Doctoral Dissertation

Development of Oxidative Amination Utilizing Hypervalent Iodine Reagents Containing (Diarylmethylene)amino Groups

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Preface

The studies presented in this thesis were conducted under the supervision of Professor Dr. Satoshi Minakata, Department of Applied Chemistry, Graduate School of Engineering, Osaka University during the period of 2016–2019 and 2021–2024.

The objects of this thesis are development of oxidative amination utilizing hypervalent iodine reagents containing (diarylmethylene)amino groups. The author hopes sincerely that the fundamental work described in this thesis contributes to further development of synthetic methods of nitrogen-containing molecules and other related fields of chemistry.

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Contents

General Introduction

1. C–N Bond Formation for the Synthesis of Nitrogen-Containing Molecules

Since nitrogen (N) is an indispensable element ubiquitously present in natural products and biologically active molecules, the development of the method for the synthesis of nitrogen-containing organic molecules has been an important research topic in organic chemistry (Figure 1).[1]

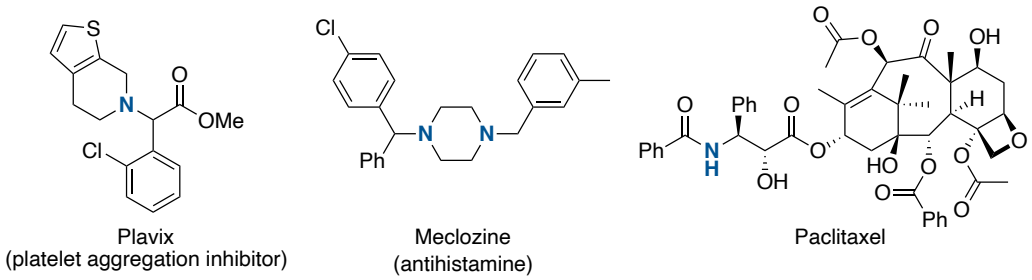
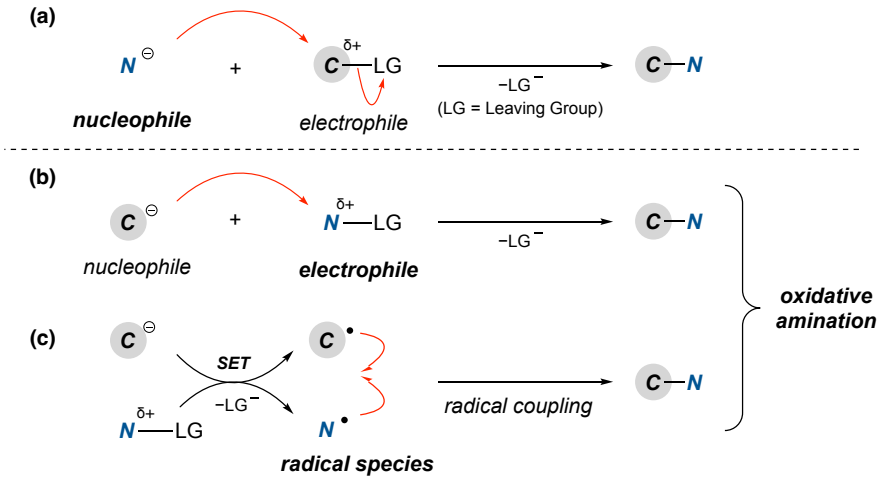


Figure 1. Nitrogen-containing molecules of pharmaceuticals and natural products

For the synthesis of a variety of nitrogen-containing molecules (amines), carbon–nitrogen bond formation reactions are the most fundamental and straightforward approaches. Representative reaction patterns for C–N bond formation are depicted in Scheme 1. The most commonly used methods involve the reaction of nitrogen nucleophiles with carbon electrophiles (Scheme 1a). Meanwhile, aminating reagents with a suitable leaving group at the nitrogen center, such as *N*-chloroamines, hydroxyamines, oxaziridines, and azo compounds, exhibit an electrophilic character of the amino groups (Figure 2). Accordingly, these reagents can serve as electrophilic aminating reagents that react with carbon nucleophiles to form a C–N bond known as electrophilic amination (Scheme 1b). In addition, since electrophilic aminating reagents can also act as single-electron oxidants, a radical reaction through single-electron transfer (SET) between the carbon nucleophiles and the aminating reagents is also possible (Scheme 1c). The latter two reaction patterns are classified as oxidative amination because they involve the oxidation process of the carbon nucleophiles, and they realize the C–N bond formation reaction that is difficult to achieve by conventional nucleophilic approaches. Therefore, the development of new methodologies for the oxidative amination has been an attractive research topic.[2]



Scheme 1. Representative reaction patterns of C–N Bond formation

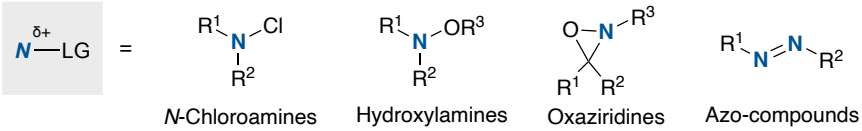


Figure 2. Typical electrophilic aminating reagents

2. Hypervalent Iodine(III) Compounds

Iodine, the heaviest halogen element practically available for organic synthesis, can have a wide range of oxidation states beyond the octet rule, up to a maximum of seven valence states, due to its large atomic radius and low electronegativity. Among iodine-based reagents, hypervalent iodine(III) compounds represent a powerful tool for oxidative transformations in organic synthesis.[3,4] The most widely used iodine(III) compounds are iodobenzene derivatives ($PhIX_2$), whose structure consists of an aryl group, electronegative heteroatom ligands (X) occupying the apical positions which can act as functional groups, and two lone pairs at the equatorial positions (Figure 3).

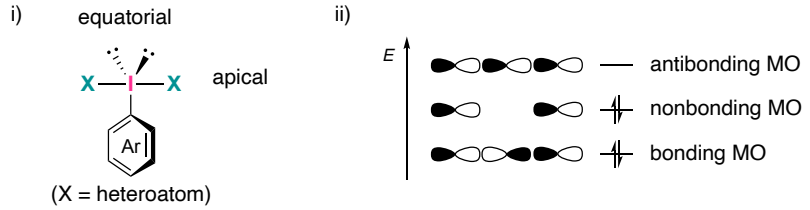
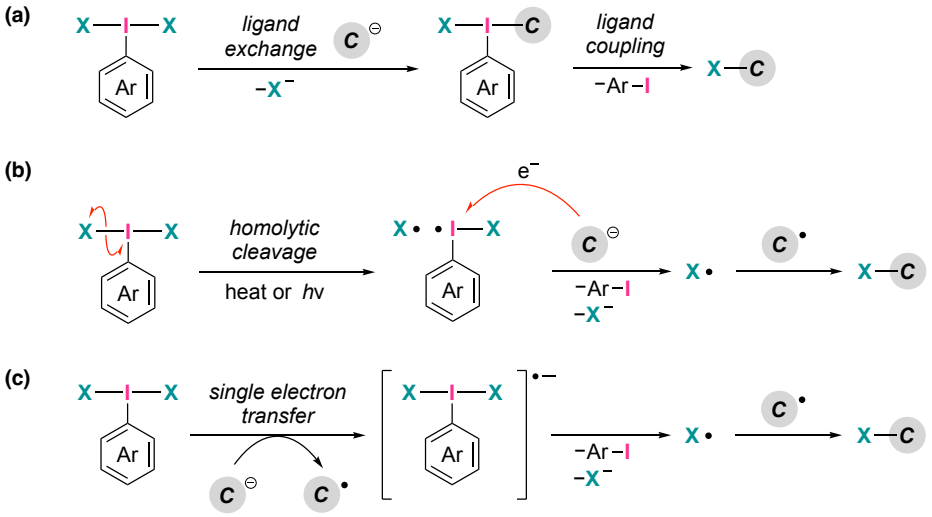


Figure 3. Features of iodine(III) compounds: i) typical structure, ii) three-center-four-electron bond

The unique reactivity of hypervalent iodine(III) reagents arises from the presence of a weak and highly polarized hypervalent (three-center-four-electron) bond (I–X) at the apical positions. In general,

the reagents undergo ligand exchange with nucleophiles, followed by ligand coupling to give the functionalized products along with the formation of monovalent iodoarenes (Scheme 2a). Moreover, the reagents show radical reactivity through a homolysis cleavage of the I–X bond under the heating or irradiation conditions (Scheme 2b) and single-electron transfer from nucleophiles (Scheme 2c). In all cases, the reduction of I(III) to I(I) is a key to promoting the reactions.



Scheme 2. Typical reactivity of hypervalent iodine(III) reagents

Given the oxidative reactivities, iodine(III) reagents containing I–N bonds are promising reagents for oxidative amination.[5] In the past decades, several hypervalent iodine(III) reagents containing transferable nitrogen functional groups such as imino (**I**),[6] bissulfonimido (**II**),[7,8] azido (**III**),[9] phthalimido (**IV**),[10,11], amide (**V**)[12], and sulfoximido (**VI**)[13] groups have been developed for use in some unique oxidative amination reactions (Figure 3).

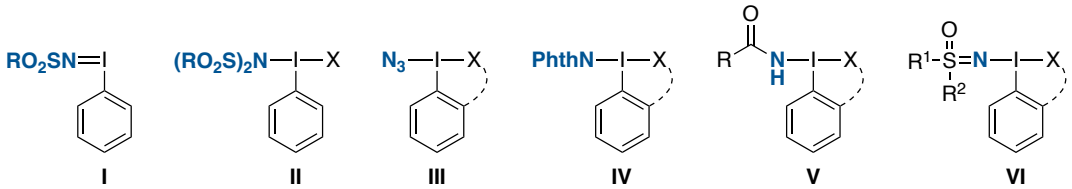
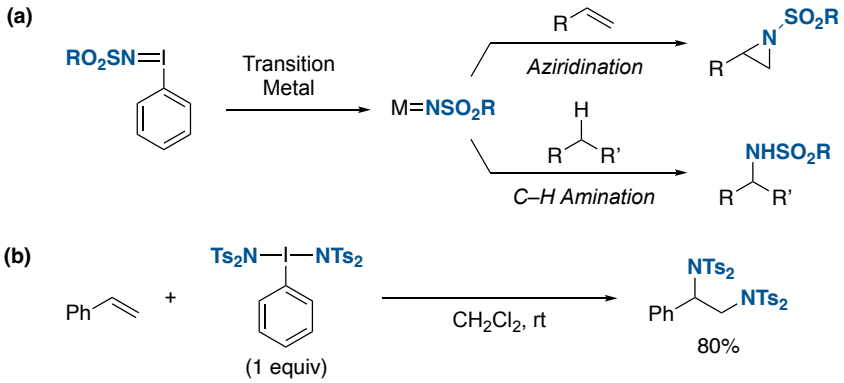


Figure 3. Representative examples of hypervalent iodine reagents that contain transferable nitrogen functional groups

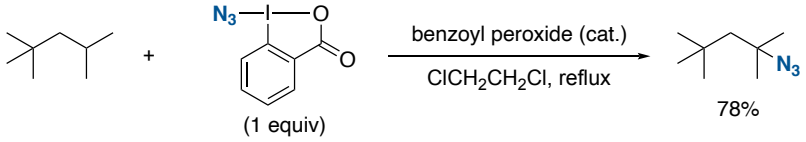
Since the first example of the general procedure for the preparation of iminoiodanes (**I**) was reported by Okawara,[6d] iminoiodanes are extensively used as a nitrene or nitrenoid precursor in the oxidative amination of unsaturated hydrocarbons and C–H bond amination (Scheme 4a).[6] Muñiz found that bisimidoiodanes (**II**) can be synthesized from (diacetoxyiodo)benzene and bissulfonylimide via a

ligand exchange, and the reagents enable diamination of alkenes (Scheme 4b).[7] However, it is frequently difficult to deprotect these amino groups installed in the products, thus hampering the synthesis of primary amines and further elaboration of the amine products.



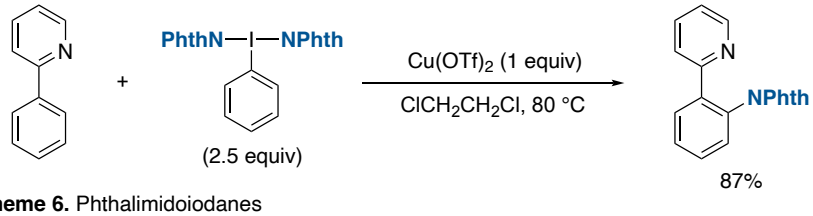
Scheme 4. a) Iminoiodanes, b) Bisimidoiodanes

Bench-stable cyclic azidoiodane (**III**) developed by Zhdankin has recently been recognized as efficient electrophilic or radical azidating reagent.[9] For instance, the azidation of C–H bonds at the tertiary carbon center in simple hydrocarbons with the reagent in the presence of benzoyl peroxide (Scheme 5).[9c] Nevertheless, it is well known that azides are hazardous substances, and the need for a laborious reduction process is a disadvantage in primary amine synthesis.



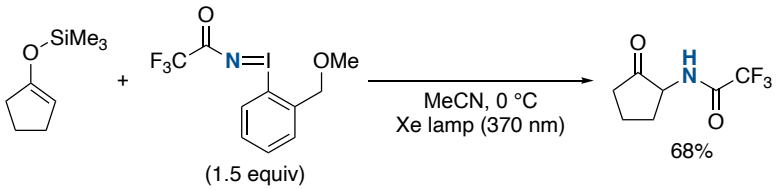
Scheme 5. Azidoiodanes

Synthetic application of phthalimidoiodane (**IV**) in oxidative amination has remained limited even though a phthaloyl group can be easily removed to provide a primary amine. As one of the few examples, copper triflate-mediated regioselective C–H amination of 2-phenylpyridines using bis(phthalimido)iodobenzene was reported by DeBoef (Scheme 6).[10e]



Scheme 6. Phthalimidoiodanes

Related to amidoiodanes (**V**) with cyclic structure, Takemoto and Kobayashi reported the synthesis of pseudocyclic amidoiodanes and their use in the α-amination of silyl enol ethers (Scheme 7).[12b] The trifluoroacetyl groups of the products can be easily deprotected under weakly acidic conditions, providing primary amines.

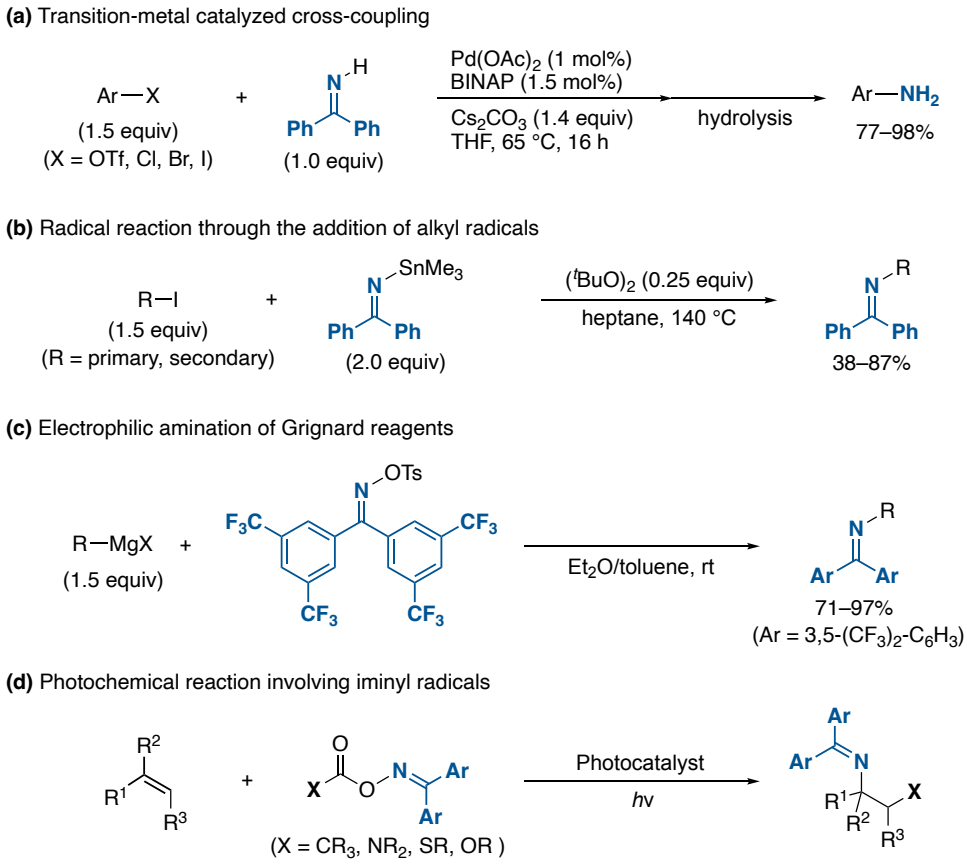


Scheme 7. Amidoiodanes

Therefore, the development of new reagents that can readily introduce modifiable nitrogen functional groups into organic skeletons in the synthesis of various nitrogen-containing compounds is still highly desired.[14]

3. Utilization of Benzophenone Imine Derivatives as Aminating Reagents

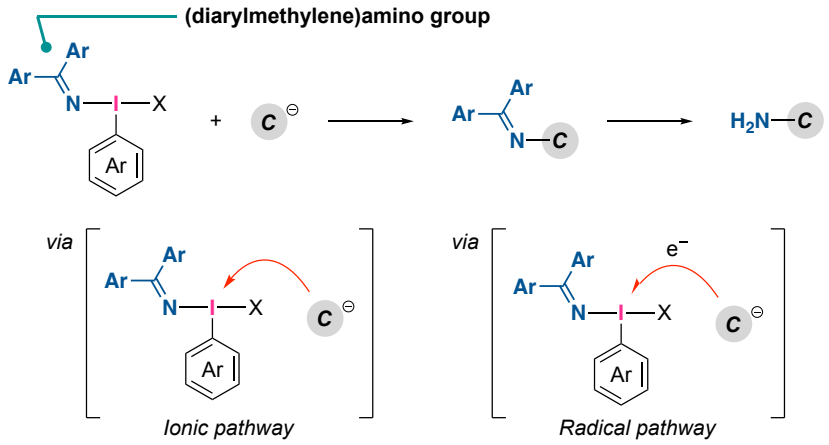
Benzophenone imine has been used as an alternative aminating reagent to ammonia[15] in transition-metal catalyzed amination[16] and catalytic C–H amination[17] because its derivatives are readily hydrolyzed to give primary amines (Scheme 8a). In addition, the radical amination by addition/elimination sequence with *N*-trimethylstannyl benzophenone imine as a radical accepter has been achieved (Scheme 8b).[18] Benzophenone imine-derived oxime derivatives function as electrophilic aminating reagents, allowing the amination of alkynyl copper reagents,[19] Grignard reagents,[20] and organoboron compounds with a copper catalyst (Scheme 8c).[21] Although iminyl radicals are also attractive species for the C–N bond formation, most of their use is in intramolecular reactions[22] for the construction of *N*-heterocycles, and examples of the intermolecular amination[23] have been reported by Glorius in the past several years. Despite these advances, the method of transferring the benzophenone imine moiety, (diarylmethylene)amino group, to organic molecules in an oxidative manner continues to be a challenging task.



Scheme 8. Utilization of benzophenone imine derivatives as nitrogen source

4. Synopsis of This Thesis

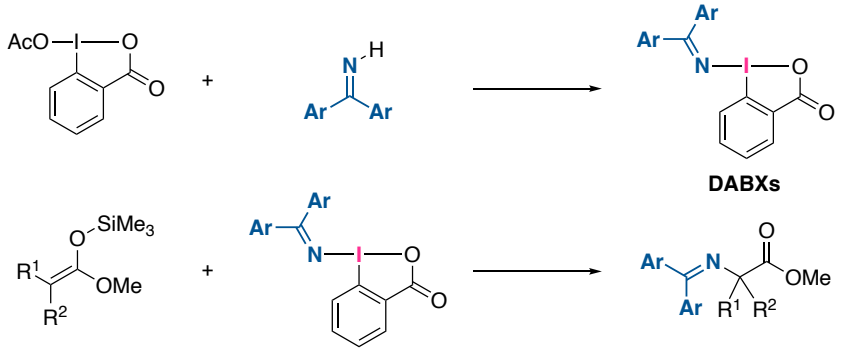
The author envisioned that the development of a novel hypervalent iodine reagent capable of introducing (diarylmethylene)amino group would lead to a new approach for the synthesis of nitrogen-containing compounds that can be readily converted to primary amines (Scheme 9). Based on the reactivity of hypervalent iodine reagents described in Scheme 2, the proposed reagents containing a (diarylmethylene)amino group are expected to act as electrophilic aminating reagents in the reaction with the carbon nucleophiles in an ionic manner. In addition, the radical reaction, in which they work as a single-electron oxidant of the carbon nucleophiles, would also be possible.



Scheme 9. Working hypothesis

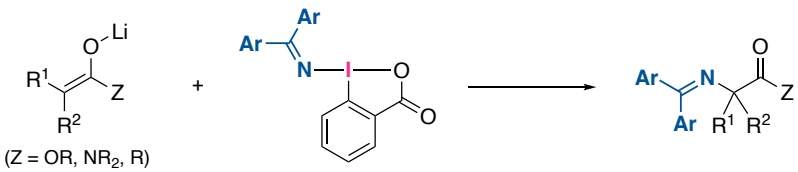
On the basis of these backgrounds, the author has developed the novel hypervalent iodine reagents containing (diarylmethylene)amino groups and oxidative amination reactions utilizing the reagents. This thesis consists of General Introduction, three Chapters, and Conclusion.

Chapter 1 describes the synthesis of (diarylmethylene)amino benziodoxolones (DABXs) and oxidative amination of silyl ketene acetals (Scheme 10).



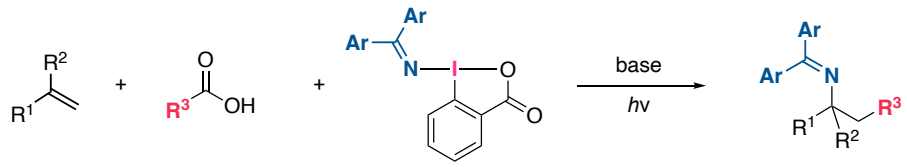
Scheme 10. Development of (diarylmethylene)amino benziodoxolones (DABXs) and oxidative amination of silyl ketene acetals

Chapter 2 deals with the oxidative amination of lithium enolates derived from various carbonyl compounds such as esters, amides, and ketones, using DABXs (Scheme 11).



Scheme 11. Oxidative amination of lithium enolates using DABXs

Chapter 3 discloses the photoexcitation of DABXs for alkylamination of alkenes with carboxylic acids (Scheme 12).



Scheme 12. Photoexitation of DABXs for alkylamination of alkenes with carboxylic acids

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Chapter 1

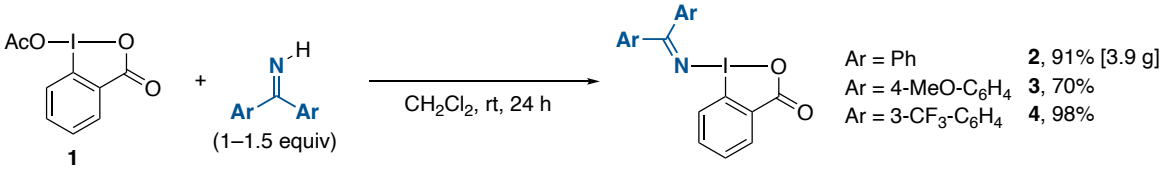
Synthesis of (Diarylmethylene)amino Benziodoxolones (DABXs) and Their Use in the Oxidative Amination of Silyl Ketene Acetals

1-1. Introduction

Based on the background described in the general introduction, the author envisioned that the synthesis of novel hypervalent iodine(III) reagents combined with benzophenone imines, which would offer a promising tool for oxidative amination to deliver modifiable amine products. Chapter 1 describes the synthesis of hypervalent iodine(III) reagents containing transferable (diarylmethylene)amino groups and their use in the oxidative amination of silyl ketene acetals.

1-2. Results and Discussion

The author initially focused on the synthesis of the hypervalent iodine reagent **2**, which has a benziodoxolone skeleton, along with the stability of the product (Scheme 1).[1] Gratifyingly, the synthesis of **2** was achieved through a simple ligand-exchange process. Indeed, acetoxyiodane **1** reacted smoothly with benzophenone imine in dichloromethane at room temperature to furnish the desired **2** in high yield, even in the case of a gram-scale synthesis (3.9 g, 91%). This simple process was successfully applied to the synthesis of derivatives containing electron-donating methoxy (**3**) and electron-withdrawing trifluoromethyl (**4**) groups.



Scheme 1. Synthesis of hypervalent iodine reagents containing benzophenone Imine-derived nitrogen functional groups

Single crystals of a representative sample of **2** suitable for X-ray crystallographic analysis were

grown through slow diffusion of an acetonitrile solution.[2] Structural data for **2** revealed that the benzophenone imine moiety was N-bound to the hypervalent iodine(III) center, which shows a typical distorted T-shaped geometry (Figure 1). The length of the I–N bond of 2.083(3) Å is somewhat longer than that observed for the sulfoximidoyl-containing hypervalent iodine reagent reported by Bolm and co-workers.[3] In the solid state, **2** exists as a monomer with no intermolecular secondary bonding interactions around the iodine center, which is consistent with the fact that it is soluble in organic solvents, such as chloroform and dichloromethane.

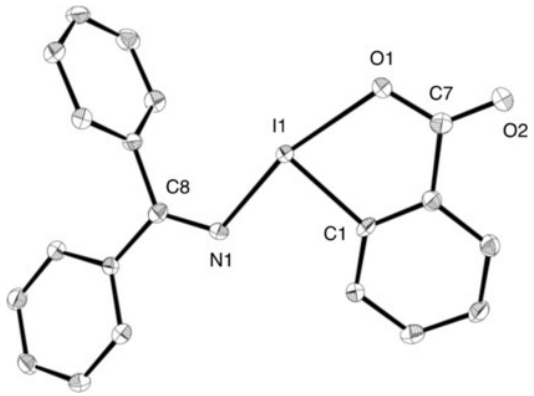


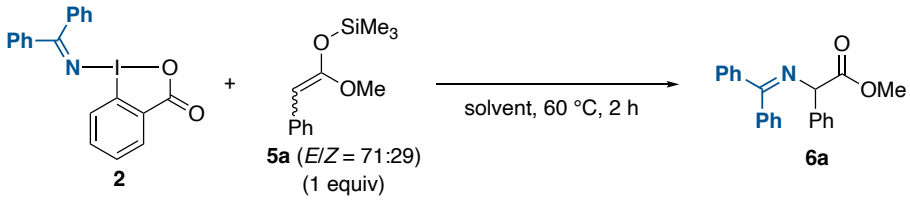
Figure 1. Crystal structure of **2**. Thermal ellispoids are shown at the 50% probability level and hydrogen atoms omitted for clarity. Slelected bond lengths [Å] and angle [°]: I1–N1 2.083(3), I1–O1 2.312(3), I1–C1 2.114(4), N1–C8 1.291(5), O1-I1-N1 165.16(10), N1-I1-C1 88.90(13), O1-I1-C1 76.56(12), I1-O1-C7 114.7(2), I1-N1-C8 115.7(2)

Oxidative amination of silyl ketene acetals is a practical and reliable strategy for preparing unnatural α-amino acid derivatives, and several transition-metal-catalyzed approaches have been reported to date, in which iminoiodanes,[4a,b] hydroxyamines,[4c] and chloramines[4d] were used as a nitrogen source. However, a remaining issue is the need for transition-metal catalysts and difficulties associated with the further elaboration of the amino group in the products. The author envisioned that the hypervalent iodine reagent **2** would be capable of aminating silyl ketene acetals without the addition of any catalyst or additive.

When the silyl ketene acetal **5a** (*E*/*Z* = 71:29), which was derived from methyl phenylacetate, was employed in the reaction with **2** in 1,2-dichloroethane at 60 °C, oxidative amination occurred to give the desired **6a** in 42% yield (Table 1, Entry 1). The results of a solvent screening revealed that the yield of **6a** could be increased to 70% when MeCN was used (Entry 2). Reactions in other polar solvents, such as DMF, THF, and $MeNO_2$, resulted in lower yields of **6a** than that in MeCN (Entries 3–5), while no desired product was formed when HFIP and toluene were used as the solvent (Entries 6 and 7). Increasing the amounts of reagents used was effective, and the use of 1.5 equivalents of **5a** gave the best result (Entries 8 and 9). The *E*/*Z* configuration of a silyl ketene acetal has little effect on the efficiency

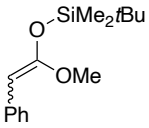
of the reaction because (*Z*)-**5a** (*E*/*Z* = 9:91) provided the same yield (Entry 2 vs. Entry 10). Silyl ketene acetals bearing a bulky silyl group, such as *tert*-butyldimethylsilyl (**7**) and triisopropylsilyl (**8**) groups, were also applicable to this amination but their reactivity was lower than that of **5a** (Entries 11 and 12). No reaction was observed with benzophenone imine-derived oxime derivatives, which can function as electrophilic aminating reagents (Entries 13 and 14).[14] Conducting the reaction at room temperature resulted in a lower yield of **5a** (Entry 15). The reaction proceeded with comparable efficiency in the dark, thus demonstrating that the reaction is a thermal process (Entry 16).

Table 1. Effect of solvents and reaction parameters on the oxidative amination of silyl ketene acetals **5a** and control experiments[a]

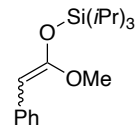


Entry	Solvent	Yield [%][b]
1	1,2-Dichloroethane	42
2	MeCN	70
3	DMF	45
4	THF	39
5	$MeNO_2$	12
6	HFIP	0
7	Toluene	0

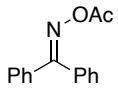
Entry	Deviation from the conditions of Entry 2	Yield [%][b]
8	**2** (1.5 equiv)	74
9	**5a** (1.5 equiv)	82
10	(*Z*)-**5a** (*E*/*Z* = 9:91) instead of **5a** (*E*/*Z* = 71:29)	70
11	**7** instead of **2**, 12 h	58
12	**8** instead of **2**, 12 h	52
13	**9** instead of **2**, 12 h	0
14	**10** instead of **2**, 12 h	0
15	rt	48
16	In the dark	66



7 (*E*/*Z* = 71:29)



8 (*E*/*Z* = 89:11)



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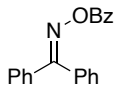

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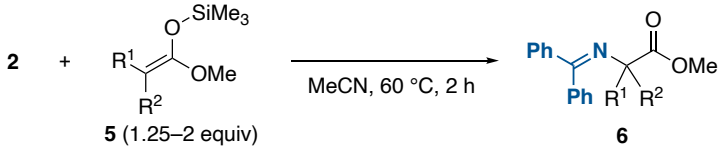
[a] Reactions were performed on a 0.2 mmol scale. [b] Determined by ^{1}H NMR analysis of the crude product.

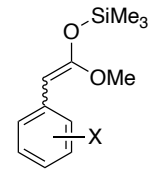
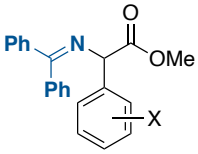
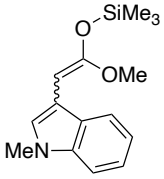
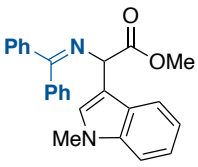
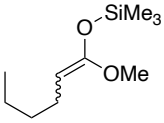
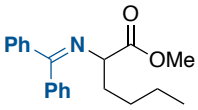
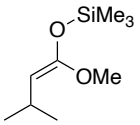
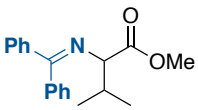
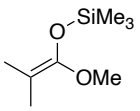
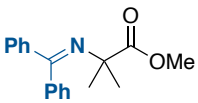
With the optimized reaction conditions in hand (Table 1, Entry 9), the substrate scope of the amination was investigated (Table 2). A series of silyl ketene acetals containing electron-rich and electron-deficient aryl groups at the 2-position were subjected to amination with **2**, and all of the reactions proceeded successfully to afford the corresponding α-amino esters in good to high yields

(Entries 1–6). The presence of a methyl substituent at the *ortho* or *meta* positions did not affect the reactivity (Entries 7 and 8). An electron-rich *N*-methylindolyl group was well tolerated under the oxidative conditions to provide the desired **6i** (Entry 9). In addition, silyl ketene acetals containing aliphatic substituents at the 2-position were also suitable for this amination. For example, substrates containing *n*-butyl (**5j**) and sterically hindered isopropyl (**5k**) groups were smoothly converted into the corresponding α-amino esters (Entries 10 and 11). Furthermore, the sterically demanding dimethyl-substituted **5l** was also transformed into **6l**, which contains an α-tertiary amine moiety, in moderate yield (Entry12).

Table 2. Substrate scope[a]



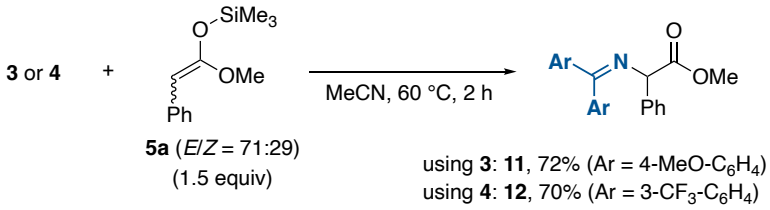
5 (1.25–2 equiv) **6**

Entry		5		6		Yield [%]
1	**5a**		X = H (*E*/*Z* = 71:29)		**6a**	78
2	**5b**		X = 4-OMe (*E*/*Z* = 93:7)		**6b**	73
3	**5c**		X = 4-Me (*E*/*Z* = 74:26)		**6c**	73
4	**5d**		X = 4-Cl (*E*/*Z* = 64:36)		**6d**	83
5	**5e**		X = 4-Br (*E*/*Z* = 63:37)		**6e**	76
6	**5f**		X = 4-CF_3 (*E*/*Z* = 40:60)		**6f**	84
7	**5g**		X = 2-Me (*E*/*Z* = 60:40)		**6g**	75
8	**5h**		X = 3-Me (*E*/*Z* = 74:26)		**6h**	75
9	**5i**[b]				**6i**	55
10	**5j**[c]				**6j**	51
11	**5k**[d]				**6k**	63
12	**5l**				**6l**	58

[a] Reactions were performed on a 0.4 mmol scale. Yields are isolated yields. The isolated products contained a small amount of dimers of **5**. [b] Reaction was conducted at RT. [c] *E*/*Z* ratios were not determined. [d] *E*/*Z* = >95:5.

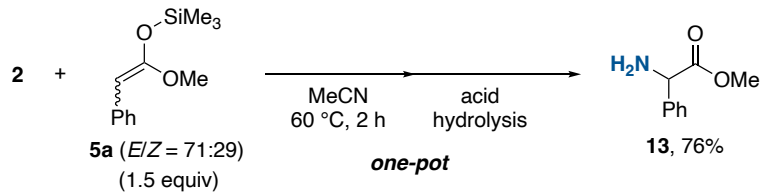
Oxidative amination was also examined using derivatives **3** and **4**, which contain electron-rich and

electron-deficient imine moieties, respectively (Scheme 2). Both reagents could be used to deliver the corresponding products in yields comparable to those for the reaction using **2**, thus indicating that the amination was not significantly influenced by the electronic properties of the imine moiety of the hypervalent iodine reagent.



Scheme 2. Oxidative amination using hypervalent iodine reagents **3** and **4**.

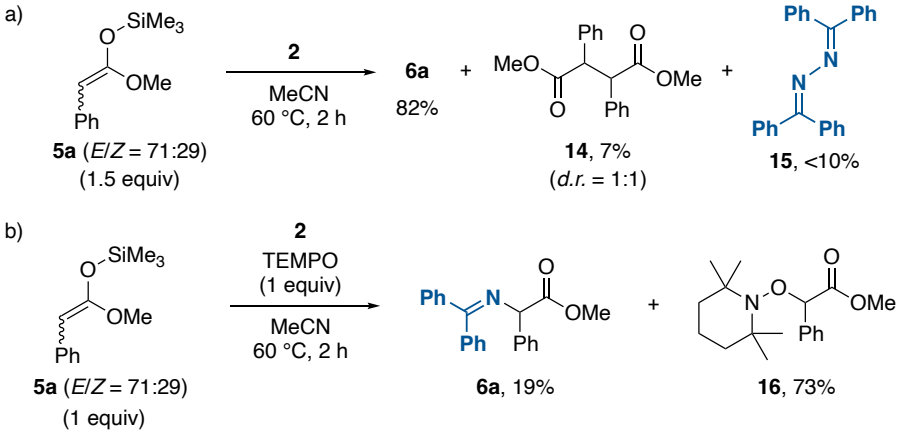
To demonstrate the usefulness of the iodine(III) reagent for the synthesis of primary amines, the one-pot synthesis of a unprotected α-amino ester was carried out (Scheme 3). A sequential one-pot method consisting of oxidative amination of **5a** with **2**, removal of the volatiles under reduced pressure, and acid hydrolysis at room temperature followed by a simple basic workup, afforded the desired product **13** in good yield. This quite simple method offers a useful and practical process for the synthesis of α-amino acid derivatives.



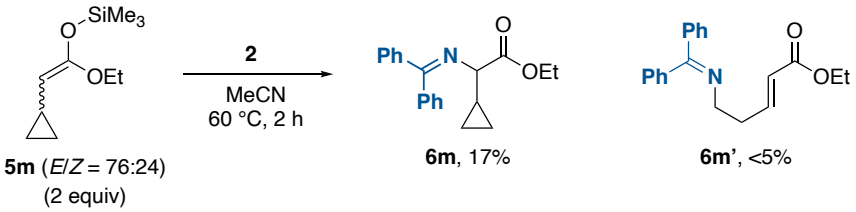
Scheme 3. Synthesis of a primary amine through a one-pot procedure

Mechanistic aspects of the oxidative amination were also investigated. Both ^{1}H NMR and GC-MS analysis of byproducts in the amination of **5a** (Table 1, Entry 9) revealed that a small amount of **14** and benzophenone azine (**15**) were generated, which were likely formed through homocoupling of the corresponding α-carbonyl radicals and iminyl radicals, respectively (Scheme 4a).[5,6] To examine this issue further, the author carried out a radical-trapping experiment using 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO). When TEMPO was added to the amination reaction of **5a**, the formation of **6a** was suppressed (19%), and **16** was produced as the main product through the trapping of an α-carbonyl radical derived from **5a** by TEMPO (Scheme 4b).[7] These results clearly

indicate that an α-carbonyl radical (**17**) as well as an iminyl radical (**18**; Scheme 6) are generated *in situ* and both participate in the amination step. A radical mechanism was further confirmed by a radical-clock experiment using the silyl ketene acetal **5m**, which contains a cyclopropyl substituent (Scheme 5).[8] When **5** m was subjected to the amination reaction conditions, the cyclopropane-containing **6m** was formed in low yield, and some ring-opening products (not fully characterized) were observed, one of which was determined to be **6m'**.

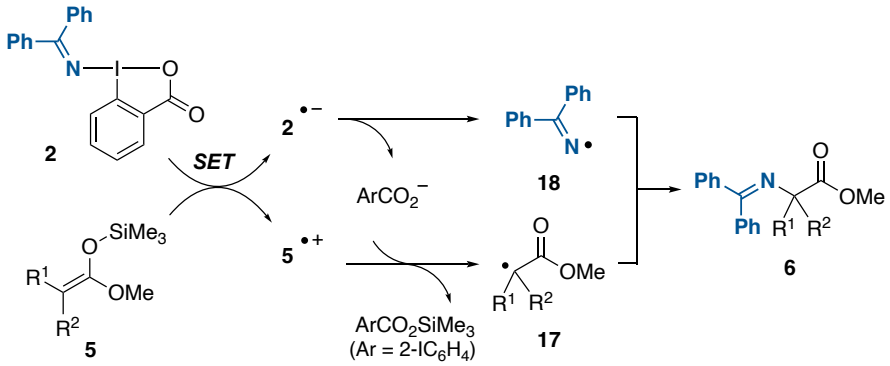


Scheme 4. Mechanistic investigations into the oxidative amination reaction: a) byproducts under the standard conditions, b) radical-trapping experimant with TEMPO



Scheme 5. Reaction of cyclopropane-containing **5m**

Based on these experimental results, a proposed reaction pathway is depicted in Scheme 6. The reaction is initiated through a single-electron transfer (SET) from the silyl ketene acetal **5** to the hypervalent iodine reagent **2**.[9,10] The resulting radical cation and anion species are then quickly decomposed to form the α-carbonyl radical **17** and the iminyl radical **18**, respectively, which are then rapidly coupled to produce the α-amino ester **6**.



Scheme 6. Proposed reaction pathway

1-3. Conclusion

In conclusion, benziodoxolone-based hypervalent iodine reagents containing a transferable (diarylmethylene)amino group (DABXs) were prepared and found to be reasonably stable under ambient conditions. A representative compound was structurally characterized by X-ray analysis. In addition, using these reagents, a transition-metal-free oxidative amination of silyl ketene acetals was developed to afford α-amino acid derivatives. These preliminary studies demonstrate that these new types of hypervalent iodine reagents can function as useful aminating reagents for the synthesis of primary amines.

1-4. Experimental Section

General Remarks

New compounds were characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{19}F{^{1}H} NMR, IR, MS, and HRMS. ^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer (^{1}H NMR, 400 MHz; ^{13}C{^{1}H} NMR, 100 MHz; ^{19}F{^{1}H} NMR, 377 MHz). ^{1}H NMR chemical shifts were determined relative to Me_4Si (0.0 ppm) as an internal standard. ^{13}C{^{1}H} NMR chemical shifts were determined relative to $CDCl_3$ (77.0 ppm). ^{19}F{^{1}H} NMR chemical shifts were determined relative to C_6F_6 (−164.9 ppm) as an external standard. Infrared spectra were recorded on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. Mass spectra were obtained on a SHIMADZU GCMS-QP2010. High-resolution mass spectra were obtained on a JEOL JMS-700 mass spectrometer (magnetic sector type mass spectrometer). Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. Cyclic voltammetry (CV) was performed with ALS-600 (BAS Inc.) system. The X-ray diffraction data of the single crystal were collected on a two-dimensional X-ray detector (PILATUS 200K/R) equipped in Rigaku XtaLAB PRO diffractometer using thin

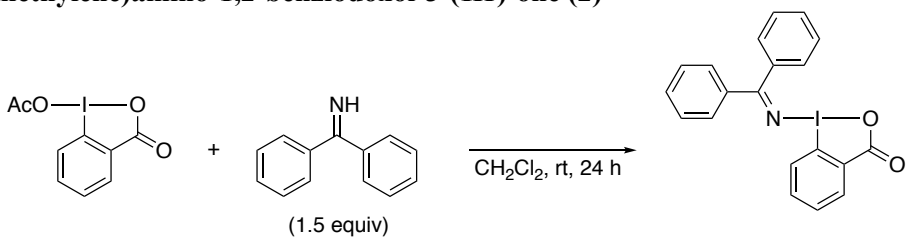
multi-layer mirror monochromated Cu-Kα radiation (λ =1.54187 Å). X-ray crystal data were collected by a Rigaku RAXIS-RAPID Imaging Plate diffractometer. All reactions were carried out under nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.) or Chromatorex NH (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F_{254} and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating. All reactions were carried out under nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.) or Chromatorex NH (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F254 and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

Materials

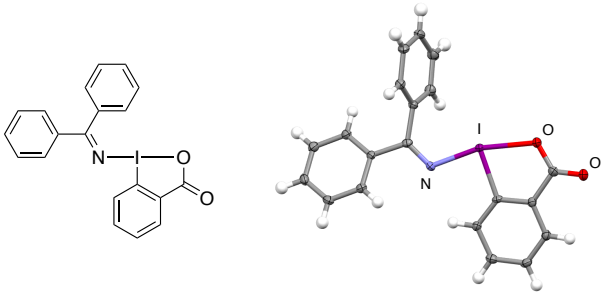
Silyl ketene acetals **5a**,[4d] (*Z*)-**5a**,[11] **5b**,[4d] **5c**,[4d] **5i**,[4d] **5j**,[4d] **5k**,[4d] **7**,[4d] and **8**[4d] were prepared according to the reported procedure, and the analytical data of **5a**,[12] **5b**,[13] **5c**,[14] **5i**,[12] **5j**,[12] and **5k**[15] were in excellent agreement with reported data. Dehydrated acetonitrile was used from a solvent purification system. All other solvents and reagents were purchased and used as obtained.

Synthesis of hypervalent iodine reagents

1-(Diphenylmethylene)amino-1,2-benziodoxol-3-(1*H*)-one (2)

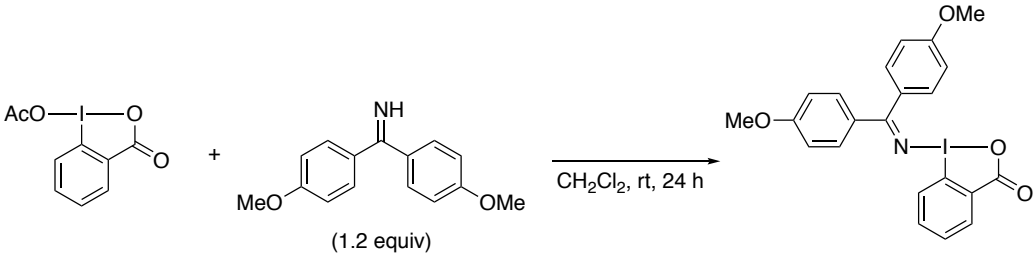


To a solution of 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one[16] (3.0 g, 10 mmol) in dichloromethane (20 mL), benzophenone imine (2.7 g, 15 mmol) was added. The mixture was stirred at room temperature for 24 h. Then, volatiles were removed under reduced pressure. The crude solid was washed with MeCN and dried under vacuum to give the product as a white solid (3.9 g, 91% yield). Recrystallization from MeCN gave a single crystal suitable for X-ray analysis. mp: 155.2 °C (decomposed); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.36 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.93–7.85 (m, 1H), 7.73–7.52 (m, 7H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39–7.30 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 180.0, 167.7, 140.9, 137.7, 133.8, 132.6, 132.4, 132.1, 131.0, 130.5, 130.1, 128.9, 128.7, 126.8, 125.7, 118.2; IR: (ATR) 3100, 3073, 1636, 1557, 1435, 1308, 1292, 823, 750 cm^{-1}; HRMS: (FAB) calcd for ($C_{20}H_{15}NO_2I$) 428.0147 ($[M+H]^+$), found *m*/*z* 428.0147



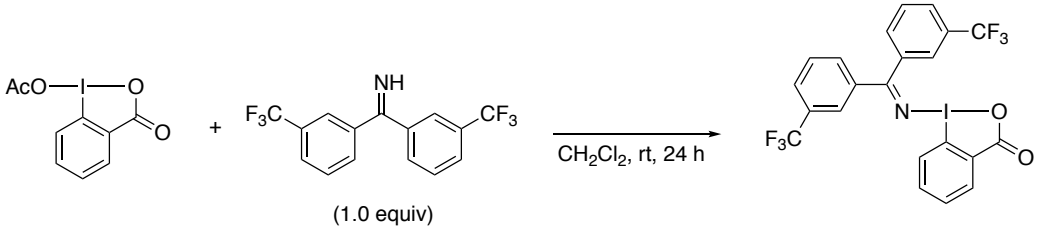
The structure of **2** was determined by X-ray structural analysis. CCDC 1906200 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-((Bis(4-methoxyphenyl)methylene)amino)-1,2-benziodoxol-3-(1*H*)-one (3)



To a solution of 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one[16] (609.3 mg, 2.0 mmol) in dichloromethane (10 mL), 4,4'-dimethoxybenzophenone imine[17] (571.5 mg, 2.4 mmol) was added. The mixture was stirred at room temperature for 24 h. Then, volatiles were removed under reduced pressure. The crude solid was washed with MeCN and dried under vacuum to give the product as a pale yellow solid (675 mg, 70% yield). mp: 111.6 °C (decomposed); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.54 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 6.4 Hz, 1H), 7.92–7.82 (m, 1H), 7.75–7.55 (m, 3H), 7.28 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.93 (s, 3H), 3.88 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 179.4, 167.8, 162.7, 161.2, 133.60, 133.58, 132.5, 131.0, 130.8, 130.3, 127.6, 126.8, 118.2, 115.1, 113.9, 55.55, 55.50 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3003, 2841, 1634, 1593, 1537, 1504, 1435, 1302, 1246, 1163, 1030, 835, 742 cm^{-1}; HRMS: (FAB) calcd for ($C_{22}H_{19}NO_4I$) 488.0359 ($[M+H]^+$), found m/z 488.0368

1-((Bis(3-(trifluoromethyl)phenyl)methylene)amino)-1,2-benziodoxol-3-(1*H*)-one (4)



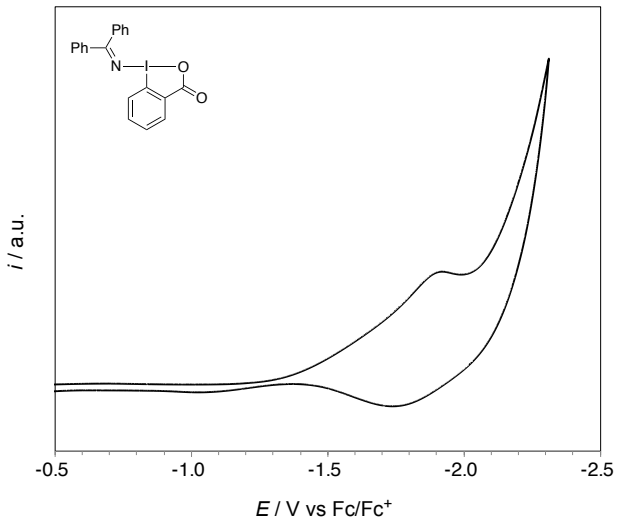
To a solution of 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one[16] (612.8 mg, 2.0 mmol) in dichloromethane (10

mL), 3,3'-bis(trifluoromethyl)benzophenone imine[17] (635.4 mg, 2.0 mmol) was added. The mixture was stirred at room temperature for 24 h. Then, volatiles were removed under reduced pressure. The crude solid was washed with MeCN and dried under vacuum to give the product as a white solid (1.1 g, 98% yield). mp: 166.8 °C (decomposed); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 7.2 Hz, 1H), 8.03–7.50 (m, 10H); ^{19}F{^{1}H} NMR: (377 MHz, $CDCl_3$) δ −63.9; IR: (ATR) 3030, 1626, 1595, 1566, 1431, 1319, 1248, 1124, 1070, 827, 748 cm^{-1}; HRMS: (FAB) calcd for ($C_{22}H_{13}F_6NO_2I$) 563.9895 ([M+H]$^{+}$), found m/z 563.9906

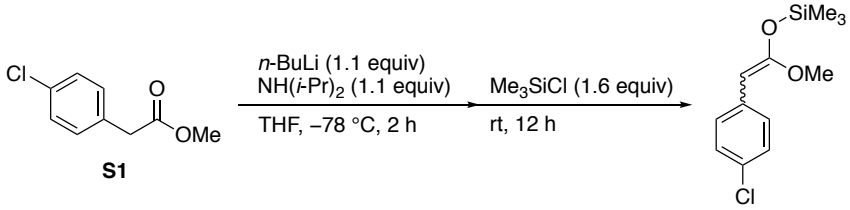
^{13}C{^{1}H} NMR signals of the compound were not detectable due to its low solubility.

CV measurement of the hypervalent iodine reagent 2

Cyclic voltammetry (CV) was performed with ALS-600 electrochemical analyzer (BAS Inc.) using a one-component cell equipped with a platinum working electrode, a platinum wire counter electrode, and Ag/Ag^{+} reference electrode, and all the measurements were carried out in an dichloromethane solution (1 x 10^{-3} M), which was prepared from distilled and degassed dichloromethane, containing tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) as the supporting electrolyte at room temperature under the Ar atmosphere at the scanning rate of 0.1 V/s. The potential values were corrected against the Fc/Fc^{+} (Fc = ferrocene) redox potential.



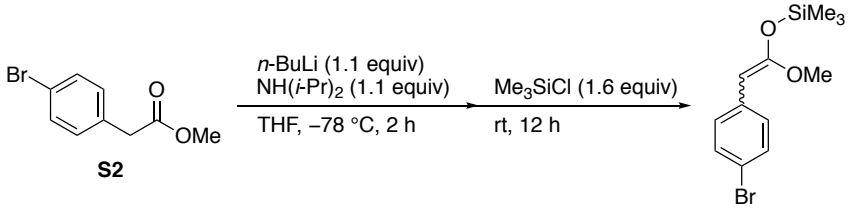
Preparation of silyl ketene acetals
((2-(4-Chlorophenyl)-1-methoxyvinyl)oxy)trimethylsilane (5d)



According to the reported procedure,[4d] the reaction using ester **S1** (7.3 g, 40 mmol), *n*-BuLi (1.6 M in hexane, 28 mL, 45 mmol), diisopropylamine (6 mL, 43 mmol), and chlorotrimethylsilane (8 mL, 63 mmol) gave the the crude mixture, which was purified by distillation to give the product as a colourless liquid (9.2 g, 90% yield). The product was obtained as a mixture of *E*/*Z* isomers (*E*/*Z* = 64:36). The configurations of the products were determined by comparing their ^{1}H NMR signals with the

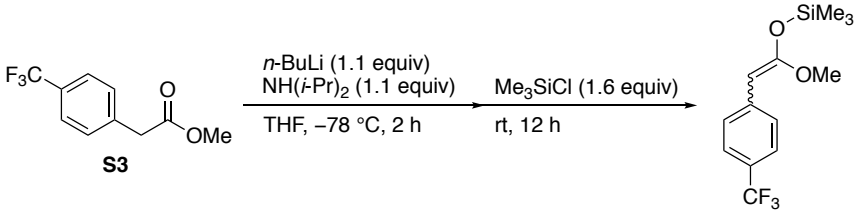
corresponding compounds.[4d] IR: (ATR) 2955, 1645, 1491, 1404, 1254, 1171, 1067, 845 cm^{-1}; MS: (EI) *m*/*z* 258 ($[M+2]^+$, 6), 256 (M^+, 16), 154 (32), 152 (100), 89 (23), 73 (41); HRMS: (EI) calcd for ($C_{12}H_{17}ClO_2Si$) 256.0686 (M^+), found *m*/*z* 256.0693; ^1H NMR signals assigned from the mixture of isomers. **(*E* isomer)** ^1H NMR: (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 2H), 7.20–7.15 (m, 2H), 4.60 (s, 1H), 3.70 (s, 3H), 0.33 (s, 9H); **(*Z* isomer)** ^1H NMR: (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 2H), 7.20–7.15 (m, 2H), 4.54 (s, 1H), 3.67 (s, 3H), 0.28 (s, 9H); $^{13}C\{^1H\}$ NMR of a mixture of *E*/*Z* isomers: (100 MHz, $CDCl_3$) δ 158.2, 155.1, 135.7, 135.3, 128.7, 128.5, 128.11, 128.08, 127.6, 127.4, 84.4, 77.7, 55.2, 53.7, 0.5, −0.2

((2-(4-Bromophenyl)-1-methoxyvinyl)oxy)trimethylsilane (5e)



According to the reported procedure,[4d] the reaction using ester **S2** (9.0 g, 40 mmol), *n*-BuLi (1.6 M in hexane, 28 mL, 45 mmol), diisopropylamine (6 mL, 43 mmol), and chlorotrimethylsilane (8 mL, 63 mmol) gave the the crude mixture, which was purified by distillation to give the product as a colourless liquid (9.4 g, 78% yield). The product was obtained as a mixture of *E*/*Z* isomers (*E*/*Z* = 63:37). The configurations of the products were determined by comparing their ^1H NMR signals with the corresponding compounds.[4d] IR: (ATR) 2959, 1641, 1400, 1252, 1171, 1067, 843, 826 cm^{-1}; MS: (EI) *m*/*z* 302 ($[M+2]^+$, 11), 300 (M^+, 14), 198 (88), 196 (100), 89 (72), 73 (87); HRMS: (EI) calcd for ($C_{12}H_{17}BrO_2Si$) 300.0181 (M^+), found *m*/*z* 300.0181; ^1H NMR signals assigned from the mixture of isomers. **(*E* isomer)** ^1H NMR: (400 MHz, $CDCl_3$) δ 7.38–7.23 (m, 4H), 4.58 (s, 1H), 3.69 (s, 3H), 0.32 (s, 9H); **(*Z* isomer)** ^1H NMR: (400 MHz, $CDCl_3$) δ 7.38–7.23 (m, 4H), 4.53 (s, 1H), 3.67 (s, 3H), 0.28 (s, 9H); $^{13}C\{^1H\}$ NMR of a mixture of *E*/*Z* isomers: (100 MHz, $CDCl_3$) δ 158.3, 155.2, 135.8, 131.01, 130.99, 128.0, 127.8, 116.6, 116.4, 84.3, 77.7, 55.2, 53.7, 0.5, −0.2 (one sp^2 signal was not observed because of overlapping)

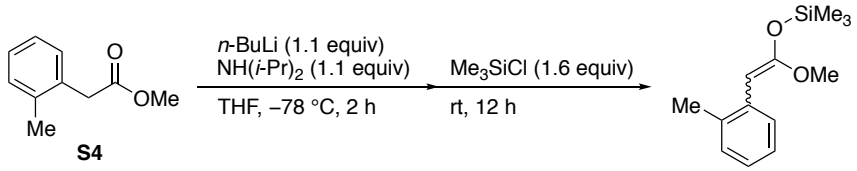
((1-Methoxy-2-(4-trifluoromethyl)phenyl)vinyl)oxy)trimethylsilane (5f)



According to the reported procedure,[4d] the reaction using ester **S3** (8.7 g, 40 mmol), *n*-BuLi (1.6 M in

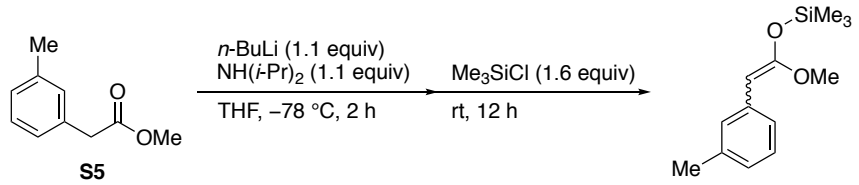
hexane, 28 mL, 45 mmol), diisopropylamine (6 mL, 43 mmol), and chlorotrimethylsilane (8 mL, 63 mmol) gave the the crude mixture, which was purified by distillation to give the product as a colourless liquid (8.2 g, 71% yield). The product was obtained as a mixture of *E*/*Z* isomers (*E*/*Z* = 40:60). The configurations of the products were determined by comparing their ^{1}H NMR signals with the corresponding compounds.[4d] IR: (ATR) 2961, 1643, 1609, 1323, 1254, 1113, 1067, 839 cm^{-1}; MS: (EI) *m*/*z* 290 (M^+, 14), 186 (100), 167 (27), 158 (24), 73 (41); HRMS: (EI) calcd for ($C_{13}H_{17}F_3O_2Si$) 290.0950 (M^+), found *m*/*z* 290.0954; ^{1}H NMR signals assigned from the mixture of isomers. **(*E* isomer)** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.56–7.45 (m, 4H), 4.69 (s, 1H), 3.75 (s, 3H), 0.37 (s, 9H); **(*Z* isomer)** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.56–7.45 (m, 4H), 4.65 (s, 1H), 3.72 (s, 3H), 0.34 (s, 9H); ^{13}C{^{1}H} NMR of a mixture of *E*/*Z* isomers: (100 MHz, $CDCl_3$) δ 159.3, 156.3, 141.2, 140.9, 126.1, 126.0, 124.96 (q, $J_{C–F}$ = 32.1 Hz), 124.95 (q, $J_{C–F}$ = 4.1 Hz), 124.91 (q, $J_{C–F}$ = 4.1 Hz), 124.89 (q, $J_{C–F}$ = 32.1 Hz), 124.73 (q, $J_{C–F}$ = 270.0 Hz), 124.71 (q, $J_{C–F}$ = 270.0 Hz), 84.0, 77.9, 55.3, 53.6, 0.4, −0.3; ^{19}F{^{1}H} NMR: (377 MHz, $CDCl_3$) δ −64.5

((1-Methoxy-2-(*o*-tolyl)vinyl)oxy)trimethylsilane (5g)



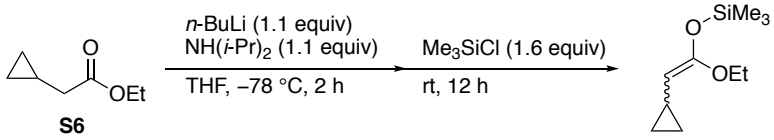
According to the reported procedure,[4d] the reaction using ester **S4** (3.3 g, 20 mmol), *n*-BuLi (1.6 M in hexane, 14 mL, 22 mmol), diisopropylamine (3 mL, 21 mmol), and chlorotrimethylsilane (4 mL, 32 mmol) gave the the crude mixture, which was purified by distillation to give the product as a colourless liquid (4.2 g, 89% yield). The product was obtained as a mixture of *E*/*Z* isomers (*E*/*Z* = 60:40). The configurations of the products were determined by comparing their ^{1}H NMR signals with the corresponding compounds.[4d] IR: (ATR) 2963, 1645, 1599, 1462, 1254, 1213, 1169, 1065, 930, 843, 745 cm^{-1}; MS: (EI) *m*/*z* 236 (M^+, 22), 132 (100), 104 (75), 103 (31), 73 (49); HRMS: (EI) calcd for ($C_{13}H_{20}O_2Si$) 236.1233 (M^+), found *m*/*z* 236.1228; ^{1}H NMR signals assigned from the mixture of isomers. **(*E* isomer)** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.73–7.65 (m, 1H), 7.17–7.07 (m, 2H), 7.00–6.94 (m, 1H), 4.72 (s, 1H), 3.66 (s, 3H), 2.26 (s, 3H), 0.34 (s, 9H); **(*Z* isomer)** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.73–7.65 (m, 1H), 7.17–7.07 (m, 2H), 7.00–6.94 (m, 1H), 4.59 (s, 1H), 3.70 (s, 3H), 2.28 (s, 3H), 0.24 (s, 9H); ^{13}C{^{1}H} NMR of a mixture of *E*/*Z* isomers: (100 MHz, $CDCl_3$) δ 157.7, 154.6, 135.3, 135.0, 133.9, 129.64, 129.62, 127.3, 127.0, 125.6, 125.5, 124.1, 123.8, 82.6, 75.7, 55.1, 54.0, 20.48, 20.46, 0.4, −0.2 (one sp^2 signal was not observed because of overlapping)

((1-Methoxy-2-(*m*-tolyl)vinyl)oxy)trimethylsilane (5h)



According to the reported procedure,[4d] the reaction using ester **S5** (3.3 g, 20 mmol), *n*-BuLi (1.6 M in hexane, 14 mL, 22 mmol), diisopropylamine (3 mL, 21 mmol), and chlorotrimethylsilane (4 mL, 32 mmol) gave the the crude mixture, which was purified by distillation to give the product as a colourless liquid (3.9 g, 82% yield). The product was obtained as a mixture of *E*/*Z* isomers (*E*/*Z* = 74:26). The configurations of the products were determined by comparing their ^{1}H NMR signals with the corresponding compounds.[4d] IR: (ATR) 2955, 1647, 1601, 1254, 1207, 1065, 841 cm^{-1}; MS: (EI) *m*/*z* 236 (M^+, 22), 132 (100), 104 (22), 73 (28); HRMS: (EI) calcd for ($C_{13}H_{20}O_2Si$) 236.1233 (M^+), found *m*/*z* 236.1230; ^{1}H NMR signals assigned from the mixture of isomers. **(*E* isomer)** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30–7.18 (m, 2H), 7.17–7.10 (m, 1H), 6.88–6.83 (m, 1H), 4.65 (s, 1H), 3.70 (s, 3H), 2.31 (s, 3H), 0.32 (s, 9H); **(*Z* isomer)** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30–7.18 (m, 2H), 7.17–7.10 (m, 1H), 6.88–6.83 (m, 1H), 4.57 (s, 1H), 3.67 (s, 3H), 2.31 (s, 3H), 0.29 (s, 9H); ^{13}C{^{1}H} NMR of a mixture of *E*/*Z* isomers: (100 MHz, $CDCl_3$) δ 157.8, 154.7, 137.5, 136.6, 128.03, 128.01, 127.2, 127.1, 124.6, 124.3, 123.6, 123.4, 85.8, 78.7, 55.2, 53.8, 21.6, 0.5, −0.2 (two sp^2 signals and one sp^3 signal were not observed because of overlapping)

((2-Cycloprpyl-1-ethoxyvinyl)oxy)trimethylsilane (5m)

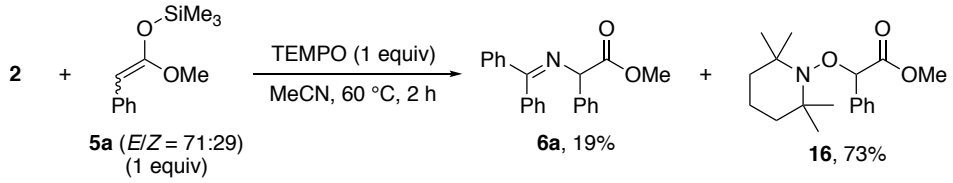


According to the reported procedure,[4d] the reaction using ester **S6** (2.5 g, 20 mmol), *n*-BuLi (1.6 M in hexane, 14 mL, 22 mmol), diisopropylamine (3 mL, 21 mmol), and chlorotrimethylsilane (4 mL, 32 mmol) gave the the crude mixture, which was purified by distillation to give the product as a colourless liquid (3.0 g, 75% yield). The product was obtained as a mixture of *E*/*Z* isomers (*E*/*Z* = 76:24). The configurations of the products were determined by comparing their ^{1}H NMR signals with the corresponding compounds.[4d] IR: (ATR) 2978, 1678, 1375, 1251, 1211, 1151, 841 cm^{-1}; MS: (EI) *m*/*z* 200 (M^+, 24), 82 (100), 75 (26), 73 (80); HRMS: (EI) calcd for ($C_{10}H_{20}O_2Si$) 200.1233 (M^+), found *m*/*z* 200.1233; ^{1}H NMR signals assigned from the mixture of isomers. **(*E* isomer)** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.88 (q, *J* = 7.2 Hz, 2H), 3.34 (d, *J* = 8.8 Hz, 1H), 1.49–1.36 (m, 1H), 1.31–1.21 (m, 3H), 0.65–0.58 (m, 2H), 0.20 (s, 9H), 0.19–0.14 (m, 2H); **(*Z* isomer)** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.64 (q, *J* = 7.2 Hz, 2H), 3.08 (d, *J* = 8.4 Hz, 1H), 1.49–1.36 (m, 1H), 1.31–1.21 (m, 3H), 0.65–0.58 (m, 2H), 0.23 (s, 9H), 0.19–0.14 (m, 2H); ^{13}C{^{1}H} NMR of a mixture of *E*/*Z* isomers: (100 MHz, $CDCl_3$) δ 155.8,

153.1, 90.5, 81.0, 63.1, 62.8, 14.9, 14.4, 7.1, 6.9, 6.4, 6.2, 0.3, −0.3

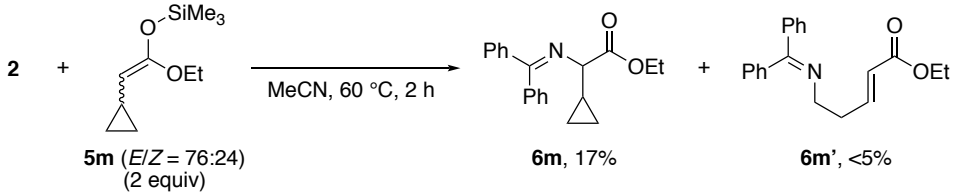
Mechanistic investigations

Oxidative amination 5a in the presence of TEMPO



An oven-dried 3 mL reaction vial containing a magnetic stir bar was charged with iodine reagent **2** (85.5 mg, 0.20 mmol), TEMPO (31.9 mg, 0.20 mmol), and MeCN (2 mL). Silyl ketene acetal **5a** (47.0 mg, 0.21 mmol) was added to the vial, and the mixture was stirred at 60 ºC for 2 h. Then, volatiles were removed under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.[18]

Oxidative amination of cyclopropane-containing 5m



A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with iodine reagent **2** (170.4 mg, 0.40 mmol) and MeCN (4 mL). Silyl ketene acetal **5m** (165.2 mg, 0.82 mmol) was added to the flask, and the mixture was stirred at 60 ºC for 2 h. Then, volatiles were removed under reduced pressure, and the residue was roughly purified by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) to give the product, which was analyzed by GC-MS (Figure S1) and ^{1}H NMR spectroscopy (Figure S2).

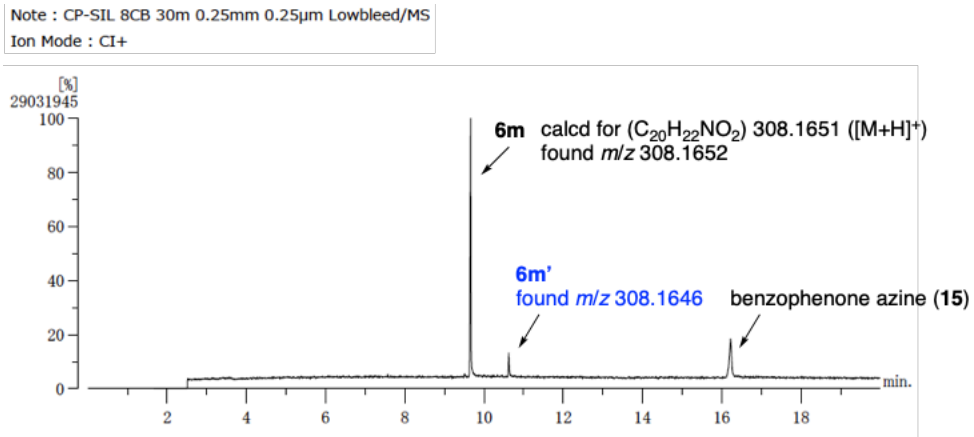


Figure S1.

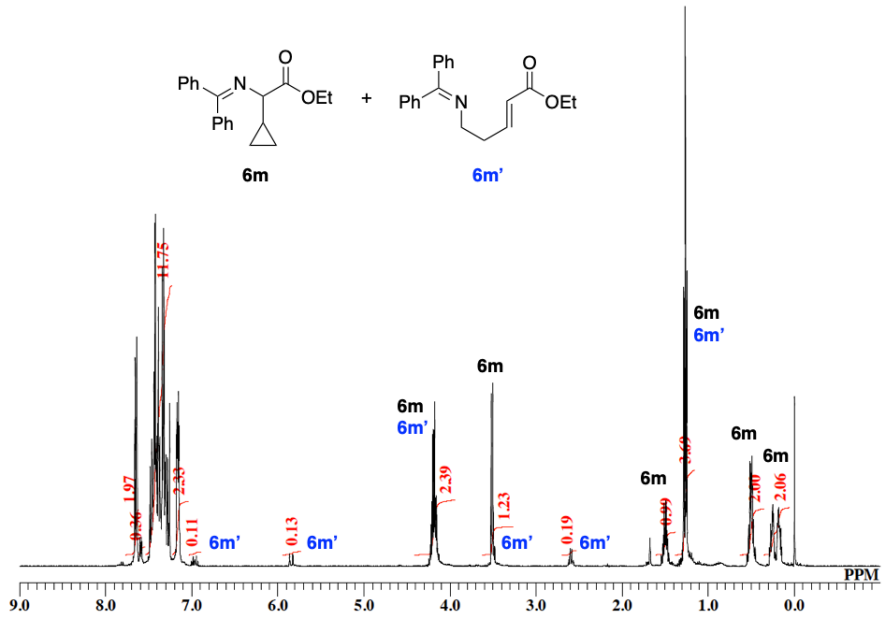
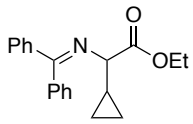


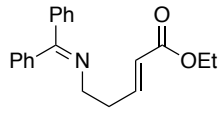
Figure S2.

Ethyl 2-cyclopropyl-2-((diphenylmethylene)amino)acetate (6m)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.73–7.60 (m, 2H), 7.56–7.28 (m, 6H), 7.22–7.12 (m, 2H), 4.29–4.09 (m, 2H), 3.51 (d, *J* = 7.6 Hz, 1H), 1.56–1.45 (m, 1H), 1.27 (dd, *J* = 7.0, 7.0 Hz, 3H), 0.56–0.40 (m, 2H), 0.31–0.14 (m, 2H); HRMS: (CI) calcd for ($C_{20}H_{22}NO_2$) 308.1651 ([M+H]$^+$), found *m*/*z* 308.1652

Ethyl (*E*)-5-((diphenylmethylene)amino)pent-2-enoate (6m')



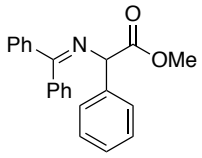
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70–7.10 (m, 10H), 6.95 (dt, *J* = 16.0, 6.8 Hz, 1H), 5.84 (d, *J* = 16.0 Hz, 1H), 4.17 (q, *J* = 6.8 Hz, 2H), 3.50 (t, *J* = 6.8 Hz, 2H), 2.59 (dt, *J* = 6.8, 6.8 Hz, 2H), 1.27 (t, *J* = 6.8 Hz, 3H); HRMS: (CI) calcd for ($C_{20}H_{22}NO_2$) 308.1651 ([M+H]$^+$), found *m*/*z* 308.1646

7. Oxidative amination of silyl ketene acetals: experimental procedure and product data

Typical procedure: An oven-dried 3 mL reaction vial or a heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with hypervalent iodine reagent **2** and MeCN. Silyl ketene acetal **5** was added to the vial or the flask, and the mixture was stirred at 60 ºC for the indicated time. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2) gave the product.

Product data

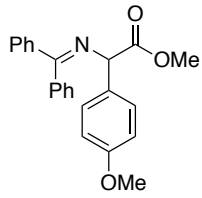
Methyl 2-((diphenylmethylene)amino)-2-phenylacetate (6a)



According to the typical procedure, the reaction using iodine reagent **2** (170.9 mg, 0.40 mmol), MeCN (2 mL), and silyl ketene acetal **5a** (133.0 mg, 0.60 mmol) was conducted at 60 ºC for 2 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) gave the product as a colorless liquid (109.3 mg), which contains a small amount of homocoupling products of **5a**. The yield of **6a** was determined by ^1H NMR analysis of the purified product which contains 0.31 mmol of **6a** (78% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.77–7.68 (m, 2H), 7.61–7.20 (m, 11H), 7.12–7.04 (m, 2H), 5.17 (s, 1H), 3.68 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.0, 170.3, 139.3, 139.1, 136.1, 130.5, 129.0, 128.8, 128.55 128.48, 128.0, 127.9, 127.8, 127.6, 69.5, 52.4

The analytical data for this compound were in excellent agreement with the reported data.[19]

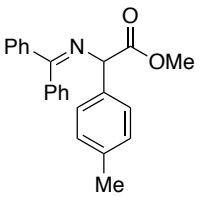
Methyl 2-((diphenylmethylene)amino)-2-(4-methoxyphenyl)acetate (6b)



According to the typical procedure, the reaction using iodine reagent **2** (170.9 mg, 0.40 mmol), MeCN (4 mL), and silyl ketene acetal **5b** (156.0 mg, 0.62 mmol) was conducted at 60 ºC for 2 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) gave the product as a colorless liquid (105.5 mg), which contains a small amount of homocoupling products of **5b**. The yield of **6b** was determined by ^1H NMR analysis of the purified product which contains 0.29 mmol of **6b** (73% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.76–7.68 (m, 2H), 7.51–7.28 (m, 8H), 7.13–7.03 (m, 2H), 6.90–6.82 (m, 2H), 5.11 (s, 1H), 3.79 (s, 3H), 3.68 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.3, 170.0, 159.1, 139.4, 136.1, 131.3, 130.4, 129.0, 128.9, 128.8, 128.5, 128.0, 127.6, 113.9, 68.9, 55.2, 52.4

The analytical data for this compound were in excellent agreement with the reported data.[19]

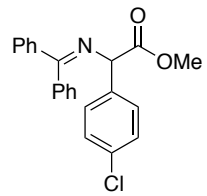
Methyl 2-((diphenylmethylene)amino)-2-(*p*-tolyl)acetate (6c)



According to the typical procedure, the reaction using iodine reagent **2** (171.5 mg, 0.40 mmol), MeCN (4 mL), and silyl ketene acetal **5c** (148.1 mg, 0.63 mmol) was conducted at 60 ºC for 2 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) gave the product (104.1 mg) as a colorless liquid, which contains a small amount of homocoupling products of **5c**. The yield of **6c** was determined by ^1H NMR analysis of the purified product which contains 0.29 mmol of **6c** (73% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.74–7.68 (m, 2H), 7.49–7.27 (m, 8H), 7.17–7.03 (m, 4H), 5.13 (s, 1H), 3.67 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.1, 170.0, 139.4, 137.5, 136.14, 136.08, 130.4, 129.2, 128.9, 128.7, 128.5, 128.0, 127.7, 127.6, 69.3, 52.3, 21.1

The analytical data for this compound were in excellent agreement with the reported data.[19]

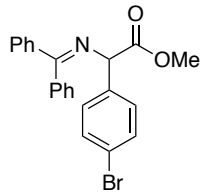
Methyl 2-(4-chlorophenyl)-2-((diphenylmethylene)amino)acetate (6d)



According to the typical procedure, the reaction using iodine reagent **2** (171.7 mg, 0.40 mmol), MeCN (4 mL), and silyl ketene acetal **5d** (135.1 mg, 0.53 mmol) was conducted at 60 ºC for 2 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) gave the product as a colorless liquid (127.5 mg), which contains a small amount of homocoupling products of **5d**. The yield of **6d** was determined by ^1H NMR analysis of the purified product which contains 0.33 mmol of **6d** (83% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.77–7.67 (m, 2H), 7.53–7.28 (m, 10H), 7.11–7.01 (m, 2H), 5.12 (s, 1H), 3.68 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 171.5, 170.7, 139.1, 137.5, 135.9, 133.6, 130.6, 129.2, 128.92, 128.88, 128.6, 128.0, 127.5, 68.8, 52.5 (one sp^2 signal was not observed because of overlapping)

The analytical data for this compound were in excellent agreement with the reported data.[19]

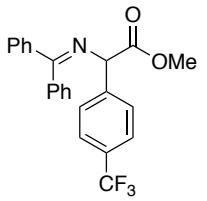
Methyl 2-(4-bromophenyl)-2-((diphenylmethylene)amino)acetate (6e)



According to the typical procedure, the reaction using iodine reagent **2** (170.8 mg, 0.40 mmol), MeCN (4 mL), and silyl ketene acetal **5e** (150.4 mg, 0.50 mmol) was conducted at 60 ºC for 2 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) gave the product as a colorless liquid (130.5 mg), which contains a small amount of homocoupling products of **5e**. The yield of **6e** was determined by ^1H NMR analysis of the purified product which contains 0.30 mmol of **6e** (76% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.75–7.66 (m, 2H), 7.57–7.20 (m, 10H), 7.14–7.01 (m, 2H), 5.11 (s, 1H), 3.67 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 171.5, 170.8, 139.1, 138.0, 135.8, 131.6, 130.6, 129.6, 128.92, 128.90, 128.6, 128.0, 127.5, 121.8, 68.8, 52.5

The analytical data for this compound were in excellent agreement with the reported data.[19]

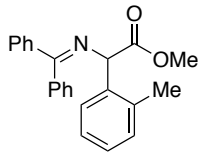
Methyl 2-((diphenylmethylene)amino)-2-(4-(trifluoromethyl)phenyl)acetate (6f)



According to the typical procedure, the reaction using iodine reagent **2** (170.7 mg, 0.40 mmol), MeCN (4 mL), and silyl ketene acetal **5f** (181.2 mg, 0.62 mmol) was conducted at 60 ºC for 2 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) gave the product as a colorless liquid (140.3 mg), which contains a small amount of homocoupling products of **5f**. The yield of **6f**. was determined by ^1H NMR analysis of the purified product which contains 0.34 mmol of **6f** (84% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.80–7.70 (m, 2H), 7.67–7.53 (m, 4H), 7.52–7.30 (m, 6H), 7.13–7.05 (m, 2H), 5.22 (s, 1H), 3.68 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 171.2, 171.1, 142.9,

139.0, 135.8, 130.7, 129.9 (q, $J_{C–F}$ = 32.1 Hz), 129.0, 128.9, 128.6, 128.3, 128.1, 127.5, 125.4 (q, $J_{C–F}$ = 4.1 Hz), 124.0 (q, $J_{C–F}$ = 270.0 Hz), 69.0, 52.5; $^{19}F\{^1H\}$ NMR: (377 MHz, $CDCl_3$) δ −63.6; IR: (ATR) 3059, 1744, 1618, 1323, 1163, 1123, 1067, 1018, 733 cm^{-1}; HRMS: (CI) calcd for ($C_{23}H_{19}F_3NO_2$) 398.1368 ($[M+H]^+$), found *m*/*z* 398.1365

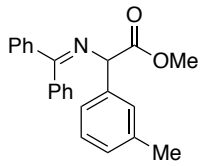
Methyl 2-((diphenylmethylene)amino)-2-(*o*-tolyl)acetate (6g)



According to the typical procedure, the reaction using iodine reagent **2** (170.5 mg, 0.40 mmol), MeCN (4 mL), and silyl ketene acetal **5g** (144.6 mg, 0.61 mmol) was conducted at 60 ºC for 2 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) gave the product as a colorless liquid (102.8 mg, 75% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.76–7.68 (m, 2H), 7.63–7.55 (m, 1H), 7.47–7.30 (m, 6H), 7.23–7.12 (m, 2H), 7.11–7.04 (m, 3H), 5.33 (s, 1H), 3.68 (s, 3H), 2.05 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.2, 170.2, 139.3, 137.9, 136.4, 135.9, 130.4, 130.3, 128.9, 128.8, 128.7, 128.6, 128.0, 127.5, 126.2, 66.5, 52.3, 19.2 (one sp^2 signal was not observed because of overlapping)

The analytical data for this compound were in excellent agreement with the reported data.[19]

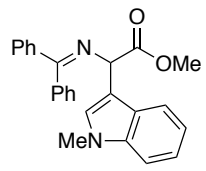
Methyl 2-((diphenylmethylene)amino)-2-(*m*-tolyl)acetate (6h)



According to the typical procedure, the reaction using iodine reagent **2** (171.2 mg, 0.40 mmol), MeCN (4 mL), and silyl ketene acetal **5h** (141.8 mg, 0.60 mmol) was conducted at 60 ºC for 2 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) gave the productas a colorless liquid (106.1 mg), which contains a small amount of homocoupling products of **5h**. The yield of **6h** was determined by ^1H NMR analysis of the purified product which contains 0.30 mmol of **6h** (75% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.77–7.68 (m, 2H), 7.56–7.29 (m, 6H), 7.28–7.15 (m, 3H), 7.14–7.03 (m, 3H), 5.13 (s, 1H), 3.68 (s, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.1, 170.2, 139.4, 138.9, 138.1, 136.1, 130.4, 129.0, 128.8, 128.6, 128.50, 128.45, 128.3, 128.0, 127.7, 124.9, 69.6, 52.4, 21.4

The analytical data for this compound were in excellent agreement with the reported data.[19]

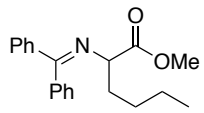
Methyl 2-((diphenylmethylene)amino)-2-(1-methyl-1*H*-indol-3-yl)acetate (6i)



A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with iodine reagent **2** (170.8 mg, 0.40 mmol) and MeCN (4 mL). Silyl ketene acetal **5i** (86% purity, 208.1 mg, 0.65 mmol) was added to the flask at −10 ºC, and the mixture was stirred at −10 ºC for 1 h and at room temperature for 5 h. Then, volatiles were removed under reduced pressure to give the crude product. Purification by flash column

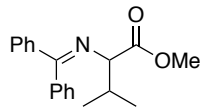
chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 9:1) gave the product as a pale-yellow liquid (84.6 mg, 55% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.76–7.68 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.50–7.17 (m, 8H), 7.16–7.05 (m, 4H), 5.49 (s, 1H), 3.76 (s, 3H), 3.68 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.4, 169.6, 139.6, 136.8, 135.9, 130.3, 128.9, 128.7, 128.5, 127.9, 127.8, 127.5, 126.2, 121.6, 120.0, 119.2, 112.6, 109.2, 63.0, 52.3, 32.8; IR: (ATR) 3053, 2951, 1738, 1616, 1472, 1153, 908 cm^{-1}; HRMS: (EI) calcd for ($C_{25}H_{22}N_2O_2$) 382.1681 (M^+), found *m*/*z* 382.1680

Methyl 2-((diphenylmethylene)amino)hexanoate (6j)



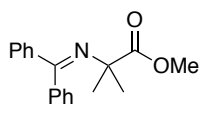
According to the typical procedure, the reaction using iodine reagent **2** (170.0 mg, 0.40 mmol), MeCN (2 mL), and silyl ketene acetal **5j** (162.0 mg, 0.80 mmol) was conducted at 60 ºC for 24 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) followed by removal of a precipitation of benzophenone azine with hexane gave the product as a colorless liquid (63.1 mg, 51% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70–7.60 (m, 2H) 7.54–7.28 (m, 6H), 7.23–7.12 (m, 2H), 4.07 (dd, *J* = 8.0, 5.4 Hz, 1H), 3.72 (s, 3H), 2.00–1.83 (m, 2H), 1.35–1.06 (m, 4H), 0.85 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.1, 170.2, 139.5, 136.4, 130.3, 128.8, 128.6, 128.5, 128.0, 127.8, 65.4, 52.0, 33.5, 28.1, 22.4, 13.9; IR: (ATR) 2955, 2930, 1736, 1622, 1445, 1196, 779 cm^{-1}; HRMS: (CI) calcd for ($C_{20}H_{24}NO_2$) 310.1807 ($[M+H]^+$), found *m*/*z* 310.1811

Methyl 2-((diphenylmethylene)amino)-3-methylbutanoate (6k)



According to the typical procedure, the reaction using iodine reagent **2** (170.9 mg, 0.40 mmol), MeCN (2 mL), and silyl ketene acetal **5k** (150.5 mg, 0.80 mmol) was conducted at 60 ºC for 12 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) followed by removal of a precipitation of benzophenone azine with hexane gave the product as a colorless liquid (74.4 mg, 63% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70–7.62 (m, 2H), 7.54–7.28 (m, 6H), 7.18–7.07 (m, 2H), 3.86 (d, *J* = 6.4 Hz, 1H), 3.72 (s, 3H), 2.36 (dqq, *J* = 6.4, 6.4, 6.4 Hz, 1H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.6, 170.5, 139.7, 136.5, 130.2, 128.8, 128.5, 128.4, 128.0, 127.9, 71.4, 51.9, 32.4, 19.5, 18.4; IR: (ATR) 2961, 1734, 1622, 1447, 1252, 1198, 1022, 781 cm^{-1}; HRMS: (CI) calcd for ($C_{19}H_{22}NO_2$) 296.1651 ($[M+H]^+$), found *m*/*z* 296.1649

Methyl 2-((diphenylmethylene)amino)-2-methylpropanoate (6l)



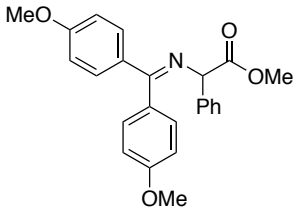
According to the typical procedure, the reaction using iodine reagent **2** (171.8 mg, 0.40 mmol), MeCN (2 mL), and silyl ketene acetal **5l** (118.9 mg, 0.68 mmol) was conducted at 60 ºC for 16 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) followed by removal of a precipitation of

benzophenone azine with hexane gave the product as a colorless liquid (65.3 mg, 58% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.60–7.51 (m, 2H), 7.47–7.25 (m, 6H), 7.19–7.11 (m, 2H), 3.29 (s, 3H), 1.54 (s, 6H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 175.7, 166.7, 141.0, 136.9, 129.9, 128.6, 128.5, 128.4, 127.9, 127.7, 63.4, 51.4, 28.8

The analytical data for this compound were in excellent agreement with the reported data.[20]

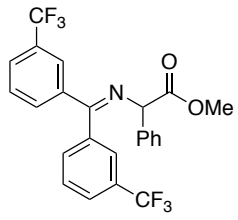
Methyl 2-((bis(4-methoxyphenyl)methylene)amino)-2-phenylacetate (11)

According to the typical procedure, the reaction using iodine reagent **3** (194.6 mg, 0.40 mmol), MeCN (4 mL), and silyl ketene acetal **5a** (135.4 mg, 0.61 mmol) was conducted at 60 ºC for 2 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) gave the product as a colorless liquid (112.1 mg, 72% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 7.2 Hz, 2H), 7.37–7.22 (m, 3H), 7.01 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.19 (s, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.68 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.3, 169.6, 161.4, 159.7, 139.4, 132.7, 130.7, 129.2, 128.4, 128.3, 127.8, 127.6, 113.8, 113.2, 69.5, 55.30, 55.26, 52.3; IR: (ATR) 2951, 2837, 1738, 1599, 1508, 1246, 1173, 1030, 908, 837 cm^{-1}; HRMS: (CI) calcd for ($C_{24}H_{24}NO_4$) 390.1705 ([M+H]$^{+}$), found m/z 390.1709

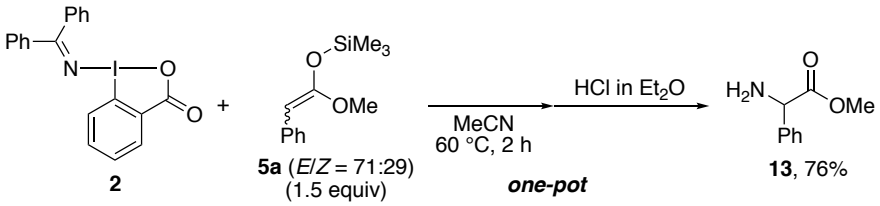


Methyl 2-((bis(3-trifluoromethyl)phenyl)methylene)amino)-2-phenylacetate (12)

According to the typical procedure, the reaction using iodine reagent **4** (222.4 mg, 0.39 mmol), MeCN (4 mL), and silyl ketene acetal **5a** (136.3 mg, 0.61 mmol) was conducted at 60 ºC for 2 h. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/CH_2Cl_2 = 99:1) gave the product as a colorless liquid (138.1 mg), which contains a small amount of homocoupling products of **5a**. The yield of **12** was determined by ^{1}H NMR analysis of the purified product which contains 0.28 mmol of **12** (70% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.83–7.76 (m, 2H), 7.73–7.61 (m, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.44–7.29 (m, 7H), 5.02 (s, 1H), 3.70 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.3, 167.2, 139.3, 138.3, 135.9, 132.2, 131.4 (q, $J_{C–F}$ = 32.1 Hz), 130.9, 130.8 (q, $J_{C–F}$ = 32.1 Hz), 129.5, 128.8, 128.7, 128.2, 127.9, 127.4 (q, $J_{C–F}$ = 4.9 Hz), 126.2 (q, $J_{C–F}$ = 4.1 Hz), 125.3 (q, $J_{C–F}$ = 4.1 Hz), 124.5 (q, $J_{C–F}$ = 4.2 Hz), 123.8 (q, $J_{C–F}$ = 270.9 Hz), 123.6 (q, $J_{C–F}$ = 271.7 Hz), 69.8, 52.5; ^{19}F{^{1}H} NMR: (377 MHz, $CDCl_3$) δ −63.7, −63.9; IR: (ATR) 3032, 1744, 1626, 1435, 1329, 1250, 1167, 1125, 1072, 908, 810, 725 cm^{-1}; HRMS: (CI) calcd for ($C_{24}H_{18}F_6NO_2$) 466.1242 ([M+H]$^{+}$), found m/z 466.1236



Synthesis of the primary amine 13 via a one-pot procedure



A heat-gun-dried 10 mL reaction flask containing a magnetic stir bar was charged with iodine reagent **2** (171.4 mg, 0.40 mmol) and MeCN (4 mL). Silyl ketene acetal **5a** (136.6 mg, 0.61 mmol) was added to the flask, and the mixture was stirred at 60 ºC for 2 h. Then, volatiles were removed under reduced pressure. THF (2 mL) and HCl (1 M in Et_2O, 5 mL) was added to the residue, and the mixture was stirred at room temperature for 5 h. The reaction mixture was diluted with H_2O (10 mL) and washed with Et_2O (3 x 10 mL), and the collected water layers was concentrated under reduced pressure. Then, the residue was basified with sat. $NaHCO_3$ aq. until pH = 9. The mixture was extracted with EtOAc (3 x 10 mL) and the collected organic layers was concentrated under reduced pressure to give the product **13** as a pale yellow liquid (50.5 mg, 76% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.45–7.20 (m, 5H), 4.63 (s, 1H), 3.71 (s, 3H), 1.94 (brs, 2H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.3, 140.1, 128.7, 127.9, 126.7, 58.6, 52.3

The analytical data for this compound were in excellent agreement with the reported data.[19]

2-5. References and Notes

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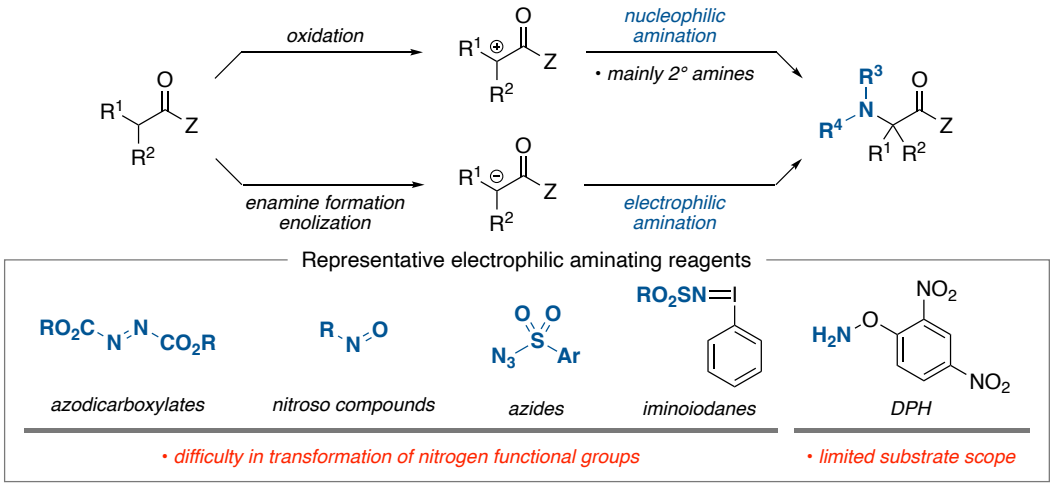
Chapter 2

α-Amination of Carbonyl Compounds Using (Diarylmethylene)amino Benziodoxolones

2-1. Introduction

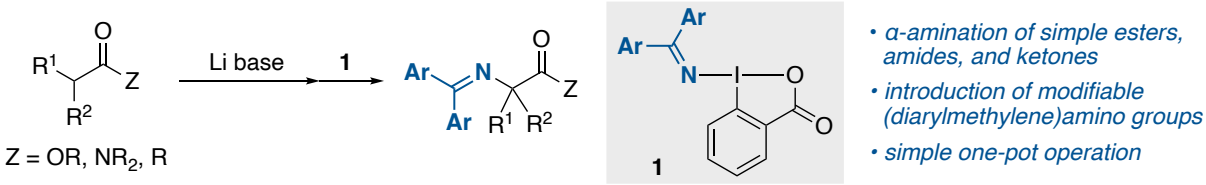
α-Amino carbonyl compounds are an important class of compounds that are frequently found in natural products and biologically active molecules.[1] Because of this, substantial efforts have been devoted to the development of methodologies for the synthesis of these types of compounds.[2] Oxidative amination in which an amino functionality is introduced at the α-position of a carbonyl compound is one of the most straightforward approaches, which can be classified into two types, namely, nucleophilic and electrophilic amination (Scheme 1, top). The nucleophilic amination strategy generally requires the preparation of electrophilic α-halogenated carbonyl compounds and the use of nucleophilic secondary amines.[3] Although some elegant umpolung strategies for the activation of carbonyl compounds have emerged,[4] the nucleophilic strategy is still not suitable for the synthesis of primary amines. The electrophilic amination of enamines, enolates, and enolate equivalents, however, represents an alternative approach. Despite the great advances associated with this type of reaction, which involves the use of several common electrophilic aminating reagents such as azodicarboxylates,[5] nitroso compounds,[6] azides,[7] and iminoiodanes,[8] a general problem is that the deprotection/modification of the amino functionalities that were installed for accessing the target molecules including primary amines requires multistep reactions under relatively harsh reaction conditions (Scheme 1, bottom).[9] In recent years, several useful α-amination reactions of carbonyl compounds have been developed with the goal of introducing a wide range of amino functionalities including readily modifiable ones.[10] Those methods, however, involve the use of activated carbonyl compounds such as acylpyrazoles and oxyindoles or separately prepared silyl enolates. Indeed, hydroxylamine derivatives, for example,

2,4-dinitrophenyl hydroxylamine (DPH), enable the direct synthesis of primary amines, but the reported methods still suffer from their limited scope.[11] In this context, the development of the general approach to α-amination that can be used to convert simple carbonyl compounds into easily modifiable α-amino carbonyl compounds, especially primary amines, remains a challenging task.



Scheme 1. Oxidative amination for the synthesis of α-amino carbonyl compounds

As described in Chapter 1, the author developed (diarylmethylene)amino benziodoxolones (DABXs) **1** and demonstrated that they can react with silyl ketene acetals to provide α-(diarylmethylene)amino esters.[12] However, the preparation and isolation of silyl ketene acetals are often laborious, thus diminishing the efficiency of the net reaction, and the amination was only feasible for ester-derived enolates. In Chapter 2, the author examined the oxidative amination of a series of lithium enolates derived from unactivated simple carbonyl compounds such as esters, amides, and ketones in the presence of **1** and lithium bases (Scheme 2).



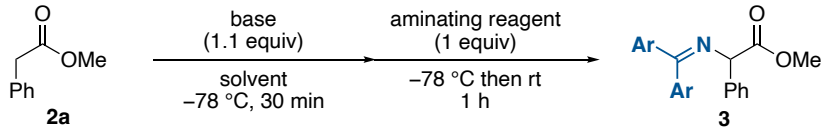
Scheme 2. This work

2-2. Results and Discussion

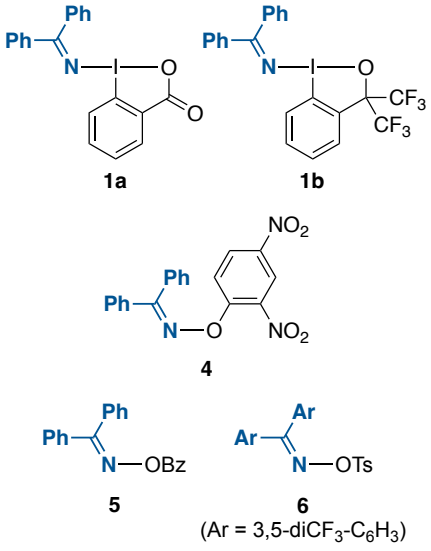
Oxidative amination of methyl phenylacetate (**2a**) through enolate formation was examined as the model reaction, and a series of metal bases were screened (Table 1). Preparing the lithium enolate of **2a**

in situ with lithium diisopropylamide (LDA) in THF at −78 °C, followed by the subsequent addition of the aminating reagent **1a** was found to provide the α-amino ester **3aa** (Ar = Ph) in 58% yield (Entry 1). The amination also proceeded using LiOtBu, but the yield of **3aa** was deceased slightly (Entry 2). When amide bases were used, the product yield was improved to 68% when the reaction was conducted with lithium hexamethyldisilazide (LiHMDS) (Entry 3), while the use of other alkali metal amides such as NaHMDS and KHMDS resulted in a lower efficiency (Entries 4 and 5). Examining the reaction in other ethereal solvents revealed that THF is suitable for this amination (Entries 3 and 6–8). Instead of **1a**, the use of the newly synthesized benziodoxole-based reagent **1b** led to a lower yield of **3aa** (Entry 9). Although benzophenone oxime derivatives can function as electrophilic aminating reagents,[13] using **4**–**6** failed to afford the target product (Entries 10–12), demonstrating the superiority of hypervalent iodine reagent **1**. Increasing the amounts of aminating reagent **1a** was effective in improving the yield, and employing 1.2 equivalents of **1a** was found to provide the highest yield of **3aa** (Entry 13). In this amination, a small amount of dimers of **2a** was obtained as a side reaction product, which is probably generated through a competitive dimerization of the lithium enolates under oxidative conditions.

Table 1. Survey of bases, solvents, and aminating reagents[a]

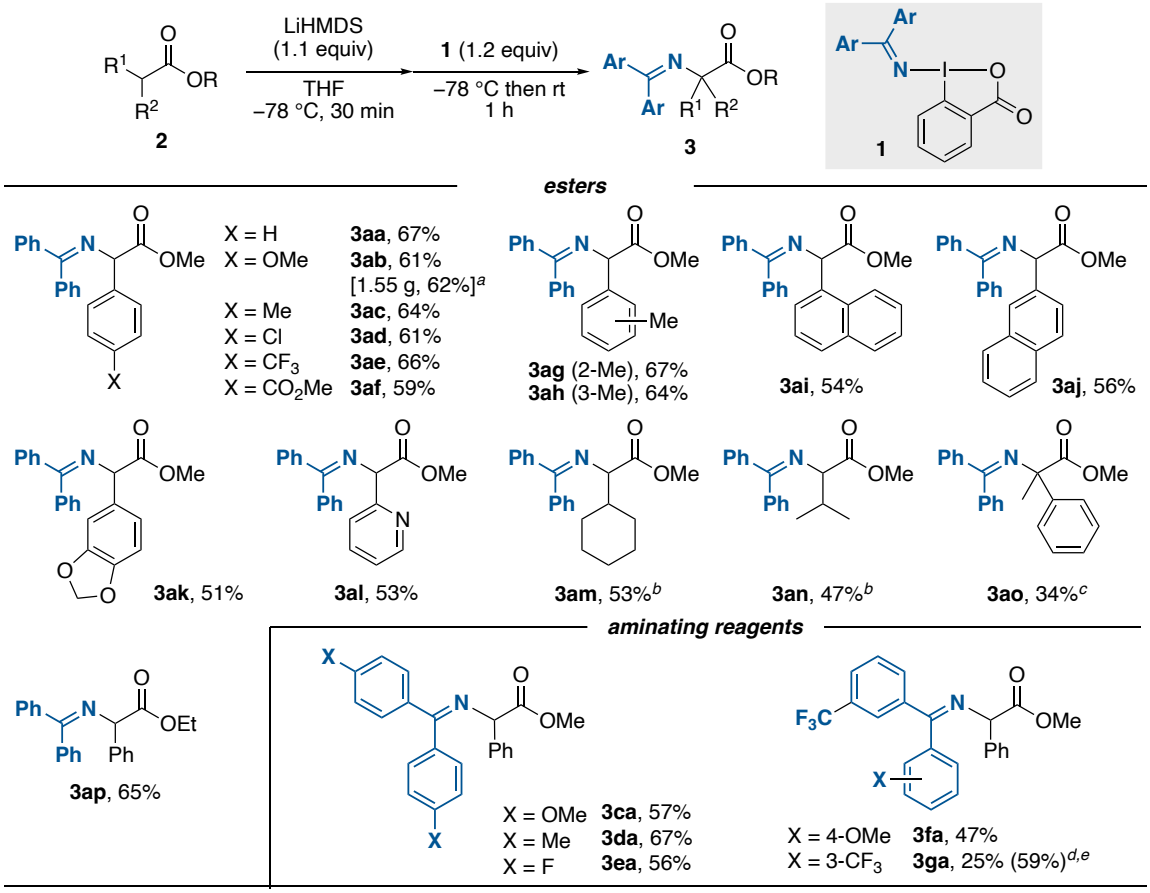


Entry	Base	Solvent	Aminating reagent	Yield [%][b]
1	LDA	THF	**1a**	58
2	LiO*t*Bu	THF	**1a**	55
3	LiHMDS	THF	**1a**	68
4	NaHMDS	THF	**1a**	51
5	LiHMDS	THF	**1a**	15
6	LiHMDS	DME	**1a**	56
7	LiHMDS	CPME	**1a**	54
8	LiHMDS	MTHP	**1a**	53
9[c]	LDA	THF	**1b**	34
10[c]	LDA	THF	**4**	<5
11[c]	LDA	THF	**5**	0
12[c]	LDA	THF	**6**	0
13[d]	LiHMDS	THF	**1a**	78 (67)[e]



[a] Reactions were performed on a 0.4 mmol scale. [b] Determined by ^{1}H NMR analysis of the crude product. A value in parenthesis is an isolated yield. [c] Reactions were performed on a 0.2 mmol scale. [d] **1a** (1.2 equiv) was used. [e] Dimers of **2a** were obtained in 7% yields (0.014 mmol).

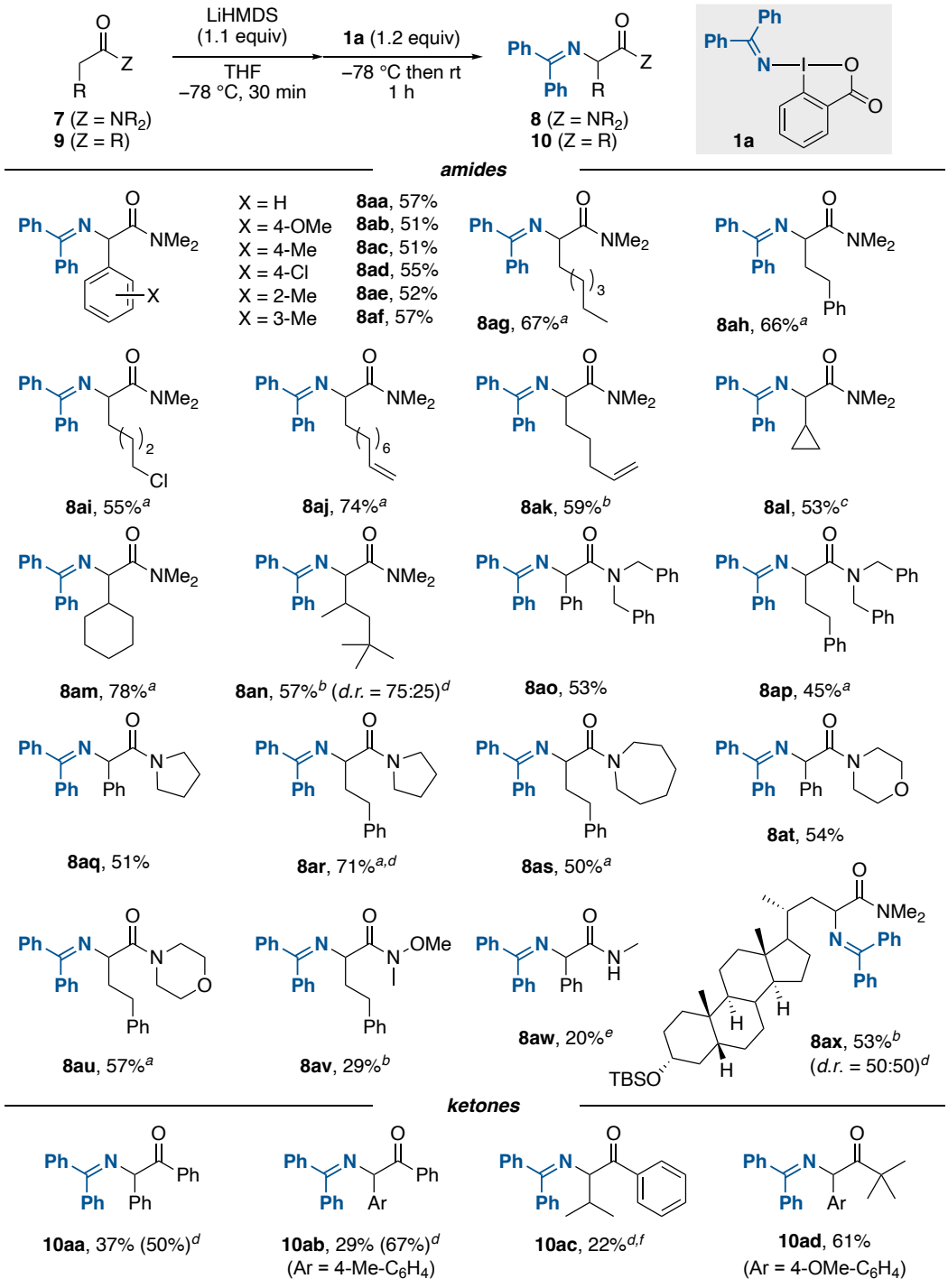
The author next evaluated the generality of the amination of esters using hypervalent iodine reagent **1** (Scheme 3). Esters bearing an aryl group at the α-position, which were converted into lithium enolates, participated in the oxidative amination with **1a**, providing the corresponding α-amino esters **3** in good yields. The synthetic utility of this one-pot method was also demonstrated by a gram-scale reaction using **2b** to afford **3ab** without any loss of yield (62%). The amination of esters bearing electron-rich as well as electron-deficient aromatic rings proceeded well (**3ab**–**3af**), in which functional groups such as chloro (**3ad**), trifluoromethyl (**3ae**), ester (**3af**) groups on the aromatic ring were well tolerated. The presence of *ortho*- and *meta*-substituents had almost no effect on the efficiency of the reaction for the formation of **3ag** and **3ah**, respectively. These results indicate that this amination is not sensitive to the electronic and steric nature of the α-aryl groups. Substrates bearing fused aromatic rings such as naphthyl (**3ai** and **3aj**) and 3,4-methylenedioxyphenyl (**3ak**) groups also reacted efficiently. The presence of a pyridyl group had no effect on the reaction, with **3al** being formed in good yield. In addition, esters including aliphatic substituents at the α-position were also suitable substrates for this amination (**3am** and **3an**). Notably, the sterically demanding **3ao** containing an α-tertiary amine moiety could be synthesized. The amination of ethyl ester also proceeded with a similar efficiency (**3ap**). The scope of the amino functionality was also investigated by using various hypervalent iodine reagents **1** containing a series of (diarylmethylene)amino groups which can be converted into useful diarylmethylamino groups. Derivatives containing electronically varied imine moieties could be used to deliver the corresponding products **3ca**–**3ga**, indicating that this amination was not significantly influenced by the electronic properties of the (diarylmethylene)amino group.



Scheme 3. Scope of esters and Aminating Reagents. Reactions were performed on a 0.2 or 0.4 mmol scale. Yields are isolated yields. [a] Reaction was conducted on a 7 mmol scale. [b] LDA was used instead of LiHMDS. [c] Lithiation was conducted for 2 h from –78 to –40 °C. [d] Determined by ^{1}H NMR analysis of the crude product. [e] *E*/*Z* mixture.

The α-amination of amides is an attractive transformation for accessing biologically important molecules.[4b,d,5c] However, owing to limited methods that are currently available for the preparation of amide-derived enolates due to the relatively low acidity of α-protons of simple amides,[14] such reactions have been limited to activated substrates.[5a,8c,10d] To our delight, the present amination using **1a** could be successfully applied to the amination of simple amides and ketones (Scheme 4). The amination of *N*,*N*-dimethyl amides bearing aryl substituents at the α-position proceeded readily when **1a** was used in the presence of LiHMDS as a base (**8aa**–**8af**). Amides that contain α-alkyl substituents show a lower acidity than those containing α-aromatic substituents, and the amination of these substrates was achieved by the use of LDA instead of LiHMDS (**8ag**–**8an**). Notably, a benzylic C–H, an alkyl chloride, and a terminal alkene (an allylic C–H) were well-tolerated under the present oxidative conditions (**8ah**–**8ak**). Interestingly, the use of *N*,*N*-dimethylhept-6-enamide as a substrate afforded only the corresponding α-aminated product **8ak** without the formation of a cyclized product. In addition, a

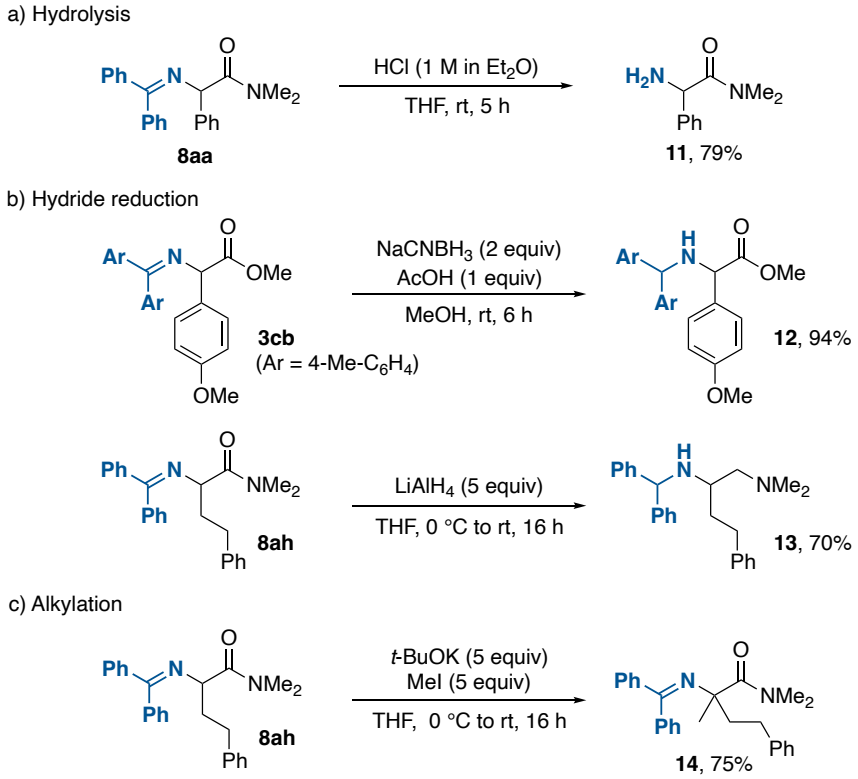
cyclopropyl group at the α-position also remained untouched in the present amination, and no ring-opening product, only the α-aminated product **8al** was obtained. These results indicate the difference in reactivity between lithium enolates and silyl ketene acetals[12] in aminations with **1** (see below). Amides containing sterically hindered alkyl substituents at the α-position also efficiently participated in the amination (**8am** and **8an**), albeit with poor diastereoselectivity. In addition, various types of secondary amine-derived amides, such as *N*,*N*-dibenzyl-, pyrrolidine-, azepane-, and morpholine-derived amides were also found to be suitable substrates (**8ao**–**8au**). This method was also applicable for a Weinreb amide and an *N*-methyl amide (**8av** and **8aw**). Moreover, the *tert*-butyldimethylsilyl (TBS)-protected lithocholic acid derivative reacted smoothly (**8ax**). α-Aminoketones could also be synthesized using the present method. Benzyl phenyl ketones readily underwent amination to provide the corresponding products although the products partially decomposed during isolation using silica gel column chromatography, which led to diminished isolated yields (**10aa** and **10ab**). Isovalerophenone was also aminated even in low yield due to the production of a considerable amount of dimers derived from the starting ketone (**10ac**). As an aliphatic ketone, a *tert*-butyl ketone could be applied to the amination (**10ad**).



Scheme 4. Scope of amides and ketones. Reactions were performed on a 0.2 or 0.4 mmol scale. Yields are isolated yields. [a] Amides (1.5 equiv), LDA (1.7 equiv), and **1a** (1equiv) were used. [b] LDA was used instead of LiHMDS. [c] $LiNCy_2$ (lithium dicyclohexylamide) was used instead of LiHMDS. [d] Determined by ^1H NMR analysis of the crude product. [e] LDA (2.2 equiv) was used instead of LiHMDS. [f] Ketone (1.5 equiv), LDA (1.7 equiv), and **1a** (1 equiv) were used.

The synthetic utility of the α-amino carbonyl compounds synthesized by the developed amination was demonstrated by transforming the products into various amine derivatives (Scheme 5). The (diarylmethylene)amino group of the amide product **8aa** was easily hydrolyzed under acidic conditions

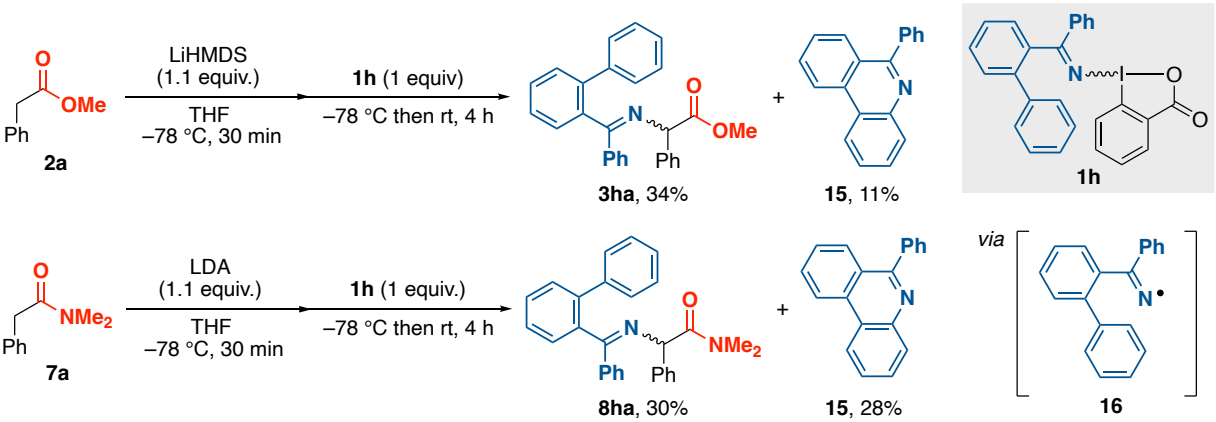
at ambient temperature to provide the α-amino amide **11**, demonstrating that the present amination is a useful tool for the synthesis of primary amines (Scheme 5a). A selective hydride reduction of the imine moiety of **3cb** to a diarylmethylamino group was successful, furnishing **12** in excellent yield (Scheme 5b). In addition, the reduction of the amide **8ah** with $LiAlH_4$ allowed for the synthesis of the diamines **13**. The α-alkylation of α-aminoamides 8ah was also feasible thus allowing an α-tertiary carbon center to be constructed (Scheme 5c). This complements the synthesis of sterically congested α-tertiary amino carbonyl compounds.



Scheme 5. Transformations of α-amino carbonyl products

Mechanistic aspects of the present oxidative amination were also investigated (Schemes 6 and 7). Based on the amination of silyl ketene acetals proceeds in a radical manner in Chapter 1 and the fact that small amounts of dimers of starting carbonyl compounds and benzophenone azine were generated under the present reaction conditions,[15] the possibility that the amination of lithium enolates proceeds through a radical pathway was studied. To confirm the participation of an iminyl radical species, an intramolecular iminyl radical trapping experiment was conducted using the hypervalent iodine reagent **1h**, resulting in the production of the α-amino ester **3ha** in 34% yield along with phenanthridine **15**

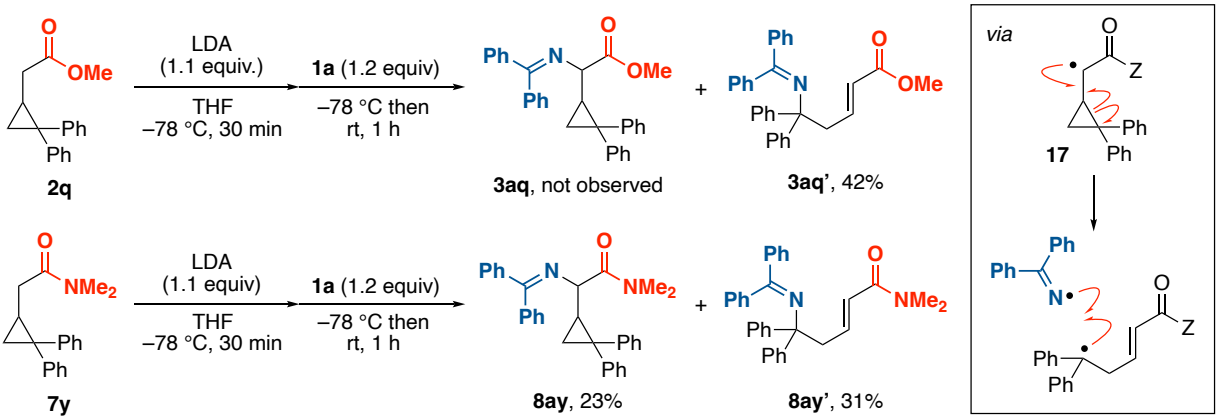
being produced (Scheme 6). Similar results were obtained in the case of the reaction with amide **7a**, in which both the α-aminated products **8ha** and **15** were also generated. Given that **15** is formed through the intramolecular trapping of the iminyl radical **16** generated *in situ*,[15b] the amination would be predicted to proceed through a radical mechanism involving the formation of an iminyl radical species. The production of a certain amount of α-aminated products **3ha** and **8ha** can be explained by a slow rate of cyclization of the iminyl radical **16**,[16] thus leading to the intermolecular coupling reaction being the preferred pathway. Meanwhile, other reaction pathways that do not involve an iminyl radical species cannot be excluded at this time (see below).



Scheme 6. Intramolecular iminyl radical trapping experiments

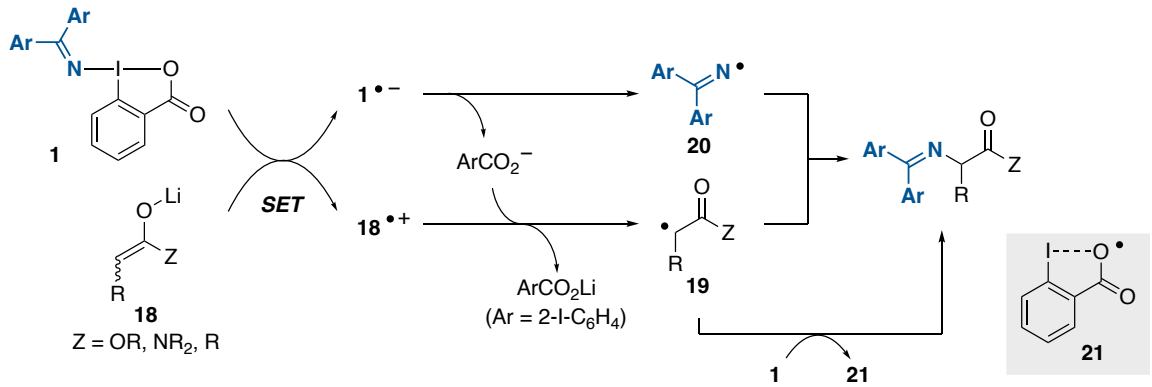
In order to confirm the participation of an α-carbonyl radical species, the author next investigated the use of substrates containing 2,2-diphenylcyclopropyl moiety at the α-position in reactions, the corresponding α-carbonyl radical is known to undergo ring-opening at a diffusion-limited rate, and therefore overcoming the intermolecular coupling (Scheme 7).[17] When the ester **2q** was subjected to the amination reaction conditions, the ring-opening product **3aq'** was formed in 42% yield and the cyclopropane-containing aminated product **3aq** was not detected, clearly indicating that an α-carbonyl radical **17** is generated in the reaction. Meanwhile, the amination of amide **7y** provided a mixture of **8ay** and **8ay'**. Although the reaction was proven to proceed preferentially through a radical pathway, the unexpected formation of **8ay** strongly indicates that the reaction of amide-derived lithium enolates involves an ionic amination process.[3f,4c,18] As mentioned above, reactions using hept-6-enamide and cyclopropaneacetamide as substrates provided only the α-aminated products **8ak** and **8al**, respectively

(Scheme 4). These products could also be preferentially formed through a radical pathway in addition to an ionic one, probably because of a relatively slow rate of cyclization and ring-opening of the corresponding α-carbonyl radical intermediates that are generated *in situ* from an aggregated lithium enolate.[19]



Scheme 7. Cyclopropane ring-opening experiments

Based on the experimental results, the proposed radical pathway as the main route for the amination of lithium enolates is depicted in Scheme 8. The reaction is initiated through a single-electron transfer (SET) from the lithium enolate **18** to the hypervalent iodine reagent **1**. The resulting radical cation and anion species are then rapidly decomposed to form the α-carbonyl radical **19** and the iminyl radical **20**, respectively, which are then rapidly coupled to produce the α-amino carbonyl compound. An alternative pathway in which the generated α-carbonyl radical **21** reacts directly with **1** cannot be excluded at this time and may be possible. The resulting *ortho*-iodobenzoyloxy radical **21** would be capable of oxidizing lithium enolates,[20,21] thereby realizing a radical-chain process.



Scheme 8. Proposed reaction pathway

2-3. Conclusion

In conclusion, the author reports a general method for the α-amination of simple carbonyl compounds by using DABXs; a rection that proceeds via the formation of a lithium enolate species. The developed amination is widely applicable to esters, ketones, and even amides. The synthetic utility of the α-aminated products was demonstrated by the facile transformation of some of them to valuable functionalized molecules. Experimental mechanistic studies revealed the unique reactivity of the hypervalent iodine reagent **1**, which enables the amination to proceed through a radical coupling of iminyl radical species and α-carbonyl radical species. It should also be noted that the amination of amide-derived lithium enolates would involve an ionic amination process. The present method offers a simple, practical, and straightforward approach to accessing easily modifiable α-amino carbonyl compounds.

2-4. Experimental Section

General Remarks

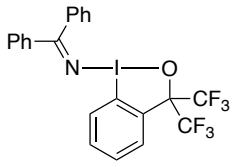
New compounds were characterized by ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, $^{19}F\{^{1}H\}$ NMR, IR, MS, and HRMS. ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer (^{1}H NMR, 400 MHz; $^{13}C\{^{1}H\}$ NMR, 100 MHz, $^{19}F\{^{1}H\}$ NMR, 377 MHz). ^{1}H NMR chemical shifts were determined relative to Me_4Si (0.0 ppm) as an internal standard. $^{13}C\{^{1}H\}$ NMR chemical shifts were determined relative to $CDCl_3$ (77.0 ppm). $^{19}F\{^{1}H\}$ NMR chemical shifts were determined relative to C_6F_6 (−164.9 ppm) as an external standard. Infrared spectra were recorded on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. Mass spectra were obtained on a SHIMADZU GCMS-QP2010 mass spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-700 mass spectrometer (magnetic sector type mass spectrometer). Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. The X-ray diffraction data of the single crystal were collected on a two-dimensional X-ray detector (PILATUS 200K/R) equipped in Rigaku XtaLAB PRO diffractometer using thin multi-layer mirror monochromated Cu-Kα radiation (λ =1.54187 Å). All reactions were carried out under nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.) or Chromatorex NH (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F_{254} and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

Materials

Hypervalent iodine reagents **1a**, **1c**, and **1f** were prepared according to the reported procedure.[12] Ester substrates were prepared according to the reported procedure.[22] Amide substrates were prepared according to the reported procedure.[23–29] Ketone substrate was prepared according to the reported procedure.[30,31] THF was distilled over sodium/benzophenone before use. All other solvents and reagents were purchased and used as obtained.

Preparation of aminating reagents and substrates

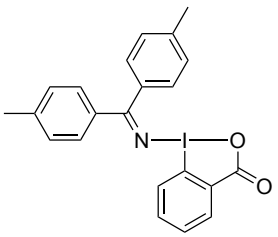
1-(Diphenylmethylene)amino-3,3-bis(trifluoromethyl)-1,2-benziodoxole (1b)



To a round-bottom flask, 1-acetoxy-3,3-bis(trifluoromethyl)-1,2-benziodoxole (2.14 g, 5 mmol) and benzophenone imine (1.83 g, 10 mmol) were dissolved in *o*-xylene (15 mL) and the flask was heated in 65 ℃ under reduced pressure (about 50 Torr.) using a diaphragm pump. Then, volatiles were removed under reduced pressure. The crude solid was washed with hexane and dried under vacuum to give the product as a white solid (1.55 g, 57% yield). Recrystallization from hexane/chloroform gave a single crystal suitable for X-ray analysis. mp: 141.2–143.8 °C (decomposed); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.87 (d, J = 8.4 Hz, 1H), 7.82–7.71 (m, 2H), 7.68–7.50 (m, 7H), 7.47–7.38 (m, 2H), 7.35–7.26 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 177.6, 140.2, 138.6, 132.0, 131.4, 131.0, 130.4, 130.1, 129.8, 128.6, 128.5, 128.3, 126.0, 123.8 (q, $J_{C–F}$ = 289.0 Hz), 115.3, 83.3–82.1 (m) (one sp^2 signal was not observed because of overlapping); ^{19}F{^{1}H} NMR: (376 MHz, $CDCl_3$) δ −78.8; IR: (ATR) 3098, 1589, 1562, 1437, 1263, 1252, 1200, 1179, 1150, 1132, 1116, 1076, 1042, 1028, 1006, 999, 945, 908, 777, 763, 752 cm^{-1}; HRMS: (EI) calcd for ($C_{22}H_{14}F_6NOI$) 549.0024 (M^+), found m/z 549.0020

The structure of **1b** was determined by X-ray structural analysis. CCDC 2216964 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

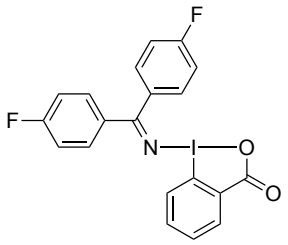
1-((Bis(4-methylphenyl)methylene)amino)-1,2-benziodoxol-3-(1*H*)-one (1d)



To a solution of 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (764.0 mg, 2.50 mmol) in dichloromethane (10 mL), 4,4'-dimethylbenzophenone imine[32] (794.0 mg, 3.79 mmol) was added. The mixture was stirred at room temperature for 24 h. Then, volatiles were removed under reduced pressure. The crude solid was washed with MeCN and dried under vacuum to give the product as a pale brown solid (925.9 mg, 81% yield). mp: 157.3 °C (decomposed); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.55 (d, J = 7.6 Hz, 1H), 8.35 (dd, J = 7.6, 1.6 Hz, 1H), 7.92–7.83 (m, 1H), 7.67–7.60 (m, 1H), 7.58 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.27–7.17 (m, 4H), 2.49 (s, 3H), 2.42 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 180.3, 167.7, 142.8, 141.4, 138.4, 135.2, 133.6, 132.6, 132.5 130.6, 130.4,

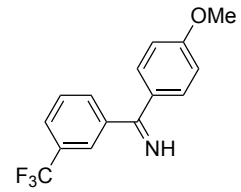
129.3, 129.0, 126.8, 125.7, 118.2, 21.6, 21.5; IR: (ATR) 3044, 2941, 2918, 1636, 1607, 1292, 835, 822, 750, 727 cm^{-1}; HRMS: (FAB+) calcd for ($C_{22}H_{19}NO_2I$) 456.0461 ($[M+H]^+$), found *m*/*z* 456.0460

1-((Bis(4-fluorophenyl)methylene)amino)-1,2-benziodoxol-3-(1*H*)-one (1e)



To a solution of 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (773.2 mg, 2.53 mmol) in dichloromethane (10 mL), 4,4'-difluorobenzophenone imine[32] (990.0 mg, 4.60 mmol) was added. The mixture was stirred at room temperature for 24 h. Then, volatiles were removed under reduced pressure. The crude solid was washed with MeCN and dried under vacuum to give the product as a white solid (921.4 mg, 79% yield). mp. 174.5 °C (decomposed); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.40–8.30 (m, 1H), 7.96–7.83 (m, 1H), 7.77–7.60 (m, 3H), 7.45–7.21 (m, 4H), 7.21–7.05 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 177.7, 167.6, 165.1 (d, $J_{C–F}$ = 253.6 Hz), 163.7 (d, $J_{C–F}$ = 252.0 Hz), 136.5 (d, J_{CF} = 3.3 Hz), 134.1 (d, $J_{C–F}$ = 2.5 Hz), 133.9, 132.7, 132.2, 131.2 (d, $J_{C–F}$ = 9.1 Hz), 130.6, 128.2 (d, J_{CF} = 9.0 Hz), 126.7, 118.2, 117.5 (d, $J_{C–F}$ = 21.5 Hz), 115.9 (d, $J_{C–F}$ = 21.4 Hz); ^{19}F{^{1}H} NMR: (377 MHz, $CDCl_3$) δ −108.8, −109.4; IR: (ATR) 3090, 3042, 1638, 1624, 1607, 1593, 1558, 1501, 1294, 1275, 1223, 1148, 849, 826, 748, 739 cm^{-1}; HRMS: (FAB+) calcd for ($C_{20}H_{13}F_2NO_2I$) 463.9959 ($[M+H]^+$), found *m*/*z* 463.9954

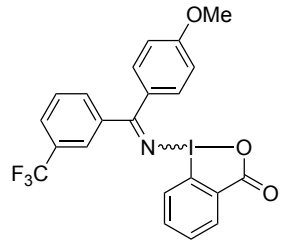
(4-Methoxyphenyl)(3-(trifluoromethyl)phenyl)methanimine



This compound was prepared according to the reported procedure.[33]

Yellow solid; mp. 37.3–38.8 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) broadened signals were observed; ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) broadened signals were observed; ^{19}F{^{1}H} NMR: (377 MHz, $CDCl_3$) δ −65.2 ; IR: (ATR) 3260, 2978, 2849, 1599, 1508, 1314, 1296, 1254, 1167, 1125, 1070, 1030, 924, 889, 841, 810 cm^{-1}; HRMS: (FAB+) calcd for ($C_{15}H_{13}F_3NO$) 280.0949 ($[M+H]^+$), found *m*/*z* 280.0950

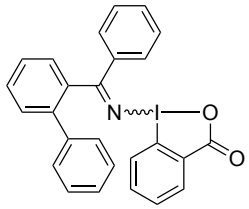
1-(((4-Methoxyphenyl)(3-(trifluoromethyl)phenyl)methylene)amino)-1,2-benziodoxol-3-(1*H*)-one (1g)



To a solution of 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (768.2 mg, 2.51 mmol) in dichloromethane (10 mL), (4-methoxyphenyl)(3-(trifluoromethyl)phenyl)methanimine (1.050 g, 3.76 mmol) was added. The mixture was stirred at room temperature for 24 h. Then, volatiles were removed under reduced pressure. The crude solid was washed with MeCN and dried under vacuum to give the product as a white solid (744.4 mg, 56% yield). The product was obtained as a mixture of *E*/*Z* isomers (62:38). mp: 163.8 °C (decomposed); ^{1}H NMR of a mixture of *E*/*Z* isomers: (400 MHz, $CDCl_3$) δ 8.55–8.49 (m, 1H), 8.40–8.32 (m, 1H), 7.95–7.84 (m,

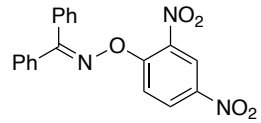
3H), 7.84–7.75 (m, 1.2H), 7.70–7.64 (m, 1H), 7.64–7.54 (m, 2.4H), 7.34–7.28 (m, 1.2H), 7.15–7.10 (m, 1.2H), 6.99–6.91 (m, 0.8H), 3.95 (s, 1.8H), 3.89 (s, 1.2H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) complicated due to mixture of *E*/*Z* isomers and C–F coupling; $^{19}F\{^{1}H\}$ NMR: (377 MHz, $CDCl_3$) δ −65.3, −65.4; IR: (ATR) 3038, 2938, 2839, 1651, 1603, 1543, 1337, 1304, 1275, 1254, 1167, 1155, 1098, 1072, 1024, 839, 824, 812, 750, 741, 708 cm^{-1}; HRMS: (FAB+) calcd for ($C_{22}H_{16}F_3NO_3I$) 526.0127 ($[M+H]^+$), found *m*/*z* 526.0131

1-(([1,1'-Biphenyl]-2-yl(phenyl)methylene)amino)-1,2-benziodoxol-3-(1*H*)-one (1h)



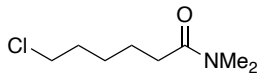
To a solution of 1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (765.9 mg, 2.50 mmol) in dichloromethane (10 mL), [1,1'-biphenyl]-2-yl(phenyl)methanimine[34] (1.067 g, 4.15 mmol) was added. The mixture was stirred at room temperature for 24 h. Then, volatiles were removed under reduced pressure. The crude solid was washed with MeCN and Et_2O, and dried under vacuum to give the product as a white solid (698.4 mg, 55% yield). The product was obtained as a single isomer, whose configuration has not been determined. mp: 154.9 °C (decomposed); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 7.83–7.74 (m, 1H), 7.74–7.65 (m, 3H), 7.65–7.49 (m, 4H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.35–7.24 (m, 3H), 7.24–7.12 (m, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 179.8, 167.7, 139.3, 139.2, 138.6, 138.3, 133.6, 132.5, 132.2, 131.9, 131.7, 131.2, 130.3, 128.74, 128.70, 128.67, 128.5, 128.3, 126.8, 126.7, 118.0 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3092, 3053, 3011, 1641, 1551, 1314, 1290, 781, 758, 739 cm^{-1}; HRMS: (FAB+) calcd for ($C_{26}H_{19}NO_2I$) 504.0461 ($[M+H]^+$), found *m*/*z* 504.0462

Diphenylmethanone *O*-(2,4-dinitrophenyl) oxime (4)



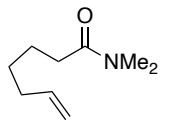
To a solution of benzophenone (372.0 mg, 2.0 mmol) in EtOH (5 mL), *O*-(2,4-dinitrophenyl) hydroxylamine (395.0 mg, 2.0 mmol) and HCl aq. (36%, 1 mL, 5.8 equiv.) was added. The mixture was stirred at 60 °C for 2 h. The precipitated solid was washed with EtOH and dried under vacuum to give the product as a white solid (445.9 mg, 61% yield). mp: 166.6–167.6 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.9 Hz, 1H), 8.47 (dd, *J* = 9.3, 2.9 Hz, 1H), 8.15 (d, *J* = 9.3 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.59–7.37 (m, 8H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 165.0, 157.3, 141.0, 136.4, 134.3, 131.3, 130.4, 129.5 129.2, 129.1, 128.7, 128.2, 121.9, 117.4 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3123, 3098, 1601, 1526, 1333, 1260, 1240, 978, 920, 883, 835, 823, 773, 741 cm^{-1}; HRMS: (FAB+) calcd for ($C_{19}H_{14}N_3O_5$) 364.0933 ($[M+H]^+$), found *m*/*z* 364.0943

6-Chloro-*N*,*N*-dimethylhexanamide (7i)



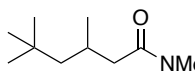
To a solution of 6-chlorohexanoic acid (2.12 g, 14.1 mmol) in $CHCl_3$ (20 mL) at 0 °C was added thionyl chloride (1.6 mL, 22.5 mmol) and dimethylformamide (12.0 μL, 0.1 mmol). The reaction mixture was stirred at ambient temperature for 3 h and then the solvent was evaporated under reduced pressure. The residue was dissolved in $CHCl_3$ (20 ml) and 50% aqueous Me_2NH (4.0 mL, 36 mmol) was slowly added at 0 °C. The reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with an aqueous saturated solution of $NaHCO_3$, and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 4:6) gave the product as a colorless oil (1.61 g, 64% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.55 (t, *J* = 6.6 Hz, 2H), 3.01 (s, 3H), 2.95 (s, 3H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.88–1.75 (m, 2H), 1.72–1.60 (m, 2H), 1.55–1.41 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.5, 44.7, 37.0, 35.1, 32.8, 32.2, 26.5, 24.1; IR: (ATR) 2936, 1639, 1495, 1460, 1396, 1265, 1126, 1057, 721 cm^{-1}; HRMS: (EI) calcd for ($C_8H_{16}ClNO$) 177.0920 (M^+), found *m*/*z* 177.0917

***N*,*N*-Dimethylhept-6-enamide (7k)**



To a solution of the dimethylamine (2 M in THF, 7.0 mL, 14.0 mmol), triethylamine (4.9 mL, 35.0 mmol), hydroxybenzotriazole (HOBt) (1.89 g, 14.0 mmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI•HCl) (2.68 g, 14.0 mmol) in $CHCl_3$ (20 mL), hept-6-enoic acid (911 mg, 7.11 mmol) was added. After being stirred at room temperature for 18 h, the reaction mixture was washed sequentially with 0.5 M aqueous HCl (20 mL), saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL). The collected organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:EtOAc = 5:5) to give the product as a pale yellow liquid (794.4 mg, 72% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.88–5.75 (m, 1H), 5.08–4.90 (m, 2H), 3.01 (s, 3H), 2.94 (s, 3H), 2.32 (t, *J* = 7.6 Hz, 2H), 2.08 (dt, *J* = 7.6, 7.2 Hz, 2H), 1.68 (tt, *J* = 7.6, 7.6 Hz, 2H), 1.44 (tt, *J* = 7.6, 7.6 Hz, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.0, 138.6, 114.5, 37.2, 35.3, 33.5, 33.2, 28.7, 24.6; IR: (ATR) 2928, 2857, 1639, 1495, 1456, 1396, 1331, 1142, 1105, 1059, 993, 908 cm^{-1}; HRMS: (CI) calcd for ($C_9H_{18}NO$) 156.1388 ([M+H]$^+$), found *m*/*z* 156.1387

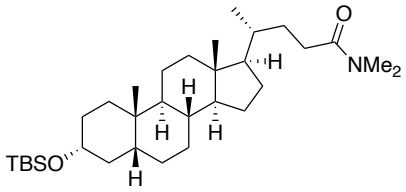
***N*,*N*,3,5,5-Pentamethylhexanamide (7n)**



To a solution of Me_2NH (2 M in THF, 5.0 mL, 10 mmol) in $CHCl_3$ (50 mL) was added NEt_3 (2.80 mL, 20 mmol). 3,5,5-trimethylhexanoyl chloride (2.12 g, 12 mmol) was then added dropwise to the mixture under 0 ºC. After stirring for 12 h at room temperature, the reaction mixture was quenched with an aqueous saturated solution of $NaHCO_3$, and the mixture was

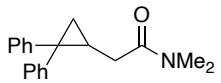
extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (hexane/EtOAc = 6:4) gave the product as a colorless liquid (1.56 g, 84% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.02 (s, 3H), 2.95 (s, 3H), 2.28 (dd, *J* = 14.4, 5.6 Hz, 1H), 2.22–2.05 (m, 2H), 1.29 (dd, *J* = 13.6, 4.0 Hz, 1H), 1.12 (dd, *J* =13.6, 6.4 Hz, 1H), 0.98, (d, *J* = 6.4 Hz, 3H), 0.91 (s, 9H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.6, 50.9, 42.8, 37.5, 35.3, 31.1, 30.0, 26.9, 22.9; IR: (ATR) 2951, 2903, 2868, 1641, 1466, 1395, 1364, 1138, 1061 cm^{-1}; HRMS: (EI) calcd for ($C_{11}H_{23}NO$) 185.1780 (M^+), found *m*/*z* 185.1783

(*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-((*tert*-Butyldimethylsilyl)oxy)-10,13-dimethyl-hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-*N*,*N*-dimethylpentanamide (7x)



To a solution of the dimethylamine (2 M in THF, 1.25 mL, 2.5 mmol), triethylamine (0.9 mL, 6.3 mmol), hydroxybenzotriazole (HOBt) (383.0 mg, 2.8 mmol), and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI•HCl) (482.0 mg, 2.5 mmol) in $CHCl_3$ (7 mL), (*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-((*tert*-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoic acid (1.23 g, 2.5 mmol) was added. After being stirred at room temperature for 18 h, the reaction mixture was washed sequentially with 0.5 M aqueous HCl (20 mL), saturated aqueous Na_2CO_3 (20 mL), and brine (20 mL). The collected organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:EtOAc = 7:3) to give the product as a white solid (488.7 mg, 38% yield). mp: 112.3–113.0 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.65–3.50 (m, 1H), 3.01 (s, 3H), 2.94 (s, 3H) 2.45–2.32 (m, 1H), 2.25–2.16 (m, 1H), 2.00–1.67 (m, 6H), 1.65–0.75 (m, 35H), 0.64 (s, 3H), 0.06 (s, 6H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.7, 72.8, 56.4, 56.0, 42.7, 42.3, 40.2, 40.1, 37.3, 36.9, 35.8, 35.6, 35.5, 35.4, 34.6, 31.2, 31.0, 30.3, 28.2, 27.3, 26.4, 26.0, 24.2, 23.4, 20.8, 18.5, 18.3, 12.0, −4.6; IR: (ATR) 2930, 2914, 2880, 2860, 1653, 1638, 1462, 1414, 1398, 1371, 1150, 1090, 1053, 1005, 870, 833, 773 cm^{-1}; HRMS: (CI) calcd for ($C_{32}H_{60}NO_2Si$) 518.4393 ($[M+H]^+$), found *m*/*z* 518.4386

2-(2,2-Diphenylcyclopropyl)-*N*,*N*-dimethylacetamide (7y)



To a solution of the dimethylamine (2 M in THF, 1 mL, 2.0 mmol), triethylamine (0.70 mL, 5 mmol), hydroxybenzotriazole (HOBt) (313 mg, 2.0 mmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI•HCl) (387.0 mg, 2.0 mmol) in $CHCl_3$ (5 mL), 2-(2,2-diphenylcyclopropyl)acetic acid (234 mg, 0.93 mmol) was added. After being stirred at room temperature for 18 h, the reaction mixture was washed sequentially with 0.5 M aqueous HCl (10 mL), saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL). The collected organic phase was

dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:EtOAc = 8:2) to give the product as a white solid (191.6 mg, 74% yield). mp: 127.6–128.6 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.36–7.32 (m, 2H), 7.28–7.20 (m, 4H), 7.20–7.08 (m, 2H), 2.93 (s, 3H), 2.63 (s, 3H), 2.26 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.20–2.11 (m, 1H), 1.95 (dd, *J* = 16.4, 8.4 Hz, 1H), 1.32–1.25 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.5, 146.8, 141.8, 130.2, 128.7, 128.20, 128.18, 126.3, 125.9, 36.9, 35.4, 35.2, 34.4, 21.2, 18.7; IR: (ATR) 2926, 2914, 1643, 1599, 1493, 1445, 1387, 1267, 1144, 1125, 1094, 1069, 1053, 1032 cm^{-1}; HRMS: (CI) calcd for ($C_{19}H_{22}NO$) 280.1701 ($[M+H]^+$), found *m*/*z* 280.1697

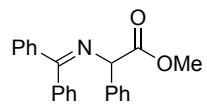
Oxidative amination of carbonyl compounds: experimental procedure and product data

Typical procedure I: A heat-gun-dried reaction flask containing a magnetic stir bar was charged with carbonyl compounds (esters, amides, or ketones) (0.40 mmol) and THF (4 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then a solution of LiHMDS (1 M in THF) (0.44 mmol) was added to the flask. The mixture was stirred at −78 °C for 30 min before hypervalent iodine reagent **1** (0.48 mmol) was added. The reaction flask was removed from a cold bath and further stirred for 1 h (The reaction mixture was allowed to warm to room temperature.). The reaction was quenched with sat. $NaHCO_3$ aq., and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product.

Typical procedure II: A heat-gun-dried reaction flask containing a magnetic stir bar was charged with diisopropylamine (0.24–0.36 mmol) and THF (1 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then *n*-BuLi (1.6 M in hexane, 0.24–0.36 mmol) was added to the flask. The mixture was stirred at −78 °C for 20 min before a solution of carbonyl compounds (0.20–0.30 mmol) in THF (1 mL) was added, and further stirred at −78 °C for 30 min. Then, hypervalent iodine reagent **1** (0.20–0.24 mmol) was added to the mixture. The reaction flask was removed from a cold bath and further stirred for 1 h (The reaction mixture was allowed to warm to room temperature.). The reaction was quenched with water, and the mixture was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Purification by flash column chromatography on NH silica gel (hexane/EtOAc) gave the product.

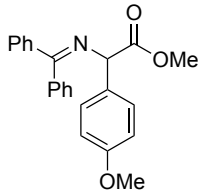
Product data

Methyl 2-((diphenylmethylene)amino)-2-phenylacetate (3aa)



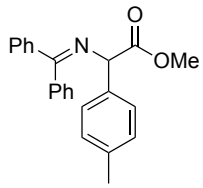
According to the typical procedure **I**, the reaction using methyl 2-phenylacetate (**2a**) (60.1 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.4 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (90.0 mg), which contains a small amount of homocoupling products of **2a**. The yield of **3aa** was determined by ^1H NMR analysis of the purified product which contains 0.27 mmol of **3aa** (67% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.77–7.68 (m, 2H), 7.54–7.20 (m, 11H), 7.15–7.03 (m, 2H), 5.16 (s, 1H), 3.68 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.0, 170.3, 139.3, 139.1, 136.0, 130.5, 128.9, 128.8, 128.53 128.47, 128.0, 127.9, 127.8, 127.6, 69.5, 52.4
The analytical data for this compound were in excellent agreement with the reported data.[35]

Methyl 2-((diphenylmethylene)amino)-2-(4-methoxyphenyl)acetate (3ab)



According to the typical procedure **I**, the reaction using methyl 2-(4-methoxyphenyl)acetate (**2b**) (72.4 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.3 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 95:5) gave the product as a colorless liquid (88.3 mg, 61% yield). **Gram-scale reaction:** A heat-gun-dried reaction flask containing a magnetic stir bar was charged with methyl 2-(4-methoxyphenyl)acetate (**2b**) (1.24 g, 6.87 mmol) and THF (60 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then a solution of LiHMDS (7.6 mL, 1 M in THF) was added to the flask. The mixture was stirred at −78 °C for 30 min before hypervalent iodine reagent **1a** (3.51 g, 8.21 mmol) was added. The reaction flask was removed from cold bath and further stirred for 1 h. (The reaction mixture was allowed to warm to room temperature.) The reaction was quenched with sat. $NaHCO_3$ aq., and the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 100:0) gave the product as a colorless liquid (1.55 g), which contains a small amount of homocoupling products of **2b**. The yield of **3ab** was determined by ^1H NMR analysis of the purified product which contains 4.28 mmol of **3ab** (62% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.74–7.65 (m, 2H), 7.49–7.41 (m, 3H), 7.41–7.26 (m, 5H), 7.13–7.03 (m, 2H), 6.90–6.80 (m, 2H), 5.11 (s, 1H), 3.78 (s, 3H), 3.67 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.2, 169.9, 159.1, 139.3, 136.1, 131.3, 130.4, 128.92, 128.88, 128.7, 128.5 128.0, 127.6, 113.8, 68.9, 55.2, 52.3
The analytical data for this compound were in excellent agreement with the reported data.[35]

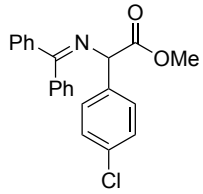
Methyl 2-((diphenylmethylene)amino)-2-(4-methylphenyl)acetate (3ac)



According to the typical procedure **I**, the reaction using methyl 2-(4-methylphenyl)acetate (**2c**) (65.1 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.6 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (90.0 mg), which contains a small amount of homocoupling products of **2c**. The yield of **3ac** was determined by ^1H NMR analysis of the purified product which contains 0.25 mmol of **3ac** (64% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.75–7.65 (m, 2H), 7.49–7.21 (m, 8H), 7.17–7.10 (m, 2H), 7.10–7.04 (m, 2H), 5.13 (s, 1H), 3.67 (s, 3H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.1, 170.0, 139.3, 137.5, 136.12, 136.06, 130.4, 129.2, 128.9, 128.7, 128.5, 128.0, 127.7, 127.6, 69.3, 52.3, 21.1

The analytical data for this compound were in excellent agreement with the reported data.[35]

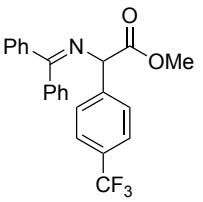
Methyl 2-(4-chlorophenyl)-2-((diphenylmethylene)amino)acetate (3ad)



According to the typical procedure **I**, the reaction using methyl 2-(4-chlorophenyl)acetate (**2d**) (72.9 mg, 0.39 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.2 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (90.4 mg), which contains a small amount of homocoupling products of **2d**. The yield of **3ad** was determined by ^1H NMR analysis of the purified product which contains 0.24 mmol of **3ad** (61% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.74–7.66 (m, 2H), 7.50–7.25 (m, 10H), 7.11–7.02 (m, 2H), 5.13 (s, 1H), 3.67 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 171.6, 170.7, 139.1, 137.5, 135.9, 133.6, 130.6, 129.2, 128.92, 128.89, 128.61, 128.59, 128.0, 127.5, 68.8, 52.5

The analytical data for this compound were in excellent agreement with the reported data.[35]

Methyl 2-((diphenylmethylene)amino)-2-(4-(trifluoromethyl)phenyl)acetate (3ae)

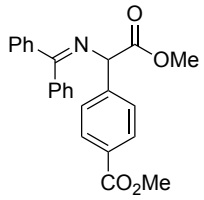


According to the typical procedure **I**, the reaction using methyl 2-(4-(trifluoromethyl)phenyl)acetate (**2e**) (87.6 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.0 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (107.8 mg), which contains a small amount of homocoupling products of **2e**. The yield of **3ae** was determined by ^1H NMR analysis of the purified product which contains 0.27 mmol of **3ae** (66% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.79–7.66 (m, 2H), 7.63–7.53 (m, 4H), 7.53–7.28 (m, 6H), 7.15–7.03 (m, 2H), 5.22 (s, 1H), 3.68 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 171.22, 171.16,

142.9, 139.0, 135.8, 130.7, 129.9 (q, J_{C-F} = 32.1 Hz), 128.98, 128.97, 128.7, 128.3, 128.1, 127.5, 125.4 (q, J_{C-F} = 4.2 Hz), 124.1 (q, J_{C-F} = 271.0 Hz), 69.1, 52.6

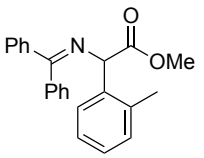
The analytical data for this compound were in excellent agreement with the reported data.[12]

Methyl 4-(1-((diphenylmethylene)amino)-2-methoxy-2-oxoethyl)benzoate (3af)



According to the typical procedure **I**, the reaction using methyl 4-(2-methoxy-2-oxoethyl)benzoate (**2f**) (83.3 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.0 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 90:10) gave the product as a colorless liquid (92.1 mg, 59% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.76–7.68 (m, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.48–7.38 (m, 4H), 7.38–7.28 (m, 2H), 7.12–7.00 (m, 2H), 5.22 (s, 1H), 3.90 (s, 3H), 3.68 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.3, 171.0, 166.8, 143.9, 139.0, 135.8, 130.6, 129.7, 129.5, 128.92, 128.90, 128.6, 128.0, 127.9, 127.5, 69.2, 52.5, 52.0; IR: (ATR) 2951, 1719, 1611, 1433, 1275, 1200., 1175, 1153, 1107, 1018, 779, 725 cm^{-1}; HRMS: (FAB+) calcd for ($C_{24}H_{22}NO_4$) 388.1549 ([M+H]$^+$), found m/z 388.1551

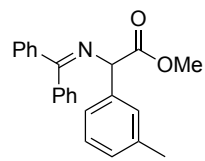
Methyl 2-((diphenylmethylene)amino)-2-(2-methylphenyl)acetate (3ag)



According to the typical procedure **I**, the reaction using methyl 2-(2-methylphenyl)acetate (**2g**) (66.0 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.2 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (93.4 mg), which contains a small amount of homocoupling products of **2g**. The yield of **3ag** was determined by ^{1}H NMR analysis of the purified product which contains 0.27 mmol of **3ag** (67% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.74–7.68 (m, 2H), 7.62–7.55 (m, 1H), 7.48–7.39 (m, 3H), 7.39–7.28 (m, 3H), 7.22–7.13 (m, 2H), 7.12–7.00 (m, 3H), 5.33 (s, 1H), 3.67 (s, 3H), 2.05 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.1, 170.2, 139.3, 137.9, 136.4, 135.9, 130.4, 130.3, 128.9, 128.8, 128.7, 128.6, 128.0, 127.49, 127.47, 126.1, 66.5, 52.3, 19.2

The analytical data for this compound were in excellent agreement with the reported data.[35]

Methyl 2-((diphenylmethylene)amino)-2-(3-methylphenyl)acetate (3ah)

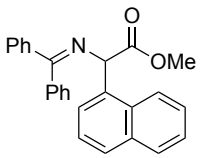


According to the typical procedure **I**, the reaction using methyl 2-(3-methylphenyl)acetate (**2h**) (66.4 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.7 mg, 0.48 mmol)

was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (89.7 mg), which contains a small amount of homocoupling products of **2h**. The yield of **3ah** was determined by ^1H NMR analysis of the purified product which contains 0.26 mmol of **3ah** (64% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.75–7.66 (m, 2H), 7.49–7.28 (m, 6H), 7.28–7.23 (m, 1H), 7.23–7.15 (m, 2H), 7.12–7.02 (m, 3H), 5.13 (s, 1H), 3.68 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.1, 170.2, 139.3, 138.9, 138.1, 136.1, 130.4, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.0, 127.6, 124.9, 69.6, 52.4, 21.4

The analytical data for this compound were in excellent agreement with the reported data.[35]

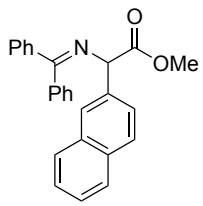
Methyl 2-((diphenylmethylene)amino)-2-(naphthalen-1-yl)acetate (3ai)



According to the typical procedure **I**, the reaction using methyl 2-(naphthalen-1-yl)acetate (**2i**) (77.9 mg, 0.39 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (204.8 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 98:2) gave the product as a pale yellow liquid (79.9 mg, 54% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 8.18–8.09 (m, 1H), 7.88–7.80 (m, 1H), 7.80–7.75 (m, 1H), 7.75–7.68 (m, 2H), 7.60–7.54 (m, 1H), 7.54–7.26 (m, 9H), 7.14–7.02 (m, 2H), 5.79 (s, 1H), 3.62 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.3, 170.4, 139.3, 136.0, 135.3, 133.9, 131.1, 130.5, 129.0, 128.8, 128.6, 128.5, 128.0, 127.7, 126.9, 126.1, 125.5, 125.4, 124.4, 67.6, 52.4 (one sp^2 signal was not observed because of overlapping)

The analytical data for this compound were in excellent agreement with the reported data.[35]

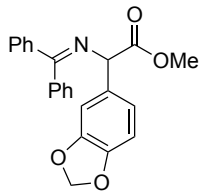
Methyl 2-((diphenylmethylene)amino)-2-(naphthalen-2-yl)acetate (3aj)



According to the typical procedure **I**, the reaction using methyl 2-(naphthalen-2-yl)acetate (**2j**) (81.1 mg, 0.41 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.2 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a pale yellow liquid (90.3 mg), which contains a small amount of homocoupling products of **1j**. The yield of **3aj** was determined by ^1H NMR analysis of the purified product which contains 0.23 mmol of **3aj** (56% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.88–7.77 (m, 4H), 7.77–7.70 (m, 2H), 7.65–7.58 (m, 1H), 7.51–7.29 (m, 8H), 7.14–7.04 (m, 2H), 5.33 (s, 1H), 3.68 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.0, 170.6, 139.3, 136.5, 136.0, 133.3, 132.9, 130.5, 129.0, 128.8, 128.5, 128.2, 128.0, 127.64, 127.60, 126.7, 126.01, 125.97, 125.8, 69.7, 52.4 (one sp^2 signal was not observed because of overlapping)

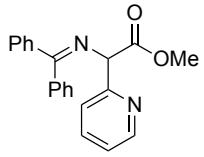
The analytical data for this compound were in excellent agreement with the reported data.[35]

Methyl 2-(benzo[*d*][1,3]dioxol-5-yl)-2-((diphenylmethylene)amino)acetate (3ak)



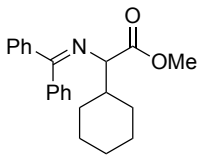
According to the typical procedure **I**, the reaction using methyl 2-(benzo[*d*][1,3]dioxol-5-yl)acetate (**2k**) (80.3 mg, 0.41 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (204.5 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 95:5) gave the product as a pale yellow liquid (78.7 mg, 51% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.74–7.66 (m, 2H), 7.48–7.43 (m, 3H), 7.43–7.37 (m, 1H), 7.37–7.30 (m, 2H), 7.13–7.05 (m, 2H), 7.05 (d, *J* = 2.0 Hz, 1H), 6.79 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.96–5.93 (m, 2H), 5.07 (s, 1H), 3.68 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.0, 170.2, 147.7, 147.1, 139.2, 136.0, 132.9, 130.5, 128.9, 128.8, 128.5, 128.0, 127.6, 121.1, 108.5, 108.1, 101.0, 69.1, 52.4; IR: (neat) 2951, 2891, 1748, 1732, 1614, 1597, 1574, 1504, 1487, 1445, 1435, 1285, 1242, 1196, 1169, 1038, 930, 810, 783, 700 cm^{-1}; HRMS: (CI) calcd for ($C_{23}H_{20}NO_4$) 374.1392 ([M+H]$^+$), found *m*/*z* 374.1396

Methyl 2-((diphenylmethylene)amino)-2-(pyridin-2-yl)acetate (3al)



According to the typical procedure **I**, the reaction using methyl 2-(pyridin-2-yl)acetate (**2l**) (59.0 mg, 0.39 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.1 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 85:15) gave the product as a orange liquid (67.8 mg, 53% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.56–8.45 (m, 1H), 7.78–7.66 (m, 4H), 7.49–7.38 (m, 4H), 7.38–7.29 (m, 2H), 7.24–7.18 (m, 1H), 7.18–7.05 (m, 2H), 5.44 (s, 1H), 3.69 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.6, 170.9, 158.4, 149.1, 139.2, 136.8, 135.7, 130.6, 129.0, 128.9, 128.6, 128.0, 127.6, 122.7, 122.6, 71.6, 52.5; IR: (ATR) 1655, 1597, 1576, 1447, 1317, 1275, 997, 941, 920 cm^{-1}; HRMS: (FAB+) calcd for ($C_{21}H_{19}N_2O_2$) 331.1447 ([M+H]$^+$), found *m*/*z* 331.1440

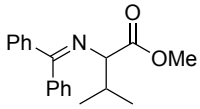
Methyl 2-cyclohexyl-2-((diphenylmethylene)amino)acetate (3am)



According to the typical procedure **II**, the reaction using diisopropylamine (25.1 mg, 0.25 mmol) and THF (1 mL), *n*-BuLi (1.6 M in hexane, 140 µL, 0.22 mmol), methyl 2-cyclohexylacetate (**2m**) (30.8 mg, 0.20 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (104.2 mg, 0.24 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (35.2 mg, 53% yield). Recrystallization from Et_2O gave a single crystal suitable for X-ray analysis. mp: 102.5–104.0 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.67–7.60 (m, 2H), 7.50–7.28 (m, 6H), 7.15–7.08 (m, 2H), 3.86 (d, *J* = 6.8 Hz, 1H), 3.71 (s, 3H), 2.11–2.00 (m,1H), 1.80–1.57 (m, 4H), 1.55–1.42 (m, 1H), 1.32–1.17 (m, 2H), 1.17–1.02 (m, 2H), 1.02–0.86 (m, 1H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ

172.6, 170.4, 139.7, 136.5, 130.2, 128.8, 128.5, 128.4, 128.01, 127.98, 71.2, 51.8, 42.0, 29.9, 28.8, 26.2, 26.1; IR: (ATR) 2936, 2914, 2847, 1744, 1622, 1489, 1447, 1429, 1325, 1288, 1267, 1229, 1194, 1159, 1136, 1072, 1022, 1001, 797, 781, 758 cm^{-1}; HRMS: (FAB+) calculated for ($C_{22}H_{25}NO_2Na$) 358.1783 ($[M+Na]^+$), found *m*/*z* 358.1779

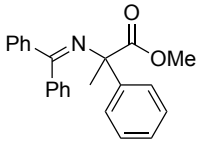
Methyl 2-((diphenylmethylene)amino)-3-methylbutanoate (3an)



According to the typical procedure **II**, the reaction using diisopropylamine (47.3 mg, 0.47 mmol), THF (2 mL), *n*-BuLi (1.6 M in hexane, 280 μL, 0.44 mmol), methyl isovalerate (**2n**) (46.6 mg, 0.40 mmol) in THF (2 mL), and hypervalent iodine reagent **1a** (204.7 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 99:1) gave the product as a pale yellow liquid (55.0 mg, 47% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.67–7.57 (m, 2H), 7.53–7.28 (m, 6H), 7.18–7.06 (m, 2H), 3.85 (d, *J* = 6.4 Hz, 1H), 3.72 (s, 3H), 2.36 (dqq, *J* = 6.4, 6.4, 6.4 Hz, 1H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.6, 170.5, 139.7, 136.5, 130.2, 128.8, 128.5, 128.4, 128.0, 127.9, 71.5, 51.8, 32.5, 19.5, 18.4

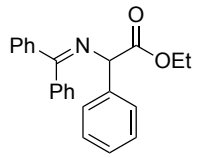
The analytical data for this compound were in excellent agreement with the reported data.[12]

Methyl 2-((diphenylmethylene)amino)-2-phenylpropanoate (3ao)



A heat-gun-dried reaction flask containing a magnetic stir bar was charged with methyl 2-phenylpropanoate (**2o**) (64.1 mg, 0.39 mmol) and THF (4 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then a solution of LiHMDS (0.44 mL, 1 M in THF) was added to the flask. The mixture was allowed to warm to −40 °C and stirred for 2 h before hypervalent iodine reagent **1a** (205.2 mg, 0.48 mmol) was added. The reaction flask was removed from cold bath and further stirred for 1 h (The reaction mixture was allowed to warm to room temperature.). Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3) gave the product as a white solid (51.0 mg), which contains a small amount of homocoupling products of **2o**. The yield of **3ao** was determined by ^1H NMR analysis of the purified product which contains 0.13 mmol of **3ao** (34% yield). mp: 81.2–85.0 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.73–7.63 (m, 4H), 7.43–7.30 (m, 8H), 7.30–7.23 (m, 1H), 7.14–7.08 (m, 2H), 3.29 (s, 3H), 1.76 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.2, 167.2, 145.9, 141.2, 136.9, 130.2, 128.6, 128.50, 128.46, 128.3, 128.0, 127.7, 127.0, 125.8, 69.0, 51.8, 28.3; IR: (KBr) 3051, 3021, 2997, 2955, 1734, 1443, 1242, 1121, 723 cm^{-1}; HRMS: (CI) calcd for ($C_{23}H_{22}NO_2$) 344.1651 ($[M+H]^+$), found *m*/*z* 344.1654

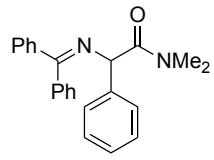
Ethyl 2-((diphenylmethylene)amino)-2-phenylacetate (3ap)



According to the typical procedure **I**, the reaction using ethyl 2-phenylacetate (**2p**) (65.3 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.6 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (88.5 mg, 65% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.75–7.67 (m, 2H), 7.52–7.20 (m, 11H), 7.14–7.03 (m, 2H), 5.14 (s, 1H), 4.18–4.06 (m, 2H), 1.18 (dd, *J* = 7.2, 7.2 Hz, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.4, 170.1, 139.3, 139.2, 136.1, 130.4, 128.9, 128.7, 128.5, 128.4, 128.0, 127.9, 127.7, 127.6, 69.6, 61.1, 14.0

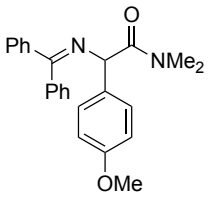
The analytical data for this compound were in excellent agreement with the reported data.[35]

2-((Diphenylmethylene)amino)-*N*,*N*-dimethyl-2-phenylacetamide (8aa)



According to the typical procedure **I**, the reaction using *N*,*N*-dimethyl-2-phenylacetamide (**7a**) (64.8 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (204.9 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 86:14) gave the product as a colorless liquid (78.1 mg, 57% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.76–7.70 (m, 2H), 7.46–7.28 (m, 10H), 7.28–7.21 (m, 1H), 7.18–7.09 (m, 2H), 5.48 (s, 1H), 2.93 (s, 3H), 2.91 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 170.8, 169.9, 139.4, 135.9, 130.4, 128.9, 128.8, 128.4, 128.0, 127.7, 127.1, 126.5, 70.3, 37.1, 36.3 (two sp^2 signals were not observed because of overlapping); IR: (ATR) 3057, 3026, 2924, 1639, 1622, 1574, 1491, 1445, 1393, 1028, 781, 727 cm^{-1}; HRMS: (CI) calcd for ($C_{23}H_{23}N_2O$) 343.1810 ([M+H]$^+$), found *m*/*z* 343.1805

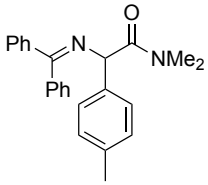
2-((Diphenylmethylene)amino)-2-(4-methoxyphenyl)-*N*,*N*-dimethylacetamide (8ab)



According to the typical procedure **I**, the reaction using 2-(4-methoxyphenyl)-*N*,*N*-dimethylacetamide (**7b**) (77.1 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.6 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane with addition of 2% NEt_3/EtOAc = 78:22) gave the product as a pale yellow solid (75.6 mg, 51% yield). mp: 143.5–145.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.77–7.69 (m, 2H), 7.48–7.36 (m, 4H), 7.36–7.30 (m, 2H), 7.30–7.21 (m, 2H), 7.18–7.08 (m, 2H), 6.90–6.82 (m, 2H), 5.41 (s, 1H), 3.77 (s, 3H), 2.92 (s, 3H), 2.90 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.1, 169.5, 158.6, 139.4, 136.0, 131.6, 130.3, 128.8, 128.7, 128.4, 127.9, 127.7, 127.6, 113.8, 69.5, 55.1, 37.0, 36.3; IR: (KBr) 3055, 2992, 2934, 2835, 1659, 1651, 1612, 1510, 1449, 1395, 1294, 1244, 1175, 1134, 1028, 818, 704 cm^{-1}; HRMS: (CI) calcd for ($C_{24}H_{25}N_2O_2$) 373.1916 ([M+H]$^+$), found *m*/*z*

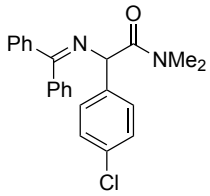
373.1913

2-((Diphenylmethylene)amino)-2-(4-methylphenyl)-*N*,*N*-dimethylacetamide (8ac)



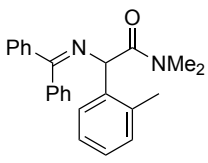
According to the typical procedure **I**, the reaction using 2-(4-methylphenyl)-*N*,*N*-dimethylacetamide (**7c**) (77.3 mg, 0.39 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.0 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane with addition of 2% NEt_3/EtOAc = 86:14) gave the product as a colorless liquid (70.9 mg, 51% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.77–7.70 (m, 2H), 7.47–7.30 (m, 6H), 7.26–7.22 (m, 2H), 7.18–7.08 (m, 4H), 5.44 (s, 1H), 2.93 (s, 3H), 2.90 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.0, 169.6, 139.4, 136.6, 136.4, 135.9, 130.3, 129.1, 128.8, 128.7, 128.4, 127.9, 127.6, 126.4, 70.1, 37.1, 36.3, 21.0; IR: (ATR) 3055, 3022, 2920, 1641, 1622, 1595, 1574, 1510, 1489, 1445, 1393, 1261, 781 cm^{-1}; HRMS: (CI) calcd for ($C_{24}H_{25}N_2O$) 357.1967 ([M+H]$^+$), found *m*/*z* 357.1971

2-(4-Chlorophenyl)-2-((diphenylmethylene)amino)-*N*,*N*-dimethylacetamide (8ad)



According to the typical procedure **I**, the reaction using 2-(4-chlorophenyl)-*N*,*N*-dimethylacetamide (**7d**) (79.0 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.4 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane with addition of 2% NEt_3/EtOAc = 86:14) gave the product as a colorless viscous liquid (82.3 mg, 55% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.75–7.69 (m, 2H), 7.49–7.23 (m, 10H), 7.15–7.06 (m, 2H), 5.42 (s, 1H), 2.92 (s, 3H), 2.90 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 170.4, 170.3, 139.1, 138.0, 135.7, 132.9, 130.5, 128.9, 128.8, 128.54, 128.47, 128.0, 127.5, 69.4, 37.0, 36.3 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3057, 3026, 2924, 1643, 1622, 1595, 1574, 1487, 1445, 1393, 1088, 1015, 781, 733 cm^{-1}; HRMS: (CI) calcd for ($C_{23}H_{22}ClN_2O$) 377.1421 ([M+H]$^+$), found *m*/*z* 377.1414

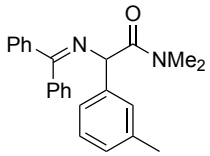
2-((Diphenylmethylene)amino)-2-(2-methylphenyl)-*N*,*N*-dimethylacetamide (8ae)



According to the typical procedure **I**, the reaction using 2-(2-methylphenyl)-*N*,*N*-dimethylacetamide (**7e**) (79.4 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.1 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane with addition of 2% NEt_3/EtOAc = 86:14) gave the product as a white solid (74.4 mg, 52% yield). mp: 143.8–146.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.74–7.67 (m, 2H), 7.57–7.50 (m, 1H), 7.47–7.35 (m, 4H), 7.35–7.26 (m, 2H), 7.23–7.12 (m, 2H), 7.12–7.00 (m, 3H), 5.39 (s, 1H), 2.94 (s, 3H), 2.76 (s, 3H), 2.03 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 170.9, 169.6, 139.2, 138.6, 136.3, 135.3,

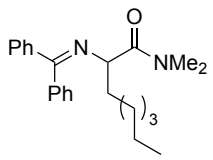
130.3, 130.2, 128.9, 128.7, 128.3, 128.2, 127.9, 127.5, 127.1, 126.1, 66.6, 36.7, 36.2, 19.4; IR: (KBr) 3034, 2936, 1645, 1634, 1609, 1593, 1574, 1487, 1393, 1285, 1134, 1018, 789, 748, 712 cm^{-1}; HRMS: (CI) calcd for ($C_{24}H_{25}N_2O$) 357.1967 ($[M+H]^+$), found *m*/*z* 357.1962

2-((Diphenylmethylene)amino)-2-(3-methylphenyl)-*N*,*N*-dimethylacetamide (8af)



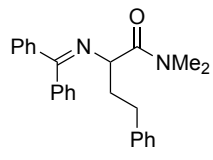
According to the typical procedure **I**, the reaction using 2-(3-methylphenyl)-*N*,*N*-dimethylacetamide (**7f**) (75.6 mg, 0.38 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (204.8 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane with addition of 2% NEt_3/EtOAc = 86:14) gave the product as a colorless liquid (77.7 mg, 57% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.78–7.70 (m, 2H), 7.48–7.29 (m, 6H), 7.25–7.09 (m, 5H), 7.09–7.02 (m, 1H), 5.44 (s, 1H), 2.93 (s, 3H), 2.91 (s, 3H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 170.9, 169.7, 139.4, 139.2, 138.1, 135.9, 130.3, 128.9, 128.7, 128.4, 128.2, 127.9, 127.8, 127.6, 127.1, 123.5, 70.2, 37.1, 36.3, 21.4; IR: (ATR) 3057, 3024, 2920, 1641, 1622, 1597, 1574, 1487, 1445, 1393, 1314, 1287, 1260, 733 cm^{-1}; HRMS: (CI) calcd for ($C_{24}H_{25}N_2O$) 357.1967 ($[M+H]^+$), found *m*/*z* 357.1965

2-((Diphenylmethylene)amino)-*N*,*N*-dimethyloctanamide (8ag)



According to the typical procedure **II**, the reaction using diisopropylamine (34.3 mg, 0.34 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 205 μL, 0.33 mmol), *N*,*N*-dimethyloctanamide (**7g**) (51.9 mg, 0.30 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (85.8 mg, 0.20 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the product as a pale yellow liquid (47.2 mg, 67% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.68–7.60 (m, 2H), 7.55–7.28 (m, 6H), 7.20–7.05 (m, 2H), 4.24 (dd, *J* = 7.8, 5.8 Hz, 1H), 2.91 (s, 3H), 2.88 (s, 3H), 2.00–1.89 (m, 1H), 1.89–1.78 (m, 1H), 1.33–1.02 (m, 8H), 0.85 (t, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.6, 168.8, 139.4, 136.9, 130.2, 128.7, 128.54, 128.50, 127.9, 127.7, 65.0, 36.8, 36.1, 34.2, 31.7, 29.0, 26.3, 22.6, 14.1; IR: (ATR) 2953, 2922, 2855, 1639, 1595, 1576, 1489, 1445, 1395, 1314, 1285, 1260, 1179, 1150, 1109, 1057, 1001, 926, 907, 779 cm^{-1}; HRMS: (CI) calculated for ($C_{23}H_{31}N_2O$) 351.2436 ($[M+H]^+$), found *m*/*z* 351.2431

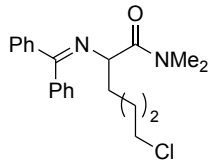
2-((Diphenylmethylene)amino)-*N*,*N*-dimethyl-4-phenylbutanamide (8ah)



According to the typical procedure **II**, the reaction using diisopropylamine (34.5 mg, 0.34 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 205 μL, 0.33 mmol), *N*,*N*-dimethyl-4-phenylbutanamide (**7h**) (57.2 mg, 0.30 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (85.8 mg, 0.20 mmol) was conducted. Purification by flash column

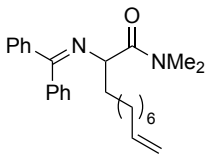
chromatography on NH silica gel (hexane/EtOAc = 8:2) gave the product as a colorless liquid (49.2 mg, 66% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72–7.62 (m, 2H), 7.48–6.98 (m, 13H), 4.20 (dd, *J* = 7.6, 6.0 Hz, 1H), 2.89 (s, 3H), 2.73–2.55 (m, 2H), 2.68 (s, 3H), 2.34–2.12 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.3, 169.5, 141.5, 139.3, 136.8, 130.2, 128.7, 128.5, 128.44, 128.41, 128.3, 128.0, 127.5, 125.8, 63.5, 36.6, 36.0, 35.5, 32.4; IR: (ATR) 2926, 1645, 1597, 1574, 1491, 1445, 1395, 1314, 1285, 1258, 1179, 1132, 1074, 1047, 1028, 1001, 926, 908, 781, 752 cm^{-1}; HRMS: (CI) calcd for ($C_{25}H_{27}N_2O$) 371.2123 ([M+H]$^+$), found *m*/*z* 371.2120

6-Chloro-2-((diphenylmethylene)amino)-*N*,*N*-dimethylhexanamide (8ai)



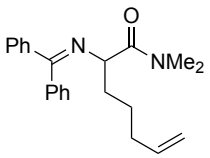
According to the typical procedure **II**, the reaction using diisopropylamine (33.1 mg, 0.33 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 205 μL, 0.33 mmol), 6-chloro-*N*,*N*-dimethylhexanamide (**7i**) (53.6 mg, 0.30 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (85.2 mg, 0.20 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 8:2) gave the product as a colorless liquid (39.1 mg, 55% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72–7.59 (m, 2H), 7.53–7.21 (m, 6H), 7.21–7.07 (m, 2H), 4.24 (dd, *J* = 6.8, 6.8 Hz, 1H), 3.50 (t, *J* = 7.0 Hz, 2H), 2.91 (s, 3H), 2.86 (s, 3H), 2.07–1.91 (m, 1H), 1.91–1.78 (m, 1H), 1.78–1.59 (m, 2H), 1.53–1.28 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.2, 169.2, 139.3, 136.7, 130.3, 128.73, 128.67, 128.6, 128.0, 127.6, 64.6, 44.8, 36.8, 36.1, 33.4, 32.2, 23.7; IR: (ATR) 2932, 1639, 1595, 1574, 1489, 1445, 1394, 1314, 1285, 1260, 1179, 1152, 1128, 1074, 1057, 1028, 1001, 982, 779, 748 cm^{-1}; HRMS: (CI) calcd for ($C_{21}H_{26}ClN_2O$) 357.1734 ([M+H]$^+$), found *m*/*z* 357.1740

2-((Diphenylmethylene)amino)-*N*,*N*-dimethylundec-10-enamide (8aj)



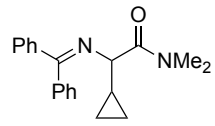
According to the typical procedure **II**, the reaction using diisopropylamine (33.7 mg, 0.33 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 205 μL, 0.33 mmol), *N*,*N*-dimethylundec-10-enamide (**7j**) (65.6 mg, 0.31 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (85.3 mg, 0.20 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the product as a pale yellow liquid (57.8 mg, 74% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72–7.60 (m, 2H), 7.53–7.28 (m, 6H), 7.21–7.11 (m, 2H), 5.88–5.72 (m, 1H), 4.98 (dd, *J* = 17.2, 2.0 Hz, 1H), 4.92 (dd, *J* = 9.8, 2.0 Hz, 1H), 4.23 (dd, *J* = 8.0, 6.0 Hz, 1H), 2.91 (s, 3H), 2.88 (s, 3H), 2.06–1.78 (m, 4H), 1.45–1.05 (m, 10H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.6, 168.8, 139.4, 139.2, 136.8, 130.2, 128.7, 128.54, 128.50, 127.9, 127.7, 114.1, 65.0, 36.8, 36.1, 34.2, 33.8, 29.3, 29.0, 28.8, 26.3; IR: (ATR) 2924, 2853, 1639, 1597, 1575, 1489, 1462, 1445, 1395, 1314, 1285, 1261, 1179, 1152, 1119, 1099, 1074, 1057, 1028, 999, 907, 779 cm^{-1}; HRMS: (CI) calcd for ($C_{26}H_{35}N_2O$) 391.2749 ([M+H]$^+$), found *m*/*z* 391.2742

2-((Diphenylmethylene)amino)-*N*,*N*-dimethylhept-6-enamide (8ak)



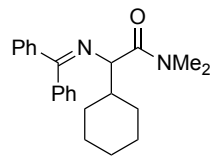
According to the typical procedure **II**, the reaction using diisopropylamine (24.8 mg, 0.25 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 140 µL, 0.22 mmol), *N*,*N*-dimethylhept-6-enamide (**7k**) (31.2 mg, 0.20 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (104.1 mg, 0.24 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 8:2) gave the product as a yellow liquid (39.5 mg, 59% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.75–7.60 (m, 2H), 7.55–7.25 (m, 6H), 7.20–7.08 (m, 2H), 5.83–5.68 (m, 1H), 5.03–4.83 (m, 2H), 4.24 (dd, *J* = 8.0, 5.6 Hz, 1H), 2.91 (s, 3H), 2.87 (s, 3H), 2.08–1.80 (m, 4H), 1.50–1.20 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.4, 168.9, 139.4, 138.5, 136.8, 130.2, 128.7, 128.6, 128.5, 127.9, 127.6, 114.6, 64.8, 36.8, 36.1, 33.6, 33.4, 25.5; IR: (ATR) 2924, 1638, 1597, 1576, 1489, 1447, 1396, 1317, 1277, 1150, 1074, 1057, 1028, 999, 941, 916, 853, 810 cm^{-1}; HRMS: (CI) calcd for ($C_{22}H_{27}N_2O$) 335.2123 ([M+H]$^+$), found *m*/*z* 335.2121

2-Cyclopropyl-2-((diphenylmethylene)amino)-*N*,*N*-dimethylacetamide (8al)



According to the typical procedure **II**, the reaction using dicyclohexylamine (41.0 mg, 0.23 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 140 µL, 0.22 mmol), 2-cyclopropyl-*N*,*N*-dimethylacetamide (**7l**) (26.3 mg, 0.21 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (103.4 mg, 0.24 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 8:2) gave the product as a pale yellow liquid (33.5 mg, 53% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.71–7.55 (m, 2H), 7.55–7.20 (m, 6H), 7.20–7.02 (m, 2H), 3.76 (d, *J* = 8.0 Hz, 1H), 3.10 (s, 3H), 2.92 (s, 3H), 1.52–1.31 (m, 1H), 0.59–0.38 (m, 2H), 0.38–0.23 (m,1H), 0.23–0.08 (m, 1H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.1, 168.7, 139.6, 136.5, 130.2, 128.8, 128.6, 128.4, 128.0, 127.9, 69.8, 37.0, 36.2, 14.9, 4.0, 2.2; IR: (ATR) 2924, 1636, 1622, 1597, 1574, 1489, 1445, 1395, 1314, 1285, 1260, 1179, 1115, 1043, 1028, 999, 847, 775 cm^{-1}; HRMS: (CI) calcd for ($C_{20}H_{23}N_2O$) 307.1810 ([M+H]$^+$), found *m*/*z* 307.1811

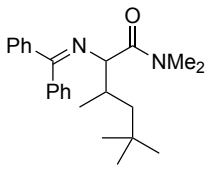
2-Cyclohexyl-2-((diphenylmethylene)amino)-*N*,*N*-dimethylacetamide (8am)



According to the typical procedure **II**, the reaction using diisopropylamine (34.7 mg, 0.34 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 205 µL, 0.33 mmol), 2-cyclohexyl-*N*,*N*-dimethylacetamide (**7m**) (50.4 mg, 0.30 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (85.7 mg, 0.20 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the product as a pale yellow liquid (54.4 mg, 78% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70–7.60 (m, 2H), 7.50–7.28 (m, 6H), 7.15–7.07 (m, 2H), 4.03 (d, *J* = 9.2 Hz, 1H), 2.90 (s, 3H), 2.86 (s, 3H), 2.20–2.08 (m, 1H), 1.93–1.78 (m, 1H), 1.78–1.60 (m, 3H), 1.60–1.48 (m, 1H), 1.33–1.17 (m, 2H), 1.17–1.00 (m, 1H),

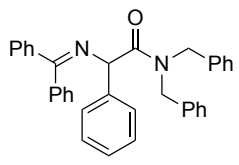
1.00–0.87 (m, 1H), 0.87–0.72 (m, 1H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 171.9, 168.7, 139.5, 137.0, 130.0, 128.7, 128.5, 128.4, 127.91, 127.90, 70.7, 42.0, 36.8, 36.0, 30.2, 29.6, 26.3, 26.1, 26.0; IR: (ATR) 2924, 2849, 1636, 1597, 1574, 1489, 1445, 1393, 1314, 1283, 1258, 1167, 1152, 1119, 1074, 1057, 1028, 988, 968, 924, 907, 779, 727 cm^{-1}; HRMS: (CI) calcd for ($C_{23}H_{29}N_2O$) 349.2280 ($[M+H]^+$), found *m*/*z* 349.2280

2-((Diphenylmethylene)amino)-*N*,*N*,3,5,5-pentamethylhexanamide (8an)



A heat-gun-dried reaction flask containing a magnetic stir bar was charged with *N*,*N*,3,5,5-pentamethylhexanamide (**7n**) (36.9 mg, 0.20 mmol) and THF (2 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then a solution of LDA (2 M in THF/heptane/ethylbenzene, 110 μL, 0.22 mmol) was added to the flask. The mixture was stirred at −78 °C for 30 min before hypervalent iodine reagent **1a** (103.4 mg, 0.24 mmol) was added. The reaction flask was removed from a cold bath and further stirred for 1 h (The reaction mixture was allowed to warm to room temperature.). The reaction was quenched with water, and the mixture was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy (*dr* = 75:25). Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the product as a pale yellow liquid (41.3 mg, 57% combined yield of diastereomers). **major isomer:** ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72–7.60 (m, 2H), 7.52–7.28 (m, 6H), 7.16–7.04 (m, 2H), 4.02 (d, *J* = 8.4 Hz, 1H), 2.97 (s, 3H), 2.88 (s, 3H), 2.32–2.19 (m, 1H), 1.32–1.21 (m, 1H), 1.04–0.92 (m, 4H), 0.86 (s, 9H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.0, 168.7, 139.7, 136.9, 130.1, 128.7, 128.45, 128.42, 128.0, 127.9, 71.9, 46.9, 37.1, 36.2, 33.7, 31.1, 30.0, 19.7; IR: (ATR) 2951, 1636, 1599, 1578, 1447, 1393, 1364, 1313, 1277, 1177, 1074, 1028, 976, 957, 810 cm^{-1}; HRMS: (EI) calcd for ($C_{24}H_{32}N_2O$) 364.2515 (M^+), found *m*/*z* 365.2520; **minor isomer:** ^{1}H NMR signals assigned from a mixture of isomers: (400 MHz, $CDCl_3$) δ 7.73–7.58 (m, 2H), 7.58–7.21 (m, 6H), 7.20–7.00 (m, 2H), 4.00 (d, *J* = 8.4 Hz, 1H), 2.93–2.82 (m, 6H), 2.32–2.19 (m, 1H), 1.50–1.40 (m, 1H), 1.06–0.78 (m, 13H); $^{13}C\{^{1}H\}$ NMR signals assigned from a mixture of isomers (observable signals): (100 MHz, $CDCl_3$) δ 172.1, 168.8, 139.5, 137.0, 130.1, 128.8, 127.9, 71.4, 46.8, 36.8, 36.0, 33.8, 31.1, 30.1, 19.7; HRMS: (EI) calcd for ($C_{24}H_{32}N_2O$) 364.2515 (M^+), found *m*/*z* 364.2524

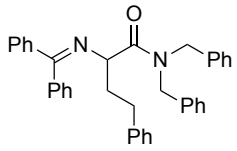
***N*,*N*-Dibenzyl-2-((diphenylmethylene)amino)-2-phenylacetamide (8ao)**



According to the typical procedure **I**, the reaction using *N*,*N*-dibenzyl-2-phenylacetamide (**7o**) (126.0 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.2 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on

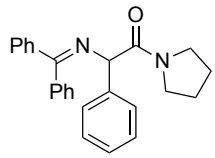
NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 90:10) gave the product as a pale yellow solid (104.0 mg, 53% yield). mp: 51.4–53.9 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.65–7.57 (m, 2H), 7.42–7.30 (m, 6H), 7.30–7.11 (m, 13H), 7.11–7.00 (m, 2H), 6.93–6.83 (m, 2H), 5.63 (s, 1H), 4.75 (d, *J* = 16.0 Hz, 1H), 4.68 (d, *J* = 14.8 Hz, 1H), 4.32 (d, *J* = 14.8 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.3, 170.1, 139.5, 139.1, 137.1, 136.7, 135.6, 130.4, 128.9, 128.8, 128.5, 128.41, 128.36, 128.3, 128.2, 127.9, 127.6, 127.23, 127.16, 127.1, 126.6, 70.7, 49.4, 47.7 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3059, 3028, 2918, 1639, 1616, 1599, 1574, 1493, 1445, 1418, 1028, 955, 781, 729 cm^{-1}; HRMS: (CI) calcd for ($C_{35}H_{31}N_2O$) 495.2436 ([M+H]$^+$), found *m*/*z* 495.2433

_N,N_-Dibenzyl-2-((diphenylmethylene)amino)-4-phenylbutanamide (8ap)



According to the typical procedure **II**, the reaction using diisopropylamine (34.6 mg, 0.34 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 205 μL, 0.33 mmol), *N*,*N*-dibenzyl-4-phenylbutanamide (**7p**) (103.4 mg, 0.30 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (85.4 mg, 0.20 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the product as a pale yellow liquid (47.0 mg, 45% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68–7.47 (m, 2H), 7.47–7.02 (m, 17H), 7.02–6.82 (m, 6H), 4.66 (d, *J* = 14.4 Hz, 1H), 4.48 (d, *J* = 14.4 Hz, 1H), 4.36 (dd, *J* = 6.8, 6.8 Hz, 1H), 4.29 (d, *J* = 16.6 Hz, 1H), 4.16 (d, *J* = 16.6 Hz, 1H), 2.65–2.49 (m, 2H), 2.49–2.33 (m, 1H), 2.12–2.00 (m, 1H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.5, 169.4, 141.3, 139.2, 137.3, 136.7, 136.2, 130.2, 128.8, 128.60, 128.56, 128.51, 128.50, 128.47, 128.4, 128.3, 127.9, 127.5, 127.3, 126.8, 125.7, 64.1, 49.0, 48.1, 35.8, 32.5 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3026, 2924, 1649, 1603, 1576, 1495, 1445, 1422, 1356, 1314, 1285, 1209, 1179, 1153, 1076, 1028, 1001, 951, 908, 781, 746, 729 cm^{-1}; HRMS: (EI) calcd for ($C_{37}H_{34}N_2O$) 522.2671 (M$^+$), found *m*/*z* 522.2668

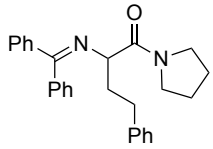
2-((Diphenylmethylene)amino)-2-phenyl-1-(pyrrolidin-1-yl)ethan-1-one (8aq)



According to the typical procedure **I**, the reaction using 2-phenyl-1-(pyrrolidin-1-yl)ethan-1-one (**7q**) (77.1 mg, 0.41 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.5 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane with addition of 2% NEt_3/EtOAc = 86:14) gave the product as a colorless viscous liquid (76.5 mg, 51% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.77–7.69 (m, 2H), 7.48–7.28 (m, 10H), 7.28–7.21 (m, 1H), 7.18–7.08 (m, 2H), 5.33 (s, 1H), 3.61–3.53 (m, 1H), 3.52–3.35 (m, 2H), 3.01–2.91 (m, 1H), 1.81–1.62 (m, 4H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 169.6, 169.5, 139.3, 139.2, 136.2, 130.3, 128.8, 128.6, 128.4, 128.3, 127.9, 127.6, 127.13, 127.10, 70.5, 46.4, 46.0, 26.1, 23.6; IR: (ATR) 3057, 3026, 2970, 2874, 1634, 1597, 1574, 1491, 1414, 1279, 1028, 781, 719 cm^{-1}; HRMS: (CI) calcd

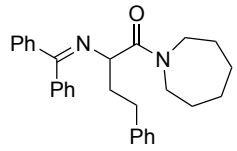
for ($C_{25}H_{25}N_2O$) 369.1967 ([M+H]$^+$), found *m*/*z* 369.1970

2-((Diphenylmethylene)amino)-4-phenyl-1-(pyrrolidin-1-yl)butan-1-one (8ar)



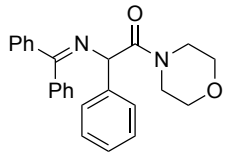
According to the typical procedure **II**, the reaction using diisopropylamine (34.5 mg, 0.34 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 205 μL, 0.33 mmol), 4-phenyl-1-(pyrrolidin-1-yl)butan-1-one (**7r**) (66.1 mg, 0.30 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (85.9 mg, 0.20 mmol) was conducted. The crude product was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard (71% NMR yield). Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the product as a pale yellow liquid (12.6 mg, 16% yield). The low isolated yield is due to difficulty in separation of the product from a side product of dimer of **7r**. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72–7.63 (m, 2H), 7.45–7.28 (m, 6H), 7.25–7.03 (m, 7H), 4.03 (dd, *J* = 6.8, 6.8 Hz, 1H), 3.50–3.35 (m, 2H), 3.05–2.93 (m, 1H), 2.77–2.58 (m, 3H), 2.23 (dd, *J* = 14.6, 7.8 Hz, 2H), 1.80–1.60 (m, 4H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.0, 169.6, 141.5, 139.3, 137.1, 130.2, 128.7, 128.43, 128.41, 128.2, 127.9, 127.5, 125.8, 64.4, 46.0, 45.7, 35.2, 32.3, 26.1, 23.9 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2967, 2949, 2926, 2872, 1638, 1576, 1495, 1423, 1339, 1314, 1285, 1252, 1227, 1180, 1169, 1074, 1028, 1001, 914, 870, 841, 781, 752 cm^{-1}; HRMS: (CI) calcd for ($C_{27}H_{29}N_2O$) 397.2280 ([M+H]$^+$), found *m*/*z* 397.2275

1-(Azepan-1-yl)-2-((diphenylmethylene)amino)-4-phenylbutan-1-one (8as)



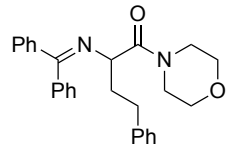
According to the typical procedure **II**, the reaction using diisopropylamine (34.9 mg, 0.34 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 205 μL, 0.33 mmol), 1-(azepan-1-yl)-4-phenylbutan-1-one (**7s**) (74.0 mg, 0.30 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (85.5 mg, 0.20 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the product as a pale yellow liquid (42.9 mg, 50% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72–7.60 (m, 2H), 7.45–7.28 (m, 6H), 7.28–7.03 (m, 7H), 4.18 (dd, *J* = 7.6, 6.4 Hz, 1H), 3.58–3.46 (m, 1H), 3.46–3.36 (m, 1H), 3.25–3.15 (m, 1H), 3.13–3.03 (m, 1H), 2.64 (dd, *J* = 7.2, 7.2 Hz, 2H), 2.43–2.28 (m, 1H), 2.20–2.07 (m, 1H), 1.75–1.58 (m, 2H), 1.55–1.43 (m, 2H) 1.43–1.35 (m, 2H), 1.35–1.20 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.6, 169.0, 141.6, 139.4, 136.7, 130.2, 128.7, 128.50, 128.47, 128.4, 128.2, 127.9, 127.6, 125.7, 63.6, 46.8, 46.4, 35.8, 32.6, 29.1, 27.3, 27.2, 26.5; IR: (ATR) 2924, 2855, 1641, 1597, 1576, 1493, 1476, 1445, 1425, 1373, 1350, 1314, 1285, 1258, 1248, 1194, 1179, 1155, 1099, 1074, 1047, 1028, 1013, 999, 907, 781 cm^{-1}; HRMS: (EI) calcd for ($C_{29}H_{32}N_2O$) 424.2515 (M$^+$), found *m*/*z* 424.2521

2-((Diphenylmethylene)amino)-1-morpholino-2-phenylethan-1-one (8at)



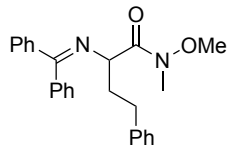
According to the typical procedure **I**, the reaction using 1-morpholino-2-phenylethan-1-one (**7t**) (81.7 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.6 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on silica gel (hexane with addition of 2% NEt_3/EtOAc = 86:14) gave the product as a white solid (82.9 mg, 54% yield). mp: 79.9–83.5 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.75–7.65 (m, 2H), 7.49–7.21 (m, 11H), 7.21–7.06 (m, 2H), 5.52 (s, 1H), 3.94–3.75 (m, 1H), 3.68–3.50 (m, 5H), 3.50–3.32 (m, 1H), 3.32–3.10 (m, 1H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 170.6, 169.5, 139.3, 139.1, 135.4, 130.6, 128.9, 128.8, 128.6, 128.5, 128.1, 127.7, 127.2, 125.9, 71.2, 66.7, 66.5, 46.4, 42.9; IR: (KBr) 2961, 2857, 1639, 1439, 1273, 1240, 1113, 972, 737, 700 cm^{-1}; HRMS: (CI) calcd for ($C_{25}H_{25}N_2O_2$) 385.1916 ([M+H]$^+$), found *m*/*z* 385.1920

2-((Diphenylmethylene)amino)-1-morpholino-4-phenylbutan-1-one (8au)



According to the typical procedure **II**, the reaction using diisopropylamine (34.9 mg, 0.35 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 205 μL, 0.33 mmol), 1-morpholino-4-phenylbutan-1-one (**7u**) (71.2 mg, 0.31 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (85.6 mg, 0.20 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the product as a yellow liquid (47.5 mg, 57% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ7.72–7.60 (m, 2H), 7.48–7.30 (m, 6H), 7.30–7.20 (m, 2H) , 7.20–7.00 (m, 5H), 4.22 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.72–3.33 (m, 7H), 3.33–3.15 (m, 1H), 2.73–2.53 (m, 2H), 2.31–2.10 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.0, 169.8, 141.2, 139.2, 136.4, 130.4, 128.72, 128.69, 128.5, 128.4, 128.3 128.1, 127.6, 126.0, 67.0, 66.7, 64.6, 45.8, 42.6, 35.8, 32.5; IR: (ATR) 3059, 3024, 2955, 2920, 2853, 1636, 1597, 1574, 1495, 1445, 1431, 1358, 1314, 1287, 1267, 1229, 1179, 1113, 1069, 1026, 1001, 966, 914, 845, 781, 752 cm^{-1}; HRMS: (CI) calcd for ($C_{27}H_{29}N_2O_2$) 413.2229 ([M+H]$^+$), found *m*/*z* 413.2224

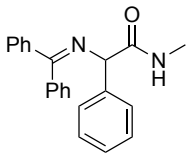
2-((Diphenylmethylene)amino)-*N*-methoxy-*N*-methyl-4-phenylbutanamide (8av)



A heat-gun-dried reaction flask containing a magnetic stir bar was charged with *N*-methoxy-*N*-methyl-4-phenylbutanamide (**7v**) (42.8 mg, 0.21 mmol) and THF (2 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then a solution of LDA (2 M in THF/heptane/ethylbenzene, 110 μL, 0.22 mmol) was added to the flask. The mixture was stirred at −78 °C for 30 min before hypervalent iodine reagent **1a** (102.1 mg, 0.24 mmol) was added. The reaction flask was removed from a cold bath and further stirred for 1 h (The reaction mixture was allowed to warm to room temperature.). The reaction was quenched with water, and the

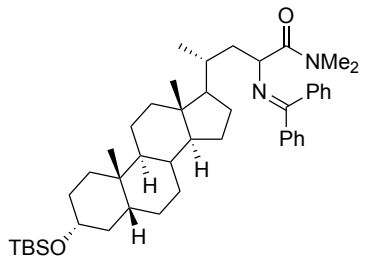
mixture was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 8:2) gave the product as a yellow liquid (22.0 mg, 29% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.71–7.60 (m, 2H), 7.43–7.28 (m, 6H), 7.25–6.98 (m, 7H), 4.24 (dd, *J* = 7.6, 6.4 Hz, 1H), 3.12 (s, 3H), 3.02 (brs, 3H), 2.67 (dd, *J* = 7.6, 6.4 Hz, 2H), 2.37 (ddt, *J* = 14.0, 6.4, 6.4 Hz, 1H), 2.13 (ddt, *J* = 14.0, 7.6, 7.6 Hz, 1H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.2, 170.0, 141.4, 139.5, 136.9, 130.2, 128.7, 128.5, 128.3, 128.2, 127.9, 127.7, 127.5, 125.7, 61.8, 60.6, 34.5, 32.4, 32.2; IR: (ATR) 2934, 2160, 1659, 1622, 1597, 1576, 1495, 1447, 1385, 1315, 1277, 1152, 1074, 1028, 989, 920, 781, 752 cm^{-1}; HRMS: (CI) calcd for ($C_{25}H_{27}N_2O_2$) 387.2073 ([M+H]$^+$), found *m*/*z* 387.2065

2-((Diphenylmethylene)amino)-*N*-methyl-2-phenylacetamide (8aw)



According to the typical procedure **II**, the reaction using diisopropylamine (88.4 mg, 0.87 mmol), THF (2 mL), *n*-BuLi (1.6 M in hexane, 550 μL, 0.88 mmol), *N*-methyl-2-phenylacetamide (**7w**) (60.0 mg, 0.40 mmol) in THF (2 mL), and hypervalent iodine reagent **1a** (205.7 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 8:2) gave the product as a yellow solid (26.0 mg, 20% yield). mp: 130.2–131.9 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.79–7.60 (m, 2H), 7.55–7.10 (m, 12H), 7.05–6.95 (m, 2H), 4.98 (s, 1H), 2.89 (d, *J* = 5.2 Hz, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.5, 169.6, 140.4, 139.1, 135.5, 130.8, 129.0, 128.7, 128.5, 128.4, 128.2, 127.52, 127.47, 127.0, 69.9, 26.1; IR: (ATR) 3370, 2936, 1657, 1622, 1601, 1574, 1518, 1491, 1449, 1398, 1373, 1319, 1148, 1047, 1030, 999, 957, 775 cm^{-1}; HRMS: (CI) calcd for ($C_{22}H_{21}N_2O$) 329.1654 ([M+H]$^+$), found *m*/*z* 329.1651

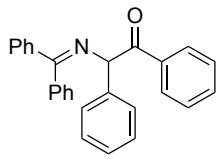
(4*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-((*tert*-Butyldimethylsilyl)oxy)-10,13-dimethyl-hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-2-((diphenylmethylene)amino)-*N*,*N*-dimethylpentanamide (8ax)



According to the typical procedure **II**, the reaction using diisopropylamine (22.9 mg, 0.22 mmol), THF (1 mL), *n*-BuLi (1.6 M in hexane, 140 μL, 0.22 mmol), (*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-((*tert*-butyldimethylsilyl)oxy)-10,13-dimethyl-hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-*N*,*N*-dimethylpentanamide (**7x**) (103.6 mg, 0.20 mmol) in THF (1 mL), and hypervalent iodine reagent **1a** (103.3 mg, 0.24 mmol) was conducted. The crude product was analyzed by ^{1}H NMR spectroscopy (*dr* = 50:50). Purification by flash column chromatography on

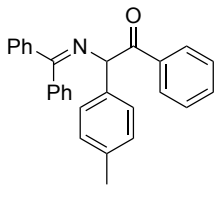
NH silica gel (hexane/EtOAc = 8:2) gave the product (74.6 mg, 53% combined yield of diastereomers). **isomer 1**: white solid; mp. 192.0–194.0 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.50–7.20 (m, 6H), 7.17–7.05 (m, 2H), 4.20 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.62–3.51 (m, 1H), 2.89 (s, 3H), 2.82 (s, 3H), 2.36–2.21 (m, 1H), 1.97–0.97 (m, 25H), 0.93–0.82 (m, 12H), 0.66 (d, *J* = 6.4 Hz, 3H), 0.62 (s, 3H), 0.05 (s, 6H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.4, 169.0, 139.5, 137.2, 130.1, 128.8, 128.4, 127.9, 127.8, 127.7, 72.8, 62.3, 56.7, 56.4, 42.8, 42.3, 40.22, 40.16, 40.1, 36.9, 36.7, 36.0, 35.8, 35.5, 34.5, 32.8, 31.0, 28.4, 27.3, 26.4, 25.9, 24.2, 23.4, 20.8, 18.3, 18.0, 12.1, −4.6; IR: (ATR) 2926, 2853, 1657, 1643, 1445, 1387, 1371, 1252, 1094, 1076, 1055, 872, 833, 773 cm^{-1}; HRMS: (EI) calcd for ($C_{45}H_{68}N_2O_2Si$) 696.5050 (M^+), found *m*/*z* 696.5053; **isomer 2**: colorless liquid; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.55–7.22 (m, 6H), 7.20 (d, *J* = 6.4 Hz, 2H), 4.40 (dd, *J* = 9.2, 4.8 Hz, 1H), 3.62–3.51 (m, 1H), 2.95 (s, 3H), 2.94 (s, 3H) 2.54–2.30 (m, 1H), 2.00–1.70 (m, 6H), 1.70–0.80 (m, 19H), 0.89 (s, 9H), 0.88 (s, 3H), 0.66 (d, *J* = 6.4 Hz, 3H), 0.57 (s, 3H), 0.06 (s, 6H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.1, 168.2, 139.5, 136.6, 130.1, 128.7, 128.5, 128.0, 127.71, 127.68, 72.8, 63.4, 56.9, 56.4, 42.7, 42.3, 40.7, 40.1, 36.92, 36.87, 36.3, 36.2, 35.8, 35.5, 34.6, 34.0, 31.0, 28.3, 27.3, 26.4, 25.9, 24.2, 23.3, 20.8, 19.0, 18.3, 12.0, −4.6; IR: (ATR) 2926, 2855, 1643, 1447, 1250, 1092, 1076, 1055, 870, 835, 773 cm^{-1}; HRMS: (EI) calcd for ($C_{45}H_{68}N_2O_2Si$) 696.5050 (M^+), found *m*/*z* 696.5037

2-((Diphenylmethylene)amino)-1,2-diphenylethan-1-one (10aa)



According to the typical procedure **I**, the reaction using 1,2-diphenylethan-1-one (**9a**) (77.9 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.6 mg, 0.48 mmol) was conducted. The crude product was analyzed by ^{1}H NMR spectroscopy using dibromomethane as an internal standard (**10aa**, 50% yield). Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a pale yellow liquid (55.5 mg, 37% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.97–7.90 (m, 2H), 7.75–7.66 (m, 2H), 7.52–7.25 (m, 13H), 7.25–7.18 (m, 1H), 7.14–7.04 (m, 2H), 5.88 (s, 1H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 197.5, 170.0, 139.3, 139.2, 136.1, 135.6, 132.7, 130.4, 129.7, 128.9, 128.8, 128.7, 128.6, 128.1, 128.0, 127.6, 127.5, 127.4, 74.2; IR: (neat) 3059, 3030, 1659, 1599, 1447, 1317, 1279, 702 cm^{-1}; HRMS: (CI) calcd for ($C_{27}H_{22}NO$) 376.1701 ([M+H]$^+$), found *m*/*z* 376.1706

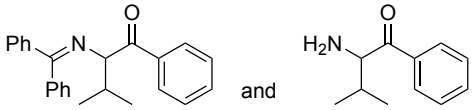
2-((Diphenylmethylene)amino)-2-(4-methylphenyl)-1-phenylethan-1-one (10ab)



According to the typical procedure **I**, the reaction using 2-(4-methylphenyl)-1-phenylethan-1-one (**9b**) (84.5 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.4 mg, 0.48 mmol) was conducted. The crude product was analyzed by ^{1}H NMR

spectroscopy using dibromomethane as an internal standard (**10ab**, 67% yield). Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (45.6 mg, 29% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.99–7.90 (m, 2H), 7.75–7.65 (m, 2H), 7.46–7.25 (m, 11H), 7.15–7.03 (m, 4H), 5.85 (s, 1H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 197.6, 169.7, 139.4, 137.1, 136.3, 136.2, 135.7, 132.6, 130.4, 129.7, 129.4, 128.9, 128.8, 128.6, 128.1, 128.0, 127.6, 127.4, 74.0, 21.1; IR: (neat) 3059, 3030, 2980, 1736, 1449, 1242, 1045, 1011, 764 cm^{-1}; HRMS: (FAB+) calcd for ($C_{28}H_{24}NO$) 390.1858 ([M+H]$^+$), found *m*/*z* 390.1865

2-((Diphenylmethylene)amino)-3-methyl-1-phenylbutan-1-one (10ac)



A heat-gun-dried reaction flask containing a magnetic stir bar was charged with diisopropylamine (68.3 mg, 0.67 mmol) and THF (2 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then *n*-BuLi (1.6 M in hexane, 415 μL, 0.66 mmol) was added to the flask. The mixture was stirred at −78 °C for 20 min before a solution of isovalerophenone (98.2 mg, 0.61 mmol) in THF (2 mL) was added, and further stirred at −78 °C for 30 min. Then, hypervalent iodine reagent **1a** (171.4 mg, 0.40 mmol) was added to the mixture. The reaction flask was removed from a cold bath and further stirred for 4 h (The reaction mixture was allowed to warm to room temperature.). The reaction was quenched with water, and the mixture was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard (**10ac**, 22% yield). To a solution of the crude product in THF (2 mL) was added HCl (1 M in Et_2O, 5 mL), and the mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with H_2O (15 mL) and washed with Et_2O (3 × 15 mL), and the water layer was concentrated to approximately 10 mL under reduced pressure (60 °C, 60 Torr). Then, the residue was further washed with Et_2O (3 × 15 mL) and basified with sat. $NaHCO_3$ aq. until pH = 9. The mixture was extracted with EtOAc (3 × 30 mL) and the collected organic layers was concentrated under reduced pressure to give the product as a brown oil (14.0 mg, 20% yield).

2-((Diphenylmethylene)amino)-3-methyl-1-phenylbutan-1-one (10ac)

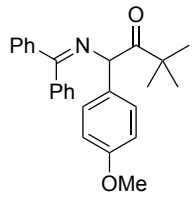
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.69 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.55–7.47 (m, 1H), 7.53–7.27 (m, 8H), 7.05–6.97 (m, 2H), 4.46 (d, *J* = 7.6 Hz, 1H), 2.55–2.42 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); HRMS: (CI) calculated for ($C_{24}H_{24}NO$) 342.1858 ([M+H]$^+$) found *m*/*z* 342.1854

2-Amino-3-methyl-1-phenylbutan-1-one

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.63–7.53 (m, 1H), 7.53–7.40 (m, 2H), 4.32 (d, *J* = 3.2 Hz, 1H), 2.18–2.00 (m, 1H), 2.00–1.50 (br, 2H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.75 (d, *J* = 6.8 Hz,

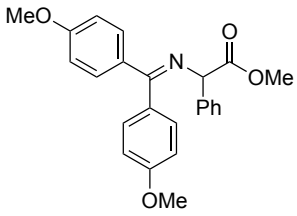
3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 203.0, 135.9, 133.1, 128.7, 128.2, 60.9, 31.7, 20.5, 15.4; IR: (ATR) 2961, 2928, 2901, 2872, 2156, 1682, 1661, 1597, 1447, 1263, 1227, 1074, 1051, 918, 879, 754 cm^{-1}; HRMS: (FAB+) calculated for ($C_{11}H_{16}NO$) 178.1232 ($[M+H]^+$) found *m*/*z* 178.1238

1-((Diphenylmethylene)amino)-1-(4-methoxyphenyl)-3,3-dimethylbutan-2-one (10ad)



According to the typical procedure **I**, the reaction using 1-(4-methoxyphenyl)-3,3-dimethylbutan-2-one (**9d**) (81.6 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1a** (205.1 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (93.6 mg, 61% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72–7.65 (m, 2H), 7.50–7.40 (m, 3H), 7.40–7.21 (m, 5H), 7.08–7.00 (m, 2H), 6.88–6.80 (m, 2H), 5.51 (s, 1H), 3.76 (s, 3H), 0.98 (s, 9H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 212.1, 168.3, 158.8, 139.3, 136.4, 131.6, 130.2, 129.3, 128.7, 128.6, 128.4, 127.9, 127.5, 113.8, 71.4, 55.1, 44.7, 26.8; IR: (neat) 3059, 2967, 2835, 1715, 1697, 1609, 1574, 1504, 1445, 1302, 1287, 1250, 1173, 1032, 986, 829 cm^{-1}; HRMS: (FAB+) calcd for ($C_{26}H_{28}NO_2$) 386.2120 ($[M+H]^+$), found *m*/*z* 386.2121

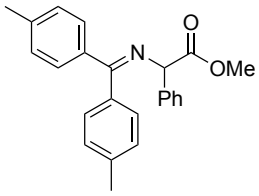
Methyl 2-((bis(4-methoxyphenyl)methylene)amino)-2-phenylacetate (3ca)



According to the typical procedure **I**, the reaction using methyl 2-phenylacetate (**2a**) (60.3 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1c** (234.0 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 93:7) gave the product as a colorless liquid (89.8 mg, 57%). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70–7.62 (m, 2H), 7.48–7.40 (m, 2H), 7.36–7.23 (m, 3H), 7.05–6.98 (m, 2H), 6.98–6.90 (m, 2H), 6.86–6.80 (m, 2H), 5.19 (s, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.68 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 172.3, 169.6, 161.4, 159.7, 139.4, 132.6, 130.7, 129.2, 128.4, 128.3, 127.8, 127.6, 113.8, 113.2, 69.4, 55.3, 55.2, 52.3

The analytical data for this compound were in excellent agreement with the reported data.[12]

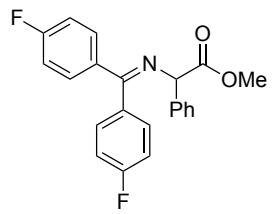
Methyl 2-((bis(4-methylphenyl)methylene)amino)-2-phenylacetate (3da)



According to the typical procedure **I**, the reaction using methyl 2-phenylacetate (**2a**) (59.9 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1d** (219.1 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (97.8 mg), which contains a small amount of homocoupling products of **2a**. The yield of **3da** was determined by

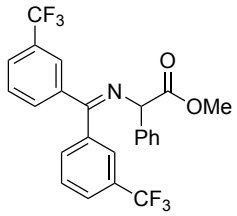
^{1}H NMR analysis of the purified product which contains 0.27 mmol of **3da** (67% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.64–7.57 (m, 2H), 7.46–7.40 (m, 2H), 7.35–7.25 (m, 3H), 7.25–7.19 (m, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 5.18 (s, 1H), 3.67 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.1, 170.4, 140.6, 139.3, 138.5, 136.9, 133.2, 129.1, 129.0, 128.7, 128.4, 127.8, 127.65, 127.60, 69.5, 52.3, 21.35, 21.34; IR: (neat) 3028, 2995, 2951, 2920, 1748, 1732, 1715, 1605, 1568, 1454, 1447, 1435, 1315, 1294, 1279, 1020, 826, 725 cm^{-1}; HRMS: (FAB+) calcd for ($C_{24}H_{24}NO_2$) 358.1807 ([M+H]$^+$), found m/z 358.1810

Methyl 2-((bis(4-fluorophenyl)methylene)amino)-2-phenylacetate (3ea)



According to the typical procedure **I**, the reaction using methyl 2-phenylacetate (**2a**) (59.1 mg, 0.39 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1e** (222.0 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave the product as a colorless liquid (85.1 mg), which contains a small amount of homocoupling products of **2a**. The yield of **3ea** was determined by ^{1}H NMR analysis of the purified product which contains 0.22 mmol of **3ea** (56% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.75–7.64 (m, 2H), 7.46–7.38 (m, 2H), 7.38–7.26 (m, 3H), 7.20–7.11 (m, 2H), 7.11–6.98 (m, 4H), 5.10 (s, 1H), 3.68 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.8, 168.2, 164.4 (d, $J_{C–F}$ = 250.3 Hz), 162.8 (d, $J_{C–F}$ = 257.8 Hz). 138.8, 135.4 (d, $J_{C–F}$ = 3.3 Hz), 131.6 (d, $J_{C–F}$ = 3.3 Hz), 131.0 (d, $J_{C–F}$ = 8.2 Hz), 129.6 (d, $J_{C–F}$ = 7.4 Hz), 128.6, 128.0, 127.8, 115.9 (d, $J_{C–F}$ = 21.4 Hz), 115.1 (d, $J_{C–F}$ = 21.4 Hz), 69.6, 52.5; ^{19}F{^{1}H} NMR: (377 MHz, $CDCl_3$) δ −112.5, −114.0; IR: (neat) 3065, 3030, 2953, 1748, 1732, 1601, 1504, 1454, 1302, 1225, 1152, 843, 700 cm^{-1}; HRMS: (FAB+) calcd for ($C_{22}H_{18}F_2NO_2$) 366.1306 ([M+H]$^+$), found m/z 366.1308

Methyl 2-((bis(3-(trifluoromethyl)phenyl)methylene)amino)-2-phenylacetate (3fa)

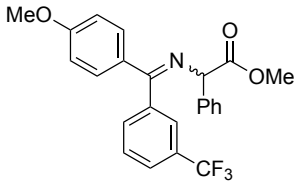


According to the typical procedure **I**, the reaction using methyl 2-phenylacetate (**2a**) (60.0 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1f** (270.6 mg, 0.48 mmol) was conducted. Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3) gave the product as a colorless liquid (90.5 mg), which contains a small amount of homocoupling products of **2a**. The yield of **3fa** was determined by ^{1}H NMR analysis of the purified product which contains 0.19 mmol of **3fa** (47% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.71–7.61 (m, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.44–7.28 (m, 7H), 5.02 (s, 1H), 3.69 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.3, 167.3, 139.3, 138.3, 135.9, 132.2, 131.4 (q, $J_{C–F}$ = 32.9 Hz), 130.9, 130.8 (q, $J_{C–F}$ = 32.1 Hz), 129.5, 128.8, 128.7, 128.2, 127.9, 127.4 (q, $J_{C–F}$ = 4.1 Hz), 126.2 (q, $J_{C–F}$ = 4.1 Hz), 125.3 (q, $J_{C–F}$ = 4.1 Hz), 124.5 (q, $J_{C–F}$ = 4.1 Hz),

123.8 (q, J_{C-F} = 270.9 Hz), 123.6 (q, J_{C-F} = 270.9 Hz), 69.8, 52.6

The analytical data for this compound were in excellent agreement with the reported data.[12]

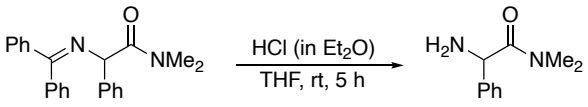
Methyl 2-(((4-methoxyphenyl)(3-(trifluoromethyl)phenyl)methylene)amino)-2-phenylacetate (3ga)



According to the typical procedure **I**, the reaction using methyl 2-phenylacetate (**2a**) (60.1 mg, 0.40 mmol), THF (4 mL), LiHMDS (0.44 mL, 1 M in THF), and hypervalent iodine reagent **1g** (251.4 mg, 0.48 mmol) was conducted. The crude product was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard (**3ga**, 59% yield). Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 95:5) gave the product as a colorless liquid (43.1 mg, 25%). The product was obtained as a mixture of *E*/*Z* isomers (69:31). ^{1}H NMR of a mixture of *E*/*Z* isomers: (400 MHz, $CDCl_3$) δ 8.00–7.95 (m, 0.3H), 7.89 (d, *J* = 8.0 Hz, 0.3H), 7.73 (d, *J* = 8.0 Hz, 0.7H), 7.66–7.54 (m, 2.7H), 7.48–7.20 (m, 6.3H), 7.05–6.95 (m, 1.3H), 6.90–6.83 (m, 1.4H), 5.24 (s, 0.3H), 4.97 (s, 0.7H), 3.89 (s, 0.9H), 3.82 (s, 2.1H), 3.70 (s, 0.9H), 3.68 (s, 2.1H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) complicated due to mixture of *E*/*Z* isomers and C–F coupling; ^{19}F{^{1}H} NMR: (377 MHz, $CDCl_3$) δ −65.1, −65.3; IR: (neat) 2953, 2839, 1748, 1732, 1601, 1506, 1339, 1252, 1155, 1130, 1072, 841, 808 cm^{-1}; HRMS: (FAB+) calcd for ($C_{24}H_{21}F_3NO_3$) 428.1474 ([M+H]$^{+}$), found *m*/*z* 428.1477

Transformations of the α-amino carbonyl products

Hydrolysis of 8aa



8aa

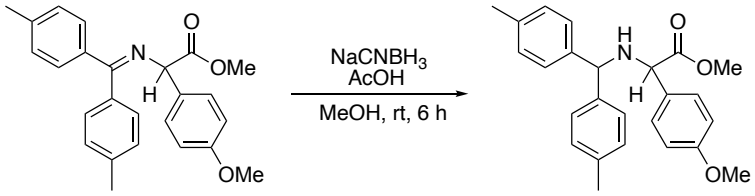
A reaction flask containing a magnetic stir bar was charged with 2-((diphenylmethylene)amino)-*N*,*N*-dimethyl-2-phenylacetamide (**8aa**) (75.3 mg, 0.22 mmol), THF (4 mL), and HCl (1 M in Et_2O, 5 mL). The mixture was stirred at room temperature for 5 h, diluted with H_2O (10 mL), and washed with Et_2O (3 x 10 mL), and the collected water layers were concentrated under reduced pressure. Then, the residue was basified with sat. $NaHCO_3$ aq. until pH = 9. The mixture was extracted with EtOAc (3 x 10 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the product as a yellow solid (31.1 mg, 79% yield).

2-Amino-*N*,*N*-dimethyl-2-phenylacetamide (11)

mp. 98.6–102.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.42–7.22 (m, 5H), 4.73 (brs, 1H), 2.99 (s, 3H), 2.85 (s, 3H) 2.12 (brs, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 172.8, 141.2, 129.0, 127.8, 127.0, 56.8,

36.6, 36.0; IR: (ATR) 3364, 3298, 2924, 2853, 1620, 1566, 1491, 1452, 1402, 1371, 1252, 1142, 962, 910, 820, 762, 719, 700 cm^{-1}; HRMS: (CI) calcd for ($C_{10}H_{15}N_2O$) 179.1184 ($[M+H]^+$), found *m/z* 179.1186

Hydride reduction of 3cb



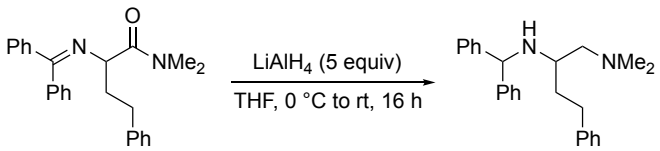
3cb

A reaction flask containing a magnetic stir bar was charged with methyl 2-((bis(4-methylphenyl)methylene)amino)-2-(4-methoxyphenyl)acetate (**3cb**) (96.5 mg, 0.25 mmol), MeOH (2 mL), $NaCNBH_3$ (31.3 mg, 0.50 mmol), and AcOH (14.4 μL) under nitrogen. The mixture was stirred at room temperature for 6 h. The reaction was quenched with H_2O, and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with sat. $NaHCO_3$ aq., dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (EtOAc) gave the product as a colorless liquid (91.6 mg, 94% yield).

Methyl 2-((bis(4-methylphenyl)methyl)amino)-2-(4-methoxyphenyl)acetate (12)

^1H NMR: (400 MHz, $CDCl_3$) δ 7.30–7.16 (m, 6H), 7.12–7.02 (m, 4H), 6.89–6.82 (m, 2H), 4.65 (s, 1H), 4.28 (s, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 2.73 (brs, 1H), 2.29 (s, 3H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 173.7, 159.3, 140.4, 140.2, 136.7, 136.6, 130.1, 129.2, 129.1, 128.6, 127.3, 127.2, 114.0, 63.5, 62.0, 55.2, 52.0, 20.99, 20.96; IR: (neat) 3329, 3001, 2951, 2835, 1738, 1611, 1585, 1510, 1454, 1435, 1304, 1250, 1173, 1034, 831, 808 cm^{-1}; HRMS: (FAB+) calcd for ($C_{25}H_{28}NO_3$) 390.2069 ($[M+H]^+$), found *m/z* 390.2071

Hydride reduction of 8ah



8ah

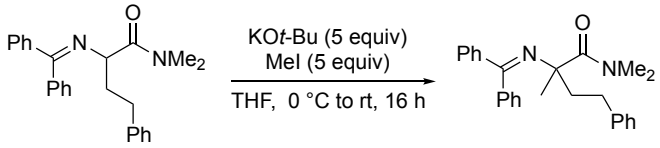
A heat-gun-dried reaction flask containing a magnetic stir bar was charged with 2-((diphenylmethylene)amino)-*N,N*-dimethyl-4-phenylbutanamide (**8ah**) (37.5 mg, 0.10 mmol) and THF (3 mL) under nitrogen. The reaction flask was cooled to 0 °C. $LiAlH_4$ (20.2 mg, 0.53 mmol) was added portionwise to the reaction mixture over a period of 10 min at 0 °C, and the resulting mixture was stirred for 16 h at room temperature. The reaction was quenched with water, and the mixture was

extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the product as a colorless liquid (25.4 mg, 70% yield).

N^2-benzhydryl-N^1,N^1-dimethyl-4-phenylbutane-1,2-diamine (13)

^1H NMR: (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 2H), 7.33–7.15 (m, 11H), 7.15–7.05 (m, 2H), 4.90 (s, 1H), 2.75–2.48 (m, 3H), 2,44 (dd, J = 12.0, 9.6 Hz, 1H), 2.25–2.06 (m, 2H), 2.05 (s, 6H), 1.83–1.62 (m, 2H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 144.6, 144.3, 142.8, 128.4, 128.34, 128.29, 128.2, 127.7, 127.5, 126.8, 126.6, 125.6, 64.0, 63.7, 51.5, 45.8, 34.5, 31.5; IR: (ATR) 2972, 2940, 2901, 2855, 2818, 2766, 1493, 1452, 1261, 1099, 1028, 866, 839, 745, 733 cm^{-1}; HRMS: (CI) calcd for ($C_{25}H_{31}N_2$) 359.2487 ($[M+H]^+$), found m/z 359.2485

Methylation of 8ah



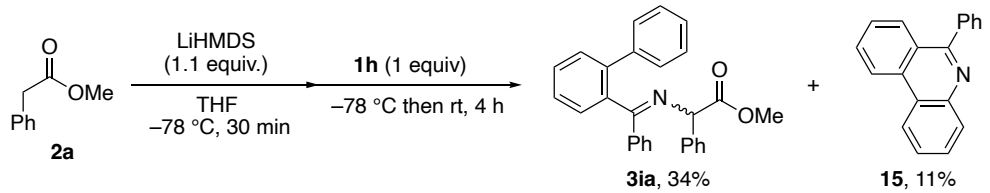
8ah

A heat-gun-dried reaction flask containing a magnetic stir bar was charged with 2-((diphenylmethylene)amino)-*N,N*-dimethyl-4-phenylbutanamide (**8ah**) (73.2 mg, 0.20 mmol) and THF (1 mL) under nitrogen. The reaction flask was cooled to 0 °C, and then a solution of KO^{t}Bu (114.4 mg, 1.02 mmol) in THF (2 mL) was added to the flask. Methyl iodide (145.6 mg, 1.03 mmol) was then added to the mixture in a dropwise manner at 0 °C, and the resulting mixture was stirred for 16 h at room temperature. The reaction was quenched with water, and the mixture was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the product as a colorless liquid (57.0 mg, 75% yield).

2-((Diphenylmethylene)amino)-*N*,*N*,2-trimethyl-4-phenylbutanamide (14)

^1H NMR: (400 MHz, $CDCl_3$) δ 7.67–7.54 (m, 2H), 7.45–7.13 (m, 11H), 7.08–6.93 (m, 2H), 3.05 (s, 3H), 3.05–2.85 (m, 1H), 2.72 (s, 3H), 2.72–2.57 (m, 1H), 2.36–2.23 (m, 1H), 2.20–2.07 (m, 1H), 1.43 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.0, 166.3, 142.7, 140.8, 137.1, 130.1, 128.7, 128.4, 128.3, 128.2, 128.0, 127.8, 127.5, 125.7, 66.4, 43.6, 38.4, 36.4, 30.5, 25.1; IR: (ATR) 2934, 1634, 1576, 1489, 1445, 1383, 1368, 1312, 1256, 1180, 1142, 1119, 1092, 1074, 1059, 1028, 1001, 953, 912, 781 cm^{-1}; HRMS: (CI) calcd for ($C_{26}H_{29}N_2O$) 385.2280 ($[M+H]^+$), found m/z 385.2277

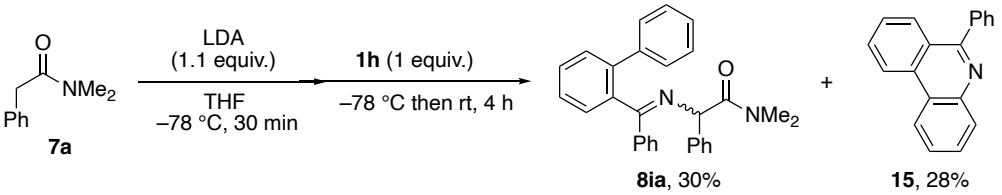
Intramolecular iminyl radical trapping experiment



A heat-gun-dried reaction flask containing a magnetic stir bar was charged with methyl 2-phenylacetate (**2a**) (28.8 mg, 0.19 mmol) and THF (1 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then a solution of LiHMDS (0.22 mL, 1 M in THF) was added to the flask. The mixture was stirred at −78 °C for 30 min before hypervalent iodine reagent **1i** (100.7 mg, 0.20 mmol) was added. The reaction flask was removed from cold bath and further stirred for 4 h. (The reaction mixture was allowed to warm to room temperature.) The reaction was quenched with sat. $NaHCO_3$ aq., and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard (**3ha**, 34% NMR yield, isomeric ratio = 52:48; **15**, 11% NMR yield). Purification by flash column chromatography on NH silica gel (hexane with addition of 2% NEt_3/EtOAc = 99:1) gave **3ha** as a colorless liquid. The product was obtained as a mixture of *E*/*Z* isomers (52:48).

Methyl-2-(([1,1'-biphenyl]-2-yl(phenyl)methylene)amino)-2-phenylacetate (3ha)

^1H NMR of a mixture of *E*/*Z* isomers: (400 MHz, $CDCl_3$) δ 7.73–7.65 (m, 1H), 7.63–7.39 (m, 4H), 7.39–7.10 (m, 11H), 7.03–6.82 (m, 2H), 5.18 (s, 0.5H), 5.05 (s, 0.5H), 3.61 (s, 1.5H), 3.47 (s, 1.5H); observable signals in the $^{13}C\{^1H\}$ NMR of a mixture of *E*/*Z* isomers: (100 MHz, $CDCl_3$) δ 171.7, 171.3, 170.5, 169.0, 140.8, 140.7, 139.8, 139.7, 139.6, 139.5, 138.9, 138.3, 134.7, 134.5, 130.3, 130.22, 130.18, 130.15, 130.1, 129.29, 129.25, 129.2, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.14, 128.08, 127.94, 127.90, 127.88, 127.84, 127.79, 127.71, 127.68, 127.57, 127.4, 127.2, 127.14, 127.10, 69.7, 69.4, 52.3, 52.1; IR: (ATR) 3055, 3026, 2949, 1734, 1616, 1449, 1246, 1200, 1153, 779, 743, 731 cm^{-1}; HRMS: (FAB+) calcd for ($C_{28}H_{24}NO_2$) 406.1807 ($[M+H]^+$), found *m*/*z* 406.1805



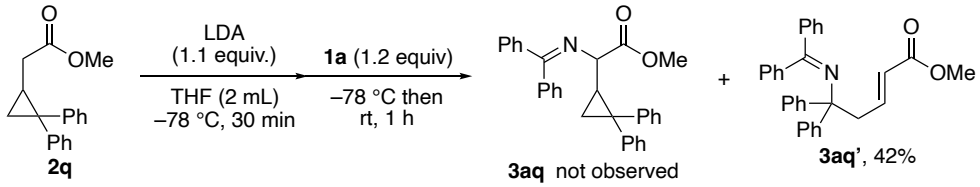
A heat-gun-dried reaction flask containing a magnetic stir bar was charged with diisopropylamine (23.9 mg, 0.24 mmol) and THF (1 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then *n*-BuLi (1.6 M in hexane, 140 μL, 0.22 mmol) was added to the flask. The mixture was stirred at −78 °C for 20 min before *N*,*N*-dimethyl-2-phenylacetamide (33.6 mg, 0.20 mmol) was added, and

further stirred at −78 °C for 30 min. Then, hypervalent iodine reagent **1h** (100.9 mg, 0.20 mmol) was added to the mixture. The reaction flask was removed from a cold bath and further stirred for 4 h (The reaction mixture was allowed to warm to room temperature.). The reaction was quenched with water, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard (**8ha**, 30% NMR yield, isomeric ratio = 63:37; **15**, 28% NMR yield). Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 85:15) gave **8ha** as a yellow liquid (14.6 mg, 17% yield). The product was obtained as a mixture of *E*/*Z* isomers (63:37).

2-(([1,1'-Biphenyl]-2-yl(phenyl)methylene)amino)-*N*,*N*-dimethyl-2-phenylacetamide (8ha)

^{1}H NMR of a mixture of *E*/*Z* isomers: (400 MHz, $CDCl_3$) δ 7.75–7.65 (m, 1.2H), 7.65–7.55 (m, 0.8H), 7.55–7.40 (m, 3H), 7.40–6.95 (m, 13.6H), 6.95–6.87 (m, 0.4H), 5.48 (s, 0.4H), 5.37 (s, 0.6H), 2.90–2.75 (m, 6H); observable signals in the $^{13}C\{^1H\}$ NMR of a mixture of *E*/*Z* isomers: (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.8, 169.5, 140.9, 140.5, 140.0, 139.9, 139.4, 139.0, 134.9, 134.8, 130.3, 130.2, 130.04, 129.99, 129.3, 129.2, 129.1, 128.7, 128.59, 128.56, 128.4, 128.2, 128.1, 128.03, 128.00, 127.9, 127.3, 127.2, 127.1, 127.0, 126.82, 126.80, 126.4, 71.0, 70.2, 36.9, 36.6, 36.2; IR: (ATR) 2926, 1736, 1639, 1614, 1576, 1493, 1476, 1447, 1393, 1373, 1242, 1159, 1132, 1042, 1030, 983, 777, 743 cm^{-1}; HRMS: (CI) calcd for ($C_{29}H_{27}N_2O$) 419.2123 ($[M+H]^+$), found *m*/*z* 419.2116

Cyclopropane ring-opening experiments

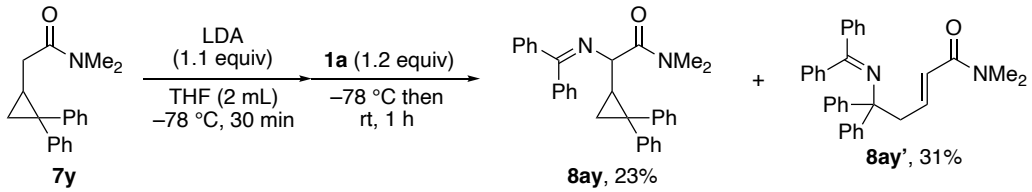


A heat-gun-dried reaction flask containing a magnetic stir bar was charged with diisopropylamine (23.6 mg, 0.23 mmol) and THF (1 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then *n*-BuLi (1.6 M in hexane, 140 μL, 0.22 mmol) was added to the flask. The mixture was stirred at −78 °C for 20 min before a solution of methyl 2-(2,2-diphenylcyclopropyl)acetate (53.1 mg, 0.20 mmol) in THF (1 mL) was added, and further stirred at −78 °C for 30 min. Then, hypervalent iodine reagent **1a** (103.4 mg, 0.24 mmol) was added to the mixture. The reaction flask was removed from a cold bath and further stirred for 1 h (The reaction mixture was allowed to warm to room temperature.). The reaction was quenched with water, and the mixture was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard (**3aq'**, 42% NMR yield). Purification by flash column chromatography on NH

silica gel (hexane/EtOAc = 95:5) gave **3aq** as a pale yellow liquid (27.2 mg, 30% yield).

Methyl (*E*)-5-((diphenylmethylene)amino)-5,5-diphenylpent-2-enoate (3aq')

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.74–7.56 (m, 2H), 7.43–7.21 (m, 7H), 7.21–7.08 (m, 7H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.83 (dt, *J* = 16.0, 7.2 Hz, 1H), 6.46 (d, *J* = 7.6 Hz, 2H), 5.61 (d, *J* = 16.0 Hz, 1H), 3.63 (s, 3H), 3.09 (dd, *J* = 7.2, 1.2 Hz, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.4, 166.5, 148.8, 145.3, 141,6, 138.5, 130.0, 128.4, 128.0, 127.8, 127.7, 127.3, 127.2, 127.1, 126.2, 123.1, 68.8, 51.3, 43.4; IR: (ATR) 3055, 3022, 2951, 1721, 1655, 1626, 1595, 1576, 1487, 1445, 1337, 1312, 1263, 1240, 1188, 1175, 1152, 1098, 1078, 1022, 1001, 974, 961, 914, 895, 835 cm^{-1}; HRMS: (EI) calcd for ($C_{31}H_{27}NO_2$) 445.2042 (M^+), found *m*/*z* 445.2036



A heat-gun-dried reaction flask containing a magnetic stir bar was charged with diisopropylamine (22.9 mg, 0.23 mmol) and THF (1 mL) under nitrogen. The reaction flask was cooled to −78 °C, and then *n*-BuLi (1.6 M in hexane, 140 μL, 0.22 mmol) was added to the flask. The mixture was stirred at −78 °C for 20 min before a solution of 2-(2,2-diphenylcyclopropyl)-*N,N*-dimethylacetamide (56.1 mg, 0.20 mmol) in THF (1 mL) was added, and further stirred at −78 °C for 30 min. Then, hypervalent iodine reagent **1a** (102.7 mg, 0.24 mmol) was added to the mixture. The reaction flask was removed from a cold bath and further stirred for 1 h (The reaction mixture was allowed to warm to room temperature.). The reaction was quenched with water, the mixture was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard (**8ay**, 23% NMR yield; **8ay'**, 31% NMR yield). Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 9:1) gave the products **8ay** (pale yellow liquid, 3.8 mg, 2% yield) and **8ay'** (colorless liquid, 13.1 mg, 6% yield).

2-(2,2-Diphenylcyclopropyl)-2-((diphenylmethylene)amino)-*N,N*-dimethylacetamide (8ay)

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70–7.60 (m, 2H), 7.55–7.40 (m, 5H), 7.40–7.20 (m, 5H), 7.20–7.10 (m, 3H), 7.10–6.92 (m, 5H), 3,63 (d, *J* = 8.8 Hz, 1H), 2.85–2.63 (m, 1H), 2.79 (s, 3H), 1.87 (s, 3H), 1.40 (dd, *J* = 5.6, 5.6 Hz, 1H), 1.10 (dd, *J* = 8.8, 5.6 Hz, 1H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 171.7, 168.6, 146.3, 141.3, 139.5, 136.9, 130.2, 129.4, 129.2, 128.9, 128.7, 128.22, 128.21, 128.16, 127.9, 127.8, 126.1, 125.9, 63.2, 35.9, 35.8, 34.7, 29.2, 17.3; IR: (ATR) 2924, 1736, 1645, 1599, 1576, 1493, 1445, 1395, 1315, 1242, 1179, 1140, 1123, 1140 1072, 1044, 1028, 1001. 986, 908 cm^{-1}; HRMS: (CI) calcd for ($C_{32}H_{31}N_2O$) 459.2436 ($[M+H]^+$), found *m*/*z* 459.2434

(*E*)-5-((Diphenylmethylene)amino)-*N*,*N*-dimethyl-5,5-diphenylpent-2-enamide (8ay')

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72–7.58 (m, 2H), 7.40–7.22 (m, 7H), 7.22–7.09 (m, 7H), 7.09–7.00 (m, 2H), 6.61 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.55–6.43 (m, 2H), 5.83 (d, *J* = 15.6 Hz, 1H), 3.07 (dd, *J* = 7.2, 1.2 Hz, 2H), 2.87 (s, 3H), 2.68 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.1, 166.9, 149.1, 141,6, 140.0, 138.5, 130.0, 128.4, 127.92, 127.89, 127.7, 127.3, 127.2, 127.1, 126.0, 124.2, 69.3, 43.8, 37.2, 35.3; IR: (ATR) 2928, 1667, 1624, 1595, 1578, 1487, 1443, 1414, 1395, 1315, 1277, 1261, 1223, 1163, 1140, 1072, 1026, 999, 972, 781, 756 cm^{-1}; HRMS: (CI) calcd for ($C_{32}H_{31}N_2O$) 459.2436 ($[M+H]^+$), found *m*/*z* 459.2430

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Chapter 3

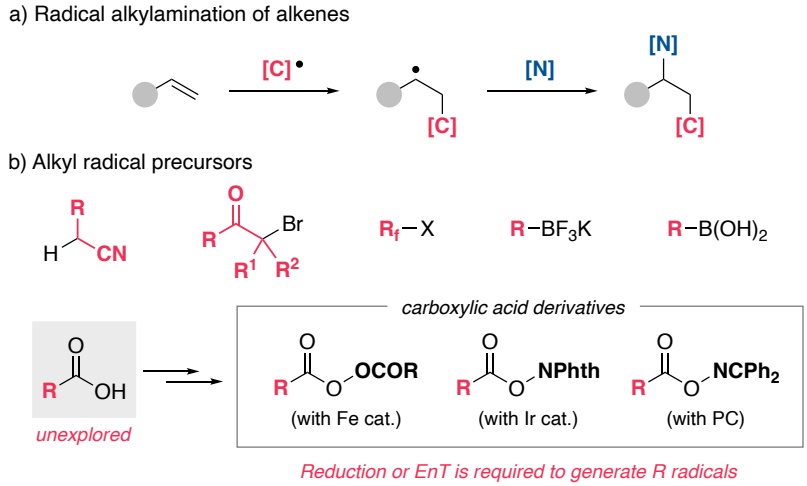
Photoexcitation of (Diarylmethylene)amino Benziodoxolones for Alkylamination of Alkenes with Carboxylic Acids

3-1. Introduction

The intermolecular carboamination of readily available alkene feedstocks, in which C–C and C–N bonds are formed simultaneously, is an attractive strategy for the rapid synthesis of structurally complex amines.[1] Although the transition-metal-catalyzed non-annulative carboamination of alkenes, mainly aryl- and alkenylamination, has been successfully developed in this area,[2–7] the method of alkylamination has rarely been explored even though it would further expand the utility of carboamination for the synthesis of various nitrogen-containing organic molecules.[5a,b]

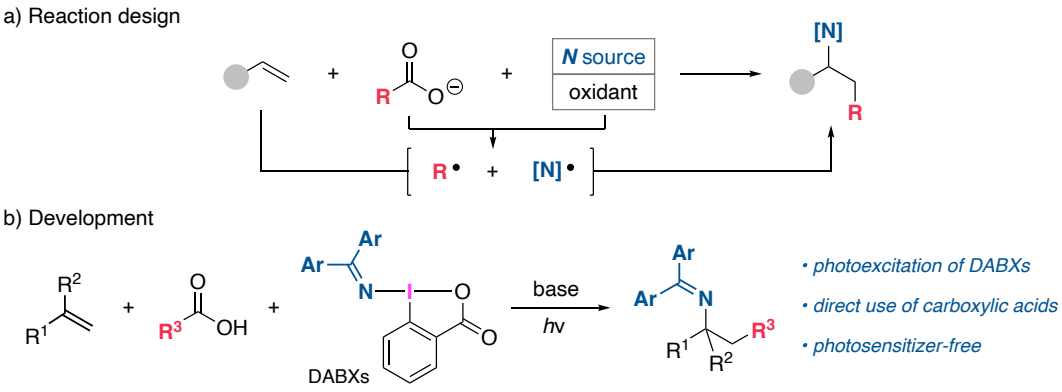
A strategy involving alkyl radical species has emerged as a useful approach for the alkylamination of alkenes (Scheme 1a).[8] Early examples of such reactions required the use of structurally specific alkyl radical precursors such as alkyl nitriles,[9] α-halocarbonyl compounds,[10] and perfluoroalkyl halides[11] (Scheme 1b). Although alkylborane derivatives have recently been utilized as alkyl radical precursors,[12,13] they still lack availability and versatility in terms of introducing the desired alkyl group. As a general alkyl radical precursor, aliphatic carboxylic acids are highly attractive because they are stable, non-toxic, and ubiquitous in nature.[14] Despite these advantages, due to their relatively high redox potential, the difficulty of selectively oxidizing carboxylic acids to generate alkyl radicals in the presence of more readily oxidized amines prevents their direct use in alkylamination reactions. Therefore, existing methods rely on the use of preactivated carboxylic acid derivatives with a higher oxidation state. For example, alkylamination reactions using diacyl peroxides[15] or redox-active esters[16] through a single electron reduction by a transition metal or a photoredox catalyst have been reported. Most recently, an elegant reaction system was reported by Glorius, in which a bifunctional oxime ester

serves as both an alkyl radical and a nitrogen-centered radical through a photo-induced triplet energy transfer mechanism.[17,18] However, these methods require additional steps for the preparation of alkyl radical precursors, which reduces the efficiency of the net reaction, and the use of appropriate catalysts.



Scheme 1. Radical alkylamination of alkenes initiated by carbon-centered radicals

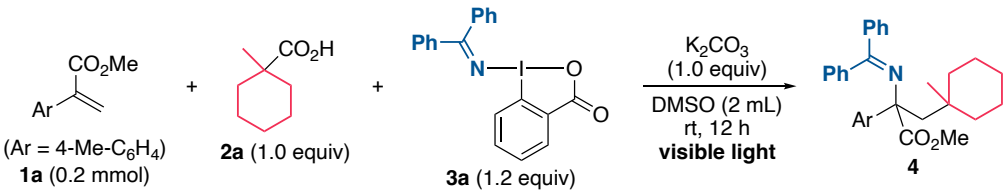
To realize a more straightforward alkylamination using pristine carboxylic acids, a new strategy employing a suitable aminating reagent and an oxidant that allows single-electron oxidation of carboxylic acids should be explored (Scheme 2a). The author developed (diarylmethylene)amino benziodoxolones (DABXs) as a unique oxidative aminating reagent that functions as a single-electron oxidant as well as an iminyl radical source in Chapters 1 and 2.[19] Accordingly, the author envisioned that DABXs would be promising bifunctional reagents that could oxidize a carboxylate and simultaneously generate an alkyl radical and an iminyl radical species, which would then participate in the regioselective alkylamination of alkenes (Scheme 2b).

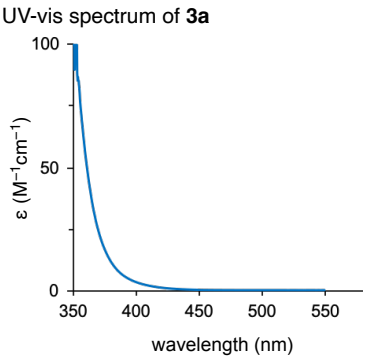


Scheme 2. This work: alkylaminanation using pristine carboxylic acids

3-2. Results and Discussion

Initially, the alkylamination of methyl 2-(*p*-tolyl)acrylate (**1a**) with 1-methylcyclohexane-1-carboxylic acid (**2a**) and DABX **3a** in DMSO in the presence of K_2CO_3 was examined (Scheme 3). However, the target reaction without irradiation did not proceed well even under heating conditions (entries 1 and 2). Indeed, a cyclic voltammetry (CV) measurement of **3a** indicated that the reduction potential of **3a** (–1.52 V vs SCE in CH_2Cl_2)[19a] is not sufficient to oxidize the carboxylate (ca. +1.2 V vs SCE). The author then focused on the photoirradiation conditions because photoexcited molecules generally behave as a better oxidant (reductant) than those in the ground state.[20] Waser recently reported that the excitation of ethynylbenziodoxolones (EBXs) with visible light increases their oxidation ability.[21] The UV-vis spectrum of **3a** (0.05 M in DMSO) was then measured, and the results showed a weak absorption in the visible light region. Based on this result, the use of a violet LED (390 nm) was examined, and, under these conditions, the alkylamination proceeded efficiently to give the desired **4** in 82% yield (entry 3). A brief screening of the wavelength of the light source revealed that the yield of **4** increased to 92% when a blue LED (467 nm) was used (entry 4), while the use of a green LED (525 nm) resulted in a very low yield of the product (entry 5). It should be noted that the present alkylamination features a photosensitizer-free reaction.





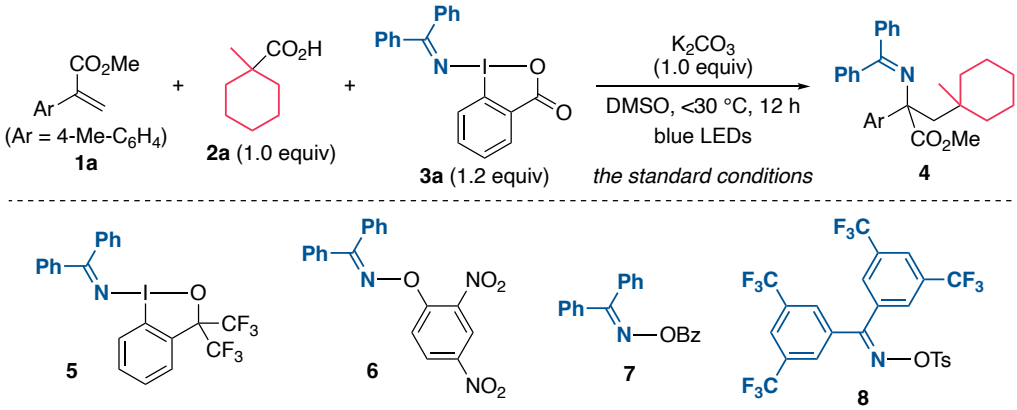
entry	light source	yield (%)
1	*w/o* LEDs	0
2	*w/o* LEDs at 60 °C	7
3	violet LEDs	82
4	**blue LEDs**	**92**
5	green LEDs	<5

Scheme 3. Initial studies on the alkylamination

The reaction conditions including bases, solvents, and aminating reagents were then surveyed

(Table 1). The alkylamination reaction also proceeded with almost the same efficiency when Na_2CO_3 and Cs_2CO_3 were used instead of K_2CO_3 (entries 2 and 3). In the absence of K_2CO_3, the yield of the product was significantly decreased, indicating that the formation of a carboxylate is necessary to promote the reaction (entry 4). Examining the reaction in other polar solvents showed that DMSO was suitable for this alkylamination (entries 5 and 6). Other oxidative aminating reagents were also investigated. The use of the benziodoxole-based reagent **5** resulted in the low efficiency, suggesting the importance of a benziodoxolone scaffold in **3a** (entry 7). The *O*-aryl oxime **6** was also found to be unsuitable for this reaction (entry 8).[22] The use of the oxime ester **7** and the *O*-sulfonyl oxime **8**, which are used as electrophilic aminating reagents,[23] failed to afford the target product (entries 9 and 10).

Table 1. Survey of bases, solvents, and aminating reagents[a]

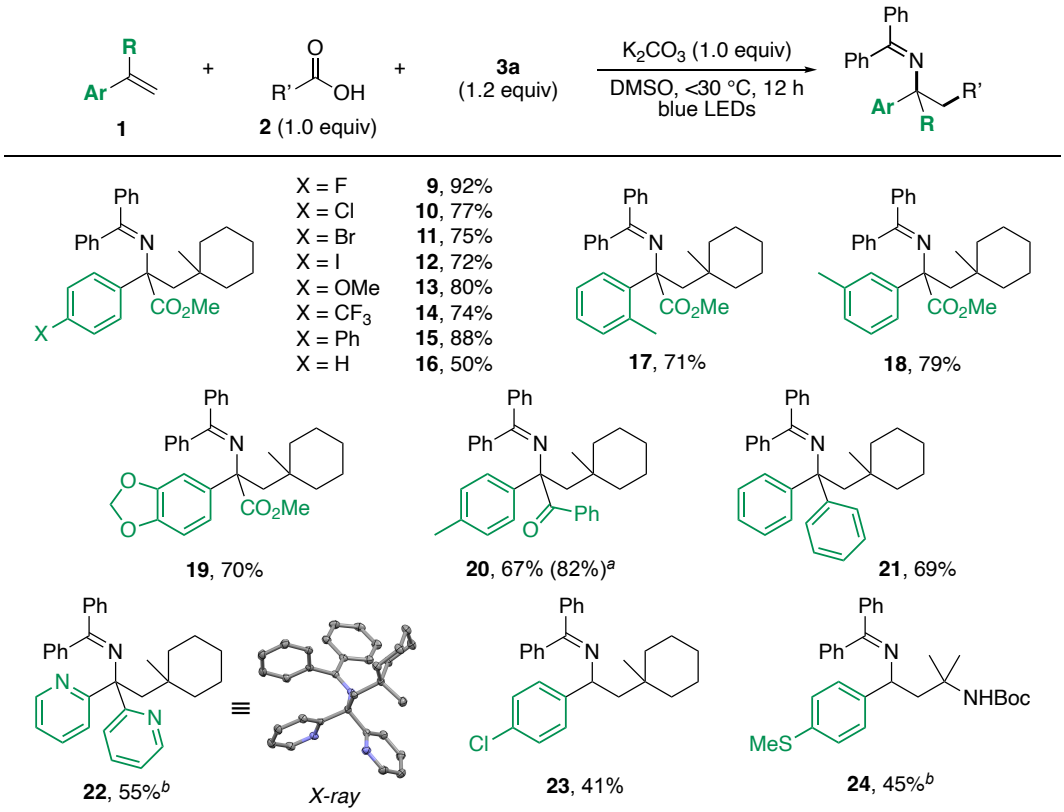


Entry	Variation from the standard conditions	Yield [%][b]
1	none	92 (84)[c]
2	Na_2CO_3 instead of K_2CO_3	92
3	Cs_2CO_3 instead of K_2CO_3	87
4	without of K_2CO_3	18
5	MeCN instead of DMSO	32
6	DMF instead of DMSO	78
7	**5** (1.0 equiv) instead of **3a**	17
8	**6** (1.0 equiv) instead of **3a**	15
9	**7** (1.0 equiv) instead of **3a**	0
10	**8** (1.0 equiv) instead of **3a**	0

[a] Reactions were performed on a 0.2 mmol scale (0.1 M). [b] Determined by ^{1}H NMR analysis of the crude product. [c] Isolated yields on 0.4 mmol scale.

With the optimized reaction conditions in hand, the scope of alkylamination was next explored (Scheme 4). In initial experiments, a series of 2-arylacrylates bearing both electron-donating and electron-withdrawing groups on the aryl moiety were subjected to the alkylamination, and all of the

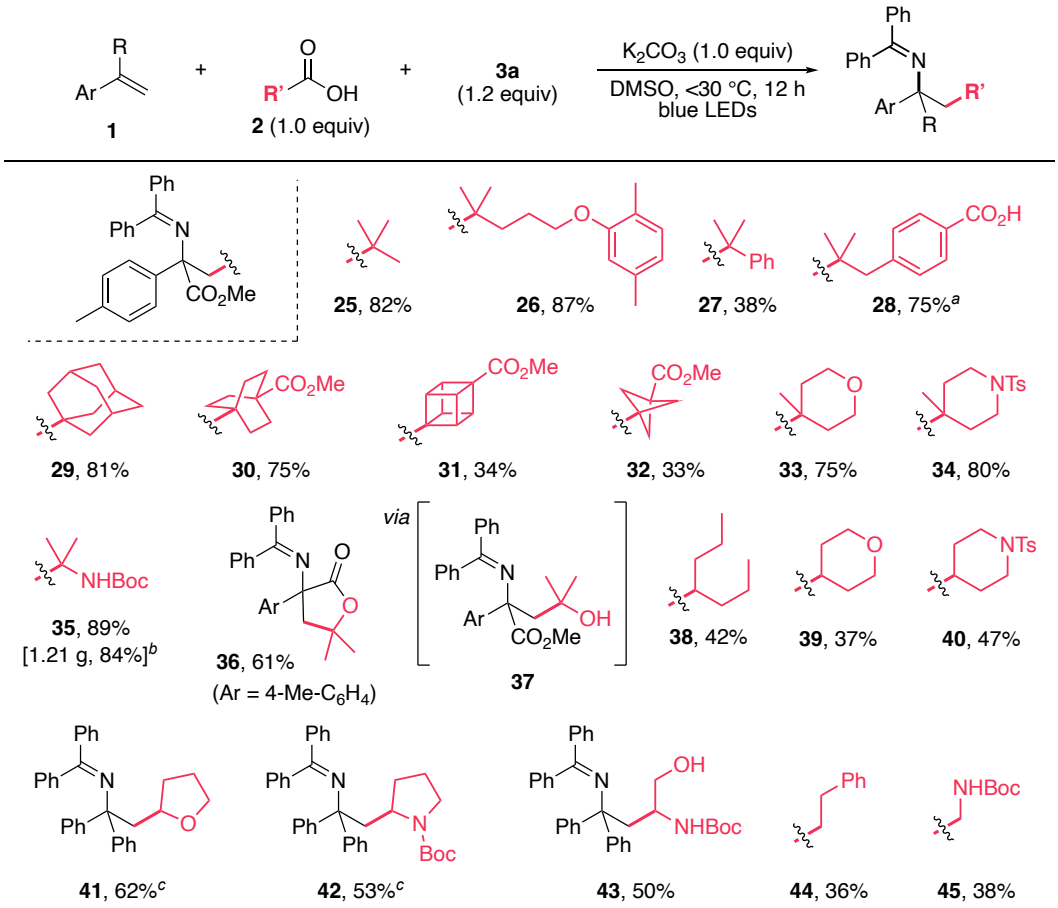
reactions proceeded effectively to afford the corresponding products in good to high yields (Scheme 4, **9**–**16**). Several functional groups including halogens (**9**–**12**) and a trifluoromethyl group (**14**) on the aromatic ring were well tolerated. The presence of a substituent at the *ortho* and *meta*-positions had little effect on the reaction efficiency in the formation of **17** and **18**, respectively. Substrates bearing a 3,4-methylenedioxyphenyl group also readily participated in the alkylamination (**19**). These reactions using 2-arylacrylates as substrates provided unnatural α-amino acid derivatives containing α-tertiary carbon centers, which are otherwise difficult to access. In addition, an α,β-unsaturated ketone (**20**), 1,1-di(hetero)arylethenes (**21** and **22**), and styrene derivatives (**23** and **24**) were also applicable for use in this alkylamiantion.



Scheme 4. Scope of styrenes. Reactions were performed on a 0.2–0.4 mmol scale. Yields are isolated yields. [a] Determined by ^{1}H NMR analysis of the crude product. [b] **2** (2 equiv), **3a** (2 equiv), and K_2CO_3 (2 equiv) were used.

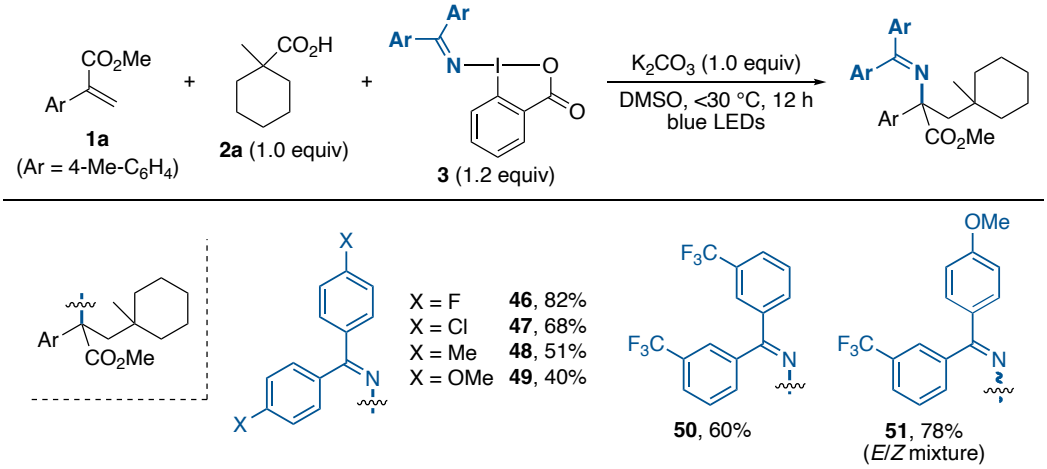
Subsequently, the scope of carboxylic acids for the alkylamination was then investigated (Scheme 5). A wide range of carboxylic acids bearing an α-quaternary carbon center could be applied to the present alkylamination, thus allowing the introduction of bulky alkyl groups (**25**–**28**). A carboxyl group on the aromatic ring was found to be inert toward decarboxylation under the oxidative conditions,

leading to the chemoselective formation of **28**. Notably, three-dimensional scaffolds with carbon skeletons such as adamantyl (**29**), bicyclo[2.2.2]octyl (**30**), cubyl (**31**), and bicyclo[1.1.1]pentyl (**32**) groups, which are of great interest as bioisosteres of the phenyl ring in medicinal chemistry,[24] could be successfully introduced. Substrates containing oxa and aza-heterocycles were also well tolerated (**33** and **34**). An α-NHBoc (**35**) and an α-hydroxy (**37**) carboxylic acids could also be used as alkylating reagents, and using the latter provided γ-lactone **36** through an intramolecular cyclization of the alkylaminated product **37**. The synthetic utility of this alkylamination was also demonstrated by a gram-scale synthesis of **35** without any loss of yield (1.21 g, 84%). Furthermore, carboxylic acids leading to secondary and primary alkyl radicals were compatible with the alkylamination, allowing the introduction of various alkyl groups including five and six-membered heterocyclic scaffolds (**38**–**45**). In particular, the product **43** with an unprotected hydroxy group was synthesized by using L-serine.



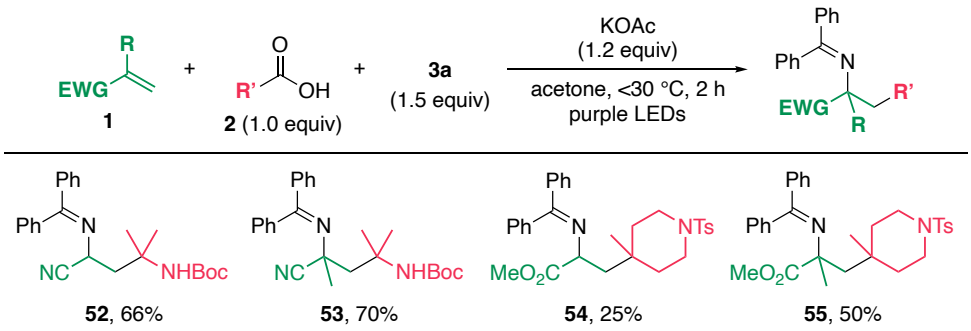
Scheme 5. Scope of carboxylic acids. Reactions were performed on a 0.2–0.4 mmol scale. Yields are isolated yields. [a] The product was isolated as the corresponding methyl ester. [b] Reaction was performed on a 2.8 mmol scale. [c] **2** (1.2 equiv), **3** (1.2 equiv), and K_2CO_3 (1.2 equiv) were uesd.

The scope of DABXs was also surveyed (Scheme 6). Derivatives containing electronically varied imine moieties could be used to deliver the corresponding products **46**–**51**, indicating that this alkylamination was not significantly influenced by the electronic property of the (diarylmethylene)amino group.



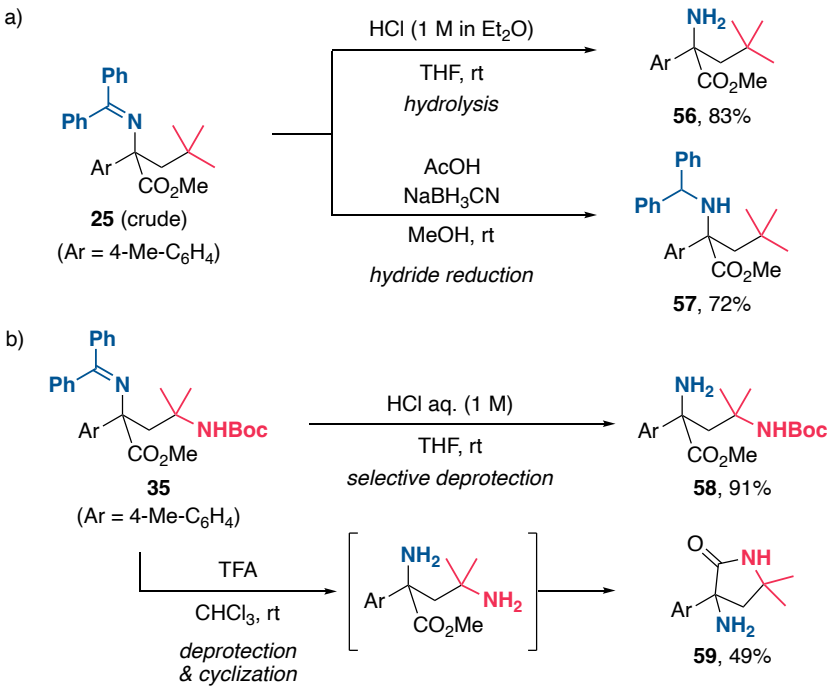
Scheme 6. Scope of aminating reagents. Reactions were performed on a 0.3–0.4 mmol scale. Yields are isolated yields.

To further expand the scope of the alkylamination, the method was applied to electron-deficient alkenes. The reaction using acrylonitrile as a substrate under the standard conditions resulted in the production of only trace amounts of the target product. A brief screening of solvents and bases revealed that the use of acetone and KOAc could promote the alkylamination (Scheme 7). The reaction of acrylonitriles with **2l** and **3a** in the presence of KOAc in acetone under irradiation conditions proceeded effectively, affording **52** and **53**. The use of violet LEDs (390 nm) instead of blue LEDs (467 nm) was able to significantly shorten the reaction time. In addition, acrylates were also subjected to alkylamination to afford the corresponding amines **54** and **55** in moderate yields. However, simple aliphatic alkenes are unsuccessful substrates, probably due to the slow rate of the addition of alkyl radicals to aliphatic alkenes.[25]



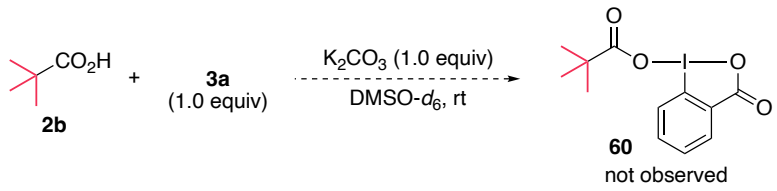
Scheme 7. Alkylamination of electron-deficient alkenes. Reactions were performed on a 0.2 mmol scale. Yield are isolated yields.

The synthetic utility of the present alkylamination was further highlighted by the derivatization of the products (Scheme 8). The facile transformation of the (diphenylmethylene)amino group of the product was demonstrated by acid hydrolysis and hydride reduction of the crude product of **25**, affording α-amino ester **56** and diphenylmethylamine **57**, respectively, in good yields (Scheme 8a). Furthermore, the chemoselective hydrolysis of the imine moiety of **35** was achieved by the treatment with aqueous HCl to provide **58** in excellent yield (Scheme 8b). Hydrolysis of both amino functionalities of **35** using trifluoroacetic acid (TFA) provided a diamine, which subsequently underwent cyclization to yield the γ-lactam **59**, a key structural motif in pharmaceuticals and natural products. These quite simple methods provide efficient and practical processes for the synthesis of a variety of useful nitrogen-containing organic molecules.



Scheme 8. Transformations of alkylaminated products

Mechanistic aspects of the alkylamination were investigated. The possibility of the ligand exchange reaction between **3a** and carboxylate to form the carboxylate-substituted hypervalent iodine compound was initially examined. When a mixture of pivalic acid (**2b**) and **3a** in the presence of K_2CO_3 in DMSO-d_6 was monitored by ^{1}H NMR (Scheme 9), no new signals were observed, and the starting materials remained, ruling out the possibility of ligand exchange (Figure 1).



Scheme 9. NMR monitoring of a mixture of **2b** and **3a**

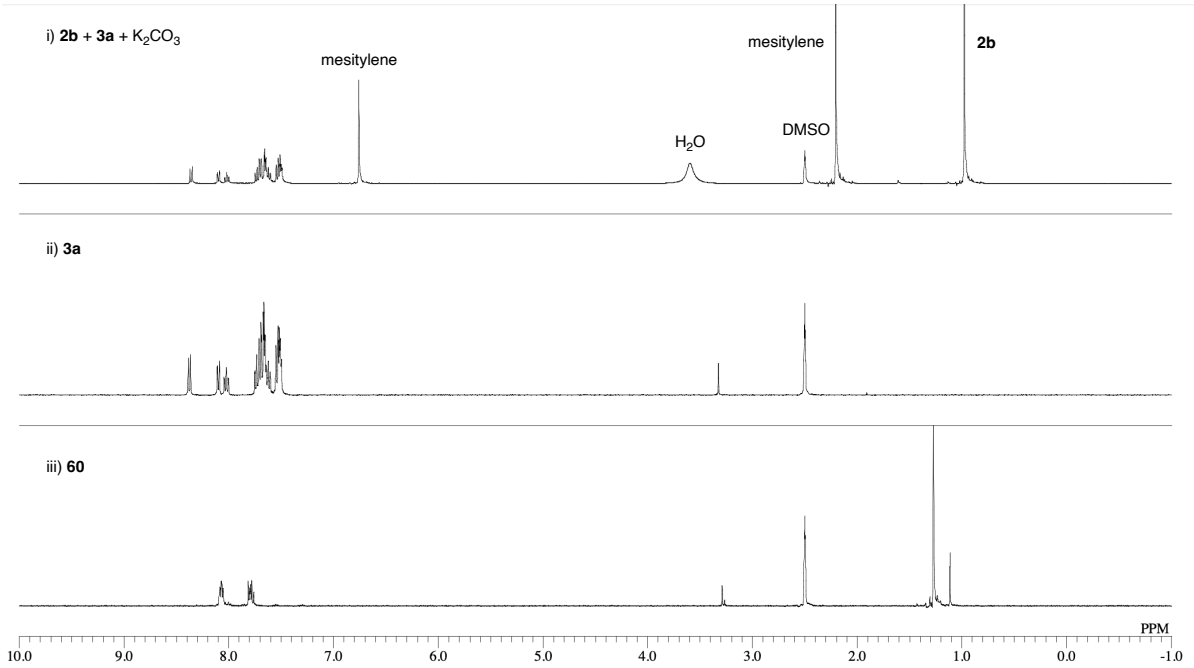


Figure 1. ^{1}H NMR spectra in DMSO-d_6: i) a mixture of **2b**, **3a**, and K_2CO_3, ii) **3a**, iii) **60**

In addition, density functional theory (DFT) calculations of the ligand exchange process at the M06-2X/6-311++G(d,g)-SDD(I) level of theory indicated that the formation of **60** is thermodynamically unfavorable (ΔG = +2.1 kcal mol^{-1}), consistent with the experimental results. The author next examined the possibility that an electron donor-acceptor (EDA) complex was formed between a carboxylate and DABXs. The UV-vis spectrum of the reaction mixture was nearly superimposable over that of **3a**

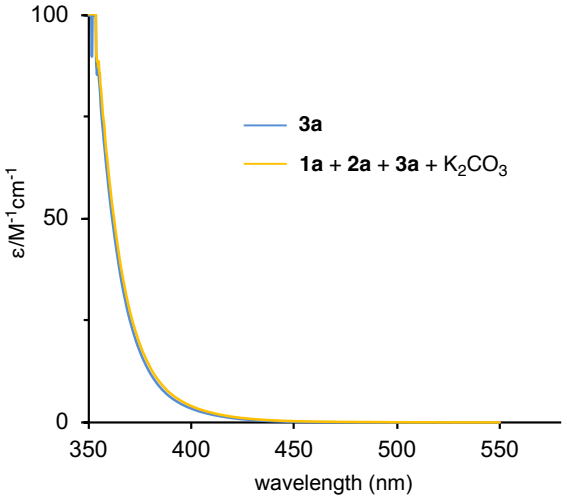


Figure 2. UV-vis absorption spectra of **3a** and the reaction mixture in DMSO.

(Figure 2), ruling out the participation of a photoactive EDA complex in the reaction. Based on these results, the author concluded that DABXs would be directly excited and initiate the reaction.

To investigate the photochemical reactivity of DABX **3a**, a series of experiments and quantum chemical calculations were performed. A fluorescence emission analysis of **3a** was first conducted in DMSO at room temperature. No significant emission signal was observed under these conditions (Figure 3), suggesting that the singlet electronically excited state, ^{1}[**3a**]*, is chemically reactive and/or that the intersystem crossing process is fast to produce the triplet state ^{3}[**3a**]*.[26] Thus, the lifetime of the singlet excited state of **3a**, ^{1}[**3a**]*, would be too short to participate in the intermolecular reaction.

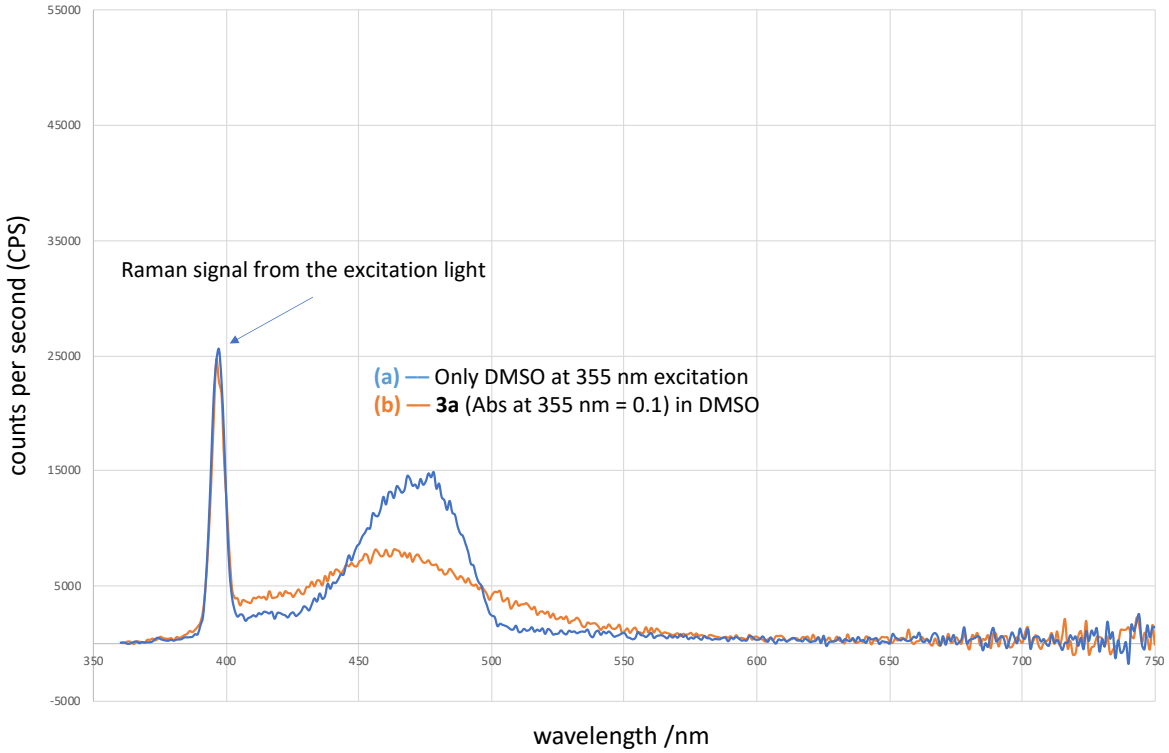


Figure 3. Emission signals from (a) DMSO and (b) **3a** in DMSO at 355 nm excitation

The author then conducted sub-microsecond transient absorption (TA) spectroscopy measurements of **3a** in DMSO using a laser flash photolysis (LFP) method (266 nm or 355 nm Nd/YAG-laser, 12 ns pulse-width, 10 Hz, 6 mJ/pulse) to gain insights into the transient species generated during the photolysis of **3a** (Figure 4).

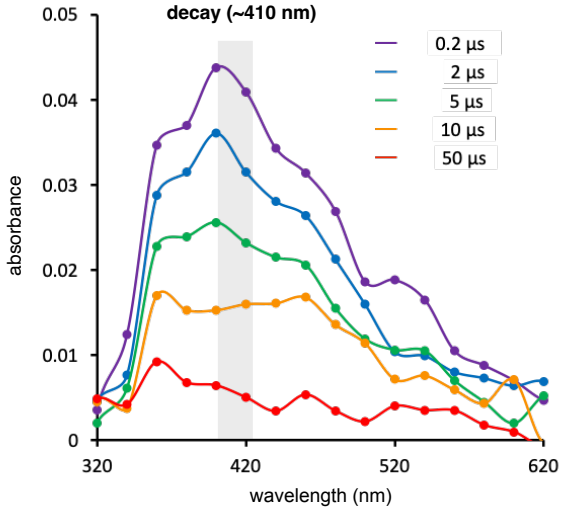
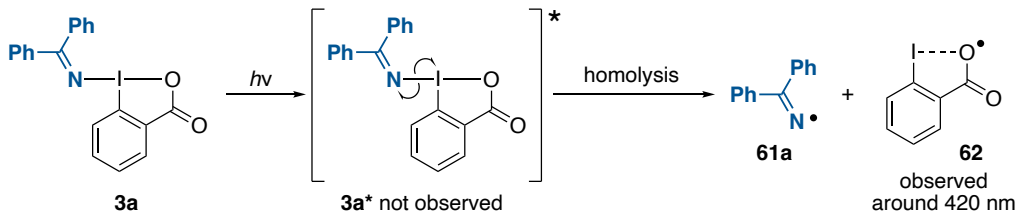


Figure 4. Sub-microsecond UV-vis transient absorption spectra of 1.7 x 10^{-4} M solution of **3a** in DMSO under air

After the LFP, a transient species absorbing at 350-600 nm with λ_{max} ~410 nm was observed under air in DMSO at 298 K. The decay time-profile monitored at 420 nm could not be reproduced by a single exponential decay-equation. The half-life ($\tau_{1/2}$) was ~6.8 µs at 298 K under an atmosphere of air. Under an argon atmosphere, the similar $\tau_{1/2}$ was found to be ~6.6 µs at 298 K, indicating that the transient species with λ_{max} ~410 nm is not quenched by molecular oxygen (O_2). These experimental results clearly suggest that the triplet excited state of **3a** is not the transient species with λ_{max} ~410 nm. Interestingly, the structural optimization of triplet state of **3a** at the UB3LYP/6-31G(d)-LanL2DZ(I) level of theory produced a pair of radicals, a diphenyl iminyl radical **61a** and *ortho*-iodobenzoyloxy radical (**62**), suggesting that the triplet **3a** spontaneously generates the radical pair after the I–N bond homolysis (Scheme 10). In addition to the generation of the transient with λ_{max} ~410 nm, the bleaching signal at ~300 nm and its second order recovering process with k_{rec} = 2.13 x 10^4 s^{-1}, $1/k$ = 63.9 µs, was observed in the LFP experiments (Figure 5). The rise in the signal is attributed to the recovering process of **3a**.



Scheme 10. Photolysis of **3a**

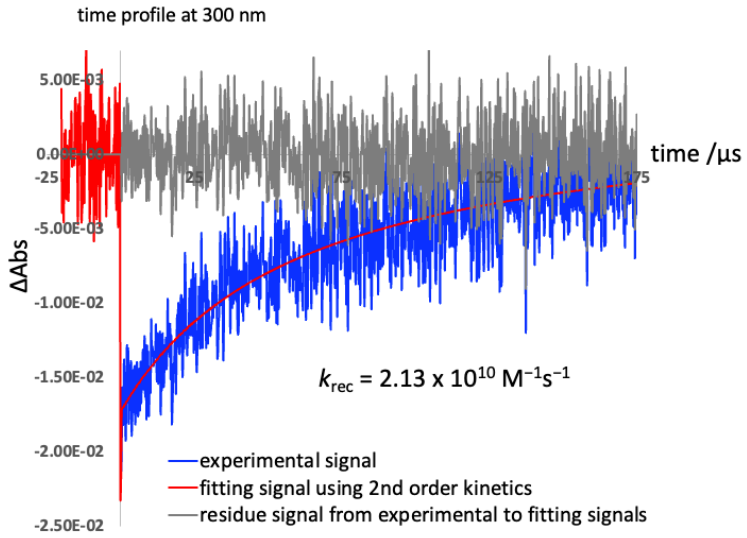


Figure 5. The time profile at 300 nm

The absorption spectra of **61a** and **62** were computed using time-dependent density functional theory (TD-DFT) calculations at the UB3LYP/6-31G(d)-LanL2DZ(I) level of theory. The computational method well reproduced the absorption spectrum of compound **3a** (Figure 6). Thus, we applied the method to simulate the absorption spectra of **61a** and **62**. Weak electronic transitions at 491 nm (f = 0.0025, ε = ~100), 353 nm (f = 0.015, ε = ~1300), and 337 nm (f = 0.018, ε = ~1300) were computed for iminyl radical **61a**, where f is the oscillator strength; ε is molar extinction coefficient in M^{-1} cm^{-1} (Figure 7a). For radical **62**, a weak transition at 758 nm (f = 0.027, ε = ~1100) and a relatively strong one at 463 nm (f = 0.125, ε = ~5000) were found over 300 nm at the same level of theory (Figure 7b). The computed results clearly suggest that the observed transient absorption at λ_{max} ~410 nm in the LFP experiments of **3a** is derived from radical **62**.

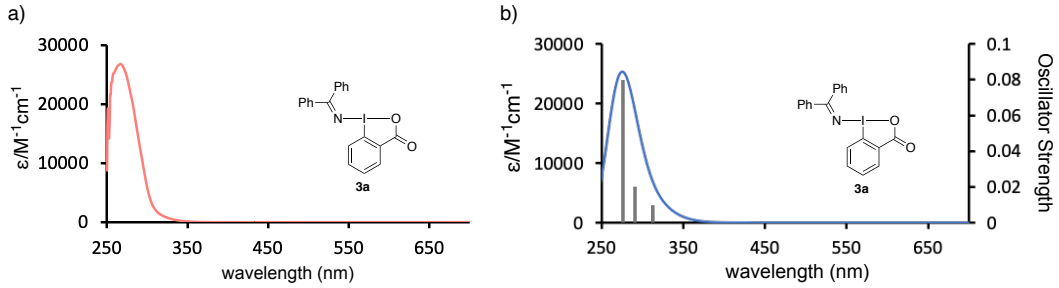


Figure 6. a) UV-vis absorption spectra of **3a** in DMSO. b) TD-DFT absorption spectrum of **3a**

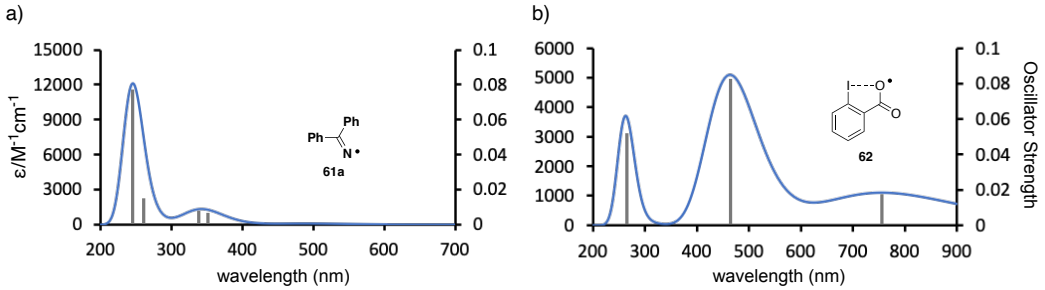


Figure 7. TD-DFT absorption spectra: a) **61a**, b) **62**

In addition, the peroxyl radical **62_O₂** was not optimized as an equilibrated structure to give a weakly bounded complex of radical **62** and O_2 during the structural optimization in the doublet state, suggesting that the reaction of **62** with O_2 is endothermic and slow. Indeed, the Gibbs energy of the complex was computed to be higher in energy by 5.8 kcal mol^{-1} than the total energy of **62** and O_2 (Figure 8). This computational result also supports the conclusion that the transient absorption with λ_{max} ~410 nm comes from radical **62**, since the transient species with λ_{max} ~410 nm was not quenched by O_2. Unfortunately, the signal of **61a** could not be clearly obtained due to the low ε and the overlap with the absorption spectra of **3a** and **62**.

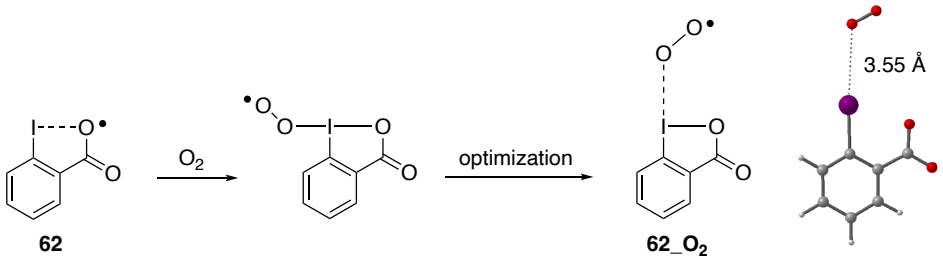


Figure 8. DFT calculations for the reaction of radical **62** with O_2

As mentioned above, the decay process of **62** was not reproduced by the first-order decay equation. However, the experimentally observed decay-signal at 420 nm was perfectly reproduced with the second-order rate equation (**61a** + **62** → **3a**, $[\mathbf{62}] = 1/(kt + 1/[\mathbf{62}]_0)$, where $[\mathbf{62}]_0 = [\mathbf{61a}]_0 = 3.88 \times 10^{-6}$ M), to give the second-order rate constant (k) of 1.7×10^{10} $M^{-1}s^{-1}$ (Figure 9), supporting the conclusion that assignment of **62** is correct. The initial concentration of **62** was determined by the bleaching signal of **3a** at 300 nm after the LFP, $Abs_{300} = -0.0231$, ε_{300} of **3a** = 5946.7. The quantitative formation of **62** from **3a** was assumed to determine the concentration.

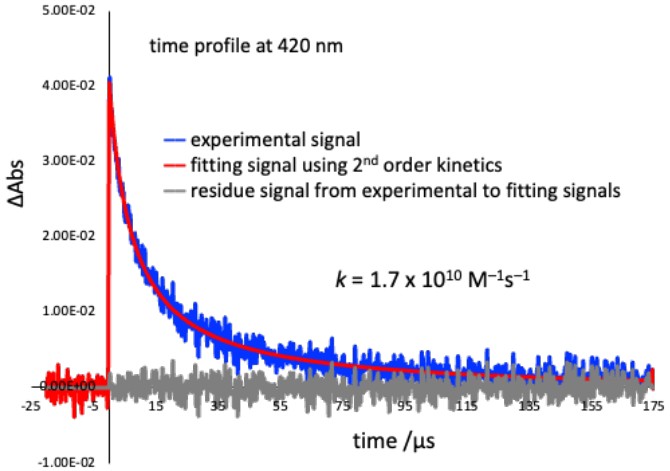
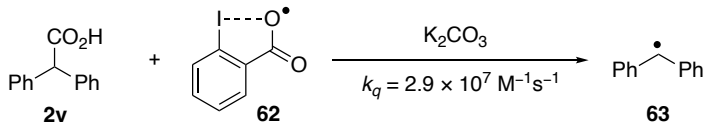


Figure 9. The time profile at 420 nm

To understand the thermal reactivity of **62**, the author then investigated the dynamic quenching of **62** with the carboxylate prepared from **2v** with K_2CO_3 to determine whether it could function as an oxidant (Scheme 11 and Figure 10). Indeed, the lifetime ($\tau = 1/k_q$) of **62** was shortened by increasing the concentration of **2v**. From the slope of the Stern-Volmer plot, k_q versus [**2v**], the quenching rate constant k_q was found to be 2.9 x 10^7 $M^{-1}s^{-1}$. Unfortunately, the resulting diphenylmethyl radical **63** (λ_{max} = 335 nm, ε = 29,900)[27] formed through the fast decarboxylation was not clearly detected, although the lifetime at 370 nm was different from that at 420 nm. The optical window was more than 370 nm for the LFP experiments. To further confirm the single-electron transfer process, the reduction potentials of **61a**, **62**, and a carboxylate of **2v** were then computed using DFT calculations at the M062X/6-31G+(d,g)-LanL2DZ(I) level of theory. Since structural optimization of the carboxyl radical species derived from **2v** resulted in the formation of the diphenylmethyl radical **63** due to the barrierless decarboxylation, the calculations were carried out using a pivalate instead. The resulting reduction potentials for **61a**, **62**, and oxidation potential for a pivalate were –1.12, +1.20, and +1.37 V vs. SCE, respectively, indicating that the single-electron oxidation of pivalate by **62** is possible although the electron transfer oxidation is slightly endothermic (ΔG_{et} = + 0.17 eV). Indeed, the estimated quenching rate constant obtained by the Rehm-Weller equation, ~1.8 x 10^7 $M^{-1}s^{-1}$, is fairly consistent with the experimentally obtained value k_q = 2.9 x 10^7 $M^{-1}s^{-1}$ (vide supra).[28]



Scheme 11. Proposed mechanism of the initial of the reaction

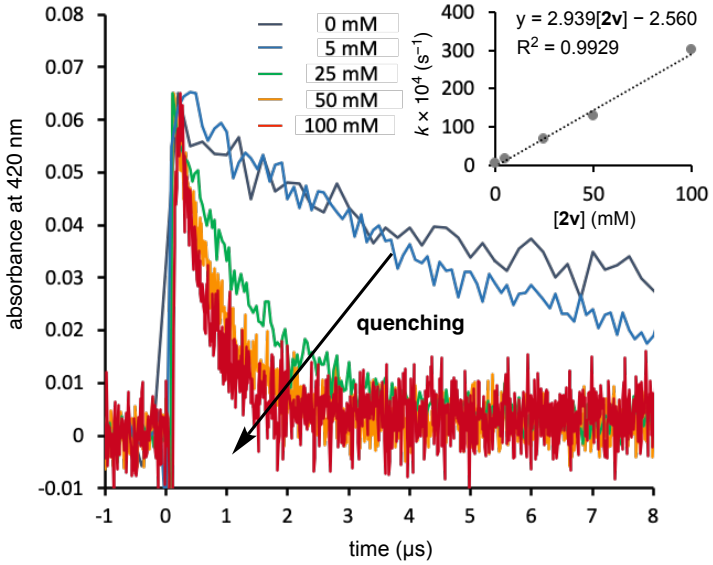
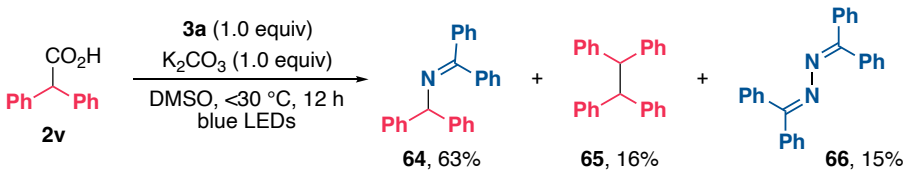


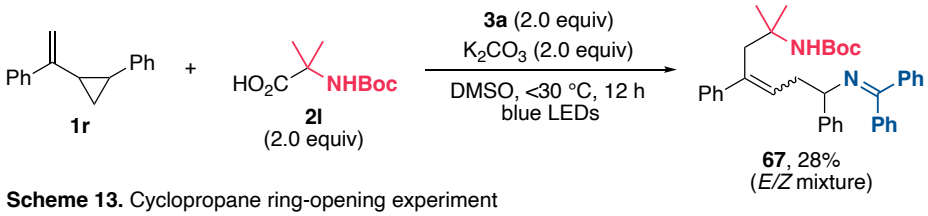
Figure 10. The time profile of **62** is obtained from UV-vis transient absorption spectra of 2.6 x 10^{-2} M solution of **3a** in DMSO under air. Stern-Volmer plot is obtained from rate constants obsorved at different concentration of **2v** at 420 nm (dynamic quenching experiments).

To confirm the generation of an iminyl radical **61a** as well as the alkyl radical **63**, the product analysis of photochemical reaction of **2v** (0.1 M) with **3a** (0.1 M) was carried out in the presence of K_2CO_3 (Scheme 12). As a result, the decarboxylative amination product **64** was obtained, accompanied by the formation of byproducts including **65** and benzophenone azine (**66**), which are apparently formed through the homocoupling of **63** and **61a**, respectively.[29] These results clearly demonstrate that the generation of **61a** and **63** under the reaction conditions, which would couple to provide **64**. Overall, the excitation of **3a** led to the formation of the iminyl radical **61a** and radical **62** that can oxidize a carboxylate to give an alkyl radical. Although there are several reports on the reactivity of radical **62** as a single-electron oxidant,[30,31] the present study is a rare example of an experimental demonstration of its reactivity.[32]



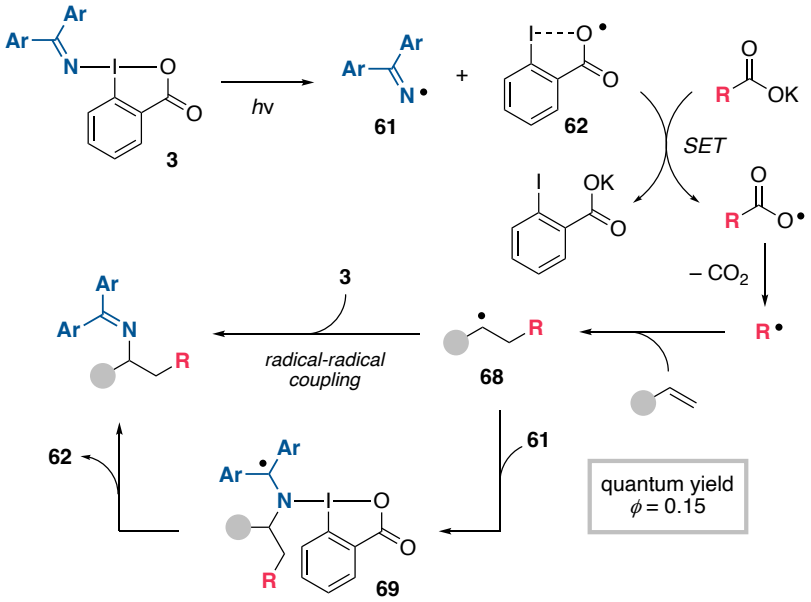
Scheme 12. Product analysis of the reaction of **2v** with **3a**

A radical mechanism was further confirmed by the use of vinylcyclopropane **1r** as an alkene substrate (Scheme 13). When **1r** was subjected to the standard alkylamination reaction conditions, no cyclopropane-containing product was observed, and several cyclopropane ring-opened products were obtained, one of which was determined to be **67**. This result clearly indicates that the reaction proceeds through radical addition of an alkyl radical to an alkene.



Scheme 13. Cyclopropane ring-opening experiment

Based on the experimental results reported herein, a proposed reaction pathway for the alkylamination is depicted in Scheme 14. As an initial step, the visible-light excitation of DABXs **3** leads to the homolysis of its I–N bond to give an iminyl radical **61** and radical **62**. A single-electron oxidation of a carboxylate by **62** then occurs. The resulting alkyl radical through a subsequent decarboxylation reacts with alkenes to form radical **68**. Given that the relative concentration of **3** is much higher than that of **61**, the radical **68** would undergo the radical addition onto **3**. The Gibbs energy barrier was then computed to be 32.0 kcal mol^{-1} at the M06-2X/6-31G+(d,g)-LanL2DZ(I) level of theory (Figure 11). The product and the radical **62** were found to be produced through the formation of the weakly bounded intermediate **69**. The re-generation of radical **62** realizes the radical-chain process. However, the result of the light ON/OFF experiments and the quantum yield (Φ = 0.15) of the alkylamination do not support an efficient radical chain process, and continuous photoirradiation is therefore required for the reaction. Therefore, an alternative pathway involving a radical–radical coupling between **68** and iminyl radical **61** cannot be excluded.



Scheme 14. Proposed reaction pathway

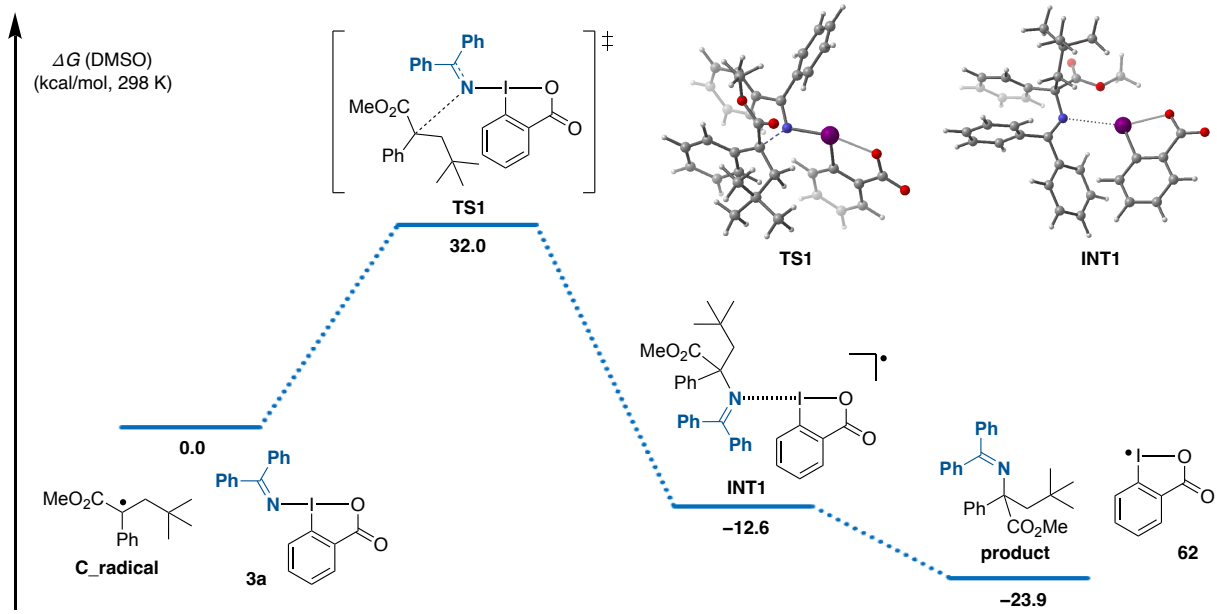


Figure 11. DFT calculations and energy level diagram of the radical addition to **3a**. Free energies (kcal/mol) are computed at the M06-2X/6-31+G(d,p)-LANL2DZ(I),CPCM(DMSO) level of theory.

3-3. Conclusion

In conclusion, the alkylamination of alkenes using pristine carboxylic acids as an alkylating reagent was enabled by photoexcitation of DABXs which function as both an oxidant and an aminating reagent. The present method has a broad substrate scope for alkenes and aliphatic carboxylic acids with good functional group tolerance. The developed alkylamination would provide a simple, scalable, and

straightforward approach to accessing readily modifiable amines. The synthetic utility of the products was clearly demonstrated by the facile transformation of some of the products into valuable nitrogen-containing molecules. Experimental and computational mechanistic studies revealed the unprecedented photochemical reactivity of DABXs. Upon visible light irradiation, *ortho*-iodobenzoyloxy radical, *in situ* generated from DABXs, oxidizes carboxylates to provide alkyl radicals.

3-4. Experimental Section

General Remarks

New compounds were characterized by ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, $^{19}F\{^{1}H\}$ NMR, IR, and HRMS. ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer (^{1}H NMR, 400 MHz; $^{13}C\{^{1}H\}$ NMR, 100 MHz, $^{19}F\{^{1}H\}$ NMR, 377 MHz). ^{1}H NMR chemical shifts were determined relative to Me_4Si (0.0 ppm) as an internal standard in $CDCl_3$ and the signals of residual undeuterated DMSO (2.50 ppm) in DMSO-d_6. $^{13}C\{^{1}H\}$ NMR chemical shifts were determined relative to $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.50 ppm). $^{19}F\{^{1}H\}$ NMR chemical shifts were determined relative to C_6F_6 (−164.9 ppm) as an external standard. Infrared spectra were recorded on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-700 mass spectrometer (magnetic sector type mass spectrometer) and JMS-T100LP. Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. Cyclic voltammetry (CV) was performed with ALS-610E (BAS Inc.) system. UV-vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The X-ray diffraction data of the single crystal were collected on a two-dimensional X-ray detector (PILATUS 200K/R) equipped in Rigaku XtaLAB PRO diffractometer using thin multi-layer mirror monochromated Cu-Kα radiation (λ =1.54187 Å). Submicrosecond laser flash photolysis (LFP) is performed with a 355 or 266 nm yttrium aluminum garnet (YAG) laser (6 mJ/pulse, 12 ns pulse width). The monitoring system consists of a 150 W Xenon arc lamp as light source, a Unisoku MD200 monochromator detection and a photomultiplier. All reactions were carried out under nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.) or Chromatorex NH (Fuji Silysia Chemical Ltd.). Light irradiation was performed by using LEDs (Kessil PR160L 390 nm (max 40W), Kessil PR160L 467 nm (max 40W), and Kessil PR160L 525 nm (max 40W)). The emission spectra of the LEDs were recorded on a HAMAMATSU Quantaurus-QY C11347-01 spectrometer. The light intensities of the LEDs were measured using Optical Power Meter PM100D (THORLABS Inc.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F_{254} and

Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

Materials

Alkenes **1a**–**1m**, **1o** and **1r** were prepared according to the reported procedure.[33,39–41] Carboxylic acids **2e**, **2j**, **2k**, and **2p** were prepared according to the reported procedure.[42,43] Hypervalent iodine reagents **3a**–**3g** and **13** were prepared according to the reported procedure.[19a,19b,44] Dehydrated THF and toluene were used from a solvent purification system. All other solvents and reagents were purchased and used as obtained.

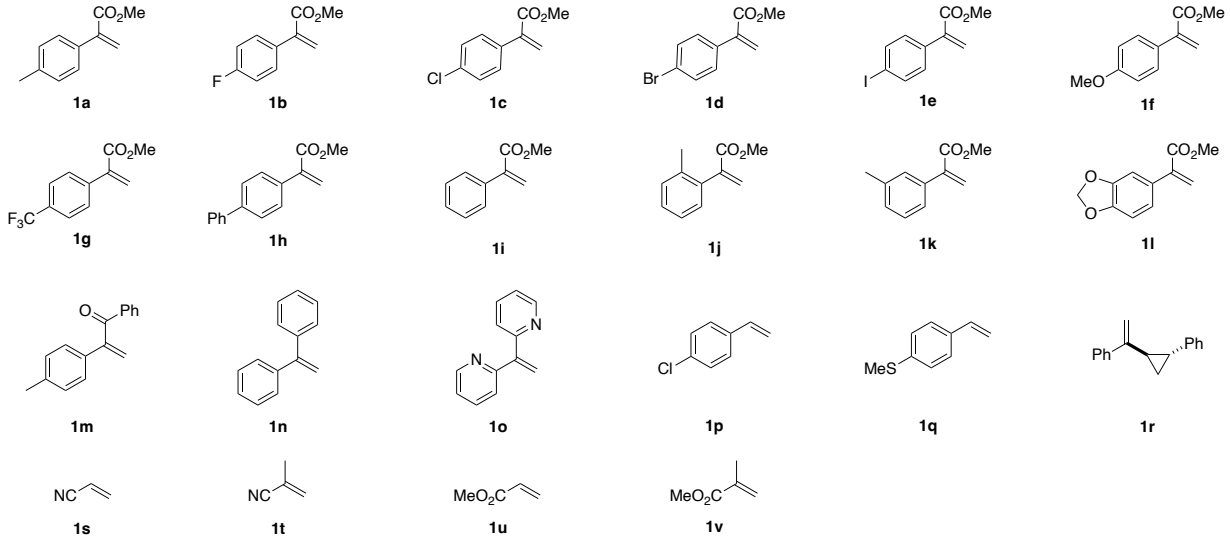


Figure S1. List of alkenes

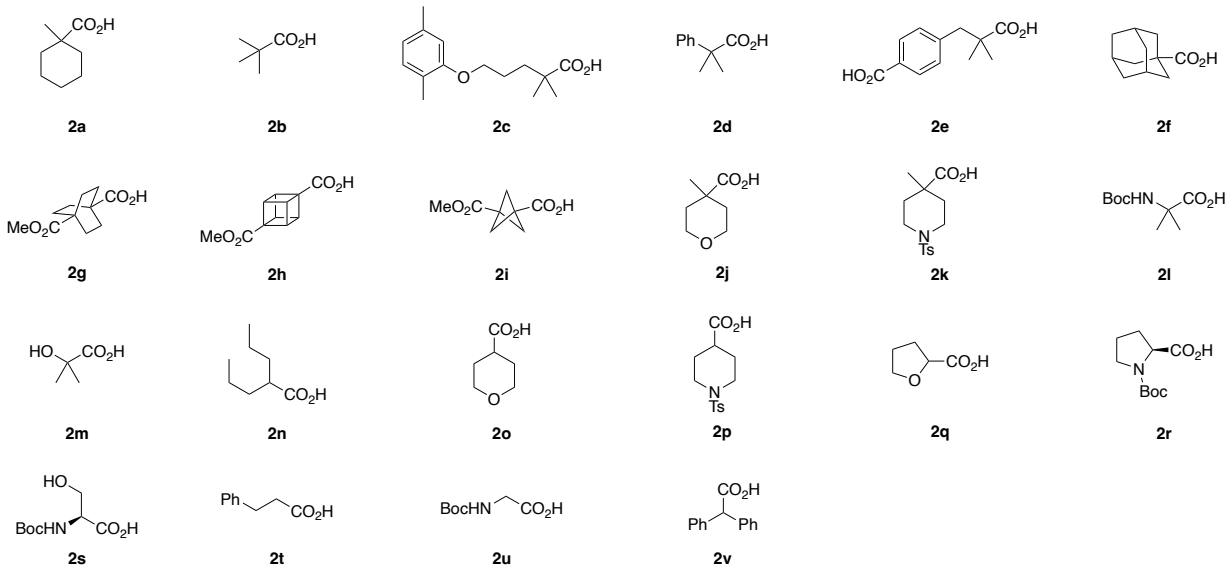


Figure S2. List of carboxylic acids

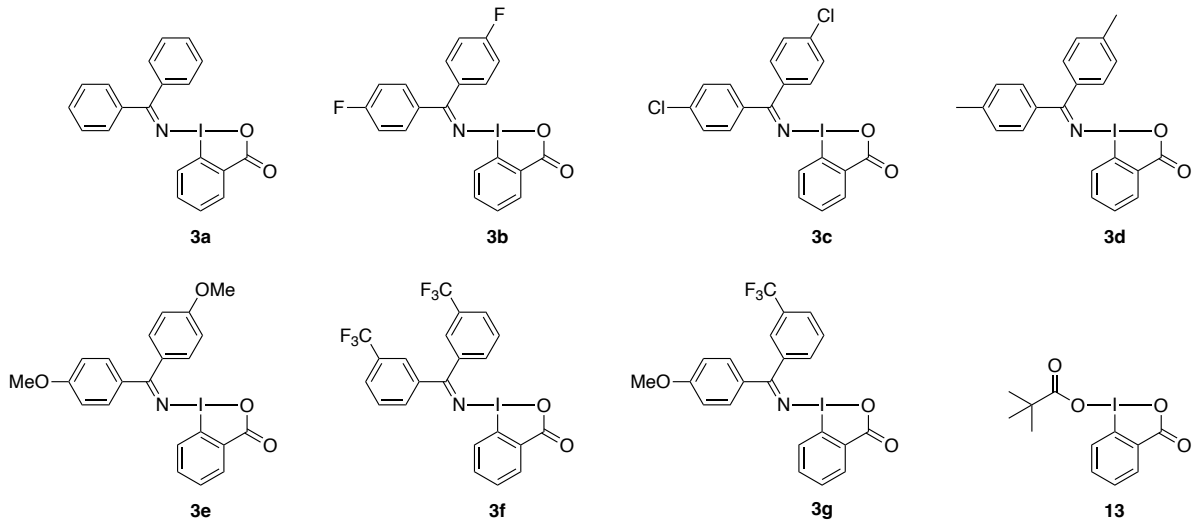
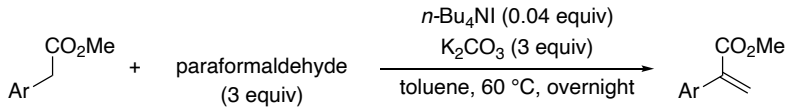


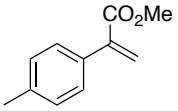
Figure S3. List of hypervalent iodine reagents

Preparation of alkenes



General procedure I: According to the reported procedure[33], to a solution of ester (1 equiv) in toluene, paraformaldehyde (3 equiv), *n*-Bu_4NI (0.04 equiv), and K_2CO_3 (3 equiv) were added at room temperature. The resulting mixture was stirred at 60 °C overnight. After cooling to room temperature, the suspension was filtered through Celite, and the filtrate was eluted with EtOAc and water. Then, the mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude mixture, which was purified by flash column chromatography on silica gel gave the desired alkene.

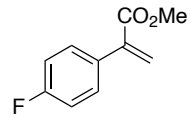
Methyl 2-(*p*-tolyl)acrylate (1a)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.31 (d, J = 1.2 Hz, 1H), 5.85 (d, J = 1.2 Hz, 1H), 3.81 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.6, 141.3, 138.2, 134.0, 129.0, 128.3, 126.3, 52.3, 21.3

The analytical data for this compound were in excellent agreement with the reported data.[34]

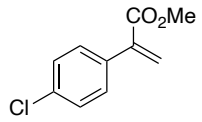
Methyl 2-(4-fluorophenyl)acrylate (1b)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.43–7.35 (m, 2H), 7.09–6.97 (m, 2H), 6.36 (d, J = 1.2 Hz, 1H), 5.87 (d, J = 1.2 Hz, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.2, 162.8 (d, $J_{C–F}$ = 246.1 Hz), 140.3, 132.8 (d, $J_{C–F}$ = 4.1 Hz), 130.22 (d, $J_{C–F}$ = 8.2 Hz), 127.1, 115.2 (d, $J_{C–F}$ = 21.4 Hz), 52.4

The analytical data for this compound were in excellent agreement with the reported data.[34]

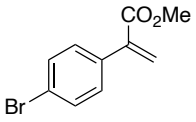
methyl 2-(4-chlorophenyl)acrylate (1c)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 4H), 6.38 (d, *J* = 1.2 Hz, 1H), 5.89 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 166.9, 140.3, 135.2, 134.4, 129.8, 128.4, 127.5, 52.4

The analytical data for this compound were in excellent agreement with the reported data.[34]

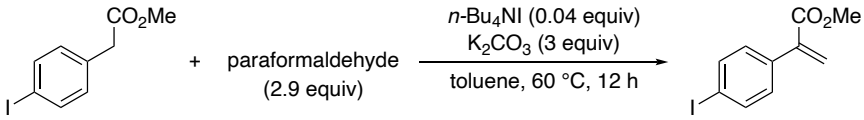
Methyl 2-(4-bromophenyl)acrylate (1d)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 0.8 Hz, 1H), 5.89 (d, *J* = 0.8 Hz, 1H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 166.8, 140.3, 135.6, 131.3, 130.1, 127.5, 122.5, 52.4

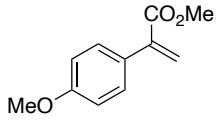
The analytical data for this compound were in excellent agreement with the reported data.[34]

Methyl 2-(4-iodophenyl)acrylate (1e)



According to the general procedure **I**, to a solution of methyl 2-(4-iodophenyl)acetate (1.64 g, 5.9 mmol) in toluene, paraformaldehyde (517.3 mg, 17 mmol), *n*-Bu_4NI (87.9 mg, 0.23 mmol), and K_2CO_3 (2.50 g, 18 mmol) were added. The resulting mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the suspension was filtered through Celite, and the filtrate was eluted with EtOAc and water. Then, the mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel (hexane/EtOAc = 95:5) gave the product as colorless oil (586.3 mg, 34% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 0.8 Hz, 1H), 5.90 (d, *J* = 0.8 Hz, 1H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 166.7, 140.3, 137.3, 136.2, 130.2, 127.6, 94.3, 52.4; IR: (ATR) 2947, 1717, 1485, 1433, 1389, 1200, 1175, 1057, 1003, 826, 810 cm^{-1}; HRMS (EI) *m*/*z*: (M^+) Calculated for $C_{10}H_9O_2I$ 287.9647; Found 287.9646

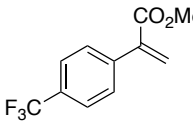
Methyl 2-(4-methoxyphenyl)acrylate (1f)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.28 (d, *J* = 1.2 Hz, 1H), 5.84 (d, *J* = 1.2 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 167.7, 159.7, 140.7, 129.6, 129.3, 125.6, 113.7, 55.4, 52.3

The analytical data for this compound were in excellent agreement with the reported data.[34]

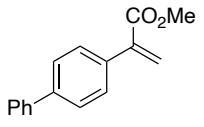
Methyl 2-(4-(trifluoromethyl)phenyl)acrylate (1g)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 6.48 (s, 1H), 5.97 (s, 1H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 166.6, 140.4, 140.3, 130.3 (q, J_{C-F} = 32.1 Hz), 128.9, 128.8, 125.2 (q, J_{C-F} = 3.2 Hz), 124.2 (q, J_{C-F} = 270.8 Hz), 52.5

The analytical data for this compound were in excellent agreement with the reported data.[34]

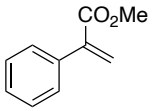
Methyl 2-([1,1'-biphenyl]-4-yl)acrylate (1h)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.62–7.55 (m, 4H), 7.49 (d, J = 8.8 Hz, 2H), 7.48–7.40 (m, 2H), 7.35 (t, J = 7.6 Hz, 1H), 6.38 (d, J = 1.2 Hz, 1H), 5.95 (d, J = 1.2 Hz, 1H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 167.4, 141.3, 141.1, 140.8, 135.8, 128.9, 128.8, 127.6, 127.2, 127.0, 126.9, 52.4

The analytical data for this compound were in excellent agreement with the reported data.[35]

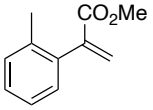
Methyl 2-phenylacrylate (1i)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.46–7.33 (m, 4H), 6.37 (d, J = 0.8 Hz, 1H), 5.90 (d, J = 0.8 Hz, 1H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 167.4, 141.5, 136.9, 128.4, 128.33, 128.27, 127.0, 52.3

The analytical data for this compound were in excellent agreement with the reported data.[34]

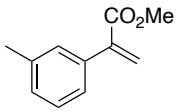
Methyl 2-(*o*-tolyl)acrylate (1j)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30–7.08 (m, 4H), 6.52 (d, J = 1.6 Hz, 1H), 5.71 (d, J = 1.6 Hz, 1H), 3.76 (s, 3H), 2.20 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 167.3, 141.8, 137.3, 136.2, 130.0, 129.6, 128.8, 128.3, 125.8, 52.4, 19.9

The analytical data for this compound were in excellent agreement with the reported data.[36]

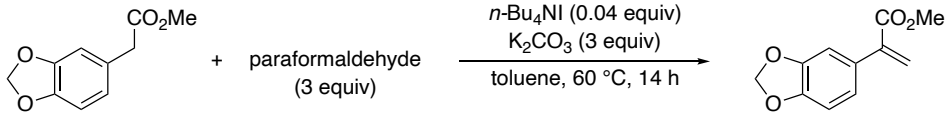
Methyl 2-(*m*-tolyl)acrylate (1k)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.28–7.10 (m, 4H), 6.33 (d, J = 1.2 Hz, 1H), 5.86 (d, J = 1.2 Hz, 1H), 3.82 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 167.6, 141.6, 137.9, 136.8, 129.12, 129.10, 128.2, 126.7, 125.5, 52.3, 21.6

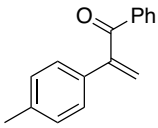
The analytical data for this compound were in excellent agreement with the reported data.[37]

Methyl 2-(benzo[*d*][1,3]dioxol-5-yl)acrylate (1l)



According to the general procedure **I**, to a solution of methyl 2-(benzo[*d*][1,3]dioxol-5-yl)acetate (1.93 g, 10 mmol) in toluene, paraformaldehyde (917.6 mg, 31 mmol), *n*-Bu_4NI (162.8 mg, 0.41 mmol), and K_2CO_3 (4.24 g, 31 mmol) were added. The resulting mixture was stirred at 60 °C for 14 h. After cooling to room temperature, the suspension was filtered through Celite, and the filtrate was eluted with EtOAc and water. Then, the mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on silica gel (hexane/EtOAc = 85:15) gave the product as yellow oil (782.4 mg, 38% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 6.93–6.86 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.25 (s, 1H), 5.95 (s, 2H), 5.81 (s, 1H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 167.4, 147.7, 147.5, 140.8, 130.7, 125.9, 122.1, 108.9, 108.0, 101.2, 52.2; IR: (ATR) 3001, 2953, 2913, 1711, 1489, 1433, 1236, 1200, 1148, 1109, 1034, 916, 816 cm^{-1}; HRMS (CI) *m/z*: ([M+H]$^+$) Calculated for $C_{11}H_{11}O_4$ 207.0657; Found 207.0652

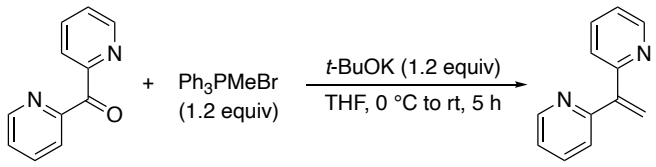
1-Phenyl-2-(*p*-tolyl)prop-2-en-1-one (1m)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.41 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.01 (s, 1H), 5.57 (s, 1H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 197.9, 148.2, 138.5, 137.2, 134.2, 133.1, 130.1, 129.4, 128.5, 127.0, 120.0, 21.3

The analytical data for this compound were in excellent agreement with the reported data.[38]

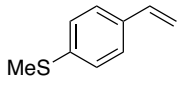
2,2'-(Ethene-1,1-diyl)dipyridine (1o)



According to the reported procedure[39], a heat-gun-dried round-bottom flask containing a magnetic stir bar was charged with Ph_3PMeBr (2.15 g, 6 mmol) and dry THF (17 mL). The suspension was cooled to 0 °C, *t*-BuOK (0.56 g, 5 mmol) was added, and the resulting yellow suspension was stirred at 0 °C for 30 min. To this suspension, a solution of di(pyridin-2-yl)methanone (0.91 g, 5 mmol) in THF (5 mL) was added slowly. The mixture was stirred at 0 °C for 4 h before being quenched with water (10 mL). The aqueous layer was extracted with AcOEt (3 × 10 mL), and the combined organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was purified by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as red oil (498.1 mg, 55% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.0, 0.8 Hz, 2H), 7.68 (ddd, *J* = 7.6, 7.6, 2.0 Hz, 2H), 7.39 (dd, *J* = 7.6, 0.8 Hz, 2H), 7.21 (ddd, *J* = 7.6, 4.0, 0.8 Hz, 2H), 6.06 (s, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 158.0, 149.5, 148.7, 136.5, 123.3, 122.7, 120.6; IR:

(ATR) 3049, 3001, 1582, 1562, 1470, 1429, 991, 924, 797, 745 cm^{-1}; HRMS (CI) *m/z*: ($[M+H]^+$) Calculated for $C_{12}H_{11}N_2$ 183.0922; Found 183.0924

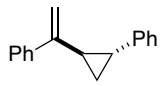
Methyl(4-vinylphenyl)sulfane (1q)



^1H NMR: (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.70 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.8 Hz, 1H), 2.49 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 138.1, 136.3, 134.7, 126.7, 113.3, 15.9 (one sp^2 signal was not observed because of overlapping)

The analytical data for this compound were in excellent agreement with the reported data.[40]

***trans*-(1-(2-Phenylcyclopropyl)vinyl)benzene (1r)**

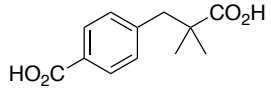


^1H NMR: (400 MHz, $CDCl_3$) δ 7.54–7.47 (m, 2H), 7.34–7.12 (m, 8H), 5.37 (s, 1H), 5.04 (s, 1H), 2.04–1.88 (m, 2H), 1.44–1.32 (m, 1H), 1.31–1.20 (m, 1H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 148.4, 142.7, 141.1, 128.6, 128.4, 127.7, 126.2, 125.87, 125.86, 109.5, 28.0, 26.6, 16.0

The analytical data for this compound were in excellent agreement with the reported data.[41]

4. Preparation of carboxylic acids

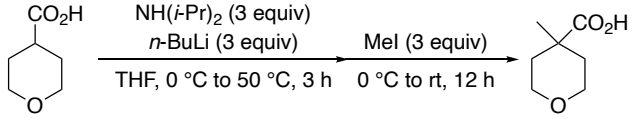
4-(2-Carboxy-2-methylpropyl)benzoic acid (2e)



^1H NMR: (400 MHz, DMSO-d_6) δ 12.6 (brs, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 2.85 (s, 2H), 1.07 (s, 6H); $^{13}C\{^1H\}$ NMR: (100 MHz, DMSO-d_6) δ 178.1, 167.3, 143.4, 130.2, 128.9, 45.2, 42.6, 24.8 (one sp^2 signal was not observed because of overlapping)

The analytical data for this compound were in excellent agreement with the reported data.[42]

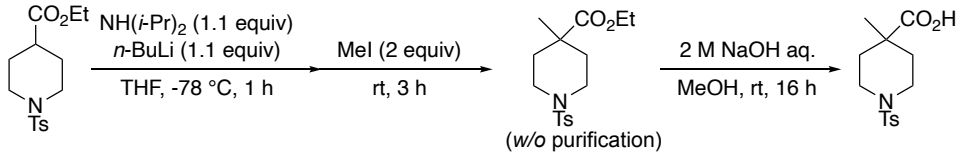
4-Methyltetrahydro-2*H*-pyran-4-carboxylic acid (2j)



A heat-gun-dried round-bottom flask containing a magnetic stir bar was charged with dry THF (30 mL) and cooled to −78 °C. Diisopropylamine (4.63 g, 46 mmol) and *n*-BuLi (1.6 M in hexane, 28 mL, 45 mmol) were added, and the solution was allowed to stir at −78 °C for 30 min. Tetrahydro-2*H*-pyran-4-carboxylic acid (1.94 g, 15 mmol) in THF (10 mL) was then added dropwise over 10 min, and the resulting solution was stirred an additional 30 min. The resulting mixture was heated at 50 °C for 3 h. The reaction mixture was cooled to 0 °C and methyl iodide (6.27 g, 44 mmol) was added dropwise. The mixture was stirred for 12 h before being quenched with water (20 mL). The

aqueous layer was washed with Et_2O (3 × 20 mL). Then, the combined aqueous layers were acidified with sat. 2 M HCl aq. until pH = 2. The mixture was extracted with Et_2O (3 x 20 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. Recrystallization from hexane/Et_2O gave the product **2j** as a brown solid (1.25 g, 58% yield). mp: 67.8–68.7 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.86–3.78 (m, 2H), 3.60–3.50 (m, 2H), 2.12–2.03 (m, 2H), 1.59–1.48 (m, 2H), 1.30 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 183.0, 65.3, 40.9, 35.2, 26.3; IR: (ATR) 2955, 2922, 2872, 1715, 1454, 1304, 1207, 1161, 1020, 880, 820 cm^{-1}; HRMS (CI) *m*/*z*: ([M+H]$^+$) Calculated for $C_7H_{13}O_3$ 145.0865; Found 145.0869

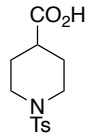
4-Methyl-1-tosylpiperidine-4-carboxylic acid (2k)



Step 1: A heat-gun-dried round-bottom flask containing a magnetic stir bar was charged with dry THF (15 mL) and cooled to −78 °C. Diisopropylamine (893.4 mg, 8.8 mmol) and *n*-BuLi (1.6 M in hexane, 5.5 mL, 8.8 mmol) were added, and the solution was allowed to stir at −78 °C for 30 min. Ethyl 1-tosylpiperidine-4-carboxylate (2.49 g, 8.0 mmol) in THF (8 mL) was then added, and the solution was stirred an additional 1 h. Methyl iodide (2.41 g, 17 mmol) was added dropwise over 10 min, and the reaction mixture was stirred at this temperature for 1 h and then allowed to warm to room temperature. The mixture was stirred for 3 h before being quenched with water (20 mL). The aqueous layer was extracted with Et_2O (3 × 20 mL), and the combined organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was directly used for the next step.

Step 2: The crude product was dissolved in the mixture of MeOH (15 mL) and aqueous NaOH aq. (2 M, 40 mL), and the solution was stirred at rt for 16 h. Then, the solution was concentrated under reduced pressure, and the resulting aqueous layer was washed with Et_2O (2 × 20 mL) to remove impurities and acidified with 2 M HCl aq. The aqueous layer was extracted with Et_2O (3 × 20 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. Recrystallization from hexane/Et_2O gave the product **2k** as a white solid (1.72 g, 72% yield). m.p.: 164.2–166.5 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.47–3.38 (m, 2H), 2.69–2.58 (m, 2H), 2.43 (s, 3H), 2.19–2.09 (m, 2H), 1.61–1.51 (m, 2H), 1.20 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 181.8, 143.6, 133.8, 129.8, 127.8, 43.6, 41.0, 34.0, 25.8, 21.7; IR: (ATR) 2978, 2936, 2862, 1688, 1346, 1329, 1207, 1173, 1157, 1090, 1057, 935, 719 cm^{-1}; HRMS (DRAT) *m*/*z*: ([M+H]$^+$) Calculated for $C_{14}H_{20}NO_4S$ 298.1113; Found 298.1100

1-Tosylpiperidine-4-carboxylic acid (2p)

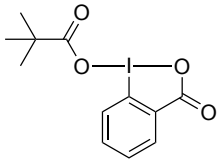


^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.73–3.60 (m, 2H), 2.55–2.40 (m, 5H), 2.37–2.25 (m, 1H), 2.10–1.95 (m, 2H), 1.93–1.75 (m, 2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 180.0, 143.8, 133.1, 129.8, 127.8, 45.5, 39.9, 27.3, 21.6

The analytical data for this compound were in excellent agreement with the reported data.[43]

Preparation of a hypervalent iodine reagent

1-Pivaloyloxy-1,2-benziodoxol-3-(1*H*)-one (60)



According to the reported procedure[44], a reaction flask containing a magnetic stir bar was charged with pivalic anhydride (5 mL) and 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one (1.32 g, 5 mmol) under nitrogen. The reaction mixture was heated up to 150 °C, while stirring vigorously until complete dissolution of the starting material (approx. 1 h). The resulting mixture was allowed to cool to room temperature and then left to settle in a freezer overnight. The white crystals were filtered, washed with Et_2O (3×5 mL) and dried, affording 1-pivaloyloxy-1,2-benziodoxol-3-(1*H*)-one as a white crystalline solid (1.08 g, 62%). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 6.8 Hz, 1H), 8.00–7.90 (m, 2H), 7.72 (dd, *J* = 7.6, 7.6 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 184.0, 168.4, 136.3, 133.3, 131.4, 129.4, 129.3, 118.7, 39.7, 27.9

The analytical data for this compound were in excellent agreement with the reported data.[44]

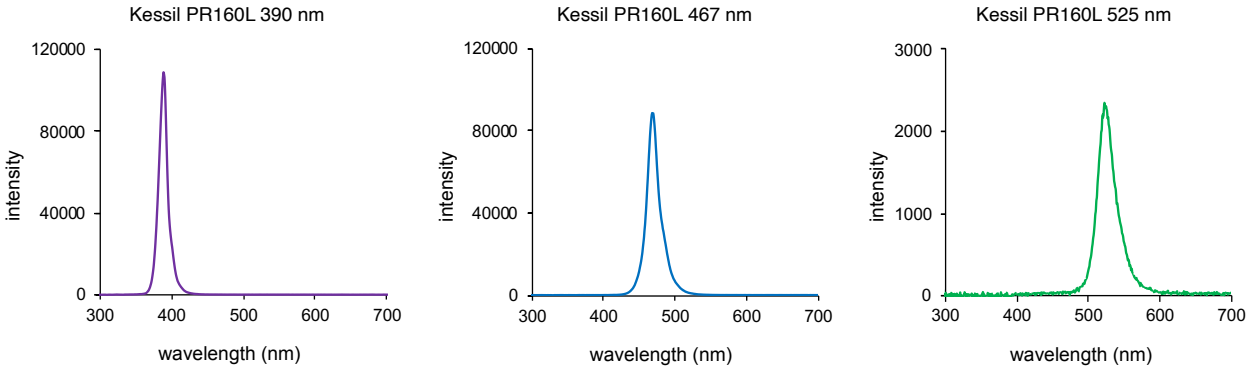
Alkylamination: experimental procedures, unsuccessful substrates, and product data

General procedure II: A reaction vial containing a magnetic stir bar was charged with alkene, carboxylic acid, iodine reagent, K_2CO_3, and DMSO. After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained at <30 °C). After 12 h of irradiation, the reaction was then quenched with H_2O. The mixture was extracted with EtOAc. The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc) gave the product.

General procedure III: A reaction vial containing a magnetic stir bar was charged with alkene, carboxylic acid, iodine reagent, KOAc, and acetone. After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 390 nm (40W, 100% intensity, 2 cm away, (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained at <30 °C). After 2 h of irradiation, the reaction was then quenched with H_2O. The mixture was extracted with EtOAc. The combined organic extracts

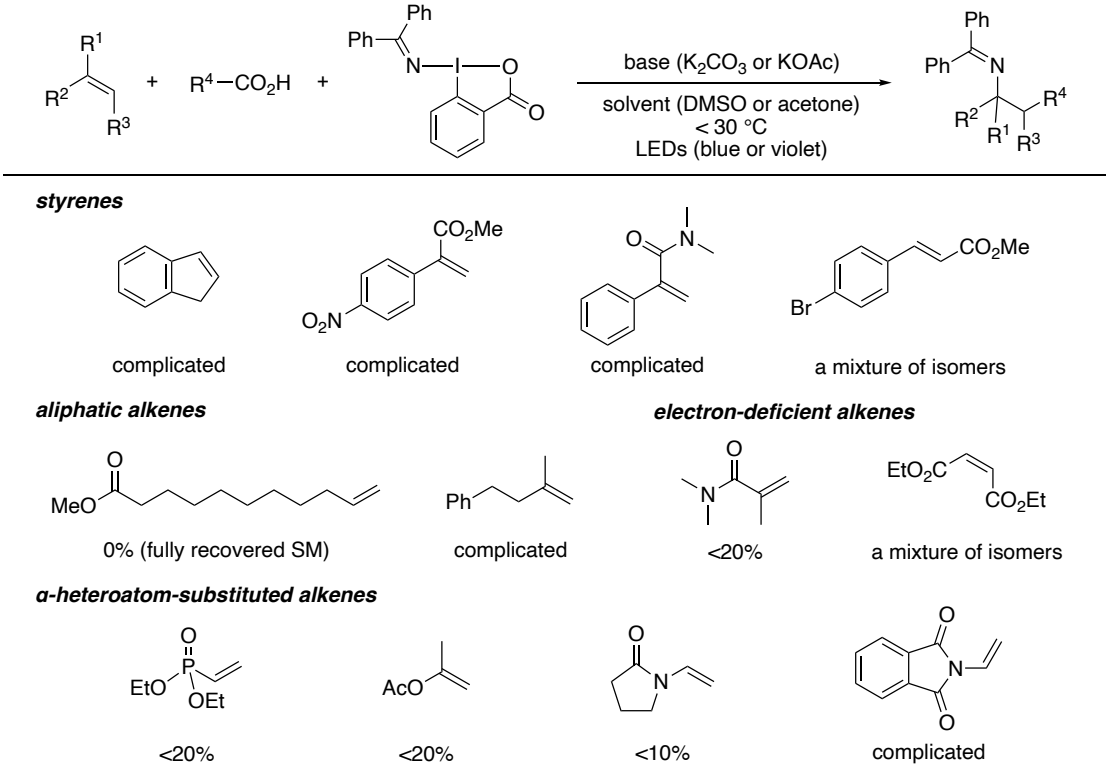
were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc) gave the product.

Emission spectra of the LEDs



Unsuccessful Substrates

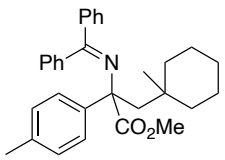
According to general procedure **II** or **III**, the reactions using alkenes listed below were examined.



Scheme S1. List of unsuccessful substrates. Yields are determined by ^{1}H NMR analysis of the crude product.

Product data

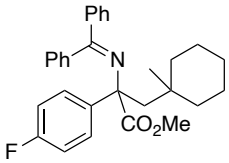
Methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (4)



According to general procedure **II**, the reaction using alkene **1a** (72.9 mg, 0.41 mmol), carboxylic acid **2a** (57.2 mg, 0.40 mmol), iodine reagent **3a** (204.8 mg, 0.48 mmol), K_2CO_3 (54.7 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 98:2) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (153.3 mg, 84% yield). Recrystallization from hexane/$CHCl_3$ gave a single crystal suitable for X-ray analysis. mp: 96.5–99.8 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 2H), 7.60–7.45 (m, 2H), 7.43–7.30 (m, 6H), 7.16–7.04 (m, 4H), 3.17 (s, 3H), 2.46 (d, J = 14.8 Hz, 1H), 2.33 (d, J = 14.8 Hz, 1H), 2.32 (s, 3H), 1.42–0.99 (m, 10H), 0.76 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.9, 165.1, 142.3, 141.4, 137.2, 136.3, 130.0, 128.9, 128.8, 128.6, 128.3, 128.1, 127.6, 126.2, 71.5, 53.1, 51.7, 40.2, 39.5, 34.3, 26.4, 25.3, 22.2, 22.1, 21.2; IR: (ATR) 2924, 2843, 1728, 1628, 1445, 1221, 1020, 820, 770 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{36}NO_2$ 454.2746; Found 454.2753

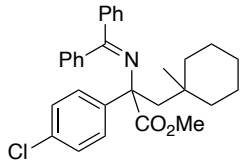
The structure of **4** was determined by X-ray structural analysis. Thermal elipsoids are drawn at the 50% probability level. CCDC 2286656 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Methyl 2-((diphenylmethylene)amino)-2-(4-fluorophenyl)-3-(1-methylcyclohexyl)propanoate (9)



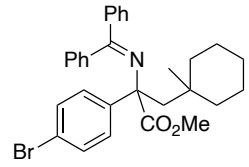
According to general procedure **II**, the reaction using alkene **1b** (74.2 mg, 0.41 mmol), carboxylic acid **2a** (56.3 mg, 0.40 mmol), iodine reagent **3a** (207.0 mg, 0.49 mmol), K_2CO_3 (55.4 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (168.3 mg, 92% yield). mp: 121.4–123.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.67–7.59 (m, 2H), 7.45–7.31 (m, 6H), 7.17–7.06 (m, 2H), 6.97 (dd, J = 9.2, 8.4 Hz, 2H), 3.18 (s, 3H), 2.45 (d, J = 15.2 Hz, 1H), 2.35 (d, J = 15.2 Hz, 1H), 1.44–0.97 (m, 10H), 0.77 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.6, 165.6, 161.6 (d, $J_{C–F}$ = 243.7 Hz), 141.2, 141.1 (d, $J_{C–F}$ = 3.3 Hz), 137.0, 130.2, 128.8, 128.54, 128.50, 128.1, 128.0 (d, $J_{C–F}$ = 8.2 Hz), 127.7, 114.9 (d, $J_{C–F}$ = 21.4 Hz), 71.3, 53.4, 51.8, 40.2, 39.5, 34.4, 26.3, 25.3, 22.2, 22.0; ^{19}F{^{1}H} NMR: (100 MHz, $CDCl_3$) δ −119.0; IR: (ATR) 2928, 1732, 1630, 1504, 1215, 1155, 1030, 841 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{30}H_{33}FNO_2$ 458.2495; Found 458.2489

Methyl 2-(4-chlorophenyl)-2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)propanoate (10)



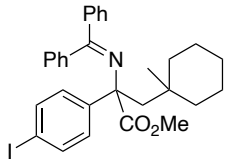
According to general procedure **II**, the reaction using alkene **1c** (79.2 mg, 0.40 mmol), carboxylic acid **2a** (56.4 mg, 0.40 mmol), iodine reagent **3a** (204.8 mg, 0.48 mmol), K_2CO_3 (58.8 mg, 0.43 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (145.7 mg, 77% yield). mp: 121.7–127.4 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 6.8 Hz, 2H), 7.66–7.54 (m, 2H), 7.44–7.30 (m, 6H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.12–7.05 (m, 2H), 3.17 (s, 3H), 2.44 (d, *J* = 14.8 Hz, 1H), 2.34 (d, *J* = 14.8 Hz, 1H), 1.44–0.99 (m, 10H), 0.76 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.5, 165.7, 144.1, 141.1, 137.0, 132.6, 130.3, 128.8, 128.6, 128.3, 128.2, 127.9, 127.7, 71.4, 53.4, 51.8, 40.2, 39.5, 34.4, 26.3, 25.3, 22.2, 22.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2916, 1728, 1634, 1489, 1443, 1209, 1030, 1013, 772, 758 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{30}H_{33}ClNO_2$ 474.2200; Found 474.2187

Methyl 2-(4-bromophenyl)-2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)propanoate (11)



According to general procedure **II**, the reaction using alkene **1d** (98.6 mg, 0.41 mmol), carboxylic acid **2a** (56.8 mg, 0.40 mmol), iodine reagent **3a** (206.0 mg, 0.48 mmol), K_2CO_3 (54.8 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (155.5 mg, 75% yield). mp: 133.2–134.4 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.2 Hz, 2H), 7.62–7.51 (m, 2H), 7.50–7.30 (m, 8H), 7.16–7.06 (m, 2H), 3.17 (s, 3H), 2.44 (d, *J* = 15.2 Hz, 1H), 2.34 (d, *J* = 15.2 Hz, 1H), 1.43–0.97 (m, 10H), 0.76 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.4, 165.7, 144.6, 141.1, 137.0, 131.3, 130.3, 128.8, 128.6, 128.3, 128.2, 127.7, 120.8, 71.4, 53.3, 51.8, 40.2, 39.5, 34.4, 26.3, 25.3, 22.2, 22.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2924, 1732, 1485, 1445, 1213 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{30}H_{33}BrNO_2$ 518.1695; Found 518.1688

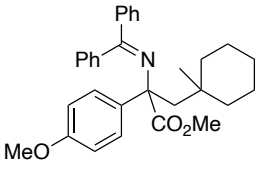
Methyl 2-((diphenylmethylene)amino)-2-(4-iodophenyl)-3-(1-methylcyclohexyl)propanoate (12)



According to general procedure **II**, the reaction using alkene **1e** (117.0 mg, 0.41 mmol), carboxylic acid **2a** (56.6 mg, 0.40 mmol), iodine reagent **3a** (205.8 mg, 0.48 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (161.8 mg, 72% yield). mp: 128.2–130.9 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 6.8 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.47–7.29 (m, 8H), 7.13–7.05 (m, 2H), 3.17 (s, 3H),

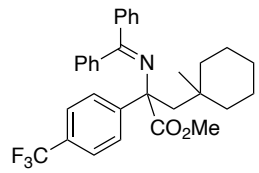
2.43 (d, J = 14.8 Hz, 1H), 2.34 (d, J = 14.8 Hz, 1H), 1.43–0.97 (m, 10H), 0.76 (s, 3H) ; $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.4, 165.7, 145.4, 141.1, 137.2, 137.0, 130.3, 128.8, 128.6, 128.5, 128.2, 127.7, 92.5, 71.5, 53.2, 51.8, 40.2, 39.6, 34.4, 26.3, 25.3, 22.2, 22.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2922, 1732, 1628, 1445, 1213, 1001 cm^{-1}; HRMS (FAB+) m/z: ($[M+H]^+$) Calculated for $C_{30}H_{33}NO_2I$ 566.1556; Found 566.1567

Methyl 2-((diphenylmethylene)amino)-2-(4-methoxyphenyl)-3-(1-methylcyclohexyl)propanoate (13)



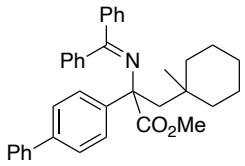
According to general procedure **II**, the reaction using alkene **1f** (76.4 mg, 0.40 mmol), carboxylic acid **2a** (56.8 mg, 0.40 mmol), iodine reagent **3a** (204.6 mg, 0.48 mmol), K_2CO_3 (55.3 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a pale yellow solid (149.7 mg, 80% yield). mp: 168.9–171.7 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, J = 6.8 Hz, 2H), 7.61–7.49 (m, 2H), 7.43–7.29 (m, 6H), 7.13–7.05 (m, 2H), 6.82 (d, J = 9.2 Hz, 2H), 3.80 (s, 3H), 3.19 (s, 3H), 2.45 (d, J = 14.4 Hz, 1H), 2.32 (d, J = 14.4 Hz, 1H), 1.44–0.99 (m, 10H), 0.78 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 175.0, 165.2, 158.4, 141.4, 137.5, 137.3, 130.1, 128.8, 128.6, 128.4, 128.1, 127.7, 127.5, 113.5, 71.2, 55.3, 53.2, 51.7, 40.2, 39.5, 34.4, 26.4, 25.3, 22.2, 22.1; IR: (ATR) 2926, 1719, 1636, 1506, 1248, 1219, 1173, 1030, 829 cm^{-1}; HRMS (FAB+) m/z: ($[M+H]^+$) Calculated for $C_{31}H_{36}NO_3$ 470.2695; Found 470.2692

Methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-(4-(trifluoromethyl)phenyl)propanoate (14)



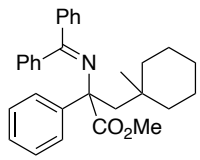
According to general procedure **II**, the reaction using alkene **1g** (92.6 mg, 0.40 mmol), carboxylic acid **2a** (56.5 mg, 0.40 mmol), iodine reagent **3a** (204.2 mg, 0.48 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (150.1 mg, 74% yield). mp: 117.8–118.9 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.85–7.76 (m, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.45–7.31 (m, 6H), 7.13–7.08 (m, 2H), 3.19 (s, 3H), 2.49 (d, J = 14.8 Hz, 1H), 2.40 (d, J = 14.8 Hz, 1H), 1.45–0.96 (m, 10H), 0.76 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.2, 166.0, 149.6, 141.0, 136.9, 130.4, 129.1 (q, J_{C-F} = 32.1 Hz), 128.8, 128.6, 128.5, 128.2, 127.8, 126.8, 125.1 (q, J_{C-F} = 4.1 Hz), 124.4 (q, J_{C-F} = 270.8 Hz), 71.7, 53.4, 51.9, 40.2, 39.6, 34.4, 26.3, 25.2, 22.1, 22.0; $^{19}F\{^1H\}$ NMR: (377 MHz, $CDCl_3$) δ −64.9; IR: (ATR) 2926, 1734, 1628, 1325, 1163, 1115, 1065, 851 cm^{-1}; HRMS (FAB+) m/z: ($[M+H]^+$) Calculated for $C_{31}H_{33}F_3NO_2$ 508.2463; Found 508.2469

Methyl 2-([1,1'-biphenyl]-4-yl)-2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)propanoate (15)



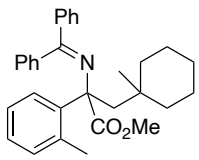
According to general procedure **II**, the reaction using alkene **1h** (96.2 mg, 0.40 mmol), carboxylic acid **2a** (57.0 mg, 0.40 mmol), iodine reagent **3a** (205.2 mg, 0.48 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (180.7 mg, 88% yield). mp: 137.2–139.6 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.8 Hz, 2H), 7.70–7.65 (m, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), δ 7.51 (d, *J* = 8.8 Hz, 2H), 7.47–7.29 (m, 9H), 7.10 (d, *J* = 7.2 Hz, 2H), 3.23 (s, 3H), 2.52 (d, *J* = 15.2 Hz, 1H), 2.40 (d, *J* = 15.2 Hz, 1H), 1.45–1.02 (m, 10H), 0.82 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.8, 165.5, 144.5, 141.3, 141.0, 139.5, 137.3, 130.2, 128.9, 128.8, 128.6, 128.3, 128.1, 127.7, 127.3, 127.1, 126.8, 71.6, 53.2, 51.8, 40.2, 39.5, 34.4, 26.4, 25.3, 22.2, 22.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2920, 1728, 1628, 1443, 1215 cm^{-1}; HRMS (FAB+) *m/z*: ([M+H]$^+$) Calculated for $C_{36}H_{38}NO_2$ 516.2903; Found 516.2900

Methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-phenylpropanoate (16)



According to general procedure **II**, the reaction using alkene **1i** (66.2 mg, 0.41 mmol), carboxylic acid **2a** (56.8 mg, 0.40 mmol), iodine reagent **3a** (206.2 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a viscous oil (87.3 mg, 50% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.77–7.63 (m, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.44–7.33 (m, 6H), 7.33–7.27 (m, 2H), 7.25–7.18 (m, 1H), 7.15–7.06 (m, 2H), 3.18 (s, 3H), 2.49 (d, *J* = 14.8 Hz, 1H), 2.35 (d, *J* = 14.8 Hz, 1H), 1.42–0.98 (m, 10H), 0.76 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.8, 165.3, 145.3, 141.3, 137.2, 130.1, 128.8, 128.6, 128.4, 128.2, 128.1, 127.7, 126.9, 126.4, 71.7, 53.3, 51.7, 40.2, 39.4, 34.4, 26.4, 25.3, 22.2, 22.1; IR: (ATR) 2922, 1728, 1628, 1445, 1213, 1030, 764 cm^{-1}; HRMS (FAB+) *m/z*: ([M+H]$^+$) Calculated for $C_{30}H_{34}NO_2$ 440.2590; Found 440.2587

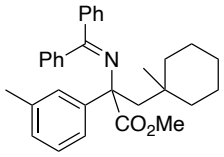
Methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-(*o*-tolyl)propanoate (17)



According to general procedure **II**, the reaction using alkene **1j** (72.2 mg, 0.41 mmol), carboxylic acid **2a** (57.8 mg, 0.41 mmol), iodine reagent **3a** (206.2 mg, 0.48 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the

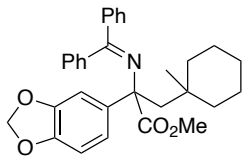
product as a white solid (128.7 mg, 71% yield). mp: 104.1–105.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.8 Hz, 2H), 7.41–7.26 (m, 4H), 7.25–6.10 (m, 8H), 3.55 (s, 3H), 2.47 (d, *J* = 14.0 Hz, 1H), 2.36 (d, *J* = 14.0 Hz, 1H), 2.20 (s, 3H), 1.54–1.10 (m, 10H), 0.98 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 175.6, 163.8, 143.6, 141.3, 137.5, 136.4, 131.7, 129.9, 128.6, 128.0, 127.4, 127.3, 126.8, 126.4, 125.3, 70.6, 52.0, 51.6, 40.4, 38.7, 34.3, 26.4, 24.5, 22.3, 22.1, 21.4 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2940, 1749, 1626, 1445, 1204, 1140, 1059 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{31}H_{36}NO_2$ 454.2746; Found 454.2750

Methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-(*m*-tolyl)propanoate (18)



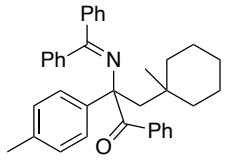
According to general procedure **II**, the reaction using alkene **1k** (70.2 mg, 0.40 mmol), carboxylic acid **2a** (57.0 mg, 0.40 mmol), iodine reagent **3a** (206.3 mg, 0.48 mmol), K_2CO_3 (56.3 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (143.3 mg, 79% yield). mp: 152.5–153.7 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.8 Hz, 2H), 7.50–7.28 (m, 8H), 7.16 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.12–7.03. (m, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 3.21 (s, 3H), 2.47 (d, *J* = 14.4 Hz, 1H), 2.36–2.25 (m, 4H), 1.43–0.96 (m, 10H), 0.78 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.9, 165.2, 145.1, 141.4, 137.6, 137.3, 130.1, 128.8, 128.5, 128.3, 128.1, 127.6, 127.0, 123.5, 71.6, 52.9, 51.8, 40.2, 39.4, 34.4, 26.4, 25.3, 22.2, 22.1, 21.9 (two sp^2 signals were not observed because of overlapping); IR: (ATR) 2920, 1724, 1636, 1443, 1211 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{31}H_{36}NO_2$ 454.2746; Found 454.2754

Methyl 2-(benzo[*d*][1,3]dioxol-5-yl)-2-((diphenylmethylene)amino)
-3-(1-methylcyclohexyl)propanoate (19)



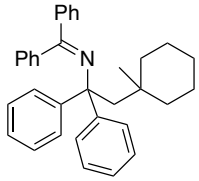
According to general procedure **II**, the reaction using alkene **1l** (42.3 mg, 0.21 mmol), carboxylic acid **2a** (28.3 mg, 0.20 mmol), iodine reagent **3a** (102.7 mg, 0.24 mmol), K_2CO_3 (27.9 mg, 0.20 mmol), and DMSO (2 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 85:15) gave the product as a pale yellow solid (67.4 mg, 70% yield). mp: 174.3–177.4 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.42–7.30 (m, 6H), 7.24–7.18 (m, 1H), 7.17–7.05 (m, 3H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.97–5.92 (m, 2H), 3.20 (s, 3H), 2.41 (d, *J* = 14.8 Hz, 1H), 2.31 (d, *J* = 14.8 Hz, 1H), 1.45–1.05 (m, 10H), 0.80 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.8, 165.3, 147.7, 146.4, 141.3, 139.5, 137.2, 130.1, 128.8, 128.6, 128.4, 128.1, 127.7, 119.7, 108.0, 107.5, 101.0, 71.4, 53.3, 51.8, 40.2, 39.5, 34.4, 26.4, 25.3, 22.2, 22.1; IR: (ATR) 2916, 2860, 1719, 1630, 1487, 1431, 1240, 1211, 1032, 934, 770 cm^{-1}; HRMS (DRAT) *m*/*z*: ($[M+H]^+$) Calculated for $C_{31}H_{34}NO_4$ 484.2488; Found 484.2465

2-((Diphenylmethylene)amino)-3-(1-methylcyclohexyl)-1-phenyl-2-(*p*-tolyl)propan-1-one (20)



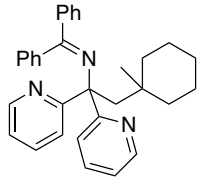
According to general procedure **II**, the reaction using alkene **1m** (90.1 mg, 0.41 mmol), carboxylic acid **2a** (56.5 mg, 0.40 mmol), iodine reagent **3a** (205.3 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and recrystallization from hexane/$CHCl_3$ gave the product as a white solid (132.9 mg, 67% yield). mp: 70.7–73.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.72 (brs, 1H), 7.72 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.51–7.27 (m, 4H), 7.25–6.31 (m, 10H), 2.51 (d, *J* = 15.2 Hz, 1H), 2.28 (s, 3H), 2.24 (d, *J* = 15.2 Hz, 1H), 1.45–0.99 (m, 8H), 0.93–0.76 (m, 2H), 0.73 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 198.0, 165.1, 141.9, 141.4, 137.3, 136.4, 134.3, 131.7, 131.3, 130.0, 129.3, 128.8, 128.6, 128.5, 128.1, 127.8, 127.4, 127.0, 75.7, 53.7, 40.9, 39.0, 34.2, 26.4, 25.7, 22.3, 22.0, 21.2; IR: (ATR) 2928, 2859, 1676, 1624, 1445, 1217, 1179, 779, 762 cm^{-1}; HRMS (CI) *m*/*z*: ([M+H]$^+$) Calculated for $C_{36}H_{38}NO$ 500.2953; Found 500.2949

***N*-(2-(1-Methylcyclohexyl)-1,1-diphenylethyl)-1,1-diphenylmethanimine (21)**



According to general procedure **II**, the reaction using alkene **1n** (72.9 mg, 0.40 mmol), carboxylic acid **2a** (57.1 mg, 0.40 mmol), iodine reagent **3a** (205.1 mg, 0.48 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 99:1) gave the product as a white solid (125.8 mg, 69% yield). mp: 104.5–107.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.60–7.20 (m, 5H), 7.17–6.95 (m, 11H), 6.70–6.30 (m, 2H), 2.47 (s, 2H), 1.46–0.97 (m, 10H), 0.78 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 164.5, 151.6, 142.4, 139.0, 129.7, 128.5, 128.1, 127.64, 127.59, 127.2, 126.6, 125.6, 68.8, 52.9, 40.1, 34.6, 26.5, 25.6, 22.3 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2920, 2859, 1626, 1489, 1445, 1263, 1028, 777, 762 cm^{-1}; HRMS (EI) *m*/*z*: (M$^+$) Calculated for $C_{34}H_{35}N$ 457.2770; Found 457.2764

***N*-(2-(1-Methylcyclohexyl)-1,1-di(pyridin-2-yl)ethyl)-1,1-diphenylmethanimine (22)**

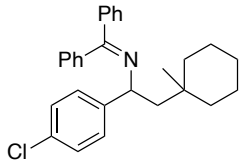


According to general procedure **II**, the reaction using alkene **1o** (40.4 mg, 0.22 mmol), carboxylic acid **2a** (56.5 mg, 0.40 mmol), iodine reagent **3a** (170.4 mg, 0.40 mmol), K_2CO_3 (56.0 mg, 0.41 mmol), and DMSO (2 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a white solid (56.1 mg, 55% yield). Recrystallization from hexane/$CHCl_3$ gave a single crystal suitable for X-ray analysis. mp: 136.1–138.4 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 4.0 Hz, 2H), 8.10–7.20 (br, 2H), 7.68 (d, *J* = 6.4 Hz, 2H), 7.53–7.40 (m, 2H), 7.40–7.31 (m, 3H), 7.12–7.08 (m, 1H), 7.08–6.98 (m, 2H), 6.97–6.87 (m, 2H), 6.80–6.40 (m, 2H),

2.81 (brs, 2H), 1.45–1.05 (m, 10H), 0.77 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 168.5, 165.1, 148.6, 141.6, 139.2, 135.8, 129.8, 128.6, 128.0, 127.4, 126.8, 122.6, 120.8, 73.4, 52.4, 39.9, 34.6, 26.4, 25.3, 22.3 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2920, 2855, 1632, 1584, 1460, 1427, 1261, 993, 768 cm^{-1}; HRMS (DRAT) *m*/*z*: ($[M+H]^+$) Calculated for $C_{32}H_{34}N_3$ 460.2753; Found 460.2758

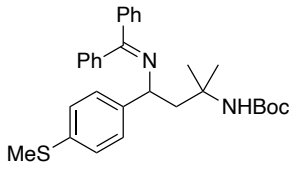
The structure of **22** was determined by X-ray structural analysis. Thermal elipsoids are drawn at the 50% probability level. CCDC 2286658 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

_N_-(1-(4-Chlorophenyl)-2-(1-methylcyclohexyl)ethyl)-1,1-diphenylmethanimine (23)



According to general procedure **II**, the reaction using alkene **1p** (63.2 mg, 0.46 mmol), carboxylic acid **2a** (57.0 mg, 0.40 mmol), iodine reagent **3a** (206.7 mg, 0.48 mmol), K_2CO_3 (56.5 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a viscous oil (67.9 mg, 41% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.48–7.28 (m, 6H), 7.26–7.13 (m, 4H), 7.03–6.93 (m, 2H), 4.48 (dd, *J* = 7.6, 4.0 Hz, 1H), 2.12 (dd, *J* = 14.4, 7.6 Hz, 1H), 1.71 (dd, *J* = 14.4, 4.0 Hz, 1H), 1.52–1.01 (m, 10H), 0.72 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 165.8, 145.9, 140.1, 137.3, 131.9, 130.0, 128.7, 128.6, 128.5, 128.4, 128.2, 127.8, 63.1, 51.7, 38.8, 38.5, 33.6, 26.5, 26.0, 22.11, 22.05 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2922, 2847, 1616, 1487, 1445, 1281, 1088, 1015, 829, 779 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{28}H_{31}ClN$ 416.2145; Found 416.2147

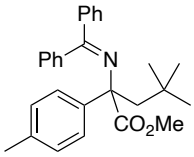
***tert*-Butyl (4-((diphenylmethylene)amino)-2-methyl-4-(4-(methylthio)phenyl)butan -2-yl)carbamate (24)**



According to general procedure **II**, the reaction using alkene **1q** (30.6 mg, 0.20 mmol), carboxylic acid **2l** (81.2 mg, 0.40 mmol), iodine reagent **3a** (170.4 mg, 0.40 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), and DMSO (2 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a white solid (45.2 mg, 45% yield). mp: 62.2–66.4 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.47–7.28 (m, 6H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 5.6 Hz, 2H), 5.48 (brs, 1H), 4.51 (dd, *J* = 10.4, 2.4 Hz, 1H), 2.46 (s, 3H), 2.34 (dd, *J* = 14.8, 10.4 Hz, 1H), 1.89 (dd, *J* = 14.8, 2.4 Hz, 1H), 1.28 (s, 9H), 1.27 (s, 3H), 1.23 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 168.0, 154.6, 143.3, 139.5, 137.1, 136.4, 130.3, 128.7, 128.6, 128.4, 128.2, 127.54, 127.48, 127.1, 78.2, 63.4, 52.6, 51.7, 28.7, 28.5, 25.8, 16.2; IR:

(ATR) 3366, 2974, 2920, 1713, 1489, 1447, 1364, 1275, 1165, 1072, 781, 770 cm^{-1}; HRMS (ESI) *m*/*z*: ($[M+H]^+$) Calculated for $C_{30}H_{37}N_2O_2S$ 489.2576; Found 489.2557

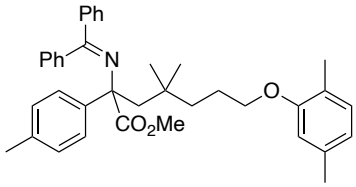
Methyl 2-((diphenylmethylene)amino)-4,4-dimethyl-2-(*p*-tolyl)pentanoate (25)



According to general procedure **II**, the reaction using alkene **1a** (71.3 mg, 0.40 mmol), carboxylic acid **2b** (40.9 mg, 0.40 mmol), iodine reagent **3a** (206.7 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (134.9 mg, 82% yield). Recrystallization from hexane/$CHCl_3$ gave a single crystal suitable for X-ray analysis. mp: 142.1–144.3 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.58–7.49 (m, 2H), 7.43–7.31 (m, 6H), 7.13–7.06 (m, 4H), 3.18 (s, 3H), 2.45 (d, *J* = 14.4 Hz, 1H), 2.37 (d, *J* = 14.4 Hz, 1H), 2.33 (s, 3H), 0.79 (s, 9H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.9, 165.4, 142.1, 141.3, 137.3, 136.4, 130.1, 128.9, 128.8, 128.6, 128.4, 128.1, 127.6, 126.3, 71.5, 52.3, 51.7, 32.0, 31.8, 21.2; IR: (ATR) 2947, 1728, 1628, 1217, 773 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{28}H_{32}NO_2$ 414.2433; Found 414.2431

The structure of **25** was determined by X-ray structural analysis. Thermal elipsoids are drawn at the 50% probability level. CCDC 2286657 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

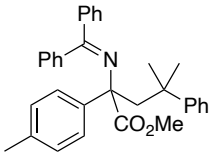
Methyl 7-(2,5-dimethylphenoxy)-2-((diphenylmethylene)amino)-4,4-dimethyl-2 -(*p*-tolyl)heptanoate (26)



According to general procedure **II**, the reaction using alkene **1a** (74.2 mg, 0.42 mmol), carboxylic acid **2c** (101.2 mg, 0.40 mmol), iodine reagent **3a** (206.2 mg, 0.48 mmol), K_2CO_3 (56.4 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (194.9 mg, 87% yield). mp: 48.8–50.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.62–7.47 (m, 2H), 7.43–7.24 (m, 6H), 7.16–7.05 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.48 (s, 1H), 3.61 (t, *J* = 6.8 Hz, 2H), 3.14 (s, 3H), 2.51 (d, *J* = 14.4 Hz, 1H), 2.38 (d, *J* = 14.4 Hz, 1H), 2.302 (s, 3H), 2.296 (s, 3H), 2.14 (s, 3H), 1.74–1.53 (m, 2H), 1.27 (t, *J* = 7.6 Hz, 2H), 0.82 (s, 3H), 0.74 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.8, 165.3, 157.2, 142.0, 141.4, 137.1, 136.44, 136.42, 130.3, 130.1, 129.0, 128.8, 128.6, 128.4, 128.1, 127.7, 126.2, 123.6, 120.5, 112.0, 71.5, 68.6, 51.7, 51.0, 40.9, 34.1, 29.1, 24.4, 21.5, 21.1, 15.9 (one sp^3 signal was not observed because of overlapping); IR: (ATR) 2947, 1728, 1628, 1508,

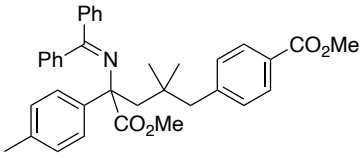
1445, 1265, 1219, 1128 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{38}H_{44}NO_3$ 562.3321; Found 562.3317

Methyl 2-((diphenylmethylene)amino)-4-methyl-4-phenyl-2-(*p*-tolyl)pentanoate (27)



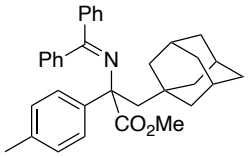
According to general procedure **II**, the reaction using alkene **1a** (72.4 mg, 0.41 mmol), carboxylic acid **2d** (66.0 mg, 0.40 mmol), iodine reagent **3a** (207.0 mg, 0.48 mmol), K_2CO_3 (56.0 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (71.9 mg, 38% yield). mp: 111.4–113.8 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.43–7.28 (m, 8H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.02–6.85 (m, 7H), 2.99 (s, 3H), 2.88 (d, *J* = 14.8 Hz, 1H), 2.80 (d, *J* = 14.8 Hz, 1H), 2.29 (s, 3H), 1.26 (s, 3H), 1.21 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.4, 165.6, 150.4, 141.7, 141.4, 137.1, 136.2, 130.0, 129.0, 128.8, 128.5, 128.3, 127.9, 127.7, 127.5, 126.3, 126.1, 124.9, 71.4, 53.7, 51.6, 37.9, 31.2, 30.2, 21.2; IR: (ATR) 2968, 1724, 1664, 1223, 1045 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{33}H_{34}NO_2$ 476.2590; Found *m*/*z* 476.2593

Methyl 4-(4-((diphenylmethylene)amino)-5-methoxy-2,2-dimethyl-5-oxo-4 -(*p*-tolyl)pentyl)benzoate (28)



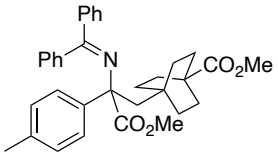
According to general procedure **II**, the reaction using alkene **1a** (71.1 mg, 0.40 mmol), carboxylic acid **2e** (89.1 mg, 0.40 mmol), iodine reagent **3a** (205.4 mg, 0.48 mmol), K_2CO_3 (112.3 mg, 0.81 mmol), and DMSO (4 mL) was conducted for 12 h. To the reaction mixture, methyl iodide (298.1 mg, 2.10 mmol) was added, and the reaction mixture was stirred at room temperature for an additional 3 h. The reaction was then quenched with H_2O (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 85:15) gave the product as a white solid (165.1 mg, 75% yield). mp: 68.1–70.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.56–7.43 (m, 2H), 7.42–7.23 (m, 6H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 6.8 Hz, 2H), 3.90 (s, 3H), 3.16 (s, 3H), 2.58–2.45 (m, 3H), 2.44 (d, *J* = 14.4 Hz, 1H), 2.32 (s, 3H), 0.84 (s, 3H), 0.63 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.7, 167.4, 165.6, 145.0, 142.0, 141.1, 136.9, 136.5, 131.1, 130.2, 129.1, 129.0, 128.8, 128.4, 128.1, 127.8, 127.6, 126.2, 71.3, 52.1, 51.7, 51.6, 51.5, 35.7, 28.7, 28.5, 21.2 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2949, 1719, 1628, 1433, 1277, 1221, 1180, 1111, 772 cm^{-1}; HRMS (EI) *m*/*z*: (M$^+$) Calculated for $C_{36}H_{37}NO_4$ 547.2723; Found 547.2720

Methyl 2-((diphenylmethylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (29)



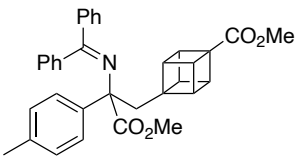
According to general procedure **II**, the reaction using alkene **1a** (71.8 mg, 0.41 mmol), carboxylic acid **2f** (72.1 mg, 0.40 mmol), iodine reagent **3a** (206.0 mg, 0.48 mmol), K_2CO_3 (55.9 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (158.8 mg, 81% yield). mp: 191.3–193.0 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 6.4 Hz, 2H), 7.62–7.44 (m, 2H), 7.43–7.28 (m, 6H), 7.17–7.03 (m, 4H), 3.19 (s, 3H), 2.44–2.27 (m, 4H), 2.22 (d, *J* = 14.4 Hz, 1H), 1.86–1.65 (m, 3H), 1.65–1.17 (m, 12H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.9, 165.2, 142.3, 141.2, 137.3, 136.3, 130.1, 128.9, 128.8, 128.6, 128.3, 128.1, 127.6, 126.2, 71.2, 53.9, 51.8, 44.3, 37.0, 34.0, 29.0, 21.2; IR: (ATR) 2895, 1721, 1624, 1219 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{34}H_{38}NO_2$ 492.2903; Found 492.2889

Methyl 4-(2-((diphenylmethylene)amino)-3-methoxy-3-oxo-2-(*p*-tolyl)propyl)bicyclo[2.2.2]octane -1-carboxylate (30)



According to general procedure **II**, the reaction using alkene **1a** (71.5 mg, 0.41 mmol), carboxylic acid **2g** (85.4 mg, 0.40 mmol), iodine reagent **3a** (205.3 mg, 0.48 mmol), K_2CO_3 (55.5 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (156.3 mg, 75% yield). mp: 75.6–83.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.53–7.32 (m, 8H), 7.13–7.05 (m, 4H), 3.55 (s, 3H), 3.16 (s, 3H), 2.37 (d, *J* = 14.4 Hz, 1H), 2.33 (s, 3H), 2.28 (d, *J* = 14.4 Hz, 1H), 1.64–1.52 (m, 6H), 1.42–1.21 (m, 6H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 178.7, 174.7, 165.7, 142.0, 141.2, 137.2, 136.5, 130.2, 129.0, 128.8, 128.6, 128.4, 128.2, 127.7, 126.2, 71.2, 51.7, 51.6, 51.2, 38.6, 32.1, 31.8, 28.9, 21.2; IR: (ATR) 2947, 2866, 1724, 1628, 1433, 1219, 1067, 1042, 1013, 752 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^+$) Calculated for $C_{34}H_{38}NO_4$ 524.2801; Found 524.2782

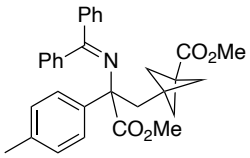
Methyl (1*s*,2*R*,3*r*,8*S*)-4-(2-((diphenylmethylene)amino)-3-methoxy-3-oxo-2-(*p*-tolyl)propyl)cubane-1-carboxylate (31)



According to general procedure **II**, the reaction using alkene **1a** (53.5 mg, 0.30 mmol), carboxylic acid **2h** (62.1 mg, 0.30 mmol), iodine reagent **3a** (154.1 mg, 0.36 mmol), K_2CO_3 (43.0 mg, 0.30 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (52.7 mg, 34% yield). mp: 76.3–78.3 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.44–7.33 (m, 6H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.11–7.07 (m, 2H), 3.92–3.86 (m, 3H), 3.61 (s, 3H), 3.35–3.27

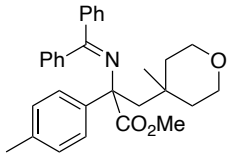
(m, 3H), 3.21 (s, 3H), 2.62 (d, *J* = 14.8 Hz, 1H), 2.53 (d, *J* = 14.8 Hz, 1H), 2.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.2, 173.2, 166.4, 141.6, 141.1, 137.0, 136.9, 130.4, 129.1, 128.8, 128.7, 128.5, 128.2, 127.8, 126.0, 71.4, 55.5, 51.8, 51.5, 47.3, 46.5, 44.2, 21.2; IR: (ATR) 2990, 1721, 1433, 1317, 1198, 1086, 1061, 770 cm^{-1}; HRMS (DART) *m*/*z*: ($[M+H]^+$) Calculated for $C_{34}H_{32}NO_4$ 518.2331; Found 518.2311

Methyl 3-(2-((diphenylmethylene)amino)-3-methoxy-3-oxo-2-(*p*-tolyl)propyl)bicyclo[1.1.1]pentane-1-carboxylate (32)



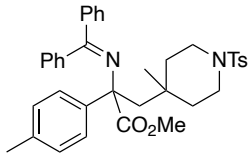
According to general procedure **II**, the reaction using alkene **1a** (69.8 mg, 0.4 mmol), carboxylic acid **2h** (67.7 mg, 0.4 mmol), iodine reagent **3a** (205.4 mg, 0.48 mmol), K_2CO_3 (53.9 mg, 0.39 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (64.2 mg, 33% yield). mp: 78.4–82.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 6.8 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.49–7.31 (m, 6H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.10–7.01 (m, 2H), 3.55 (s, 3H), 3.28 (s, 3H), 2.54 (d, *J* = 15.2 Hz, 1H), 2.47 (d, *J* = 15.2 Hz, 1H), 2.34 (s, 3H), 1.75 (dd, *J* = 9.6, 2.0 Hz, 3H), 1.67 (dd, *J* = 9.6, 2.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.1, 170.5, 167.0, 140.9, 140.5, 137.1, 136.8, 130.4, 129.0, 128.7, 128.6, 128.4, 128.2, 127.9, 126.4, 70.5, 53.6, 52.0, 51.5, 41.1, 38.8, 37.1, 21.2; IR: (ATR) 2949, 2914, 2876, 1728, 1628, 1435, 1229, 1200, 1177, 1063 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{31}H_{32}NO_4$ 482.2331; Found 482.2320

Methyl 2-((diphenylmethylene)amino)-3-(4-methyltetrahydro-2*H*-pyran-4-yl)-2-(*p*-tolyl)propanoate (33)



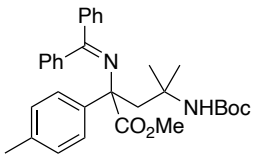
According to general procedure **II**, the reaction using alkene **1a** (71.5 mg, 0.41 mmol), carboxylic acid **2j** (57.9 mg, 0.40 mmol), iodine reagent **3a** (206.2 mg, 0.48 mmol), K_2CO_3 (55.0 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (135.8 mg, 75% yield). mp: 128.4–131.0 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.61–7.46 (m, 2H), 7.45–7.30 (m, 6H), 7.18–7.05 (m, 4H), 3.62–3.36 (m, 4H), 3.13 (s, 3H), 2.54 (d, *J* = 14.8 Hz, 1H), 2.38 (d, *J* = 14.8 Hz, 1H), 2.32 (s, 3H), 1.52–1.49 (m, 1H), 1.42–1.28 (m, 2H), 1.07–0.97 (m, 1H), 0.86 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.6, 165.5, 141.9, 141.3, 137.0, 136.5, 130.2, 129.0, 128.8, 128.6, 128.5, 128.1, 127.7, 126.2, 71.3, 63.84, 63.76, 53.6, 51.7, 40.0, 39.2, 32.1, 24.1, 21.2; IR: (ATR) 2949, 1728, 1628, 1443, 1215, 1180, 1020 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{30}H_{34}NO_3$ 456.2539; Found 456.2547

Methyl 2-((diphenylmethylene)amino)-3-(4-methyl-1-tosylpiperidin-4-yl)-2-(*p*-tolyl)propanoate (34)



According to general procedure **II**, the reaction using alkene **1a** (69.7 mg, 0.40 mmol), carboxylic acid **2l** (120.1 mg, 0.40 mmol), iodine reagent **3a** (205.3 mg, 0.48 mmol), K_2CO_3 (55.6 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 80:20) gave the product as a white solid (195.3 mg, 80% yield). mp: 126.7–131.3 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 6.8 Hz, 2H), 7.57–7.28 (m, 10H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 6.8 Hz, 2H), 3.12–2.93 (m, 2H), 3.06 (s, 3H), 2.60–2.50 (m, 2H), 2.42–2.25 (m, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 1.70–1.61 (m, 1H), 1.47–1.35 (m, 2H), 1.22–1.14 (m, 1H), 0.55 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.5, 165.7, 143.3, 141.7, 141.2, 136.8, 133.2, 130.4, 129.7, 129.2, 128.8, 128.60, 128.57, 128.2, 127.8, 127.7, 126.1, 71.4, 52.3, 51.7, 42.4, 42.2, 38.1, 38.0, 32.2, 24.6, 21.6, 21.2 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2949, 2942, 2859, 1728, 1346, 1221, 1182, 1092, 930, 725 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^+$) Calculated for $C_{37}H_{41}N_2O_4S$ 609.2787; Found 609.2766

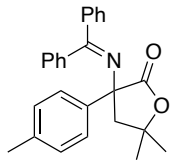
Methyl 4-((*tert*-butoxycarbonyl)amino)-2-((diphenylmethylene)amino)-4-methyl-2-(*p*-tolyl)pentanoate (35)



According to general procedure **II**, the reaction using alkene **1a** (71.1 mg, 0.40 mmol), carboxylic acid **2l** (81.4 mg, 0.40 mmol), iodine reagent **3a** (207.3 mg, 0.49 mmol), K_2CO_3 (56.3 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a white solid (184.1 mg, 89% yield). mp: 101.9–105.3 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.49–7.28 (m, 8H), 7.15–7.05 (m, 4H), 5.46 (brs, 1H), 3.13 (s, 3H), 2.79 (d, *J* = 14.8 Hz, 1H), 2.64 (d, *J* = 14.8 Hz, 1H), 2.33 (s, 3H), 1.33 (s, 3H), 1.24 (s, 9H), 1.01 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.9, 167.5, 154.5, 141.1, 141.0, 136.75, 136.71, 130.4, 129.1, 129.0, 128.8, 128.5, 128.2, 127.6, 126.5, 78.1, 71.6, 53.0, 51.8, 50.8, 29.7, 28.9, 28.5, 21.2; IR: (ATR) 3387, 2976, 1724, 1697, 1530, 1364, 1279, 1229, 1171, 1080, 1047, 770 cm^{-1}; HRMS (EI) *m*/*z*: (M$^+$) Calculated for $C_{32}H_{38}N_2O_4$ 514.2832; Found 514.2829

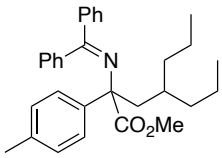
Gram-scale reaction: According to general procedure, the reaction using alkene **1a** (496.8 mg, 2.8 mmol), carboxylic acid **2l** (570.4 mg, 2.8 mmol), iodine reagent **3a** (1.44 g, 3.4 mmol), K_2CO_3 (389.2 mg, 2.8 mmol), and DMSO (20 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a white solid (1.21 g, 84% yield).

3-((Diphenylmethylene)amino)-5,5-dimethyl-3-(*p*-tolyl)dihydrofuran-2(3*H*)-one (36)



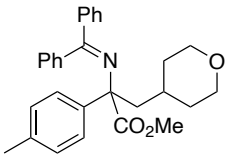
According to general procedure **II**, the reaction using alkene **1a** (35.8 mg, 0.20 mmol), carboxylic acid **2m** (21.0 mg, 0.20 mmol), iodine reagent **3a** (103.0 mg, 0.24 mmol), K_2CO_3 (28.2 mg, 0.20 mmol), and DMSO (2 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as colorless oil (46.5 mg, 61% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.42–7.20 (m, 4H), 7.19–7.05 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 7.6 Hz, 2H), 2.73 (d, *J* = 13.6 Hz, 1H), 2.62 (d, *J* = 13.6 Hz, 1H), 2.26 (s, 3H), 1.50 (s, 3H), 1.26 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 176.7, 170.0, 140.7, 137.74, 137.67, 137.2, 130.5, 128.71, 128.69, 128.1, 128.0, 127.8, 127.53, 127.47, 81.0, 71.6, 48.0, 29.9, 28.5, 21.1; IR: (ATR) 2974, 2924, 2872, 1763, 1622, 1445, 1267, 1138, 816, 756 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{26}H_{26}NO_2$ 384.1964; Found 384.1973

Methyl 2-((diphenylmethylene)amino)-4-propyl-2-(*p*-tolyl)heptanoate (38)



According to general procedure **II**, the reaction using alkene **1a** (71.1 mg, 0.40 mmol), carboxylic acid **2n** (58.3 mg, 0.40 mmol), iodine reagent **3a** (205.8 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a viscous oil (76.5 mg, 42% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 6.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.44–7.30 (m, 6H), 7.17–7.05 (m, 4H), 3.17 (s, 3H), 2.33 (s, 3H), 2.28 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.13 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.52–0.89 (m, 9H), 0.72–0.56 (m, 6H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.7, 165.9, 141.5, 141.4, 137.1, 136.3, 130.1, 128.9, 128.7, 128.54, 128.48, 128.0, 127.7, 126.4, 71.9, 51.6, 45.9, 37.0, 36.6, 32.6, 21.2, 19.5, 19.2, 14.4, 14.3; IR: (ATR) 2953, 2926, 2870, 1732, 1630, 1445, 1221, 770 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{38}NO_2$ 456.2903; Found 456.2907

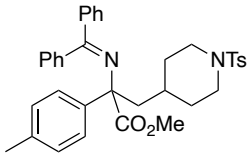
Methyl 2-((diphenylmethylene)amino)-3-(tetrahydro-2*H*-pyran-4-yl)-2-(*p*-tolyl)propanoate (39)



According to general procedure **II**, the reaction using alkene **1a** (72.3 mg, 0.41 mmol), carboxylic acid **2o** (53.0 mg, 0.41 mmol), iodine reagent **3a** (206.0 mg, 0.48 mmol), K_2CO_3 (56.0 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (65.9 mg, 37% yield). mp: 78.4–81.6 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.8 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.43–7.32 (m, 6H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 3.82–3.70 (m, 2H), 3.24 (s, 3H), 3.27–3.11 (m, 2H), 2.35 (s, 3H), 2.26 (dd, *J* = 14.0, 5.6

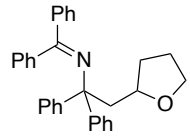
Hz, 1H), 2.19 (dd, *J* = 14.8, 6.8 Hz, 1H), 1.70–1.60 (m, 1H), 1.32–1.10 (m, 4H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.5, 166.7, 141.3, 141.2, 137.1, 136.7, 130.3, 129.1, 128.7, 128.6, 128.4, 128.2, 127.8, 126.3, 71.3, 68.1, 51.8, 47.6, 34.6, 34.4, 31.1, 21.2 (one sp^3 signal was not observed because of overlapping); IR: (ATR) 2949, 2916, 2837, 1728, 1628, 1443, 1221, 1130 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{29}H_{32}NO_3$ 442.2382; Found 442.2371

Methyl 2-((diphenylmethylene)amino)-2-(*p*-tolyl)-3-(1-tosylpiperidin-4-yl)propanoate (40)



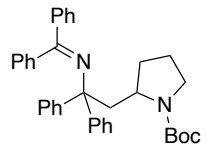
According to general procedure **II**, the reaction using alkene **1a** (69.8 mg, 0.40 mmol), carboxylic acid **2p** (112.8 mg, 0.40 mmol), iodine reagent **3a** (204.4 mg, 0.48 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 80:20) gave the product as a white solid (110.8 mg, 47% yield). mp: 92.6–94.3 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.43–7.30 (m, 6H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 3.62–3.47 (m, 2H), 3.20 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H), 2.25 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.14 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.09–1.96 (m, 2H), 1.87–1.76 (m, 1H), 1.41–1.11 (m, 4H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.2, 166.9, 143.4, 141.1, 141.0, 136.9, 136.7, 133.3, 130.4, 129.6, 129.1, 128.7, 128.4, 128.2, 127.82, 127.79, 126.2, 71.2, 51.8, 46.8, 46.43, 46.39, 32.8, 32.7, 31.2, 21.6, 21.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2920, 2843, 1728, 1445, 1339, 1225, 1163, 1092, 934, 725 cm^{-1}; HRMS (DART) *m*/*z*: ($[M+H]^+$) Calculated for $C_{36}H_{39}N_2O_4S$ 595.2631; Found 595.2630

***N*-(1,1-Diphenyl-2-(tetrahydrofuran-2-yl)ethyl)-1,1-diphenylmethanimine (41)**



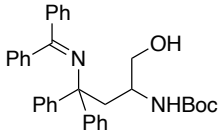
According to general procedure **II**, the reaction using alkene **1n** (71.2 mg, 0.40 mmol), carboxylic acid **2q** (56.1 mg, 0.48 mmol), iodine reagent **3a** (205.8 mg, 0.48 mmol), K_2CO_3 (64.9 mg, 0.48 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (106.8 mg, 62% yield). mp: 61.4–69.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.43–7.28 (m, 5H), 7.25–7.17 (m, 1H), 7.17–6.93 (m, 10H), 6.52 (d, *J* = 7.6 Hz, 2H), 3.79–3.67 (m, 2H), 3.51 (ddd, *J* = 8.0, 8.0, 8.0 Hz, 1H), 2.92 (dd, *J* = 13.2, 3.2 Hz, 1H), 2.40 (dd, *J* = 13.2, 9.2 Hz, 1H), 1.80–1.57 (m, 2H), 1.57–1.42 (m, 1H), 1.07–0.93 (m, 1H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 166.8, 149.9, 149.8, 142.1, 138.7, 129.9, 128.5, 128.2, 128.1, 127.9, 127.8, 127.5, 127.3, 126.8, 125.93, 125.88, 76.9, 67.9, 66.8, 46.8, 32.6, 26.4 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3055, 2864, 1624, 1489, 1445, 1273, 1063, 764 cm^{-1}; HRMS (DART) *m*/*z*: ($[M+H]^+$) Calculated for $C_{31}H_{30}NO$ 432.2327; Found 432.2338

***tert*-Butyl 2-(2-((diphenylmethylene)amino)-2,2-diphenylethyl)pyrrolidine-1-carboxylate (42)**



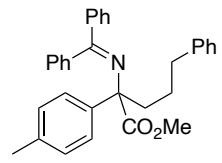
According to general procedure **II**, the reaction using alkene **1n** (71.4 mg, 0.40 mmol), carboxylic acid **2r** (103.6 mg, 0.48 mmol), iodine reagent **3a** (205.5 mg, 0.48 mmol), K_2CO_3 (68.3 mg, 0.49 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (111.6 mg, 53% yield). mp: 72.1–76.2 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.60–7.27 (m, 4H), 7.20–6.40 (m, 14H), 3.74–2.93 (m, 4H), 2.43–2.21 (m, 1H), 1.93–1.50 (m, 4H), 1.39 (s, 9H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 166.4, 154.6, 150.1, 149.3, 142.1, 138.8, 129.9, 128.5, 128.3, 128.14, 128.06, 127.8, 127.7, 127.5, 127.3, 126.5, 125.8, 79.3, 68.5, 55.4, 46.4, 44.9, 31.0, 28.8, 23.7 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2972, 1686, 1626, 1445, 1391, 1364, 1165, 1099, 762, 731 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^+$) Calculated for $C_{36}H_{39}N_2O_2$ 531.3012; Found 531.3023

***tert*-Butyl (4-((diphenylmethylene)amino)-1-hydroxy-4,4-diphenylbutan-2-yl)carbamate (43)**



According to general procedure **II**, the reaction using alkene **1n** (72.9 mg, 0.40 mmol), carboxylic acid **2s** (82.8 mg, 0.40 mmol), iodine reagent **3a** (206.1 mg, 0.48 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 70:30) gave the product as a white solid (103.6 mg, 50% yield). mp: 99.1–101.5 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.2 Hz, 2H), 7.41–7.28 (m, 5H), 7.23–6.99 (m, 9H), 6.94 (t, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 7.8 Hz, 2H), 5.60 (brs, 1H), 3.53–3.44 (m, 2H), 3.44–3.24 (m, 2H), 2.71 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.62–2.47 (m, 1H), 1.33 (s, 9H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 168.7, 157.0, 148.0, 147.7, 141.5, 138.4, 130.4, 128.6, 128.2, 128.1, 128.01, 127.94, 127.8, 127.4, 127.2, 126.9, 126.4, 126.2, 79.4, 69.2, 67.0, 51.5, 43.3, 28.4 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 3441, 3055, 2972, 2930, 2870, 1688, 1491, 1445, 1366, 1246, 1165, 1028, 764 cm^{-1}; HRMS (ESI) *m*/*z*: ([M+Na]$^+$) Calculated for $C_{34}H_{36}N_2O_3Na$ 543.2624; Found 543.2617

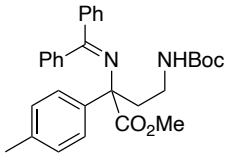
Methyl 2-((diphenylmethylene)amino)-5-phenyl-2-(*p*-tolyl)pentanoate (44)



According to general procedure **II**, the reaction using alkene **1a** (71.6 mg, 0.41 mmol), carboxylic acid **2t** (61.4 mg, 0.41 mmol), iodine reagent **3a** (205.0 mg, 0.48 mmol), K_2CO_3 (56.8 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) gave the product as a white solid (67.9 mg, 36% yield). mp: 146.0–148.3 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.42–7.28 (m, 4H), 7.28–7.09 (m, 7H), 7.06 (d, *J* = 6.8 Hz, 2H), 6.80 (d, *J* = 7.6 Hz, 2H), 3.28 (s, 3H), 2.60–2.36 (m, 2H), 2.34 (s,

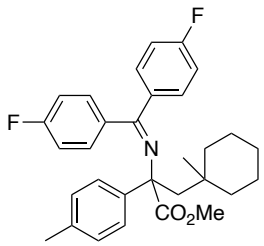
3H), 2.21–2.08 (m, 2H), 1.77–1.35 (m, 2H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.4, 167.1, 142.3, 141.22, 141.19, 137.1, 136.5, 130.2, 129.0, 128.72, 128.70, 128.5, 128.3, 128.1, 127.8, 126.4, 125.8, 71.4, 51.8, 40.2, 36.0, 25.0, 21.2 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2945, 1726, 1634, 1223 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{32}H_{32}NO_2$ 462.2433; Found 462.2424

Methyl 4-((*tert*-butoxycarbonyl)amino)-2-((diphenylmethylene)amino)-2-(*p*-tolyl)butanoate (45)



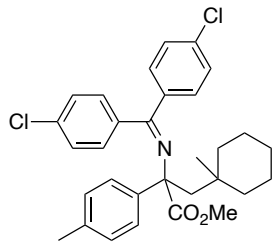
According to general procedure **II**, the reaction using alkene **1a** (71.1 mg, 0.40 mmol), carboxylic acid **2u** (70.4 mg, 0.40 mmol), iodine reagent **3a** (205.8 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 85:15) gave the product as a white solid (73.2 mg, 38% yield). mp: 68.2–72.5 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.44–7.30 (m, 6H), 7.20–7.09 (m, 4H), 4.84 (brs, 1H), 3.21 (s, 3H), 3.22–2.95 (m, 2H), 2.55–2.30 (m, 2H), 2.35 (s, 3H), 1.29 (s, 9H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 173.8, 168.0, 155.9, 141.1, 140.1, 137.0, 136.8, 130.5, 129.3, 128.9, 128.8, 128.5, 128.2, 127.8, 126.3, 78.7, 71.4, 51.9, 41.6, 36.4, 28.4, 21.2; IR: (ATR) 3408, 2924, 2853, 1732, 1709, 1506, 1229, 1167, 779, 770 cm^{-1}; HRMS (ESI) *m*/*z*: ($[M+Na]^+$) Calculated for $C_{30}H_{34}N_2O_4Na$ 509.2416; Found 509.2425

Methyl 2-((bis(4-fluorophenyl)methylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (46)



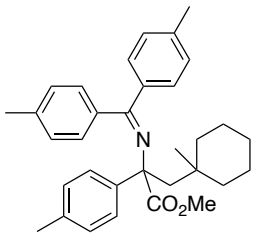
According to general procedure **II**, the reaction using alkene **1a** (71.6 mg, 0.41 mmol), carboxylic acid **2a** (57.0 mg, 0.40 mmol), iodine reagent **3b** (223.2 mg, 0.48 mmol), K_2CO_3 (57.3 mg, 0.41 mmol), and DMSO (4 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (160.1 mg, 82% yield). mp: 59.7–62.9 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.69–7.62 (m, 2H), 7.46–7.37 (m, 2H), 7.10–6.96 (m, 8H), 3.24 (s, 3H), 2.43 (d, *J* = 14.4 Hz, 1H), 2.33–2.27 (m, 4H), 1.47–1.02 (m, 10H), 0.78 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 174.9, 164.3 (d, J_{C-F} = 249.4 Hz), 163.3, 162.4 (d, J_{C-F} = 247.0 Hz), 142.0, 137.5 (d, J_{C-F} = 3.3 Hz), 136.5, 133.0 (d, J_{C-F} = 3.3 Hz), 130.7 (d, J_{C-F} = 8.2 Hz), 130.3 (d, J_{C-F} = 8.2 Hz), 129.0, 126.2, 115.1 (d, J_{C-F} = 22.3 Hz), 114.9 (d, J_{C-F} = 23.0 Hz), 71.5, 53.1, 51.8, 40.1, 39.5, 34.4, 26.4, 25.1, 22.2, 22.1, 21.2; $^{19}F\{^{1}H\}$ NMR: (377 MHz, $CDCl_3$) δ −113.7, −114.7; IR: (ATR) 2924, 1730, 1628, 1599, 1503, 1223, 1152, 835 cm^{-1}; HRMS (FAB+) *m*/*z*: ($[M+H]^+$) Calculated for $C_{31}H_{34}F_2NO_2$ 490.2558; Found 490.2570

Methyl 2-((bis(4-chlorophenyl)methylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (47)



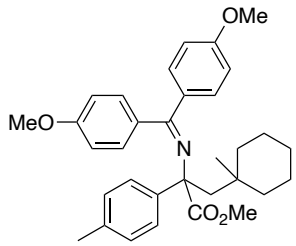
According to general procedure **II**, the reaction using alkene **1a** (53.3 mg, 0.30 mmol), carboxylic acid **2a** (42.5 mg, 0.30 mmol), iodine reagent **3c** (179.2 mg, 0.36 mmol), K_2CO_3 (42.3 mg, 0.31 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (105.9 mg, 68% yield). mp: 78.7–81.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.26 (s, 3H), 2.43 (d, *J* = 14.8 Hz, 1H), 2.31 (s, 3H), 2.31 (d, *J* = 14.8 Hz, 1H), 1.47–1.01 (m, 10H), 0.78 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.8, 163.2, 141.8, 139.5, 136.64, 136.57, 135.3, 134.5, 130.0, 129.8, 129.0, 128.4, 128.0, 126.2, 71.7, 53.0, 51.9, 40.0, 39.6, 34.4, 26.4, 25.1, 22,2, 22.1, 21.2; IR: (ATR) 2922, 1730, 1628, 1585, 1487, 1211, 1090, 1013, 818, 746 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^+$) Calculated for $C_{31}H_{34}NO_2Cl_2$ 522.1967; Found 522.1962

Methyl 2-((di-*p*-tolylmethylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (48)



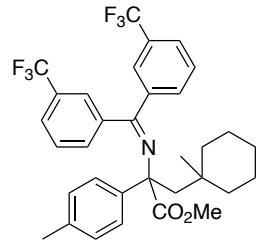
According to general procedure **II**, the reaction using alkene **1a** (53.7 mg, 0.30 mmol), carboxylic acid **2a** (42.9 mg, 0.30 mmol), iodine reagent **3d** (164.3 mg, 0.36 mmol), K_2CO_3 (43.0 mg, 0.31 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (74.1 mg, 51% yield). mp: 65.3–67.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.62–7.49 (m, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.21–7.12 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 3.16 (s, 3H), 2.45 (d, *J* = 14.4 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H), 2.33 (s, 3H), 2.30 (d, *J* = 14.4 Hz, 1H), 1.44–0.97 (m, 10H), 0.74 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 175.1, 165.3, 142.6, 140.1, 139.2, 138.0, 136.2, 134.5, 128.85, 128.79, 128.6, 128.3, 126.3, 71.4, 53.1, 51.7, 40.3, 39.5, 34.4, 26.4, 25.4, 22.3, 22.1, 21.52, 21.46, 21.2 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2920, 1730, 1605, 1508, 1443, 1211, 1180, 1038, 814, 731cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^+$) Calculated for $C_{33}H_{40}NO_2$ 482.3059; Found 482.3040

Methyl 2-((bis(4-methoxyphenyl)methylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (49)



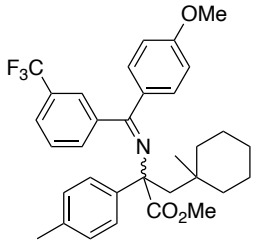
According to general procedure **II**, the reaction using alkene **1a** (56.6 mg, 0.32 mmol), carboxylic acid **2a** (43.2 mg, 0.30 mmol), iodine reagent **3e** (178.5 mg, 0.37 mmol), K_2CO_3 (43.6 mg, 0.32 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (61.4 mg, 40% yield). mp: 89.3–92.7 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.8 Hz, 2H), 7.62–7.46 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.90–6.79 (m, 4H), 3.84 (s, 3H), 3.83 (s, 3H), 3.18 (s, 3H), 2.45 (d, *J* = 14.8 Hz, 1H), 2.33 (s, 3H), 2.30 (d, *J* = 14.8 Hz, 1H), 1.42–0.97 (m, 10H), 0.74 (s, 3H); ^{13}C {^{1}H} NMR: (100 MHz, $CDCl_3$) δ 175.3, 164.5, 161.2, 159.3, 142.6, 136.2, 134.9, 130.4, 130.0, 129.7, 128.9, 126.3, 113.3, 113.0, 71.3, 55.4, 55.3, 53.2, 51.8, 40.2, 39.5, 34.4, 26.4, 25.3, 22.2, 22.1, 21.2; IR: (ATR) 2924, 1726, 1599, 1506, 1246, 1173, 1032, 831 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{33}H_{40}NO_4$ 514.2957; Found 514.2940

Methyl 2-((bis(3-(trifluoromethyl)phenyl)methylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (50)



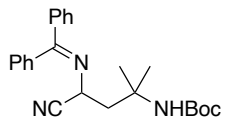
According to general procedure **II**, the reaction using alkene **1a** (53.9 mg, 0.31 mmol), carboxylic acid **2a** (42.4 mg, 0.30 mmol), iodine reagent **3f** (204.6 mg, 0.36 mmol), K_2CO_3 (41.5 mg, 0.30 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a viscous oil (105.8 mg, 60% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.42 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.29–7.11 (m, 3H), 7.08 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 3.37 (s, 3H), 2.42 (d, *J* = 14.4 Hz, 1H), 2.37 (d, *J* = 14.4 Hz, 1H), 2.28 (s, 3H), 1.51–0.99 (m, 10H), 0.87 (s, 3H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 174.5, 162.8, 141.4, 141.3, 137.6, 137.0, 131.9, 131.3, 130.9 (q, $J_{C–F}$ = 32.1 Hz), 130.2 (q, $J_{C–F}$ = 32.1 Hz), 129.1, 128.9, 128.4, 127.0 (q, $J_{C–F}$ = 3.3 Hz), 126.2, 125.2 (q, $J_{C–F}$ = 3.2 Hz), 125.1 (q, $J_{C–F}$ = 3.3 Hz), 124.1 (q, $J_{C–F}$ = 270.9 Hz), 123.8 (q, $J_{C–F}$ = 270.8 Hz), 71.8, 53.0, 52.0, 39.8, 39.6, 34.4, 26.3, 24.9, 22.2, 22.1, 21.0 (one sp^2 signal was not observed because of overlapping); ^{19}F{^{1}H} NMR: (100 MHz, $CDCl_3$) δ −65.3, −65.4; IR: (ATR) 2926, 1732, 1327, 1240, 1213, 1165, 1123, 1072, 806 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{33}H_{34}F_6NO_2$ 590.2494; Found 590.2499

Methyl 2-(((4-methoxyphenyl)(3-(trifluoromethyl)phenyl)methylene)amino)-3-(1-methylcyclohexyl)-2-(*p*-tolyl)propanoate (51)



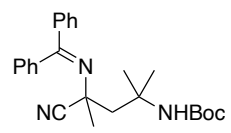
According to general procedure **II**, the reaction using alkene **1a** (55.1 mg, 0.31 mmol), carboxylic acid **2a** (42.6 mg, 0.30 mmol), iodine reagent **3g** (190.1 mg, 0.36 mmol), K_2CO_3 (41.7 mg, 0.30 mmol), and DMSO (3 mL) was conducted for 12 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 95:5) and gel permeation chromatography (GPC, $CHCl_3$ as an eluent) gave the product as a white solid (129.1 mg, 78% yield). The product was obtained as a mixture of *E*/*Z* isomers. mp: 73.6–77.8 °C; ^{1}H NMR of a mixture of *E*/*Z* isomers: (400 MHz, $CDCl_3$) δ 7.95 (s, 0.4H), 7.89 (d, *J* = 7.6 Hz, 0.4H), 7.67–7.37 (m, 4H), 7.36–7.20 (m, 2H), 7.15 (s, 0.6H), 7.10 (d, *J* = 8.4 Hz, 0.6H), 7.04–6.96 (m, 2H), 6.90–6.83 (m, 2H), 3.85 (s, 1.2H), 3.82 (s, 1.8H), 3.30 (s, 1.8H), 3.21 (s, 1.2H), 2.55–2.20 (m, 5H), 1.49–1.00 (m, 10H), 0.85 (s, 1.8H), 0.75 (s, 1.2H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) complicated due to mixture of *E*/*Z* isomers and C–F coupling; ^{19}F{^{1}H} NMR: (100 MHz, $CDCl_3$) δ −65.2, −65.3; IR: (ATR) 2926, 1730, 1599, 1508, 1331, 1250, 1165, 1125, 1072, 1032, 804 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{33}H_{37}F_3NO_3$ 552.2726; Found 552.2729

***tert*-Butyl (4-cyano-4-((diphenylmethylene)amino)-2-methylbutan-2-yl)carbamate (52)**



According to general procedure **III**, the reaction using alkene **1s** (11.3 mg, 0.21 mmol), carboxylic acid **2l** (40.6 mg, 0.20 mmol), iodine reagent **3a** (128.5 mg, 0.30 mmol), KOAc (23.2 mg, 0.24 mmol), and acetone (3 mL) was conducted for 2 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as colorless oil (51.6 mg, 66% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.58–7.48 (m, 3H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.32–7.20 (m, 2H), 4.83 (brs, 1H), 4.36 (dd, *J* = 7.2, 5.6 Hz, 1H), 2.41 (dd, *J* = 14.4, 5.6 Hz, 1H), 2.33 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.32 (s, 9H), 1.28 (s, 6H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 173.3, 154.3, 138.4, 135.3, 131.4, 129.6, 129.19, 129.15, 128.4, 127.4, 119.9, 79.0, 51.8, 50.1, 44.4, 28.5, 28.3, 27.2; IR: (ATR) 3364, 2974, 2930, 1713, 1493, 1447, 1366, 1246, 1159, 1074, 772 cm^{-1}; HRMS (DART) *m*/*z*: ([M+H]$^+$) Calculated for $C_{24}H_{30}N_3O_2$ 392.2338; Found 392.2319

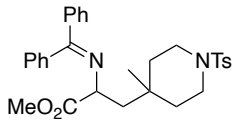
***tert*-Butyl (4-cyano-4-((diphenylmethylene)amino)-2-methylpentan-2-yl)carbamate (53)**



According to general procedure **III**, the reaction using alkene **1t** (13.7 mg, 0.20 mmol), carboxylic acid **2l** (40.3 mg, 0.20 mmol), iodine reagent **3a** (128.3 mg, 0.30 mmol), KOAc (23.1 mg, 0.24 mmol), and acetone (3 mL) was conducted for 2 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as colorless oil (56.7 mg, 70% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.57–7.46 (m, 3H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.30–7.22 (m, 2H),

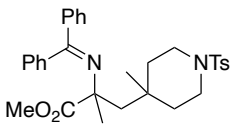
5.70 (brs, 1H), 2.46 (d, *J* = 14.8 Hz, 1H), 2.28 (d, *J* = 14.8 Hz, 1H), 1.65 (s, 3H), 1.50 (s, 3H), 1.44 (s, 3H), 1.36 (s, 9H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 168.3, 154.5, 139.4, 135.0, 131.0, 129.8, 128.7, 128.4, 120.7, 78.7, 55.5, 53.7, 52.9, 31.6, 28.9, 28.6, 26.8 (two sp^2 signals were not observed because of overlapping); IR: (ATR) 3360, 2976, 2928, 1715, 1497, 1447, 1364, 1271, 1163, 1067, 773 cm^{-1}; HRMS (DART) *m*/*z*: ($[M+H]^+$) Calculated for $C_{25}H_{32}N_3O_2$ 406.2495; Found 406.2478

Methyl 2-((diphenylmethylene)amino)-3-(4-methyl-1-tosylpiperidin-4-yl)propanoate (54)



According to general procedure **III**, the reaction using alkene **1u** (17.6 mg, 0.20 mmol), carboxylic acid **2k** (59.9 mg, 0.20 mmol), iodine reagent **3a** (128.3 mg, 0.30 mmol), KOAc (23.9 mg, 0.24 mmol), and acetone (6 mL) was conducted for 2 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a viscous oil (26.2 mg, 25% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.53–7.38 (m, 4H), 7.38–7.28 (m, 4H), 7.21–7.08 (m, 2H), 4.15 (dd, *J* = 6.8, 4.8 Hz, 1H), 3.68 (s, 3H), 3.18–3.02 (m, 2H), 2.92–2.77 (m, 2H), 2.44 (s, 3H), 1.98 (dd, *J* = 14.4, 4.8 Hz, 1H), 1.86 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.54–1.38 (m, 2H), 1.38–1.21 (m, 2H), 0.62 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 173.4, 170.1, 143.6, 139.3, 136.3, 133.3, 130.7, 129.8, 129.1, 128.9, 128.7, 128.3, 127.8, 127.7, 62.6, 52.5, 44.4, 42.22, 42.19, 37.1, 36.3, 31.1, 24.0, 21.7; IR: (ATR) 2920, 2855, 1732, 1447, 1344, 1325, 1092, 928, 721 cm^{-1}; HRMS (DART) *m*/*z*: ($[M+H]^+$) Calculated for $C_{30}H_{35}N_2O_4S$ 519.2318; Found 519.2307

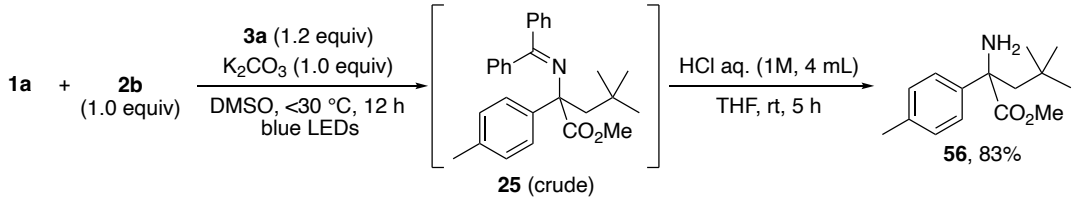
Methyl 2-((diphenylmethylene)amino)-2-methyl-3-(4-methyl-1-tosylpiperidin-4-yl)propanoate (55)



According to general procedure **III**, the reaction using alkene **1v** (21.1 mg, 0.21 mmol), carboxylic acid **2k** (59.6 mg, 0.20 mmol), iodine reagent **3a** (128.1 mg, 0.30 mmol), KOAc (23.1 mg, 0.24 mmol), and acetone (6 mL) was conducted for 2 h. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product as a viscous oil (53.1 mg, 50% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.45–7.28 (m, 8H), 7.17–7.04 (m, 2H), 3.35 (s, 3H), 3.42–3.26 (m, 2H), 2.74–2.56 (m, 2H), 2.42 (s, 3H), 2.10 (d, *J* = 14.8 Hz, 1H), 1.91 (d, *J* = 14.8 Hz, 1H), 1.84–1.65 (m, 2H), 1.59–1.47 (m, 2H), 1.34 (s, 3H), 0.92 (s, 3H); $^{13}C\{^{1}H\}$ NMR: (100 MHz, $CDCl_3$) δ 175.9, 165.7, 143.5, 141.2, 137.7, 133.2, 130.1, 129.7, 128.6, 128.5, 128.1, 127.9, 127.8, 66.8, 55.1, 51.7, 42.3, 37.8, 37.7, 32.1, 26.9, 22.8, 21.7 (one sp^2 and one sp^3 signals were not observed because of overlapping); IR: (ATR) 3671, 2972, 2901, 1728, 1445, 1342, 1161, 1092, 926, 725 cm^{-1}; HRMS (DART) *m*/*z*: ($[M+H]^+$) Calculated for $C_{31}H_{37}N_2O_4S$ 533.2474; Found 533.2475

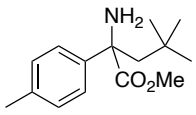
Transformation of the products

1. Hydrolysis of 25



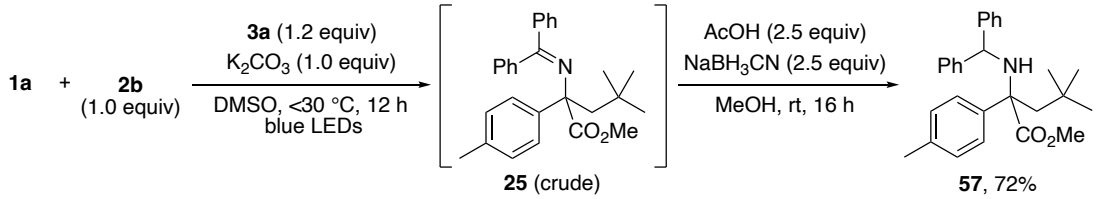
A reaction vial containing a magnetic stir bar was charged with alkene **1a** (73.0 mg, 0.41 mmol), carboxylic acid **2b** (41.3 mg, 0.40 mmol), iodine reagent **3a** (205.5 mg, 0.48 mmol), K_2CO_3 (55.6 mg, 0.41 mmol), and DMSO (4 mL). After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained at <30 °C). After 12 h of irradiation, the reaction was then quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. After THF (10 mL), and HCl (1 M in Et_2O, 10 mL) was added to the residue with a magnetic stir bar, the mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with H_2O, washed with Et_2O (3 x 10 mL), and the collected water layers were concentrated under reduced pressure. Then, the residue was basified with sat. $NaHCO_3$ aq. until pH = 9. The mixture was extracted with EtOAc (3 x 10 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the product **56** as a yellow oil (82.8 mg, 83% yield).

Methyl 2-amino-4,4-dimethyl-2-(*p*-tolyl)pentanoate (56)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 3.68 (s, 3H), 2.33 (d, J = 14.8 Hz, 1H), 2.32 (s, 3H), 2.01 (brs, 2H), 1.97 (d, J = 14.8 Hz, 1H), 0.96 (s, 9H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 177.0, 142.1, 137.0, 129.1, 125.3, 63.8, 52.4, 51.5, 31.7, 31.3, 21.0; IR: (ATR) 2951, 1728, 1510, 1435, 1194, 1177, 820, 756 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{15}H_{24}NO_2$ 250.1807; Found 250.1803

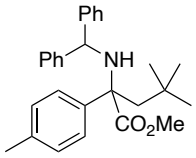
2. Hydride reduction of 25



A reaction vial containing a magnetic stir bar was charged with alkene **1a** (72.8 mg, 0.41 mmol), carboxylic acid **2b** (40.6 mg, 0.40 mmol), iodine reagent **3a** (205.5 mg, 0.48 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), and DMSO (4 mL). After the vial was purged with nitrogen and sealed with a screw cap,

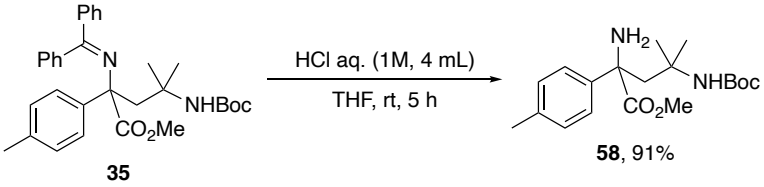
the mixture was stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained at <30 °C). After 12 h of irradiation, the reaction was then quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 15 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. After MeOH (4 mL), $NaCNBH_3$ (63.4 mg, 1.0 mmol), and AcOH (61.2 mg, 1.0 mmol) were added to the residue with a magnetic stir bar under N_2, the mixture was stirred at room temperature for 16 h. The reaction was quenched with H_2O, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with sat. $NaHCO_3$ aq., dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 60:40) gave the product **57** as a colorless oil (119.0 mg, 72% yield).

Methyl 2-(benzhydrylamino)-4,4-dimethyl-2-(*p*-tolyl)pentanoate (57)



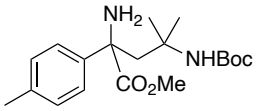
^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.28–7.15 (m, 8H), 7.15–7.06 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.81 (s, 1H), 3.15 (s, 3H), 2.28 (s, 3H), 2.22 (d, *J* = 14.8 Hz, 1H), 2.15 (d, *J* = 14.8 Hz, 1H), 0.72 (s, 9H); ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$) δ 175.5, 145.52, 145.47 138.6, 136.8, 128.5, 128.24, 128.20, 127.7, 127.5, 127.3, 126.4, 67.7, 61.5, 51.3, 50.2, 31.3, 31.2, 21.1 (one sp^2 signal was not observed because of overlapping); IR: (ATR) 2949, 2922, 1728, 1450, 1169, 820, 743 cm^{-1}; HRMS (FAB+) *m*/*z*: ([M+H]$^+$) Calculated for $C_{28}H_{34}NO_2$ 416.2590; Found 416.2588

3. Deprotection of 35



A 10 mL reaction vial containing a magnetic stir bar was charged with **35** (103.2 mg, 0.20 mmol), THF (4 mL), and HCl aq. (1 M, 4 mL). The mixture was stirred at room temperature for 5 h, diluted with H_2O (10 mL), and washed with Et_2O (3 x 10 mL). Then, the combined aqueous layers were basified with sat. $NaHCO_3$ aq. until pH = 9. The mixture was extracted with EtOAc (3 x 10 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the product **58** as colorless oil (64.1 mg, 91% yield).

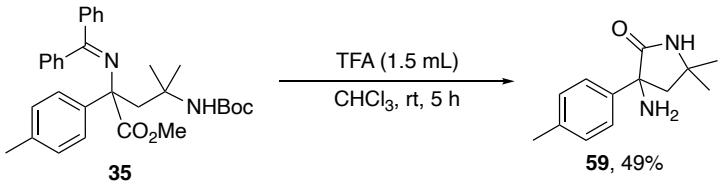
Methyl 2-amino-4-((*tert*-butoxycarbonyl)amino)-4-methyl-2-(*p*-tolyl)pentanoate (58)



^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.48 (brs, 1H), 3.69 (s, 3H), 2.46 (d, *J* = 15.2 Hz, 1H), 2.33 (s, 3H), 2.32

(d, J = 15.2 Hz, 1H), 2.12 (brs, 2H), 1.42 (s, 9H), 1.31 (s, 3H), 1.23 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 176.3, 154.9, 141.2, 137.4, 129.4, 125.1, 78.5, 63.0, 53.0, 52.7, 48.5, 29.0, 28.7, 27.2, 21.0; IR: (ATR) 3292, 2974, 2928, 1713, 1506, 1363, 1234, 1165, 1065, 822 cm^{-1}; HRMS (ESI) m/z: ($[M+H]^+$) Calculated for $C_{19}H_{31}N_2O_4$ 351.2284; Found 351.2283

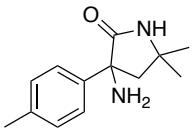
4. Deprotection and cyclization of 35



35 **59**, 49%

A 10 mL reaction vial containing a magnetic stir bar was charged with **35** (101.7 mg, 0.20 mmol), $CHCl_3$ (3 mL), and trifluoroacetic acid (1.5 mL). The mixture was stirred at room temperature for 5 h, diluted with H_2O (10 mL), and washed with Et_2O (3 x 10 mL). Then, the combined aqueous layers were basified with sat. $NaHCO_3$ aq. until pH = 9. The mixture was extracted with EtOAc (3 x 10 mL), and the collected organic layers were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the product **59** as an off-white solid (21.6 mg, 49% yield).

3-Amino-5,5-dimethyl-3-(*p*-tolyl)pyrrolidin-2-one (59)



mp: 178.2–180.5 °C; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.38 (brs, 1H), 2.52 (d, J = 14.0 Hz, 1H), 2.33 (s, 3H), 2.17 (d, J = 14.0 Hz, 1H), 1.90 (brs, 2H), 1.38 (s, 3H), 1.10 (s, 3H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 178.7, 141.8, 137.2, 129.3, 126.1, 63.9, 53.0, 52.8, 31.3, 29.5, 21.2; IR: (ATR) 3343, 3088, 2968, 2920, 1692, 1647, 1508, 1186, 814, 723 cm^{-1}; HRMS (EI) m/z: (M^+) Calculated for $C_{13}H_{18}N_2O$ 218.1419; Found 218.1421

NMR monitoring of the mixture of 2b and 3a in DMSO-d_6

A 3 mL reaction vial containing a magnetic stir bar was charged with pivalic acid **2b** (5.3 mg, 0.05 mmol), iodine reagent **3a** (21.6 mg, 0.05 mmol), K_2CO_3 (6.8 mg, 0.05 mmol), and DMSO-d_6 (1 mL). After the vial was purged with N_2 and sealed with a screw cap, the mixture was stirred at room temperature for 3 h. Mesitylene was added to the mixture as an internal standard before the mixture was transferred into an NMR tube. The resulting ^1H NMR spectrum is shown in Figure 1.

DFT calculations of the ligand exchange between 2b and 3a

Density functional theory (DFT) computations were performed in Gaussian 16, Revision C.01.[45] Molecular geometries were optimized using M06-2X density functional in the 6-311++G(d,p)-SDD(I) basis set with the SMD solvation model (DMSO). Frequency calculations were performed at the same level of theory as that used for geometry optimization to characterize the stationary points as either

minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency). The thermal energy corrections were calculated for the optimized geometry at M06-2X level of theory in the 6-311++G(d,p)-SDD(I) basis set with the SMD solvation model (DMSO).

Calculated energies and thermochemical parameters

structure	*E* [hartree]	*H* [hartree]	*TS* [hartree]	*G* [hartree]
2b	-346.989396	-346.833147	0.041467	-346.874615
3a	-986.927007	-986.618354	0.073565	-986.691919
60	-777.244516	-776.996057	0.066475	-777.062532
Benzophenone imine	-556.667961	-556.451282	0.049391	-556.500673

Cartesian coordinates of computed structures

2b

C	0.93699	-0.18877	-0.00003
O	1.51012	-1.24922	-0.00002
C	-0.56842	0.01261	-0.00001
O	1.61172	0.97509	-0.00003
H	2.55995	0.77055	-0.00002
C	-0.95715	0.80388	-1.25766
H	-0.64882	0.27653	-2.16472
H	-2.04364	0.92044	-1.28250
H	-0.50352	1.79644	-1.25948
C	-1.25846	-1.34873	-0.00011
H	-0.98865	-1.92884	0.88500
H	-2.34123	-1.20180	-0.00012
H	-0.98860	-1.92871	-0.88528
C	-0.95706	0.80366	1.25784
H	-0.50352	1.79626	1.25974
H	-2.04356	0.92009	1.28285
H	-0.64853	0.27621	2.16478

3a

I	-1.00050	-0.76495	-0.30870
O	-3.17737	-1.76301	-0.20644
O	-5.33013	-1.20965	0.04902
N	0.58226	0.62408	-0.37742
C	-2.35188	0.85814	0.04921
C	-1.89334	2.15552	0.19127
H	-0.84012	2.39017	0.12609
C	-2.84001	3.15184	0.42325
H	-2.50713	4.17676	0.53900
C	-4.19400	2.83840	0.50706
H	-4.92046	3.62186	0.68747
C	-4.61361	1.52222	0.36207
H	-5.66182	1.25502	0.42729
C	-3.68887	0.50450	0.12917
C	-4.13605	-0.94127	-0.01941
C	1.76732	0.21751	-0.14381
C	2.85066	1.24839	-0.13148
C	2.53452	2.59414	0.08392
H	1.50384	2.87502	0.26572
C	3.53507	3.55572	0.07768
H	3.28473	4.59507	0.25628
C	4.85963	3.18586	-0.15441
H	5.63974	3.93865	-0.16136
C	5.17914	1.84989	-0.37278
H	6.20679	1.55818	-0.55563
C	4.17998	0.88078	-0.35491
H	4.43687	-0.15816	-0.52711
C	2.15494	-1.20148	0.11426
C	1.94367	-2.16941	-0.86845
H	1.53394	-1.88197	-1.83197
C	2.27920	-3.49709	-0.61654
H	2.12315	-4.24616	-1.38400
C	2.81688	-3.85735	0.61503
H	3.07322	-4.89192	0.81216
C	3.03264	-2.88873	1.59387
H	3.45319	-3.16912	2.55260
C	2.71608	-1.55908	1.34170
H	2.89295	-0.79925	2.09549

60				**Benzophenone imine**			
I	-0.29531	-1.08794	-0.00009	C	-0.00884	1.15127	0.01764
O	-4.47646	-1.22492	0.00053	C	1.27683	0.38806	0.04190
C	-1.43520	0.71151	-0.00010	C	2.37826	0.85611	-0.68017
C	-0.88403	1.97845	-0.00025	C	1.40626	-0.77012	0.81404
H	0.18513	2.13560	-0.00039	C	3.59110	0.17779	-0.62930
C	-1.77350	3.05253	-0.00023	H	2.28091	1.74308	-1.29766
H	-1.37609	4.06069	-0.00035	C	2.62535	-1.43658	0.87828
C	-3.15115	2.84467	-0.00006	H	0.55724	-1.14125	1.37757
H	-3.82419	3.69350	-0.00004	C	3.71791	-0.96708	0.15342
C	-3.66441	1.55423	0.00009	H	4.43543	0.54085	-1.20394
H	-4.73237	1.37016	0.00022	H	2.72067	-2.32495	1.49196
C	-2.79656	0.46471	0.00006	H	4.66433	-1.49400	0.19567
O	1.38830	0.21244	0.00005	C	-1.28912	0.38437	-0.03397
C	2.54776	-0.41744	-0.00023	C	-1.37494	-0.83393	-0.71361
O	2.61962	-1.63149	-0.00054	C	-2.43307	0.90963	0.57458
C	3.74154	0.53355	0.00012	C	-2.58980	-1.50800	-0.79507
C	-3.29558	-0.95259	0.00017	H	-0.49641	-1.25036	-1.19375
O	-2.33894	-1.84389	-0.00013	C	-3.64183	0.22780	0.50563
C	5.03698	-0.27305	-0.00118	H	-2.36319	1.84996	1.10878
H	5.10662	-0.90802	-0.88696	C	-3.72346	-0.98123	-0.18285
H	5.88692	0.41428	-0.00097	H	-2.64923	-2.44552	-1.33581
H	5.10744	-0.90956	0.88342	H	-4.52060	0.63788	0.99016
C	3.65894	1.41231	-1.25521	H	-4.66718	-1.51184	-0.23914
H	3.66847	0.80307	-2.16346	N	-0.06357	2.42615	0.04215
H	2.75108	2.01856	-1.25171	H	0.87525	2.82459	0.10797
H	4.52342	2.08089	-1.28309				
C	3.65988	1.40974	1.25731				
H	2.75205	2.01605	1.25571				
H	3.67003	0.79866	2.16433				
H	4.52441	2.07822	1.28594				

UV-vis absorption spectra of 3a and the reaction mixture in DMSO

All samples were prepared using dry DMSO which were degassed by bubbling with N_2 gas for 30 min before use. **Sample A**: A 10 mL volumetric flask was charged with **3a** (213.8 mg, 0.50 mmol) and DMSO (10 mL). The solution was transferred to 1 cm^2 quartz cuvette. **Sample B**: A 10 mL volumetric flask was charged with **1a** (90.3 mg, 0.51 mmol), **2a** (71.3 mg, 0.50 mmol), **3a** (213.2 mg, 0.50 mmol), K_2CO_3 (70.2 mg, 0.51 mmol), and DMSO (10 mL). The solution was transferred to 1 cm^2 quartz cuvette. The resulting UV-vis absorption spectra are shown in Figure 2.

Fluorescence emission analysis and sub-nanosecond transient absorption (TA) spectroscopy measurement of 3a in DMSO

No signal corresponding to the singlet excited state was observed by sub-nanosecond transient absorption (TA) spectroscopy measurements of **3a** in DMSO, while *ortho*-iodobenzoyloxy radical (**62**) with λ_{max} ~410 nm was observed within the time resolution of ~200 ps even though no rise signal at 410 nm was observed (Figure S2).

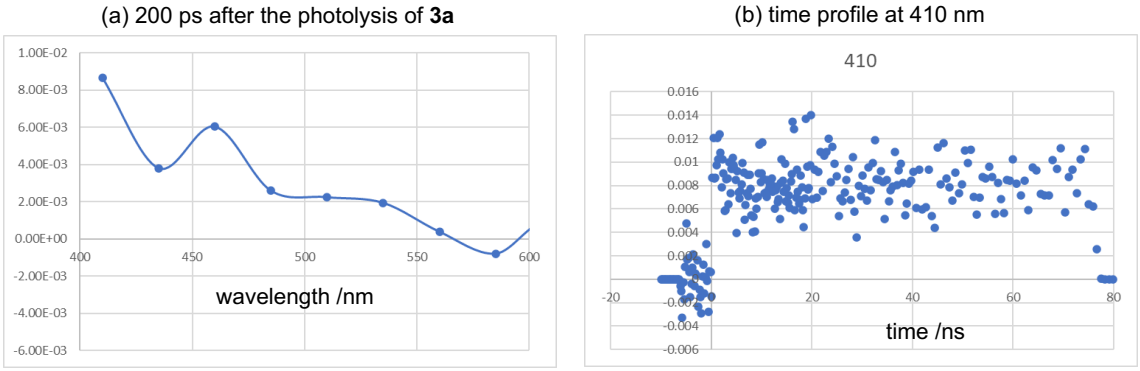


Figure S4. Sub-nanosecond transient absorption spectroscopy in the photolysis of **3a**. (a) Transient absorption spectrum right after the photolysis. (b) The time profile at 410 nm

Sub-microsecond transient absorption (TA) spectroscopy measurement of 3a in DMSO using laser flash photolysis (LFP) method

A 25 mL of stock solution of **3a** (1.7 x 10^{-4} M) in DMSO was prepared for the transient absorption (TA) spectroscopy measurements using laser flash photolysis (LFP) method with Nd-YAG laser (266 or 355 nm, 6 mJ, 12 ns pulse width). The sub-microsecond TA spectra were measured using 1.5 mL of the solution under an air or argon atmosphere at 298 K (Figure 4). The quenching experiments of **62** the carboxylate prepared from **2v** with K_2CO_3 were performed in the presence of different concentration of the carboxylate (5 mM, 25 mM, 50 mM, and 100 mM) (Scheme 10).

TD-DFT calculations: absorption spectra of 3a, 61a, 62, and 2-iodobenzoate (62 anion)

Density functional theory (DFT) computations were performed in Gaussian 16, Revision C.01.[45] Molecular geometries were optimized using UB3LYP density functional in the 6-31G(d)-LANL2DZ(I) basis set with the SMD solvation model (DMSO). Frequency calculations were performed at the same level of theory as that used for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency). The thermal energy corrections were calculated for the optimized geometry at UB3LYP level of theory in the 6-31G(d)-LANL2DZ(I) basis set with the SMD solvation model (DMSO).

DFT calculations for the reaction of radical 62 with O_2

Density functional theory (DFT) computations were performed in Gaussian 16, Revision C.01.[45] Molecular geometries were optimized using UB3LYP density functional in the 6-31G(d)-LANL2DZ(I) basis set. Frequency calculations were performed at the same level of theory as that used for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency). The thermal energy corrections were calculated for the optimized geometry at UB3LYP level of theory in the 6-31G(d)-LANL2DZ(I) basis set. Molecular structure visualizations were obtained using CYLview.[46]

Calculated energies and thermochemical parameters

structure	*E* [hartree]	*H* [hartree]	*TS* [hartree]	*G* [hartree]
62	-430.916699	-430.815605	0.045810	-430.861415
O_2	-150.320040	-150.312951	0.023286	-150.336237
62_O_2	-581.234092	-581.124480	0.063954	-581.188434

Cartesian coordinates of computed structures

62

C	-0.42020	-0.61928	0.00000
C	-3.16060	-1.09429	-0.00001
C	-1.29966	0.46502	-0.00002
C	-0.88426	-1.93190	0.00003
C	-2.26211	-2.16377	0.00003
C	-2.67849	0.21054	-0.00003
H	-0.18953	-2.76446	0.00006
H	-2.62798	-3.18658	0.00006
H	-3.34845	1.06505	-0.00006
H	-4.23038	-1.27897	-0.00001
C	-0.86380	1.89248	-0.00006
O	0.39093	2.20236	0.00008
O	-1.65908	2.84198	0.00002
I	1.69729	-0.27816	-0.00001

O_2

O	0.00000	0.00000	0.60719
O	0.00000	0.00000	-0.60719

62_O_2

C	1.17413	-0.58071	-0.00035
C	3.95681	-0.63177	-0.00406
C	1.87943	0.62460	-0.00052
C	1.83479	-1.80676	-0.00200
C	3.23174	-1.82585	-0.00386
C	3.28103	0.58404	-0.00240
H	1.27544	-2.73596	-0.00184
H	3.74935	-2.78105	-0.00516
H	3.81276	1.53094	-0.00250
H	5.04238	-0.65092	-0.00551
C	1.23040	1.96779	0.00119
O	-0.05682	2.08277	0.00297
O	1.87010	3.02856	0.00101
I	-0.96867	-0.56784	0.00250
O	-4.50901	-0.29907	0.00478
O	-5.06311	0.78079	-0.01448

Determination of computed reduction potentials

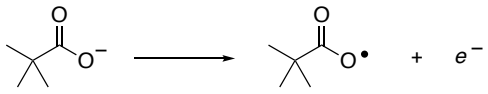
Density functional theory (DFT) computations were performed in Gaussian 16, Revision C.01.[45] Molecular geometries were optimized using M06-2X density functional in the

6-31+G(d,p)-LANL2DZ(I) basis set with the CPCM solvation model (DMSO). Frequency calculations were performed at the same level of theory as that used for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency). The thermal energy corrections were calculated for the optimized geometry at M06-2X level of theory in the 6-31+G(d,p)-LANL2DZ(I) basis set with the CPCM solvation model (DMSO).[30c]

The redox potentials were determined according to the following equation[47]

$$E^{o}_{1/2} = -\frac{G_{(red)} - G_{(ox)}}{nF} - E^{o,SHE}_{1/2} + E^{o,SCE}_{1/2}$$

Where n is the number of electrons transferred (n = 1 in this case), F is Faraday's constant (23.061 kcal mol^{-1} V^{-1}), $E^{o,SHE}_{1/2}$ is the absolute value for the standard hydrogen electrode (SHE, value = 4.281 V), and $E^{o,SCE}_{1/2}$ is the potential of the saturated calomel electrode (SCE) relative to SHE in DMSO (value = −0.279 V).[48] $G_{(red)}$ and $G_{(ox)}$ are the Gibbs free energies in DMSO as gathered from DFT calculations.

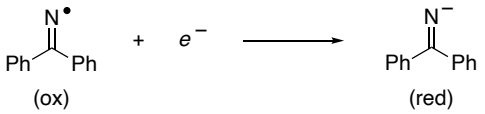


(red) **Piv_anion** (ox) **Piv_radical**

$G_{(red)}$ = −346.327593 Hartree, $G_{(ox)}$ = −346.109512 Hartree

$G_{(red)} - G_{(ox)}$ = {(−346.327593) − (−346.109512)} × 627.51 = −136.85 kcal mol^{-1}

$E^{o}_{1/2}$ = 1.37 V vs. SCE



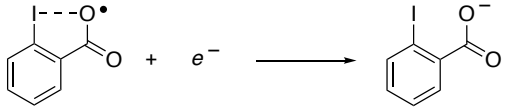
(ox) **61a** (red) **61a anion**

$G_{(red)}$ = −555.86733 Hartree

$G_{(ox)}$ = −555.74103 Hartree

$G_{(red)} - G_{(ox)}$ = {(−555.86733) − (−555.74103)} × 627.51 = −79.25 kcal mol^{-1}

$E^{o}_{1/2}$ = −1.12 V vs. SCE



(ox) **62** (red) **62 anion**

$G_{(red)}$ = −430.884557 Hartree, $G_{(ox)}$ = −430.672886 Hartree

$G_{(red)} - G_{(ox)}$ = {(−430.884557) − (−430.672886)} × 627.51 = −132.83 kcal mol^{-1}

$E^{o}_{1/2}$ = 1.20 V vs. SCE

Calculated energies and thermochemical parameters

structure	*E* [hartree]	*H* [hartree]	*TS* [hartree]	*G* [hartree]
Piv_anion	-346.430955	-346.288871	0.038722	-346.327593
Piv_radical	-346.211418	-346.069620	0.039892	-346.109512
61a	-555.894277	-555.690403	0.050627	-555.741030
61a anion	-556.021413	-555.819685	0.046728	-555.867331
62	-430.730447	-430.628101	0.044784	-430.672886
62 anion	-430.942846	-430.841586	0.042971	-430.884557

Cartesian coordinates of computed structures

Piv_anion

C	0.51682	0.00740	-0.00001
C	0.99091	-0.74368	1.25183
H	2.08623	-0.79514	1.27205
H	0.66033	-0.23377	2.16431
H	0.59329	-1.76170	1.26414
C	1.10880	1.41638	-0.00080
H	2.20421	1.36197	-0.00070
H	0.79208	1.97719	-0.88493
H	0.79195	1.97823	0.88262
C	0.99106	-0.74515	-1.25090
H	0.59351	-1.76321	-1.26202
H	0.66050	-0.23636	-2.16402
H	2.08639	-0.79654	-1.27100
C	-1.04016	0.03173	-0.00005
O	-1.61436	-1.09175	-0.00004
O	-1.61978	1.15040	-0.00006

Piv_radical

C	0.53874	-0.00588	-0.00007
C	0.99321	-0.75287	1.26351
H	2.08636	-0.79731	1.27005
H	0.66446	-0.23629	2.16997
H	0.60171	-1.77283	1.27507
C	1.07472	1.43007	-0.00377
H	2.16796	1.39751	-0.00322
H	0.75451	1.97811	-0.89474
H	0.75381	1.98299	0.88394
C	0.99485	-0.76014	-1.25869
H	0.60318	-1.78008	-1.26497
H	0.66742	-0.24867	-2.16851
H	2.08800	-0.80481	-1.26347
C	-0.98450	-0.03351	-0.00073
O	-1.69208	-1.02385	-0.00030
O	-1.56912	1.15078	-0.00041

61a

N	0.00000	2.41247	0.00006
C	0.00001	1.15013	0.00004
C	-1.29917	0.40537	0.03645
C	-3.74912	-0.92618	0.16615
C	-1.41455	-0.77845	0.77321
C	-2.41325	0.91946	-0.63628
C	-3.63399	0.25204	-0.57287
C	-2.63985	-1.43845	0.83991
H	-0.55130	-1.17716	1.29774
H	-2.31314	1.83203	-1.21557
H	-4.49336	0.64882	-1.10353
H	-2.72703	-2.35357	1.41651
H	-4.70053	-1.44620	0.21413
C	1.29918	0.40536	-0.03642
C	3.74911	-0.92623	-0.16621
C	2.41333	0.91950	0.63616
C	1.41449	-0.77854	-0.77307
C	2.63977	-1.43856	-0.83981
C	3.63406	0.25207	0.57270
H	2.31328	1.83213	1.21537
H	0.55118	-1.17729	-1.29748

H	2.72689	-2.35374	-1.41633
H	4.49348	0.64890	1.10324
H	4.70051	-1.44625	-0.21422

61a anion

N	0.00004	2.53186	0.00022
C	0.00004	1.27224	0.00010
C	-1.27979	0.43332	0.02845
C	-3.71502	-0.98310	0.18704
C	-1.38908	-0.73041	0.80174
C	-2.41388	0.86767	-0.66872
C	-3.61649	0.16639	-0.60146
C	-2.59661	-1.42568	0.89376
H	-0.51986	-1.09254	1.34625
H	-2.33498	1.77548	-1.26129
H	-4.47947	0.51448	-1.16249
H	-2.66298	-2.31466	1.51488
H	-4.65265	-1.52735	0.24831
C	1.27984	0.43327	-0.02841
C	3.71496	-0.98333	-0.18716
C	2.41419	0.86792	0.66813
C	1.38881	-0.73084	-0.80118
C	2.59628	-1.42621	-0.89327
C	3.61675	0.16657	0.60079
H	2.33551	1.77603	1.26027
H	0.51939	-1.09320	-1.34522
H	2.66240	-2.31550	-1.51398
H	4.47995	0.51490	1.16133
H	4.65254	-1.52765	-0.24849

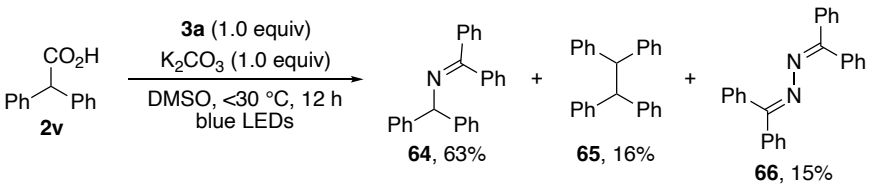
62

C	-0.48462	-0.61230	-0.00009
C	-3.23692	-0.81243	-0.00001
C	-1.24330	0.55104	-0.00001
C	-1.05683	-1.87676	-0.00016
C	-2.44976	-1.96533	-0.00013
C	-2.63549	0.44174	0.00006
H	-0.44747	-2.77365	-0.00021
H	-2.91638	-2.94471	-0.00017
H	-3.22413	1.35344	0.00014
H	-4.31816	-0.89466	0.00003
C	-0.59326	1.90288	0.00002
O	0.71101	1.92760	-0.00033
O	-1.25431	2.93576	0.00028
I	1.61233	-0.36642	0.00005

62 anion

C	-0.32257	-0.57654	-0.00000
C	-2.96261	-1.47035	-0.00006
C	-1.34951	0.37498	-0.00004
C	-0.60399	-1.94687	0.00001
C	-1.92103	-2.39624	-0.00003
C	-2.66680	-0.11294	-0.00006
H	0.20791	-2.66631	0.00004
H	-2.12274	-3.46273	-0.00003
H	-3.45943	0.62678	-0.00009
H	-3.99578	-1.80272	-0.00009
C	-1.18347	1.91170	-0.00010
O	-0.01911	2.36986	-0.00020
O	-2.25229	2.57219	0.00013
I	1.76606	-0.13083	0.00005

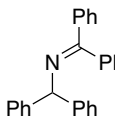
Product analysis of the reaction of 2v with 3a



A 3 mL reaction vial containing a magnetic stir bar was charged with carboxylic acid **2v** (63.9 mg, 0.20 mmol), iodine reagent **3a** (129.0 mg, 0.30 mmol), K_2CO_3 (42.4 mg, 0.31 mmol), and DMSO (3 mL). After the vial was purged with N_2 and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480

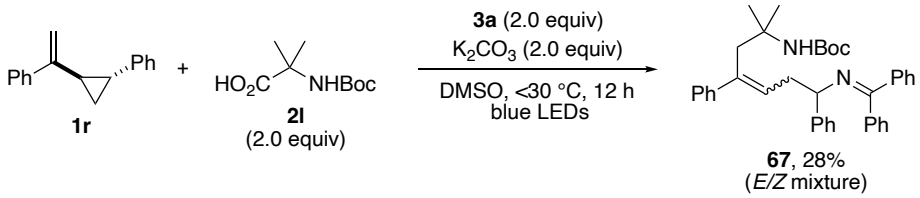
mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained at <30 °C). After 12 h of irradiation, the reaction was then quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product, which was analyzed by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

_N_-Benzhydryl-1,1-diphenylmethanimine (64)



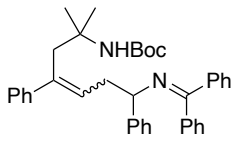
^1H NMR: (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 8.2, 1.6 Hz, 2H), 7.49–7.23 (m, 14H), 7.23–7.16 (m, 2H), 7.15–6.98 (m, 2H), 5.55 (s, 1H); $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 167.1, 145.0, 140.0, 136.9, 130.2, 128.9, 128.61, 128.55, 128.5, 128.1, 127.9, 127.7, 126.8, 70.0; The analytical data for this compound were in excellent agreement with the reported data.[49]

Cyclopropane ring-opening experiment



A reaction vial containing a magnetic stir bar was charged with alkene **1r** (67.0 mg, 0.30 mmol), carboxylic acid **2l** (122.4 mg, 0.60 mmol), iodine reagent **3a** (257.0 mg, 0.60 mmol), K_2CO_3 (82.6 mg, 0.60 mmol), and DMSO (3 mL). After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained at <30 °C). After 12 h of irradiation, the reaction was then quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 15 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on NH silica gel (hexane/EtOAc = 90:10) gave the product **67** as a viscous oil (46.2 mg, 28% yield). The product was obtained as a mixture of *E*/*Z* isomers.

Methyl 2-(benzhydrylamino)-4,4-dimethyl-2-(*p*-tolyl)pentanoate (67)

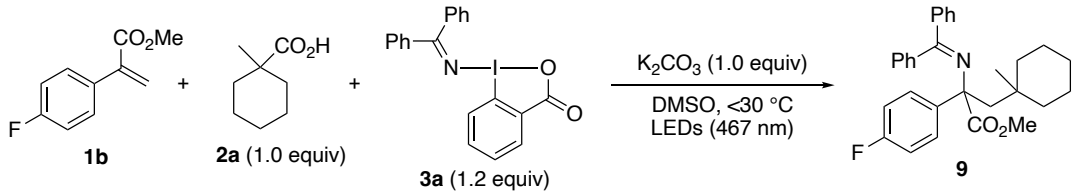


^1H NMR signals assigned from a mixture of *E*/*Z* isomers: (400 MHz, $CDCl_3$) δ 7.73–7.56 (m, 2H), 7.56–7.26 (m, 9H), 7.24–7.06 (m, 6H), 7.06–6.89 (m, 3H), 5.48 (dd, J = 7.6, 7.2 Hz, 0.7H), 5.43 (dd, J = 8.0, 7.2 Hz, 0.3H), 4.47 (dd, J = 7.7, 5.8 Hz, 0.7H), 4.36 (dd, J = 6.8, 6.8 Hz, 0.3H), 4.17 (brs, 0.7H), 4.12 (brs, 0.3H), 2.90–2.50 (m, 4H), 1.41–1.17 (m, 9H), 1.17–0.92 (m, 6H); $^{13}C\{^1H\}$ NMR signals assigned from a mixture of *E*/*Z* isomers (observable signals): (100 MHz, $CDCl_3$) δ 166.9, 166.5, 154.2, 145.4, 144.6, 144.4, 141.6, 140.03, 140.0, 139.4, 139.3, 137.13, 137.09, 130.4, 130.0, 128.71, 128.67, 128.6, 128.43, 128.41,

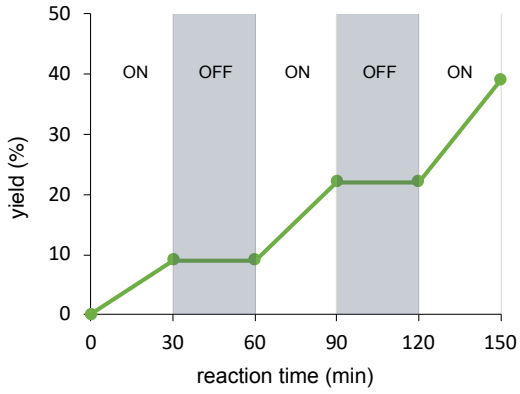
128.35, 128.30, 128.2, 128.09, 128.06, 127.92, 127.89, 127.4, 127.3, 126.9, 126.8, 126.7, 126.5, 126.4, 78.4, 67.0, 66.8, 53.5, 52.9, 49.3, 39.4, 39.0, 28.5, 27.9; IR: (ATR) 2972, 2930, 1715, 1491, 1364, 1165, 1074, 777 cm^{-1}; HRMS (ESI) *m/z*: ($[M+H]^+$) Calculated for $C_{38}H_{43}N_2O_2$ 559.3325; Found 559.3326

Light on/off experiments

A 10 mL 0.1 M stock solution of alkene **1b** (236.5 mg, 1.31 mmol) were prepared in DMSO. A 3 mL reaction vial containing a magnetic stir bar was charged with carboxylic acid **2a** (0.20 mmol), iodine reagent **3a** (0.24 mmol), K_2CO_3 (0.20 mmol), and the stock solution (2 mL). Five parallel reaction mixtures in five vials were prepared. After the vials were purged with N_2 and sealed with a screw cap, the mixtures were stirred and irradiated with a Kessil lamp 467 nm (40W, 100% intensity, 2 cm away (The measured light intensity is >480 mW.)) with a cooling fun (The reaction temperature within the reaction vial was maintained at <30 °C). After 30 min of irradiation, the lamp was turned off and one vial was quenched. After another 30 min in dark, another vial was quenched. Then, the lamp was turned on for another 30 min. Repeat the same procedure until the last vial was quenched. The crudes were analyzed by ^1H NMR spectroscopy using 1,1,1,2-tetrachloroethane as an internal standard.



entry	time (min)	light	yield (%)
1	30	on	9
2	60	off	9
3	90	on	22
4	120	off	22
5	150	on	39



Quantum yield experiments

Chemical actinometer for quantum yield measurement

One of the most reliable and widely used chemical actinometers to measure photon fluxes is ferrioxalate, which upon irradiation decomposes according to the following equations:

$$Fe(C_2O_4)_3^{3+} \xrightarrow{hv} Fe^{2+} + C_2O_4^{-} + 2C_2O_4^{2-}$$

$$Fe^{2+} + 3\,phen \longrightarrow Fe(phen)_3^{2+}$$

The number of ferrous ions generated during the photochemical reaction is determined by conversion to the colored tris-phenanthroline complex, which absorbs the light at 510 nm (ε = 11100 M^{-1} cm^{-1}). The complexation between ferric ions and phenanthroline is not considerable, and their complex does not have absorption at 510 nm.

Procedure for measurement:

1. 120 mg of $K_3[Fe(C_2O_4)_3]\bullet 3H_2O$ was dissolved in 20 mL of 0.05 M H_2SO_4 (1).
2. 5 mg of 1,10-phenanthroline monohydrate and 1.12 g of $CH_3COONa\bullet 3H_2O$ were dissolved in 5 mL of 0.5 M H_2SO_4 (2).
3. 3 mL of solution (1) was taken and irradiated with Xe lamp 365 nm for 0, 10, 20 and 30 s, respectively. After each irradiation, 0.5 mL of solution (2) was added and the absorption spectra were measured.
4. The changes in absorbance at 510 nm with respect to irradiation time were used to calculate the amount of light as the equation below:

$$I\,(\text{mol/s}) = \frac{\text{moles of } Fe^{2+}}{\Phi_\lambda \times t \times F} = \frac{V_1 \times V_3 \times \Delta A_{510}}{10^3 \times V_2 \times l \times \varepsilon_{510} \times \Phi_\lambda \times t}$$

V_1: irradiated volume (3 mL)

V_2: aliquot of irradiated solution taken for determining ferrous ions (3 mL)

V_3: final volume (3.5 mL)

ΔA_{510}: absorbance difference between solutions before and after irradiation

l: optical pathlength of irradiation cell (1 cm)

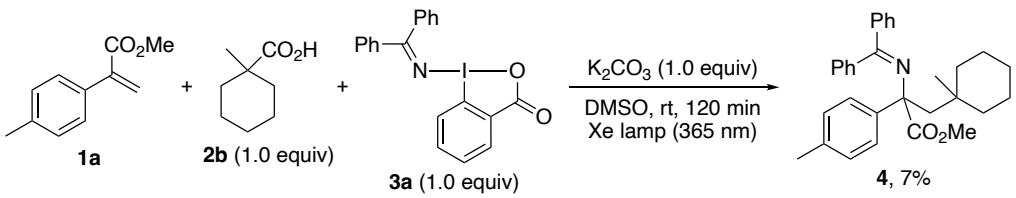
ε_{510}: molar extinction coefficient of $Fe(phen)_3^{2+}$ at 510 nm (11100 $M^{-1}cm^{-1}$)

Φ_λ: quantum yield of ferrous ions generation at the irradiation wavelength (Φ_{365} = 1.21)

t: irradiation time

F: mean function of light absorbed by the ferrioxalate solution

Time (s)	A_{510}	ΔA_{510}	I (mol/s)	I (mol/min)	I_{avg} (mol/min)
0	0	-	-	-	3.8×10^{-7}
10	0.25	0.25	6.5×10^{-9}	3.9×10^{-7}	
20	0.48	0.48	6.3×10^{-9}	3.8×10^{-7}	
30	0.71	0.71	6.2×10^{-9}	3.7×10^{-7}	



A reaction vial containing a magnetic stir bar was charged with alkene **1a** (20.3 mg, 0.12 mmol),

carboxylic acid **2a** (14.6 mg, 0.10 mmol), iodine reagent **3a** (42.1 mg, 0.10 mmol), K_2CO_3 (13.8 mg, 0.10 mmol), and DMSO (3 mL). After the vial was purged with nitrogen and sealed with a screw cap, the mixture was stirred and irradiated with a Xe lamp (2 cm away). After 120 min of irradiation, the reaction was then quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to give the crude product which was analyzed by ^1H NMR spectroscopy using 1,1,1,2-tetrachloroethane as an internal standard (**4**, 7% yield). The quantum yield (Φ) was determined according to the following equation:

$$\Phi = \frac{0.007\ (\text{mmol})}{3.8\times10^{-7}\ (\text{mol/min}) \times 120\ (\text{min})} = 0.154$$

DFT calculations and energy level diagram of the radical addition to 3a

Density functional theory (DFT) computations were performed in Gaussian 16, Revision C.01.[45] Molecular geometries were optimized using M06-2X density functional in the 6-31+G(d,p)-LANL2DZ(I) basis set with the CPCM solvation model (DMSO). Frequency calculations were performed at the same level of theory as that used for geometry optimization to characterize the stationary points as either minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency). Intrinsic Reaction Coordinate (IRC) calculations were performed to confirm that the first-order saddle points found were real transition states connecting the reactants and the products. The thermal energy corrections were calculated for the optimized geometry at M06-2X level of theory in the 6-31+G(d,p)-LANL2DZ(I) basis set with the CPCM solvation model (DMSO). Molecular structure visualizations were obtained using CYLview.[46]

Calculated energies and thermochemical parameters

structure	*E* [hartree]	*H* [hartree]	*TS* [hartree]	*G* [hartree]
C_radical	-695.096153	-694.776539	0.062448	-694.838987
3a	-986.664392	-986.354526	0.074327	-986.428854
TS1	-1681.738508	-1681.108154	0.108722	-1681.216876
INT1	-1681.809131	-1681.175714	0.112212	-1681.287927
product	-1251.075380	-1250.546786	0.086210	-1250.632996
62	-430.730447	-430.628101	0.044784	-430.672886

Cartesian coordinates of computed structures

C_radical				C	1.07195	-0.26190	-0.27002
C	3.50565	-1.61450	0.20557	C	1.95096	0.15562	0.75358
C	2.65331	-2.03844	-0.81501	C	3.14366	-0.51767	0.99034
C	1.45006	-1.38013	-1.04313	H	4.44037	-2.13441	0.38929

H	2.92540	-2.88651	-1.43534
H	0.80685	-1.72673	-1.84472
H	1.67901	0.99640	1.38043
H	3.79289	-0.18689	1.79489
C	-0.21723	0.38437	-0.49180
C	-0.42098	1.82563	-0.30749
O	-1.51674	2.36871	-0.35826
O	0.71094	2.53008	-0.12277
C	0.54445	3.94148	0.03832
H	1.54661	4.33999	0.18216
H	0.08511	4.37292	-0.85317
H	-0.08085	4.15346	0.90771
C	-1.41956	-0.39524	-0.92633
H	-1.13729	-1.13376	-1.68531
H	-2.13515	0.29287	-1.38508
C	-2.16148	-1.16085	0.21296
C	-2.58702	-0.19184	1.32058
H	-3.15867	-0.72630	2.08728
H	-1.71595	0.26327	1.80620
H	-3.20883	0.61480	0.92001
C	-3.40728	-1.79954	-0.41172
H	-3.13205	-2.49524	-1.21238
H	-3.97017	-2.35776	0.34420
H	-4.06953	-1.03616	-0.83449
C	-1.27936	-2.26310	0.80947
H	-0.39961	-1.85085	1.31370
H	-1.85198	-2.83666	1.54681
H	-0.93268	-2.95603	0.03411

3a

I	-0.97503	-0.73992	-0.12865
O	-3.08101	-1.79629	0.00675
O	-5.26811	-1.32464	0.16196
N	0.55954	0.66342	-0.21788
C	-2.37526	0.85986	-0.01301
C	-1.97027	2.18503	-0.03035
H	-0.92334	2.44924	-0.10259
C	-2.96305	3.16445	0.04963
H	-2.67254	4.20972	0.03912
C	-4.30904	2.80956	0.14070
H	-5.06955	3.58054	0.20201
C	-4.67654	1.46731	0.15257
H	-5.71581	1.16358	0.22187
C	-3.70361	0.46900	0.07435
C	-4.08214	-0.99707	0.08438
C	1.76420	0.24858	-0.09377
C	2.85036	1.27195	-0.06106
C	2.54883	2.60853	0.23379
H	1.52336	2.88212	0.45823
C	3.55706	3.56528	0.25184
H	3.31806	4.59664	0.48998
C	4.87601	3.19898	-0.03018
H	5.66208	3.94719	-0.01585
C	5.18185	1.87130	-0.32361
H	6.20440	1.58235	-0.54312
C	4.17410	0.90757	-0.33370
H	4.41772	-0.12529	-0.56228
C	2.15579	-1.19087	0.02415
C	1.96328	-2.05803	-1.05677
H	1.57384	-1.67561	-1.99711
C	2.29390	-3.40724	-0.93149
H	2.15114	-4.07662	-1.77319
C	2.80895	-3.89020	0.27088
H	3.06151	-4.94093	0.36875
C	3.00653	-3.02296	1.34719
H	3.41034	-3.39825	2.28170
C	2.69203	-1.67184	1.22319
H	2.85384	-0.99070	2.05385

TS1

C	2.62818	-0.26648	-1.19714
C	3.87158	-1.85020	-3.06918
C	4.01394	-0.31632	-1.20537
C	1.83899	-0.94571	-2.10744
C	2.47976	-1.75082	-3.05135
C	4.63521	-1.13006	-2.15431
H	0.76200	-0.84692	-2.08120
H	1.88138	-2.29543	-3.77440
H	5.71938	-1.17464	-2.16071
H	4.35954	-2.47991	-3.80515
C	4.81047	0.52545	-0.23545
O	4.08639	1.28680	0.50859
O	6.03923	0.45637	-0.21611
I	1.78393	0.99426	0.28895
C	-1.03481	1.30701	-0.51719
C	-0.91810	2.70636	-0.06121

C	-0.63629	5.39737	0.72304
C	-0.46436	3.03999	1.22776
C	-1.23976	3.75373	-0.94511
C	-1.09376	5.08118	-0.55889
C	-0.32554	4.37125	1.61437
H	-0.25081	2.25862	1.95423
H	-1.58876	3.51628	-1.94555
H	-1.33410	5.87302	-1.26108
H	0.01627	4.60307	2.61800
H	-0.52639	6.43405	1.02374
C	-2.22363	0.95128	-1.32016
C	-4.49528	0.31353	-2.84384
C	-2.13374	0.06465	-2.40209
C	-3.47246	1.52245	-1.02011
C	-4.59803	1.20336	-1.77217
C	-3.25802	-0.25153	-3.15755
H	-1.17339	-0.36992	-2.65453
H	-3.55725	2.20510	-0.17953
H	-5.55718	1.64451	-1.51991
H	-3.16796	-0.94031	-3.99183
H	-5.37322	0.06379	-3.43129
N	-0.14714	0.33399	-0.21996
C	-3.34384	-3.46313	-1.48057
C	-1.97459	-3.36626	-1.73410
C	-1.17454	-2.56672	-0.92982
C	-1.70951	-1.83076	0.14176
C	-3.08476	-1.94437	0.38981
C	-3.88942	-2.75349	-0.41365
H	-3.97571	-4.08620	-2.10578
H	-1.52877	-3.91612	-2.55730
H	-0.11103	-2.52101	-1.13537
H	-3.53877	-1.40887	1.21290
H	-4.95101	-2.82531	-0.19774
C	-0.76179	-1.05426	0.99652
C	-1.24869	-0.12451	2.05967
O	-0.58585	0.19661	3.03499
O	-2.43559	0.42626	1.79259
C	-2.97805	1.30484	2.78746
H	-3.97065	1.56992	2.42824
H	-3.04067	0.78748	3.74629
H	-2.35903	2.19778	2.88908
C	0.47788	-1.81863	1.43099
H	1.08587	-1.15195	2.04420
H	1.07091	-2.08948	0.54810
C	0.27814	-3.11288	2.28616
C	-0.21601	-4.31993	1.47541
H	-0.13841	-5.21937	2.09649
H	-1.25927	-4.21695	1.16677
H	0.39321	-4.47527	0.57795
C	1.66948	-3.45531	2.84162
H	2.05157	-2.64625	3.47330
H	1.62457	-4.36749	3.44569
H	2.38532	-3.62155	2.02838
C	-0.68155	-2.88128	3.45912
H	-1.69279	-2.63887	3.10931
H	-0.75167	-3.79532	4.05871
H	-0.33775	-2.06732	4.10286

INT1

C	-3.71902	0.43159	0.36634
C	-5.85308	2.00196	1.14213
C	-4.96273	-0.16131	0.54037
C	-3.50568	1.78745	0.57481
C	-4.59098	2.57275	0.96490
C	-6.03789	0.63838	0.93300
H	-2.52389	2.23041	0.43869
H	-4.44277	3.63537	1.12903
H	-7.00789	0.17056	1.06770
H	-6.69016	2.62135	1.44524
C	-5.14240	-1.63606	0.31726
O	-4.08122	-2.29745	-0.03885
O	-6.23607	-2.17537	0.46961
I	-2.13547	-0.81069	-0.25339
C	1.10207	1.34496	-0.23504
C	0.05908	2.31154	-0.71108
C	-1.90207	4.10211	-1.61643
C	-0.69721	2.02051	-1.85675
C	-0.16996	3.51660	-0.03413
C	-1.15021	4.40363	-0.48174
C	-1.67142	2.90806	-2.30456
H	-0.50002	1.09740	-2.39248
H	0.41203	3.76050	0.84920
H	-1.32463	5.32872	0.05821
H	-2.24727	2.67218	-3.19385
H	-2.66264	4.79331	-1.96553
C	2.18212	1.93308	0.62435

C	4.18227	3.07979	2.20217
C	2.16464	1.76335	2.01028
C	3.17734	2.71924	0.03462
C	4.18185	3.27721	0.81944
C	3.16623	2.33388	2.79737
H	1.36288	1.19687	2.47578
H	3.17647	2.86893	-1.04187
H	4.96717	3.86352	0.35253
H	3.14860	2.19585	3.87384
H	4.96625	3.51561	2.81333
N	0.97666	0.13118	-0.61311
C	1.93221	-0.95589	-0.32833
C	3.37553	-0.51013	-0.58665
C	4.33869	-0.38740	0.41398
C	3.71238	-0.11269	-1.88746
C	5.61089	0.10838	0.12407
H	4.10743	-0.64695	1.44026
C	4.97655	0.38847	-2.18105
H	2.97263	-0.18801	-2.68069
C	5.93579	0.49842	-1.17225
H	6.34075	0.20211	0.92245
H	5.21282	0.69330	-3.19584
H	6.92326	0.89000	-1.39577
C	1.63082	-1.48993	1.10791
H	2.11519	-0.79183	1.79498
H	0.55332	-1.35379	1.25676
C	1.96292	-2.93772	1.56287
C	3.41051	-3.36922	1.29113
H	3.53228	-4.41746	1.58637
H	3.66910	-3.28269	0.23164
H	4.12514	-2.77886	1.87135
C	1.72446	-2.94679	3.08220
H	0.68526	-2.69109	3.31872
H	1.93131	-3.94063	3.49264
H	2.37753	-2.22662	3.58732
C	1.01551	-3.97627	0.93742
H	1.08923	-4.91488	1.49657
H	-0.02767	-3.64131	0.97005
H	1.27765	-4.20459	-0.09846
C	1.57502	-2.07341	-1.33470
O	2.37964	-2.77207	-1.90866
O	0.25513	-2.23538	-1.47108
C	-0.16192	-3.28030	-2.36119
H	0.23497	-3.09795	-3.36077
H	0.18546	-4.24927	-1.99749
H	-1.25023	-3.24482	-2.36817

product

C	1.40492	-0.37317	-0.16823
C	2.70530	-1.12425	-0.14401
C	5.11814	-2.55651	-0.10742
C	2.77658	-2.38494	0.46652
C	3.85957	-0.58855	-0.72797
C	5.05747	-1.30437	-0.71482
C	3.97252	-3.09391	0.48623
H	1.88211	-2.79319	0.92468
H	3.82550	0.38725	-1.20214
H	5.94203	-0.87935	-1.17846
H	4.01527	-4.06572	0.96808
H	6.05126	-3.11089	-0.09176
C	1.50739	1.08747	-0.50315
C	1.75034	3.80660	-1.10404
C	1.21988	1.55021	-1.78876
C	1.96338	1.98461	0.46818
C	2.07052	3.34017	0.17276
C	1.33690	2.90880	-2.08682
H	0.91351	0.84913	-2.56018
H	2.20903	1.62025	1.46224
H	2.39980	4.03433	0.93984
H	1.10708	3.26190	-3.08726
H	1.83342	4.86429	-1.33349
N	0.35203	-1.04089	0.10438
C	-1.01587	-0.49894	0.17813
C	-1.06455	0.81618	0.96304
C	-1.35818	2.05085	0.38486
C	-0.69671	0.78700	2.31472
C	-1.29888	3.22534	1.13609
H	-1.60835	2.12251	-0.66716
C	-0.62938	1.95529	3.06759
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C	-0.93519	3.18390	2.47942
H	-1.52385	4.17474	0.65952
H	-0.33841	1.90659	4.11245
H	-0.88307	4.09837	3.06214
C	-1.56709	-0.44459	-1.28152
H	-1.12966	0.44928	-1.73418

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C	-3.08475	-0.47676	-1.61646
C	-3.93151	0.53558	-0.83242
H	-4.98688	0.39372	-1.09142
H	-3.82602	0.40262	0.24835
H	-3.66744	1.56691	-1.08184
C	-3.17641	-0.13667	-3.11350
H	-2.62195	-0.86418	-3.71720
H	-4.22088	-0.14826	-3.44237
H	-2.76656	0.85912	-3.31597
C	-3.69335	-1.87596	-1.41813
H	-4.66516	-1.92117	-1.92115
H	-3.05291	-2.65735	-1.84120
H	-3.87170	-2.10293	-0.36419
C	-1.83146	-1.56719	0.94342
O	-2.69818	-1.32227	1.75540
O	-1.52211	-2.80688	0.56805
C	-2.26546	-3.85666	1.19817
H	-2.12564	-3.81792	2.27976
H	-3.32841	-3.76424	0.96483
H	-1.86581	-4.78305	0.79165

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C	-0.48462	-0.61230	-0.00009
C	-3.23692	-0.81243	-0.00001
C	-1.24330	0.55104	-0.00001
C	-1.05683	-1.87676	-0.00016
C	-2.44976	-1.96533	-0.00013
C	-2.63549	0.44174	0.00006
H	-0.44747	-2.77365	-0.00021
H	-2.91638	-2.94471	-0.00017
H	-3.22413	1.35344	0.00014
H	-4.31816	-0.89466	0.00003
C	-0.59326	1.90288	0.00002
O	0.71101	1.92760	-0.00033
O	-1.25431	2.93576	0.00028
I	1.61233	-0.36642	0.00005

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Conclusion

The research reported in this thesis focused on the development of oxidative amination reactions utilizing the novel hypervalent iodine reagents containing (diarylmethylene)amino groups.

In Chapter 1, the synthesis of (diarylmethylene)amino benziodoxolones (DABXs) as a new class of hypervalent iodine-based aminating reagents were achieved. They could be used in the oxidative amination of silyl ketene acetals without the addition of a transition metal catalyst, which is required in existing methods. Furthermore, investigation of the reaction mechanism suggested that the reaction proceeds via a radical pathway involving α-carbonyl radicals and iminyl radicals.

In Chapter 2, the oxidative amination of lithium enolates, which can be readily prepared *in situ* from various carbonyl compounds such as esters, amides, and ketones, with DABXs was accomplished. The reaction proceeds efficiently in a one-pot manner to afford the corresponding α-amino carbonyl compounds. Mechanistic studies indicated that the reaction involves both ionic and radical pathways.

In Chapter 3, the photoexcitation of DABXs for three-component alkylamination of alkenes with carboxylic acids as an alkylating reagent was achieved. Various alkenes and carboxylic acids could be applied to this alkylamination. Transient absorption spectroscopy and computational mechanistic studies disclosed the unique photochemical reactivity of DABXs, which undergoes homolysis of their I–N bonds to give an iminyl radical and an *ortho*-iodobenzoyloxy radical. Moreover, it was found that the *ortho*-iodobenzoyloxy radical participates in the single-electron oxidation of carboxylates.

A wide variety of nitrogen-containing organic molecules (amines) can be synthesized by using the developed methods. As amines are useful building blocks, the methods find wide application in the synthesis of natural products and biologically active molecules. The knowledge gained from the above studies provides novel strategies for the oxidative amination using hypervalent iodine-based aminating reagents.

List of Publications

The content of this thesis has been published in the following papers.

1) Synthesis of Hypervalent Iodine(III) Reagents Containing a Transferable (Diarylmethylene)amino Group and Their Use in the Oxidative Amination of Silyl Ketene Acetals
Kensuke Kiyokawa, Daichi Okumatsu, Satoshi Minakata
Angew. Chem., Int. Ed. **2019**, *58*, 8907–8911.

2) α-Amination of Carbonyl Compounds by Using Hypervalent Iodine-Based Aminating Reagents Containing a Transferable (Diarylmethylene)amino Group
Daichi Okumatsu, Kazuki Kawanaka, Shunpei Kainuma, Kensuke Kiyokawa, Satoshi Minakata
Chem. Eur. J. **2023**, *29,* e202203722.

3) Photoexcitation of (diarylmethylene)amino benziodoxolones for alkylamination of styrene derivatives with carboxylic acids
Daichi Okumatsu, Kensuke Kiyokawa, Linh Tran Bao Nguyen, Manabu Abe, Satoshi Minakata
Chem. Sci. **2024**, *15*, 1068–1076.

Supplementary List of Publications

1) Hypervalent Iodine(III)-Mediated Decarboxylative Acetoxylation at Tertiary and Benzylic Carbon Centers
Kensuke Kiyokawa, Daichi Okumatsu, Satoshi Minakata
Beilstein J. Org. Chem. **2018**, *14*, 1046–1050.

2) *para*-Selective dearomatization of phenols by I(I)/I(III) catalysis-based fluorination
Timo Stünkel, Kathrin Siebold, Daichi Okumatsu, Kazuki Murata, Louise Ruyet, Constantin G. Daniliuc, Ryan Gilmour
Chem. Sci. **2023**, *14*, 13574–13580.

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