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Doctoral Dissertation

Studies on Nickel-Catalyzed Activation of Inert Bonds
for Rearrangement of Aryl Imidates and
Chemical Recycling/Skeletal Editing of Persistent Polymers

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January 2026

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The University of Osaka

Preface and Acknowledgements

The research presented in this thesis was carried out under the direction of Professor Mamoru Tobisu of the Department of Applied Chemistry, Graduate School of Engineering, the University of Osaka. The author joined the Tobisu Laboratory in April 2020 and advanced to the doctoral program from April 2023 to March 2024. This thesis focuses on nickel-catalyzed inert bond activation as a platform for developing rearrangement reactions as well as chemical recycling and skeletal-editing strategies for persistent polymers. The completion of this work was made possible through the generous support and encouragement of many individuals. The author would like to express sincere gratitude to all of them.

First, the author expresses his deepest appreciation to Professor Mamoru Tobisu for his invaluable guidance and unwavering support throughout the doctoral journey. Since the author joined the Tobisu Laboratory as an undergraduate student, Professor Tobisu has provided an environment in which the author was encouraged to freely explore new ideas, along with extensive advice and constructive discussions on how to effectively develop and reflect those ideas in research. Furthermore, when the author sought to expand into research areas beyond the primary scope of the laboratory, Professor Tobisu kindly arranged numerous opportunities for discussions and valuable advice from many researchers. The author was also fortunate to be given opportunities to engage in external collaborative research, which greatly contributed to the development of a broad scientific perspective and the refinement of experimental skills. In addition, Professor Tobisu supported the author's professional development by providing the opportunity to undertake a three-month visiting research stay in the research group of Professor Robert J. Phipps at University of Cambridge. These experiences were not only essential for the smooth progress of the research but also invaluable in shaping the author's growth toward becoming an independent and proactive researcher. The author is deeply grateful for his mentorship.

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January 2026

Satoshi Ogawa

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General Introduction

0.1. Transformation of Inert Bonds by Metal Catalysts

Organic molecules are fundamentally built from atoms linked by covalent bonds. In organic synthesis, target molecular architectures are constructed by repeated formation of new chemical bonds. In this process, cleavage of certain pre-existing chemical bonds in the starting materials is required at an early stage of the overall transformation. Traditionally, synthetic strategies have relied on substrates bearing intrinsically reactive bonds, as such bonds can be selectively cleaved under mild conditions. For example, addition reactions are initiated by π -bond cleavage, whereas substitution reactions are initiated by σ -bond cleavage. Enabling the transformation of chemical bonds that have traditionally been considered difficult to cleave would open new possibilities in organic synthesis. However, the types of chemical bonds that can be readily exploited remain limited (Figure 0.1).

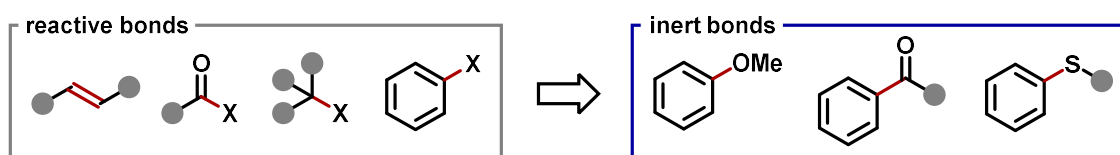


Figure 0.1. Expanding the Repertoire of Cleavable Bonds: Towards New Possibilities in Organic Synthesis

The advent of transition-metal complexes has enabled the activation of chemical bonds that were previously difficult to cleave, such as Ar–X bonds, thereby allowing transformations exemplified by cross-coupling reactions (Figure 0.2).¹ A key elementary step that underpins these bond-activation processes is “oxidative addition.” Oxidative addition² involves cleavage of a bond within an organic substrate, resulting in the formation of two new metal–ligand bonds. In this process, the metal center is formally oxidized, typically by two units in the case of mononuclear complexes. Because the reaction both increases the oxidation state of the metal and incorporates new ligands, it is referred to as “oxidative addition.” This elementary step plays a central role in numerous catalytic and stoichiometric transformations mediated by transition metals. It often serves as the entry point for modifying the functional-group connectivity of organic molecules.

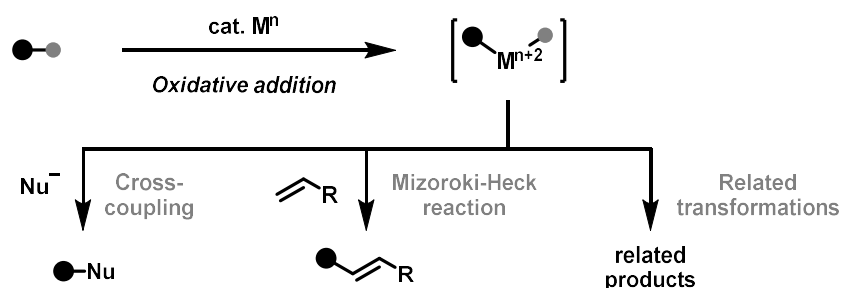
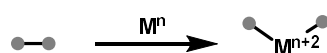


Figure 0.2. Catalytic Transformations Initiated by Oxidative Addition

Given its fundamental role in transforming otherwise inert bonds, it is essential to understand the factors that facilitate oxidative addition. A series of general trends help predict the reactivity of metal complexes toward oxidative addition. These trends arise from the formal increase in charge and the coordination number of the metal center that typically accompanies this elementary step. Because oxidative addition increases the partial positive character of the metal center, complexes bearing more electron-rich metal centers tend to undergo this step more readily than those containing electron-poor metal centers.³ Although the actual change in partial charge is smaller than the change in formal oxidation state, this enhanced reactivity can be rationalized by a ground-state, thermodynamic effect. Because of these electronic considerations, employing strongly electron-donating ligands increases the electron density at the metal, thereby further facilitating this elementary step (Figure 0.3). In addition, nickel—being a relatively electropositive transition metal capable of stabilizing high-valent states—serves as a particularly suitable metal center for promoting oxidative addition.⁴ In light of these electronic considerations, computational studies comparing the activation barriers for oxidative addition of various electrophiles to nickel and palladium complexes have shown that these barriers are markedly lower for nickel (Figure 0.4).⁵ These reduced barriers at nickel enable the use of electrophiles that are considerably less reactive under palladium catalysis, such as phenol derivatives,⁶ aromatic nitriles,⁷ and even aryl fluorides.⁸ Consequently, low-valent nickel complexes bearing electron-donating ligands have been widely utilized as catalysts for activating otherwise inert bonds.

Oxidative addition



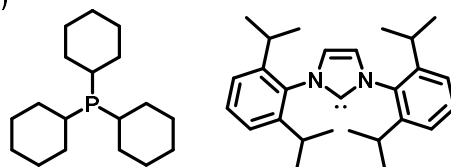
oxidation state: $n \rightarrow n+2$
d-electrons: $x \rightarrow x+2$
coordination number: $m \rightarrow m+2$

■ The electron-rich metal center facilitates oxidative addition.

• Strong σ donor ligand

- increase electron density at metal center

ex)



• Nickel

- smaller atomic radius
- less electronegative
- electron-rich Ni(0)

■ Strong σ donor ligand + Ni(0) $\rightarrow$ electron-rich metal center

Figure 0.3. Promotion of oxidative addition step

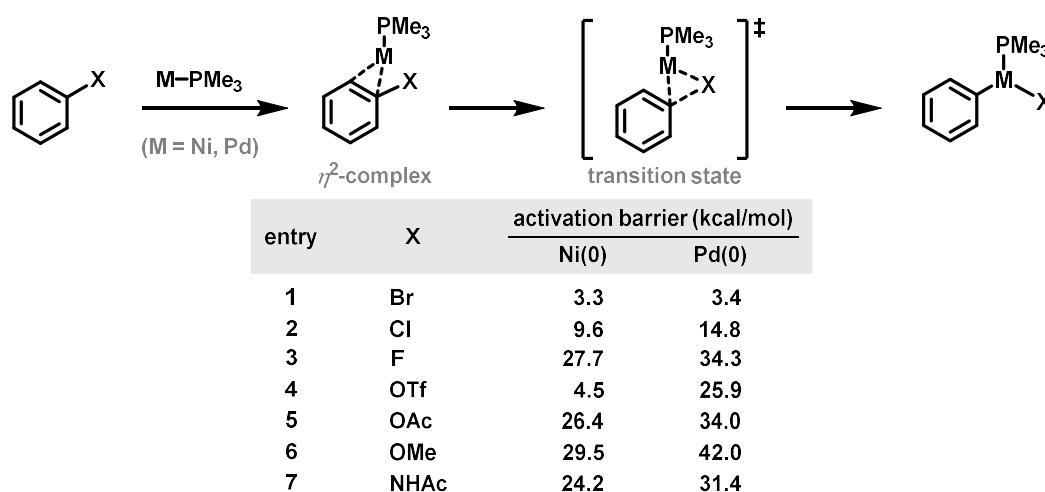


Figure 0.4. Comparison of Oxidative Addition Reactivity of Ni(0) and Pd(0)

In addition to these electronic considerations, oxidative addition can also be promoted through substrate-based strategies. A well-established approach involves the use of directing groups, which are polar functional groups capable of coordinating to the metal center.⁹ Such coordination not only enforces a preorganized favorable geometry that positions the reacting bond close to the metal, but also delivers a substantial enthalpic driving force for oxidative addition. This arises because the energetic cost associated with cleavage of the inert C–X bond is offset by the formation of a thermodynamically stabilized metallacyclic intermediate,¹⁰ typically a five-membered chelate featuring strong metal–heteroatom interactions. Collectively, these effects enable directing-group assistance to lower activation barriers and facilitate oxidative addition to otherwise inert bonds (Figure 0.5).

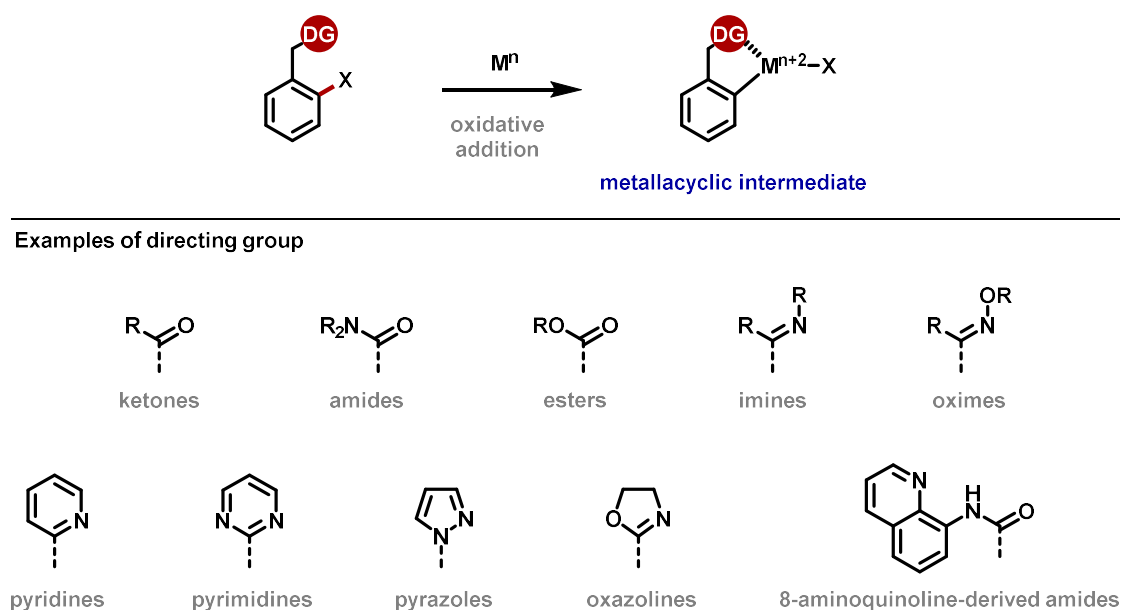


Figure 0.5. Promotion of Oxidative Addition by a Directing Group

0.2. Activation of Inert Bonds in Low Molecular Weight Compounds

In the synthetic chemistry of low molecular weight compounds, among the various inert bonds that could be targeted, the activation of carbon–oxygen bonds—particularly those linking aryl groups to oxygen—is especially attractive from both synthetic and practical standpoints. Aryl motifs are ubiquitous in pharmaceuticals and functional materials, and their selective modification is therefore a cornerstone of modern organic synthesis. To this end, aryl halides have been extensively used as electrophilic aryl sources. However, aryl halides are far less accessible from natural sources and are not employed as coupling partners in biosynthetic pathways. In contrast, phenol-derived electrophiles offer a key advantage in terms of feedstock availability. Phenols are naturally abundant aromatic compounds and can also be readily prepared from easily accessible aromatic precursors. Notably, phenolic units constitute approximately 30% of lignin, a major component of wood biomass, making phenols renewable and highly attractive aromatic feedstocks (Figure 0.6).¹¹

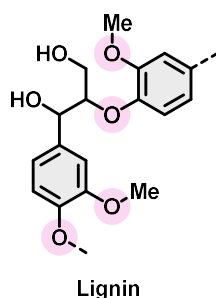


Figure 6. Structure of Lignin

Despite this promise, the direct transformation of phenols requires cleavage of the inherently strong C–O bond, which has long been regarded as challenging. Traditionally, substitution of the hydroxyl group has necessitated its prior conversion into a better leaving group, such as a triflate. While effective, this strategy relies on expensive fluorinated sulfonylating reagents and inevitably generates fluorine-containing waste. From both economic and environmental perspectives, the development of fluorine-free leaving groups would therefore be highly desirable. However, simple alkoxy groups, such as methoxy substituents, generally exhibit poor leaving ability, resulting in low reactivity and limited synthetic utility under conventional catalytic conditions. In recent years, several groups have reported that nickel catalysis enables the activation of otherwise unreactive C–O bonds in phenyl esters and anisole derivatives, allowing their direct use in substitution reactions (Figure 0.7a).⁶ However, all of these transformations proceed through cross-coupling-type pathways, in which the oxygen-based leaving group is expelled and not incorporated into the product framework. In this context, the author sought to explore a complementary reaction mode, namely a rearrangement-type transformation of phenol derivatives in which the departing oxygen functionality is retained within the product (Figure 0.7b).

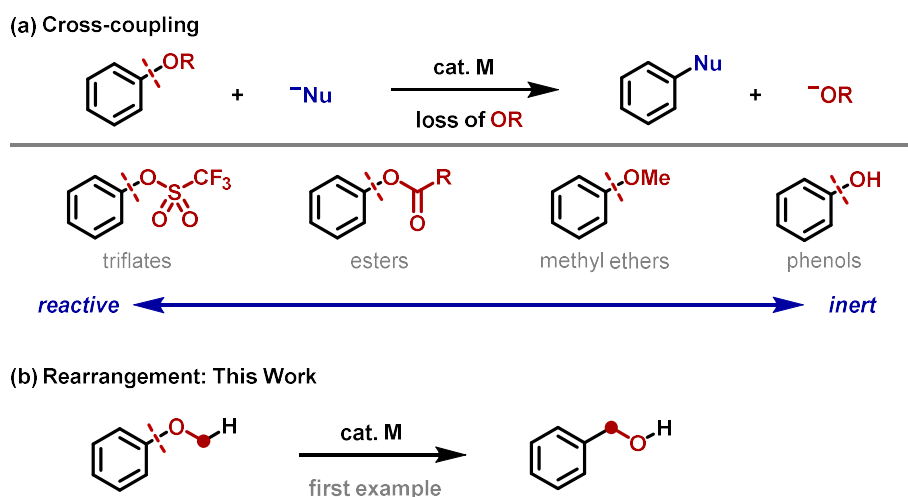


Figure 0.7. Transition Metal Catalyzed Inert C–O Bonds Transformation

0.3. Challenges in the Chemical Transformation of Polymeric Materials

In contrast to synthetic chemistry of low molecular weight compounds, the chemical transformation of polymeric materials remains far more challenging, especially for those composed solely of strong covalent bonds. Polymeric materials are indispensable organic materials in modern society owing to their favorable combination of light weight, mechanical strength, and processability, which underpins their widespread industrial and everyday use. However, because most polymers are ultimately discarded after use, contemporary society faces serious challenges related to environmental pollution and resource depletion. In this context, increasing attention has been directed toward the development

of chemical transformation strategies for post-consumer polymers. Representative approaches include chemical recycling,¹² in which polymers are depolymerized into their constituent monomers, as well as skeletal editing strategies¹³ that transform polymer backbones into structurally distinct polymeric materials. Nevertheless, most reported transformations are limited to relatively reactive functional groups¹⁴ or modifications of side chains.¹⁵ As a result, chemical recycling and backbone-level skeletal editing of persistent polymers composed exclusively of strong covalent bonds remain highly challenging.

0.3.1. Chemical Recycling

In the context of post-consumer polymer management, polymer recycling strategies can be broadly classified into four categories:¹⁶ thermal recycling (incineration), mechanical recycling,¹⁷ non-selective chemical recycling (pyrolysis, gasification etc.) and selective chemical recycling¹². Globally, post-consumer plastic recycling rates remain stubbornly low, with only about 9% of plastic waste recycled in 2019 when incineration is not counted as recycling.^{12b} The most prevalent approach is thermal recycling, in which heat generated by incineration is recovered for energy use. However, once polymers are combusted, the carbon resources are irreversibly converted into carbon dioxide, resulting in a loss of material value. Furthermore, most comprehensive analyses clearly favour recycling (material/chemical recycling) over incineration in terms of total energy use, greenhouse gas production and other environmental factors.¹⁸ The second most common approach is mechanical recycling, whereby plastics are mechanically reprocessed into new plastic products. Because repeated melt-processing and remolding typically lead to a reduction in molecular weight and a concomitant loss of thermal and mechanical robustness, the number of feasible recycling cycles is inherently limited. Non-selective chemical recycling strategies, such as pyrolysis and gasification, utilize heat to convert plastic waste into chemical feedstocks. In contrast to selective depolymerization, these methods rarely produce monomers in high yield, thereby necessitating subsequent chemical upgrading or resulting in downcycling to lower-value products. Although non-selective chemical recycling approaches can recover some value from consumed polymers, they remain fundamentally limited as routes to closed-loop, monomer-based recycling. From the perspective of sustainable resource utilization, selective chemical recycling is therefore regarded as the most ideal recycling strategy. In such processes, polymers are efficiently depolymerized into their original monomers, enabling high-quality circular use of carbon resources. The intrinsic difficulty of chemical recycling arises from two major factors. First, polymer backbones are typically composed of highly stable covalent bonds, such as carbon–carbon and carbon–oxygen linkages, which are inherently resistant to cleavage. Second, to obtain a single, well-defined degradation product, backbone scission must proceed in a highly site-selective manner.¹⁹ Consequently, the development of controlled depolymerization strategies that overcome issues of both the intrinsic stability of polymer backbones and the requirement for positional selectivity

is indispensable for advancing chemical recycling technologies (Figure 0.8).

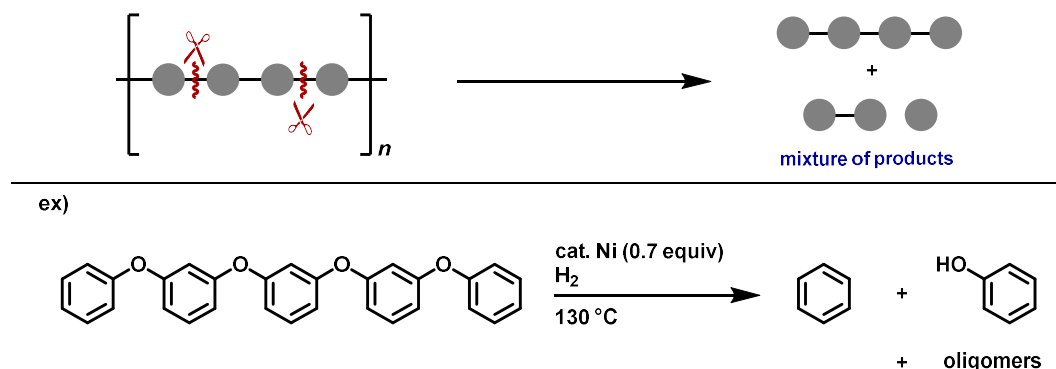


Figure 0.8. Intrinsic Challenges in the Chemical Recycling of Persistent Polymers

These challenges are particularly pronounced for many persistent polymers, such as poly(ether ether ketone) (PEEK),²⁰ poly(phenylene sulfide) (PPS), poly(tetrafluoroethylene) (PTFE), polysulfone (PSU), and poly(ethersulfone) (PESU), which are extensively used in demanding industrial applications owing to their exceptional thermal stability and chemical resistance (Figure 0.9). Structurally, these polymers consist almost entirely of strong covalent bonds in their main chains, including C–C, C–O, C–S, and C–F linkages, rendering their controlled chemical transformation highly challenging.

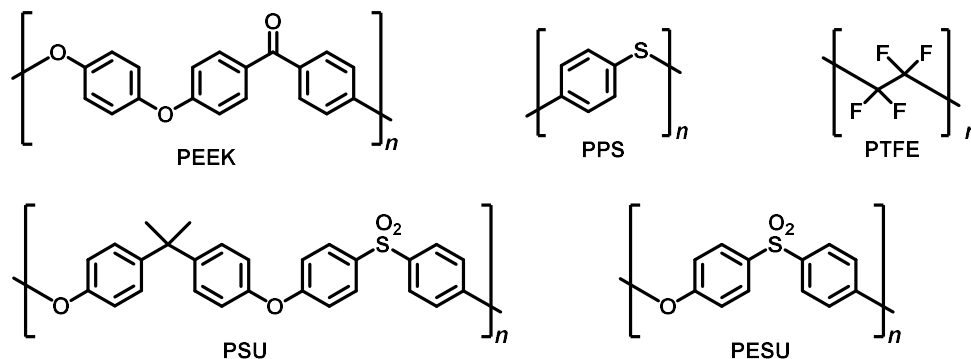


Figure 0.9. Example of Persistent Polymers

In this context, the author presents a new design strategy for persistent polymers based on insights from nickel-catalyzed activation of inert bonds using directing groups, and develop polymers that retain high thermal and chemical stability while enabling chemical recycling.

0.3.2. Skeletal Editing of Polymer Backbones

In recent years, skeletal editing²¹ has emerged as a powerful strategy in low molecular weight compounds, enabling framework modification at a post-synthetic stage through the insertion, deletion, or exchange of atoms (Figure 0.10). By allowing direct modification of the molecular backbone, skeletal editing provides rapid access to structural analogues that would otherwise require laborious de novo synthesis. This capability is particularly valuable for late-stage diversification, where efficient exploration of chemical space is essential for optimizing function and properties. As a result, skeletal editing has become an increasingly important tool for expanding chemical diversity beyond the limits of conventional functional-group interconversions.

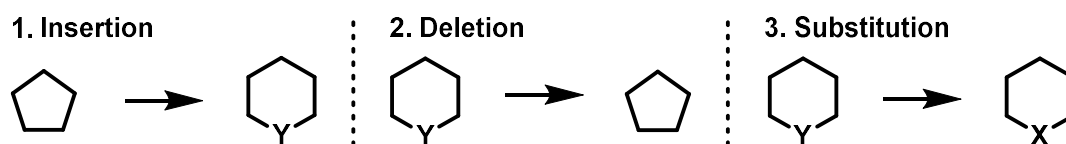


Figure 0.10. Skeletal Editing

Among these transformations, unimolecular fragment coupling (UFC) reactions²² have attracted particular attention (Figure 0.11). In this reaction mode, extrusion of a small, thermodynamically stable molecule from the backbone is followed by recombination of the resulting fragments, leading to the formation of a new covalent bond. Representative examples include decarboxylation²³ (the removal of CO₂) and decarbonylation²⁴ (the removal of CO). Utilizing unimolecular fragment coupling (UFC) as a skeletal-editing strategy enables the transformation of existing molecular skeletons by deleting various functional groups and forming new chemical bonds, thereby affording entirely different molecular frameworks that are otherwise difficult to access by conventional synthetic routes.

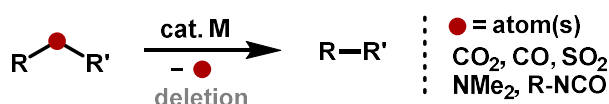


Figure 0.11. Unimolecular Fragment Coupling (UFC) Reaction

In contrast, modification of the polymer backbone¹³ has received comparatively less attention, although several studies have appeared in the literature over the past few decades.²⁵ In recent years, Zhukhovitskiy and co-workers have reported skeletal editing in the context of polymer backbones, envisioning a transformation platform that enables site-selective reactions across a range of polymer backbones, including commodity materials. This method is promising for three reasons: first, it opens access to functional polymers that were previously challenging to synthesize, or to existing polymers derived from new feedstocks; second, it permits the conversion of one polymer type into another, with associated changes in material properties; and third, it allows the breakdown of polymer backbones

that are otherwise difficult to degrade.

In this context, the author explores reactions that involve the deletion of atom units directly from the polymer backbone, representing a new mode of skeletal editing for new polymer frameworks (Figure 0.12).

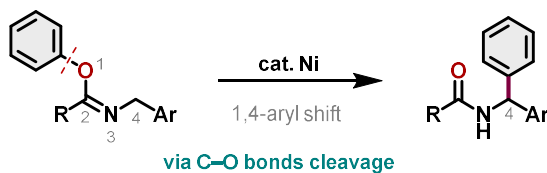


Figure 0.12. This Work: Skeletal Editing of Polymer Backbone

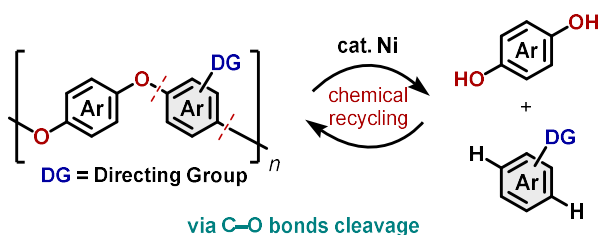
0.4. Outline of This Thesis

In this thesis, transformation reactions of small molecules and polymers were developed on the basis of nickel-catalyzed activation of inert bonds. This doctoral dissertation consists of the following four chapters.

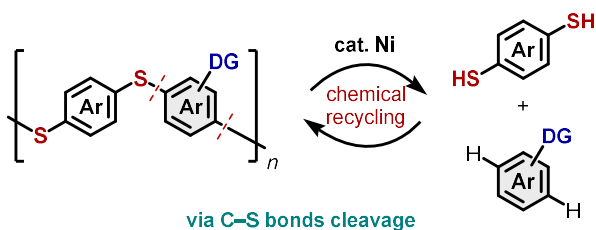
Chapter 1 describes the nickel-catalyzed 1,4-aryl migration of aryl *N*-benzylimidates. This rearrangement is clearly distinguished from the classical thermal Chapman rearrangement, which proceeds via a 1,3-aryl migration of aryl *N*-benzylimidates.



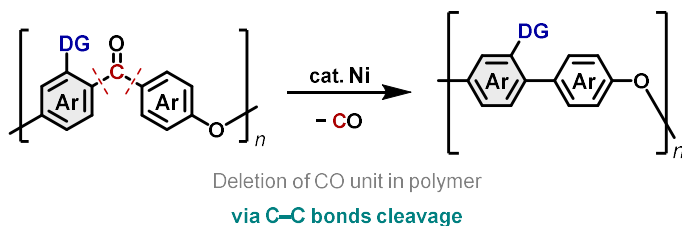
Chapter 2 describes the synthesis of phenylene ether-based polymers bearing a directing group (DG) and their catalytic degradation into monomer or monomer precursors via nickel-catalyzed C(sp²)–O bond cleavage. This work represents the first example of utilizing DG strategy for the cleavage of the main chain of polymeric materials.



Chapter 3 describes the synthesis of directing group-integrated poly(phenylene sulfide)s and its controlled degradation through nickel-catalyzed C(sp²)–S bond cleavage. This study also reveals that the crystallinity of the polymers is tunable by the design of the directing group.



Chapter 4 describes the skeletal transformation of poly(aryl ether ketone) into poly(aryl ether) through a nickel-catalyzed decarbonylation reaction.



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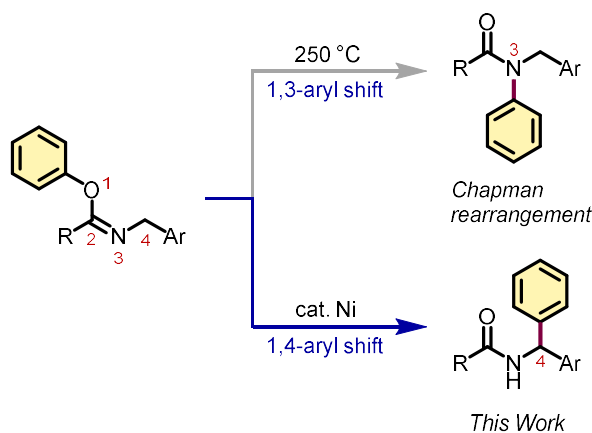
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Chapter 1

Nickel-Catalyzed 1,4-Aryl Rearrangement of Aryl *N*-Benzylimidates via C–O and C–H Bond Cleavage

1.1. Introduction

Unimolecular rearrangement reactions represent a fundamental class of chemical reactions and have attracted interest in terms of both the mechanisms involved as well as synthetic applications.¹ Therefore, the exploration of new modes of unimolecular rearrangement continues to be a subject of considerable interests. Aryl imidates are derivatives of phenols and can readily be prepared from the corresponding secondary amides. These compounds are known to undergo a 1,3-migration of an *O*-aryl group to form tertiary amides via the cleavage of the C–O bond (Chapman rearrangement, Scheme 1.1, top).² The Chapman rearrangement is a thermal reaction, in which the cleavage of an aryl ether moiety proceeds via intramolecular nucleophilic aromatic substitution by the nitrogen atom.^{2c,e} The author report herein that a distinctly different rearrangement pathway of aryl imidates emerges when a nickel catalyst is used. In this reaction, a 1,4-aryl shift via the cleavage of C–O and C–H bonds occurs, leading to the formation of a new C–C bond (Scheme 1.1, bottom).³



Scheme 1.1. Aryl Migration of Aryl Imidates: a 1,3 vs. a 1,4-shift.

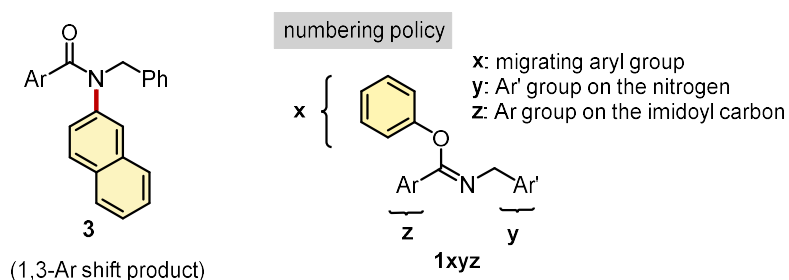
1.2. Results and Discussion

Inspired by previous work on nickel-mediated C–O bond activation reactions,⁴ the author hypothesized that a nickel catalyst would promote the oxidative addition of aryl imidates, thereby allowing the Chapman rearrangement to proceed under milder conditions. The author examined the Ni(0)-catalyzed reaction of aryl *N*-benzyl imidate **1aaa** in toluene at 160 °C in the presence of various ligands (Table 1.1). Although virtually no reaction occurred in the absence of ligands (Entry 1) or when PCy₃ (Entry 2) or IPr (Entry 3) were used, amide **2aaa** was unexpectedly formed in 49% yield when dcype was used as the ligand (Entry 5). Interestingly, decreasing the amount of dcype to 1 equiv

relative to Ni(cod)₂ significantly diminished the yield of **2aaa** (Entry 8). In this reaction, the *O*-aryl group migrated to the benzylic position of **1aaa** (1,4-aryl shift) with the formation of a new C–C bond, rather than the expected C–N bond formation that is normally observed for the Chapman rearrangement (*i.e.*, the formation of **3aaa**). It should be noted that imide **1aaa** undergoes the Chapman rearrangement to form **3aaa** in 35% yield when heated in the absence of a nickel catalyst at 250 °C (Scheme 1.2).

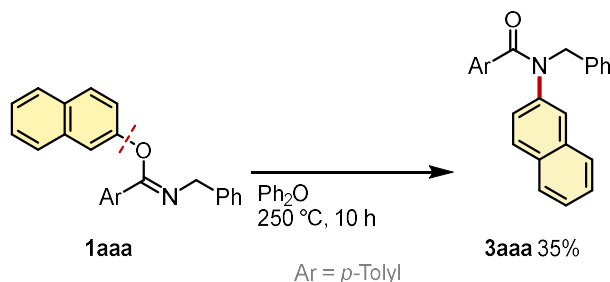
Table 1.1. Nickel-Catalyzed 1,4-Aryl Migration of Aryl Imide **1**^a

Entry	Ar	Ligand	Yield of 2 [%] ^b	Recovered 1 [%] ^b
1	<i>p</i> -Tolyl (1aaa)	None	(0)	(100)
2	<i>p</i> -Tolyl (1aaa)	PCy ₃	(0)	(50)
3	<i>p</i> -Tolyl (1aaa)	IPr ^c	(2)	(1)
4	<i>p</i> -Tolyl (1aaa)	Dcypm	(8)	(66)
5	<i>p</i> -Tolyl (1aaa)	Dcype	49 (46)	(13)
6	<i>p</i> -Tolyl (1aaa)	Dppe	(11)	(59)
7	<i>p</i> -Tolyl (1aaa)	Dcypp	(1)	(67)
8	<i>p</i> -Tolyl (1aaa)	Dcype ^d	(12)	(41)
9	<i>p</i> -Tolyl (1aaa)	Dcype ^e	(11)	(36)
10	<i>p</i> -(CF ₃)C ₆ H ₄ (1aab)	Dcype	40	---
11	<i>p</i> -(MeO)C ₆ H ₄ (1aac)	Dcype	35	---
12	3,5-(Me) ₂ C ₆ H ₃ (1aad)	Dcype	52	(0)
13	3,5-(CF ₃) ₂ C ₆ H ₃ (1aae)	Dcype	31	---
14	3,5-(^t Bu) ₂ C ₆ H ₃ (1aaf)	Dcype	41	---



^aReaction conditions: imide **1** (0.20 mmol), Ni(cod)₂ (0.020 mmol), dcype (0.040 mmol) in dioxane (1.5 mL) at 160 °C for 18 h. ^bIsolated yields are shown. Values in the parentheses refer to the yield for the reaction performed in toluene and was determined by GC analysis. ^cIPr was generated in situ from IPr·HCl and KO^tBu (20 mol% each). ^dDcype (10 mol%) was used in dioxane. ^eRun at 120 °C IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; dcypm = 1,2-

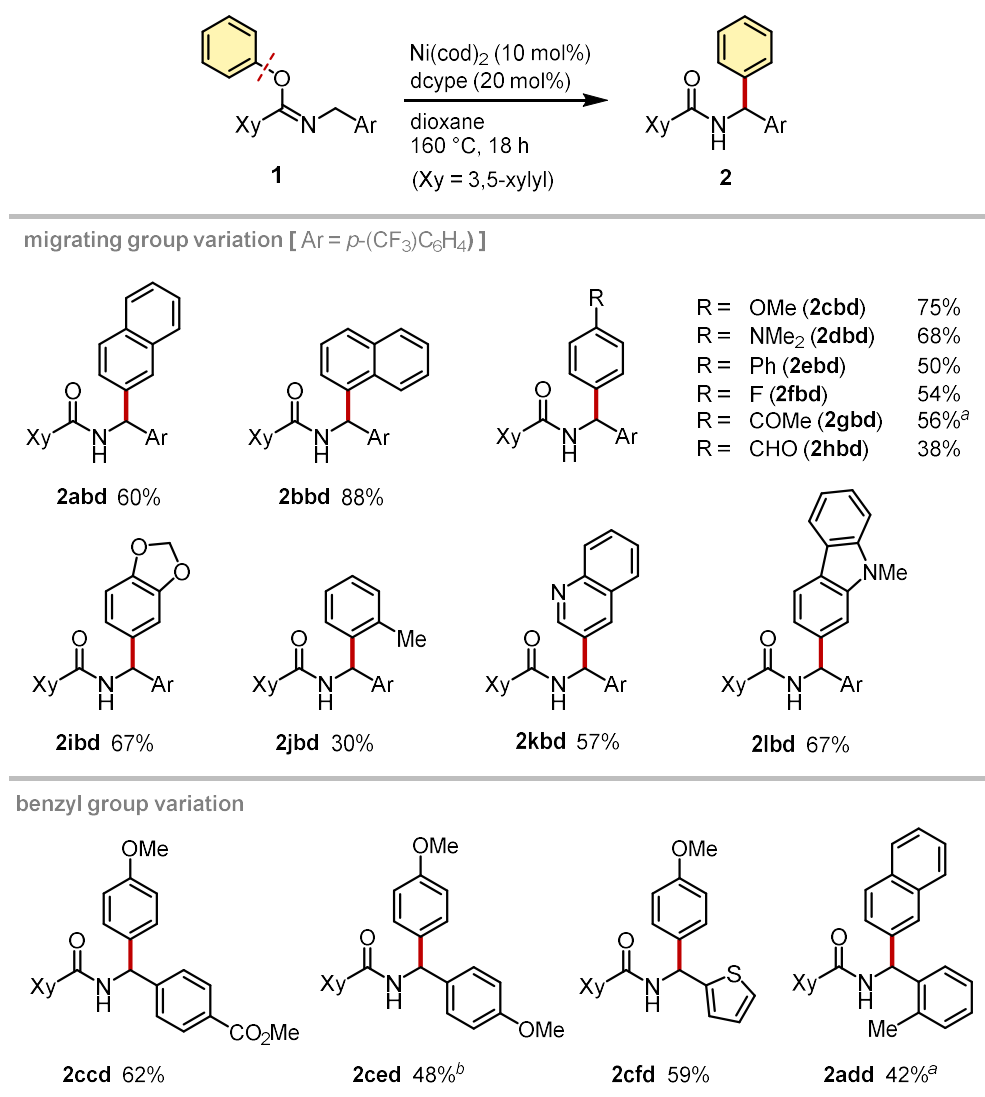
bis(dicyclohexylphosphino)methane; dcype = 1,2-bis(dicyclohexylphosphino)ethane; dppe = 1,2-bis(diphenylphosphino)ethane; dcyp = 1,2-bis(dicyclohexylphosphino)propane.



Scheme 1.2. Chapman Rearrangement

The author next examined the effect of an aryl group that is attached to the imide carbon in the hope of improving the yield of rearrangement product **2**. However, the yield of **2** was not significantly affected by the nature of the aryl group, with a 3,5-xylyl group giving a slightly increased yield (52% yield, Entry 12). In this case, although the starting imide **1aad** was completely consumed, the only detectable byproducts were hydrolysis products (*i.e.*, 2-naphthol and NH-amide, ca. 10% each), and neither biaryl nor a 1,3-Ar shift product were detected.

Having the optimized catalytic conditions in hand, the scope of this rearrangement reaction was explored (Figure 1.1). Regarding the scope of the migrating aryl group, both 1- and 2-naphthyl groups can be used to form the corresponding amides **2abd** and **2bbd**. Imidates derived from non-*p*-extended phenol derivatives were also found to undergo the 1,4-migration reaction, with an array of functional groups, such as OMe (**1cbd**), NMe₂ (**1dbd**), F (**1fbd**), ketone (**1gbd**), aldehyde (**1hbd**) and acetal (**1ibd**), being compatible. This reaction is relatively sensitive to the steric demand, as exemplified by the diminished yield of an imide derived from 2-cresole (*i.e.*, **2jbd**). This reaction is also applicable to heteroaryl imidates, such as **1kbd** and **1lbd**, thus allowing for access to heteroaryl(aryl)methylamine derivatives. Although this 1,4-migration is limited to aryl imidates bearing an *N*-benzyl group, a range of benzyl groups, including electron-rich (**1ced**), electron-deficient (**1ccd**), bulky (**1add**) and heteroaryl (**1cfd**) substituents are all tolerated.



^aRun in *n*Bu₂O at 180 °C. ^bRun for 48 h.

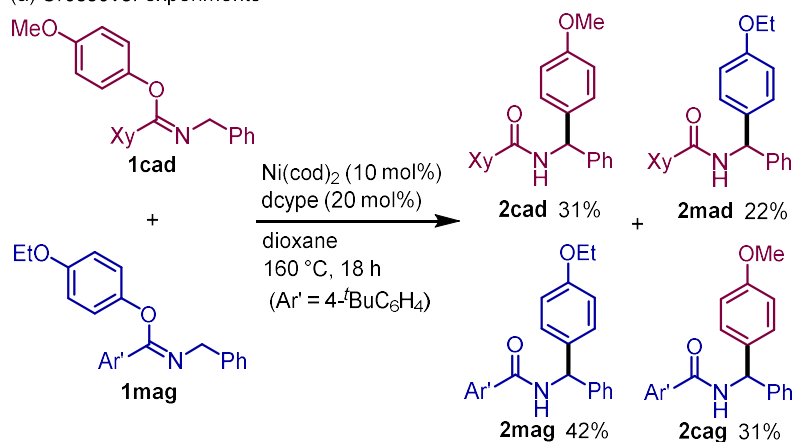
Figure 1.1. Scope of the Nickel-Catalyzed 1,4-Aryl Migration of Aryl Imidates

To obtain insights into the mechanism responsible for this reaction, a crossover experiment was performed using a mixture of imidates **1cad** and **1mag** (Scheme 1.3a). In addition to products formed by intramolecular rearrangement (*i.e.*, **2cad**: 31% and **2mag**: 42%), significant amounts of crossover products were also formed (**2mad**: 22%, **2cag**: 31%), indicating that the fragments involved in this rearrangement reaction are interchangeable under the reaction conditions being used. A kinetic isotope effect of 4.2 was observed by comparing the initial rates of **1cad** and **1cad-*d*₂**, in which the benzylic hydrogens are deuterated (Scheme 1.3b).

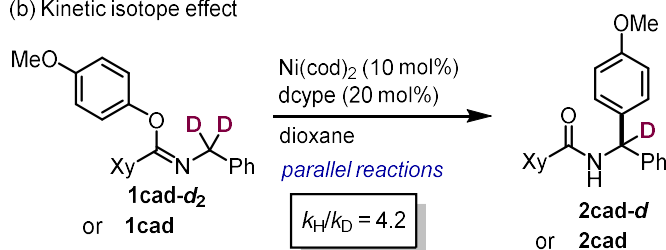
These results indicate that the cleavage of a C–H bond is involved as the rate-determining step. An independently synthesized Chapman rearrangement product **3cad** was not converted into a 1,4-Ar shift product **2cad** under the nickel-catalyzed conditions, which excludes the intermediacy of **3cad** in the

present nickel-catalyzed rearrangement reaction (Scheme 1.3c). A possible mechanism for this nickel-catalyzed 1,4-aryl migration reaction of aryl imidates is shown in Scheme 1.3d. The reaction is likely initiated by the oxidative addition of the C(aryl)–O bond of imidate **1**, which provides Ar–Ni(II)–OC(=NBn)R (**A**). If the imidate ligand on the nickel center in **A** serves as an internal base to abstract a hydrogen atom at the benzylic position and the benzylic carbon is simultaneously metalated, then benzylnickel intermediate **B** is generated. This process can be viewed as a variant of the well-known concerted metalation/deprotonation pathway⁵ in which a base and the C–H bond to be cleaved are in the same fragment. An imidate moiety can subsequently be tautomerized to amide **C**, which leads to the formation of final product **2** via reductive elimination.⁶ The results of the crossover experiment (Scheme 1.3a) suggest that the fragments in intermediate **A** and/or **B** can be exchanged under the nickel-catalyzed conditions used.

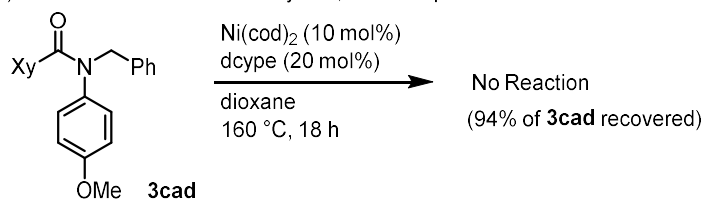
(a) Crossover experiments



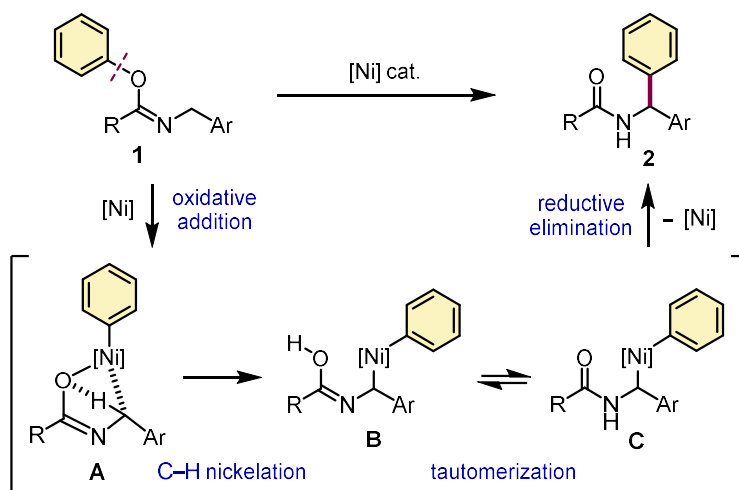
(b) Kinetic isotope effect



(c) Exclusion of the intermediacy of 1,3-Ar shift product



(d) Possible mechanism

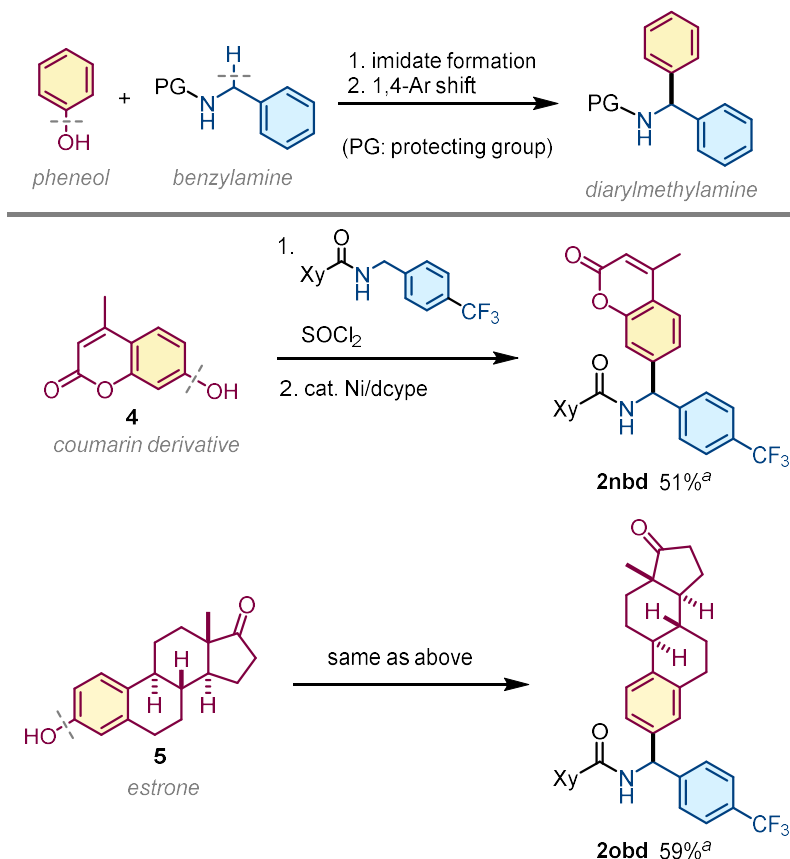


Scheme 1.3. Mechanistic Studies

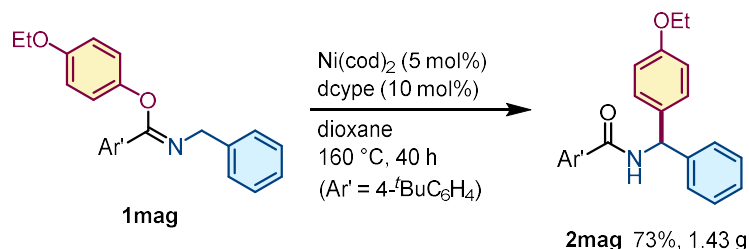
Since the starting imidates used in this rearrangement reaction can be readily prepared from the corresponding phenols and benzylamines, the overall transformation can be regarded as the C-H

arylation of benzylamines using phenols as an aryl source (Scheme 1.4a). Given that a phenol substructure is present in a number of biologically active compounds, this protocol allows such complex phenol derivatives to be introduced into the benzylic position of benzylamines and to be converted to intricate diarylmethylamine derivatives, which represents another class of structural motifs of medicinal importance.⁷ In fact, coumarin derivative **4** and estrone (**5**) were successfully coupled with benzylamines to generate elaborate diarylmethylamines **2nbd** and **2obd**, respectively. It should also be noted that this catalytic protocol is scalable, as demonstrated by a gram scale synthesis of **2mag** (73% yield, 1.43 g, Scheme 1.4b).

(a) Rapid access to complex diarylmethylamines from phenols and benzylamines



(b) Gram scale synthesis



^aYields refer to those for the 1,4migration reaction step.

Scheme 1.4. Synthetic Applications

1.3. Conclusion

In summary, the author report on the development of nickel-catalyzed 1,4-aryl migration reactions of aryl imidates, which proceed through the cleavage of C–O and C–H bonds. This rearrangement pathway is distinctly different from the classical thermal Chapman rearrangement, in which the 1,3-migration of an *O*-aryl group of aryl imidates occurs. This protocol is synthetically useful, because it allows elaborate diarylamine derivatives to be accessed from phenol and benzylamine building blocks. The further exploration of catalytic transformations involving the activation of inert C–O bonds is currently underway.

1.4. Experimental Section

I. General Information

¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a JEOL ECS-400 spectrometer in CDCl₃. ²H NMR spectra were recorded in CHCl₃. The chemical shifts in ¹H NMR spectra were recorded relative to tetramethylsilane (δ 0.00). The chemical shifts in ²H NMR spectra were recorded relative to CDCl₃ (δ 7.26). The chemical shifts in ¹³C NMR spectra were recorded relative to CDCl₃ (δ 77.0). The chemical shifts in ¹⁹F NMR spectra were recorded relative to hexafluorobenzene (δ –163.00). The data is reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{–1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO₂ (Silica Gel 60N (spherical, neutral) (40–50 μ m, KANTO CHEMIXAL CO., INC.) and NH Silica (Silica Gel 60 (spherical) NH₂ (40–50 μ m)). Some of the compounds were purified by LC-908 HPLC (GPC). Microwave synthesis was performed by Biotage[®] Initiator+.

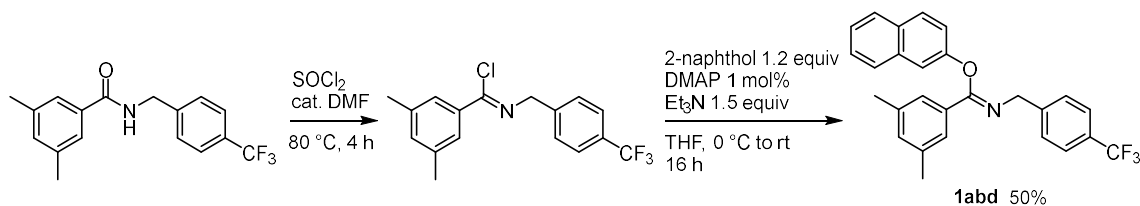
II. Materials

Toluene (deoxygenated) (FUJI FILM Wako Chemicals) and 1,4-dioxane (super dehydrated) (FUJI FILM Wako Chemicals) were used as received. Ni(cod)₂ was purchased from Strem Chemicals and used as received. PCy₃ (Sigma-Aldrich), dcype (Sigma-Aldrich), dppe (TCI), dcypm (FUJI FILM Wako Chemicals), dcypm (Sigma-Aldrich), IPr·HCl (TCI) and were purchased from commercial suppliers and used as received.

III. Synthesis of Starting Materials

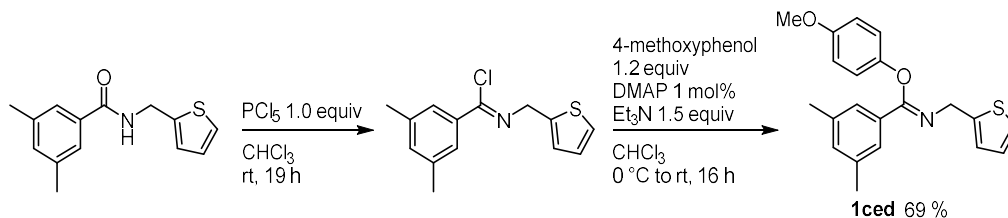
Synthesis of Aryl *N*-Benzylimidates

General procedure A: Synthesis of imidate with SOCl₂.¹



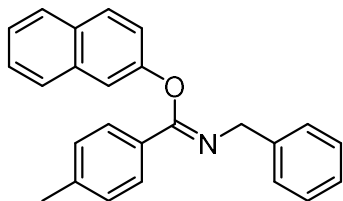
3,5-Dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzamide (1.56 g, 5.1 mmol), DMF (2 drops) and SOCl_2 (5 mL) were added to a 50 mL two-necked flask. After the mixture was stirred at 80 °C for 4 h, the resulting mixture was concentrated to give the corresponding imidoyl chloride, which was used in the next step without further purification. The imidoyl chloride was added dropwise to a solution of 2-naphthol (893 mg, 6.2 mmol), Et_3N (1.1 mL, 7.9 mmol) and DMAP (15 mg, 0.12 mmol) in THF (10 mL) at 0 °C. After the addition was complete, the reaction mixture was stirred at rt for 16 h. After the precipitate ($\text{Et}_3\text{N}\cdot\text{HCl}$) was filtered off, the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (eluent: hexane/ EtOAc = 97/3) to give naphthalen-2-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (**1abd**) as a white solid (1.10 g, 50%). Aryl *N*-benzylimidates **1aaa**, **1aab**, **1aac**, **1aad**, **1aae**, **1aaf**, **1abd**, **1bbd**, **1cbd**, **1dbd**, **1ebd**, **1fbd**, **1gbd**, **1hbd**, **1ibd**, **1jbd**, **1kbd**, **1add**, **1cad**, **1cad-*d*₂**, **1nbd** and **1obd** were prepared in a similar manner.

General Procedure B: Synthesis of imide with PCl_5 .²



PCl_5 (1.27 g, 6.1 mmol) was added at 0 °C to a solution of 3,5-dimethyl-*N*-(thiophen-2-ylmethyl)benzamide (1.48 g, 6.0 mmol) in CHCl_3 (30 mL). After the mixture was stirred at rt for 19 h, the resulting mixture was concentrated to give the corresponding imidoyl chloride (brown oil), which was used in the next step without further purification. The imidoyl chloride was added dropwise at 0 °C to a solution of 4-methoxyphenol (910 mg, 7.3 mmol), Et_3N (1.8 mL, 12.9 mmol) and DMAP (16 mg, 0.13 mmol) in CHCl_3 (12 mL). After the addition was complete, the reaction mixture was stirred at rt for 16 h. After the precipitate ($\text{Et}_3\text{N}\cdot\text{HCl}$) was filtered off, the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (eluent: hexane/ EtOAc = 100/0 to 95/5) to give 4-methoxyphenyl 3,5-dimethyl-*N*-(thiophen-2-ylmethyl)benzimidate (**1ced**) as a pale yellow oil (1.47 g, 69%). Aryl *N*-benzylimidates **1acd**, **1ccd** and **1mag** were prepared in a similar manner.

Naphthalen-2-yl *N*-benzyl-4-methylbenzimidate (**1aaa**).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:17$), which was determined by ^1H NMR.

White solid (5.67 g, 87%). R_f 0.58 (SiO_2 , Hexane/EtOAc = 3/1). Mp 59.1-61.4 °C.

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.30 (s, 3H), 4.76 (s, 2H), 7.10 (s, 1H), 7.12 (s, 1H), 7.14 (d, $J = 2.8$ Hz, 1H), 7.22-7.42 (m, 8H), 7.59 (d, $J = 8.2$ Hz, 1H), 7.74-7.86 (m, 4H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.40, 51.82, 110.84, 117.69, 124.46, 126.62, 126.66, 126.92, 127.68, 127.79, 128.32, 128.67, 129.14, 129.59, 129.79, 130.20, 134.17, 139.87, 141.18, 153.20, 153.73.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.41 (s, 3H), 4.63 (s, 2H), 7.50 (d, $J = 8.2$ Hz, 2H), 7.67 (d, $J = 1.8$ Hz, 1H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.47, 53.61, 118.42, 122.61, 125.05, 126.10, 126.30, 126.76, 127.48, 127.93, 128.19, 128.78, 130.99, 134.08, 140.38, 140.73, 151.24, 161.18. Other peaks are overlapped with those of a major isomer.

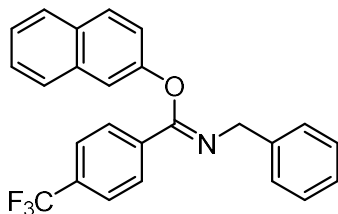
E/Z Mixture

IR (KBr): 3030 m, 2892 m, 1653 s, 1626 s, 1597 s, 1508 s, 1463 m, 1455 m, 1352 s, 1272 s, 1244 s, 1206 m, 1165 s, 1063 s, 1112 s, 993 s, 880 m, 854 s, 813 s, 746 s, 735 s, 601 m.

MS, m/z (relative intensity, %): 351 (M^+ , 33), 232 (41), 208 (42), 127 (11), 120 (14), 119 (97), 115 (13), 92 (38), 91 (100), 65 (26).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{25}\text{H}_{22}\text{NO}$: 352.1696. Found: 352.1706.

Naphthalen-2-yl *N*-benzyl-4-(trifluoromethyl)benzimidate (1aab).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:20$), which was determined by ^1H NMR.

Colorless oil (415 mg, 10%). R_f 0.71 (SiO_2 , Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 4.80 (s, 2H), 7.12 (d, $J = 2.1$ Hz, 1H), 7.24-7.28 (m, 2H), 7.32-7.42 (m, 6H), 7.57 (m, 3H), 7.78-7.84 (m, 2H), 8.05 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 52.15, 110.98, 117.49, 123.76 (q, $J = 272.2$ Hz), 124.83, 125.41 (q, $J = 3.8$ Hz), 126.88, 126.92, 126.94, 127.75, 127.83, 128.44, 129.05, 129.80, 130.54, 132.43 (q, $J = 32.6$ Hz), 134.08, 136.08, 139.31, 152.41, 152.70.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 4.58 (s, 2H), 7.71-7.72 (m, 7H), 7.87-7.90 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 54.01, 125.24 (q, $J = 3.8$ Hz), 126.30, 126.69, 127.50, 128.35, 128.74, 129.33, 129.40, 131.60. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

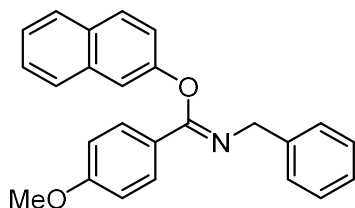
^{19}F NMR (CDCl_3 , 376 MHz) δ : -64.17, -63.84.

IR (KBr): 3058 m, 3032 m, 1663 s, 1627 s, 1598 s, 1510 s, 1464 s, 1408 s, 1324 s, 1243 m, 1163 s, 1123 s, 1067 s, 1017 s, 984 m, 958 m, 942 m, 843 s, 811 m, 744 s, 697 s, 616 m.

MS, m/z (relative intensity, %): 405 (M^+ , 3), 262 (11), 91 (100).

HRMS (DART $^+$, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{25}\text{H}_{19}\text{F}_3\text{NO}$: 406.1413. Found: 406.1420.

Naphthalen-2-yl *N*-benzyl-4-methoxybenzimidate (1aac).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:20$), which was determined by ^1H NMR.

White solid (853 mg, 23%). R_f 0.64 (SiO_2 , Hexane/EtOAc = 1/1). Mp 71.5-73.2 $^\circ\text{C}$.

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 3.74 (s, 3H), 4.74 (s, 2H), 6.79-6.83 (m, 2H), 7.15 (d, $J = 2.3$ Hz, 1H), 7.20-7.25 (m, 2H), 7.29-7.42 (m, 6H), 7.60 (d, $J = 7.8$ Hz, 1H), 7.75-7.79 (m, 2H), 7.87-7.90 (m, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 51.76, 55.22, 100.77, 113.74, 117.64, 124.46, 124.95, 126.60, 126.67, 126.90, 127.67, 127.79, 128.31, 129.58, 130.20, 130.39, 134.19, 139.93, 153.25, 153.49, 161.72.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.83 (s, 3H), 4.66 (s, 2H), 8.18-8.22 (m, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) Peaks are not clearly observed.

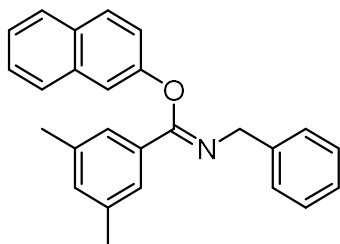
E/Z Mixture

IR (KBr): 2359 w, 1698 m, 1683 m, 1652 s, 1636 m, 1558 s, 1540 s, 1515 m, 1507 s, 1456 s, 1261 m, 1243 s, 1160 m, 1051 m, 1024 m, 837 m, 757 m, 700 m, 607 w, 582 w.

MS, m/z (relative intensity, %): 367 (M^+ , 18), 232 (14), 135 (100), 107 (10), 92 (10), 91 (48), 77 (16).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{22}NO_2$: 368.1645. Found: 368.1647.

Naphthalen-2-yl *N*-benzyl-3,5-dimethylbenzimidate (1aad).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:13$), which was determined by 1H NMR.

Colorless oil (638 mg, 54%). R_f 0.68 (SiO_2 , Hexane/EtOAc = 1/1).

Major isomer

1H NMR ($CDCl_3$, 400 MHz) δ : 2.38 (s, 6H), 4.90 (s, 2H), 7.13 (s, 1H), 7.29-7.55 (m, 9H), 7.73-7.74 (m, 3H), 7.86-7.92 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 21.16, 51.93, 110.68, 117.63, 124.41, 126.37, 126.62, 126.89, 127.63, 127.81, 128.30, 129.56, 130.19, 132.47, 132.71, 134.16, 137.94, 139.71, 153.18, 154.08.

Minor isomer

1H NMR ($CDCl_3$, 400 MHz) δ : 2.50 (s, 6H), 4.75 (s, 2H), 7.23 (s, 1H), 7.58-7.61 (m, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 21.26, 53.60, 118.42, 122.59, 125.01, 125.84, 126.06, 126.27, 126.81, 127.44, 128.12, 128.74, 130.84, 130.97, 131.70, 134.06, 138.15, 140.75, 151.16, 161.44. Other peaks are overlapped with those of a major isomer.

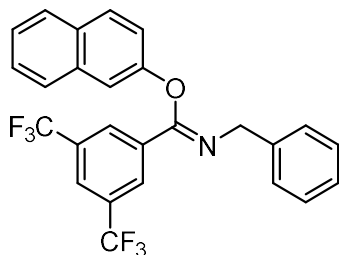
E/Z Mixture

IR (KBr): 3058 w, 3028 w, 2915 w, 1660 s, 1629 s, 1599 s, 1509 m, 1463 m, 1317 m, 1246 m, 1211 s, 1185 s, 1161 s, 1087 s, 1027 m, 962 m, 845 m, 809 m, 746 m, 697 m.

MS, m/z (relative intensity, %): 365 (M^+ , 24), 232 (25), 222 (21), 133 (81), 105 (31), 92 (10), 91 (100), 79 (12), 77 (11), 65 (10).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{26}H_{24}NO$: 366.1852. Found: 366.1862.

Naphthalen-2-yl *N*-benzyl-3,5-bis(trifluoromethyl)benzimidate (1aae).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:37), which was determined by ^1H NMR.

Yellow oil (118 mg, 8%). R_f 0.72 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 4.77 (s, 2H), 7.13 (d, $J = 2.3$ Hz, 1H), 7.28-7.48 (m, 8H), 7.64 (d, $J = 8.2$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.87 (d, $J = 9.2$ Hz, 1H), 7.90 (s, 1H), 8.41 (s, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 52.48, 110.89, 117.27, 122.95 (q, $J = 273.2$ Hz), 124.41 (m, $J = 3.4$ Hz), 125.06, 126.98, 127.09, 127.83, 127.89, 128.53, 128.63 (q, $J = 2.9$ Hz), 130.01, 130.89, 132.01 (q, $J = 33.6$ Hz), 134.05, 135.22, 138.77, 150.93, 152.30.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 4.56 (s, 2H), 8.03 (br, 4H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) Peaks were not observed due to low concentration of the minor isomer.

E/Z Mixture

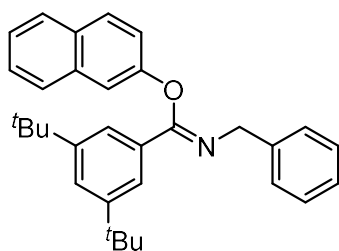
^{19}F NMR (CDCl_3 , 376 MHz) δ : -64.17.

IR (KBr): 3062 m, 3026 w, 1811 w, 1667 s, 1629 s, 1600 s, 1512 s, 1496 m, 1458 s, 1414 w, 1385 s, 1352 m, 1279 s, 1233 m, 1209 m, 1165 s, 1133 s, 1014 m, 960 m, 909 m, 835 m, 810 m, 729 m, 694 s, 682 s.

MS, m/z (relative intensity, %): 473 (M^+ , 1), 330 (50), 227 (100), 115 (27).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{26}\text{H}_{18}\text{F}_6\text{NO}$: 474.1287. Found: 474.1289.

Naphthalen-2-yl *N*-benzyl-3,5-di-*tert*-butylbenzimidate (1aaf).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:7.0), which was determined

by ^1H NMR.

White solid (499 mg, 12%). R_f 0.70 (NH silica, Hexane/EtOAc = 1/1). Mp 91.8-92.8 °C.

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 1.25 (s, 18H), 4.80 (s, 2H), 7.17-7.45 (m, 10H), 7.61 (d, J = 8.2 Hz, 1H), 7.74-7.78 (m, 4H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 31.29, 34.80, 51.89, 111.37, 117.98, 123.05, 124.42, 125.04, 126.56, 126.79, 126.95, 127.66, 127.79, 128.29, 129.63, 130.09, 131.85, 134.20, 139.97, 150.76, 153.32, 154.65.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 1.33 (s, 18H), 4.61 (s, 2H), 7.47-7.50 (m, 2H), 7.54-7.55 (m, 1H), 7.71-7.72 (m, 1H), 7.82-7.90 (m, 4H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 31.34, 34.92, 53.67, 118.55, 121.45, 122.38, 122.74, 123.32, 124.21, 125.62, 126.10, 126.28, 127.50, 127.71, 128.78, 129.36, 131.03, 134.12, 140.89, 151.05, 151.27, 162.41.

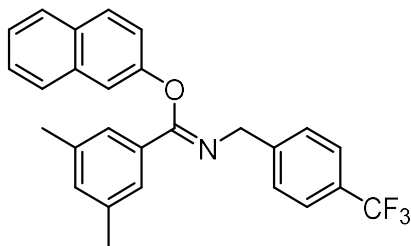
E/Z Mixture

IR (KBr): 2965 s, 2911 s, 2866 m, 1665 s, 1627 s, 1597 s, 1508 s, 1460 s, 1450 m, 1361 s, 1318 m, 1242 s, 1206 s, 1160 s, 1093 s, 1009 m, 963 m, 885 m, 809 m, 750 m, 734 s, 705 m.

MS, m/z (relative intensity, %): 449 (M^+ , 20), 306 (11), 232 (32), 218 (13), 217 (71), 133 (17), 91 (100), 57 (26).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{32}\text{H}_{36}\text{NO}$: 450.2791. Found: 450.2792.

Naphthalen-2-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1abd).



The product was obtained as a mixture of geometrical isomers ($E:Z$ = 1:9.5), which was determined by ^1H NMR.

White solid (1.10 g, 50%). R_f 0.68 (NH silica, Hexane/EtOAc = 1/1). Mp 108.2-109.1 °C.

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.28 (s, 6H), 4.78 (s, 2H), 7.04 (s, 1H), 7.13 (m, 1H), 7.19-7.24 (m, 1H), 7.24-7.27 (m, 1H), 7.35-7.44 (m, 2H), 7.50-7.52 (m, 2H), 7.56-7.58 (m, 4H), 7.62 (d, J = 8.2 Hz, 1H), 7.77-7.82 (m, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.22, 51.43, 110.79, 117.60, 124.62, 124.29 (q, J = 271.3 Hz), 124.62,

125.25 (q, $J = 3.8$ Hz), 126.41, 126.77, 126.93, 127.71, 128.01, 128.91 (q, $J = 32.3$ Hz), 129.68, 130.35, 132.23, 133.02, 134.16, 138.14, 143.87, 153.06.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.39 (s, 6H), 4.63 (s, 2H), 7.19 (s, 2H), 7.46 (d, $J = 1.8$ Hz, 1H), 7.48 (s, 2H), 7.66 (m, 2H), 7.85-7.89 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.33, 53.19, 118.54, 122.52, 125.08 (q, $J = 3.8$ Hz), 125.80, 126.26, 127.03, 127.50, 127.76, 128.88, 130.68, 131.09, 131.97, 134.08, 138.37, 144.93, 151.07, 154.94, 162.14. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

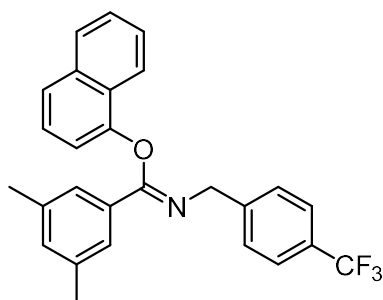
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.62.

IR (KBr): 2898 m, 1663 s, 1628 s, 1598 s, 1511 s, 1464 m, 1418 m, 1324 s, 1247 m, 1159 s, 1118 m, 1087 s, 1066 s, 961 m, 915 m, 840 s, 746 s, 732 s, 691 m.

MS, m/z (relative intensity, %): 433 (M^+ , 4), 290 (22), 159 (100), 133 (41), 115 (17), 109 (13), 105 (12).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{27}\text{H}_{23}\text{F}_3\text{NO}$: 434.1726. Found: 434.1729.

Naphthalen-1-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1bbd).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:10$), which was determined by ^1H NMR.

Yellow oil (149 mg, 8%). R_f 0.66 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.25 (s, 6H), 4.77 (s, 2H), 6.64 (d, $J = 7.8$ Hz, 1H), 7.05 (s, 1H), 7.19-7.24 (m, 1H), 7.49-7.62 (m, 9H), 7.87-7.89 (m, 1H), 8.42 (d, $J = 7.8$ Hz, 1H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.20, 51.30, 109.02, 121.54, 122.47, 124.30 (q, $J = 271.9$ Hz), 124.52, 125.26 (q, $J = 3.8$ Hz), 125.66, 126.10, 126.13, 126.88, 127.86, 128.04, 128.91 (q, $J = 32.3$ Hz), 133.11, 134.90, 138.16, 143.85, 150.77.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.42 (s, 6H), 4.59 (s, 2H), 7.28 (s, 1H), 7.38 (d, $J = 7.8$ Hz, 2H), 7.64 (m, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.38, 52.99, 118.47, 122.07, 124.89 (q, $J = 3.8$ Hz), 125.48, 125.78, 125.92, 126.44, 126.84, 127.64, 132.06, 132.21, 138.45, 155.28. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

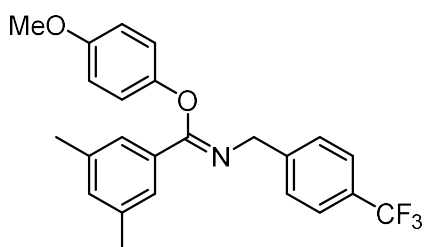
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.56.

IR (KBr): 3053 w, 2918 w, 1738 w, 1661 m, 1618 m, 1577 w, 1507 w, 1461 w, 1392 m, 1324 s, 1233 m, 1162 s, 1123 s, 1094 s, 1066 s, 1018 m, 857 w, 820 m, 791 m, 779 m, 769 m.

MS, m/z (relative intensity, %): 433 (M^+ , 1), 290 (30), 159 (100), 133 (19), 115 (14), 109 (12).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{27}\text{H}_{23}\text{F}_3\text{NO}$: 434.1726. Found: 434.1733.

4-Methoxyphenyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1cbd).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:4.2$), which was determined by ^1H NMR.

Yellow oil (425 mg, 17%). R_f 0.68 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.28 (s, 6H), 3.74 (s, 3H), 4.76 (s, 2H), 6.76-6.85 (m, 4H), 7.03 (s, 1H), 7.45 (s, 2H), 7.51-7.60 (m, 4H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.22, 51.27, 55.57, 114.87, 117.18, 124.31 (q, $J = 271.9$ Hz), 125.23 (q, $J = 3.8$ Hz), 126.48, 128.00, 128.81 (q, $J = 32.6$ Hz), 132.57, 132.65, 137.96, 144.13, 149.23, 155.00, 155.51.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.37 (s, 6H), 3.82 (s, 3H), 4.60 (s, 2H), 6.92-6.95 (m, 2H), 7.12 (s, 3H), 7.14-7.17 (m, 2H), 7.27 (d, $J = 7.8$ Hz, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.31, 53.11, 55.52, 114.25, 122.97, 125.06 (q, $J = 3.8$ Hz), 125.69, 126.96, 130.81, 131.81, 138.30, 145.13, 146.71, 156.50, 162.47. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

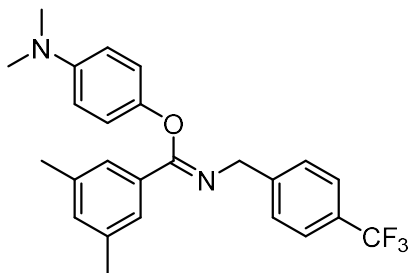
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.56 (s, 1F).

IR (KBr): 2916 w, 1733 w, 1654 m, 1606 w, 1504 s, 1456 w, 1418 w, 1324 s, 1246 w, 1178 s, 1122 m, 1066 m, 1036 w, 1018 w, 821 m, 778 w.

MS, m/z (relative intensity, %): 413 (M^+ , 1), 291 (11), 290 (55), 160 (28), 159 (100), 123 (28), 109 (29), 95 (13).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{23}F_3NO_2$: 414.1675. Found: 414.1665.

4-(Dimethylamino)phenyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1dbd).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:4.5$), which was determined by 1H NMR.

Yellow oil (397 mg, 12%). R_f 0.76 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

1H NMR ($CDCl_3$, 400 MHz) δ : 2.28 (s, 6H), 2.87 (s, 6H), 4.76 (s, 2H), 6.62–6.66 (m, 2H), 6.80–6.83 (m, 2H), 7.02 (s, 1H), 7.46 (s, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.58 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 21.22, 41.20, 51.25, 114.09, 117.05, 124.33 (q, $J = 271.6$ Hz), 125.19 (q, $J = 3.8$ Hz), 126.49, 128.01, 128.72 (q, $J = 32.6$ Hz), 132.50, 132.88, 137.85, 144.33, 146.72, 147.00, 155.91.

Minor isomer

1H NMR ($CDCl_3$, 400 MHz) δ : 2.36 (s, 6H), 2.95 (s, 6H), 4.60 (s, 2H), 6.76–6.79 (m, 2H), 6.91 (s, 1H), 7.06–7.08 (m, 2H), 7.11 (s, 3H), 7.17 (d, $J = 8.2$ Hz, 1H), 7.29 (d, $J = 7.8$ Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 21.31, 41.09, 53.14, 113.26, 122.47, 125.01 (q, $J = 3.8$ Hz), 125.67, 126.98, 131.66, 138.21, 144.11, 148.05. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

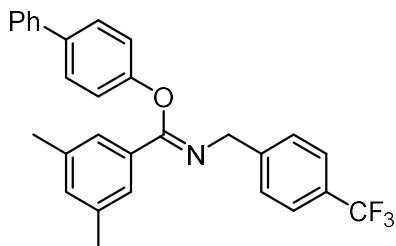
^{19}F NMR ($CDCl_3$, 376 MHz) δ : -63.53.

IR (KBr): 2918 s, 2802 m, 1733 s, 1669 m, 1653 s, 1616 s, 1608 s, 1516 s, 1508 s, 1324 s, 1202 s, 1162 s, 1123 s, 1066 m, 850 m, 820 m.

MS, m/z (relative intensity, %): 426 (M^+ , 9), 291 (11), 290 (55), 160 (11), 159 (100), 136 (42), 109 (13).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{26}F_3N_2O$: 427.1992. Found: 427.1997.

[1,1'-Biphenyl]-4-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1ebd).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:9.1$), which was determined by ^1H NMR.

Yellow oil (188 mg, 10%). R_f 0.67 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.29 (s, 6H), 4.78 (s, 2H), 6.96-7.00 (m, 2H), 7.06 (s, 1H), 7.30-7.33 (m, 1H), 7.38-7.42 (m, 2H), 7.47-7.48 (m, 1H), 7.49-7.50 (m, 2H), 7.51-7.53 (m, 5H), 7.58-7.60 (m, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.22, 51.37, 116.34, 122.48, 124.30 (q, $J = 272.0$ Hz), 125.25 (q, $J = 3.5$ Hz), 126.41, 126.74, 127.06, 128.00, 128.59, 128.76, 128.89 (q, $J = 32.3$ Hz), 132.35, 132.93, 135.73, 138.11, 140.17, 143.91, 154.85.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.38 (s, 6H), 4.64 (s, 2H), 7.14 (s, 1H), 7.16 (s, 2H), 7.27-7.29 (m, 4H), 7.61-7.62 (m, 4H), 7.64 (s, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.31, 53.21, 121.99, 125.10 (q, $J = 3.8$ Hz), 125.74, 127.10, 127.30, 127.89, 127.94, 130.68, 131.93, 137.83, 138.35, 152.78. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

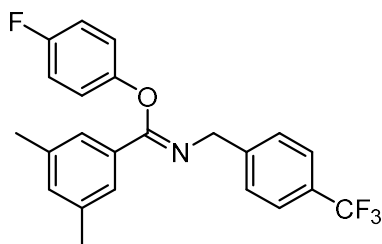
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.53.

IR (KBr): 3057 m, 3032 s, 2918 s, 1661 s, 1605 s, 1513 s, 1485 s, 1450 m, 1417 s, 1325 s, 1216 s, 1169 s, 1123 s, 1066 s, 1018 s, 821 s, 761 s, 697 s.

MS, m/z (relative intensity, %): 459 (M^+ , 7), 290 (30), 159 (100), 133 (74), 109 (11), 105 (21).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{29}\text{H}_{25}\text{F}_3\text{NO}$: 460.1883. Found: 460.1889.

4-Fluorophenyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1fbd).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:4.8$), which was determined by ^1H NMR.

Yellow oil (2.06 g, 85%). R_f 0.74 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.28 (s, 6H), 4.75 (s, 2H), 6.83–6.87 (m, 2H), 6.91–6.97 (m, 2H), 7.05 (s, 1H), 7.44 (s, 2H), 7.51 (d, $J = 7.8$ Hz, 2H), 7.59 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.19, 51.27, 116.44 (d, $J = 23.0$ Hz), 117.35 (d, $J = 8.6$ Hz), 124.28 (q, $J = 271.9$ Hz), 125.27 (q, $J = 3.8$ Hz), 126.45, 127.98, 128.94 (q, $J = 32.3$ Hz), 132.12, 132.88, 138.12, 143.83, 151.33 (d, $J = 1.9$ Hz), 154.96, 158.20 (d, $J = 241.5$ Hz).

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.38 (s, 6H), 4.60 (s, 2H), 7.06–7.11 (m, 2H), 7.13 (s, 3H), 7.17–7.20 (m, 2H), 7.26 (d, $J = 7.8$ Hz, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.29, 53.07, 115.81 (d, $J = 23.0$ Hz), 123.57 (d, $J = 8.6$ Hz), 125.11 (q, $J = 3.8$ Hz), 125.69, 126.97, 130.49, 131.99, 138.37, 143.86, 149.07 (d, $J = 2.9$ Hz), 159.66 (d, $J = 242.5$ Hz), 161.98. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

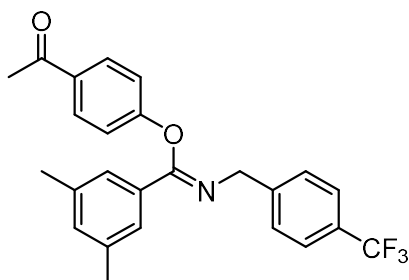
^{19}F NMR (CDCl_3 , 376 MHz) δ : -122.19 (s, 1F, *major isomer*), -119.64 (s, 1F, *minor isomer*), -63.59 (s, 3F, major/minor isomers overlapped).

IR (KBr): 2916 m, 1666 s, 1618 s, 1606 s, 1505 s, 1419 s, 1331 s, 1318 s, 1288 m, 1186 s, 1159 s, 1120 s, 1067 s, 1038 m, 903 m, 864 s, 830 s, 782 s, 739 m, 696 m, 671 s.

MS, m/z (relative intensity, %): 401 (M^+ , 1), 291 (16), 290 (76), 160 (18), 159 (100), 133 (16), 116 (11), 109 (35).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{23}\text{H}_{20}\text{F}_4\text{NO}$: 402.1476. Found: 402.1478.

4-Acetylphenyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1gbd).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:13$), which was determined by ^1H NMR.

White solid (1.63 g, 63%). R_f 0.60 (NH silica, Hexane/EtOAc = 1/1). Mp 91.1–91.8 °C.

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.30 (s, 6H), 2.55 (s, 3H), 4.73 (s, 2H), 6.95–6.98 (m, 2H), 7.08 (s,

1H), 7.47 (s, 2H), 7.51 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 8.2$ Hz, 2H), 7.90–7.93 (m, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.22, 26.42, 51.38, 115.77, 124.23 (q, $J = 272.2$ Hz), 125.31 (q, $J = 3.8$ Hz), 126.25, 127.94, 129.03 (q, $J = 32.3$ Hz), 130.93, 131.71, 131.96, 133.24, 138.29, 143.47, 153.82, 159.03, 196.55.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.39 (s, 6H), 2.62 (s, 3H), 4.63 (s, 2H), 7.15 (s, 3H), 7.32–7.34 (m, 2H), 8.03–8.05 (m, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.32, 26.61, 122.30, 125.72, 127.03, 129.87, 132.17, 133.77, 138.46.

Other peaks are overlapped with those of a major isomer.

E/Z Mixture

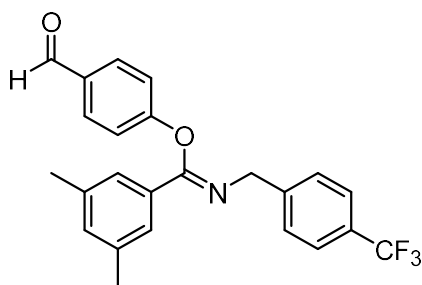
^{19}F NMR (CDCl_3 , 376 MHz) δ : –63.62.

IR (KBr): 3002 m, 2918 m, 1659 s, 1649 s, 1599 s, 1584 s, 1504 s, 1418 s, 1358 m, 1327 s, 1227 m, 1160 m, 1121 m, 1088 m, 1019 m, 912 m, 847 s, 828 s, 817 s, 719 m, 686 m, 592 s.

MS, m/z (relative intensity, %): 425 (M^+ , 9), 134 (10), 133 (100), 105 (24).

HRMS (DART $^+$, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{25}\text{H}_{23}\text{F}_3\text{NO}_2$: 426.1675. Found: 426.1685.

4-Formylphenyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1hbd).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:12$), which was determined by ^1H NMR.

White solid (1.86 g, 75%). R_f 0.64 (SiO_2 , Hexane/EtOAc = 1/1). Mp 99.9–101.0 °C.

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.30 (s, 6H), 4.74 (s, 2H), 7.04 (d, $J = 8.7$ Hz, 2H), 7.09 (s, 1H), 7.48 (s, 2H), 7.51 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 8.2$ Hz, 2H), 7.81–7.85 (m, 2H), 9.90 (s, 1H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.22, 51.34, 116.41, 122.88, 124.21 (q, $J = 271.9$ Hz), 125.35 (q, $J = 3.8$ Hz), 126.29, 127.97, 129.14 (q, $J = 32.6$ Hz), 131.16, 131.49, 132.27, 133.43, 138.39, 143.25, 160.00, 190.50.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.39 (s, 6H), 4.64 (s, 2H), 7.16 (s, 3H), 7.41 (d, $J = 8.2$ Hz, 2H), 7.94–7.96 (m, 2H), 10.01 (s, 1H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.32, 53.22, 125.35 (q, $J = 3.8$ Hz), 125.74, 127.06, 133.13, 138.51, 191.14. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

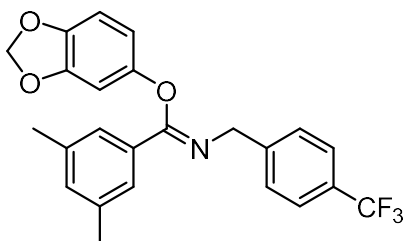
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.65.

IR (KBr): 2918 w, 2839 w, 1698 s, 1668 s, 1599 s, 1505 s, 1419 m, 1324 s, 1239 m, 1156 m, 1115 m, 1082 m, 943 m, 903 m, 824 s, 768 m, 719 m, 597 m, 501 m.

MS, m/z (relative intensity, %): 411 (M^+ , 11), 134 (17), 133 (100), 105 (40), 79 (15), 77 (14).

HRMS (DART $^+$, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{24}\text{H}_{21}\text{F}_3\text{NO}_2$: 412.1519. Found: 412.1525.

Benzo[d][1,3]dioxol-5-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1bd).



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:4.6$), which was determined by ^1H NMR.

Yellow oil (674 mg, 27%). R_f 0.70 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.29 (s, 6H), 4.77 (s, 2H), 5.93 (s, 2H), 6.30 (dd, $J = 8.2, 2.3$ Hz, 1H), 6.49 (d, $J = 2.3$ Hz, 1H), 6.64 (d, $J = 8.7$ Hz, 1H), 7.05 (s, 1H), 7.45 (s, 2H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.24, 51.27, 99.09, 101.51, 108.05, 108.25, 124.30 (q, $J = 272.2$ Hz), 125.26 (q, $J = 3.8$ Hz), 126.42, 127.99, 128.87 (q, $J = 32.3$ Hz), 132.42, 132.78, 138.03, 143.03, 144.02, 148.52, 150.30, 155.16.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.37 (s, 6H), 4.61 (s, 2H), 5.99 (s, 2H), 6.67 (dd, $J = 8.2, 2.3$ Hz, 1H), 6.77 (d, $J = 2.3$ Hz, 1H), 6.82 (d, $J = 8.2$ Hz, 1H), 7.10-7.13 (m, 3H), 7.29 (d, $J = 8.2$ Hz, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.31, 53.15, 104.48, 107.91, 114.40, 125.11 (q, $J = 3.8$ Hz), 125.67, 126.97, 130.61, 131.89, 138.33, 144.60, 144.99, 147.63, 147.86, 162.48. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.59, -63.53.

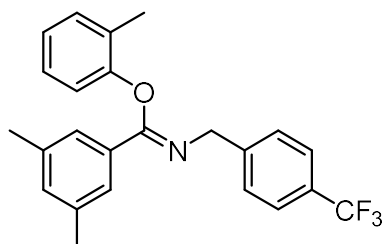
IR (KBr): 3009 w, 2916 m, 1735 w, 1661 m, 1618 m, 1606 m, 1483 s, 1446 m, 1417 m, 1325 s, 1246

m, 1171 s, 1125 s, 1066 s, 1038 s, 1019 m, 949 m, 932 m, 821 s, 681 w, 595 w.

MS, m/z (relative intensity, %): 427 (M^+ , 1), 290 (41), 160 (21), 159 (100), 137 (17), 133 (11), 109 (24), 107 (10), 79 (12).

HRMS (DART⁺, $[M+H]^+$) Calcd for $C_{24}H_{21}F_3NO_3$: 428.1468. Found: 428.1474.

***o*-Tolyl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1jbd).**



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:4.3$), which was determined by 1H NMR.

Pale yellow oil (105 mg, 4%). R_f 0.80 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

1H NMR ($CDCl_3$, 400 MHz) δ : 2.28 (s, 6H), 2.44 (s, 3H), 4.71 (s, 2H), 6.57 (dd, $J = 7.8, 1.4$ Hz, 1H), 6.91–7.01 (m, 2H), 7.05 (s, 1H), 7.15 (s, 1H), 7.45 (s, 2H), 7.51 (d, $J = 7.8$ Hz, 2H), 7.58 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 16.21, 21.23, 51.23, 114.80, 122.65, 124.31 (q, $J = 271.9$ Hz), 125.24 (q, $J = 3.8$ Hz), 125.60, 126.19, 126.92, 127.07, 128.02, 128.86 (q, $J = 32.3$ Hz), 131.52, 132.84, 138.02, 138.35, 144.02, 153.42.

Minor isomer

1H NMR ($CDCl_3$, 400 MHz) δ : 2.29 (s, 3H), 2.39 (s, 6H), 4.58 (s, 2H), 7.27 (d, $J = 7.3$ Hz, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 16.55, 21.34, 53.06, 122.52, 125.02 (q, $J = 3.8$ Hz), 126.79, 129.65, 130.69, 130.85, 130.96, 131.85, 132.51, 145.15, 151.74, 155.55, 161.52. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

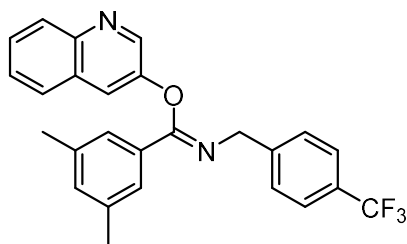
^{19}F NMR ($CDCl_3$, 376 MHz) δ : -63.59, -63.53.

IR (KBr): 2920 w, 1661 m, 1618 w, 1605 w, 1587 w, 1490 m, 1418 w, 1324 s, 1226 m, 1176 s, 1117 s, 1066 m, 1018 w, 820 w, 751 w.

MS, m/z (relative intensity, %): 397 (M^+ , 2), 290 (43), 160 (11), 159 (100), 133 (15), 109 (21).

HRMS (DART⁺, $[M+H]^+$) Calcd for $C_{24}H_{23}F_3NO$: 398.1726. Found: 398.1729.

Quinolin-3-yl 3,5-dimethyl-N-(4-(trifluoromethyl)benzyl)benzimidate (1kbd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:3.1), which was determined by ^1H NMR.

Brown oil (1.06 g, 40%). R_f 0.64 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.29 (s, 6H), 4.80 (s, 2H), 7.07 (s, 1H), 7.32 (d, $J = 2.8$ Hz, 1H), 7.46-7.64 (m, 9H), 8.08 (d, $J = 8.2$ Hz, 1H), 8.87 (d, $J = 3.2$ Hz, 1H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.19, 51.47, 117.58, 124.20 (q, $J = 271.3$ Hz), 125.31 (q, $J = 3.8$ Hz), 125.75, 126.38, 126.91, 127.06, 127.52, 127.93, 128.44 (q, $J = 31.2$ Hz), 129.20, 131.37, 133.32, 138.39, 143.01, 144.39, 147.42, 148.74, 153.77.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.42 (s, 6H), 4.64 (s, 2H), 7.19 (s, 1H), 7.22 (s, 2H), 7.26-7.28 (m, 2H), 7.68-7.72 (m, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 8.00 (d, $J = 2.3$ Hz, 1H), 8.14 (d, $J = 8.2$ Hz, 1H), 8.91 (d, $J = 2.8$ Hz, 1H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.32, 53.18, 116.47, 126.06, 127.01, 127.45, 129.98, 132.27, 138.51, 143.39, 144.34, 145.39, 146.74, 161.47. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

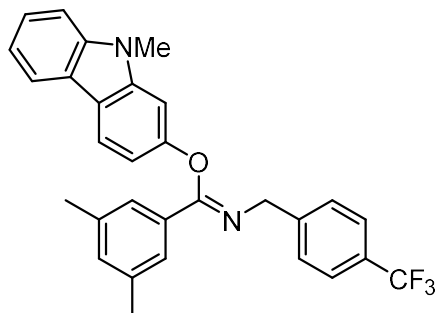
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.62.

IR (KBr): 3055 m, 3010 m, 2919 s, 1737 m, 1668 s, 1603 s, 1497 m, 1464 m, 1418 m, 1324 s, 1269 m, 1162 s, 1123 s, 1066 s, 987 m, 858 s, 820 s, 781 s, 750 s, 612 m.

MS, m/z (relative intensity, %): 434 (M^+ , 7), 159 (24), 134 (10), 133 (100), 105 (28), 79 (11).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{26}\text{H}_{22}\text{F}_3\text{N}_2\text{O}$: 435.1679. Found: 435.1682.

9-Methyl-9H-carbazol-2-yl 3,5-dimethyl-N-(4-(trifluoromethyl)benzyl)benzimidate (1lbd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:8.5), which was determined by ^1H NMR.

White solid (1.35 g, 68%). R_f 0.62 (NH silica, Hexane/EtOAc = 1/1). Mp 128.5-132.1 °C.

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.28 (s, 6H), 3.69 (s, 3H), 4.81 (s, 2H), 6.83–6.87 (m, 2H), 7.04 (s, 1H), 7.19–7.23 (m, 1H), 7.32–7.34 (m, 1H), 7.40–7.42 (m, 1H), 7.51–7.53 (m, 2H), 7.56–7.57 (m, 4H), 7.94 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.24, 29.13, 51.44, 95.83, 108.27, 108.35, 118.23, 119.26, 119.66, 121.42, 122.48, 124.29 (q, J = 272.2 Hz), 125.06, 125.22 (q, J = 3.8 Hz), 126.44, 128.02, 128.84 (q, J = 32.6 Hz), 132.65, 132.84, 138.03, 141.25, 142.02, 144.08, 154.49, 155.22.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.40 (s, 6H), 3.81 (s, 3H), 4.65 (s, 2H), 7.11–7.15 (m, 2H), 7.27–7.30 (m, 3H), 7.48 (s, 1H), 8.06–8.10 (m, 2H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.35, 53.23, 102.24, 113.78, 119.05, 119.89, 120.00, 120.55, 125.84, 127.04, 128.35, 130.84, 131.91, 138.35. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

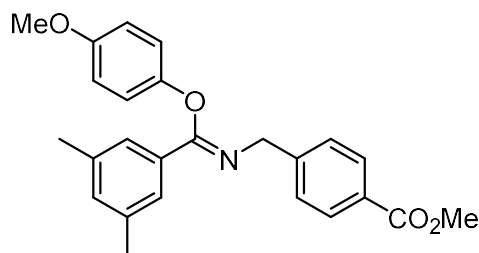
^{19}F NMR (CDCl_3 , 376 MHz) δ : –63.56.

IR (KBr): 3052 w, 2940 w, 1662 s, 1631 s, 1600 s, 1497 m, 1468 s, 1458 s, 1418 s, 1360 m, 1328 s, 1233 m, 1203 m, 1181 s, 1113 s, 1067 m, 1017 m, 955 m, 863 m, 808 s, 745 s, 594 m.

MS, m/z (relative intensity, %): 486 (M^+ , 3), 290 (50), 168 (11), 159 (100).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{30}\text{H}_{26}\text{F}_3\text{N}_2\text{O}$: 487.1992. Found: 487.1998.

Methyl 4-(((3,5-dimethylphenyl)(4-methoxyphenoxy)methylene)amino)methyl)benzoate (1ccd**).**



The product was obtained as a mixture of geometrical isomers ($E:Z = 1:4.1$), which was determined by ^1H NMR. Based on NOSEY spectroscopy of compound **1ccd**, the stereochemistry of the major isomer was determined to have a Z configuration.

Colorless oil (545 mg, 55%). R_f 0.54 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.28 (s, 6H), 3.74 (s, 3H), 3.91 (s, 3H), 4.76 (s, 2H), 6.76-6.85 (m, 4H), 7.03 (s, 1H), 7.45-7.49 (m, 4H), 8.00-8.02 (m, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.21, 51.45, 52.00, 55.57, 114.86, 117.18, 126.48, 127.65, 128.42, 129.52, 129.67, 132.61, 137.93, 145.43, 149.26, 154.97, 155.41, 167.13.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.36 (s, 6H), 3.82 (s, 3H), 3.89 (s, 3H), 4.60 (s, 2H), 6.92-6.94 (m, 2H), 7.12 (s, 3H), 7.15-7.17 (m, 2H), 7.24 (d, $J = 8.7$ Hz, 2H), 7.93-7.95 (m, 2H).

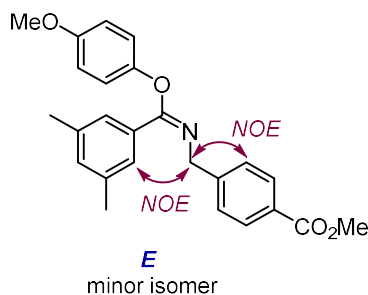
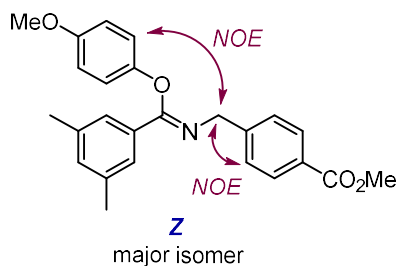
^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.30, 51.97, 53.35, 55.52, 114.25, 122.96, 125.71, 126.66, 131.78, 134.30, 138.25. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

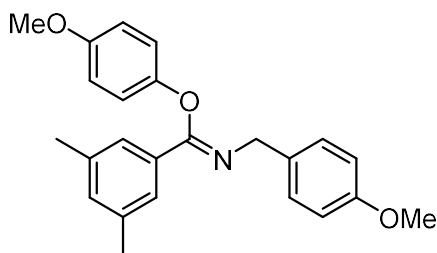
IR (KBr): 3002 m, 2950 m, 1718 s, 1653 s, 1609 m, 1505 s, 1456 m, 1435 m, 1278 s, 1204 s, 1179 s, 1105 m, 1036 m, 823 m, 755 m.

MS, m/z (relative intensity, %): 403 (M^+ , 5), 281 (11), 280 (48), 150 (15), 149 (100), 133 (21), 123 (19), 121 (33), 90 (14).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{25}\text{H}_{26}\text{NO}_4$: 404.1856. Found: 404.1868.



4-Methoxyphenyl *N*-(4-methoxybenzyl)-3,5-dimethylbenzimidate (1ced).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:5.1), which was determined by ¹H NMR.

Colorless oil (2.37 g, 79%). *R*_f 0.56 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

¹H NMR (CDCl₃, 400 MHz) δ : 2.26 (s, 6H), 3.74 (s, 3H), 3.80 (s, 3H), 4.65 (s, 2H), 6.76-6.88 (m, 6H), 7.00 (s, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.44 (s, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 21.20, 51.24, 55.25, 55.78, 113.72, 114.82, 117.12, 126.47, 129.03, 132.17, 132.39, 132.86, 137.81, 149.45, 154.47, 154.84, 158.35.

Minor isomer

¹H NMR (CDCl₃, 400 MHz) δ : 2.36 (s, 6H), 3.78 (s, 3H), 3.81 (s, 3H), 4.49 (s, 2H), 6.90-6.92 (m, 2H), 7.07-7.16 (m, 6H). Other peaks are overlapped with those of a major isomer.

¹³C NMR (CDCl₃, 101 MHz) δ : 21.31, 52.95, 55.21, 55.51, 113.53, 114.18, 122.97, 125.77, 127.83, 131.56, 133.12, 138.11. Other peaks are overlapped with those of a major isomer.

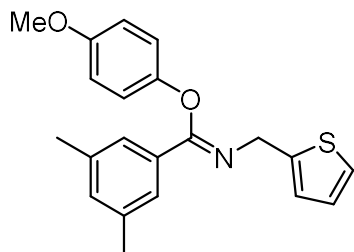
E/Z Mixture

IR (KBr): 2951 w, 2911 w, 1654 m, 1607 m, 1504 s, 1463 m, 1440 w, 1317 m, 1301 m, 1245 s, 1178 s, 1088 m, 1035 m, 821 m, 779 w, 517 w.

MS, *m/z* (relative intensity, %): 375 (*M*⁺, 3), 122 (45), 121 (100), 91 (11), 78 (10), 77 (15).

HRMS (DART⁺, [*M*+*H*]⁺) Calcd for C₂₄H₂₆NO₃: 376.1907. Found: 376.1910.

4-Methoxyphenyl 3,5-dimethyl-*N*-(thiophen-2-ylmethyl)benzimidate (1cfd).



The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:4.0), which was determined by ¹H NMR.

Pale yellow oil (1.47 g, 69%). *R*_f 0.68 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.27 (s, 6H), 3.74 (s, 3H), 4.88 (s, 2H), 6.76-6.86 (m, 4H), 6.95 (d, J = 3.7 Hz, 2H), 7.01 (s, 1H), 7.21 (t, J = 3.2 Hz, 1H), 7.43 (s, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.21, 47.00, 55.57, 114.83, 117.31, 122.99, 124.11, 124.31, 126.57, 126.65, 132.56, 137.85, 143.45, 149.26, 154.99, 155.27.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.37 (s, 6H), 3.81 (s, 3H), 4.70 (s, 2H), 6.91-6.93 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.31, 49.58, 55.51, 114.17, 122.66, 123.50, 125.73, 126.50, 131.75, 138.21, 145.03, 146.60, 156.41, 162.36. Other peaks are overlapped with those of a major isomer.

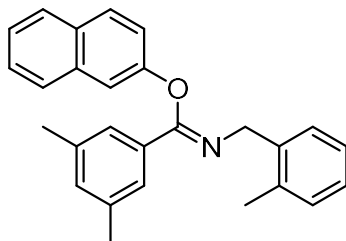
E/Z Mixture

IR (KBr): 2948 w, 2913 w, 1655 m, 1604 w, 1503 s, 1462 w, 1440 w, 1314 m, 1245 m, 1190 m, 1091 m, 1034 m, 822 m, 779 w, 698 m.

MS, m/z (relative intensity, %): 351 (M^+ , 3), 228 (26), 220 (15), 123 (11), 99 (20), 98 (49), 97 (100), 53 (19), 44 (14).

HRMS (DART⁺, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_2\text{S}$: 352.1366. Found: 352.1368.

Naphthalen-2-yl 3,5-dimethyl-*N*-(2-methylbenzyl)benzimidate (1add).



The product was obtained as a mixture of geometrical isomers ($E:Z$ = 1:13), which was determined by ^1H NMR.

White solid (1.05 g, 46%). R_f 0.68 (NH silica, Hexane/EtOAc = 1/1). Mp 61.2-62.7 °C.

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.26 (s, 6H), 2.32 (s, 3H), 4.71 (s, 2H), 7.02 (s, 1H), 7.14-7.17 (m, 4H), 7.25-7.28 (m, 1H), 7.33-7.37 (m, 1H), 7.39-7.43 (m, 2H), 7.55 (s, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.76-7.81 (m, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 19.28, 21.22, 50.00, 110.76, 117.72, 124.45, 125.77, 125.91, 126.41, 126.64, 126.79, 126.96, 127.69, 128.18, 129.61, 130.00, 130.21, 132.52, 132.73, 134.21, 136.19, 137.84, 137.98, 153.27.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.37 (s, 6H), 2.41 (s, 3H), 4.51 (s, 2H), 7.08-7.10 (m, 3H), 7.46 (m,

2H), 7.68 (m, 2H), 7.84-7.87 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 19.02, 21.33, 51.65, 118.49, 122.64, 125.04, 125.65, 126.09, 126.25, 126.51, 127.49, 127.91, 128.78, 129.65, 130.92, 131.01, 131.72, 138.20, 153.99. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

IR (KBr): 3008 m, 2918 m, 2231 s, 1662 s, 1629 m, 1605 s, 1508 s, 1456 s, 1377 m, 1316 s, 1248 s, 1212 s, 1187 s, 1166 s, 1083 m, 1038 m, 960 m, 908 m, 856 s, 746 s.

MS, m/z (relative intensity, %): 379 (M^+ , 5), 133 (33), 105 (100), 79 (15), 77 (13).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{27}\text{H}_{26}\text{NO}$: 380.2009. Found: 380.2009.

IV. Optimization Studies

Table S1.1. Screening of Transition Metal^a

Reaction scheme: **1aaa** $\xrightarrow[\text{160 } ^\circ\text{C, 18h}]{\text{Ni precursor (10 mol\%), dcype (20 mol\%)}}$ **2aaa**

Entry	Ni precursor	Yield of 2aaa [%]	Recovery of 1aaa [%]
1	$\text{Ni}(\text{cod})_2$	51	12
2	$\text{NiCl}_2 \cdot \text{DME}$	0	94
3	$\text{NiBr}_2 \cdot \text{DME}$	0	100
4	$\text{Ni}(\text{OAc})_2$	0	71
5	$\text{Ni}(\text{OTf})_2$	0	89
7 ^b	$\text{Ni}(\text{dcype})(\text{CO})_2$	13	50
8	$\text{NiCl}_2 \cdot \text{DME} / \text{Mn}$ (1 equiv)	0	91
9	$\text{Ni}(\text{acac})_2 / \text{BuLi}$ (20 mol%)	12	42
10	$\text{Ni}(\text{acac})_2 / \text{MeMgI}$ (20 mol%)	0	0
11 ^c	$\text{Pd}_2(\text{dba})_3$ (5 mol%)	0	60
12 ^c	$[\text{RhCl}(\text{cod})]_2$ (5 mol%)	0	84
13 ^c	none	0	100

^a Reaction conditions: **1aaa** (0.20 mmol), catalyst (0.020 or 0.010 mmol), dcype (0.040 mmol), and dioxane (1.5 mL) in a screw capped vial under N_2 at 160 $^\circ\text{C}$ for 18h. Yields were determined by GC using pentadecane as an internal standard.

^b With dcype 10 mol% instead of 20 mol%

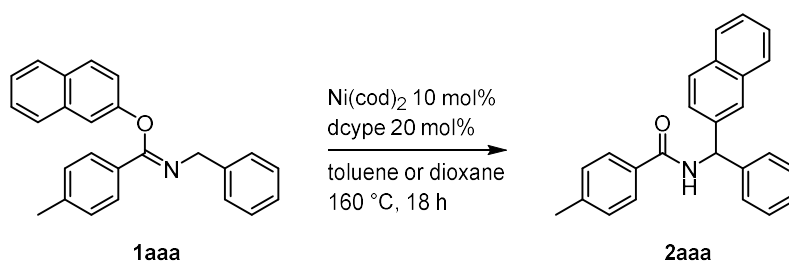
^c In toluene instead of dioxane

Table S1.2. Screening of Solvent^a

Solvent	Yield of 2aaa
toluene	46%
mesitylene	44%
dioxane	51% (isolated yield 49%)
dibutyl ether	51%
CPME	49%
diglyme	37%
DMF	19%
DMAc	27%
DMI	16%
DMSO	19%
<i>tert</i> -amyl alcohol	0.3%
octane	34%
ethylcyclohexane	43%

^a Reaction conditions: **1aaa** (0.20 mmol), Ni(cod)₂ (0.020 mmol), dcype (0.040 mmol), and solvent (1.5 mL) in a screw capped vial under N₂ at 160 °C for 18 h. Yields were determined by GC using pentadecane as an internal standard.

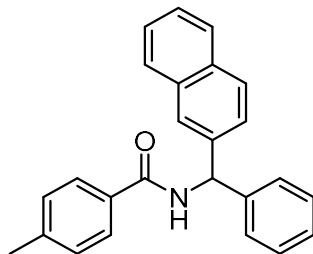
V. A Typical Procedure



In a glovebox filled with nitrogen, aryl *N*-benzylimidate **1aaa** (73.5 mg, 0.21 mmol), Ni(cod)₂ (5.5 mg, 0.020 mmol), dcype (16.9 mg, 0.040 mmol) and solvent (1.5 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 160 °C for 18 h. The resulting mixture was then evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 9/1 to 7/3) to give **2aaa** as a white solid (36.3 mg, 49%).

Spectroscopic Data of Products

4-Methyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzamide (2aaa).



White solid (36.3 mg, 49%). R_f 0.54 (SiO₂, Hexane/EtOAc = 1/1). Mp 187.2-188.1 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.40 (s, 3H), 6.61 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 7.23 (s, 1H), 7.26 (d, J = 0.9 Hz, 1H), 7.29-7.41 (m, 6H), 7.45-7.49 (m, 2H), 7.73-7.83 (m, 6H).

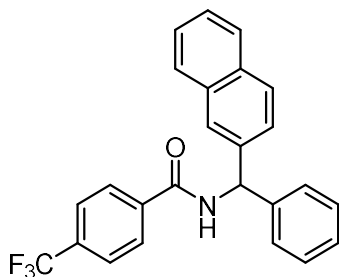
¹³C NMR (CDCl₃, 101 MHz) δ : 21.47, 57.45, 125.66, 126.05, 126.07, 126.28, 127.06, 127.62, 127.64, 127.99, 128.59, 128.76, 129.28, 131.25, 132.72, 133.24, 138.82, 141.36, 142.21, 166.43.

IR (KBr): 3325 m, 3055 m, 2923 m, 1634 s, 1540 s, 1506 s, 1454 m, 1329 s, 1281 m, 1189 m, 1121 m, 817 s, 754 s, 734 m, 698 s, 655 m, 576 m, 474 s.

MS, m/z (relative intensity, %): 352 (10), 351 (M^+ , 37), 351 (49), 233 (13), 232 (64), 215 (15), 120 (11), 119 (100), 104 (19), 91 (35).

HRMS (DART+, [$M+H$]⁺) Calcd for C₂₅H₂₂NO: 352.1696. Found: 352.1694.

N-(Naphthalen-2-yl(phenyl)methyl)-4-(trifluoromethyl)benzamide (2aab).



White solid (36.9 mg, 40%). R_f 0.66 (SiO₂, Hexane/EtOAc = 1/1). Mp 193.1-193.2 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 6.61 (d, J = 7.8 Hz, 1H), 6.83 (d, J = 7.3 Hz, 1H), 7.30-7.40 (m, 6H), 7.46-7.50 (m, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.74 (s, 1H), 7.77-7.81 (m, 1H), 7.82-7.84 (m, 2H), 7.94 (d, J = 8.2 Hz, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 57.79, 123.58 (q, J = 273.2 Hz), 125.46, 125.71 (q, J = 3.4 Hz), 126.10, 126.26, 126.45, 127.57, 127.66, 127.86, 127.97, 128.77, 128.89, 132.79, 133.22, 133.43 (q, J = 32.6 Hz), 137.37, 138.28, 140.85, 165.26.

¹⁹F NMR (CDCl₃, 376 MHz) δ : -64.23.

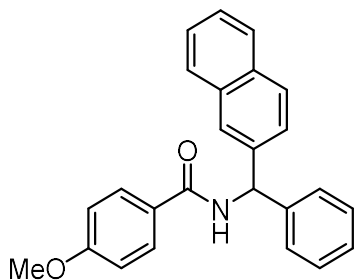
IR (KBr): 3297 m, 1644 s, 1539 s, 1507 m, 1327 s, 1165 s, 1128 s, 1110 m, 1068 m, 1016 m, 860 m,

813 m, 750 m, 719 w, 697 m, 477 m.

MS, m/z (relative intensity, %): 406 (18), 405 (M^+ , 64), 233 (17), 232 (80), 217 (15), 216 (26), 215 (52), 202 (13), 173 (78), 154 (19), 145 (66), 129 (24), 128 (11), 127 (23), 105 (12), 104 (100), 77 (18).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{19}F_3NO$: 406.1413. Found: 406.1414.

4-Methoxy-*N*-(naphthalen-2-yl(phenyl)methyl)benzamide (2aac).



White solid (26.3 mg, 35%). R_f 0.48 (SiO_2 , Hexane/EtOAc = 1/1). Mp 162.7-163.3 °C.

1H NMR ($CDCl_3$, 400 MHz) δ : 3.84 (s, 3H), 6.60 (d, J = 7.8 Hz, 1H), 6.71 (d, J = 7.8 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 7.27-7.36 (m, 5H), 7.39 (dd, J = 8.2 Hz, J = 1.8 Hz, 1H), 7.44-7.49 (m, 2H), 7.74 (s, 1H), 7.76-7.82 (m, 5H).

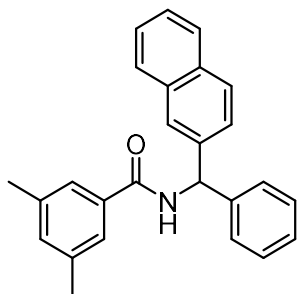
^{13}C NMR ($CDCl_3$, 101 MHz) δ : 55.40, 57.45, 113.77, 125.67, 126.05, 126.27, 126.37, 127.58, 127.60, 127.64, 127.98, 128.55, 128.74, 128.90, 132.71, 133.24, 138.92, 141.44, 162.32, 166.02.

IR (KBr): 3289 m, 3057 w, 1635 s, 1605 s, 1539 s, 1504 s, 1456 w, 1438 w, 1337 m, 1297 m, 1253 s, 1181 m, 1033 m, 847 m, 813 m, 751 m, 698 m, 477 m.

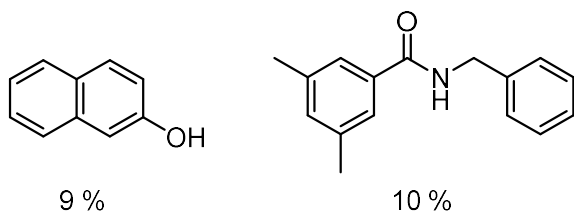
MS, m/z (relative intensity, %): 367 (M^+ , 20), 233 (11), 232 (56), 215 (10), 136 (10), 135 (100), 107 (10), 77 (18).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{22}NO_2$: 368.1645. Found: 368.1644.

3,5-Dimethyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzamide (2aad).



The only detectable byproducts were hydrolysis products (*i.e.*, 2-naphthol 9 % and NH-amide 10 % yield: yields was determined by GC using pentadecane as an internal standard.).



White solid (37.6 mg, 52%). R_f 0.62 (SiO₂, Hexane/EtOAc = 1/1). Mp 179.5-180.2 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.34 (s, 6H), 6.61 (d, J = 7.8 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 7.13 (s, 1H), 7.27-7.35 (m, 5H), 7.39 (dd, J = 8.7 Hz, J = 1.8 Hz, 1H), 7.43 (s, 2H), 7.45-7.48 (m, 2H), 7.74 (s, 1H), 7.76-7.78 (m, 1H), 7.79-7.81 (m, 2H).

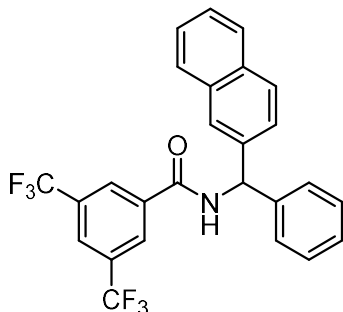
¹³C NMR (CDCl₃, 101 MHz) δ : 21.19, 57.40, 124.78, 125.68, 126.05, 126.08, 126.26, 127.57, 127.59, 127.64, 127.97, 128.54, 128.72, 132.70, 133.23, 133.27, 134.13, 138.33, 138.83, 141.35, 166.85.

IR (KBr): 3298 s, 3052 m, 1634 s, 1602 s, 1539 s, 1455 m, 1348 m, 1336 m, 1244 s, 892 m, 860 m, 841 m, 816 s, 748 s, 713 s, 699 s, 590 m, 556 m, 478 s.

MS, m/z (relative intensity, %): 366 (13), 365 (M^+ , 43), 233 (14), 232 (74), 215 (18), 134 (23), 133 (100), 127 (10), 105 (43), 104 (21), 79 (15), 77 (17).

HRMS (DART⁺, $[M+H]^+$) Calcd for C₂₆H₂₄NO: 366.1852. Found: 366.1850.

***N*-(Naphthalen-2-yl(phenyl)methyl)-3,5-bis(trifluoromethyl)benzamide (2aae).**



White solid (29.9 mg, 31%). R_f 0.72 (SiO₂, Hexane/EtOAc = 1/1). Mp 192.9-193.2 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 6.60 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 6.9 Hz, 1H), 7.31-7.40 (m, 6H), 7.47-7.51 (m, 2H), 7.73 (s, 1H), 7.76-7.81 (m, 1H), 7.82-7.85 (m, 2H), 8.01 (s, 1H), 8.26 (s, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 58.12, 122.82 (q, J = 273.2 Hz), 125.26 (m, J = 3.4 Hz), 125.41, 126.24, 126.37, 126.53, 127.39 (q, J = 1.9 Hz), 127.60, 127.68, 127.97, 128.01, 128.86, 128.94, 132.23 (q, J = 33.9 Hz), 132.82, 133.17, 136.06, 137.84, 140.41, 163.63.

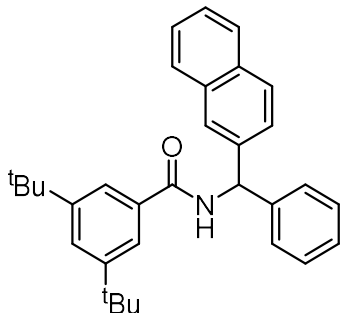
¹⁹F NMR (CDCl₃, 376 MHz) δ : -64.08.

IR (KBr): 3292 m, 1637 s, 1616 m, 1539 s, 1455 m, 1380 w, 1331 m, 1277 s, 1172 m, 1141 s, 908 m, 845 m, 815 m, 754 m, 700 m, 681 m, 477 m.

MS, m/z (relative intensity, %): 474 (16), 473 (M^+ , 90), 241 (65), 232 (77), 217 (13), 216 (32), 215 (69), 212 (34), 207 (50), 129 (22), 127 (20), 104 (100), 73 (41).

HRMS (DART+, [M+H]⁺) Calcd for C₂₆H₁₈F₆NO: 474.1287. Found: 474.1294.

3,5-Di-*tert*-butyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzamide (2aaf).



White solid (36.9 mg, 41%). R_f 0.70 (SiO₂, Hexane/EtOAc = 1/1). Mp 221.1-221.6 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 1.34 (s, 18H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 7.29-7.40 (m, 5H), 7.43 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.46-7.50 (m, 2H), 7.60 (t, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 1.8 Hz, 2H), 7.77-7.85 (m, 4H).

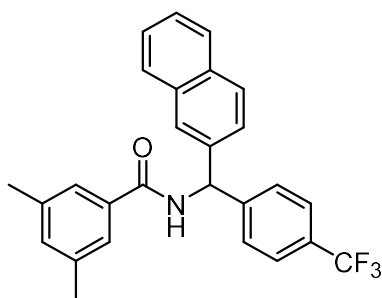
¹³C NMR (CDCl₃, 101 MHz) δ : 31.37, 34.98, 57.52, 121.15, 125.71, 126.01, 126.09, 126.17, 126.31, 127.63, 127.68, 128.01, 128.62, 128.78, 132.73, 133.24, 133.79, 138.86, 141.37, 151.37, 167.59.

IR (KBr): 3256 s, 2961 s, 1634 s, 1592 m, 1539 s, 1522 s, 1363 m, 1275 m, 1249 m, 889 m, 810 m, 748 s, 708 s, 696 s, 477 m.

MS, *m/z* (relative intensity, %): 450 (13), 449 (M⁺, 35), 233 (19), 232 (100), 218 (16), 217 (55), 215 (12), 207 (11), 133 (18), 104 (13), 73 (11), 57 (25).

HRMS (DART+, [M+H]⁺) Calcd for C₃₂H₃₆NO: 450.2791. Found: 450.2793.

4-Methyl-*N*-(naphthalen-2-yl(phenyl)methyl)benzamide (2abd).



White solid (52.2 mg, 60%). R_f 0.64 (SiO₂, Hexane/EtOAc = 1/1). Mp 199.0-200.0 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.33 (s, 6H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 7.14 (s, 1H), 7.35 (dd, *J* = 8.2 Hz, *J* = 1.8 Hz, 1H), 7.42 (s, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.48-7.51 (m, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.69 (s, 1H), 7.75-7.79 (m, 1H), 7.82-7.84 (m, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 21.19, 57.27, 124.04 (q, *J* = 271.9 Hz), 124.81, 125.49, 125.65 (q, *J* = 3.8 Hz), 126.44, 126.57, 126.61, 127.67, 127.75, 127.98, 128.96, 129.70 (q, *J* = 32.3 Hz), 132.84,

133.21, 133.53, 133.71, 137.93, 138.44, 145.28, 167.04.

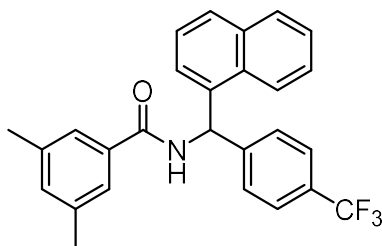
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.74.

IR (KBr): 3285 s, 1636 s, 1602 s, 1527 s, 1327 s, 1249 m, 1160 s, 1121 s, 1068 m, 1021 m, 862 m, 848 s, 814 m, 737 m, 607 m, 473 s.

MS, m/z (relative intensity, %): 433 (M^+ , 20), 300 (35), 134 (19), 133 (100), 105 (31).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{27}\text{H}_{23}\text{F}_3\text{NO}$: 434.1726. Found: 434.1722.

3,5-Dimethyl-*N*-(naphthalen-1-yl(4-(trifluoromethyl)phenyl)methyl)benzamide (2bbd).



White solid (62.7 g, 88%). R_f 0.66 (SiO_2 , Hexane/EtOAc = 1/1). Mp 228.6-229.7 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 2.32 (s, 6H), 6.72 (d, J = 7.8 Hz, 1H), 7.14 (s, 1H), 7.16 (d, J = 6.9 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.39 (s, 2H), 7.42 (d, J = 6.9 Hz, 1H), 7.48 (d, J = 8.2 Hz, 2H), 7.51-7.55 (m, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.2 Hz, 1H), 7.90-7.94 (m, 1H), 8.06-8.09 (m, 1H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.19, 53.89, 123.39, 124.07 (q, J = 272.0 Hz), 124.78, 125.20, 125.63 (q, J = 3.8 Hz), 126.20, 126.23, 127.10, 127.70, 128.95, 129.10, 129.66 (q, J = 31.6 Hz), 131.20, 133.52, 133.56, 134.04, 136.40, 138.45, 145.21, 166.84.

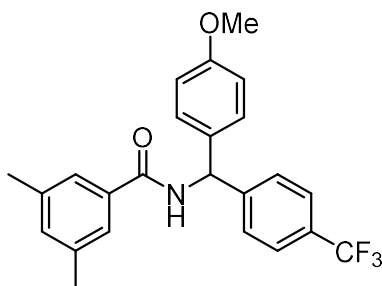
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.71.

IR (KBr): 3302 s, 3042 w, 1628 s, 1598 s, 1527 s, 1421 w, 1324 s, 1244 m, 1157 s, 1125 s, 1071 s, 1019 m, 859 m, 832 w, 803 m, 776 s, 709 m, 692 m, 623 w.

MS, m/z (relative intensity, %): 433 (M^+ , 19), 300 (24), 134 (120), 133 (100), 105 (32), 79 (12).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{27}\text{H}_{23}\text{F}_3\text{NO}$: 434.1726. Found: 434.1727.

***N*-((4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2cbd).**



White solid (62.9 mg, 75%). R_f 0.60 (SiO_2 , Hexane/EtOAc = 1/1). Mp 184.7-184.9 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 2.34 (s, 6H), 3.79 (s, 3H), 6.39 (d, $J = 7.3$ Hz, 1H), 6.70 (d, $J = 7.3$ Hz, 1H), 6.88 (d, $J = 8.7$ Hz, 2H), 7.14 (s, 1H), 7.17 (d, $J = 8.7$ Hz, 2H), 7.40-7.42 (m, 4H), 7.58 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.19, 55.28, 56.65, 114.28, 124.06 (q, $J = 272.2$ Hz), 124.76, 125.53 (q, $J = 3.8$ Hz), 127.46, 128.99, 129.47 (q, $J = 32.6$ Hz), 132.82, 133.44, 133.78, 138.38, 145.69, 159.24, 166.90.

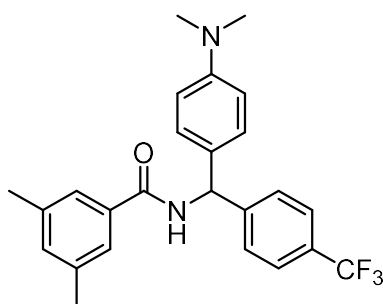
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.71.

IR (KBr): 3301 s, 2954 m, 2912 m, 2837 m, 1633 s, 1604 s, 1532 m, 1512 s, 1328 s, 1247 s, 1167 s, 1120 s, 1071 s, 1035 s, 1021 s, 862 s, 825 s, 768 m, 711 m, 688 m, 604.

MS, m/z (relative intensity, %): 414 (10), 413 (M^+ , 42), 280 (27), 207 (12), 134 (43), 133 (100), 105 (33), 79 (11), 73 (12).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{24}\text{H}_{23}\text{F}_3\text{NO}_2$: 414.1675. Found: 414.1678.

***N*-(4-(Dimethylamino)phenyl)(4-(trifluoromethyl)phenyl)methyl-3,5-dimethylbenzamide (2dbd).**



White solid (58.2 mg, 68%). R_f 0.52 (SiO_2 , Hexane/EtOAc = 1/1). Mp 217.2-217.8 $^\circ\text{C}$.

^1H NMR (CDCl_3 , 400 MHz) δ : 2.34 (s, 6H), 2.95 (s, 6H), 6.34 (d, $J = 7.3$ Hz, 1H), 6.62 (d, $J = 7.3$ Hz, 1H), 6.69 (d, $J = 8.7$ Hz, 2H), 7.10 (d, $J = 8.7$ Hz, 2H), 7.14 (s, 1H), 7.40 (s, 2H), 7.44 (d, $J = 7.8$ Hz, 2H), 7.58 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.19, 40.41, 56.88, 112.50, 124.15 (q, $J = 272.2$ Hz), 124.74, 125.42 (q, $J = 3.8$ Hz), 127.28, 128.20, 128.77, 129.19 (q, $J = 32.6$ Hz), 133.33, 133.93, 138.34, 146.06, 150.14, 166.84.

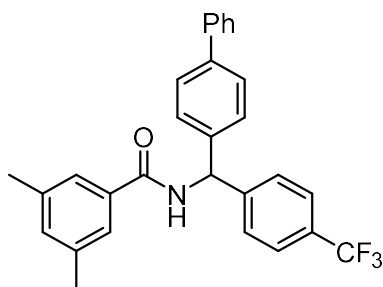
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.65.

IR (KBr): 3289 s, 2916 m, 1633 s, 1604 s, 1522 s, 1324 s, 1247 s, 1163 s, 1119 s, 1069 s, 1019 m, 947 m, 861 s, 809 s, 751 m, 689 m, 603 m.

MS, m/z (relative intensity, %): 427 (14), 426 (M^+ , 49), 293 (17), 281 (17), 279 (11), 278 (59), 277 (20), 276 (12), 165 (12), 147 (11), 134 (20), 133 (100), 122 (24), 105 (48), 103 (12), 79 (22), 77 (21).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{25}\text{H}_{26}\text{F}_3\text{N}_2\text{O}$: 427.1992. Found: 427.1988.

***N*-([1,1'-Biphenyl]-4-yl(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2ebd).**



White solid (45.6 mg, 50%). R_f 0.68 (SiO₂, Hexane/EtOAc = 1/1). Mp 219.4-220.4 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.36 (s, 6H), 6.51 (d, J = 7.3 Hz, 1H), 6.70 (d, J = 7.3 Hz, 1H), 7.16 (s, 1H), 7.33-7.38 (m, 3H), 7.43-7.49 (m, 6H), 7.56-7.63 (m, 6H).

¹³C NMR (CDCl₃, 101 MHz) δ : 21.23, 56.97, 124.04 (q, J = 272.2 Hz), 124.78, 125.70 (q, J = 3.8 Hz), 127.07, 127.55, 127.68, 127.71, 128.15, 128.84, 129.74 (q, J = 32.6 Hz), 133.55, 133.73, 138.47, 139.61, 140.34, 141.01, 145.34, 166.98.

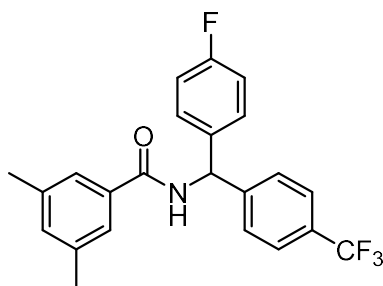
¹⁹F NMR (CDCl₃, 376 MHz) δ : -63.74.

IR (KBr): 3278 s, 3031 w, 1637 s, 1605 s, 1527 s, 1486 m, 1329 s, 1247 m, 1165 s, 1122 s, 1072 m, 1018 m, 870 s, 819 s, 763 s, 701 s, 664 m, 620 m.

MS, m/z (relative intensity, %): 459 (M^+ , 27), 326 (16), 134 (41), 133 (100), 105 (39), 79 (13), 77 (12).

HRMS (DART+, [$M+H$]⁺) Calcd for C₂₉H₂₅F₃NO: 460.1883. Found: 460.1885.

***N*-((4-Fluorophenyl)(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (1fbd).**



White solid (46.1 g, 54%). R_f 0.68 (SiO₂, Hexane/EtOAc = 1/1). Mp 198.8-199.1 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.35 (s, 6H), 6.45 (d, J = 7.3 Hz, 1H), 6.65 (br, 1H), 7.05 (t, J = 8.7 Hz, 2H), 7.16 (s, 1H), 7.22-7.26 (m, 2H), 7.40-7.42 (m, 4H), 7.61 (d, J = 7.8 Hz, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 21.20, 56.47, 115.88 (d, J = 22.0 Hz), 123.96 (q, J = 272.2 Hz), 124.74, 125.73 (q, J = 3.5 Hz), 127.62, 129.39 (d, J = 8.6 Hz), 129.83 (q, J = 32.6 Hz), 133.60, 136.46 (d, J = 3.8 Hz), 138.48, 145.15, 162.29 (d, J = 247.3 Hz), 166.93.

¹⁹F NMR (CDCl₃, 376 MHz) δ : -115.22 (s, 1F), -63.80 (s, 3F).

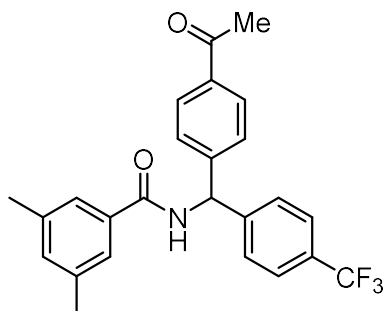
IR (KBr): 3332 s, 1635 s, 1604 s, 1539 m, 1511 m, 1333 s, 1248 m, 1226 m, 1162 s, 1119 s, 1072 s,

1017 s, 915 m, 877 m, 864 s, 825 s, 767 s, 751 s, 716 m, 687 m, 634 m, 602 s, 553 m, 531 s.

MS, m/z (relative intensity, %): 401 (M^+ , 32), 134 (33), 133 (100), 105 (32), 79 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{20}F_4NO$: 402.1476. Found: 402.1479.

***N*-((4-Acetylphenyl)(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2gbd).**



The general procedure was followed, except that the reaction temperature was 180 °C in dibutyl ether.

White solid (45.7 mg, 56%). R_f 0.50 (SiO_2 , Hexane/EtOAc = 1/1). Mp 189.3-190.6 °C.

1H NMR ($CDCl_3$, 400 MHz) δ : 2.36 (s, 6H), 2.60 (s, 3H), 6.53 (d, J = 7.8 Hz, 1H), 6.64 (d, J = 7.3 Hz, 1H), 7.17 (s, 1H), 7.39-7.43 (m, 6H), 7.63 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 21.23, 26.68, 56.93, 123.89 (q, J = 272.2 Hz), 124.75, 125.90 (q, J = 3.8 Hz), 127.72, 127.88, 129.00, 130.15 (q, J = 32.6 Hz), 133.46, 133.71, 136.65, 138.55, 144.64, 145.67, 166.99, 197.48.

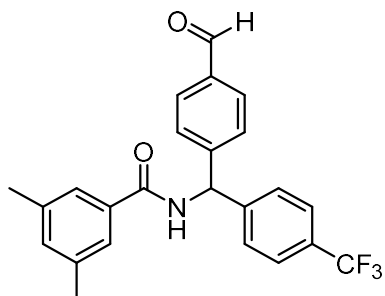
^{19}F NMR ($CDCl_3$, 376 MHz) δ : -63.87.

IR (KBr): 3294 s, 1688 s, 1636 s, 1604 s, 1519 s, 1423 m, 1358 m, 1326 s, 1268 s, 1237 m, 1158 s, 1117 s, 1068 s, 1017 s, 962 s, 862 s, 833 s, 815 s, 752 s, 687 s, 613 s, 588 s.

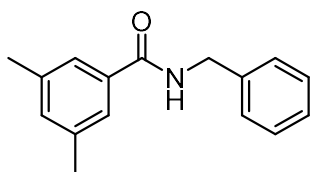
MS, m/z (relative intensity, %): 425 (M^+ , 22), 292 (13), 134 (17), 133 (100), 105 (27).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{23}F_3NO_2$: 426.1675. Found: 426.1676.

***N*-((4-Formylphenyl)(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2hbd).**



The only detectable byproducts were hydrolysis products (*i.e.*, NH-amide 33 % yield, yields was determined by GC using pentadecane as an internal standard.).



33 %

White solid (32.5 mg, 38%). R_f 0.52 (SiO₂, Hexane/EtOAc = 1/1). Mp 198.9-200.1 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.35 (s, 6H), 6.54 (d, J = 7.8 Hz, 1H), 6.81 (br, 1H), 7.17 (s, 1H), 7.40-7.41 (m, 4H), 7.46 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 7.8 Hz, 2H), 9.99 (s, 1H).

¹³C NMR (CDCl₃, 101 MHz) δ : 21.20, 57.01, 123.84 (q, J = 272.2 Hz), 124.79, 125.94 (q, J = 3.8 Hz), 127.95, 128.12, 130.22 (q, J = 32.6 Hz), 130.30, 133.34, 133.76, 135.85, 138.54, 144.41, 147.18, 167.09, 191.62.

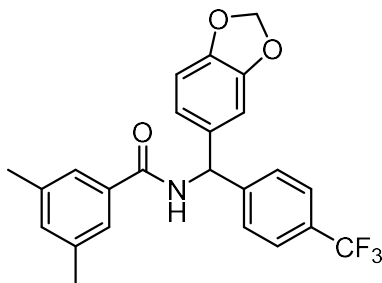
¹⁹F NMR (CDCl₃, 376 MHz) δ : -63.87.

IR (KBr): 3286 s, 1698 s, 1635 s, 1605 s, 1530 m, 1327 s, 1212 m, 1164 s, 1121 s, 1068 s, 1017 s, 863 s, 826 s, 807 s, 769 m, 692 m, 611m.

MS, m/z (relative intensity, %): 412 (13), 411 (M⁺, 43), 134 (19), 133 (100), 105 (23).

HRMS (DART⁺, [M+H]⁺) Calcd for C₂₄H₂₁F₃NO₂: 412.1519. Found: 412.1513.

***N*-(Benzo[d][1,3]dioxol-5-yl(4-(trifluoromethyl)phenyl)methyl)-3,5-dimethylbenzamide (2ibd).**



White solid (58.1 mg, 67%). R_f 0.60 (SiO₂, Hexane/EtOAc = 1/1). Mp 176.0-176.4 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.33 (s, 6H), 5.94 (d, J = 0.9 Hz, 2H), 6.34 (d, J = 7.3 Hz, 1H), 6.71-6.78 (m, 4H), 7.14 (s, 1H), 7.39-7.41 (m, 4H), 7.57 (d, J = 8.2 Hz, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 21.16, 56.94, 101.27, 108.09, 108.47, 121.22, 124.02 (q, J = 272.2 Hz), 124.77, 125.56 (q, J = 2.9 Hz), 127.45, 129.57 (q, J = 32.3 Hz), 133.46, 133.68, 134.58, 138.37, 145.46, 147.28, 148.12, 166.92.

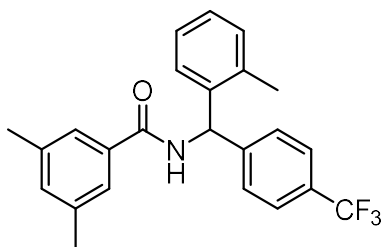
¹⁹F NMR (CDCl₃, 376 MHz) δ : -63.74.

IR (KBr): 3289 s, 1634 s, 1603 s, 1526 s, 1504 s, 1487 s, 1328 s, 1251 s, 1164 s, 1124 s, 1072 m, 1039 m, 939 m, 859 s, 798 m, 711 m, 662 w.

MS, m/z (relative intensity, %): 428 (12), 427 (M⁺, 42), 294 (24), 134 (38), 133 (100), 105 (35), 79 (13).

HRMS (DART+, [M+H]⁺) Calcd for C₂₄H₂₁F₃NO₃: 428.1468. Found: 428.1469.

3,5-Dimethyl-N-(*o*-tolyl(4-(trifluoromethyl)phenyl)methyl)benzamide (2jbd).



White solid (25.6 g, 30%). R_f 0.64 (SiO₂, Hexane/EtOAc = 1/1). Mp 192.7-193.3 °C.

¹H NMR (CDCl₃, 400 MHz) δ: 2.36 (s, 6H), 2.40 (s, 3H), 6.54 (d, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 7.16 (s, 1H), 7.19 (q, *J* = 4.1 Hz, 1H), 7.25 (d, *J* = 5.0 Hz, 2H), 7.38-7.41 (m, 4H), 7.59 (d, *J* = 8.2 Hz, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ: 19.48, 21.21, 54.03, 124.05 (q, *J* = 271.3 Hz), 124.73, 125.58 (q, *J* = 3.8 Hz), 126.45, 127.30, 127.63, 128.08, 129.57 (q, *J* = 32.3 Hz), 131.06, 133.52, 133.61, 136.72, 138.46, 138.80, 145.17, 166.77.

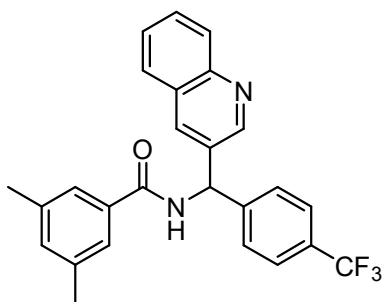
¹⁹F NMR (CDCl₃, 376 MHz) δ: -63.74.

IR (KBr): 3294 s, 3043 m, 2917 m, 1637 s, 1527 m, 1325 m, 1244 m, 1170 s, 1126 s, 1068 m, 1018 m, 865 s, 835 s, 755 s, 732 s, 613 s, 449 m.

MS, *m/z* (relative intensity, %): 397 (M⁺, 32), 179 (47), 134 (17), 133 (100), 105 (39), 79 (15), 77 (12).

HRMS (DART+, [M+H]⁺) Calcd for C₂₄H₂₃F₃NO: 398.1726. Found: 398.1727.

3,5-Dimethyl-N-(quinolin-3-yl(4-(trifluoromethyl)phenyl)methyl)benzamide (2kbd).



White solid (48.6 mg, 57%). R_f 0.32 (SiO₂, Hexane/EtOAc = 1/1). Mp 211.2-211.5 °C.

¹H NMR (CDCl₃, 400 MHz) δ: 2.32 (s, 6H), 6.67 (d, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 7.15 (s, 1H), 7.43 (s, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.97 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 8.91 (br, 1H).

¹³C NMR (CDCl₃, 101 MHz) δ: 21.15, 55.22, 123.86 (q, *J* = 272.2 Hz), 124.85, 125.93 (q, *J* = 2.9 Hz), 127.26, 127.51, 127.84, 129.09, 129.93, 130.19 (q, *J* = 32.6 Hz), 133.32, 133.41, 133.70, 134.47,

138.48, 144.11, 147.43, 150.24, 167.15.

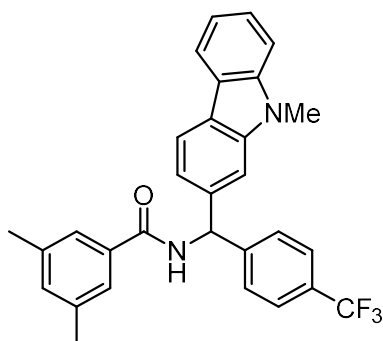
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.84.

IR (KBr): 3268 s, 1642 s, 1603 m, 1524 s, 1495 m, 1329 s, 1242 m, 1166 s, 1119 s, 1071 s, 1018 m, 862 s, 785 m, 754 s, 749 s, 717 m.

MS, m/z (relative intensity, %): 434 (M^+ , 14), 301 (27), 207 (10), 134 (16), 133 (100), 105 (39), 79 (15), 77 (13).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{26}\text{H}_{22}\text{F}_3\text{N}_2\text{O}$: 435.1679. Found: 435.1686.

3,5-Dimethyl-*N*-((9-methyl-9H-carbazol-2-yl)(4-(trifluoromethyl)phenyl)methyl)benzamide (2lbd).



White solid (65.6 mg, 67%). R_f 0.56 (SiO_2 , Hexane/EtOAc = 1/1). Mp 235.8-237.0 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 2.33 (s, 6H), 3.78 (s, 3H), 6.65 (d, J = 7.3 Hz, 1H), 6.84 (d, J = 7.3 Hz, 1H), 7.10 (dd, J = 8.2, 1.4 Hz, 1H), 7.14 (s, 1H), 7.21-7.25 (m, 1H), 7.29 (s, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.43 (s, 2H), 7.46-7.49 (m, 3H), 7.59 (d, J = 8.2 Hz, 2H), 8.04-8.07 (m, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.19, 29.12, 57.93, 108.11, 108.55, 118.36, 119.18, 120.34, 120.87, 122.23, 122.52, 124.09 (q, J = 272.2 Hz), 124.79, 125.53 (q, J = 3.8 Hz), 126.01, 127.55, 129.49 (q, J = 32.6 Hz), 133.46, 133.83, 138.35, 138.41, 141.07, 141.40, 145.86, 166.96.

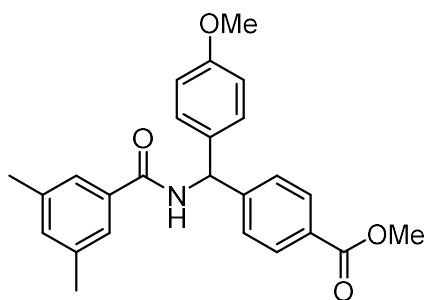
^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.65.

IR (KBr): 3263 s, 3061 m, 2919 m, 1634 s, 1604 s, 1539 s, 1497 m, 1468 m, 1454 m, 1420 m, 1323 s, 1254 s, 1165 s, 1123 s, 1069 s, 1017 m, 862 s, 834 m, 818 s, 748 s, 726 s, 684 w, 666 w, 654 m, 618 m, 506 m, 449 m.

MS, m/z (relative intensity, %): 487 (20), 486 (M^+ , 62), 354 (23), 353 (100), 182 (18), 167 (16), 134 (26), 133 (74), 105 (35), 79 (12).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{30}\text{H}_{26}\text{F}_3\text{N}_2\text{O}$: 487.1992. Found: 487.1993.

Methyl 4-((3,5-dimethylbenzamido)(4-methoxyphenyl)methyl)benzoate (2ccd).



White solid (50.2 mg, 62%). R_f 0.48 (SiO₂, Hexane/EtOAc = 1/1). Mp 184.2-184.5 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.34 (s, 6H), 3.79 (s, 3H), 3.90 (s, 3H), 6.41 (d, J = 7.3 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H), 6.86-6.89 (m, 2H), 7.14 (s, 1H), 7.16-7.19 (m, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.40 (s, 2H), 7.99-8.01 (m, 2H).

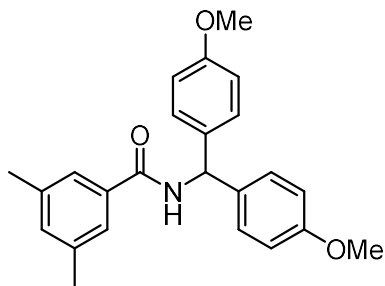
¹³C NMR (CDCl₃, 101 MHz) δ : 21.20, 52.10, 55.28, 56.71, 114.213, 124.74, 127.15, 128.97, 129.12, 129.90, 133.00, 133.37, 133.90, 138.36, 146.78, 159.16, 166.79, 166.84.

IR (KBr): 3304 s, 2949 w, 1729 s, 1636 s, 1604 m, 1529 s, 1515 s, 1457 w, 1435 m, 1274 s, 1251 s, 1186 m, 1106 m, 1036 w, 1020 m, 864 m, 810 m, 764 m, 736 m, 699 m.

MS, m/z (relative intensity, %): 404 (13), 403 (M^+ , 45), 270 (30), 134 (30), 133 (100), 105 (30), 79 (10).

HRMS (DART+, [$M+H$]⁺) Calcd for C₂₅H₂₆NO₄: 404.1856. Found: 404.1851.

***N*-(Bis(4-methoxyphenyl)methyl)-3,5-dimethylbenzamide (2ced).**



White solid (37.5 mg, 48%). R_f 0.48 (SiO₂, Hexane/EtOAc = 1/1). Mp 180.2-182.3 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.34 (s, 6H), 3.79 (s, 3H), 3.90 (s, 3H), 6.34 (d, J = 7.8 Hz, 1H), 6.57 (d, J = 7.8 Hz, 1H), 6.85-6.89 (m, 4H), 7.13 (s, 1H), 7.19-7.22 (m, 4H), 7.40 (s, 2H).

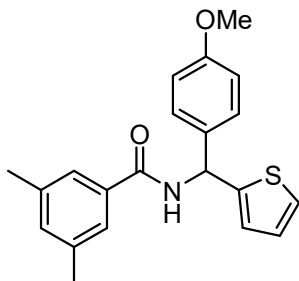
¹³C NMR (CDCl₃, 101 MHz) δ : 21.21, 55.27, 56.17, 113.98, 124.72, 128.59, 133.18, 133.91, 134.27, 138.28, 158.83, 166.69.

IR (KBr): 3326 s, 3004 m, 2931 m, 2833 s, 1635 s, 1605 s, 1508 s, 1463 m, 1323 m, 1306 m, 1281 m, 1238 s, 1176 s, 1111 m, 1032 s, 862 s, 815 s, 767 m, 687 s, 669 m, 582 s, 569 m.

MS, m/z (relative intensity, %): 376 (23), 375 (M^+ , 84), 243 (12), 242 (60), 227 (30), 226 (18), 211 (16), 207 (12), 134 (70), 133 (100), 105 (39), 103 (10), 79 (18), 77 (16).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{24}H_{26}NO_3$: 376.1907. Found: 376.1904.

***N*-((4-Methoxyphenyl)(thiophen-2-yl)methyl)-3,5-dimethylbenzamide (2cfd).**



White solid (45.0 mg, 59%). R_f 0.60 (SiO_2 , Hexane/EtOAc = 1/1). Mp 174.0-175.1 °C.

1H NMR ($CDCl_3$, 400 MHz) δ : 2.34 (s, 6H), 3.80 (s, 3H), 6.59 (d, J = 8.2 Hz, 1H), 6.74 (d, J = 7.8 Hz, 1H), 6.86-6.96 (m, 4H), 7.13 (s, 1H), 7.23-7.25 (m, 1H), 7.31-7.33 (m, 2H), 7.40 (s, 2H).

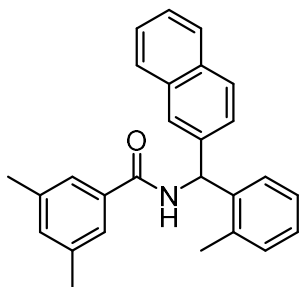
^{13}C NMR ($CDCl_3$, 101 MHz) δ : 21.19, 52.75, 55.26, 114.01, 124.77, 125.06, 125.73, 126.89, 128.38, 133.28, 133.35, 134.03, 138.30, 146.20, 159.17, 166.57.

IR (KBr): 3287 s, 3042 w, 2999 m, 2964 w, 2833 w, 1639 s, 1604 s, 1535 s, 1512 s, 1462 m, 1379 m, 1342 m, 1284 m, 1244 s, 1183 s, 1029 s, 859 s, 839 m, 801 m, 697 s, 533 w.

MS, m/z (relative intensity, %): 352 (17), 351 (M^+ , 69), 218 (42), 203 (15), 202 (11), 187 (17), 134 (156), 133 (100), 115 (11), 110 (12), 105 (41), 103 (11), 79 (19), 77 (17).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{21}H_{22}NO_2S$: 352.1366. Found: 352.1359.

3,5-Dimethyl-*N*-(naphthalen-2-yl(o-tolyl)methyl)benzamide (2add).



The general procedure was followed, except that the reaction temperature was 180 °C in dibutyl ether.

White solid (31.2 mg, 42%). R_f 0.58 (SiO_2 , Hexane/EtOAc = 1/1). Mp 157.6-158.3 °C.

1H NMR ($CDCl_3$, 400 MHz) δ : 2.35 (s, 6H), 2.38 (s, 3H), 6.64 (d, J = 7.8 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 7.14 (s, 1H), 7.18-7.24 (m, 4H), 7.39 (dd, J = 8.2 Hz, J = 1.8 Hz, 1H), 7.44 (s, 2H), 7.45-7.48 (m, 2H), 7.66 (s, 1H), 7.74-7.76 (m, 1H), 7.80-7.83 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 19.53, 21.22, 54.48, 124.77, 125.87, 125.97, 126.02, 126.21, 126.23, 127.00, 127.60, 127.68, 127.95, 128.50, 130.90, 132.70, 133.24, 133.32, 133.99, 136.67, 138.37, 138.44, 139.34, 166.61.

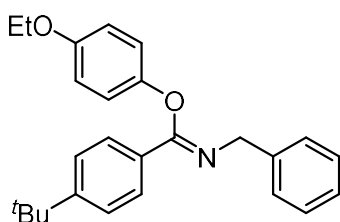
IR (KBr): 3294 s, 3047 m, 2917 m, 1627 s, 1602 s, 1525 s, 1458 m, 1334 m, 1240 m, 1051 m, 912 m, 860 m, 820 m, 770 m, 751 s, 725 w, 696 m, 483 m, 477 m.

MS, m/z (relative intensity, %): 379 (M^+ , 23), 246 (35), 230 (25), 229 (23), 228 (13), 215 (12), 207 (12), 134 (17), 133 (100), 127 (11), 118 (14), 105 (47), 103 (12), 91 (12), 79 (19), 77 (18), 73 (11).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{27}H_{26}NO$: 380.2009. Found: 380.2012.

VI. Gram-Scale Reaction

VI-1. Synthesis of the starting imidate 1mag



4-Ethoxyphenyl *N*-benzyl-4-(tert-butyl)benzimidate (1mag). This compound was prepared according to general procedure B. The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:5.7), which was determined by 1H NMR.

Colorless oil (2.75 g, 71%). R_f 0.60 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

1H NMR ($CDCl_3$, 400 MHz) δ : 1.28 (s, 9H), 1.37 (t, J = 7.1 Hz, 3H), 3.94 (q, J = 7.0 Hz, 2H), 4.73 (s, 2H), 6.75-6.86 (m, 4H), 7.30-7.34 (m, 4H), 7.40 (d, J = 7.8 Hz, 2H), 7.48 (s, 1H), 7.76-7.79 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 14.85, 31.12, 34.78, 51.63, 63.80, 115.44, 117.07, 125.26, 126.51, 127.76, 128.28, 128.52, 130.06, 140.14, 149.35, 153.91, 154.23, 154.27.

Minor isomer

1H NMR ($CDCl_3$, 400 MHz) δ : 1.35 (s, 9H), 1.41 (t, J = 7.1 Hz, 3H), 3.94 (q, J = 6.9 Hz, 2H), 4.62 (s, 2H), 6.90-6.92 (m, 2H), 7.15-7.23 (m, 9H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 14.90, 31.19, 34.86, 53.48, 63.69, 114.79, 122.97, 125.38, 126.22, 126.69, 128.06, 128.15. Other peaks are overlapped with those of a major isomer.

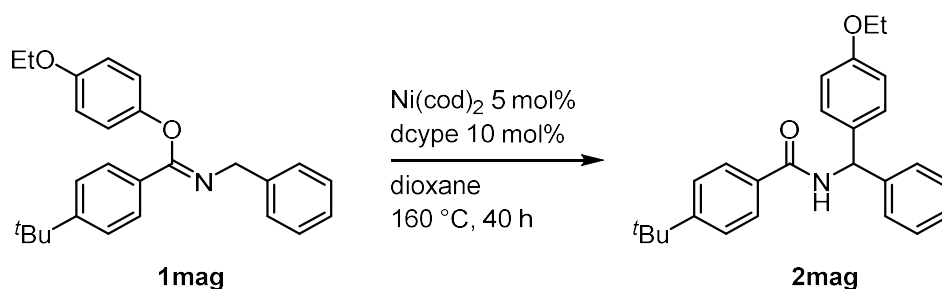
E/Z Mixture

IR (KBr): 2964 m, 2903 m, 1660 s, 1608 w, 1503 m, 1477 m, 1269 m, 1242 m, 1202 s, 1186 s, 1112 m, 1062 s, 1017 w, 823 m, 778 w, 733 m, 697 m.

MS, m/z (relative intensity, %): 387 (M^+ , 6), 251 (16), 250 (172), 161 (14), 116 (11), 109 (24), 92 (60), 91 (100), 65 (14).

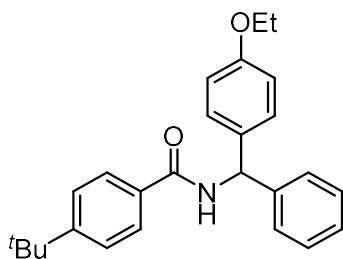
HRMS (DART+, $[M+H]^+$) Calcd for $C_{26}H_{30}NO_2$: 388.2271. Found: 388.2274.

VI-2. Gram-Scale Reaction



In a glovebox filled with nitrogen, aryl *N*-benzylimidate **1mag** (1.96 g, 5.0 mmol), Ni(cod)₂ (69.5 mg, 0.25 mmol), dcype (214.2 mg, 0.50 mmol) and 1,4-dioxane (25 mL) were added to a 200 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 160 °C for 40 h. This mixture was then evaporated to dryness, and the residue was purified by flash column chromatography using hexane/EtOAc = 17/3 as the eluent to give **2mag** as a white solid (1.43 g, 73%).

4-(*tert*-Butyl)-*N*-((4-ethoxyphenyl)(phenyl)methyl)benzamide (2mag).



White solid (1.43 g, 73%). *R*_f 0.60 (SiO₂, Hexane/EtOAc = 1/1). Mp 166.1-166.9 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 1.32 (s, 9H), 1.40 (t, *J* = 6.9 Hz, 3H), 4.00 (q, *J* = 7.0 Hz, 2H), 6.39 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.83-6.86 (m, 2H), 7.17-7.20 (m, 2H), 7.24-7.45 (m, 5H), 7.42-7.45 (m, 2H), 7.74-7.77 (m, 2H).

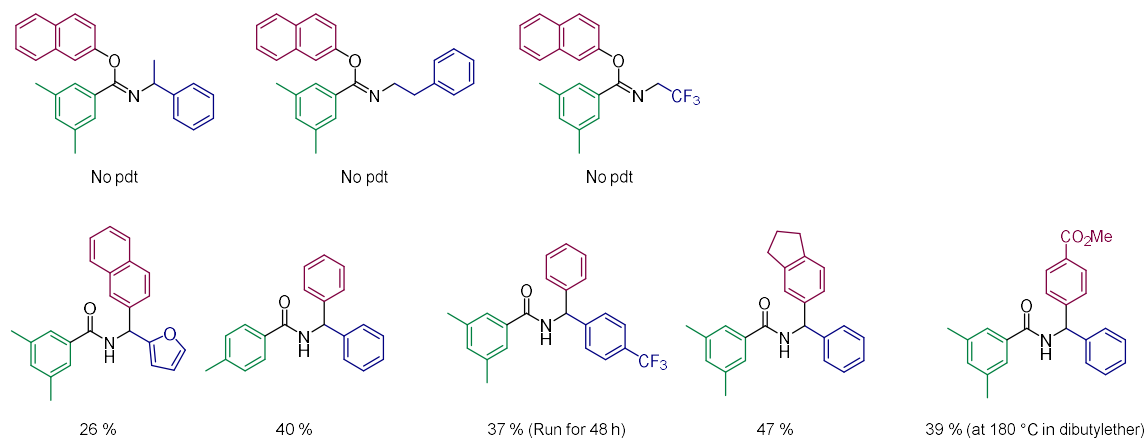
¹³C NMR (CDCl₃, 101 MHz) δ : 14.79, 31.10, 34.88, 56.71, 63.39, 114.53, 125.47, 126.85, 127.32, 128.58, 128.71, 131.33, 133.53, 141.73, 155.09, 158.25, 166.27.

IR (KBr): 3308 s, 2965 s, 2908 m, 2869 m, 1628 s, 1539 s, 1507 s, 1455 m, 1361 m, 1322 m, 1303 m, 1243 s, 1173 s, 1116 m, 1048 s, 923 m, 855 m, 824 m, 747 m, 702 s.

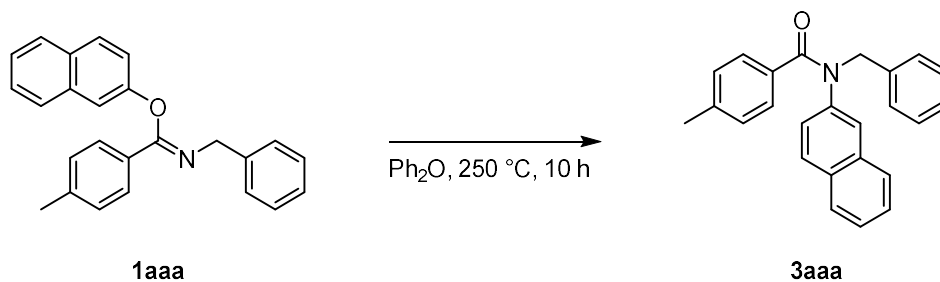
MS, *m/z* (relative intensity, %): 388 (28), 387 (*M*⁺, 97), 310 (10), 227 (10), 226 (57), 211 (15), 181 (10), 162 (14), 161 (100), 146 (14), 123 (11), 118 (25), 105 (16), 104 (27), 91 (16).

HRMS (DART⁺, [*M*+H]⁺) Calcd for C₂₆H₃₀NO₂: 388.2271. Found: 388.2271.

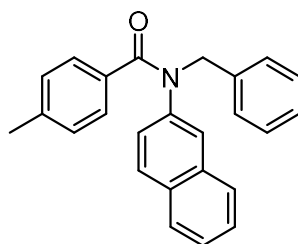
VII. Additional Scope and Limitations



VIII. Chapman Rearrangement of **1aaa**



In a glovebox filled with nitrogen, imidate **1aaa** (71.1 mg, 0.20 mmol) and Ph₂O (1.5 mL) were added to a 5 mL pressure-resistant vial and it was closed with a resealable septum. The mixture was stirred at 250 °C for 10 h using a microwave reactor. This mixture was purified by flash column chromatography using hexane/EtOAc (1/9) as the eluent to give **3aaa** as a yellow oil (25.1 mg, 35 %). ***N*-Benzyl-4-methyl-*N*-(naphthalen-2-yl)benzamide (3aaa).**



Yellow oil (25.1 mg, 35%). R_f 0.58 (SiO₂, Hexane/EtOAc = 1/1).

¹H NMR (CDCl₃, 400 MHz) δ : 2.20 (s, 3H), 5.22 (s, 2H), 6.91 (d, J = 8.2 Hz, 2H), 7.04 (dd, J = 8.7, 2.3 Hz, 1H), 7.22–7.35 (m, 7H), 7.39 (d, J = 2.3 Hz, 1H), 7.41–7.44 (m, 2H), 7.61–7.63 (m, 2H), 7.72–7.74 (m, 1H).

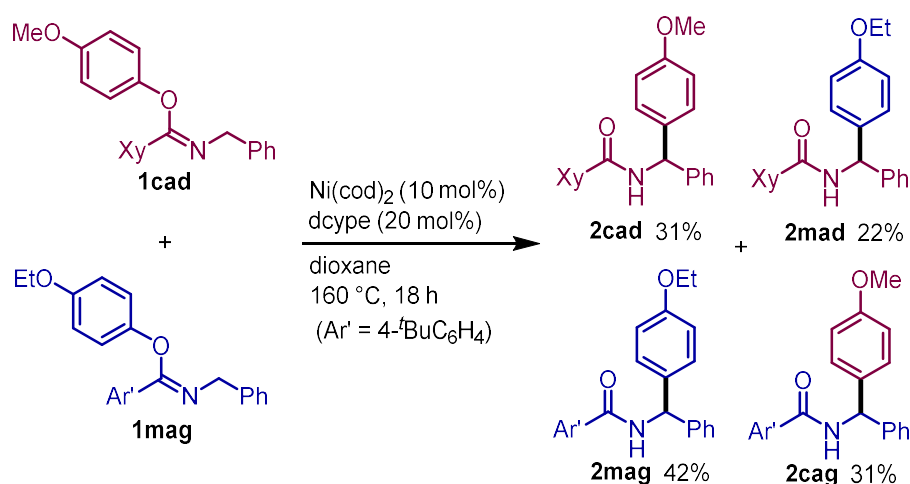
¹³C NMR (CDCl₃, 101 MHz) δ : 21.30, 54.15, 125.45, 126.12, 126.41, 127.30, 127.57, 127.76, 128.35, 128.45, 128.83, 128.96, 131.50, 132.84, 133.28, 137.63, 139.95, 141.31, 170.68.

IR (KBr): 3059 m, 2923 m, 1645 s, 1599 s, 1508 s, 1441 m, 1388 m, 1304 m, 1290 m, 1182 m, 832 m, 819 m, 748 s, 700 s.

MS, m/z (relative intensity, %): 351 (M^+ , 21), 232 (26), 119 (100), 91 (60), 65 (12).

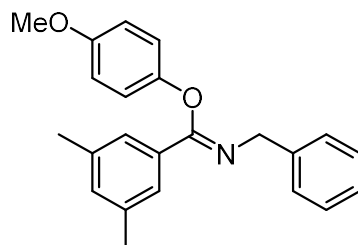
HRMS (DART+, $[M+H]^+$) Calcd for $C_{25}H_{22}NO$: 352.1696. Found: 352.1695.

IX. Crossover Experiments



In a glovebox filled with nitrogen, aryl *N*-benzylimidates **1cad** (67.4 mg, 2.0 mmol) and **1mag** (76.2 mg, 2.0 mmol), $Ni(cod)_2$ (12.6 mg, 0.46 mmol), dcype (34.9 mg, 0.83 mmol) and 1,4-dioxane (3 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 160 °C for 18 h. The resulting mixture was then evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 9/1 to 7/3) and GPC to give crossover products **2mad** (22%) and **2cag** (31%) and intramolecular migration products **2cad** (31%) and **2mag** (42%).

4-Methoxyphenyl *N*-benzyl-3,5-dimethylbenzimidate (**1cad**).



This compound was prepared according to general procedure A. The product was obtained as a mixture of geometrical isomers ($E:Z = 1:5.4$), which was determined by 1H NMR.

Colorless oil (672 mg, 32%). R_f 0.72 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.27 (s, 6H), 3.81 (s, 3H), 4.72 (s, 2H), 6.76-6.80 (m, 2H), 7.82-7.85 (m, 2H), 7.01 (s, 1H), 7.24-7.26 (m, 2H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.39-7.41 (m, 2H), 7.45 (s, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.22, 51.77, 55.58, 114.83, 117.14, 126.48, 126.58, 127.85, 128.32, 132.43, 132.82, 137.85, 140.01, 149.41, 154.76, 154.86.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.36 (s, 6H), 3.81 (s, 3H), 4.56 (s, 2H), 6.91-6.93 (m, 2H), 7.10-7.12 (m, 4H), 7.15-7.18 (m, 5H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.31, 53.52, 55.52, 114.19, 122.99, 125.76, 126.22, 126.77, 128.13, 131.60, 138.14. Other peaks are overlapped with those of a major isomer.

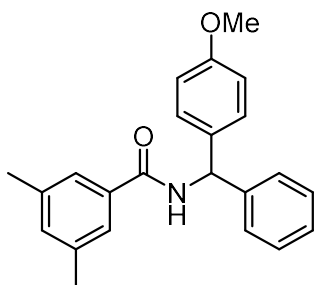
E/Z Mixture

IR (KBr): 3003 w, 2914 m, 1734 w, 1655 s, 1604 m, 1504 s, 1454 m, 1317 m, 1244 m, 1203 s, 1178 s, 1091 m, 1035 m, 824 m, 774 w, 730 m, 698 m.

MS, m/z (relative intensity, %): 345 (M^+ , 2), 222 (41), 92 (24), 91 (100), 65 (15).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_2$: 346.1802. Found: 346.1802.

***N*-(4-Methoxyphenyl)(phenyl)methyl-3,5-dimethylbenzamide (2cad).**



White solid (20.7 mg, 31%). R_f 0.60 (SiO_2 , Hexane/EtOAc = 1/1). Mp 160.3-160.6 $^\circ\text{C}$.

^1H NMR (CDCl_3 , 400 MHz) δ : 2.33 (s, 6H), 3.78 (d, $J = 0.9$ Hz, 3H), 6.39 (d, $J = 7.7$ Hz, 1H), 6.66 (d, $J = 7.8$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 2H), 7.12 (s, 1H), 7.20 (d, $J = 8.7$ Hz, 2H), 7.25-7.36 (m, 5H), 7.40 (s, 2H).

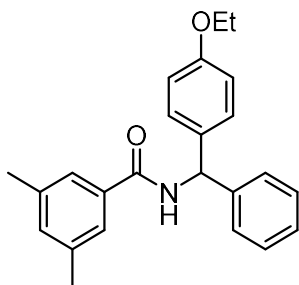
^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.19, 55.23, 56.69, 113.99, 124.72, 127.34, 128.59, 128.74, 133.18, 133.70, 134.19, 138.25, 141.68, 158.85, 166.73.

IR (KBr): 3339 s, 2918 m, 1634 s, 1601 s, 1539 s, 1515 s, 1465 m, 1305 m, 1238 s, 1183 s, 1120 m, 1034 s, 911 m, 861 s, 817 s, 789 m, 763 m, 726 s, 700 s, 573 s.

MS, m/z (relative intensity, %): 346 (18), 345 (M^+ , 70), 212 (46), 197 (12), 134 (38), 133 (100), 105 (39), 104 (19), 79 (16), 77 (18).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_2$: 346.1802. Found: 346.1802.

***N*-((4-Ethoxyphenyl)(phenyl)methyl)-3,5-dimethylbenzamide (2mad).**



White solid (15.7 mg, 22%). R_f 0.60 (SiO₂, Hexane/EtOAc = 1/1). Mp 144.7-144.9 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 1.40 (t, J = 6.9 Hz, 3H), 2.35 (s, 6H), 4.01 (q, J = 7.0 Hz, 2H), 6.39 (d, J = 8.2 Hz, 1H), 6.60 (d, J = 7.3 Hz, 1H), 6.84-6.88 (m, 2H), 7.13 (s, 1H), 7.17-7.21 (m, 2H), 7.27-7.37 (m, 5H), 7.41 (s, 2H).

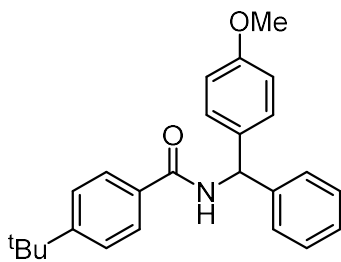
¹³C NMR (CDCl₃, 101 MHz) δ : 14.81, 21.22, 56.71, 63.41, 114.54, 124.72, 127.35, 128.61, 128.74, 133.21, 133.51, 134.20, 138.30, 141.70, 158.27, 166.72.

IR (KBr): 3292 s, 3031 m, 2978 m, 2918 m, 1635 s, 1602 s, 1508 s, 1475 m, 1327 m, 1304 m, 1243 s, 1176 s, 1116 m, 1048 s, 922 m, 861 m, 820 m, 759 m, 699 s, 597 m.

MS, m/z (relative intensity, %): 360 (17), 359 (M⁺, 64), 226 (44), 134 (25), 133 (100), 105 (38), 104 (17), 79 (14), 77 (14).

HRMS (DART⁺, [M+H]⁺) Calcd for C₂₄H₂₆NO₂: 360.1958. Found: 360.1964.

***4*-(*tert*-Butyl)-*N*-((4-methoxyphenyl)(phenyl)methyl)benzamide (2cag).**



White solid (31.8 mg, 31%). R_f 0.60 (SiO₂, Hexane/EtOAc = 1/1). Mp 180.1-181.3 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 1.33 (s, 9H), 3.79 (d, 3H), 6.40 (d, J = 7.3 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 6.85-6.89 (m, 2H), 7.12-7.22 (m, 2H), 7.27-7.36 (m, 5H), 7.43-7.46 (m, 2H), 7.74-7.77 (m, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 31.13, 34.91, 55.29, 56.77, 114.05, 125.54, 126.85, 127.33, 127.41, 128.65, 128.73, 131.33, 133.72, 141.70, 155.18, 158.91, 166.31.

IR (KBr): 3310 s, 2964 s, 2870 m, 1636 s, 1614 m, 1540 s, 1508 s, 1321 m, 1248 s, 1176 s, 1114 m, 1031 s, 853 s, 837 s, 800 m, 744 m, 696 s, 675 s, 621 m, 594 m, 546 m.

MS, m/z (relative intensity, %): 374 (27), 373 (M⁺, 100), 212 (58), 197 (20), 196 (10), 162 (14), 161

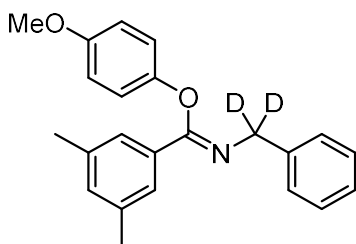
(97), 153 (12), 146 (14), 134 (13), 118 (25), 109 (14), 105 (17), 104 (29), 91 (19), 77 (12).

HRMS (DART+, [M+H]⁺) Calcd for C₂₅H₂₈NO₂: 374.2115. Found: 374.2116.

X. Kinetic Studies

X-1. Synthesis of 1cad-d₂.

This compound was prepared according to General Procedure A using amide derived from benzylamine-d₂.



4-Methoxyphenyl 3,5-dimethyl-N-(phenylmethyl-d₂)benzimidate (1cad-d₂). The product was obtained as a mixture of geometrical isomers (*E*:*Z* = 1:5.2), which was determined by ¹H NMR.

Colorless oil (1.02 g, 65%, 97%D). R_f 0.62 (NH silica, Hexane/EtOAc = 1/1).

Major isomer

¹H NMR (CDCl₃, 400 MHz) δ: 2.27 (s, 6H), 3.73 (s, 3H), 6.75-6.79 (m, 2H), 6.82-6.86 (m, 2H), 7.01 (s, 1H), 7.15-7.18 (m, 1H), 7.23-7.26 (m, 1H), 7.31-7.41 (m, 4H), 7.45 (s, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ: 21.20, 51.20 (m), 55.57, 114.83, 117.15, 126.49, 126.60, 127.89, 128.31, 132.43, 132.84, 137.83, 139.87, 149.43, 154.80, 154.86.

Minor isomer

¹H NMR (CDCl₃, 400 MHz) δ: 2.36 (s, 6H), 3.80 (s, 3H), 6.90-6.92 (m, 2H), 7.10-7.12 (m, 3H). Other peaks are overlapped with those of a major isomer.

¹³C NMR (CDCl₃, 101 MHz) δ: 21.30, 55.51, 114.19, 122.99, 125.76, 126.25, 126.81, 128.13, 131.05, 131.59, 138.14, 140.86, 146.84, 156.34, 161.87.

E/Z Mixture

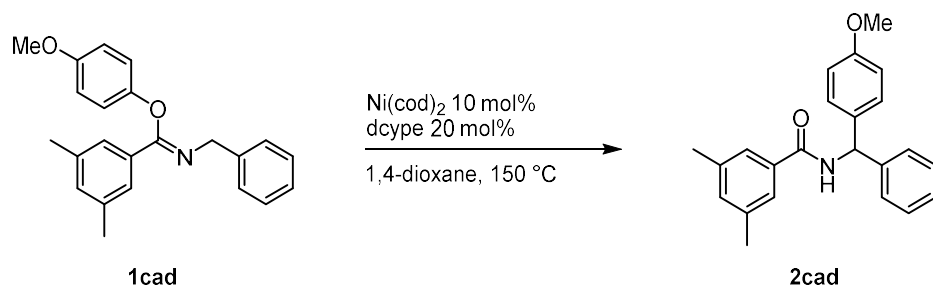
²H-NMR (CHCl₃, 61.37 MHz) δ: 4.56 (minor), 4.73 (major).

IR (KBr): 2949 w, 2914 w, 1654 m, 1604 w, 1503 s, 1447 w, 1316 w, 1243 w, 1206 m, 1186 s, 1102 w, 1035 m, 823 w, 714 w.

MS, *m/z* (relative intensity, %): 347 (M⁺, 3), 225 (12), 224 (59), 123 (14), 94 (47), 93 (100), 92 (33), 66 (10).

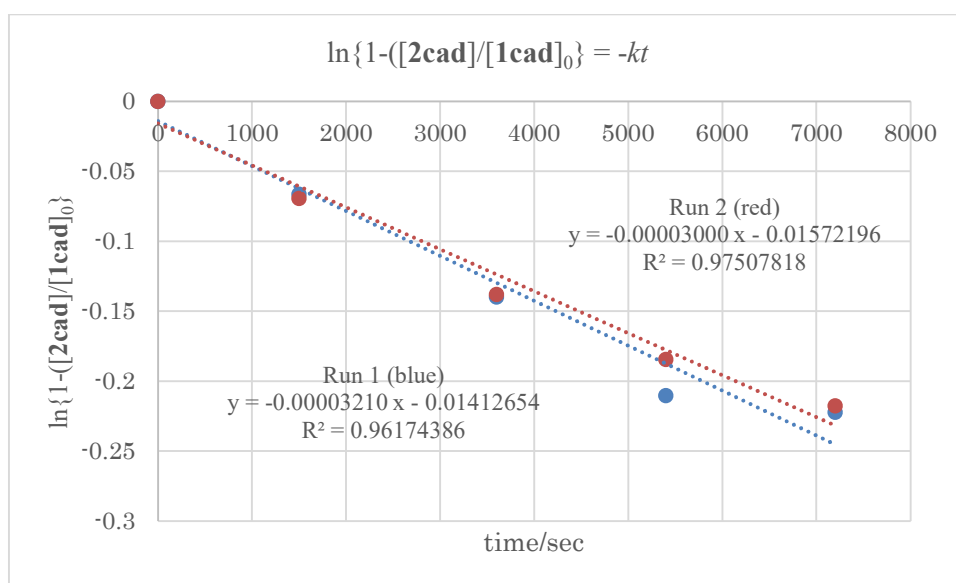
HRMS (DART+, [M+H]⁺) Calcd for C₂₃H₂₂D₂NO₂: 348.1927. Found: 348.1936.

X-2. Kinetic studies

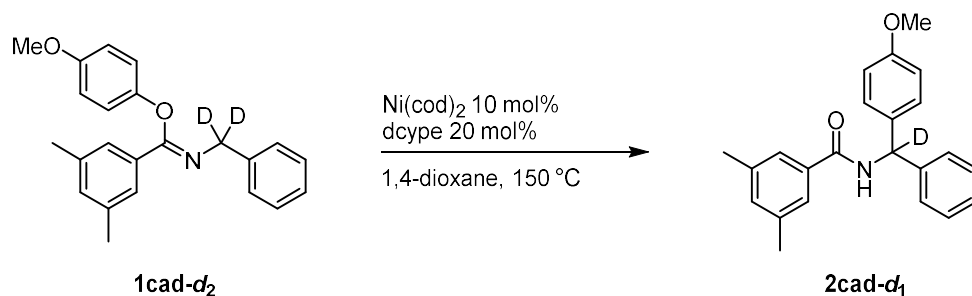


In a glovebox filled with nitrogen, imidate **1cad** (210.4 mg, 0.6 mmol), Ni(cod)₂ (16.2 mg, 0.06 mmol), dcype (51.4 mg, 0.12 mmol) and 1,4-dioxane (4.5 mL) were added to a 30 mL pressure-resistant vial and it was closed with a resealable septum. The mixture was stirred at 150 °C. An aliquot of the crude reaction mixture was taken through the septum using a syringe at the indicated time, was diluted with EtOAc and was analyzed by GC. The yields of **1cad** and **2cad** were determined based on the calibration curves. The same experiment was repeated twice.

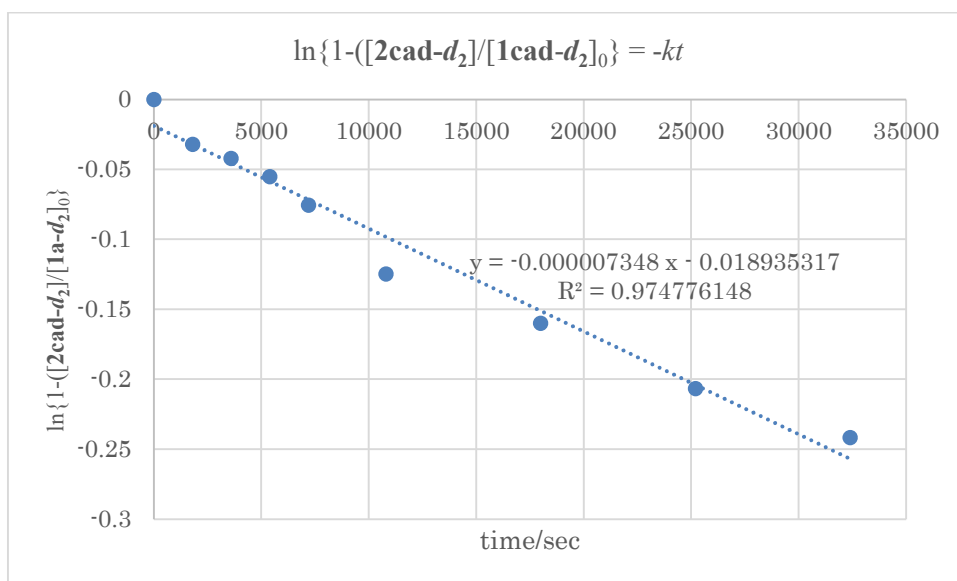
Time / s	Run 1			Run 2		
	GC yields (%)		$\ln\{1-[2\text{cad}]/[1\text{cad}]_0\}$	GC yields (%)		$\ln\{1-[2\text{cad}]/[1\text{cad}]_0\}$
	1cad	2cad		1cad	2cad	
0	98	0	0	96	0	0
1500	74	6	-0.0665	74	6	-0.0694
3600	71	13	-0.140	65	12	-0.138
5400	59	18	-0.210	59	16	-0.184
7200	49	20	-0.222	53	19	-0.218



The same experiment was conducted using **1cad-d₂** (213.2 mg, 0.61 mmol) as the substrate. The results are summarized below.



Time / s	GC yields (%)		$\ln\{1-[2cad-d_1]/[1cad-d_2]_0\}$
	1cad-d₂	2cad-d₁	
0	97	0	0
1800	82	3	-0.0320
3600	79	4	-0.0421
5400	75	5	-0.0552
7200	71	7	-0.0754
10800	63	11	-0.125
18000	53	14	-0.160
25200	54	18	-0.207
32400	46	21	-0.241

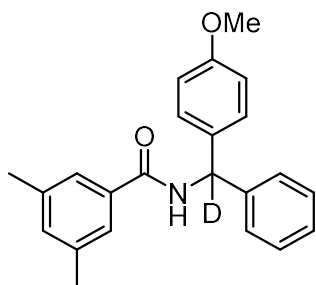


The reaction of **2cad** and **2cad-d₂** followed first-order kinetics with respect to the concentration of the

substrate. Rate constants for these reactions, which were determined by the slopes obtained in the $\ln(1 - ([\text{substrate}])/[\text{starting material}]_0)$ vs time plot shown above, were summarized in the following table. The kinetic isotope effect ($k_{\text{H}}/k_{\text{D}}$) was determined to be 4.2, indicating that the C–H bond cleavage process is involved in the turnover-limiting step in this catalytic reaction.

	$k_{\text{obs}} / \text{s}^{-1}$ (Run 1)	$k_{\text{obs}} / \text{s}^{-1}$ (Run 2)	Average	KIE
1a	3.21×10^{-5}	3.00×10^{-5}	3.11×10^{-5}	4.2
1a-<i>d</i>₂	7.35×10^{-6}	--	7.35×10^{-6}	

N*-((4-Methoxyphenyl)(phenyl)methyl-*d*)-3,5-dimethylbenzamide (**2cad-*d).**



White solid (58.6 mg, 94%D). R_f 0.52 (SiO₂, Hexane/EtOAc = 1/1). Mp 161.4-162.0 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.34 (s, 6H), 3.78 (s, 3H), 6.64 (s, 1H), 6.87 (d, J = 7.8 Hz, 2H), 7.12 (s, 1H), 7.20 (d, J = 8.5 Hz, 2H), 7.29-7.34 (m, 5H), 7.40 (s, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 21.19, 55.24, 56.39 (d, J = 20.6 Hz, **2cad-*d***), 56.71 (**2cad**), 113.91, 114.01, 124.73, 127.34, 128.61, 128.74, 133.19, 133.66, 134.22, 138.27, 141.64, 158.89, 166.75.

²H-NMR (CHCl₃, 61.37 MHz) δ : 6.39.

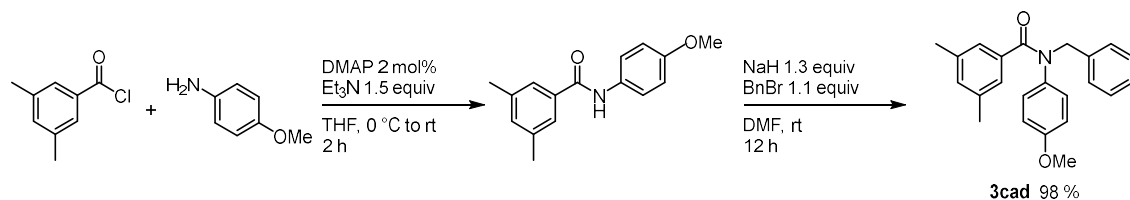
IR (KBr): 3335 s, 3054 w, 3004 w, 2918 m, 2838 w, 1628 s, 1600 s, 1531 s, 1512 s, 1465 m, 1298 m, 1246 s, 1182 m, 1035 s, 911 m, 861 m, 797 w, 764 w, 726 m, 701m, 644 w, 618 w, 582 m, 570 m.

MS, m/z (relative intensity, %): 347 (28), 346 (M⁺, 51), 214 (13), 213 (32), 198 (10), 134 (38), 133 (100), 105 (42), 104 (14), 79 (16), 77 (16).

HRMS (DART⁺, [M+H]⁺) Calcd for C₂₃H₂₃DNO₂: 347.1864. Found: 347.1867.

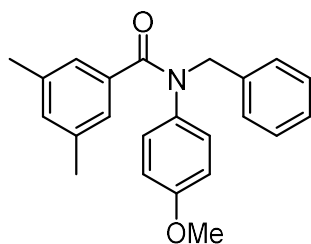
XI. The reaction of 3cad under Typical Procedure

XI-1. Synthesis of 3cad.³



3,5-Dimethylbenzoyl chloride (1.71 g, 10.1 mmol) was added at 0 °C to a solution of 4-methoxyaniline (1.41 g, 11.4 mmol), Et₃N (2.0 mL, 14.3 mmol) and DMAP (24.8 mg, 0.20 mmol) in THF (20 mL). The mixture was then allowed to warm to room temperature, and stirred for 2 h. The mixture was quenched with 1 M HCl(aq) and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure to afford corresponding amide (white solid), which was used in the next step without further purification. Benzyl bromide (2.20 g, 12.9 mmol) was added to a solution of NaH (60 % dispersion in paraffin liquid, 0.55 g, 13.3 mmol) and the amide in DMF (40 mL). After the addition was complete, the reaction mixture was stirred at rt for 12 h. The mixture was quenched with sat. NaHCO₃(aq) and extracted with hexane/Et₂O = 1/1 (240 mL). The combined organic layers were washed three times with water (240 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (eluent: hexane/EtOAc = 4/1 to 3/2) to give *N*-Benzyl-*N*-(4-methoxyphenyl)-3,5-dimethylbenzamide (**3cad**) as a colorless oil (3.43 g, 98%).

N-Benzyl-*N*-(4-methoxyphenyl)-3,5-dimethylbenzamide (**3cad**).



Colorless oil. R_f 0.48 (SiO₂, Hexane/EtOAc = 1/1).

¹H NMR (CDCl₃, 400 MHz) δ: 2.11 (s, 6H), 3.58 (s, 3H), 5.05 (s, 2H), 6.59 (d, *J* = 8.7 Hz, 2H), 6.78 (br, 3H), 6.94 (s, 2H), 7.16–7.29 (m, 5H).

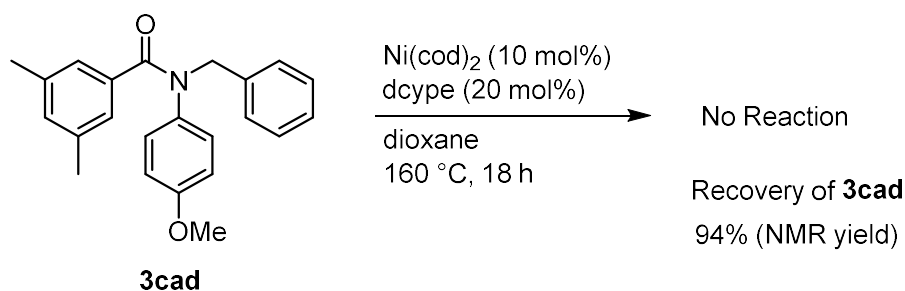
¹³C NMR (CDCl₃, 101 MHz) δ: 20.79, 53.53, 54.86, 113.69, 126.11, 126.96, 128.10, 128.25, 128.60, 130.74, 135.79, 135.92, 136.80, 137.39, 157.59, 170.59.

IR (KBr): 3031 m, 3005 m, 2918 m, 2837 w, 1640 s, 1604 s, 1584 m, 1510 s, 1440 s, 1389 s, 1325 s, 1298 m, 1249 s, 1212 m, 1180 m, 1108 w, 1080 w, 1029 m, 979 w, 890 w, 858 m, 837 s, 778 w, 755 s, 728 m, 701 s, 623 m, 553 m, 541 m.

MS, m/z (relative intensity, %): 346 (M^+ , 25), 345 (82), 344 (15), 212 (59), 196 (10), 134 (30), 133 (100), 105 (78), 103 (17), 91 (56), 79 (29), 77 (27), 65 (10).

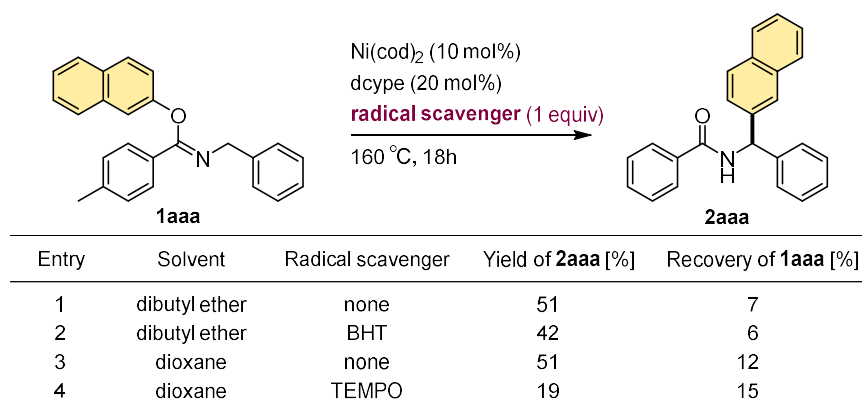
HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{24}NO_2$: 346.1802. Found: 346.1811.

XI-2. The reaction of **3cad** under Typical Procedure



Yields were determined by 1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. This result rules out the 1,3 aryl shift pathway ($1cad \rightarrow 3cad \rightarrow 2cad$) during the 1,4 aryl shift reaction ($1cad \rightarrow 2cad$).

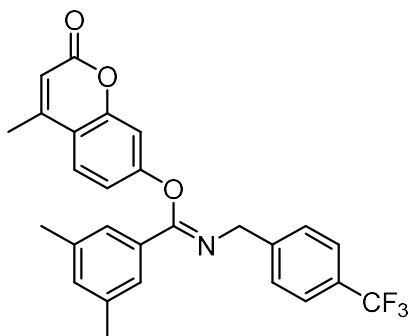
XII. The reaction of **1aaa** with radical scavengers



To rule out the radical pathway, the reaction was performed with radical scavengers. In a glovebox filled with nitrogen, aryl *N*-benzylimidate **1aaa** (73.5 mg, 0.21 mmol), $Ni(cod)_2$ (5.5 mg, 0.020 mmol), dcype (16.9 mg, 0.040 mmol), radical scavengers (1 equiv) and solvent (1.5 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 160 °C for 18 h. Yields were determined by GC using pentadecane as an internal standard. In the presence of a radical scavenger, the reaction still proceeded, indicating that a radical pathway is unlikely.

XIII. Synthetic Applications

4-Methyl-2-oxo-2*H*-chromen-7-yl (3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1nbd).



This imidate was synthesized according to the general procedure A using 4-methylumbelliferone (1.06 g, 6.0 mmol), except that the solvent was CHCl_3 . This compound was obtained as a mixture of geometrical isomers ($E:Z = 1:9.5$), which was determined by ^1H NMR.

White solid (1.98 g, 85%). R_f 0.72 (NH silica, Hexane/EtOAc = 1/1). Mp 52.2–55.5 °C.

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.30 (s, 6H), 2.38 (d, $J = 0.92$ Hz, 3H), 4.75 (s, 2H), 6.17 (d, $J = 1.4$ Hz, 1H), 6.86–6.89 (m, 2H), 7.08 (s, 1H), 7.47 (s, 2H), 7.49–7.52 (m, 3H), 7.59 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 18.64, 21.20, 51.35, 104.24, 112.56, 113.07, 115.28, 124.20 (q, $J = 272.2$ Hz), 125.31 (q, $J = 3.8$ Hz), 126.23, 127.92, 129.04 (q, $J = 32.3$ Hz), 131.52, 133.32, 138.35, 143.36, 152.07, 153.54, 154.98, 157.85, 160.61.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 2.39 (s, 6H), 2.45 (d, $J = 1.4$ Hz, 3H), 4.63 (s, 2H), 6.26 (d, $J = 1.4$ Hz, 1H), 7.15 (s, 3H), 7.20–7.23 (m, 1H), 7.27–7.29 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 18.74, 21.29, 53.25, 110.81, 113.92, 116.99, 118.87, 125.05, 125.67, 127.02, 129.92, 132.23, 138.49, 144.35, 152.21, 154.30, 156.03, 160.86, 161.33. Other peaks are overlapped with those of a major isomer.

E/Z Mixture

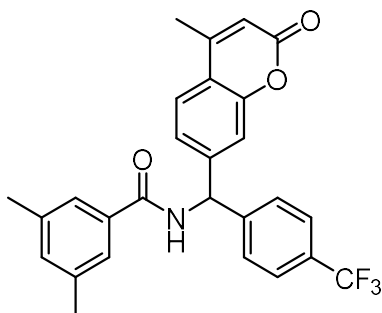
^{19}F NMR (CDCl_3 , 376 MHz) δ : –63.62.

IR (KBr): 3058 w, 2920 m, 2868 w, 1734 s, 1666 s, 1610 s, 1564 m, 1505 m, 1418 s, 1387 s, 1325 s, 1267 s, 1133 s, 1066 s, 1016 s, 851 s, 821 s, 685 m.

MS, m/z (relative intensity, %): 465 (M^+ , 9), 134 (10), 133 (100), 105 (24).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{27}\text{H}_{23}\text{F}_3\text{NO}_3$: 466.1625. Found: 466.1636.

3,5-Dimethyl-*N*-((4-methyl-2-oxo-2*H*-chromen-7-yl)(4-(trifluoromethyl)phenyl)methyl)benzamide (2nbd).



The typical procedure was followed using **1nbd** (96.8 mg, 0.21 mmol).

White solid (49.5 mg, 51%). R_f 0.32 (SiO₂, Hexane/EtOAc = 1/1). Mp 208.3-210.3 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 2.35 (s, 6H), 2.42 (d, J = 0.92 Hz, 3H), 6.25 (d, J = 0.92 Hz, 1H), 6.55 (d, J = 7.8 Hz, 1H), 6.89 (d, J = 7.3 Hz, 1H), 7.16 (s, 1H), 7.24 (dd, J = 8.2, 1.8 Hz, 1H), 7.30 (d, J = 1.4 Hz, 1H), 7.42-7.45 (m, 4H), 7.59 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 8.2 Hz, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 18.64, 21.21, 56.73, 115.09, 115.53, 119.39, 123.69, 123.83 (q, J = 272.2 Hz), 124.82, 125.16, 125.96 (q, J = 3.8 Hz), 128.02, 130.29 (q, J = 32.6 Hz), 133.33, 133.73, 138.50, 144.32, 145.13, 152.07, 153.74, 160.52, 167.17.

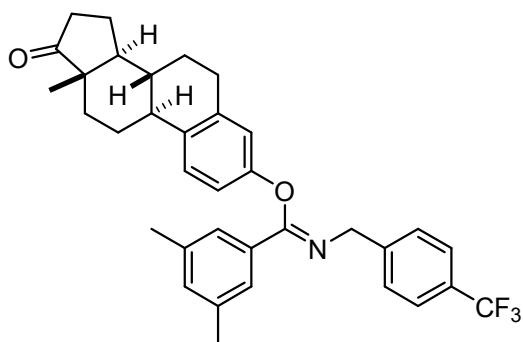
¹⁹F NMR (CDCl₃, 376 MHz) δ : -63.90.

IR (KBr): 3248 s, 3064 m, 1723 s, 1634 s, 1602 s, 1539 s, 1417 m, 1386 m, 1327 s, 1176 m, 1115 s, 1069 m, 1017 m, 888 m, 861 s, 819 m, 750 m, 712 s, 683 m.

MS, m/z (relative intensity, %): 465 (M⁺, 30), 332 (16), 134 (31), 133 (100), 105 (31).

HRMS (DART⁺, [M+H]⁺) Calcd for C₂₇H₂₃F₃NO₃: 466.1625. Found: 466.1619.

13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 3,5-dimethyl-*N*-(4-(trifluoromethyl)benzyl)benzimidate (1obd).



This imidate was synthesized according to the general procedure A using estrone (1.18 g, 4.4 mmol, 1.1 equiv), except that the solvent was CHCl₃. The product was obtained as a mixture of geometrical isomers ($E:Z$ = 1:8.3), which was determined by ¹H NMR.

White solid (1.21 g, 54%). R_f 0.76 (NH silica, Hexane/EtOAc = 1/1). Mp 74.4-78.2 °C.

Major isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 0.90 (s, 3H), 1.37-1.66 (m, 7H), 1.93-2.22 (m, 5H), 2.30 (s, 6H), 2.47-2.54 (m, 1H), 2.79-2.81 (m, 2H), 4.72 (s, 2H), 6.62 (d, J = 2.8 Hz, 1H), 6.72 (dd, J = 8.2, 2.8 Hz, 1H), 7.06 (s, 1H), 7.17 (d, J = 8.7 Hz, 1H), 7.49-7.52 (m, 4H), 7.56-7.58 (m, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 13.81, 21.24, 21.52, 25.74, 26.31, 29.44, 31.48, 35.81, 38.05, 43.93, 47.92, 50.33, 51.36, 113.33, 115.74, 124.28 (q, J = 272.2 Hz), 125.17 (q, J = 3.8 Hz), 126.32, 126.81, 127.96, 128.80 (q, J = 31.6 Hz), 132.64, 132.84, 134.03, 138.00, 138.45, 144.03, 153.31, 155.10, 220.84.

Minor isomer

^1H NMR (CDCl_3 , 400 MHz) δ : 0.93 (s, 3H), 2.37 (s, 6H), 2.93-2.95 (m, 2H), 4.61 (s, 2H), 6.97-6.98 (m, 1H), 7.11 (s, 3H), 7.29-7.33 (m, 3H). Other peaks are overlapped with those of a major isomer.

^{13}C NMR (CDCl_3 , 101 MHz) δ : 21.30, 26.44, 31.53, 44.16, 47.97, 50.41, 53.22, 119.38, 122.06, 125.04 (q, J = 3.8 Hz), 125.68, 126.16, 127.00, 130.81, 131.81, 136.17, 137.62, 138.28, 145.14, 151.07, 162.43. Other peaks are overlapped with those of a major isomer.

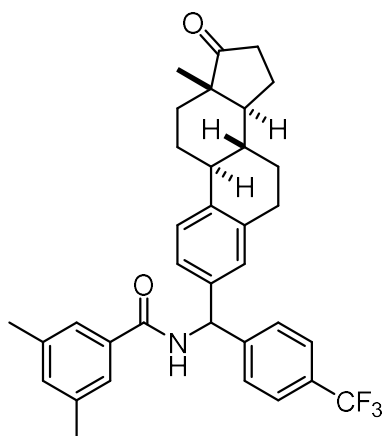
E/Z Mixture

^{19}F NMR (CDCl_3 , 376 MHz) δ : -63.56.

IR (KBr): 2929 m, 2865 m, 1740 s, 1659 m, 1605 m, 1493 m, 1455 w, 1417 m, 1324 s, 1229 m, 1161 s, 1122 s, 1066 s, 1018 m, 820 m.

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{35}\text{H}_{37}\text{F}_3\text{NO}_2$: 560.2771. Found: 560.2781.

3,5-Dimethyl-*N*-((14-methyl-15-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)(4-(trifluoromethyl)phenyl)methyl)benzamide (2obd).



The typical procedure was followed using **1nbd** (111.8 mg, 0.20 mmol).

White solid (66.1 mg, 59%). R_f 0.48 (SiO_2 , Hexane/EtOAc = 1/1). M.p. 142.7-144.4 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 0.90 (s, 3H), 1.41-1.68 (m, 6H), 1.95-2.18 (m, 4H), 2.26-2.54 (m, 8H),

2.47–2.54 (m, 1H), 2.87–2.90 (m, 2H), 6.39 (d, $J = 7.8$ Hz, 1H), 6.69 (d, $J = 7.3$ Hz, 1H), 7.00–7.01 (m, 1H), 7.03–7.05 (m, 1H), 7.15 (s, 1H), 7.29 (d, $J = 8.2$ Hz, 1H), 7.41 (s, 2H), 7.44 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 13.77, 21.20, 21.51, 25.61, 26.33, 29.39, 31.48, 35.78, 37.96, 44.28, 47.89, 50.39, 56.96, 124.05 (q, $J = 271.9$ Hz), 124.74, 124.94, 125.03, 125.56 (q, $J = 4.2$ Hz), 126.01, 127.48, 128.34, 128.43, 129.48 (q, $J = 32.5$ Hz), 133.44, 133.76, 137.26, 138.14, 138.37, 139.65, 145.53, 166.87, 220.77.

^{19}F NMR (CDCl_3 , 376 MHz) δ : –63.71.

IR (KBr): 3311 m, 2929 m, 2863 m, 1737 s, 1639 s, 1603 s, 1522 s, 1472 m, 1455 m, 1411w, 1324 s, 1240 m, 1163 s, 1123 s, 1068 s, 1017 m, 862 m, 822 m, 757 s.

HRMS (DART⁺, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{35}\text{H}_{37}\text{F}_3\text{NO}_2$: 560.2771. Found: 560.2762.

1.5. References

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For Experimental Section

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Chapter 2

Controlled Degradation of Chemically Stable Poly(Aryl Ethers) via Directing Group-Assisted Catalysis

2.1. Introduction

Serious concerns about the long-term environmental impact caused by plastic pollution are prompting us to transition away from single-use plastics toward a more sustainable and circular polymer economy.¹ To this end, mechanical recycling has been implemented on an industrial scale. However, the physical properties of the recycled materials are frequently compromised compared to the original ones, and mechanical recycling cannot be universally applied to all plastics.² A more ideal approach is chemical recycling, wherein polymers are transformed back into monomers or other well-defined small molecules that could subsequently be repolymerized.³ Although this approach is appealing in principle, successful examples have primarily been limited to the polymers that contain chemically labile bonds in their main chains encompassing esters,⁴ acetals,⁵ disulfides,⁶ and silyl ethers⁷ (Figure 2.1a). Polymers that consist of strong covalent bonds, such as C–C or C(aryl)–O bonds, often exhibit high robustness, which in turn makes depolymerization into monomers a challenge due to the lack of mild methods that could be used to cleave these bonds. Therefore, only a limited array of techniques has been documented for depolymerizing such polymers. For instance, polyolefins may be depolymerized by heating above the ceiling temperature (T_{ceiling}), which is defined as the temperature at which the rates of polymerization and depolymerization of these polymers are equal. However, the T_{ceiling} for common robust polyolefins exceeds 400 °C,⁸ which poses difficulties in controlling degradation into well-defined monomers. Alternatively, multi-step post-polymerization modifications⁹ such as C–H oxidation¹⁰ and dehydrogenation¹¹ have been employed to promote the cleavage of C–C bonds in polymer backbones. These methods, however, also tend to yield a mixture of products that are unsuitable for repolymerization.

Herein, we introduce a directing group (DG) that serves as a design principle for depolymerizable polymers devoid of labile chemical bonds in their main chain (Figure 2.1b). DG is a heteroatom-containing functional group that coordinates to a transition metal catalyst to facilitate the cleavage of strong covalent bonds by forming a stable metalacyclic intermediate.¹² DGs are strategically used to develop catalytic reactions that involve the activation of strong σ -bonds in low molecular weight compounds.¹³ Surprisingly, however, the DG strategy has not been exploited for the cleavage of the main chain of polymeric materials. It is noteworthy that a DG does not fundamentally alter the thermal and chemical stability of neighboring covalent bonds but rather promotes their cleavage only in the presence of a suitable catalyst. Therefore, the robust nature of parent polymers is anticipated to be preserved with the introduction of DGs.

As a proof-of-concept study, the author's investigation focuses on assessing the impact of a DG on the depolymerization of polymers containing a phenylene ether unit, because it has been demonstrated that cleavage of the C(aryl)–O bond can be accelerated by a directing group (DG) in a nickel-catalyzed process.¹⁴ Phenylene ethers serve as crucial structural motifs in several durable polymers, notably, poly(phenylene ether)s (PPEs) and poly(ether ether ketone)s (PEEKs). While previous studies have reported the direct depolymerization of these materials using heterogeneous catalysts,¹⁵ chemical oxidation,¹⁶ or nucleophilic aromatic substitution methods,¹⁷ the resultant degraded products were obtained in forms that were unsuitable for straightforward repolymerization into the parent phenylene ether-based polymers. Herein, we demonstrate that a DG strategy enables the development of phenylene ether-based polymers capable of undergoing degradation to yield well-defined low-molecular-weight compounds, which can subsequently be repolymerized into the parent polymers.

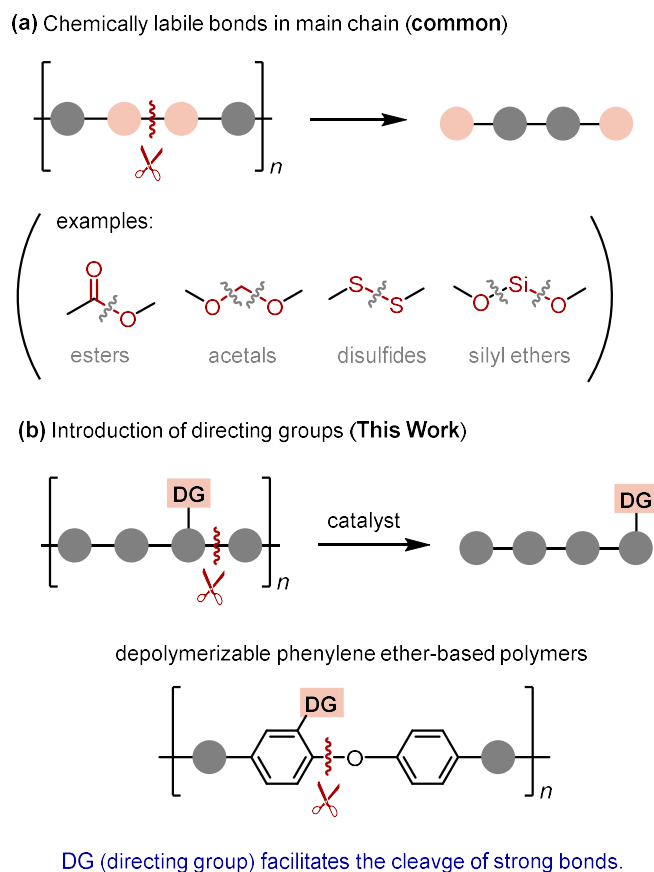


Figure 2.1. Strategies for the Design of Depolymerizable Polymers.

2.2. Results and Discussion

Preparation of DG-installed polymers. The study was initiated by investigating the effect of directing groups (DGs) on the efficiency of the catalytic cleavage of a C(aryl)–O bond in model monomeric substrates **1** (Figure S2.1). Building upon previous studies,^{14a} diphenyl ether derivatives **1a–d** were reacted with HSiMe(OMe)₂ (reductant) in the presence of Ni(cod)₂ (a catalyst precursor) and PCy₃ (a ligand) in toluene at 80 °C for 18 h. Although the reaction did not occur when a substrate had no DG (Entry 1), the introduction of 2-pyridyl (Entry 2), ester (Entry 3) and amide (Entry 4) groups facilitated the reductive cleavage of C(aryl)–O bonds to form **2**, with a 2-pyridyl group being the most effective. Therefore, we decided to employ a 2-pyridyl group as the DG for the development of depolymerizable polymers. A PPE-based polymer bearing a 2-pyridyl group (**DG-PPE**) was synthesized by polycondensation via nucleophilic aromatic substitution (S_NAr) using an initiator (Figure 2.2a).¹⁸ Thus, the reaction of 4-fluorophenol derivative **3** in the presence of KH (1.0 equiv, base) and 4,4'-difluorobenzophenone (0.63 mol%, initiator) in NMP at 200 °C for 4 h afforded the desired **DG-PPE** in a 62% isolated yield upon reprecipitation from CHCl₃/MeOH. The relatively high dispersity of **DG-PPE** (*D* = 3.01) compared with the value reported in Yokozawa's work (*D* = 1.1) can be attributed to the higher polymerization temperature used in this study, which induced undesired main-chain cleavage as a side reaction (Figure S2.3). A PEEK-based polymer bearing a 2-pyridyl group (**DG-PEEK1**) was also synthesized using a similar method of polycondensation between hydroquinone derivative **4** and 4,4'-difluorobenzophenone derivative **5** in the presence of a catalytic amount of Cs₂CO₃ in NMP at 150–180 °C (Figure 2.2b).¹⁹ The polycondensation of bis(phenol) derivative **6** and difluoride **5** afforded a PEEK derivative that possesses fewer 2-pyridyl groups (one pyridine ring per two ether moieties for **DG-PEEK2** vs. one pyridine per one ether for **DG-PEEK1**, Figure 2.2c). All DG-installed polymers were characterized by ¹H and ¹³C NMR and MALDI-TOF MS (see Section 2.4, Experimental Section).

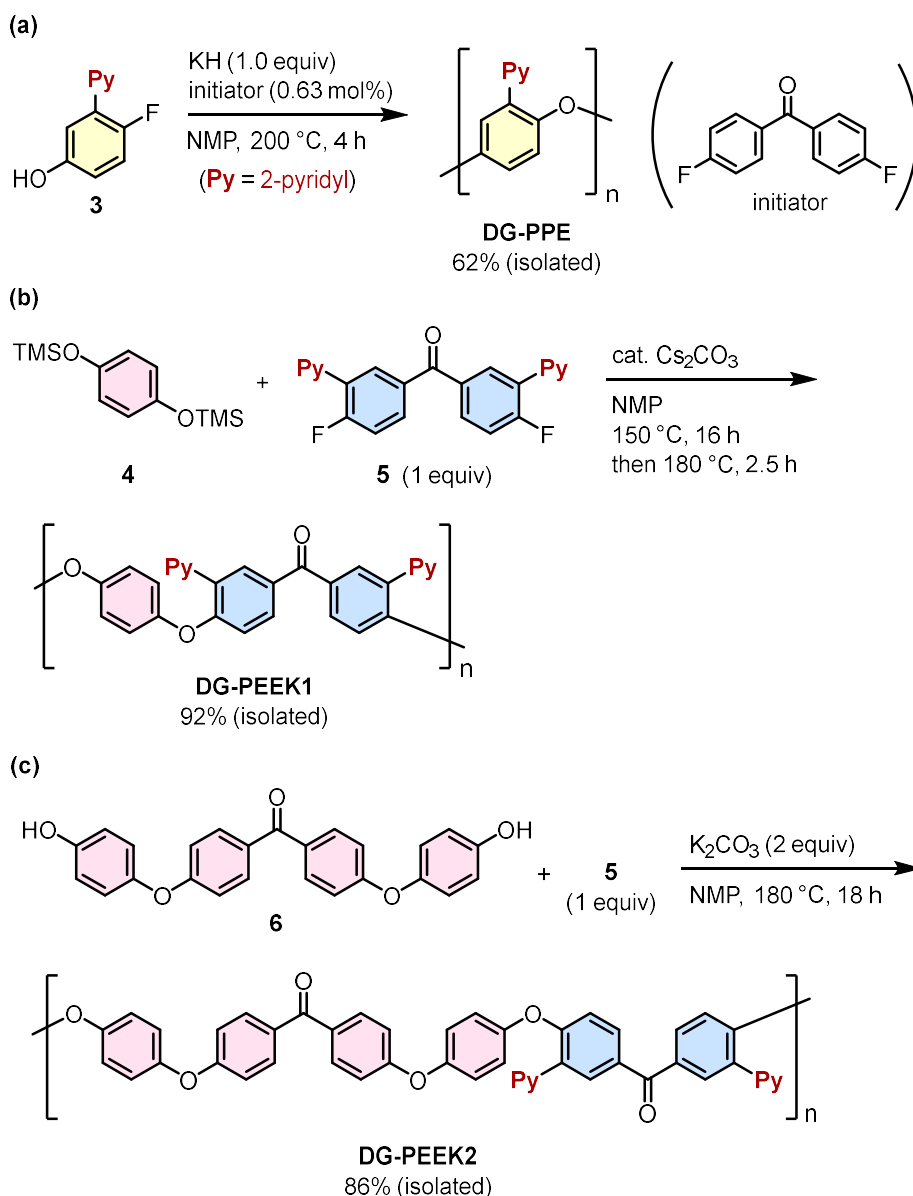


Figure 2.1. Synthesis of **DG-PPE**, **DG-PEEK1** and **DG-PEEK2**

Properties of DG-installed polymers. The physical properties of DG-installed polymers are summarized in Table 2.1. All DG-installed polymers exhibited notable thermal stability with high decomposition temperatures at 5% weight loss (T_{d5} = 399-465 °C). The T_{d5} values measured under air are comparable to those measured under nitrogen. **DG-PPE** displayed the transition temperature (T_g) of 143 °C, which is significantly higher than that reported for a parent PPE (83 °C).²⁰ Similarly, **DG-PEEK1** exhibited a markedly higher T_g value of 182 °C, showcasing that the introduction of DGs does not compromise the exceptional heat resistance of PEEK (T_g = 143 °C). **DG-PEEK2** also exhibited a comparable T_g value (172 °C), indicating that the feed ratio of DGs has minimal impact on thermal properties. None of the DG-installed polymers synthesized in this study exhibited discernible T_m

values. This departure from the behavior of the parent PPE ($T_m = 290\text{ }^{\circ}\text{C}$) and that of PEEK ($T_m = 344\text{ }^{\circ}\text{C}$) underscores the significant influence of the DG incorporation on polymer crystallinity.

The chemical stabilities of **DG-PPE** and **DG-PEEK1** were investigated through immersion in five distinct solutions for 24 h: aqueous HCl (12 M), aqueous NaOH (10 M), aqueous H₂O₂ (30%), AcOH and boiling water. SEC analysis of the recovered polymeric materials after neutralization revealed no change in molecular weight after these treatments (Figure 2.3a for **DG-PPE**; Figure 2.3b for **DG-PEEK1**). Additionally, minimal differences were observed in the FT-IR spectra before and after exposure to the solutions (Figure 2.3c for **DG-PPE**; Figure 2.3d for **DG-PEEK1**), indicating the stability of these polymers towards strong acids, bases, and oxidants.

Table 2.1. Properties of **DG-PPE**, **DG-PEEK1** and **DG-PEEK2**.

Entry	Polymer	M_w [kDa] ^a	$\bar{D}$ ^a	T_g [$^{\circ}\text{C}$] ^b	T_{d5} [$^{\circ}\text{C}$] ^c
1	DG-PPE	4.98	3.01	143	399 (419)
2	DG-PEEK1	27.2	1.81	182	465 (473)
3	DG-PEEK2	59.0	2.21	172	437 (451)
4	PPE ^d	--- ^e	--- ^e	83	(390) ^f
5	PEEK ^g	--- ^e	--- ^e	143	576

^a Weight average molecular weights and dispersities were determined by size-exclusion chromatography in CHCl₃ by comparison with low dispersity polystyrene standards.

^b Glass transition temperature as determined by DSC thermogram (exo up, 10 $^{\circ}\text{C}/\text{min}$, second run).

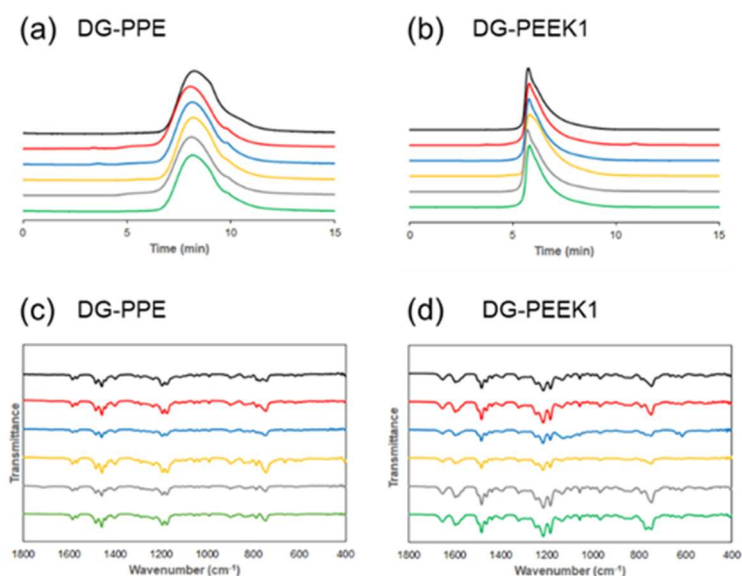
^c Decomposition temperature at 5% weight loss as determined by TGA thermogram (10 $^{\circ}\text{C}/\text{min}$ under nitrogen gas flow). The values in parentheses refer to those measured under air, unless otherwise noted.

^d Values for poly(*p*-phenylene oxide), which are cited from ref. 20.

^e Not determined due to insolubility in organic solvents at room temperature.

^f Decomposition temperature at 2% weight loss that was reported in ref. 20.

^g Values for a sample purchased from Aldrich (Cat. No. 456640).



^aSEC (a, b) and FT-IR (c, d) analysis measured after neutralization for polymer samples treated with the following solutions at rt for 24 h: black, none; red, HCl (12 M); blue, NaOH (10 M); orange, H₂O₂ (30%); gray, AcOH; green, boiling water.

Figure 2.3. Chemical Stability of **DG-PPE** and **DG-PEEK1**.^a

Controlled degradation of DG-installed polymers. Having confirmed the thermal and chemical stability of DG-introduced polymers **DG-PPE**, **DG-PEEK1** and **DG-PEEK2**, we next investigated their catalytic degradation. On the basis of model studies (Figure S2.1), nickel-catalyzed reductive degradation of these polymers with hydrosilane was investigated. The reaction of **DG-PPE** with HSiMe(OMe)₂ (2 equiv per monomer unit) in the presence of a Ni(cod)₂/PCy₃ catalyst in toluene at 80 °C for 18 h afforded phenol **7** in an isolated yield of 64% (Figure 2.4a). These nickel-catalyzed conditions were successfully applied to disassemble **DG-PEEK1**, selectively yielding hydroquinone component **8** and benzophenone component **9** in isolated yields of 78 and 87%, respectively (Figure 2.4b). Similarly, **DG-PEEK2** underwent degradation to afford **9** (80%) and **10** (68%) under analogous conditions (Figure 2.4c). Notably, the site-selective cleavage of C(aryl)–O bonds positioned ortho to the directing group occurred, while other C(aryl)–O bonds remained intact. The resultant structurally well-defined degraded products were converted back into the parent polymers in a few chemical steps (Figure 2.4d). For instance, phenol **7** was ortho-fluorinated to form **3** by palladium catalysis,²¹ which enabled its use in the polymerization of **DG-PPE**. Compound **9**, which was generated from the degradation of **DG-PEEK1** and **DG-PEEK2**, was transformed into fluorinated benzophenone **5** through oxidation and ortho-fluorination. Consequently, the straightforward recycling of **DG-PEEK1** was feasible by reacting **5** with a degraded product **8**. Similarly, **DG-PEEK2** was chemically recycled by oxidizing degraded product **10** into ketone **6**, which was followed by condensation with **5** (see

Section 2.4, Experimental Section). Of particular significance is the pivotal role played by the directing group in the ortho-fluorination step, as well as its contribution to the depolymerization process. This underscores the advantageous utilization of directing groups in the strategic design of recyclable polymers.

The method for depolymerizing DG-installed polymers exhibits remarkable specificity, and diverges from conventional approaches used for polymers containing labile chemical bonds, such as simple acids or bases. For example, polyethylene terephthalate (PET) undergoes efficient depolymerization under basic conditions (condition A, Figure 2.4e),²² whereas **DG-PEEK1** remains entirely stable under these circumstances. Conversely, the nickel-catalyzed conditions utilized for **DG-PEEK1** degradation (condition B, Figure 2.4e) exhibit no impact on PET, underscoring the selectivity of this catalyst system toward substrates featuring DGs. This orthogonal behavior bears significant advantages for the design of chemical recycling protocols, particularly when addressing polymer mixtures.

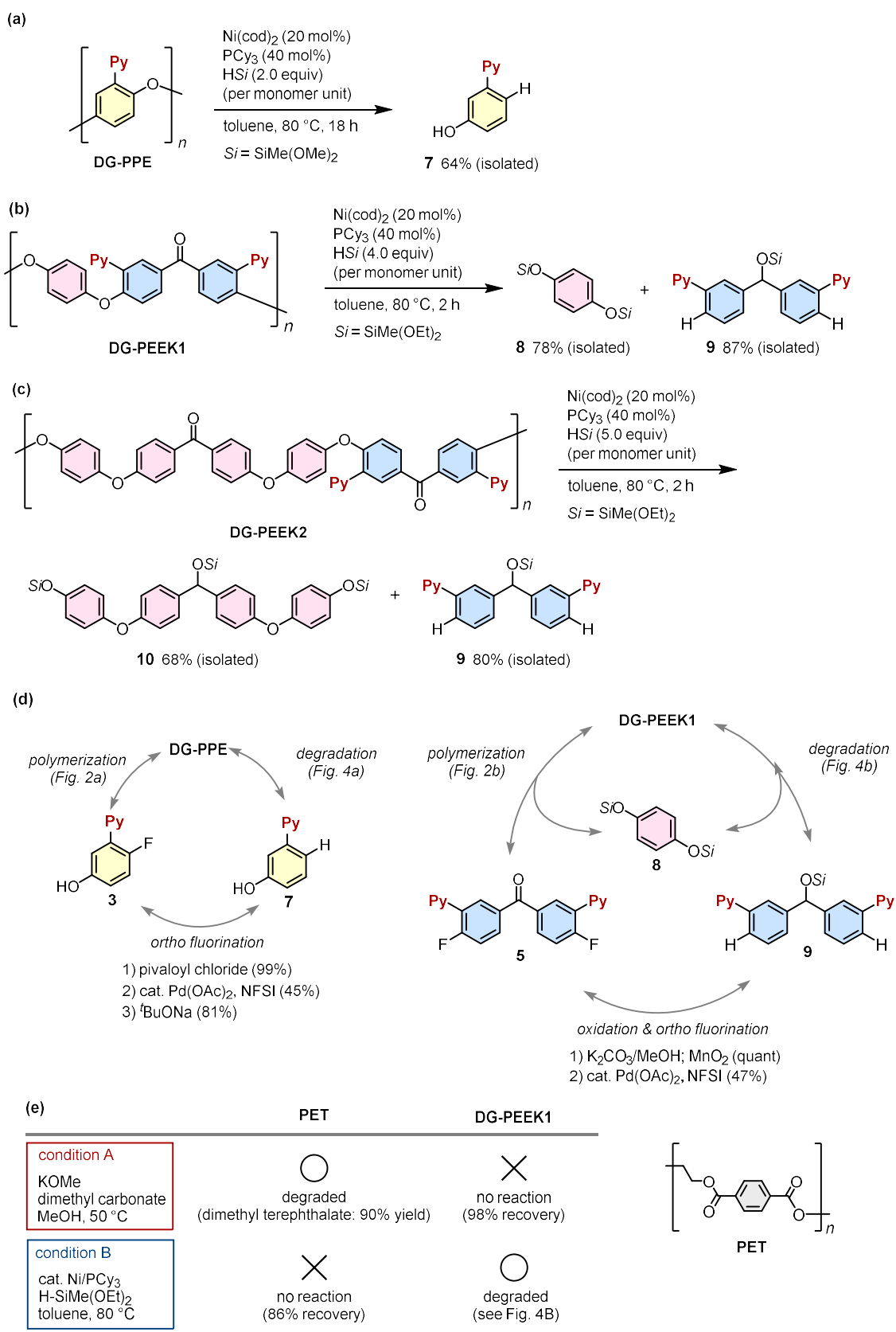


Figure 2.4. Controlled Degradation of DG-PPE and DG-PEEK1.

2.3. Conclusion

While the demand for polymer materials that could be depolymerized into monomers is on the rise, current design strategies are limited mostly to the incorporation of labile covalent bonds, such as esters, into their main chains. This work presented herein showcases a novel approach: polymers composed of strong covalent bonds can be selectively degraded into well-defined monomers by integrating the concept of a directing group. This directing group facilitates the cleavage of robust chemical bonds within the polymer's main chain through the formation of stable metalacyclic intermediates with transition metal catalysts. It is important to note that the introduction of pyridine directing groups did not compromise the chemical stability of the polymers in the absence of a catalyst, which shows promise as a potent strategy for designing robust polymers that are chemically recyclable. The application of this strategy to other resilient polymers is currently under investigation, which is expected to open new avenues for the design and recycling of sustainable materials.

2.4. Experimental Section

I. General Information

^1H , ^{13}C , ^{11}B and ^{19}F NMR spectra were recorded on a JEOL ECS-400 spectrometer in CDCl_3 . The chemical shifts in ^1H NMR spectra were recorded relative to CHCl_3 (δ 7.26) unless otherwise noted. The chemical shifts in ^{13}C NMR spectra were recorded relative to CDCl_3 (δ 77.0). The chemical shifts in ^{11}B NMR spectra were recorded relative to boron trifluoride diethyl etherate (δ 0.00). The chemical shifts in ^{19}F NMR spectra were recorded relative to hexafluorobenzene (δ -163.00). The data is reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer, JEOL JMS-700 or JEOL JMS-S3000. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-2014 gas chromatograph, equipped with a flame ionization detector. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with Biotage Isolera[®] equipped with Biotage[®] S_fär. Microwave synthesis was performed by Biotage[®] Initiator+. Analytical SEC was performed on a Hitachi High-Technologies Corporation L-2420/L-2130 equipped with a Shodex K-803L using chloroform (CHCl_3) as an eluent (40 °C, 1 ml/min) calibrated with polystyrene standards. Thermogravimetric analyses (TGA) were performed on a Hitachi High-Tech NEXTA STA200RV at 10 °C/min under N_2 flow. The glass transition temperatures (T_g) of the polymers were recorded on a Hitachi High-Tech NEXTA DSC2000.

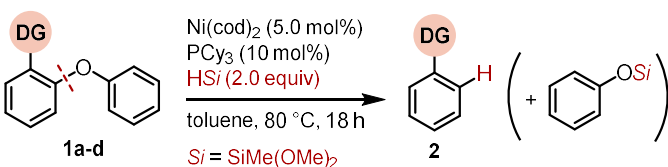
II. Materials

All commercially available reagents and solvents were supplied from TCI, WAKO, Aldrich and Strem Chemicals. Ni(cod)₂ was purchased from Strem Chemicals and used as received. PEEK (pellet forms) was purchased from Sigma–Aldrich Japan. 1,4-Bis((trimethylsilyl)oxy)benzene [CAS: 2117-24-0] was prepared from hydroquinone [CAS: 123-31-9] according to the literature method¹. Ethyl 2-phenoxybenzoate [CAS: 41755-76-4]², 2-(2-phenoxyphenyl)pyridine [CAS: 358741-46-5]³ and *N,N*-diethyl-2-phenoxybenzamide [CAS: 76279-43-1]⁴ were prepared according to the literature methods.

III. Effect of Directing Group in Ni-Catalyzed Reductive Cleavage of Model Substrate

Several functional groups have been tested as a directing group for use in Ni-catalyzed reductive cleavage of diphenyl ether derivatives.

A typical procedure: In a glovebox filled with nitrogen, diphenyl ether **1b** (58.3 mg, 0.24 mmol), HSiMe(OMe)₂ (54.8 mg, 0.52 mmol), Ni(cod)₂ (3.3 mg, 0.012 mmol), PCy₃ (6.7 mg, 0.024 mmol) and toluene (0.75 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 80 °C for 18 h. The resulting mixture was then evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 96/4 to 68/32) to give 2-phenylpyridine **2b** (74%).



Entry	DG	Yield of 2 ^[a] (%)	Recovered 1 (%)
1	H (1a)	0	89
2	2-pyridyl (1b)	74 ^[b]	0
3	CO ₂ Et (1c)	54	0
4	CONEt ₂ (1d)	27	48
5 ^[c]	2-pyridyl (1b)	0	>99
6 ^[d]	2-pyridyl (1b)	<5	>99
7 ^[e]	2-pyridyl (1b)	<5	>99
8 ^[f]	2-pyridyl (1b)	28	72

Figure S2.1. Effect of Directing Group in Ni-Catalyzed Reductive Cleavage of Model Substrate **1**.

^aThe yields were determined by GC analysis using dodecane as an internal standard.

^bIsolated yield.

^cWithout Ni(cod)₂.

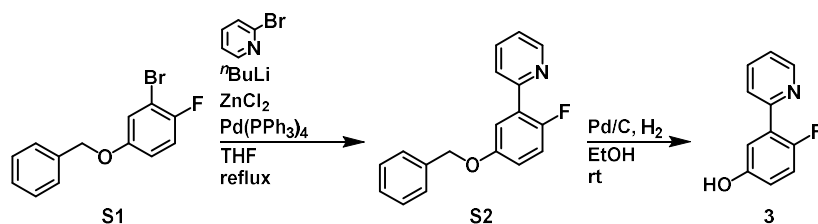
^dWithout PCy₃.

^eWithout HSiMe(OMe)₂.

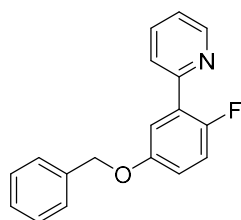
^fAt 40 °C.

IV. Preparation of Starting Materials

Synthesis of 4-fluoro-3-(pyridin-2-yl)phenol (**3**)



2-(5-(Benzyloxy)-2-fluorophenyl)pyridine (S2). This compound was synthesized using a literature procedure⁵, with minor modifications. **S1**⁶ (2.17 g, 7.7 mmol) was cooled to −78 °C in THF (12 mL) under N₂. ⁿBuLi (5.3 mL of a 1.6 M solution in hexane, 8.5 mmol) was added dropwise and stirred for 30 min. ZnCl₂ (5.29 g, 38.5 mmol) was cannulated into the reaction mixture as a THF solution (90 mL), and the mixture was stirred for an additional 30 min. 2-bromopyridine (1.52 g, 9.6 mmol) and Pd(PPh₃)₄ (428 mg, 5 mol%) were dissolved in THF (12 mL) and cannulated into the reaction mixture. The reaction mixture was degassed then refluxed for 16 hours. The reaction mixture was cooled to rt and diluted with water. After the removing THF in vacuum, The aqueous phase was extracted with EtOAc. The combined extracts were dried over Na₂SO₄ and concentrated. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 96/4 to 68/32) to give **S2** as a white solid (1.17 g, 54%).



White solid. R_f 0.43 (Hexane/EtOAc = 5/1). M.p. 99.4–100.2 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 8.72 (d, *J* = 4.6 Hz, 1H), 7.81–7.79 (m, 1H), 7.76–7.72 (m, 1H), 7.64 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.46–7.44 (m, 2H), 7.40–7.37 (m, 2H), 7.34–7.31 (m, 1H), 7.26–7.24 (m, 1H), 7.10–7.05 (m, 1H), 6.98–6.94 (m, 1H), 5.10 (s, 2H).

The chemical shifts in ¹H NMR spectra were recorded relative to tetramethylsilane (δ 0.00).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 155.1, 155.0 (d, $J = 242.5$ Hz), 153.1 (d, $J = 2.9$ Hz), 149.6, 136.8, 136.4, 128.5, 128.0, 127.7 (d, $J = 13.4$ Hz), 127.5, 124.5 (d, $J = 10.5$ Hz), 122.5, 117.3 (d, $J = 8.6$ Hz), 117.1 (d, $J = 25.9$ Hz), 115.5 (d, $J = 2.9$ Hz), 70.6.

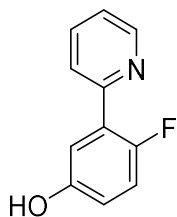
^{19}F NMR (CDCl_3 , 376 MHz) δ : -128.6 (s, 1F).

IR (KBr): 3071 w, 3033 w, 2950 w, 2876 w, 1584 s, 1569 m, 1501 s, 1460 s, 1442 s, 1406 s, 1383 s, 1328 s, 1292 m, 1269 m, 1254 m, 1240 m, 1222 s, 1195 s, 1006 s, 993 s, 904 m, 843 m, 816 s, 776 m, 754 s, 725 s, 696 s, 554 m.

MS, m/z (relative intensity, %): 280 (M^+ , 6), 279 (31), 92 (19), 91 (100), 65 (22).

HRMS (DART+, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{18}\text{H}_{15}\text{NOF}$: 280.1132. Found: 280.1137

4-Fluoro-3-(pyridin-2-yl)phenol (3). This compound was synthesized using a literature procedure⁵, with minor modifications. **S2** (2.31 g, 8.3 mmol), Pd/C (2.02 g, 0.83 mmol) and EtOH were added to a 500 mL round-bottom flask. The reaction mixture was flushed with H_2 and stirred for 16 h, then filtered through celite and rinsed with EtOAc. After removing the solvent in vacuo, the crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 90/10 to 20/80) to give **3** as a white solid (1.34 g, 86%).



White solid. R_f 0.50 (Hexane/EtOAc = 1/1). M.p. 150.0–151.1 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 8.71–8.69 (m, 1H), 7.82–7.77 (m, 2H), 7.52–7.49 (m, 1H), 7.33–7.28 (m, 1H), 7.05–7.00 (m, 2H), 6.84 (dt, $J = 8.7, 3.6$ Hz, 1H).

The chemical shifts in ^1H NMR spectra were recorded relative to tetramethylsilane (δ 0.00).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 154.0 (d, $J = 241.5$ Hz), 153.2 (d, $J = 1.9$ Hz), 153.1 (d, $J = 1.9$ Hz), 149.0, 137.3, 126.7 (d, $J = 14.4$ Hz), 125.3 (d, $J = 8.6$ Hz), 122.8, 118.0 (d, $J = 1.9$ Hz), 117.1 (d, $J = 24.9$ Hz), 117.0.

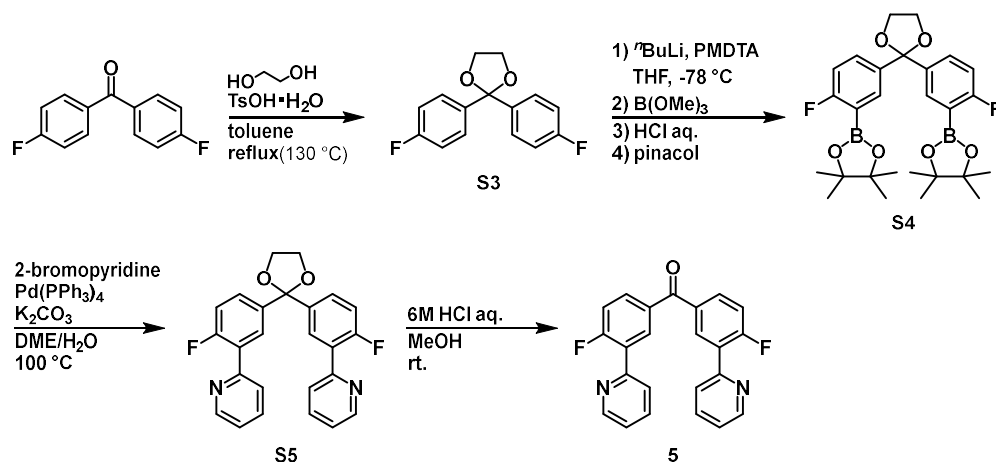
^{19}F NMR (CDCl_3 , 376 MHz) δ : -130.3 (s, 1F).

IR (KBr): 3081 br, 1615 m, 1593 s, 1566 m, 1508 s, 1471 s, 1454 s, 1423 s, 1354 s, 1327 m, 1256 m, 1237 s, 1227 s, 1202 s, 1155 m, 1059 m, 1001 m, 869 m, 828 m, 799 m, 792 m, 763 s, 751 s, 728 s, 714 m, 627 m, 611 m.

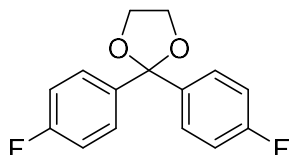
MS, m/z (relative intensity, %): 190 (14), 189 (M^+ , 100), 161 (43), 160 (13), 135 (30), 133 (14).

HRMS (DART+, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{11}\text{H}_9\text{NOF}$: 190.0663. Found: 190.0665

Synthesis of bis(4-fluoro-3-(pyridin-2-yl)phenyl)methanone (**5**)



2,2-Bis(4-fluorophenyl)-1,3-dioxolane (S3). CAS[1616861-44-9] This compound was synthesized using a literature procedure⁷, with minor modifications. 4,4'-Difluorobenzophenone (21.3 g, 97.7 mmol), ethylene glycol (27.6 g, 444.1 mmol), *p*-toluenesulfonic acid monohydrate (190 mg, 1.1 mmol) and toluene (100 mL) were added to a 300 mL round-bottom flask. The mixture was refluxed for 2 days with a Dean–Stark apparatus for azeotropic removal of H_2O . The resulting mixture was cooled to rt and washed with saturated aqueous solution of NaHCO_3 and with water. The aqueous phase was extracted with Et_2O twice. After drying the combined organic extracts with Na_2SO_4 and removing the solvent in vacuo, **S3** was obtained as a colorless oil (25.3 g, 99%). This compound was used in the next step without further purification.



Colorless oil. R_f 0.62 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 7.48–7.44 (m, 4H), 7.04–6.99 (m, 4H), 4.06 (s, 4H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 162.6 (d, $J = 247.3$ Hz), 137.7 (d, $J = 2.9$ Hz), 128.1 (d, $J = 7.7$ Hz), 115.0 (d, $J = 21.1$ Hz), 108.7, 64.9.

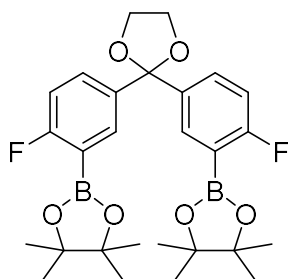
^{19}F NMR (CDCl_3 , 376 MHz) δ : -115.4 .

IR (KBr): 2979 w, 2893 w, 1604 m, 1507 s, 1269 w, 1223 s, 1155 m, 1080 s, 1014 m, 992 m, 946 m, 834 s, 602 w, 577 s, 545 w.

MS, m/z (relative intensity, %): 262 (M^+ , 14), 231 (18), 202 (14), 201 (54), 190 (31), 168 (73), 167 (100), 124 (28), 123 (100), 95 (94), 75 (31).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{F}_2$: 263.0878. Found: 263.0878.

2,2'-((1,3-Dioxolane-2,2-diyl)bis(6-fluoro-3,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S4). This compound was synthesized using a literature procedure^{8,9,10}, with minor modifications. *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDTA) (2.9 mL, 13.8 mmol) was added at $-78\text{ }^{\circ}\text{C}$ under N_2 to $n\text{BuLi}$ (8.6 mL of a 1.6 M solution in hexane, 13.8 mmol) followed by dropwise addition of 2,2-bis(4-fluorophenyl)-1,3-dioxolane (1.49 g, 5.7 mmol) in THF (6 mL). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, then B(OMe)_3 (4.67 g, 44.9 mmol) was slowly added. The reaction mixture was warmed to rt and then stirred for 19 h. THF (18 mL) was added, then the reaction mixture was stirred for an additional 1 h. To the resulting mixture, water (10 mL) was added, followed by aqueous HCl (5%, 25 mL). The reaction mixture was stirred for 4 h. THF was removed under reduced pressure. The remaining aqueous phase was extracted with EtOAc. After drying the organic phase with Na_2SO_4 and removing the solvent in vacuo, the boronic acid product was obtained as a white solid. Pinacol (1.78 g, 15.1 mmol) was added to a stirred solution of this boronic acid in hexane (20 mL) and the reaction mixture was stirred for 4 h at rt. The resulting hexane solution was dried with over Na_2SO_4 , filtered with EtOAc, and the solvent was removed in vacuo. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 75/25) to give **S4** as a white solid (1.17 g, 40%).



White solid. R_f 0.58 (Hexane/EtOAc = 1/1). M.p. $143.8\text{--}145.1\text{ }^{\circ}\text{C}$.

^1H NMR (CDCl_3 , 400 MHz) δ : 7.91 (dd, $J = 5.5, 2.3\text{ Hz}$, 2H), 7.52–7.48 (m, 2H), 6.97 (t, $J = 8.9\text{ Hz}$, 2H), 4.05 (s, 4H), 1.35 (s, 24H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 167.0 (d, $J = 252.1\text{ Hz}$), 137.2 (d, $J = 2.9\text{ Hz}$), 134.36 (d, $J = 8.6\text{ Hz}$), 131.5 (d, $J = 9.6\text{ Hz}$), 115.06 (d, $J = 24.9\text{ Hz}$), 108.8, 83.9, 64.9, 24.8.

^{19}F NMR (CDCl_3 , 376 MHz) δ : -103.9 .

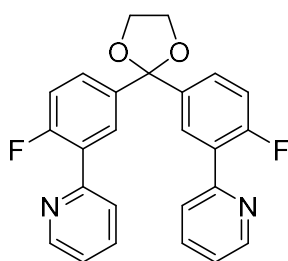
^{11}B NMR (CDCl_3 , 128 MHz) δ : 30.1.

IR (KBr): 2979 m, 2893 w, 1614 s, 1585 w, 1488 m, 1419 s, 1372 s, 1346 s, 1328 s, 1289 m, 1269 m, 1254 m, 1215 s, 1200 s, 1144 s, 1091 m, 1069 s, 998 m, 962 m, 851 m, 743 w, 673 w, 607 m.

MS, m/z (relative intensity, %): 514 (M^+ , 3), 294 (41), 293 (100), 292 (65), 249 (14), 193 (11), 149 (13), 101 (14), 83 (16), 43 (15).

HRMS (DART+, $[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{27}\text{H}_{35}\text{O}_6\text{B}_2\text{F}_2$: 515.2582. Found: 515.2607.

2,2'-((1,3-Dioxolane-2,2-diyl)bis(6-fluoro-3,1-phenylene))dipyridine (S5). This compound was synthesized using a literature procedure¹¹, with minor modifications. To a 50 mL two-necked flask, 2-bromopyridine (1.09 g, 6.9 mmol), Pd(PPh₃)₄ (261 mg, 9.8 mol%), K₂CO₃ (967 mg, 7.0 mmol), 2,2'-((1,3-dioxolane-2,2-diyl)bis(6-fluoro-3,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1.17 g, 2.3 mmol), water (8 mL) and DME (8 mL) were added. The reaction mixture was degassed then refluxed for 19 h. The reaction mixture was cooled to rt and diluted with H₂O and extracted with EtOAc. The combined extracts were dried over Na₂SO₄ and concentrated. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 50/50 to 10/90) to give **S5** as a yellow oil (669 mg, 71%).



Yellow oil. R_f 0.20 (Hexane/EtOAc = 1/1).

¹H NMR (CDCl₃, 400 MHz) δ : 8.72 (td, J = 3.0, 1.5 Hz, 2H), 8.18 (dd, J = 7.6, 2.5 Hz, 2H), 7.74–7.72 (m, 4H), 7.55–7.51 (m, 2H), 7.26–7.22 (m, 2H), 7.12 (dd, J = 11.0, 8.7 Hz, 2H), 4.10 (s, 4H).

¹³C NMR (CDCl₃, 101 MHz) δ : 160.1 (d, J = 250 Hz), 153.3, 149.7, 138.4 (d, J = 3.8 Hz), 136.2, 128.8 (d, J = 2.9 Hz), 128.5 (d, J = 8.6 Hz), 127.2 (d, J = 12.5 Hz), 124.5 (d, J = 8.6 Hz), 122.4, 116.0 (d, J = 24.0 Hz), 108.6, 65.1.

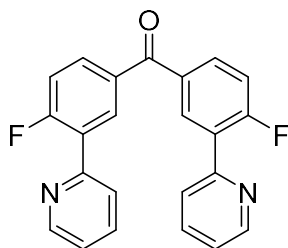
¹⁹F NMR (CDCl₃, 376 MHz) δ : –118.2.

IR (KBr): 3055 m, 3006 m, 2895 m, 1611 m, 1587 s, 1567 m, 1496 s, 1463 s, 1441 m, 1407 m, 1295 m, 1250 m, 1212 m, 1184 m, 1089 m, 1061 m, 1038 m, 1013 m, 996 s, 946 m, 907 m, 828 s, 790 s, 746 s, 648 m, 638 m, 627 m, 614 m, 474 m.

MS, m/z (relative intensity, %): 416 (M⁺, 2), 245 (19), 244 (100), 200 (21), 172 (20).

HRMS (DART⁺, [M+H]⁺) Calcd for C₂₅H₁₉N₂O₂F₂: 417.1409. Found: 417.1414.

Bis(4-fluoro-3-(pyridin-2-yl)phenyl)methanone (5). This compound was synthesized using a literature procedure¹², with minor modifications. An aqueous HCl (10%, 2 mL) was added to a solution of 2,2'-((1,3-dioxolane-2,2-diyl)bis(6-fluoro-3,1-phenylene))dipyridine (160 mg, 0.38 mmol) in MeOH (2 mL) and the mixture was stirred at rt for 16 h. An aqueous solution of NaOH (10%, 2 mL) was added to the reaction mixture, and the aqueous layer was extracted with EtOAc. The combined extracts were dried over Na₂SO₄ and concentrated. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 80/20 to 50/50) to give **5** as a white solid (132 mg, 92%).



White solid. R_f 0.40 (Hexane/EtOAc = 1/1). M.p. 139.2–139.9 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 8.72–8.71 (m, 2H), 8.45 (dd, J = 7.8, 2.3 Hz, 2H), 7.90–7.86 (m, 2H), 7.83–7.76 (m, 4H), 7.32–7.27 (m, 4H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 193.7, 162.9 (d, J = 257.8 Hz), 152.3, 149.9, 136.5, 134.1 (d, J = 3.8 Hz), 133.5 (d, J = 4.8 Hz), 132.2 (d, J = 9.6 Hz), 127.8 (d, J = 12.5 Hz), 124.4 (d, J = 8.6 Hz), 122.8, 116.6 (d, J = 24.0 Hz).

^{19}F NMR (CDCl_3 , 376 MHz) δ : –111.8.

IR (KBr): 3079 w, 3056 w, 3005 w, 1657 s, 1604 m, 1588 s, 1570 m, 1497 m, 1463 s, 1442 m, 1392 m, 1328 m, 1306 m, 1294 m, 1285 m, 1254 s, 1220 s, 1139 m, 1119 m, 1061 m, 971 m, 930 m, 842 s, 788 s, 761 s, 752 s, 742 s, 706 m, 607 s.

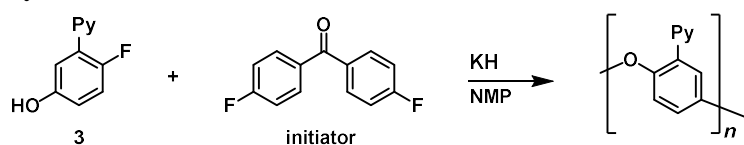
MS, m/z (relative intensity, %): 373 (15), 372 (M^+ , 59), 371 (37), 352 (20), 351 (14), 343 (14), 295 (22), 294 (100), 200 (18), 172 (38), 145 (10), 125 (14), 78 (11).

HRMS (DART+, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{23}\text{H}_{15}\text{N}_2\text{OF}_2$: 373.1147. Found: 373.1152.

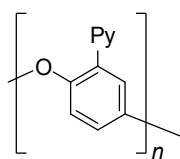
V. Synthesis and Characterization of DG-PPE, DG-PEEK1 and DG-PEEK2

V-1. Synthesis of DG-polymers

Synthesis of DG-PPE



This compound was synthesized using a literature procedure¹³, with minor modifications. In a glovebox filled with nitrogen, **3** (764.3 mg, 4.0 mmol), 4,4'-difluorobenzophenone (5.2 mg, 0.024 mmol), KH (168.0 mg, 4.2 mmol) and NMP (2.7 mL) were added to a 5 mL pressure-resistant vial and it was closed with a resealable septum. The mixture was stirred at 200 °C for 4 h using a microwave reactor. After cooling to rt, the polymer is precipitated by adding the viscous reaction mixture slowly to vigorously stirred MeOH. The polymer is purified by stirring with acetone. After drying in a vacuum oven, **DG-PPE** was obtained as a white powder (426.2 mg, 62%).



$M_w = 4980$, $M_w/M_n = 3.01$.

^1H NMR (CDCl_3 , 400 MHz) δ : 8.62 (s, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 7.63 (t, $J = 7.1$ Hz, 1H), 7.57 (s, 1H), 7.17–7.16 (m, 1H), 6.96 (d, $J = 8.7$ Hz, 1H), 6.86 (dd, $J = 8.7$, 2.7 Hz, 1H).

The chemical shifts in ^1H NMR spectra were recorded relative to tetramethylsilane (δ 0.00).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 154.2, 153.5, 149.8, 149.5, 136.1, 132.9, 124.9, 122.3, 121.0, 120.6, 119.6.

IR (ATR): 2359 w, 2340 w, 1585 m, 1567 w, 1483 s, 1458 s, 1442 m, 1399 m, 1311 w, 1289 w, 1235 m, 1197 s, 1176 s, 1119 w, 992 w, 901 w, 890 w, 842 w, 833 w, 812 w, 786 m, 772 m, 742 m, 618 w.

The observed peak interval in the MALDI-TOF MS spectrum was 169, which is consistent with the mass of the repeating unit of **DG-PPE**.

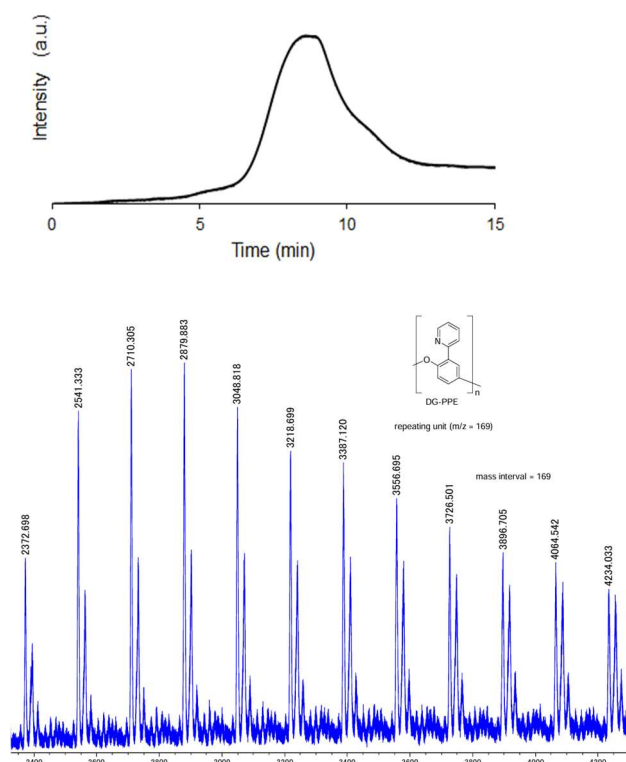


Figure S2.2. SEC and MALDI-TOF Spectrum of **DG-PPE**.

The relatively high dispersity of **DG-PPE** ($M_w/M_n = 3.01$) compared with the value reported in Yokozawa's work ($M_w/M_n = 1.1$)¹³ can be attributed to the higher polymerization temperature used in this study. While Yokozawa conducted polymerization at 150 °C, monomer **3** required 200 °C for efficient polymerization due to the pyridine ring being a weaker electron-withdrawing group compared to a cyano group used in the Yokozawa's work. The elevated temperature likely led to main-chain cleavage reactions as side reactions under the author's polymerization conditions, resulting in the higher dispersity observed. Specifically, aryloxide can attack the carbon ortho to the pyridine group (Figure S2.3). We confirmed that this side reaction pathway occurred using a model substrate **1d** by reacting with *p*-cresol under the conditions used for polymerization (i.e., in NMP at 200 °C).

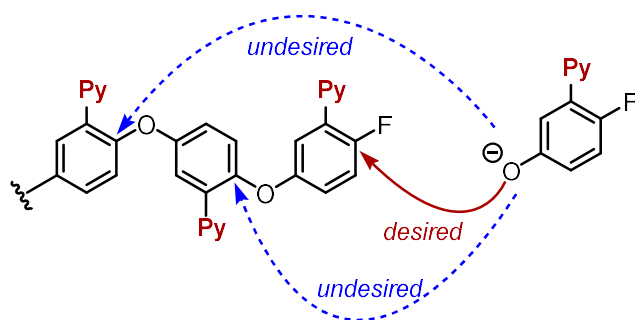
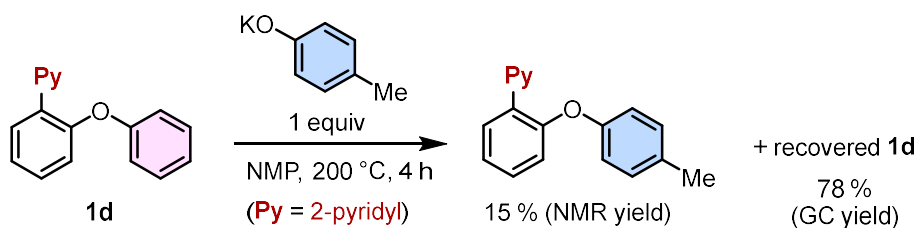


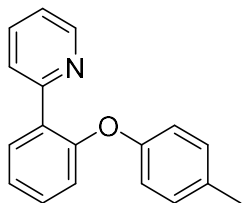
Figure S2.3. One of the Possible Side Reactions under the Polymerization Conditions.

Proof of side reaction pathway



In a glovebox filled with nitrogen, *p*-cresol (113 mg, 1.0 mmol), KH (43.2 mg, 1.1 mmol) and NMP (0.70 mL) were added to a 5 mL pressure-resistant vial. After stirring the reaction mixture at rt for 30 min, **1d** (244 mg, 1.0 mmol) and NMP (0.30 mL) were added to the vial and it was closed with a resealable septum. The mixture was stirred at 200 °C for 4 h using a microwave reactor. Water (20 mL) was added to the reaction mixture, and the aqueous layer was extracted with EtOAc. The combined extracts were dried over Na₂SO₄ and concentrated to give crude product. The crude product was analyzed by ¹H NMR with 1,1,2,2-tetrachloroethane as an internal standard, which revealed that 2-(2-(*p*-tolylloxy)phenyl)pyridine was formed in 15 % yield. Yield of recovered **1d** was determined by GC using dodecane as an internal standard. These results indicate that main chain cleavage can occur under the polymerization conditions, which leads to high dispersity of the resulting polymer.

2-(2-(*p*-Tolyloxy)phenyl)pyridine.



Colorless oil. R_f 0.58 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 8.69–8.68 (m, 1H), 7.92 (dd, J = 7.8, 1.8 Hz, 1H), 7.88–7.86 (m, 1H), 7.65 (td, J = 7.7, 2.0 Hz, 1H), 7.33 (td, J = 7.8, 1.8 Hz, 1H), 7.26–7.17 (m, 2H), 7.09 (d, J = 8.2 Hz, 2H), 6.96 (dd, J = 8.2, 0.9 Hz, 1H), 6.89–6.85 (m, 2H), 2.30 (s, 3H).

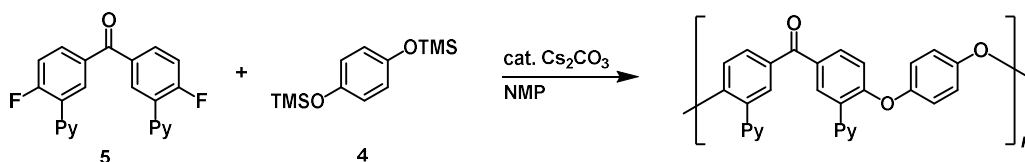
^{13}C NMR (CDCl_3 , 101 MHz) δ : 155.2, 155.0, 154.6, 149.4, 135.9, 132.5, 131.6, 131.4, 130.2, 130.0, 124.9, 123.8, 122.0, 119.4, 118.4, 20.6.

IR (KBr): 3058 w, 3033 w, 2924 w, 1604 w, 1585 m, 1506 s, 1489 s, 1462 w, 1453 w, 1423 w, 1227 s, 913 w, 876 w, 831 w, 745 s.

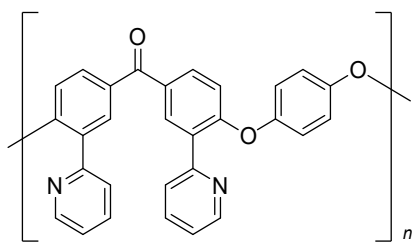
MS, m/z (relative intensity, %): 262 (13), 261 (M^+ , 73), 260 (100), 244 (35), 127 (12), 109 (17).

HRMS (DART $^+$, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{18}\text{H}_{16}\text{NO}$: 262.1226. Found: 262.1230.

Synthesis of DG-PEEK1



The synthesis of **DG-PEEK1** was performed following a modified procedure from reported literature.¹⁴ To a 100 mL two-necked flask, **5** (6.14 g, 16.5 mmol), 1,4-bis((trimethylsilyl)oxy)benzene (**4**, 4.21 g, 16.5 mmol), and NMP (33 mL) were added. The flask is equipped with a reflux condenser, and the reaction mixture is stirred under N_2 atmosphere at rt. After the reactants were completely dissolved, Cs_2CO_3 (184 mg, 3.4 mol%) were added, and the mixture was heated to 150 °C using an oil bath. After stirring the reaction mixture at 150 °C for 18 h, it was stirred at 180 °C for further 2.5 h. After cooling to rt, the polymer was precipitated by pouring the viscous reaction mixture slowly to a vigorously stirred MeOH. The polymer is purified by stirring in acetone. After drying in a vacuum oven, **DG-PEEK1** was obtained as a white powder (6.73 g, 92%).



$M_w = 27200$, $M_w/M_n = 1.81$.

^1H NMR (CDCl_3 , 400 MHz) δ : 8.68 (d, $J = 4.6$ Hz, 2H), 8.38 (d, $J = 2.4$ Hz, 2H), 7.86 (d, $J = 7.8$ Hz, 2H), 7.81 (dd, $J = 8.5$, 2.1 Hz, 2H), 7.70 (td, $J = 7.8$, 1.8 Hz, 2H), 7.23 (td, $J = 6.2$, 1.1 Hz, 2H), 7.05 (s, 4H), 6.97 (d, $J = 8.2$ Hz, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 194.0, 158.3, 154.3, 152.1, 149.6, 136.1, 133.9, 133.0, 131.9, 130.8, 124.8, 122.4, 121.2, 117.5.

IR (ATR): 3055 w, 3006 w, 1655 w, 1599 m, 1586 m, 1498 m, 1485 s, 1463 w, 1440 w, 1323 w, 1248 m, 1218 s, 1186 s, 1136 w, 1058 w, 969 w, 748 m.

The observed peak interval in the MALDI-TOF MS spectrum was 442, which is consistent with the mass of the repeating unit of **DG-PEEK1**.

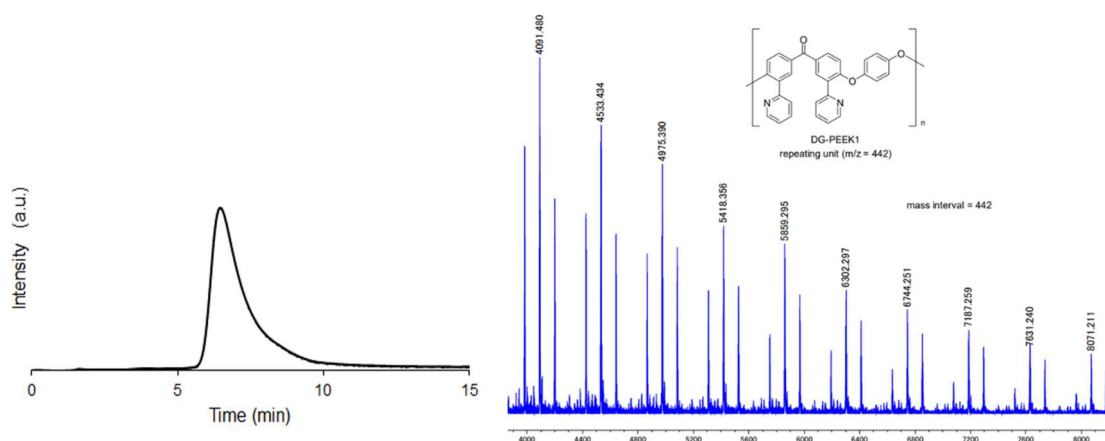
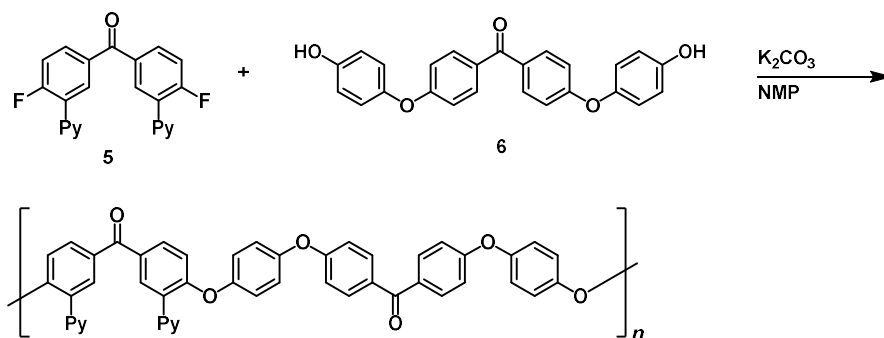
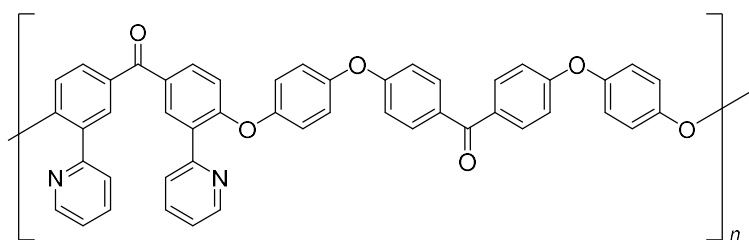


Figure S2.4. SEC and MALDI-TOF Spectrum of **DG-PEEK1**.

Synthesis of DG-PEEK2



To a 30 mL two-necked flask, **5** (391 mg, 0.98 mmol), **6**¹⁵ (368 mg, 0.99 mmol), K_2CO_3 (302 mg, 2.2 mmol) and NMP (4 mL) were added. The flask is equipped with a reflux condenser, and the reaction mixture is stirred under N_2 atmosphere at rt. After the reactants are completely dissolved, the reaction mixture was stirred at 180 °C for 18 h. After cooling to rt, the polymer is precipitated by adding the viscous reaction mixture slowly to vigorously stirred MeOH. The polymer was purified by stirring with acetone. After drying in a vacuum oven, **DG-PEEK2** was obtained as a white powder (619 mg, 86%).



$M_w = 59000$, $M_w/M_n = 2.21$.

1H NMR ($CDCl_3$, 396 MHz) δ : 8.69 (d, $J = 4.1$ Hz, 2H), 8.40 (d, $J = 1.8$ Hz, 2H), 7.88 (d, $J = 8.2$ Hz, 2H), 7.84 (dd, $J = 8.6, 2.3$ Hz, 2H), 7.79 (d, $J = 8.6$ Hz, 4H), 7.71 (td, $J = 7.7, 1.5$ Hz, 2H), 7.24 (dd, $J = 7.0, 5.2$ Hz, 2H), 7.12–6.99 (m, 14H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ : 194.1, 194.0, 161.4, 158.2, 154.4, 152.4, 151.7, 149.7, 136.0, 133.9, 133.1, 132.22, 132.18, 131.9, 131.0, 124.8, 122.4, 121.7, 121.1, 117.6, 116.8.

IR (ATR): 3065 w, 3004 w, 1653 w, 1598 m, 1487 s, 1464 w, 1306 w, 1279 w, 1247 m, 1221 s, 1188 s, 1161 m, 929 w, 850 w, 751 m.

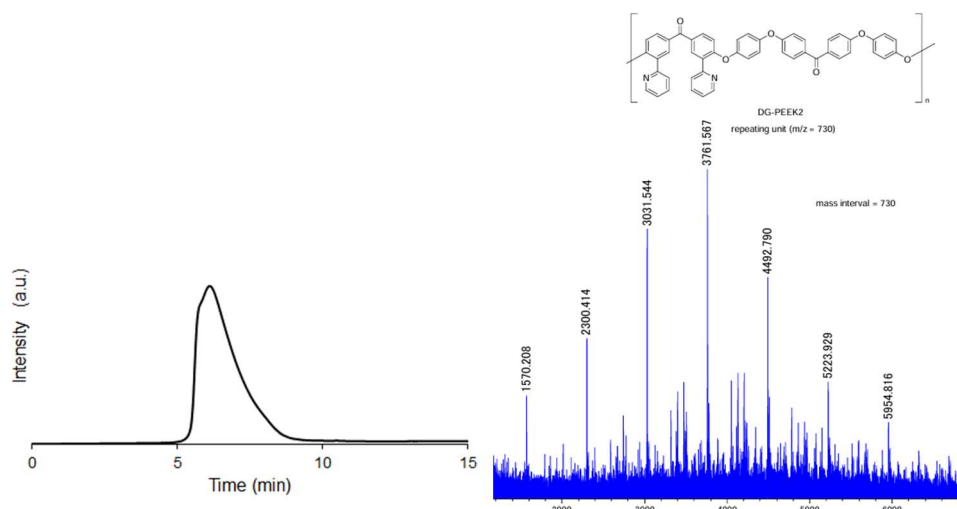


Figure S2.5. SEC Chart of DG-PEEK2.

V-2. Thermal properties of DG-polymers

Differential Scanning Calorimetry (DSC) Thermograms

DG-PPE: Thermal transitions were assessed with differential scanning calorimetry using a Hitachi High-Tech NEXTA DSC2000 and 2–3 mg of polymer material. Samples were heated to 350 °C and then cooled to 30 °C at 10 °C/min. Samples were again heated to 350 °C at 10 °C/min. Thermal data was assessed from the second heating cycle. T_g value of **DG-PPE** was determined to be 143 °C (Figure S2.6).

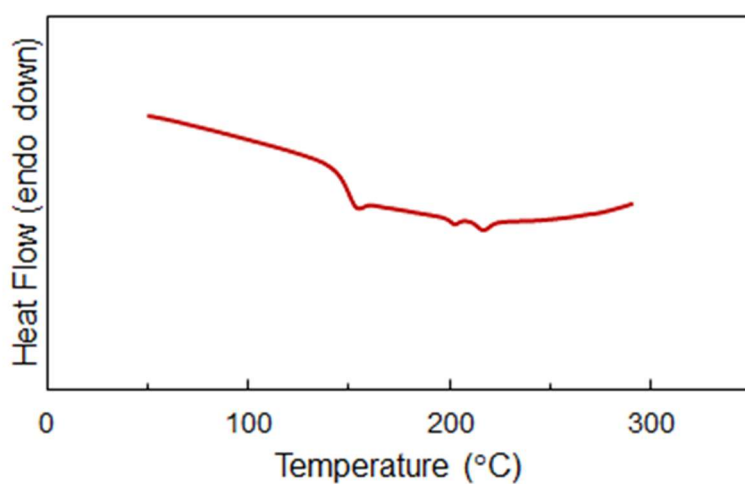


Figure S2.6. DSC Second Heating Thermogram of DG-PPE.

DG-PEEK1, DG-PEEK2, PEEK: Thermal transitions were assessed with differential scanning calorimetry using a Hitachi High-Tech NEXTA DSC2000 and 1–10 mg of polymer material. Samples were heated to 400 °C and then cooled to 30 °C at 10 °C/min. Samples were again heated to 400 °C at 10 °C/min. Thermal data was assessed from the second heating cycle. PEEK without DG was purchased from Sigma–Aldrich Japan (pellet forms, Cat. No. 456640.). T_g values for **DG-PEEK1** and **DG-PEEK2** were determined to be 182 and 172 °C, respectively, with no T_m being observed (Figure S2.7 and S2.8). The parent PEEK without DGs has T_g of 143 °C and T_m of 344 °C (Figure S2.9).

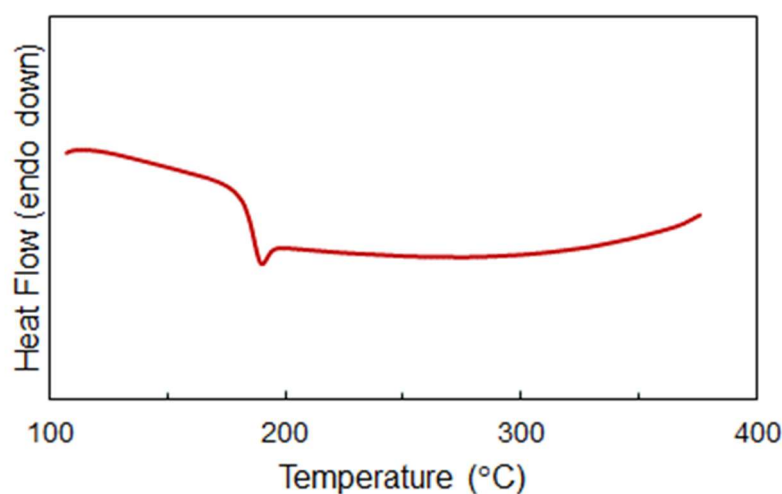


Figure S2.7. DSC Second Heating Thermogram of **DG-PEEK1**.

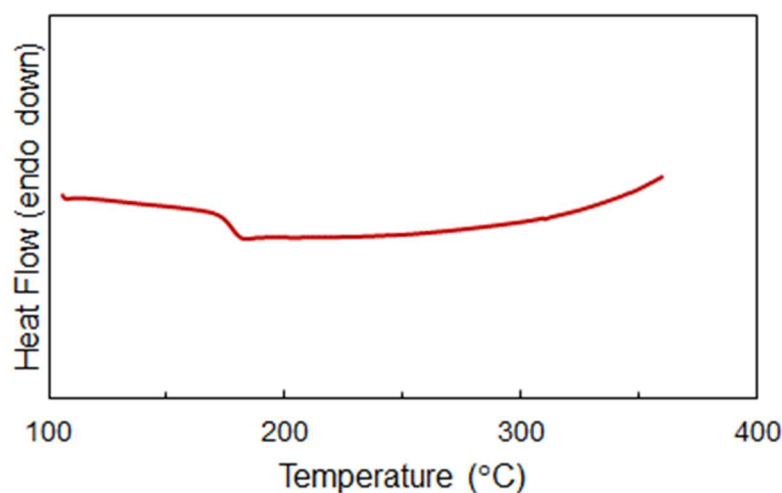


Figure S2.8. DSC Second Heating Thermogram of **DG-PEEK2**.

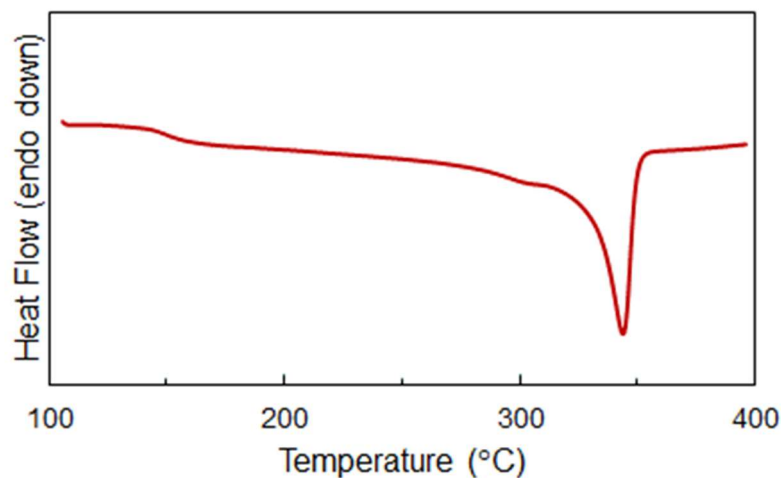


Figure S2.9. DSC Second Heating Thermogram of PEEK.

Thermogravimetric Analysis (TGA)

DG-PPE: Thermogravimetric analysis was performed using a Hitachi High-Tech NEXTA STA200RV and 3–6 mg of polymer material. Samples were heated at a rate of 10 °C/min from 40 °C to 600 °C under N₂ or air flow. Decomposition temperatures are reported at 5% mass loss (T_{d5}). T_{d5} of **DG-PPE** was determined to be 399 °C (N₂) and 419 °C (air) (Figure S2.10).

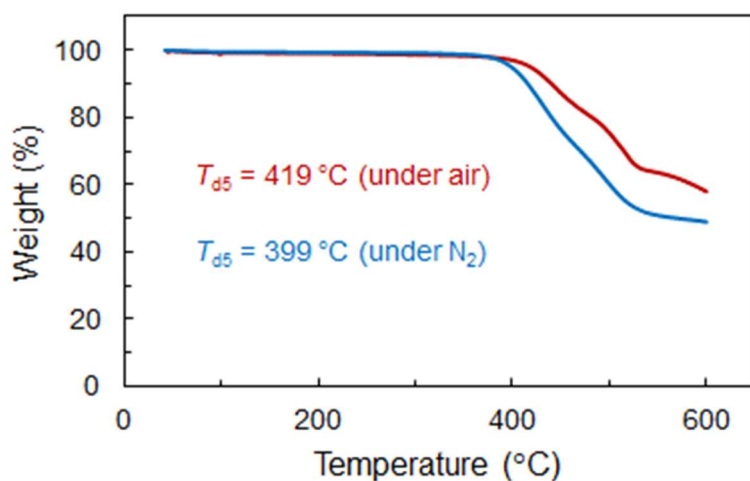


Figure S2.10. TGA of **DG-PPE**.

PEEK, DG-PEEK1 and DG-PEEK2: Thermogravimetric analysis was performed using a Hitachi High-Tech NEXTA STA200RV and 1–10 mg of polymer material. Samples were heated at a rate of

10 °C/min from 30 °C to 600 °C under N₂ or air flow. Decomposition temperatures are reported at 5% mass loss (T_{d5}). T_{d5} of **DG-PEEK1** was determined to be 465 (N₂) and 473 °C (air) (Figure S2.11). T_{d5} of **DG-PEEK2** was determined to be 437 (N₂) and 451 °C (air) (S12). The parent PEEK without DGs had T_{d5} of 576 °C (Figure S2.13).

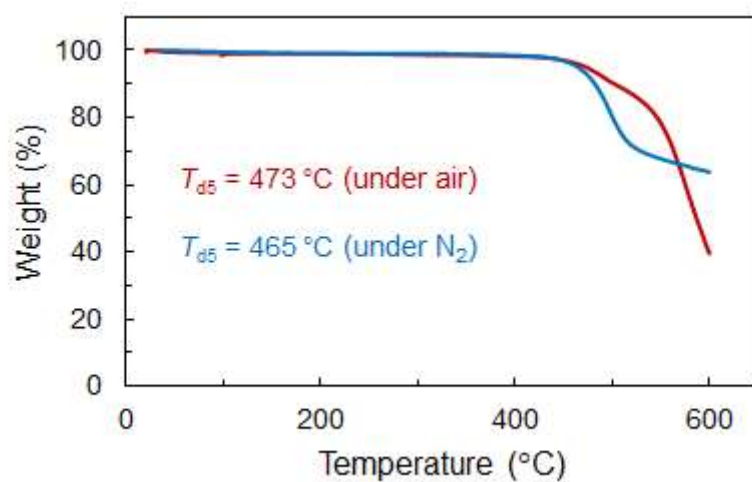


Figure S2.11. TGA of **DG-PEEK1**.

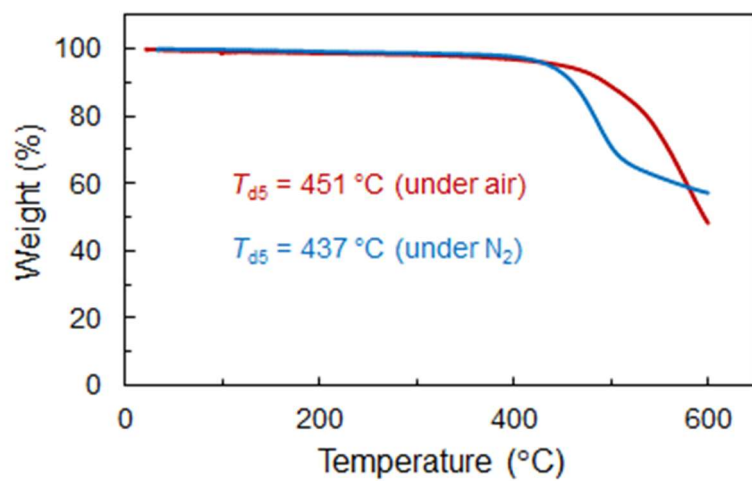


Figure S2.12. TGA of **DG-PEEK2**.

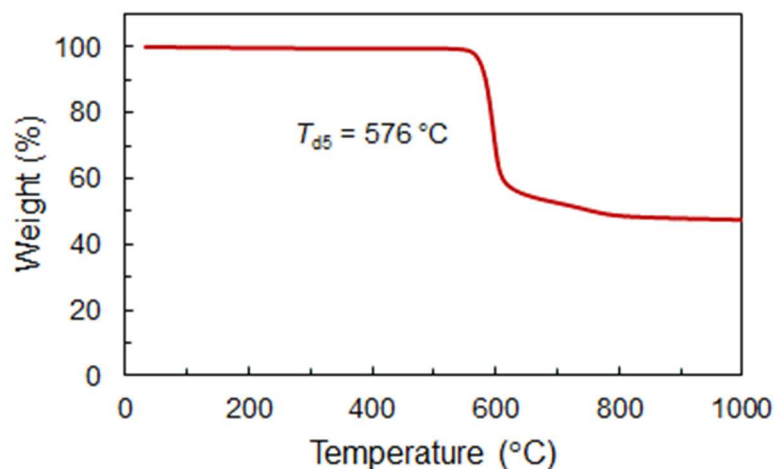
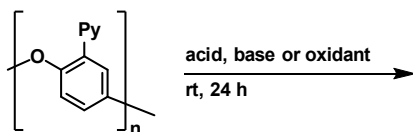


Figure S2.13. TGA of PEEK.

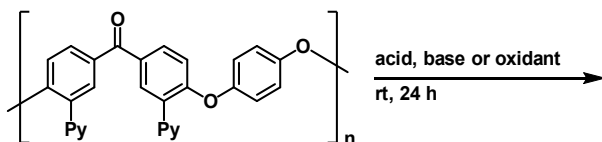
VI. Chemical Stability of DG-PPE and DG-PEEK1

VI-1. Stability of DG-PPE in different solutions



DG-PPE (5.0 mg) was introduced into a 10 mL vial with a Teflon-sealed screwcap, along with a magnetic stirring bar. Subsequently, a solution (1.0 mL) containing HCl (12 M), NaOH (10 M), H₂O₂ (30%), AcOH or water was added to the vial, and the mixture was stirred for 24 h at rt (or heated to 100°C in the case of water). Following neutralization, the mixture was extracted with CHCl₃ (2 mL × 3). The combined extracts were dried, and the solid obtained was subjected to FT-IR spectroscopic analysis using an ATR detector. A portion of the solid was dissolved in HPLC-grade CHCl₃, filtered through a syringe filter, and subsequently analyzed via SEC analysis.

VI-2. Stability of DG-PEEK1 in different solutions

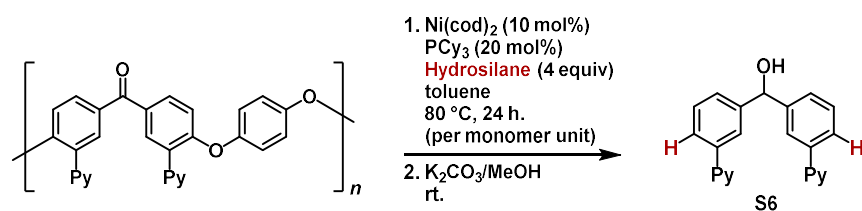


DG-PEEK1 (5.0 mg) was introduced into a 10 mL vial with a Teflon-sealed screwcap, along with a magnetic stirring bar. Subsequently, a solution (1.0 mL) containing HCl (12 M), NaOH (10 M), H₂O₂ (30%), AcOH or water was added to the vial, and the mixture was stirred for 24 h at rt (or heated to 100°C in the case of water). Following neutralization, the mixture was extracted with CHCl₃ (2 mL ×

3). The combined extracts were dried, and the solid obtained was subjected to FT-IR spectroscopic analysis using an ATR detector. A portion of the solid was dissolved in HPLC-grade CHCl₃, filtered through a syringe filter, and subsequently analyzed via SEC analysis.

VII. Optimization of Depolymerization Conditions

VII-1. Optimization of C–O bond cleavage in DG-PEEK1



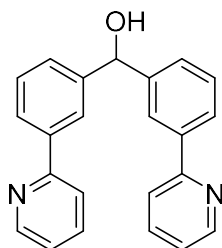
Entry	Hydrosilane	Yield [%]
1	HSiEt ₃	0
2 ^[a]	(HSiMe ₂)O	32
3	HSiMe(OMe) ₂	36
4	HSiMe(OEt) ₂	51 (89) ^[b]
5	HSiMe(OTMS) ₂	0
6	HSi(OMe) ₃	25
7	HSi(OEt) ₃	26

Figure S2.14. Screening of Hydrosilane in C–O Bond Cleavage Reaction with **DG-PEEK1**.

^a3 Equiv of hydrosilane was used. ^bWith 20 mol% catalyst.

In a glovebox filled with nitrogen, **DG-PEEK1** (0.20 mmol), Ni(cod)₂ (0.020 mmol), PCy₃ (0.04 mmol), hydrosilane (0.80 mmol) and toluene (1.0 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 80 °C for 24 h. The resulting mixture was then evaporated to dryness, and the residue was hydrolyzed with saturated solution of K₂CO₃ in MeOH (1.0 mL) at rt for 4 h. After removing MeOH in vacuo, the crude mixture was purified by flash column chromatography (eluent: hexane/EtOAc = 80/20 to 30/70) to give **S6** as a white solid. Among the hydrosilanes examined, HSiMe(OEt)₂ resulted in the formation of a degraded product in highest yield.

Bis(3-(pyridin-2-yl)phenyl)methanol (S6).



White solid. R_f 0.12 (Hexane/EtOAc = 1/1). M.p. 134.1–136.3 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 8.66 (d, J = 5.0 Hz, 2H), 8.06 (s, 2H), 7.87 (d, J = 7.3 Hz, 2H), 7.75–7.68 (m, 4H), 7.46–7.40 (m, 4H), 7.23–7.20 (m, 2H), 6.01 (s, 1H), 2.90 (br, 1H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 157.3, 149.5, 144.5, 139.4, 136.8, 128.9, 127.3, 126.1, 125.3, 122.2, 120.9, 76.0.

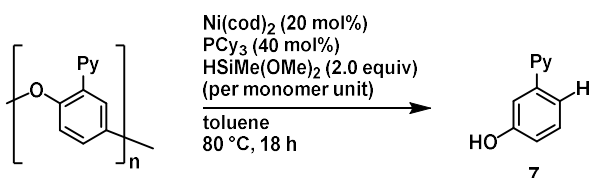
IR (KBr): 3331 br, 3061 m, 2960 m, 2927 m, 1652 w, 1586 s, 1567 s, 1464 s, 1435 s, 1417 m, 1268 m, 1173 m, 1153 m, 1096 m, 1054m, 998 m, 911 w, 775 s, 753 s, 703 m, 640 w, 617 w.

MS, m/z (relative intensity, %): 338 (M^+ , 26), 337 (24), 260 (18), 182 (12), 157 (13), 156 (100), 155 (17), 154 (29), 127 (14), 78 (23).

HRMS (DART+, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}$: 339.1492. Found: 339.1493.

VIII. Typical Procedures for Depolymerization

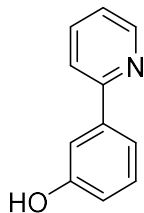
VIII-1. Depolymerization of DG-PPE



In a glovebox filled with nitrogen, **DG-PPE** (21.1 mg, 0.13 mmol), $\text{Ni}(\text{cod})_2$ (6.9 mg, 0.025 mmol), PCy_3 (16.4 mg, 0.058 mmol), $\text{HSiMe}(\text{OMe})_2$ (27.7 mg, 0.26 mmol) and toluene (0.5 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 80 °C for 18 h. The resulting mixture was then evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 90/10 to 50/50) to give **7** as a white solid (13.6 mg, 64%).

Note: When $\text{HSiMe}(\text{OEt})_2$ was used, instead of $\text{HSiMe}(\text{OMe})_2$, **7** was obtained in lower yield of 30%, along with its silylated derivative (5%).

3-(Pyridin-2-yl)phenol (7).



White solid. R_f 0.50 (Hexane/EtOAc = 1/1). M.p. 101.3–102.7 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 8.64–8.63 (m, 1H), 7.74 (td, J = 7.8, 1.8 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.50 (t, J = 1.8 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.27–7.22 (m, 2H), 6.85 (dd, J = 8.0, 1.6 Hz, 1H).

The chemical shifts in ^1H NMR spectra were recorded relative to tetramethylsilane (δ 0.00).

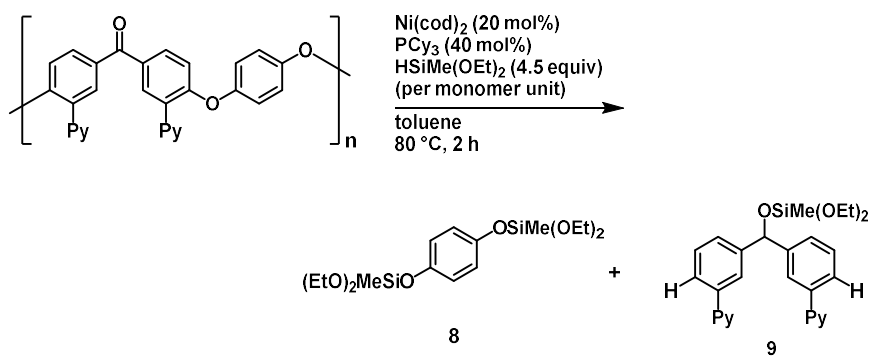
^{13}C NMR (CDCl_3 , 101 MHz) δ : 157.5, 157.1, 149.0, 140.2, 137.4, 130.0, 122.4, 121.6, 118.8, 116.7, 114.6.

IR (KBr): 2794 br, 2667 s, 2607 s, 1593 s, 1567 s, 1468 s, 1430 s, 1352 s, 1313 s, 1281 s, 1243 m, 1216 s, 1156 s, 1082 m, 1006 s, 999 s, 897 s, 872 m, 807 m, 771 s, 746 m, 729 m, 700 s, 631 m, 618 m, 538 m.

MS, m/z (relative intensity, %): 172 (16), 171 (M^+ , 100), 170 (24), 154 (13), 143 (40), 142 (19), 141 (14), 117 (49), 115 (23), 89 (12), 63 (12), 51 (13).

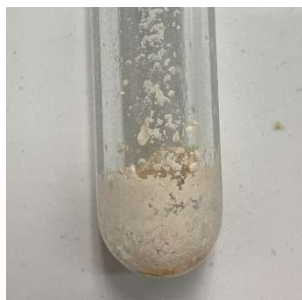
HRMS (DART+, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{11}\text{H}_{10}\text{NO}$: 172.0757. Found: 172.0758

VIII-2. Depolymerization of DG-PEEK1



In a glovebox filled with nitrogen, **DG-PEEK1** (87.1 mg, 0.20 mmol), $\text{Ni}(\text{cod})_2$ (11.7 mg, 0.043 mmol), PCy_3 (22.5 mg, 0.080 mmol), hydrosilane (115.0 mg, 0.86 mmol) and toluene (0.40 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 80 °C for 2 h. The resulting mixture was then evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 60/40) to give **8** as a colorless oil (57.7 mg, 78%) and **9** as a yellow oil (80.4 mg, 87%). Column chromatography was performed with SiO_2 (Silica Gel 60N (spherical, neutral) (40–50 μm , KANTO CHEMIXAL CO., INC.).

(A)

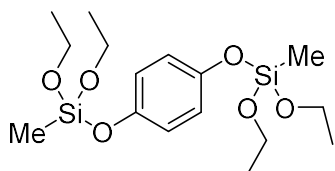


(B)



Pictures of the reaction mixture before heating (A) and after heating at 80 °C for 24 h (B).

1,4-Bis((diethoxy(methyl)silyl)oxy)benzene (8).



Colorless oli. R_f 0.73 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 6.84 (s, 4H), 3.87 (q, J = 7.0 Hz, 8H), 1.23 (t, J = 7.1 Hz, 12H), 0.23 (s, 6H).

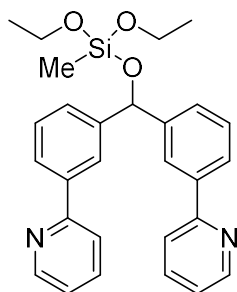
^{13}C NMR (CDCl_3 , 101 MHz) δ : 148.5, 120.0, 58.7, 18.1, -6.8.

IR (KBr): 2976 m, 2927 w, 2888 w, 1506 s, 1267 m, 1241 m, 1167 m, 1107 s, 1082 s, 954 s, 839 m, 784 m, 775m.

MS, m/z (relative intensity, %): 376 (11), 375 (28), 374 (M^+ , 100), 226 (19), 133 (37), 105 (16), 89 (16), 77 (26).

HRMS (EI^+ , M^+) Calcd for $\text{C}_{16}\text{H}_{30}\text{O}_6\text{Si}_2$: 374.1581. Found: 374.1588.

2,2'-((((Diethoxy(methyl)silyl)oxy)methylene)bis(3,1-phenylene))dipyridine (9).



Yellow oil. R_f 0.64 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 8.68–8.66 (m, 2H), 8.04 (s, 2H), 7.90–7.88 (m, 2H), 7.74–7.68 (m, 4H), 7.51 (d, J = 7.8 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.22–7.18 (m, 2H), 6.20 (s, 1H), 3.73 (q, J = 7.0 Hz, 4H), 1.14 (t, J = 7.1 Hz, 6H), 0.10 (s, 3H).

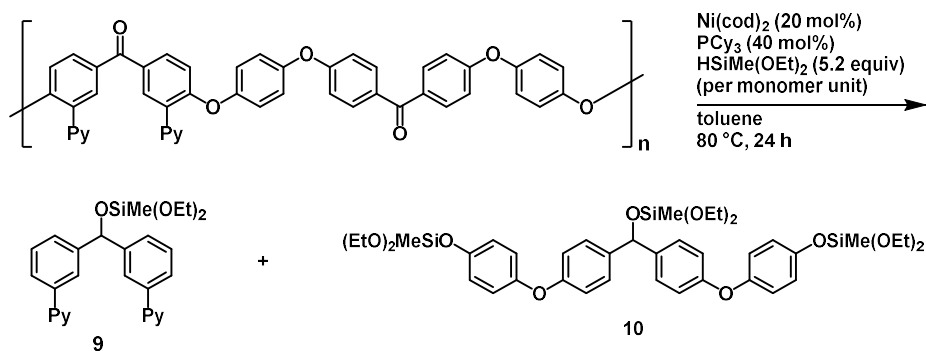
^{13}C NMR (CDCl_3 , 101 MHz) δ : 157.4, 149.6, 144.6, 139.4, 136.6, 128.8, 127.2, 125.9, 125.1, 122.0, 120.6, 76.1, 58.4, 18.1, –6.4.

IR (KBr): 2973 m, 2924 w, 2886 w, 1584 m, 1566 w, 1462 m, 1436 m, 1417 w, 1265 w, 1167 w, 1099 s, 1074 s, 957 m, 876 w, 824 w, 773 m, 746 m.

MS, m/z (relative intensity, %): 472 (12), 471 (39), 470 (M^+ , 100), 322 (15), 321 (36), 320 (41), 319 (12), 316 (10), 302 (17), 288 (18), 244 (13), 242 (16), 226 (23), 190 (14), 133 (27), 105 (21), 89 (24), 77 (39).

HRMS (ESI $^+$, $[\text{M}+\text{Na}]^+$): Calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_3\text{NaSi}$: 493.1918. Found: 493.1925.

VIII-3. Depolymerization of DG-PEEK2



In a glovebox filled with nitrogen, **DG-PEEK2** (77.9 mg, 0.11 mmol), $\text{Ni}(\text{cod})_2$ (6.2 mg, 0.023 mmol), PCy_3 (12.0 mg, 0.043 mmol), $\text{HSiMe}(\text{OEt})_2$ (69.4 mg, 0.52 mmol) and toluene (0.4 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 80 °C for 2 h. The resulting mixture was then evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/ EtOAc = 100/0 to 60/40) to give **9** as a yellow oil (39.9 mg, 80%) and **10** as a colorless oil (57.6 mg, 68%). Column chromatography was performed with SiO_2 (Silica Gel 60N (spherical, neutral) (40–50 μm , KANTO CHEMICAL CO., INC.).

(A)



(B)

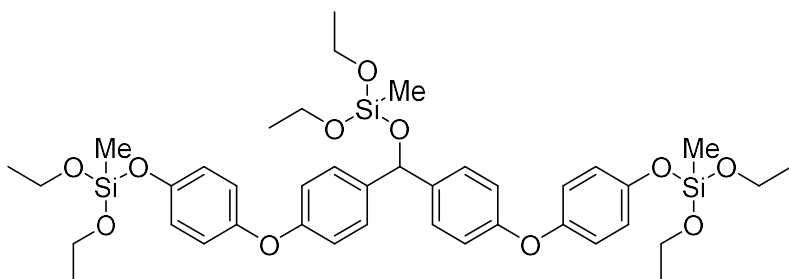


(C)



Pictures of the reaction mixture before heating (A) and after heating at 80 °C for 2 h (B) and 24 h (C).

((((((Diethoxy(methyl)silyl)oxy)methylene)bis(4,1-phenylene))bis(oxy))bis(4,1-phenylene))bis(oxy))bis(diethoxy(methyl)silane) (10).



Colorless oil. R_f 0.75 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 7.29 (d, J = 8.6 Hz, 4H), 6.94-6.87 (m, 12H), 5.94 (s, 1H), 3.89 (q, J = 6.9 Hz, 8H), 3.70 (q, J = 7.2 Hz, 4H), 1.24 (t, J = 7.0 Hz, 12H), 1.14 (t, J = 7.0 Hz, 6H), 0.25 (s, 6H), 0.05 (s, 3H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 157.3, 151.0, 150.0, 138.6, 127.7, 120.5, 120.4, 117.5, 75.1, 58.8, 58.4, 18.1, -6.5, -6.8.

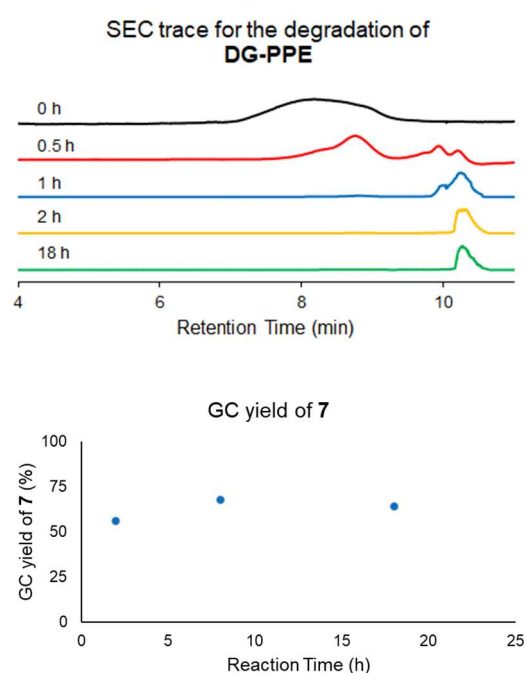
IR (KBr): 2975 m, 2927 w, 2889 w, 1497 s, 1267 m, 1227 s, 1197 w, 1166 m, 1104 s, 1079 s, 954 m, 875 w, 827 m, 807 m, 786 m.

HRMS (FAB $^+$, M^+): Calcd for $\text{C}_{40}\text{H}_{56}\text{O}_{11}\text{Si}_3$: 796.3130. Found: 796.3141.

IX. Time-course Study

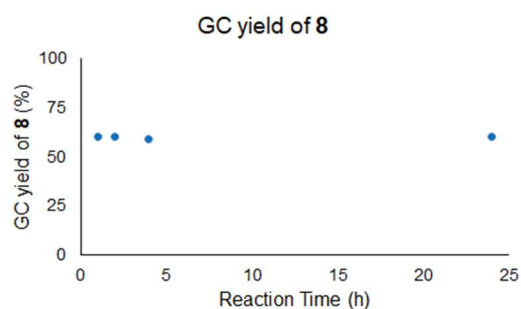
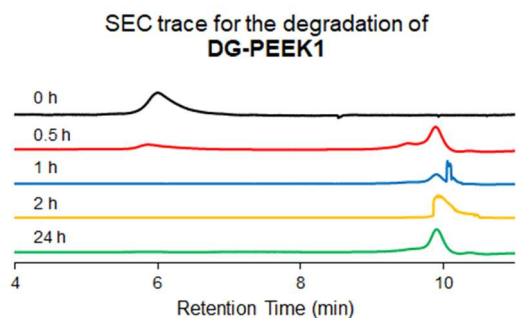
IX -1. Time-course of the degradation of DG-PPE

Reactions were set up according to the typical Procedure outlined above on a 0.13 mmol scale. Time points were taken as separate reactions. To track degradation of DG-PPE via molecular weight, a portion of resulting mixture was subjected to SEC analysis. The yields of **7** was determined by GC using pentadecane as an internal standard. SEC analysis showed that the polymeric materials disappeared within 2 h, but the yield of monomer **7** increased slightly with extended reaction time (50% at 2 hours; 64% at 18 hours).



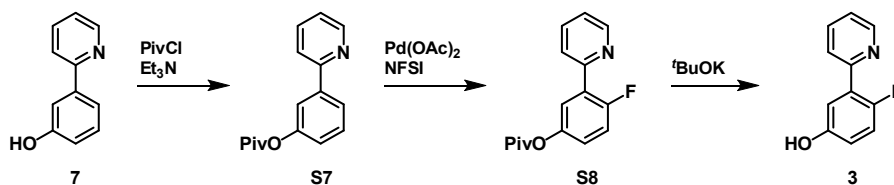
IX -2. Time-course of the degradation of DG-PEEK1

Reactions were set up according to the typical Procedure outlined above on a 0.10 mmol scale. Time points were taken as separate reactions. To track degradation of DG-PEEK1 via molecular weight, a portion of resulting mixture was subjected to SEC analysis. The yields of **7** was determined by GC using pentadecane as an internal standard. SEC traces and GC measurements showed that degradation of **DG-PEEK1** were completed within 2 h.

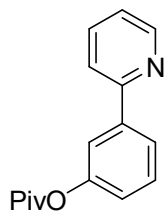


X. Repolymerization of Monomeric Products into Original DG-Polymers

X -1. Conversion of **7** to **3** for Repolymerization to DG-PPE



3-(Pyridin-2-yl)phenyl pivalate (S7). To a 50 mL two-necked flask, **7** (700.2 mg, 4.1 mmol), pivaloyl chloride (0.54 mL, 4.4 mmol), Et₃N (1.2 mL, 8.7 mmol) and THF (16 mL) were added at 0 °C. The reaction mixture was warmed to rt and then stirred for 13 h. The resulting mixture was filtered, and THF was evaporated in vacuo. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 80/20 to 70/30) to give **S7** as a pale yellow oil (1.03 g, 99%).



Pale yellow oil. R_f 0.54 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 8.70–8.68 (m, 1H), 7.84–7.81 (m, 1H), 7.78–7.72 (m, 3H), 7.48 (t, J = 7.8 Hz, 1H), 7.26–7.22 (m, 1H), 7.13–7.11 (m, 1H), 1.38 (s, 9H).

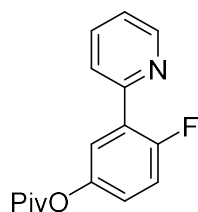
^{13}C NMR (CDCl_3 , 101 MHz) δ : 177.0, 156.3, 151.6, 149.6, 140.9, 136.8, 129.6, 123.9, 122.5, 122.1, 120.7, 120.1, 39.1, 27.2.

IR (KBr): 3066 w, 2975 w, 2872 w, 1749 s, 1584 m, 1567 w, 1472 m, 1460 m, 1277 m, 1181 m, 1167 m, 1117 s, 767 m.

MS, m/z (relative intensity, %): 255 (M^+ , 20), 172 (14), 171 (100), 143 (27), 117 (12), 85 (24), 57 (96), 41 (14).

HRMS (ESI $^+$, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_2$: 256.1332. Found: 256.1339.

4-Fluoro-3-(pyridin-2-yl)phenyl pivalate (S8). This compound was synthesized using a literature procedure,¹⁶ with minor modifications. In a glovebox filled with nitrogen, 3-(pyridin-2-yl)phenyl pivalate (26.1 mg, 0.10 mmol), $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.010 mmol), NFSI (79.3 mg, 0.25 mmol), acetonitrile (0.1 mL) and benzonitrile (4.3 mL) were added to a 5 mL pressure-resistant vial and it was closed with a resealable septum. The mixture was stirred at 170 °C for 2 h using a microwave reactor. After cooling to rt, the resulting mixture was evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 95/5 to 50/50) to give **S8** as a colorless oil (12.7 mg, 45%).



Colorless oil. R_f 0.54 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 8.72–8.70 (m, 1H), 7.84–7.81 (m, 1H), 7.77–7.71 (m, 2H), 7.27–7.24 (m, 1H), 7.16 (dd, J = 10.3, 8.9 Hz, 1H), 7.09–7.05 (m, 1H), 1.35 (s, 9H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 177.0, 157.7 (d, J = 248.2 Hz), 152.3 (d, J = 2.9 Hz), 149.6, 147.2 (d, J = 2.9 Hz), 136.5, 128.0 (d, J = 13.4 Hz), 124.5 (d, J = 10.5 Hz), 123.5 (d, J = 3.8 Hz), 123.4 (d, J = 9.6 Hz), 122.7, 116.9 (d, J = 25.9 Hz), 39.0, 27.1.

^{19}F NMR (CDCl_3 , 376 MHz) δ : -122.5.

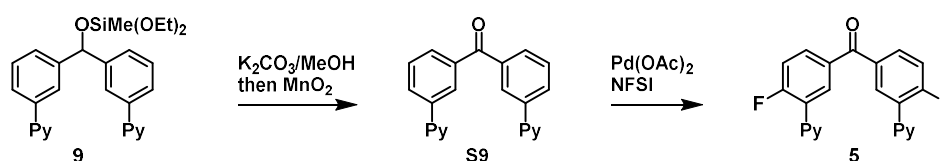
IR (KBr): 3073 w, 2977 s, 2939 m, 2875 m, 1749 s, 1586 s, 1571 m, 1496 s, 1462 s, 1408 m, 1272 m, 1239 m, 1171 m, 1120 s, 1057 m, 1027 m, 916 m, 831 m, 791 m, 770 s, 615 m.

MS, m/z (relative intensity, %): 273 (M^+ , 20), 190 (14), 189 (100), 161 (28), 85 (34), 57 (95), 41 (14).

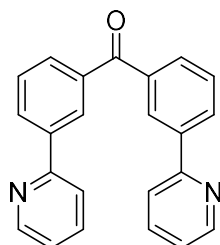
HRMS (DART $^+$, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{16}\text{H}_{17}\text{FNO}_2$: 274.1238. Found: 274.1244.

4-Fluoro-3-(pyridin-2-yl)phenol (3). This compound was synthesized using a literature procedure¹⁷, with minor modifications. To a 10 mL round-bottom flask, 4-fluoro-3-(pyridin-2-yl)phenyl pivalate (52.3 mg, 0.19 mmol), ^tBuONa (58.5 mg, 0.61 mmol) and MeOH (1 mL) were added at 0 °C. After stirring at rt for 4 h, the reaction was quenched by adding saturated aqueous solution of NH₄Cl and the resulting mixture was extracted with EtOAc. The combined extracts were dried over Na₂SO₄ and concentrated. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 95/5 to 50/50) to give 4-fluoro-3-(pyridin-2-yl)phenol (**3**) as a white solid (29.3 mg, 81%).

X -2. Conversion of 9 to 5 for Repolymerization to DG-PEEK1



Bis(3-(pyridin-2-yl)phenyl)methanone (S9). CAS[851540-82-4] Compound **9** (97.8 mg, 0.21 mmol) was hydrolyzed with saturated solution of K₂CO₃ in MeOH (1.0 mL) at rt for 30 min. After removing MeOH in vacuo, toluene (2.0 mL) and MnO₂ (263.3 mg, 3.0 mmol) were added. The mixture was stirred at rt for 17 h. The resulting mixture was filtered, and toluene was evaporated in vacuo to give **S9** as a white solid (70.2 mg, 100%).



White solid. R_f 0.28 (Hexane/EtOAc = 1/1). M.p. 140.6–141.0 °C.

¹H NMR (CDCl₃, 400 MHz) δ : 8.70 (dd, J = 4.6, 0.9 Hz, 2H), 8.44 (t, J = 1.8 Hz, 2H), 8.29 (dd, J = 7.8, 1.4 Hz, 2H), 7.87 (d, J = 7.8 Hz, 2H), 7.80–7.75 (m, 4H), 7.62 (t, J = 7.8 Hz, 2H), 7.28–7.25 (m, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 196.5, 156.4, 149.8, 139.7, 138.1, 137.0, 131.0, 130.5, 128.8, 128.4, 122.6, 120.7.

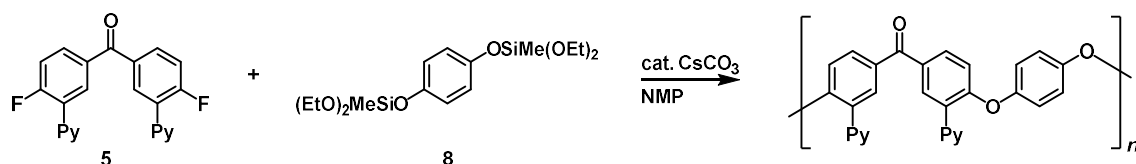
IR (KBr): 3064 w, 3049 w, 1972 w, 1921 w, 1650 s, 1596 s, 1581 s, 1563 s, 1473 m, 1433 s, 1313 s, 1298 m, 1246 s, 1168 m, 1144 m, 1086 m, 992 m, 976 m, 914 m, 816 m, 780 s, 756 s, 748 s, 736 s, 692 m, 649 s, 618 m.

MS, m/z (relative intensity, %): 336 (M⁺, 67), 335 (53), 307 (16), 258 (100), 207 (63), 182 (13), 154 (51), 127 (34).

HRMS (DART+, [M+H]⁺): Calcd for C₂₃H₁₇N₂O: 337.1335. Found: 337.1335.

Bis(4-fluoro-3-(pyridin-2-yl)phenyl)methanone (5). This compound was synthesized using a literature procedure,¹⁶ with minor modifications. In a glovebox filled with nitrogen, bis(3-(pyridin-2-yl)phenyl)methanone (67.9 mg, 0.20 mmol), Pd(OAc)₂ (6.1 mg, 0.027 mmol), NFSI (334.5 mg, 1.1 mmol), acetonitrile (0.36 mL) and benzonitrile (18.0 mL) were added to a 20 mL pressure-resistant vial and it was closed with a resealable septum. The mixture was stirred at 160 °C for 2 h using a microwave reactor. After cooling to rt, saturated solution of K₂CO₃ in MeOH (1.0 mL) was added. The resulting mixture was then evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 52/48) to give **5** as a white solid (35.1 mg, 47%).

Repolymerization to DG-PEEK1.



DG-PEEK1 was synthesized using monomers obtained from depolymerization experiments. To a 20 mL two-necked flask, compound **5** (743.6 mg, 2.0 mmol), compound **8** (750.2 mg, 2.0 mmol), and NMP (4 mL) were added. The flask is equipped with a reflux condenser, and the reaction mixture is stirred under N₂ atmosphere at rt. After the reactants were completely dissolved, Cs₂CO₃ (23.4 mg, 3.6 mol%) was added, and the mixture was heated to 150 °C using an oil bath. After stirring the reaction mixture at 150 °C for 18 h, it was stirred at 180 °C for further 3 h. After cooling to rt, the polymer was precipitated by adding the viscous reaction mixture slowly to vigorously stirred MeOH. The polymer was purified by stirring with acetone. After drying in a vacuum oven, **DG-PEEK1** was obtained as a white powder (806.1 mg, 92%). The spectroscopic data of the repolymerized **DG-PEEK1** was in agreement with that of the original **DG-PEEK1**. The values of M_w , T_g and T_{d5} were comparable to those obtained for the original **DG-PEEK1** (T_{d5} = 474 °C, T_g = 179 °C, M_w = 35400, M_w/M_n = 2.37).

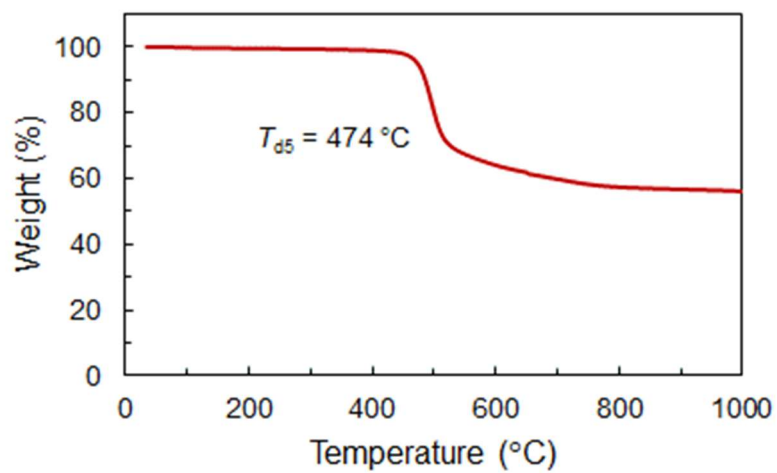


Figure S2.15. TGA of **DG-PEEK1** Obtained by Repolymerization.

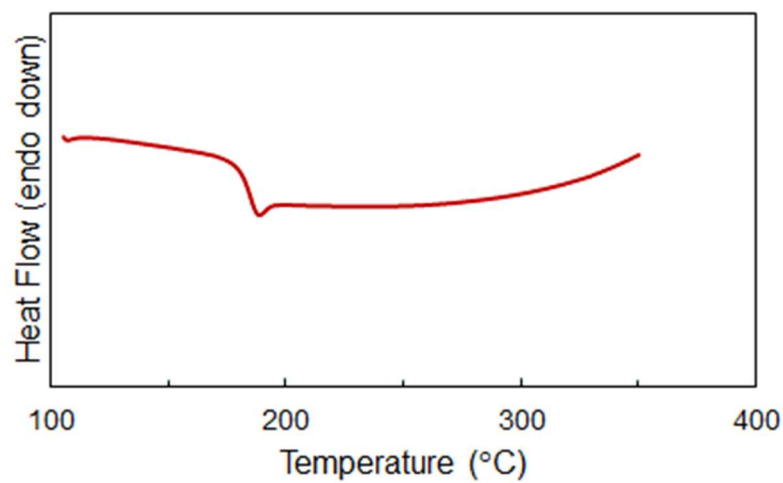


Figure S2.16. DSC Second Heating Thermogram of **DG-PEEK1** Obtained by Repolymerization.

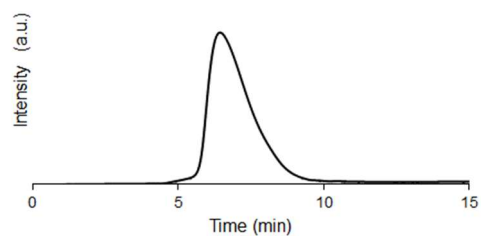
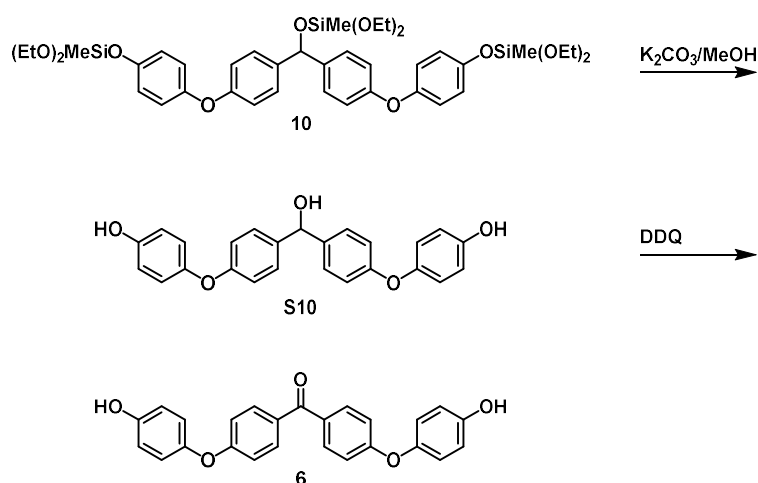
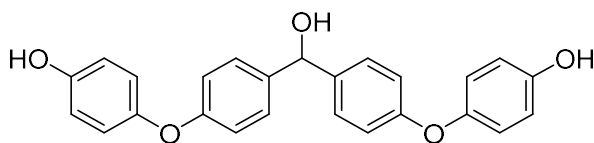


Figure S2.17. SEC Chart of **DG-PEEK1** Obtained by Repolymerization.

X-3. Conversion of 10 to 6 for repolymerization to DG-PEEK2



4,4'-(((Hydroxymethylene)bis(4,1-phenylene))bis(oxy))diphenol (S10). Compound **10** (75.1 mg, 0.094 mmol) was hydrolyzed with a saturated solution K_2CO_3 in MeOH (3.0 mL) at rt for 1 h. After neutralizing using HCl aq, the mixture was extracted with EtOAc. The combined extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 60/40 to 50/50) to give **S10** as a white solid (35.5 mg, 94%).



White solid. R_f 0.24 (Hexane/EtOAc = 1/1). M.p. 168.8–169.9 °C.

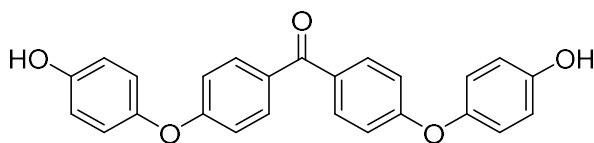
^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ : 9.33 (br, 2H), 7.27 (d, J = 8.7 Hz, 4H), 6.85–6.79 (m, 8H), 6.74 (m, 4H), 5.78 (br, 1H), 5.61 (s, 1H).

^{13}C NMR ($\text{DMSO}-d_6$, 101 MHz) δ : 157.1, 153.8, 148.0, 139.8, 127.6, 120.8, 116.6, 116.2, 73.3.

IR (KBr): 3302 br, 1606 s, 1504 s, 1457 s, 1374 m, 1337 m, 1262 s, 1228 s, 1165 s, 1103 m, 1010 m, 988 m, 879 m, 830 s, 758 m, 604 m, 561 m, 502 m.

HRMS (MALDI⁺, $[\text{M}]^+$): Calcd for $\text{C}_{25}\text{H}_{20}\text{O}_5$: 400.1305. Found: 400.1298.

Bis(4-(4-hydroxyphenoxy)phenyl)methanone (6). [CAS: 42592-70-1] This compound was synthesized using a literature procedure,¹⁸ with minor modifications. DDQ (46.7 mg, 0.21 mmol) was added to a solution of 4,4'-(((hydroxymethylene)bis(4,1-phenylene))bis(oxy))diphenol (77.8 mg, 0.19 mmol) in dioxane (1.2 mL). The reaction mixture immediately turned deep green. The mixture was stirred at rt for 14 h. The resulting white precipitate was filtered off, and dioxane was evaporated in vacuo. The obtained crude compound was purified by flash column chromatography (eluent: hexane/EtOAc = 60/40 to 35/65) to give **6** as a white solid (65.8 mg, 85%).



White solid. R_f 0.32 (Hexane/EtOAc = 1/1).

^1H NMR (DMSO- d_6 , 400 MHz) δ : 9.50 (s, 1H), 7.70 (d, J = 8.7 Hz, 2H), 6.98-6.95 (m, 4H), 6.82 (d, J = 9.2 Hz, 2H).

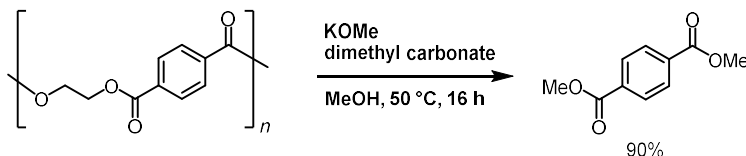
^{13}C NMR (DMSO- d_6 , 101 MHz) δ : 193.1, 162.1, 154.7, 146.5, 132.1, 131.1, 121.8, 116.5, 115.9.

HRMS (EI $^+$, M^+): Calcd for $\text{C}_{25}\text{H}_{18}\text{O}_5$: 398.1154. Found: 398.1162.

XI. Orthogonal Depolymerization

Post-consumer polyethylene terephthalate (PET) in beverage bottles was used for this study. PET beverage bottles were washed with water, dried, and shredded to flake form (ca. 1 mm squares) prior to use.

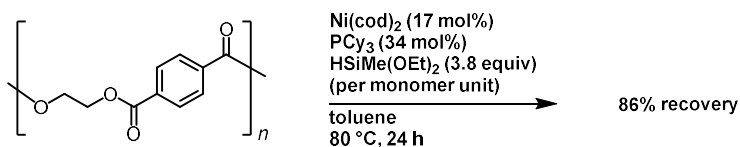
Depolymerization of PET under basic conditions



This reaction was conducted based on the literature procedure.¹⁹

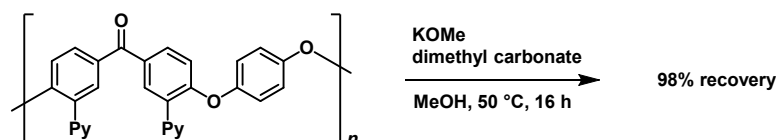
PET (108.3 mg, 0.53 mmol), KOMe (10.8 mg, 0.15 mmol), dimethyl carbonate (1.5 mL) and MeOH (0.20 mL) were added to a 10 mL vial with a Teflon-sealed screwcap with a magnetic stirring bar. The reaction mixture was degassed and stirred at 50 °C for 16 h. The resulting mixture was then evaporated to dryness, and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 85/15 to 50/50) to give dimethyl terephthalate as a white solid (98.9 mg, 90%). The spectroscopic data of the product was in agreement with that reported in the literature.

Attempted depolymerization of PET under Ni-catalyzed conditions



In a glovebox filled with nitrogen, PET (52.2 mg, 0.27 mmol), Ni(cod)₂ (13.0 mg, 0.047 mmol), PCy₃ (25.6 mg, 0.091 mmol), hydrosilane (137.2 mg, 1.02 mmol) and toluene (0.50 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 80 °C for 24 h. The resulting mixture was filtered, and the residue was washed with MeOH. PET was recovered (45.0 mg, 86%). This result is consistent with the fact that in Ni-catalyzed reductive C–O bond cleavage reactions with hydrosilane, an ester group remains unreacted.²⁰

Attempted depolymerization of DG-PEEK1 under basic conditions



DG-PEEK1 (90.3 mg, 0.20 mmol), KOMe (4.4 mg, 0.063 mmol), dimethyl carbonate (0.6 mL) and MeOH (0.080 mL) were added to a 5 mL vial with a Teflon-sealed screwcap with a magnetic stirring bar. The reaction mixture was degassed and stirred at 50 °C for 18 h. The resulting mixture was filtered, and the residue was washed with MeOH. **DG-PEEK1** was recovered (88.2 mg, 98%).

2.5. References

- (1) Vollmer, I.; Jenks, M. J. F.; Roelands, M. C. P.; White, R. J.; van Harmelen, T.; de Wild, P.; van der Laan, G. P.; Meirer, F.; Keurentjes, J. T. F.; Weckhuysen, B. M. *Angew. Chem., Int. Ed.*, 2020, **59**, 15402–15423.
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For Experimental Section

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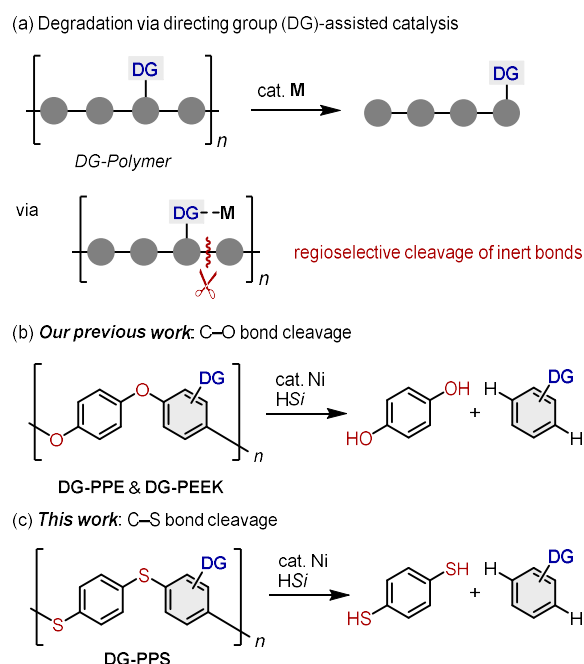
Chapter 3

Directing Group-Integrated Poly(Phenylene Sulfide): Achieving Chemical Stability and Controlled Degradability

3.1. Introduction

With growing concerns about the environmental pollution caused by plastics, chemical recycling, which converts polymers back into monomers or their precursor forms, is becoming increasingly important.^{1,2} While this approach is promising in theory, the practical success of chemical recycling has primarily been limited to polymers containing chemically labile bonds,³ such as esters,⁴⁻⁸ disulfides,⁹⁻¹³ and silyl ethers,^{14,15} in their main chains. Developing methods to transform other classes of polymers (e.g., those consisting of strong covalent bonds) back into monomers or their precursors could significantly advance the realization of a sustainable and circular polymer economy. One potential strategy to address this challenge is to integrate the directing group (DG) as a design principle to create chemically recyclable polymers without sacrificing chemical and thermal stability (DG-polymers, Scheme 3.1a). As discussed in Chapter 2, DGs are functional groups that interact with transition metal catalysts to facilitate the site-selective bond cleavage by forming stable metallacyclic intermediates. The concept of directing group has been widely used to transform strong covalent bonds in small molecules, such as C–C or C(aryl)–O bonds.¹⁶⁻²⁰ Based on this strategy, Chapter 2 describes the selective disassembly of poly(aryl ether)s bearing DGs into monomer precursors via nickel-catalyzed C–O bond cleavage (Scheme 3.1b).²¹ These polymers exhibited excellent chemical and thermal stability and allowed orthogonal degradation with polyethylene terephthalate (PET). To further explore the potential of DG-polymers, this chapter aims to extend the DG strategy to poly(phenylene sulfide) (PPS). This study also demonstrates that the crystallinity of the polymers is tunable by the design of the DG.

PPS, which is composed of robust Ar–S–Ar bonds, is a high-performance thermoplastic polymer widely used in industries for applications such as electrical insulators and metal part replacements due to its exceptional chemical and thermal stability. However, the direct degradation of PPS into low-molecular-weight compounds are sparse, with only a few examples documented.²²⁻²⁸ Notably, the regeneration of the original polymers from the degradation products has remained challenging.²⁹ Herein, the author report on the development of directing group- integrated PPS, which can be selectively disassembled into monomer precursors (Scheme 3.1c).



Scheme 3.1. Strategies for the Design of Chemically Recyclable Polymers

3.2. Results and Discussion

Synthesis of DG-integrated PPS. To achieve both sustainability and high performance in material design, two scientific requirements must be addressed: (1) optimizing the ratio of DG incorporation to maintain or fine-tune the desired material properties, and (2) elucidating the impact of DG structure on thermal properties and crystallinity. To this end, four DG-PPS variants were synthesized *via* nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$) using dithiol monomers with varying chain lengths (**1** and **2**) and dichloride monomers bearing two types of DGs: 2-pyridyl (**3**) and 4,7-phenanthroline (**4**) (Table 3.1). The latter directing group was selected based on the hypothesis that its increased planarity and rigidity, resulting from the absence of rotatable bonds between the main chain and the DG, would enhance crystallinity. A typical polymerization procedure involved the reaction of dithiol **1** with dichloride **3** in the presence of K_2CO_3 (2.2 equiv) in NMP at 185 °C for 5 h to yield **DG-PPS1** in a 92% isolated yield. Following the same procedure, **DG-PPS2**, **DG-PPS3** and **DG-PPS4** were synthesized. While **DG-PPS2** was soluble in CHCl_3 , **DG-PPS1**, **DG-PPS3** and **DG-PPS4** were only sparingly soluble or insoluble in all tested organic solvents (*i.e.*, CHCl_3 , DMSO, THF), precluding molecular weight determination. The weight average molecular weight (M_{w}) of **DG-PPS2**, determined by SEC with polystyrene standards, was 212 kDa. DG-installed polymers were characterized by ^1H and ^{13}C NMR spectroscopy and MALDI-TOF MS (see Section 3.4, Experimental Section).

Table 3.1. Synthesis of **DG-PPSs**

entry	polymer	dithiol	dichloride	yield of DG-PPS (%)	M_w [kDa]	M_w/M_n	T_{d5} [°C]	T_g [°C]
1	DG-PPS1	1	3	92	(300) ^a	1.36	443	123
2	DG-PPS2	2	3	70	212	1.20	412	126
3	DG-PPS3	1	4	92	— ^b	— ^b	418	236
4	DG-PPS4	2	4	94	— ^b	— ^b	418	262

dithiol monomers

1 **2**

dichloride monomers

3 **4**

polymers

DG-PPS1 **DG-PPS3**

DG-PPS2 **DG-PPS4**

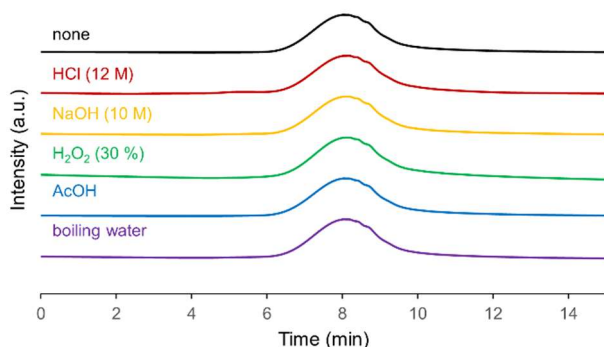
^aDetermined by SEC analysis of the fraction of **DG-PPS1** that was soluble in CHCl_3 . ^bNot determined due to insolubility in organic solvents at rt.

Properties of DG-integrated PPSs. Thermogravimetric analysis (TGA) revealed that all DG-PPSs exhibit high thermal stability with 5% weight loss temperatures (T_{d5}) ranging from 412 to 443 °C (Table 3.1). Notably, the integration of 2-pyridyl or 4,7-phenanthroline groups into the PPS backbone does not compromise thermal stability when compared to the parent PPS. Differential scanning calorimetry (DSC) analysis determined the glass transition temperature (T_g) of **DG-PPS1** to be 123 °C, which is higher than that of the parent PPS (88 °C)³⁰ (Scheme S3.13). **DG-PPS2** exhibited a comparable T_g value (126 °C), indicating that the DG incorporation ratio has a minimal impact on the thermal properties. **DG-PPS3** and **DG-PPS4**, which bear 4,7-phenanthroline groups as DGs, exhibit substantially higher T_g values of 236 °C and 262 °C, respectively. These results demonstrate that the structure of DG can effectively modulate the thermal properties of the resulting polymers. **DG-PPS1–4** did not display clear melt transition temperature (T_m) below 350 °C (Scheme S3.9–S

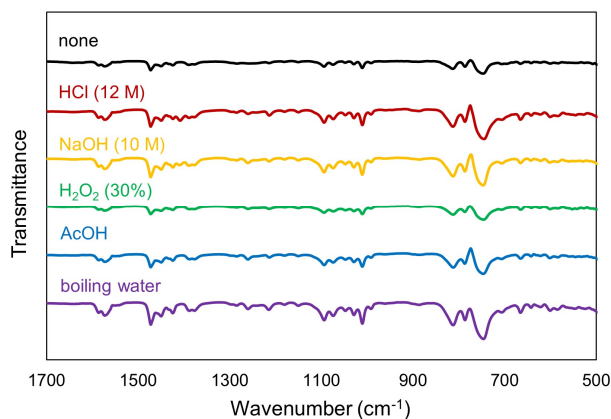
3.12). However, in the case of **DG-PPS4**, X-ray diffraction (XRD) analysis revealed a crystalline nature with a crystallinity of 75% (Scheme S3.8). This finding demonstrates that the crystallinity of the polymers is tunable through careful design of the DG structure.

The chemical stability of **DG-PPS1** was evaluated by subjecting it to various harsh conditions, including aqueous HCl (12 M), aqueous NaOH (10 M), aqueous H₂O₂ (30%), AcOH, and boiling water. After 24 hours of immersion, size exclusion chromatography (SEC) analysis of the recovered polymers (neutralized when necessary) revealed no change in molecular weight (Scheme 3.2a). FT-IR spectra recorded before and after treatment with these reagents showed only minor differences (Scheme 3.2b). Furthermore, the integrity of the directing groups was confirmed by the successful Ni-catalyzed depolymerization (vide infra) following exposure to these conditions, indicating their resistance to degradation (see Section 3.4, Experimental Section). These results demonstrate the exceptional chemical stability of DG-PPSs.

(a) SEC trace



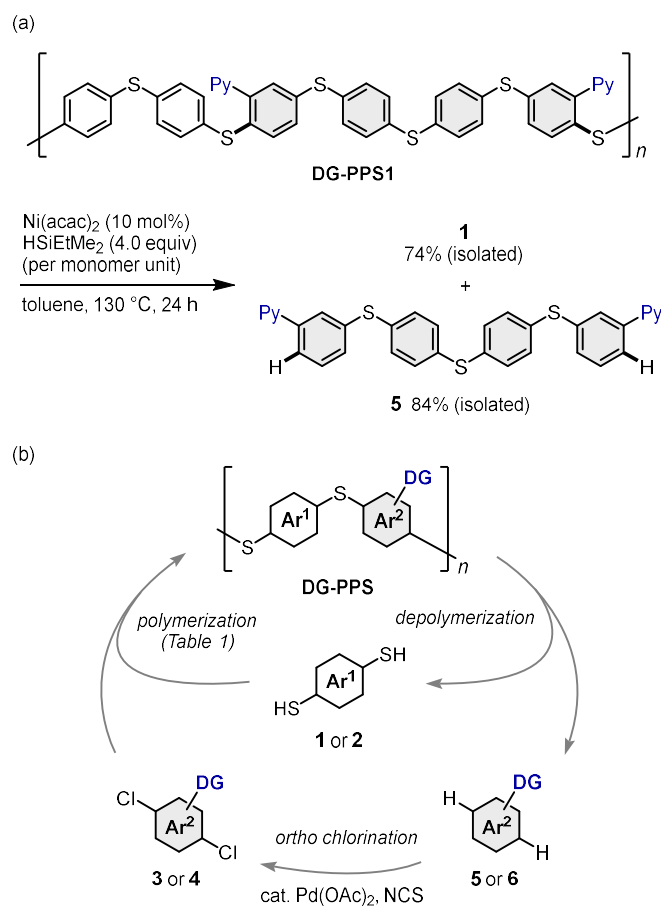
(b) FT-IR analysis



Scheme 3.2. Chemical Stability of **DG-PPS1**

Catalytic depolymerization of DG-integrated PPS. To identify suitable catalytic conditions for the selective degradation of DG-PPSs into well-defined monomer precursors, we initially screened catalysts that were previously used for the C(aryl)–S bond cleavage in small molecules (see Section 3.4, Experimental Section).^{31,32} As a result, the following conditions were established: the reaction of **DG-PPS1** with HSiEtMe₂ (4 equiv per monomer unit) in the presence of Ni(acac)₂ catalyst in toluene at 130 °C for 24 h yielded dithiol **1** (74%) and DG-containing fragment **5** (84%) (Scheme 3.3a). Notably, unlike the previous reports on Ni or Pd-catalyzed reductive cleavage of PPS using hydrosilane,²⁶ overreduction of the SH group in **1** was suppressed to approximately 6%, as determined by GC-MS analysis (see Section 3.4, Experimental Section). Control experiments using model compounds suggest that this selectivity arises from the interaction of DGs with the Ni catalyst, which not only promotes cleavage of adjacent C(aryl)–S bonds in **DG-PPS1** but also inhibits degradation of DG-free C(aryl)–S bonds (Scheme S3.25).

Under these reaction conditions, controlled decomposition of **DG-PPS2**, **DG-PPS3** and **DG-PPS4** was achieved (Scheme 3.3b). For **DG-PPS2**, independent of the DG feed ratio, the polymer was disassembled to **2** (62%) and **5** (78%) under identical conditions (entry 2). Similarly, **DG-PPS3** and **DG-PPS4** underwent controlled degradation to **1** (71%) and **6** (84%), and **2** (62%) and **6** (68%), respectively (entries 3, 4), demonstrating that a 4,7-phenanthroline backbone serves as an effective DG. The resultant structurally well-defined small molecules were subsequently converted back into the original polymers through *ortho*-chlorination. For example, the reaction of **5** with NCS (3 equiv) in the presence of Pd(OAc)₂ catalyst at 120 °C³³ produced the original monomer **3** in 53% isolated yield. Similarly, this palladium-catalyzed *ortho*-chlorination of **6** afforded **4** in 70% yield. Notably, this step was also enabled by the assistance of the DG, underscoring the utility of utilizing DG in the design of recyclable polymer.



entry	polymer	yields of depolymerization		yield of chlorination ^a
		dithiol (%)	arene (%)	dichloride (%)
1	DG-PPS1	1 (74)	5 (84)	3 (53)
2	DG-PPS2	2 (62)	5 (78)	3 (53)
3	DG-PPS3	1 (71)	6 (84)	4 (70)
4	DG-PPS4	2 (62)	6 (68)	4 (70)

Scheme 3.3. Chemical Recycling of **DG-PPS**

^a **5** (or **6**) (1 equiv), Pd(OAc)₂ (10 mol%), NCS (3 equiv) and acetonitrile at 120 °C for 18 h.

3.3. Conclusion

In summary, we developed directing group-integrated poly(phenylene sulfide)s, which are chemically recyclable while retaining heat and chemical resistance. In the presence of a nickel catalyst and hydrosilane, these polymers can be selectively disassembled into monomers or monomer precursors without excessive reductive degradation of the SH groups, which are essential for repolymerization. Moreover, we demonstrate that incorporating 4,7-phenanthroline as the directing group significantly enhanced both the *T_g* values and crystallinity, compared to the 2-pyridyl group. These findings provide a foundation for designing sustainable yet high-performance materials.

Ongoing studies are exploring the application of the directing group strategy to other resilient polymers.

3.4. Experimental Section

I. General Information

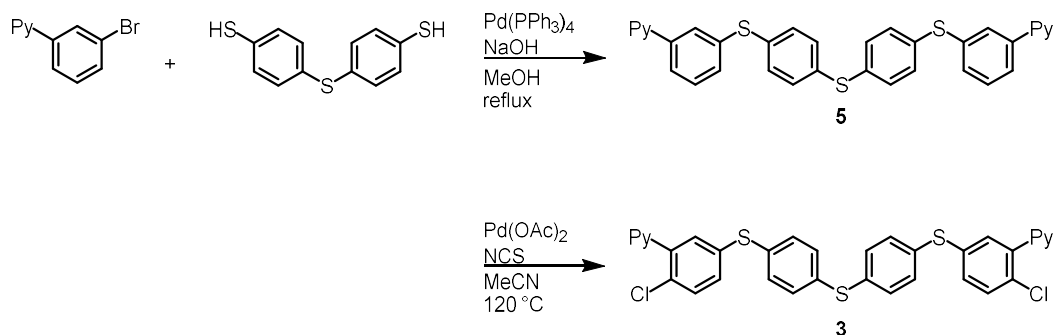
^1H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer in CDCl_3 . The chemical shifts in ^1H NMR spectra were recorded relative to tetramethylsilane (δ 0.00) unless otherwise noted. The chemical shifts in ^{13}C NMR spectra were recorded relative to CDCl_3 (δ 77.0). The data is reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer, or JEOL JMS-S3000. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-2014 gas chromatograph, equipped with a flame ionization detector. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with Biotage Isolera[®] equipped with Biotage[®] Sfar. Analytical SEC was performed on a Hitachi High-Technologies Corporation L-2420/L-2130 equipped with a Shodex K-803L using chloroform (CHCl_3) as an eluent (40 °C, 1 ml/min) calibrated with polystyrene standards. Thermogravimetric analyses (TGA) were performed on a Hitachi High-Tech NEXTA STA200RV at 10 °C/min under N_2 flow. The glass transition temperatures (T_g) of the polymers were recorded on a Hitachi High-Tech NEXTA DSC2000. Powder X-ray diffraction (PXRD) patterns were recorded using a XRD Aeris (Malvern Panalytical) instrument in the 2θ region of 3–50°. The measurements were performed with Cu-K α radiation (λ = 1.5418 Å) at a scanning rate of 1.0° min⁻¹ under an applied voltage of 40 kV and a current of 7.5 mA.

II. Materials

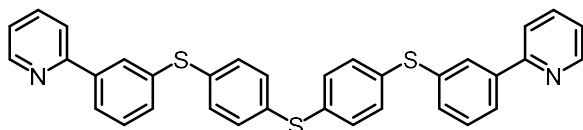
All commercially available reagents and solvents were supplied from TCI, WAKO, Aldrich and Strem Chemicals. $\text{Ni}(\text{acac})_2$ was purchased from Aldrich and used as received. 2-(3-Bromophenyl)pyridine was prepared from (3-bromophenyl)boronic acid [CAS: 89598-96-9] according to the literature method.¹ 1,4-Naphthalenediamine was prepared from 1-amino-4-nitronaphthalene [CAS: 776-34-1] according to the literature method.²

III. Preparation of Starting Materials

Synthesis of bis(4-((4-chloro-3-(pyridin-2-yl)phenyl)thio)phenyl)sulfane (3)



Bis(4-((3-(pyridin-2-yl)phenyl)thio)phenyl)sulfane (5). This compound was synthesized following a literature procedure,³ with minor modifications. To a 50 mL two-necked flask, 2-(3-bromophenyl)pyridine (4.42 g, 19.8 mmol), 4,4'-thiobisbenzenethiol (1.65 g, 6.6 mmol), $\text{Pd(PPh}_3)_4$ (993 mg, 0.86 mmol), NaOH (2.27 g, 56.8 mmol) and MeOH (13 mL) were added. The reaction mixture was degassed and then refluxed for 12 h. After cooling to rt, the reaction was quenched by adding saturated aqueous solution of NH_4Cl and the resulting mixture was extracted with CHCl_3 . The combined extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 80/20, then CHCl_3) and the resulting product was recrystallized from hexane / CHCl_3 (5/1) to give **5** as a white solid (2.90 g, 79%).



White solid. R_f 0.49 (Hexane/EtOAc = 1/1). M.p. 192.9–193.2 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 8.68 (d, J = 4.0 Hz, 2H), 8.03 (t, J = 1.6 Hz, 2H), 7.91 (dt, J = 7.2, 1.8 Hz, 2H), 7.74 (td, J = 7.5, 1.9 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.45–7.38 (m, 4H), 7.28–7.22 (m, 10H).

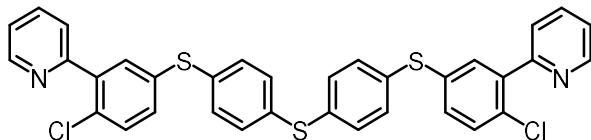
^{13}C NMR (CDCl_3 , 101 MHz) δ : 156.4, 149.7, 140.5, 136.9, 135.5, 135.3, 134.0, 132.2, 131.6, 130.9, 130.2, 129.7, 126.2, 122.5, 120.6.

IR (KBr): 3055 w, 3012 w, 1590 m, 1557 m, 1474 m, 1427 m, 1402 m, 809 s, 768 s, 742 m, 694 m.

HRMS (DART+, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{34}\text{H}_{25}\text{N}_2\text{S}_3$: 557.1174. Found: 557.1179.

Bis(4-((4-chloro-3-(pyridin-2-yl)phenyl)thio)phenyl)sulfane (3). This compound was synthesized using a literature procedure,⁴ with minor modifications. Compound **5** (1.34 g, 2.4 mmol), Pd(OAc)_2 (55 mg, 0.25 mmol), NCS (961 mg, 7.2 mmol) and MeCN (100 mL) were added to a 250 mL vial with a Teflon-sealed screwcap. The reaction mixture was stirred at 120 °C for 18 h. After the removing

MeCN in vacuo, the crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 70/30) and SEC to give **3** as a white solid (806 mg, 53%).



White solid. R_f 0.64 (Hexane/EtOAc = 1/1). M.p. 131.5–132.0 °C.

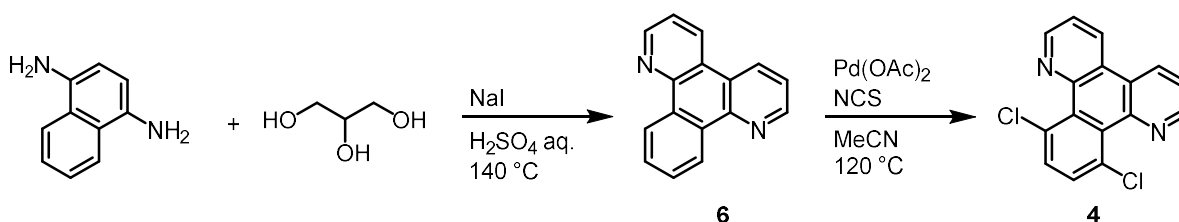
^1H NMR (CDCl_3 , 400 MHz) δ : 8.71–8.69 (m, 2H), 7.76 (td, J = 7.8, 1.9 Hz, 2H), 7.63–7.61 (m, 4H), 7.41 (d, J = 8.0 Hz, 2H), 7.31–7.22 (m, 12H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 155.9, 149.6, 139.9, 136.0, 134.6, 134.4, 134.3, 134.0, 132.2, 131.6, 131.5, 131.4, 130.9, 124.8, 122.7.

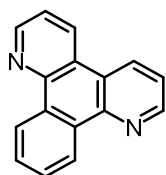
IR (KBr): 3044 w, 1589 m, 1567 m, 1473 s, 1453 s, 1433 m, 1375 m, 1096 s, 1029 s, 1007 s, 908 m, 822 s, 785 s, 747 s.

HRMS (DART $^+$, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{34}\text{H}_{23}\text{N}_2\text{S}_3^{35}\text{Cl}_2$: 625.0395. Found: 625.0391.

Synthesis of 9,12-Dichlorobenzo[f][4,7]phenanthroline (**4**)



Benzo[f][4,7]phenanthroline (6**).** This compound was synthesized using a literature procedure,⁵ with minor modifications. Glycerol (6.3 mL, 86.2 mmol) was added to a solution of naphthalene-1,4-diamine (4.53 g, 28.6 mmol) and NaI (129 mg, 0.86 mol) in aqueous H_2SO_4 (80%, 60 mL) at 140 °C. The mixture was then heated at 140 °C for 9 h while distilling the water formed during this period. After cooling to rt, the dark solution was carefully poured into ice and then basified to pH 9–10 with NaOH. The resulting mixture was then extracted with CHCl_3 . The combined extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 50/50) to give **6** as a yellow solid (3.87 g, 56%).



Yellow solid. R_f 0.64 (Hexane/EtOAc = 1/1). M.p. 162.4–163.2 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 9.27 (q, J = 3.2 Hz, 2H), 9.02–9.01 (m, 2H), 8.80–8.78 (m, 2H), 7.84 (q, J = 3.2 Hz, 2H), 7.61–7.58 (m, 2H).

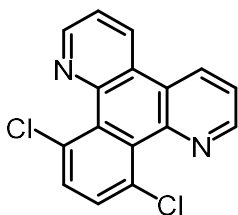
^{13}C NMR (CDCl_3 , 101 MHz) δ : 149.5, 146.5, 132.4, 130.7, 129.1, 124.6, 123.4, 122.1.

IR (KBr): 3070 w, 1584 m, 1529 m, 1460 m, 1420 s, 1396 s, 802 s, 791 s, 741 s, 691 m, 619 m.

MS, m/z (relative intensity, %): 230 (M^+ , 100), 231 (18), 229 (36), 115 (21).

HRMS (DART+, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{16}\text{H}_{11}\text{N}_2$: 231.0917. Found: 231.0908.

9,12-Dichlorobenzo[f][4,7]phenanthroline (4). This compound was synthesized using a literature procedure,⁴ with minor modifications. Compound **6** (57.5 mg, 0.25 mmol), $\text{Pd}(\text{OAc})_2$ (5.8 mg, 0.026 mmol), NCS (99.1 mg, 0.74 mmol) and MeCN (10 mL) were added to a 20 mL vial with a Teflon-sealed screwcap. The reaction mixture was stirred at 120 °C for 18 h. After removing MeCN in vacuo, the crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 30/70) to give **4** as a white solid (52.0 mg, 70%).



White solid. R_f 0.67 (Hexane/EtOAc = 1/1). M.p. 193.2–194.2 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 9.04 (dd, J = 4.4, 1.6 Hz, 2H), 8.75 (d, J = 8.4, 2H), 7.74 (s, 2H), 7.62 (q, J = 4.1 Hz, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 147.9, 145.7, 132.7, 131.6, 131.2, 130.2, 124.4, 122.8.

IR (KBr): 3079 w, 1592 m, 1561 m, 1531 m, 1461 m, 1406 s, 1309 m, 1154 m, 1124 s, 1026 s, 827 m, 786 s, 666 m, 601 s.

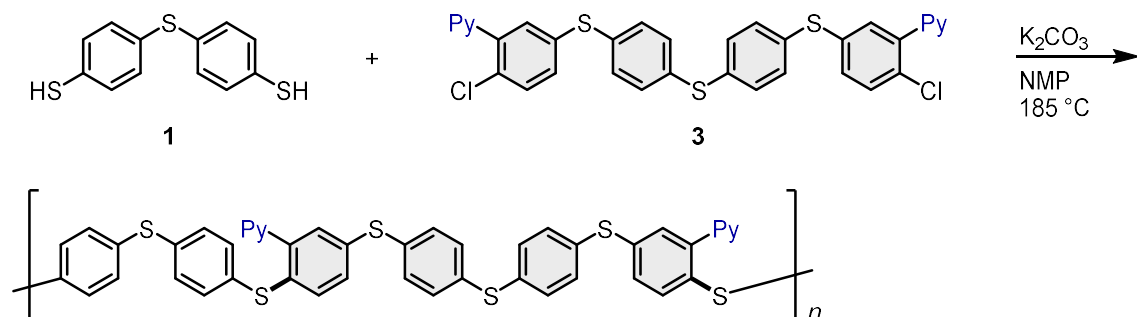
MS, m/z (relative intensity, %): 299 (M^+ , 21), 301 (12), 300 (70), 298 (100), 263 (32), 149 (15), 87 (12).

HRMS (DART+, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{16}\text{H}_9\text{N}_2^{35}\text{Cl}_2$: 299.0137. Found: 299.0124.

IV. Synthesis and Characterization of DG-PPS

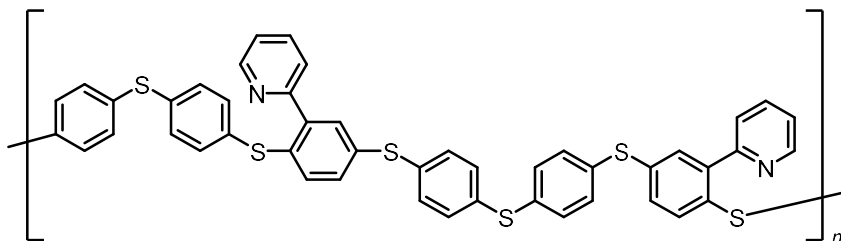
IV-1. Synthesis of DG-Polymers

General Procedure



The synthesis of **DG-PPS1** was performed following a modified procedure from reported literature.⁶ To a 20 mL two-necked flask, **3** (1.33 g, 2.1 mmol), **1** (534 mg, 2.1 mmol), K_2CO_3 (641 mg, 4.6 mmol) and NMP (2.5 mL) were added. The flask is equipped with a reflux condenser, and the reaction mixture is stirred at $185\text{ }^\circ\text{C}$ for 5 h under N_2 atmosphere. After cooling to rt, the polymer was precipitated by pouring the viscous reaction mixture slowly to a vigorously stirred MeOH. The resulting solid was washed with acetone.

After drying in a vacuum oven, **DG-PPS1** was obtained as a light brown powder (1.56 g, 92%).



$M_w = 300000$, $M_w/M_n = 1.36$.

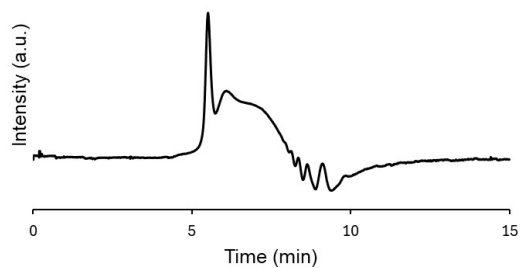
M_n was determined by SEC analysis of the fraction of **DG-PPS1** that was soluble in $CHCl_3$

1H NMR (CD_2Cl_2 , 400 MHz) δ : 8.60 (br, 2H), 7.67–7.19 (br, 28H).

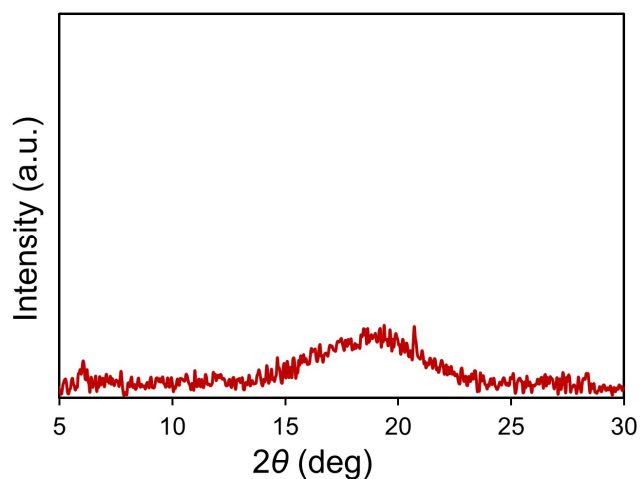
^{13}C NMR ($CDCl_3$, 101 MHz) δ : 157.3, 149.6, 149.0, 141.8, 136.2, 134.7, 134.6, 134.4, 134.3, 134.0, 132.7, 132.0, 131.6, 131.5, 131.5, 124.8, 124.1, 122.5.

IR (ATR): 3005 w, 1573 m, 1472 m, 1449 m, 1424 m, 1388 w, 14215 w, 1093 m, 1074 m, 1029 w, 1011 m, 812 m, 787 m, 744 s, 665 m, 602 w.

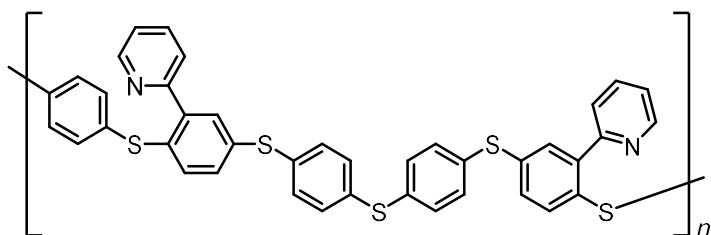
Scheme S3.1. SEC Spectrum of **DG-PPS1**.



Scheme S3.2. XRD Patterns of **DG-PPS1**.



Synthesis of **DG-PPS2**



DG-PPS2



The general procedure was followed, except that **2** was used instead of **1**.

A white powder (486.3 mg, 70%).

$M_w = 212000$, $M_w/M_n = 1.20$.

^1H NMR (CDCl_3 , 400 MHz) δ : 8.63 (d, $J = 3.6$ Hz, 2H), 7.67 (t, $J = 6.8$ Hz, 2H), 7.49 (d, $J = 11.2$ Hz, 4H), 7.26–7.11 (m, 18H).

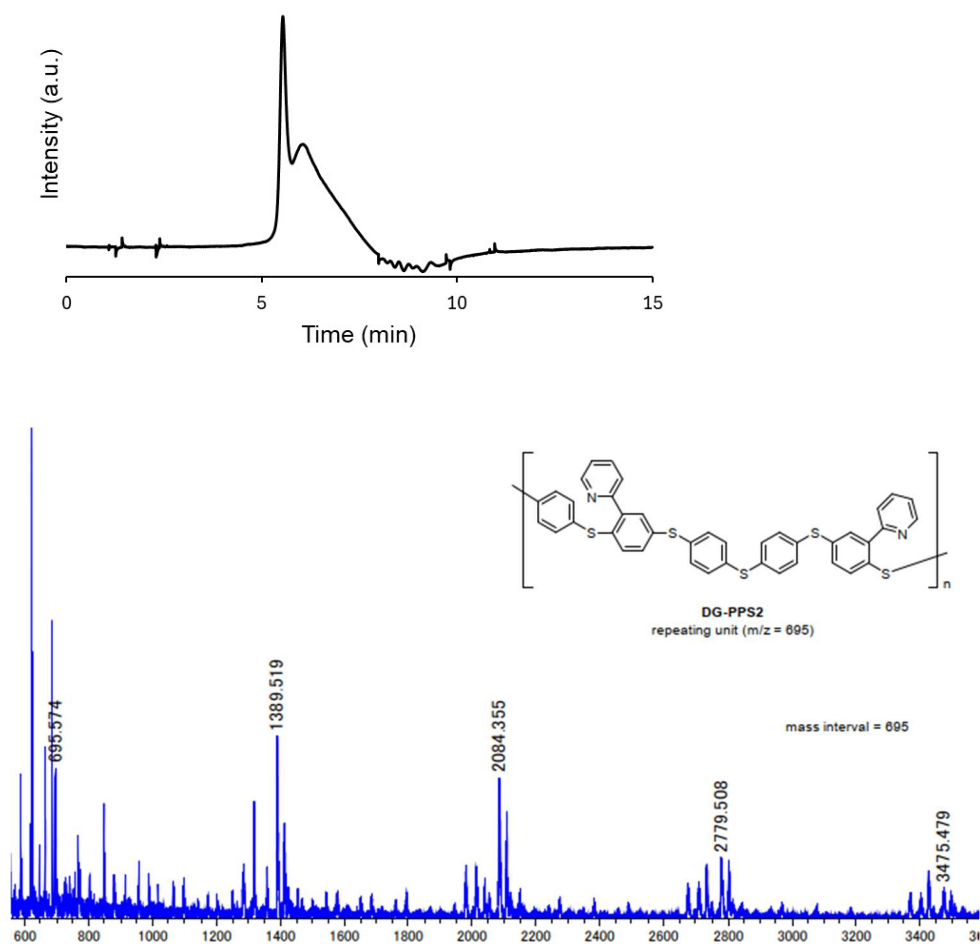
^{13}C NMR (CDCl_3 , 101 MHz) δ : 157.2, 149.0, 141.9, 136.1, 134.7, 134.6, 134.4, 134.4, 134.1, 132.7,

132.5, 132.2, 131.6, 131.5, 131.4, 124.0, 122.4.

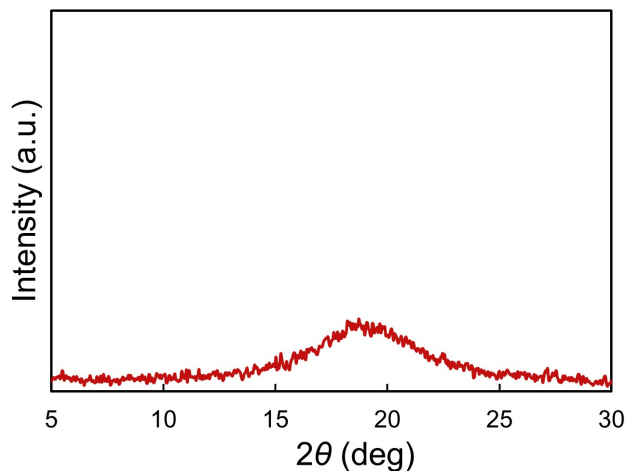
IR (ATR): 3005 w, 1586 m, 1573 m, 1472 s, 1449 m, 1424 m, 1377 w, 1215 w, 1094 m, 1074 m, 1030 w, 1011 m, 814 m, 787 m, 745 s, 665 w, 601 w.

The observed peak interval in the MALDI-TOF MS spectrum was 694, which is consistent with the mass of the repeating unit of **DG-PPS2**.

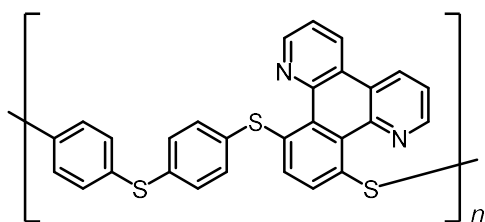
Scheme S3.3. SEC and MALDI-TOF MS Spectrum of **DG-PPS2**.



Scheme S3.4. XRD Patterns of DG-PPS2.



Synthesis of DG-PPS3



The general procedure was followed, except that **4** was used instead of **3**.

A light brown powder (1.31 g, 92%).

¹H and ¹³C NMR spectra were recorded on a JEOL RESONANCE ECA-500 in DMSO-*d*₆ at 150 °C. The chemical shifts in ¹H NMR spectra were recorded relative to DMSO-*d*₆ (δ 2.50). The chemical shifts in ¹³C NMR spectra were recorded relative to DMSO-*d*₆ (δ 39.51). Even at 150 °C, **DG-PPS3** was only sparingly soluble in DMSO-*d*₆. The following resonances were observed for the soluble fraction of **DG-PPS3**.

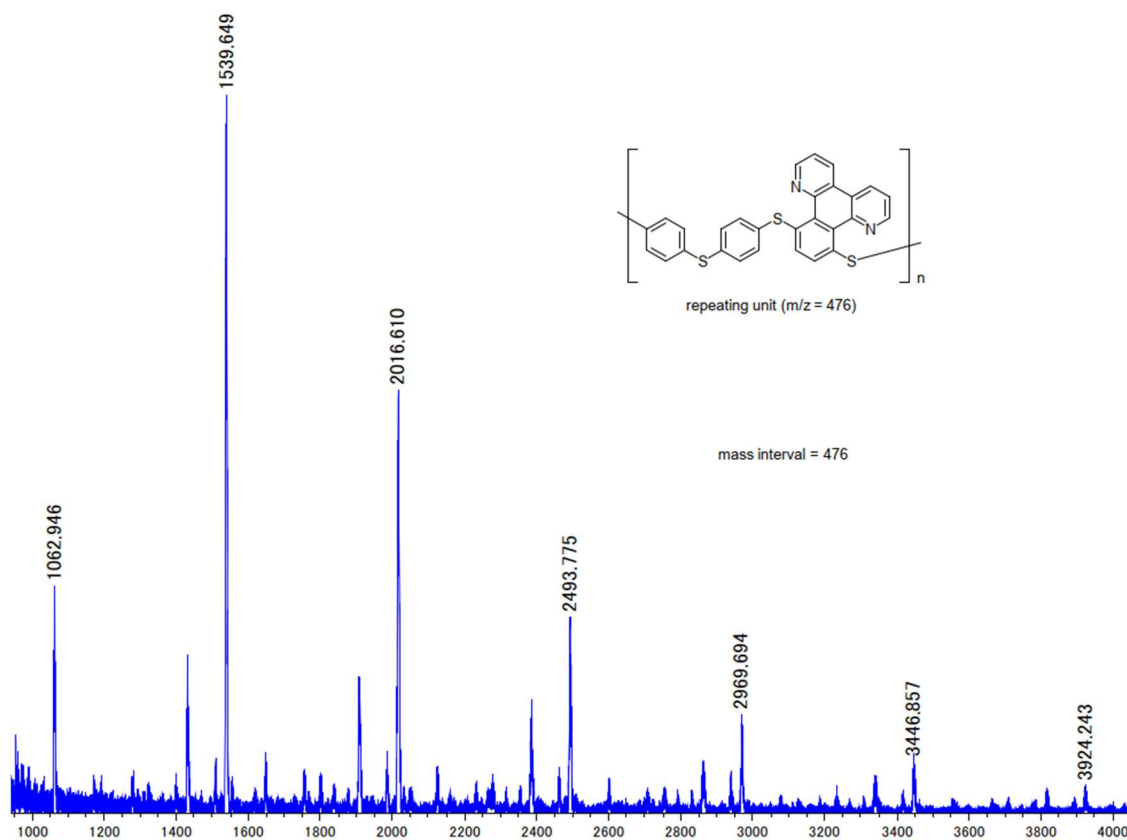
¹H NMR (DMSO-*d*₆, 500 MHz) δ : 9.18–9.04 (m, 4H), 7.81–7.10 (m, 12H).

¹³C NMR (DMSO-*d*₆, 126 MHz) δ : 146.0, 145.8, 145.2, 134.7, 133.6, 131.1, 130.8, 130.3, 130.2, 127.6, 122.8, 121.7.

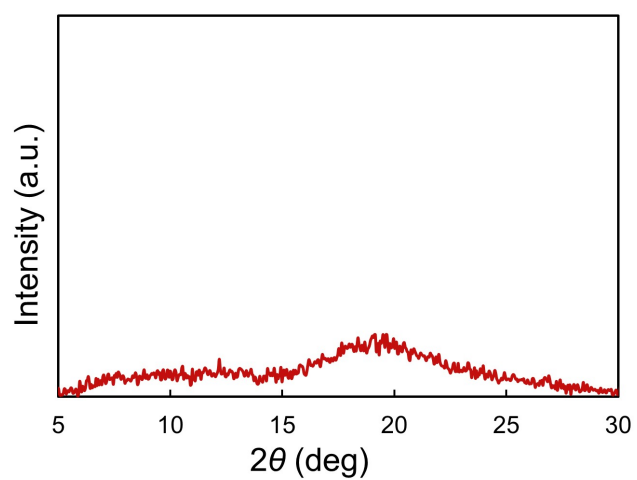
IR (KBr): 3060 w, 1589 m, 1561 s, 1538 m, 1472 m, 1395 s, 1308 w, 1260 w, 1163 m, 1127 m, 1094 m, 1068 m, 1012 s, 814 s, 784 s, 742 m, 658 s, 607 m.

The observed peak interval in the MALDI-TOF MS spectrum was 477, which is consistent with the mass of the repeating unit of **DG-PPS3**.

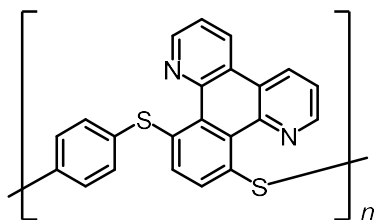
Scheme S3.5. MALDI-TOF MS Spectrum of **DG-PPS3**.



Scheme S3.6. XRD Patterns of **DG-PPS3**.



Synthesis of DG-PPS4



The general procedure was followed, except that **4** was used instead of **3** and **2** was used instead of **1**. A light brown powder (1.03 g, 94%).

^1H and ^{13}C NMR spectra were recorded on a JEOL RESONANCE ECA-500 in $\text{DMSO}-d_6$ at 150 °C. The chemical shifts in ^1H NMR spectra were recorded relative to $\text{DMSO}-d_6$ (δ 2.50). The chemical shifts in ^{13}C NMR spectra were recorded relative to $\text{DMSO}-d_6$ (δ 39.51). Even at 150 °C, **DG-PPS4** was only sparingly soluble in $\text{DMSO}-d_6$. The following resonances were observed for the soluble fraction of **DG-PPS4**. The following resonances were observed for the soluble fraction of **DG-PPS4**.

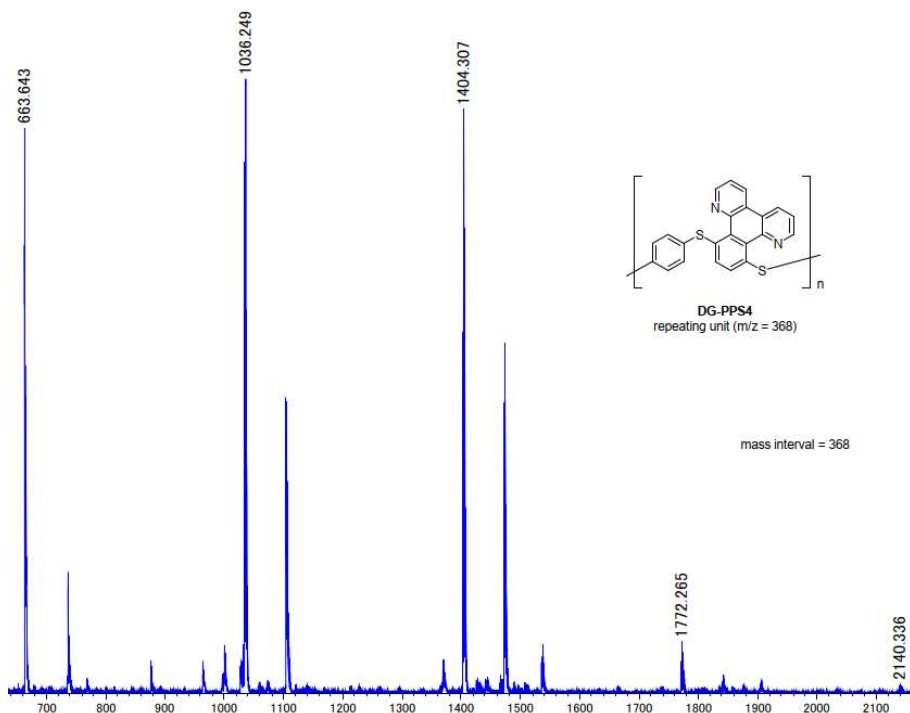
^1H NMR ($\text{DMSO}-d_6$, 500 MHz) δ : 9.21–9.01 (m, 4H), 7.84–7.27 (m, 8H).

^{13}C NMR ($\text{DMSO}-d_6$, 126 MHz) δ : 147.2, 146.0, 145.9, 134.9, 130.3, 127.9, 127.5, 123.4, 121.9, 121.7.

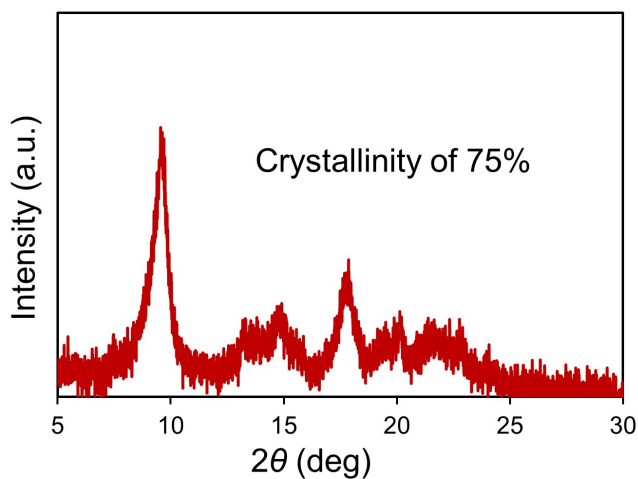
IR (KBr): 3059 w, 1589 m, 1561 s, 1538 m, 1459 m, 1394 s, 1308 w, 1264 w, 1162 m, 1127 m, 1095 w, 1029 m, 1014 m, 815 m, 784 s, 658 s, 606 m.

The observed peak interval in the MALDI-TOF MS spectrum was 368, which is consistent with the mass of the repeating unit of **DG-PPS4**.

Scheme S3.7. SEC and MALDI-TOF MS Spectrum of **DG-PPS4**.



Scheme S3.8. XRD Patterns of **DG-PPS4**.

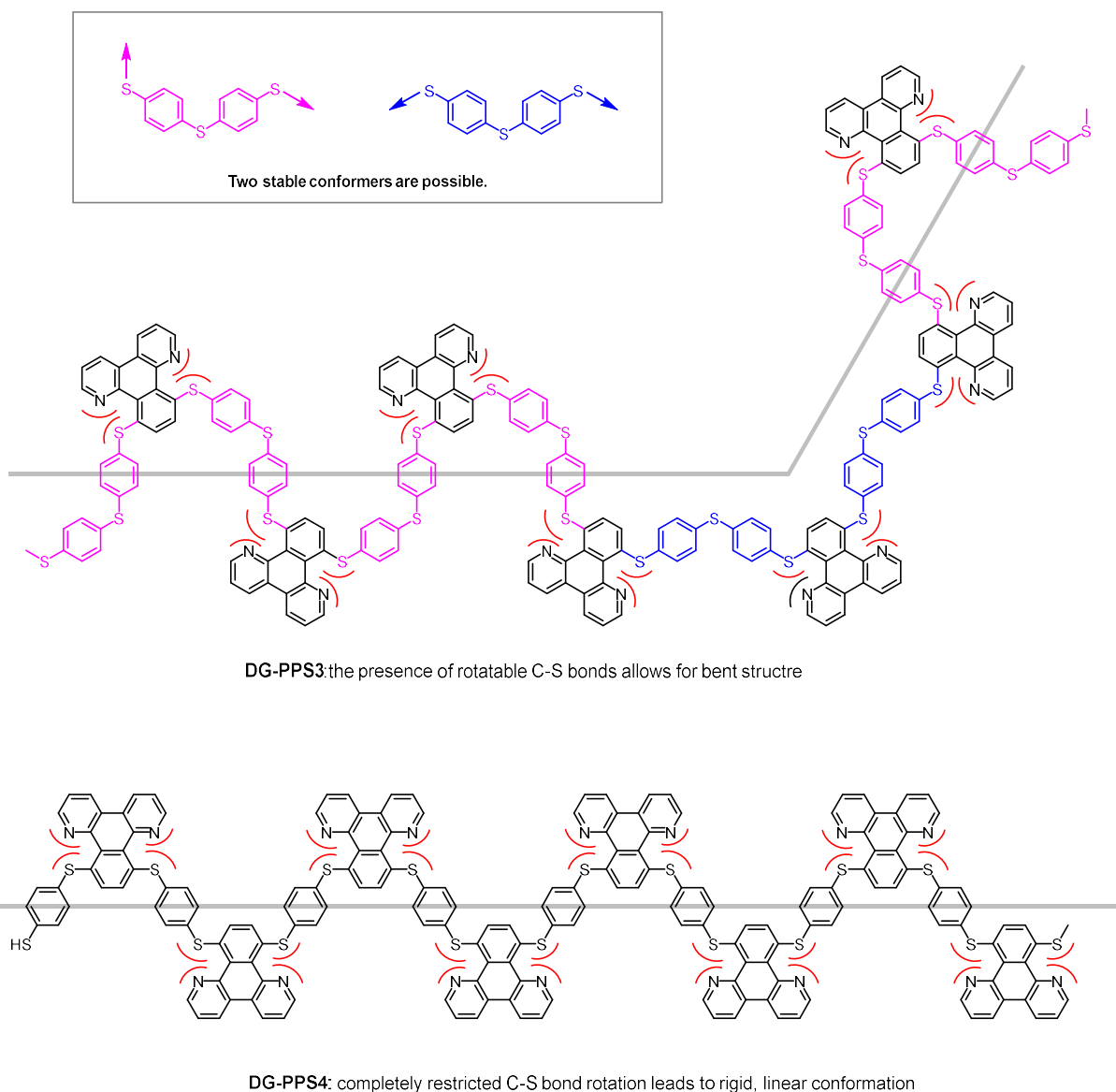


The degree of crystallinity (X_C) of the polymers was determined using X-ray diffraction (XRD) analysis in the 2θ range of 3–30°. The crystallinity was calculated using the following equation:

$$X_C = I_C / (I_C + I_A) \times 100 (\%)$$

where I_C represents the integrated intensity of the crystalline peaks, and I_A denotes the integrated intensity of the amorphous halo. To distinguish between crystalline and amorphous contributions, the XRD profiles of amorphous halo were deconvoluted by fitting a Gaussian function to the diffraction pattern in the 2θ range of 15–25°.

The difference in crystallinity between **DG-PPS3** and **DG-PPS4** can be attributed to their structural flexibility. **DG-PPS3** contains a more extended phenylene sulfide linker, which allows for two stable conformers (pink and blue substructures in the figure below) without introducing significant steric repulsion with the bulky directing groups. This increased flexibility allows the polymer chains to adopt a bent conformation, resulting in lower crystallinity. In contrast, **DG-PPS4** lacks rotatable C–S bonds, restricting it to a predominantly linear structure to minimize steric interactions with the directing groups (see figure below). This rigidity enhances intermolecular interactions, promoting effective packing in the solid state and leading to higher crystallinity

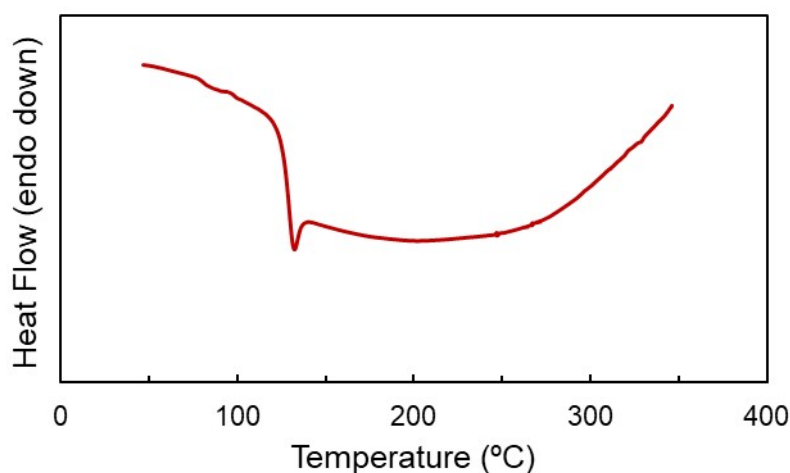


IV-2. Thermal Properties of DG-PPSs

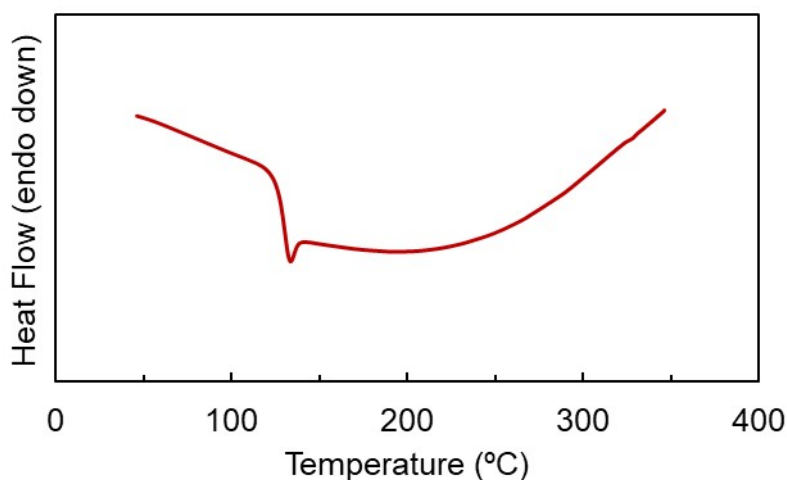
Differential Scanning Calorimetry (DSC) Thermograms

Thermal transitions were assessed with differential scanning calorimetry using a Hitachi High-Tech NEXTA DSC2000 and 1–10 mg of polymer material. Samples were heated to 350 °C and then cooled to 30 °C at 10 °C/min. Samples were again heated to 350 °C at 10 °C/min. Thermal data was assessed from the second heating cycle. PPS without DG was purchased from Sigma–Aldrich Japan (powder forms, Cat. No. 182354.). T_g values for **DG-PPS1**, **DG-PPS2**, **DG-PPS3** and **DG-PPS4** were determined to be 123, 126, 236 and 262 °C, respectively. In each DG-PPS, T_m were not observed (Schemes S3.9, S3.10, S3.11 and S3.12). The parent PPS without DGs has T_g of 88 °C and T_m of 283 °C (Scheme S3.13).

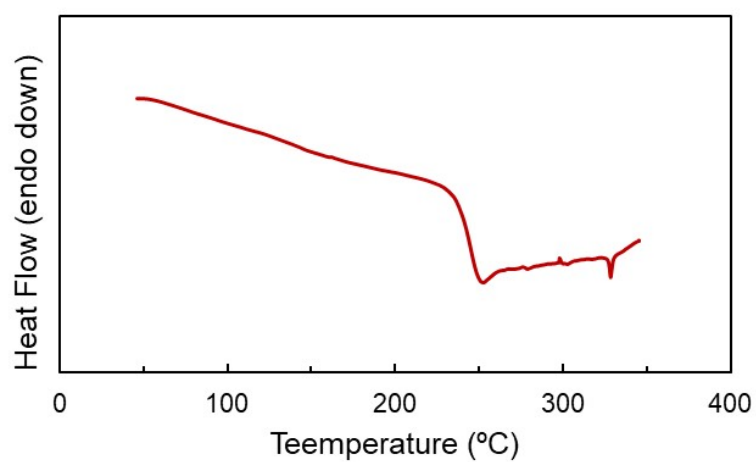
Scheme S3.9. DSC Second Heating Thermogram of **DG-PPS1**.



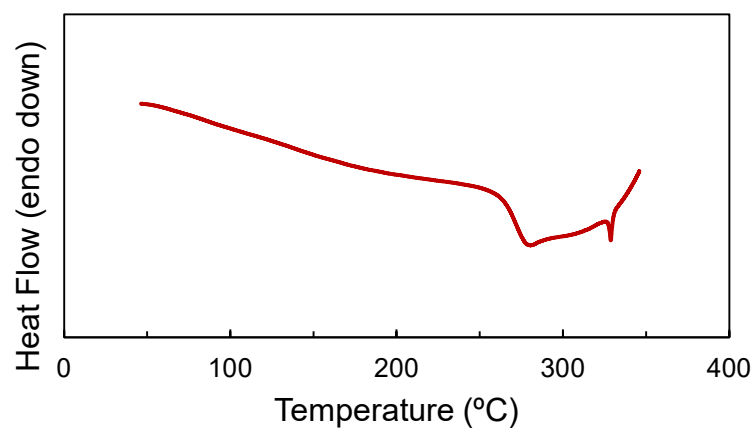
Scheme S3.10. DSC Second Heating Thermogram of **DG-PPS2**.



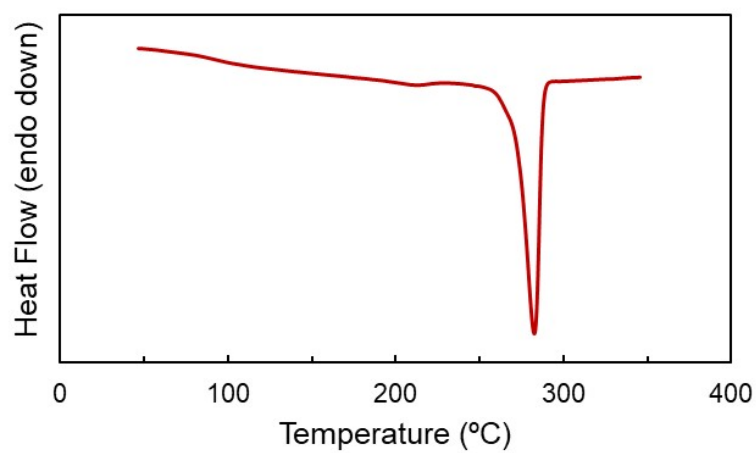
Scheme S3.11. DSC Second Heating Thermogram of **DG-PPS3**.



Scheme S3.12. DSC Second Heating Thermogram of **DG-PPS4**.



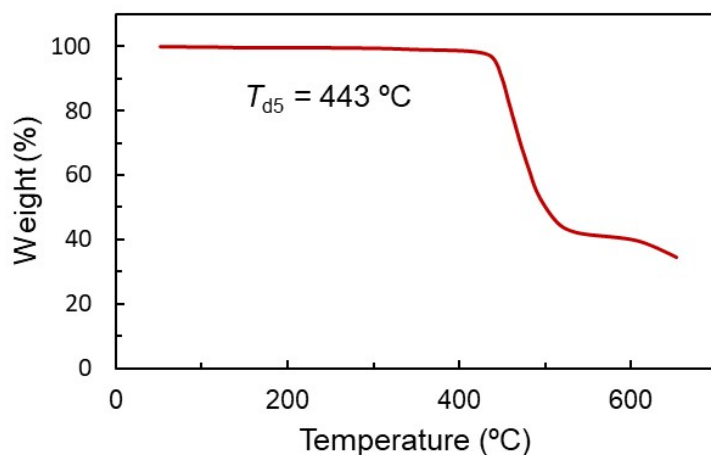
Scheme S3.13. DSC Second Heating Thermogram of **PPS**.



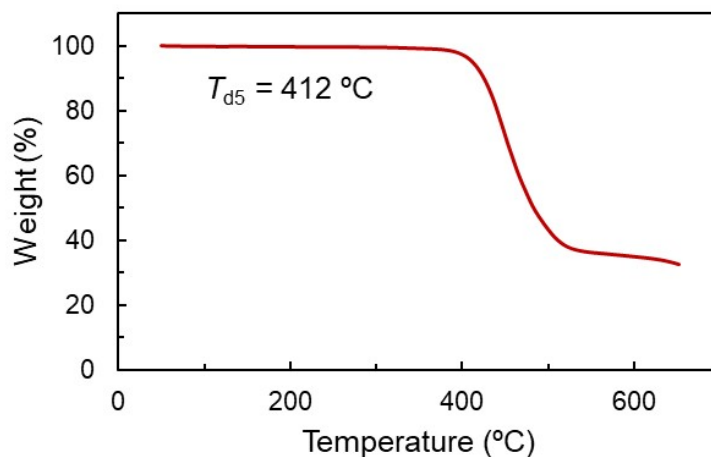
Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using a Hitachi High-Tech NEXTA STA200RV and 1–10 mg of polymer material. Samples were heated at a rate of 10 °C/min from 30 °C to 800 °C under N₂ flow. Decomposition temperatures are reported at 5% mass loss (T_{d5}). T_{d5} of **DG-PPS1**, **DG-PPS2**, **DG-PPS3** and **DG-PPS4** were determined to be 443, 412, 418 and 418 °C, respectively (Scheme S3.14, S3.15, S3.16 and S3.17). The parent PPS without DGs had T_{d5} of 459 °C (Scheme S3.18).

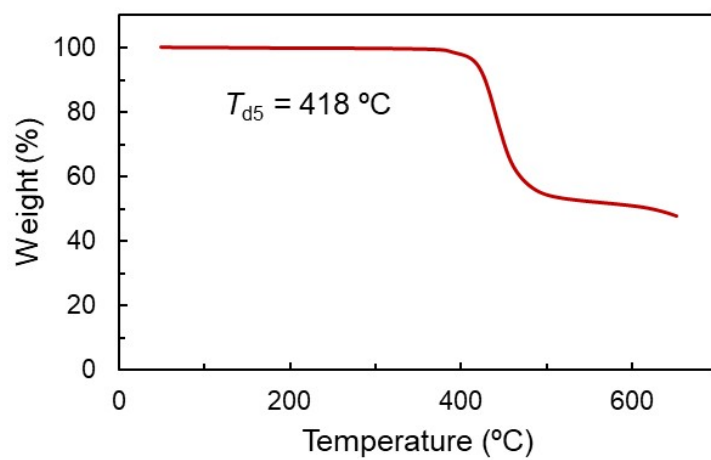
Scheme S3.14. TGA of **DG-PPS1**.



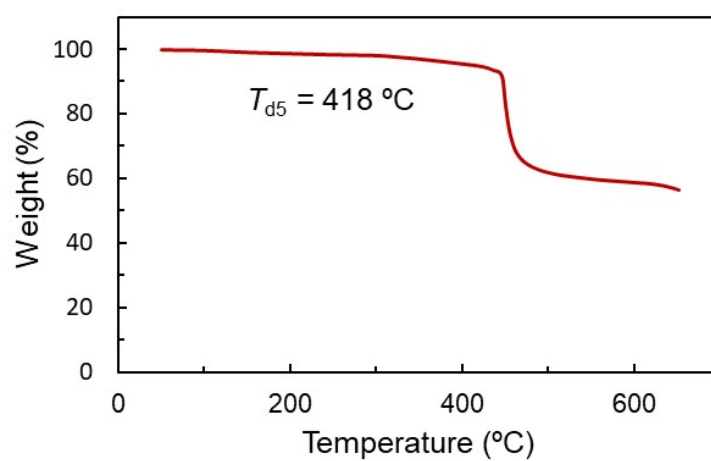
Scheme S3.15. TGA of **DG-PPS2**.



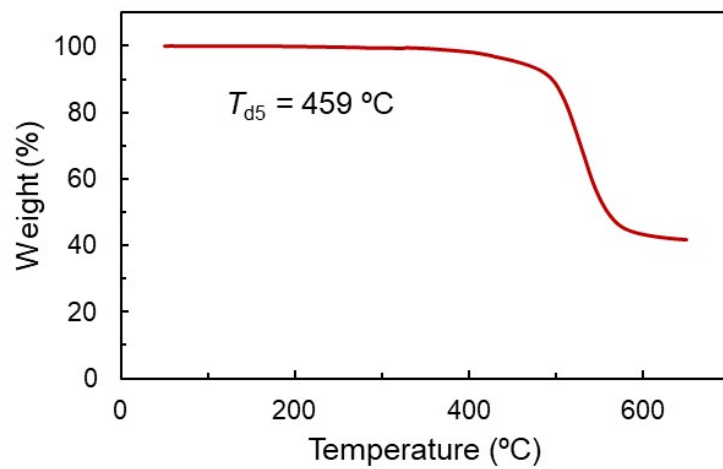
Scheme S3.16. TGA of DG-PPS3.



Scheme S3.17. TGA of DG-PPS4.



Scheme S3.18. TGA of PPS.



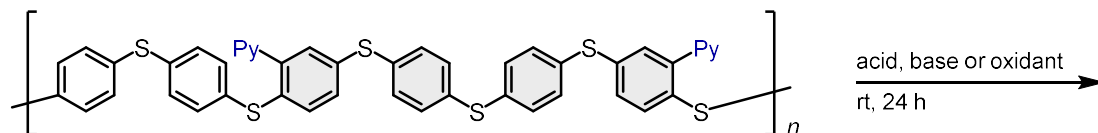
IV-3. Solubility of the DG-PPSs

Table S3.1. Solubility of the DG-PPSs

polymer	CHCl ₃ (40 °C)	THF (60 °C)	DMF (100 °C)	o-dichlorobenzene (100 °C)
DG-PPS1	sparingly soluble	sparingly soluble	sparingly soluble	sparingly soluble
DG-PPS2	soluble	soluble	insoluble	soluble
DG-PPS3	sparingly soluble	insoluble	insoluble	sparingly soluble
DG-PPS4	insoluble	insoluble	insoluble	insoluble

V. Chemical Stability of DG-PPS

V-1. Stability of DG-PPS1 in Different Solutions



DG-PPS1 (5.0 mg) was introduced into a 10 mL vial with a Teflon-sealed screwcap, along with a magnetic stirring bar. Subsequently, a solution (1.0 mL) containing HCl (12 M), NaOH (10 M), H₂O₂ (30%), AcOH or water was added to the vial, and the mixture was stirred for 24 h at rt (or heated to 100°C in the case of water). Following neutralization, the mixture was extracted with CHCl₃ (2 mL × 3). The combined extracts were dried, and the solid obtained was subjected to FT-IR spectroscopic analysis using an ATR detector. A portion of the solid was dissolved in HPLC-grade CHCl₃, filtered through a syringe filter, and subsequently analyzed via SEC analysis.

Furthermore, to assess the integrity of the directing groups, Ni-catalyzed depolymerization reactions on **DG-PPS1** were performed after treatment with HCl, NaOH, H₂O₂, AcOH, and boiling water. In all cases, depolymerization proceeded smoothly, indicating that the directing groups remained intact and that **DG-PPS1** retains its chemical recyclability even after exposure to these conditions.

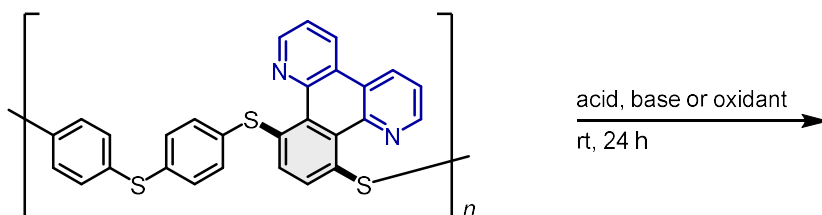
1. pretreatment
 2. Ni(acac)₂ (10 mol%)
 HSiEtMe₂ (4.0 equiv)
 (per monomer unit)
 toluene, 130 °C, 24 h

1

5

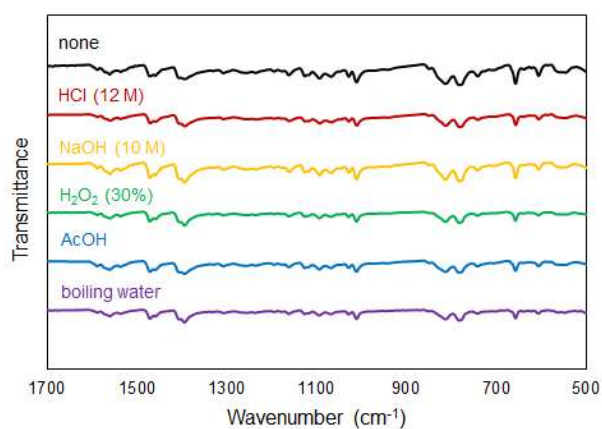
DG-PPS1

V-2. Stability of DG-PPS3 in Different Solutions



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Scheme S3.19. FT-IR analysis

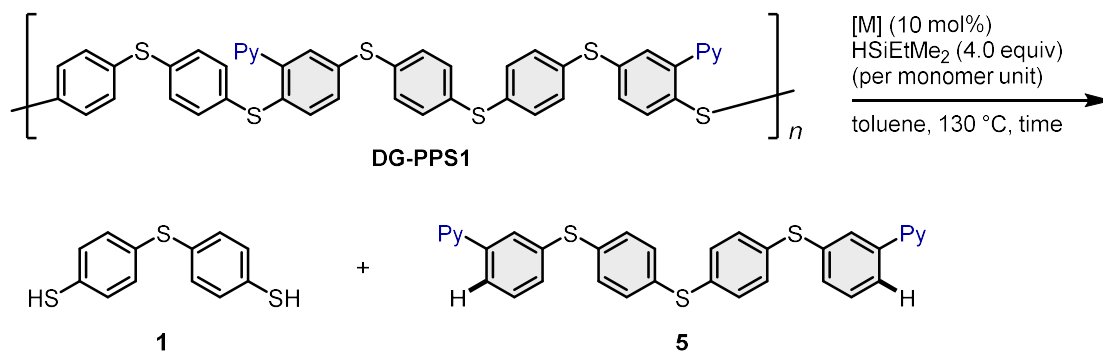


VI. Typical Procedures for Controlled Decomposition

VI-1. Optimization of C–S Bond Cleavage in DG-PPS1

In a glovebox filled with nitrogen, **DG-PPS1** (0.10 mmol), catalyst (0.010 mmol), hydrosilane (0.40 mmol) and toluene (0.4 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 130 °C. The resulting mixture was filtered, and toluene was evaporated in vacuo. The crude mixture was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 20/80) to give **1** and **5** as white solids respectively.

Table S3.3. Optimization of C–S Bonds Cleavage of **DG-PPS1**

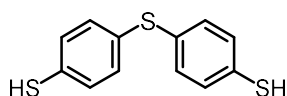


entry	[M]	time (h)	Yield of 1 (%)	Yield of 5 (%)
1 ^a	[Rh(CO) ₂ Cl] ₂	18	78	67
2 ^a	Ni(cod) ₂	18	60	43
3	Ni(cod) ₂	18	67	70
4 ^c	NiCl ₂	48	19	23
5 ^c	NiCl ₂ •PPh ₃	48	47	69
6 ^c	NiCl ₂ •dme	48	45	76
7 ^c	Ni(OAc) ₂	48	32	24
8 ^c	Ni(acac) ₂	48	75	80
9	Ni(acac) ₂	48	66	84
10	Ni(acac) ₂	24	74	84
11	Ni(acac) ₂	2	n.d.	n.d.

^aWith metal catalyst 20 mol% instead of 10 mol%.

^bWith Mn (6.0 equiv) as reductant.

4,4'-Thiodibenzenethiol (**1**). [CAS: 19362-77-7]



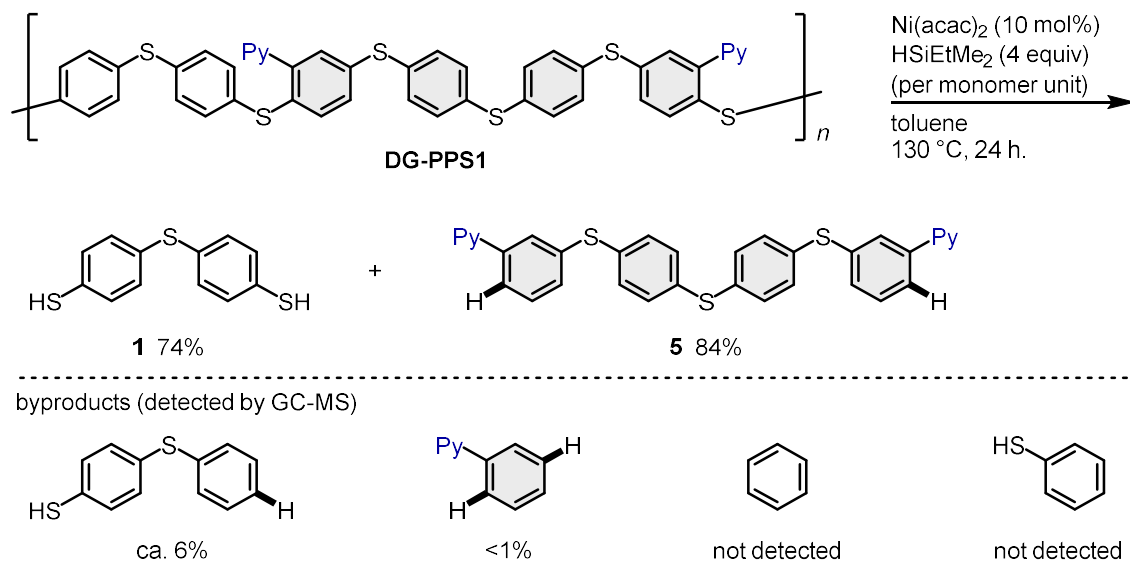
White solid. *R*_f 0.71 (Hexane/EtOAc = 1/1).

¹H NMR (CDCl₃, 400 MHz) δ : 7.29–7.15 (m, 8H), 3.46 (s, 2H).

¹³C NMR (CDCl₃, 101 MHz) δ : 132.9, 131.7, 130.1.

HRMS (DART⁺, [M+H]⁺): Calcd for C₁₂H₁₁S₂: 251.0017. Found: 251.0021.

VI-2. Controlled Decomposition of DG-PPS1



In a glovebox filled with nitrogen, **DG-PPS1** (81.2 mg, 0.10 mmol), Ni(acac)₂ (3.0 mg, 0.012 mmol), HSiEtMe₂ (35.3 mg, 0.40 mmol) and toluene (0.4 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 130 °C for 24 h. The resulting mixture was filtered, and toluene was evaporated in vacuo. The crude mixture was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 20/80) to give **1** as a white solid (18.8 mg, 74%) and **5** as a white solid (47.1 mg, 84%). The detectable byproducts were overreduction products (i.e., ca. 6 % of 4-(phenylthio)benzenethiol was formed, as determined by GC using eicosane as an internal standard). SEC analysis further confirmed that no high molecular weight compounds remained after the catalytic depolymerization of **DG-PPS1**.

(B)

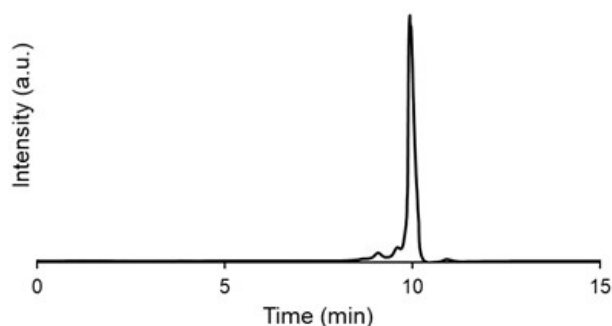


(B)

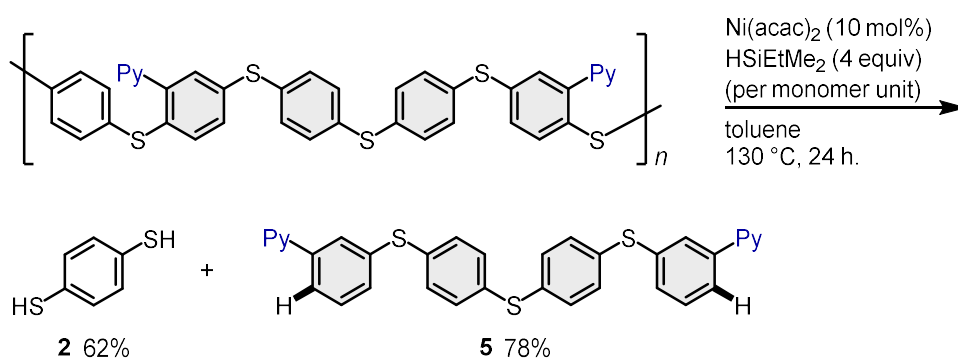


Pictures of the reaction mixture before heating (A) and after heating at 130 °C for 24 h (B).

Scheme S3.20. SEC Chart of **DG-PPS1** after heating at 130 °C for 24 h in the presence of Ni catalyst.



VI-3. Controlled Decomposition of DG-PPS2



In a glovebox filled with nitrogen, **DG-PPS2** (74.3 mg, 0.11 mmol), $\text{Ni}(\text{acac})_2$ (2.7 mg, 0.011 mmol), HSiEtMe_2 (37.0 mg, 0.42 mmol) and toluene (0.4 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 130 °C for 24 h. The resulting mixture was filtered, and toluene was evaporated in vacuo. The crude mixture was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 20/80) to give **2** as a white solid (9.4 mg, 62%) and **5** as a white solid (46.5 mg, 78%).

(A)

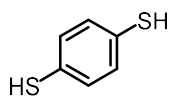


(B)



Pictures of the reaction mixture before heating (A) and after heating at 130 °C for 24 h (B).

Benzene-1,4-dithiol (2). [CAS: 624-39-5]



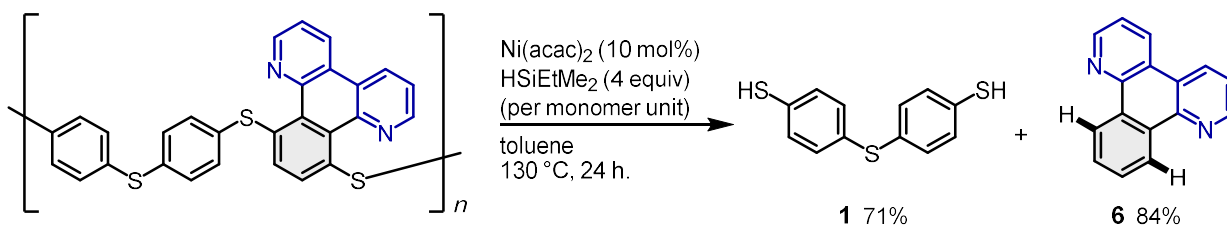
White solid. R_f 0.58 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 7.16 (s, 4H), 3.42 (s, 2H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 130.31, 127.91.

HRMS (DART+, $[\text{M}]^+$): Calcd for $\text{C}_6\text{H}_6\text{S}_2$: 141.9905. Found: 141.9902.

VI-4. Controlled Decomposition of DG-PPS3



In a glovebox filled with nitrogen, **DG-PPS3** (47.9 mg, 0.10 mmol), $\text{Ni}(\text{acac})_2$ (2.6 mg, 0.010 mmol), HSiEtMe_2 (39.4 mg, 0.45 mmol) and toluene (0.4 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 130 °C for 24 h. The resulting mixture was filtered, and toluene was evaporated in vacuo. The crude mixture was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 70/30) to give **1** as a white solid (17.8 mg, 71%) and **6** as a white solid (19.4 mg, 84%).

(A)

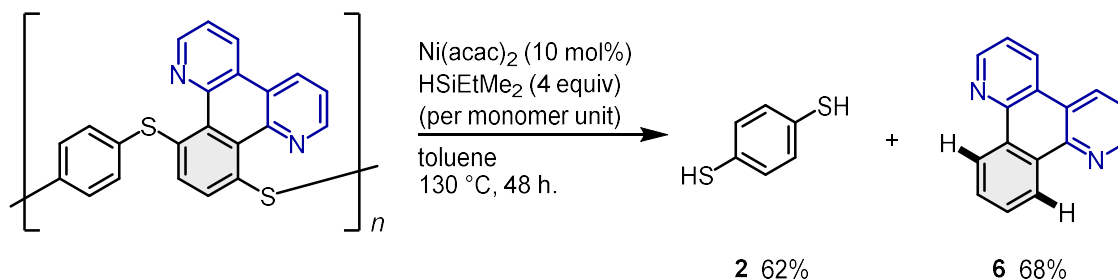


(B)



Pictures of the reaction mixture before heating (A) and after heating at 130 °C for 24 h (B).

VI-5. Controlled Decomposition of DG-PPS4.



In a glovebox filled with nitrogen, **DG-PPS4** (36.2 mg, 0.098 mmol), Ni(acac)_2 (3.3 mg, 0.013 mmol), HSiEtMe_2 (40.0 mg, 0.45 mmol) and toluene (0.4 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at $130\text{ }^\circ\text{C}$ for 48 h. The resulting mixture was filtered, and toluene was evaporated in vacuo. The crude mixture was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 70/30) to give **2** as a white solid (8.6 mg, 62%) and **6** as a white solid (15.4 mg, 68%).

(A)



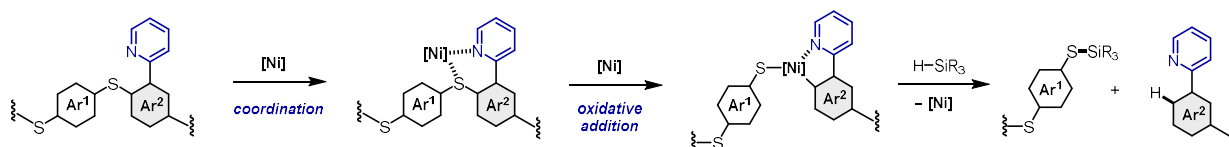
(B)



Pictures of the reaction mixture before heating (A) and after heating at $130\text{ }^\circ\text{C}$ for 24 h (B).

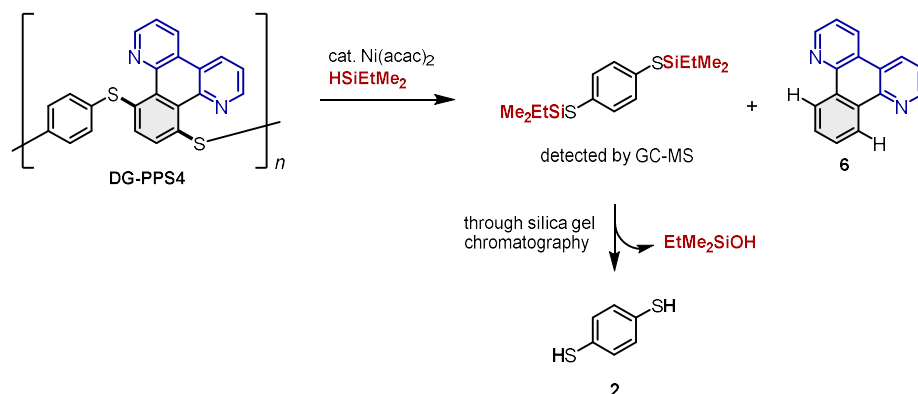
VI-6. Possible Mechanism of Controlled Decomposition DG-PPS.

The plausible pathway for C–S bond cleavage was illustrated. This includes key metallacyclic intermediates, providing a clearer depiction of how the directing groups interact with the transition metal catalyst.



The silyl thiolate intermediate was confirmed by GC-MS analysis in the depolymerization reaction of **DG-PPS4** (see the figure below). However, due to the intrinsic lability of the S–Si bond, the silyl thiolate readily undergoes hydrolysis during the workup process, generating the corresponding thiol and silanol. While the thiol can be detected, the silanol is likely lost due to its volatility, making its

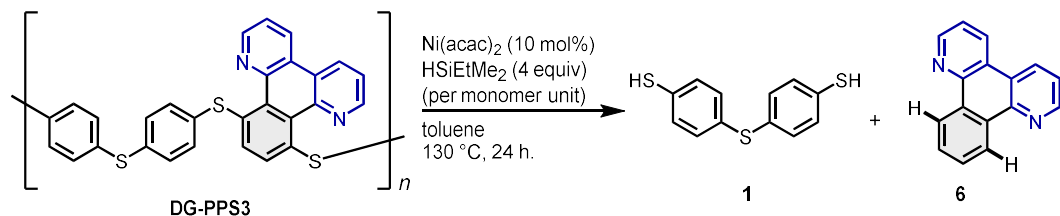
direct observation challenging.



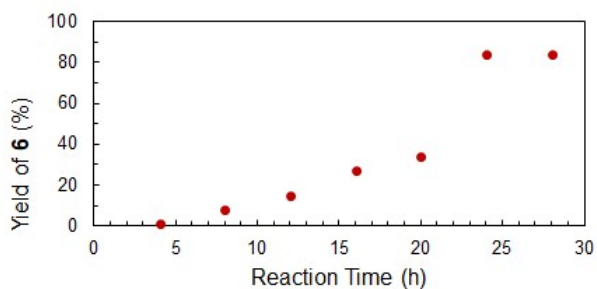
VII. Time-Course Study

To track the degradation process of **DG-PPS3**, a portion of resulting mixture was subjected to GC analysis. The yields of **6** was determined by GC using eicosane as an internal standard. These results indicate that the formation rate of **6** accelerates as the reaction progresses, likely due to the increased solubility of the reactants as the polymer chains shorten.

Scheme S3.21. Time-course Study on the Degradation of **DG-PPS3**.



entry	time	Yield of 6 (%)
1	4	1
2	8	8
3	12	15
4	16	27
5	20	34
6	24	84
7	28	84



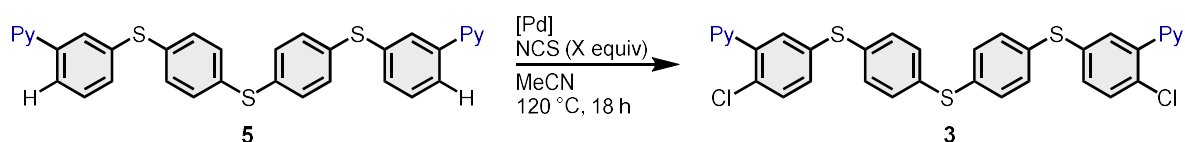
VIII. Repolymerization of Monomeric Products into Original DG-Polymers

VIII-1. Pd-catalyzed Ortho-chlorination

Compound **5** (1 equiv), Pd(OAc)₂ (10 mol%), NCS (X equiv) and MeCN were added to a vial with a Teflon-sealed screwcap. The reaction mixture was stirred at 120 °C for 18 h. After the removing MeCN in vacuo, the crude product was analyzed by ¹H NMR with 1,1,2,2- tetrachloroethane as an internal standard.

Screening different palladium precursors and varying the equivalents of NCS did not lead to any improvement in yield. Notably, neither overchlorinated products nor mono-chlorinated byproducts were detected, suggesting that overchlorination and regioselectivity are not the primary factors limiting the yield (53%).

Table S3.4. Optimization of Pd-catalyzed Ortho-chlorination of **5**.

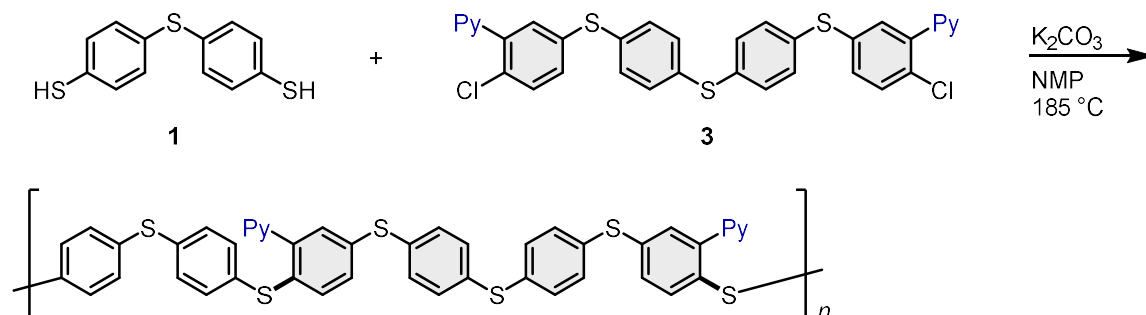


entry	[Pd]	X	yield of 3 (%) ^a
1	PdCl ₂	3.0	40
2	Pd(OAc) ₂	3.0	55 (53) ^b
3	Pd(OAc) ₂	2.0	57 (53) ^b

^a NMR yields

^b isolated yields

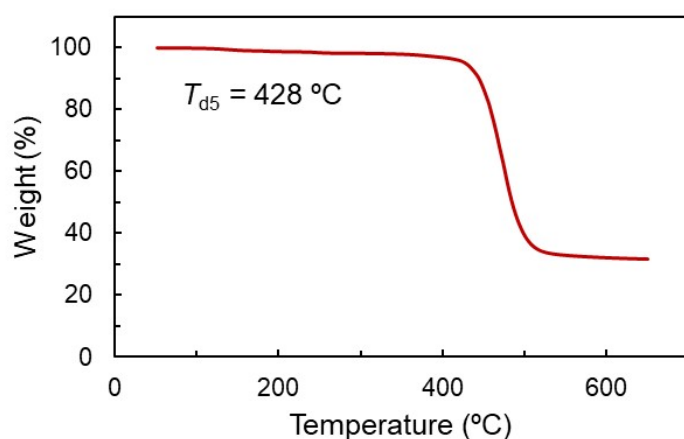
VIII-2. Repolymerization to DG-PPS1.



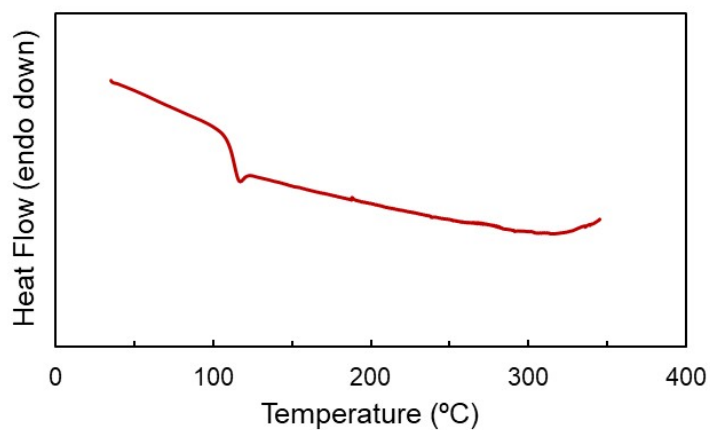
DG-PPS1 was synthesized using **1** and **3**, which were derived from controlled decomposition of **DG-PPS1**. To a 5 mL two-necked flask, **3** (132.6 g, 0.21 mmol), **1** (53.3 mg, 0.21 mmol), K₂CO₃ (64.4 mg, 0.47 mmol) and NMP (0.25 mL) were added. The flask is equipped with a reflux condenser, and the

reaction mixture is stirred under N₂ atmosphere at 185 °C for 5 h. After cooling to rt, the polymer was precipitated by pouring the viscous reaction mixture slowly to a vigorously stirred MeOH. The resulting solid was washed with acetone. After drying in a vacuum oven, DG-PPS1 was obtained as a gray powder (128 mg, 75%). The values of T_g and T_{d5} were comparable to those obtained for the original **DG-PPS1** (T_{d5} = 428 °C, T_g = 108 °C).

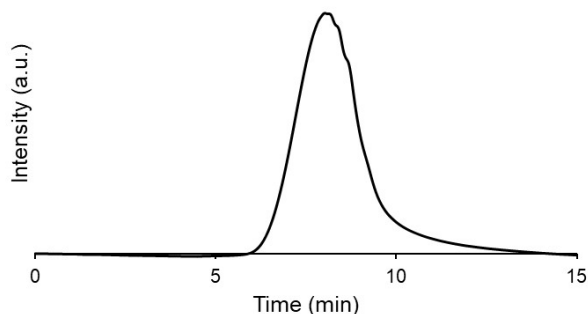
Scheme S3.22. TGA of **DG-PPS1** Obtained by Repolymerization.



Scheme S3.23. DSC Second Heating Thermogram of **DG-PPS1** Obtained by Repolymerization.



Scheme S3.24. SEC Chart of **DG-PPS1** Obtained by Repolymerization.



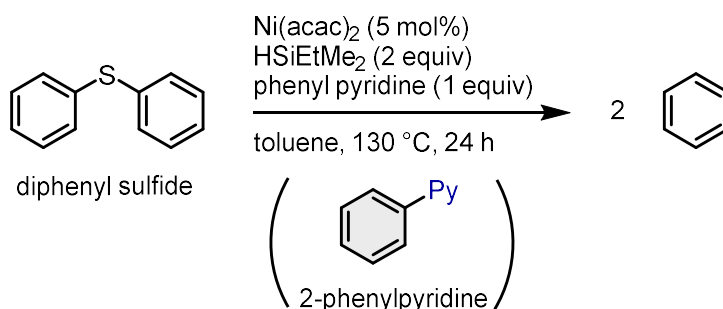
$$M_w = 13200, M_w/M_n = 1.62$$

IX. Control Experiments Using Model Compounds

In a glovebox filled with nitrogen, diphenyl sulfide (36.7 mg, 0.20 mmol), 2-phenylpyridine (32.6 mg, 0.21 mmol), Ni(acac)₂ (2.9 mg, 0.011 mmol), HSiEtMe₂ (35.4 mg, 0.40 mmol) and toluene (0.4 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 130 °C for 24 h. After cooling to room temperature, the reaction mixture was added eicosane. The yields were determined by GC analysis using eicosane as an internal standard.

The results are shown in Scheme S3.22. These results indicate that the Ni-catalyzed reductive cleavage of a C–S bond can occur even in the absence of a directing group (entry 1). However, this process is significantly inhibited by the presence of 2-phenylpyridine (entry 2), indicating that the nickel catalyst is deactivated by the coordination with 2-phenylpyridine.

Scheme S3.25. Control Experiments Using Model Compounds.



entry	recover of diphenyl sulfide (%)
w/o 2-phenylpyridine	43
w/ 2-phenylpyridine	90

3.5. References

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For Experimental Section

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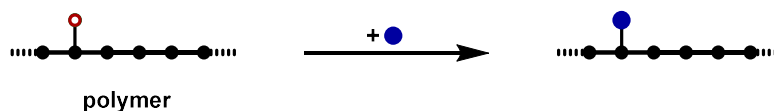
Chapter 4

Skeletal Editing of Polymer Backbone via Nickel-Catalyzed Decarbonylation: Poly(Aryl Ethers) from Poly(Aryl Ether Ketones)

4.1. Introduction

Postpolymerization modification represents a powerful strategy for precisely tuning polymer functions and properties through molecular-level structural editing. Most reported examples to date have focused on transformations of pendant functional groups and the resulting changes in material properties (Figure 4.1a).¹ In contrast, transformations of the polymer backbone are generally challenging. As a result, accessing polymers with distinct backbone structures typically requires the synthesis of new monomers followed by their polymerization. Only recently, modification of the polymer backbone itself has gained attention. Emerging studies have demonstrated that backbone-level structural transformations provide a complementary approach to conventional side-chain functionalization and enable tunable control over material properties.² Backbone editing reactions can be broadly classified into three categories: (1) deletion or insertion of atomic units,³ (2) rearrangement^{3g,4} and (3) cyclization or ring opening⁵ (Figure 4.1b).

(a) Modification of side chain in a polymer structure



(b) Modification of the polymer backbone

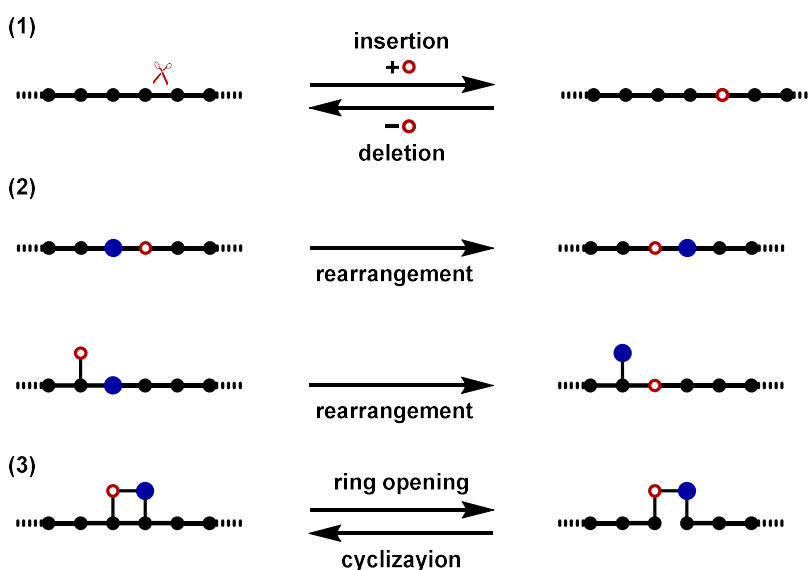


Figure 4.1. Postpolymerization Modification

Among these, transformations that effectively delete atom unit from the polymer backbone remain exceedingly rare, with only a single example reported to date, highlighting the inherent difficulty of such conversions (Figure 4.2).^{3a} The Ramberg–Bäcklund reaction was employed to excise sulfur atoms as SO₂ from poly(arylmethylene sulfone) backbones, thereby converting them into poly(arylene vinylene)s. In this transformation, the α -position of the sulfone is brominated, followed by an intramolecular nucleophilic substitution to form an episulfone intermediate, which subsequently eliminates SO₂ to afford the target polymer. The resulting polymer gained the useful optical properties characteristic of conjugated polymers, which were absent in the precursor material.

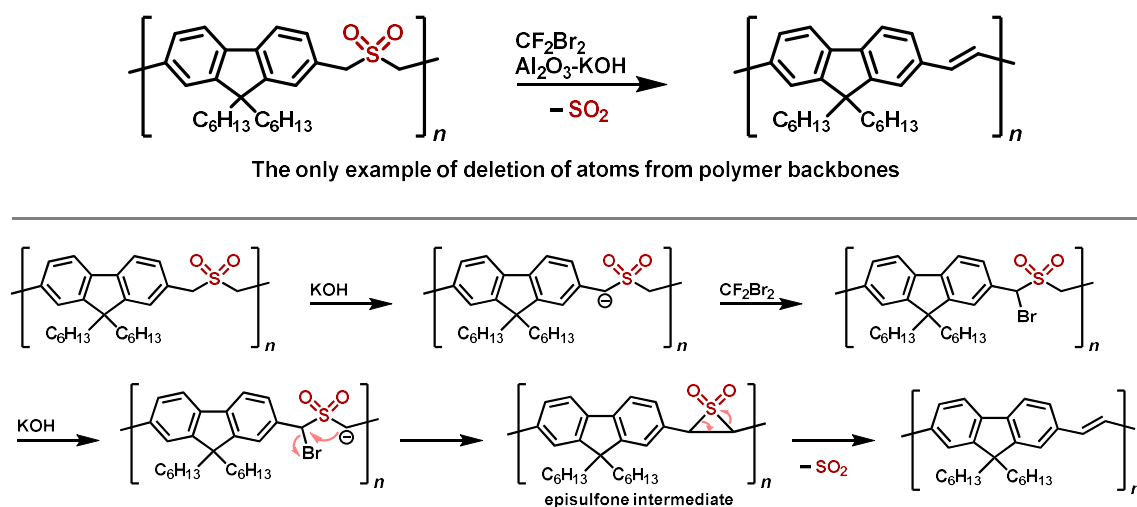


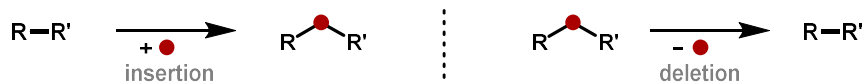
Figure 4.2. The Only Example of Atom-Deletion-Type Skeletal Editing of Polymer

In recent years, a variety of “skeletal editing” reactions⁶ that insert, delete, or replace atomic units within an existing molecular framework have been reported in small-molecule synthesis (Figure 4.3a). Among these transformations is the unimolecular fragment coupling (UFC) reaction,⁷ in which an atom is eliminated from the molecular backbone and the resulting fragments recombine intramolecularly to form a new chemical bond. For example, decarboxylation reactions⁸ involving the loss of CO₂ and decarbonylation reactions⁹ involving the extrusion of CO have been reported. A decarbonylative UFC of diaryl ketones has also been reported. This transformation is inherently challenging because it requires cleavage of a robust carbon–carbon bond. Consequently, catalytic turnover is difficult to achieve, and stoichiometric amounts of a metal complex are typically required (Figure 4.3b, left).¹⁰ The first example of the decarbonylation of diaryl ketones was reported in 2004 by Brookhart et al.,^{10a} who demonstrated that a stoichiometric rhodium complex mediates the conversion of diaryl ketones into biaryl products. In 2017, Tobisu and Chatani et al. reported that this transformation can also be promoted by a nickel complex.^{10b} A highly electron-donating *N*-heterocyclic carbene ligand is essential to generate a nickel center sufficiently electron-rich to facilitate the challenging oxidative addition of a carbon–carbon bond. The resulting electron-rich nickel species

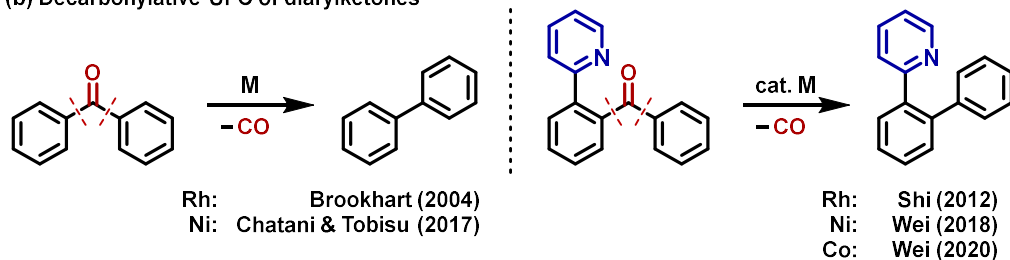
binds the eliminated CO strongly, which prevents regeneration of the electron-rich nickel species required for oxidative addition of the carbon–carbon bond, thereby inhibiting catalytic turnover. In contrast, *catalytic* C–C bond cleavage of diaryl ketones has been achieved when ketones bearing a directing group are employed (Figure 4.3b, right).¹¹ In 2012, Shi and co-workers developed a rhodium-catalyzed decarbonylative UFC of unstrained ketones using a pyridyl directing group. Subsequently, Wei and co-workers disclosed nickel- or cobalt-catalyzed decarbonylative UFC reactions based on a similar directing-group strategy. In these transformations, the directing group promotes oxidative addition of the C–C bond, thereby enabling catalytic decarbonylation. However, despite these advances, no examples have demonstrated the application of these reactions to polymeric materials, where the activation and controlled cleavage of C–C bonds within polymer backbones remain a significant challenge.¹²

In this study, the author explored the decarbonylation of polyketones as a postpolymerization skeletal-editing strategy that removes an embedded atomic unit from the polymer backbone (Figure 4.3c). To achieve this, the author focused on polymers integrated with a directing group (DG). The author has previously demonstrated that incorporating a DG enables site-selective cleavage of the polymer main chain. Through this controlled backbone scission, the polymer can be transformed into monomers or monomer precursors under suitable metal catalysis (Chapter 2 and 3).

(a) Skeletal editing of small-molecular frameworks



(b) Decarbonylative UFC of diarylketones



(c) This work

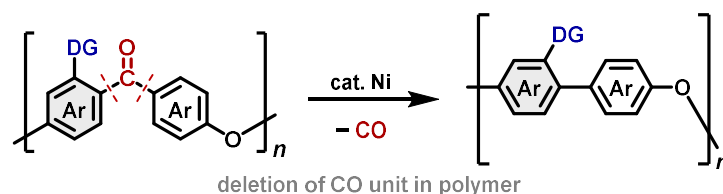


Figure 4.3. Skeletal Editing of Small-Molecule Frameworks and This Work

4.2. Results and Discussion

Synthesis of DG-Integrated Polymer. The author initially designed **DG-PEEK3** as a PEEK-based polymer bearing a 2-pyridyl group. **DG-PEEK3** was synthesized by polycondensation via nucleophilic aromatic substitution (S_NAr). When a benzophenone derivative **1** was heated in the presence of K_2CO_3 (1.2 equiv) in NMP at 180 °C for 24 h, a precipitate was formed (Figure 4.4). However, the resulting solid was insoluble in common organic solvents including NMP and $CHCl_3$, which made detailed characterization difficult.

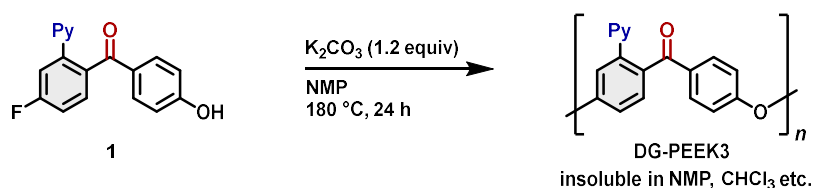


Figure 4.4. Synthesis of a PEEK-type Polymer Bearing Pyridine Directing Groups

To address the solubility issue, the author next turned attention to the synthesis of polymers containing a bisphenol A unit, which was expected to improve solubility. Following the synthetic route outlined in Figure 4.5, the synthesis of the required monomer **2** was investigated.

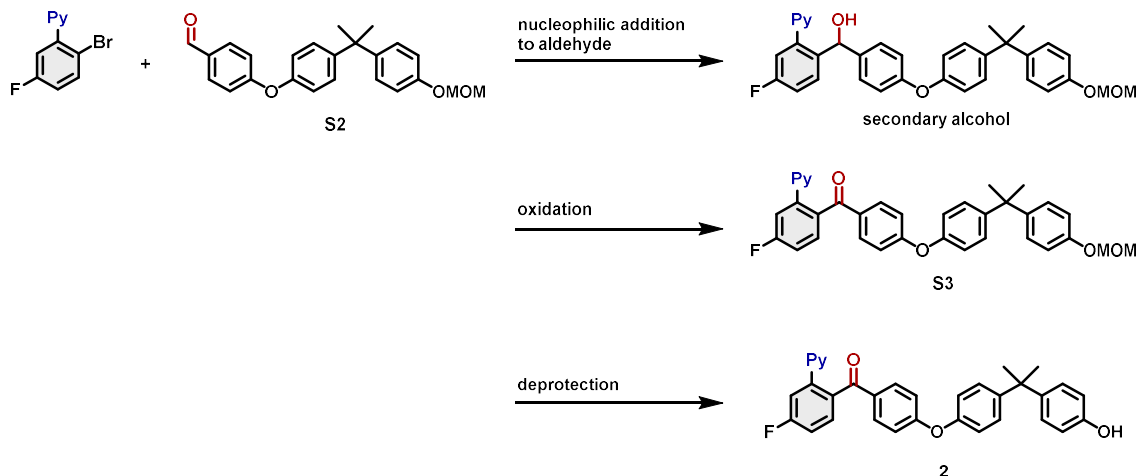


Figure 4.5. Synthetic Route of Monomer **2**

Initially, a nucleophilic addition to the aldehyde was carried out using $nBuLi$ to afford the corresponding secondary alcohol (Figure 4.6a, condition A). However, during the lithiation step, a rearrangement occurred, resulting in the formation of a regioisomer as a byproduct. This byproduct could not be separated from the desired product by purification using flash column chromatography. Therefore, the resulting mixture was subsequently subjected to oxidation with MnO_2 , affording the corresponding ketones (Figure 4.6b). Purification of the ketone by flash column chromatography

allowed the separation of the desired product **S3** from the regioisomer, which were obtained in a 1.3:1 ratio (desired product:regioisomer) with isolated yields of 23% and 18%, respectively. Subsequently, in order to enhance both the yield and selectivity, the reaction was conducted using a Grignard reagent (Figure 4.6a, condition B). As a result, the formation of the byproduct was largely suppressed, and the desired product was obtained predominantly. The obtained crude secondary alcohol was oxidized with MnO_2 , and the resulting ketone was purified by flash column chromatography to afford **S3** in 49% yield, whereas the regioisomer could not be isolated. Finally, **2** was obtained by deprotection of **S3** via treatment with hydrochloric acid (see Section 4.4, Experimental Section).

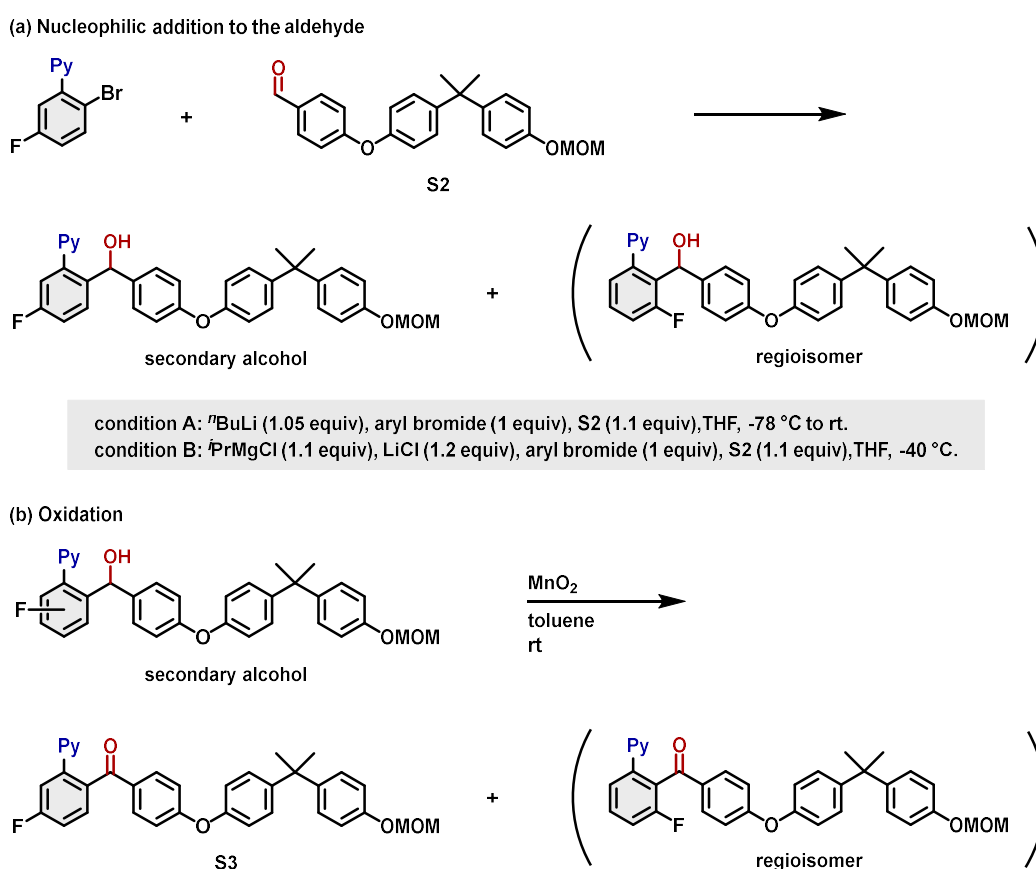


Figure 4.6. Synthesis of **S3** via Nucleophilic Addition to the Aldehyde and Subsequent Oxidation

The resulting monomer **2** was then subjected to polymerization. Specifically, the reaction of a benzophenone derivative **2** in the presence of K_2CO_3 (1.2 equiv) in NMP at $180\text{ }^{\circ}\text{C}$ for 14 h to give **DG-PEEK4** in a 92% isolated yield (Figure 4.7). The weight-average molecular weight (M_w) of **DG-PEEK4**, determined by SEC with polystyrene standards, was 10.9 kDa.

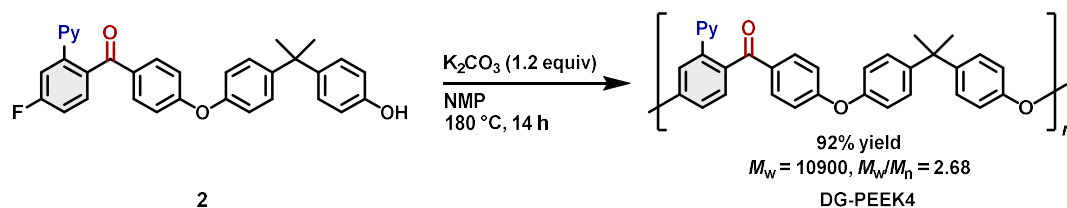
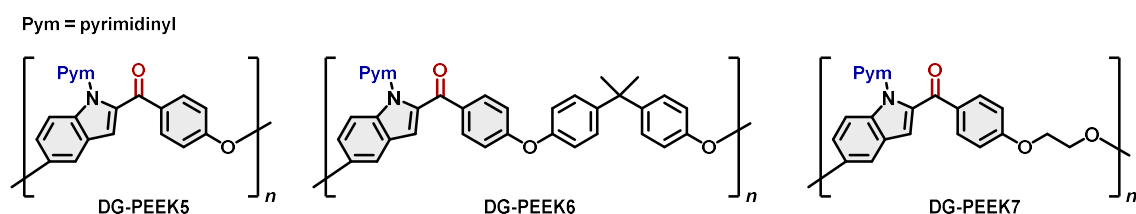


Figure 4.7. Synthesis of a DG-Integrated PEEK-Type Polymer with Bisphenol A Unit

On the basis of previous reports¹¹ in small-molecule synthesis demonstrating that indole-type substrates bearing a pyrimidine directing group (DG) undergo decarbonylation with higher efficiency, the corresponding polymers were also synthesized (Figure 4.8). However, when condensation reaction was conducted under conditions similar to those used for **DG-PEEK3** and **DG-PEEK4**, only insoluble products were obtained.



Condition: Monomer **S6** (323 mg, 0.97 mmol), K_2CO_3 (373 mg, 2.7 mmol), and NMP (1 mL) at 180 °C for 21 h.

Figure 4.8. Synthesis of DG-Integrated Polymers Bearing Pyrimidine Directing group

Therefore, the reaction time was reduced in an attempt to lower the molecular weight and synthesize a polymer soluble in organic solvents, which would allow easier characterization (Figure 4.9). The reaction of an indole derivative monomer **S12** in the presence of K_2CO_3 (1.4 equiv) in NMP at 180 °C for 6 h to afford **DG-PEEK7** in a 78% isolated yield. The resulting polymer was insoluble in $CHCl_3$ and THF, but was soluble in DMSO.

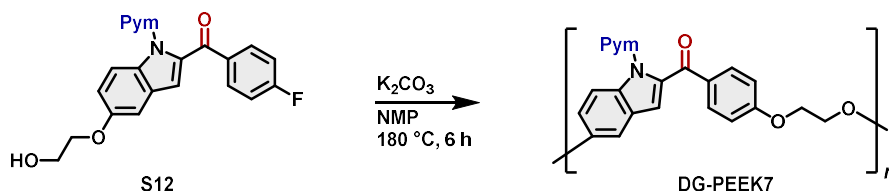


Figure 4.9. Synthesis of **DG-PEEK7**

Catalytic Decarbonylation of DG-Integrated Polymer. To identify suitable catalytic conditions for decarbonylation of **DG-PEEK4**, the author initially screened catalysts that were previously used for the decarbonylation of diary ketones in small molecules chemistry (Figure 4.10).^{11b} As a result, the

desired decarbonylative product (**DG-PAE1**) was obtained when heated with Ni(cod)₂ and IMes in dioxane at 150 °C for 36 h. The weight-average molecular weight (M_w) of **DG-PAE1**, determined by SEC with polystyrene standards, was 3.34 kDa. This value is lower than that of the corresponding polymer (**DG-PEEK4**) prior to the decarbonylation reaction.

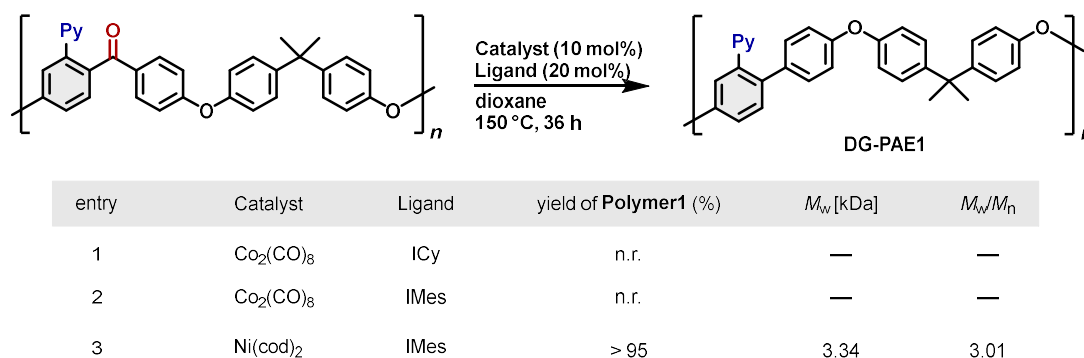


Figure 4.10. Optimization for Decarbonylation of **DG-PEEK4**

To elucidate the origin of this decrease in molecular weight (M_w), the decarbonylation reaction was examined using low-molecular-weight model substrates **3** (1 equiv) and **4** (1 equiv) (Figure 4.11). As a result, decarbonylative product compound **5** and compound **6** were obtained in yields of 86% and 5%, respectively. These results suggest that, in addition to the desired decarbonylation, cleavage of the C–O bond adjacent to the benzophenone unit may also occur under these conditions, which could account for the decrease in molecular weight observed in the reaction of **DG-PEEK4**. Based on the product yields, decarbonylation and C–O bond cleavage occur in a ratio of approximately 17.2:1 (derived from 86:5).

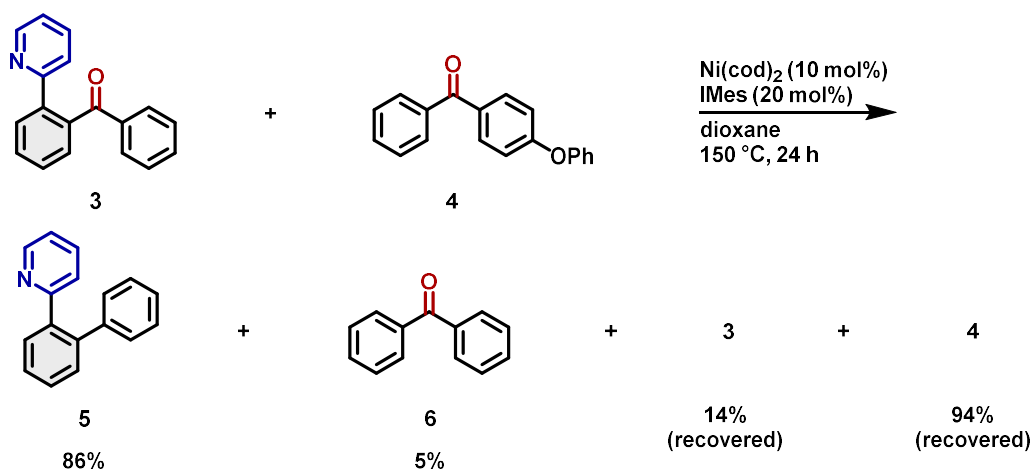


Figure 4.11. Mechanistic Insight into the Decrease in Molecular Weight Probed by Model Substrates

Given that the degree of polymerization (n) of **DG-PEEK4**, estimated from its molecular weight ($M_w = 10900$), is 22.5, a single polymer chain can be considered to contain 22.5 ketone units proximal to the DG and 45 C–O bonds adjacent to the benzophenone unit. If the reaction rate is assumed to be proportional to the number of reactive sites, such that the number of C–O bonds is twice that of the ketone units, the results shown in Figure 4.11, where decarbonylation and C–O bond cleavage occur in a ratio of approximately 17.2:1, would predict a ratio of approximately 8.6:1 for decarbonylation and C–O bond cleavage in the reaction of **DG-PEEK4**. On this basis, it can be estimated that approximately 2.6 C–O bond cleavage events occur before all ketone units (22.5 per chain) undergo decarbonylation along a polymer chain. As a result, the molecular weight (M_w) is reduced to approximately 3.03 kDa, assuming degradation into oligomers of comparable chain length. Notably, this estimation ($M_w = 3.03$ kDa) based on the model reaction is in good agreement with the experimental results ($M_w = 3.34$ kDa) obtained for decarbonylation of **DG-PEEK4** (Figure 4.10, entry 3).

The progress of the decarbonylation reaction of **DG-PEEK4** was evaluated using ^{13}C NMR and FT-IR analysis (Figure 4.12). In the ^{13}C NMR spectrum, the signal at 196.2 ppm, which corresponds to the carbonyl carbon of the ketone, disappeared after the reaction. In addition, the IR spectrum showed the disappearance of the carbonyl stretching band at 1650 cm^{-1} . These results indicate that the carbonyl groups in **DG-PEEK4** were selectively removed, strongly supporting that skeletal editing of the polymer backbone was successfully achieved.

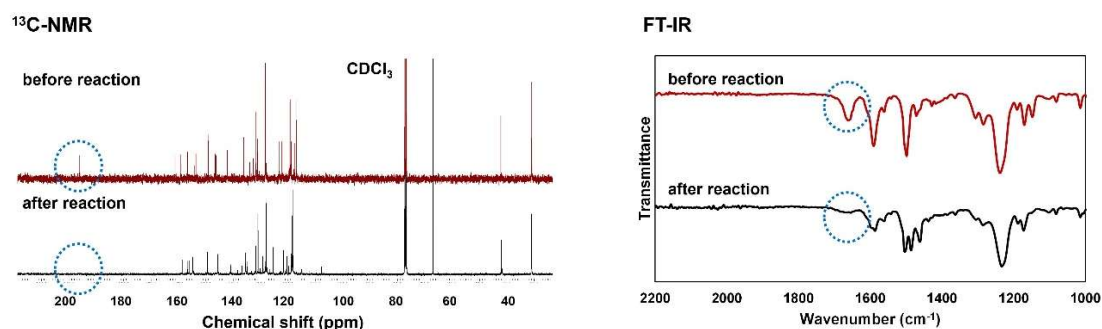


Figure 4.12. ^{13}C NMR and FT-IR Spectra Before and After Decarbonylation Reaction of **DG-PEEK4**

A similar decarbonylation reaction was carried out on **DG-PEEK7**. However, the resulting solid was insoluble in organic solvents, preventing the evaluation of reaction progress by ^{13}C NMR spectroscopy. In addition, in the IR spectrum, the signals corresponding to the carbonyl carbons overlapped with other signals, making assessment via IR also unfeasible.

4.3. Conclusion

In summary, the author demonstrated that a skeletal transformation from poly(aryl ether ketone) to poly(aryl ether) via a nickel-catalyzed decarbonylation reaction. By integrating a directing group into polymer backbone, the author demonstrated that atom-deletion-type skeletal editing involving the cleavage of otherwise inert bonds can be realized within the polymer backbone. Despite these advances, a decrease in molecular weight remains a limitation in the context of backbone editing via atomic excision. To address this issue, the author is currently optimizing reaction conditions and catalyst systems to improve selectivity toward skeletal-editing reactions over competing pathways that lead to molecular-weight loss. Furthermore, the incorporation of linkers containing chemically robust bonds, in place of ether bonds, that remain inert under skeletal-editing reaction conditions is being considered, as this may help suppress molecular weight loss while retaining the desired chemical transformations. Building on the insights gained in this work, further studies are being pursued to explore atom-deletion-type skeletal editing in other classes of polymers.

4.4. Experimental Section

I. General Information

^1H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer in CDCl_3 . The chemical shifts in ^1H NMR spectra were recorded relative to tetramethylsilane (δ 0.00) unless otherwise noted. The chemical shifts in ^{13}C NMR spectra were recorded relative to CDCl_3 (δ 77.0). The data is reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer, or JEOL JMS-S3000. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-2014 gas chromatograph, equipped with a flame ionization detector. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with Biotage Isolera[®] equipped with Biotage[®] Sfar.

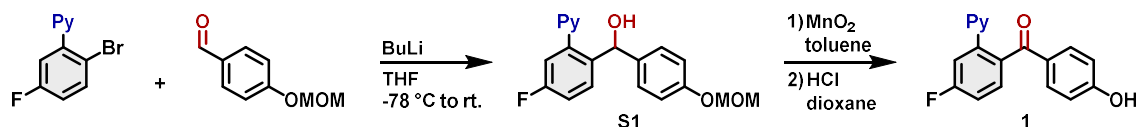
II. Materials

1,4-dioxane (super dehydrated) (FUJI FILM Wako Chemicals) were used as received. $\text{Ni}(\text{cod})_2$ was purchased from Strem Chemicals and used as received. $\text{ICy}\cdot\text{HBF}_4$ (TCI) and IMes (TCI) were purchased from commercial suppliers and used as received.

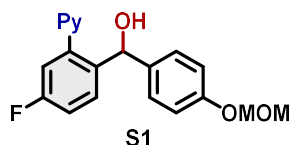
III. Preparation of Starting Materials

Synthesis of DG-PEEK3

Monomer Synthesis



(4-Fluoro-2-(pyridin-2-yl)phenyl)(4-(methoxymethoxy)phenyl)methanol (S1). This compound was synthesized using a literature procedure,¹ with minor modifications. Phenyl pyridine derivative (1.28 g, 5.0 mmol) was cooled to -78 °C in THF (15 mL) under N₂. ⁿBuLi (3.6 mL of a 1.6 M solution in hexane, 5.8 mmol) was added dropwise and stirred for 1.5 h. The aldehyde derivative (1.02 g, 6.1 mmol) was cannulated into the reaction mixture as a THF solution, and the mixture was stirred at rt for 8 h. After the quenching with NH₄Cl aq., the aqueous phase was extracted with EtOAc. The combined extracts were dried over Na₂SO₄ and concentrated. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 30/70) to give **S1** as a yellow oil (1.39 g, 81%).



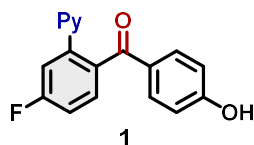
Yellow oil. R_f 0.36 (Hexane/EtOAc = 1/1).

MS, *m/z* (relative intensity, %): 340 (17), 339 (M⁺, 73), 338 (38), 294 (24), 277 (11), 276 (21), 248 (15), 201 (30), 200 (100), 174 (11), 173 (28), 172 (16), 80 (62), 78 (11), 45 (92).

(4-Fluoro-2-(pyridin-2-yl)phenyl)(4-hydroxyphenyl)methanone (1). This compound was synthesized using a literature procedure,^{2,3} with minor modifications.

To a round-bottom flask, **S1** (1.39 g, 4.1 mmol), MnO₂ (5.37 g, 61.7 mmol), and toluene (40 mL) were added. The mixture was stirred at rt for 20 h. The resulting mixture was filtered, and toluene was evaporated in vacuo to give the ketone (pale yellow oil), which was used in the next step without further purification.

The ketone and 4 M HCl in dioxane (40 mL) were added to a round-bottom flask, and the mixture was stirred at rt for 14 h. After removal of the solvent, aqueous NaHCO₃ aq. and EtOAc were added. The combined extracts were dried over Na₂SO₄ and concentrated. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 90/10 to 25/75) to give **1** as a white solid (1.08 g, 92%).



White solid. R_f 0.36 (Hexane/EtOAc = 1/1).

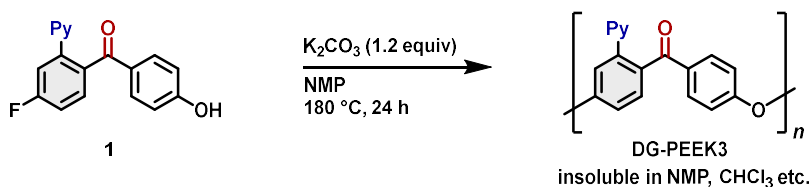
^1H NMR (DMSO- d_6 , 400 MHz) δ : 10.27 (s, 1H), 8.30 (d, J = 4.7 Hz, 1H), 7.78–7.66 (m, 3H), 7.50–7.36 (m, 4H), 7.20–7.17 (m, 1H), 6.67 (d, J = 8.7 Hz, 2H).

^{13}C NMR (DMSO- d_6 , 101 MHz) δ : 194.5, 162.5, 161.6, 155.2, 148.8, 141.6, 137.0, 136.0, 131.5, 131.1, 128.9, 122.9, 122.7, 115.7, 115.3, 115.0.

^{19}F NMR (DMSO- d_6 , 376 MHz) δ : -112.0 (q, 1F).

MS, m/z (relative intensity, %): 293 (M^+ , 29), 265 (18), 264 (89), 201 (14), 200 (100), 145 (16), 125 (11), 121 (19), 93 (17), 65 (24).

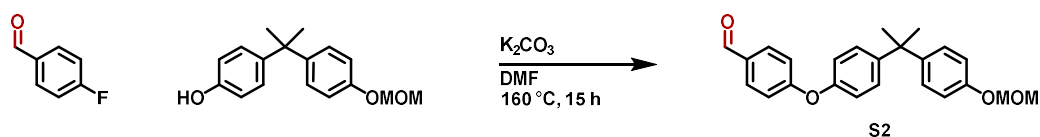
Polymerization



To a 10 mL two-necked flask, **1** (570 mg, 1.94 mmol), K_2CO_3 (324 mg, 2.34 mmol), and NMP (2 mL) were added. The flask is equipped with a reflux condenser, and the reaction mixture is stirred under N_2 atmosphere at rt. After the reactants were completely dissolved, the mixture was heated to 180 °C for 24 h using an oil bath, and a precipitate was formed. The resulting precipitate was insoluble in THF, CHCl_3 , DMSO, and AcOH.

Synthesis of DG-PEEK4

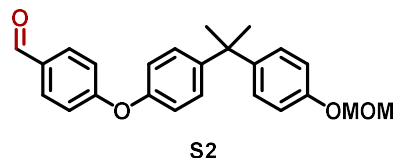
Monomer Synthesis



4-(4-(2-(4-(Methoxymethoxy)phenyl)propan-2-yl)phenoxy)benzaldehyde (S2). This compound was synthesized using a literature procedure,⁴ with minor modifications.

To a 200 mL two-necked flask, aldehyde (2.85 g, 23 mmol), phenol derivative (5.75 g, 21 mmol), K_2CO_3 (11.5 mg, 83.2 mmol) and DMF (50 mL) were added. The flask is equipped with a reflux condenser, and the reaction mixture is stirred under N_2 atmosphere at 160 °C for 15 h. The reaction mixture was cooled to rt and diluted with water. The aqueous phase was extracted with Et_2O . The

combined extracts were dried over Na₂SO₄ and concentrated. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 60/40) to give **S2** as a pale yellow oil (6.65 g, 84%).

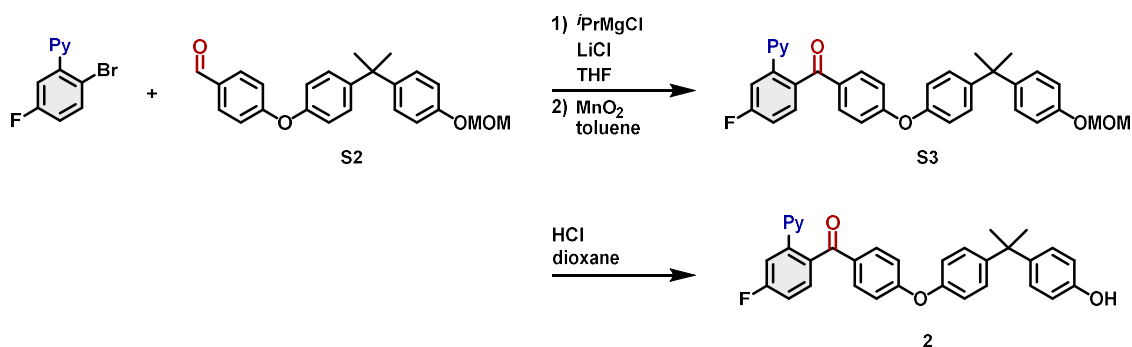


Pale yellow oil. R_f 0.60 (Hexane/EtOAc = 1/1).

¹H NMR (CDCl₃, 400 MHz) δ : 9.92 (s, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.26 (t, *J* = 4.5 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 3.7 Hz, 2H), 6.96 (d, *J* = 3.9 Hz, 2H), 5.16 (s, 3H), 3.49 (s, 3H), 1.68 (s, 6H).

¹³C NMR (CDCl₃, 101 MHz) δ : 190.8, 163.4, 155.2, 152.7, 147.6, 143.7, 131.9, 131.1, 128.4, 127.7, 119.8, 117.4, 115.7, 94.5, 56.0, 42.1, 31.0.

MS, *m/z* (relative intensity, %): 377 (11), 376 (M⁺, 37), 362 (28), 361 (86), 331 (39), 45 (100).

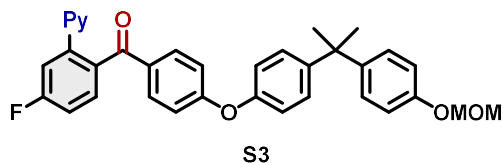


(4-Fluoro-2-(pyridin-2-yl)phenyl)(4-(4-(2-(4-(methoxymethoxy)phenyl)propan-2-yl)phenoxy)phenyl)methanone (S3). This compound was synthesized using a literature procedure,^{2,5} with minor modifications.

LiCl (264 mg, 6.2 mmol) and phenyl pyridine derivative (1.28 g, 5.1 mmol) were cooled to −40 °C in THF (10 mL) under N₂. *t*PrMgCl (2.8 mL of a 2 M solution in hexane, 5.6 mmol) was added dropwise and stirred for 1.5 h. **S2** (2.16 g, 5.7 mmol) was cannulated into the reaction mixture as a THF solution (5 mL), and the mixture was stirred at −40 °C for 1 h. After the quenching with NH₄Cl aq., the aqueous phase was extracted with EtOAc. The combined extracts were concentrated and purified by flash column chromatography to give the crude product (white solid), which was used in the next step without further purification.

To a round-bottom flask, obtained white solid, MnO₂ (5.39 g, 62 mmol), and toluene (40 mL) were added. The mixture was stirred at rt for 21 h. The resulting mixture was filtered, and toluene was evaporated in vacuo to give the crude product. The crude product was purified by flash column

chromatography to give **S3** as a white solid (1.37 g, 49%).



White solid. R_f 0.58 (Hexane/EtOAc = 1/1). M.p. 46.9–51.1 °C.

^1H NMR (CDCl_3 , 400 MHz) δ : 8.43–8.42 (m, 1H), 7.66–7.62 (m, 2H), 7.61–7.57 (m, 1H), 7.55–7.52 (dd, J = 8.4, 5.6 Hz, 1H), 7.48–7.43 (m, 2H), 7.23–7.13 (m, 5H), 7.09 (ddd, J = 7.4, 4.9, 0.9 Hz, 1H), 6.97–6.94 (m, 2H), 6.88–6.80 (m, 4H), 5.16 (s, 2H), 3.48 (s, 3H), 1.66 (s, 6H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 163.4, 161.5, 155.8, 155.1, 153.1, 149.2, 147.1, 143.8, 142.2, 136.4, 135.5, 132.2, 131.7, 131.2, 128.2, 127.7, 123.0, 122.4, 119.3, 116.9, 116.0, 115.7, 115.3, 94.5, 55.9, 42.0, 30.9.

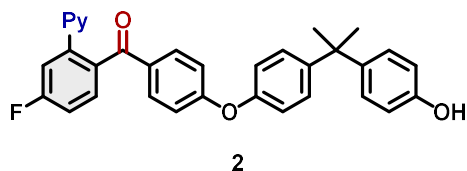
^{19}F NMR (CDCl_3 , 376 MHz) δ : –110.9 (td, J = 8.7, 5.8 Hz, 1F).

IR (ATR): 2966 w, 1662 m, 1606 m, 1590 m, 1567 w, 1497 s, 1473 w, 1308 m, 1284 m, 1237 s, 1171 m, 1150 m, 1079 w, 1003 m, 933 m, 875 w, 833 m, 752 m, 579 w.

HRMS (DART⁺, $[\text{M}+\text{H}]^+$): Calcd for $\text{C}_{35}\text{H}_{31}\text{FNO}_4$: 548.2232. Found: 548.2241.

(4-Fluoro-2-(pyridin-2-yl)phenyl)(4-(4-(2-(4-hydroxyphenyl)propan-2-yl)phenoxy)phenyl)methanone (2).

This compound was prepared from **S3** in a manner similar to that used for Compound **1**.³

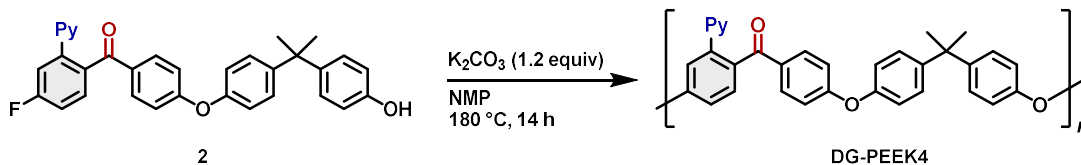


White solid. R_f 0.52 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 8.44–8.42 (m, 1H), 7.68–7.43 (m, 6H), 7.22–7.06 (m, 6H), 6.92–6.80 (m, 4H), 6.73–6.70 (m, 2H), 5.29–5.75 (1H), 1.64 (s, 6H).

^{19}F NMR (CDCl_3 , 376 MHz) δ : –110.7 (q, 1F).

Polymerization



To a 10 mL two-necked flask, **2** (588 mg, 1.17 mmol), K_2CO_3 (201 mg, 1.46 mmol), and NMP (1.2 mL) were added. The flask is equipped with a reflux condenser, and the reaction mixture is stirred

under N₂ atmosphere at rt. After the reactants were completely dissolved, the mixture was heated to 180 °C for 14 h using an oil bath. After cooling to rt, the polymer was precipitated by pouring the viscous reaction mixture slowly to a vigorously stirred MeOH. The polymer is purified by stirring in MeOH. After drying in a vacuum oven, **DG-PEEK4** was obtained as a white powder (519 mg, 92%).



$M_w = 10900$, $M_w/M_n = 2.68$.

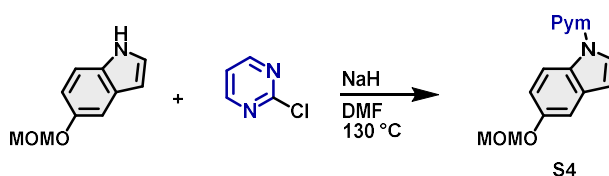
¹H NMR (CDCl₃, 400 MHz) δ : 8.39 (s, 1H), 7.66 (d, $J = 8.5$ Hz, 2H), 7.56–7.50 (m, 2H), 7.40–7.36 (m, 2H), 7.26–7.20 (m, 4H), 7.08–7.00 (m, 4H), 6.84 (dd, $J = 20.3, 8.4$ Hz, 4H), 1.69 (s, 6H).

¹³C NMR (CDCl₃, 101 MHz) δ : 196.2, 161.2, 159.0, 156.6, 153.9, 153.3, 149.1, 146.6, 146.2, 142.1, 136.3, 133.9, 132.5, 131.8, 131.1, 128.2, 128.2, 123.1, 122.1, 119.3, 119.0, 118.7, 117.6, 117.0, 42.2, 30.9.

IR (ATR): 1661 w, 1590 m, 1498 s, 1471 w, 1284 m, 1238 s, 1170 m, 1147 w, 1014 w, 933 m, 910 w, 834 w, 731 m.

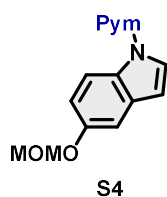
Synthesis of DG-PEEK5, DG-PEEK6 and DG-PEEK7

Monomer Synthesis for DG-PEEK5



5-(Methoxymethoxy)-1-(pyrimidin-2-yl)-1H-indole (S4). This compound was synthesized using a literature procedure,⁶ with minor modifications.

To a 100 mL two-necked flask, the indole (2.26 g, 12.8 mmol), NaH (60% dispersion in mineral oil, 602 mg, 15.1 mmol) and DMF (24 mL) were added. After stirring at 0 °C for 30 min, 2-chloropyrimidine (1.88 g, 16.5 mmol) was added in. The resulting mixture was stirred at 130 °C for 17 h. Then the mixture was cooled to room temperature, washed with water and extracted with EtOAc. After drying with Na₂SO₄, the organic phase was concentrated and purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 60/40) to give **S4** as a yellow solid (2.58 g, 79%).

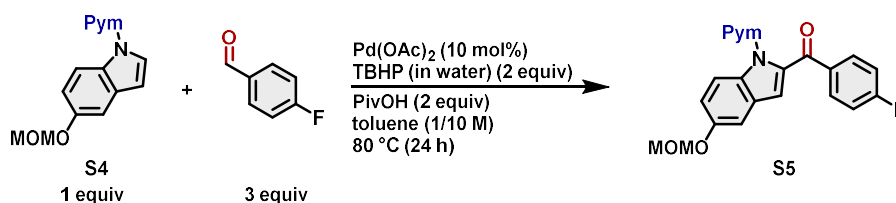


Yellow solid. R_f 0.68 (Hexane/EtOAc = 1/1).

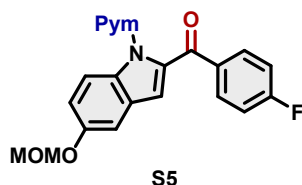
^1H NMR (CDCl_3 , 400 MHz) δ : 8.71 (d, J = 8.9 Hz, 1H), 8.65 (d, J = 4.8 Hz, 2H), 8.25 (d, J = 3.7 Hz, 1H), 7.30 (d, J = 2.3 Hz, 1H), 7.07 (dd, J = 9.2, 2.5 Hz, 1H), 6.99 (t, J = 4.8 Hz, 1H), 6.64 (d, J = 3.4 Hz, 1H), 5.24 (s, 2H), 3.54 (s, 3H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 158.0, 157.6, 152.9, 132.1, 131.1, 126.5, 117.0, 115.9, 114.1, 107.0, 106.7, 95.3, 55.9.

MS, m/z (relative intensity, %): 256 (18), 255 (M^+ , 100), 226 (11), 225 (67), 211 (16), 210 (86), 182 (60), 155 (10), 79 (15), 45 (81).



(4-Fluorophenyl)(5-(methoxymethoxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)methanone (S5). This compound was synthesized using a literature procedure,⁷ with minor modifications. A 100 mL two-necked flask was charged with **S4** (1.04 g, 4.0 mmol), then, aldehyde (1.61 g, 13.0 mmol), $\text{Pd}(\text{OAc})_2$ (113 mg, 0.5 mmol), TBHP (70% aqueous solution, 1.06 g), PivOH (884 mg, 8.7 mmol) were added to the flask. Then the flask was evacuated and backfilled with N_2 and then toluene (40 mL) was added. The mixture was stirred at 80 °C. After cooling the reaction mixture to room temperature, the mixture was diluted with ethyl acetate, and washed with NaOH aq., $\text{Na}_2\text{S}_2\text{O}_3$ aq. and brine. Then, the organic layer was dried over Na_2SO_4 , and concentrated to give the crude product. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 60/40) to give **S5** as a yellow oil (1.21 g, 79%).



Yellow oil. R_f 0.44 (Hexane/EtOAc = 1/1).

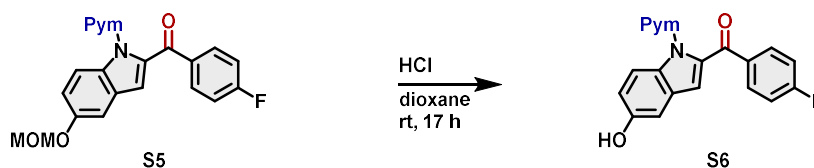
^1H NMR (CDCl_3 , 400 MHz) δ : 8.60 (d, J = 4.8 Hz, 2H), 8.37 (d, J = 9.2 Hz, 1H), 7.97 (dd, J = 8.7, 5.5 Hz, 2H), 7.35 (d, J = 2.3 Hz, 1H), 7.17 (dd, J = 9.0, 2.4 Hz, 1H), 7.10 (t, J = 8.6 Hz, 2H), 7.04 (t,

$J = 4.8$ Hz, 1H), 7.02 (s, 1H), 5.24 (s, 2H), 3.53 (s, 3H).

^{13}C NMR (CDCl_3 , 101 MHz) δ : 186.2, 165.5, 157.9, 157.1, 153.5, 137.4, 134.4, 133.9, 132.0, 128.7, 117.7, 117.2, 115.5, 115.4, 114.7, 107.7, 95.2, 56.0.

^{19}F NMR (CDCl_3 , 376 MHz) δ : -106.6—-106.7 (m, 1F).

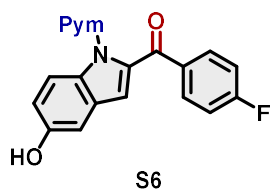
MS, m/z (relative intensity, %): 378 (16), 377 (M^+ , 62), 362 (22), 347 (16), 332 (32), 276 (18), 252 (13), 123 (51), 95 (28), 45 (100).



(4-Fluorophenyl)(5-hydroxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)methanone (S6).

This compound was prepared from S5 in a manner similar to that used for Compound 1.³

87% yield.



Yellow solid. R_f 0.63 (Hexane/acetone = 1/2).

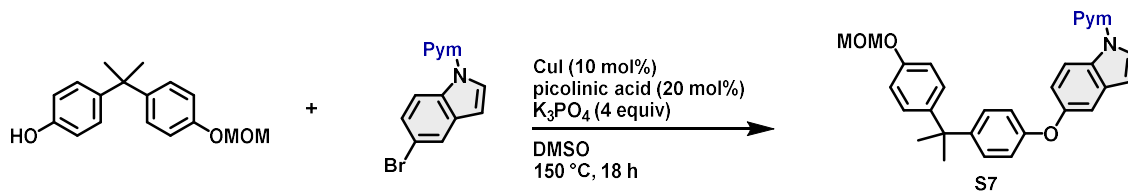
^1H NMR (acetone- d_6 , 400 MHz) δ : 8.69 (d, $J = 4.8$ Hz, 2H), 8.30 (d, $J = 8.9$ Hz, 1H), 8.24 (s, 1H), 7.97 (ddd, $J = 12.0, 5.4, 3.1$ Hz, 2H), 7.29–7.23 (m, 3H), 7.15 (d, $J = 2.3$ Hz, 1H), 7.03–7.01 (m, 2H).

^{13}C NMR (acetone- d_6 , 101 MHz) δ : 186.2, 166.1, 159.1, 158.0, 154.4, 138.4, 135.7, 133.3, 132.7, 130.0, 118.4, 117.0, 116.2, 116.1, 114.6, 107.0.

^{19}F NMR (acetone- d_6 , 376 MHz) δ : -108.0—-108.1 (m, 1F).

MS, m/z (relative intensity, %): 334 (22), 333 (M^+ , 97), 305 (15), 304 (36), 239 (16), 238 (100), 209 (11), 207 (30), 123 (22), 95 (44), 75 (15), 73 (14).

Monomer Synthesis for DG-PEEK6

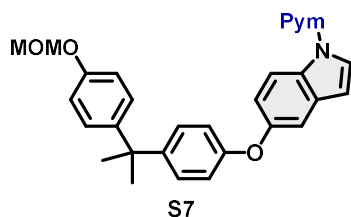


5-(4-(2-(4-(Methoxymethoxy)phenyl)propan-2-yl)phenoxy)-1-(pyrimidin-2-yl)-1H-indole (S7).

This compound was synthesized using a literature procedure,⁸ with minor modifications.

To a 50 mL two-necked flask, phenol (1.48 g, 5.4 mmol), indole (1.24 g, 4.5 mmol), CuI (105 mg, 0.55 mmol), picolinic acid (137 mg, 1.1 mmol), K_3PO_4 (3.47 g, 16.3 mmol) and DMSO (11 mL) were

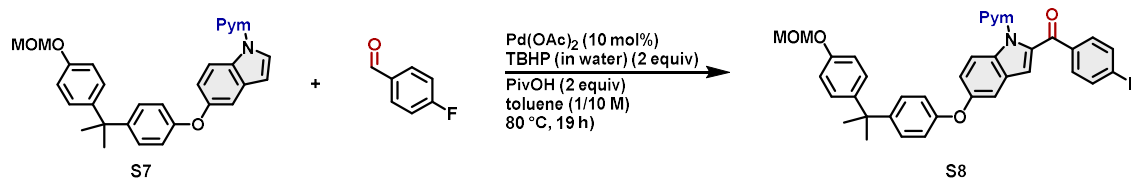
added. The flask is equipped with a reflux condenser, and the reaction mixture is stirred under N₂ atmosphere at 150 °C for 18 h. The reaction mixture was cooled to room temperature and diluted with water (100 mL). The crude product was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na₂SO₄, concentrated in vacuo and the residue was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 80/20) to give **S7** as a yellow oil (1.34 g, 64%).



Yellow oil. R_f 0.35 (Hexane/EtOAc = 3/1).

¹H NMR (CDCl₃, 400 MHz) δ : 8.77 (d, *J* = 8.9 Hz, 1H), 8.70 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 3.7 Hz, 1H), 7.16 (td, *J* = 4.5, 2.4 Hz, 4H), 7.09–7.05 (m, 2H), 6.95–6.89 (m, 4H), 6.63 (d, *J* = 3.7 Hz, 1H), 5.16 (s, 2H), 3.48 (s, 3H), 1.65 (s, 6H).

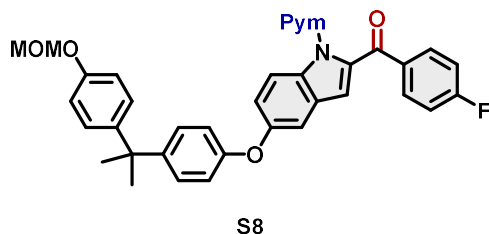
MS, *m/z* (relative intensity, %): 466 (18), 465 (M⁺, 54), 451 (18), 450 (54), 433 (14), 420 (12), 210 (12), 195 (15), 182 (10), 45 (100).



(4-Fluorophenyl)(5-(4-(2-(4-(methoxymethoxy)phenyl)propan-2-yl)phenoxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)methanone (S8).

This compound was prepared from **S7** in a manner similar to that used for Compound **S5**.⁷

91% yield.



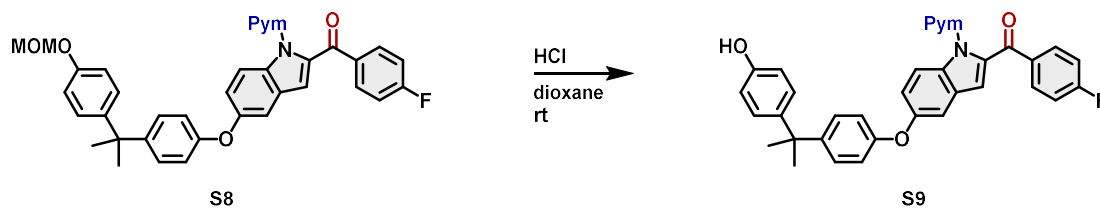
White solid. R_f 0.52 (Hexane/EtOAc = 1/1).

¹H NMR (CDCl₃, 400 MHz) δ : 8.63 (d, *J* = 4.8 Hz, 2H), 8.42 (d, *J* = 9.2 Hz, 1H), 8.02–7.98 (m, 2H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.22–7.06 (m, 8H), 7.02 (d, *J* = 0.7 Hz, 1H), 6.93 (ddd, *J* = 17.5, 6.7, 2.1 Hz, 4H), 5.16 (s, 2H), 3.48 (s, 3H), 1.66 (s, 6H).

¹³C NMR (CDCl₃, 101 MHz) δ : 186.1, 165.5, 157.9, 157.0, 156.0, 155.0, 152.7, 145.2, 144.1, 137.6,

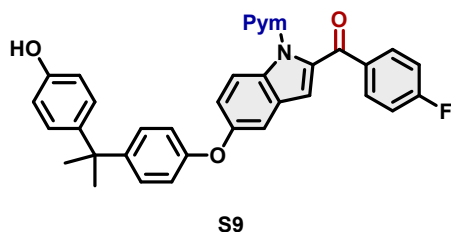
134.6, 134.2, 132.0, 128.8, 127.9, 127.7, 119.6, 117.4, 117.3, 115.6, 115.5, 114.6, 111.7, 94.4, 56.0, 41.9, 31.0.

^{19}F NMR (CDCl_3 , 376 MHz) δ : -106.4 (m, 1F).



(4-Fluorophenyl)(5-(4-(2-(4-hydroxyphenyl)propan-2-yl)phenoxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)methanone (S9).

This compound was prepared from **S8** in a manner similar to that used for Compound **1**.³
82% yield.

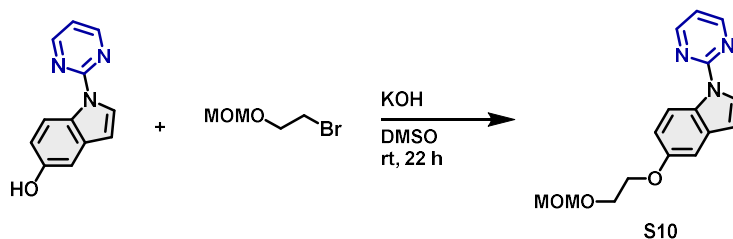


White solid. R_f 0.40 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 8.62 (d, J = 5.0 Hz, 2H), 8.40 (d, J = 9.2 Hz, 1H), 8.01–7.97 (m, 2H), 7.29 (d, J = 2.3 Hz, 1H), 7.22–7.06 (m, 8H), 7.02 (d, J = 0.5 Hz, 1H), 6.90 (dd, J = 6.6, 2.1 Hz, 2H), 6.72 (dd, J = 6.5, 2.2 Hz, 2H), 1.64 (s, 6H).

^{19}F NMR (CDCl_3 , 376 MHz) δ : -106.3 (m, 1F).

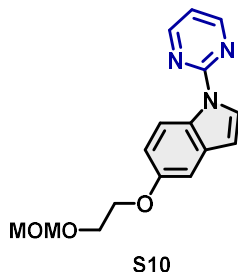
Monomer Synthesis for DG-PEEK7



5-(2-(Methoxymethoxy)ethoxy)-1-(pyrimidin-2-yl)-1H-indole (S10). This compound was synthesized using a literature procedure,⁹ with minor modifications.

To a solution of the indole (299 mg, 1.4 mmol) in DMSO (1 mL) was added potassium hydroxide (179 mg, 3.2 mmol). The reaction mixture was stirred at room temperature for 10 min. Then, 1-bromo-2-(methoxymethoxy)ethane (229 mg, 1.35 mmol) was added and the reaction mixture was stirred at room temperature for 13 h. Then, the reaction mixture was diluted with ethyl acetate and water. The

organic layer was dried over Na₂SO₄, and concentrated to give the crude product. The crude product was purified by flash column chromatography (eluent: hexane/EtOAc = 100/0 to 60/40) to give **S10** as a white solid (172 mg, 42%).

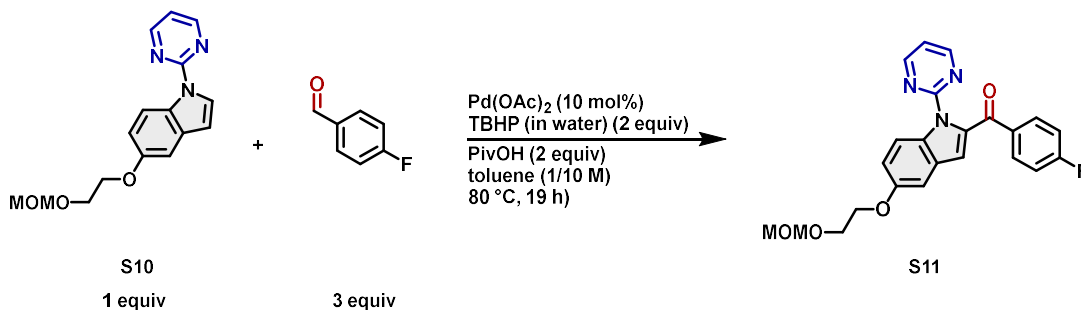


White solid. R_f 0.40 (Hexane/EtOAc = 1/1).

¹H NMR (CDCl₃, 400 MHz) δ : 8.70–8.65 (m, 3H), 8.24 (d, *J* = 3.7 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 7.02–7.00 (m, 2H), 6.63–6.62 (m, 1H), 4.75 (s, 2H), 4.23 (t, *J* = 4.8 Hz, 2H), 3.96–3.93 (m, 2H), 3.43 (s, 3H).

¹³C NMR (CDCl₃, 101 MHz) δ : 158.1, 157.6, 154.5, 132.0, 130.4, 126.3, 117.0, 115.9, 113.2, 106.7, 104.2, 96.6, 67.8, 66.1, 55.3.

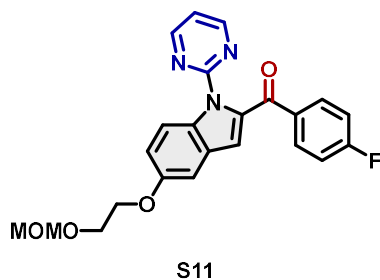
MS, *m/z* (relative intensity, %): 300 (14), 299 (M⁺, 83), 268 (10), 225 (24), 224 (13), 223 (49), 212 (13), 211 (86), 210 (60), 194 (16), 183 (25), 182 (46), 89 (36), 79 (14), 59 (38), 45 (100).



(4-Fluorophenyl)(5-(2-(methoxymethoxy)ethoxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)methanone (S11).

This compound was prepared from **S10** in a manner similar to that used for Compound **S5**.⁷

74% yield.

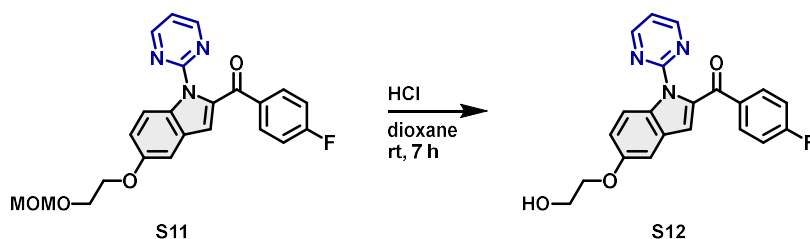


Brown oil. R_f 0.40 (Hexane/EtOAc = 1/1).

^1H NMR (CDCl_3 , 400 MHz) δ : 8.60 (d, $J = 4.8$ Hz, 2H), 8.35 (d, $J = 9.9$ Hz, 1H), 7.99–7.96 (m, 2H), 7.14–7.02 (m, 6H), 4.75 (s, 2H), 4.22 (t, $J = 4.8$ Hz, 2H), 3.95 (t, $J = 4.7$ Hz, 2H), 3.42 (s, 3H).

^{19}F NMR (CDCl_3 , 376 MHz) δ : -106.7 (m, 1F).

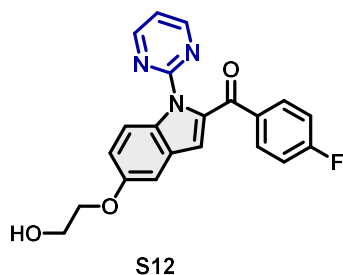
MS, m/z (relative intensity, %): 422 (16), 421 (58), 345 (27), 333(39), 332 (20), 276 (13), 238 (14), 123 (80), 95 (28), 89 (39), 59 (42), 45 (100).



(4-Fluorophenyl)(5-(2-hydroxyethoxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)methanone (S12).

This compound was prepared from **S11** in a manner similar to that used for Compound **1**.³

78% yield.



Yellow solid. R_f 0.60 (Hexane/EtOAc = 1/1).

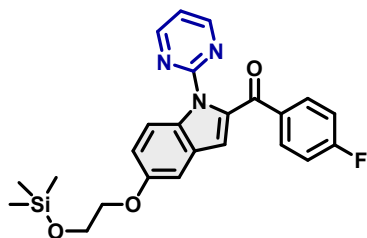
^1H NMR (acetone- d_6 , 400 MHz) δ : 8.70 (d, $J = 4.8$ Hz, 2H), 8.35 (d, $J = 9.2$ Hz, 1H), 8.00–7.96 (m, 2H), 7.29–7.24 (m, $J = 6.8, 2.0$ Hz, 4H), 7.11–7.08 (m, 2H), 4.12 (t, $J = 4.9$ Hz, 2H), 3.92–3.88 (m, 2H).

^{13}C NMR (acetone- d_6 , 101 MHz) δ : 186.1, 166.2, 159.1, 157.9, 156.4, 138.4, 135.6, 133.7, 132.7, 129.7, 118.6, 117.5, 116.2, 116.2, 114.8, 105.3, 71.0, 61.4.

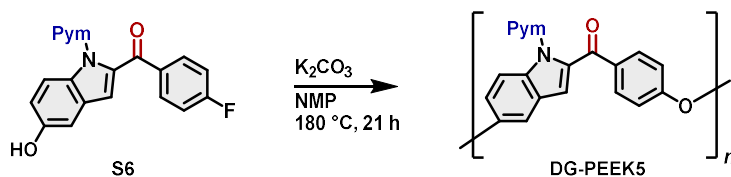
^{19}F NMR (acetone- d_6 , 376 MHz) δ : -109.0 (m, 1F).

After silylation with BSTFA, the resulting product was analyzed by GC-MS.

MS, m/z (relative intensity, %): 450 (19), 449 (M^+ , 57), 405 (15), 377 (21), 334 (20), 333 (89), 305 (12), 304 (12), 238 (32), 180 (13), 148 (17), 123 (92), 117 (21), 95 (28), 75 (11), 73 (100).



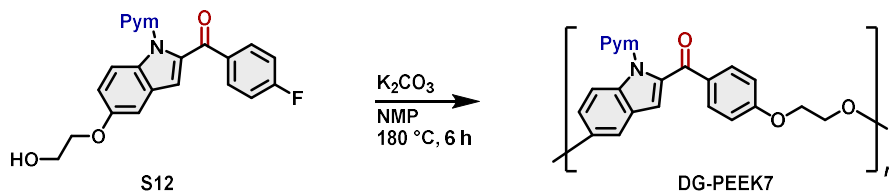
Polymerization (reaction time = 21 h)



To a 10 mL two-necked flask, **S6** (323 mg, 0.97 mmol), K_2CO_3 (373 mg, 2.7 mmol), and NMP (1 mL) were added. The flask is equipped with a reflux condenser, and the reaction mixture is stirred under N_2 atmosphere at rt. After the reactants were completely dissolved, the mixture was heated to $180\text{ }^\circ\text{C}$ for 21 h using an oil bath, and a black precipitate was formed. The resulting precipitate was insoluble in THF and $CHCl_3$.

DG-PEEK6 and **DG-PEEK7** were prepared in a similar manner using **S9** or **S12**. Both polymers were insoluble in organic solvents.

Polymerization (reaction time = 6 h)



To a 10 mL two-necked flask, **S12** (370 mg, 0.98 mmol), K_2CO_3 (187 mg, 1.35 mmol), and NMP (1 mL) were added. The flask is equipped with a reflux condenser, and the reaction mixture is stirred under N_2 atmosphere at rt. After the reactants were completely dissolved, the mixture was heated to $180\text{ }^\circ\text{C}$ for 6 h using an oil bath. After cooling to rt, the polymer was precipitated by pouring the viscous reaction mixture slowly to a vigorously stirred MeOH. The polymer is purified by stirring in MeOH. After drying in a vacuum oven, **DG-PEEK7** was obtained as a dark brown powder (273 mg, 78%).

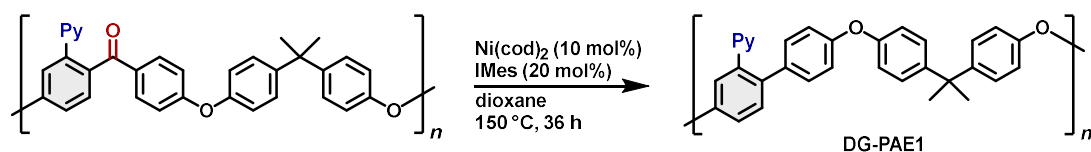
Due to broad signals, only the characteristic peaks are reported.

^1H NMR ($\text{DMSO-}d_6$, 400 MHz) δ : 8.75–7.11 (br, 11H), 4.64–3.74 (br, 4H).

^{13}C NMR ($\text{DMSO-}d_6$, 101 MHz) δ : 185.3.

IR (KBr): 3367 br, 1619 s, 1598 s, 1577 s, 1520 s, 1508 s, 1447 s, 1426 s, 1324 m, 1226 s, 1170 s, 1121 m, 1050 m, 844 w, 806 w, 765 w.

IV. Decarbonylation of DG-PEEK4



In a glovebox filled with nitrogen, **DG-PEEK4** (0.10 mmol), Ni(cod)_2 (0.01 mmol), IMes (0.02 mmol) and dioxane (1.5 mL) were added to a 5 mL vial with a Teflon-sealed screwcap. The mixture was stirred at 150 °C for 36 h. The resulting mixture was precipitated by pouring the viscous reaction mixture slowly to a vigorously stirred MeOH.

The solid obtained was subjected to FT-IR spectroscopic analysis using an ATR detector. The solid was dissolved in HPLC-grade CHCl_3 , filtered through a syringe filter, and subsequently analyzed via SEC analysis.

$M_w = 3340$, $M_w/M_n = 3.01$.

^1H NMR (CDCl_3 , 400 MHz) δ : 8.58 (s, 1H), 7.44–7.30 (m, 4H), 7.19–6.85 (m, 15H), 1.67 (s, 6H).

IR (ATR): 2363 w, 1587 m, 1503 s, 1486 s, 1462 m, 1233 s, 1173 w, 831 w, 750 m, 418 w.

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For Experimental Section

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Conclusions

In this doctoral dissertation, based on the activation of inert bonds by nickel catalyst, the author achieved novel transformations of both small molecules and polymers.

In Chapter 1, nickel-catalyzed 1,4-aryl migration of aryl *N*-benzylimidates was developed. To date, reactions involving the cleavage of C(sp²)-O bonds in phenol derivatives by transition metal catalysis have been largely limited to cross-coupling-type reactions, and, to the best of the author's knowledge, there is no example that the leaving group (OR group) is incorporated into the product. In this study, by combining the cleavage of C-O bonds with C-H bond activation, the recombination of the leaving group was achieved, thereby realizing a novel rearrangement reaction.

In Chapter 2, the synthesis of phenylene-ether-type polymers bearing directing groups and their catalytic depolymerization via C(sp²)-O bond cleavage by a nickel catalyst are described. It was demonstrated that, through the introduction of directing groups, selective polymer degradation can be achieved without compromising the high thermal and chemical stability of the polymers.

In Chapter 3, the design principle of "main-chain cleavage via directing group-assisted catalysis," discovered in Chapter 2, was applied to polyphenylene sulfide-type polymers, enabling catalytic depolymerization via C(sp²)-S bond cleavage. Furthermore, by designing the introduced directing groups, we controlled the glass transition temperature and crystallinity of the polymers, demonstrating the potential to balance both practicality and recyclability.

In Chapter 4, the skeletal transformation from poly(aryl ether ketone)s to poly(aryl ether)s via nickel-catalyzed decarbonylation was realized. By utilizing directing groups, it was demonstrated that atom-deletion-type skeletal editing involving the cleavage of inert bonds is feasible in polymer backbones.

In summary, this thesis study accomplished (i) the development of novel reactions based on the activation of inert bonds (Chapter 1), (ii) chemoselective bond cleavage for chemical recycling (Chapters 2 and 3), and (iii) skeletal editing of polymer main chains via atom unit-elimination reactions (Chapter 4). The findings of this research provide new guidelines for the chemical recycling and skeletal modification of otherwise persistent polymers composed solely of robust covalent bonds, and are expected to contribute to the advancement of sophisticated chemical transformations of post-consumer polymers.

List of Publications

1. **Ogawa, S.**; Tobisu, M.
Nickel-Catalyzed 1,4-Aryl Rearrangement of Aryl *N*-Benzylimidates via C–O and C–H Bond Cleavage.
Chem. Commun. **2022**, 58, 7909–7911.
2. **Ogawa, S.**; Morita, H.; Hsu, Y.-I.; Uyama, H.; Tobisu, M.
Controlled Degradation of Chemically Stable Poly(Aryl Ethers) *via* Directing Group-Assisted Catalysis.
Chem. Sci. **2024**, 15, 17556–17561.
3. **Ogawa, S.**; Takenaka, N.; Hsu, Y.-I.; Uyama, H.; Tobisu, M.
Directing Group-Integrated Poly(Phenylene Sulfide): Achieving Chemical Stability and Controlled Degradability.
Macromolecules **2025**, 58, 4257–4261.
4. **Ogawa, S.**; Ohtani, H.; Tobisu, M.
Skeletal Editing of Polymer Backbone via Nickel-Catalyzed Decarbonylation: Poly(Aryl Ethers) from Poly(Aryl Ether Ketones).
in preparation.

Supplementary Publication

1. Fujimoto, H.; Nishioka, T.; Imachi, K.; **Ogawa, S.**; Nishimura, R.; Tobisu, M.
Generation of Stereocenters via Single-Carbon-Atom Doping Using *N*-Isocyanides.
J. Am. Chem. Soc. **2025**, 147, 8138–8144.

Although this study is not discussed in detail in the main chapters, it is conceptually related to Chapter 4. In this work, the author contributed to the development of synthetic methods for (*N*-isocyanoimino)phosphorane (PINC) derivatives through examination of reaction conditions inspired by the Appel reaction. Given that these reagents can be utilized for skeletal modification via single-carbon atom insertion, their application to polymeric materials may enable the development of new atom insertion-type or cyclization-type skeletal editing strategies for polymer backbones.