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Author(s)	Ohta, Ryousuke; Shio, Yasunori; Akiyama, Toshiki et al.
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Supporting Information

Carbon-(sp^2)-carbon(sp^3) Bond-forming Cross-coupling Reactions Using Sulfur-Modified Au-Supported Nickel Nanoparticle Catalyst

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Contents

1. General Information

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-AL-300 (300 MHz), JEOL JNM-AL-400 (400 MHz) or JEOL ECA-500 (500 MHz) with tetramethylsilane as an internal standard. Chemistation (TOKYO RIKAKIKAI CO., LTD, PPS-CTRL) was used for heating reactions using SANi. GC-MS analyses were performed by GCMS-QP2010 SE (Shimadzu corporation). Au mesh was purchased from Sanwa Metal CO. LTD. Column chromatography was carried out with silica gel (Kanto Chemical Co. Inc., Silica Gel 60 N, spherical neutral) unless otherwise stated. Transmission Electron Microscope (TEM) analyses were performed by JEOL JEM-2100F. Focused Ion Beam (FIB) treatment were performed by JEOL JIB-4600F

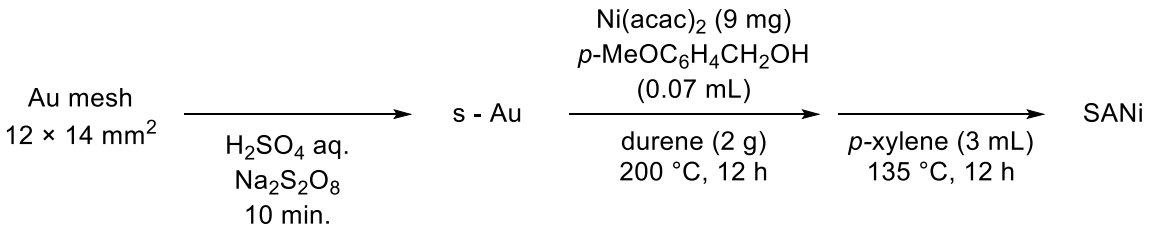
Experiment materials

Solvent were dried by molecular sieves 3A or 4A. Commercial reagents and argon gas were used as received. TLC (Merck silica gel 60 F^{254}) was used for monitoring reactions.

General consideration

Unless otherwise indicated, all reactions were carried out under argon atmosphere. Reactions were monitored by thin layer chromatography.

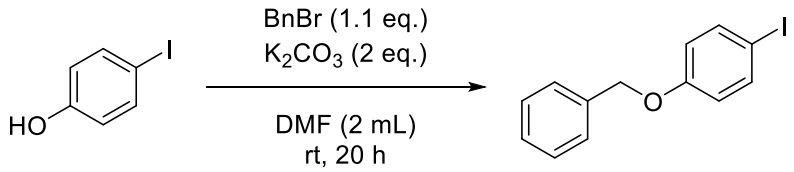
2. Preparation of SANi



$Na_2S_2O_8$ (4 g) was gradually added to 98% H_2SO_4 (4.7 g) in a flask at 0 ℃ with stirring. 17 mL of water cooled in ice bath was added to the solution to maintain the temperature below 15 ℃. After stirring at this temperature, the ice bath was removed and the mixture was stirred at room temperature for 30 min to obtain piranha solution. Au (100 mesh, 12 × 14 mm^2) was placed in piranha solution (3 mL) at 25 ℃ for 10 min, and then rinsed in succession with H_2O (1 mL × 6) and EtOH (1 mL × 6). The sample was placed in a flask and dried under reduced pressure for 10 min. The resulting sulfur-modified Au [s-Au] was placed in a solution of $Ni(acac)_2$ (9 mg) in and 4-methoxybenzylalcohol (0.07 mL) in durene (2 g) and the reaction mixture was stirred at 200 ℃ for 12 h under a N_2 atmosphere. Then the plate was rinsed with *p*-xylene (1 mL × 6) and dried under reduced pressure for 20 min. The obtained mesh was placed in *p*-xylene (3 mL) and heated at 135 ℃ for 12 h. The mesh was rinsed with *p*-xylene (1 mL × 6) and dried under reduced pressure for 20 min to give SANi.

3.Preparation of aryl halides

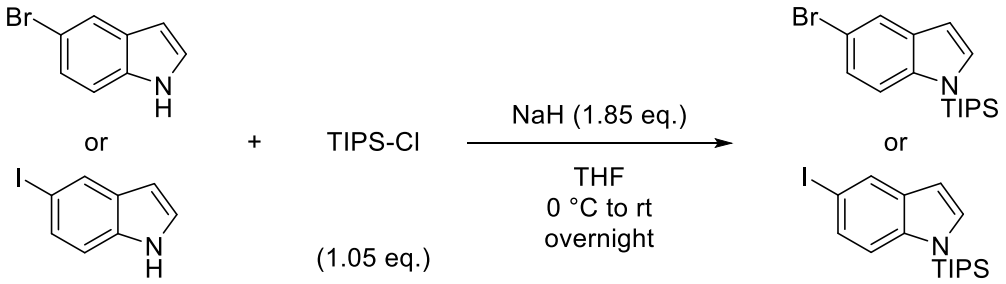
4-Benzyloxyiodobenzene (**1e**)[S1]



In a flame-dried round bottom flask (20 mL), 4-iodophenol (507 mg, 2.3 mmol, 1.0 equiv.) was dissolved in DMF (2 mL). Then, potassium carbonate (644 mg, 4.66 mmol, 2.0 equiv.) and benzyl bromide (0.3 mL, 2.52 mmol, 1.1 equiv.) were added, and the reaction mixture was stirred at room temperature for 20 h. The reaction was stopped by adding sat. NH_4Cl aq. (10 mL). The aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residual crude product was purified by silica gel column chromatography (*n*-hexane : AcOEt = 10 : 1) to afford **1e** (528 mg, 1.7 mmol, 74%) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.55 (d, J = 9.2 Hz, 2H), 7.42-7.31 (m, 5H), 6.75 (d, J = 9.2 Hz, 2H), 5.03 (s, 2H)); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 158.7, 138.3, 136.5, 128.7, 128.2, 127.5, 117.3, 83.1, 70.1; mp: 61-62 ℃ (recrystallized from *n*-hexane/*i*-PrOH, needle).

5-Bromo-1-(triisopropylsilyl)indole (**1h'**)[S2] and 5-iodo-1-(triisopropylsilyl)indole (**1h**)[S3]



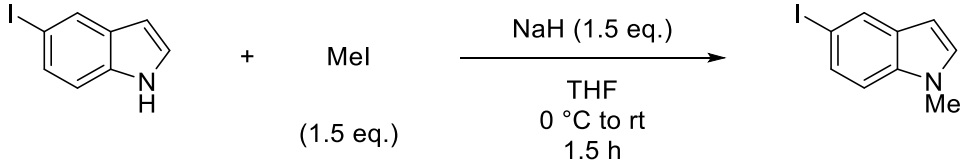
In a flame-dried round bottom flask (50 mL), 5-bromoindole (648 mg, 3.3 mmol, 1 eq.) was dissolved in THF (13 mL), cooled to 0 ℃ and sodium hydride (245 mg, 6.13 mmol, 1.85 eq. 60% oil suspension) was added in portions. The mixture was allowed to warm to room temperature with stirring for 1 h. The reaction mixture was again cooled to 0 ℃ and triisopropylsilyl chloride (0.74 mL, 3.49 mmol, 1.05 eq.) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was stopped by adding 2 N H_3PO_4 (5 mL). The aqueous layer was extracted with *n*-hexane. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residual crude product was purified by silica gel column chromatography (100% *n*-hexane) to afford **1o** (1160 mg, 3.29 mmol, 99%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.72 (d, J = 2.0 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.25-7.20 (m, 2H), 6.56 (d, J = 3.2 Hz, 1H), 1.73-1.61 (m, 3H), 1.12 (d, J = 8.0 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 139.5, 133.3, 132.5, 124.1, 123.1, 115.2, 113.1, 104.4, 18.1, 12.8.

1h (859 mg, 2.15 mmol, 90%) as a colorless oil was prepared by same procedure from 5-iodoindole (578 mg, 2.38 mmol).

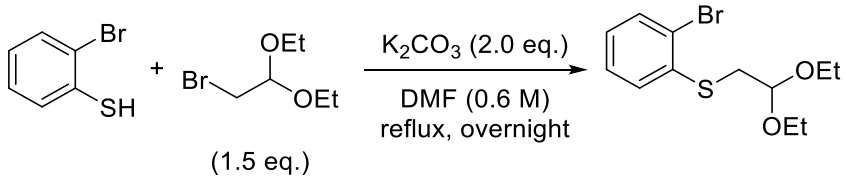
^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.95 (d, J = 1.7 Hz, 1H), 7.38 (dd, J = 8.7, 1.8 Hz, 1H), 7.27 (d, J = 8.7 Hz, 1H), 7.20 (d, J = 3.2 Hz, 1H), 6.54 (dd, J = 3.2, 0.7 Hz, 1H), 1.67 (m, 3H), 1.12 (d, J = 7.5 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 140.0, 134.1, 132.1, 129.6, 129.4, 115.8, 104.1, 83.5, 18.1, 12.8.

5-Iodo-1-methylindole (**1i**)[S4]



In a flame-dried round bottom flask (50 mL), 5-iodoindole (519 mg, 2.14 mmol) was dissolved in THF (7.2 mL), cooled to 0 ℃ and sodium hydride (134 mg, 3.35 mmol, 1.57 eq. 60% oil suspension) was added slowly. After stirring for 30 min at 0 ℃, methyl iodide (0.2 mL, 3.21 mmol, 1.5 eq.) was added in dropwise. The mixture was then warmed up to room temperature, and the resulting reaction mixture was monitored by TLC. The reaction was quenched by sat. NH_4Cl aq. (5 mL) and extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residual crude product was purified by flash silica gel column chromatography (*n*-hexane : AcOEt = 10 : 1) to afford **1i** (542 mg, 2.11 mmol, 98%) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.94 (s, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.39 (d, J = 2.4 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 135.8, 131.0, 129.8, 129.6, 129.6, 111.2, 100.2, 82.8, 32.9; mp: 41-43 ℃ (recrystallized from *n*-hexane/*i*-PrOH, needle).

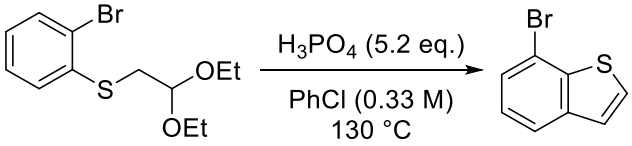
(2-Bromophenyl)(2,2-diethoxyethyl)sulfane (**9**)[S5]



In a flame-dried round bottom flask (20 mL), a mixture of 2-bromothiophenol (0.52 mL, 4.4 mmol, 1 eq.) and K_2CO_3 (1.2 g, 8.7 mmol, 2.0 eq.) were dissolved DMF (7.2 mL), and it was stirred at 60 ℃ for 1 h. Then 2-bromoacetaldehyde diethyl acetal (1.0 mL, 6.5 mmol, 1.5 eq.) was added. The mixture was stirred for overnight under reflux (175 ℃) until the reaction was completed based on TLC analysis. It was cooled to room temperature and extracted with AcOEt. The combined organic layer was washed with 5% NaOH aqueous solution and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residual crude product was purified by flash silica gel column chromatography (*n*-hexane : AcOEt = 10 : 1) to afford (2-Bromophenyl)(2,2-diethoxyethyl)sulfane **9** (1.19 g, 3.9 mmol, 88%) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.53 (dd, J = 8.0, 1.3 Hz, 1H), 7.36 (dd, J = 7.9, 1.5 Hz, 1H), 7.26-7.23 (m, 1H), 7.03-7.01 (m, 1H), 4.70 (t, J = 5.6 Hz, 1H), 3.72-3.66 (m, 2H), 3.60-3.53 (m, 2H), 3.14 (d, J =

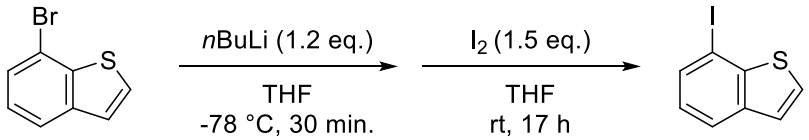
5.5 Hz, 2H), 1.20 (t, J = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 137.8, 133.0, 128.8, 127.7, 126.8, 123.9, 101.6, 62.3, 36.8, 15.3.

7-Bromobenzothiophene (**10**)[S5]



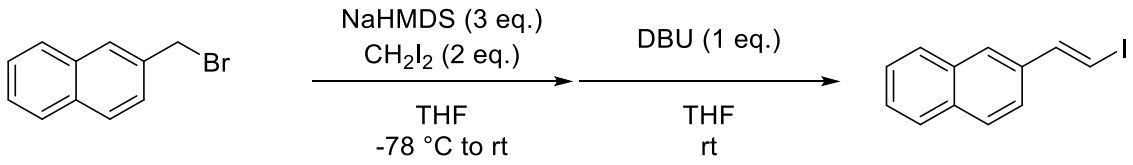
In a test tube (15 Φ), (2-bromophenyl)(2,2-diethoxyethyl)sulfane (305 mg, 1.0 mmol, 1 eq.) and phosphoric acid (0.3 mL, 5.2 mmol, 5.2 eq.) were dissolved in chlorobenzene (3 mL). The mixture was stirred at 130 ℃ for 19 h. Then the mixture was cooled to room temperature, the reaction was quenched by addition of sat. $NaHCO_3$ aq., and extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residual crude product was purified by flash silica gel column chromatography (100% *n*-hexane) to afford 7-bromothiophene **10** (193 mg, 0.90 mmol, 90%) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.77 (d, J = 8.0 Hz, 1H), 7.51-7.49 (m, 2H), 7.44 (d, J = 5.4 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 141.6, 140.6, 127.3, 127.2, 125.6, 124.8, 122.6, 116.0.

7-Iodobenzothiophene (**1J**)[S6]



THF (16 mL) and *n*-BuLi (1.6 M *n*-hexane solution, 5.0 mL, 8.0 mmol, 1.2 eq.) was placed in a flame-dried round bottom flask (100 mL). To the mixture was added a solution of 7-bromothiophene **10** (1.42 g, 6.66 mmol, 1 eq.) in THF (24 mL) at -78 ℃. After stirring for 0.5 h at -78 ℃, I_2 (2.54 g, 10 mmol, 1.5 eq.) was added. The mixture was gradually warmed up to room temperature. After stirring for 17 h, the reaction was quenched by addition of sat. $Na_2S_2O_3$ aq. and extracted with *n*-hexane. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residual crude product was purified by flash silica gel column chromatography (100% *n*-hexane) to afford 7-iodobenzothiophene **1j** (146 mg, 0.56 mmol, 8%) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.81 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.4 Hz, 1H), 7.58 (d, J = 5.5 Hz, 1H), 7.52 (d, J = 5.5 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 146.4, 139.2, 133.8, 126.8, 125.6, 125.4, 123.5, 87.5.

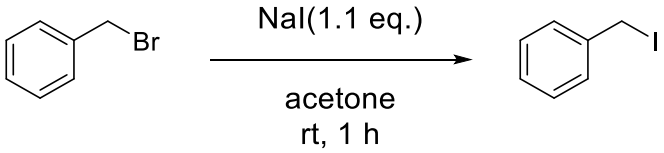
(*E*)-2-(2-Iodovinyl)naphthalene (**1k**)[S7]



In a flame-dried round bottom flask (50 mL), a solution of CH_2I_2 (0.48 mL, 6.0 mmol, 1.5 eq.) in THF (1.5 mL) was added dropwise to a solution of LiHMDS (2.2 g, 12.0 mmol, 3.0 eq.) in THF (8 mL) and Et_2O (8 mL) at -78 ℃ in the dark. After 20 min, a solution of the 2-(bromomethyl)naphthalene (885 mg, 4.0 mmol, 1 eq.) in THF (3 mL) was added dropwise. The reaction mixture was stirred for 90 min then removed from the cold bath to warm to rt. After 30 min, DBU (0.60 mL, 4.0 mmol, 1 eq.) was added dropwise and the solution stirred for 1 h before Et_2O (30 mL) was added. The mixture was filtered through a plug of celite/silica (approximately 3 cm celite over 3 cm silica) and the solvent removed under reduced pressure. The residual crude product was purified by flash silica gel column chromatography (100% *n*-hexane) to afford (*E*)-2-(2-iodovinyl)naphthalene **1k** (790 mg, 2.81 mmol, 70%) as a yellow solid.

^{1}H NMR (400 MHz; $CDCl_3$) δ : 7.82-7.77 (m, 3H), 7.66 (s, 1H), 7.58 (d, J = 14.7 Hz, 1H), 7.46 (m, 3H), 6.95 (d, J = 15.1 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ : 145.1, 135.2, 133.4, 133.2, 128.5, 128.2, 127.8, 126.6, 126.5, 126.3, 122.8, 77.0; mp: 88-90 ℃ (recrystallized from *n*-hexane/*i*-PrOH, plate).

Benzyl iodide (**1q**)[S8]



In a flame-dried round bottom flask (50 mL), NaI (495 mg, 3.3 mmol) was added to a solution of benzyl bromide (513 mg, 3.0 mmol) in acetone (10 mL). After stirring at rt for 1 h, the mixture was filtered and concentrated in vacuo. The residual crude product was purified by open silica gel column chromatography (100% *n*-hexane) to afford benzyl iodide (587 mg, 2.69 mmol, 89%) as a ruby red oil.

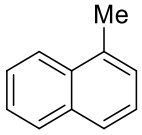
^{1}H NMR (400 MHz; $CDCl_3$) δ :7.39-7.37 (m, 2H), 7.31-7.21 (m, 3H), 4.46 (s, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ : 139.4, 128.9, 128.8, 128.0, 5.9

4. SANi-catalyzed ligand-free kumada coupling

General procedure (Table 2, Entry 1)

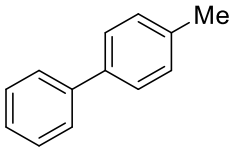
In a test tube (15 Φ), a mixture of 1-iodonaphthalene **1a** (64.5 mg, 0.254 mmol) was dissolved in toluene (2 mL) in the presence of SANi under an argon atmosphere. MeMgI **2a'** (3 M Et_2O solution, 0.25 mL, 0.75 mmol) was added into the reaction mixture and heated at 80 ℃ for 19 h without stirring. After the reaction mixture had been cooled to room temperature, the SANi was removed from the reaction mixture and rinsed several times with EtOH. Then, sat. NH_4Cl aq. (5 mL) was added into the reaction mixture, and the reaction mixture was extracted with AcOEt. The organic layer was washed with brine, dried over

Na_2SO_4 and concentrated under reduced pressure. The residual crude product was purified by flash silica gel column chromatography (100% *n*-hexane) to afford 1-methylnaphthalene **3a** (29.2 mg, 0.205 mmol, 81%) as a colorless oil.



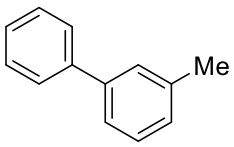
1-Methylnaphthalene (**3a**)[S9]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.99 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.54-7.46 (m, 2H), 7.37 (dd, J = 7.6, 7.6 Hz, 1H), 7.31 (d, J = 6.9 Hz, 1H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 134.2, 133.5, 132.6, 128.5, 126.5, 126.3, 125.7, 125.6, 125.5, 124.1, 19.4.



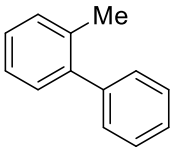
4-Phenyltoluene (**3b**)[S10]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.58 (d, J = 7.3 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.43 (dd, J = 7.3, 7.3 Hz, 2H), 7.33 (dd, J = 7.3, 7.3 Hz, 1H), 7.25 (d, J = 8.2 Hz, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 141.1, 138.3, 137.0, 129.5, 128.7, 128.7, 127.0, 126.9, 21.1; mp: 42-43 ℃ (recrystallized from *n*-hexane/*i*-PrOH, needle).



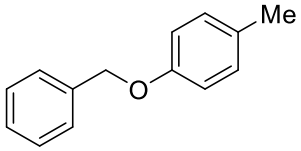
3-Phenyltoluene (**3c**)[S11]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.63-7.59 (m, 2H), 7.47-7.40 (m, 4H), 7.37-7.33 (m, 2H), 7.18 (d, J = 7.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 141.3, 141.2, 138.2, 128.7, 128.6, 128.0, 128.0, 127.2, 127.1, 124.2, 21.5.



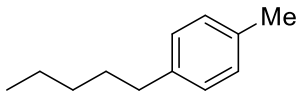
2-Phenyltoluene (**3d**)[S10]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.41 (dd, J = 7.1, 7.1 Hz, 2H), 7.33 (m, 3H), 7.28-7.22 (m, 4H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 141.9, 141.8, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 20.4.



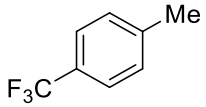
4-Benzyloxytoluene (**3e**)[S12]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.43 (d, J = 7.3 Hz, 2H), 7.38 (dd, J = 7.3, 7.3 Hz, 2H), 7.32 (dd, J = 7.3, 7.3 Hz, 1H), 7.08 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.2 Hz, 2H), 5.04 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 156.7, 137.3, 130.2, 130.0, 128.6, 127.9, 127.5, 114.7, 70.1, 20.5; mp: 35-36 ℃; (recrystallized from *n*-hexane/*i*-PrOH, plate).



4-Pentyltoluene (**3f**)[S13]

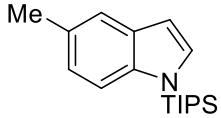
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.09 (s, 4H), 2.57 (t, J = 7.7 Hz, 2H), 2.32 (s, 3H), 1.63-1.56 (m, 2H), 1.36-1.29 (m, 4H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 139.9, 135.0, 128.9, 128.3, 35.5, 31.6, 31.4, 22.6, 21.0, 14.1.



4-Trifluoromethyltoluene (**3g**)

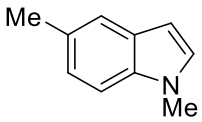
Colorless oil; The yield was determined by GC-MS due to the volatility of the product.

GC Method: 50 ℃ hold for 1 min, followed by a temperature increase of 20 ℃/min to 130 ℃, and hold for 5 min (total run time: 10 min). Retention time: 2.32 min.



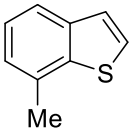
5-Methyl-1-(triisopropylsilyl)indole (**3h**)[S14]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.41 (m, 2H), 7.20 (d, J = 3.1 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.53 (d, J = 3.1 Hz, 1H), 2.43 (s, 3H), 1.73-1.64 (m, 3H), 1.13 (d, J = 7.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 139.1, 131.8, 131.8, 129.0, 122.9, 120.4, 113.6, 104.3, 21.3, 18.2, 13.0.



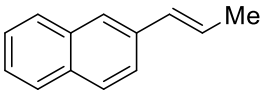
1,5-Dimethylindole (**3i**)[S15]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.96 (s, 1H), 7.46 (d, J = 8.7 Hz, 1H), 7.10 (d, J = 8.7 Hz, 1H), 7.01 (d, J = 3.2 Hz, 1H), 6.41 (d, J = 3.2 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 135.2, 128.9, 128.8, 128.5, 123.2, 120.6, 109.0, 100.3, 33.0, 21.5



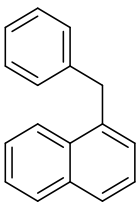
7-Methylbenzothiophene (**3J**)[S16]

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.69 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 5.7 Hz, 1H), 7.37 (d, J = 5.2 Hz, 1H), 7.31 (m, 1H), 7.16 (d, J = 7.4 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 140.0, 139.4, 132.1, 125.8, 124.6, 124.6, 124.4, 121.3, 20.5.



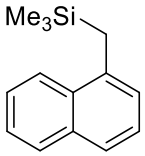
(*E*)-2-(1-Propen-1-yl)naphthalene (**3k**)[S17]

White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.78-7.76 (m, 3H), 7.65 (s, 1H), 7.56 (dd, J = 8.6, 1.7 Hz, 1H), 7.45-7.38 (m, 2H), 6.56 (d, J = 14.0 Hz, 1H), 6.37 (m, 1H), 1.94 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 135.4, 133.7, 132.6, 131.2, 128.1, 127.9, 127.6, 126.2, 126.1, 125.4, 125.2, 123.5, 18.7; mp: 41-42 ℃ (recrystallized from *n*-hexane/*i*-PrOH, plate).



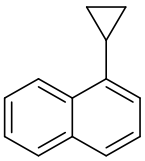
1-Benzylnaphthalene (**3l**)[S18]

Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ : 8.03-7.99 (m, 1H), 7.89-7.86 (m, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.49-7.41 (m, 3H), 7.31-7.26 (m, 3H), 7.22-7.20 (m, 3H), 4.47 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 140.6, 136.6, 133.9, 132.1, 128.7, 128.7, 128.4, 127.3, 127.1, 126.0, 126.0, 125.6, 124.3, 39.0; mp: 58-59 ℃ (recrystallized from *n*-hexane/*i*-PrOH, plate).



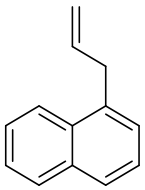
1-(Trimethylsilylmethyl)naphthalene (**3m**)[S19]

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ : 8.00-7.98 (m, 1H), 7.89-7.87 (m, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.52-7.47 (m, 2H), 7.41 (dd, J = 7.6, 7.6 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H), 2.62 (s, 2H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 137.3, 134.0, 131.7, 128.6, 125.6, 125.4, 125.3, 125.0, 124.8, 124.7, 23.5, -1.00.



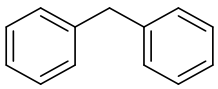
1-Cyclopropylnaphthalene (**3n**)[S20]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.44 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.60-7.50 (m, 2H), 7.43-7.39 (m, 1H), 7.31-7.29 (m, 1H), 2.39-2.35 (m, 1H), 1.12-1.07 (m, 2H), 0.82-0.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 139.2, 133.6, 128.6, 126.6, 125.8, 125.7, 125.6, 124.5, 123.9, 13.4, 9.3, 6.5



1-allylnaphthalene (**3o**)[S21]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.05 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.55-7.48 (m, 2H), 7.44 (dd, J = 7.8, 7.8 Hz, 1H), 7.37 (d, J = 6.9 Hz, 1H), 6.19-6.10 (m, 1H), 5.15-5.10 (m, 2H), 3.87 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 137.1, 136.2, 133.9, 132.1, 128.8, 127.1, 126.4, 125.9, 125.7, 125.6, 124.2, 116.3, 37.4



Diphenylmethane (**3q**)[S22]

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.33-7.28 (m, 4H), 7.24-7.20 (m, 6H), 4.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 141.2, 129.0, 128.6, 126.2, 42.0

5. Reusability of SANi in the ligand-free Kumada coupling (Table 4)

In a test tube (15 Φ), a mixture of 4-phenyliodobenzene **1b** (70.0 mg, 0.25 mmol) was dissolved in toluene (2 mL) in the presence of SANi under an argon atmosphere. MeMgBr **2a** (3 M Et_2O solution, 0.25 mL, 0.75 mmol) was added into the reaction mixture and heated at 80 ℃ without stirring. The reaction was monitored using GC-MS. After completion, the reaction mixture had been cooled to room temperature, the SANi was removed from the reaction mixture and rinsed several times with toluene and EtOH. The yields of **3b** were determined by GC-MS. The recovered SANi plate was again subject to the above reaction. This procedure was repeated a total of 5 times.

GC Method: 50 ℃ hold for 1 min, followed by a temperature increase of 40 ℃/min to 230 ℃, and hold for 4.5 min (total run time: 10 min). Retention time: 5.04 min.

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1e

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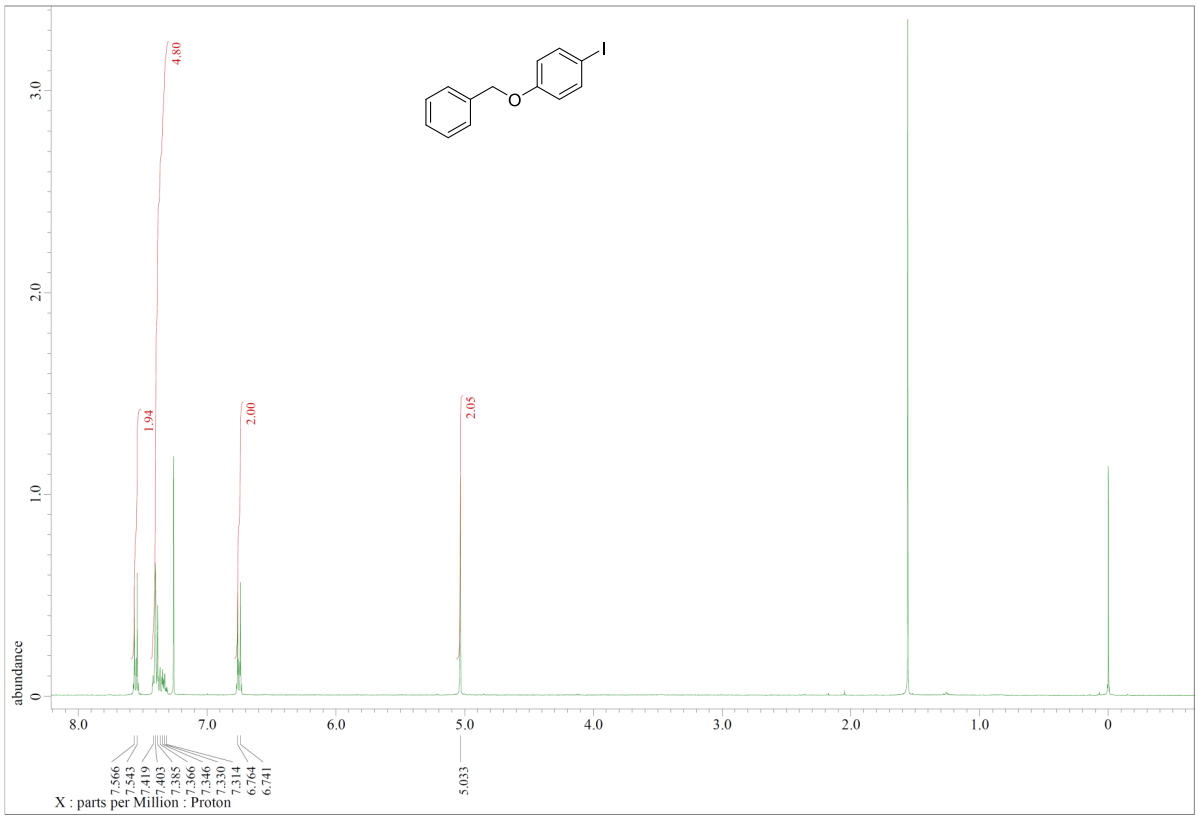

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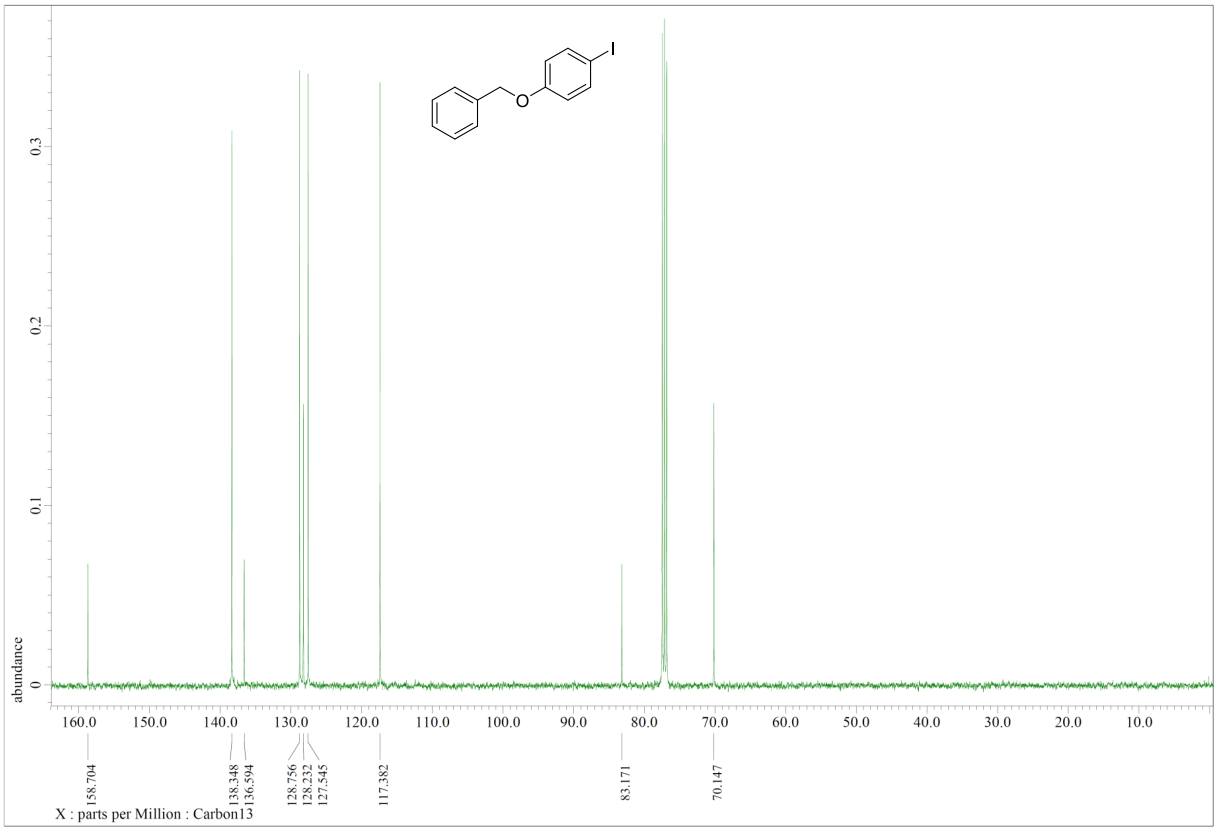

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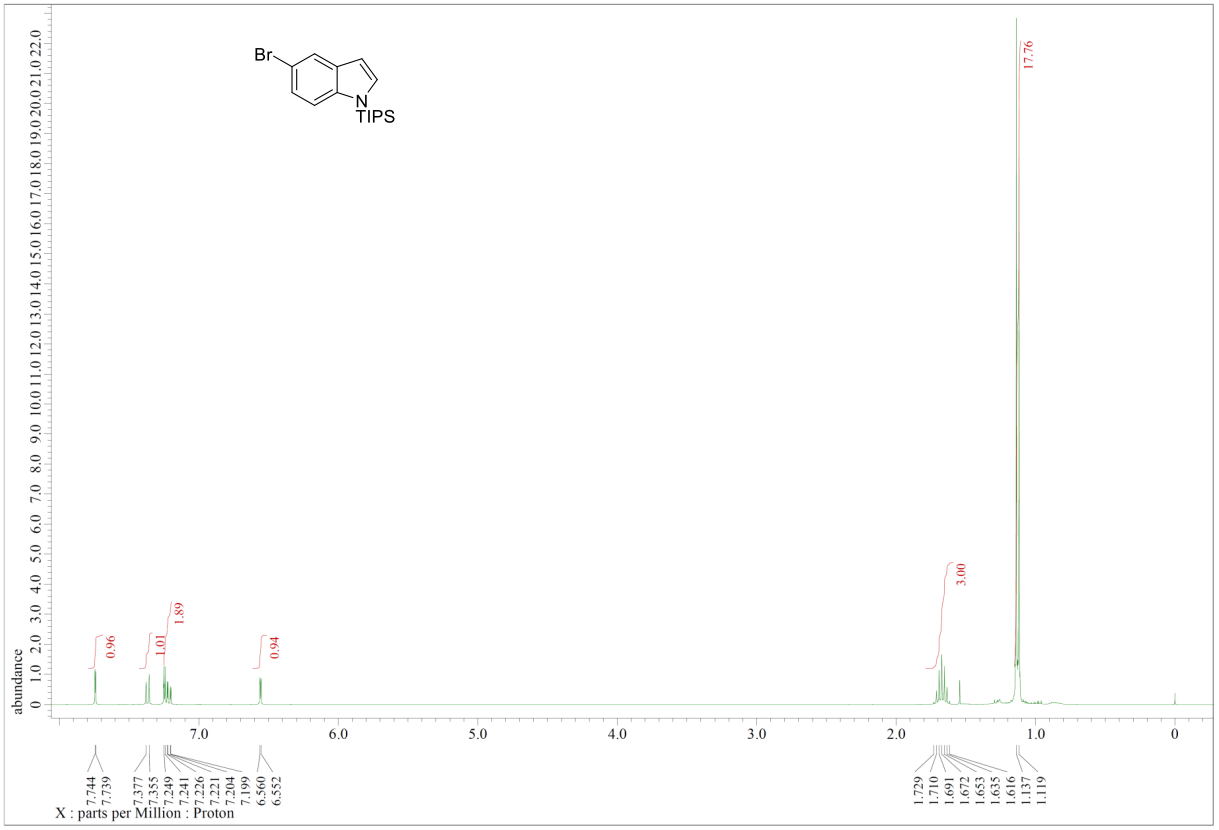

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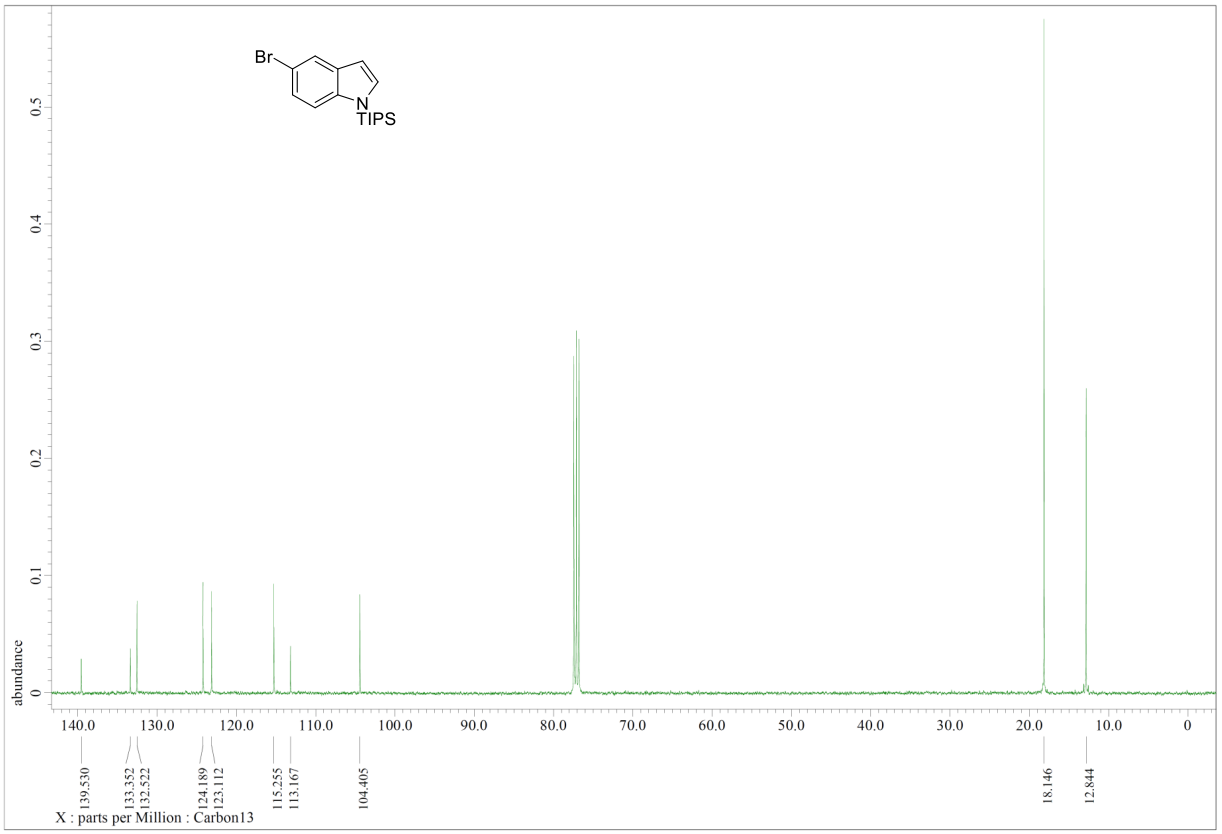

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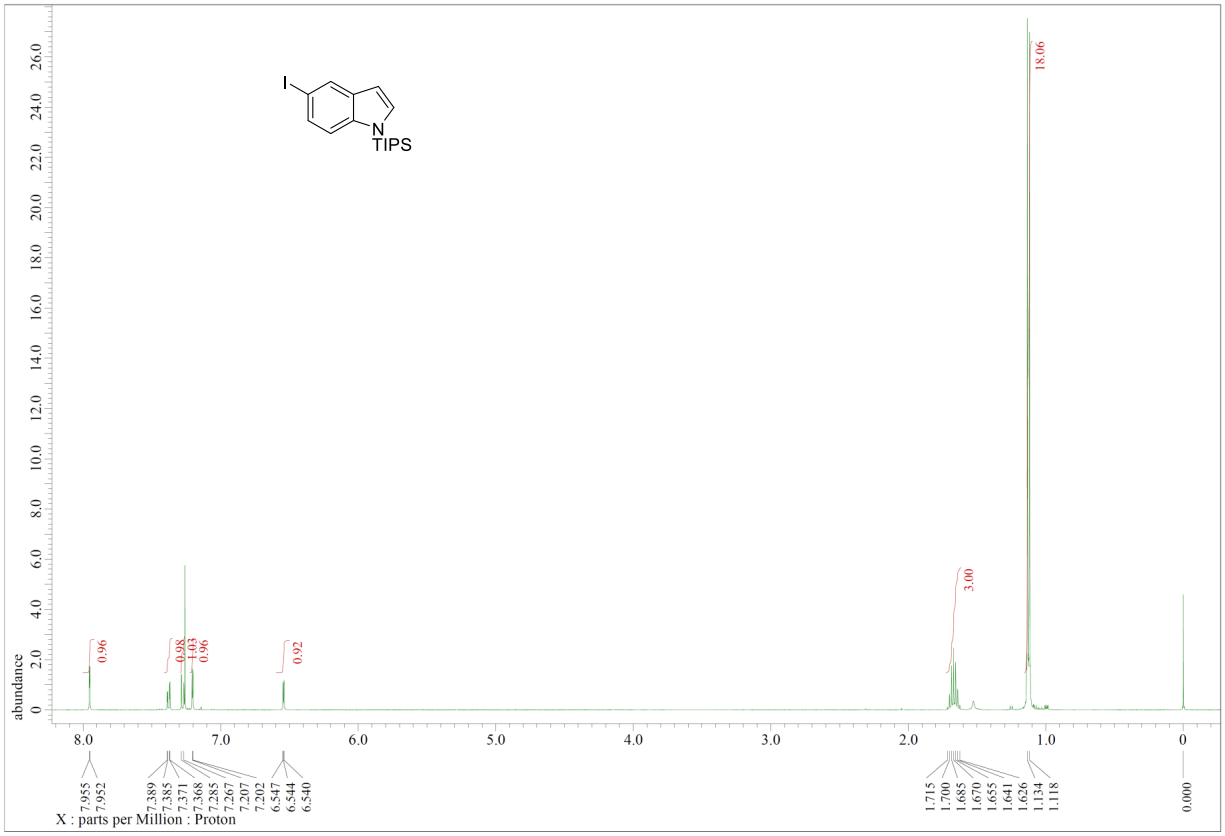

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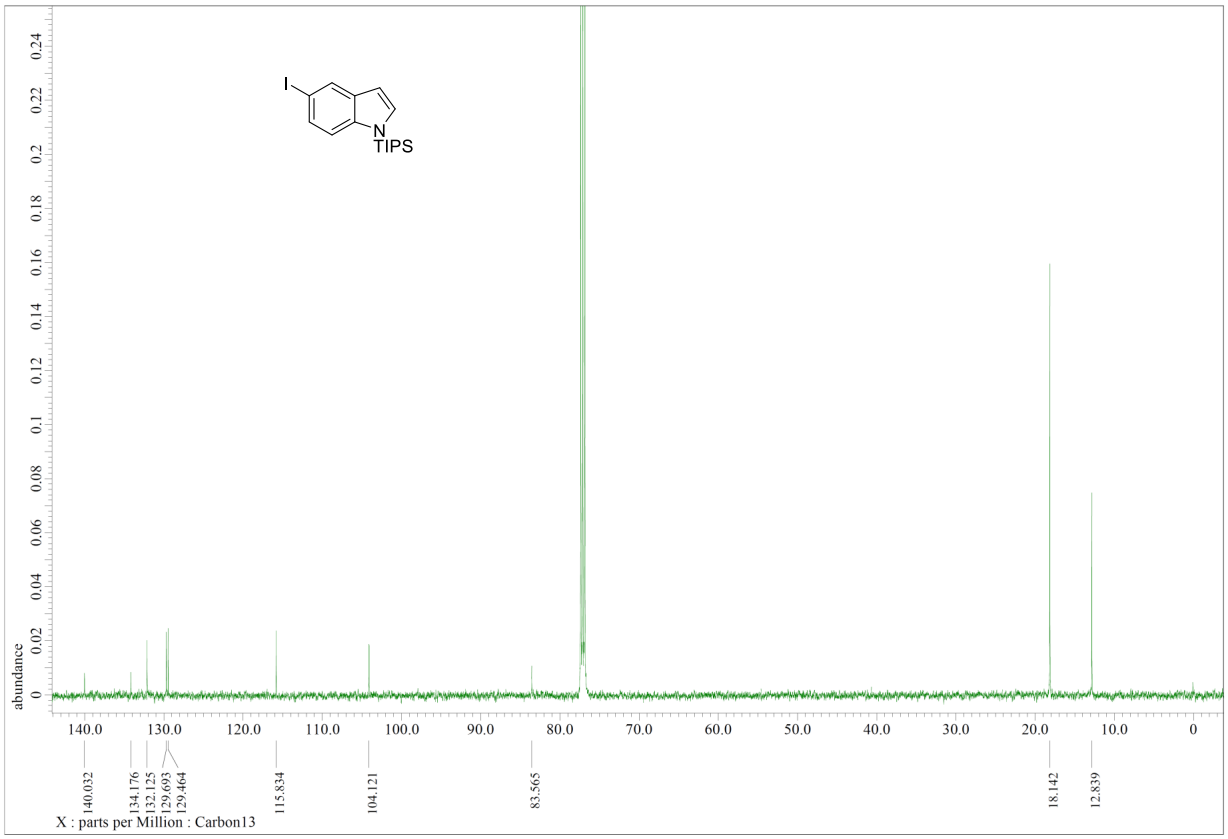

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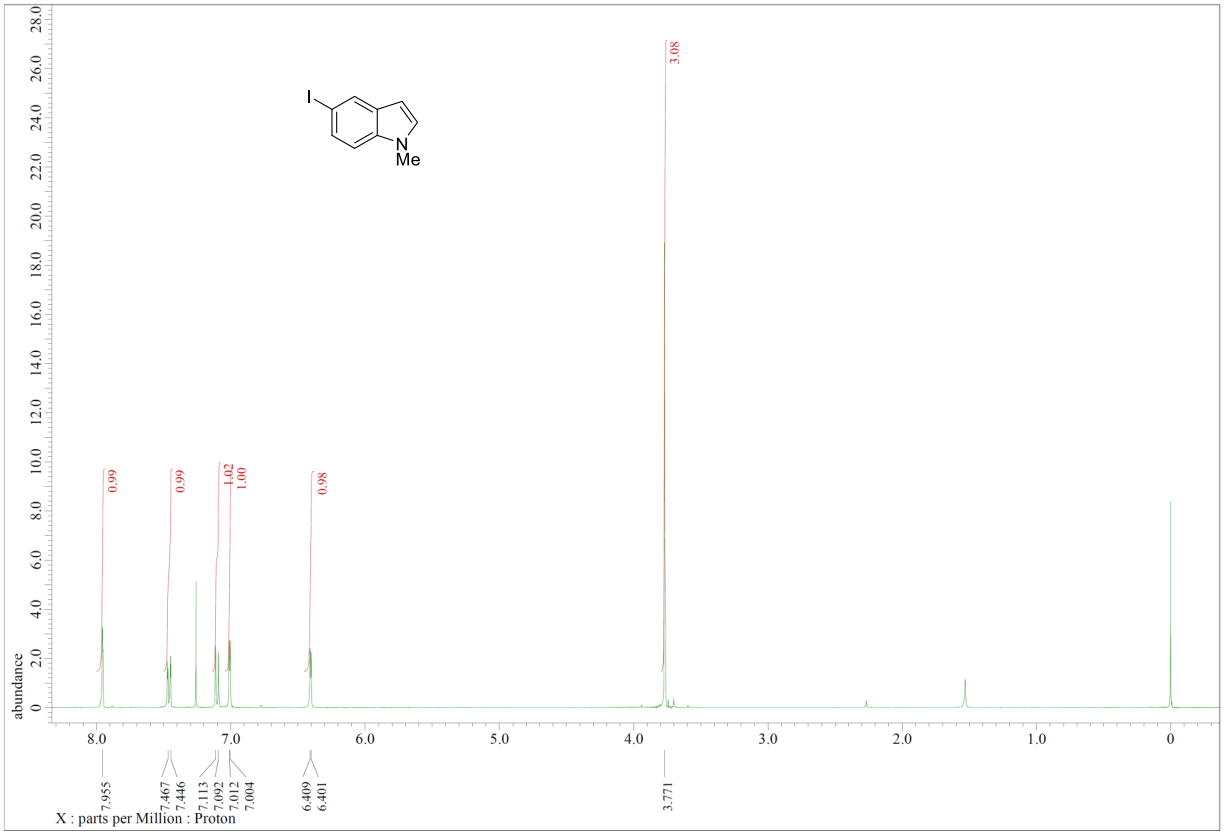

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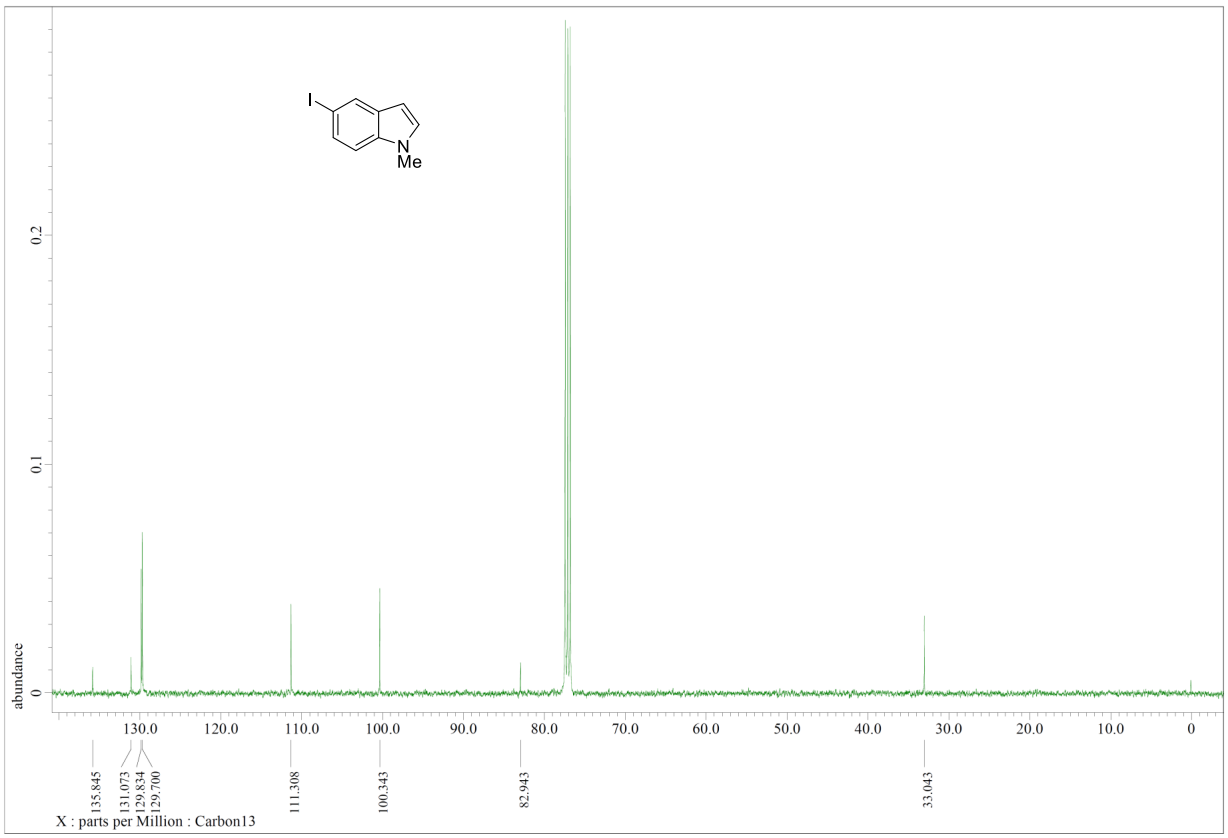

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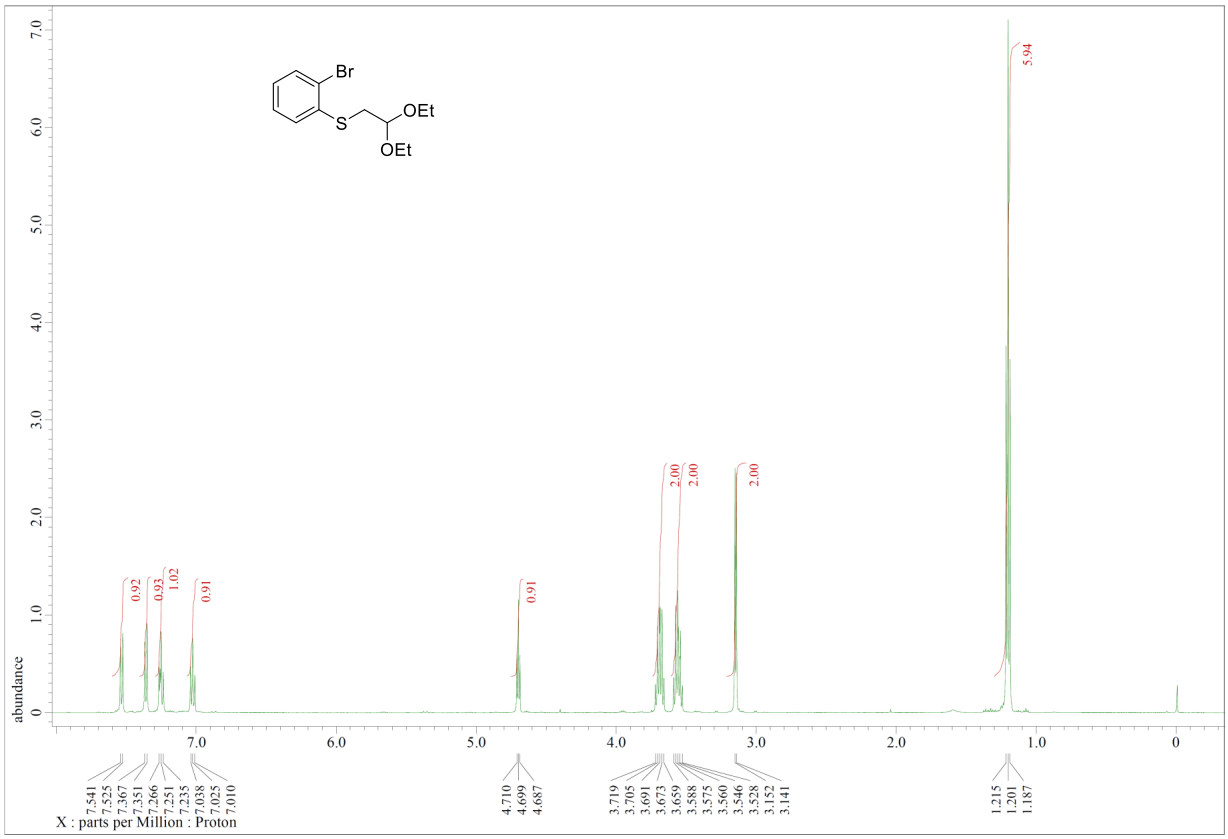

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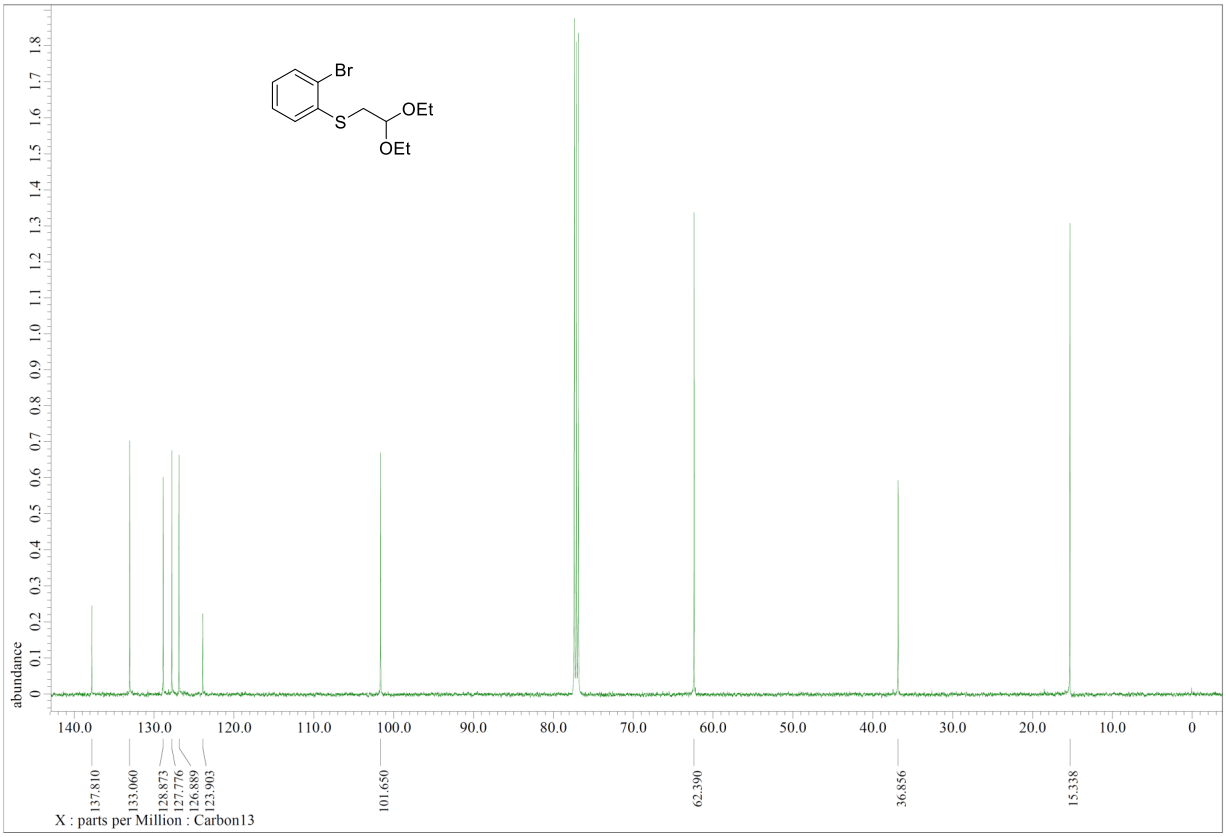

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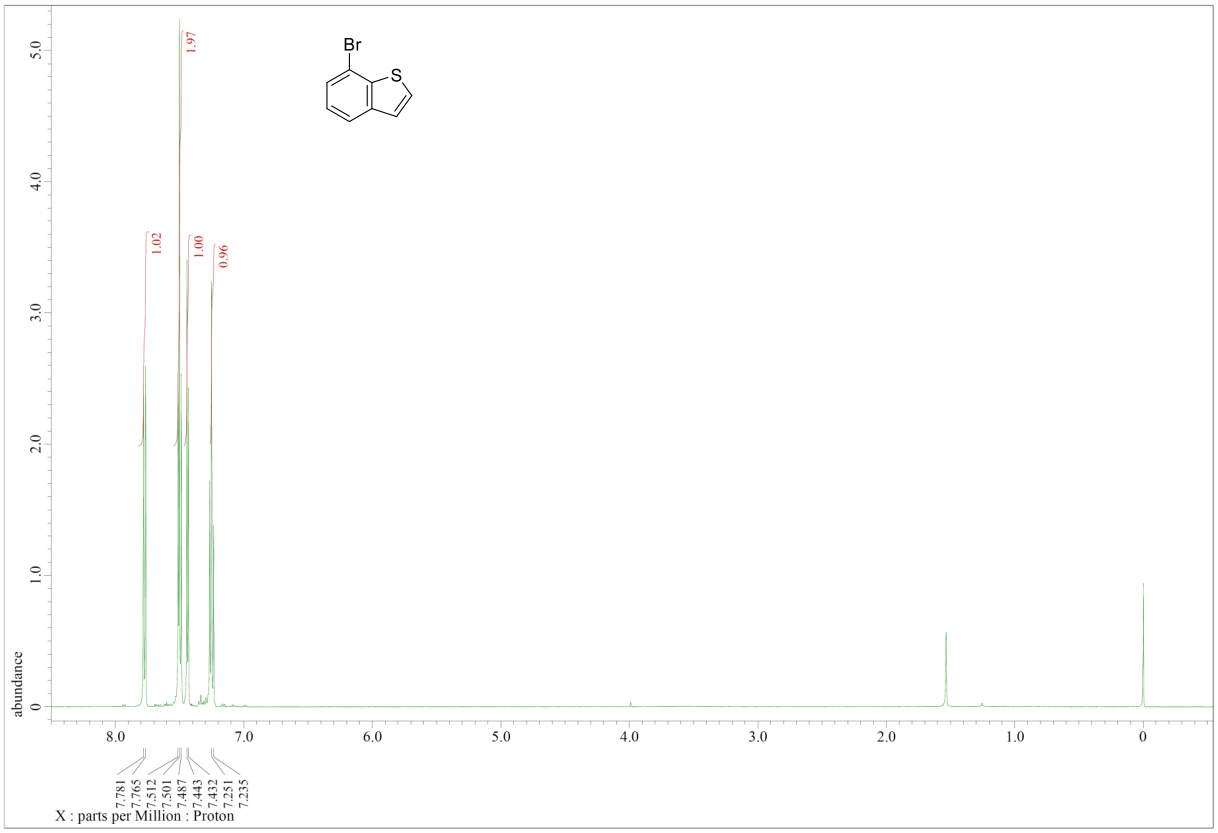

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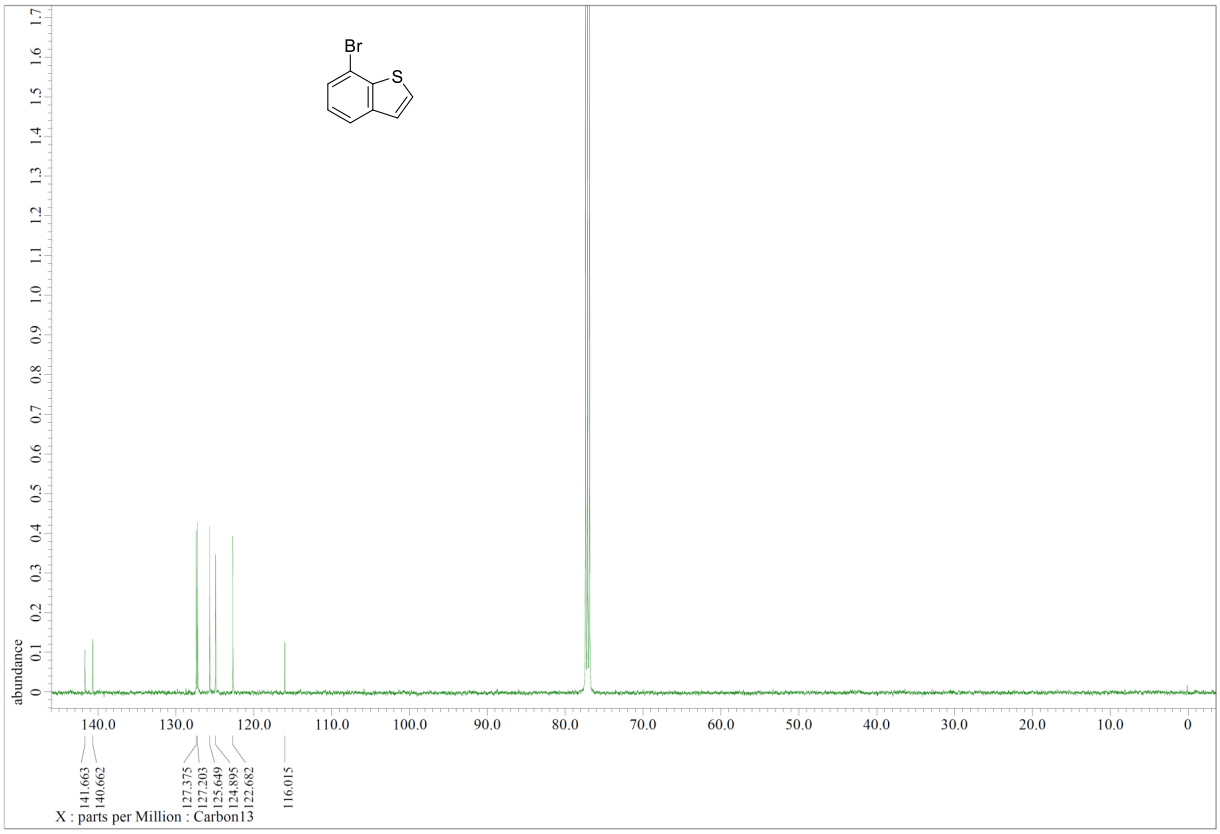

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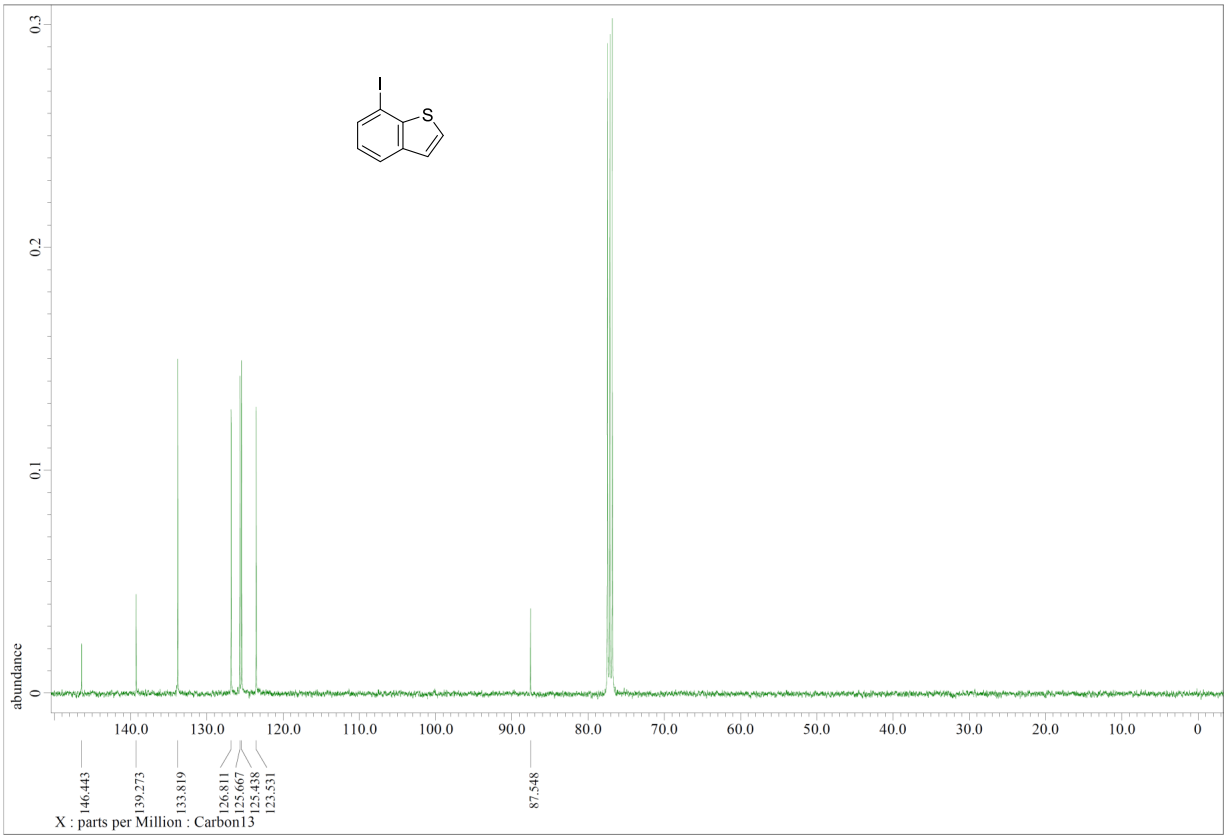

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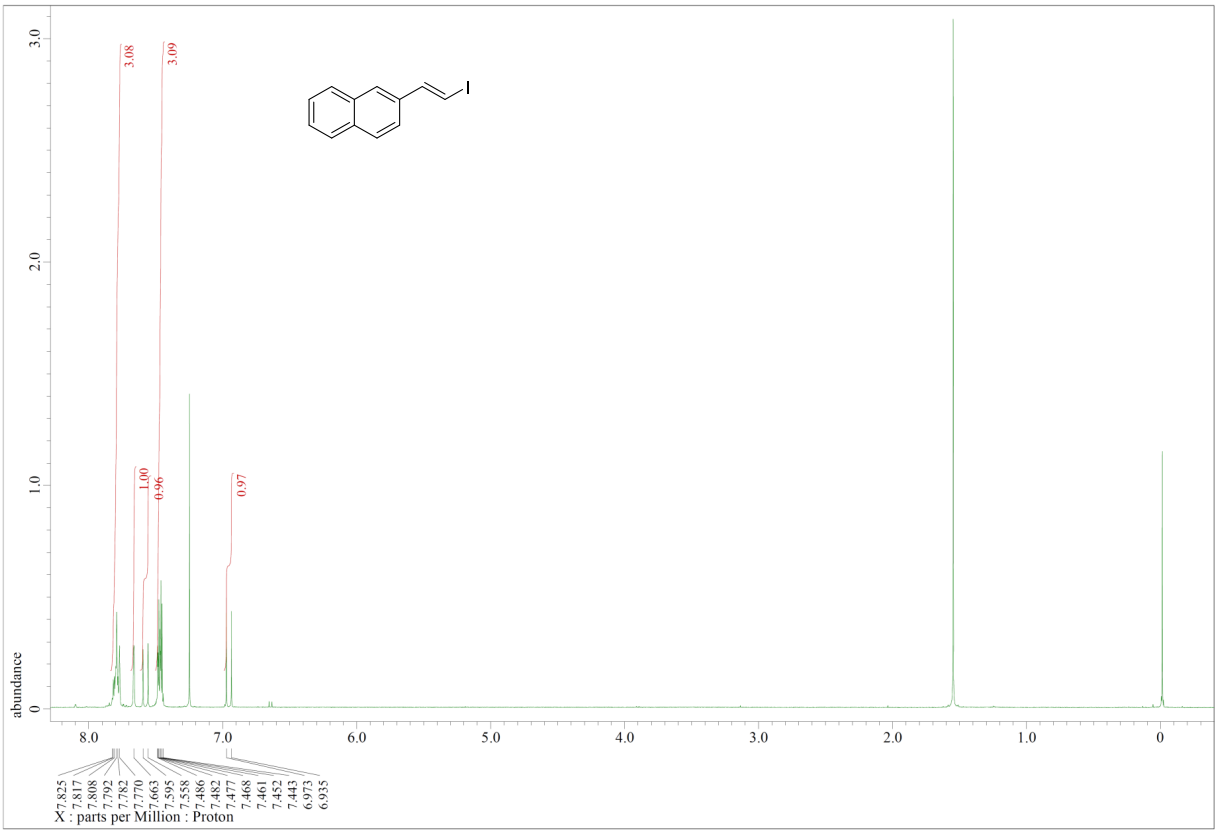

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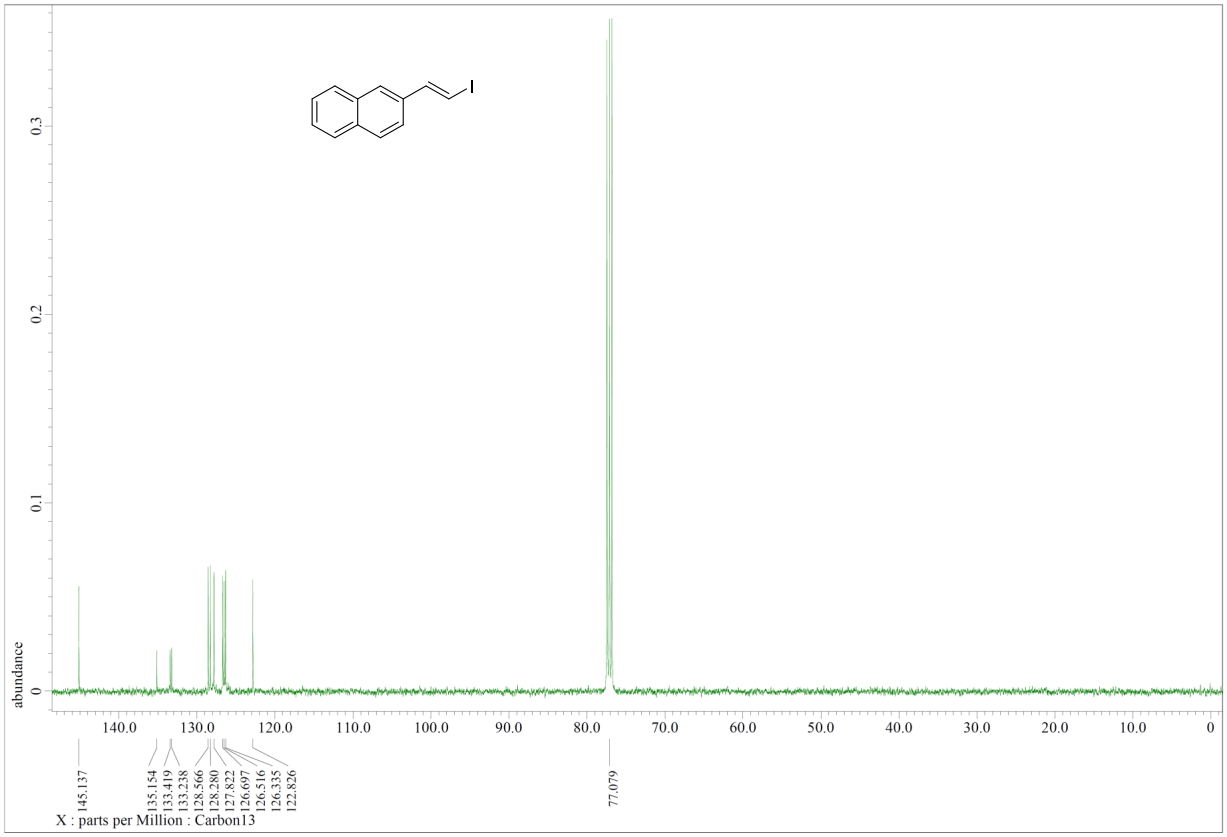

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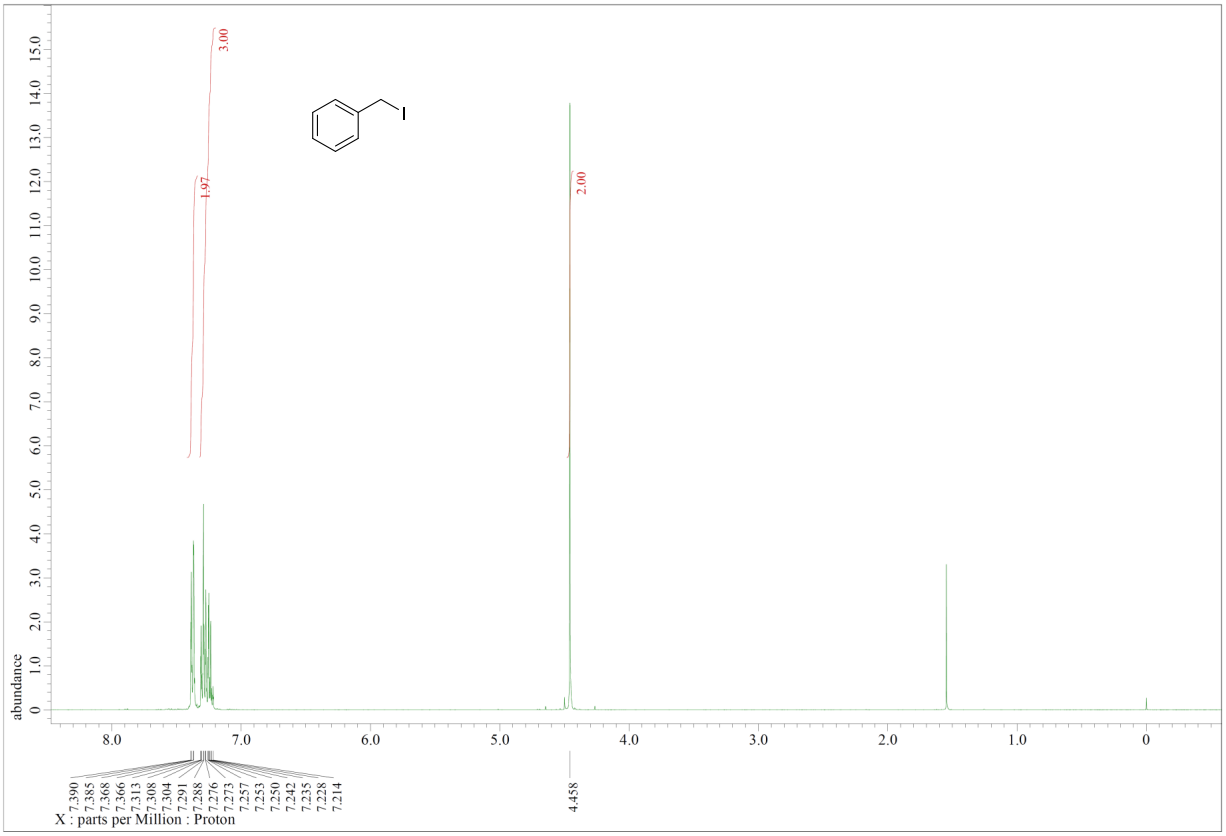

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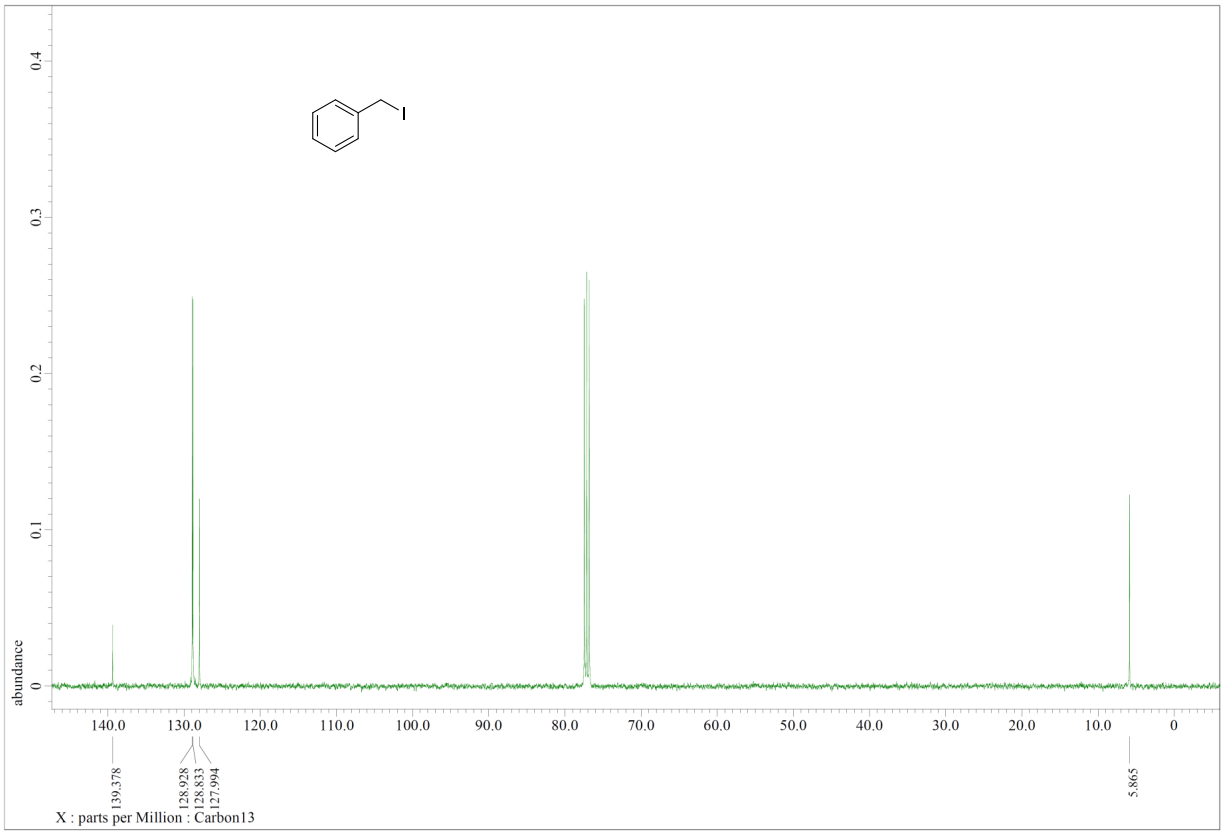

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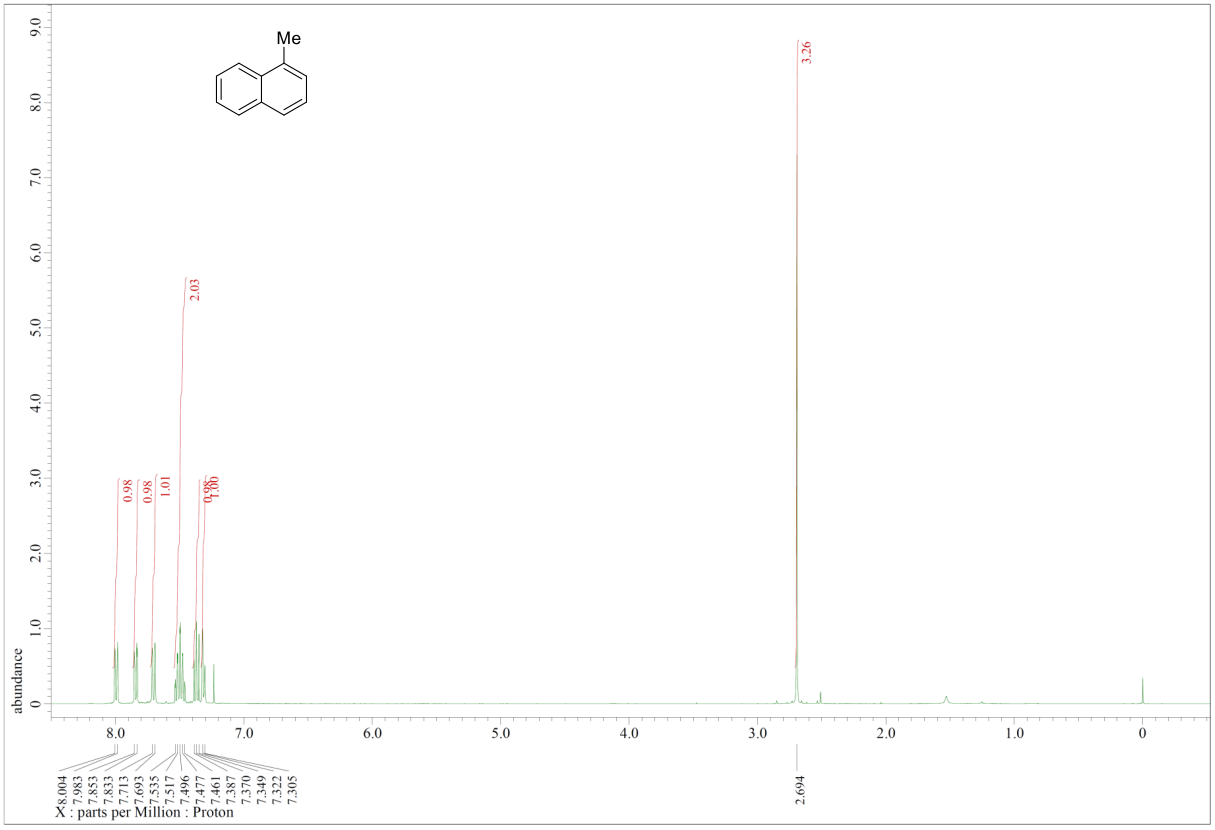

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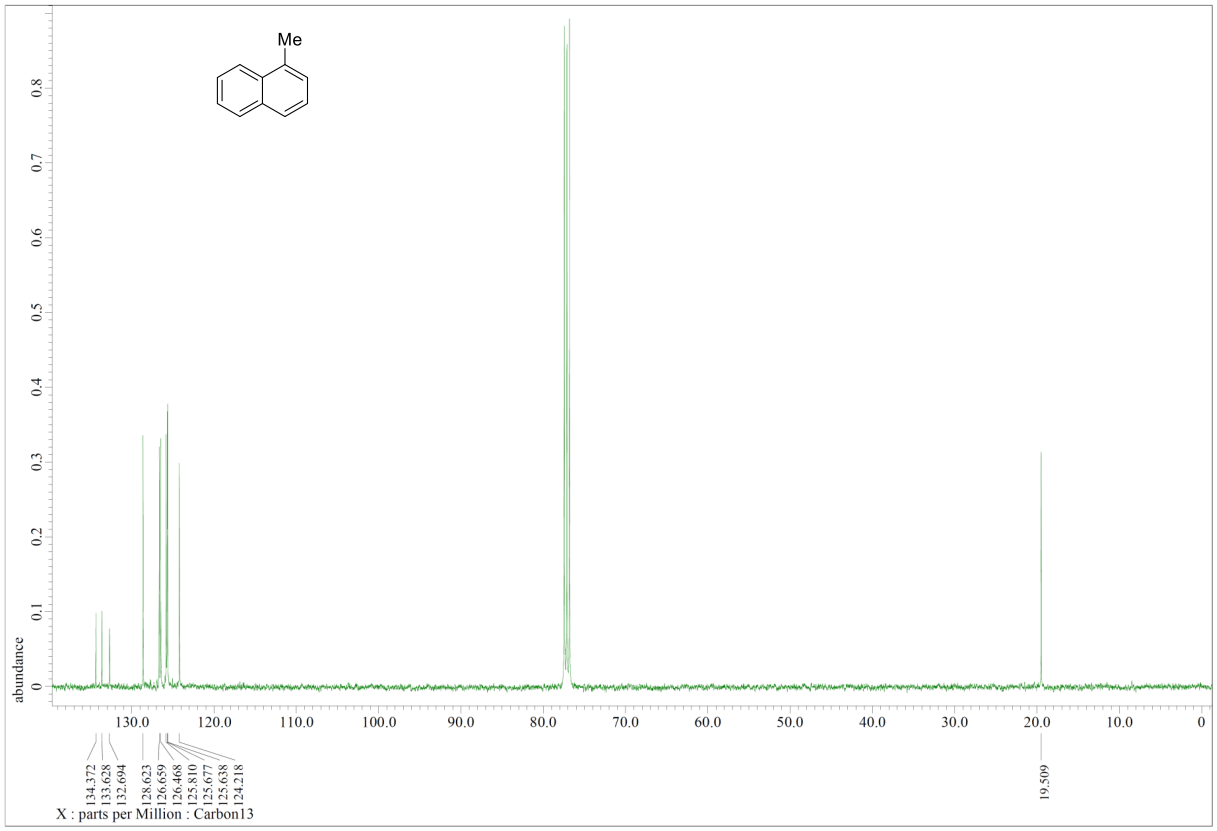

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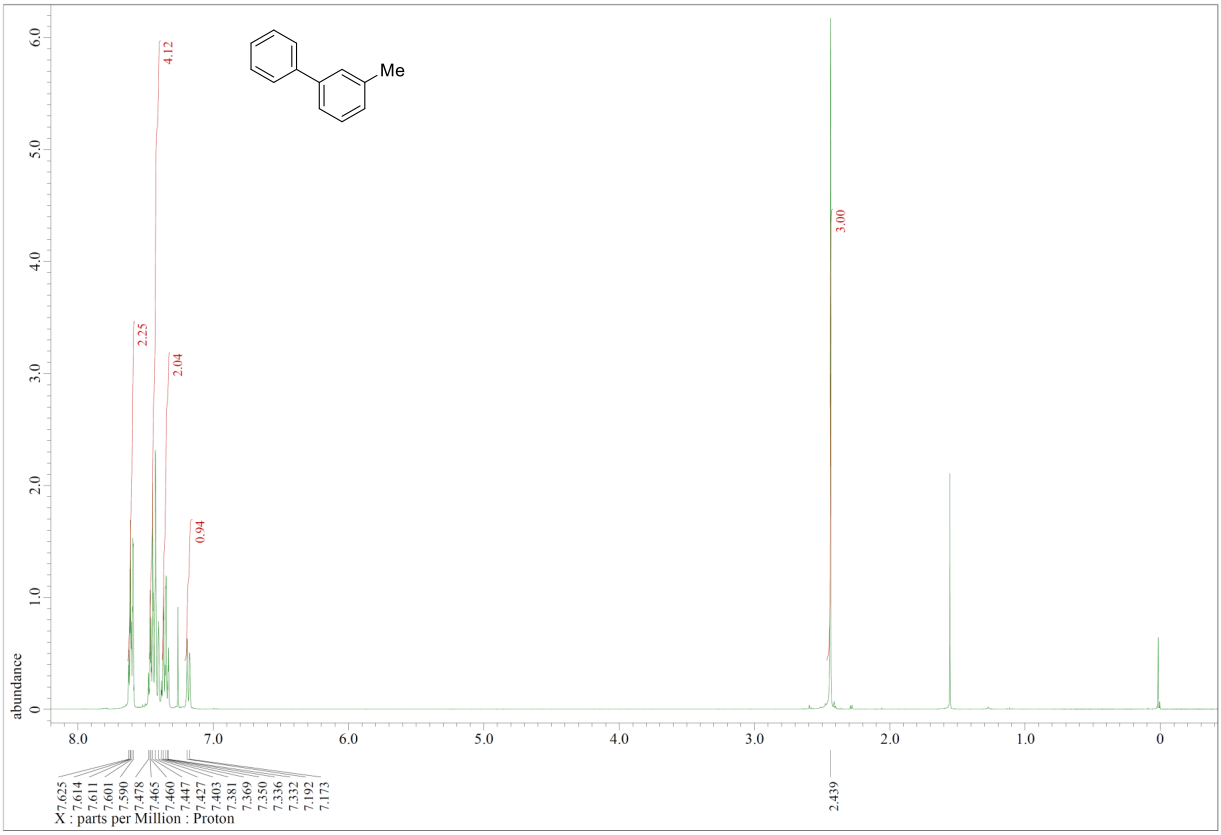

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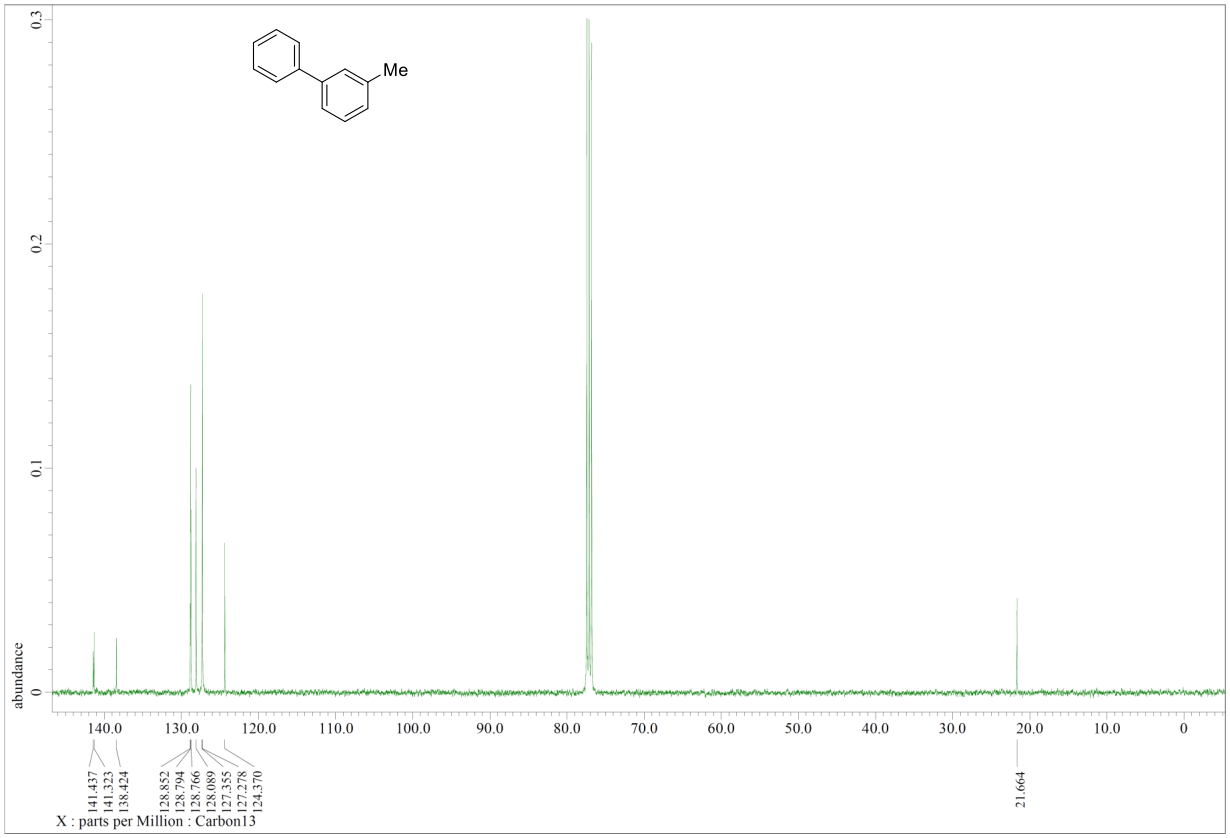

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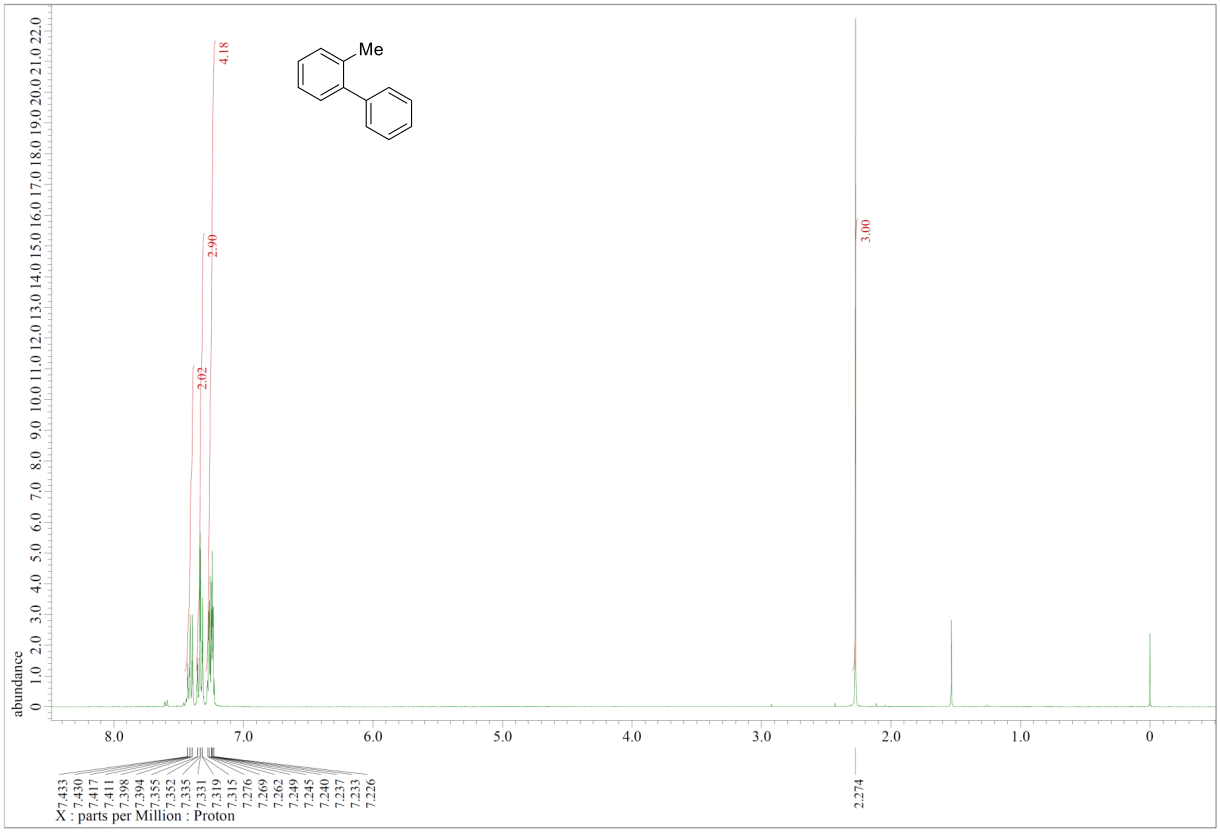

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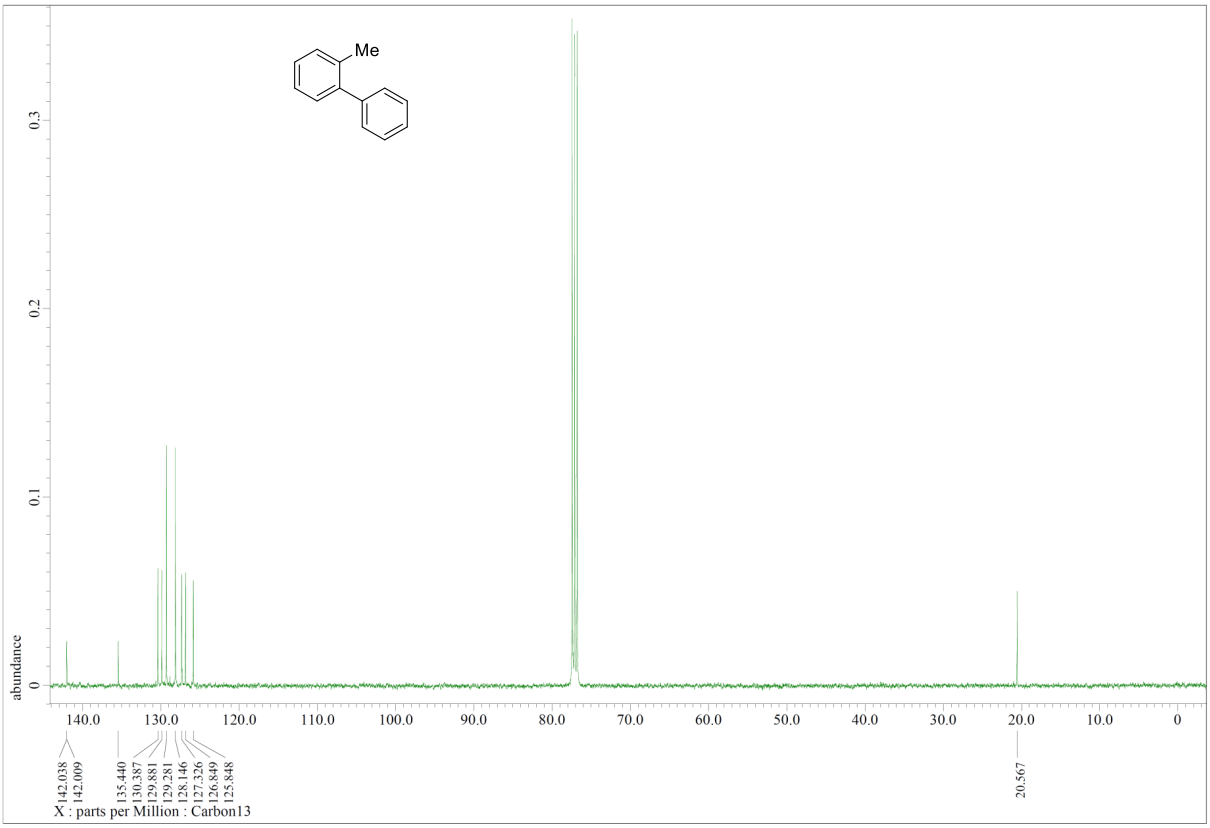

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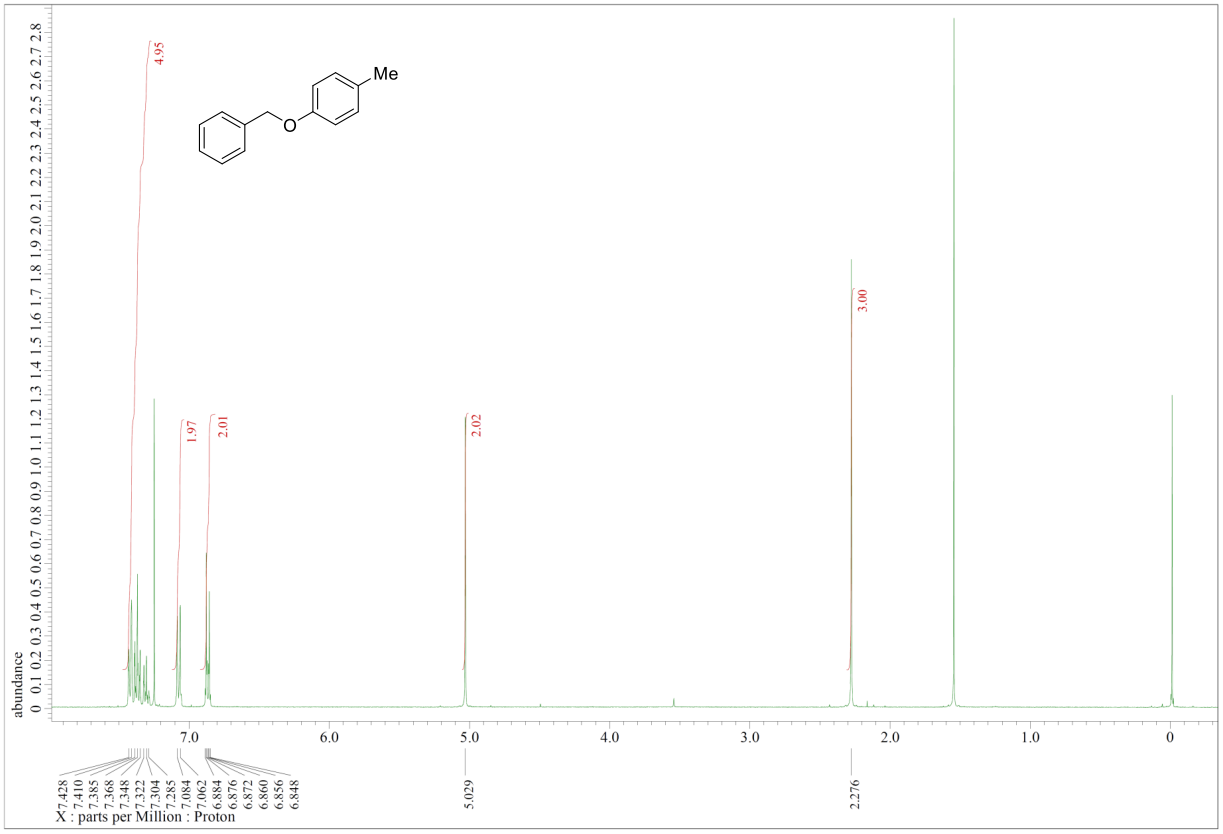

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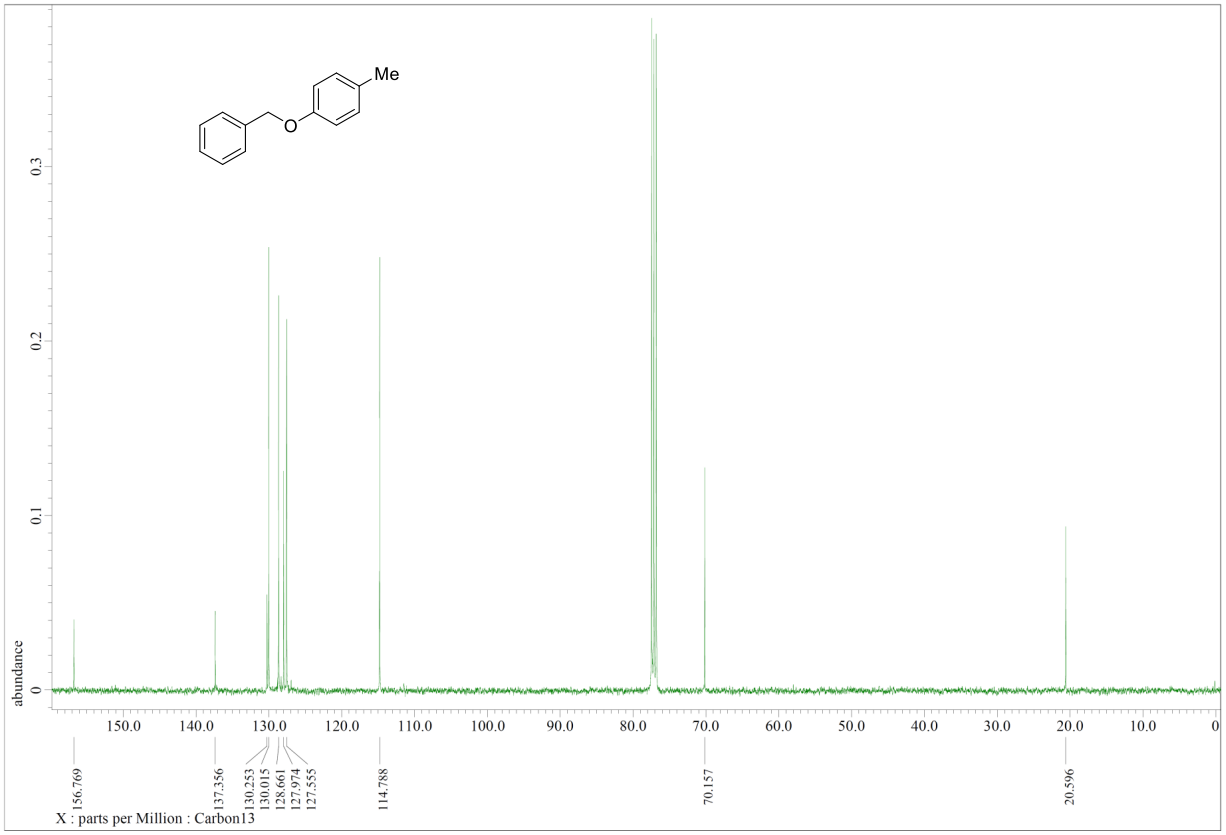

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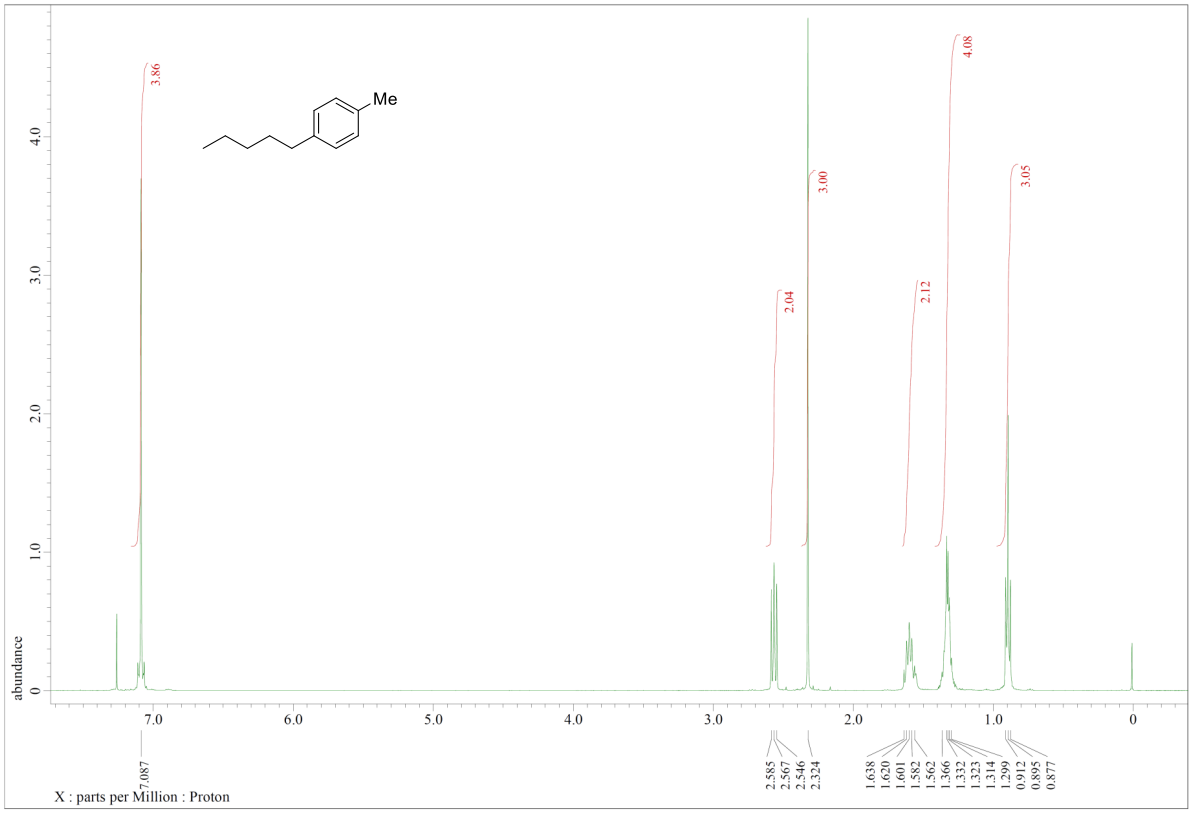

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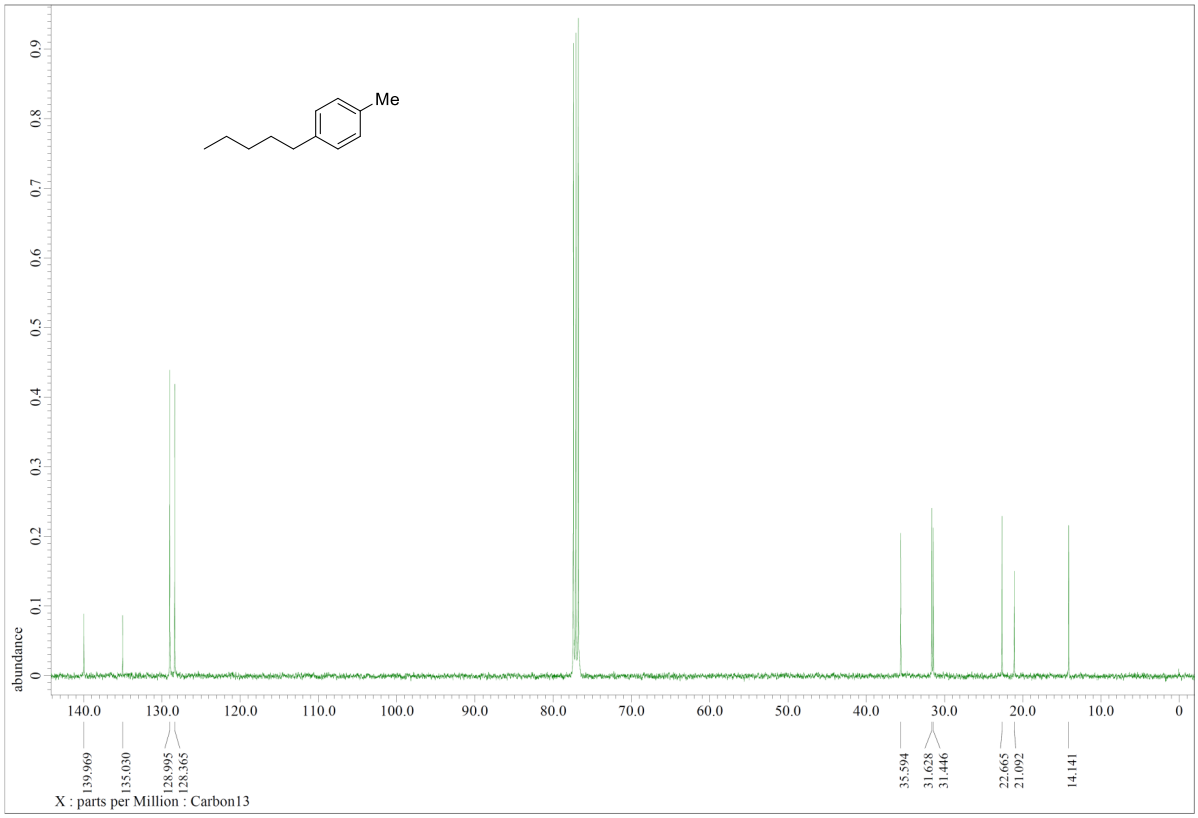

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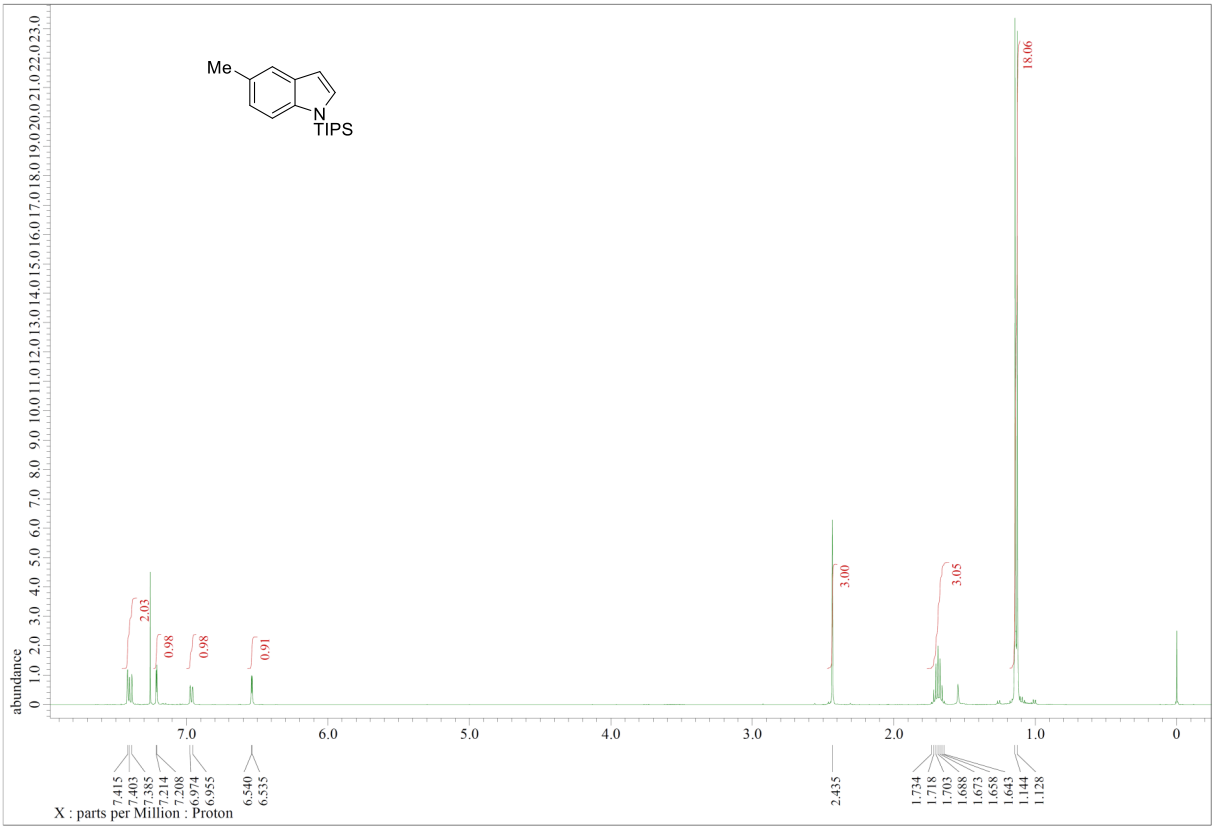

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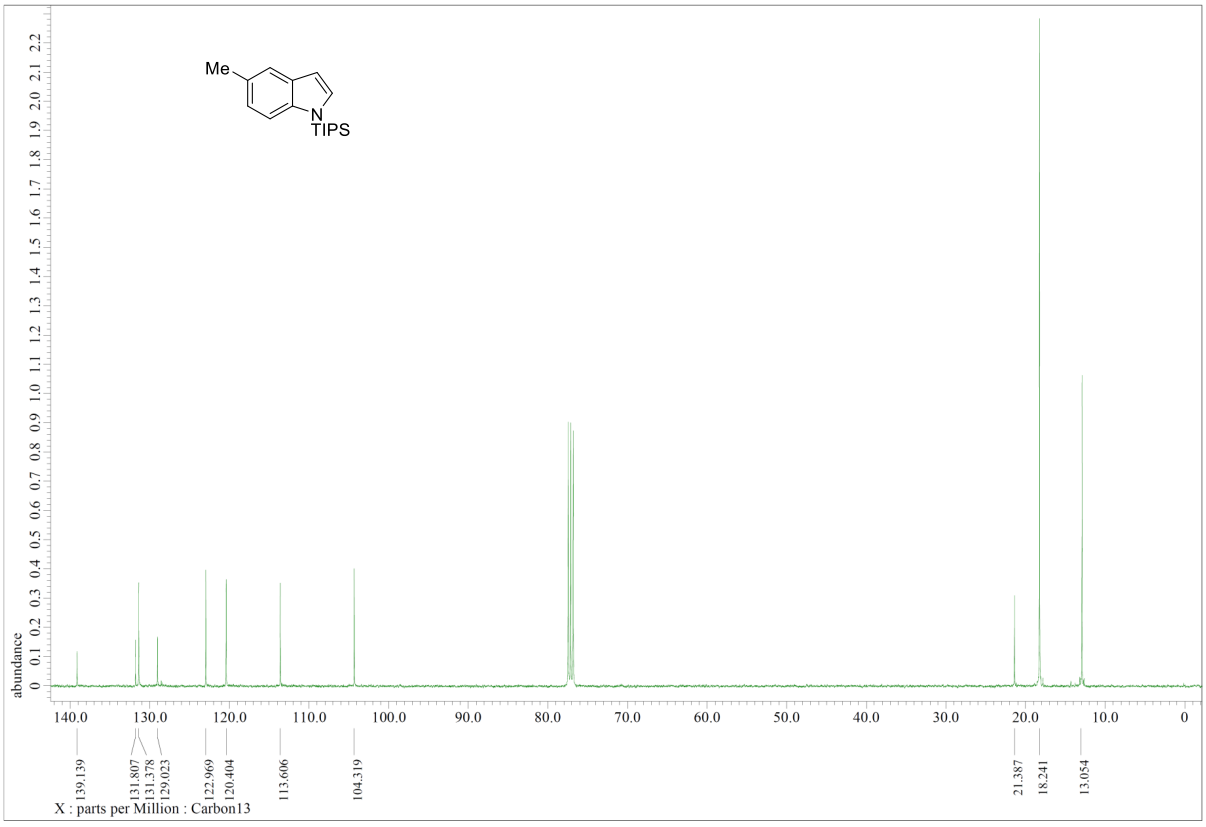

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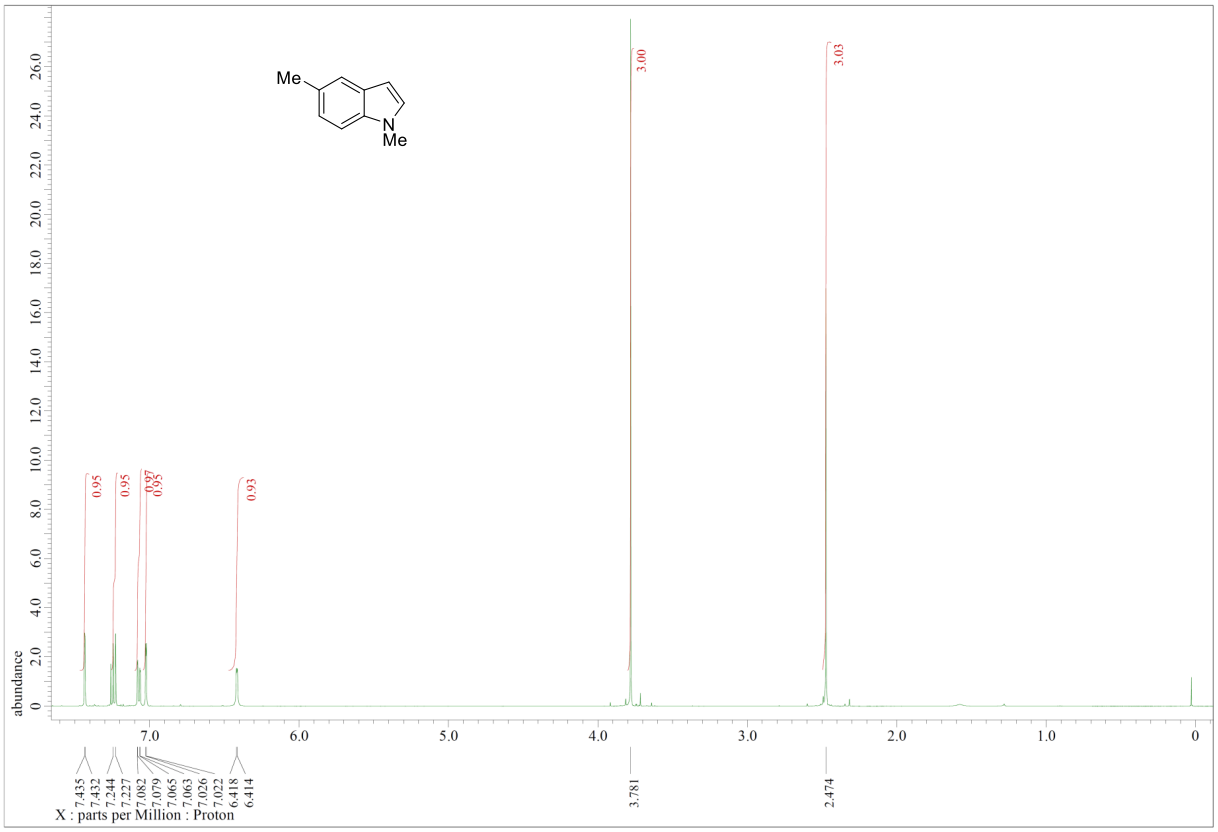

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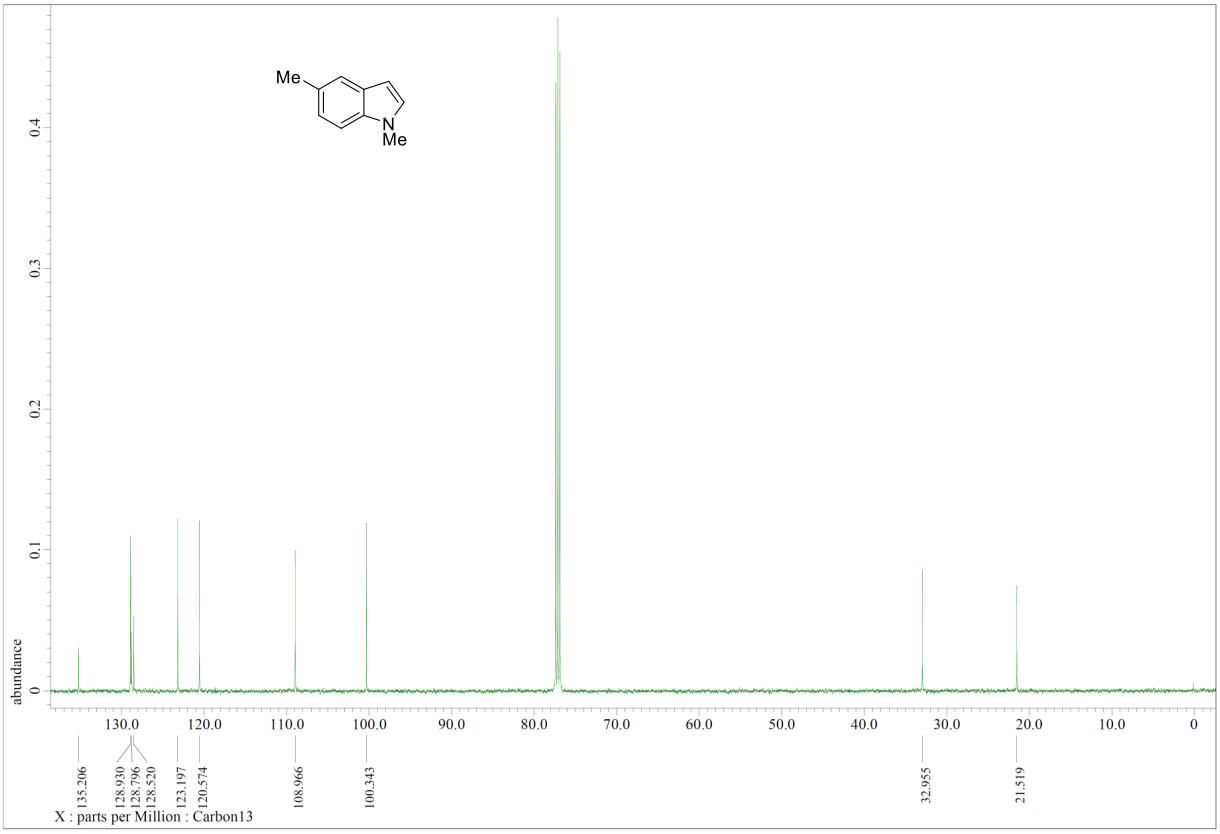

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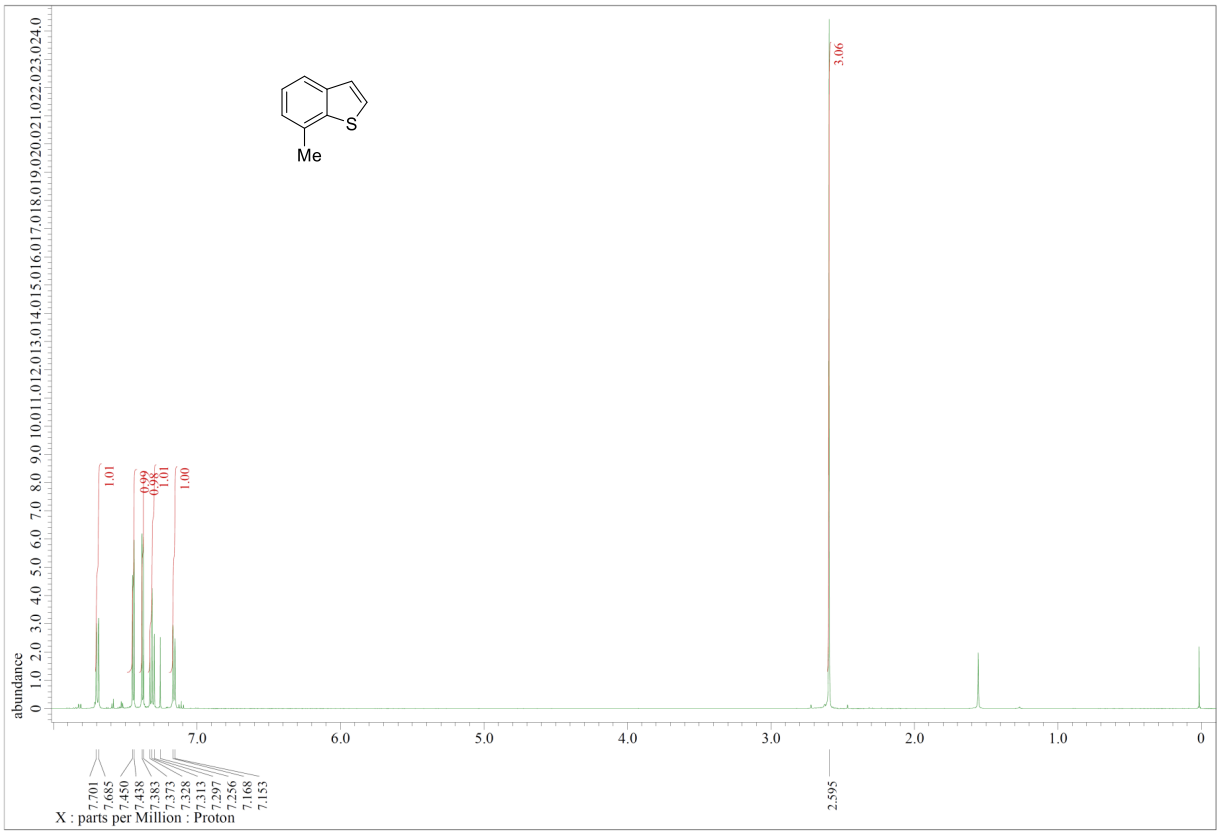

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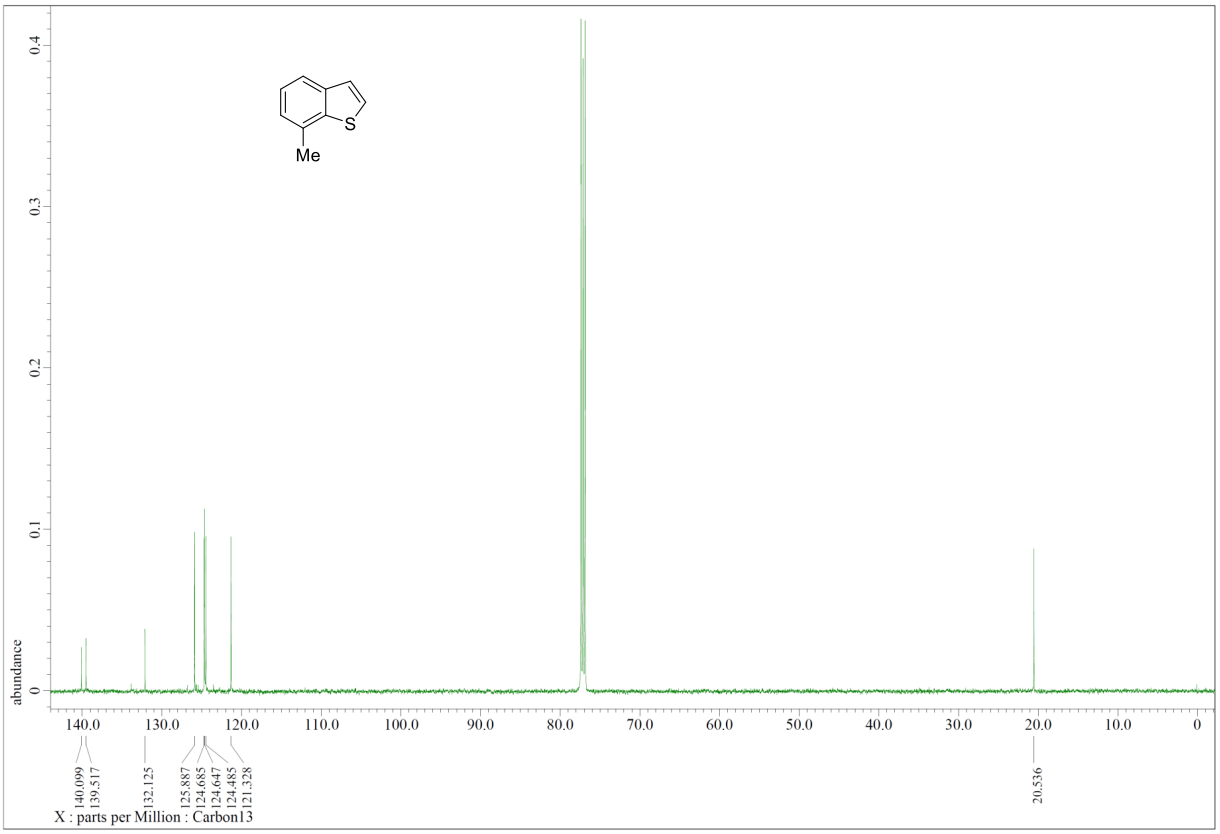

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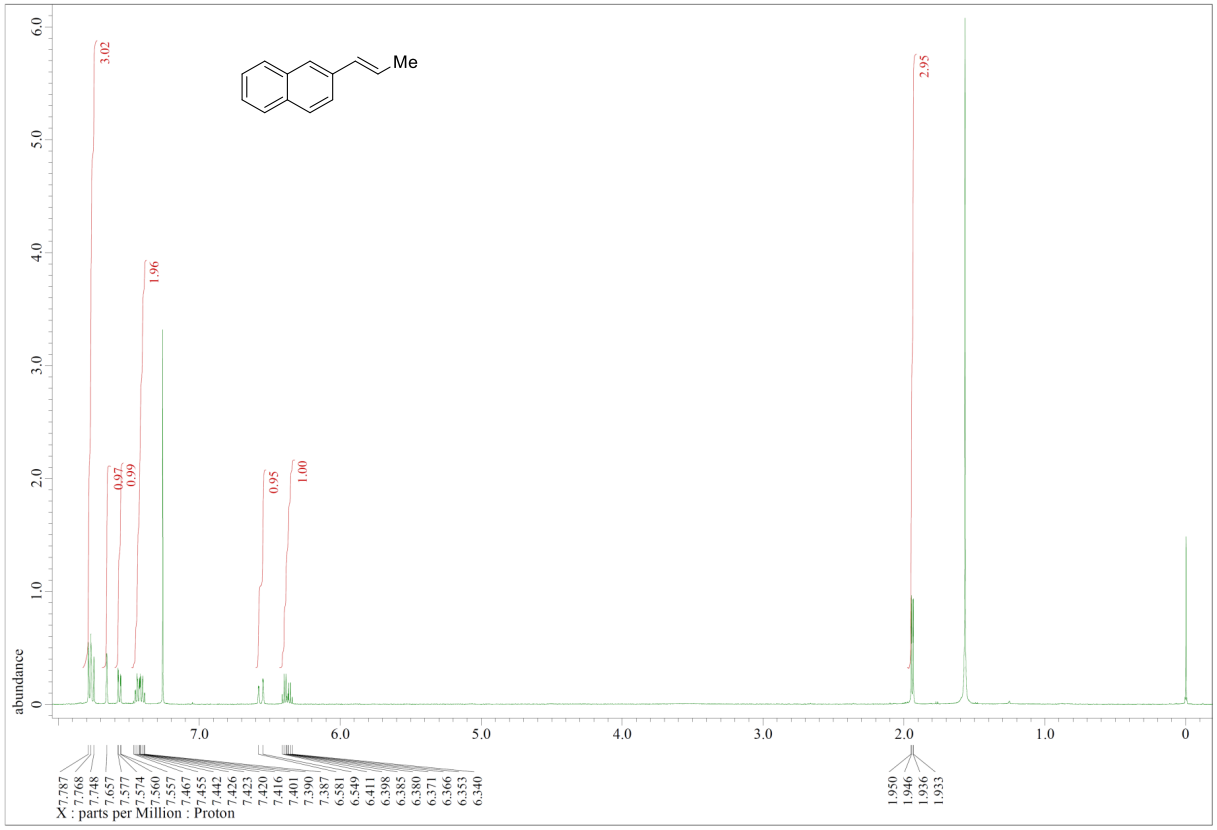

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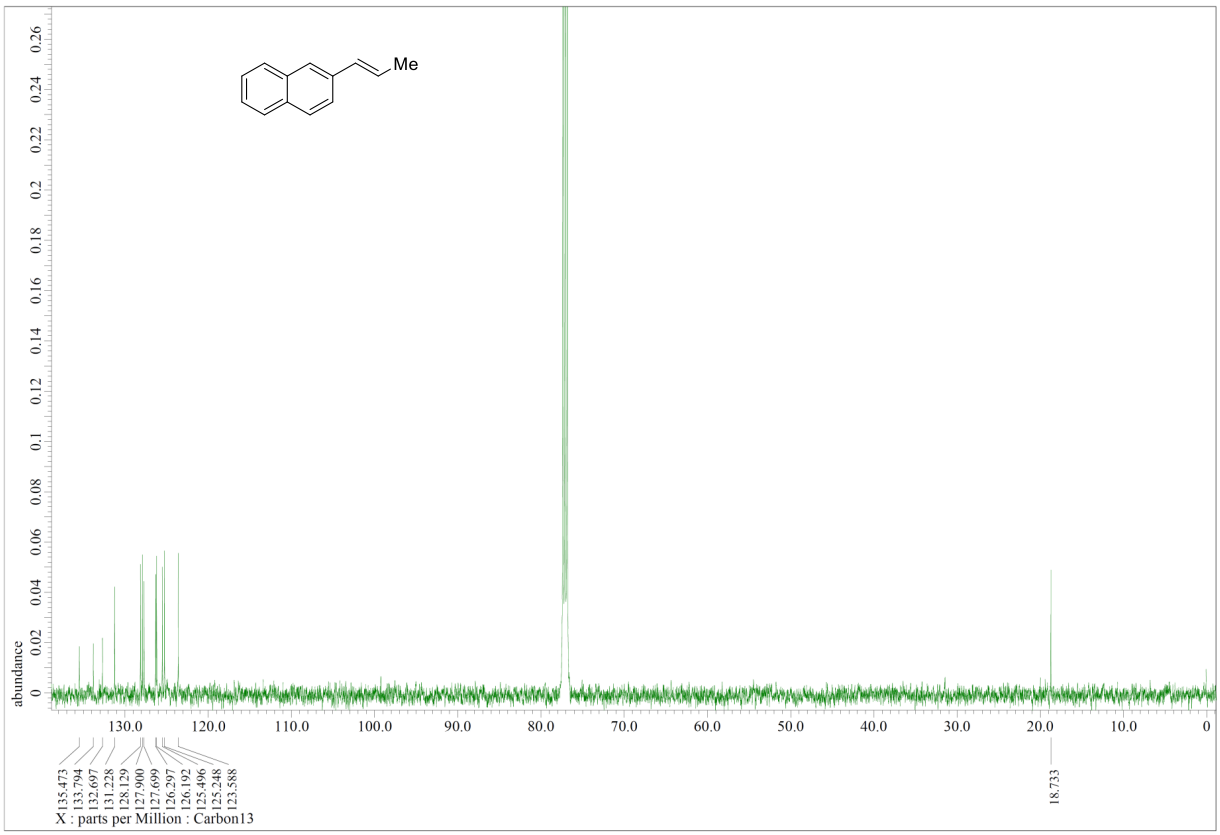

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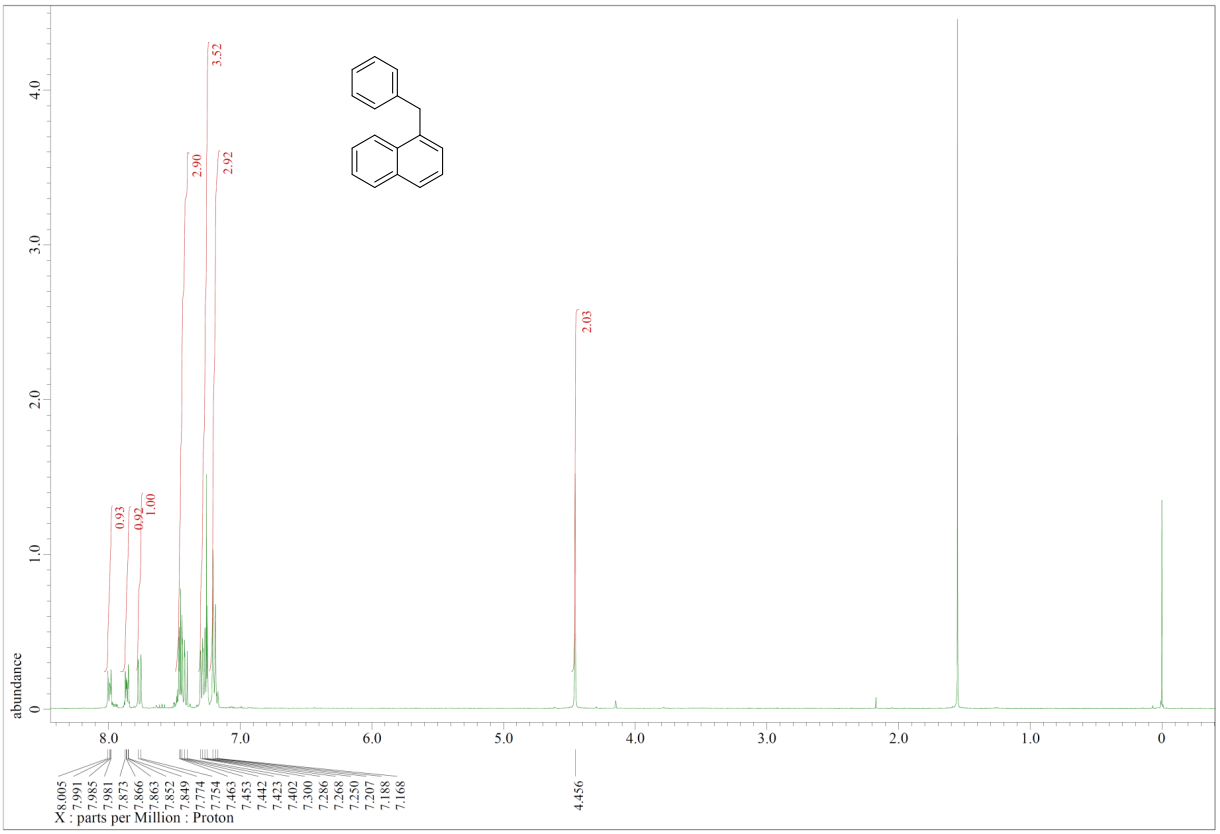

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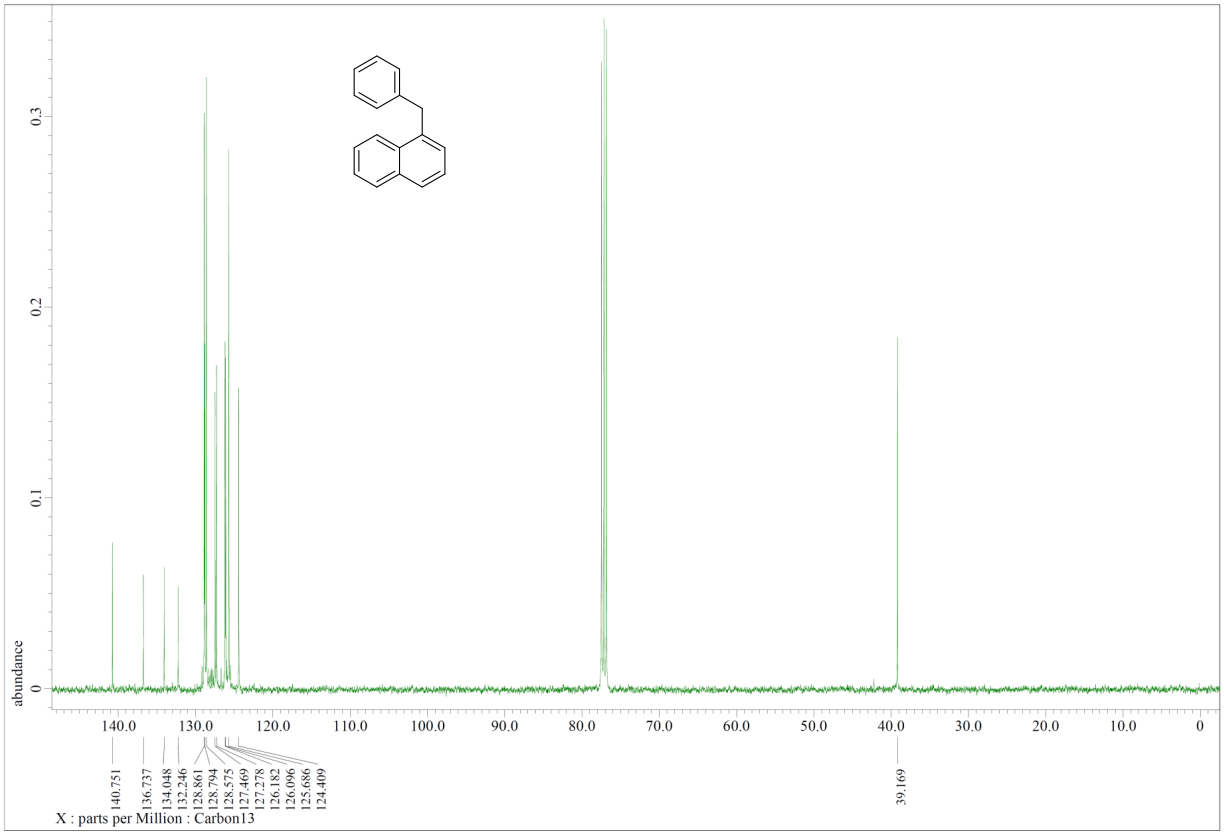

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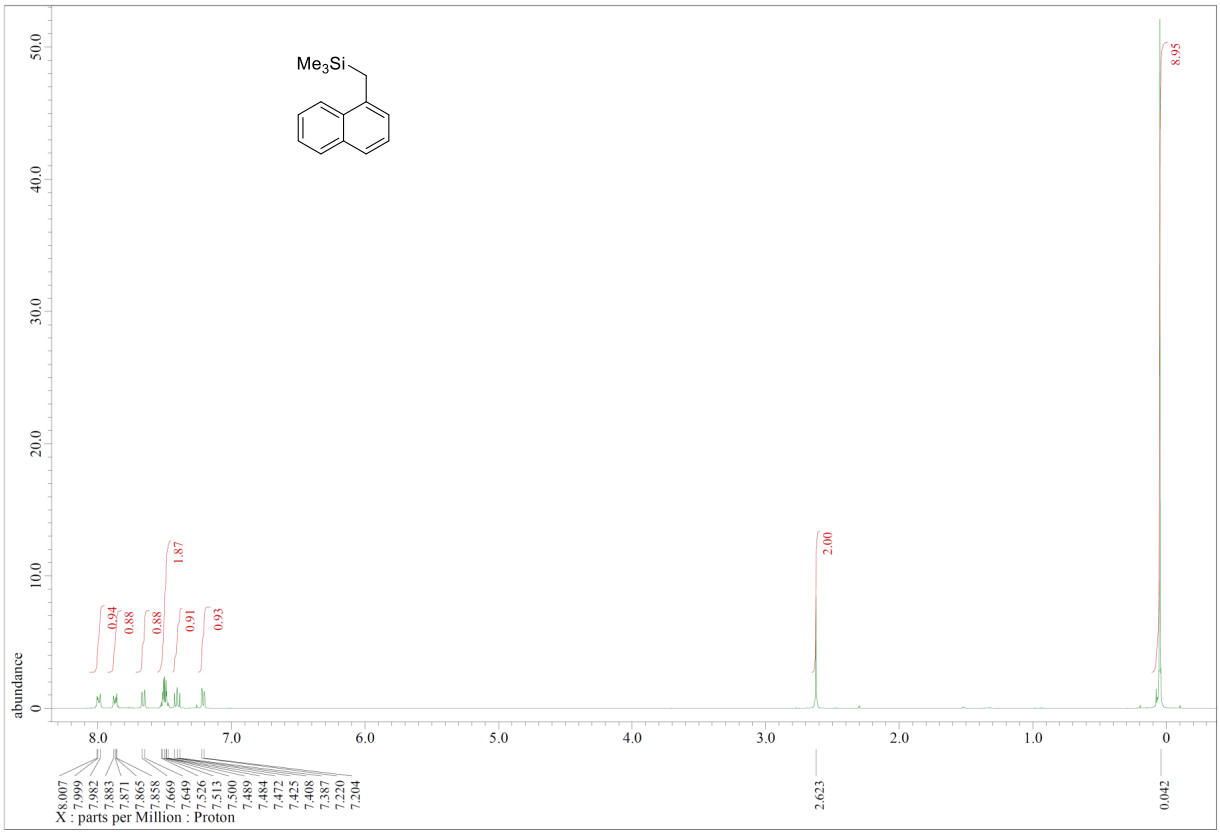

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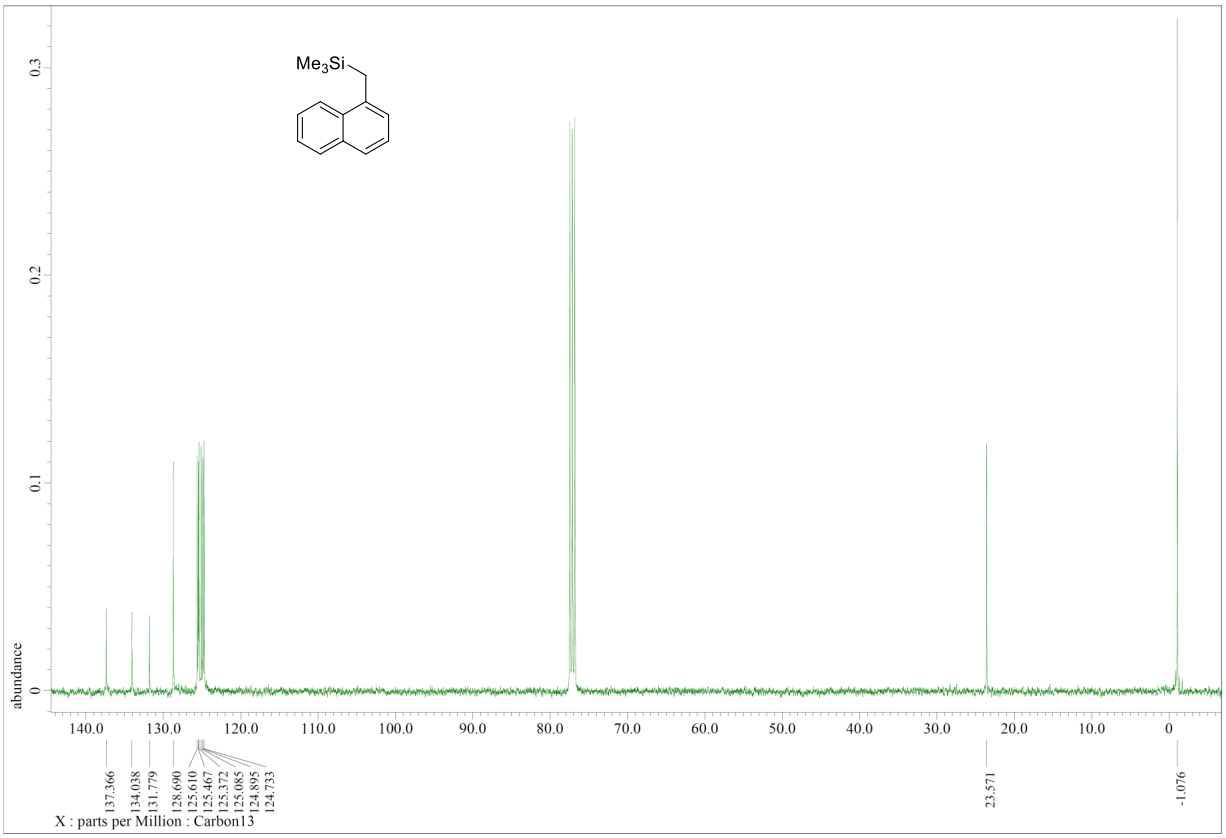

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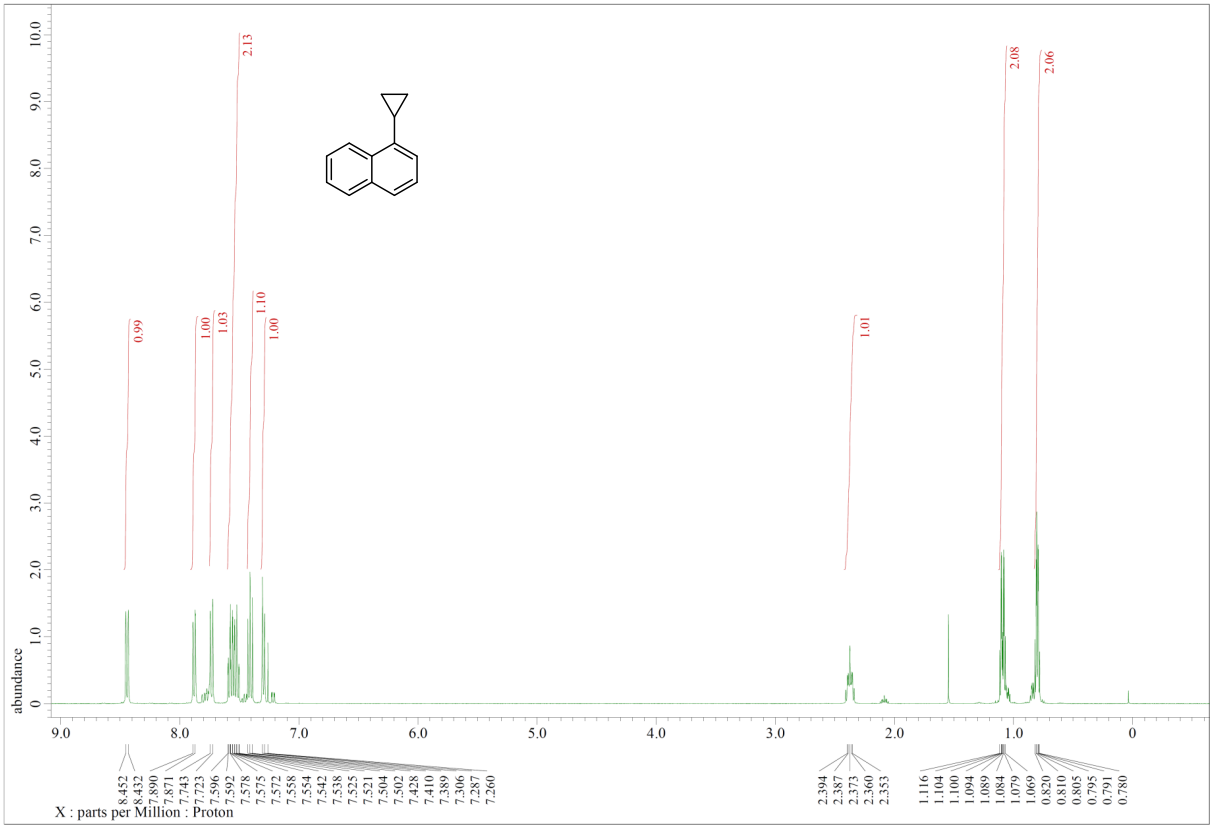

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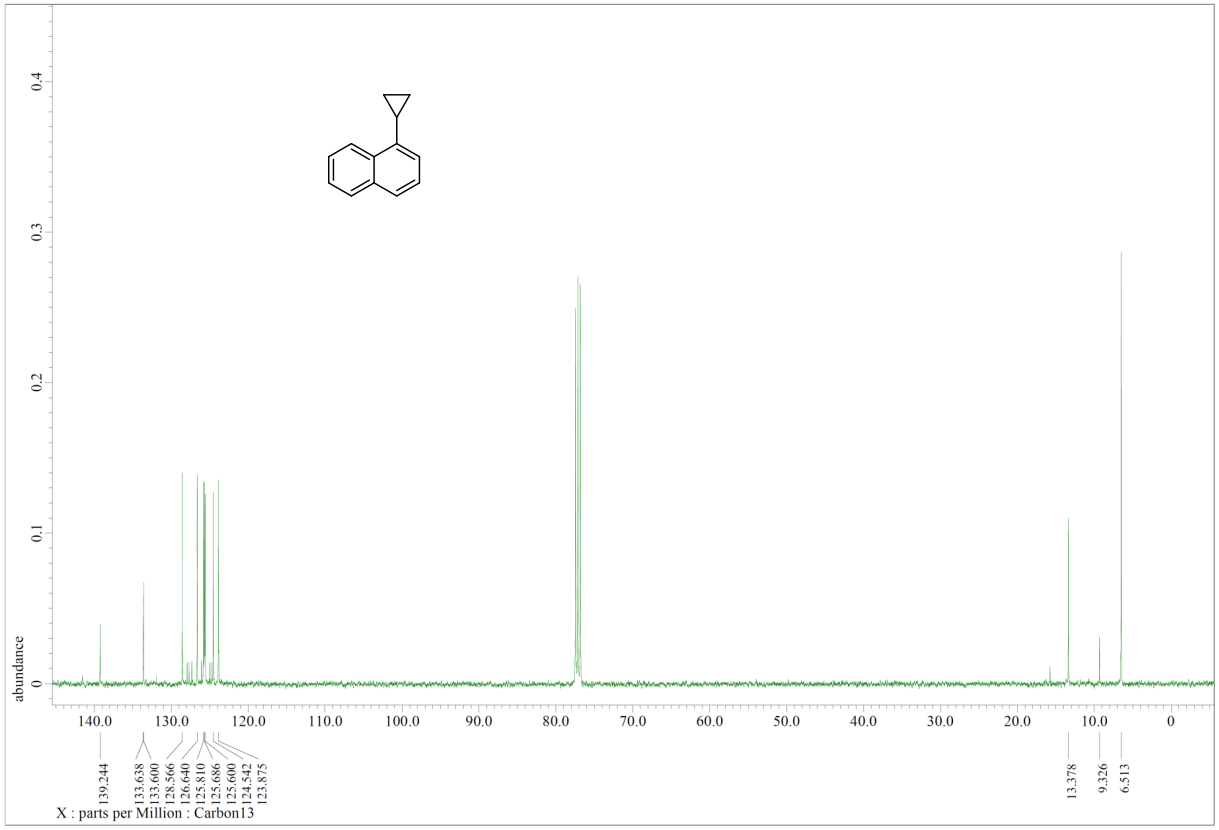

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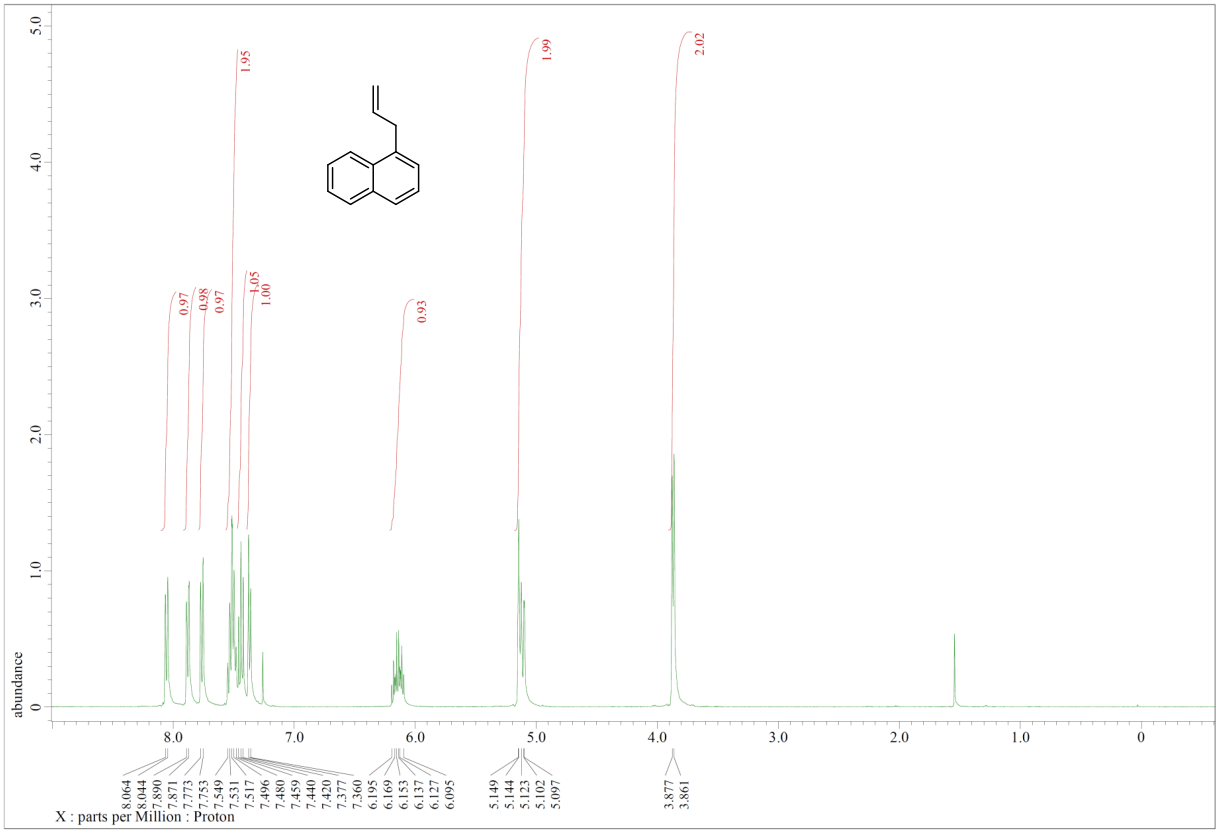

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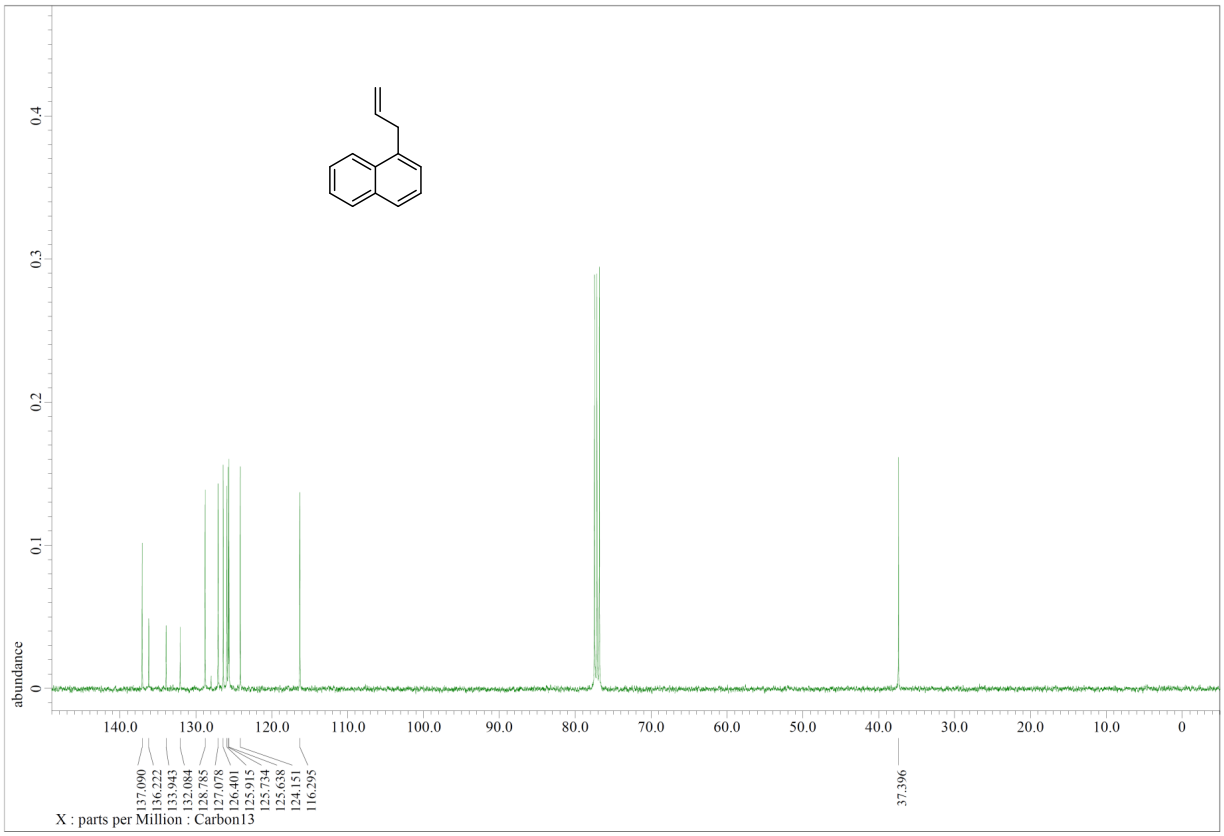

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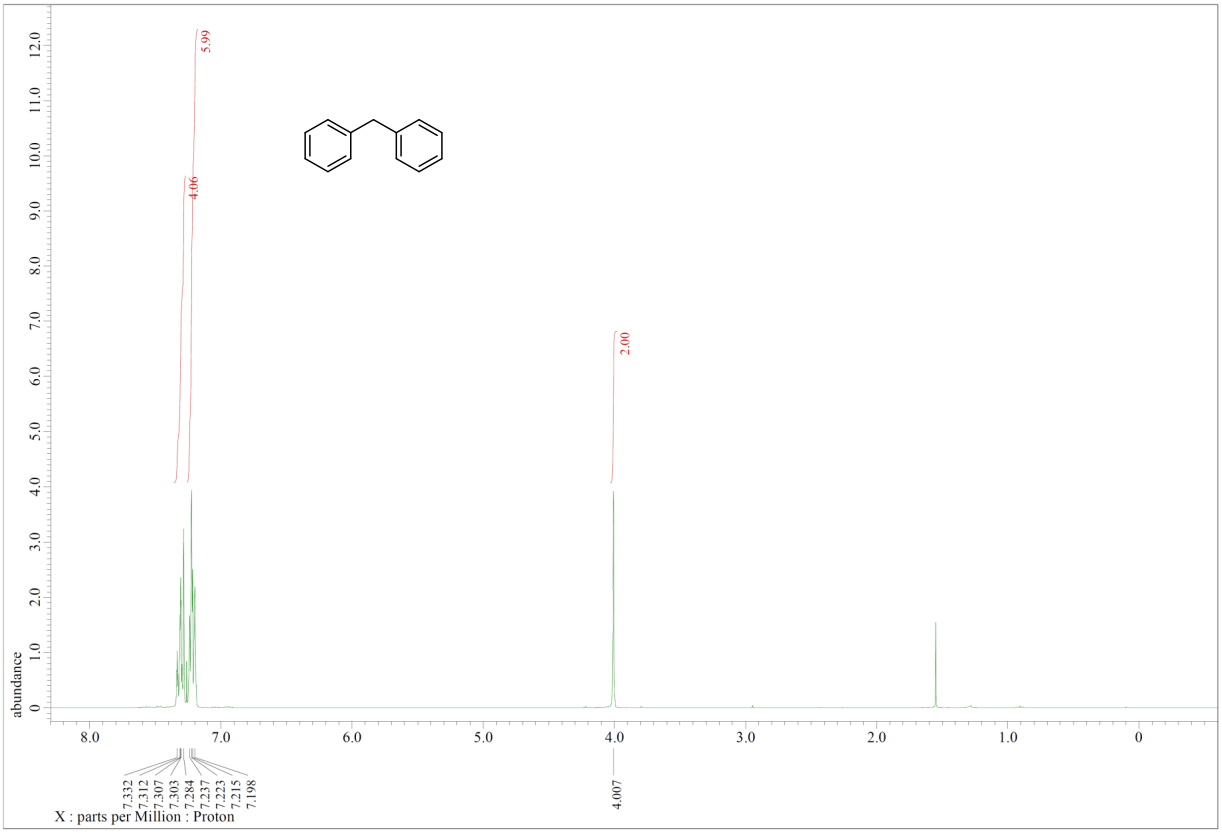

3q $CDCl_3$