

Supporting Information

Palladium-Catalyzed Silylation Reaction between Benzylic Halides and Silylboronate

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Table of Contents

1. General information	2
2. Procedure for the synthesis of Benzylic Halides 1a-1v	3
3. Procedure for the synthesis of benzylic silanes 2a-2v	5
4. Enantiopecific Pd-catalyzed silylation of secondary benzylic halides	12
5. References	16
6. NMR spectra for the products	17

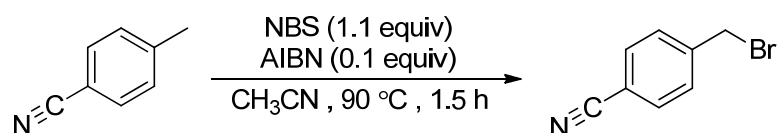
1. General information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^1H -NMR and ^{13}C -NMR spectra were recorded at 25 °C on Bruker Advance 400M NMR spectrometers (CDCl_3 as solvent). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 7.26 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and *etc.* Coupling constants are reported as a J value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 77.16 triplet). High-resolution EI mass spectra (HR-EI-MS) were recorded on a GCT CA127 Micronass UK mass Spectrometer. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

2. Procedure for the synthesis of benzylic halides 1a-1v

1a-1m were purchased from commercial suppliers and used without further purification, other benzylic halides were prepared following the procedure below and the analytical data of the products were consistent with the literature values.¹⁻⁷

2.1 Representative Procedure for the synthesis of benzylic halides 1n-1q, 1s



4-methylbenzonitrile (1.17 g, 10 mmol, 1.0 equiv) was dissolved in acetonitrile (20 mL) under N₂, NBS (1.96 g, 1.1 equiv) and AIBN (0.16 g, 0.1 equiv) were slowly added and the mixture was stirred for 1.5 h at 90 °C. After the reaction was completed, the solvent was removed in vacuo, following the residue was treated with toluene at 0 °C and the solution was filtrated. After removal of the solvent in vacuo, purification by silica gel column chromatography yielded the target products.

4-(bromomethyl)benzonitrile (1n)¹, yield 42%. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 4.48 (s, 2H).

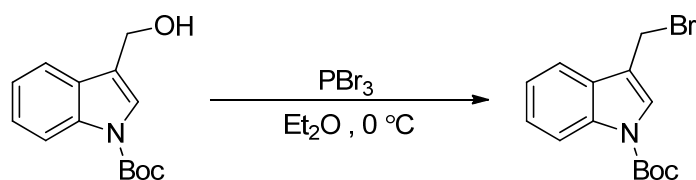
methyl 4-(bromomethyl)benzoate (1o)², yield 68%. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.3 Hz, 2 H), 7.46 (d, *J* = 8.3 Hz, 2 H), 4.50 (s, 2 H), 3.92 (s, 3 H).

1-(4-(bromomethyl)phenyl)ethanone (1p)¹, yield 85%. ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 4.50 (s, 2H), 2.60 (s, 3H).

4-(bromomethyl)phenyl acetate (1q)³, yield 48%. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 4.50 (s, 2H), 2.32 (s, 3H).

1-(bromomethyl)-4-(phenylethynyl)benzene (1s)⁴, yield 65%. ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.46 (m, 4H), 7.42 – 7.30 (m, 5H), 4.49 (s, 2H).

2.3 Representative Procedure for the synthesis of Benzylic Halides 1r, 1t



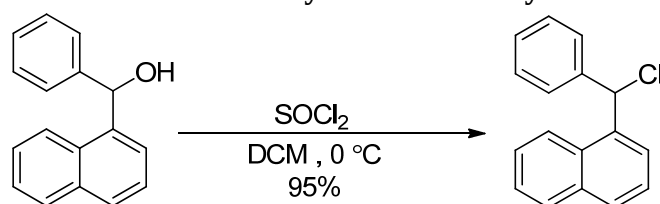
PBr₃ (0.35 equiv) was slowly added to a solution of the corresponding alcohol (5 mmol, 1.0 equiv) in Et₂O (20 mL) at 0 °C, and the mixture was stirred for 2 h at 0 °C. After the reaction was completed, the mixture was quenched with aqueous sodium bicarbonate slowly. The organic layer was extracted with Et₂O, washed with aqueous

sodium bicarbonate and brine. The combined organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure to give the target product which was used without further purification.

1-(bromomethyl)-4-vinylbenzene (1r), colorless liquid, yield 96%. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (q, *J* = 8.3 Hz, 4H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H), 4.49 (s, 2H).

tert-butyl-3-(bromomethyl)-1H-indole-1-carboxylate (1t)⁵, yield 94%. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (bs, 1H), 7.63-7.61 (m, 2H), 7.31-7.26 (m, 2H), 4.62 (s, 2H), 1.62 (s, 9H).

2.2 Representative Procedure for the synthesis of Benzylic Halides 1u, 1v

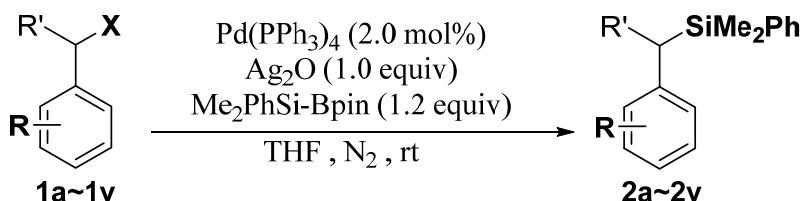


To a solution of the alcohol (10 mmol) in DCM (50 mL) at 0 °C, SOCl₂ (2 mL, 2.0 equiv) was slowly added, the mixture was stirred for 2 h at 0 °C. After the reaction was completed, the diluted aqueous sodium bicarbonate was slowly added to quench the reaction, after that Et₂O (50 ml) was added, the mixture was washed with diluted aqueous sodium bicarbonate for several times until the pH of the aqueous layer was larger than 7. Then the organic layer was washed with brine and dried over Na₂SO₄, filtered and concentrated under reduced pressure to give the target products as yellowish or white solid, which was used without further purification.

1-(chloro(phenyl)methyl)naphthalene (1u)⁶, yield 95%. ¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.01 (m, 1H), 7.93 – 7.87 (m, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.55 – 7.41 (m, 5H), 7.41 – 7.24 (m, 3H), 6.57 (s, 1H).

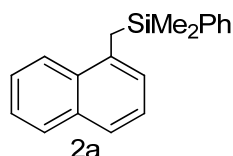
2-(chloro(phenyl)methyl)naphthalene (1v)⁷, yield 92%. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (m, 4H), 7.40 (m, 5H), 7.32 – 7.16 (m, 3H), 6.21 (s, 1H).

3. Procedure for the synthesis of benzylicsilanes 2a-2v

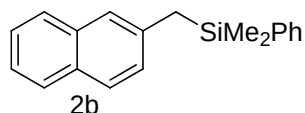


A dry 25-mL Schlenk tube containing a magnetic stirring bar was charged with compound **1** (0.3 mmol, if compound **1** was solid), Pd(PPh₃)₄ (2.0 mol%, 6.9 mg, 0.006 mmol), Ag₂O (1.0 equiv, 69.5 mg, 0.3 mmol), which was evacuated and backfilled with N₂. Then, the solvent THF (2 mL) was added into this mixture under N₂. After that, compound **1** (0.3 mmol, if compound **1** was liquid), Ph(Me)₂SiB(pin) (94.4 mg, 0.36 mmol, 1.2 equiv) was added under N₂. The reaction was stirred at room temperature for 24 or 36 h. After the reaction was completed, the mixture was diluted with dichloromethane and filtered through a pad of Celite. The Celite bed was washed with 3×5 mL dichloromethane. The organic layer was concentrated in vacuo. Purification by silica gel column chromatography afforded the target product.

Characterization Data for benzylicsilanes 2a-2v

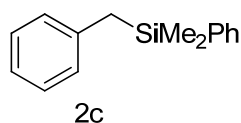


dimethyl(naphthalen-1-ylmethyl)(phenyl)silane (2a). White solid, yield 85%. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.51 – 7.33 (m, 6H), 7.15 (d, *J* = 7.0 Hz, 1H), 2.84 (s, 2H), 0.27 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 138.87, 136.54, 134.05, 133.79, 131.88, 129.23, 128.69, 127.91, 125.84, 125.58, 125.40, 125.13, 125.01, 124.84, 22.85, -2.74. HRMS (EI) calculated for C₁₉H₂₀Si: 276.1334, found: 276.1335. ²⁹Si NMR (79 MHz, CDCl₃) δ (ppm): -2.92.

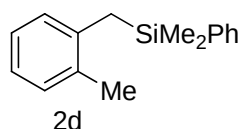


dimethyl(naphthalen-2-ylmethyl)(phenyl)silane (2b). White solid, yield 72%. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.71 (t, *J* = 7.2 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.47 – 7.35 (m, 6H), 7.11 (dd, *J* = 8.4, 1.5 Hz, 1H), 2.51 (s, 2H), 0.31 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 138.57, 137.57, 133.90, 133.88, 131.22, 129.25, 128.14, 127.90, 127.70, 127.62, 127.16, 125.88, 125.73, 124.56, 26.65, -3.26. HRMS

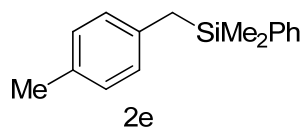
(EI) calculated for $C_{19}H_{20}Si$: 276.1334, found: 276.1330. ^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm): -3.52.



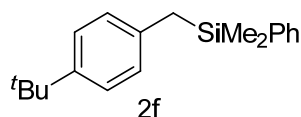
benzyldimethyl(phenyl)silane (2c). Colorless oil, yield 81%. 1H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.44 – 7.35 (m, 3H), 7.22 (t, J = 7.6 Hz, 2H), 7.10 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 7.6 Hz, 2H), 2.35 (s, 2H), 0.29 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.79, 138.61, 133.84, 129.18, 128.44, 128.24, 127.86, 124.21, 26.31, -3.33. HRMS (EI) calculated for $C_{15}H_{18}Si$: 226.1178, found: 226.1180. ^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm): -3.74.



dimethyl(2-methylbenzyl)(phenyl)silane (2d). Colorless oil, yield 62%. 1H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H), 7.44 – 7.31 (m, 3H), 7.15 – 6.99 (m, 3H), 6.98 – 6.89 (m, 1H), 2.34 (s, 2H), 2.11 (s, 3H), 0.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.92, 138.24, 135.02, 133.76, 130.24, 129.20, 129.05, 127.87, 125.71, 124.41, 23.16, 20.34, -2.94. HRMS (EI) calculated for $C_{16}H_{20}Si$: 240.1334, found: 240.1332. ^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm): -3.69.

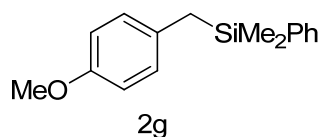


dimethyl(4-methylbenzyl)(phenyl)silane (2e). Colorless oil, yield 79%. 1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.43 – 7.38 (m, 3H), 7.05 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 2.32 (s, 2H), 0.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.82, 136.46, 133.85, 133.49, 129.13, 128.96, 128.34, 127.85, 25.64, 21.05, -3.30. HRMS (EI) calculated for $C_{16}H_{20}Si$: 240.1334, found: 240.1333. ^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm): -3.98.

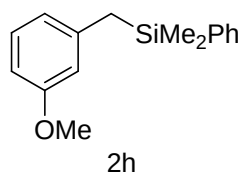


(4-(tert-butyl)benzyl)dimethyl(phenyl)silane (2f). White solid, yield 81%. 1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 2H), 7.45 – 7.40 (m, 3H), 7.29 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 2.36 (s, 2H), 1.38 (s, 9H), 0.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.95, 137.93, 135.48, 132.85, 128.11, 127.14, 126.84, 124.12,

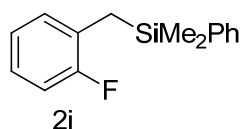
76.48, 76.16, 75.84, 33.35, 30.62, 24.51, -4.18. HRMS (EI) calculated for $C_{19}H_{26}Si$: 282.1804, found: 282.1806. ^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm): -3.89.



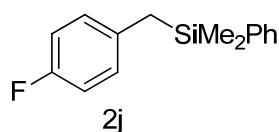
(4-methoxybenzyl)dimethyl(phenyl)silane (2g). White solid, yield 59%. 1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.39 – 7.32 (m, 3H), 6.85 (d, J = 8.7 Hz, 2H), 6.75 (d, J = 8.7 Hz, 2H), 3.77 (s, 3H), 2.24 (s, 2H), 0.24 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.79, 138.79, 133.86, 131.61, 129.24, 129.13, 127.84, 113.78, 55.37, 24.95, -3.32. HRMS (EI) calculated for $C_{16}H_{20}OSi$: 256.1283, found: 256.1280. ^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm): -3.99.



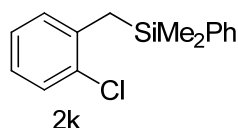
(3-methoxybenzyl)dimethyl(phenyl)silane (2h). Colorless oil, yield 70%. 1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 2H), 7.44 – 7.33 (m, 3H), 7.13 (t, J = 7.9 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 6.48 (s, 1H), 3.72 (s, 3H), 2.32 (s, 2H), 0.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.53, 141.41, 138.59, 133.86, 129.18, 129.11, 127.85, 121.02, 113.93, 109.88, 55.09, 26.49, -3.31. HRMS (EI) calculated for $C_{16}H_{20}OSi$: 256.1283, found: 256.1285. ^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm): -3.69.



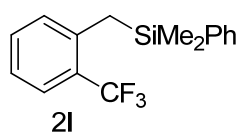
(2-fluorobenzyl)dimethyl(phenyl)silane (2i). Colorless oil, yield 63%. 1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.43 – 7.34 (m, 3H), 7.13 – 7.03 (m, 1H), 7.03 – 6.85 (m, 3H), 2.34 (s, 2H), 0.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.48 (d, J_{CF} = 242.9 Hz), 138.41, 133.76, 130.65 (d, J_{CF} = 5.0 Hz), 129.26, 127.89, 127.01 (d, J_{CF} = 16.7 Hz), 125.81 (d, J_{CF} = 7.8 Hz), 123.79 (d, J_{CF} = 3.5 Hz), 115.14 (d, J_{CF} = 22.4 Hz), 18.84 (d, J_{CF} = 2.2 Hz), -3.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.07. HRMS (EI) calculated for $C_{15}H_{17}FSi$: 244.1084, found: 244.1086. ^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm): -3.06.



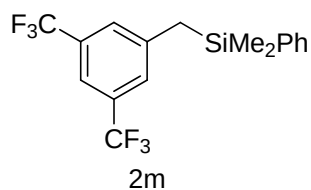
(4-fluorobenzyl)dimethyl(phenyl)silane (2j). White solid, yield 87%. ^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.42 (m, 2H), 7.42 – 7.31 (m, 3H), 6.98 – 6.78 (m, 4H), 2.30 (s, 2H), 0.28 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.51 (d, $J_{\text{CF}} = 241.4$ Hz), 138.26, 135.26 (d, $J_{\text{CF}} = 3.0$ Hz), 133.84, 129.47 (d, $J_{\text{CF}} = 7.5$ Hz), 129.27, 127.90, 114.95 (d, $J_{\text{CF}} = 21.1$ Hz), 25.39, -3.42. ^{19}F NMR (376 MHz, CDCl_3) δ -120.06. HRMS (EI) calculated for $\text{C}_{15}\text{H}_{17}\text{FSi}$: 244.1084, found: 244.1083. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -3.74.



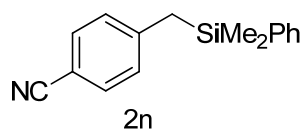
(2-chlorobenzyl)dimethyl(phenyl)silane (2k). Colorless oil, yield 72%. ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.50 (m, 2H), 7.44 – 7.37 (m, 3H), 7.37 – 7.32 (m, 1H), 7.14 – 7.01 (m, 2H), 7.01 – 6.93 (m, 1H), 2.55 (s, 2H), 0.34 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.53, 138.22, 133.79, 133.01, 130.13, 129.52, 129.27, 127.91, 126.50, 125.65, 23.71, -3.01. HRMS (EI) calculated for $\text{C}_{15}\text{H}_{17}\text{ClSi}$: 260.0788, found: 260.0786. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -2.65.



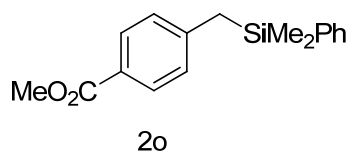
dimethyl(phenyl)(2-(trifluoromethyl)benzyl)silane (2l). Colorless oil, yield 82%. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 7.8$ Hz, 1H), 7.56 – 7.50 (m, 2H), 7.43 – 7.36 (m, 3H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.18 (t, $J = 7.6$ Hz, 1H), 7.00 (d, $J = 7.8$ Hz, 1H), 2.57 (s, 2H), 0.28 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.43 (q, $J_{\text{CF}} = 1.7$ Hz), 138.54, 133.82, 131.32, 130.80, 129.34, 128.00, 127.51 (q, $J_{\text{CF}} = 29.1$ Hz), 126.24 (q, $J_{\text{CF}} = 5.7$ Hz), 124.86 (q, $J_{\text{CF}} = 273.5$ Hz), 124.34, 23.11 (q, $J_{\text{CF}} = 1.7$ Hz), -3.01. ^{19}F NMR (376 MHz, CDCl_3) δ -59.51. HRMS (EI) calculated for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{Si}$: 294.1052, found: 294.1048. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -2.57.



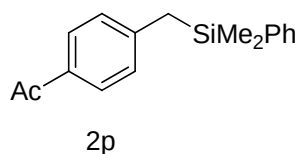
(3,5-bis(trifluoromethyl)benzyl)dimethyl(phenyl)silane (2m). Colorless oil, yield 49%. ^1H NMR (400 MHz, CDCl_3) δ 7.57 (s, 1H), 7.44 – 7.31 (m, 5H), 7.25 (bs, 2H), 2.42 (s, 2H), 0.30 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.67, 136.59, 133.74, 131.27 (q, $J_{\text{CF}} = 32.9$ Hz), 129.76, 128.17 (m), 128.11, 123.59 (q, $J_{\text{CF}} = 272.6$ Hz), 118.17 (m, $J_{\text{CF}} = 4.0$ Hz), 27.17, -3.77. ^{19}F NMR (376 MHz, CDCl_3) δ -63.03. HRMS (EI) calculated for $\text{C}_{17}\text{H}_{16}\text{F}_6\text{Si}$: 362.0925, found: 362.0927. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -2.86.



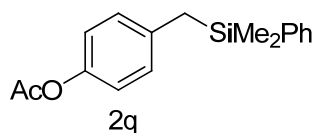
4-((dimethyl(phenyl)silyl)methyl)benzonitrile (2n). White solid, yield 51%. ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 8.3$ Hz, 2H), 7.42 – 7.32 (m, 5H), 6.96 (d, $J = 8.3$ Hz, 2H), 2.38 (s, 2H), 0.28 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.36, 137.19, 133.75, 132.02, 129.57, 128.89, 128.01, 119.54, 107.86, 27.76, -3.50. HRMS (EI) calculated for $\text{C}_{16}\text{H}_{17}\text{NSi}$: 251.1130, found: 251.1127. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -3.01.



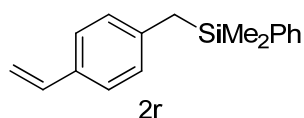
methyl 4-((dimethyl(phenyl)silyl)methyl)benzoate (2o). White solid, yield 73%. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.3$ Hz, 2H), 7.48 – 7.40 (m, 2H), 7.40 – 7.32 (m, 3H), 6.97 (d, $J = 8.4$ Hz, 2H), 3.89 (s, 3H), 2.38 (s, 2H), 0.27 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.45, 146.09, 137.80, 133.79, 129.64, 129.39, 128.26, 127.94, 126.25, 51.97, 27.28, -3.42. HRMS (EI) calculated for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Si}$: 284.1233, found: 284.1231. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -3.33.



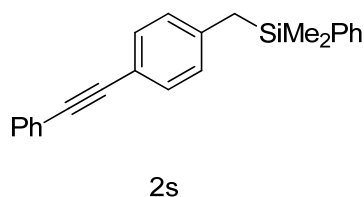
1-(4-((dimethyl(phenyl)silyl)methyl)phenyl)ethanone(2p). White solid, yield 70%. ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.73 (m, 2H), 7.47 – 7.42 (m, 2H), 7.41 – 7.32 (m, 3H), 6.99 (d, $J = 8.2$ Hz, 2H), 2.56 (s, 3H), 2.40 (s, 2H), 0.28 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.89, 146.49, 137.73, 133.77, 133.68, 129.40, 128.52, 128.38, 127.94, 27.33, 26.53, -3.41. HRMS (EI) calculated for $\text{C}_{17}\text{H}_{20}\text{OSi}$: 268.1283, found: 268.1285. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -3.27.



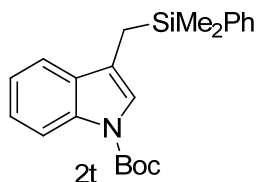
4-((dimethyl(phenyl)silyl)methyl)phenyl acetate (2q). Colorless oil, yield 73%. ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.44 (m, 2H), 7.41 – 7.34 (m, 3H), 6.99 – 6.88 (m, 4H), 2.32 (s, 2H), 2.29 (s, 3H), 0.29 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.73, 147.72, 138.30, 137.35, 133.81, 129.22, 129.09, 127.87, 121.18, 25.72, 21.24, -3.38. HRMS (EI) calculated for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Si}$: 284.1233, found: 284.1234. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -3.74.



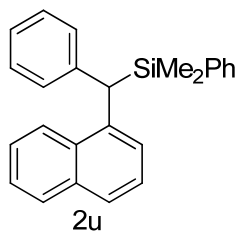
dimethyl(phenyl)(4-vinylbenzyl)silane (2r). Colorless oil, yield 79%. ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.41 (m, 2H), 7.37 – 7.31 (m, 3H), 7.25 – 7.20 (m, 2H), 6.88 (d, J = 8.1 Hz, 2H), 6.65 (dd, J = 17.6, 10.9 Hz, 1H), 5.65 (dd, J = 17.6, 1.0 Hz, 1H), 5.14 (dd, J = 10.9, 0.9 Hz, 1H), 2.29 (s, 2H), 0.24 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.71, 138.50, 136.94, 133.84, 133.71, 129.21, 128.56, 127.88, 126.19, 112.24, 26.24, -3.33. HRMS (EI) calculated for $\text{C}_{17}\text{H}_{20}\text{Si}$: 252.1334, found: 252.1336. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -3.74.



dimethyl(phenyl)(4-(phenylethynyl)benzyl)silane (2s). White solid, yield 80%. ^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.53 (m, 2H), 7.53 – 7.46 (m, 2H), 7.45 – 7.31 (m, 8H), 6.95 (d, J = 8.2 Hz, 2H), 2.37 (s, 2H), 0.31 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.67, 138.11, 133.82, 131.63, 131.56, 129.30, 128.43, 128.41, 128.10, 127.90, 123.72, 118.90, 89.92, 88.74, 26.82, -3.39. HRMS (EI) calculated for $\text{C}_{23}\text{H}_{22}\text{Si}$: 326.1491, found: 326.1494. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -3.54.

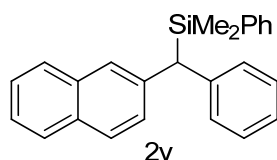


tert-butyl-3-((dimethyl(phenyl)silyl)methyl)-1H-indole-1-carboxylate (2t). Colorless oil, yield 95%. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (bs, 1H), 7.50 – 7.37 (m, 2H), 7.33 – 7.22 (m, 4H), 7.22 – 7.16 (m, 1H), 7.11 – 7.05 (m, 1H), 7.00 (bs, 1H), 2.20 (s, 2H), 1.55 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.94, 138.76, 135.37, 133.79, 131.56, 129.27, 127.92, 124.13, 122.15, 121.56, 119.38, 117.80, 115.12, 83.16, 28.37, 13.30, -2.89. HRMS (EI) calculated for $\text{C}_{22}\text{H}_{27}\text{NO}_2\text{Si}$: 365.1811, found: 365.1810. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -3.55.



dimethyl(naphthalen-1-yl(phenyl)methyl)(phenyl)silane (2u). Colorless oil, yield 76%. ^1H NMR (400 MHz, CDCl_3) δ 8.12 – 8.04 (m, 1H), 7.81 – 7.74 (m, 1H), 7.66 (d,

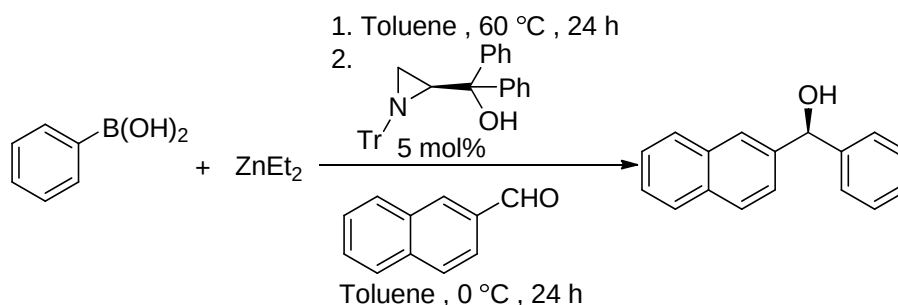
$J = 8.2$ Hz, 1H), 7.52 (dd, $J = 7.2, 1.1$ Hz, 1H), 7.41 – 7.28 (m, 6H), 7.28 – 7.22 (m, 2H), 7.17 – 7.00 (m, 5H), 4.56 (s, 1H), 0.37 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.40, 138.39, 137.99, 134.56, 134.53, 133.00, 129.22, 128.94, 128.69, 128.16, 127.72, 126.73, 125.95, 125.44, 125.15, 125.11, 124.25, 40.07, -2.17, -2.78. HRMS (EI) calculated for $\text{C}_{25}\text{H}_{24}\text{Si}$: 352.1647, found: 352.1643. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -2.76.



dimethyl(naphthalen-2-yl(phenyl)methyl)(phenyl)silane (2v). Colorless oil, yield 68%. ^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.71 (m, 1H), 7.66 (d, $J = 8.7$ Hz, 2H), 7.56 (s, 1H), 7.42 – 7.22 (m, 8H), 7.22 – 7.16 (m, 4H), 7.14 – 7.07 (m, 1H), 3.91 (s, 1H), 0.32 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.34, 140.08, 137.67, 134.59, 133.70, 131.71, 129.31, 129.19, 128.39, 127.75, 127.72, 127.65, 127.61, 126.94, 125.91, 125.42, 125.12, 45.93, -2.92, -2.95. HRMS (EI) calculated for $\text{C}_{25}\text{H}_{24}\text{Si}$: 352.1647, found: 352.1645. ^{29}Si NMR (79 MHz, CDCl_3) δ (ppm): -2.38.

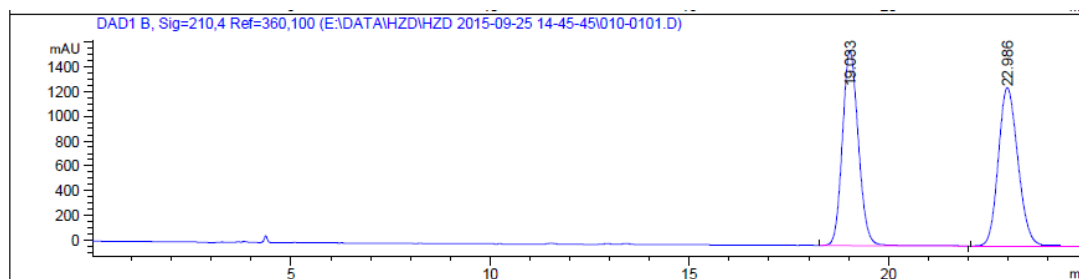
4. Enantioselective Pd-catalyzed silylation of secondary benzylic halides

4.1 Preparation of Enantioenriched naphthalen-2-yl(phenyl)methanol



(S)-naphthalen-2-yl(phenyl)methanol was prepared following the reported procedure^{8,9}. To a solution of boronic acid (2.4 equiv) in toluene was added diethylzinc (7.2 equiv, 1.0 M in toluene), the solution was heated and stirred at 65 °C for 24 h. Upon cooling to 0 °C, (S)-diphenyl(1-tritylaziridin-2-yl)methanol¹⁰ (5 mol%) was added as a solution in toluene. After stirring for 10 min, aldehyde (0.8 g, 5 mmol, 1.0 equiv) was added as a solution in toluene, and the solution was stirred at 0 °C for 20 h before quenching with 1N HCl. The product was extracted with EA, washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. Purification by flash chromatography afforded the target compound. Analytical Data are consistent with the literature values. The alcohol product was determined to be 92% ee by chiral HPLC analysis (OD, *i*-PrOH/hexane = 10/90, 0.8 mL/min, 210 nm, *tr* (major) = 19.0 min, *tr* (minor) = 23.0 min).

Racemic Product

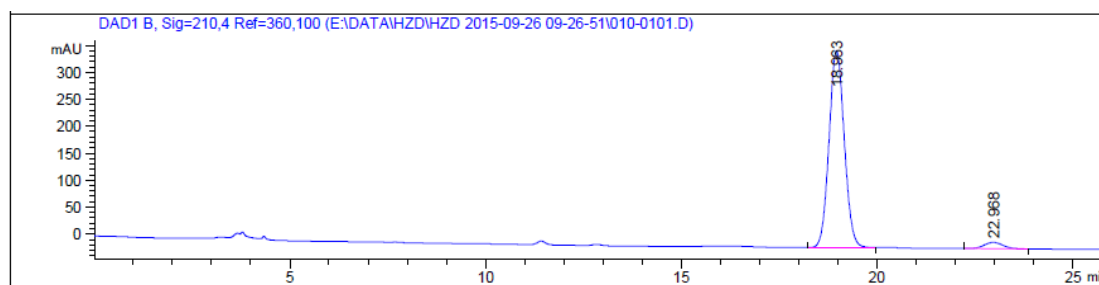


Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.033	BB	0.4308	4.35612e4	1574.48486	49.9084
2	22.986	BBA	0.5331	4.37211e4	1278.21021	50.0916

Totals : 8.72823e4 2852.69507

Enantioenriched Product

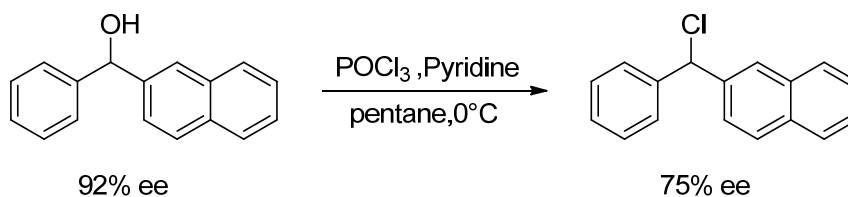


Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.963	BB	0.4196	9896.63867	365.90189	96.1803
2	22.968	BB	0.5130	393.03671	11.84835	3.8197

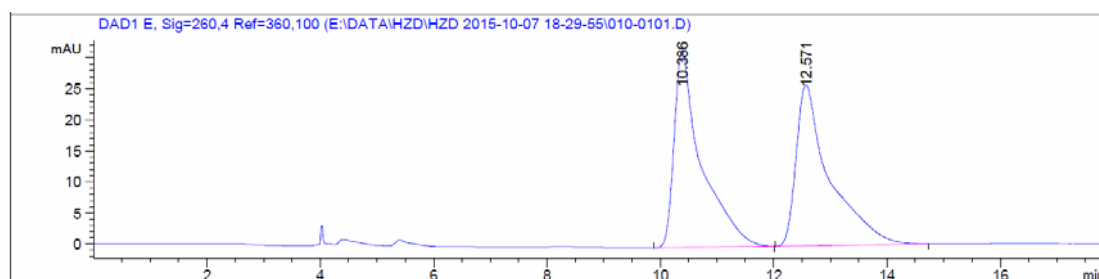
Totals : 1.02897e4 377.75024

4.2 Preparation of Enantioenriched 2-(chloro(phenyl)methyl)naphthalene



Enantioenriched 2-(chloro(phenyl)methyl)naphthalene was prepared following the similar reported procedure¹¹. A flame-dried 100 mL round-bottom flask was charged with (*R*)-(4-chlorophenyl)(phenyl)methanol (5 mmol, 92% ee). Hexane (60 mL) and pyridine (1.2 mL, 15 mmol) were added, and the mixture was cooled to 0 °C. Phosphorus oxychloride (750 μ L, 8 mmol) was added, and the reaction was stirred at 0 °C for 5 h. Saturated sodium bicarbonate (~30 mL) was added, and the organic layer was extracted with Et₂O (3 $\times$ 15 mL). The combined organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure to afford the target product as a white solid which was used in the next step without further purification. The chloride product was determined to be 75% ee by chiral HPLC analysis (AD-H, *i*-PrOH/hexane = 0/100, 0.8mL/min, 260 nm, tr (major) = 10.4 min, tr (minor) = 12.7 min). The absolute configuration of the chloride product was not determined.

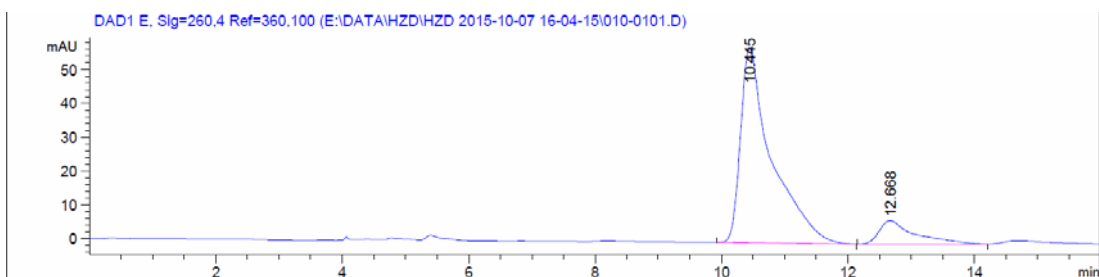
Racemic Product



Signal 4: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.386	BB	0.4641	1060.04590	31.70172	49.8564
2	12.571	BB	0.5708	1066.15356	25.98098	50.1436

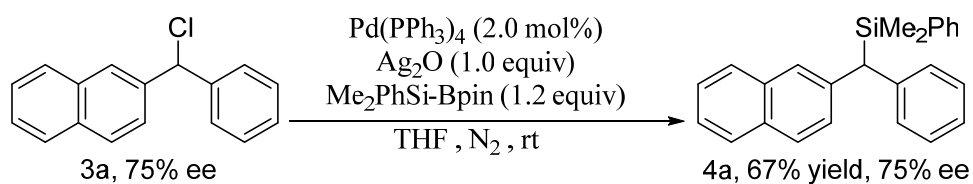
Enantioenriched Product



Signal 4: DAD1 E, Sig=260,4 Ref=360,100

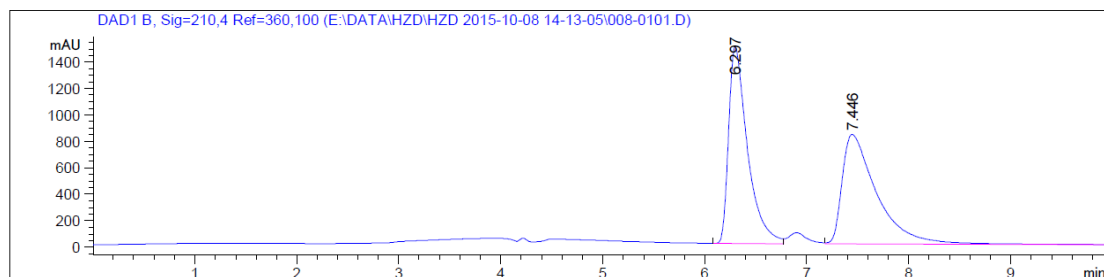
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.445	BB	0.4747	1975.42322	57.79980	87.6468
2	12.668	BB	0.5534	278.42169	7.00912	12.3532

4.3 Enantionspecific silylation



The procedure was following the method for the synthesis of benzylicsilanes 2v. The silane product was determined to be 75% ee by chiral HPLC analysis (IC, *i*-PrOH/hexane = 0/100, 0.8 mL/min, 210 nm, tr (major) = 6.5 min, tr (minor) = 7.8 min). The absolute configuration of the silane product was not determined.

Racemic Product

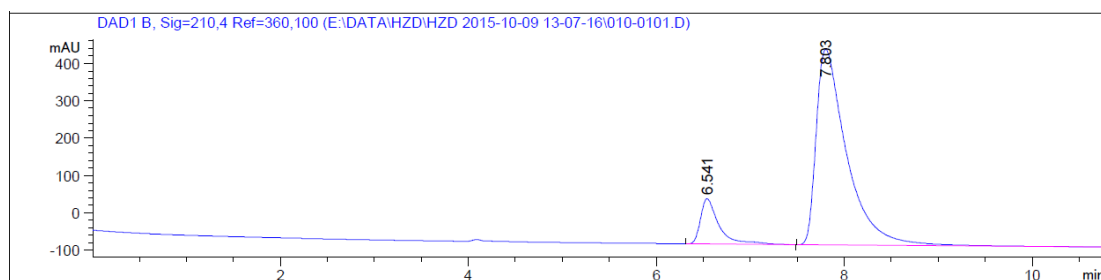


Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.297	BV	0.1899	1.91352e4	1489.42700	49.6075
2	7.446	VBA	0.3443	1.94380e4	826.80048	50.3925

Totals : 3.85732e4 2316.22748

Enantioenriched Product

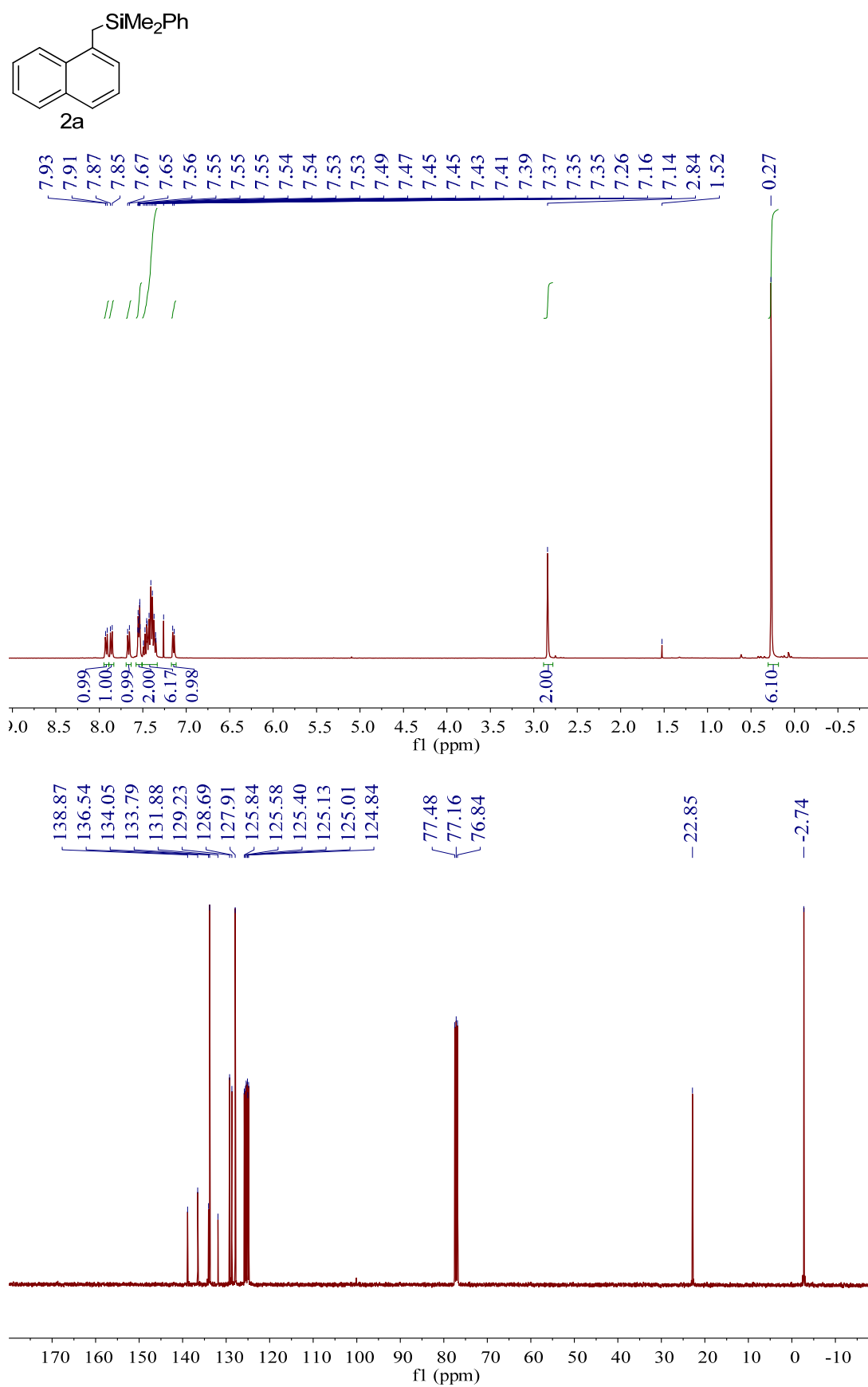


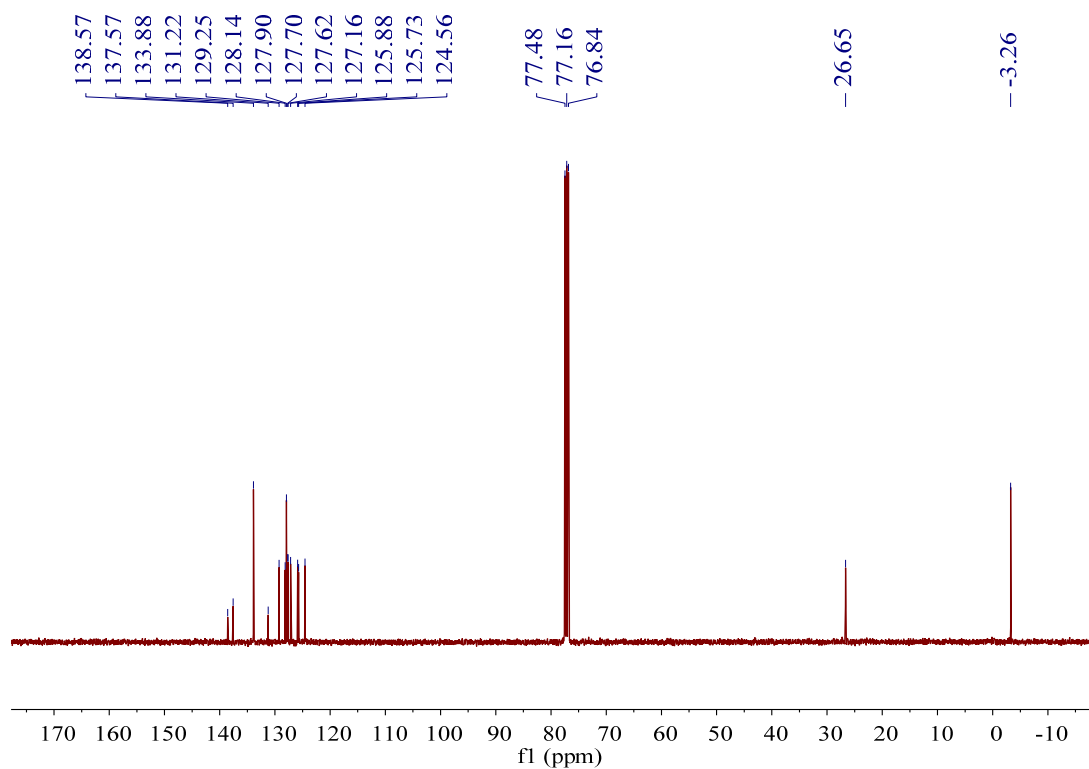
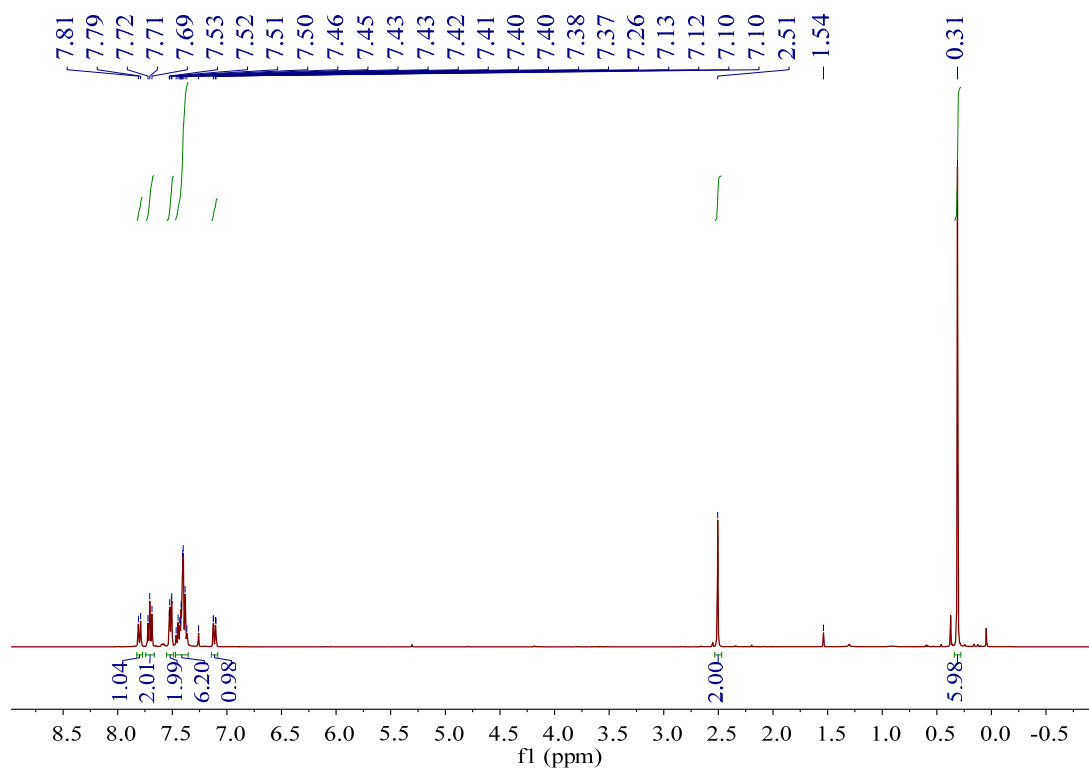
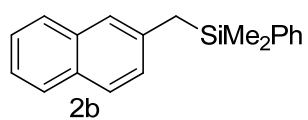
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.541	BB	0.1995	1654.48108	120.99983	12.2554
2	7.803	BBA	0.3318	1.18455e4	523.97119	87.7446

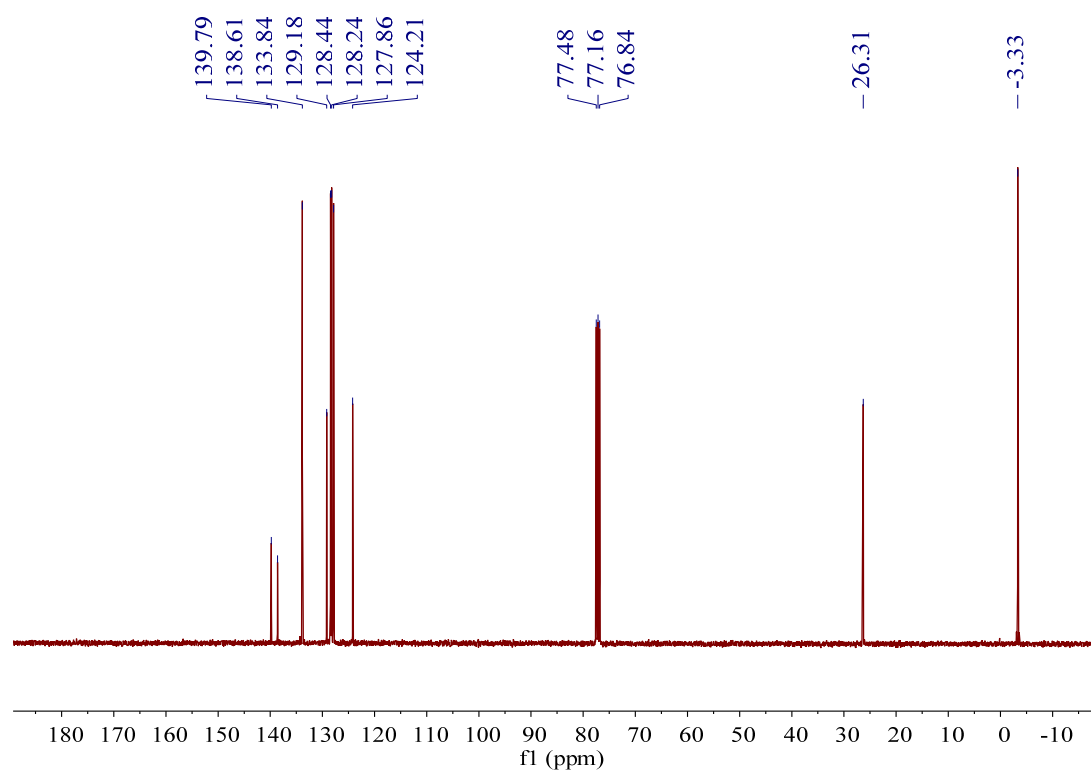
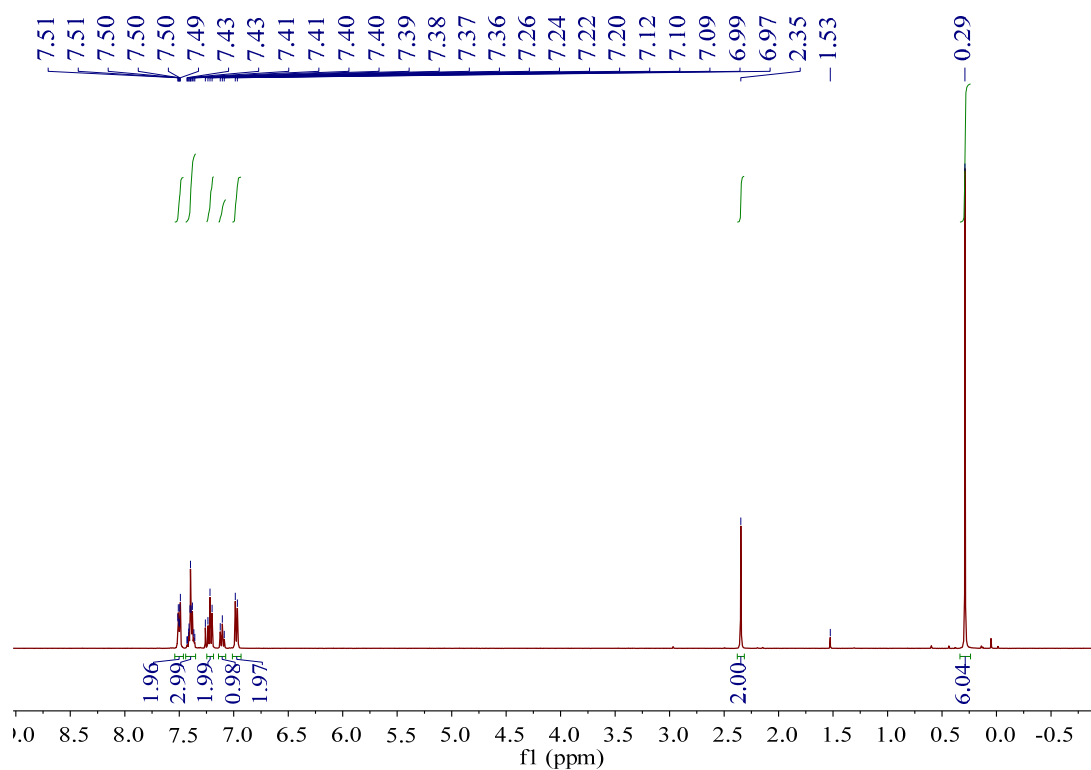
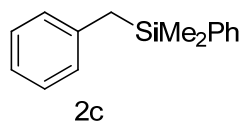
5. References for supporting information

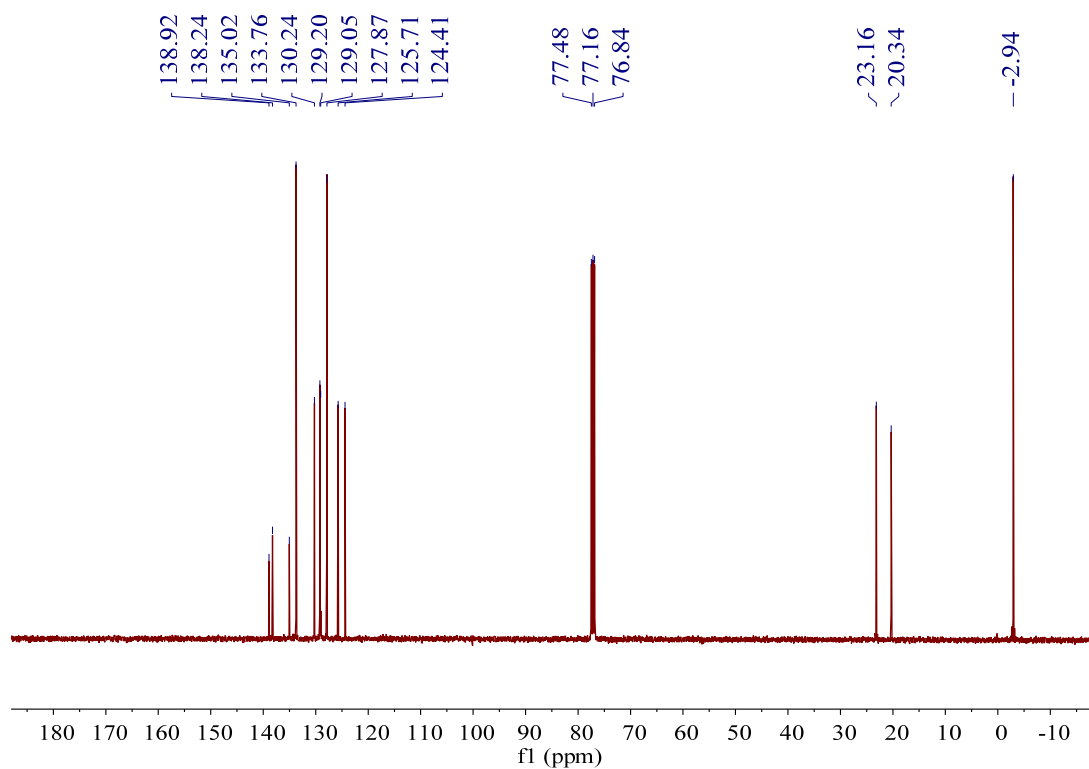
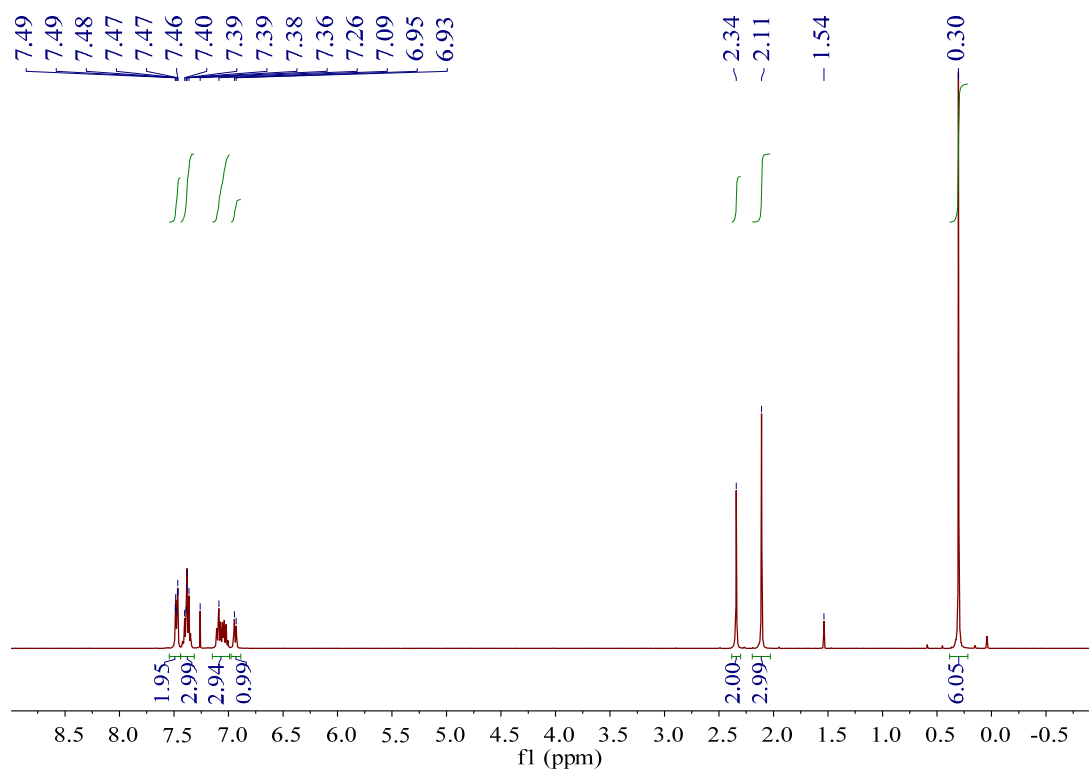
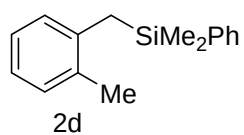
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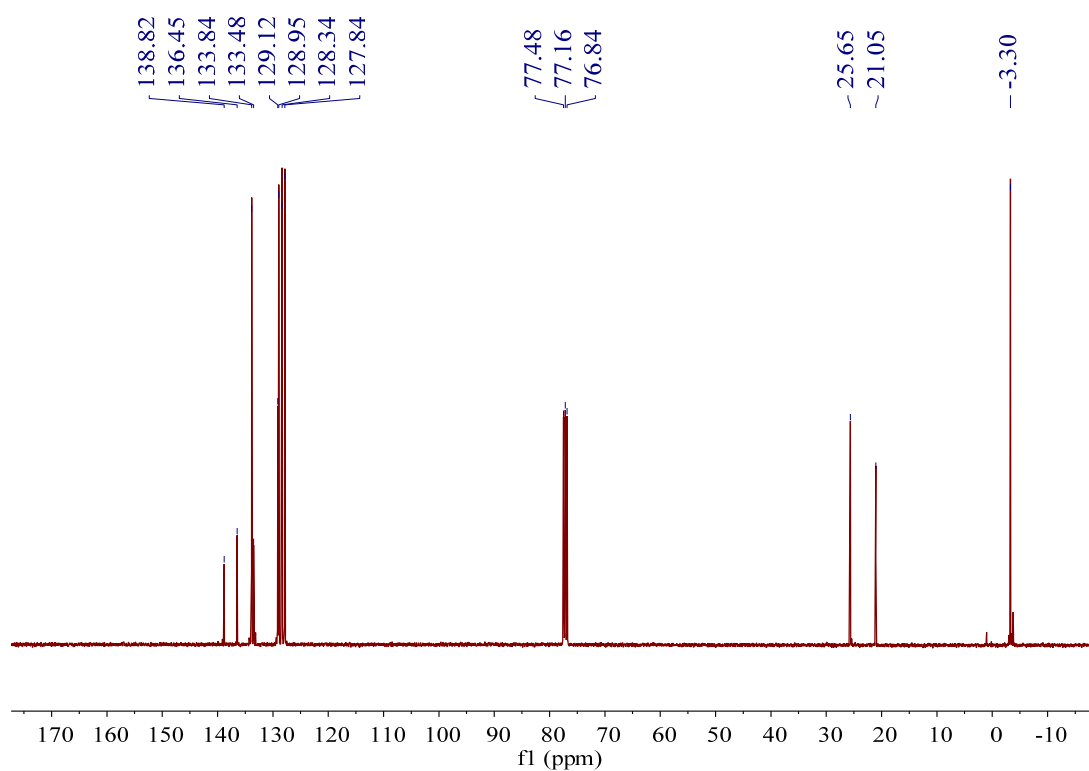
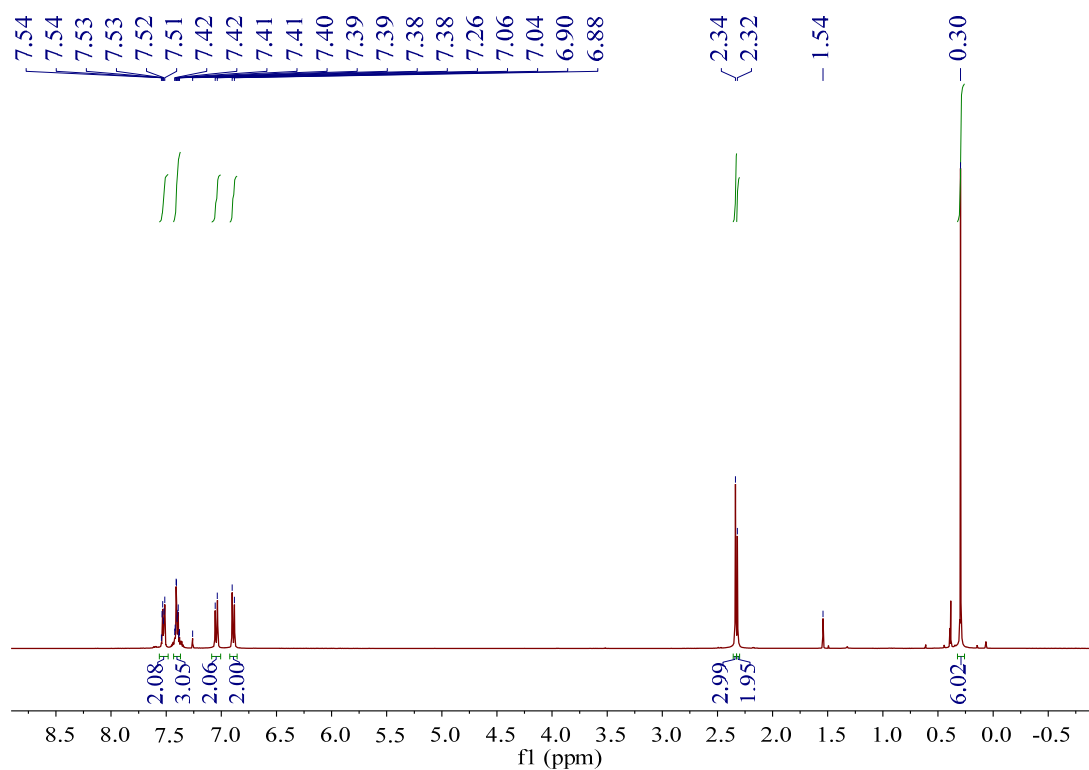
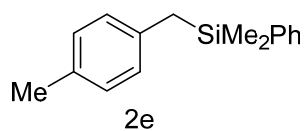
6. NMR spectra for the products

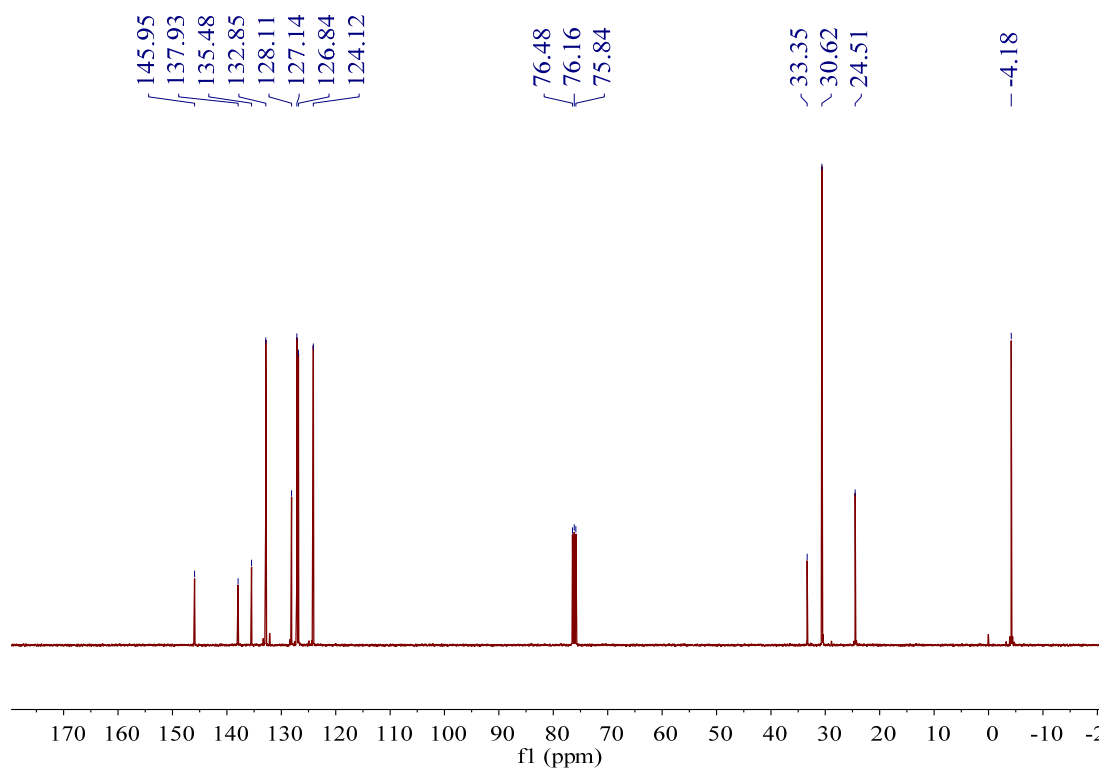
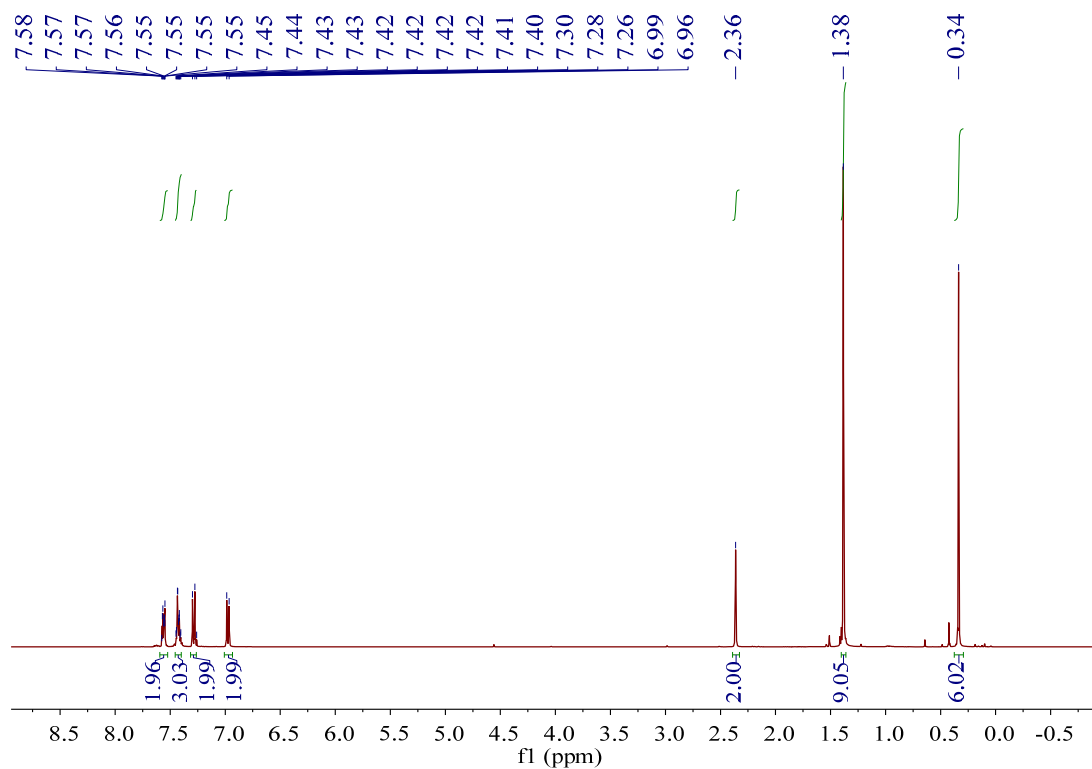
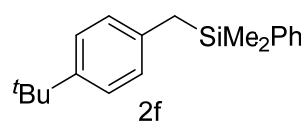


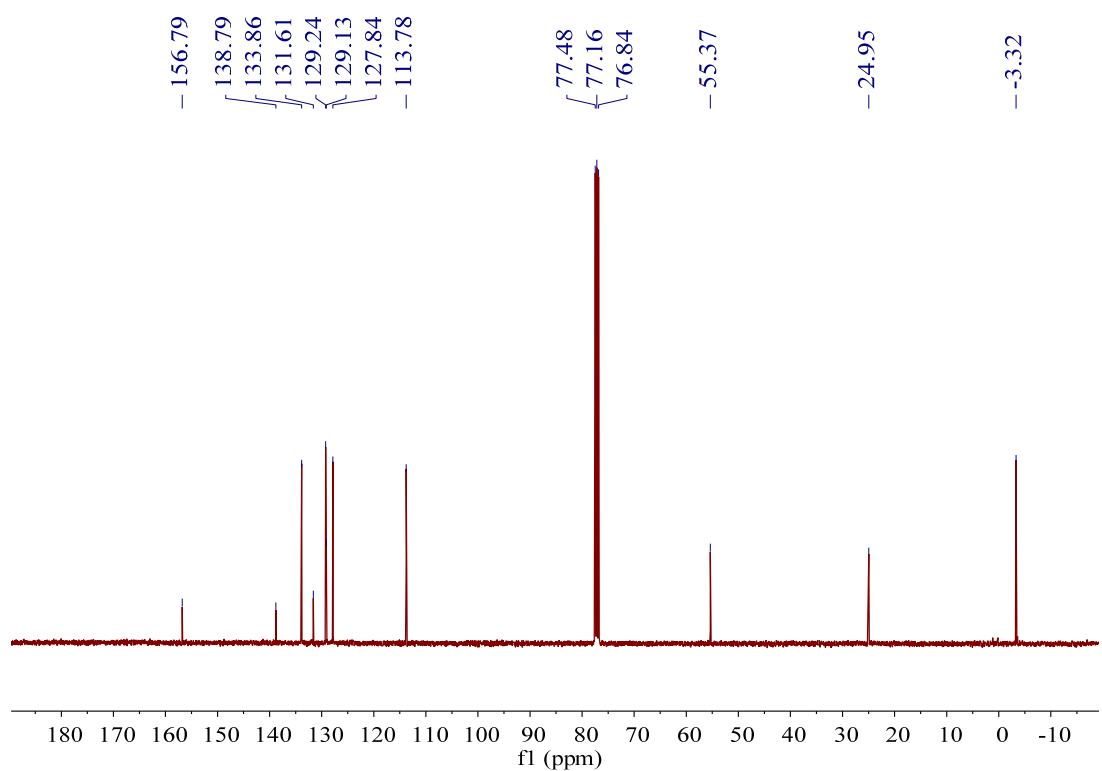
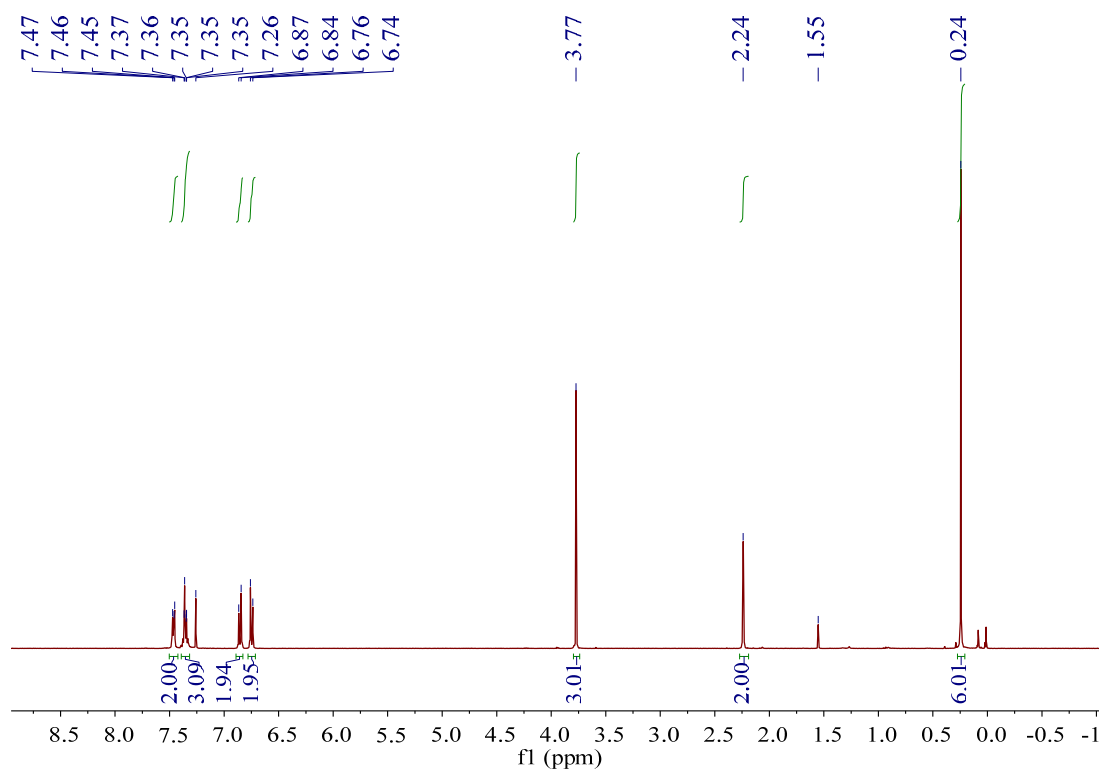
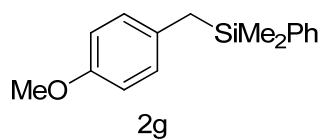


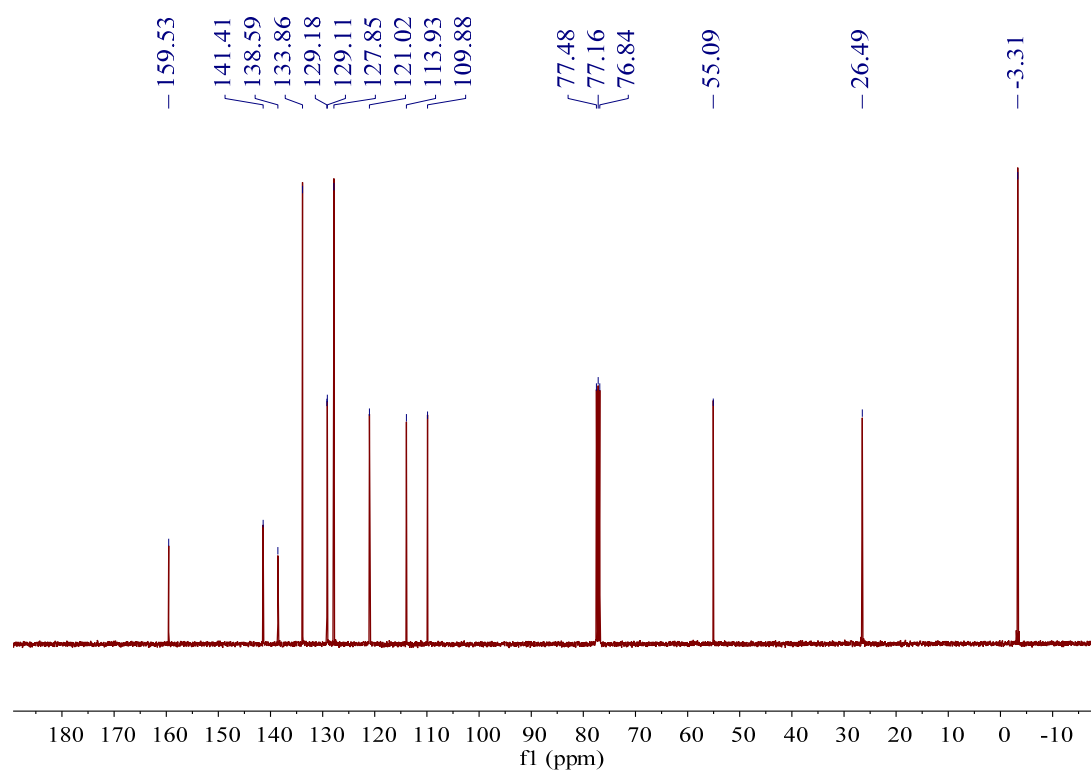
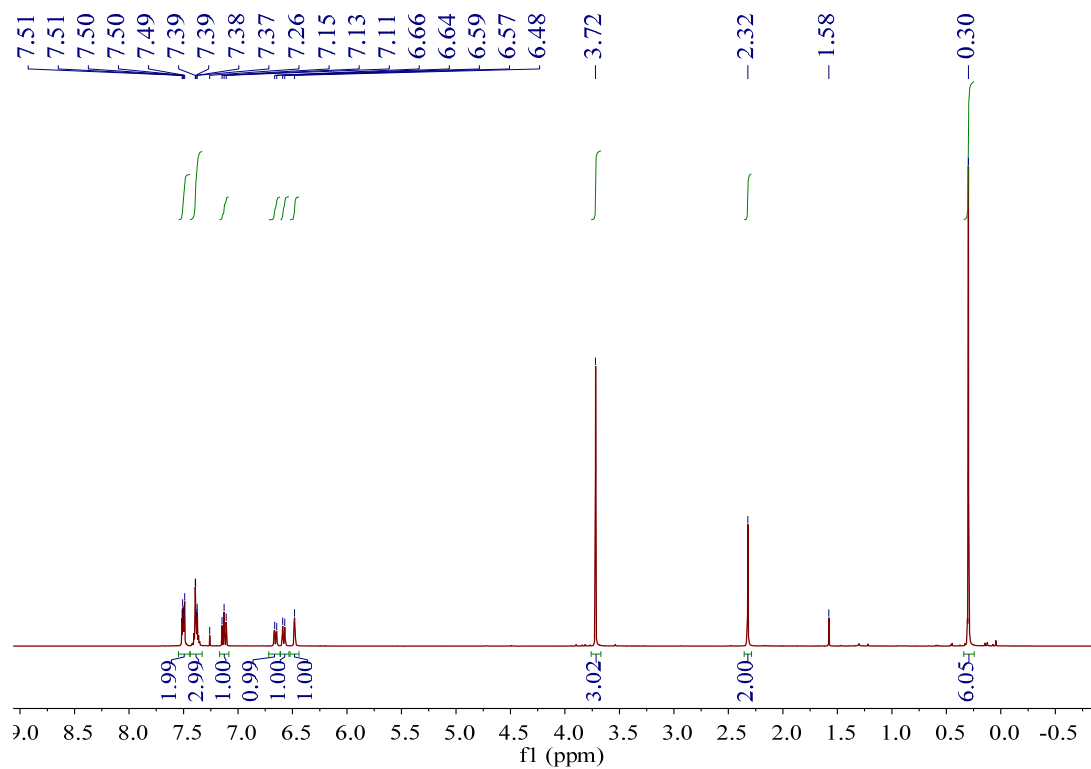
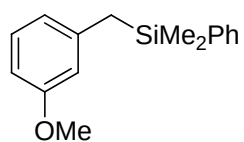


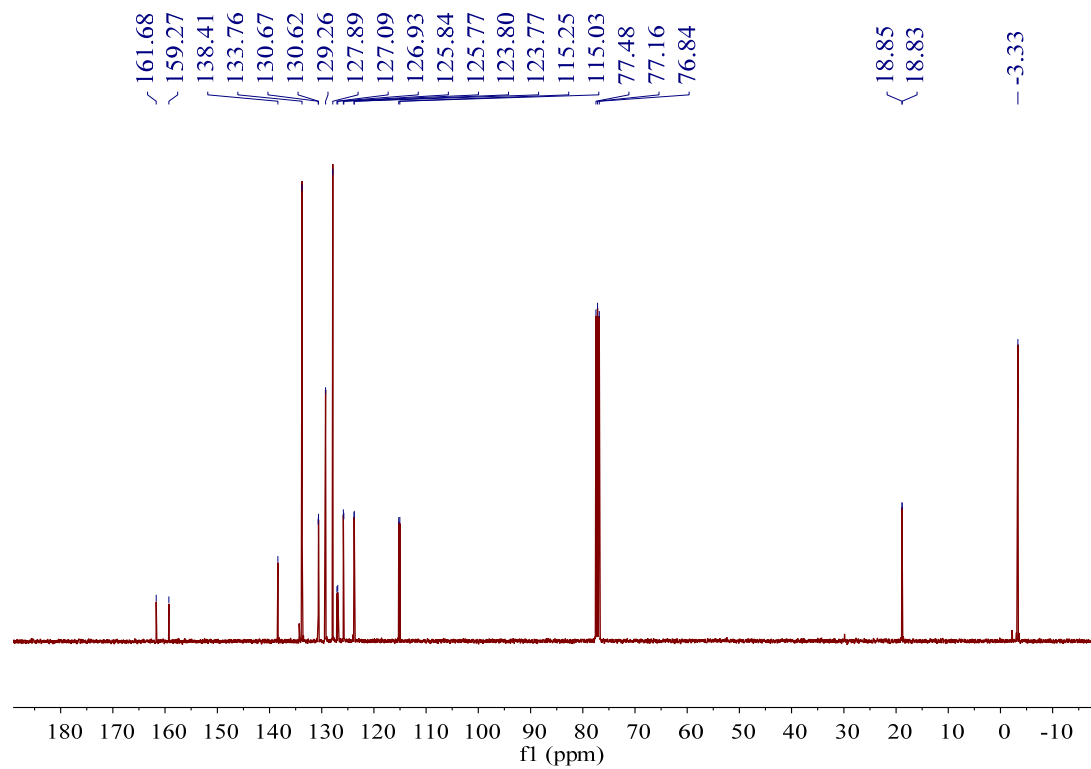
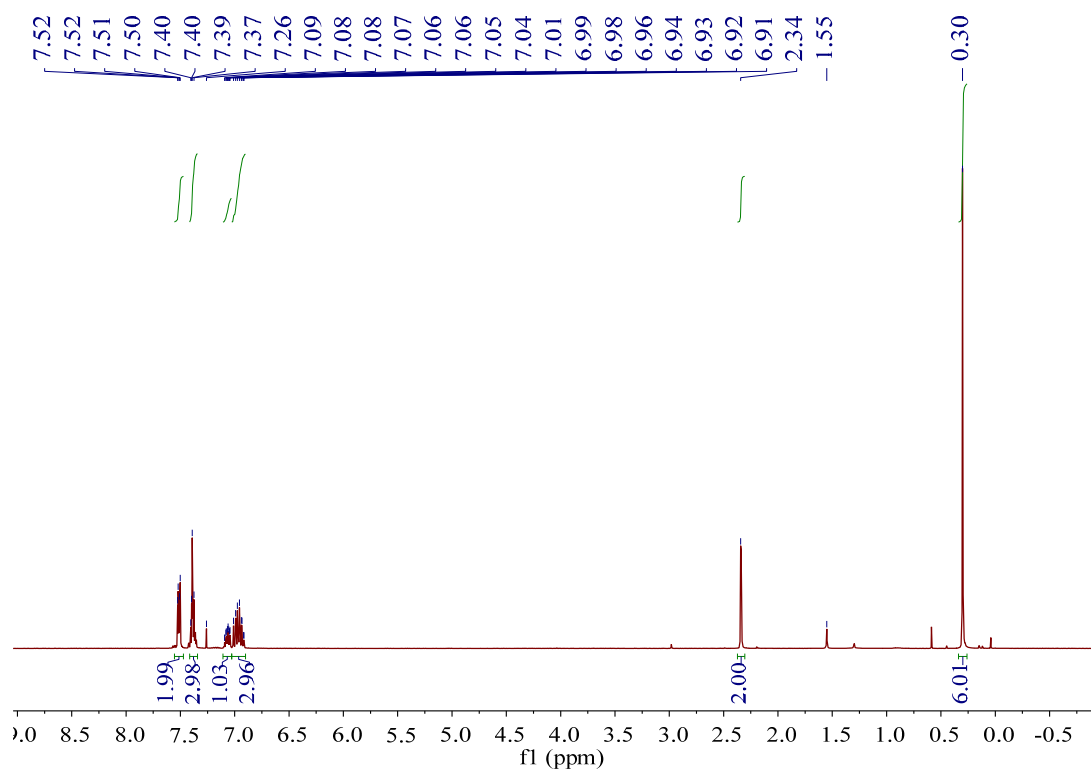
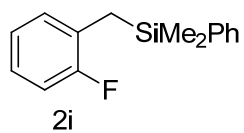




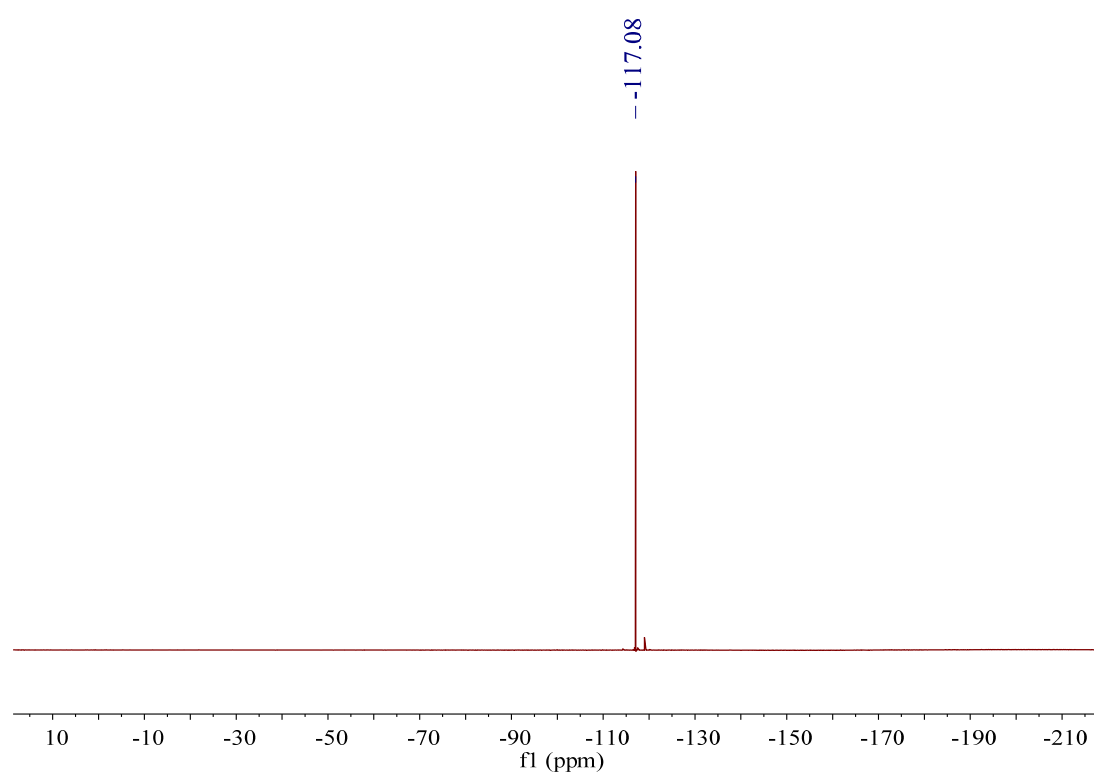


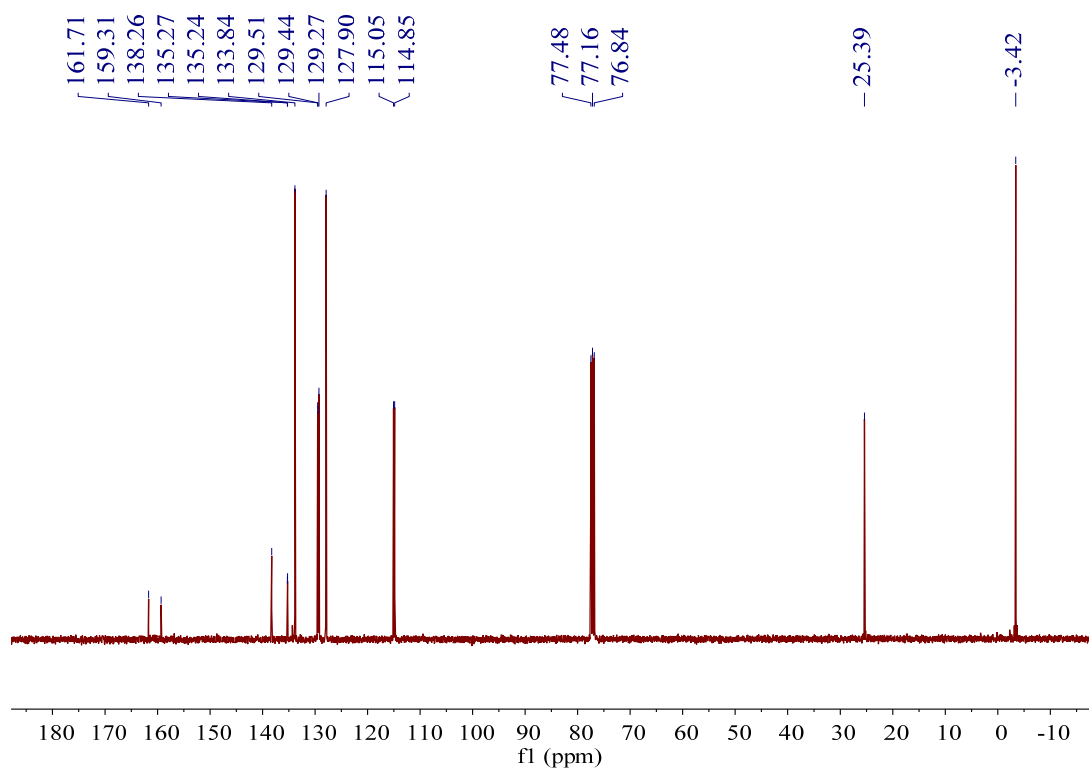
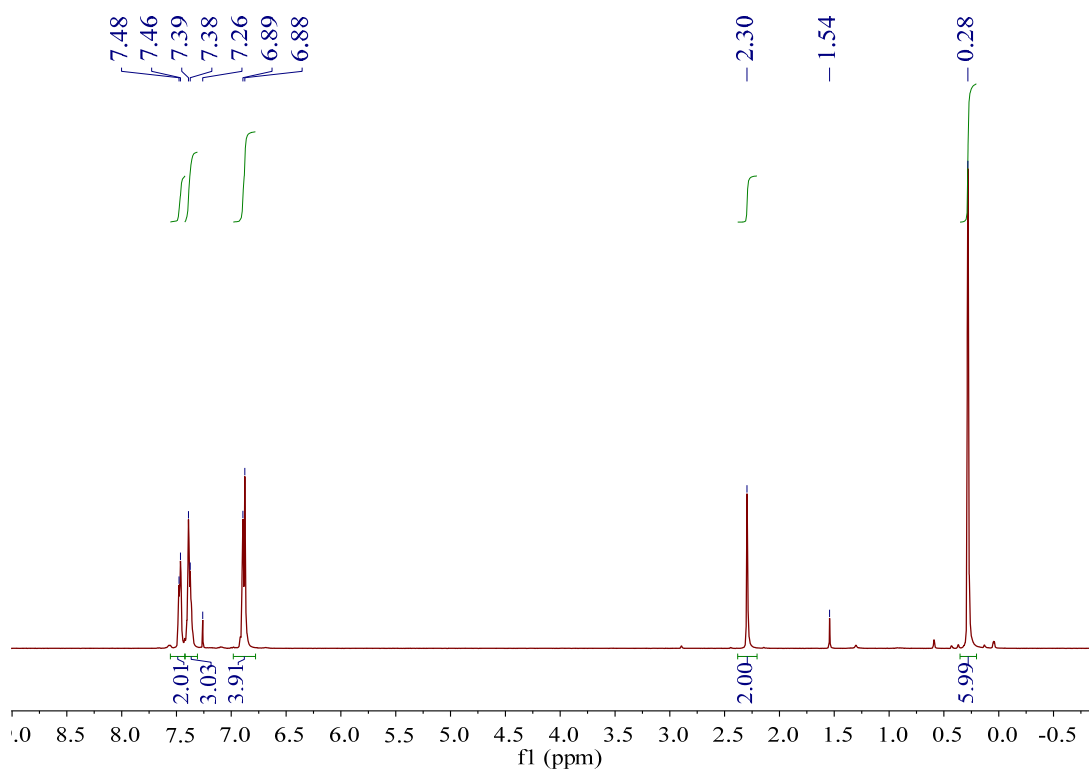
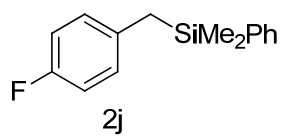




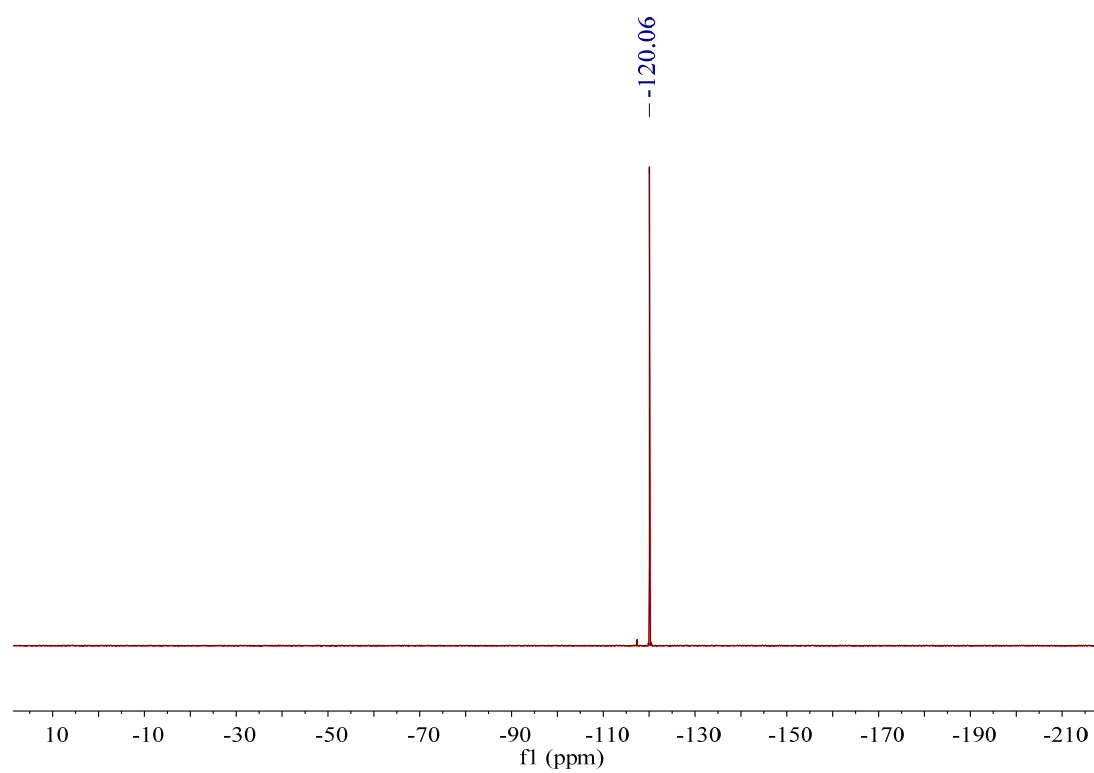


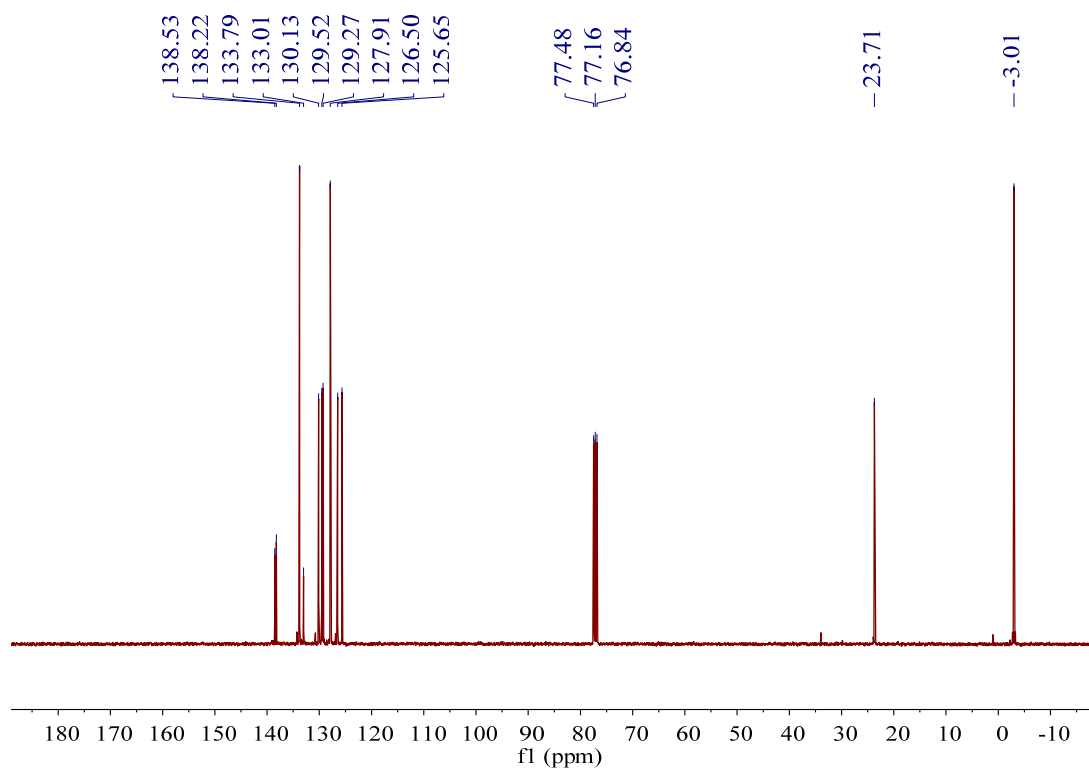
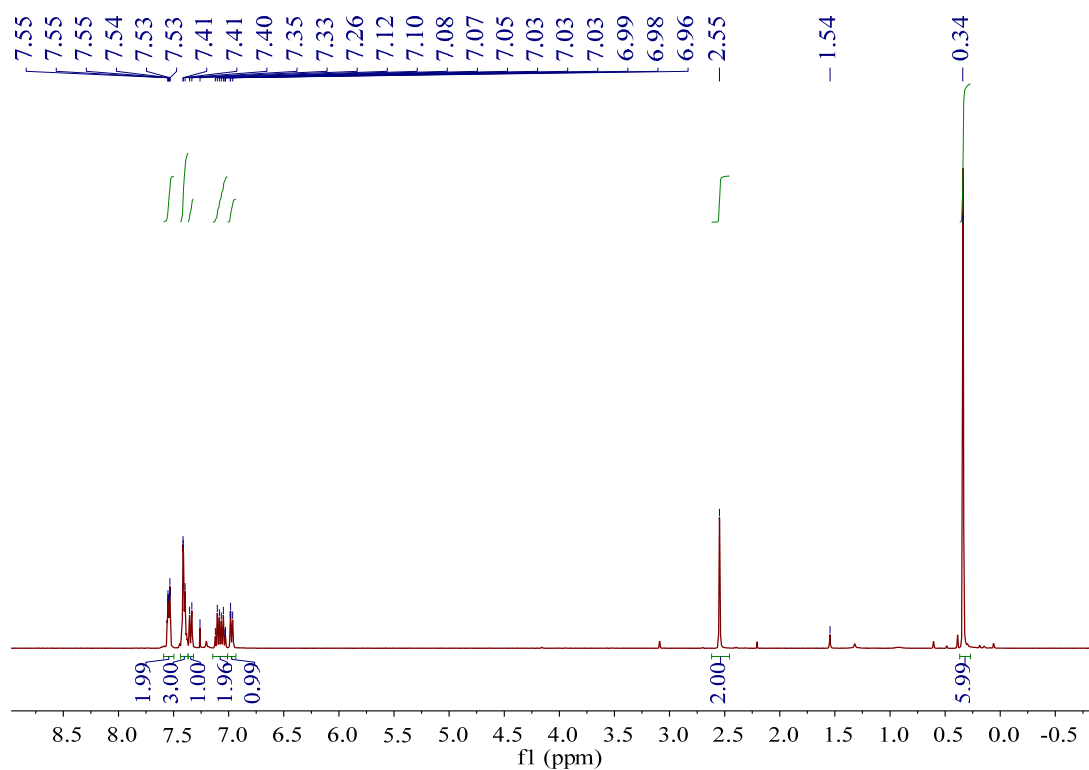
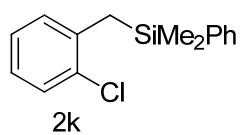
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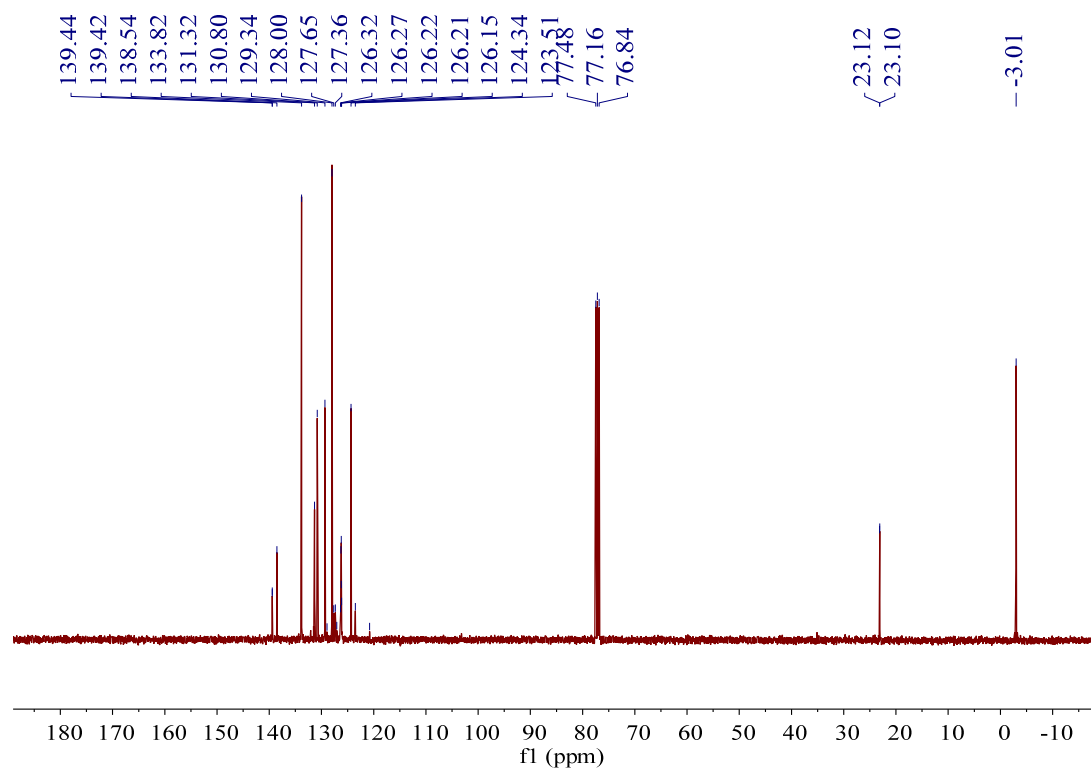
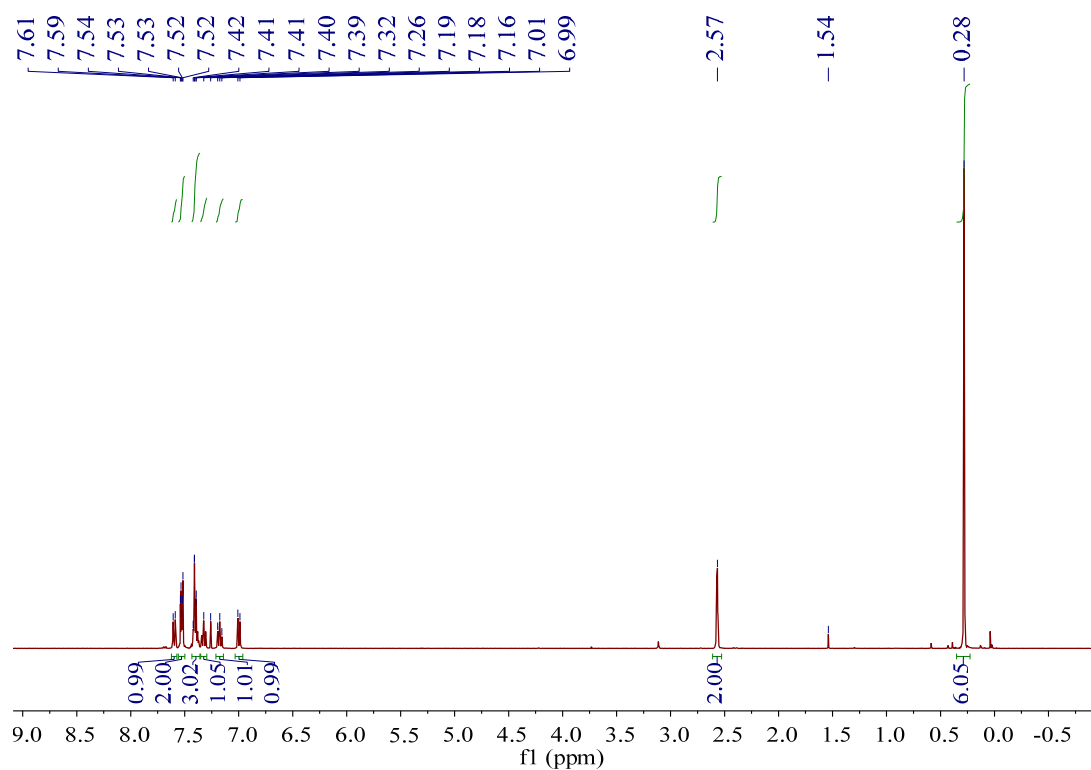
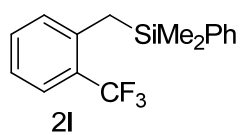




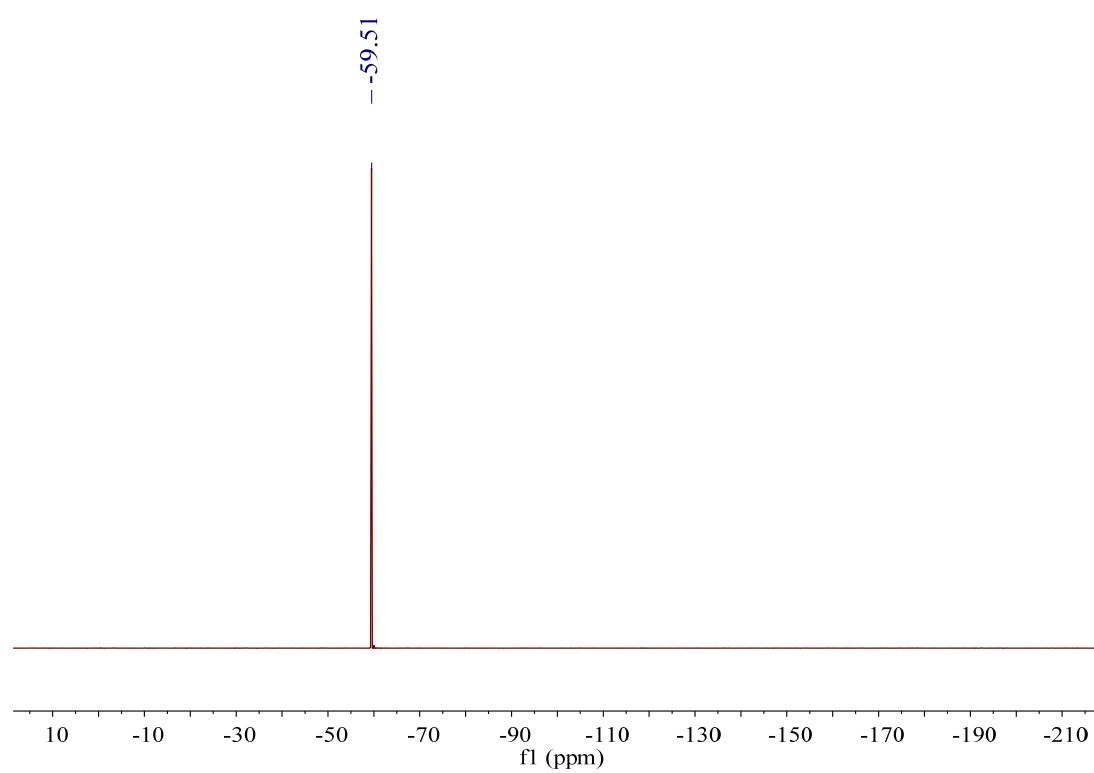
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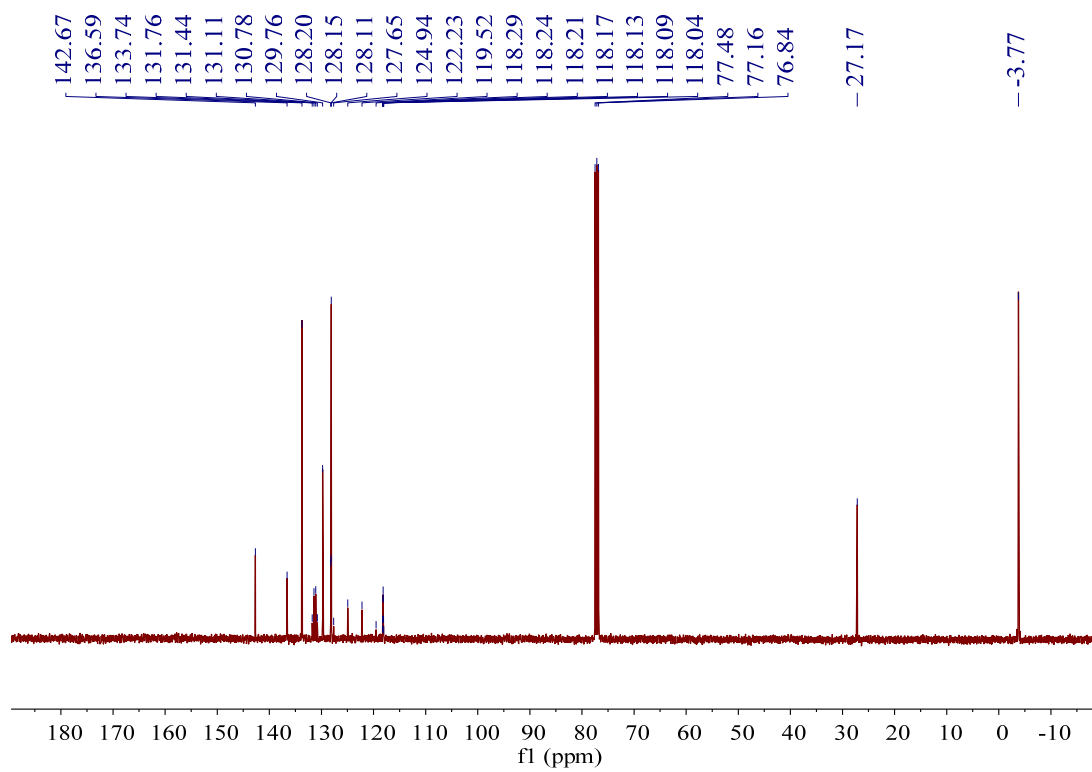
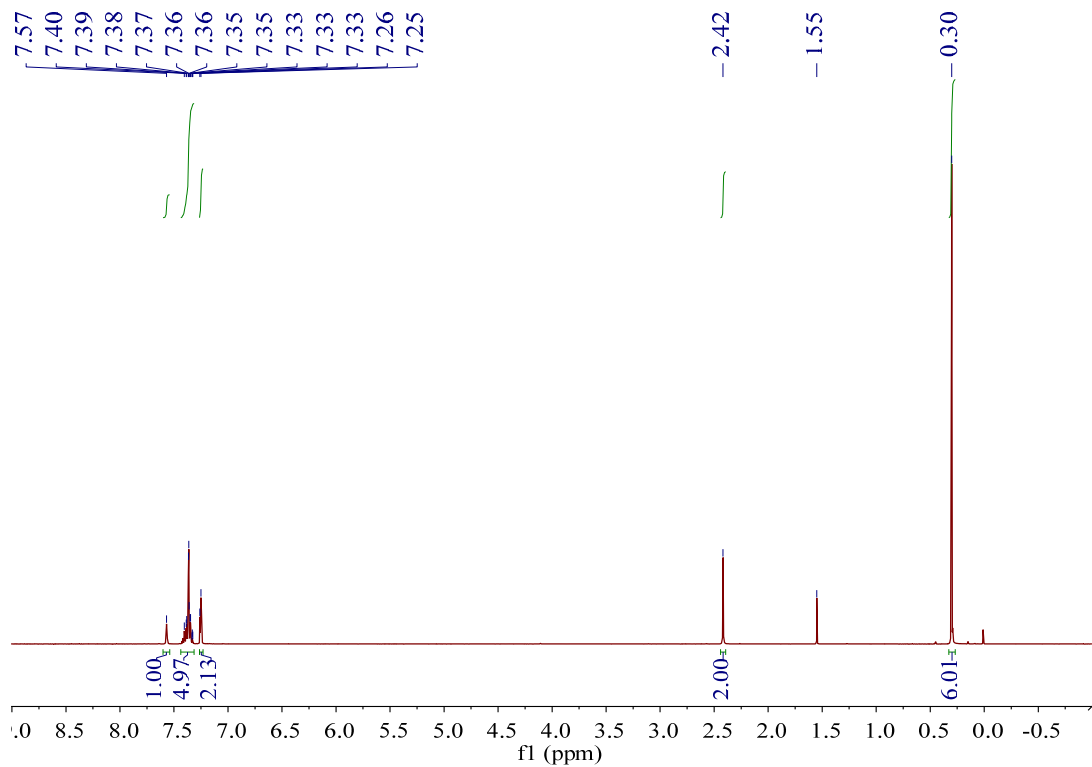
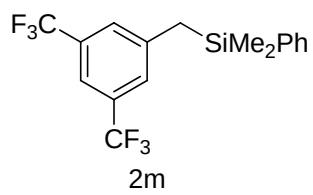




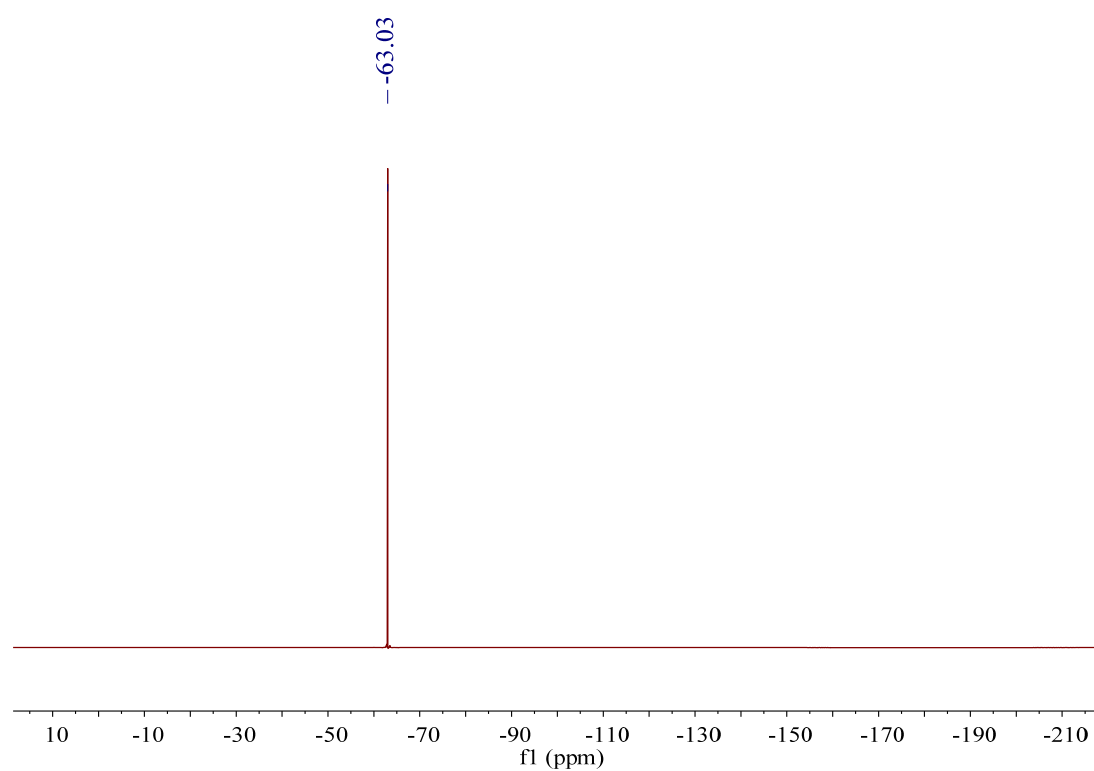


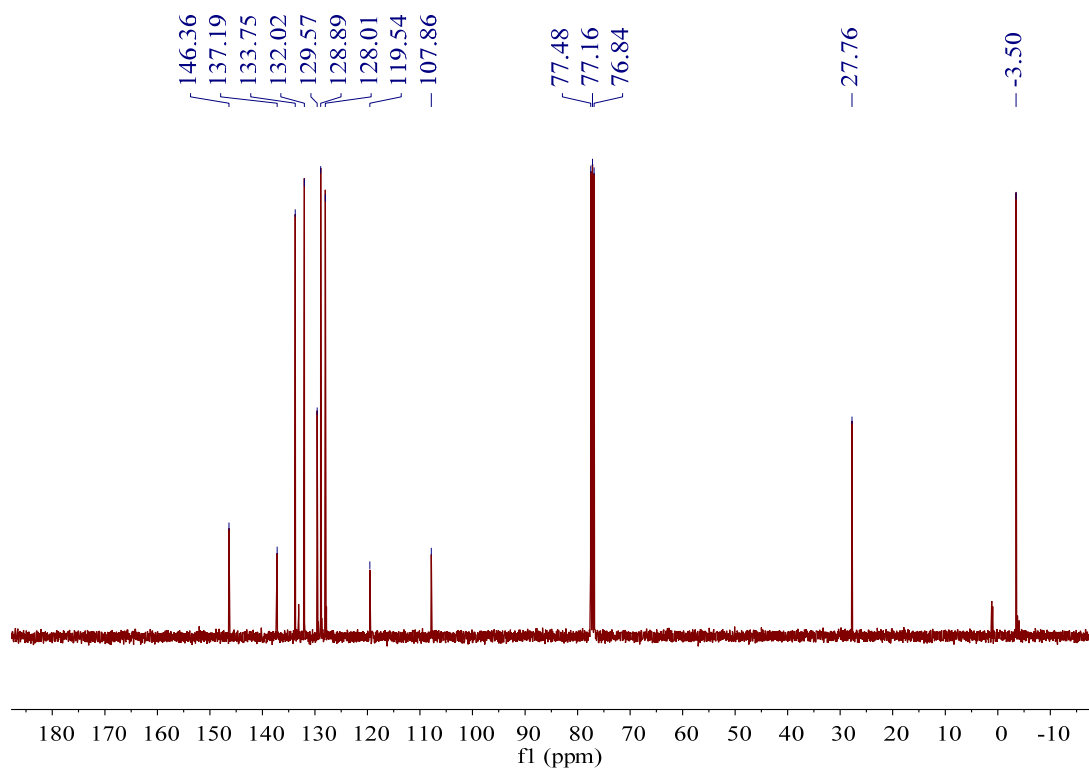
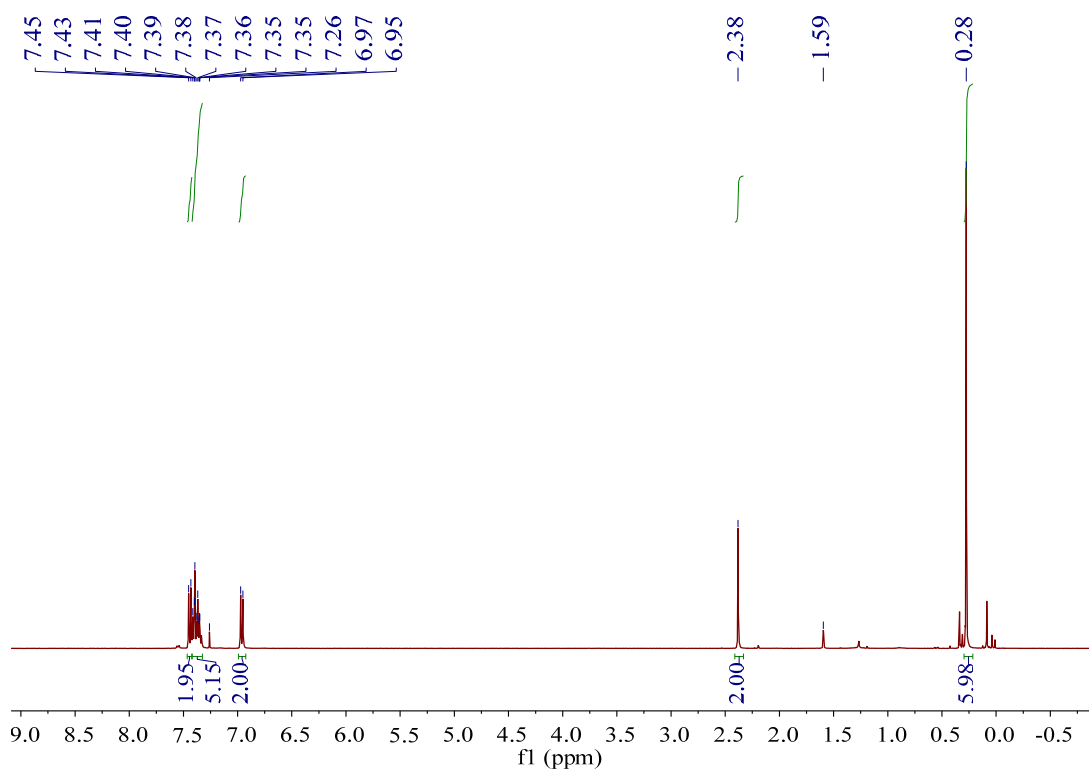
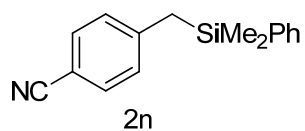
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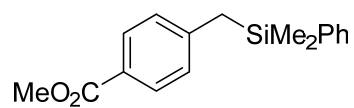




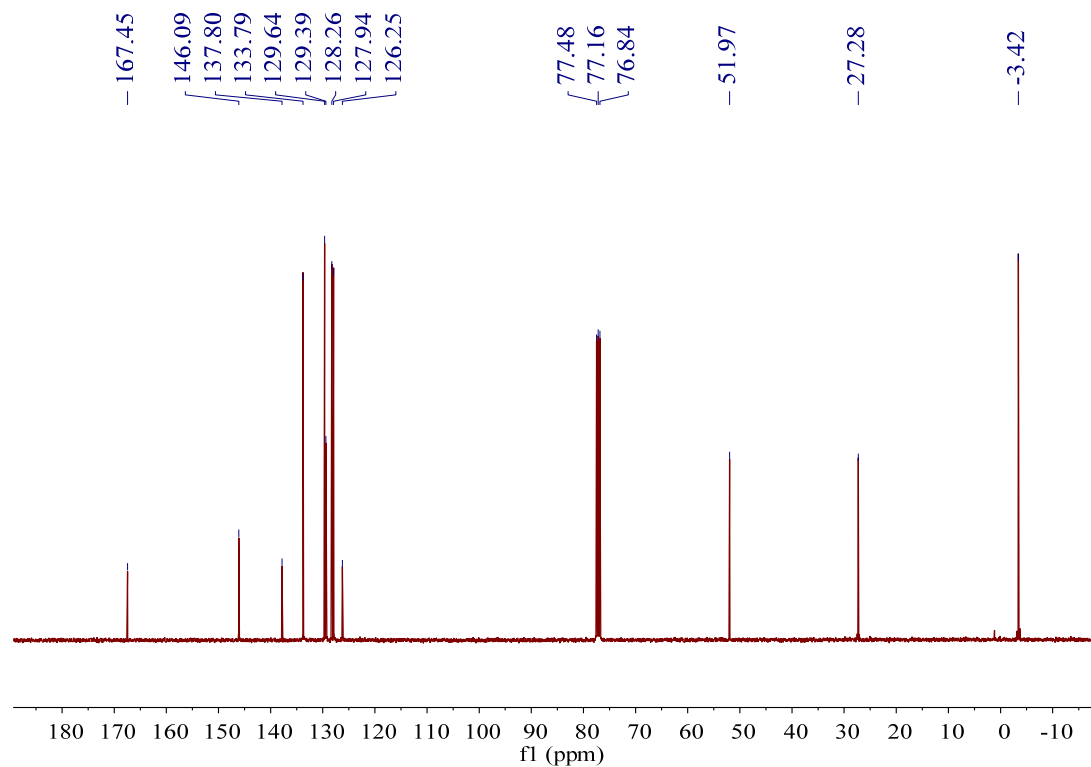
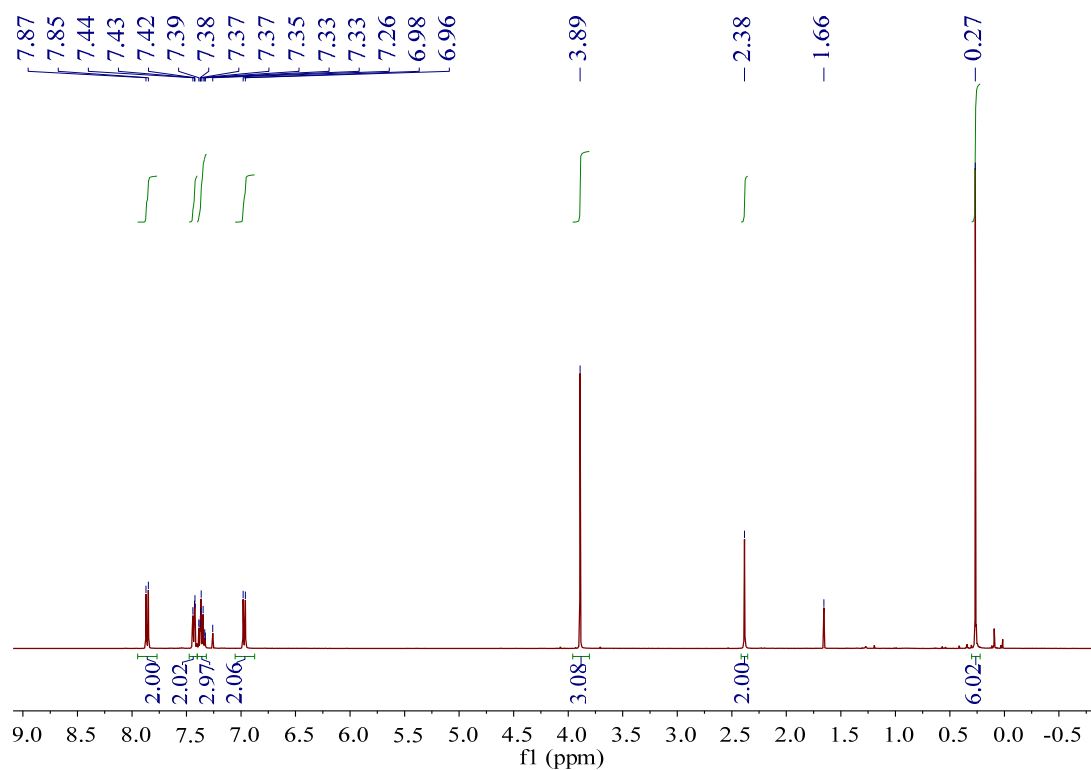
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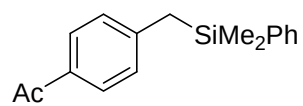






2o





2p

