Supplementary Information

Silacyclization through Palladium-Catalyzed Intermolecular Silicon-Based C(sp^2)−C(sp^3) Cross-Coupling

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1. General Information

All reactions were set up using standard Schlenk techniques and carried out under a N_2 atmosphere with dry solvents. Commercially available chemicals were obtained from Infinity Scientific, Heowns, Admas, Alfa Aesar, J&K, Sigma-Aldrich, Sinocompound, Energy Chemical, and TCI and used as received unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} glass plates. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 365 nm) and/or iodine.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV 400 spectrometer at 400MHz (^{1}H NMR), 100MHz (^{13}C NMR) and 376MHz (^{19}F NMR) using $CDCl_3$ as solvent. Proton and carbon chemical shifts are reported relative to the solvent used as an internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm).

GC-MS spectra were obtained using electron ionization (Thermo Scientific Trace 300/GC-System and ISQ/QD). High-resolution mass spectra (HRMS) of product were recorded on Varian 7.0T FTMS with ESI resource or Q Exactive GC-Orbitrap MS. Flash chromatography was performed on silica gel (200-300 mesh) by standard techniques.

The procedures for preparation of the *o*-iodophenols were described in the literatures.[1-2]

2. Synthesis of Starting Materials

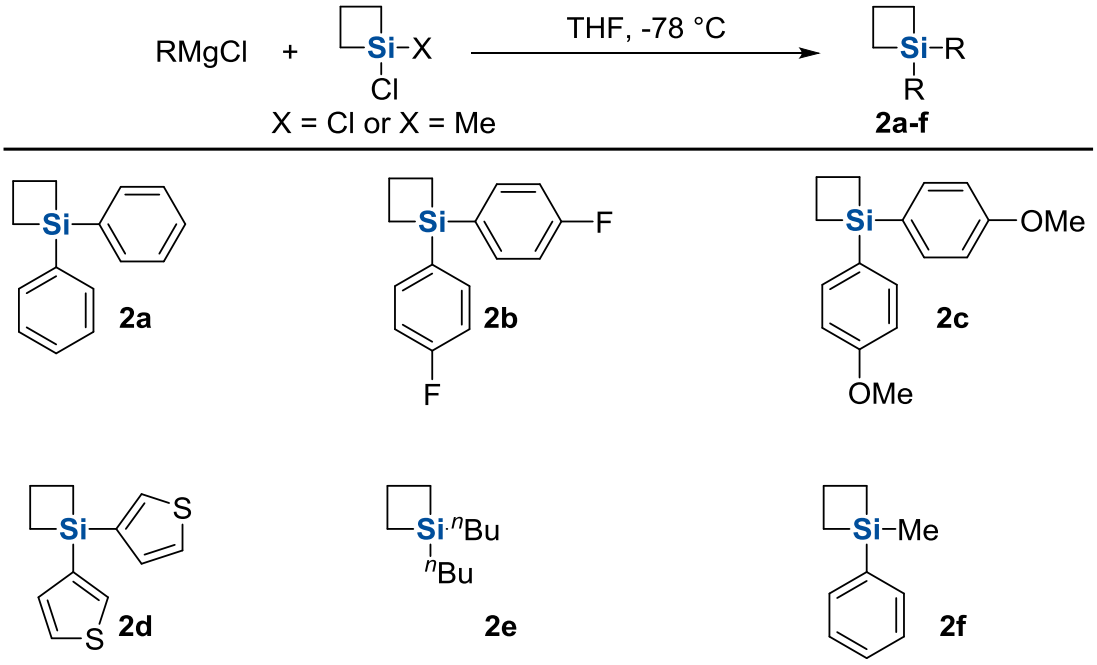
2.1. General method for preparation of silacyclobutanes

The preparation of silacyclobutanes with symmetrical or non-symmetrical substitution was described following a literature procedure.[3]

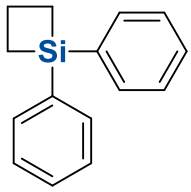
Procedure A: Arylmagnesium bromide or alkylmagnesium bromide (2.83 M in THF, 30 mL, 85 mmol) was added to a solution of 1,1-dichlorosilacyclobutane (5.99 g, 42 mmol), which was prepared according to the literatures[4] in THF (20 mL) at -78 ℃ for 30 min. The cloudy suspension was stirred for another 30 min. and refluxed overnight. The reaction was quenched by water (1 mL) and slowly added brine (100 mL). The organic phase was then separated and the aqueous phase was extracted with Et_2O (2 × 100 mL). The combined organic phase was dried (Na_2SO_4) and concentrated under vacuum to give the crude product as a colorless oil, which was further purified by

flash chromatography (PE) and reversed-phase column to give colorless liquid **2a-e** (40-80% yield).

Procedure B: Phenylmagnesium bromide (2.83 M in THF, 15 mL, 42.5 mmol) was added to a solution of 1-chloro-1-methylsiletane (5.04 g, 42 mmol) in THF (20 mL) at -78 ℃ for 30 min. The cloudy suspension was stirred for another 30 min. and refluxed overnight. The reaction was quenched by water (1 mL) and slowly added brine (100 mL). The organic phase was then separated and the aqueous phase was extracted with Et_2O (2 × 100 mL). The combined organic phase was dried (Na_2SO_4) and concentrated under vacuum to give the crude product as a colorless oil, which was further purified by flash chromatography (PE) and reversed-phase column to give colorless liquid **2f** (70% yield).

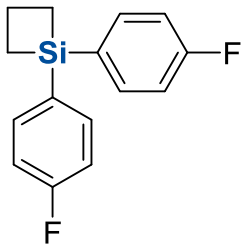


1,1-Diphenylsiletane (2a)



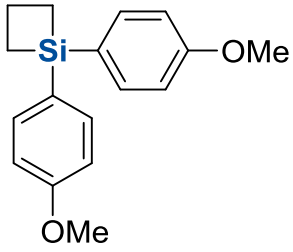
Following the general procedure A to give the desired product 7.52 g, 80% yield, colorless liquid. $\mathbf{R_f}$ (PE): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.70 (m, 4H), 7.63 – 7.37 (m, 6H), 2.41 (p, *J* = 8.2 Hz, 2H), 1.81 – 1.37 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.51, 134.63, 129.80, 128.11, 18.49, 14.02. **MS** (EI) calcd. For $C_{15}H_{16}Si$ $[M]^+$: 224.1021. Found: 224.0688.

1,1-Bis(4-fluorophenyl)siletane (2b)



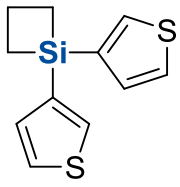
Following the general procedure A to give the desired product 7.64 g, 70% yield, colorless liquid. **R_f** (PE): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 6.6 Hz, 4H), 7.12 (t, *J* = 8.2 Hz, 4H), 2.26 (p, *J* = 8.4, 7.7 Hz, 2H), 1.49 (t, *J* = 8.3 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.29 (d, *J* = 249.4 Hz), 136.64 (d, *J* = 7.5 Hz), 131.80 (d, *J* = 3.8 Hz), 115.44 (d, *J* = 19.9 Hz), 18.29, 14.21. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.48. **MS** (EI) calcd. For $C_{15}H_{14}F_2Si$ $[M]^+$: 260.0833. Found: 260.0671.

1,1-Bis(4-methoxyphenyl)siletane (2c)



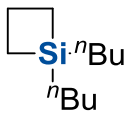
Following the general procedure A to give the desired product 8.35 g, 70% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 4H), 6.97 (d, *J* = 8.5 Hz, 4H), 3.85 (s, 6H), 2.25 (p, *J* = 8.1 Hz, 2H), 1.53 – 1.39 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.03, 136.21, 127.70, 113.88, 55.20, 18.26, 14.41. **MS** (EI) calcd. For $C_{17}H_{20}O_2Si$ $[M]^+$: 284.1233. Found: 284.0612.

3,3'-(Siletane-1,1-diyl)dithiophene (2d)



Following the general procedure A to give the desired product 7.43 g, 75% yield, colorless liquid. **R_f** (PE): 0.7. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 2H), 7.50 (dd, *J* = 4.8, 2.6 Hz, 2H), 7.35 (dd, *J* = 4.8, 1.0 Hz, 2H), 2.32 (p, *J* = 8.2 Hz, 2H), 1.53 (t, *J* = 8.3 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.14, 134.32, 132.02, 126.30, 18.56, 15.57. **MS** (EI) calcd. For $C_{11}H_{12}S_2Si$ $[M]^+$: 236.0150. Found: 235.9756.

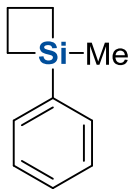
1,1-Dibutylsiletane (2e)



Following the general procedure A to give the desired product 3.1 g, 40% yield, colorless liquid. **R_f** (PE): 0.7. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.06

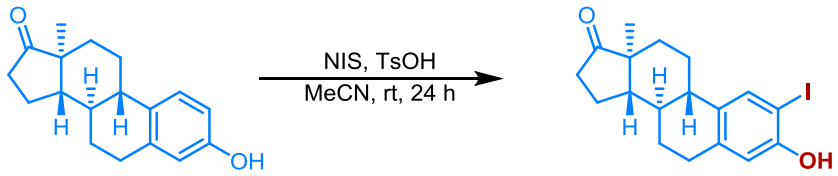
(p, *J* = 8.3 Hz, 2H), 1.57 – 1.31 (m, 8H), 0.99 – 0.94 (t, *J* = 8.0 Hz, 4H), 0.91 (t, *J* = 6.9 Hz, 6H), 0.82 – 0.67 (t, *J* = 8.0 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 26.54, 26.18, 18.63, 15.02, 14.00, 12.31. **MS** (EI) calcd. For $C_{11}H_{24}Si$ $[M]^+$: 184.1647. Found: 184.1602.

1-Methyl-1-phenylsiletane (2f)

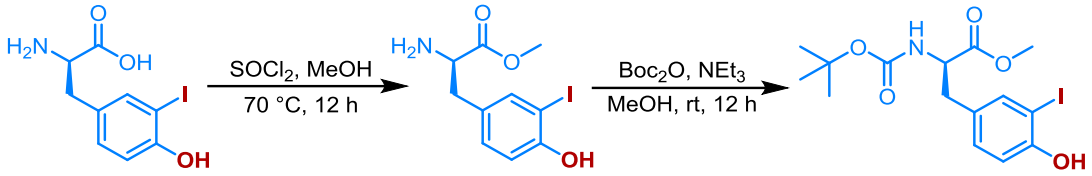


Following the general procedure B to give the desired product 4.76 g, 70% yield, colorless liquid. **R_f** (PE): 0.9. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.50 – 7.38 (m, 3H), 2.23 (p, *J* = 8.2 Hz, 2H), 1.38 – 1.29 (m, 2H), 1.27 – 1.14 (m, 2H), 0.59 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.82, 133.63, 129.55, 128.06, 18.39, 14.49, -1.64. **MS** (EI) calcd. For $C_{10}H_{14}Si$ $[M]^+$: 162.0865. Found: 162.0860.

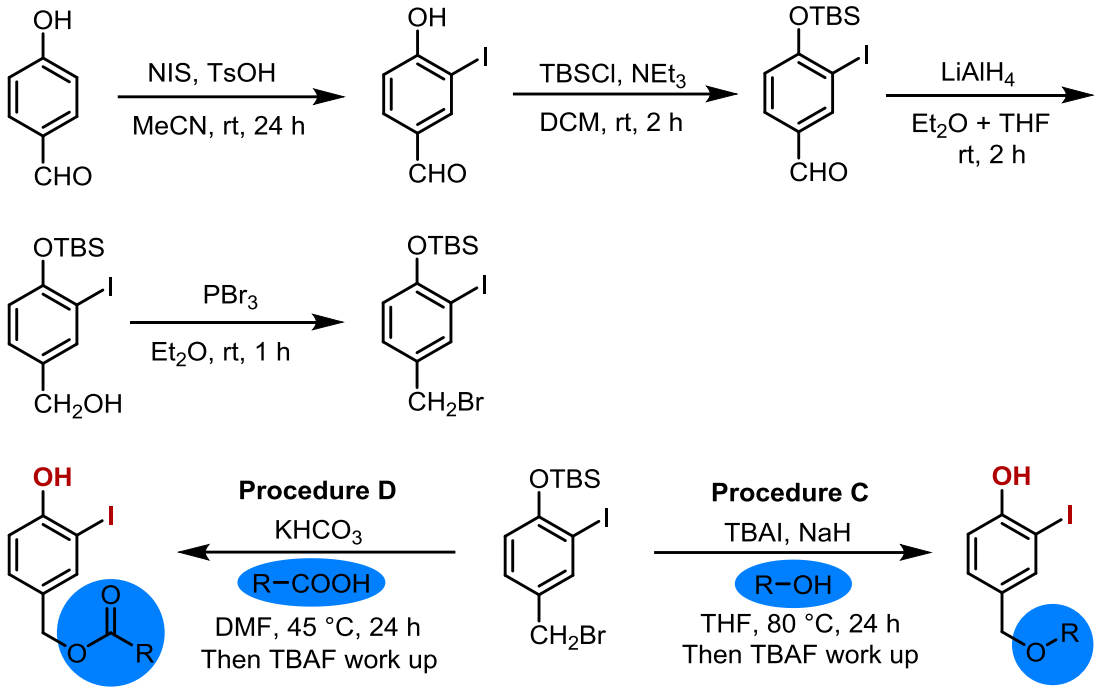
2.2. General procedures for preparation of natural product and drug derivatives



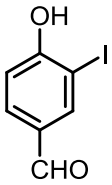
Procedure A: Estrone (811 mg, 3.0 mmol) was dissolved in $CHCl_3$ (20 mL) and N-Iodosuccinimide (743 mg, 3.3 mmol) was added. The mixture was heated to 70 ℃ with stirring for 6 h. After cooling to ambient temperature, EtOAc (50 mL) was added and the organic layer was washed with brine (20 mL), dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude residue was purified by column chromatography (2% to 10% EA/PE) to give the desired product 832 mg, 70% yield, white solid. **R_f** (PE/EA 5:2): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 6.74 (s, 1H), 5.19 (s, 1H), 2.84 (dd, *J* = 8.9, 4.2 Hz, 2H), 2.51 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.26 – 2.16 (m, 1H), 2.11 (dd, *J* = 17.7, 8.9 Hz, 1H), 2.05 – 1.93 (m, 2H), 1.63 (dd, *J* = 8.8, 3.3 Hz, 1H), 1.60 – 1.33 (m, 6H), 0.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.01, 152.83, 139.22, 135.14, 134.66, 115.06, 82.62, 50.42, 48.07, 43.74, 38.18, 35.99, 31.55, 29.24, 26.41, 26.05, 21.70, 13.95. **HRMS** (EI) calcd. For $C_{18}H_{21}IO_2$ $[M]^+$: 396.0586. Found: 396.0580.



Procedure B: $SOCl_2$ (119 mg, 1.1 mmol) was added to MeOH (2 mL) at -5 ℃ before the addition of 3-iodotyrosine (307 mg, 1.0 mmol). The reaction mixture was heated to 70 ℃ with stirring for 8 h. After the reaction was complete, the mixture was cooled to ambient temperature and stirred for an additional 4 h. After the addition of Et_2O (1 mL), the formed precipitate was filtered off and dried under reduced pressure. The crude product was dissolved in MeOH (2 mL) before the addition of Boc_2O (262 mg, 1.2 mmol) and NEt_3 (303 mg, 3.0 mmol). The reaction mixture was stirred at ambient temperature for 12 h. After the reaction was completed, the mixture was adjusted to pH = 3 by the addition of HCl (1 M) and organics were extracted with EtOAc (3x10 mL). The combined organics were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude residue was purified by column chromatography (PE/EA 2:1) to give the desired product as a white solid (0.30 g, 70% yield). $\mathbf{R_f}$ (PE/EA 2:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 6.94 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.54 (s, 1H), 5.10 (d, *J* = 8.3 Hz, 1H), 4.57 – 4.42 (m, 1H), 3.69 (s, 3H), 2.99 (dd, *J* = 14.0, 5.8 Hz, 1H), 2.89 (dd, *J* = 14.0, 6.3 Hz, 1H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.30, 155.27, 154.50, 139.25, 130.72, 129.70, 115.08, 84.96, 80.33, 54.55, 52.42, 36.94, 28.33. **HRMS** (ESI) calcd. For $C_{15}H_{20}INNaO_5$ $[M+Na]^+$: 444.0284. Found: 444.0285.

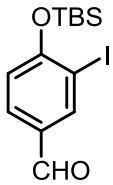


4-Hydroxy-3-iodobenzaldehyde



4-Hydroxybenzaldehyde (12.2 g, 100.0 mmol) and TsOH (17.2 g, 100.0 mmol) was dissolved in MeCN (200 mL) and N-iodosuccinimide (24.8 g, 110.0 mmol) was added. The mixture was stirred at ambient temperature for 24 h before the solvent was filtered and evaporated under reduced pressure to give the crude residue as a yellow oil, which was used directly for the next step without further purification (19.8 g, 80% yield).

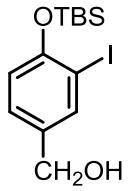
4-((Tert-butyldimethylsilyl)oxy)-3-iodobenzaldehyde



4-Hydroxy-3-iodobenzaldehyde (19.8 g, 80.0 mmol) and NEt_3 (12.1 g, 120.0 mmol) was dissolved in DCM (100 mL) then TBSCl (18.0 g, 120.0 mmol) was added slowly. The mixture was stirred at ambient temperature for 2 h before the solvent was filtered and evaporated under reduced pressure. The crude residue was purified by column chromatography (PE/EA 20:1) to give the desired product as yellow oil (29.0 g, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.27 (d, *J* = 2.1 Hz, 1H), 7.73 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 1.05 (s, 9H), 0.31 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.43, 160.58, 141.67, 131.58, 131.32, 118.21, 91.12, 25.79, 18.45, -3.96. **MS** (EI) calcd.

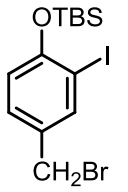
For $C_{13}H_{19}IO_2Si$ $[M]^+$: 362.0199. Found: 361.9253.

(4-((Tert-butyldimethylsilyl)oxy)-3-iodophenyl)methanol



4-((Tert-butyldimethylsilyl)oxy)-3-iodobenzaldehyde (29.0 g, 80.0 mmol) was dissolved in mixture solvent (Et_2O/THF 4:1, 100 mL). $LiAlH_4$ (3.0 g, 80.0 mmol) was added slowly to the solution at ambient temperature then the mixture was stirred for 2 h before the solvent was filtered and evaporated under reduced pressure. The crude residue was purified by column chromatography (PE/EA 5:1) to give the desired product as yellow oil (26.2 g, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.0 Hz, 1H), 7.18 (d, *J* = 6.2 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.54 (s, 2H), 1.97 (s, 1H), 1.06 (s, 9H), 0.27 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.84, 138.47, 135.44, 128.36, 118.49, 90.62, 64.18, 25.98, 18.48, -3.88. **MS** (EI) calcd. For $C_{13}H_{21}IO_2Si$ $[M]^+$: 364.0355. Found: 364.0180.

(4-(Bromomethyl)-2-iodophenoxy)(tert-butyl)dimethylsilane

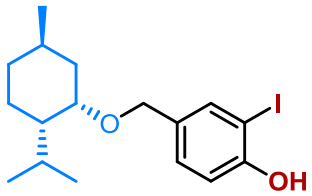


(4-((Tert-butyldimethylsilyl)oxy)-3-iodophenyl)methanol (26.2 g, 72.0 mmol) was dissolved in Et_2O (100 mL). PBr_3 (19.5 g, 72.0 mmol) was added slowly to the solution at ambient temperature then the mixture was stirred for 1 h before the solvent was evaporated under reduced pressure. The crude residue was purified by column chromatography (PE/DCM 5:1) to give the desired product as colorless oil (30.0 g, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.3 Hz, 1H), 7.24 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 4.41 (s, 2H), 1.07 (s, 9H), 0.29 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.50, 140.21, 132.22, 130.29, 118.39, 90.57, 32.43, 25.94, 18.47, -3.89. **MS** (EI) calcd. For $C_{13}H_{20}BrIOSi$ $[M]^+$: 425.9511. Found: 425.8456.

Procedure C: Following a literature's procedure,[5] a 100 mL round-bottom flask was charged with 60 wt% NaH in mineral oil (400 mg, 10.0 mmol). The NaH was washed three times with hexanes (5 mL) and once with THF (5 mL). THF (40 mL) was added to the flask and the mixture was cooled to ambient temperature. A solution of the

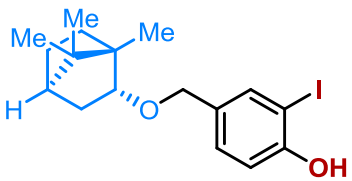
alcoholic natural product (3 mmol) in THF (5 mL) was added dropwise. TBAI (111 mg, 0.3 mmol) was added to the reaction mixture at once followed by the dropwise addition of the corresponding benzyl bromides (2.13 g, 5 mmol). The reaction mixture was stirred at 80 ℃ for 24 h. and then the reaction was quenched with TBAF and water. The product was extracted with EA. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography on silica gel afforded the pure product as colorless oil or white solid (50-81% yield).

2-Iodo-4-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)phenol



Following the general procedure C to give the desired product 0.94 g, 81% yield, colorless liquid. $\mathbf{R_f}$ (PE/EA 5:1): 0.7. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 2.0 Hz, 1H), 7.20 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.03 (s, 1H), 4.56 (d, *J* = 11.3 Hz, 1H), 4.31 (d, *J* = 11.3 Hz, 1H), 3.18 (td, *J* = 10.6, 4.1 Hz, 1H), 2.28 (pd, *J* = 7.0, 2.6 Hz, 1H), 2.18 (dd, *J* = 12.3, 1.9 Hz, 1H), 1.66 (ddt, *J* = 13.1, 10.0, 3.1 Hz, 2H), 1.45 – 1.22 (m, 2H), 1.15 – 0.87 (m, 9H), 0.74 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.54, 138.12, 132.92, 130.00, 115.02, 85.33, 78.74, 69.17, 48.18, 40.26, 34.51, 31.59, 25.51, 23.24, 22.42, 21.10, 16.09. **HRMS** (ESI) calcd. For $C_{17}H_{25}IO_2$ $[M]^+$: 388.0899. Found: 388.0892.

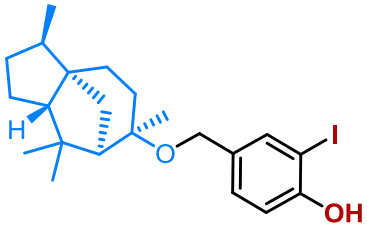
2-Iodo-4-((((1*S*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)phenol



Following the general procedure C to give the desired product 0.93 g, 80% yield, colorless liquid. $\mathbf{R_f}$ (PE/EA 5:1): 0.7. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 1.9 Hz, 1H), 7.21 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 5.27 (s, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 4.32 (d, *J* = 11.9 Hz, 1H), 3.66 (ddd, *J* = 9.4, 3.4, 1.8 Hz, 1H), 2.17 – 2.09 (m, 1H), 2.08 – 2.02 (m, 1H), 1.72 (tt, *J* = 7.5, 3.6 Hz, 1H), 1.65 (t, *J* = 4.6 Hz,

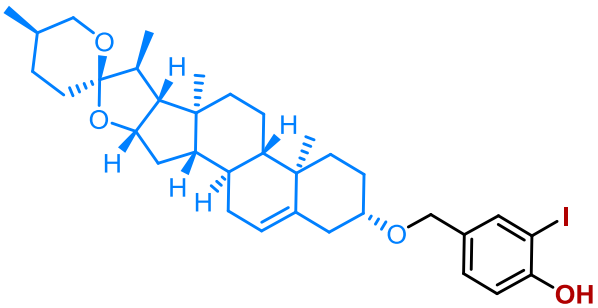
1H), 1.36 – 1.19 (m, 2H), 1.07 (dd, *J* = 13.0, 3.4 Hz, 1H), 0.89 (s, 3H), 0.84 (d, *J* = 8.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.12, 137.24, 133.91, 129.58, 114.90, 85.63, 84.56, 70.49, 49.42, 48.04, 45.16, 36.29, 28.40, 26.90, 19.93, 19.02, 14.20. **HRMS** (ESI) calcd. For $C_{17}H_{23}IO_2$ $[M]^+$: 386.0743. Found: 386.0739.

2-Iodo-4-((((3*R*,3a*S*,6*R*,7*R*,8a*S*)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulen-6-yl)oxy)methyl)phenol



Following the general procedure C to give the desired product 0.68 g, 50% yield, colorless liquid. **R_f** (PE/EA 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.21 (d, *J* = 10.3 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 5.29 (s, 1H), 4.33 (d, *J* = 2.8 Hz, 2H), 1.96 (dd, *J* = 13.0, 6.8 Hz, 1H), 1.91 – 1.88 (m, 1H), 1.84 – 1.78 (m, 1H), 1.77 – 1.69 (m, 2H), 1.67 – 1.60 (m, 2H), 1.59 – 1.49 (m, 2H), 1.48 – 1.42 (m, 1H), 1.41 – 1.37 (m, 2H), 1.30 (d, *J* = 4.8 Hz, 6H), 1.26 (s, 1H), 0.99 (s, 3H), 0.85 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.98, 137.49, 134.18, 129.81, 114.88, 85.70, 79.37, 61.77, 57.03, 56.56, 54.08, 43.50, 41.59, 41.43, 37.19, 33.27, 31.48, 28.96, 27.37, 25.48, 25.19, 15.74. **HRMS** (ESI) calcd. For $C_{22}H_{31}INaO_2$ $[M+Na]^+$: 477.1266. Found: 477.1262.

2-Iodo-4-((((4*S*,5'*R*,6a*R*,6b*S*,8a*S*,8b*R*,9*S*,10*R*,11a*S*,12a*S*,12b*S*)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl)oxy)methyl)phenol

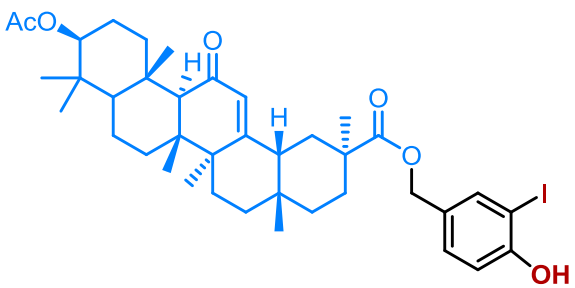


Following the general procedure C to give the desired product 1.16 g, 60% yield, white solid. **R_f** (PE/EA 5:2): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.1 Hz,

1H), 7.20 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 5.53 (d, *J* = 1.5 Hz, 1H), 5.34 (d, *J* = 5.0 Hz, 1H), 4.41 (d, *J* = 11.0 Hz, 3H), 3.47 (dd, *J* = 11.1, 4.2 Hz, 1H), 3.37 (t, *J* = 10.9 Hz, 1H), 3.25 (tt, *J* = 10.8, 4.5 Hz, 1H), 2.40 (ddd, *J* = 13.3, 4.8, 2.3 Hz, 1H), 2.33 – 2.18 (m, 1H), 1.93 (dtd, *J* = 43.7, 13.5, 12.2, 5.3 Hz, 5H), 1.81 – 1.70 (m, 2H), 1.70 – 1.56 (m, 5H), 1.48 (qd, *J* = 12.4, 11.7, 5.5 Hz, 5H), 1.29 (td, *J* = 12.8, 6.3 Hz, 1H), 1.21 – 1.04 (m, 3H), 1.02 (s, 3H), 0.97 (d, *J* = 6.9 Hz, 4H), 0.78 (d, *J* = 2.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.42, 140.94, 137.75, 133.20, 129.90, 121.56, 114.99, 109.47, 85.69, 80.96, 78.73, 68.84, 66.97, 62.16, 56.62, 50.18, 41.72, 40.38, 39.89, 39.19, 37.29, 37.14, 32.20, 31.94, 31.53, 31.48, 30.40, 28.89, 28.51, 20.97, 19.53, 17.27, 16.43, 14.67. **HRMS** (ESI) calcd. For $C_{34}H_{48}IO_4$ $[M+H]^+$: 647.2597. Found: 647.2597.

Procedure D: Following a literature procedure,[6] natural acid (3.0 mmol) and $KHCO_3$ (0.60 g, 6.0 mmol) were placed in a 100 mL flame-dried Schlenk tube. Then 20mL of DMF was added to dissolve the mixture. The solution was warmed up to 40 ˚C. After half an hour later of stirring at 40 ˚C, the corresponding benzyl bromide (2.13 g, 5.0 mmol) was added. After 24 hours of heating at 40 ˚C, the reaction was quenched with TBAF and 500 mL of H_2O. The aqueous solution was extracted with 7x100 mL of EA. The combined organic solutions were washed with 1 M $NaHCO_3$ and water, dried over $MgSO_4$ and filtered. Removal of volatile components under reduced pressure afforded crude product, which was purified by flash column chromatography to yield the pure product as colorless oil or white solid.

4-Hydroxy-3-iodobenzyl(2*S*,4a*S*,6a*S*,6b*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-acetoxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylate



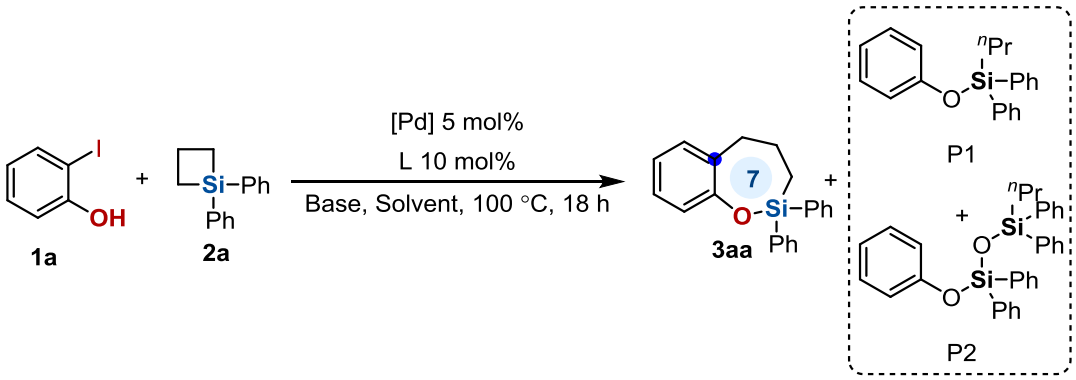
Following the general procedure D to give the desired product 0.67 g, 41% yield, white solid. **R_f** (PE/EA 5:3): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.0 Hz,

1H), 7.23 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.11 (s, 1H), 5.51 (s, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 4.96 (d, *J* = 11.7 Hz, 1H), 2.78 (dt, *J* = 13.6, 3.7 Hz, 1H), 2.33 (s, 1H), 2.04 (s, 3H), 2.01 – 1.94 (m, 2H), 1.92 – 1.86 (m, 1H), 1.79 (td, *J* = 13.8, 4.5 Hz, 1H), 1.73 – 1.53 (m, 6H), 1.43 – 1.36 (m, 3H), 1.33 (s, 3H), 1.27 (s, 1H), 1.24 (d, *J* = 7.1 Hz, 3H), 1.15 (s, 3H), 1.13 (s, 3H), 1.10 (s, 3H), 1.00 (ddd, *J* = 16.5, 13.9, 3.5 Hz, 2H), 0.89 – 0.83 (m, 6H), 0.78 (d, *J* = 10.9 Hz, 1H), 0.73 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.31, 176.28, 171.22, 169.48, 155.36, 138.80, 130.74, 130.48, 128.50, 115.40, 85.47, 80.79, 65.02, 61.83, 60.55, 55.13, 48.36, 45.53, 44.04, 43.32, 41.16, 38.91, 38.17, 37.73, 37.05, 32.82, 31.89, 31.27, 28.61, 28.31, 28.17, 26.56, 23.68, 23.40, 21.44, 18.79, 16.81, 16.55, 14.32. **HRMS** (ESI) calcd. For $C_{39}H_{53}INaO_6$ $[M+Na]^+$: 767.2785. Found: 767.2788.

3. Pd-Catalyzed Ring Expansion Reaction between Silacyclobutanes and 2-Iodophenols

3.1. Reaction condition optimization

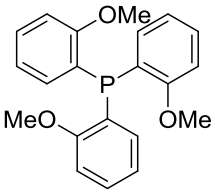
Table S1 Optimization of reaction conditions[a]



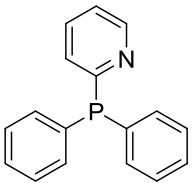
Entry	[Pd] Source	Ligand	Base	Solvent	Yield [%][b]
1	$Pd_2(dba)_3$	IPr•HCl	NEt_3	DMF	28
2	$Pd_2(dba)_3$	IPr•HCl	NEt_3	MeCN	24
3	$Pd_2(dba)_3$	IMes•HCl	NEt_3	MeCN	Trace
4	$Pd_2(dba)_3$	ICy•HCl	NEt_3	MeCN	Trace
5	$Pd_2(dba)_3$	IPr•HCl	Pyridine	MeCN	N.P.
6	$Pd_2(dba)_3$	IPr•HCl	Piperidine	MeCN	17
7	$Pd_2(dba)_3$	IPr•HCl	HTMP	MeCN	21

8	$Pd_2(dba)_3$	IPr•HCl	Pempidine	MeCN	28
9	PdIPr(allyl)Cl	-	Pempidine	MeCN/DMF 10 :1	46
10	$Pd_2(dba)_3$	$P(^tBu)_3$	Pempidine	MeCN/DMF 10 :1	43
11	$[Pd(allyl)Cl]_2$	L_1	Pempidine	MeCN/DMF 10 :1	35
12	$[Pd(allyl)Cl]_2$	DPPP	Pempidine	MeCN/DMF 10 :1	57
13	$[Pd(allyl)Cl]_2$	L_2	Pempidine	MeCN/DMF 10 :1	51
14	$[Pd(allyl)Cl]_2$	DiPPF	Pempidine	MeCN/DMF 10 :1	41
15	$[Pd(allyl)Cl]_2$	L_3	Pempidine	MeCN/DMF 10 :1	41
16	$[Pd(allyl)Cl]_2$	L_4	Pempidine	MeCN/DMF 10 :1	56
17	$[Pd(allyl)Cl]_2$	^{t}BuDavePhos	Pempidine	MeCN/DMF 10 :1	66
18	$Pd(OAc)_2$	^{t}BuDavePhos	Pempidine	MeCN/DMF 10 :1	65
19	$Pd(nbd)Cl_2$	^{t}BuDavePhos	Pempidine	MeCN/DMF 10 :1	72
20	$Pd(MeCN)_2Cl_2$	^{t}BuDavePhos	Pempidine	MeCN/DMF 10 :1	80
21	$Pd(MeCN)_2Cl_2$	^{t}BuDavePhos	NEt_3	MeCN/DMF 10 :1	57
22	$Pd(MeCN)_2Cl_2$	^{t}BuDavePhos	Pempidine/NEt_3 1:1	MeCN/DMF 10 :1	76
23	$Pd(MeCN)_2Cl_2$	^{t}BuDavePhos	Pempidine/NEt_3 1:4	MeCN/DMF 10 :1	64
24[c]	$Pd(MeCN)_2Cl_2$	^{t}BuDavePhos	Pempidine/NEt_3 4:1	MeCN/DMF 10 :1	82 (72)

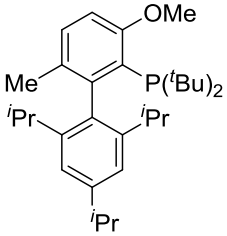
[a] Reactions were carried out by using [Pd] catalyst (5 mol%), ligand (10 mol%), base (0.20 mmol), **1a** (0.11 mmol) **2a** (0.10 mmol) in 1.0 mL solvent for 18 h at 100 ℃ under an N_2 atmosphere. [b] Yield was determined by GC-MS analysis of the mixture, and values in parentheses indicated the isolated yield. N.P.: No product detected. [c] 20 mol% ligand was added.



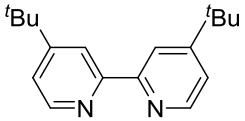
L_1



L_2

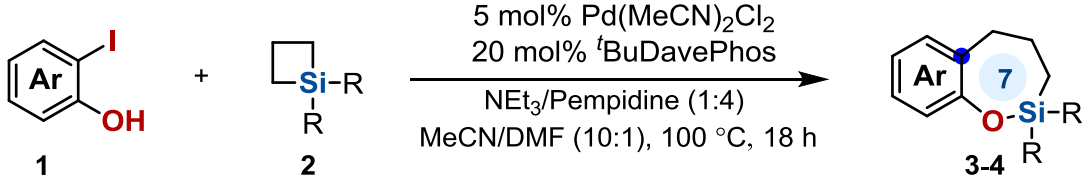


L_3



L_4

3.2. General procedure

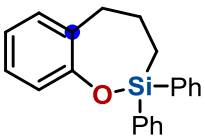


General procedure A: The 25 mL Schlenk tube was added 2-iodophenols **1** (0.22 mmol), silacyclobutanes **2** (0.2 mmol), $Pd(MeCN)_2Cl_2$ (2.6 mg, 5 mol%), ^{t}BuDavePhos (13.6 mg, 20 mol%), NEt_3 (0.08 mmol), pempidine (0.32 mmol), DMF (91 μL) and MeCN (0.91 mL). The formed mixture was stirred at 100 ℃ under N_2 for 18 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (200-300 mesh) by standard technique to afford product **3-4**.

General procedure B: The 25 mL Schlenk tube was added 2-iodophenols **1** (0.22 mmol), silacyclobutans **2** (0.2 mmol), $Pd(MeCN)_2Cl_2$ (2.6 mg, 5 mol%), ^{t}BuDavePhos (13.6 mg, 20 mol%), NEt_3 (0.08 mmol), pempidine (0.32 mmol), DMF (91 μL) and MeCN (0.91 mL). The formed mixture was stirred at 100 ℃ under N_2 for 8 h, then $Pd(MeCN)_2Cl_2$ (2.6 mg, 5 mol%) was added to Schlenk tube and heated for another 10 h. Finally the solution was cooled to room temperature, the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (200-300 mesh) by standard techniques to afford product **3-4**.

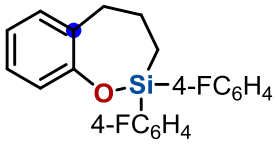
3.3. Characterization of products 3-4

2,2-Diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3aa)



Following the general procedure A to give the desired product 45.5mg, 72% yield, colorless liquid. $\mathbf{R_f}$ (PE/DCM 5:1): 0.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.8, 1.7 Hz, 4H), 7.52 – 7.37 (m, 6H), 7.21 – 7.11 (m, 2H), 7.06 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.96 (td, *J* = 7.3, 1.3 Hz, 1H), 2.93 – 2.80 (m, 2H), 2.02 (dt, *J* = 13.2, 6.9 Hz, 2H), 1.36 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.60, 135.26, 134.33, 132.23, 130.20, 128.14, 128.12, 127.88, 122.32, 120.94, 32.75, 22.88, 12.20. **HRMS** (ESI) calcd. For $C_{21}H_{20}OSi$ $[M+H]^+$: 317.1362. Found: 317.1360.

9-Fluoro-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ab)



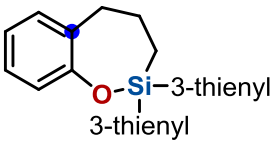
Following the general procedure A to give the desired product 54.9 mg, 78% yield, colorless liquid. $\mathbf{R_f}$ (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.61 (dd, *J* = 8.5, 6.2

Hz, 4H), 7.10 (q, *J* = 8.6 Hz, 6H), 7.02 – 6.90 (m, 2H), 2.87 – 2.75 (m, 2H), 1.98 (p, *J* = 6.9 Hz, 2H), 1.31 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.49 (d, *J* = 249.8 Hz), 154.27, 136.41 (d, *J* = 7.6 Hz), 132.18, 130.79, 130.64 (d, *J* = 3.7 Hz), 127.99, 122.57, 120.85, 115.50 (d, *J* = 19.8 Hz), 32.76, 22.84, 12.48. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.26. **HRMS** (EI) calcd. For $C_{21}H_{18}F_2OSi$ $[M]^+$: 352.1095. Found: 352.1089.

2,2-Bis(4-methoxyphenyl)-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ac)

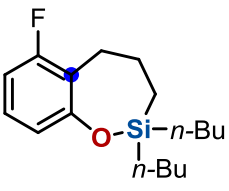
Following the general procedure A to give the desired product 51.1 mg, 68% yield, colorless liquid. **R_f** (PE/DCM 5:2): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.6, 2.4 Hz, 4H), 7.20 – 7.09 (m, 2H), 7.05 – 6.99 (m, 1H), 6.96 (dd, *J* = 8.5, 2.5 Hz, 5H), 3.85 (s, 6H), 2.93 – 2.76 (m, 2H), 2.16 – 1.92 (m, 2H), 1.31 (td, *J* = 7.0, 2.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.25, 154.70, 135.97, 132.42, 130.62, 127.81, 126.51, 122.19, 120.97, 113.86, 55.16, 32.82, 22.98, 12.61. **HRMS** (EI) calcd. For $C_{23}H_{24}O_3Si$ $[M]^+$: 376.1495. Found: 376.1488.

2,2-Di(thiophen-3-yl)-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ad)



Following the general procedure A to give the desired product 40.7 mg, 62% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 2.6, 1.1 Hz, 2H), 7.34 (dd, *J* = 4.8, 2.6 Hz, 2H), 7.18 (dd, *J* = 4.8, 1.1 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.92 – 6.83 (m, 2H), 2.89 – 2.72 (m, 2H), 2.00 – 1.85 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.19, 136.12, 134.84, 132.66, 131.65, 130.75, 127.92, 126.26, 122.55, 121.04, 33.08, 23.00, 14.40. **HRMS** (EI) calcd. For $C_{17}H_{16}OS_2Si$ $[M]^+$: 328.0412. Found: 328.0406.

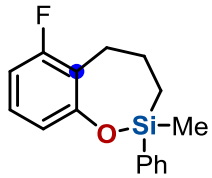
2,2-Dibutyl-6-fluoro-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3be)



Following the general procedure A to give the desired product 41.2 mg, 70% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.7. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 6.87 (m, 2H), 6.81 (dd, *J* = 7.1, 3.6 Hz, 2H), 2.86 – 2.71 (m, 2H), 1.86 (p, *J* = 6.7 Hz, 2H), 1.46 – 1.24 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 6H), 0.82 (t, *J* = 6.8 Hz, 2H), 0.73 (dd, *J* =

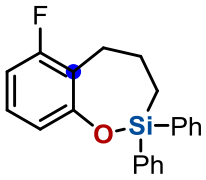
9.6, 6.3 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.58 (d, *J* = 243.8 Hz), 142.40 (d, *J* = 12.2 Hz), 135.96, 125.21 (d, *J* = 3.6 Hz), 121.45 (d, *J* = 7.5 Hz), 114.35 (d, *J* = 19.3 Hz), 33.17, 33.15, 26.40, 24.88, 22.97, 13.75, 13.73, 12.95. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -133.99. **HRMS** (ESI) calcd. For $C_{17}H_{27}FOSi$ $[M]^+$: 294.1815. Found: 294.1807.

6-Fluoro-2-methyl-2-phenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3bf)



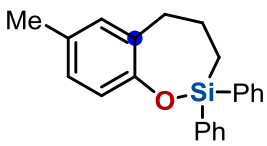
Following the general procedure A to give the desired product 34.3 mg, 63% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.7. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.25 (dtd, *J* = 7.1, 5.6, 5.2, 2.2 Hz, 3H), 6.92 – 6.81 (m, 1H), 6.62 – 6.43 (m, 2H), 2.60 (dt, *J* = 7.1, 4.6 Hz, 2H), 1.86 – 1.66 (m, 2H), 0.97 (ddd, *J* = 15.1, 8.7, 6.4 Hz, 1H), 0.83 (ddd, *J* = 15.1, 6.9, 5.9 Hz, 1H), 0.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.19 (d, *J* = 243.9 Hz), 155.47 (d, *J* = 11.5 Hz), 136.35, 133.47, 131.09, 131.00, 130.19, 128.16, 108.72 (d, *J* = 54.0 Hz), 108.50 (d, *J* = 28.3 Hz), 32.52, 22.99 (d, *J* = 1.5 Hz), 14.12, -2.07. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.39. **HRMS** (ESI) calcd. For $C_{16}H_{17}FOSi$ $[M]^+$: 272.1033. Found: 272.1031.

6-Fluoro-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ba)



Following the general procedure A to give the desired product 48.1 mg, 72% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.58 (m, 4H), 7.49 – 7.35 (m, 6H), 7.02 (dd, *J* = 8.4, 6.8 Hz, 1H), 6.74 (dd, *J* = 10.0, 2.7 Hz, 1H), 6.63 (td, *J* = 8.3, 2.6 Hz, 1H), 2.82 – 2.72 (m, 2H), 2.04 – 1.91 (m, 2H), 1.33 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.12 (d, *J* = 244.2 Hz), 155.39 (d, *J* = 11.6 Hz), 134.70, 134.15, 130.91 (d, *J* = 9.8 Hz), 130.25, 128.09, 127.90 (d, *J* = 3.3 Hz), 108.87 (d, *J* = 20.9 Hz), 108.28 (d, *J* = 22.9 Hz), 32.06, 22.77, 12.04. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.30. **HRMS** (ESI) calcd. For $C_{21}H_{20}FOSi$ $[M+H]^+$: 335.1267. Found: 335.1268.

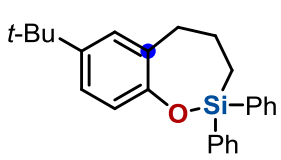
7-Methyl-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ca)



Following the general procedure A to give the desired product 42.9 mg, 65% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.5.

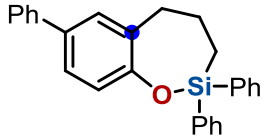
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.7, 1.7 Hz, 4H), 7.44 (ddt, *J* = 10.7, 8.6, 4.8 Hz, 6H), 6.96 (d, *J* = 9.9 Hz, 3H), 2.88 – 2.78 (m, 2H), 2.31 (s, 3H), 2.03 (p, *J* = 6.9 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.25, 135.40, 134.35, 131.84, 131.47, 131.26, 130.15, 128.29, 128.07, 120.61, 32.78, 22.93, 20.73, 12.29. **HRMS** (ESI) calcd. For $C_{22}H_{23}OSi$ $[M+H]^+$: 331.1518. Found: 331.1518.

7-(Tert-butyl)-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3da)



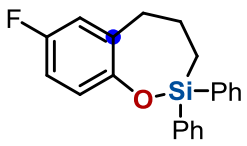
Following the general procedure A to give the desired product 41.7 mg, 56% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.6. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.7, 1.7 Hz, 4H), 7.48 – 7.35 (m, 6H), 7.16 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 2.89 – 2.74 (m, 2H), 2.00 (dt, *J* = 13.2, 6.9 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 2H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.20, 144.90, 135.56, 134.33, 131.12, 130.12, 128.09, 127.52, 124.65, 120.13, 34.24, 33.07, 31.72, 22.91, 12.13. **HRMS** (ESI) calcd. For $C_{25}H_{29}OSi$ $[M+H]^+$: 373.1988. Found: 373.1988.

2,2,7-Triphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ea)



Following the general procedure B to give the desired product 56.4 mg, 72% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.7, 1.7 Hz, 4H), 7.59 – 7.52 (m, 2H), 7.46 – 7.35 (m, 9H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 2.95 – 2.79 (m, 2H), 2.18 – 1.92 (m, 2H), 1.37 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.27, 141.04, 135.30, 135.19, 134.31, 132.44, 130.26, 129.42, 128.79, 128.16, 126.92, 126.79, 126.53, 121.23, 32.99, 22.90, 12.22. **MS** (EI) calcd. For $C_{27}H_{24}OSi$ $[M]^+$: 392.1596. Found: 392.1581.

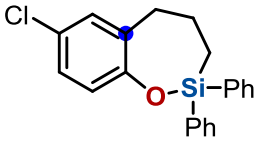
7-Fluoro-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3fa)



Following the general procedure A to give the desired product 53.4 mg, 80% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.9, 1.6 Hz, 4H), 7.50 – 7.35 (m, 6H), 6.95 (ddt, *J* = 6.2, 4.7, 1.4 Hz, 1H), 6.86 – 6.77 (m, 2H), 2.86 – 2.72 (m, 2H), 2.11 – 1.94 (m, 2H), 1.35 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.97 (d, *J* = 239.4 Hz), 150.40 (d, *J* = 2.4 Hz), 134.92, 134.31, 133.76 (d, *J* = 7.6

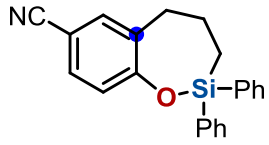
Hz), 130.32, 128.17, 121.62 (d, J = 8.4 Hz), 116.79 (d, J = 22.6 Hz), 113.93 (d, J = 22.7 Hz), 32.79, 22.68, 12.15. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -122.47. **HRMS** (ESI) calcd. For $C_{21}H_{20}FOSi$ $[M+H]^+$: 335.1267. Found: 335.0076.

7-Chloro-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ga)



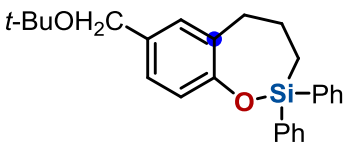
Following the general procedure A to give the desired product 49.0 mg, 70% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.8, 1.7 Hz, 4H), 7.55 – 7.34 (m, 6H), 7.10 (dq, J = 5.1, 2.7 Hz, 2H), 7.01 – 6.87 (m, 1H), 2.90 – 2.65 (m, 2H), 2.13 – 1.94 (m, 2H), 1.36 (t, J = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.14, 134.67, 134.19, 133.94, 130.28, 130.22, 128.10, 127.56, 126.77, 122.07, 32.58, 22.58, 12.05. **HRMS** (EI) calcd. For $C_{21}H_{19}ClOSi$ $[M]^+$: 350.0894. Found: 351.0886.

2,2-Diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine-7-carbonitrile (3ha)



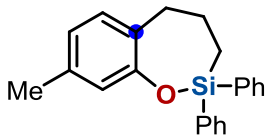
Following the general procedure A to give the desired product 42.2 mg, 62% yield, colorless liquid. **R_f** (PE/DCM 5:2): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, J = 2.1 Hz, 1H), 7.39 (s, 1H), 7.35 – 7.28 (m, 5H), 7.22 (dt, J = 14.6, 7.3 Hz, 6H), 2.94 – 2.81 (m, 2H), 2.05 (p, J = 6.8 Hz, 2H), 1.38 (t, J = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.57, 133.95, 133.50, 133.17, 130.20, 129.71, 128.05, 127.89, 127.60, 119.22, 105.57, 33.08, 22.73, 12.05. **HRMS** (ESI) calcd. For $C_{22}H_{19}NNaOSi$ $[M+Na]^+$: 364.1134. Found: 364.1739.

7-(Tert-butoxymethyl)-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ia)



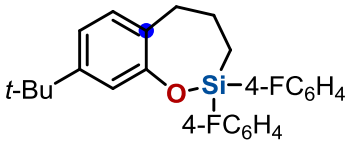
Following the general procedure B to give the desired product 56.3 mg, 70% yield, colorless liquid. **R_f** (PE/DCM 5:2): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.8, 1.7 Hz, 4H), 7.49 – 7.34 (m, 6H), 7.18 – 7.07 (m, 2H), 6.99 (d, J = 8.0 Hz, 1H), 4.36 (s, 2H), 2.97 – 2.75 (m, 2H), 1.99 (tt, J = 7.4, 5.6 Hz, 2H), 1.33 (t, J = 7.0 Hz, 2H), 1.30 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.75, 135.31, 134.35, 133.41, 131.97, 130.17, 130.14, 128.10, 127.24, 120.77, 73.40, 63.99, 32.89, 27.86, 22.77, 12.31. **HRMS** (ESI) calcd. For $C_{26}H_{30}O_2Si$ $[M]^+$: 402.2015. Found: 402.2008.

8-Methyl-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ja)



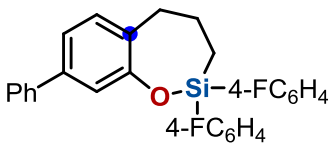
Following the general procedure A to give the desired product 40.3 mg, 61% yield, colorless liquid. $\mathbf{R_f}$ (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.59 (m, 4H), 7.48 – 7.35 (m, 6H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 6.75 (dd, *J* = 7.5, 1.8 Hz, 1H), 2.82 – 2.73 (m, 2H), 2.29 (s, 3H), 1.97 (dt, *J* = 13.3, 6.9 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.31, 137.65, 135.35, 134.19, 130.25, 130.02, 128.81, 127.98, 122.88, 121.40, 32.25, 22.86, 21.00, 12.01. **HRMS** (ESI) calcd. For $C_{22}H_{22}OSi$ $[M]^+$: 330.1440. Found:330.1433.

8-(Tert-butyl)-2,2-bis(4-fluorophenyl)-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3lb)



Following the general procedure A to give the desired product 61.2 mg, 75% yield, colorless liquid. $\mathbf{R_f}$ (PE/DCM 5:1): 0.6. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 4H), 7.12 – 7.05 (m, 4H), 7.04 – 6.99 (m, 2H), 6.95 (dd, *J* = 7.8, 2.0 Hz, 1H), 2.85 – 2.72 (m, 2H), 1.96 (ddd, *J* = 10.7, 8.7, 5.4 Hz, 2H), 1.34 (t, *J* = 7.0 Hz, 2H), 1.27 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.45 (d, *J* = 250.0 Hz), 153.79, 151.48, 136.46 (d, *J* = 7.7 Hz), 130.68 (d, *J* = 3.8 Hz), 130.30, 129.23, 119.30, 118.32, 115.43 (d, *J* = 19.9 Hz), 34.50, 32.61, 31.43, 23.08, 13.01. **HRMS** (ESI) calcd. For $C_{25}H_{27}F_2OSi$ $[M+H]^+$: 409.1799. Found: 409.1798.

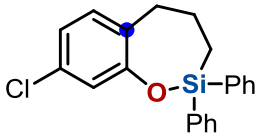
2,2-Bis(4-fluorophenyl)-8-phenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3mb)



Following the general procedure A to give the desired product 68.5 mg, 80% yield, colorless liquid. $\mathbf{R_f}$ (PE/DCM 5:1): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 4H), 7.61 – 7.56 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (dtd, *J* = 7.3, 5.2, 4.6, 1.9 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.13 (dd, *J* = 10.0, 7.8 Hz, 4H), 2.92 – 2.82 (m, 2H), 2.04 (ddd, *J* = 11.3, 8.9, 5.6 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.38 (d, *J* = 249.8 Hz), 154.48, 141.13, 140.65, 136.29 (d, *J* = 8.0

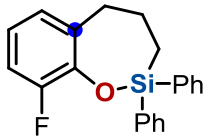
Hz), 134.50, 131.02, 128.74, 127.75, 127.25, 126.97, 121.13, 119.29, 115.42 (d, *J* = 19.9 Hz), 32.39, 22.75, 12.34. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.62. **HRMS** (ESI) calcd. For $C_{27}H_{23}F_2OSi$ $[M+H]^+$: 429.1486. Found: 429.2047.

8-Chloro-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ka)



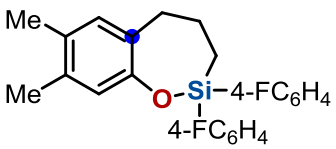
Following the general procedure A to give the desired product 53.9 mg, 77% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.9, 1.7 Hz, 4H), 7.50 – 7.36 (m, 6H), 7.10 – 6.98 (m, 2H), 6.91 (dd, *J* = 8.0, 2.1 Hz, 1H), 2.86 – 2.67 (m, 2H), 1.98 (p, *J* = 6.9 Hz, 2H), 1.35 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.32, 134.79, 134.25, 132.56, 131.35, 130.76, 130.39, 128.23, 122.43, 121.18, 32.27, 22.73, 11.98. **HRMS** (EI) calcd. For $C_{21}H_{19}ClOSi$ $[M]^+$: 350.0894. Found: 350.0887.

9-Fluoro-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3nb)



Following the general procedure A to give the desired product 42.0 mg, 63% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.7, 1.7 Hz, 4H), 7.42 (tdd, *J* = 8.5, 7.2, 4.8 Hz, 6H), 6.96 (ddd, *J* = 10.0, 6.9, 2.9 Hz, 1H), 6.89 – 6.79 (m, 2H), 2.95 – 2.78 (m, 2H), 2.03 (dq, *J* = 8.8, 6.7 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.46 (d, *J* = 244.7 Hz), 142.36 (d, *J* = 11.7 Hz), 135.23, 134.72, 134.23, 130.36, 128.18, 125.51 (d, *J* = 3.2 Hz), 122.05 (d, *J* = 7.6 Hz), 114.80 (d, *J* = 19.3 Hz), 33.12 (d, *J* = 2.5 Hz), 22.93, 12.91. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -132.31. **HRMS** (ESI) calcd. For $C_{21}H_{19}FNaOSi$ $[M+Na]^+$: 357.1087. Found: 357.1080.

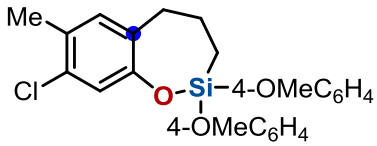
2,2-Bis(4-fluorophenyl)-7,8-dimethyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ob)



Following the general procedure A to give the desired product 41.8 mg, 55% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51

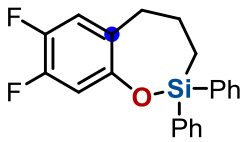
(dd, *J* = 8.4, 6.2 Hz, 4H), 7.00 (t, *J* = 8.9 Hz, 4H), 6.76 (s, 1H), 6.70 (s, 1H), 2.73 – 2.60 (m, 2H), 2.10 (s, 3H), 2.08 (s, 3H), 1.86 (qd, *J* = 6.9, 4.1 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.31 (d, *J* = 249.9 Hz), 151.85, 136.26 (d, *J* = 7.7 Hz), 135.93, 131.71, 130.82 (d, *J* = 4.0 Hz), 130.13, 128.80, 121.69, 115.30 (d, *J* = 19.7 Hz), 32.26, 22.86, 19.40, 18.79, 12.44. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.92. **HRMS** (ESI) calcd. For $C_{23}H_{22}F_2OSi$ $[M]^+$: 380.1408. Found: 380.1401.

8-Chloro-2,2-bis(4-methoxyphenyl)-7-methyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3pc)



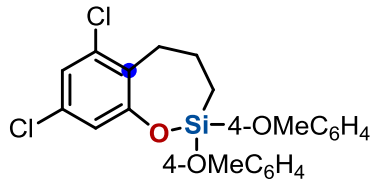
Following the general procedure A to give the desired product 52.6 mg, 62% yield, colorless liquid. **R_f** (PE/DCM 5:2): 0.2. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 4H), 7.00 (s, 1H), 6.98 – 6.91 (m, 5H), 3.83 (s, 6H), 2.81 – 2.65 (m, 2H), 2.27 (s, 3H), 1.95 (dt, *J* = 13.1, 6.9 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.35, 153.17, 135.93, 132.43, 132.19, 130.93, 129.22, 126.17, 121.29, 113.94, 55.17, 32.39, 22.91, 19.19, 12.56. **HRMS** (ESI) calcd. For $C_{24}H_{25}ClNaO_3Si$ $[M+Na]^+$: 447.1159. Found: 447.1158.

7,8-Difluoro-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ra)



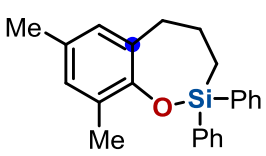
Following the general procedure A to give the desired product 54.2 mg, 77% yield, colorless liquid. **R_f** (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.59 (m, 4H), 7.48 – 7.35 (m, 6H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 6.75 (dd, *J* = 7.5, 1.8 Hz, 1H), 2.82 – 2.73 (m, 2H), 2.29 (s, 3H), 1.97 (dt, *J* = 13.3, 6.9 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.8 (dd, *J* = 262.6, 20.2 Hz), 148.1 (dd, *J* = 284.82, 23.2 Hz), 144.29 (d, *J* = 12.4 Hz), 134.40, 134.14, 130.36, 128.14, 117.91 (d, *J* = 18.2 Hz), 117.90 (d, *J* = 17.2 Hz), 109.85 (d, *J* = 18.5 Hz), 32.14, 22.58, 12.03. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.09 (d, *J* = 21.5 Hz), -146.88 (d, *J* = 22.1 Hz). **HRMS** (ESI) calcd. For $C_{21}H_{18}F_2OSi$ $[M]^+$: 352.1095. Found: 352.1089.

6,8-Dichloro-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3sc)



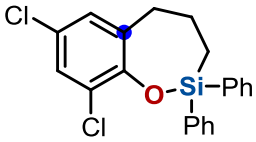
Following the general procedure A to give the desired product 53.3 mg, 60% yield, colorless liquid. **R*f*** (PE/DCM 5:2): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.54 (m, 4H), 7.21 (d, *J* = 2.6 Hz, 1H), 6.99 (d, *J* = 2.6 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 4H), 3.82 (s, 6H), 2.88 – 2.71 (m, 2H), 2.02 (p, *J* = 6.7 Hz, 2H), 1.37 (t, *J* = 6.9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) 161.43, 149.61, 136.04, 135.62, 128.94, 127.99, 126.47, 126.38, 125.50, 113.88, 55.16, 33.66, 22.82, 13.10. **HRMS** (ESI) calcd. For $C_{23}H_{22}Cl_2NaO_3Si$ $[M+Na]^+$: 467.0613. Found: 467.0611.

7,9-Dimethyl-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ta)



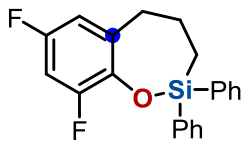
Following the general procedure A to give the desired product 37.2 mg, 54% yield, colorless liquid. **R*f*** (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.2 Hz, 4H), 7.43 (dt, *J* = 14.5, 7.2 Hz, 6H), 6.85 (s, 1H), 6.80 (s, 1H), 2.80 (t, *J* = 6.3 Hz, 2H), 2.28 (s, 3H), 2.12 (s, 3H), 2.02 (p, *J* = 6.9 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.47, 135.58, 134.30, 131.29, 130.82, 130.02, 129.76, 128.64, 128.56, 127.92, 32.66, 22.77, 20.61, 16.91, 11.90. **HRMS** (ESI) calcd. For $C_{23}H_{25}OSi$ $[M+H]^+$: 345.1675. Found: 345.1671.

7,9-Dichloro-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3ua)



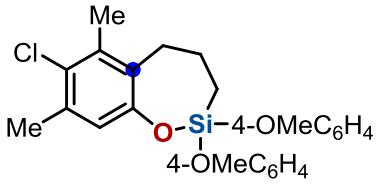
Following the general procedure A to give the desired product 51.4 mg, 67% yield, colorless liquid. **R*f*** (PE/DCM 5:1): 0.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.9, 1.6 Hz, 4H), 7.47 – 7.35 (m, 6H), 7.22 (d, *J* = 2.6 Hz, 1H), 6.99 (d, *J* = 2.6 Hz, 1H), 2.86 – 2.68 (m, 2H), 2.03 (tt, *J* = 6.8, 5.2 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.50, 135.40, 134.36, 134.26, 130.51, 128.99, 128.17, 128.09, 126.53, 126.46, 33.59, 22.69, 12.65. **MS** (EI) calcd. For $C_{21}H_{18}Cl_2OSi$ $[M]^+$: 384.0504. Found: 384.0521.

7,9-Difluoro-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (3va)



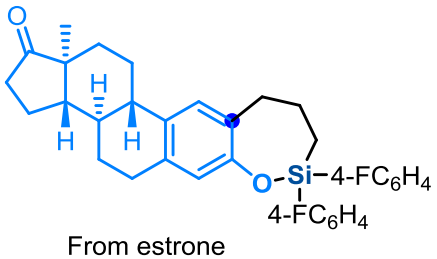
Following the general procedure A to give the desired product 50.0 mg, 71% yield, colorless liquid. **R*f*** (PE/DCM 5:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 4H), 7.51 – 7.35 (m, 6H), 6.70 (ddd, *J* = 10.7, 8.3, 2.9 Hz, 1H), 6.61 (dd, *J* = 8.7, 2.6 Hz, 1H), 2.95 – 2.70 (m, 2H), 2.11 – 1.97 (m, 2H), 1.52 – 1.28 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.44 (dd, *J* = 276.7, 11.1 Hz), 155.04 (dd, *J* = 286.84, 13.1 Hz), 135.68 (d, *J* = 8.1 Hz), 134.27, 134.09, 130.35, 128.10, 111.73 (dd, *J* = 22.0, 3.5 Hz), 102.89 (d, *J* = 26.3 Hz), 102.66 (d, *J* = 26.2 Hz), 33.22, 22.65, 12.78. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.39, -127.66. **HRMS** (EI) calcd. For $C_{21}H_{18}F_2OSi$ $[M]^+$: 352.1095. Found: 352.1088.

7-Chloro-2,2-bis(4-methoxyphenyl)-6,8-dimethyl-2,3,4,5-tetrahydrobenzo[*f*][1,2] oxasilepine (3wc)



Following the general procedure A to give the desired product 41.1 mg, 47% yield, colorless liquid. **R*f*** (PE/DCM 5:2): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.6 Hz, 4H), 6.94 (d, *J* = 8.6 Hz, 4H), 6.75 (s, 1H), 3.83 (s, 6H), 2.85 (t, *J* = 6.7 Hz, 2H), 2.35 (s, 3H), 2.30 (s, 3H), 1.90 (p, *J* = 6.8 Hz, 2H), 1.18 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.29, 153.03, 135.89, 134.91, 134.76, 128.92, 128.28, 126.45, 120.19, 113.90, 55.19, 28.02, 21.03, 20.85, 16.88, 10.85. **HRMS** (ESI) calcd. For $C_{25}H_{27}ClNaO_3Si$ $[M+Na]^+$: 461.1316. Found: 461.1315.

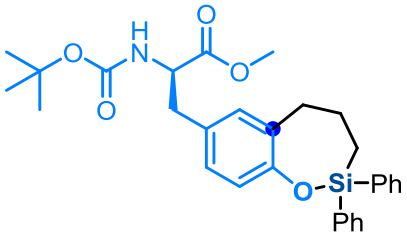
(3a*S*,3b*R*,12b*S*,14a*S*)-8,8-Bis(4-fluorophenyl)-14a-methyl-2,3,3a,3b,4,5,8,9,10,11, 12b,13,14,14a-tetradecahydro-1H-cyclopenta[7,8]phenanthro[3,2-*f*][1,2]oxasilepi n-1-one (4a)



From estrone

Following the general procedure A to give the desired product 45.4 mg, 43% yield, colorless liquid. **R_f** (PE/EA 10:1): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.12 – 7.06 (m, 4H), 7.00 (s, 1H), 6.73 (s, 1H), 2.90 – 2.81 (m, 2H), 2.74 (q, *J* = 5.8 Hz, 2H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.30 – 2.20 (m, 1H), 2.15 (q, *J* = 9.7, 9.3 Hz, 1H), 2.10 – 2.03 (m, 1H), 2.02 – 1.88 (m, 3H), 1.72 – 1.36 (m, 7H), 1.31 (t, *J* = 6.8 Hz, 2H), 0.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.13, 164.45 (d, *J* = 249.8 Hz), 152.17, 136.37 (d, *J* = 7.7 Hz), 136.21, 133.67, 130.93 (d, *J* = 3.3 Hz), 129.16, 127.63, 120.61, 115.47 (d, *J* = 19.9 Hz), 50.63, 48.15, 44.19, 38.46, 36.02, 32.71, 31.77, 29.20, 26.73, 26.07, 22.97, 21.74, 14.03, 12.33. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.86. **HRMS** (ESI) calcd. For $C_{33}H_{34}F_2O_2Si$ $[M+Na]^+$: 551.2194. Found: 551.2190.

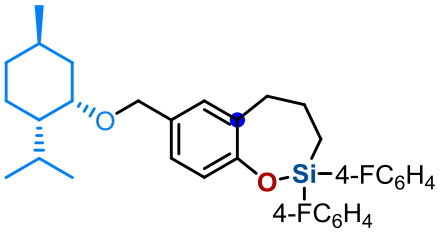
Methyl-(*R*)-2-((*tert*-butoxycarbonyl)amino)-3-(2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepin-7-yl)propanoate (4b)



From tyrosine

Following the general procedure B to give the desired product 63.1 mg, 61% yield, colorless liquid. **R_f** (PE/EA 5:1): 0.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.56 (m, 4H), 7.40 (tt, *J* = 8.2, 5.8 Hz, 6H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.89 – 6.84 (m, 2H), 4.96 (d, *J* = 8.4 Hz, 1H), 4.53 (q, *J* = 6.7 Hz, 1H), 3.66 (s, 3H), 2.99 (t, *J* = 5.1 Hz, 2H), 2.83 – 2.73 (m, 2H), 1.97 (dt, *J* = 13.1, 6.9 Hz, 2H), 1.42 (s, 9H), 1.32 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.65, 155.23, 153.65, 135.18, 134.30, 132.30, 131.53, 130.23, 129.70, 128.61, 128.12, 120.98, 79.99, 54.72, 52.19, 37.78, 32.81, 28.45, 22.93, 12.24. **HRMS** (ESI) calcd. For $C_{30}H_{35}NNaO_5Si$ $[M+Na]^+$: 540.2182. Found: 540.2179.

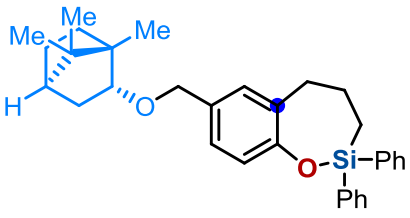
2,2-Bis(4-fluorophenyl)-7-((((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (4c)



From L-Menthol

Following the general procedure A to give the desired product 86.3 mg, 83% yield, colorless liquid. **R_f** (PE/EA 10:1): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (ddd, *J* = 8.3, 6.2, 1.9 Hz, 4H), 7.15 – 7.04 (m, 6H), 6.94 (d, *J* = 7.9 Hz, 1H), 4.56 (d, *J* = 11.1 Hz, 1H), 4.31 (d, *J* = 11.1 Hz, 1H), 3.14 (td, *J* = 10.5, 4.1 Hz, 1H), 2.79 (dd, *J* = 7.4, 5.2 Hz, 2H), 2.28 (pd, *J* = 7.0, 2.7 Hz, 1H), 2.18 (dtd, *J* = 12.2, 3.9, 1.9 Hz, 1H), 1.98 (p, *J* = 6.9 Hz, 2H), 1.64 (ddt, *J* = 13.5, 9.6, 3.1 Hz, 2H), 1.44 – 1.20 (m, 4H), 0.94 (d, *J* = 6.5 Hz, 4H), 0.89 (d, *J* = 7.1 Hz, 4H), 0.69 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.49 (d, *J* = 249.8 Hz), 153.65, 136.42 (d, *J* = 7.6 Hz), 133.12, 131.95, 130.72, 130.62, 127.87, 120.66, 115.49 (d, *J* = 20.0 Hz), 78.57, 70.25, 48.41, 40.47, 34.73, 32.85, 31.74, 25.62, 23.39, 22.75, 22.53, 21.18, 16.18, 12.55. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.46. **HRMS** (ESI) calcd. For $C_{32}H_{38}F_2NaO_2Si$ $[M+Na]^+$: 543.2507. Found:543.2505.

2,2-Diphenyl-7-((((1*S*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)methyl)-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (4d)

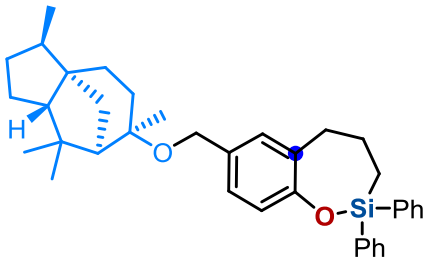


From Borneol

Following the general procedure A to give the desired product 72.3 mg, 75% yield, colorless liquid. **R_f** (PE/EA 10:1): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 4.0 Hz, 4H), 7.36 – 7.27 (m, 6H), 7.09 – 6.96 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 4.28 (d, *J* = 11.8 Hz, 1H), 3.78 – 3.46 (m, 1H), 2.73 (dd, *J* = 7.6, 5.1 Hz, 2H), 2.09 – 1.95 (m, 2H), 1.91 (p, *J* = 6.7 Hz, 2H), 1.64 (tt, *J* = 7.9, 3.7 Hz, 1H),

1.56 (t, *J* = 4.6 Hz, 1H), 1.31 – 1.21 (m, 2H), 1.22 – 1.14 (m, 2H), 0.99 (dd, *J* = 12.9, 3.3 Hz, 1H), 0.80 (d, *J* = 1.4 Hz, 3H), 0.77 (s, 3H), 0.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.64, 135.16, 134.23, 133.13, 131.81, 130.08, 129.74, 128.00, 126.88, 120.56, 84.20, 71.42, 49.26, 47.90, 45.05, 36.21, 32.76, 28.30, 26.81, 22.76, 19.84, 18.91, 14.10, 12.18. **HRMS** (ESI) calcd. For $C_{32}H_{38}O_2Si$ $[M]^+$: 482.2641. Found: 482.2634.

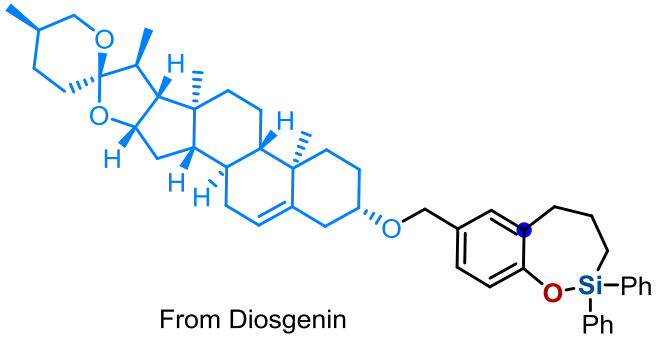
2,2-Diphenyl-7-((((3*R*,3a*S*,6*R*,7*R*,8a*S*)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulen-6-yl)oxy)methyl)-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (4e)



From Cedrol

Following the general procedure B to give the desired product 77.0 mg, 70% yield, colorless liquid. **R_f** (PE/EA 20:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.8, 1.7 Hz, 4H), 7.43 – 7.35 (m, 6H), 7.10 (dd, J = 8.1, 2.3 Hz, 1H), 7.07 (d, J = 2.2 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 4.36 (dd, J = 2.6 Hz, 2H), 2.86 – 2.72 (m, 2H), 1.98 (dt, J = 11.9, 6.2 Hz, 3H), 1.92 (t, J = 5.7 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.79 – 1.66 (m, 2H), 1.69 – 1.59 (m, 2H), 1.53 – 1.48 (m, 2H), 1.45 (dt, J = 9.2, 2.3 Hz, 1H), 1.43 – 1.37 (m, 2H), 1.34 – 1.32 (m, 8H), 1.31 (s, 1H), 1.00 (s, 3H), 0.85 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.68, 135.37, 134.36, 133.44, 131.87, 130.28, 130.17, 128.11, 127.36, 120.71, 79.13, 62.74, 57.11, 56.59, 54.09, 43.52, 41.63, 41.48, 37.22, 33.33, 32.91, 31.54, 28.98, 27.42, 25.51, 25.24, 22.79, 15.76, 12.27. **HRMS** (ESI) calcd. For $C_{37}H_{46}NaO_2Si$ $[M+Na]^+$: 573.3165. Found: 573.3166.

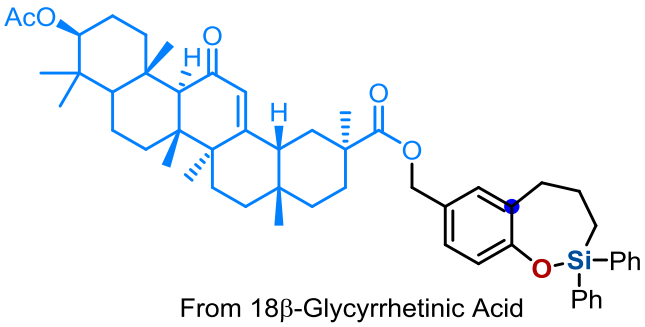
2,2-Diphenyl-7-((((4*S*,5'*R*,6a*R*,6b*S*,8a*S*,8b*R*,9*S*,10*R*,11a*S*,12a*S*,12b*S*)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-*b*]furan-10,2'-pyran]-4-yl)oxy)methyl)-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (4f)



From Diosgenin

Following the general procedure A to give the desired product 117.2 mg, 79% yield, colorless liquid. **R_f** (PE/EA 5:1): 0.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 4H), 7.43 – 7.37 (m, 6H), 7.12 – 7.09 (m, 2H), 6.99 (d, *J* = 7.9 Hz, 1H), 5.48 – 5.22 (m, 1H), 4.62 – 4.32 (m, 3H), 3.53 – 3.45 (m, 1H), 3.39 (t, *J* = 10.9 Hz, 1H), 3.28 (tt, *J* = 11.1, 4.5 Hz, 1H), 2.81 (t, *J* = 6.3 Hz, 2H), 2.50 – 2.39 (m, 1H), 2.28 (t, *J* = 12.4 Hz, 1H), 2.05 – 1.83 (m, 7H), 1.83 – 1.71 (m, 2H), 1.72 – 1.56 (m, 5H), 1.58 – 1.43 (m, 5H), 1.34 (t, *J* = 6.9 Hz, 2H), 1.30 – 1.11 (m, 4H), 1.04 (s, 3H), 0.99 (d, *J* = 7.0 Hz, 4H), 0.80 (t, *J* = 3.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.01, 141.23, 135.24, 134.34, 132.65, 132.10, 130.36, 130.20, 128.11, 127.48, 121.38, 120.82, 109.43, 80.97, 78.71, 69.98, 66.99, 62.24, 56.68, 50.25, 41.74, 40.41, 39.94, 39.30, 37.39, 37.19, 32.87, 32.25, 32.00, 31.58, 31.53, 30.45, 28.94, 28.59, 22.79, 21.00, 19.56, 17.29, 16.44, 14.68, 12.29. **HRMS** (ESI) calcd. For $C_{49}H_{62}NaO_4Si$ $[M+Na]^+$: 765.4315. Found: 765.5041.

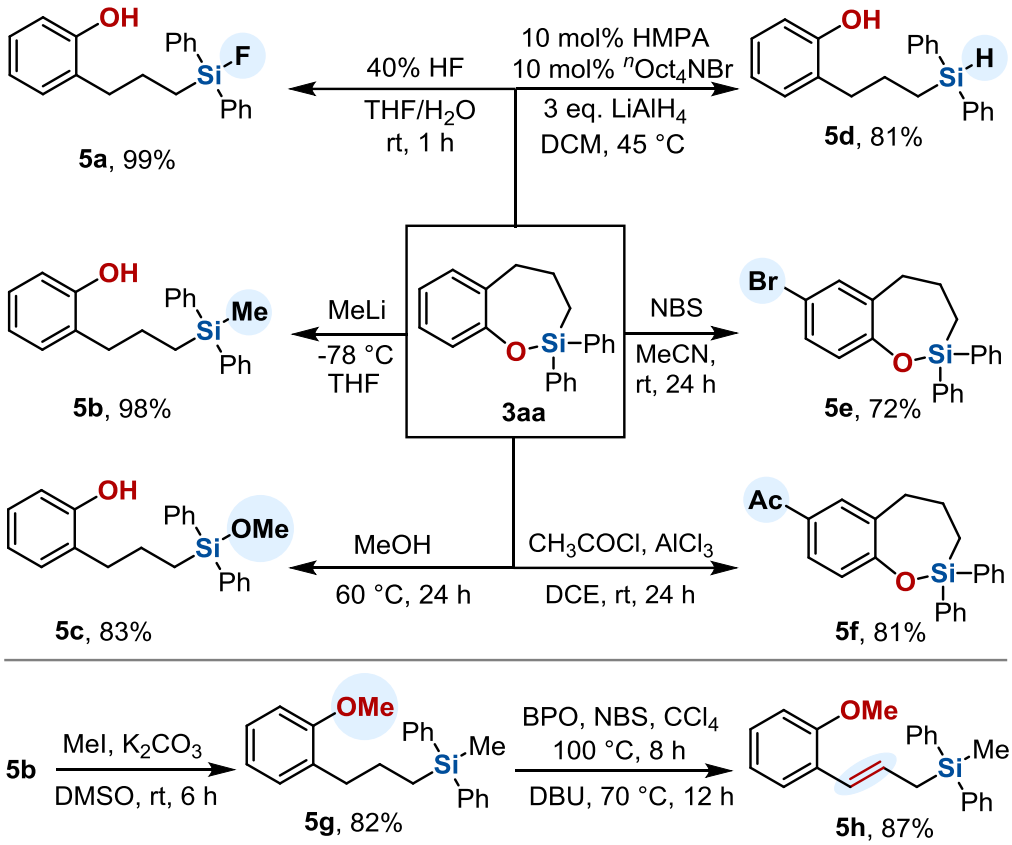
(2,2-Diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepin-7-yl)methyl(2*S*,4a*S*,6a*S*,6b*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-acetoxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylate (4g)



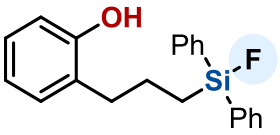
From 18β-Glycyrrhetinic Acid

Following the general procedure A to give the desired product 87.4 mg, 52% yield, colorless liquid. **R$_f$** (PE/EA 5:1): 0.6. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 4H), 7.39 (dtdd, *J* = 11.0, 8.5, 5.9, 2.1 Hz, 6H), 7.16 – 7.11 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 1H), 5.58 (s, 1H), 5.12 (d, *J* = 11.9 Hz, 1H), 5.00 (d, *J* = 11.9 Hz, 1H), 2.96 – 2.74 (m, 3H), 2.33 (s, 1H), 2.05 (s, 3H), 2.03 – 1.94 (m, 4H), 1.91 (t, *J* = 3.1 Hz, 1H), 1.82 – 1.71 (m, 1H), 1.69 – 1.53 (m, 6H), 1.52 – 1.37 (m, 3H), 1.33 (s, 3H), 1.29 (t, *J* = 6.9 Hz, 3H), 1.25 (t, *J* = 3.5 Hz, 3H), 1.15 (s, 3H), 1.13 (s, 3H), 1.09 (s, 3H), 1.00 – 0.96 (m, 2H), 0.87 (d, *J* = 1.8 Hz, 6H), 0.79 (d, *J* = 11.2 Hz, 1H), 0.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.01, 176.46, 171.17, 169.31, 154.75, 135.16, 134.32, 132.34, 131.17, 130.24, 130.22, 130.08, 128.61, 128.41, 128.14, 120.99, 80.78, 66.12, 61.83, 55.16, 48.25, 45.45, 44.07, 43.30, 41.21, 38.92, 38.19, 37.78, 37.08, 32.83, 32.64, 31.85, 31.38, 29.85, 28.59, 28.37, 28.19, 26.57, 26.54, 23.72, 23.44, 22.73, 21.47, 18.82, 17.52, 16.83, 16.57, 12.05. **HRMS** (MADLI-TOF) calcd. For $C_{54}H_{68}NaO_6Si$ $[M+Na]^+$: 863.4683. Found: 863.4683.

4. Synthetic Utilities of Products 3aa and 5b



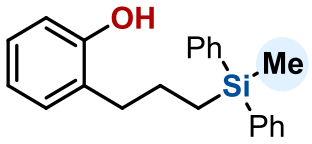
2-(3-(Fluorodiphenylsilyl)propyl)phenol (5a)



Conversion of 3aa to 5a: To a 0 ℃ solution of **3aa** (63.2 mg, 0.20 mmol) in THF (2 mL) was added slowly 48% hydrofluoric acid (25 µL, 0.60 mmol). The mixture was allowed to warm to room temperature, stirred for 1 h and the solvent was removed with a rotary evaporator. The residue was partitioned between ethyl acetate and water. The aqueous phase was extracted with ethyl acetate, the combined organics were washed with water until neutral, washed with sat. NaCl, dried over $MgSO_4$ and concentrated in vacuo, the crude mixture was purified by column chromatography on reversed phase column to give **5a** as a colorless oil (66.5 mg, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 4H), 7.36 – 7.20 (m, 6H), 6.97 – 6.89 (m, 2H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 4.58 (s, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.69 (q, *J* = 8.2, 7.7 Hz, 2H), 1.16 (q, *J* = 8.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) 153.52, 134.23 (d, *J* = 2.0 Hz), 133.48 (d, *J* = 16.3 Hz), 130.69, 130.50, 128.19,

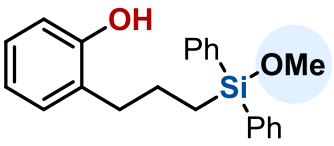
127.85, 127.33, 120.85, 115.35, 33.23, 22.83, 13.93 (d, J = 14.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -171.23. **HRMS** (EI) calcd. For $C_{21}H_{21}FOSi$ $[M\text{-}F]^+$: 317.1362. Found: 317.1311.

2-(3-(Methyldiphenylsilyl)propyl)phenol (5b)



Conversion of 3aa to 5b: Following a literature procedure,[7] **3aa** (63.2 mg, 0.20 mmol) was dissolved in THF (2 mL) at -78 ℃, MeLi (0.60 mmol) was added into the reaction mixture, which was stirred at -78 ℃ for 30 min and at room temperature for 24 h. The reaction was quenched by adding saturated aqueous ammonium chloride solution, then the mixture was acidified to pH 4-5 with aqueous HCl (1 M). The mixture was extracted with diethyl ether. The combined organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. The volatiles were removed in vacuo, and the crude mixture was purified by column chromatography on reversed phase column to afford **5b** (65.1 mg, 98%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.5, 1.9 Hz, 4H), 7.36 (dtd, J = 7.0, 5.2, 2.2 Hz, 6H), 7.07 (dd, J = 7.4, 1.7 Hz, 2H), 6.86 (t, J = 7.5 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 4.60 (s, 1H), 2.65 (t, J = 7.6 Hz, 2H), 1.73 (dtd, J = 12.4, 9.2, 8.5, 6.8 Hz, 2H), 1.31 – 1.10 (m, 2H), 0.55 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.44, 137.26, 134.50, 130.37, 129.15, 128.10, 127.84, 127.14, 120.76, 115.23, 33.71, 24.14, 14.11, -4.39. **HRMS** (EI) calcd. For $C_{22}H_{24}OSi$ $[M\text{-}CH_3]^+$: 317.1362. Found: 317.1312.

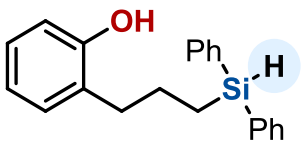
2-(3-(Methoxydiphenylsilyl)propyl)phenol (5c)



Conversion of 3aa to 5c: **3aa** (63.2 mg, 0.20 mmol) was dissolved in MeOH (1 mL), which was stirred at 60 ℃ for 24 h. and the crude mixture was purified by column chromatography on reversed phase column to afford compound **5c** (57.8 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.8, 1.6 Hz, 4H), 7.50 – 7.37 (m, 6H), 7.16 – 7.05 (m, 2H), 6.86 (td, J = 7.4, 1.2 Hz, 1H), 6.81 (dd, J = 7.9, 1.2 Hz, 1H), 5.83 (s, 1H), 3.58 (s, 3H), 2.70 (dd, J = 8.3, 6.7 Hz, 2H), 1.83 (p, J = 7.7 Hz, 2H), 1.23 (t, J

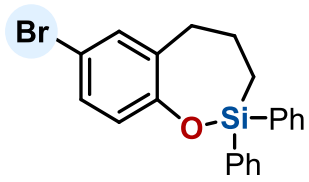
= 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.12, 134.88, 134.27, 130.40, 130.17, 128.12, 127.90, 127.40, 120.61, 115.73, 51.81, 32.81, 23.79, 13.07. **HRMS** (EI) calcd. For $C_{22}H_{24}O_2Si$ [M-OMe]$^+$: 317.1362. Found: 317.1311.

2-(3-(Diphenylsilyl)propyl)phenol (5d)



Conversion of 3aa to 5d: Following a literature procedure,[8] a vial was charged with a DCM suspension (1 mL) of $LiAlH_4$ (22.8 mg, 0.60 mmol), (^{n}Oct)$_4$NBr (11.2 mg, 0.02 mmol), **3aa** (63.2 mg, 0.20 mmol) and HMPA (3.6 mg, 0.02 mmol) was added at room temperature, and then the solution was stirred at 45 ℃ for 24 h. The solution was diluted with hexane (4 mL) and filtered through a silica gel pad. The volatiles were removed in vacuo, the crude mixture was purified by column chromatography on reversed phase column to afford compound **5d** (51.5 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.7, 1.8 Hz, 4H), 7.46 – 7.33 (m, 6H), 7.09 (ddd, *J* = 7.2, 4.0, 2.4 Hz, 2H), 6.87 (td, *J* = 7.4, 1.2 Hz, 1H), 6.74 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.91 (t, *J* = 3.7 Hz, 1H), 4.61 (s, 1H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.82 (tt, *J* = 9.1, 6.8 Hz, 2H), 1.30 – 1.19 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.54, 135.28, 134.50, 130.50, 129.69, 128.13, 128.08, 127.29, 120.89, 115.36, 33.38, 24.76, 12.16. **HRMS** (EI) calcd. For $C_{21}H_{22}OSi$ [M-H]$^+$: 317.1362. Found: 317.1312.

7-Bromo-2,2-diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepine (5e)

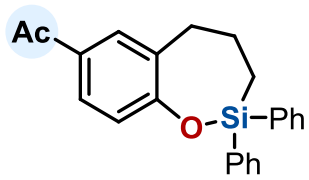


Conversion of 3aa to 5e: **3aa** (63.2 mg, 0.2 mmol) was dissolved in MeCN (200 mL) and *N*-bromosuccinimide (38.7 mg, 2.2 mmol) was added. The mixture was stirred at ambient temperature for 24 h before the solvent was filtered and evaporated under reduced pressure. The crude residue was purified by column chromatography (PE/DCM 5:1) to give the desired product **5e** as yellow oil (56.7 mg, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.9, 1.6 Hz, 4H), 7.35 – 7.20 (m, 6H), 7.12 – 7.04 (m, 2H), 6.74 (d, *J* = 9.2 Hz, 1H), 2.68 – 2.55 (m, 2H), 1.93 – 1.78 (m, 2H), 1.20 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.80,

134.73, 134.59, 134.28, 133.22, 130.65, 130.38, 128.20, 122.69, 114.44, 32.62, 22.68, 12.13. **HRMS** (EI) calcd. For $C_{21}H_{19}BrOSi$ $[M]^+$: 394.0389. Found: 394.0381.

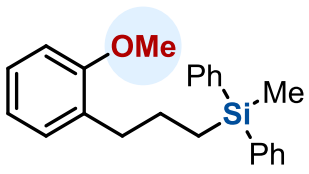
Stille coupling of 5e with tributyl(phenyl)stannane: The 25 mL Schlenk tube was added **5e** (78.8 mg, 0.20 mmol), tributyl(phenyl)stannane (147.2 mg, 0.40 mmol), $Pd(PPh_3)_4$ (11.5 mg, 5 mol%), NEt_3 (0.4 mmol) and toluene (1.0 mL). The formed mixture was stirred at 110 ℃ under N_2 for 24 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (200-300 mesh) to afford product **3ea** as yellow oil (51.0 mg, 65%).

1-(2,2-Diphenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2]oxasilepin-7-yl)ethan-1-one (5f)



Conversion of 3aa to 5f: Acetyl chloride (17.2 mg, 0.22 mmol) and $AlCl_3$ (29.3 mg, 0.22 mmol) was dissolved in DCE (1 mL) and **3aa** (63.2 mg, 0.20 mmol) was added. The mixture was stirred at ambient temperature for 24 h before the solvent was filtered and evaporated under reduced pressure. The crude residue was purified by column chromatography (PE/DCM 5:1) to give the desired product **5f** as yellow oil (58.0 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (dq, *J* = 4.5, 2.4 Hz, 2H), 7.59 – 7.51 (m, 4H), 7.42 – 7.25 (m, 6H), 6.97 (d, *J* = 8.9 Hz, 1H), 2.83 – 2.70 (m, 2H), 2.46 (s, 3H), 2.00 – 1.87 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.34, 159.34, 134.57, 134.25, 132.49, 131.85, 131.38, 130.47, 129.04, 128.24, 121.02, 32.86, 26.56, 22.71, 12.18. **HRMS** (EI) calcd. For $C_{23}H_{22}O_2Si$ $[M]^+$: 358.1389. Found: 358.1382.

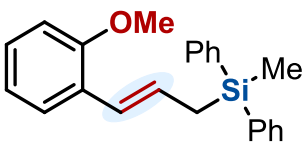
(3-(2-Methoxyphenyl)propyl)(methyl)diphenylsilane (5g)



Conversion of 5b to 5g: K_2CO_3 (82.8 mg, 0.60 mmol) and MeI (85.2 mg, 0.60 mmol) was dissolved in DMSO (2 mL) and **5b** (66.4 mg, 0.20 mmol) was added. The mixture was stirred at ambient temperature for 6 h before the solvent was filtered and evaporated under reduced pressure to give the crude residue **5g** as a yellow oil, which was used directly for the next step without further

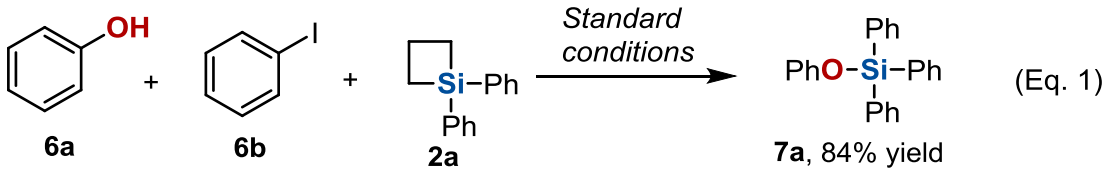
purification.

(E)-(3-(2-Methoxyphenyl)allyl)(methyl)diphenylsilane (5h)



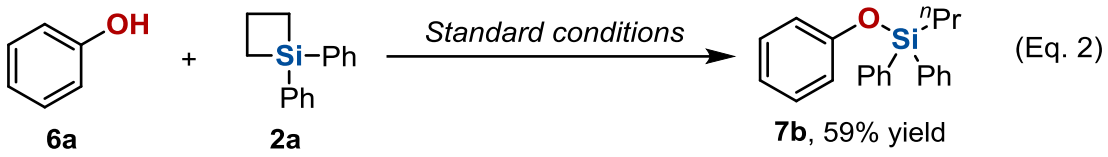
Conversion of 5g to 5h: a mixture of **5g** (69.2 mg, 0.2 mmol), *N*-bromosuccinimide (42.2 mg, 0.24 mmol), and benzoyl peroxide (0.1 equiv.) in CCl_4 (2 mL) was stirred at 100 ℃ for 8 h. Then DBU (2 equiv.) was added, which were stirred at 70 ℃ for 12 hours under argon atmosphere. After cooling down to room temperature, the mixture was evaporated in vacuo. Purification of the residue by column chromatography on reversed phase column afforded the **5h** (59.8 mg, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.53 (m, 4H), 7.39 (d, *J* = 6.9 Hz, 6H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.14 (m, 1H), 6.97 – 6.82 (m, 2H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 16.0, 8.1 Hz, 1H), 3.82 (s, 3H), 2.46 – 2.20 (d, *J* = 9.5 Hz, 2H), 0.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.12, 136.67, 134.63, 129.31, 127.86, 127.55, 127.40, 127.31, 126.29, 124.42, 120.64, 110.88, 55.51, 21.91, -4.54. **HRMS** (EI) calcd. For $C_{23}H_{24}OSi$ $[M]^+$: 344.1596. Found: 344.1590.

5. Mechanistic Experiments



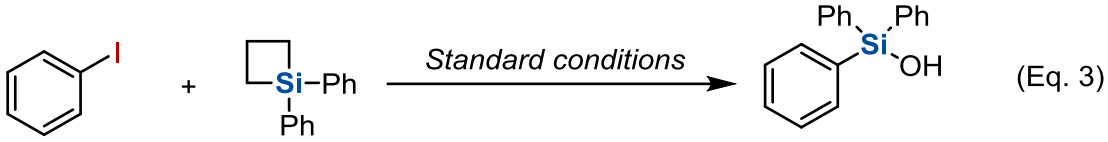
Equation 1: The 25 mL Schlenk tube was added phenol **6a** (0.22 mmol), Silacyclobutane derivatives **2a** (0.2 mmol), iodobenzene **6b** (0.22 mmol), $Pd(MeCN)_2Cl_2$ (2.6 mg, 5 mol%), ^{t}BuDavePhos (13.6 mg, 20 mol%), NEt_3 (0.08 mmol), Pempidine (0.32 mmol), DMF (91 μL) and MeCN (0.91 mL). The formed mixture was stirred at 100 ℃ under N_2 for 18 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (200-300 mesh) by standard techniques to afford product **7a** (isolated yield 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.47 (m, 6H), 7.31 (t, *J* = 7.4 Hz, 3H), 7.24 (t, *J* = 7.2 Hz, 6H), 7.03 – 6.95 (m,

2H), 6.75 (dd, *J* = 14.5, 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.20, 135.66, 133.73, 130.44, 129.45, 128.09, 121.71, 120.21.



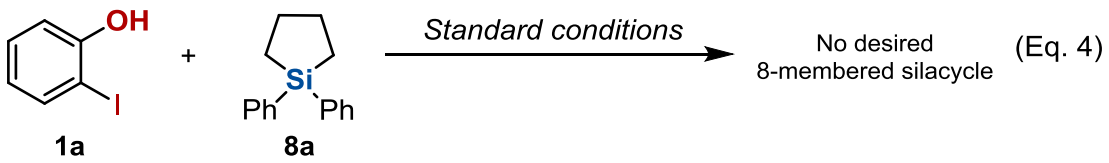
6a **2a** **7b**, 59% yield (Eq. 2)

Equation 2: The 25 mL Schlenk tube was added phenol **6a** (0.22 mmol), Silacyclobutane **2a** (0.2 mmol), $Pd(MeCN)_2Cl_2$ (2.6 mg, 5 mol%), ^{t}BuDavePhos (13.6 mg, 20 mol%), NEt_3 (0.08 mmol), Pempidine (0.32 mmol), DMF (91 μL) and MeCN (0.91 mL). The formed mixture was stirred at 100 ℃ under N_2 for 18 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (200-300 mesh) by standard techniques to afford product **7b** (isolated yield 59%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.1 Hz, 4H), 7.27 (dq, *J* = 14.0, 7.1 Hz, 6H), 7.01 (t, *J* = 7.7 Hz, 2H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 1.34 (h, *J* = 7.4 Hz, 2H), 1.19 – 1.08 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.23, 134.72, 130.07, 129.37, 127.95, 121.43, 119.89, 18.12, 16.71, 16.59.



6b **2a** **7c**, 86% yield (Eq. 3)

Equation 3: The 25 mL Schlenk tube was added Iodobenzene **6b** (0.22 mmol), Silacyclobutane **2a** (0.2 mmol), $Pd(MeCN)_2Cl_2$ (2.6 mg, 5 mol%), ^{t}BuDavePhos (13.6 mg, 20 mol%), NEt_3 (0.08 mmol), Pempidine (0.32 mmol), DMF (91 μL) and MeCN (0.91 mL). The formed mixture was stirred at 100 ℃ under N_2 for 18 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum directly. The crude product was purified by column chromatography on silica gel (200-300 mesh) by standard techniques to afford product **7c** (86% isolated yield).



Equation 4: The 25 mL Schlenk tube was added 2-Iodophenol **1a** (0.22 mmol), 1,1-diphenylsilolane **8a** (0.2 mmol), $Pd(MeCN)_2Cl_2$ (2.6 mg, 5 mol%), ^{t}BuDavePhos (13.6 mg, 20 mol%), NEt_3 (0.08 mmol), Pempidine (0.32 mmol), DMF (91 μL) and MeCN (0.91 mL). The formed mixture was stirred at 100 ℃ under N_2 for 18 h. The solution was then cooled to room temperature, and the solvent was removed under vaccum directly. The crude product was detected by GC-MS and no corresponding target product was found. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 4H), 7.30 – 7.18 (m, 6H), 1.78 – 1.63 (m, 4H), 1.13 – 0.84 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.97, 134.83, 129.25, 127.91, 27.79, 12.21.

6. References

1) M. J. Bosiak, *ACS Catal*., 2016, **6**, 2429.

2) Q. Zhou, F. Lu, D. Liu, Q. Lu and W. Xiao, *Org. Chem. Front*., 2018, **5**, 3098.

3) J. D. Sunderhaus, H. Lam and G. B. Dudley, *Org. Lett*., 2003, **5**, 4571.

4) B. Fan, J. Zhang, R. Li and W. Fan, *Catal. Lett.*, 2008, **121**, 297.

5) N. Kennedy and T. Cohen, *J. Org. Chem.*, 2015, **80**, 8134.

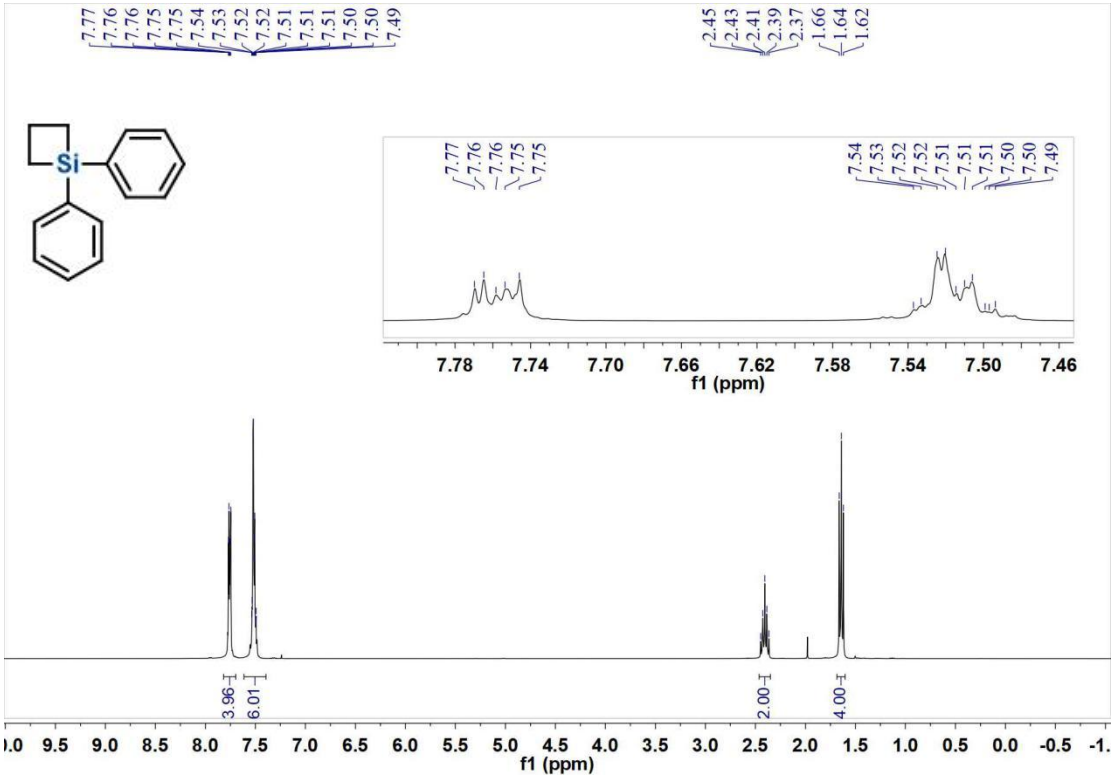
6) S. A. Nair, B. Lee and D. G. Hangauer, *Synthesis* 1995, **7**, 810.

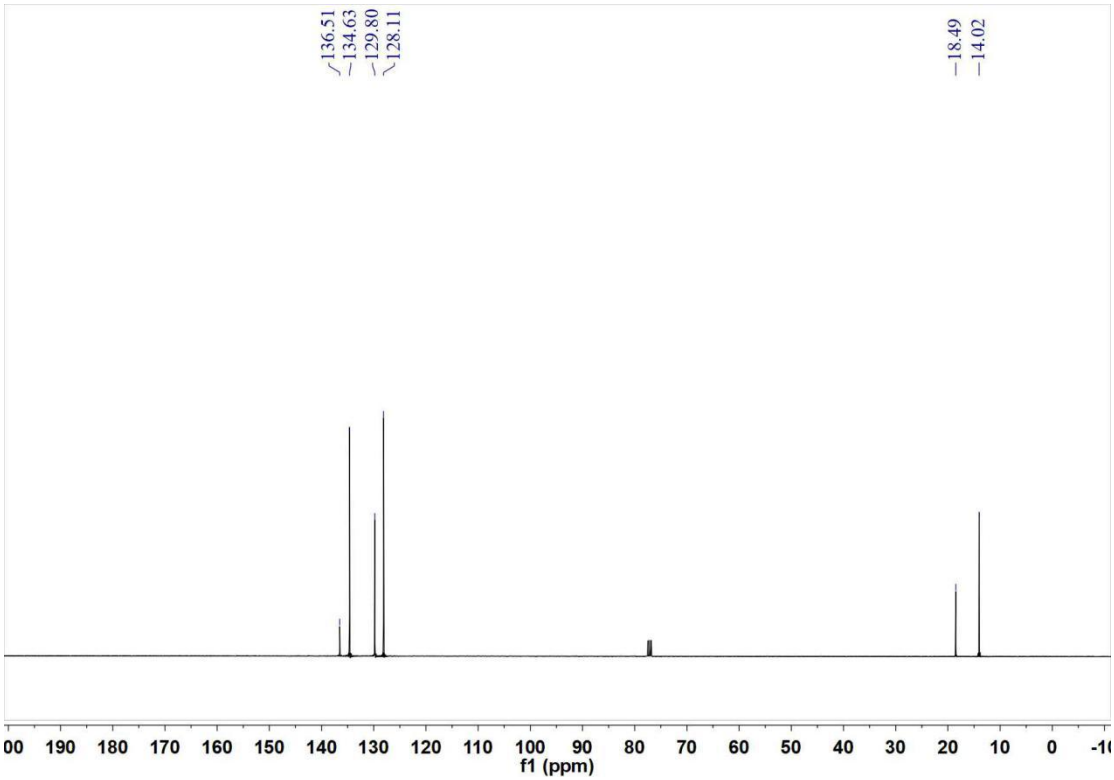
7) Y. Hua, P. Asgari, T. Avullala and J. Jeon, *J. Am. Chem. Soc.*, 2016, **138**, 7982.

8) Y. Qin, J. Han, C. Ju and D. Zhao, *Angew. Chem. Int. Ed.*, 2020, **59**, 8481.

7. NMR Spectra

2a





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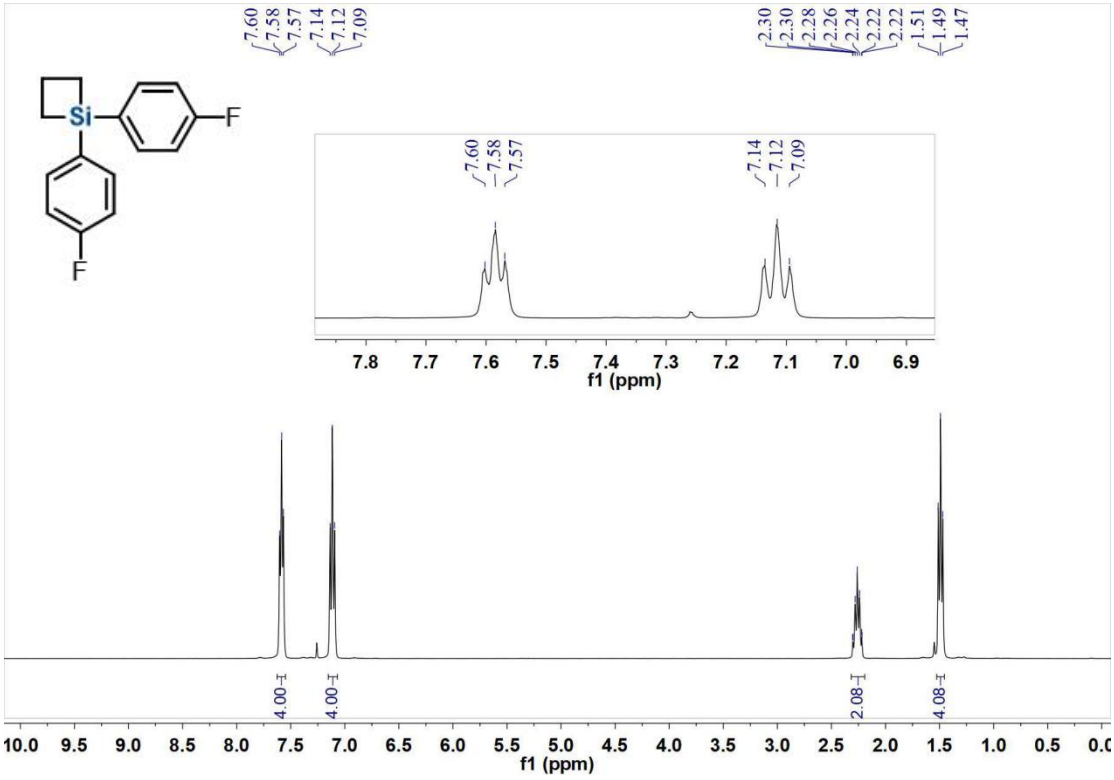
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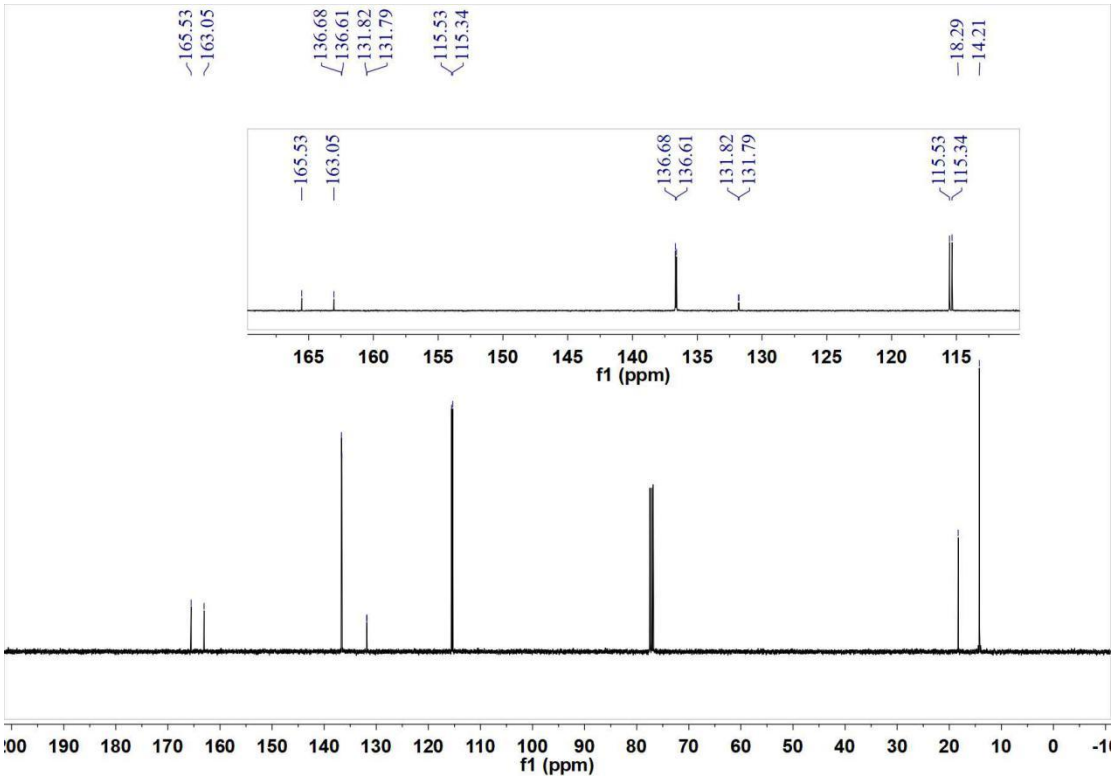
7.57
7.14
7.12
7.09
2.30
2.30
2.28
2.26
2.24
2.22
2.22
1.51
1.49
1.47
Si
F
F
4.00
4.00
2.08
4.08
f1 (ppm)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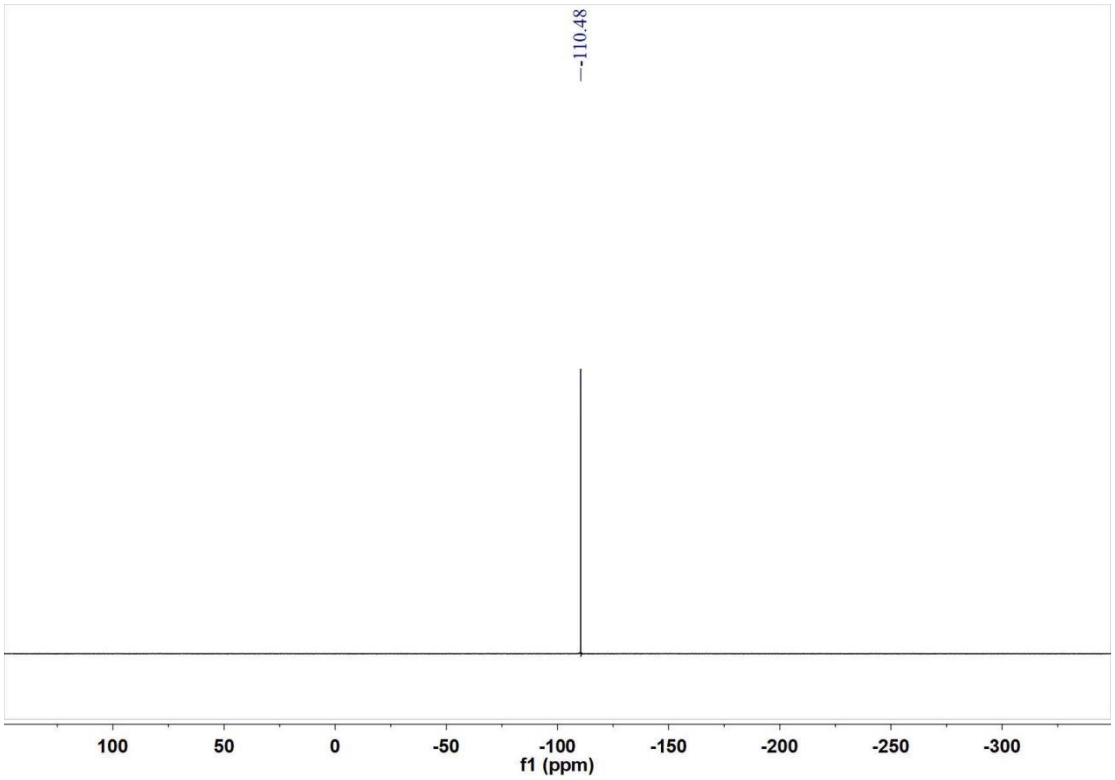
136.68
136.61
131.82
131.79
115.53
115.34
18.29
14.21
f1 (ppm)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100
50
0
-50
-100
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-200
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-300
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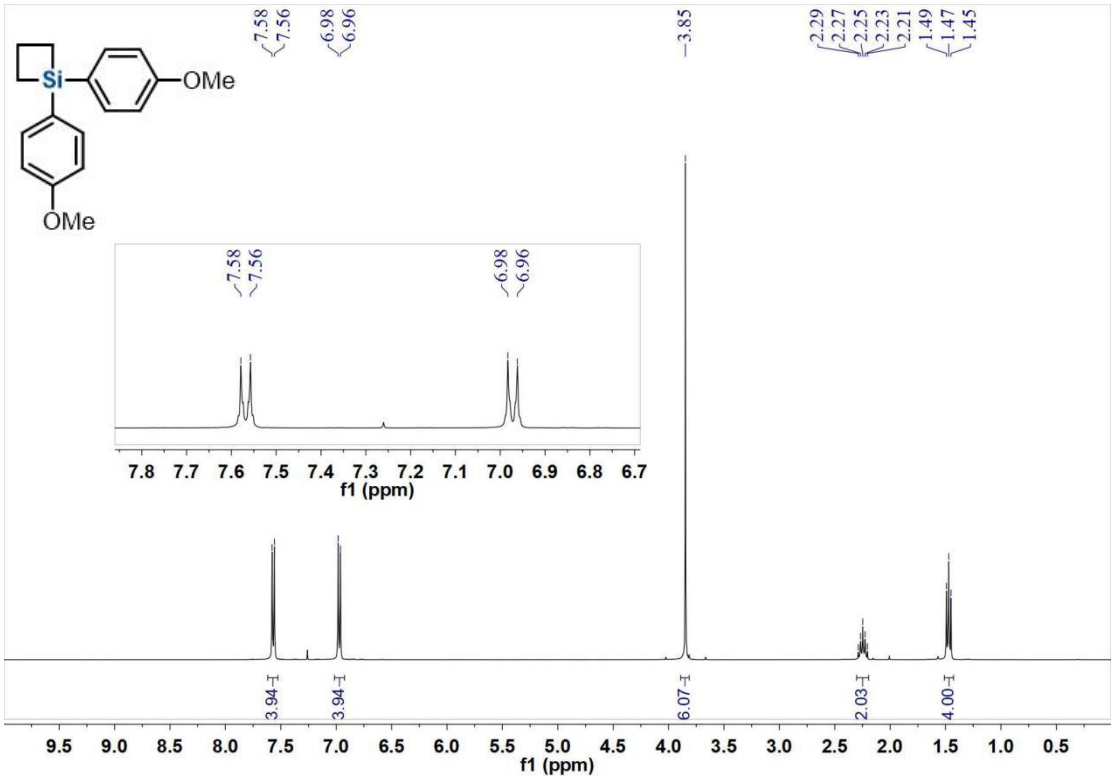
2c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OMe
OMe
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7.56
6.98
6.96
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2.29
2.27
2.25
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1.49
1.47
1.45
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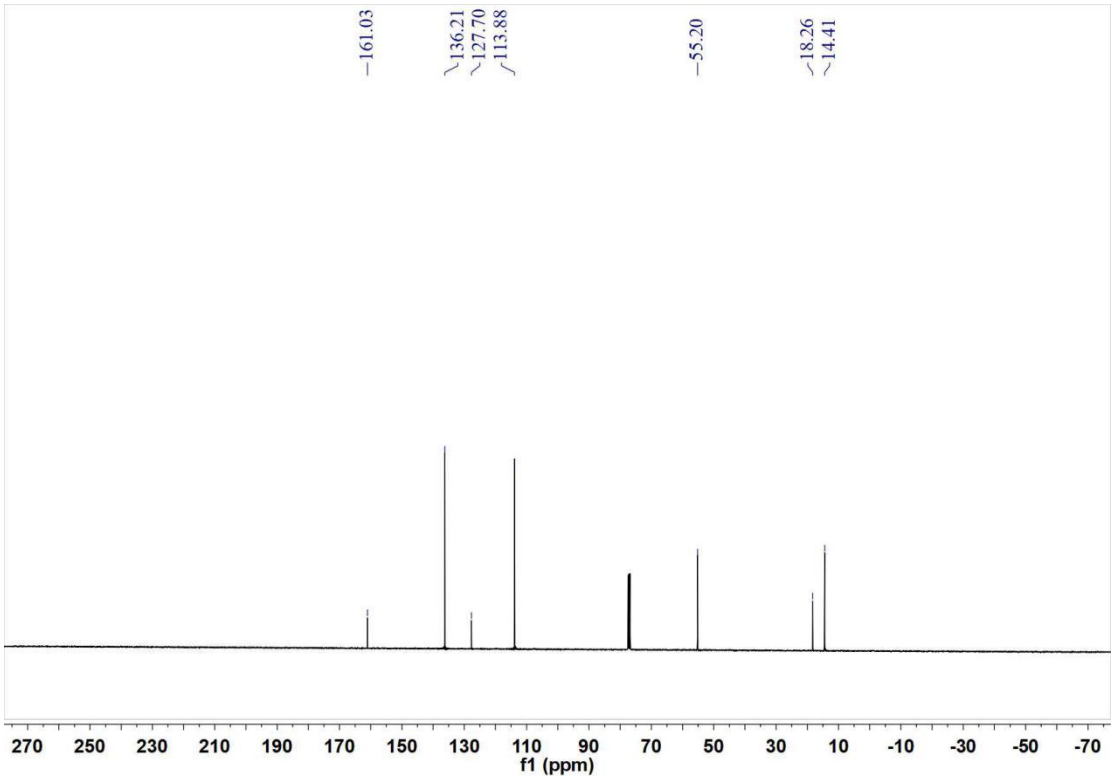
3.94
6.07
2.03
4.00
f1 (ppm)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55.20
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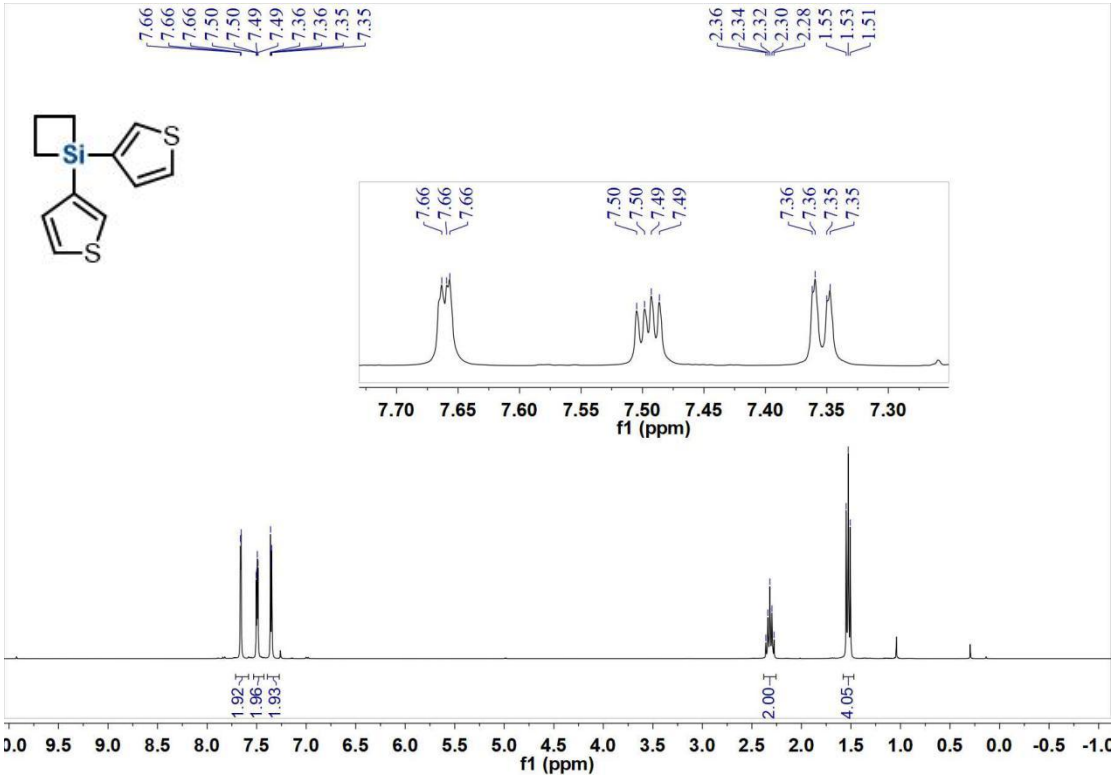
f1 (ppm)

2d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7.66
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7.35
7.35
2.36
2.34
2.32
2.30
2.28
1.55
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1.51
Si
S
S
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1.92
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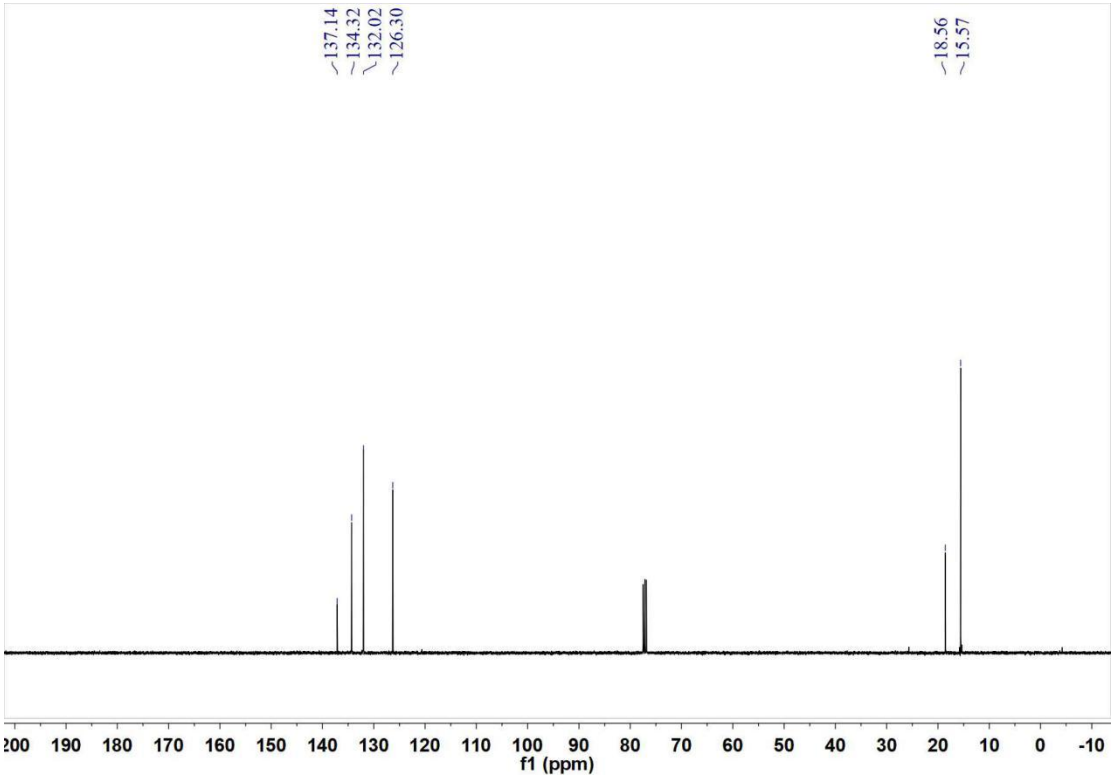
1.93
2.00
4.05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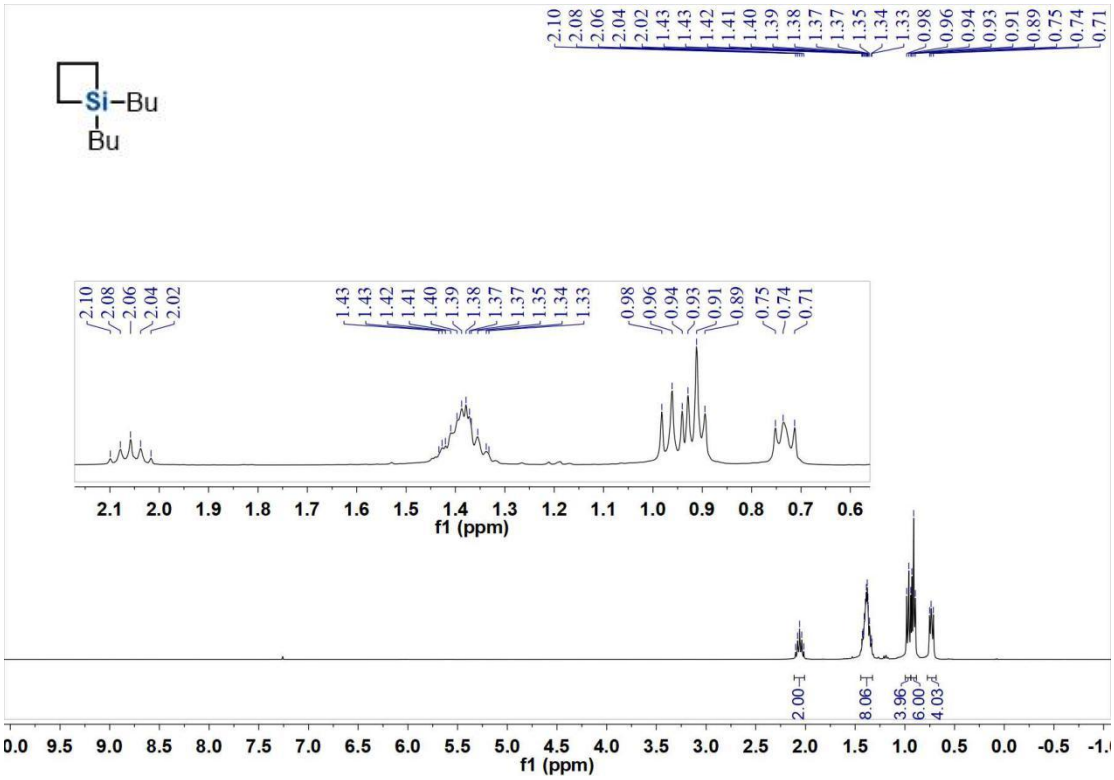
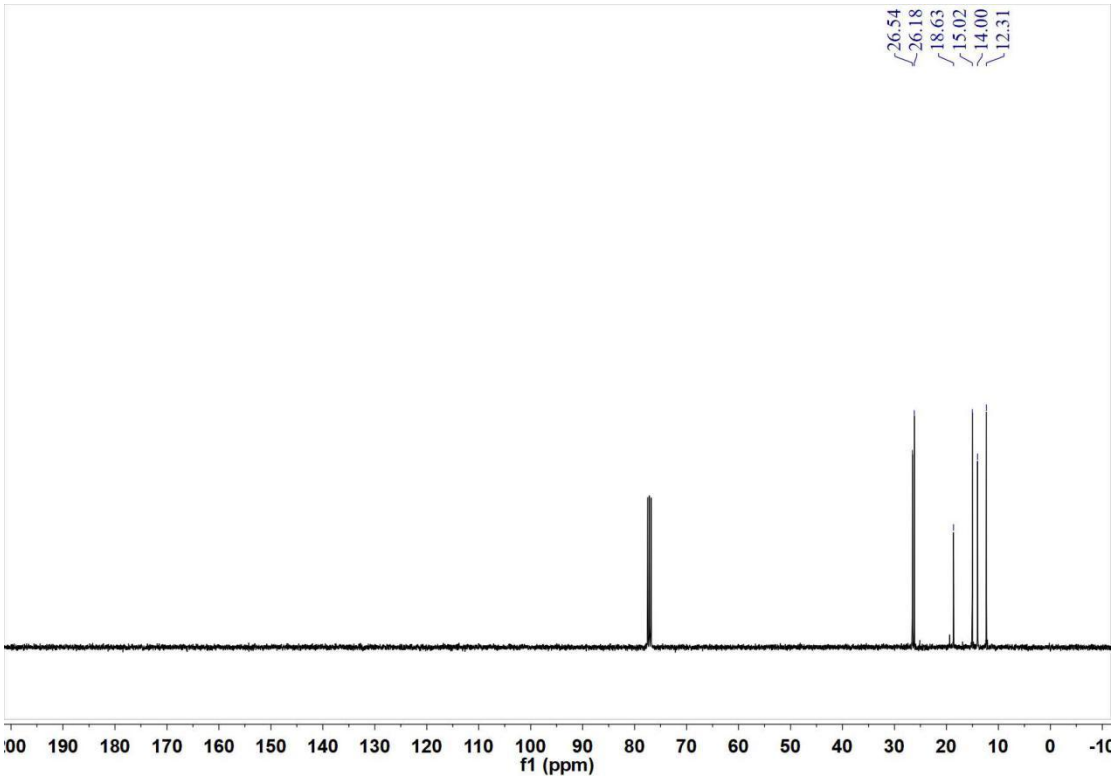
2e





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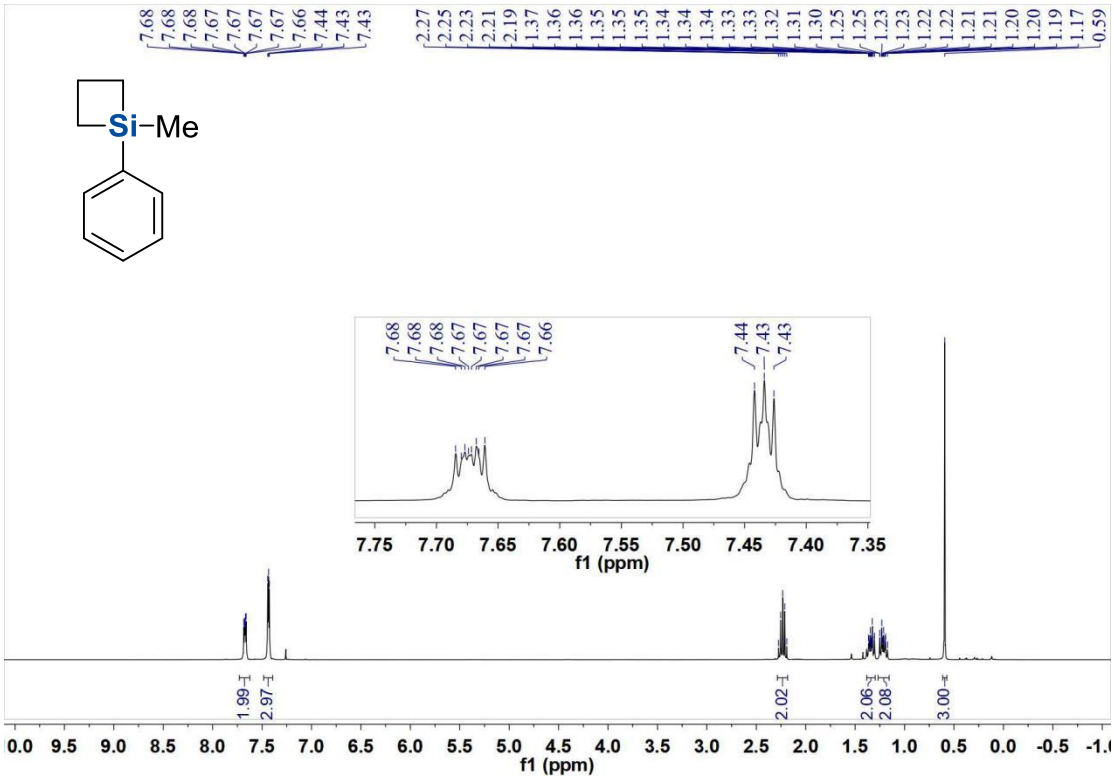
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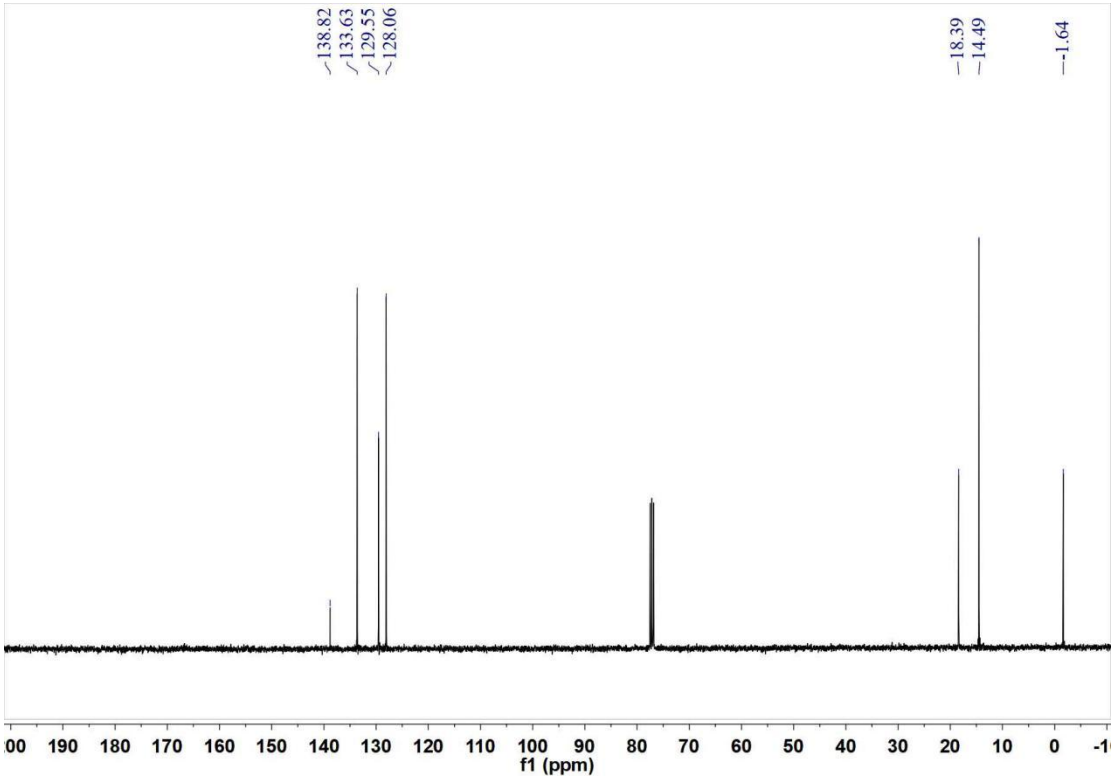
2.27 2.25 2.23 2.21 2.19 1.37 1.36 1.36 1.35 1.35 1.35 1.34 1.34 1.34 1.33 1.33 1.32 1.31 1.30 1.25 1.25 1.23 1.23 1.22 1.22 1.21 1.21 1.20 1.20 1.19 1.17 0.59
Si–Me
7.68 7.68 7.68 7.67 7.67 7.67 7.67 7.66
7.44 7.43 7.43
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
1.99 2.97 2.02 2.06 2.08 3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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18.39 14.49 1.64
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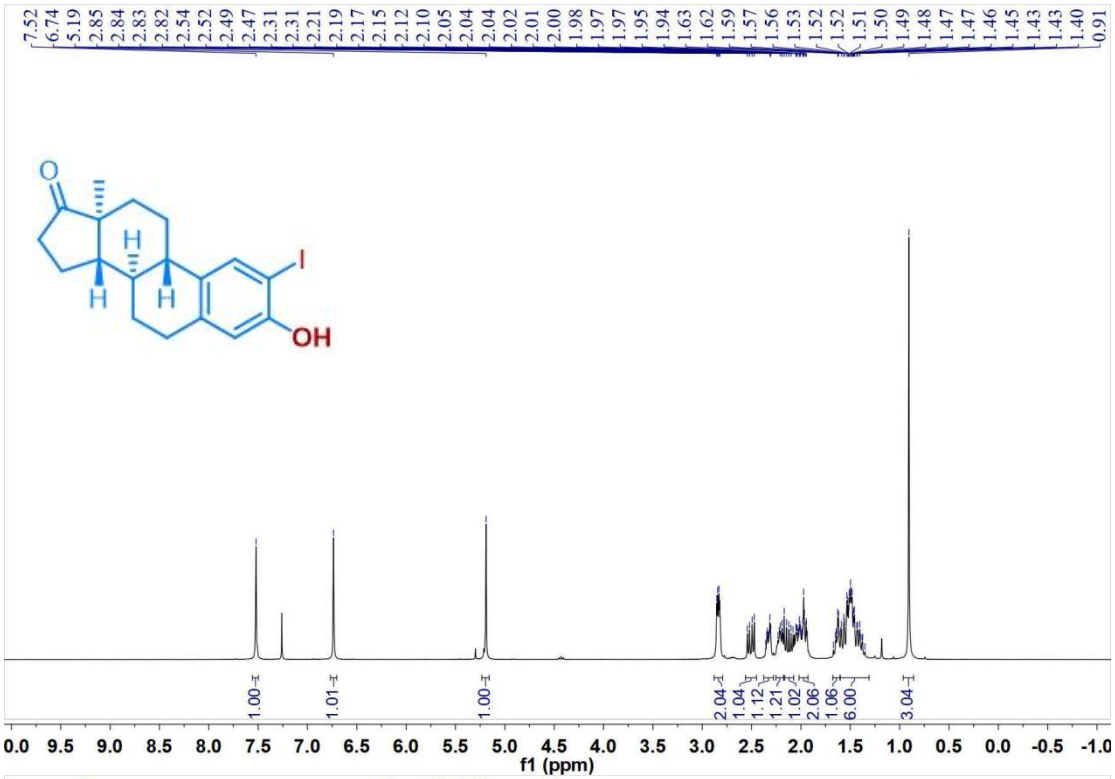
f1 (ppm)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O
H
H
H
I
OH
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0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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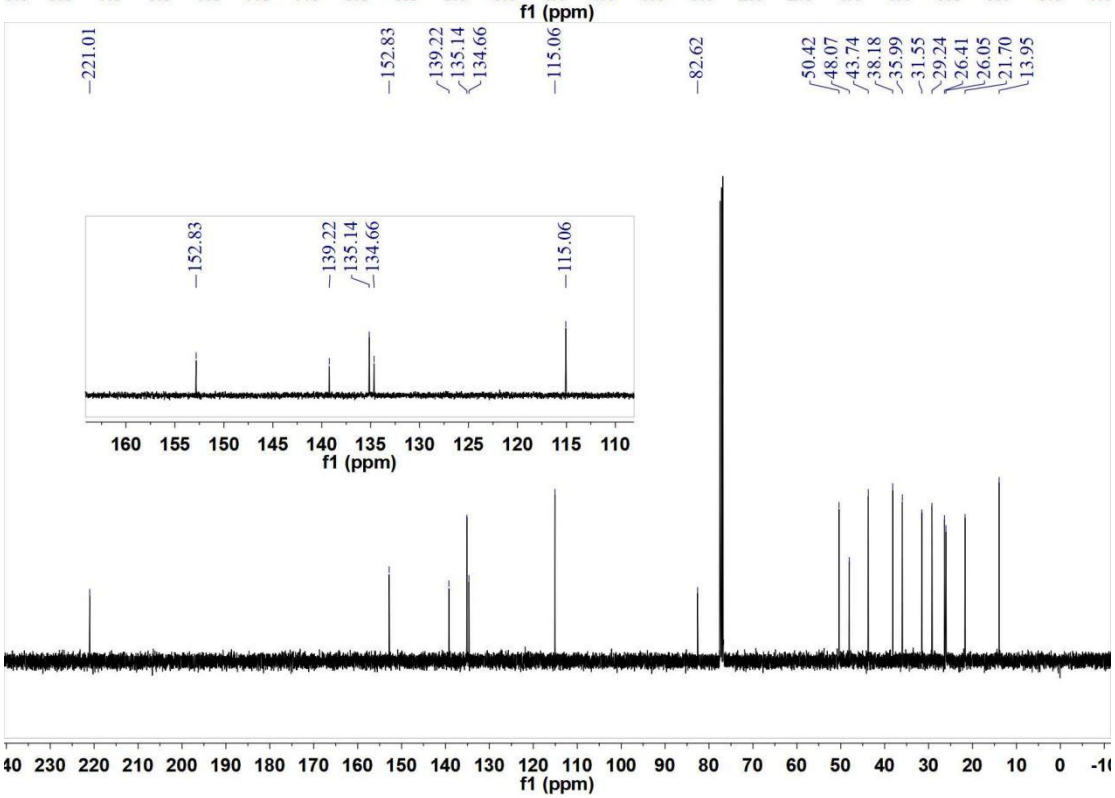
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31.55
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26.41
26.05
21.70
13.95
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f1 (ppm)
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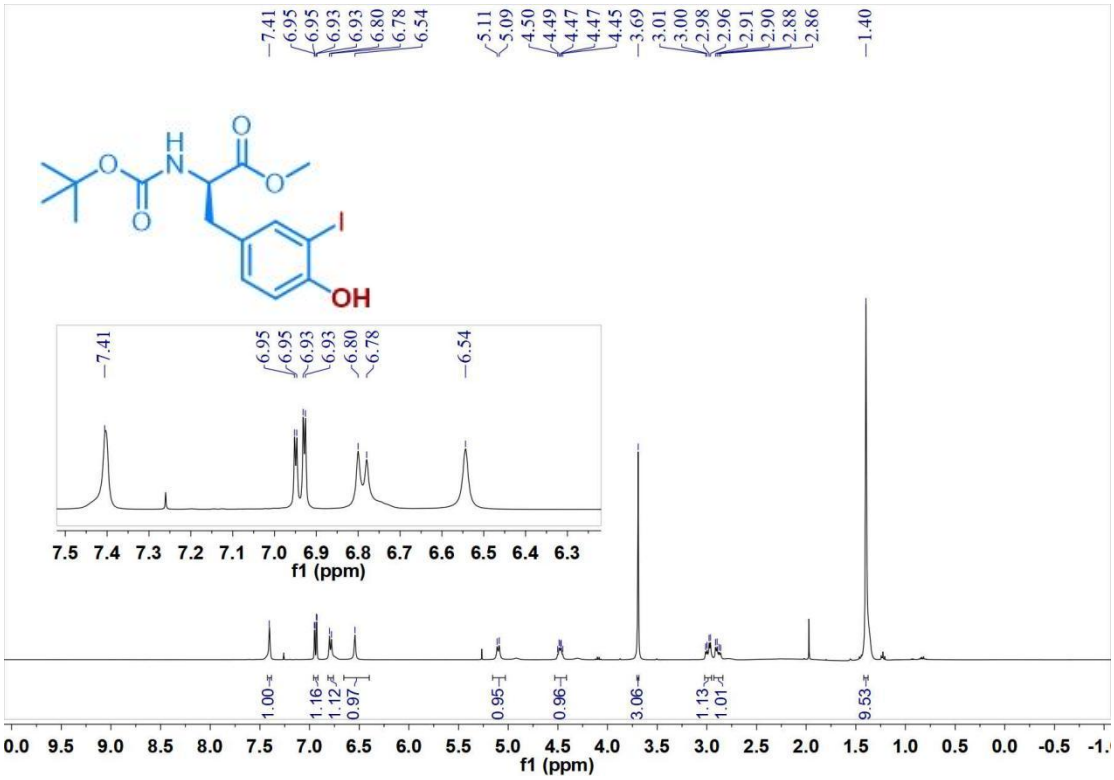
f1 (ppm)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4.47
4.47
4.45
3.69
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3.00
2.98
2.96
2.91
2.90
2.88
2.86
1.40
O
H
N
O
O
O
O
I
OH
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3
f1 (ppm)
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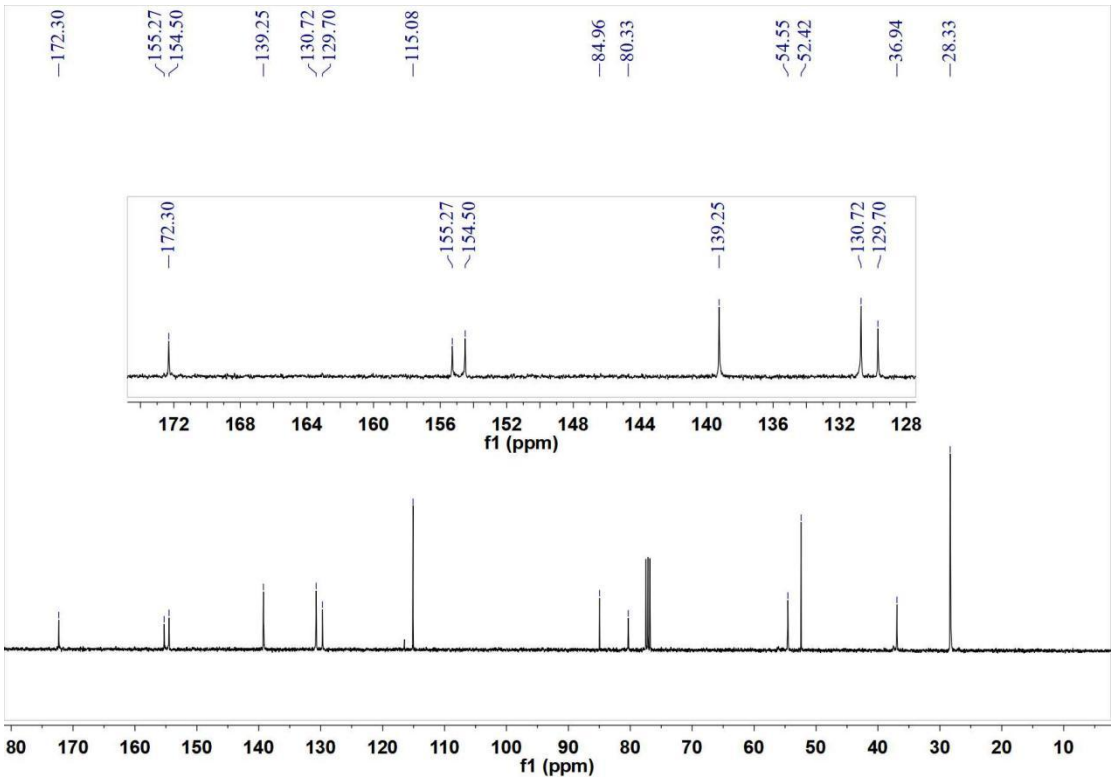
1.16
1.12
0.97
0.95
0.96
3.06
1.13
1.01
9.53
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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54.55
52.42
36.94
28.33
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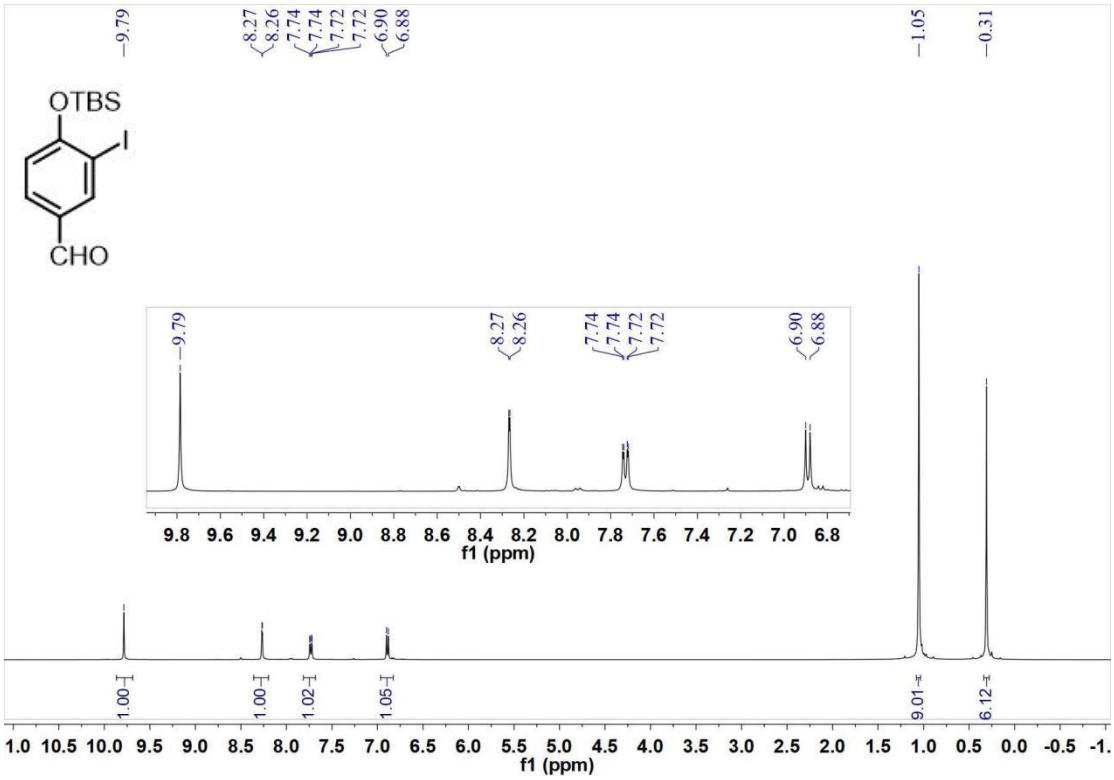
f1 (ppm)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6.88
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OTBS
I
CHO
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1.00
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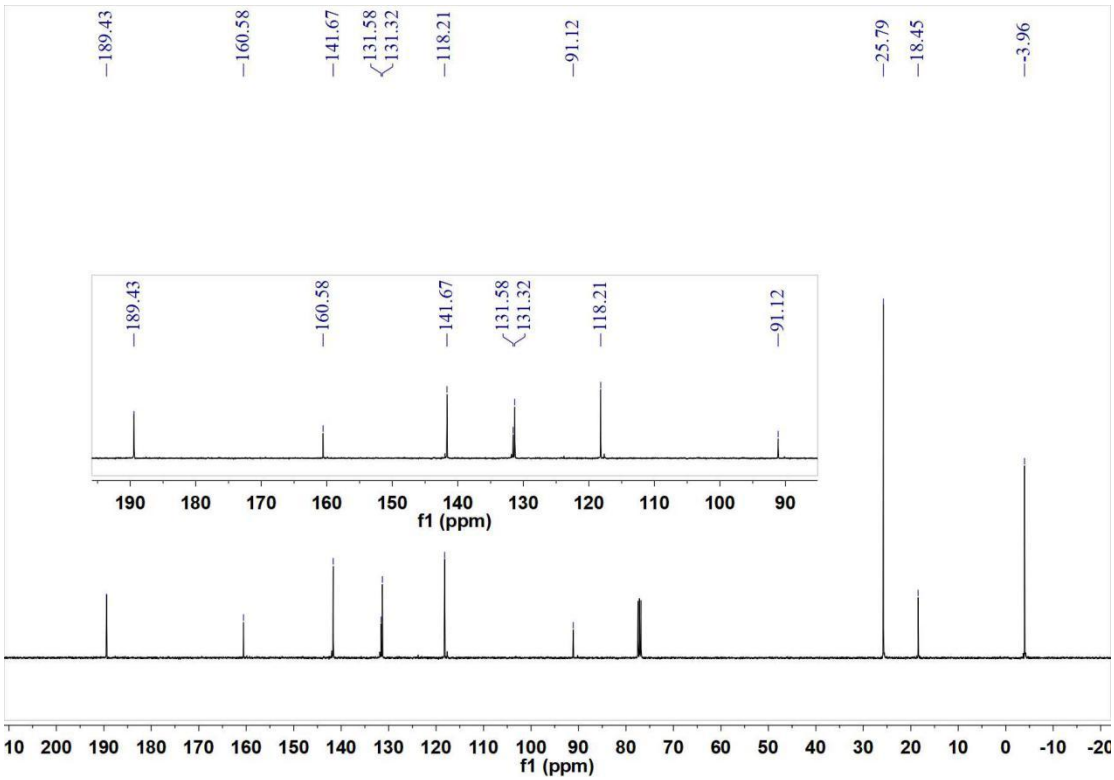
9.01
6.12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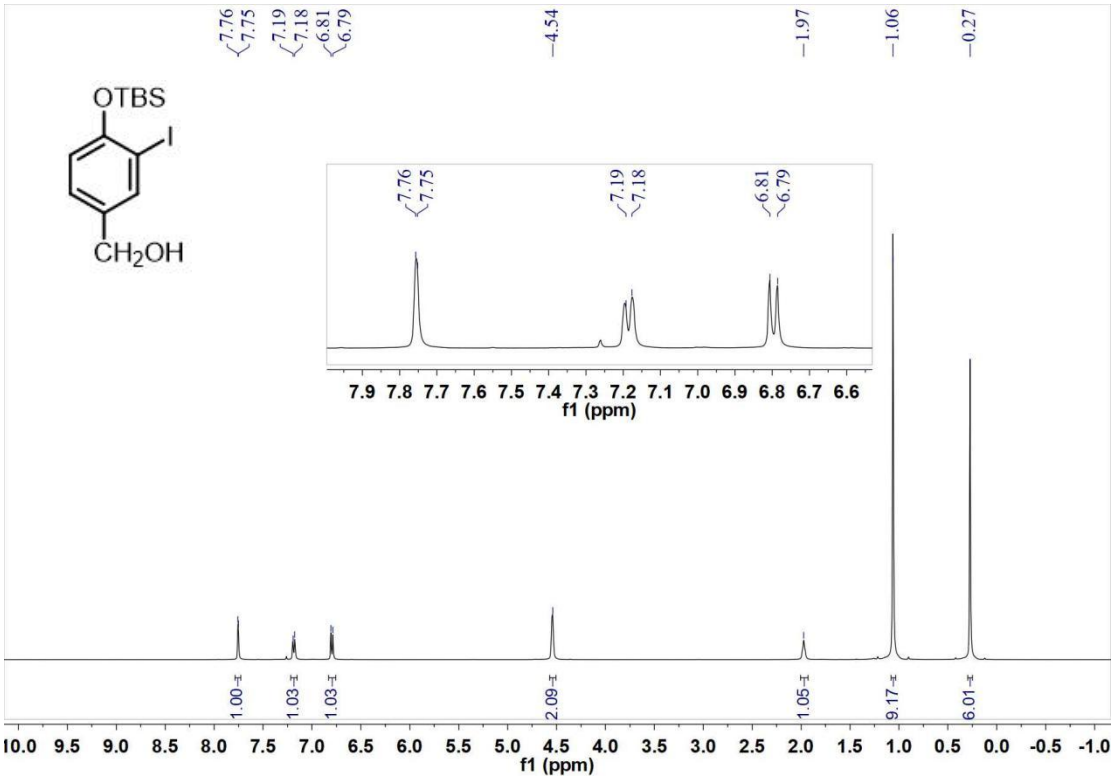
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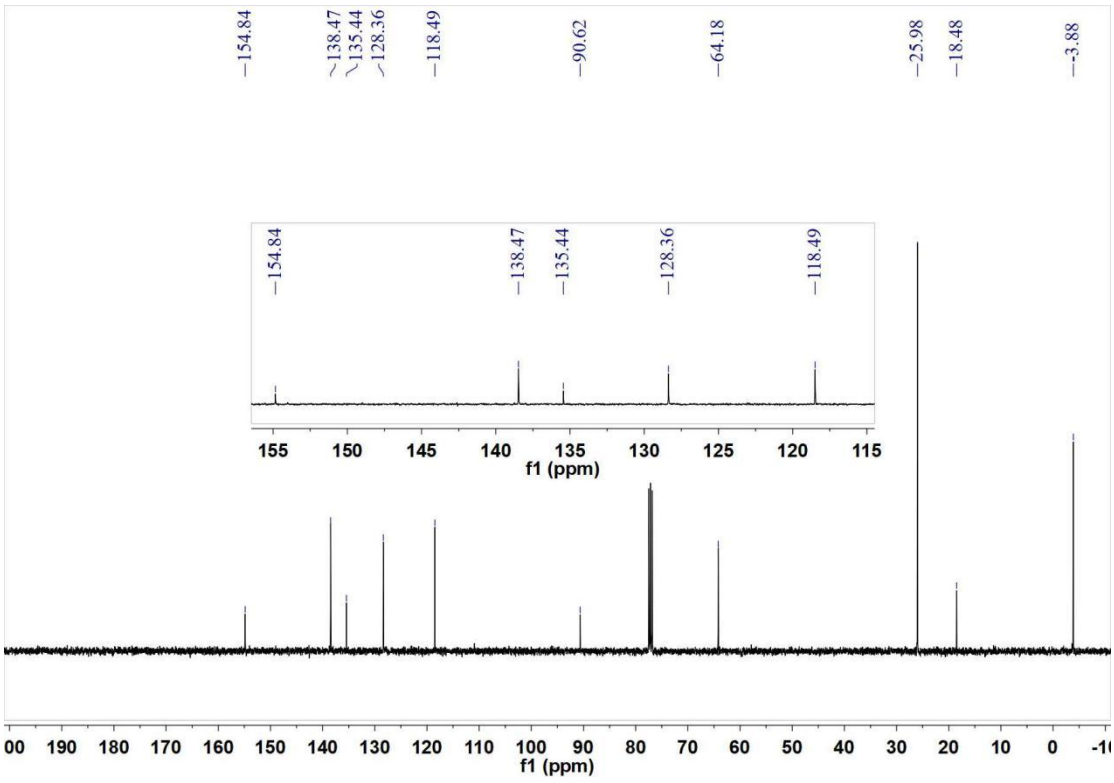
6.01
f1 (ppm)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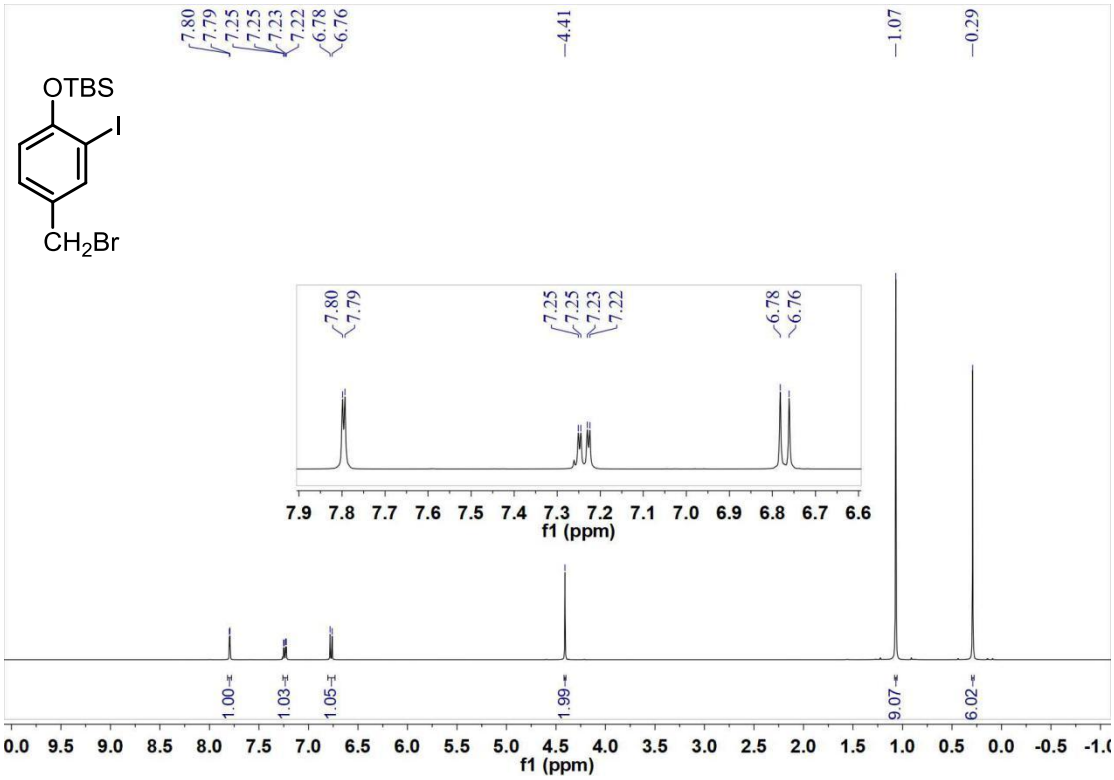
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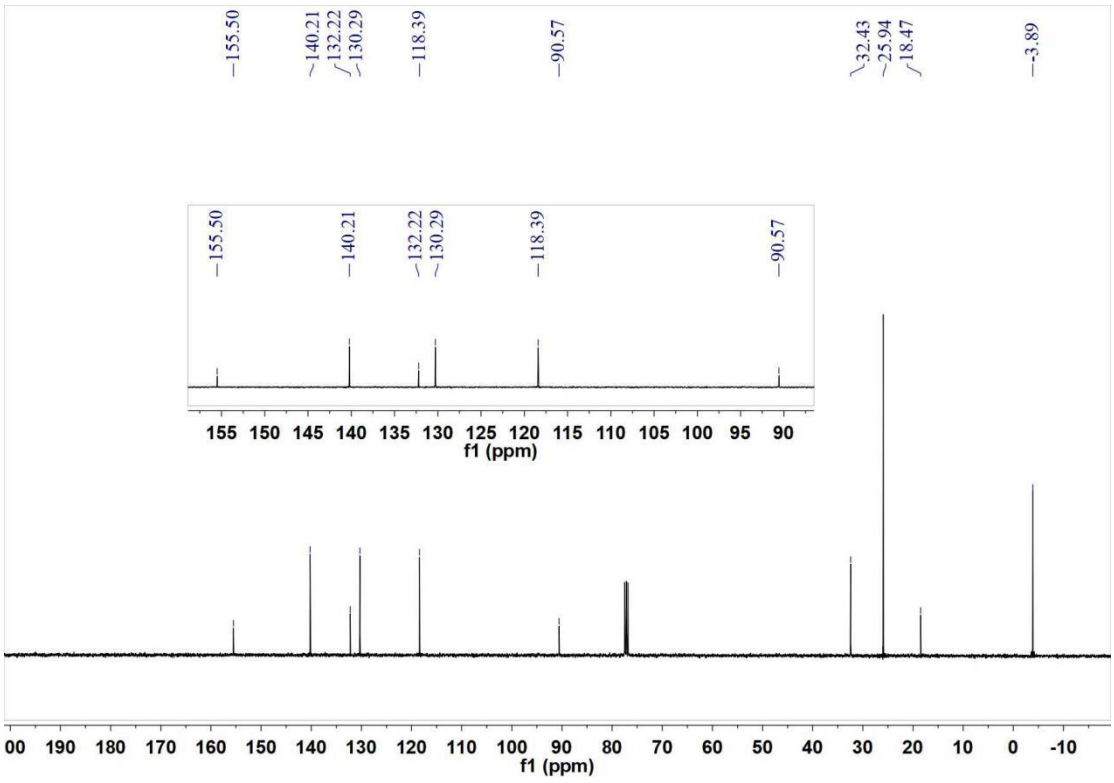
9.07
6.02
f1 (ppm)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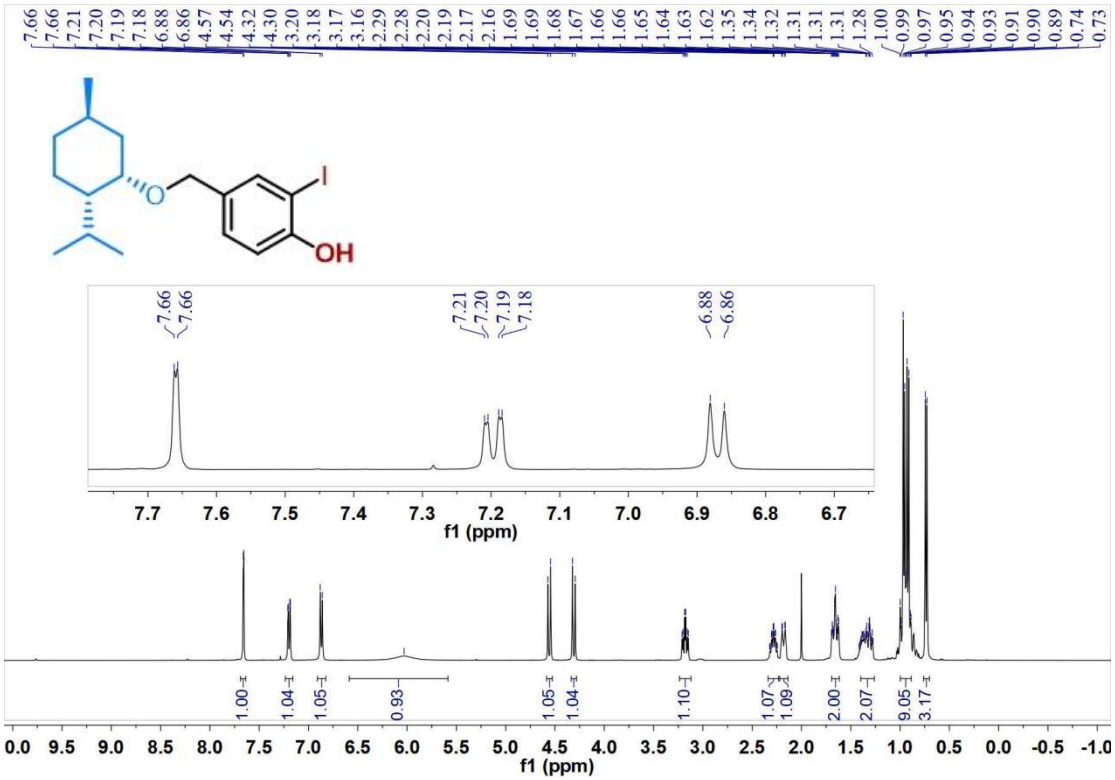
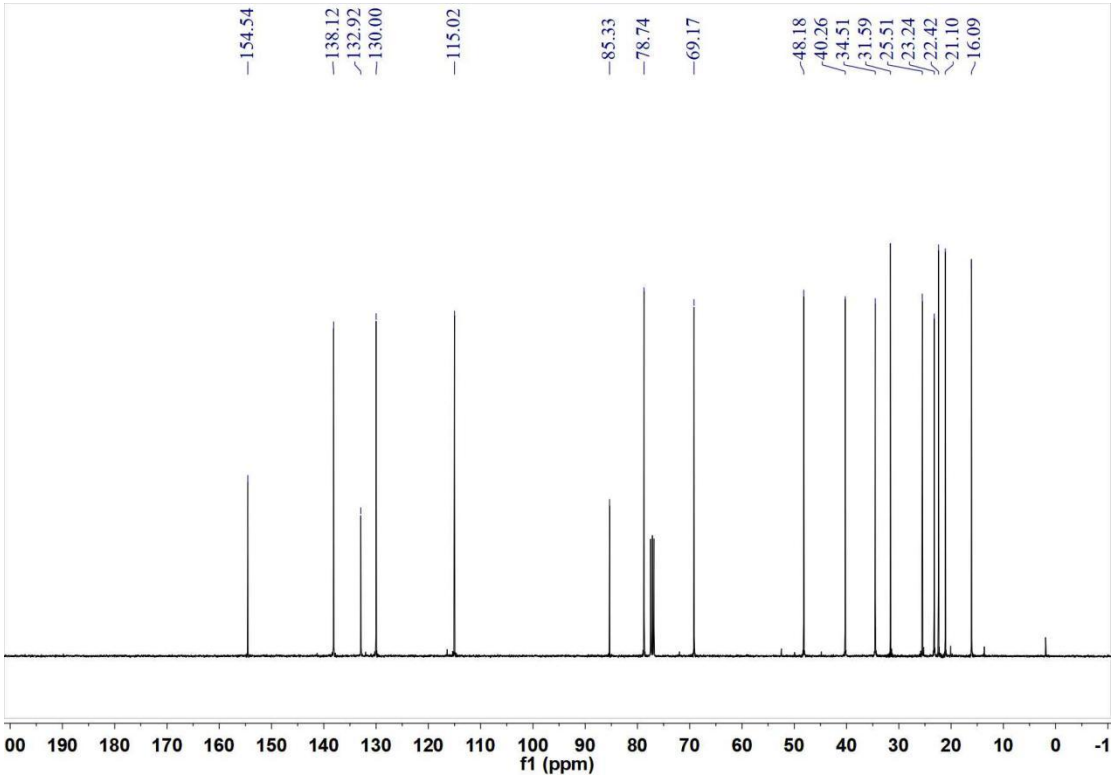

7.66 7.66 7.21 7.20 7.19 7.18 6.88 6.86 4.57 4.54 4.32 4.30 3.20 3.18 3.17 3.16 2.29 2.28 2.20 2.19 2.17 2.16 1.69 1.69 1.68 1.67 1.66 1.66 1.65 1.64 1.63 1.62 1.35 1.34 1.32 1.31 1.31 1.28 1.00 0.99 0.97 0.95 0.94 0.93 0.91 0.90 0.89 0.74 0.73
I
O
OH
7.66 7.66 7.21 7.20 7.19 7.18 6.88 6.86
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
1.00 1.04 1.05 0.93 1.05 1.04 1.10 1.07 1.09 2.00 2.07 9.05 3.17
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


154.54 138.12 132.92 130.00 115.02 85.33 78.74 69.17 48.18 40.26 34.51 31.59 25.51 23.24 22.42 21.10 16.09
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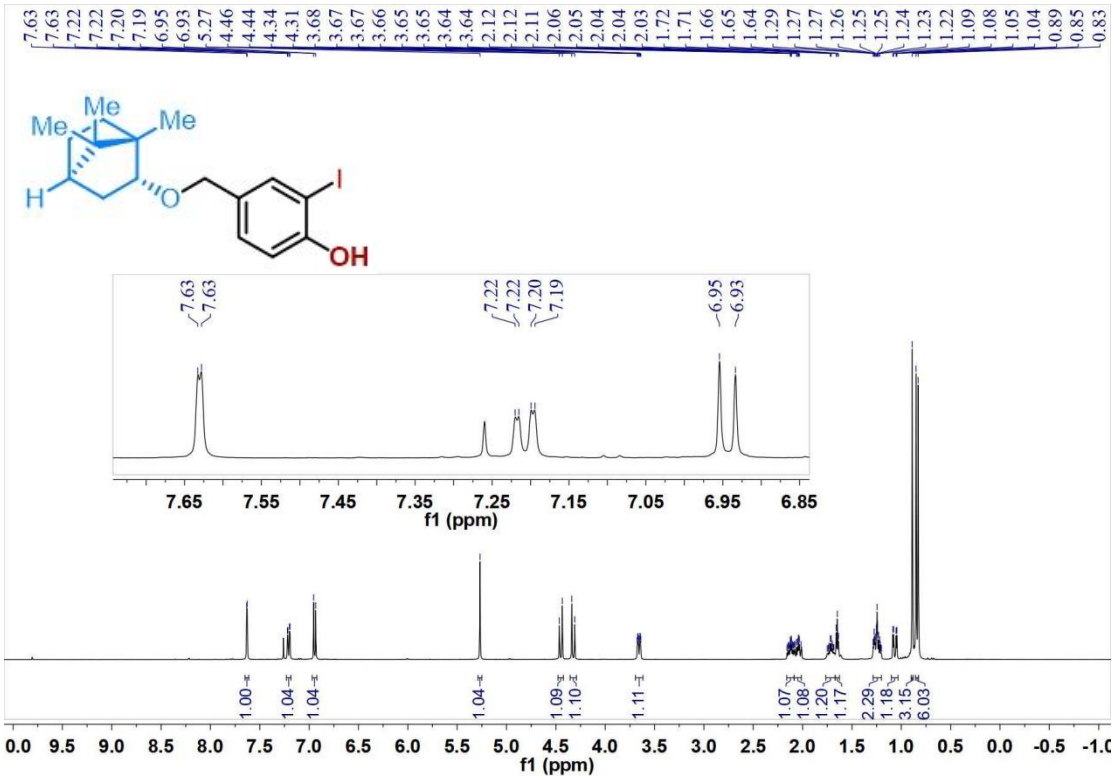
f1 (ppm)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Me
Me
H
O
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OH
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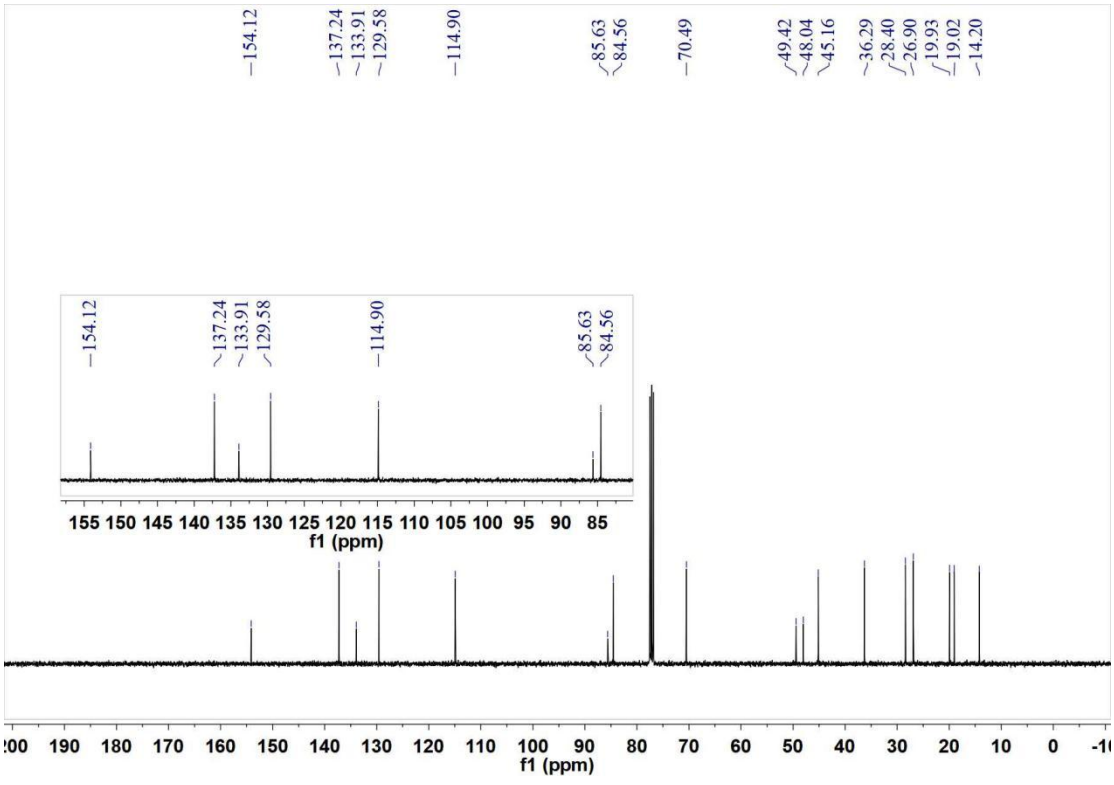
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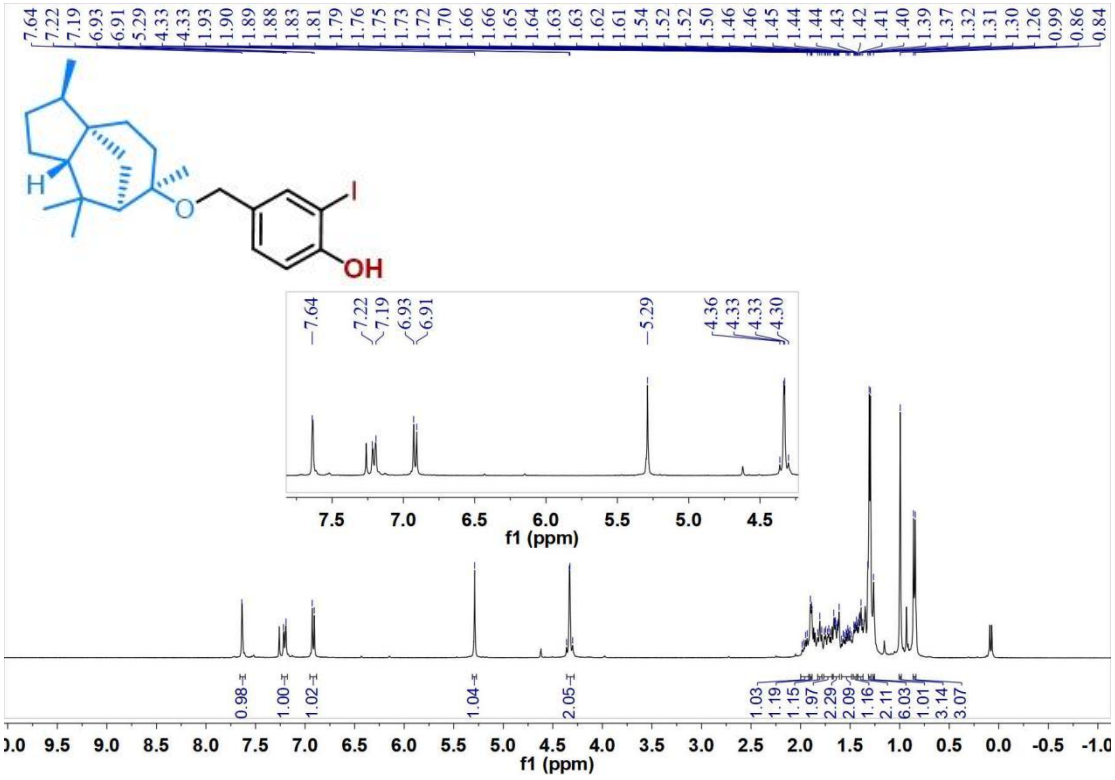
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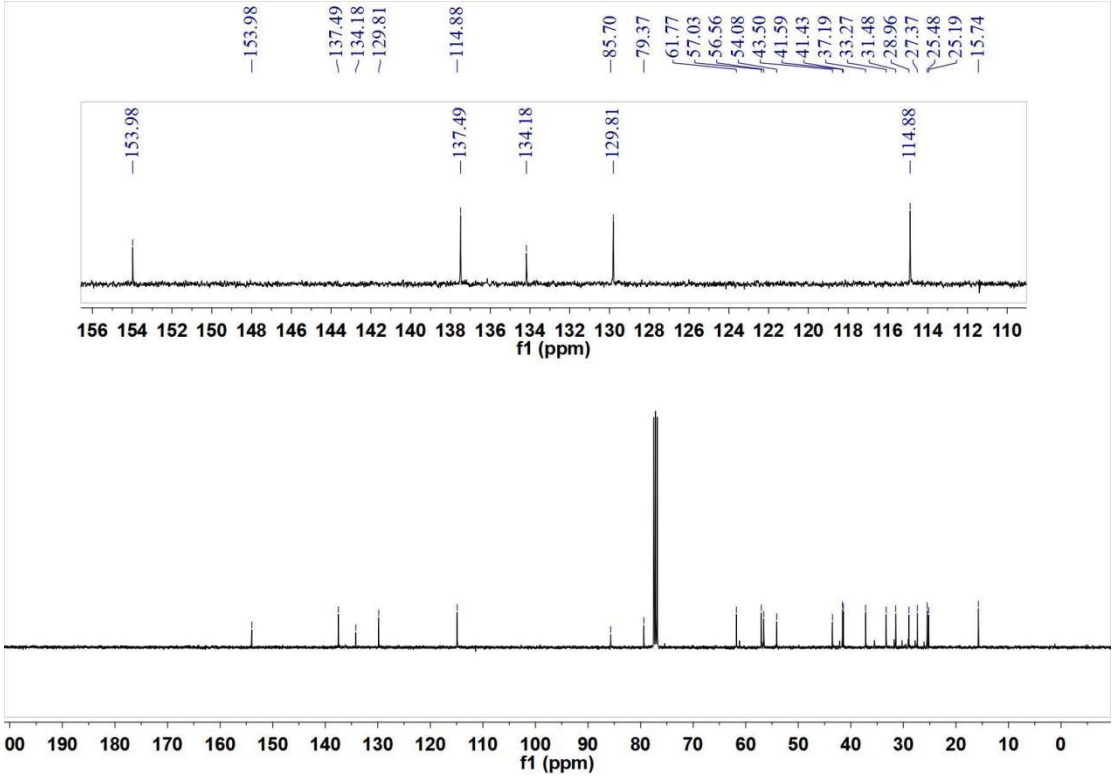
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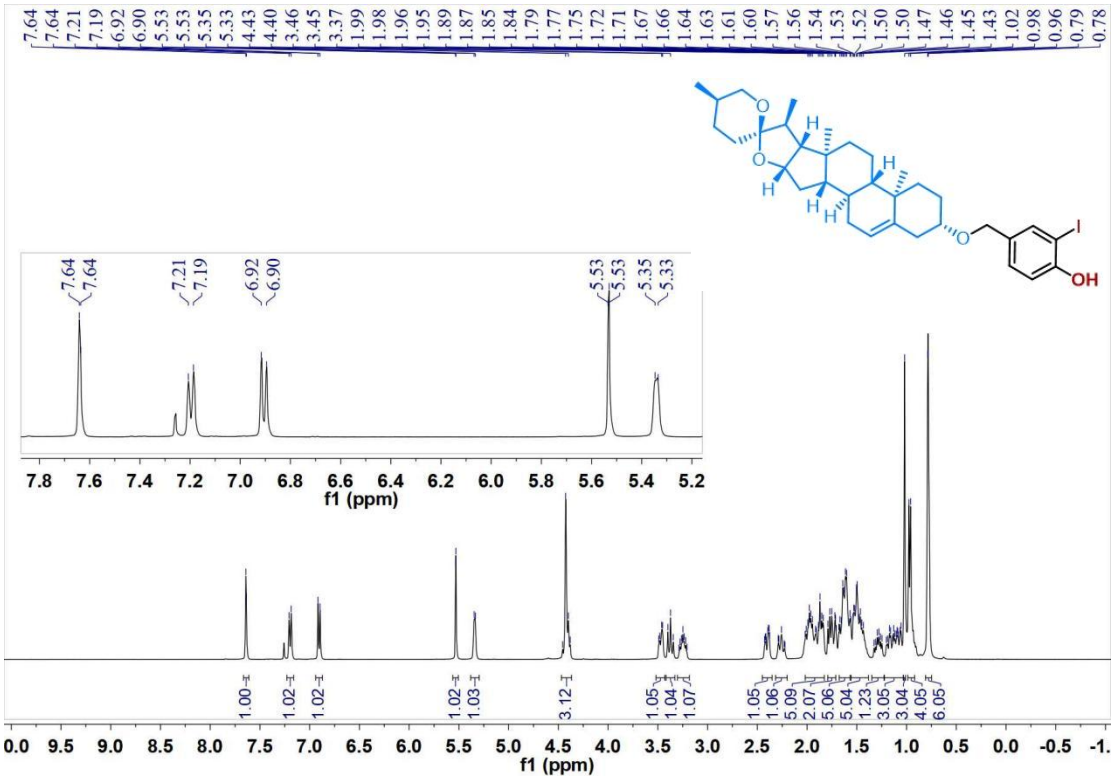
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1.57
1.56
1.54
1.53
1.52
1.50
1.50
1.47
1.46
1.45
1.43
1.02
0.98
0.96
0.79
0.78
O
O
H
H
H
H
O
I
OH
f1 (ppm)
1.00
1.02
1.02
1.02
1.03
3.12
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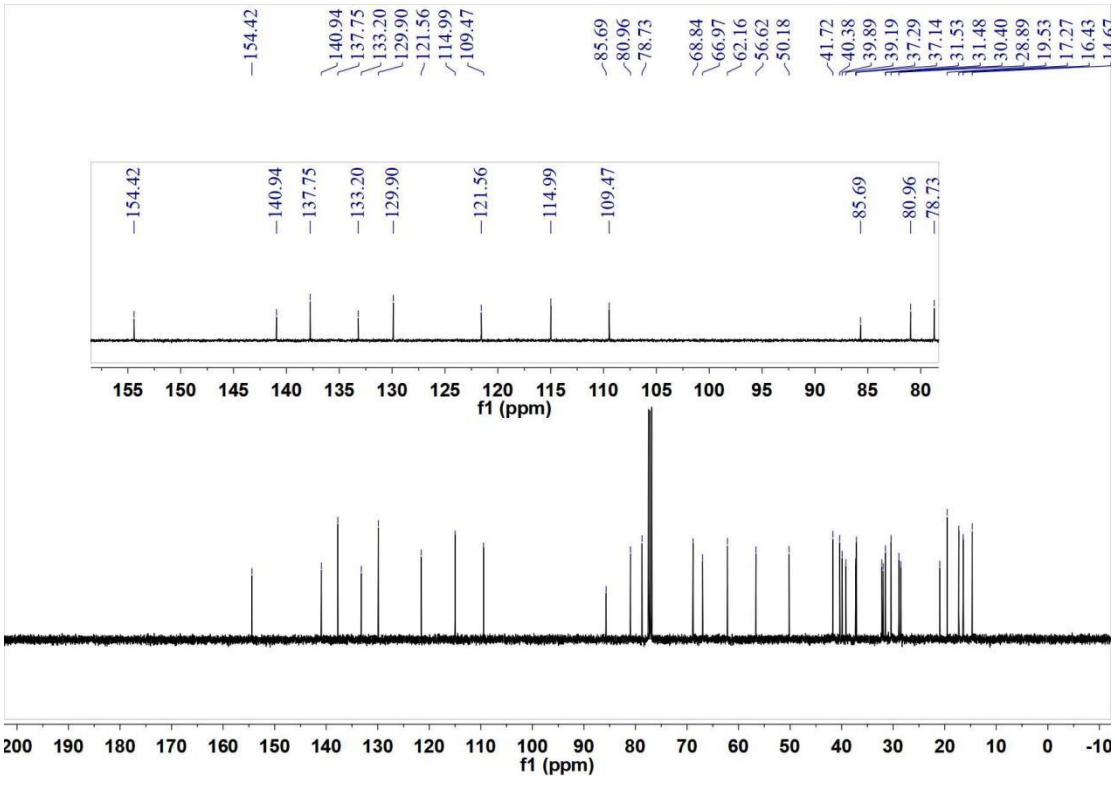
f1 (ppm)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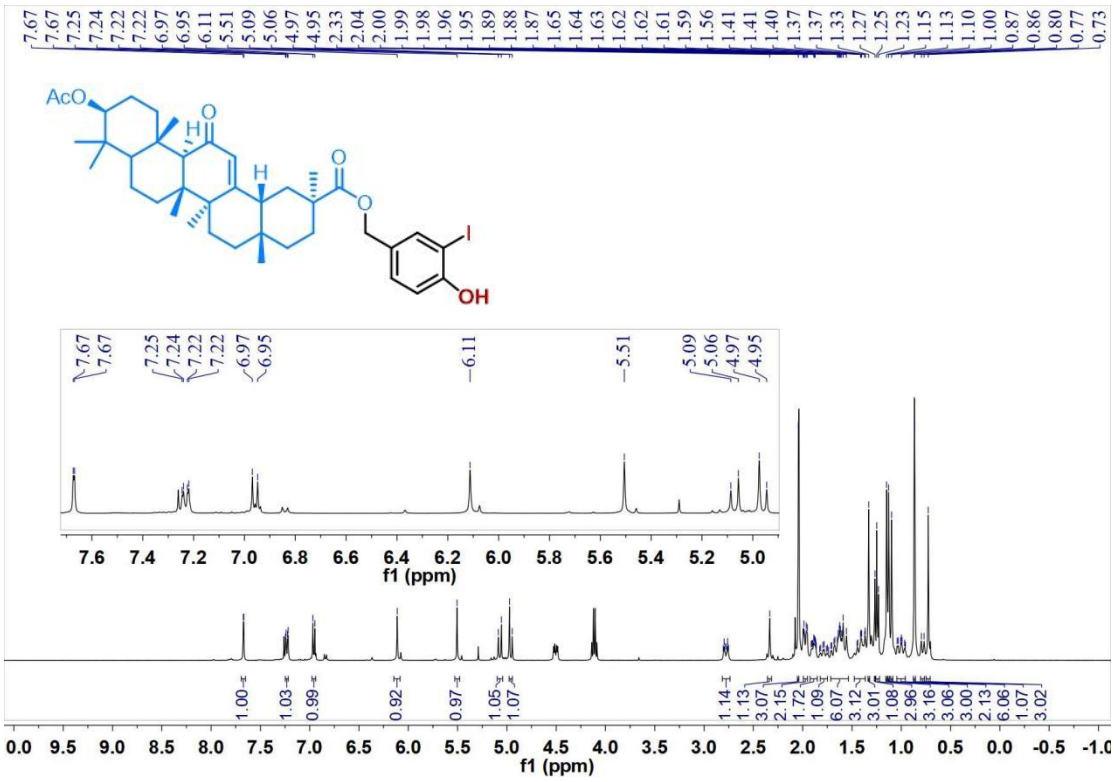
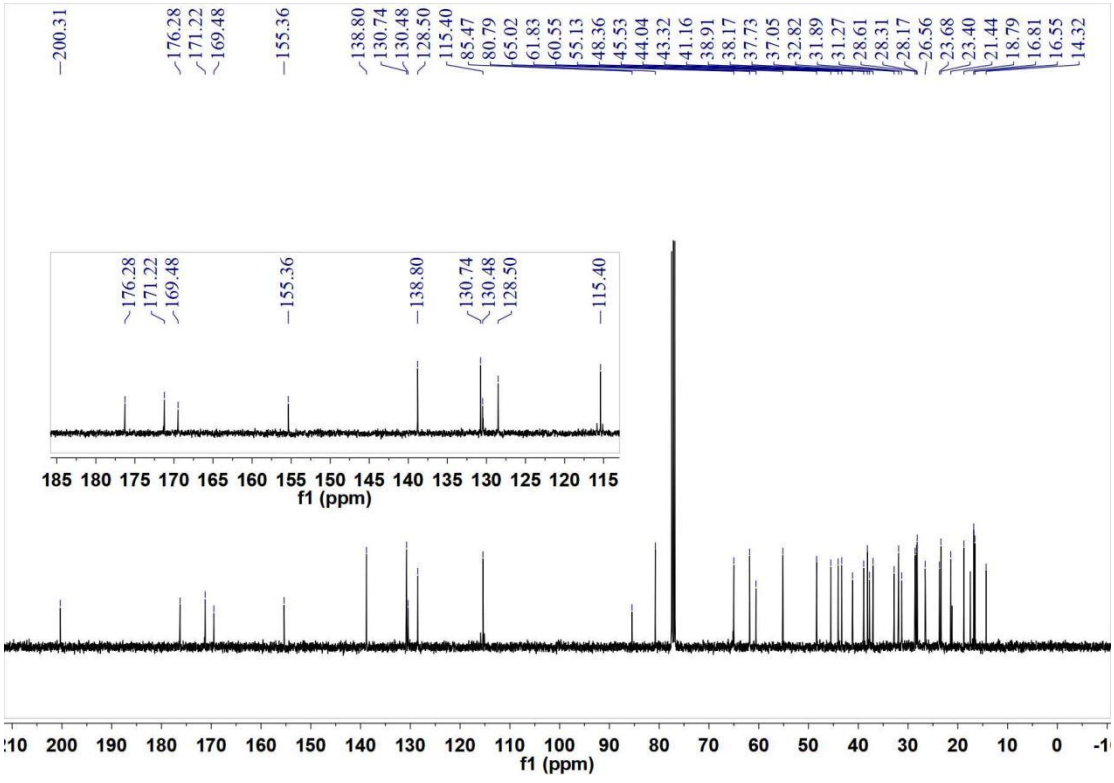
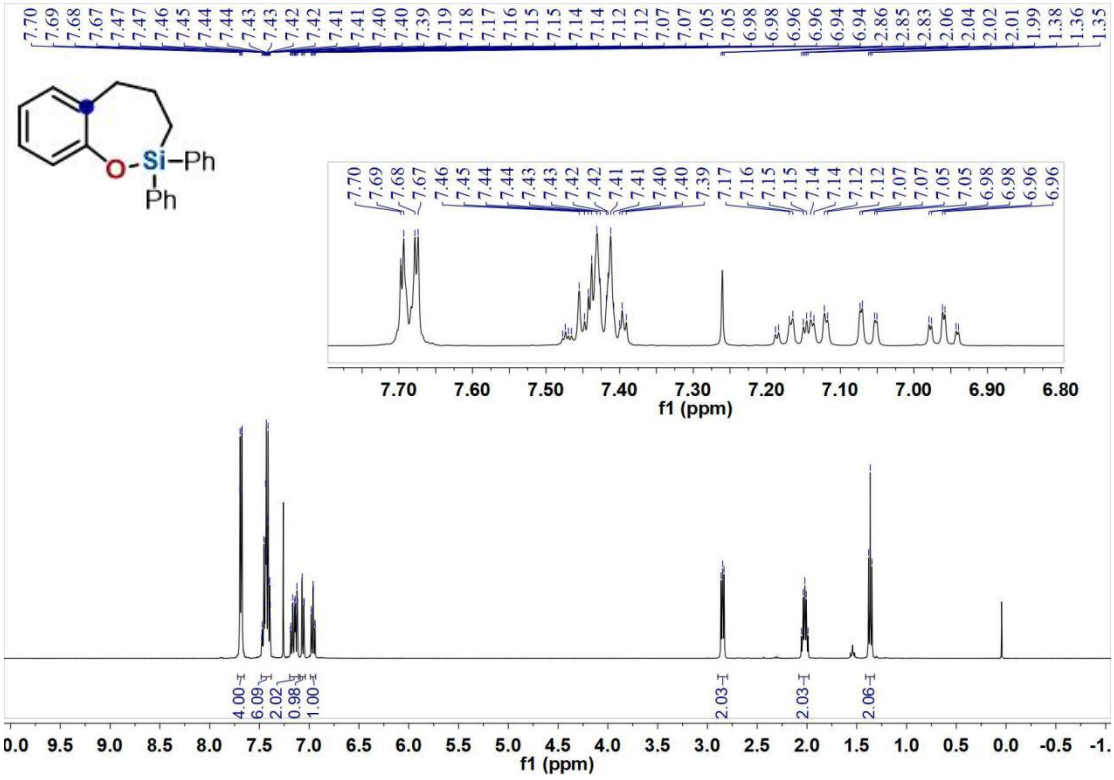
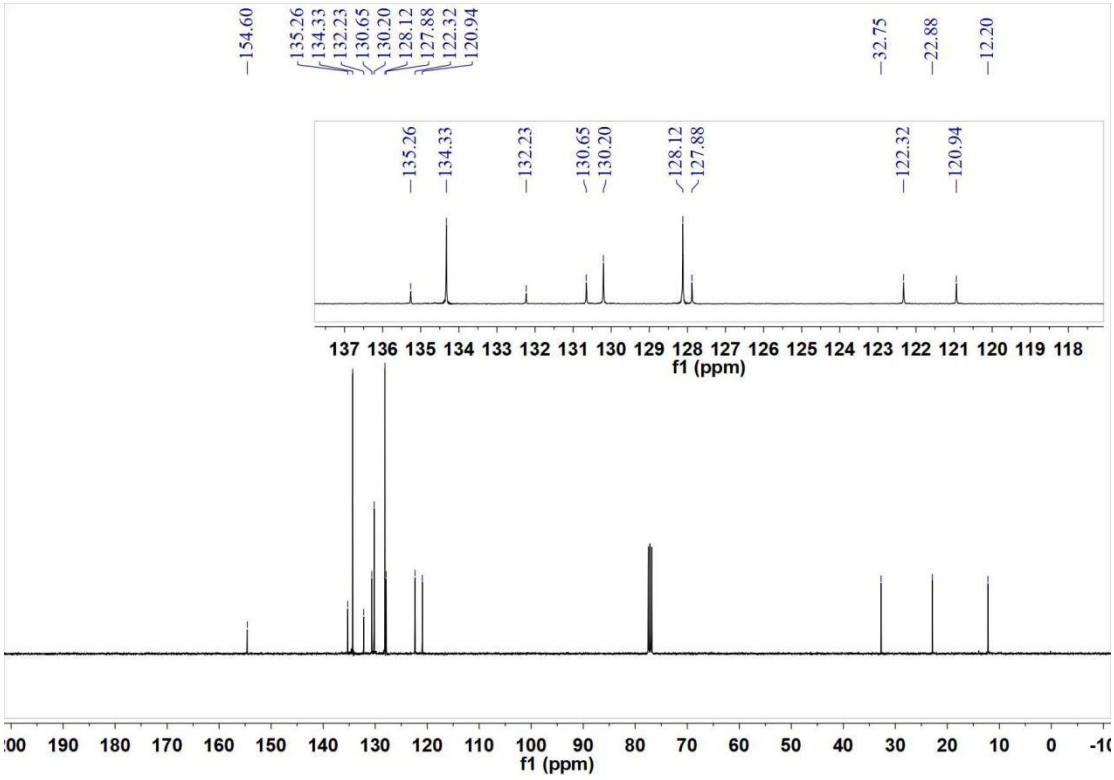
80.96
78.73
68.84
66.97
62.16
56.62
50.18
41.72
40.38
39.89
39.19
37.29
37.14
31.53
31.48
30.40
28.89
19.53
17.27
16.43
f1 (ppm)
f1 (ppm)


AcO
O
H
H
O
O
I
OH
f1 (ppm)

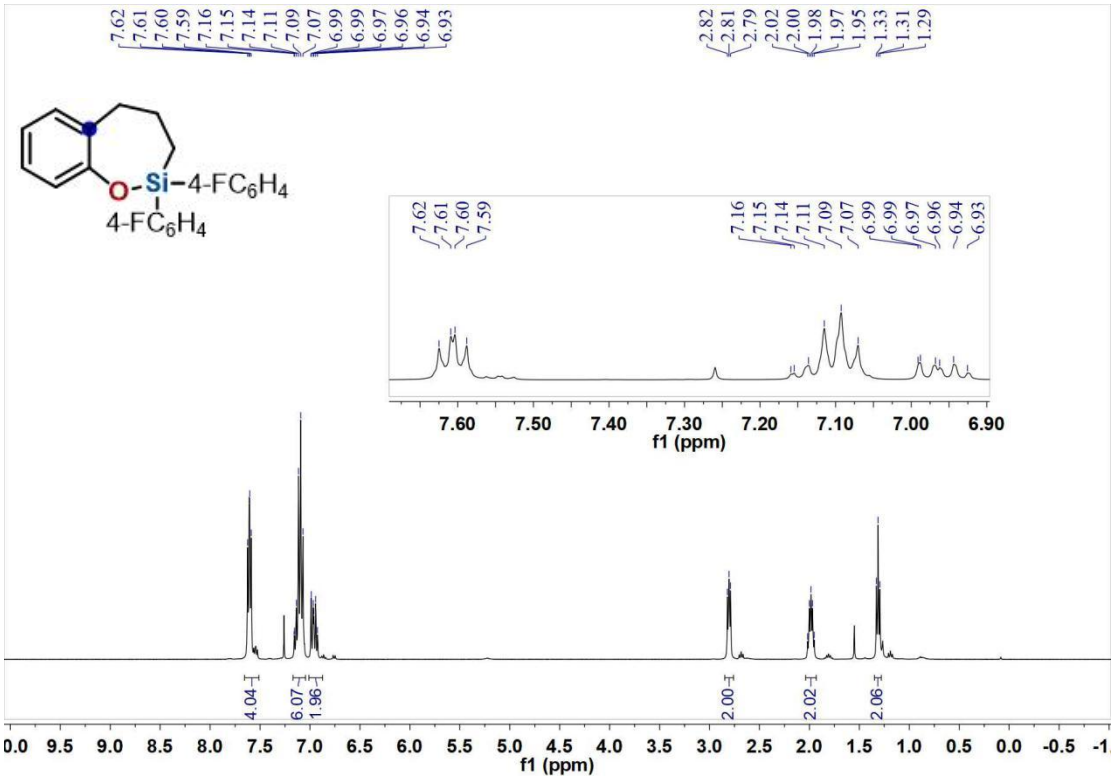

f1 (ppm)

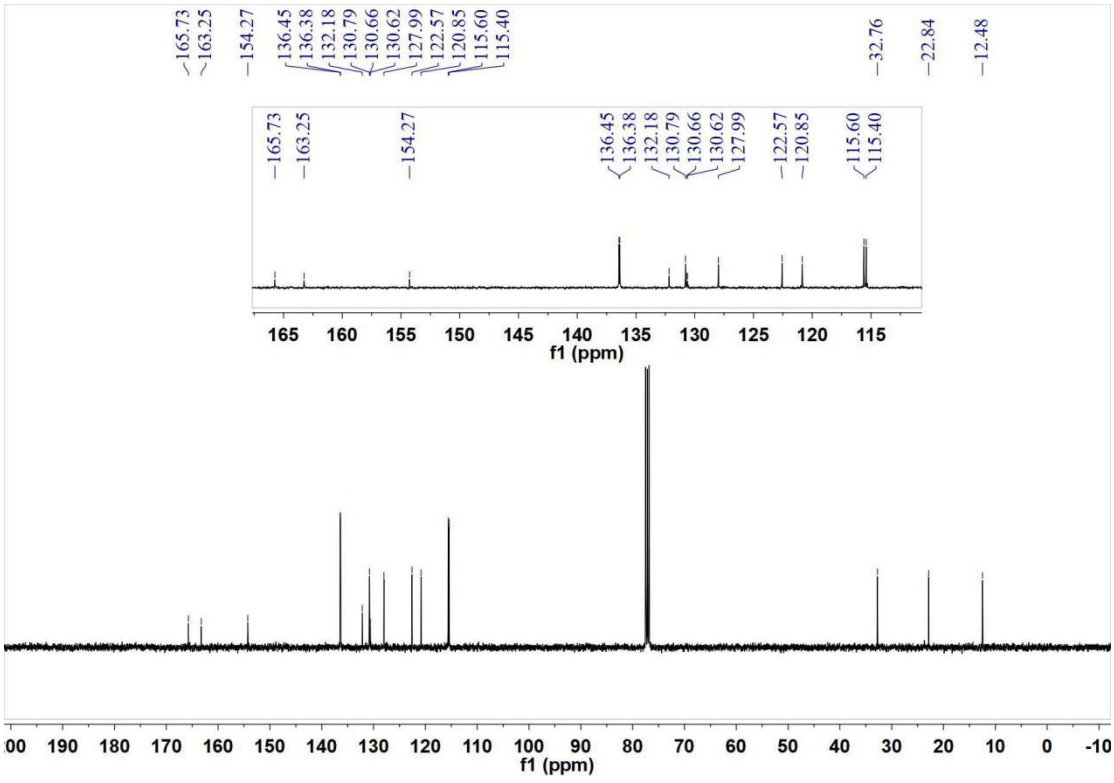
3aa

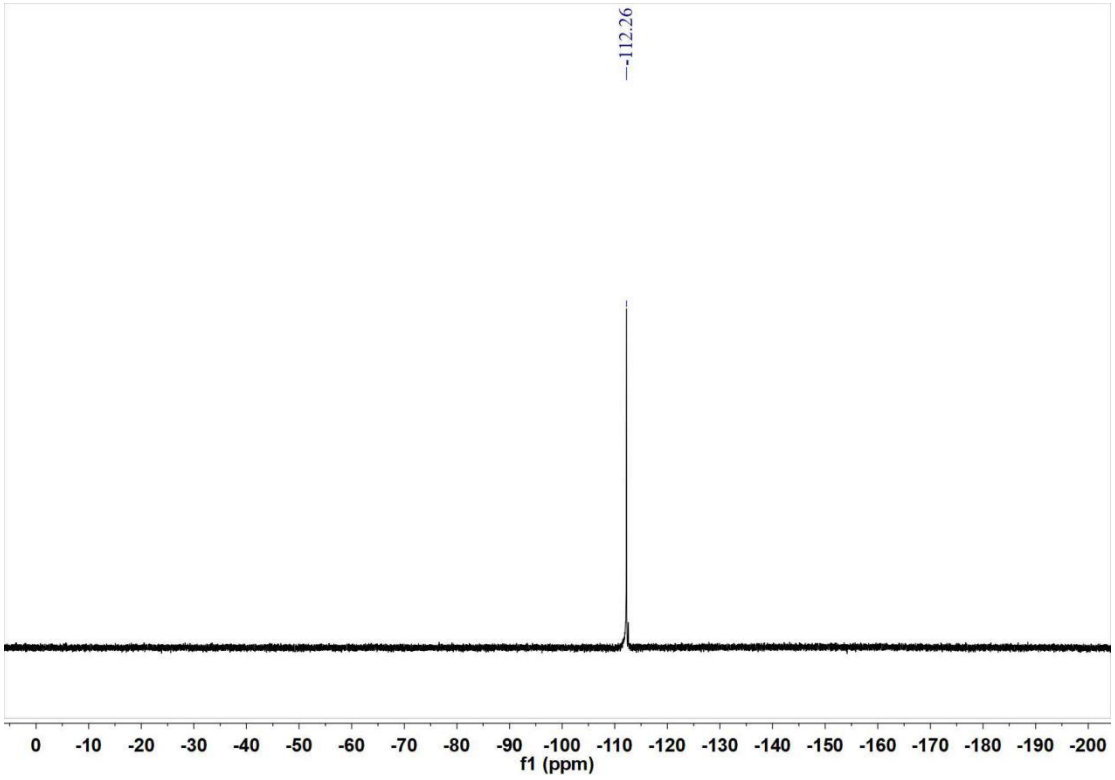

7.70 7.69 7.68 7.67 7.47 7.47 7.46 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.19 7.18 7.17 7.16 7.15 7.15 7.14 7.14 7.12 7.12 7.07 7.07 7.05 7.05 6.98 6.98 6.96 6.96 6.94 2.86 2.85 2.83 2.06 2.04 2.02 2.01 1.99 1.38 1.36 1.35
O-Si-Ph
Ph
4.00 6.09 2.02 0.98 1.00 2.03 2.03 2.06
f1 (ppm)


154.60 135.26 134.33 132.23 130.65 130.20 128.12 127.88 122.32 120.94 32.75 22.88 12.20
f1 (ppm)

3ab


7.62
7.61
7.60
7.59
7.16
7.15
7.14
7.11
7.09
7.07
6.99
6.99
6.97
6.96
6.94
6.93
2.82
2.81
2.79
2.02
2.00
1.98
1.97
1.95
1.33
1.31
1.29
O-Si-4-FC6H4
4-FC6H4
4.04
6.07
1.96
2.00
2.02
2.06
f1 (ppm)


165.73
163.25
154.27
136.45
136.38
132.18
130.79
130.66
130.62
127.99
122.57
120.85
115.60
115.40
32.76
22.84
12.48
f1 (ppm)


-112.26
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
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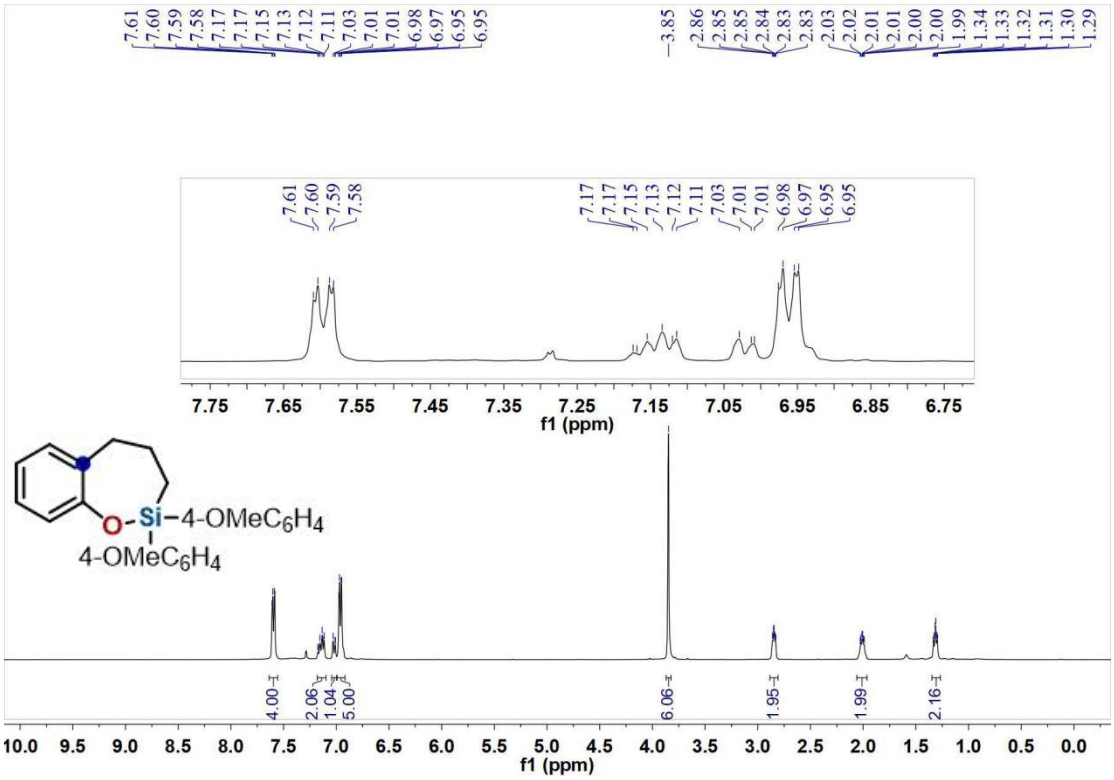
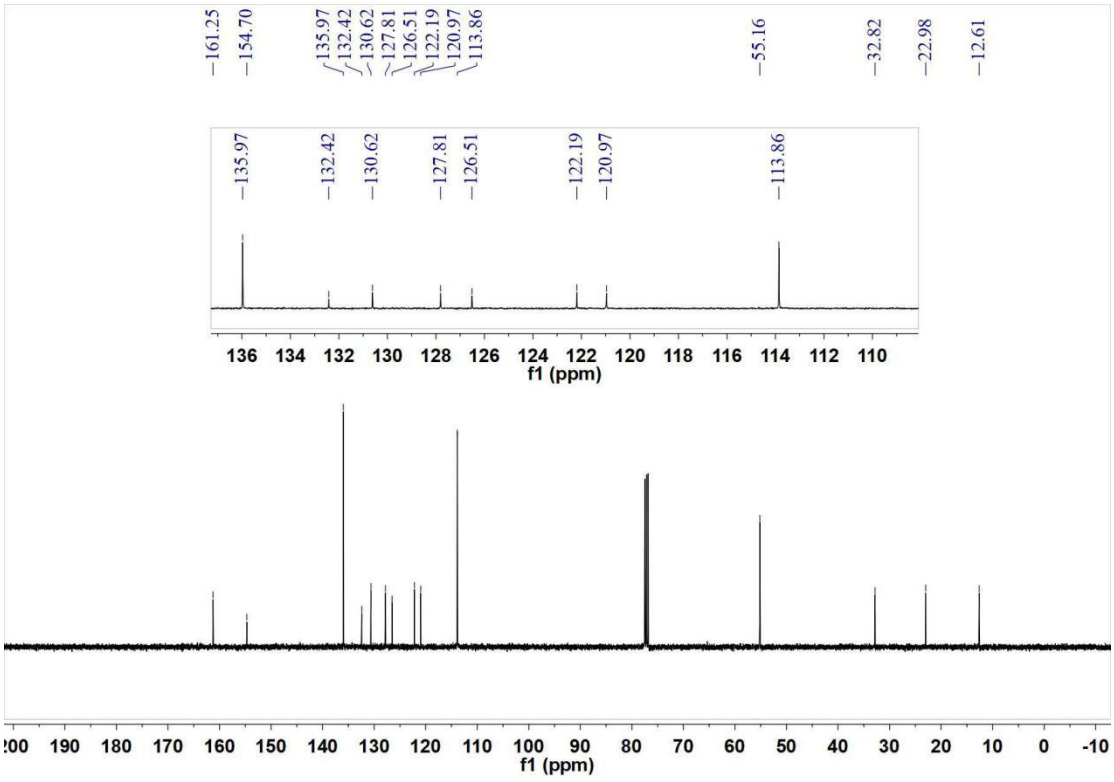
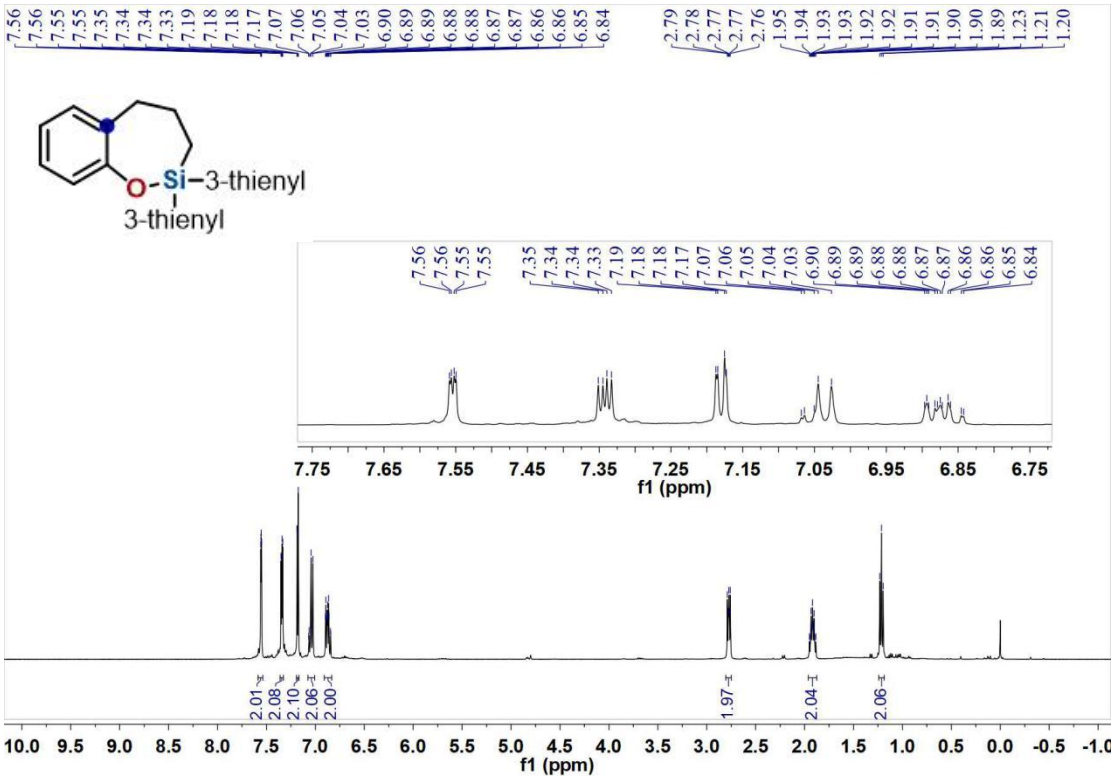
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

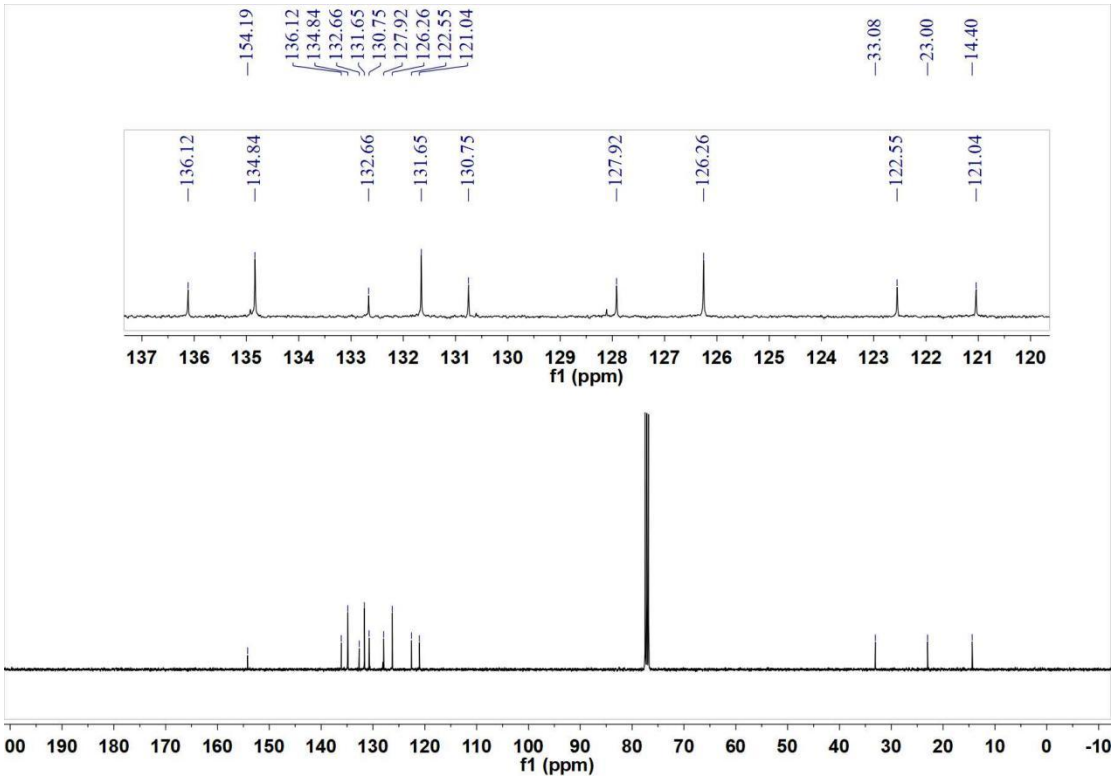
3ac


7.61
7.60
7.59
7.58
7.17
7.17
7.15
7.13
7.12
7.11
7.03
7.01
7.01
6.98
6.97
6.95
6.95
3.85
2.86
2.85
2.85
2.84
2.83
2.83
2.03
2.02
2.01
2.01
2.00
2.00
1.99
1.34
1.33
1.32
1.31
1.30
1.29
f1 (ppm)
O-Si-4-OMeC6H4
4-OMeC6H4
4.00
2.06
1.04
5.00
6.06
1.95
1.99
2.16
f1 (ppm)

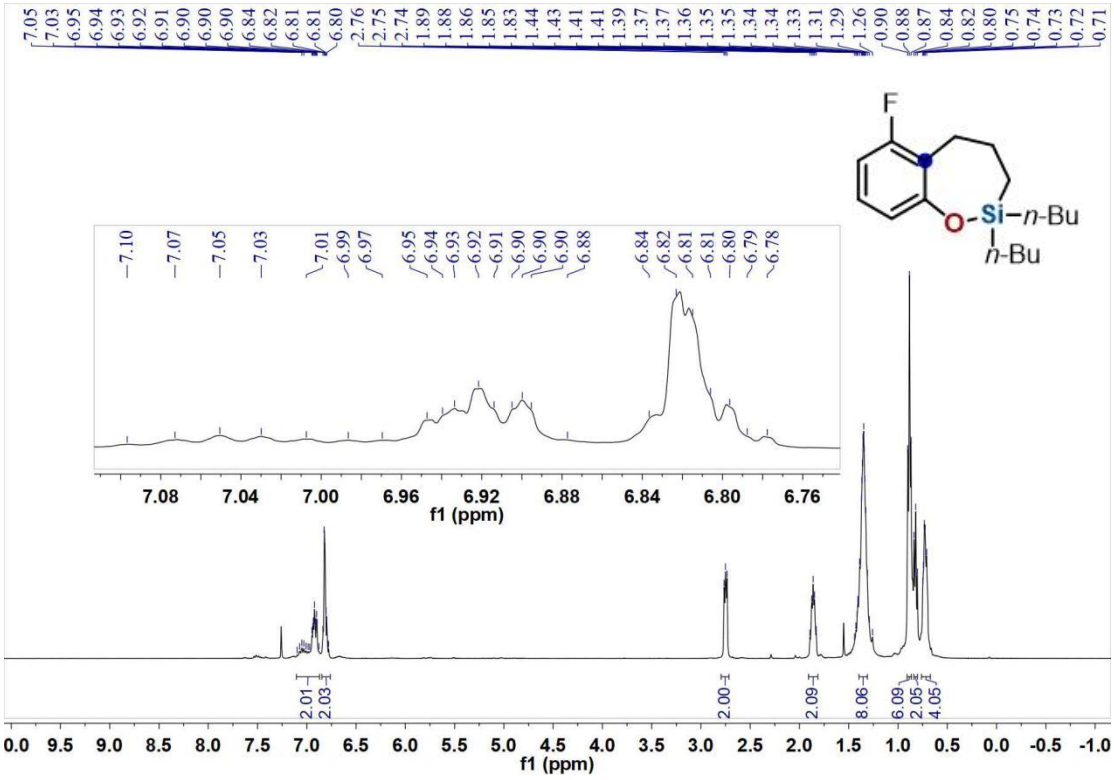

161.25
154.70
135.97
132.42
130.62
127.81
126.51
122.19
120.97
113.86
55.16
32.82
22.98
12.61
f1 (ppm)
f1 (ppm)

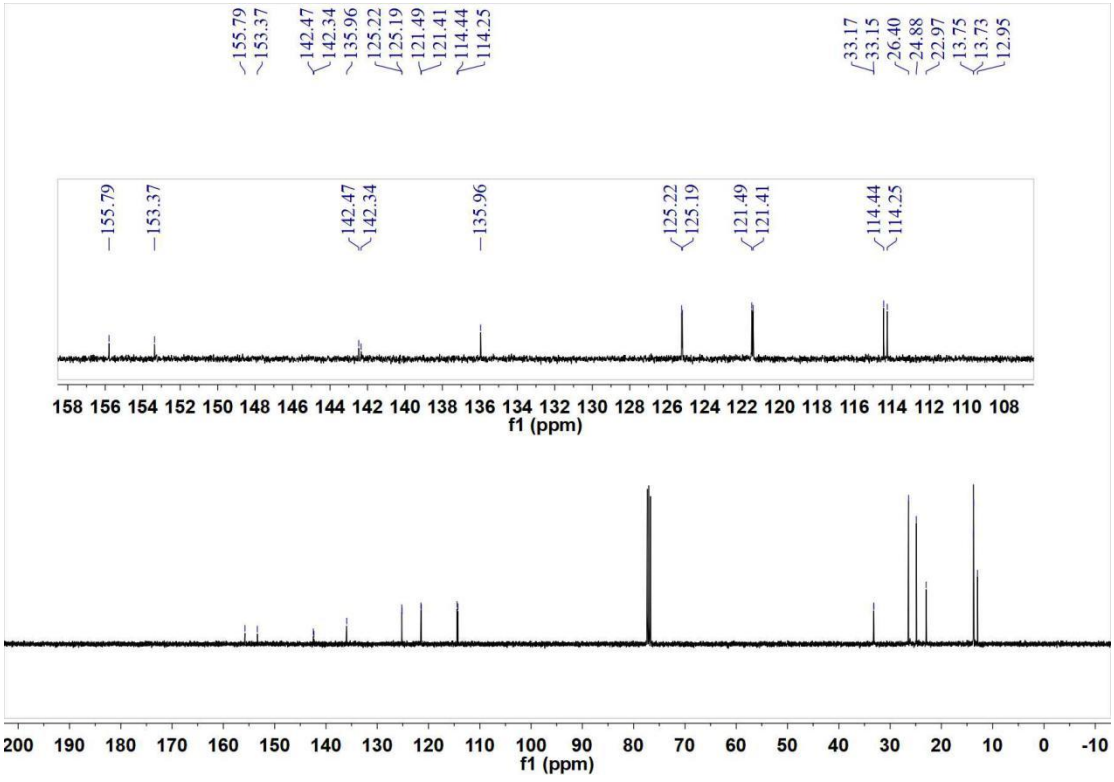
3ad

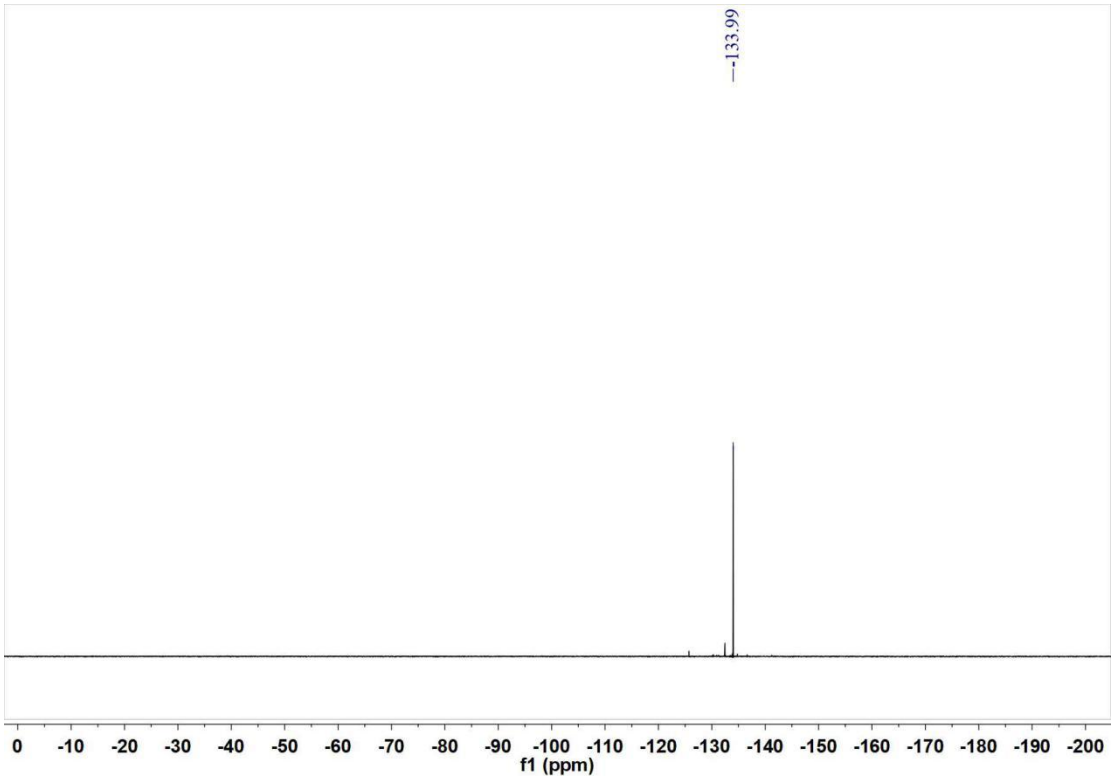




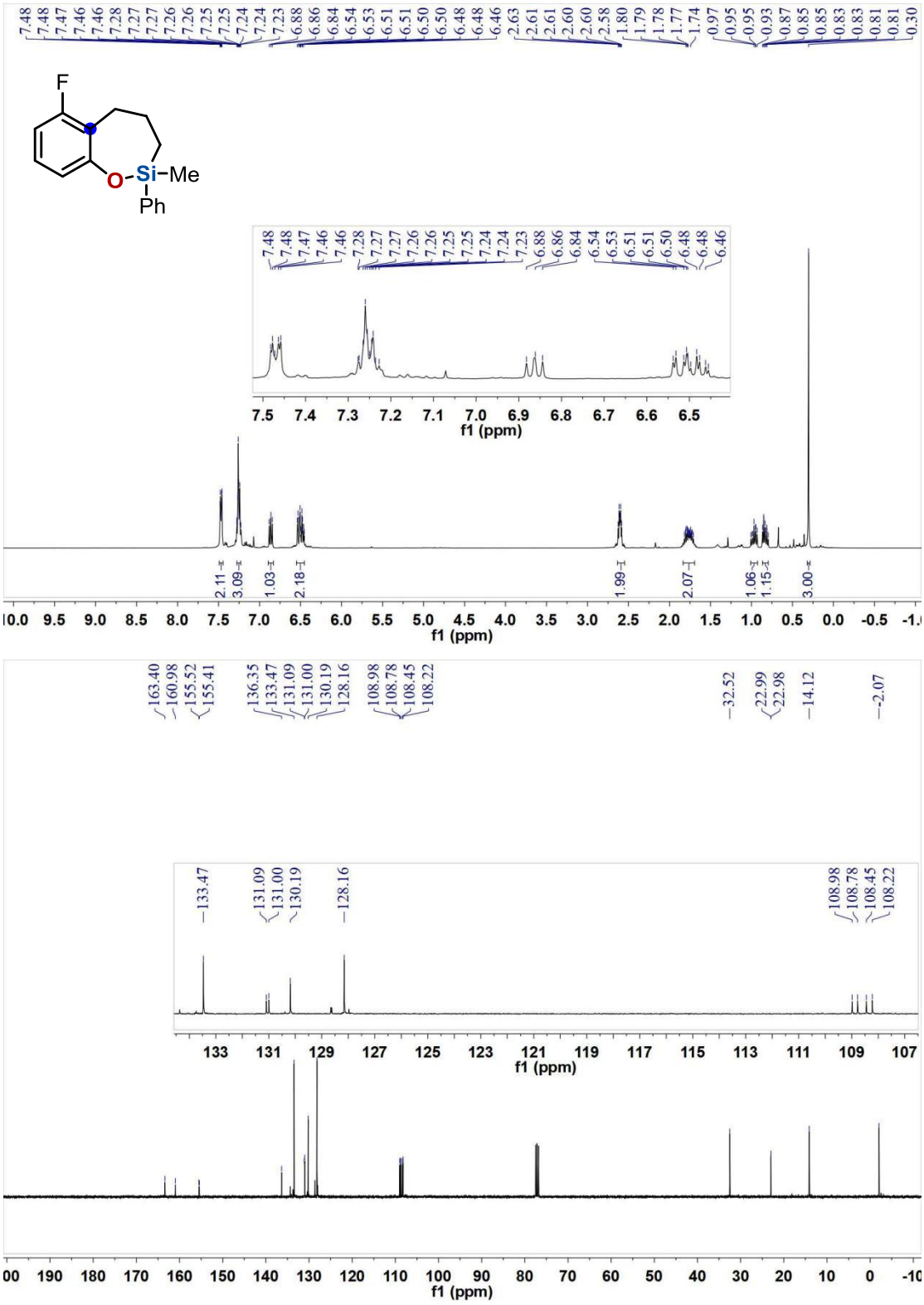
3be

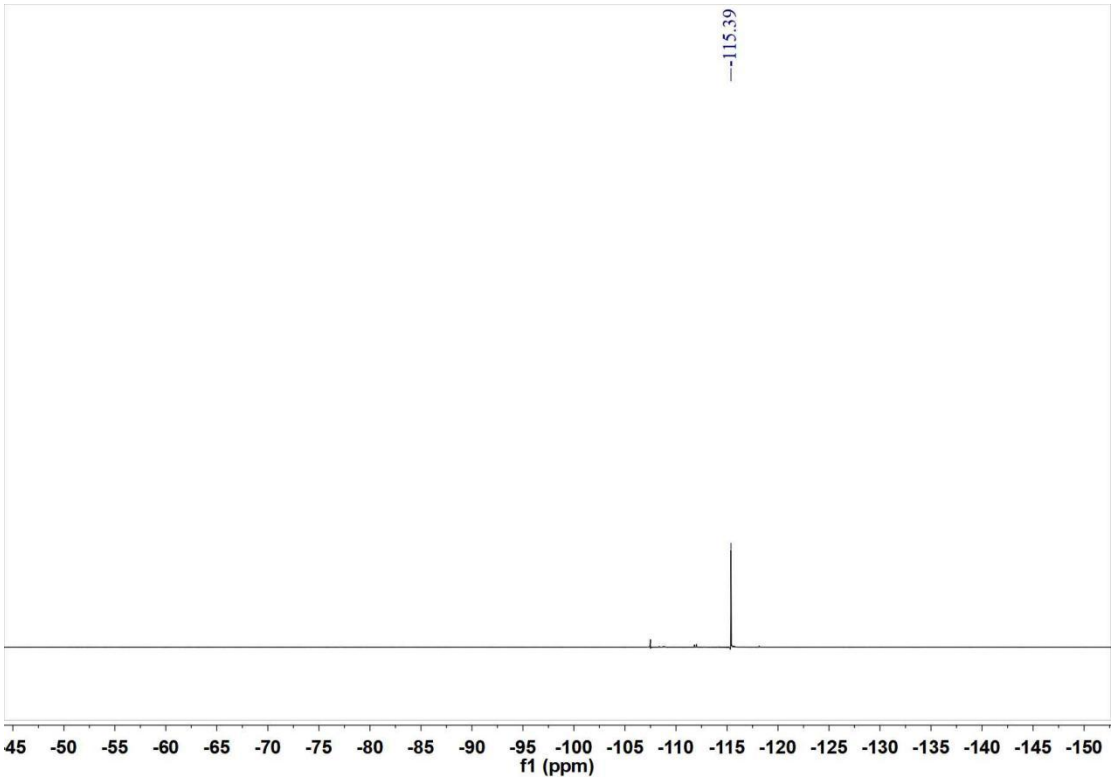




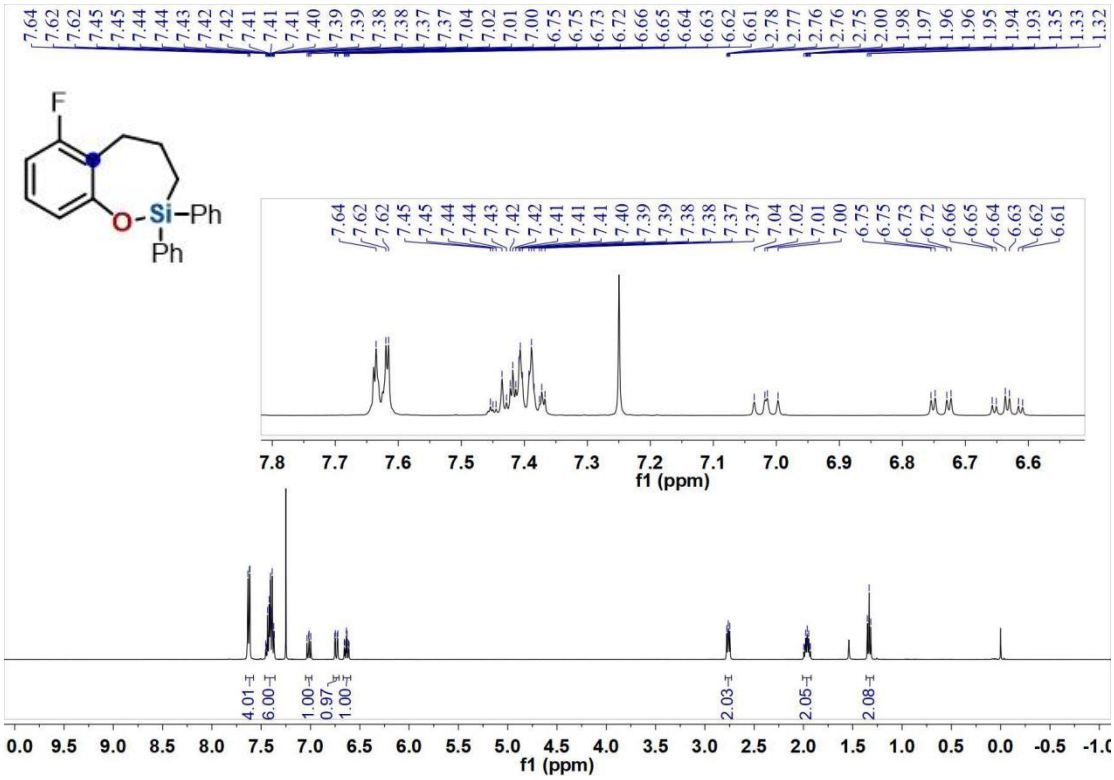

-133.99
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

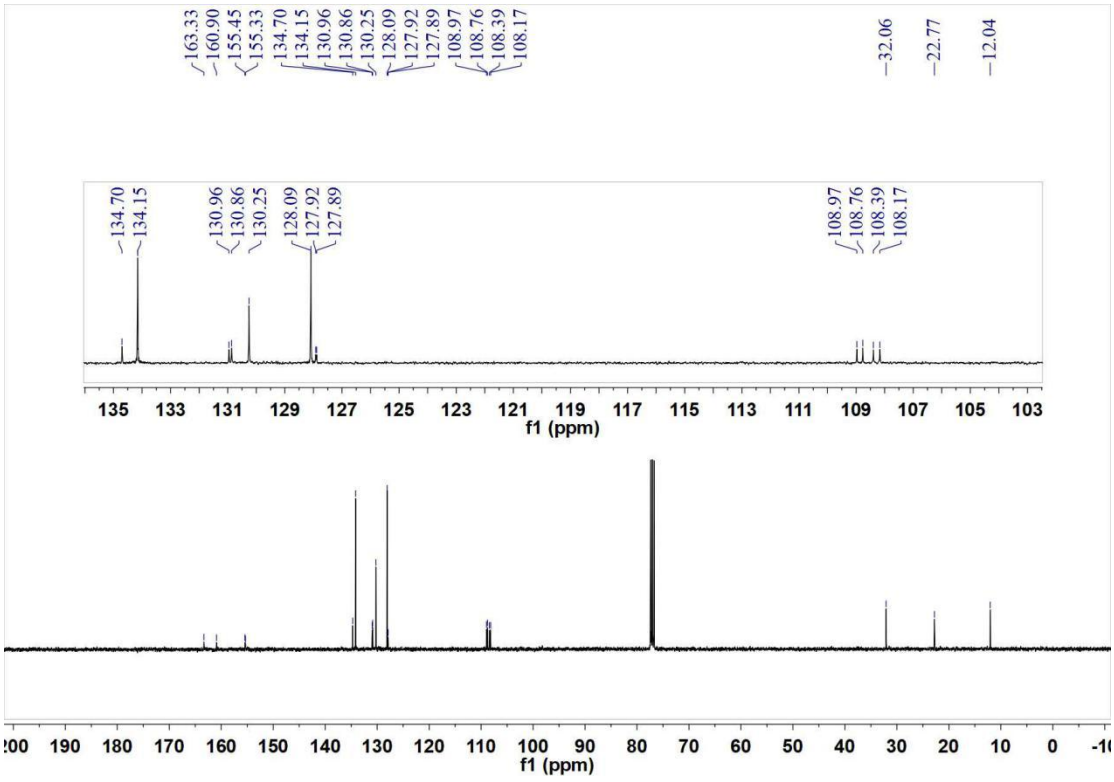
3bf

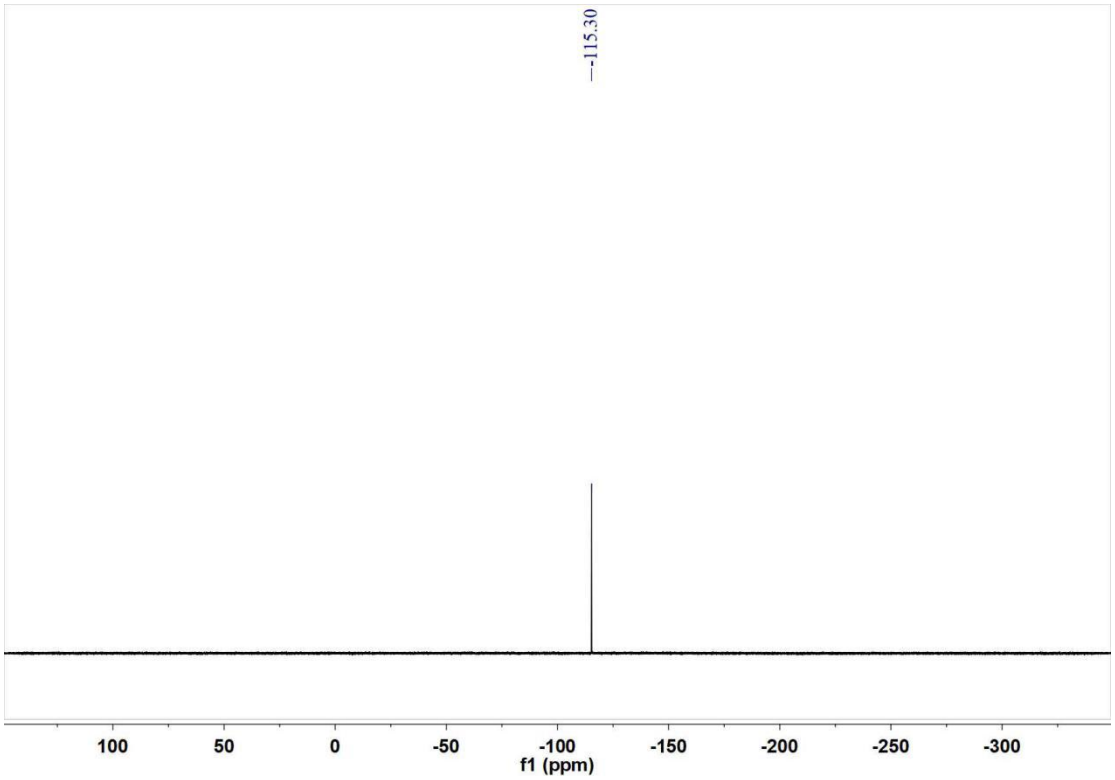



-115.39
45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)

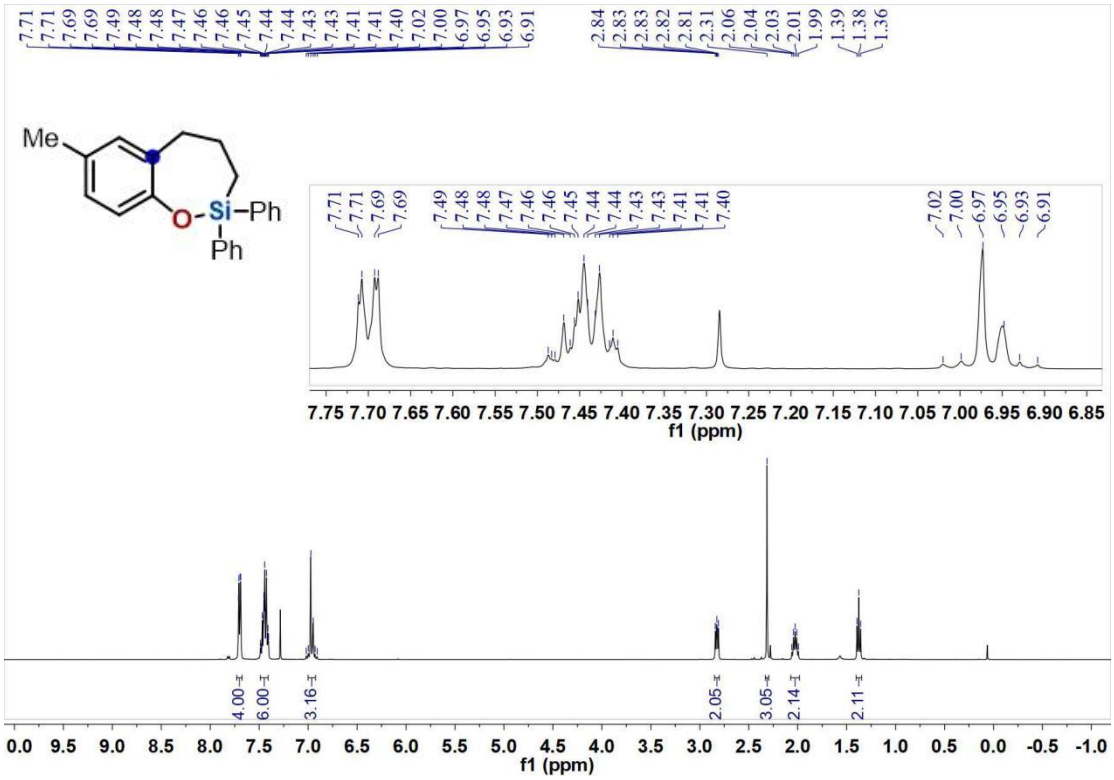
3ba

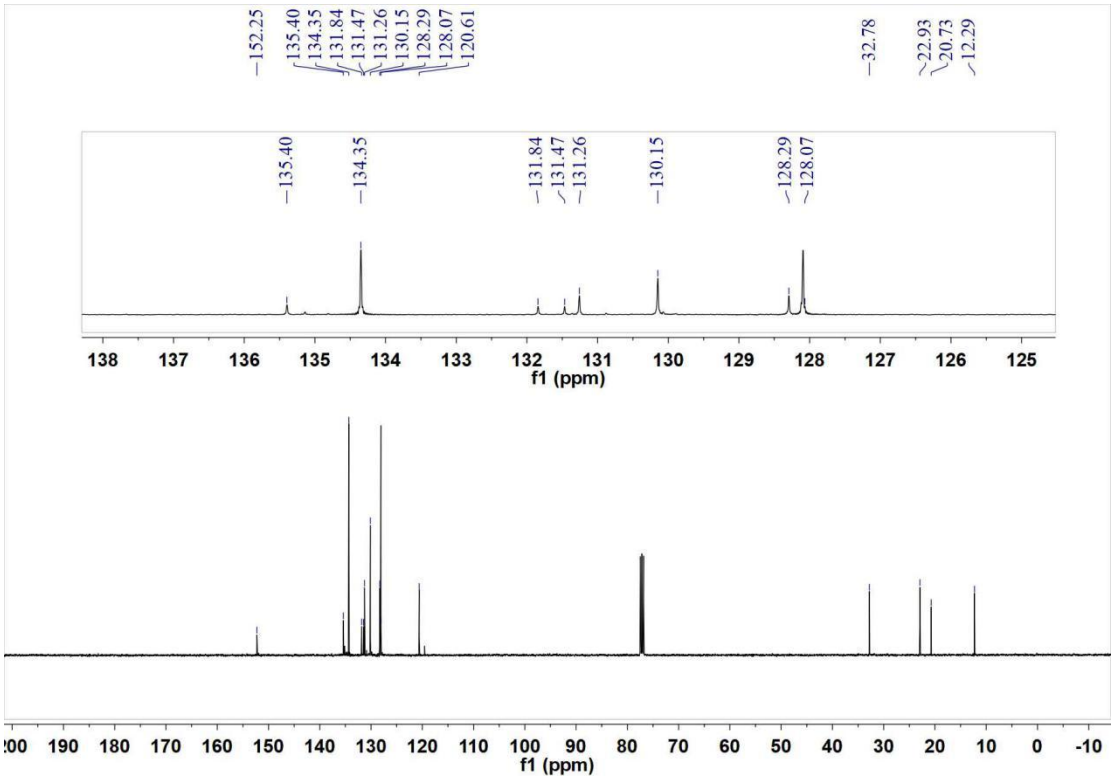




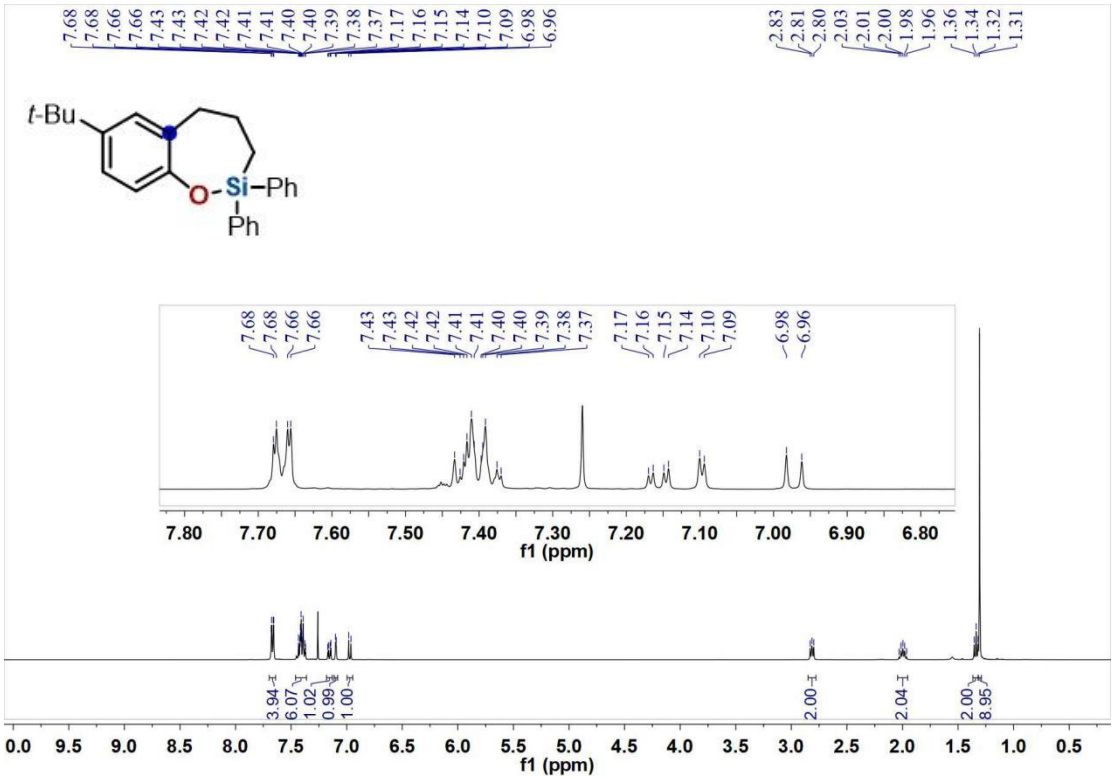

-115.30
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

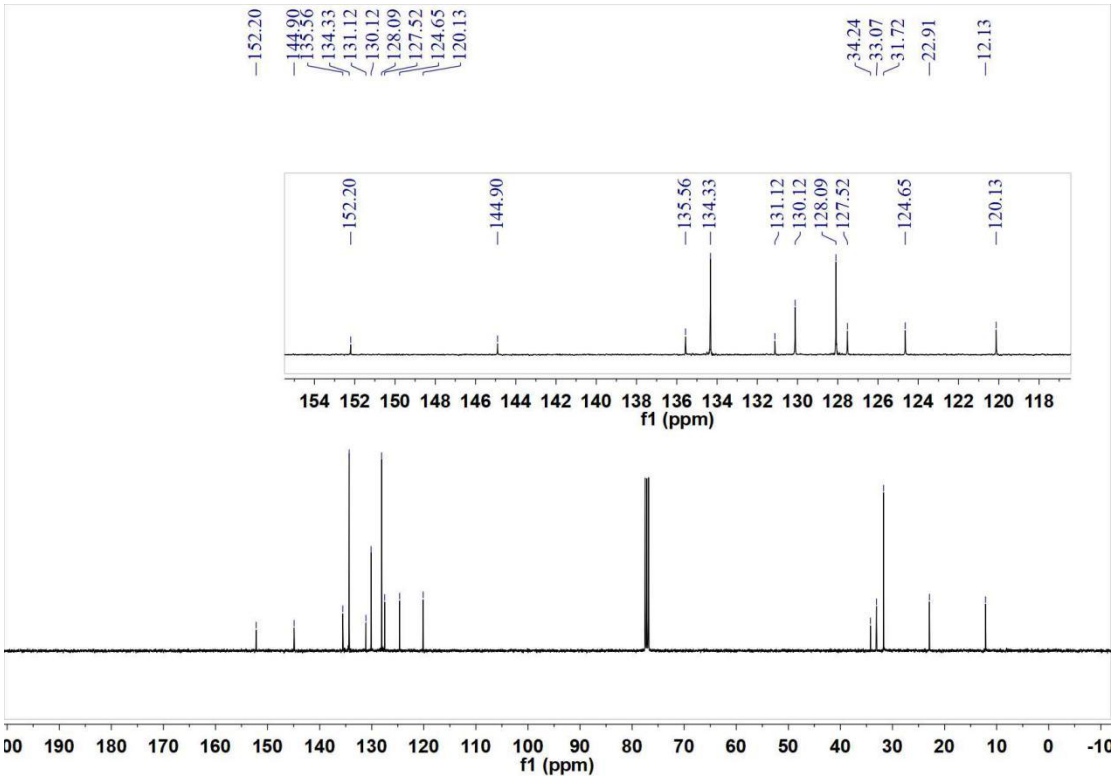
3ca



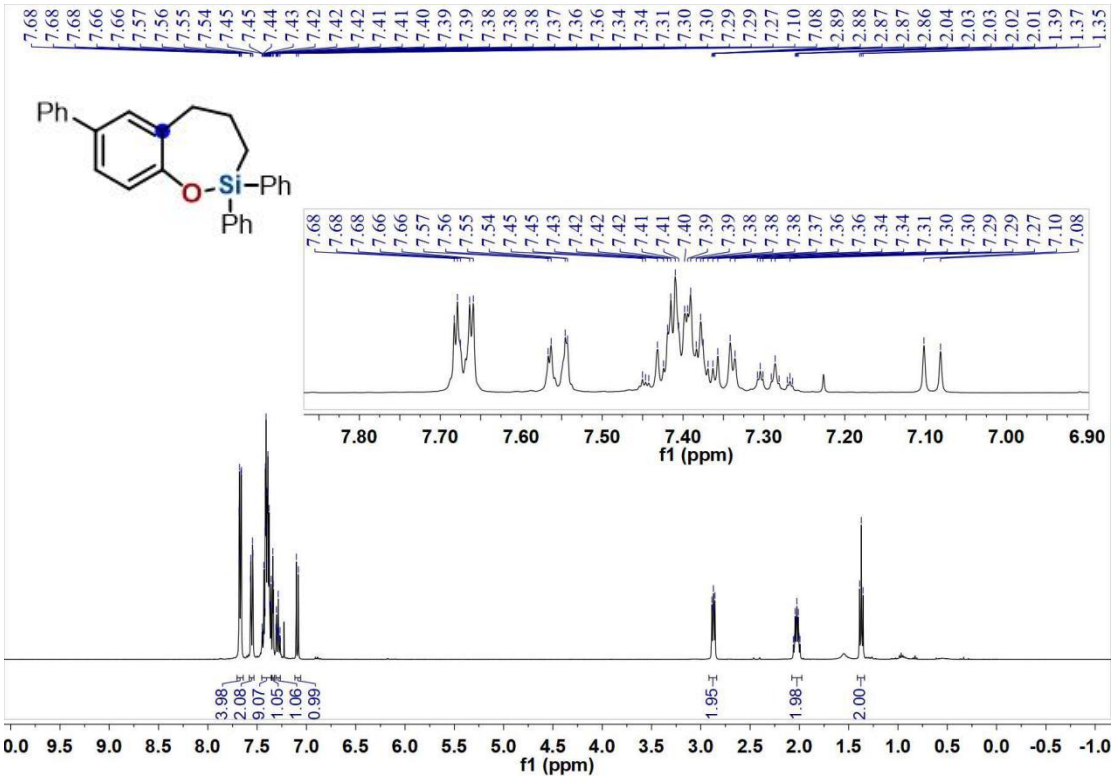


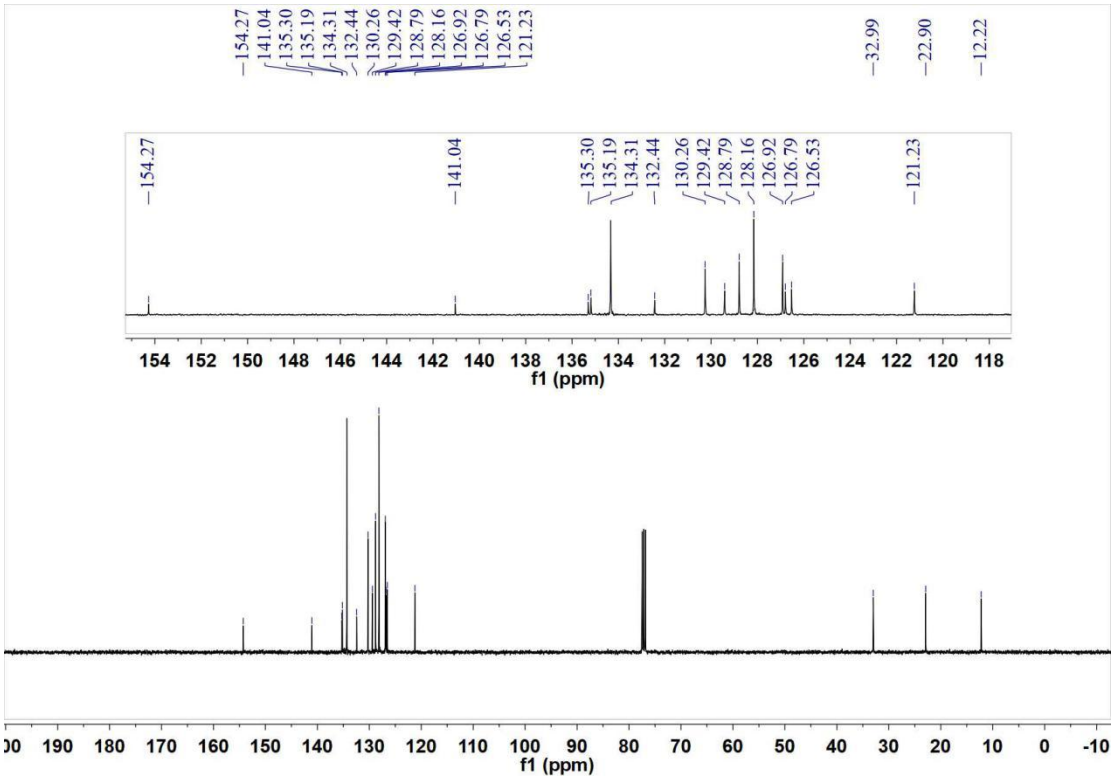
3da


7.68 7.68 7.66 7.66 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.37 7.17 7.16 7.15 7.14 7.10 7.09 6.98 6.96
2.83 2.81 2.80 2.03 2.01 2.00 1.98 1.96 1.36 1.34 1.32 1.31
t-Bu
O-Si-Ph
Ph
7.80 7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80
f1 (ppm)
3.94 6.07 1.02 0.99 1.00 2.00 2.04 2.00 8.95
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

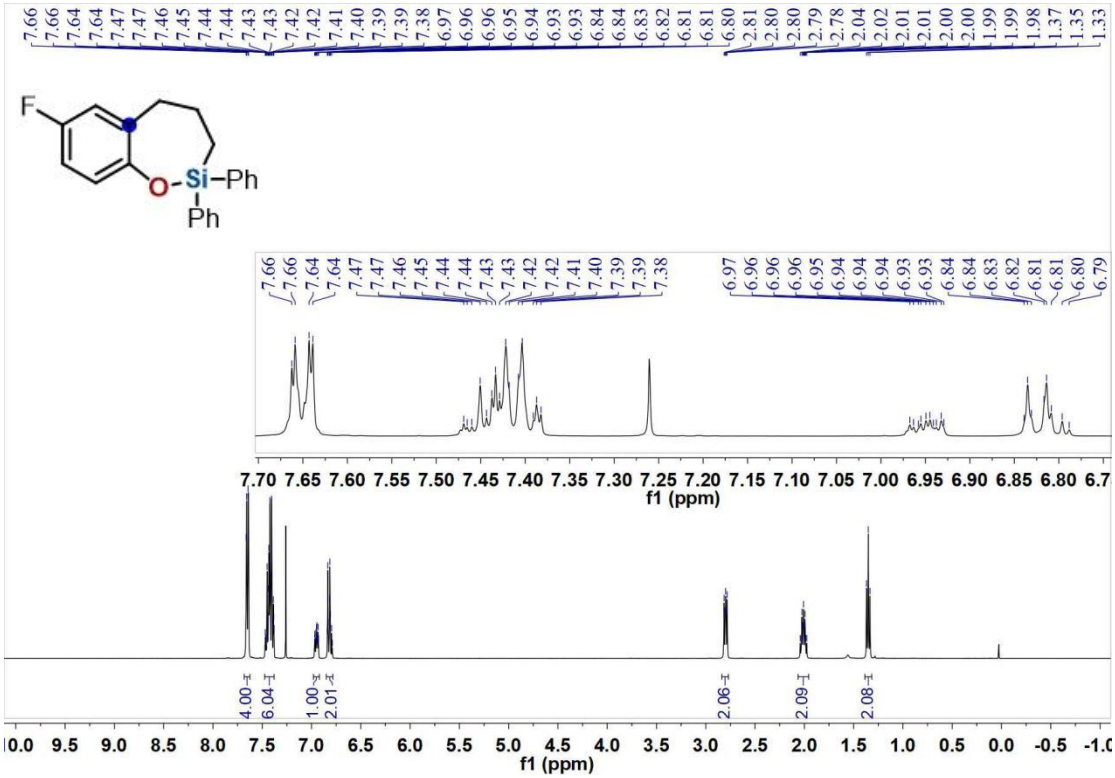

152.20 144.90 135.56 134.33 131.12 130.12 128.09 127.52 124.65 120.13
34.24 33.07 31.72 22.91 12.13
154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

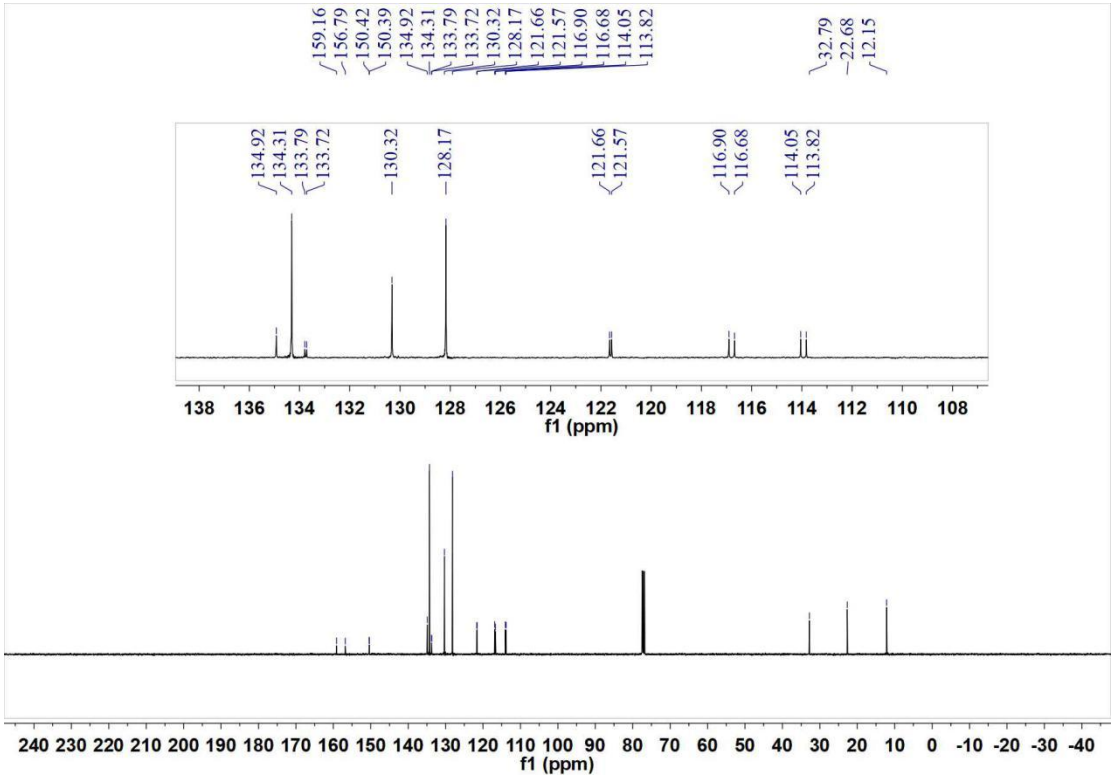
3ea

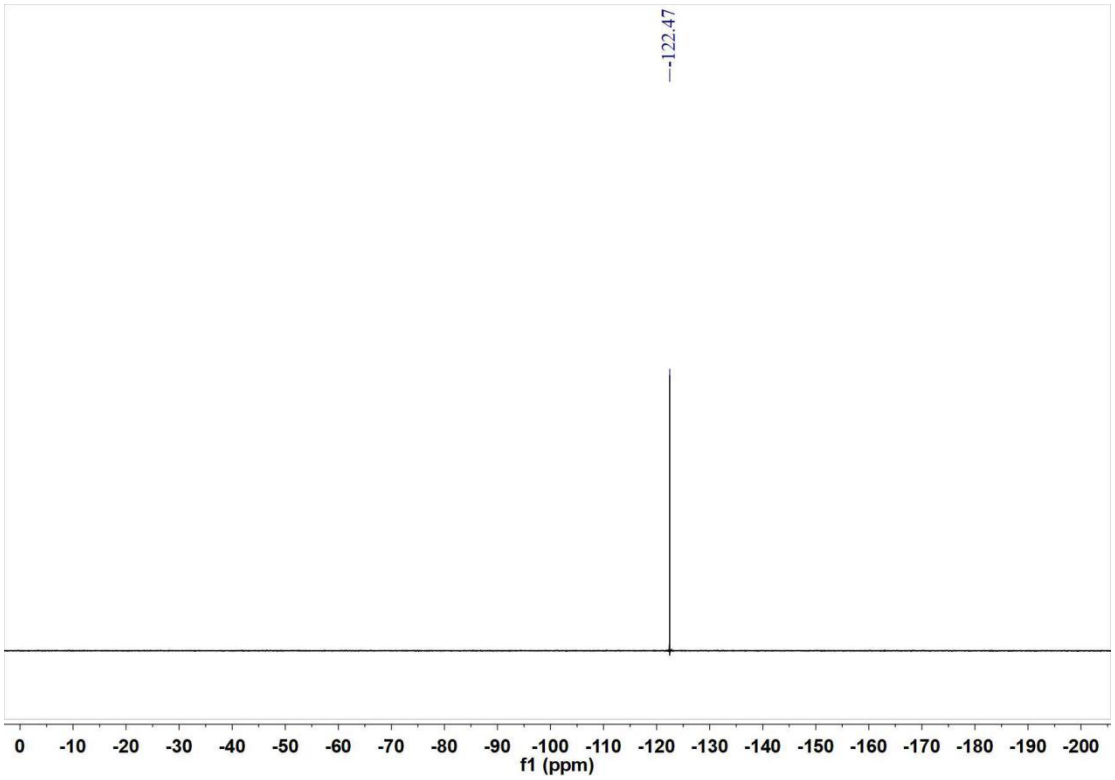




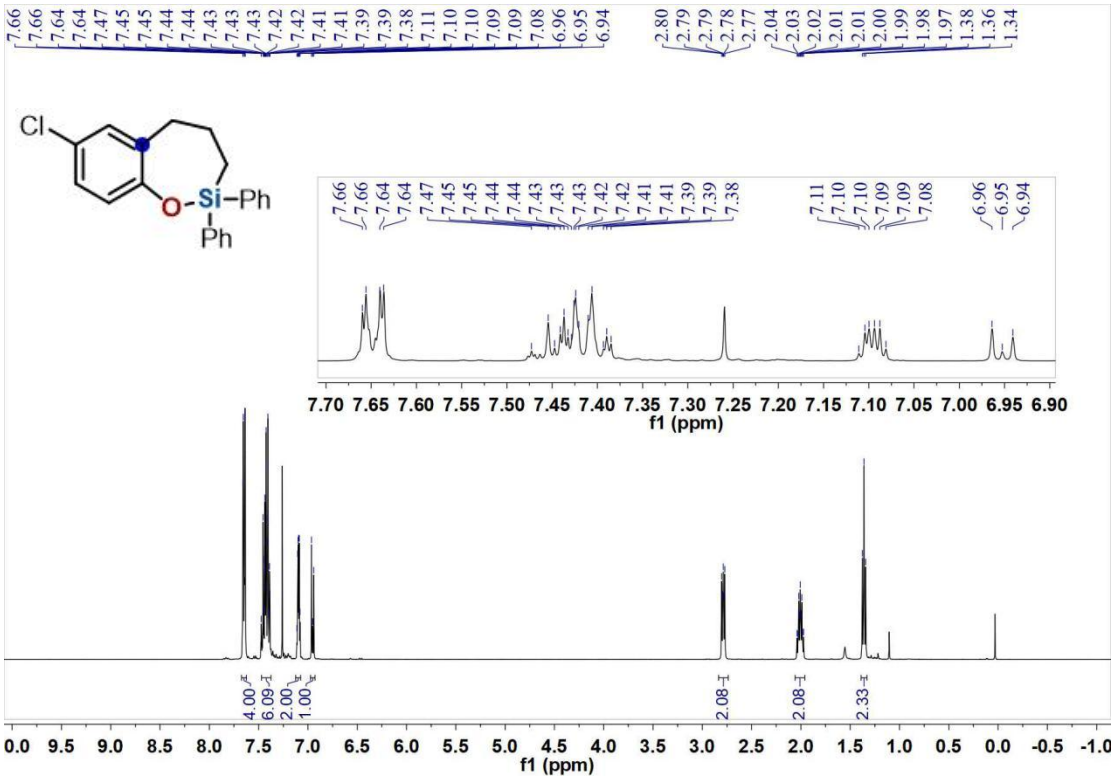
3fa

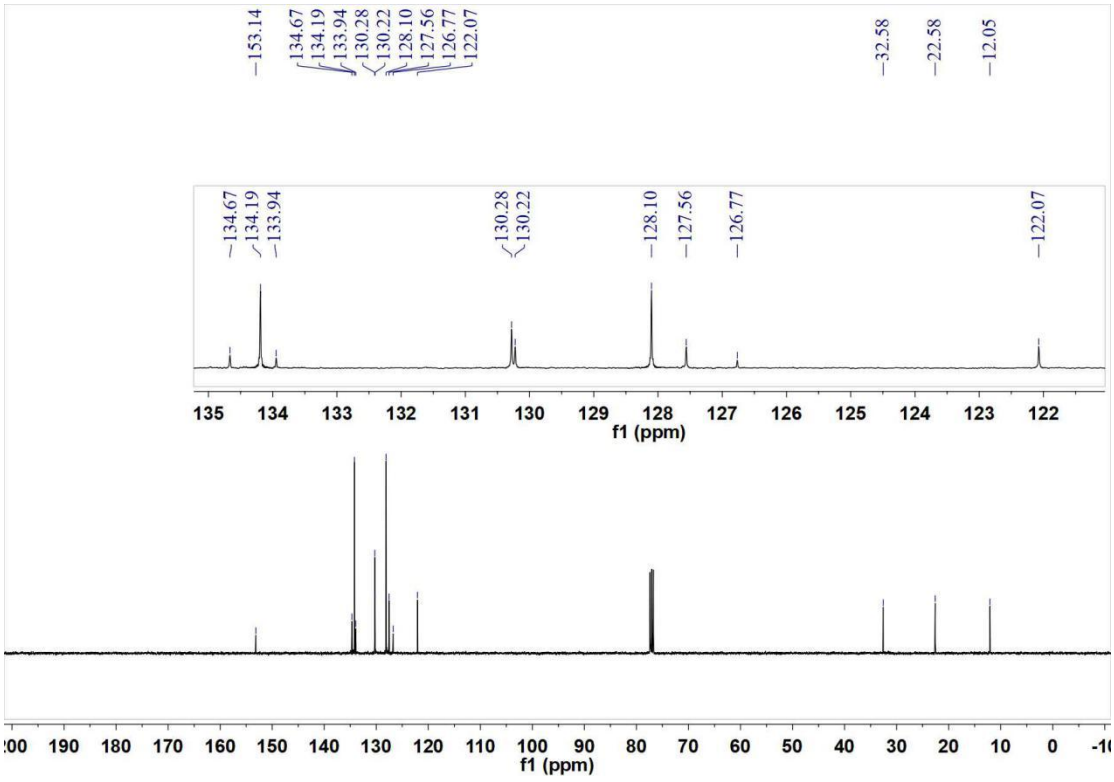




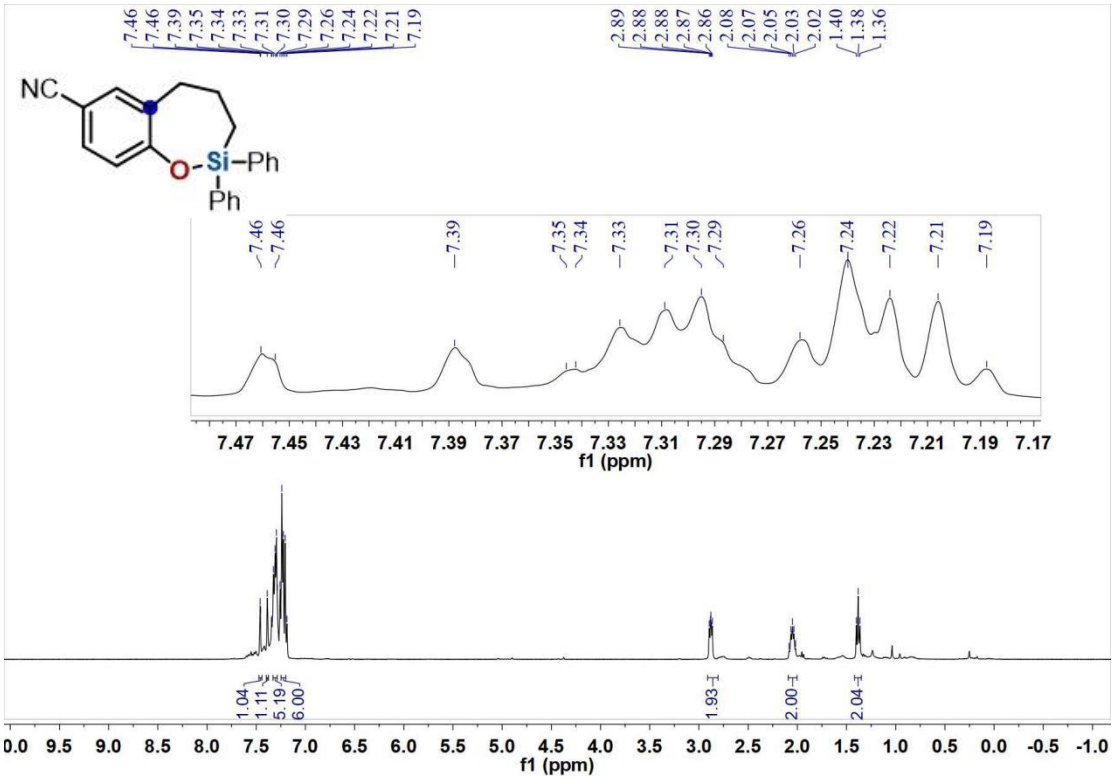

-122.47
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

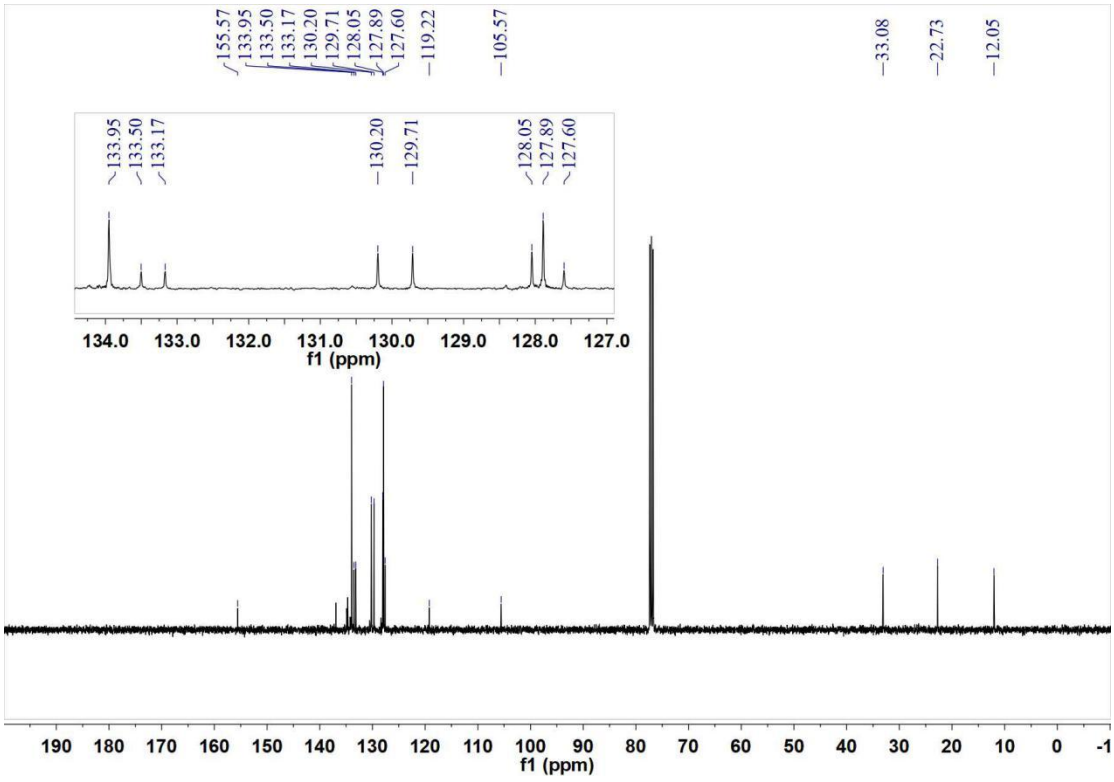
3ga



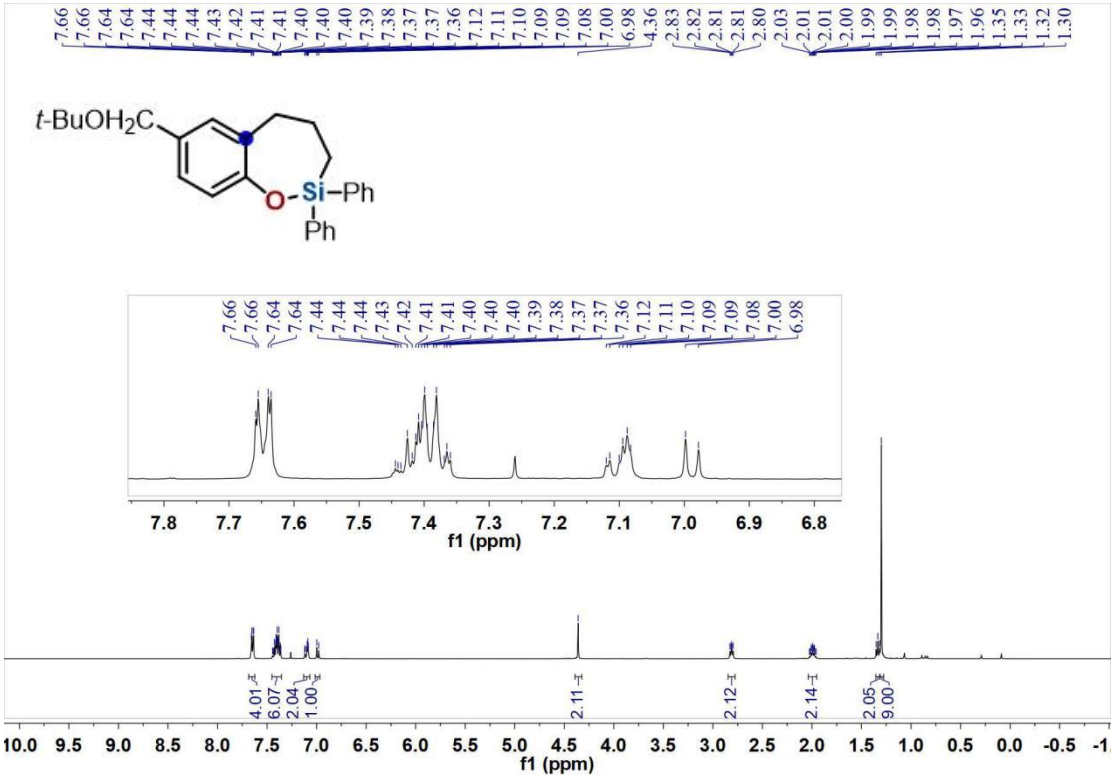


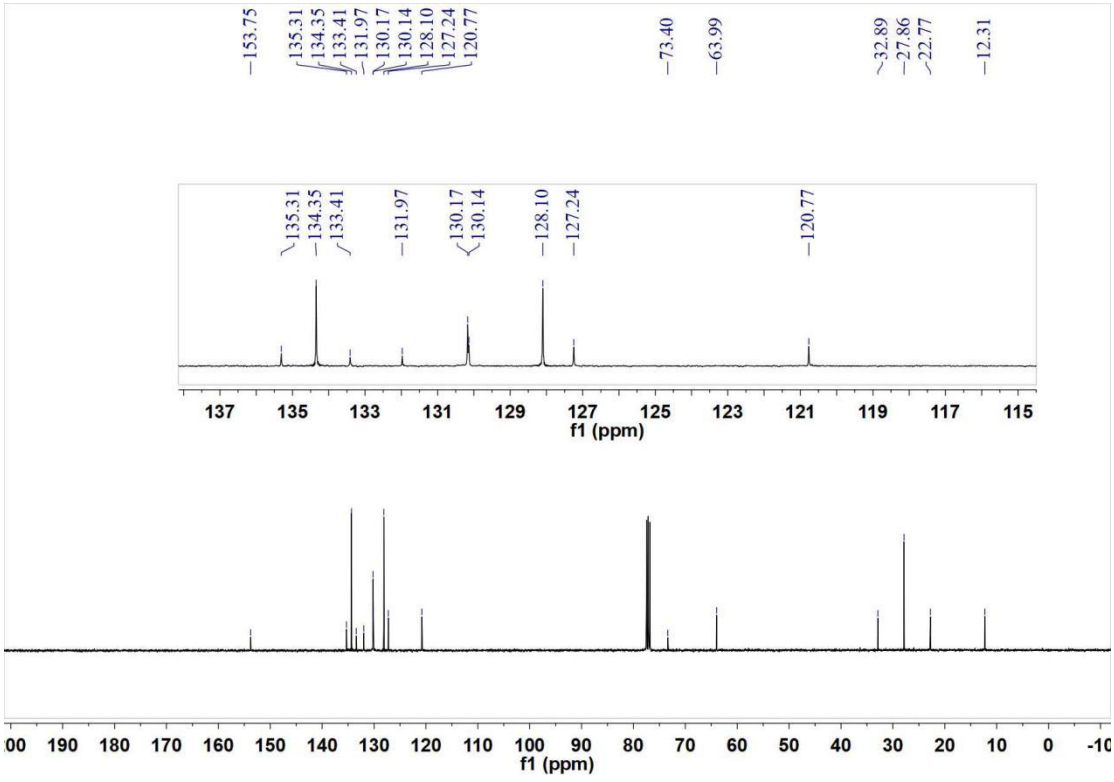
3ha



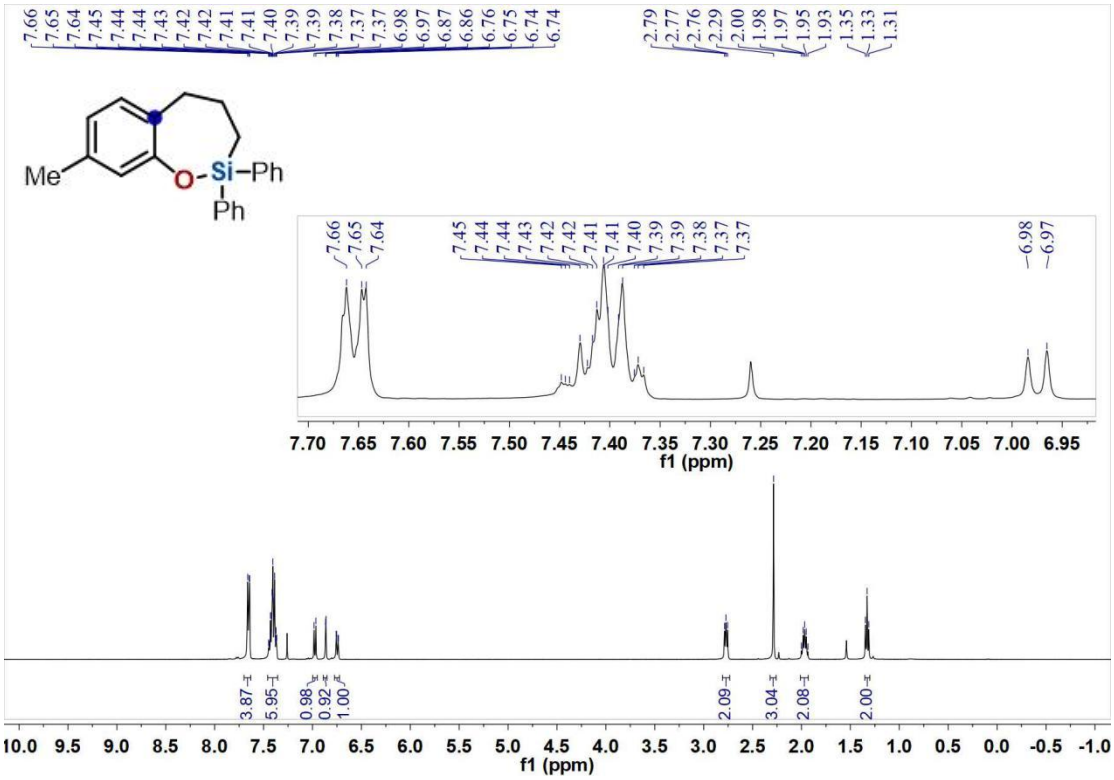


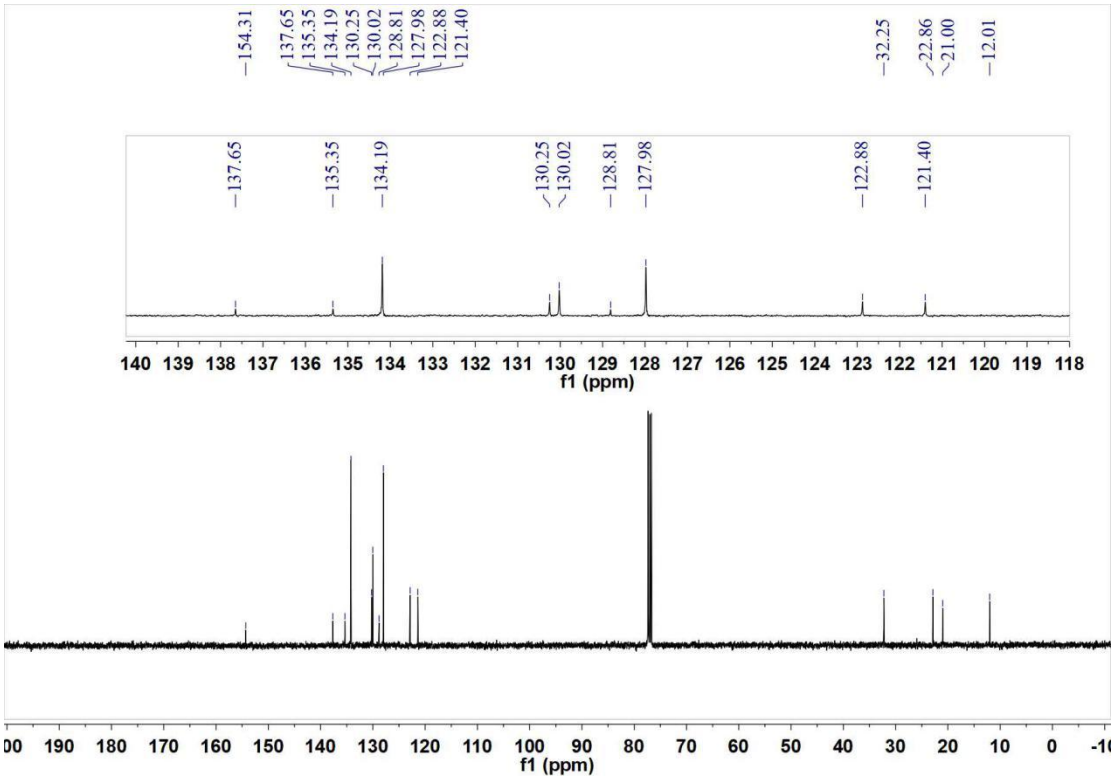
3ia



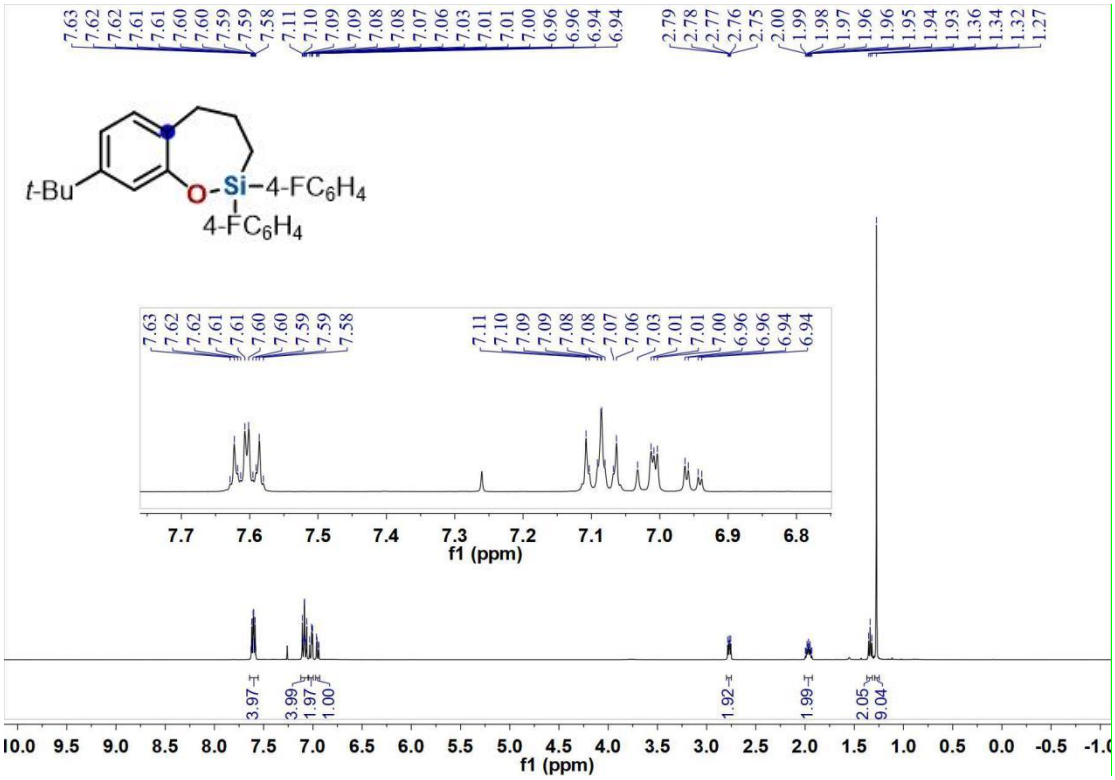


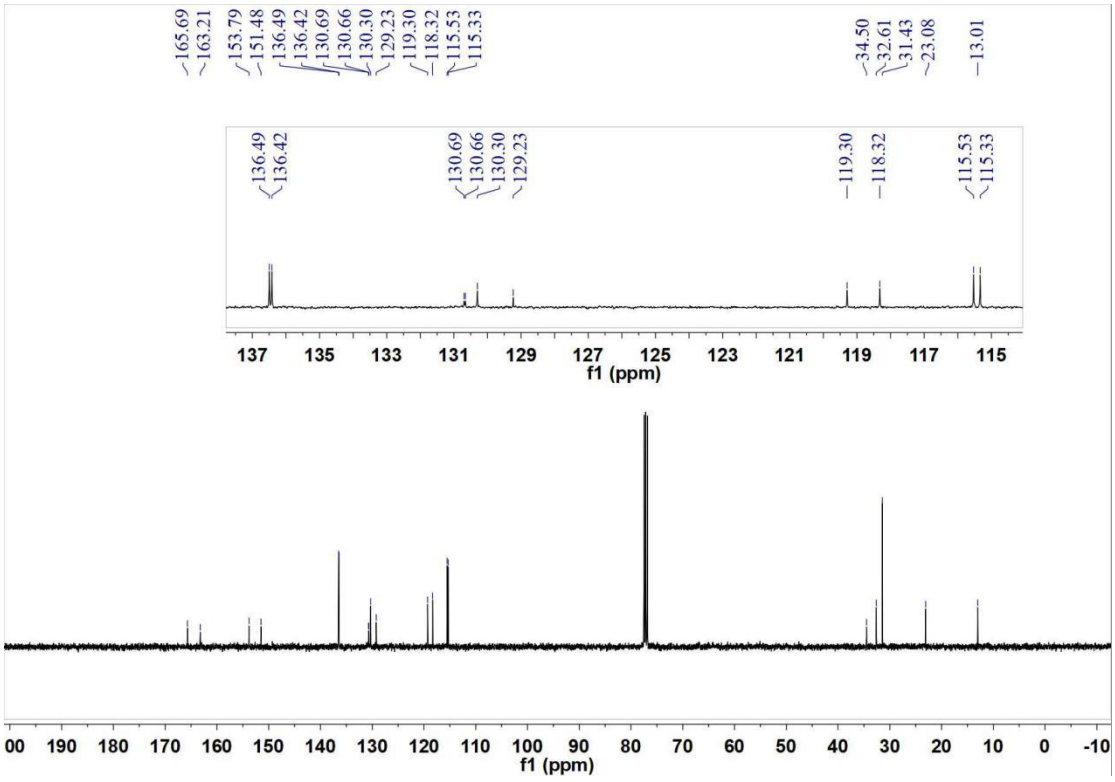
3ja



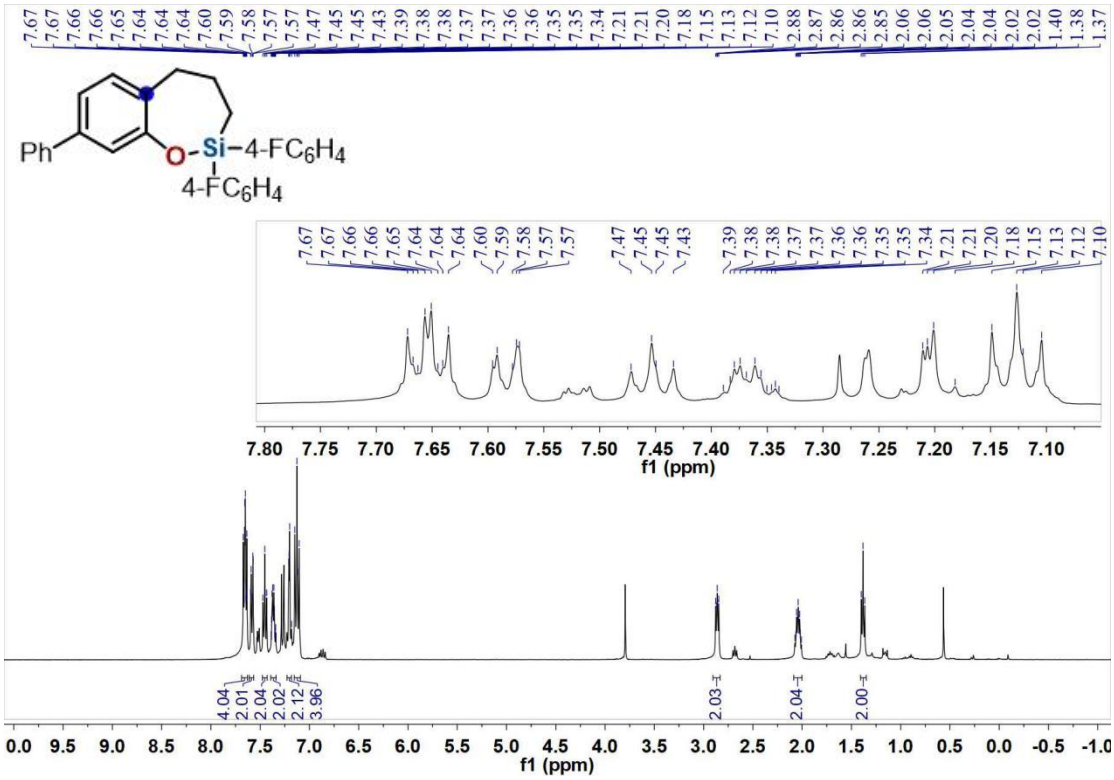


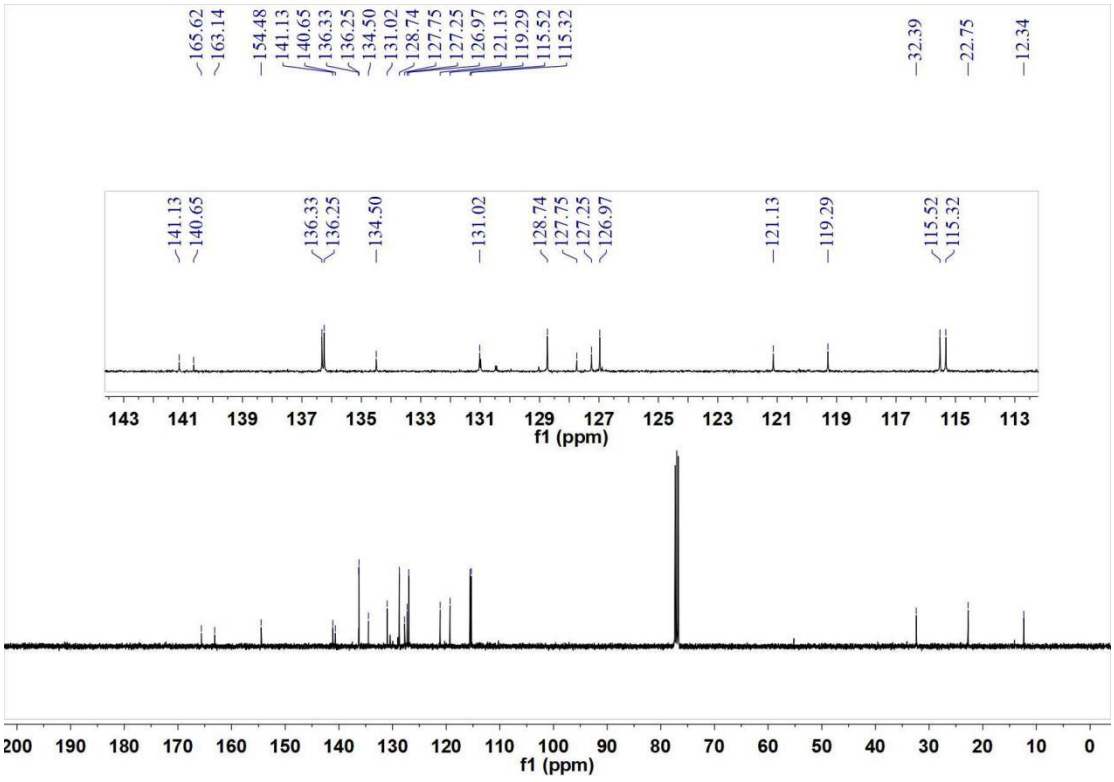
3lb

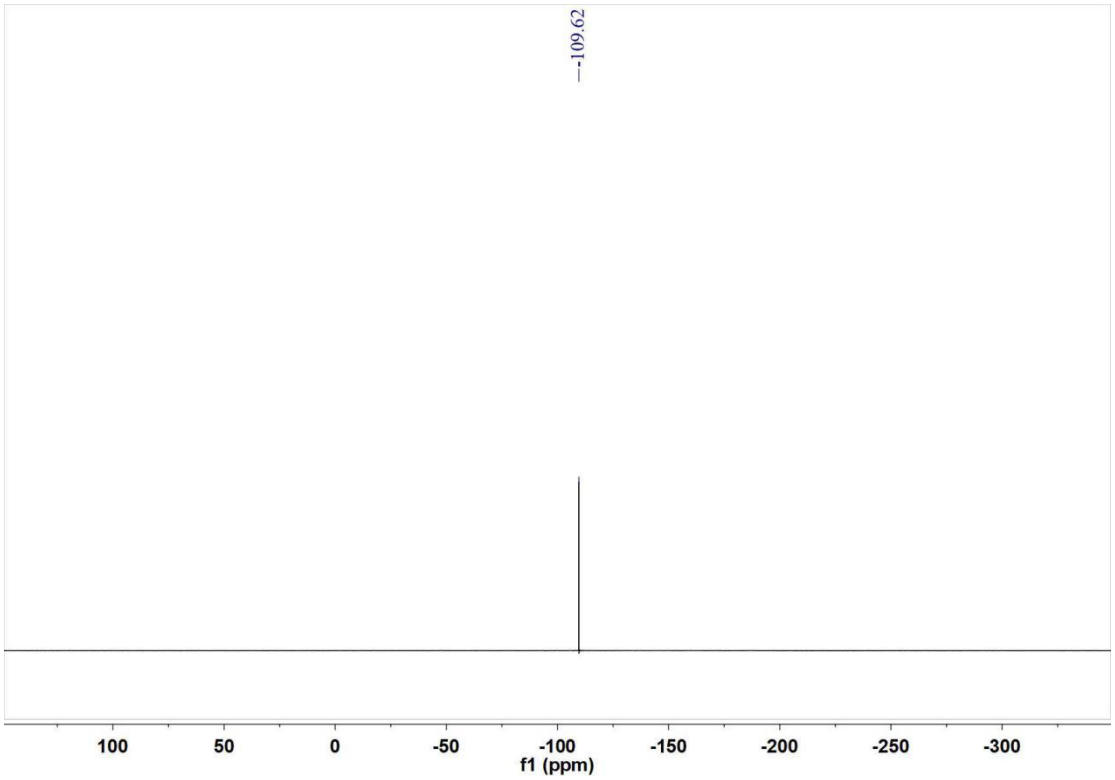




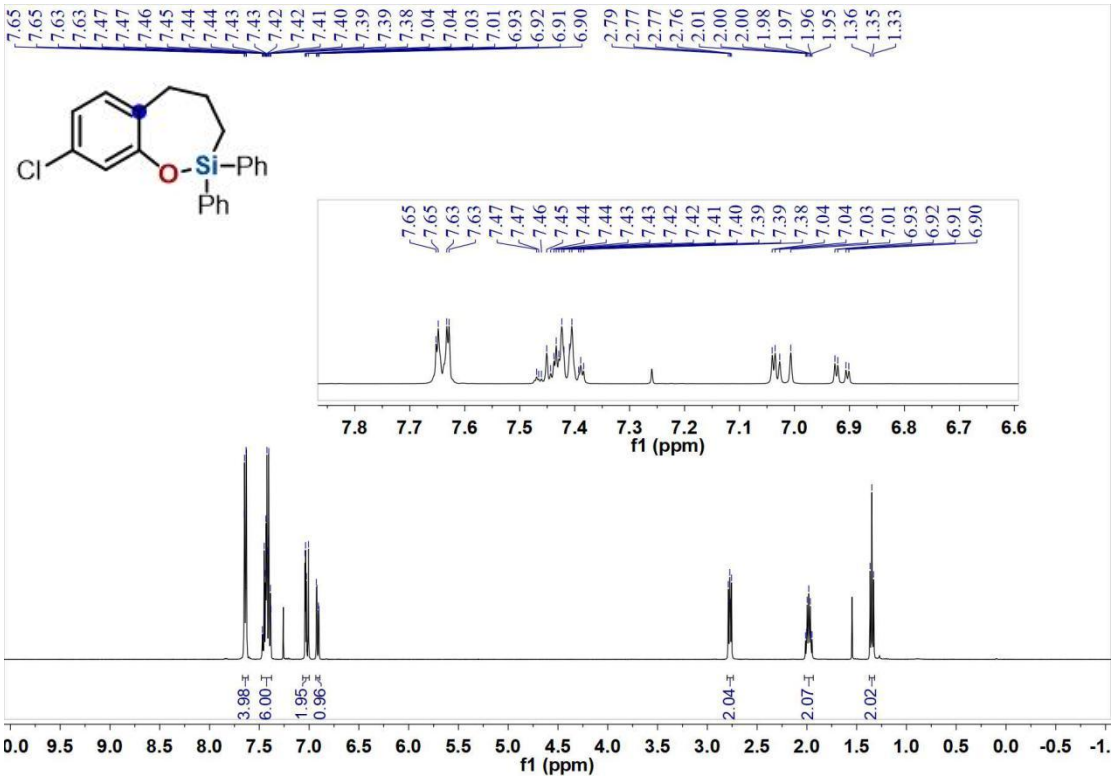
3mb

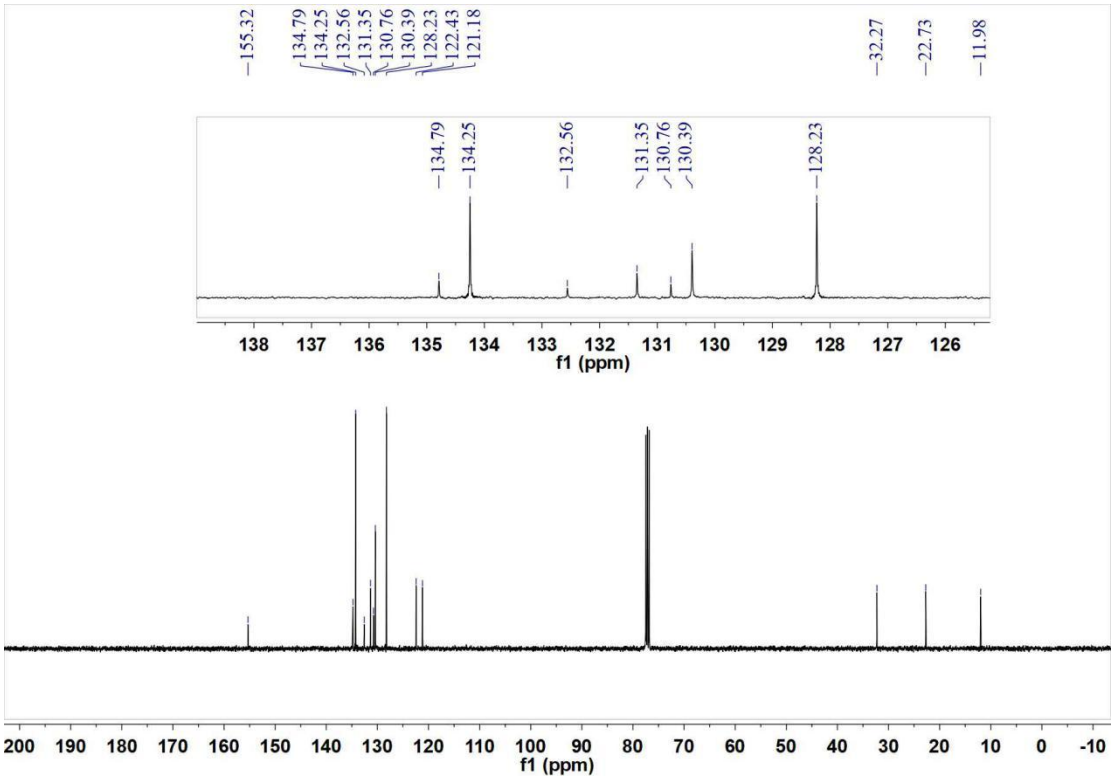




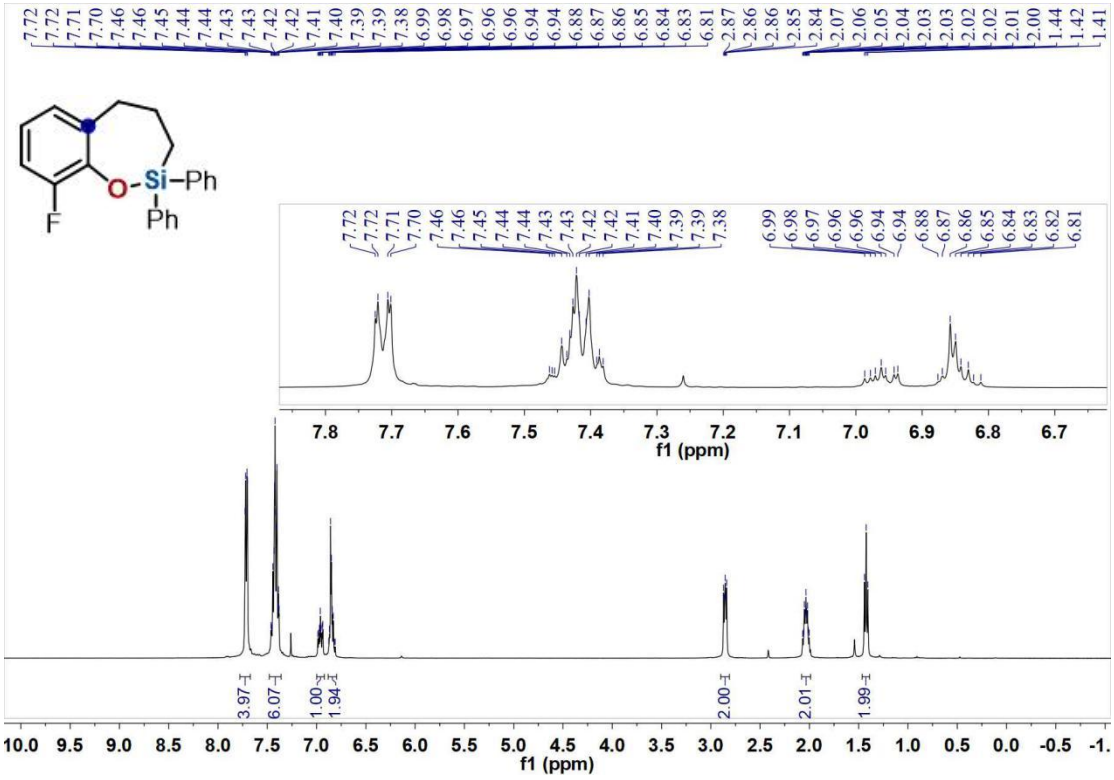

-109.62
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

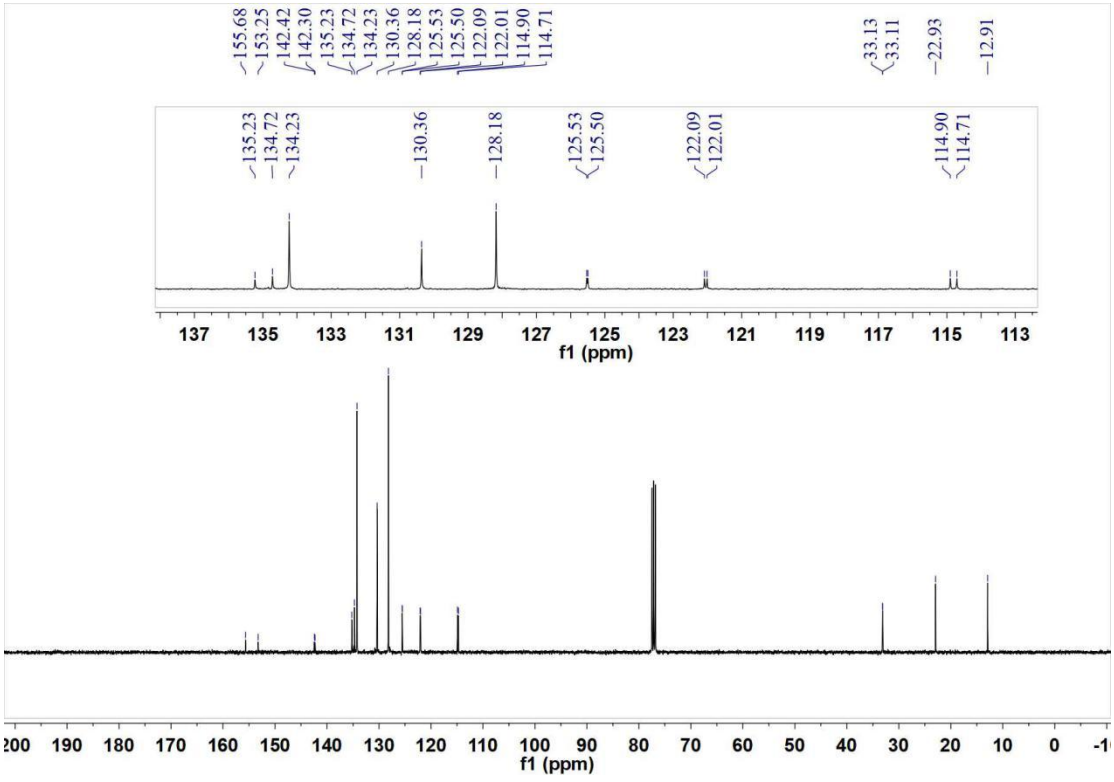
3ka

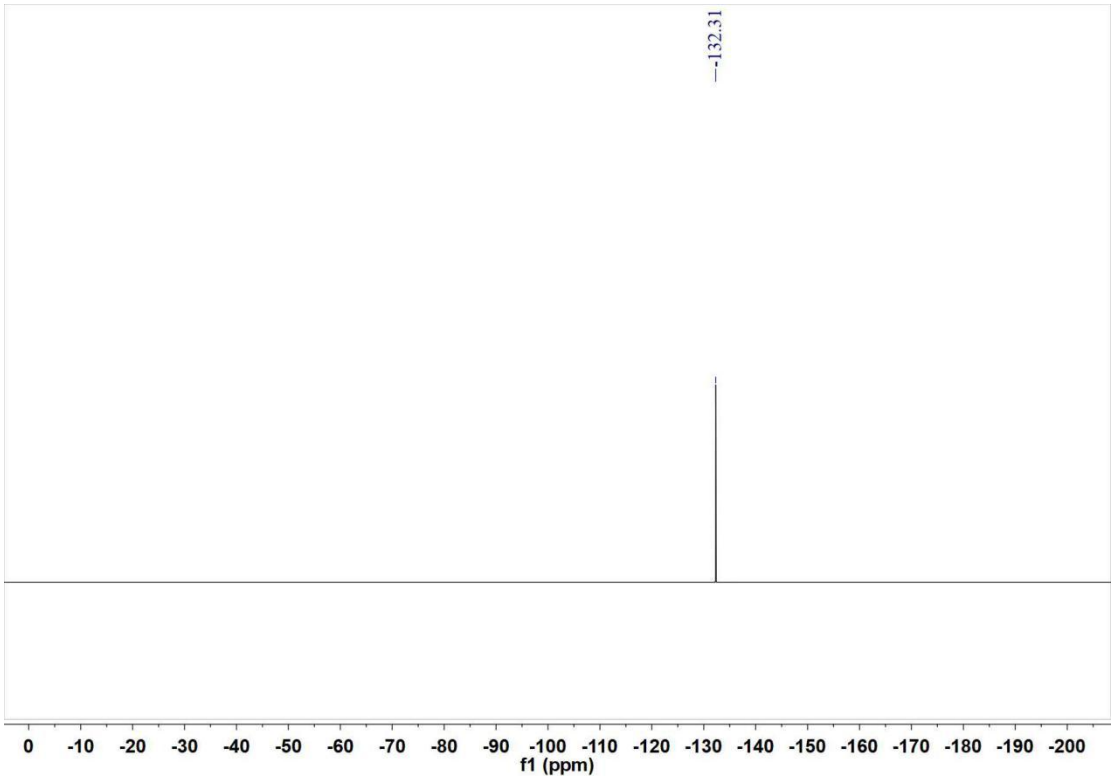

7.65 7.65 7.63 7.63 7.47 7.47 7.46 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.40 7.39 7.39 7.38 7.04 7.04 7.03 7.01 6.93 6.92 6.91 6.90
2.79 2.77 2.77 2.76 2.01 2.00 2.00 1.98 1.97 1.96 1.95 1.36 1.35 1.33
Cl
O
Si
Ph
Ph
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
3.98
6.00
1.95
0.96
2.04
2.07
2.02
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


155.32
134.79 134.25 132.56 131.35 130.76 130.39 128.23 122.43 121.18
32.27 22.73 11.98
138 137 136 135 134 133 132 131 130 129 128 127 126
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

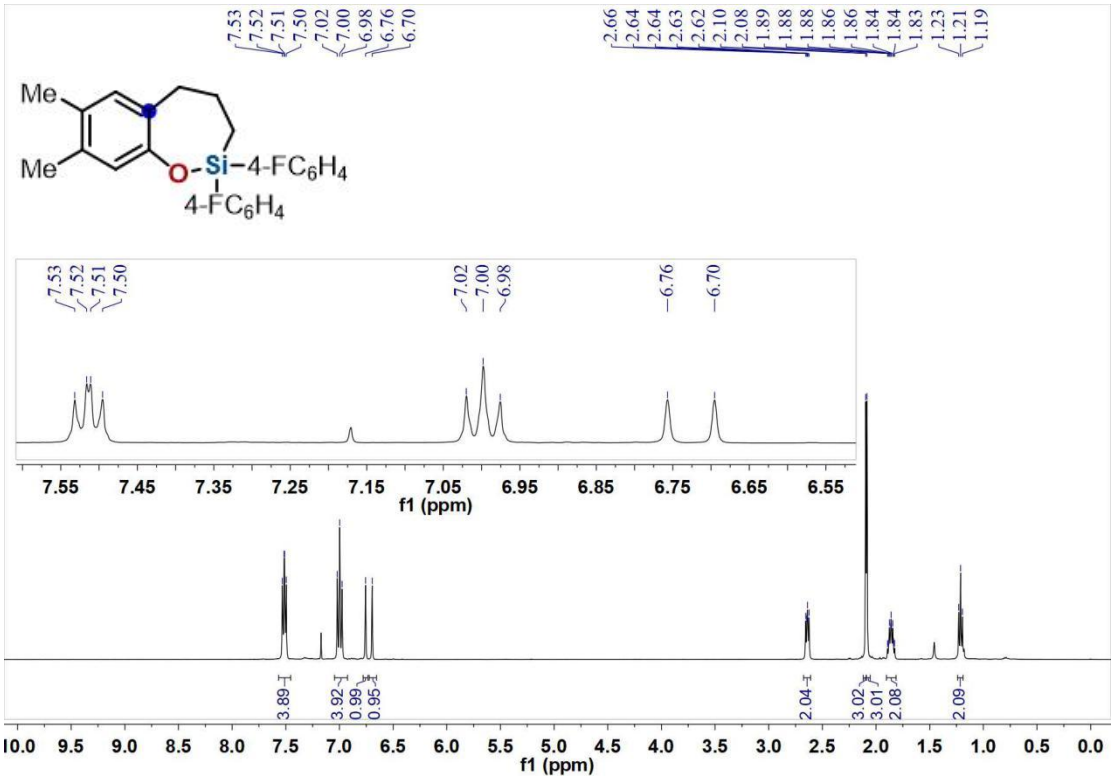
3nb

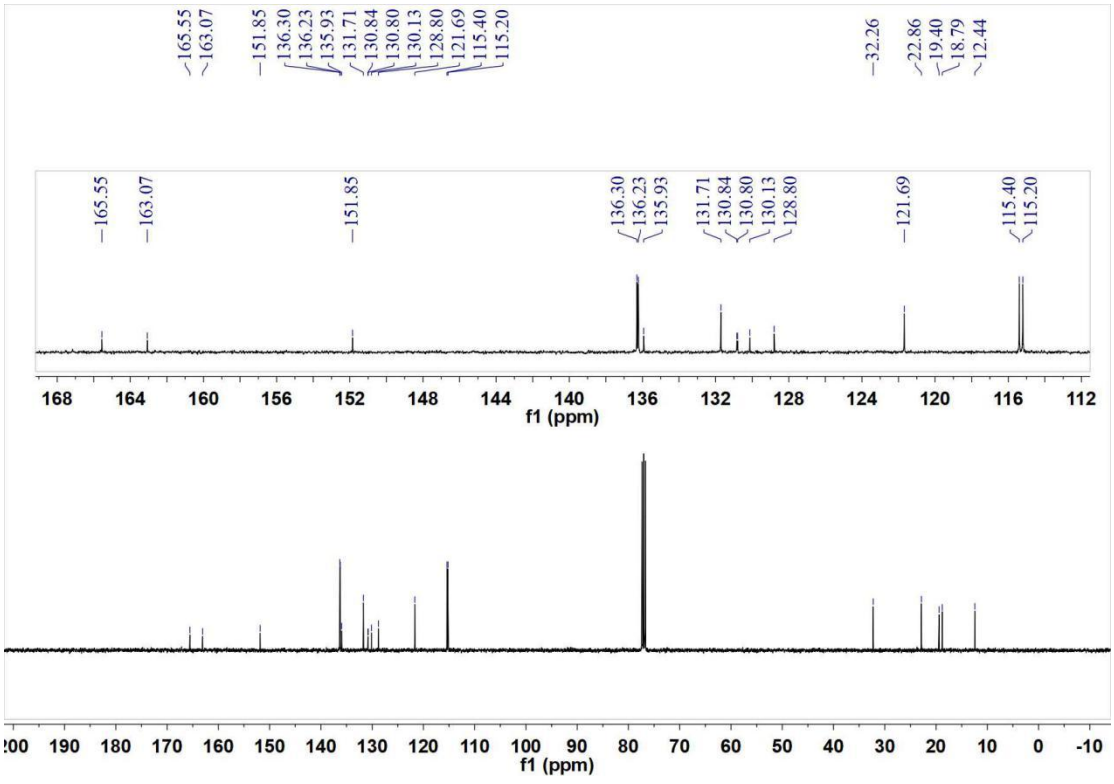


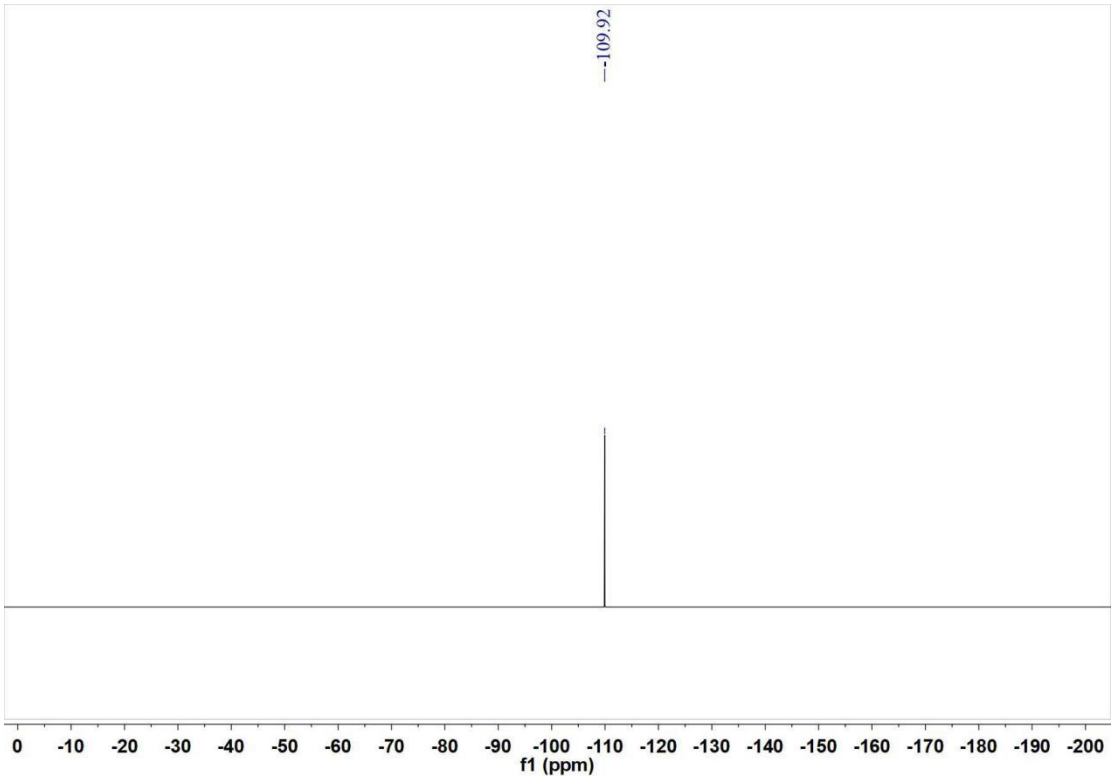



-132.31
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

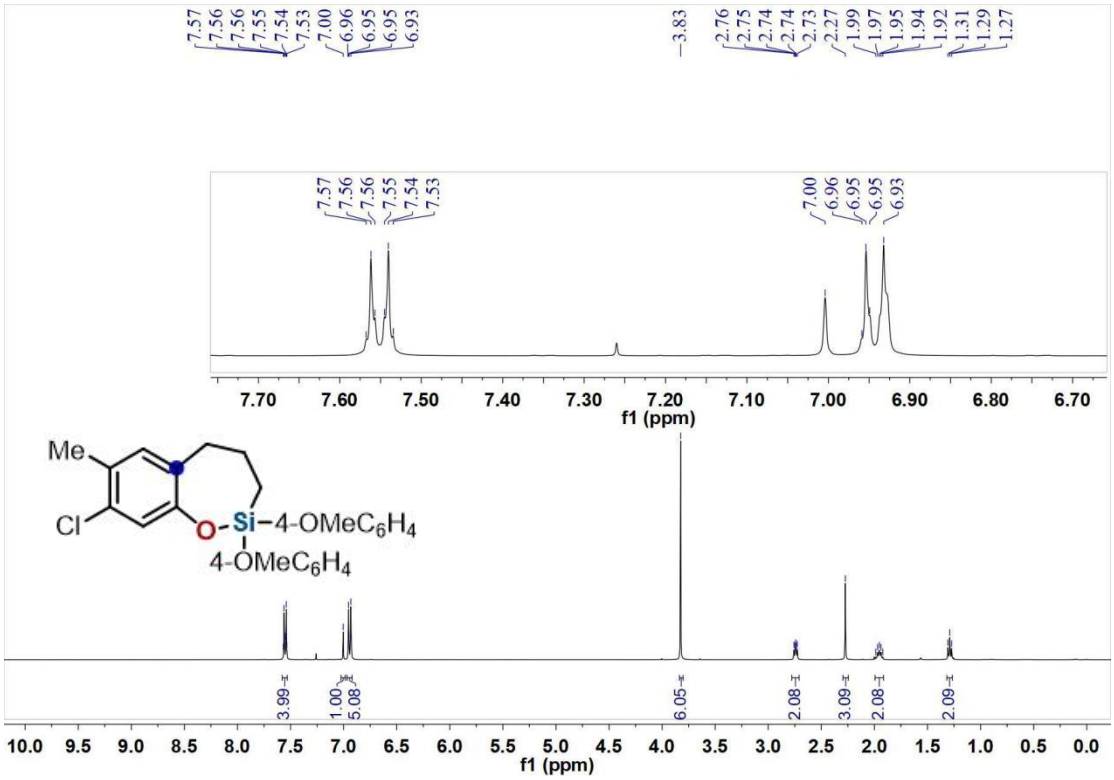
3ob

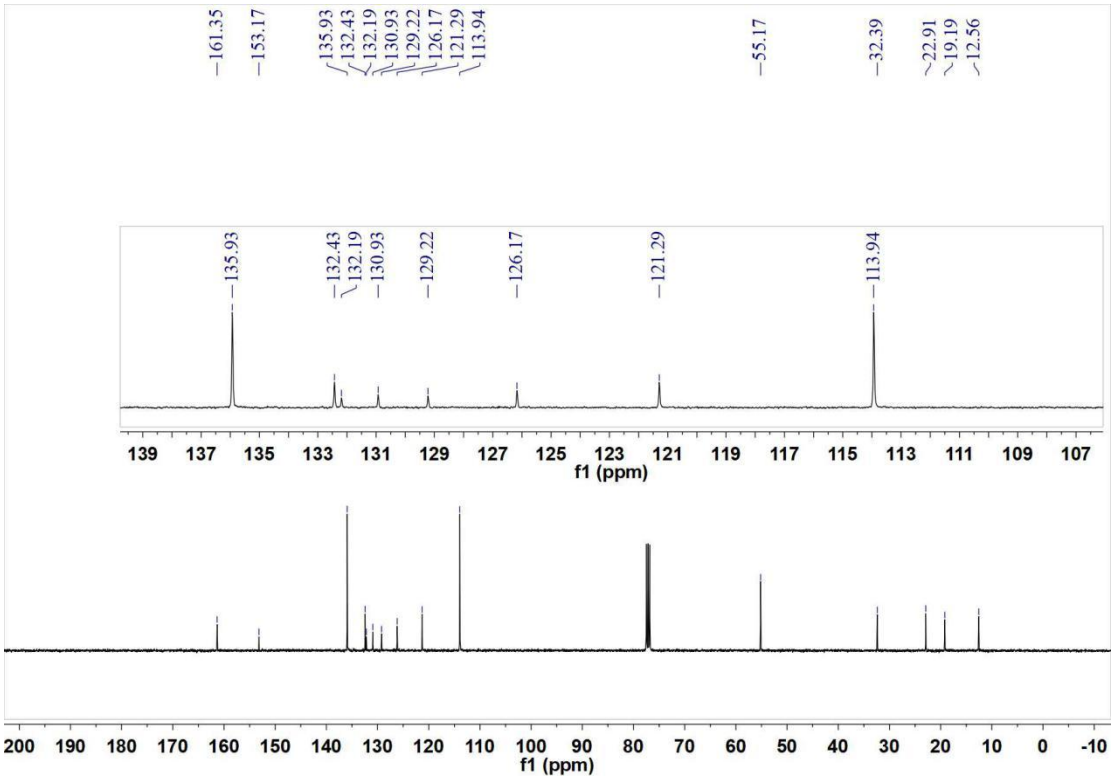

7.53
7.52
7.51
7.50
7.02
7.00
6.98
6.76
6.70
2.66
2.64
2.64
2.63
2.62
2.10
2.08
1.89
1.88
1.88
1.86
1.86
1.84
1.84
1.83
1.23
1.21
1.19
Me
Me
O-Si-4-FC6H4
4-FC6H4
3.89
3.92
0.99
0.95
2.04
3.02
3.01
2.08
2.09
f1 (ppm)


165.55
163.07
151.85
136.30
136.23
135.93
131.71
130.84
130.80
130.13
128.80
121.69
115.40
115.20
32.26
22.86
19.40
18.79
12.44
f1 (ppm)

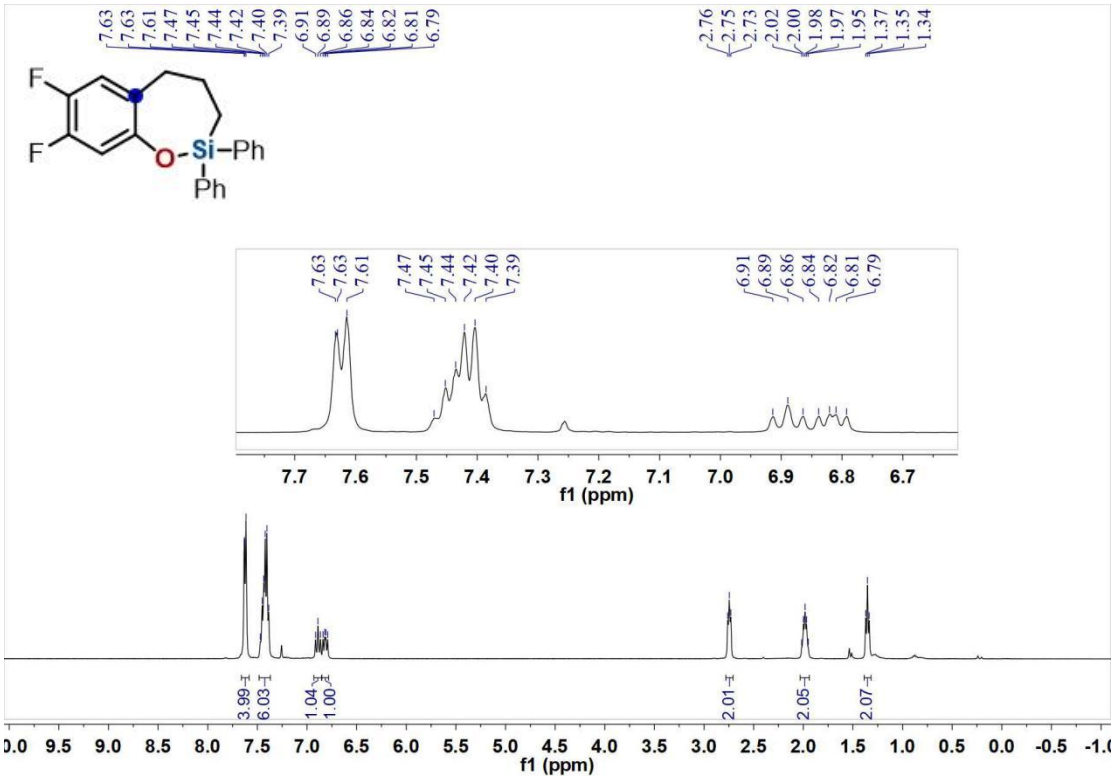

-109.92
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

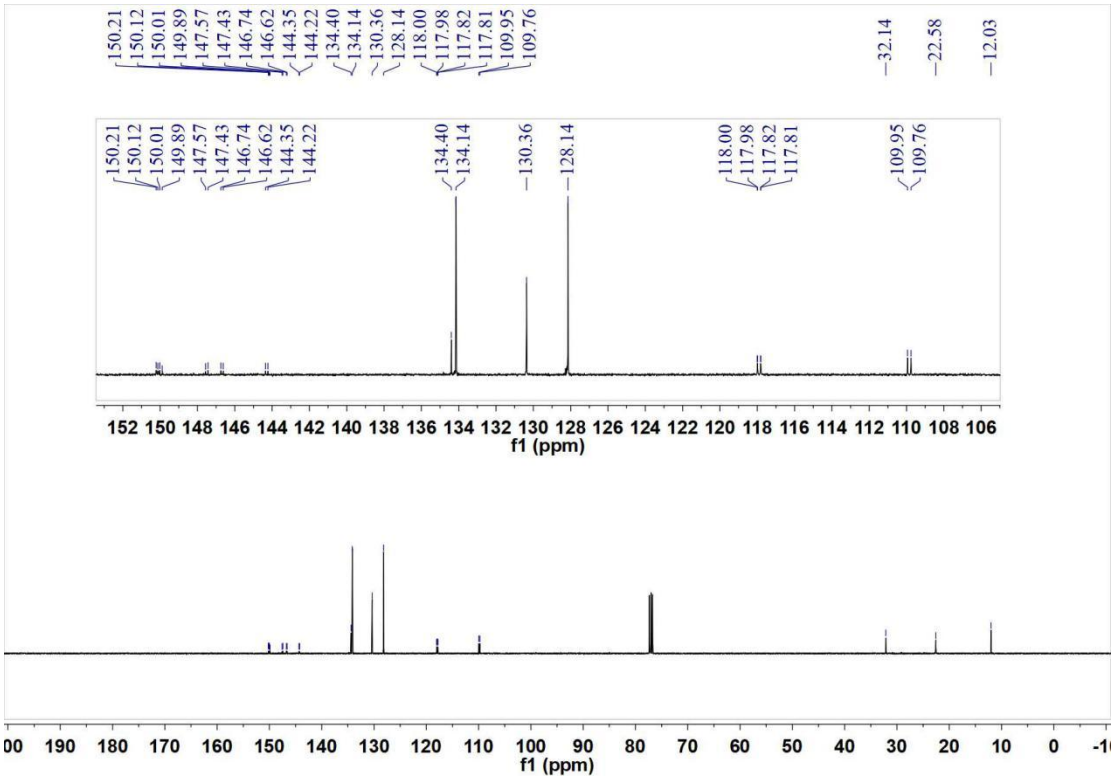
3pc

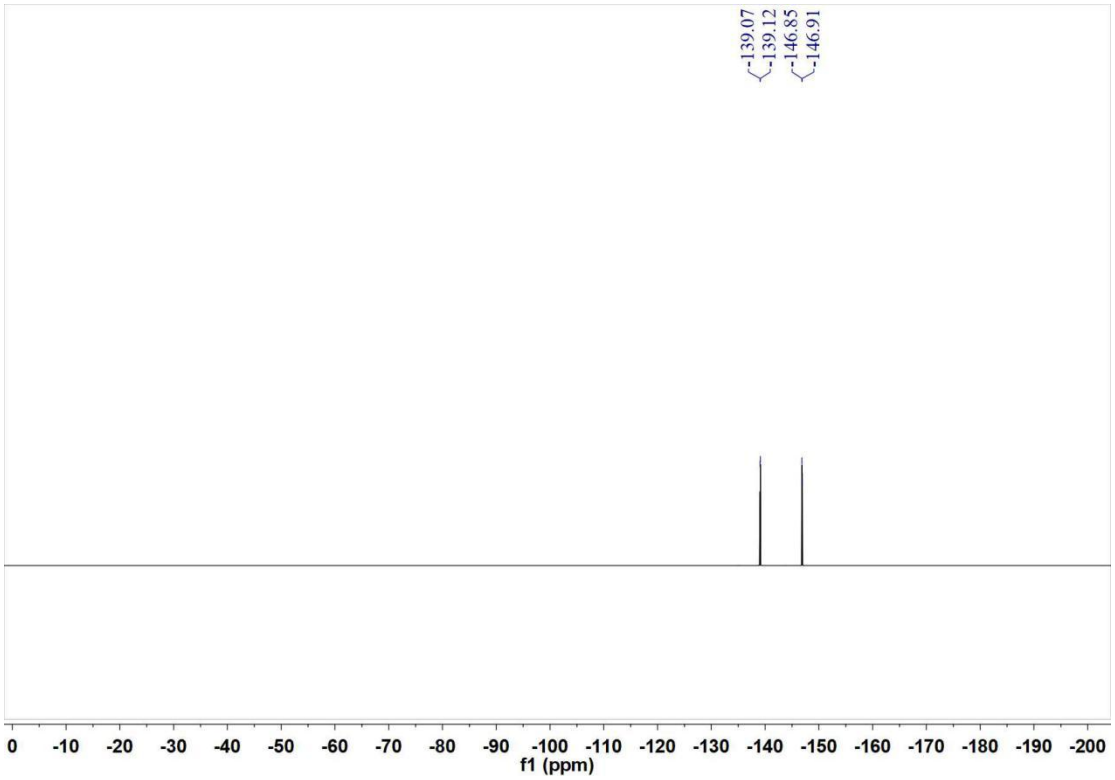

7.57
7.56
7.56
7.55
7.54
7.53
7.00
6.96
6.95
6.95
6.93
3.83
2.76
2.75
2.74
2.74
2.73
2.27
1.99
1.97
1.95
1.94
1.92
1.31
1.29
1.27
Me
Cl
O-Si-4-OMeC6H4
4-OMeC6H4
3.99
1.00
5.08
6.05
2.08
3.09
2.08
2.09
f1 (ppm)


161.35
153.17
135.93
132.43
132.19
130.93
129.22
126.17
121.29
113.94
55.17
32.39
22.91
19.19
12.56
f1 (ppm)

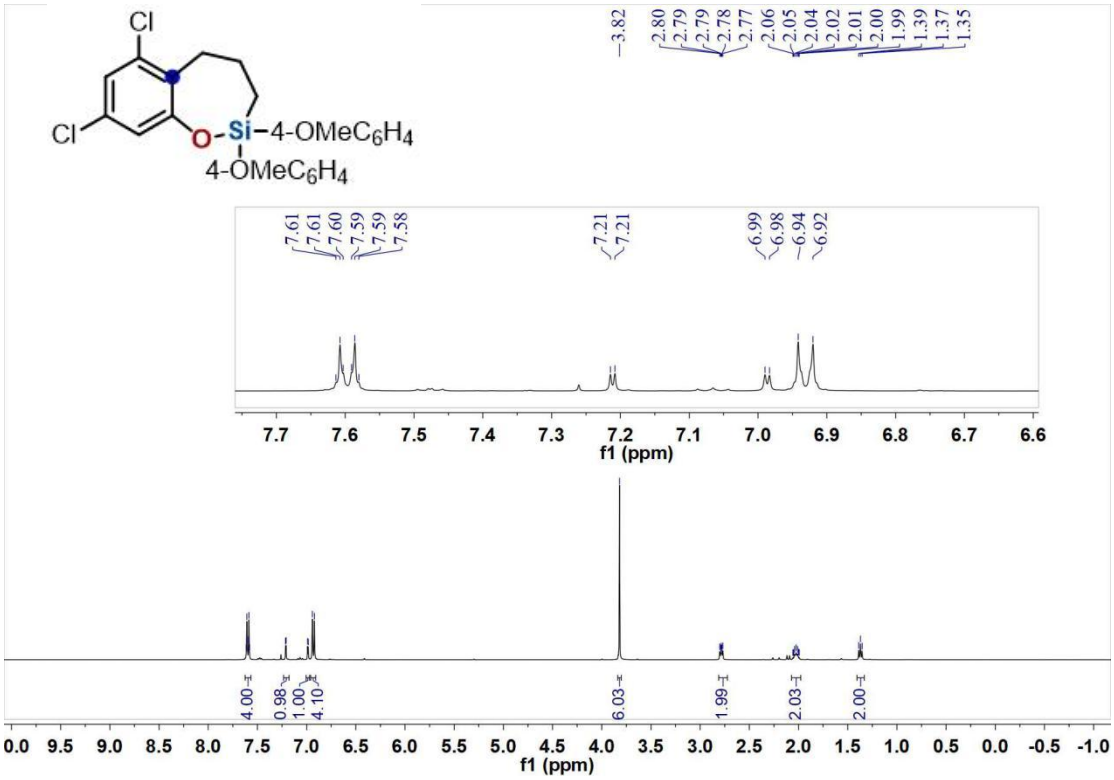
3ra

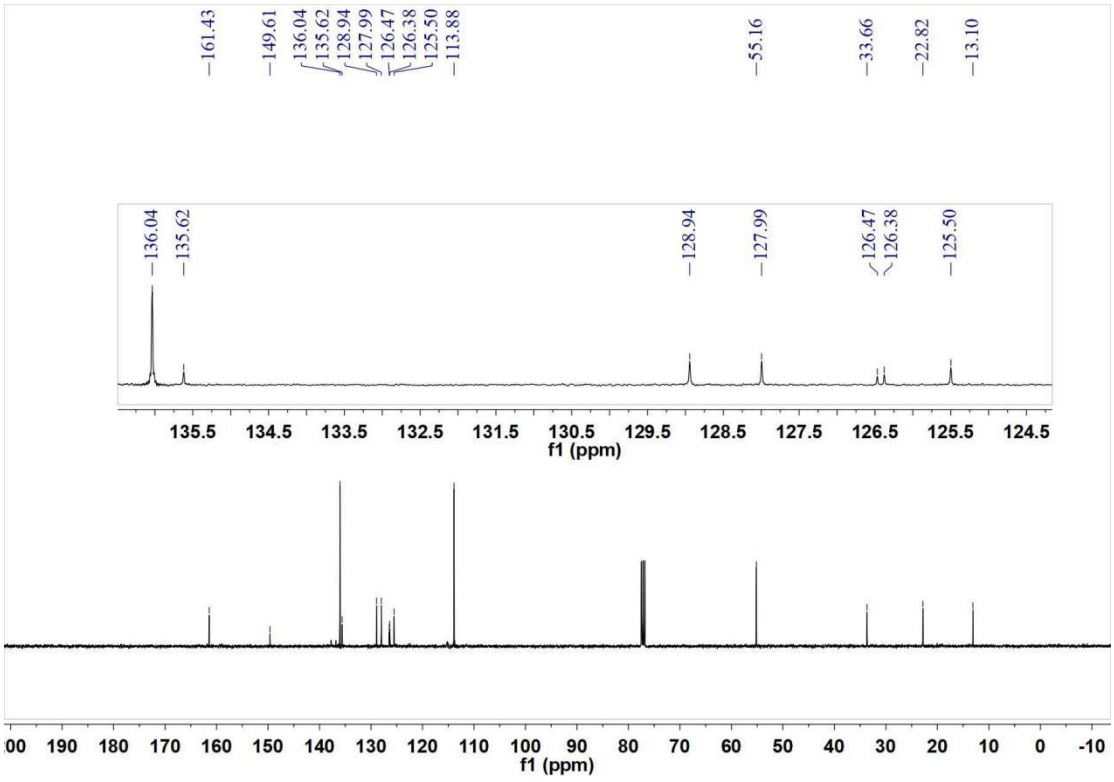

7.63
7.63
7.61
7.47
7.45
7.44
7.42
7.40
7.39
6.91
6.89
6.86
6.84
6.82
6.81
6.79
2.76
2.75
2.73
2.02
2.00
1.98
1.97
1.95
1.37
1.35
1.34
F
F
O
Si
Ph
Ph
3.99
6.03
1.04
1.00
2.01
2.05
2.07
f1 (ppm)


150.21
150.12
150.01
149.89
147.57
147.43
146.74
146.62
144.35
144.22
134.40
134.14
130.36
128.14
118.00
117.98
117.82
117.81
109.95
109.76
32.14
22.58
12.03
f1 (ppm)

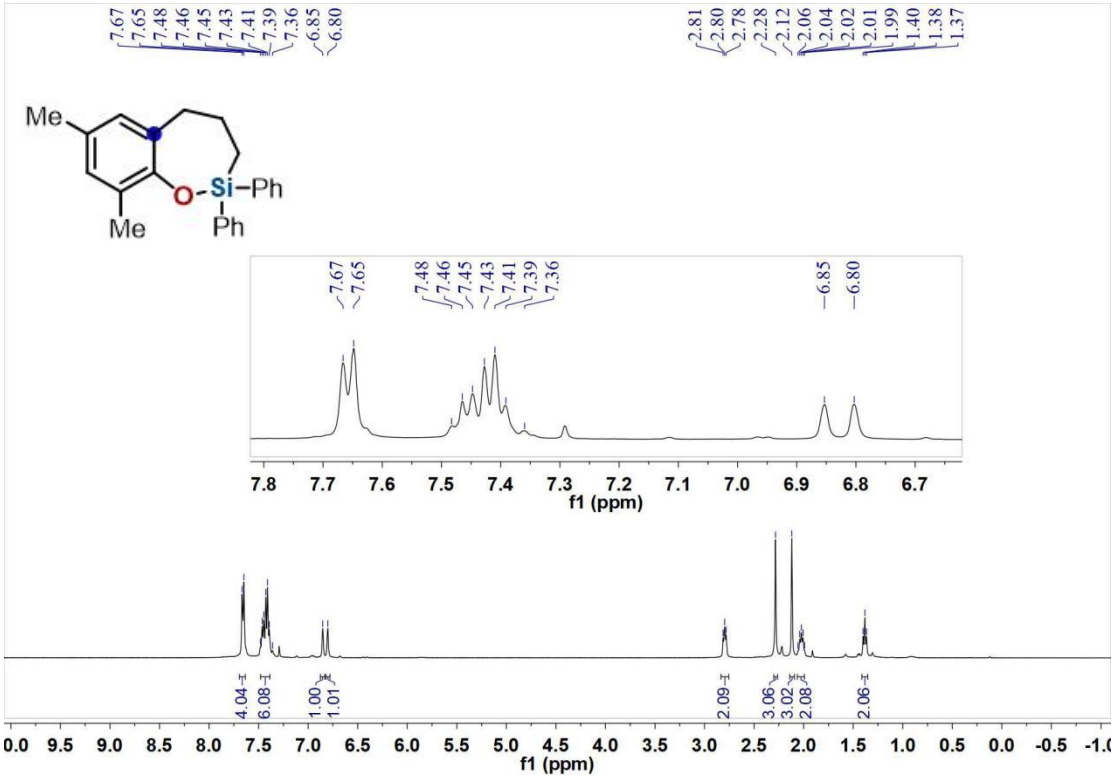

-139.07
-139.12
-146.85
-146.91
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

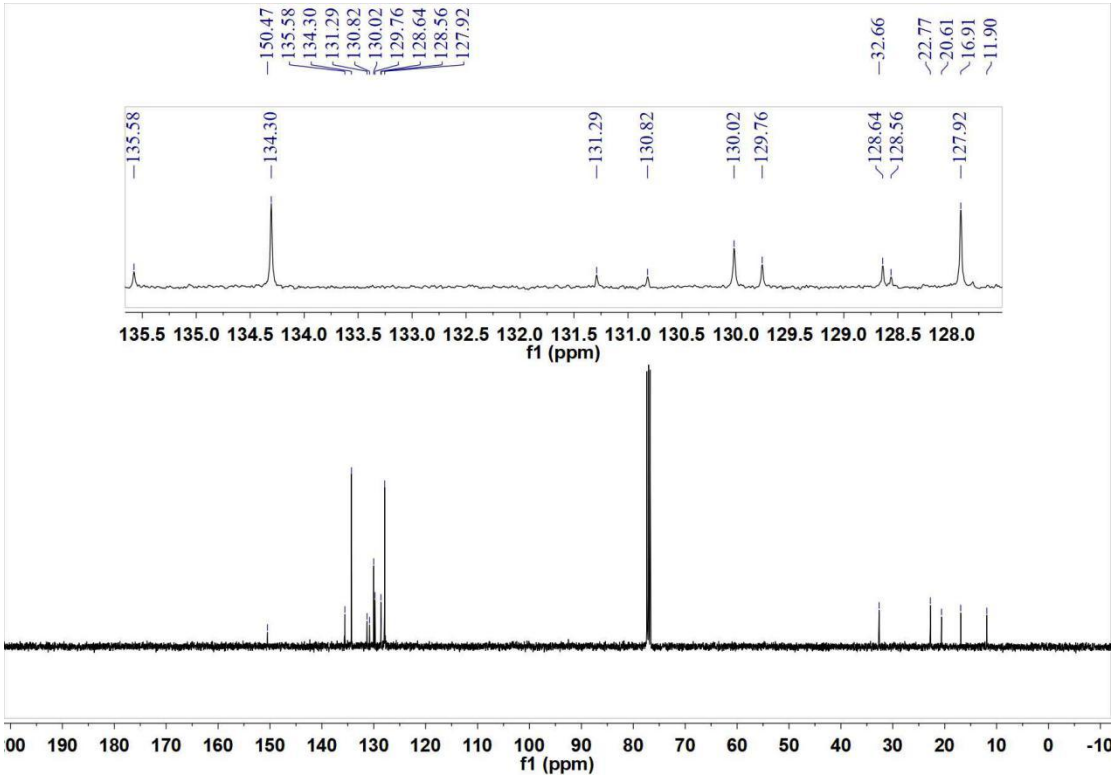
3sc


Cl
Cl
O-Si-4-OMeC6H4
4-OMeC6H4
3.82
2.80
2.79
2.79
2.78
2.77
2.06
2.05
2.04
2.02
2.01
2.00
1.99
1.39
1.37
1.35
7.61
7.61
7.60
7.59
7.59
7.58
7.21
7.21
6.99
6.98
6.94
6.92
f1 (ppm)
4.00
0.98
1.00
4.10
6.03
1.99
2.03
2.00
f1 (ppm)

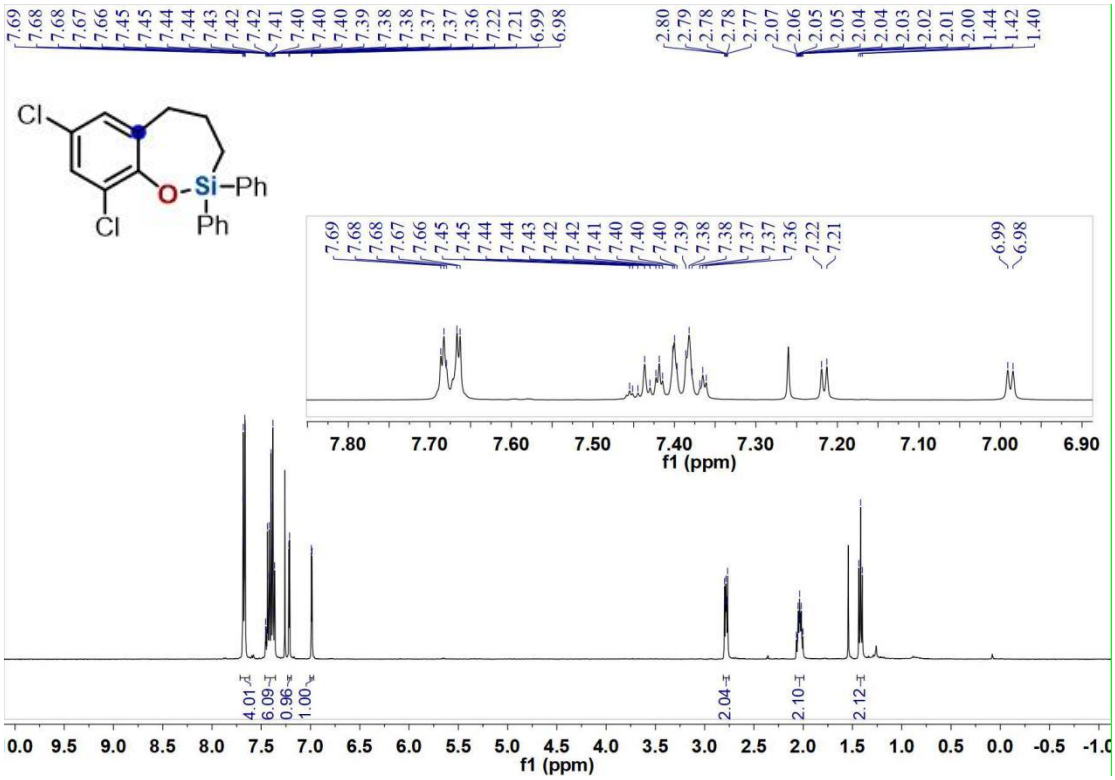

161.43
149.61
136.04
135.62
128.94
127.99
126.47
126.38
125.50
113.88
55.16
33.66
22.82
13.10
136.04
135.62
128.94
127.99
126.47
126.38
125.50
f1 (ppm)
f1 (ppm)

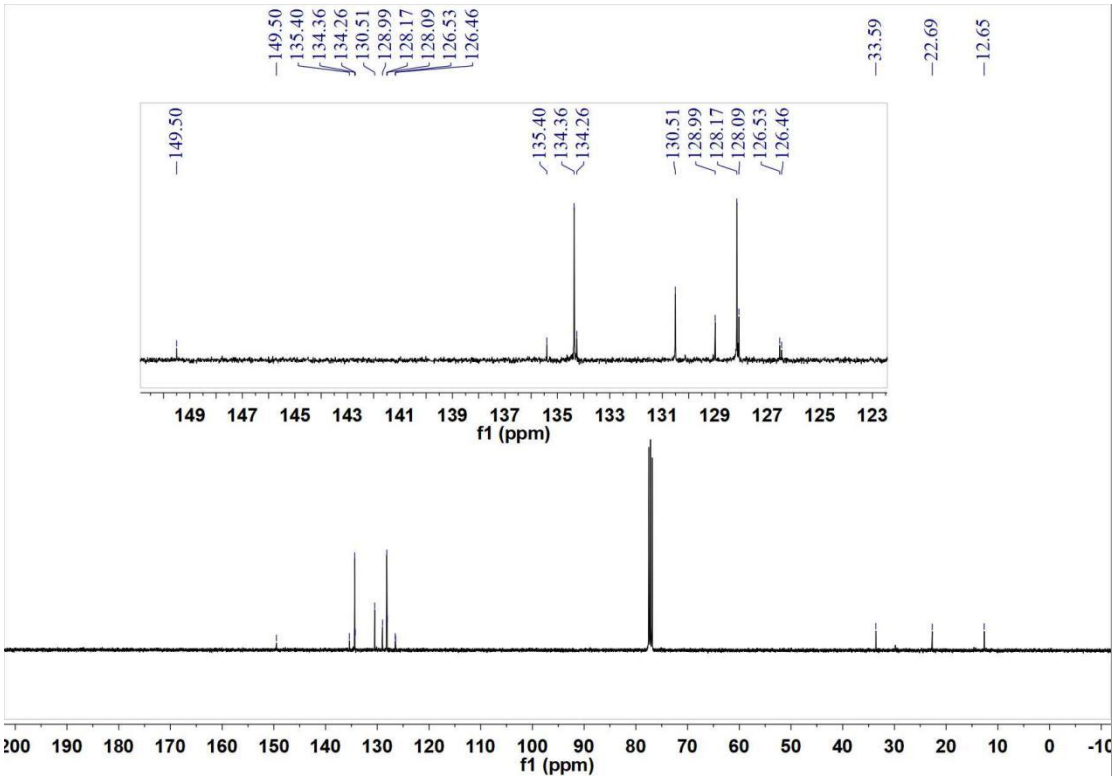
3ta


7.67
7.65
7.48
7.46
7.45
7.43
7.41
7.39
7.36
6.85
6.80
2.81
2.80
2.78
2.28
2.12
2.06
2.04
2.02
2.01
1.99
1.40
1.38
1.37
Me
O
Si
Ph
Ph
Me
f1 (ppm)
4.04
6.08
1.00
1.01
2.09
3.06
3.02
2.08
2.06

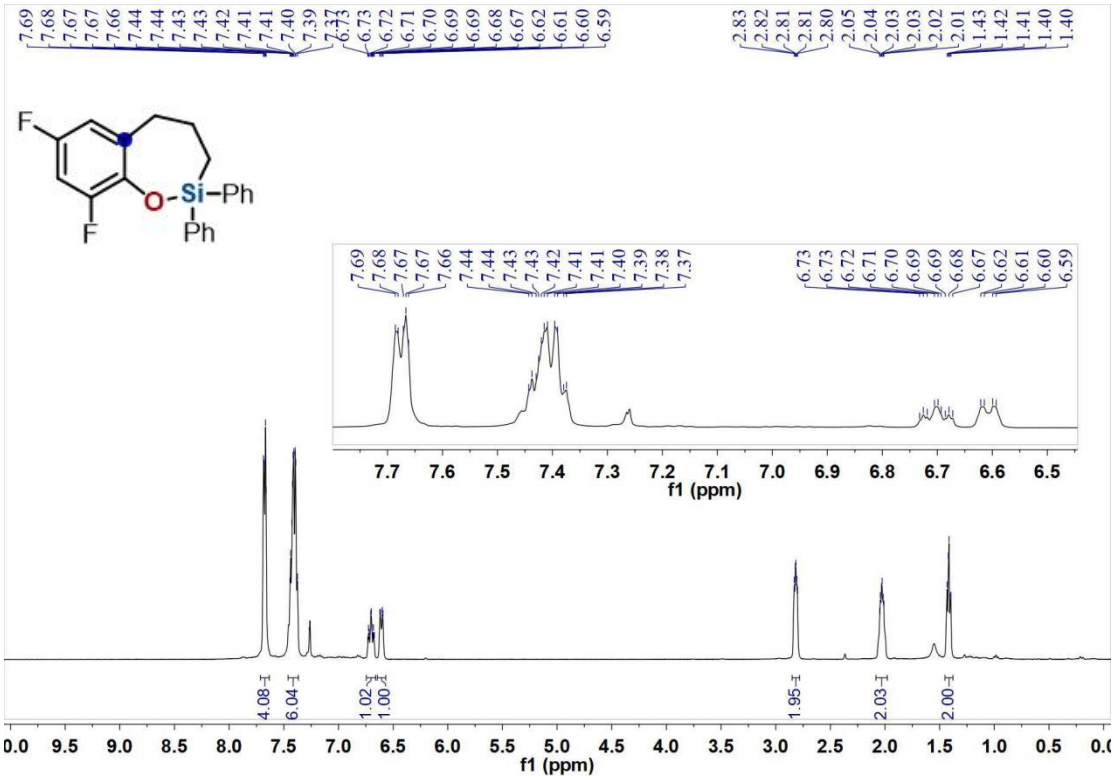

150.47
135.58
134.30
131.29
130.82
130.02
129.76
128.64
128.56
127.92
32.66
22.77
20.61
16.91
11.90
f1 (ppm)

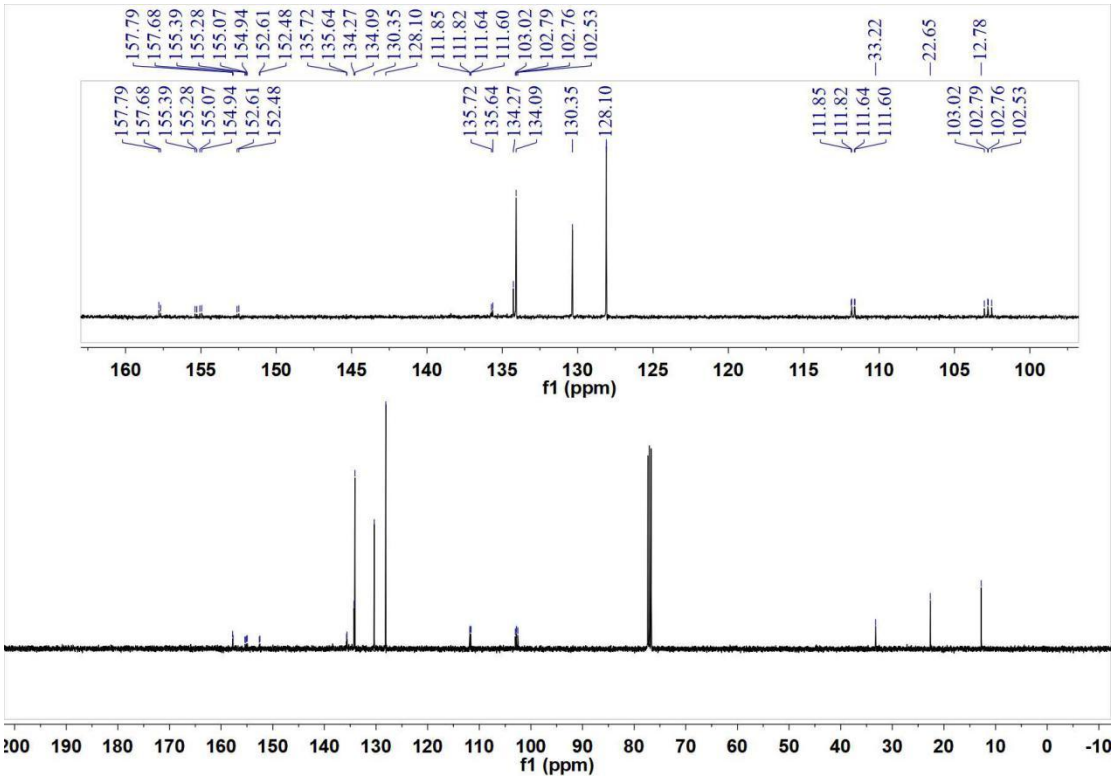
3ua

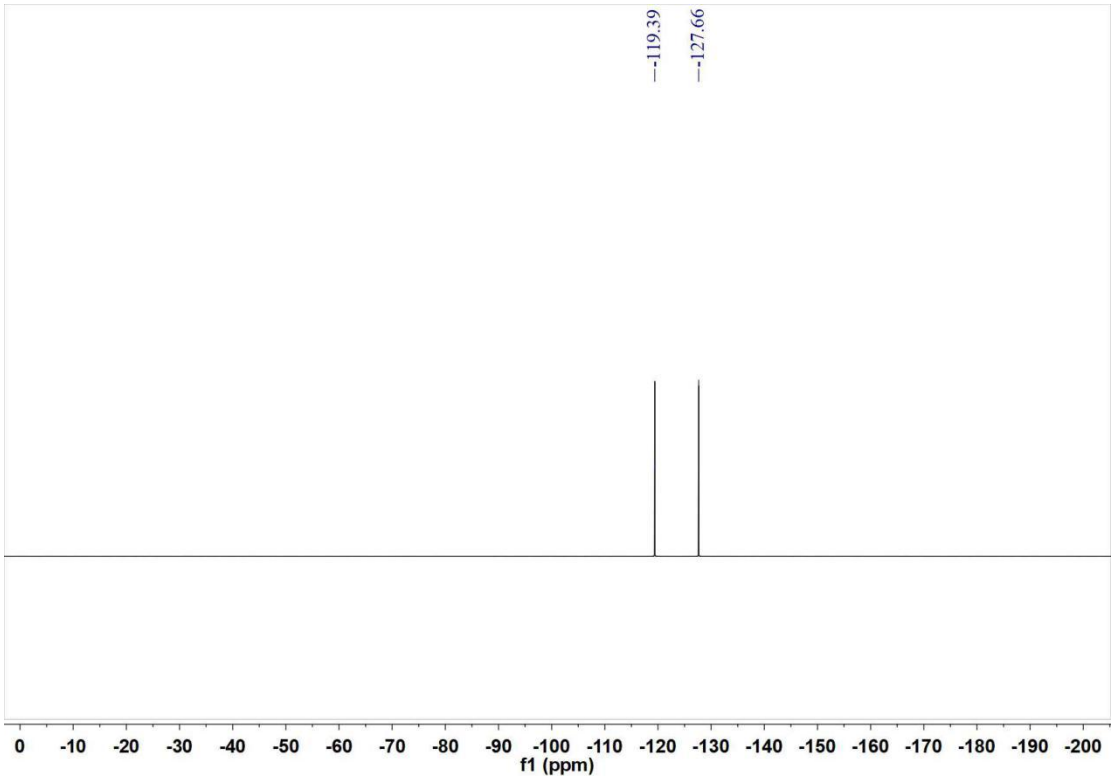




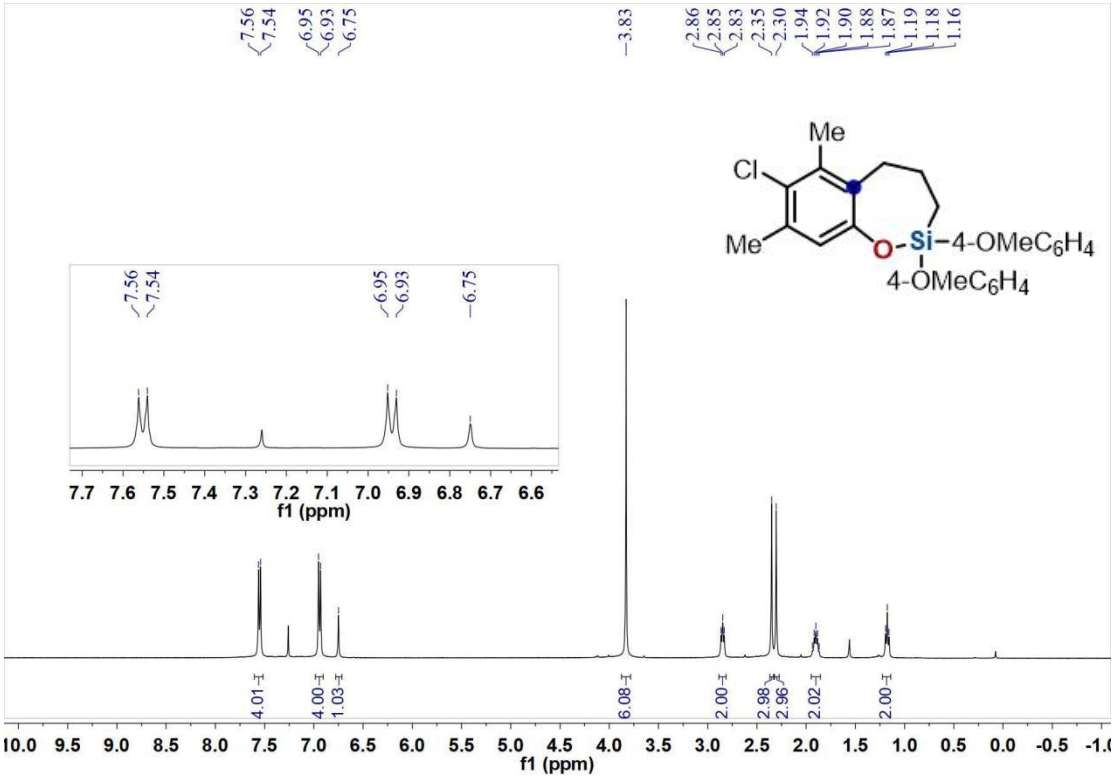
3va

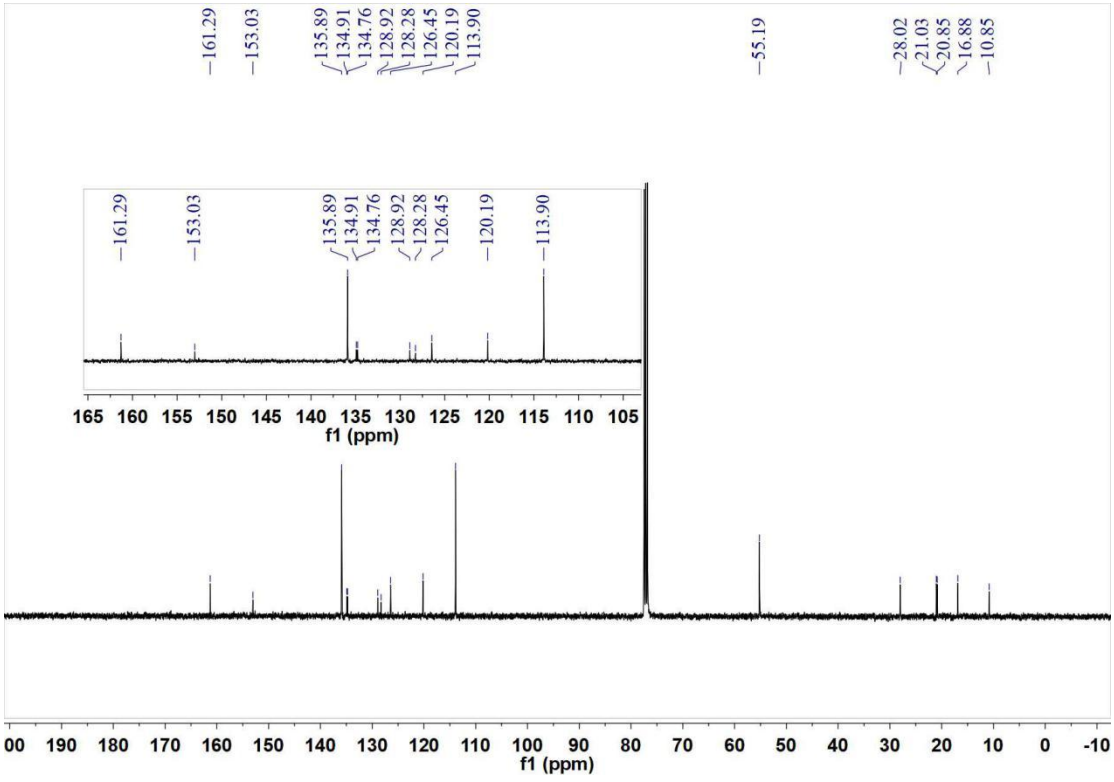




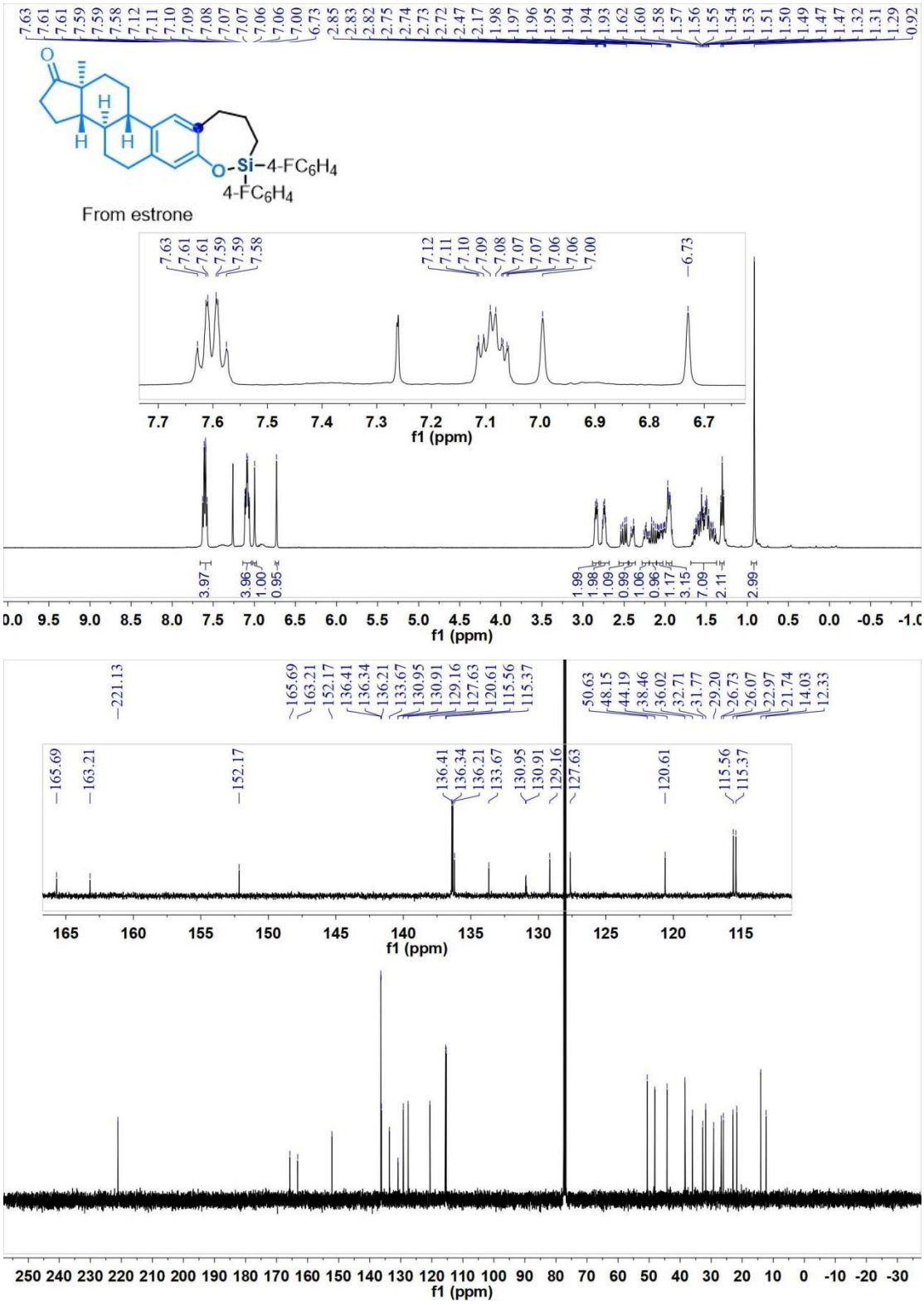

-119.39
-127.66
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

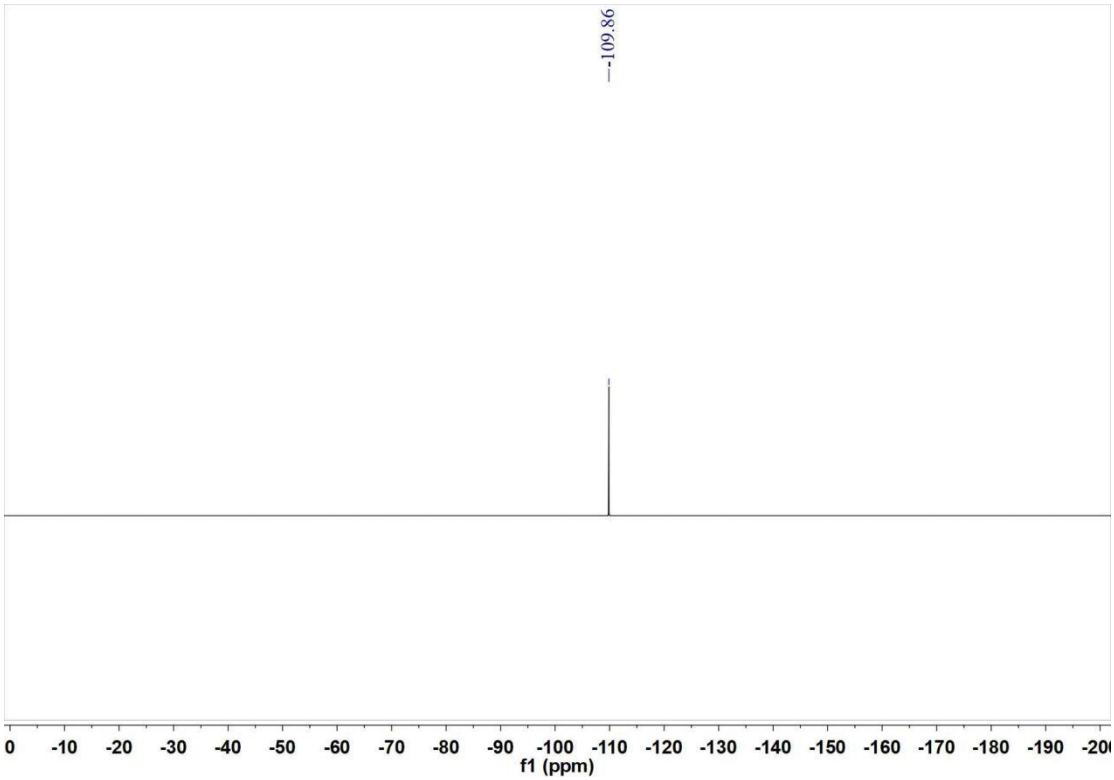
3wc


7.56
7.54
6.95
6.93
6.75
3.83
2.86
2.85
2.83
2.35
2.30
1.94
1.92
1.90
1.88
1.87
1.19
1.18
1.16
Me
Cl
Me
O-Si-4-OMeC6H4
4-OMeC6H4
4.01
4.00
1.03
6.08
2.00
2.98
2.96
2.02
2.00
f1 (ppm)

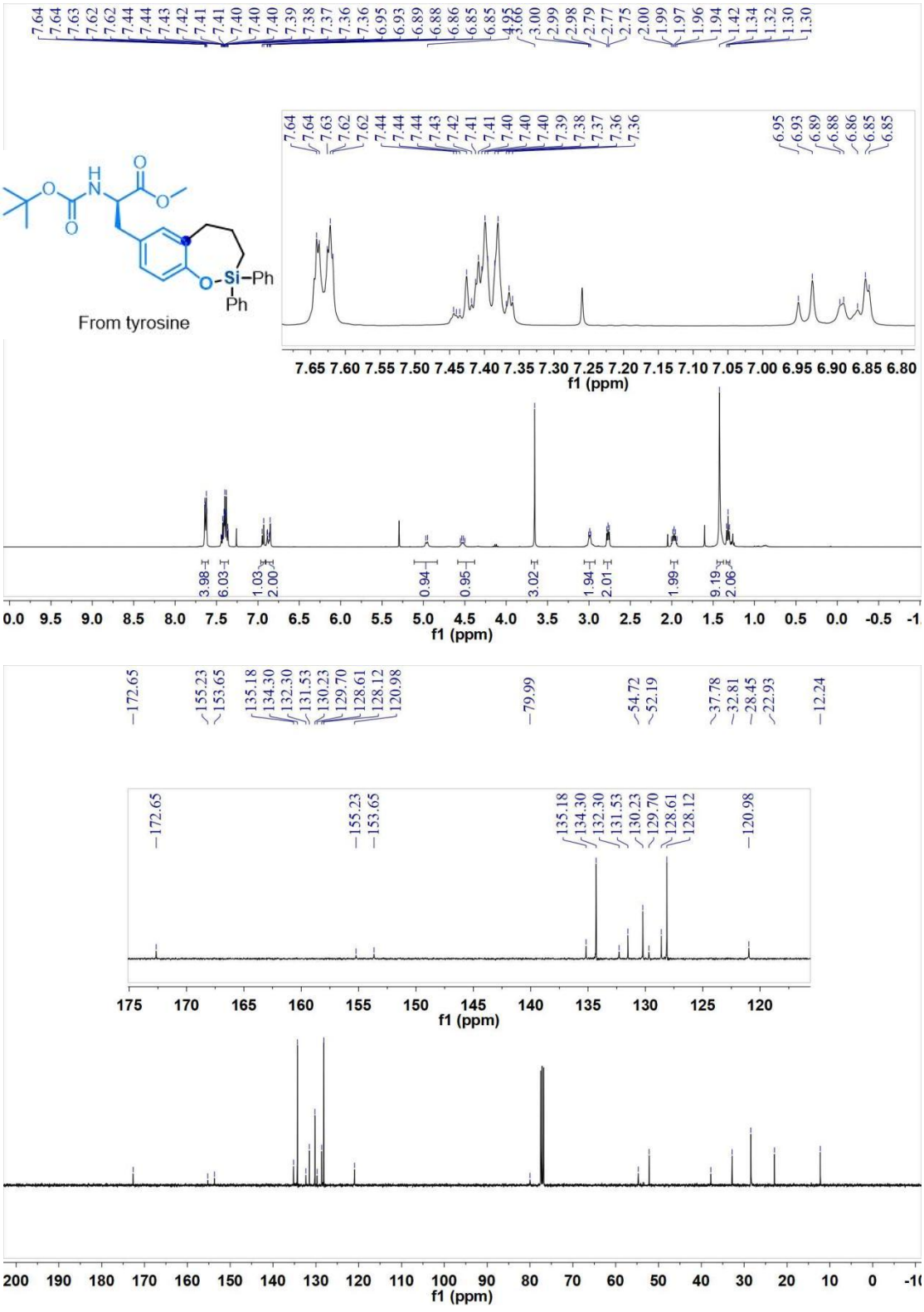

161.29
153.03
135.89
134.91
134.76
128.92
128.28
126.45
120.19
113.90
55.19
28.02
21.03
20.85
16.88
10.85
f1 (ppm)

4a

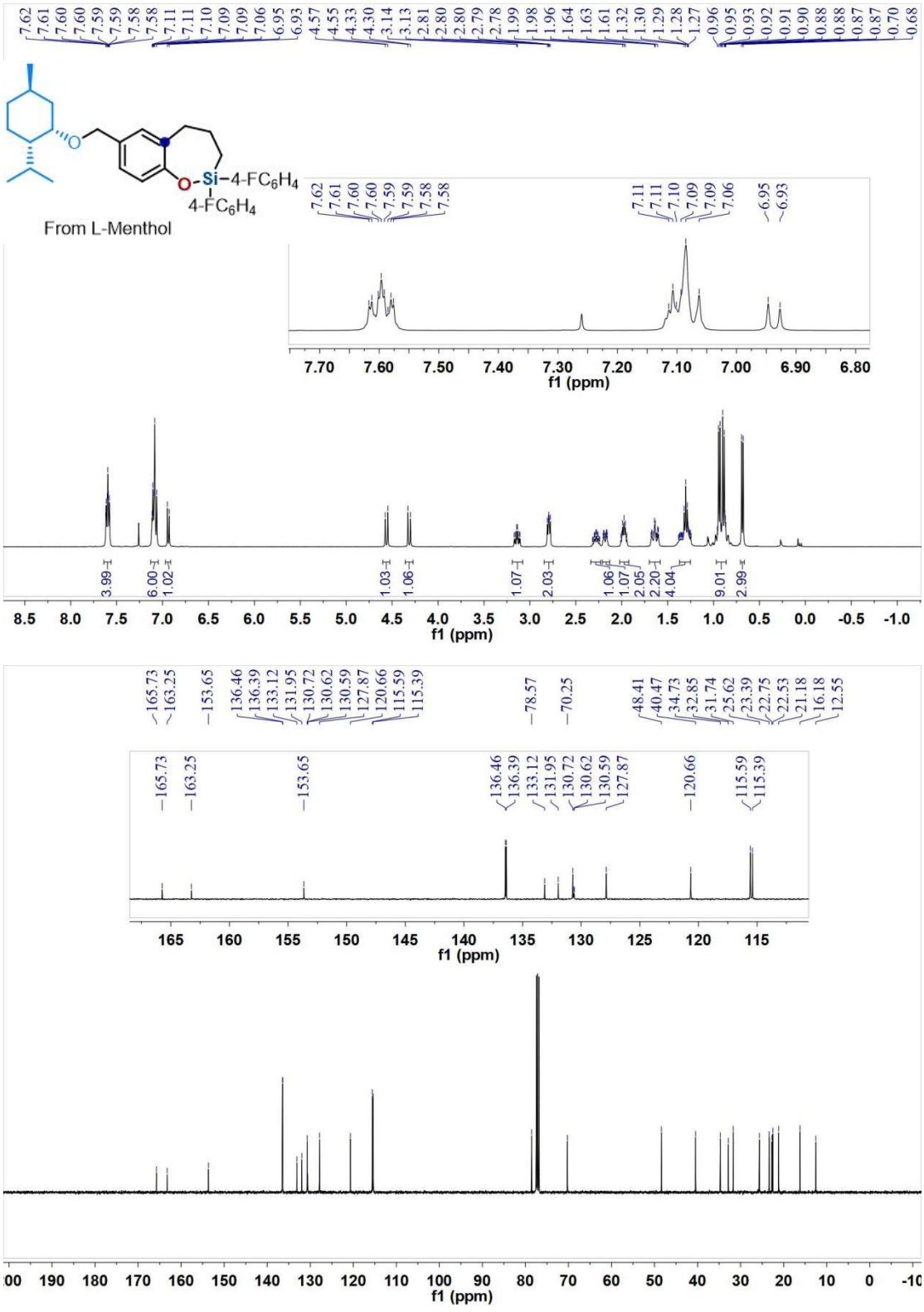


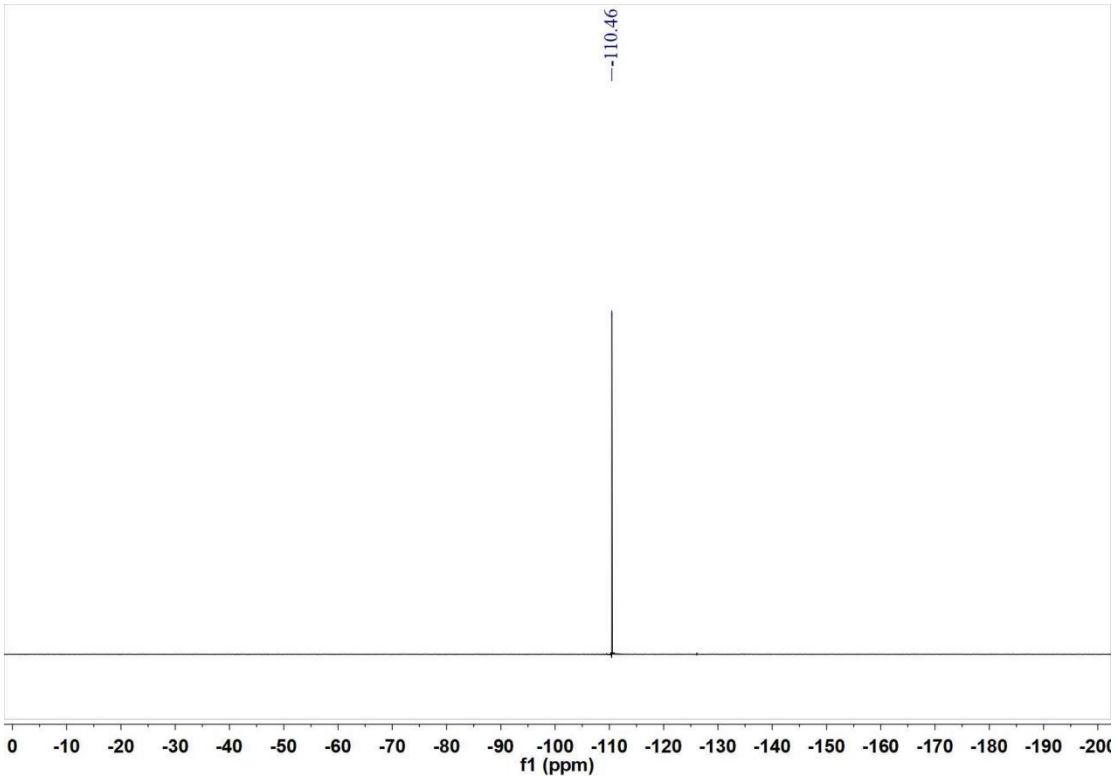

-109.86
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

4b

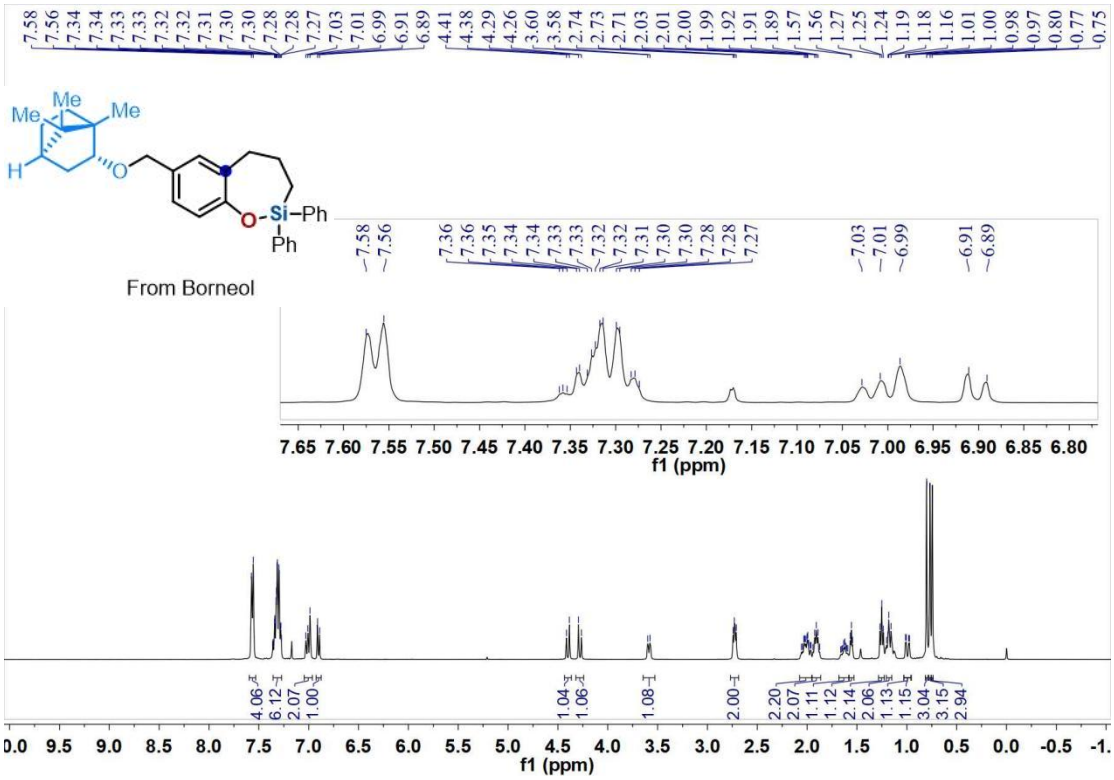


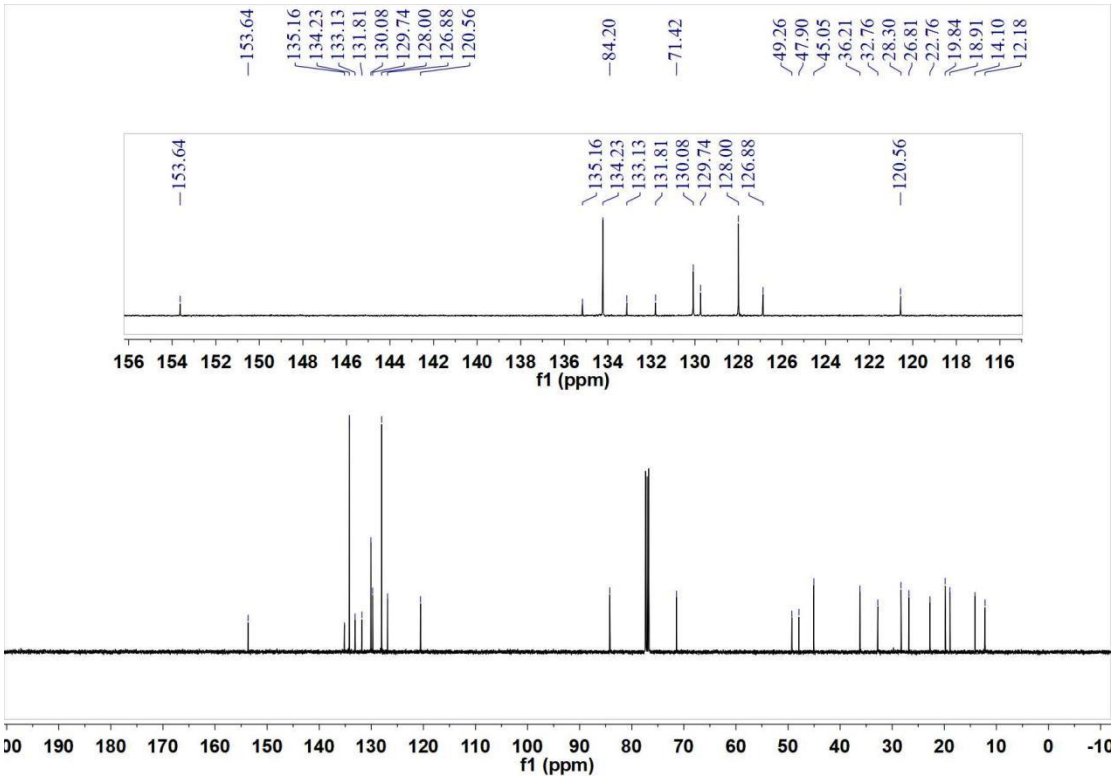
4c



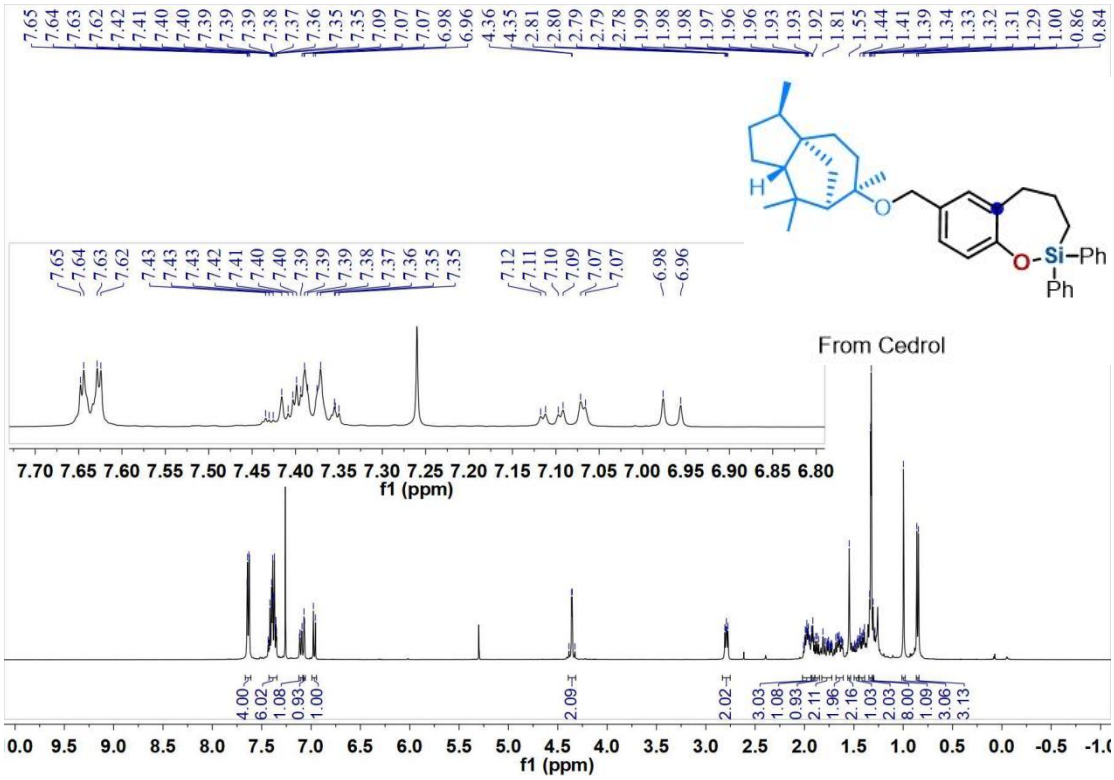

-110.46
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

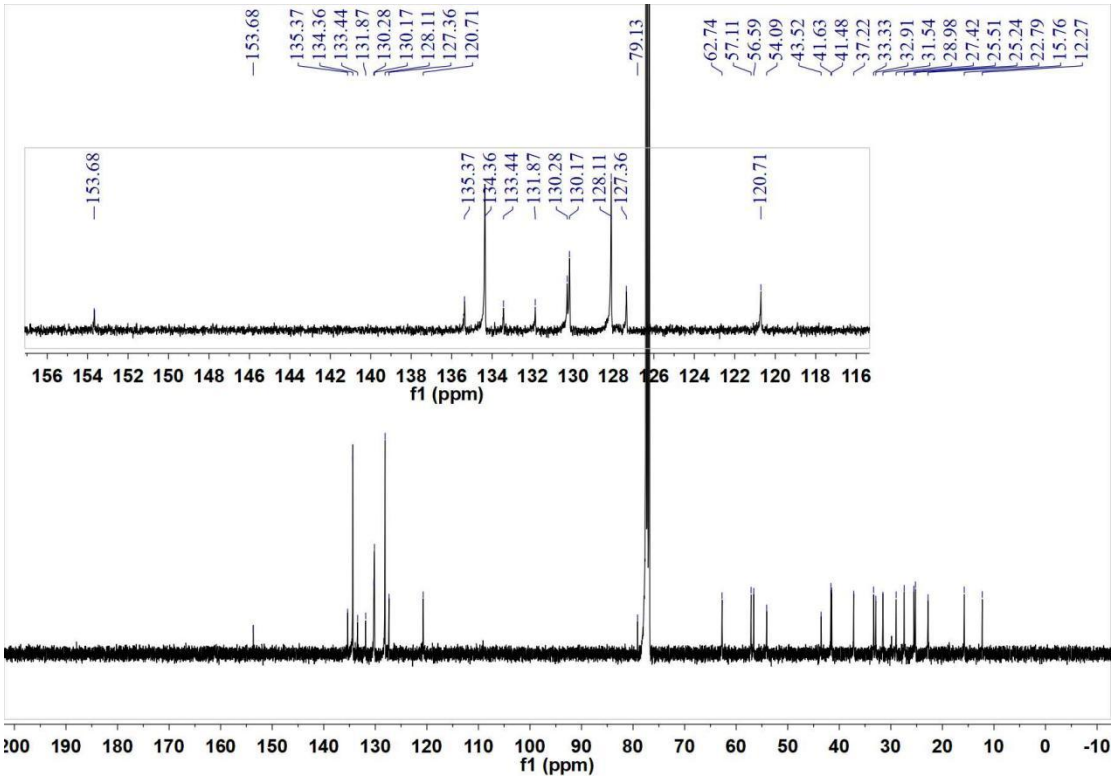
4d



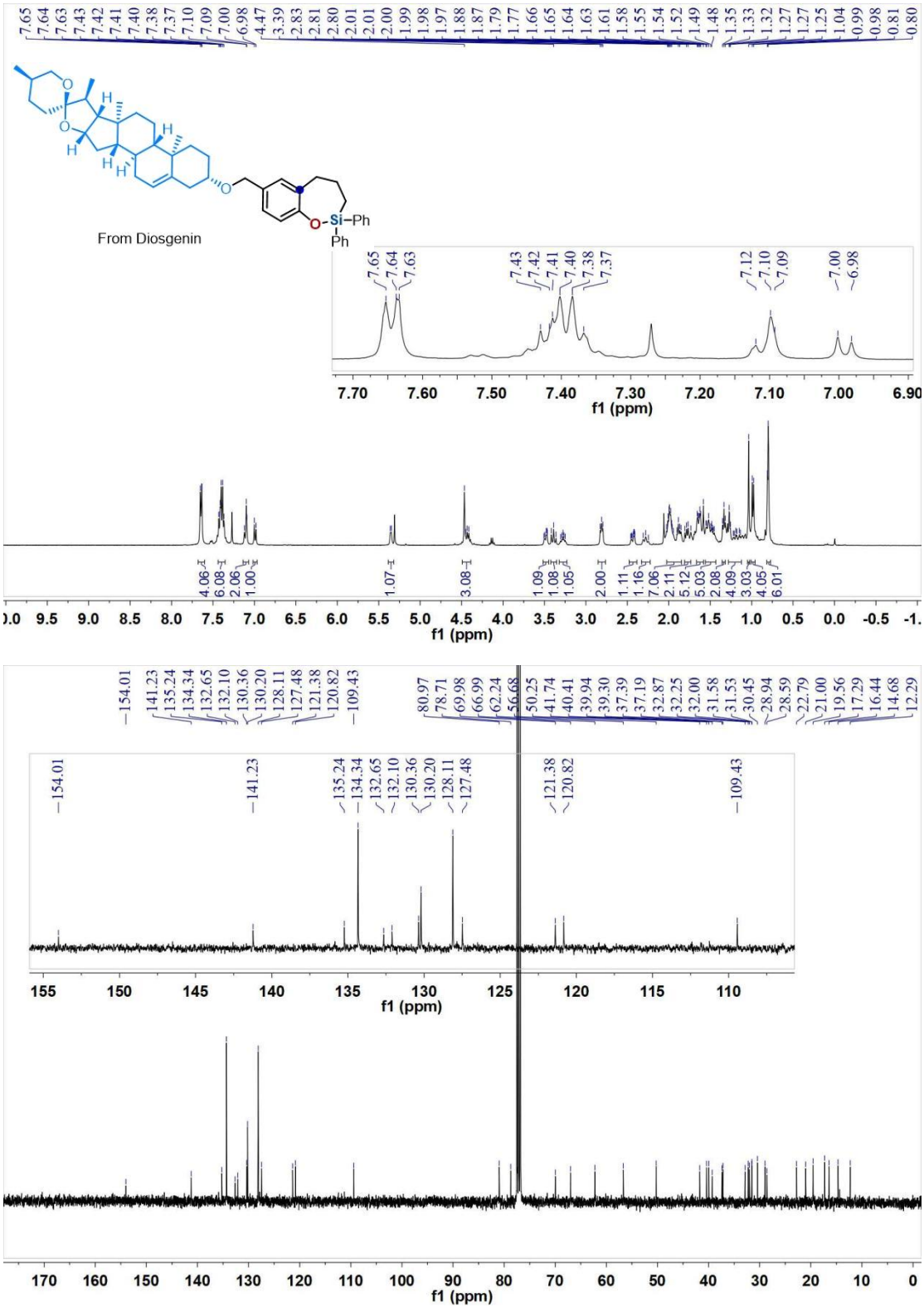


4e

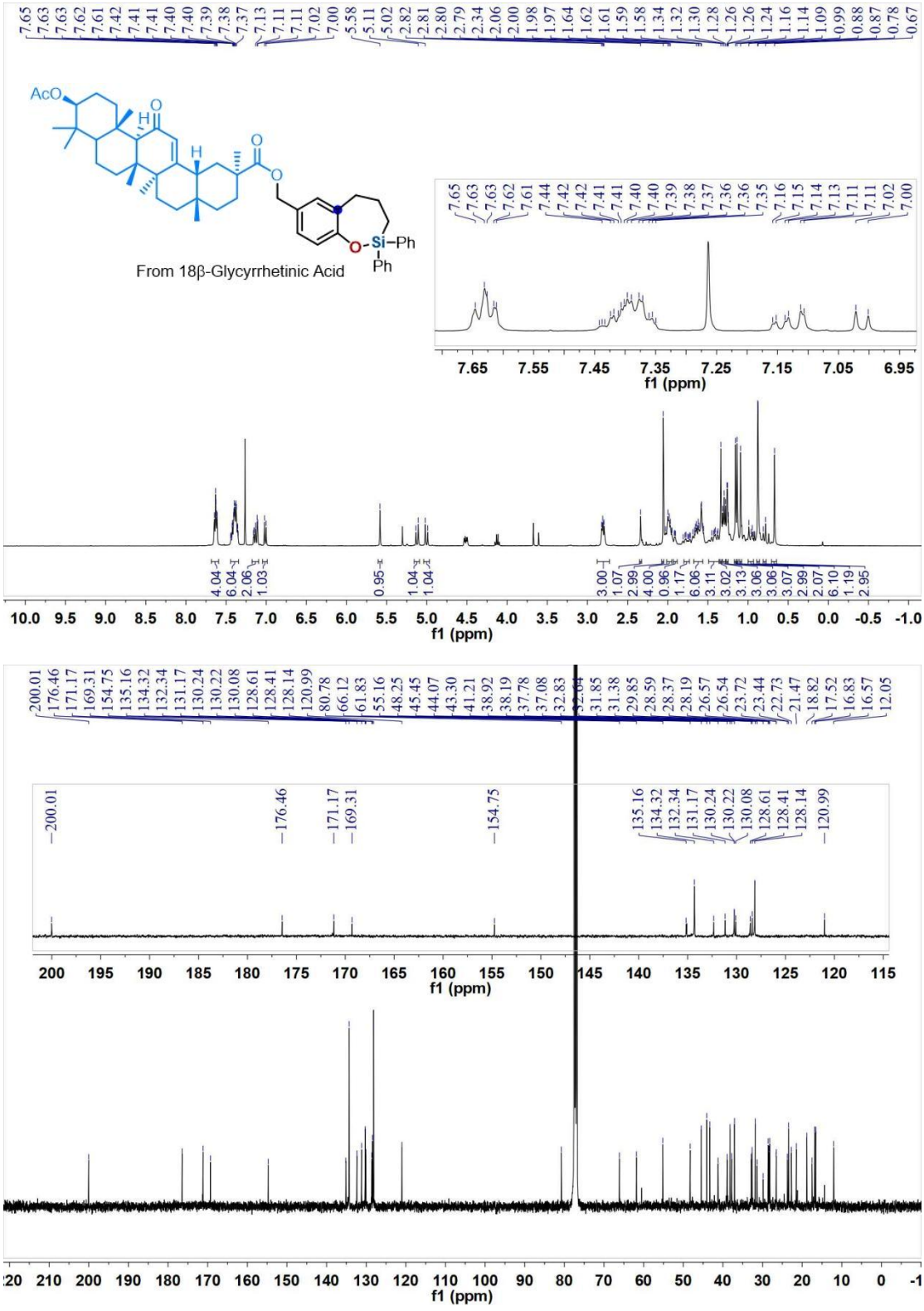




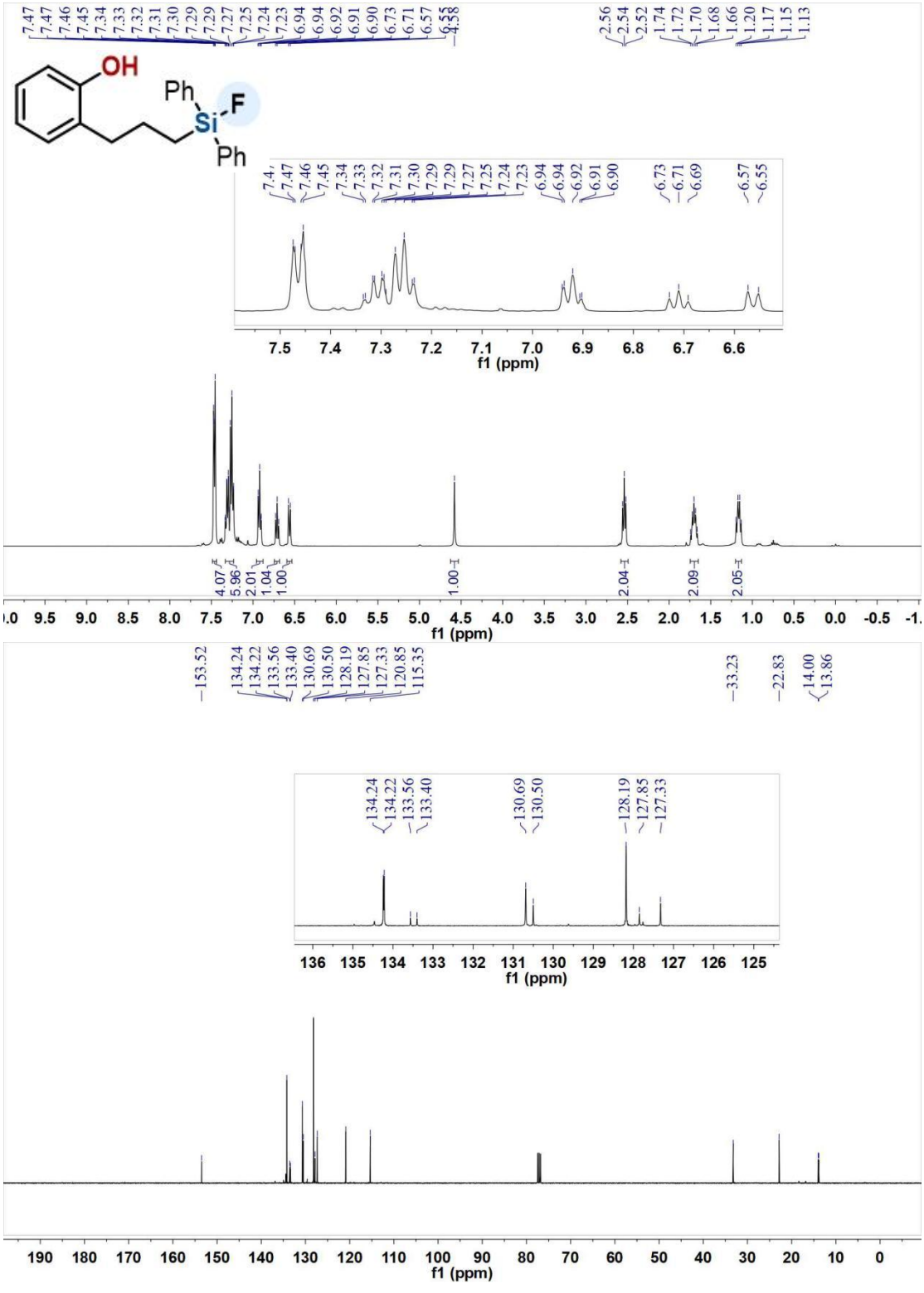
4f

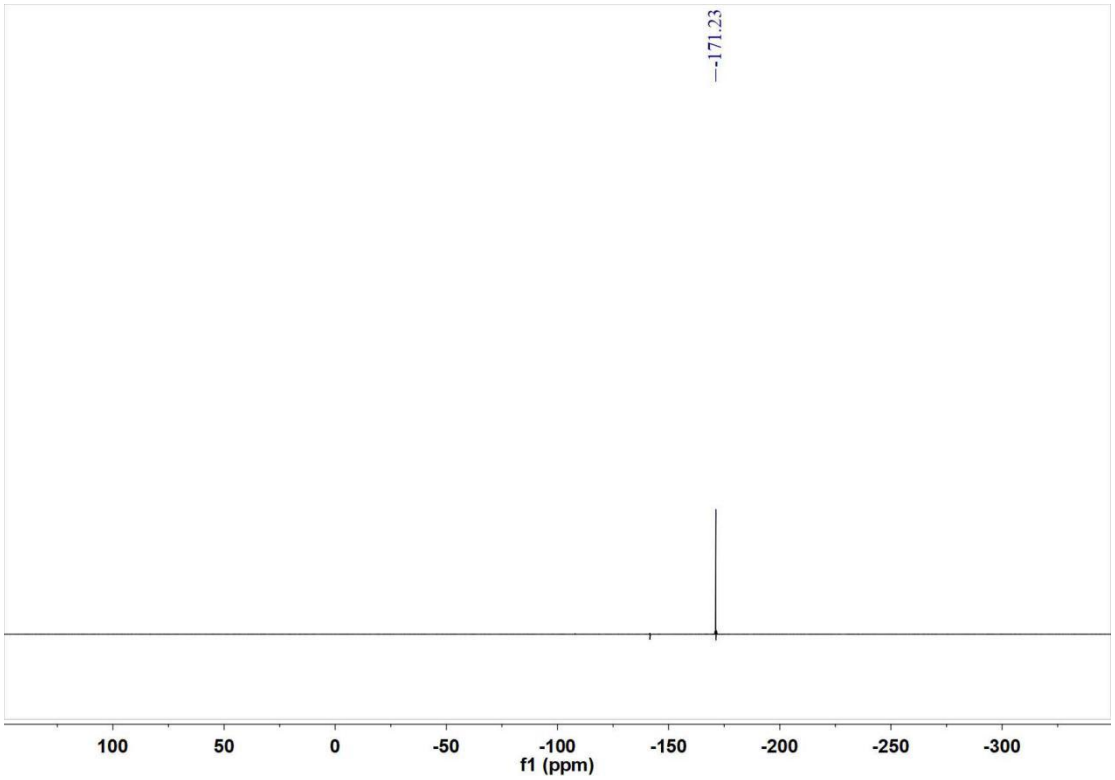


4g

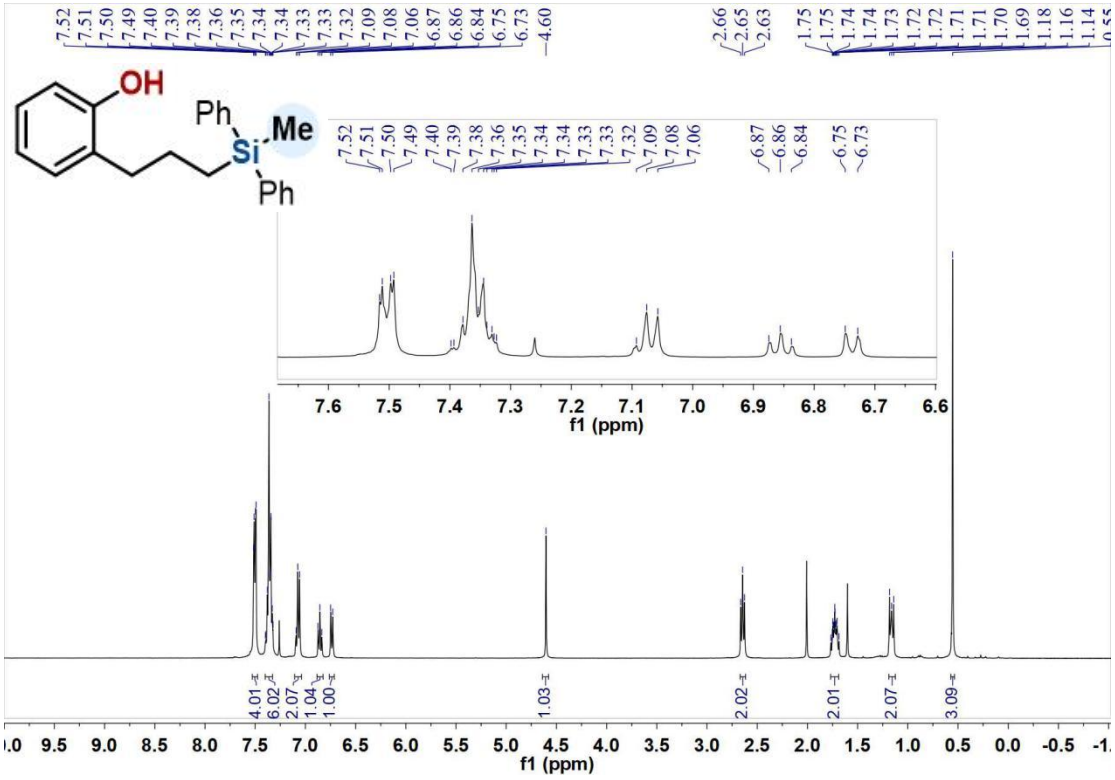

AcO
O
H
H
O
O
O
Si–Ph
Ph
From 18β-Glycyrrhetinic Acid
f1 (ppm)
f1 (ppm)
f1 (ppm)

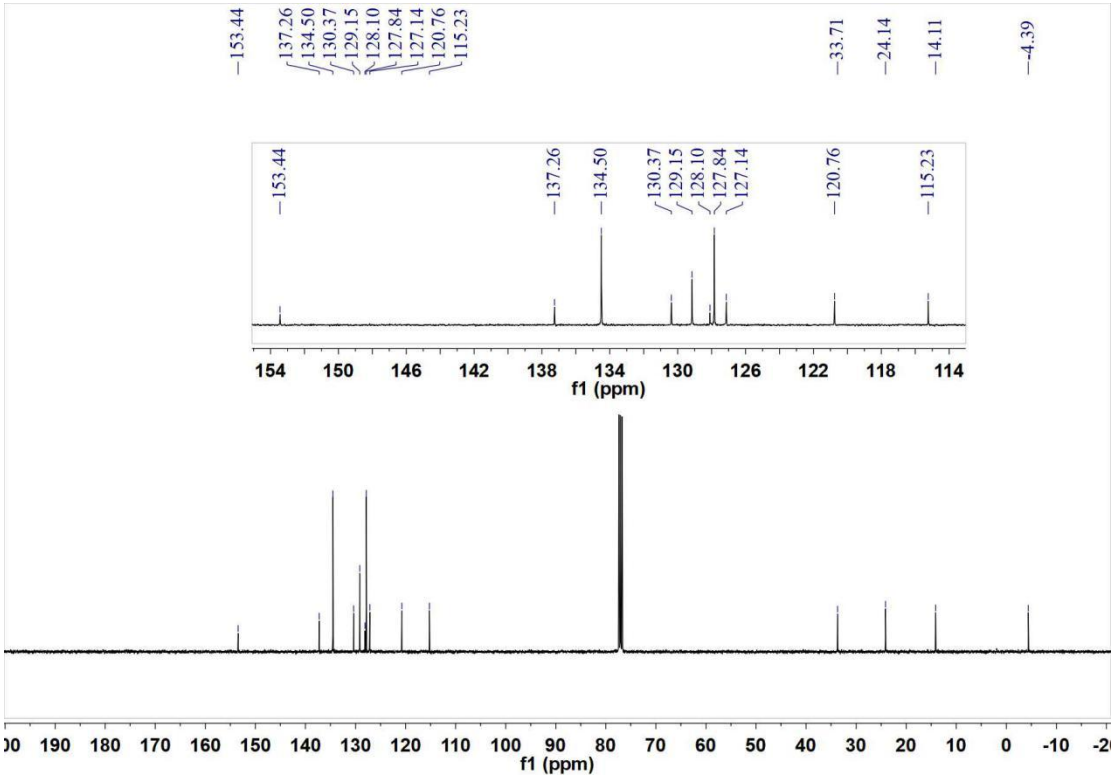
5a



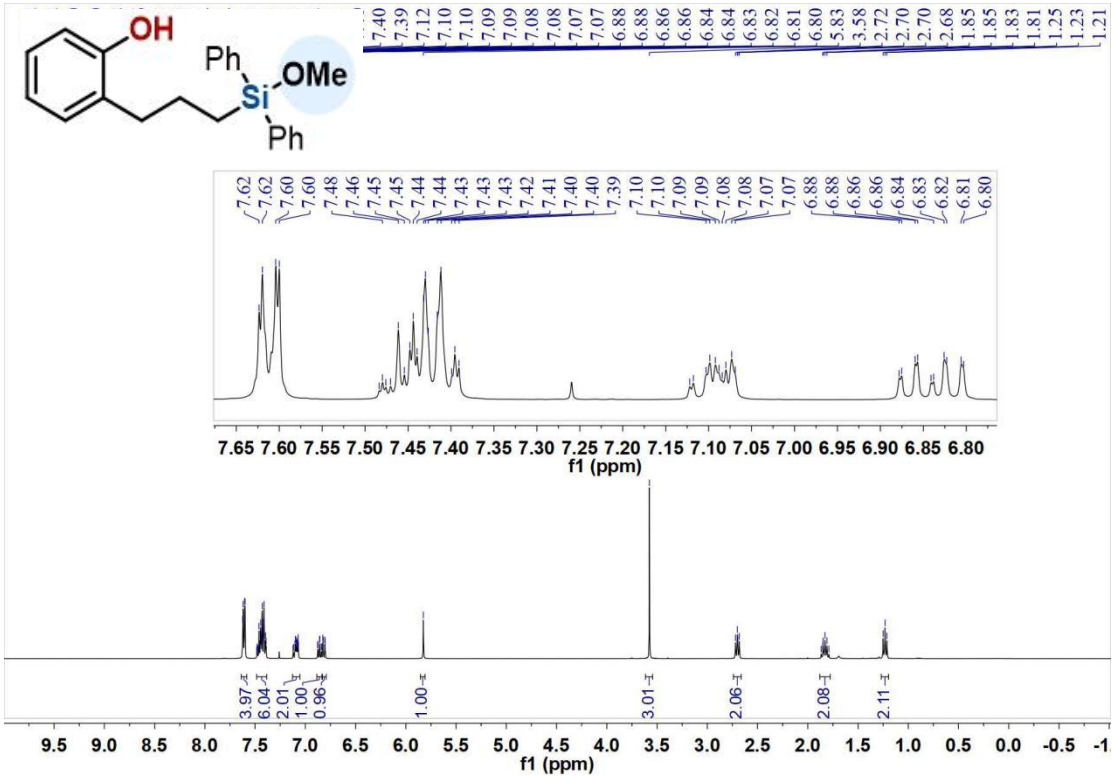

-171.23
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

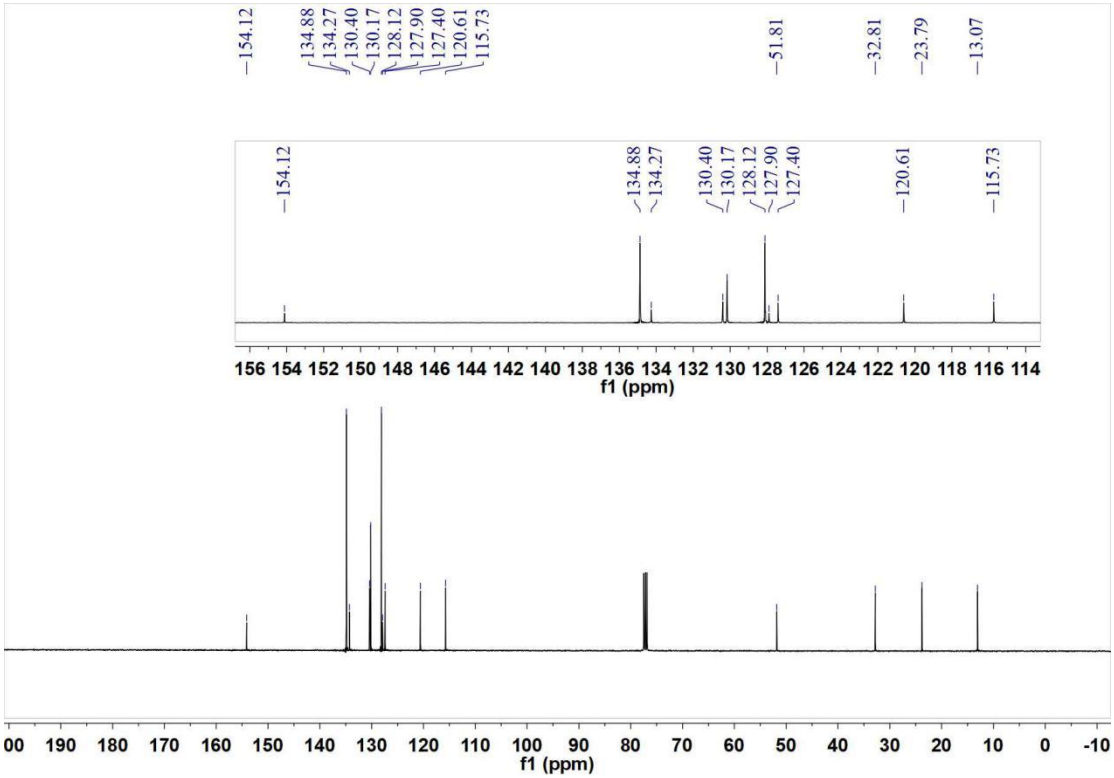
5b



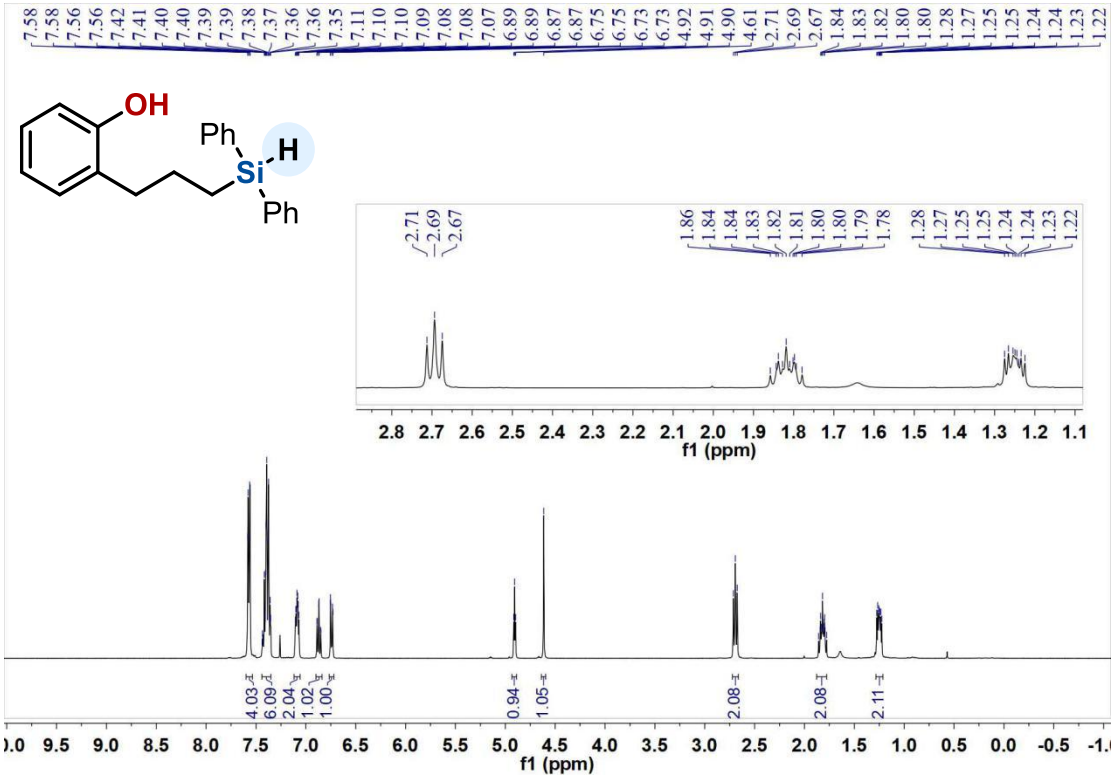


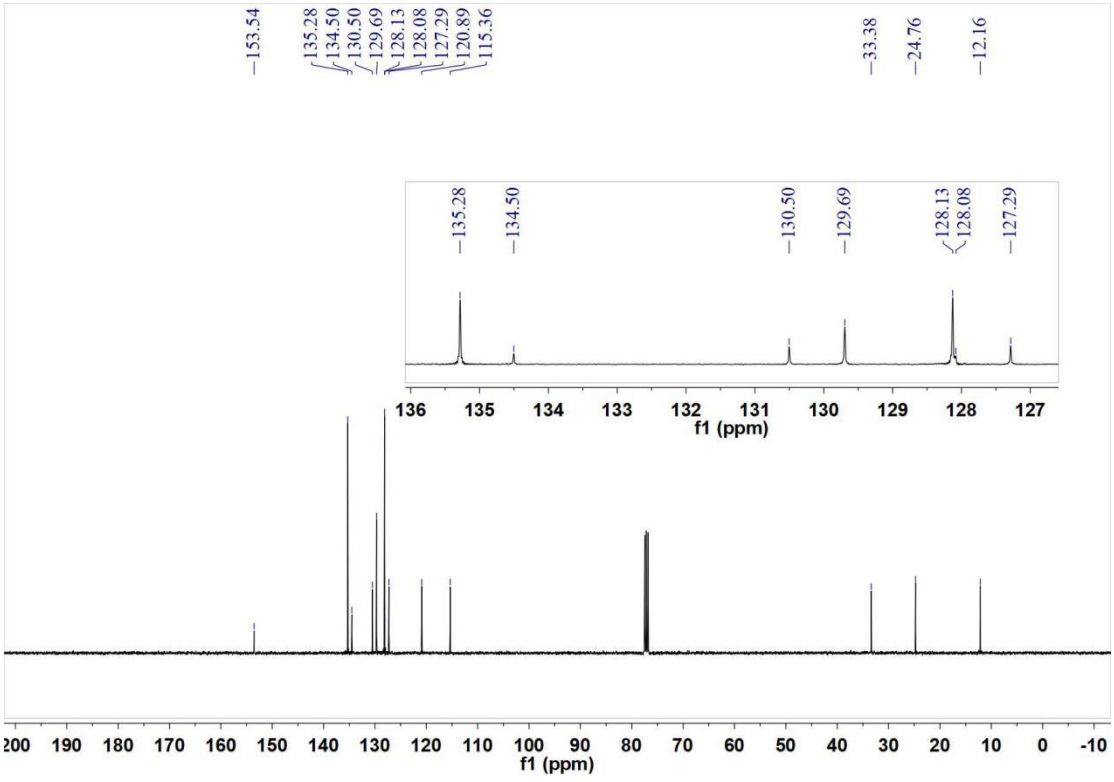
5c



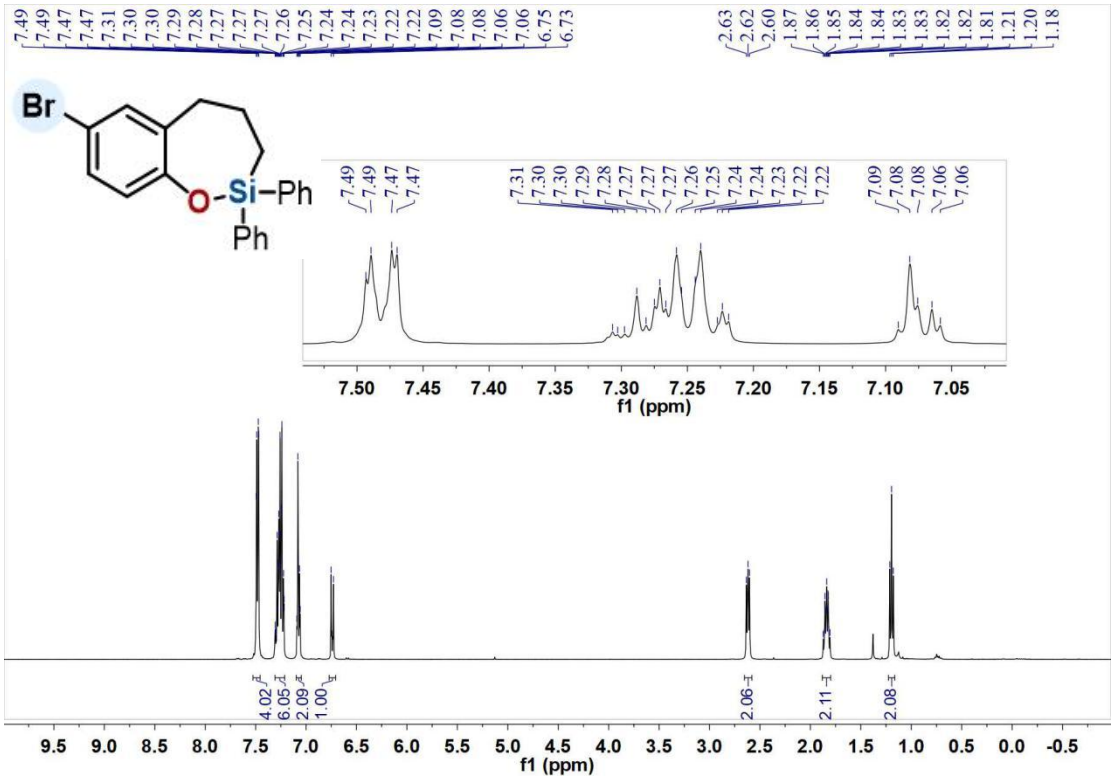


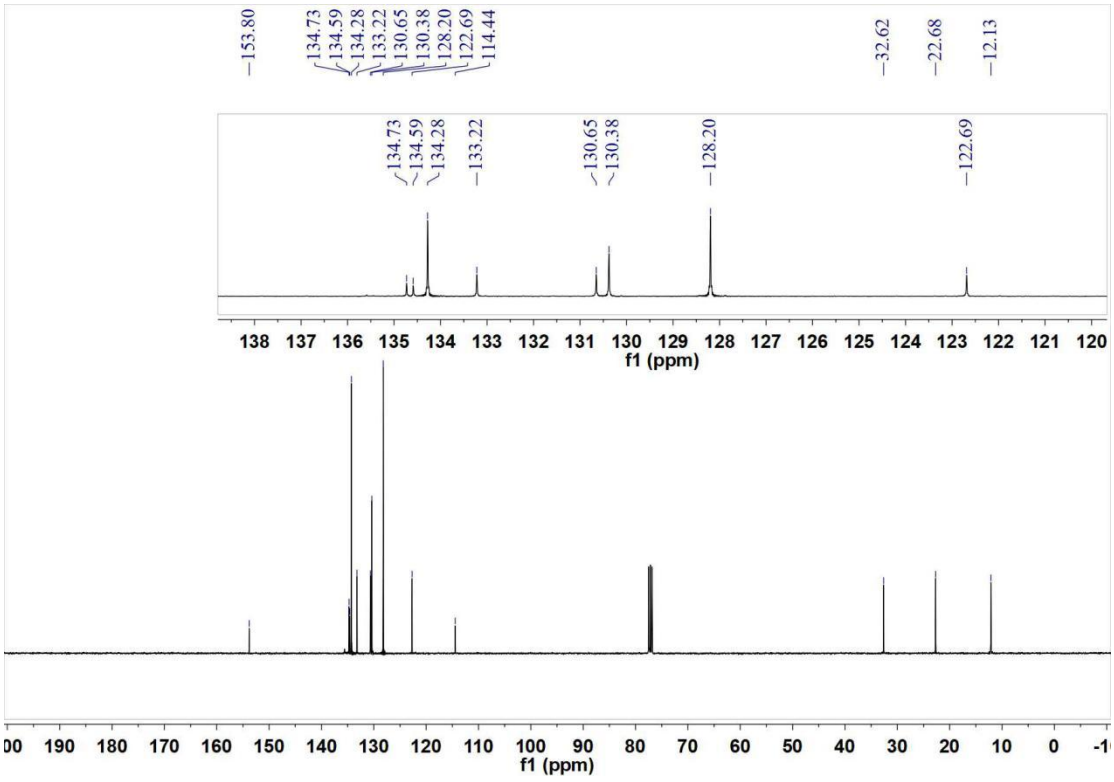
5d



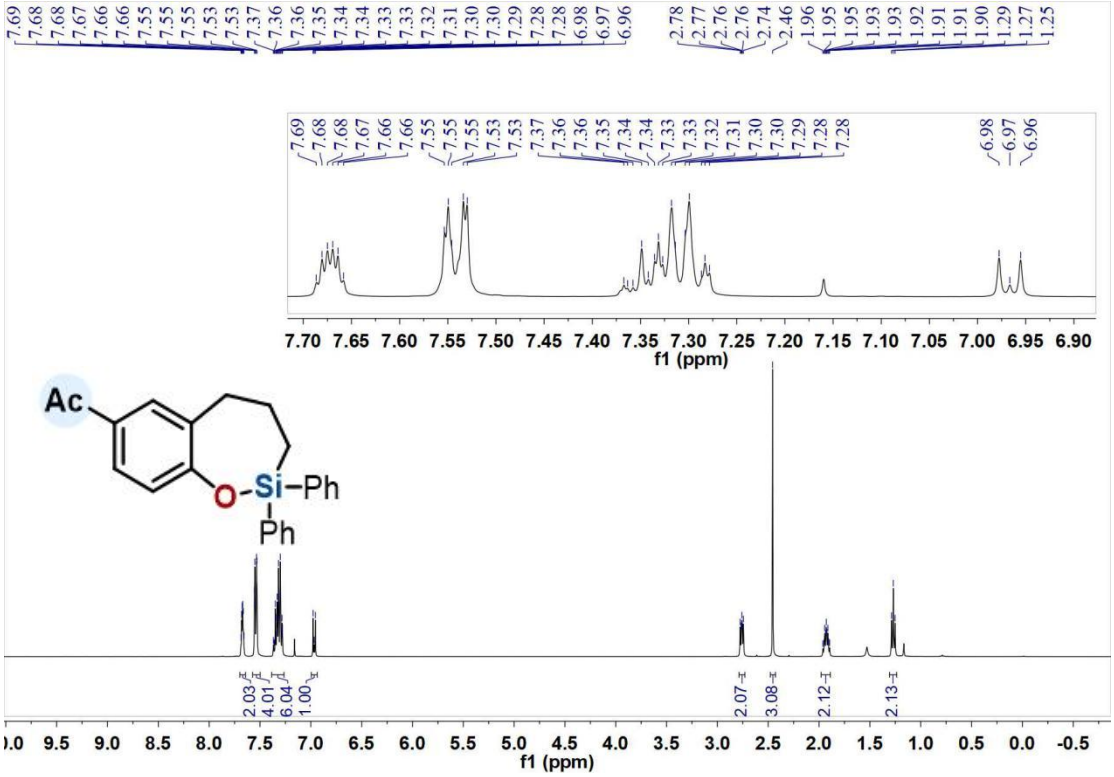


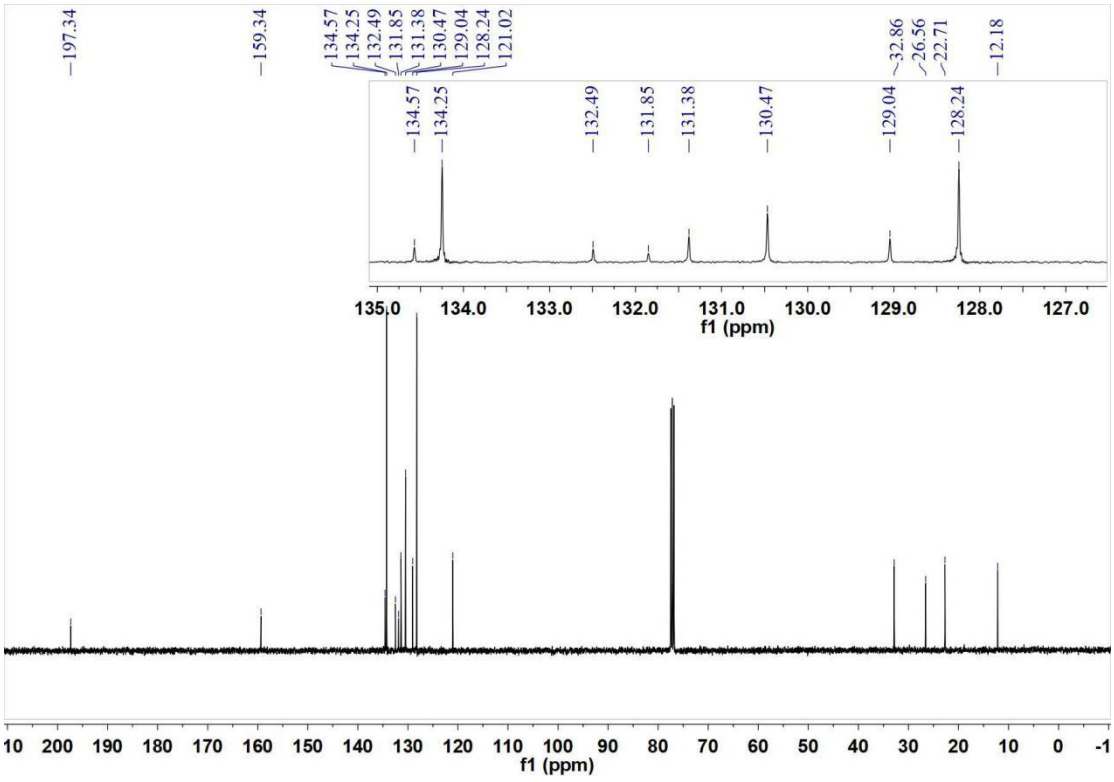
5e



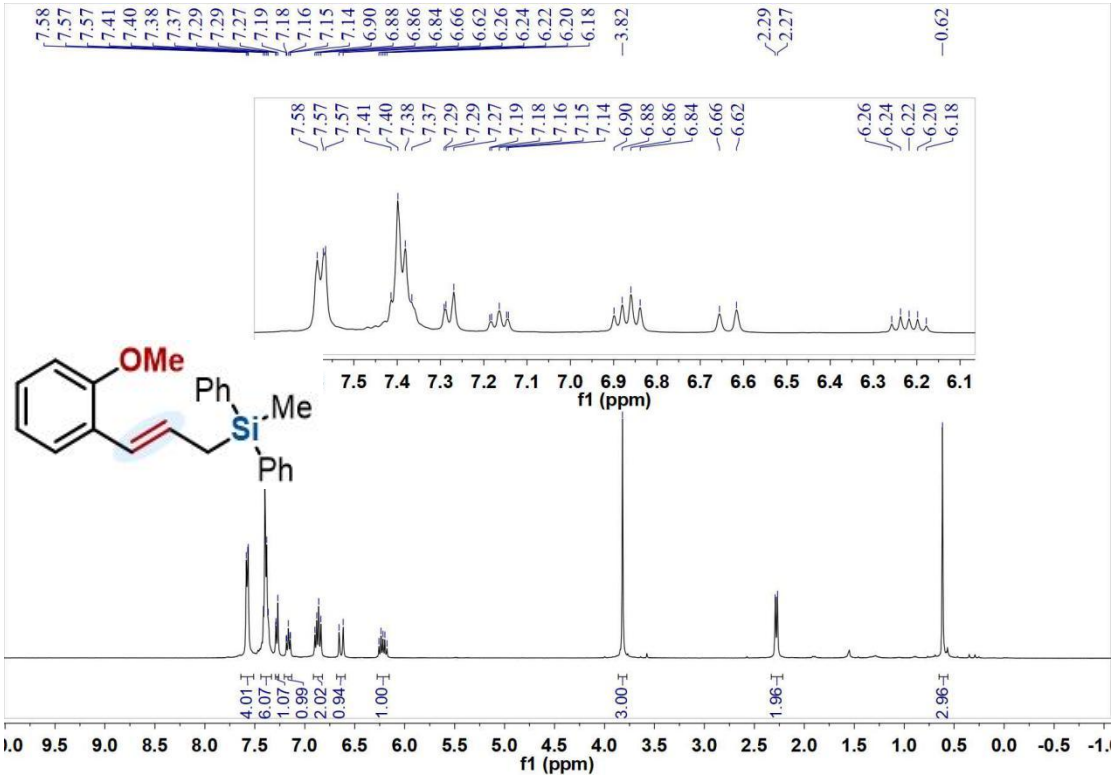


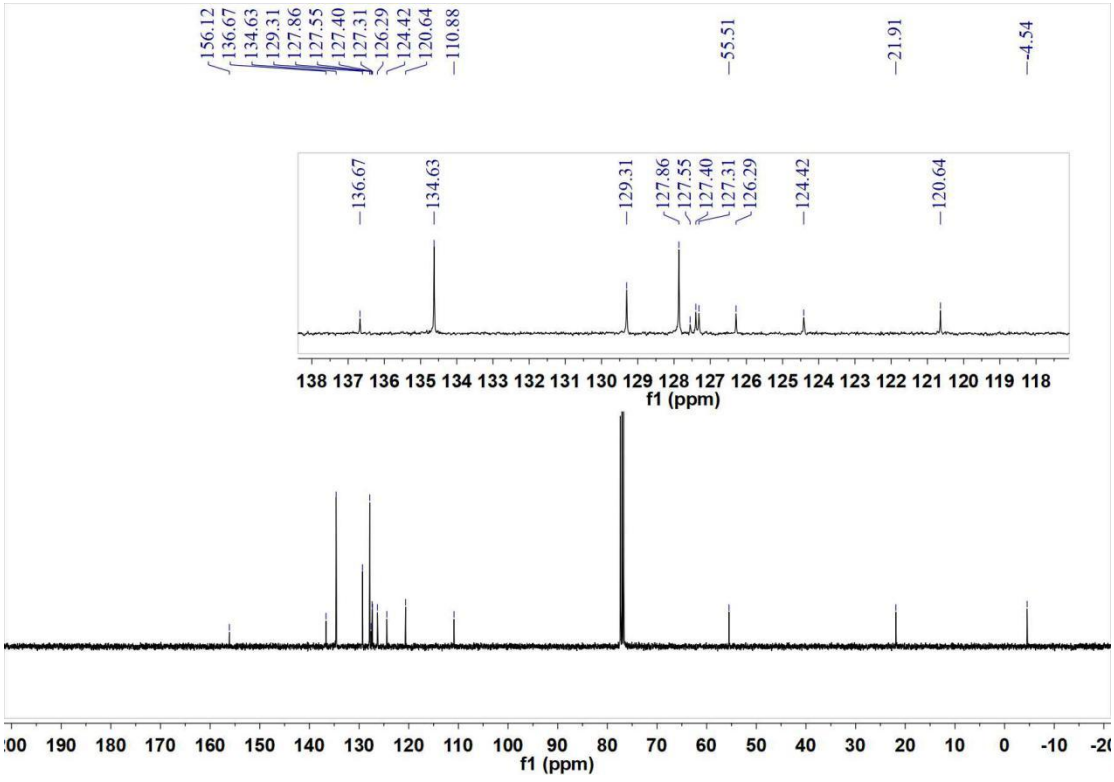
5f



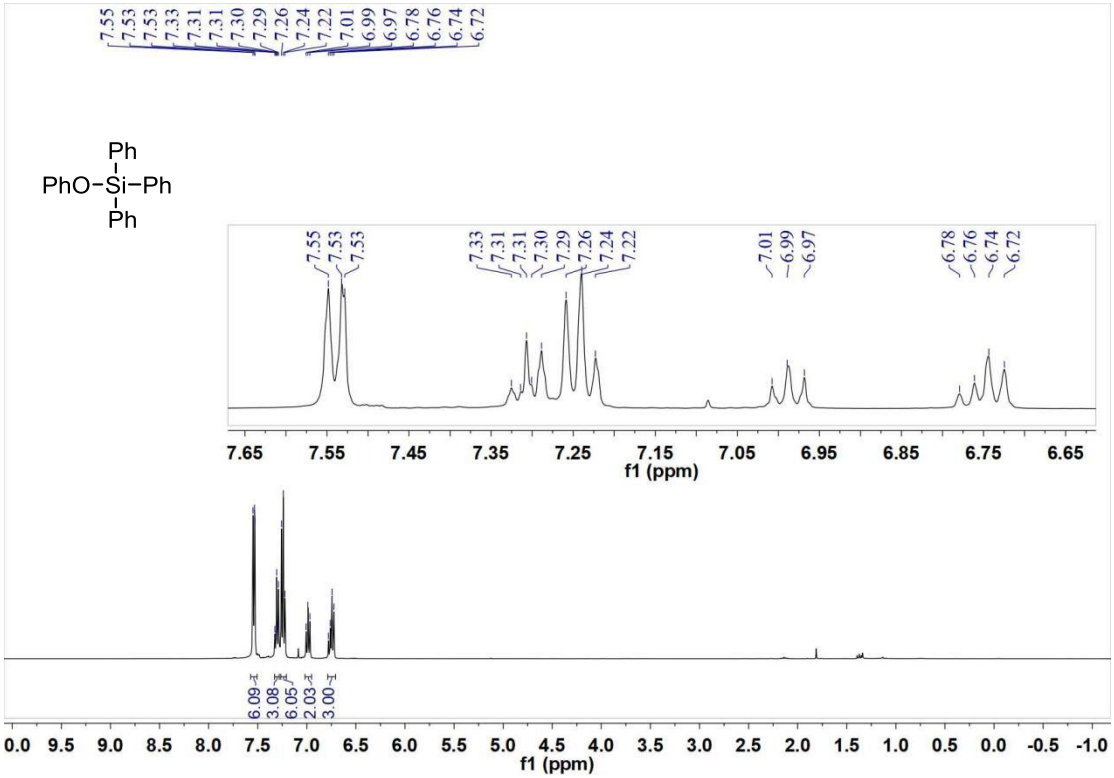


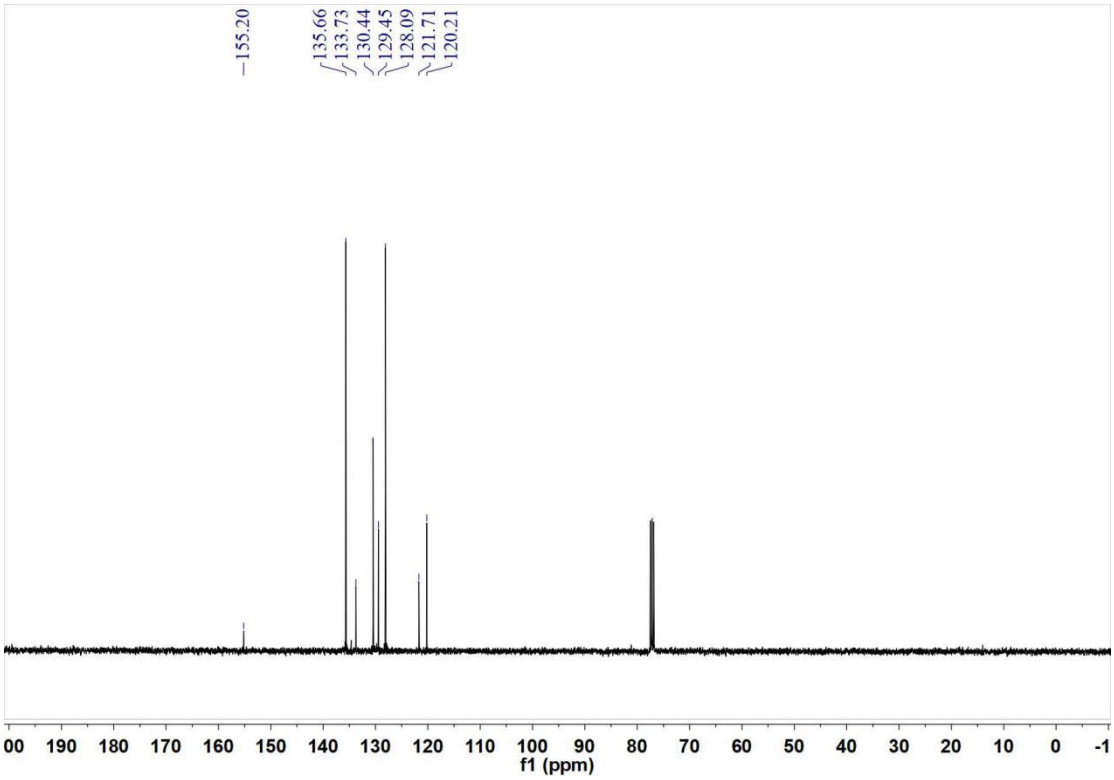
5h


7.58 7.57 7.57 7.41 7.40 7.38 7.37 7.29 7.29 7.27 7.19 7.18 7.16 7.15 7.14 6.90 6.88 6.86 6.84 6.66 6.62 6.26 6.24 6.22 6.20 6.18 3.82 2.29 2.27 0.62
OMe
Ph
Si
Me
Ph
4.01 6.07 1.07 0.99 2.02 0.94 1.00 3.00 1.96 2.96
f1 (ppm)

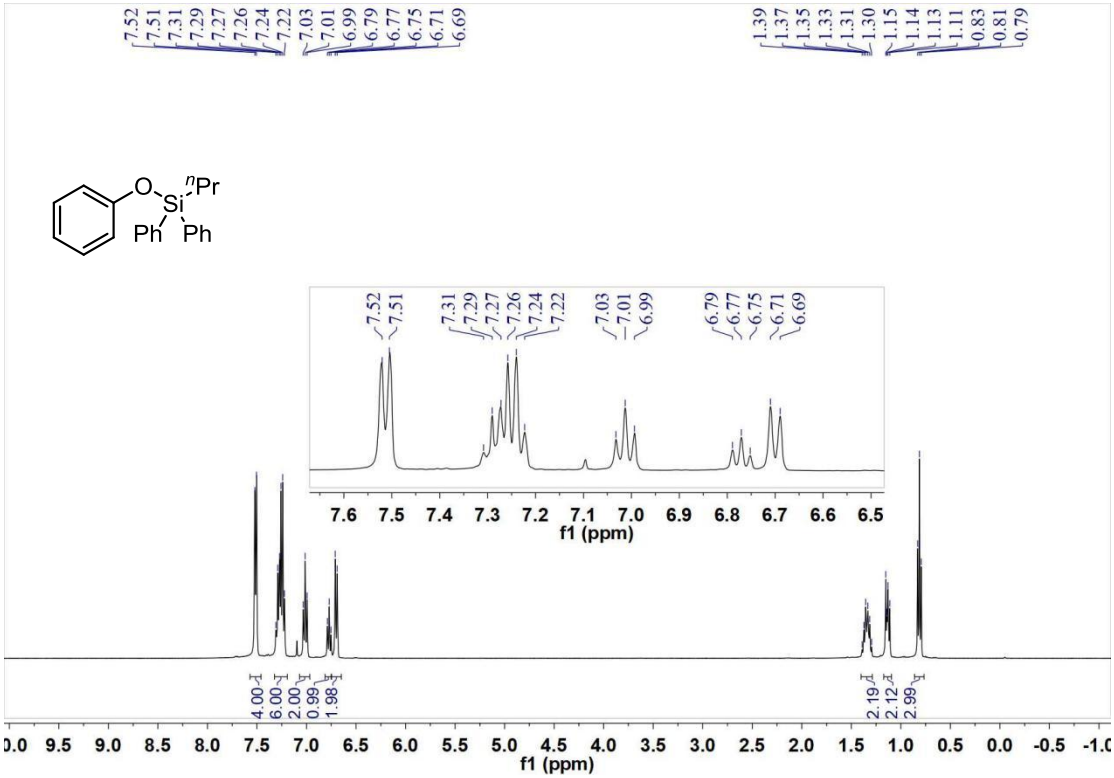

156.12 136.67 134.63 129.31 127.86 127.55 127.40 127.31 126.29 124.42 120.64 110.88 55.51 21.91 4.54
f1 (ppm)

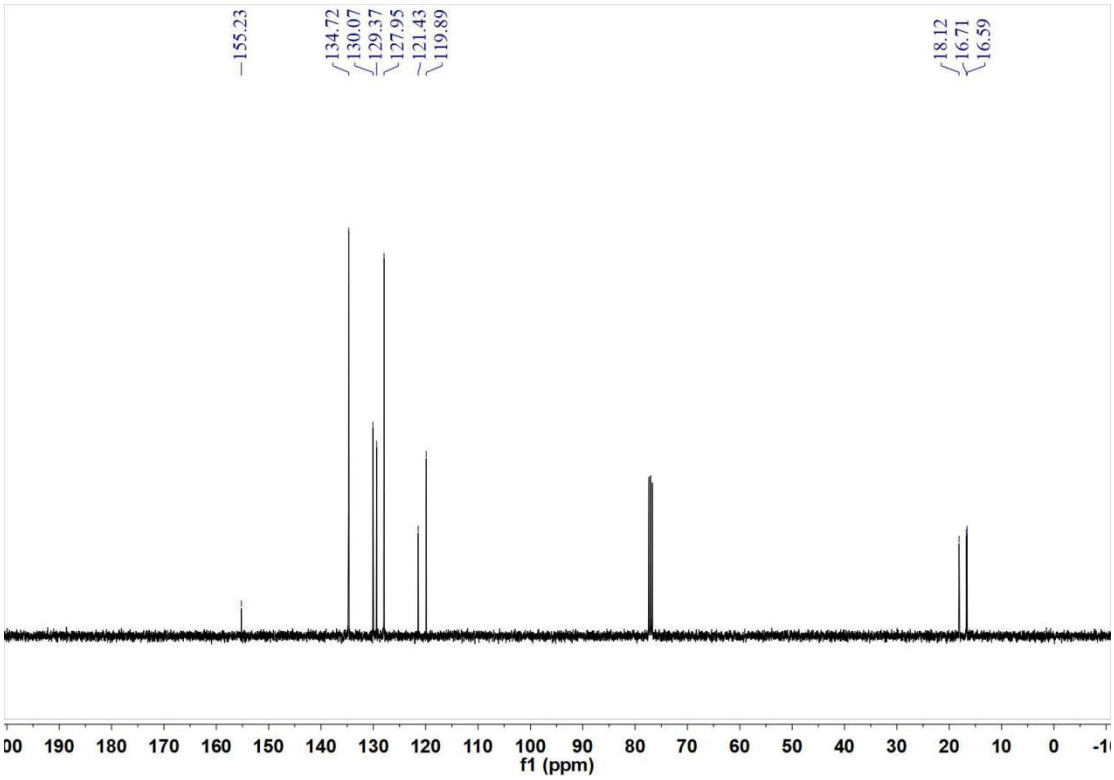
7a


7.55
7.53
7.53
7.33
7.31
7.31
7.30
7.29
7.26
7.24
7.22
7.01
6.99
6.97
6.78
6.76
6.74
6.72
Ph
PhO–Si–Ph
Ph
f1 (ppm)
6.09
3.08
6.05
2.03
3.00
f1 (ppm)

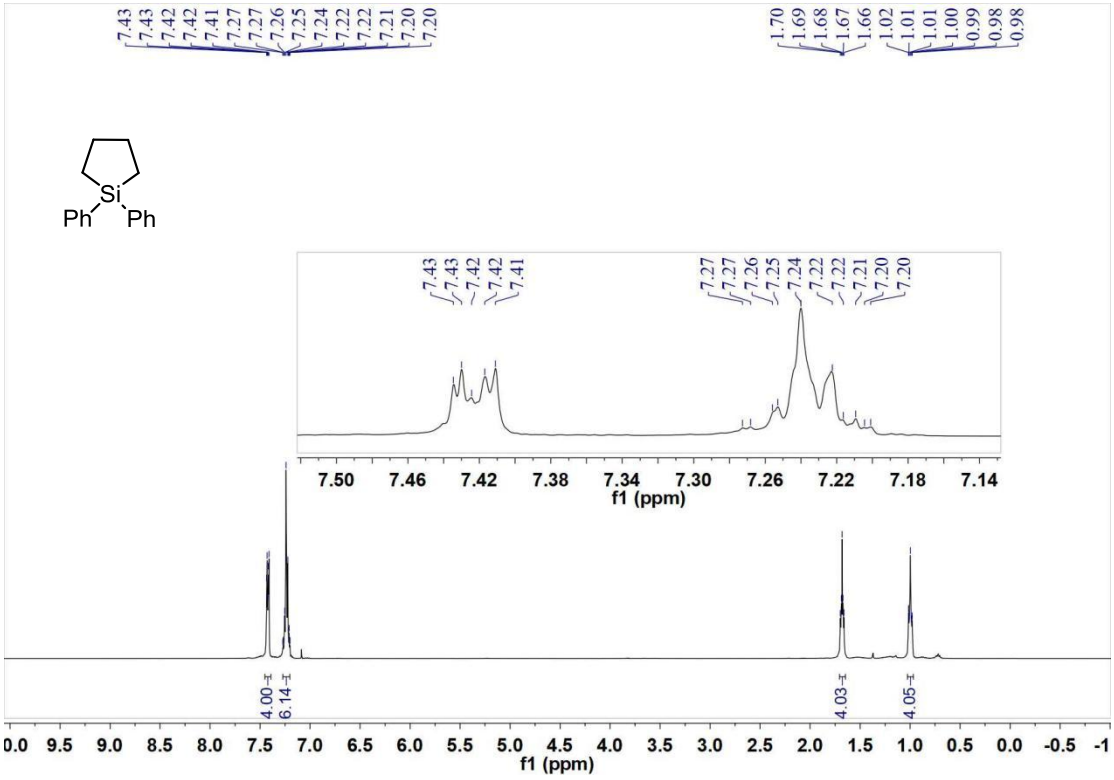

155.20
135.66
133.73
130.44
129.45
128.09
121.71
120.21
f1 (ppm)

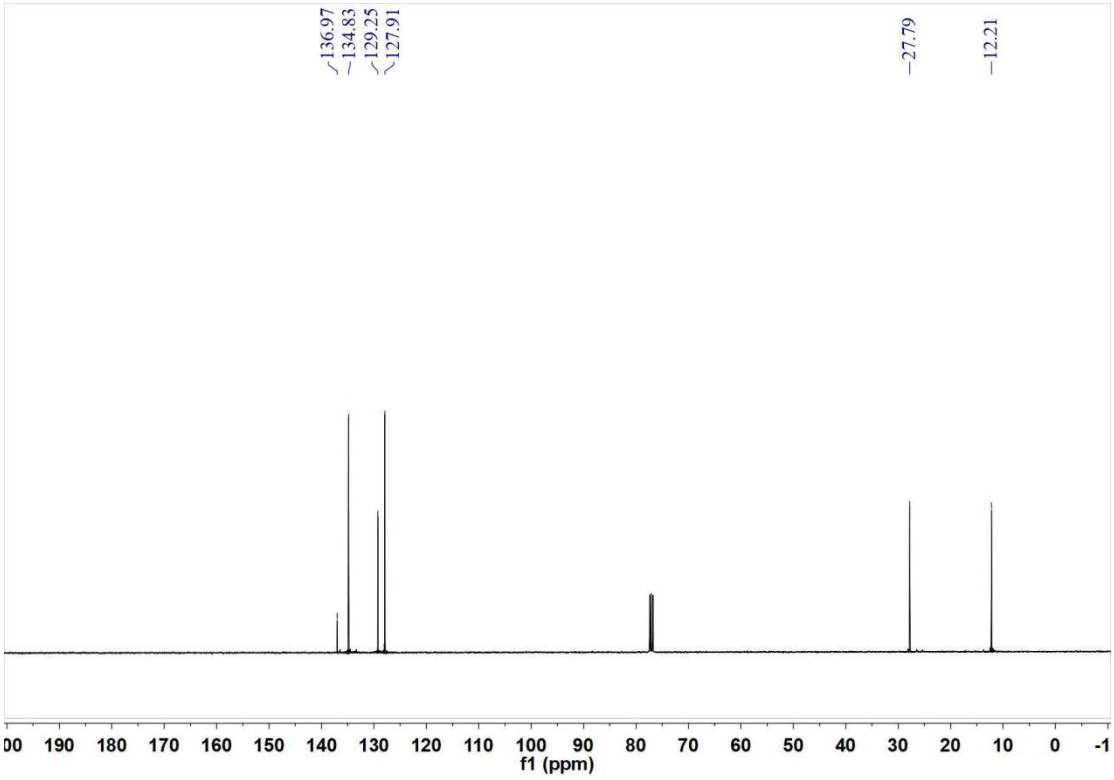
7b


7.52
7.51
7.31
7.29
7.27
7.26
7.24
7.22
7.03
7.01
6.99
6.79
6.77
6.75
6.71
6.69
1.39
1.37
1.35
1.33
1.31
1.30
1.15
1.14
1.13
1.11
0.83
0.81
0.79
O
Si
nPr
Ph
Ph
4.00
6.00
2.00
0.99
1.98
2.19
2.12
2.99
f1 (ppm)


155.23
134.72
130.07
129.37
127.95
121.43
119.89
18.12
16.71
16.59
f1 (ppm)

8a


7.43
7.43
7.42
7.42
7.41
7.27
7.27
7.26
7.25
7.24
7.22
7.22
7.21
7.20
7.20
1.70
1.69
1.68
1.67
1.66
1.02
1.01
1.01
1.00
0.99
0.98
0.98
Si
Ph
Ph
4.00
6.14
4.03
4.05
f1 (ppm)


136.97
134.83
129.25
127.91
27.79
12.21
f1 (ppm)