# Supporting Information

## Palladium-Catalyzed Silaborative Carbocyclizations of 1,6-Diynes

Qian Zhang,[†] Qiu-Ju Liang,[†] Jian-Lin Xu,[†] Yun-He Xu*[,†] and Teck-Peng Loh[†,‡,§]

[†]*Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*

[‡]*Institute of Advanced Synthesis, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing, Jiangsu, 210009, P. R. China*

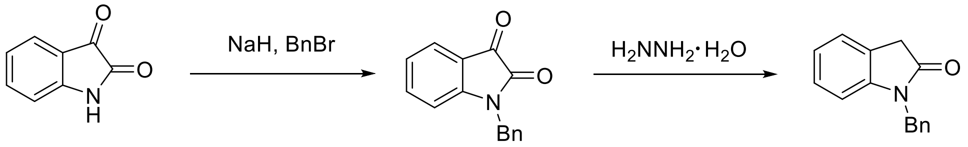
[§]*Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637616*

# I. General Information:

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware under a positive pressure of argon using dry solvents. Reagents were commercially purchased and were used as received without further purification for the reactions. Proton nuclear magnetic resonance ($^{1}$H NMR) and carbon nuclear magnetic resonance ($^{13}$C NMR) spectroscopy were performed on a Bruker Advance 400M NMR spectrometers. Chemical shifts $^{1}$H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-*d* (*J* = 7.264, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and etc. The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as δ in units of parts per million (ppm) relative to the signal of chloroform-d (*J* = 77.16, triplet). High resolution mass spectral analysis (HRMS) was performed on Water XEVO G2 Q-TOF (Waters Corporation). Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system. Preparative high performance liquid chromatography (Preparative HPLC) was performed on Shimadzu LC-20AP.

# II. Experimental Procedures：

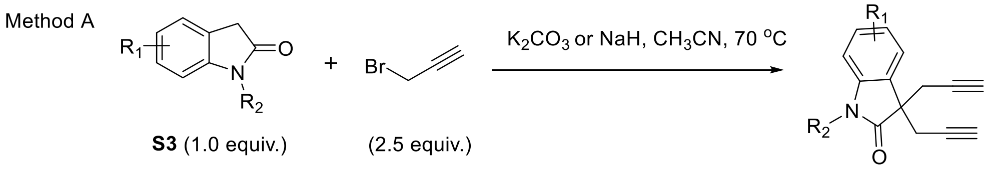
## 2.1.1 Procedures for Synthesis of *N*-protected oxindoles.



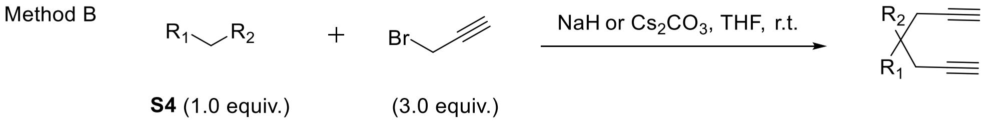

***N*-Benzylindoline-2,3-dione (S2):** Isatin (**S1**) (1.0 equiv.) was dissolved in *N*, *N*-dimethylformamide, and the resultant solution was cooled to 0 ℃. Sodium hydride (60% dispersion in mineral oil, 1.2 equiv.) was added in resulting in a purple suspension. After 15 min at 0 ℃, benzyl bromide (1.2 equiv.) was added dropwise, and the brown solution was maintained at 0 ℃ for 15 min. Ice-cooled water was added to the mixture, and a precipitate formed. The precipitate was filtered, washed with water and PE. The resulting solid was recrystallized from hot ethanol, filtered under reduced pressure to afford isatin **S2** (94%) as red-needlelike crystals.

***N*-Benzylindoline-2-one (S3):** A suspension of *N*-protected isatin **S2** (1.0 equiv.) and hydrazine hydrate (30.0 equiv.) was heated to 130 ℃ for 6h. The solution was then cooled to r.t. and 1M HCl was added until the PH < 7 resulting in a yellow suspension. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous $NaHCO_3$, then dried over $Na_2SO_4$ and concentrated to obtain the product **S3** (90%) as yellow oil.

## 2.1.2 Procedures for synthesis of 1,6-heptadiyne.



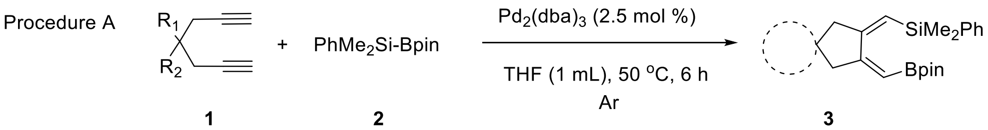

Method A: 3-Bromoprop-1-yne (2.5 equiv.) was added dropwise in a mixture of *N*-protected 2-oxindole **S3** (1.0 equiv.), potassium carbonate (6.0 equiv.) or sodium hydride (60% dispersion in mineral oil, 3.0 equiv.) in dry acetonitrile, and the solution was heated at 70 ℃ for 6 h. After cooling to room temperature the solid material was filtered off and the filtrate was evaporated under reduced pressure. Then purification of the crude product on a silica gel column chromatography using PE/EtOAc (10:1) to get the desired 1,6-heptadiyne derivatives.




Method B: 3-Bromoprop-1-yne (3.0 equiv.) was added dropwise in a mixture of **S4** (1.0 equiv.), sodium hydride (60% dispersion in mineral oil, 4.0 equiv.) or cesium carbonate (4.0 equiv.) in dry tetrahydrofuran. After stirring for 9 h at room temperature, the solid material was filtered off and the filtrate was evaporated under reduced pressure. Then purification of the crude product on a silica gel column chromatography using PE/EtOAc to get the desired 1,6-heptadiyne derivatives.

All substrates were prepared according to the previously reported procedure[1-9].

## 2.2 General Method for the Silaborative Cyclization Reactions.

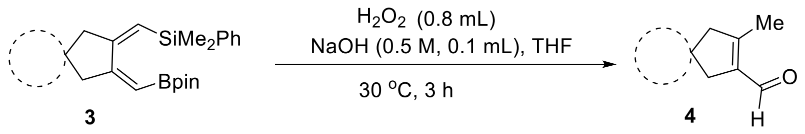



Procedure A: 1,6-diynes **1**(0.2 mmol), $Pd_2(dba)_3$ (0.005 mmol, 4.6 mg) and 1 mL THF were added into an oven dried 15 mL tube equipped with a stirring bar under argon atmosphere. Then $Me_2PhSi$-Bpin (0.24 mmol, 62.9 mg) were added to the tube. The solution was stirred at 50 $^{o}$C for 6 hours. After cooling to the room temperature, the reaction mixture was diluted with water, DCM, and further extracted with DCM (two times). Then the combined aqueous layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo. The residue was purified by Preparative HPLC to get product **3**.

## 2.3 Typical Procedures for Derivation.

### 2.3.1 Typical Procedures for Oxidation[10-11].

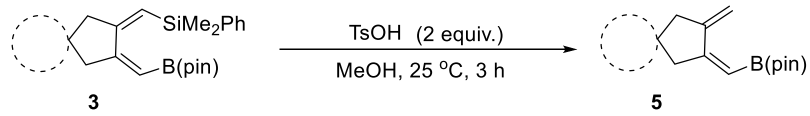
Procedure B




Procedure B: The alkenyl boronate ester **3** was prepared according to the above procedure A from **1** without further working up. The mixture was dissolved in THF (1.0 mL) and cooled to 0 ℃. Then, aqueous 0.5 M NaOH (0.1 mL) was added, followed by 30% aq. $H_2O_2$ (0.8 mL) was added dropwise via syringe at 0 ℃. The resulting mixture was allowed to stir at room temperature for 3 hours. Then saturated aqueous $Na_2S_2O_3$ was added dropwise. The mixture was diluted with $H_2O$ and extracted with DCM. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel with PE/EtOAc (8:2) as the eluent to afford product **4**.

### 2.3.2 Typical Procedures for Protonation[12].

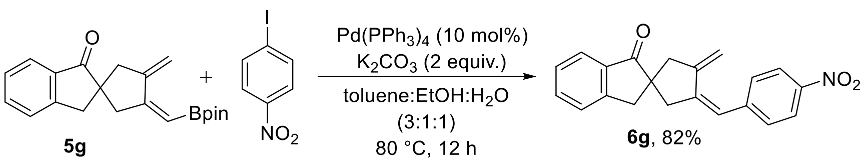
Procedure C




Procedure C: The alkenyl boronate ester **3** was prepared according to the above procedure A from **1** without further working up. A solution of **3** (0.20 mmol) and TsOH (68.9 mg, 0.40 mmol) in MeOH (1 mL) was stirred at room temperature for 3 h. The reaction mixture was diluted with water and DCM, and was further extracted with DCM (two times). After washed with brine, saturated aqueous $NaHCO_3$, and dried with $MgSO_4$, filtered, the combined organic layers were concentrated in vacuo. Purification by column chromatography on silica gel with PE/EtOAc/$CH_3CN$ (100:6:6) as the eluent to get product **5**.

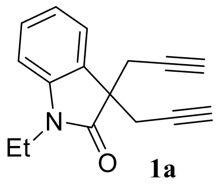
### 2.3.3 General Procedure for Suzuki-Miyaura cross coupling reaction[13].

Procedure D



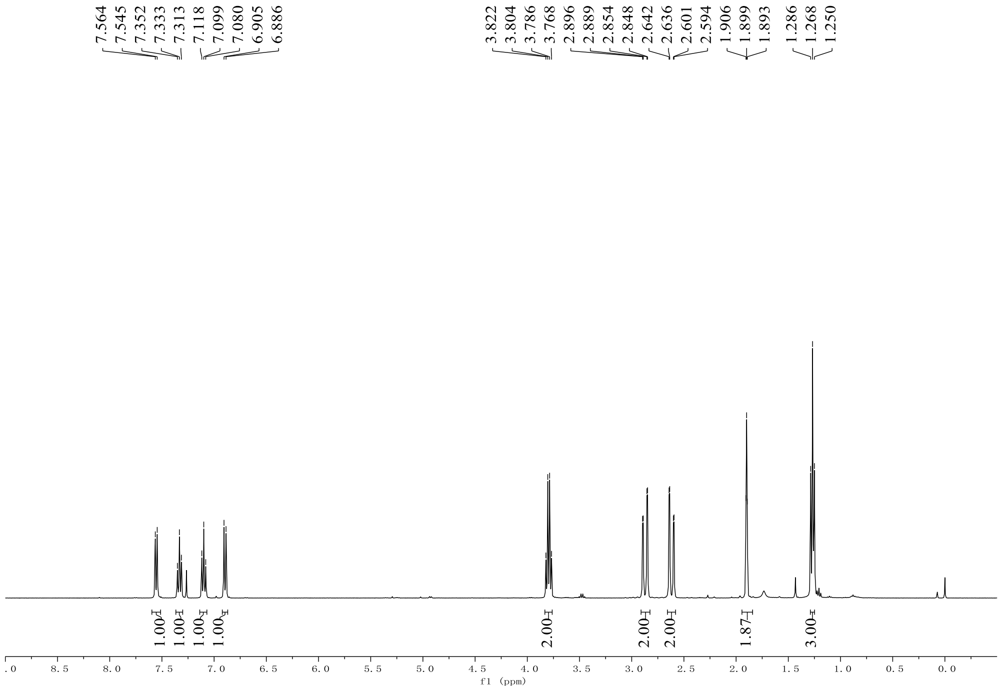

Procedure D: The alkenyl boronate ester **5g** was prepared according to the above procedure C from 3g. The starting material **5g** (67.2 mg, 0.2 mmol) was added in a dried tube under argon atmosphere. $Pd(PPh_3)_4$ (23.2 mg, 0.02 mmol), toluene 1.5 mL, EtOH 0.5 mL and aqueous $K_2CO_3$ (0.8 M, 0.5 mL, 0.4 mmol) were then added successively. At last 1-Iodo-4-nitrobenzene (99.6 mg, 0.4 mmol) was added into the tube. The reaction was allowed to stir at 80 $^{o}$C. After stirring for 12 hours, the reaction was quenched with water and the aqueous layer was extracted with DCM (two times). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was subjected to by column chromatography on silica gel with PE/EtOAc/$CH_3CN$ (100:6:6) to afford the product **6g** as a yellow oil.

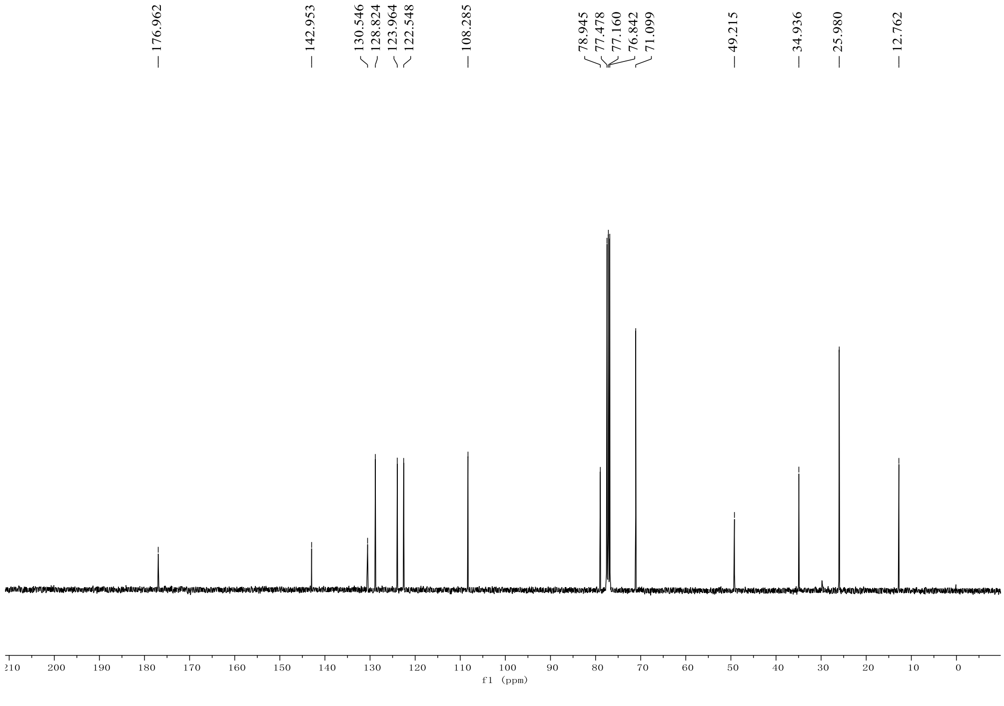
## III. Characterization Data and Spectrum of Starting Materials and Products.

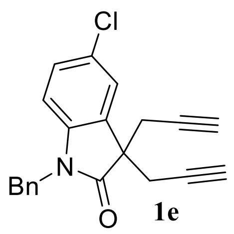


**1a**

According to the method A to get the product **1a** (1.22 g, 27%) as white solid. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 3.79 (q, *J* = 7.2 Hz, 2H), 2.87, 2.62 (ABd, *J* = 16.8, 2.8 Hz, 4H), 1.90 (t, *J* = 2.8 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 176.96, 142.95, 130.55, 128.82, 123.96, 122.55, 108.29, 78.94, 71.10, 49.22, 34.94, 25.98, 12.76; **HRMS** (ESI) m/z calculated for $C_{16}H_{16}NO$ $[M+H]^+$: 238.1232, found: 238.1235.

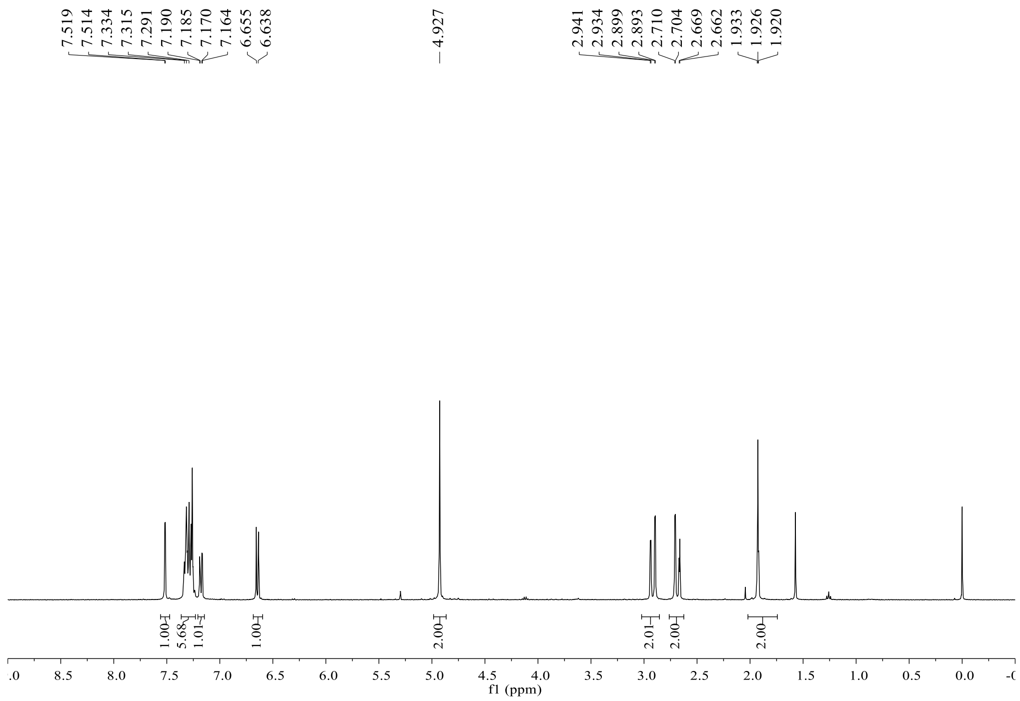


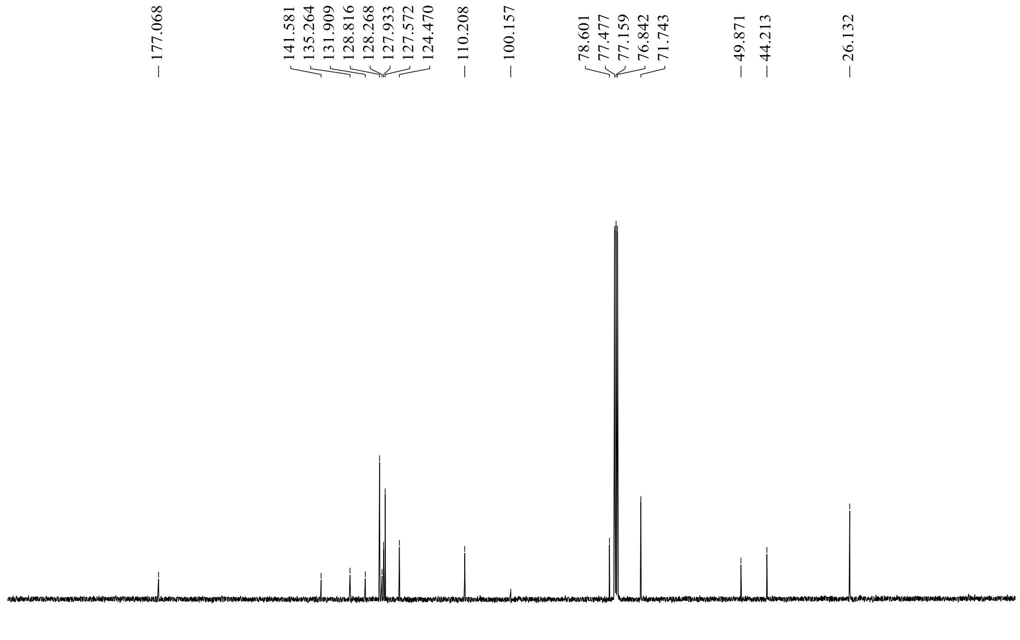


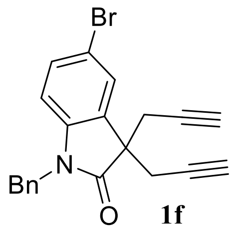


**1e**

According to above method A to get the product **1e** (0.66 g, 20%) as yellow solid. **$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 2.0 Hz, 1H), 7.33 - 7.29 (m, 5H), 7.18 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.65 (d, *J* = 6.8 Hz, 1H), 4.93 (s, 2H), 2.92, 2.68 (ABd, *J* = 16.8, 2.8 Hz, 4H), 1.93 (t, *J* = 2.8 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 177.07, 141.58, 135.26, 131.91, 128.82, 128.27, 127.93, 127.57, 124.47, 110.21, 100.16, 78.60, 71.74, 49.87, 44.21, 26.13; **HRMS** (ESI) m/z calculated for $C_{21}H_{17}NOCl$ $[M+H]^{+}$: 334.0999, found: 334.0998.

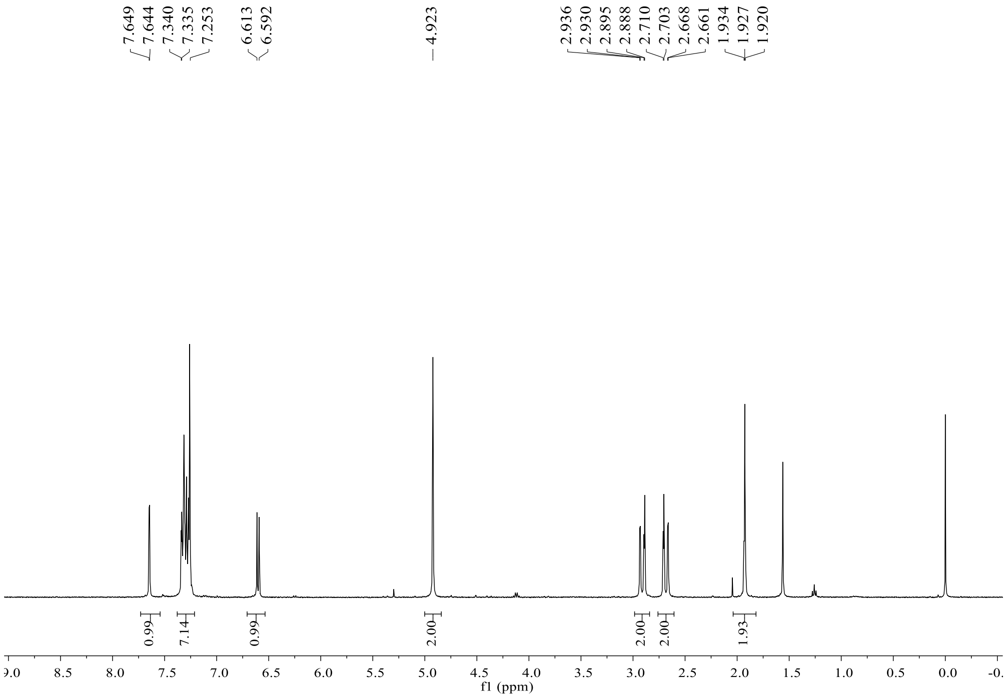


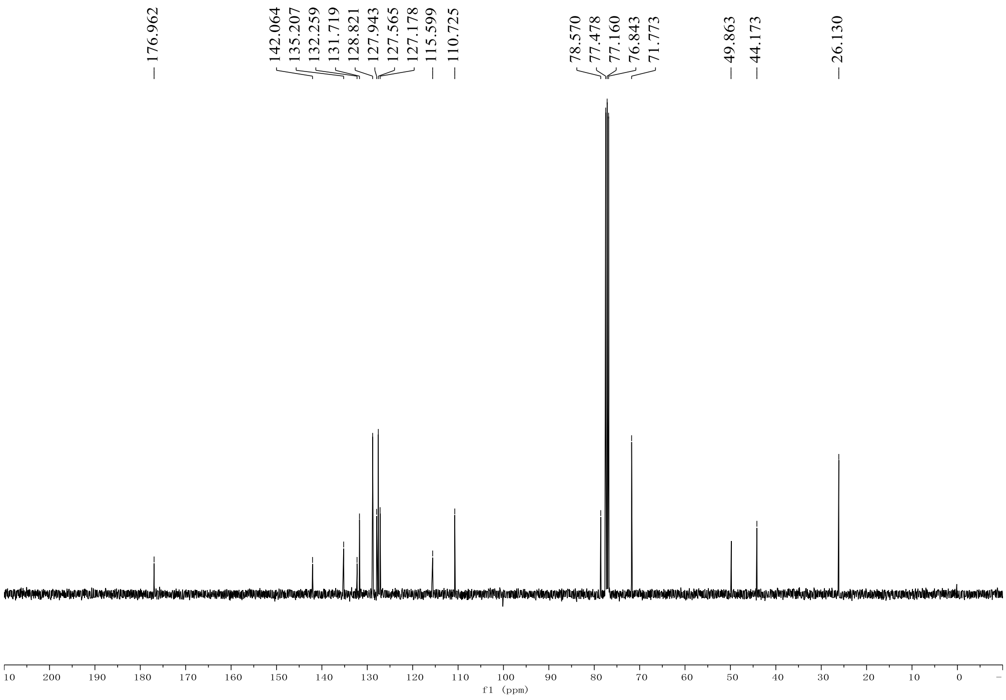



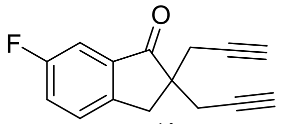



**1f**

According to above method A to get the product **1f** (0.50 g, 21%) as yellow solid. **$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.64 (d, $J$ = 2.0 Hz, 1H), 7.34 - 7.25 (m, 6H), 6.60 (d, $J$ = 8.4 Hz, 1H), 4.92 (s, 2H), 2.93, 2.68 (ABd, $J$ = 16.4, 2.8 Hz, 4H), 1.93 (t, $J$ = 2.8 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 176.96, 142.06, 135.21, 132.26, 131.72, 128.82, 127.94, 127.57, 127.18, 115.60, 110.73, 78.57, 71.77, 49.86, 44.17, 26.13; **HRMS** (ESI) m/z calculated for $C_{21}H_{17}NOBr$ $[M+H]^+$: 378.0494, found: 378.0497.



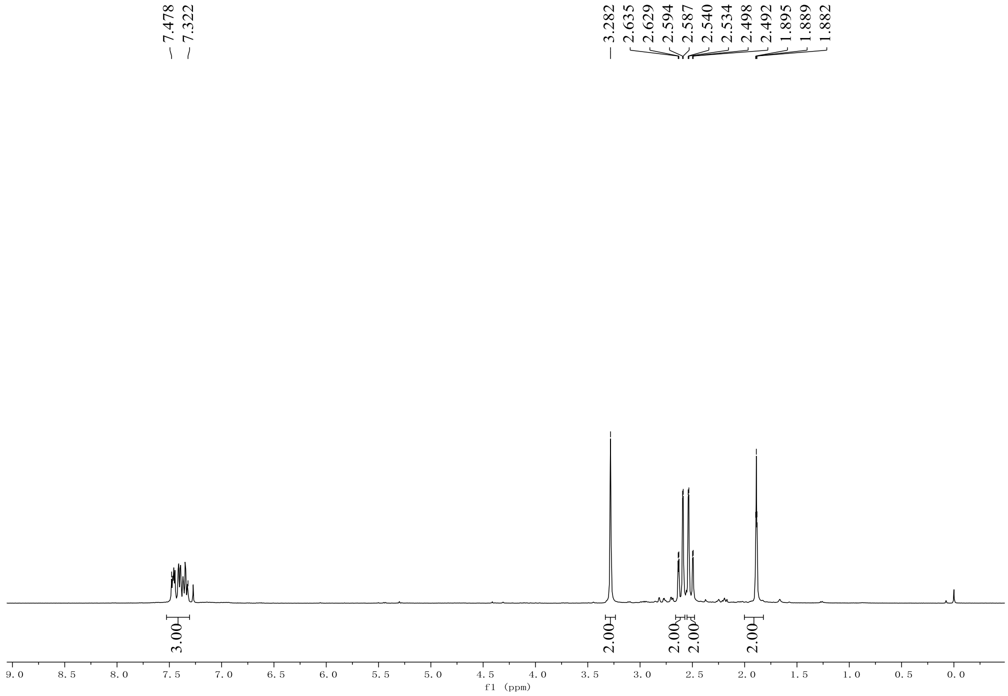



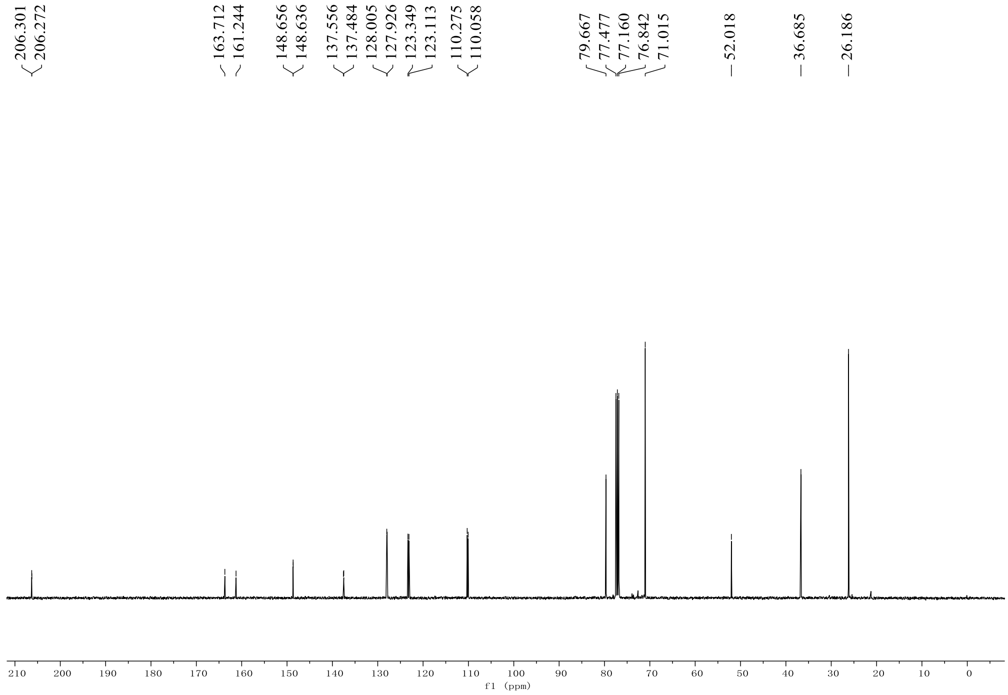


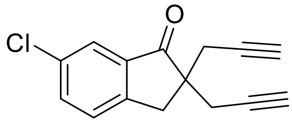
**1j**

According to above method A to get the product **1j** (1.17 g, 52%) as yellow solid.

[1]**H NMR** (400 MHz, CDCl3): δ 7.48 - 7.32 (m, 3H), 3.28 (s, 2H), 2.61, 2.52 (ABd, *J* = 16.4, 2.4 Hz, 4H), 1.89 (t, *J* = 2.4 Hz, 2H); [13]**C NMR** (101 MHz, $CDCl_3$): δ 206.29 (d, *J* = 2.9 Hz), 162.48 (d, *J* = 249.3 Hz), 148.65 (d, *J* = 2.0 Hz), 137.52 (d, *J* = 7.3 Hz), 127.97 (d, *J* = 8.0 Hz), 123.23 (d, *J* = 23.8 Hz), 110.17 (d, *J* = 21.9 Hz), 79.67, 71.01, 52.02, 36.69, 26.19; **HRMS** (ESI) m/z calculated for $C_{15}H_{12}OF$ $[M+H]^+$: 227.0872, found: 227.0869; [19]**F NMR** (376 MHz, $CDCl_3$): δ -114.08 Hz (s, 1F).



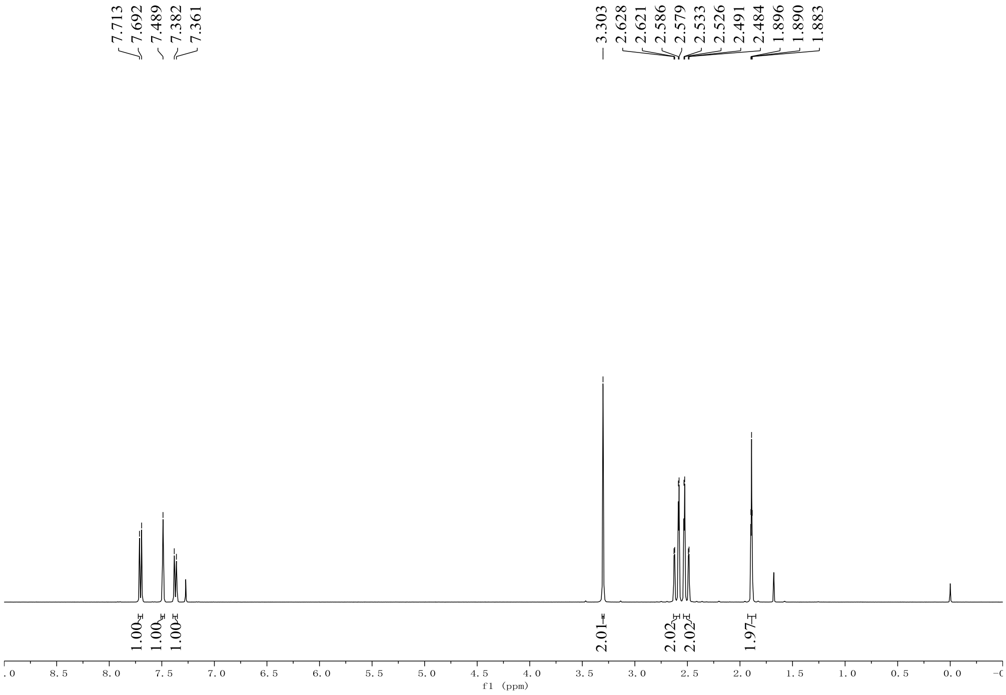



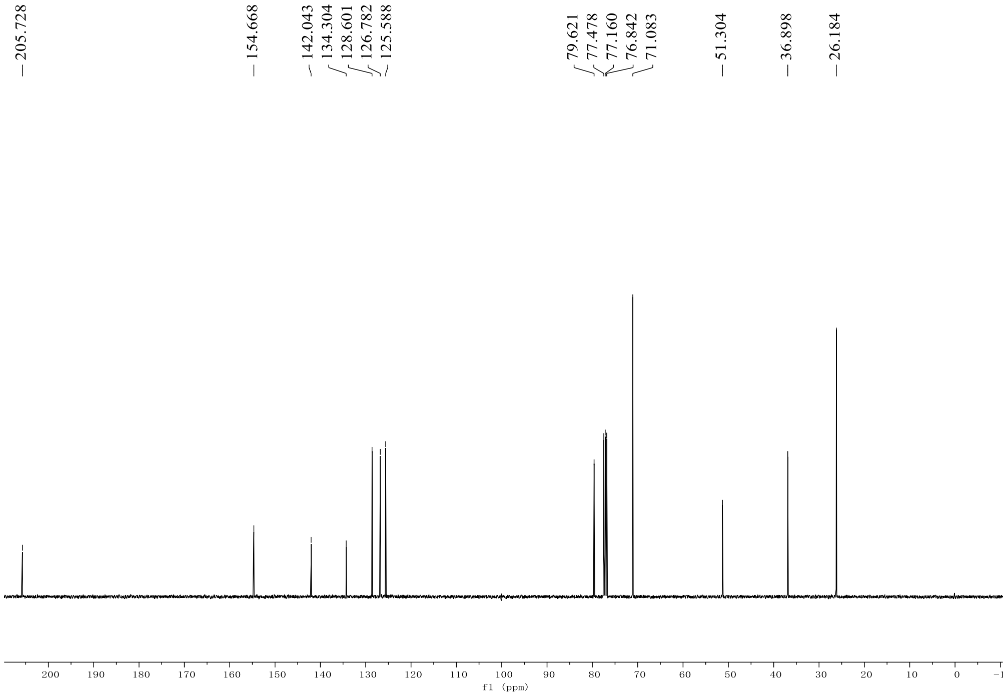


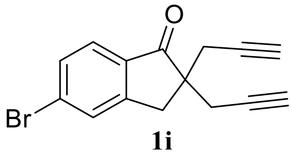
**1h**

According to above method A to get the product **1h** (1.02 g, 42%) as pale yellow solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 3.30 (s, 2H), 2.61, 2.51 (ABd, *J* = 16.8, 2.8 Hz, 4H), 1.89 (t, *J* = 2.4 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 205.73, 154.67, 142.04, 134.30, 128.60, 126.78, 125.59, 79.62, 71.08, 51.30, 36.90, 26.18; **HRMS** (ESI) m/z calculated for $C_{15}H_{12}OCl$ $[M+H]^+$: 243.0577, found: 243.0578.



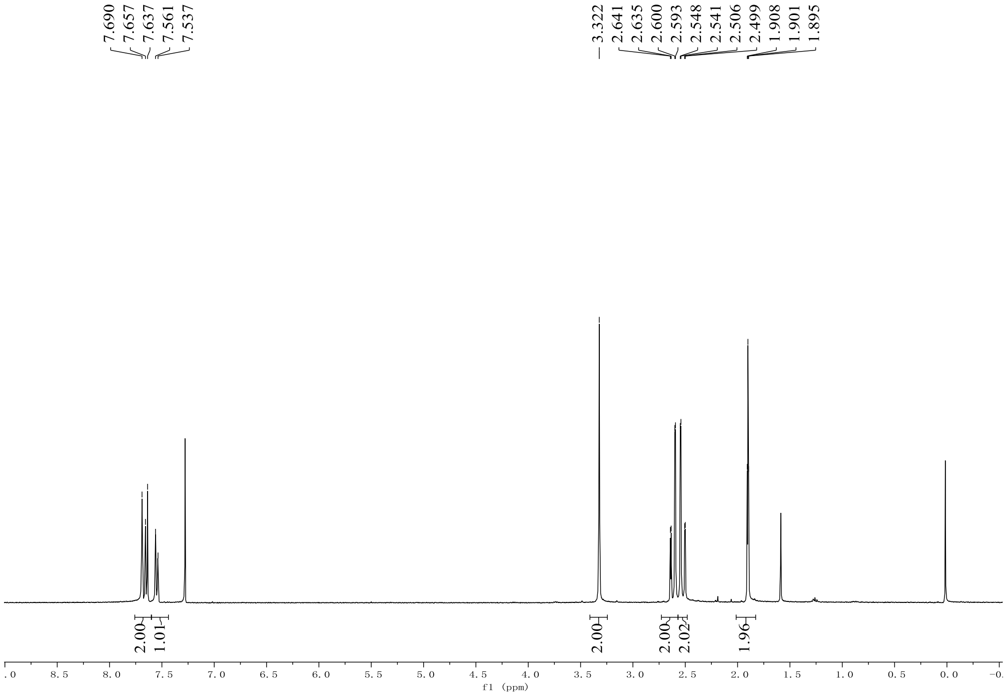



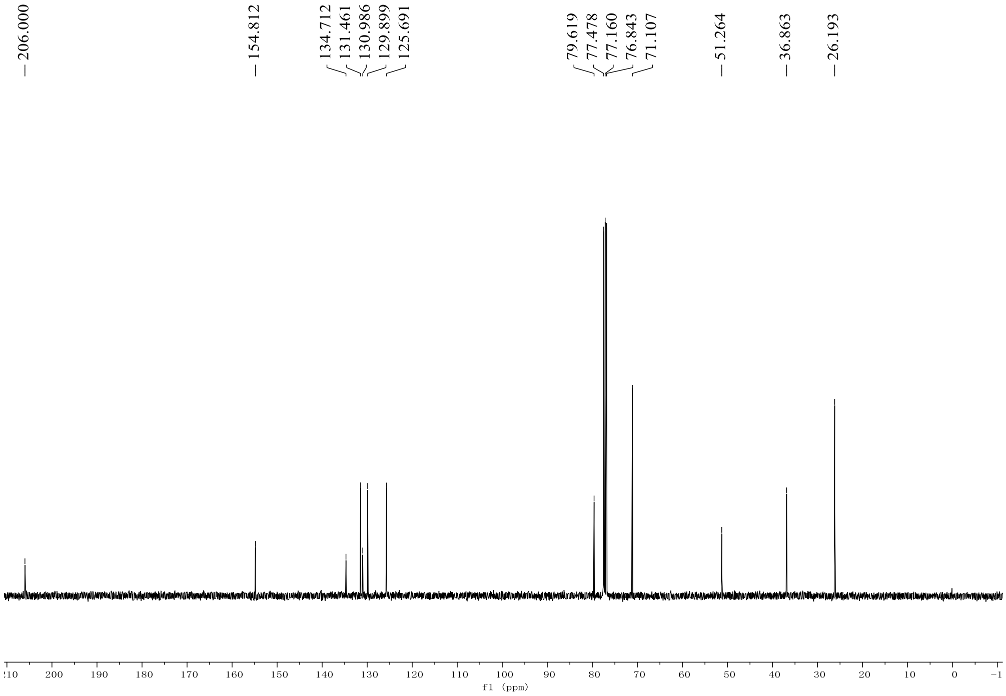


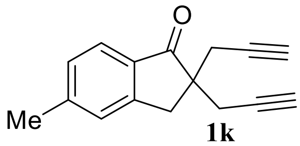
**1i**

According to above method A to get the product **1i** (1.27 g, 44%) as pale yellow solid.

**$^{1}$H NMR** (400 MHz, CDCl3): δ 7.69 - 7.54 (m, 3H), 3.32 (s, 2H), 2.62, 2.53 (ABd, *J* = 16.4, 2.4 Hz, 4H), 1.90 (t, *J* = 2.4 Hz, 2H); **$^{13}$C NMR** (101 MHz, CDCl3): δ 206.00, 154.81, 134.71, 131.46, 130.99, 129.90, 125.69, 79.62, 71.11, 51.26, 36.86, 26.19; **HRMS** (ESI) m/z calculated for $C_{15}H_{12}BrO$ $[M+H]^{+}$: 287.0072, found: 287.0073.



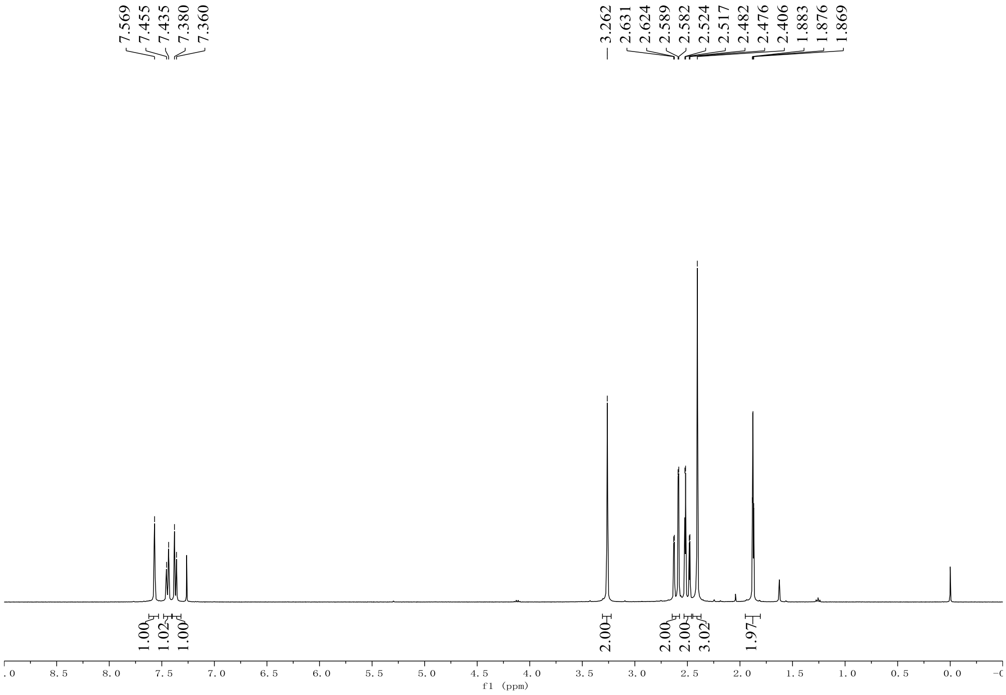



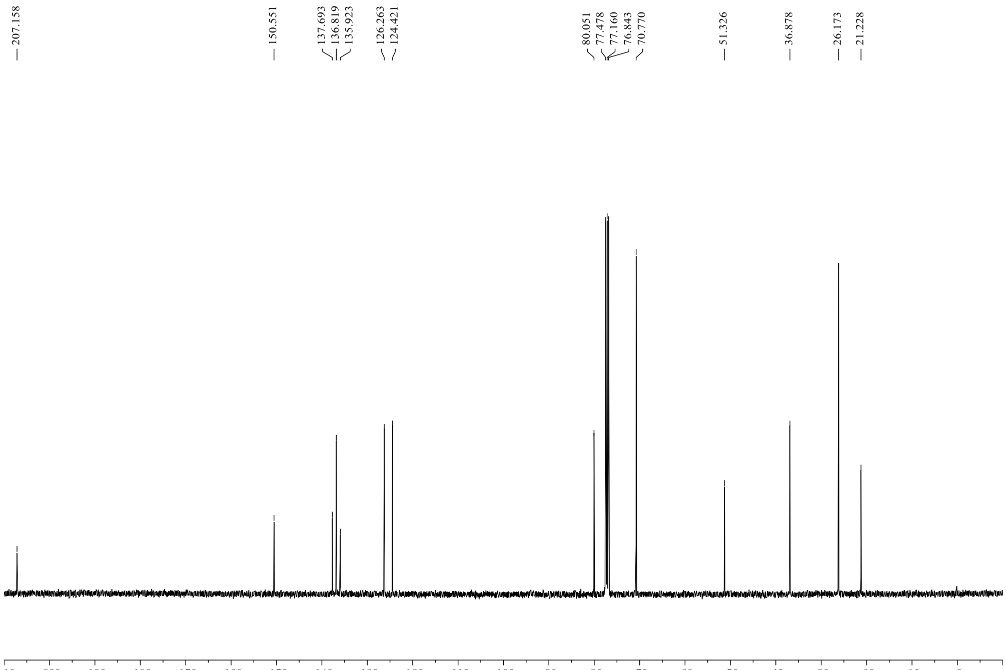


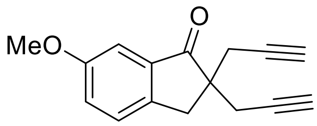
**1k**

According to above method A to get the product **1k** (1.38 g, 62%) as yellow solid.

**[1]H NMR** (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.45 - 7.36 (m, 2H), 3.26 (s, 2H), 2.61, 2.50 (ABd, *J* = 16.8, 2.8 Hz, 4H), 2.41 (s, 3H), 1.87 (t, *J* = 2.8 Hz, 2H); **[13]C NMR** (101 MHz, $CDCl_3$): δ 207.16, 150.55, 137.69, 136.82, 135.92, 126.26, 124.42, 80.05, 70.77, 51.33, 36.88, 26.17, 21.23; **HRMS** (ESI) m/z calculated for $C_{16}H_{15}O$ $[M+H]^+$: 223.1123, found: 223.1125.



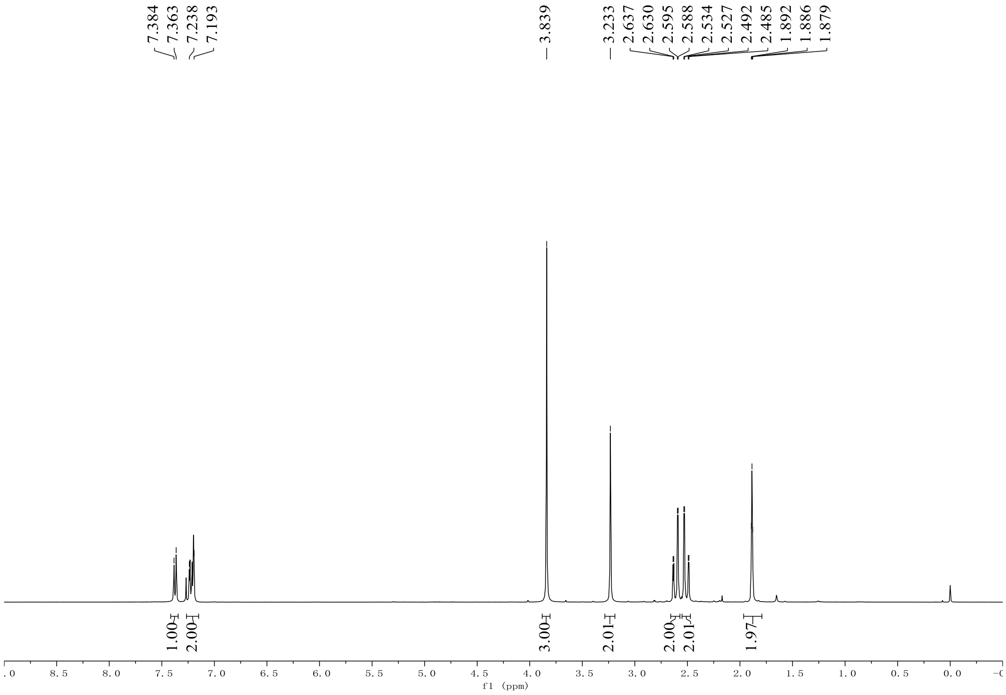



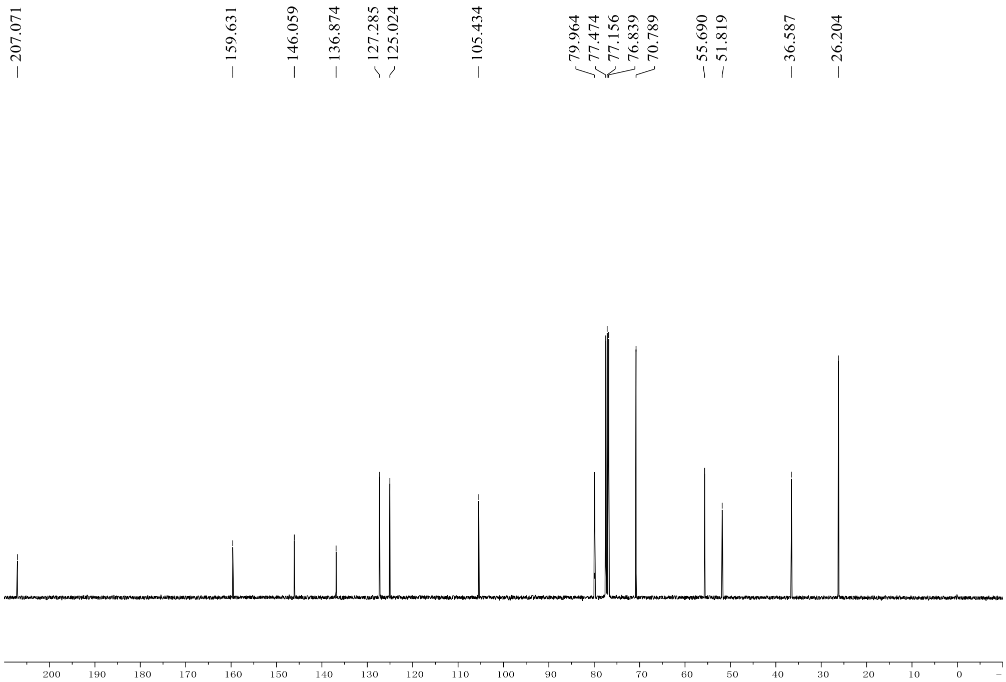


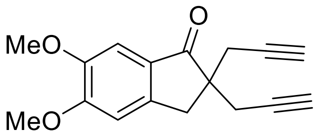
**1l**

According to above method A to get the product **1l** (1.67 g, 70%) as yellow solid.

**[1]H NMR** (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.4 Hz, 1H), 7.24 - 7.19 (m, 2H), 3.84 (s, 3H), 3.23 (s, 2H), 2.61, 2.51 (ABd, *J* = 16.8, 2.8 Hz, 4H), 1.89 (t, *J* = 2.4 Hz, 2H); **[13]C NMR** (101 MHz, $CDCl_3$): δ 207.07, 159.63, 146.06, 136.87, 127.28, 125.02, 105.43, 79.96, 70.79, 55.69, 51.82, 36.59, 26.20; **HRMS** (ESI) m/z calculated for $C_{16}H_{15}O_2$ $[M+H]^+$: 239.1072, found: 239.1071.



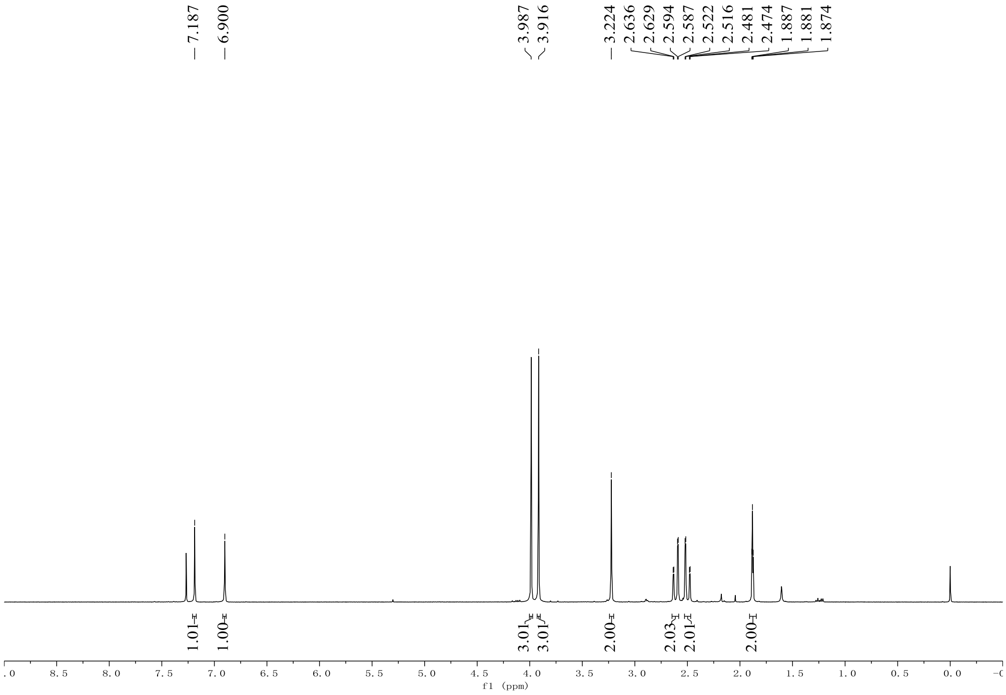


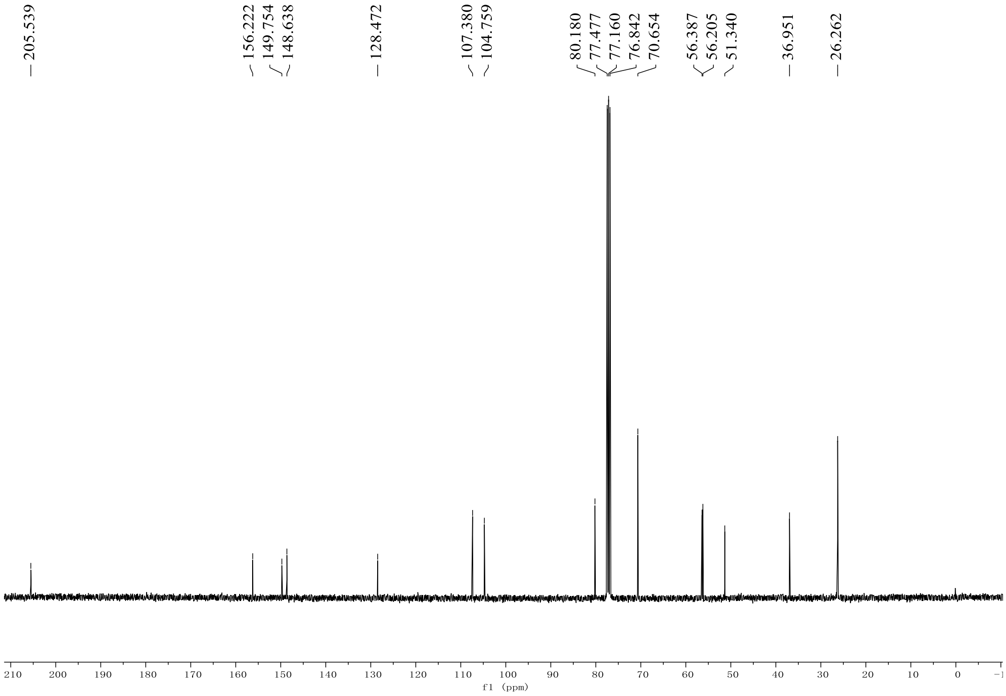


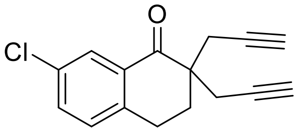
**1m**

According to above method A to get the product **1m** (0.58 g, 44%) as yellow solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.19 (s, 1H), 6.90 (s, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 3.22 (s, 2H), 2.61, 2.50 (ABd, $J$ = 16.8, 2.8 Hz, 4H), 1.88 (t, $J$ = 2.8 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 205.54, 156.22, 149.75, 148.64, 128.47, 107.38, 104.76, 80.18, 70.65, 56.39, 56.20, 51.34, 36.95, 26.26; **HRMS** (ESI) m/z calculated for $C_{17}H_{17}O_3$ $[M+H]^+$: 269.1178, found: 269.1178.



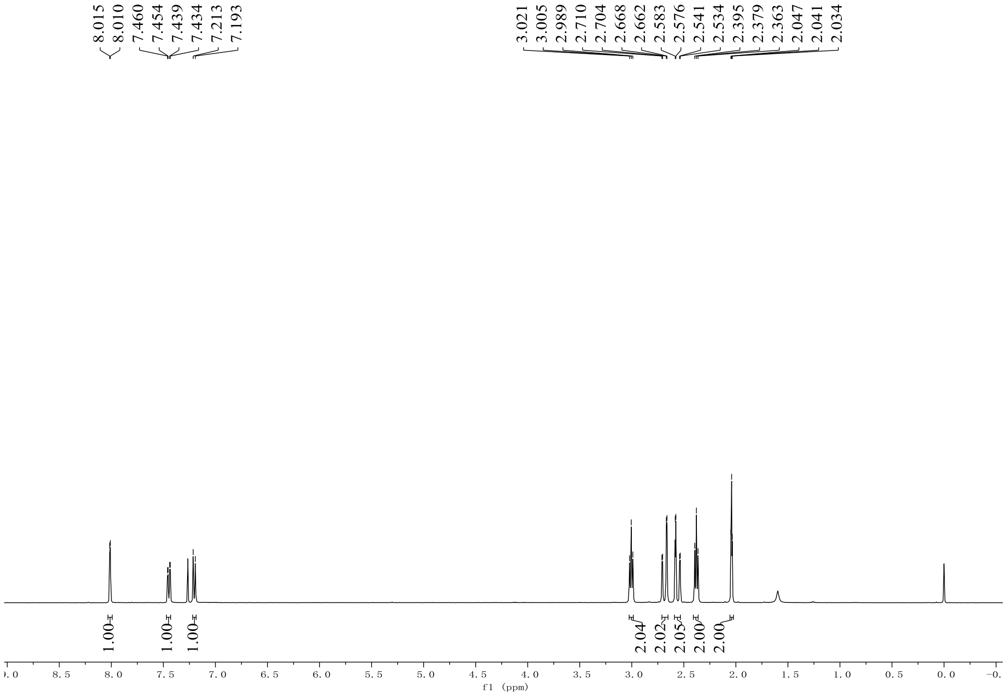


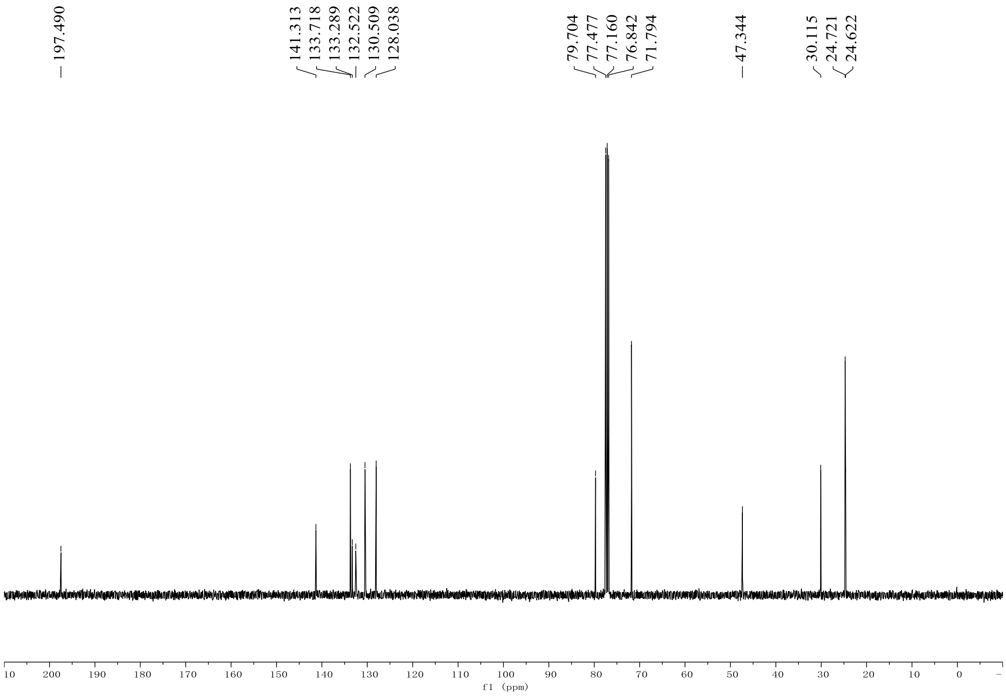


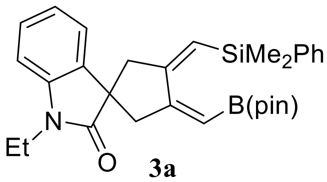

**1o**

According to above method A to get the product **1o** (0.67 g, 47%) as yellow solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.0 Hz, 1H), 7.45 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 3.00 (t, *J* = 6.4 Hz, 2H), 2.68, 2.56 (ABd, *J* = 16.4, 2.4 Hz, 4H), 2.38 (t, *J* = 6.4 Hz, 2H), 2.04 (t, *J* = 2.4 Hz, 2H); **$^{13}$C NMR** (101 MHz, CDCl3): δ 197.49, 141.31, 133.72, 133.29, 132.52, 130.51, 128.04, 79.70, 71.79, 47.34, 30.12, 24.72, 24.62; **HRMS** (ESI) m/z calculated for $C_{16}H_{14}OCl$ $[M+H]^+$: 257.0733, found: 257.0735.



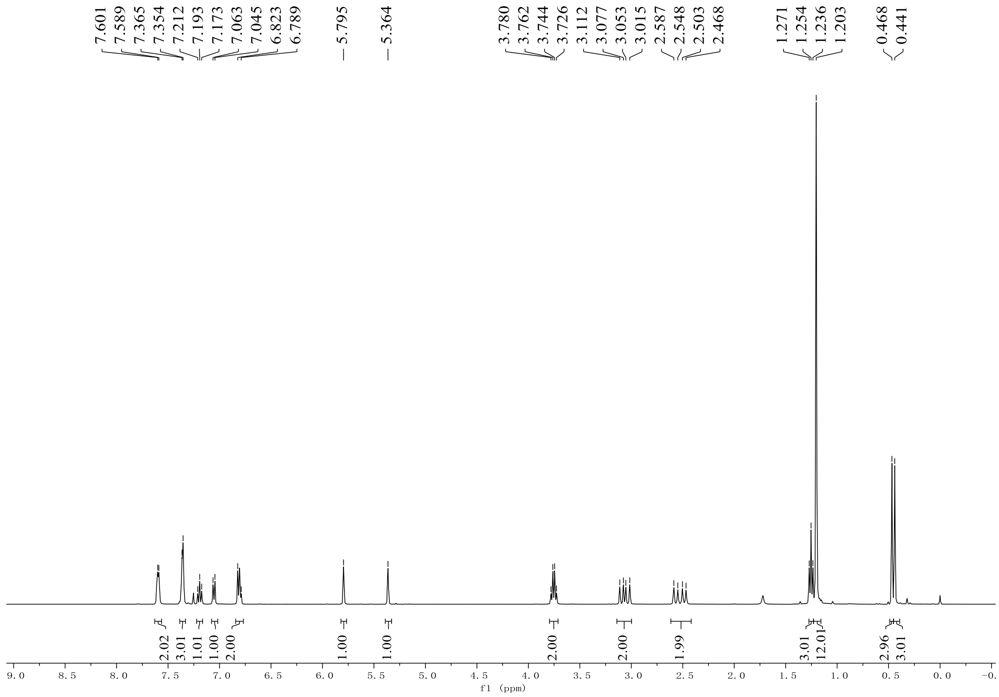



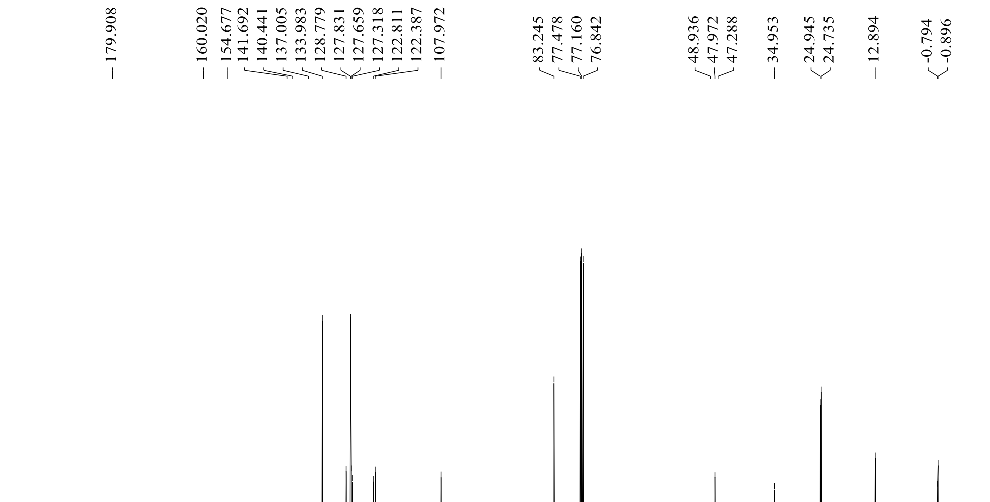


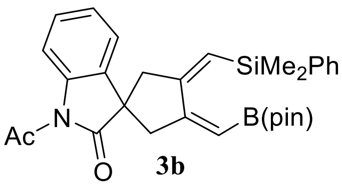

**3a**

According to above procedure A to get the product **3a** (89.9 mg, 90%) as yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.59 (m, 2H), 7.36 – 7.35 (m, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.82 – 6.79 (m, 2H), 5.80 (s, 1H), 5.36 (s, 1H), 3.75 (q, *J* = 7.2 Hz, 2H), 3.09 (d, *J* = 14.0 Hz, 1H), 3.03 (d, *J* = 15.2 Hz, 1H), 2.57 (d, *J* = 15.4 Hz, 1H), 2.48 (d, *J* = 14.0 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 12H), 0.46 (s, 3H), 0.44 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 179.91, 160.02, 154.68, 141.69, 140.44, 137.01, 133.98, 128.78, 127.83, 127.66, 127.32, 122.81, 122.39, 107.97, 83.25, 48.94, 47.97, 47.29, 34.95, 24.94, 24.74, 12.89, -0.79, -0.90; **HRMS** (ESI) m/z calculated for $C_{30}H_{39}BNO_3Si$ $[M+H]^+$: 500.2792, found: 500.2807; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 29.48 (s).

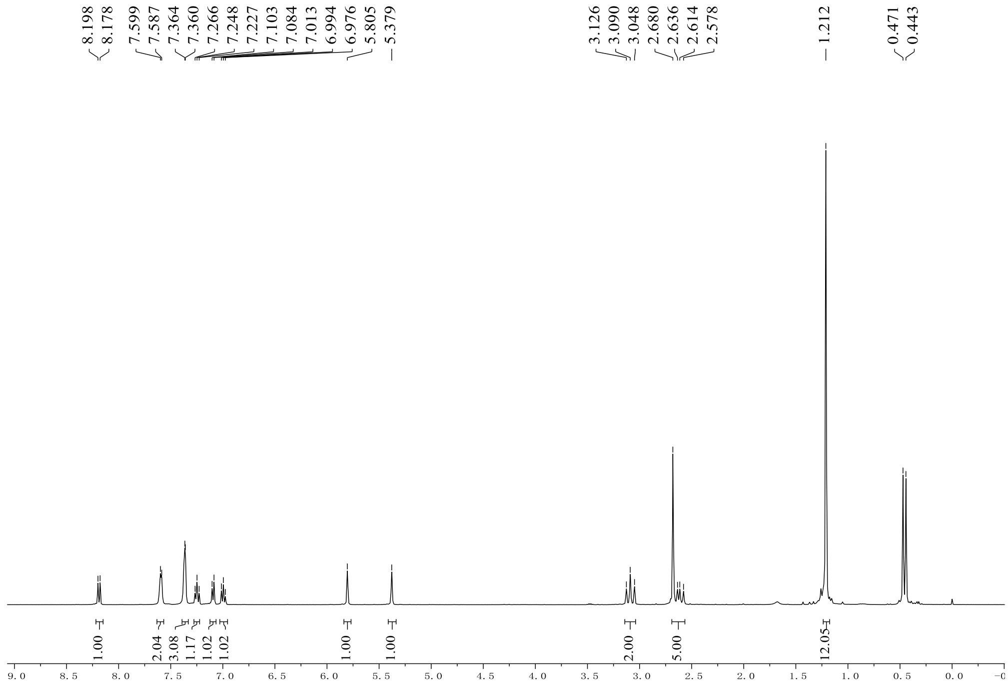


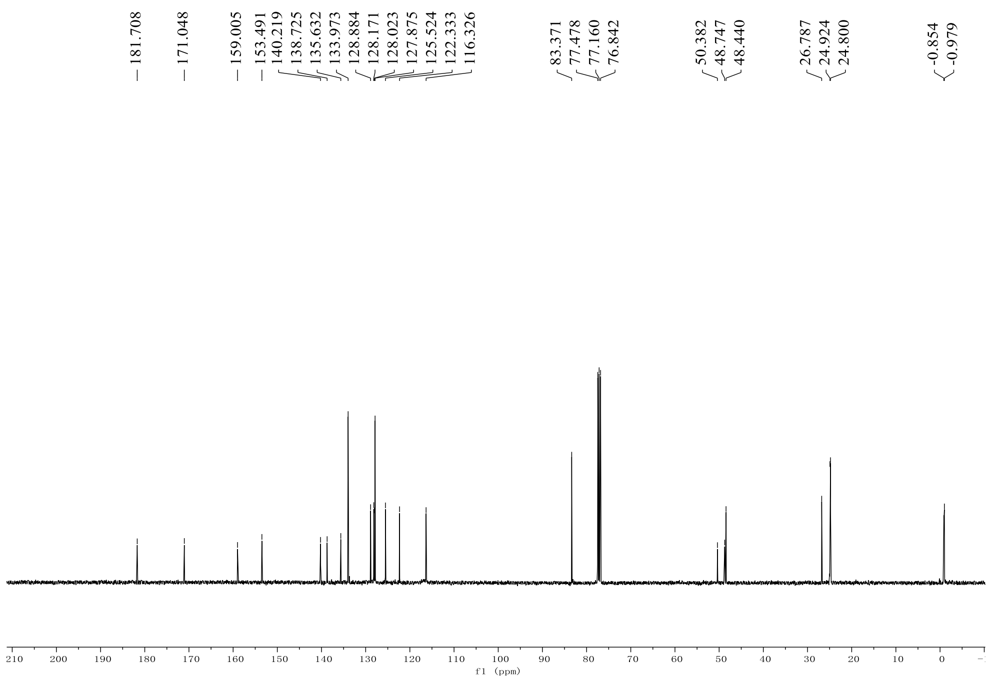



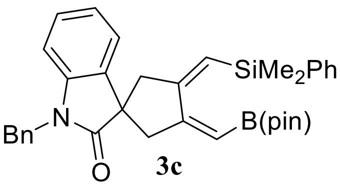



According to above procedure A to get the product **3b** (92.3 mg, 92%) as yellow solid.

**[1]H NMR** (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.58 (m, 2H), 7.36 - 7.36 (m, 3H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 5.80 (s, 1H), 5.38 (s, 1H), 3.11 (d, *J* = 14.4 Hz, 1H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.68 (s, 3H) 2.64 – 2.56 (m, 2H), 1.21 (s, 12H), 0.47 (s, 3H), 0.44 (s, 3H); **[13]C NMR** (101 MHz, $CDCl_3$): δ 181.71, 171.05, 159.00, 153.49, 140.22, 138.73, 135.63, 133.97, 128.88, 128.17, 128.02, 127.87, 125.52, 122.33, 116.33, 83.37, 50.38, 48.75, 48.44, 26.79, 24.92, 24.80, -0.85, -0.98; **HRMS** (ESI) m/z calculated for $C_{30}H_{37}BNO_4Si$ $[M+H]^+$: 514.2585, found: 514.2590; **[11]B NMR** (128.4 MHz, $CDCl_3$): δ 29.31 (s).



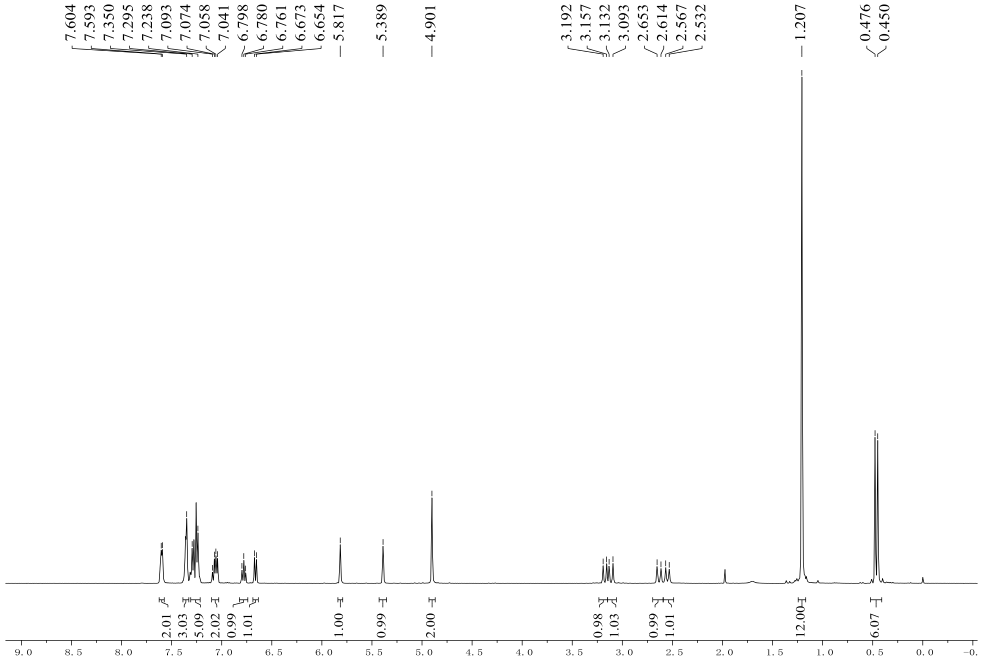



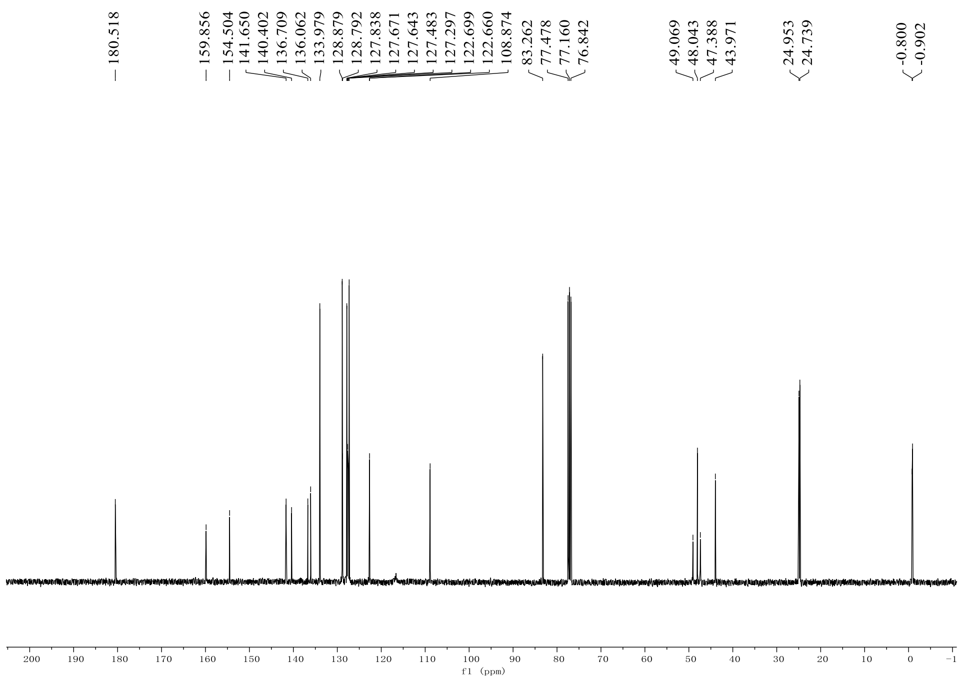


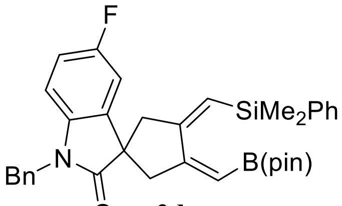
**3c**

According to above procedure A to get the product **3c** (103.3 mg, 92%) as pale yellow oil.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.59 (m, 2H), 7.36 - 7.35 (m, 3H), 7.29 - 7.24 (m, 5H), 7.09 - 7.04 (m, 2H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 5.80 (s, 1H), 5.38 (s, 1H), 4.90 (s, 2H), 3.17 (d, *J* = 14.0 Hz, 1H), 3.11 (d, *J* = 15.6 Hz, 1H), 2.63 (d, *J* = 15.6 Hz, 1H), 2.55 (d, *J* = 14.0 Hz, 1H), 1.21 (s, 12H), 0.48 (s, 3H), 0.45 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.52, 159.86, 154.50, 141.65, 140.40, 136.71, 136.06, 133.98, 128.88, 128.79, 127.84, 127.67, 127.64, 127.48, 127.30, 122.70, 122.66, 108.87, 83.26, 49.07, 48.04, 47.39, 43.97, 24.95, 24.74, -0.80, -0.90; **HRMS** (ESI) m/z calculated for $C_{35}H_{41}BNO_3Si$ $[M+H]^+$: 562.2944, found: 562.2947; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 29.33 (s).



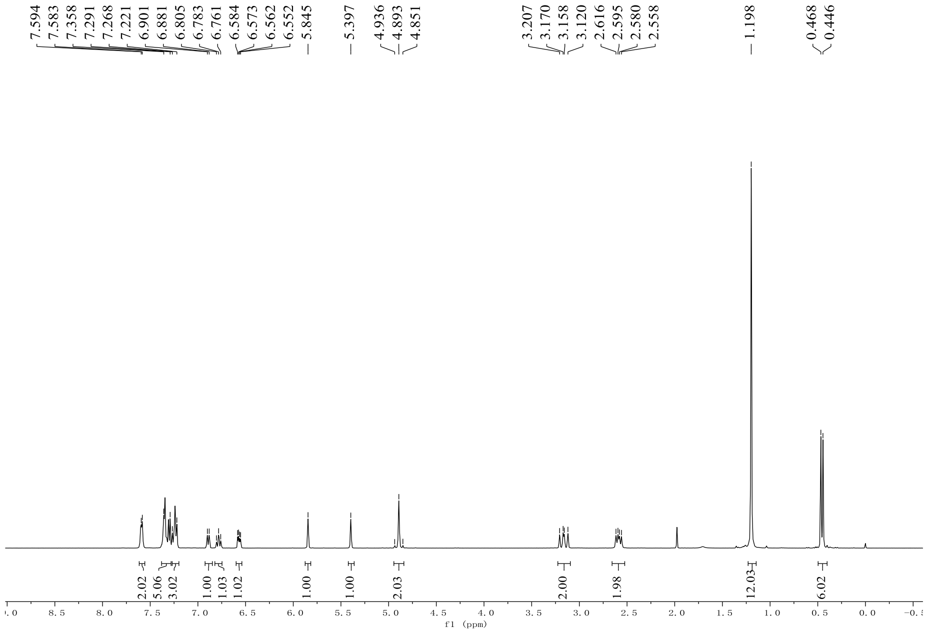



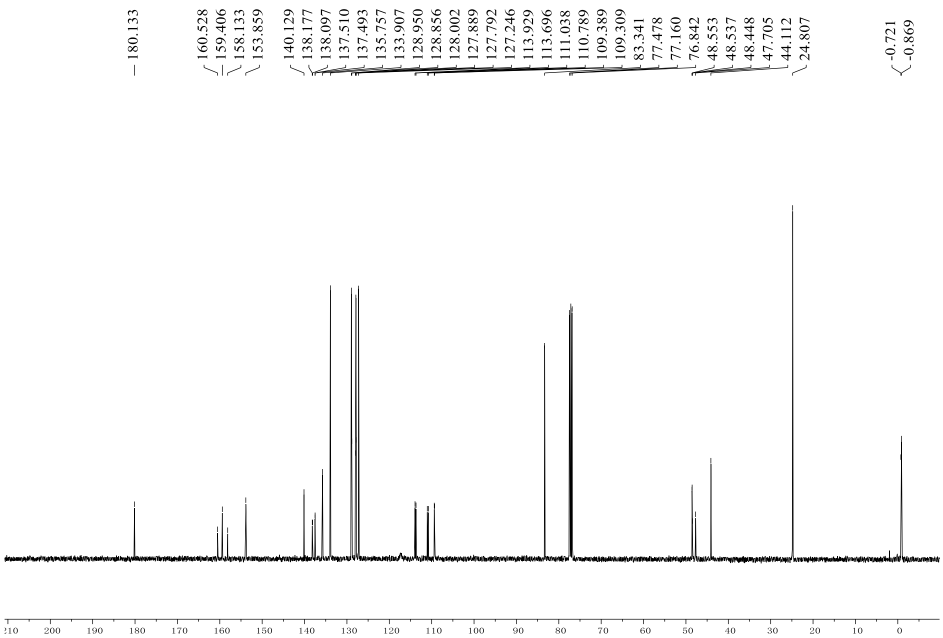


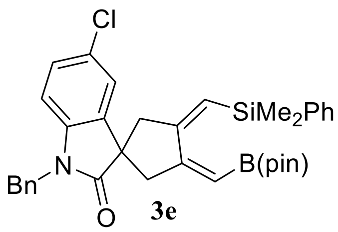
**3d**

According to above procedure A to get the product **3d** (104.2 mg, 90%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.59 – 7.58 (m, 2H), 7.36 - 7.29 (m, 5H), 7.27 - 7.22 (m, 3H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.78 (t, *J* = 8.9 Hz, 1H), 6.57 (dd, *J* = 8.5, 4.0 Hz, 1H), 5.85 (s, 1H), 5.40 (s, 1H), 4.91, 4.87 (AB, *J* = 16.8 Hz, 2H), 3.19 (d, *J* = 14.8 Hz, 1H), 3.14 (d, *J* = 15.2 Hz, 1H), 2.60 (d, *J* = 14.4 Hz, 1H), 2.58 (d, *J* = 14.8 Hz, 1H), 1.20 (s, 12H), 0.47 (s, 3H), 0.45 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 180.13, 159.41, 159.33 (d, *J* = 241.9 Hz), 153.86, 140.13, 138.14 (d, *J* = 8.1 Hz), 137.50 (d, *J* = 1.7 Hz), 135.76, 133.91, 128.95, 128.86, 128.00, 127.89, 127.79, 127.25, 113.81 (d, *J* = 23.5 Hz), 110.91 (d, *J* = 25.1 Hz), 109.35 (d, *J* = 8.1 Hz), 83.34, 48.54 (d, *J* = 1.6 Hz), 48.45, 47.71, 44.11, 24.81, -0.72, -0.87; **HRMS** (ESI) m/z calculated for $C_{35}H_{40}BFNO_3Si$ $[M+H]^+$: 580.2855, found: 580.2851; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 27.92 (s); **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -120.06 Hz (s, 1F).



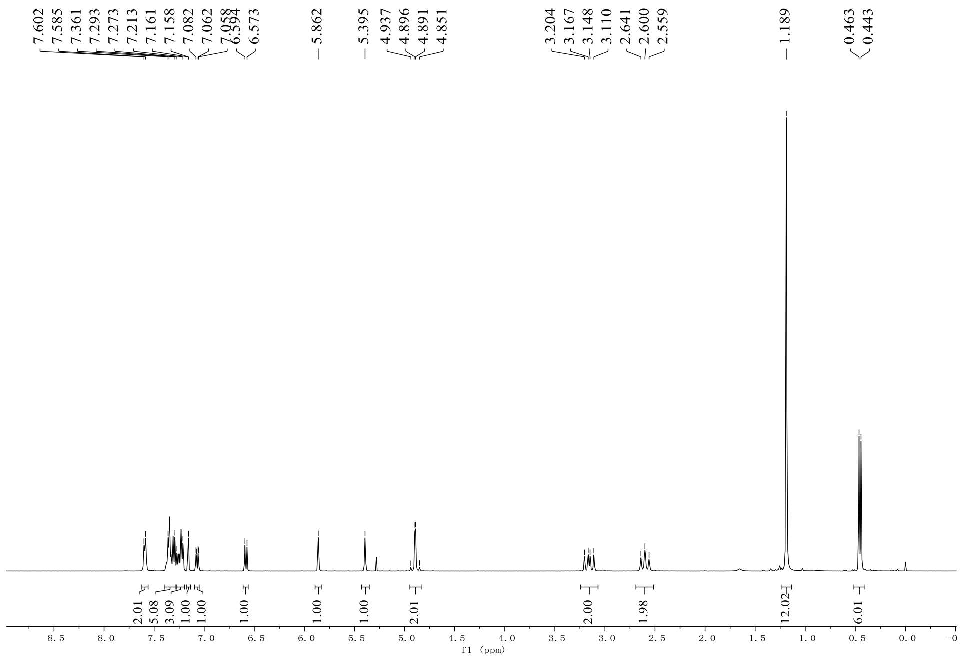



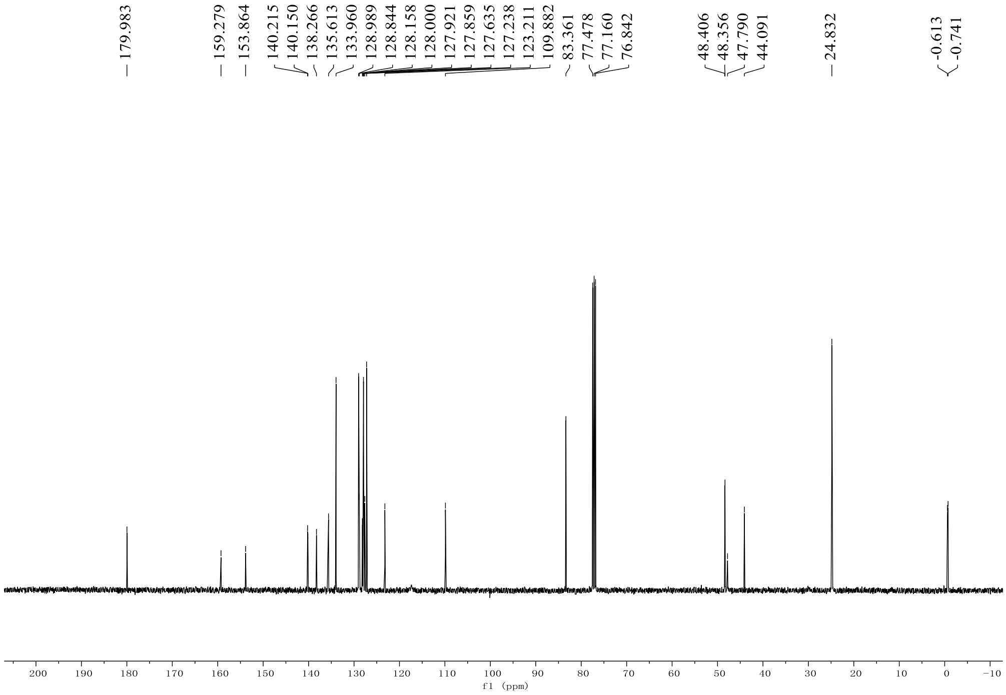


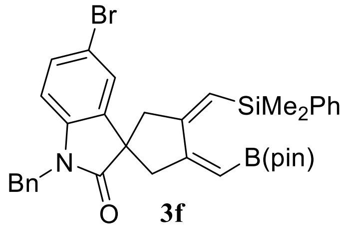

**3e**

According to above procedure A to get the product **3e** (111.9 mg, 94%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.59 (m, 2H), 7.36 - 7.29 (m, 5H), 7.27 - 7.21 (m, 3H), 7.16 (d, *J* = 1.1 Hz, 1H), 7.07 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.58 (d, *J* = 8.3 Hz, 1H), 5.86 (s, 1H), 5.39 (s, 1H), 4.90, 4.88 (AB, *J* = 16.4 Hz, 2H), 3.19 (d, *J* = 14.8 Hz, 1H), 3.13 (d, *J* = 15.2 Hz, 1H), 2.62 (d, *J* = 16.0 Hz, 1H), 2.58 (d, *J* = 16.0 Hz, 1H), 1.19 (s, 12H), 0.46 (s, 3H), 0.44 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 179.98, 159.28, 153.86, 140.21, 140.15, 138.27, 135.61, 133.96, 128.99, 128.84, 128.16, 128.00, 127.92, 127.86, 127.64, 127.24, 123.21, 109.88, 83.36, 48.40, 48.36, 47.79, 44.09, 24.83, -0.61, -0.74; **HRMS** (ESI) m/z calculated for $C_{35}H_{40}BClNO_3Si$ $[M+H]^+$: 596.2559, found: 596.2558; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 30.01 (s).



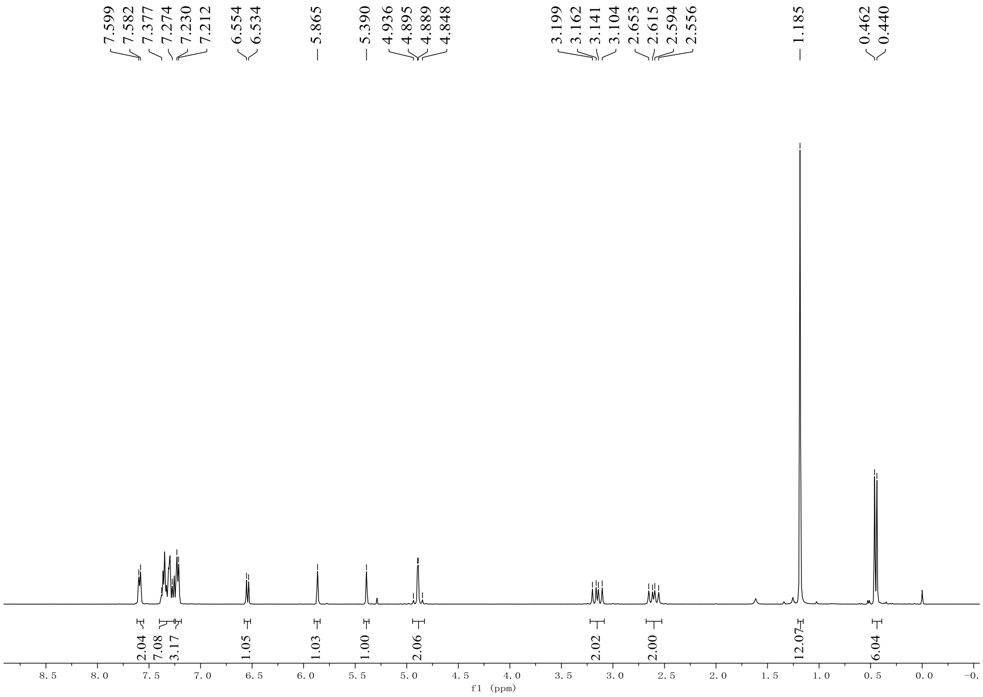



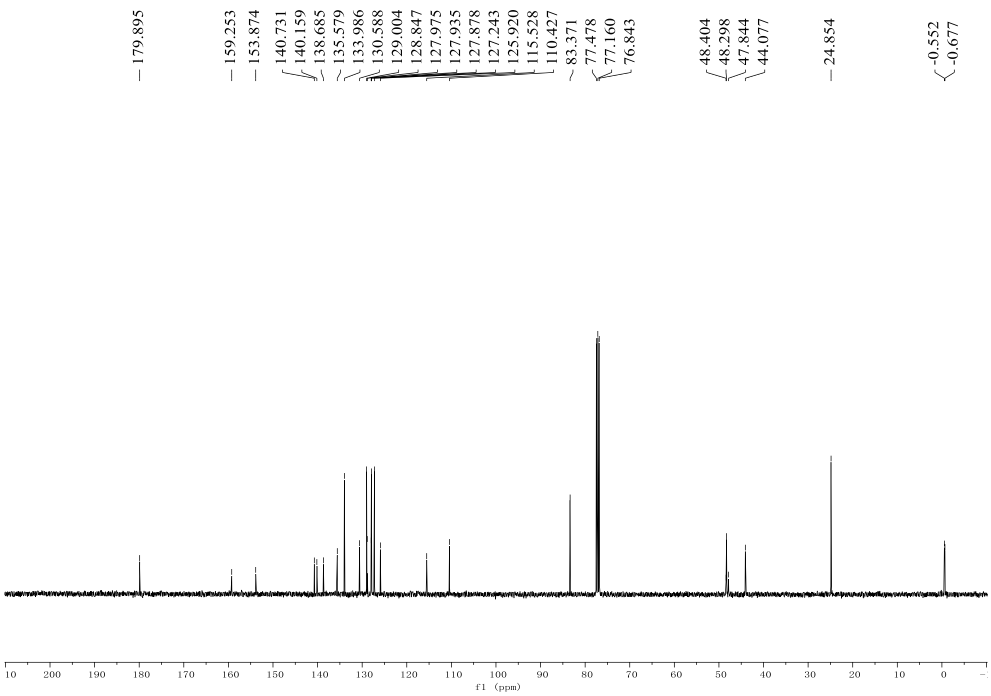


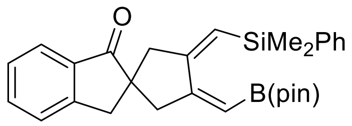
**3f**

According to above procedure A to get the product **3f** (115.0 mg, 90%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.58 (m, 2H), 7.38 - 7.27 (m, 7H), 7.23 - 7.21 (m, 3H), 6.54 (d, *J* = 8.3 Hz, 1H), 5.87 (s, 1H), 5.39 (s, 1H), 4.92, 4.90 (AB, *J* = 16.4 Hz, 2H), 3.18 (d, *J* = 14.8 Hz, 1H), 3.12 (d, *J* = 14.8 Hz, 1H), 2.63 (d, *J* = 15.2 Hz, 1H), 2.57 (d, *J* = 15.2 Hz, 1H), 1.19 (s, 12H), 0.46 (s, 3H), 0.44 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 179.89, 159.25, 153.87, 140.73, 140.16, 138.69, 135.58, 133.99, 130.59, 129.00, 128.85, 127.98, 127.93, 127.88, 127.24, 125.92, 115.53, 110.43, 83.37, 48.40, 48.30, 47.84, 44.08, 24.85, -0.55, -0.68; **HRMS** (ESI) m/z calculated for $C_{35}H_{40}BBrNO_3Si$ $[M+H]^+$: 640.2054, found: 640.2060; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 28.79 (s).



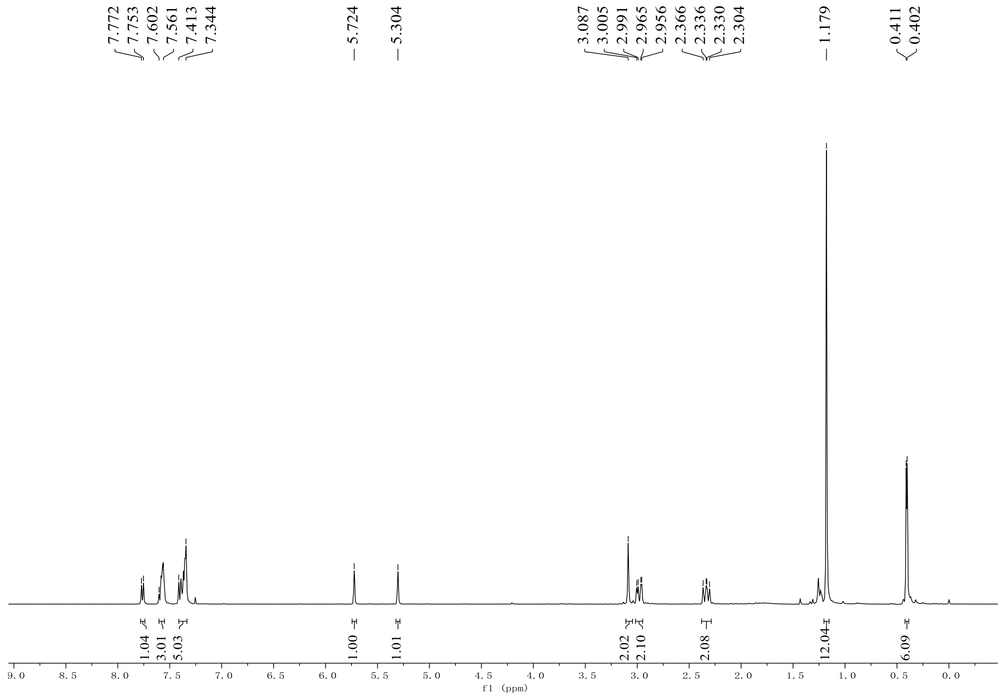



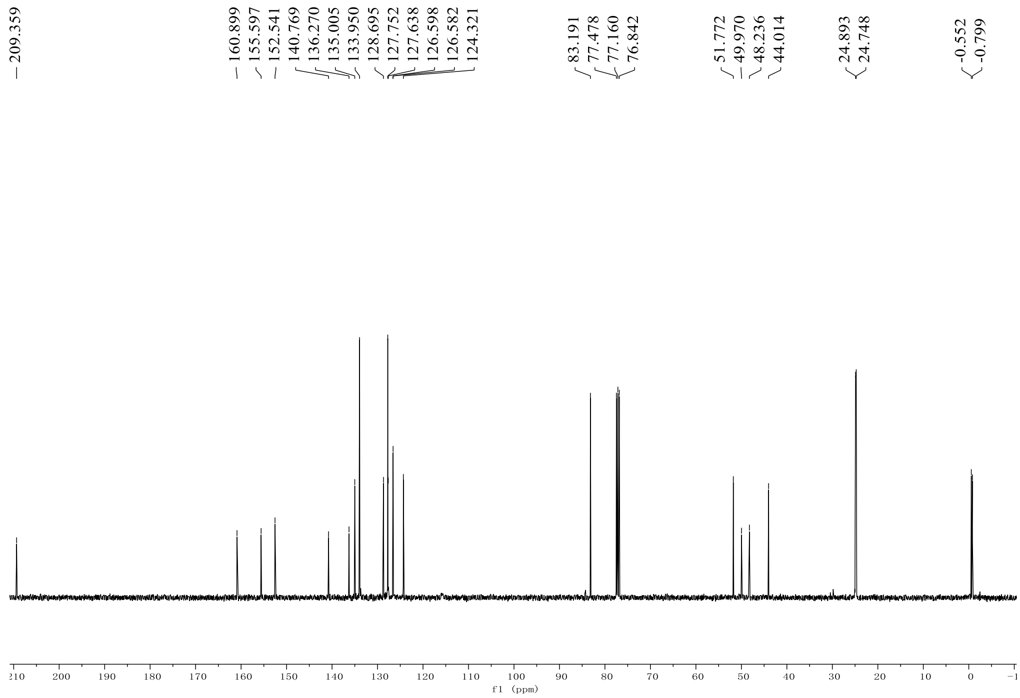


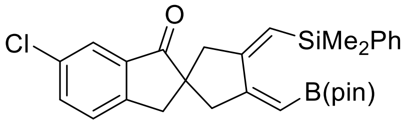

**3g**

According to above procedure A to get the product **3g** (84.8 mg, 90%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.56 (m, 3H), 7.41 - 7.34 (m, 5H), 5.72 (s, 1H), 5.30 (s, 1H), 3.09 (s, 2H), 2.98 (d, *J* = 16.0 Hz, 1H), 2.97 (d, *J* = 14.0 Hz, 1H), 2.35 (d, *J* = 14.0 Hz, 1H), 2.32 (d, *J* = 12.8 Hz, 1H), 1.18 (s, 12H), 0.41 (s, 3H), 0.40 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 209.36, 160.90, 155.60, 152.54, 140.77, 136.27, 135.01, 133.95, 128.69, 127.75, 127.64, 126.60, 126.58, 124.32, 83.19, 51.77, 49.97, 48.24, 44.01, 24.89, 24.75, -0.55, -0.80; **HRMS** (ESI) m/z calculated for $C_{29}H_{36}BO_3Si$ $[M+H]^+$: 471.2527, found: 471.2529; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 28.61 (s).



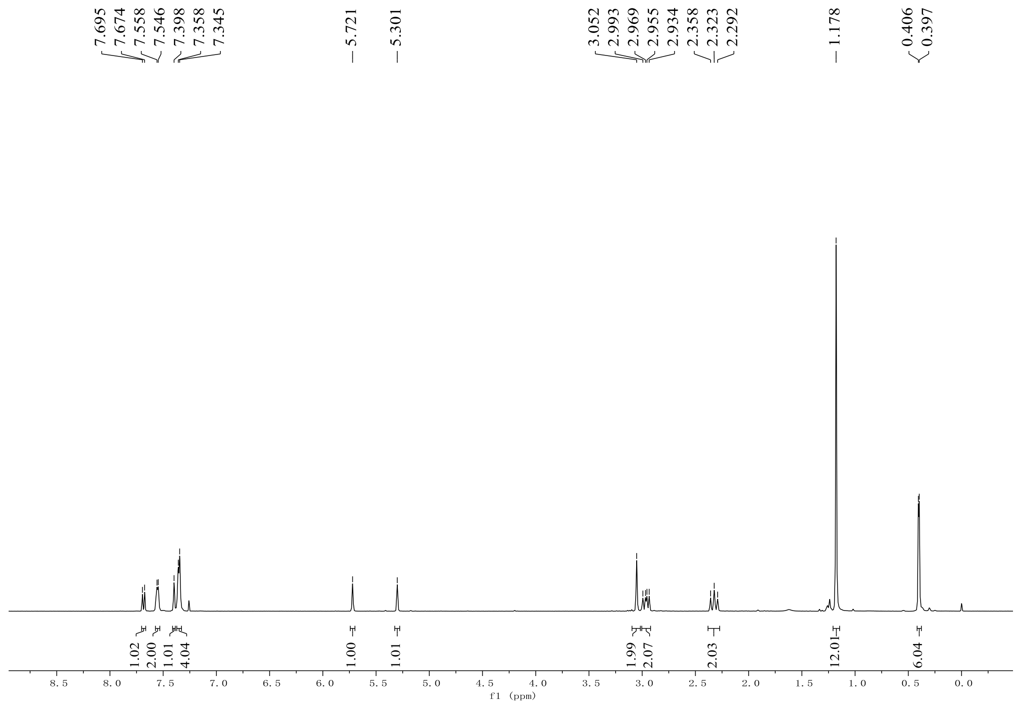



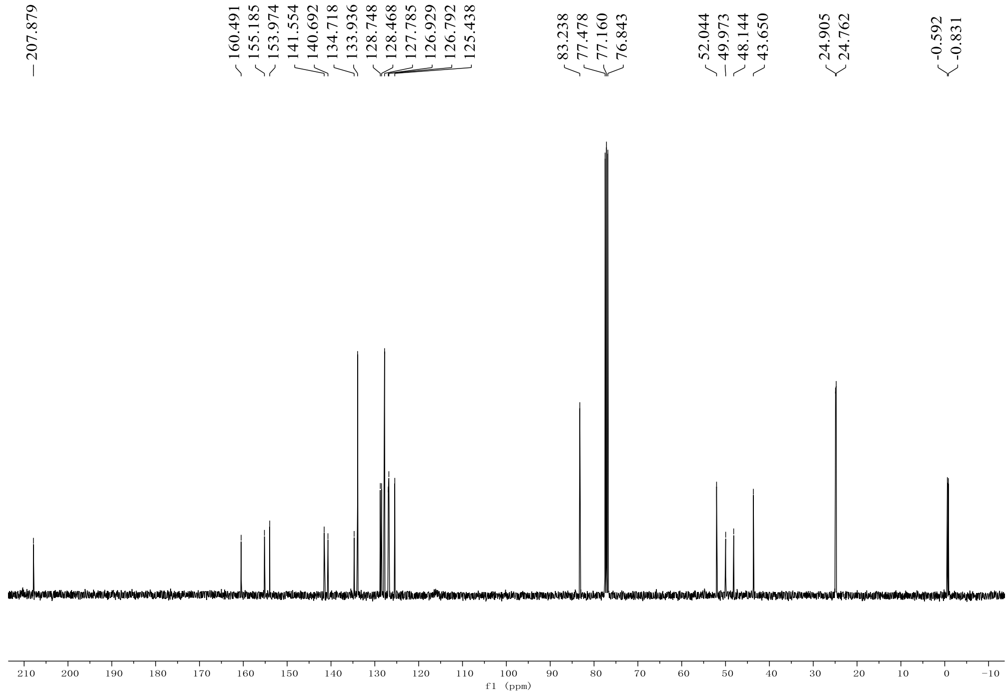


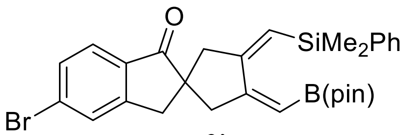
**3h**

According to above procedure A to get the product **3h** (91.8 mg, 91%) as yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.55 (m, 2H), 7.40 (s, 1H), 7.36 – 7.34 (m, 4H), 5.72 (s, 1H), 5.30 (s, 1H), 3.05 (s, 2H), 2.97 (d, *J* = 15.2 Hz, 1H), 2.95 (d, *J* = 14.0 Hz, 1H), 2.34 (d, *J* = 15.2 Hz, 1H), 2.30 (d, *J* = 12.4 Hz, 1H), 1.18 (s, 12H), 0.41 (s, 3H), 0.40 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 207.88, 160.49, 155.18, 153.97, 141.55, 140.69, 134.72, 133.94, 128.75, 128.47, 127.78, 126.93, 126.79, 125.44, 83.24, 52.04, 49.97, 48.14, 43.65, 24.90, 24.76, -0.59, -0.83; **HRMS** (ESI) m/z calculated for $C_{29}H_{35}BClO_3Si$ $[M+H]^+$: 505.2137, found: 505.2147; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 28.26 (s).



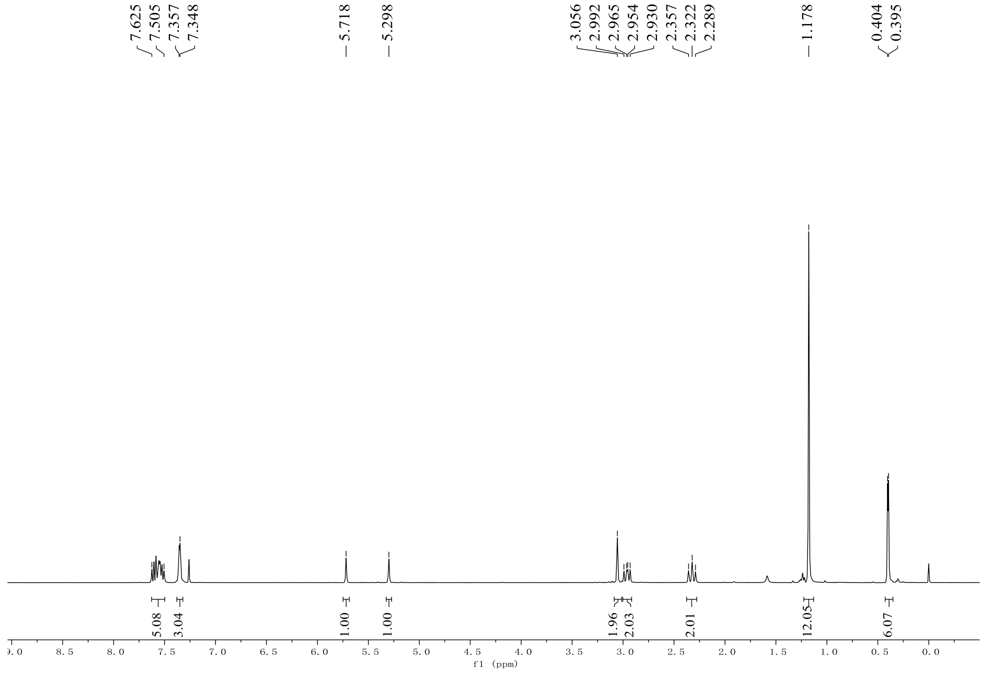


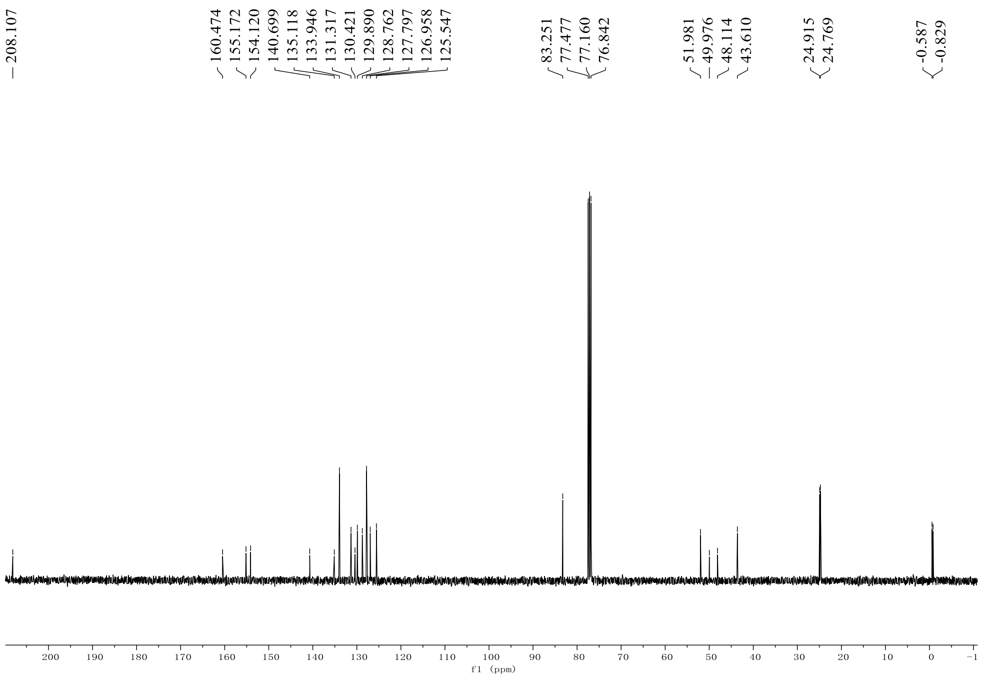


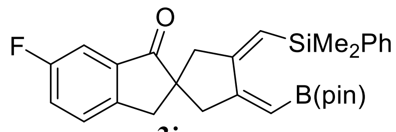
**3i**

According to above procedure A to get the product **3i** (54.8 mg, 50%) as pale yellow oil**.**

[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.62 – 7.50 (m, 5H), 7.36 – 7.35 (m, 3H), 5.72 (s, 1H), 5.30 (s, 1H), 3.06 (s, 2H), 2.97 (d, *J* = 15.2 Hz, 1H), 2.95 (d, *J* = 14.0 Hz, 1H), 2.33 (d, *J* = 14.0 Hz, 1H), 2.30 (d, *J* = 13.2 Hz, 1H), 1.18 (s, 12H), 0.41 (s, 3H), 0.40 (s, 3H); [13]**C NMR** (101 MHz, $CDCl_3$): δ 208.11, 160.47, 155.17, 154.12, 140.70, 135.12, 133.95, 131.32, 130.42, 129.89, 128.76, 127.80, 126.96, 125.55, 83.25, 51.98, 49.98, 48.11, 43.61, 24.92, 24.77, -0.59, -0.83; **HRMS** (ESI) m/z calculated for $C_{29}H_{35}BBrO_3Si$ [M+H]+: 549.1632, found: 549.1645; [11]**B NMR** (128.4 MHz, $CDCl_3$): δ 29.67 (s).



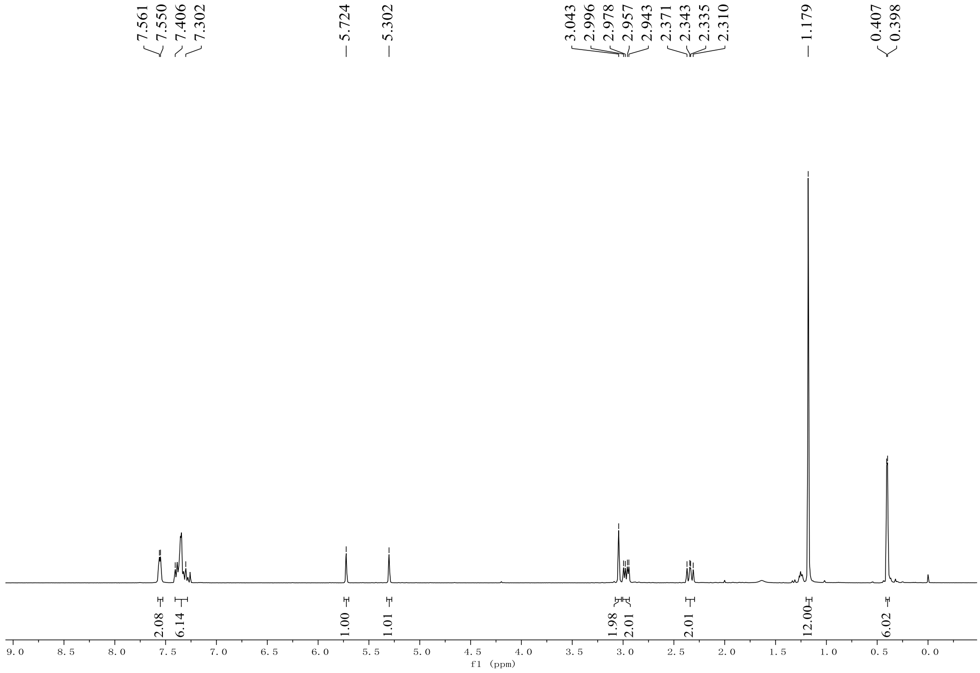


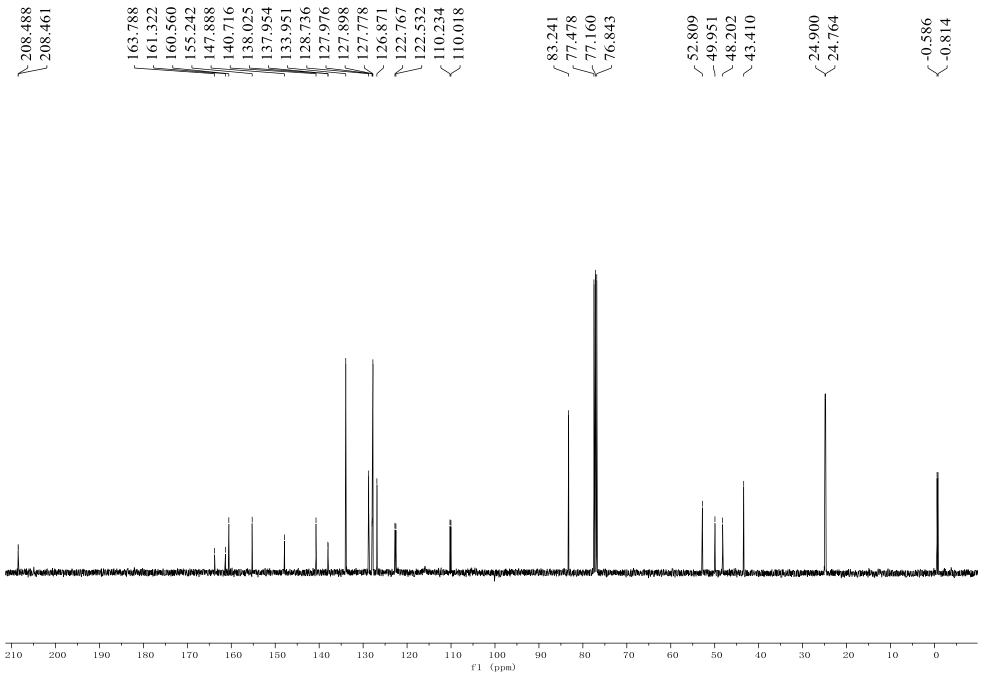


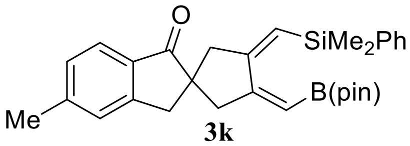

**3j**

According to above procedure A to get the product **3j** (86.9 mg, 89%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.55 (m, 2H), 7.41 - 7.30 (m, 6H), 5.72 (s, 1H), 5.30 (s, 1H), 3.04 (s, 2H), 2.98 (d, *J* = 15.6 Hz, 1H), 2.96 (d, *J* = 14.4 Hz, 1H), 2.35 (d, *J* = 14.4 Hz, 1H), 2.32 (d, *J* = 13.2 Hz, 1H), 1.18 (s, 12H), 0.41 (s, 3H), 0.40 (s, 3H); **$^{13}$C NMR** (101 MHz, CDCl3): δ 208.47 (d, *J* = 2.7 Hz), 162.55 (d, *J* = 249.1 Hz), 160.56, 155.24, 147.89, 140.72, 137.99 (d, *J* = 7.2 Hz), 133.95, 128.74, 127.94 (d, *J* = 7.9 Hz), 127.78, 126.87, 122.65 (d, *J* = 23.7 Hz), 110.13 (d, *J* = 21.8 Hz), 83.24, 52.81, 49.95, 48.20, 43.41, 24.90, 24.76, -0.59, -0.81; **HRMS** (ESI) m/z calculated for $C_{29}H_{35}FBO_3Si$ [M+H]+: 489.2433, found: 489.2443; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 29.65 (s); **$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -114.32 Hz (s, 1F).



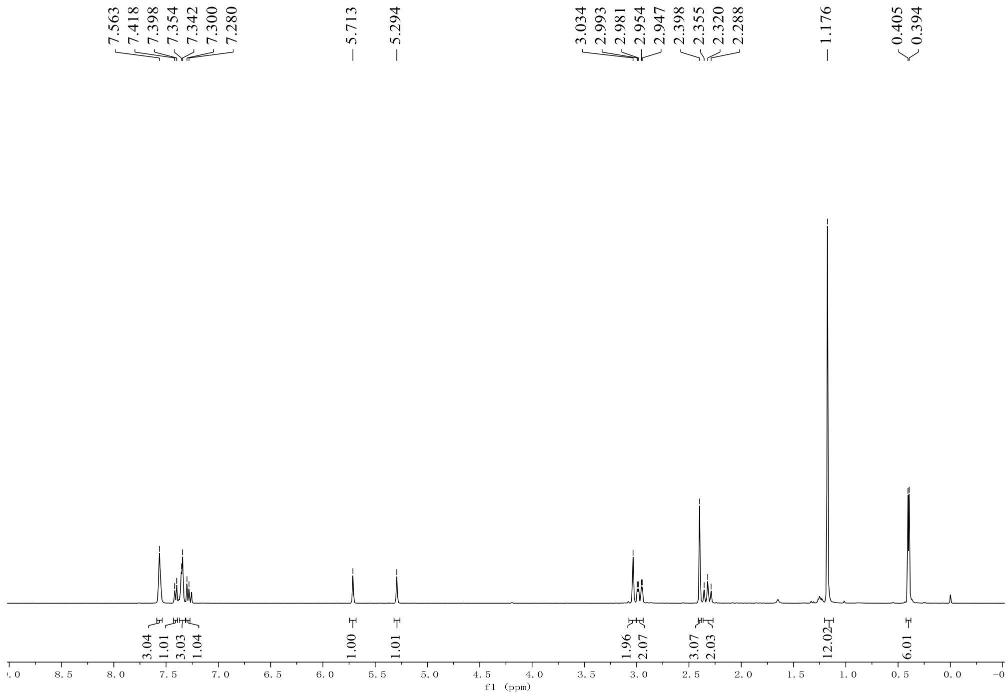



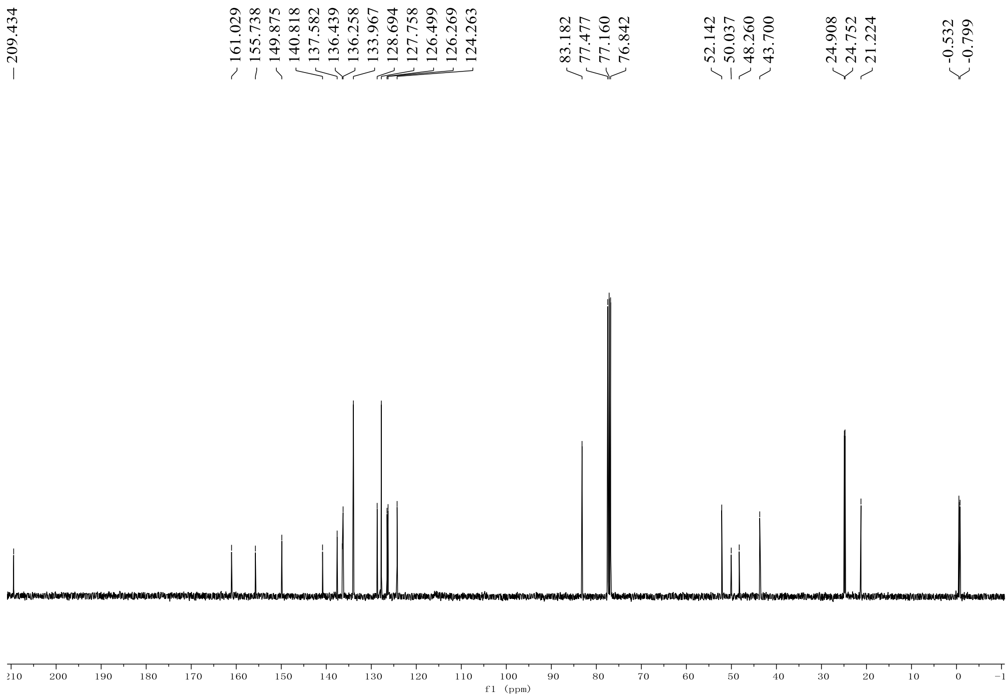


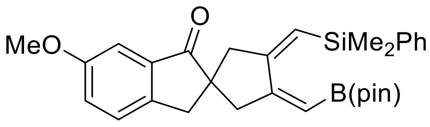
3k

According to above procedure A to get the product **3k** (93.0 mg, 96%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.57 – 7.55 (m, 3H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.35 - 7.34 (m, 3H), 7.29 (d, *J* = 7.7 Hz, 1H), 5.71 (s, 1H), 5.29 (s, 1H), 3.03 (s, 2H), 2.97 (d, *J* = 15.6 Hz, 1H), 2.96 (d, *J* = 14.0 Hz, 1H), 2.40 (s, 3H), 2.33 (d, *J* = 14.0 Hz, 1H), 2.30 (d, *J* = 12.8 Hz, 1H), 1.18 (s, 12H), 0.40 (s, 3H), 0.39 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 209.43, 161.03, 155.74, 149.87, 140.82, 137.58, 136.44, 136.26, 133.97, 128.69, 127.76, 126.50, 126.27, 124.26, 83.1, 52.14, 50.04, 48.26, 43.70, 24.91, 24.75, 21.22, -0.53, -0.80; **HRMS** (ESI) m/z calculated for $C_{30}H_{38}BO_3Si$ $[M+H]^+$: 485.2683, found: 485.2686; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 29.12 (s).



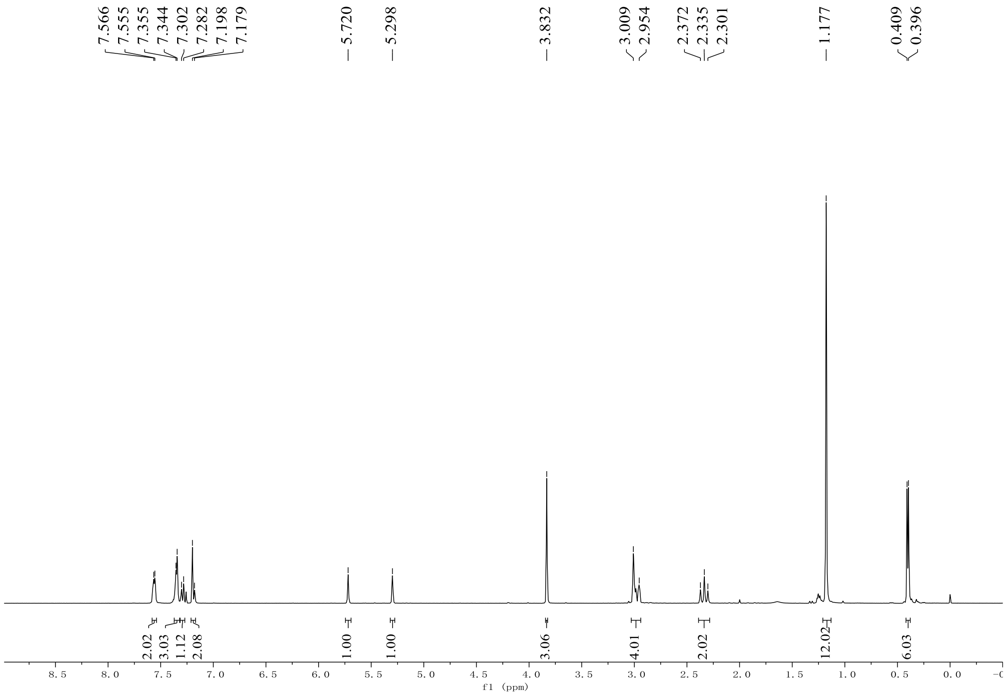



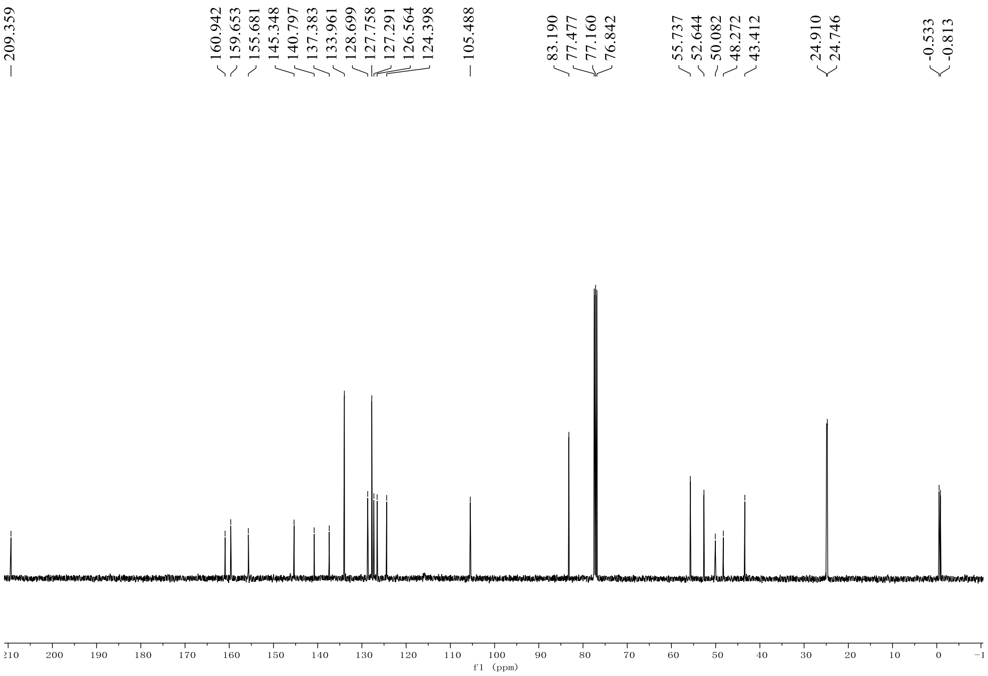


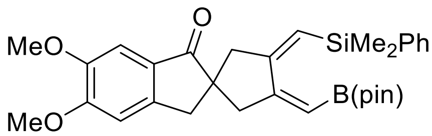
**3l**

According to above procedure A to get the product **3l** (87.0 mg, 87%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.57 – 7.55 (m, 2H), 7.35 - 7.34 (m, 3H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.20 – 7.18 (m, 2H), 5.72 (s, 1H), 5.30 (s, 1H), 3.83 (s, 3H), 3.01 – 2.95 (m, 4H), 2.35 (d, *J* = 14.8 Hz, 1H), 2.32 (d, *J* = 13.6 Hz, 1H), 1.18 (s, 12H), 0.41 (s, 3H), 0.40 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 209.36, 160.94, 159.65, 155.68, 145.35, 140.80, 137.38, 133.96, 128.70, 127.76, 127.29, 126.56, 124.40, 105.49, 83.19, 55.74, 52.64, 50.08, 48.27, 43.41, 24.91, 24.75, -0.53, -0.81; **HRMS** (ESI) m/z calculated for $C_{30}H_{38}BO_4Si$ $[M+H]^+$: 501.2632, found: 501.2636; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 29.66 (s);



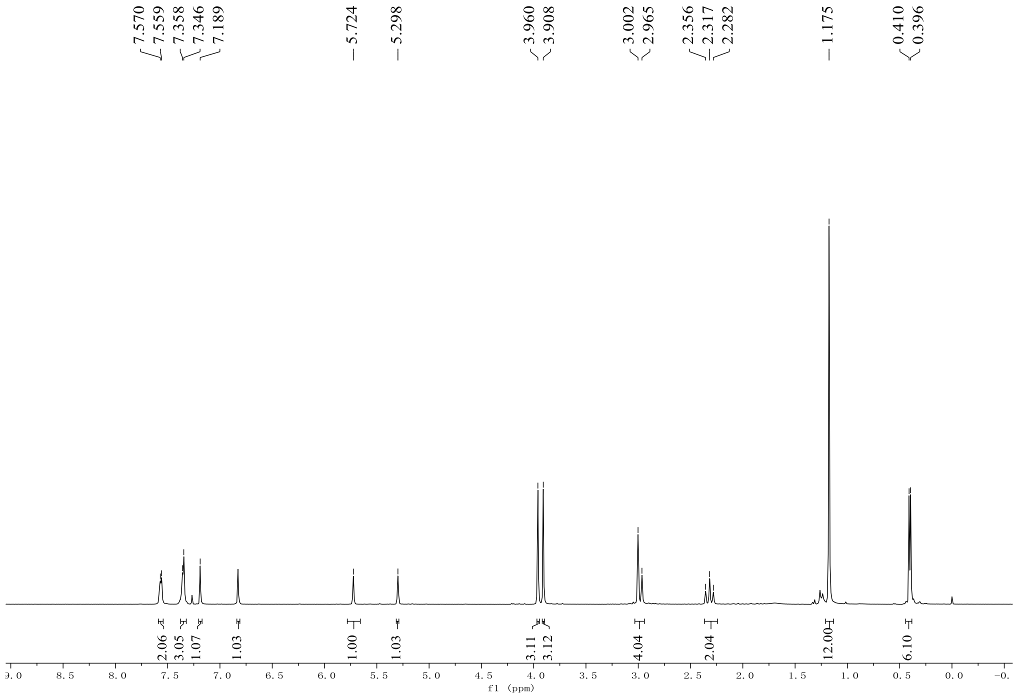


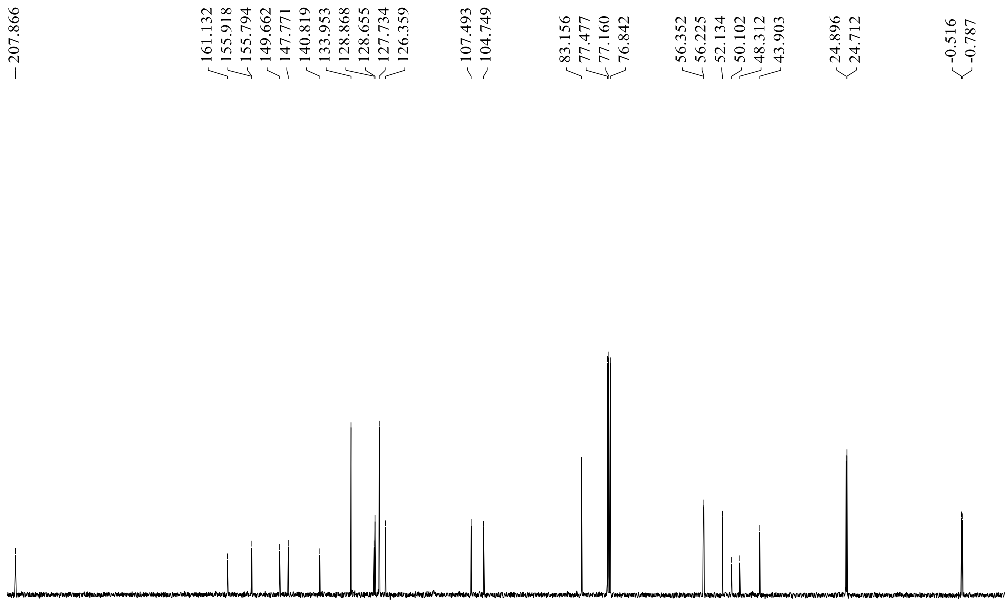


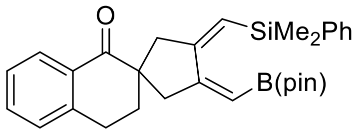

**3m**

According to above procedure A to get the product **3m** (96.5 mg, 91%) as pale yellow solid.

**[1]H NMR** (400 MHz, $CDCl_3$): δ 7.57 – 7.55 (m, 2H), 7.36 - 7.35 (m, 3H), 7.19 (s, 1H), 6.83 (s, 1H), 5.72 (s, 1H), 5.30 (s, 1H), 3.96 (s, 3H), 3.91 (s, 3H), 3.00 – 2.96 (m, 4H), 2.34 (d, *J* = 15.6 Hz, 1H), 2.30 (d, *J* = 14.0 Hz, 1H), 1.18 (s, 12H), 0.41 (s, 3H), 0.40 (s, 3H); **[13]C NMR** (101 MHz, CDCl3): δ 207.87, 161.13, 155.92, 155.79, 149.66, 147.77, 140.82, 133.95, 128.87, 128.66, 127.73, 126.36, 107.49, 104.75, 83.16, 56.35, 56.23, 52.13, 50.10, 48.31, 43.90, 24.90, 24.71, -0.52, -0.79; **HRMS** (ESI) m/z calculated for $C_{31}H_{40}BO_5Si$ [M+H]+: 531.2738, found: 531.2745; **[11]B NMR** (128.4 MHz, $CDCl_3$): δ 30.36 (s).



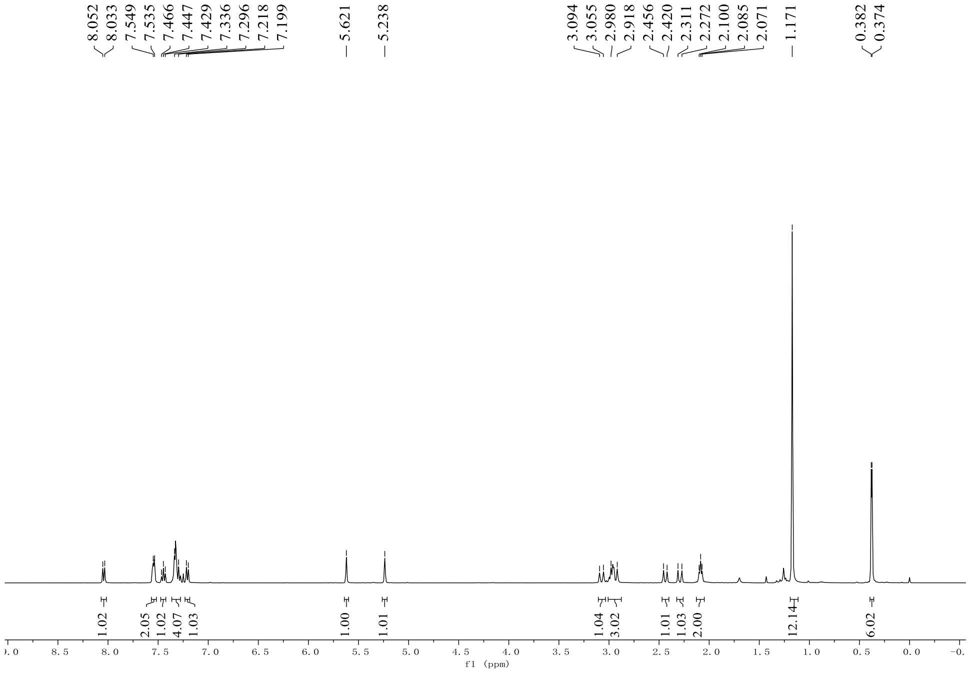



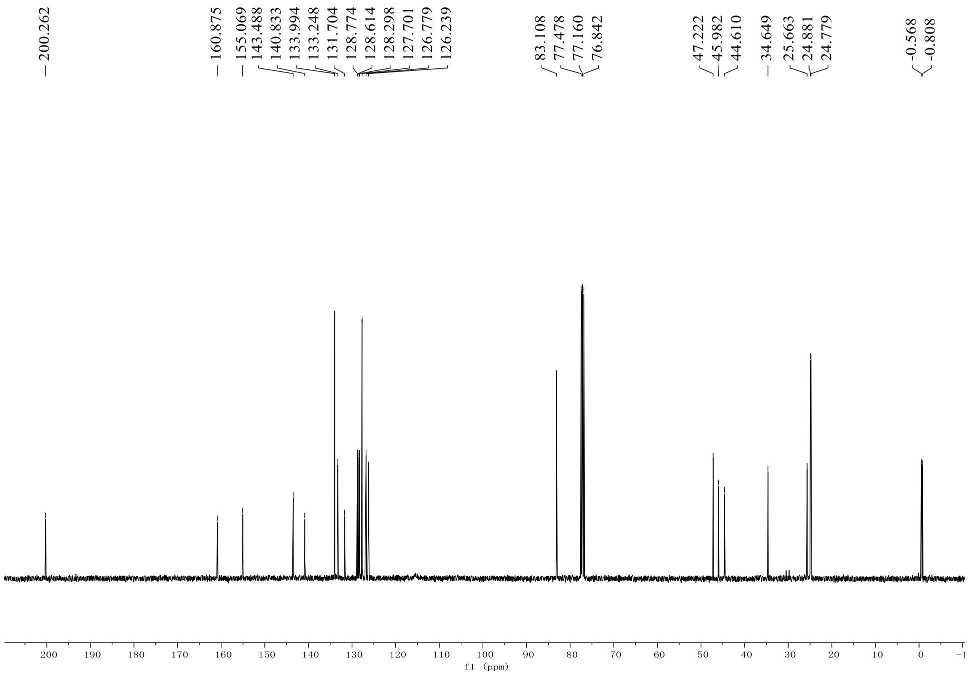


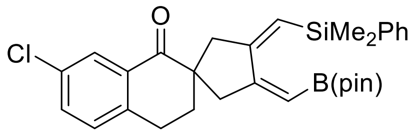

**3n**

According to above procedure A to get the product **3n** (79.4 mg, 82%) as pale yellow oil.

**[1]H NMR** (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.34 – 7.29 (m, 4H),7.21 (d, *J* = 7.6 Hz, 1H), 5.62 (s, 1H), 5.24 (s, 1H), 3.07 (d, *J* = 15.4 Hz, 1H), 2.98 – 2.92 (m, 3H), 2.44 (d, *J* = 14.2 Hz, 1H), 2.29 (d, *J* = 15.5 Hz, 1H), 2.09 (t, *J* = 5.9 Hz, 2H), 1.17 (s, 12H), 0.38 (s, 3H), 0.37 (s, 3H); **[13]C NMR** (101 MHz, $CDCl_3$): δ 200.26, 160.88, 155.07, 143.49, 140.83, 133.99, 133.25, 131.70, 128.77, 128.61, 128.30, 127.70, 126.78, 126.24, 83.11, 47.22, 45.98, 44.61, 34.65, 25.66, 24.88, 24.78, -0.57, -0.81; **HRMS** (ESI) m/z calculated for $C_{30}H_{38}BO_3Si$ $[M+H]^+$: 485.2683, found: 485.2690; **[11]B NMR** (128.4 MHz, $CDCl_3$): δ 28.72 (s).



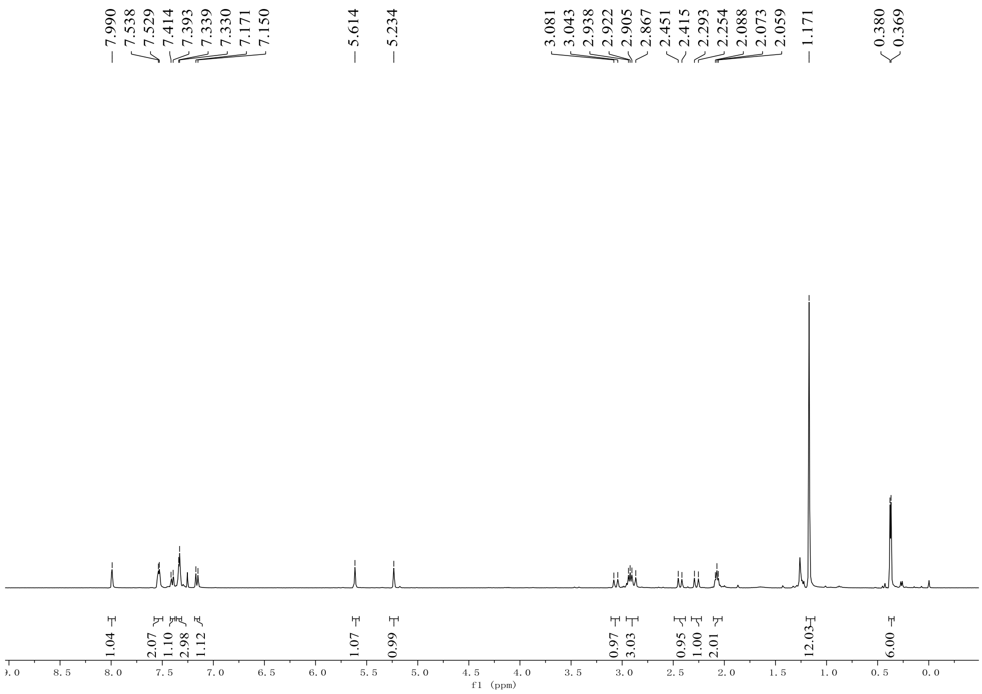



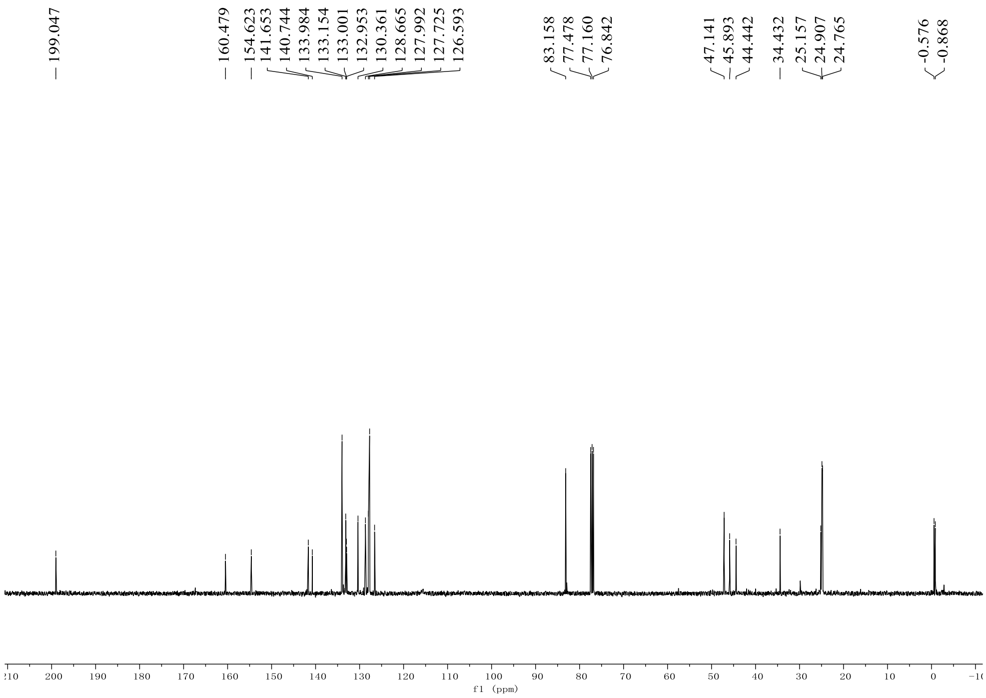


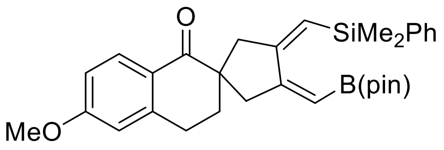

**3o**

According to above procedure A to get the product **3o** (86.0 mg, 83%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.54 – 7.53 (m, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.16 (d, *J* = 8.2 Hz, 1H), 5.62 (s, 1H), 5.24 (s, 1H), 3.06 (d, *J* = 15.4 Hz, 1H), 2.94 – 2.87 (m, 3H), 2.43 (d, *J* = 14.3 Hz, 1H), 2.27 (d, *J* = 15.4 Hz, 1H), 2.07 (t, *J* = 6.2 Hz, 2H), 1.17 (s, 12H), 0.38 (s, 3H), 0.37 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 199.05, 160.48, 154.62, 141.65, 140.74, 133.98, 133.15, 133.00, 132.95, 130.36, 128.67, 127.99, 127.72, 126.59, 83.16, 47.14, 45.89, 44.44, 34.43, 25.16, 24.91, 24.77, -0.58, -0.87; **HRMS** (ESI) m/z calculated for $C_{30}H_{37}BClO_3Si$ $[M+H]^+$: 519.2294, found: 519.2295; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 30.02 (s).



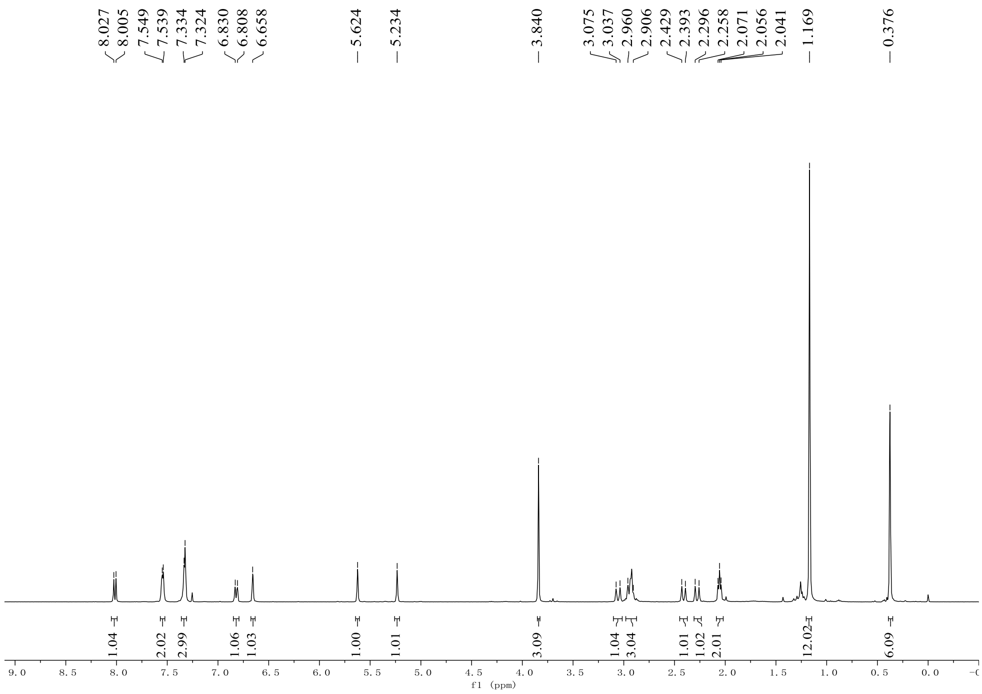



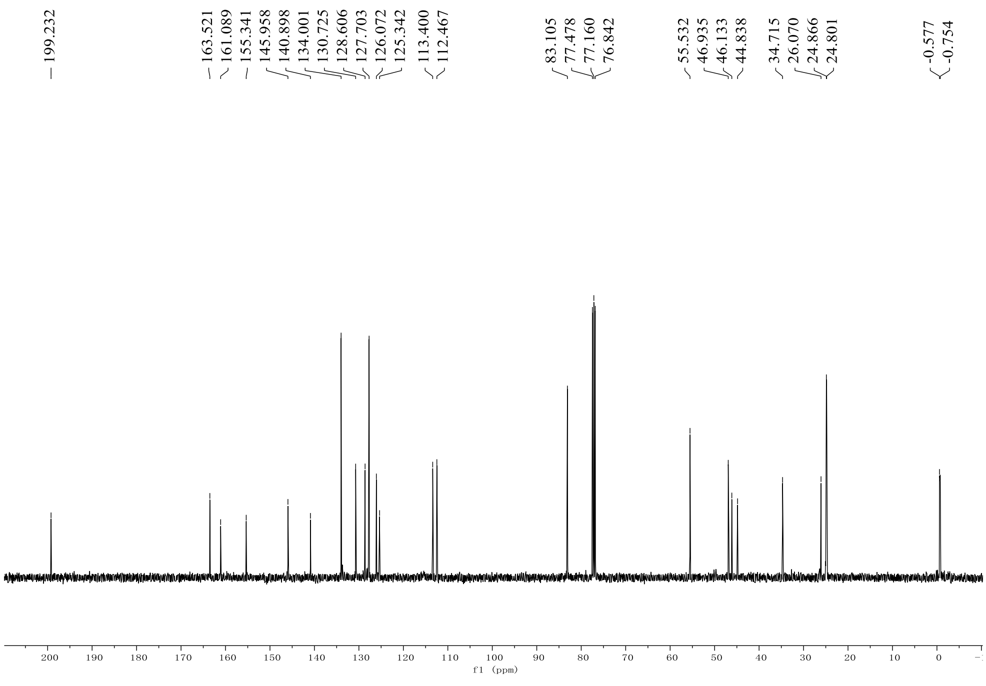


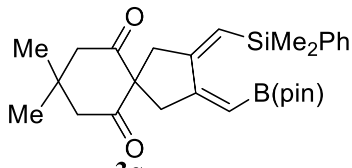

**3p**

According to above procedure A to get the product **3p** (91.5 mg, 89%) as yellow oil.

**$^{1}$H NMR** (400 MHz, CDCl$_3$): δ 8.02 (d, $J$ = 8.7 Hz, 1H), 7.55 – 7.54 (m, 2H), 7.34 – 7.32 (m, 3H), 6.82 (d, $J$ = 8.7 Hz, 1H), 6.66 (s, 1H), 5.62 (s, 1H), 5.23 (s, 1H), 3.84 (s, 3H), 3.05 (d, $J$ = 15.4 Hz, 1H), 2.96 – 2.91 (m, 3H), 2.41 (d, $J$ = 14.2 Hz, 1H), 2.28 (d, $J$ = 15.4 Hz, 1H), 2.06 (t, $J$ = 6.2 Hz, 2H), 1.17 (s, 12H), 0.38 (s, 6H); **$^{13}$C NMR** (101 MHz, CDCl$_3$): δ 199.23, 163.52, 161.09, 155.34, 145.96, 140.90, 134.00, 130.73, 128.61, 127.70, 126.07, 125.34, 113.40, 112.47, 83.10, 55.53, 46.93, 46.13, 44.84, 34.71, 26.07, 24.87, 24.80, -0.58, -0.75; **HRMS** (ESI) m/z calculated for $C_{31}H_{40}BO_4Si$ [M+H]$^+$: 515.2789, found: 515.2792; **$^{11}$B NMR** (128.4 MHz, CDCl$_3$): δ 29.83 (s).



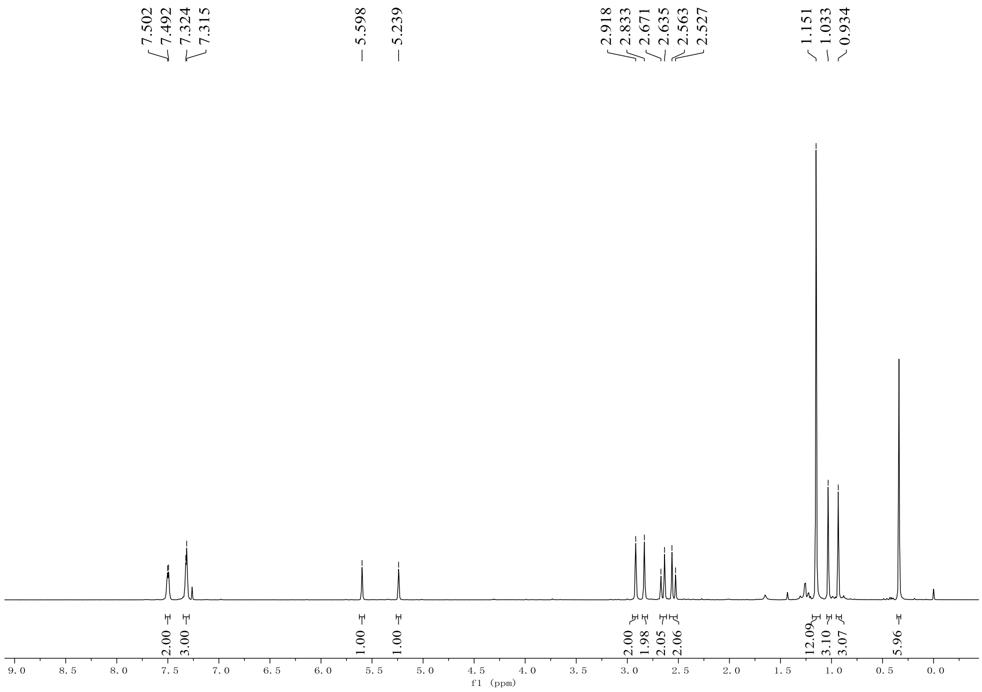



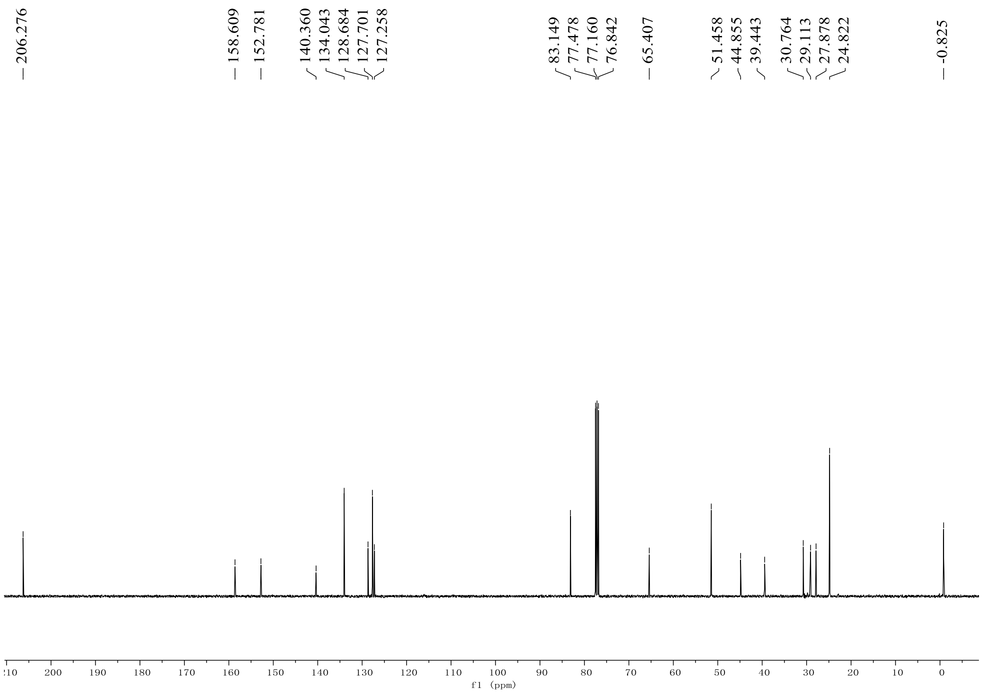


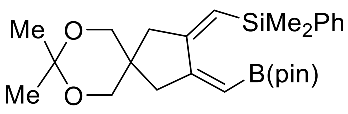
**3q**

According to above procedure A to get the product **3q** (84.1 mg, 88%) as pale yellow oil.

**[1]H NMR** (400 MHz, $CDCl_3$): δ 7.50 – 7.49 (m, 2H), 7.32 – 7.15 (m, 3H), 5.60 (s, 1H), 5.24 (s, 1H), 2.92 (s, 2H), 2.83 (s, 2H), 2.65, 2.55 (AB, $J$ = 14.4 Hz, 4H), 1.15 (s, 12H), 1.03 (s, 3H), 0.93 (s, 3H), 0.34 (s, 6H); **[13]C NMR** (101 MHz, $CDCl_3$) δ 206.28, 158.61, 152.78, 140.36, 134.04, 128.68, 127.70, 127.26, 83.15, 65.41, 51.46, 44.86, 39.44, 30.76, 29.11, 27.88, 24.82, -0.82; **HRMS** (ESI) m/z calculated for $C_{28}H_{40}BO_4Si$ $[M+H]^+$: 479.2789, found: 479.2801; **[11]B NMR** (128.4 MHz, $CDCl_3$): δ 29.13 (s).



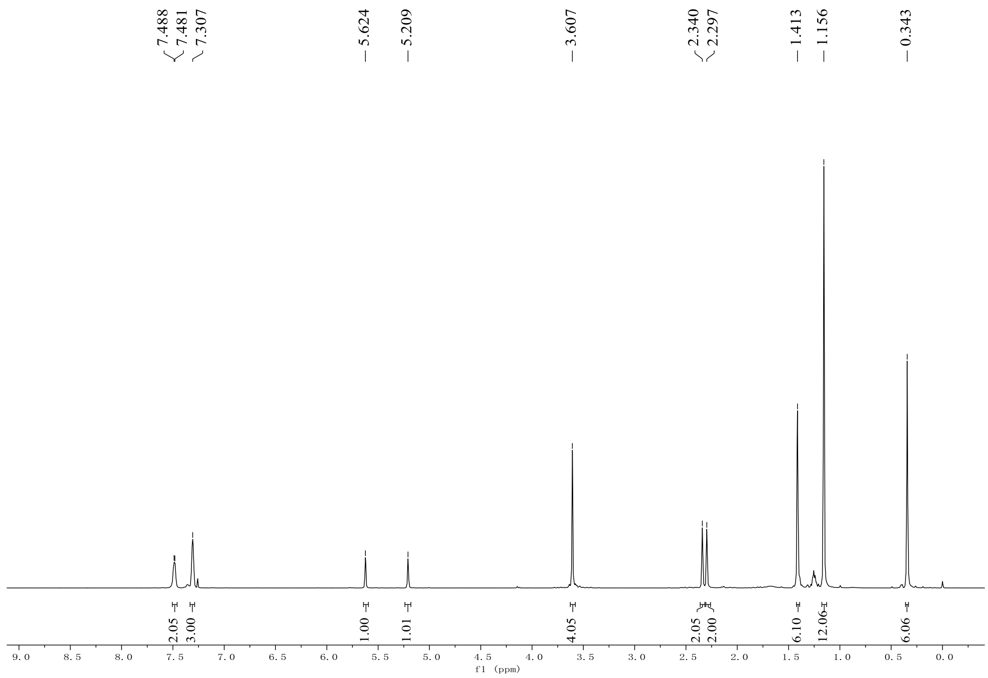


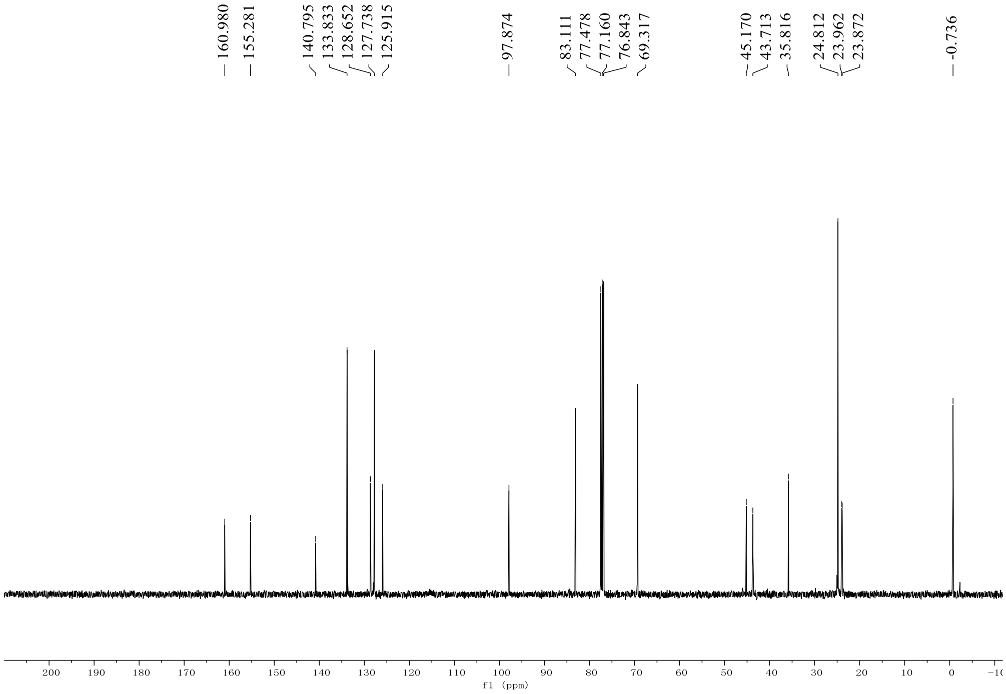


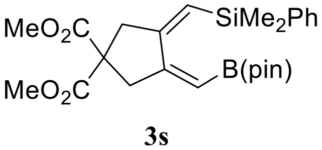

**3r**

According to above procedure A to get the product **3r** (78.2 mg, 86%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.49 – 7.48 (m, 2H), 7.32 – 7.30 (m, 3H), 5.62 (s, 1H), 5.21 (s, 1H), 3.61 (s, 4H), 2.34 (s, 2H), 2.30 (s, 2H), 1.41 (s, 6H), 1.16 (s, 12H), 0.34 (s, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 160.98, 155.28, 140.80, 133.83, 128.65, 127.74, 125.91, 97.87, 83.11, 69.32, 45.17, 43.71, 35.82, 24.81, 23.96, 23.87, -0.74; **HRMS** (ESI) m/z calculated for $C_{26}H_{40}BO_4Si$ $[M+H]^+$: 455.2789, found: 455.2794; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 29.65 (s).



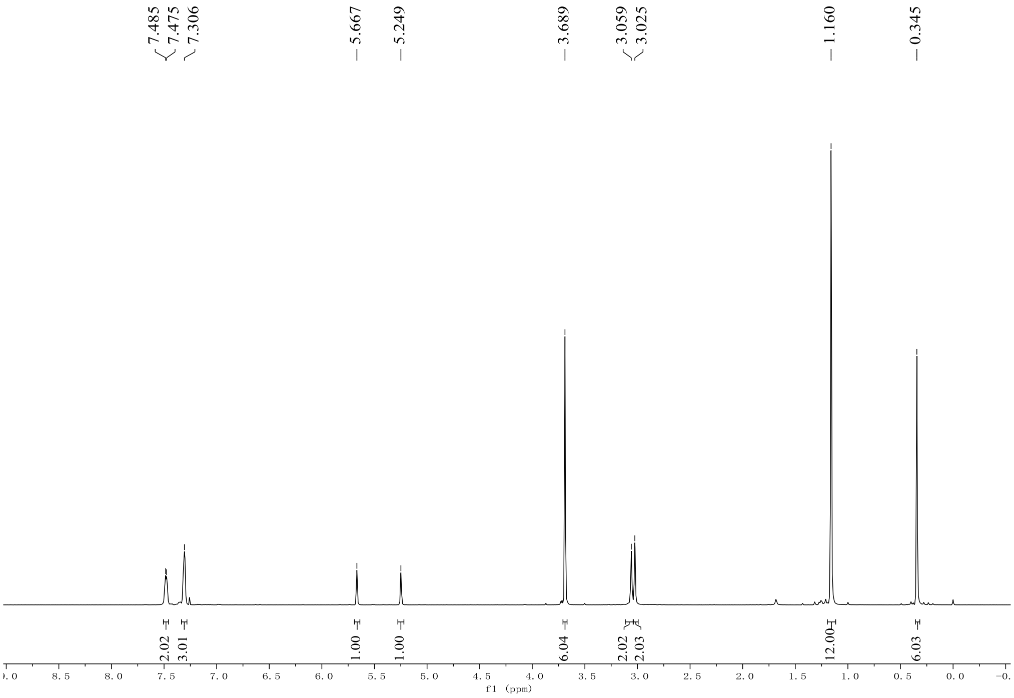



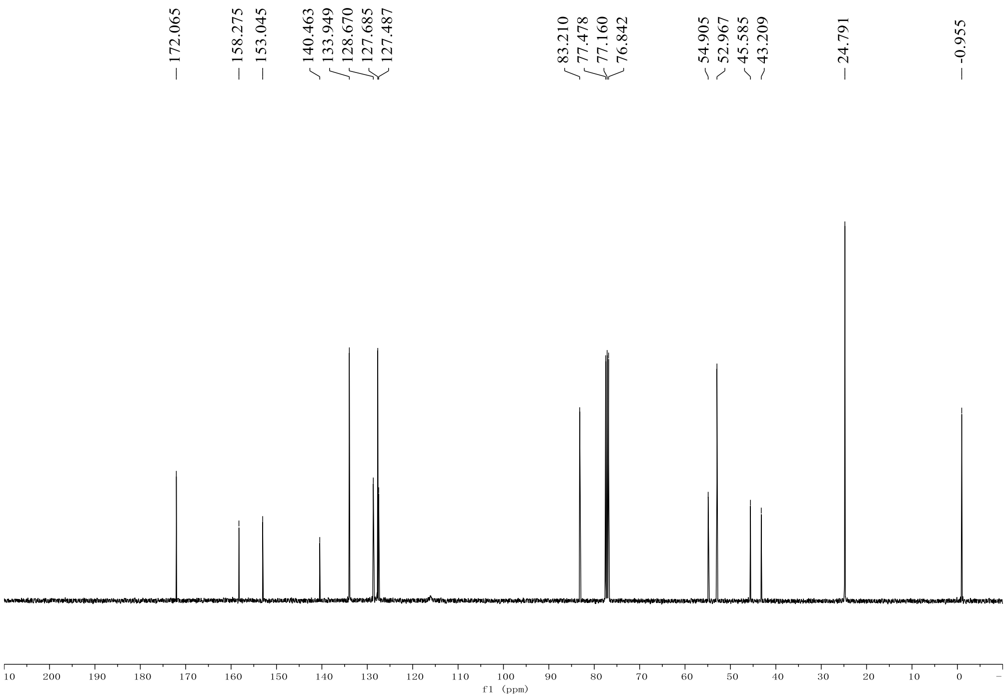


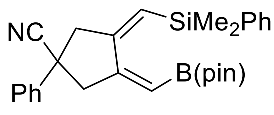
**3s**

According to above procedure A to get the product **3s** (83.7 mg, 89%) as pale yellow solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.49 – 7.47 (m, 2H), 7.31 – 7.30 (m, 3H), 5.67 (s, 1H), 5.25 (s, 1H), 3.69 (s, 6H), 3.06 (s, 2H), 3.03 (s, 2H), 1.16 (s, 12H), 0.34 (s, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 172.06, 158.28, 153.05, 140.46, 133.95, 128.67, 127.69, 127.49, 83.21, 54.91, 52.97, 45.58, 43.21, 24.79, -0.96; **HRMS** (ESI) m/z calculated for $C_{25}H_{36}BO_6Si$ $[M+H]^+$: 471.2374, found: 471.2374; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 28.61 (s).



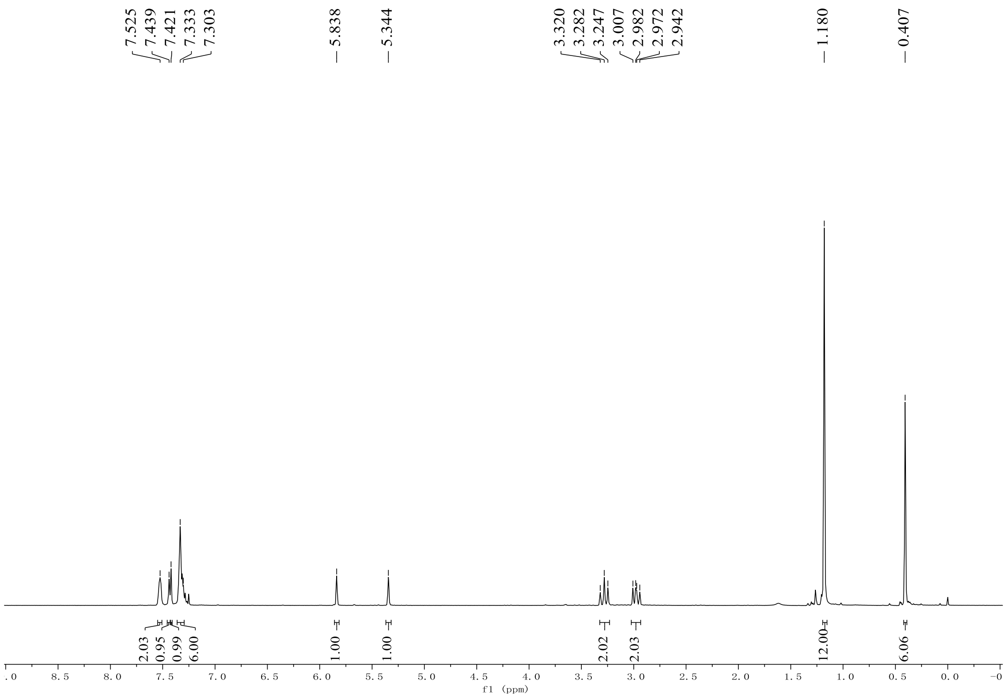


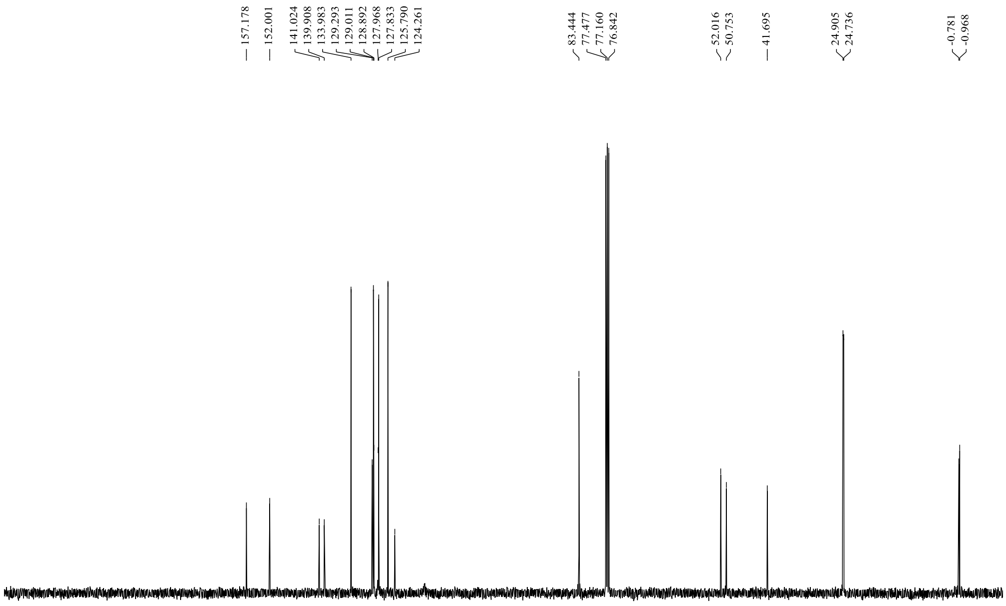


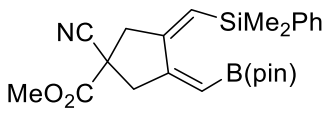
**3t**

According to above procedure A to get the product **3t** (79.1 mg, 87%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.53 – 7.52 (m, 2H), 7.44 (s, 1H), 7.42 (s, 1H), 7.34 – 7.30 (m, 6H), 5.84 (s, 1H), 5.34 (s, 1H), 3.30 (d, $J$ = 15.2 Hz, 1H), 3.26 (d, $J$ = 14.0 Hz, 1H), 2.99 (d, $J$ = 14.0 Hz, 1H), 2.96 (d, $J$ = 16.0 Hz, 1H), 1.18 (s, 12H), 0.41 (s, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 157.18, 152.00, 141.02, 139.91, 133.98, 129.29, 129.01, 128.89, 127.97, 127.83, 125.79, 124.26, 83.44, 52.02, 50.75, 41.69, 24.90, 24.74, -0.78, -0.97; **HRMS** (ESI) m/z calculated for $C_{28}H_{35}BNO_2Si$ $[M+H]^+$: 456.2530, found: 456.2534; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 29.49 (s).



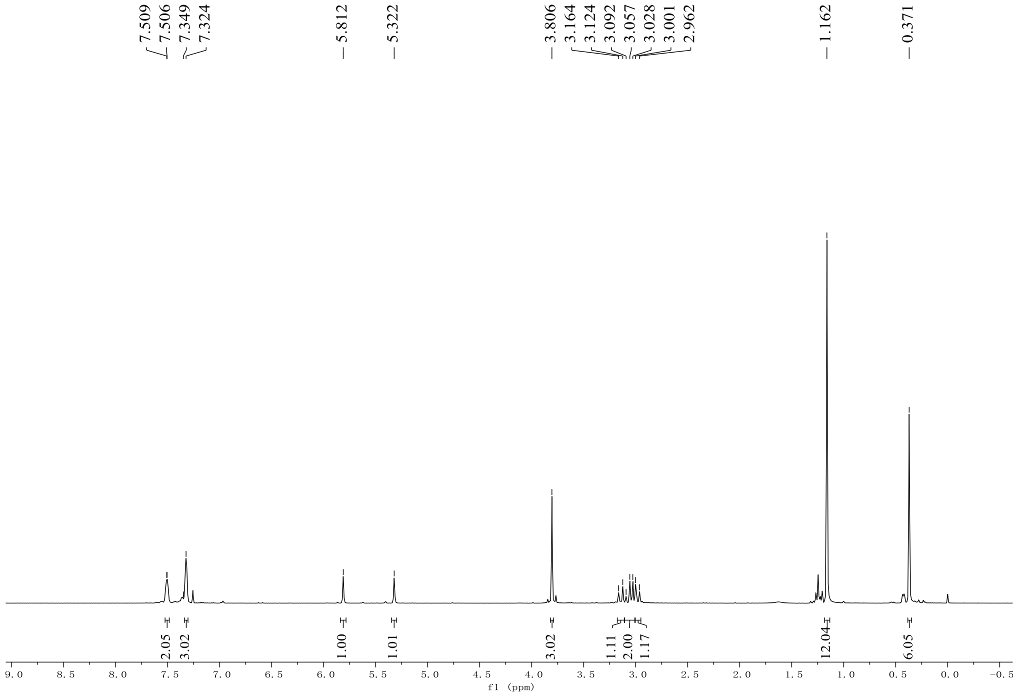


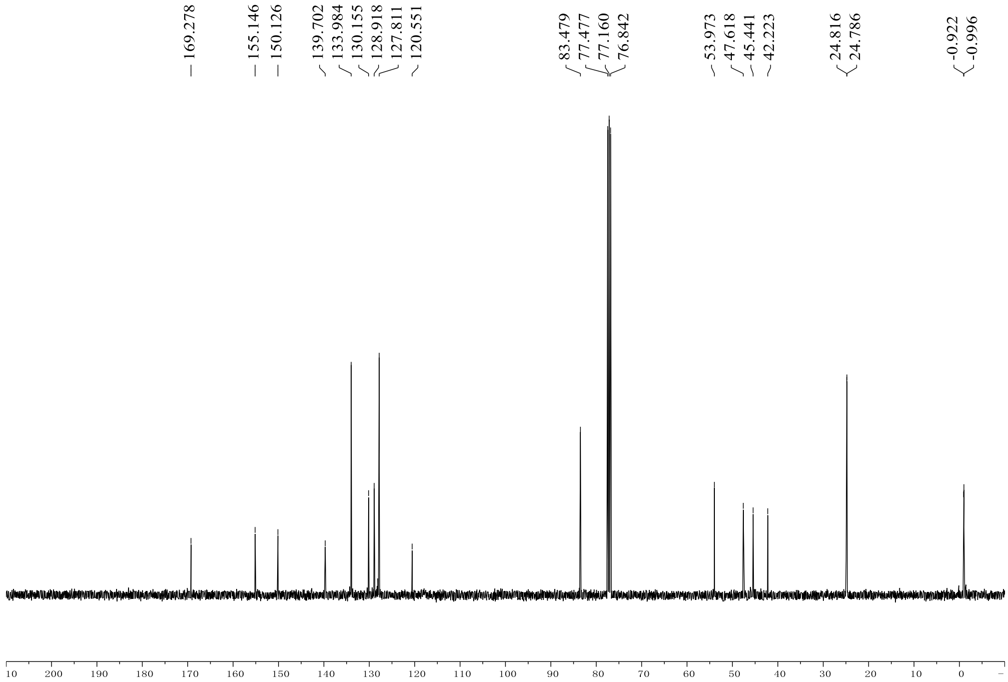


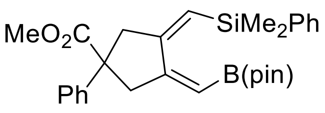

**3u**

According to above procedure A to get the product **3u** (44.6 mg, 51%) as yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.51 – 7.50 (m, 2H), 7.35 – 7.32 (m, 3H), 5.81 (s, 1H), 5.32 (s, 1H), 3.81 (s, 3H), 3.14 (d, $J$ = 16.0 Hz, 1H), 3.09 – 3.03 (m, 2H), 2.98 (d, $J$ = 16.0 Hz, 1H), 1.16 (s, 12H), 0.37 (s, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 169.28, 155.15, 150.13, 139.70, 133.98, 130.15, 128.92, 127.81, 120.55, 83.48, 53.97, 47.62, 45.44, 42.22, 24.82, 24.79, -0.92, -1.00; **HRMS** (ESI) m/z calculated for $C_{24}H_{33}BNO_4Si$ $[M+H]^+$: 438.2272, found: 438.2278; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 29.13 (s).



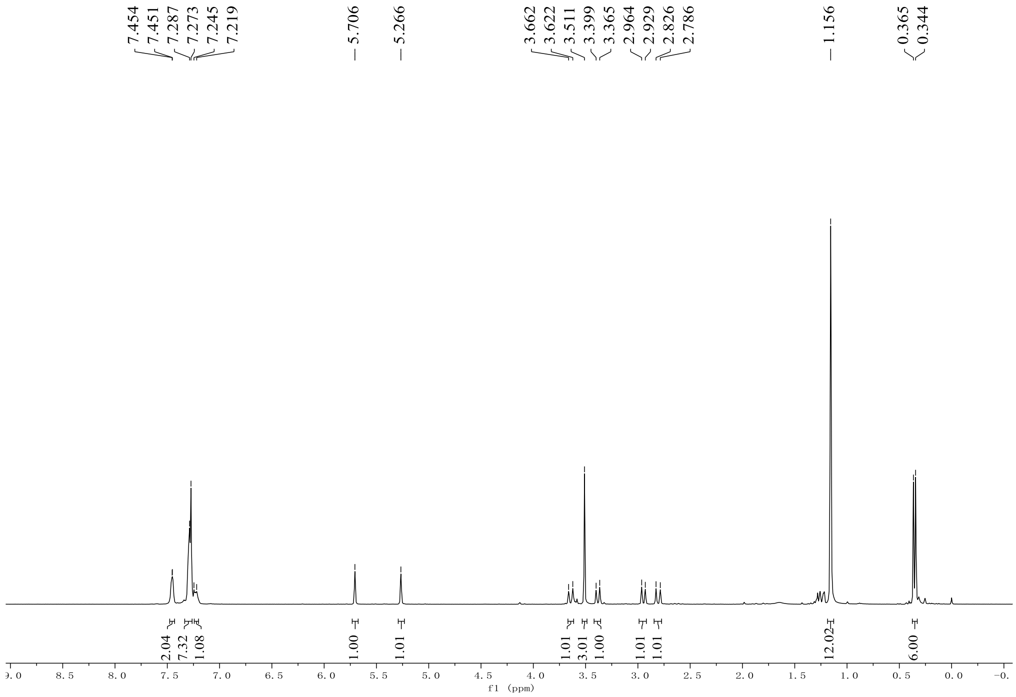



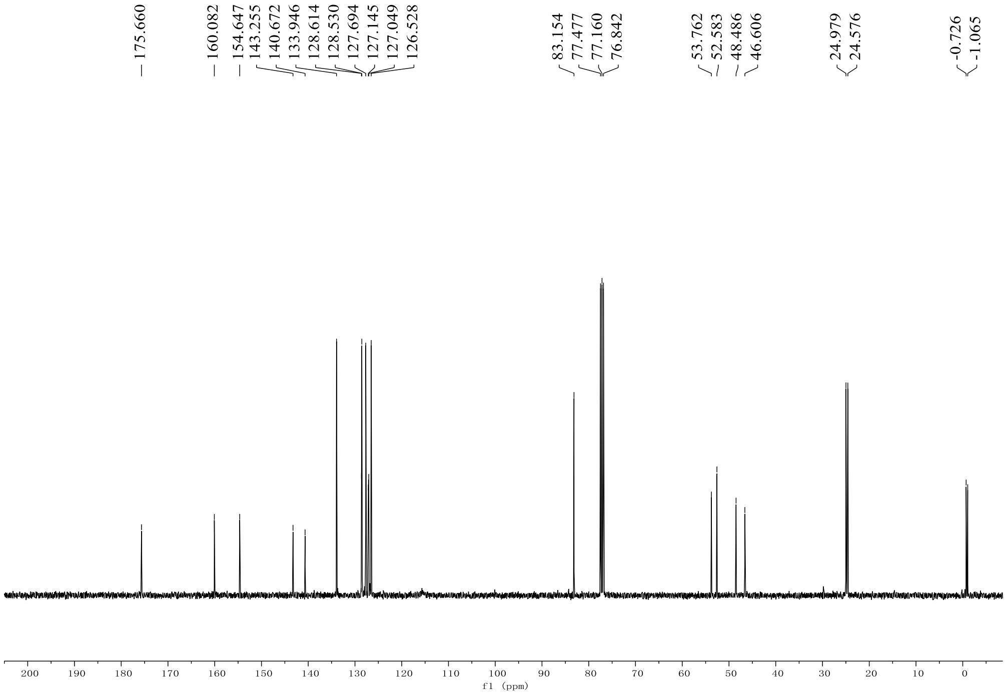


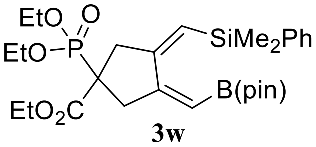

**3v**

According to above procedure A to get the product **3v** (79.1 mg, 81%) as yellow oil.

**[1]H NMR** (400 MHz, $CDCl_3$): δ 7.54 – 7.45 (m, 2H), 7.29 – 7.27 (m, 7H), 7.25 – 7.22 (m, 1H), 5.71 (s, 1H), 5.27 (s, 1H), 3.64 (d, *J* = 16.0 Hz, 1H), 3.51 (s, 3H), 3.38 (d, *J* = 13.6 Hz, 1H), 2.95 (d, *J* = 13.6 Hz, 1H), 2.81 (d, *J* = 16.0 Hz, 1H), 1.16 (s, 12H), 0.37 (s, 3H), 0.34 (s, 3H); **[13]C NMR** (101 MHz, $CDCl_3$): δ 175.66, 160.08, 154.65, 143.26, 140.67, 133.95, 128.61, 128.53, 127.69, 127.15, 127.05, 126.53, 83.15, 53.76, 52.58, 48.49, 46.61, 24.98, 24.58, -0.73, -1.07; **HRMS** (ESI) m/z calculated for $C_{29}H_{38}BO_4Si$ $[M+H]^+$: 489.2632, found: 489.2639; **[11]B NMR** (128.4 MHz, $CDCl_3$): δ 28.78 (s).



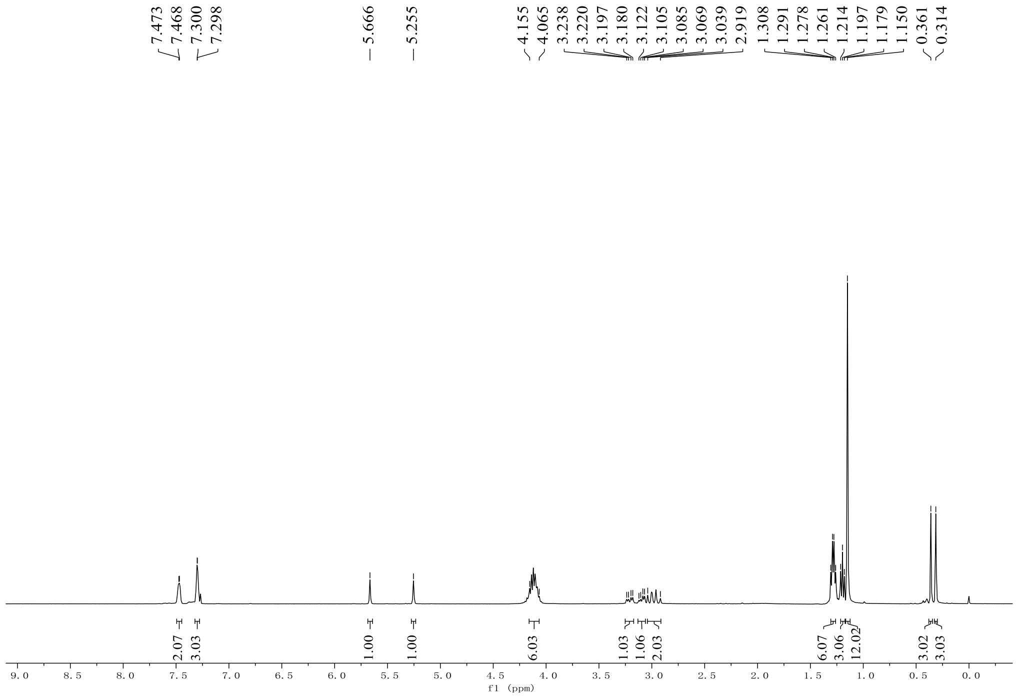


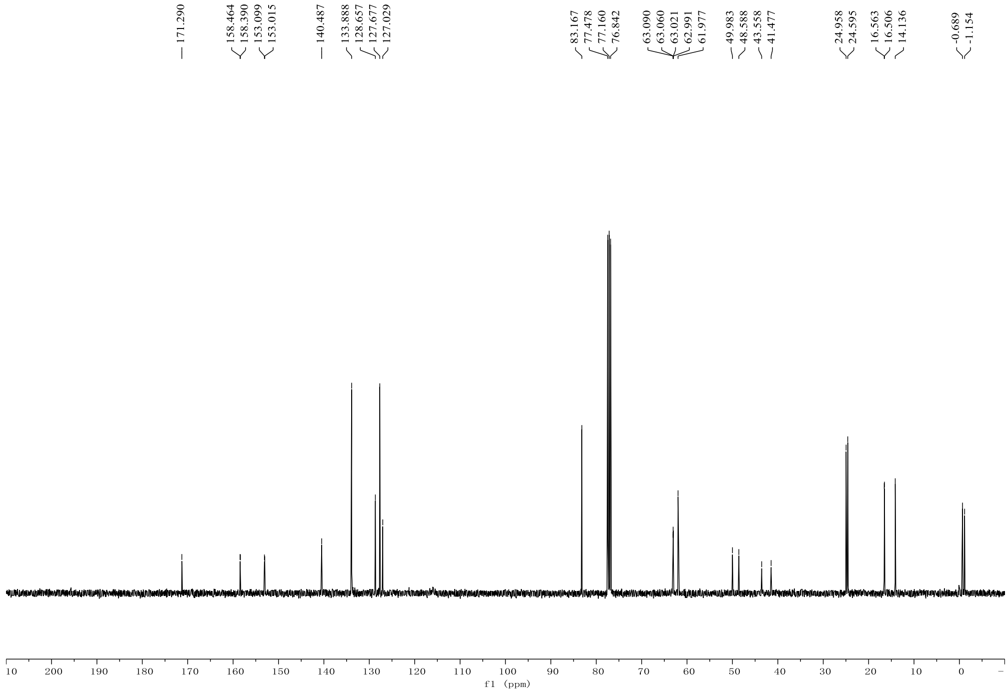


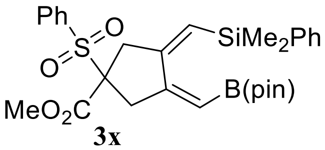
**3w**

According to above procedure A to get the product **3w** (94.5 mg, 84%) as yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.49 – 7.45 (m, 2H), 7.31 – 7.29 (m, 3H), 5.67 (s, 1H), 5.25 (s, 1H), 4.16 – 4.06 (m, 6H), 3.21 (dd, *J* = 16.2, 6.9 Hz, 1H), 3.10 (dd, *J* = 14.5, 6.7 Hz, 1H), 3.04 – 2.92 (m, 2H), 1.28 (q, *J* = 6.8 Hz, 6H), 1.20 (t, *J* = 6.8 Hz, 3H), 1.15 (s, 12H), 0.36 (s, 3H), 0.31 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 171.29, 158.43 (d, *J* = 7.5 Hz), 153.02 (d, *J* = 8.5 Hz), 140.49, 133.89, 128.66, 127.68, 127.03, 83.17, 63.07 (d, *J* = 3.03 Hz), 63.01 (d, *J* = 3.03 Hz), 61.98, 49.29 (d, *J* = 140.89 Hz),42.52 (d, *J* = 210.18 Hz), 24.96, 24.60, 16.53 (d, *J* = 5.8 Hz), 14.14, -0.69, -1.15; **HRMS** (ESI) m/z calculated for $C_{28}H_{45}BPO_7Si$ $[M+H]^+$: 563.2765, found: 563.2768; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 29.13 (s).



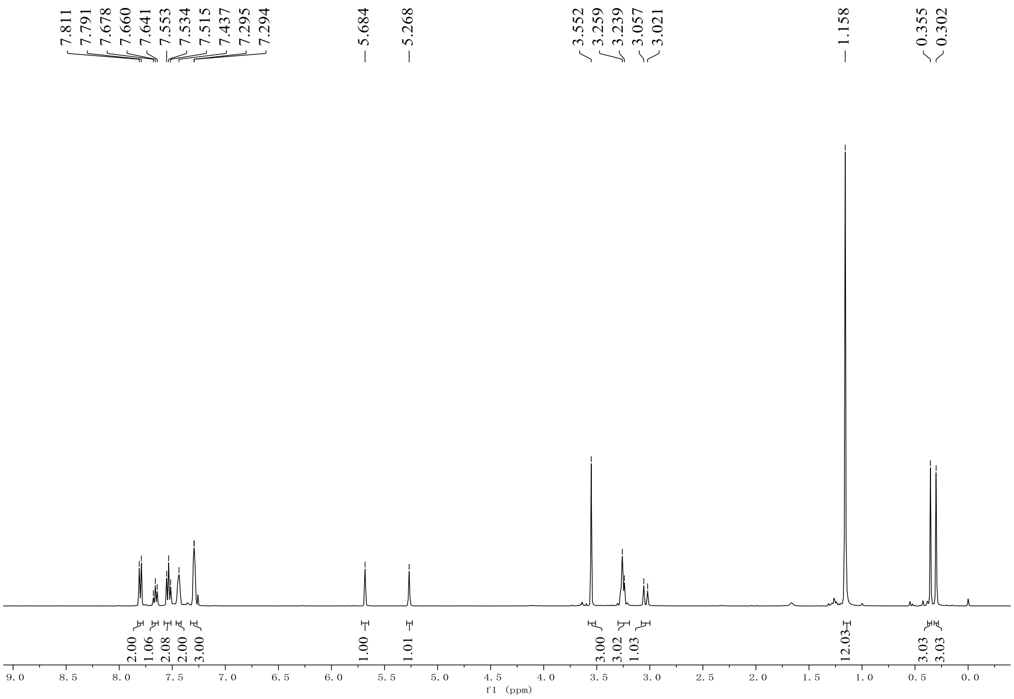



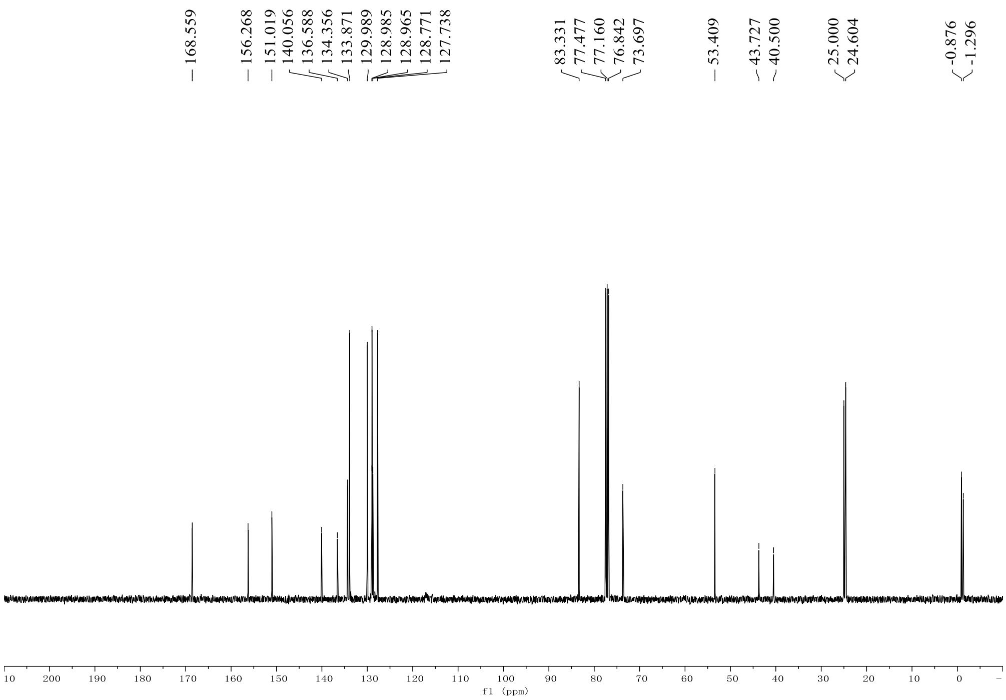


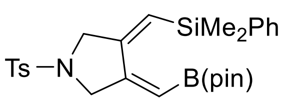
**3x**

According to above procedure A to get the product **3x** (96.2 mg, 87%) as yellow solid.

**[1]H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.43 (m, 2H), 7.30 – 7.29 (m, 3H), 5.68 (s, 1H), 5.27 (s, 1H), 3.55 (s, 3H), 3.26 – 3.02 (m, 3H), 3.04 (d, *J* = 14.4 Hz, 1H), 1.16 (s, 12H), 0.36 (s, 3H), 0.30 (s, 3H); **[13]C NMR** (101 MHz, $CDCl_3$): δ 168.56, 156.27, 151.02, 140.06, 136.59, 134.36, 133.87, 129.99, 128.99, 128.97, 128.77, 127.74, 83.33, 73.70, 53.41, 43.73, 40.50, 25.00, 24.60, -0.88, -1.30; **HRMS** (ESI) m/z calculated for $C_{29}H_{38}BSO_6Si$ $[M+H]^+$: 553.2251, found: 553.2261; **[11]B NMR** (128.4 MHz, $CDCl_3$): δ 29.13 (s).



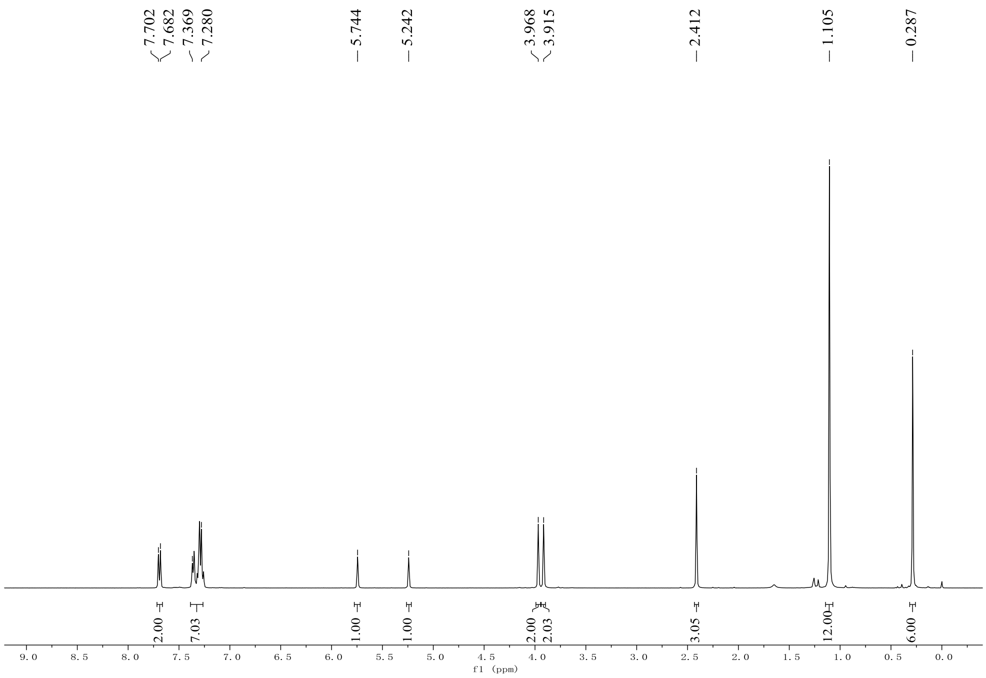


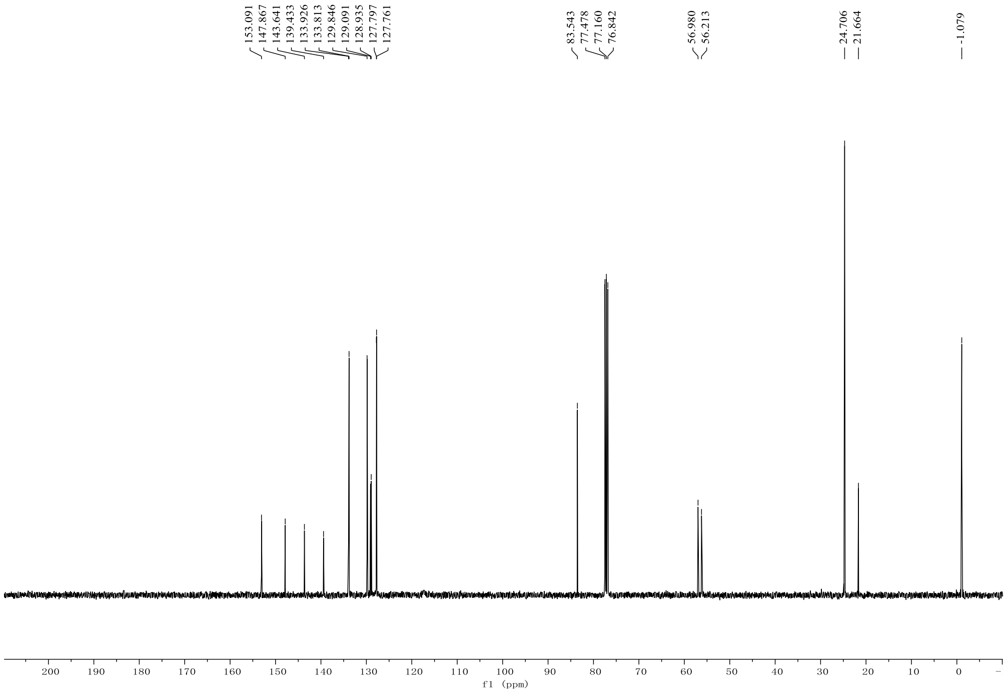


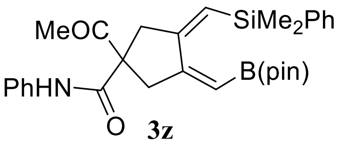

**3y**

According to above procedure A to get the product **3y** (96.5 mg, 85%) as yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.28 (m, 7H), 5.74 (s, 1H), 5.24 (s, 1H), 3.97 (s, 2H), 3.91 (s, 2H), 2.41 (s, 3H), 1.11 (s, 12H), 0.29 (s, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 153.09, 147.87, 143.64, 139.43, 133.93, 133.81, 129.85, 129.09, 128.94, 127.80, 127.76, 83.54, 56.98, 56.21, 24.71, 21.66, -1.08; **HRMS** (ESI) m/z calculated for $C_{27}H_{37}BSNO_4Si$ $[M+H]^+$: 510.2306, found: 510.2311; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 28.78 (s).



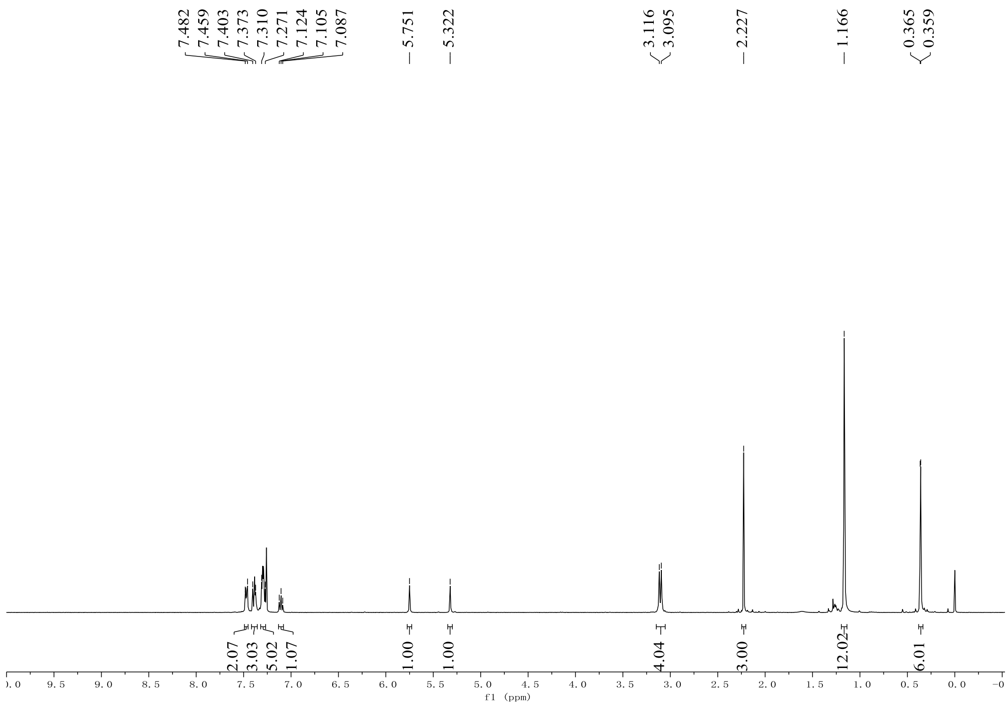


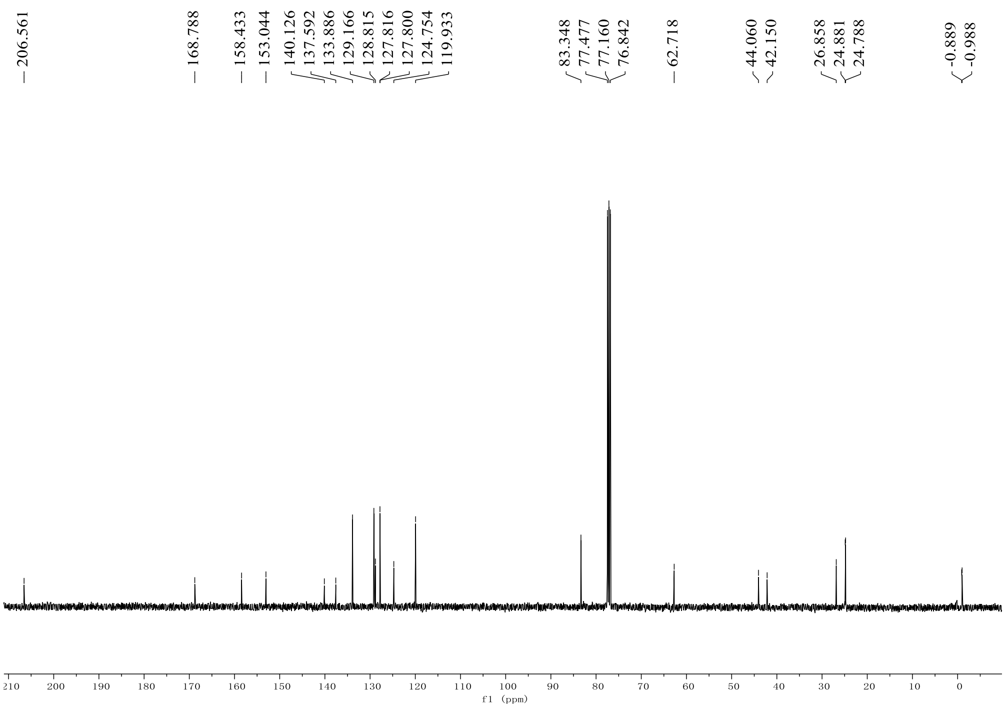


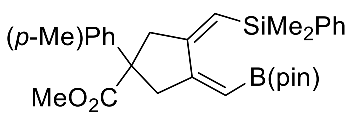
**3z**

According to above procedure A to get the product **3z** (89.7 mg, 87%) as yellow oil.

[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.48 – 7.46 (m, 2H), 7.40 – 7.37 (m, 3H), 7.31 – 7.27 (m, 5H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.75 (s, 1H), 5.32 (s, 1H), 3.11 – 3.09 (m, 4H), 2.23 (s, 3H), 1.17 (s, 12H), 0.37 (s, 6H), 0.36 (s, 6H); [13]**C NMR** (101 MHz, $CDCl_3$): δ 206.56, 168.79, 158.43, 153.04, 140.13, 137.59, 133.89, 129.17, 128.81, 127.82, 127.80, 124.75, 119.93, 83.35, 62.72, 44.06, 42.15, 26.86, 24.88, 24.79, -0.89, -0.99. **HRMS** (ESI) m/z calculated for $C_{30}H_{39}BNO_4Si$ $[M+H]^+$: 516.2741, found: 516.2747; [11]**B NMR** (128.4 MHz, $CDCl_3$): δ 28.63 (s).



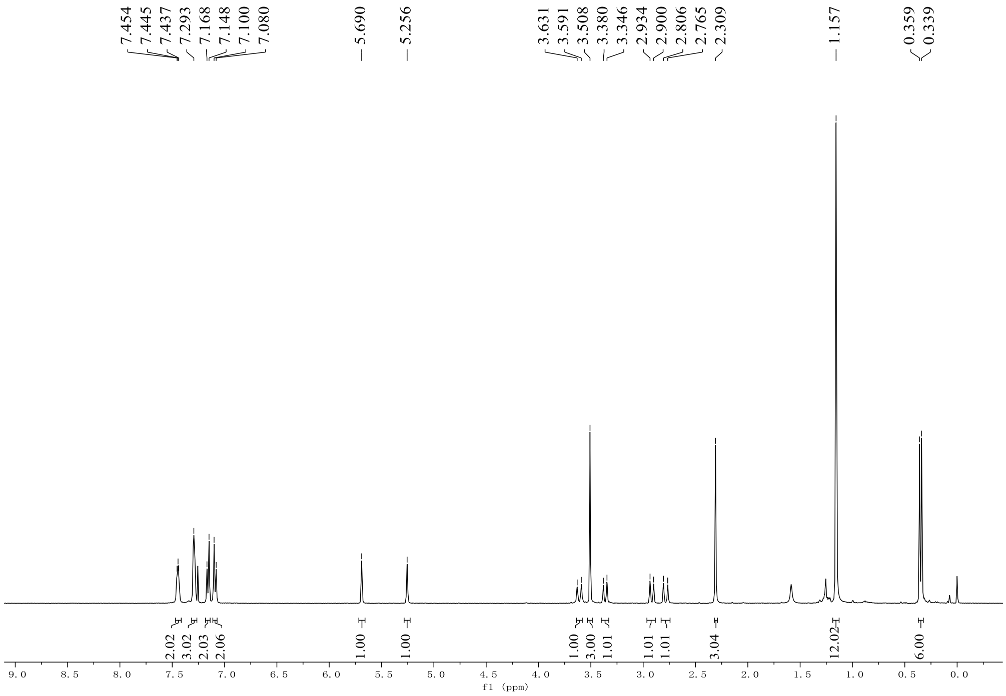


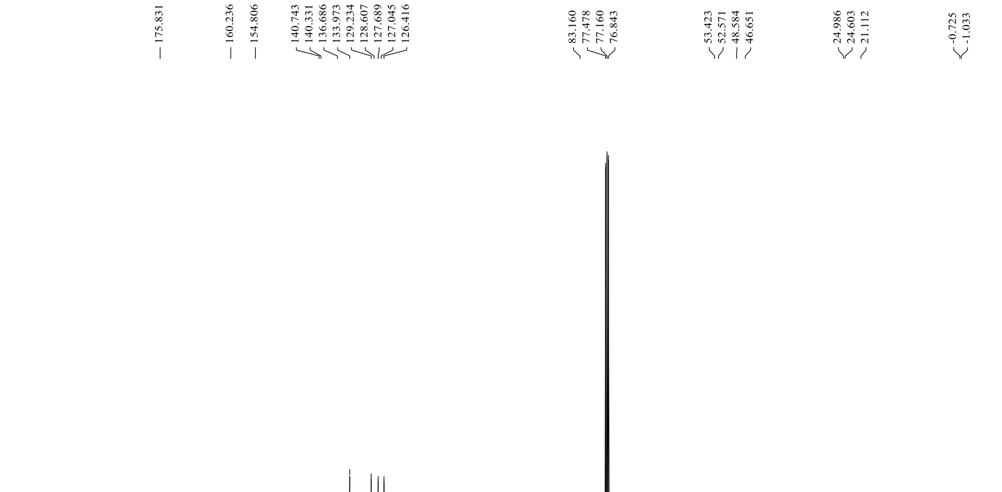


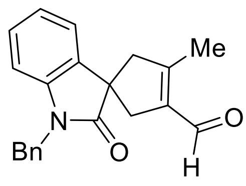

**3aa**

According to above procedure A to get the product **3aa** (78.4 mg, 78%) as pale yellow solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.47 – 7.41 (m, 2H), 7.30 – 7.28 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.69 (s, 1H), 5.26 (s, 1H), 3.61 (d, *J* = 15.8 Hz, 1H), 3.51 (s, 3H), 3.36 (d, *J* = 13.8 Hz, 1H), 2.92 (d, *J* = 13.6 Hz, 1H), 2.79 (d, *J* = 16.2 Hz, 1H), 2.31 (s, 3H), 1.16 (s, 12H), 0.36 (s, 3H), 0.34 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 175.83, 160.24, 154.81, 140.74, 140.33, 136.69, 133.97, 129.23, 128.61, 127.69, 127.05, 126.42, 83.16, 53.42, 52.57, 48.58, 46.65, 24.99, 24.60, 21.11, -0.72, -1.03; **HRMS** (ESI) m/z calculated for $C_{30}H_{40}BO_4Si$ $[M+H]^+$: 503.2789, found: 503.2800; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 30.01 (s).



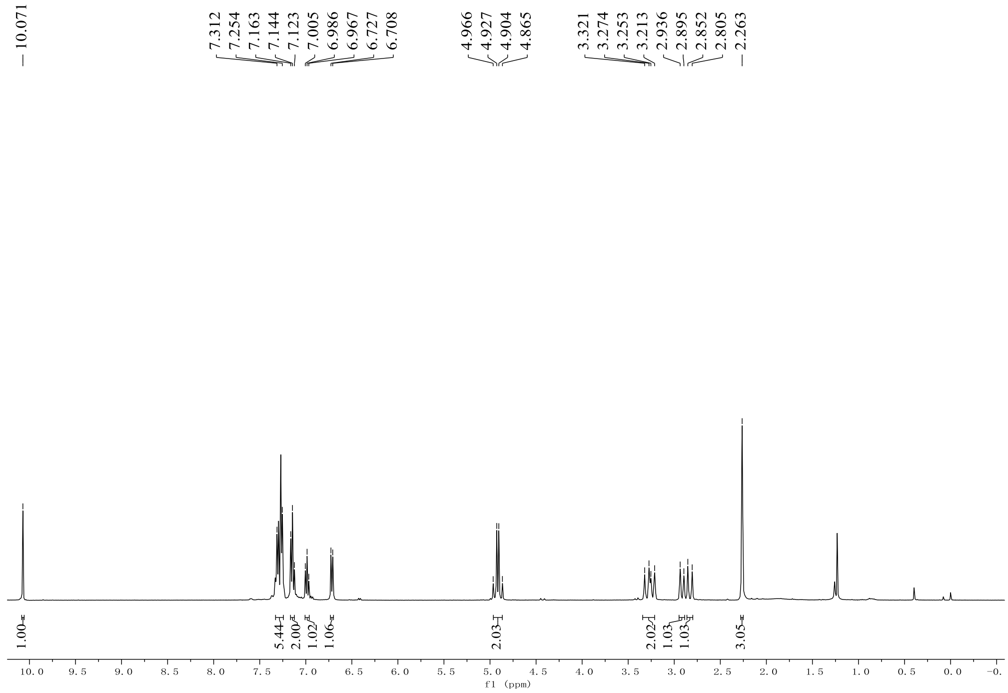


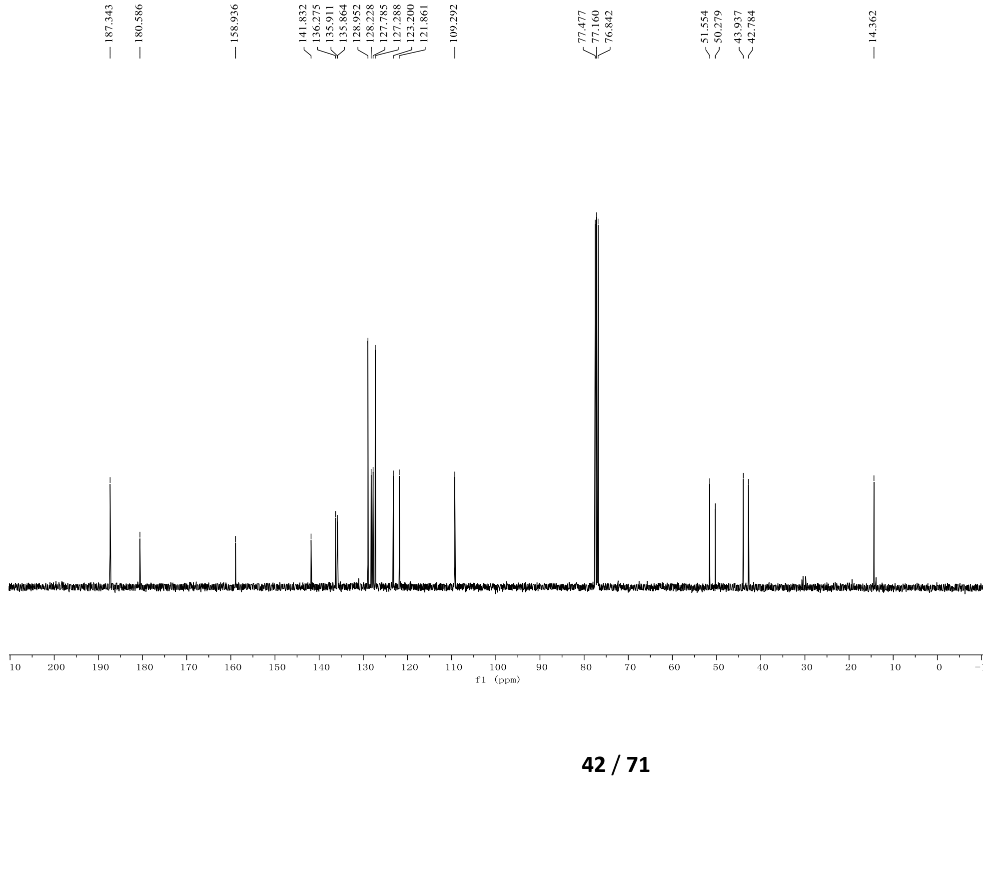


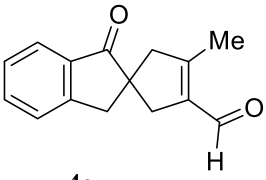
**4c**

According to above procedure B to get the product **4c** (45.6 mg, 72%) as pale yellow solid.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 7.31 – 7.25 (m, 5H), 7.14 (t, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 4.94, 4.89 (AB, *J* = 15.6 Hz, 2H), 3.30 (d, *J* = 18.8 Hz, 1H), 3.23 (d, *J* = 16.2 Hz, 1H), 2.92 (d, *J* = 16.2 Hz, 1H), 2.83 (d, *J* = 18.8 Hz, 1H), 2.26 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 187.34, 180.59, 158.94, 141.83, 136.28, 135.91, 135.86, 128.95, 128.23, 127.79, 127.29, 123.20, 121.86, 109.29, 51.55, 50.28, 43.94, 42.78, 14.36; **HRMS** (ESI) m/z calculated for $C_{21}H_{20}NO_2$ $[M+H]^+$: 318.1494, found: 318.1494.



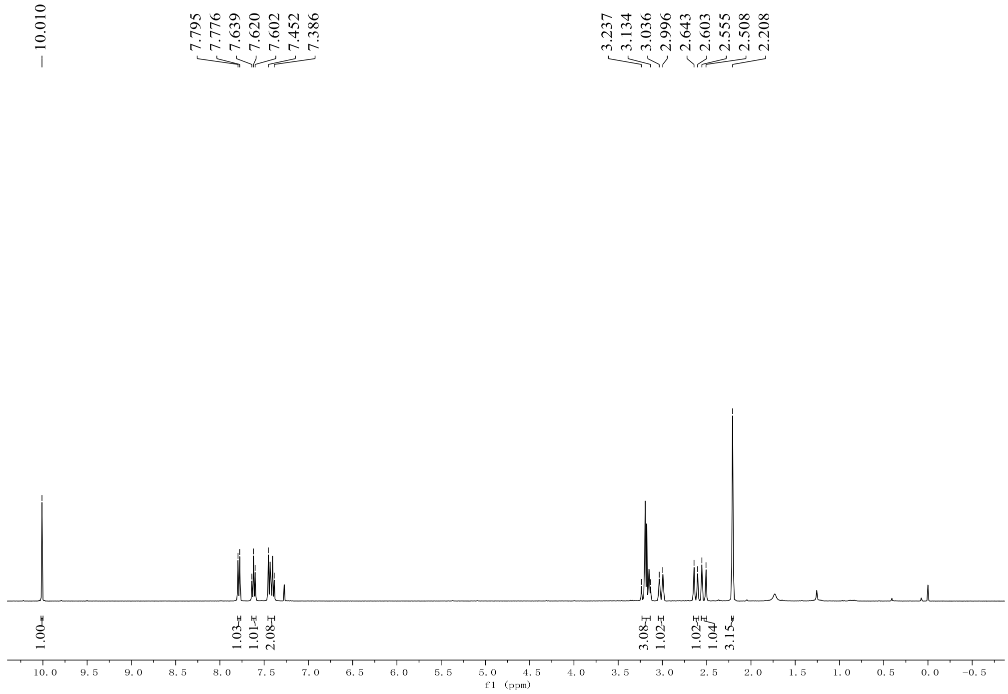


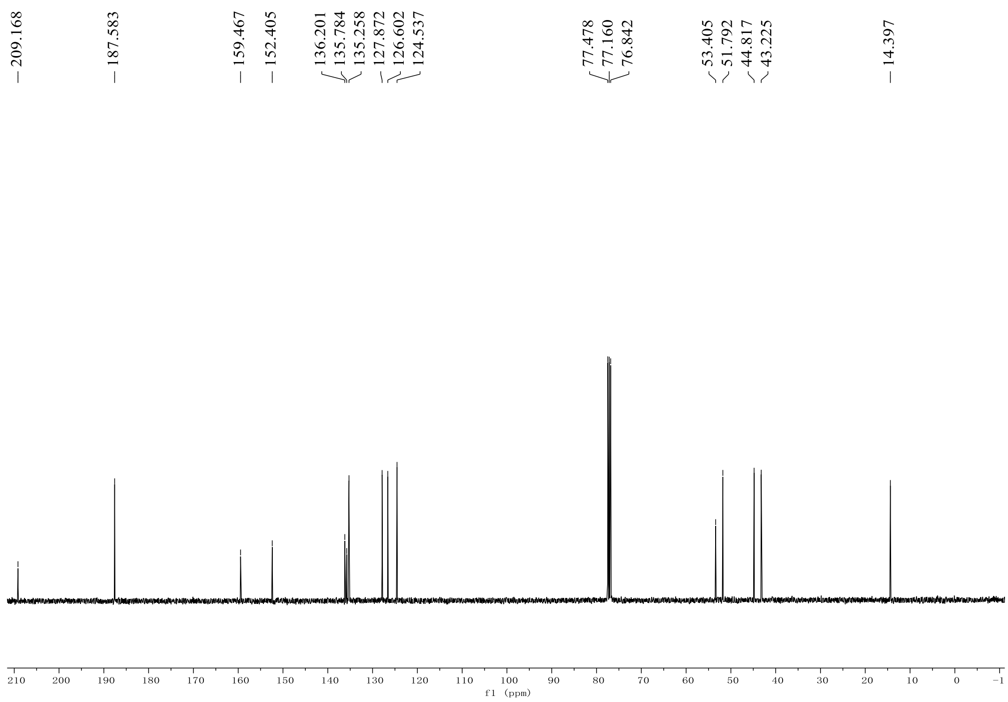


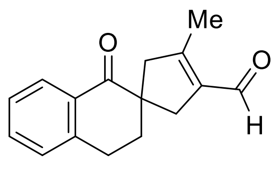

**4g**

According to above procedure B to get the product **4g** (34.1 mg, 75%) as yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.40 (m, 2H), 3.24 – 3.13 (m, 3H), 3.02 (d, *J* = 15.9 Hz, 1H), 2.62 (d, *J* = 16.1 Hz, 1H), 2.53 (d, *J* = 18.7 Hz, 1H), 2.21 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 209.17, 187.58, 159.47, 152.41, 136.20, 135.78, 135.26, 127.87, 126.60, 124.54, 53.41, 51.79, 44.82, 43.23, 14.40; **HRMS** (ESI) m/z calculated for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1072, found: 227.1068.



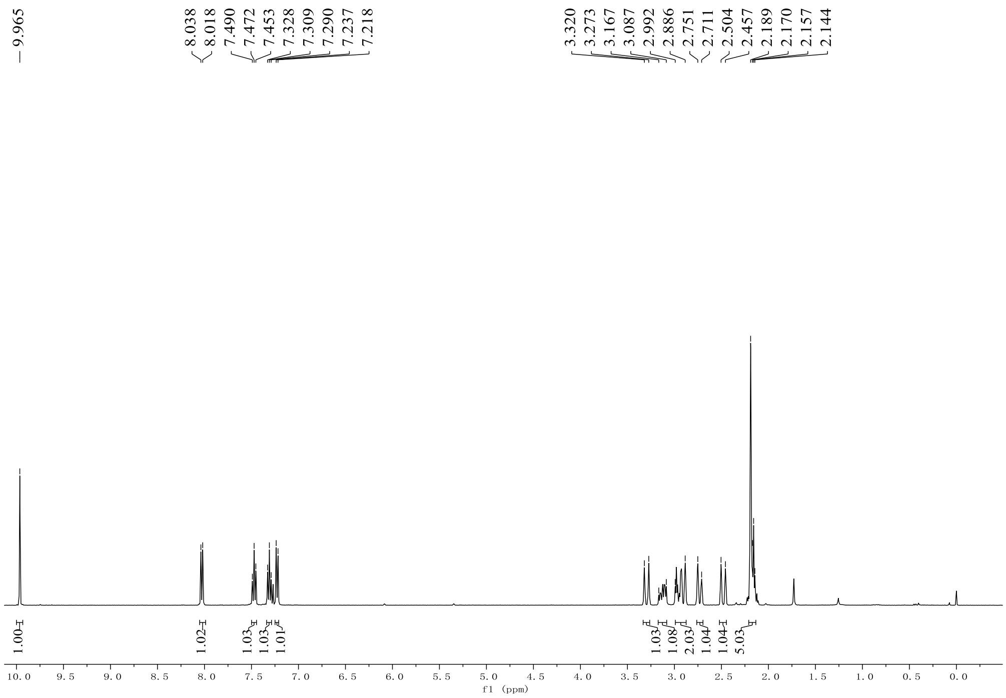



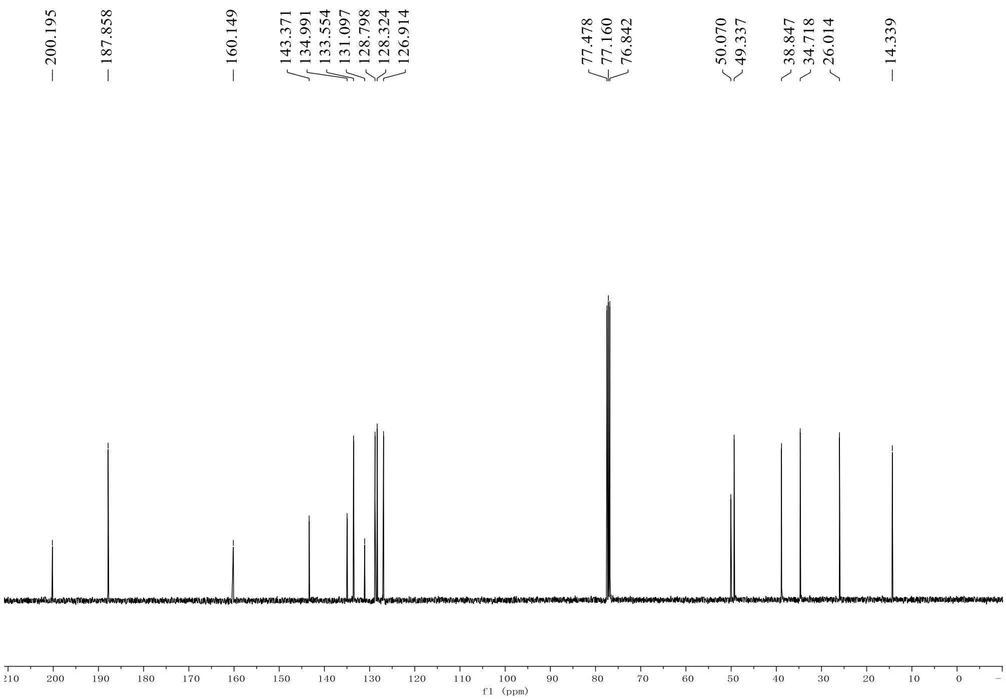


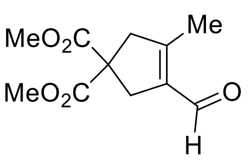
**4n**

According to above procedure B to get the product **4n** (34.8 mg, 72%) as pale yellow oil.

**[1]H NMR** (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 3.30 (d, *J* = 18.7 Hz, 1H), 3.17 – 3.09 (m, 1H), 2.99 – 2.89 (m, 2H), 2.73 (d, *J* = 16.2 Hz, 1H), 2.48 (d, *J* = 18.7 Hz, 1H), 2.18 (s, 3H), 2.16 (t, *J* = 5.2 Hz, 2H) ; **[13]C NMR** (101 MHz, $CDCl_3$): δ 200.19, 187.86, 160.15, 143.37, 134.99, 133.55, 131.10, 128.80, 128.32, 126.91, 50.07, 49.34, 38.85, 34.72, 26.01, 14.34; **HRMS** (ESI) m/z calculated for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1229, found: 241.1225.



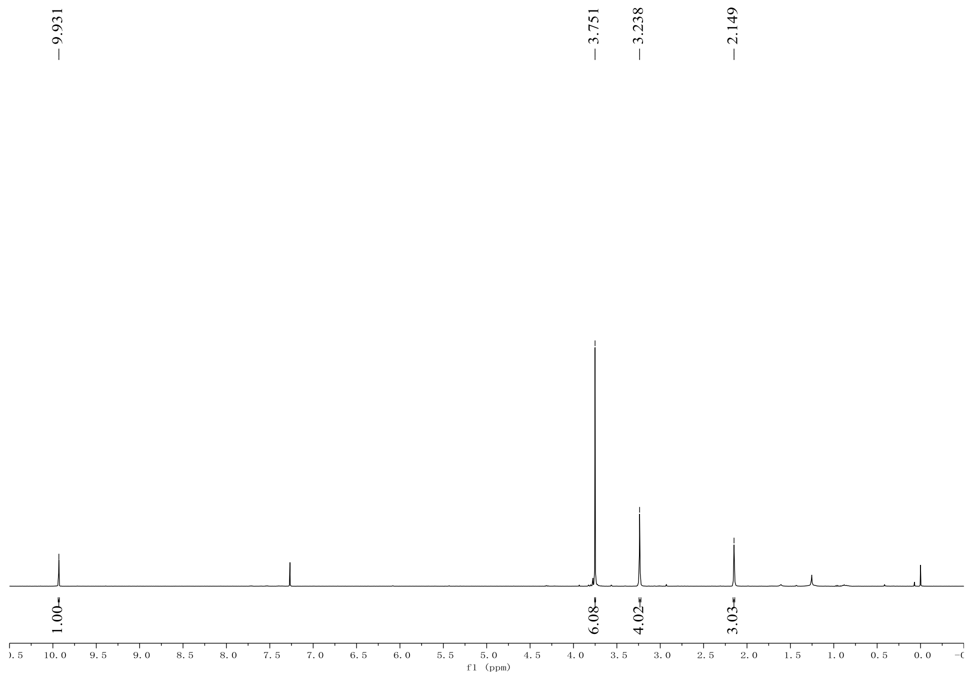


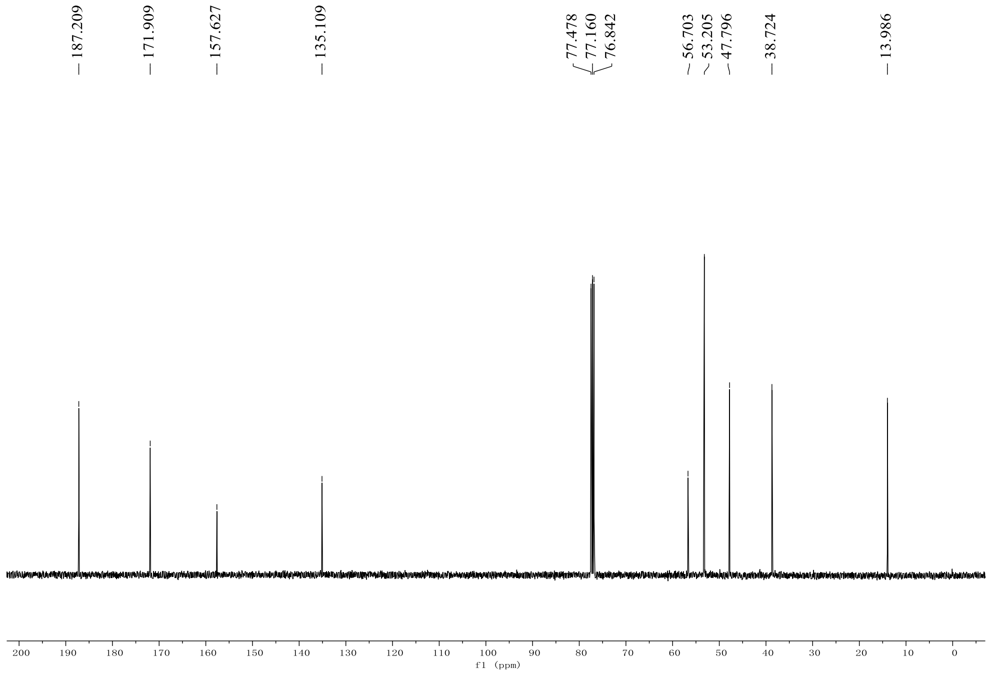


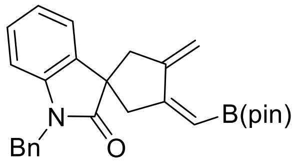
**4s**

According to above procedure B to get the product **4s** (35.2 mg, 78%) as pale yellow oil.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 3.75 (s, 6H), 3.24 (s, 4H), 2.15 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 187.21, 171.92, 157.62, 135.12, 56.71, 53.20, 47.80, 38.73, 13.98; **HRMS** (ESI) m/z calculated for $C_{11}H_{15}O_5$ $[M+H]^+$: 227.0919, found: 227.0918.



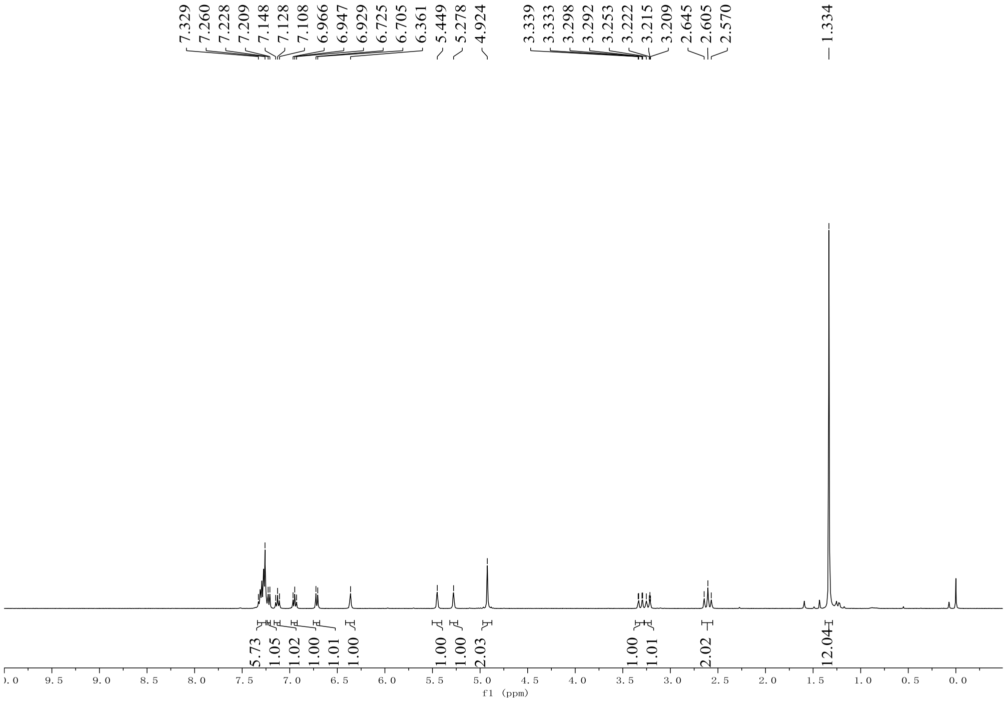


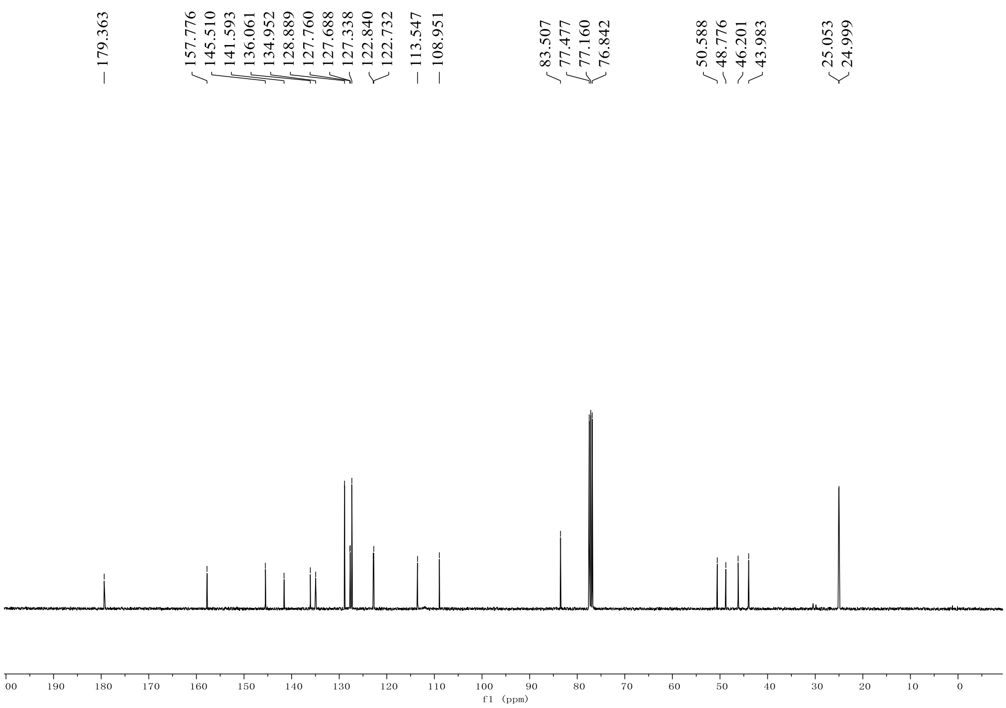


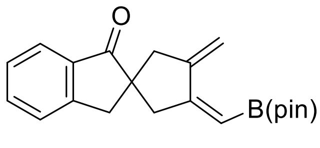

**5c**

According to above procedure C to get the product **5c** (64.4 mg, 75%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.33 – 7.25 (m, 5 H), 7.22 (d, $J$ = 7.6 Hz, 1H), 7.13 (t, $J$ = 8.0 Hz, 1H), 6.95 (t, $J$ = 7.8 Hz, 1H), 6.71 (d, $J$ = 7.6 Hz, 1H), 6.36 (s, 1H), 5.45 (s, 1H), 5.28 (s, 1H), 4.92 (s, 2H), 3.32 (dd, $J$ = 16.0, 2.4 Hz, 1H), 3.23 (dt, $J$ = 14.8, 2.4 Hz, 1H), 2.60 (t, $J$ = 15.0 Hz, 2H),1.33 (s, 12H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 179.36, 157.78, 145.51, 141.59, 136.06, 134.95, 128.89, 127.76, 127.69, 127.34, 122.84, 122.73, 113.55, 108.95, 83.51, 50.59, 48.78, 46.20, 43.98, 25.05, 25.00. **HRMS** (ESI) m/z calculated for $C_{27}H_{31}BNO_3$ $[M+H]^+$: 428.2397, found: 428.2402; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 30.37 (s).



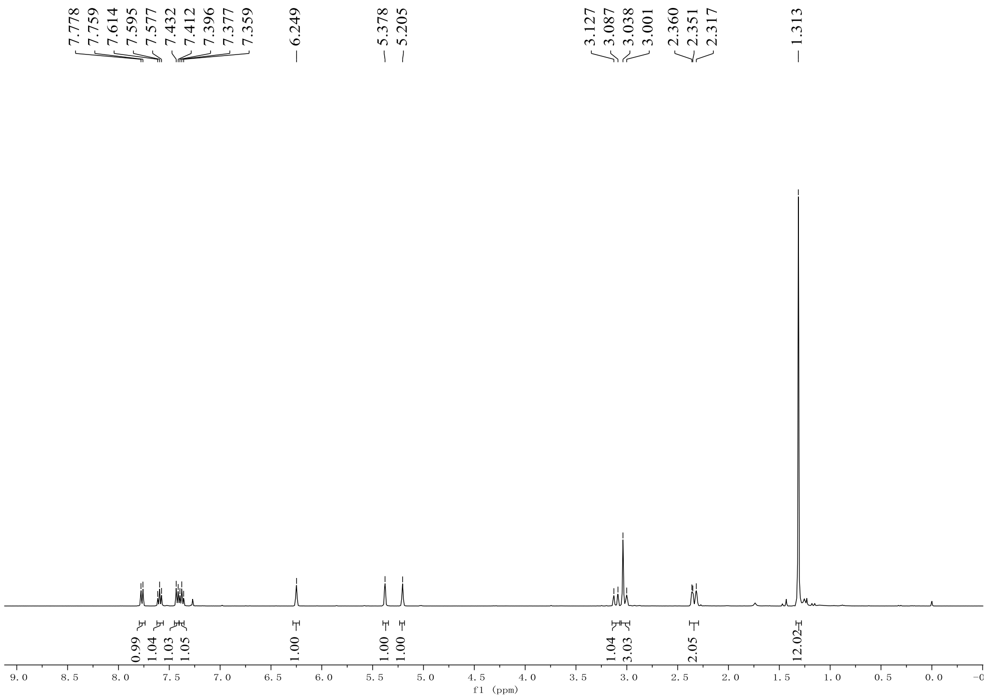



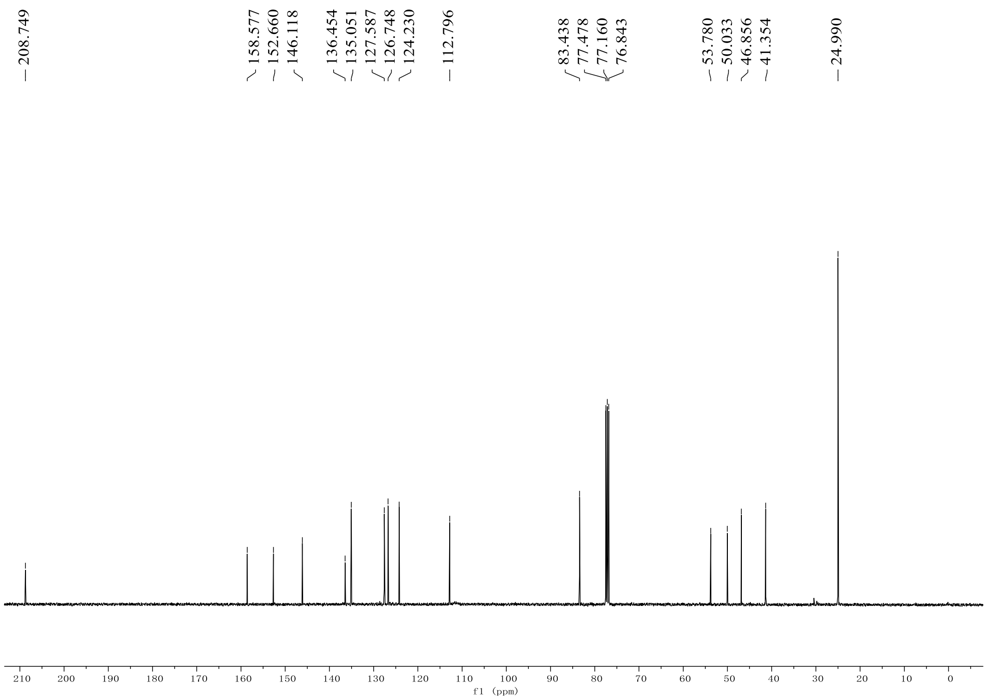


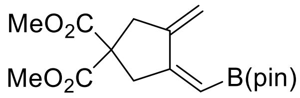

**5g**

According to above procedure C to get the product 5g (41.2 mg, 61%) as pale yellow oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 6.25 (s, 1H), 5.38 (s, 1H), 5.21 (s, 1H), 3.11 (d, *J* = 14.4 Hz, 1H), 3.04 – 3.00 (m, 3H), 2.34 (d, *J* = 17.2 Hz, 1H), 2.33 (d, *J* = 13.6 Hz, 1H),1.31 (s, 12H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 208.75, 158.58, 152.66, 146.12, 136.45, 135.05, 127.59, 126.75, 124.23, 112.80, 83.44, 53.78, 50.03, 46.86, 41.35, 24.99; **HRMS** (ESI) m/z calculated for $C_{21}H_{26}BO_3$ $[M+H]^+$: 337.1975, found: 337.1978; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 30.31 (s).

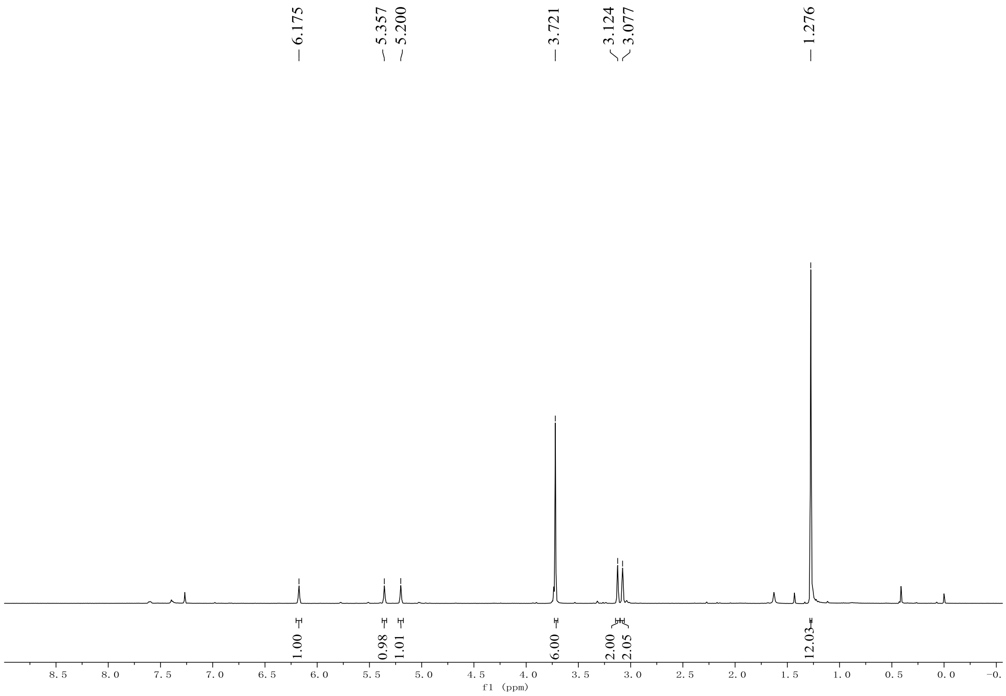


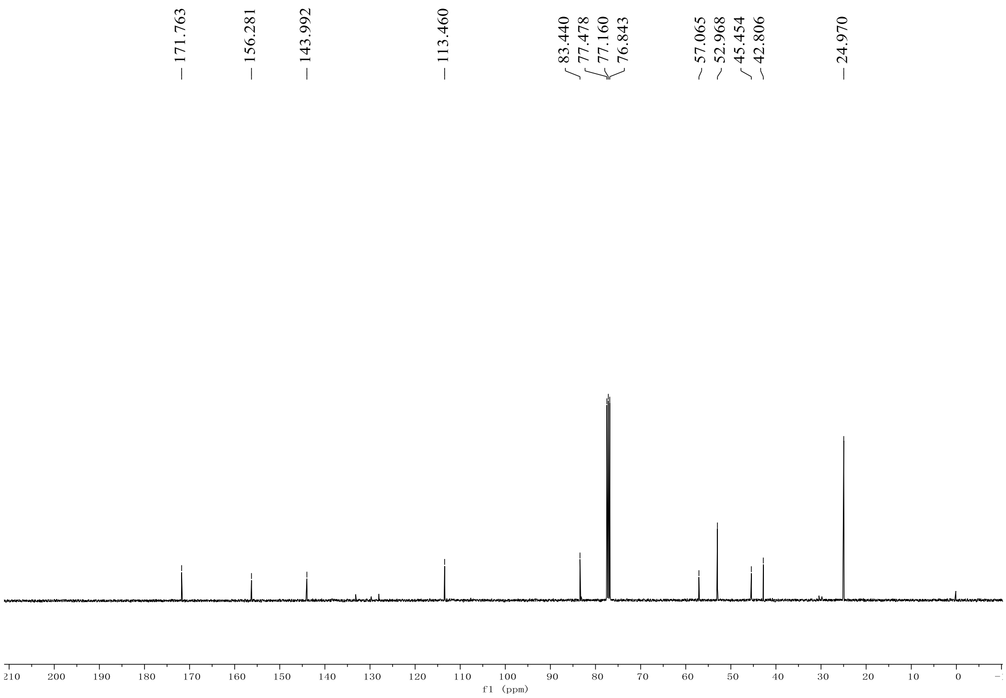



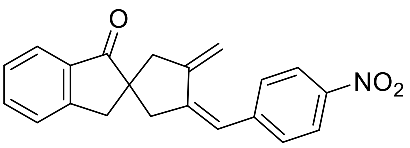


**5s**

According to above procedure C to get the product **5s** (47.0 mg, 70%) as pale yellow oil.
**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 6.17 (s, 1H), 5.36 (s, 1H), 5.20 (s, 1H), 3.72 (s, 6H), 3.12 (s, 2H), 3.08 (s, 2H), 1.28 (s, 12H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 171.76, 156.28, 143.99, 113.46, 83.44, 57.07, 52.97, 45.45, 42.81, 24.97; **HRMS** (ESI) m/z calculated for $C_{17}H_{26}BO_6$ $[M+H]^+$: 337.1822, found: 337.1824; **$^{11}$B NMR** (128.4 MHz, $CDCl_3$): δ 29.83 (s).

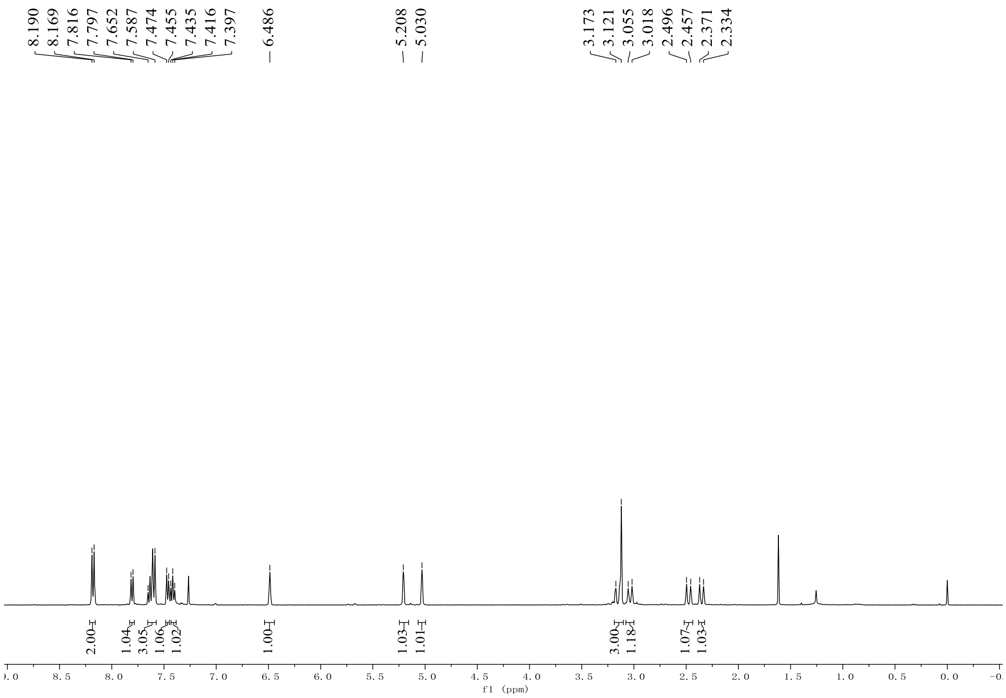


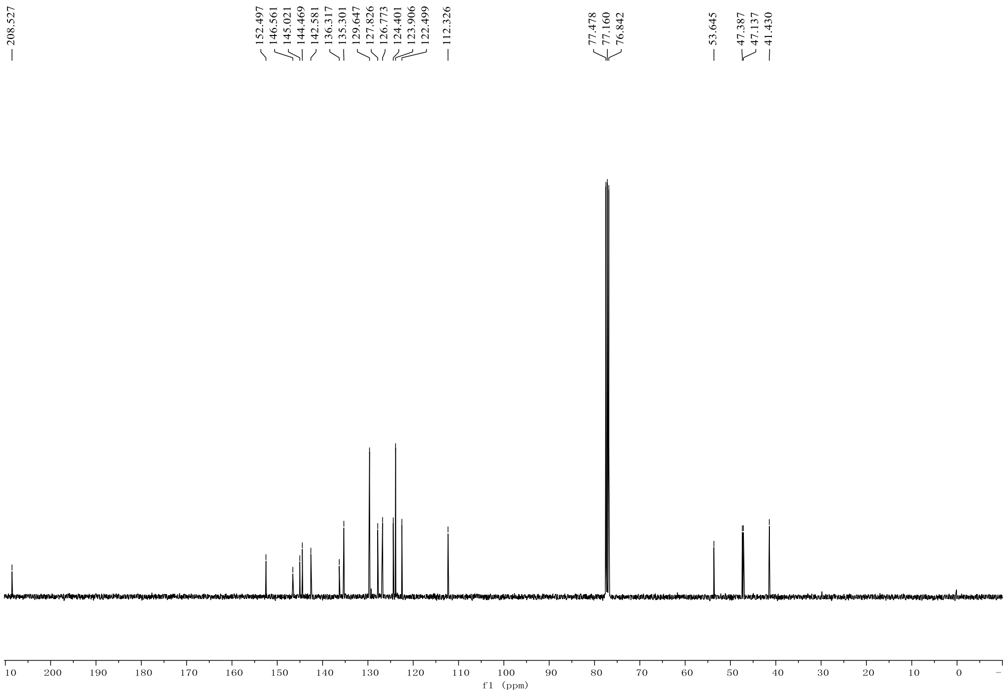





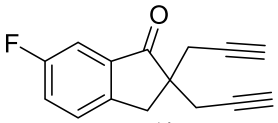

**6g**

According to above procedure D to get the product **6g** (54.3 mg, 82%) as yellow oil.
**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.59 (m, 3H),7.46 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 6.49 (s, 1H), 5.21 (s, 1H), 5.03 (s, 1H), 3.17 – 3.12 (m, 3H), 3.04 (d, *J* = 14.9 Hz, 1H), 2.48 (d, *J* = 15.9 Hz, 1H), 2.35 (d, *J* = 14.9 Hz, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$): δ 208.53, 152.50, 146.56, 145.02, 144.47, 142.58, 136.32, 135.30, 129.65, 127.83, 126.77, 124.40, 123.91, 122.50, 112.33, 53.64, 47.39, 47.14, 41.43; **HRMS** (ESI) m/z calculated for $C_{21}H_{18}NO_3$ $[M+H]^+$: 332.1287, found: 332.1282.

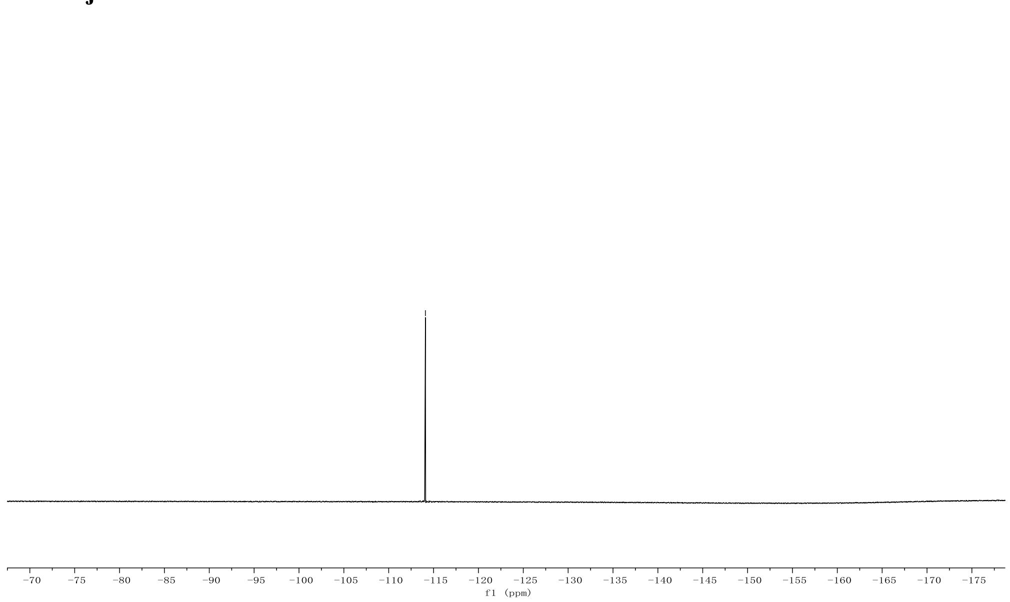


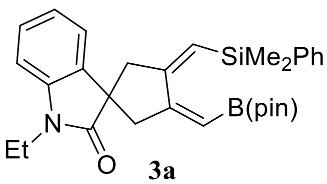
**[19]F NMR spectrum of 1j (376 MHz, $CDCl_3$).**



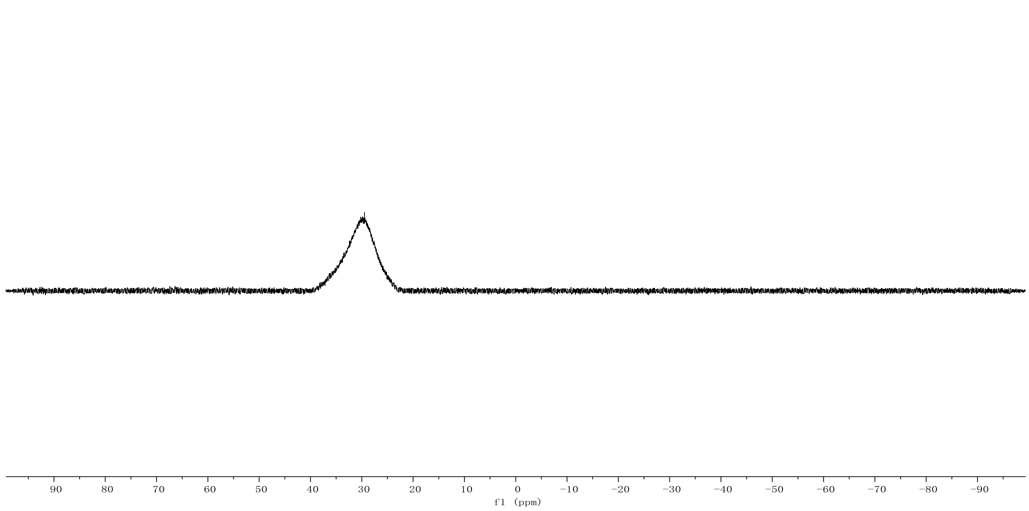

**1j**



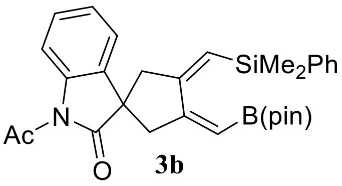

**[11]B NMR spectrum of 3a (128.4 MHz, $CDCl_3$)**



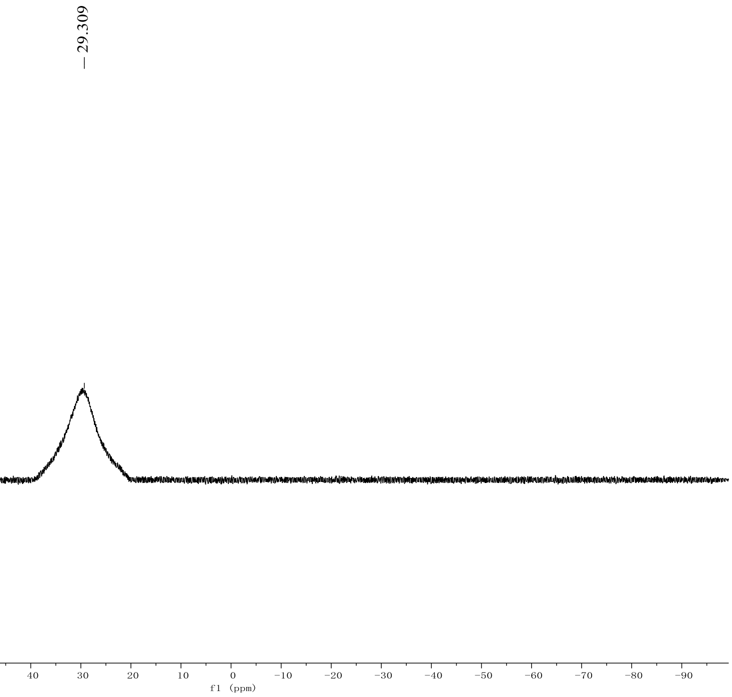

**3a**



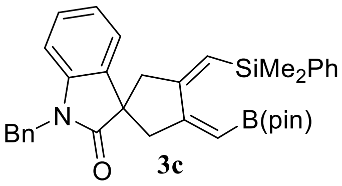
## $^{11}$B NMR spectrum of 3b (128.4 MHz, $CDCl_3$)



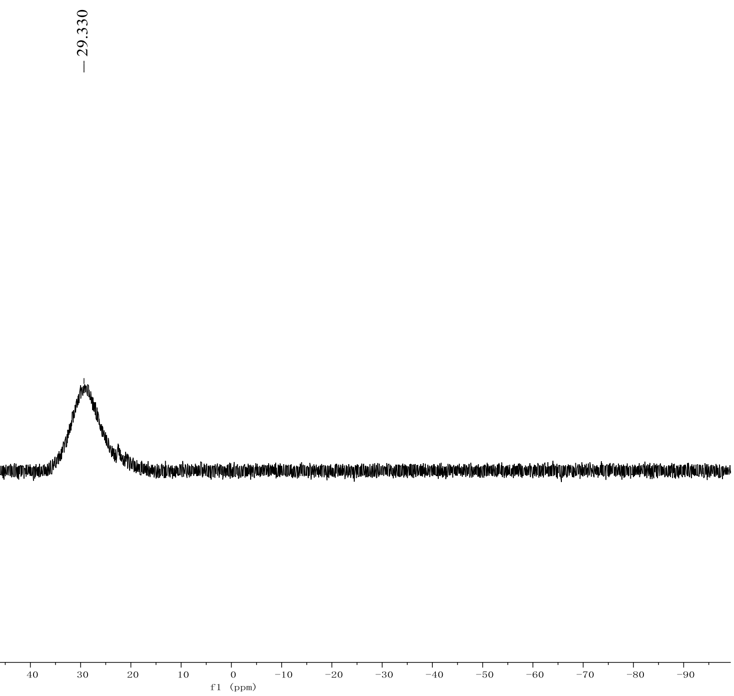

**3b**



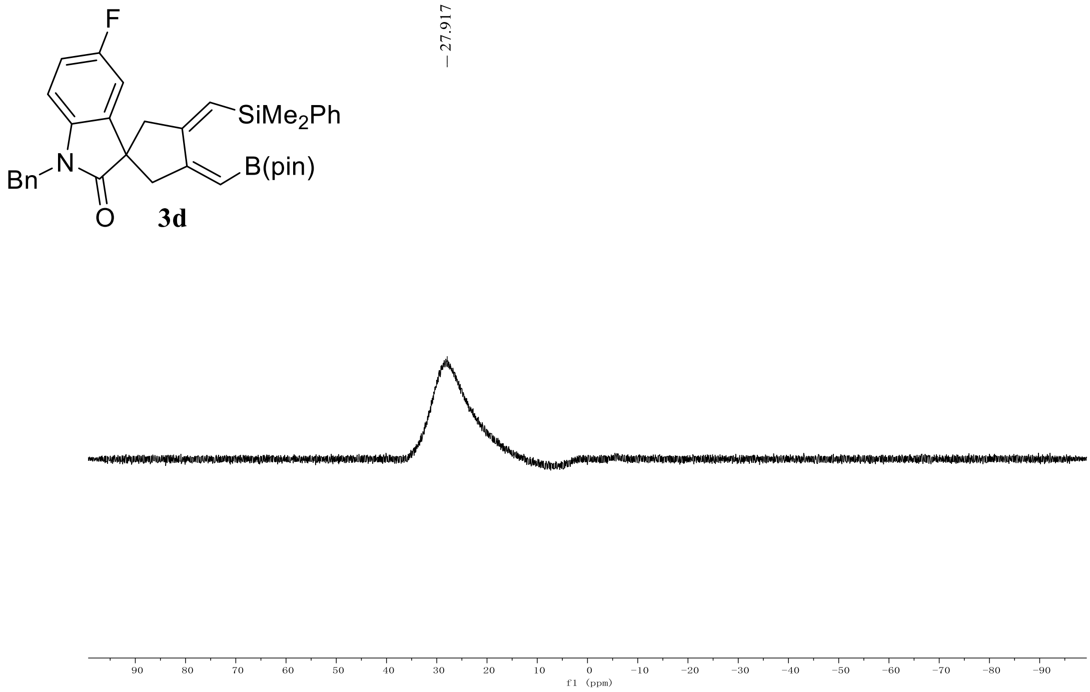

## $^{11}$B NMR spectrum of 3c (128.4 MHz, $CDCl_3$)



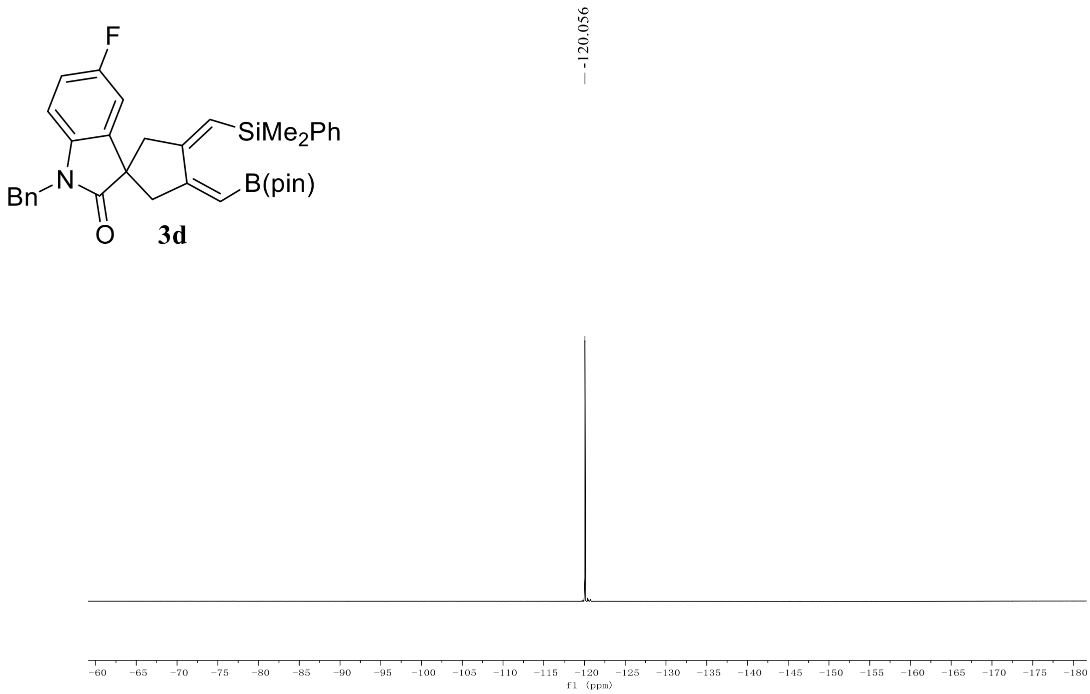

**3c**



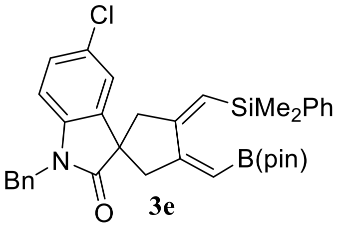
**$^{11}$B NMR spectrum of 3d (128.4 MHz, $CDCl_3$)**



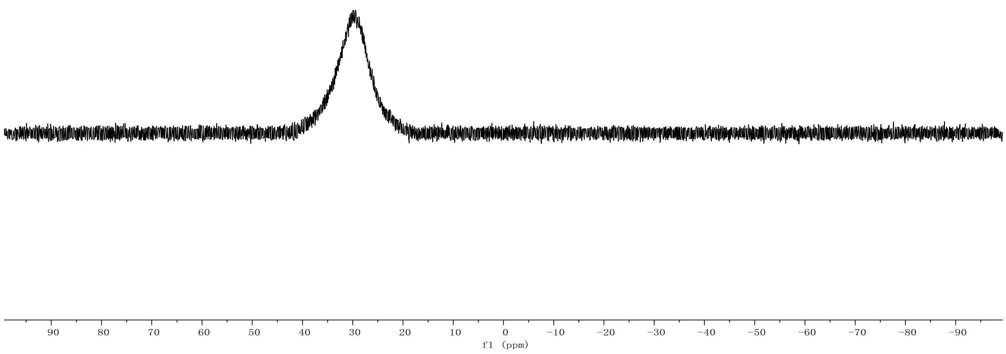

**$^{19}$F NMR spectrum of 3d (376 MHz, $CDCl_3$).**



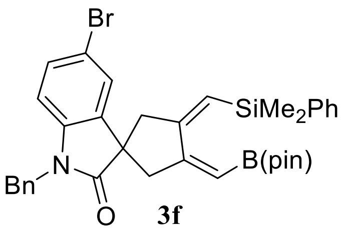
**[11]B NMR spectrum of 3e (128.4 MHz, $CDCl_3$)**



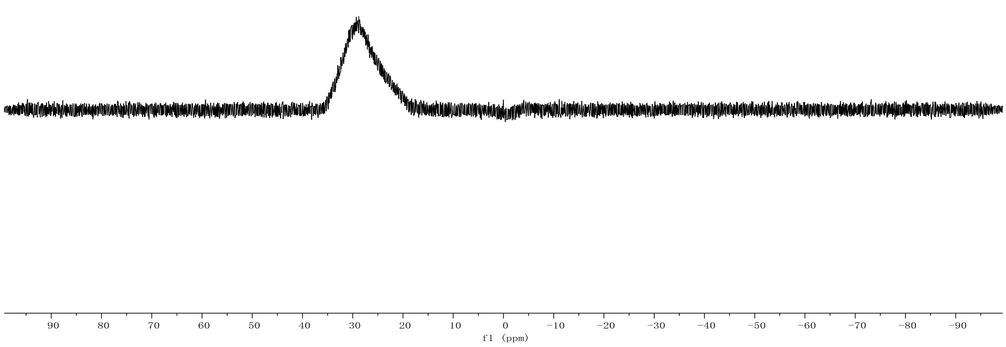

3e



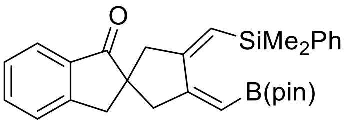

**[11]B NMR spectrum of 3f (128.4 MHz, $CDCl_3$)**



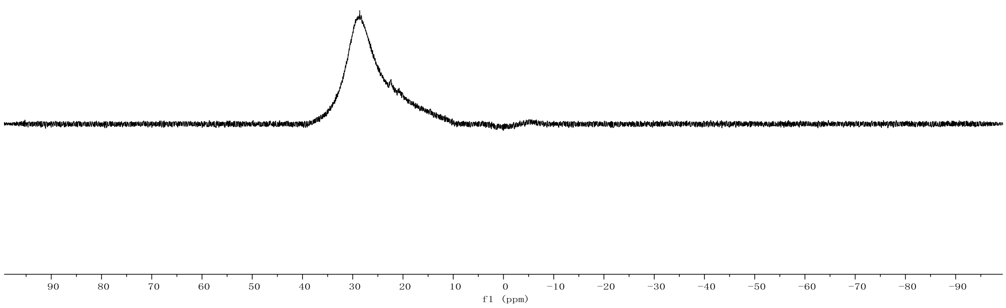

3f



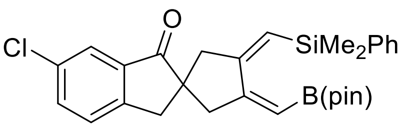
**$^{11}$B NMR spectrum of 3g (128.4 MHz, $CDCl_3$)**



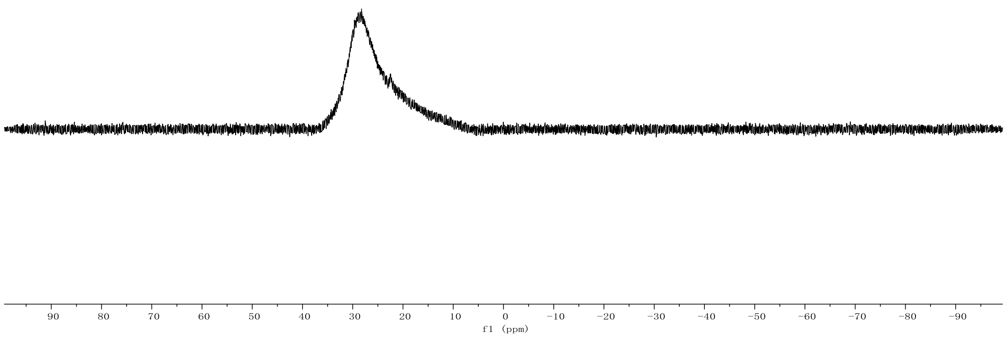

**3g**



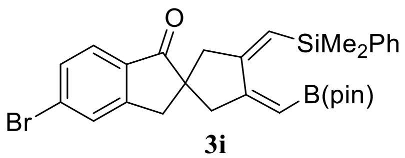

**$^{11}$B NMR spectrum of 3h (128.4 MHz, $CDCl_3$)**



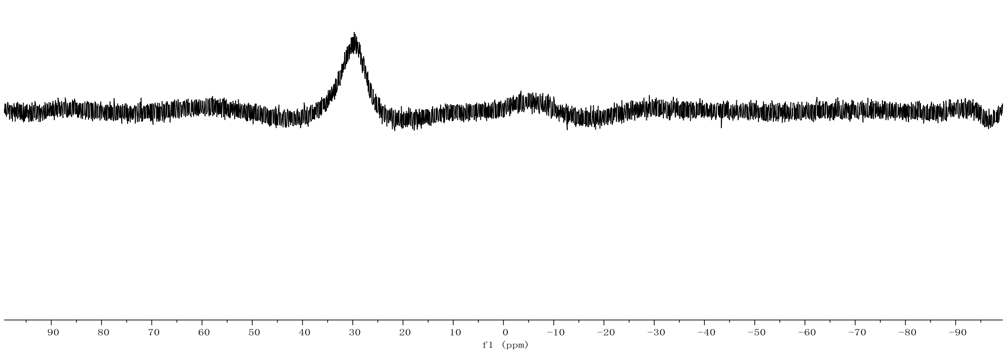

**3h**



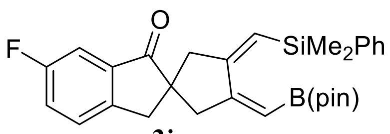
**$^{11}$B NMR spectrum of 3i (128.4 MHz, $CDCl_3$)**



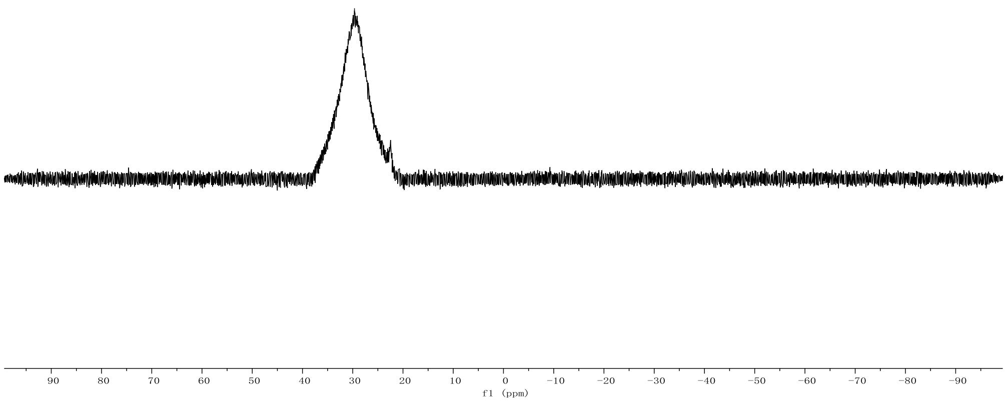

3i



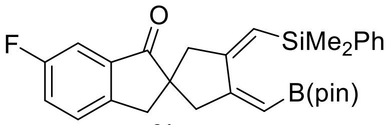

**$^{11}$B NMR spectrum of 3j (128.4 MHz, $CDCl_3$)**



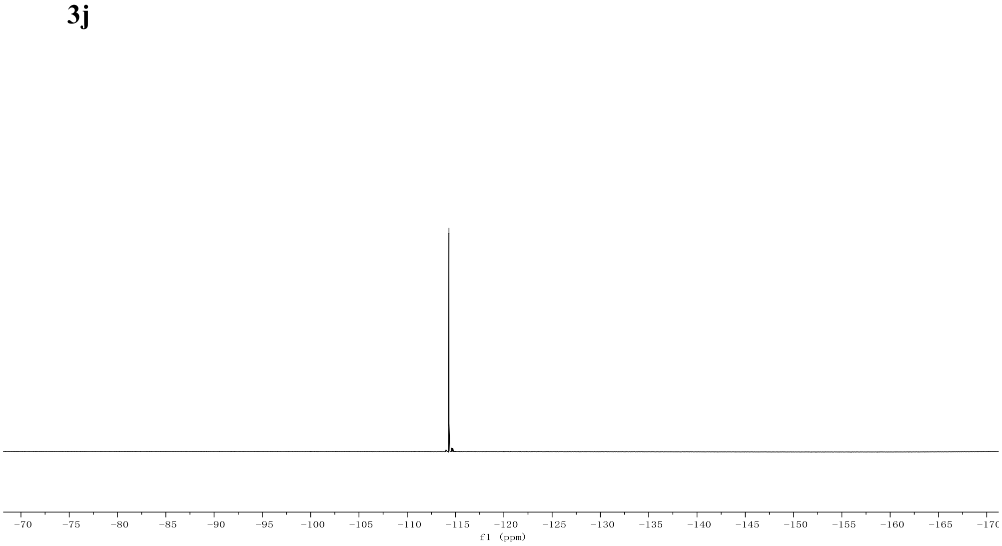

3j



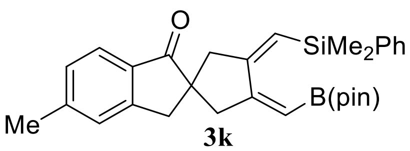
**19F NMR spectrum of 3j (376 MHz, CDCl3)**



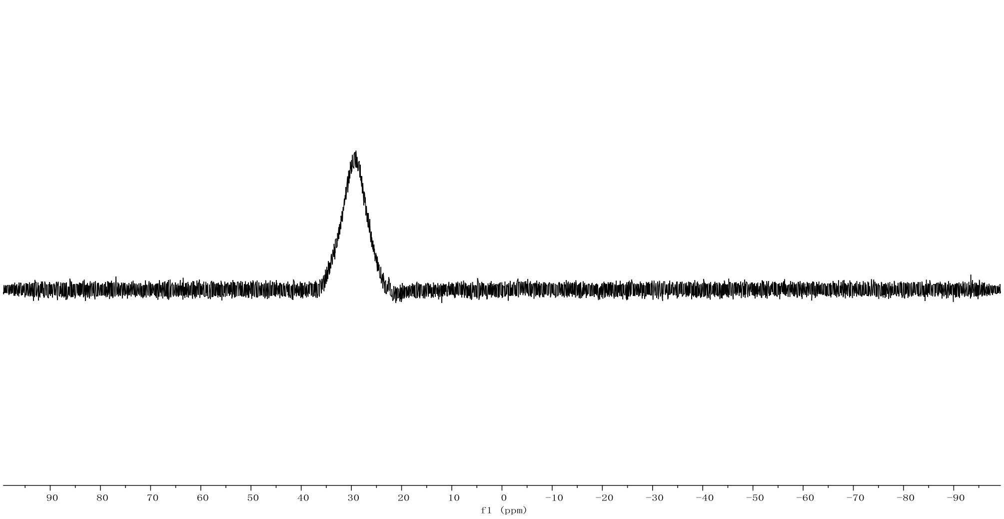

**3j**



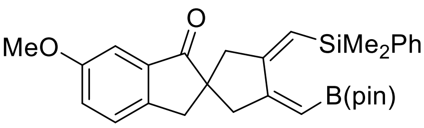

**$^{11}$B NMR spectrum of 3k (128.4 MHz, CDCl$_3$)**



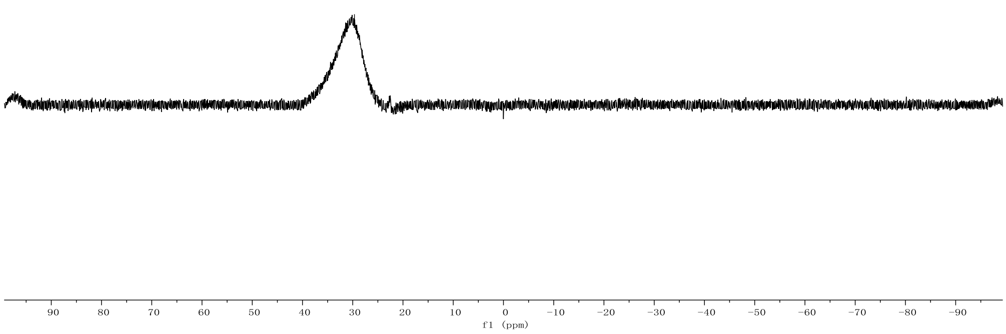

**3k**



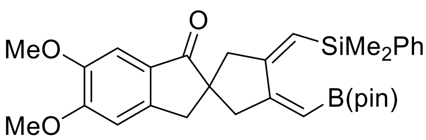
**$^{11}$B NMR spectrum of 3l (128.4 MHz, $CDCl_3$)**



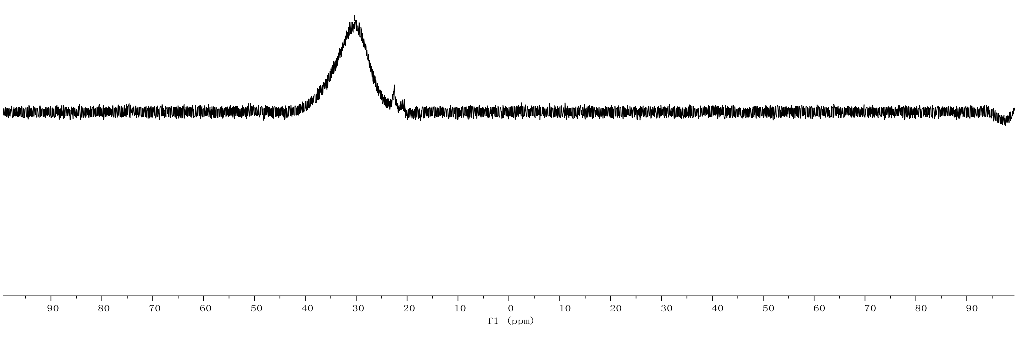

**3l**



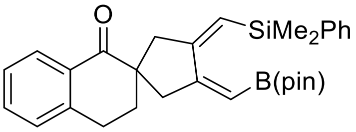

**$^{11}$B NMR spectrum of 3m (128.4 MHz, $CDCl_3$)**



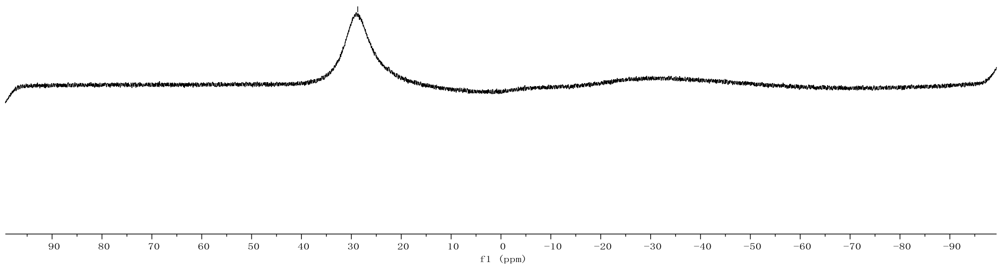

**3m**



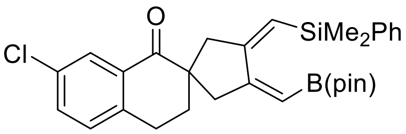
**$^{11}$B NMR spectrum of 3n (128.4 MHz, $CDCl_3$)**



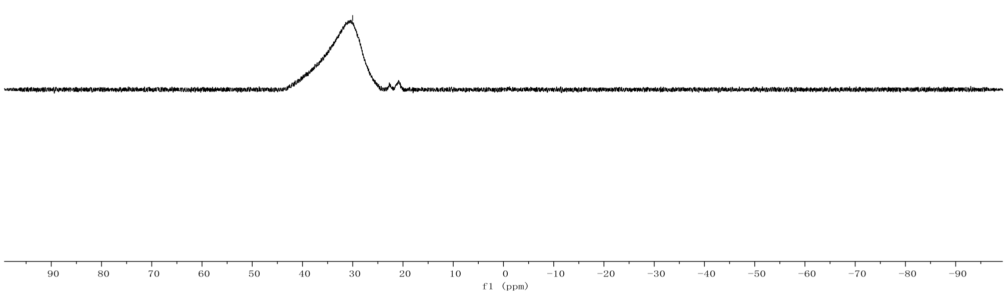

3n



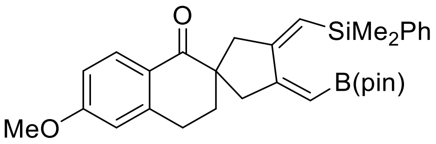

**$^{11}$B NMR spectrum of 3o (128.4 MHz, $CDCl_3$)**



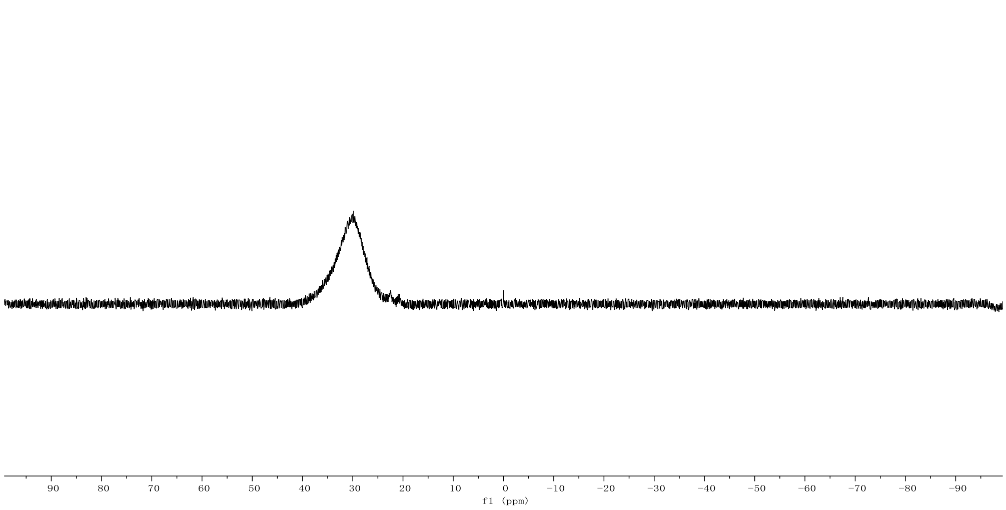

3o



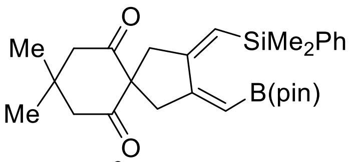
## $^{11}$B NMR spectrum of 3p (128.4 MHz, $CDCl_3$)



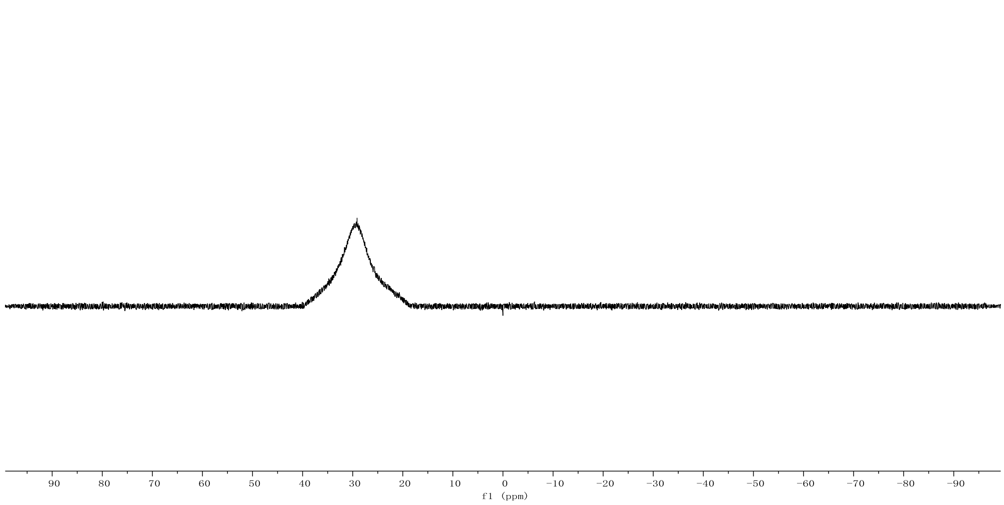

**3p**



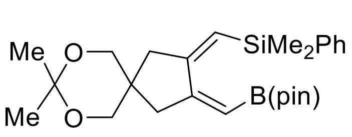

## $^{11}$B NMR spectrum of 3q (128.4 MHz, $CDCl_3$)



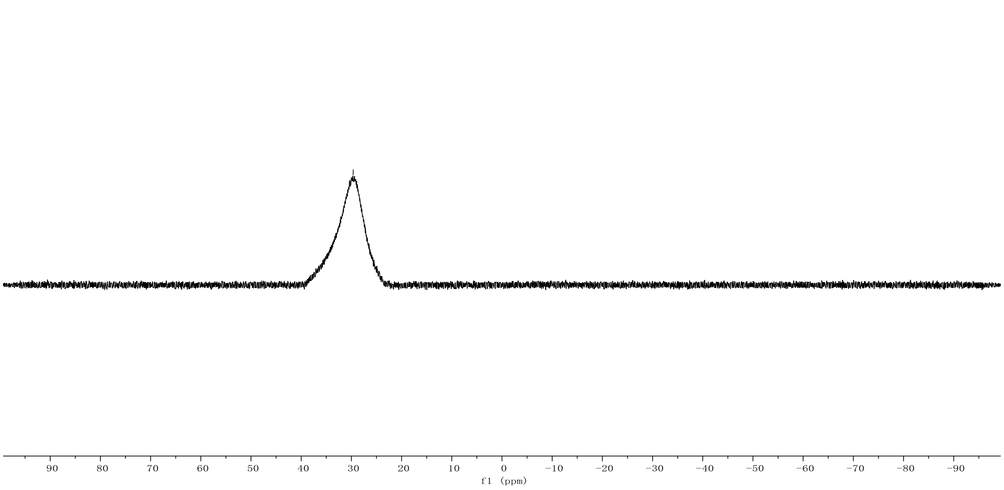

**3q**



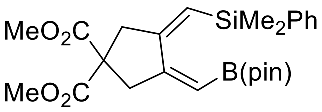
## $^{11}$B NMR spectrum of 3r (128.4 MHz, $CDCl_3$)



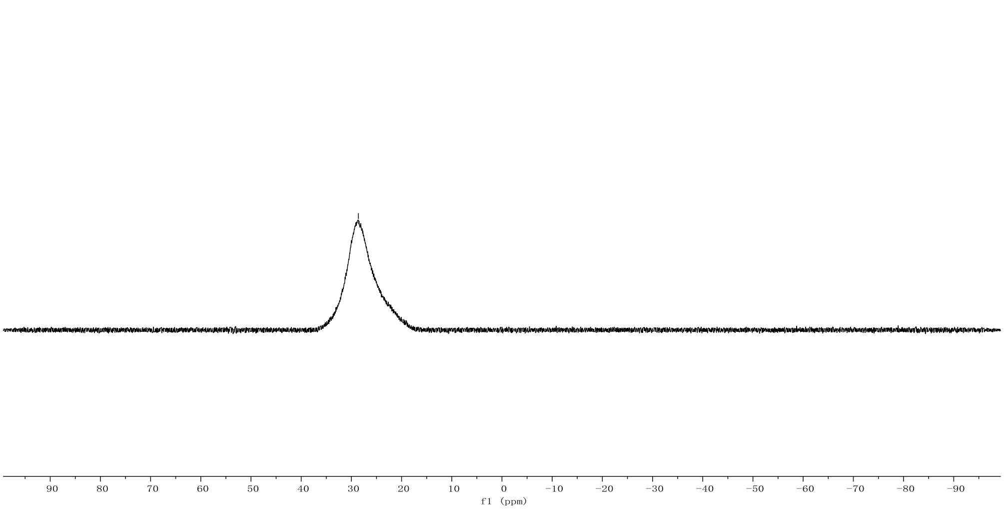

**3r**



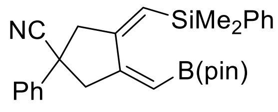

## $^{11}$B NMR spectrum of 3s (128.4 MHz, $CDCl_3$)



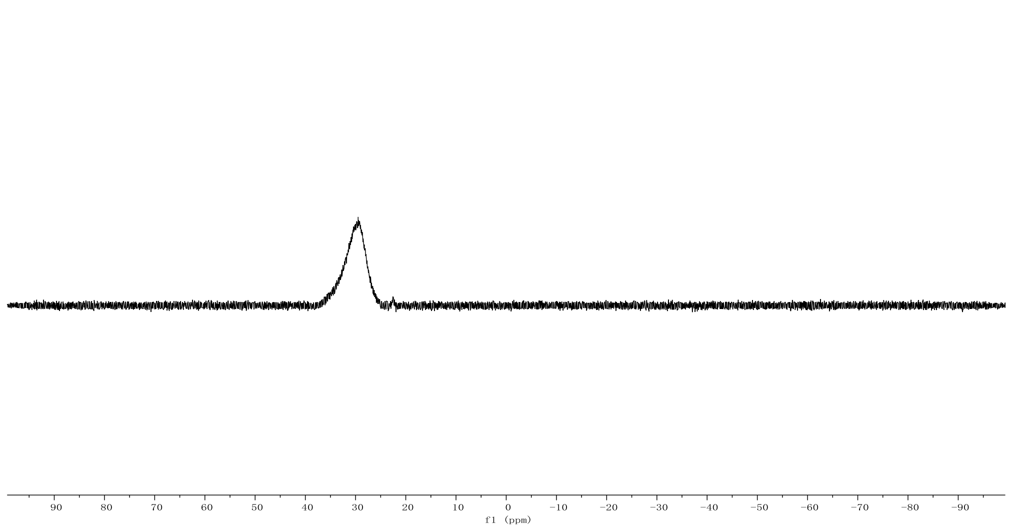

**3s**



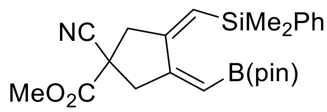
$^{11}$B NMR spectrum of 3t (128.4 MHz, $CDCl_3$)



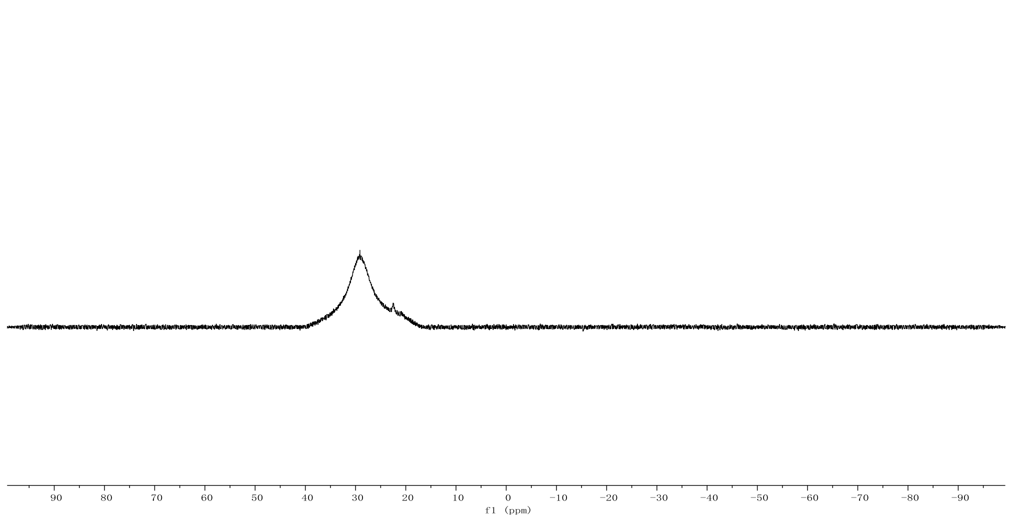

**3t**



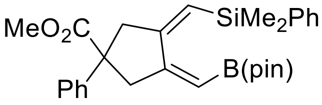

$^{11}$B NMR spectrum of 3u (128.4 MHz, $CDCl_3$)



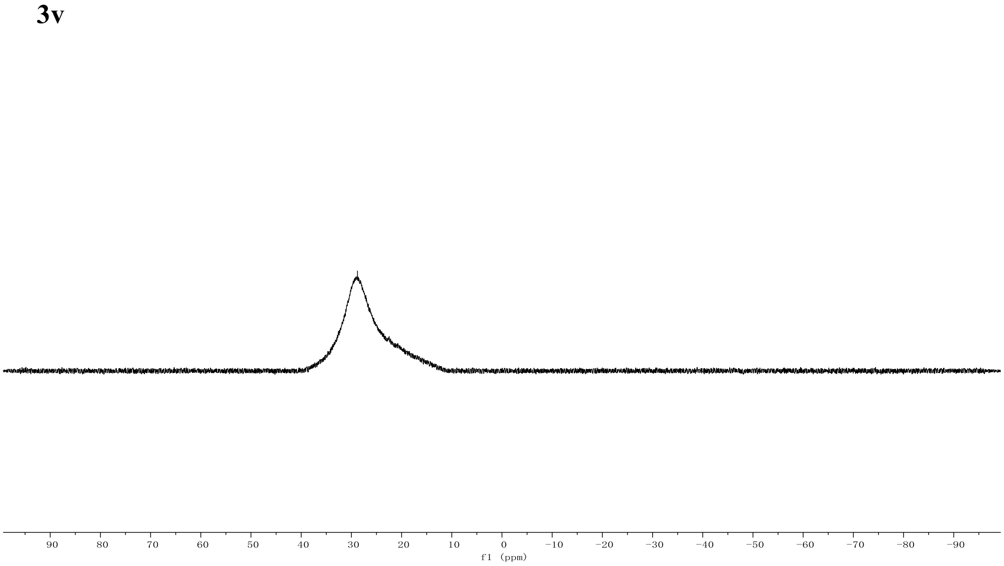

**3u**



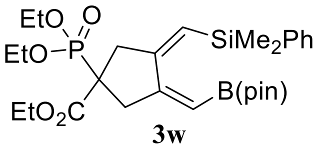
**$^{11}$B NMR spectrum of 3v (128.4 MHz, $CDCl_3$)**



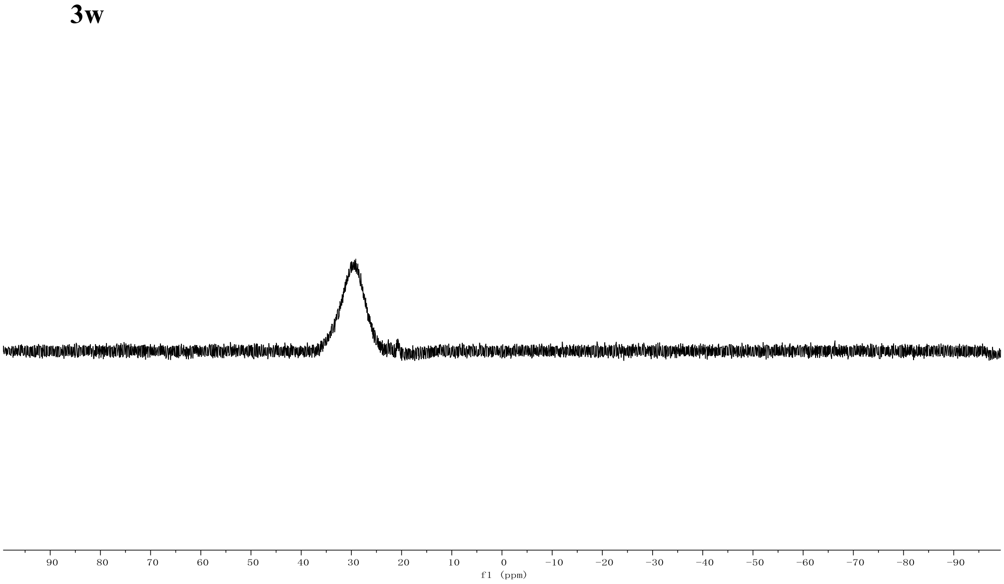

**3v**



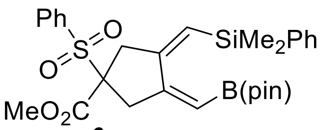

**$^{11}$B NMR spectrum of 3w (128.4 MHz, $CDCl_3$)**



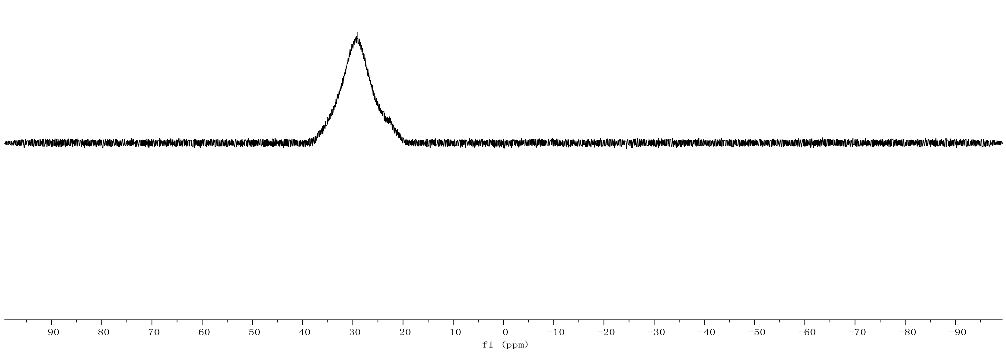

**3w**



## $^{11}$B NMR spectrum of 3x (128.4 MHz, $CDCl_3$)

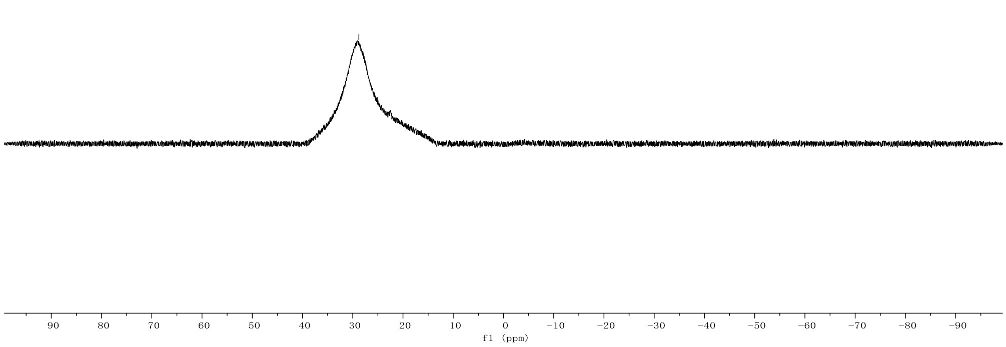



**3x**

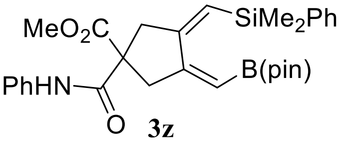



## $^{11}$B NMR spectrum of 3y (128.4 MHz, $CDCl_3$)

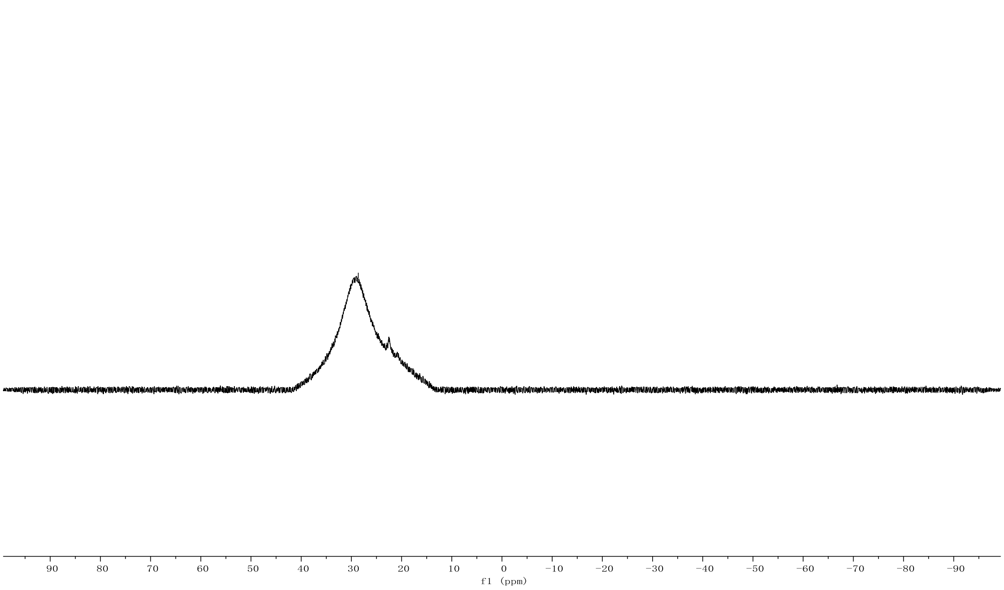

**3y**



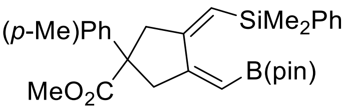
**$^{11}$B NMR spectrum of 3z (128.4 MHz, $CDCl_3$)**



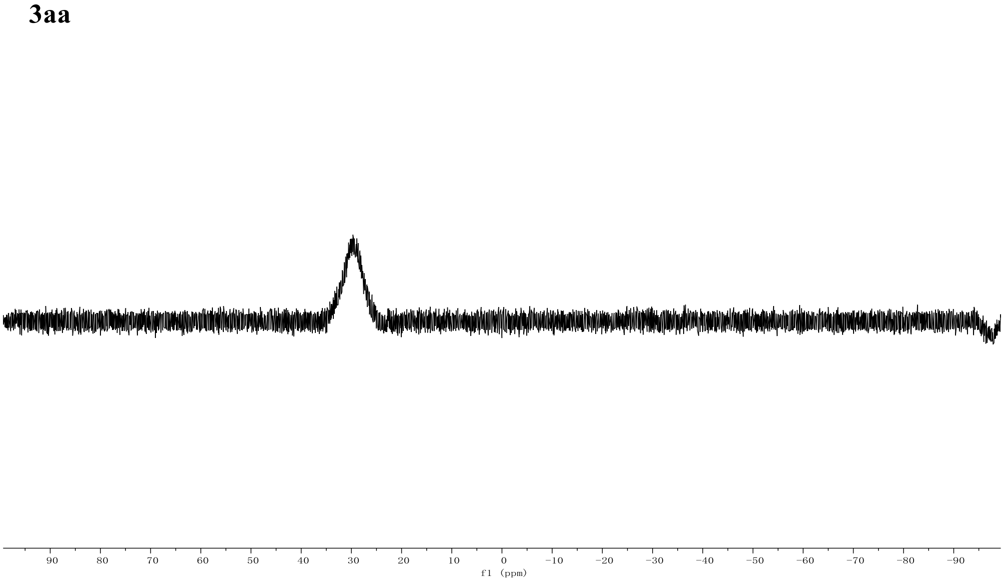

**3z**



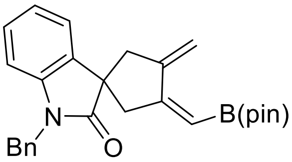

**$^{11}$B NMR spectrum of 3aa (128.4 MHz, $CDCl_3$)**



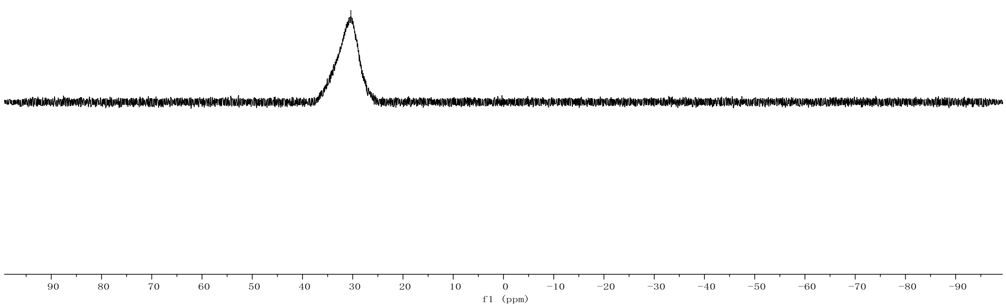

**3aa**



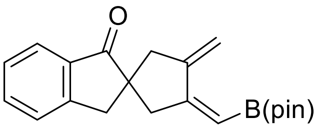
**$^{11}$B NMR spectrum of 5c (128.4 MHz, $CDCl_3$)**



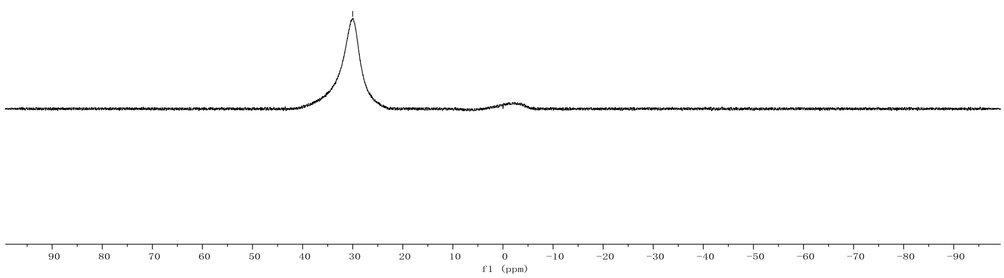
5c



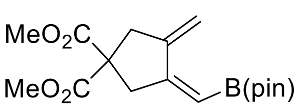

**$^{11}$B NMR spectrum of 5g (128.4 MHz, $CDCl_3$)**



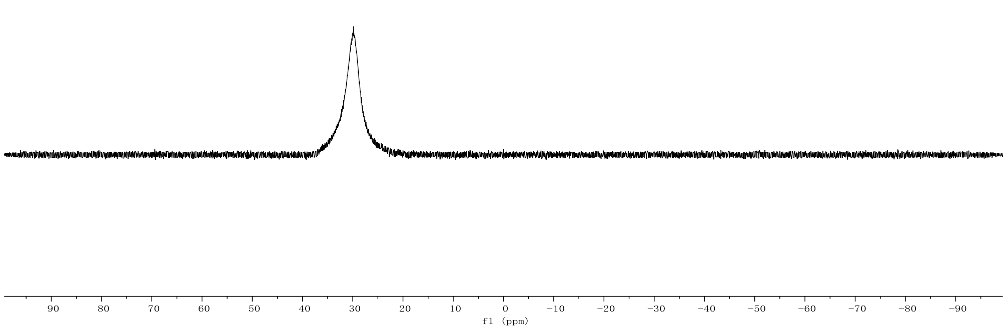
5g




**$^{11}$B NMR spectrum of 5s (128.4 MHz, $CDCl_3$)**



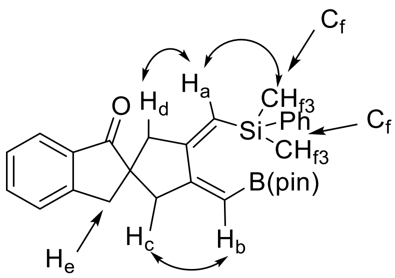
**5s**



## IV. Stereochemistry Analysis of Products.

**Relative configuration analysis of (*Z*, *Z*)-3g:** The relative configuration of compound **3g** was determined from $^{1}H$-$^{13}C$ HMBC 2D NMR and 1D-NOE spectroscopy (**Figure S1, S2**). Firstly, HMBC correlations from $H_f$ and $H_a$ to $C_f$ help to assign the peak of proton $H_a$ in 1H NMR spectrum. Therefore, the correlation from $H_a$ and $H_d$ based on 1D-NOE experiment can confirm the relative configuration of vinylsilane fragment. Similarly, the correlation from $H_b$ and $H_c$ based on 1D-NOE experiment also determines the vinylboronate fragment with a ***Z***-configuration (**Figure S2**).

**Figure S1.** HMBC spectroscopy of **3g**.




**(Z,Z) 3g**

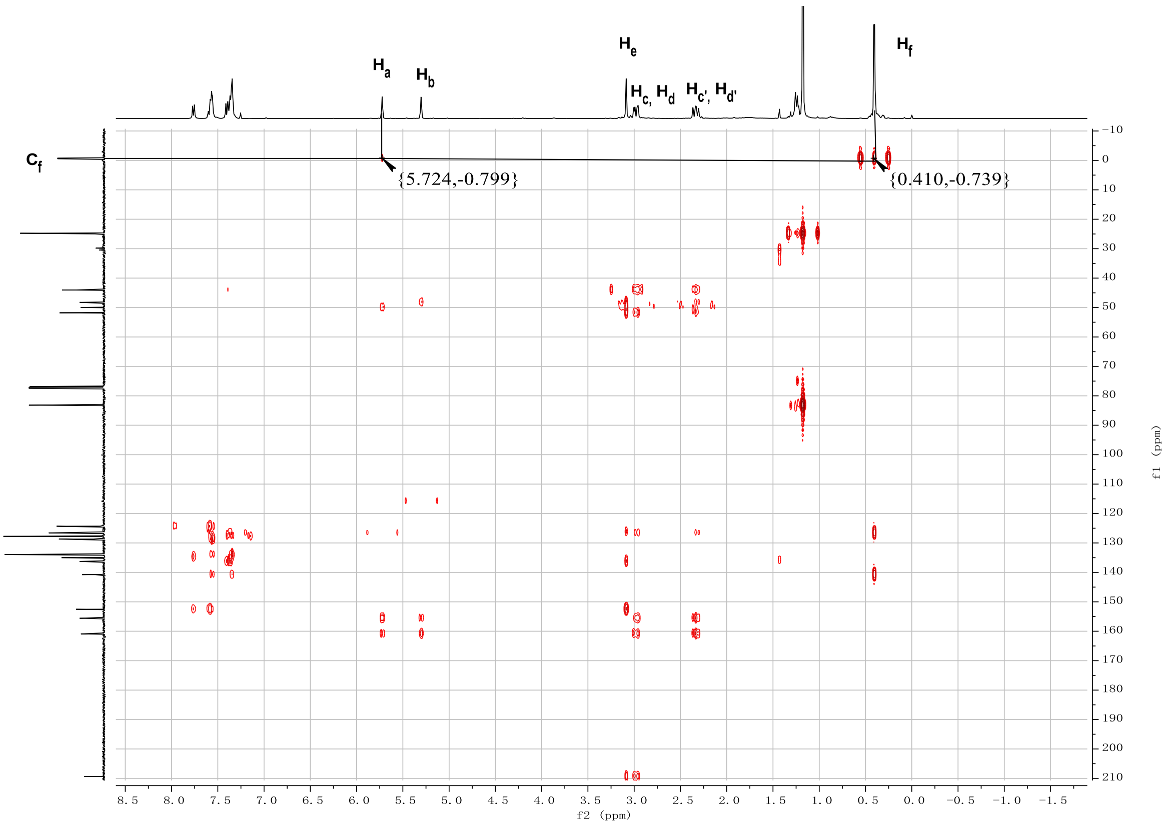
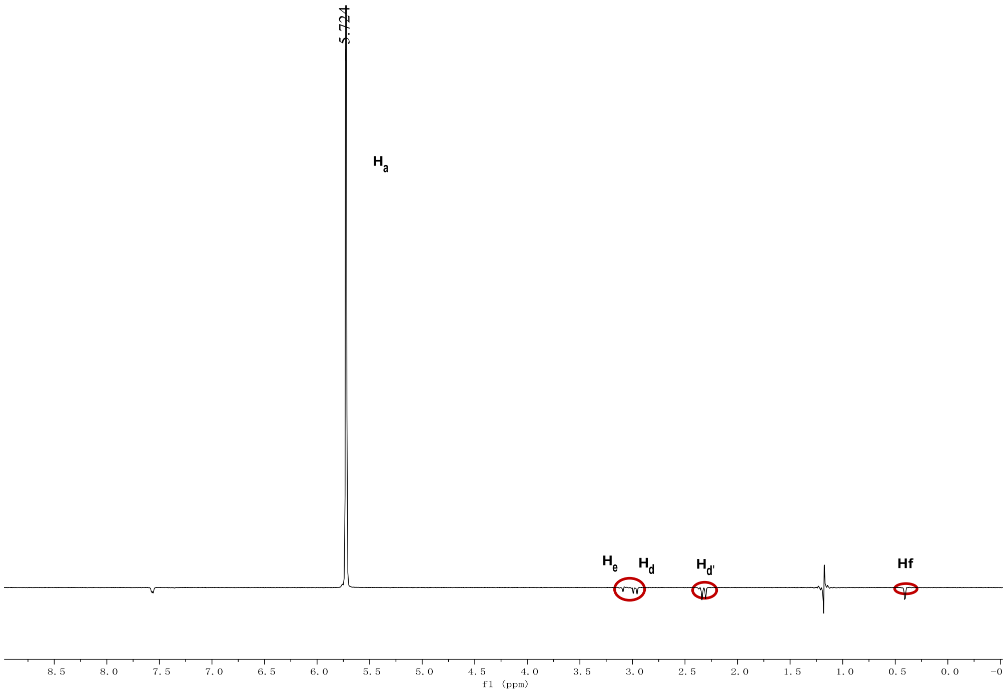
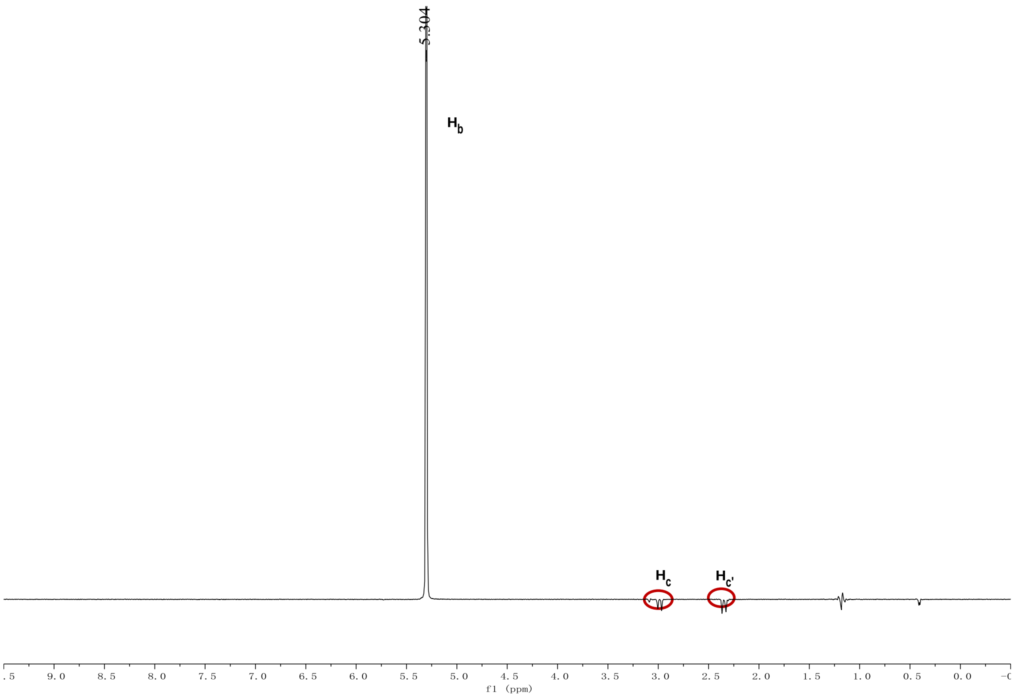


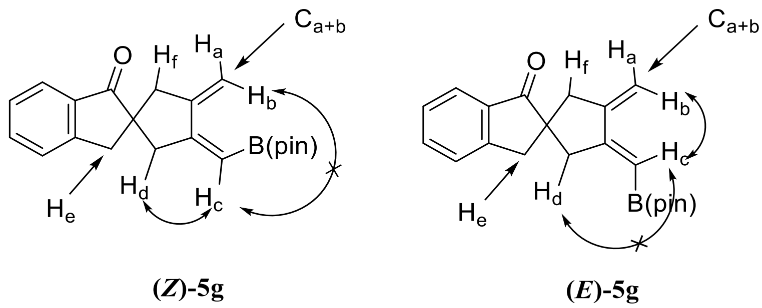
**Figure S2.** 1D-NOE spectroscopy of **3g.**



**Relative configuration analysis of (*Z*)-5g:** From chemical shift values of vinyl protons $H_a$, $H_b$, $H_c$ were assigned at δ 6.249, 5.378, 5.205, respectively. HSQC correlations from $H_a$ and $H_b$ to $C_{a+b}$ help to verify the peak of proton $H_c$ in $^1$H NMR spectrum (**Figure S3**). In consequence, the 1D-NOE correlation from $H_c$ and $H_d$ observed could determine the vinylboronate fragment of compound **5g** with a ***Z***-configuration (**Figure S4**).

**Figure S3.** HSQC spectroscope of **5g**.



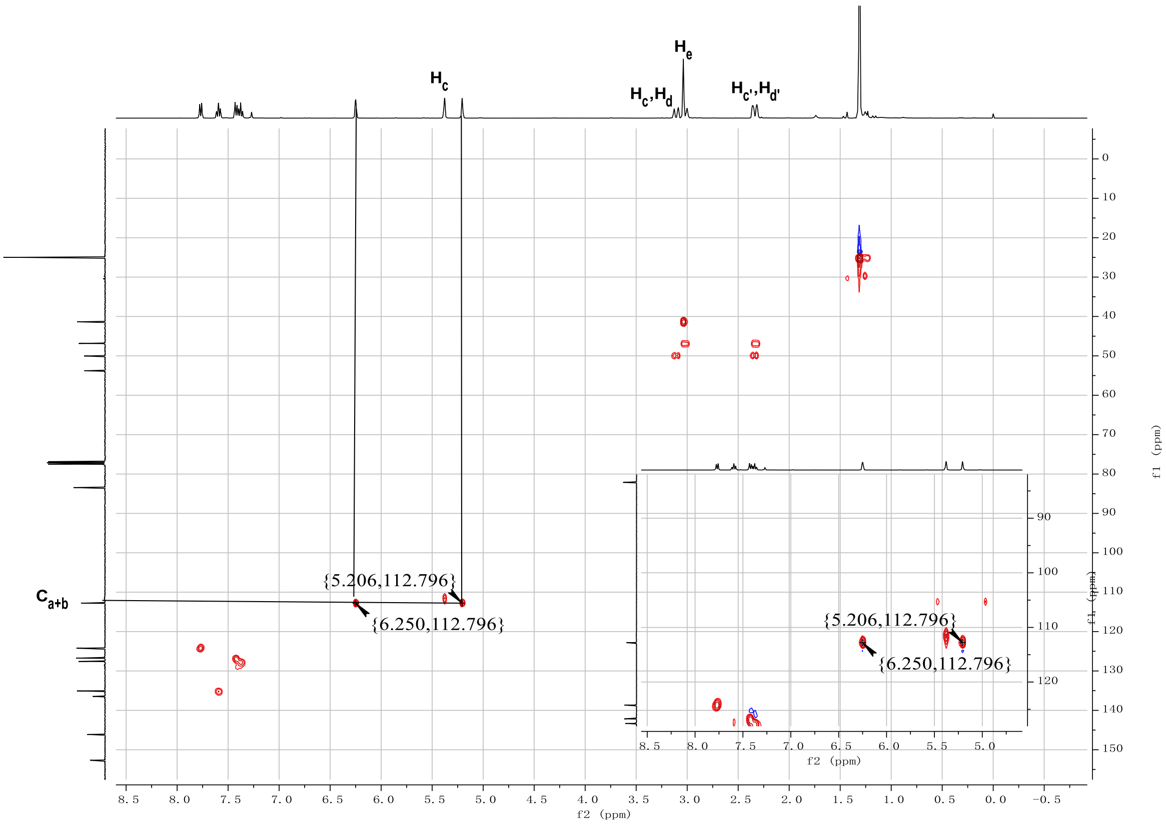
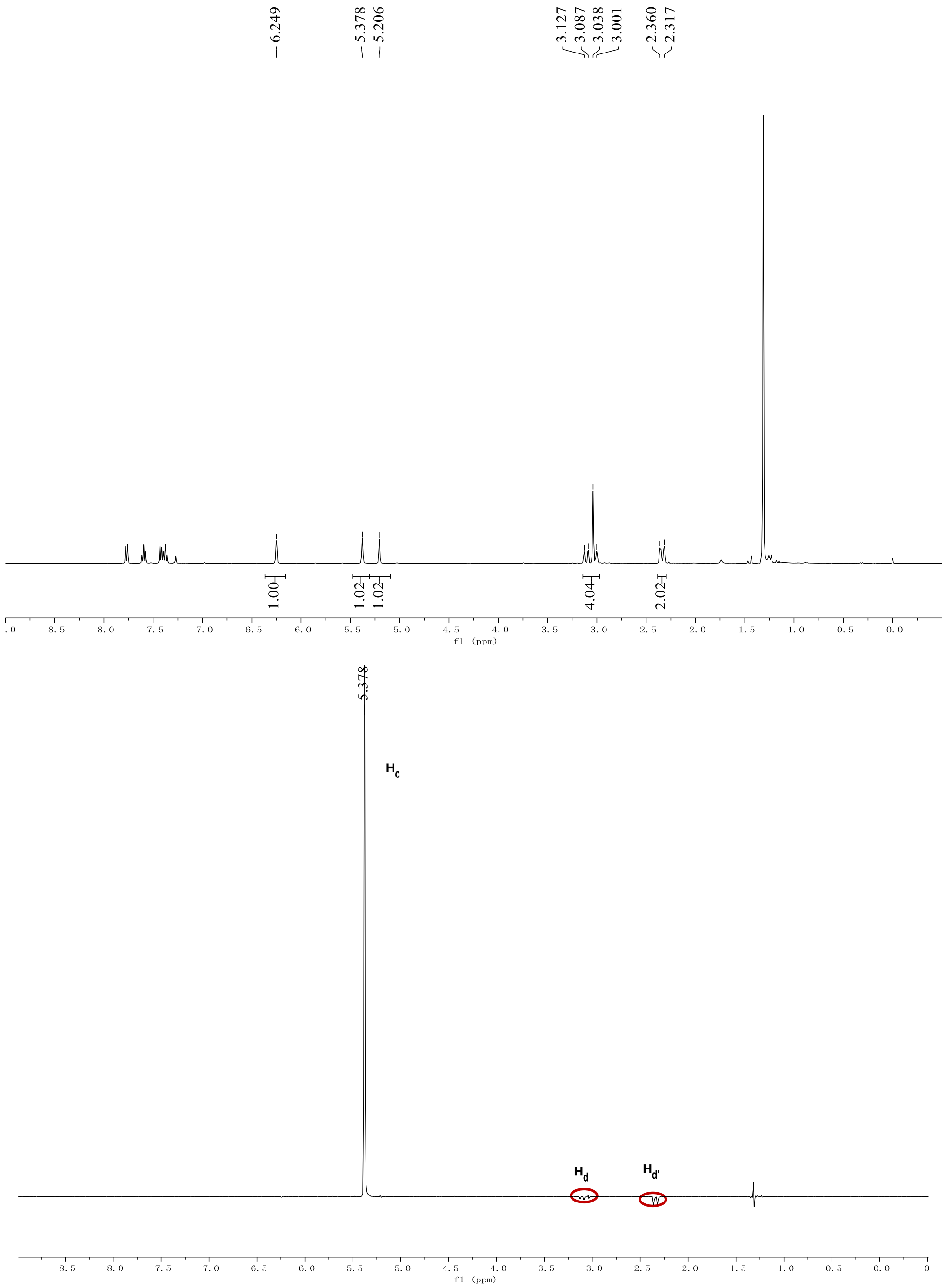



**Figure S4.** 1D-NOE spectrum of **5g.**



## V. References


1. F. Zhou, C. Tan, J. Tang, Y.-Y. Zhang, W.-M. Gao, H.-H. Wu, Y.-H. Yu and J. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 10994.
2. H. E. Fried and F. G. Bordwel, *J. Org. Chem.*, 1991, **56**, 4218.
3. J. M. Ellis, L. E. Overman, H. R. Tanner and J. Wang, *J. Org. Chem.*, 2008, **73**, 9151.
4. A.-C. Cantet, H. Carreyre, J.-P. Gesson, M.-P. Jouannetaud and B. Renoux, *J. Org. Chem.*, 2008, **73**, 2875.
5. O. I. Artyushin, S. N. Osipov, G.-V. Röschenthaler and I. L. Odinets, *Synthesis* 2009, **21**, 3579.
6. H. Clavier, L. Giordano and A. Tenaglia, *Angew. Chem. Int. Ed.*, 2012, **51**, 8648.
7. J.-M. Yang, X.-Y. Tang, Y. Wei and M. Shi, *Adv. synth. catal.*, 2013, **355**, 3545.
8. S. Kotha and R. Ali, *Tetrahedron*, 2015, **71**, 1597.
9. A. S. K. Hashmi, T. Häffner, M. Rudolph and F. Rominger, *Chem. Eur. J.*, 2011, **17**, 8195.
10. M. Fujinaga, T. Murafuji, K. Kurotobi and Y. Sugihara, *Tetrahedron*, 2009, **65**, 7115.
11. L.T. Kliman, S. N. Mlynarski, G. E. Ferris and J. P. Morken, *Angew. Chem. Int. Ed.*, 2012, **51**, 521.
12. R. R. Singidi, A. M. Kutney, J. C. Gallucci and T. V. RajanBabu, *J. Am. Chem. Soc.*, 2010, **132**, 13078.
13. S. E. Korkis, D. J. Burns and H. W. Lam, *J. Am. Chem. Soc.*, 2016, **138**, 12252.