Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-Catalyzed Silylation Reactions of Propargyl Epoxides: Easy Access to 2,3-Allenols and Stereodefined Alkenes

Xi-Hao Chang,[a] Zheng-Li Liu,[a] Yun-Cheng Luo,[a] Chao Yang,[a] Xiao-Wei Liu,[a] Bing-Chao Da,[a] Jie-Jun Li,[a] Tanveer Ahmad,[a] Teck-Peng Loh*[a,b,c] and Yun-He Xu*[a]

[a] Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China

[b] Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing, 211816, China

[c] Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University

E-mail: xyh0709@ustc.edu.cn

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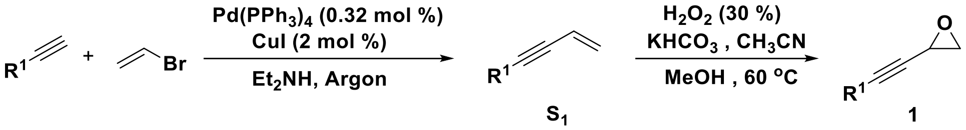
General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded at 25 ℃ on a Bruker Advance 400M NMR spectrometers ($CDCl_3$ as solvent). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of chloroform-*d* (δ 77.00 triplet). High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF.

2. Experimental Procedures

2.1 Procedures for the Synthesis of Starting Materials [1, 2, 3]

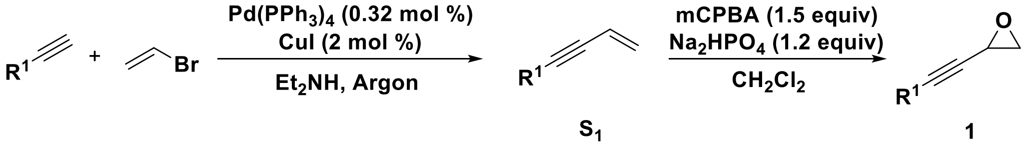
Method A:



S_1: In an oven dried flask, a mixture of $Pd(PPh_3)_4$ (55 mg, 0.048 mmol, 0.32 mol %) and CuI (57 mg, 0.3 mmol, 2 mol %) were dissolved in Et_2NH (7.5 mL) under argon. After cooling to –10 ℃, alkyne (15 mmol) and vinyl bromide (20 mL, 1.0 M in THF, 20 mmol) were added. The reaction mixture was kept stirring at room temperature for 20 h. The reaction mixture was poured in H_2O, and extracted with Et_2O. The organic phase was washed with HCl (1 M), dried with $MgSO_4$ and concentrated to give crude compound. The crude product was purified by column chromatography over silica gel to give pure product **S_1**.

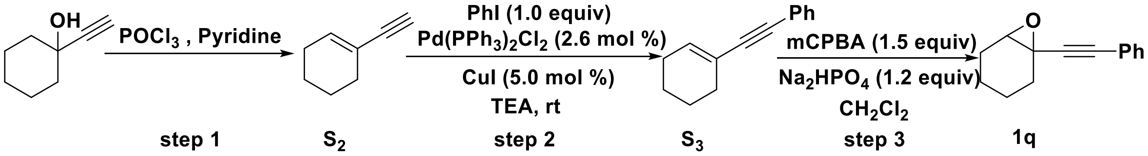
1: In an oven dried flask with S_1 (1.0 equiv) and $KHCO_3$ (25 mol %) was added MeOH (2.0 mL/mmol). To the resulting solution, 30% hydrogen peroxide (2.2 equiv) and acetonitrile (2.0 equiv) were added and the mixture was stirring at 60 ℃ until the S_1 was disappeared. The mixture was cooled to room temperature and added ethyl acetate, washed with H_2O. The organic phase was dried over anhydrous Na_2SO_4, concentrated under reduced pressure to give crude compound. The crude product was purified by column chromatography over silica gel to give the pure product **1**.

Method B:



1: The procedures for the synthesis of S_1 are same as method A. A dried flask was charged with the S_1 (1.0 equiv) and CH_2Cl_2 (3.0 mmol/mL) and cooled to 0 ℃. mCPBA (1.5 equiv) and Na_2HPO_4 (1.2 equiv) was added subsequently and the stirring was continued for overnight. The reaction mixture was diluted with saturated aqueous solution of Na_2CO_3, $Na_2S_2O_3$, NaOH (2N) and extracted with CH_2Cl_2. The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuo. The crude product was purified by column chromatography over silica gel to give the pure product **1**.

Synthesis of 1-(phenylethynyl)-7-oxabicyclo[4.1.0]heptane (1q) [3, 4]

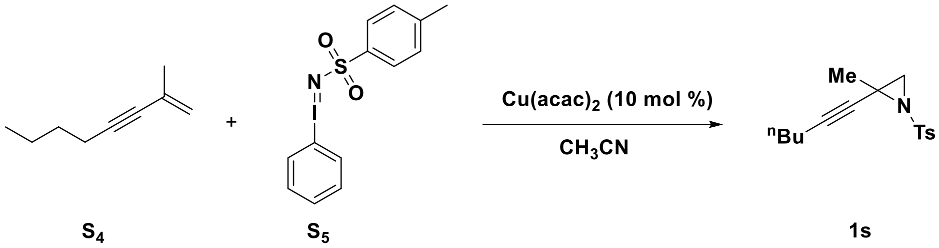


Step 1: A dried flask was charged with 1-ethynylcyclohexanol (1.0 equiv) and pyridine (0.5 mmol/mL) and cooled to 0 ℃. $POCl_3$ (1.5 equiv) was added dropwise and stirred for 5 hours at room temperature. The reaction mixture was then cooled to 0 ℃ and ice was added to quench the reaction. The layers were separated and the aqueous layer was extracted with Et_2O. The combined extracts were washed with saturated aqueous solution of $NaHCO_3$ and dried over anhydrous $MgSO_4$. After filtration the solvent was removed in vacuo and the product was purified by column chromatography. The product **S_2** was isolated as colorless oil in 40% yield.

Step 2: To a solution of compound PhI (1.0 equiv) and **S_2** (1.0 equiv) in solvent of Et_3N (8.5 mmol/ml) at 0 ℃ was added $PdCl_2(PPh_3)_2$ (2.6 mol %) and CuI (5.0 mol %). The reaction mixture was stirred at ambient temperature for 12 h. The reaction mixture was then filtered and concentrated under vacuo. The crude product was purified by column chromatography over silica gel to give the pure product **S_3** in 64% yield.

Step 3: A dried flask was charged with the **S_3** (1.0 equiv) and CH_2Cl_2 (3.0 mmol/mL) and cooled to 0 ℃. mCPBA (1.5 equiv) and Na_2HPO_4 (1.2 equiv) was added subsequently and the stirring was continued for overnight. The reaction mixture was diluted with saturated aqueous solution of Na_2CO_3, $Na_2S_2O_3$, NaOH (2N) and extracted with CH_2Cl_2. The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuo. The crude product was purified by column chromatography over silica gel to give the pure product **1q** in 54% yield.

Synthesis of 2-(hex-1-yn-1-yl)-2-methyl-1-tosylaziridine (1s) [5, 6]



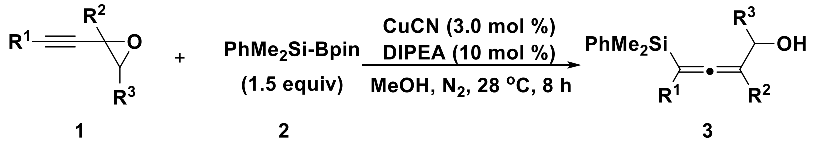
S_4 (2-methyloct-1-en-3-yne): To a mixture of hex-1-yne (1.0 equiv), $PdCl_2(PPh_3)_2$ (2.0 mol%), CuI (4.0 mol%) and TEA (1.0 mmol/mL) were added the compound 2-bromoprop-1-ene (1.0 mol/L in THF, 1.5 equiv). The mixture was stirred at 25 ℃ for about three hours until the starting material hex-1-yne was completely consumed (monitored by TLC). Then the mixture was diluted with ethyl acetate and the organic phase was washed with HCl (1 M). Then the solution was washed with saturated ammonium chloride again. The aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo, the residue was purified by column chromatography to afford the product **S_4** in 72% yield.

S_5: Diacetoxyiodobenzene (1.0 equiv) was added to a solution of KOH (2.5 equiv) and p-toluenesulfonamide (1.0 equiv) in methanol (4.0 mmol/ml) at 8 ℃. A yellow color developed within one minute. The cooling bath was removed, and the solution was allowed to warm to rt with stirring for 3 hours. Water (4.5 mmol/ml) was added and the reaction was refrigerated overnight. The precipitate was collected by filtration and dried overnight through a vacuum pump to afford a light yellow solid which was used without further purification or characterization in 62% yield.

1s (2-(hex-1-yn-1-yl)-2-methyl-1-tosylaziridine): To a mixture of **S_5** (1.0 equiv), Cu(acac)$_2$ (10.0 mol %) and acetonitrile (0.4 mmol/mL) were added the compound **S_4** (3.0 equiv). The mixture was stirred at 25 ℃ until the starting material **S_5** was completely consumed (monitored by TLC). Then the mixture was diluted with ethyl acetate and the organic phase was washed with water. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo, the residue was purified by column chromatography to afford the product **1s** as yellow oil in 37% yield.

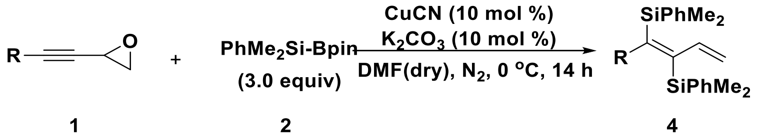
2.2 Procedures for the Synthesis of Products

General Procedures for the Synthesis of 3a-3r



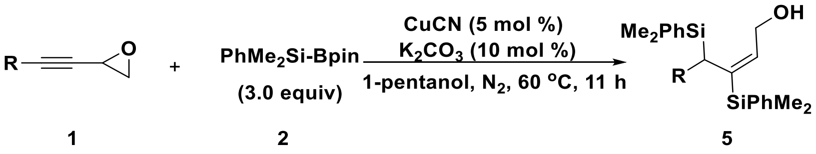
In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.006 mmol (0.54 mg, 3 mol %) CuCN and 0.02 mmol (2.58 mg, 10 mol %) DIPEA were added into 1.2 mL of MeOH under nitrogen atmosphere. Then 0.2 mmol **1** (1.0 equiv), 0.3 mmol (78.7 mg, 1.5 equiv) PhMe$_2$Si-Bpin were added to the tube subsequently under nitrogen atmosphere. The final solution was continued to stir for 8 h at room temperature (28 ^{o}C). Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography over silica gel to give the product **3.**

General Procedures for the Synthesis of 4a-4l



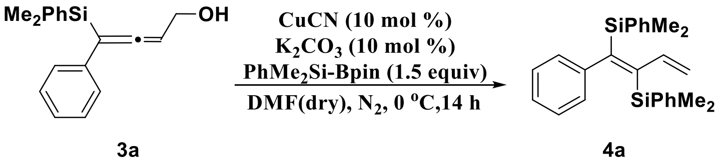
In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (1.79 mg, 10 mol %) CuCN and 0.02 mmol (2.8 mg, 10 mol %) K_2CO_3 were added into 1.2 mL of dry DMF under nitrogen atmosphere. Then 0.2 mmol **1** (1.0 equiv), 0.6 mmol (157 mg, 3.0 equiv) PhMe$_2$Si-Bpin were added to the tube subsequently under nitrogen atmosphere. The final solution was continued to stir for 14 h at 0 ^{o}C. Then the solution was diluted with DCM and washed with saturated ammonium chloride (15 mL×3). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography over 200-300 mesh basic aluminum oxide to give the product **4.**

General Procedures for the Synthesis of 5a-5g



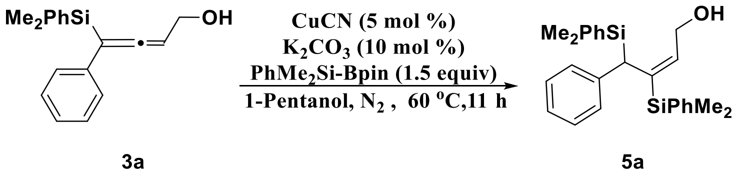
In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01 mmol (0.9 mg, 5 mol %) CuCN and 0.02 mmol (2.8 mg, 10 mol %) K_2CO_3 were added into 1.2 mL of 1-pentanol under nitrogen atmosphere. Then 0.2 mmol **1** (1.0 equiv), 0.6 mmol (157 mg, 3.0 equiv) PhMe$_2$Si-Bpin were added to the tube subsequently under nitrogen atmosphere. The final solution was continued to stir for 11 h at 60 °C. Then the solution was diluted with DCM and washed with brine (15 mL×3). The organic layer was added about 10g silica gel and stirred for 3 h. Then the solution was filtered and evaporated in vacuo. The residue was purified by column chromatography over silica gel to give the product **5.**

Procedures for the Synthesis of 4a from 3a



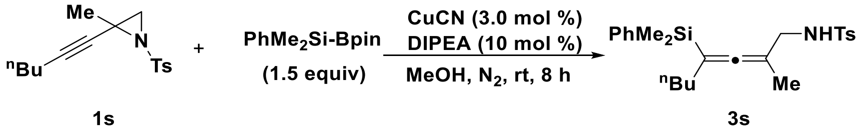
In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.02 mmol (1.79 mg, 10 mol %) CuCN and 0.02 mmol (2.8 mg, 10 mol %) K_2CO_3 were added into 1.2 mL of dry DMF under nitrogen atmosphere. Then 0.2 mmol **3a** (1.0 equiv), 0.3 mmol (78.7 mg, 1.5 equiv) $PhMe_2Si$-Bpin were added to the tube subsequently under nitrogen atmosphere. The final solution was continued to stir for 14 h at 0 °C. Then the solution was diluted with DCM and washed with saturated ammonium chloride (15 mL×3). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography over 200-300 mesh basic aluminum oxide. The product of **4a** was isolated as colorless oil in 71% yield (56.2 mg).

Procedures for the Synthesis of 5a from 3a



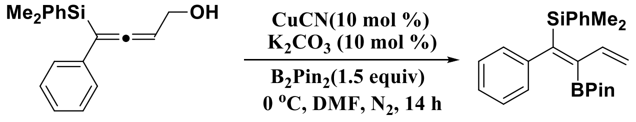
In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.01 mmol (0.9 mg, 5 mol %) CuCN and 0.02 mmol (2.8 mg, 10 mol %) K_2CO_3 were added into 1.2 mL of 1-pentanol under nitrogen atmosphere. Then 0.2 mmol **3a** (1.0 equiv), 0.3 mmol (78.7 mg, 1.5 equiv) $PhMe_2Si$-Bpin were added to the tube subsequently under nitrogen atmosphere. The final solution was continued to stir for 11 h at 60 °C. Then the solution was diluted with DCM and washed with brine (15 mL×3). The organic layer was added about 10g silica gel and stirred for 3 h. Then the solution was filtered and evaporated in vacuo. The residue was purified by column chromatography over silica gel. The product of **5a** was isolated as colorless oil in 82% yield (E/Z=95:5) (67.9 mg).

Procedures for the Synthesis of 3s from 1s



In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.006 mmol (0.54 mg, 3 mol %) CuCN and 0.02 mmol (2.58 mg, 10 mol %) DIPEA were added into 1.2 mL of MeOH under nitrogen atmosphere. Then 0.2 mmol **1s** (1.0 equiv), 0.3 mmol (78.7 mg, 1.5 equiv) $PhMe_2Si$-Bpin were added to the tube subsequently under nitrogen atmosphere. The final solution was continued to stir for 8 h at room temperature (25 °C). Then the solution was diluted with DCM and filtered through Celite. The final filtrate was concentrated under vacuum to afford the crude product which was isolated through flash column chromatography over silica gel. The product of **3s** was isolated as white solid in 98% yield (83.8 mg).

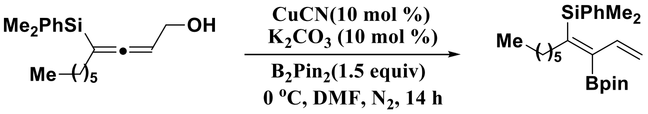
Procedures for the Synthesis of 6a from 3a



3a **6a**

In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.03 mmol (2.7 mg, 10 mol %) CuCN, 0.03 mmol (4.1 mg, 10 mol %) K_2CO_3 and 0.45 mmol (114.3 mg, 1.5 equiv) B_2Pin_2 were added into 1.5 mL of dry DMF under nitrogen atmosphere. Then 0.3 mmol **3a** (1.0 equiv) was added to the tube under nitrogen atmosphere. The final solution was continued to stir for 14 h at 0°C. Then the solution was diluted with DCM and washed with saturated ammonium chloride (15 mL×3). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography over silica gel. The product of **6a** was isolated as white solid in 94% yield (Z/E=73:17) (109.8 mg).

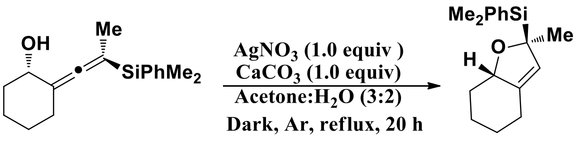
Procedures for the Synthesis of 6b from 3a



3a **6b**

In an oven dried 15 mL Schlenk tube equipped with a stirring bar, 0.024 mmol (2.2 mg, 10 mol %) CuCN, 0.024 mmol (3.3 mg, 10 mol %) K_2CO_3 and 0.36 mmol (91.4 mg, 1.5 equiv) B_2Pin_2 were added into 1.3 mL of dry DMF under nitrogen atmosphere. Then 0.24 mmol **3a** (1.0 equiv) was added to the tube under nitrogen atmosphere. The final solution was continued to stir for 14 h at 0°C. Then the solution was diluted with DCM and washed with saturated ammonium chloride (15 mL×3). The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography over silica gel. The product of **6b** was isolated as colorless oil in 85% yield (Z/E=84:16) (81.1 mg).

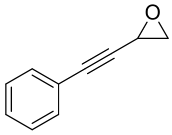
Procedures for the Synthesis of 7 from 3p [7, 8]



3p **7**

To a well-stirred solution of allene **3p** (0.228 mmol, 1.0 equiv) in 1.5 mL of acetone and 1.0 mL of H_2O was added $AgNO_3$ (0.228 mmol, 1.0 equiv) and $CaCO_3$ (0.228 mmol, 1.0 equiv) in the dark. The mixture was refluxed at 100 ℃ for 20 h. After refluxing, the mixture was cooled to room temperature and added water, the product was extracted with DCM (10 mL×2). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography over silica gel to afford the product of **7** as yellow oil in 62% yield (38.6 mg).

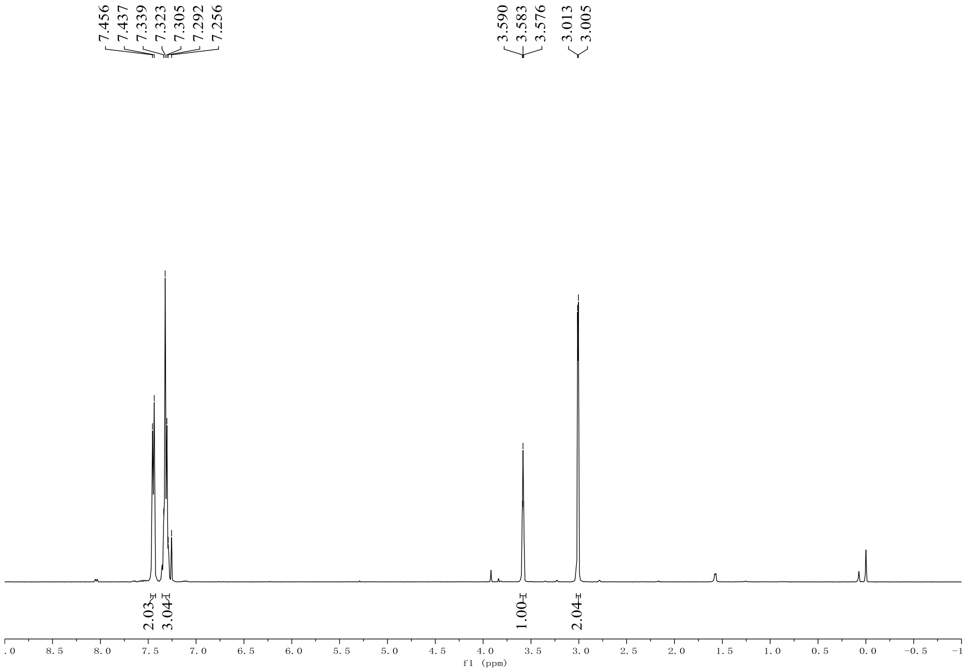
Characterization Data and Spectrum of Starting Materials and Products

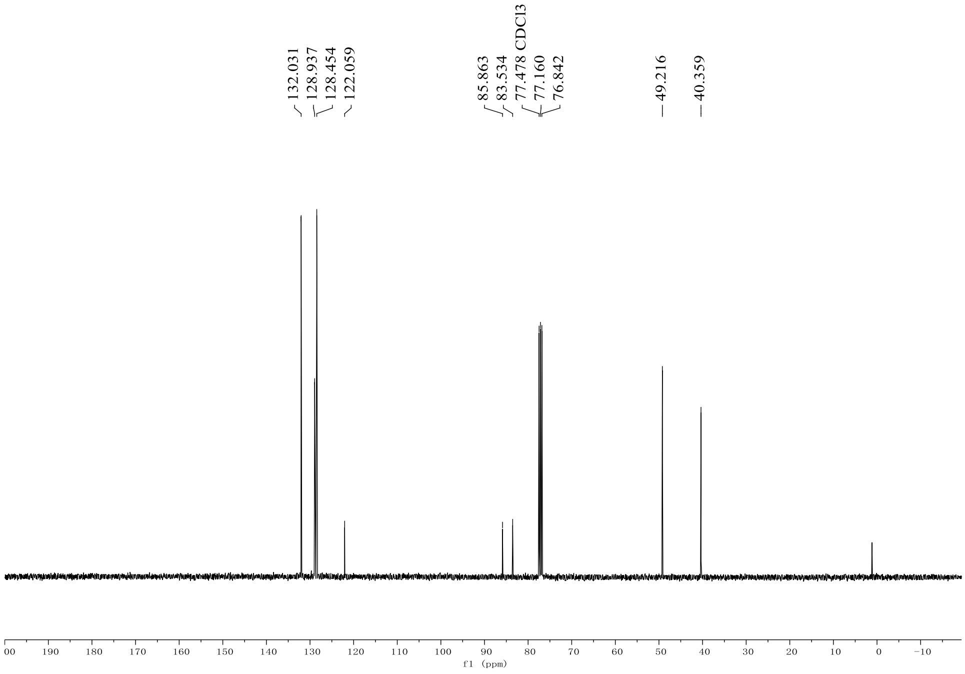


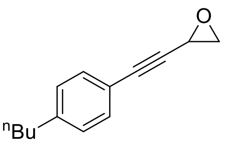
2-(phenylethynyl)oxirane (1a), R_f = 0.50 (Petroleum ether : EtOAc = 19:1), yellow oil. The procedures are according to the above method A in 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.35-7.28 (m, 3H), 3.58 (t, *J* = 2.8 Hz, 1H), 3.01 (d, *J* = 3.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.0, 128.94, 128.45, 122.06, 85.86, 83.53, 49.22, 40.36.

HRMS (ESI) m/z calculated for $C_{10}H_9O$ $[M+H]^+$: 145.0653, found: 145.0656.





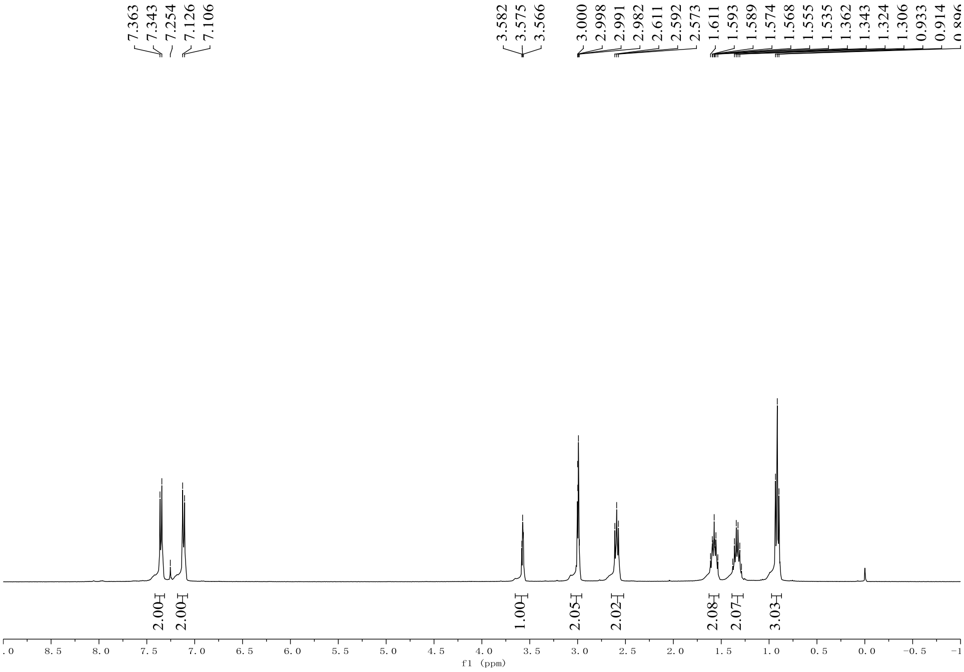


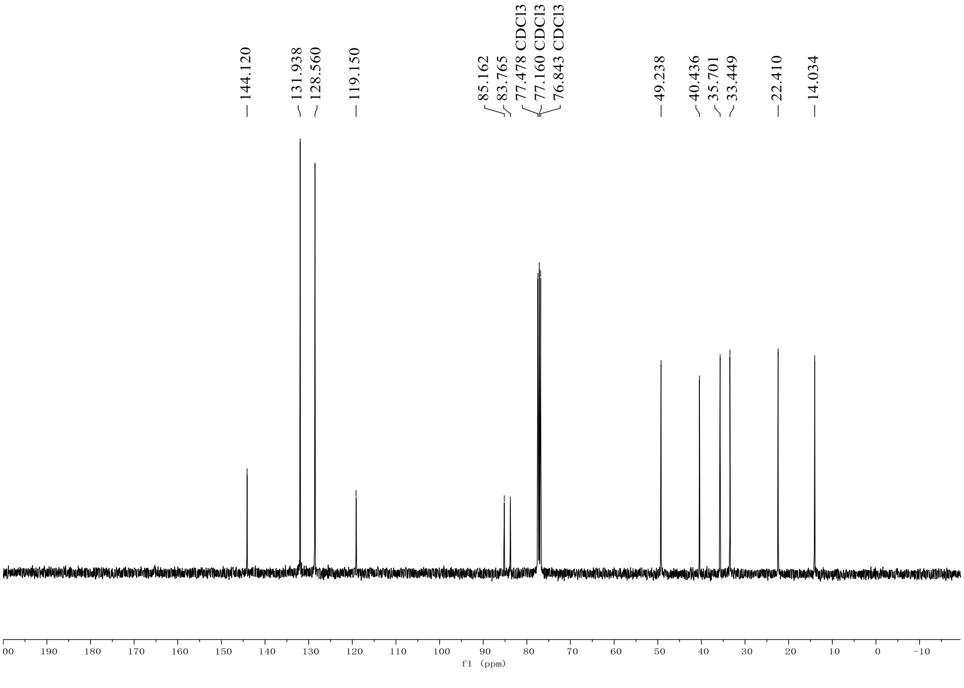
2-((4-butylphenyl)ethynyl)oxirane (1b), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), yellow oil. The procedures are according to the above method B in 56% yield.

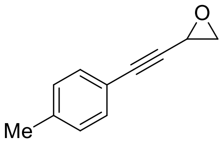
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.57 (t, *J* = 3.2 Hz, 1H), 3.05-2.96 (m, 2H), 2.65-2.52 (m, 2H), 1.63-1.52 (m, 2H), 1.39-1.27 (m , 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.12, 131.94, 128.56, 119.15, 85.16, 83.77, 49.24, 40.44, 35.70, 33.45, 22.41, 14.03.

HRMS (ESI) m/z calculated for $C_{14}H_{17}O$ [M+H]$^+$: 201.1279, found: 201.1285.





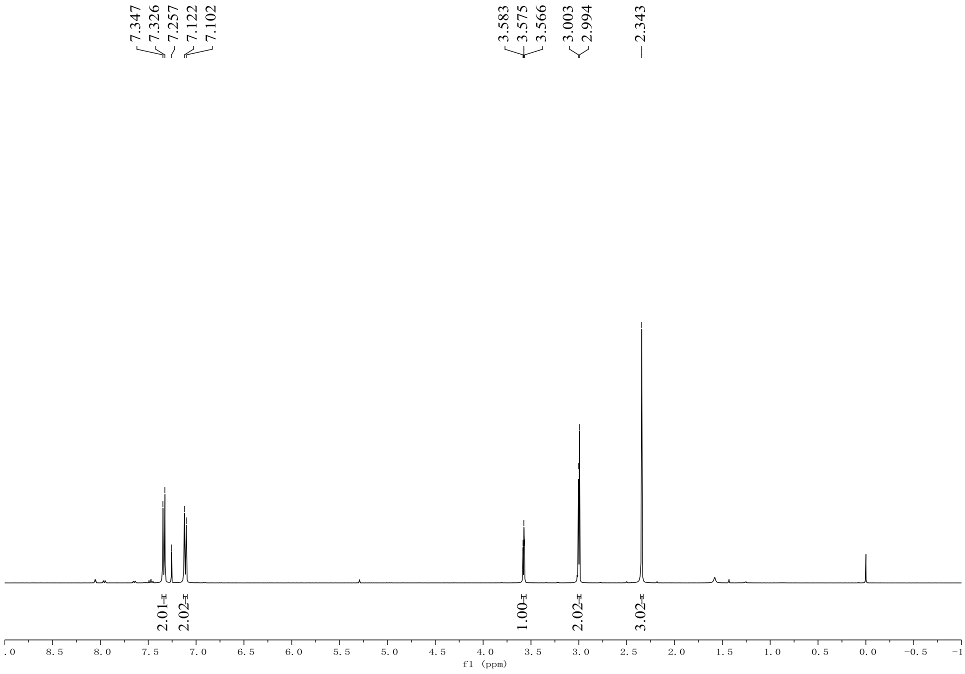


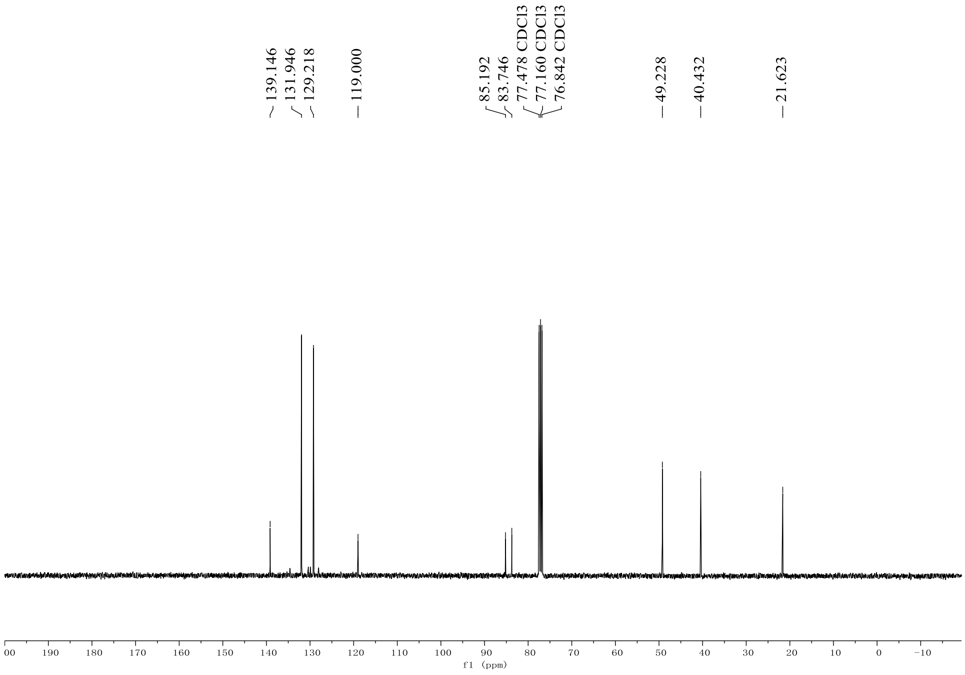
2-(*p*-tolylethynyl)oxirane (1c), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), yellow oil. The procedures are according to the above method B in 57% yield.

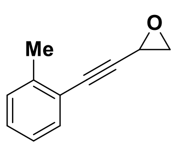
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.57 (t, *J* = 3.4 Hz, 1H), 3.00 (d, *J* = 3.6 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.15, 131.95, 129.22, 119.00, 85.19, 83.75, 49.23, 40.43, 21.62.

HRMS (ESI) m/z calculated for $C_{11}H_{10}ONa$ [M+Na]$^+$: 181.0629, found: 181.0622.

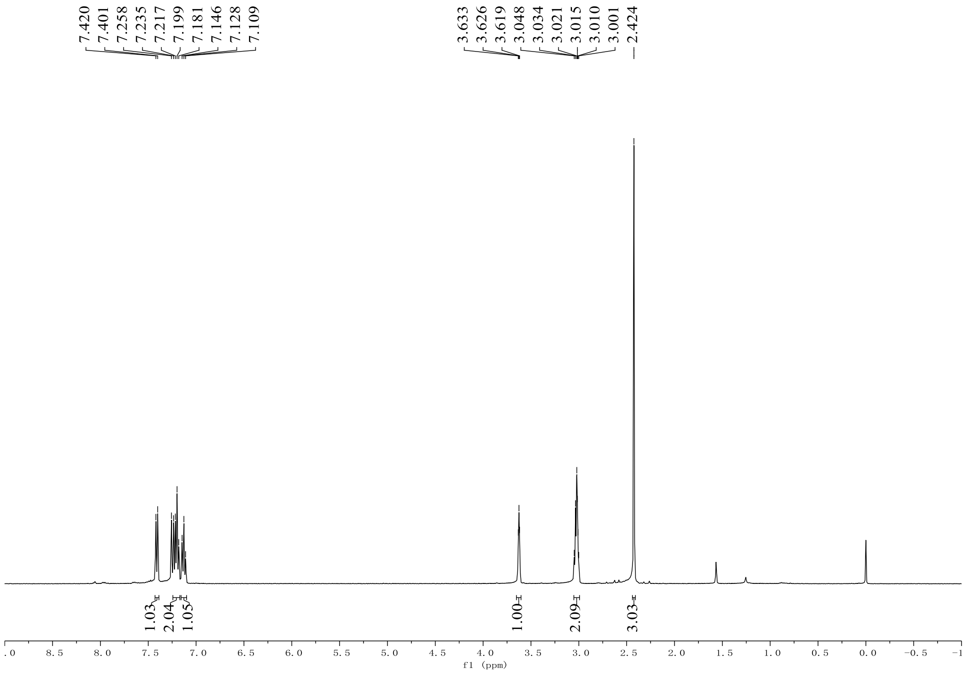


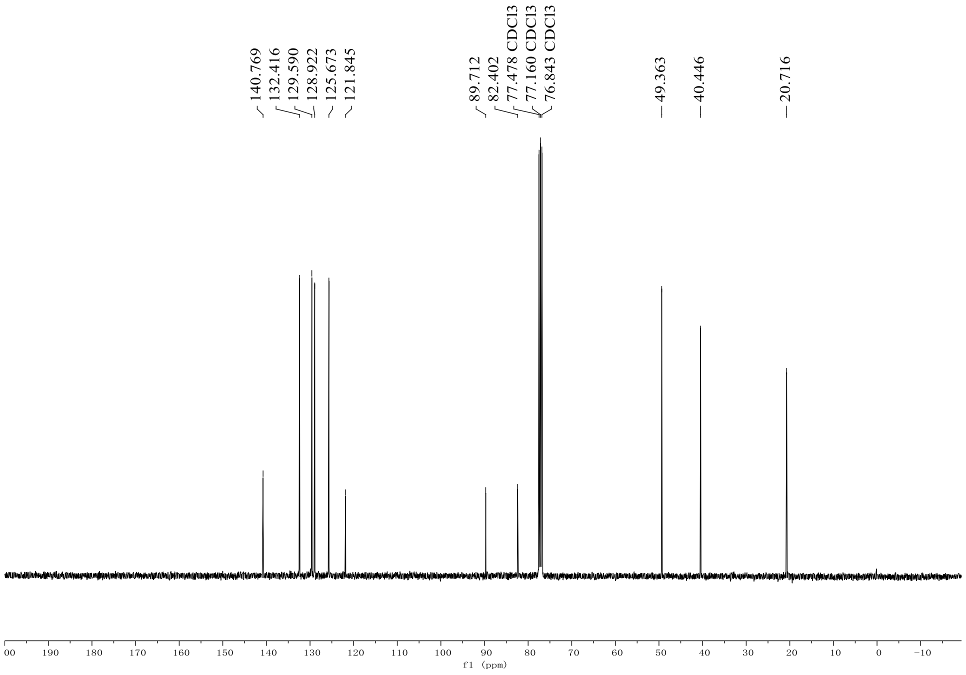


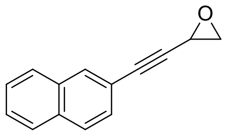


2-(*o*-tolylethynyl)oxirane (1d), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), yellow oil. The procedures are according to the above method B in 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.24-3.17 (m, 2H), 7.16-7.10 (m, 1H), 3.63 (t, *J* = 2.8 Hz, 1H), 3.05-2.99 (m, 2H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.77, 132.42, 129.59, 128.92, 125.67, 121.85, 89.71, 82.40, 49.36, 40.45, 20.72.

HRMS (ESI) m/z calculated for $C_{11}H_{11}O$ $[M+H]^+$: 159.0810, found: 159.0809.





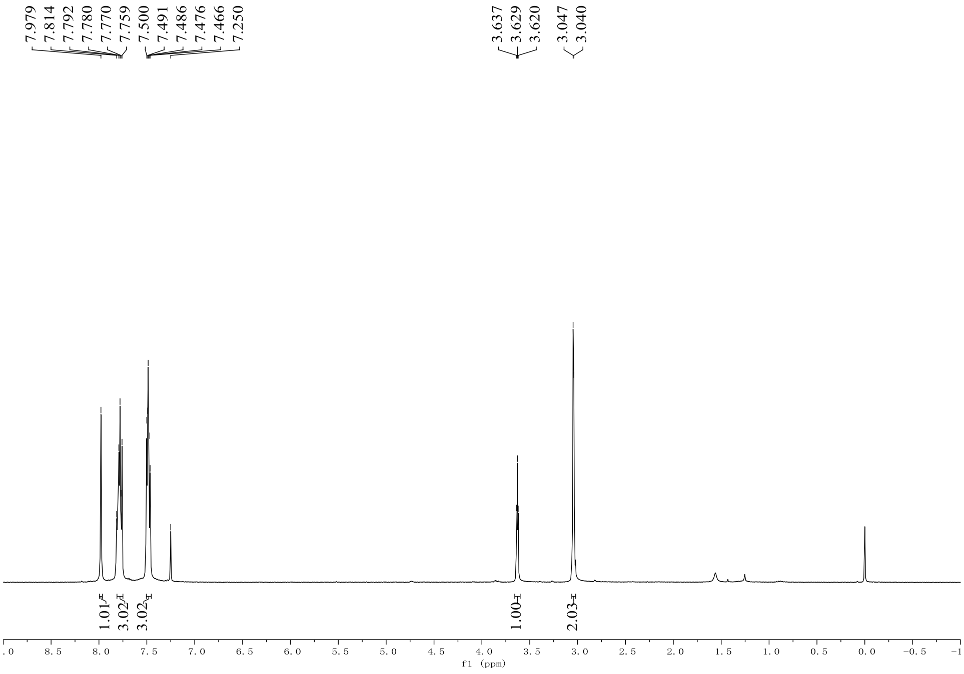


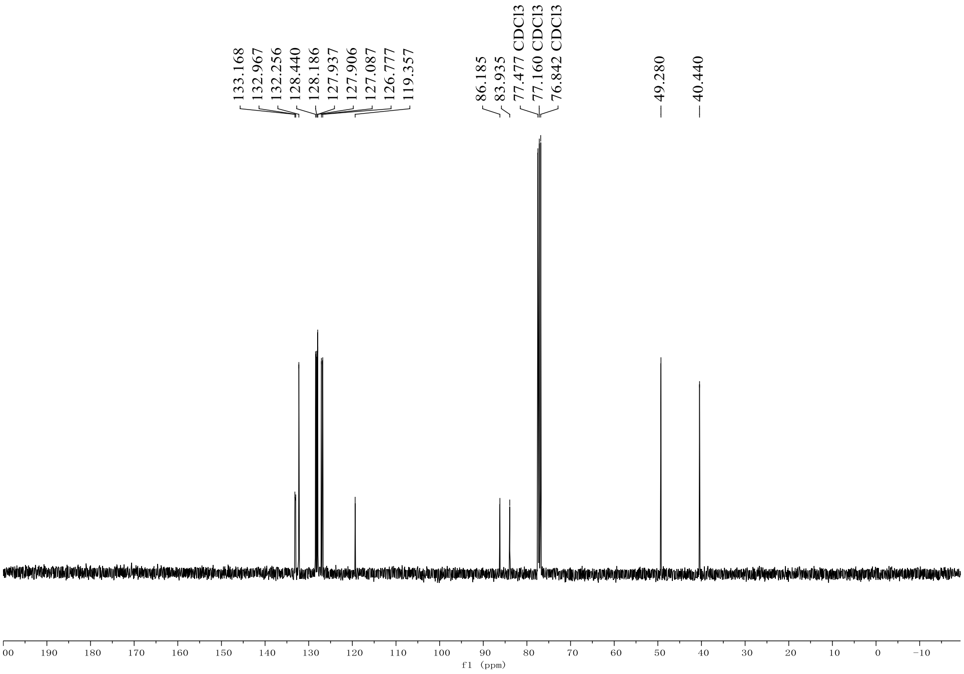
2-(naphthalen-2-ylethynyl)oxirane (1e), R_f = 0.50 (Petroleum ether : EtOAc = 19:1), yellow solid. The procedures are according to the above method B in 45% yield.

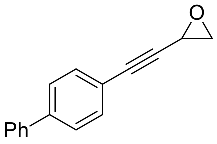
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.82-7.75 (m, 3H), 7.51-7.45 (m, 3H), 3.63 (t, *J* = 3.4 Hz, 1H), 3.04 (d, *J* = 2.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.17, 132.97, 132.26, 128.44, 128.19, 127.94, 127.91, 127.09, 126.78, 119.36, 86.19, 83.94, 49.28, 40.44.

HRMS (ESI) m/z calculated for $C_{14}H_{11}O$ $[M+H]^+$: 195.0810, found: 195.0814.





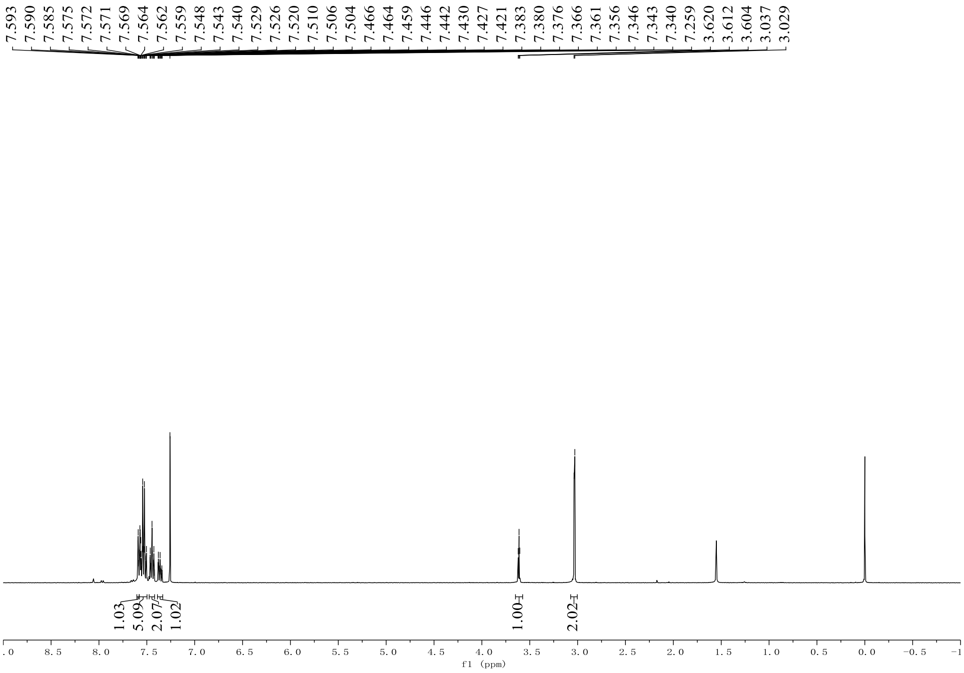


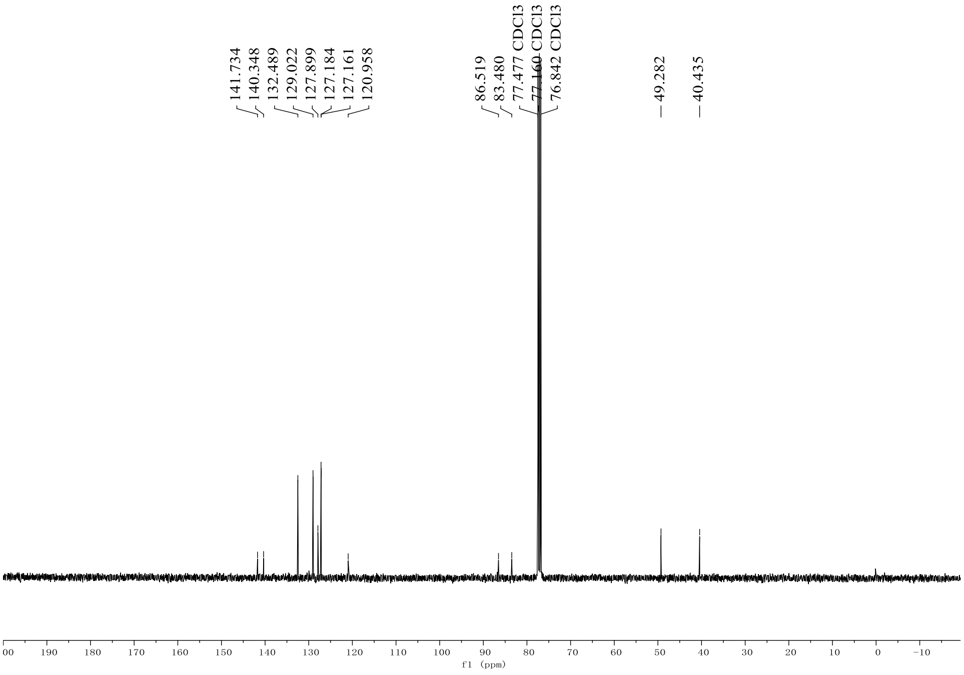
2-([1,1’-biphenyl]-4-ylethynyl)oxirane (1f), R_f = 0.50 (Petroleum ether : EtOAc = 19:1), yellow solid. The procedures are according to the above method B in 67% yield.

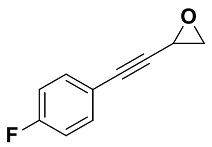
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 1H), 7.58-7.50 (m, 5H), 7.48-7.42 (m, 2H), 7.39-7.33 (m, 1H), 3.61 (t, *J* = 3.2 Hz, 1H), 3.03 (d, *J* = 3.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.73, 140.35, 132.49, 129.02, 127.90, 127.18, 127.16, 120.96, 86.52, 83.48, 49.28, 40.44.

HRMS (ESI) m/z calculated for $C_{16}H_{13}O$ [M+H]$^+$: 221.0966, found: 221.0972.







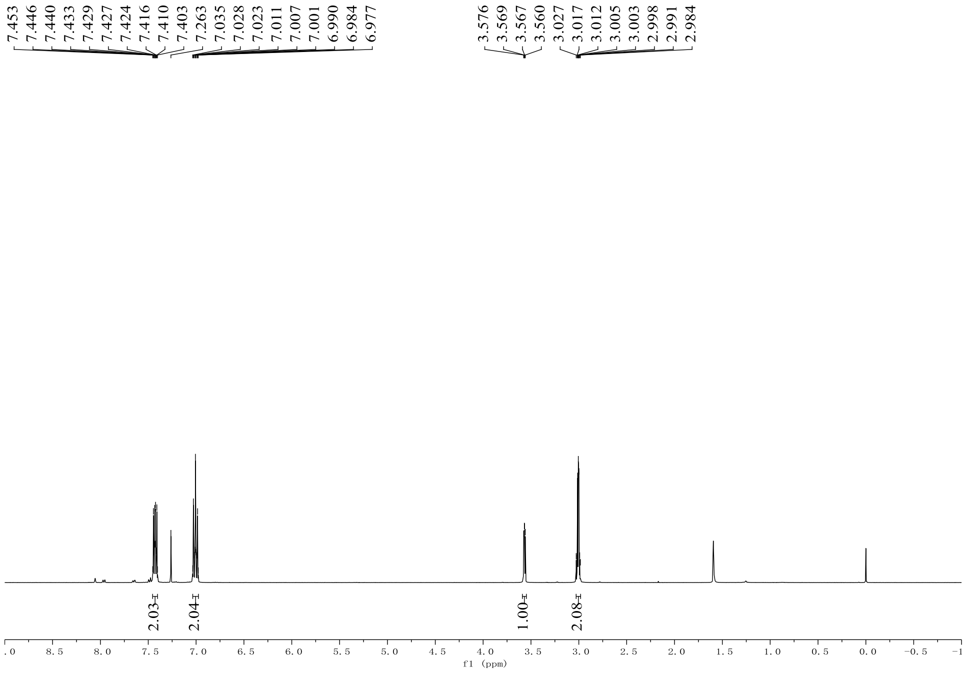
2-((4-fluorophenyl)ethynyl)oxirane (1g), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), yellow oil. The procedures are according to the above method B in 58% yield.

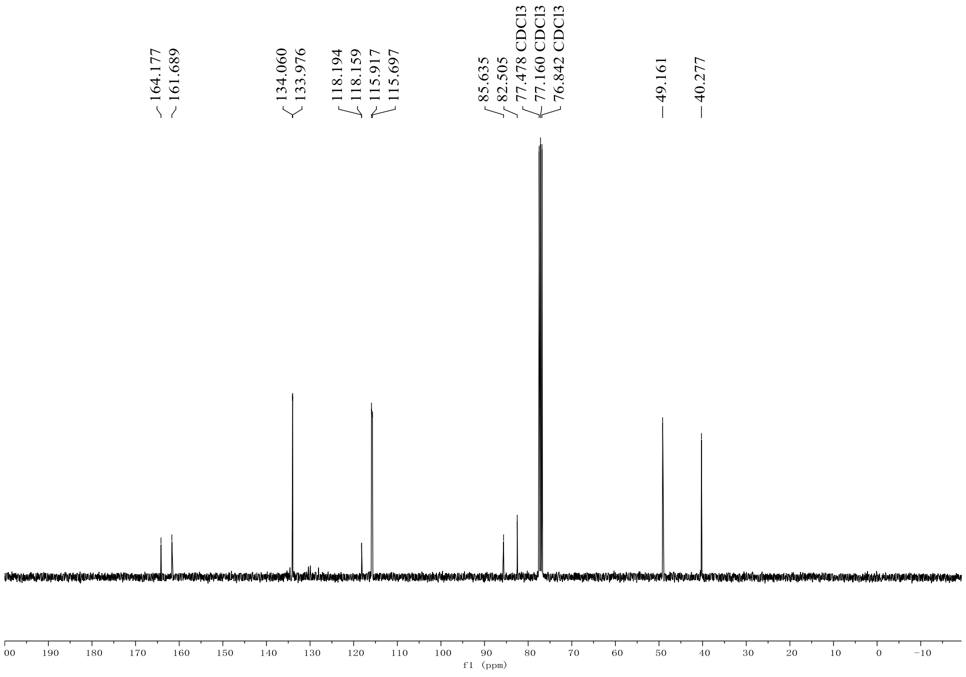
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.04-6.97 (m, 2H), 3.57 (dd, *J* = 3.6, 2.8 Hz, 1H), 3.03-2.98 (m, 2H).

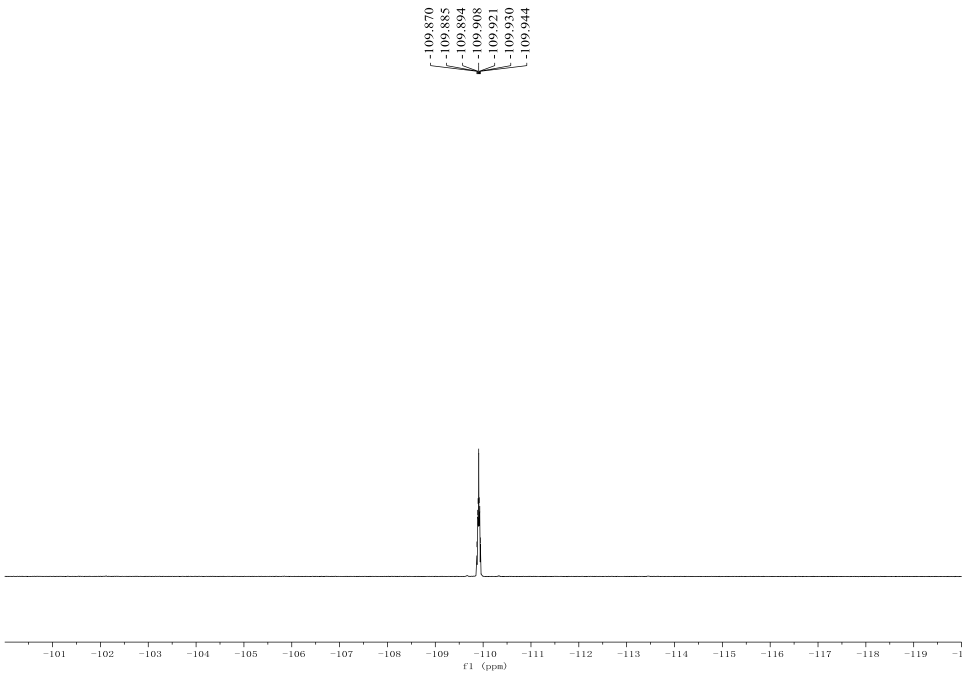
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.93 (d, *J* = 251.3 Hz), 134.02 (d, *J* = 8.5 Hz), 118.18 (d, *J* = 3.5 Hz), 115.81 (d, *J* = 22.2 Hz), 85.64, 82.50, 49.16, 40.28.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.91 (m, 1F).

HRMS (ESI) m/z calculated for $C_{10}H_8FO$ $[M+H]^+$: 163.0559, found: 163.0555.






-109.870
-109.885
-109.894
-109.908
-109.921
-109.930
-109.944
−101
−102
−103
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−106
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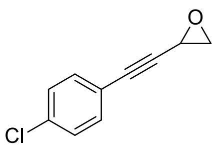
−119
−1
f1 (ppm)

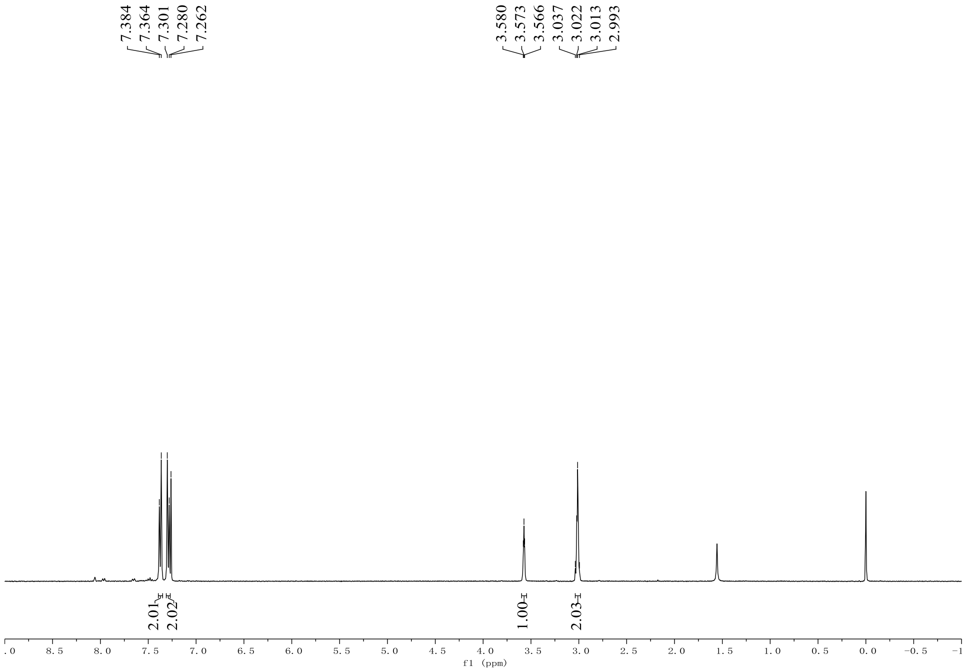


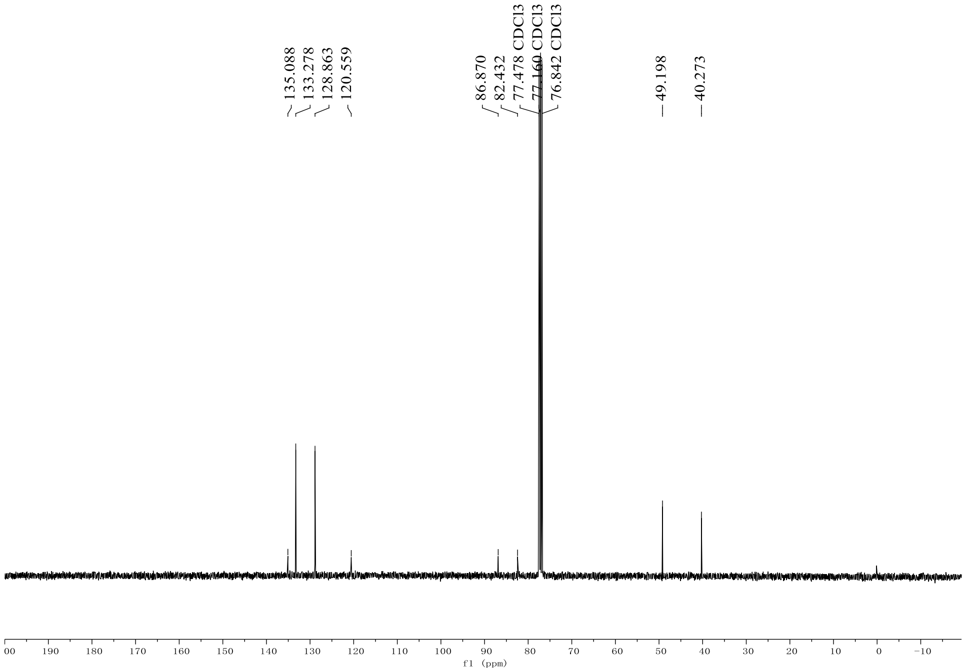
2-((4-chlorophenyl)ethynyl)oxirane (1h), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), yellow solid. The procedures are according to the above method B in 56% yield.

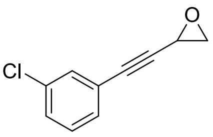
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.57 (t, *J* = 2.8 Hz, 1H), 3.04-2.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.09, 133.28, 128.86, 120.56, 86.87, 82.43, 49.20, 40.27.

HRMS (ESI) m/z calculated for $C_{10}H_8ClO$ $[M+H]^+$: 179.0264, found: 179.0265.





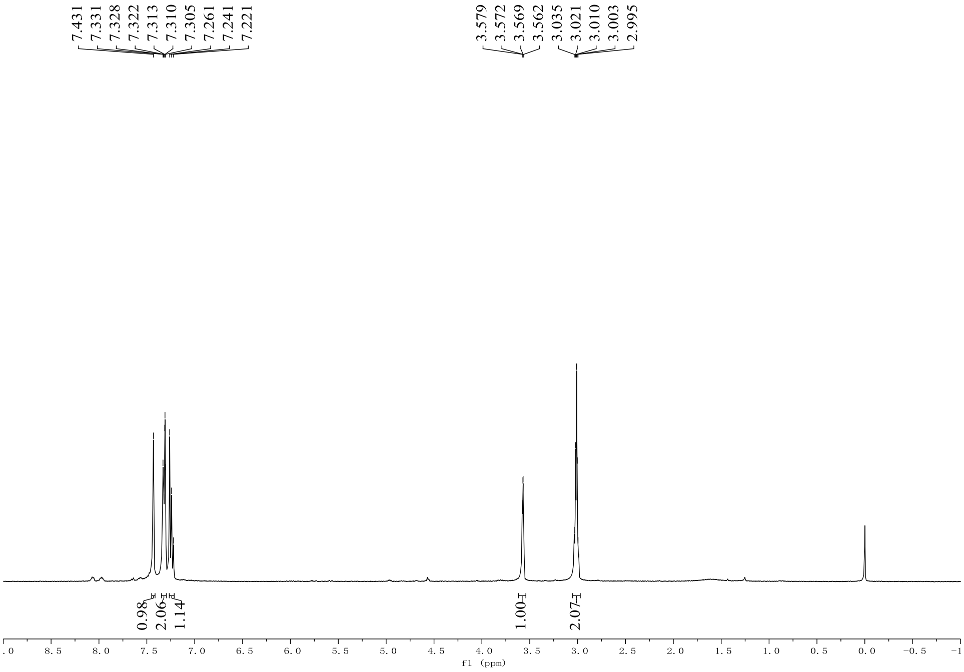


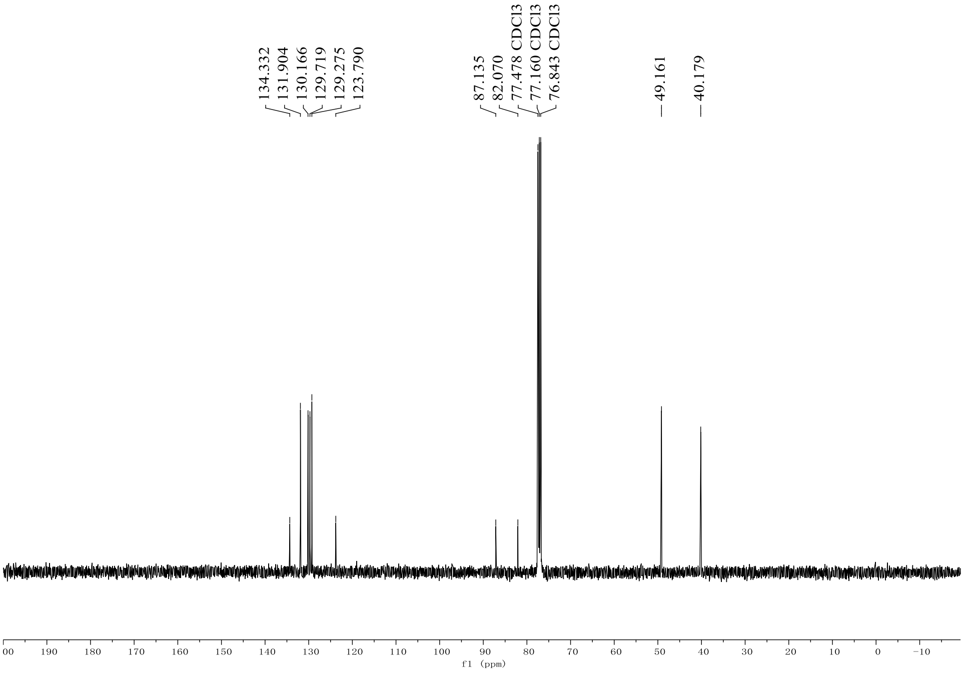
2-((3-chlorophenyl)ethynyl)oxirane (1i), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), yellow oil. The procedures are according to the above method B in 54% yield.

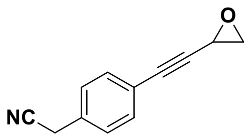
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.34-7.29 (m, 2H), 7.27-7.21 (m, 1H), 3.57 (dd, *J* = 4.0, 2.8 Hz, 1H), 3.05-2.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.33, 131.90, 130.17, 129.72, 129.28, 123.79, 87.14, 82.07, 49.16, 40.18.

HRMS (ESI) m/z calculated for $C_{10}H_8ClO$ $[M+H]^+$: 179.0264, found: 179.0266.





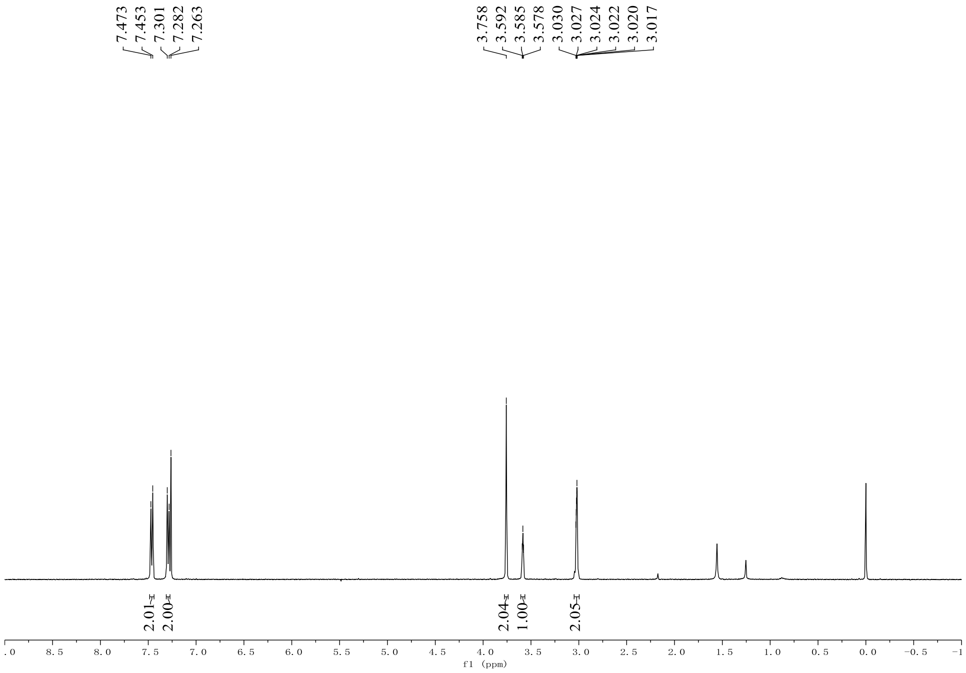


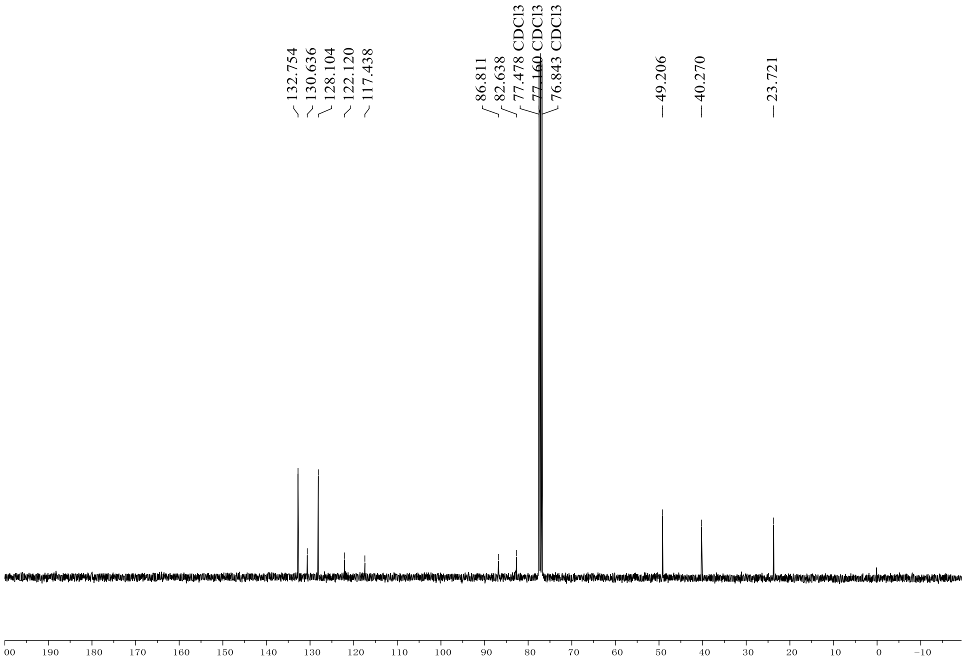
2-(4-(oxiran-2-ylethynyl)phenyl)acetonitrile (1j), R_f = 0.40 (Petroleum ether : EtOAc = 4:1), yellow solid. The procedures are according to the above method B in 40% yield.

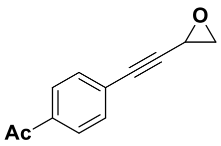
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 3.76 (s, 2H), 3.58 (t, *J* = 2.8 Hz, 1H), 3.05-3.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.75, 130.64, 128.10, 122.12, 117.44, 86.81, 82.64, 49.21, 40.27, 23.72.

HRMS (ESI) m/z calculated for $C_{12}H_{10}NO$ $[M+H]^+$: 184.0762, found: 184.0765.





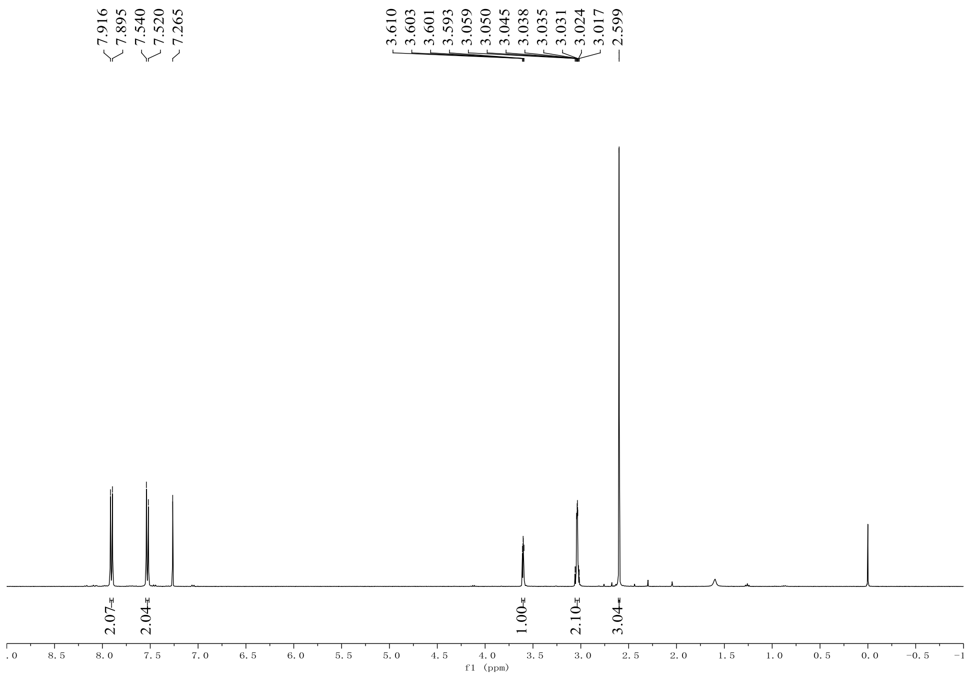


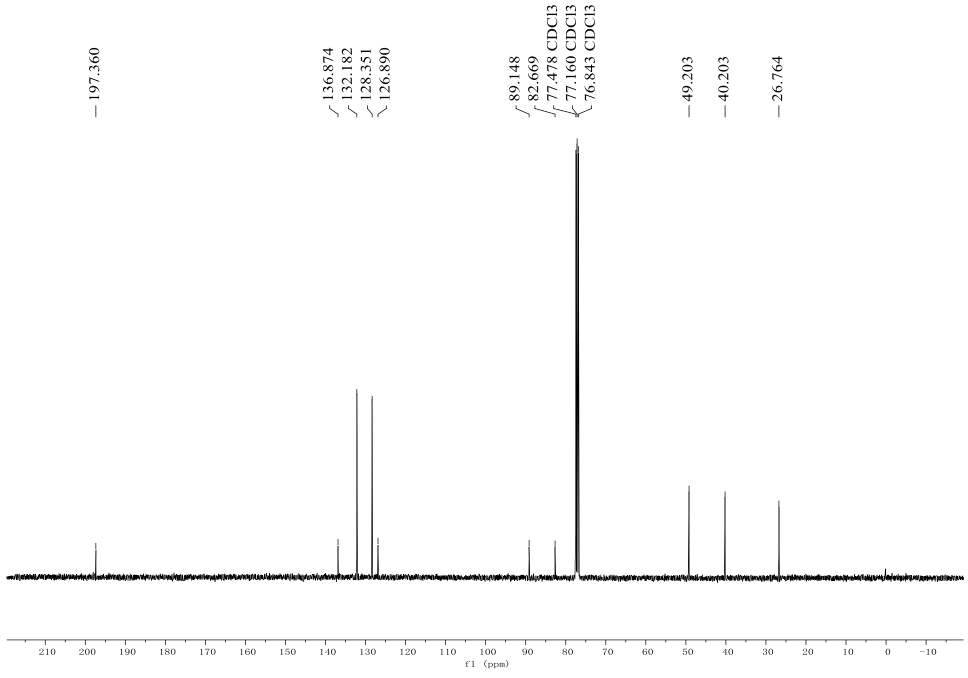
1-(4-(oxiran-2-ylethynyl)phenyl)ethanone (1k), R_f = 0.50 (Petroleum ether : EtOAc = 4:1), yellow solid. The procedures are according to the above method B in 52% yield.

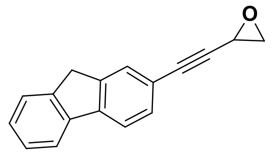
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 3.60 (dd, *J* = 3.8, 3.0 Hz, 1H), 3.06-3.01 (m, 2H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.36, 136.87, 132.18, 128.35, 126.89, 89.15, 82.67, 49.20, 40.20, 26.76.

HRMS (ESI) m/z calculated for $C_{12}H_{11}O_2$ $[M+H]^+$: 187.0759, found: 187.0756.





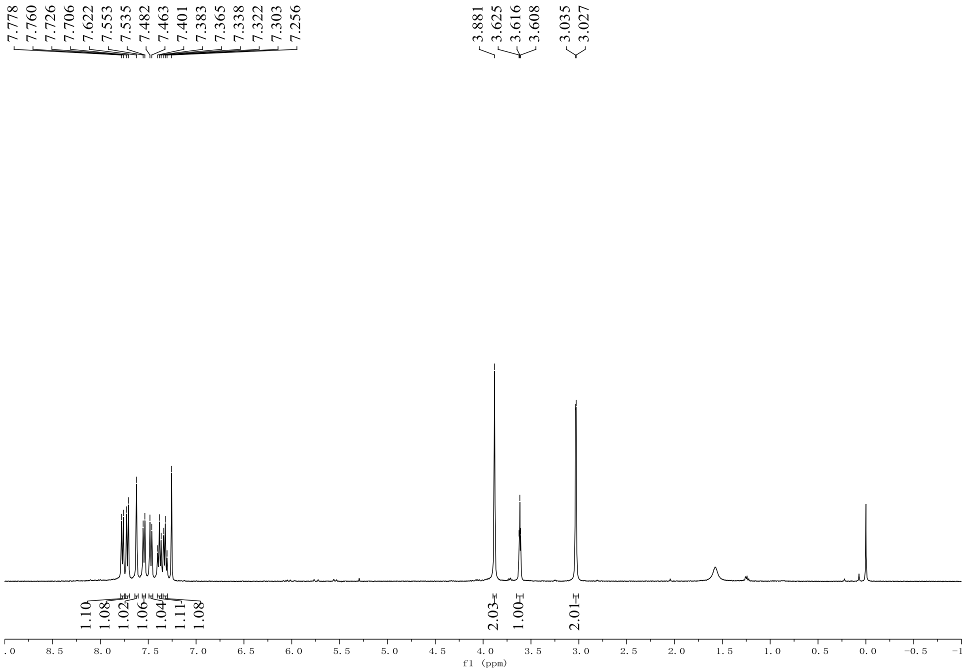


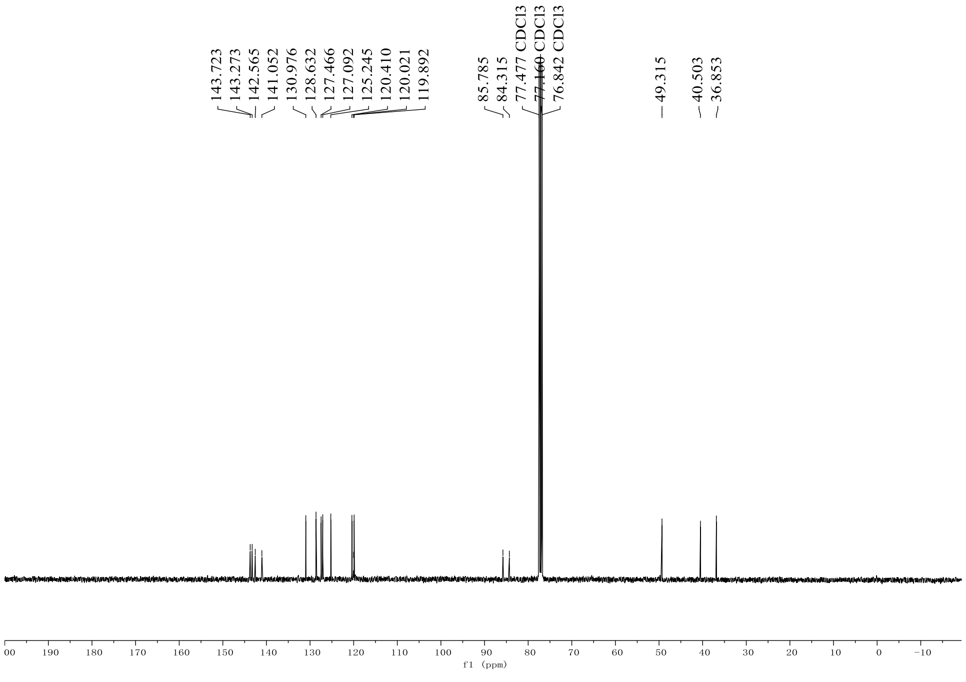
2-((9H-fluoren-2-yl)ethynyl)oxirane (1l), R_f = 0.40 (Petroleum ether : EtOAc = 19:1), yellow solid. The procedures are according to the above method B in 34% yield.

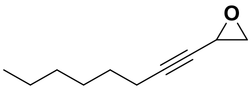
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.62 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.41-7.36 (m, 1H), 7.35-7.29 (m, 1H), 3.88 (s, 2H), 3.62 (t, *J* = 3.4 Hz, 1H), 3.03 (d, *J* = 3.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.72, 143.27, 142.57, 141.05, 130.98, 128.63, 127.47, 127.09, 125.25, 120.41, 120.02, 119.89, 85.79, 84.32, 49.32, 40.50, 36.85.

HRMS (ESI) m/z calculated for $C_{17}H_{13}O$ $[M+H]^+$: 233.0966, found: 233.0969.





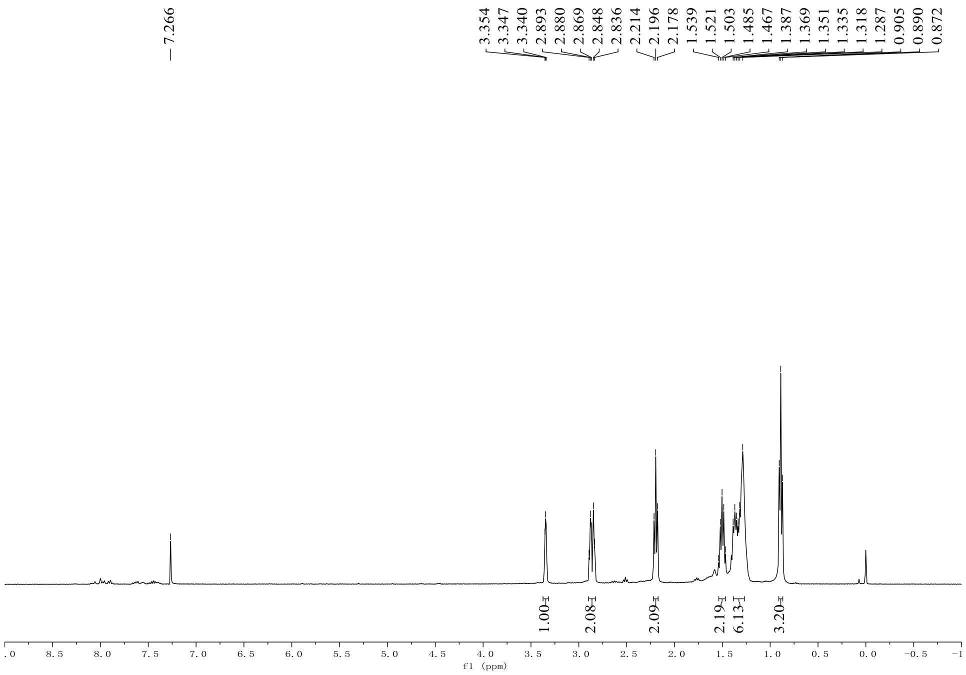


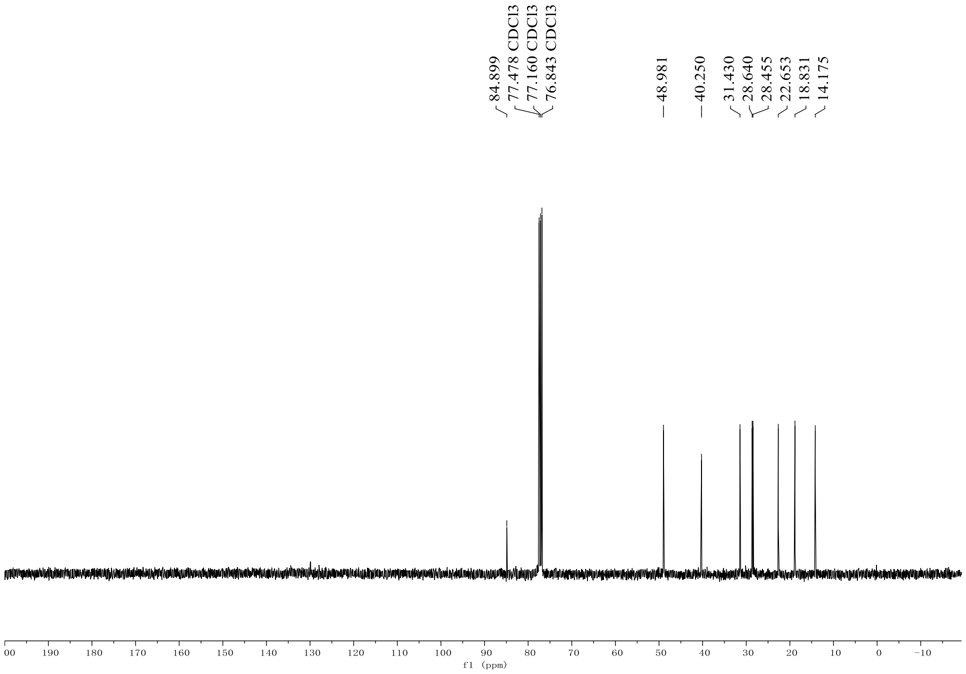
2-(oct-1-yn-1-yl)oxirane (1m), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), yellow oil. The procedures are according to the above method B in 38% yield.

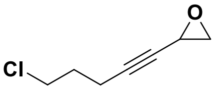
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 (t, *J* = 2.8 Hz, 1H), 2.90-2.83 (m, 2H), 2.20 (t, *J* = 7.2 Hz, 2H), 1.54-1.47 (m, 2H), 1.39-1.27 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 84.90, 76.84, 48.98, 40.25, 31.43, 28.64, 28.46, 22.65, 18.83, 14.18.

HRMS (ESI) m/z calculated for $C_{10}H_{17}O$ [M+H]$^+$: 153.1279, found: 153.1280.





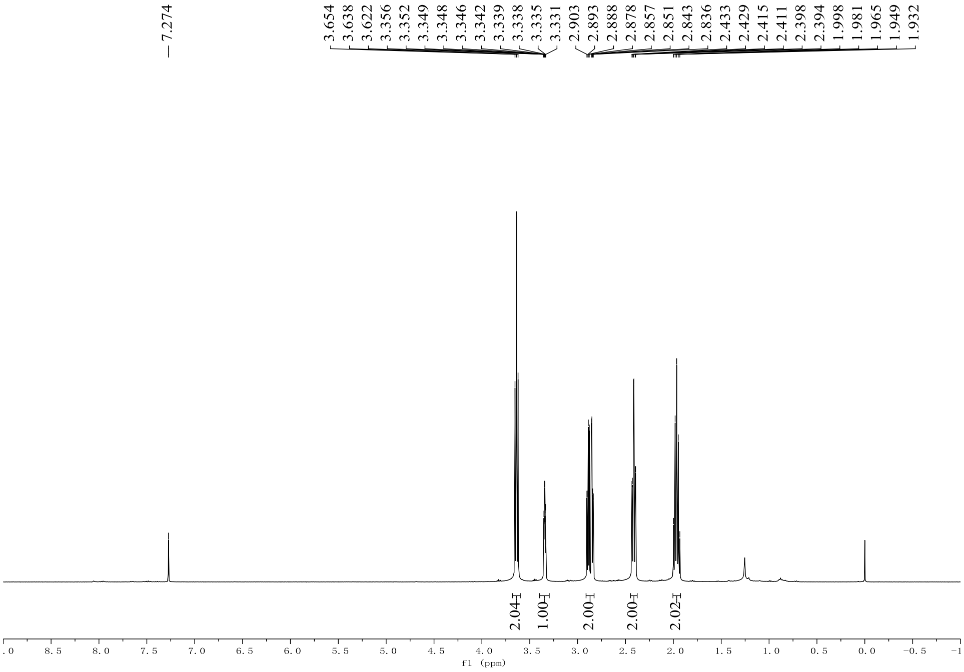


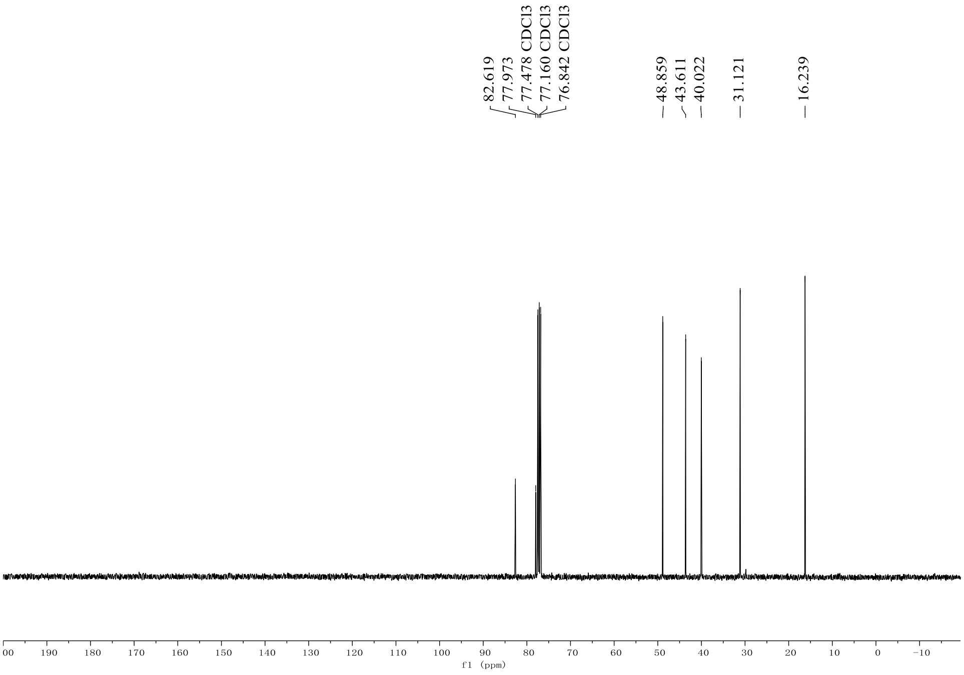
2-(5-chloropent-1-yn-1-yl)oxirane (1n), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), yellow oil. The procedures are according to the above method B in 25% yield.

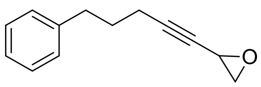
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (t, *J* = 6.4 Hz, 2H), 3.38-3.30 (m, 1H), 2.91-2.82 (m, 2H), 2.41 (td, *J* = 7.0, 1.6 Hz, 2H), 2.00-1.92 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.62, 77.97, 48.86, 43.61, 40.02, 31.12, 16.24.

HRMS (APCI) m/z calculated for $C_7H_{10}ClO$ $[M+H]^+$: 145.0420, found: 145.0409.





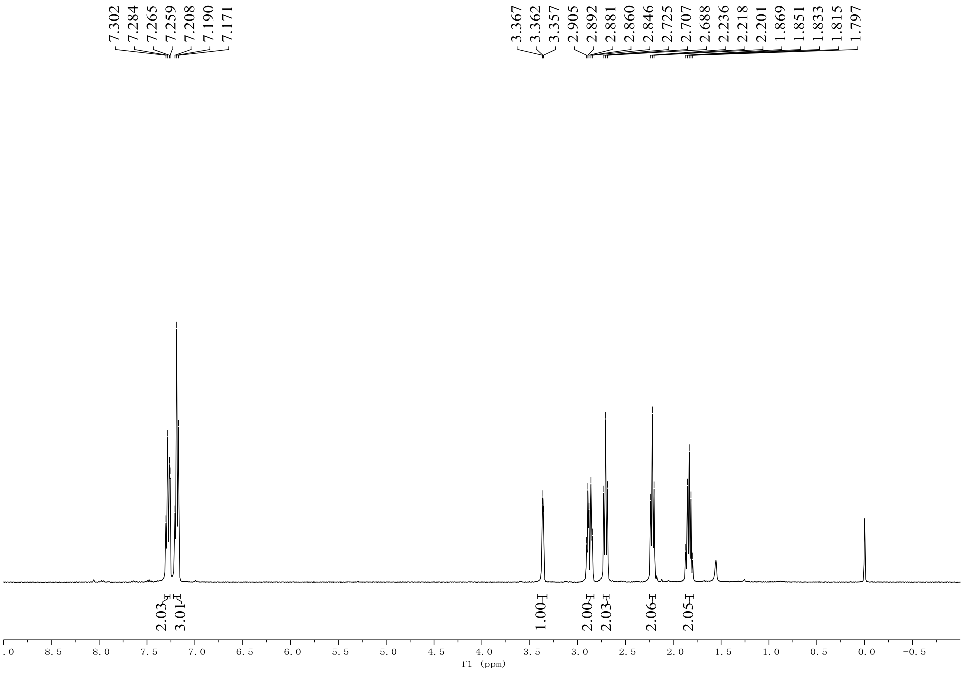


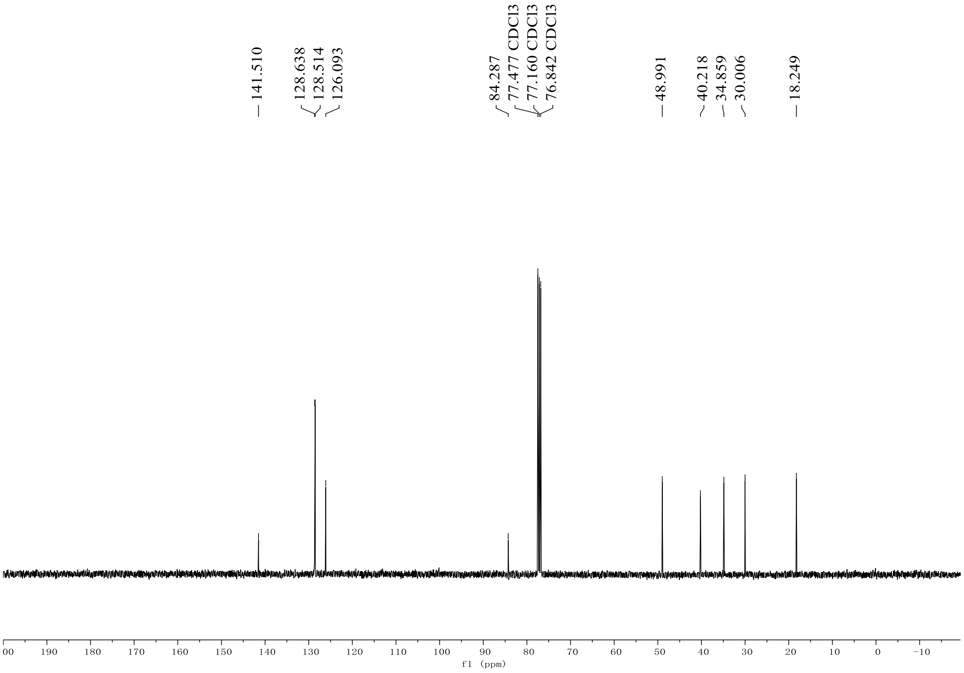
2-(5-phenylpent-1-yn-1-yl)oxirane (1o), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), yellow oil. The procedures are according to the above method B in 50% yield.

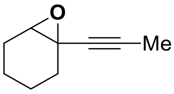
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.22-7.15 (m, 3H), 3.36 (t, *J* = 2.0 Hz, 1H), 2.91-2.83 (m, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.22 (t, *J* = 7.0 Hz, 2H), 1.88-1.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.51, 128.64, 128.51, 126.09, 84.29, 77.48, 48.99, 40.22, 34.86, 30.01, 18.25.

HRMS (ESI) m/z calculated for $C_{13}H_{14}ONa$ [M+ Na]$^+$: 209.0942, found: 209.0936.





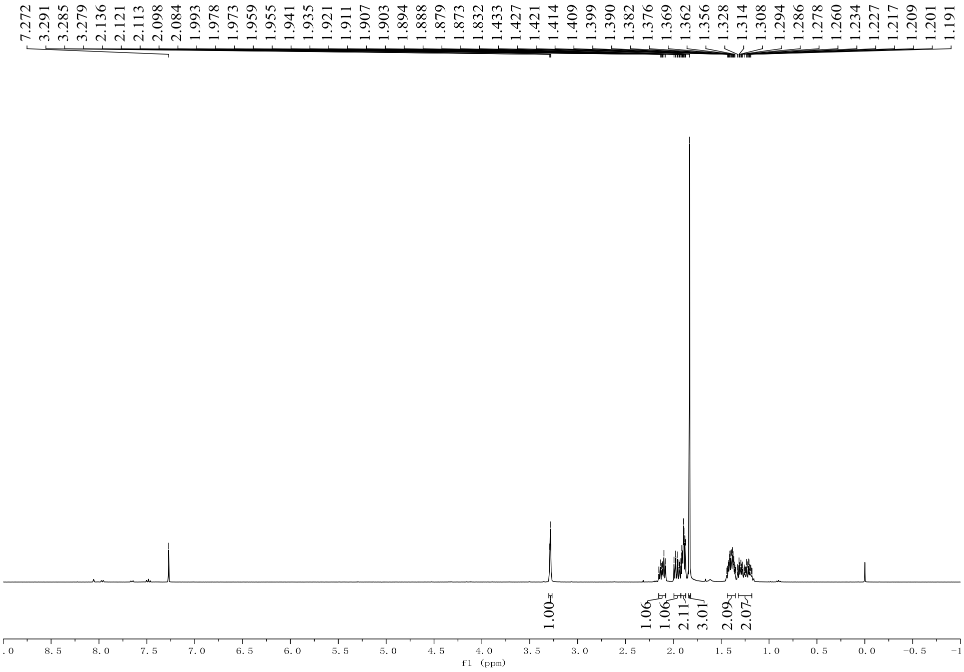


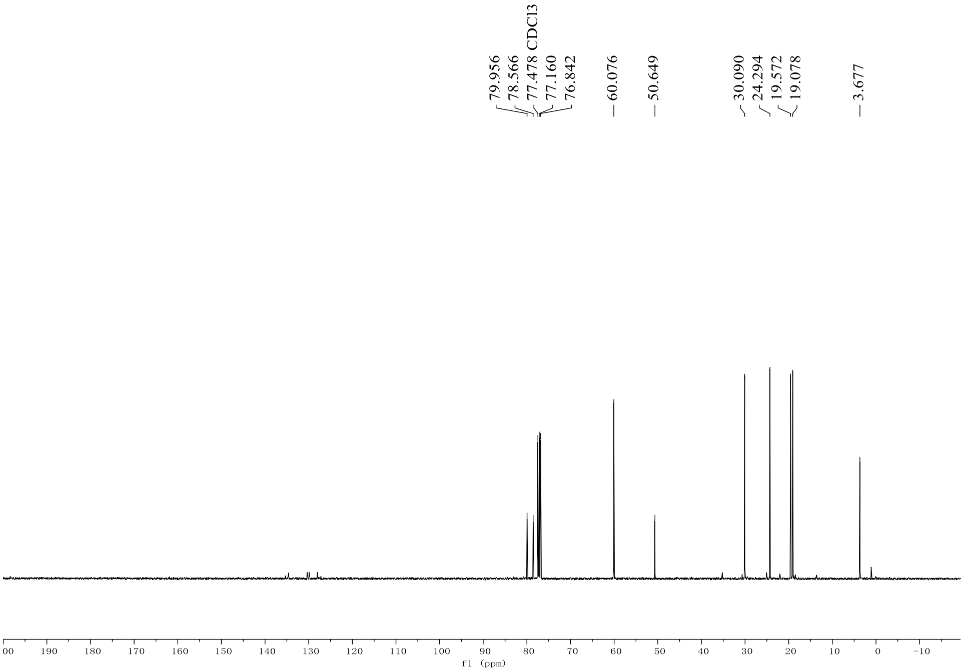
1-(prop-1-yn-1-yl)-7-oxabicyclo[4.1.0]heptane (1p), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), colorless oil. It was prepared according to the previously reported procedure[3] in 18% overall yield.

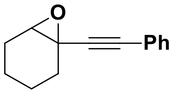
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 (t, *J* = 2.4 Hz, 1H), 2.16-2.08 (m, 1H), 1.99-1.92 (m, 1H), 1.92-1.87 (m, 2H), 1.83 (s, 3H), 1.44-1.35 (m, 2H), 1.32-1.17 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 79.96, 78.57, 60.08, 50.65, 30.09, 24.29, 19.57, 19.08, 3.68.

HRMS (ESI) m/z calculated for $C_9H_{13}O$ [M+ H]$^+$: 137.0966, found: 137.0963.





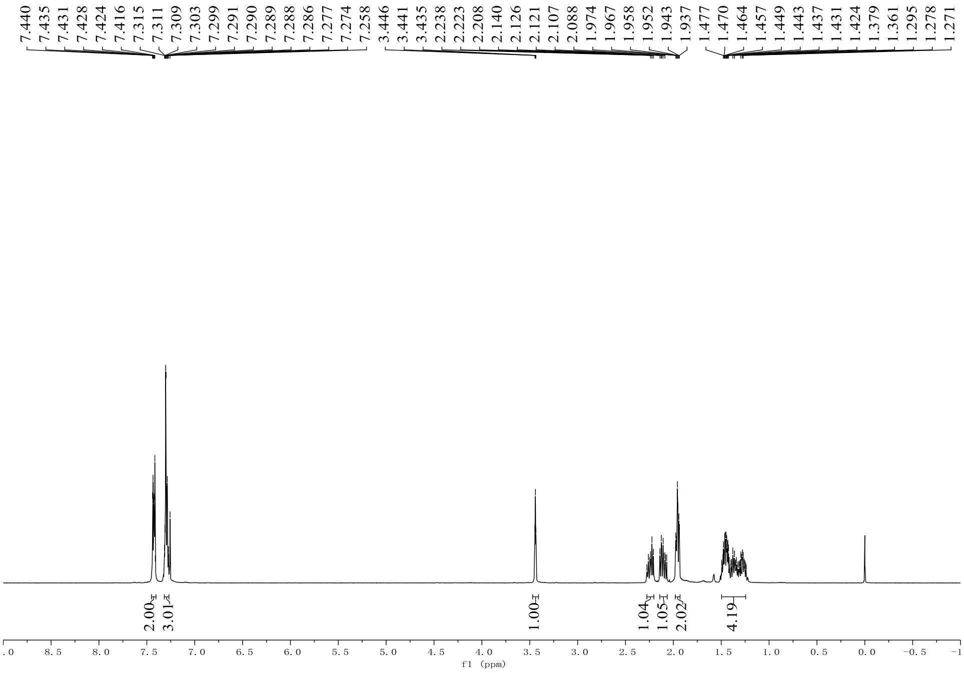


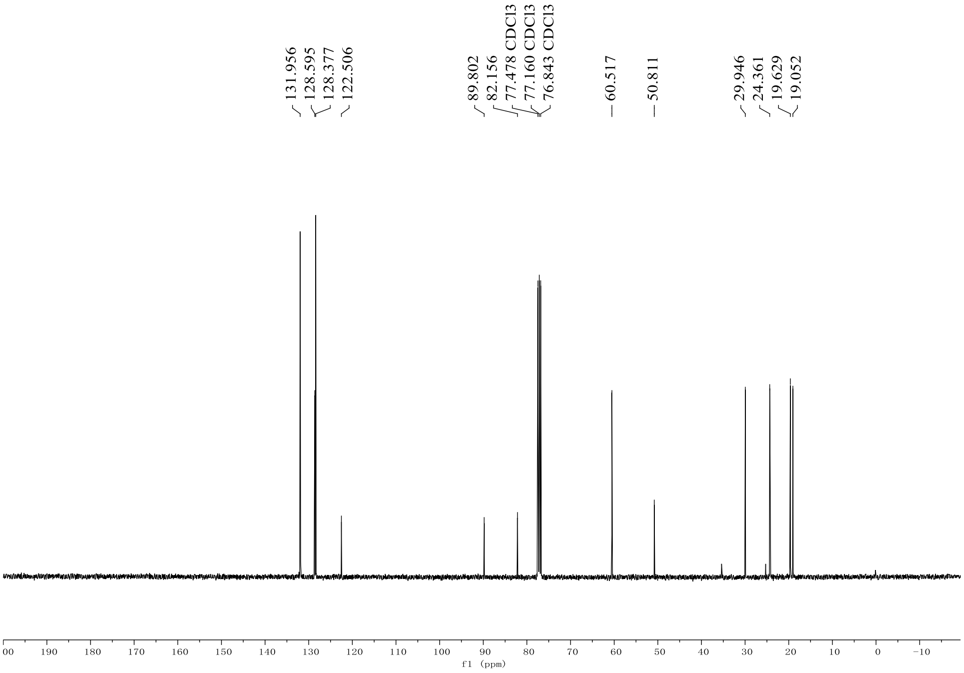
1-(phenylethynyl)-7-oxabicyclo[4.1.0]heptane (1q), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), yellow oil. It was prepared according to the procedures described above.

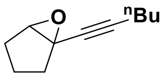
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.32-7.27 (m, 3H), 3.44 (t, *J* = 2.2 Hz, 1H), 2.28-2.20 (m, 1H), 2.15-2.07 (m, 1H), 1.98-1.93 (m, 2H), 1.50-1.24 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.96, 128.60, 128.38, 122.51, 89.80, 82.16, 60.52, 50.81, 29.95, 24.36, 19.63, 19.05.

HRMS (ESI) m/z calculated for $C_{14}H_{15}O$ $[M+H]^+$: 199.1123, found: 199.1119.





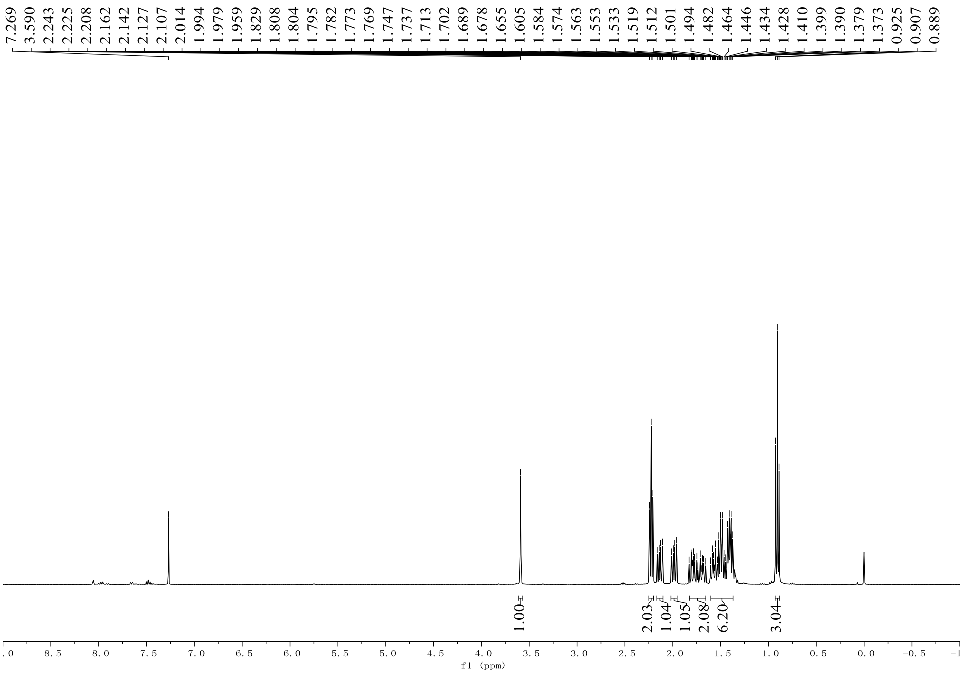


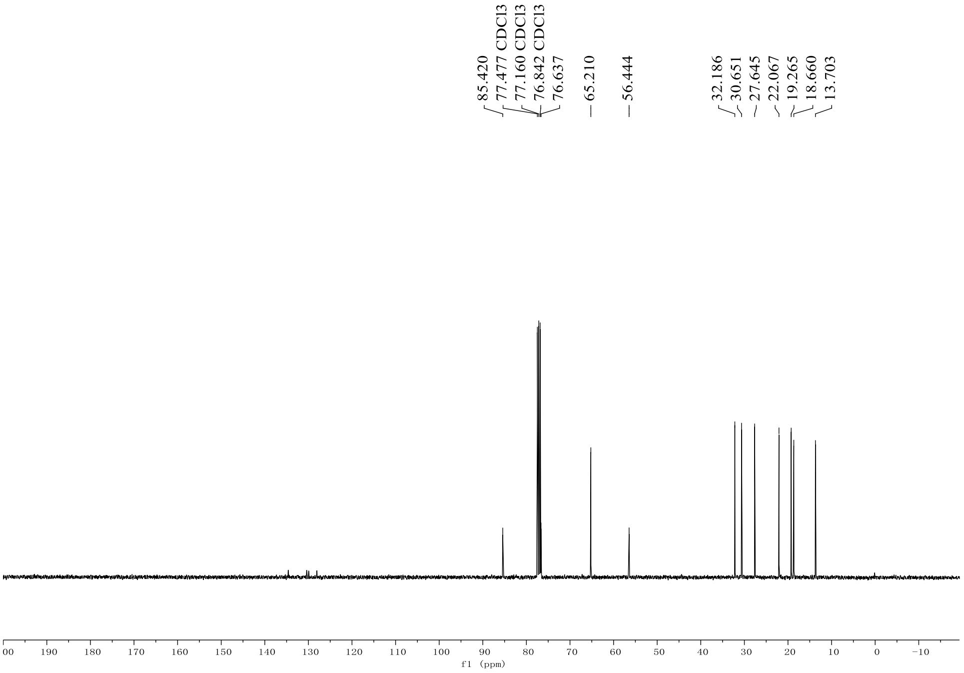
1-(hex-1-yn-1-yl)-6-oxabicyclo[3.1.0]hexane (1r), R_f = 0.55 (Petroleum ether : EtOAc = 19:1), colorless oil. It was prepared according to the previously reported procedure[3] in 20% overall yield.

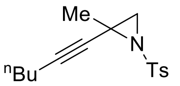
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59 (s, 1H), 2.23 (t, *J* = 7.0 Hz, 2H), 2.13 (dd, *J* = 14.0, 8.0 Hz, 1H), 1.99 (dd, *J* = 14.0, 8.0 Hz, 1H), 1.83-1.65 (m, 2H), 1.60-1.37 (m, 6H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 85.42, 76.64, 65.21, 56.44, 32.19, 30.65, 27.65, 22.07, 19.27, 18.66, 13.70.

HRMS (ESI) m/z calculated for $C_{11}H_{17}O$ $[M+H]^+$: 165.1279, found: 165.1281.





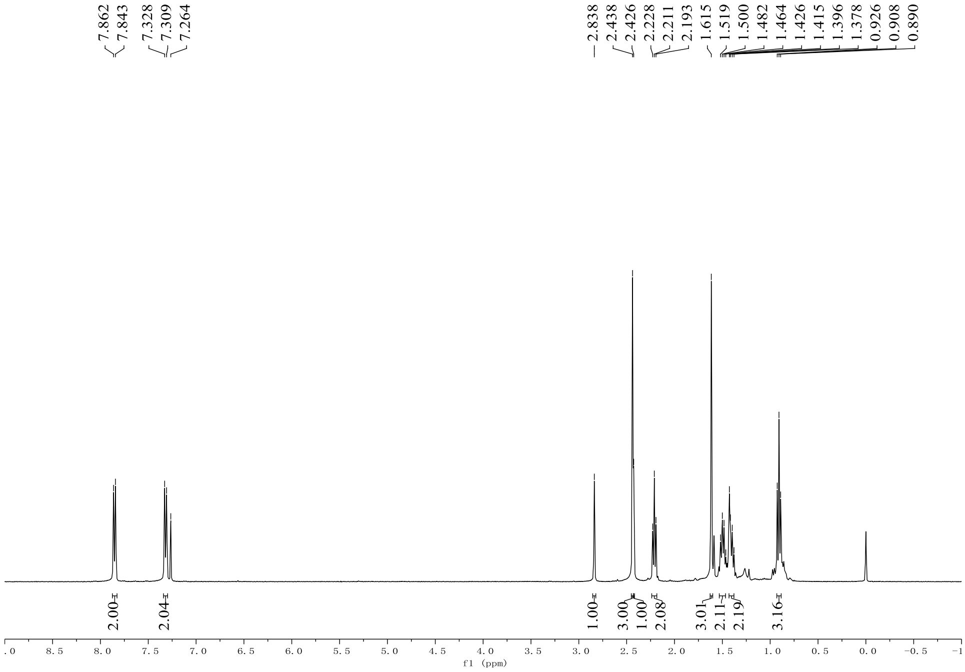


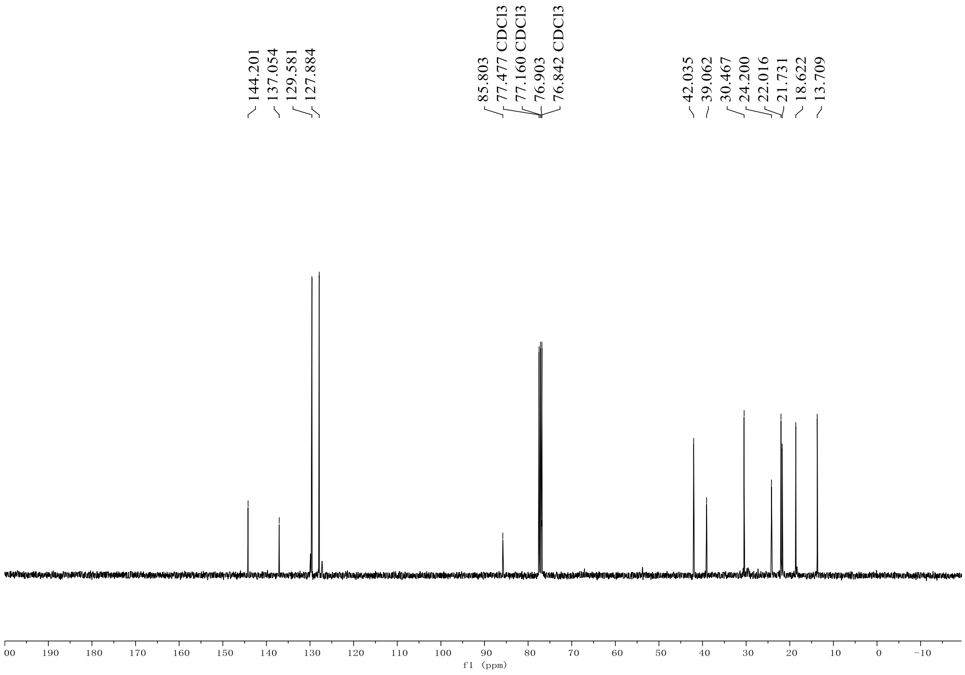
2-(hex-1-yn-1-yl)-2-methyl-1-tosylaziridine (1s), R_f = 0.50 (Petroleum ether : EtOAc = 6:1), yellow oil. It was prepared according to the procedures described above.

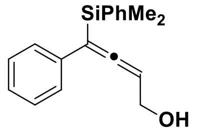
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 2.84 (s, 1H), 2.44 (s, 3H), 2.43 (s, 1H), 2.21 (t, *J* = 7.0 Hz, 2H), 1.62 (s, 3H), 1.53-1.47 (m, 2H), 1.43-1.38 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.20, 137.05, 129.58, 127.88, 85.80, 76.90, 42.04, 39.06, 30.47, 24.20, 22.02, 21.73, 18.62, 13.71.

HRMS (ESI) m/z calculated for $C_{16}H_{22}NO_2S$ [M+ H]$^+$: 292.1371, found: 292.1368.



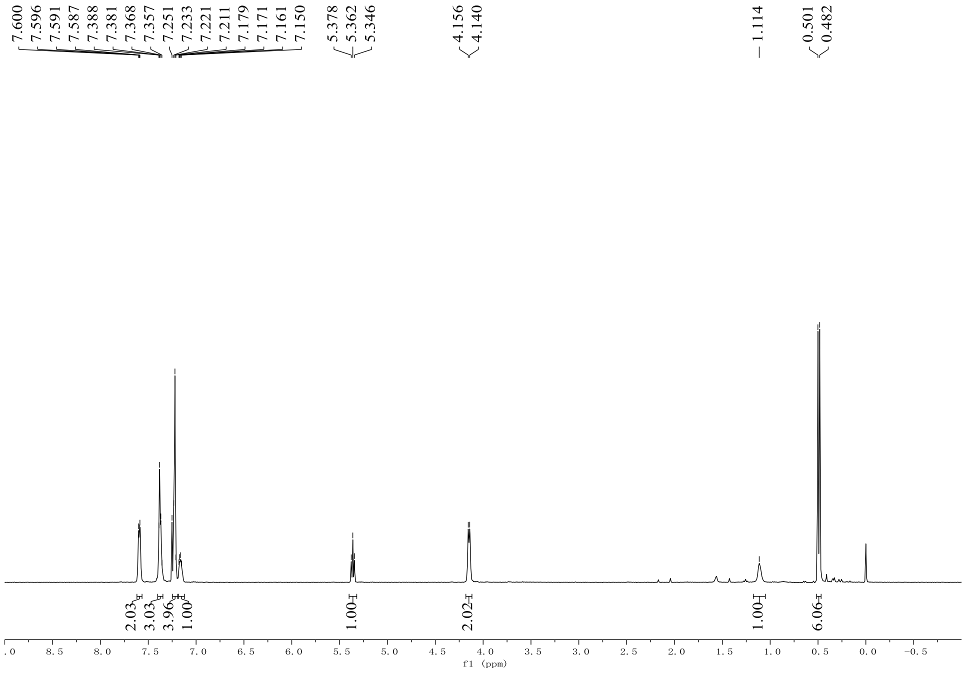


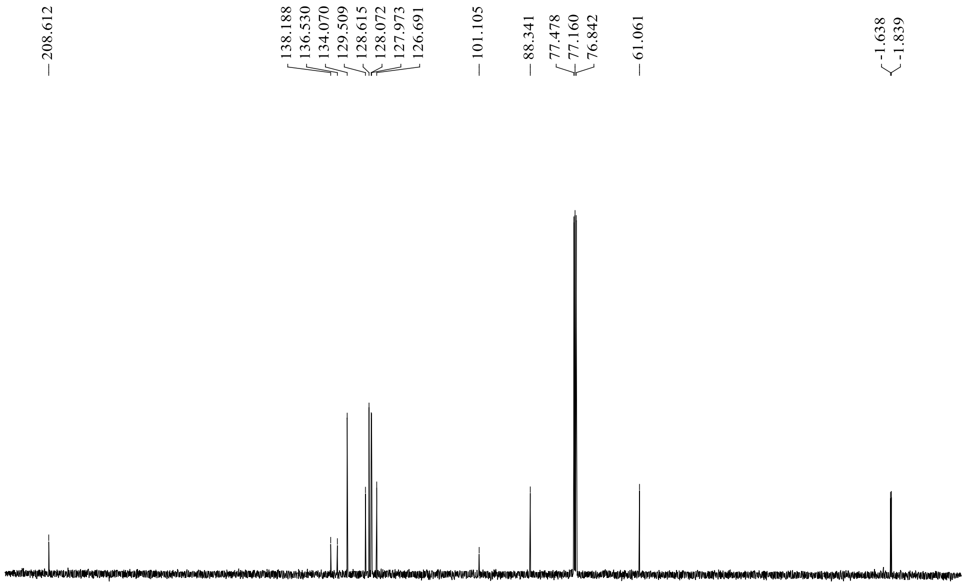


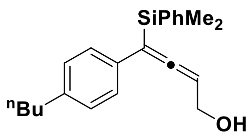
4-(dimethyl(phenyl)silyl)-4-phenylbuta-2,3-dien-1-ol (3a). This compound was prepared via the general procedures described above and was obtained as yellow oil in 92% yield (51.6 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.57 (m, 2H), 7.40-7.35 (m, 3H), 7.25-7.19 (m, 4H), 7.18-7.12 (m, 1H), 5.36 (t, *J* = 6.4 Hz, 1H), 4.15 (d, *J* = 6.4 Hz, 2H), 1.11 (s, 1H), 0.50 (s, 3H), 0.48 (s, 3H).

13C NMR (101 MHz, $CDCl_3$) δ 208.61, 138.19, 136.53, 134.07, 129.51, 128.62, 128.07, 127.97, 126.69, 101.11, 88.34, 61.06, -1.64, -1.84.

HRMS (ESI) m/z calculated for $C_{18}H_{21}OSi$ $[M+H]^+$: 281.1362, found: 281.1364.





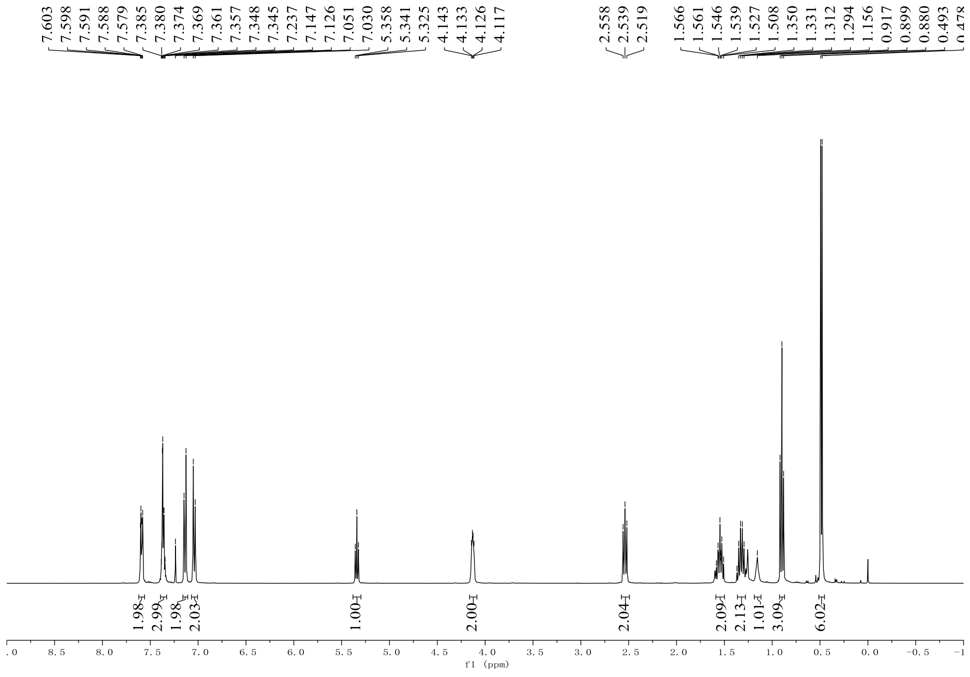


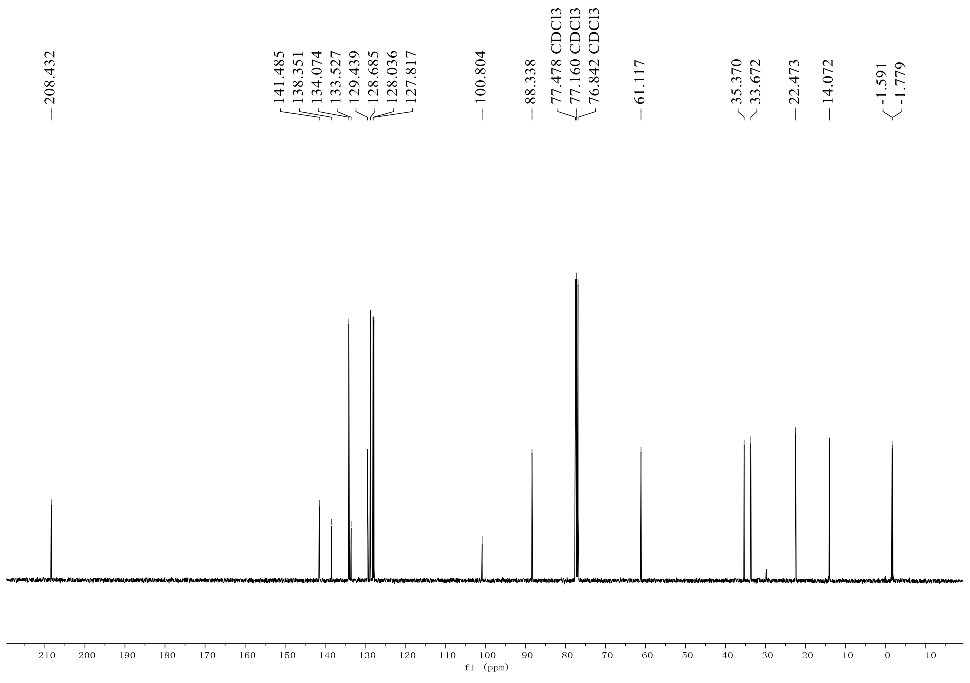
4-(4-butylphenyl)-4-(dimethyl(phenyl)silyl)buta-2,3-dien-1-ol (3b). This compound was prepared via the general procedures described above and was obtained as yellow oil in 84% yield (56.7 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

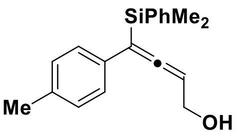
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.56 (m, 2H), 7.39-7.33 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 5.34 (t, *J* = 6.8 Hz, 1H), 4.1-4.09 (m, 2H), 2.54 (t, *J* = 7.8 Hz, 2H), 1.59-1.50 (m, 2H), 1.37-1.28 (m, 2H), 1.16 (s, 1H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.49 (s, 3H), 0.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.43, 141.49, 138.35, 134.07, 133.53, 129.44, 128.69, 128.04, 127.82, 100.80, 88.34, 61.12, 35.37, 33.67, 22.47, 14.07, -1.59, -1.78.

HRMS (ESI) m/z calculated for $C_{22}H_{28}OSiNa$ $[M+Na]^+$: 359.1807, found: 359.1809.





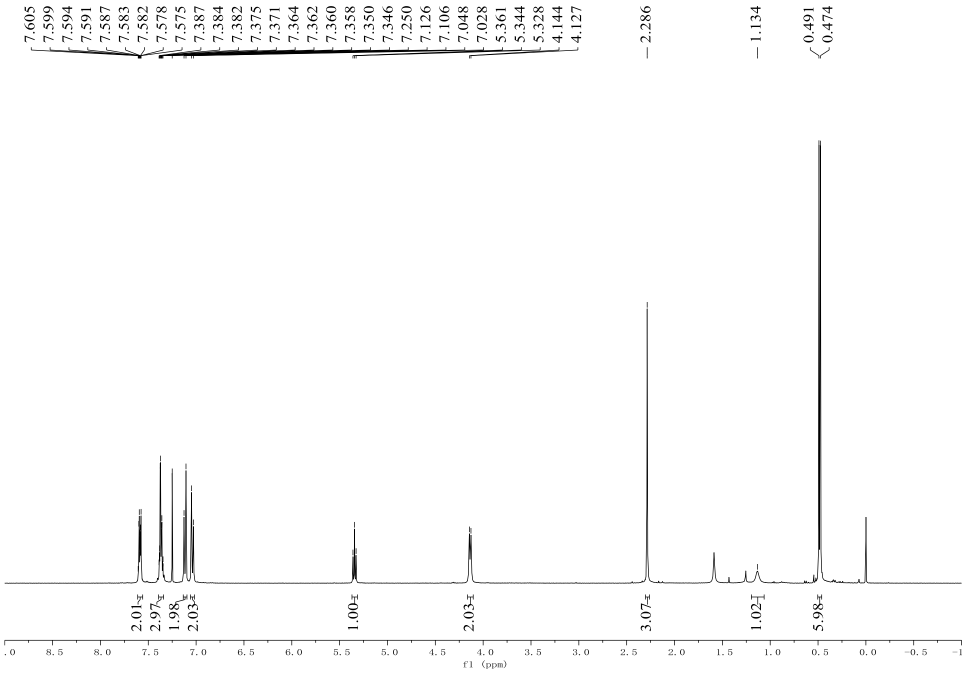


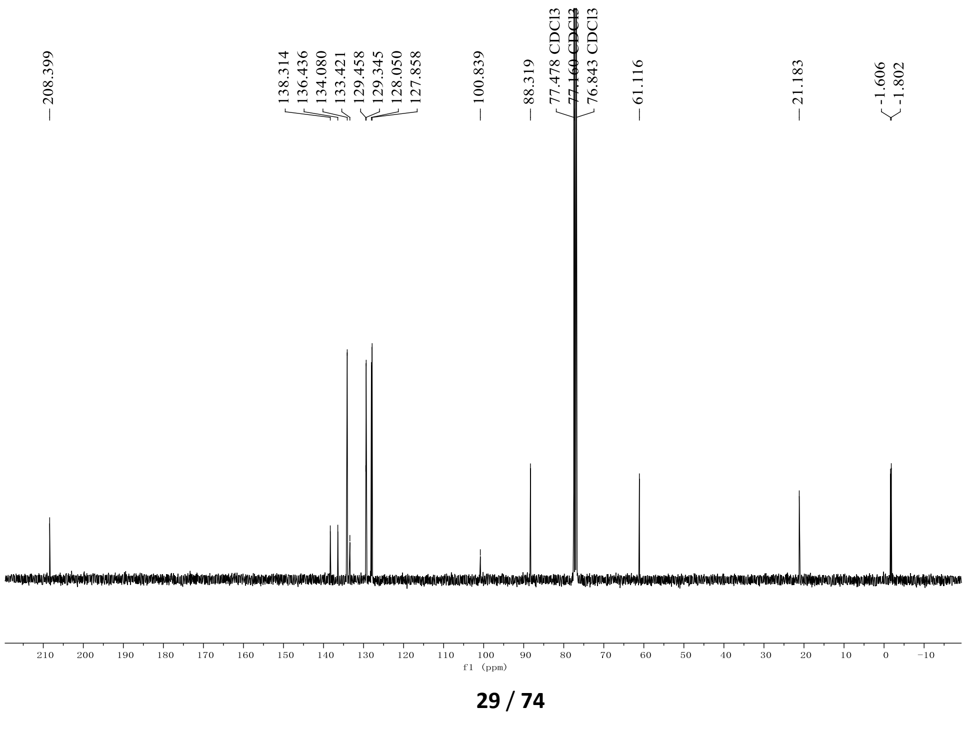
4-(dimethyl(phenyl)silyl)-4-(*p*-tolyl)buta-2,3-dien-1-ol (3c). This compound was prepared by the general procedure described above and was obtained as yellow oil in 87% yield (51.4 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

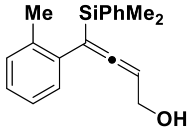
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 2H), 7.39-7.34 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.34 (t, *J* = 6.6 Hz, 1H), 4.14 (d, *J* = 6.8 Hz, 2H), 2.29 (s, 3H), 1.13 (s, 1H), 0.49 (s, 3H) 0.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.40, 138.31, 136.44, 134.08, 133.42, 129.46, 129.35, 128.05, 127.86, 100.84, 88.32, 61.12, 21.18, -1.61, -1.80.

HRMS (ESI) m/z calculated for $C_{19}H_{22}OSiNa$ $[M+Na]^+$: 317.1338, found: 317.1335.





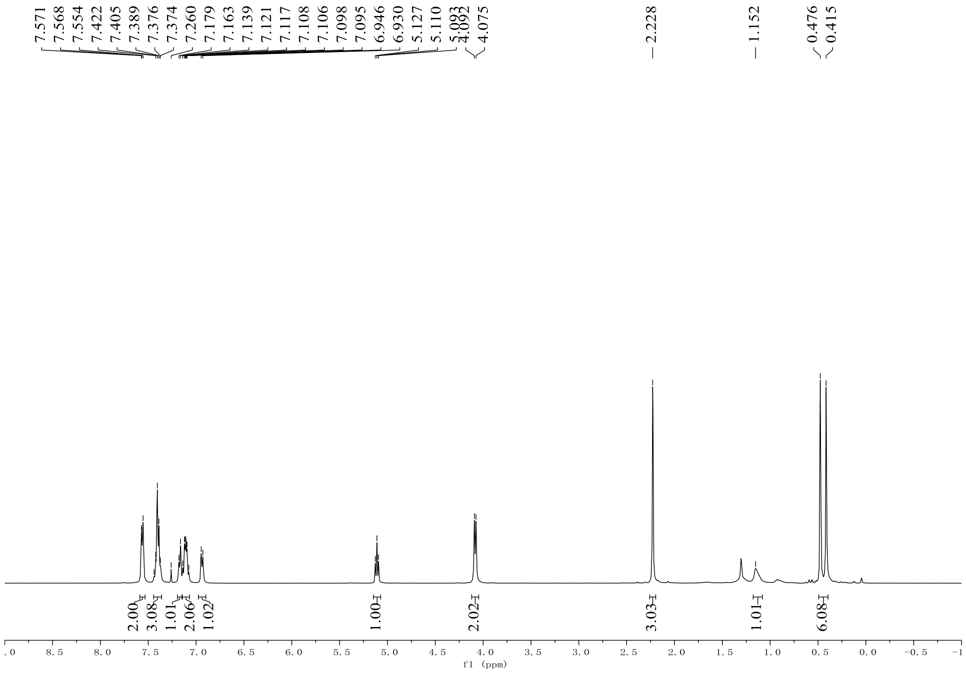


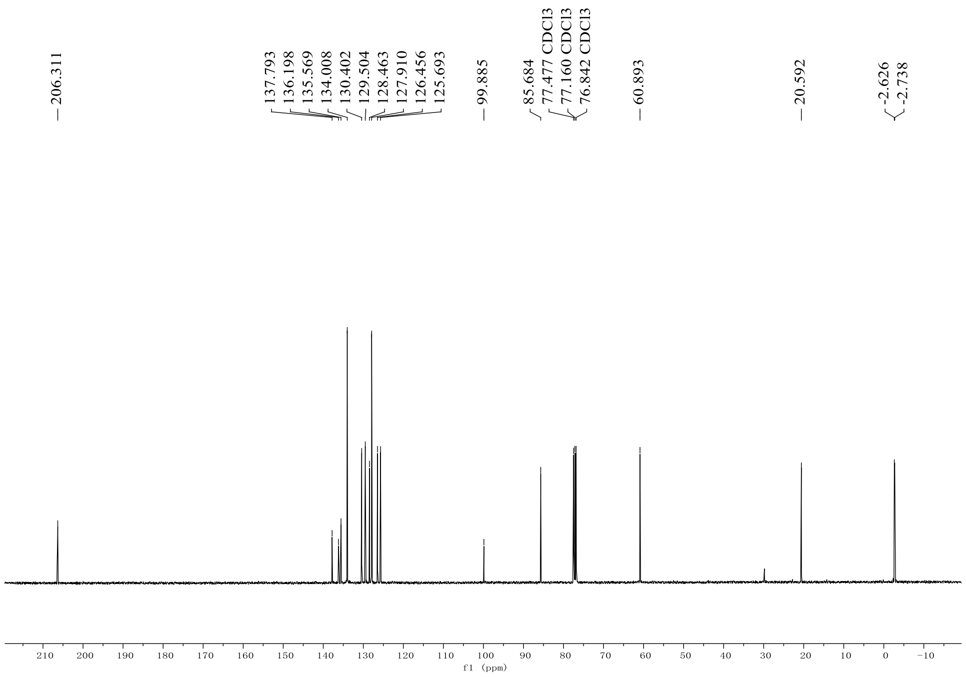
4-(dimethyl(phenyl)silyl)-4-(*o*-tolyl)buta-2,3-dien-1-ol (3d). This compound was prepared by the general procedure described above and was obtained as yellow oil in 83% yield (48.6 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

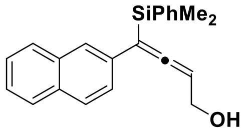
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.53 (m, 2H), 7.45-7.36 (m, 3H), 7.17 (d, *J* = 6.4 Hz, 1H), 7.14-7.07 (m, 2H), 6.94 (d, *J* = 6.4 Hz, 1H), 5.11 (t, *J* = 6.8 Hz, 1H), 4.08 (d, *J* = 6.8 Hz, 2H), 2.23 (s, 3H), 1.15 (s, 1H), 0.48 (s, 3H), 0.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.31, 137.79, 136.20, 135.57, 134.01, 130.40, 129.50, 128.46, 127.91, 126.46, 125.69, 99.89, 85.68, 60.89, 20.59, -2.63, -2.74.

HRMS (ESI) m/z calculated for $C_{19}H_{22}OSiNa$ $[M+Na]^+$: 317.1338, found: 317.1334.





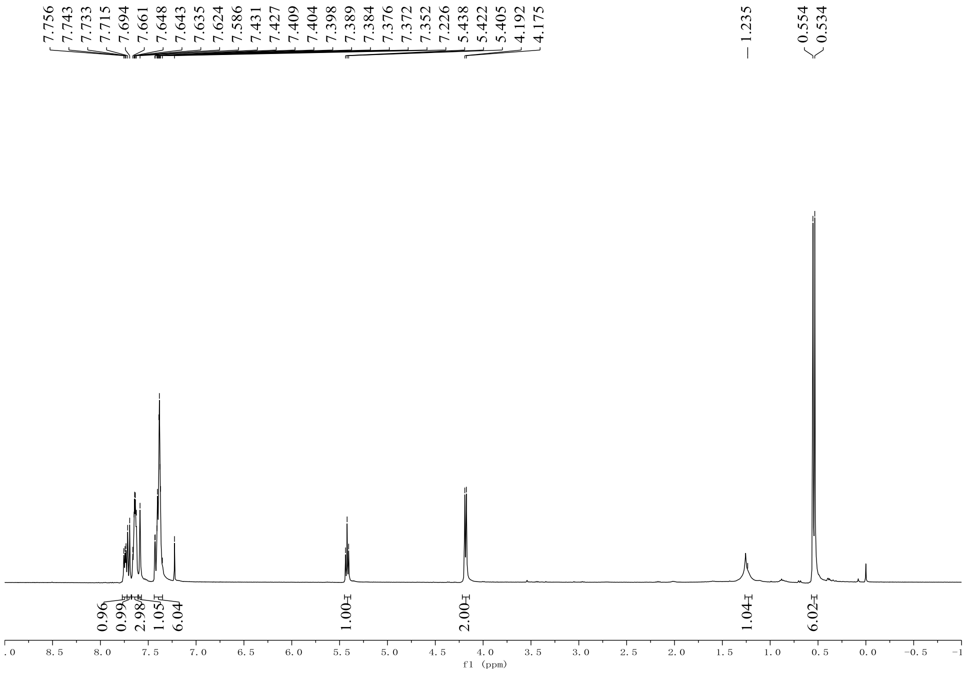


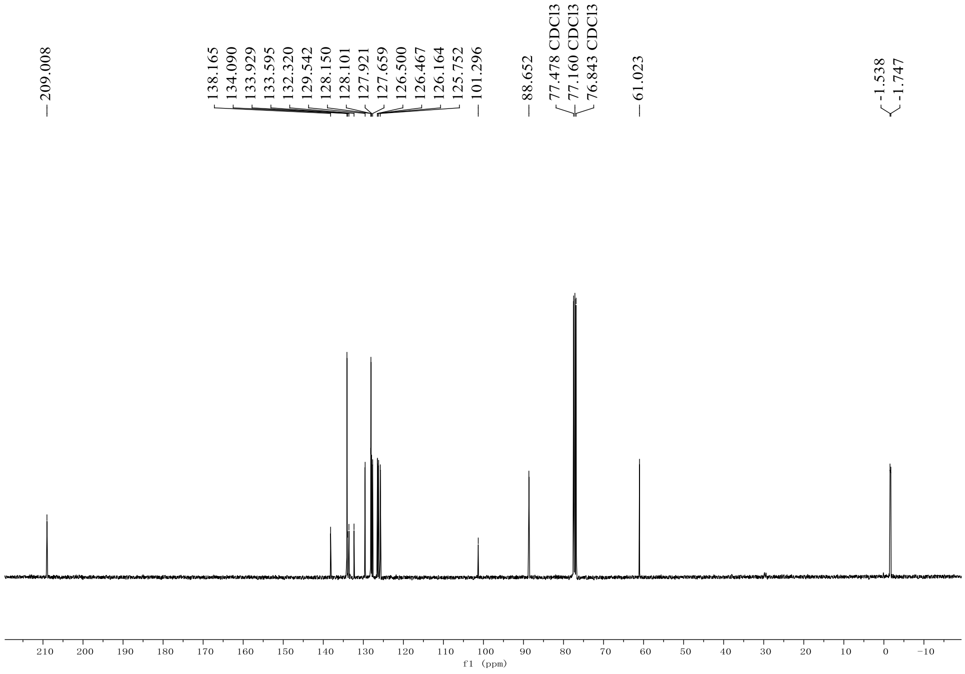
4-(dimethyl(phenyl)silyl)-4-(naphthalen-2-yl)buta-2,3-dien-1-ol (3e). This compound was prepared by the general procedure described above and was obtained as yellow oil in 66% yield (43.5 mg). R_f = 0.40 (Petroleum ether : EtOAc = 4:1).

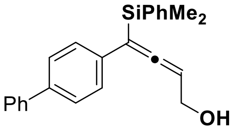
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.72 (m, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.67-7.61 (m, 3H), 7.59 (s, 1H), 7.44-7.35 (m, 6H), 5.42 (t, *J* = 6.6 Hz, 1H), 4.18 (d, *J* = 6.8 Hz, 2H), 1.23 (s, 1H), 0.55 (s, 3H), 0.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.01, 138.17, 134.09, 133.93, 133.60, 132.32, 129.54, 128.15, 128.10, 127.92, 127.66, 126.50, 126.47, 126.16, 125.75, 101.30, 88.65, 61.02, -1.54, -1.75.

HRMS (ESI) m/z calculated for $C_{22}H_{22}OSiNa$ $[M+Na]^+$: 353.1338, found: 353.1337.





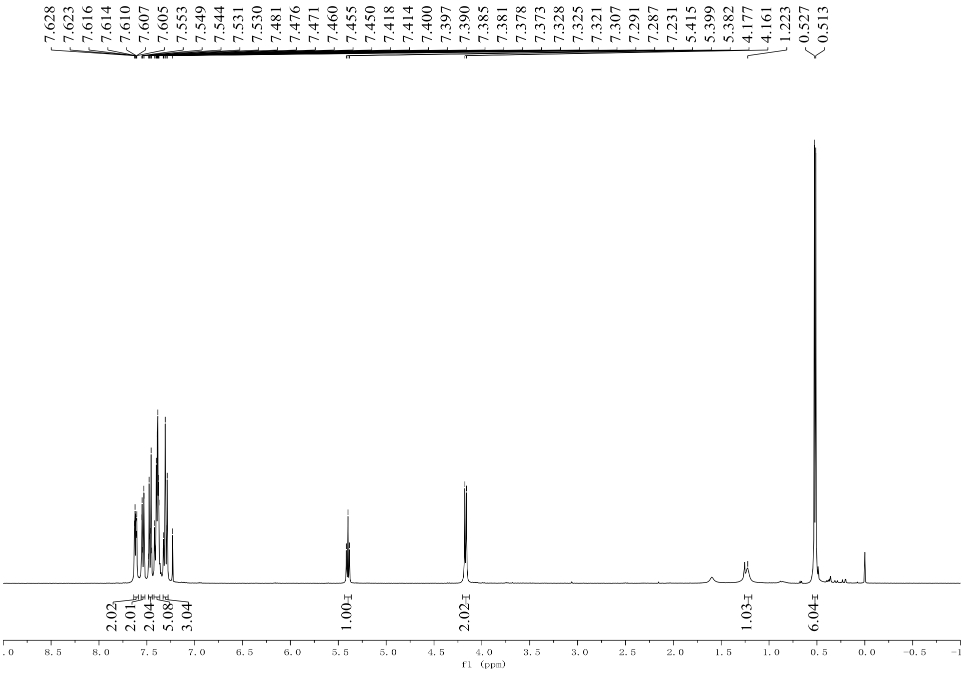


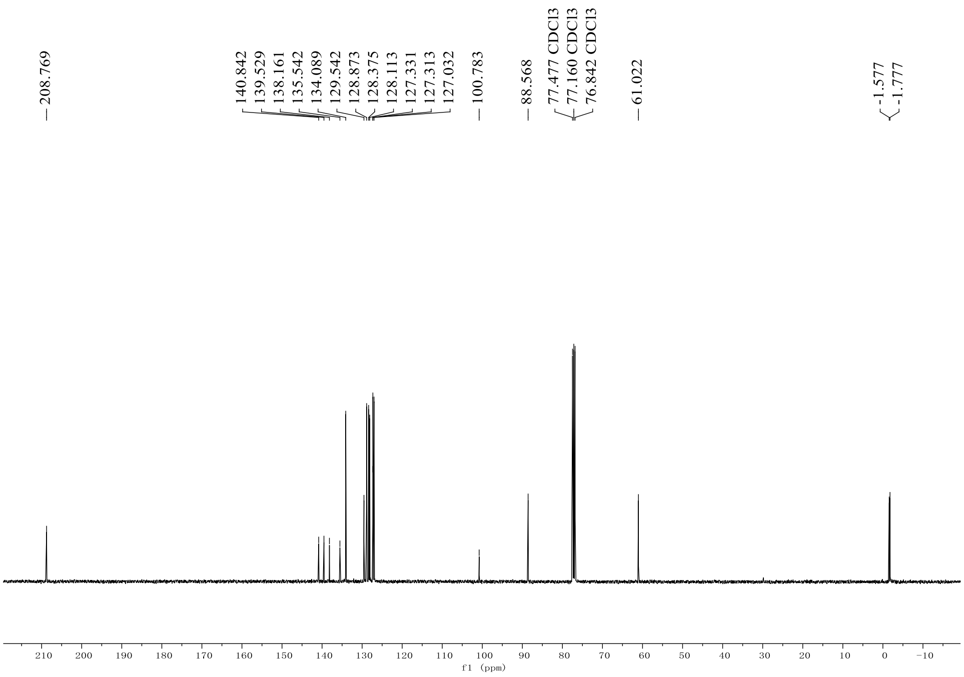
4-([1,1'-biphenyl]-4-yl)-4-(dimethyl(phenyl)silyl)buta-2,3-dien-1-ol (3f). This compound was prepared by the general procedure described above and was obtained as yellow oil in 60% yield (42.5 mg). R_f = 0.45 (Petroleum ether : EtOAc = 4:1).

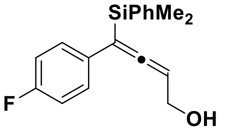
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.59 (m, 2H), 7.56-7.52 (m, 2H), 7.48-7.44 (m, 2H), 7.43-7.36 (m, 5H), 7.33-7.28 (m, 3H), 5.40 (t, *J* = 6.6 Hz, 1H), 4.17 (d, *J* = 6.4 Hz, 2H), 1.22 (s, 1H), 0.53 (s, 3H), 0.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.77, 140.84, 139.53, 138.16, 135.54, 134.09, 129.54, 128.87, 128.38, 128.11, 127.33, 127.31, 127.03, 100.78, 88.57, 61.02, -1.58, -1.78.

HRMS (ESI) m/z calculated for $C_{24}H_{24}OSiNa$ $[M+Na]^+$: 379.1494, found: 379.1500.







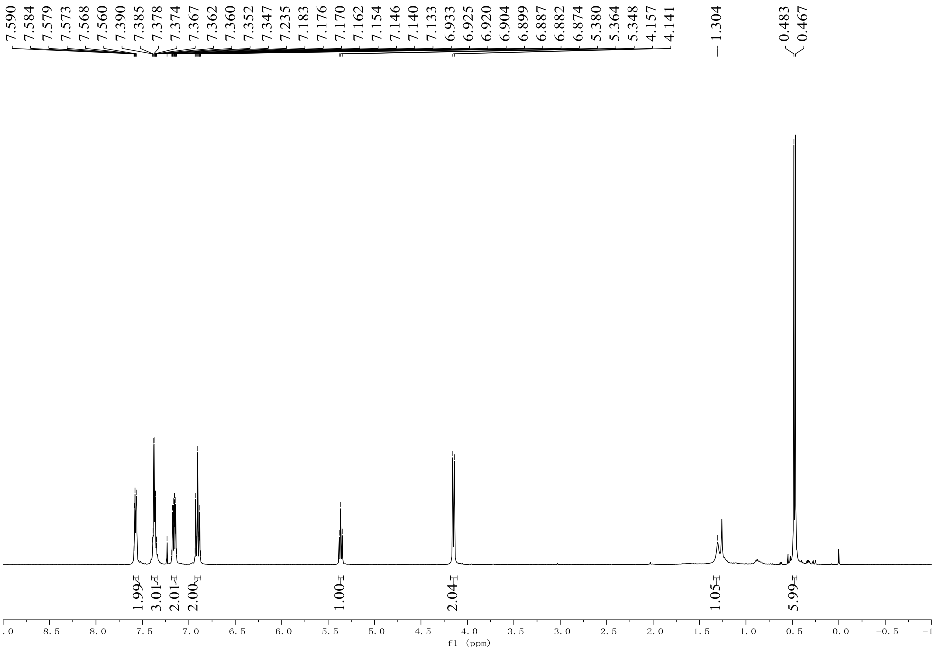
4-(dimethyl(phenyl)silyl)-4-(4-fluorophenyl)buta-2,3-dien-1-ol (3g). This compound was prepared by the general procedure described above and was obtained as yellow oil in 76% yield (45.2 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

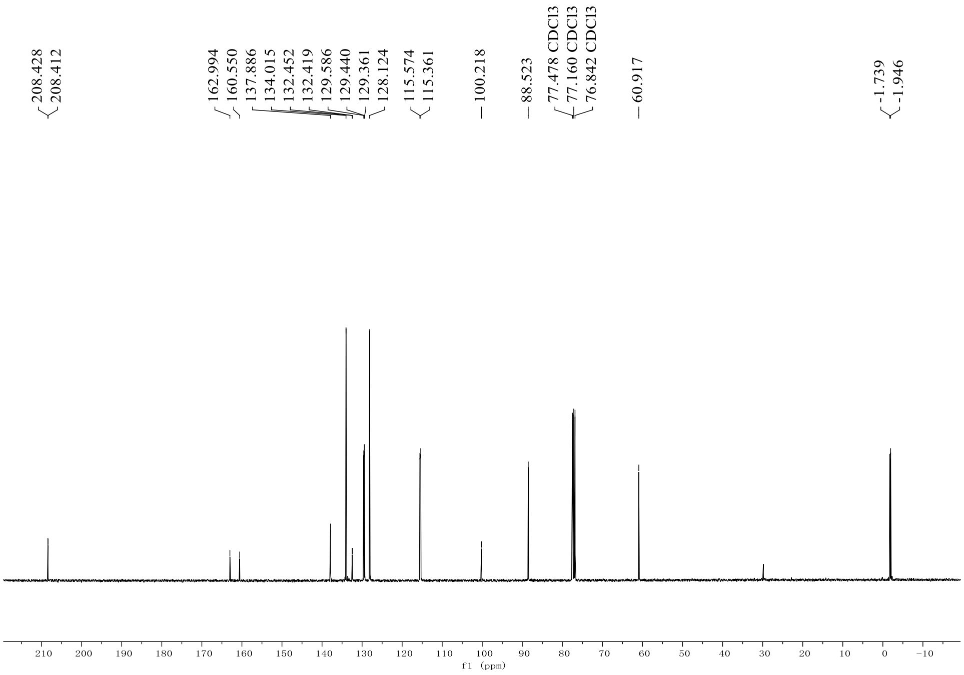
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 2H), 7.40-7.34 (m, 3H), 7.19-7.13 (m, 2H), 6.93-6.87 (m, 2H), 5.36 (t, *J* = 6.4 Hz, 1H), 4.15 (d, *J* = 6.4 Hz, 2H), 1.30 (s, 1H), 0.48 (s, 3H), 0.47 (s, 3H).

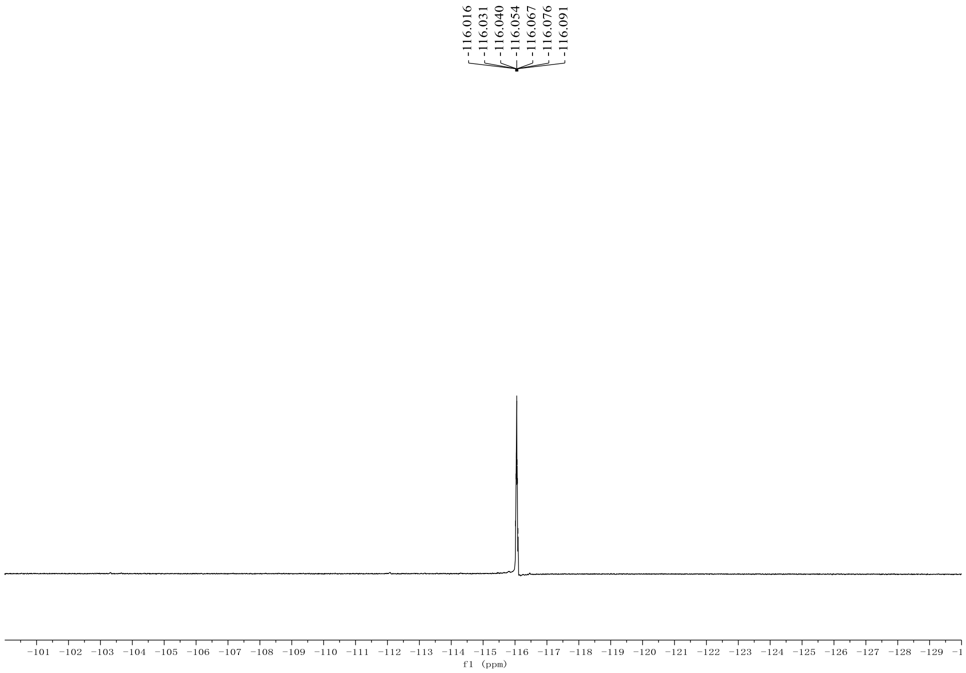
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.42 (d, *J* =1.6 Hz),161.77 (d, *J* =246.8 Hz), 137.89, 134.02, 132.43 (d, *J* =3.3 Hz), 129.59, 129.40 (d, *J* =8.0 Hz), 128.12, 115.47 (d, *J* =21.5 Hz), 100.22, 88.52, 60.92, -1.74, -1.95.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.05 (m, 1F).

HRMS (ESI) m/z calculated for $C_{18}H_{19}FOSiNa$ $[M+Na]^+$: 321.1087, found: 321.1090.



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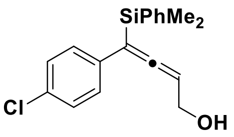
f1 (ppm)

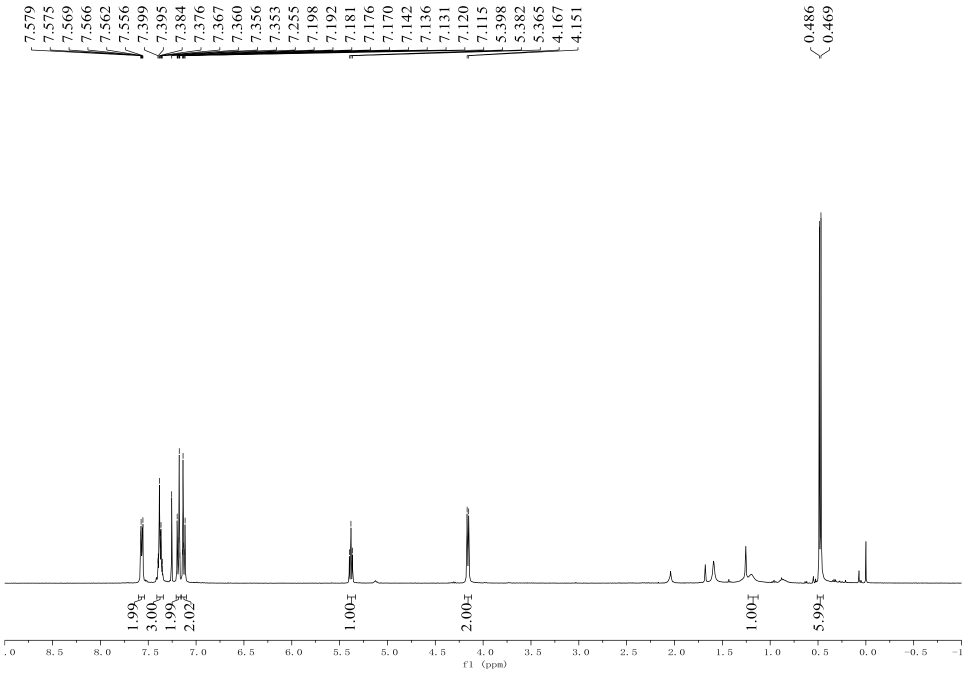


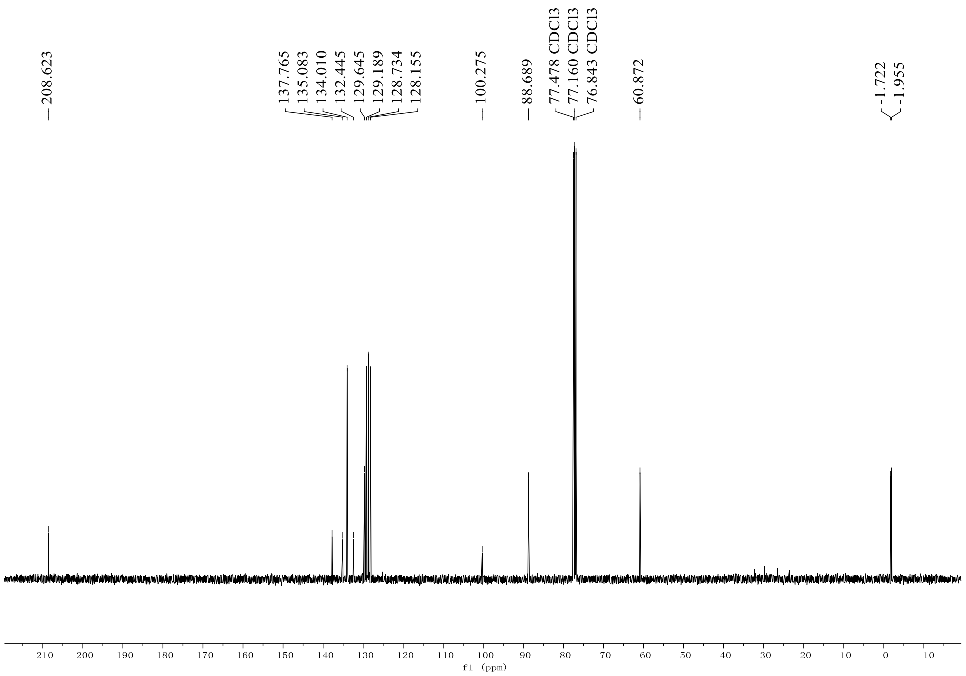
4-(4-chlorophenyl)-4-(dimethyl(phenyl)silyl)buta-2,3-dien-1-ol (3h). This compound was prepared by the general procedure described above and was obtained as yellow oil in 68% yield (43.0 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

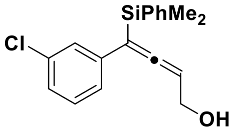
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.54 (m, 2H), 7.41-7.34 (m, 3H), 7.21-7.16 (m, 2H), 7.15-7.10 (m, 2H), 5.38 (t, *J* = 6.6 Hz, 1H), 4.16 (d, *J* = 6.4 Hz, 2H), 1.20 (s, 1H), 0.49 (s, 3H), 0.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.62, 137.77, 135.08, 134.01, 132.45, 129.65, 129.19, 128.73, 128.16, 100.28, 88.69, 60.87, -1.72, -1.96.

HRMS (ESI) m/z calculated for $C_{18}H_{20}ClOSi$ $[M+H]^+$: 315.0972, found: 315.0977.





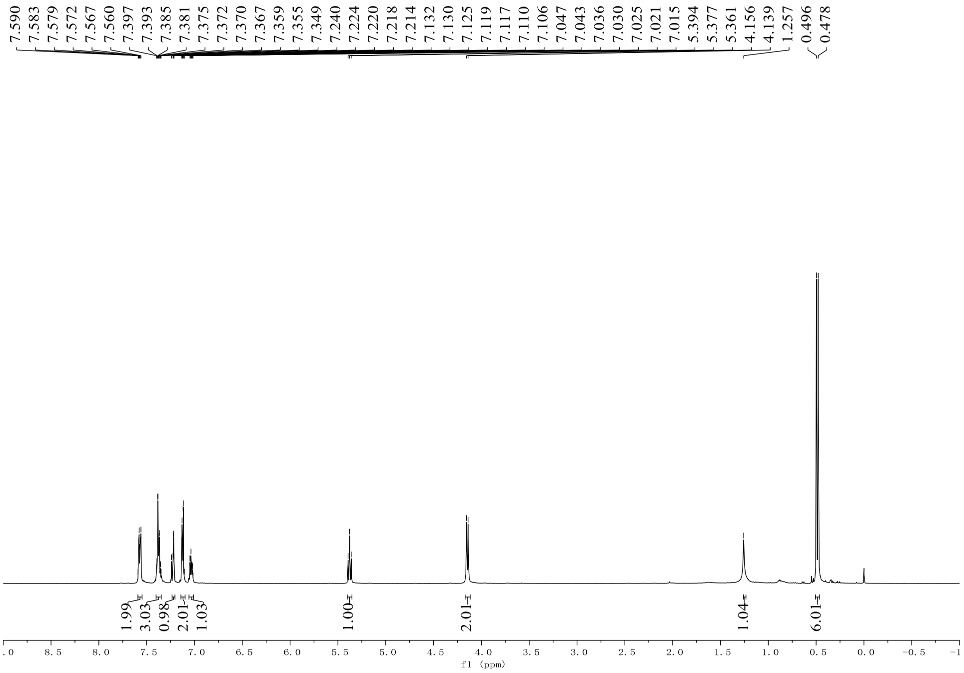


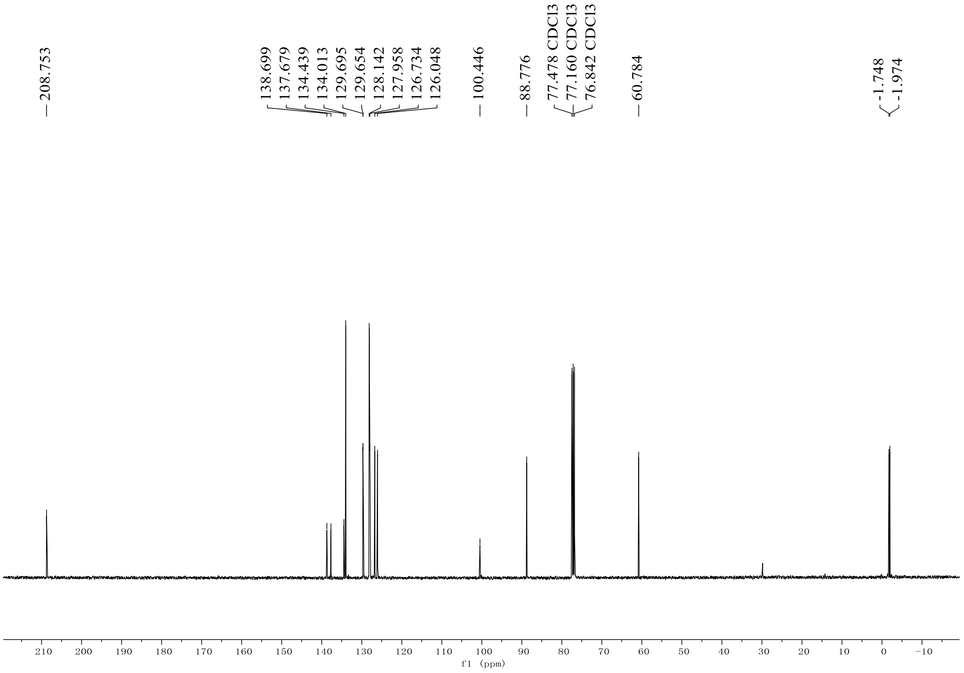
4-(3-chlorophenyl)-4-(dimethyl(phenyl)silyl)buta-2,3-dien-1-ol (3i). This compound was prepared by the general procedure described above and was obtained as yellow oil in 66% yield (41.7 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

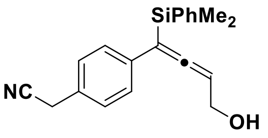
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.40-7.35 (m, 3H), 7.23-7.21 (m, 1H), 7.14-7.10 (m, 2H), 7.06-7.01 (m, 1H), 5.38 (t, *J* = 6.6 Hz, 1H), 4.15 (d, *J* = 6.8 Hz, 2H), 1.26 (s, 1H), 0.50 (s, 3H), 0.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.75, 138.70, 137.68, 134.44, 134.01, 129.70, 129.65, 128.14, 127.96, 126.73, 126.05, 100.45, 88.78, 60.78, -1.75, -1.97.

HRMS (ESI) m/z calculated for $C_{18}H_{19}ClOSiNa$ $[M+Na]^+$: 337.0791, found: 337.0787.





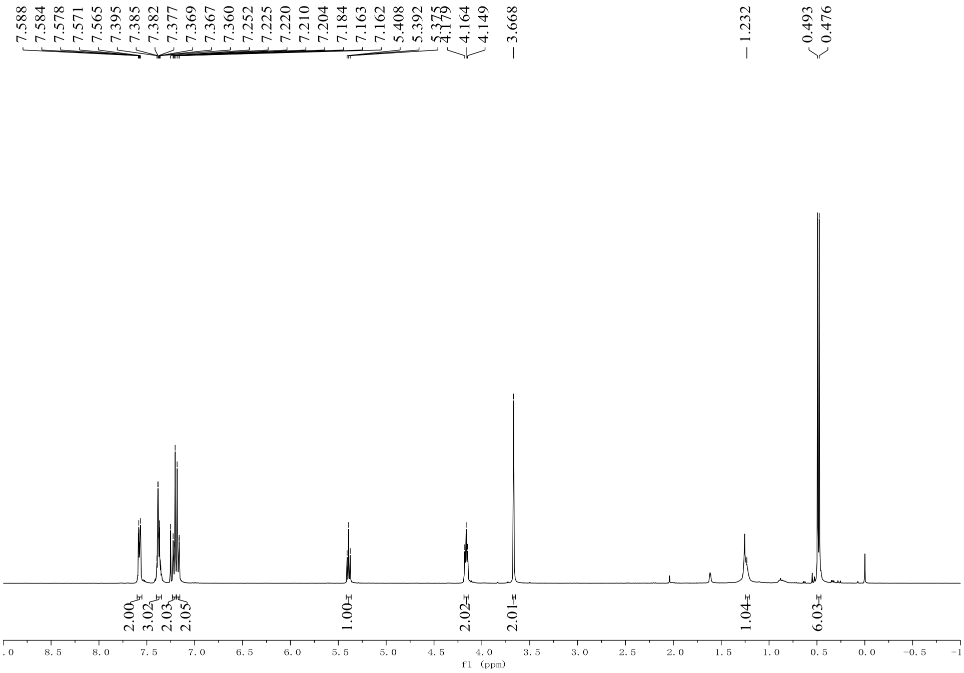


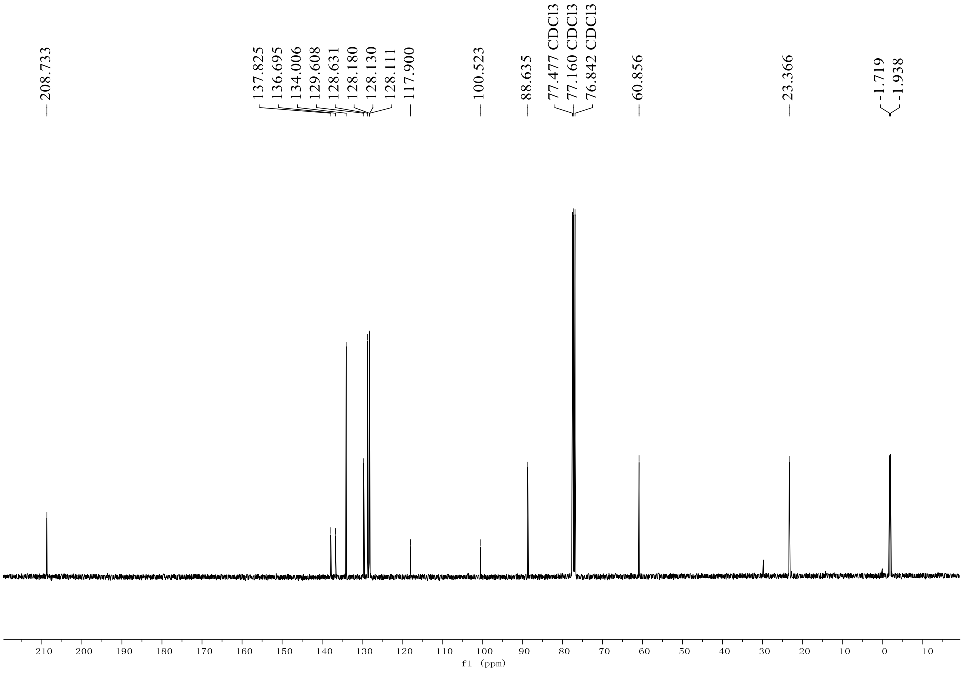
2-(4-(1-(dimethyl(phenyl)silyl)-4-hydroxybuta-1,2-dien-1-yl)phenyl) acetonitrile (3j). This compound was prepared by the general procedure described above and was obtained as yellow oil in 79% yield (50.7 mg). R_f = 0.35 (Petroleum ether : EtOAc = 7:3).

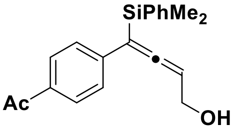
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 2H), 7.40-7.35 (m, 3H), 7.23-7.19 (m, 2H), 7.19-7.15 (m, 2H), 5.39 (t, *J* = 6.6 Hz, 1H), 4.16 (t, *J* = 6.0 Hz, 2H), 3.67 (s, 2H), 1.23 (s, 1H), 0.49 (s, 3H), 0.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.73, 137.83, 136.70, 134.01, 129.61, 128.63, 128.18, 128.13, 128.11, 117.90, 100.52, 88.64, 60.86, 23.37, -1.72, -1.94.

HRMS (ESI) m/z calculated for $C_{20}H_{21}NOSiNa$ $[M+Na]^+$: 342.1290, found: 342.1287.





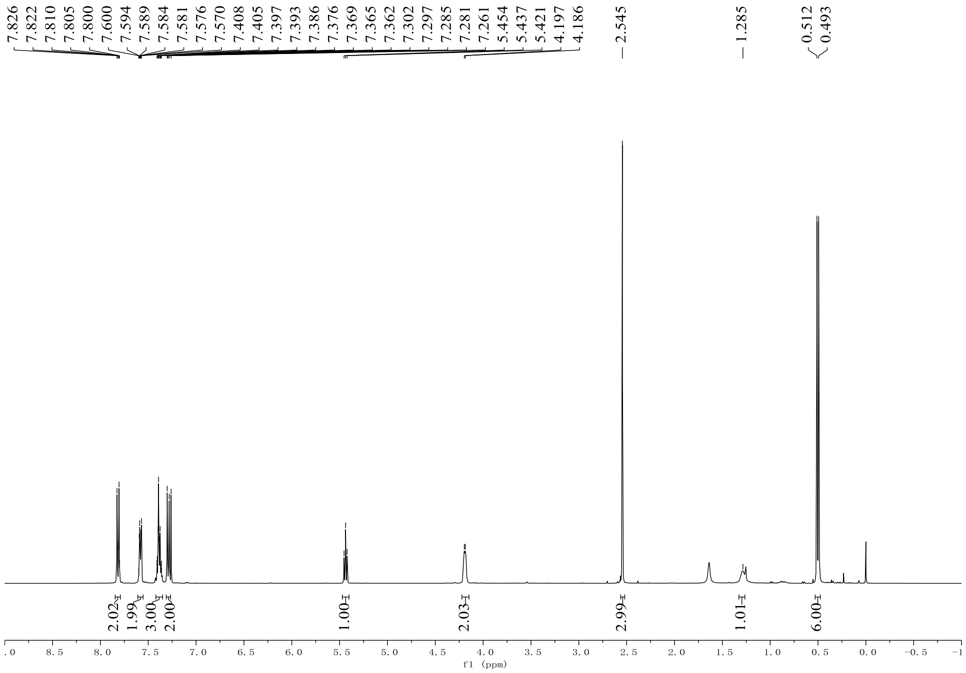


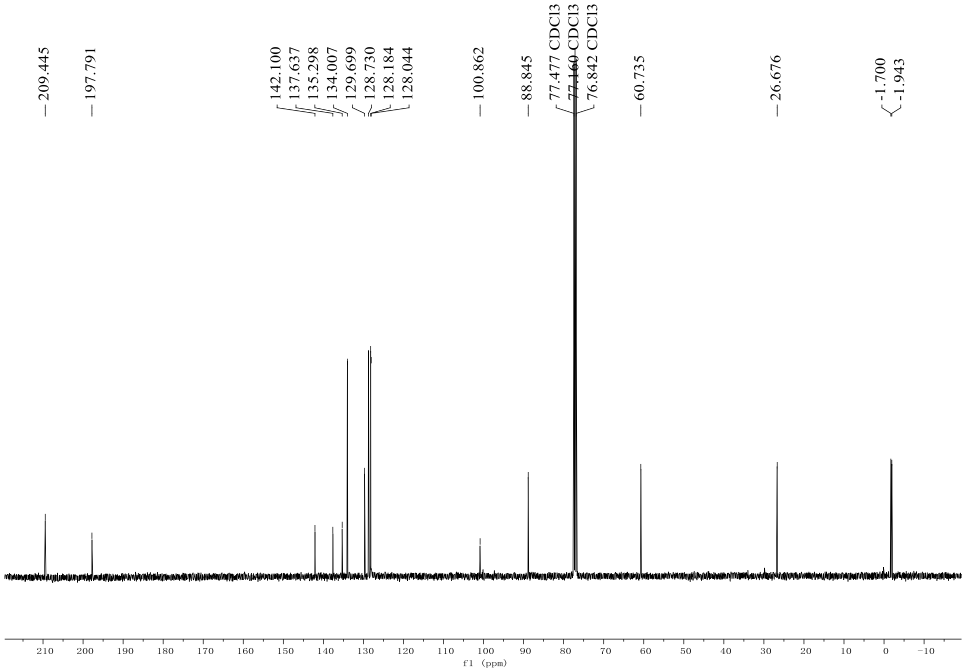
1-(4-(1-(dimethyl(phenyl)silyl)-4-hydroxybuta-1,2-dien-1-yl)phenyl)ethan-1-one (3k). This compound was prepared by the general procedure described above and was obtained as yellow oil in 32% yield (20.9 mg). R_f = 0.50 (Petroleum ether : EtOAc = 7:3).

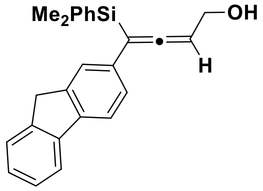
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.79 (m, 2H), 7.61-7.55 (m, 2H), 7.42-7.35 (m, 3H), 7.31-7.27 (m, 2H), 5.44 (t, *J* = 6.6 Hz, 1H), 4.19 (d, *J* = 4.4 Hz, 2H), 2.54 (s, 3H), 1.28 (s, 1H), 0.51 (s, 3H), 0.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.45, 197.79, 142.10, 137.64, 135.30, 134.01, 129.70, 128.73, 128.18, 128.04, 100.86, 88.85, 60.74, 26.68, -1.70, -1.94.

HRMS (ESI) m/z calculated for $C_{20}H_{23}O_2Si$ $[M+H]^+$: 323.1467, found: 323.1474.





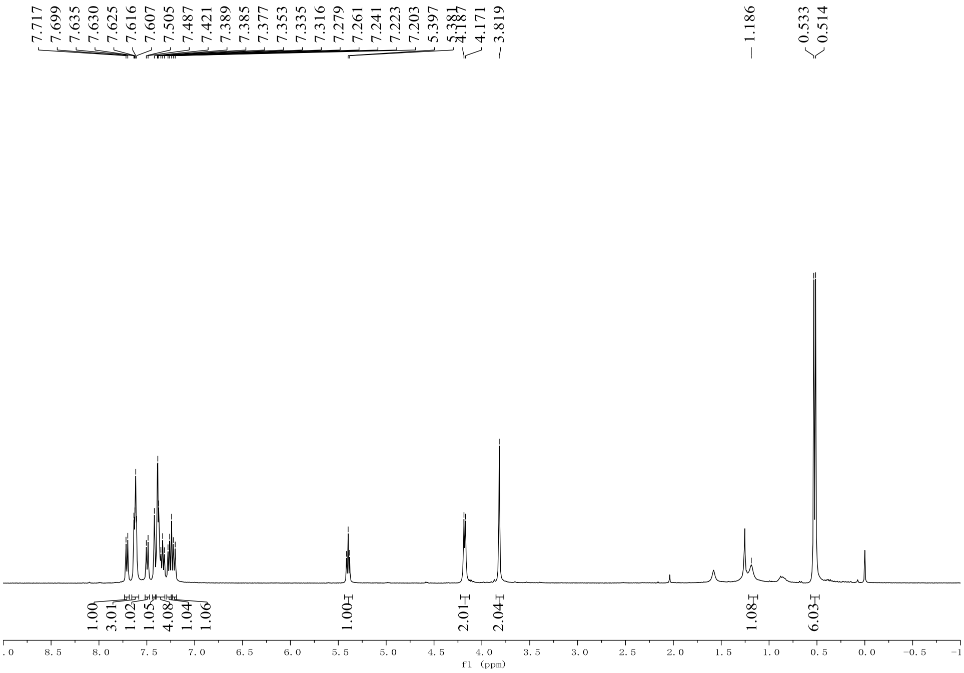


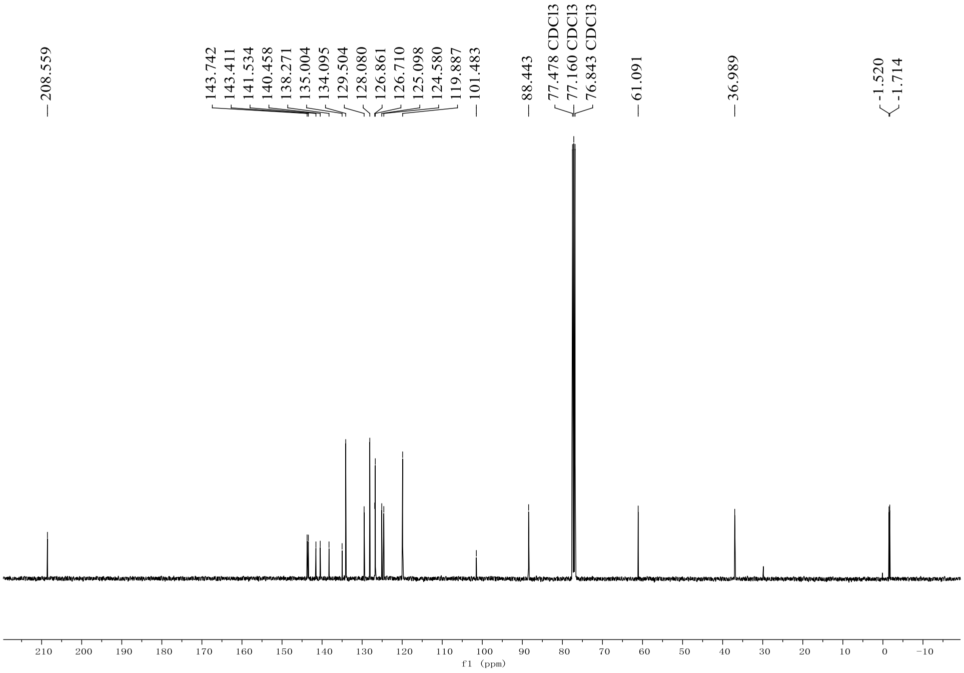
4-(dimethyl(phenyl)silyl)-4-(9H-fluoren-2-yl)buta-2,3-dien-1-ol (3l). This compound was prepared by the general procedure described above and was obtained as yellow oil in 51% yield (37.6 mg). R_f = 0.45 (Petroleum ether : EtOAc = 4:1).

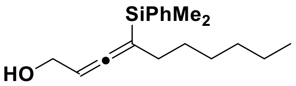
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.2 Hz, 1H), 7.66-7.58 (m, 3H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.42 (s, 1H), 7.40-7.31 (m, 4H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 5.40 (t, *J* = 6.6 Hz, 1H), 4.18 (d, *J* = 6.4 Hz, 2H), 3.82 (s, 2H), 1.19 (s, 1H), 0.53 (s, 3H), 0.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.56, 143.74, 143.41, 141.53, 140.46, 138.27, 135.00, 134.10, 129.50, 128.08, 126.86, 126.71, 125.10, 124.58, 119.89, 101.48, 88.44, 61.09, 36.99, -1.52, -1.71 .

HRMS (ESI) m/z calculated for $C_{25}H_{25}OSi$ $[M+H]^+$: 369.1675, found: 369.1678.





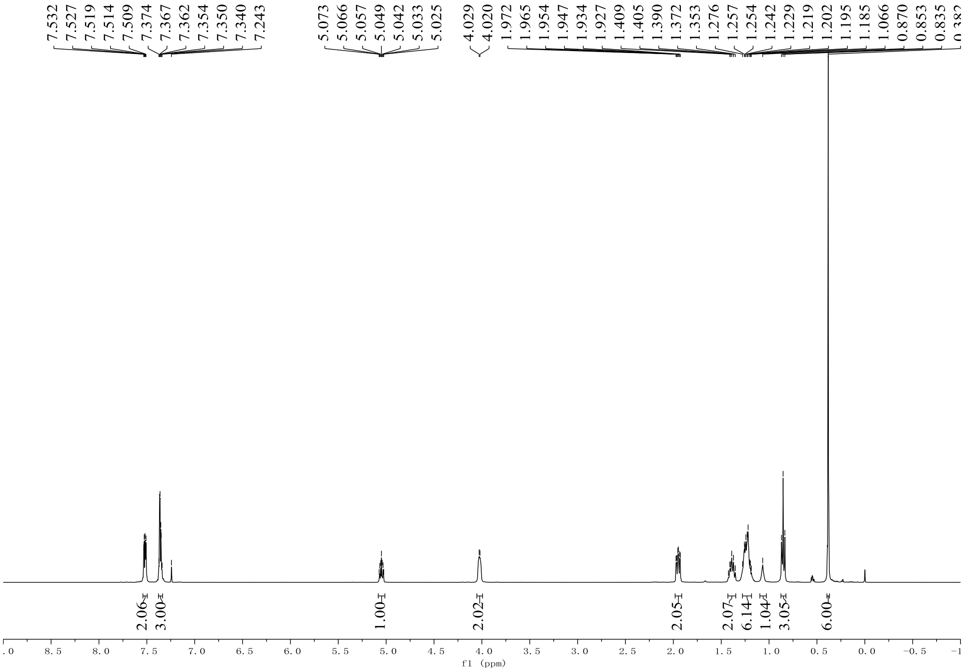


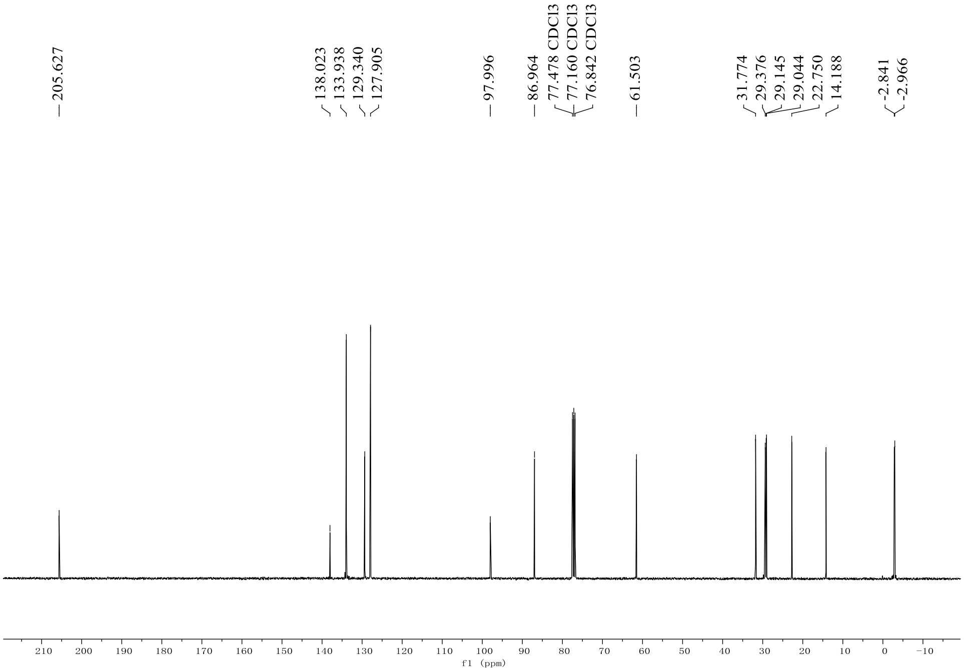
4-(dimethyl(phenyl)silyl)deca-2,3-dien-1-ol (3m). This compound was prepared by the general procedure described above and was obtained as colorless oil in 85% yield (49.0 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

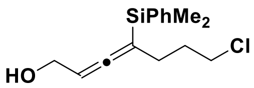
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.38-7.34 (m, 3H), 5.08-5.02 (m, 1H), 4.02 (d, *J* = 3.6Hz, 2H), 1.95 (td, *J* = 7.6, 2.8 Hz, 2H), 1.43-1.35 (m, 2H), 1.28-1.18 (m, 6H), 1.07 (s, 1H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.38 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.63, 138.02, 133.94, 129.34, 127.91, 98.00, 86.96, 61.50, 31.77, 29.38, 29.15, 29.04, 22.75, 14.19, -2.84, -2.97.

HRMS (ESI) m/z calculated for $C_{18}H_{28}OSiNa$ $[M+Na]^+$: 311.1807, found: 311.1804.





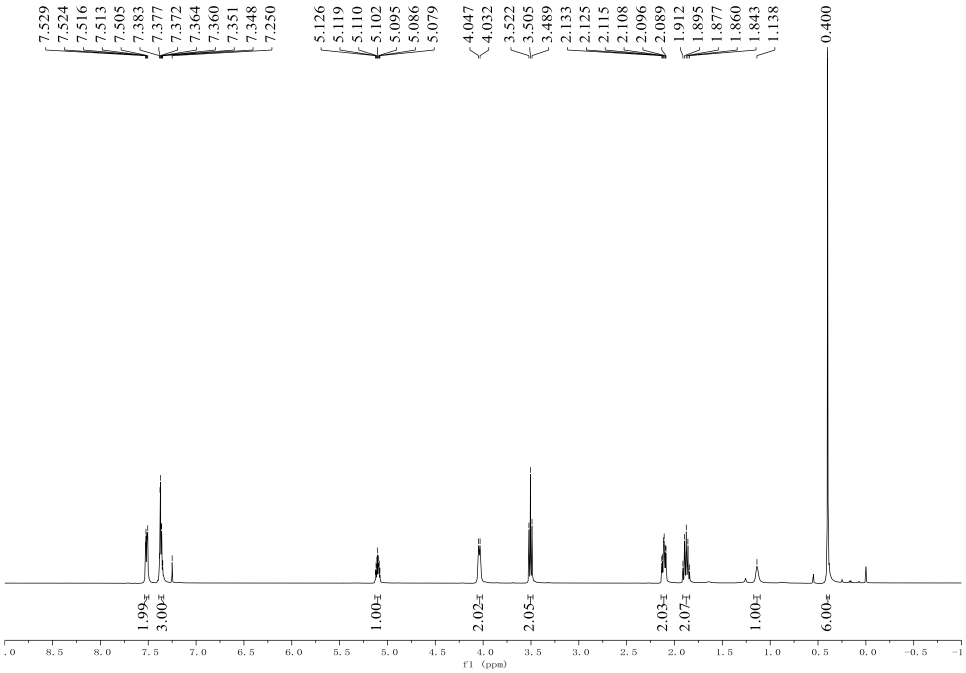


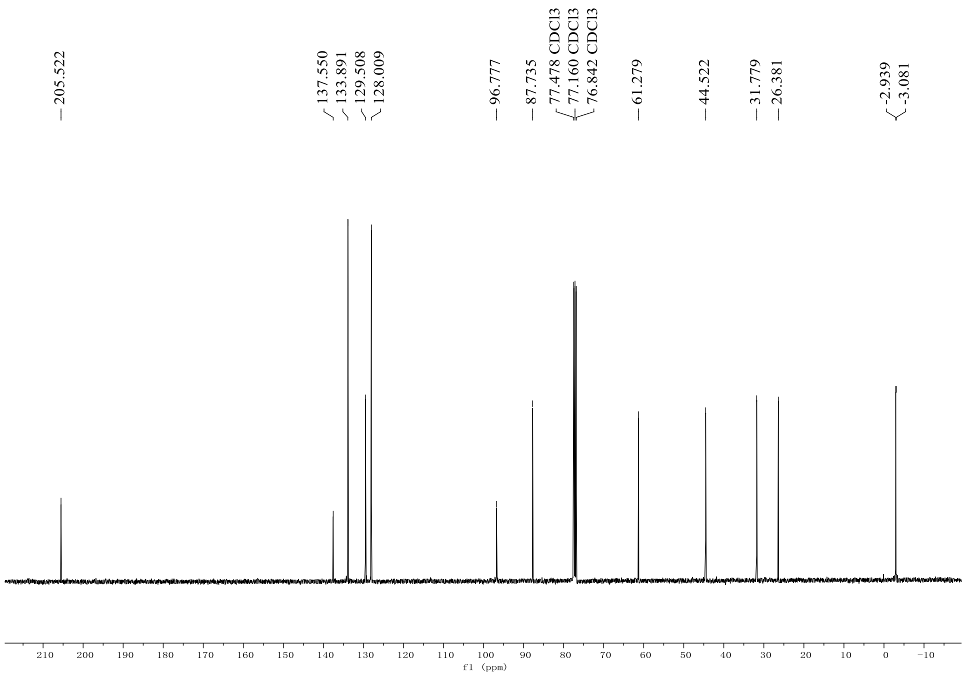
7-chloro-4-(dimethyl(phenyl)silyl)hepta-2,3-dien-1-ol (3n). This compound was prepared by the general procedure described above and was obtained as colorless oil in 88% yield (49.2 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

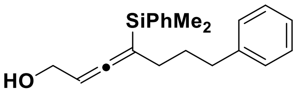
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.49 (m, 2H), 7.39-7.34 (m, 3H), 5.10 (tt, *J* = 6.4, 3.0 Hz, 1H), 4.04 (d, *J* = 6.0 Hz, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.11 (td, *J* = 7.2, 3.0 Hz, 2H), 1.92-1.84 (m, 2H), 1.14 (s, 1H), 0.40 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.52, 137.55, 133.89, 129.51, 128.01, 96.78, 87.74, 61.28, 44.52, 31.78, 26.38, -2.94, -3.08.

HRMS (ESI) m/z calculated for $C_{15}H_{21}ClOSiNa$ $[M+Na]^+$: 303.0948, found: 303.0945.





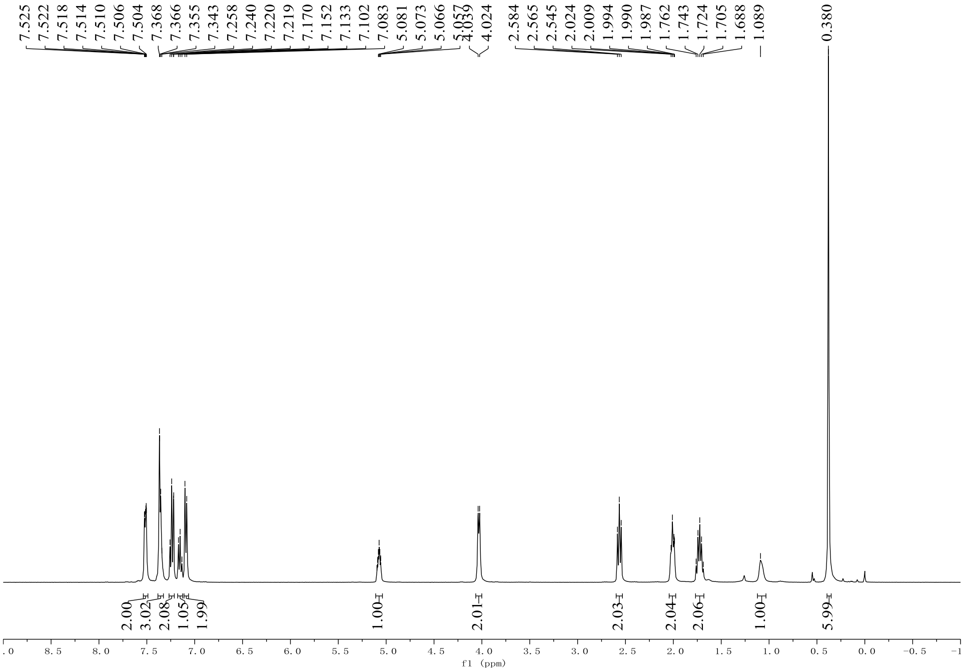


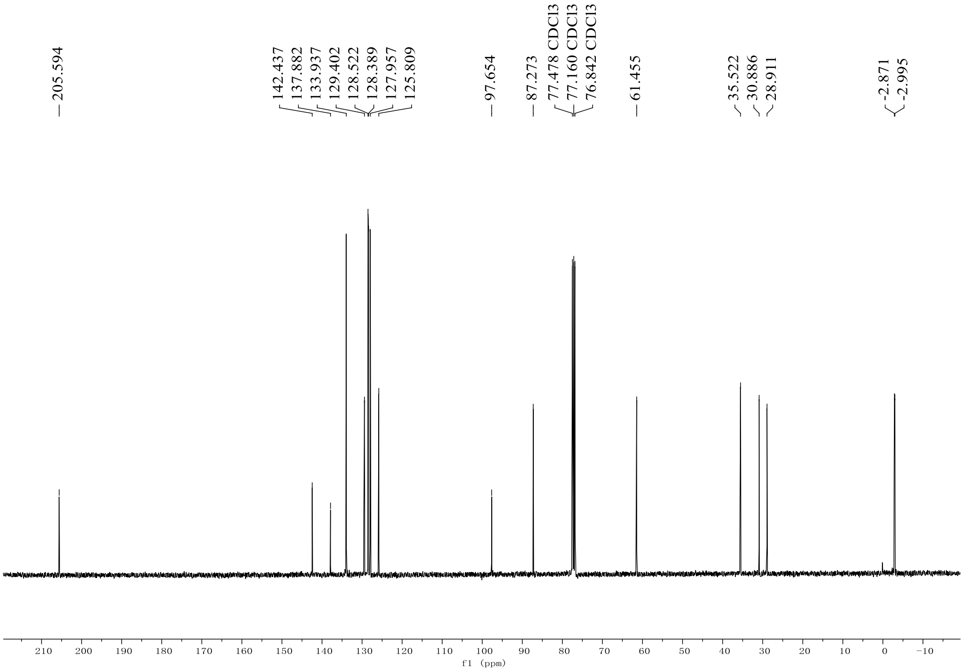
4-(dimethyl(phenyl)silyl)-7-phenylhepta-2,3-dien-1-ol (3o). This compound was prepared by the general procedure described above and was obtained as colorless oil in 86% yield (55.5 mg). $R_f = 0.50$ (Petroleum ether : EtOAc = 4:1).

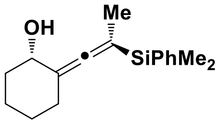
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.49 (m, 2H), 7.39-7.33 (m, 3H), 7.27-7.21 (m, 2H), 7.18-7.12 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 5.11-5.04 (m, 1H), 4.03 (d, *J* = 6.0 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.04- 1.98 (m, 2H), 1.77-1.67 (m, 2H), 1.09 (s, 1H), 0.38 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.59, 142.44, 137.88, 133.94, 129.40, 128.52, 128.39, 127.96, 125.81, 97.65, 87.27, 61.46, 35.52, 30.89, 28.91, -2.87, -3.00.

HRMS (ESI) m/z calculated for $C_{21}H_{26}OSiNa$ $[M+Na]^+$: 345.1651, found: 345.1648.





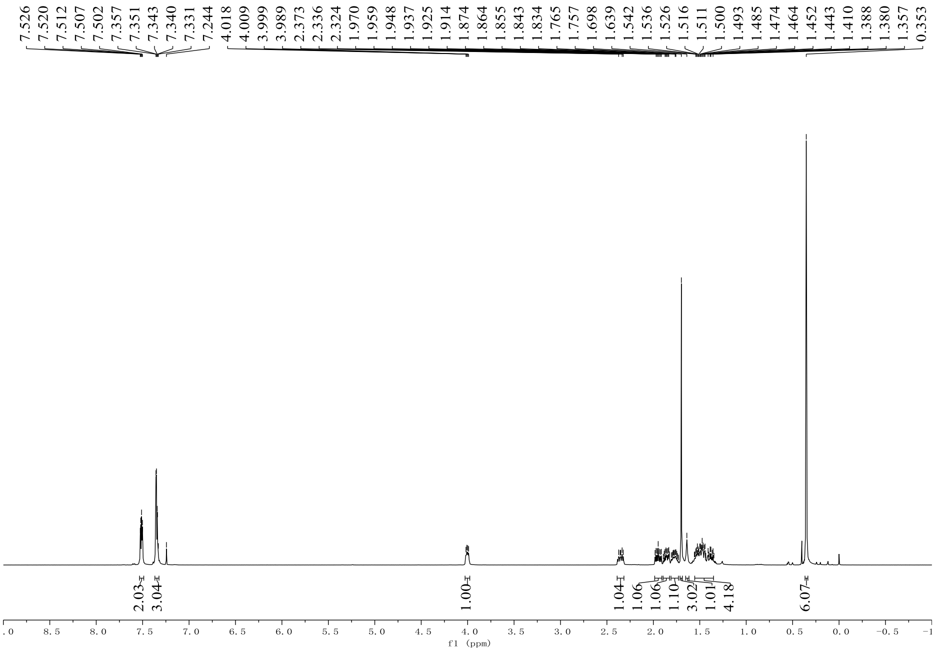


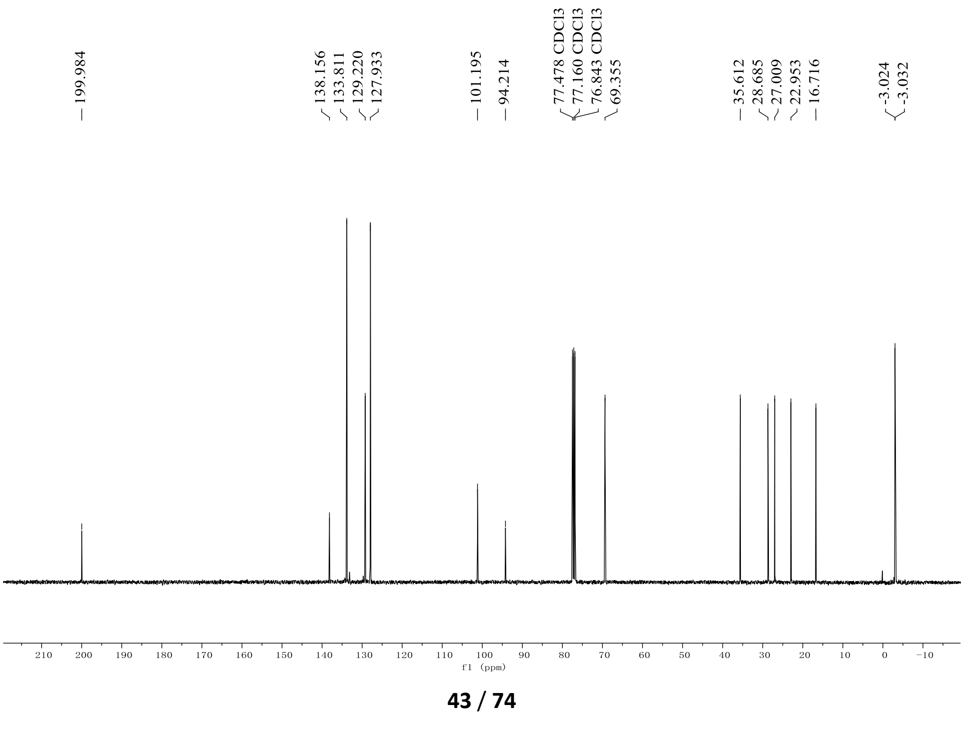
2-(2-(dimethyl(phenyl)silyl)prop-1-en-1-ylidene)cyclohexan-1-ol (3p). This compound was prepared by the general procedure described above and was obtained as colorless oil in 93% yield (50.7 mg). The stereochemical assignment was corroborated by NOE measurements of the product of **7c** derivatives formed from selected allenol upon treatment with $AgNO_3$.[7, 8] R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

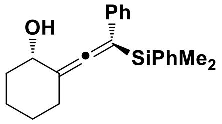
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.37-7.32 (m, 3H), 4.00 (dd, *J* = 7.8, 3.8 Hz, 1H), 2.39-2.32 (m, 1H), 1.99-1.91 (m, 1H), 1.90-1.82 (m, 1H), 1.81-1.73 (m, 1H), 1.70 (s, 3H), 1.64 (s, 1H), 1.56-1.35 (m, 4H), 0.35 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.98, 138.16, 133.81, 129.22, 127.93, 101.20, 94.21, 69.36, 35.61, 28.69, 27.01, 22.95, 16.72, -3.02, -3.03.

HRMS (ESI) m/z calculated for $C_{17}H_{24}OSiNa$ [M+Na]$^+$: 295.1494, found: 295.1497.





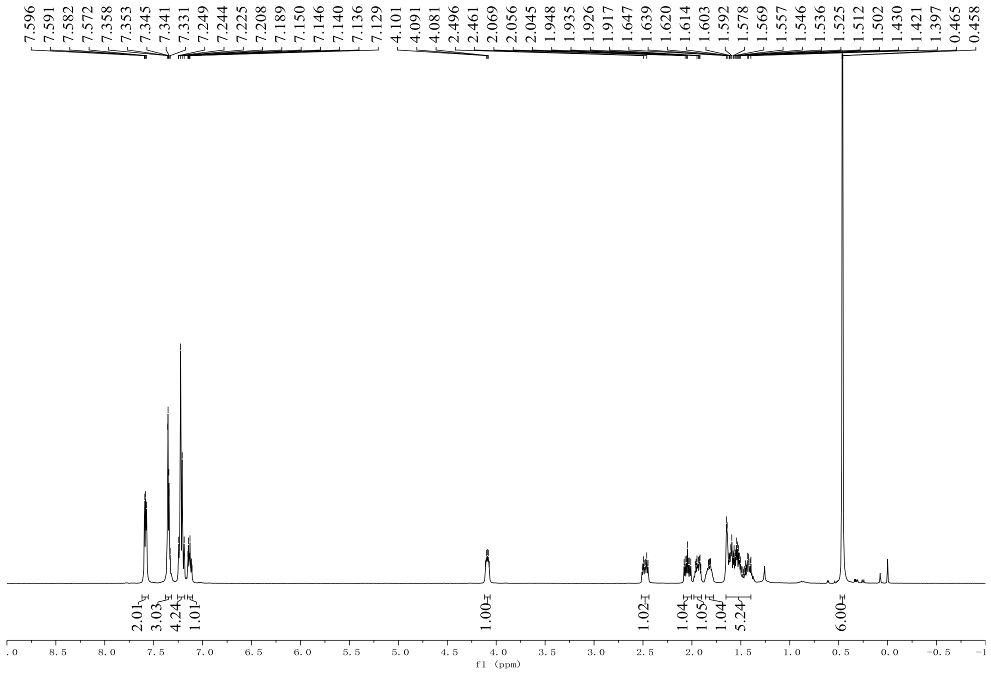


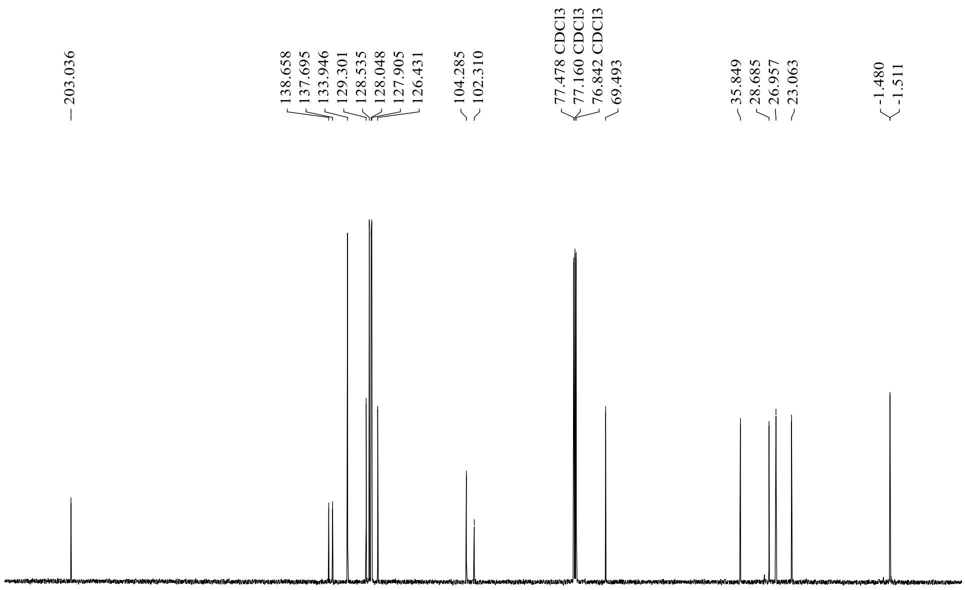
2-(2-(dimethyl(phenyl)silyl)-2-phenylvinylidene)cyclohexan-1-ol (3q). This compound was prepared by the general procedure described above and was obtained as colorless oil in 92% yield (61.5 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

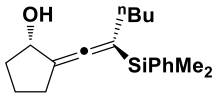
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 2H), 7.38-7.32 (m, 3H), 7.26-7.18 (m, 4H), 7.16-7.10 (m, 1H), 4.12-4.06 (m, 1H), 2.52-2.44 (m, 1H), 2.09-2.00 (m, 1H), 1.98-1.90 (m, 1H), 1.87-1.77 (m, 1H), 1.65-1.40 (m, 5H), 0.47 (s, 3H), 0.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.04, 138.66, 137.70, 133.95, 129.30, 128.54, 128.05, 127.91, 126.43, 104.29, 102.31, 69.49, 35.85, 28.69, 26.96, 23.06, -1.48, -1.51.

HRMS (ESI) m/z calculated for $C_{22}H_{26}OSiNa$ $[M+Na]^+$: 357.1651, found: 357.1653.





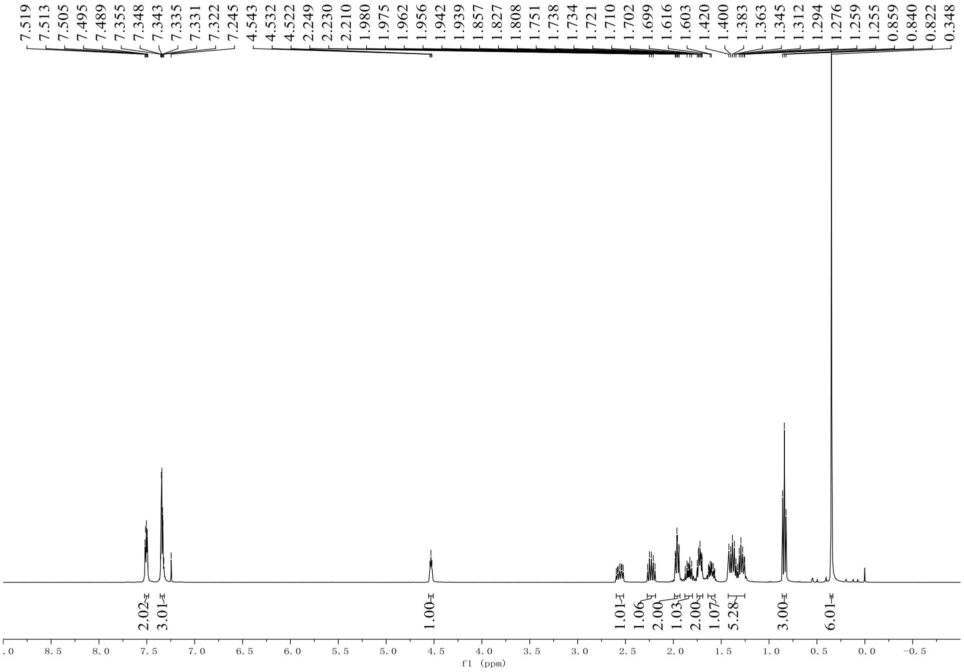


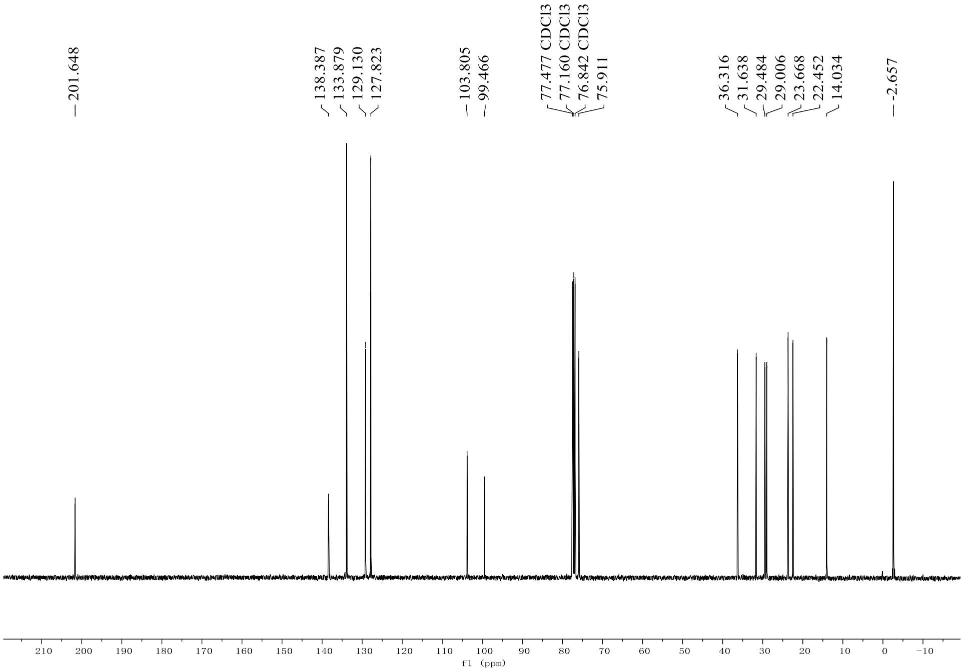
2-(2-(dimethyl(phenyl)silyl)hex-1-en-1-ylidene)cyclopentan-1-ol (3r). This compound was prepared by the general procedure described above and was obtained as colorless oil in 96% yield (57.5 mg). R_f = 0.50 (Petroleum ether : EtOAc = 4:1).

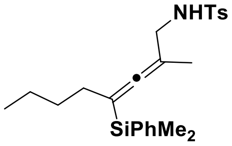
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 2H), 7.36-7.32 (m, 3H), 4.53 (t, *J* = 4.2 Hz, 1H), 2.60-2.52 (m, 1H), 2.27-2.19 (m, 1H), 1.99-1.93 (m, 2H), 1.88-1.80 (m, 1H), 1.75-1.69 (m, 2H), 1.64-1.57 (m, 1H), 1.43-1.25 (m, 5H), 0.84 (t, *J* = 7.4 Hz, 3H), 0.35 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.65, 138.39, 133.88, 129.13, 127.82, 103.81, 99.47, 75.91, 36.32, 31.64, 29.48, 29.01, 23.67, 22.45, 14.03, -2.66.

HRMS (ESI) m/z calculated for $C_{19}H_{28}OSiNa$ [M+Na]$^+$: 323.1807, found: 323.1808.





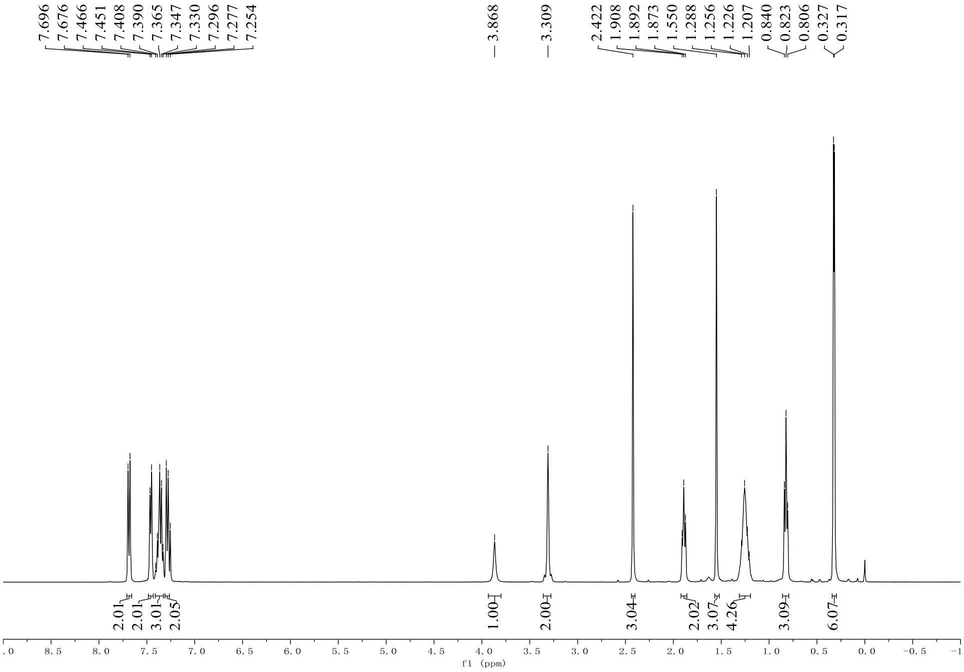


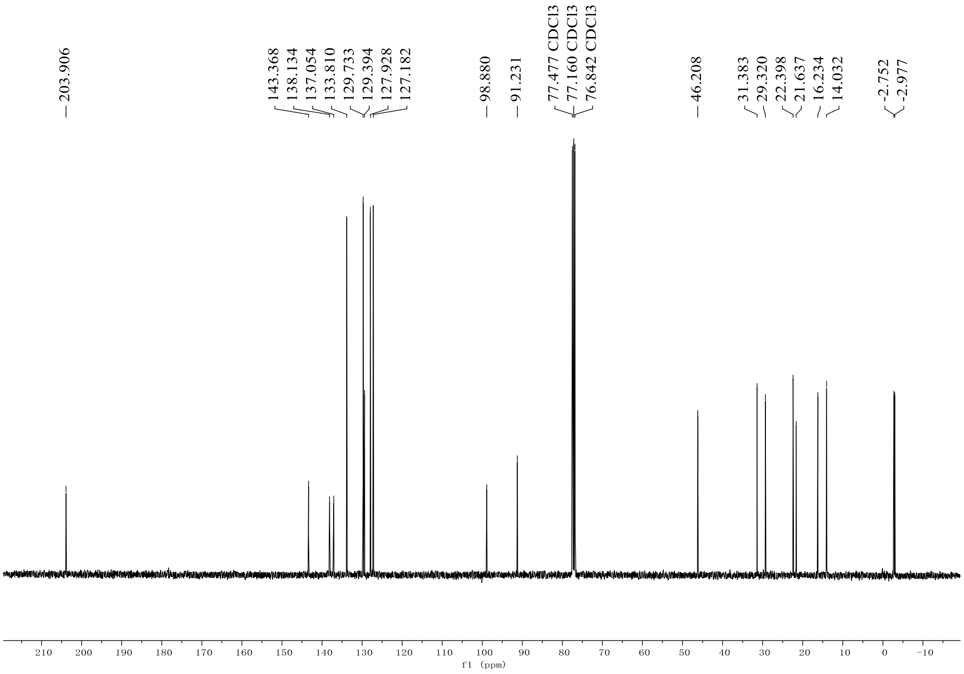
N-(4-(dimethyl(phenyl)silyl)-2-methylocta-2,3-dien-1-yl)-4-methylbenzenesulfonamide (3s). This compound was prepared according to the procedures described above and was obtained as white solid in 98% yield (83.8 mg). $R_f = 0.30$ (Petroleum ether : EtOAc = 9:1).

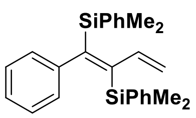
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 6.0 Hz, 2H), 7.41-7.33 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 2H), 3.87 (s, 1H), 3.31 (s, 2H), 2.42 (s, 3H), 1.89 (t, *J* = 7.1 Hz, 2H), 1.55 (s, 3H), 1.32-1.17 (m, 4H), 0.82 (t, *J* = 6.8 Hz, 3H), 0.33 (s, 3H), 0.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.91, 143.37, 138.13, 137.05, 133.81, 129.73, 129.39, 127.93, 127.18, 98.88, 91.23, 46.21, 31.38, 29.32, 22.40, 21.64, 16.23, 14.03, -2.75, -2.98.

HRMS (ESI) m/z calculated for $C_{24}H_{33}NO_2SSiNa$ $[M+Na]^+$: 450.1899, found: 450.1907.





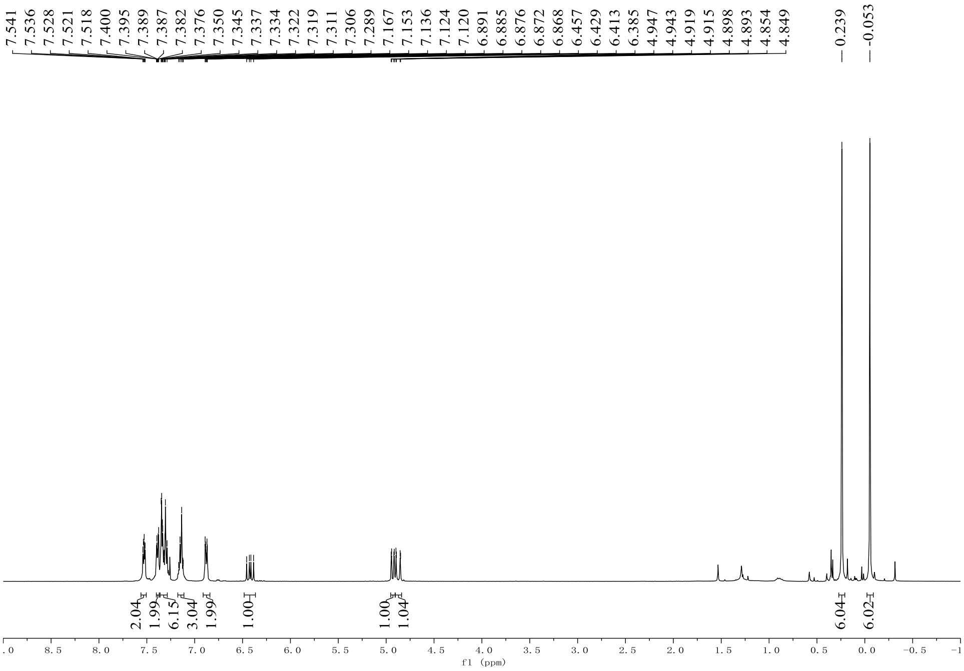


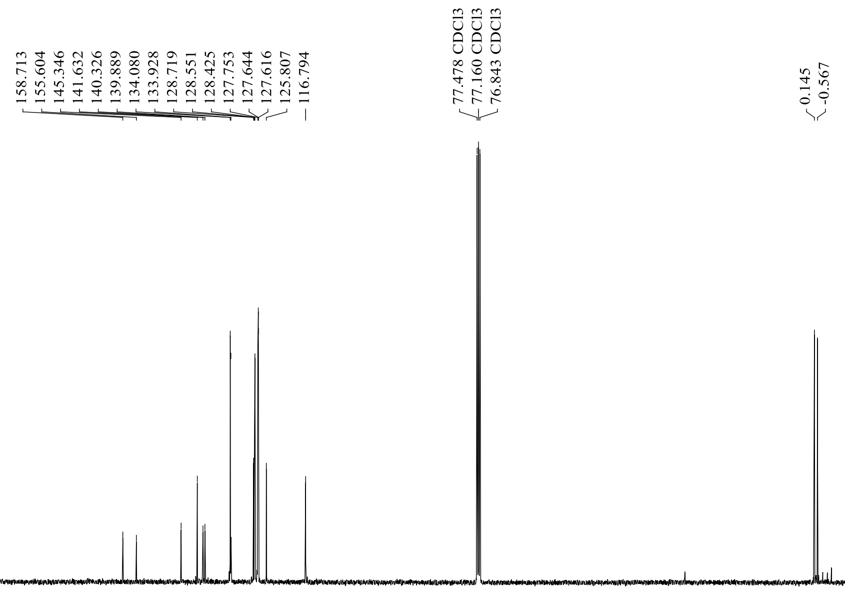
(*E*)-(1-phenylbuta-1,3-diene-1,2-diyl)bis(dimethyl(phenyl)silane (4a). This compound was prepared via the general procedure described above and was obtained as colorless oil in 77% yield (61.4 mg). The configuration of the product was determined by NOESY and HMBC correlation analysis. $R_f = 0.80$ (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 2H), 7.40-7.37 (m, 2H), 7.36-7.29 (m, 6H), 7.18-7.11 (m, 3H), 6.91-6.84 (m, 2H), 6.42 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.93 (dd, *J* = 11.2, 1.8 Hz, 1H), 4.87 (dd, *J* = 17.6, 1.8 Hz, 1H), 0.24 (s, 6H), -0.05 (s, 6H).

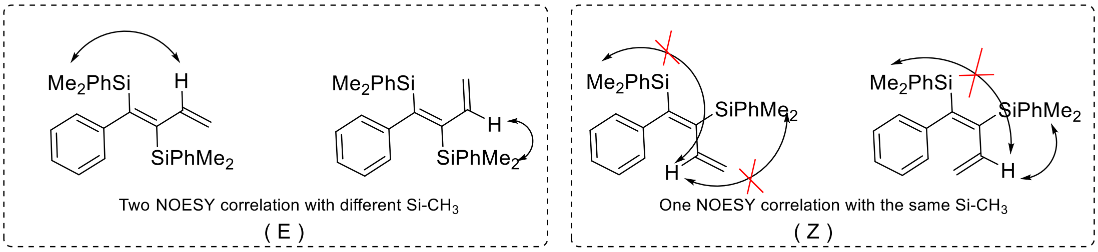
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.71, 155.60, 145.35, 141.63, 140.33, 139.89, 134.08, 133.93, 128.72, 128.55, 128.43, 127.75, 127.64, 127.62, 125.81, 116.79, 0.15, -0.57.

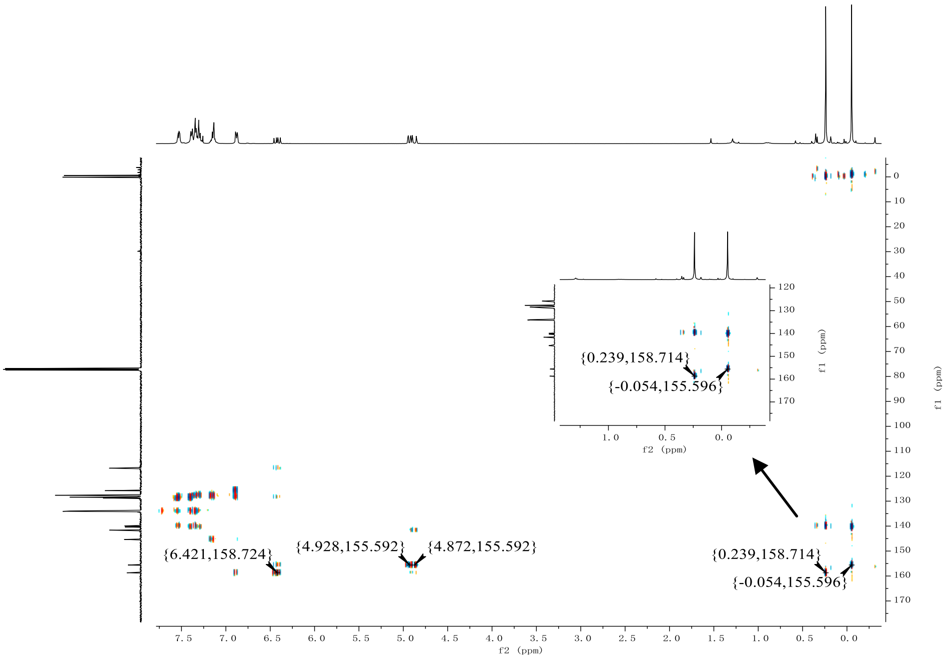
HRMS (ESI) m/z calculated for $C_{26}H_{30}Si_2Na$ $[M+Na]^+$: 421.1784, found: 421.1782.

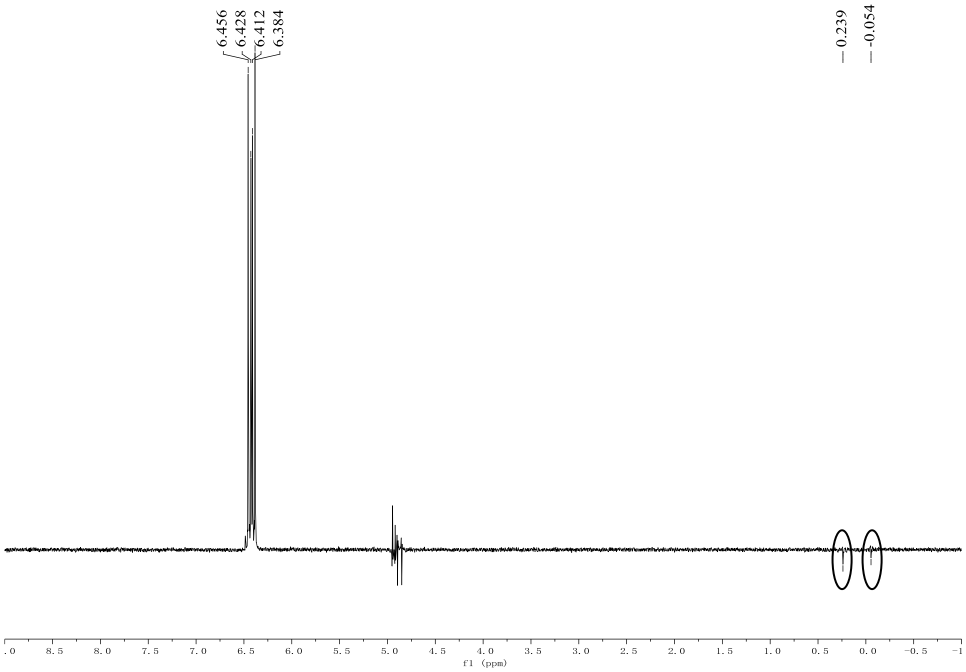


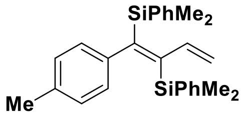


The configuration of product **4a** was determined by NOESY and HMBC correlation analysis. It can be concluded that the 6H (δ=0.24 ppm) are from the same $Si(CH_3)_2$ group and next 6H (δ = -0.05 ppm) are from the other $Si(CH_3)_2$ group judged from the following HMBC spectrum.







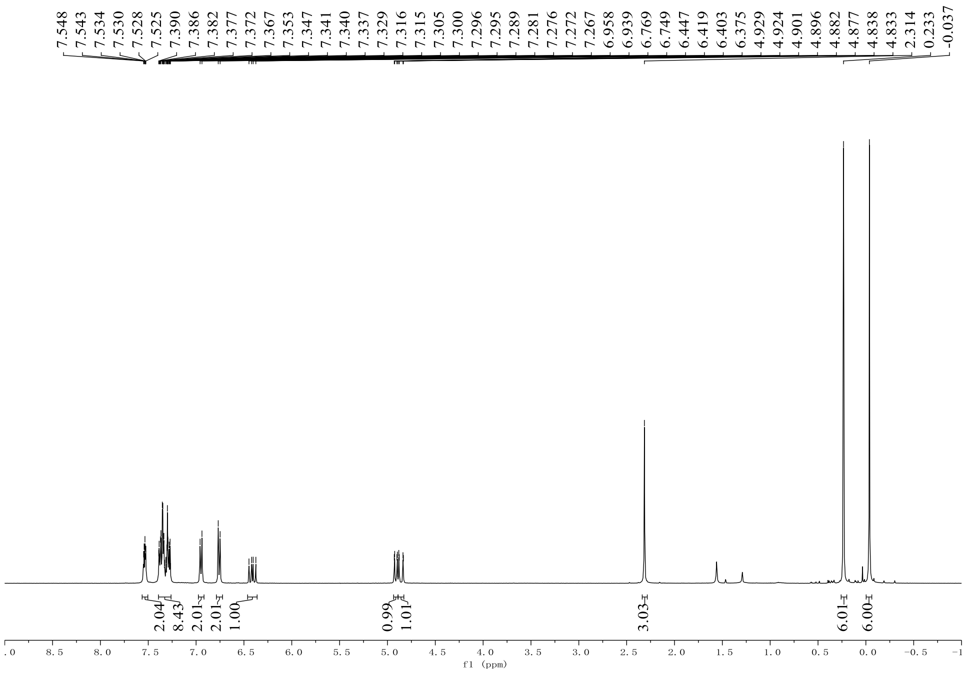


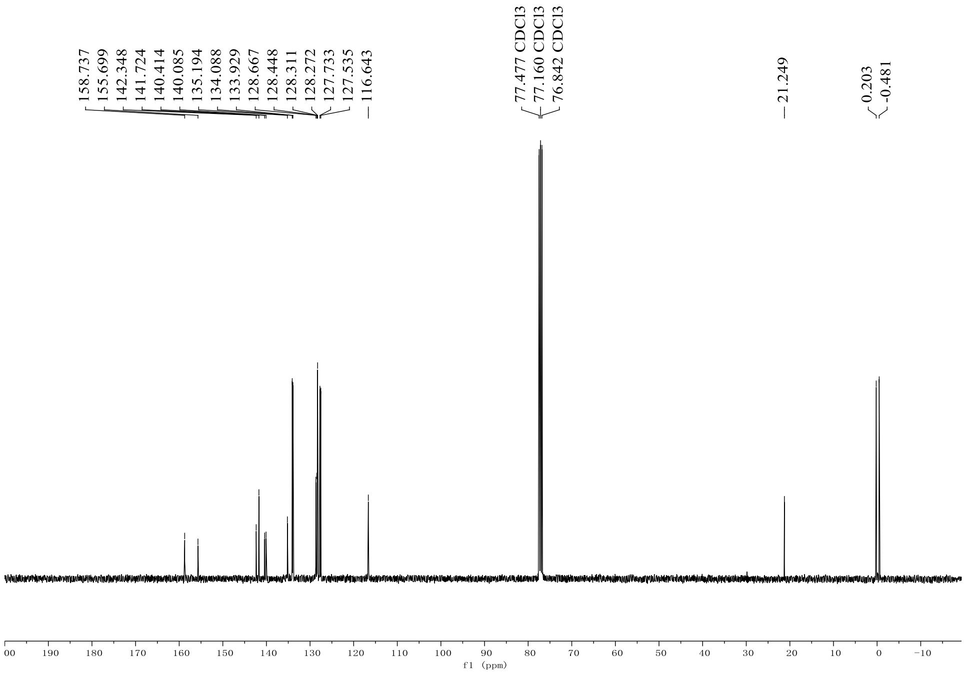
(*E*)-(1-(*p*-tolyl)buta-1,3-diene-1,2-diyl)bis(dimethyl(phenyl)silane) (4b). This compound was prepared via the general procedure described above and was obtained as yellow oil in 71% yield (58.9 mg). R_f = 0.80 (Petroleum ether).

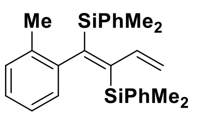
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.50 (m, 2H), 7.39-7.26 (m, 8H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.41 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.91 (dd, *J* = 11.2, 1.8 Hz, 1H), 4.86 (dd, *J* = 17.6, 1.8 Hz, 1H), 2.31 (s, 3H), 0.23 (s, 6H), -0.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.74, 155.70, 142.35, 141.72, 140.41, 140.09, 135.19, 134.09, 133.93, 128.67, 128.45, 128.31, 128.27, 127.73, 127.54, 116.64, 21.25, 0.20, -0.48.

HRMS (ESI) m/z calculated for $C_{27}H_{32}Si_2Na$ $[M+Na]^+$: 435.1940, found: 435.1952.





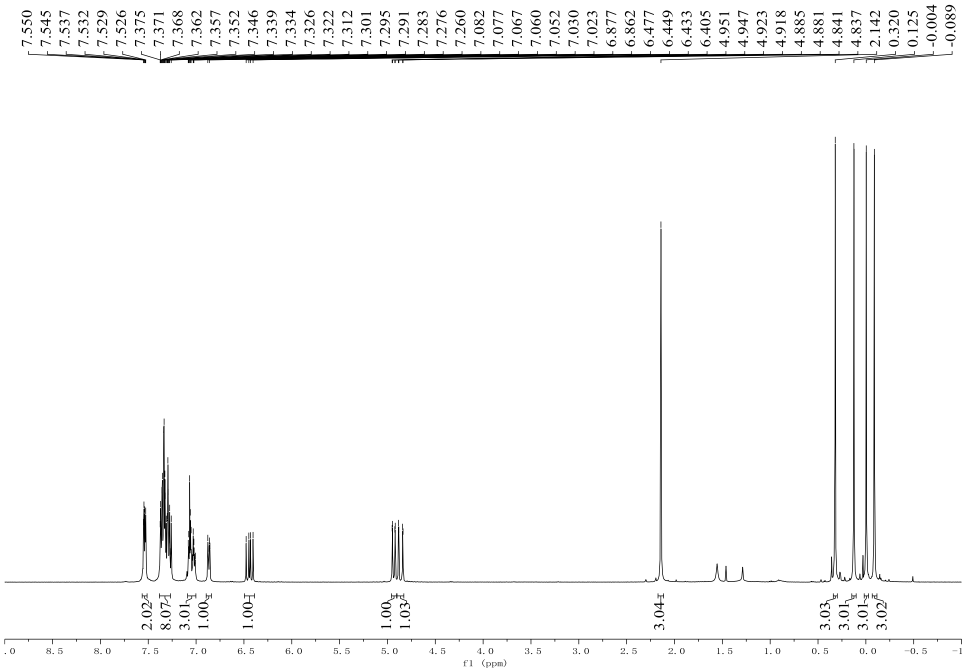


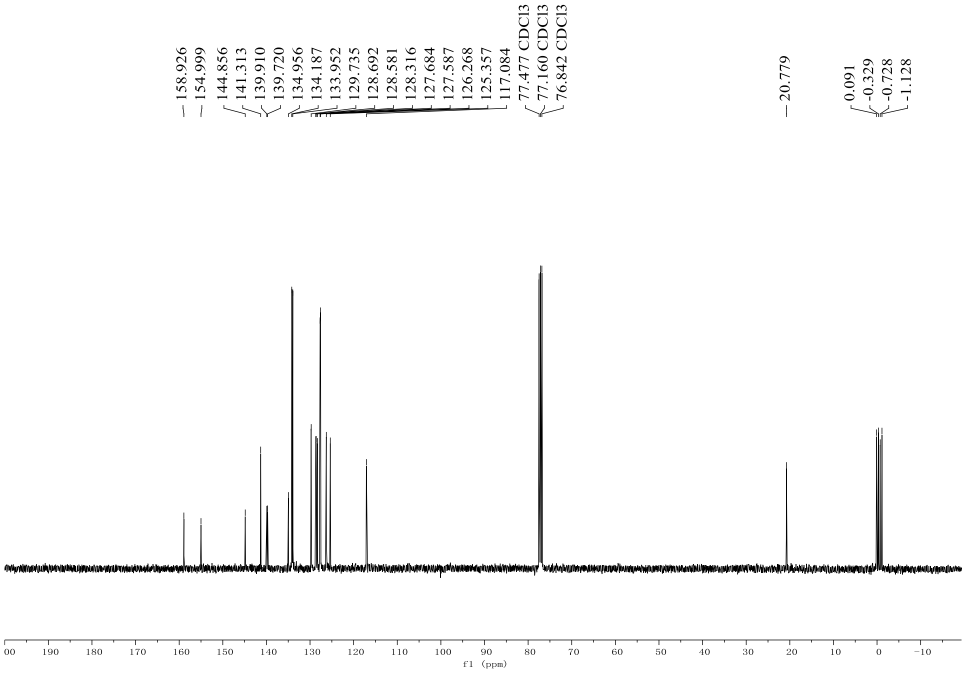
(*E*)-(1-(*o*-tolyl)buta-1,3-diene-1,2-diyl)bis(dimethyl(phenyl)silane) (4c). This compound was prepared via the general procedure described above and was obtained as yellow oil in 67% yield (55.4 mg). $R_f = 0.80$ (Petroleum ether).

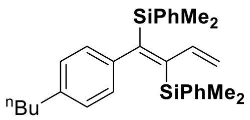
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 2H), 7.38-7.27 (m, 8H), 7.09-7.00 (m, 3H), 6.89-6.84 (m, 1H), 6.44 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.93 (dd, *J* = 11.2, 1.7 Hz, 1H), 4.86 (dd, *J* = 17.6, 1.7 Hz, 1H), 2.14 (s, 3H), 0.32 (s, 3H), 0.12 (s, 3H), -0.00 (s, 3H), -0.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.93, 155.00, 144.86, 141.31, 139.91, 139.72, 134.96, 134.19, 133.95, 129.74, 128.69, 128.58, 128.32, 127.68, 127.59, 126.27, 125.36, 117.08, 20.78, 0.09, -0.33, -0.73, -1.13.

HRMS (ESI) m/z calculated for $C_{27}H_{32}Si_2Na$ $[M+Na]^+$: 435.1940, found: 435.1954.





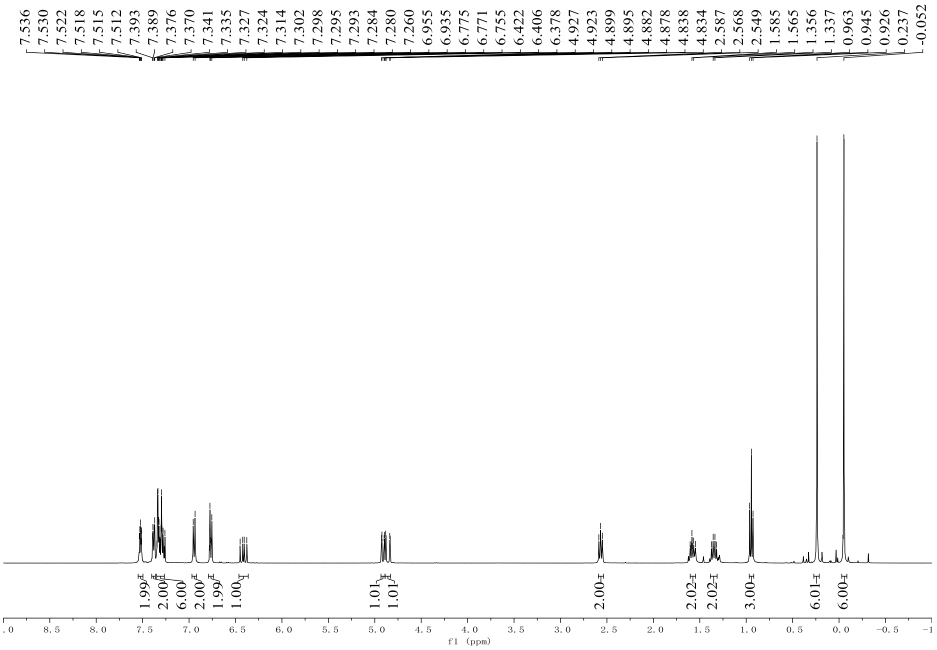


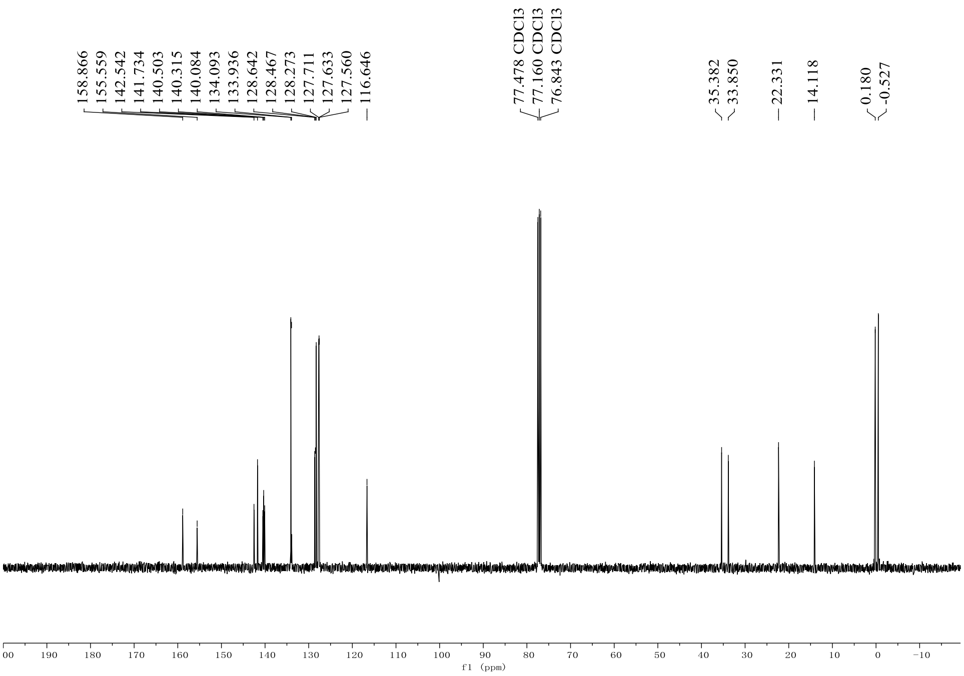
(*E*)-(1-(4-butylphenyl)buta-1,3-diene-1,2-diyl)bis(dimethyl(phenyl)silane) (4d). This compound was prepared via the general procedure described above and was obtained as colorless oil in 77% yield (69.8 mg). $R_f = 0.80$ (Petroleum ether).

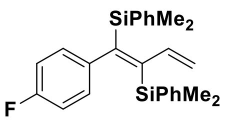
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.50 (m, 2H), 7.40-7.36 (m, 2H), 7.35-7.27 (m, 6H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.79-6.74 (m, 2H), 6.41 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.91 (dd, *J* = 11.2, 1.8 Hz, 1H), 4.86 (dd, *J* = 17.6, 1.8 Hz, 1H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.60-1.55 (m, 2H), 1.39-1.31 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.24 (s, 6H), -0.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.87, 155.56, 142.54, 141.73, 140.50, 140.32, 140.08, 134.09, 133.94, 128.64, 128.47, 128.27, 127.71, 127.63, 127.56, 116.65, 35.38, 33.85, 22.33, 14.12, 0.18, -0.53.

HRMS (ESI) m/z calculated for $C_{30}H_{38}Si_2Na$ $[M+Na]^+$: 477.2410, found: 477.2404.







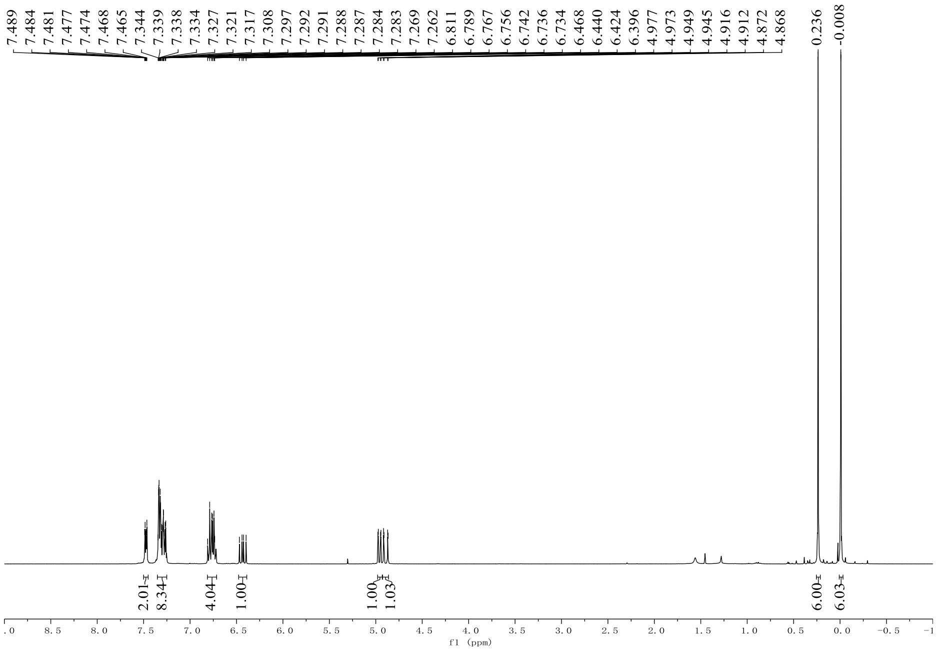
(*E*)-(1-(4-fluorophenyl)buta-1,3-diene-1,2-diyl)bis(dimethyl(phenyl)silane) (4e). This compound was prepared via the general procedure described above and was obtained as yellow oil in 71% yield (59.3 mg). $R_f = 0.80$ (Petroleum ether).

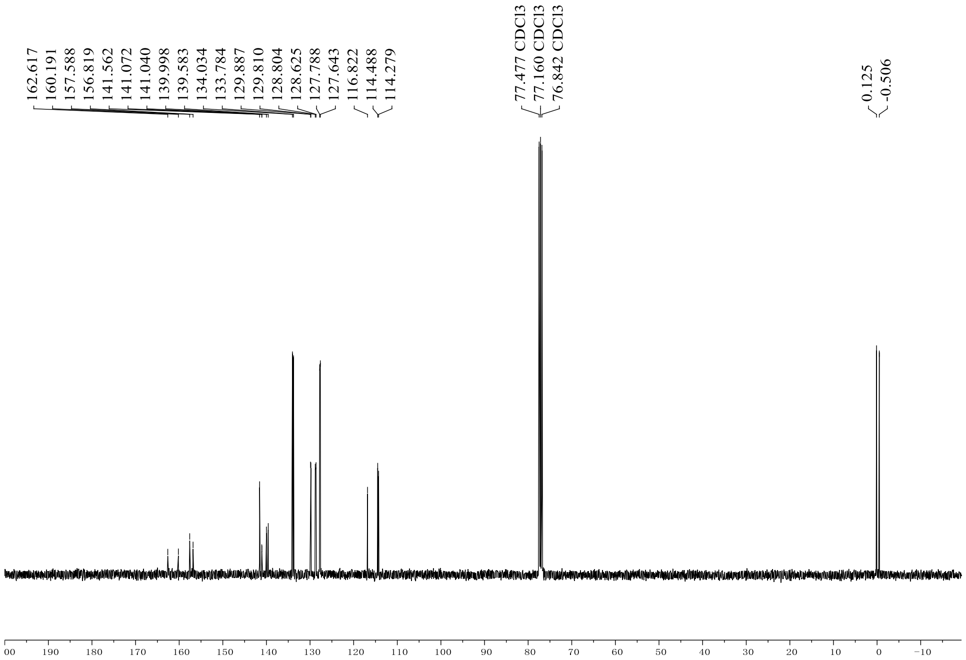
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2H), 7.35-7.25 (m, 8H), 6.81-6.71 (m, 4H), 6.43 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.96 (dd, *J* = 11.2, 1.8 Hz, 1H), 4.89 (dd, *J* = 17.6, 1.8 Hz, 1H), 0.24 (s, 6H), -0.01 (s, 6H).

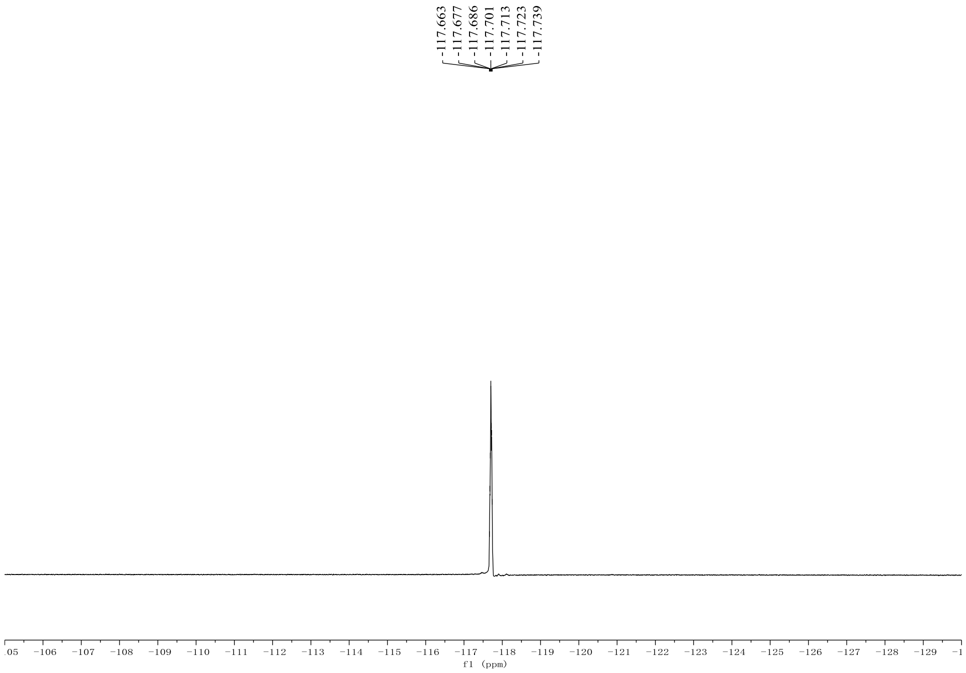
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.40 (d, *J* = 245.03 Hz), 157.59, 156.82, 141.56, 141.06 (d, *J* = 3.2 Hz), 140.00, 139.58, 134.03, 133.78, 129.85 (d, *J* = 7.8 Hz), 128.80, 128.63, 127.72 (d, *J* = 14.6 Hz), 116.82, 114.49, 114.28, 0.13, -0.51.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.70 (m, 1F).

HRMS (ESI) m/z calculated for $C_{26}H_{29}FSi_2Na$ $[M+Na]^+$: 439.1690, found: 439.1690.







-117.663
-117.677
-117.686
-117.701
-117.713
-117.723
-117.739
05
−106
−107
−108
−109
−110
−111
−112
−113
−114
−115
−116
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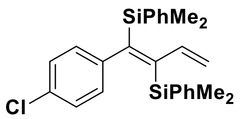
−129
−1
f1 (ppm)

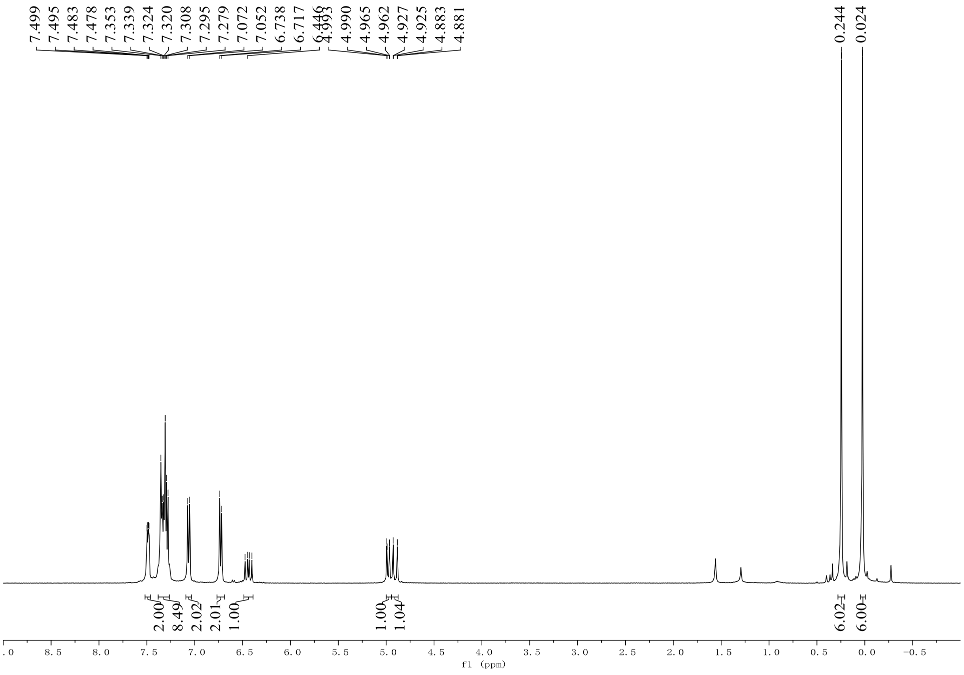


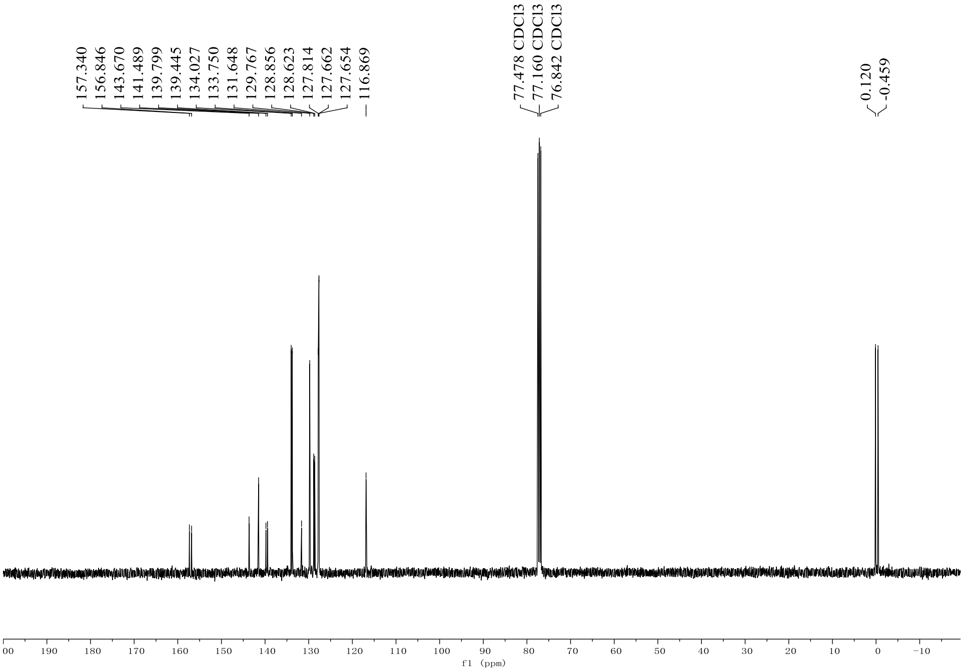
(*E*)-(1-(4-chlorophenyl)buta-1,3-diene-1,2-diyl)bis(dimethyl(phenyl)silane) (4f). This compound was prepared via the general procedure described above and was obtained as yellow oil in 70% yield (60.1 mg). R$_f$ = 0.80 (Petroleum ether).

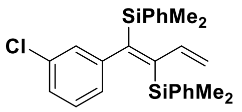
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52-7.46 (m, 2H), 7.38-7.26 (m, 8H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.44 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.98 (dd, *J* = 11.2, 1.1 Hz, 1H), 4.90 (dd, *J* = 17.6, 1.1 Hz, 1H), 0.24 (s, 6H), 0.02 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 157.34, 156.85, 143.67, 141.49, 139.80, 139.45, 134.03, 133.75, 131.65, 129.77, 128.86, 128.62, 127.81, 127.66, 127.65, 116.87, 0.12, -0.46.

HRMS (ESI) m/z calculated for C$_{26}$H$_{29}$ClSi$_2$Na [M+Na]$^+$: 455.1394, found: 455.1397.





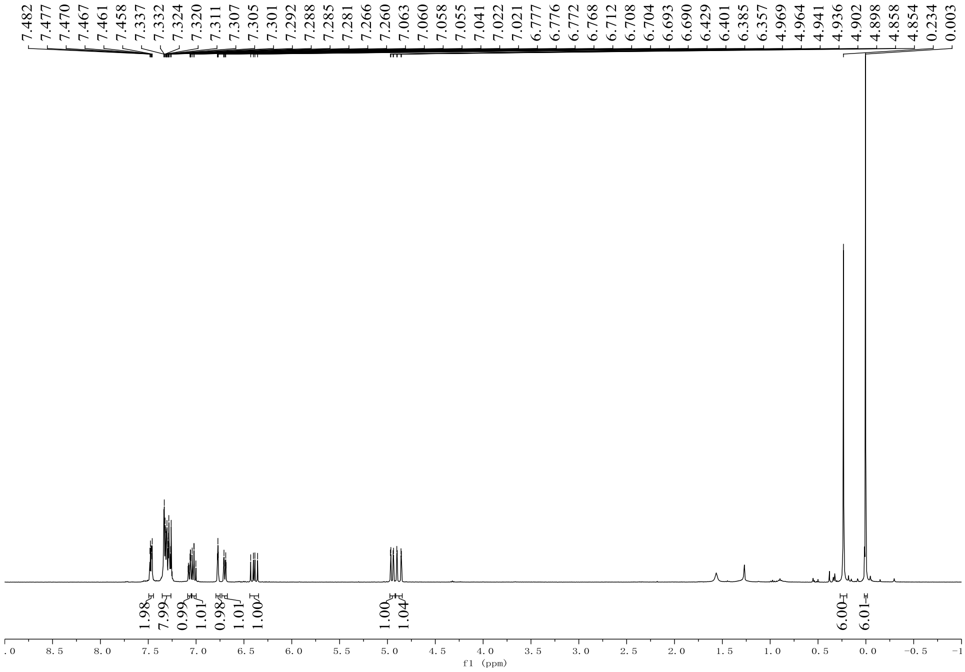


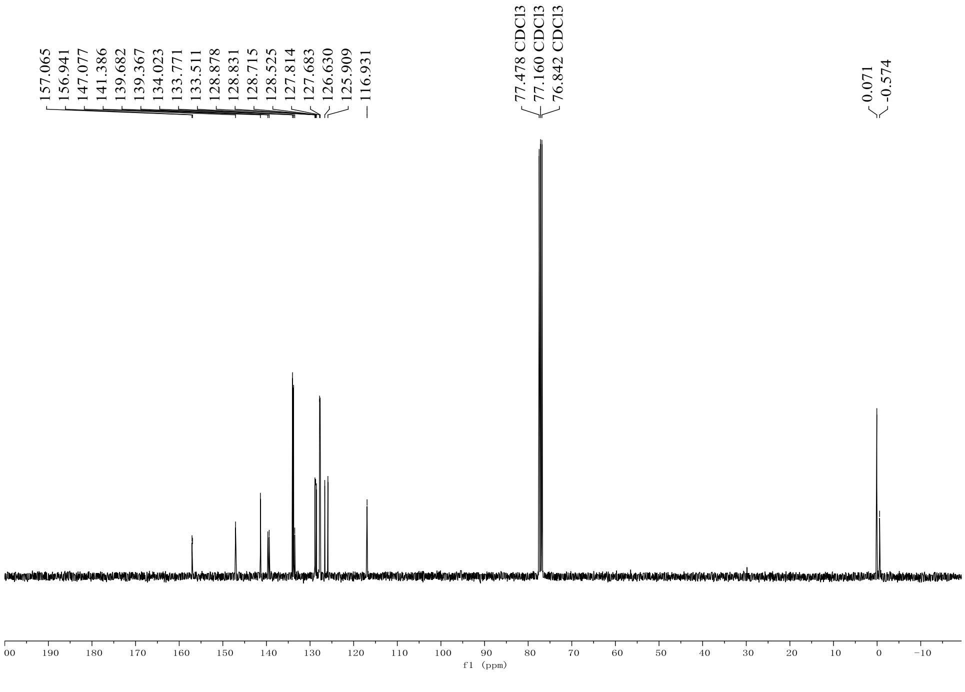
(*E*)-(1-(3-chlorophenyl)buta-1,3-diene-1,2-diyl)bis(dimethyl(phenyl)silane) (4g). This compound was prepared via the general procedure described above, but the reaction time was prolonged to 20 h, and it was obtained as yellow oil in 65% yield (56.0 mg). $R_f = 0.80$ (Petroleum ether).

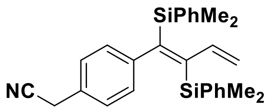
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2H), 7.35-7.26 (m, 8H), 7.09-7.05 (m, 1H), 7.04-7.00 (m, 1H), 6.79-6.75 (m, 1H), 6.70 (dt, *J* = 7.2, 1.4 Hz, 1H), 6.39 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.95 (dd, *J* = 11.2, 1.8 Hz, 1H), 4.88 (dd, *J* = 17.6, 1.8 Hz, 1H), 0.23 (s, 6H), 0.00 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.07, 156.94, 147.08, 141.39, 139.68, 139.37, 134.02, 133.77, 133.51, 128.88, 128.83, 128.72, 128.53, 127.81, 127.68, 126.63, 125.91, 116.93, 0.07, -0.57.

HRMS (ESI) m/z calculated for $C_{26}H_{29}ClSi_2Na$ $[M+Na]^+$: 455.1394, found: 455.1410.





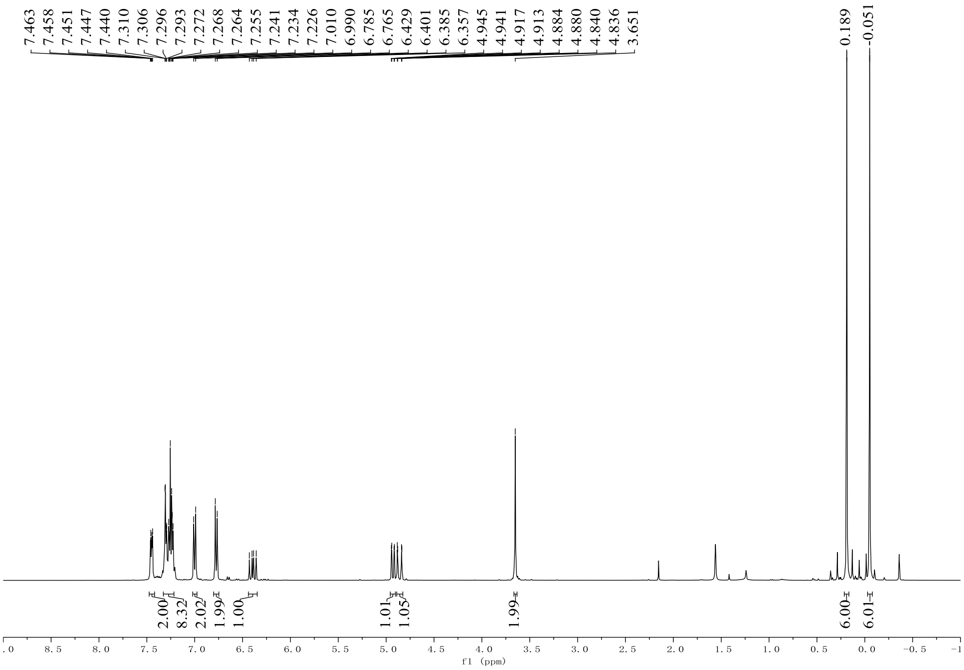


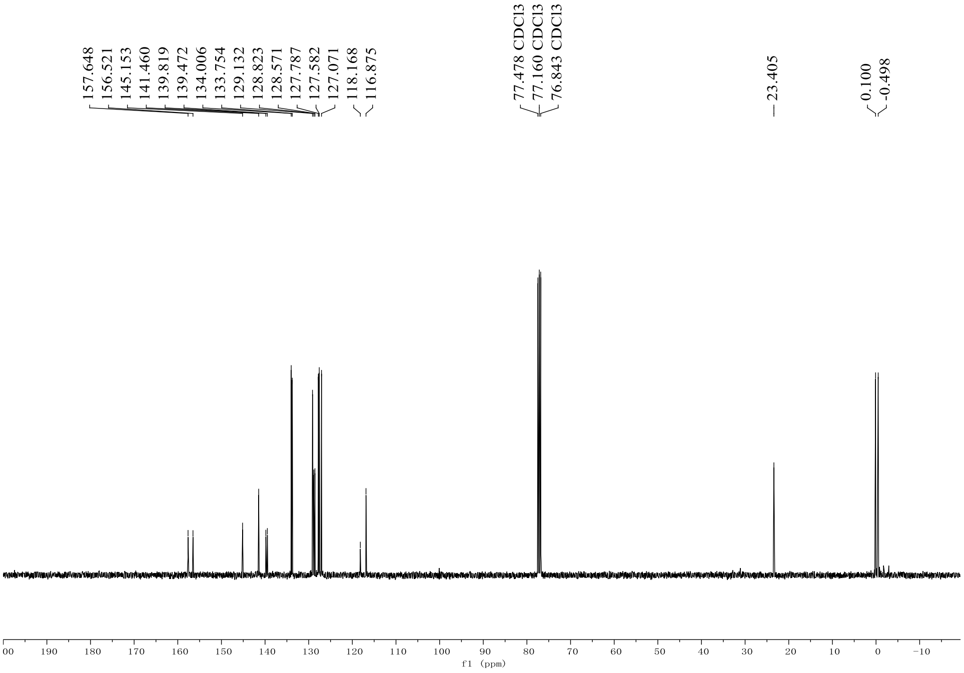
(*E*)-2-(4-(1,2-bis(dimethyl(phenyl)silyl)buta-1,3-dien-1-yl)phenyl)acetonitrile (4h). This compound was prepared via the general procedure described above and was obtained as yellow oil in 75% yield (65.8 mg). $R_f = 0.50$ (Petroleum ether : EtOAc = 19:1).

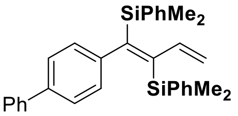
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 2H), 7.33-7.22 (m, 8H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.39 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.93 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.86 (dd, *J* = 17.6, 1.6 Hz, 1H), 3.65 (s, 2H), 0.19 (s, 6H), -0.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.65, 156.52, 145.15, 141.46, 139.82, 139.47, 134.01, 133.75, 129.13, 128.82, 128.57, 127.79, 127.58, 127.07, 118.17, 116.88, 23.41, 0.10, -0.50.

HRMS (ESI) m/z calculated for $C_{28}H_{31}NSi_2Na$ $[M+Na]^+$: 460.1893, found: 460.1900.





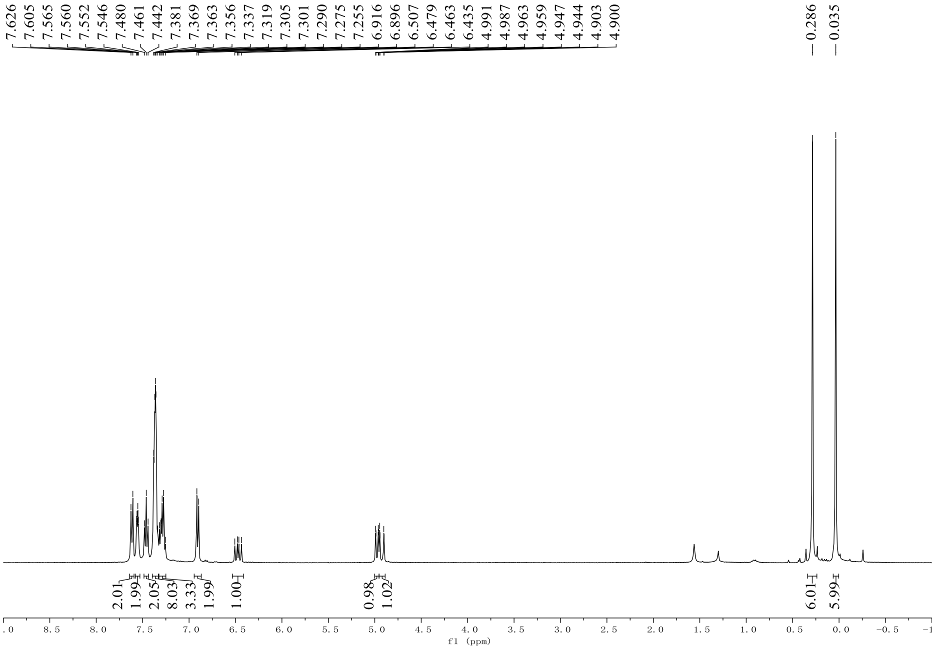


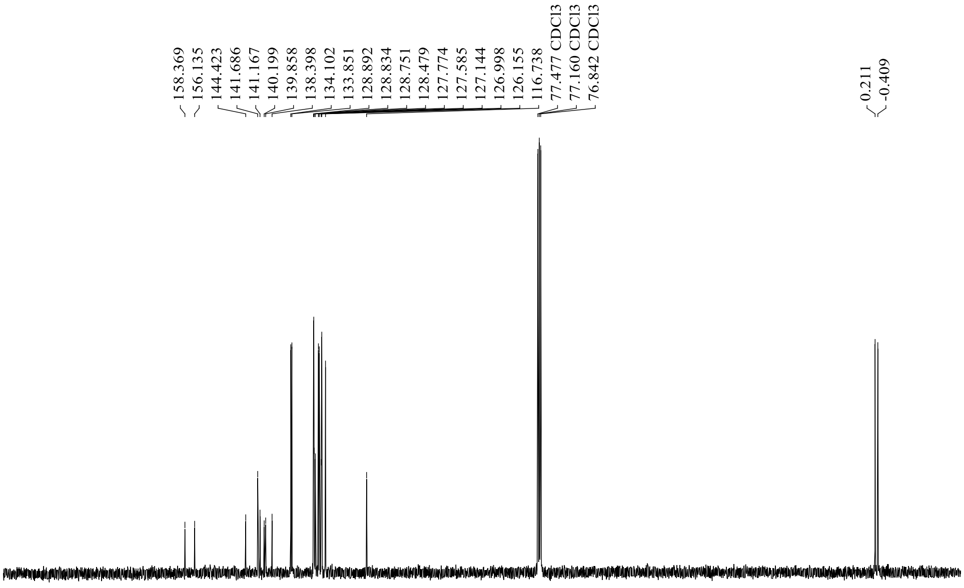
(*E*)-(1-([1,1'-biphenyl]-4-yl)buta-1,3-diene-1,2-diyl)bis(dimethyl(phenyl)silane) (4i). This compound was prepared via the general procedure described above, but the reaction time was prolonged to 20 h, and it was obtained as yellow oil in 67% yield (63.1 mg). R_f = 0.70 (Petroleum ether).

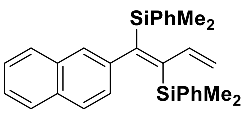
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.58-7.53 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40-7.33 (m, 8H), 7.32-7.24 (m, 3H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.47 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.97 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.92 (dd, *J* = 17.6, 1.2 Hz, 1H), 0.29 (s, 6H), 0.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.37, 156.14, 144.42, 141.69, 141.17, 140.20, 139.86, 138.40, 134.10, 133.85, 128.89, 128.83, 128.75, 128.48, 127.77, 127.59, 127.14, 127.00, 126.16, 116.74, 0.21, -0.41.

HRMS (ESI) m/z calculated for $C_{32}H_{34}Si_2Na$ $[M+Na]^+$: 497.2097, found: 497.2090.





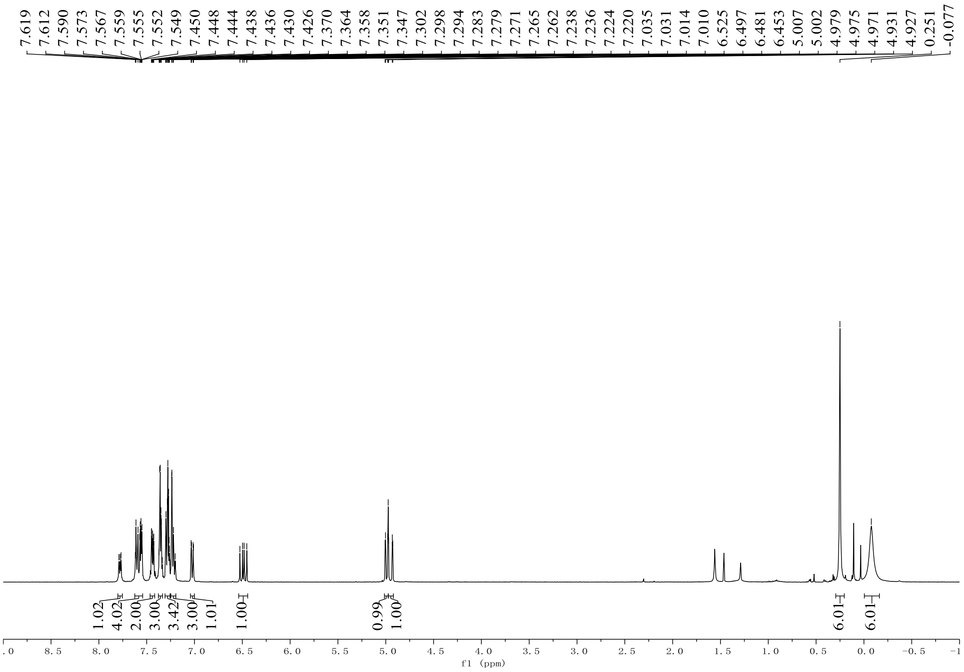


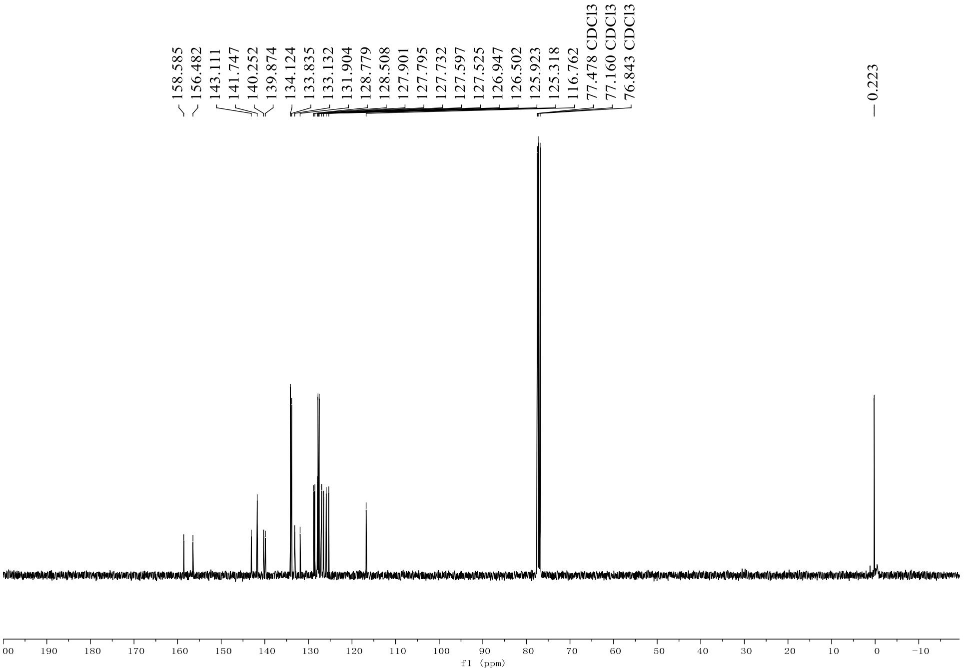
(*E*)-(1-(naphthalen-2-yl)buta-1,3-diene-1,2-diyl)bis(dimethyl(phenyl)silane) (4j). This compound was prepared via the general procedure described above, but the reaction time was prolonged to 20 h, and it was obtained as yellow solid in 68% yield (61.3 mg). R_f = 0.70 (Petroleum ether).

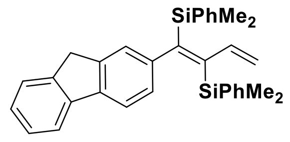
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.75 (m, 1H), 7.62-7.54 (m, 4H), 7.46-7.42 (m, 2H), 7.38-7.33 (m, 3H), 7.31-7.25 (m, 3H), 7.25-7.19 (m, 3H), 7.02 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.49 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.99 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.95 (dd, *J* = 17.6, 1.6 Hz, 1H), 0.25 (s, 6H), -0.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.59, 156.48, 143.11, 141.75, 140.25, 139.87, 134.12, 133.84, 133.13, 131.90, 128.78, 128.51, 127.90, 127.80, 127.73, 127.60, 127.53, 126.95, 126.50, 125.92, 125.32, 116.76, 0.22.

HRMS (ESI) m/z calculated for $C_{30}H_{32}Si_2Na$ $[M+Na]^+$: 471.1940, found: 471.1928.





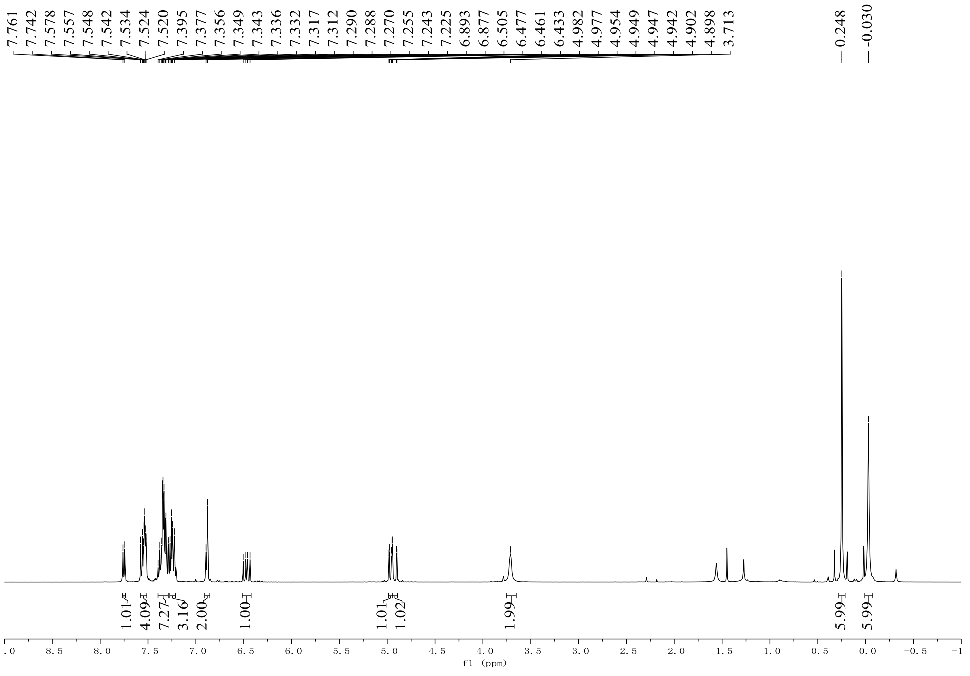


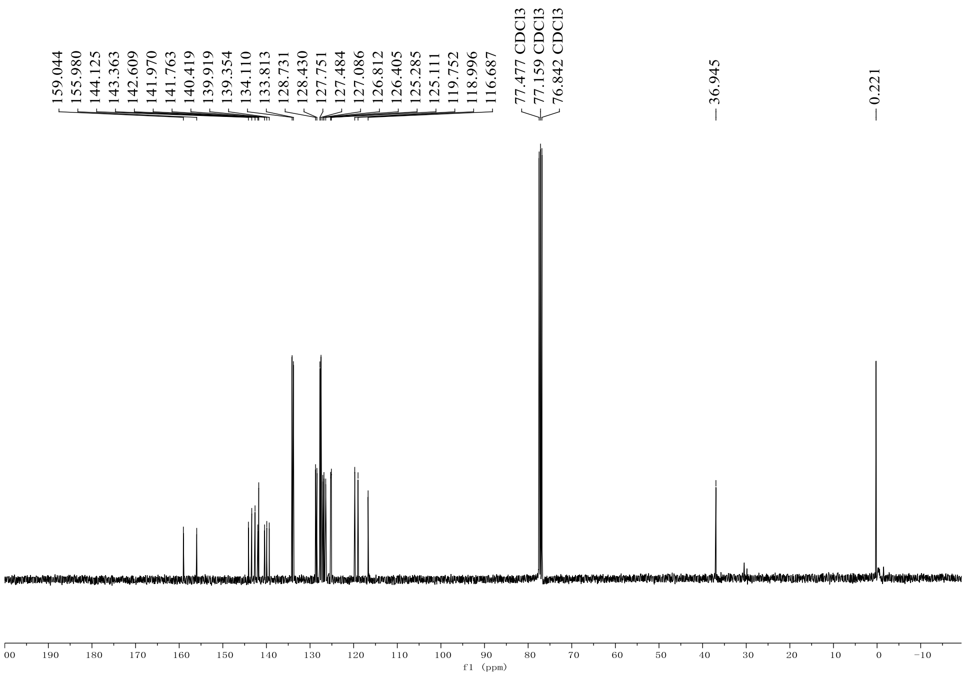
(*E*)-(1-(9H-fluoren-2-yl)buta-1,3-diene-1,2-diyl)bis(dimethyl(phenyl)silane) (4k). This compound was prepared via the general procedure described above and was obtained as white solid in 50% yield (48.9 mg). $R_f = 0.70$ (Petroleum ether).

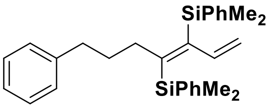
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.58-7.51 (m, 4H), 7.40-7.29 (m, 7H), 7.27-7.21 (m, 3H), 6.91-6.85 (m, 2H), 6.47 (dd, *J* = 17.6, 11.2 Hz, 1H), 4.97 (dd, *J* = 11.2, 1.8 Hz, 1H), 4.92 (dd, *J* = 17.6, 1.8 Hz, 1H), 3.71 (s, 2H), 0.25 (s, 6H), -0.03 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.04, 155.98, 144.13, 143.36, 142.61, 141.97, 141.76, 140.42, 139.92, 139.35, 134.11, 133.81, 128.73, 128.43, 127.75, 127.48, 127.09, 126.81, 126.41, 125.29, 125.11, 119.75, 119.00, 116.69, 36.95, 0.22.

HRMS (ESI) m/z calculated for $C_{33}H_{34}Si_2Na$ $[M+Na]^+$: 509.2097, found: 509.2100.





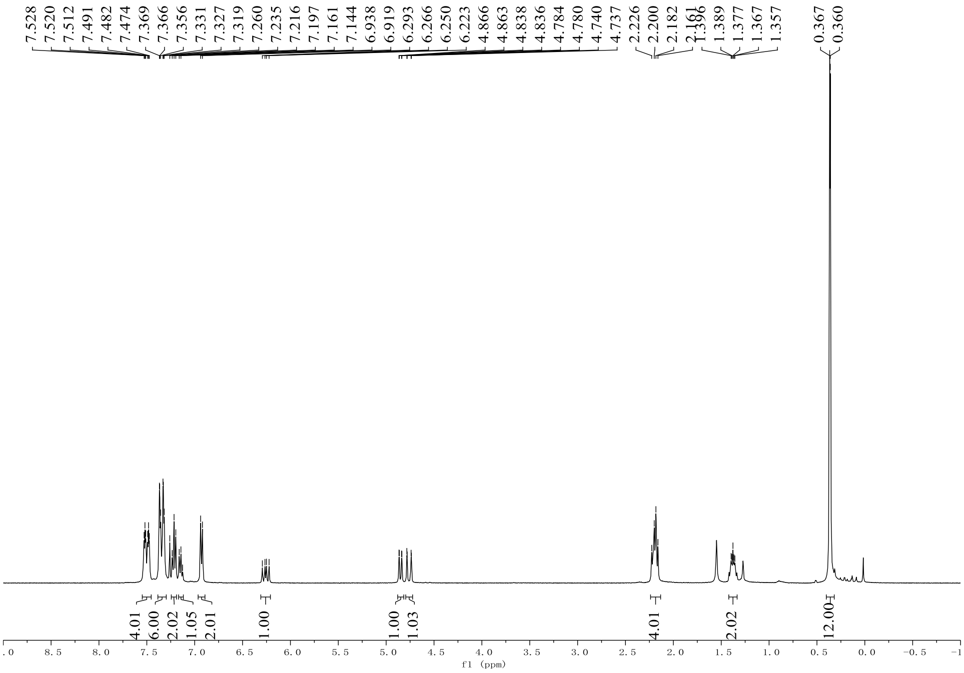


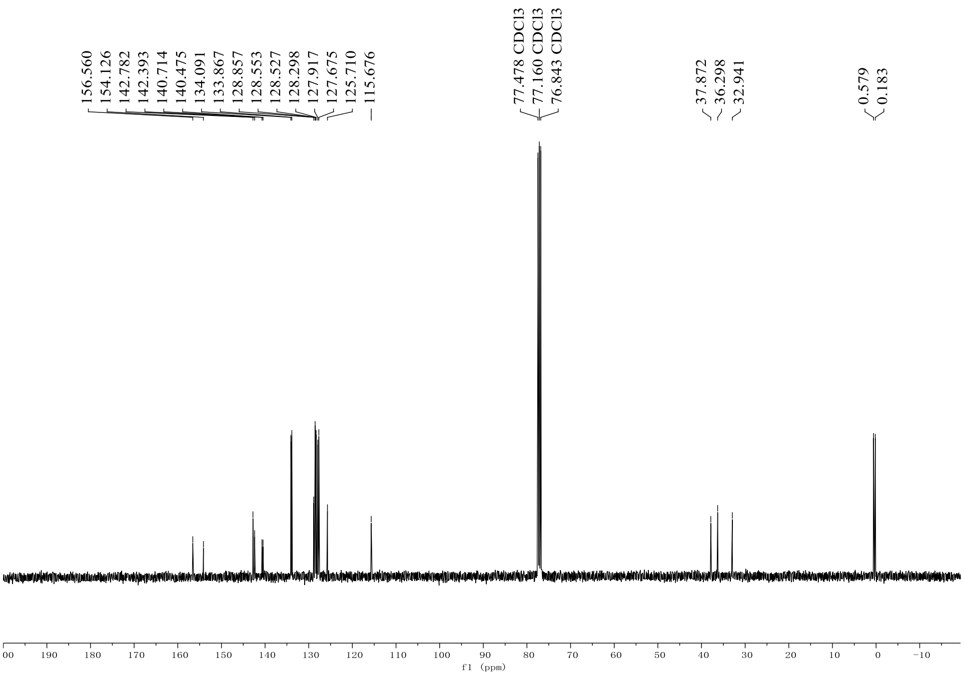
(*E*)-(7-phenylhepta-1,3-diene-3,4-diyl)bis(dimethyl(phenyl)silane) (4l). This compound was prepared via the general procedure described above and was obtained as colorless oil in 35% yield (31.1 mg). R_f = 0.70 (Petroleum ether).

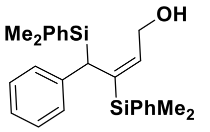
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.45 (m, 4H), 7.38-7.30 (m, 6H), 7.25-7.19 (m, 2H), 7.17-7.12 (m, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.26 (dd, *J* = 17.2, 10.8 Hz, 1H), 4.85 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.76 (dd, *J* = 17.2, 1.2 Hz, 1H), 2.24-2.13 (m, 4H), 1.42-1.33 (m, 2H), 0.37 (s, 6H), 0.36 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.56, 154.13, 142.78, 142.39, 140.71, 140.48, 134.09, 133.87, 128.86, 128.55, 128.53, 128.30, 127.92, 127.68, 125.71, 115.68, 37.87, 36.30, 32.94, 0.58, 0.18.

HRMS (ESI) m/z calculated for $C_{29}H_{36}Si_2Na$ $[M+Na]^+$: 463.2253, found: 463.2262.





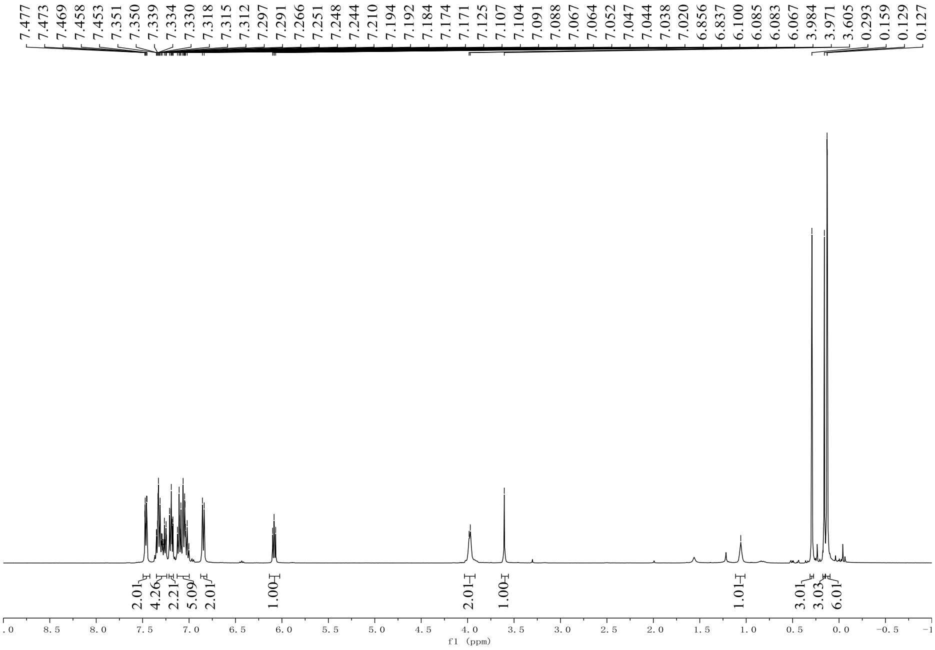


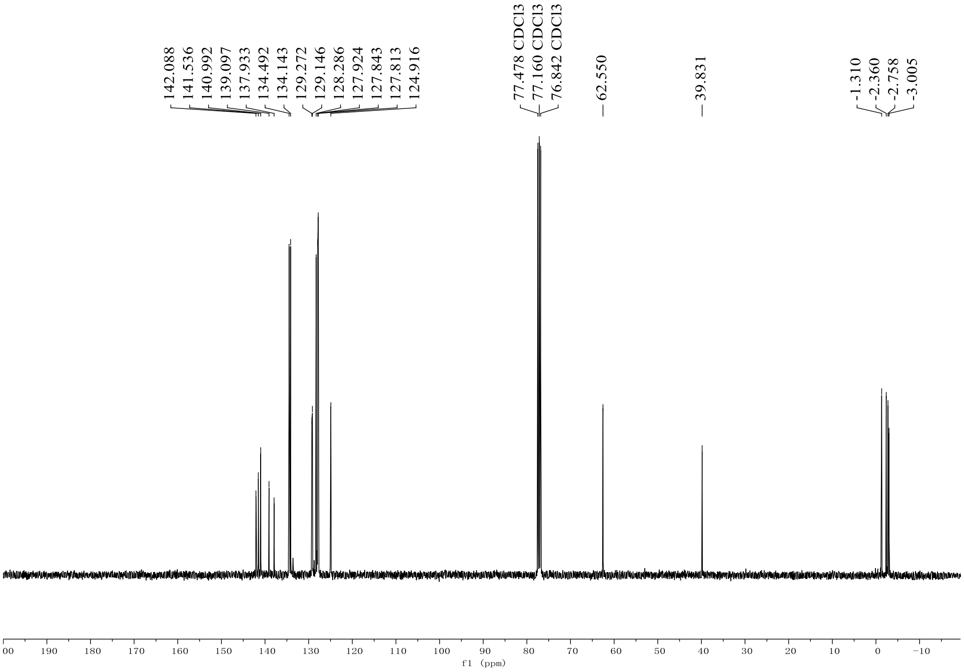
(*E*)-3,4-bis(dimethyl(phenyl)silyl)-4-phenylbut-2-en-1-ol (5a). This compound was prepared via the general procedure described above and was obtained as colorless oil of inseparable mixture (E/Z=95:5) in 83% yield (69.3 mg). The data of ^{1}H and ^{13}C NMR described following is for the *E* isomer. The configuration of the product was determined by NOESY and HMBC correlation analysis. R_f = 0.30 (Petroleum ether : EtOAc = 9:1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50-7.42 (m, 2H), 7.35-7.24 (m, 4H), 7.22-7.17 (m, 2H), 7.13-7.00 (m, 5H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.08 (dd, *J* = 7.0, 6.2 Hz, 1H), 4.02-3.92 (m, 2H), 3.61 (s, 1H), 1.06 (s, 1H), 0.29 (s, 3H), 0.16 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H).

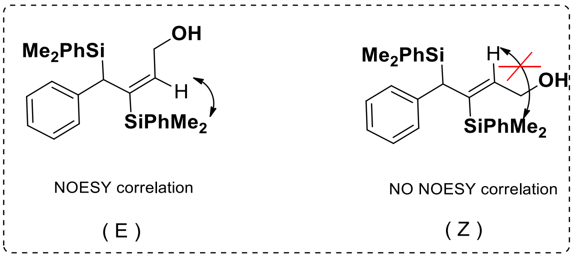
^{13}C NMR (101 MHz, CDCl$_3$) δ 142.09, 141.54, 140.99, 139.10, 137.93, 134.49, 134.14, 129.27, 129.15, 128.29, 127.92, 127.84, 127.81, 124.92, 62.55, 39.83, -1.31, -2.36, -2.76, -3.01.

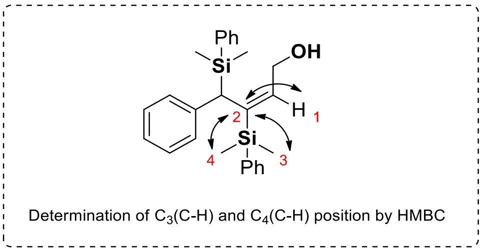
HRMS (ESI) m/z calculated for $C_{26}H_{32}OSi_2Na$ [M+Na]$^+$: 439.1889, found: 439.1889.



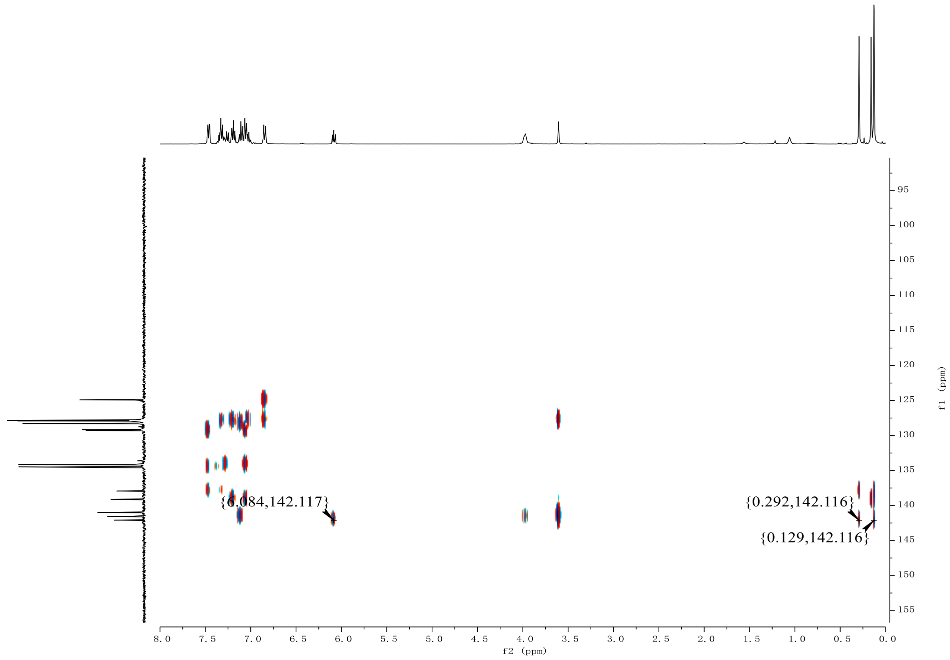


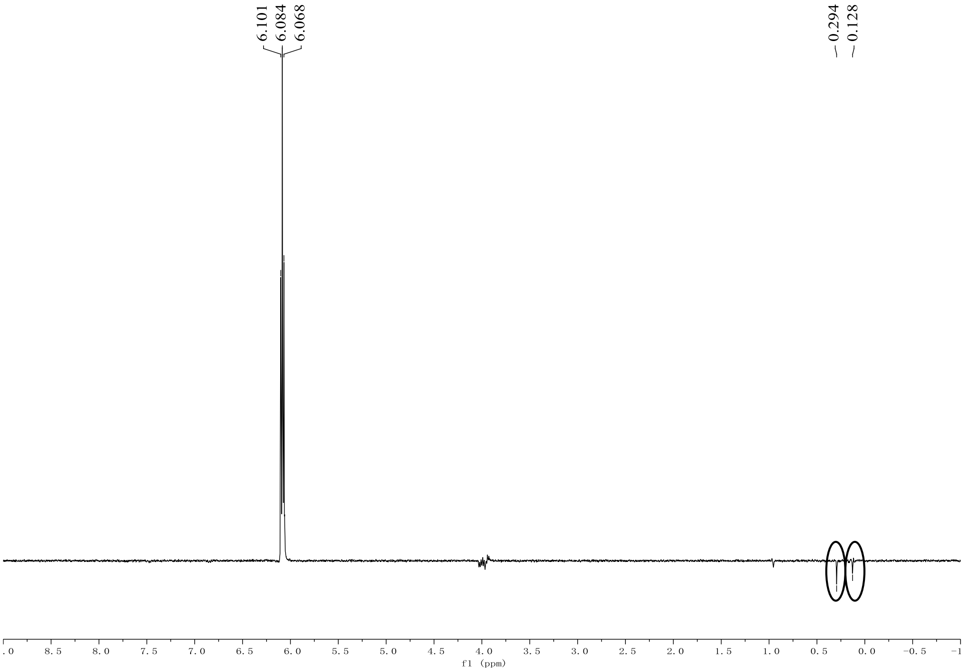
The configuration of product **5a** was determined by NOESY and HMBC correlation analysis.

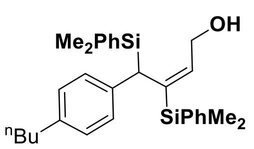




Determination of C_3(C-H) and C_4(C-H) position by HMBC





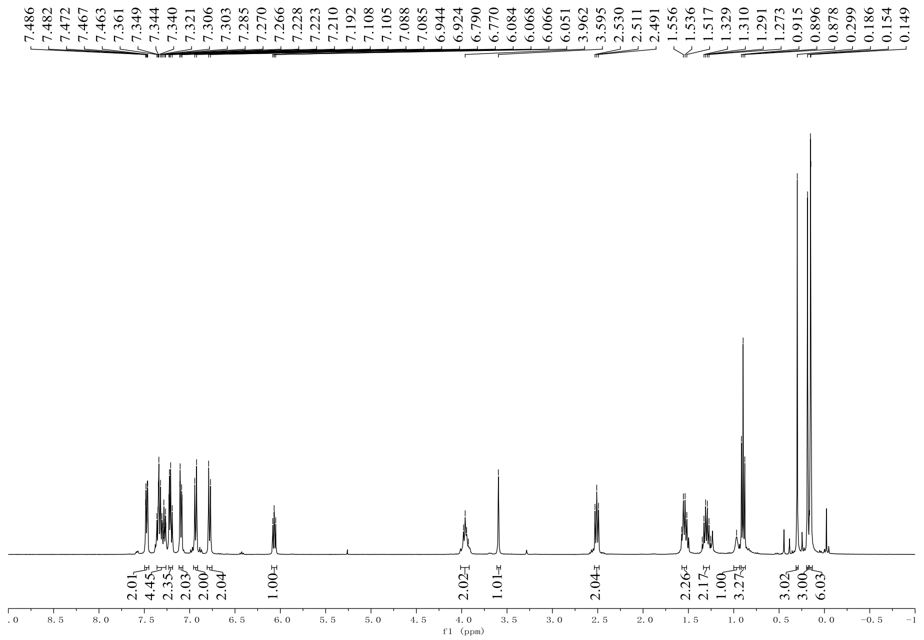


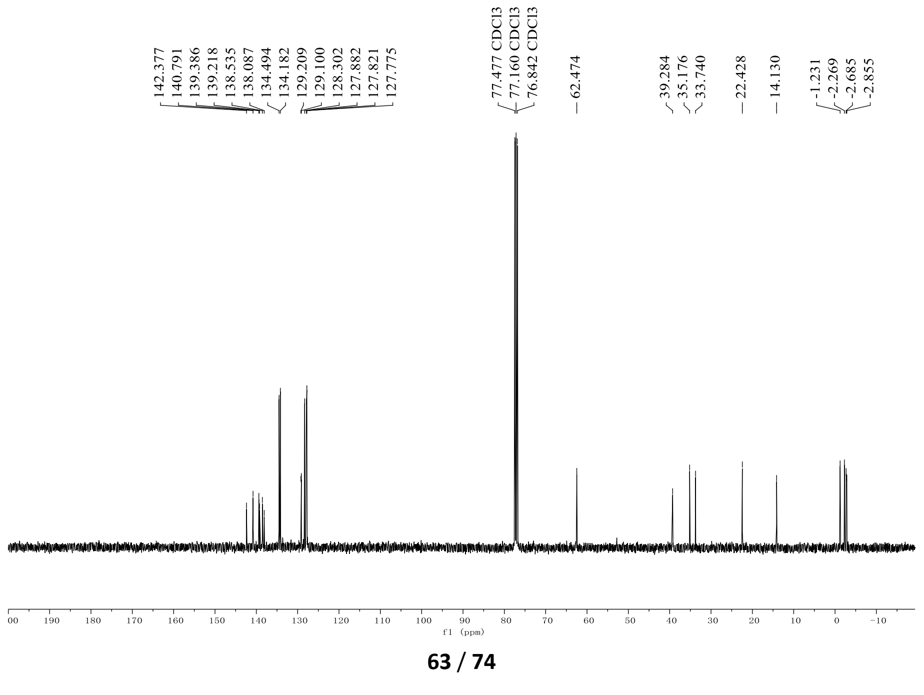
(E)-4-(4-butylphenyl)-3,4-bis(dimethyl(phenyl)silyl)but-2-en-1-ol (5b). This compound was prepared via the general procedure described above and was obtained as yellow solid of inseparable mixture (E/Z=95:5) in 70% yield (66.2 mg). The data of ^{1}H and ^{13}C NMR following is for the *E* isomer. R_f = 0.40 (Petroleum ether : EtOAc = 9:1).

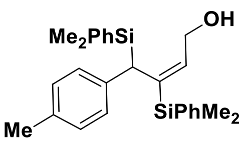
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2H), 7.36-7.26 (m, 4H), 7.23-7.18 (m, 2H), 7.12-7.07 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.07 (dd, *J* = 7.0, 6.2 Hz, 1H), 4.01-3,91 (m, 2H), 3.60 (s, 1H), 2.51 (t, *J* = 7.8 Hz, 2H), 1.57-1.52 (m, 2H), 1.34-1.26 (m, 2H), 0.97 (s, 1H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.30 (s, 3H), 0.19 (s, 3H), 0.16 (s, 3H), 0.15 (s, 3H) .

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.38, 140.79, 139.39, 139.22, 138.54, 138.09, 134.49, 134.18, 129.21, 129.10, 128.30, 127.88, 127.82, 127.78, 62.47, 39.28, 35.18, 33.74, 22.43, 14.13, -1.23, -2.27, -2.69, -2.86.

HRMS (ESI) m/z calculated for $C_{30}H_{40}OSi_2Na$ $[M+Na]^+$: 495.2515, found: 495.2522.





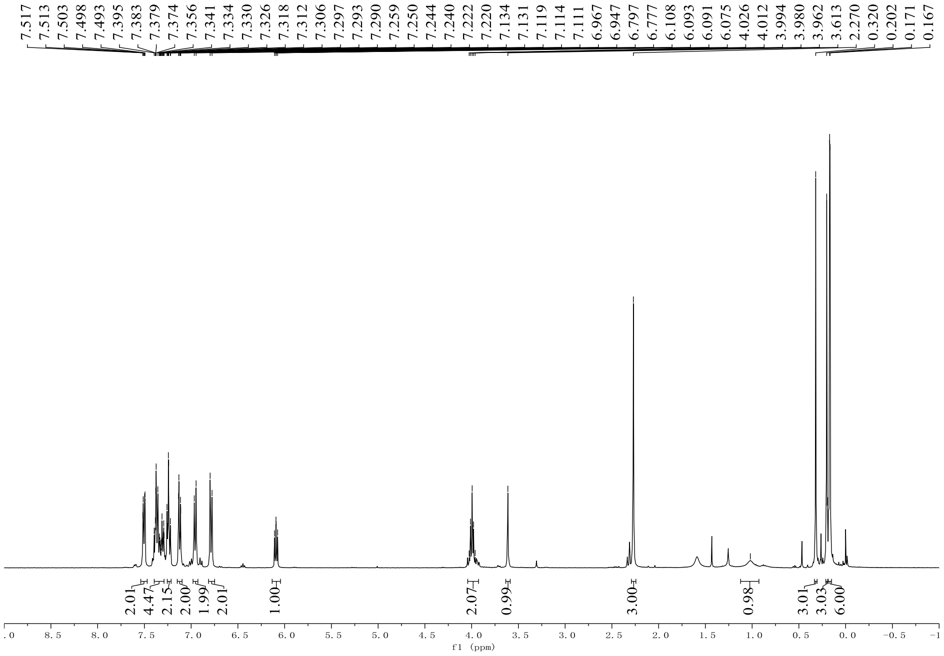


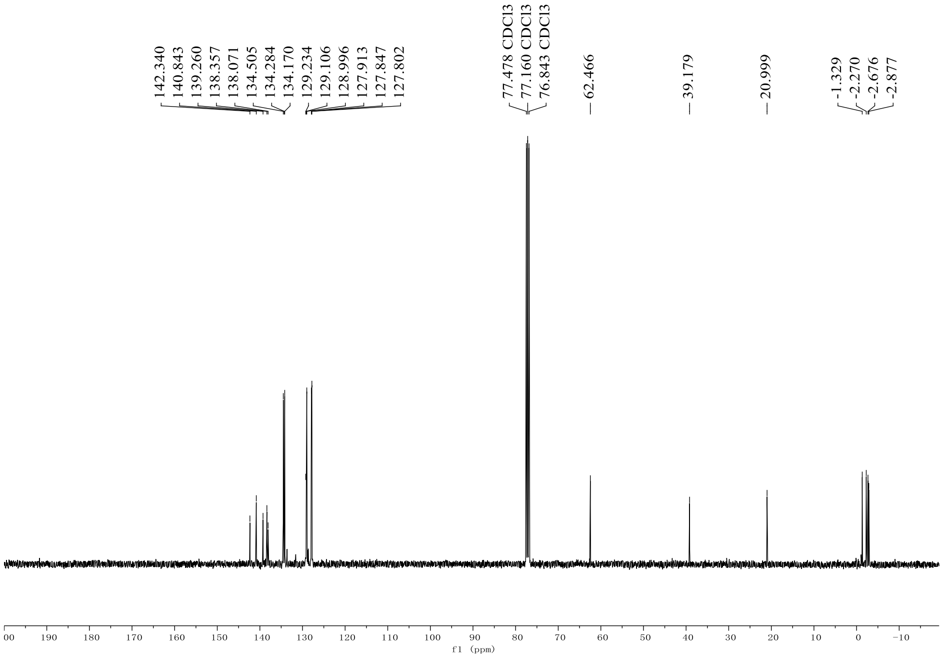
(*E*)-3,4-bis(dimethyl(phenyl)silyl)-4-(p-tolyl)but-2-en-1-ol (5c). This compound was prepared via the general procedure described above and was obtained as yellow oil of inseparable mixture (E/Z=92:8) in 62% yield (53.1 mg). The data of ^{1}H and ^{13}C NMR described following is for the *E* isomer. R_f = 0.30 (Petroleum ether : EtOAc = 9:1).

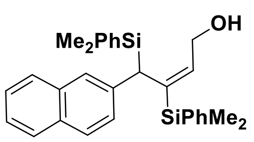
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.47 (m, 2H), 7.39-7.29 (m, 4H), 7.26-7.21 (m, 2H), 7.15-7.10 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.09 (dd, *J* = 7.0, 6.2 Hz, 1H), 4.04-3.93 (m, 2H), 3.61 (s, 1H), 2.27 (s, 3H), 1.02 (s, 1H), 0.32 (s, 3H), 0.20 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.34, 140.84, 139.26, 138.36, 138.07, 134.51, 134.28, 134.17, 129.23, 129.11, 129.00, 127.91, 127.85, 127.80, 62.47, 39.18, 21.00, -1.33, -2.27, -2.68, -2.88.

HRMS (ESI) m/z calculated for $C_{27}H_{34}OSi_2Na$ $[M+Na]^+$: 453.2046, found: 453.2040.





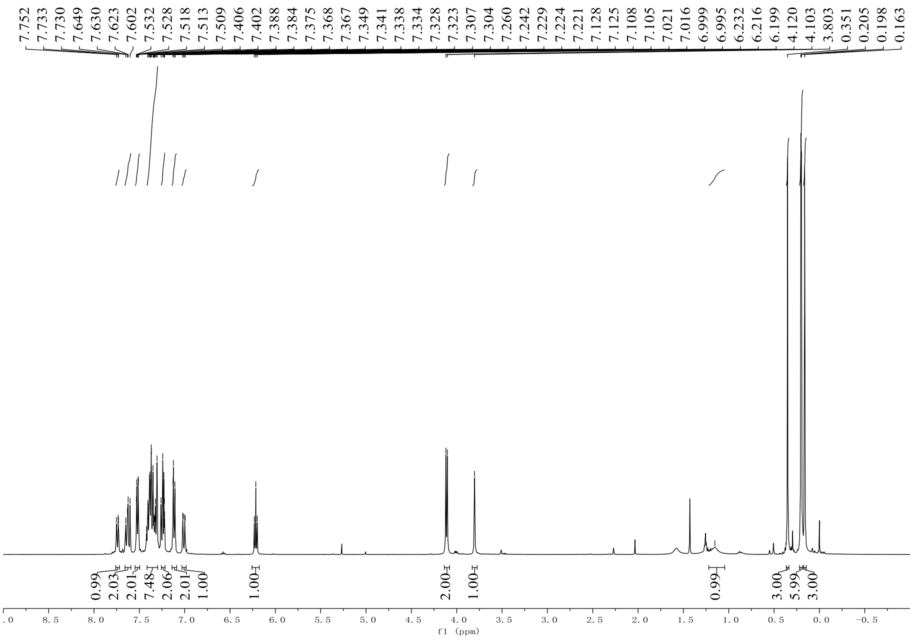


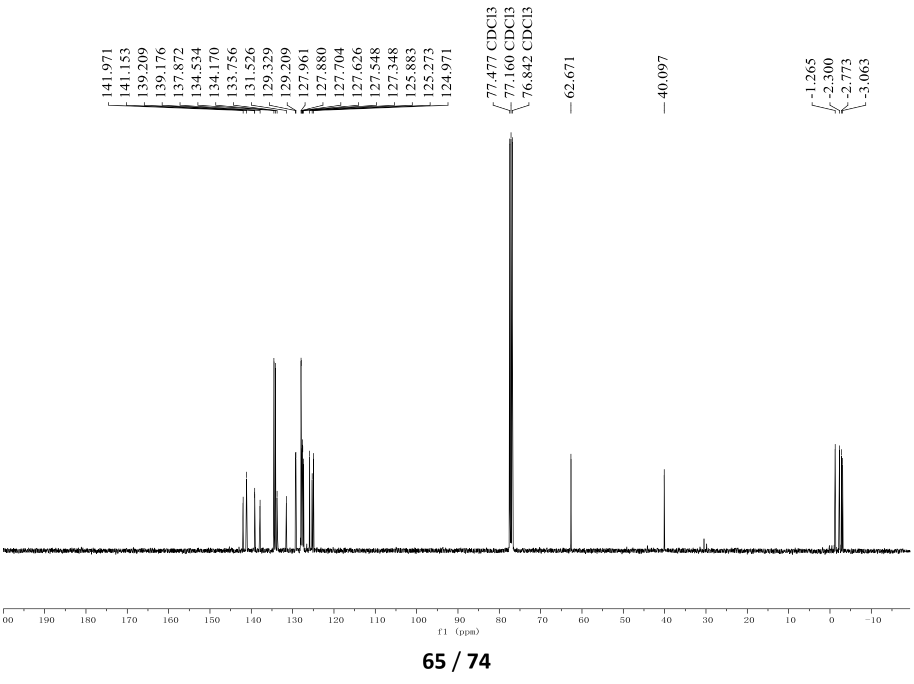
(*E*)-3,4-bis(dimethyl(phenyl)silyl)-4-(naphthalen-2-yl)but-2-en-1-ol (5d). This compound was prepared by the general procedure described above and was obtained as yellow oil of inseparable mixture (E/Z=94:6) in 54% yield (50.5 mg). The data of ^{1}H and ^{13}C NMR described following is for the *E* isomer. R_f = 0.30 (Petroleum ether : EtOAc = 9:1).

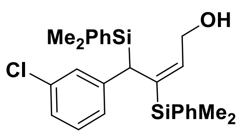
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.72 (m, 1H), 7.66-7.59 (m, 2H), 7.55-7.50 (m, 2H), 7.41-7.30 (m, 7H), 7.25-7.21 (m, 2H), 7.14-7.09 (m, 2H), 7.01 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.22 (t, *J* = 6.6 Hz, 1H), 4.11 (d, *J* = 6.8 Hz, 2H), 3.80 (s, 1H), 1.15 (s, 1H), 0.35 (s, 3H), 0.21 (s, 3H), 0.20 (s, 3H), 0.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.97, 141.15, 139.21, 139.18, 137.87, 134.53, 134.17, 133.76, 131.53, 129.33, 129.21, 127.96, 127.88, 127.70, 127.63, 127.55, 127.35, 125.88, 125.27, 124.97, 62.67, 40.10, -1.27, -2.30, -2.77, -3.06.

HRMS (ESI) m/z calculated for $C_{30}H_{34}OSi_2Na$ $[M+Na]^+$: 489.2046, found: 489.2052.





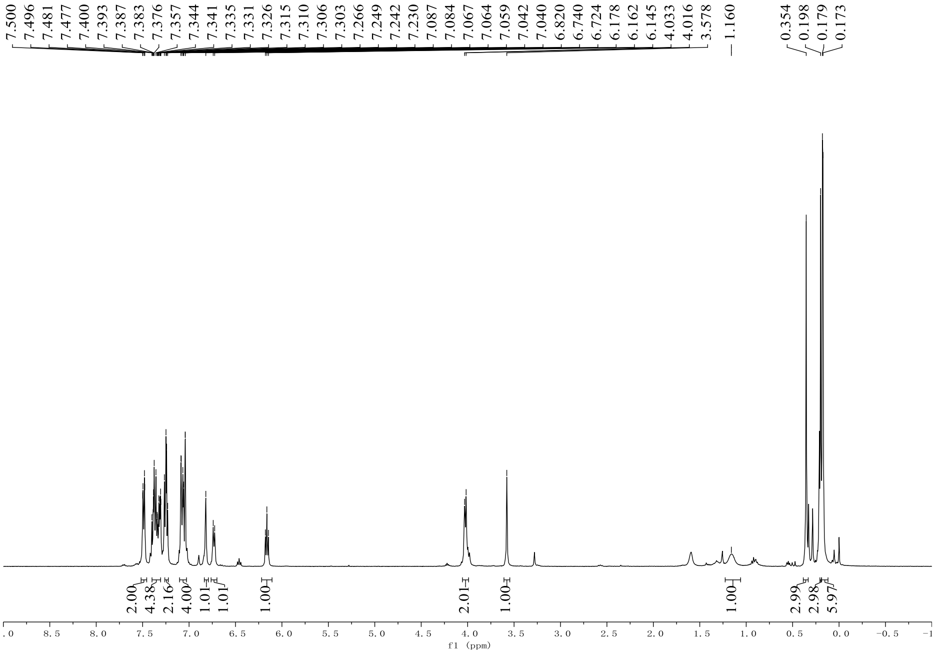


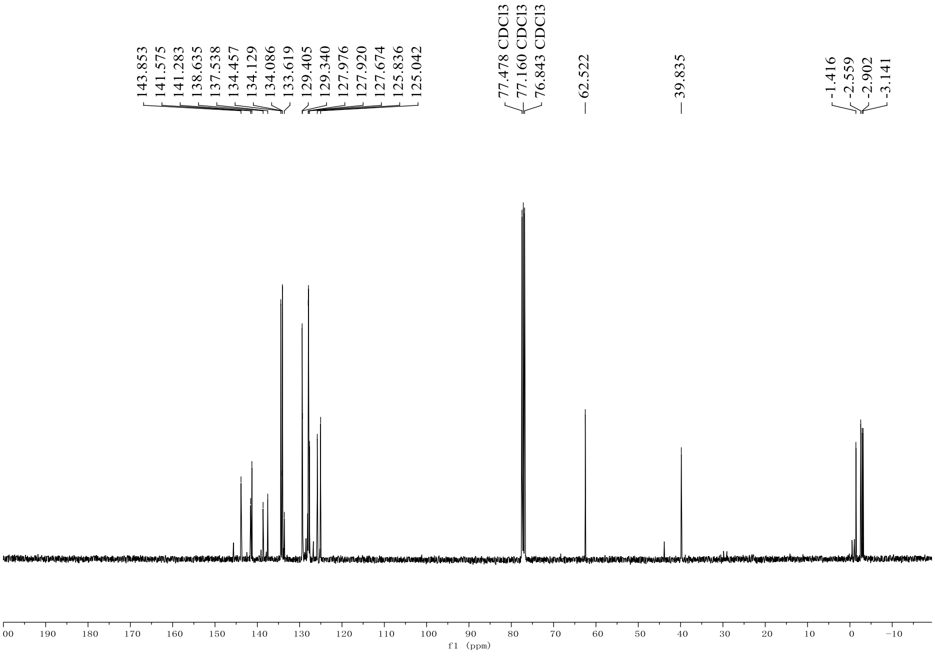
(*E*)-4-(3-chlorophenyl)-3,4-bis(dimethyl(phenyl)silyl)but-2-en-1-ol (5e). This compound was prepared via the general procedure described above and was obtained as yellow oil of inseparable mixture (E/Z=88:12) in 76% yield (68.2 mg). The data of ^{1}H and ^{13}C NMR described following is for the *E* isomer. R_f = 0.30 (Petroleum ether : EtOAc = 9:1).

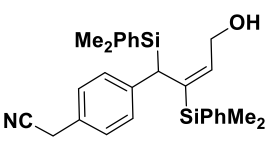
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.46 (m, 2H), 7.40-7.31 (m, 4H), 7.26-7.22 (m, 2H), 7.10-7.03 (m, 4H), 6.82 (s, 1H), 6.73 (d, *J* = 6.4 Hz, 1H), 6.16 (t, *J* = 6.6 Hz, 1H), 4.02 (d, *J* = 6.8 Hz, 2H), 3.58 (s, 1H), 1.16 (s, 1H), 0.35 (s, 3H), 0.20 (s, 3H), 0.18 (s, 3H), 0.17 (s, 3H) .

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.85, 141.58, 141.28, 138.64, 137.54, 134.46, 134.13, 134.09, 133.62, 129.41, 129.34, 127.98, 127.92, 127.67, 125.84, 125.04, 62.52, 39.84, -1.42, -2.56, -2.90, -3.14.

HRMS (ESI) m/z calculated for $C_{26}H_{31}ClOSi_2Na$ $[M+Na]^+$: 473.1500, found: 473.1509.





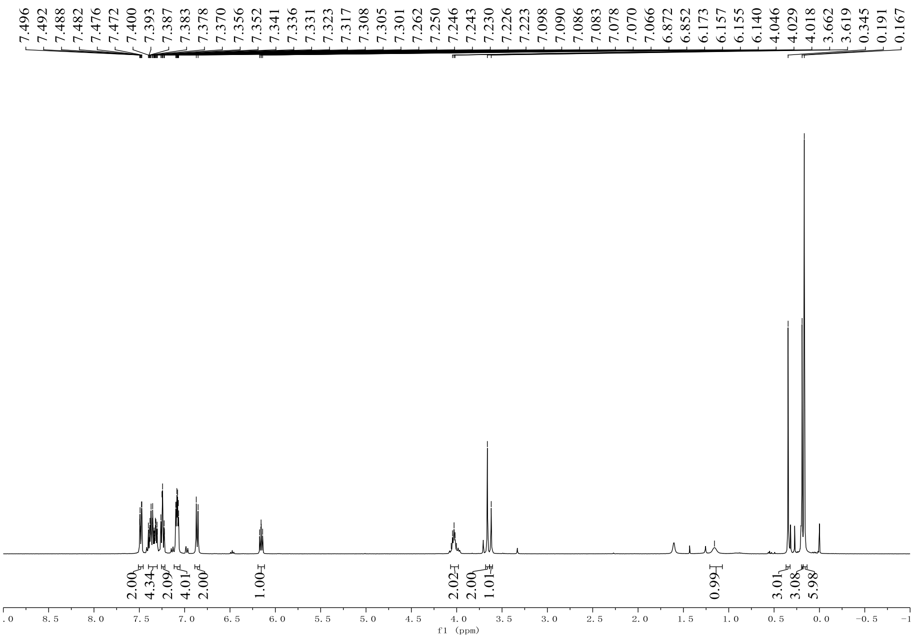


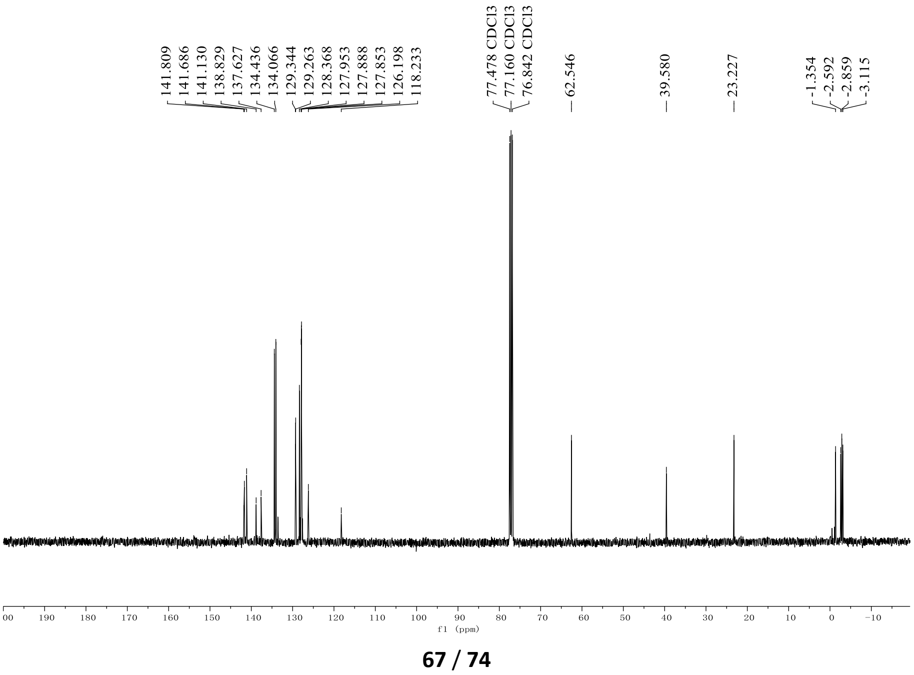
(*E*)-2-(4-(1,2-bis(dimethyl(phenyl)silyl)-4-hydroxybut-2-en-1-yl)phenyl)acetonitrile (5f). This compound was prepared via the general procedure described above and was obtained as colorless oil of inseparable mixture (E/Z=89:11) in 80% yield (72.7 mg). The data of ^{1}H and ^{13}C NMR described following is for the *E* isomer. R_f = 0.30 (Petroleum ether : EtOAc = 4:1).

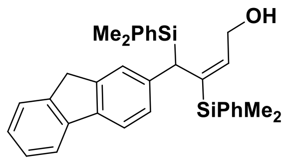
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.46 (m, 2H), 7.40-7.30 (m, 4H), 7.26-7.22 (m, 2H), 7.12-7.05 (m, 4H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.16 (dd, *J* = 7.0, 6.2 Hz, 1H), 4.07-3.98 (m, 2H), 3.66 (s, 2H), 3.62 (s, 1H), 1.16 (s, 1H), 0.35 (s, 3H), 0.19 (s, 3H), 0.17 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.81, 141.69, 141.13, 138.83, 137.63, 134.44, 134.07, 129.34, 129.26, 128.37, 127.95, 127.89, 127.85, 126.20, 118.23, 62.55, 39.58, 23.23, -1.35, -2.59, -2.86, -3.12.

HRMS (ESI) m/z calculated for $C_{28}H_{33}NOSi_2Na$ $[M+Na]^+$: 478.1998, found: 478.2011.





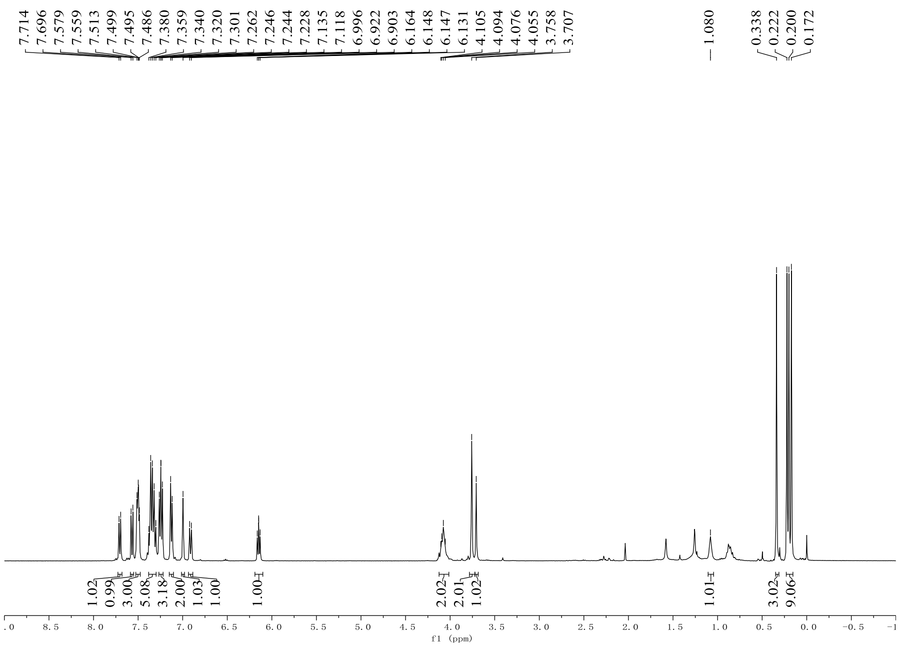


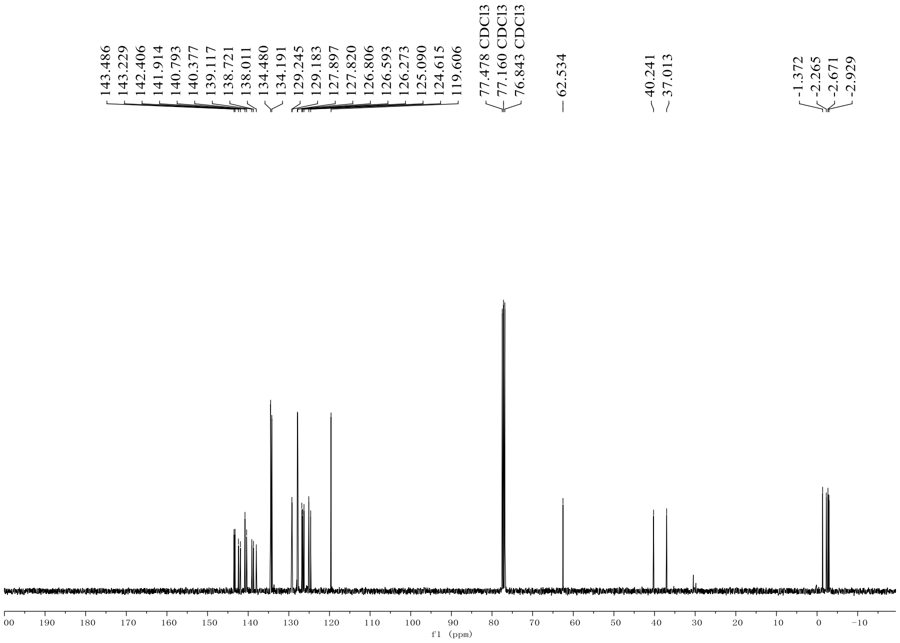
(*E*)-3,4-bis(dimethyl(phenyl)silyl)-4-(9H-fluoren-2-yl)but-2-en-1-ol (5g). This compound was prepared via the general procedure described above and was obtained as yellow oil of inseparable mixture (E/Z=96:4) in 71% yield (71.2 mg). The data of ^{1}H and ^{13}C NMR described following is for the *E* isomer. R_f = 0.30 (Petroleum ether : EtOAc = 9:1).

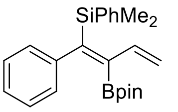
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.53-7.47 (m, 3H), 7.39-7.29 (m, 5H), 7.27-7.21 (m, 3H), 7.13 (d, *J* = 6.8 Hz, 2H), 7.00 (s, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.15 (dd, *J* = 6.8, 6.4 Hz, 1H), 4.12-4.02 (m, 2H), 3.76 (s, 2H), 3.71 (s, 1H), 1.08 (s, 1H), 0.34 (s, 3H), 0.22 (s, 3H), 0.20 (s, 3H), 0.17 (s, 3H) .

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.49, 143.23, 142.41, 141.91, 140.79, 140.38, 139.12, 138.72, 138.01, 134.48, 134.19, 129.25, 129.18, 127.90, 127.82, 126.81, 126.59, 126.27, 125.09, 124.62 , 119.61, 62.53, 40.24, 37.01, -1.37, -2.27, -2.67, -2.93.

HRMS (ESI) m/z calculated for $C_{33}H_{36}OSi_2Na$ $[M+Na]^+$: 527.2202, found: 527.2200.





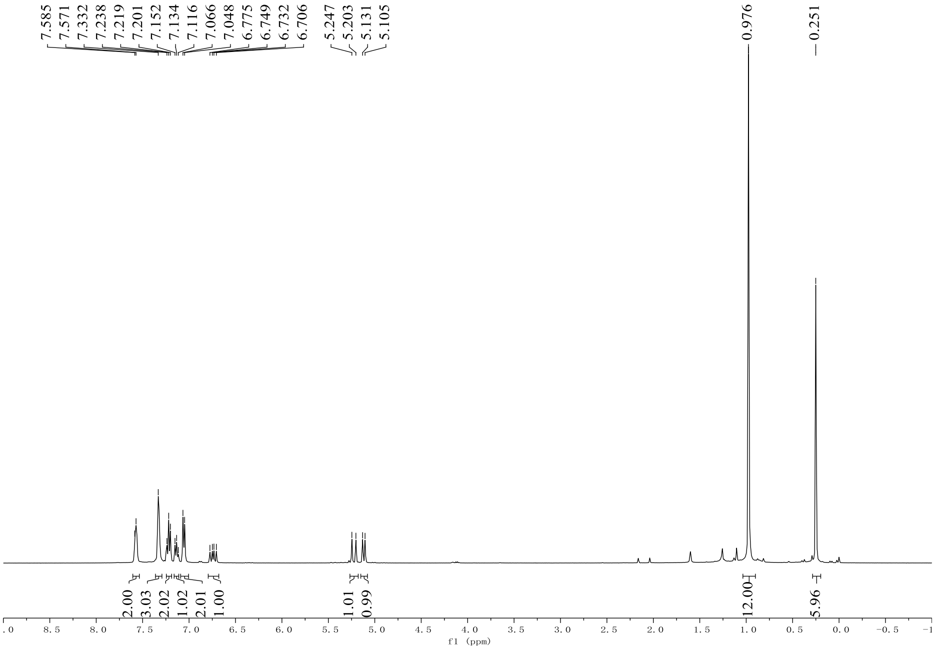


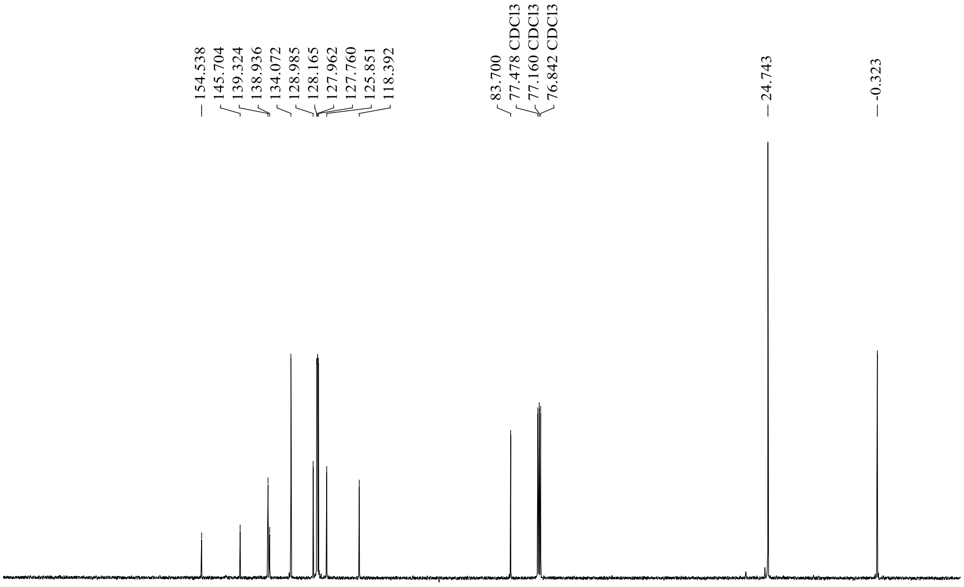
(*Z*)-dimethyl(phenyl)(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)silane (6a). This compound was prepared via the procedure described above and was obtained as white solid of inseparable mixture (Z/E = 73:17) in 94% yield (109.8 mg). The data of ^{1}H and ^{13}C NMR described following is for the *Z* isomer. The configuration of the product was determined by NOESY correlation analysis. R_f = 0.70 (Petroleum ether : EtOAc = 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.54 (m, 2H), 7.33 (s, 3H), 7.24-7.19 (m, 2H), 7.16-7.11 (m, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 6.74 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.23 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 0.98 (s, 12H), 0.25 (s, 6H).

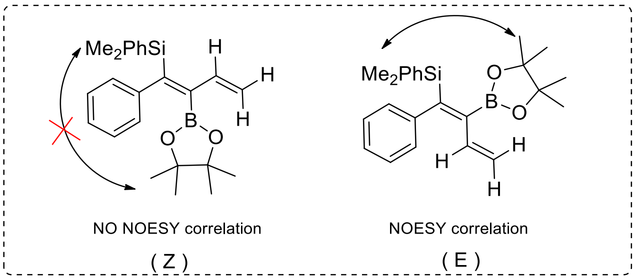
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.54, 145.70, 139.32, 138.94, 134.07, 128.99, 128.17, 127.96, 127.76, 125.85, 118.39, 83.70, 24.74, -0.32.

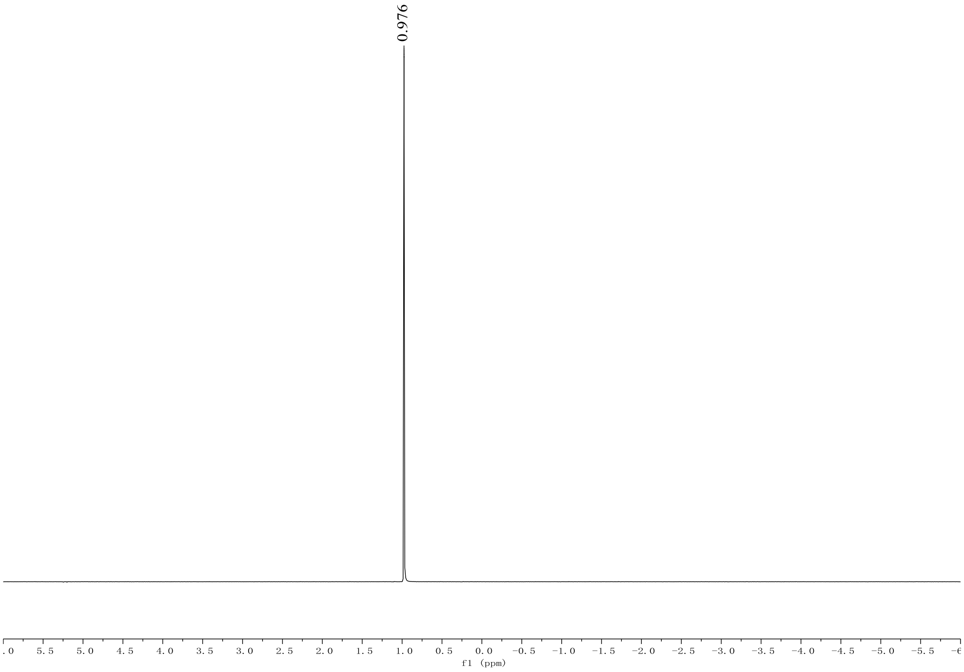
HRMS (ESI) m/z calculated for $C_{24}H_{31}BO_2SiNa$ [M+Na]$^+$: 413.2084, found: 413.2085.

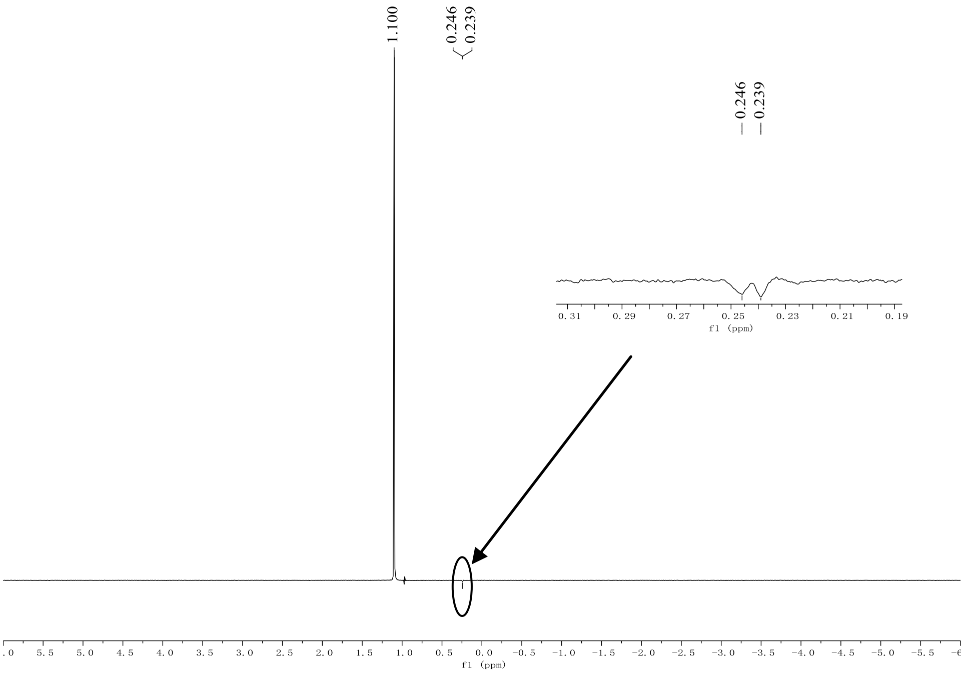


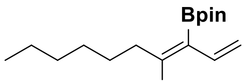


The configuration of product **6a** was determined by NOESY correlation analysis.







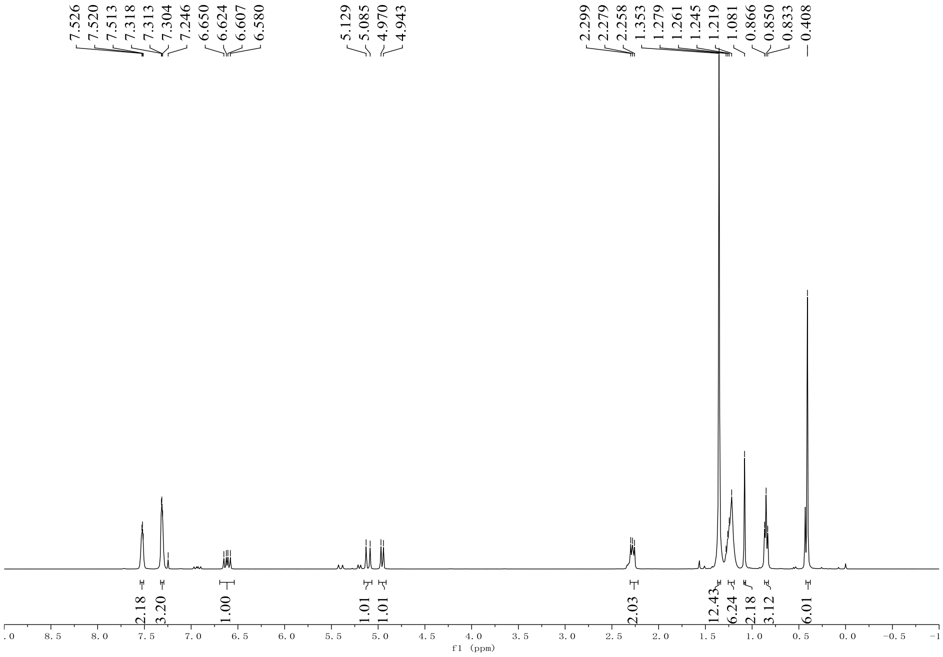


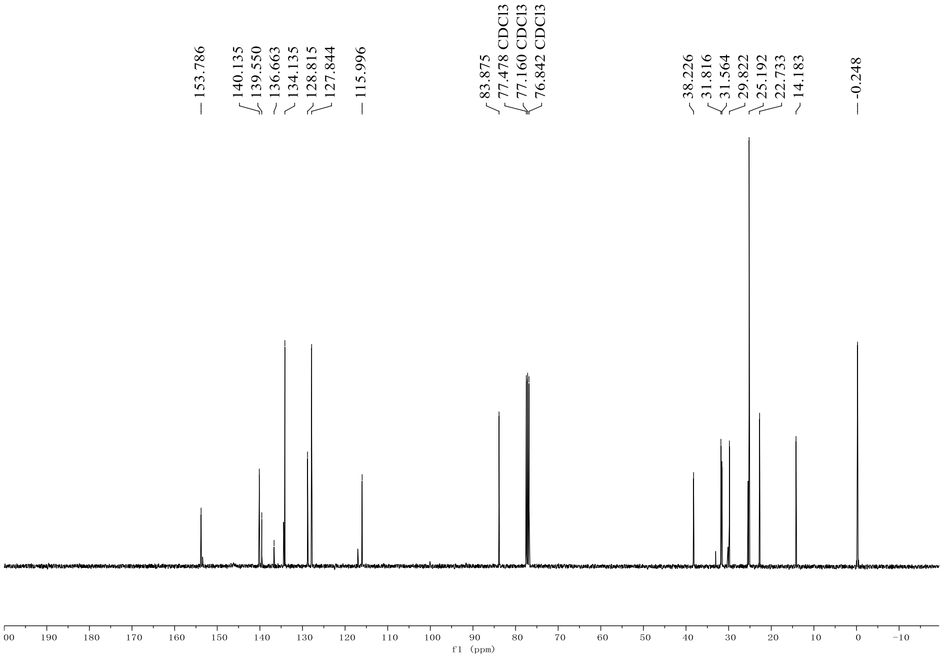
(*Z*)-dimethyl(phenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-1,3-dien-4-yl)silane (6b). This compound was prepared via the procedure described above and was obtained as colorless oil of inseparable mixture (Z/E = 84:16) in 85% yield (81.1 mg). The data of ^{1}H and ^{13}C NMR described following is for the *Z* isomer. The configuration of the product was determined by NOESY correlation analysis. R_f = 0.70 (Petroleum ether : EtOAc = 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.33-7.29 (m, 3H), 6.62 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.11 (d, *J* = 17.6 Hz, 1H), 4.96 (d, *J* = 10.8 Hz, 1H), 2.30-2.22 (m, 2H), 1.35 (s, 12H), 1.26-1.19 (m, 6H), 1.08 (s, 2H), 0.85 (t, *J* = 6.6 Hz, 3H), 0.41 (s, 6H).

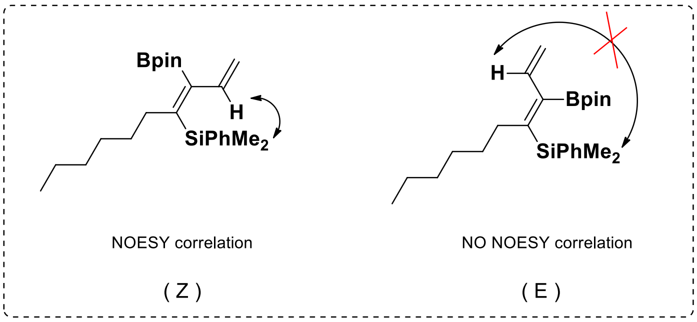
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.79, 140.14, 139.55, 136.66, 134.14, 128.82, 127.84, 116.00, 83.88, 38.23, 31.82, 31.56, 29.82, 25.19, 22.73, 14.18, -0.25.

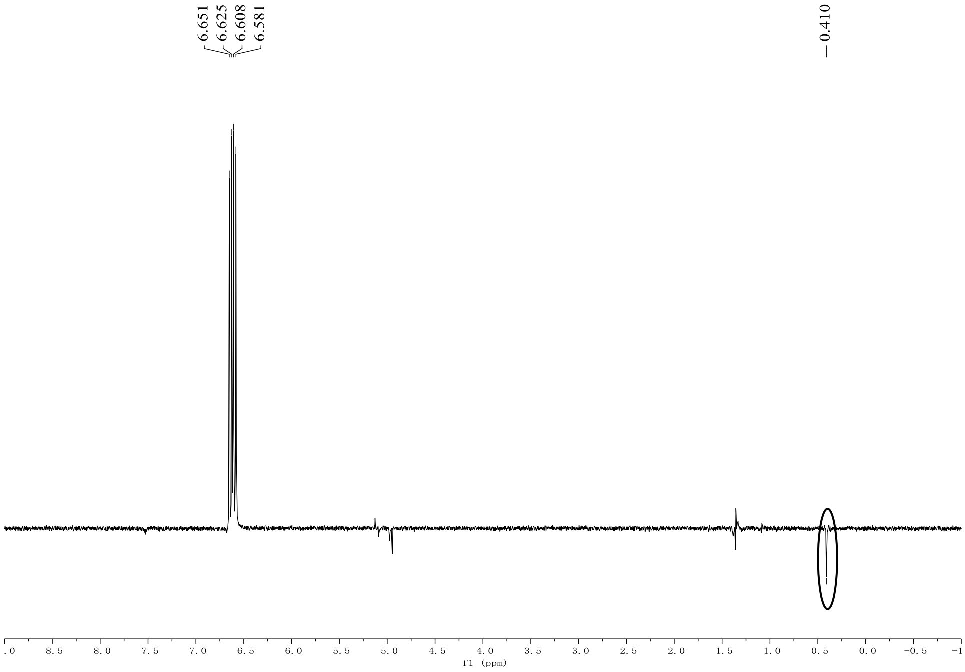
HRMS (ESI) m/z calculated for $C_{24}H_{40}BO_2Si$ $[M+H]^+$: 399.2891, found: 399.2893.

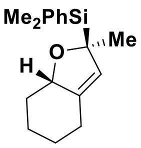




The configuration of the product **6b** was determined by NOESY correlation analysis.





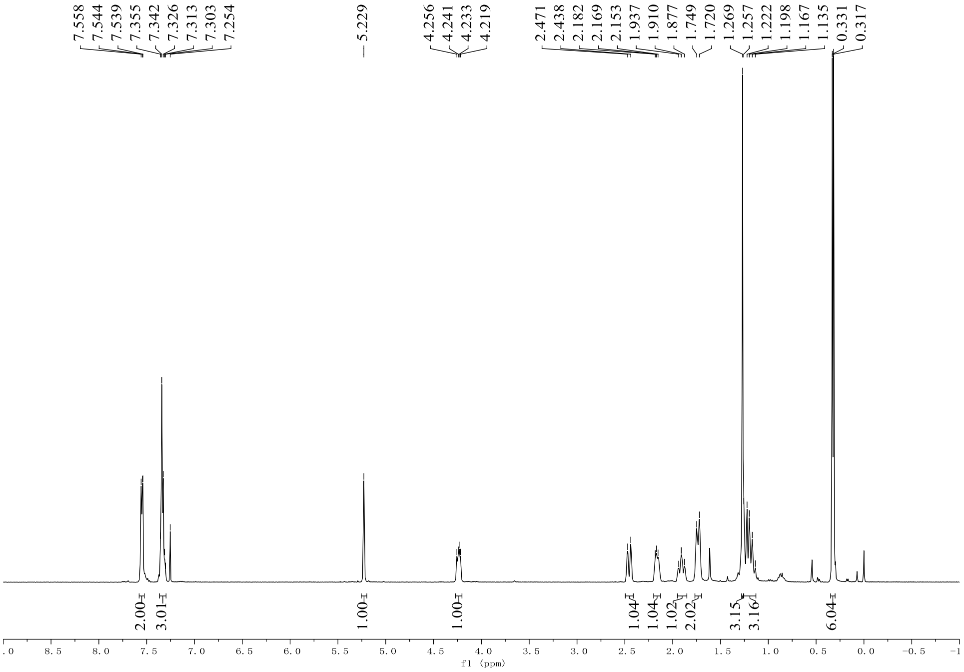


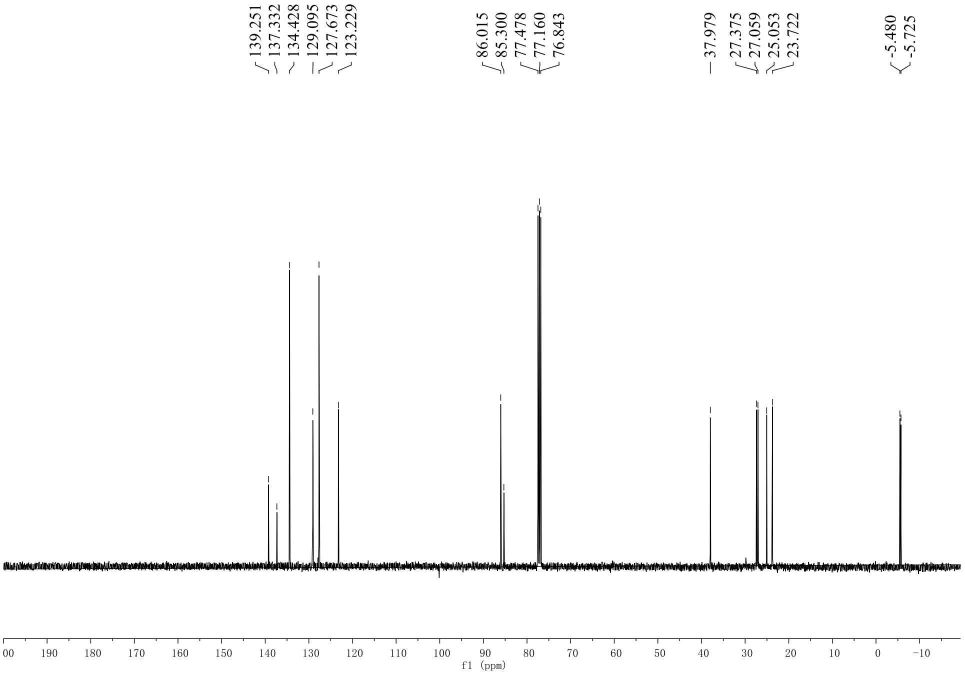
Dimethyl(-2-methyl-2,4,5,6,7,7a-hexahydrobenzofuran-2-yl)(phenyl)silane (7). This compound was prepared via the procedure described above and was obtained as yellow oil in 62% yield (38.6 mg). The configuration of the product was determined by NOESY correlation analysis.[7, 8] R_f = 0.60 (Petroleum ether : EtOAc = 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.52 (m, 2H), 7.36-7.30 (m, 3H), 5.23 (s, 1H), 4.24 (dd, *J* = 9.0, 5.8 Hz, 1H), 2.45 (d, *J* = 13.2 Hz, 1H), 2.20-2.13 (m, 1H), 1.91 (t, *J* = 12.0 Hz, 1H), 1.73 (d, *J* = 11.6 Hz, 2H), 1.27 (s, 3H), 1.26-1.13 (m, 3H), 0.33 (s, 3H), 0.32 (s, 3H).

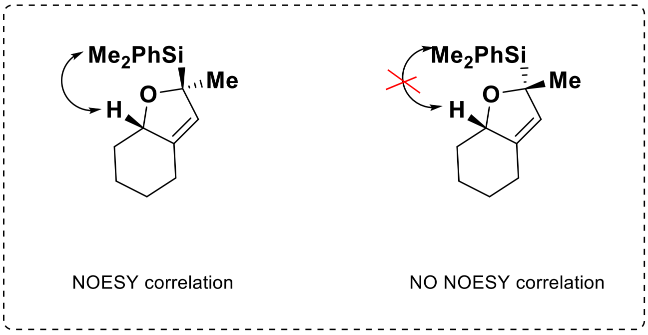
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.25, 137.33, 134.43, 129.10, 127.67, 123.23, 86.02, 85.30, 37.98, 27.38, 27.06, 25.05, 23.72, -5.48, -5.73.

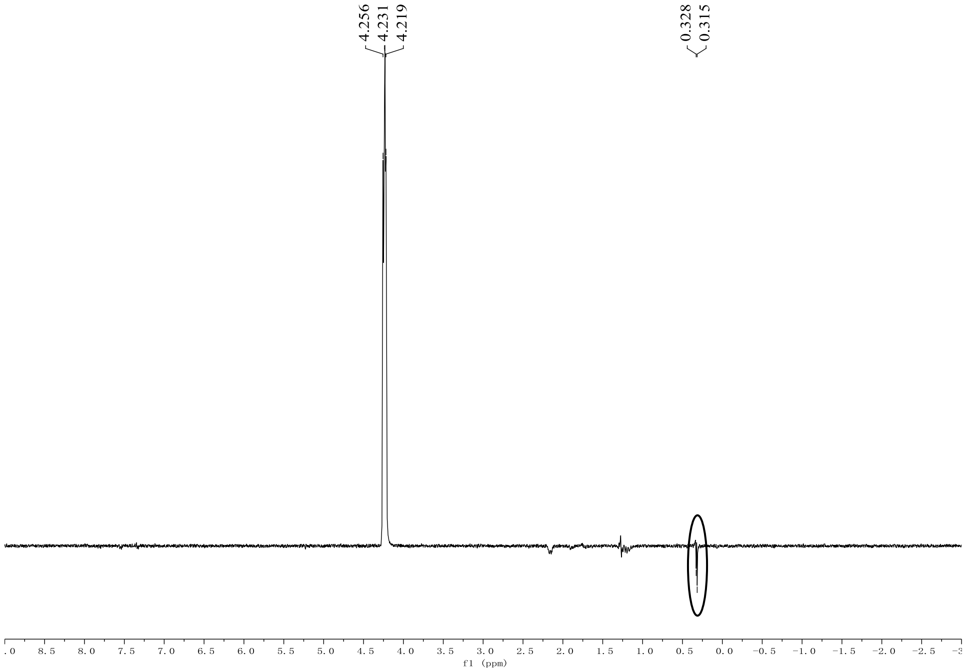
HRMS (ESI) m/z calculated for $C_{17}H_{24}OSiNa$ $[M+Na]^+$: 295.1494, found: 295.1484.





The configuration of product **7** was determined by NOESY correlation analysis.





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