

Supporting Information

**Copper-Catalyzed Asymmetric Silylation of Propargyl Dichlorides:
Access to Enantioenriched Functionalized Allenylsilanes**

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Supporting Information

1 General Information.....	S-2
2 General Procedures for the Preparation of Dichloropropargyl Substrates.....	S-2
3 Optimization of the Reaction Conditions of Racemic Silyl-substituted Allenes.....	S-10
4 General Procedures for the Synthesis of Racemic Silyl-substituted Allenes	S-10
5 General Procedures for the Synthesis of Enantioenriched Silyl-substituted Allenes	S-23
6 General Procedures for the One-pot Synthesis of Enantioenriched Disilyl-substituted Allenes	S-30
7 Further Transformations of Silyl-substituted Chloroallenes.....	S-31
8 Gram-scaled Synthesis of Racemic Silyl-substituted Allenes.....	S-34
9 Determination of the Absolute Configuration of Compound (<i>S</i>)- 3p	S-35
10 References.....	S-36
11 ¹ H NMR, ¹⁹ F NMR, ¹³ C NMR and HPLC Spectra of the Substrates and Products.....	S-37
12 Crystal Data for (<i>E, S</i>)- 14	S-108

1 General Information

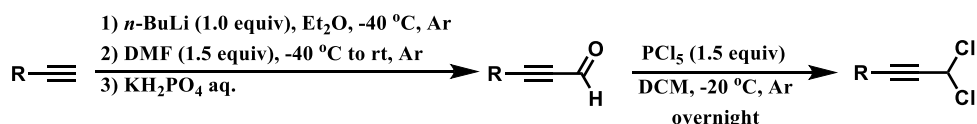
Experiments involving air sensitive components were performed in glovebox. Et₃N and DCE were fractionally distilled. Other reagents were commercially purchased and were used as received without further purification for the reactions. Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectra were performed on a Bruker Advance 400M NMR spectrometer (CDCl₃). Chemical shifts ¹H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe₄ (δ 0.00 ppm) and relative to the signal of chloroform-*d* (δ 7.26 ppm, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); tt (triplet of triplets); td (triplet of doublets); m (multiplets) and *etc.* The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (¹³C NMR) are reported as in units of parts per million (ppm) downfield from SiMe₄ (0.00) and relative to the signal of chloroform-*d* (*J* = 77.03, triplet). High resolution mass spectral analysis (HRMS) were performed on Water XEVO G2 Q-TOF (Waters Corporation) and GCT Premier. The enantiomeric excesses were determined by HPLC analysis on Chiral Daicel Chiralpak OD-H, OJ, ID columns. Optical rotations were recorded on an Anton Paar MCP 200 polarimeter at 589 nm in dichloromethane.

Experimental Procedure:

2 General Procedures for the Preparation of Dichloropropargyl Substrates (GP1) .

All substrates were prepared according to the reported literatures.¹⁻³

The general procedure A¹

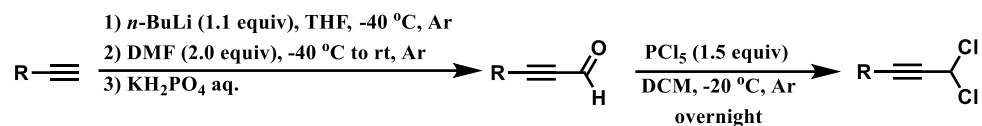


Step 1: To a solution of 1-alkyne (2.61 mL, 20 mmol) in dry Et₂O (20 mL) at -40 °C was added dropwise 2.5 M *n*-BuLi (12.5 mL, 20 mmol) followed by the addition of anhydrous DMF (2.4 mL, 30 mmol) in one portion. The clear reaction mixture was allowed to warm up to room temperature and stirred until full conversion (TLC monitoring). The solution was then poured into a biphasic mixture of 100 mL 10% KH₂PO₄ aqueous solution and ether (80 mL) at 0 °C. The mixture was stirred vigorously, and layers were partitioned. The aqueous layer was extracted with ether (3 x 50 mL). The organic layers were collected, combined, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The crude product obtained was used in the following chloration step without further purification.

Step 2: The crude product was dissolved in dry CH₂Cl₂ (40 mL) and cooled to -20 °C. Then, PCl₅ (6.2 g, 30 mmol) was added portion wise and the reaction mixture was stirred overnight. It was quenched by the addition of saturated NaHCO₃ solution at -20 °C. The mixture allowed to warm back to 25 °C, water was added to completely neutralize the solution. The aqueous phase was extracted by CH₂Cl₂ (3 x 50 mL), the organic phases were collected, dried over Na₂SO₄, concentrated under reduced pressure. Purification by column chromatography on

silica gel (eluent: petroleum ether) provided the desired compound.

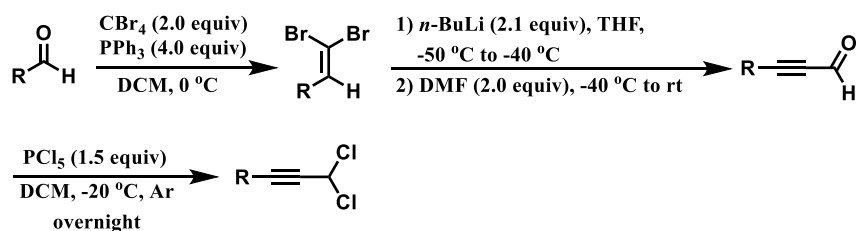
The general procedure B ²



Step 1: A dried, argon-flushed flask equipped with a magnetic stirring bar was charged with dry THF (40 mL) and ethynylcyclohexane (4.33 g, 40 mmol). The solution was cooled to $-40\text{ }^\circ\text{C}$ and *n*-BuLi (17.6 mL, 44 mmol, 2.5 M in hexane) was added dropwise. The reaction mixture was stirred for 1 hour at $-40\text{ }^\circ\text{C}$ followed by the addition of dry DMF (5.85 g, 80.0 mmol). Then, the reaction mixture was allowed to warm up to room temperature until the starting material was completely consumed (monitored by TLC). The solution was then poured into a biphasic mixture of 200 mL 10% KH_2PO_4 aqueous solution and ether (160 mL) at $0\text{ }^\circ\text{C}$. The mixture was stirred vigorously, and layers were partitioned. The aqueous layer was extracted with ether (3 x 50 mL). The organic layers were collected, combined, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was purified by column chromatography (eluent: PE/EA = 95:5) to afford the product (3.37 g) as colorless oil.

Step 2: The above product was dissolved in dry CH_2Cl_2 (40 mL) and cooled to $-20\text{ }^\circ\text{C}$. Then, PCl_5 (12.5 g, 60 mmol) was added portion wise and the reaction mixture was stirred overnight. It was quenched by the addition of saturated NaHCO_3 solution at $-20\text{ }^\circ\text{C}$. The mixture allowed to warm back to room temperature, water was added to completely neutralize the solution. The aqueous phase was extracted by CH_2Cl_2 (3 x 50 mL), the organic phases were collected, dried over Na_2SO_4 , concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: PE) provided the desired compound (4.05 g) as slightly yellow oil. (85% yield over two steps)

The general procedure C ^{1,3}

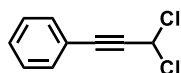


Step 1: Under argon atmosphere, a solution of triphenylphosphine (4.0 equiv) and tetrabromomethane (2.0 equiv) in DCM (0.15 M) was stirred at $0\text{ }^\circ\text{C}$ for 30 minutes. Then the corresponding aldehyde was added over a period of five minutes, and the mixture was stirred at $0\text{ }^\circ\text{C}$ for one hour. After addition of water, the layers were separated, and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was dry-loaded on silica and subjected to flash chromatography (silica, DCM/PE).

Step 2: Under argon atmosphere, *n*-BuLi (2.1 equiv, 2.5 M in hexane) was added over a

period of 30 minutes via syringe pump to a solution of *gem*-dibromoolefine (1.0 equiv) in dry THF (0.4 M) at -50 °C, and the mixture was stirred at -40 °C for 15 minutes. After addition of dry DMF (2.0 equiv) at once, the mixture was allowed to warm to room temperature and stirred for one hour. The mixture was added to a stirring solution of aqueous NaH₂PO₄/Et₂O (1:1). After five minutes, the layers were separated and the aqueous layer was extracted with Et₂O (3 x 50 mL). The combined organic layers were dried over Na₂SO₄, the solvent was removed under reduced pressure and the crude product was subjected to flash chromatography (silica, EA/PE).

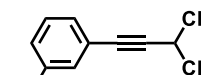
Step 3: The crude product was dissolved in dry CH₂Cl₂ (1.0 M) and cooled to -20 °C. Then, PCl₅ (1.5 equiv) was added portion wise and the reaction mixture was stirred overnight. It was quenched by the addition of saturated NaHCO₃ solution at -20 °C. The mixture allowed to warm back to 25 °C, water was added to completely neutralize the solution. The aqueous phase was extracted by CH₂Cl₂ (3 x 50 mL); the organic phases were collected, dried over Na₂SO₄, concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: PE) provided the desired compound.



1a

Prepared according to the general procedure **B** using corresponding aldehyde (2.60 g, 20 mmol). The product **1a** was isolated in 84% yield (3.11 g) by column chromatography as yellow oil.

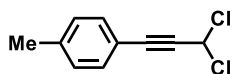
Eluent: petroleum ether. **¹H NMR (400 MHz, CDCl₃):** δ 7.50 – 7.48 (m, 2H), 7.42 – 7.33 (m, 3H), 6.49 (s, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 132.08, 129.94, 128.59, 120.69, 90.03, 84.17, 56.12. **HRMS (EI):** m/z calculated for C₉H₆Cl₂ [M]⁺: 183.9841, found: 183.9840. **IR (KBr):** 2225, 1491, 1444, 1279, 1236, 757, 722, 687.



1b

Prepared according to the general procedure **B** using corresponding aldehyde (2.88 g, 20 mmol). The product **1b** was isolated in 67% yield (2.67 g) by column chromatography as yellow oil.

Eluent: petroleum ether. **¹H NMR (400 MHz, CDCl₃):** δ 7.32 – 7.28 (m, 2H), 7.26 – 7.24 (m, 1H), 7.22 – 7.19 (m, 1H), 6.49 (s, 1H), 2.34 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 138.24, 132.47, 130.69, 129.01, 128.34, 120.38, 90.18, 83.72, 56.03, 21.15. **HRMS (EI):** m/z calculated for C₁₀H₈Cl₂ [M]⁺: 197.9998, found: 198.0010. **IR (KBr):** 2233, 1485, 1293, 1243, 1035, 785, 723, 688.

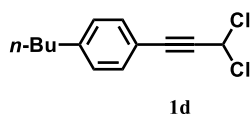


1c

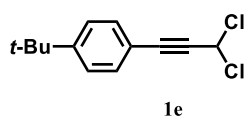
Prepared according to the general procedure **B** using corresponding aldehyde (1.44 g, 10 mmol). The product **1c** was isolated in 71% yield (1.42 g) by column chromatography as yellow solid.

Eluent: petroleum ether. **¹H NMR (400 MHz, CDCl₃):** δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.49 (s, 1H), 2.37 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 140.21, 131.86,

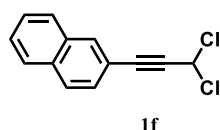
129.22, 117.50, 90.28, 83.52, 56.14, 21.60. **HRMS (EI):** m/z calculated for $C_{10}H_8Cl_2 [M]^+$: 197.9998, found: 197.9997. **IR (KBr):** 2224, 1509, 1282, 1232, 1197, 1023, 1007, 823, 723, 692.



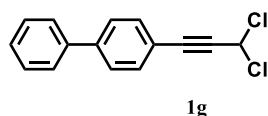
Prepared according to the general procedure **B** using corresponding aldehyde (2.05 g, 11 mmol). The product **1d** was isolated in 87% yield (2.31 g) by column chromatography as yellow oil. **Eluent:** petroleum ether. **1H NMR (400 MHz, $CDCl_3$):** δ 7.41 – 7.39 (m, 2H), 7.17 – 7.15 (m, 2H), 6.49 (s, 1H), 2.62 (t, $J = 7.6$ Hz, 2H), 1.62 – 1.55 (m, 2H), 1.39 – 1.29 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 145.19, 131.88, 128.58, 117.69, 90.35, 83.54, 56.15, 35.64, 33.26, 22.26, 13.88. **HRMS (EI):** m/z calculated for $C_{13}H_{14}Cl_2 [M]^+$: 240.0467, found: 240.0484. **IR (KBr):** 2225, 1510, 1283, 1237, 1195, 1023, 1005, 835, 723, 696.



Prepared according to the general procedure **B** using corresponding aldehyde (2.79 g, 15 mmol). The product **1e** was isolated in 72% yield (2.60 g) by column chromatography as yellow solid. **Eluent:** petroleum ether. **1H NMR (400 MHz, $CDCl_3$):** δ 7.43 – 7.41 (m, 2H), 7.38 – 7.36 (m, 2H), 6.49 (s, 1H), 1.31 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 153.32, 131.73, 125.49, 117.53, 90.28, 83.55, 56.16, 34.94, 31.10. **HRMS (EI):** m/z calculated for $C_{13}H_{14}Cl_2 [M]^+$: 240.0467, found: 240.0475. **IR (KBr):** 2226, 1505, 1464, 1271, 1239, 1195, 1021, 1005, 835, 724, 688.

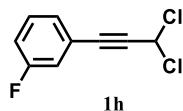


Prepared according to the general procedure **C** using corresponding aldehyde (1.62 g, 9 mmol). The product **1f** was isolated in 45% yield (0.95 g) by column chromatography as yellow solid. **Eluent:** petroleum ether. **1H NMR (400 MHz, $CDCl_3$):** δ 8.04 (s, 1H), 7.85 – 7.81 (m, 3H), 7.56 – 7.49 (m, 3H), 6.55 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 133.45, 132.68, 132.64, 128.26, 128.01, 127.85, 127.49, 126.88, 117.79, 90.30, 84.21, 56.05. **HRMS (EI):** m/z calculated for $C_{13}H_8Cl_2 [M]^+$: 233.9998, found: 234.0007. **IR (KBr):** 2222, 1498, 1280, 1266, 1242, 1196, 1025, 1014, 828, 750, 715, 687.

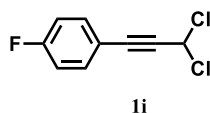


Prepared according to the general procedure **B** using corresponding aldehyde (2.47 g, 12 mmol). The product **1g** was isolated in 52% yield (1.63 g) by column chromatography as yellow solid. **Eluent:** dichloromethane /petroleum ether = 20:80. **1H NMR (400 MHz, $CDCl_3$):** δ 7.61 – 7.55

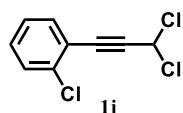
(m, 6H), 7.48 – 7.44 (m, 2H), 7.40 – 7.36 (m, 1H), 6.52 (s, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 142.60, 139.96, 132.41, 128.94, 127.99, 127.13, 127.10, 119.37, 89.87, 84.61, 56.03 ppm; **HRMS (EI):** m/z calculated for C₁₅H₁₀Cl₂ [M]⁺: 260.0154, found: 260.0162. **IR (KBr):** 2222, 1497, 1288, 1232, 1197, 1027, 1002, 840, 766, 718, 689.



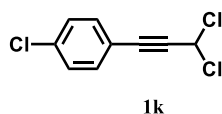
Prepared according to the general procedure **B** using corresponding aldehyde (1.48 g, 10 mmol). The product **1h** was isolated in 43% yield (0.87 g) by column chromatography as yellow oil. **Eluent:** petroleum ether. **¹H NMR (400 MHz, CDCl₃):** δ 7.36 – 7.26 (m, 2H), 7.21 – 7.18 (m, 1H), 7.14 – 7.09 (m, 1H), 6.47 (s, 1H). **¹⁹F NMR (376 MHz, CDCl₃):** δ -112.11. **¹³C NMR (100 MHz, CDCl₃):** δ 162.26 (d, *J* = 246.2 Hz), 130.17 (d, *J* = 8.5 Hz), 127.88 (d, *J* = 3.2 Hz), 122.4 (d, *J* = 9.4 Hz), 118.80 (d, *J* = 23.2 Hz), 117.26 (d, *J* = 21.0 Hz), 88.30 (d, *J* = 3.4 Hz), 84.71, 55.60. **HRMS (EI):** m/z calculated for C₉H₅Cl₂F[M]⁺: 201.9747, found: 201.9749. **IR (KBr):** 2237, 1609, 1583, 1487, 1296, 1244, 1176, 1154, 1024, 875, 786, 723, 679.



Prepared according to the general procedure **B** using corresponding aldehyde (1.4 g, 9.4 mmol). The product **1i** was isolated in 78% yield (1.50 g) by column chromatography as yellow oil. **Eluent:** petroleum ether. **¹H NMR (400 MHz, CDCl₃):** δ 7.50 – 7.45 (m, 2H), 7.08 – 7.02 (m, 2H), 6.47 (s, 1H). **¹⁹F NMR (376 MHz, CDCl₃):** δ -112.77. **¹³C NMR (100 MHz, CDCl₃):** δ 163.40 (d, *J* = 250.5 Hz), 134.07 (d, *J* = 8.6 Hz), 116.70 (d, *J* = 3.6 Hz), 115.91 (d, *J* = 22.17 Hz), 88.83, 83.85, 55.85. **HRMS (EI):** m/z calculated for C₉H₅Cl₂F[M]⁺: 201.9747, found: 201.9757. **IR (KBr):** 2229, 1601, 1479, 1283, 1237, 1157, 1014, 836, 726, 696.

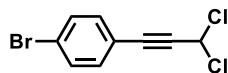


Prepared according to the general procedure **B** using corresponding aldehyde (0.5 g, 3.0 mmol). The product **1j** was isolated in 50% yield (0.33 g) by column chromatography as yellow oil. **Eluent:** petroleum ether. **¹H NMR (400 MHz, CDCl₃):** δ 7.52 (dd, *J*₁ = 7.6 Hz, *J*₂ = 1.7 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.33 (td, *J*₁ = 7.6 Hz, *J*₂ = 1.7 Hz, 1H), 7.25 (td, *J*₁ = 7.2 Hz, *J*₂ = 1.3 Hz, 1H), 6.53 (s, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 136.52, 133.72, 130.87, 129.49, 126.58, 120.72, 88.57, 86.45, 55.69. **HRMS (EI):** m/z calculated for C₉H₅Cl₃[M]⁺: 217.9451, found: 217.9462. **IR (KBr):** 2230, 1474, 1435, 1293, 1250, 1068, 1035, 1003, 756, 727, 690.



Prepared according to the general procedure **B** using corresponding aldehyde (3.46 g, 21.0 mmol). The product **1k** was isolated in 88% yield (4.06 g) by column chromatography as yellow solid.

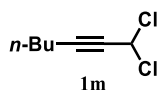
Eluent: petroleum ether. **¹H NMR (400 MHz, CDCl₃):** δ 7.44 – 7.41 (m, 2H), 7.36 – 7.32 (m, 2H), 6.47 (s, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 136.11, 133.18, 128.90, 119.05, 88.62, 84.87, 55.73. **HRMS (EI):** m/z calculated for C₉H₅Cl₃[M]⁺: 217.9451, found: 217.9461. **IR** (KBr): 2225, 1491, 1279, 1232, 1090, 1004, 830, 761, 717, 687.



1l

Prepared according to the general procedure **B** using corresponding aldehyde (2.47 g, 11.8 mmol). The product **1l** was isolated in 80% yield (2.50 g) by column chromatography as white solid.

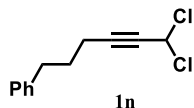
Eluent: petroleum ether. **¹H NMR (400 MHz, CDCl₃):** δ 7.52 – 7.49 (m, 2H), 7.37 – 7.34 (m, 2H), 6.47 (s, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 133.32, 131.83, 124.41, 119.52, 88.67, 85.02, 55.71. **HRMS (EI):** m/z calculated for C₉H₅Cl₂Br[M]⁺: 261.8946, found: 261.8950. **IR** (KBr): 2224, 1582, 1487, 1278, 1239, 1207, 1069, 1011, 826, 749, 718, 686.



1m

Prepared according to the general procedure **A** using corresponding aldehyde (2.97 g, 27.0 mmol). The product **1m** was isolated in 66% yield (2.94 g) by column chromatography as colorless oil.

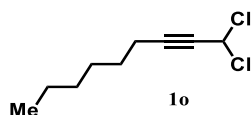
Eluent: petroleum ether (b.p. = 30 – 60 °C). **¹H NMR (400 MHz, CDCl₃):** δ 6.26 (t, *J* = 2.0 Hz, 1H), 2.32 (td, *J*₁ = 7.0 Hz, *J*₂ = 2.0 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.46 – 1.37 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 92.42, 76.32, 56.05, 29.87, 21.90, 18.55, 13.51. **HRMS (EI):** m/z calculated for C₇H₁₀Cl₂ [M]⁺: 164.0154, found: 164.0151. **IR** (KBr): 2959, 2928, 2858, 2239, 1465, 1379, 1254, 1197, 1159, 815, 725, 685.



1n

Prepared according to the general procedure **B** using corresponding aldehyde (1.1 g, 6.4 mmol). The product **1n** was isolated in 45% yield (0.66 g) by column chromatography as colorless oil.

Eluent: petroleum ether (b.p. = 30 – 60 °C). **¹H NMR (400 MHz, CDCl₃):** δ 7.31 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 6.27 (t, *J* = 2.0 Hz, 1H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.32 (td, *J*₁ = 7.1 Hz, *J*₂ = 2.0 Hz, 2H), 1.88 (q, *J* = 7.0 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 141.03, 128.53, 128.46, 126.10, 91.90, 76.92, 55.98, 34.64, 29.38, 18.20. **HRMS (EI):** m/z calculated for C₁₂H₁₂Cl₂ [M]⁺: 226.0311, found: 226.0321. **IR** (KBr): 3027, 2945, 2861, 2238, 1496, 1455, 1426, 1255, 1198, 1158, 862, 722, 699.

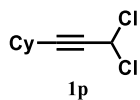


1o

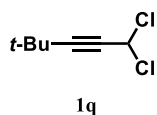
Prepared according to the general procedure **A** using corresponding aldehyde (1.34 g, 9.7 mmol). The product **1o** was isolated in 68% yield (1.28 g) by column chromatography as colorless oil.

Eluent: petroleum ether (b.p. = 30 – 60 °C). **¹H NMR (400 MHz, CDCl₃):** δ 6.27 (t, *J* = 4.0 Hz, 1H), 2.31 (td, *J*₁ = 7.1 Hz, *J*₂ = 2.0 Hz, 2H), 1.58 – 1.51 (m, 2H), 1.42 – 1.34 (m, 2H),

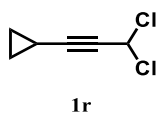
1.33 – 1.26 (m, 4H), 0.90 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 92.51, 76.34, 56.05, 31.20, 28.45, 27.79, 22.47, 18.85, 13.99. HRMS (EI): m/z calculated for $\text{C}_7\text{H}_9\text{Cl}_2$ $[\text{M}-\text{C}_2\text{H}_5]^+$: 163.0076, found: 163.0087. IR (KBr): 2956, 2930, 2860, 2322, 2238, 1752, 1690, 1466, 1458, 1428, 1380, 1328, 1252, 1198, 1158, 1030, 958, 814, 780, 718, 684.



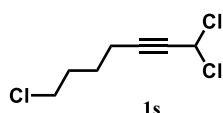
Prepared according to the general procedure **B** using corresponding aldehyde (3.4 g, 25.0 mmol). The product **1p** was isolated in 85% yield (4.06 g) by column chromatography as pale yellow oil. **Eluent**: petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ 6.28 (d, $J = 1.8$ Hz, 1H), 2.54 – 2.49 (m, 1H), 1.83 – 1.78 (m, 2H), 1.73 – 1.66 (m, 2H), 1.52 – 1.44 (m, 3H), 1.36 – 1.30 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 96.00, 76.53, 56.13, 31.73, 29.03, 25.68, 24.60. HRMS (EI): m/z calculated for $\text{C}_9\text{H}_{12}\text{Cl}_2$ $[\text{M}]^+$: 190.0311, found: 190.0306. IR (KBr): 2934, 2856, 2234, 1449, 1252, 1197, 1165, 888, 864, 722, 688.



Prepared according to the general procedure **B** using corresponding aldehyde (2.3 g, 20.9 mmol). The product **1q** was isolated in 34% yield (1.18 g) by column chromatography as colorless oil. **Eluent**: petroleum ether (b.p. = 30 – 60 °C). ^1H NMR (400 MHz, CDCl_3): δ 6.26 (s, 1H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 99.66, 75.18, 56.10, 30.20, 27.65. HRMS (EI): m/z calculated for $\text{C}_6\text{H}_7\text{Cl}_2$ $[\text{M}-\text{CH}_3]^+$: 148.9919, found: 148.9918. IR (KBr): 2973, 2931, 1701, 1368, 1270, 1210, 841, 819, 728, 698.

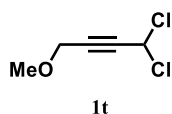


Prepared according to the general procedure **A** using corresponding aldehyde (0.33 g, 3.5 mmol). The product **1r** was isolated in 55% yield (0.29 g) by column chromatography as colorless oil. **Eluent**: petroleum ether (b.p. = 30 – 60 °C). ^1H NMR (400 MHz, CDCl_3): δ 6.24 (d, $J = 1.7$ Hz, 1H), 1.40 – 1.33 (m, 1H), 0.91 – 0.85 (m, 2H), 0.83 – 0.78 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 95.76, 71.66, 56.58, 9.13, 0.00. HRMS (EI): m/z calculated for $\text{C}_6\text{H}_6\text{Cl}_2$ $[\text{M}]^+$: 147.9841, found: 147.9843. IR (KBr): 2238, 1428, 1361, 1257, 1196, 1165, 1056, 1032, 889, 814, 794, 720, 678.

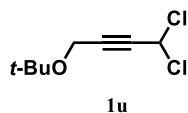


Prepared according to the general procedure **B** using corresponding aldehyde (2.23 g, 15.4 mmol). The product **1s** was isolated in 52% yield (1.60 g) by column chromatography as colorless oil. **Eluent**: petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ 6.26 (t, $J = 2.0$ Hz, 1H), 3.58 (t, $J = 6.4$ Hz, 2H), 2.39 (td, $J_1 = 7.0$ Hz, $J_2 = 1.9$ Hz, 2H), 1.93 – 1.86 (m, 2H), 1.76 – 1.69 (m, 2H).

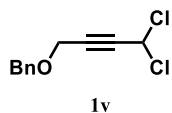
¹³C NMR (100 MHz, CDCl₃): δ 91.26, 76.94, 55.83, 44.29, 31.39, 25.03, 18.19. **HRMS (EI):** m/z calculated for C₇H₉Cl₂ [M-Cl]⁺: 163.0076, found: 163.0076. **IR (KBr):** 2957, 2869, 2323, 2239, 1455, 1431, 1255, 1198, 1160, 976, 812, 723, 684.



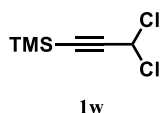
Prepared according to the general procedure **A** using corresponding aldehyde (3.2 g, 32.6 mmol). The product **1t** was isolated in 37% yield (1.87 g) by column chromatography as pale yellow oil. **Eluent:** petroleum ether (b.p. = 30 – 60 °C) /diethyl ether = 90:10. **¹H NMR (400 MHz, CDCl₃):** δ 6.30 (t, *J* = 1.7 Hz, 1H), 4.22 (d, *J* = 1.7 Hz, 2H), 3.41 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 86.29, 81.61, 59.56, 58.00, 55.05. **HRMS (EI):** m/z calculated for C₅H₅Cl₂O [M-H]⁺: 150.9712, found: 150.9713. **IR (KBr):** 2238, 1718, 1340, 1308, 1254, 1198, 1148, 1094, 993, 810, 737, 697.



Prepared according to the general procedure **A** using corresponding aldehyde (1.95 g, 13.9 mmol). The product **1u** was isolated in 84% yield (2.27 g) by column chromatography as pale yellow oil. **Eluent:** ethyl acetate /petroleum ether = 2:98. **¹H NMR (400 MHz, CDCl₃):** δ 6.29 (t, *J* = 1.7 Hz, 1H), 4.20 (d, *J* = 1.6 Hz, 2H), 1.25 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ 88.56, 79.90, 74.96, 55.39, 50.39, 27.45. **HRMS (EI):** m/z calculated for C₇H₉Cl₂O[M-CH₃]⁺: 179.0025, found: 179.0026. **IR (KBr):** 2978, 2230, 1602, 1472, 1393, 1368, 1253, 1191, 1148, 1067, 887, 843, 730.

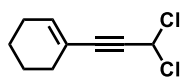


Prepared according to the general procedure **B** using corresponding aldehyde (2.24 g, 12.9 mmol). The product **1v** was isolated in 56% yield (1.64 g) by column chromatography as yellow oil. **Eluent:** diethyl ether /petroleum ether = 2:98. **¹H NMR (400 MHz, CDCl₃):** δ 7.39 – 7.30 (m, 5H), 6.30 (t, *J* = 1.7 Hz, 1H), 4.61 (s, 2H), 4.28 (d, *J* = 1.7 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 136.87, 128.54, 128.18, 128.11, 86.46, 81.69, 72.04, 56.96, 55.09. **HRMS (EI):** m/z calculated for C₁₁H₉Cl₂O[M-H]⁺: 227.0025, found: 227.0029. **IR (KBr):** 3032, 2982, 2859, 2229, 1496, 1455, 1354, 1253, 1199, 1161, 1144, 1074, 1028, 940, 807, 730, 698.



Prepared according to the general procedure **A** using corresponding aldehyde (1.4 g, 11.1 mmol). The product **1w** was isolated in 50% yield (1.00 g) by column chromatography as colorless oil. **Eluent:** ethyl acetate /petroleum ether (b.p. = 30 – 60 °C) = 1:99. **¹H NMR (400 MHz, CDCl₃):** δ 6.22 (s, 1H), 0.22 (s, 9H). **¹³C NMR (100 MHz, CDCl₃):** δ 99.44, 96.75, 55.69, 0.00. **HRMS (EI):** m/z calculated for C₅H₇Cl₂Si [M-CH₃]⁺: 164.9689, found: 164.9691. **IR (KBr):**

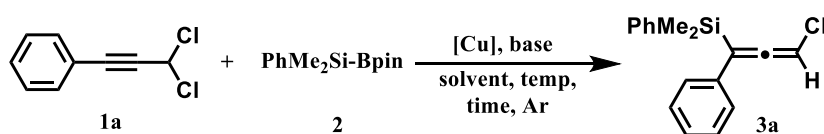
2925, 2854, 2228, 1911, 1458, 1376, 1252, 1114, 846, 731, 699.



1x

Prepared according to the general procedure **B** using corresponding aldehyde (1.61 g, 12.0 mmol). The product **1x** was isolated in 84% yield (1.91 g) by column chromatography as yellow oil. **Eluent:** petroleum ether (b.p. = 30 – 60 °C). **¹H NMR (400 MHz, CDCl₃):** δ 6.39 (s, 1H), 6.27 (p, *J* = 1.9 Hz, 1H), 2.15 – 2.11 (m, 4H), 1.68 – 1.56 (m, 4H). **¹³C NMR (100 MHz, CDCl₃):** δ 138.81, 118.91, 92.01, 81.79, 56.35, 28.33, 25.74, 21.99, 21.22. **HRMS (EI):** *m/z* calculated for C₉H₁₀Cl₂[M]⁺: 188.0154, found: 188.0150. **IR (KBr):** 2936, 2861, 2222, 1628, 1449, 1435, 1274, 1224, 1195, 1137, 1078, 1049, 1005, 931, 919, 848, 799, 729, 685.

3 Optimization of the Reaction Conditions of Racemic Silyl-substituted Allenes.

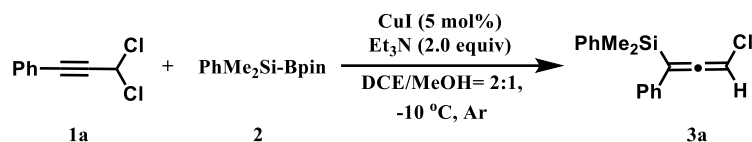


entry	cat. (mol%)	base (equiv)	solvent (mL)	temp (°C)	time (h)	yield (%)
1	CuTc (10)	NaOMe (4.0)	DCE	-30	36	0
2	CuTc (10)	NaOMe (2.0)	DCE	-30	36	54
3	CuTc (10)	NaOMe (2.0)	DCE	-10	36	60
4	CuTc (10)	NaOMe (2.0)	DCE	rt	36	6
5	CuTc (10)	NaOMe (2.0)	MeOH	-10	36	62
6	CuTc (10)	Et ₃ N (2.0)	MeOH	-10	45	72
7	CuTc (10)	Et ₃ N (2.0)	DCE/MeOH= 2:1	-10	45	76
8	CuTc (10)	Et ₃ N (2.0)	<i>i</i> -PrOH	-10	24	23
9	CuTc (10)	Et ₃ N (2.0)	<i>t</i> -AmOH	-10	24	10
10	CuCl (10)	Et ₃ N (2.0)	DCE/MeOH= 2:1	-10	20	76
11	CuBr (10)	Et ₃ N (2.0)	DCE/MeOH= 2:1	-10	20	76
12	CuCN (10)	Et ₃ N (2.0)	DCE/MeOH= 2:1	-10	20	63
13	CuI (5)	Et ₃ N (2.0)	DCE/MeOH= 2:1	-10	2	79 ^c
14	--	Et ₃ N (2.0)	DCE/MeOH= 2:1	-10	2	--
15	CuI (5)	--	DCE/MeOH= 2:1	-10	2	--

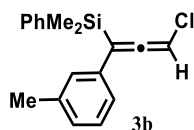
^aUnless noted otherwise, the reaction was conducted with **1a** (0.2 mmol), **2** (0.4 mmol, 2.0 equiv), copper catalyst (0.02 mmol, 10 mol %), and base (0.4 mmol, 2.0 equiv) in indicated dry solvent (1.5 mL) for corresponding time under argon atmosphere. ^bNMR yield with 1,3,5-trimethylbenzene as internal standard. ^cIsolated yield.

4. General Procedure for the Synthesis of Racemic Silyl-substituted Allenes. (GP2)

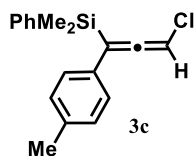
4.1 Procedures for Synthesis of Products 3a-3x.



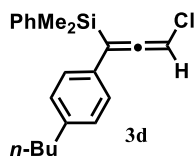
3a: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then removed it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1a** (37 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 2 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3a** (45.0 mg, 79%) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.60 – 7.57 (m, 2H), 7.41 – 7.34 (m, 3H), 7.25 – 7.17 (m, 5H), 6.20 (s, 1H), 0.52 (s, 3H), 0.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 209.13, 139.01, 137.11, 136.00, 131.65, 130.65, 130.46, 130.14, 129.67, 113.03, 89.62, 0.06, 0.00. HRMS (EI): m/z calculated for C₁₇H₁₇ClSi[M]⁺: 284.0783, found: 284.0798. IR (KBr): 3053, 3021, 2959, 1921, 1490, 1428, 1304, 1251, 1211, 1113, 917, 835, 814, 781, 743, 696, 646.



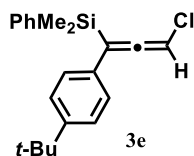
3b: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then removed it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1b** (39.8 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3b** (36.9 mg, 62%) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.60 – 7.57 (m, 2H), 7.39 – 7.35 (m, 3H), 7.13 – 7.07 (m, 2H), 7.02 – 6.99 (m, 2H), 6.18 (s, 1H), 2.26 (s, 3H), 0.52(s, 3H), 0.51(s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 208.98, 140.27, 139.09, 137.01, 136.00, 131.59, 131.14, 130.47, 130.45, 130.09, 127.51, 113.12, 89.46, 23.43, 0.07, 0.00. HRMS (EI): m/z calculated for C₁₈H₁₉ClSi[M]⁺: 298.0939, found: 298.0941. IR (KBr): 3050, 2959, 2924, 2868, 1924, 1602, 1487, 1458, 1428, 1296, 1248, 1112, 949, 822, 781, 730, 699, 648.



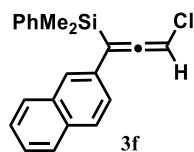
3c: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1c** (39.8 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 3 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3c** (42.9 mg, 72%) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.60 - 7.58 (m, 2H), 7.39 - 7.34 (m, 3H), 7.14 (d, *J* = 6.7 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 6.19 (s, 1H), 2.29 (s, 3H), 0.51 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 208.68, 139.50, 139.03, 135.87, 133.84, 131.46, 131.25, 130.27, 129.99, 112.65, 89.42, 23.09, 0.00, -0.07. HRMS (EI): *m/z* calculated for C₁₈H₁₉ClSi[M]⁺: 298.0939, found: 298.0951. IR (KBr): 3050, 3022, 2958, 2920, 1919, 1508, 1428, 1317, 1303, 1251, 1207, 1113, 908, 819, 780, 733, 701, 656.



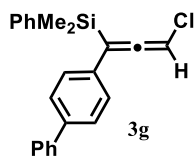
3d: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1d** (48.2 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3d** (51.4 mg, 75%) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.60 - 7.58 (m, 2H), 7.39 - 7.35 (m, 3H), 7.17 - 7.14 (m, 2H), 7.06 - 7.04 (m, 2H), 6.19 (s, 1H), 2.54 (t, *J* = 8.0 Hz, 2H), 1.58 - 1.52 (m, 3H), 1.36 - 1.27 (m, 2H), 0.89 (t, *J* = 7.9 Hz, 3H), 0.52 (s, 3H), 0.51 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 208.71, 144.53, 139.07, 135.87, 134.00, 131.43, 130.59, 130.25, 129.97, 112.71, 89.39, 37.23, 35.38, 24.26, 15.85, 0.00, -0.07. HRMS (EI): *m/z* calculated for C₂₁H₂₅ClSi[M]⁺: 340.1409, found: 340.1408. IR (KBr): 3050, 2957, 2929, 2858, 1919, 1507, 1457, 1428, 1310, 1251, 1213, 1113, 909, 835, 780, 734, 700, 658.



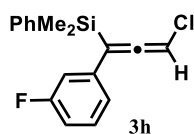
3e: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et_3N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to $-10\text{ }^\circ\text{C}$, **1e** (48.2 mg, 0.2 mmol, 1.0 equiv) and $\text{PhMe}_2\text{Si-Bpin}$ (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 3 hours at $-10\text{ }^\circ\text{C}$. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3e** (62.8 mg, 87%) as yellow oil. **$^1\text{H NMR}$ (400 MHz, CDCl_3)**: δ 7.61 - 7.59 (m, 2H), 7.39 - 7.34 (m, 3H), 7.27 - 7.25 (m, 2H), 7.20 - 7.18 (m, 2H), 6.19 (s, 1H), 1.27(s, 9H), 0.52 (s, 3H), 0.51(s, 3H). **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)**: δ 208.83, 152.68, 139.08, 135.84, 133.70, 131.41, 130.04, 129.96, 127.46, 112.47, 89.41, 36.45, 33.13, 0.00, -0.10 . **HRMS (EI)**: m/z calculated for $\text{C}_{21}\text{H}_{25}\text{ClSi}[\text{M}]^+$: 340.1409, found: 340.1412. **IR (KBr)**: 3051, 2962, 2920, 2851, 1918, 1508, 1428, 1364, 1252, 1112, 913, 835, 813, 780, 732, 701, 654.



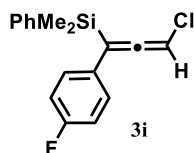
3f: A dried screw-vial seal tube was charged with CuI (3.8 mg, 0.01 mmol, 10 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et_3N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to $-10\text{ }^\circ\text{C}$, **1f** (47 mg, 0.2 mmol, 1.0 equiv) and $\text{PhMe}_2\text{Si-Bpin}$ (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at $-10\text{ }^\circ\text{C}$. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3f** (71.7 mg, 52%) as yellow oil. **$^1\text{H NMR}$ (400 MHz, CDCl_3)**: δ 7.70 - 7.77 (m, 2H), 7.59 - 7.66 (m, 4H), 7.35 - 7.45 (m, 6H), 6.27 (s, 1H), 0.58(s, 3H), 0.57(s, 3H). **$^{13}\text{C NMR}$ (100 MHz, CDCl_3)**: δ 209.48, 138.94, 135.95, 135.28, 134.65, 134.39, 131.61, 130.19, 130.10, 130.06, 129.54, 129.50, 128.39, 128.16, 113.12, 89.82, 0.07, 0.00. **HRMS (EI)**: m/z calculated for $\text{C}_{21}\text{H}_{19}\text{ClSi}[\text{M}]^+$: 334.0939, found: 334.0946. **IR (KBr)**: 3052, 2958, 2920, 2850, 1916, 1596, 1504, 1427, 1406, 1288, 1251, 1185, 1113, 961, 914, 820, 735, 701, 656.



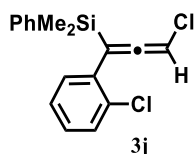
3g: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et_3N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to $-10\text{ }^\circ\text{C}$, **1g** (52.2 mg, 0.2 mmol, 1.0 equiv) and $\text{PhMe}_2\text{Si-Bpin}$ (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 3.5 hours at $-10\text{ }^\circ\text{C}$. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3g** (45.5 mg, 63%) as yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.63 – 7.60 (m, 2H), 7.55 – 7.52 (m, 2H), 7.48 – 7.46 (m, 2H), 7.40 – 7.38 (m, 6H), 7.33 – 7.30 (m, 2H), 6.24 (s, 1H), 0.55 (s, 3H), 0.54 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 209.14, 142.40, 142.36, 138.86, 135.88, 135.85, 131.56, 130.77, 130.72, 130.05, 129.35, 129.20, 128.88, 112.51, 89.65, 0.00, -0.09. HRMS (EI): m/z calculated for $\text{C}_{23}\text{H}_{21}\text{ClSi}[\text{M}]^+$: 360.1096, found: 360.1108. IR (KBr): 3051, 3028, 2958, 1918, 1600, 1485, 1447, 1427, 1404, 1317, 1251, 1213, 1136, 1111, 1007, 909, 837, 780, 734, 697, 659.



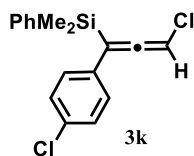
3h: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et_3N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to $-10\text{ }^\circ\text{C}$, **1h** (40.6 mg, 0.2 mmol, 1.0 equiv) and $\text{PhMe}_2\text{Si-Bpin}$ (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 3 hours at $-10\text{ }^\circ\text{C}$. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3h** (41.9 mg, 69%) as yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.58 – 7.56 (m, 2H), 7.41 – 7.36 (m, 3H), 7.21 – 7.16 (m, 1H), 6.99 – 6.87 (m, 3H), 6.22 (s, 1H), 0.52 (s, 3H), 0.51 (s, 3H). $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -112.77. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 207.41, 162.78 (d, $J = 244.8$ Hz), 137.45 (d, $J = 7.5$ Hz), 136.44, 133.87, 129.89 (d, $J = 8.3$ Hz), 129.72, 128.14, 124.04 (d, $J = 2.8$ Hz), 115.2, 115.0, 114.59, 114.38, 110.23, 87.80, -2.13, -2.22. HRMS (EI): m/z calculated for $\text{C}_{17}\text{H}_{16}\text{SiClF}[\text{M}]^+$: 302.0688, found: 302.0698. IR (KBr): 3053, 2960, 1927, 1608, 1583, 1483, 1428, 1315, 1241, 1113, 984, 874, 830, 785, 733, 701, 647.



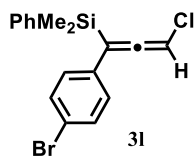
3i: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1i** (40.6 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3i** (46.6 mg, 77%) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.58 – 7.56 (m, 2H), 7.40 – 7.35 (m, 3H), 7.20 – 7.17 (m, 2H), 6.94 – 6.90 (m, 2H), 6.22 (s, 1H), 0.51 (s, 3H), 0.50 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ -114.16. ¹³C NMR (100 MHz, CDCl₃): δ 209.08 (d, *J* = 1.8 Hz), 164.4 (d, *J* = 246.2 Hz), 138.80, 136.05, 133.10 (d, *J* = 3.4 Hz), 132.15 (d, *J* = 8.1 Hz), 131.86, 130.31, 117.72 (d, *J* = 21.5 Hz), 112.17, 89.89, 0.07, 0.00. HRMS (EI): *m/z* calculated for C₁₇H₁₆SiClF[M]⁺: 302.0688, found: 302.0703. IR (KBr): 3069, 2959, 2922, 1922, 1598, 1505, 1428, 1312, 1252, 1232, 1159, 1113, 908, 837, 781, 734, 701, 657.



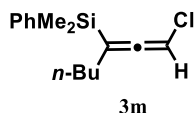
3j: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1j** (43.9 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 3.5 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3j** (31.1 mg, 49%) as colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.55 – 7.52 (m, 2H), 7.38 – 7.33 (m, 4H), 7.15 – 7.07 (m, 2H), 6.92 – 6.90 (m, 1H), 6.04 (s, 1H), 0.47 (s, 3H), 0.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 206.35, 136.26, 134.76, 133.98, 132.39, 129.82, 129.61, 129.46, 128.14, 127.90, 126.53, 108.78, 86.72, -2.74, -2.85. HRMS (EI): *m/z* calculated for C₁₇H₁₆SiCl₂[M]⁺: 318.0393, found: 318.0391. IR (KBr): 3068, 2958, 1921, 1489, 1428, 1312, 1252, 1208, 1113, 1011, 908, 830, 780, 733, 700.



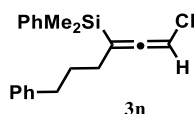
3k: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1k** (43.9 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3k** (38.4 mg, 60%) as yellow oil. **¹H NMR (400 MHz, CDCl₃):** δ 7.57 – 7.55 (m, 2H), 7.40 – 7.34 (m, 3H), 7.21 – 7.18 (m, 2H), 7.16 – 7.13 (m, 2H), 6.22 (s, 1H), 0.51 (s, 3H), 0.50 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 209.37, 138.71, 136.07, 135.74, 135.70, 131.92, 131.79, 130.95, 130.36, 112.22, 90.04, 0.08, 0.00. **HRMS (EI):** m/z calculated for C₁₇H₁₆SiCl₂[M]⁺: 318.0393, found: 318.0392. **IR (KBr):** 3069, 3051, 2958, 1922, 1589, 1488, 1428, 1312, 1252, 1209, 1113, 1092, 1014, 905, 830, 781, 732, 701, 653.



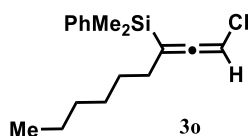
3l: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1l** (52.8 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3l** (37.8 mg, 52%) as yellow oil. **¹H NMR (400 MHz, CDCl₃):** δ 7.57 – 7.55 (m, 2H), 7.40 – 7.33 (m, 5H), 7.09 – 7.06 (m, 2H), 6.21 (s, 1H), 0.51 (s, 3H), 0.50 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 209.29, 138.61, 136.16, 135.99, 133.83, 132.02, 131.86, 130.29, 123.82, 112.21, 90.00, 0.00, -0.09. **HRMS (EI):** m/z calculated for C₁₇H₁₆SiClBr[M]⁺: 361.9888, found: 361.9901. **IR (KBr):** 3068, 3050, 2958, 1921, 1584, 1484, 1427, 1397, 1311, 1252, 1207, 1111, 1073, 1010, 906, 824, 736, 703, 652.



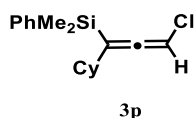
3m: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1m** (33 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3m** (39.8 mg, 75%) as slightly yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.53 – 7.51 (m, 2H), 7.39 – 7.35 (m, 3H), 5.91 (t, *J* = 2.4 Hz, 1H), 2.03 (tt, *J*₁ = 7.2 Hz, *J*₂ = 2.0 Hz, 2H), 1.40 (q, *J* = 7.4 Hz, 2H), 1.32 – 1.22 (m, 2H), 0.84 (t, *J* = 7.3 Hz), 0.42 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 203.67, 136.66, 133.85, 129.45, 127.90, 109.90, 86.70, 30.63, 29.64, 22.15, 13.84, -3.25, -3.35. HRMS (EI): *m/z* calculated for C₁₄H₁₈SiCl[M-CH₃]⁺: 249.0861, found: 249.0870. IR (KBr): 3069, 2959, 2930, 1932, 1465, 1428, 1304, 1250, 1113, 1017, 835, 817, 780, 734, 700.



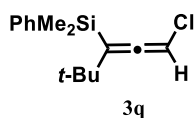
3n: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1n** (45 .4 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3n** (43 mg, 66%) as colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.54 – 7.50 (m, 2H), 7.39 - 7.35 (m, 3H), 7.24 – 7.22 (m, 2H), 7.18 – 7.15 (m, 1H), 7.11 – 7.09 (m, 2H), 5.96 – 5.93 (m, 1H), 2.62 – 2.50 (m, 2H), 2.10 – 2.06 (m, 2H), 1.80 – 1.72 (m, 2H), 0.43 (s, 3H), 0.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 203.74, 142.17, 136.54, 133.89, 129.55, 128.49, 128.31, 127.99, 125.76, 109.51, 87.05, 35.11, 30.22, 29.39, -3.25, -3.38. HRMS (EI): *m/z* calculated for C₂₀H₂₃SiCl[M]⁺: 326.1252, found: 326.1257. IR (KBr): 3067, 3025, 2934, 2857, 1931, 1603, 1496, 1454, 1428, 1303, 1250, 1112, 1066, 1030, 997, 815, 780, 745, 699, 647.



3o: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1o** (38.6 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3o** (44.7 mg, 76%) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.53 – 7.50 (m, 2H), 7.38 – 7.34 (m, 3H), 5.90 (t, *J* = 2.4 Hz, 1H), 2.02 (td, *J*₁ = 7.2 Hz, *J*₂ = 1.1 Hz, 2H), 1.44 – 1.38 (m, 2H), 1.28 – 1.18 (m, 6H), 0.85 (t, *J* = 6.7 Hz, 3H), 0.42 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 203.70, 136.68, 133.86, 129.46, 127.92, 109.92, 86.72, 31.62, 29.97, 28.75, 28.48, 22.60, 14.07, -3.23, -3.34. HRMS (EI): *m/z* calculated for C₁₇H₂₅SiCl[M]⁺: 292.1409, found: 292.1415. IR (KBr): 3070, 2958, 2928, 2857, 1933, 1428, 1305, 1250, 1113, 835, 816, 780, 733, 699.

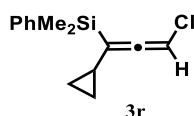


3p: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1p** (38.2 mg, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3p** (38.6 mg, 66%) as colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.54 – 7.51 (m, 2H), 7.40 – 7.33 (m, 3H), 5.91 (d, *J* = 1.4 Hz, 1H), 1.92 (t, *J* = 9.8 Hz, 1H), 1.71 – 1.66 (m, 4H), 1.59 (s, 1H), 1.22 – 1.08 (m, 5H), 0.42 (s, 3H), 0.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 203.93, 137.10, 133.85, 129.37, 127.86, 115.30, 87.11, 39.59, 33.57, 33.53, 26.40, 26.34, 25.93, -2.67, -2.76. HRMS (EI): *m/z* calculated for C₁₇H₂₃SiCl[M]⁺: 290.1252, found: 290.1264. IR (KBr): 3069, 2926, 2852, 1926, 1448, 1428, 1286, 1250, 1113, 1022, 977, 819, 759, 730, 700, 651.

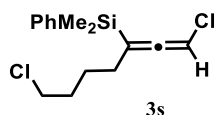


3q: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white

suspension. Then the tube was cooled to $-10\text{ }^{\circ}\text{C}$, **1q** (33.0 mg, 0.2 mmol, 1.0 equiv) and $\text{PhMe}_2\text{Si-Bpin}$ (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at $-10\text{ }^{\circ}\text{C}$. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3q** (33.3 mg, 63%) as yellow oil. **$^1\text{H NMR}$ (400 MHz, CDCl_3):** δ 7.55 – 7.53 (m, 2H), 7.36 – 7.33 (m, 3H), 5.89 (s, 1H), 1.03 (s, 9H), 0.49 (s, 3H), 0.47 (s, 3H). **$^{13}\text{C NMR}$ (100 MHz, CDCl_3):** δ 204.78, 138.94, 134.75, 130.05, 128.65, 120.69, 87.66, 37.20, 31.81, 0.22, 0.00. **HRMS (EI):** m/z calculated for $\text{C}_{14}\text{H}_{18}\text{SiCl}[\text{M}-\text{CH}_3]^+$: 249.0861, found: 249.0864. **IR** (KBr): 3069, 2964, 1933, 1428, 1363, 1292, 1113, 953, 837, 820, 777, 745, 701, 657.

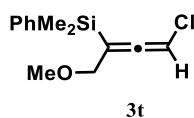


3r: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et_3N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to $-10\text{ }^{\circ}\text{C}$, **1r** (29.8 mg, 0.2 mmol, 1.0 equiv) and $\text{PhMe}_2\text{Si-Bpin}$ (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at $-10\text{ }^{\circ}\text{C}$. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3r** (34.1 mg, 69%) as colorless oil. **$^1\text{H NMR}$ (400 MHz, CDCl_3):** δ 7.58 – 7.55 (m, 2H), 7.40 – 7.36 (m, 3H), 5.93 (d, $J = 1.0\text{ Hz}$, 1H), 1.17 – 1.10 (m, 1H), 0.78 – 0.68 (m, 2H), 0.55 – 0.47 (m, 2H), 0.46 (s, 3H), 0.46 (s, 3H). **$^{13}\text{C NMR}$ (100 MHz, CDCl_3):** δ 201.24, 136.67, 133.95, 129.48, 127.90, 114.97, 87.98, 10.29, 9.55, 9.30, -3.02, -3.11. **HRMS (EI):** m/z calculated for $\text{C}_{14}\text{H}_{17}\text{SiCl}[\text{M}]^+$: 248.0783, found: 248.0791. **IR** (KBr): 3070, 3003, 2960, 2926, 1930, 1428, 1315, 1250, 1201, 1113, 999, 855, 833, 814, 779, 735, 700.

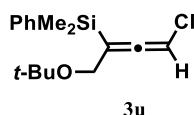


3s: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et_3N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to $-10\text{ }^{\circ}\text{C}$, **1s** (39.9 mg, 0.2 mmol, 1.0 equiv) and $\text{PhMe}_2\text{Si-Bpin}$ (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 3.5 hours at $-10\text{ }^{\circ}\text{C}$. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column

chromatography on silica gel (eluent: PE) to obtain the desired product **3s** (57.4 mg, 96%) as slightly yellow oil. **¹H NMR (400 MHz, CDCl₃):** δ 7.53 – 7.50 (m, 2H), 7.39 – 7.34 (m, 3H), 5.94 (t, *J* = 2.4 Hz, 1H), 3.45 (t, *J* = 6.6 Hz, 2H), 2.06 (td, *J*₁ = 7.2 Hz, *J*₂ = 2.4 Hz, 2H), 1.77 – 1.68 (m, 2H), 1.61 – 1.56 (m, 2H), 0.43 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 203.73, 136.37, 133.83, 129.59, 128.00, 109.29, 87.12, 44.75, 31.80, 29.09, 25.64, -3.31, -3.43. **HRMS (EI):** *m/z* calculated for C₁₄H₁₇SiCl₂[M-CH₃]⁺: 283.0471, found: 283.0480. **IR (KBr):** 3069, 2957, 1933, 1447, 1428, 1305, 1251, 1112, 997, 835, 816, 781, 735, 701, 649.

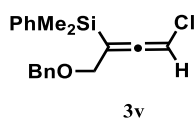


3t: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1t** (30.6 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 3.5 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE/Et₂O = 97:3) to obtain the desired product **3t** (41.5 mg, 82%) as colorless oil. **¹H NMR (400 MHz, CDCl₃):** δ 7.56 – 7.53 (m, 2H), 7.39 – 7.36 (m, 3H), 5.98 (t, *J* = 2.1 Hz, 1H), 4.04 – 3.96 (m, 2H), 3.25 (s, 3H), 0.46 (s, 6H). **¹³C NMR (100 MHz, CDCl₃):** δ 203.97, 136.13, 133.86, 129.57, 127.93, 107.38, 86.99, 71.15, 58.10, -3.08, -3.12. **HRMS (EI):** *m/z* calculated for C₁₃H₁₇SiClO[M]⁺: 252.0732, found: 252.0740. **IR (KBr):** 3069, 2925, 2821, 1940, 1912, 1428, 1369, 1311, 1250, 1192, 1113, 969, 910, 837, 818, 781, 734, 700.

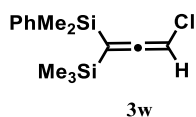


3u: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, and **1u** (39.0 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE/Et₂O = 98:2) to obtain the desired product **3u** (56.8 mg, 96%) as slightly yellow oil. **¹H NMR (400 MHz, CDCl₃):** δ 7.57 – 7.54 (m, 2H), 7.38 – 7.25 (m, 3H), 5.93 (t, *J* = 2.1 Hz, 1H), 4.01 (d, *J* = 2.1 Hz, 2H), 1.09 (s, 9H), 0.46 (s, 3H), 0.45 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 203.71, 136.73, 134.00, 129.34, 127.76,

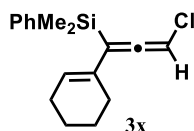
109.26, 86.67, 73.66, 61.43, 27.34, -2.62, -2.66. **HRMS (EI):** m/z calculated for $C_{15}H_{20}SiClO[M-CH_3]^+$: 279.0966, found: 279.0968. **IR (KBr):** 3070, 2974, 2933, 1940, 1428, 1389, 1363, 1304, 1249, 1194, 1114, 1076, 880, 837, 817, 781, 733, 700.



3v: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et_3N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to $-10\text{ }^\circ\text{C}$, and **1v** (45.8 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at $-10\text{ }^\circ\text{C}$. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE/ Et_2O = 98:2) to obtain the desired product **3v** (61.3 mg, 93%) as yellow oil. **¹H NMR (400 MHz, $CDCl_3$):** δ 7.55 – 7.52 (m, 2H), 7.39 – 7.32 (m, 4H), 7.31 – 7.27 (m, 2H), 7.24 – 7.22 (m, 2H), 5.99 (t, J = 2.0 Hz, 1H), 4.41 (q, J = 11.8 Hz, 2H), 4.16 – 4.08 (m, 2H), 0.46 (s, 6H). **¹³C NMR (100 MHz, $CDCl_3$):** δ 204.34, 137.81, 136.19, 133.91, 129.55, 128.33, 127.94, 127.85, 127.63, 107.42, 87.00, 72.09, 68.76, -2.98, -3.05. **HRMS (EI):** m/z calculated for $C_{19}H_{21}SiO[M-Cl]^+$: 293.1356, found: 293.1363. **IR (KBr):** 3067, 2958, 2852, 1940, 1911, 1455, 1428, 1350, 1304, 1250, 1113, 837, 817, 781, 734, 698.

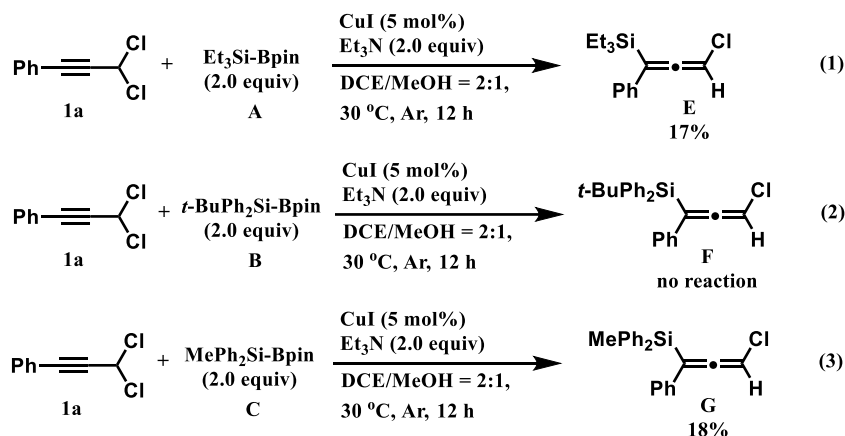


3w: A dried screw-vial seal tube was charged with CuI (3.8 mg, 0.01 mmol, 10 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et_3N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to $-10\text{ }^\circ\text{C}$, **1w** (36.2 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 3.5 hours at $-10\text{ }^\circ\text{C}$. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3w** (21.2 mg, 38%) as slightly yellow oil. **¹H NMR (400 MHz, $CDCl_3$):** δ 7.54 – 7.51 (m, 2H), 7.39 – 7.35 (m, 3H), 5.66 (s, 1H), 0.46 (s, 6H), 0.04 (s, 9H). **¹³C NMR (100 MHz, $CDCl_3$):** δ 209.09, 137.76, 134.19, 129.71, 128.14, 103.49, 81.16, 0.00, -1.42, -1.49. **HRMS (EI):** m/z calculated for $C_{14}H_{21}ClSi_2[M]^+$: 280.0865, found: 280.0879. **IR (KBr):** 3070, 2959, 1922, 1429, 1273, 1251, 1112, 883, 842, 807, 751, 732, 700.



3x: A dried screw-vial seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the tube was cooled to -10 °C, **1x** (37.8 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 3 hours at -10 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3x** (25.9 mg, 45%) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.55 – 7.52 (m, 2H), 7.38 – 7.34 (m, 3H), 6.03 (s, 1H), 5.70 (t, *J* = 3.6 Hz, 1H), 2.13 – 2.10 (m, 2H), 2.02 – 1.99 (m, 2H), 1.66 – 1.60 (m, 2H), 1.55 – 1.48 (m, 2H), 0.46 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 207.36, 139.25, 135.32, 133.78, 132.28, 130.76, 129.39, 114.53, 88.97, 29.59, 27.69, 24.25, 23.47, 0.00, -0.06. HRMS (EI): *m/z* calculated for C₁₇H₂₁SiCl[M]⁺: 288.1096, found: 288.1097. IR (KBr): 3068, 2931, 2858, 1909, 1709, 1585, 1428, 1311, 1250, 1188, 1113, 998, 838, 777, 731, 700, 652.

4.2 The results of reactions between different silylboronates with **1a**.



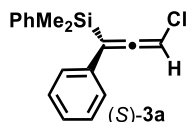
Procedures for the reaction between **1a** and silylboronate **A**:

E: A dried seal tube was charged with CuI (1.9 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, dry Et₃N (40.5 mg, 0.4 mmol, 2.0 equiv), dry DCE (1.0 mL) and dry MeOH (0.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then **1a** (37.0 mg, 0.2 mmol, 1.0 equiv) and Et₃Si-Bpin (96.9 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 12 hours at 30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30

was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (*S*)-**3c** (36.8 mg, 62%) as yellow oil.

$[\alpha]_{\text{D}}^{20} +208.9^{\circ}$ ($c = 1.19$, CH_2Cl_2)

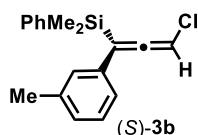
The enantiomeric excess of (*S*)-**3c** was determined by chiral HPLC analysis on Chiralcel OJ column. Conditions: hexane/isopropanol = 99:1, flow rate = 0.5 mL/min, UV-Vis detection at $\lambda = 273$ nm, $t_{\text{R}1} = 10.2$ min (minor), $t_{\text{R}2} = 16.1$ min (major), 20 °C, ee = 90%.



(*S*)-**3a**: A dried screw-vial seal tube was charged with CuF_2 (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol%) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1a** (37 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence via syringe. It was continued to stir for 4 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (*S*)-**3a** (33.2 mg, 56%) as yellow oil.

$[\alpha]_{\text{D}}^{20} +199.7^{\circ}$ ($c = 1.00$, CH_2Cl_2)

The enantiomeric excess of (*S*)-**3a** was determined by chiral HPLC analysis on Chiralcel OJ column. Conditions: hexane/isopropanol = 99:1, flow rate = 0.5 mL/min, UV-Vis detection at $\lambda = 273$ nm, $t_{\text{R}1} = 10.4$ min (minor), $t_{\text{R}2} = 14.3$ min (major), 20 °C, ee = 89%.

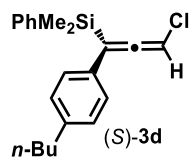


(*S*)-**3b**: A dried screw-vial seal tube was charged with CuF_2 (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol%) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1b** (39.8 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4.5 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (*S*)-**3b** (48.2 mg, 81%) as yellow oil.

$[\alpha]_{\text{D}}^{20} +92.8^{\circ}$ ($c = 1.19$, CH_2Cl_2)

The enantiomeric excess of (*S*)-**3b** was determined by chiral HPLC analysis on Chiralcel OD-H column. Conditions: hexane/isopropanol = 100:0, flow rate = 0.6 mL/min, UV-Vis

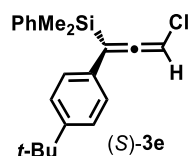
detection at $\lambda = 210$ nm, $t_{R1} = 13.3$ min (major), $t_{R2} = 22.4$ min (minor), 20 °C, ee = 91%.



(S)-**3d**: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol%) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1d** (48.2 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence via syringe. It was continued to stir for 7 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (S)-**3d** (35.4 mg, 52%) as yellow oil.

$[\alpha]_D^{20} +110.9^\circ$ (c = 1.02, CH₂Cl₂)

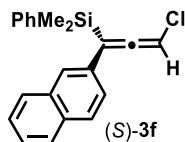
The enantiomeric excess of (S)-**3d** was determined by chiral HPLC analysis on Chiralcel OD-H column. Conditions: hexane/isopropanol = 100:0, flow rate = 0.6 mL/min, UV-Vis detection at $\lambda = 210$ nm, $t_{R1} = 12.1$ min (major), $t_{R2} = 15.3$ min (minor), 20 °C, ee = 88%.



(S)-**3e**: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1e** (48.2 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence via syringe. It was continued to stir for 15 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (S)-**3e** (47.7 mg, 70%) as yellow oil.

$[\alpha]_D^{20} +100.3^\circ$ (c = 1.06, CH₂Cl₂)

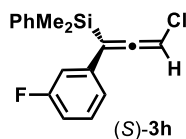
The enantiomeric excess of (S)-**3e** was determined by chiral HPLC analysis on Chiralcel OJ column. Conditions: hexane/isopropanol = 95:5, flow rate = 0.6 mL/min, UV-Vis detection at $\lambda = 210$ nm, $t_{R1} = 5.6$ min (minor), $t_{R2} = 6.9$ min (major), 20 °C, ee = 88%.



(S)-**3f**: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1f** (47.0 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence via syringe. It was continued to stir for 15 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (S)-**3f** (41.5 mg, 62%) as yellow oil.

[α]_D²⁰ +151.2° (c = 1.21, CH₂Cl₂)

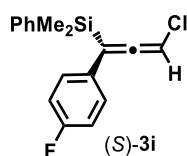
The enantiomeric excess of (S)-**3f** was determined by chiral HPLC analysis on Chiralcel OJ column. Conditions: hexane/isopropanol = 98:2, flow rate = 0.5 mL/min, UV-Vis detection at λ = 273 nm, t_{R1} = 13.6 min (minor), t_{R2} = 26.4 min (major), 20 °C, ee = 90%.



(S)-**3h**: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1h** (40.6 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence via syringe. It was continued to stir for 10 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (S)-**3h** (29 mg, 48%) as yellow oil.

[α]_D²⁰ +37.7° (c = 1.71, CH₂Cl₂)

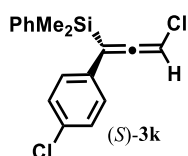
The enantiomeric excess of (S)-**3h** was determined by chiral HPLC analysis on Chiralcel OD-H column. Conditions: hexane/isopropanol = 100:0, flow rate = 0.6 mL/min, UV-Vis detection at λ = 210 nm, t_{R1} = 13.7 min (major), t_{R2} = 15.7 min (minor), 20 °C, ee = 86%.



(*S*)-**3i**: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1i** (40.6 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence via syringe. It was continued to stir for 4 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (*S*)-**3i** (33.3 mg, 55%) as yellow oil.

$[\alpha]_{\text{D}}^{20} +216.9^{\circ}$ (c = 1.06, CH₂Cl₂)

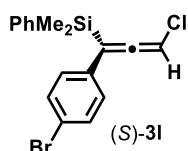
The enantiomeric excess of (*S*)-**3i** was determined by chiral HPLC analysis on Chiralcel OD-H column. Conditions: hexane/isopropanol = 100:0, flow rate = 0.6 mL/min, UV-Vis detection at $\lambda = 210$ nm, $t_{\text{R}1} = 11.3$ min (major), $t_{\text{R}2} = 13.0$ min (minor), 20 °C, ee = 86%.



(*S*)-**3k**: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1k** (43.9 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence via syringe. It was continued to stir for 4 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (*S*)-**3k** (42.4 mg, 66%) as yellow oil.

$[\alpha]_{\text{D}}^{20} +256.6^{\circ}$ (c = 1.10, CH₂Cl₂)

The enantiomeric excess of (*S*)-**3k** was determined by chiral HPLC analysis on Chiralcel OD-H column. Conditions: hexane/isopropanol = 100:0, flow rate = 0.6 mL/min, UV-Vis detection at $\lambda = 210$ nm, $t_{\text{R}1} = 12.5$ min (major), $t_{\text{R}2} = 14.3$ min (minor), 20 °C, ee = 86%.

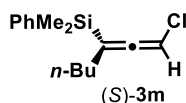


(*S*)-**3l**: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room

temperature to form a white solution. Then the tube was cooled to -30 °C, **11** (52.8 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 15 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (*S*)-**31** (45.3 mg, 62%) as yellow oil.

$[\alpha]_D^{20}$ -54.1° (c = 0.63, CH₂Cl₂)

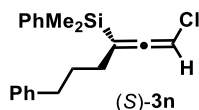
The enantiomeric excess of (*S*)-**31** was determined by chiral HPLC analysis on Chiralcel OJ column. Conditions: hexane/isopropanol = 95:5, flow rate = 0.6 mL/min, UV-Vis detection at λ = 273 nm, t_{R1} = 6.9 min (minor), t_{R2} = 9.5 min (major), 20 °C, ee = 84%.



(*S*)-**3m**: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L₅** (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1m** (33.0 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (*S*)-**3m** (45.9 mg, 87%) as slightly yellow oil.

$[\alpha]_D^{20}$ -32.9° (c = 0.78, CH₂Cl₂)

The enantiomeric excess of (*S*)-**3m** was determined by chiral HPLC analysis on Chiralcel OJ column. Conditions: hexane/isopropanol = 100:0, flow rate = 0.2 mL/min, UV-Vis detection at λ = 210 nm, t_{R1} = 21.0 min (major), t_{R2} = 23.0 min (minor), 20 °C, ee = 84%.

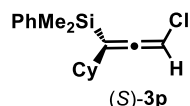


(*S*)-**3n**: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L₅** (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1n** (45.4 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE/Et₂O = 98:2) to obtain

the desired product (*S*)-**3n** (57.6 mg, 88%) as colorless oil.

$[\alpha]_{\text{D}}^{20} +6.5^{\circ}$ ($c = 1.49$, CH_2Cl_2)

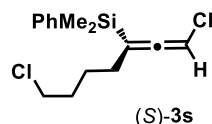
The enantiomeric excess of (*S*)-**3n** was determined by chiral HPLC analysis on Chiralcel OD-H column. Conditions: hexane/isopropanol = 100:0, flow rate = 0.3 mL/min, UV-Vis detection at $\lambda = 210$ nm, $t_{\text{R}1} = 44.1$ min (minor), $t_{\text{R}2} = 46.5$ min (major), 20 °C, ee = 80%.



(*S*)-**3p**: A dried screw-vial seal tube was charged with CuF_2 (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, and **1p** (38.2 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence via syringe. It was continued to stir for 4 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product (*S*)-**3p** (51.7 mg, 89%) as slightly yellow oil.

$[\alpha]_{\text{D}}^{20} +17.3^{\circ}$ ($c = 1.10$, CH_2Cl_2)

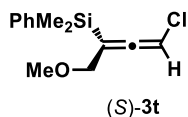
The enantiomeric excess of (*S*)-**3p** was determined by chiral HPLC analysis on Chiralcel OD-H column. Conditions: hexane/isopropanol = 99:1, flow rate = 0.5 mL/min, UV-Vis detection at $\lambda = 210$ nm, $t_{\text{R}1} = 6.5$ min (minor), $t_{\text{R}2} = 6.9$ min (major), 20 °C, ee = 80%.



(*S*)-**3s**: A dried screw-vial seal tube was charged with CuF_2 (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1s** (39.9 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence via syringe. It was continued to stir for 4 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH_2Cl_2 (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE/Et₂O = 98:2) to obtain the desired product (*S*)-**3s** (40.8 mg, 68%) as colorless oil.

$[\alpha]_{\text{D}}^{20} -11.2^{\circ}$ ($c = 1.35$, CH_2Cl_2)

The enantiomeric excess of (*S*)-**3s** was determined by chiral HPLC analysis on Chiralcel OJ column. Conditions: hexane/isopropanol = 95:5, flow rate = 0.7 mL/min, UV-Vis detection at $\lambda = 210$ nm, $t_{\text{R}1} = 6.2$ min (minor), $t_{\text{R}2} = 12.0$ min (major), 20 °C, ee = 83%.

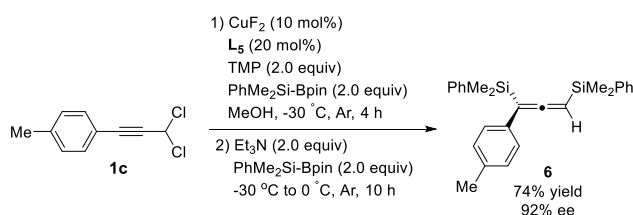


(S)-**3t**: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol, 10 mol %) and ligand **L**₅ (19.5 mg, 0.04 mmol, 20 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol, 2.0 equiv) and extra dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white solution. Then the tube was cooled to -30 °C, **1t** (30.6 mg, 0.2 mmol, 1.0 equiv) and PhMe₂Si-Bpin (105 mg, 0.4 mmol, 2.0 equiv) were added in sequence *via* syringe. It was continued to stir for 4 hours at -30 °C. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE/Et₂O = 99:1) to obtain the desired product (S)-**3t** (44.5 mg, 88%) as slightly yellow oil.

[α]_D²⁰ -29.8° (c = 0.99, CH₂Cl₂)

The enantiomeric excess of (S)-**3t** was determined by chiral HPLC analysis on Chiralcel OJ column. Conditions: hexane/isopropanol = 95:5, flow rate = 0.7 mL/min, UV-Vis detection at λ = 210 nm, t_{R1} = 7.3 min (minor), t_{R2} = 8.7 min (major), 20 °C, ee = 70%.

6 General Procedures for the One-pot Synthesis of Enantioenriched Disilyl-substituted Allenes.



6: A dried screw-vial seal tube was charged with CuF₂ (2.0 mg, 0.02 mmol) and ligand **L**₅ (19.5 mg, 0.04 mmol) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, TMP (56.5 mg, 0.4 mmol) and dry MeOH (1.0 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form an off-white solution. Then the tube was cooled to -30 °C, **1c** (39.8 mg, 0.2 mmol) and PhMe₂Si-Bpin (105 mg, 0.4 mmol) were added in sequence *via* syringe. It was continued to stir for 4 hours at -30 °C, the final yellow solution was added dry Et₃N (40.5 mg, 0.4 mmol). It was continued to stir for 20 minutes at -30 °C, PhMe₂Si-Bpin (105 mg, 0.4 mmol) was added dropwise *via* syringe. The system was warmed to 0 °C, and stirred 10 hours at this temperature. The tube was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **6** (59 mg, 74 %) as yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.57 – 7.54 (m, 4H), 7.38 – 7.33 (m, 6H), 7.11 -7.09 (m, 2H), 7.02 – 7.00 (m, 2H), 5.09 (s, 1H), 2.28 (s, 1H), 0.44 (s, 3H), 0.43 (s, 6H), 0.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 213.67, 140.40, 140.22, 137.10, 135.88, 135.61, 135.43, 131.03, 130.96, 130.88, 129.66, 129.33, 91.07, 78.04, 22.85, 0.36, 0.26, 0.01, 0.00. HRMS (EI): m/z calculated for

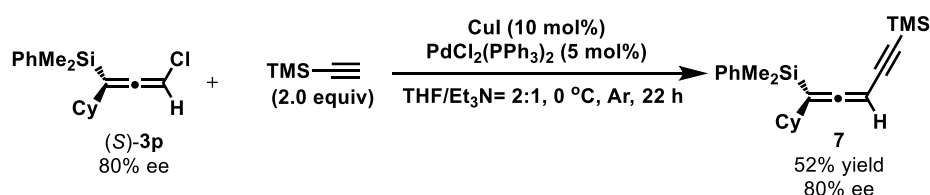
$C_{26}H_{30}Si_2[M]^+$: 398.1881, found: 398.1894. **IR** (KBr): 2957, 1901, 1508, 1428, 1304, 1251, 1115, 914, 829, 730, 699, 656.

$[\alpha]_D^{20} +54.0^\circ$ ($c = 0.80$, CH_2Cl_2)

The enantiomeric excess of **6** was determined by chiral HPLC analysis on Chiralcel OJ column. Conditions: hexane/isopropanol = 97:3, flow rate = 0.1 mL/min, UV-Vis detection at $\lambda = 214$ nm, $t_{R1} = 33.7$ min (major), $t_{R2} = 47.1$ min (minor), 20 °C, ee = 92%.

7 Further Transformations of Silyl-substituted Chloroallenes.

7.1 General Procedure for Sonogashira Coupling Reaction.

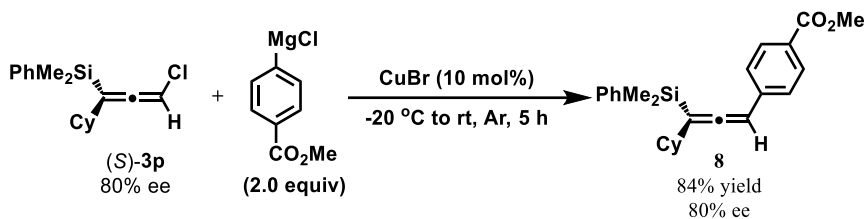


7: A dried screw-vial seal tube was charged with CuI (3.8 mg, 0.02 mmol, 10 mol %) and PdCl₂(PPh₃)₂ (7.0 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, (S)-**3p** (58.2mg, 0.2 mmol, 1.0 equiv), a dried and degassed mixture of THF (2.0 mL) and Et₃N (1.0 mL) were added into it. The atmosphere of the tube was displaced by argon for 20 minutes, then it was cooled to 0 °C for 10 minutes, trimethylsilylacetylene (39.3 mg, 0.4 mmol, 2.0 equiv) was introduced dropwise via syringe. The reaction mixture was stirred for 22 hours at 0 °C under dark environment. The tube was opened quickly at room temperature, the final black solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **7** (36.7 mg, 52%) as brown oil. **¹H NMR (400 MHz, CDCl₃)**: δ 7.56 – 7.53 (m, 2H), 7.37 – 7.33 (m, 3H), 5.14 (d, $J = 1.9$ Hz, 1H), 1.87 – 1.83 (m, 1H), 1.72 – 1.66 (m, 4H), 1.58 – 1.56 (m, 1H), 1.19 – 1.10 (m, 5H), 0.42 (s, 3H), 0.41 (s, 3H), 0.19. **¹³C NMR (100 MHz, CDCl₃)**: δ 212.52, 137.64, 133.71, 129.06, 127.62, 103.30, 99.38, 94.01, 71.50, 38.99, 33.63, 33.60, 26.35, 26.30, 25.81, 0.00, -2.46, -2.79. **HRMS (EI)**: m/z calculated for $C_{22}H_{32}Si_2[M]^+$: 352.2037, found: 352.2036. **IR** (KBr): 3069, 2927, 2852, 2153, 1913, 1428, 1370, 1112, 1062, 999, 842, 733, 700.

$[\alpha]_D^{20} +2560.0^\circ$ ($c = 0.20$, CH_2Cl_2)

The enantiomeric excess of **7** was determined by chiral HPLC analysis on Chiralcel OD-H&OD-H column. Conditions: hexane/isopropanol = 100:0, flow rate = 0.2 mL/min, UV-Vis detection at $\lambda = 260$ nm, $t_{R1} = 48.3$ min (major), $t_{R2} = 50.1$ min (minor), 20 °C, ee = 80%.

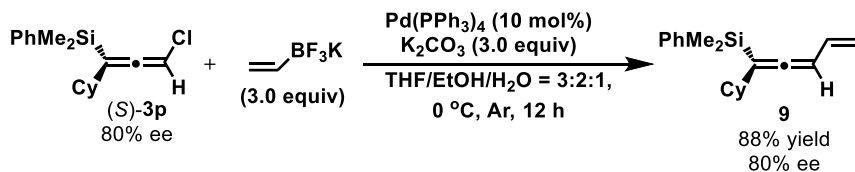
7.2 General Procedure for Kumada Reaction.⁴



8: An oven-dried, argon-flushed Schlenk tube equipped with a magnetic stirring bar and a septum was charged with methyl 4-iodobenzoate (157.2 mg, 0.6 mmol) in THF (0.6 mL). *i*-PrMgCl LiCl (0.49 mL, 0.64 mmol, 1.3 M in THF) was added at -20 °C and the mixture was stirred for 1 hour at this temperature. The CuBr (2.8 mg, 0.02 mmol, 10 mol%) and (S)-3p (58.2 mg, 0.2 mmol) were added quickly under argon atmosphere. The reaction mixture was stirred at room temperature (20 °C) until (S)-3p was consumed completely (TLC). The solution was diluted with DCM (10 mL), then poured into an ice-cooled saturated aqueous NH₄Cl solution (15 mL). After extraction with DCM (3 x 20 mL), the organic layers were dried (Na₂SO₄), filtered, and concentrated *in vacuo*. Product **8** was purified as yellow oil (65.7 mg, 84%) by flash column chromatography on silica gel (eluent: distilled PE/Et₂O = 100:0 ~ 96:4). **¹H NMR (400 MHz, CDCl₃):** δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.50 (m, 2H), 7.38 – 7.31 (m, 3H), 7.27 (d, *J* = 8.3 Hz, 2H), 5.98 (s, 1H), 3.89 (s, 3H), 1.98 – 1.93 (m, 1H), 1.80 – 1.73 (m, 2H), 1.67 – 1.63 (m, 2H), 1.60 – 1.54 (m, 1H), 1.21 – 1.07 (m, 5H), 0.42 (s, 3H), 0.40 (s, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 209.39, 169.46, 143.96, 140.18, 136.18, 132.39, 131.67, 130.23, 129.76, 127.82, 108.76, 93.40, 54.35, 42.03, 36.89, 36.52, 28.97, 28.36, 0.00, -0.03. **HRMS (ED):** *m/z* calculated for C₂₅H₃₀O₂Si [M]⁺: 390.2015, found: 390.2018. **IR (KBr):** 3069, 2925, 2851, 1911, 1720, 1605, 1434, 1276, 1173, 1111, 1017, 974, 817, 734, 699. $[\alpha]_D^{20} +801.1^\circ$ (*c* = 0.80, CH₂Cl₂)

The enantiomeric excess of **8** was determined by chiral HPLC analysis on Chiralcel OD-H column. Conditions: hexane/isopropanol = 98:2, flow rate = 0.6 mL/min, UV-Vis detection at λ = 260 nm, *t*_{R1} = 7.2 min (major), *t*_{R2} = 7.8 min (minor), 20 °C, ee = 80%.

7.3 General Procedure for Suzuki Coupling Reaction.



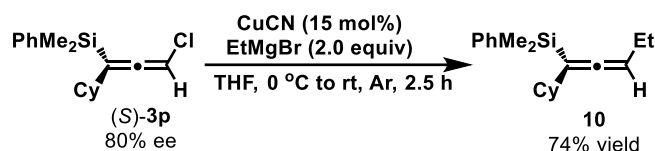
9: A dried argon-flushed Schlenk tube was charged with K₂CO₃ (83 mg, 0.6 mmol, 3.0 equiv), potassium vinyltrifluoroborate (107.2 mg, 0.6 mmol, 3.0 equiv) and Pd(PPh₃)₄ (23.1 mg, 0.02 mmol, 10 mol %) under Ar. Then a degassed mixture of THF (1.2 mL), EtOH (0.8 mL) and H₂O (0.4 mL) was added into it under Ar. The tube was cooled to 0 °C for 5 minutes, (S)-3p (58.2 mg, 0.2 mmol, 1.0 equiv) was introduced under Ar. The Schlenk tube was sealed and the reaction mixture was stirred at 0 °C for 12 hours under dark environment. The final black solution was quenched by water (5 mL) and the aqueous phase was extracted with CH₂Cl₂ (3 x 15 mL). The combined organic phases were dried over Na₂SO₄, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: PE). Product **9** was obtained as yellow oil (49.7 mg, 88%). **¹H NMR (400 MHz, CDCl₃):** δ 7.54 – 7.52 (m,

2H), 7.36 – 7.33 (m, 3H), 6.21 – 6.12 (m, 1H), 5.67 (d, $J = 10.3$ Hz, 1H), 5.09 (d, $J = 17.0$ Hz, 1H), 4.82 (d, $J = 10.1$ Hz, 1H), 1.83 – 1.79 (m, 1H), 1.68 – 1.64 (m, 4H), 1.58 (s, 1H), 1.17 – 1.07 (m, 5H), 0.37 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 211.41, 140.75, 136.46, 136.17, 131.41, 130.09, 114.81, 105.28, 93.75, 41.33, 36.51, 36.33, 28.96, 28.94, 28.40, 0.00, -0.05. **HRMS (EI)**: m/z calculated for $\text{C}_{19}\text{H}_{26}\text{Si}$ $[\text{M}]^+$: 282.1798, found: 282.1810. **IR** (KBr): 3069, 2925, 2852, 1913, 1612, 1448, 1428, 1248, 1112, 1028, 986, 888, 851, 818, 774, 731, 699, 650.

$[\alpha]_{\text{D}}^{20}$ -113.6° ($c = 1.00$, CH_2Cl_2)

The enantiomeric excess of **9** was determined by chiral HPLC analysis on Chiralcel OJ-H&OJ column. Conditions: hexane/isopropanol = 98:2, flow rate = 0.5 mL/min, UV-Vis detection at $\lambda = 260$ nm, $t_{\text{R}1} = 16.1$ min (major), $t_{\text{R}2} = 16.8$ min (minor), 20 °C, ee = 80%.

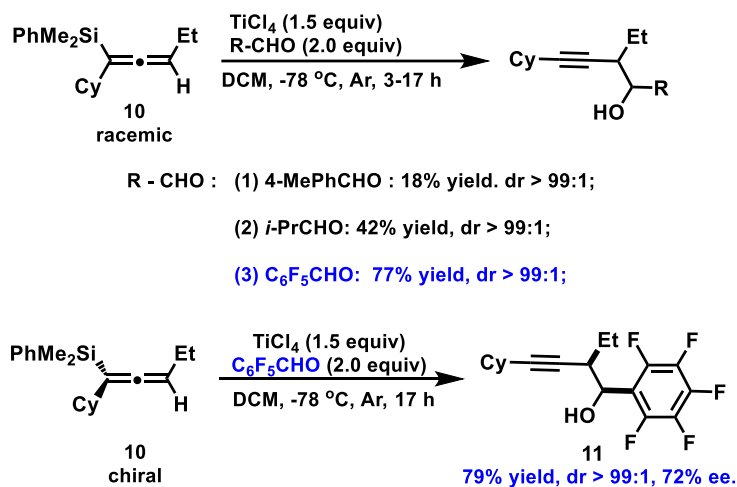
7.4 Copper-catalyzed Derivation Reactions of Chloroallenes.⁵



10: A dried screw-vial seal tube was charged with CuCN (1.4 mg, 0.015 mmol, 15 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, (*S*)-**3p** (29.1 mg, 0.1 mmol, 1.0 equiv) and dry THF (1.0 mL) were added into it. It was cooled to 0 °C for further 5 minutes, the Ethylmagnesiumbromide (3.0 M in Et₂O, 67 μL, 0.2 mmol, 2.0 equiv) was added dropwise *via* syringe. The reaction mixture was allowed to warm back to room temperature and stir for 2.5 hours. The reaction mixture was quenched by saturated aqueous NH₄Cl solution and the aqueous phase was extracted with Et₂O (3 x 15 mL). The combined organic phases were dried over Na₂SO₄, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: PE/Et₂O = 99.5:0.5). Product **10** was obtained as colorless oil (21.1 mg, 74%). ^1H NMR (400 MHz, CDCl_3): δ 7.54 – 7.52 (m, 2H), 7.35 – 7.32 (m, 3H), 4.95 (td, $J_1 = 6.0$ Hz, $J_2 = 1.6$ Hz, 1H), 2.00 – 1.93 (m, 2H), 1.78 – 1.73 (m, 1H), 1.66 – 1.64 (m, 4H), 1.59 – 1.57 (m, 1H), 1.17 – 1.06 (m, 5H), 0.98 (t, $J = 7.4$ Hz, 3H), 0.34 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 208.61, 141.41, 136.14, 131.07, 129.87, 104.02, 91.04, 40.85, 36.46, 36.25, 28.99, 28.97, 28.43, 23.80, 16.10, 0.00, -0.01. **HRMS (EI)**: m/z calculated for $\text{C}_{19}\text{H}_{28}\text{Si}$ $[\text{M}]^+$: 284.1955, found: 284.1953. **IR** (KBr): 2925, 2853, 1913, 1448, 1260, 1112, 1023, 888, 818, 776, 732, 700.

The product **10** can't be separated by HPLC, the subsequent TiCl₄-mediated addition of **10** to aldehyde afforded the homopropargylic alcohol. At beginning, we tried the 4-methylbenzaldehyde and isobutyraldehyde to react with the racemic allenylsilane **10** in the presence of different Lewis acids. Finally, it was found that only TiCl₄ could afford the desired products with excellent dr ratios albeit in low yields. Therefore, we consider that a highly reactive reactant possibly could favor a better yield of the desired product *via* a rapid nucleophilic addition process. Then the pentafluorobenzaldehyde was tested to react with the racemic allenylsilane **10** and enantioenriched allenylsilane **10** respectively. In both cases, the desired products were obtained in good yields and with excellent distereoselectivities. And

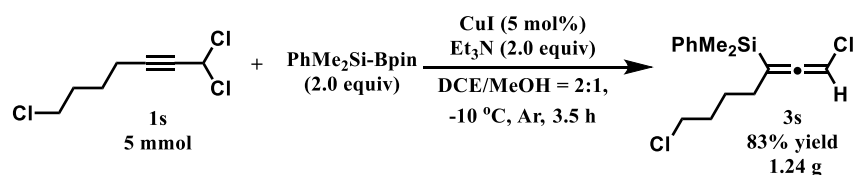
the chirality of the enantioenriched allenylsilane **10** was also well transformed during the synthesis of homoallylic alcohol product **11**. The detailed results are shown as below:



11: A dried argon-flushed Schlenk tube was charged with **10** (42.7 mg, 0.15 mmol), 2,3,4,5,6-pentafluorobenzaldehyde (58.8 mg, 0.3 mmol). It was added dry DCM (0.5 mL) and cooled to -78 °C for further 5 minutes, TiCl₄ solution (43.1 mg, dissolved in 0.2 mL dry DCM) was added dropwise at -78 °C, the mixture was stirred for 17 hours at this temperature. Then the solution was diluted with EA and quenched by 2N HCl aq., After stirring at room temperature for 10 minutes, the mixture was neutralized to pH = 7 with NaHCO₃ aq., the organic layer was separated. The aqueous layer was extracted with EA (3 x 20 mL), the combined organic phases were dried over Na₂SO₄, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: PE/EA = 90:10). Product **11** was obtained as yellow oil (41.0 mg, 79%). ¹H NMR (400 MHz, CDCl₃): δ 4.91 (dd, *J*₁ = 8.0 Hz, *J*₂ = 8.0 Hz, 1H), 2.85 (dt, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 2.82 – 2.76 (m, 1H), 2.43 – 2.36 (m, 1H), 1.85 – 1.78 (m, 2H), 1.73 – 1.64 (m, 2H), 1.54 – 1.40 (m, 5H), 1.35 – 1.28 (m, 3H), 1.03 (t, *J* = 8.0 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃): -142.38 – -142.46 (m, 1F), -154.88 – -154.99 (m, 2F), -161.97 – -162.11 (m, 2F). ¹³C NMR (100 MHz, CDCl₃): δ 146.27 – 146.04 (m), 143.84 – 143.56 (m), 142.12 – 141.66 (m), 138.94 – 138.58 (m), 136.45 – 136.08 (m), 115.50 – 115.18 (m), 90.56, 77.32, 69.06, 41.61, 32.84, 29.08, 25.82, 25.01, 24.86, 11.69. **HRMS (EI):** *m/z* calculated for C₁₈H₁₉F₅O [M]⁺: 346.1356, found: 346.1359. **IR (KBr):** 2955, 2911, 2875, 1892, 1428, 1249, 1112, 1089, 1015, 896, 839, 806, 730, 699. $[\alpha]_D^{20} +3.0^\circ$ (c = 1.23, CH₂Cl₂)

The enantiomeric excess of **11** was determined by chiral HPLC analysis on Chiralcel OJ column. Conditions: hexane/isopropanol = 99:1, flow rate = 0.5 mL/min, UV-Vis detection at λ = 220 nm, *t*_{R1} = 7.3 min (major), *t*_{R2} = 7.9 min (minor), 20 °C, ee = 72%.

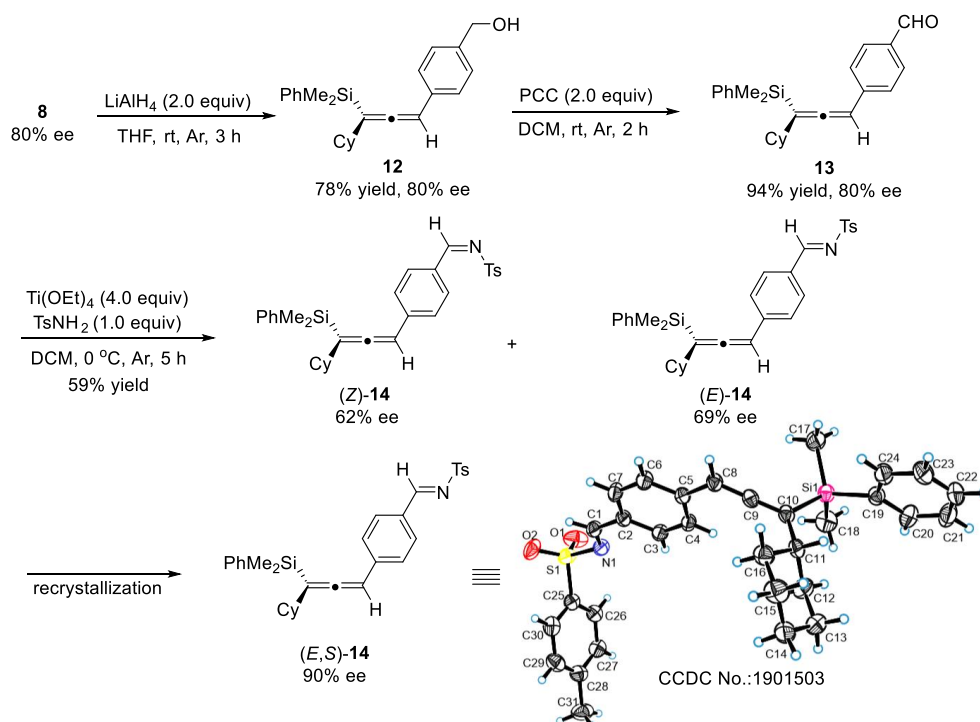
8 Gram-scaled Synthesis of Racemic Silyl-substituted Allenes.



A dried screw-vial flask was charged with CuI (47.5 mg, 0.25 mmol) in glove box, then

moved it out of the glove box. The flask was equipped with an argon balloon, dry Et₃N (1.0 g, 10.0 mmol), dry DCE (25.0 mL) and dry MeOH (12.5 mL) were added into it. The mixture was stirred for 1 hour at room temperature to form a white suspension. Then the flask was cooled to -10 °C, **1s** (1.0 g, 5.0 mmol) and PhMe₂Si-Bpin (2.63 g, 10.0 mmol) were added in sequence via syringe. It was continued to stir for 3.5 hours at -10 °C. The flask was opened quickly at room temperature, the final solution was filtered through celite using CH₂Cl₂ (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE) to obtain the desired product **3s** (1.24 g, 83%) as pale yellow oil.

9 Determination of the Absolute Configuration of Compound (*S*)-**3p**.



Step 1: In an oven-dried 35 mL screw-vial seal tube equipped with a stirring bar, **8** (78.1 mg, 0.2 mmol) was dissolved in 2 mL of dry THF under argon atmosphere. The solution was added LiAlH₄ (15.2 mg, 0.4 mmol) in four batches at 20 °C. The final solution was continued to stir for 3 hours at room temperature (20 °C). Then the reaction was quenched with water and excess amount of saturated potassium sodium tartrate was introduced, and the solution was stirred for 1 hour at room temperature (20 °C). The final solution was extracted with ethyl acetate (4 x 15 mL), and the combined organic layers were washed with saturated brine (5 mL) and dried over anhydrous Na₂SO₄. The filtrate was concentrated under vacuum to afford the crude product which was purified through flash column chromatography (Eluent: PE/EA = 90:10) to furnish the related product **12** (56.6 mg, 78%, 80% ee) as yellow oil.

Step 2: A dried screw-vial seal tube equipped with an argon balloon, **12** (72.5 mg, 0.2 mmol) and dry DCM (1.0 mL) were introduced. PCC (86.2 mg, 0.4 mmol) was added into it, the mixture was continued to stir for 2 hours at 25 °C. Then the final solution was filtered through celite using CH₂Cl₂ (30 mL) and the solvent was evaporated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent:

PE/EA = 90:10) to obtain the desired product **13** (67.5 mg, 94%, 80% ee) as yellow oil.

Step 3:⁶ A dried screw-vial seal tube equipped with an argon balloon was charged with 4-methylbenzenesulfonamide (59.9 mg, 0.35 mmol), **13** (126.3 mg, 0.35 mmol, dissolved in 1.8 mL dry DCM). It was cooled to 0 °C for further 10 minutes, Ti(OEt)₄ (319.4 mg, 1.4 mmol) was added dropwise via syringe. The tube was stirred for 5 hours at this temperature and monitored by TLC. The reaction mixture was quenched at 0 °C by addition of H₂O (6 mL), the turbid solution was filtered through celite, and the filter cake was washed with DCM (50 mL). The filtrate was concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography on silica gel (eluent: PE/EA = 90:10) to obtain the mixture of desired product (*Z*)-**14** (62% ee) and (*E*)-**14** (69% ee) as yellow solid (106.1 mg, 59%). After several recrystallization in mixed solvent (DCM/ PE = 1:1) at 5 °C, the single product (*E*)-**14** was obtained as white solid (90% ee). Finally, single-crystal X-ray diffraction analysis produced the molecular structure of (*E*)-**14** with (*S*)-configuration (CCDC No.:1901503). ¹H NMR (400 MHz, CDCl₃): δ 8.96 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 6.6 Hz, 2H), 7.36 – 7.25 (m, 7H), 5.98 (s, 1H), 2.42 (s, 3H), 2.00 – 1.91 (m, 1H), 1.79 – 1.73 (m, 2H), 1.69 – 1.62 (m, 2H), 1.59 – 1.56 (m, 1H), 1.22 – 1.09 (m, 5H), 0.42 (s, 3H), 0.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 209.60, 172.01, 146.90, 146.76, 139.88, 138.07, 136.16, 134.36, 132.29, 132.18, 131.83, 130.39, 130.31, 128.52, 109.09, 93.63, 42.15, 36.95, 36.59, 28.96, 28.35, 24.10, 0.00, -0.03. HRMS (ESI): *m/z* Calcd. for C₃₁H₃₅NO₂SSiNa [M+Na]⁺: 536.2055, found: 536.2058. IR (KBr): 2955, 2910, 2875, 1892, 1428, 1249, 1112, 896, 839, 806, 730, 699.

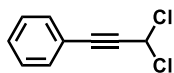
[α]_D²⁰ +80.6° (c = 0.46, CH₂Cl₂)

The enantiomeric excess of (*E, S*)-**14** was determined by chiral HPLC analysis on Chiralcel Chiralpak ID column. Conditions: hexane/isopropanol = 90:10, flow rate = 0.6 mL/min, UV-Vis detection at λ = 210 nm, t_{R1} = 41.0 min (minor), t_{R2} = 42.8 min (major), 20 °C, ee = 90%.

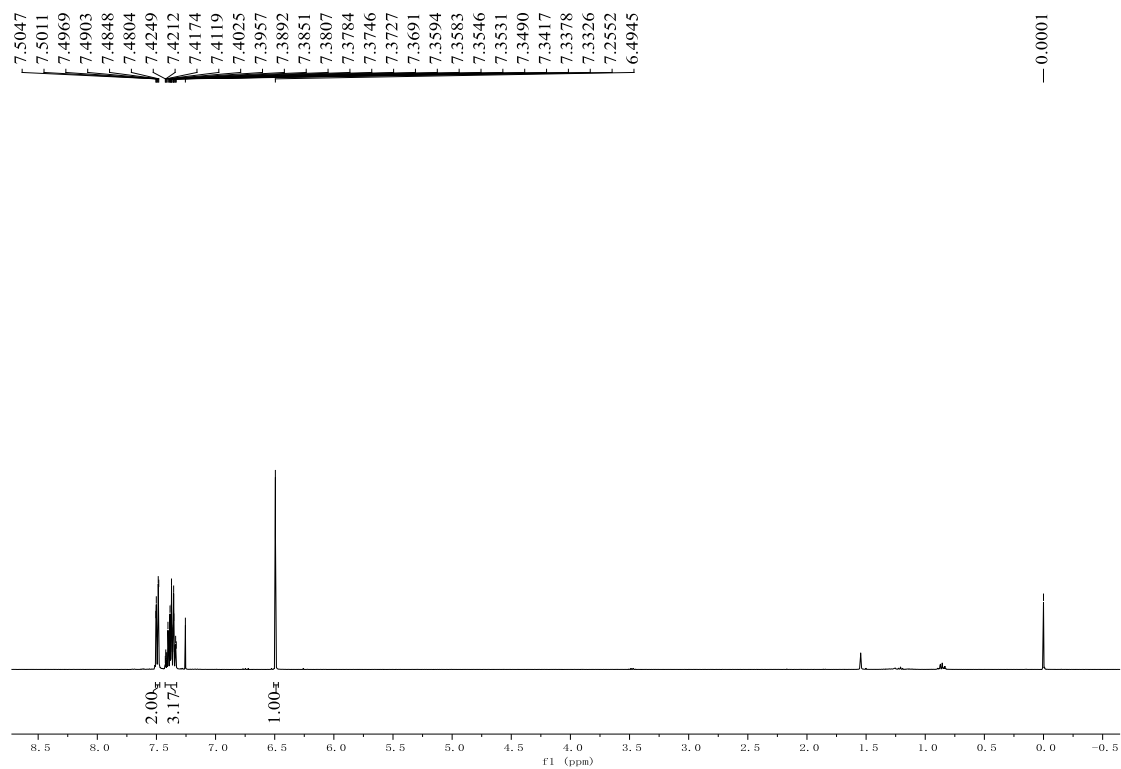
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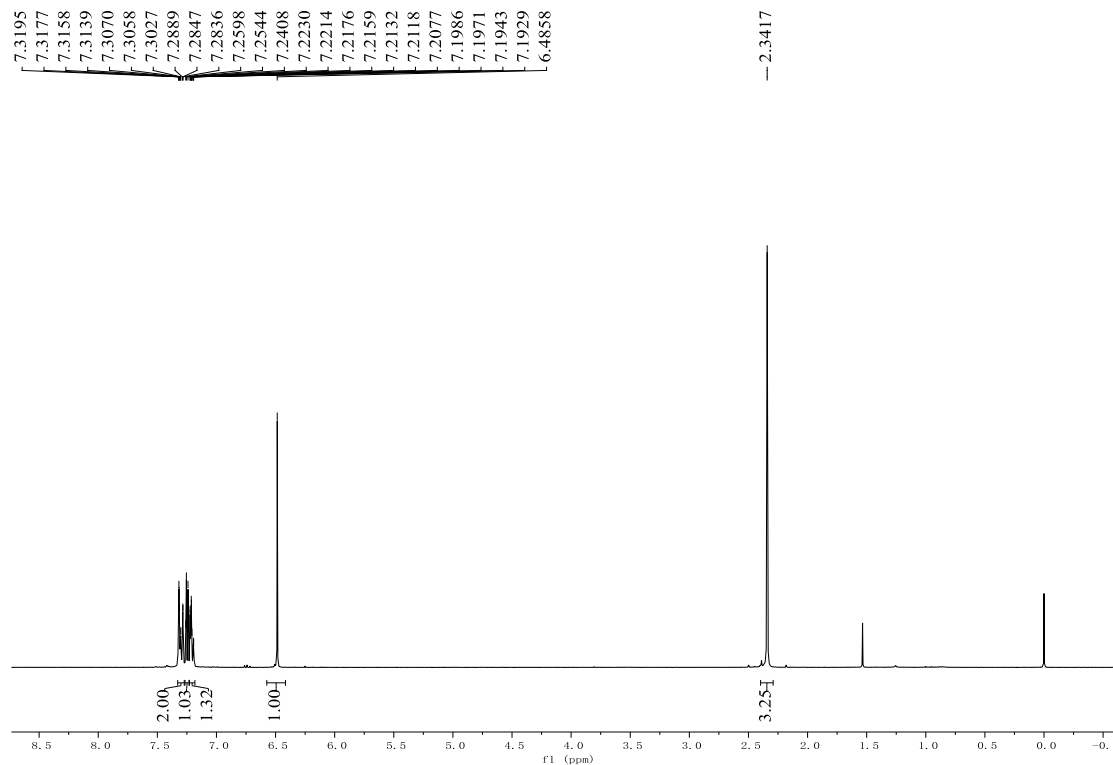
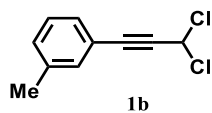
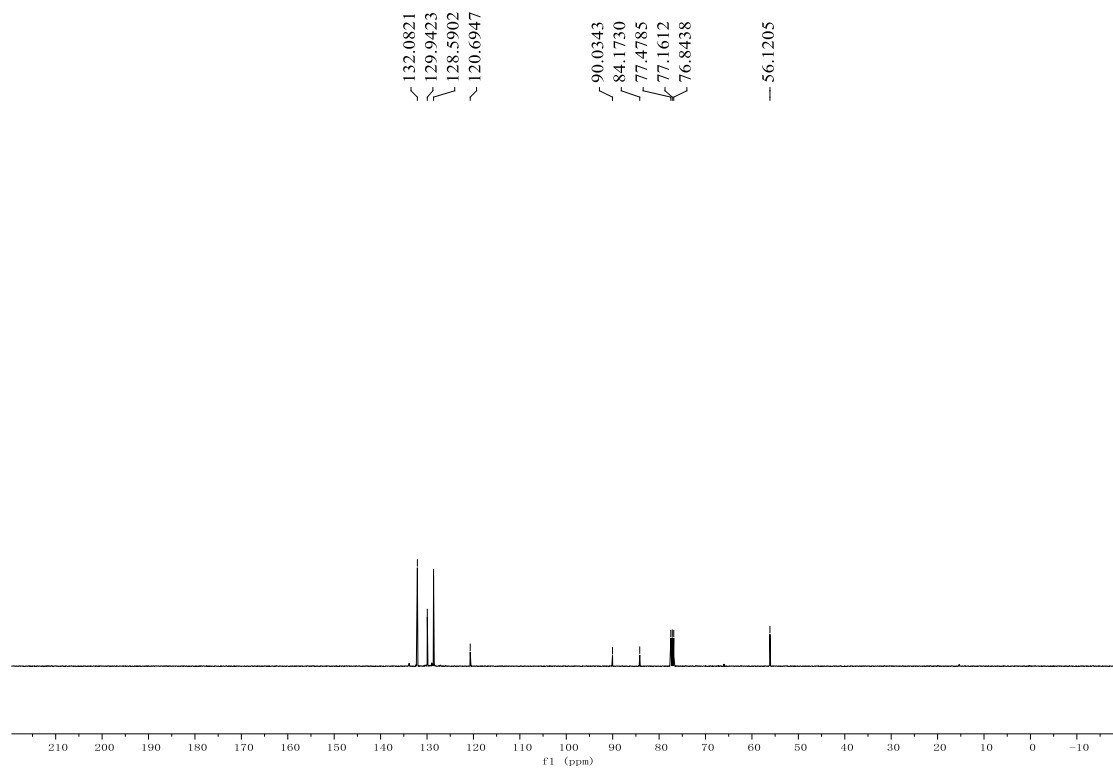
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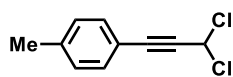
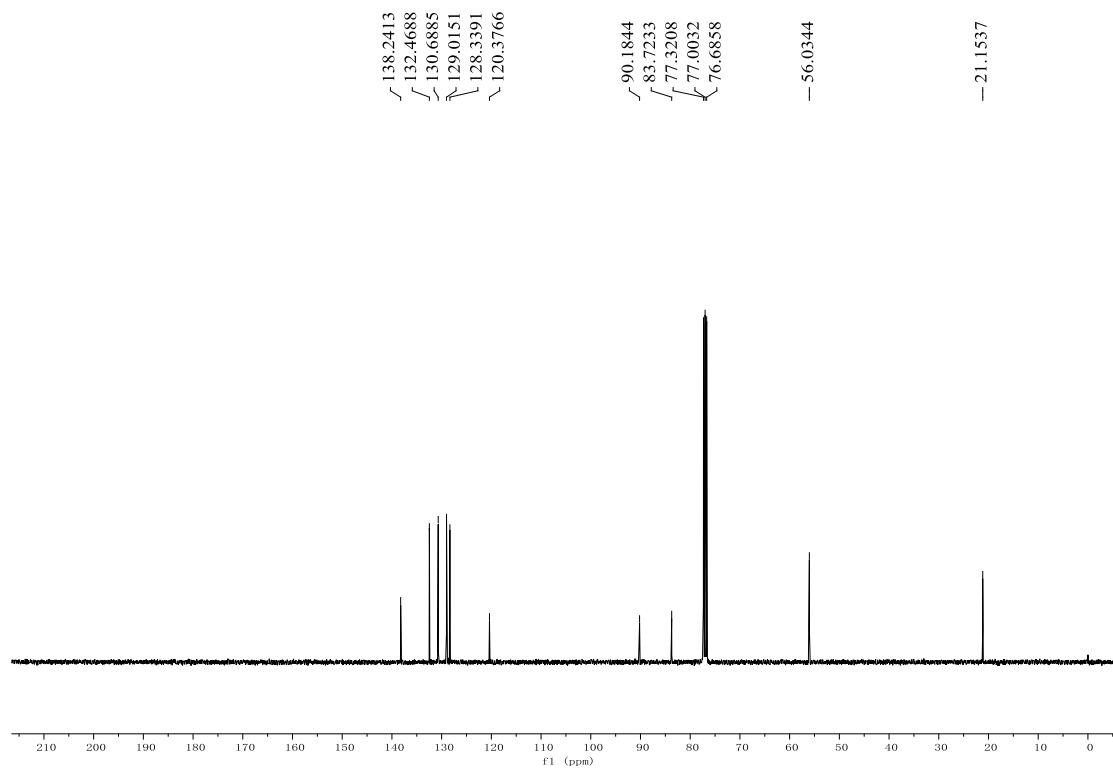
11 ¹H NMR, ¹⁹F NMR, ¹³C NMR and HPLC Spectra of the Substrates and Products.



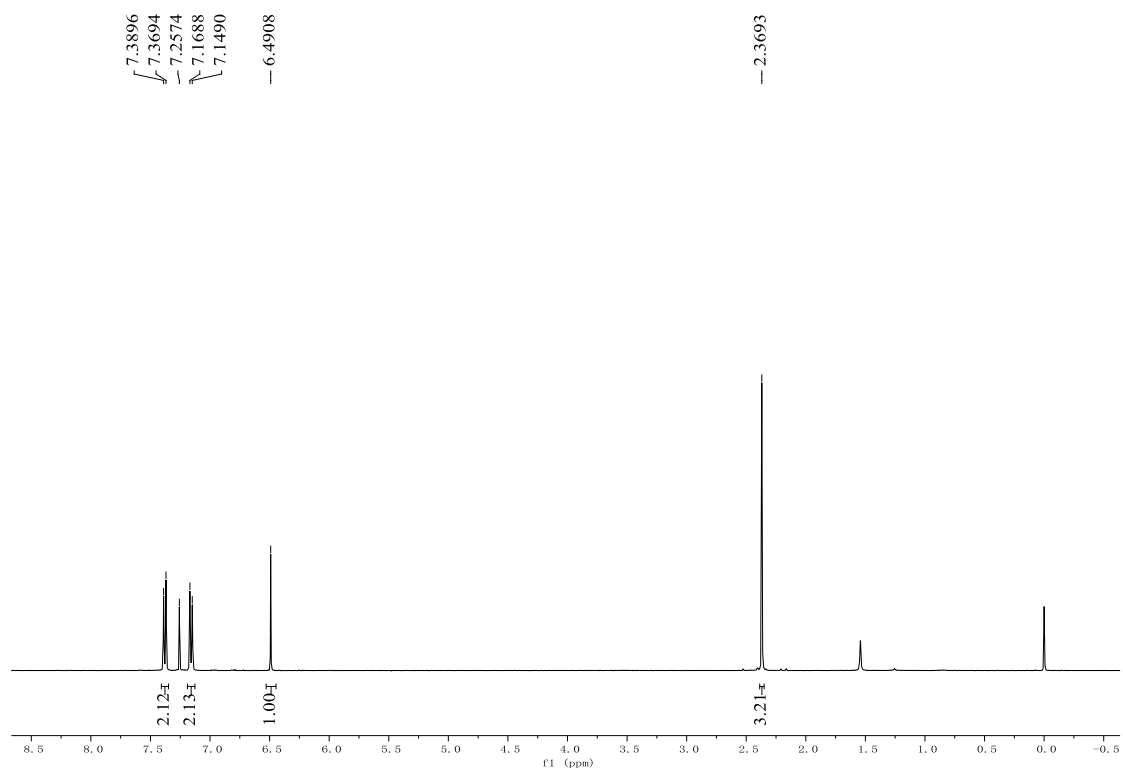
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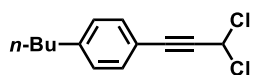
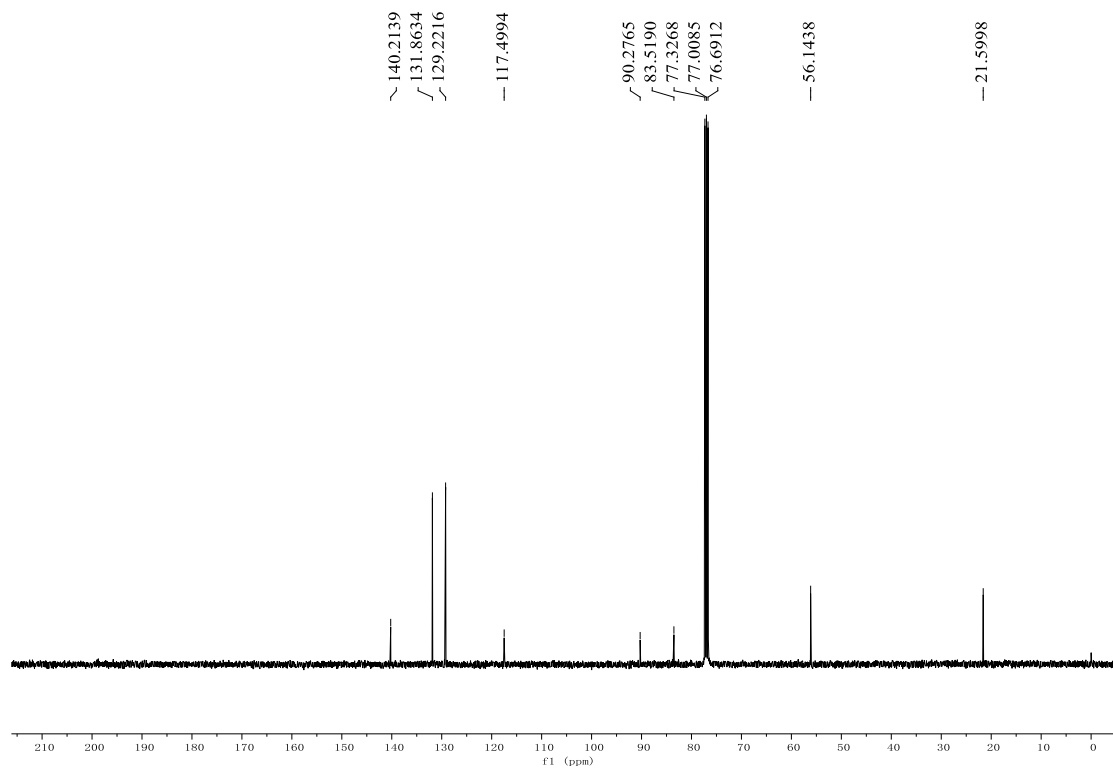




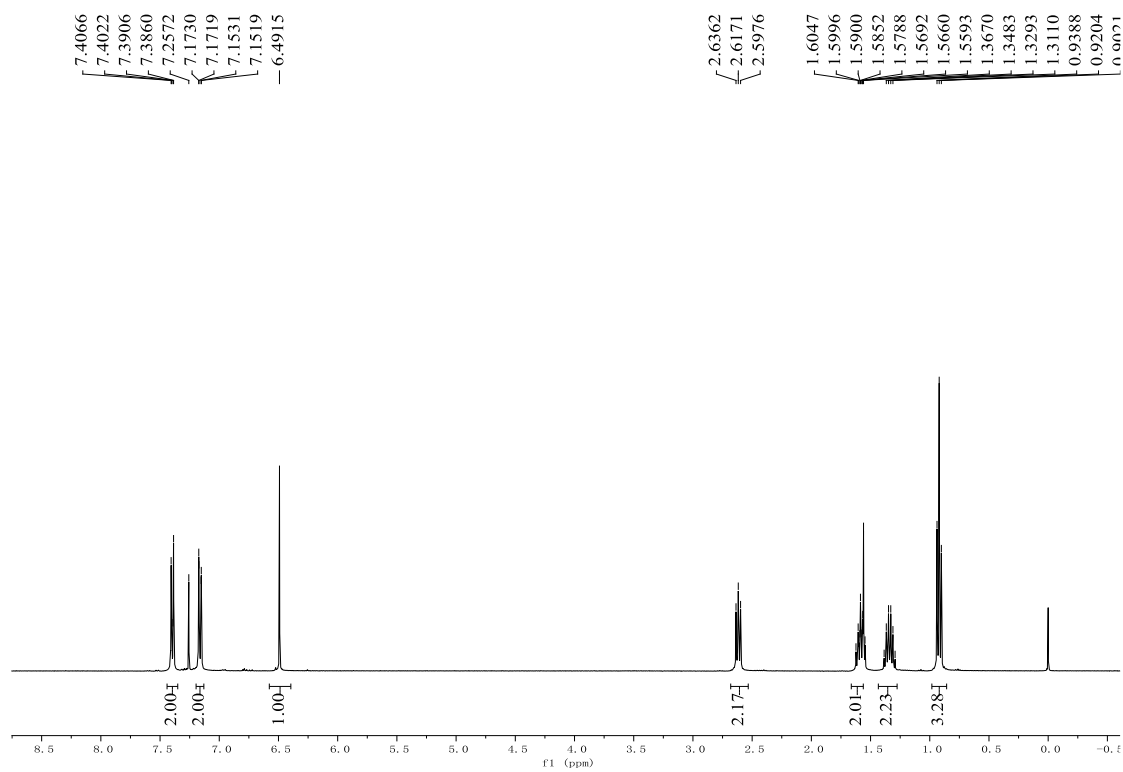


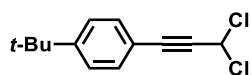
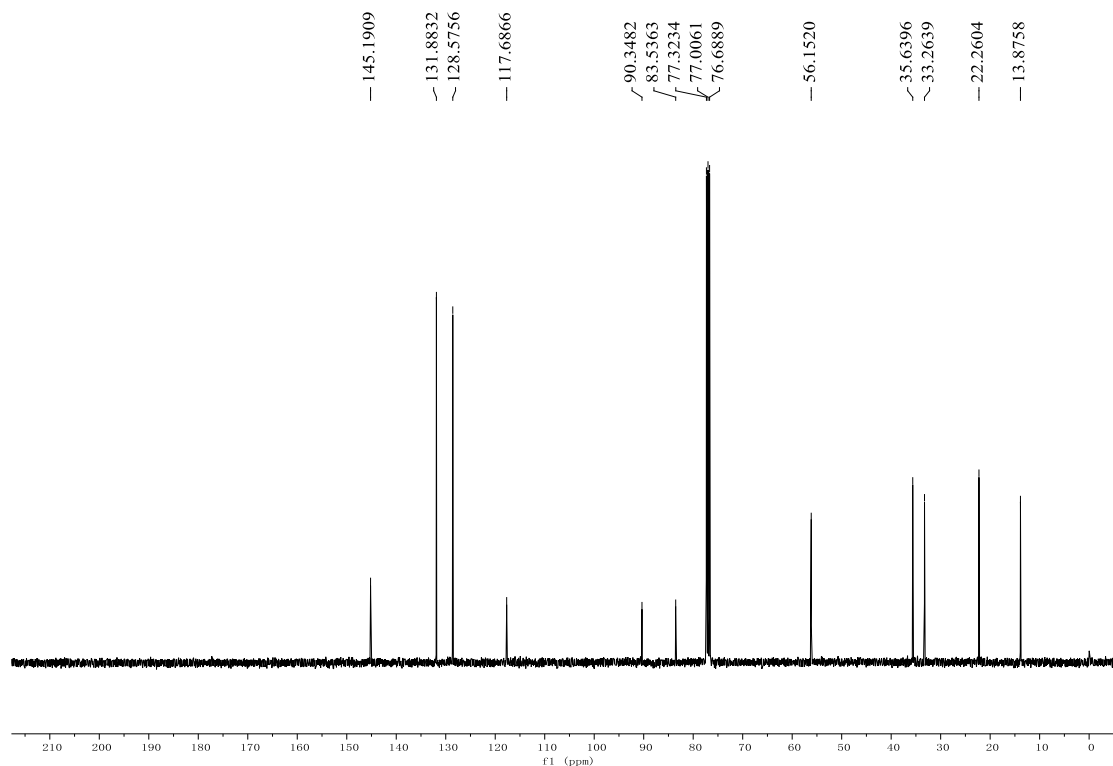
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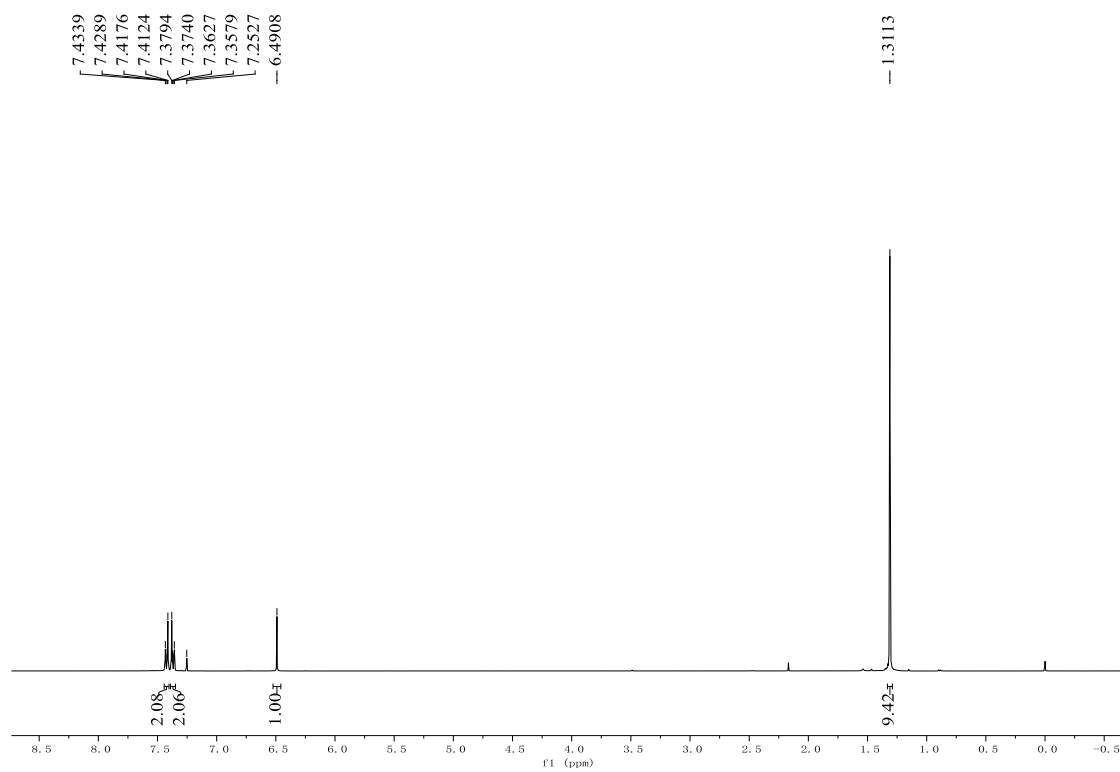


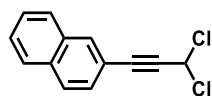
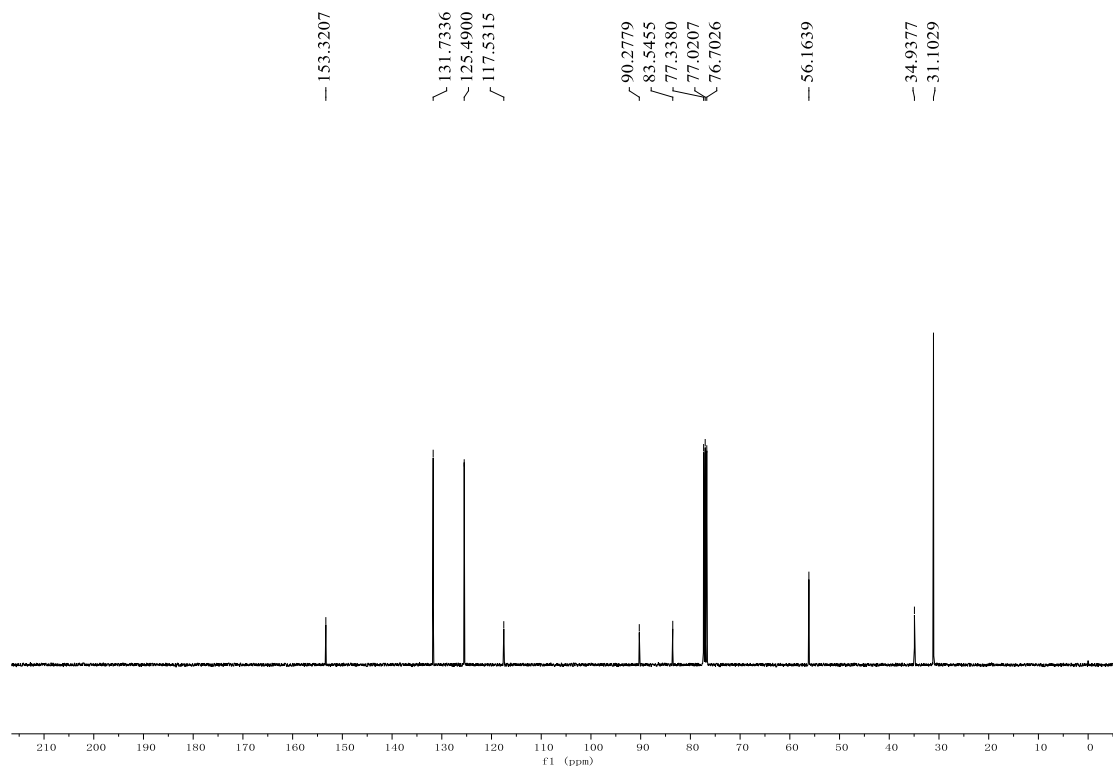
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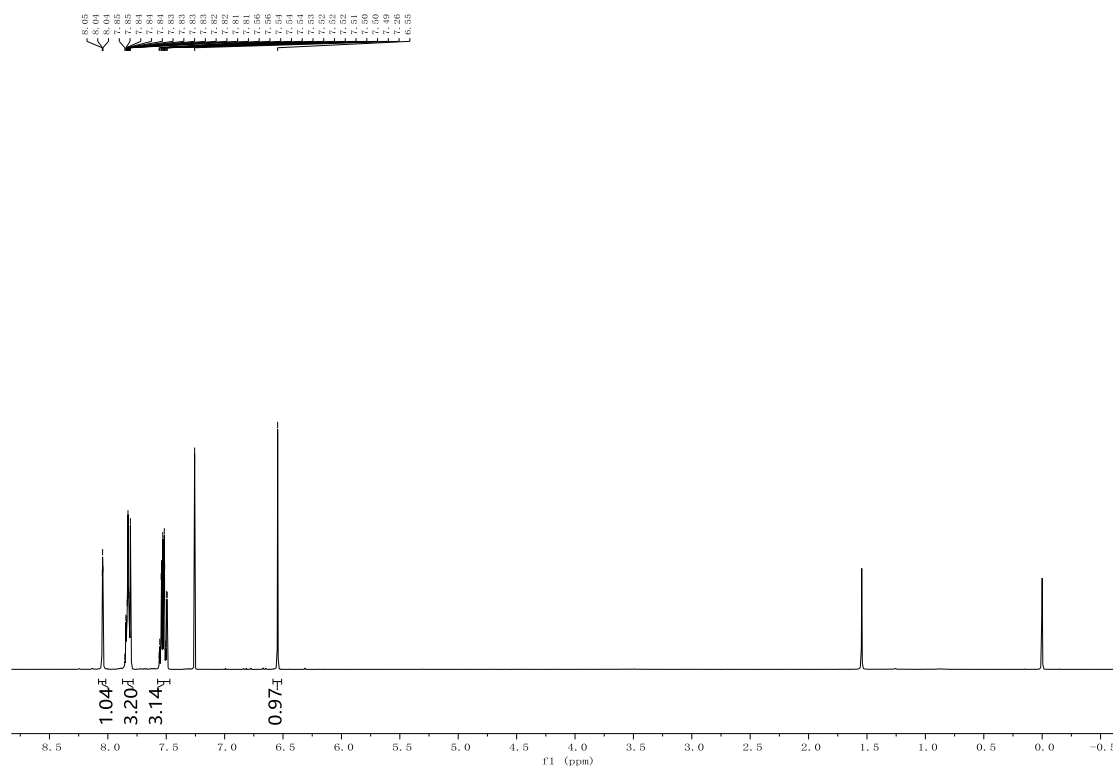


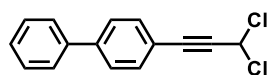
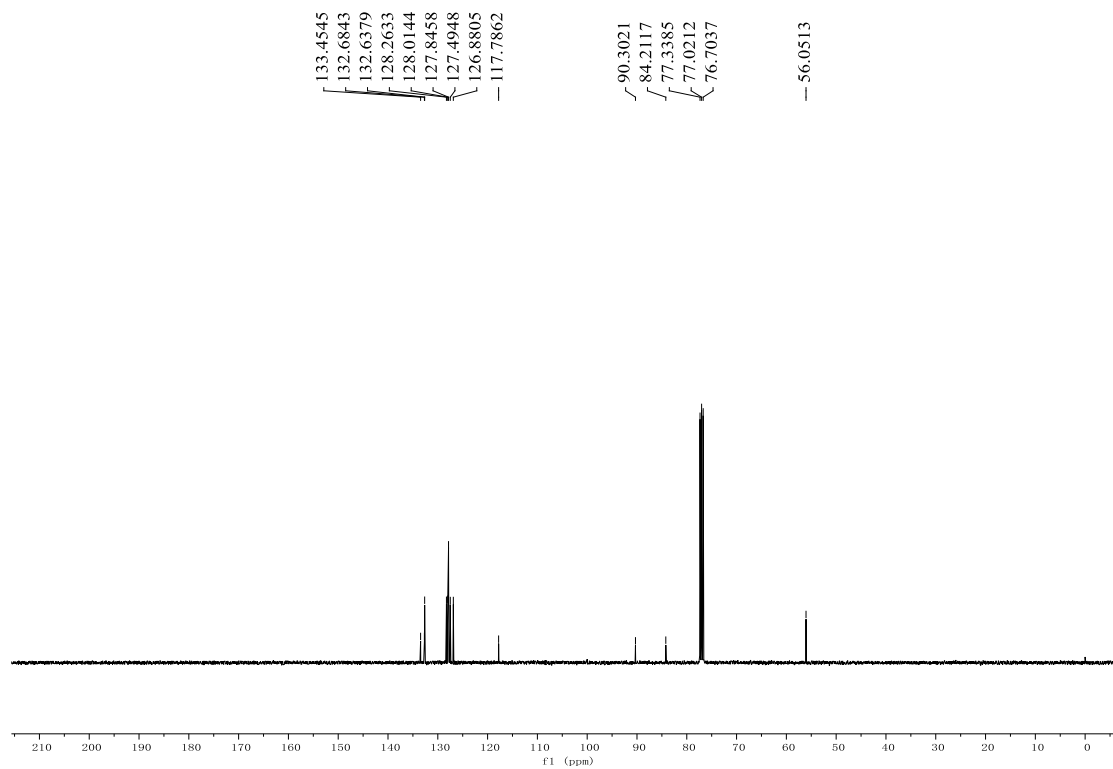
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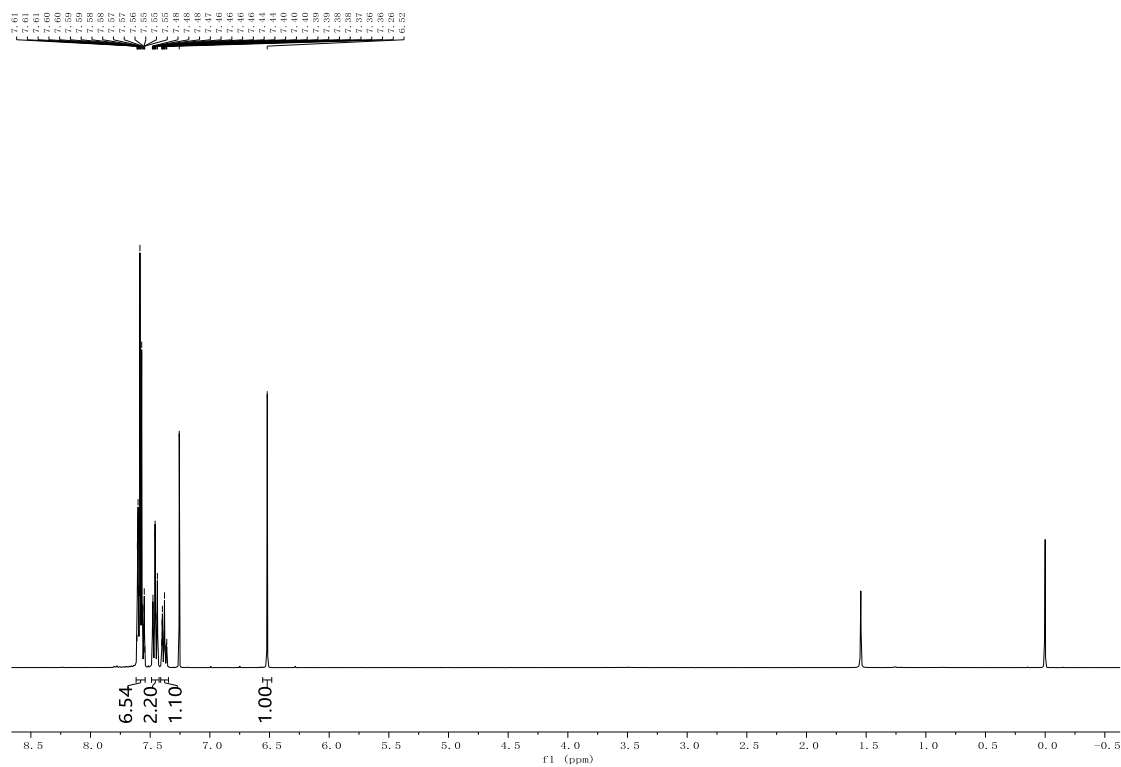


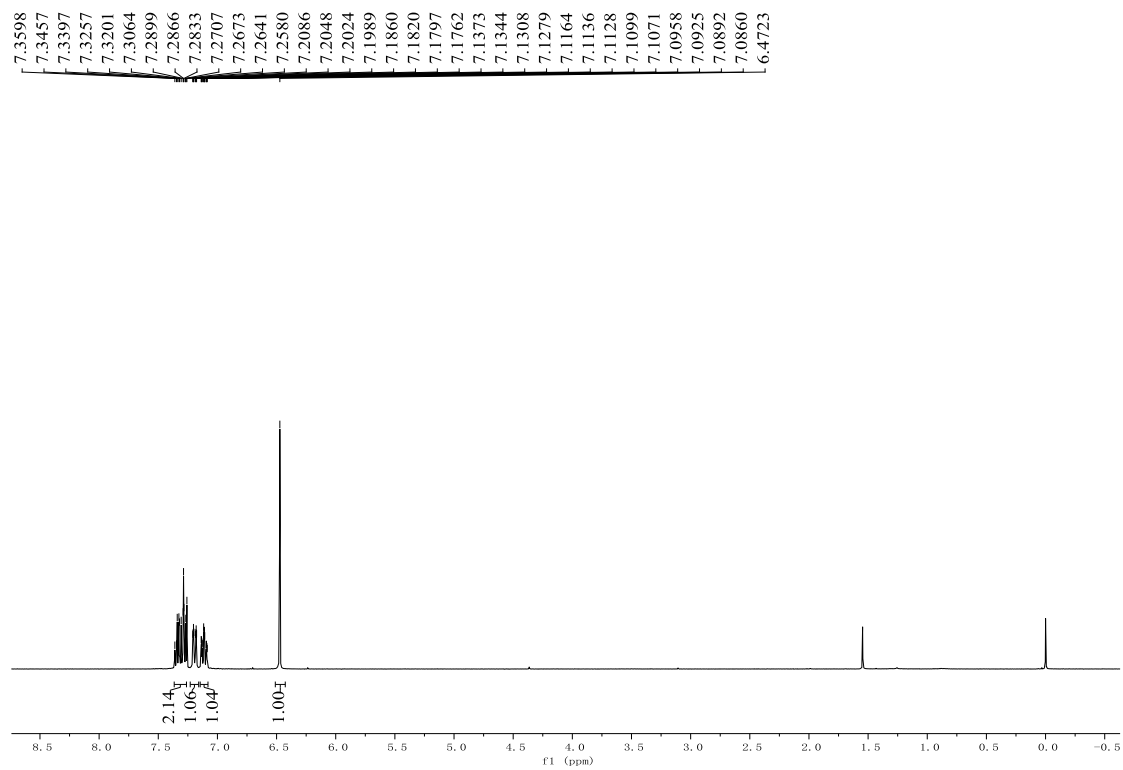
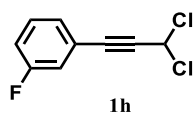
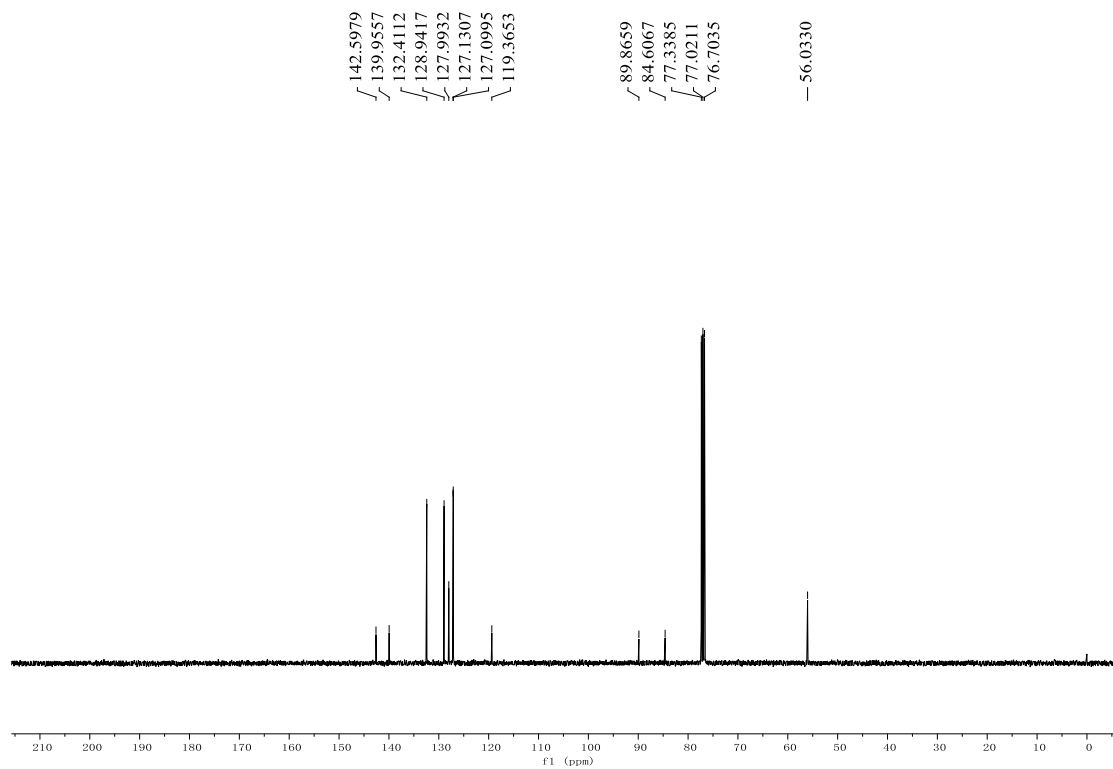
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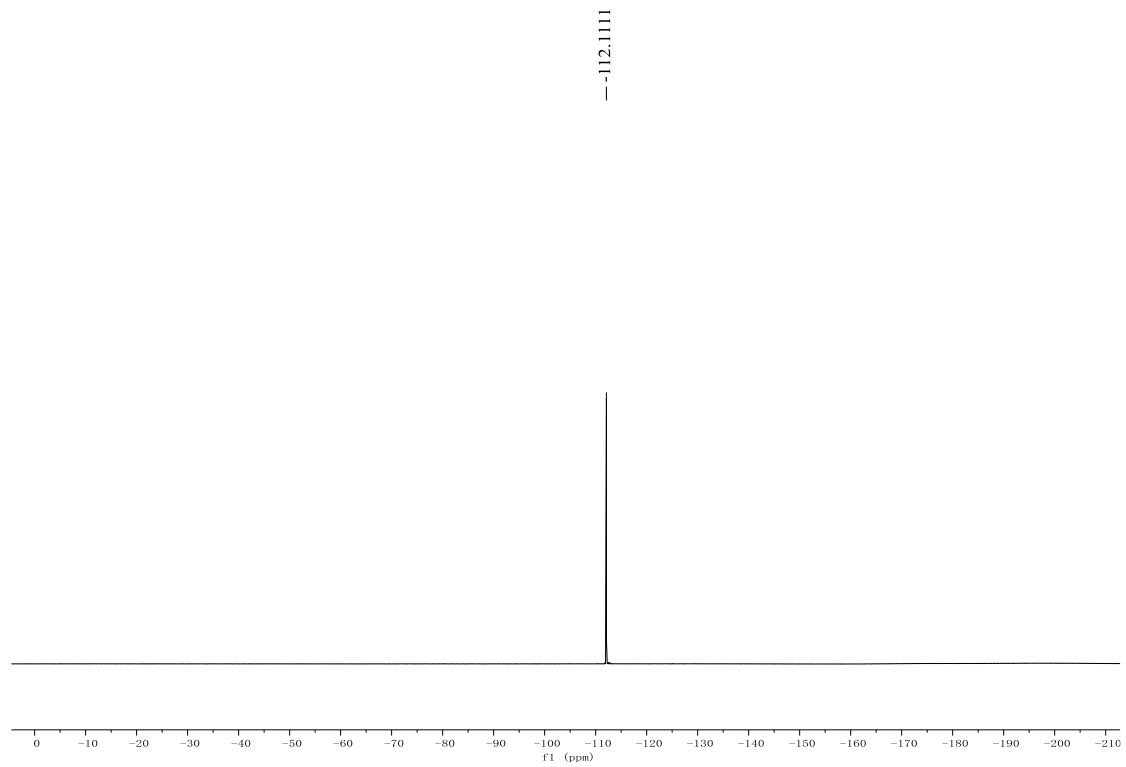




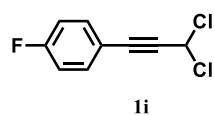
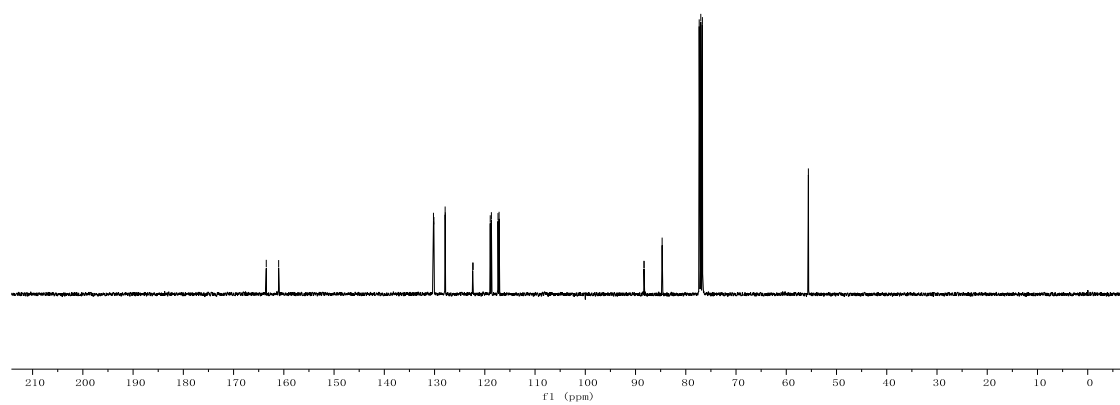
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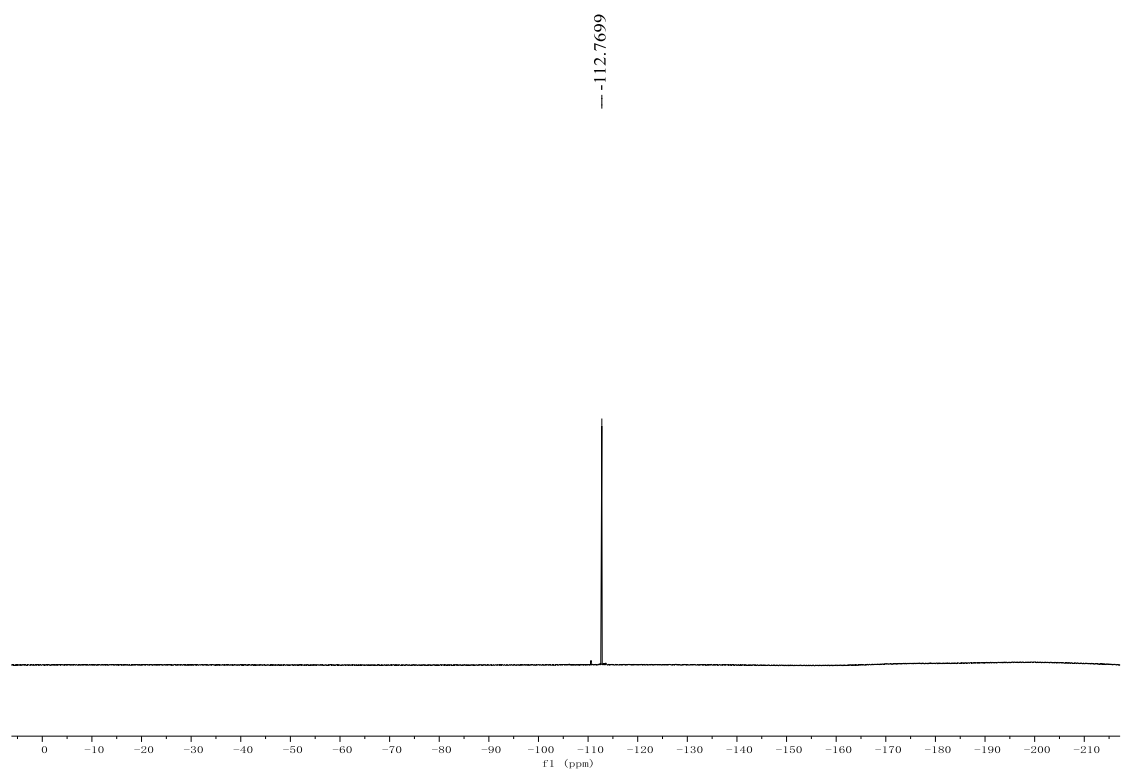
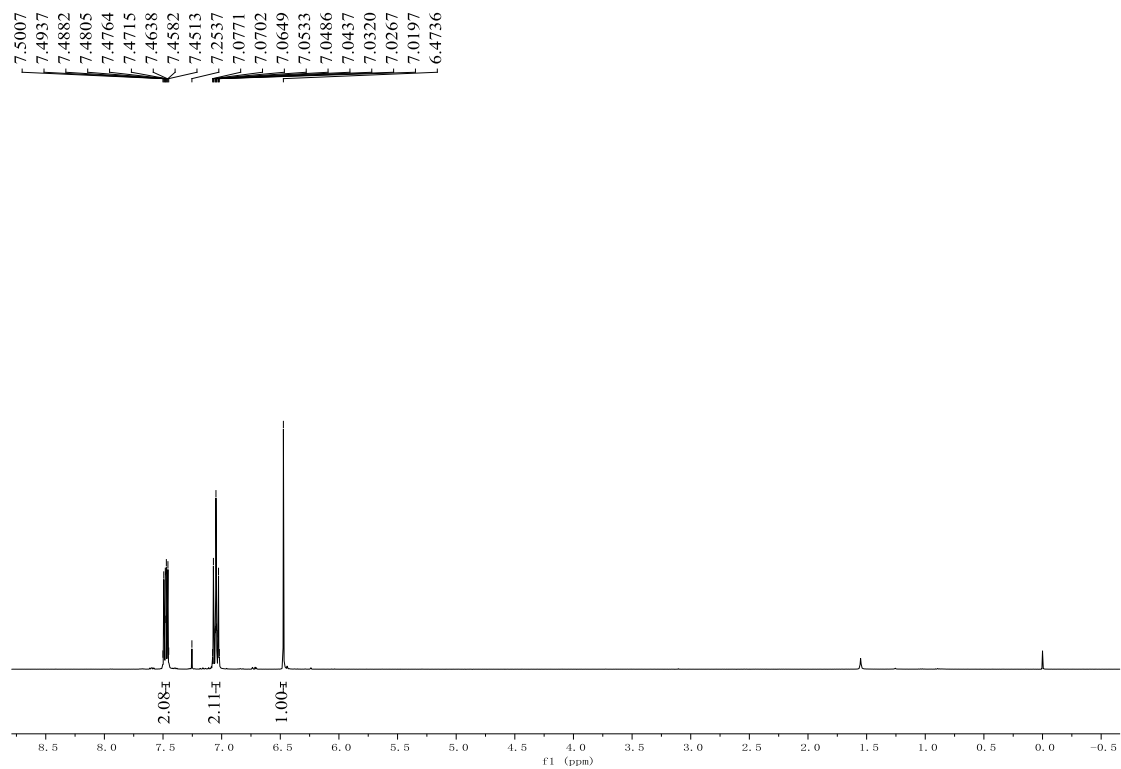


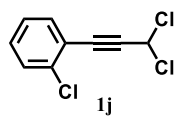
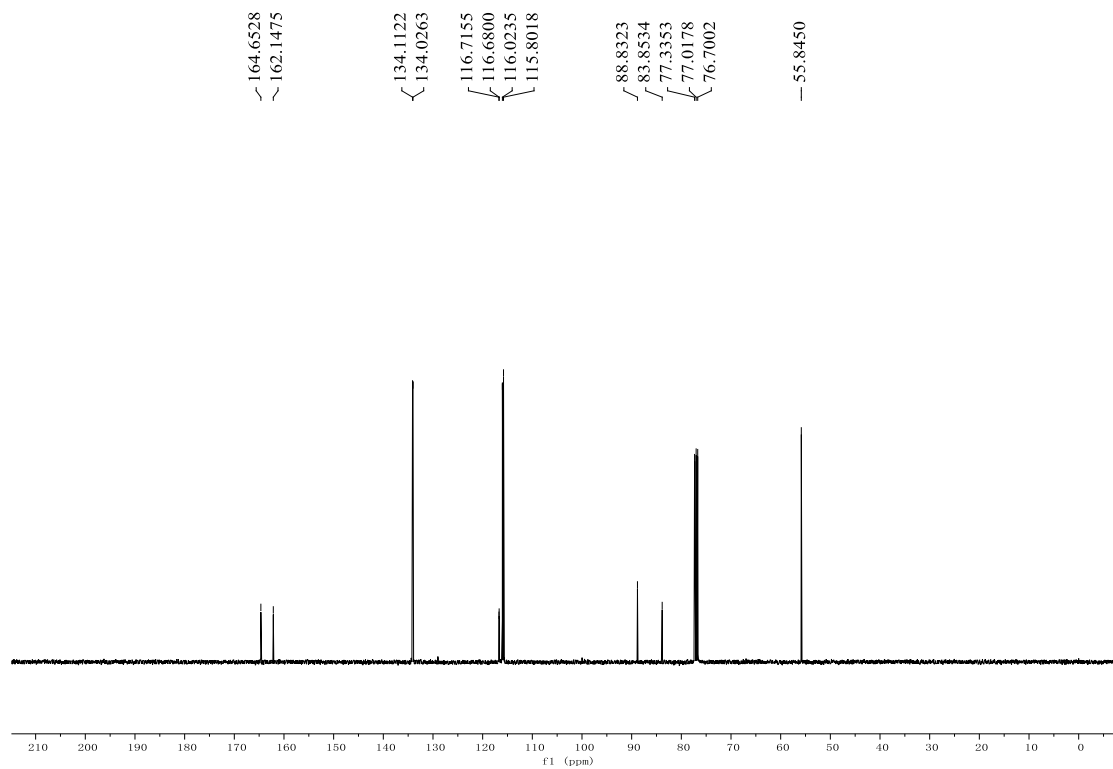


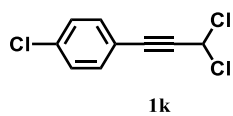
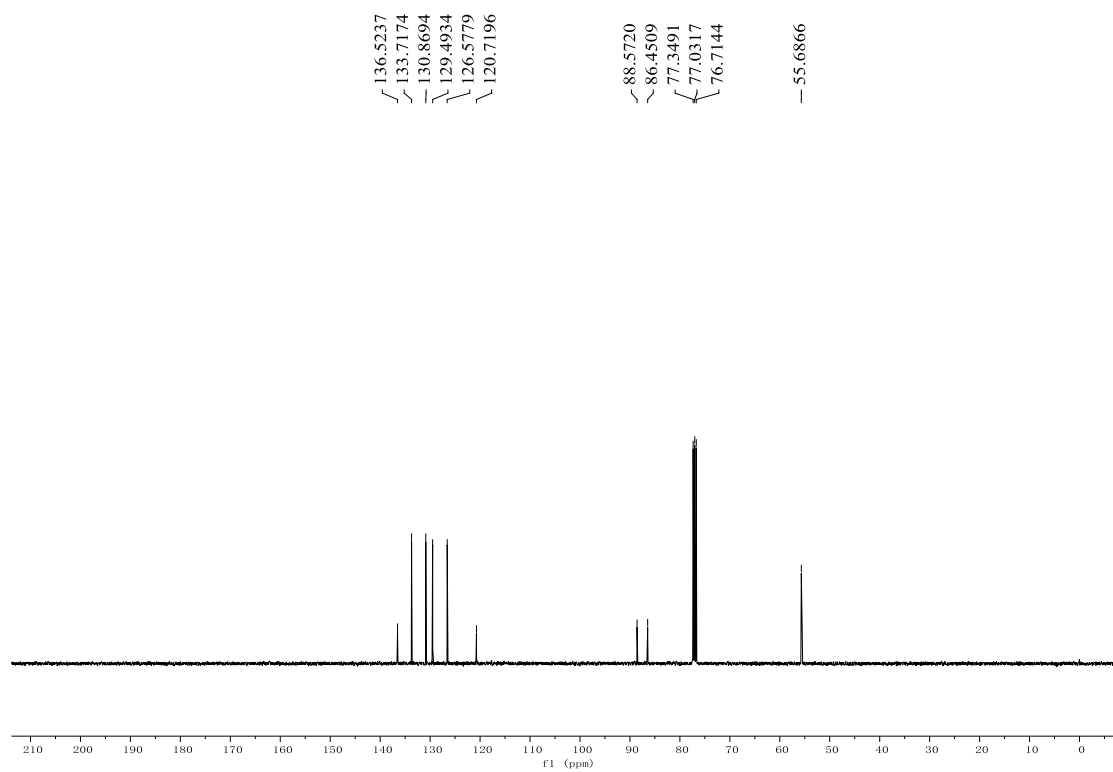
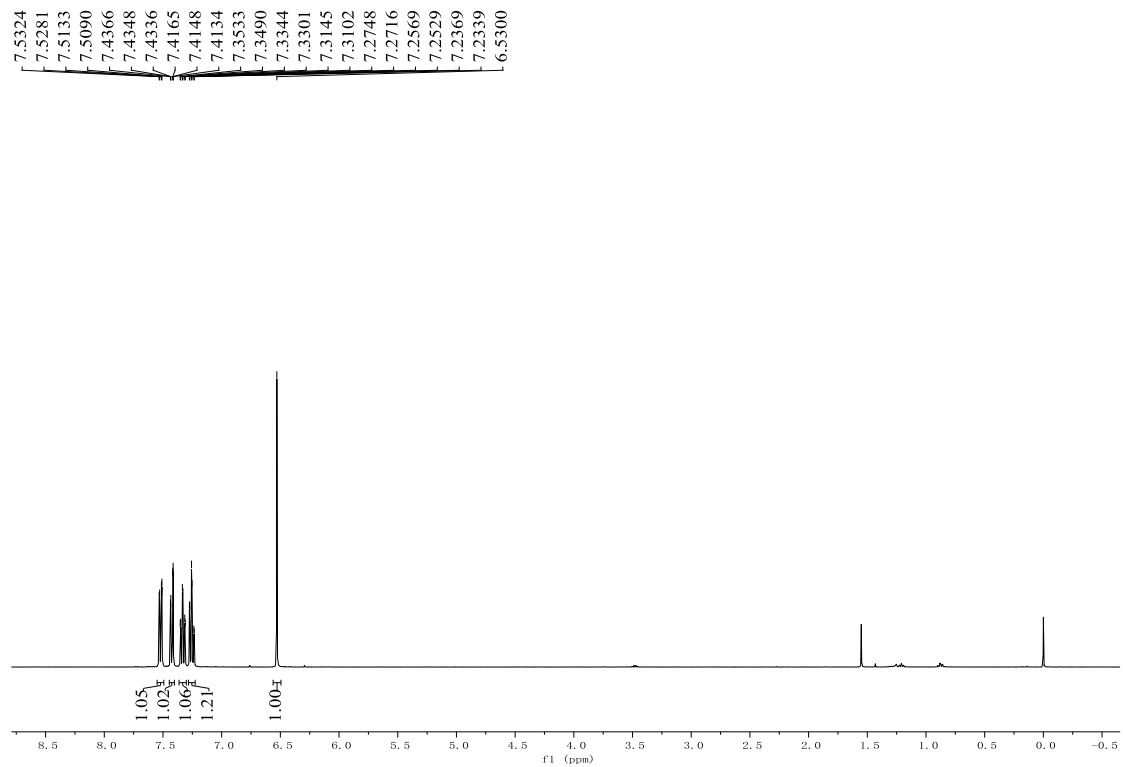


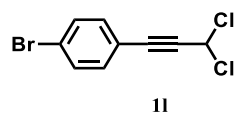
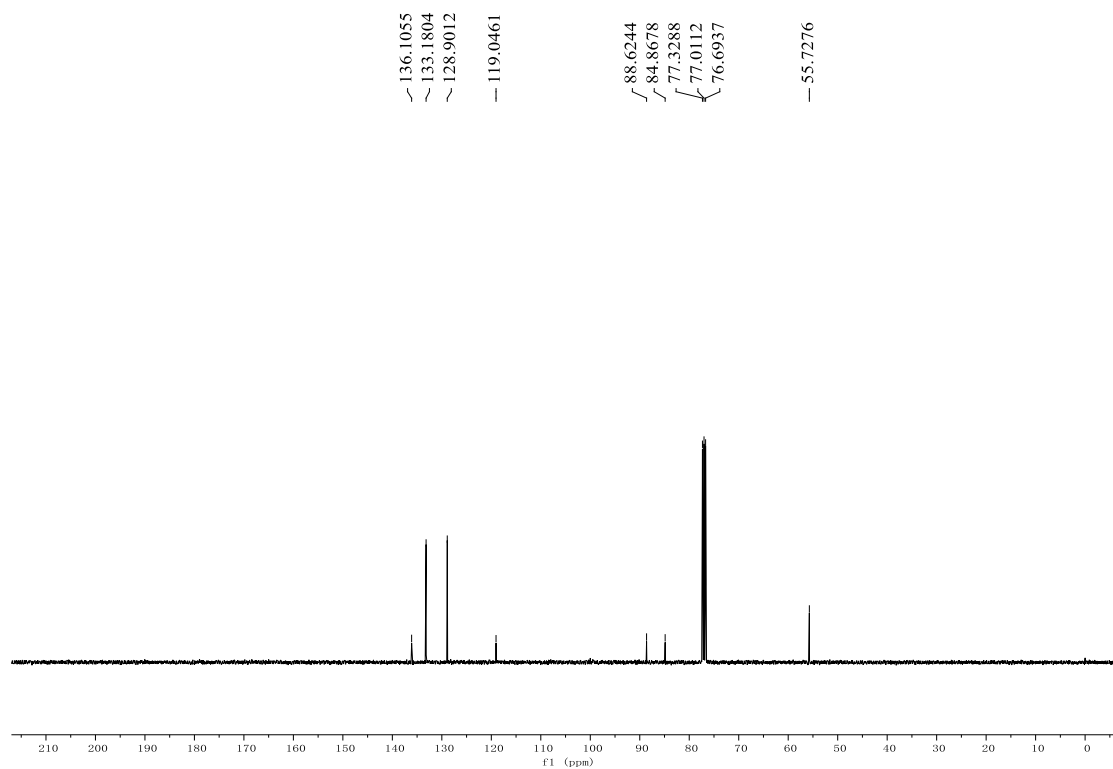
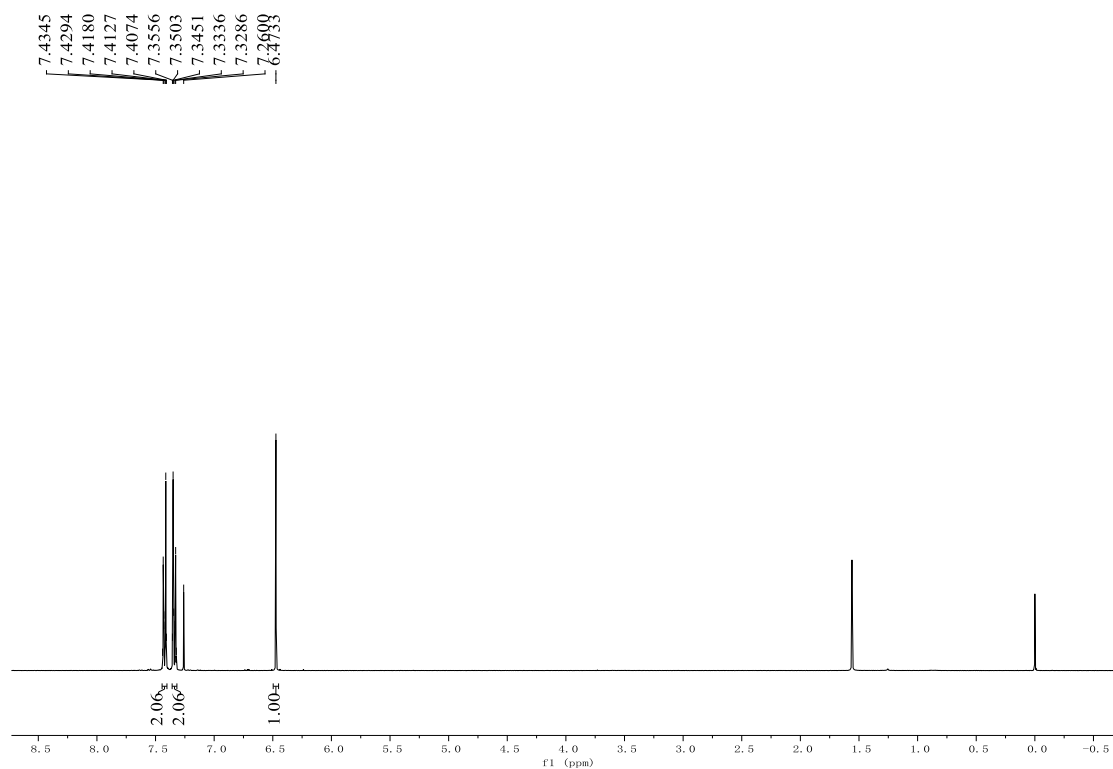
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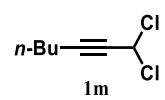
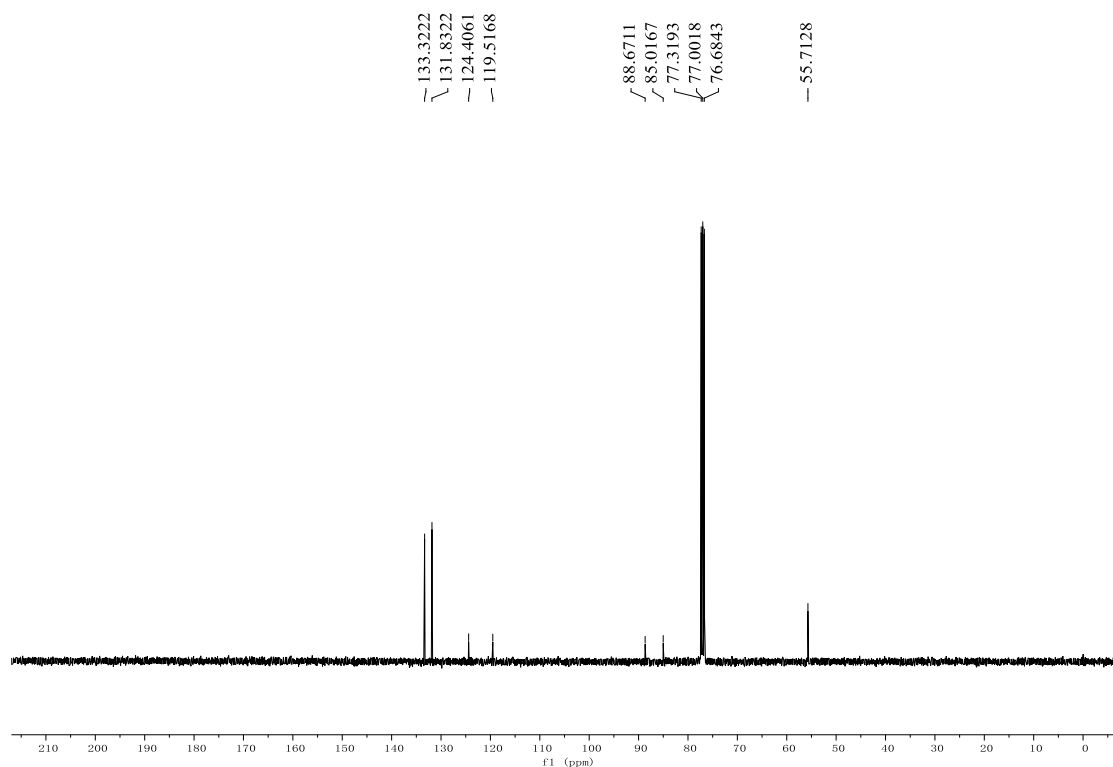
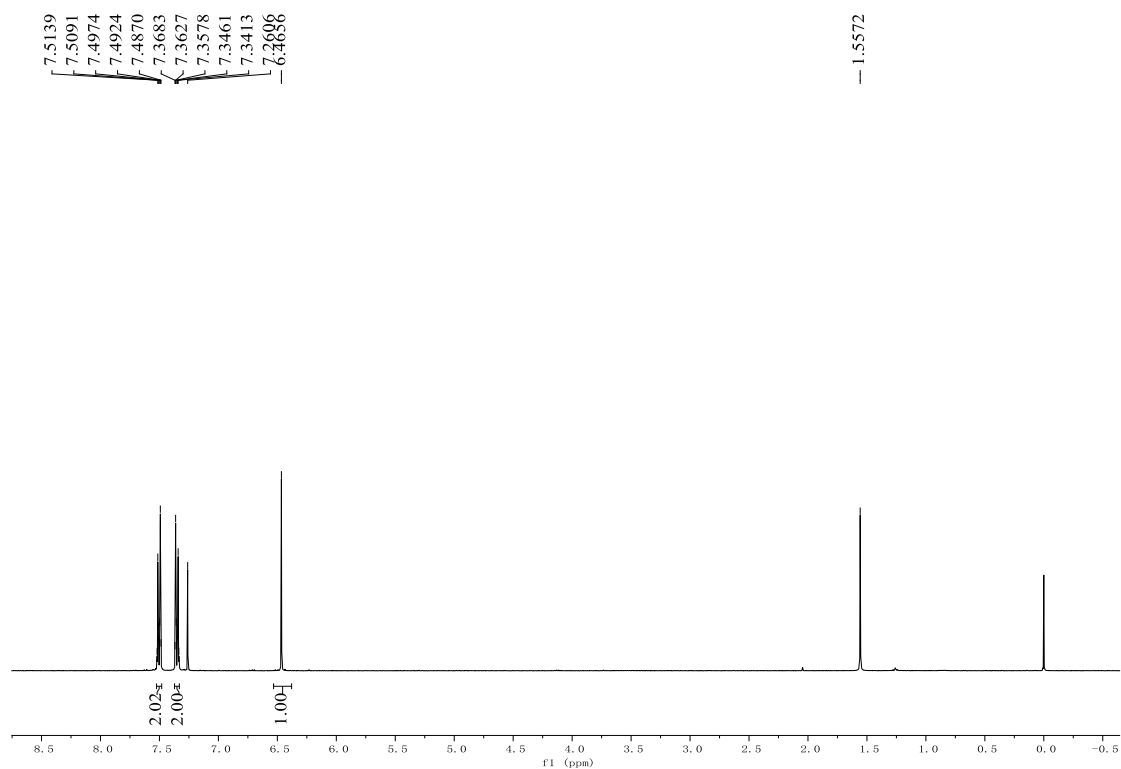


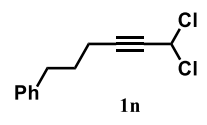
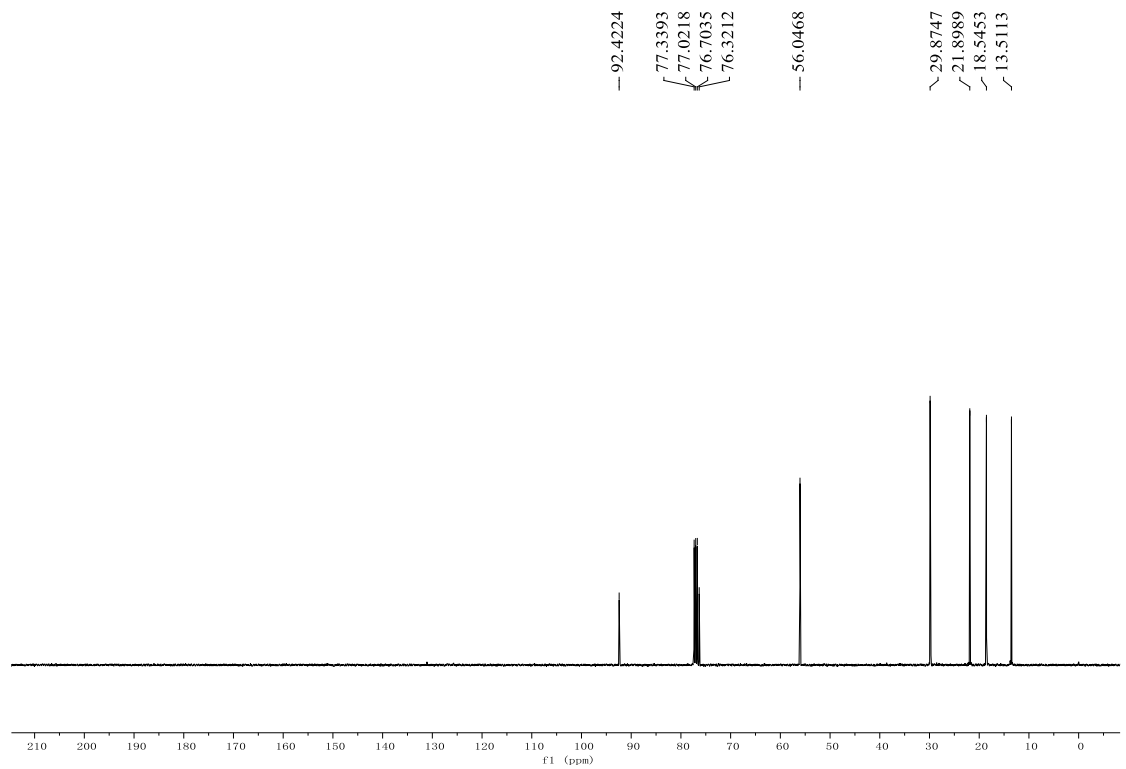
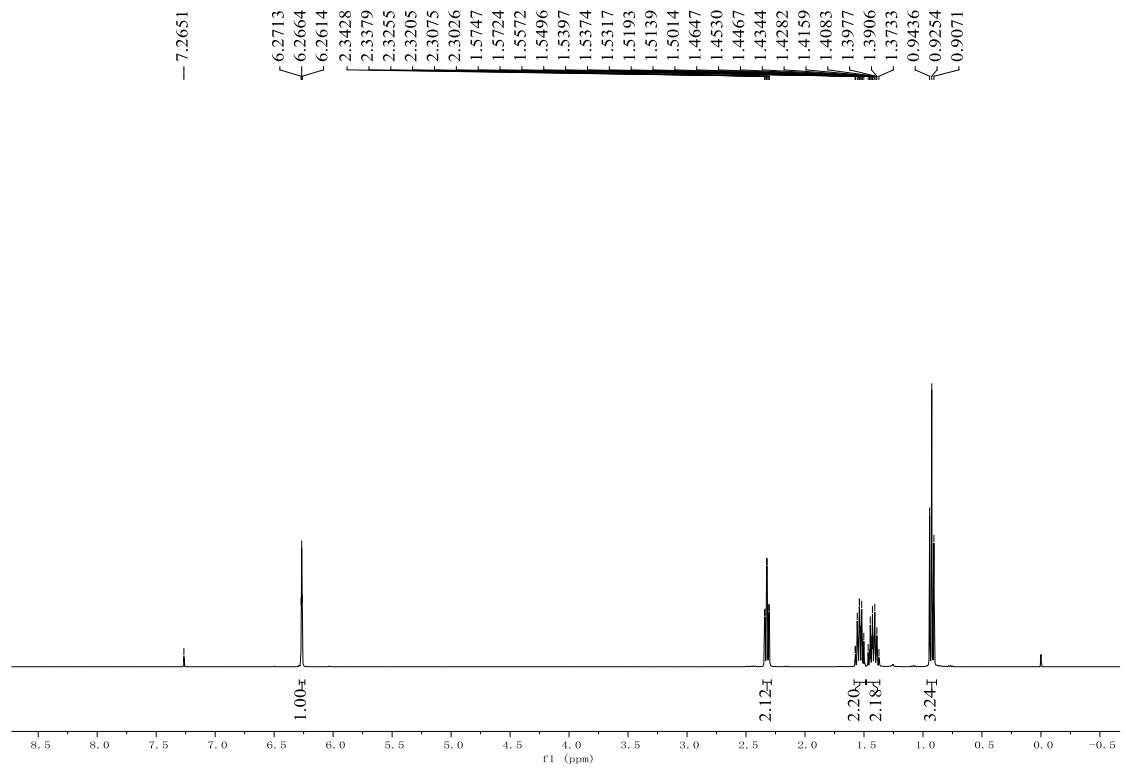


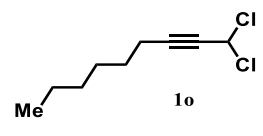
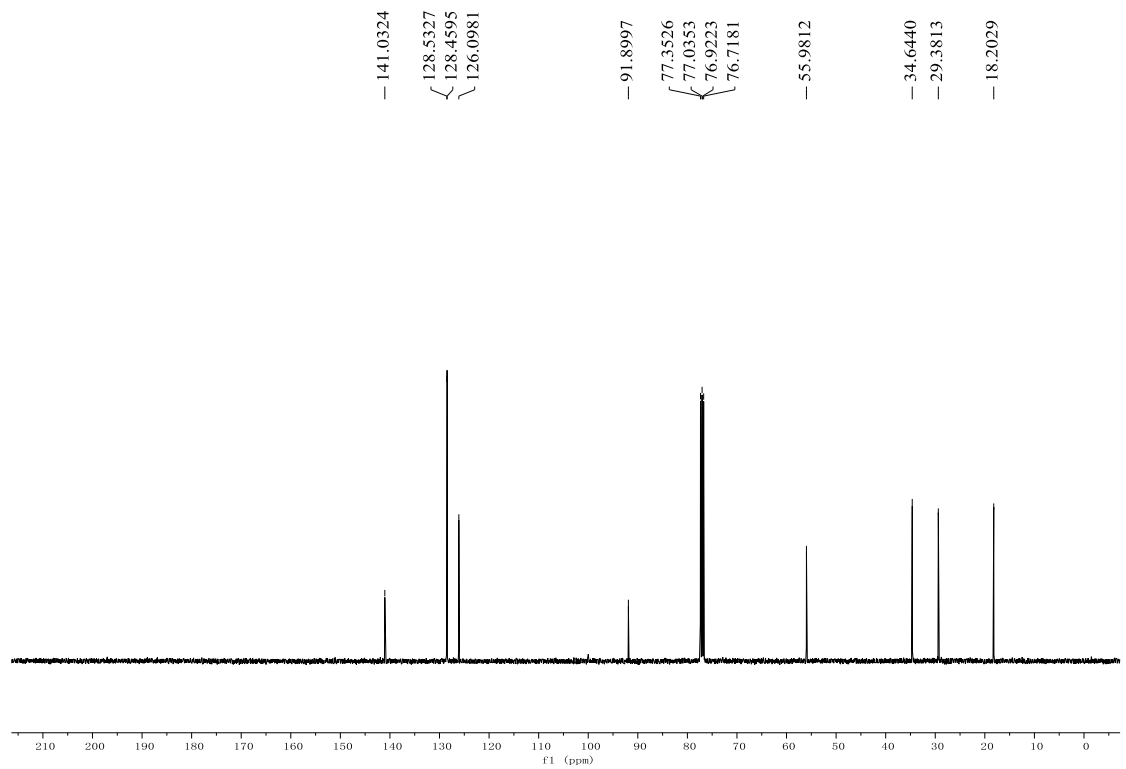
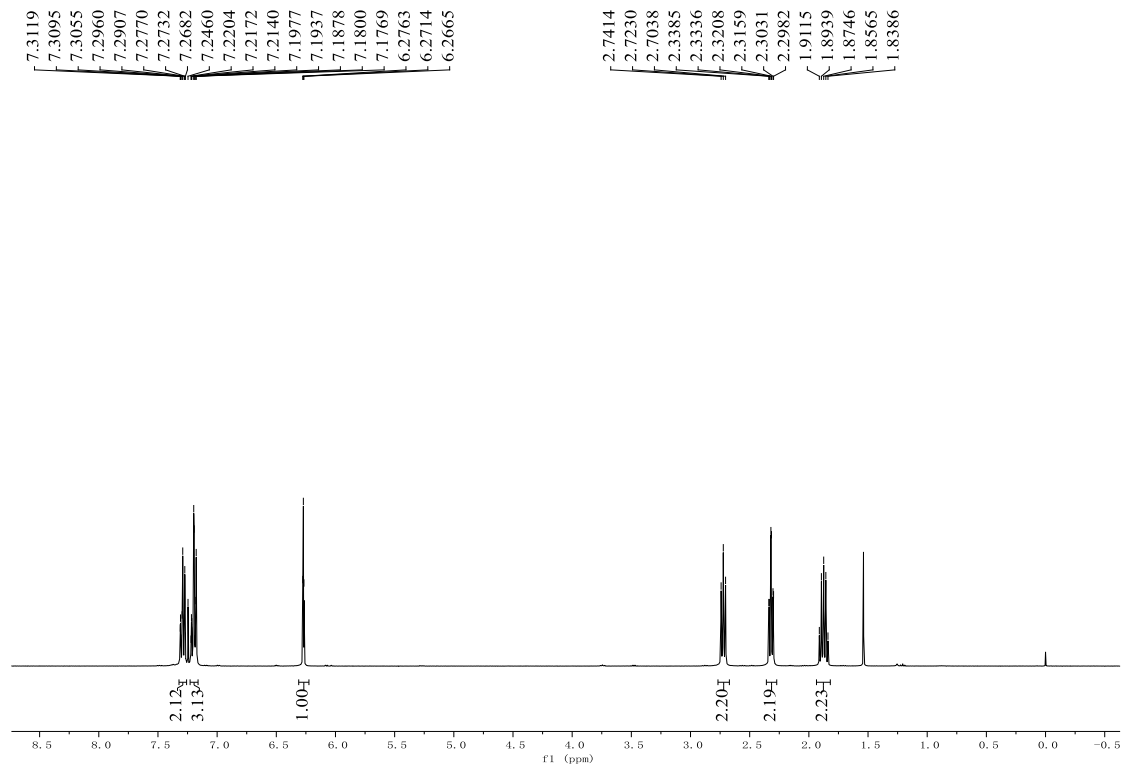


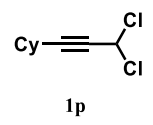
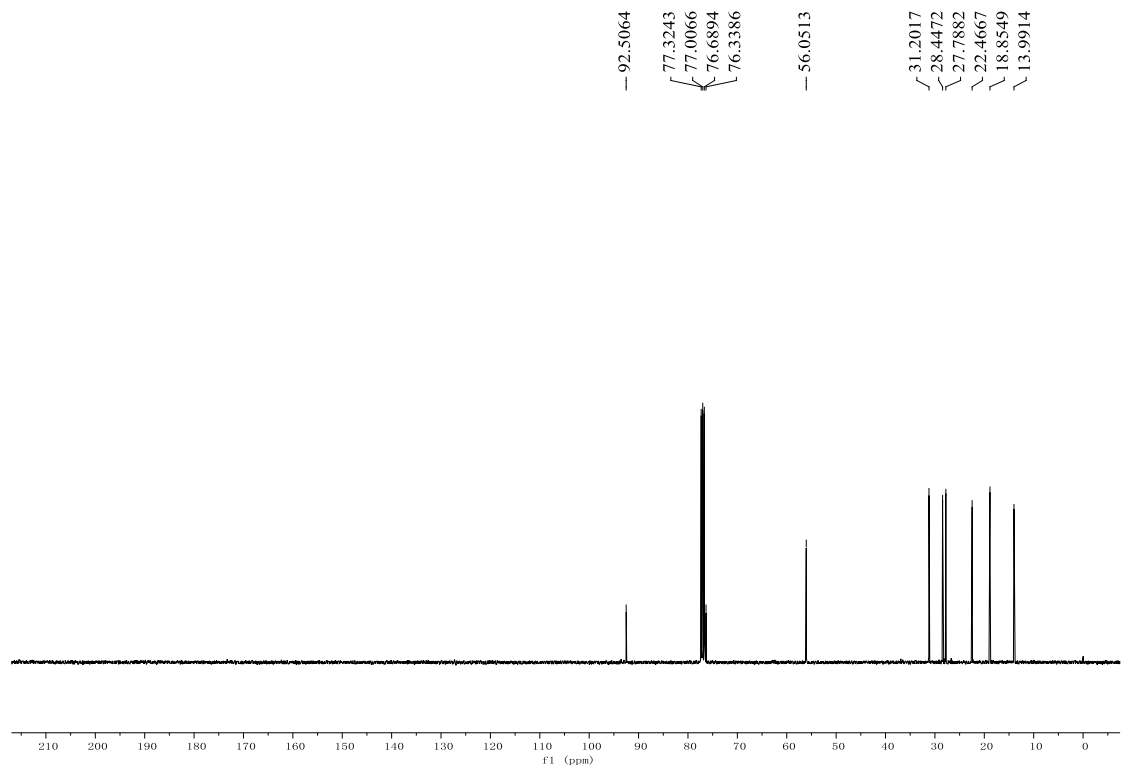
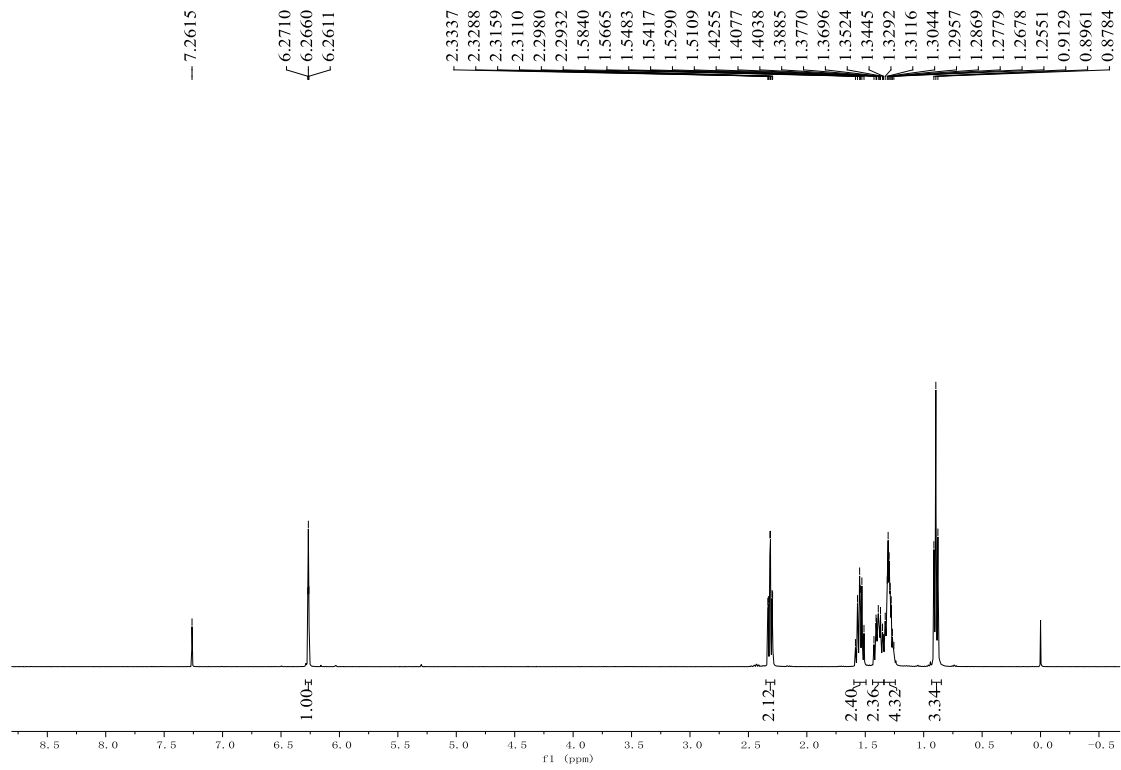


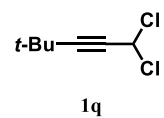
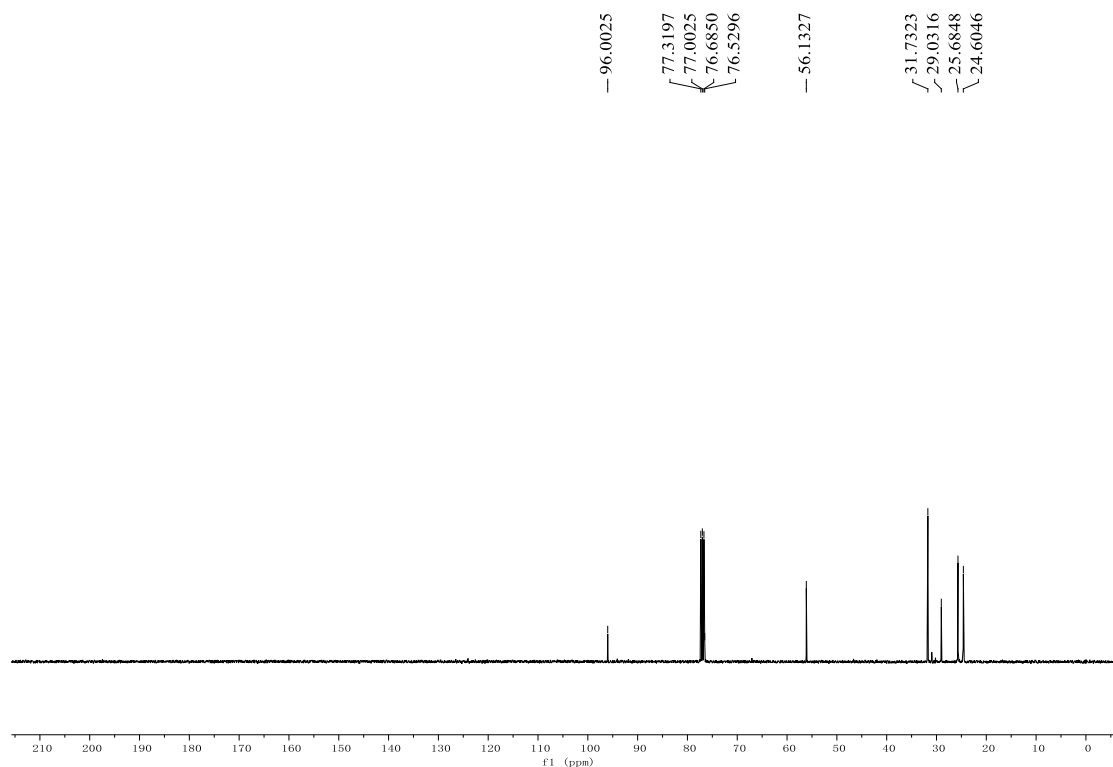
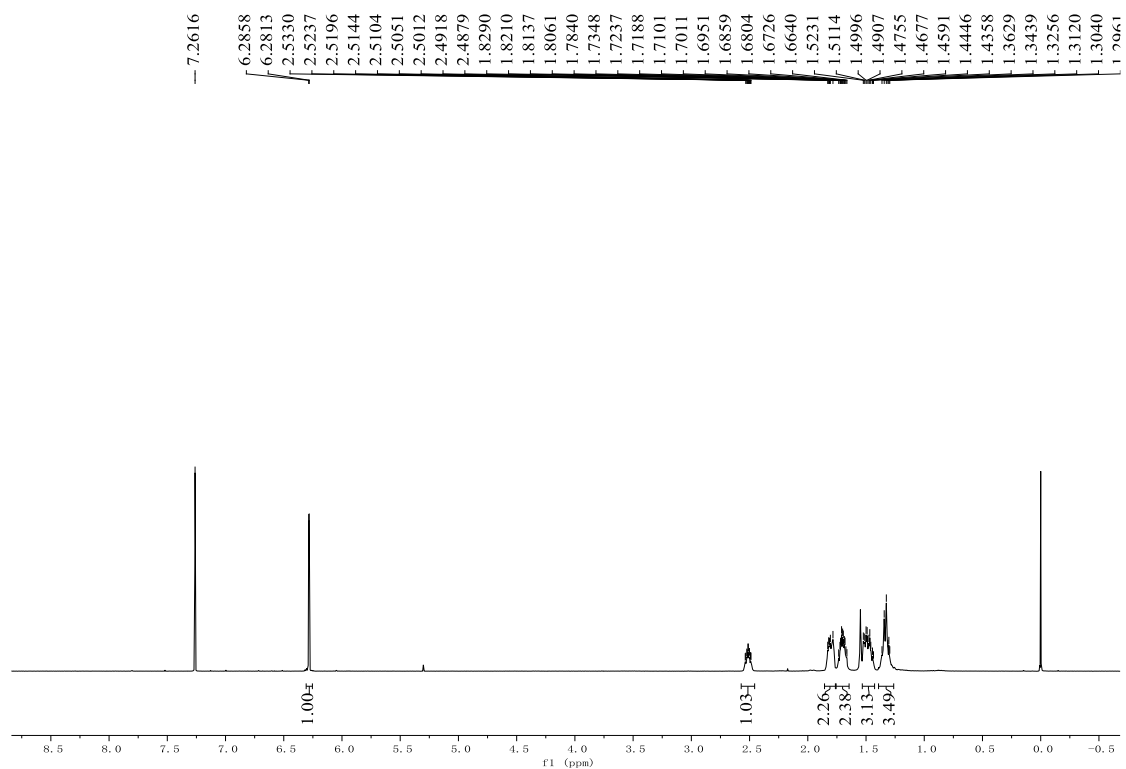


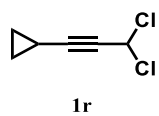
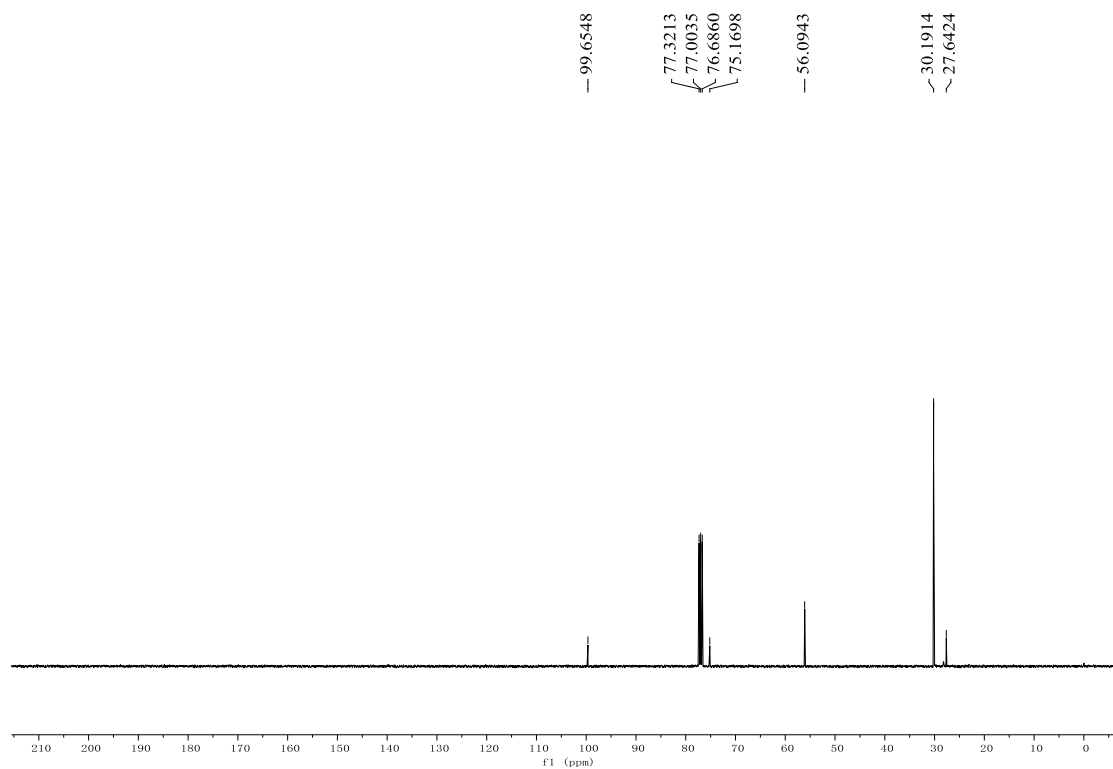
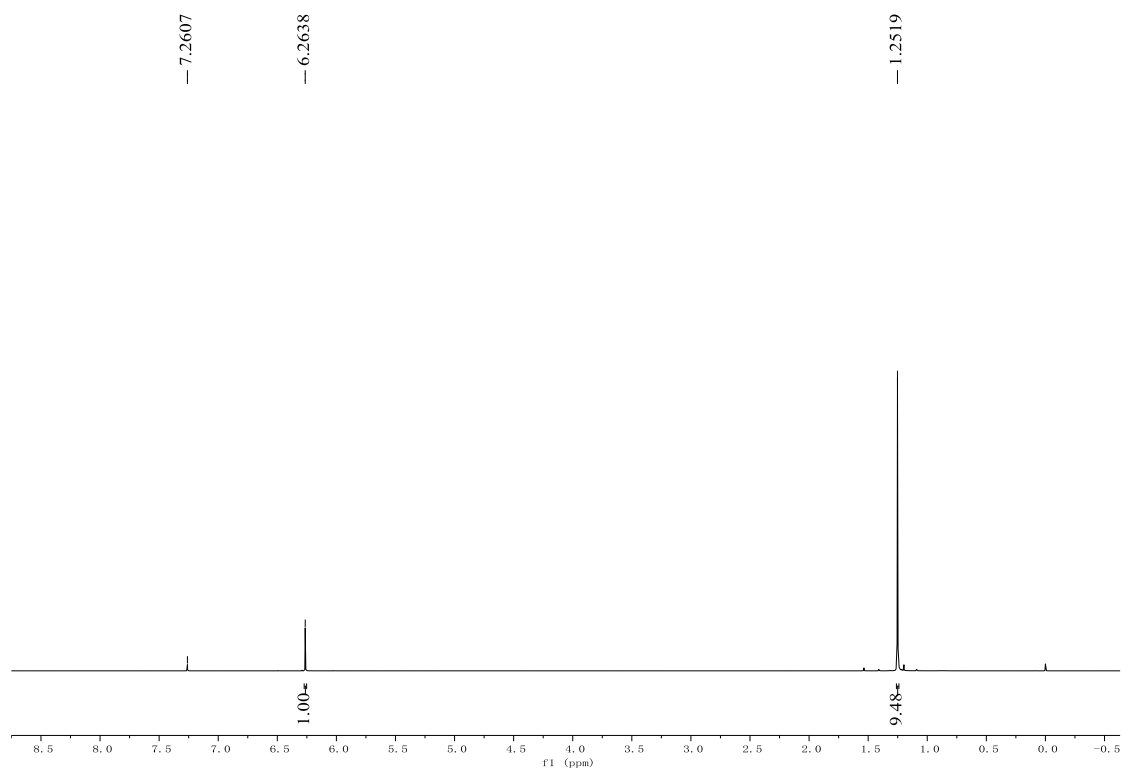


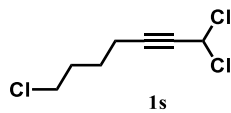
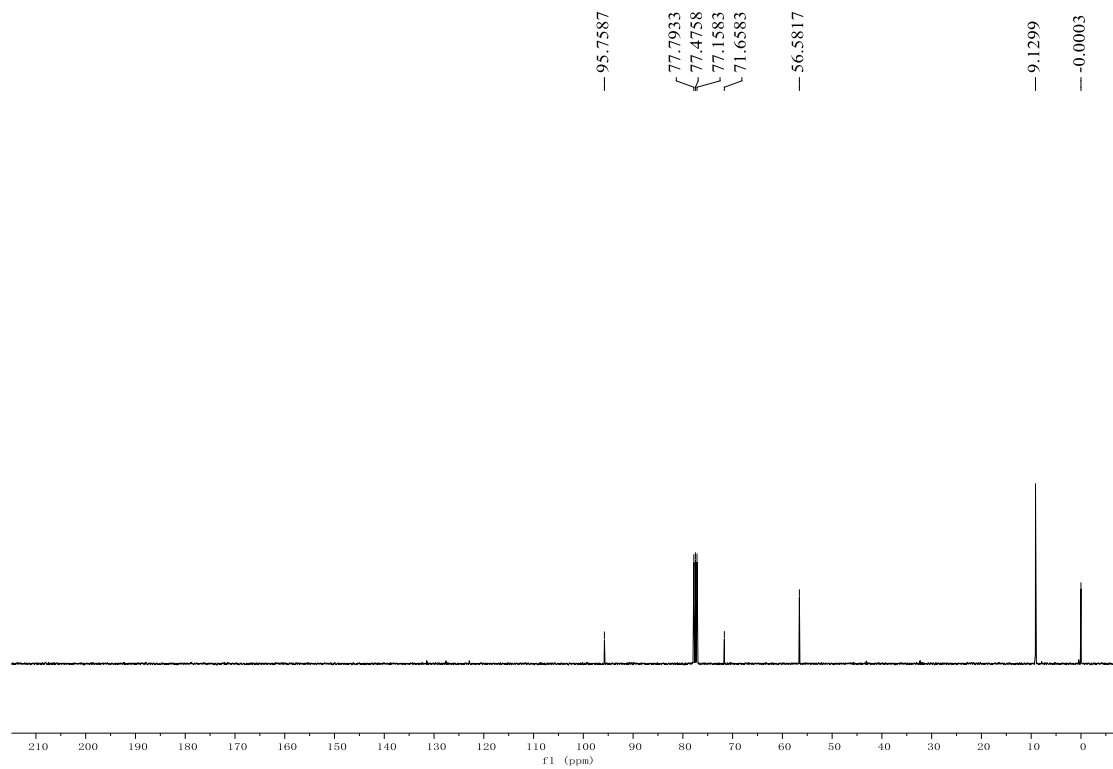
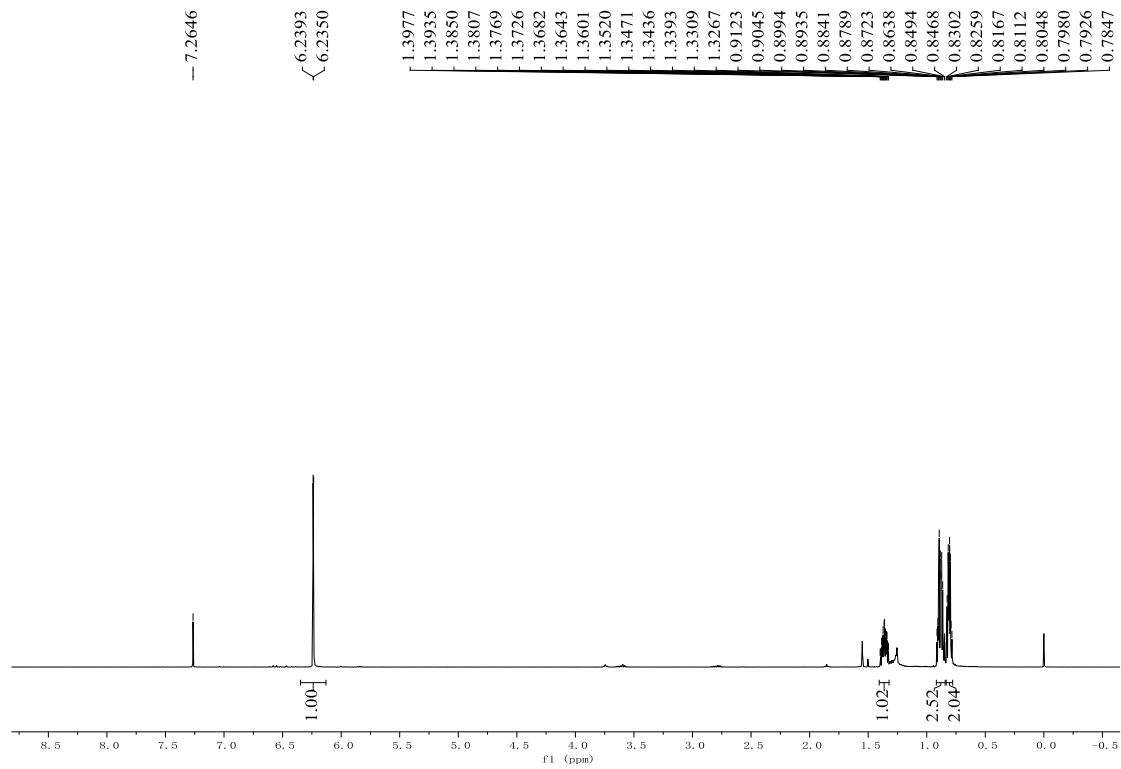


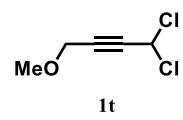
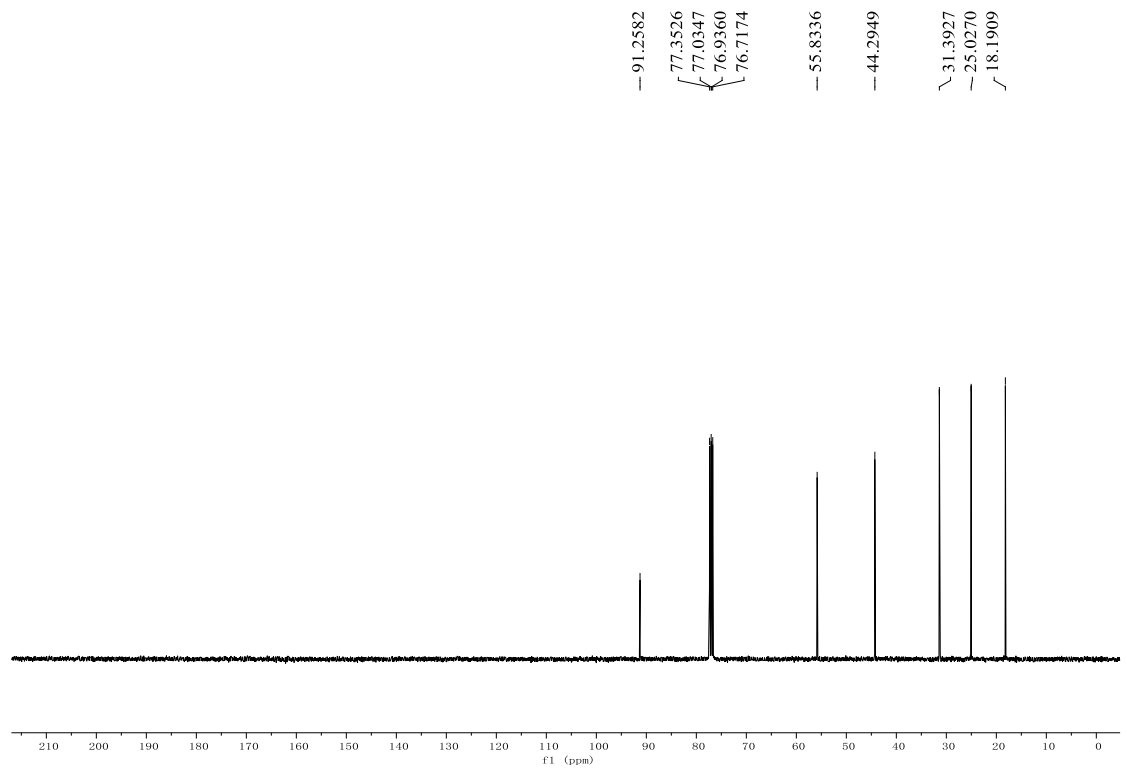
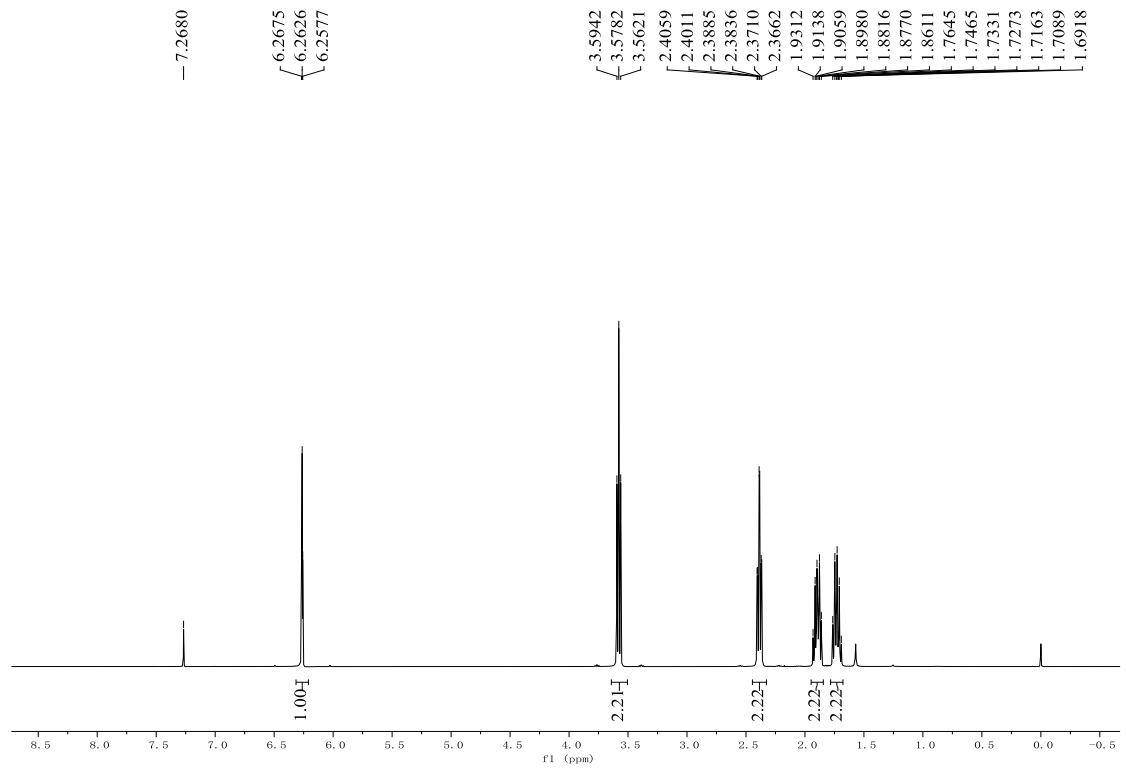


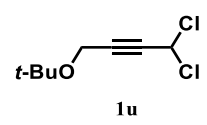
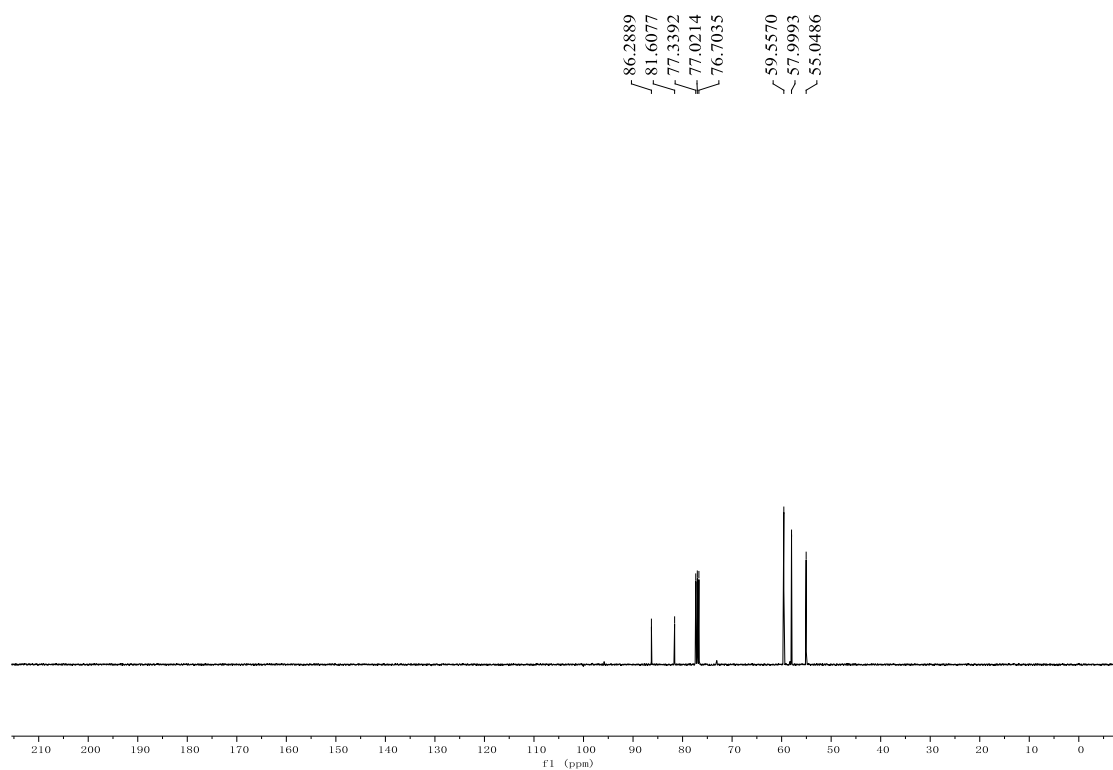
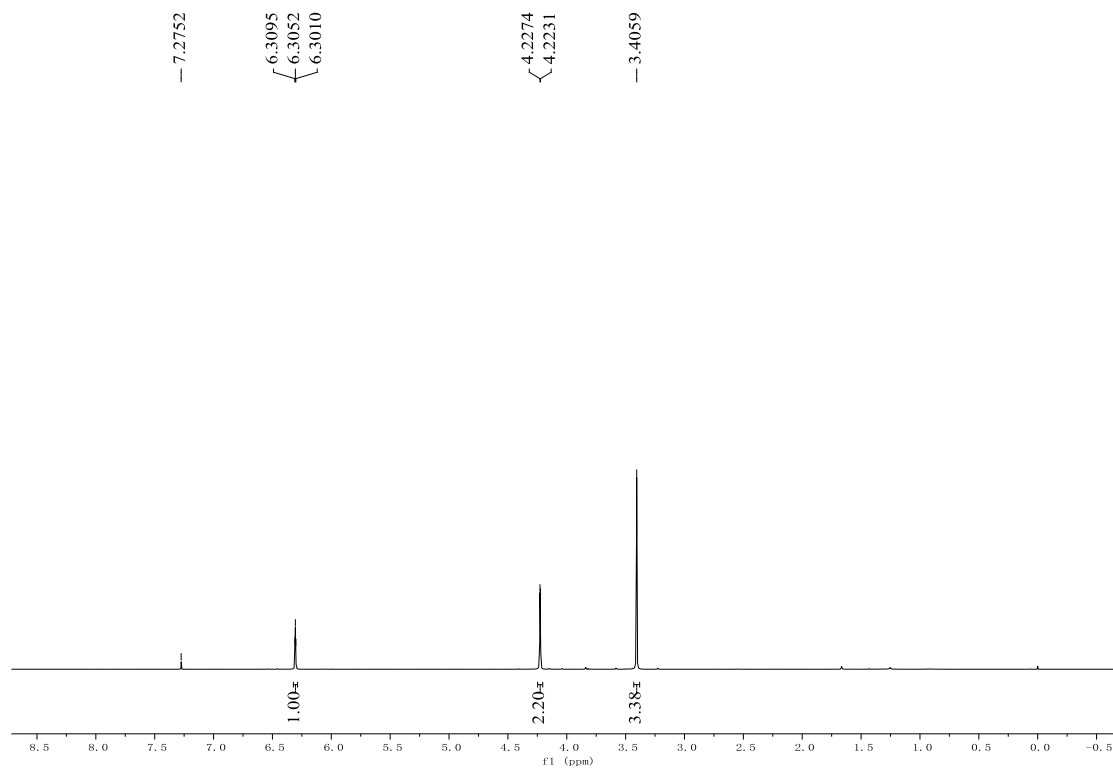


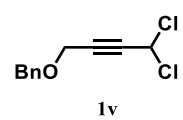
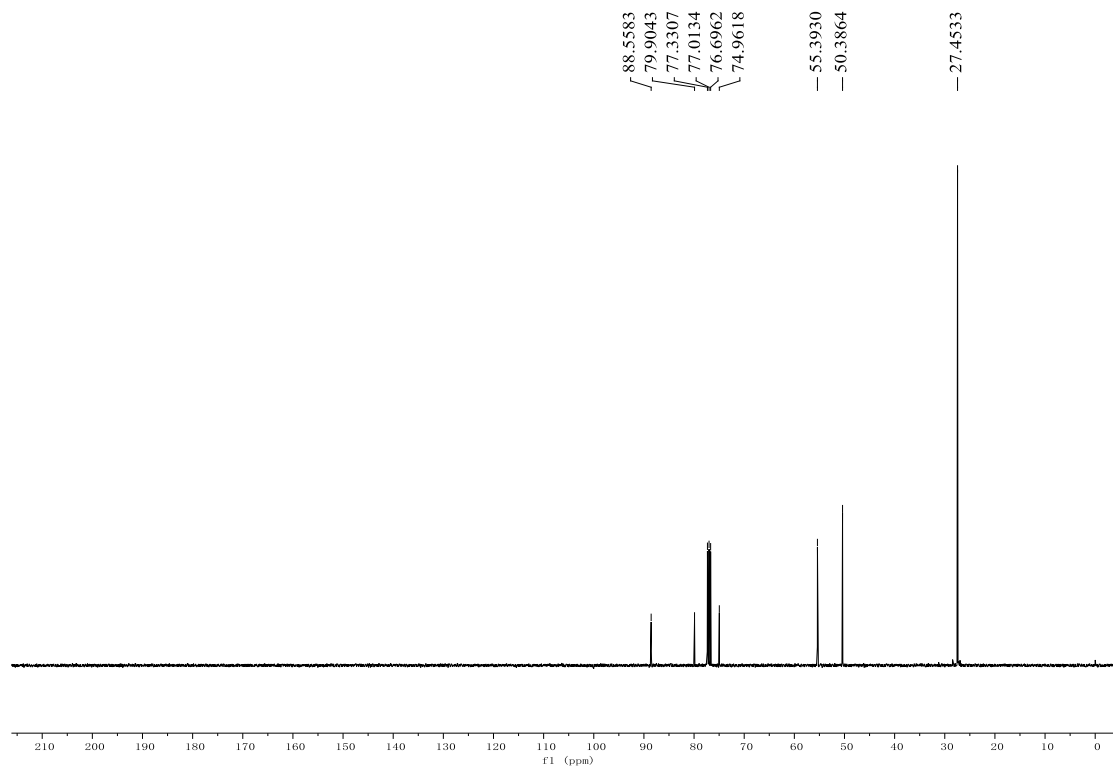
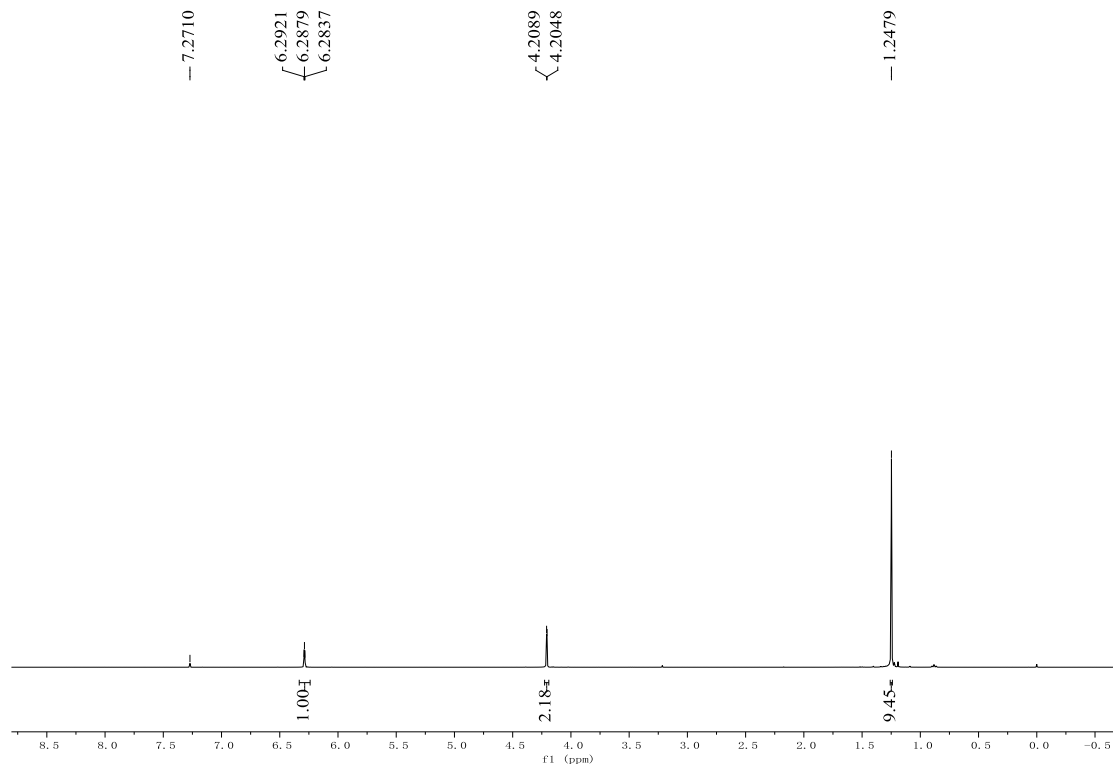


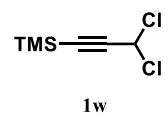
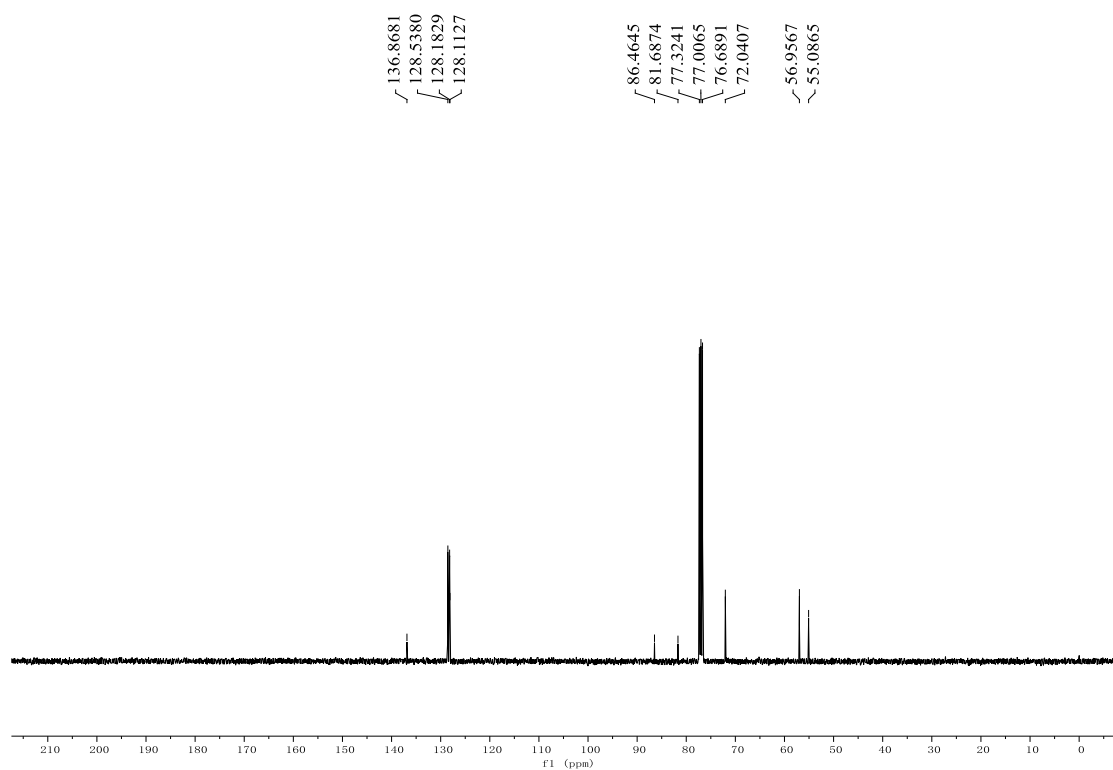
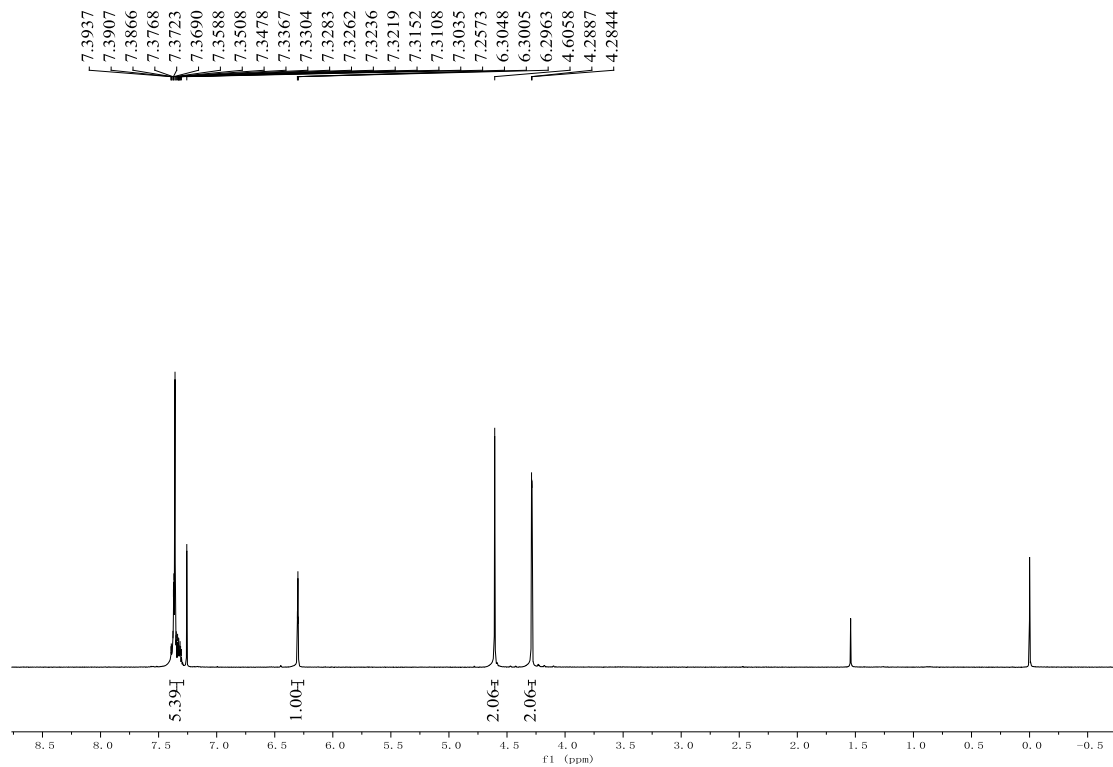


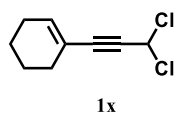
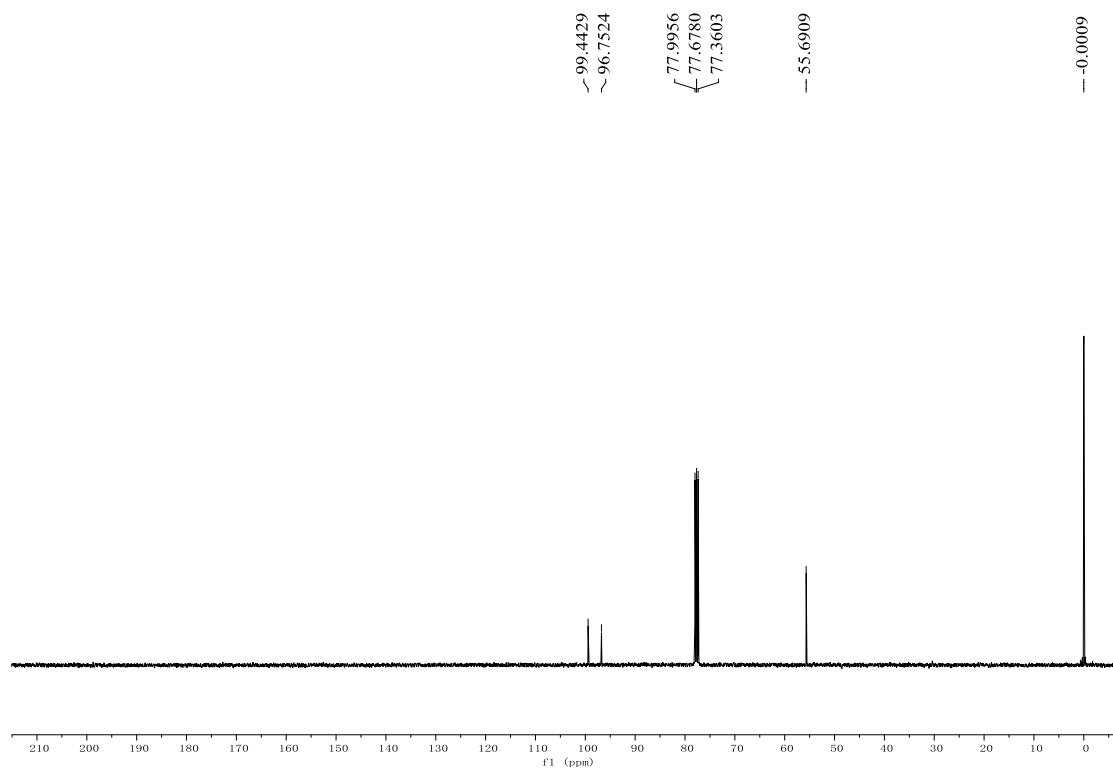
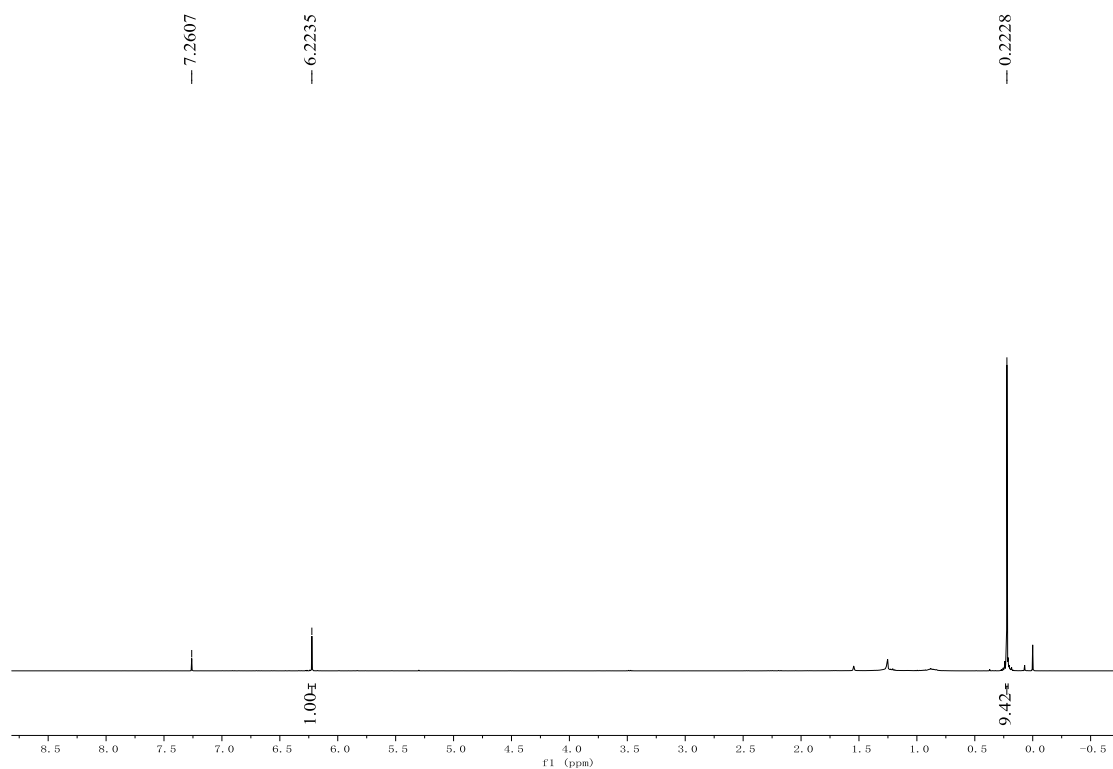


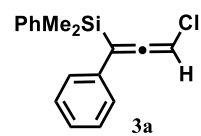
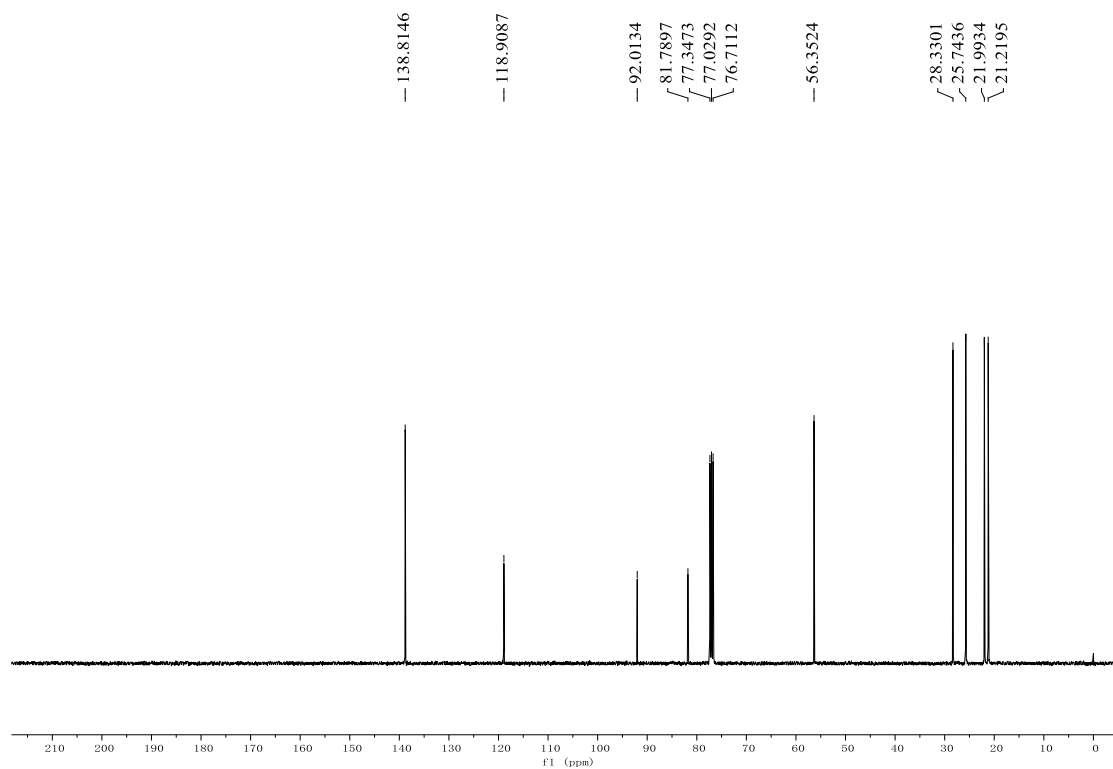
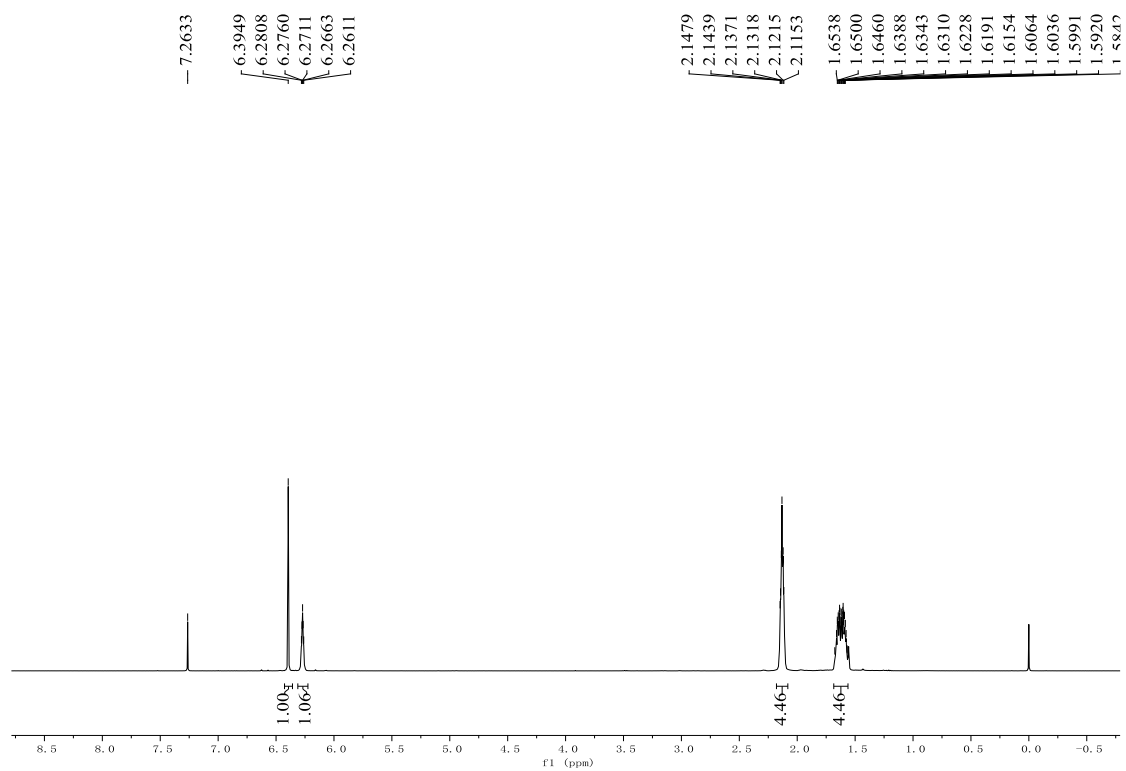


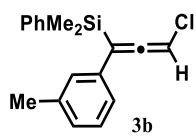
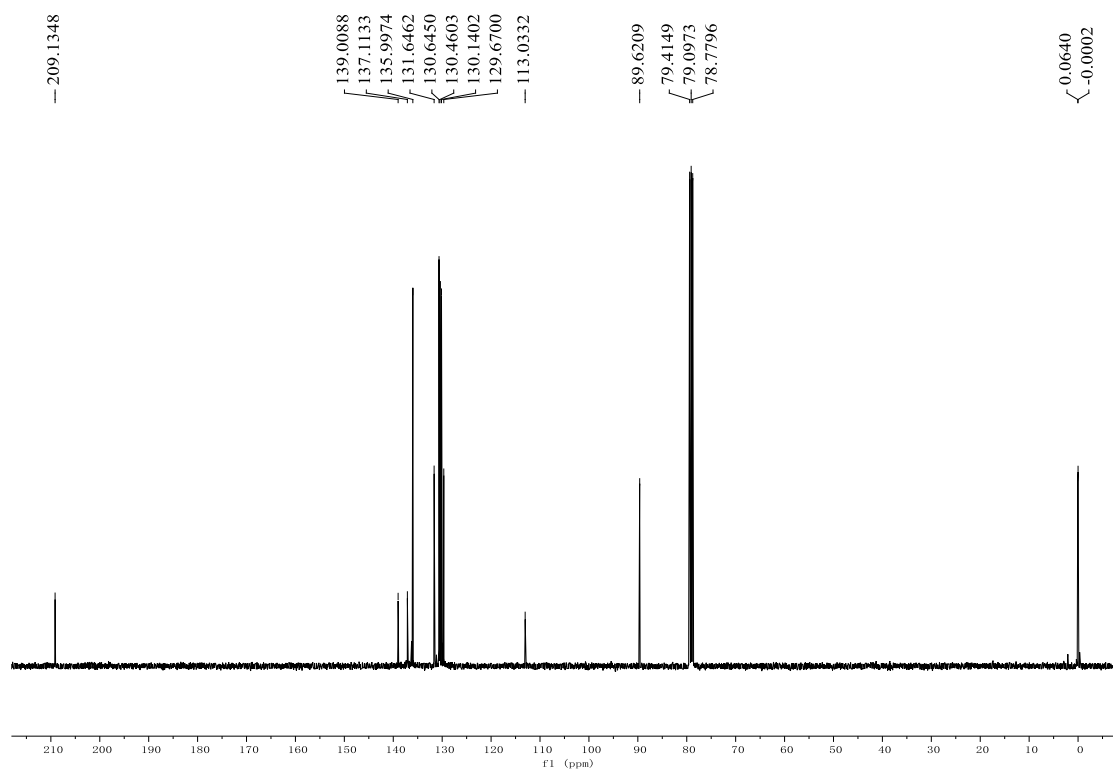
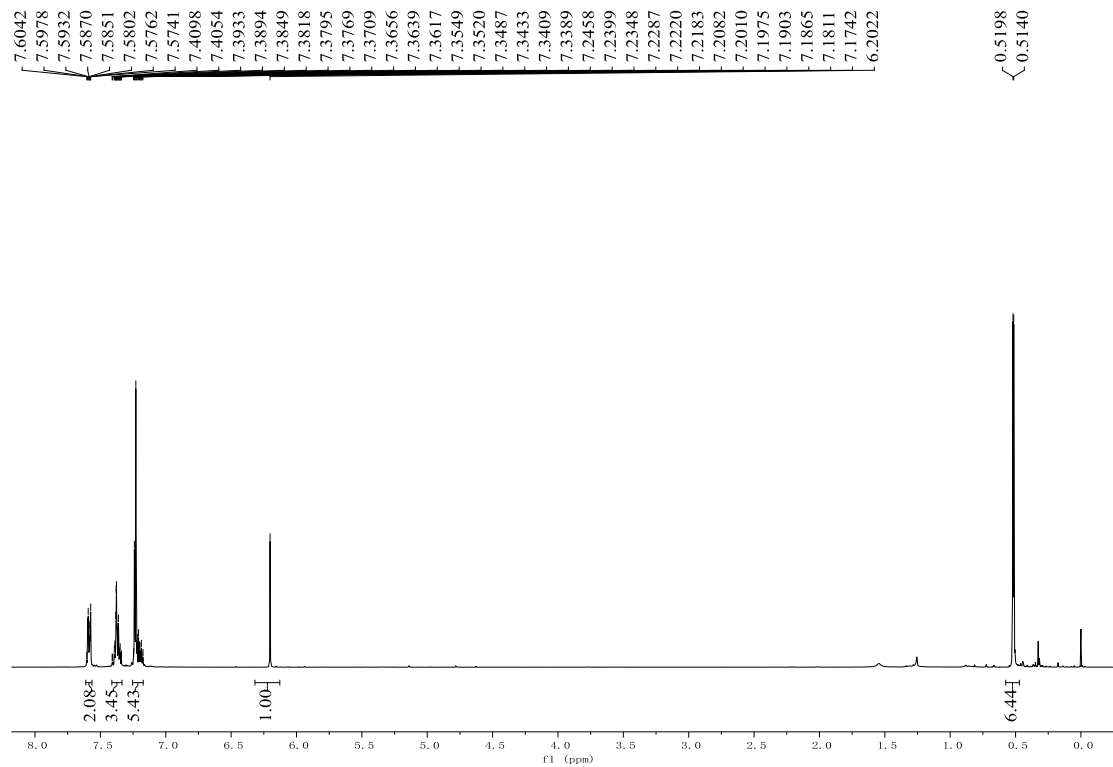


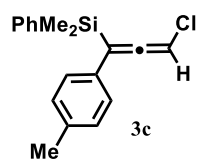
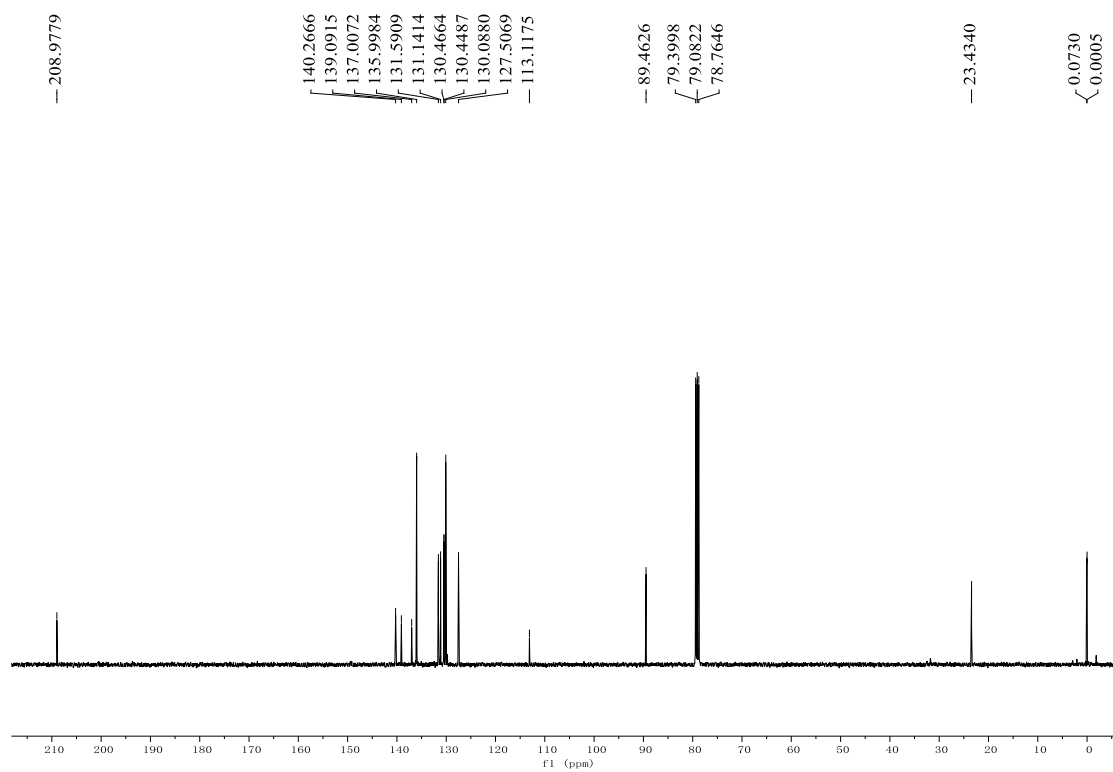
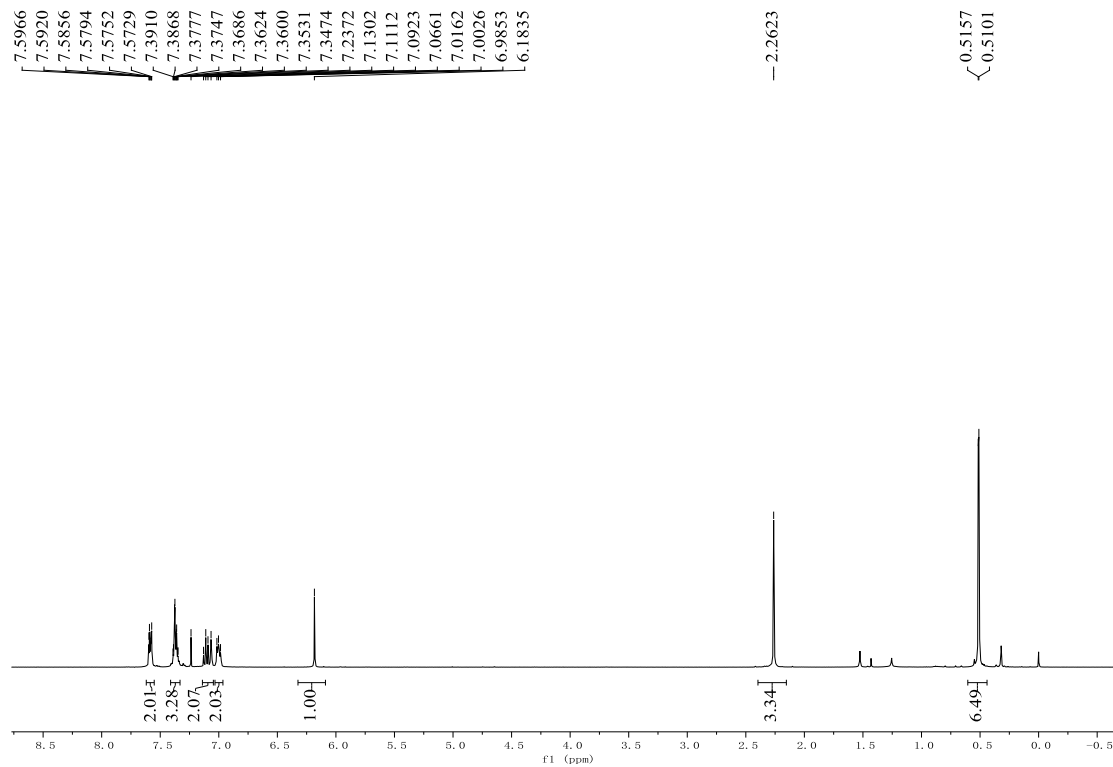


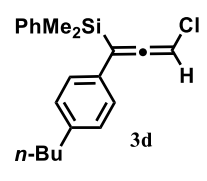
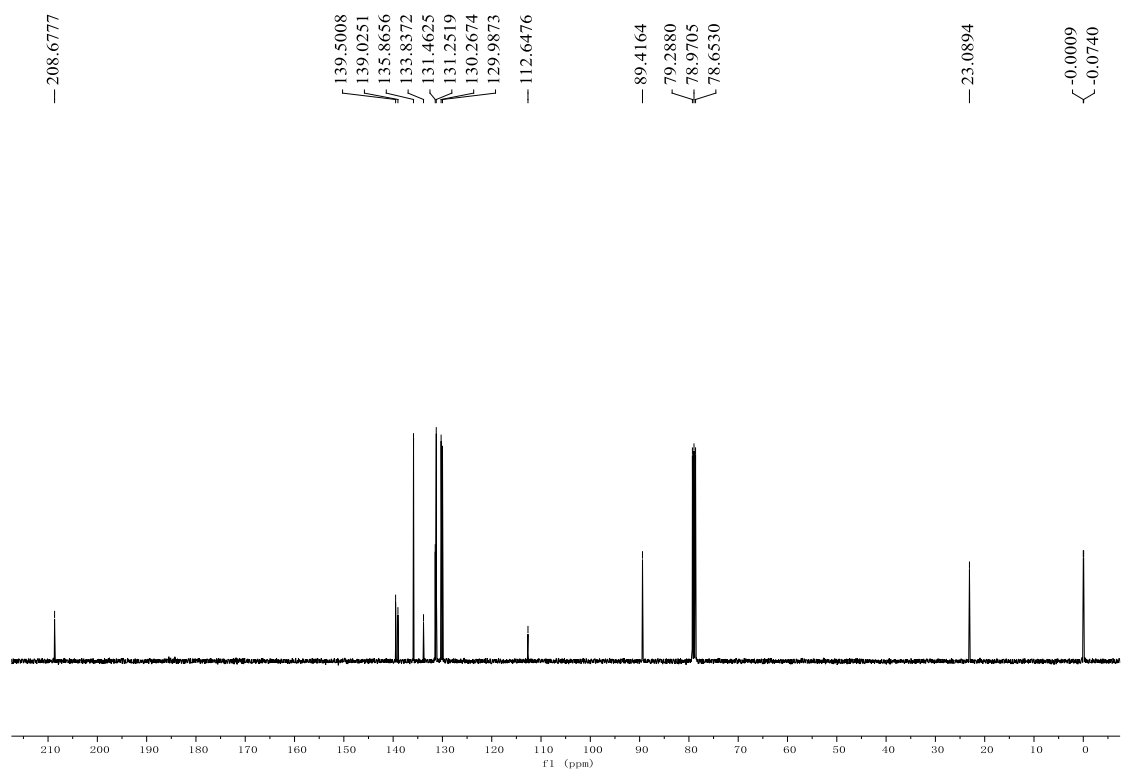
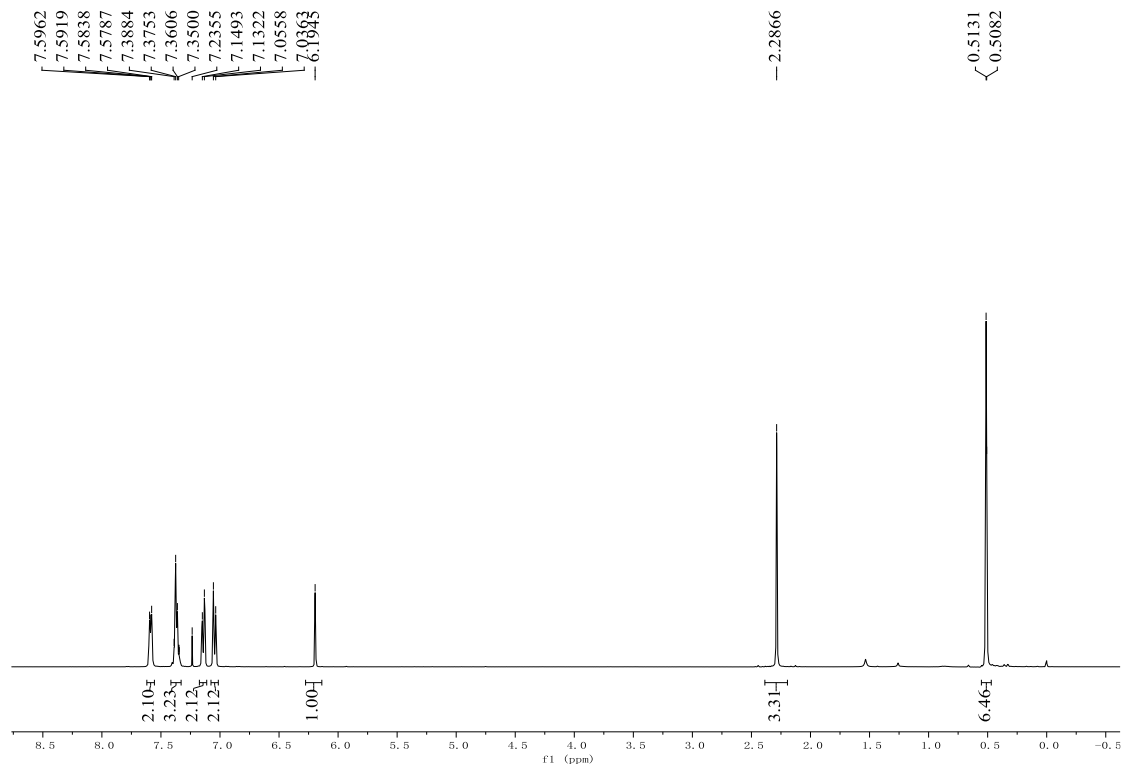


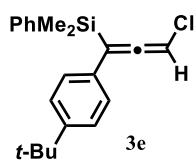
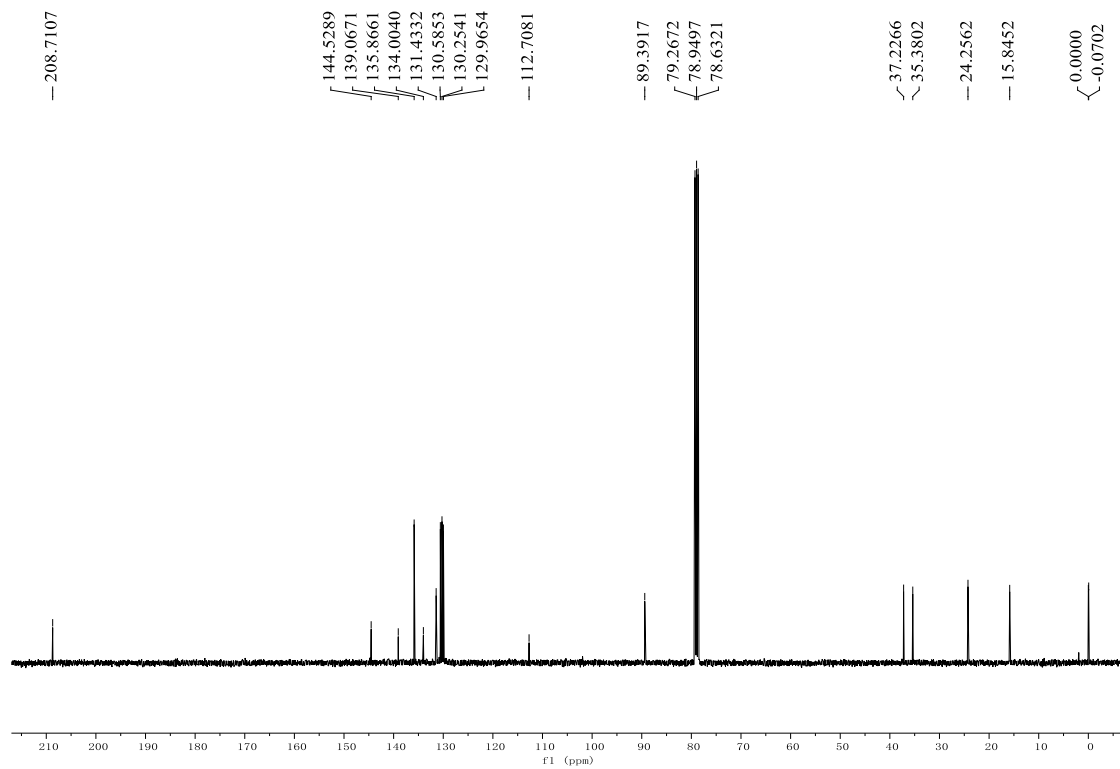
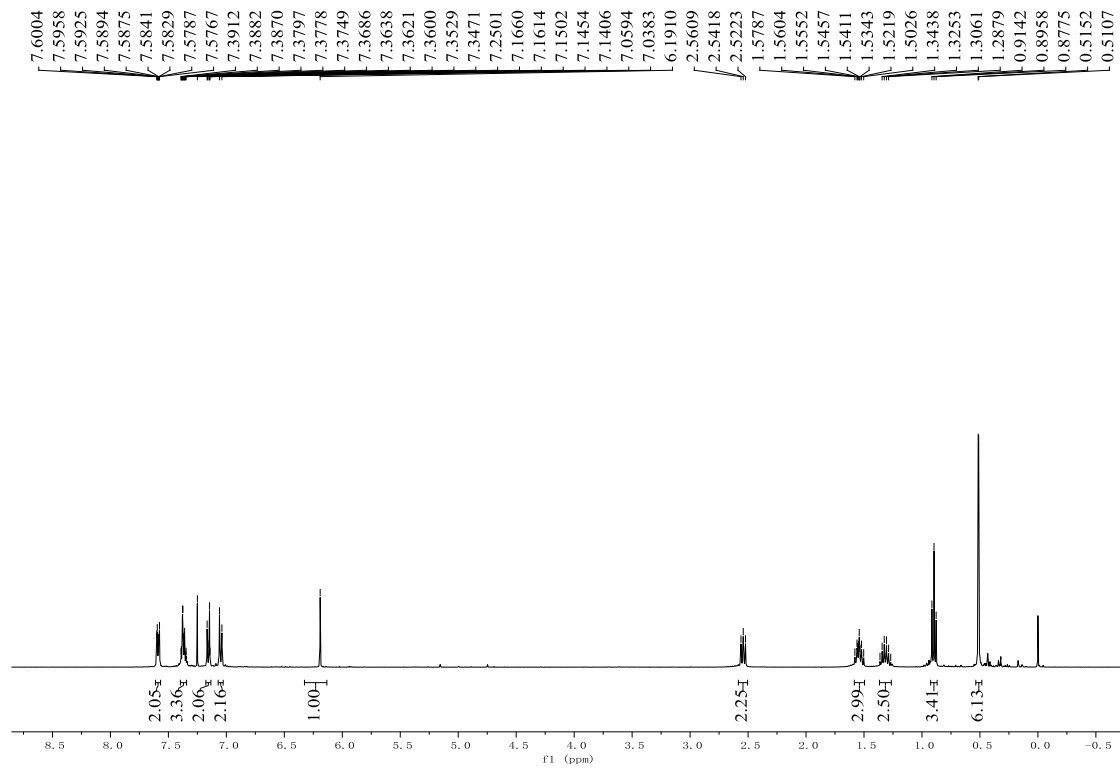


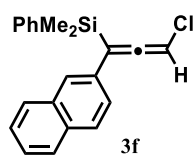
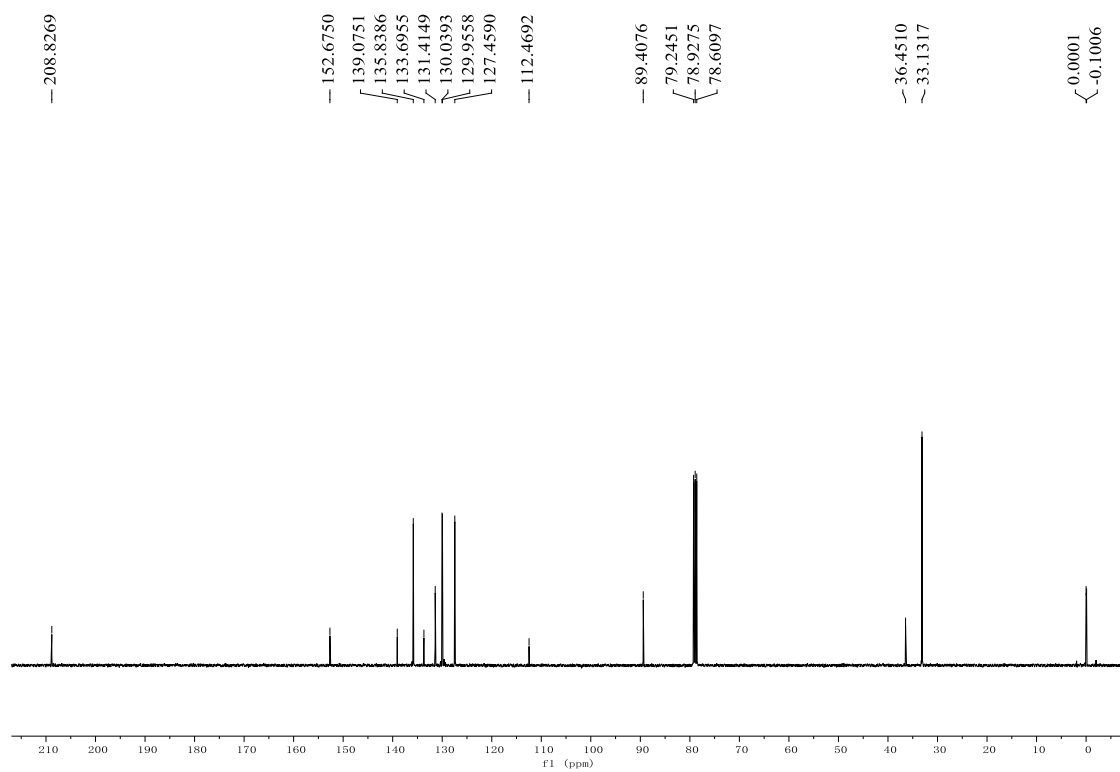
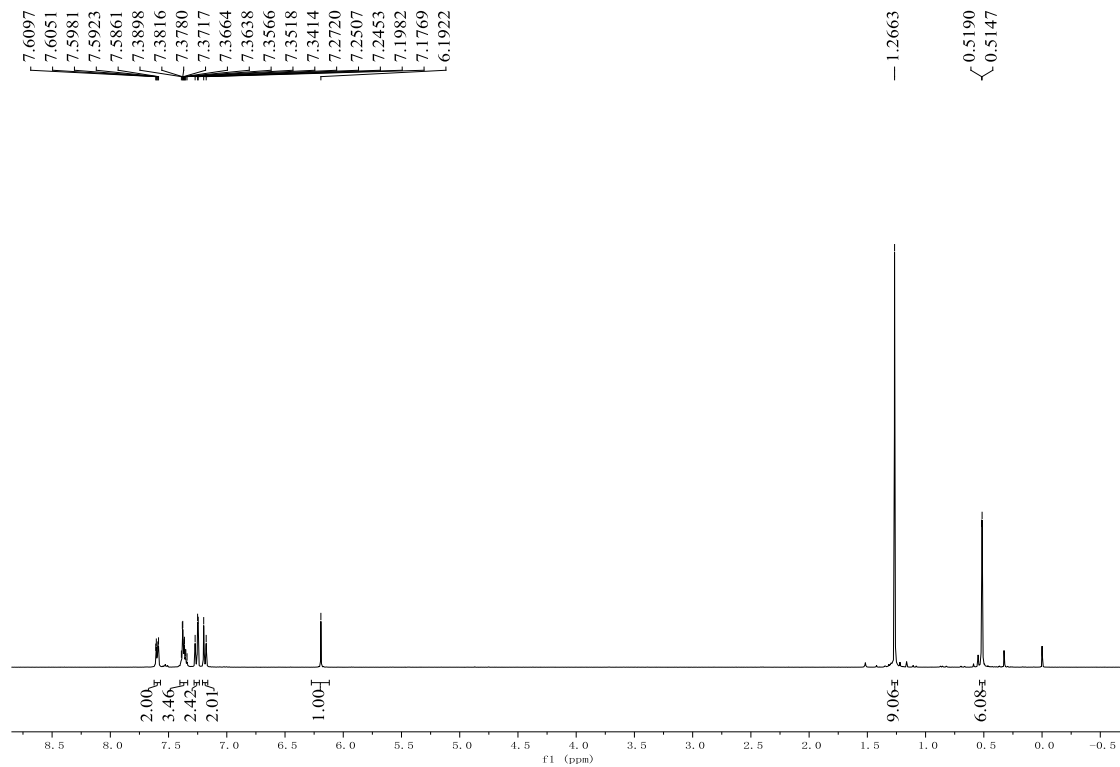


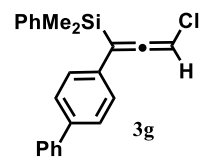
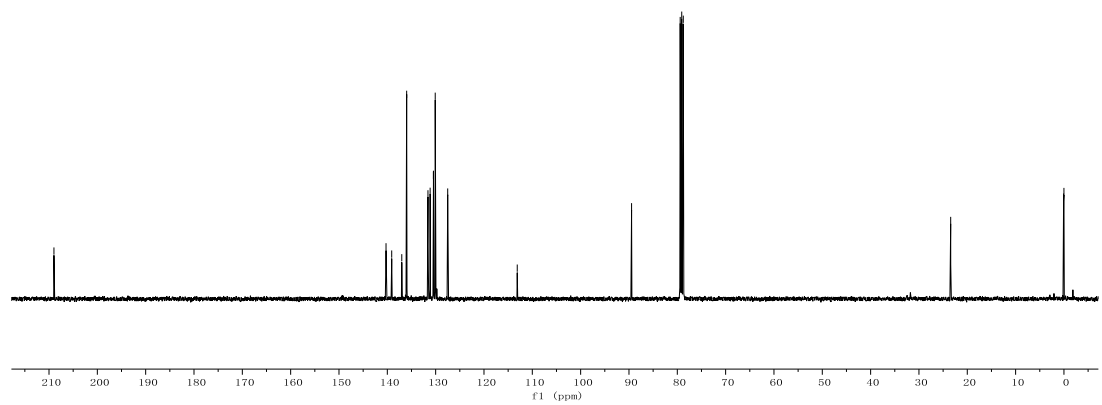
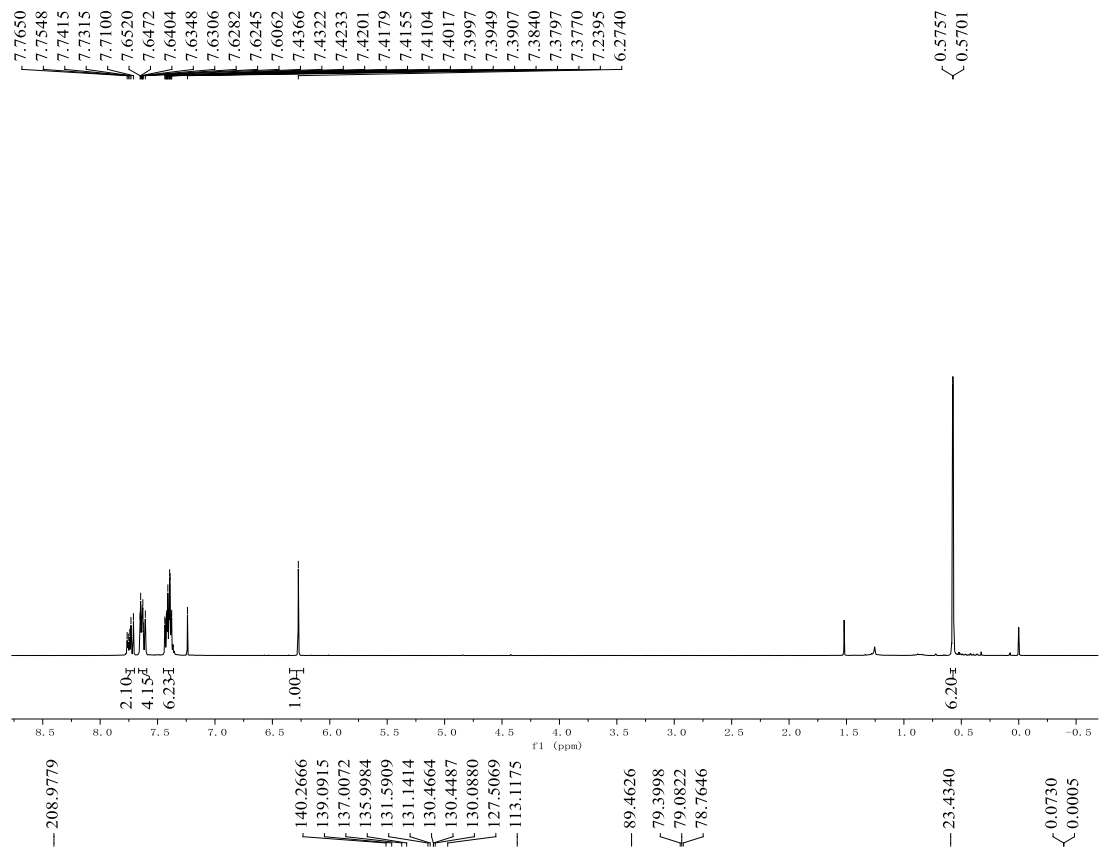


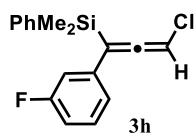
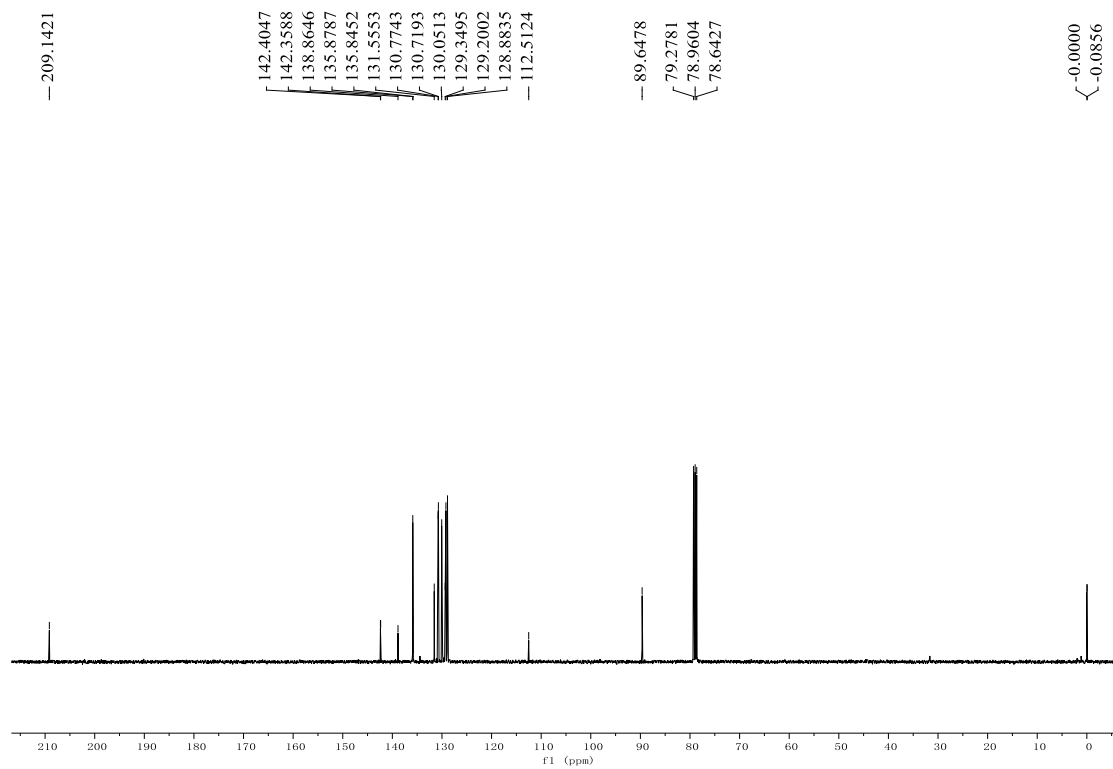
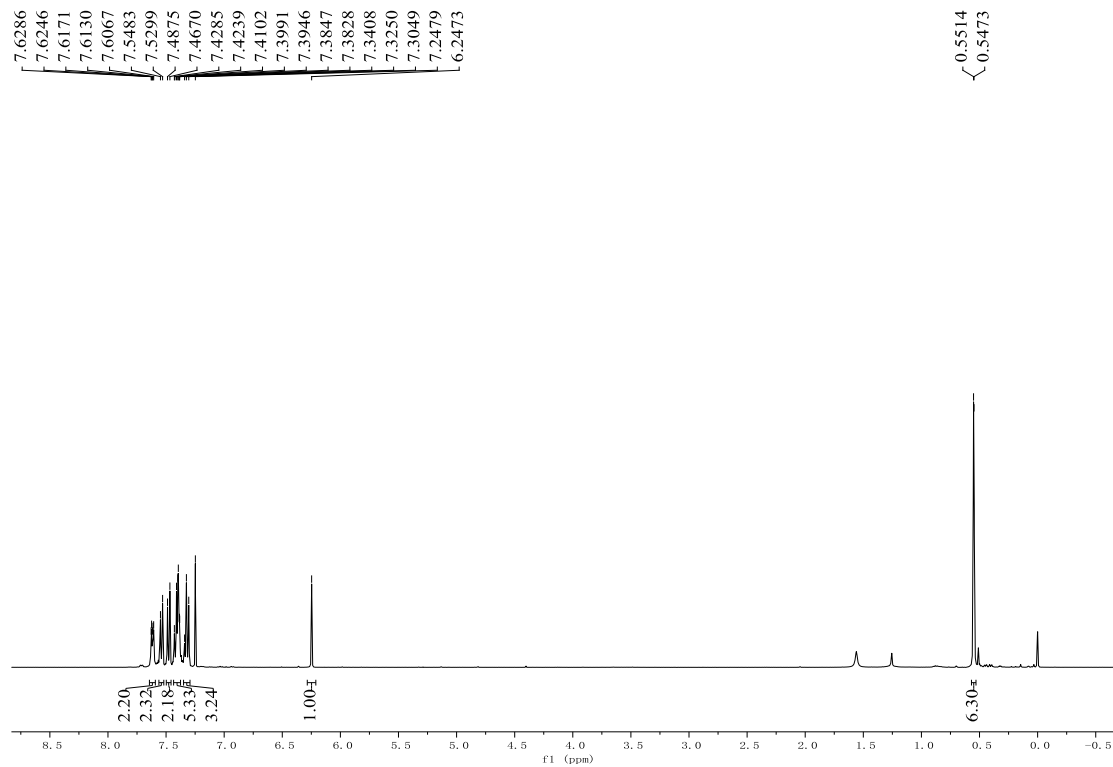


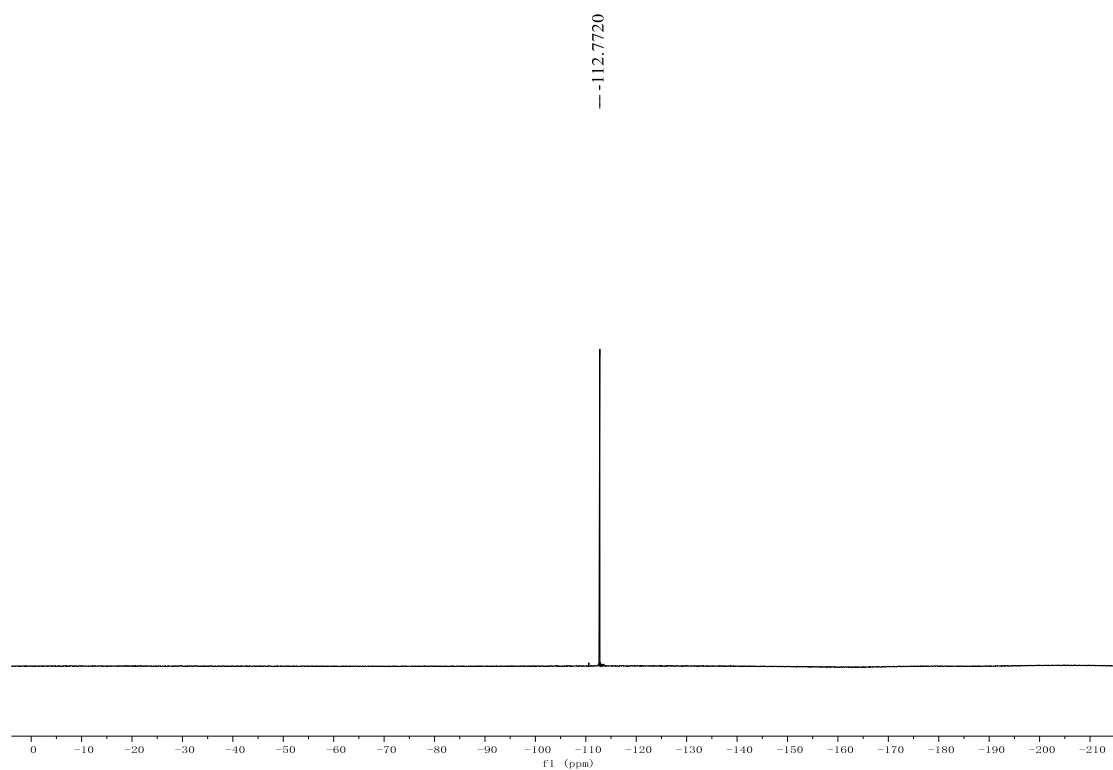
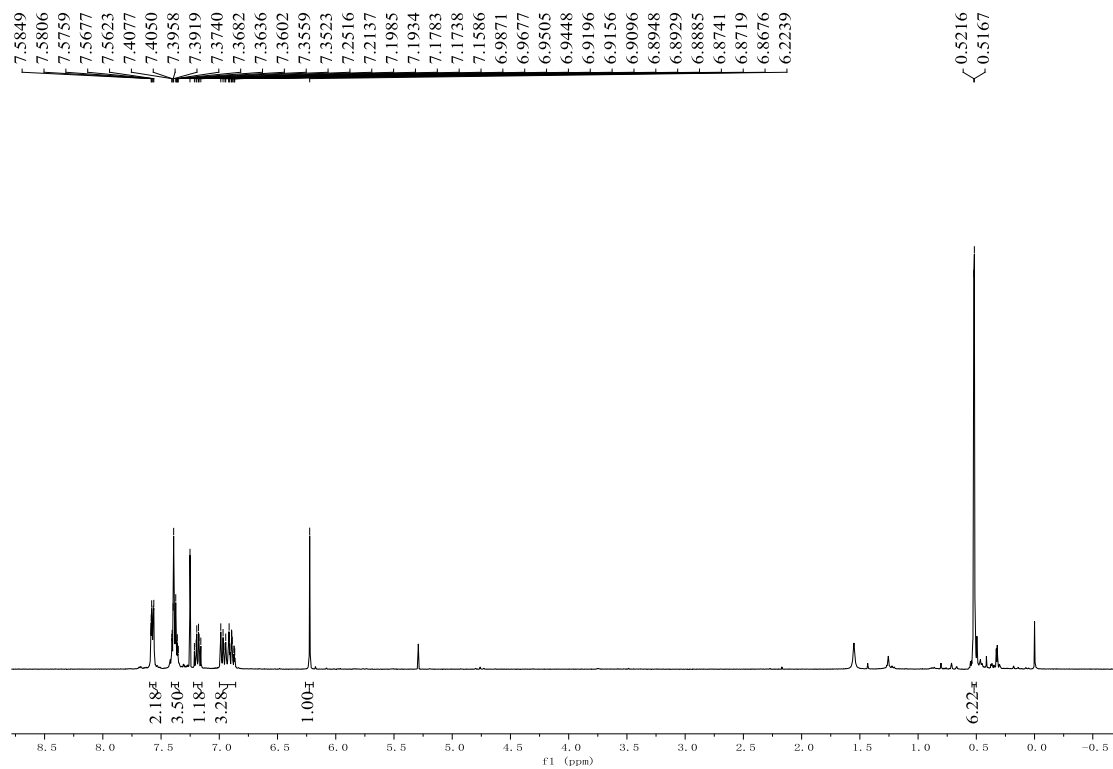


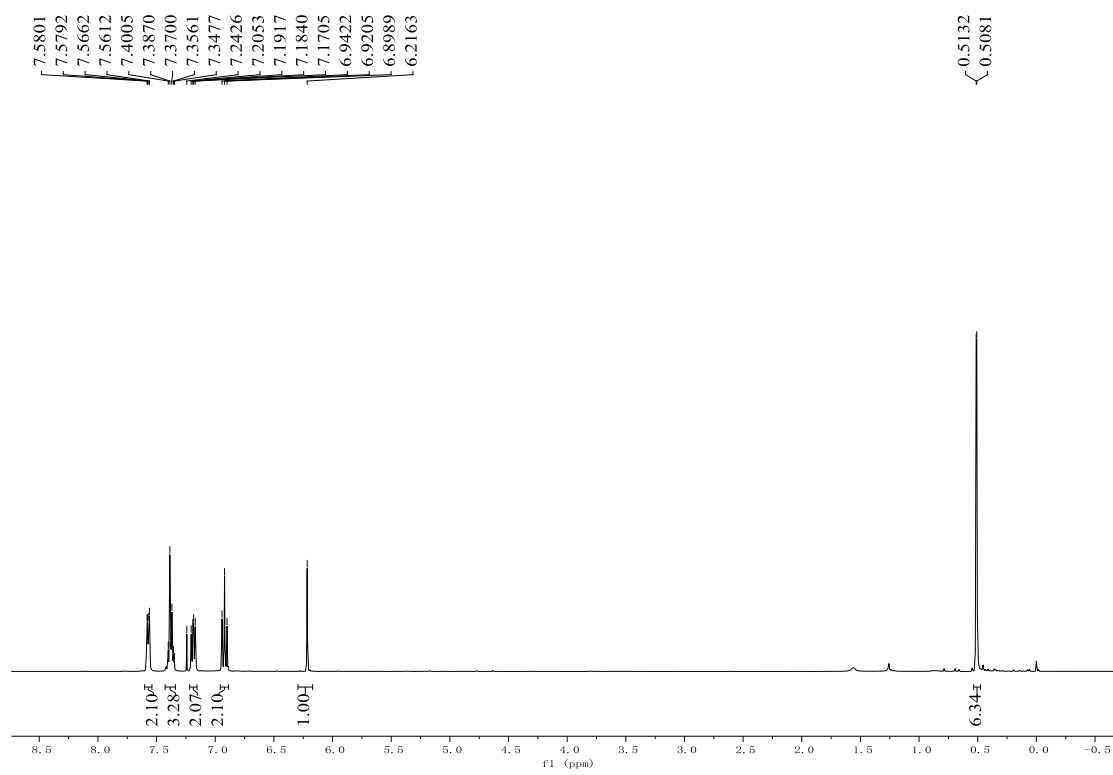
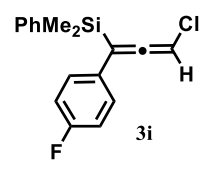
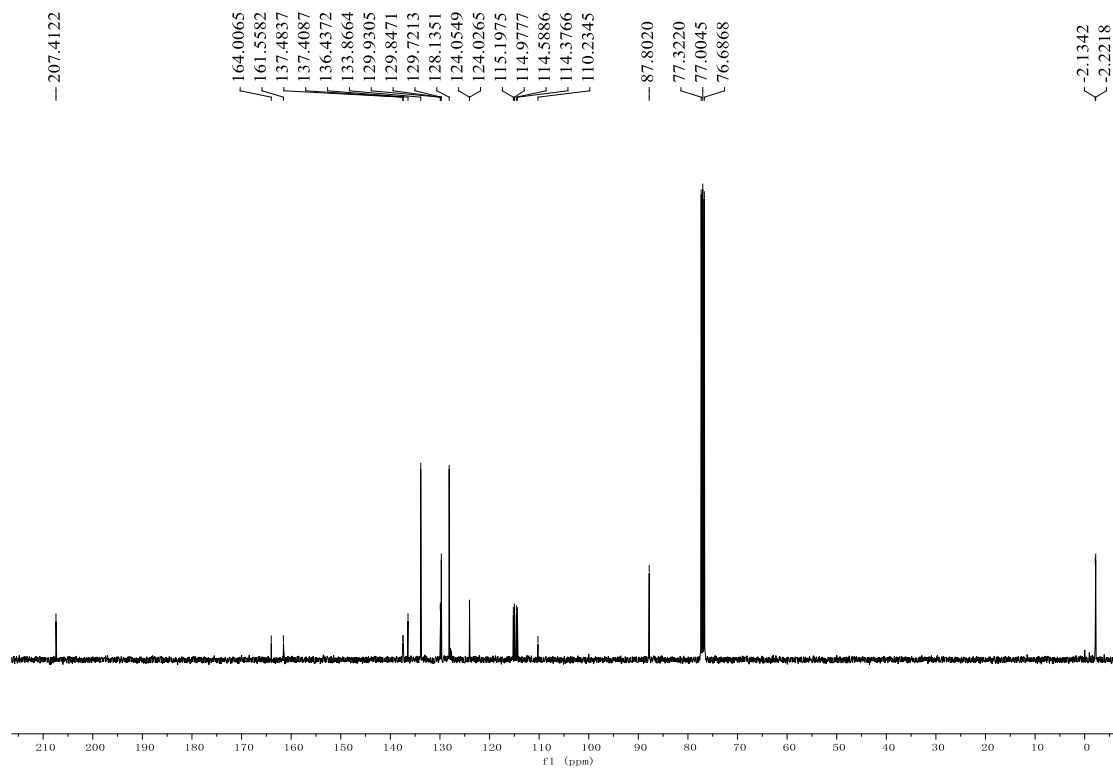


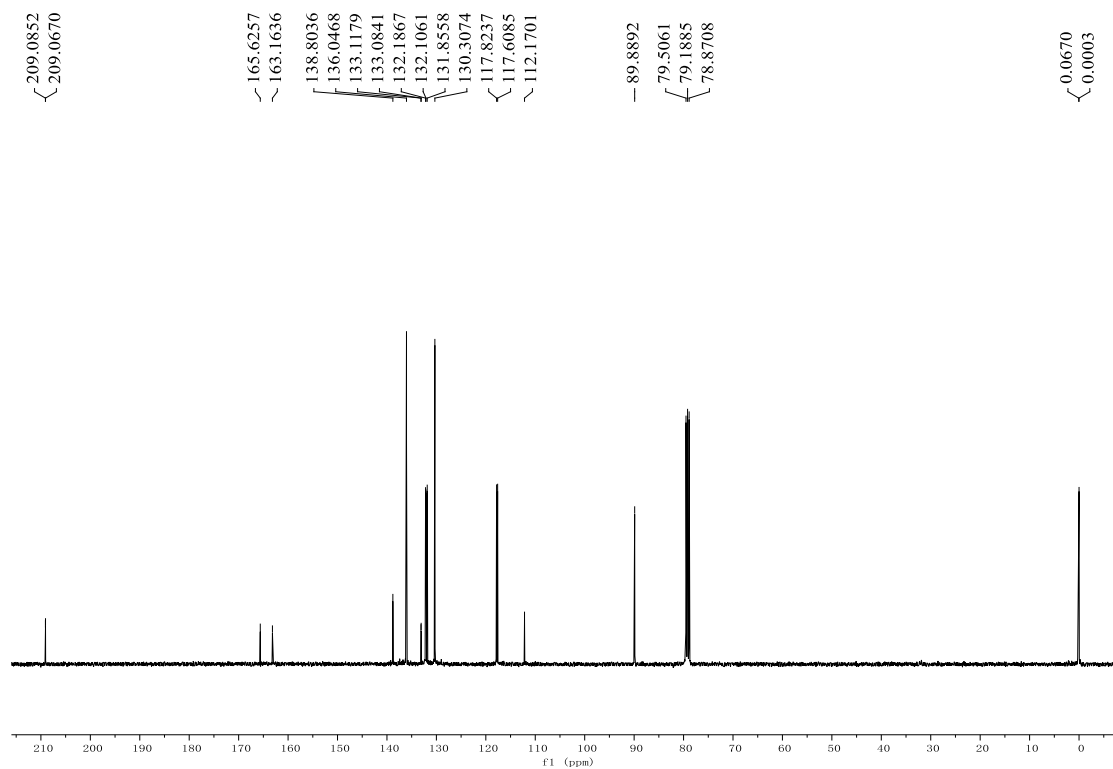
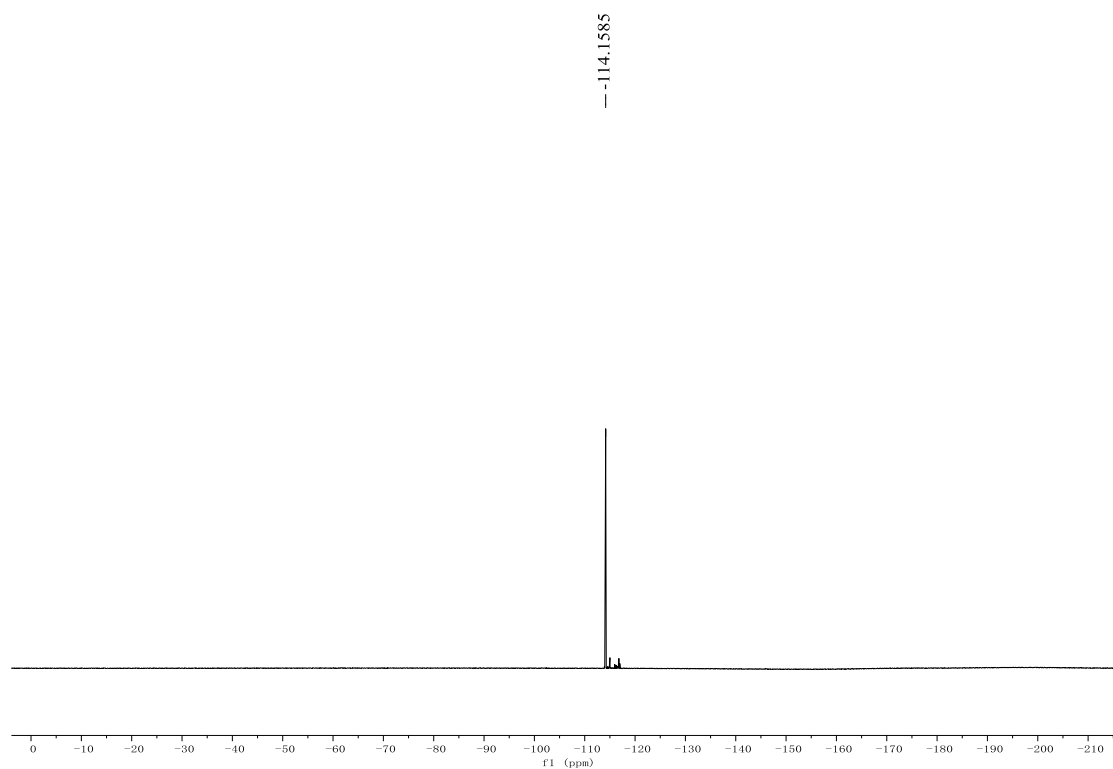


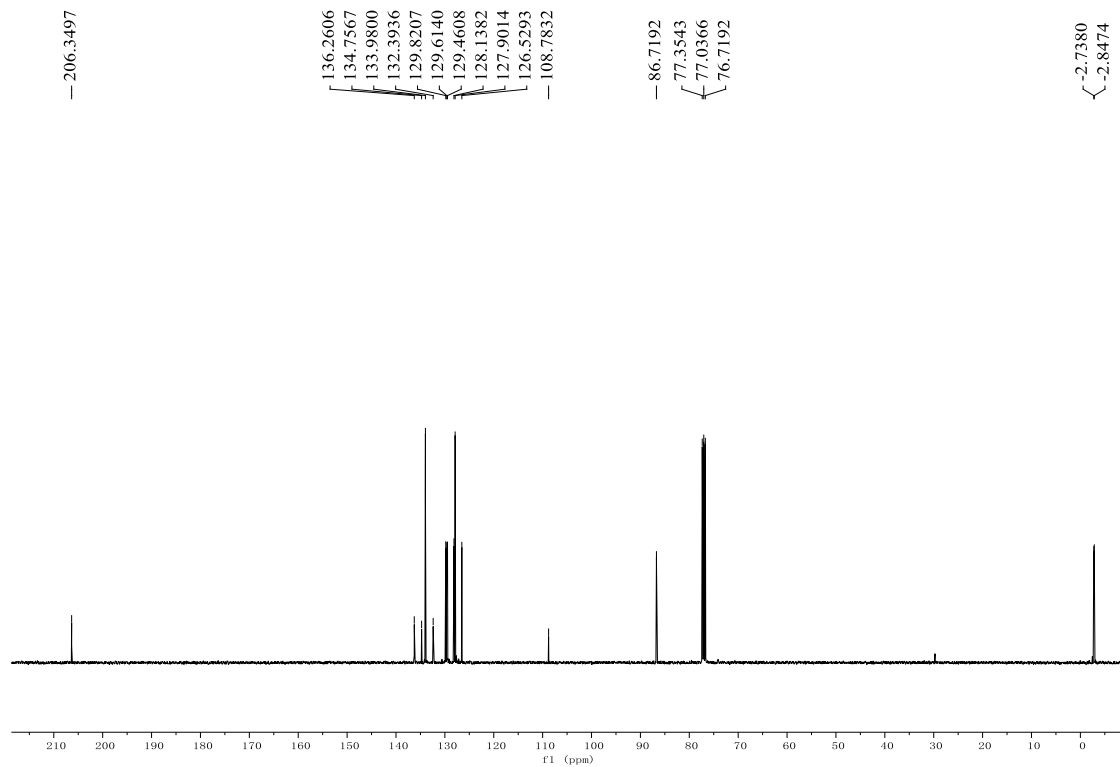
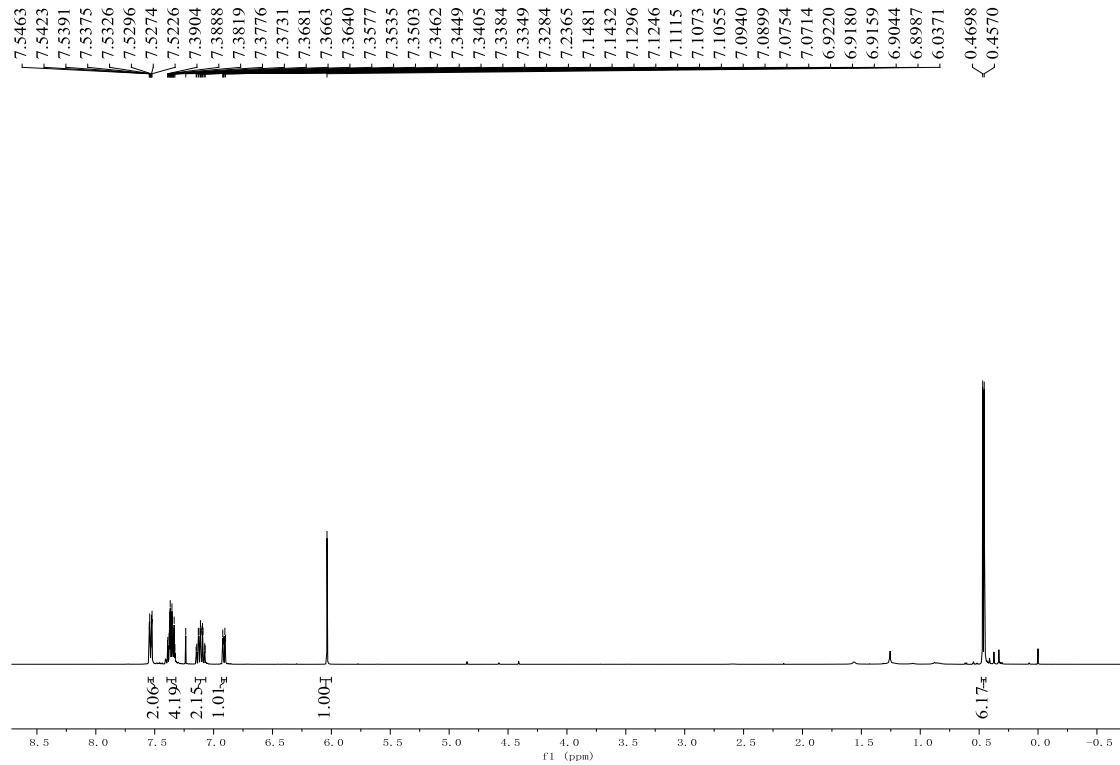
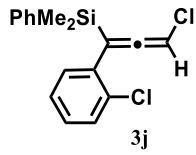


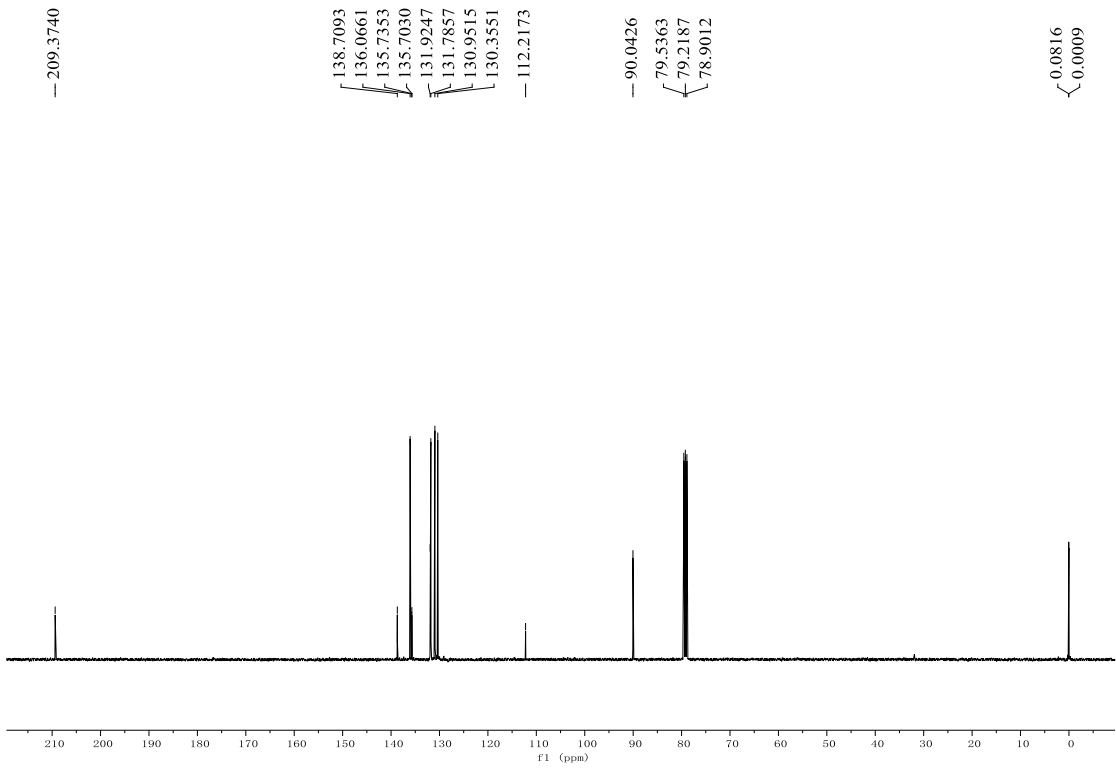
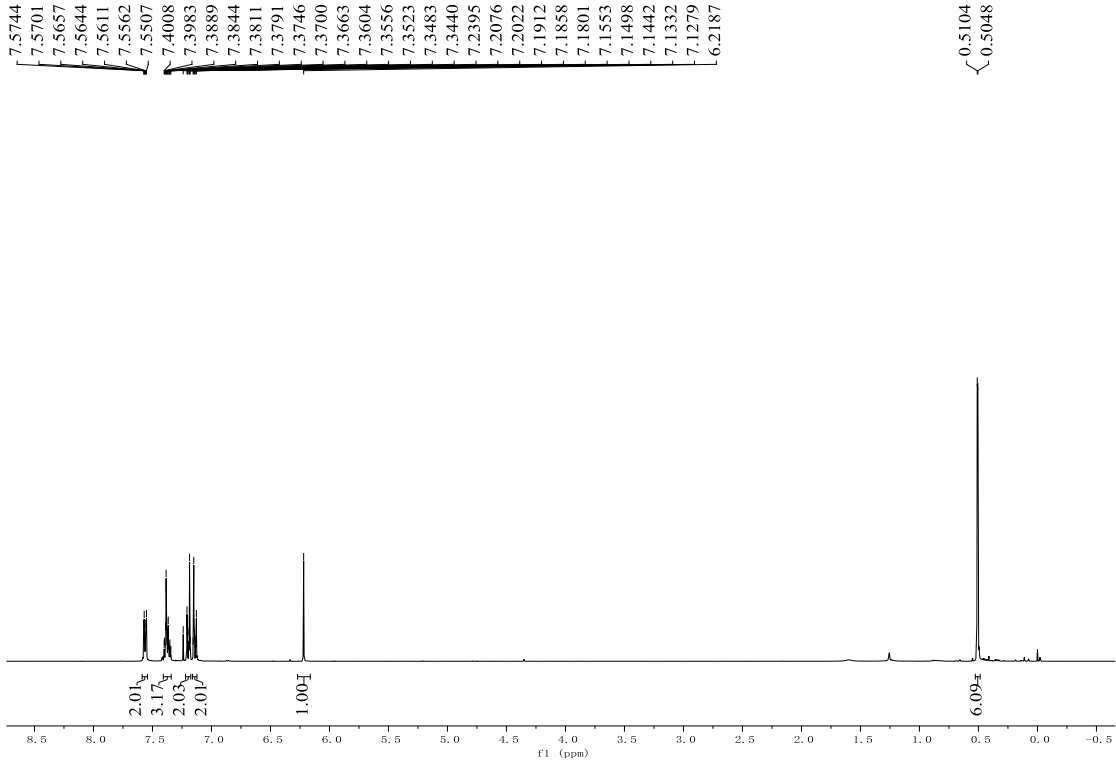
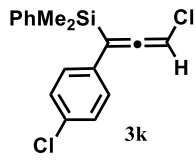


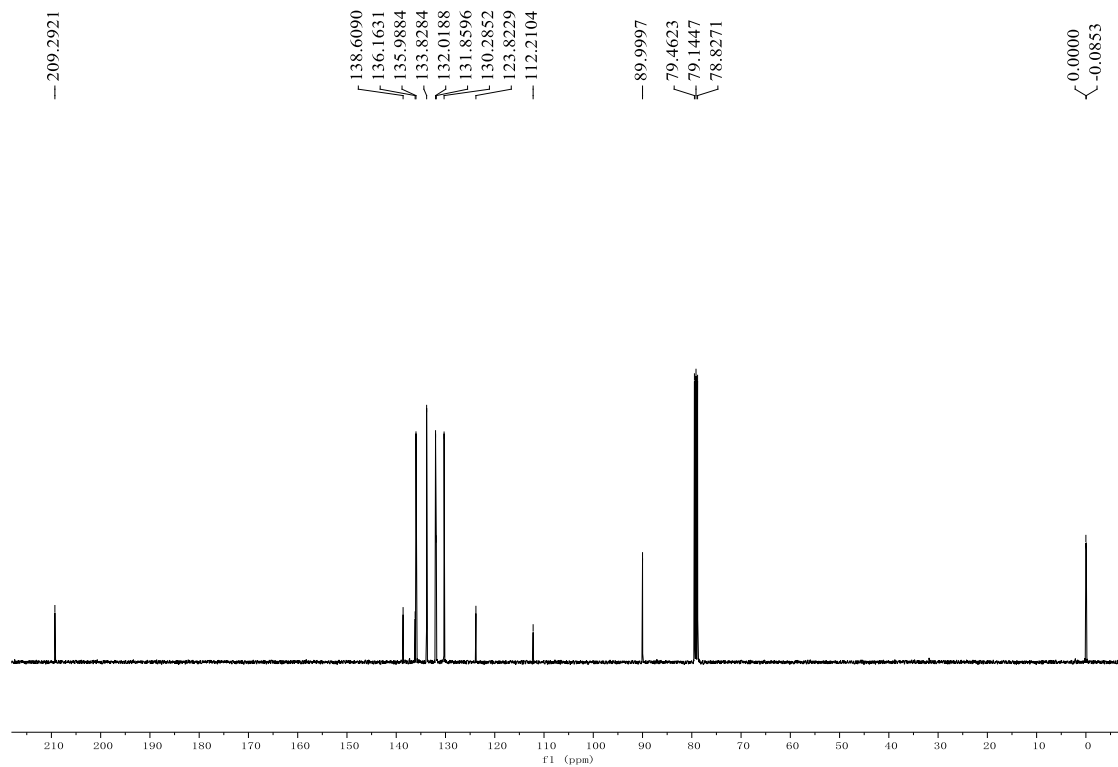
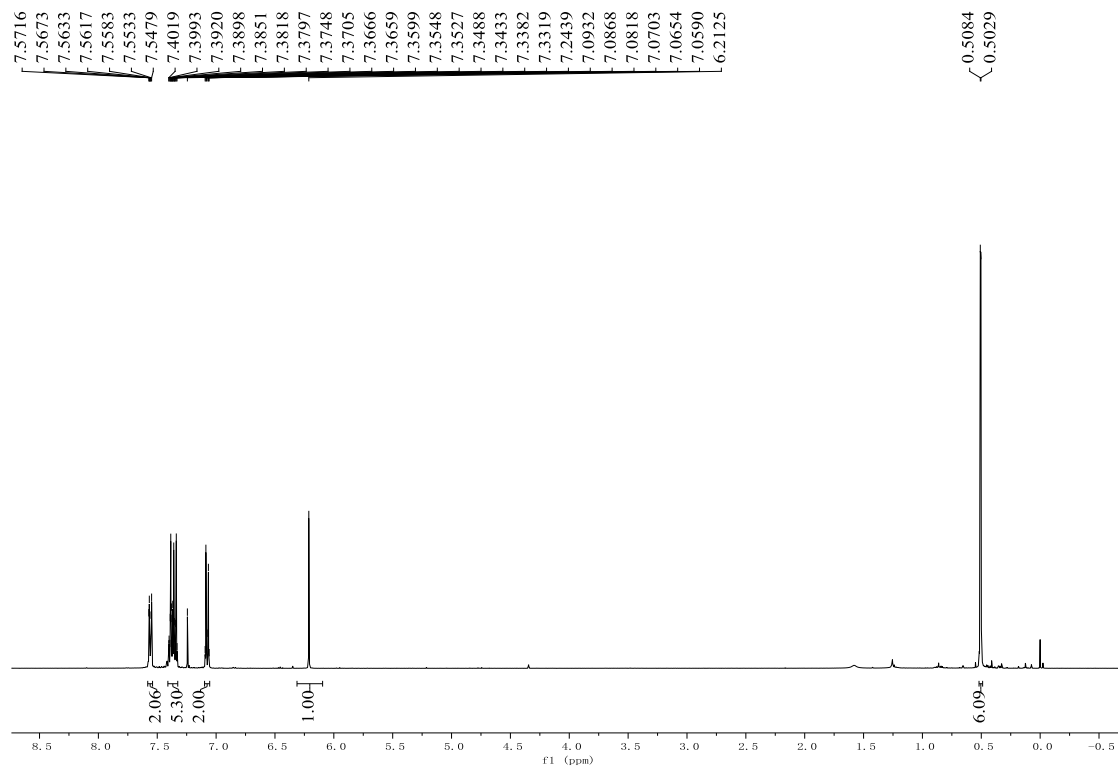
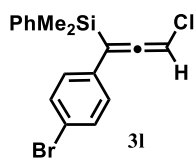


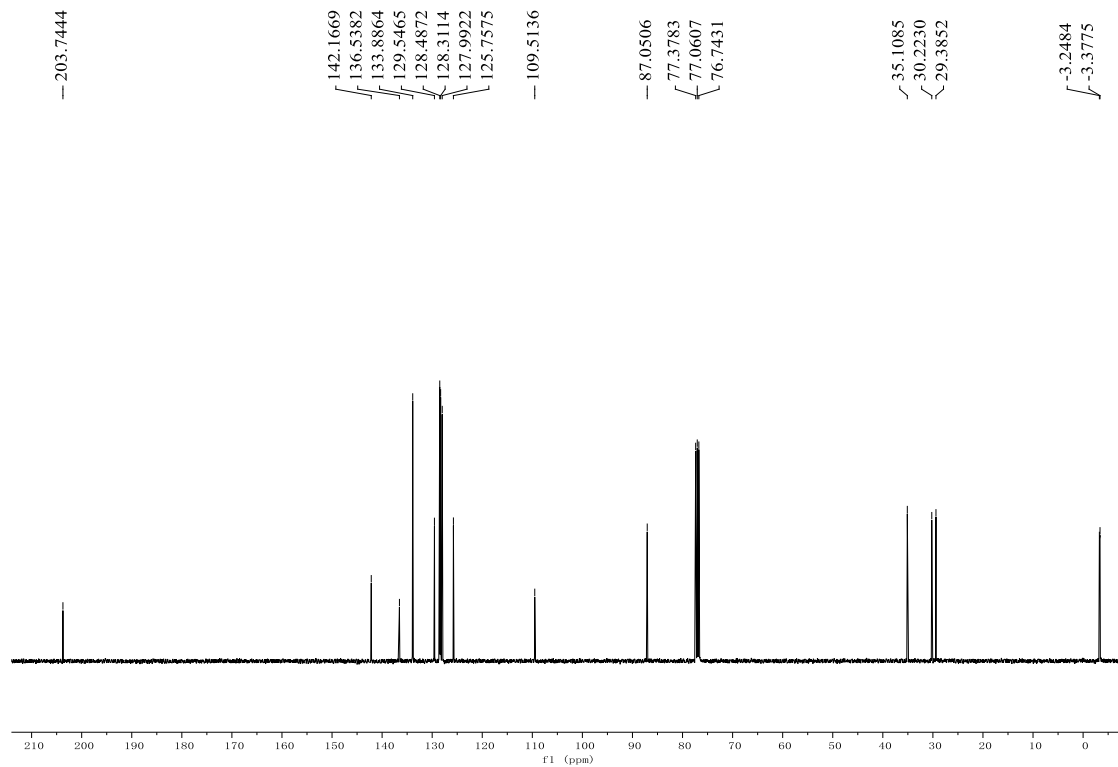
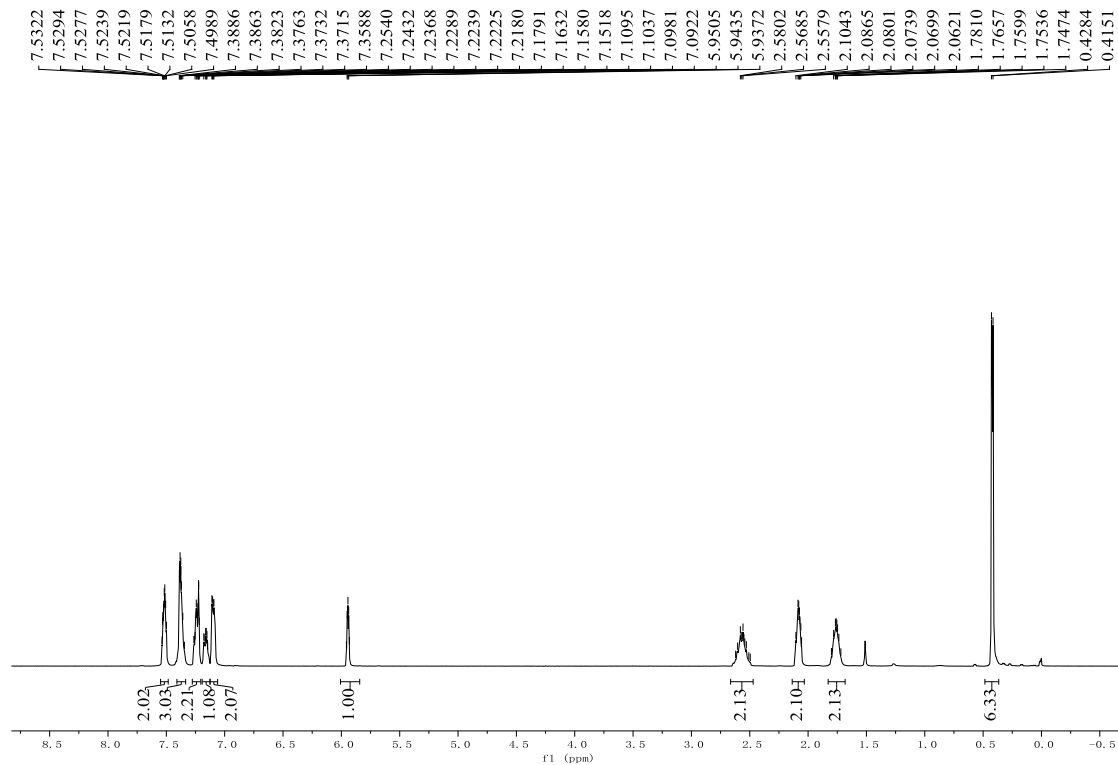
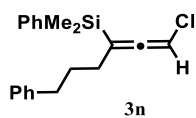


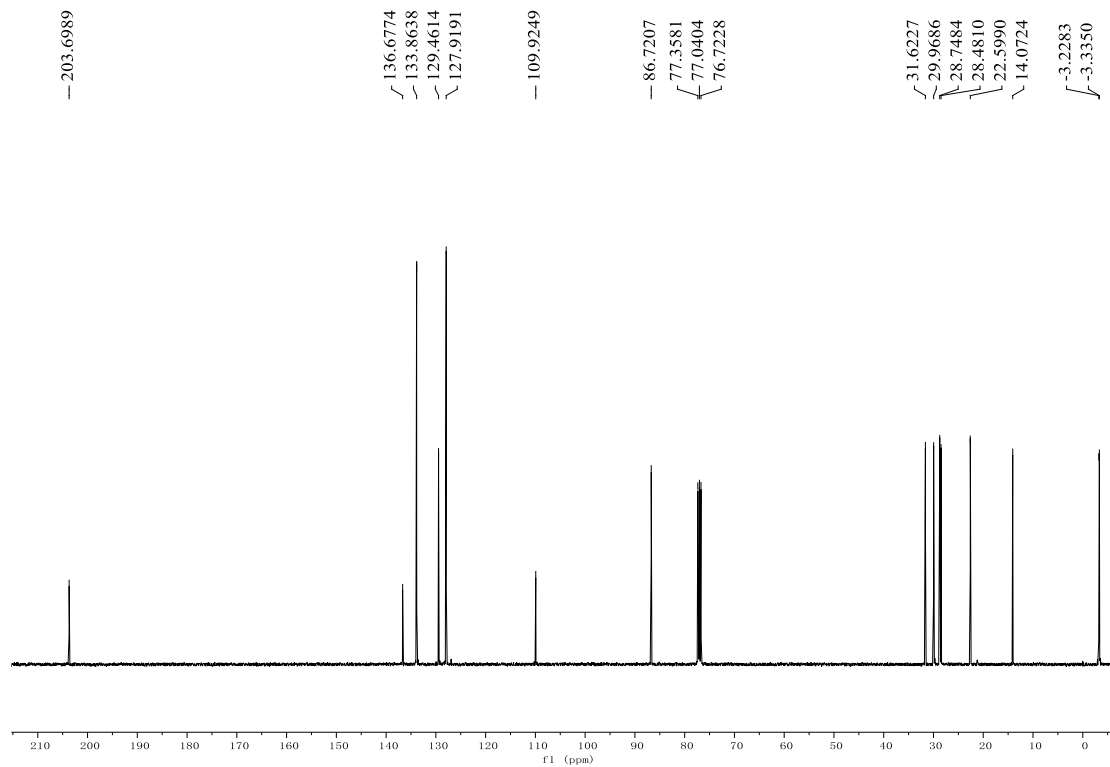
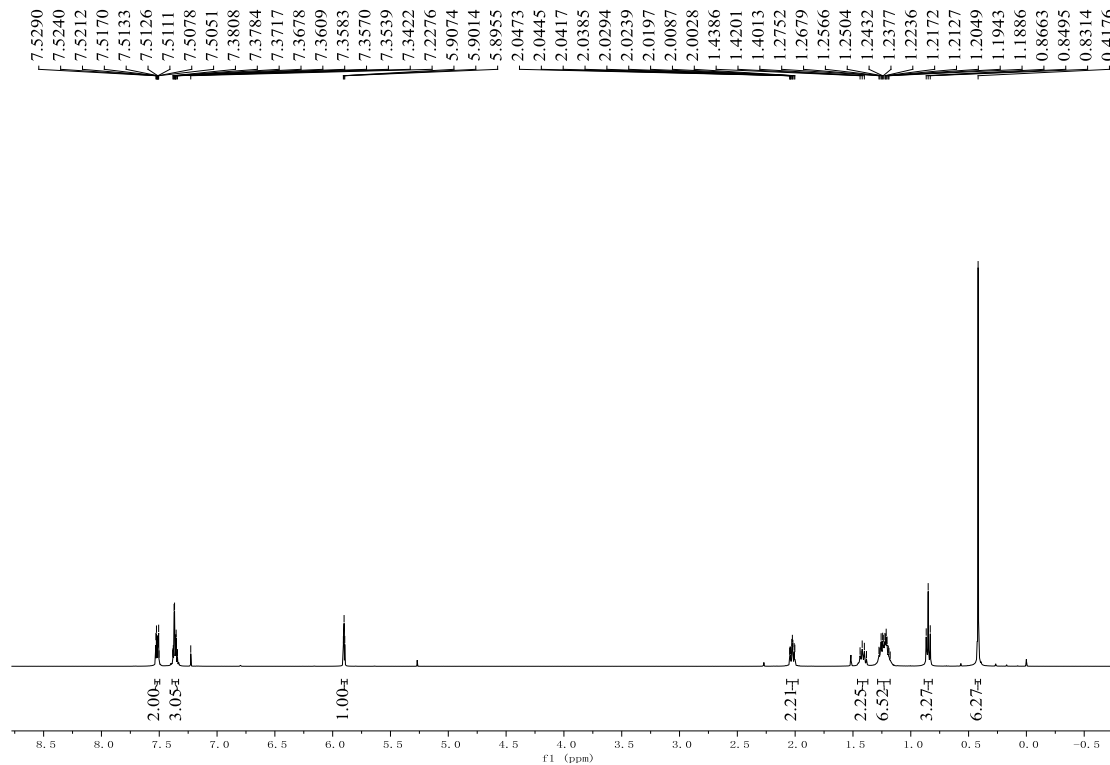
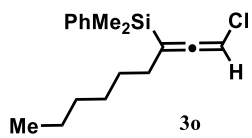


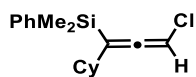




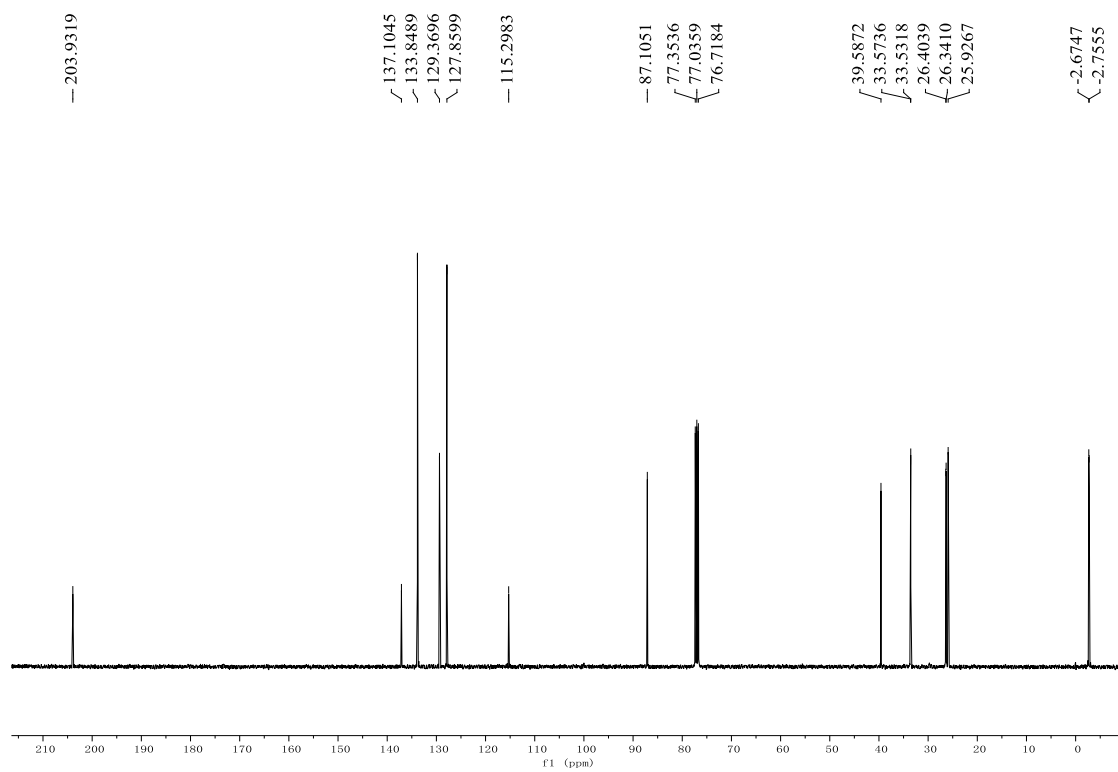
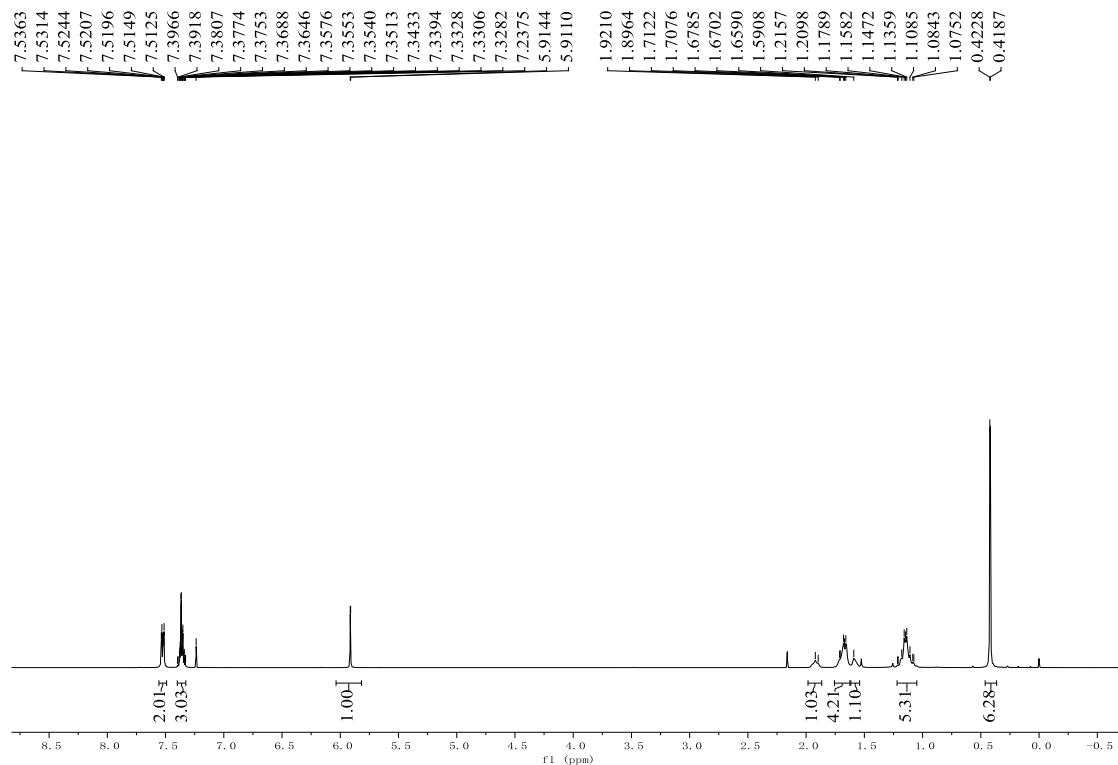


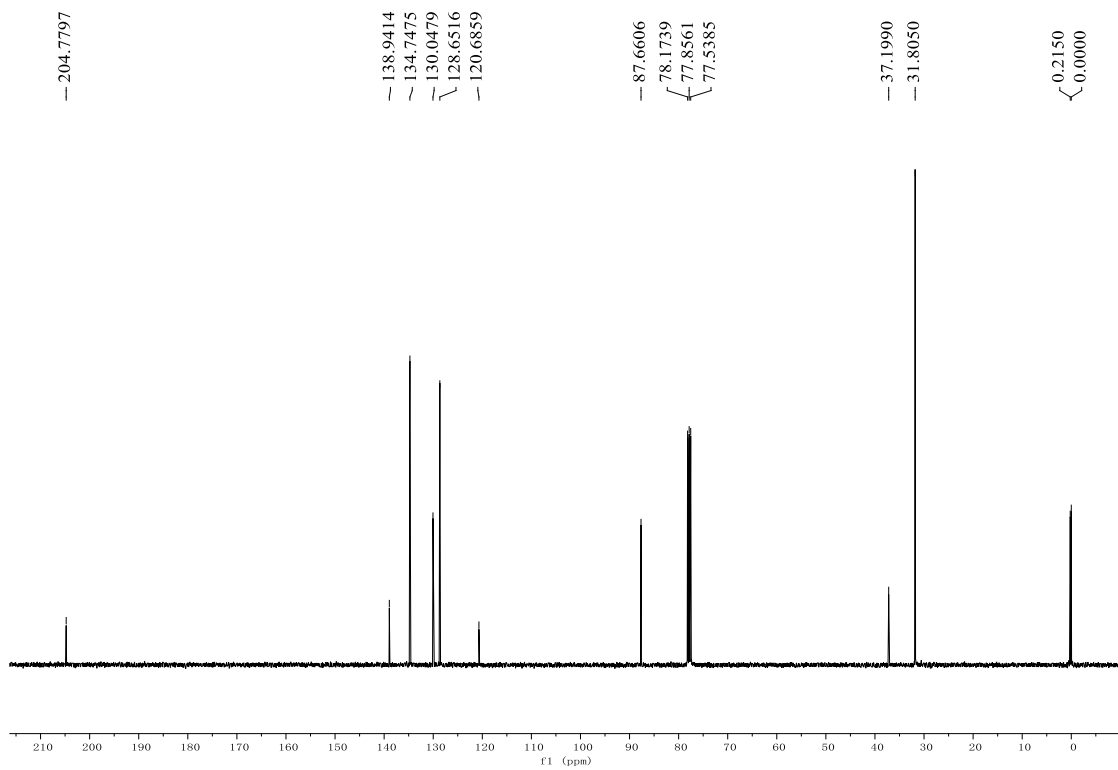
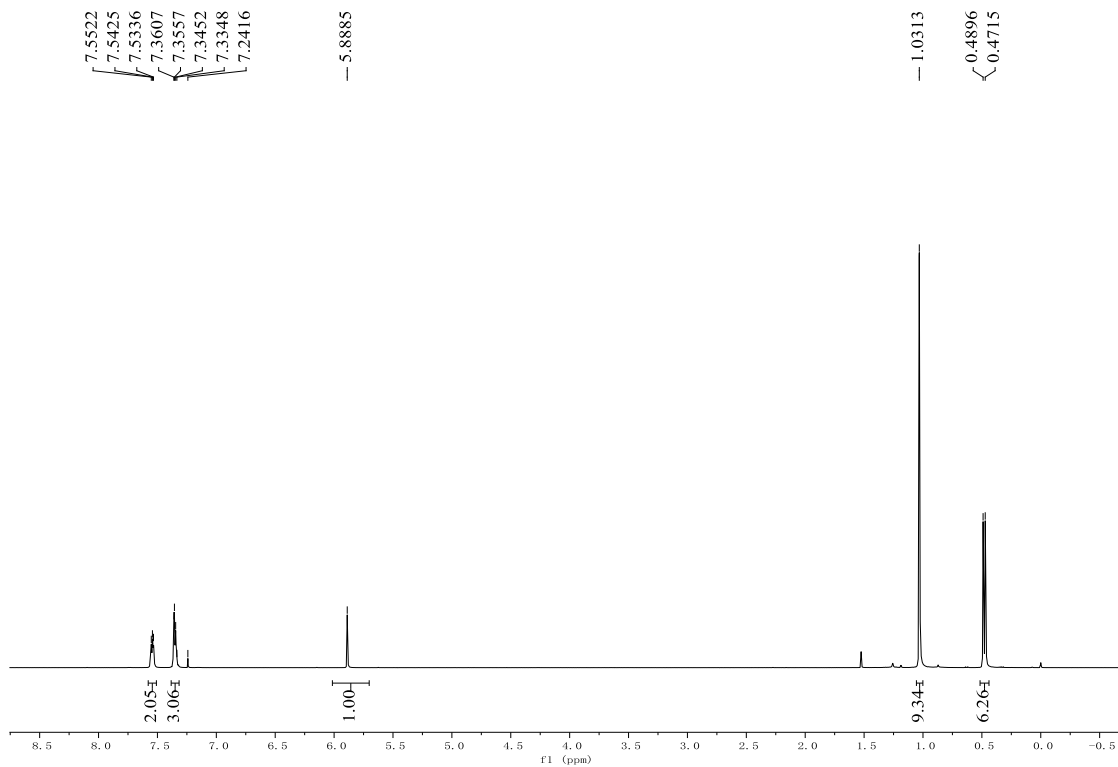
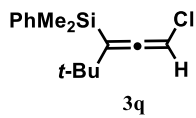


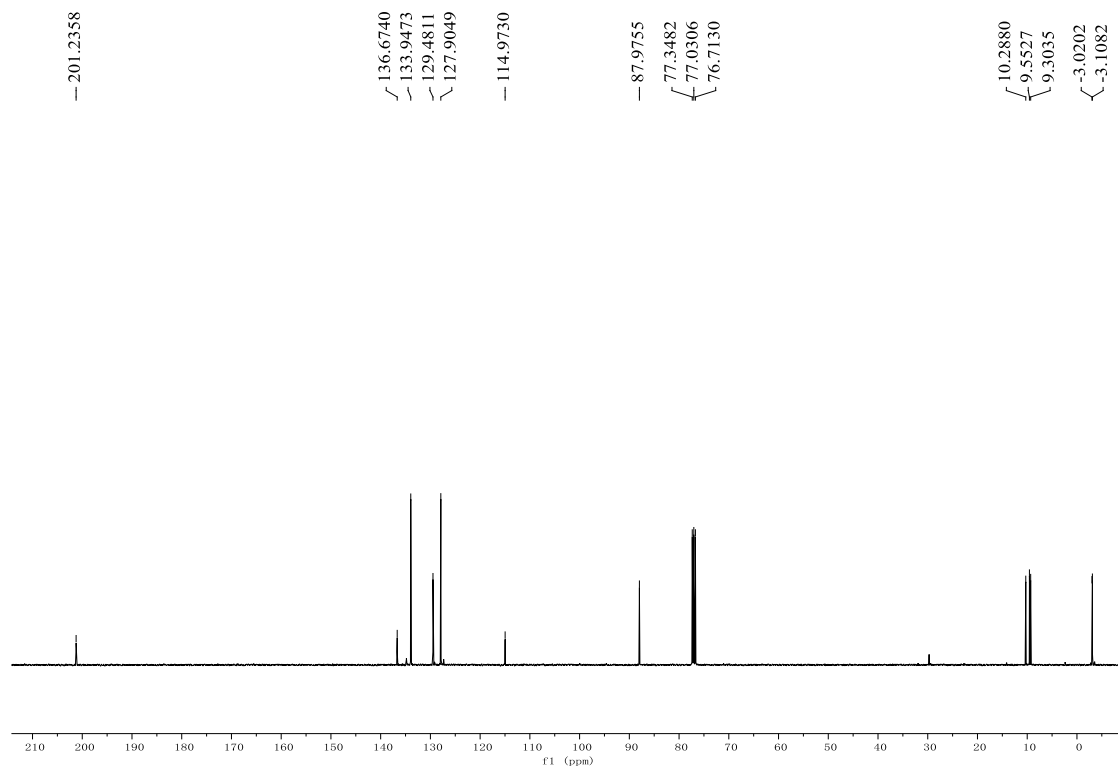
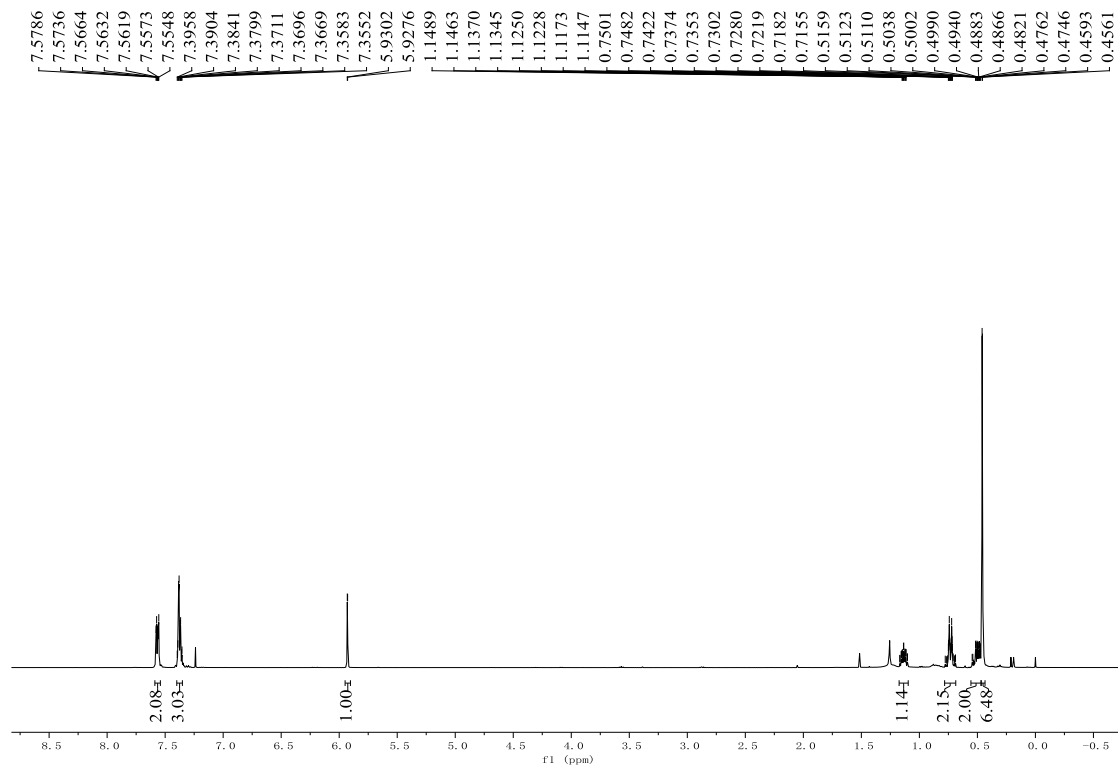
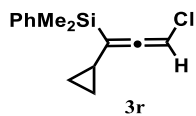


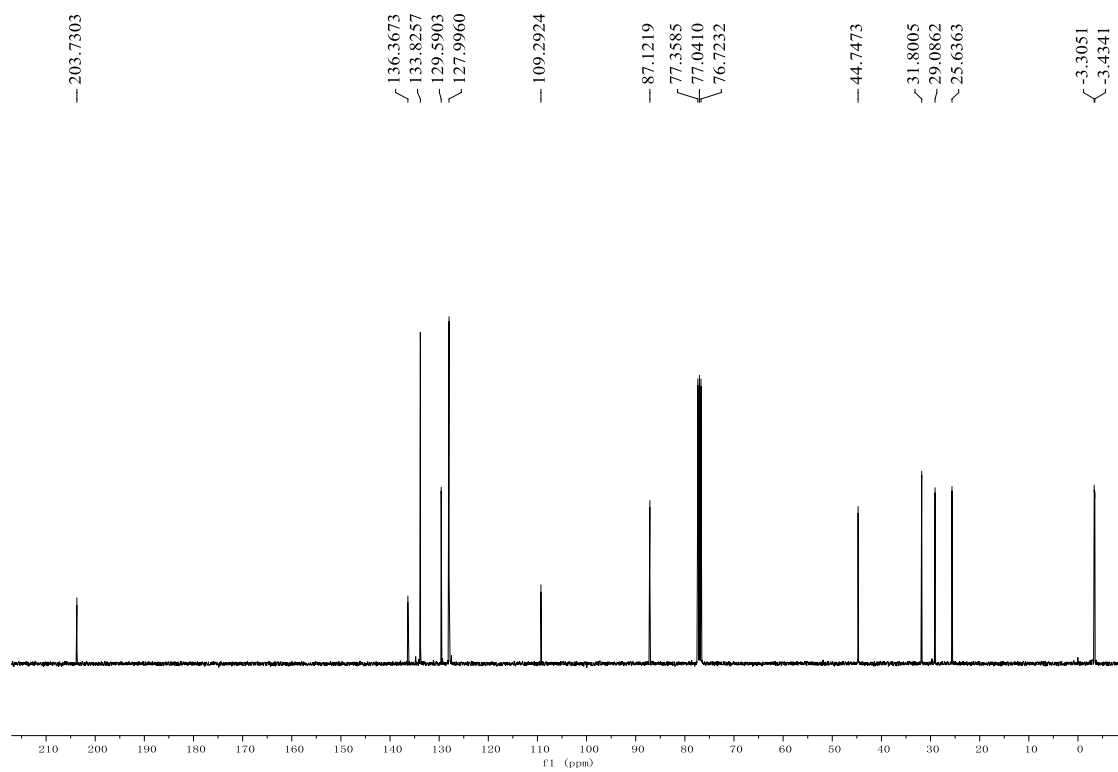
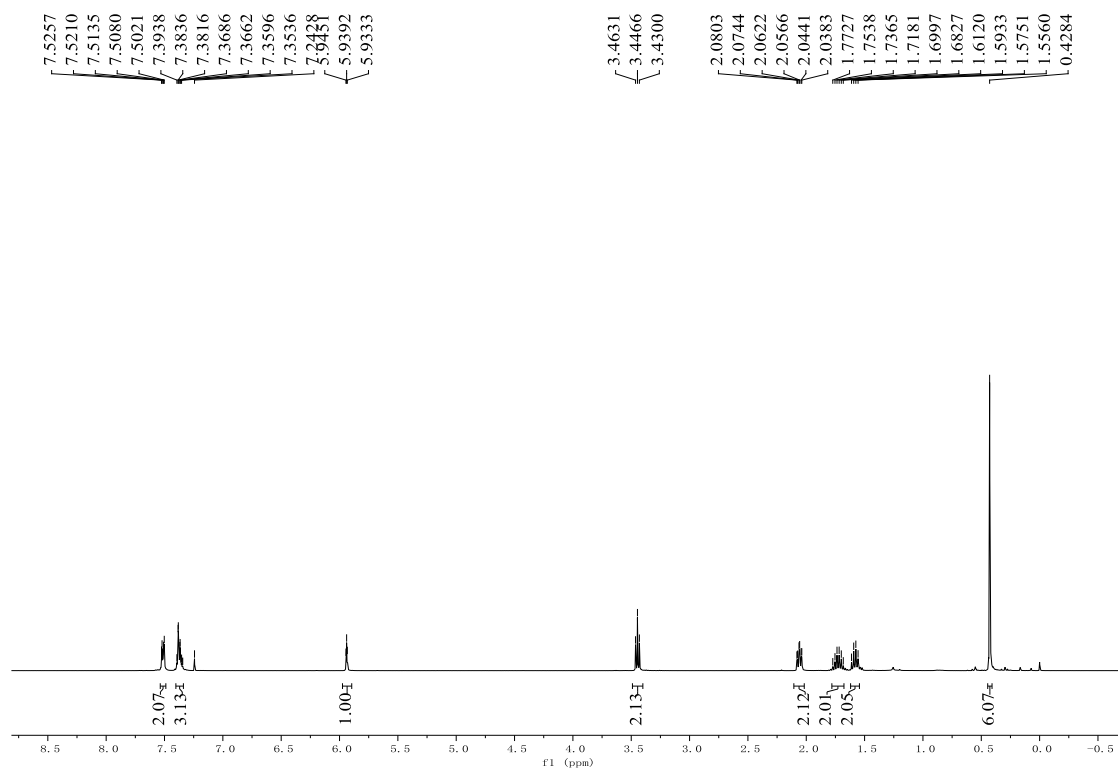
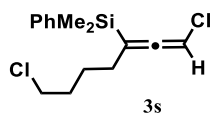


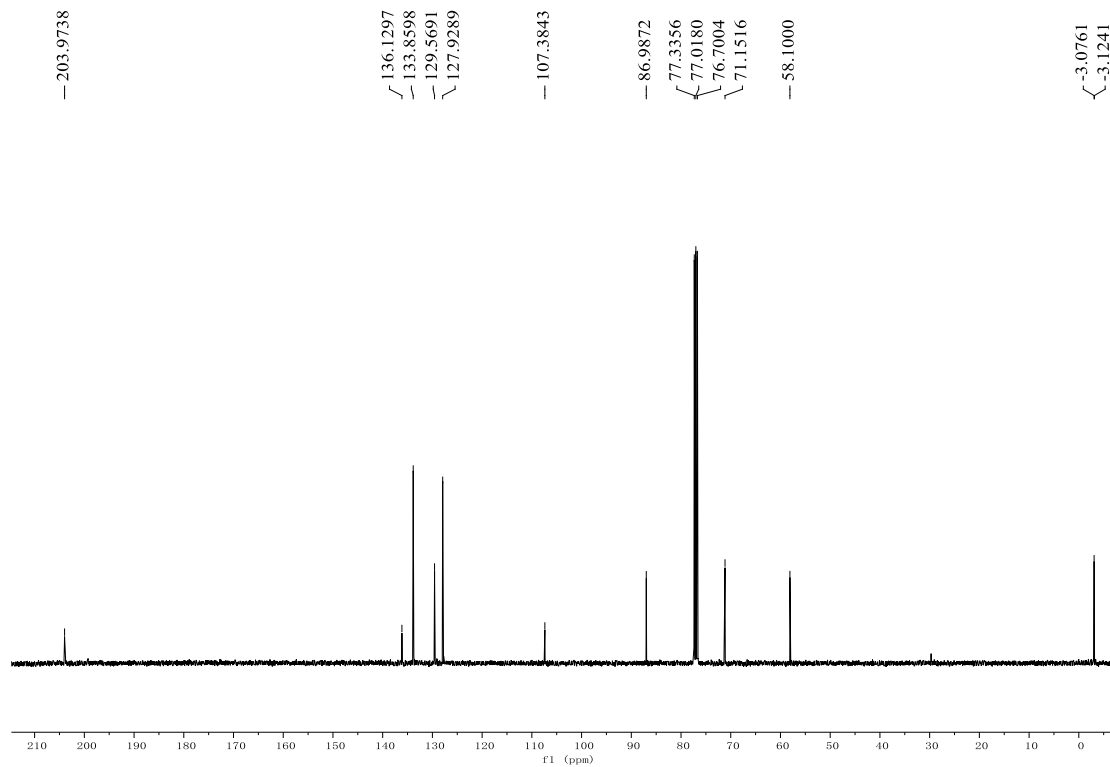
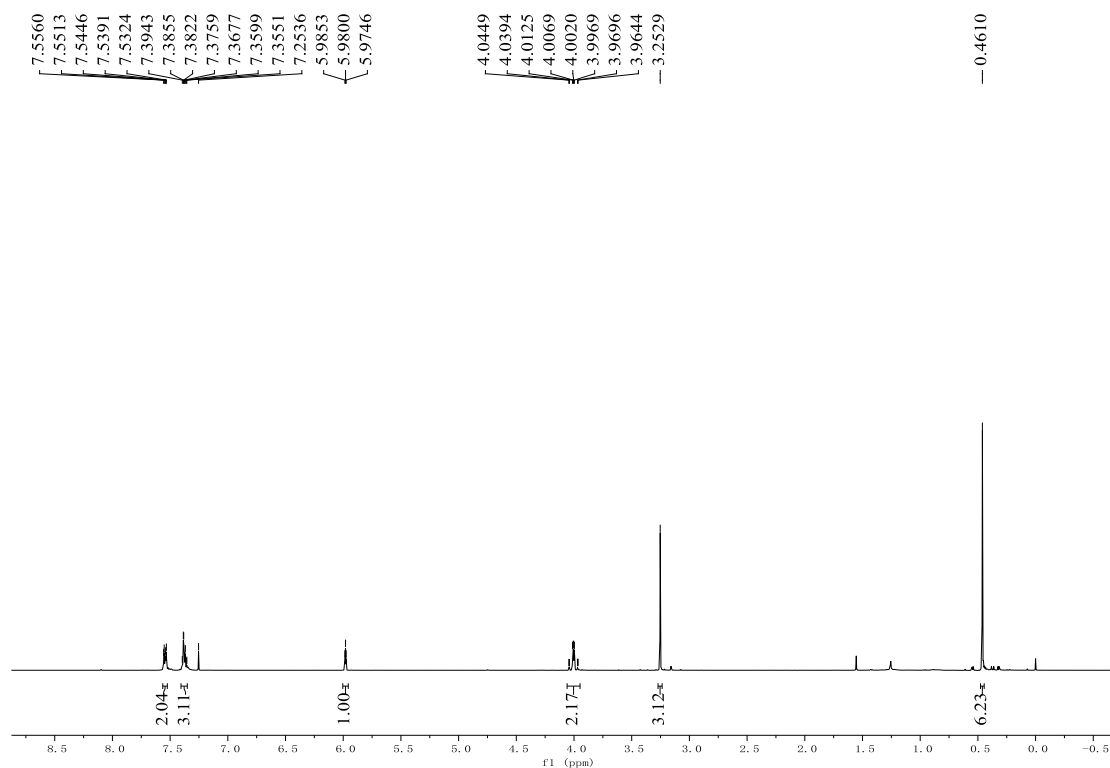
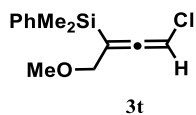
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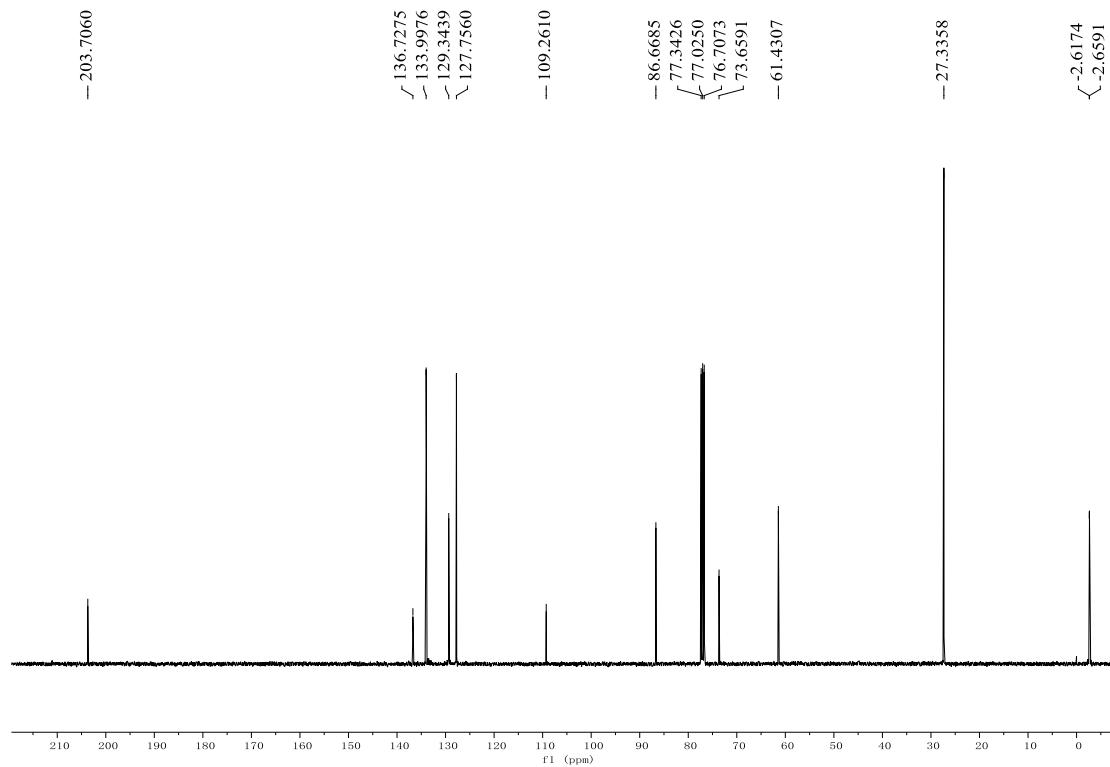
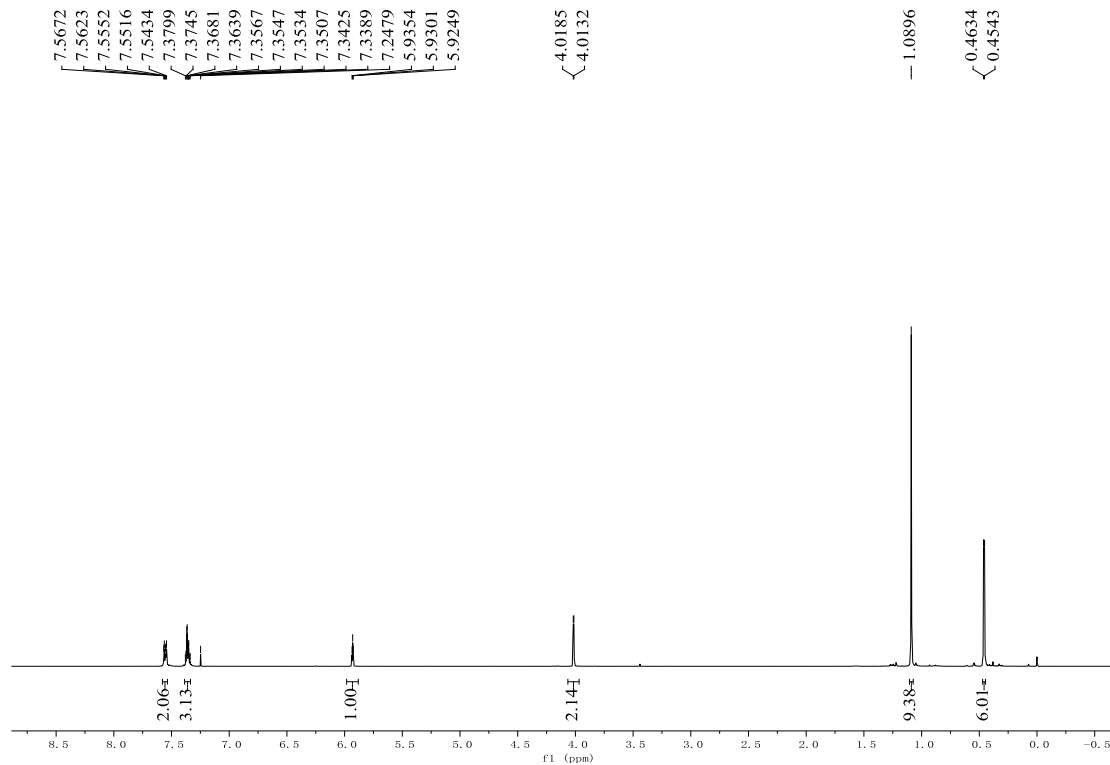
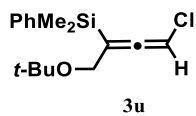


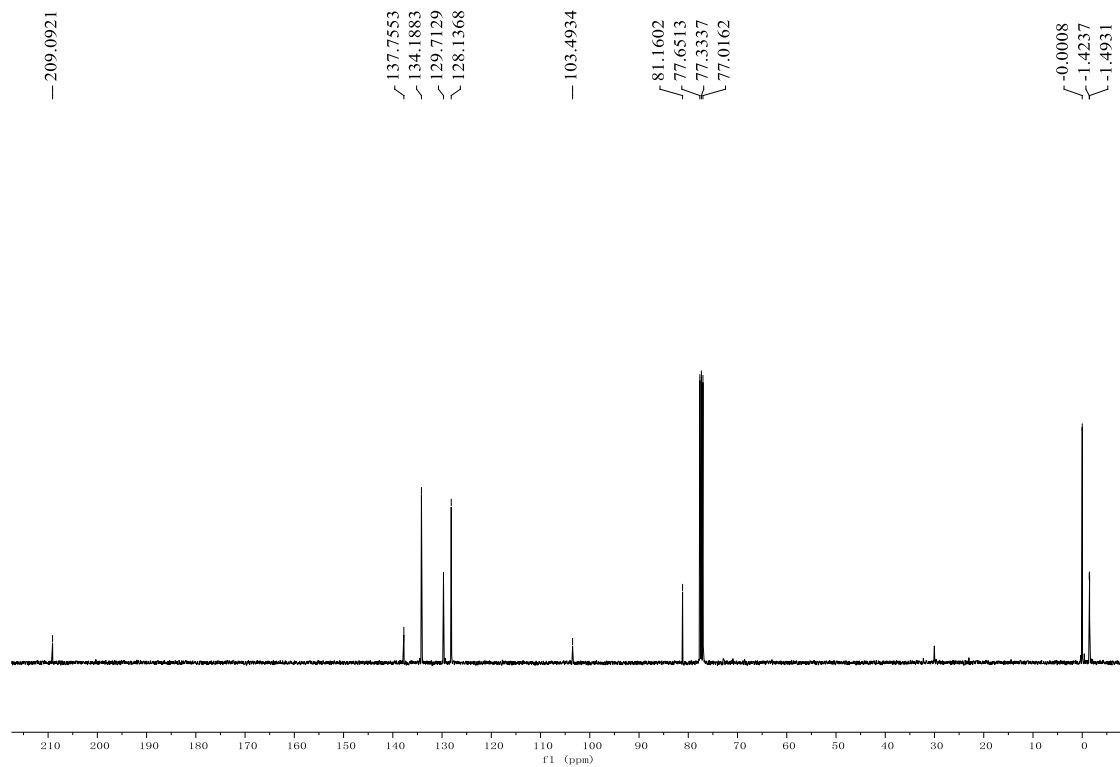
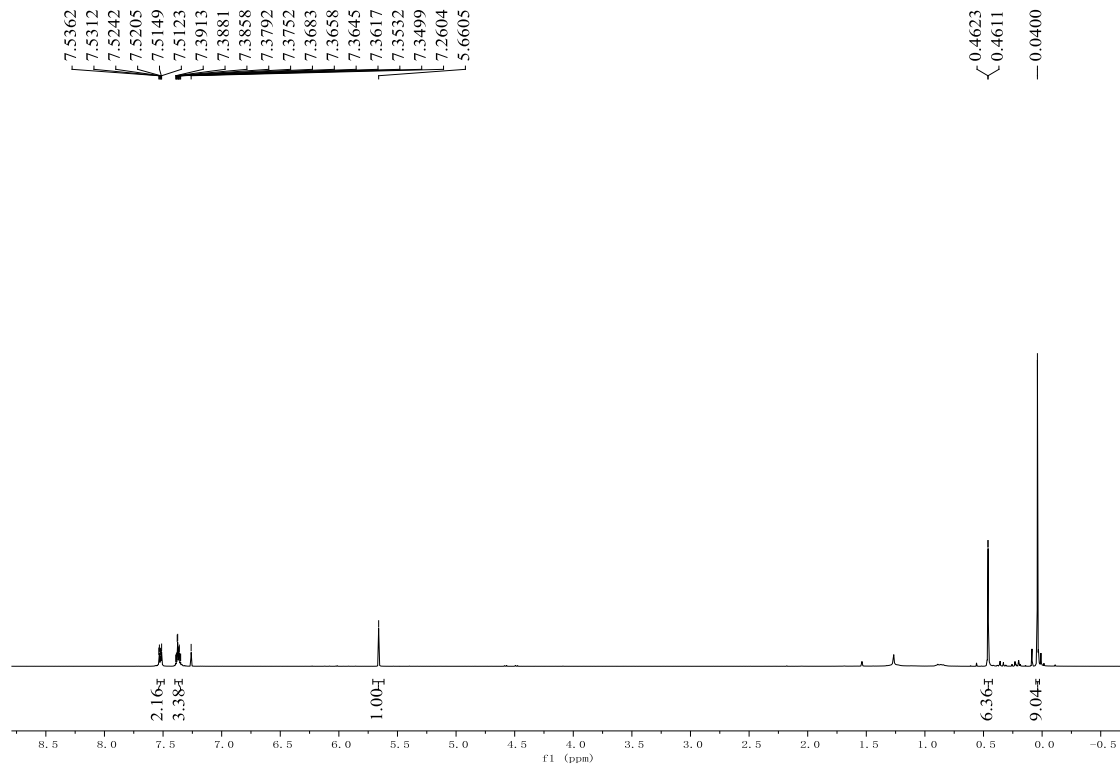
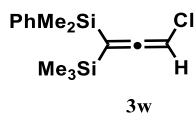


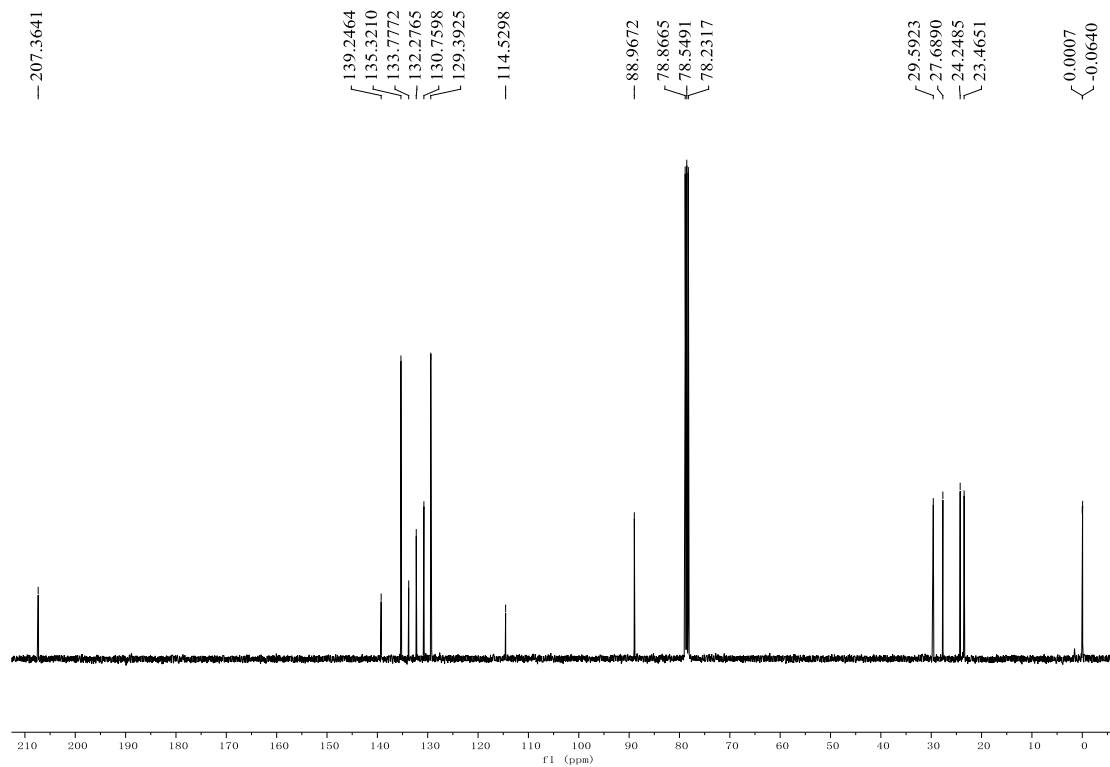
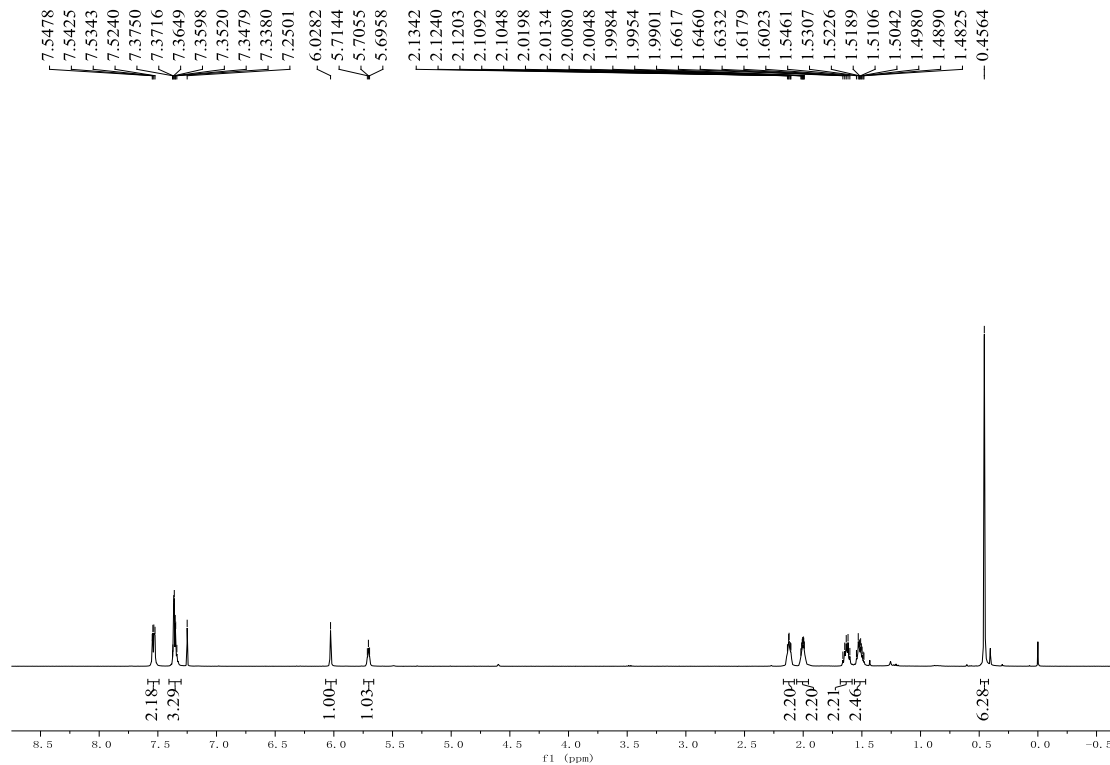
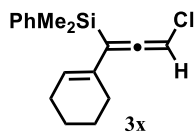


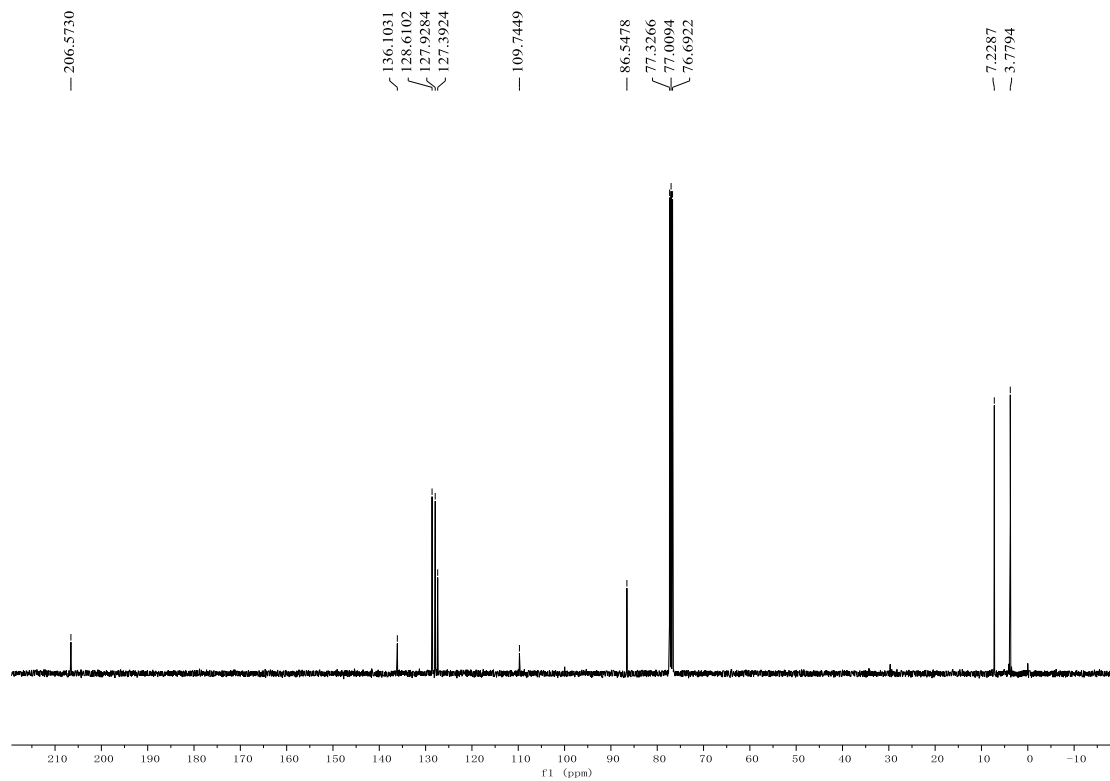
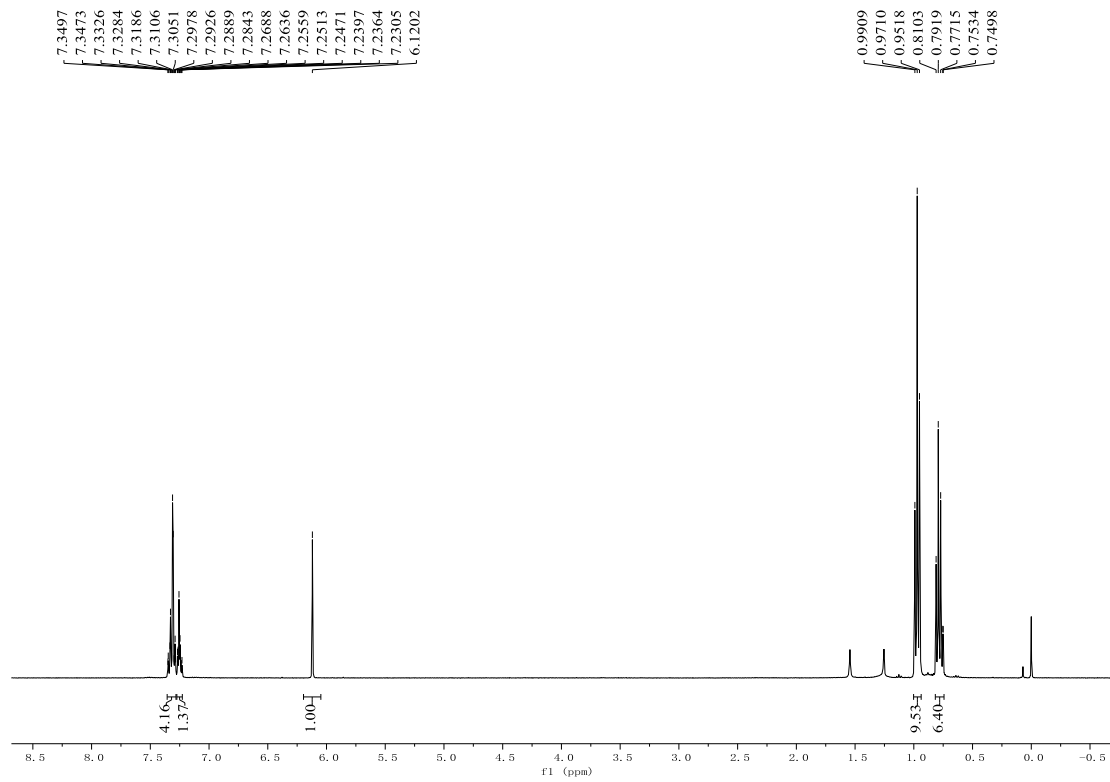
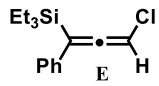


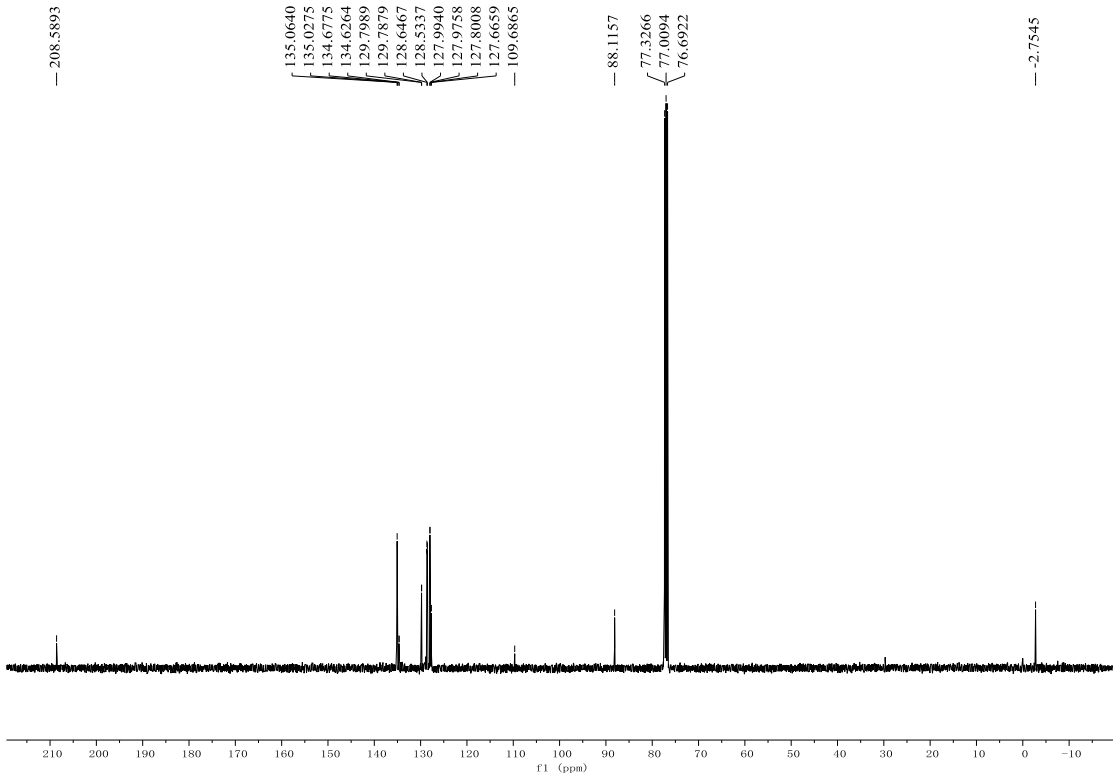
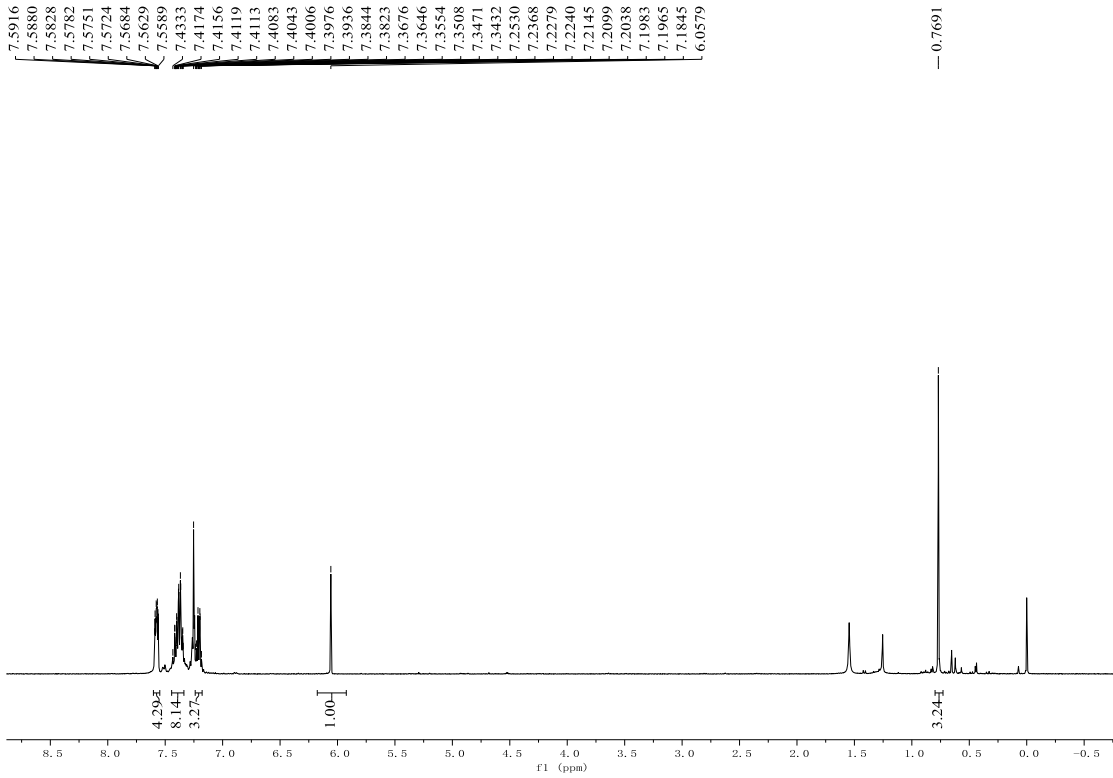
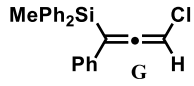


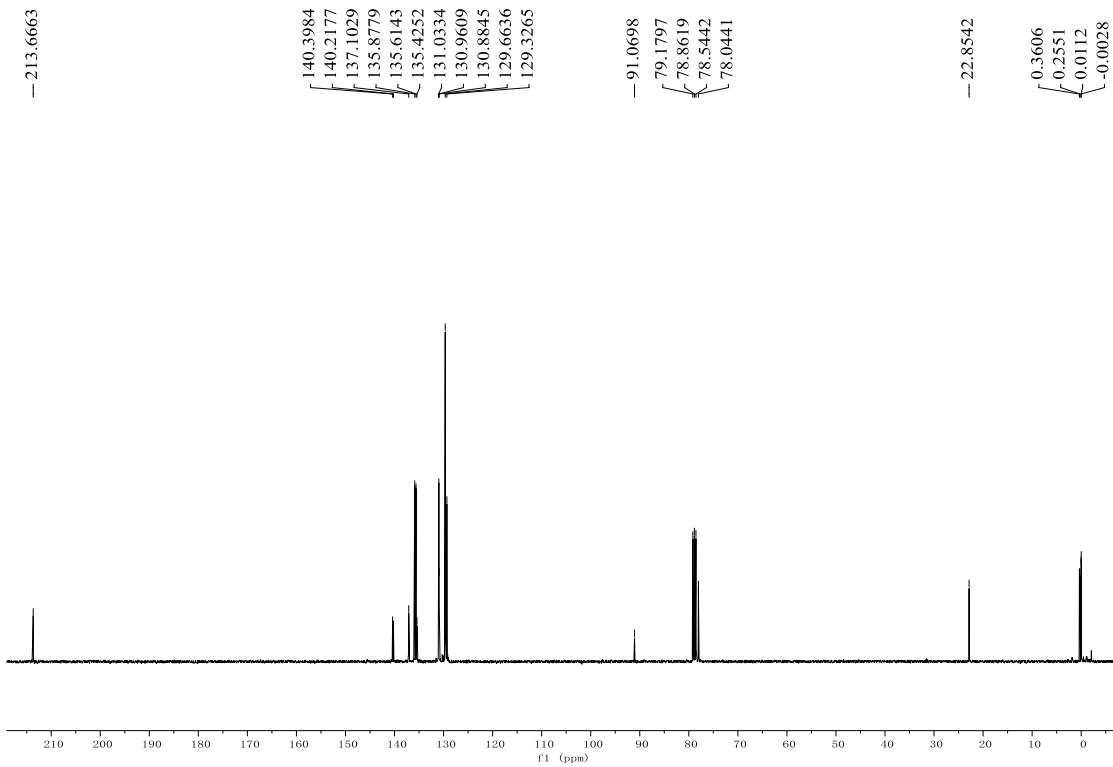
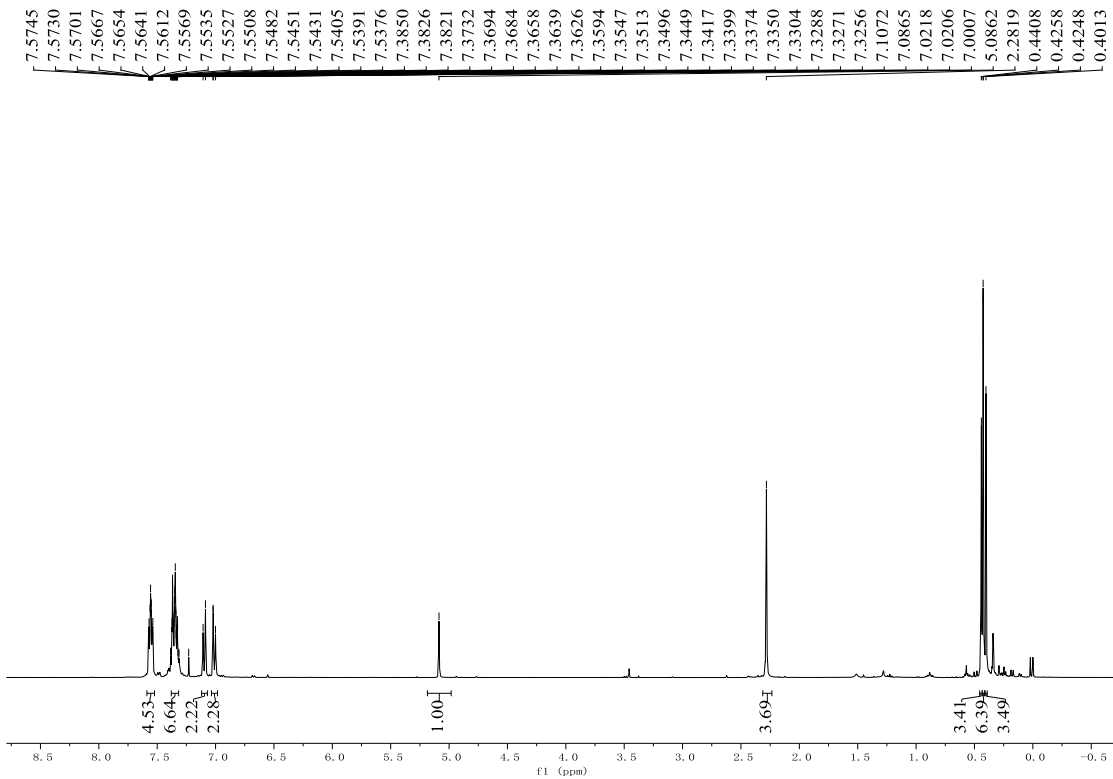
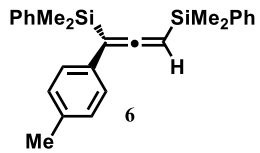


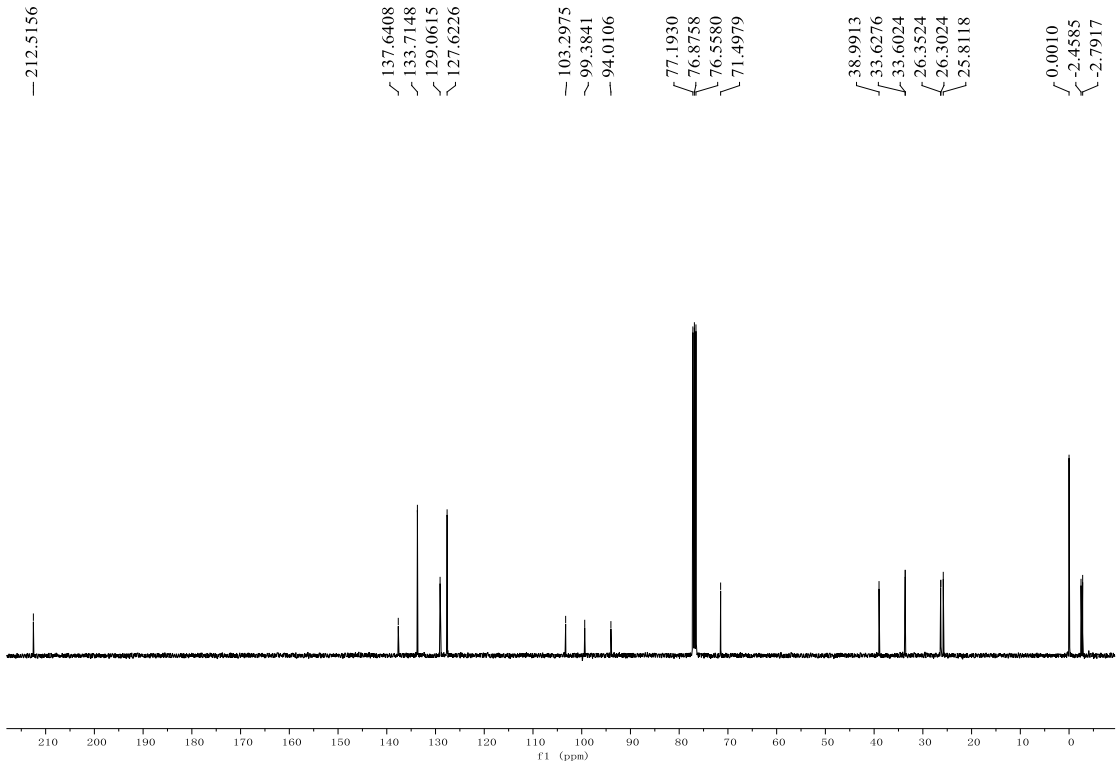
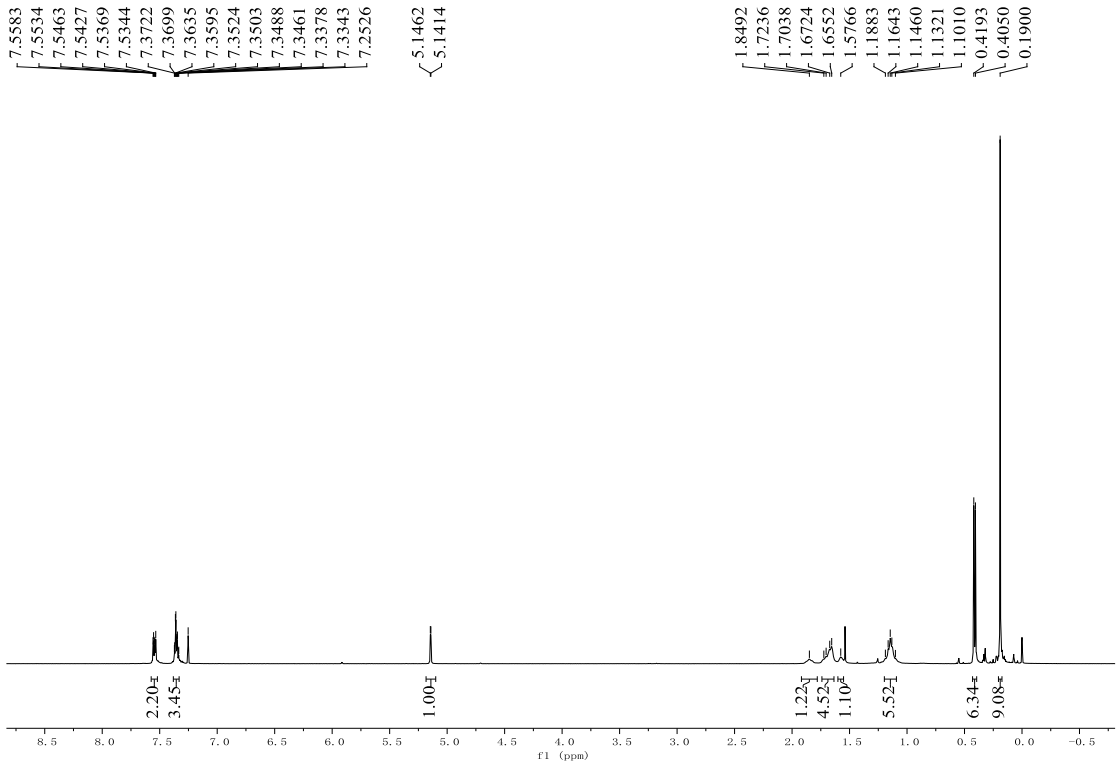
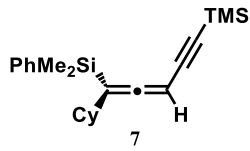


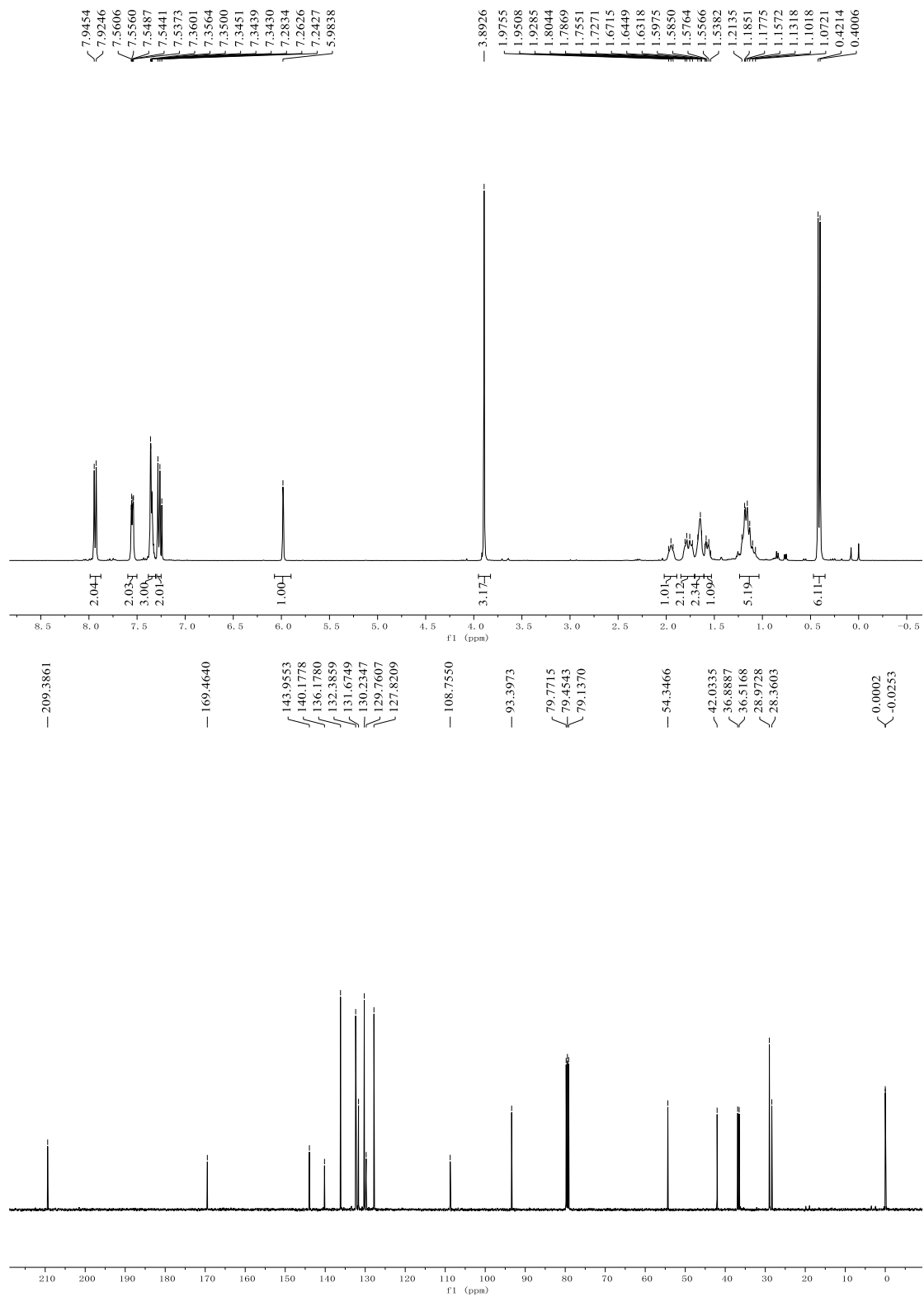
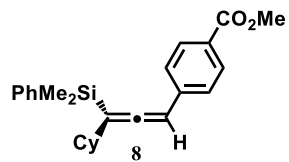


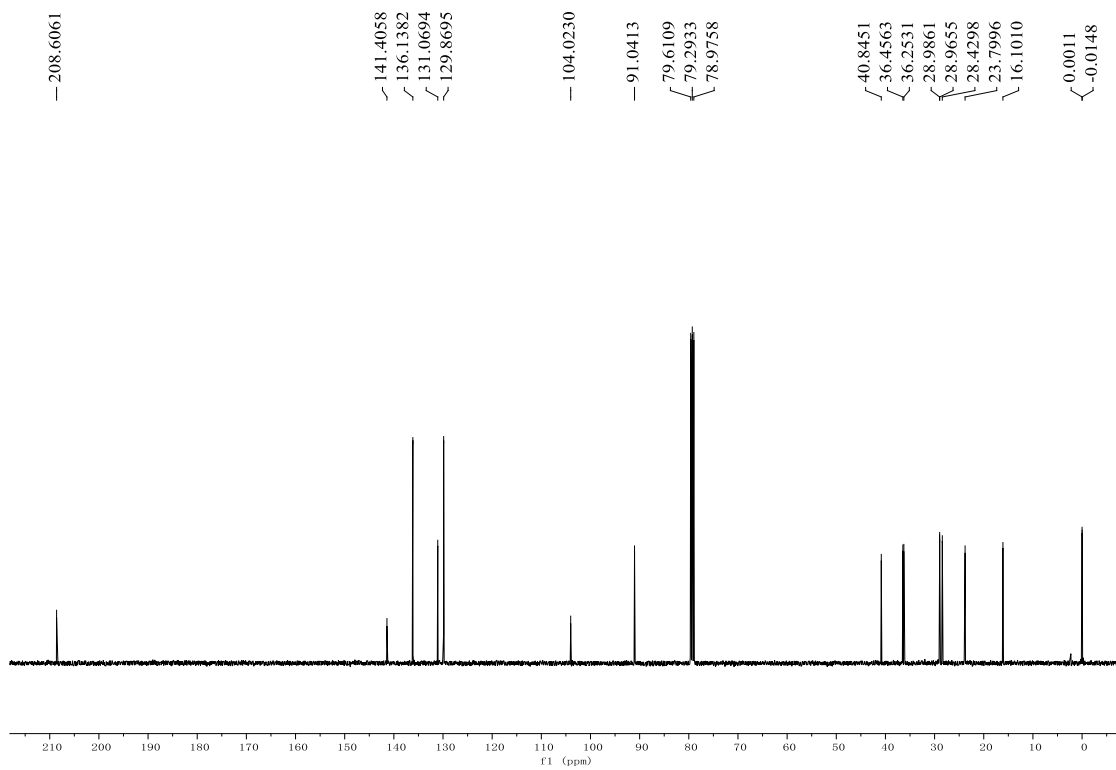
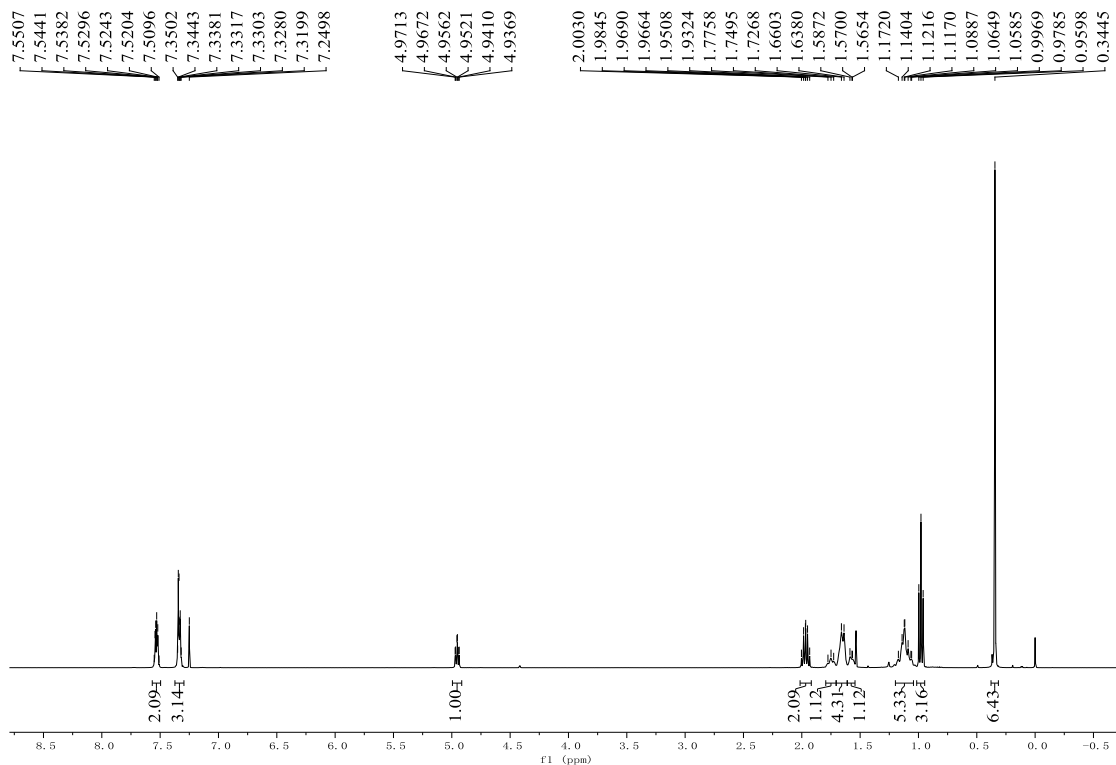
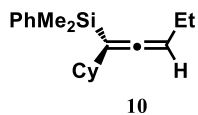


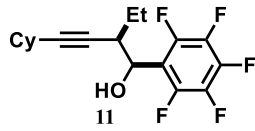




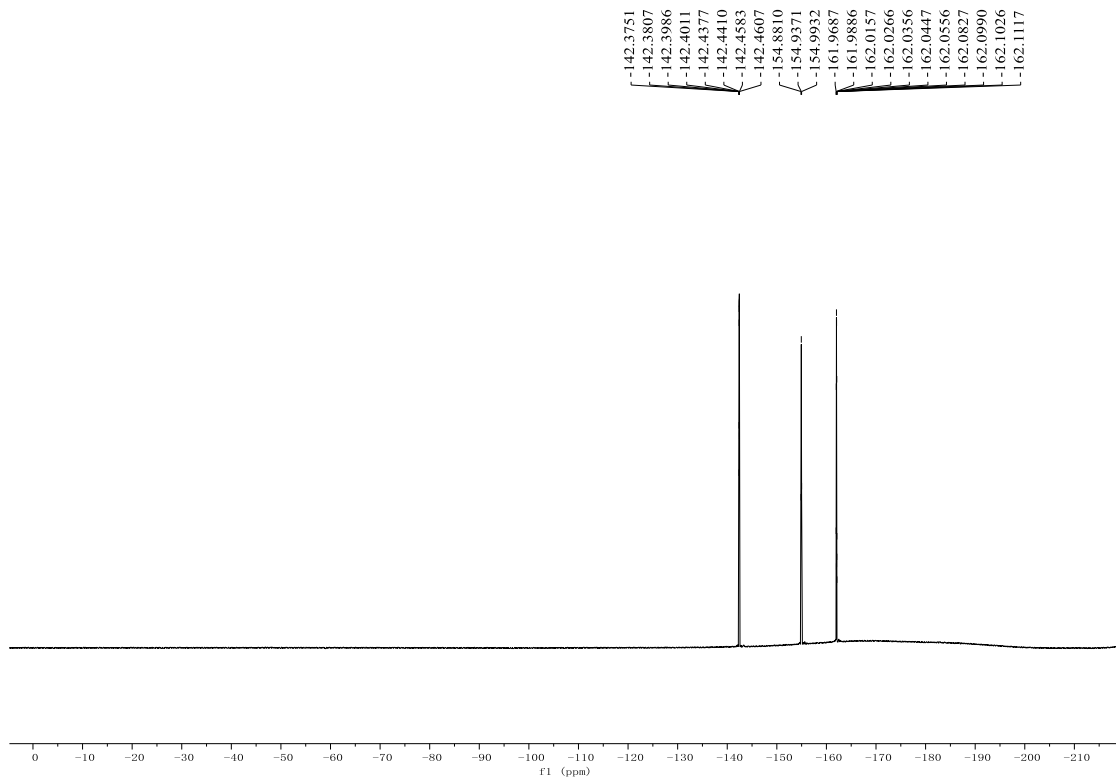
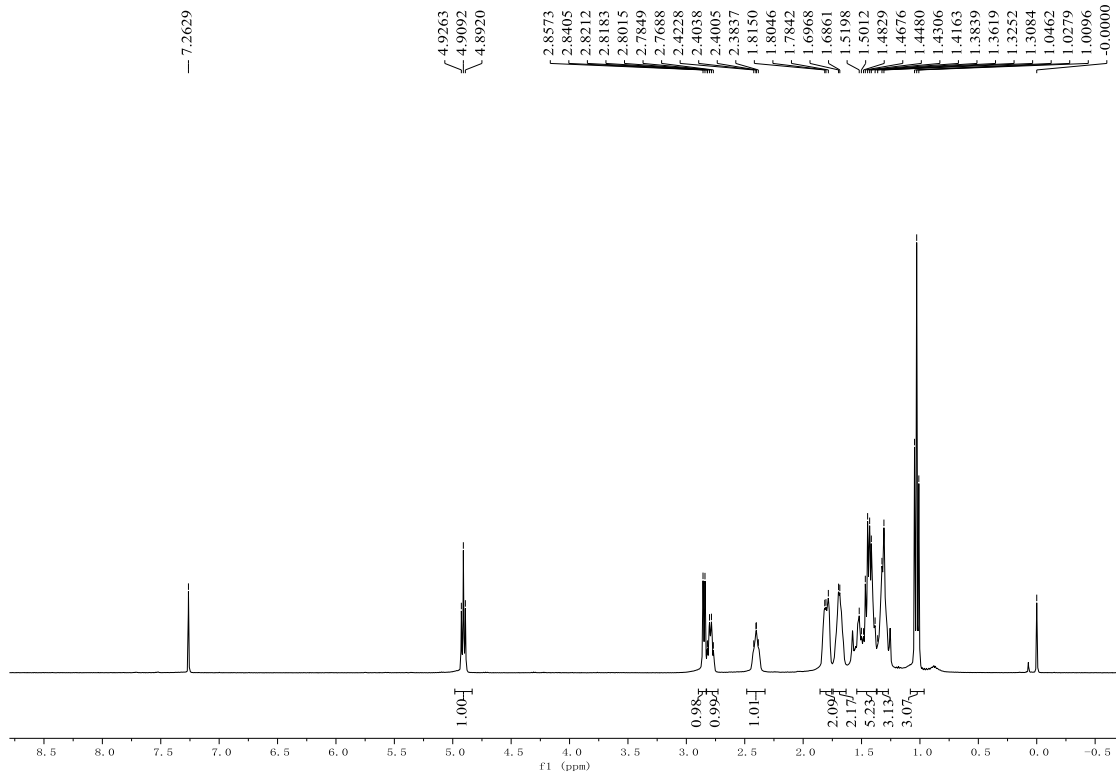


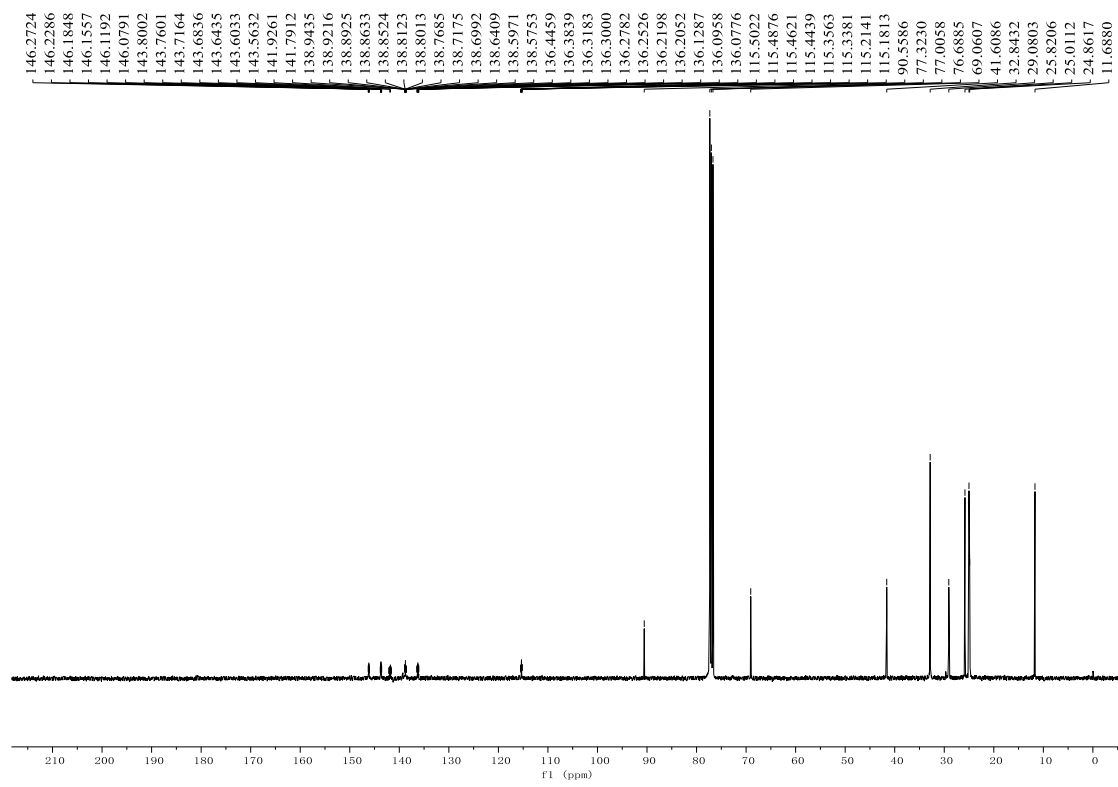


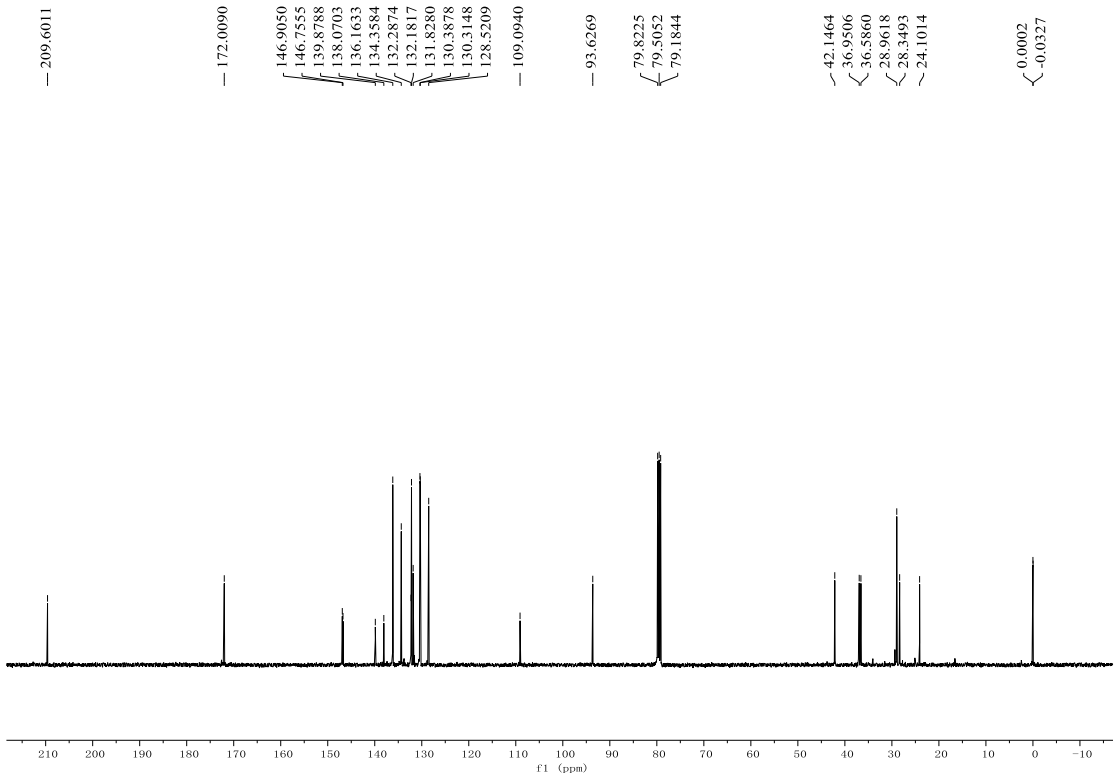
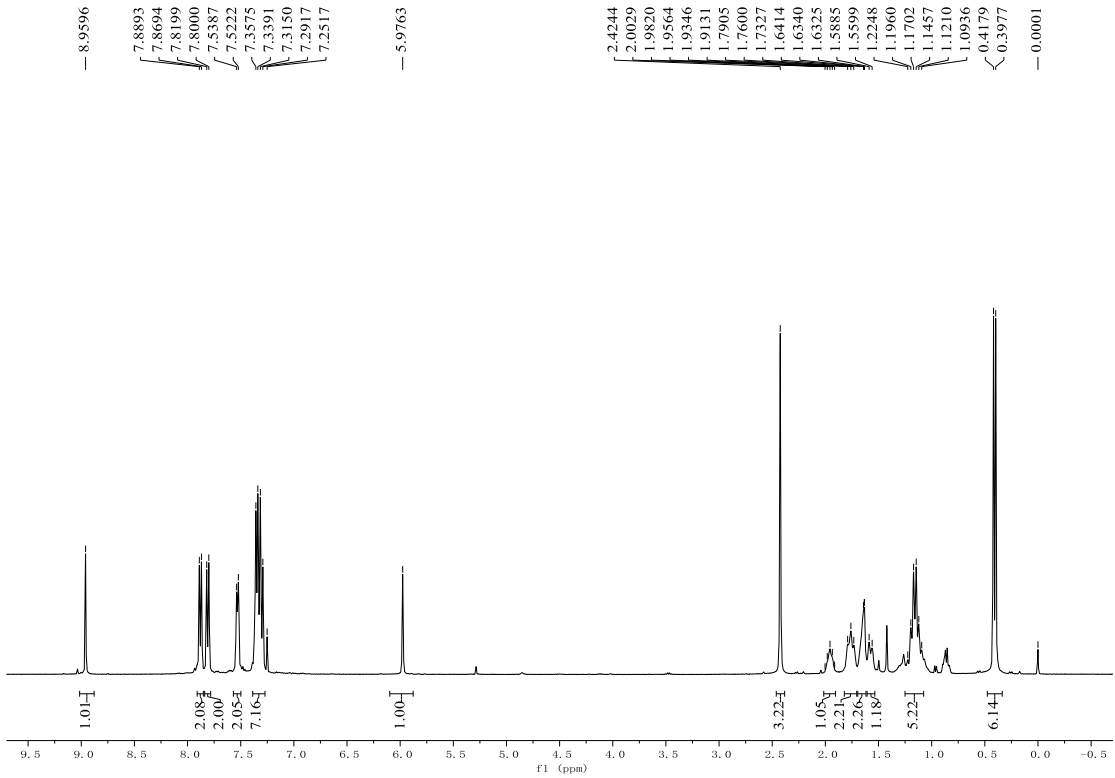
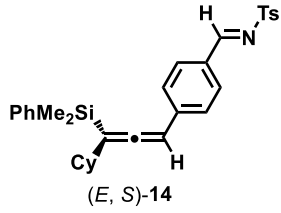


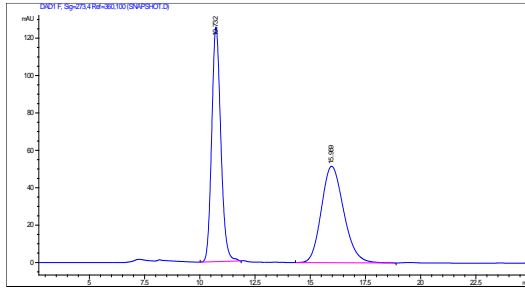
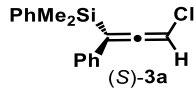


- 7.2629





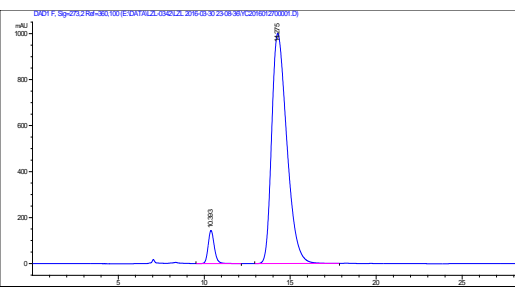




Signal 6: DAD1 F, Sig=273,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.732	BB	0.4399	3591.40381	125.50317	49.7873
2	15.969	BB	1.0798	3622.09546	51.54496	50.2127

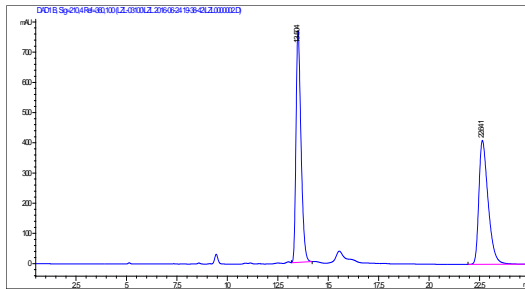
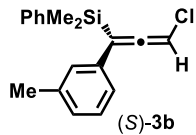
Totals : 7213.49927 177.04812



Signal 6: DAD1 F, Sig=273,2 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.393	BB	0.3862	3578.50073	143.85506	5.5179
2	14.275	BB	0.9323	6.12742e4	1000.72412	94.4821

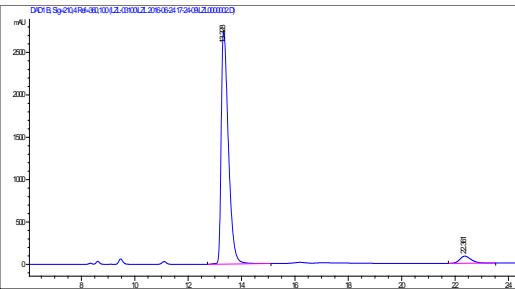
Totals : 6.48527e4 1144.57918



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.504	VB	0.2639	1.32739e4	766.93518	50.4324
2	22.641	BBA	0.4808	1.30463e4	410.49673	49.5676

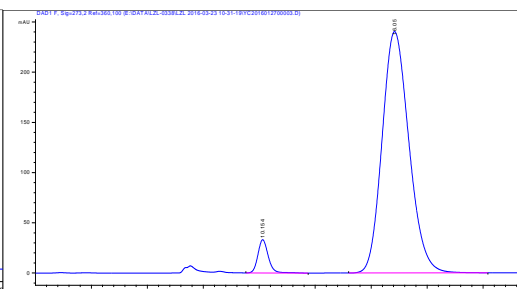
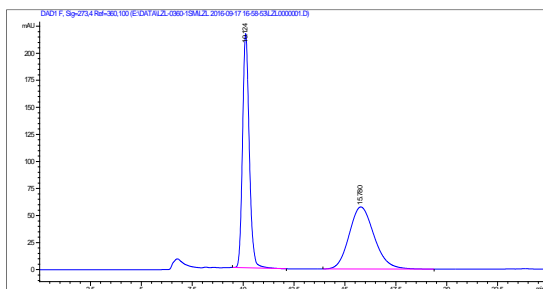
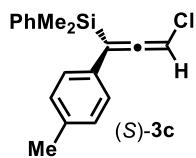
Totals : 2.63202e4 1177.43192



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.328	MM	0.3258	5.41048e4	2767.78076	95.6240
2	22.361	MM	0.4820	2476.00220	85.62308	4.3760

Totals : 5.65808e4 2853.40384



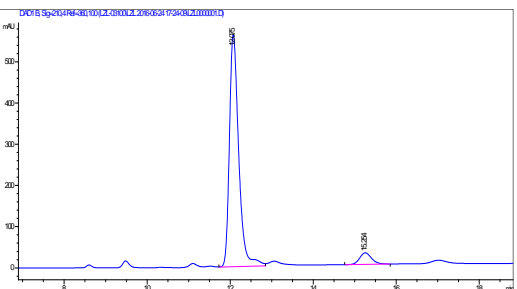
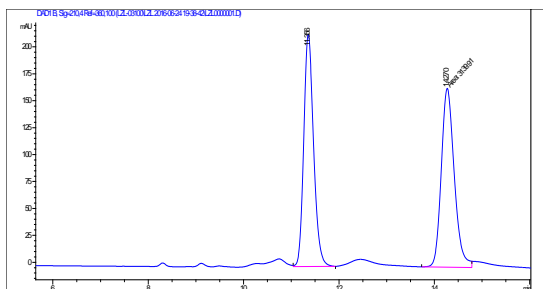
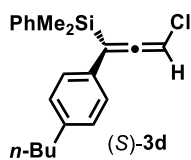
Signal 6: DAD1 F, Sig=273,4 Ref=360,100

Signal 6: DAD1 F, Sig=273,2 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.124	BB	0.3544	4979.08789	216.41650	50.4753	1	10.154	BB	0.4824	1061.86340	33.08468	5.0306
2	15.780	BB	1.2984	4885.31738	57.31890	49.5247	2	16.053	BB	1.0671	2.00462e4	240.33324	94.9694

Totals : 9864.40527 273.73540

Totals : 2.11081e4 273.41792



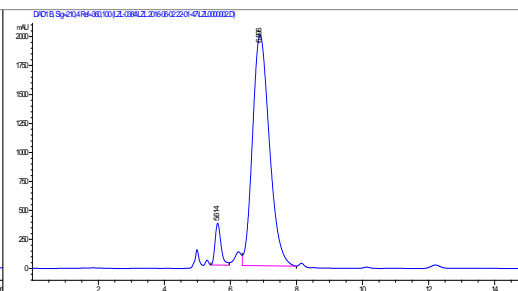
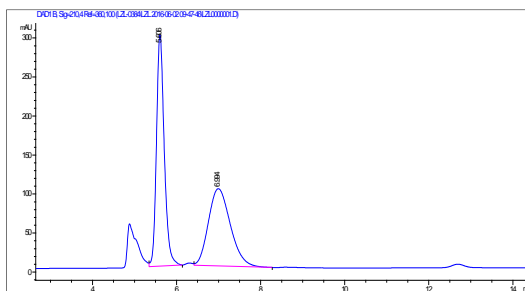
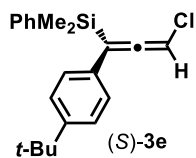
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.356	VB	0.2189	3086.63818	215.75822	49.5722	1	12.075	BV	0.2349	8745.37695	563.86841	94.0550
2	14.270	MF	0.3151	3139.91113	166.08830	50.4278	2	15.254	BB	0.3042	552.77844	28.01121	5.9450

Totals : 6226.54932 381.84653

Totals : 9298.15540 591.87962



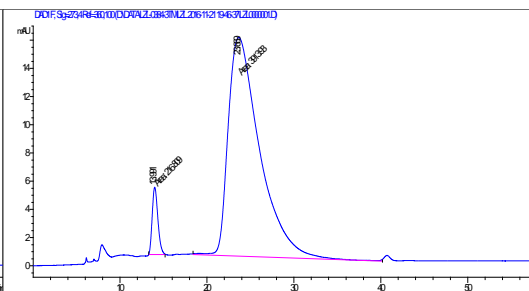
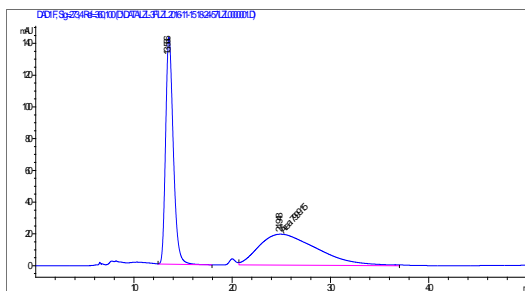
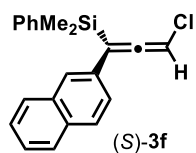
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.606	VB	0.1941	3813.20703	296.42584	51.4836	1	5.614	BV	0.1903	4482.46338	362.29968	5.9778
2	6.994	VB	0.5650	3593.44165	99.11376	48.5164	2	6.896	VB	0.5493	7.05032e4	1990.26440	94.0222

Totals : 7406.64868 395.53960

Totals : 7.49856e4 2352.56409



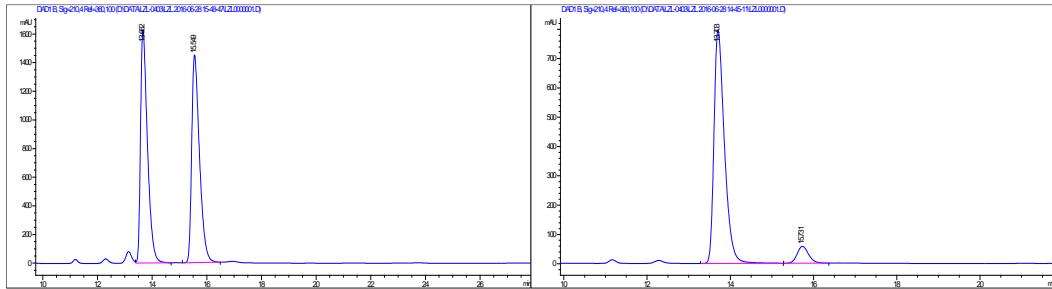
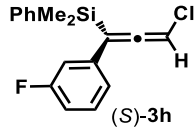
Signal 6: DAD1 F, Sig=273,4 Ref=360,100

Signal 6: DAD1 F, Sig=273,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.566	BB	0.8334	7751.22900	142.77934	49.2130	1	13.991	MM	0.7562	216.80930	4.77854	5.2487
2	24.948	FM	6.8567	7999.15332	19.44358	50.7870	2	23.669	MF	4.2004	3913.93481	15.53017	94.7513

Totals : 1.57504e4 162.22292

Totals : 4130.74411 20.30871



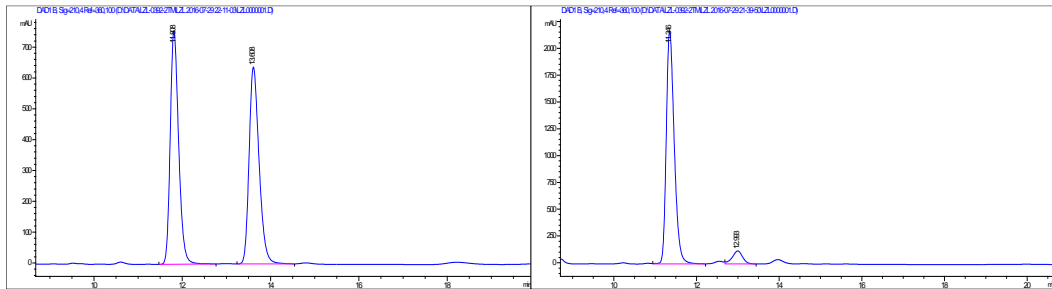
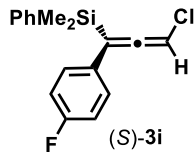
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.662	VB	0.2653	2.86453e4	1628.08557	50.0092	1	13.703	BB	0.2648	1.38577e4	797.02148	92.6725
2	15.549	BB	0.2983	2.86348e4	1450.60510	49.9908	2	15.731	BB	0.2935	1095.70715	57.70712	7.3275

Totals : 5.72801e4 3078.69067

Totals : 1.49534e4 854.72861



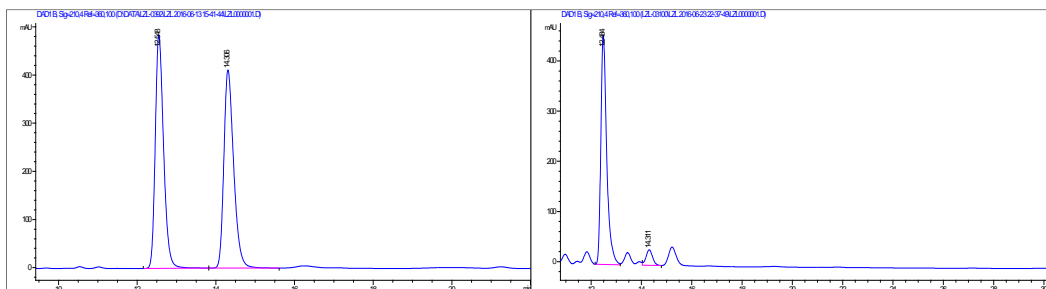
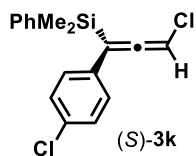
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.808	BB	0.2043	1.00042e4	756.65826	50.0224	1	11.346	VB	0.2062	2.90800e4	2171.68506	93.3462
2	13.608	BB	0.2406	9995.26074	638.74432	49.9776	2	12.993	VB	0.2602	2072.83862	120.78619	6.6538

Totals : 1.99995e4 1395.40259

Totals : 3.11529e4 2292.47125



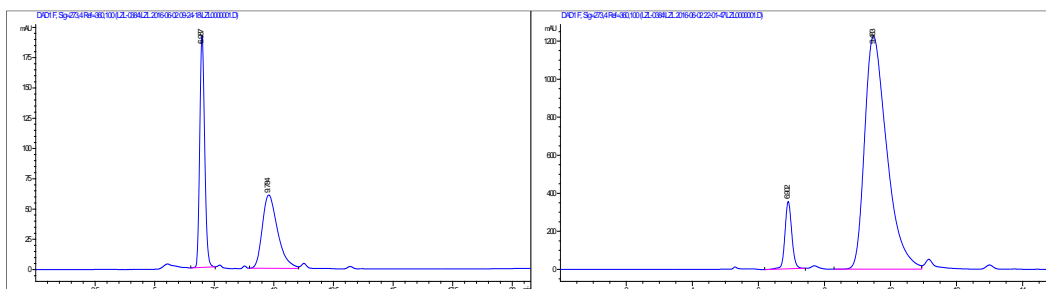
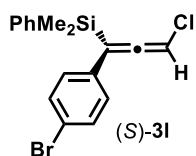
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.548	BB	0.2258	7142.16895	484.89758	50.0441	1	12.484	BV	0.2433	7428.21875	457.80365	92.9746
2	14.306	BB	0.2641	7129.57031	411.59836	49.9559	2	14.311	VB	0.2794	561.29901	30.97358	7.0254

Totals : 1.42717e4 896.49594

Totals : 7989.51776 488.77723



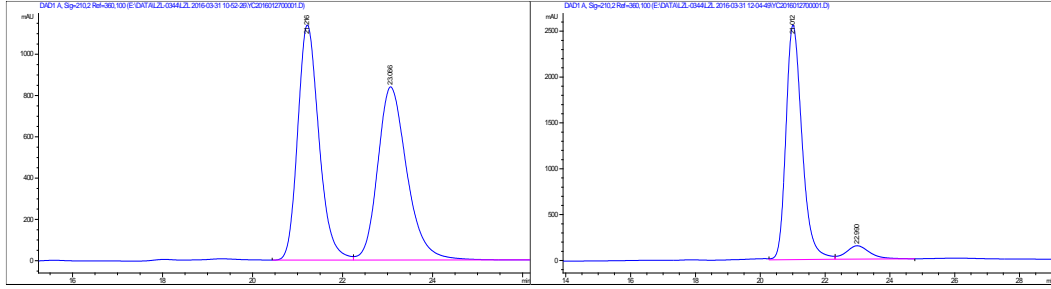
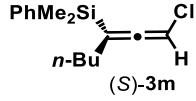
Signal 6: DAD1 F, Sig=273,4 Ref=360,100

Signal 6: DAD1 F, Sig=273,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.987	BB	0.2199	2717.19019	191.09383	50.1123	1	6.902	BB	0.2209	5075.59766	354.83728	8.1639
2	9.784	BV	0.6854	2705.01660	60.52993	49.8877	2	9.483	BV	0.6992	5.70957e4	1226.25073	91.8361

Totals : 5422.20679 251.62375

Totals : 6.21713e4 1581.08801



Signal 1: DAD1 A, Sig=210,2 Ref=360,100

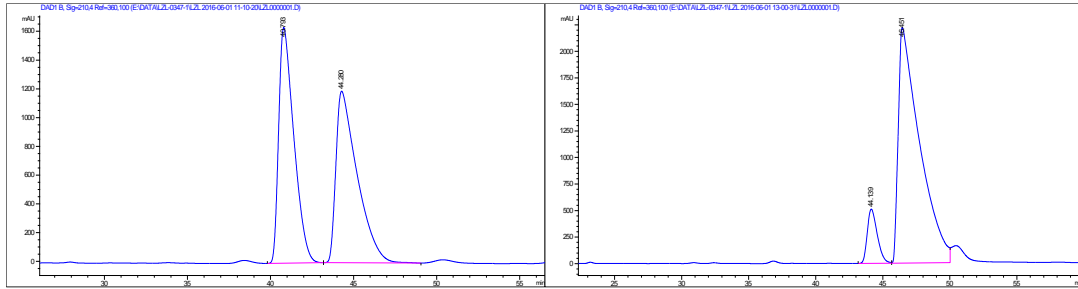
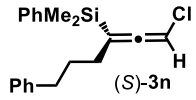
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.216	BV	0.5166	3.73452e4	1138.87988	49.6501
2	23.066	VBA	0.6844	3.78716e4	839.37390	50.3499

Totals : 7.52168e4 1978.25378

Signal 1: DAD1 A, Sig=210,2 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.012	VV	0.5188	8.82884e4	2557.44604	92.2333
2	22.990	VB	0.7542	7434.56201	145.96889	7.7667

Totals : 9.57230e4 2703.41493



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

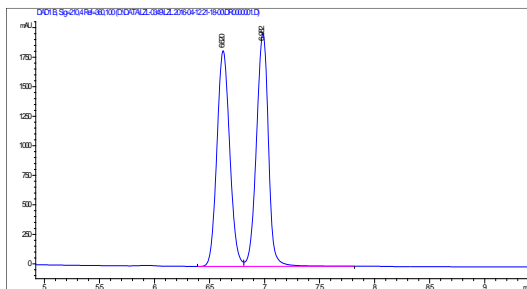
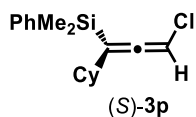
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.793	BB	0.9402	1.03974e5	1638.86658	49.5261
2	44.280	BB	1.2463	1.05964e5	1192.88843	50.4739

Totals : 2.09938e5 2831.75500

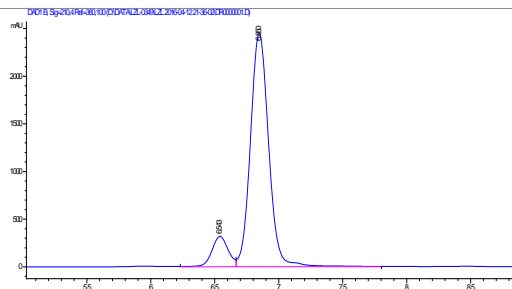
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.139	BV	0.7887	2.64267e4	511.59106	9.7186
2	46.451	VV	1.4307	2.45493e5	2219.03320	90.2814

Totals : 2.71919e5 2730.62427



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



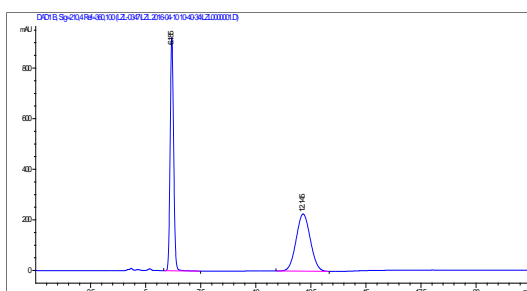
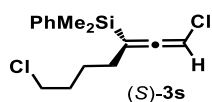
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.620	BV	0.1261	1.47516e4	1828.96484	49.7436
2	6.982	VB	0.1180	1.49036e4	1974.97961	50.2564

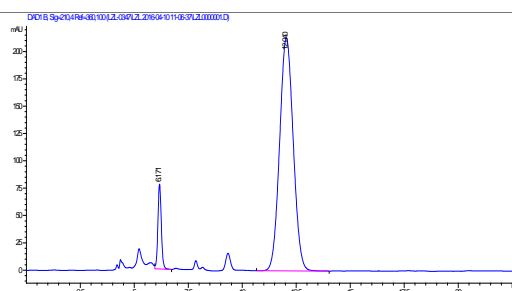
Totals : 2.96552e4 3803.94446

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.543	VV	0.1348	2813.73413	319.26279	10.3824
2	6.850	VV	0.1537	2.42873e4	2449.73193	89.6176

Totals : 2.71010e4 2768.99472



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



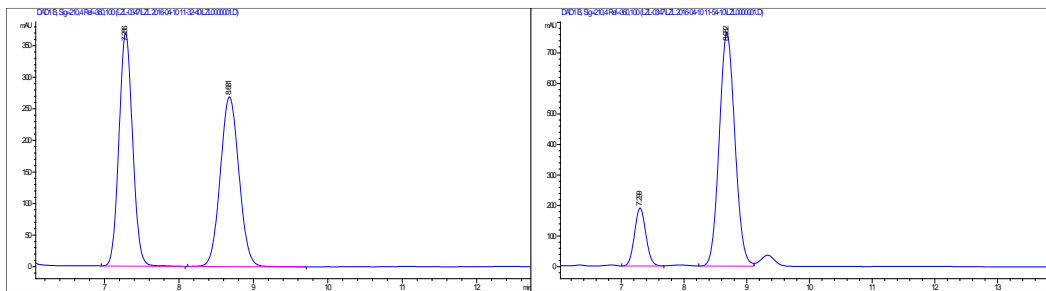
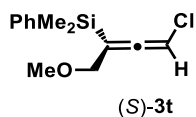
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.185	BB	0.1720	1.01137e4	922.02484	50.0180
2	12.145	BB	0.6997	1.01064e4	226.02942	49.9820

Totals : 2.02201e4 1148.05426

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.171	VB	0.1710	858.67053	77.63022	8.4166
2	12.040	BB	0.6853	9343.46484	213.21170	91.5834

Totals : 1.02021e4 290.84192



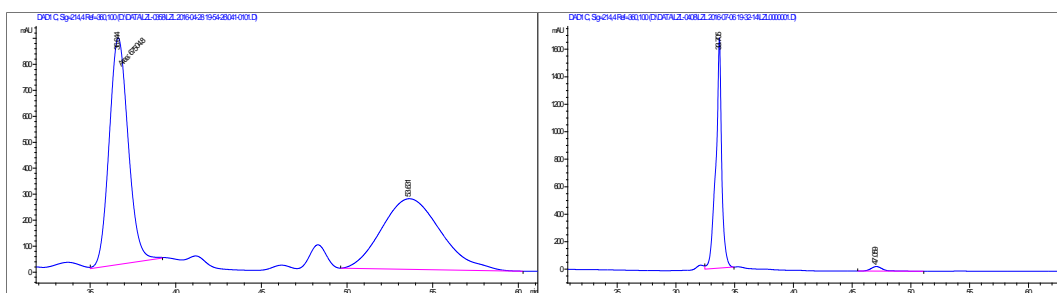
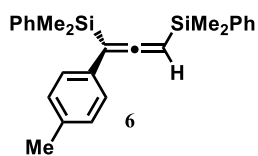
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.286	BB	0.1981	4682.50098	368.83368	50.0304	1	7.299	BV	0.1972	2395.32202	189.80386	15.2877
2	8.681	BB	0.2708	4676.80371	268.99612	49.9696	2	8.682	BV	0.2709	1.32730e4	763.28540	84.7123

Totals : 9359.30469 637.82980

Totals : 1.56683e4 953.08926



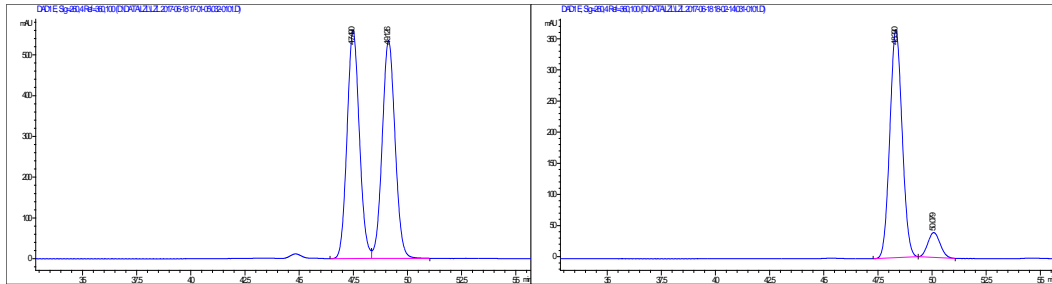
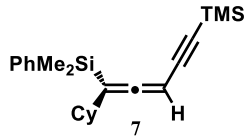
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.644	MF	1.3214	7.04392e4	888.44092	51.9406	1	33.705	VB	0.4654	5.76402e4	1675.46606	96.2515
2	53.631	BB	3.4392	6.51756e4	271.83408	48.0594	2	47.059	BB	1.0501	2244.77319	33.23087	3.7485

Totals : 1.35615e5 1160.27499

Totals : 5.98850e4 1708.69693



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

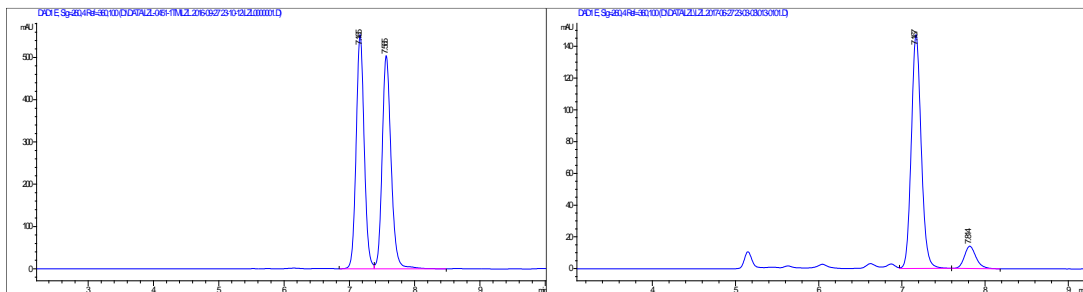
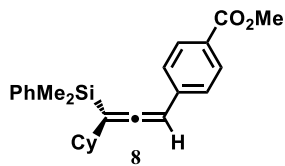
Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.490	BV	0.6046	2.21081e4	559.93231	50.0481
2	49.126	VB	0.5930	2.20656e4	535.21979	49.9519

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.330	BB	0.6058	1.43922e4	365.14581	90.1630
2	50.079	BB	0.6060	1570.22803	39.82764	9.8370

Totals : 4.41737e4 1095.15210

Totals : 1.59625e4 404.97345



Signal 5: DAD1 E, Sig=260,4 Ref=360,100

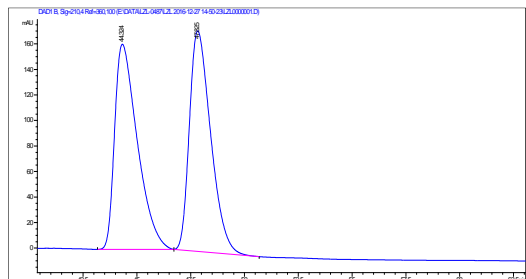
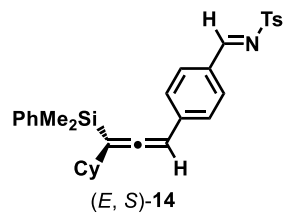
Signal 4: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.165	BV	0.1317	4733.23047	553.94714	49.6984
2	7.565	VB	0.1448	4790.68701	504.41898	50.3016

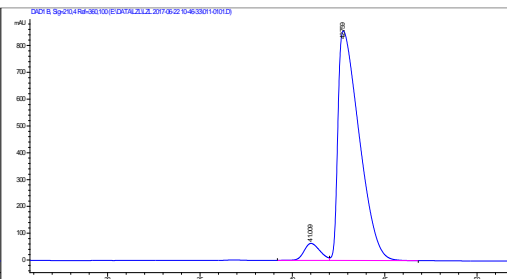
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.167	VB	0.1285	1216.48901	147.12424	89.9513
2	7.814	BB	0.1489	135.89771	14.04717	10.0487

Totals : 9523.91748 1058.36612

Totals : 1352.38672 161.17141



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



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.324	BB	1.1011	1.17833e4	160.76486	49.7724	1	41.009	BV	0.9078	3784.01025	63.44725	5.2536
2	47.825	BB	1.0527	1.18910e4	172.81844	50.2276	2	42.759	VB	1.1437	6.82433e4	856.37207	94.7464
Totals :				2.36743e4	333.58330		Totals :				7.20273e4	919.81932	

12 Crystal Data for (*E, S*)-14.

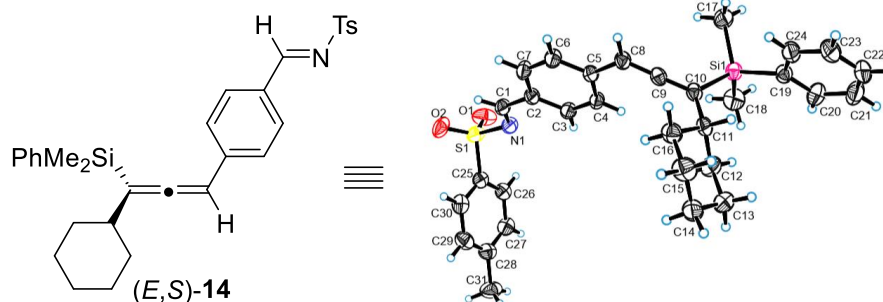


Table Crystal data and structure refinement for lzl-86.	
Identification code	lzl-86
Empirical formula	C ₃₁ H ₃₅ NO ₂ SSi
Formula weight	513.75
Temperature/K	290(2)
Crystal system	monoclinic
Space group	C2
a/Å	12.12950(10)
b/Å	13.86570(10)
c/Å	17.2627(2)
α / °	90
β / °	104.7730(10)
γ / °	90
Volume/Å ³	2807.34(5)
Z	4
ρ _{calc} /cm ³	1.216
μ /mm ⁻¹	1.643
F(000)	1096.0
Crystal size/mm ³	0.230 × 0.220 × 0.150
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.878 to 142.544
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -18 ≤ l ≤ 20
Reflections collected	10139
Independent reflections	5264 [R _{int} = 0.0265, R _{sigma} = 0.0328]
Data/restraints/parameters	5264/1/328
Goodness-of-fit on F ²	1.029
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0350, wR ₂ = 0.0938
Final R indexes [all data]	R ₁ = 0.0362, wR ₂ = 0.0955
Largest diff. peak/hole / e Å ⁻³	0.28/-0.15
Flack parameter	-0.011(11)