

Supporting Information

Stereo-divergent synthesis of silyl-enynes via palladium-catalyzed coupling of alkynes and iodosilanes

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General information

Unless otherwise noted, all reactions were carried out under N₂ atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (300-400 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ¹H NMR (400 MHz), ¹³C NMR (100 MHz), ²⁹Si NMR (79 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer and ¹⁹F NMR (471 MHz) spectra were recorded on a Bruker Avance (500 MHz) spectrometer, using CDCl₃ as the solvent and TMS as internal standard; chemical shifts were quoted in parts per million and *J* values were given in hertz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. High resolution mass spectrometry (HRMS) was performed on a Waters Micromass (APCI-TOF and ESI-TOF).

Optimization of Reaction Conditions

Reaction of alkynes and iodosilanes.

Table S1: Optimization of ligands.^a

1a + Me₃SiI $\xrightarrow[\text{DCE, 40 °C, 12 h}]{\text{Pd}_2(\text{dba})_3 \text{ (2.5 mol\%)}, \text{Ligand (5 mol\%)}, \text{Et}_3\text{N}}$

3a (E) + **4a (Z)**

81%
E/Z 24:76

73%
E/Z 26:74

56%
E/Z 23:77

77%
E/Z 17:83

83%
E/Z 20:80

69%
E/Z 38:62

51%
E/Z 16:84

70%
E/Z 5:95

63%
E/Z 19:81

92%
E/Z 37:63

trace

60%
E/Z 36:64

60%
E/Z 93:7

42%
E/Z 74:26

46%
E/Z 69:31

60%
E/Z 81:19

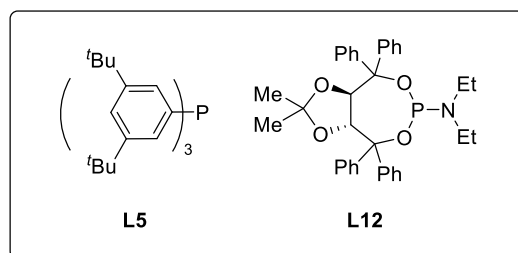
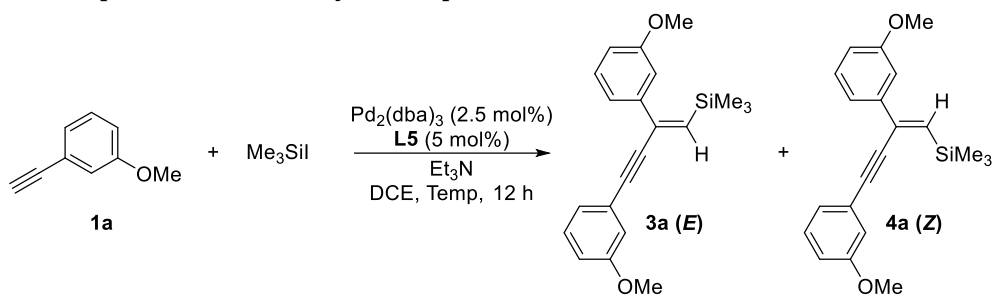
56%
E/Z 75:25

83%
E/Z 80:20

78%
E/Z 95:5

17%
E/Z 40:60

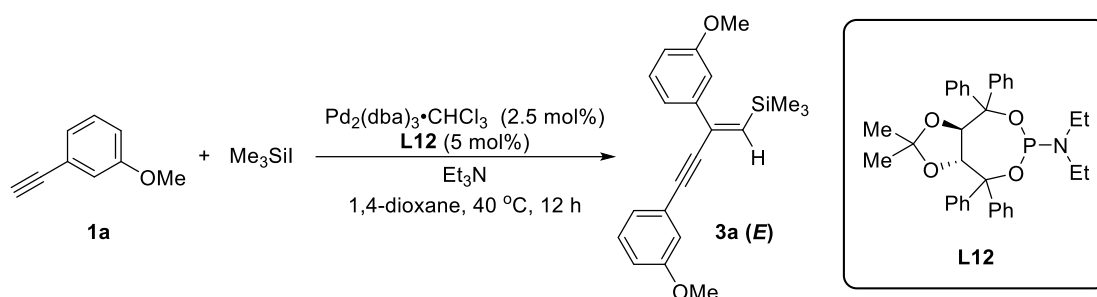
^a Reaction conditions: **1a** (1.0 mmol), **Me₃SiI** (1.0 mmol), Pd₂(dba)₃ (2.5 mol%), ligand (5 mol%), Et₃N (3.5 mmol), DCE (0.5 mL), 40 °C for 12 h, isolated yield.

Table S2: Optimization of catalysts, temperature and solvents.^a

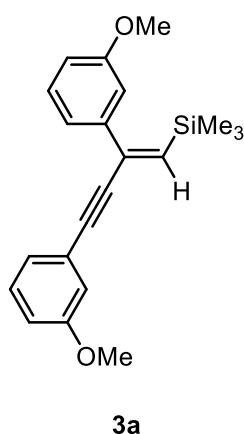
Entry	[Pd]	Ligand	Temp (°C)	Solvent	3a(E)+4a(Z)	3a(E):4a(Z)
1	$\text{Pd}_2(\text{dba})_3$	/	40	DCE	51	22:78
2	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L5	40	DCE	79	4:96
3	$\text{Pd}(\text{dba})_2$	L5	40	DCE	75	5:95
4	$\text{Pd}(\text{OAc})_2$	L5	40	DCE	68	4:96
5	$\text{Pd}(\text{acac})_2$	L5	40	DCE	71	5:95
6	$\text{Pd}(\text{cod})\text{Cl}_2$	L5	40	DCE	71	9:91
7	$\text{Pd}(\text{MeCN})_2\text{Cl}_2$	L5	40	DCE	63	8:92
8	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L5	r.t.(23)	DCE	65	4:96
9	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L5	30	DCE	78	4:96
10	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L5	40	DCE	80	4:96
11	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L5	50	DCE	72	4:96
12	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L5	60	DCE	70	7:93
13	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L5	70	DCE	62	8:92
14	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L5	40	Toluene	82	4:96
15	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L5	40	1,4-dioxane	85	5:95
16	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L5	40	Et_3N	56	7:93
17	$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$	L12	40	1,4-dioxane	83	95:5

^a Reaction conditions: **1a** (1.0 mmol), **Me₃SiH** (1.0 mmol), [Pd] (5 mol%), **L5/L12** (5 mol%), Et_3N (3.5 mmol), solvent (0.5 mL) for 12 h, isolated yield.

Typical procedure for the synthesis of **3a**.



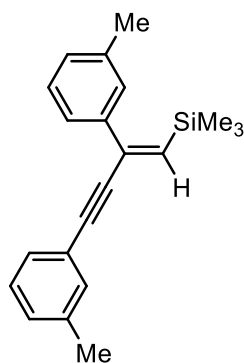
A 10 mL Schlenk flask equipped with a magnetic stirbar and rubber septum was flame-dried, allowed to cool to room temperature under vacuum, and refilled with N_2 . The flask was briefly opened, charged with the given **L12** (14.4 mg, 0.025 mmol) and palladium catalyst (13.0 mg, 0.0125 mmol), and the septum was replaced. The flask was evacuated and refilled with nitrogen 3 times. 1,4-dioxane (0.5 mL), alkyne **1a** (132 mg, 0.13 mL, 1 mmol), triethylamine (0.5 mL, 3.5 mmol) and Me_3SiH (200 mg, 0.14 mL, 1 mmol) were added sequentially via syringe at room temperature with stirring. The reaction was allowed to stir at 40 °C in an oil bath for 12 h after the addition was completed. The reaction mixture was quenched by water. The aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with saturated aqueous sodium chloride solution (30 mL), dried over anhydrous sodium sulfate, filtered, concentrated in vacuo, and under reduced pressure and then purified by silica column (PE) to get the product **3a**.



(E)-(2,4-bis(3-methoxyphenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (140.0 mg, 83%). ^1H NMR (400 MHz, CDCl_3) δ 7.27 (t, J = 8.0 Hz, 1H), 7.22-7.17 (m, 1H), 7.07-7.02 (m,

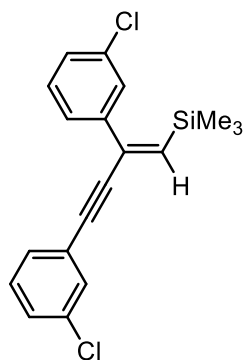
2H), 7.01-6.97 (m, 2H), 6.90-6.83 (m, 2H), 6.48 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.32, 159.31, 141.6, 138.9, 129.4, 129.1, 124.3, 120.9, 116.3, 115.0, 113.9, 113.7, 91.9, 89.6, 55.29, 55.26, 0.0. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.7. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{O}_2\text{Si}$, 337.1618; found 337.1608.



3b

(*E*)-(2,4-di-*m*-tolylbut-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (126.2 mg, 83%). ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.25 (m, 5H), 7.24-7.09 (m, 3H), 6.45 (s, 1H), 2.38 (s, 3H), 2.31 (s, 3H), 0.0 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 140.7, 139.5, 138.0, 137.6, 132.3, 129.2, 129.1, 128.84, 128.82, 128.3, 128.0, 125.5, 123.2, 92.1, 89.8, 21.5, 21.3, 0.1. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.9. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{Si}$, 305.1720; found 305.1709.

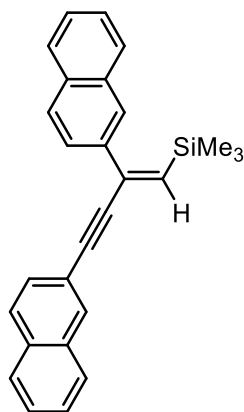


3c

(*E*)-(2,4-bis(3-chlorophenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (154.8 mg, 90%). ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.40 (m, 2H), 7.36-7.23 (m, 5H), 7.22 (d, $J = 7.6$ Hz,

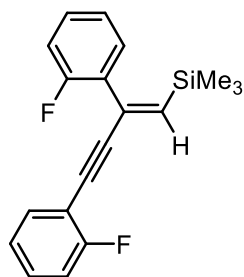
1H), 6.53 (s, 1H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.5, 142.1, 137.3, 134.3, 134.1, 131.5, 129.8, 129.6, 129.5, 128.7, 128.5, 128.3, 126.5, 124.9, 92.7, 88.5, 0.0. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.4. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{Cl}_2\text{Si}$, 345.0628; found 345.0633.



3d

(E)-(2,4-di(naphthalen-2-yl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (154.3 mg, 82%). ^1H NMR (400 MHz, CDCl_3) δ 8.12 (s, 1H), 8.07 (s, 1H), 8.01-7.94 (m, 3H), 7.89-7.82 (m, 3H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.69-7.51 (m, 5H), 6.78 (s, 1H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.0, 139.3, 138.2, 133.12, 133.06, 133.0, 132.9, 131.7, 128.5, 128.2, 128.1, 127.9, 127.4, 126.8, 126.6, 126.48, 126.45, 126.3, 120.7, 92.7, 90.5, 0.2. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.6. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{25}\text{Si}$, 377.1720; found 377.1725.

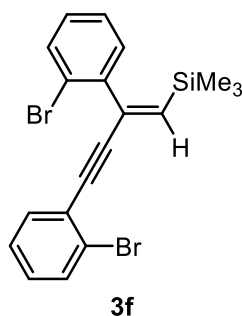


3e

(E)-(2,4-bis(2-fluorophenyl)but-1-en-3-yn-1-yl)trimethylsilane

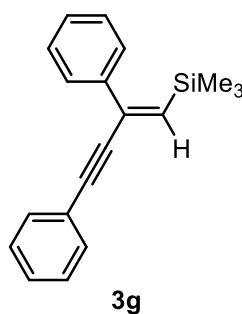
The mobile phase for flash chromatography: PE. Colorless oil. (100.4 mg, 65%). ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, $J = 6.8$ Hz, 1H), 7.45-7.33 (m, 3H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.20-7.10 (m, 3H), 6.78 (s, 1H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ

162.6 (d, $J = 252.0$ Hz), 159.6 (d, $J = 247.2$ Hz), 145.5, 133.6 (d, $J = 0.7$ Hz), 131.9, 131.0 (d, $J = 3.2$ Hz), 130.1 (d, $J = 8.0$ Hz), 129.9 (d, $J = 8.0$ Hz), 128.0 (d, $J = 16.0$ Hz), 124.0 (d, $J = 3.6$ Hz), 123.9 (d, $J = 3.6$ Hz), 115.8 (d, $J = 21.6$ Hz), 115.5 (d, $J = 20.8$ Hz), 111.9 (d, $J = 15.6$ Hz), 96.3 (d, $J = 3.6$ Hz), 82.5, -0.7. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.1. ^{19}F NMR (471 MHz, CDCl_3) δ -109.7, -114.5. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_2\text{Si}$, 313.1219; found 313.1211.



(*E*)-(2,4-bis(2-bromophenyl)but-1-en-3-yn-1-yl)trimethylsilane

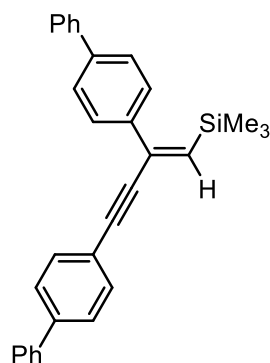
The mobile phase for flash chromatography: PE. Colorless oil. (90.7 mg, 42%). ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.0$ Hz, 1H), 7.55 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.44 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.33-7.29 (m, 2H), 7.24-7.18 (m, 2H), 7.12 (td, $J = 7.6, 1.6$ Hz, 1H), 6.65 (s, 1H), -0.10 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 140.9, 137.6, 133.4, 132.8, 132.5, 130.9, 129.5, 127.2, 127.0, 125.8, 125.5, 123.0, 95.0, 88.7, -0.6. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.1. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{Br}_2\text{Si}$, 434.9617; found 434.9594.



(*E*)-(2,4-diphenylbut-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (118.8 mg, 86%). ^1H NMR (400 MHz, CDCl_3) δ 7.56-7.49 (m, 4H), 7.44-7.37 (m, 3H), 7.36-7.33 (m, 3H), 6.55 (s, 1H), 0.04 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.4, 140.7, 139.2, 131.7, 128.4, 128.3, 128.1, 128.1, 123.4, 92.3, 89.7, 0.1. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.72.

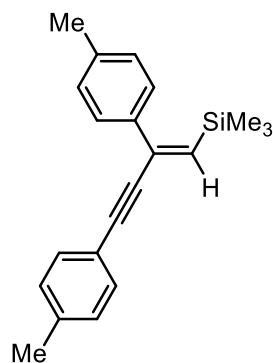
HRMS (APCI-TOF) m/z : $[M + H]^+$ Calcd for $C_{19}H_{21}Si$, 277.1407; found 277.1413.



3h

(E)-(2,4-di([1,1'-biphenyl]-4-yl)but-1-en-3-yn-1-yl)trimethylsilane

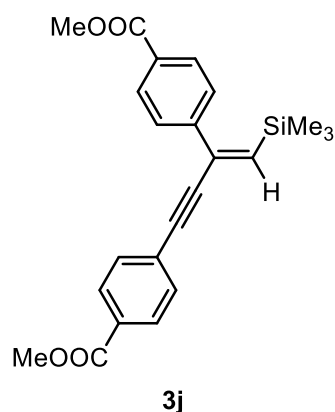
The mobile phase for flash chromatography: PE. White solid. (156.3 mg, 73%). mp 116-118 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.69-7.59 (m, 6H), 7.58-7.51 (m, 6H), 7.50-7.43 (m, 4H), 7.40-7.35 (m, 2H), 6.54 (s, 1H), 0.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 141.1, 141.0, 140.7, 140.4, 139.7, 138.8, 132.2, 129.0, 128.94, 128.90, 127.8, 127.6, 127.2, 127.13, 127.08, 126.8, 122.3, 93.0, 89.6, 0.2. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -8.9. HRMS (APCI-TOF) m/z : $[M + H]^+$ Calcd for $C_{31}H_{29}Si$, 429.2033; found 429.2034.



3i

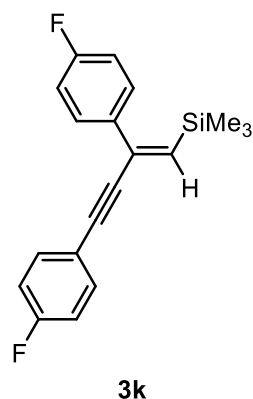
(E)-(2,4-di-p-tolylbut-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (114.1 mg, 75%). 1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 4H), 7.20 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.46 (s, 1H), 2.42 (s, 3H), 2.37 (s, 3H), 0.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 139.4, 138.4, 138.0, 137.9, 131.6, 129.1, 128.8, 128.3, 120.4, 91.9, 89.7, 21.6, 21.4, 0.2. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -8.9. HRMS (APCI-TOF) m/z : $[M + H]^+$ Calcd for $C_{21}H_{25}Si$, 305.1720; found 305.1713.



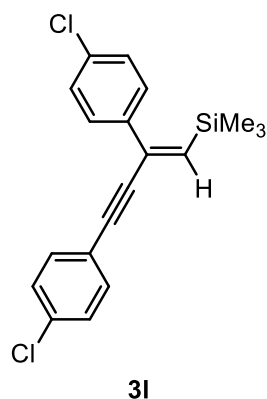
(*E*)-dimethyl 4,4'-(4-(trimethylsilyl)but-3-en-1-yn-1,3-diyl)dibenzoate

The mobile phase for flash chromatography: PE. Colorless oil. (147.0 mg, 90%). ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 2H), 7.97 (d, $J = 8.4$ Hz, 2H), 7.54-7.46 (m, 4H), 6.58 (s, 1H), 3.92 (s, 3H), 3.89 (s, 3H), -0.04 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 166.3, 144.7, 143.9, 137.6, 131.4, 129.7, 129.6, 129.4, 128.3, 94.2, 89.2, 52.10, 52.07, -0.2. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{24}\text{NaO}_4\text{Si}$, 415.1336; found 415.1347.



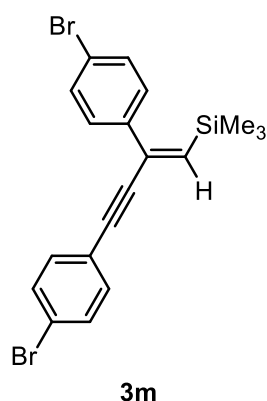
(*E*)-(2,4-bis(4-fluorophenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (140.5 mg, 86%). ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.38 (m, 4H), 7.11-6.97 (m, 4H), 6.46 (s, 1H), -0.01 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.7 (d, $J = 245.0$ Hz), 162.6 (d, $J = 248.0$ Hz), 141.8, 137.9, 136.7 (d, $J = 3.2$ Hz), 133.6 (d, $J = 8.4$ Hz), 130.1 (d, $J = 8.0$ Hz), 119.3 (d, $J = 3.6$ Hz), 115.7 (d, $J = 22.0$ Hz), 115.1 (d, $J = 21.6$ Hz), 91.8, 88.7, 0.1. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.7. ^{19}F NMR (471 MHz, CDCl_3) δ -110.4, -114.0. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_2\text{Si}$, 313.1219; found 313.1223.



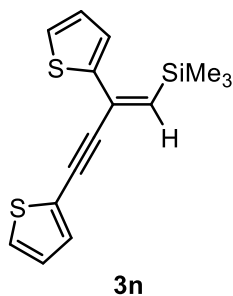
(*E*)-(2,4-bis(4-chlorophenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. White solid. (141.2 mg, 82%). mp 60-62 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.33 (m, 6H), 7.32-7.26 (m, 2H), 6.51 (s, 1H), 0.00 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 142.6, 138.9, 137.6, 134.5, 134.1, 132.9, 129.7, 128.8, 128.4, 121.6, 92.7, 88.7, 0.1. ²⁹Si NMR (79 MHz, CDCl₃) δ -8.6. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₉H₁₉Cl₂Si, 345.0628; found 345.0619.



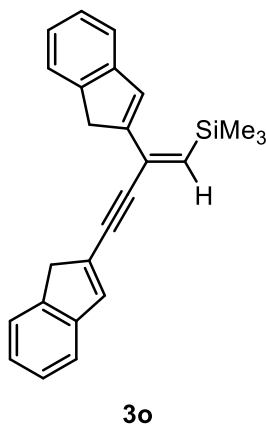
(*E*)-(2,4-bis(4-bromophenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. White solid. (183.6 mg, 85%). mp 75-77 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.32-7.26 (m, 4H), 6.51 (s, 1H), 0.00 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 142.6, 139.4, 137.6, 133.1, 131.7, 131.3, 130.0, 122.8, 122.3, 122.1, 92.8, 88.8, 0.1. ²⁹Si NMR (79 MHz, CDCl₃) δ -8.6. HRMS (APCI-TOF) m/z: [M + H]⁺ Calcd for C₁₉H₁₉Br₂Si, 434.9617; found 434.9593.



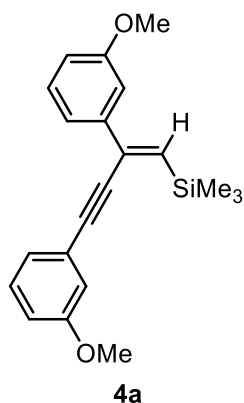
(Z)-(2,4-di(thiophen-2-yl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (82.1 mg, 57%). ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.44 (m, 1H), 7.34-7.32 (m, 1H), 7.31-7.28 (m, 1H), 7.27-7.24 (m, 1H), 7.21 (d, $J = 4.8$ Hz, 1H), 7.13 (d, $J = 4.8$ Hz, 1H), 6.42 (s, 1H), 0.05 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 141.0, 133.4, 129.9, 128.8, 128.2, 125.4, 125.3, 123.9, 122.3, 91.4, 84.1, 0.0. ^{29}Si NMR (79 MHz, CDCl_3) δ -9.1. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{17}\text{S}_2\text{Si}$, 289.0535; found 289.0527.



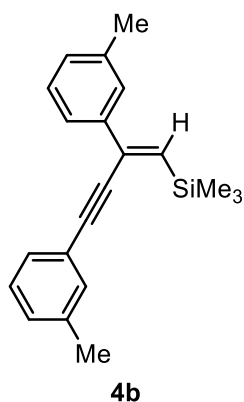
(E)-(2,4-di(1H-inden-2-yl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (45.8 mg, 26%). ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.25 (m, 4H), 7.19-7.09 (m, 3H), 7.07-7.00 (m, 3H), 6.20 (s, 1H), 3.51 (s, 2H), 3.46 (s, 2H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.6, 145.0, 144.2, 143.4, 143.1, 137.5, 136.9, 133.8, 130.8, 127.4, 127.0, 126.7, 126.0, 125.5, 123.7, 121.8, 121.6, 93.4, 90.0, 42.6, 38.0, -0.6. ^{29}Si NMR (79 MHz, CDCl_3) δ -9.2. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{25}\text{Si}$, 353.1720; found 353.1722.



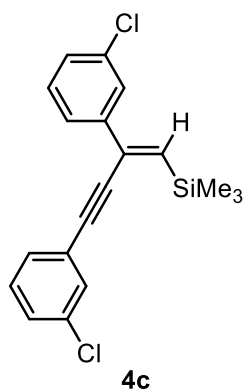
(Z)-(2,4-bis(3-methoxyphenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (142.8 mg, 85%). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.33-7.26 (m, 3H), 7.15-7.13 (m, 1H), 7.06 (dd, $J = 2.8, 1.6$ Hz, 1H), 6.95-6.85 (m, 2H), 6.68 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 0.33 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.7, 159.5, 141.0, 138.3, 136.9, 129.6, 129.4, 124.4, 124.1, 118.6, 116.6, 114.8, 113.9, 111.8, 93.9, 89.4, 55.4, -0.7. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.32. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{O}_2\text{Si}$, 337.1618; found 337.1610.



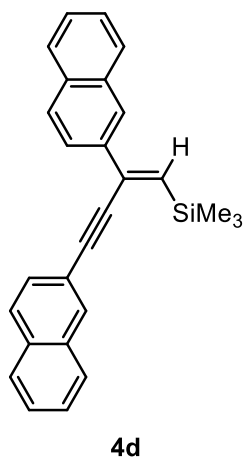
(Z)-(2,4-di-*m*-tolylbut-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (106.5 mg, 70%). ^1H NMR (400 MHz, CDCl_3) δ 7.62 (s, 1H), 7.40 (s, 1H), 7.36-7.26 (m, 4H), 7.19 (dd, $J = 11.9, 7.7$ Hz, 2H), 6.70 (s, 1H), 2.45 (s, 3H), 2.42 (s, 3H), 0.38 (s, 7H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.6, 138.2, 137.9, 137.4, 132.0, 129.4, 129.1, 128.6, 128.5, 128.3, 126.7, 123.3, 94.1, 89.4, 21.7, 21.4, -0.7. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.0. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{Si}$, 305.1720; found 305.1724.



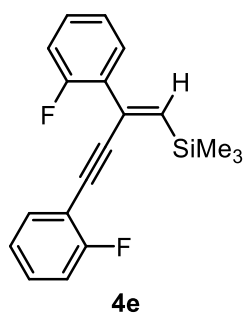
(Z)-(2,4-bis(3-chlorophenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (142.8 mg, 83%). ^1H NMR (400 MHz, CDCl_3) δ 7.75 (s, 1H), 7.68-7.60 (m, 1H), 7.55 (t, $J = 1.6$ Hz, 1H), 7.44 (d, $J = 7.6$ Hz, 1H), 7.40-7.27 (m, 4H), 6.76 (s, 1H), 0.38 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.1, 140.2, 135.4, 134.50, 134.45, 131.2, 129.8, 129.7, 129.0, 128.4, 126.2, 124.8, 124.3, 92.7, 90.1, -0.8. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.51. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{Cl}_2\text{Si}$, 345.0628; found 345.0643.



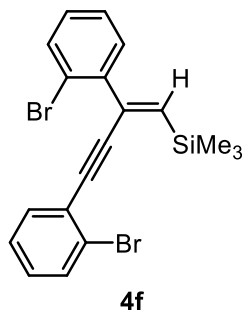
(Z)-(2,4-di(naphthalen-2-yl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (154.0 mg, 82%). ^1H NMR (400 MHz, CDCl_3) δ 8.43 (s, 1H), 8.20 (s, 1H), 8.03 (d, $J = 7.6$ Hz, 2H), 7.93 (dd, $J = 10.8, 6.0$ Hz, 5H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.67-7.53 (m, 4H), 6.99 (s, 1H), 0.54 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.3, 137.2, 136.8, 133.4, 133.3, 133.1, 133.0, 131.4, 128.7, 128.3, 128.2, 128.0, 127.9, 127.7, 126.9, 126.8, 126.4, 126.4, 125.8, 123.7, 120.7, 94.6, 90.1, -0.6. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.7. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{25}\text{Si}$, 377.1720; found 377.1713.



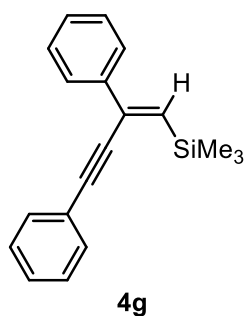
(Z)-(2,4-bis(2-fluorophenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (113.9 mg, 73%). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (td, $J = 8.0, 2.0$ Hz, 1H), 7.35 (td, $J = 7.6, 1.6$ Hz, 1H), 7.21-7.09 (m, 2H), 7.06-6.90 (m, 4H), 6.58 (s, 1H), 0.22 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.9 (d, $J = 252.0$ Hz), 160.0 (d, $J = 250.4$ Hz), 145.1 (d, $J = 5.6$ Hz), 133.3 (d, $J = 1.6$ Hz), 131.8, 130.2 (d, $J = 11.2$ Hz), 130.1, 129.5 (d, $J = 8.4$ Hz), 128.5 (d, $J = 10.8$ Hz), 124.15 (d, $J = 4.0$ Hz), 124.10 (d, $J = 4.0$ Hz), 116.3 (d, $J = 22.8$ Hz), 115.7 (d, $J = 20.8$ Hz), 112.0 (d, $J = 15.6$ Hz), 94.7 (d, $J = 3.2$ Hz), 86.3, -0.9. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.9. ^{19}F NMR (471 MHz, CDCl_3) δ -109.2, -115.5. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_2\text{Si}$, 313.1219; found 313.1203.



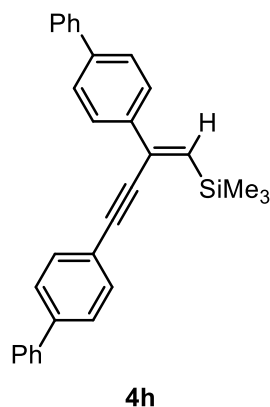
(Z)-(2,4-bis(2-bromophenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (151.2 mg, 70%). ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.60 (m, 2H), 7.54-7.47 (m, 2H), 7.37-7.24 (m, 2H), 7.21-7.11 (m, 2H), 6.38 (s, 1H), 0.39 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.4, 142.9, 136.9, 133.4, 133.2, 132.6, 130.2, 129.6, 129.0, 127.4, 127.1, 125.6, 125.4, 121.5, 93.7, 92.6, -0.7. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.6. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{Br}_2\text{Si}$, 434.9617; found 434.9590.



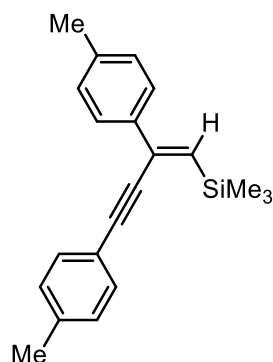
(Z)-(2,4-diphenylbut-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (105.4 mg, 76%). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 7.6$ Hz, 2H), 7.64 (dd, $J = 7.6, 2.1$ Hz, 2H), 7.51-7.37 (m, 6H), 6.78 (s, 1H), 0.44 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.5, 137.7, 137.2, 131.5, 128.6, 128.4, 128.3, 126.1, 123.4, 94.0, 89.7, -0.7. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.88. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{21}\text{Si}$, 277.1407; found 277.1413.



(Z)-(2,4-di([1,1'-biphenyl]-4-yl)but-1-en-3-yn-1-yl)trimethylsilane

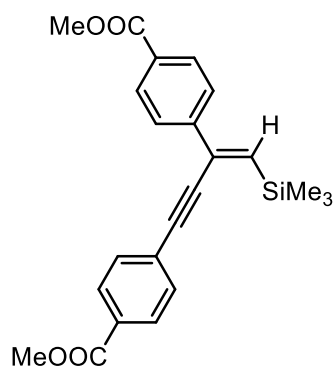
The mobile phase for flash chromatography: PE. White solid. (156.2 mg, 73%). mp 65-67 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.0$ Hz, 2H), 7.74-7.65 (m, 10H), 7.52 (t, $J = 7.6$ Hz, 4H), 7.47-7.37 (m, 2H), 6.82 (s, 1H), 0.45 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.3, 141.1, 140.7, 140.4, 138.4, 137.7, 136.8, 132.0, 129.0, 128.9, 127.8, 127.5, 127.3, 127.15, 127.12, 126.6, 122.3, 94.1, 90.3, -0.6. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.8. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{29}\text{Si}$, 429.2033; found 429.2035.



4i

(Z)-(2,4-di-*p*-tolylbut-1-en-3-yn-1-yl)trimethylsilane

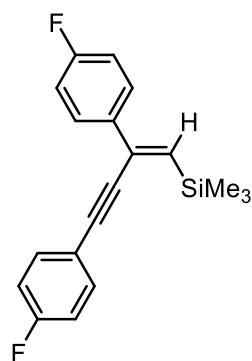
The mobile phase for flash chromatography: PE. White solid. (82.1 mg, 54%). mp 45-47 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 7.6 Hz, 4H), 6.63 (s, 1H), 2.40 (s, 3H), 2.39 (s, 3H), 0.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.7, 138.2, 137.2, 136.8, 136.0, 131.4, 129.3, 129.1, 126.0, 120.5, 94.1, 89.2, 21.7, 21.3, -0.7. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.1. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{Si}$, 305.1720; found 305.1731.



4j

(Z)-dimethyl 4,4'-(4-(trimethylsilyl)but-3-en-1-yne-1,3-diyl)-dibenzoate

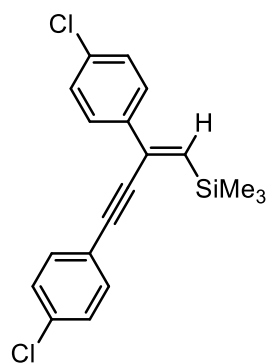
The mobile phase for flash chromatography: PE. White solid. (188.2 mg, 96%). mp 97-99 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.04-8.01 (m, 4H), 7.77 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 6.82 (s, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 166.3, 143.2, 141.6, 135.8, 131.3, 129.9, 129.8, 129.73, 129.68, 127.6, 125.9, 93.5, 91.7, 52.3, 52.1, -0.9. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.5. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{25}\text{O}_4\text{Si}$, 393.1517; found 393.1519.



4k

(Z)-(2,4-bis(4-fluorophenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. White solid. (127.9 mg, 82%). mp 54-56 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.74 (dd, $J = 8.4, 5.2$ Hz, 2H), 7.53 (dd, $J = 8.4, 5.6$ Hz, 2H), 7.09 (td, $J = 8.8, 3.2$ Hz, 4H), 6.63 (s, 1H), 0.35 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.0 (d, $J = 246.0$ Hz), 162.8 (d, $J = 249.0$ Hz), 137.5 (d, $J = 0.9$ Hz), 135.9, 135.6 (d, $J = 3.2$ Hz), 133.4 (d, $J = 8.4$ Hz), 127.8 (d, $J = 8.4$ Hz), 119.4 (d, $J = 3.6$ Hz), 116.0 (d, $J = 22.4$ Hz), 115.3 (d, $J = 21.6$ Hz), 93.1, 89.1 (d, $J = 1.6$ Hz), -0.8. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.9. ^{19}F NMR (471 MHz, CDCl_3) δ -110.2, -113.8. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_2\text{Si}$, 313.1219; found 313.1207.

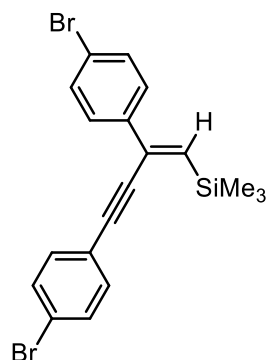


4l

(Z)-(2,4-bis(4-chlorophenyl)but-1-en-3-yn-1-yl)trimethylsilane

The mobile phase for flash chromatography: PE. White solid. (128.6 mg, 75%). mp 66-68 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 4H), 6.70 (s, 1H), 0.35 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.8, 137.7, 135.7, 134.8, 134.3, 132.7, 129.0, 128.5, 127.4, 121.6, 93.1, 90.1, -0.8. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.69. ^{19}F NMR (471 MHz, Chloroform- d) δ -110.2, -113.8. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{Cl}_2\text{Si}$, 345.0628; found

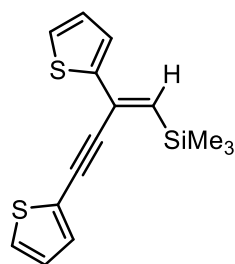
345.0644.



4m

(Z)-(2,4-bis(4-bromophenyl)but-1-en-3-yn-1-yl)trimethylsilane

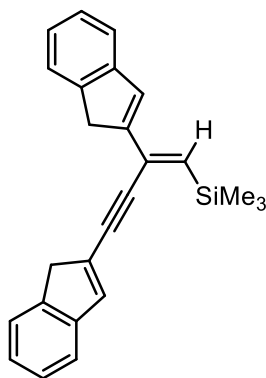
The mobile phase for flash chromatography: PE. White solid. (181.4 mg, 84%). mp 66-68 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 8.4 Hz, 2H), 7.55-7.47 (m, 4H), 7.39 (d, J = 8.4 Hz, 2H), 6.70 (s, 1H), 0.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.0, 138.2, 135.8, 132.8, 131.9, 131.5, 127.7, 123.0, 122.5, 122.0, 93.1, 90.2, -0.8. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.6. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{Br}_2\text{Si}$, 434.9617; found 434.9603.



4n

(Z)-(2,4-di(thiophen-2-yl)but-1-en-3-yn-1-yl)trimethylsilane

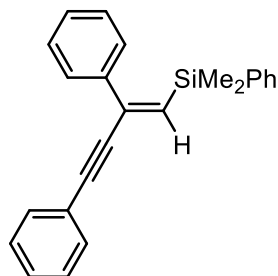
The mobile phase for flash chromatography: PE. Colorless oil. (79.2 mg, 55%). ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 1.6 Hz, 1H), 7.52 (d, J = 2.0 Hz, 1H), 7.37 (d, J = 4.8 Hz, 1H), 7.33 (dd, J = 5.2, 3.2 Hz, 1H), 7.28 (dd, J = 5.2, 3.2 Hz, 1H), 7.20 (d, J = 4.8 Hz, 1H), 6.51 (s, 1H), 0.30 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.3, 135.8, 131.7, 129.7, 128.7, 126.0, 125.7, 125.1, 123.0, 122.4, 89.0, 88.0, -0.7. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.95. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{17}\text{S}_2\text{Si}$, 289.0535; found 289.0528.



4o

(Z)-(2,4-di(1*H*-inden-2-yl)but-1-en-3-yn-1-yl)trimethylsilane

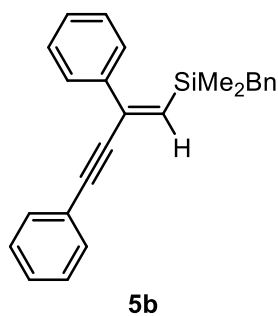
The mobile phase for flash chromatography: PE. Colorless oil. (51.1 mg, 29%). ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.40 (m, 4H), 7.36-7.26 (m, 3H), 7.24-7.18 (m, 3H), 6.39 (s, 1H), 3.69 (s, 2H), 3.64 (s, 2H), 0.36 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.6, 145.0, 144.2, 143.4, 143.1, 137.4, 136.9, 133.8, 130.8, 127.4, 127.0, 126.7, 125.9, 125.5, 123.74, 123.73, 121.8, 121.6, 93.4, 90.0, 42.6, 38.0, -0.6. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.2. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{25}\text{Si}$, 353.1720; found 353.1721.



5a

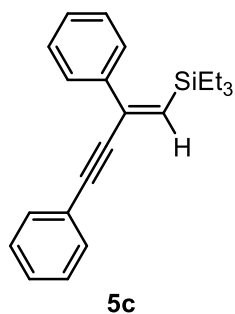
(E)-(2,4-diphenylbut-1-en-3-yn-1-yl)dimethyl(phenyl)silane

The mobile phase for flash chromatography: PE. Colorless oil. (133.5 mg, 79%). ^1H NMR (400 MHz, CDCl_3) δ 7.67-7.59 (m, 2H), 7.61-7.54 (m, 2H), 7.55-7.48 (m, 2H), 7.50-7.42 (m, 3H), 7.44-7.35 (m, 6H), 6.77 (s, 1H), 0.29 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.41, 140.37, 139.2, 138.8, 133.8, 131.7, 129.1, 128.43, 128.38, 128.2, 128.1, 128.0, 123.3, 92.3, 90.2, -1.3. ^{29}Si NMR (79 MHz, CDCl_3) δ -13.2. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{23}\text{Si}$, 339.1564; found 339.1554.



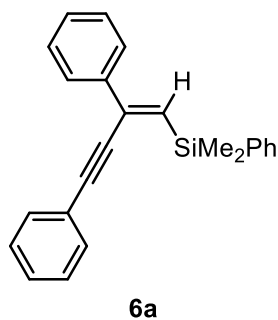
(E)-benzyl(2,4-diphenylbut-1-en-3-yn-1-yl)dimethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (151.4 mg, 86%). ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.50 (m, 2H), 7.49-7.34 (m, 8H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.17 (t, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 7.2$ Hz, 2H), 6.53 (s, 1H), 2.16 (s, 2H), -0.02 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 140.1, 139.7, 139.2, 131.7, 128.41, 128.38, 128.35, 128.26, 128.15, 124.3, 123.3, 92.3, 90.1, 26.5, -1.9. ^{29}Si NMR (79 MHz, CDCl_3) δ -8.1. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{25}\text{Si}$, 353.1720; found 353.1708.



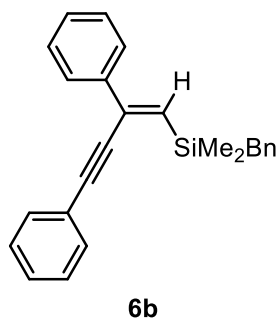
(E)-(2,4-diphenylbut-1-en-3-yn-1-yl)triethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (33.4 mg, 21%). ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.43 (m, 4H), 7.38-7.35 (m, 3H), 7.33-7.28 (m, 3H), 6.42 (s, 1H), 0.86 (t, $J = 8.0$ Hz, 9H), 0.45 (q, $J = 8.0$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.1, 140.1, 138.5, 131.8, 128.4, 128.3, 128.23, 128.17, 128.1, 123.4, 92.6, 89.4, 7.6, 4.7. ^{29}Si NMR (79 MHz, CDCl_3) δ -1.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{NaSi}$, 341.1696; found 341.1713.



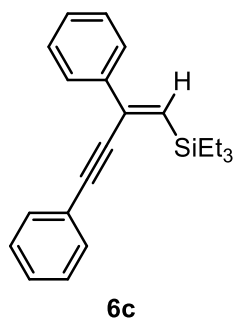
(Z)-(2,4-diphenylbut-1-en-3-yn-1-yl)dimethyl(phenyl)silane

The mobile phase for flash chromatography: PE. Colorless oil. (150.4 mg, 89%). ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 7.6$ Hz, 2H), 7.89-7.84 (m, 2H), 7.60-7.52 (m, 7H), 7.51-7.44 (m, 4H), 6.99 (s, 1H), 0.81 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 138.8, 138.5, 135.1, 134.0, 131.5, 129.1, 128.58, 128.55, 128.4, 127.9, 126.2, 123.2, 94.7, 89.7, -1.7. ^{29}Si NMR (79 MHz, CDCl_3) δ -12.3. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{23}\text{Si}$, 339.1564; found 339.1557.



(Z)-benzyl(2,4-diphenylbut-1-en-3-yn-1-yl)dimethylsilane

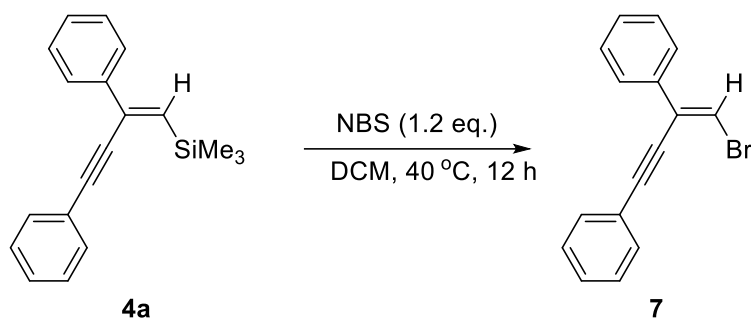
The mobile phase for flash chromatography: PE. Colorless oil. (162.0 mg, 92%). ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 7.2$ Hz, 2H), 7.55 (dd, $J = 7.6, 2.4$ Hz, 2H), 7.40-7.27 (m, 6H), 7.21 (t, $J = 7.6$ Hz, 2H), 7.12-7.03 (m, 3H), 6.60 (s, 1H), 2.45 (s, 2H), 0.32 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.0, 139.4, 138.0, 135.6, 131.5, 128.7, 128.6, 128.5, 128.45, 128.42, 128.3, 126.1, 124.2, 123.2, 94.5, 89.7, 25.6, -2.7. ^{29}Si NMR (79 MHz, CDCl_3) δ -7.2. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{25}\text{Si}$, 353.1720; found 353.1710.



(Z)-(2,4-diphenylbut-1-en-3-yn-1-yl)triethylsilane

The mobile phase for flash chromatography: PE. Colorless oil. (40.0 mg, 25%). ^1H NMR (400 MHz, CDCl_3) δ 7.84-7.76 (m, 2H), 7.60-7.52 (m, 2H), 7.45-7.32 (m, 6H), 6.66 (s, 1H), 1.08 (t, $J = 7.7$ Hz, 9H), 0.94-0.84 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.9, 137.9, 135.0, 131.5, 128.6, 128.5, 128.4, 128.3, 126.2, 123.5, 93.1, 90.0, 7.8, 4.1. ^{29}Si NMR (79 MHz, CDCl_3) δ -0.5. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{NaSi}$, 341.1696; found 341.1713.

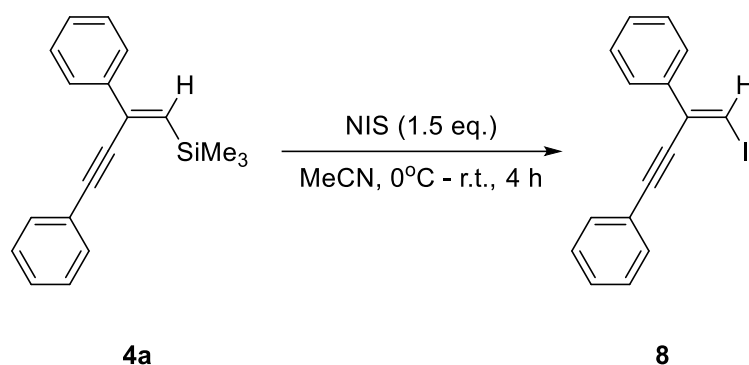
Procedures for the synthesis of 7 and 8.



(Z)-(4-bromobut-3-en-1-yn-1,3-diyl)dibenzene

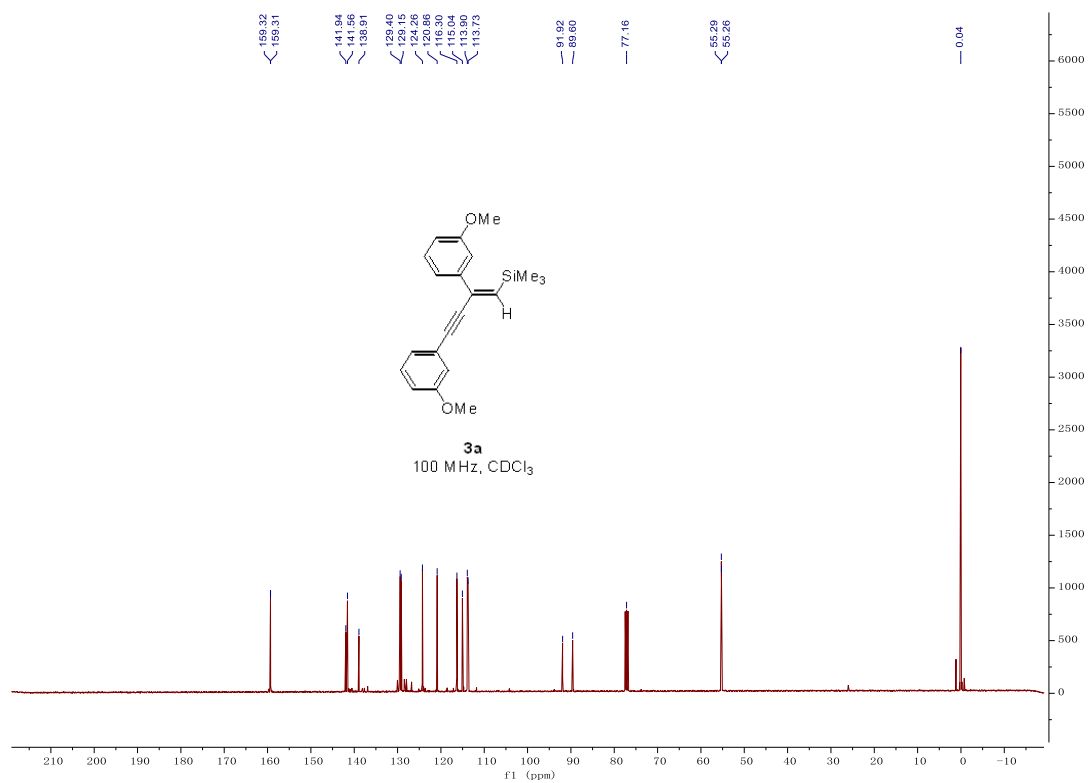
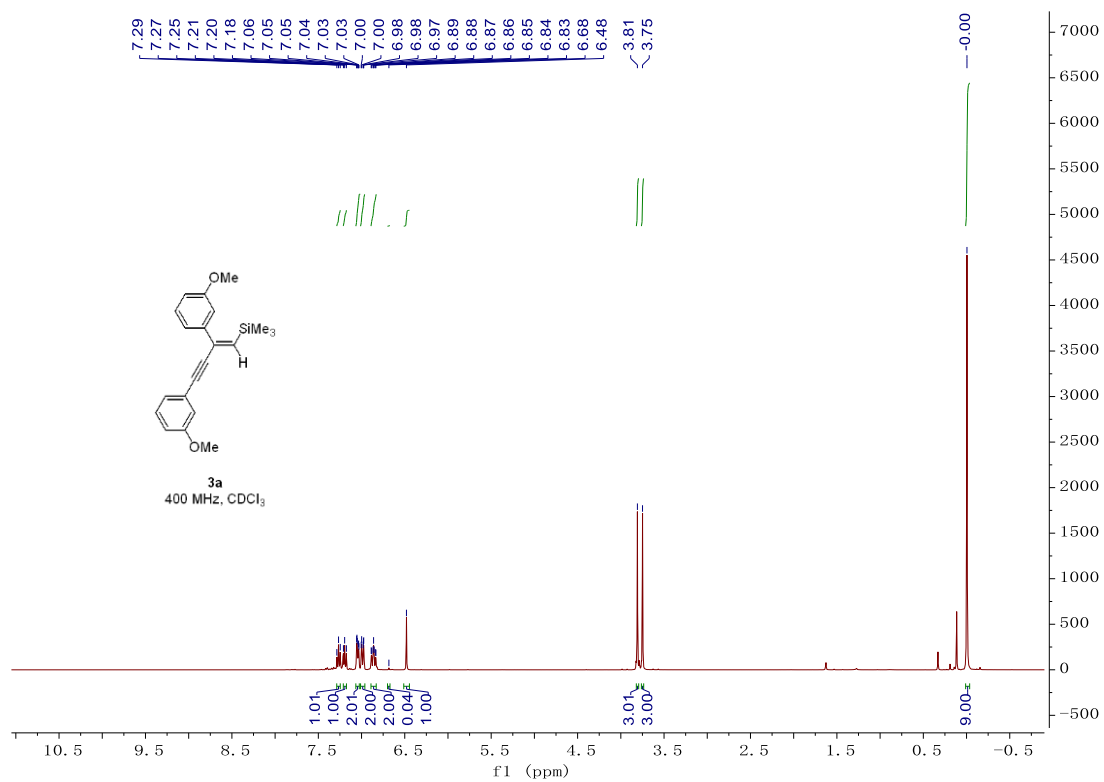
A vial was charged with **4a** (138 mg, 0.5 mmol) and NBS (106.8 mg, 0.6 mmol). Then DCM (6 mL) was added and the reaction mixture was stirred at 40 °C in an oil bath for 12 h. Upon reaction completion, the reaction mixture was diluted with DCM (5 mL) and water (10 mL) was then added. The organic layer was separated, and the aqueous layer was extracted with DCM (2 $\times$ 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude product. The mobile phase for flash chromatography: PE. Colorless oil. (114.2 mg, 81%). ^1H NMR (400 MHz, CDCl_3) δ 7.72-7.59 (m, 4H), 7.46-7.36 (m, 6H), 7.06 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.9, 131.9, 130.4, 129.0, 128.8, 128.7, 128.5, 126.4, 122.8, 113.3, 98.0, 86.7. HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{12}\text{Br}$, 283.0117; found

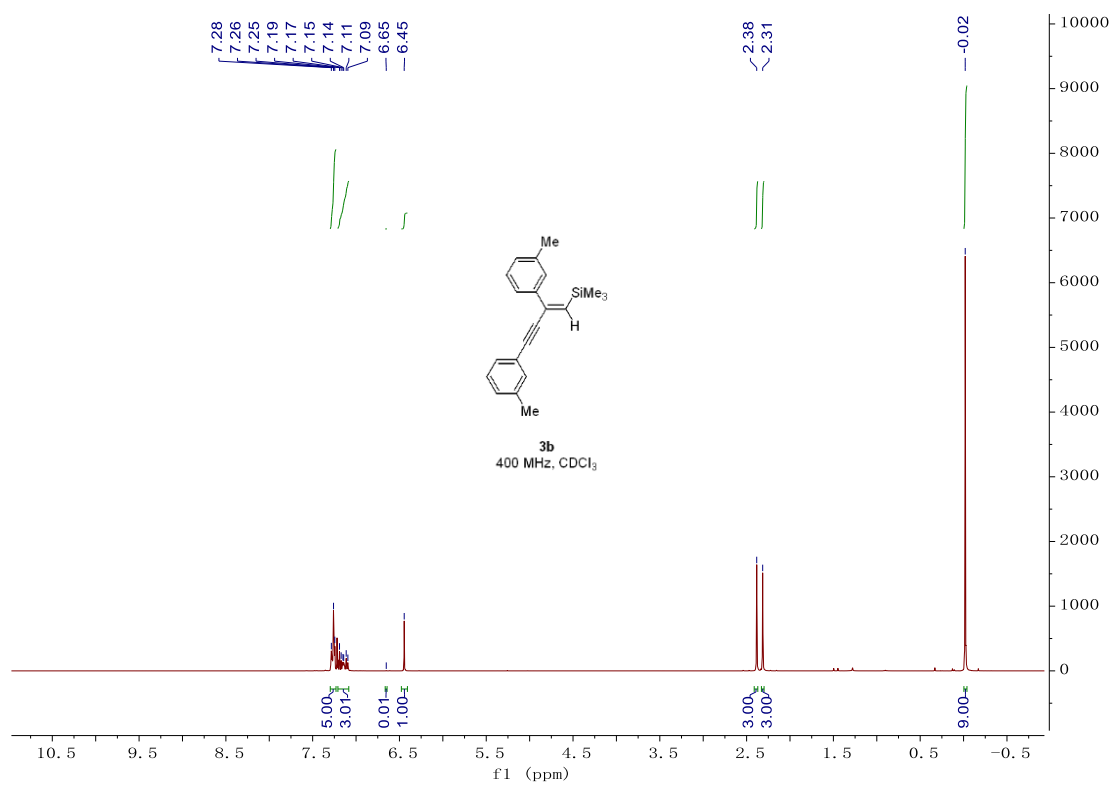
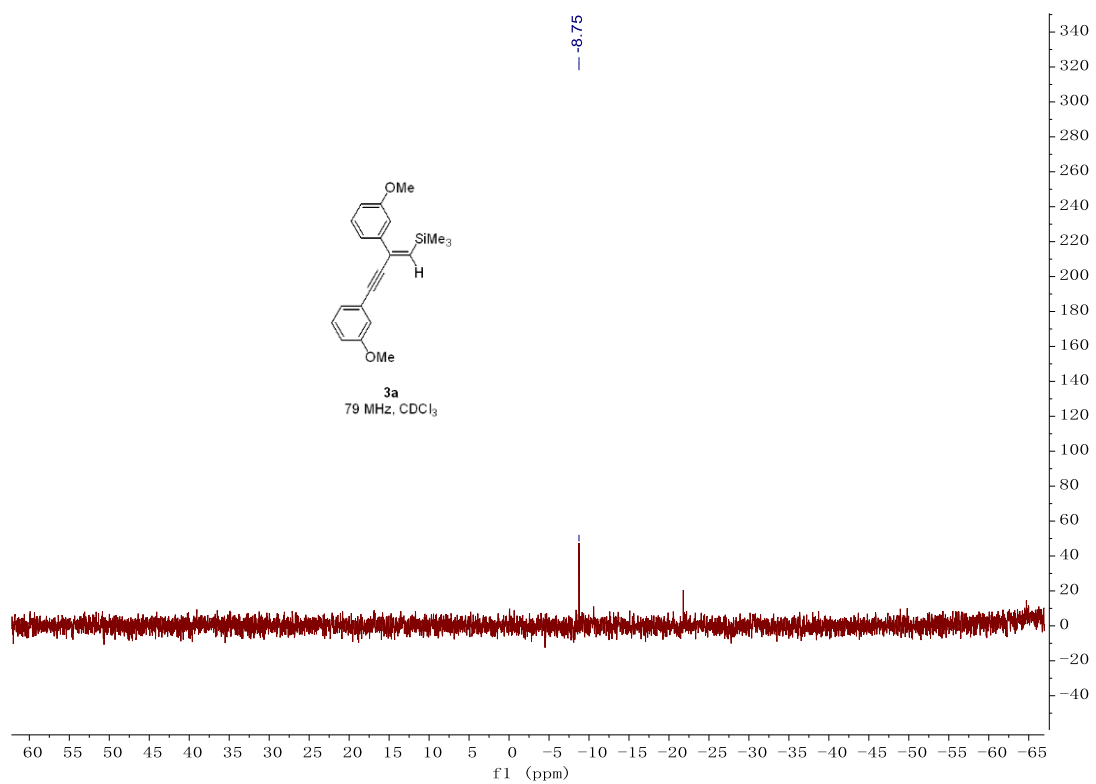
283.0121.

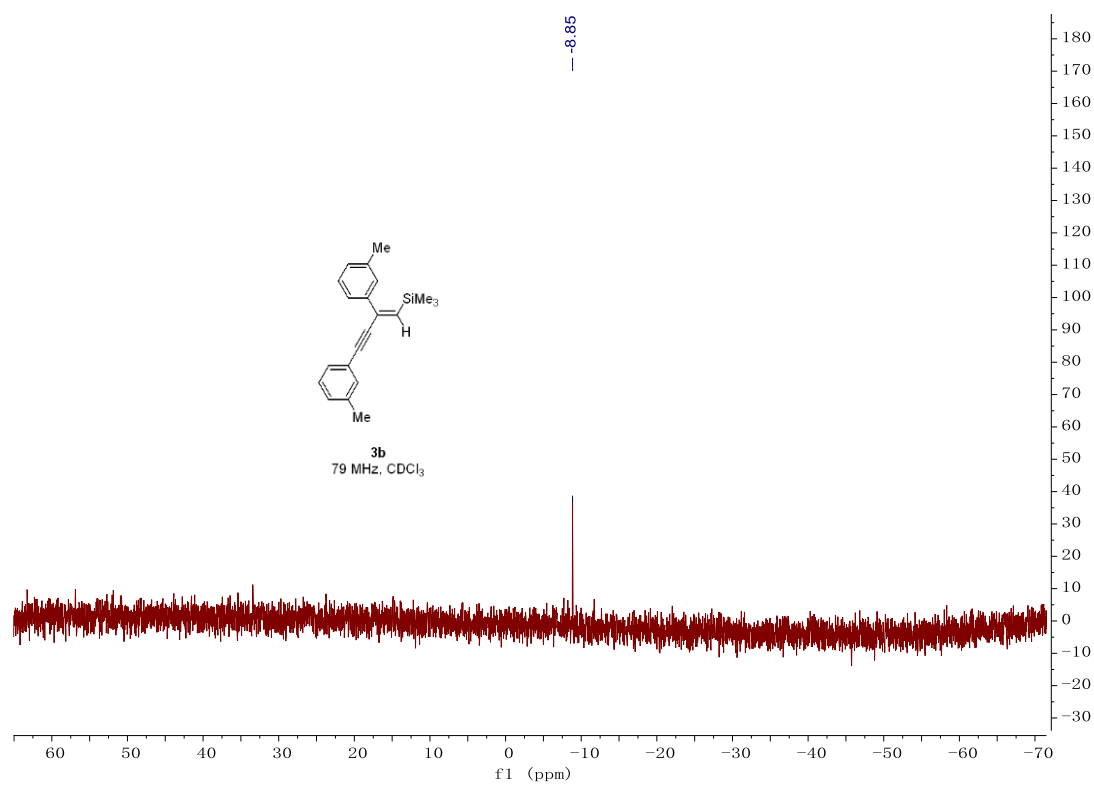
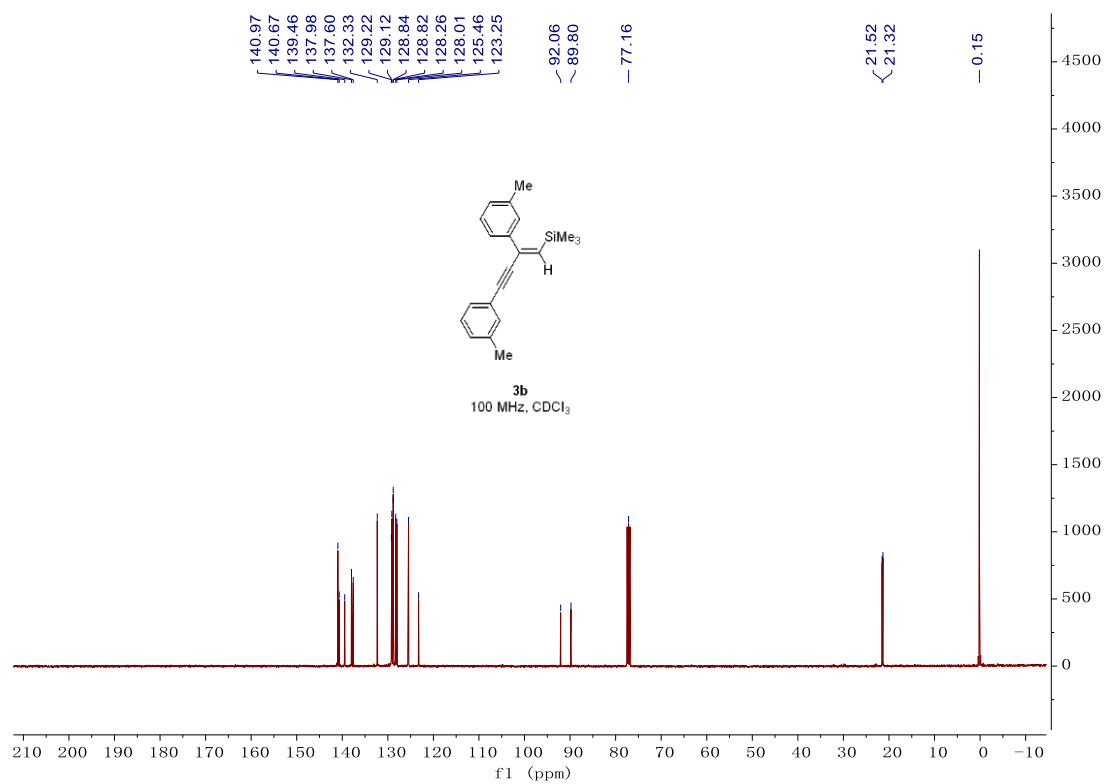


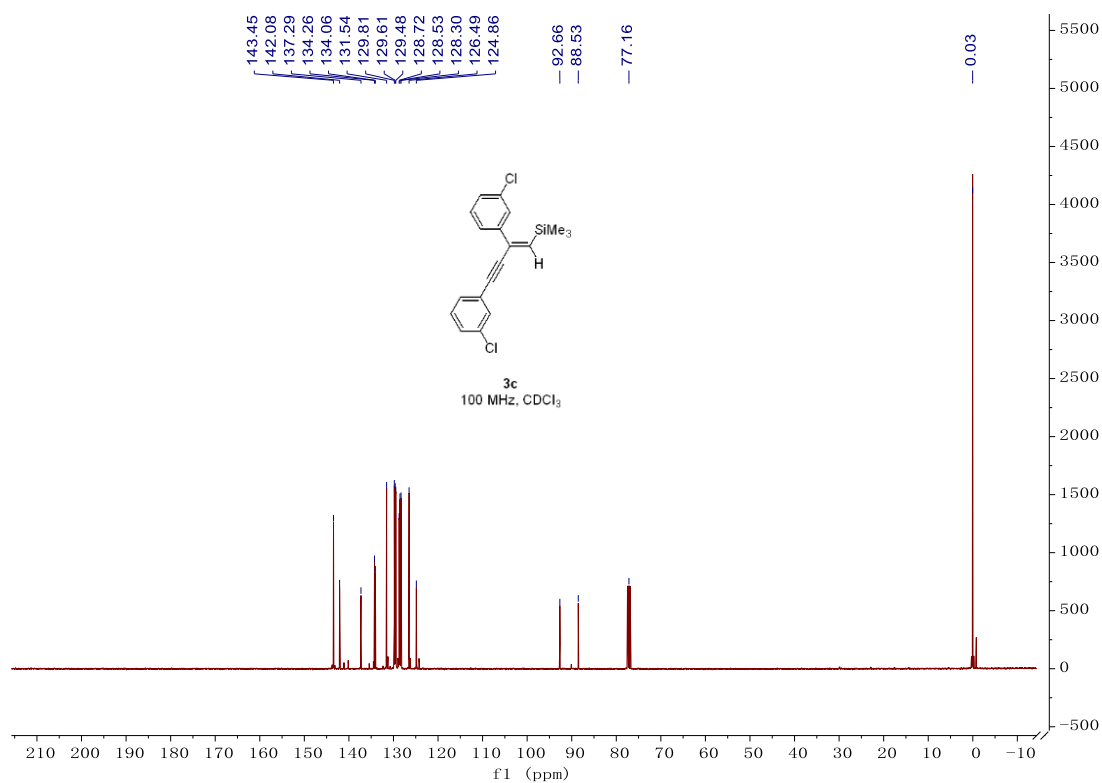
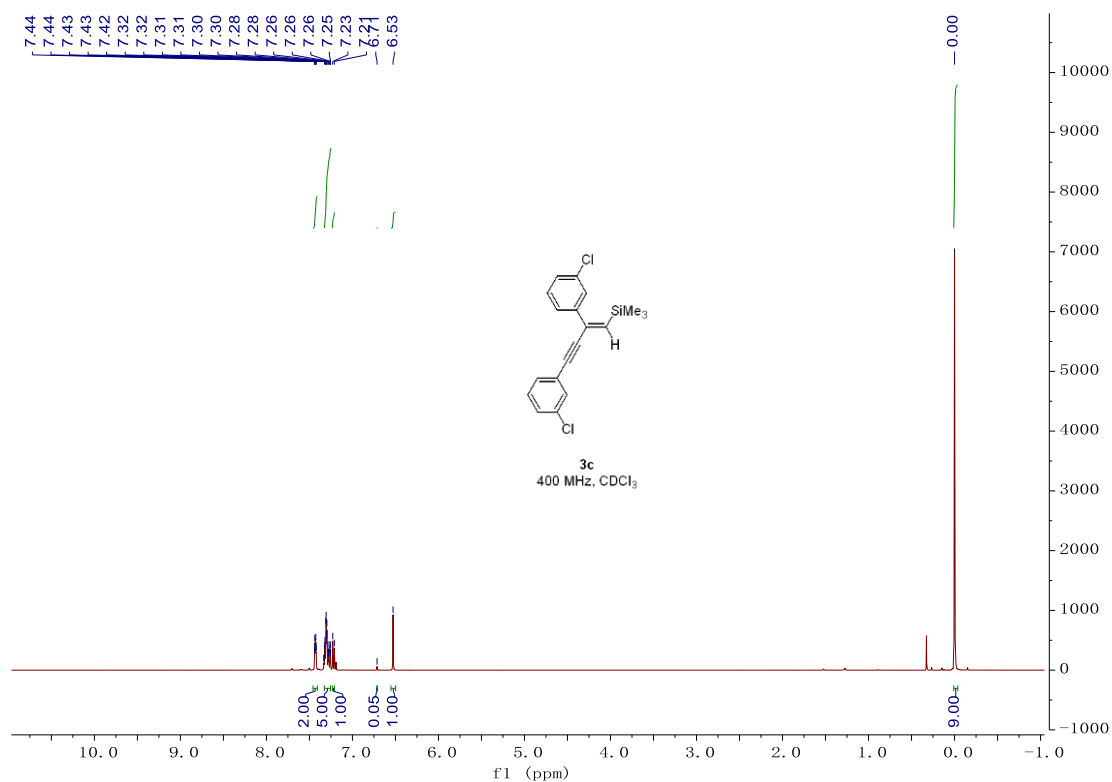
(Z)-(4-iodobut-3-en-1-yn-1,3-diyl)dibenzene

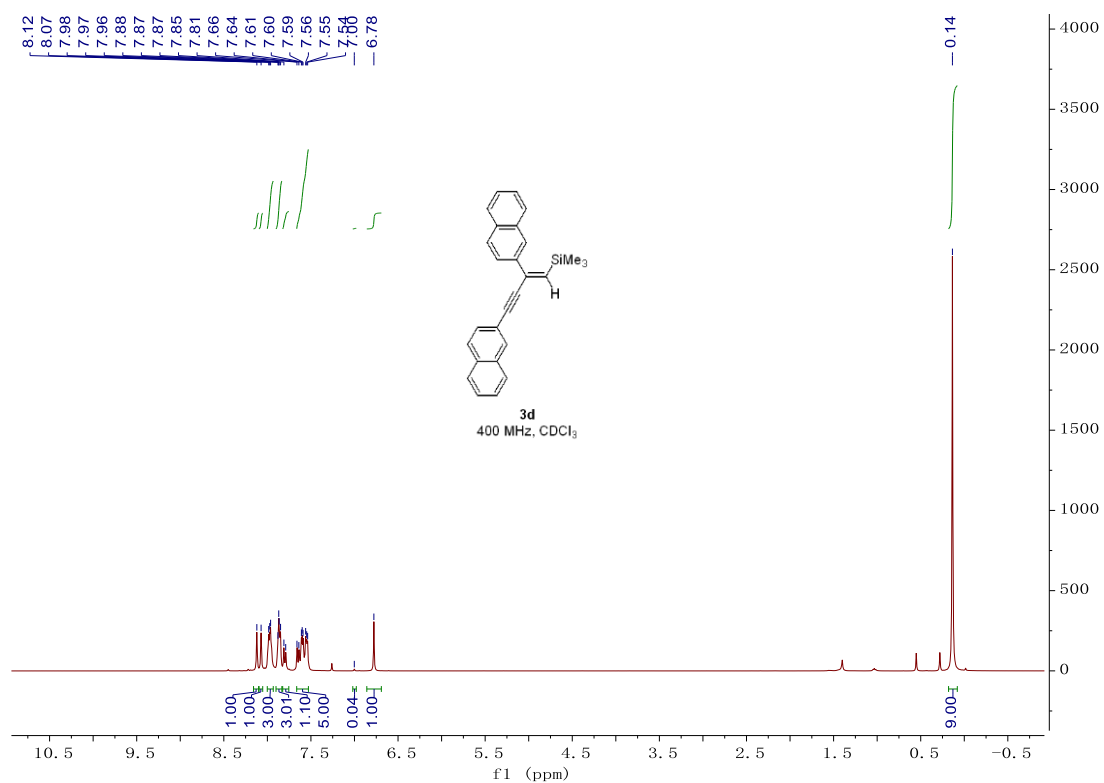
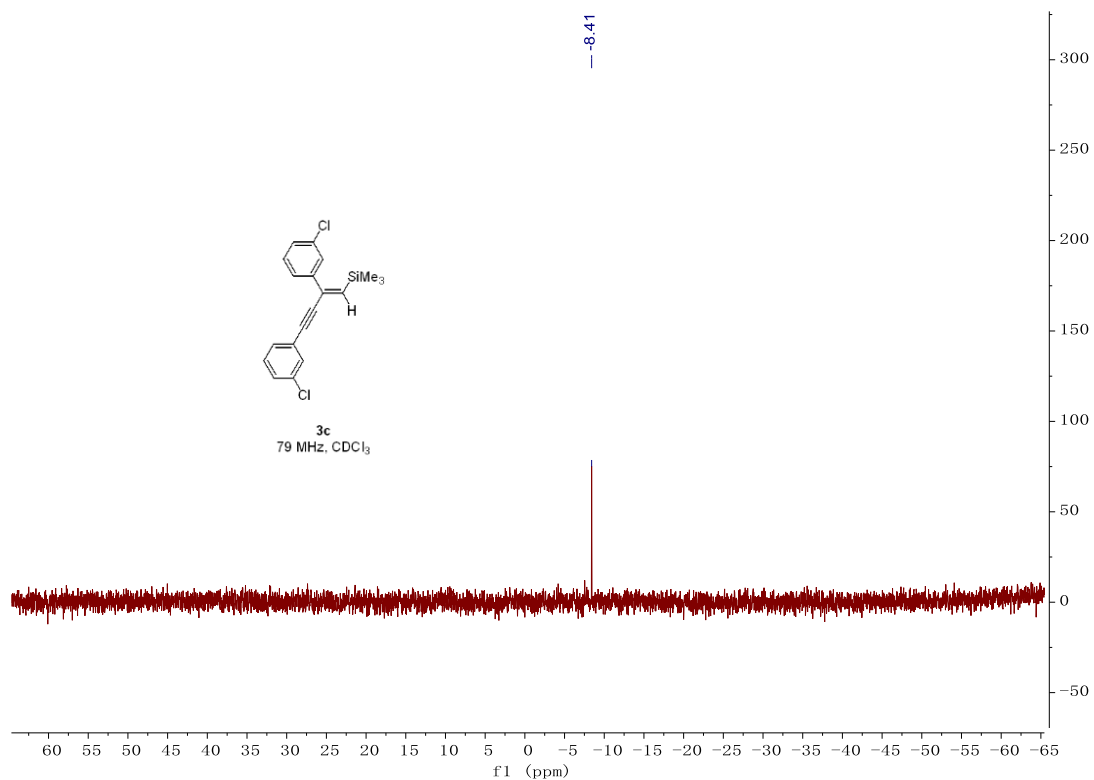
To a magnetically stirred solution of **4a** (138 mg, 0.5 mmol) in acetonitrile (5 mL) was added *N*-iodosuccinimide (NIS) (56 mg, 0.25 mmol) in one portion at 0 °C. After 30 min, another portion of NIS (56 mg, 0.25 mmol) was added. After 2.5 h, the reaction mixture was allowed to warm to room temperature and was stirred for another hour, time after which NIS (28 mg, 0.13 mmol) was added. After another 30 min, NIS (28 mg, 0.13 mmol) was added and the mixture was further stirred for 30 min. A saturated aqueous solution of Na₂S₂O₃ was then added to the reaction mixture and the resulting aqueous layer was extracted 3 times with diethyl ether. The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and the solvent removed in vacuo to give a yellow oil. The mobile phase for flash chromatography: PE. Colorless oil. (140.3 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.64 (m, 4H), 7.47-7.36 (m, 6H), 7.27 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 137.8, 136.6, 131.9, 129.0, 128.72, 128.69, 128.5, 126.4, 122.8, 96.9, 90.2, 87.1. HRMS (APCI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₂I, 330.9978; found 330.9957.

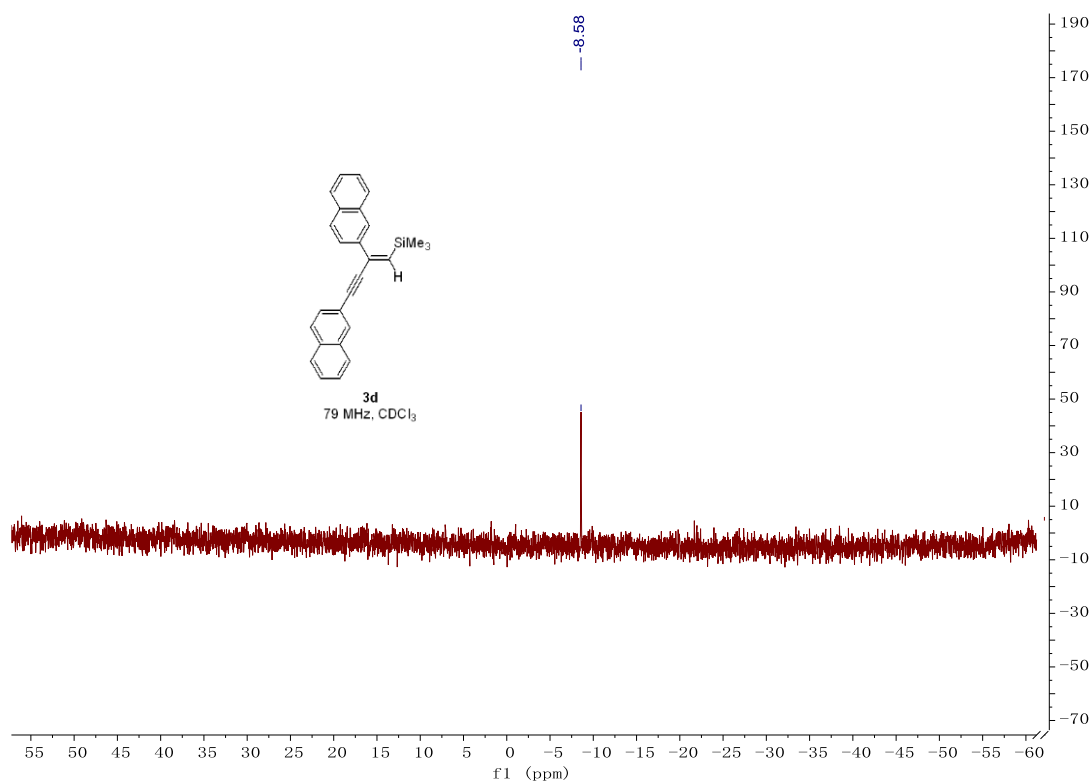
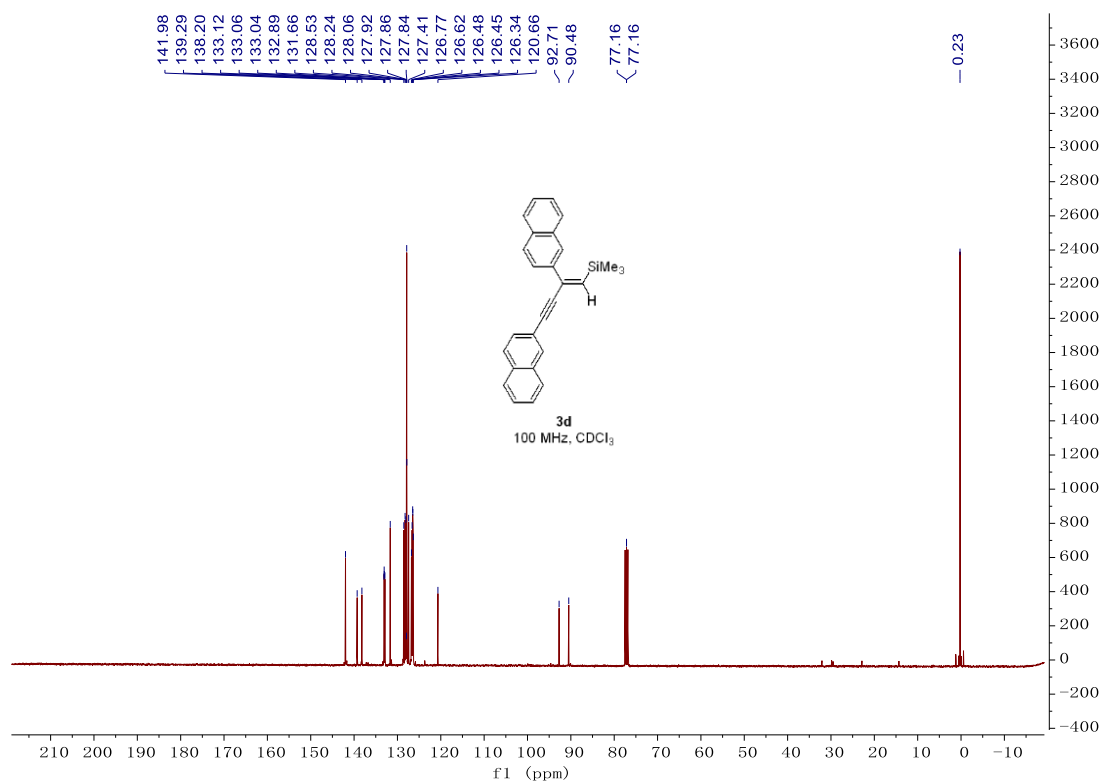


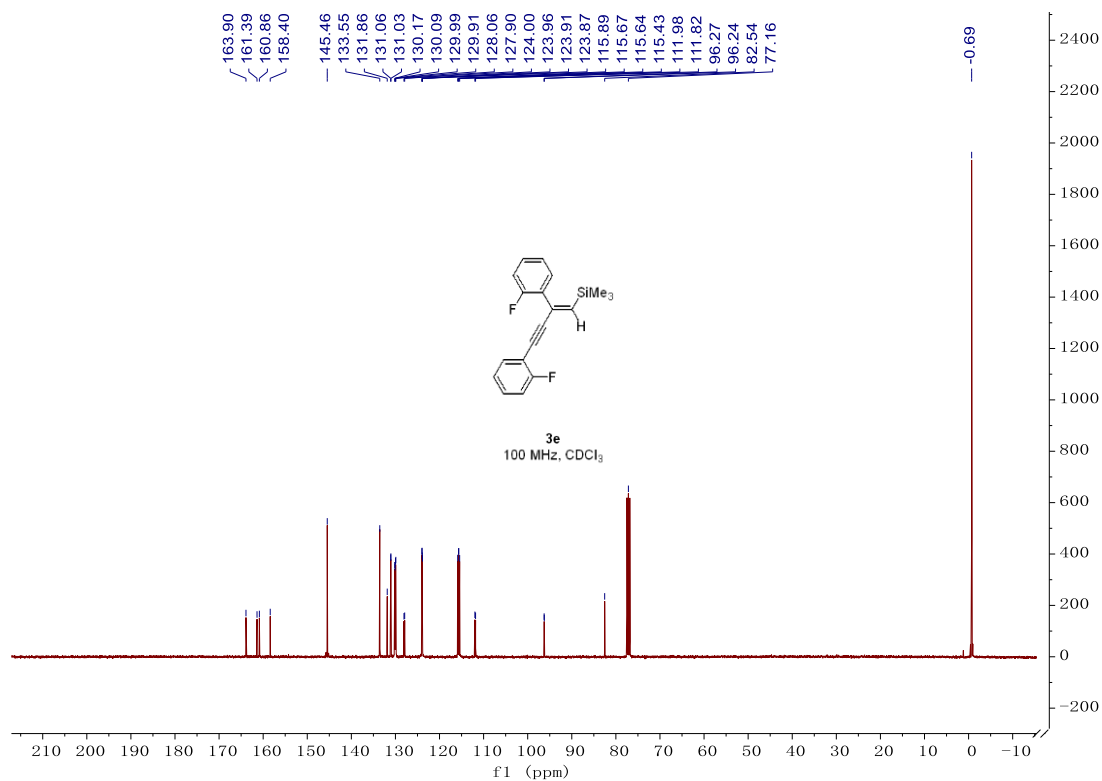
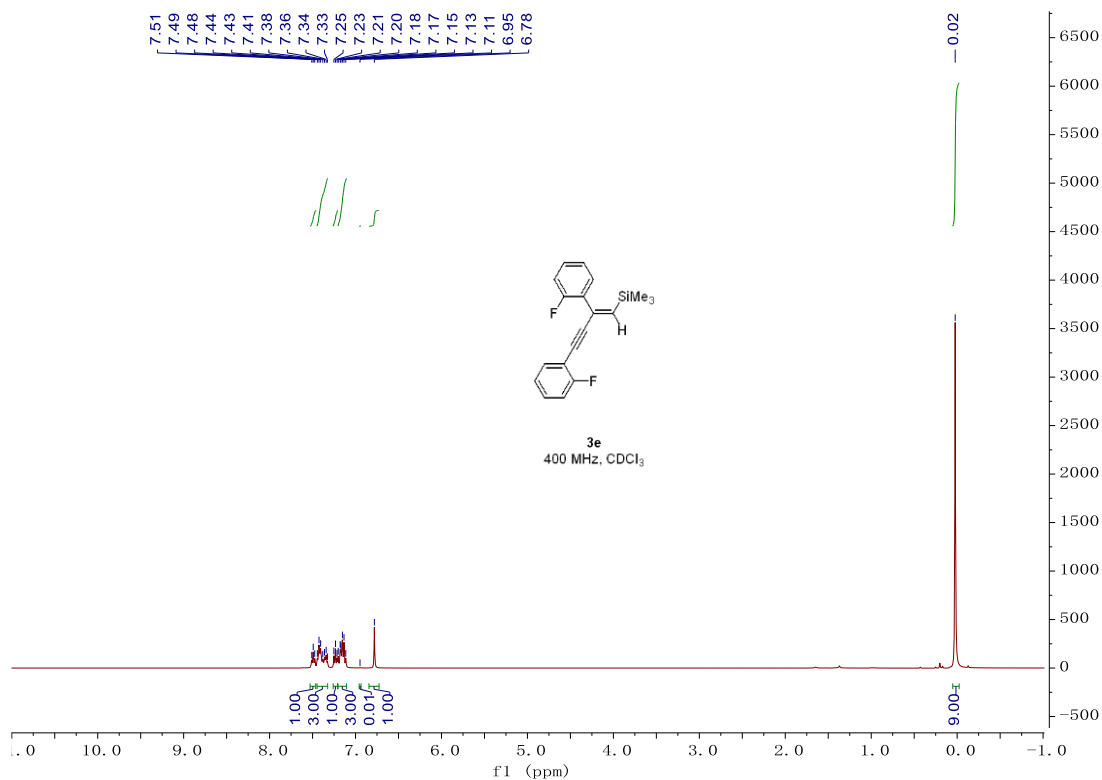


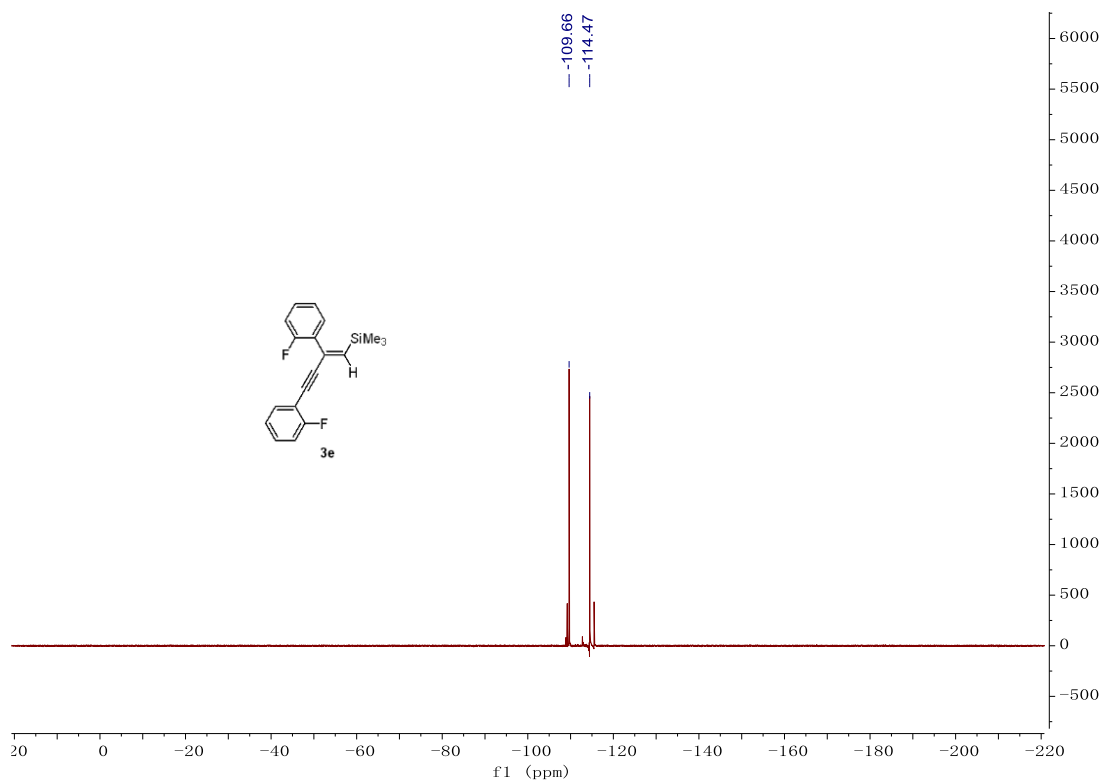
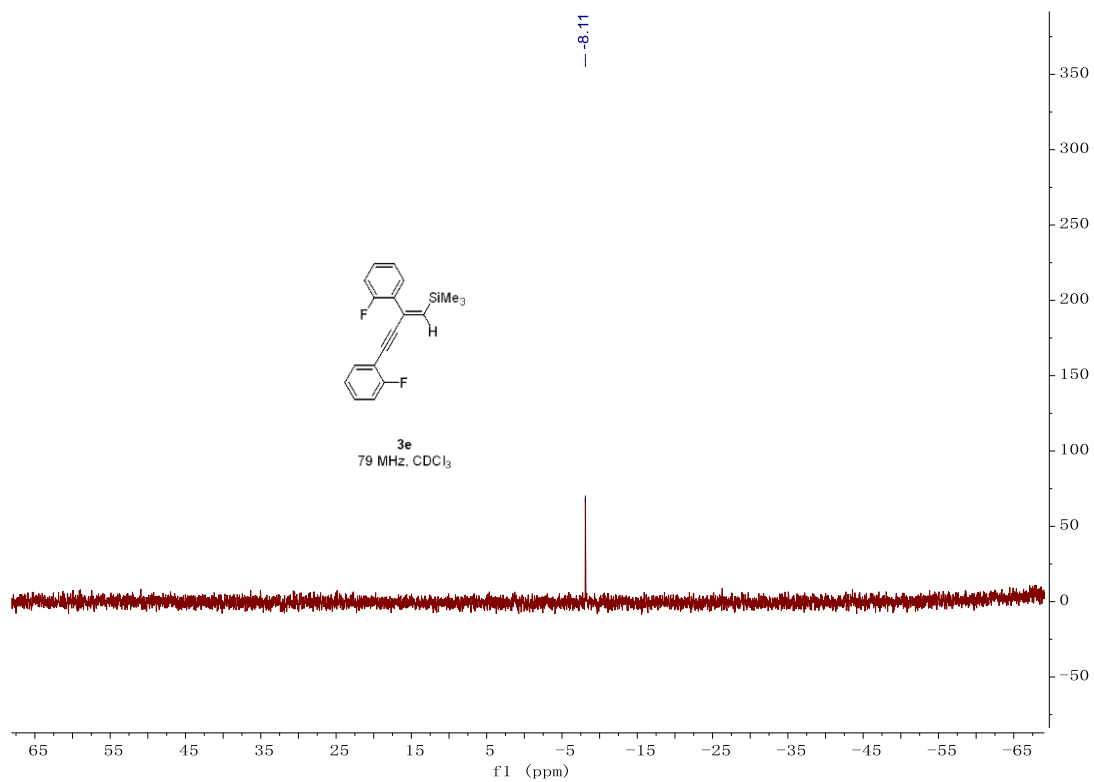


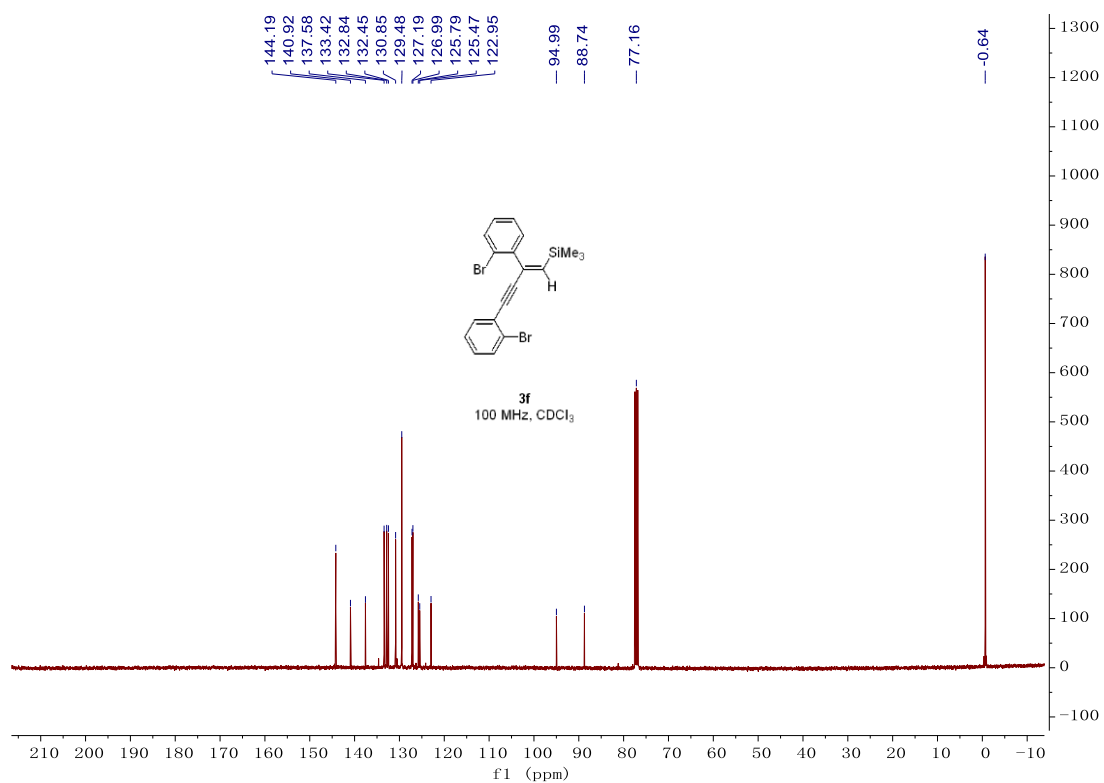
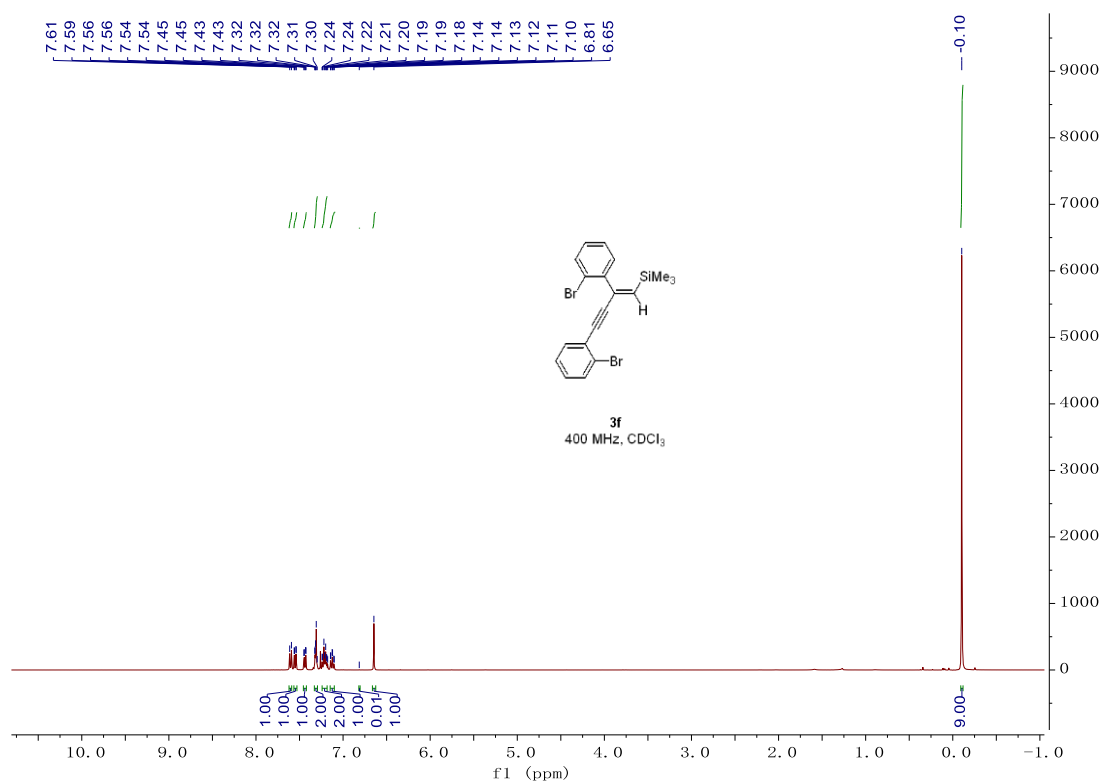


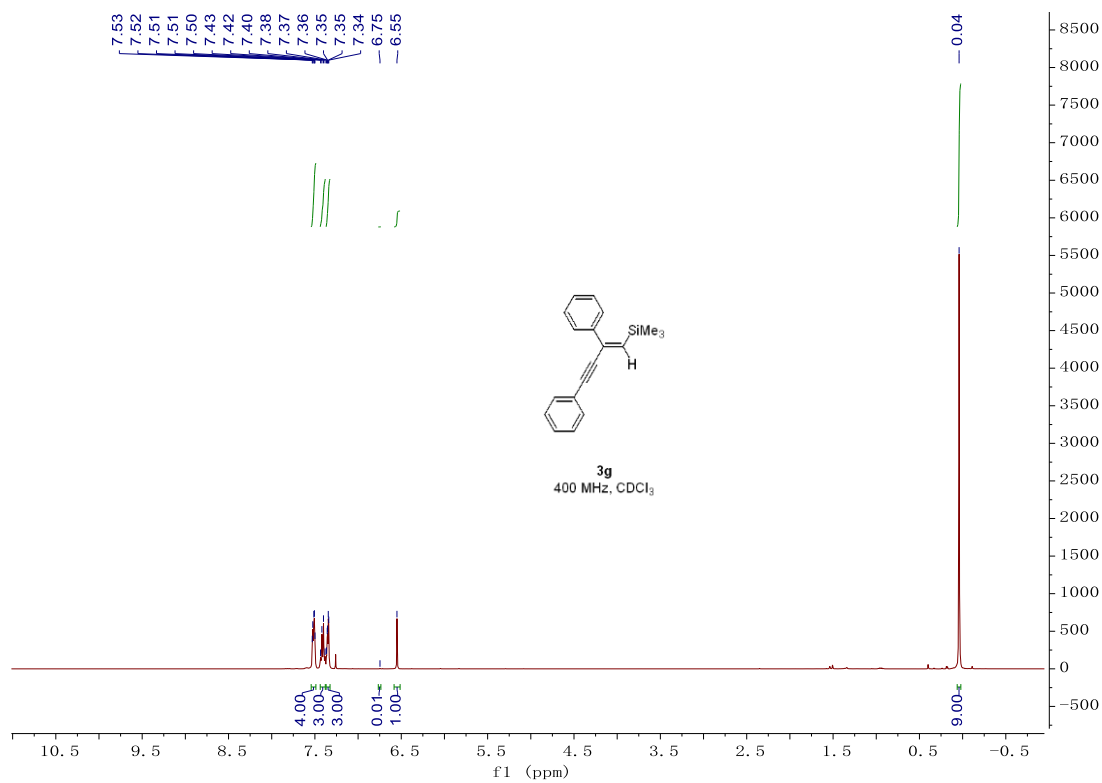
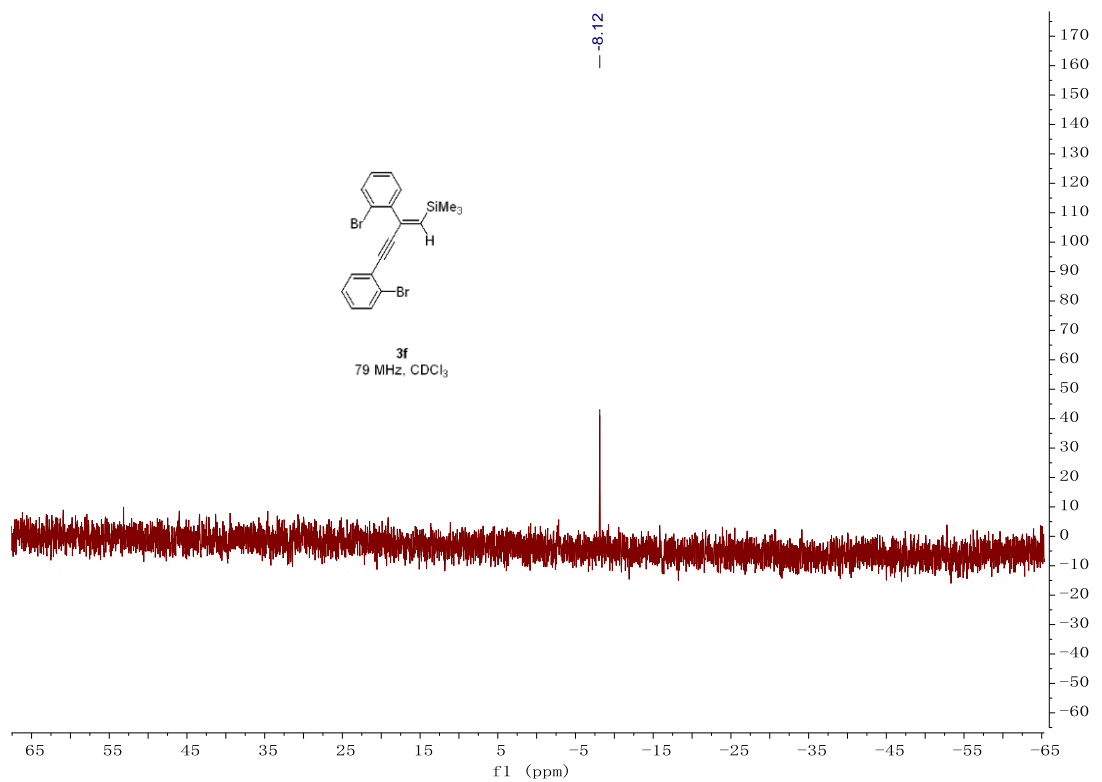


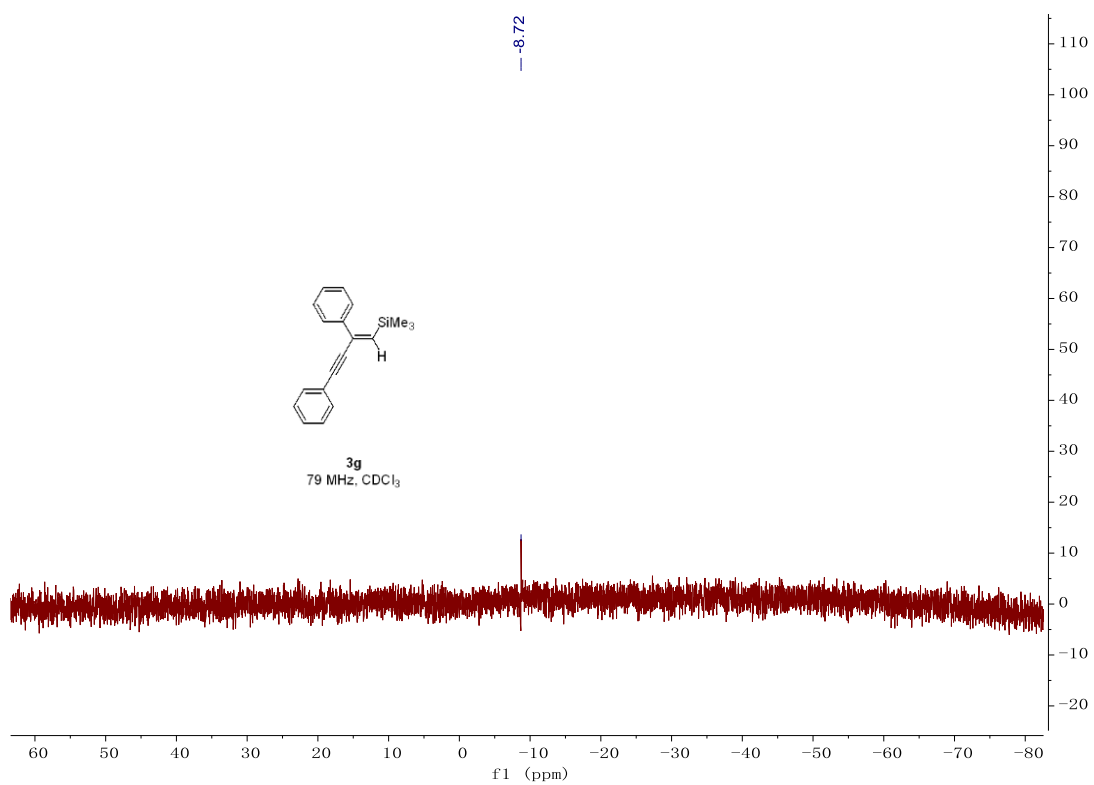
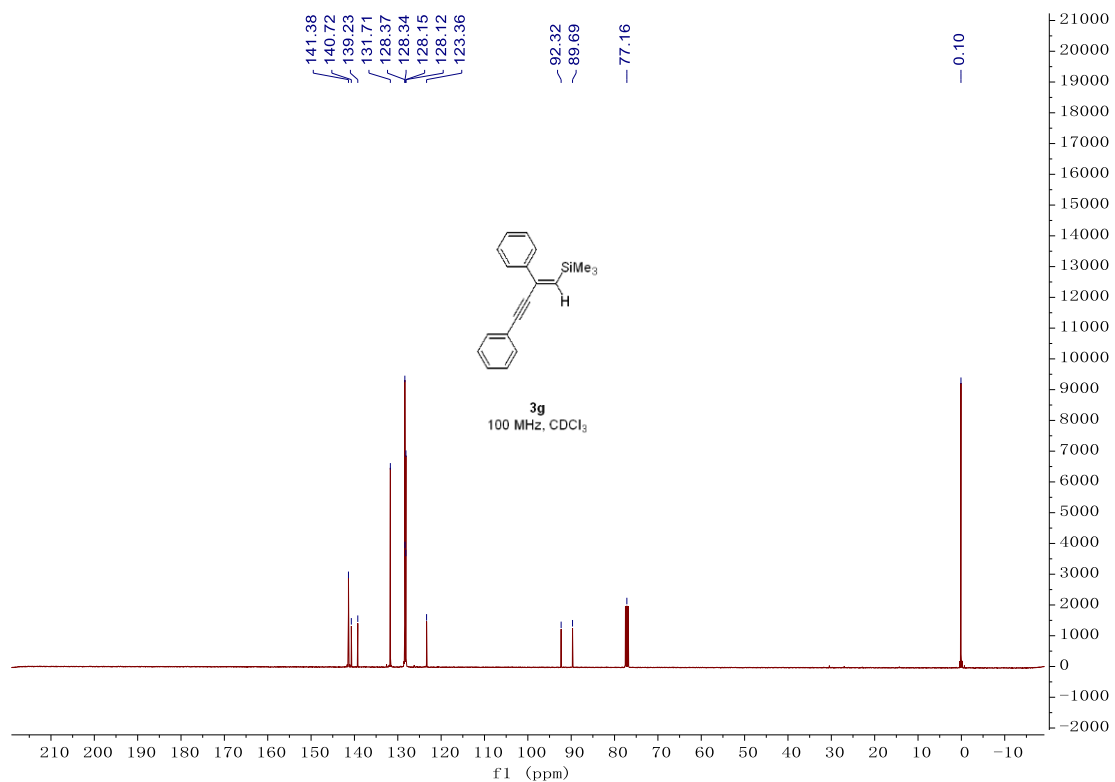


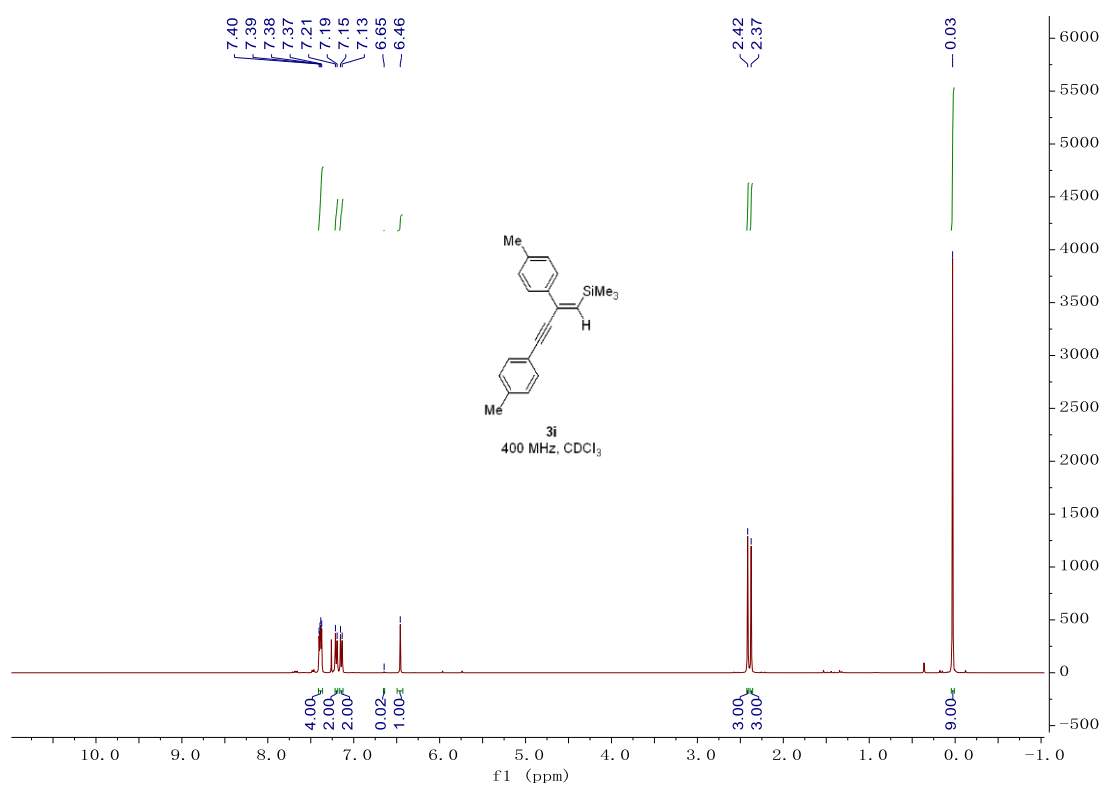
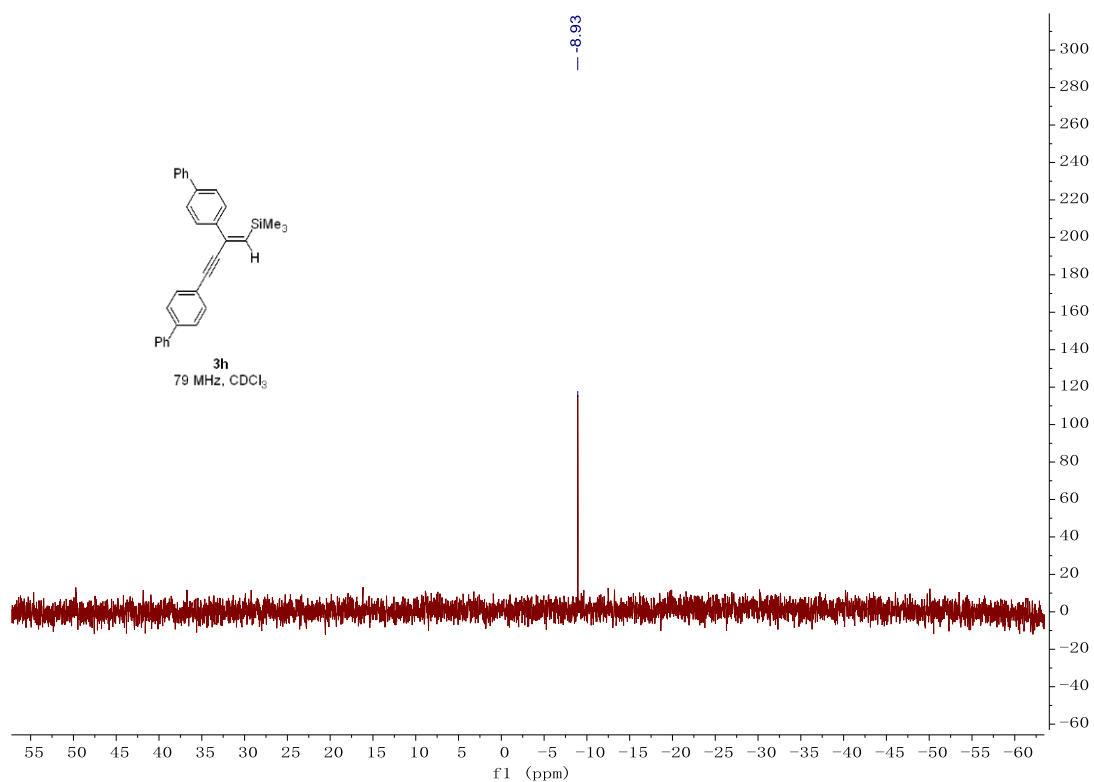


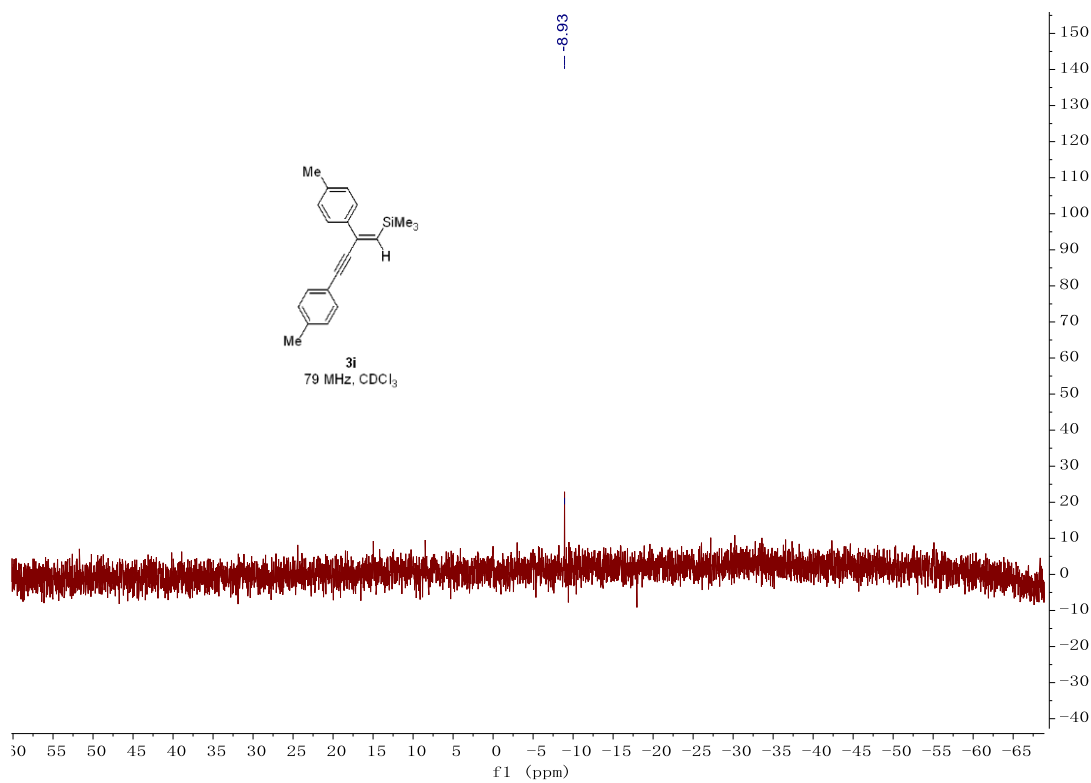
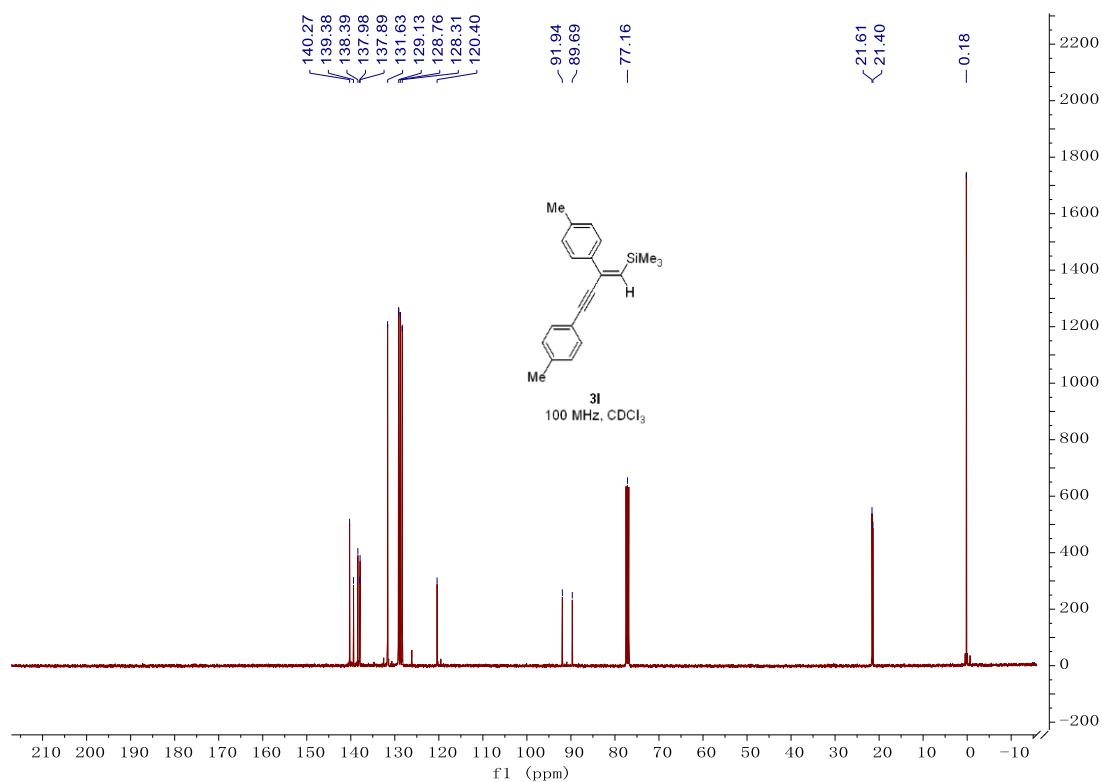


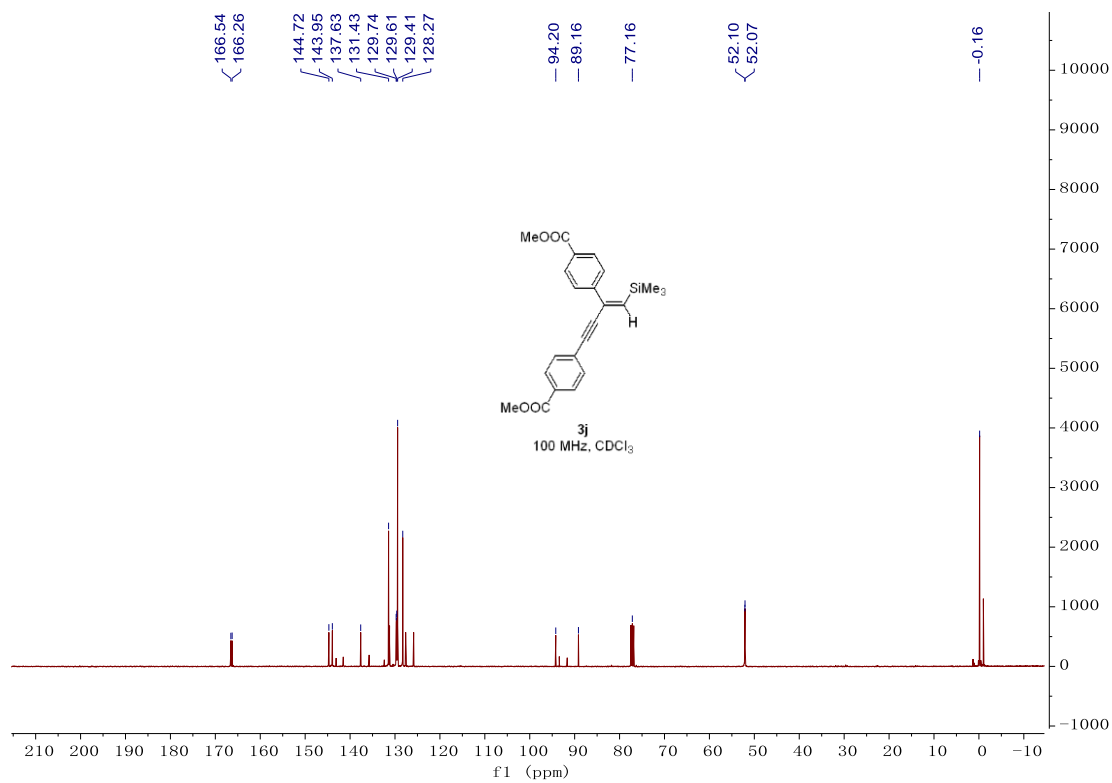
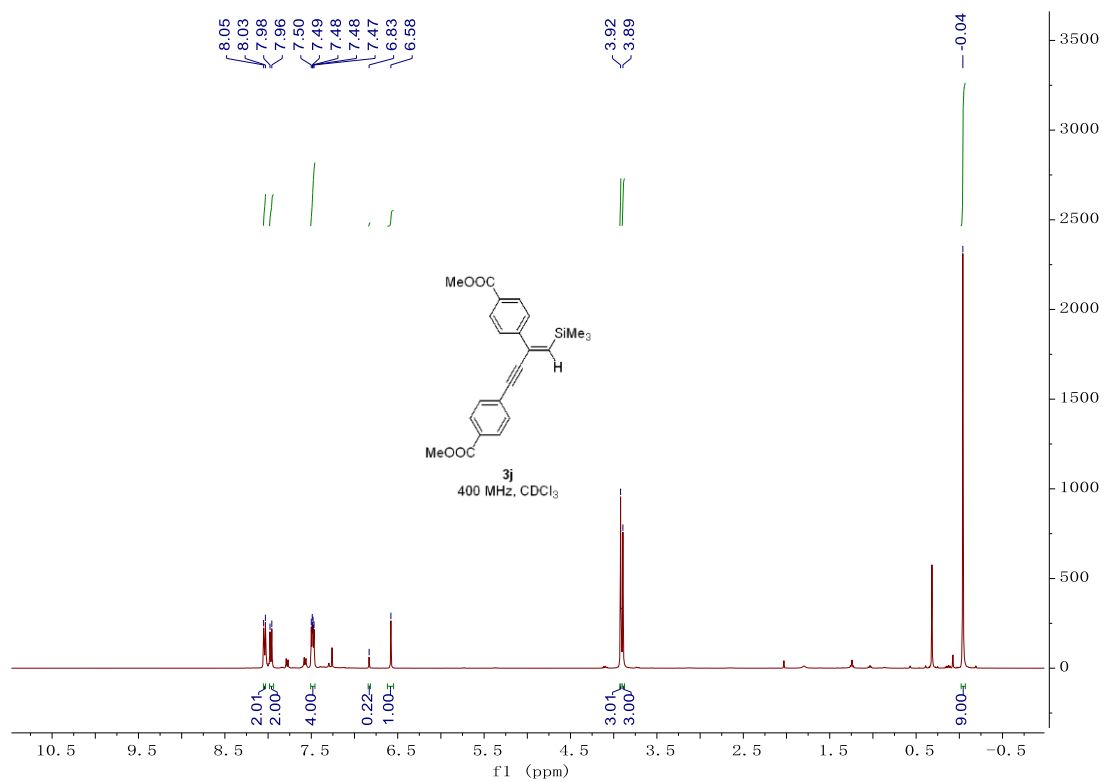


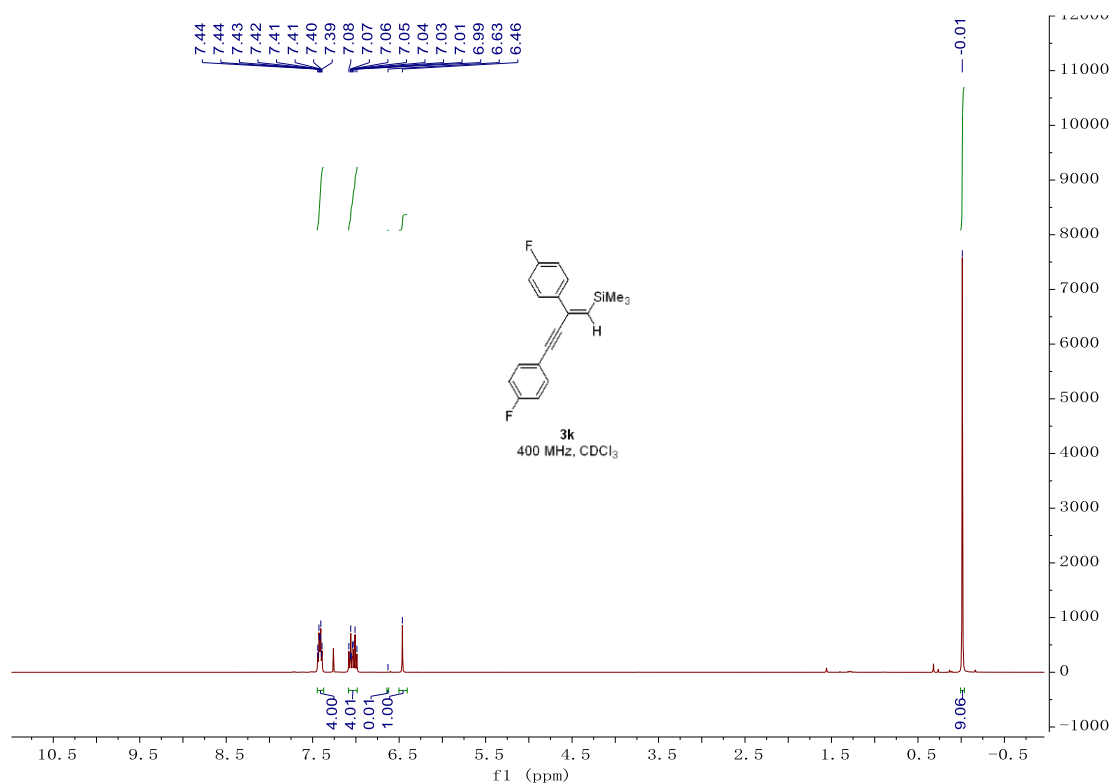
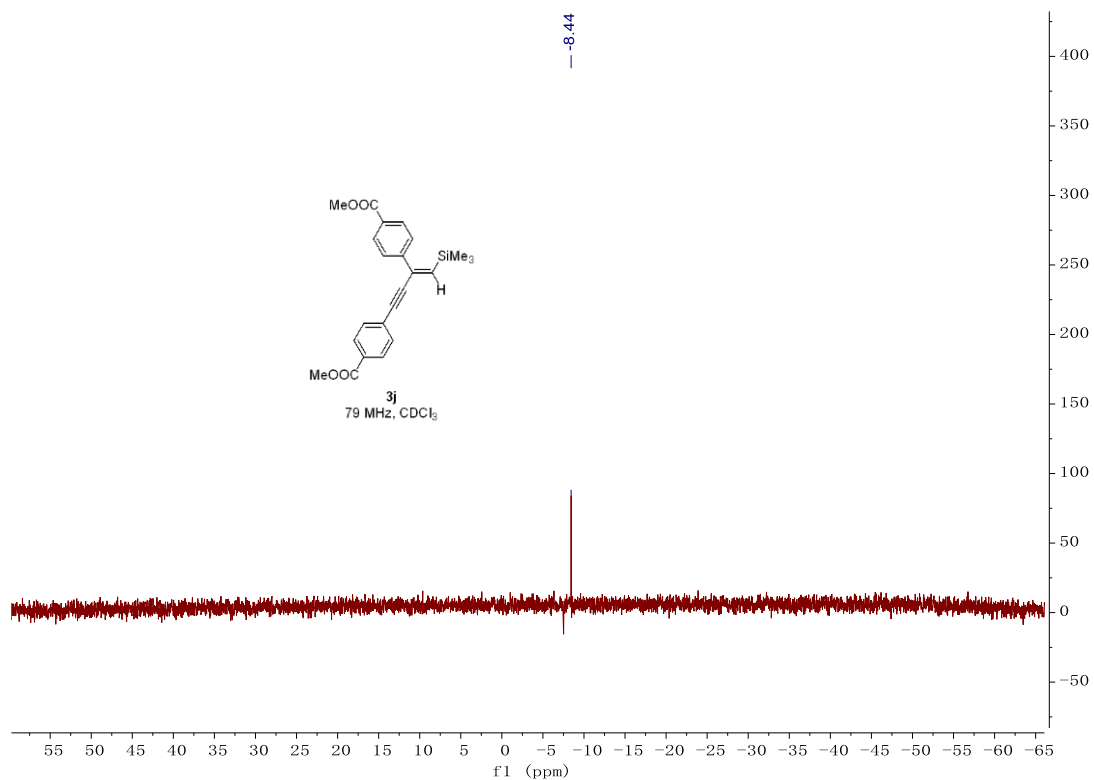


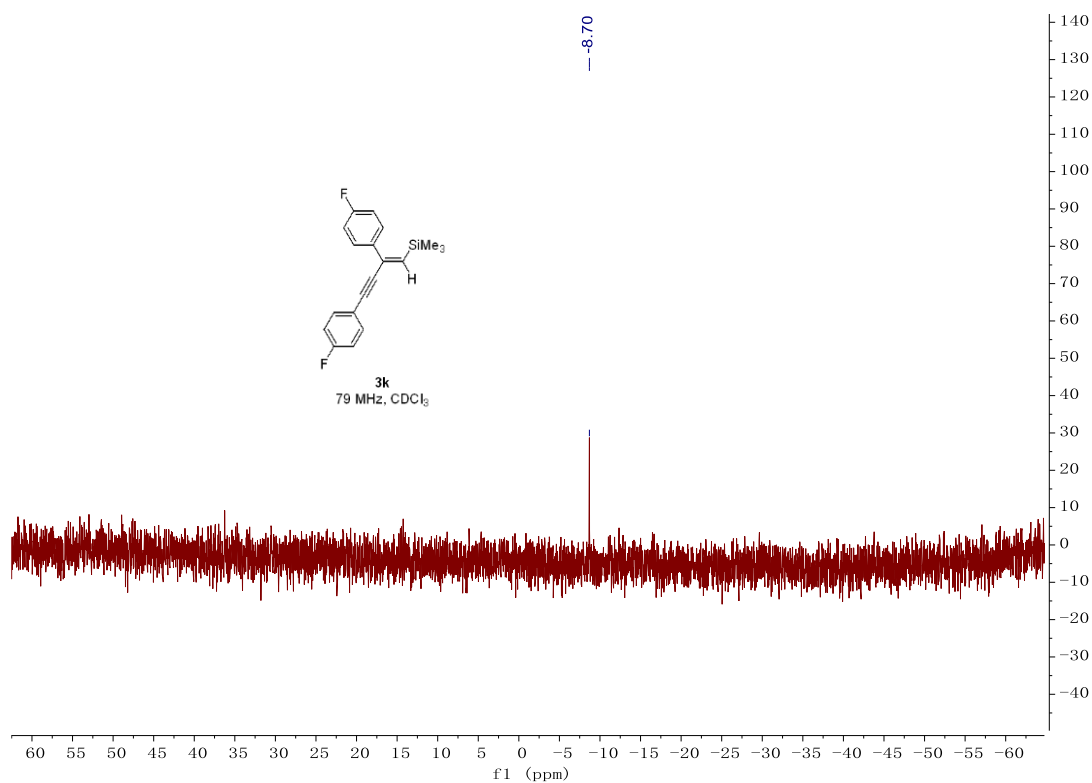
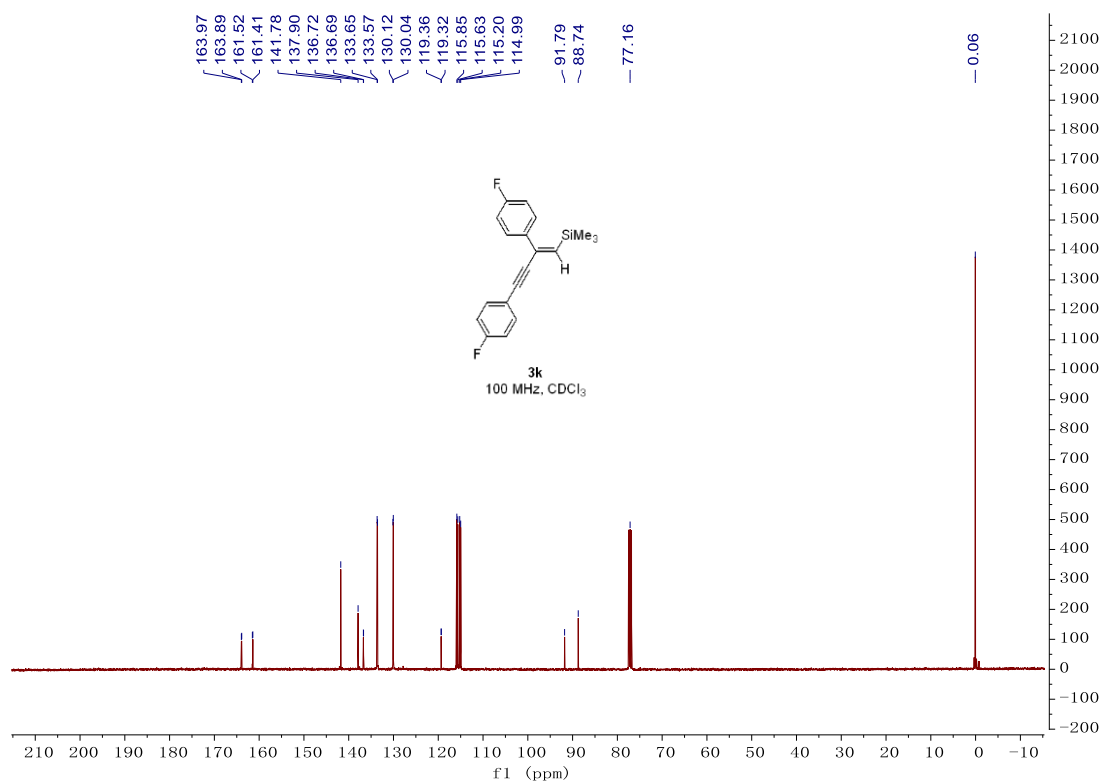


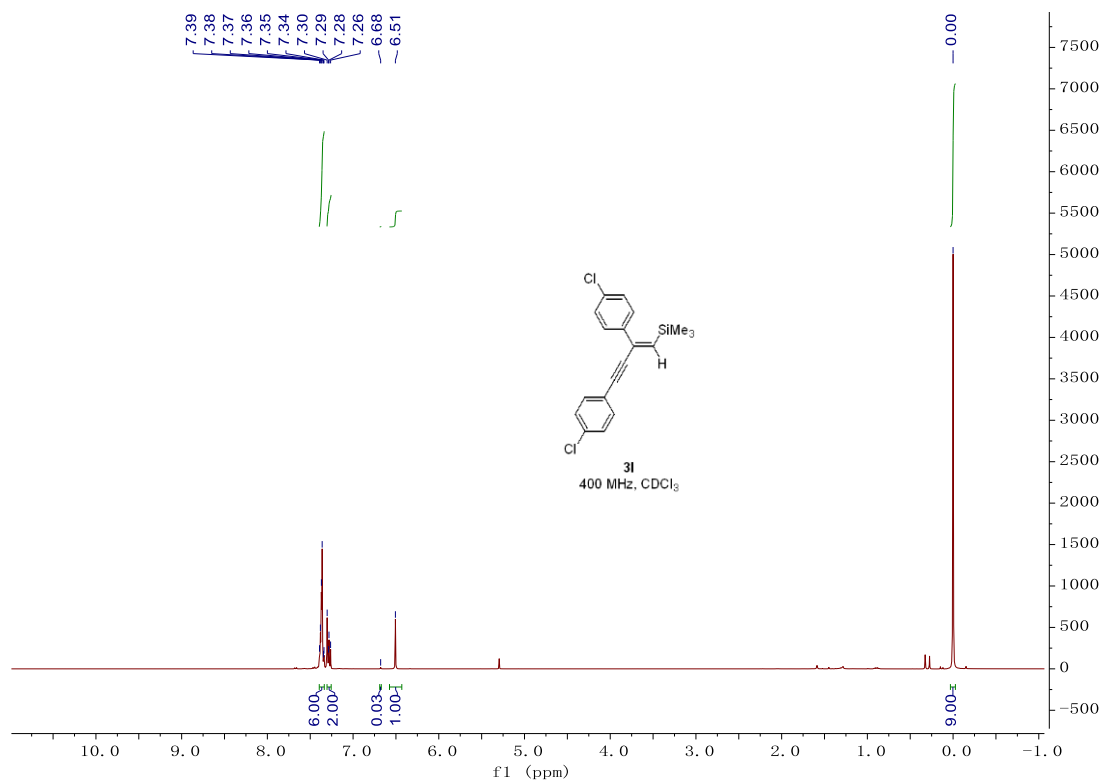
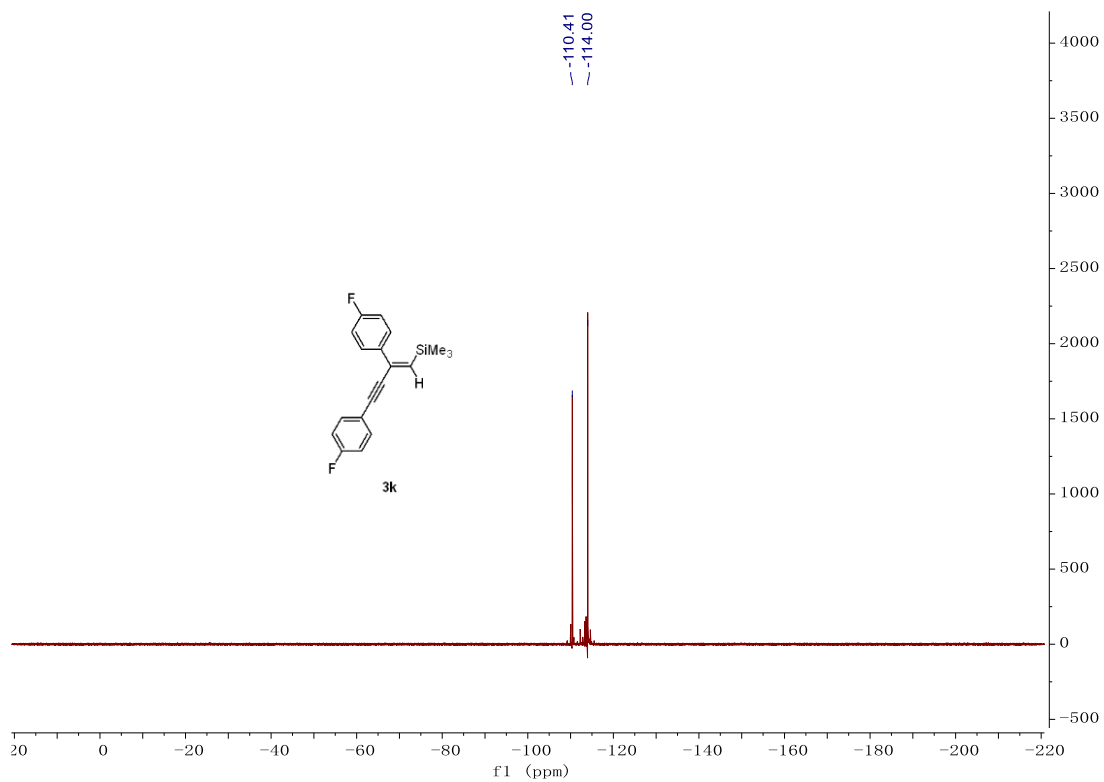


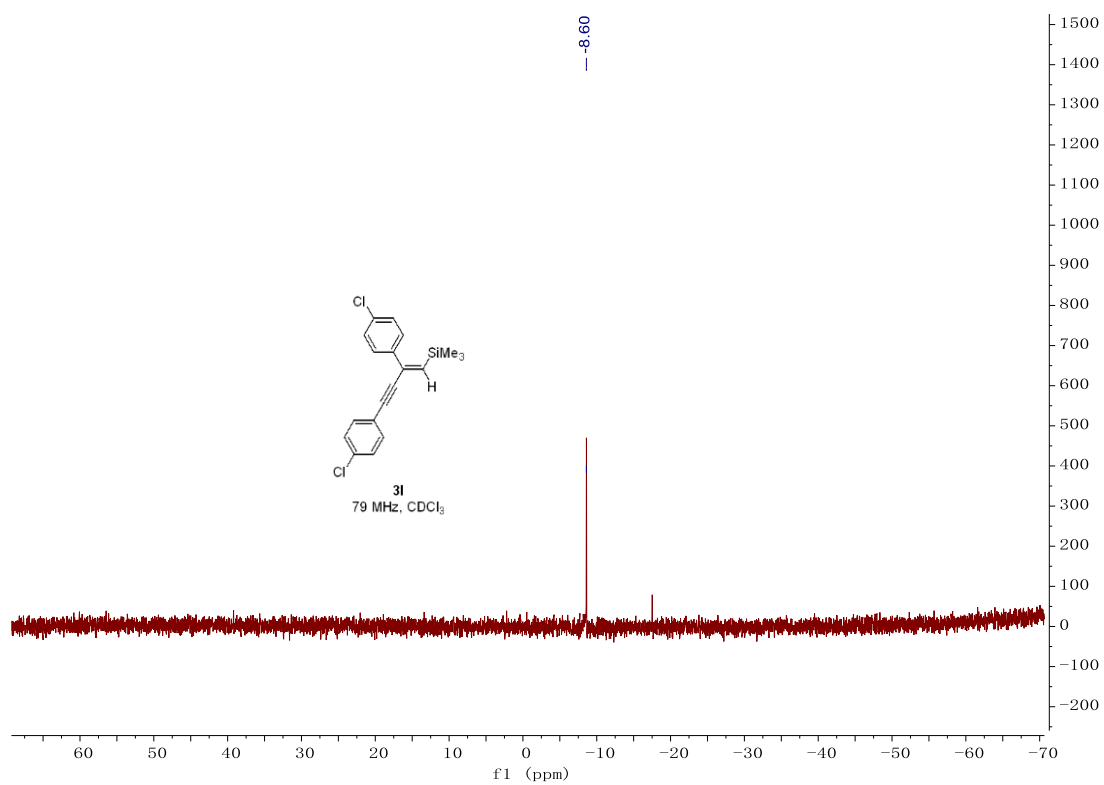
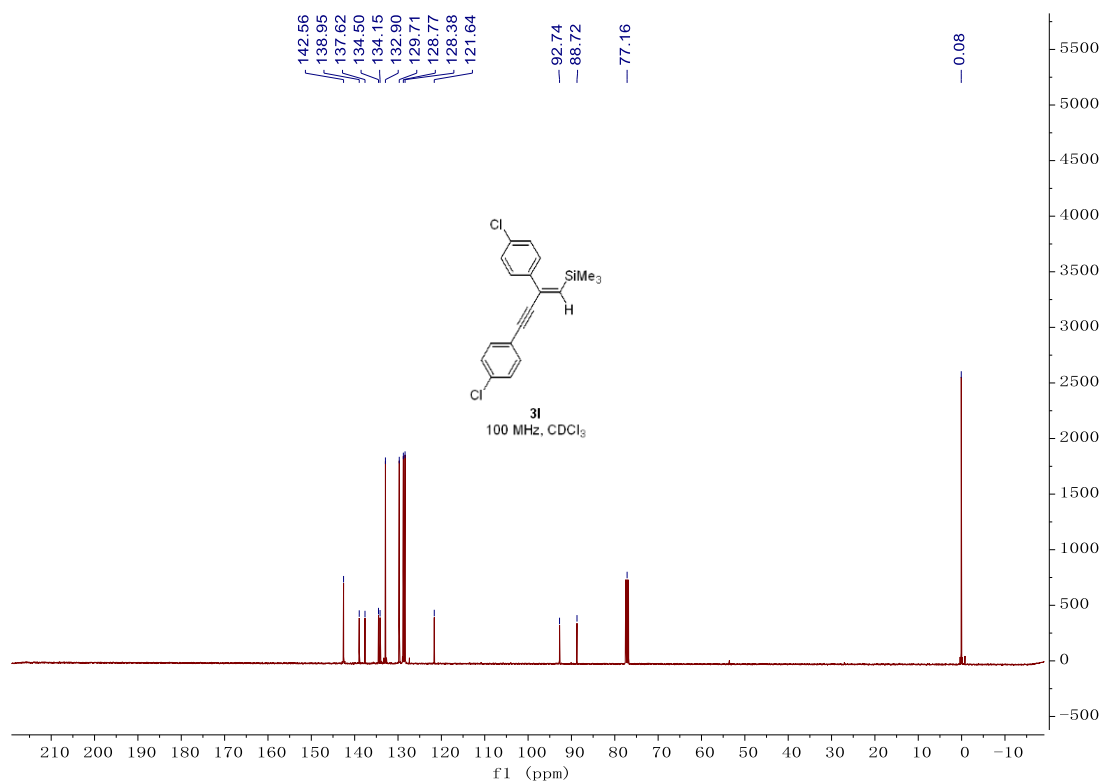


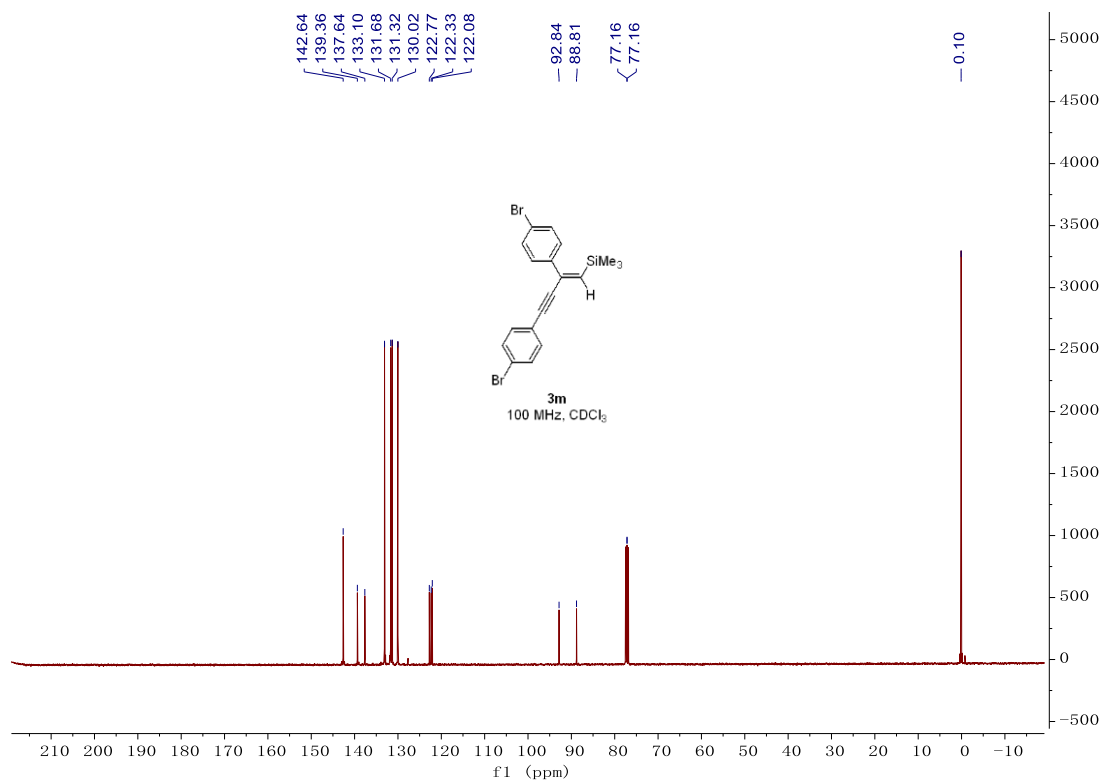
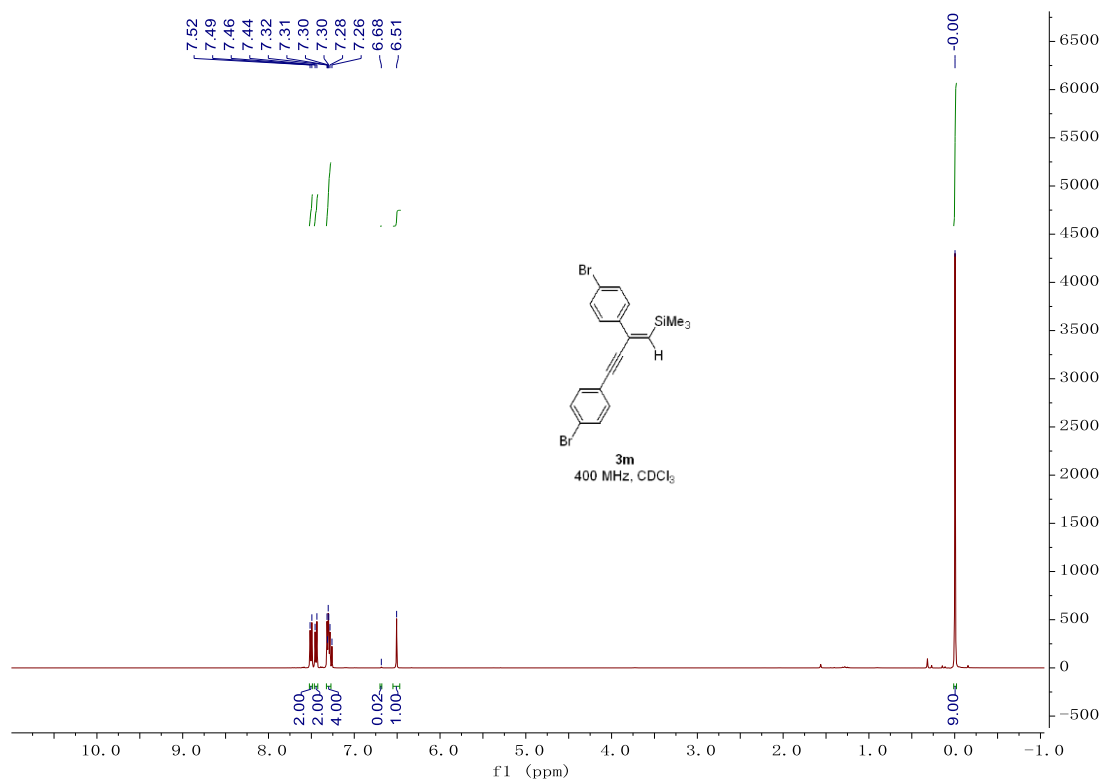


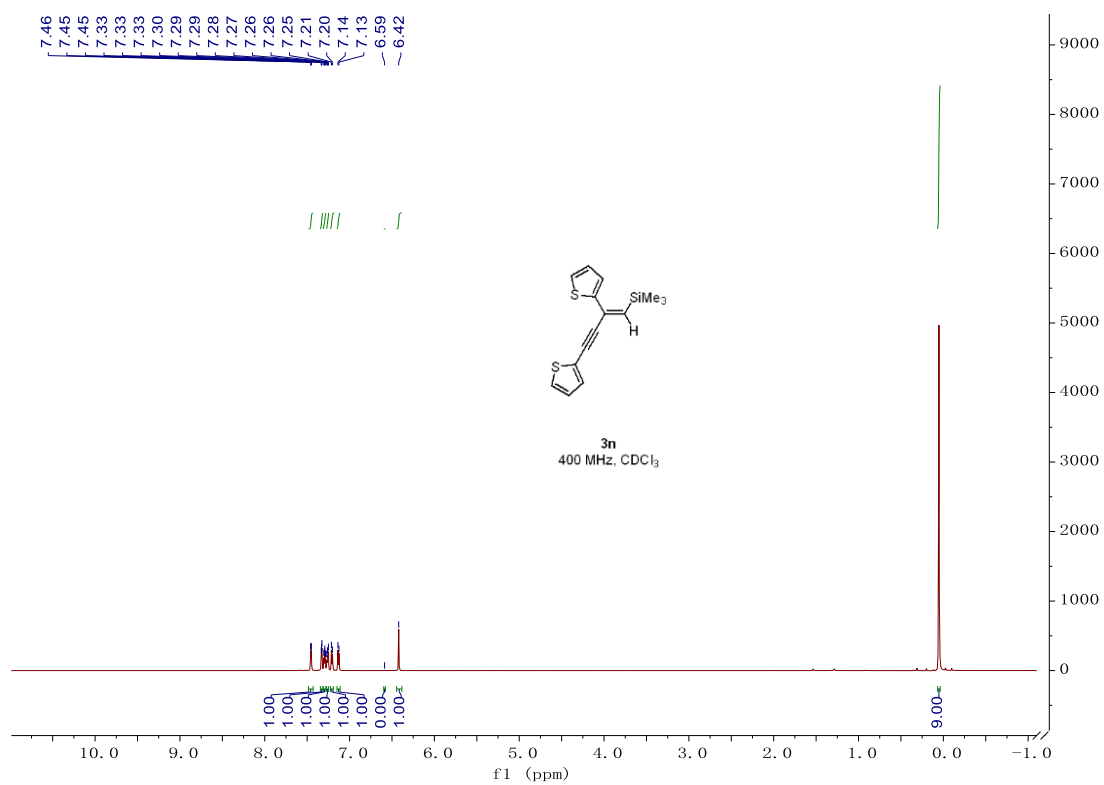
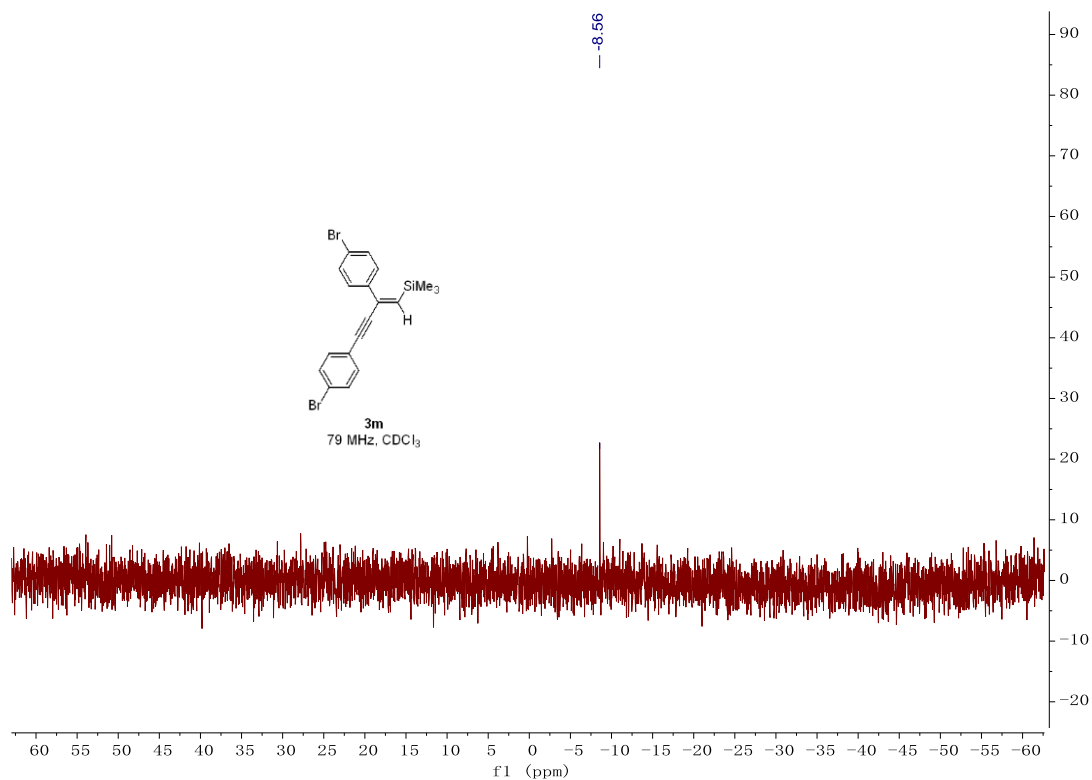


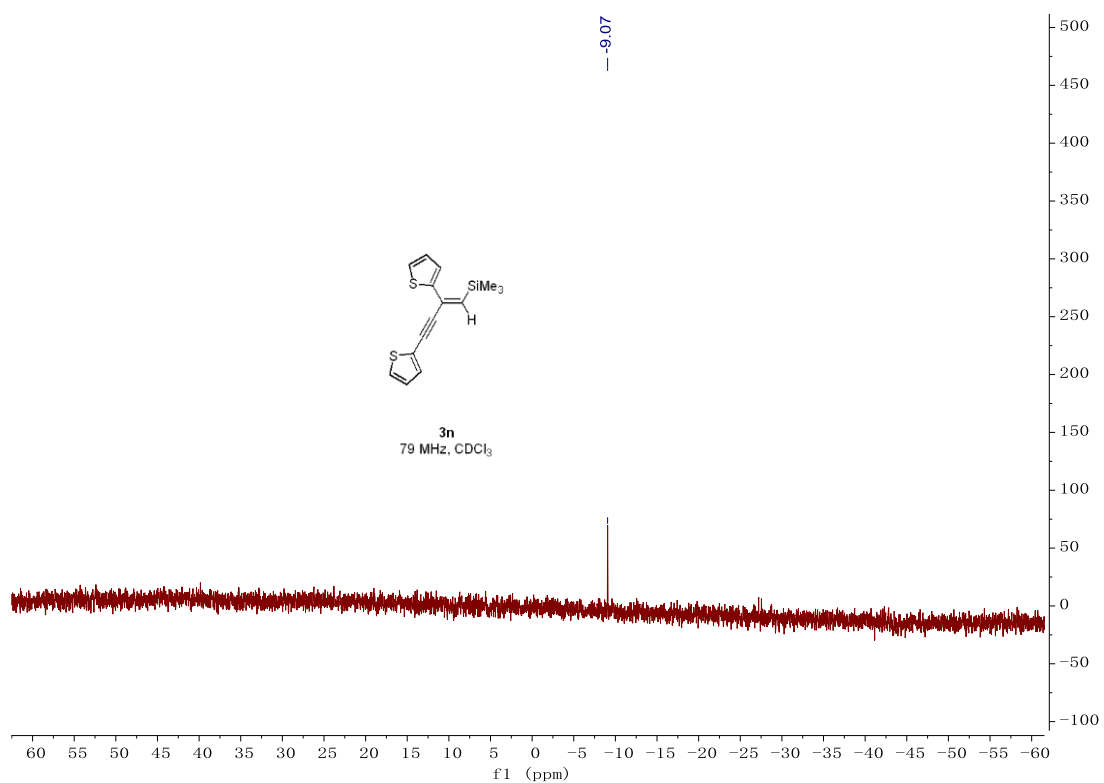
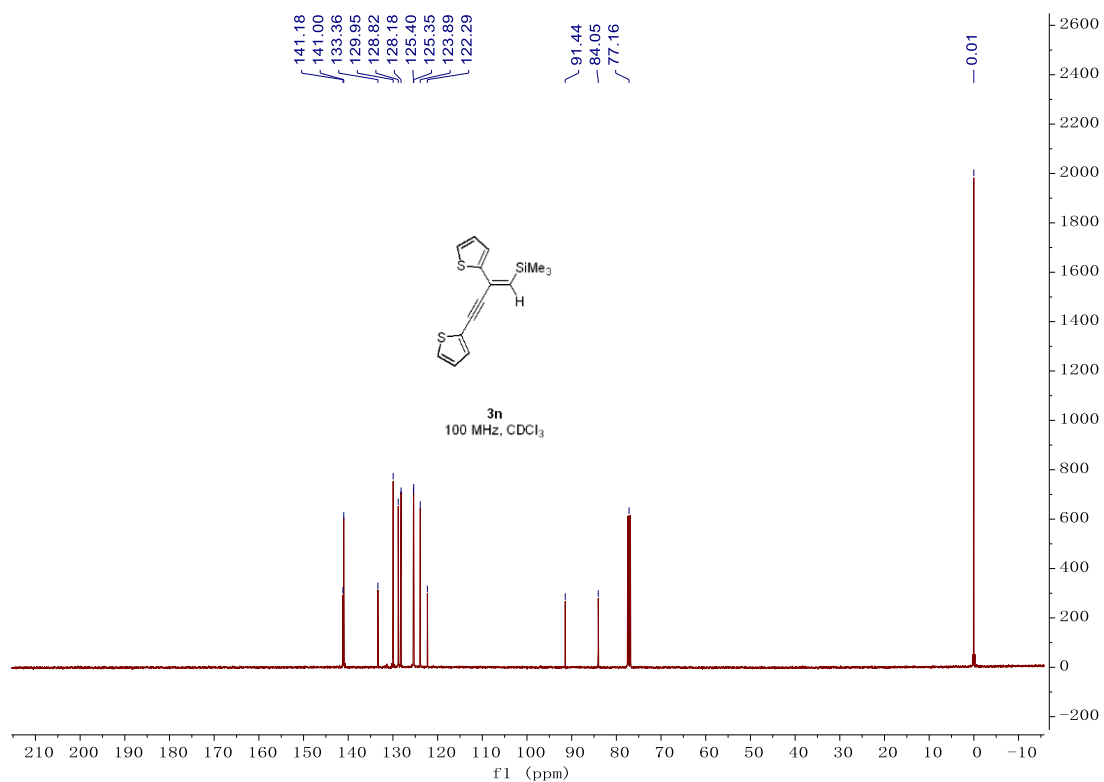


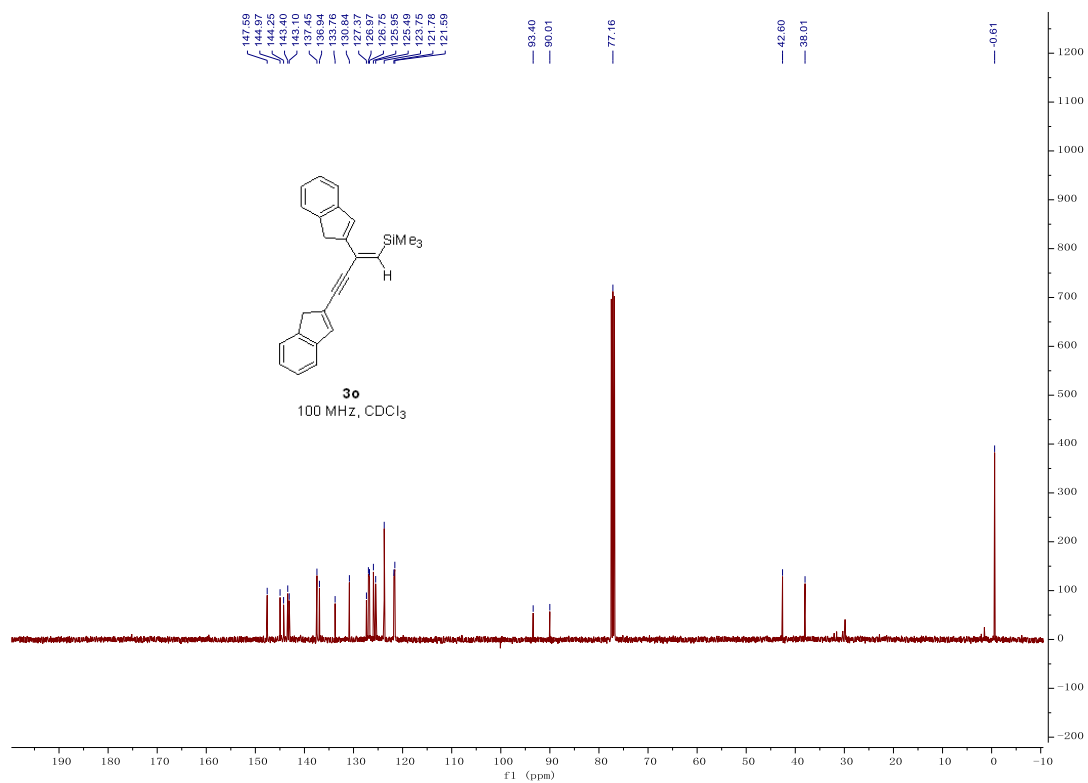
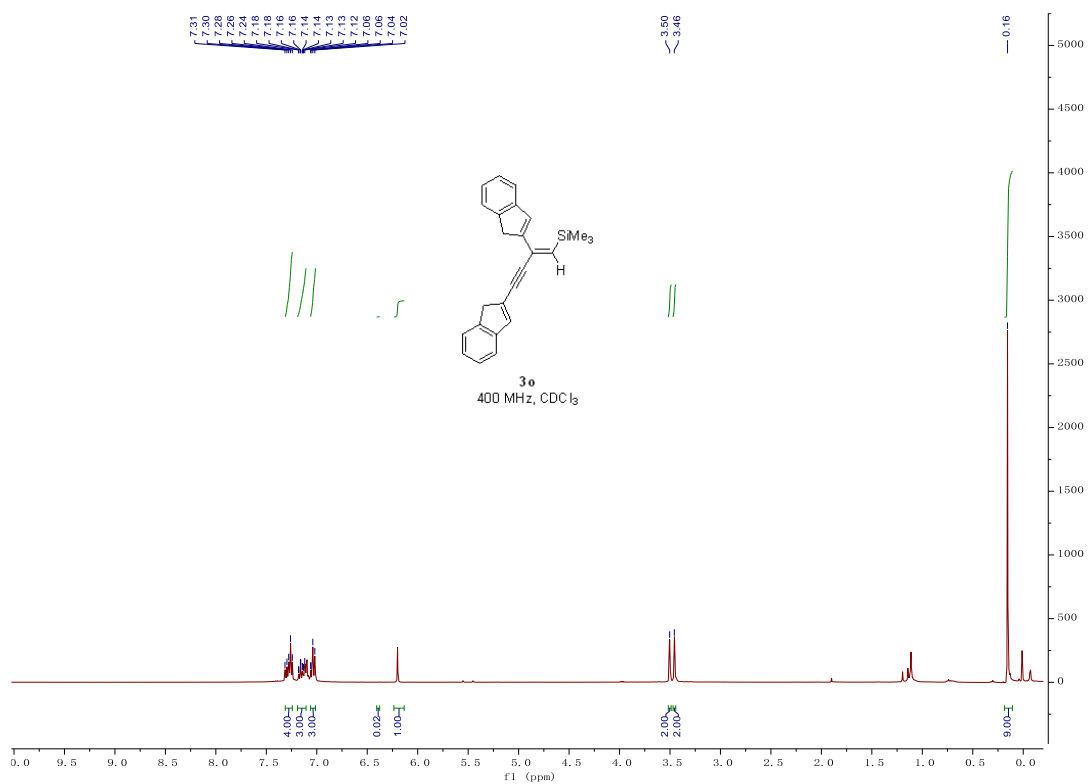


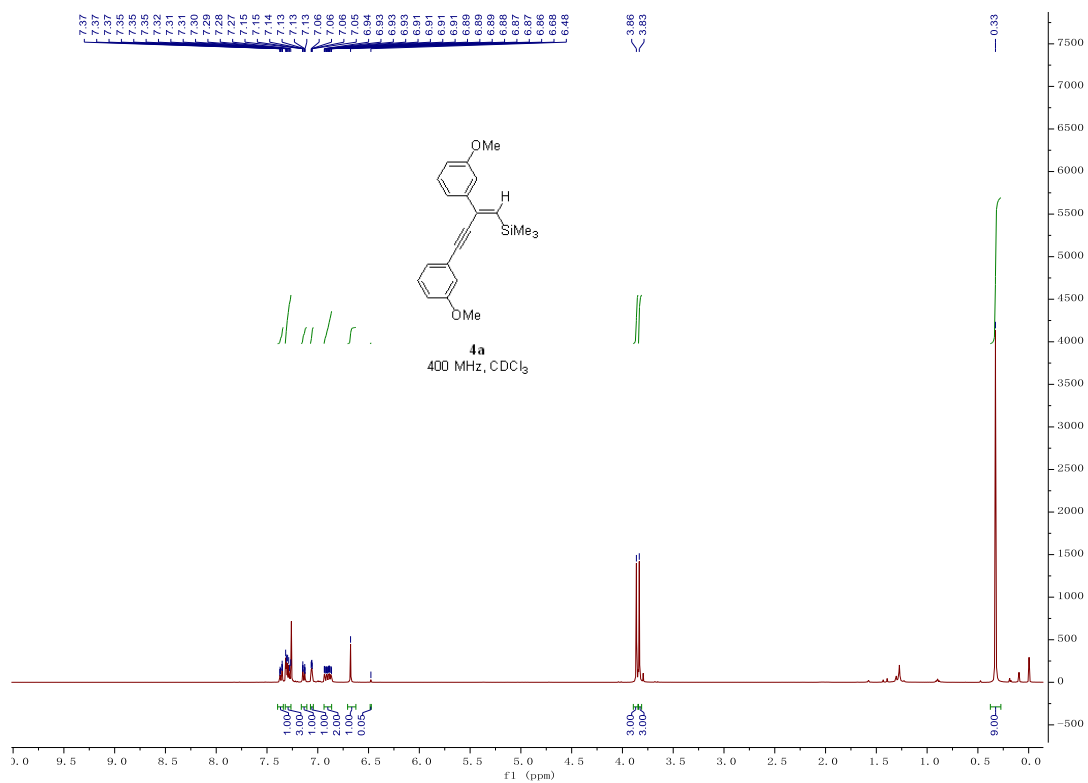
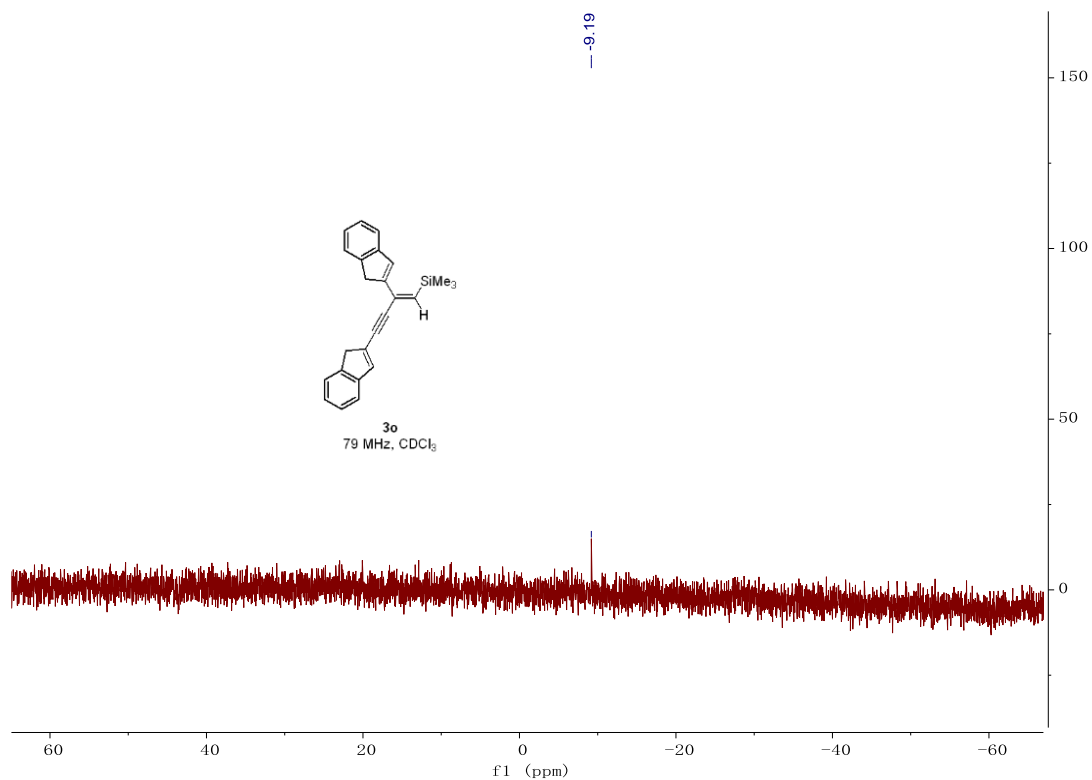


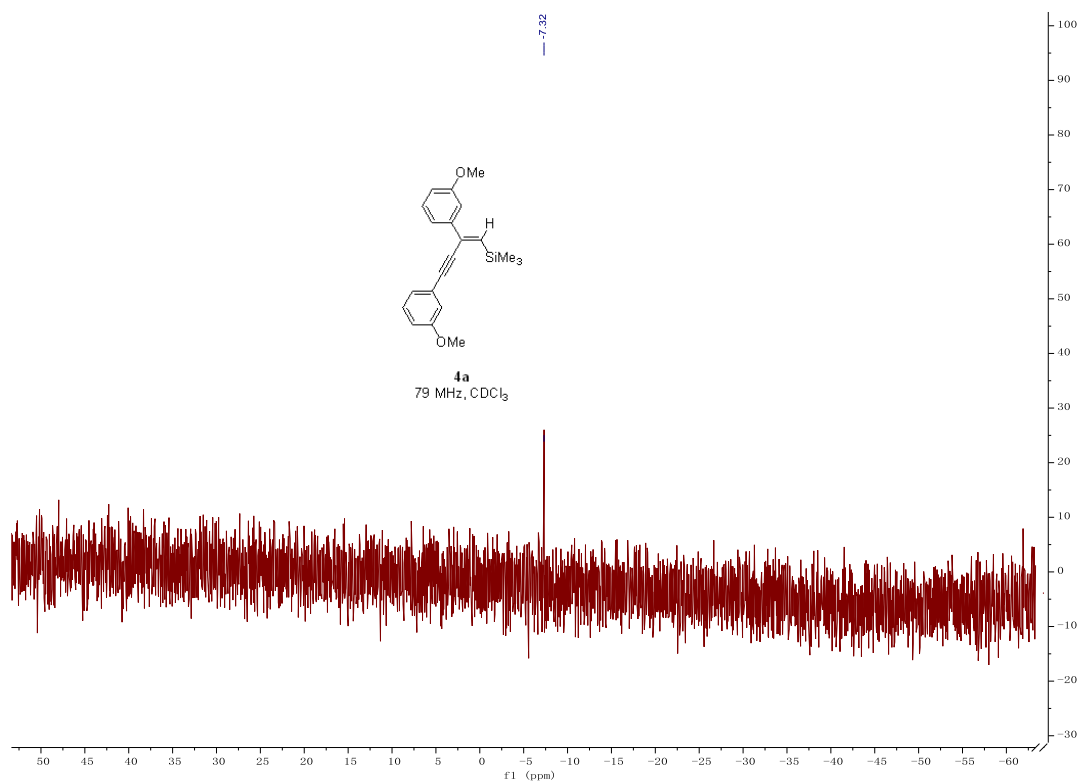
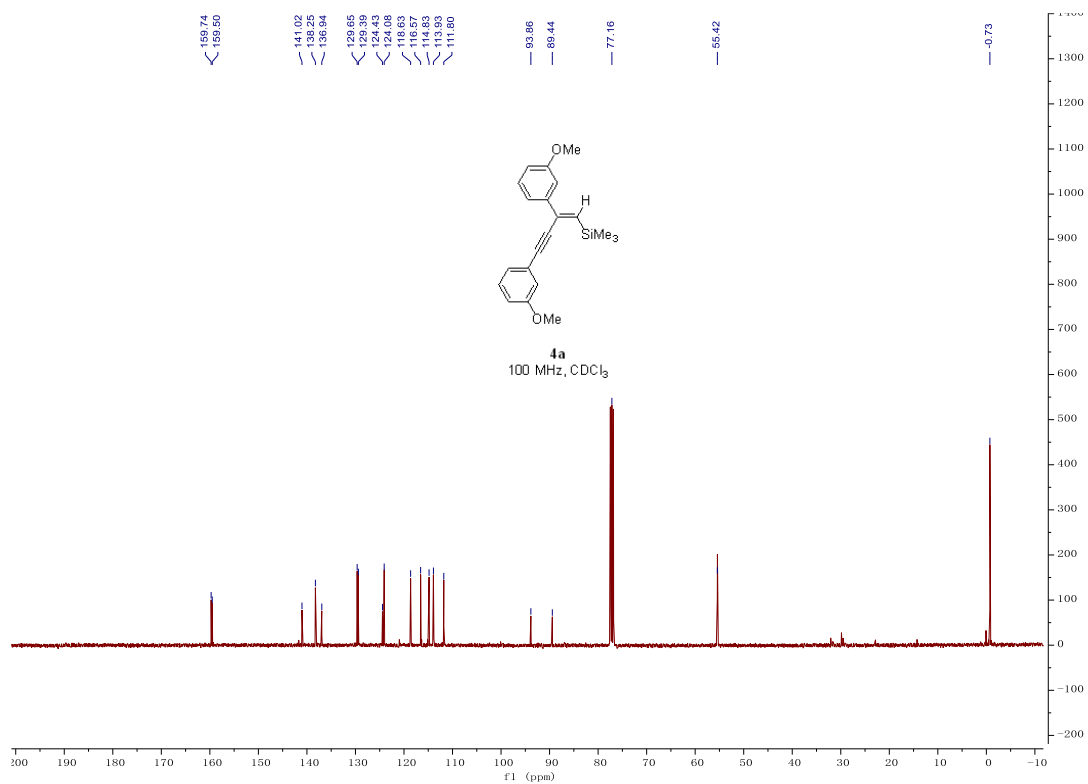


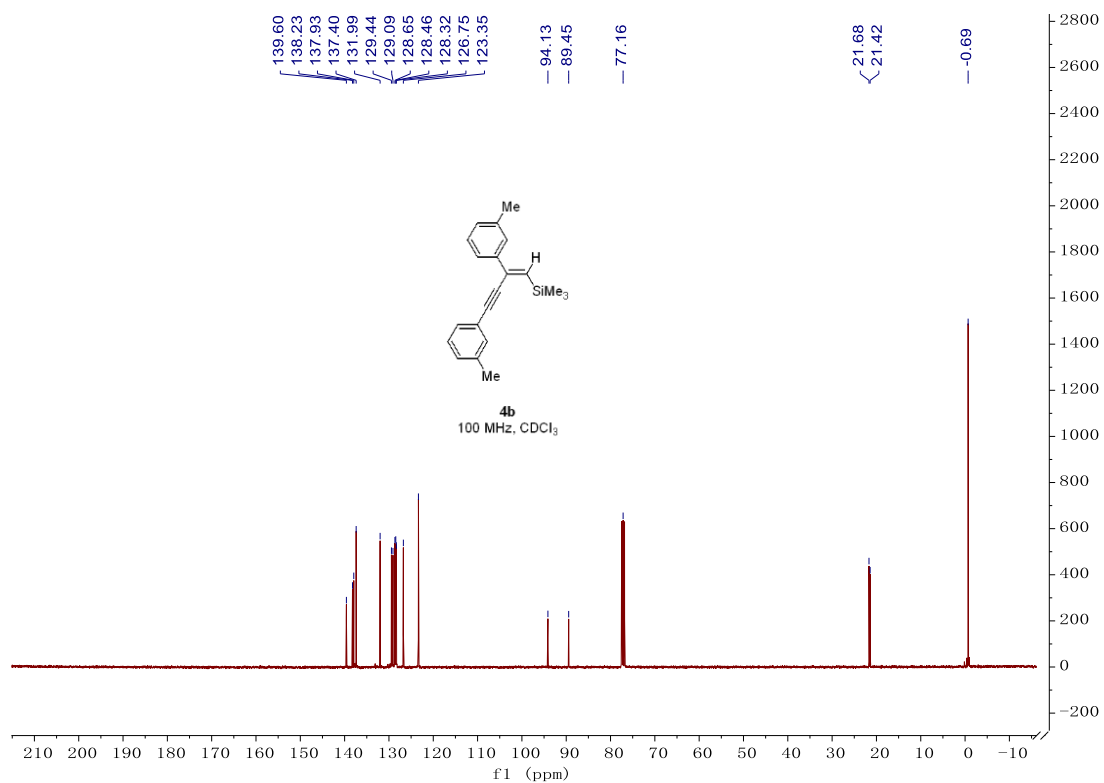
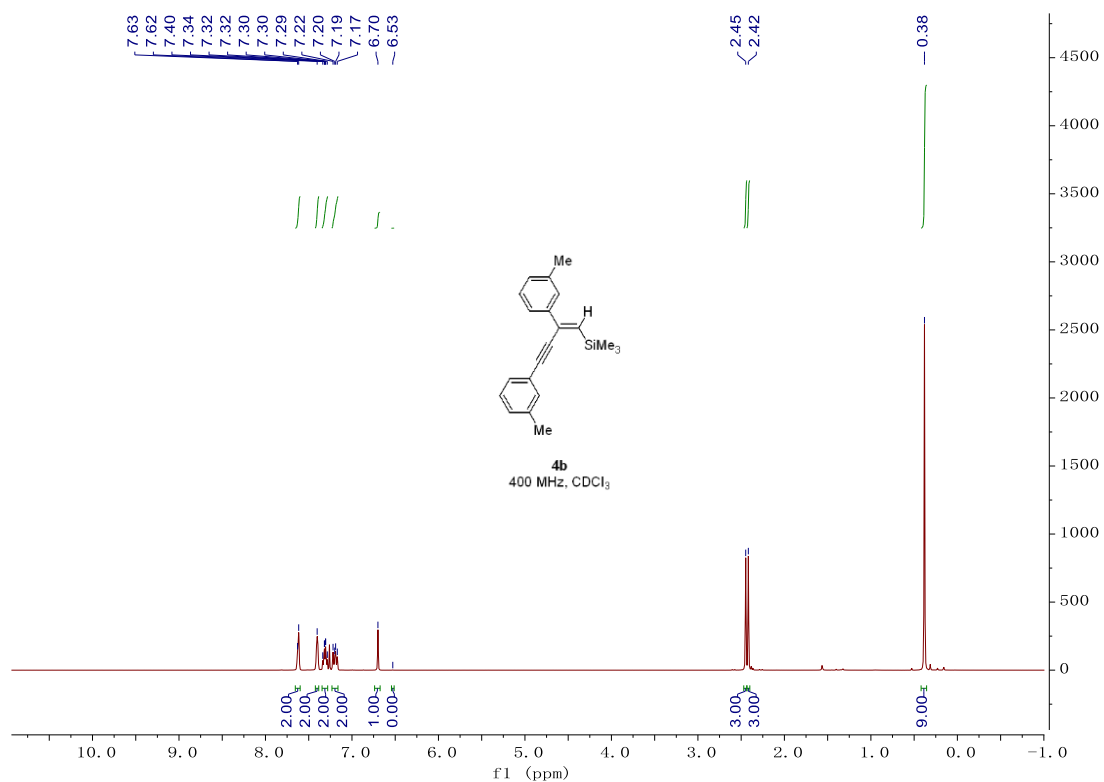


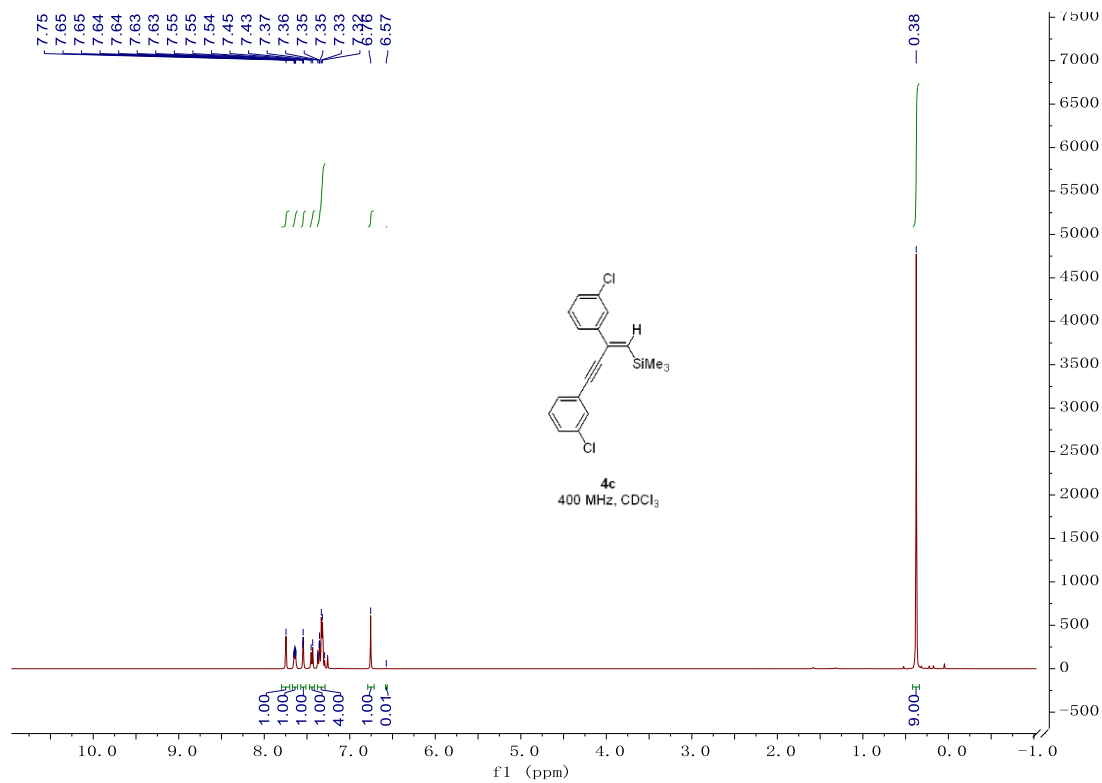
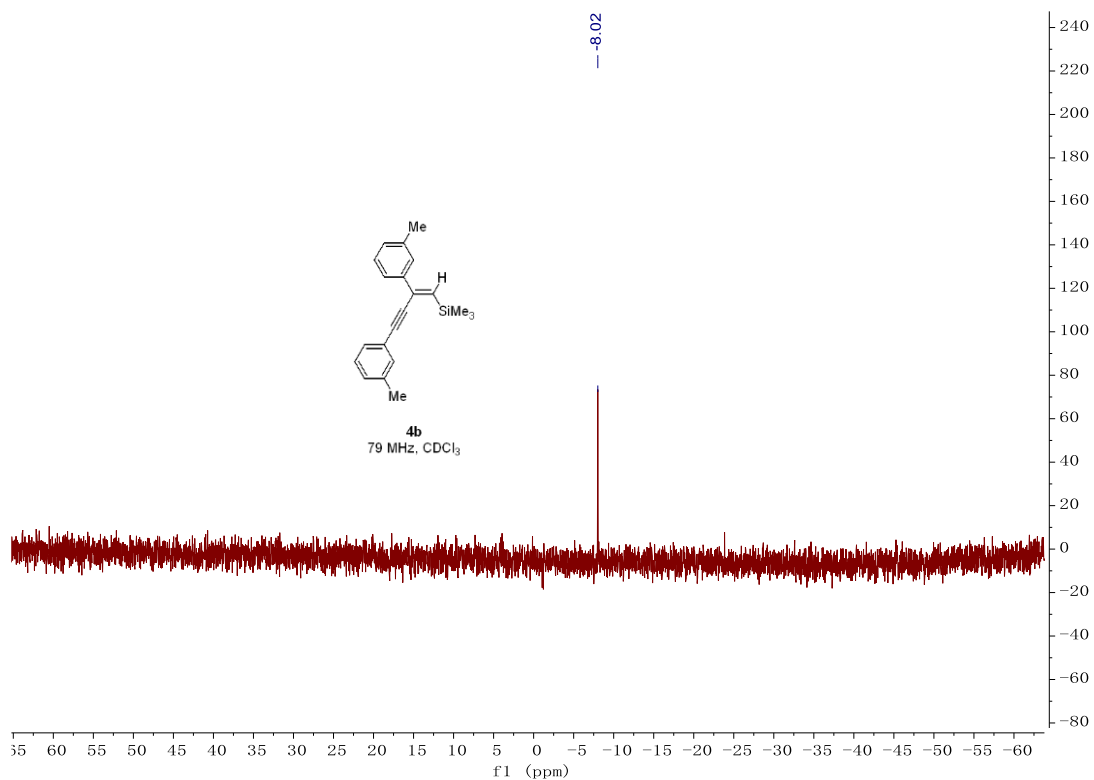


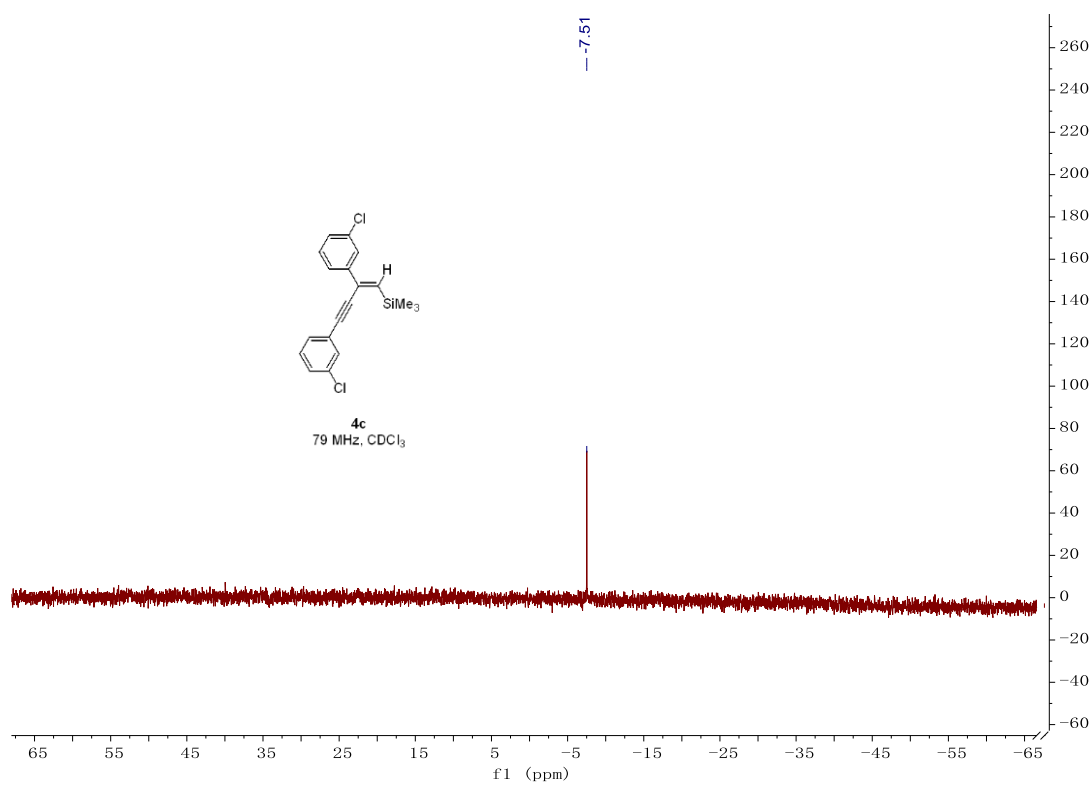
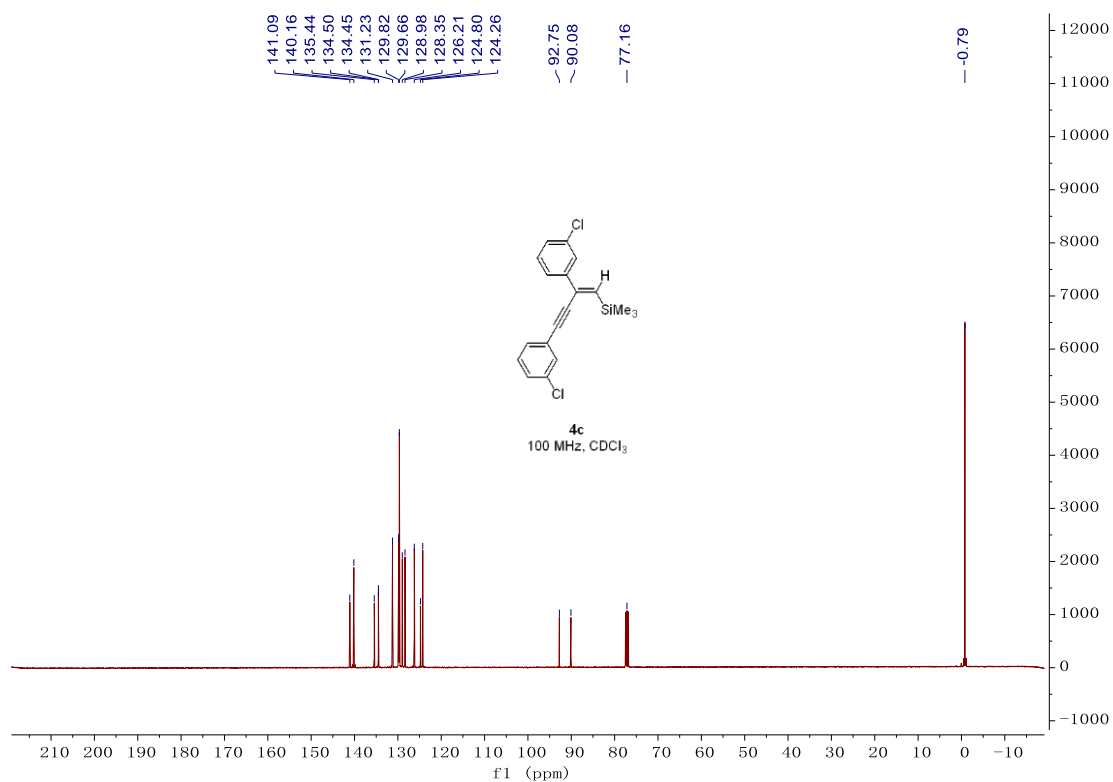


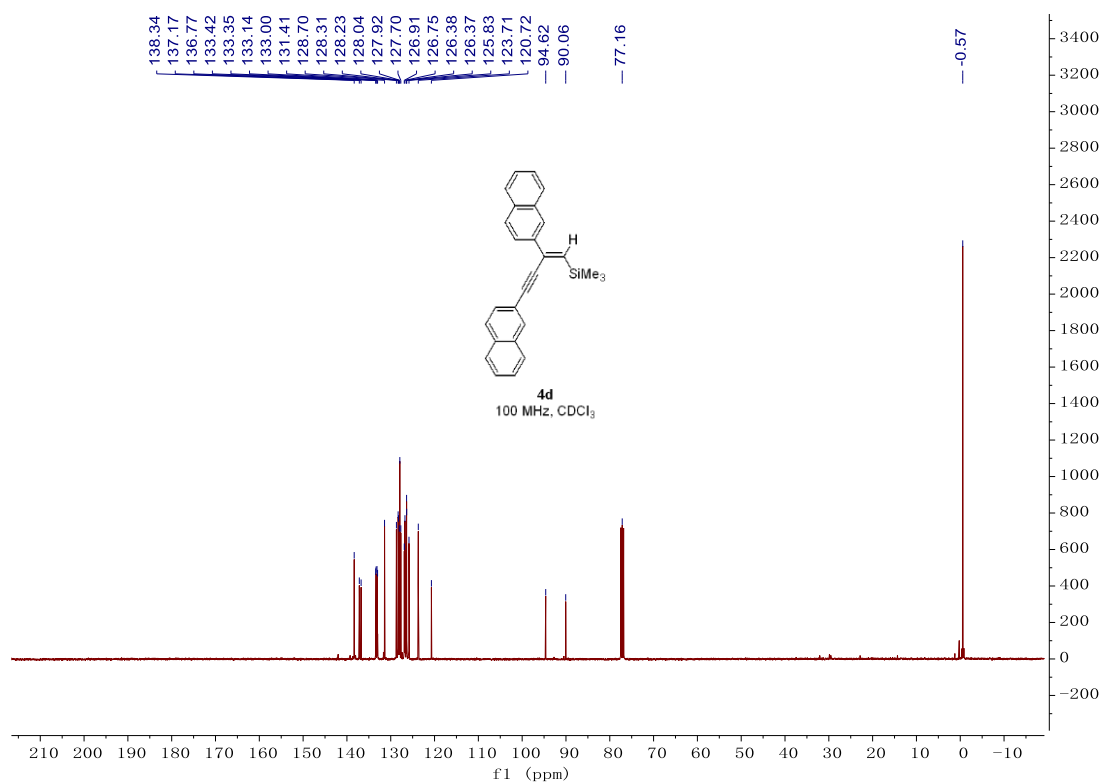
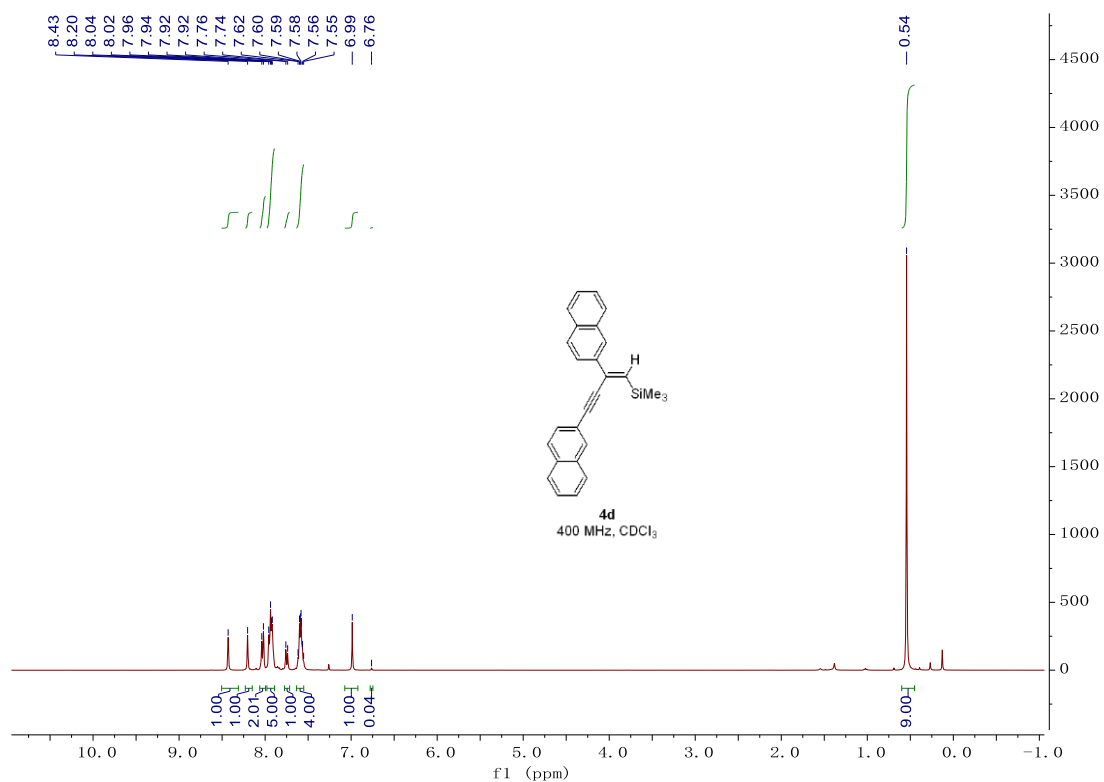


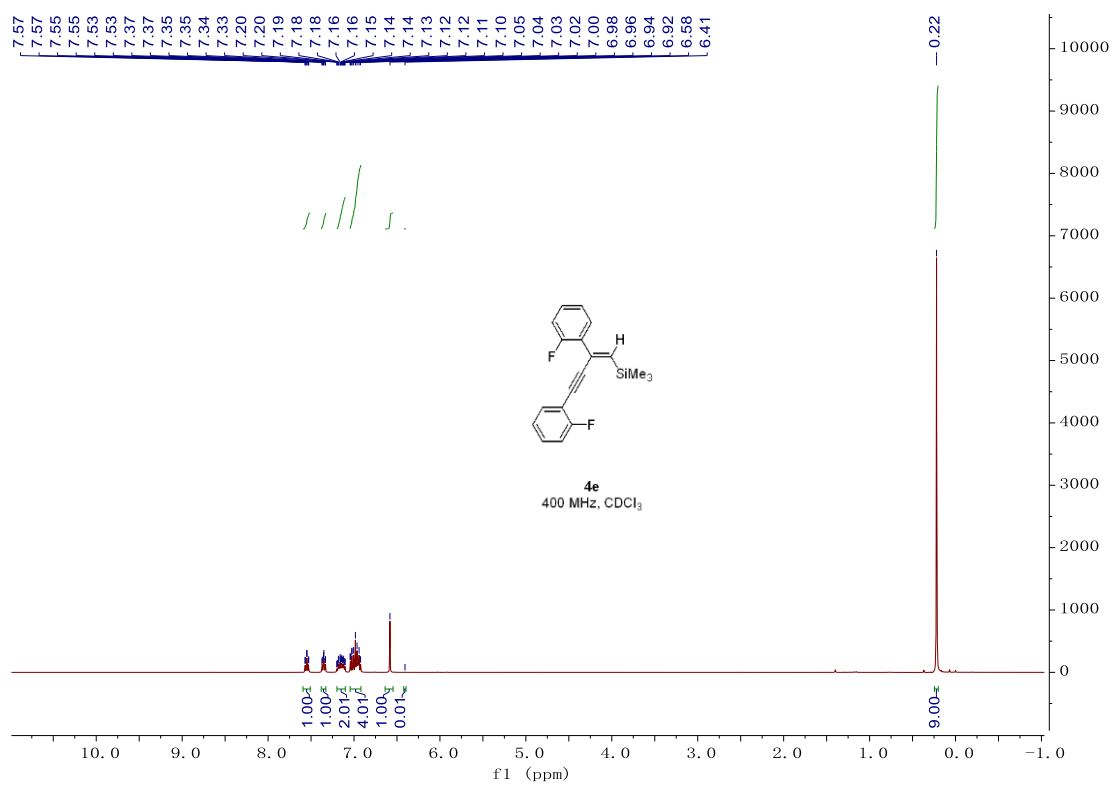
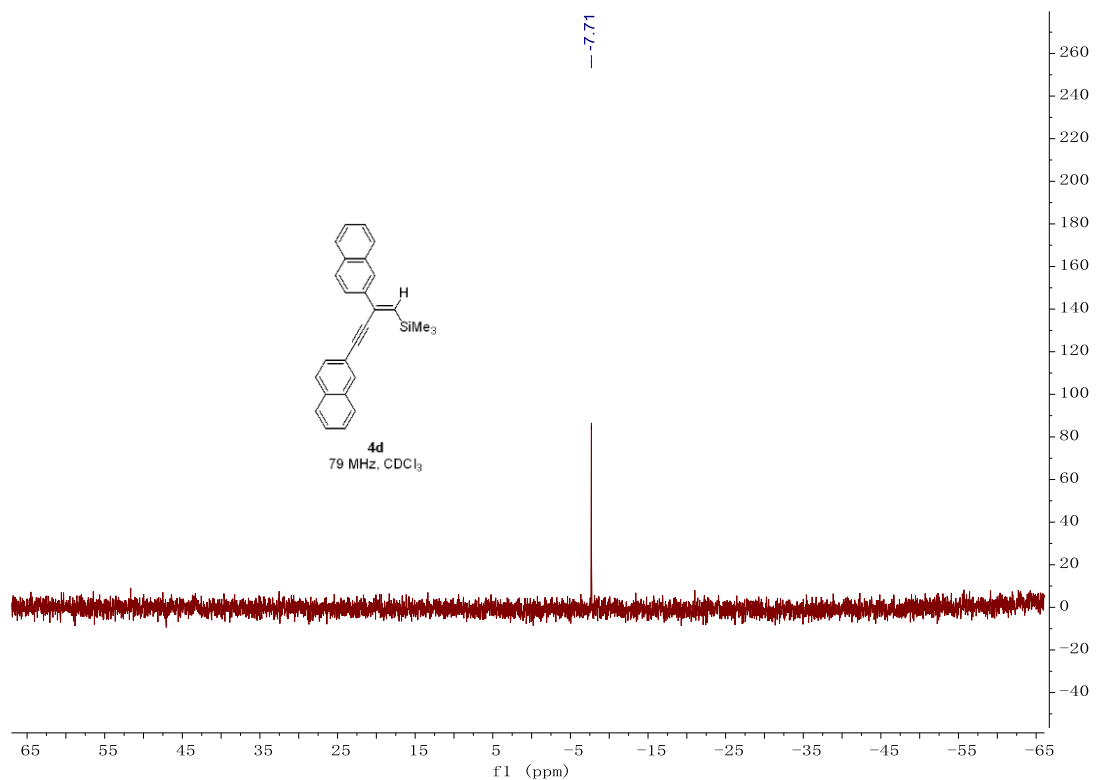


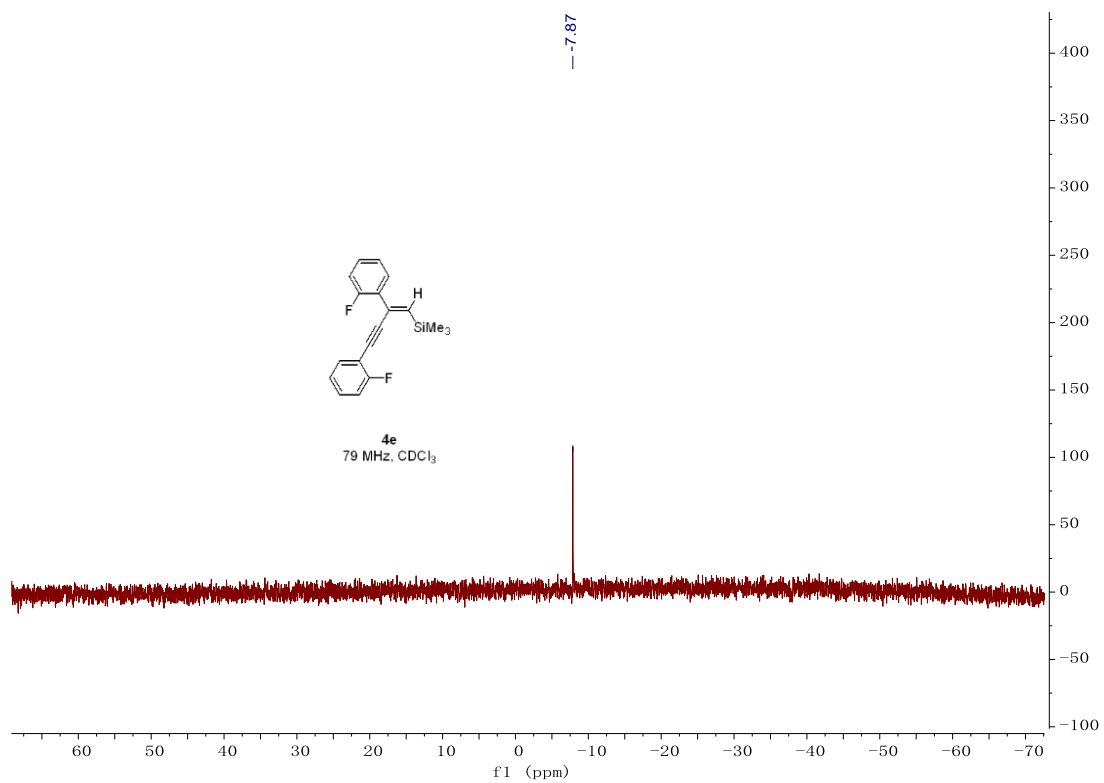
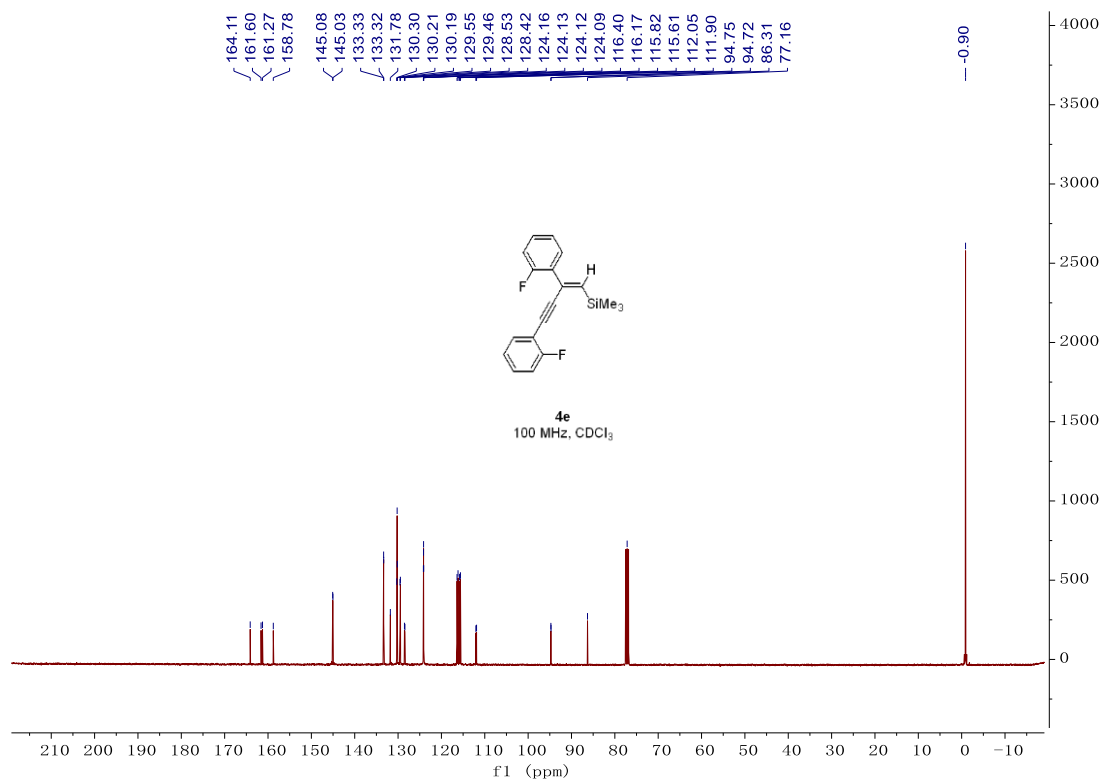


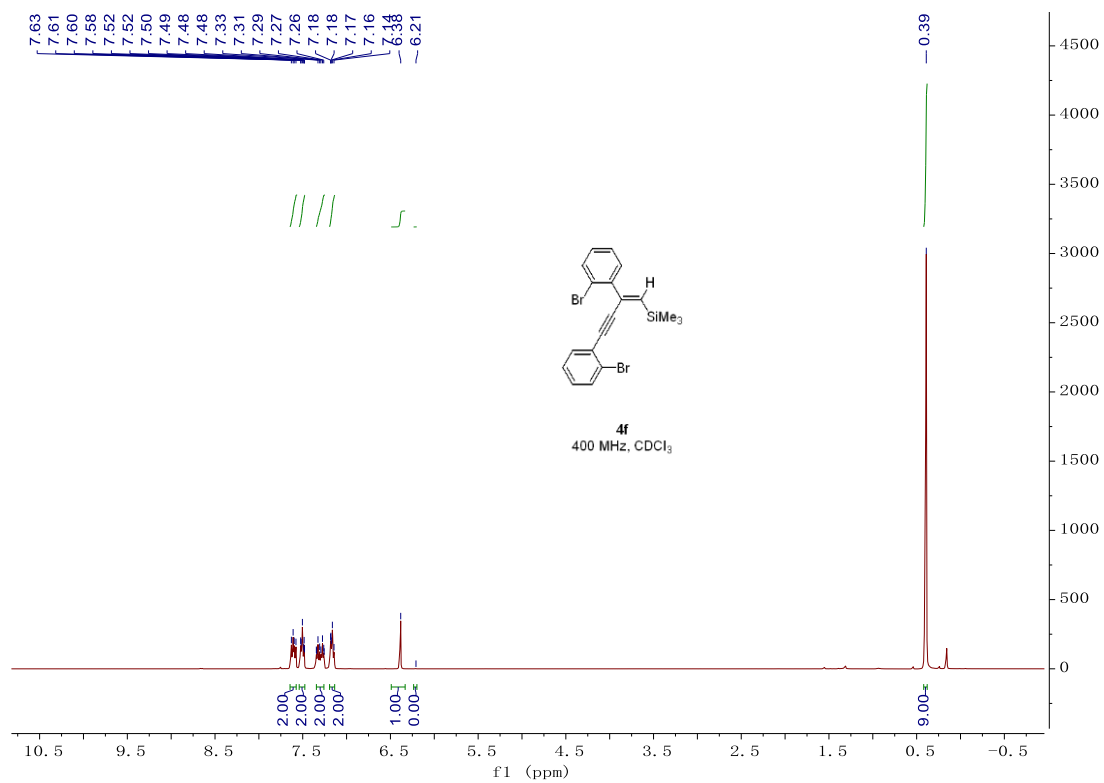
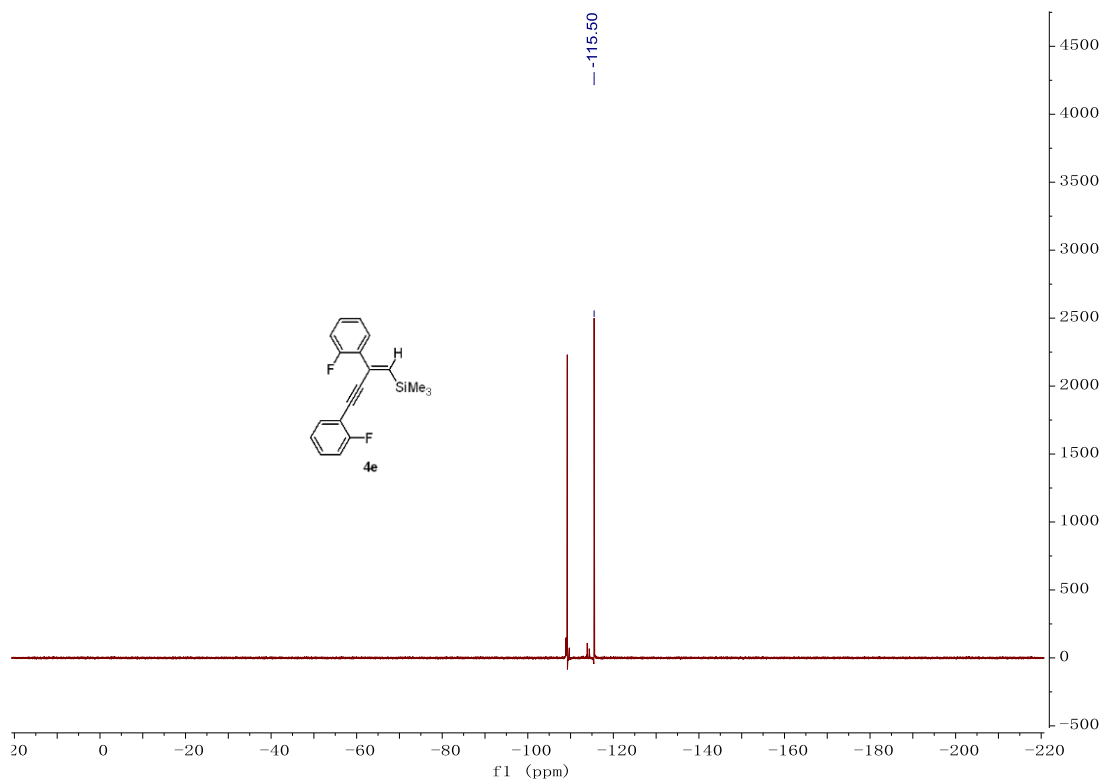


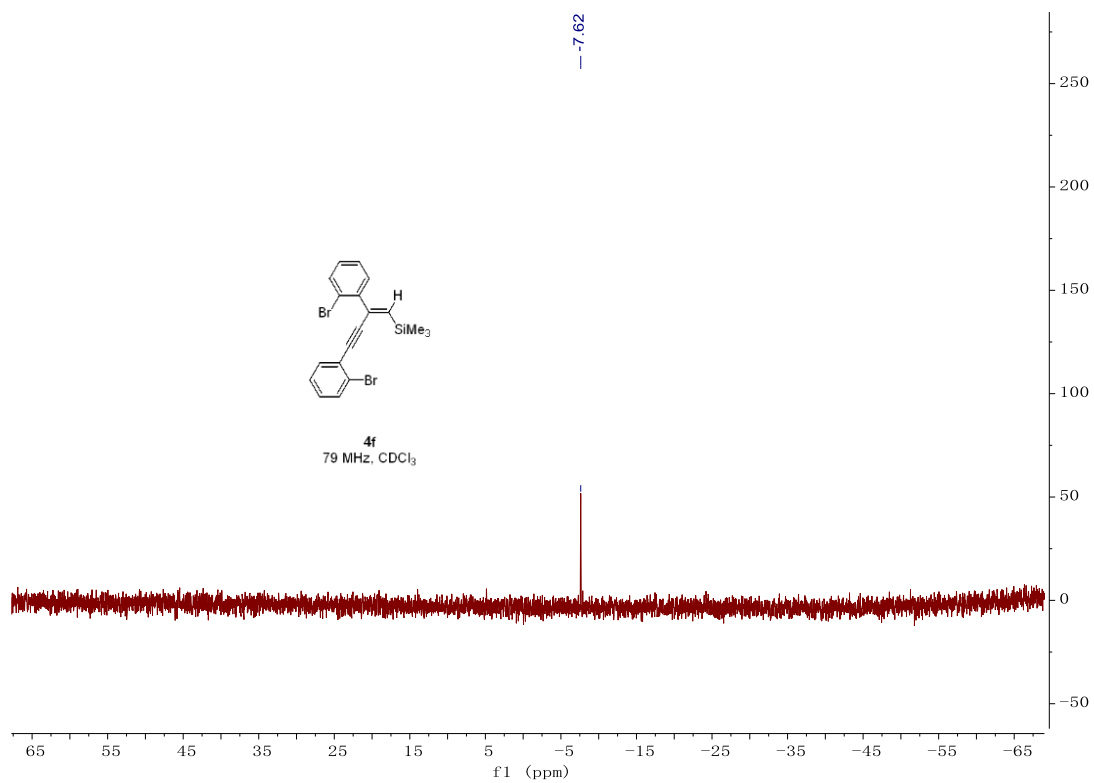
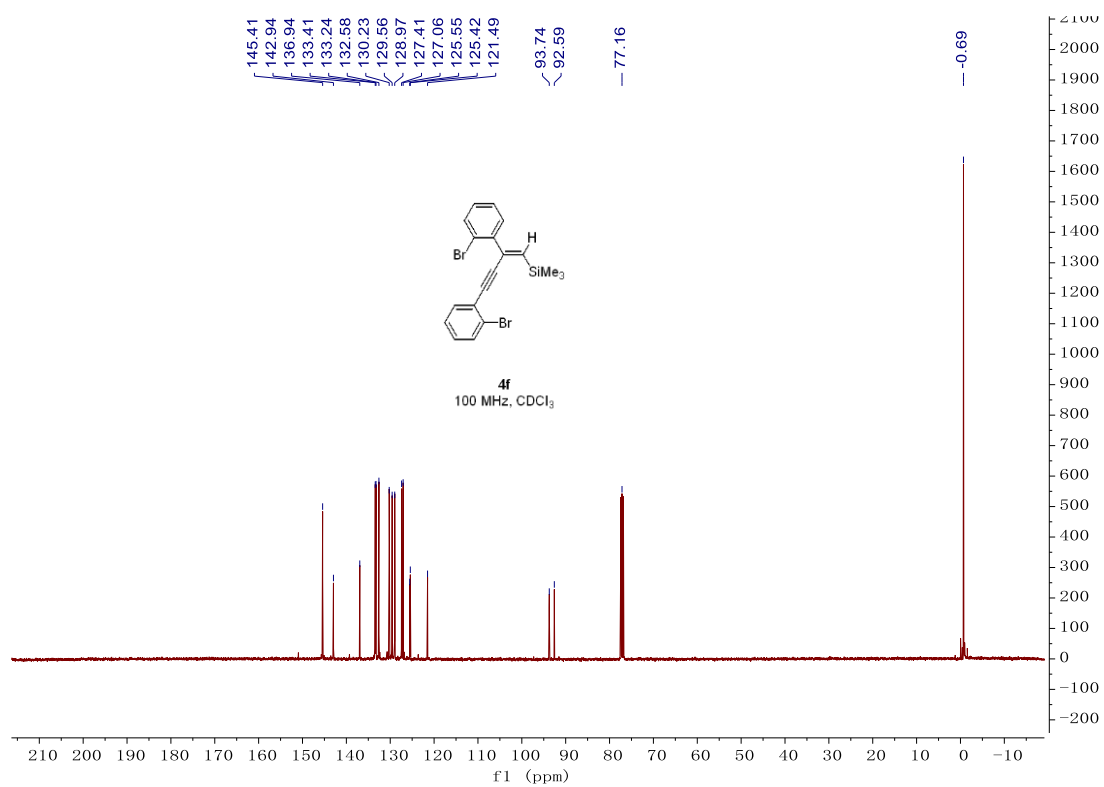


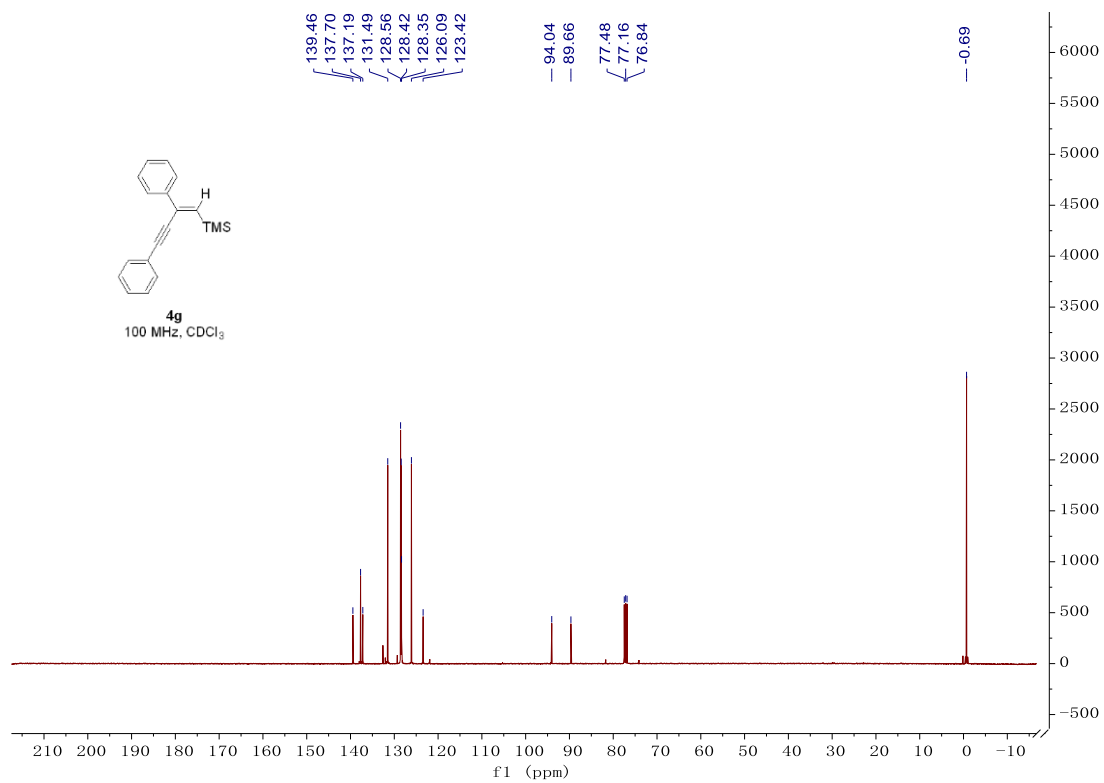
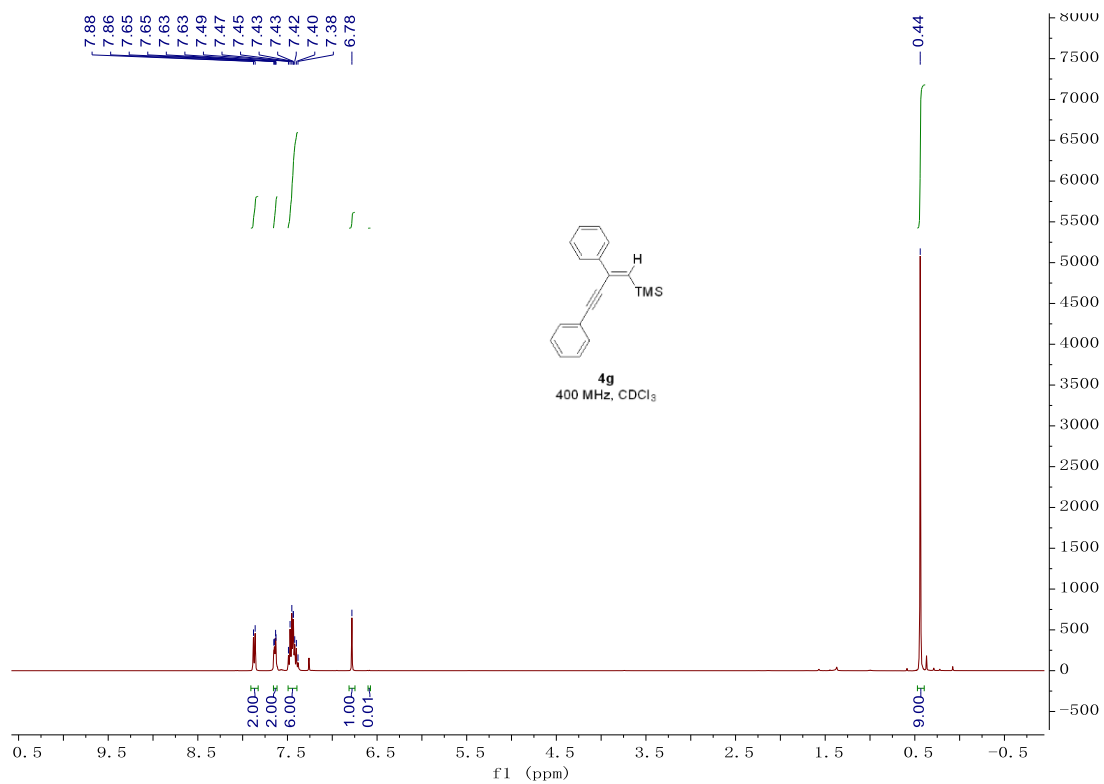


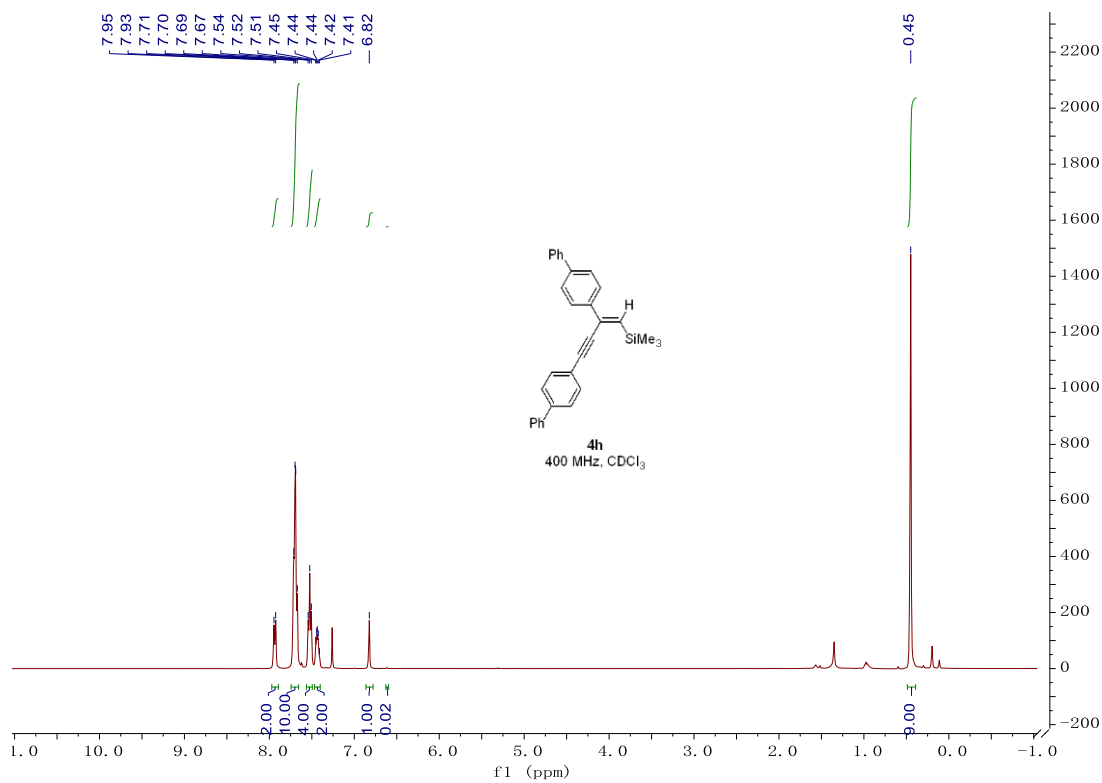
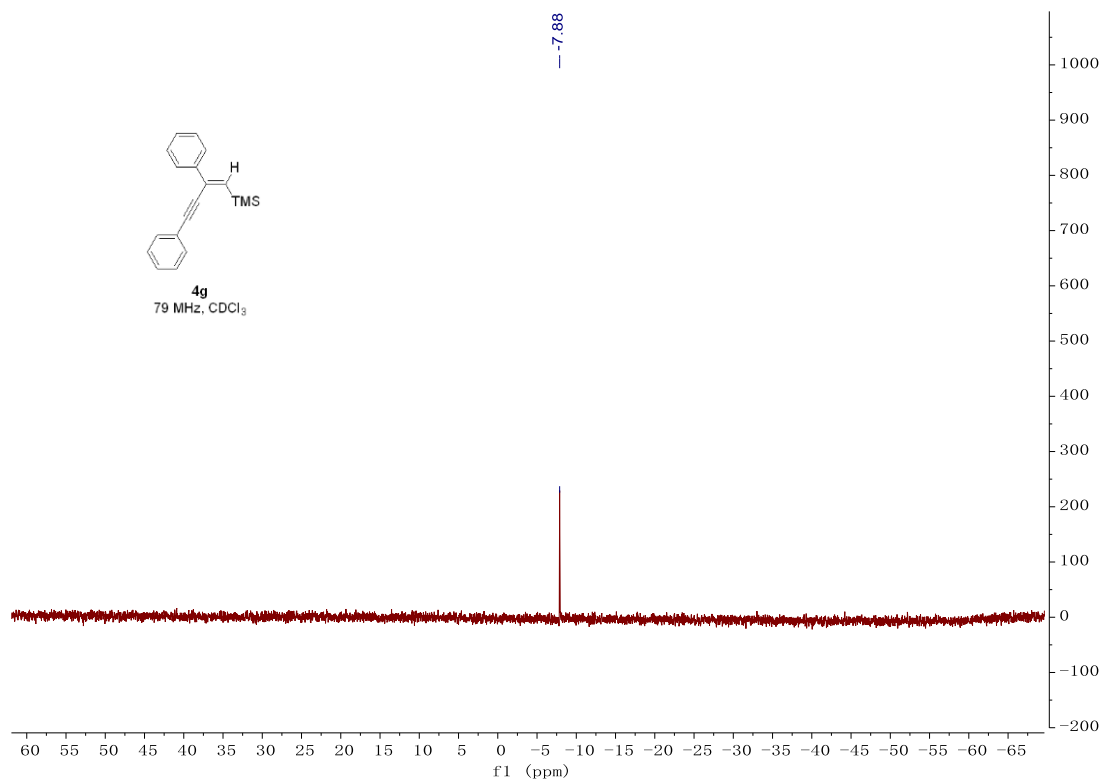


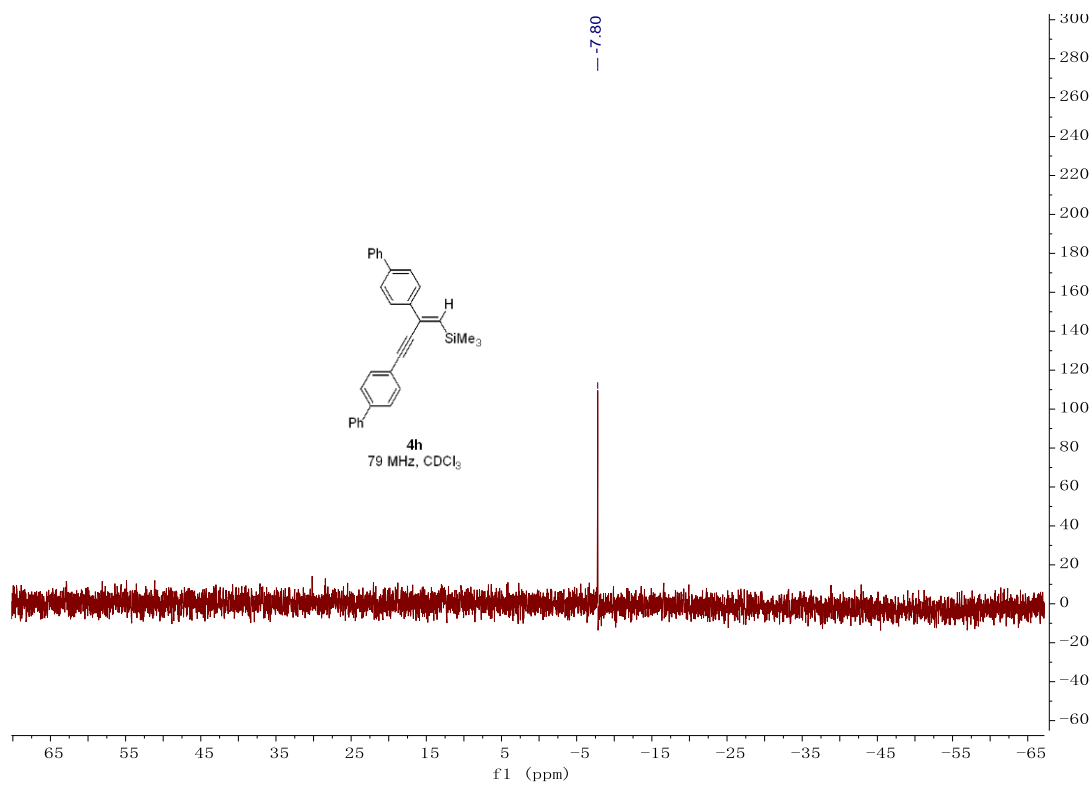
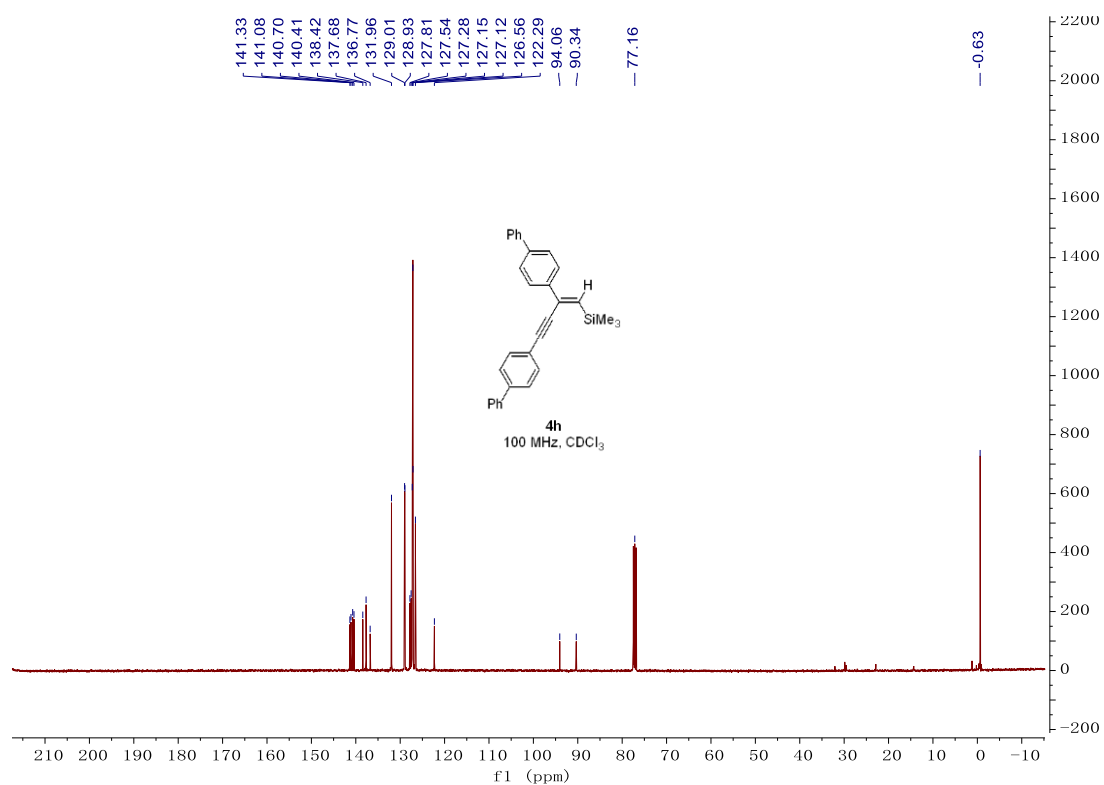


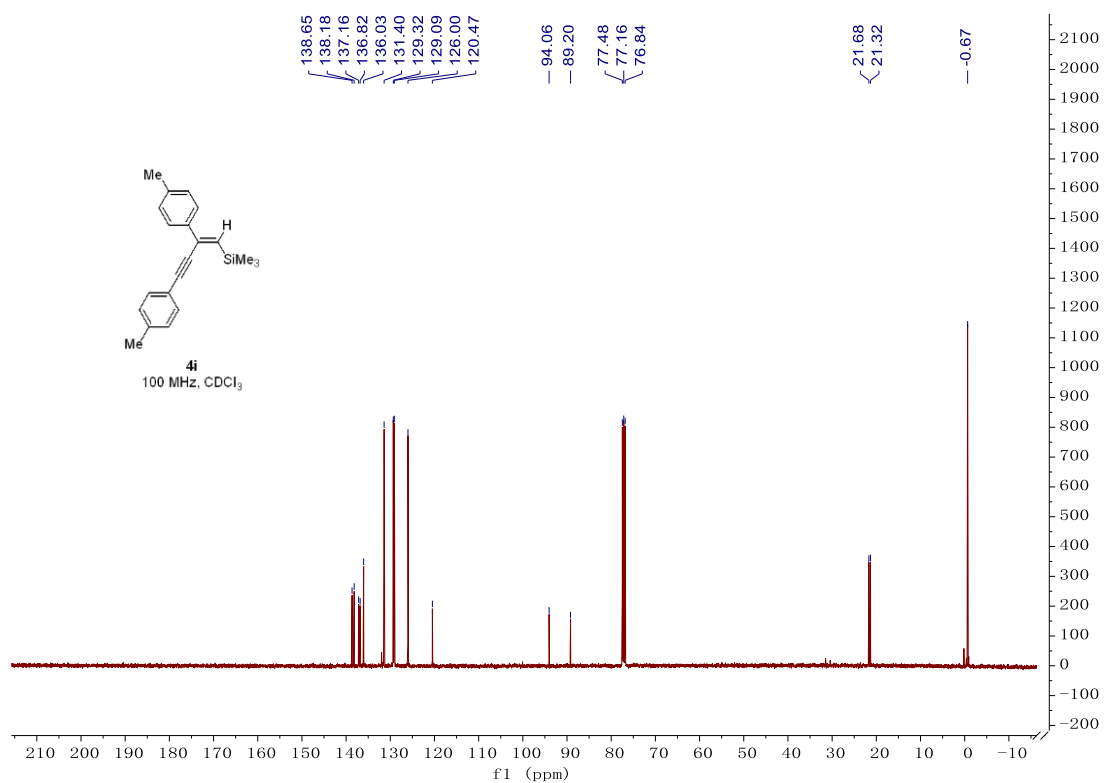
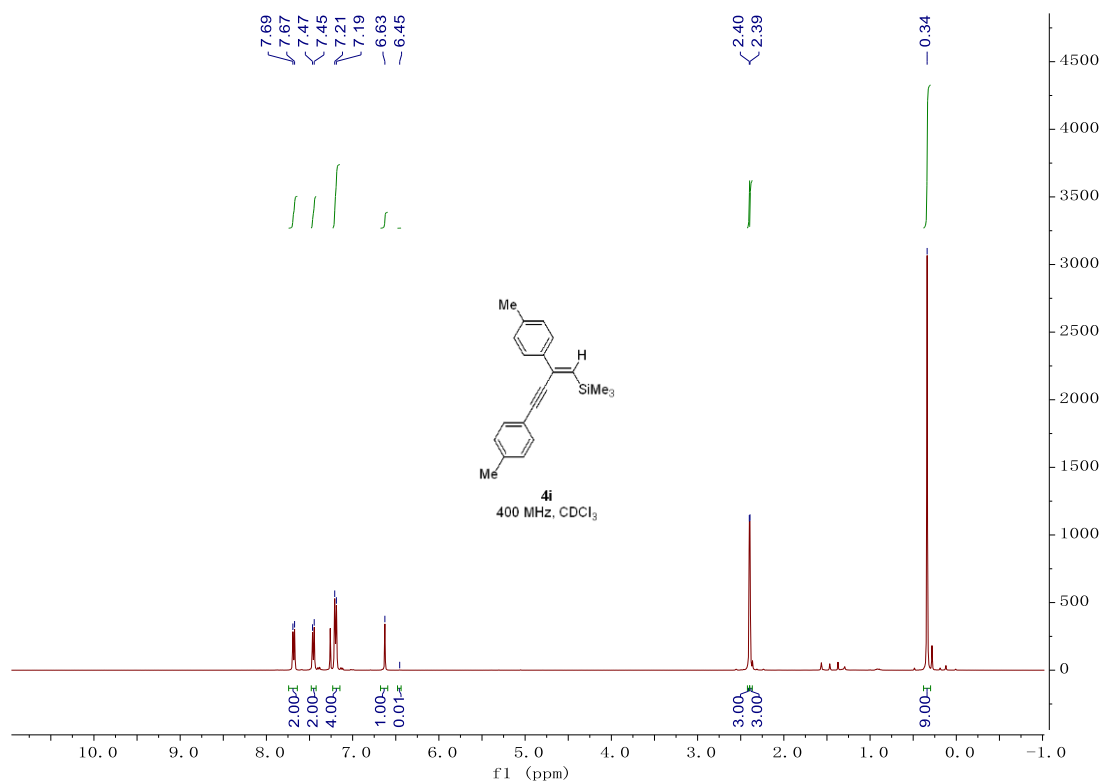


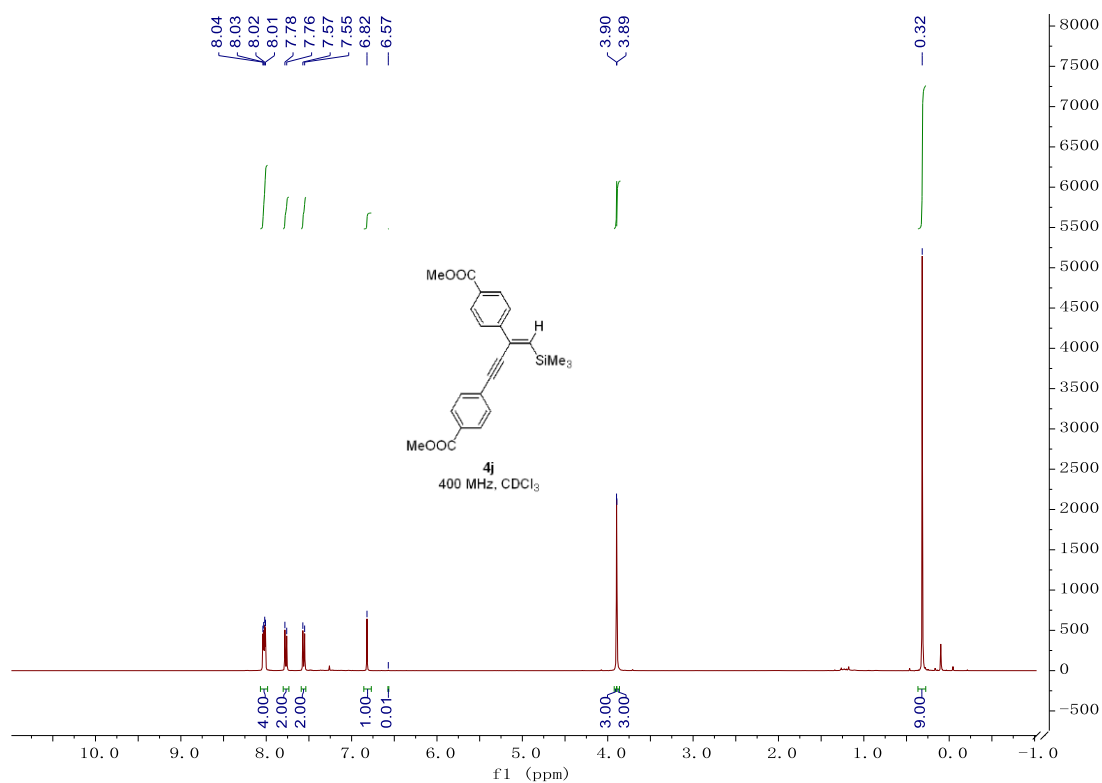
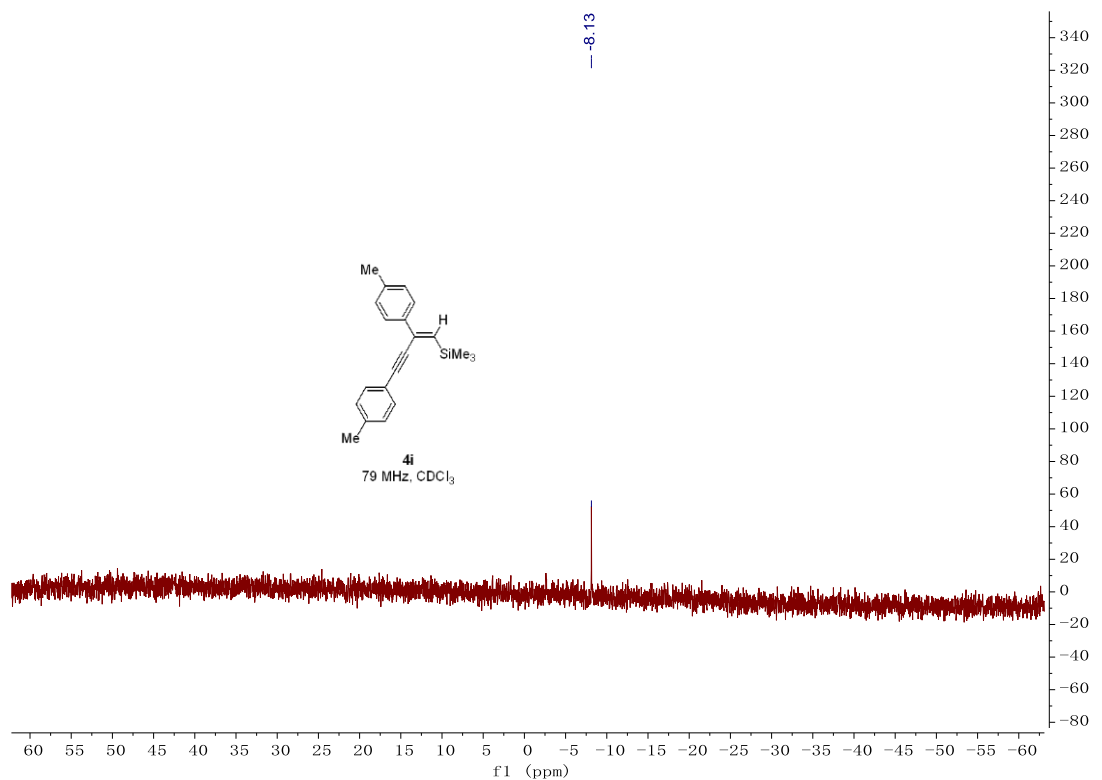


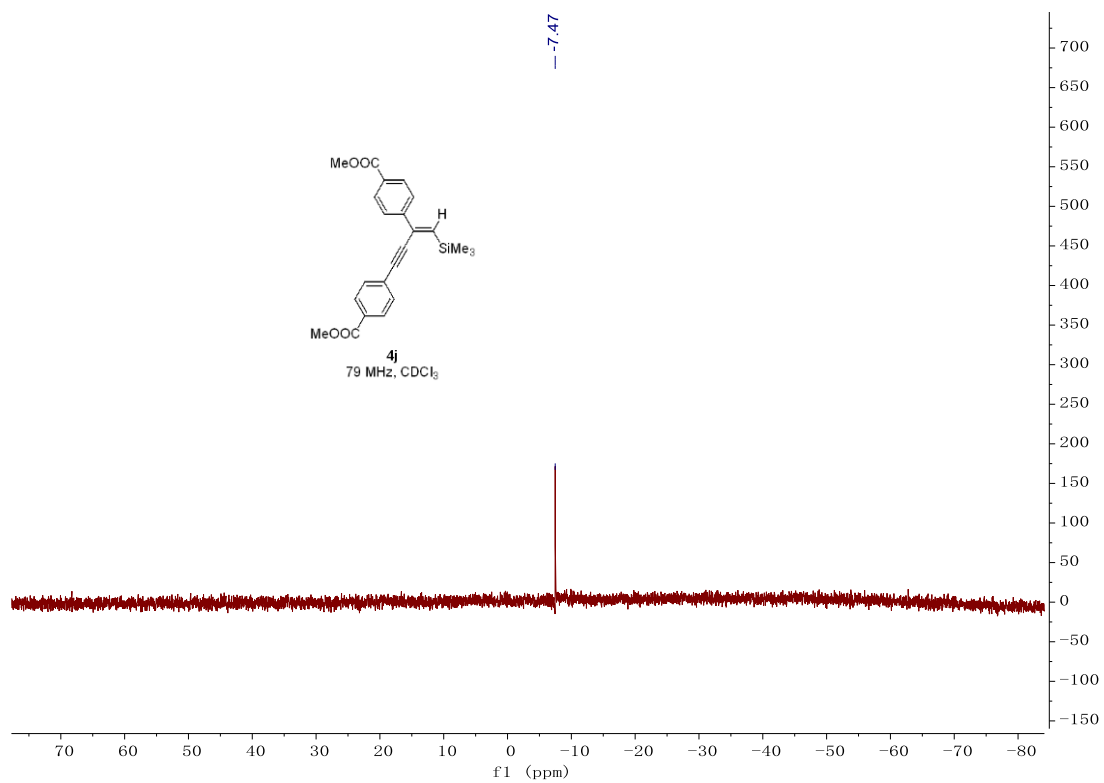
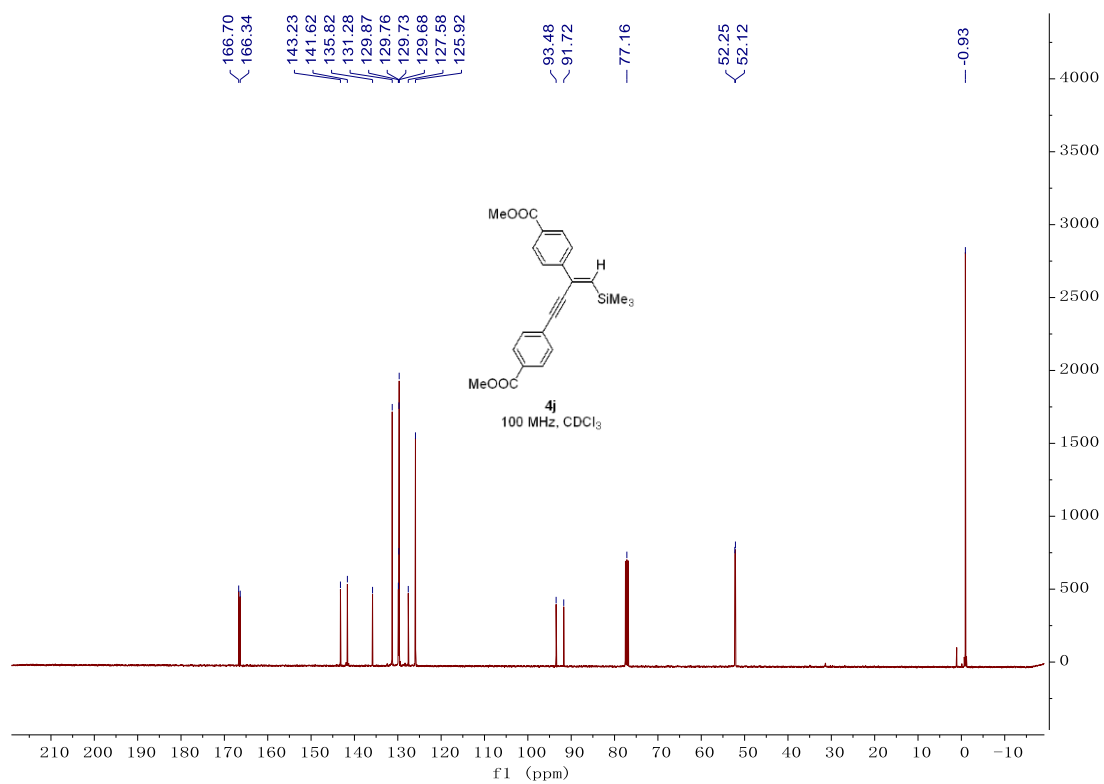


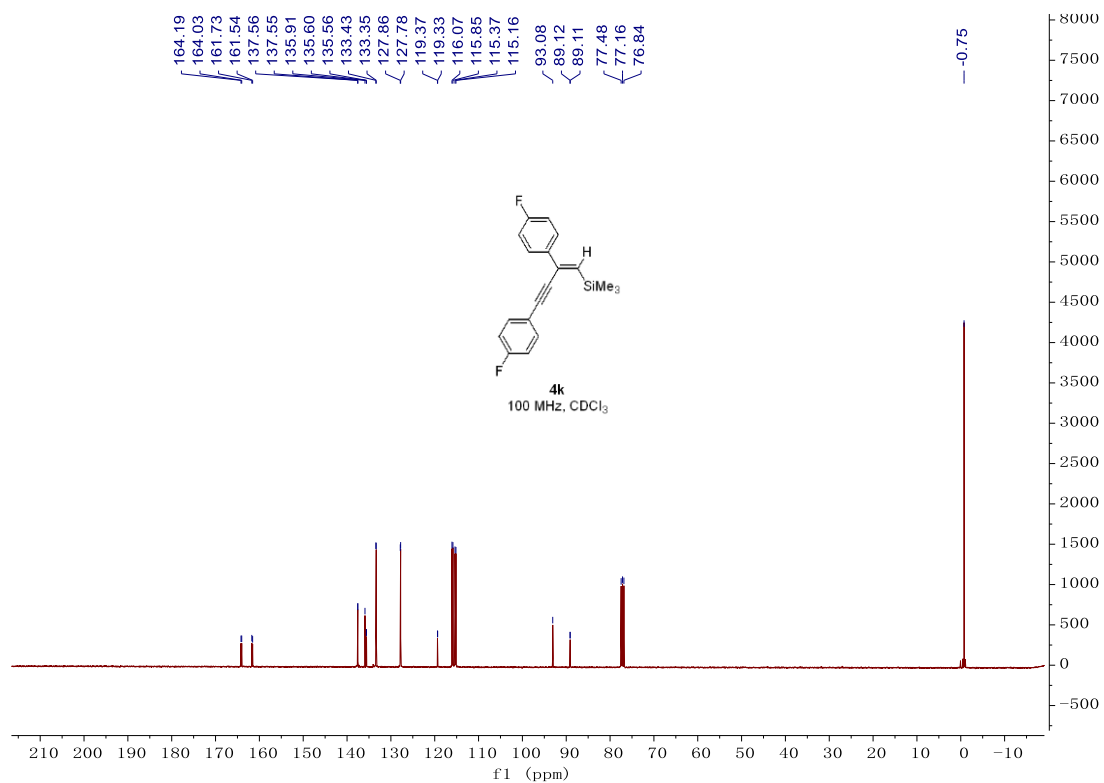
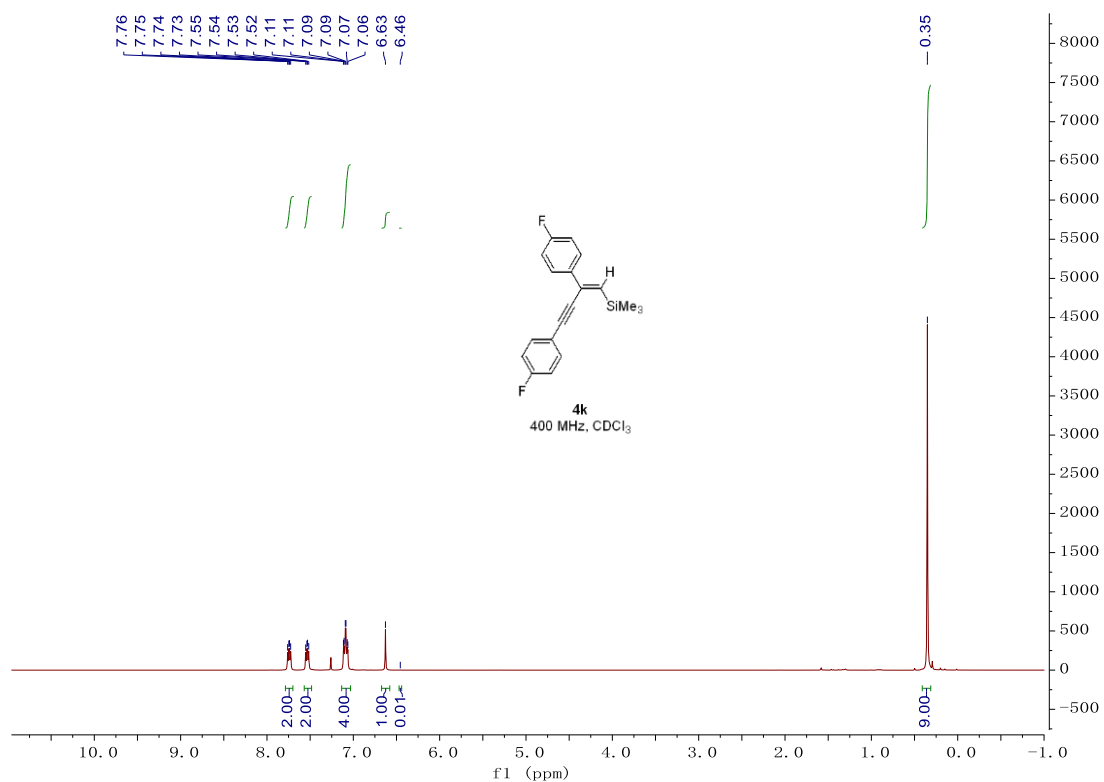


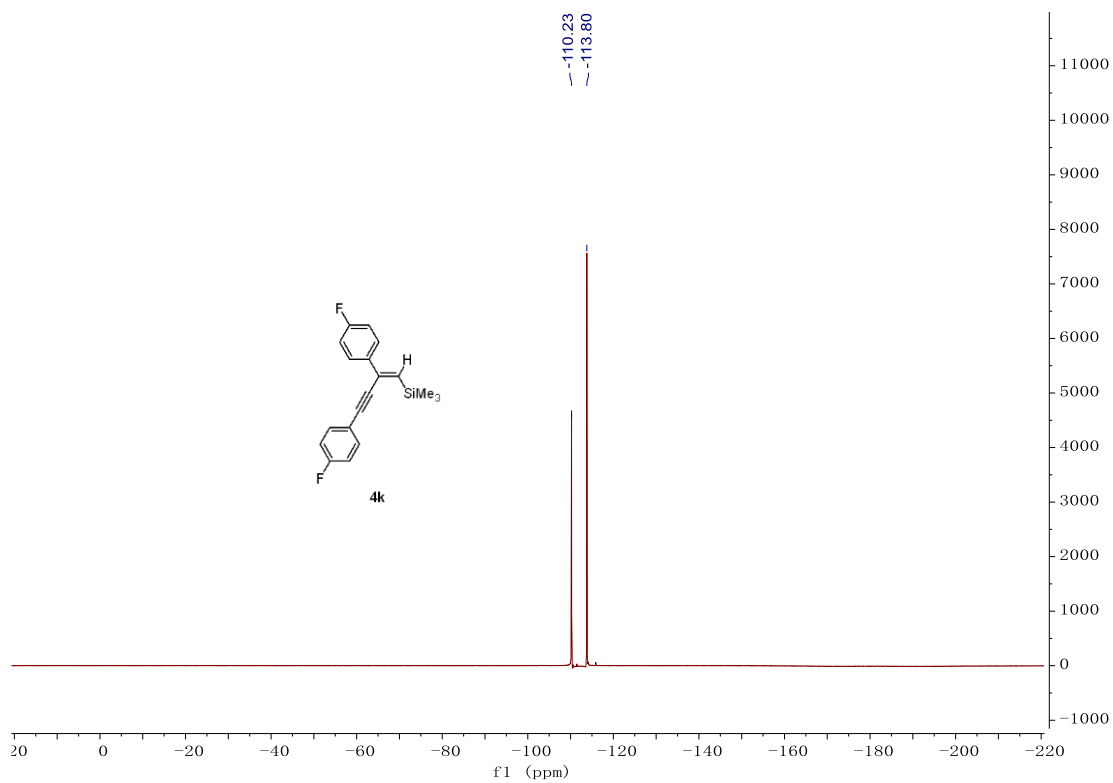
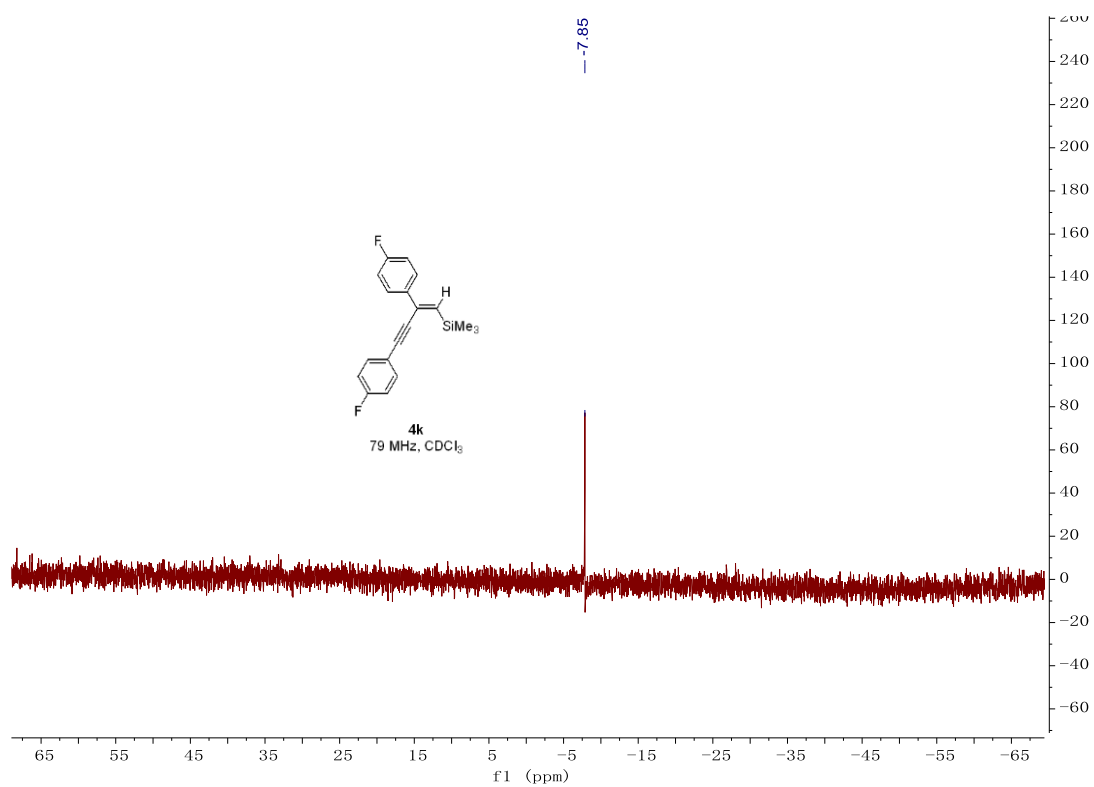


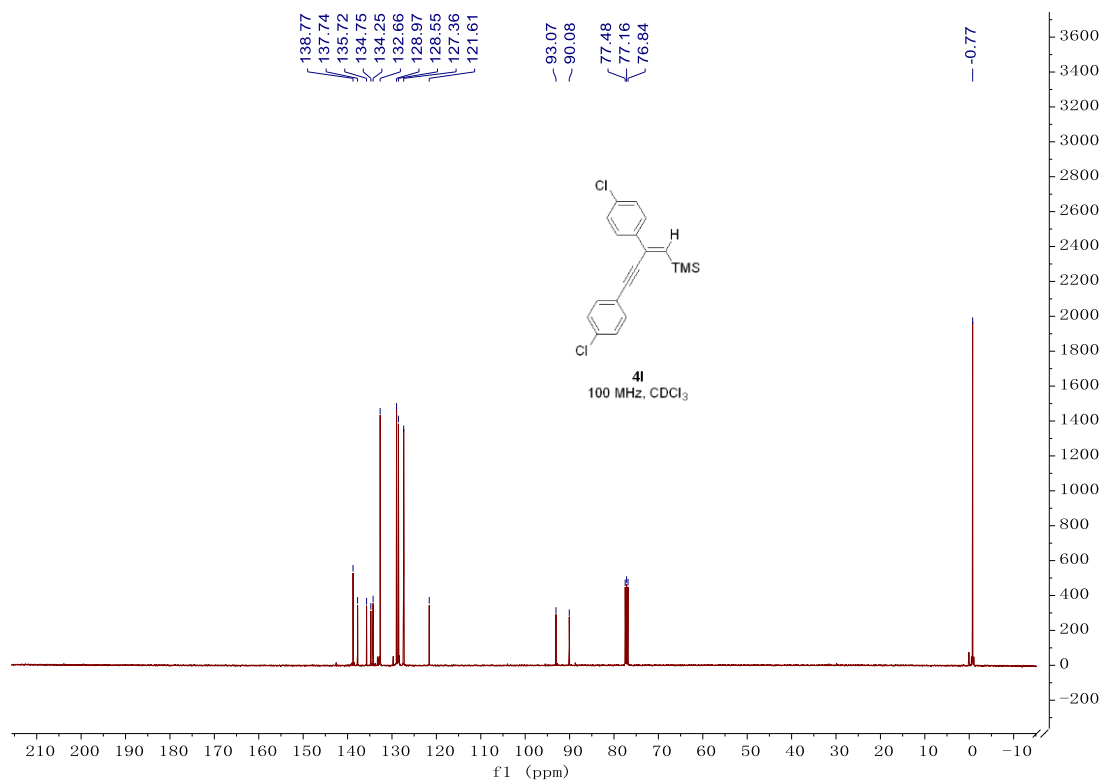
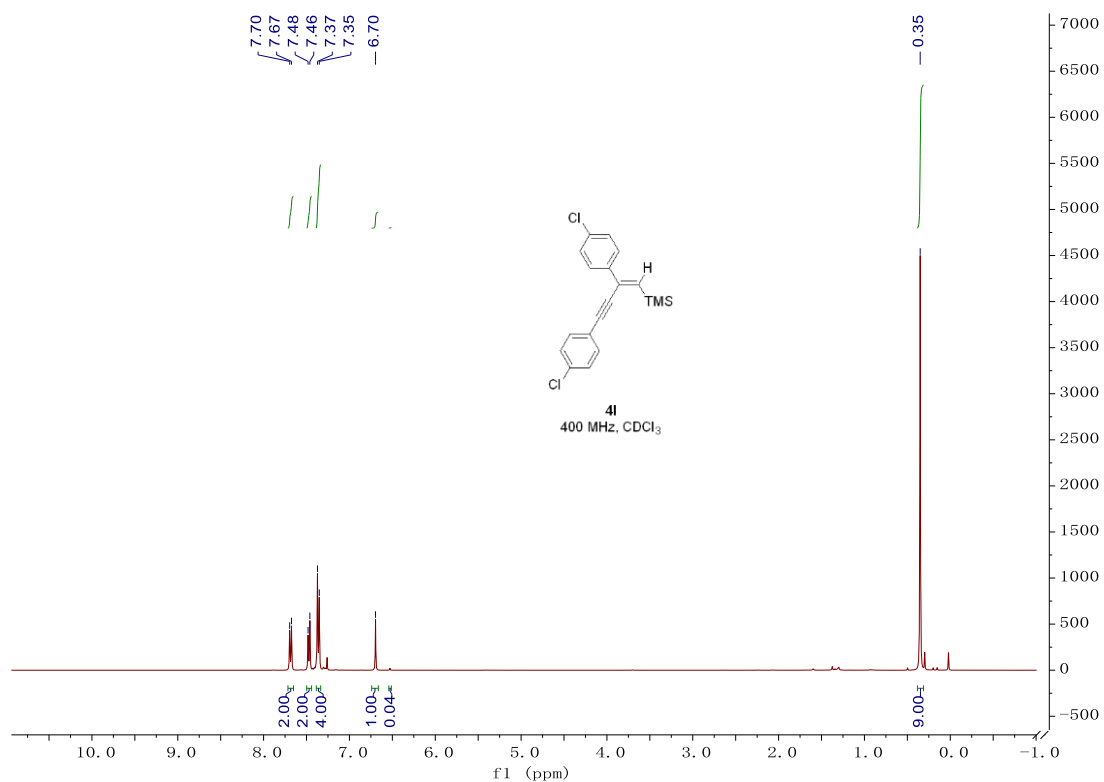


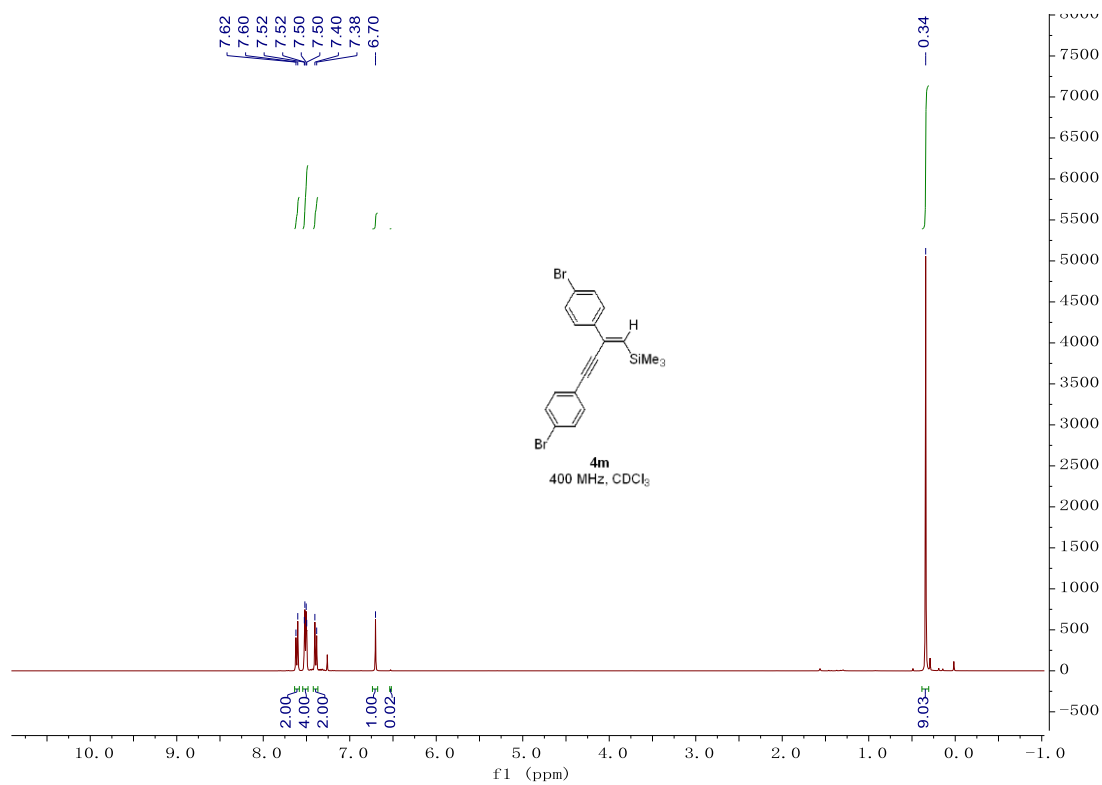
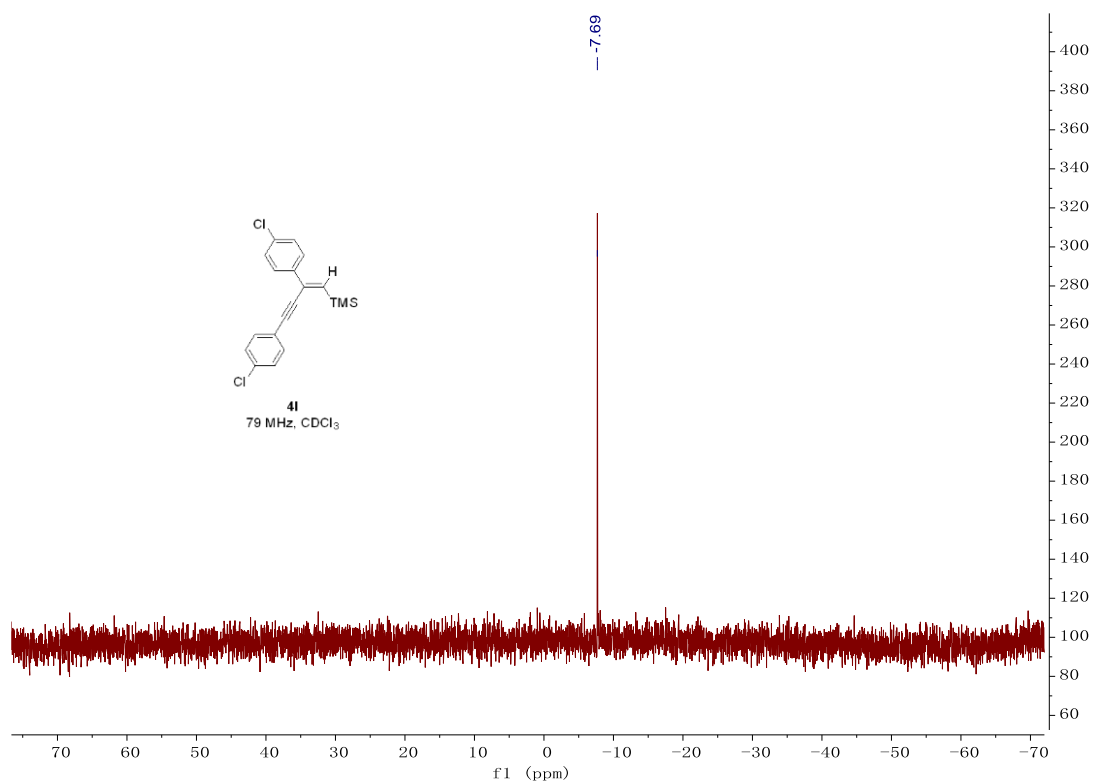


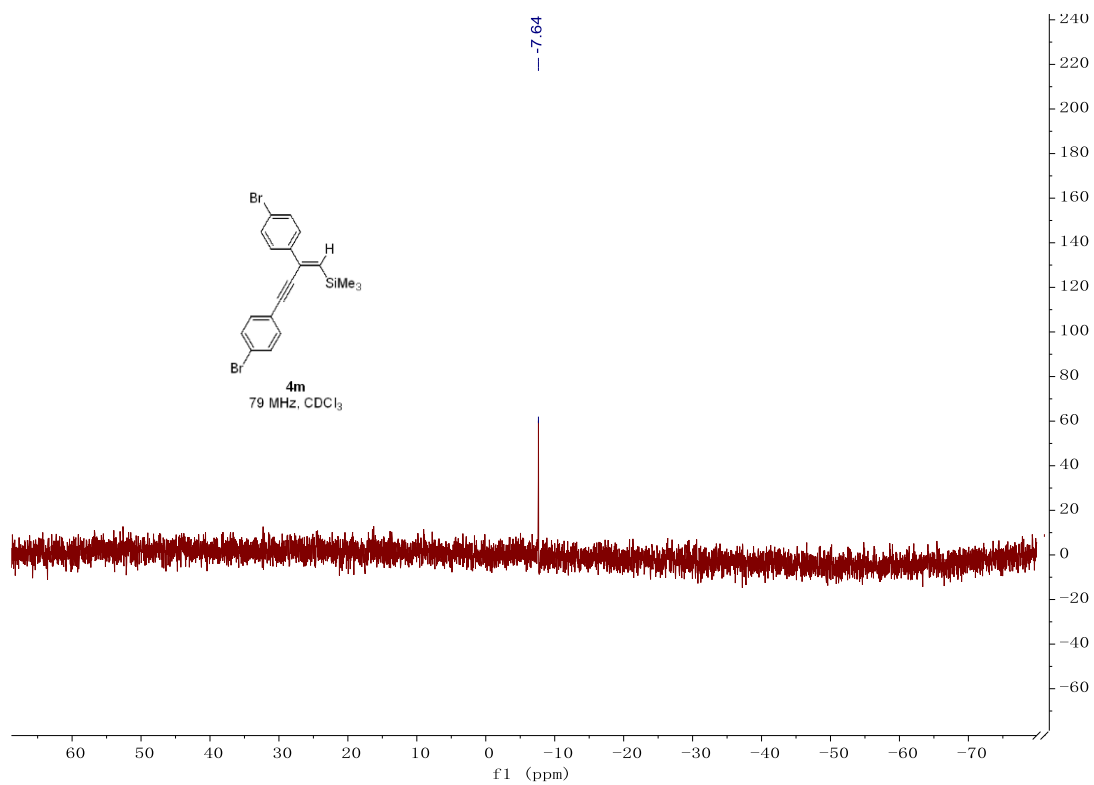
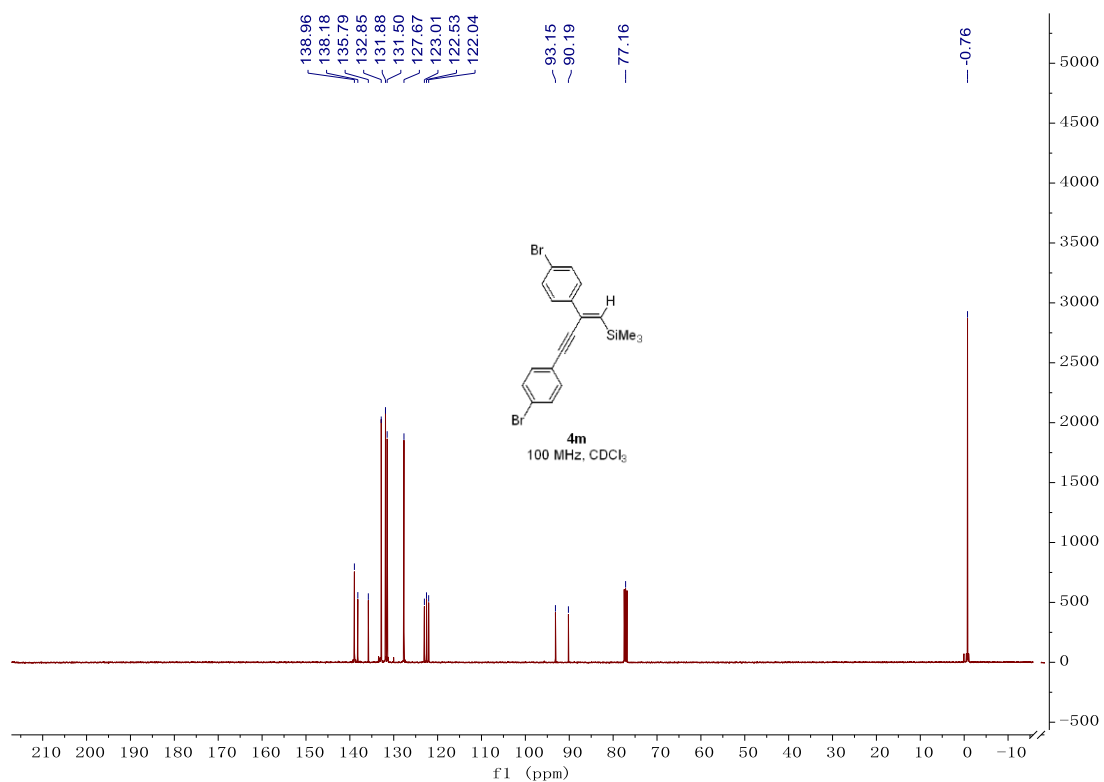


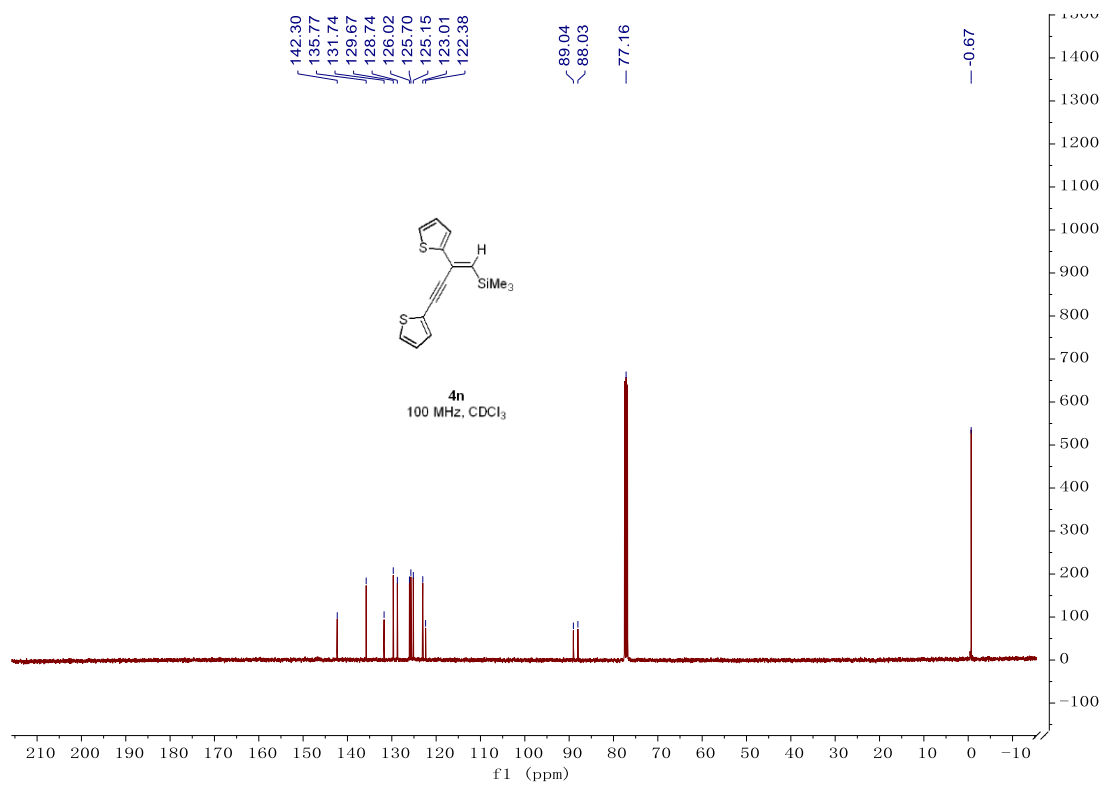
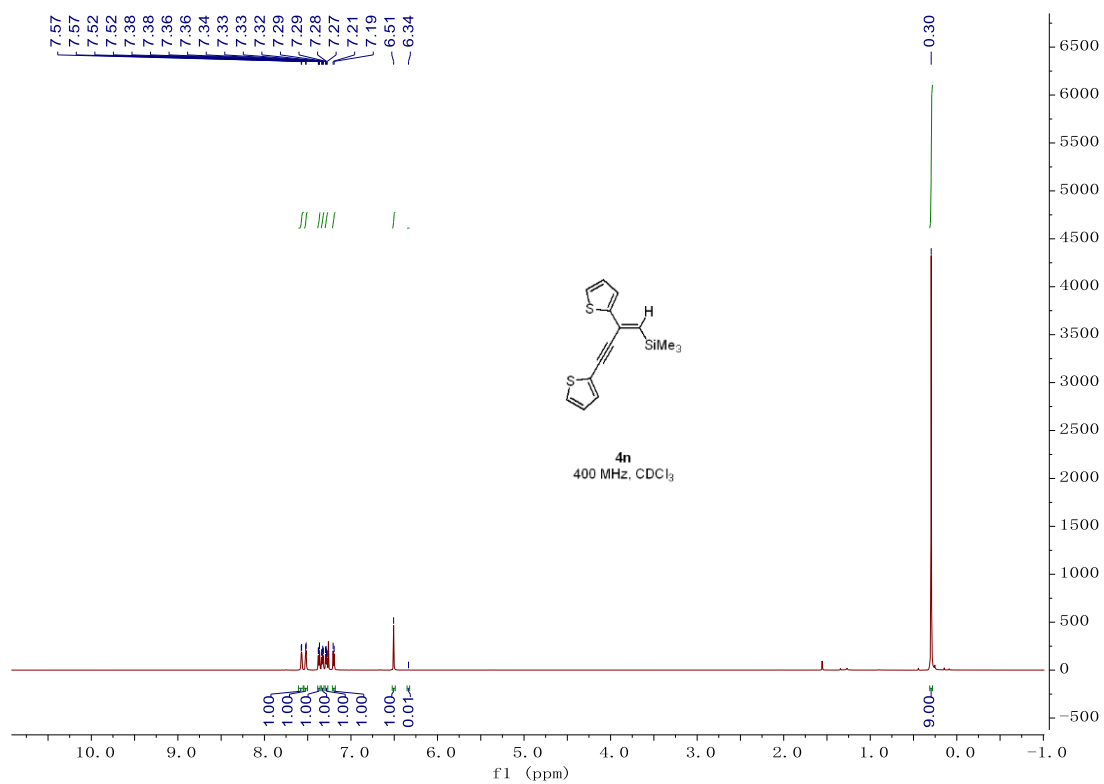


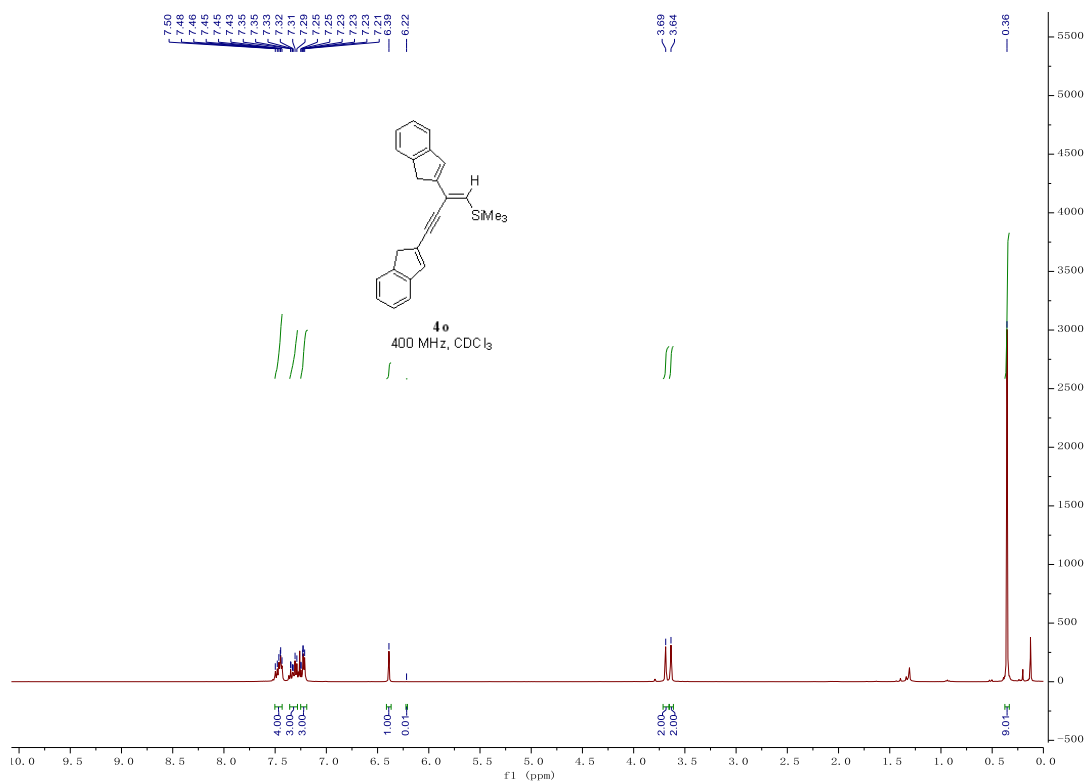
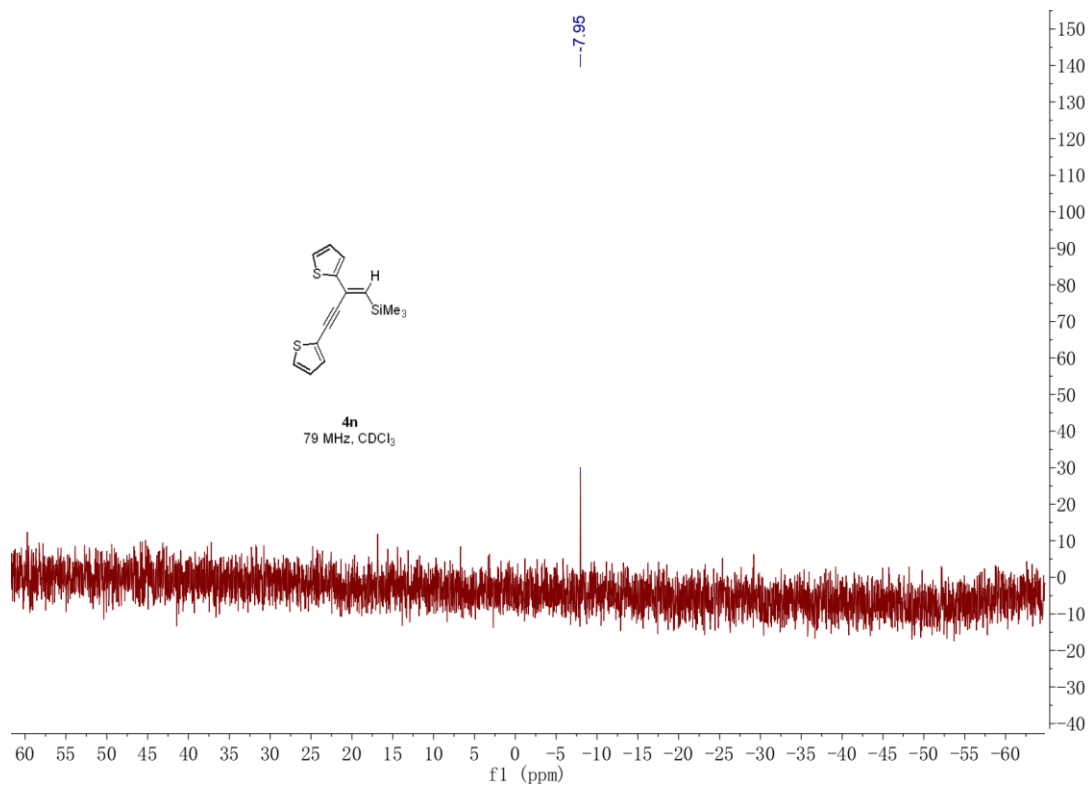


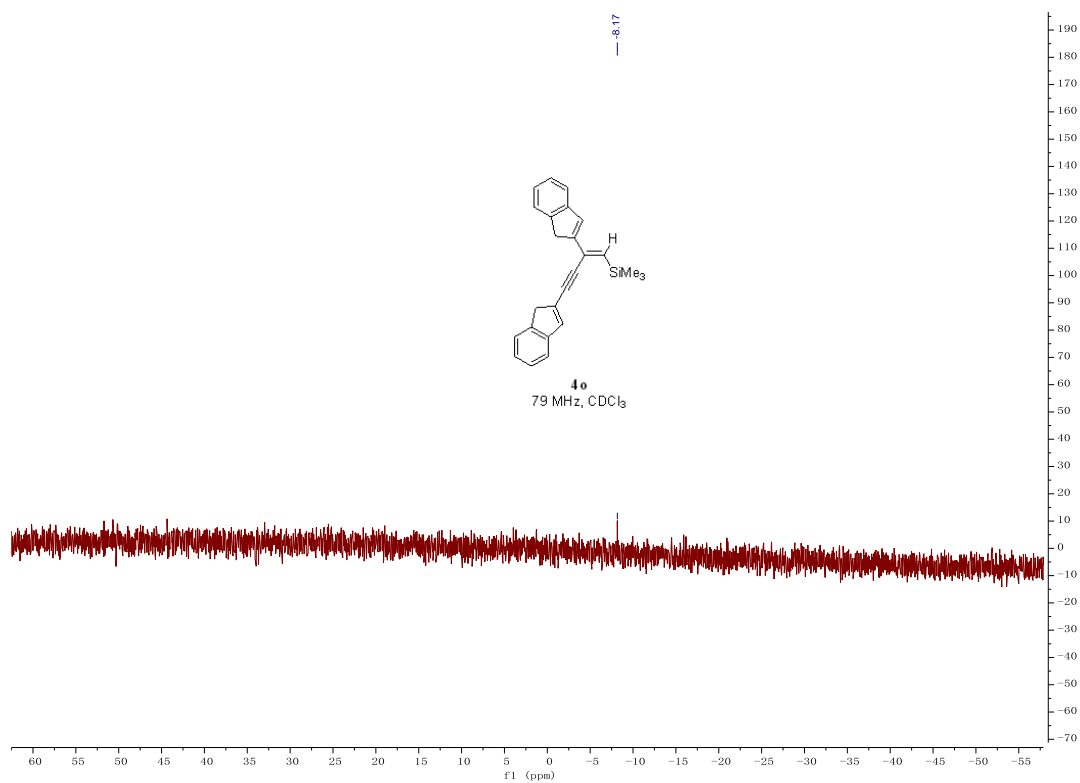
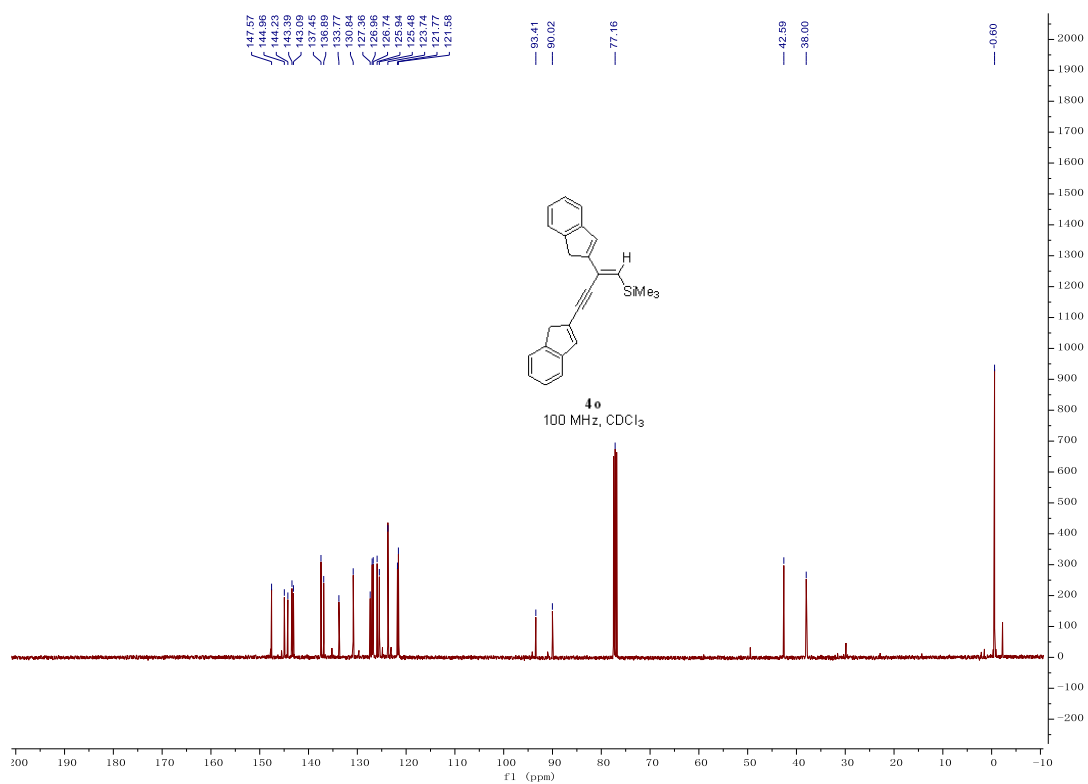


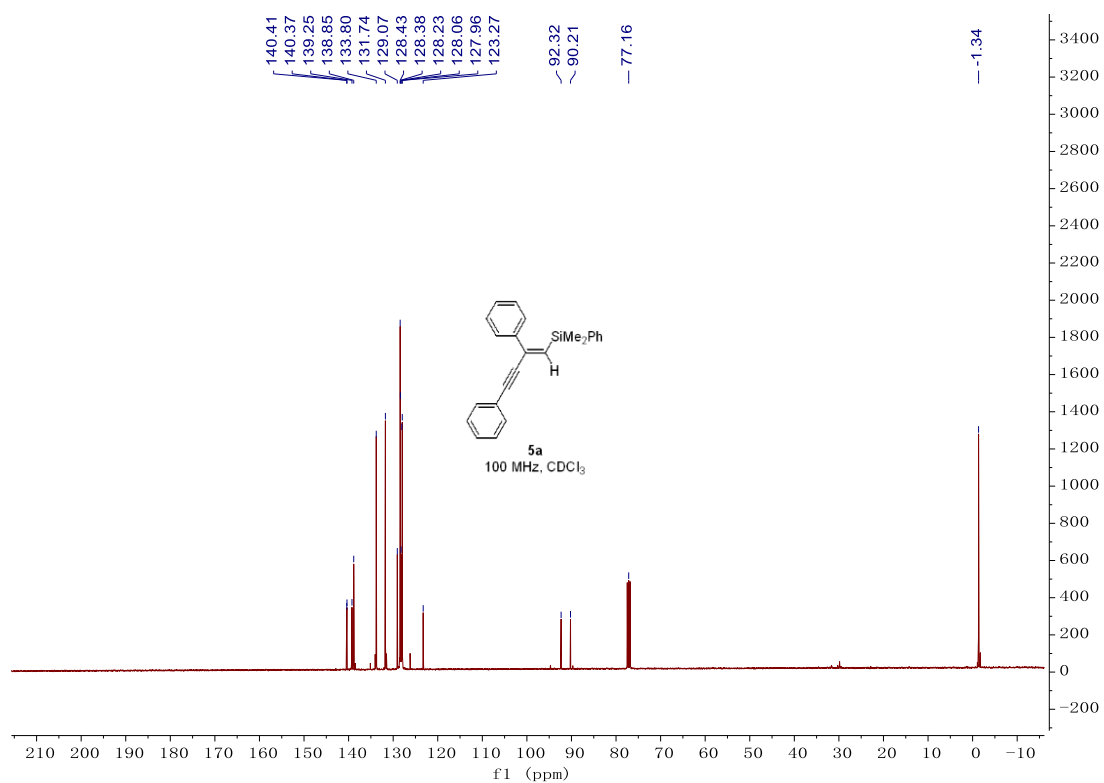
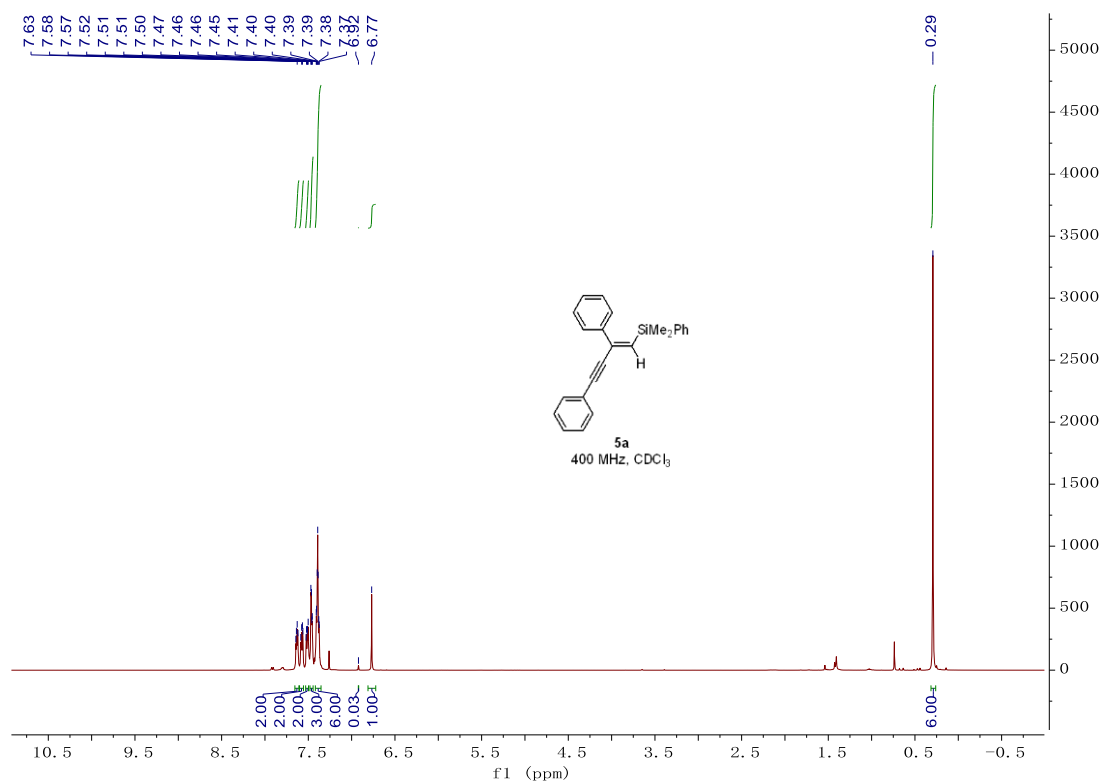


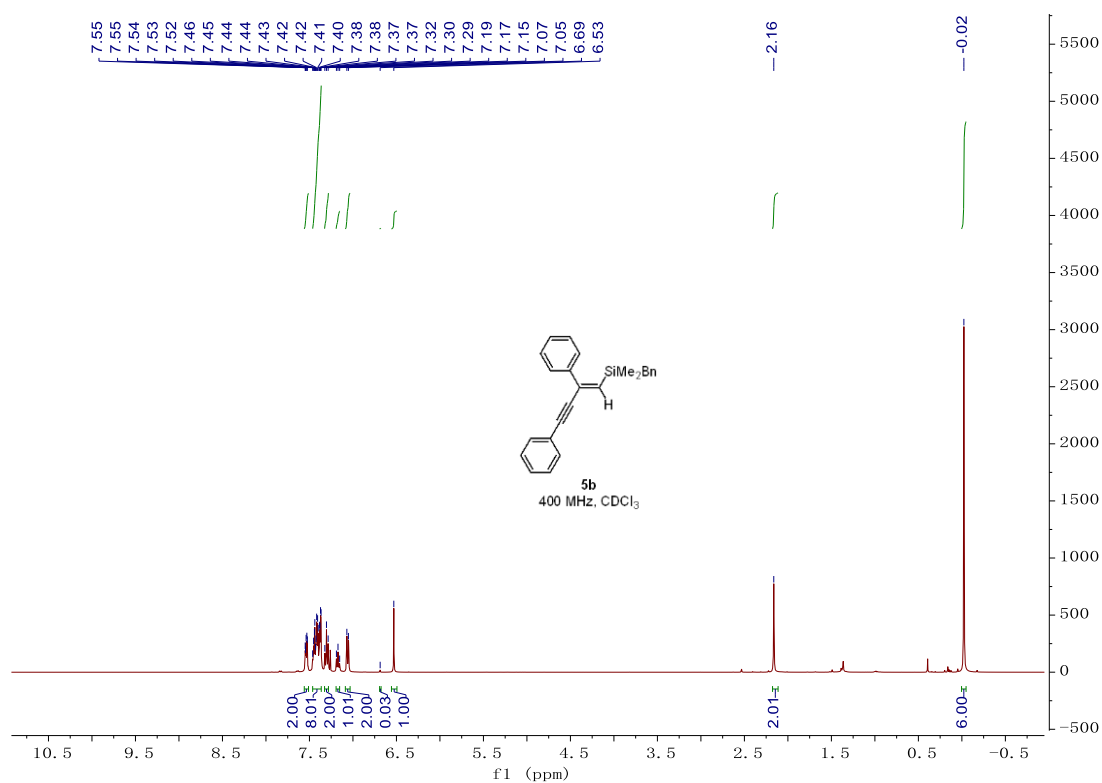
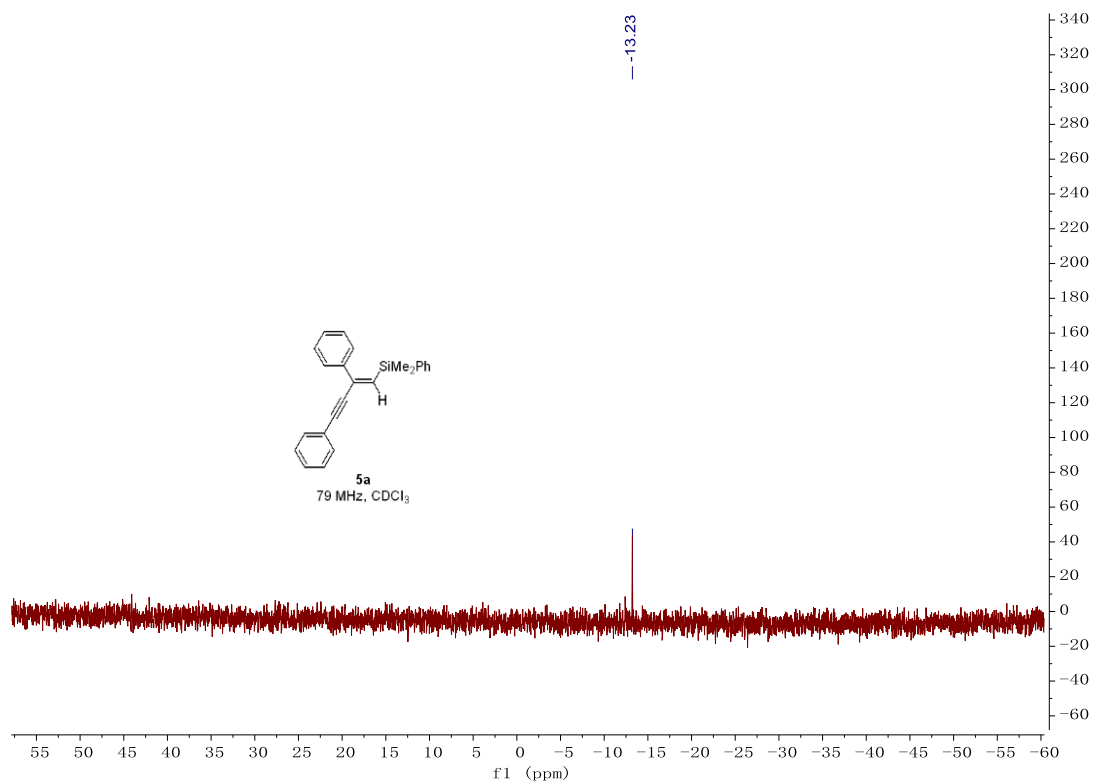


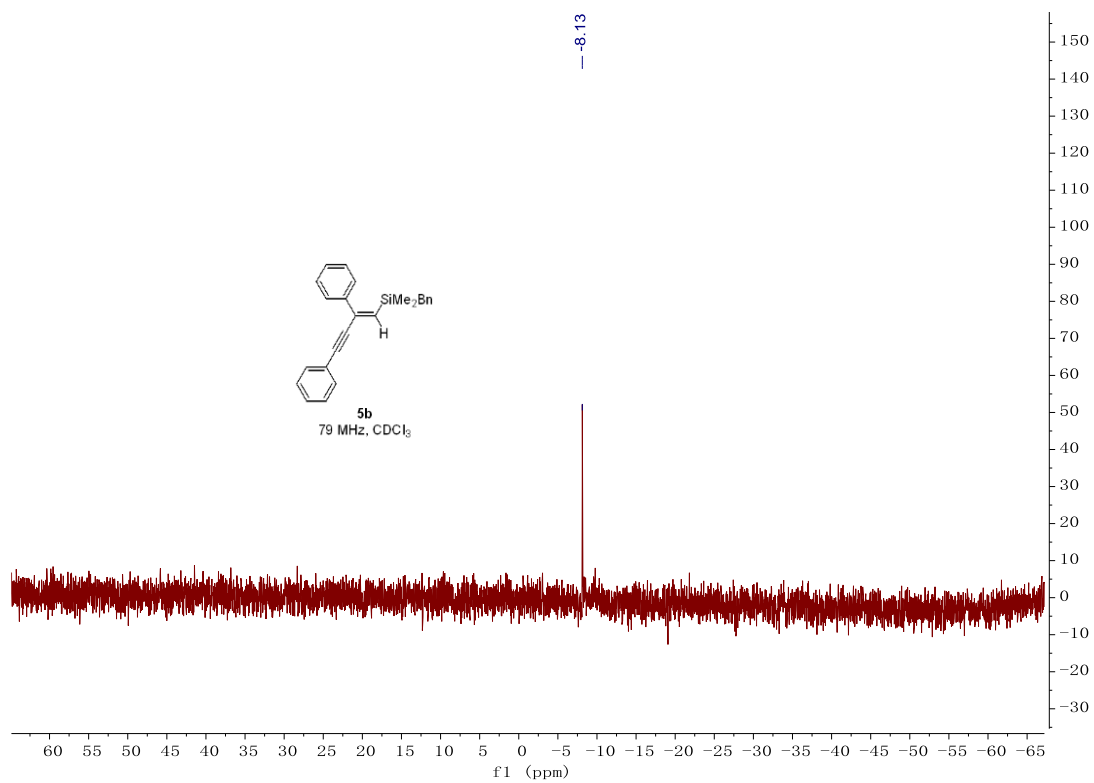
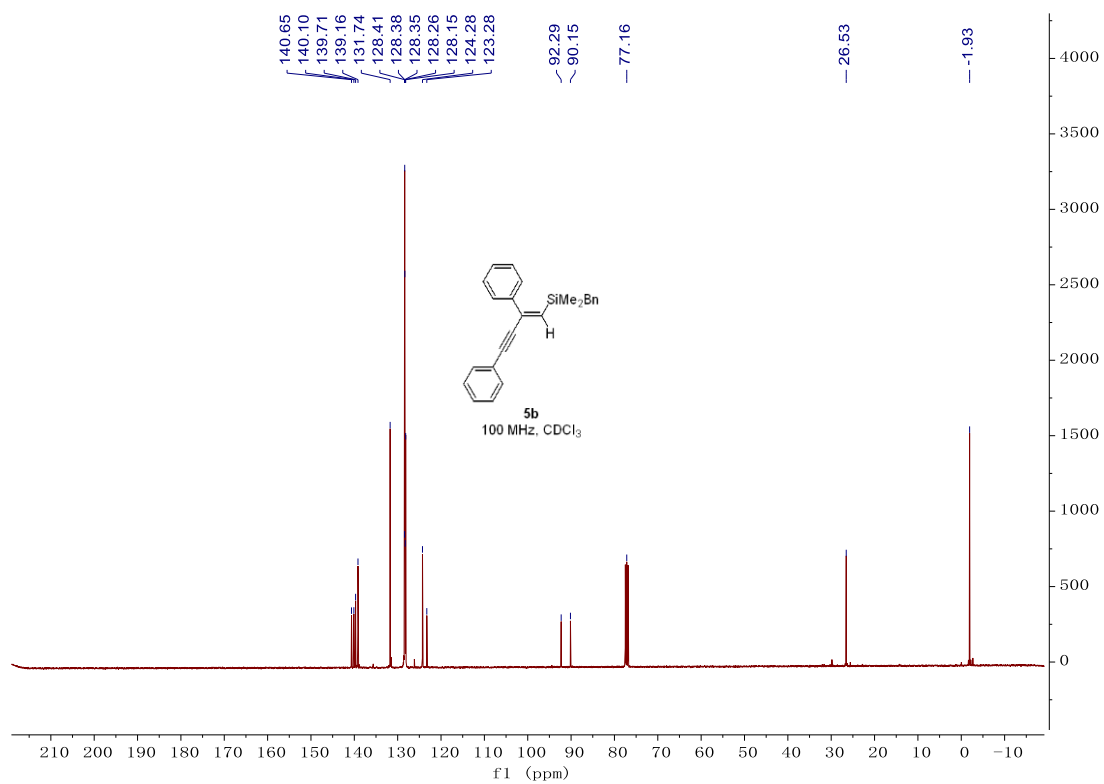


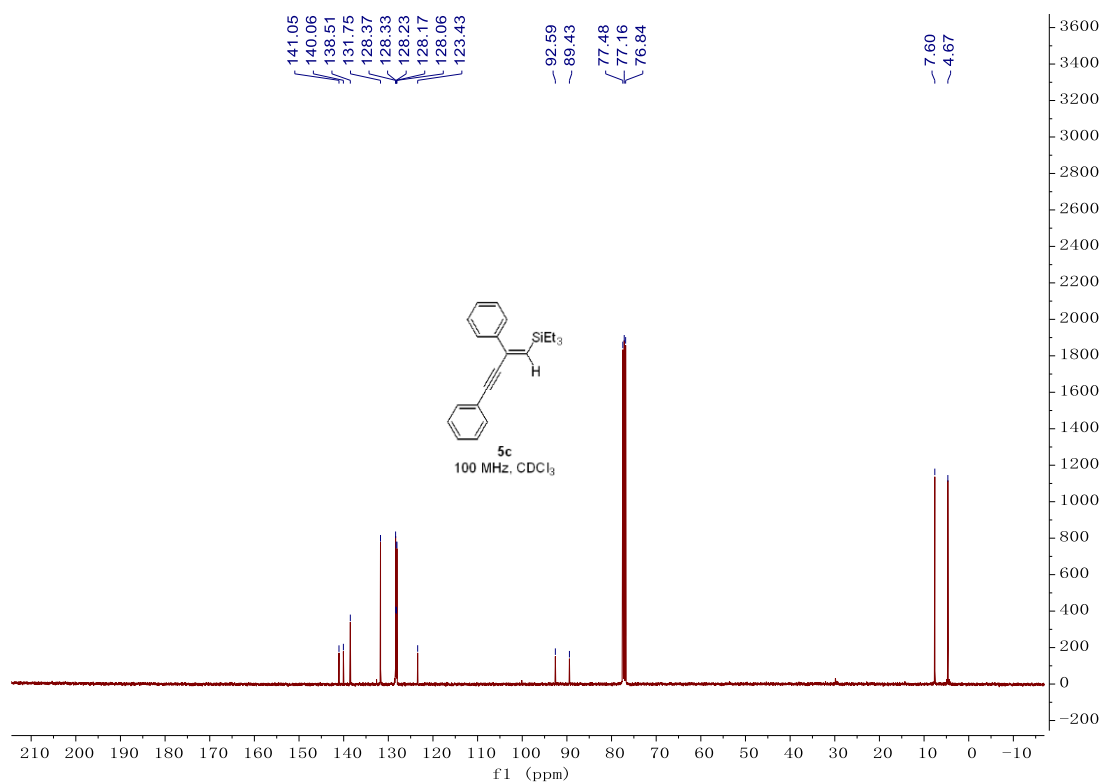
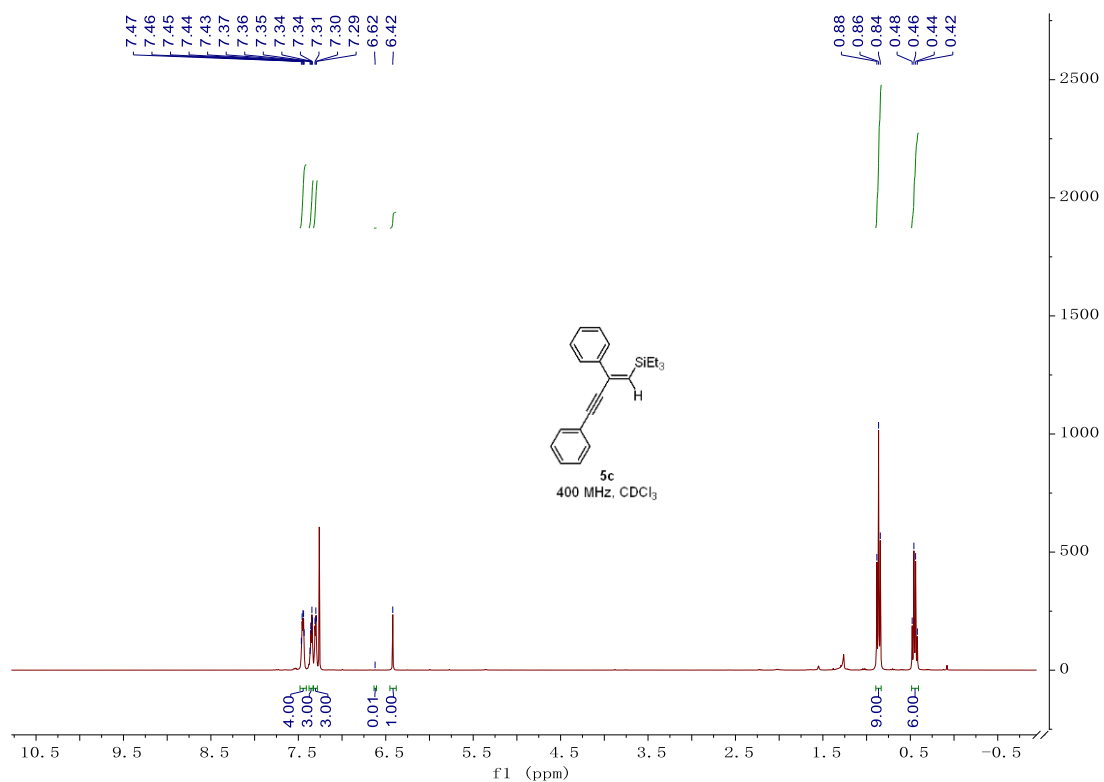


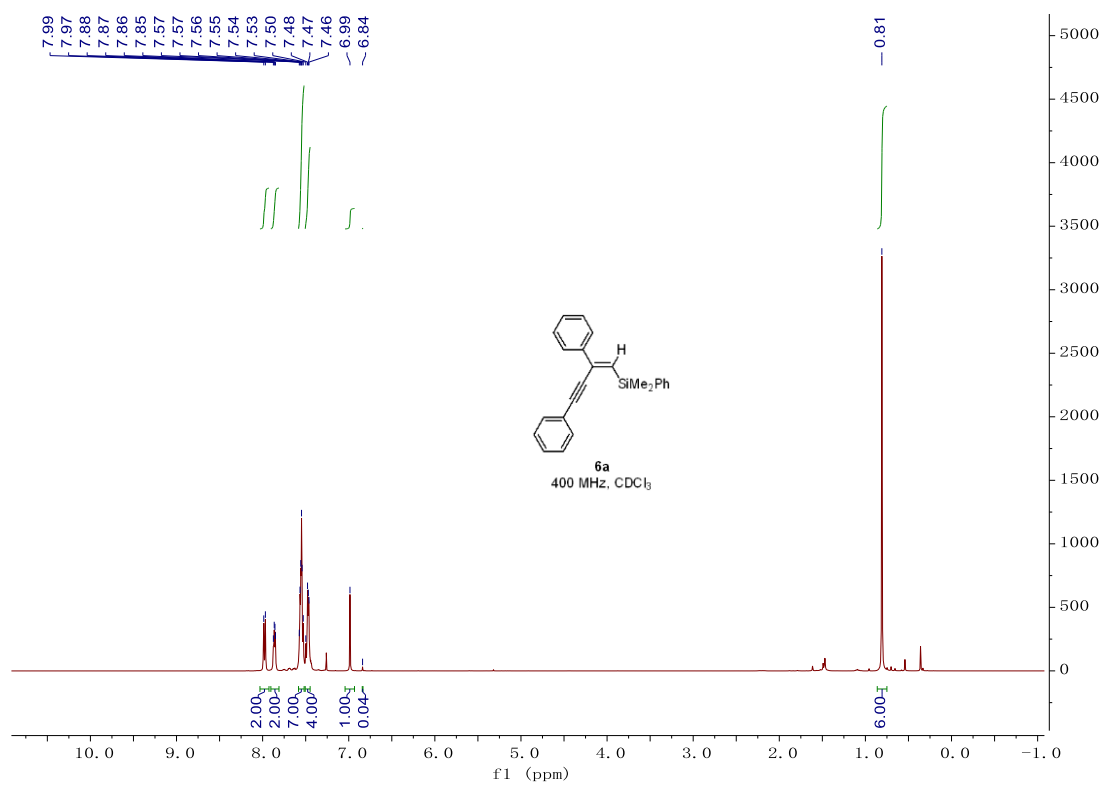
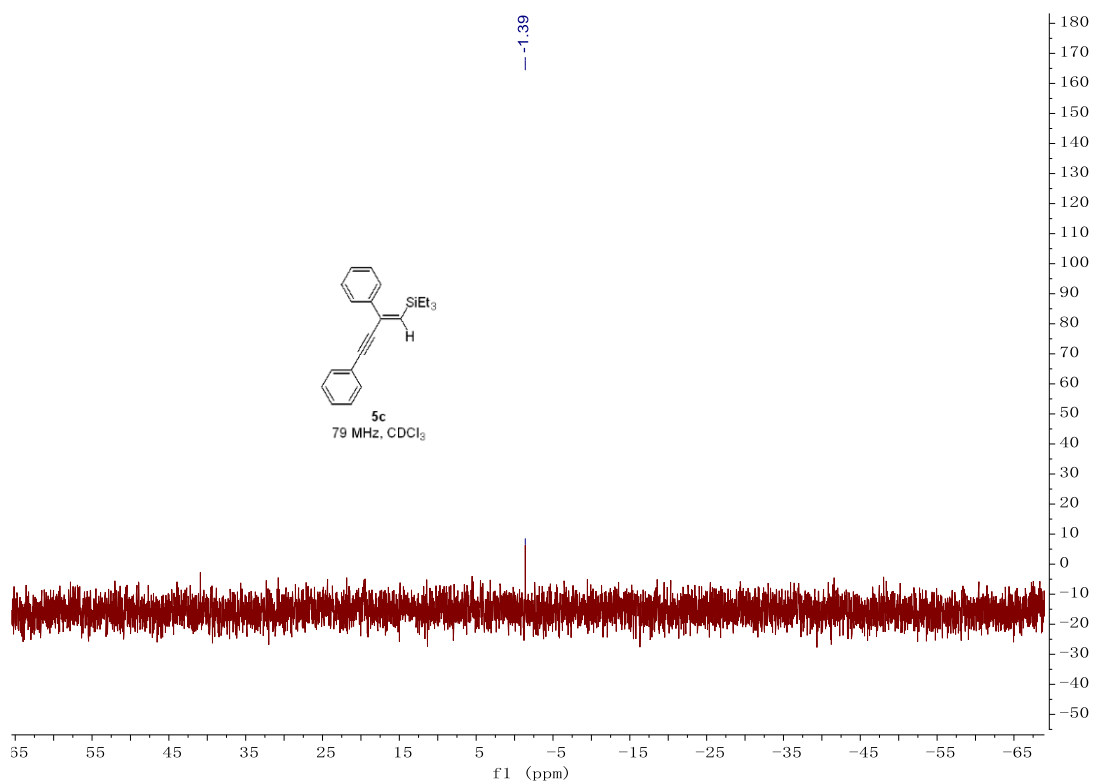


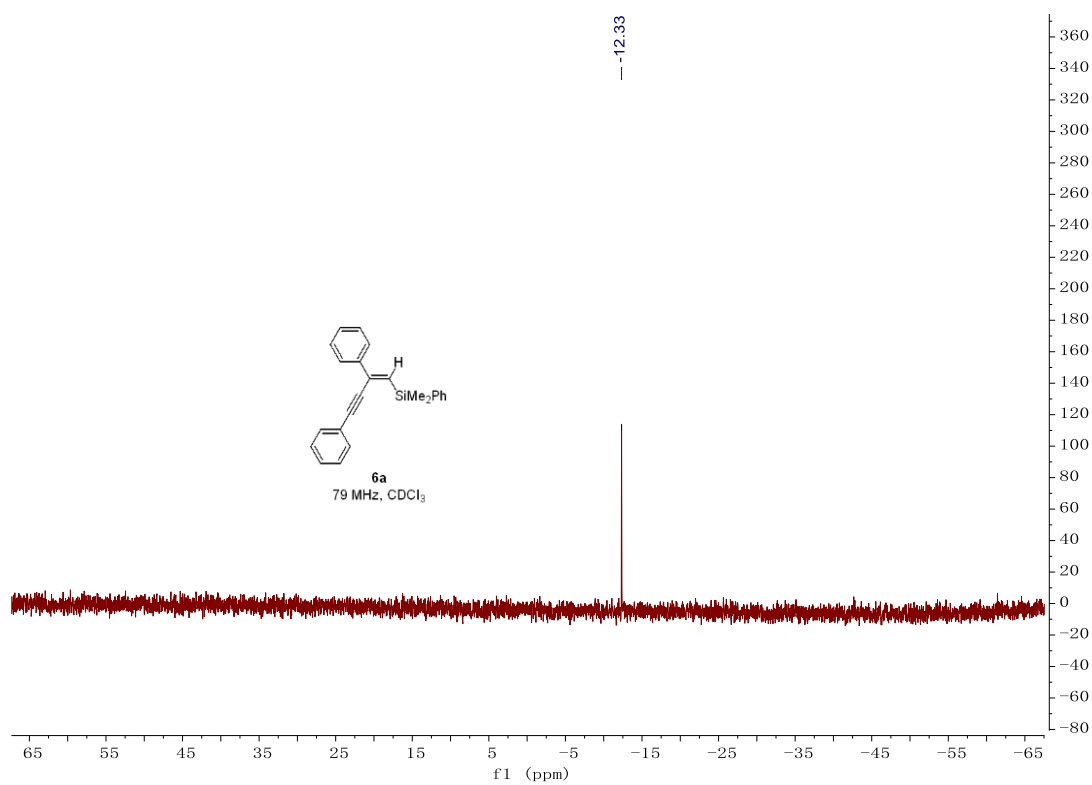
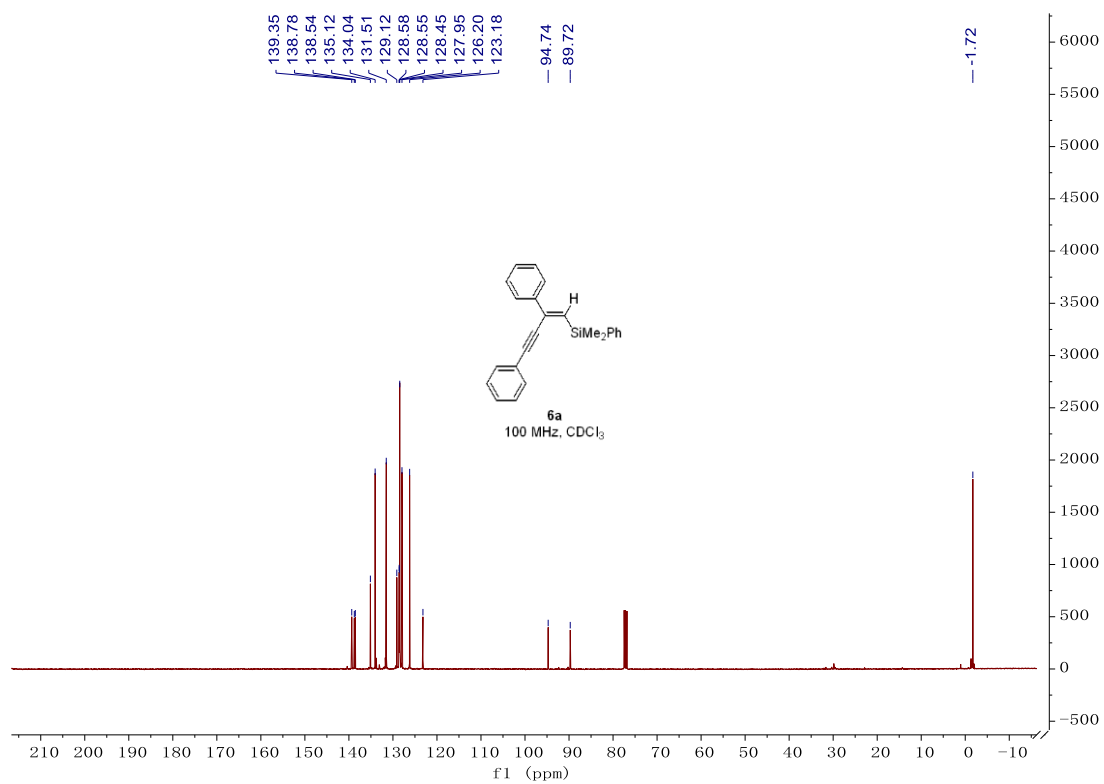


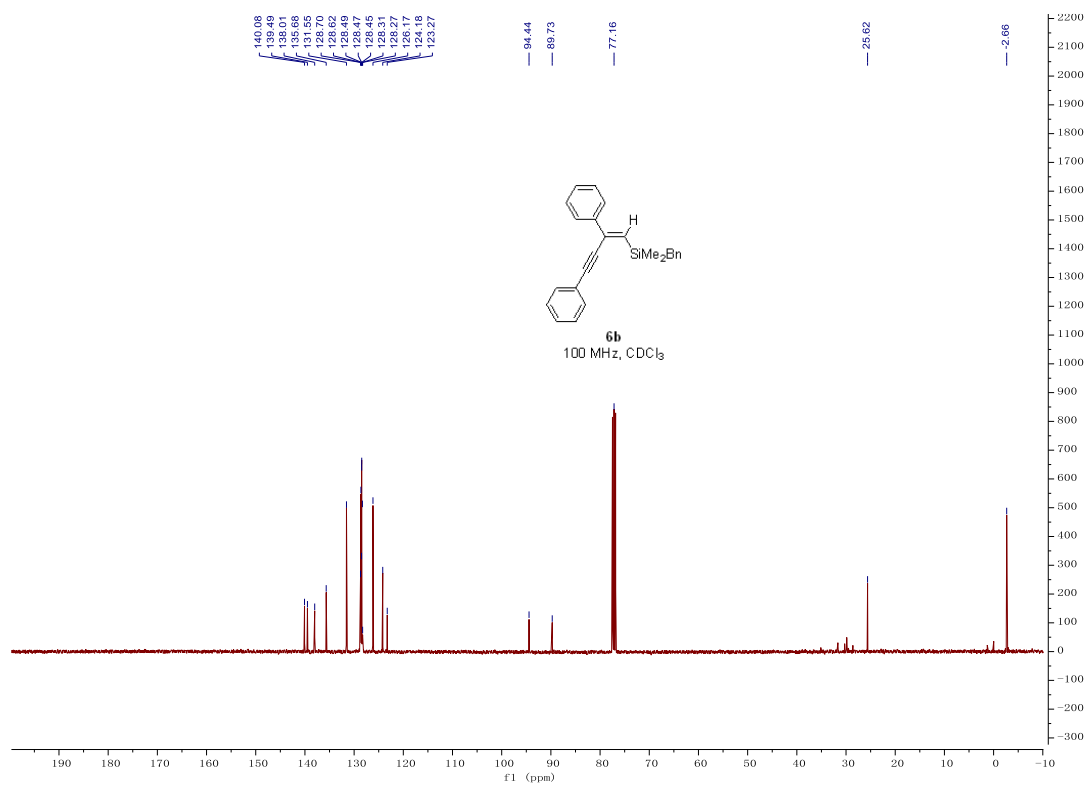
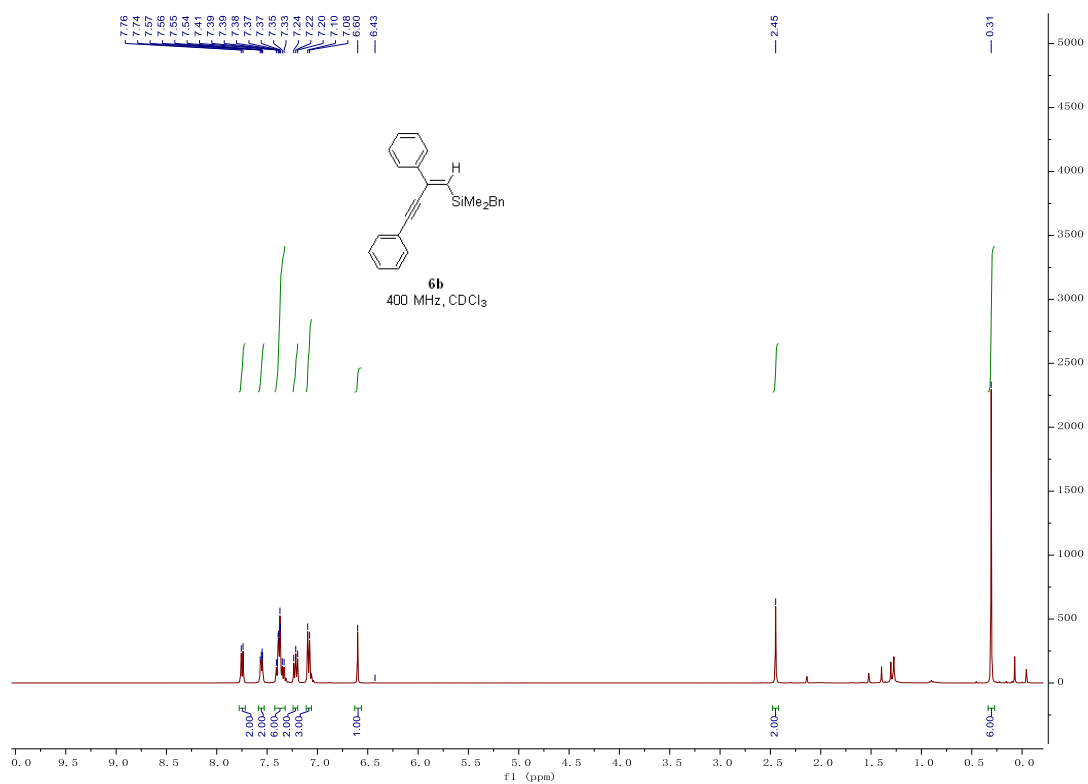


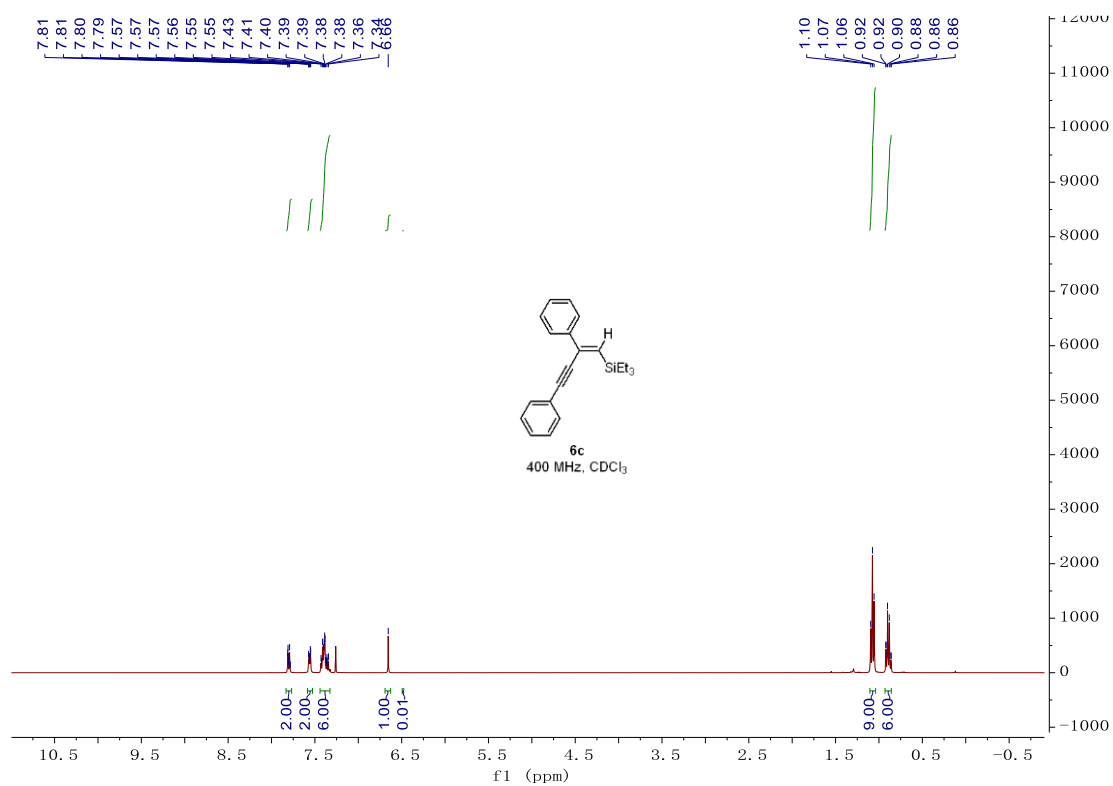
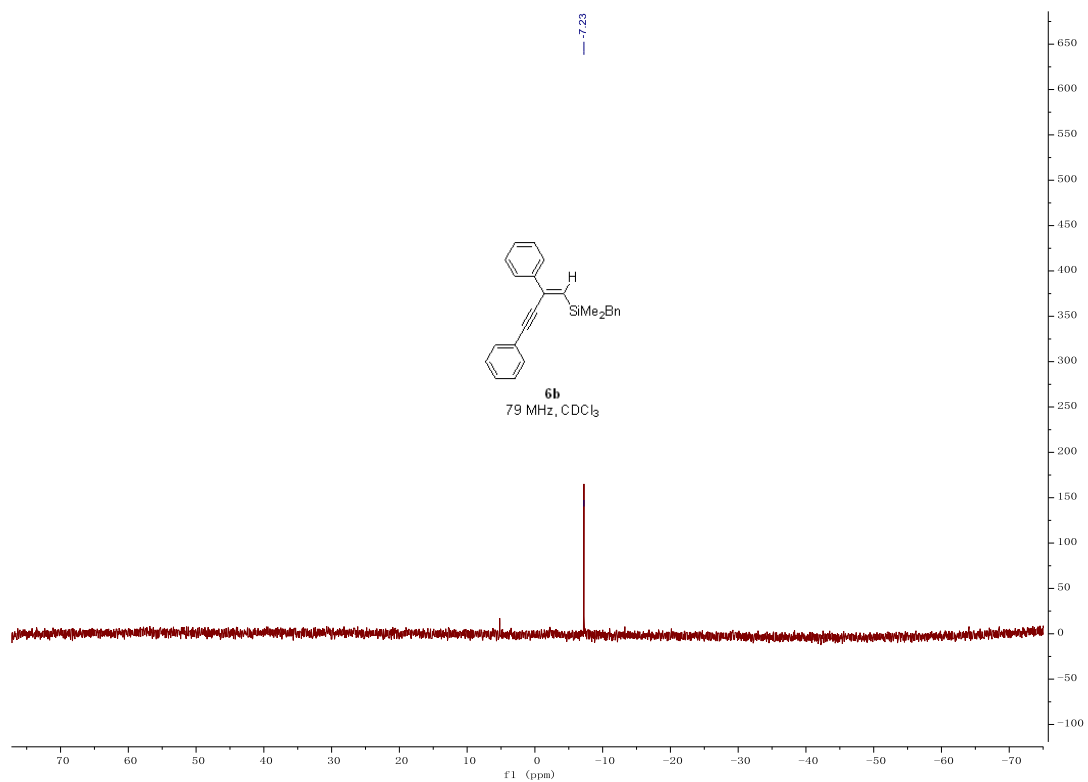


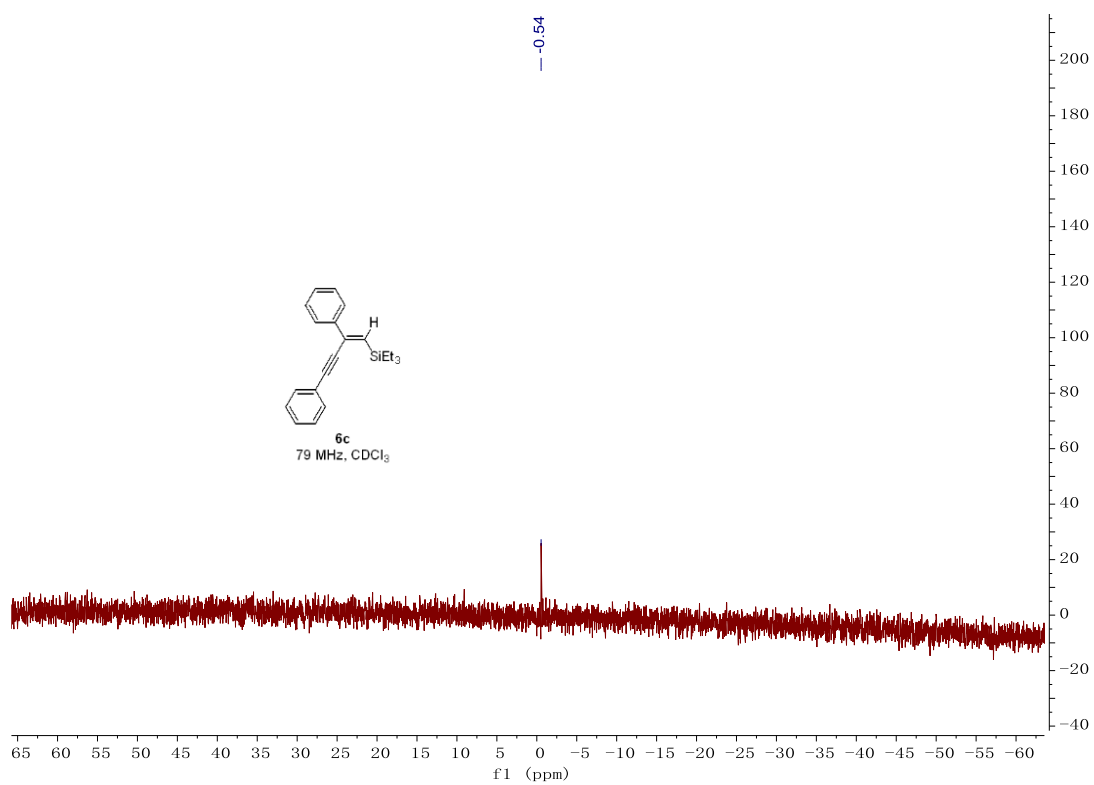
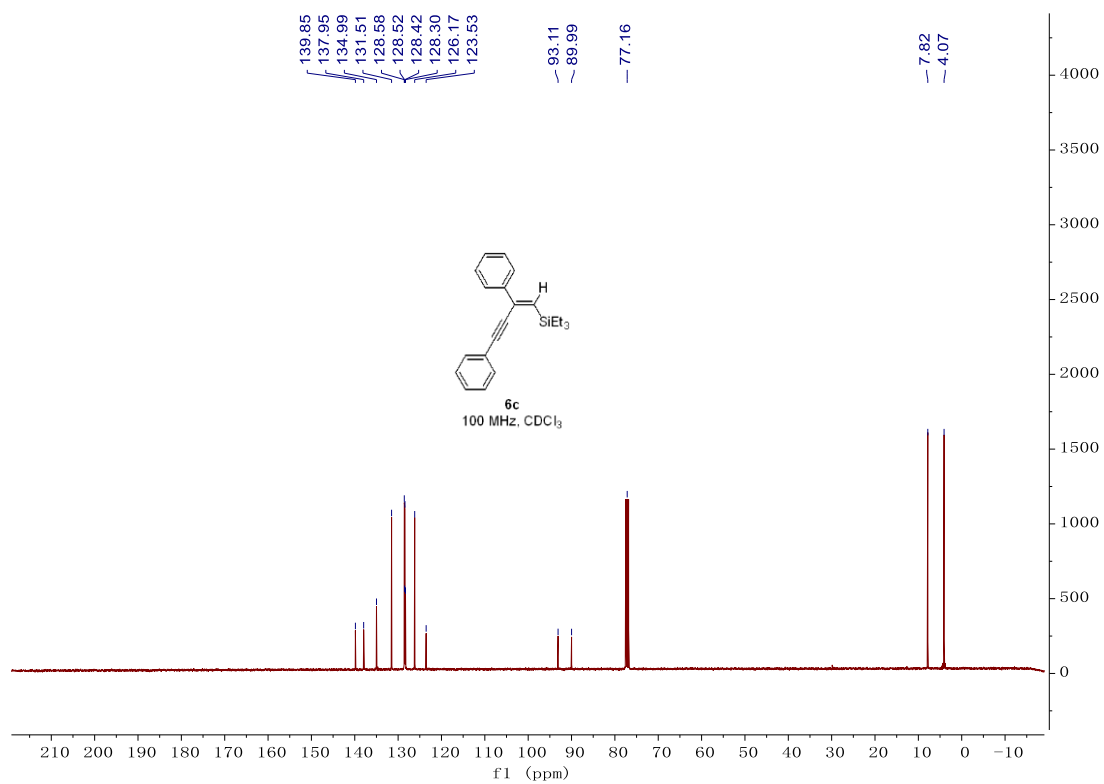


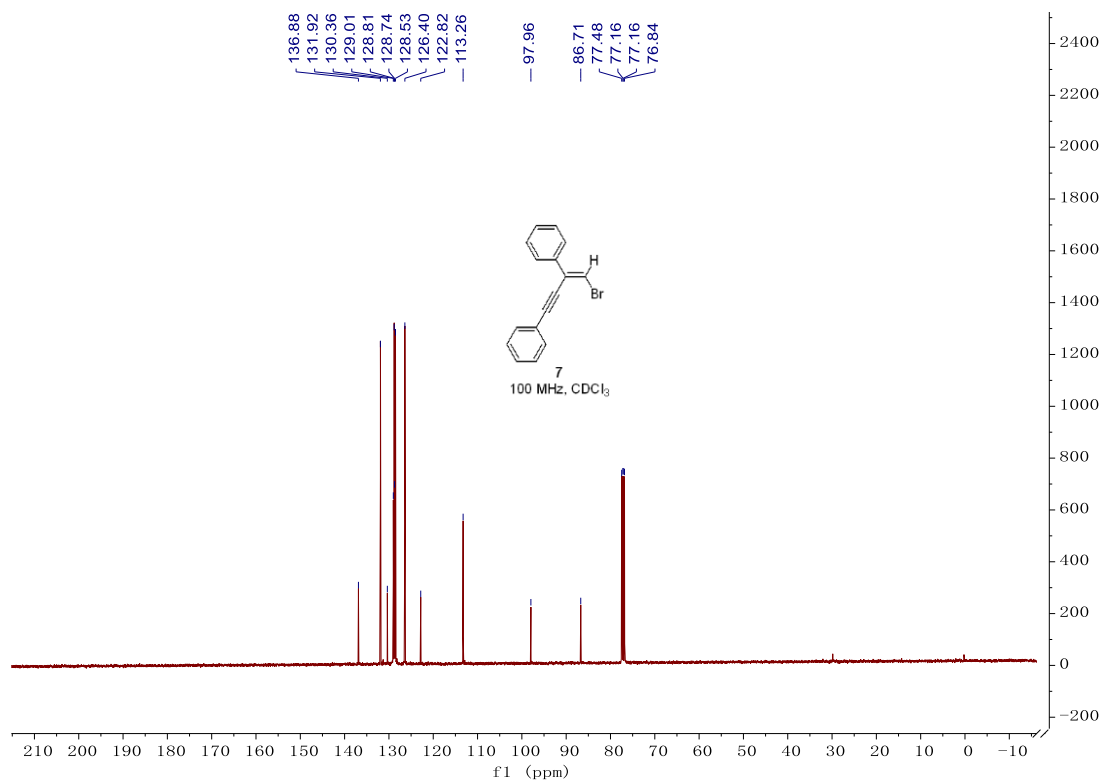
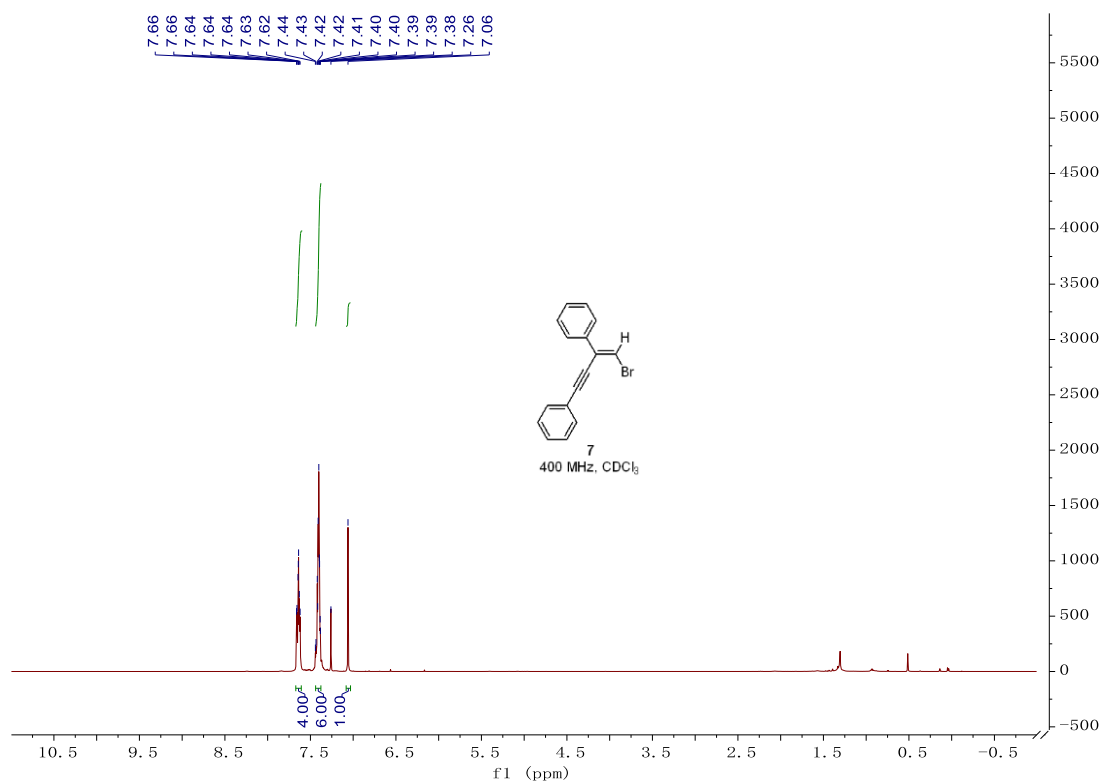


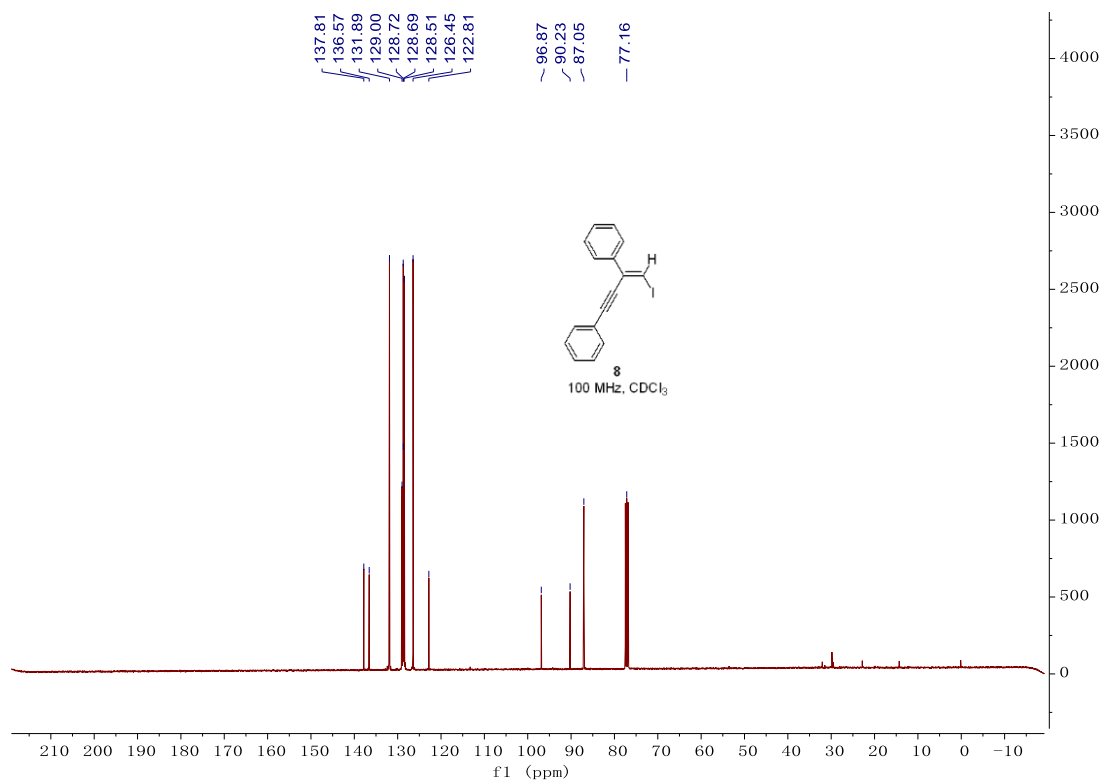
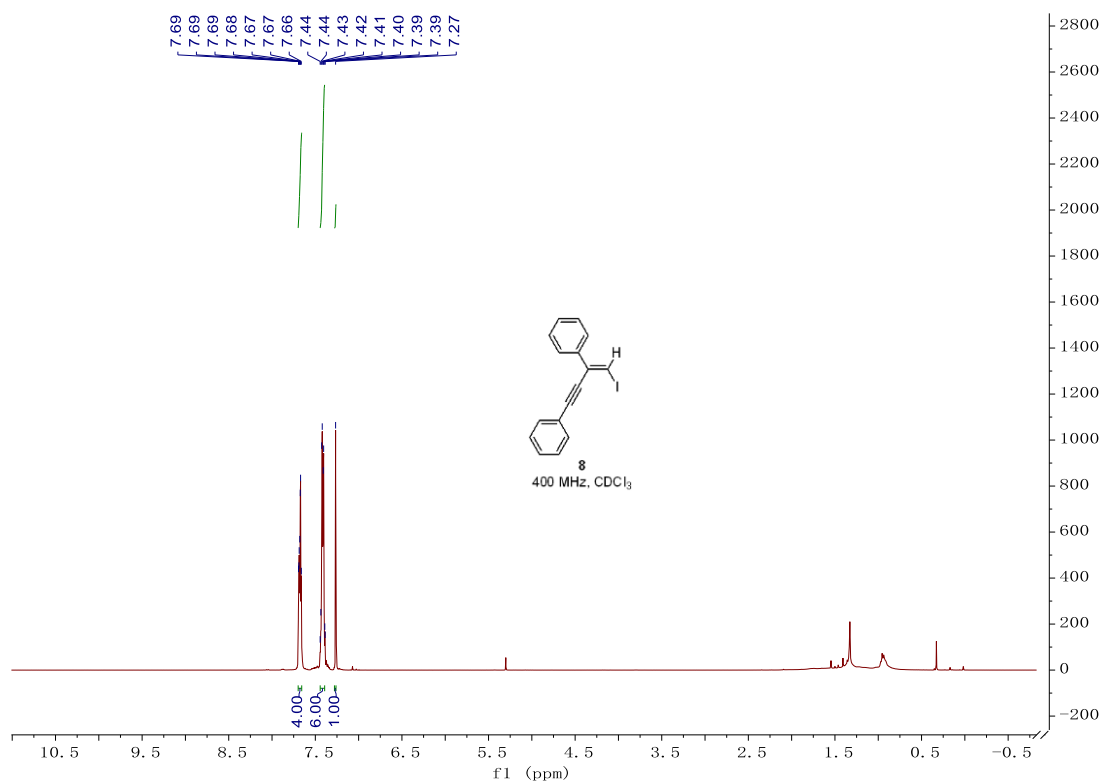












Crystallographic data for 3m (CCDC 2131880)

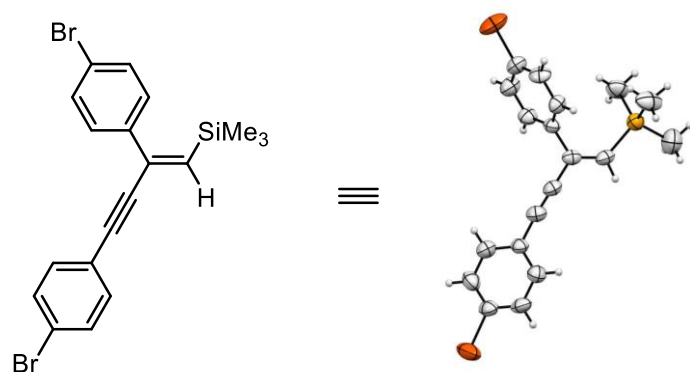


Table S3 Crystal data and structure refinement for mo211211a_pl.

Identification code	mo211211a_pl
Empirical formula	C ₁₉ H ₁₈ Br ₂ Si
Formula weight	434.24
Temperature/K	296.15
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	6.1450(14)
b/Å	15.369(4)
c/Å	20.888(5)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1972.7(8)
Z	4
ρ _{calc} /cm ³	1.462
μ/mm ⁻¹	4.165
F(000)	864.0
Crystal size/mm ³	0.15 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.29 to 61.052
Index ranges	-8 ≤ h ≤ 8, -21 ≤ k ≤ 21, -28 ≤ l ≤ 27
Reflections collected	21792
Independent reflections	5645 [R _{int} = 0.1323, R _{sigma} = 0.1309]
Data/restraints/parameters	5645/0/203
Goodness-of-fit on F ²	0.962
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0549, wR ₂ = 0.1061
Final R indexes [all data]	R ₁ = 0.1665, wR ₂ = 0.1363
Largest diff. peak/hole / e Å ⁻³	0.60/-0.46
Flack parameter	-0.011(18)

Crystallographic data for 4m (CCDC 2141725)

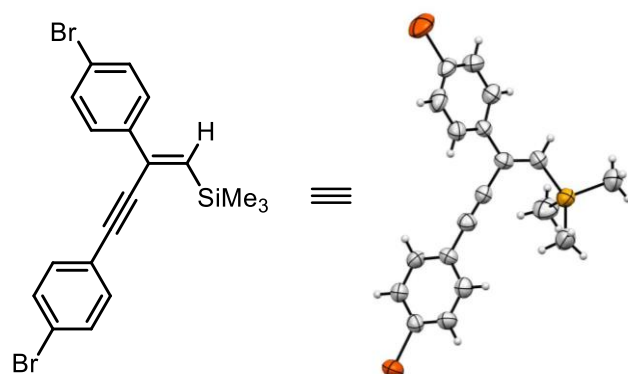


Table S4 Crystal data and structure refinement for mo211215a.

Identification code	mo211215a
Empirical formula	C ₁₉ H ₁₈ Br ₂ Si
Formula weight	434.24
Temperature/K	296.15
Crystal system	monoclinic
Space group	C2/c
a/Å	28.886(8)
b/Å	6.1944(12)
c/Å	22.938(6)
α /°	90
β /°	111.585(9)
γ /°	90
Volume/Å ³	3816.4(16)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.512
μ/mm^{-1}	4.306
F(000)	1728.0
Crystal size/mm ³	0.15 × 0.15 × 0.12
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.82 to 61.052
Index ranges	-41 ≤ h ≤ 40, -8 ≤ k ≤ 8, -27 ≤ l ≤ 32
Reflections collected	17550
Independent reflections	5243 [R _{int} = 0.0902, R _{sigma} = 0.1131]
Data/restraints/parameters	5243/0/202
Goodness-of-fit on F ²	0.973
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0546, wR ₂ = 0.0950
Final R indexes [all data]	R ₁ = 0.1907, wR ₂ = 0.1268
Largest diff. peak/hole / e Å ⁻³	0.37/-0.55