Electronic supplementary information

Synthesis of 1,4-enynes via nickel-catalyzed cross-coupling of allylic alcohols with alkynylzinc reagents

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1. General information

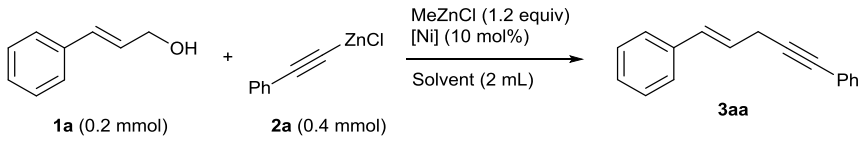
All reactions were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. All chemicals were purchased as reagent grade and used without further purification unless otherwise noted. Toluene and THF were purified by JC Meyer Phoenix Solvent Systems. DME, *n*Bu_2O, and 1,4-dioxane were distilled under nitrogen over sodium and degassed prior to use. DMF, DMA, and NMP was dried over 4 Å molecular sieves, fractionally distilled under reduced pressure, and stored under a nitrogen atmosphere. $ZnCl_2$ and LiCl were purchased from commercial vendors and dried under vacuum at 140 ℃ for 12 h prior to use. MeMgCl was purchased from commercial vendors and used as received. MeZnCl was prepared via reaction of $ZnCl_2$ with 1.0 equiv of MeMgCl in the presence of 2.0 equiv of LiCl. Concentration of MeZnCl was titrated using Knochel's method.[1] Allyl alcohols were prepared according to literature methods.[2] NMR spectra were recorded on a Bruker av400 or Bruker av500 spectrometer at 25 ℃. The chemical shifts of the ^1H NMR spectra were referenced to TMS, and the chemical shifts of the ^{13}C NMR spectra were referenced to internal solvent resonance. The chemical shifts of the ^{19}F NMR spectra were referenced to external CF_3COOH. High-resolution mass spectra (HRMS) were acquired on a Thermo Fisher LTQ Orbitrap XL mass spectrometer.

2. Preparation of alkynylzinc reagents

To a stirred solution of terminal alkyne (5 mmol) in THF (5 mL) was added dropwise *n*BuLi (2.5 M solution in hexane, 2.1 mL, 5.25 mmol) at −78 ℃. After the mixture was stirred for 1 h at −78 °C, dried $ZnCl_2$ (715.5 mg, 5.25 mmol) in THF (5 mL) was added. The cooling bath was removed after 15 min, and the resulting mixture was slowly warmed to room temperature with stirring. The concentration of the resulting alkynylzinc solution was titrated using Knochel's method.[1]

3. Optimization of reaction conditions

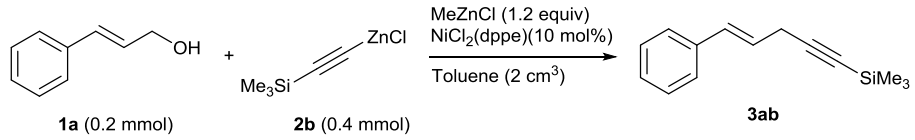
Table S1. Optimization of reaction conditions employing (*E*)-3-phenylprop-2-en-1-ol and PhC≡CZnCl as the model substrates[a]



Entry	[Ni]	Solvent	Temp. (℃)	Time (h)	Yield (%)[b]
1	$NiCl_2(PMe_3)_2$	toluene	120	16	–
2[c]	$Ni(OTf)_2$	toluene	120	16	25
3[c]	$NiBr_2$	toluene	120	16	54
4	$NiBr_2$(glyme)	toluene	120	16	–
5	$NiCl_2(PCy_3)_2$	toluene	120	16	–
6	$NiCl_2(PPh_3)_2$	toluene	120	16	–
7	$NiCl_2$(dppe)	toluene	120	16	63
8	$NiCl_2$(dppf)	toluene	120	16	48
9	$NiCl_2$(dppe)	toluene	120	24	74
10	$NiCl_2$(dppe)	toluene	120	34	76
11	$NiCl_2$(dppe)	toluene	110	24	88[d]
12	$NiCl_2$(dppe)	toluene	100	24	82
13	$NiCl_2$(dppe)	*n*Bu_2O	110	24	66
14	$NiCl_2$(dppe)	toluene/*n*Bu_2O (3/1)	110	24	82
15	$NiCl_2$(dppe)	dioxane	110	24	36
16	$NiCl_2$(dppe)	DME	110	24	<5
17	$NiCl_2$(dppe)	NMP	110	24	–
18[e]	$NiCl_2$(dppe)	toluene	110	24	70

[a] Unless otherwise specified, the reactions were carried out according to the conditions indicated by the above equation. [b] NMR yield, determined by ^{1}H NMR spectra using $C_2H_2Cl_4$ as an internal standard. [c] 10 mol% of dppe was employed. [d] Isolated yields. [e] 5 mol% of $NiCl_2$(dppe) was used.

Table S2. Optimization of reaction conditions employing (*E*)-3-phenylprop-2-en-1-ol and $Me_3SiC{\equiv}CZnCl$ as the model substrates[a]



1a (0.2 mmol) **2b** (0.4 mmol) **3ab**

Entry	Temp. (℃)	Time (h)	Yield (%)[b]
1	110	24	99
2[c]	110	16	90[d]
3[e]	110	24	53[d]
4[f]	110	24	99
5[f]	100	24	99
6[f]	90	24	96
7[f]	100	18	97

[a] Unless otherwise specified, the reactions were carried out according to the conditions indicated by the above equation. [b] Isolated yields. [c] 5 mol% of $NiCl_2$(dppe) was used. [d] NMR yield, determined by ^{1}H NMR spectra using $C_2H_2Cl_4$ as an internal standard. [e] No MeZnCl was used. [f] 0.3 mmol of alkynylzinc reagent was employed.

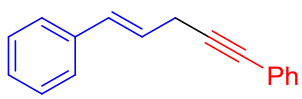
4. General procedure for the catalytic coupling

(1) ArC≡CZnCl was used as the nucleophile: $NiCl_2$(dppe) (10.6 mg, 10 mol%) and allyl alcohol (0.5 mL, 0.4 M solution in THF, 0.2 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeZnCl (0.42 mL, 0.57 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of ArC≡CZnCl (1 mL, 0.4 M solution in THF, 0.4 mmol) was added. The mixture was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (2 mL) was added. The resulting mixture was heated at 110 ℃ (oil bath temperature) for 24 h and then cooled to room temperature. A 20% aqueous solution of NH_4Cl (10 mL) was added. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel).

(2) Me_3SiC≡CZnCl was used as the nucleophile: $NiCl_2$(dppe) (10.6 mg, 10 mol%) and allyl alcohol (0.5 mL, 0.4 M in THF, 0.2 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeZnCl (0.42 mL, 0.57 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of Me_3SiC≡CZnCl (0.65 mL, 0.46 M solution in THF, 0.3mmol) was added. The resulting solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (2 mL) was added. The reaction mixture was heated at 100 ℃ (oil bath temperature) for 24 h and then cooled to room temperature. A 20% aqueous solution of NH_4Cl (10 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel).

5. Characterization data

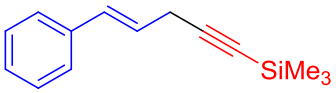
(*E*)-pent-1-en-4-yne-1,5-diyldibenzene (**3aa**)[3]



Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 38.4 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.42 (m, 2H), 7.41–7.36 (m, 2H), 7.34–7.27 (m, 5H), 7.25–7.19 (m, 1H), 6.71 (dt, *J* = 15.7, 1.6 Hz, 1H), 6.25 (dt, *J* = 15.7, 5.7 Hz, 1H), 3.36 (dd, *J* = 5.6, 1.8

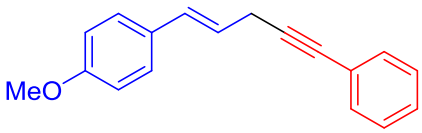
Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.22, 131.77, 131.55, 128.67, 128.39, 127.97, 127.48, 126.41, 124.38, 123.77, 86.87, 83.00, 23.15.

(*E*)-trimethyl(5-phenylpent-4-en-1-yn-1-yl)silane (**3ab**)[4]



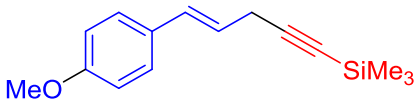
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 42.7 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.35 (m, 2H), 7.35–7.29 (m, 2H),7.28–7.20 (m, 1H), 6.65 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.17 (dt, *J* = 15.7, 5.7 Hz, 1H), 3.19 (dd, *J* = 5.7, 1.9 Hz, 2H), 0.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.22, 131.58, 128.65, 127.47, 126.40, 124.12, 103.76, 87.23, 23.60, 0.25.

(*E*)-1-methoxy-4-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3ba**)[4]



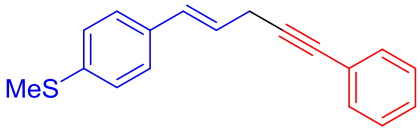
Eluent: EtOAc/petroleum ether 1/60 (v/v), light yellow oil, yield 43.2 mg (87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.41 (m, 2H), 7.35–7.26 (m, 5H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.64 (dt, *J* = 15.6, 1.9 Hz, 1H), 6.11 (dt, *J* = 15.7, 5.7 Hz, 1H), 3.80 (s, 3H), 3.34 (dd, *J* = 5.7, 1.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.14, 131.76, 130.92, 130.04, 128.37, 127.92, 127.54, 123.83, 122.15, 114.07, 87.17, 82.82, 55.41, 23.10.

(*E*)-(5-(4-methoxyphenyl)pent-4-en-1-yn-1-yl)trimethylsilane (**3bb**)[4]



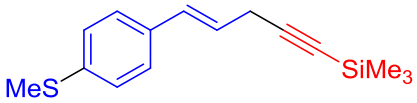
Eluent: EtOAc/petroleum ether 1/60 (v/v), light yellow oil, yield 48.5 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d,*J* = 8.7 Hz, 2H), 6.84 (d,*J* = 8.7 Hz, 2H), 6.56 (dt, *J* = 15.8, 1.8 Hz, 1H), 6.01 (dt, *J* = 15.7, 5.7 Hz, 1H), 3.80 (s, 3H), 3.15 (dd, *J* = 5.7, 1.8 Hz, 2H), 0.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.12, 130.92, 130.01, 127.51, 121.88, 114.04, 104.07, 86.97, 55.39, 23.55, 0.26.

(*E*)-methyl(4-(5-phenylpent-1-en-4-yn-1-yl)phenyl)sulfane (**3ca**)



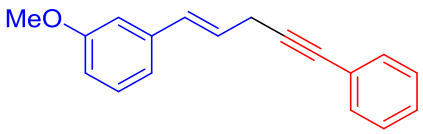
Eluent: EtOAc/petroleum ether 1/150 (v/v), light yellow oil, yield 41.2 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.43 (m, 2H), 7.33–7.27 (m, 5H), 7.20 (d, *J* =8.4 Hz, 2H), 6.66 (dt, *J* = 15.7, 1.8 Hz, 1H), 6.20 (dt, *J* = 15.7, 5.7 Hz, 1H), 3.36 (dd, *J* = 5.7, 1.8 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.50, 134.22, 131.76, 130.90, 128.39, 127.97, 126.82, 123.83, 123.74, 86.84, 83.02, 23.13, 16.02. HRMS (ESI): m/z 265.1056 $[M+H]^+$, calcd. for $C_{18}H_{17}S$ 265.1051.

(*E*)-trimethyl(5-(4-(methylthio)phenyl)pent-4-en-1-yn-1-yl)silane (**3cb**)



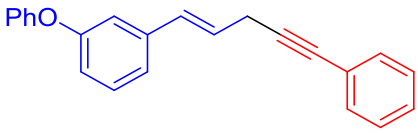
Eluent: EtOAc/petroleum ether 1/120 (v/v), yellow oil, yield 51.6 mg (99%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (d, *J* = 6.7 Hz, 2H), 7.19 (d, *J* = 6.7 Hz, 2H), 6.57 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.11 (dt, *J* = 15.7, 5.7 Hz, 1H), 3.16 (dd, *J* = 5.7, 1.8 Hz, 2H), 2.47 (s, 3H), 0.19 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.49, 134.21, 130.91, 126.82, 126.80, 123.57, 103.71, 87.23, 23.57, 16.02, 0.24. HRMS (ESI): m/z 283.0947 $[M+Na]^+$, calcd. for $C_{15}H_{20}NaSSi$ 283.0953.

(*E*)-1-methoxy-3-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3d**)



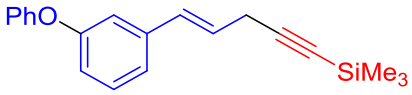
Eluent: EtOAc/petroleum ether 1/60 (v/v), light yellow oil, yield 42.3 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.41 (m, 2H), 7.35–7.26 (m, 5H), 6.85 (dt, *J* = 8.8 Hz,2H), 6.64 (dt, *J* = 15.7, 1.8 Hz, 1H), 6.10 (dt, *J* = 15.7, 5.7 Hz, 1H), 3.80 (s, 3H), 3.34 (dd, *J* = 5.7, 1.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.16, 131.77, 130.94, 130.06, 128.38, 127.92, 127.55, 123.85, 122.16, 114.09, 87.18, 82.83, 55.42, 23.10. HRMS (ESI): m/z 249.1296 $[M+H]^+$, calcd. for $C_{18}H_{17}O$ 249.1279.

(*E*)-1-phenoxy-3-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3ea**)



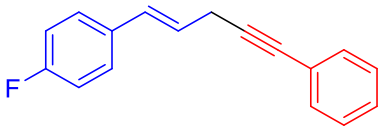
Eluent: EtOAc/petroleum ether 1/60 (v/v), light yellow oil, yield 51.4 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.40 (m, 2H), 7.37–7.23 (m, 6H), 7.16–7.07 (m, 2H), 7.05 (t, *J* = 1.9 Hz, 1H), 7.03–6.98 (m, 2H), 6.91–6.85 (m, 1H), 6.67 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.22 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.34 (dd, *J* = 5.6, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.57, 157.40, 139.17, 131.78, 131.01, 129.95, 129.89, 128.39, 128.00, 125.27, 123.70, 123.33, 121.60, 118.94, 118.07, 116.76, 86.62, 83.12, 23.10. HRMS (ESI): m/z 311.1455 $[M+H]^+$, calcd. for $C_{23}H_{19}O$ 311.1436.

(*E*)-trimethyl(5-(3-phenoxyphenyl)pent-4-en-1-yn-1-yl)silane (**3eb**)



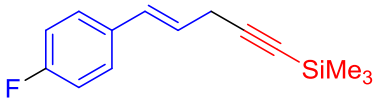
Eluent: EtOAc/petroleum ether 1/60 (v/v), light yellow oil, yield 55.6 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.29 (m, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.13–7.06 (m, 2H), 7.05–6.97 (m, 3H), 6.90–6.83 (m, 1H), 6.59 (dt, *J* = 15.8, 1.9 Hz, 1H), 6.12 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.15 (dd, *J* = 5.6, 1.9 Hz, 2H), 0.18 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.52, 157.39, 139.16, 131.02, 129.92, 129.87, 125.01, 123.32, 121.60, 118.90, 118.02, 116.77, 103.49, 87.38, 23.55, 0.24. HRMS (ESI): m/z 329.1358 $[M+Na]^+$, calcd. for $C_{20}H_{22}NaOSi$ 329.1338.

(*E*)-1-fluoro-4-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3fa**)[5]



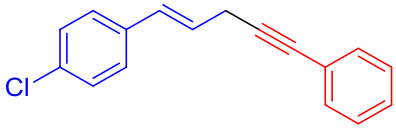
Eluent: EtOAc/petroleum ether 1/200 (v/v), colorless oil, yield 36.8 mg (78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.42 (m, 2H), 7.37–7.27 (m, 5H), 6.99 (t, *J* = 8.8 Hz,2H), 6.67 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.16 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.34 (dd, *J* = 5.6, 1.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.32 (d, *J* = 246.3 Hz), 133.39 (d, *J* = 3.6 Hz), 131.77, 130.41, 128.40, 128.01, 127.88 (d, *J* = 8.2 Hz), 124.14 (d, *J* = 2.2 Hz), 123.73, 115.50 (d, *J* = 22.0 Hz), 86.73, 83.08, 23.08. ^{19}F NMR (471 MHz, $CDCl_3$): δ –114.91.

(*E*)-(5-(4-fluorophenyl)pent-4-en-1-yn-1-yl)trimethylsilane (**3fb**)



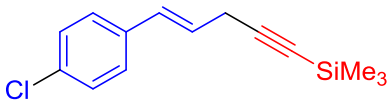
Eluent: EtOAc/petroleum ether 1/120 (v/v), colorless oil, yield 46.1 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.28 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 1H,2H), 6.59 (dt, *J* = 15.8, 1.8 Hz, 1H), 6.07 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.16 (dd, *J* = 5.7, 1.9 Hz, 2H), 0.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.29 (d, *J* = 246.4 Hz), 133.35 (d, *J* = 3.4 Hz), 130.41, 127.86 (d, *J* = 8.0 Hz), 123.85 (d, *J* = 2.3 Hz), 115.53 (d, *J* = 21.6 Hz), 103.59, 87.34, 23.53, 0.24. ^{19}F NMR (471 MHz, $CDCl_3$): δ–114.92. HRMS (ESI): m/z 233.1151 $[M+H]^+$, calcd. for $C_{14}H_{18}FSi$ 233.1162.

(*E*)-1-chloro-4-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3ga**)[4]



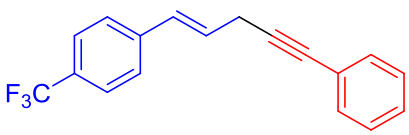
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 26.7 mg (53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.41 (m, 2H), 7.34–7.27 (m, 6H), 6.66 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.22 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.35 (dd, *J* = 5.6, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.72, 133.07, 131.76, 130.38, 128.81, 128.41, 128.04, 127.62, 125.10, 123.66, 86.53, 83.20, 23.11.

(*E*)-(5-(4-chlorophenyl)pent-4-en-1-yn-1-yl)trimethylsilane (**3gb**)



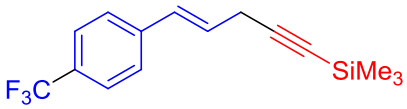
Eluent: EtOAc/petroleum ether 1/120 (v/v), light yellow oil, yield 46.7 mg (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (s, 4H), 6.58 (dt, *J* = 15.7, 1.8 Hz, 1H), 6.13 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.17 (dd, *J* = 5.6, 1.8 Hz, 2H), 0.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.69, 133.05, 130.39, 128.79, 127.61, 124.83, 103.37, 87.49, 23.57, 0.24. HRMS (ESI): m/z 249.0884 $[M+H]^+$, calcd. for $C_{14}H_{18}ClSi$ 249.0866.

(*E*)-1-(5-phenylpent-1-en-4-yn-1-yl)-4-(trifluoromethyl)benzene (**3ha**)



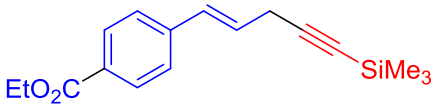
Eluent: EtOAc/petroleum ether 1/200 (v/v), colorless oil, yield 48.1 mg (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.51–7.41 (m, 4H), 7.36–7.27 (m, 3H), 6.75 (d, *J* = 15.8 Hz, 1H), 6.35 (dt, *J* = 15.7, 5.5 Hz, 1H), 3.39 (dd, *J* = 5.6, 1.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.70, 131.79, 130.37, 129.32 (q, *J* = 32.5 Hz), 128.44, 128.12, 127.22, 126.58, 125.65 (q, *J* = 3.8 Hz), 124.37 (q, *J* = 271.4 Hz), 123.60, 86.18, 83.44, 23.19. ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.44. HRMS (ESI): m/z 287.1060 $[M+H]^+$, calcd. for $C_{18}H_{14}F_3$ 287.1048.

(*E*)-trimethyl(5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yn-1-yl)silane (**3hb**)



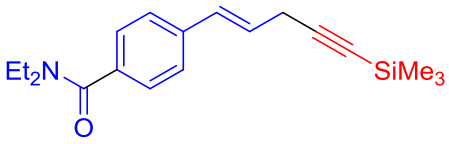
Eluent: EtOAc/petroleum ether 1/120 (v/v), yellow oil, yield 51.7 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 6.68 (d, *J* = 15.8Hz, 1H), 6.26 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.21 (dd, *J* = 5.6, 1.9 Hz, 2H), 0.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.66, 130.37,129.29 (q, *J* = 32.4 Hz), 126.94, 126.56, 125.62 (q, *J* = 3.8 Hz), 124.36 (q, *J* = 271.8 Hz), 103.00, 87.81, 23.64, 0.22. ^{19}F NMR (471 MHz, $CDCl_3$): δ –62.43. HRMS (ESI): m/z 305.0945 $[M+Na]^+$, calcd. for $C_{15}H_{17}F_3NaSi$ 305.0949.

ethyl (*E*)-4-(5-(trimethylsilyl)pent-1-en-4-yn-1-yl)benzoate (**3i**)



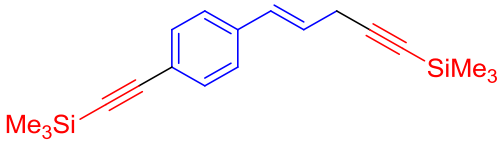
Eluent: EtOAc/petroleum ether 1/10 (v/v), light yellow oil, yield 40.3 mg (70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 15.7 Hz, 1H), 6.29 (dt, *J* = 15.7, 5.6 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.21 (dd, *J* = 5.6, 1.9 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.20 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.57, 141.55, 130.80, 129.99, 129.26, 126.84, 126.23, 103.07, 87.71, 61.03, 23.68, 14.48, 0.22. HRMS (ESI): m/z 309.1300 $[M+Na]^+$, calcd. for $C_{17}H_{22}NaO_2Si$ 309.1287.

(*E*)-N,N-diethyl-4-(5-(trimethylsilyl)pent-1-en-4-yn-1-yl)benzamide (**3j**)



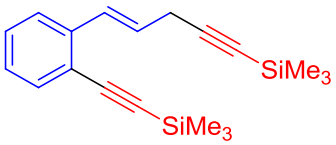
Eluent: EtOAc/petroleum ether 1/3 (v/v), light yellow oil, yield 40.3 mg (64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 5.6 Hz, 1H), 3.54 (b, 2H), 3.26 (b, 2H), 3.19 (dd, *J* = 5.7, 1.9 Hz, 2H), 1.24 (b, 3H), 1.11 (b, 3H), 0.20 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.20, 138.02, 136.13, 130.85, 126.79, 126.30, 125.26, 103.36, 87.44, 43.38, 39.37, 23.58, 14.35, 13.02, 0.21. HRMS (ESI): m/z 314.1937 $[M+H]^+$, calcd. for $C_{19}H_{28}NOSi$ 314.1940.

(*E*)-trimethyl(5-(4-((trimethylsilyl)ethynyl)phenyl)pent-4-en-1-yn-1-yl)silane (**3k**)



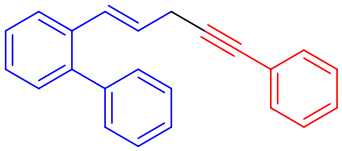
Eluent: EtOAc/petroleum ether 1/120 (v/v), light yellow oil, yield 45.9 mg (74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.60 (d, *J* = 15.7 Hz, 1H), 6.17 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.18 (dd, *J* = 5.7, 1.8 Hz, 2H), 0.25 (s, 9H), 0.19 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.31, 132.29, 130.97, 126.19, 125.23, 121.96, 105.27, 103.36, 94.79, 87.48, 23.63, 0.24, 0.13. HRMS (ESI): m/z 311.1664 $[M+H]^+$, calcd. for $C_{19}H_{27}Si_2$ 311.1651.

(*E*)-trimethyl(5-(2-((trimethylsilyl)ethynyl)phenyl)pent-4-en-1-yn-1-yl)silane (**3l**)



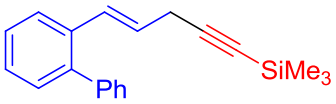
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 56.4mg (91%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.26 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.15 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.02 (d, *J* = 15.7 Hz, 1H), 6.25 (dt, *J* = 15.7, 6.1 Hz, 1H), 3.22 (dd, *J* = 6.1, 1.8 Hz, 2H), 0.27 (s, 9H), 0.18 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ139.01, 133.11, 129.85, 128.76, 127.03, 126.52, 125.38, 121.42, 103.81, 103.71, 99.18, 86.61, 24.04, 0.28, 0.20. HRMS (ESI): m/z 333.1454 $[M+Na]^+$, calcd. for $C_{19}H_{26}NaSi_2$ 333.1471.

(*E*)-2-(5-phenylpent-1-en-4-yn-1-yl)-1,1'-biphenyl (**3ma**)



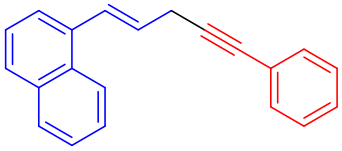
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 52.3 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.59 (m, 1H), 7.43–7.21 (m, 13H), 6.77 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.20 (dt, *J* = 15.7, 5.5 Hz, 1H), 3.28 (dd, *J* = 5.5, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.09, 140.89, 135.10, 131.71, 130.37, 130.33, 129.97, 128.25, 128.19, 127.83, 127.59, 127.39, 127.05, 125.94, 124.82, 123.68, 86.81, 83.14, 23.24. HRMS (ESI): m/z 317.1284 $[M+Na]^+$, calcd. for $C_{23}H_{18}Na$ 317.1306.

(*E*)-(5-([1,1'-biphenyl]-2-yl)pent-4-en-1-yn-1-yl)trimethylsilane (**3mb**)



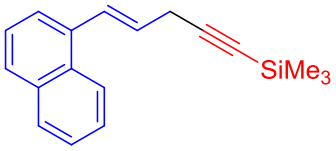
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 57.8 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.62 (m, 1H), 7.53–7.45 (m, 2H), 7.45–7.32 (m, 6H), 6.76 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.17 (dt, *J* = 15.7, 5.4 Hz, 1H), 3.18 (dd, *J* = 5.5, 1.9 Hz, 2H), 0.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.03, 140.82, 135.19, 130.36, 130.32, 129.91, 128.16, 127.54, 127.36, 127.10, 126.04, 124.64, 103.53, 87.29, 23.66, 0.14. HRMS (ESI): m/z 313.1392 $[M+Na]^+$, calcd. for $C_{20}H_{22}NaSi$ 313.1388.

(*E*)-1-(5-phenylpent-1-en-4-yn-1-yl)naphthalene (**3na**)[6]



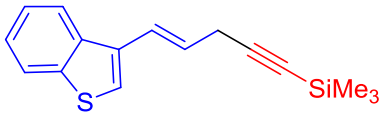
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 41.4 mg (77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19–8.10 (m, 1H), 7.88–7.82 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H),7.55–7.40 (m, 6H), 7.35–7.27 (m, 3H), 6.27 (dt, *J* = 15.4, 5.5 Hz, 1H), 3.48 (dd, *J* = 5.4, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.11, 133.72, 131.79, 131.29, 128.91, 128.61, 128.43, 128.00, 127.88, 127.54, 126.13, 125.88, 125.77, 124.05, 124.02, 123.80, 86.89, 83.29, 23.56.

(*E*)-trimethyl(5-(naphthalen-1-yl)pent-4-en-1-yn-1-yl)silane (**3nb**)



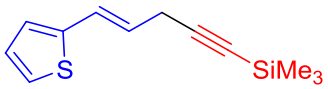
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 52.5 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–8.09 (m, 1H), 7.86–7.81 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 7.0 Hz, 1H), 7.53–7.39 (m, 4H), 6.17 (dt, *J* = 15.5, 5.4 Hz, 1H), 3.28 (dd, *J* = 5.4, 2.0 Hz, 2H), 0.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.02, 133.74, 131.32, 128.88, 128.62, 127.85, 127.11, 126.09, 125.86, 125.76, 123.97, 123.90, 103.80, 87.70, 23.97, 0.28. HRMS (ESI):m/z 287.1227$[M+Na]^+$,calcd. for $C_{18}H_{20}NaSi$ 287.1232.

(*E*)-(5-(benzo[b]thiophen-3-yl)pent-4-en-1-yn-1-yl)trimethylsilane (**3o**)



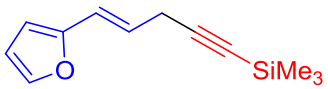
Eluent: EtOAc/petroleum ether 1/100 (v/v), light yellow oil, yield 32.8 mg (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.83 (m, 2H), 7.46–7.32 (m, 3H), 6.94 (d, *J* = 15.7 Hz, 1H), 6.24 (dt, *J* = 15.7, 5.5 Hz, 1H), 3.24 (dd, *J* = 5.5, 1.9 Hz, 2H), 0.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.53, 137.89, 133.87, 125.89, 124.55, 124.35, 123.86, 123.01, 122.02, 121.64, 103.54, 87.65, 23.86, 0.27. HRMS (ESI): m/z 271.0966 $[M+H]^+$, calcd. for $C_{16}H_{19}SSi$ 271.0977.

(*E*)-trimethyl(5-(thiophen-2-yl)pent-4-en-1-yn-1-yl)silane (**3p**)



Eluent: EtOAc/petroleum ether 1/100 (v/v), light yellow oil, yield 40.1mg (91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 (d, *J* = 5.0 Hz, 1H), 6.98–6.91 (m, 2H), 6.76 (d, *J* = 15.5 Hz, 1H), 6.00 (dt, *J* = 15.6, 5.6 Hz, 1H), 3.15 (dd, *J* = 5.6, 1.9 Hz, 2H), 0.19 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.20, 127.40, 125.31, 124.74, 123.98, 123.77, 103.29, 87.46, 23.35, 0.23. HRMS (ESI): m/z 221.0839 $[M+H]^+$, calcd. for $C_{12}H_{17}SSi$ 221.0820.

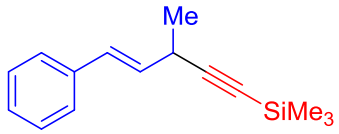
(*E*)-(5-(furan-2-yl)pent-4-en-1-yn-1-yl)trimethylsilane (**3q**)



Eluent: EtOAc/petroleum ether 1/100 (v/v), light yellow oil, yield 20.8 mg (51%). ^{1}H NMR

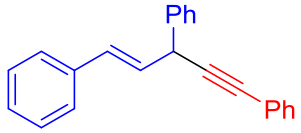
(500 MHz, $CDCl_3$): δ 7.33 (d, *J* = 1.8 Hz, 1H), 6.47 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.36 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.21 (d, *J* = 3.3 Hz, 1H), 6.11 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.16 (dd, *J* = 5.6, 1.9 Hz, 2H), 0.19 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.78, 141.84, 122.83, 120.04, 111.31, 107.34, 103.29, 87.50, 23.29, 0.23. HRMS (ESI): m/z 205.1066 $[M+H]^+$,calcd. for $C_{12}H_{17}OSi$ 205.1049.

(*E*)-trimethyl(3-methyl-5-phenylpent-4-en-1-yn-1-yl)silane (**3r**)[7]



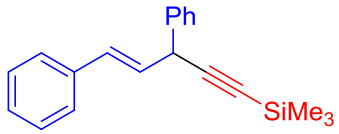
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 44.9 mg (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.34 (m, 2H), 7.30 (t, *J* = 7.6 Hz,2H), 7.21 (tt, *J* = 7.2, 2.2 Hz,1H), 6.61 (dd, *J* = 15.7, 1.6 Hz, 1H), 6.14 (dd, *J* = 15.7, 6.1 Hz, 1H), 3.39–3.30 (m, 1H), 1.35 (d, *J* = 7.1 Hz, 3H), 0.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.29, 131.03, 129.69, 128.65, 127.44, 126.48, 108.77, 86.62, 30.07, 21.82, 0.35.

(*E*)-pent-1-en-4-yne-1,3,5-triyltribenzene (**3sa**)[8]



Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 54.6 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.45 (m, 4H), 7.43–7.35 (m, 4H), 7.34–7.25 (m, 6H), 7.22 (tt, *J* = 7.2, 2.1 Hz, 1H), 6.78 (dd, *J* = 15.6, 1.4 Hz, 1H), 6.35 (dd, *J* = 15.6, 6.5 Hz, 1H), 4.76 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.45, 136.98, 131.86, 130.60, 129.77, 128.86, 128.68, 128.40, 128.17, 127.90, 127.68, 127.25, 126.67, 123.59, 88.96, 85.55, 41.37.

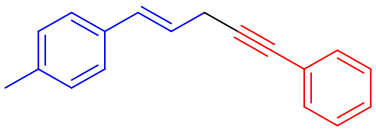
(*E*)-(3,5-diphenylpent-4-en-1-yn-1-yl)trimethylsilane (**3sb**)[8]



Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 52.4 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.39 (m, 2H), 7.39–7.17 (m, 8H), 6.69 (dd, *J* = 15.6, 1.5 Hz, 1H), 6.23 (dd, *J* = 15.6, 6.6 Hz, 1H), 4.55 (dd, *J* = 6.6, 1.5 Hz, 1H), 0.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.09, 136.97, 130.54, 129.67, 128.78, 128.65, 127.83, 127.65, 127.16,

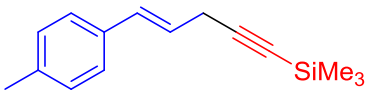
126.65, 105.44, 89.86, 41.73, 0.28.

(*E*)-1-methyl-4-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3ta**)[5]



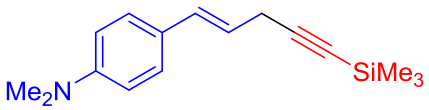
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 36.2 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.40 (m, 2H), 7.35–7.23 (m, 5H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.67 (d, *J* = 15.7 1H), 6.18 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.34 (dd, *J* = 5.7, 1.8 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.23, 134.44, 131.76, 131.38, 129.36, 128.37, 127.92, 126.30, 123.82, 123.30, 87.06, 82.90, 23.12, 21.31.

(*E*)-trimethyl(5-(*p*-tolyl)pent-4-en-1-yn-1-yl)silane (**3tb**)



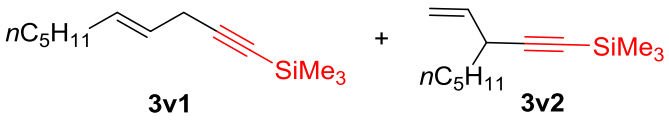
Eluent: EtOAc/petroleum ether 1/200 (v/v), colorless oil, yield 44.8 mg (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.59 (d, *J* = 15.7 Hz, 1H), 6.09 (dt, *J* = 15.7, 5.7 Hz, 1H), 3.16 (dd, *J* = 5.7, 1.8 Hz, 2H), 2.32 (s, 3H), 0.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.22, 134.44, 131.41, 129.34, 126.29, 123.05, 103.96, 87.07, 23.58, 21.31, 0.26. HRMS (ESI):m/z 229.1419$[M+H]^+$, calcd. for $C_{15}H_{21}Si$ 229.1412.

(*E*)-N,N-dimethyl-4-(5-(trimethylsilyl)pent-1-en-4-yn-1-yl)aniline (**3u**)



Eluent: EtOAc/petroleum ether 1/60 (v/v), light yellow oil, yield 48.9 mg (95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 15.7 Hz, 1H), 5.94 (dt, *J* = 15.7, 5.8 Hz, 1H), 3.14 (dd, *J* = 5.8, 1.8 Hz, 2H), 2.95 (s, 6H), 0.19 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.05, 131.32, 127.27, 125.80, 119.71, 112.57, 104.57, 86.62, 40.70, 23.60, 0.28. HRMS (ESI): m/z 258.1676 $[M+H]^+$, calcd. for $C_{16}H_{24}NSi$ 258.1678.

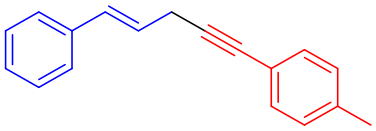
(*E*)-dec-4-en-1-ynyltrimethylsilane (**3v1**) and trimethyl(3-vinyloct-1-ynyl)silane (**3v2**)[9]



3v1 **3v2**

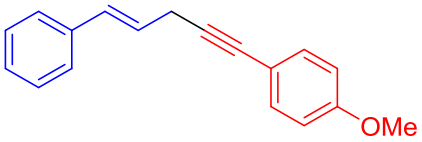
Eluent: petroleum ether, colorless oil, yield 26.9 mg (a mixture of **3v1** and **3v2**, 65% overall yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79–5.71 (m, 0.9H), 5.71–5.63 (m, 1H), 5.42–5.34 (m, 1H), 5.28 (dt, *J* = 17.0, 1.6 Hz, 0.9H), 5.07 (dt, *J* = 10.1, 1.5 Hz, 0.9H), 3.10–3.03 (m, 0.9H), 2.96–2.92 (m, 2H), 2.05–1.98 (m, 2H), 1.54–1.21 (m, 14H), 0.93–0.84 (m, 6H), 0.162 (s, 9H), 0.16 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.08, 132.67, 123.59, 115.07, 107.73, 104.94, 87.46, 86.20, 36.58, 35.34, 32.39, 31.64, 31.55, 29.08, 26.65, 23.24, 22.68, 22.66, 14.21, 14.16, 0.34, 0.28.

(*E*)-1-methyl-4-(5-phenylpent-4-en-1-yn-1-yl)benzene (**3ac**)[3]



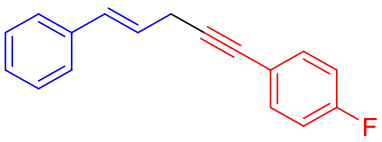
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 45.9 mg (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.26 (m, 6H), 7.25–7.18 (m, 1H), 7.10 (d, *J* = 7.8 Hz,2H), 6.70 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.24 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.35 (dd, *J* = 5.7, 1.9 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.97, 137.26, 131.63, 131.46, 129.14, 128.65, 127.44, 126.40, 124.54, 120.68, 86.05, 83.05, 23.17, 21.56.

(*E*)-1-methoxy-4-(5-phenylpent-4-en-1-yn-1-yl)benzene (**3ad**)[3]



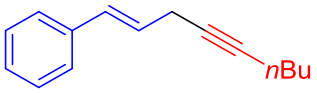
Eluent: EtOAc/petroleum ether 1/60 (v/v), light yellow oil, yield 44.6 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.35 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (tt, *J* = 7.2, 2.4 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.70 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.24 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.79 (s, 3H), 3.34 (dd, *J* = 5.7, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.36, 137.27, 133.11, 131.41, 128.65, 127.43, 126.40, 124.65, 115.90, 113.99, 85.25, 82.75, 55.38, 23.17.

(*E*)-1-fluoro-4-(5-phenylpent-4-en-1-yn-1-yl)benzene (**3ae**)[10]



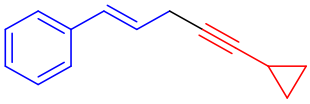
Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 37.6 mg (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.35 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27–7.19 (m, 1H), 6.99 (t, *J* = 8.8 Hz,2H), 6.69 (dt, *J* = 15.6, 1.9 Hz, 1H), 6.24 (dt, *J* = 15.8, 5.7 Hz, 1H), 3.34 (dd, *J* = 5.7, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.37 (d, *J* = 248.4 Hz), 137.17, 133.57 (d, *J* = 8.3 Hz), 131.63, 128.69, 127.54, 126.41, 124.26, 119.84 (d, *J* = 3.4 Hz), 115.61 (d, *J* = 21.9 Hz), 86.55 (d, *J* = 1.5 Hz), 81.90, 23.09. ^{19}F NMR (471 MHz, $CDCl_3$): δ –111.78.

(*E*)-non-1-en-4-yn-1-ylbenzene (**3af**)[8]



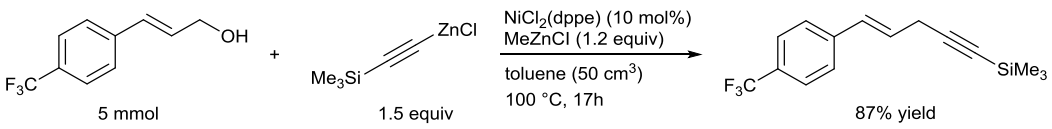
Eluent: EtOAc/petroleum ether 1/200 (v/v), colorless oil, yield 30.9 mg (78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.34 (m, 2H), 7.33–7.27 (m, 2H), 7.24–7.19 (m, 1H), 6.64 (dt, *J* = 15.7, 1.9 Hz, 1H), 6.18 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.14–3.08 (m, 2H), 2.27–2.19 (m, 2H), 1.56–1.48 (m, 2H), 1.48–1.39 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.39, 130.92, 128.63, 127.31, 126.35, 125.43, 83.12, 76.77, 31.26, 22.55, 22.12, 18.66, 13.80.

(*E*)-(5-cyclopropylpent-1-en-4-yn-1-yl)benzene (**3ag**)[10]



Eluent: EtOAc/petroleum ether 1/200 (v/v), light yellow oil, yield 34.6 mg (95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.33 (m, 2H), 7.32–7.26 (m, 2H), 7.23–7.18 (m, 1H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.15 (dt, *J* = 15.7, 5.7 Hz, 1H), 3.07 (dt, *J* = 5.7, 1.9 Hz, 2H), 1.32–1.22 (m, 1H), 0.78–0.71 (m, 2H), 0.70–0.64 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.33, 130.98, 128.61, 127.32, 126.34, 125.28, 85.93, 72.31, 22.54, 8.18, –0.27.

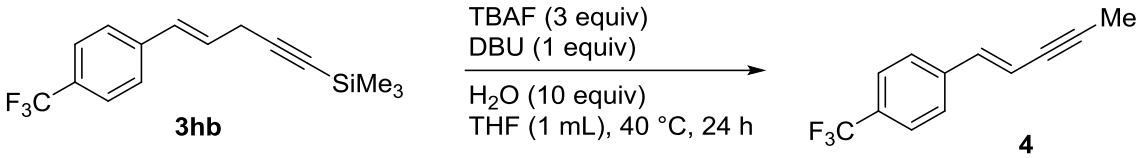
6. Gram scale reaction



$NiCl_2$(dppe) (0.264 g, 10 mol %), (*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (1.01 g, 5 mmol) and THF (3 mL) were charged to a Schlenk tube. To the stirred mixture was added MeZnCl (8.34 mL, 0.72 M solution in THF, 6 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of alkynylzinc reagent (16.3 mL, 0.46 M solution in THF, 7.5 mmol) was added, and the solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (50 mL) was added. and the reaction mixture was heated at 100 ℃ (oil bath) for 17 h, allowed to cool to rt. A 20% aqueous solution of NH_4Cl (60 mL) was added. The mixture was extracted with ethyl acetate (3 × 60 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 120:1) to afford the desired coupling product (1.23 g, 87%).

7. Transformation of 1,4-enynes

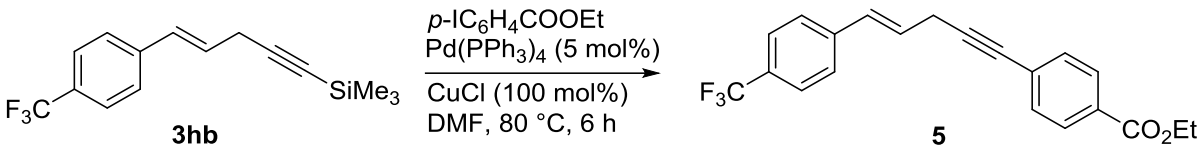
(1) Transformation of **3hb** to (*E*)-1-(pent-1-en-3-yn-1-yl)-4-(trifluoromethyl)benzene (**4**)[11]



1,4-enyne **3hb** (28.2 mg, 0.1 mmol) was dissolved in anhydrous THF (1 mL) under N_2 atmosphere in a Schlenk tube. Then, H_2O (18 mg, 1 mmol), DBU (15.2 mg, 0.1 mmol), and TBAF (0.3 mL, 1 M solution in THF, 0.3 mmol) were added into the solution. The mixture was stirred at 40 ℃ for 24 h. The reaction mixture was poured into water and extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure to give a crude product. The crude product was purified by column chromatography (eluent: petroleum ether) to give **4**[12] (15.1 mg, 72%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 16.2 Hz, 1H), 6.22 (d, *J* = 16.1 Hz, 1H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.06, 138.57, 130.03 (q, *J* = 32.7 Hz), 126.29, 125.76 (q, *J* = 3.8 Hz), 124.23 (q, *J* = 272.5 Hz), 111.78, 90.22, 78.64, 4.70. ^{19}F NMR (471 MHz, $CDCl_3$): δ –62.62.

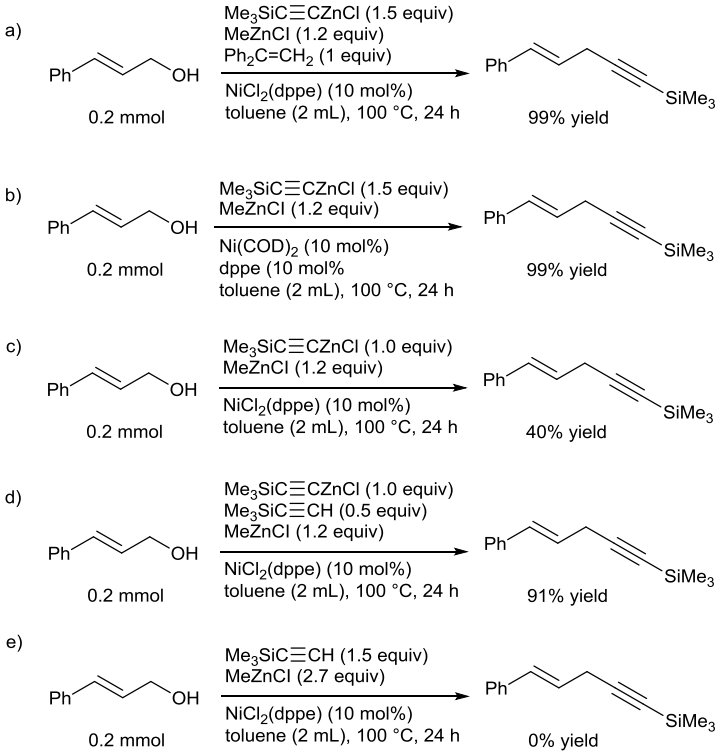
The reaction did not yield a naphthalene derivative under the present conditions. In the absence of H_2O and DBU the reaction gave **4** in very low yield. In the absence of DBU the reaction gave **4** in good yield along with a small amount of unidentified side products.

(2) Transformation of **3hb** to ethyl (*E*)-4-(5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yn-1-yl) benzoate (**5**)[13]



$Pd(PPh_3)_4$ (11.6 mg, 5 mol %), CuCl (19.8 mg, 0.2 mmol), dry DMF (1 mL), **3hb** (112.8 mg, 0.4 mmol) and ethyl 4-iodobenzoate (55.2 mg, 0.2 mmol) were successively added to a Schlenk tube at room temperature. The mixture was heated at 80 ℃ (oil bath) for 6 h with stirring. After cooled to room temperature, the mixture was quenched with 1 M HCl and extracted with diethyl ether. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. Filtration and concentration with a rotary evaporator gave a viscous oil which was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) to give **5** (58.6 mg, 82%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.65–7.38 (m, 6H), 6.74 (d, *J* = 15.7 Hz, 1H), 6.42-6.27 (m, 1H), 4.38 (q, *J* = 6.8 Hz, 2H), 3.41 (d, *J* = 4.2 Hz, 2H), 1.40 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.24, 140.54, 131.67, 130.63, 129.82, 129.58, 129.30, 128.21, 126.69, 126.59, 125.67 (q, *J* = 3.7 Hz), 124.33 (q, *J* = 272.3 Hz), 89.45, 82.82, 61.26, 23.26, 14.45. ^{19}F NMR (471 MHz, $CDCl_3$): δ –62.47. HRMS (ESI): m/z 359.1256 $[M+H]^+$, calcd. for $C_{21}H_{18}F_3O_2$ 359.1259.

8. Mechanistic studies



(a) $NiCl_2$(dppe) (10.6 mg, 10 mol %) and cinnamyl alcohol (0.5 mL, 0.4 M solution in THF, 0.2 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeZnCl (0.42 mL, 0.57 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of $Me_3SiC{\equiv}CZnCl$ (0.65 mL, 0.46 M solution in THF, 0.3 mmol) was added. The resulying solution was stirred for an additional 5 min. Solvent was removed in vacuo and toluene (2 mL) and $Ph_2C{=}CH_2$ (36 mg, 0.2 mmol) was successively added. The reaction mixture was heated at 100 ℃ (oil bath) for 24 h and then cooled to room temperature. The reaction mixture was passed through a short pad of celite (eluting with ethyl acetate) and then concentrated under reduced pressure. The yield (99%) was determined by NMR spectral analysis using 1,1,2,2-tetrachloroethane as an internal standard.

(2) $Ni(COD)_2$ (5.5 mg, 10 mol %), dppe (8 mg, 10 mol %) and cinnamyl alcohol (0.5 mL, 0.4 M solution in THF, 0.2 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeZnCl (0.42 mL, 0.57 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of $Me_3SiC{\equiv}CZnCl$ (0.65 mL, 0.46 M solution in THF, 0.3 mmol) was added. The resulting mixture was stirred for an additional 5 min. Solvent was removed in vacuo and toluene (2 mL) was added. The reaction mixture was heated at 100 ℃ (oil bath) for 24 h and then cooled to room temperature. The resulting mixture was passed through a short pad of celite (eluting with ethyl acetate) and then concentrated under reduced pressure. The yield (99%) was determined by NMR spectral analysis using 1,1,2,2-tetrachloroethane as an internal standard.

(3) $NiCl_2$(dppe) (10.6 mg, 10 mol %) and cinnamyl alcohol (0.5 mL, 0.4 M in THF, 0.2 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeZnCl (0.42 mL, 0.57 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of $Me_3SiC{\equiv}CZnCl$ (0.44 mL, 0.46 M solution in THF, 0.2 mmol) was added. The resulting solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (2 mL) was added. The reaction mixture was heated at 100 ℃ (oil bath) for 24 h and then cooled to room temperature. The mixture was passed through a short pad of celite (eluting with ethyl acetate) and then concentrated under reduced pressure. The yield (40%) was determined by NMR spectral analysis using 1,1,2,2-tetrachloroethane as an internal standard.

(4) $NiCl_2$(dppe) (10.6 mg, 10 mol %) and cinnamyl alcohol (0.5 mL, 0.4 M in THF, 0.2 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeZnCl (0.42 mL, 0.57 M solution in THF, 0.24 mmol) at room temperature. After the mixture was stirred for 5 min, a solution of $Me_3SiC{\equiv}CZnCl$ (0.44 mL, 0.46 M solution in THF, 0.2 mmol) was added. The resulting solution was stirred for an additional 5 min. Solvent was removed in vacuo and then toluene (2 mL) and $Me_3SiC{\equiv}CH$ (9.8 mg, 0.1 mmol) was successively added. The reaction mixture was heated at 100 ℃ (oil bath) for 24 h and then cooled to room temperature. The mixture was passed through a short pad of celite (eluting with ethyl acetate) and concentrated under reduced pressure. The yield (91%) was determined by NMR spectral analysis using 1,1,2,2-tetrachloroethane as an internal standard.

(5) $NiCl_2$(dppe) (10.6 mg, 10 mol %) and cinnamyl alcohol (0.5 mL, 0.4 M in THF, 0.2 mmol) were charged to a Schlenk tube under nitrogen. To the stirred mixture was added MeZnCl (0.95 mL, 0.57 M solution in THF, 0.54 mmol) at room temperature. After the mixture was stirred for 5 min, solvent was removed in vacuo and then toluene (2 mL) and ethynyltrimethylsilane (29.5 mg, 0.3 mmol) were added. The reaction mixture was heated at 100 ℃ (oil bath) for 24 h with stirring and then cooled to room temperature. The resulting mixture was passed through a short pad of celite with ethyl acetate and concentrated under reduced pressure. The residue was determined using ^{1}H NMR spectrum. No expected product was observed.

9. References

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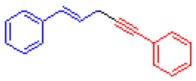
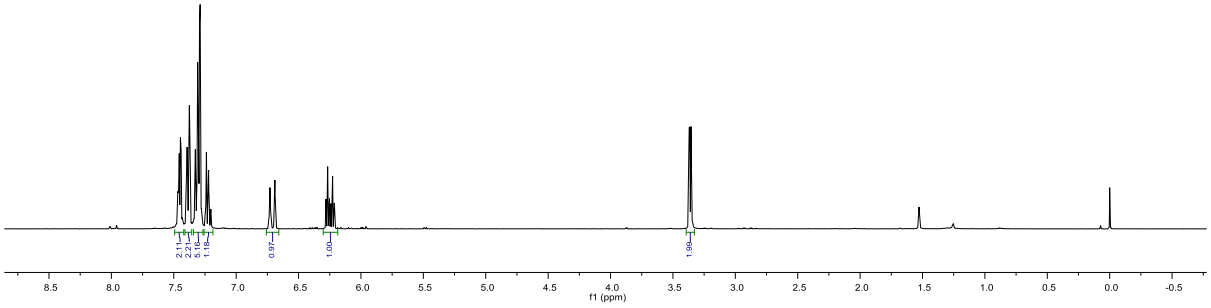
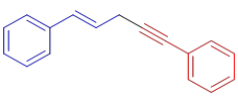
10. Copies of NMR spectra of the reaction products

(1) (*E*)-pent-1-en-4-yne-1,5-diyldibenzene (**3aa**)

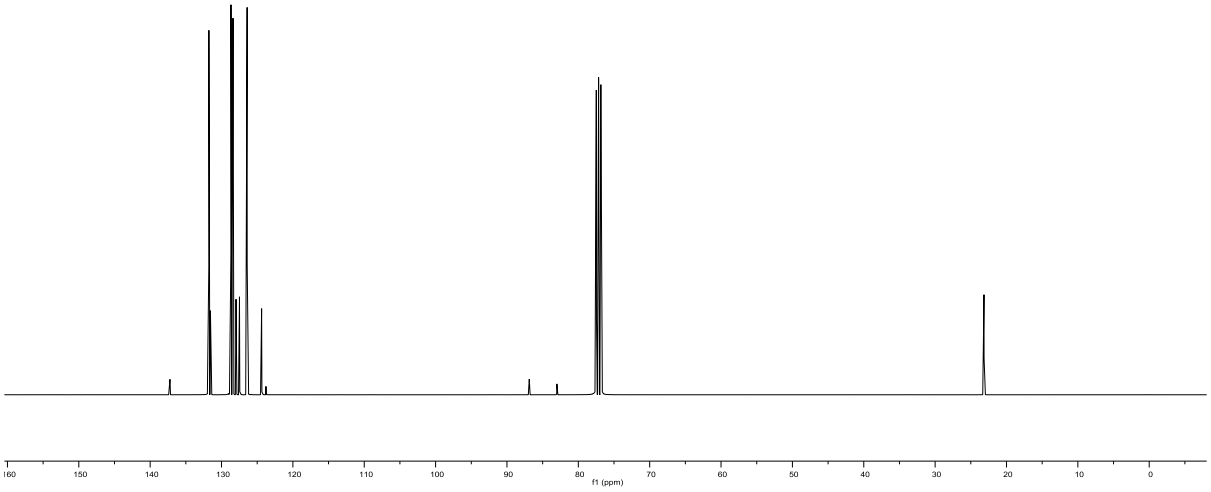


^{1}H NMR (400 MHz, $CDCl_3$)

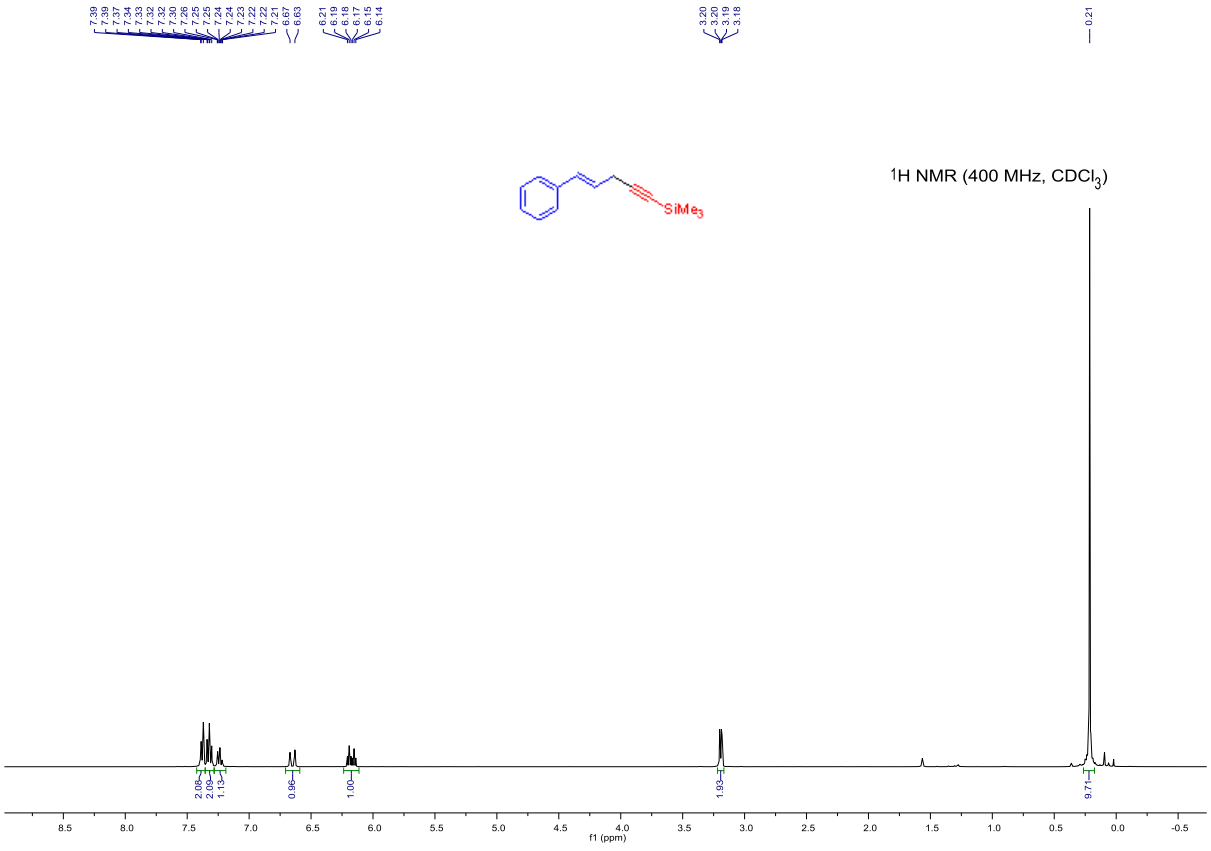


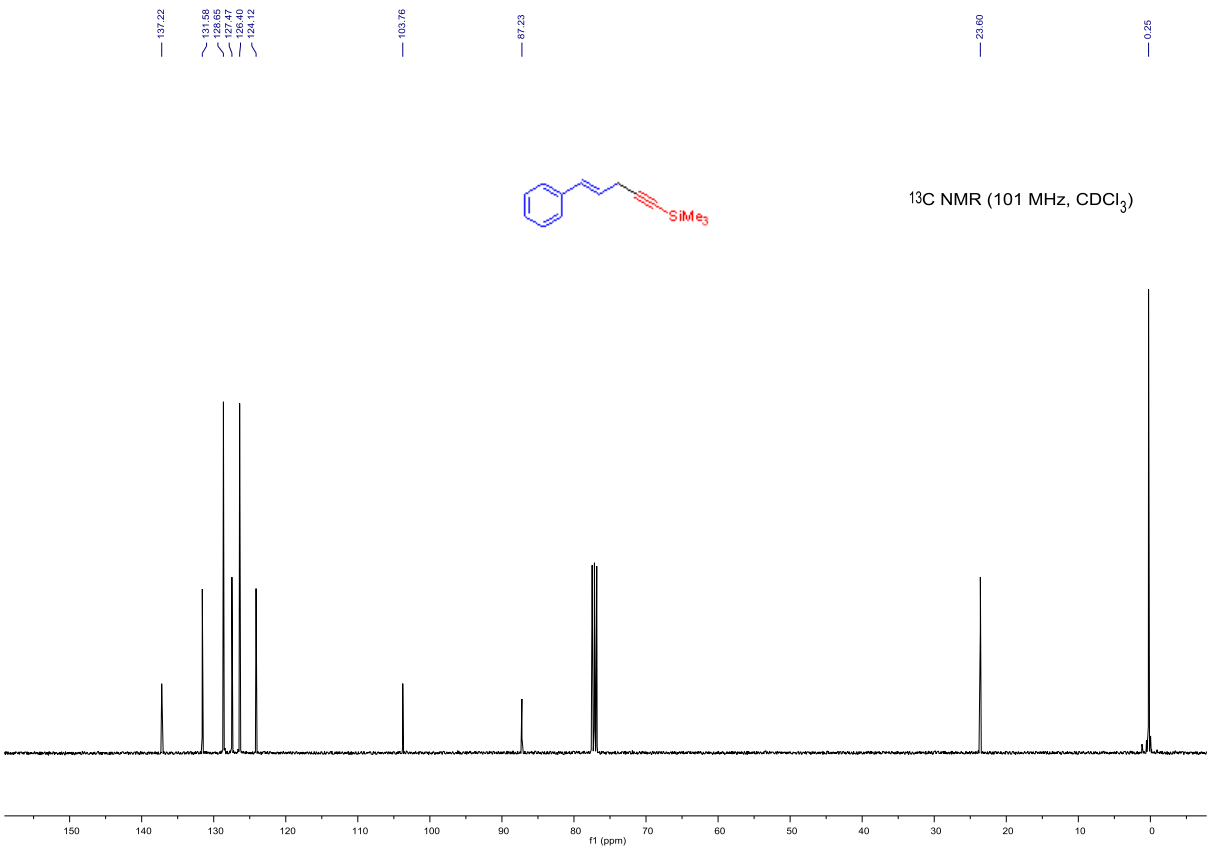


^{13}C NMR (101 MHz, $CDCl_3$)

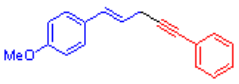


(2) (*E*)-trimethyl(5-phenylpent-4-en-1-yn-1-yl)silane (**3ab**)

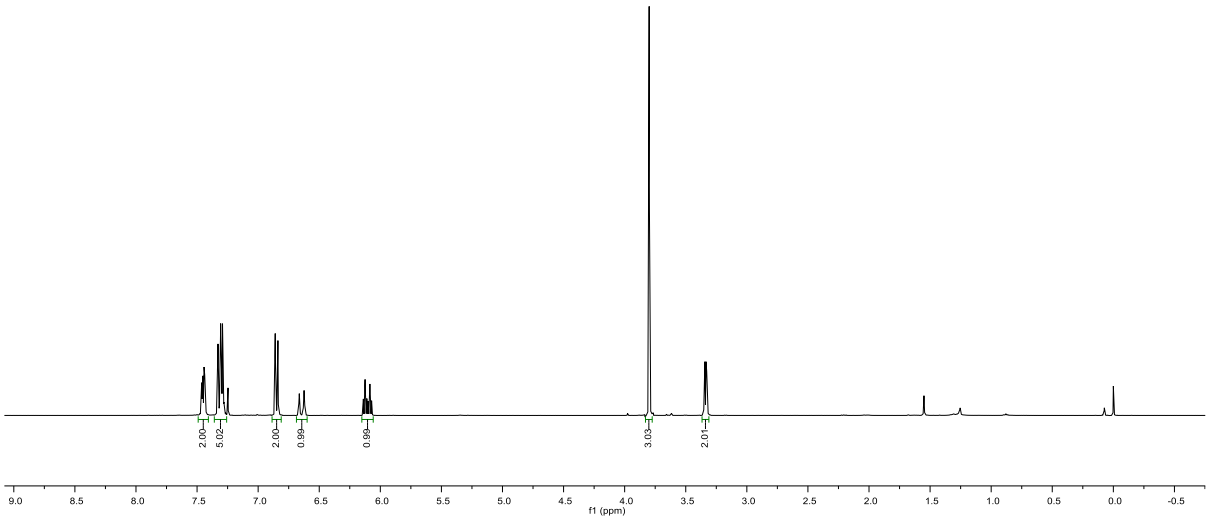


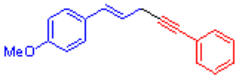


(3) (*E*)-1-methoxy-4-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3ba**)

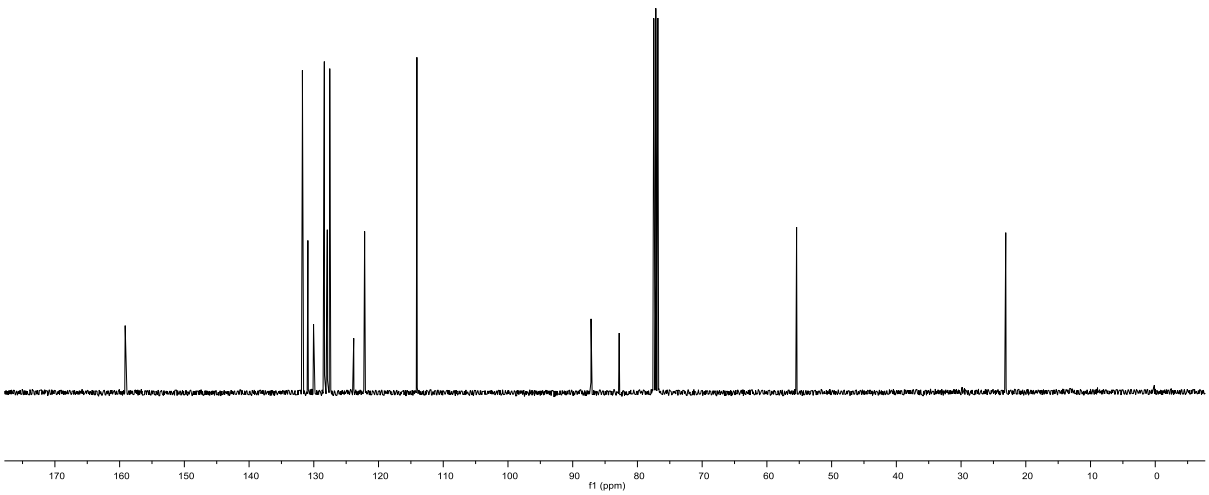


^{1}H NMR (400 MHz, $CDCl_3$)

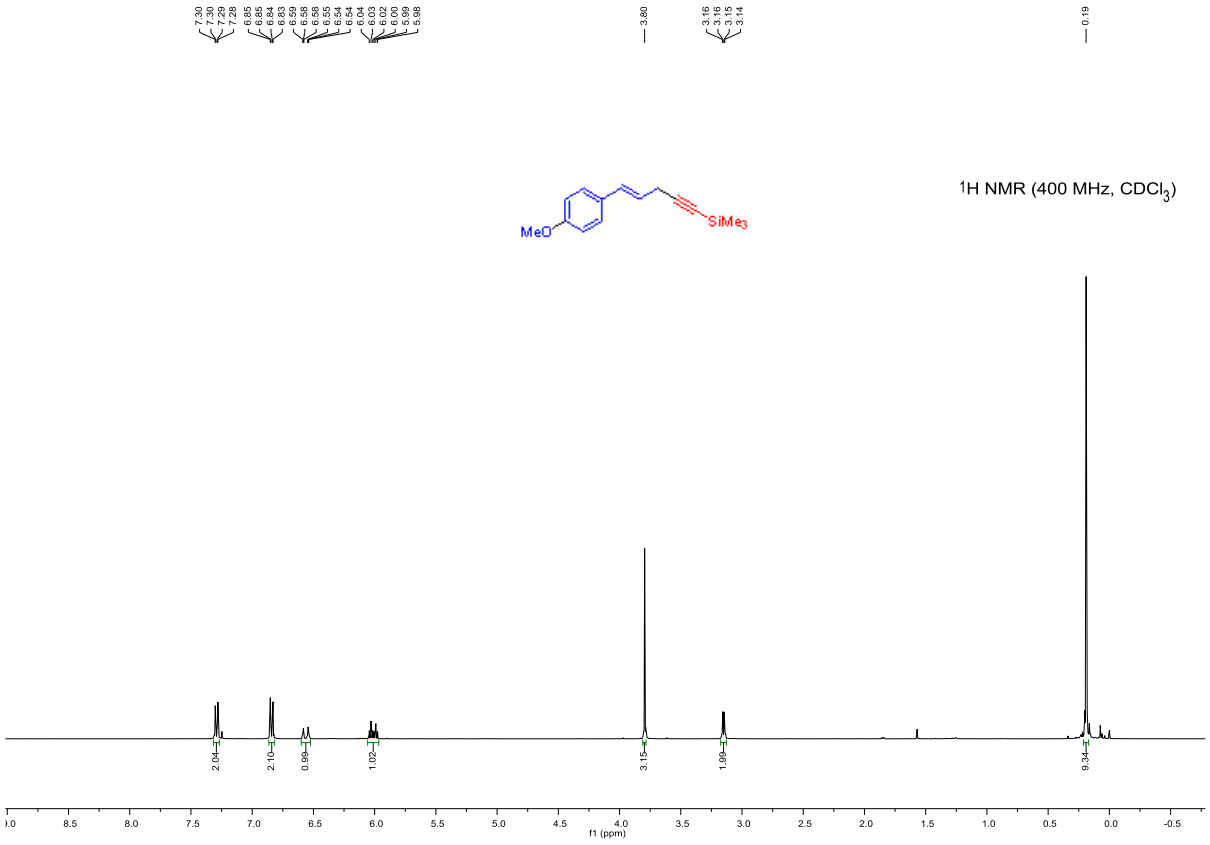


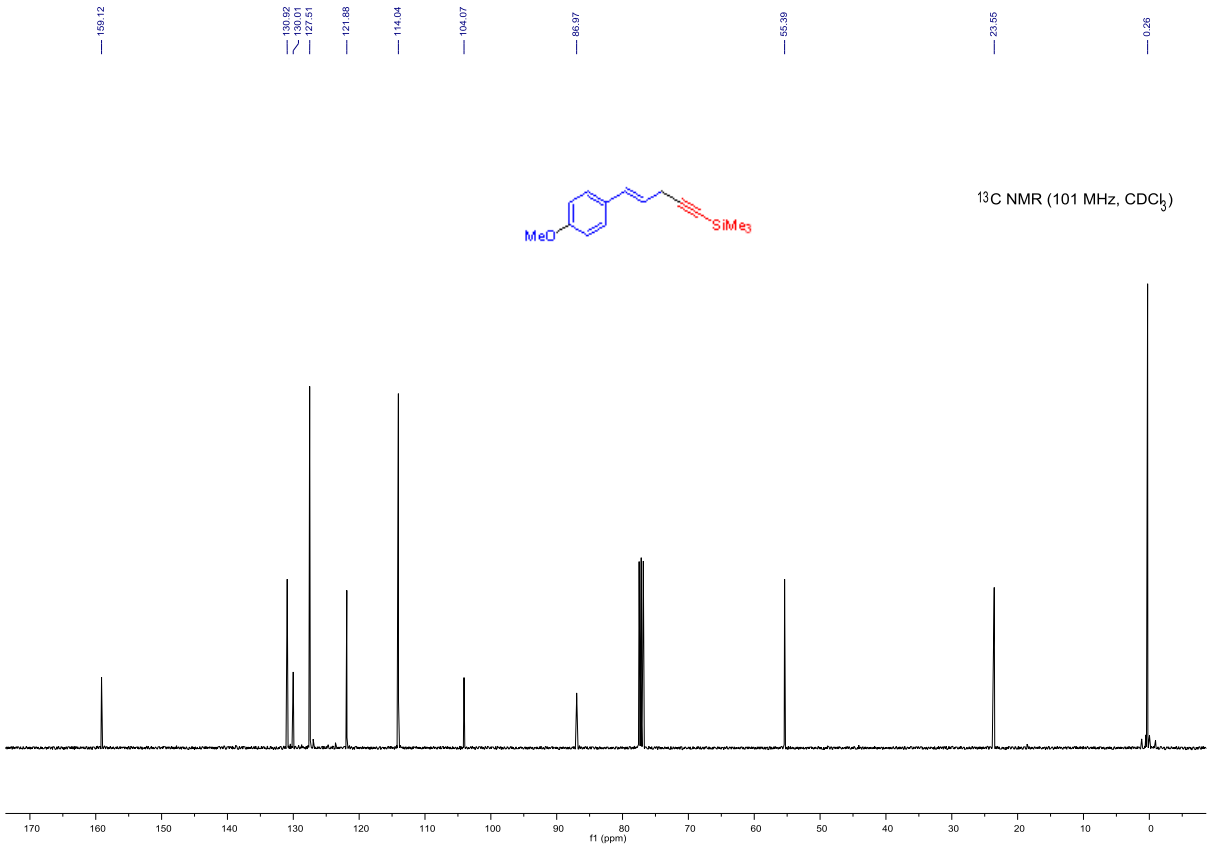


^{13}C NMR (101 MHz, $CDCl_3$)

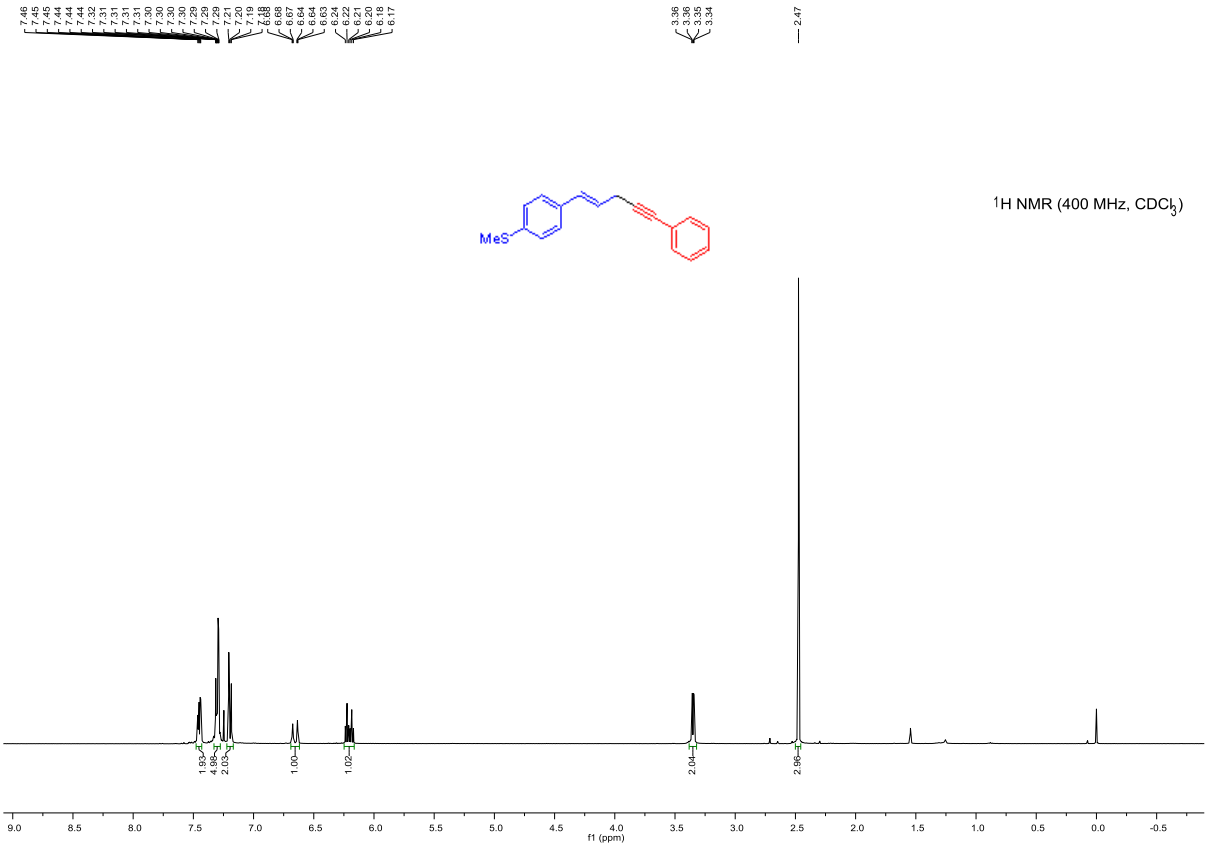


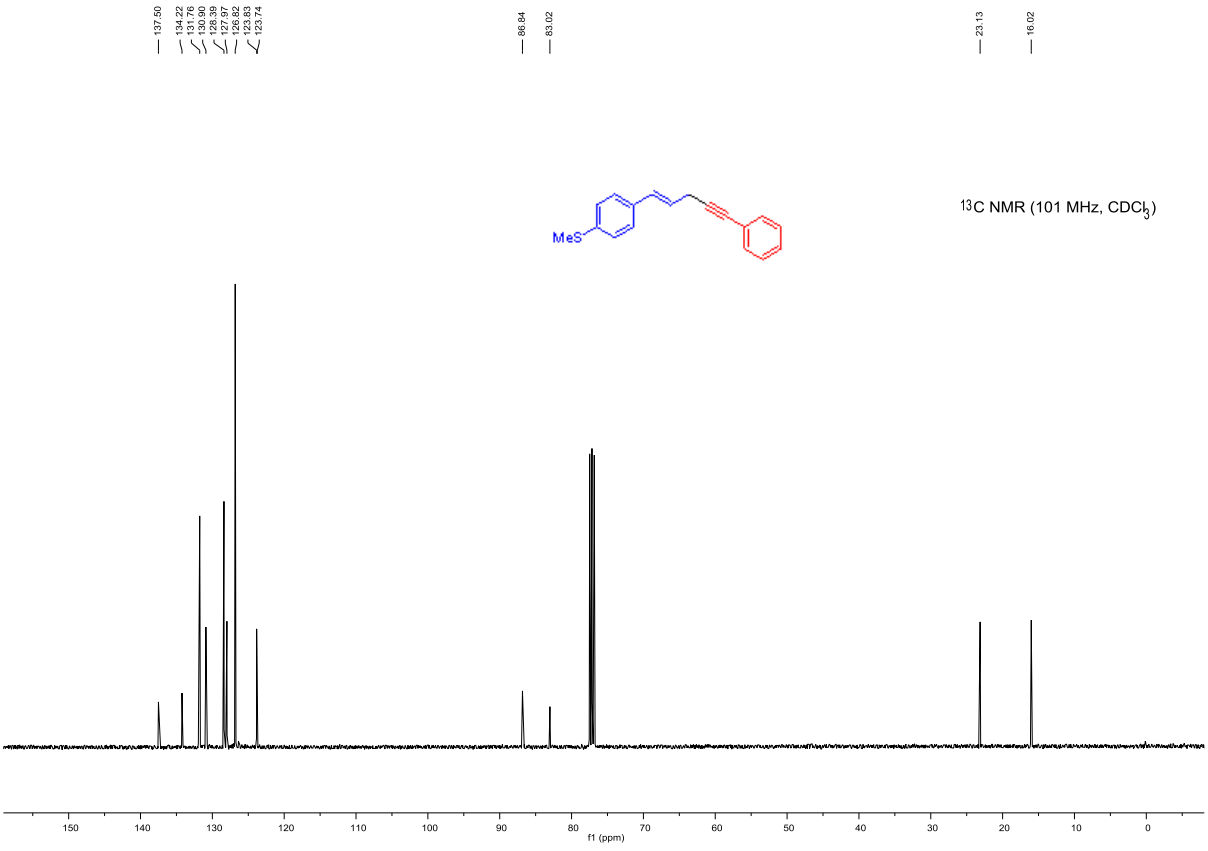
(4) (*E*)-(5-(4-methoxyphenyl)pent-4-en-1-yn-1-yl)trimethylsilane (**3bb**)



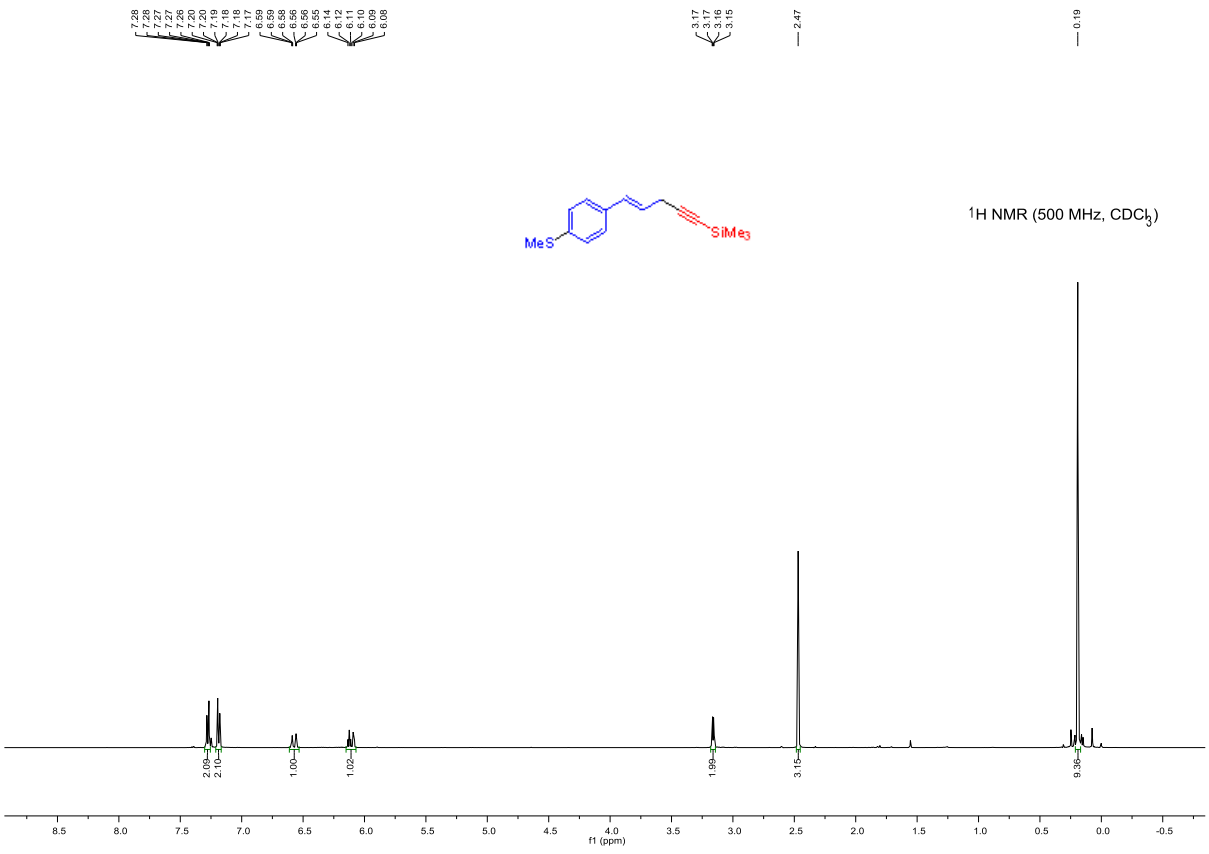


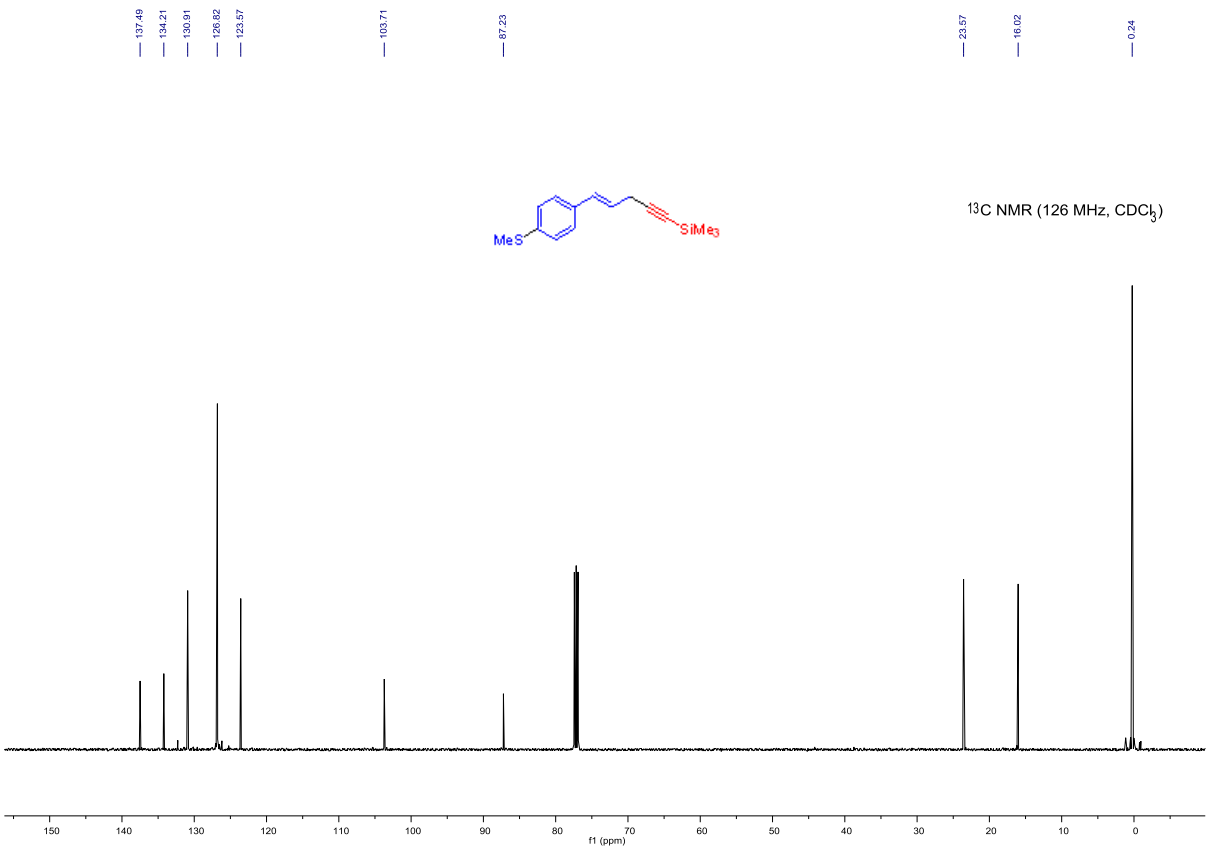
(5) (*E*)-methyl(4-(5-phenylpent-1-en-4-yn-1-yl)phenyl)sulfane (**3ca**)



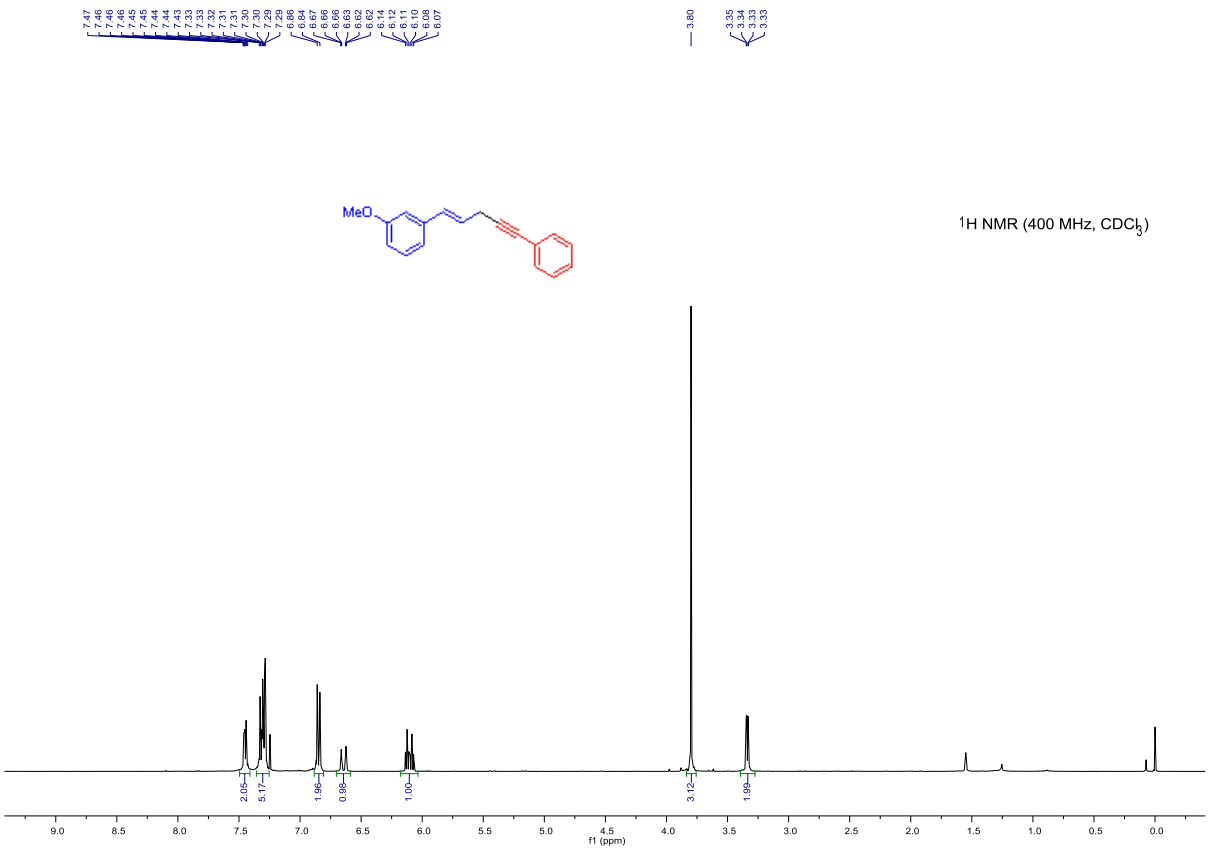


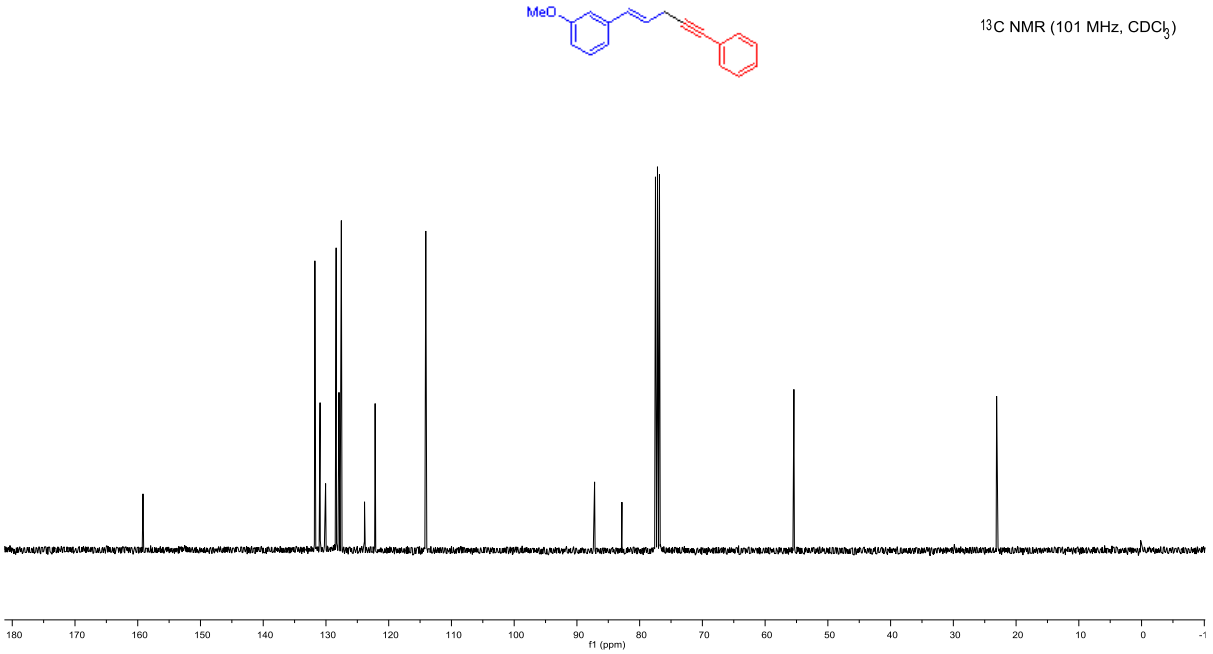
(6) (*E*)-trimethyl(5-(4-(methylthio)phenyl)pent-4-en-1-yn-1-yl)silane (**3cb**)



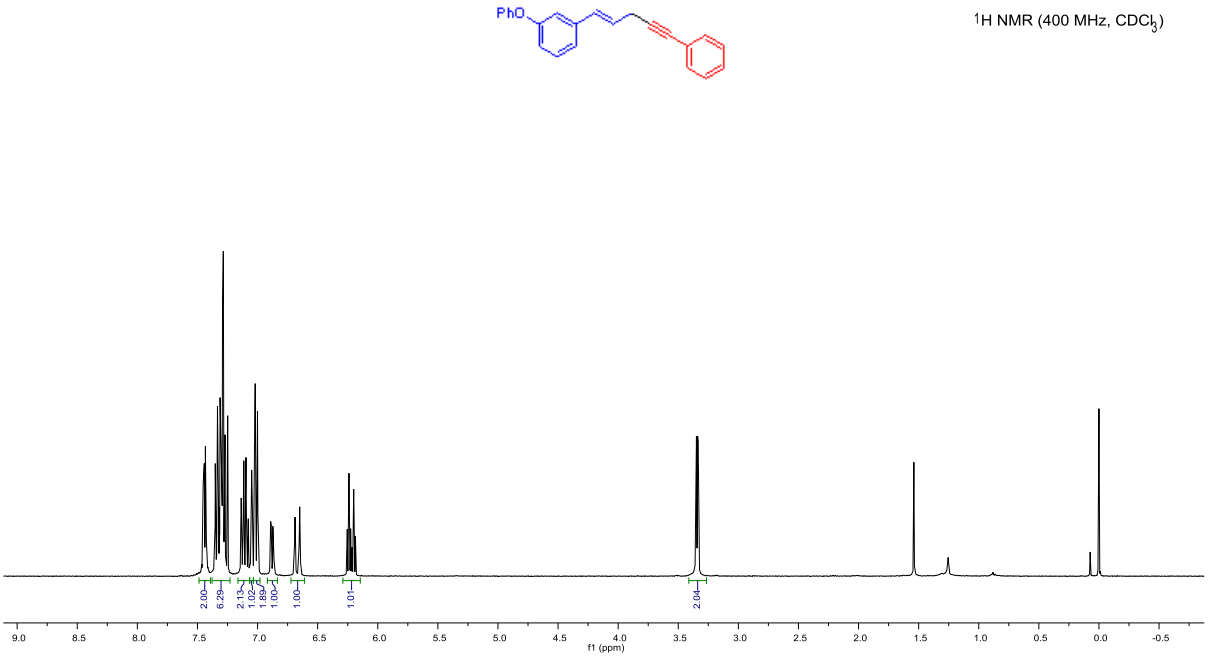


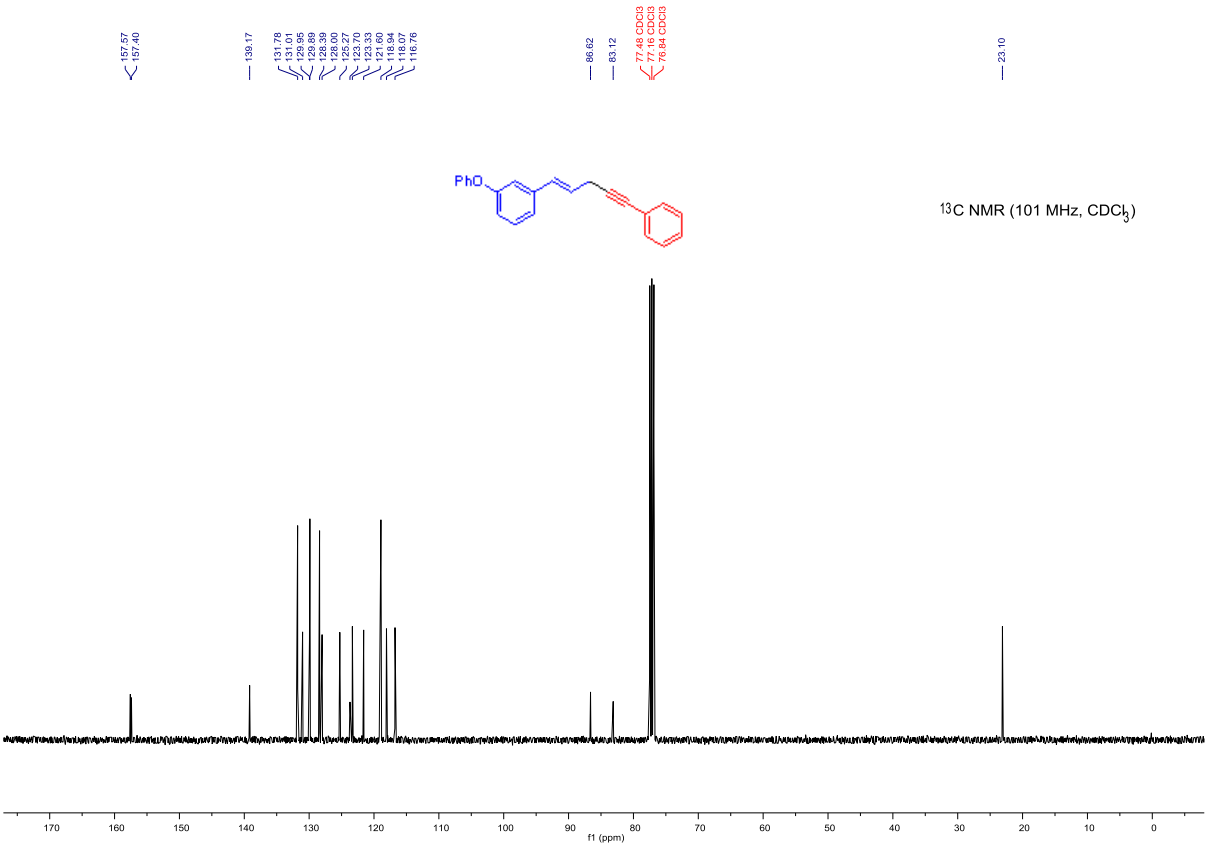
(7) (*E*)-1-methoxy-3-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3d**)



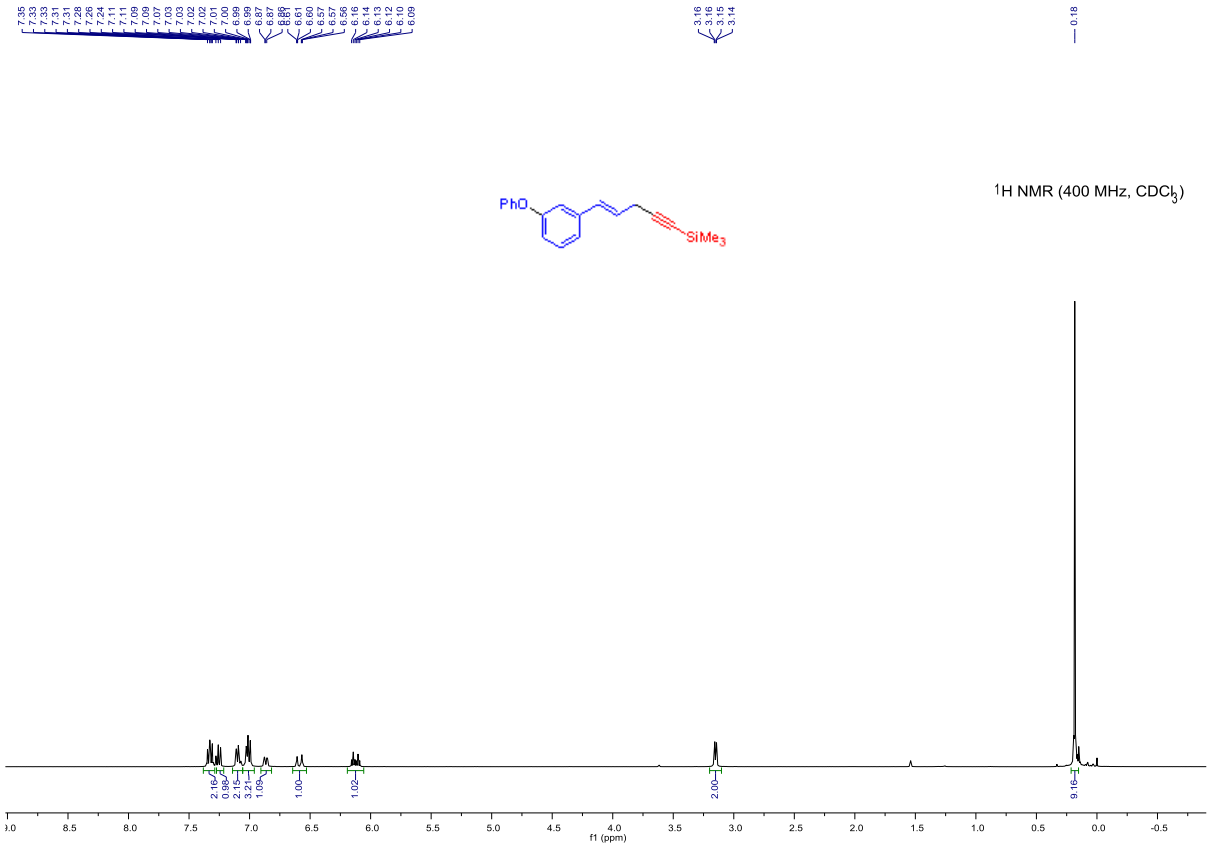


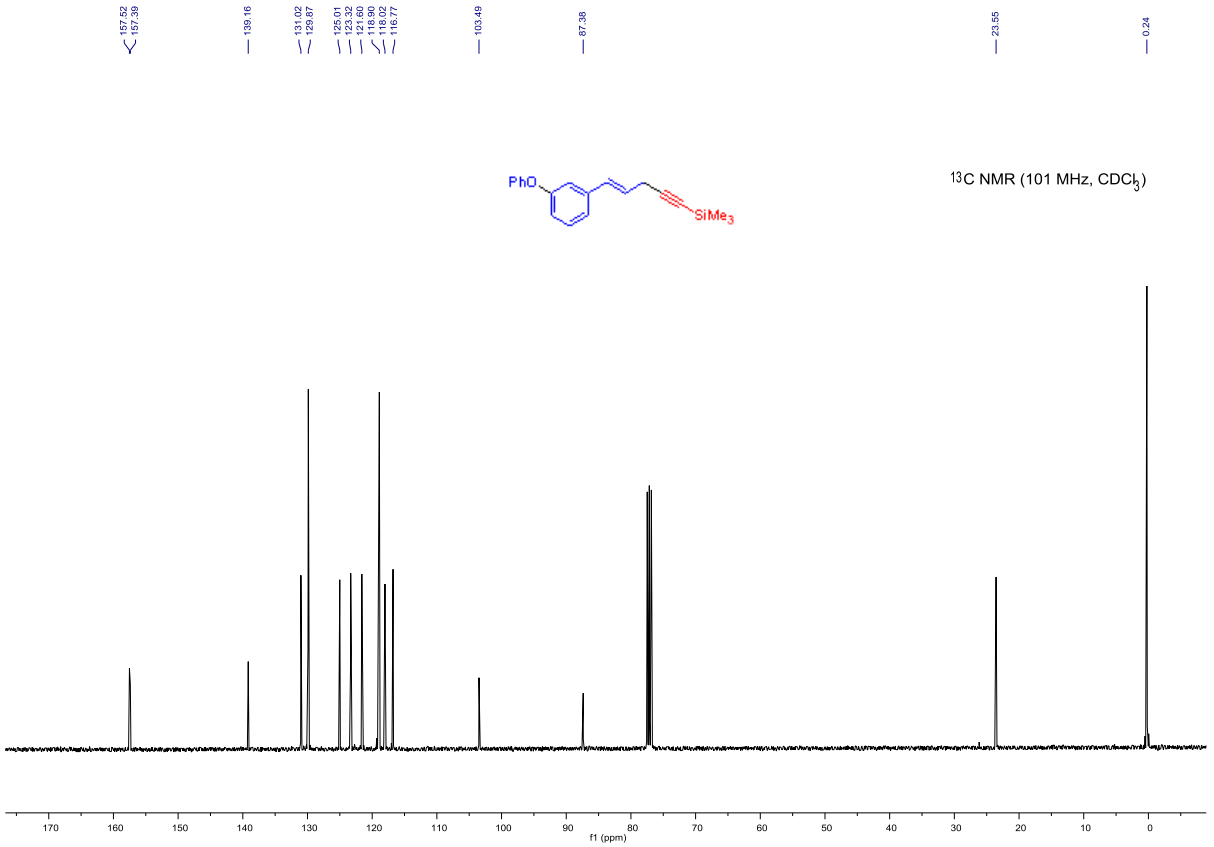
(8) (*E*)-1-phenoxy-3-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3ea**)



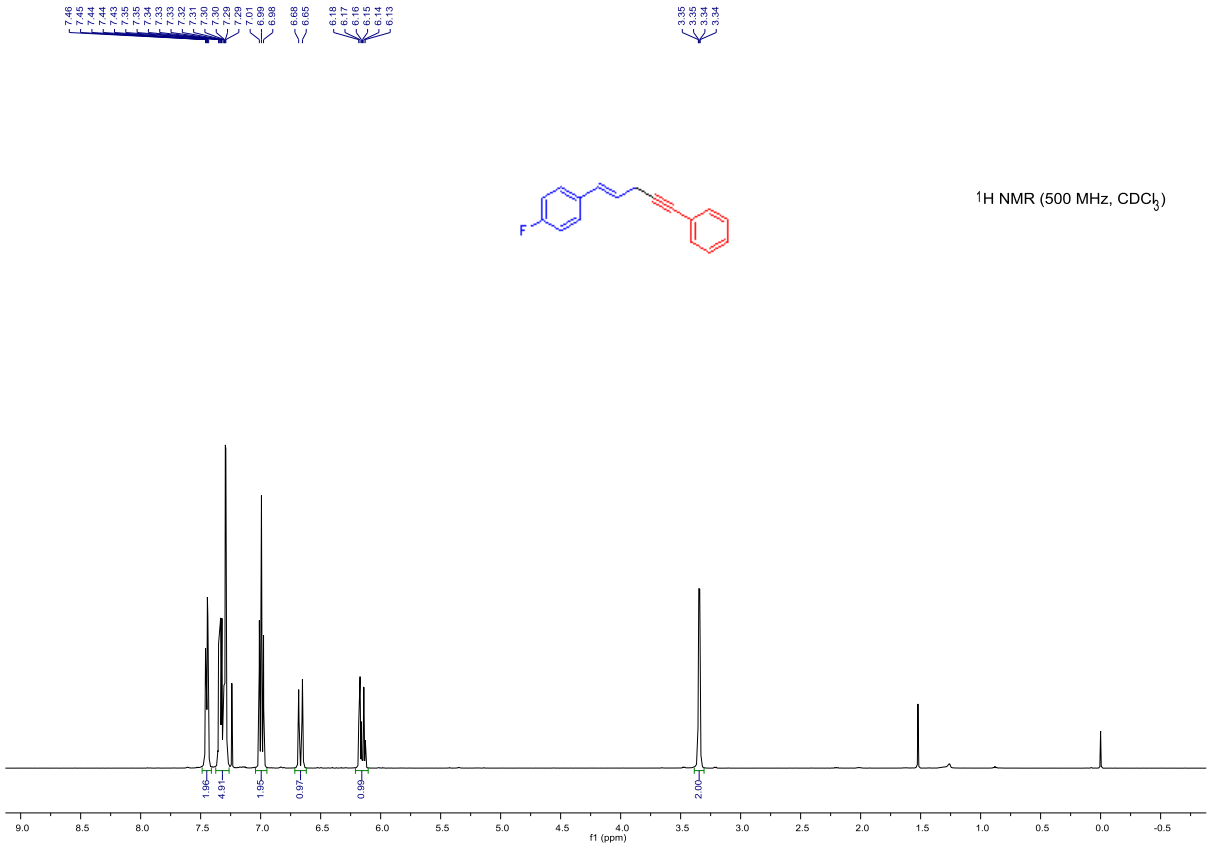


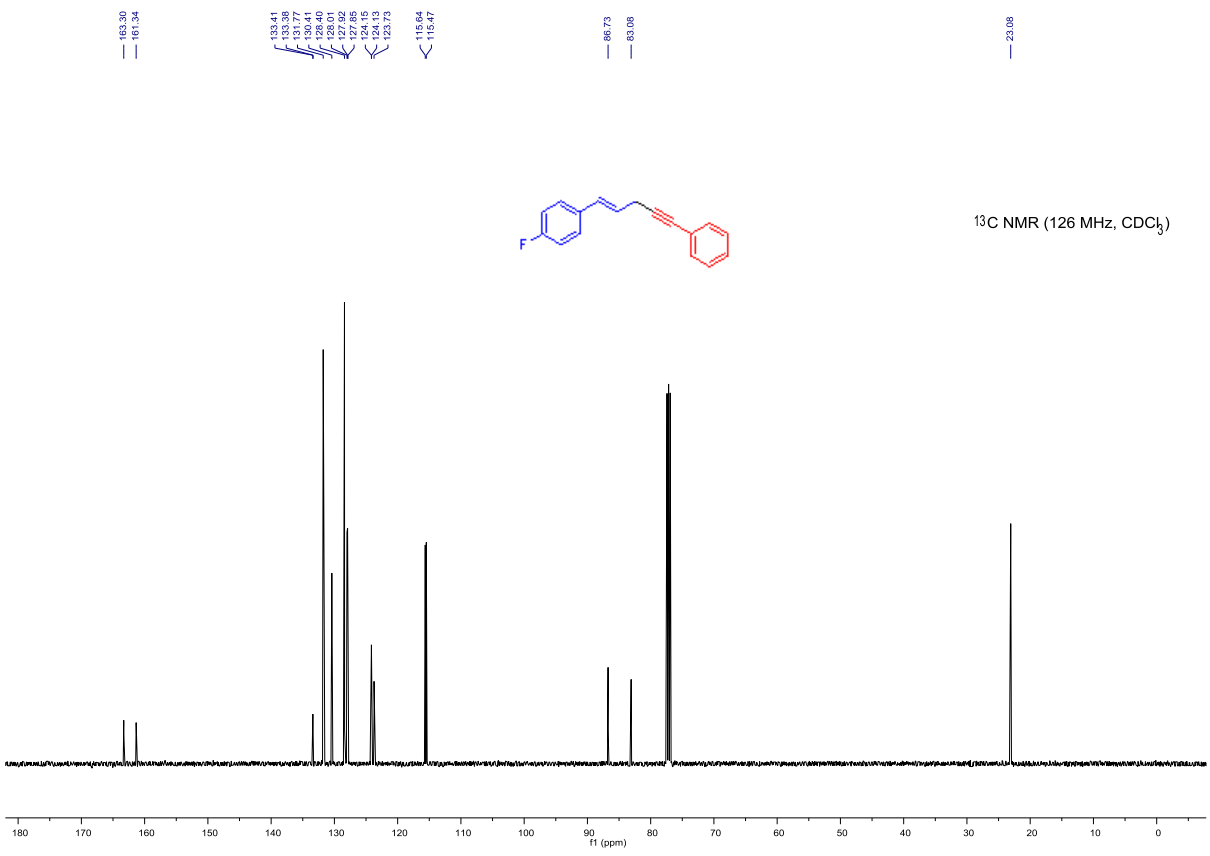
(9) (*E*)-trimethyl(5-(3-phenoxyphenyl)pent-4-en-1-yn-1-yl)silane (**3eb**)

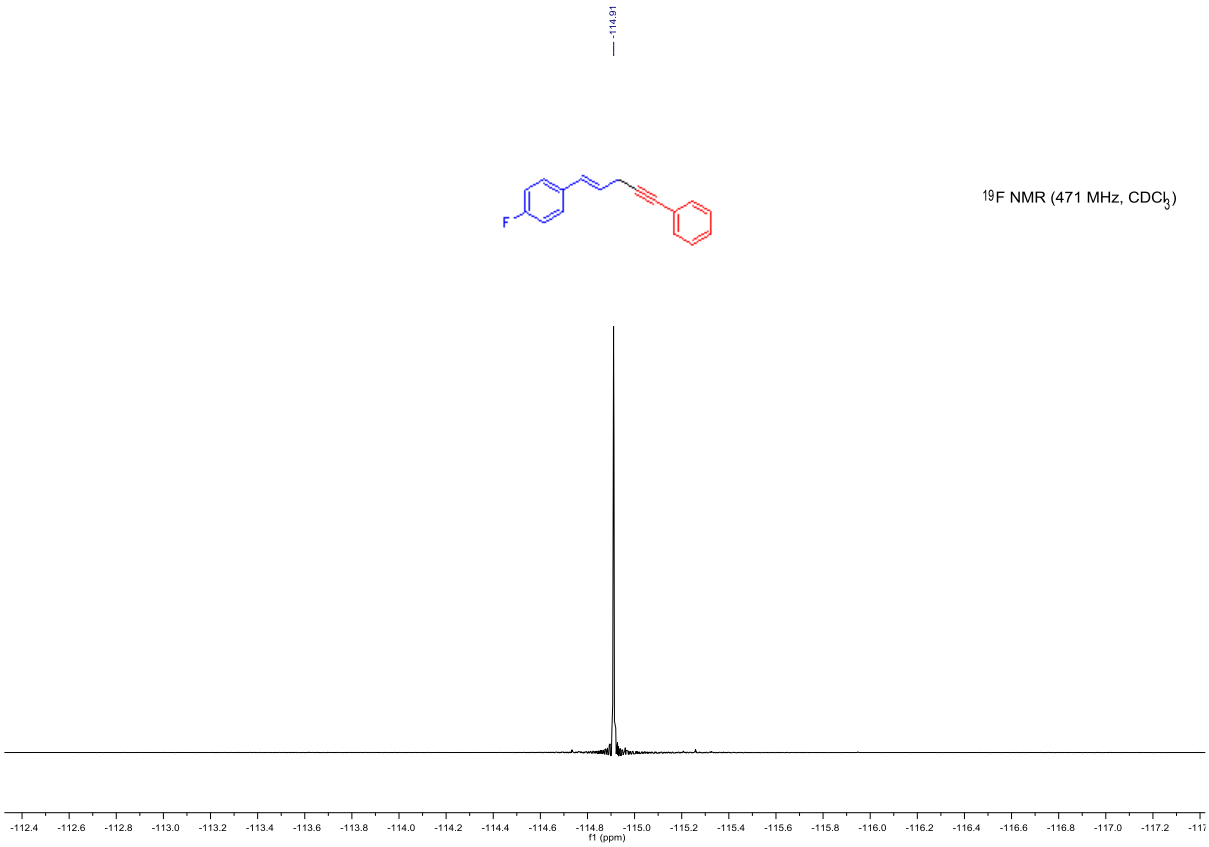




(10) (*E*)-1-fluoro-4-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3fa**)

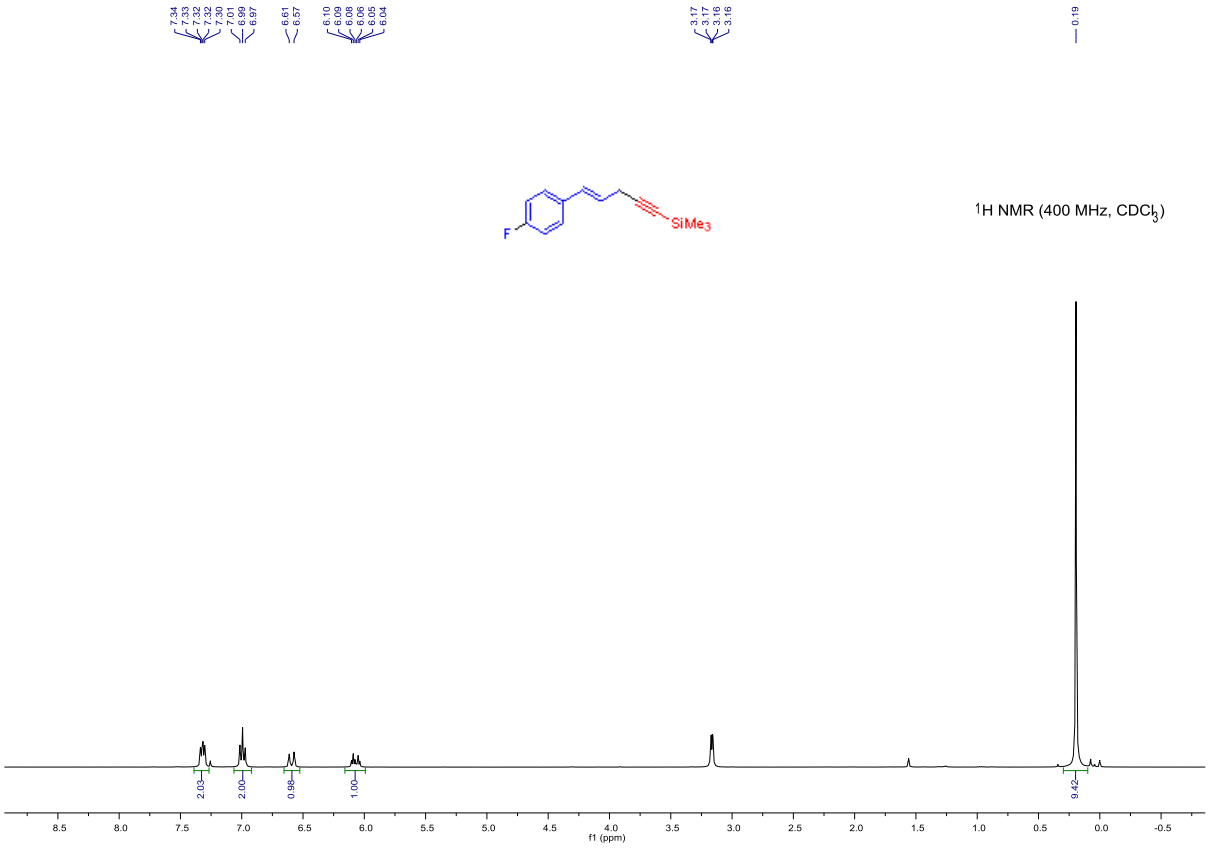


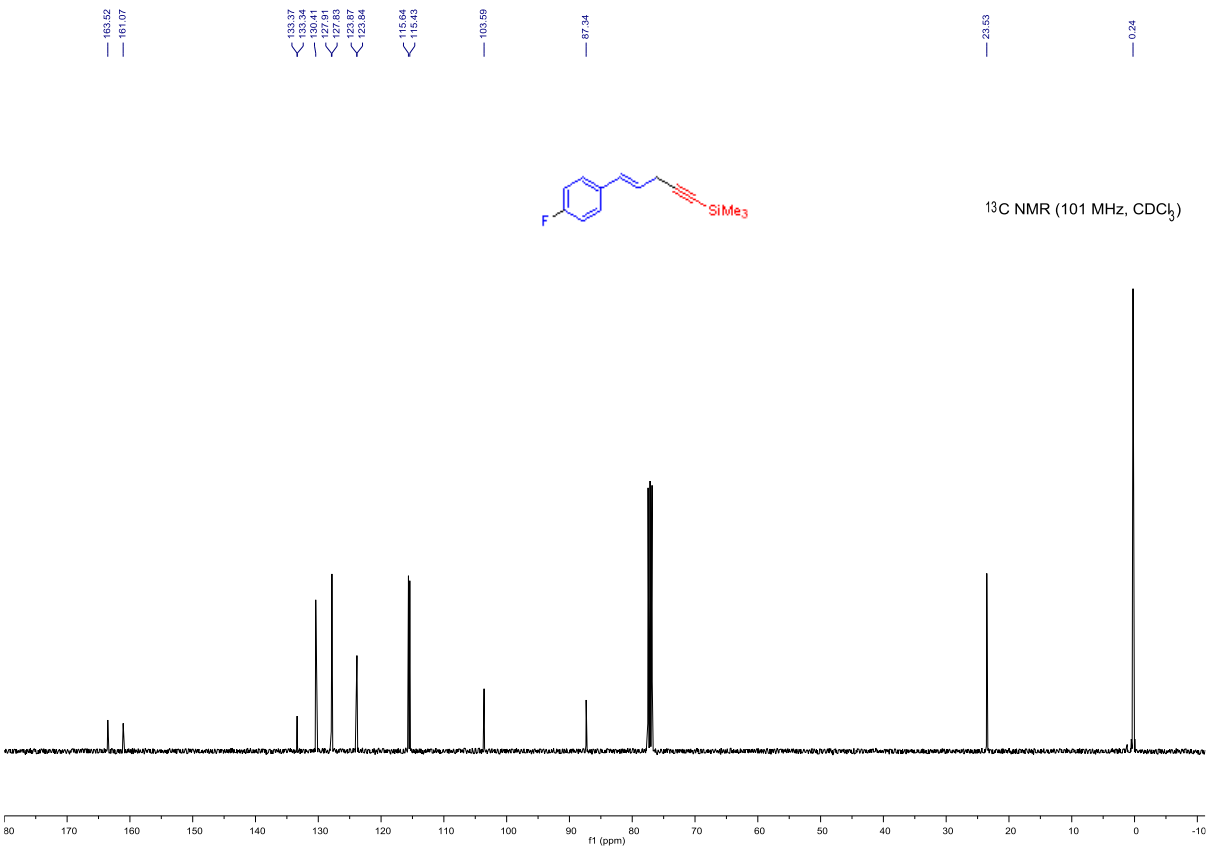




^{19}F NMR (471 MHz, $CDCl_3$)

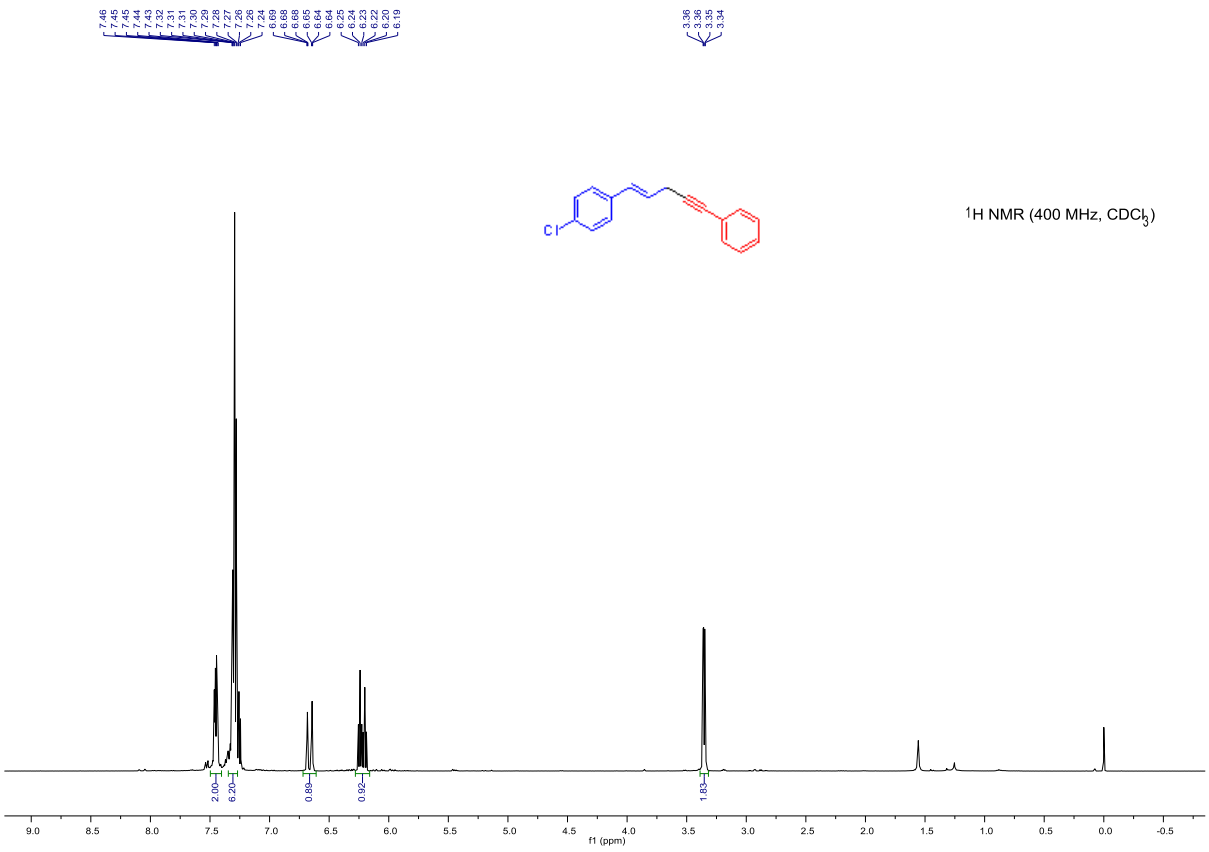
(11) (E)-(5-(4-fluorophenyl)pent-4-en-1-yn-1-yl)trimethylsilane (**3fb**)



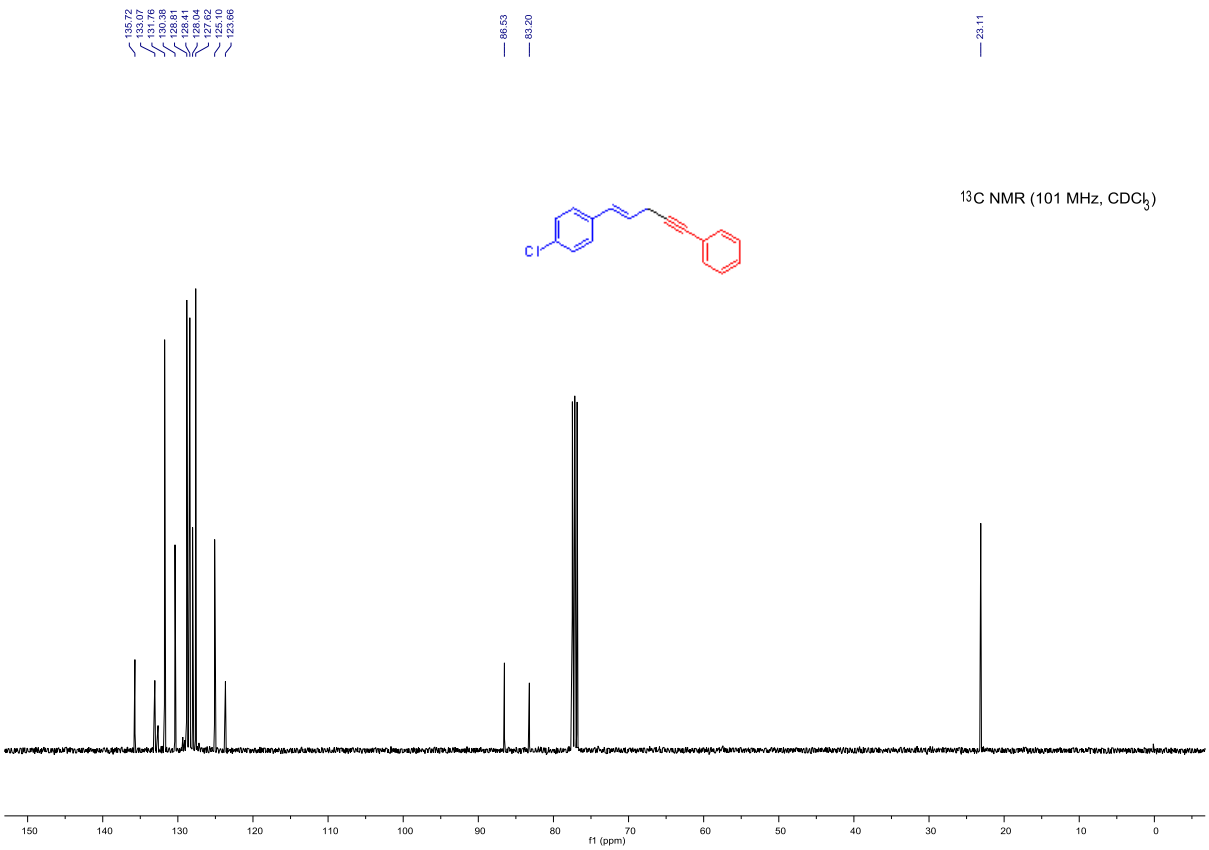


^{19}F NMR (471 MHz, $CDCl_3$)

(12) (*E*)-1-chloro-4-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3ga**)

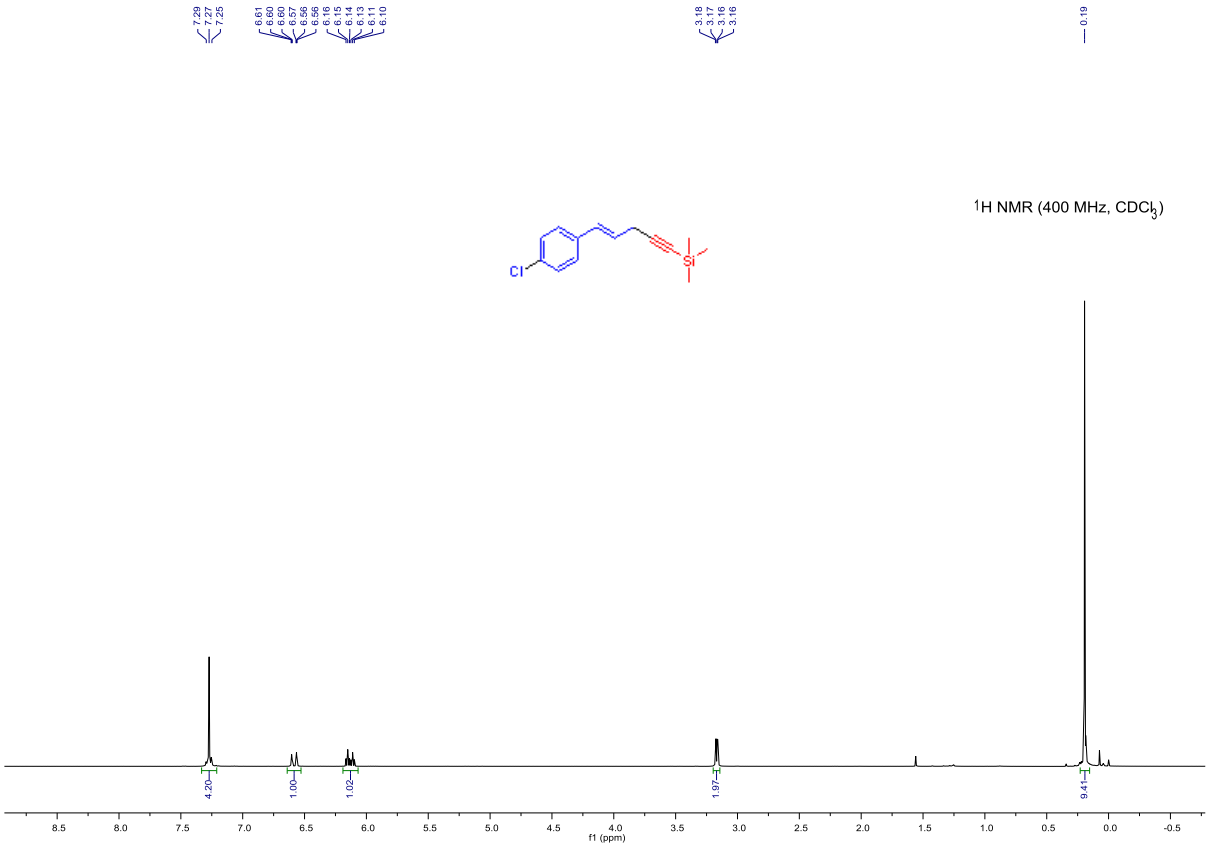


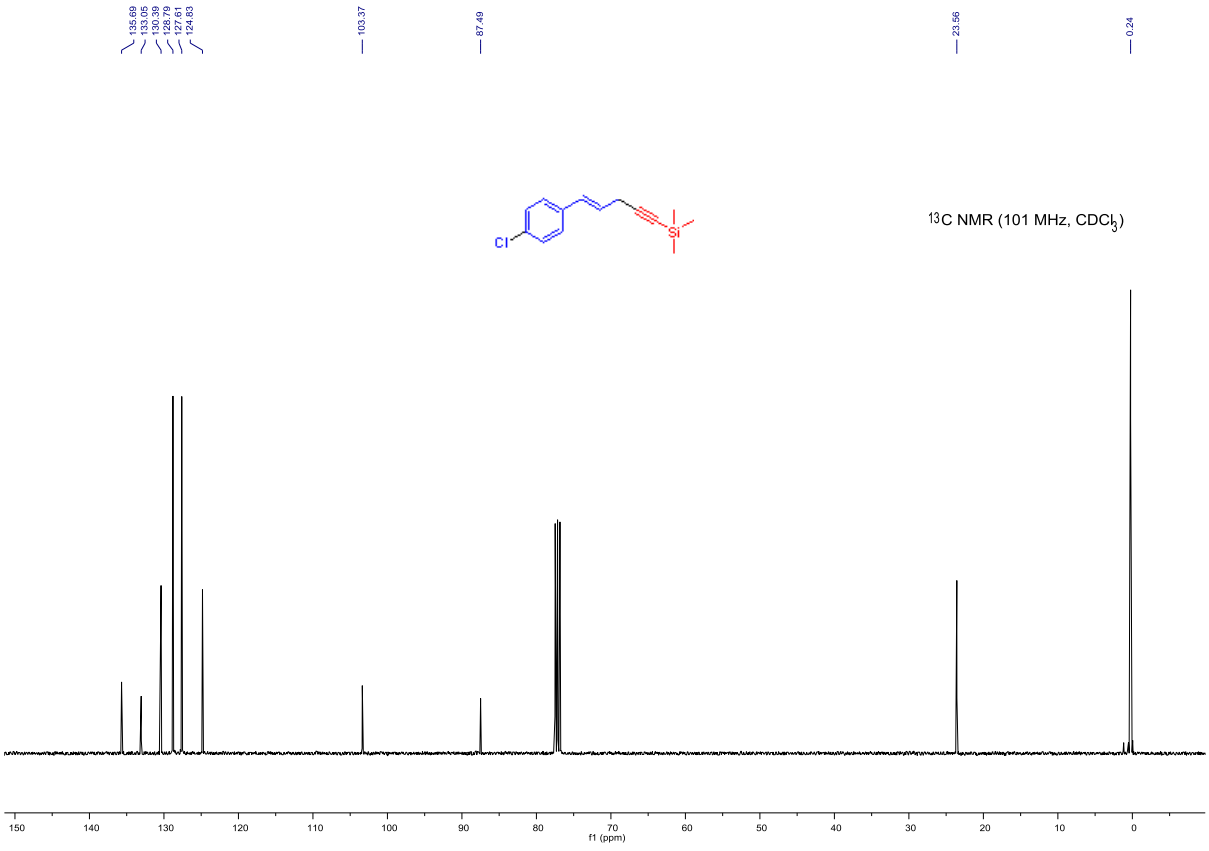
^{1}H NMR (400 MHz, $CDCl_3$)



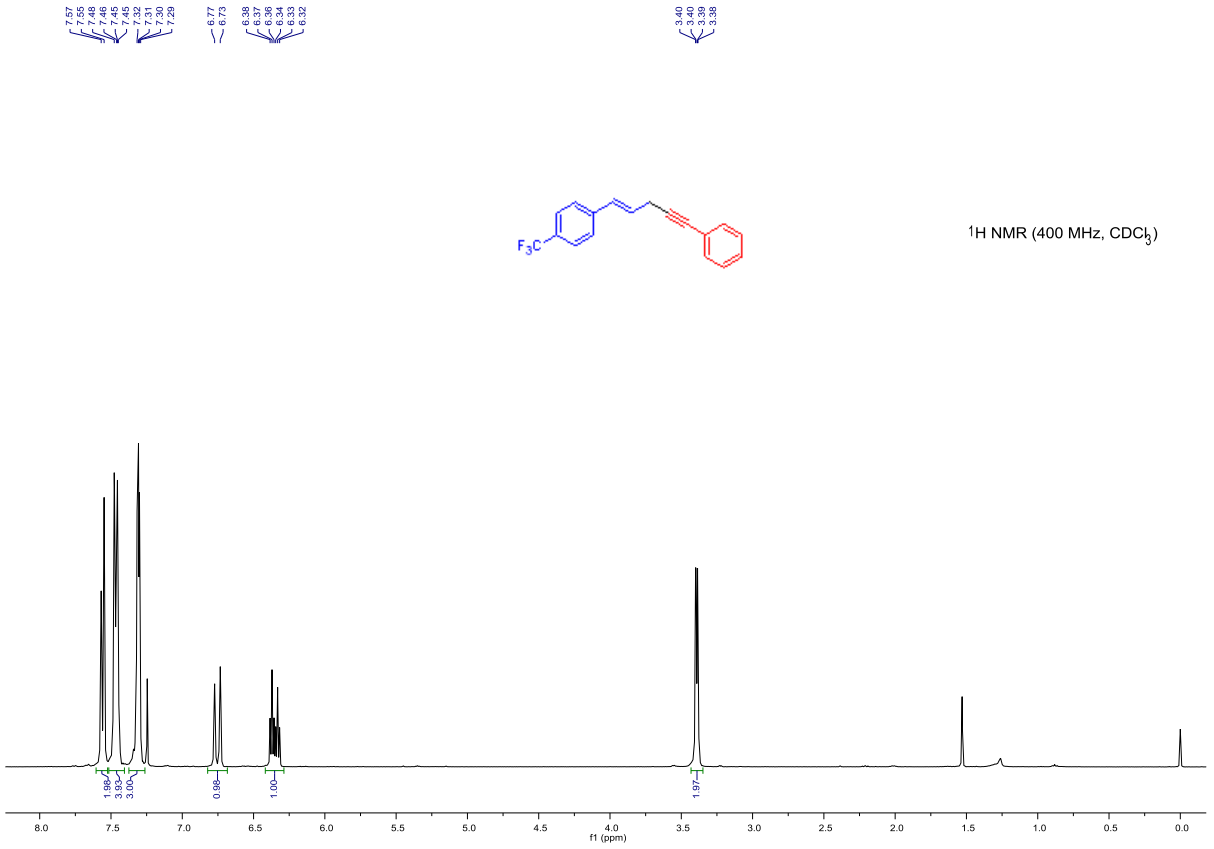
^{13}C NMR (101 MHz, $CDCl_3$)

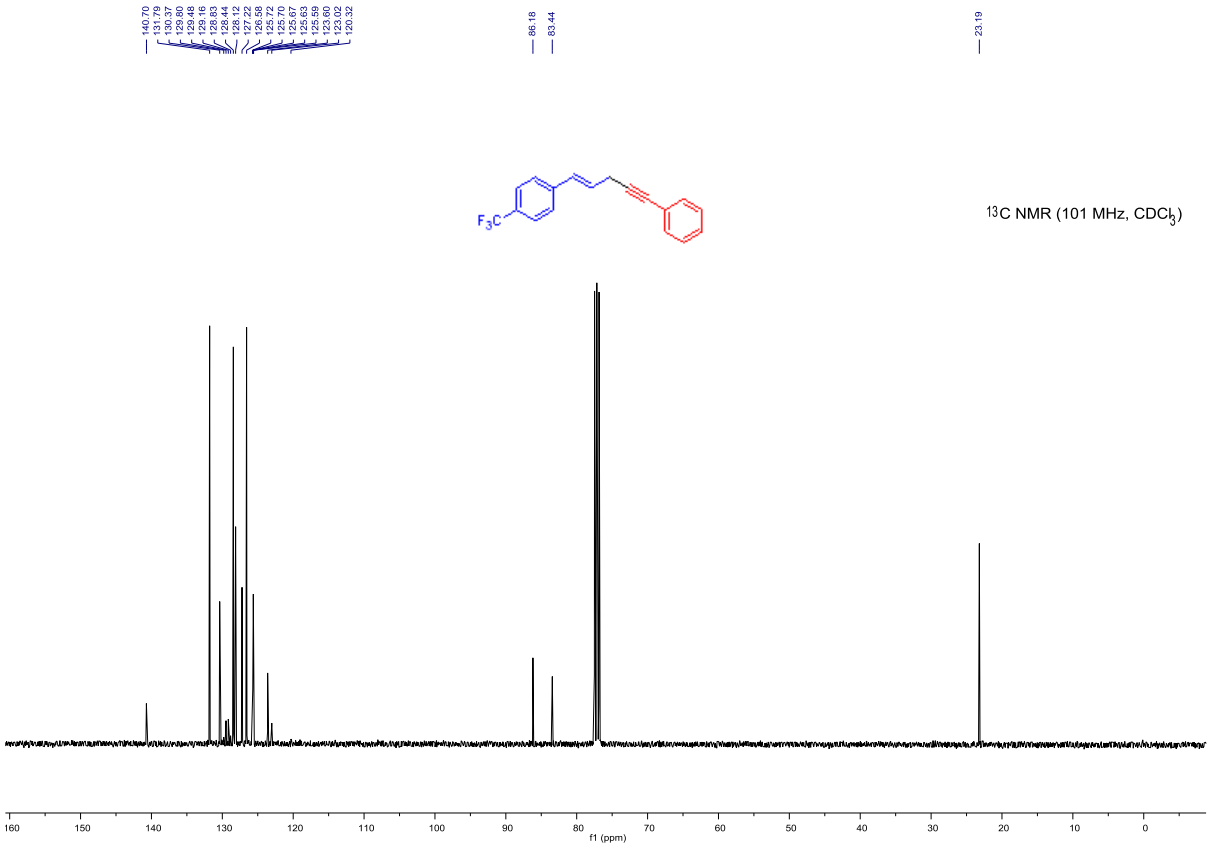
(13) (*E*)-(5-(4-chlorophenyl)pent-4-en-1-yn-1-yl)trimethylsilane (**3gb**)

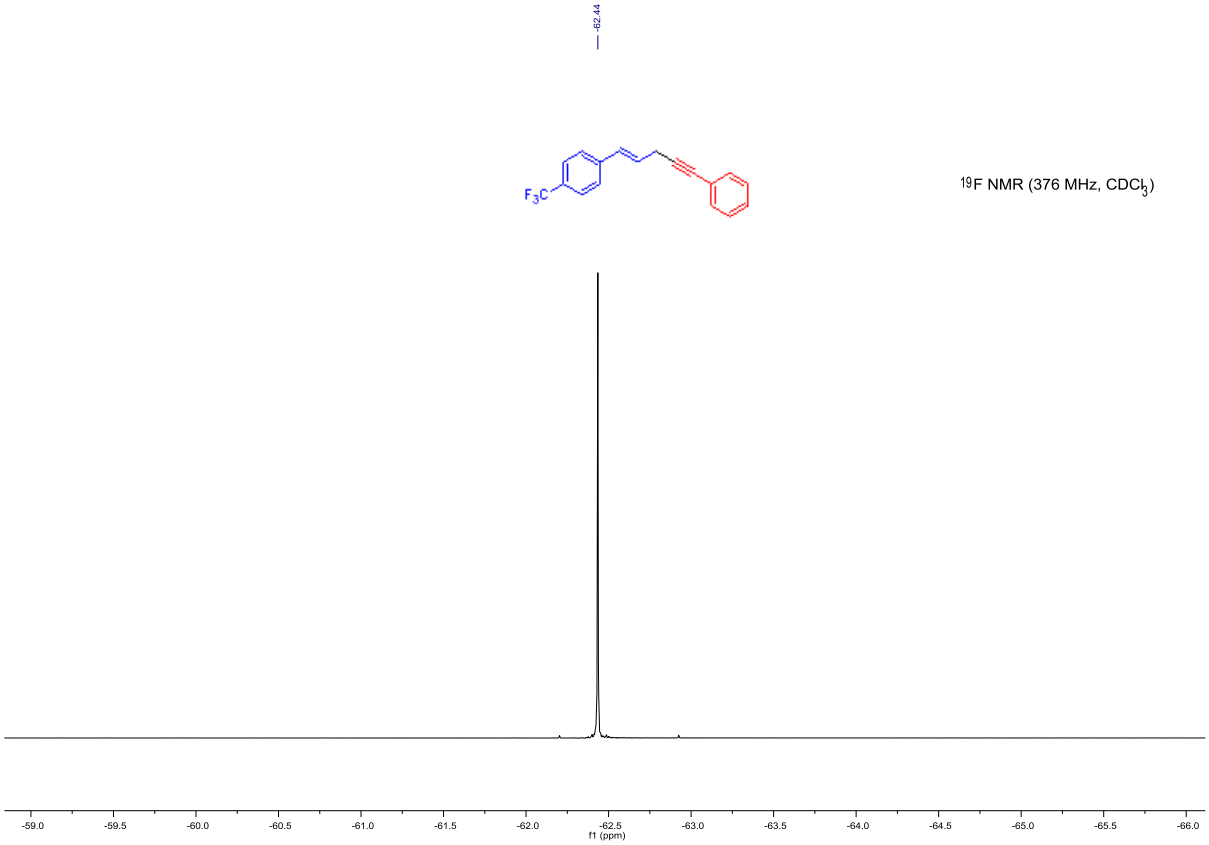




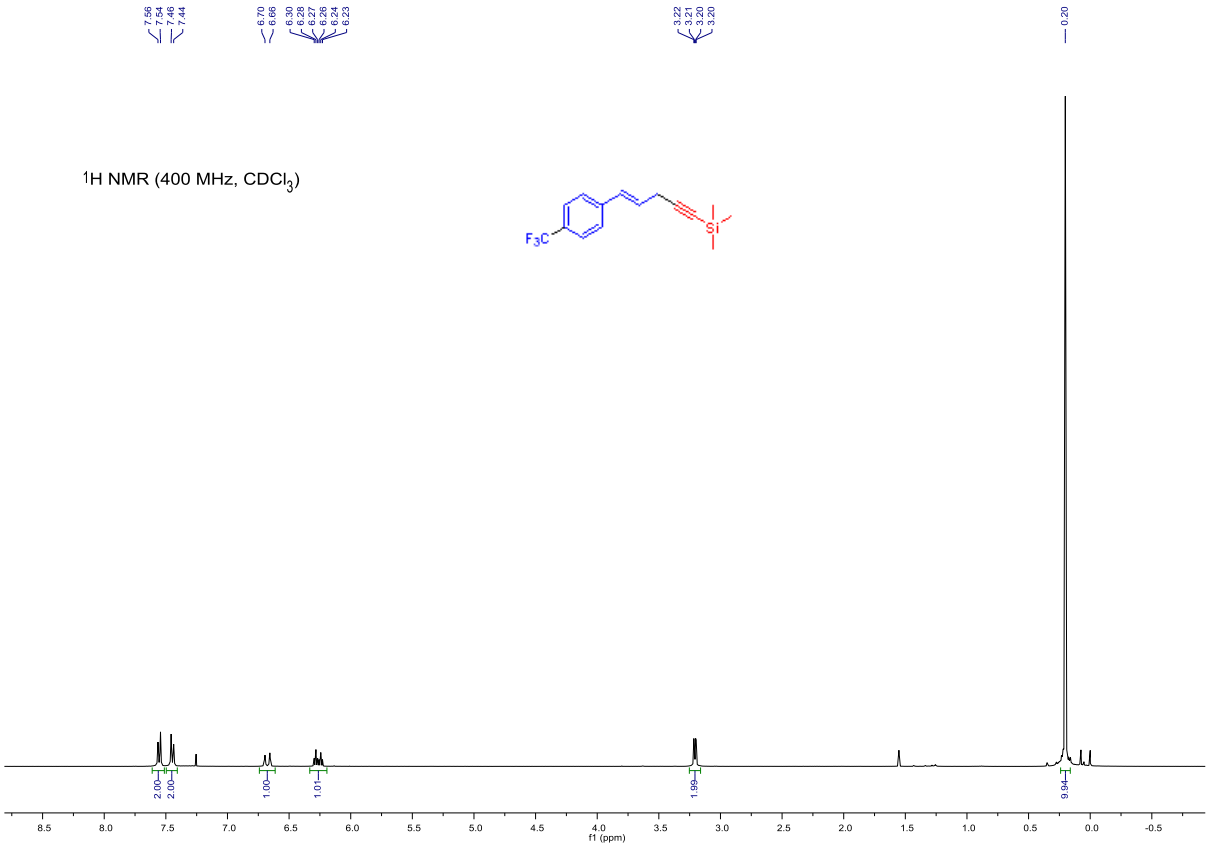
(14) (*E*)-1-(5-phenylpent-1-en-4-yn-1-yl)-4-(trifluoromethyl)benzene (**3ha**)

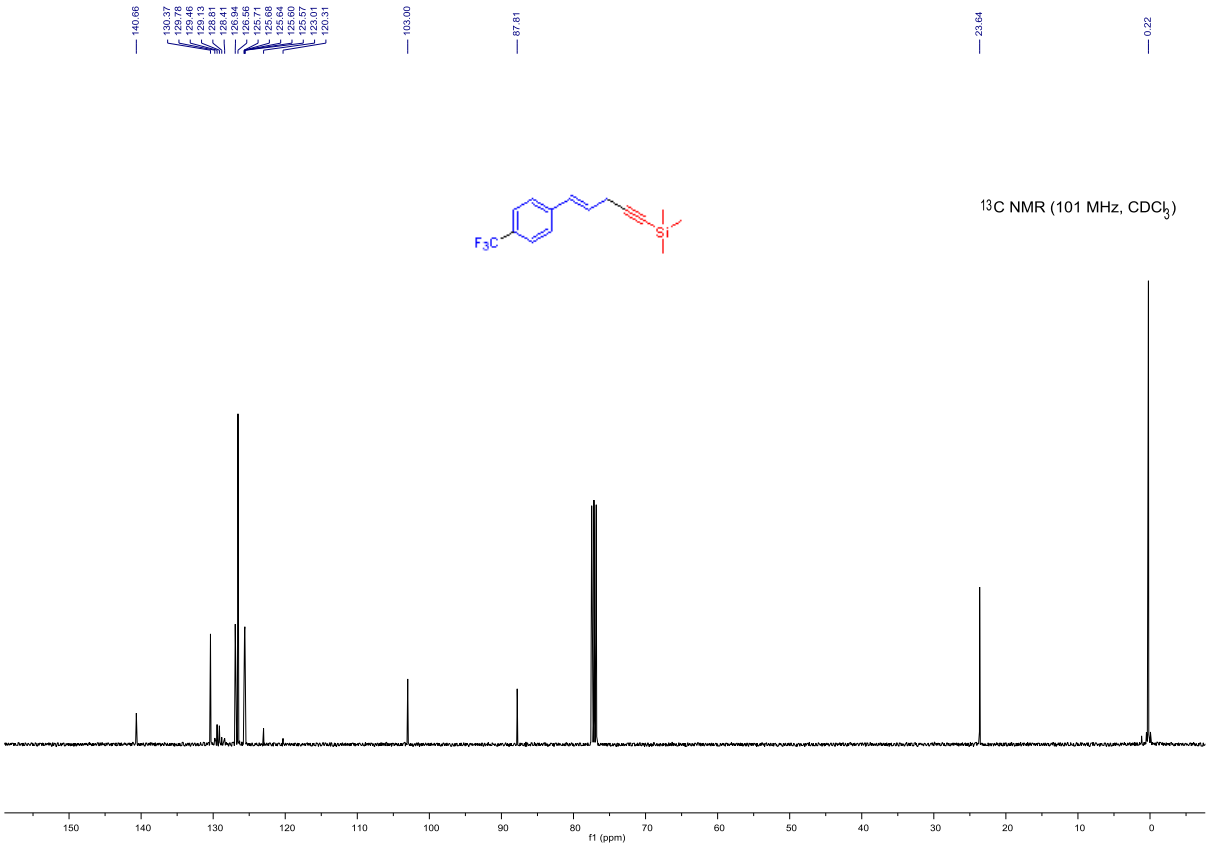


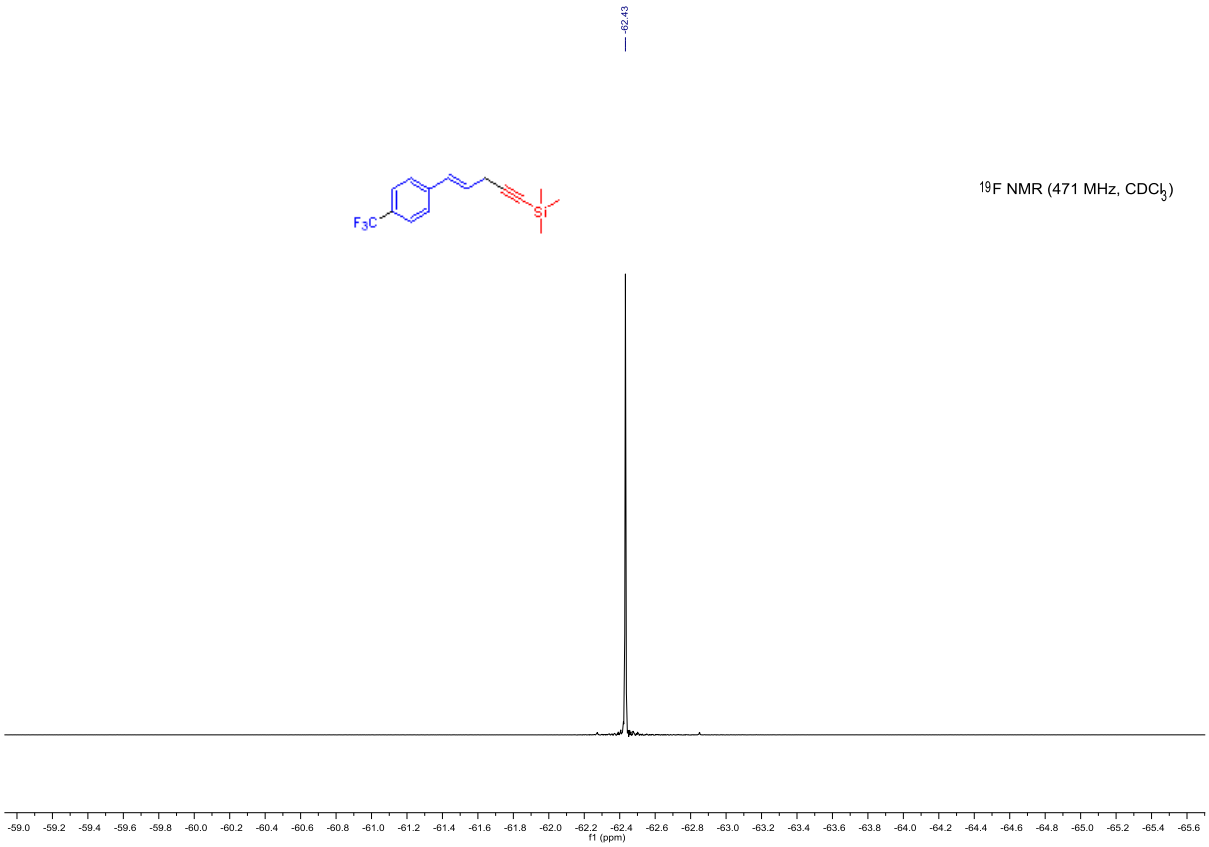



-62.44
F3C
19F NMR (376 MHz, CDCl3)
-59.0
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
f1 (ppm)

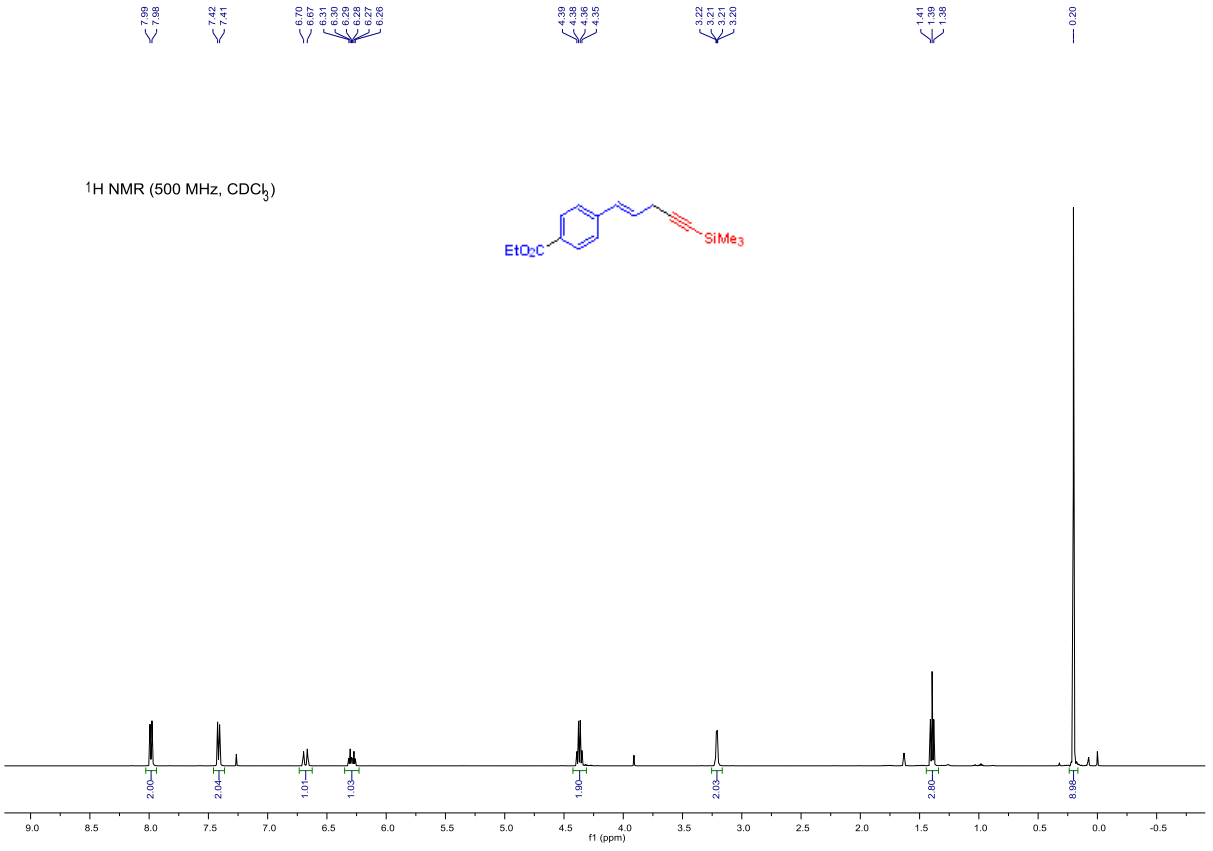
(15) (*E*)-trimethyl(5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yn-1-yl)silane (**3hb**)

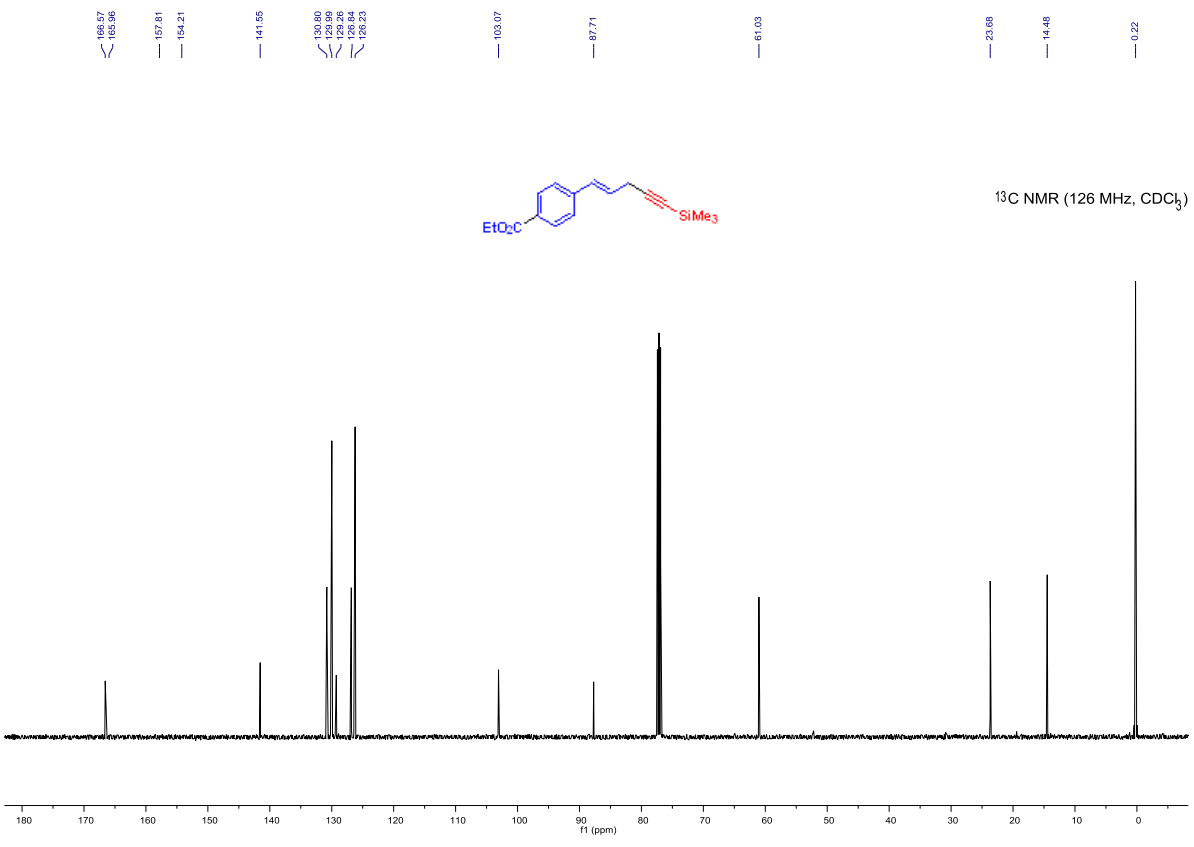




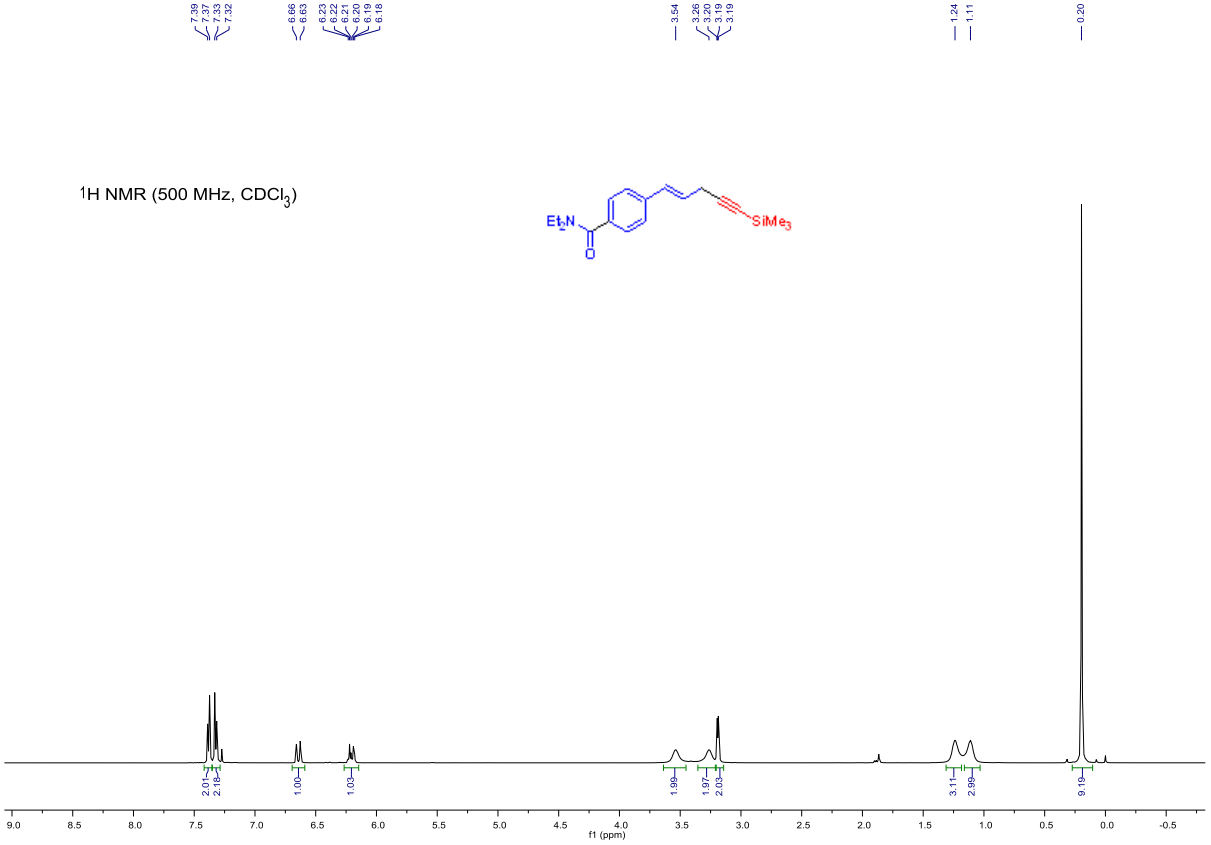

-62.43
F3C
Si
19F NMR (471 MHz, CDCl3)
-59.0 -59.2 -59.4 -59.6 -59.8 -60.0 -60.2 -60.4 -60.6 -60.8 -61.0 -61.2 -61.4 -61.6 -61.8 -62.0 -62.2 -62.4 -62.6 -62.8 -63.0 -63.2 -63.4 -63.6 -63.8 -64.0 -64.2 -64.4 -64.6 -64.8 -65.0 -65.2 -65.4 -65.6
f1 (ppm)

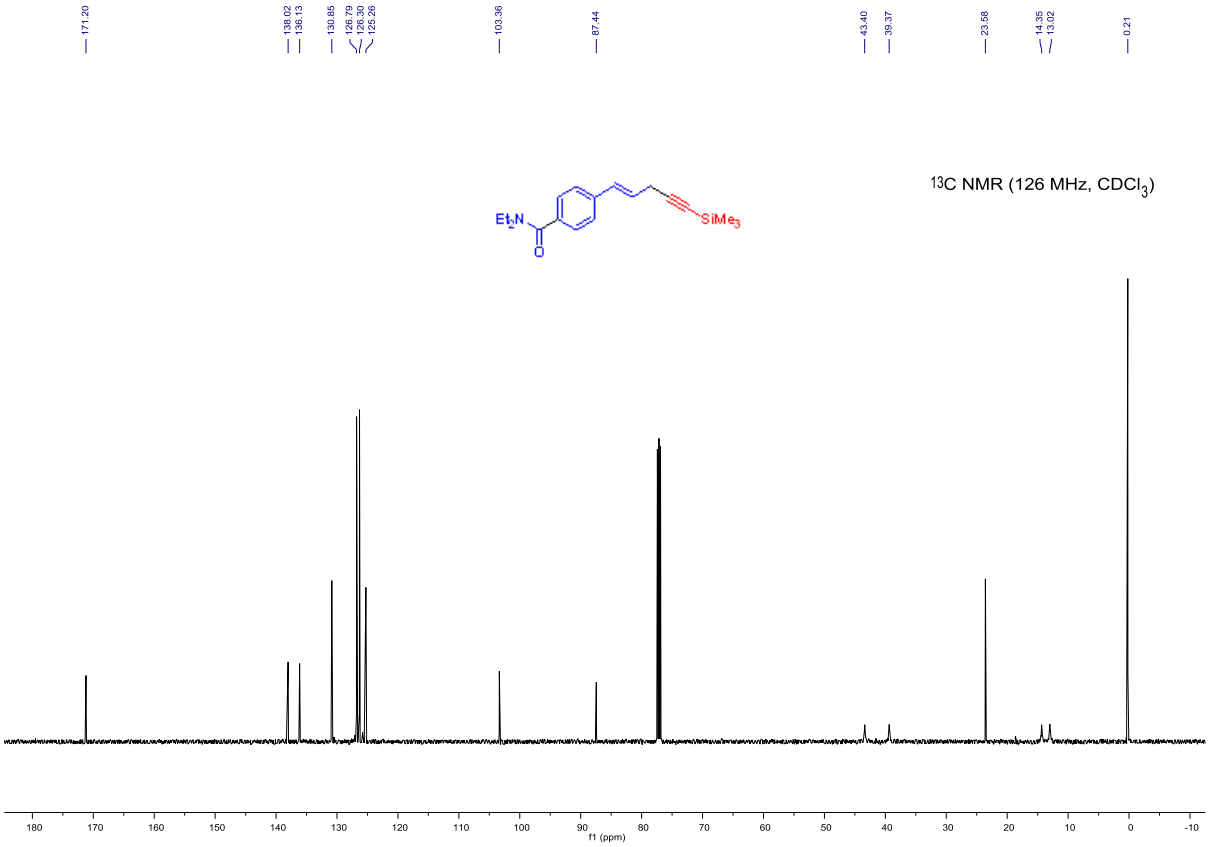
(16) ethyl (*E*)-4-(5-(trimethylsilyl)pent-1-en-4-yn-1-yl)benzoate (**3i**)



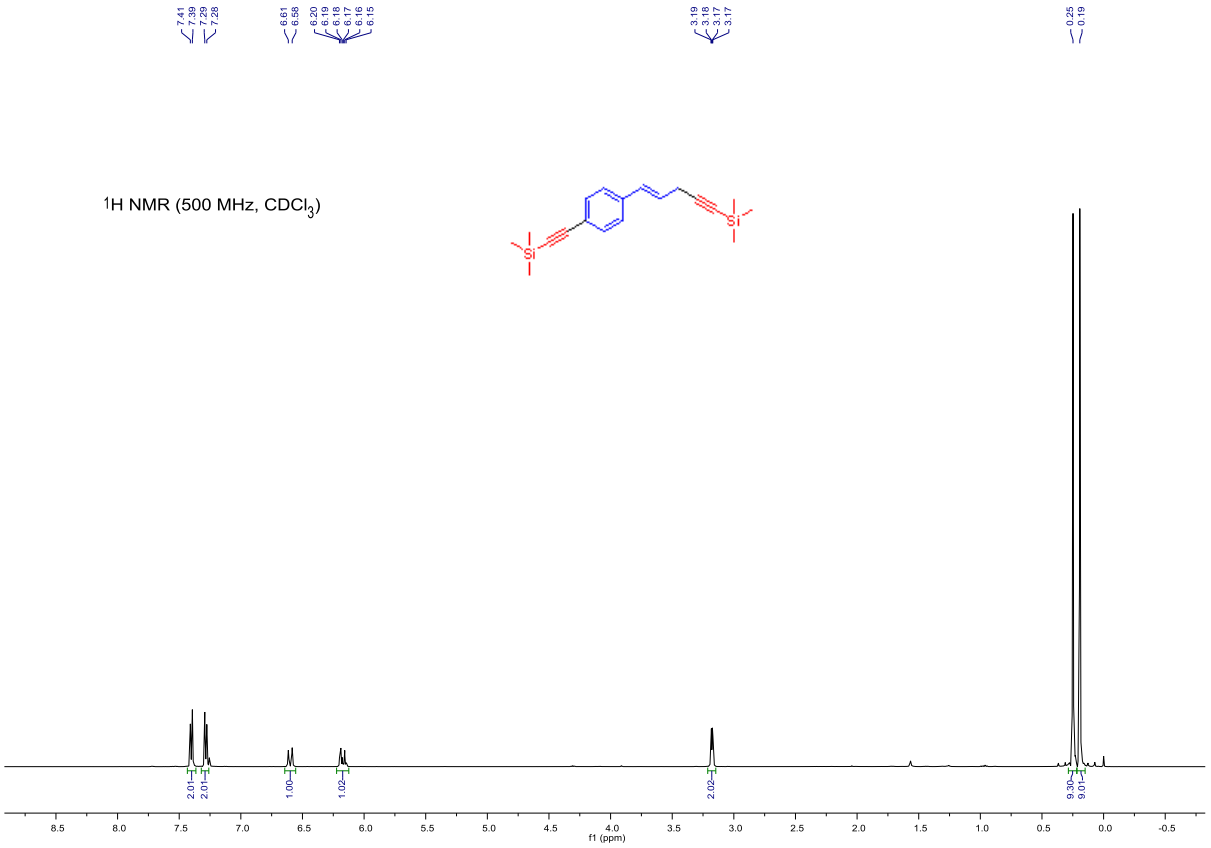


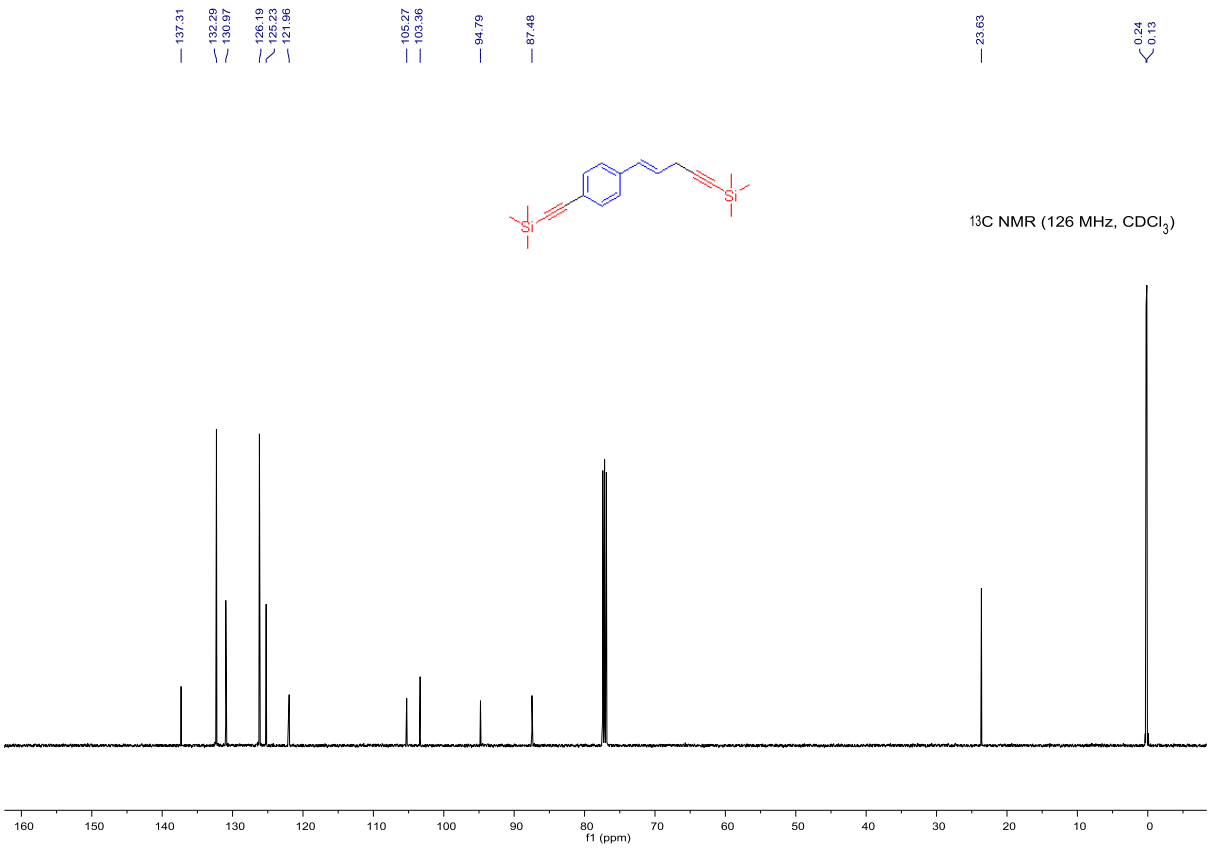
(17) (*E*)-N,N-diethyl-4-(5-(trimethylsilyl)pent-1-en-4-yn-1-yl)benzamide (**3j**)



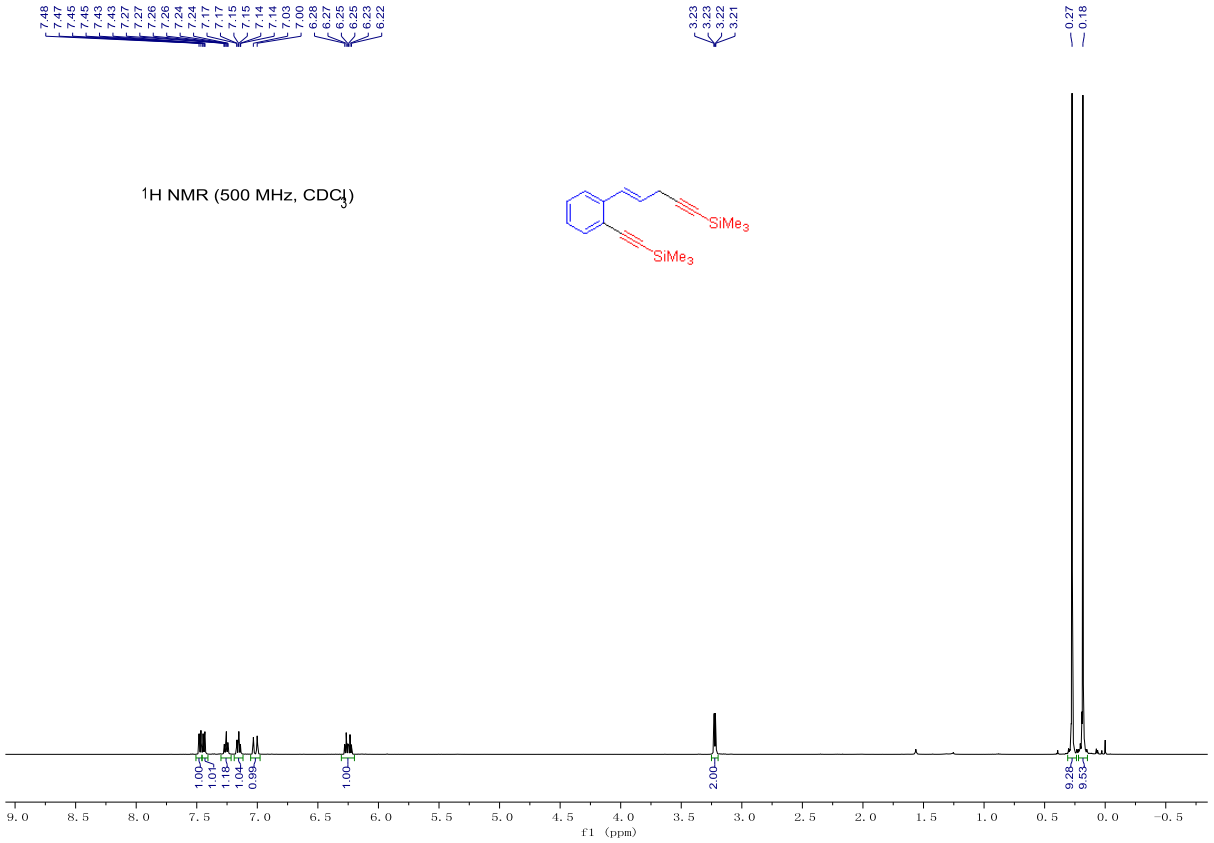


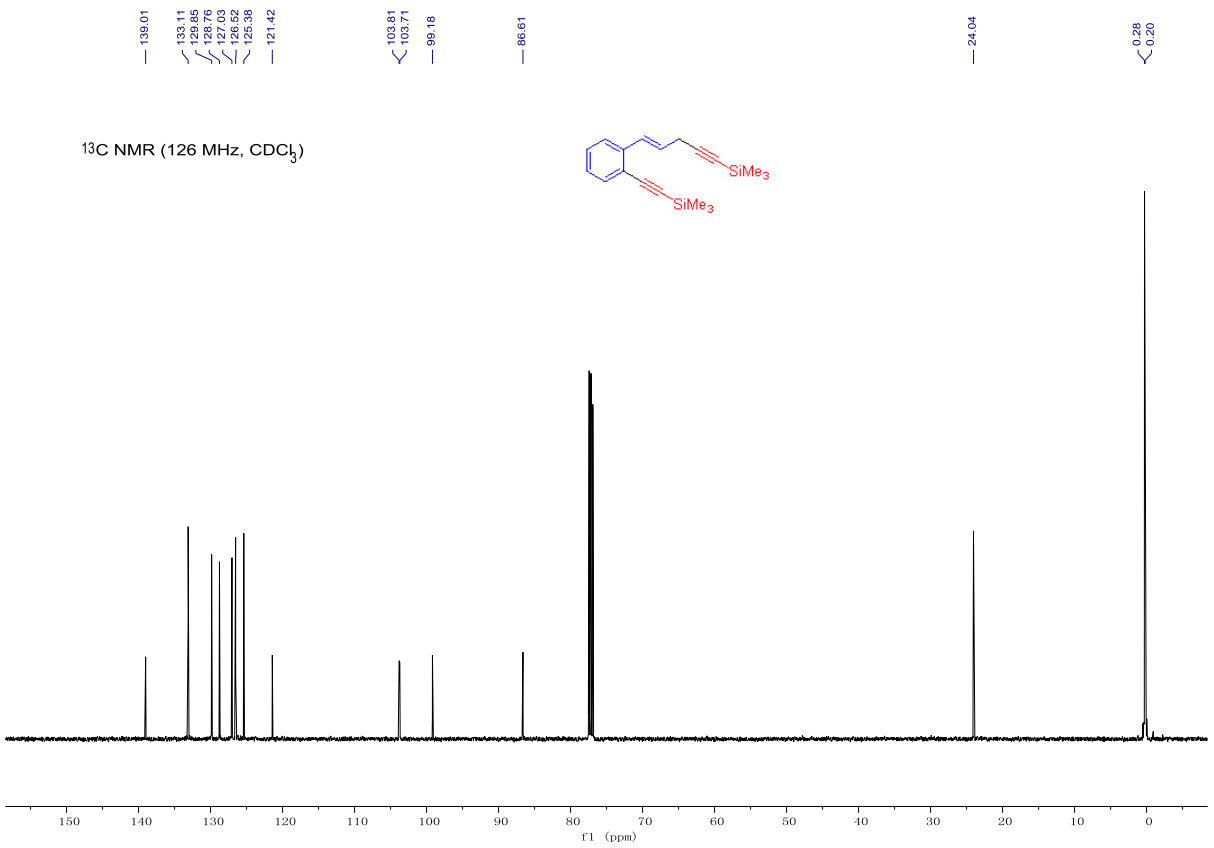
(18) (*E*)-trimethyl(5-(4-((trimethylsilyl)ethynyl)phenyl)pent-4-en-1-yn-1-yl)silane (**3k**)



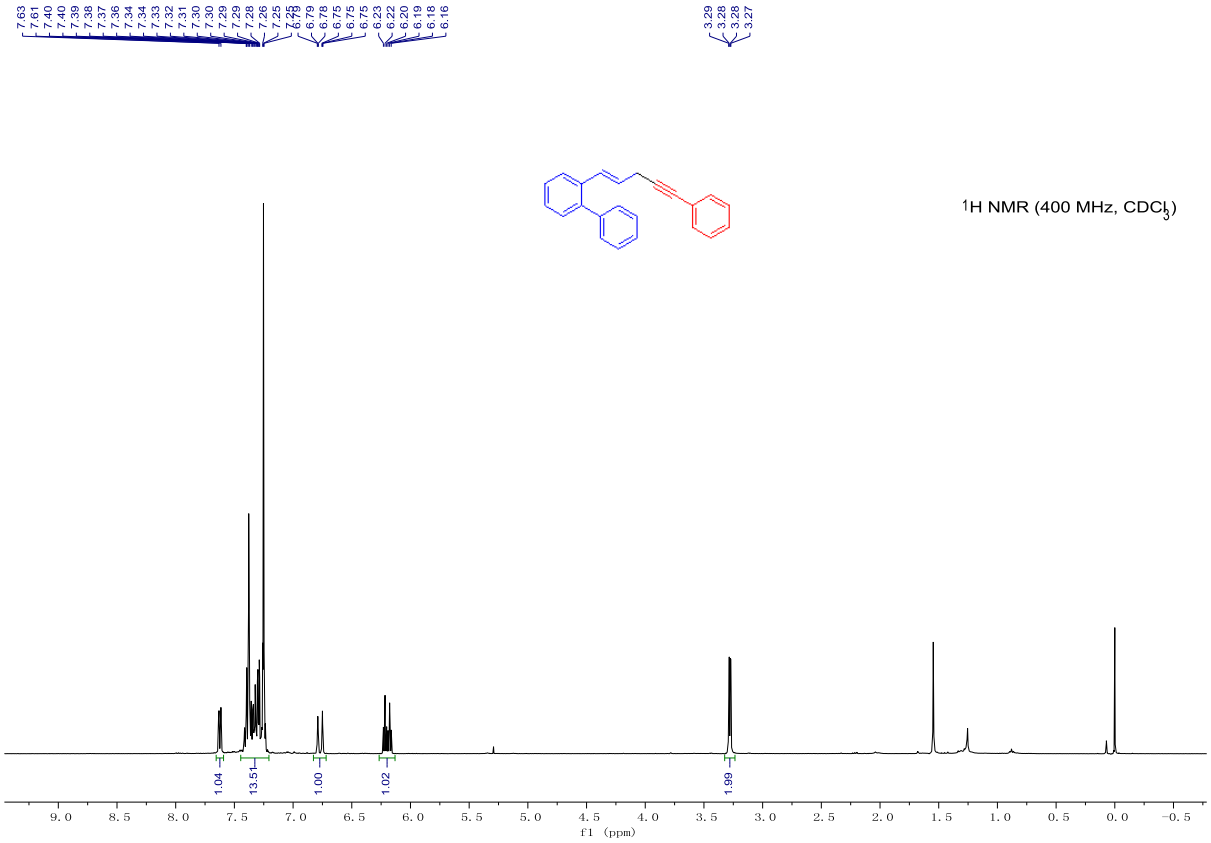


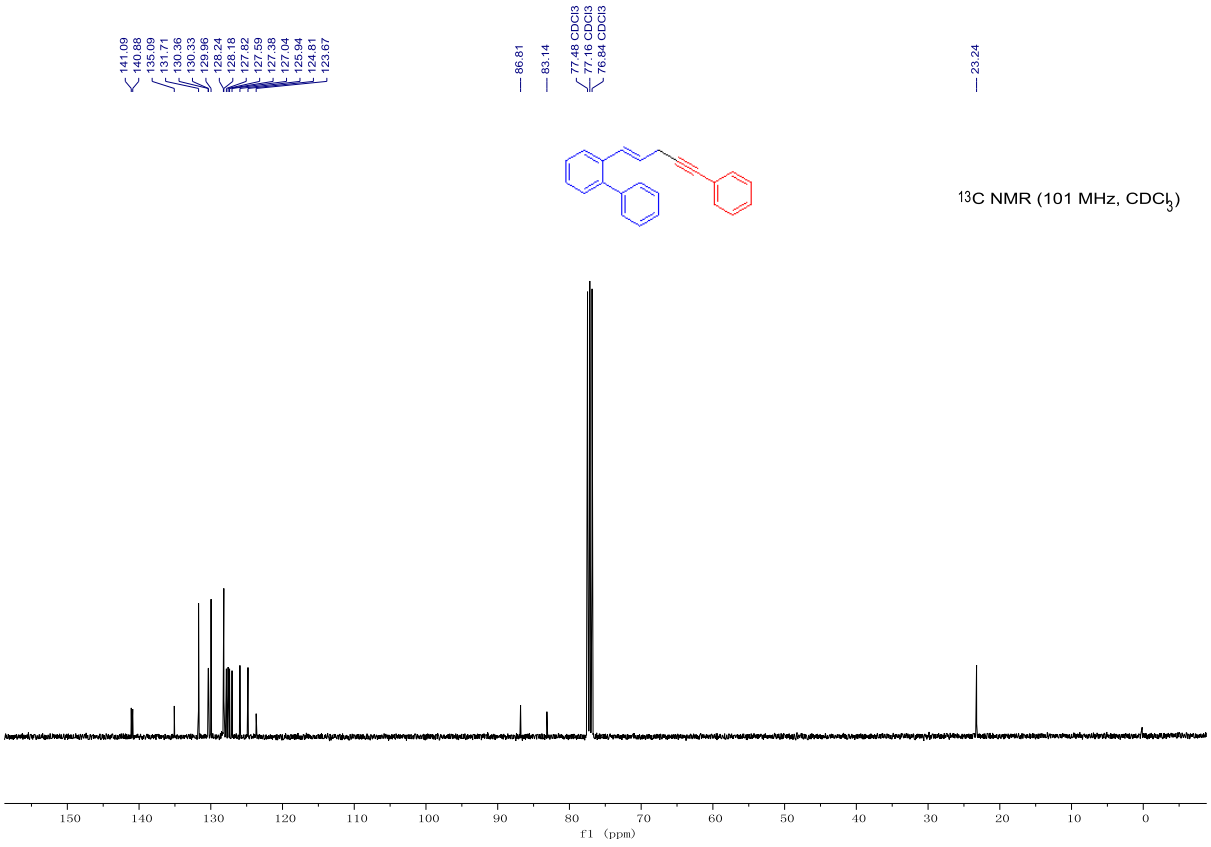
(19) (*E*)-trimethyl(5-(2-((trimethylsilyl)ethynyl)phenyl)pent-4-en-1-yn-1-yl)silane (**3l**)



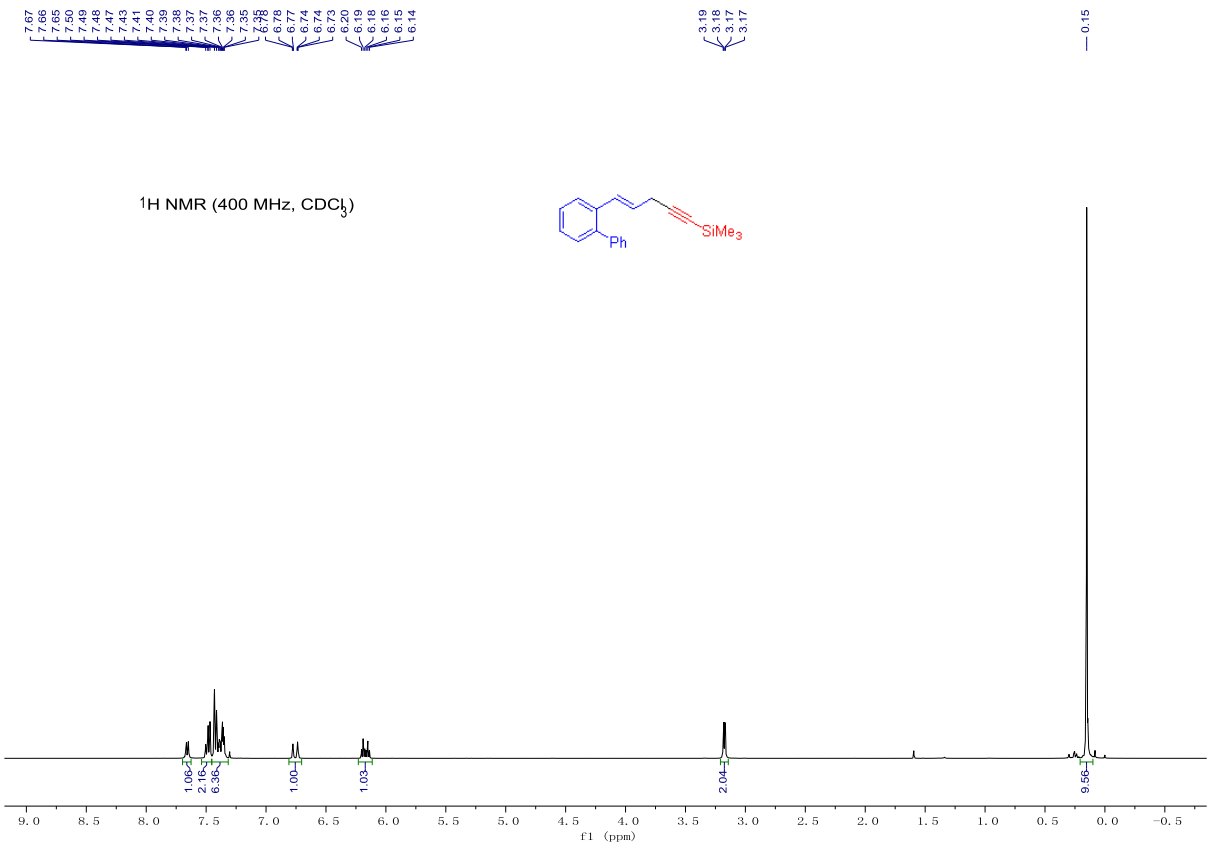


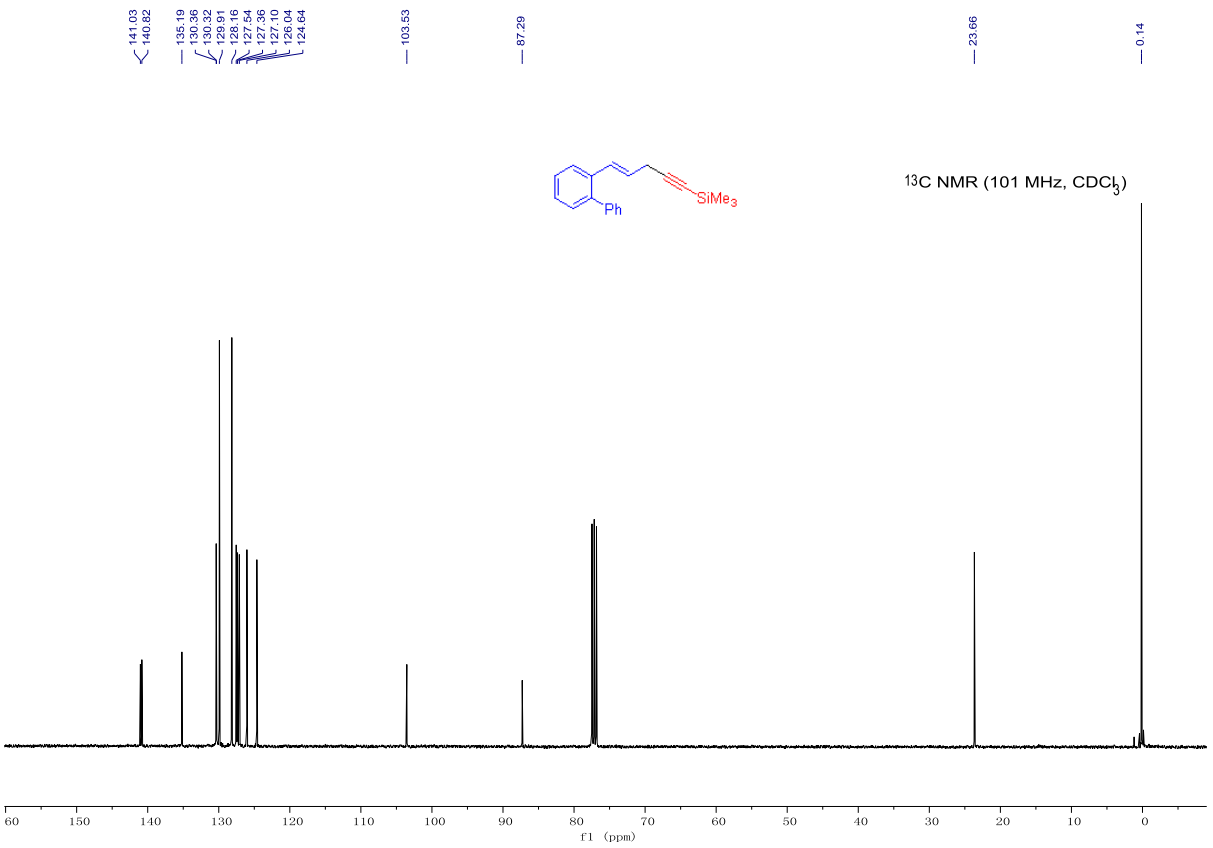
(20) (*E*)-2-(5-phenylpent-1-en-4-yn-1-yl)-1,1'-biphenyl (**3ma**)



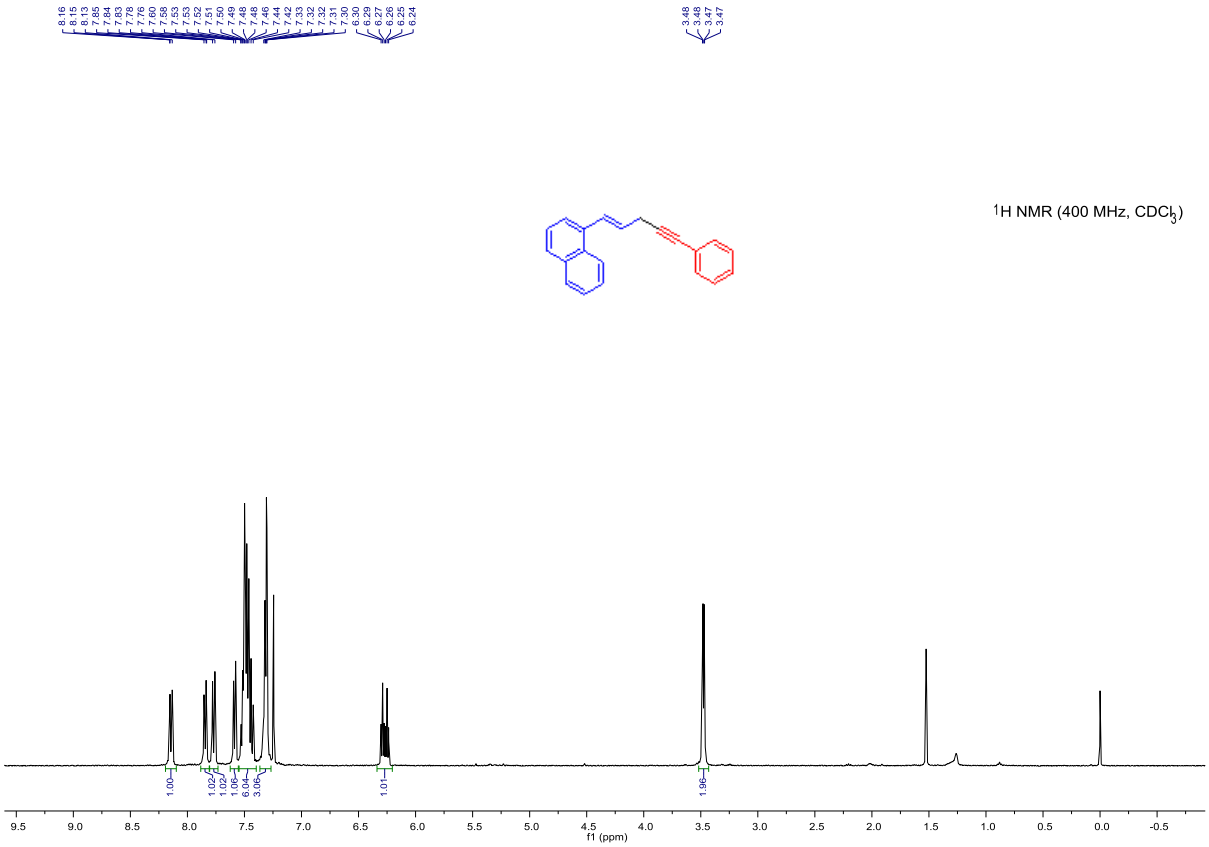


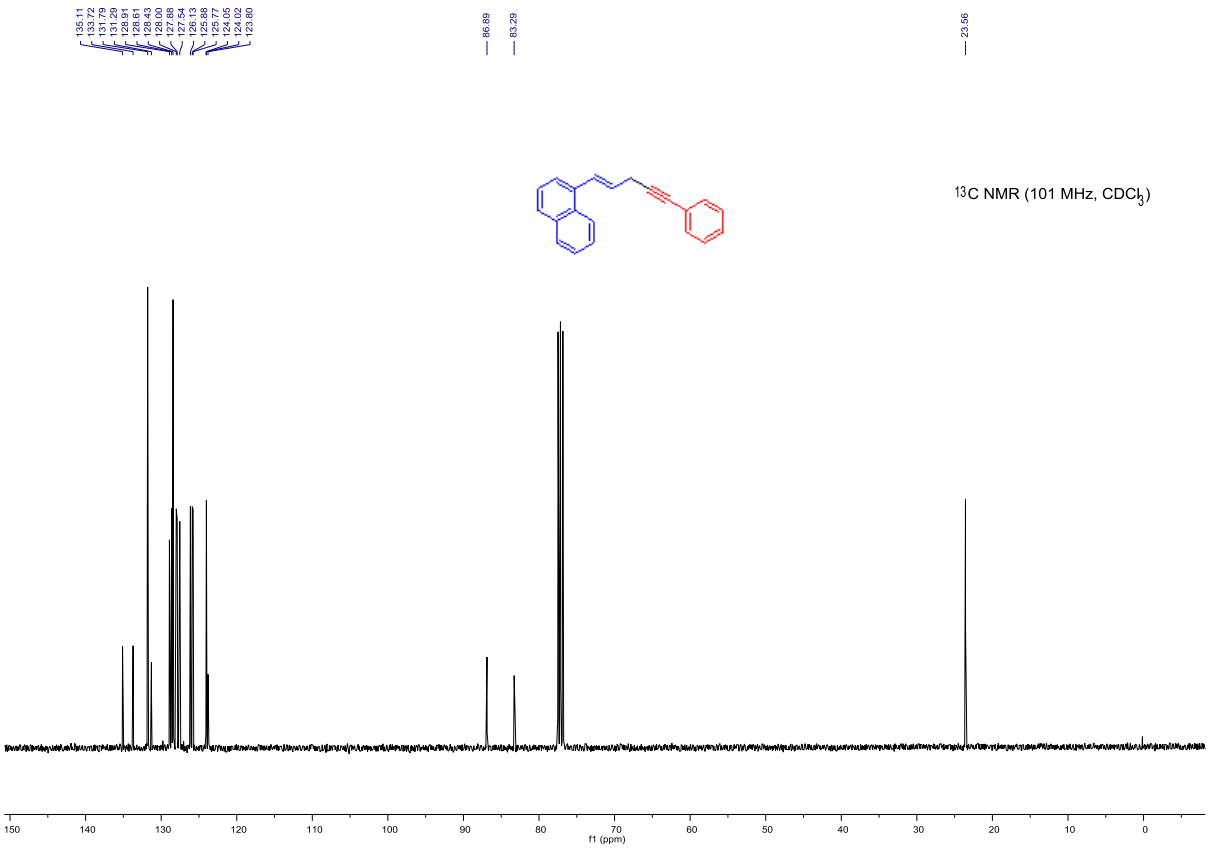
(21) (*E*)-(5-([1,1'-biphenyl]-2-yl)pent-4-en-1-yn-1-yl)trimethylsilane (**3mb**)



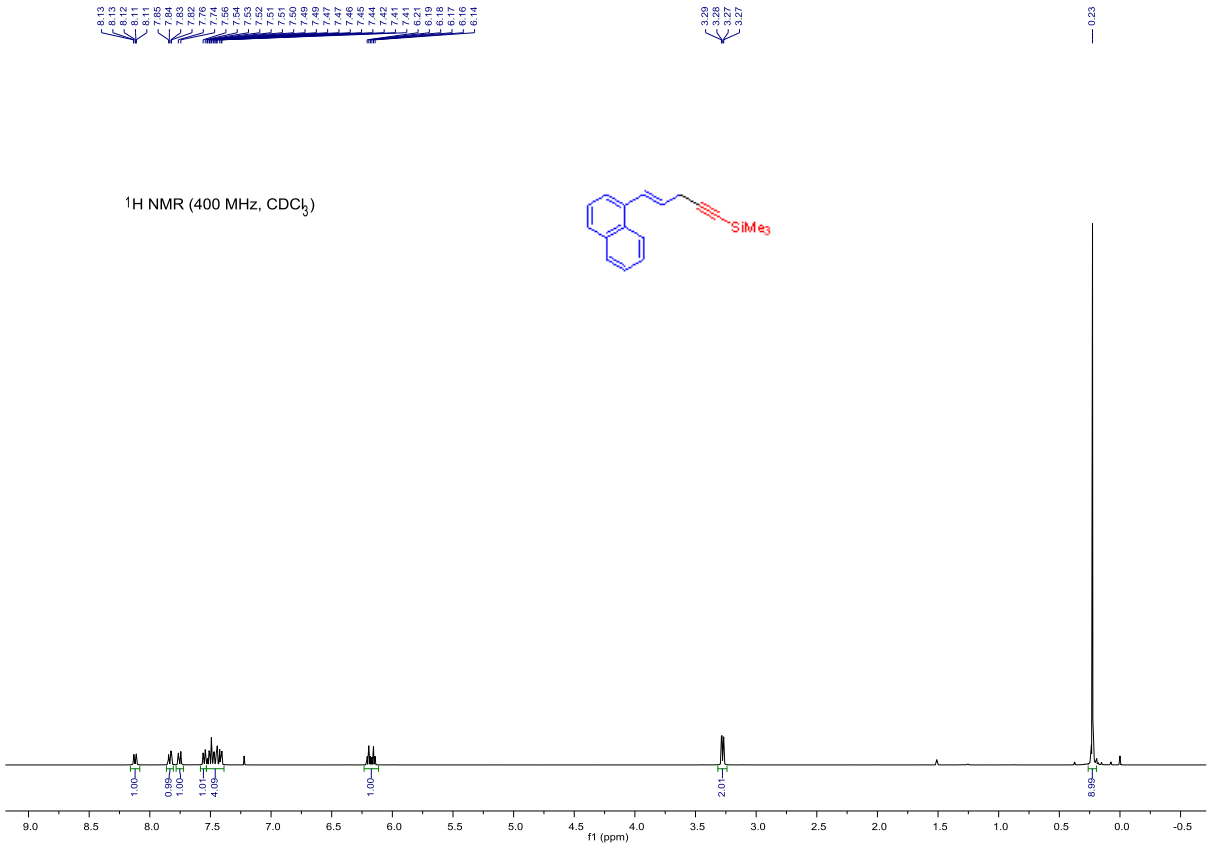


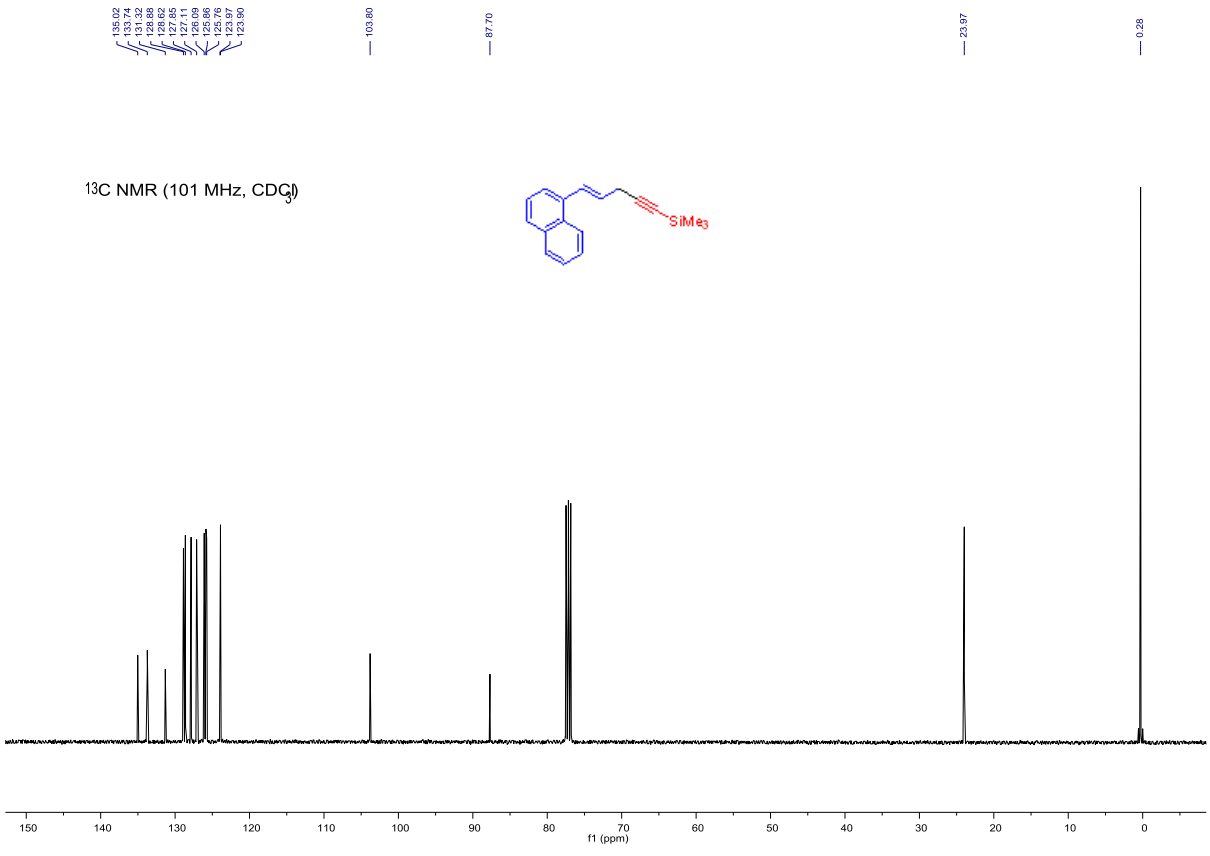
(22) (*E*)-1-(5-phenylpent-1-en-4-yn-1-yl)naphthalene (**3na**)



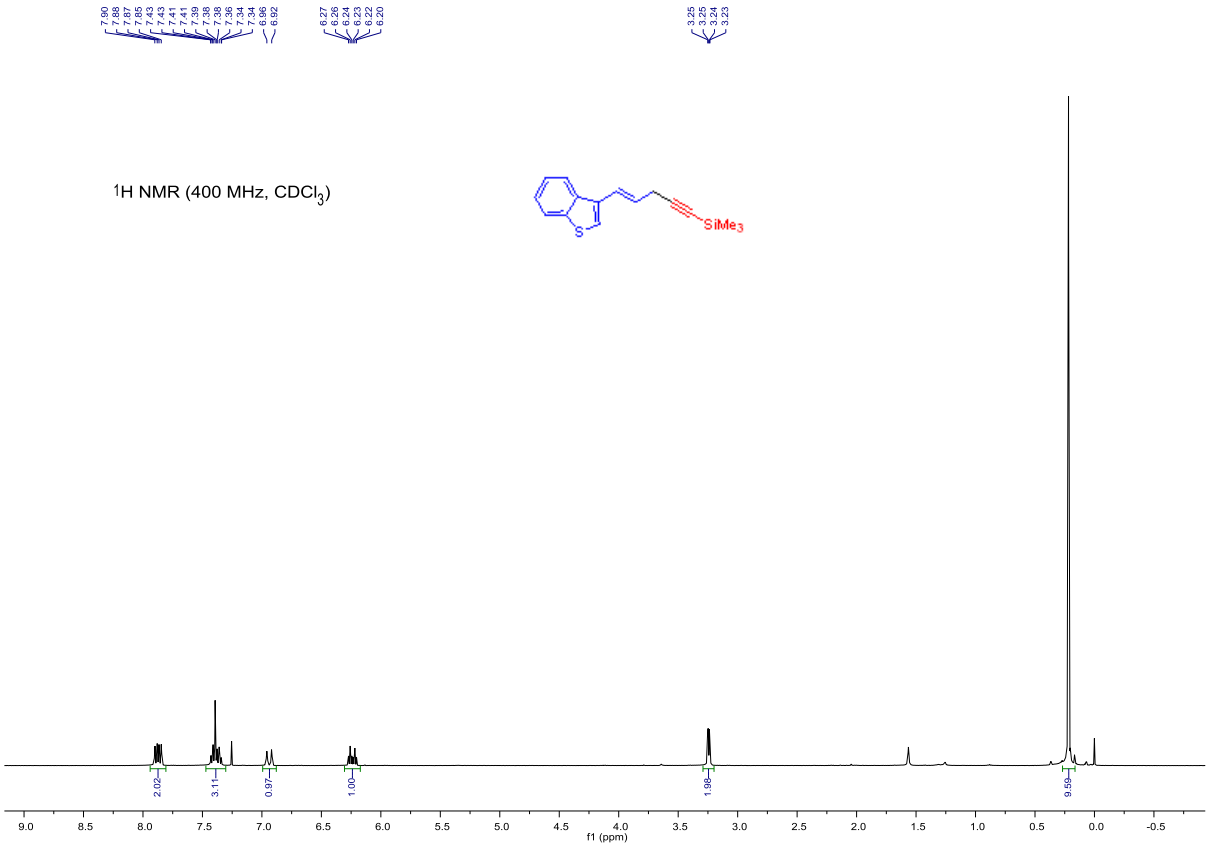


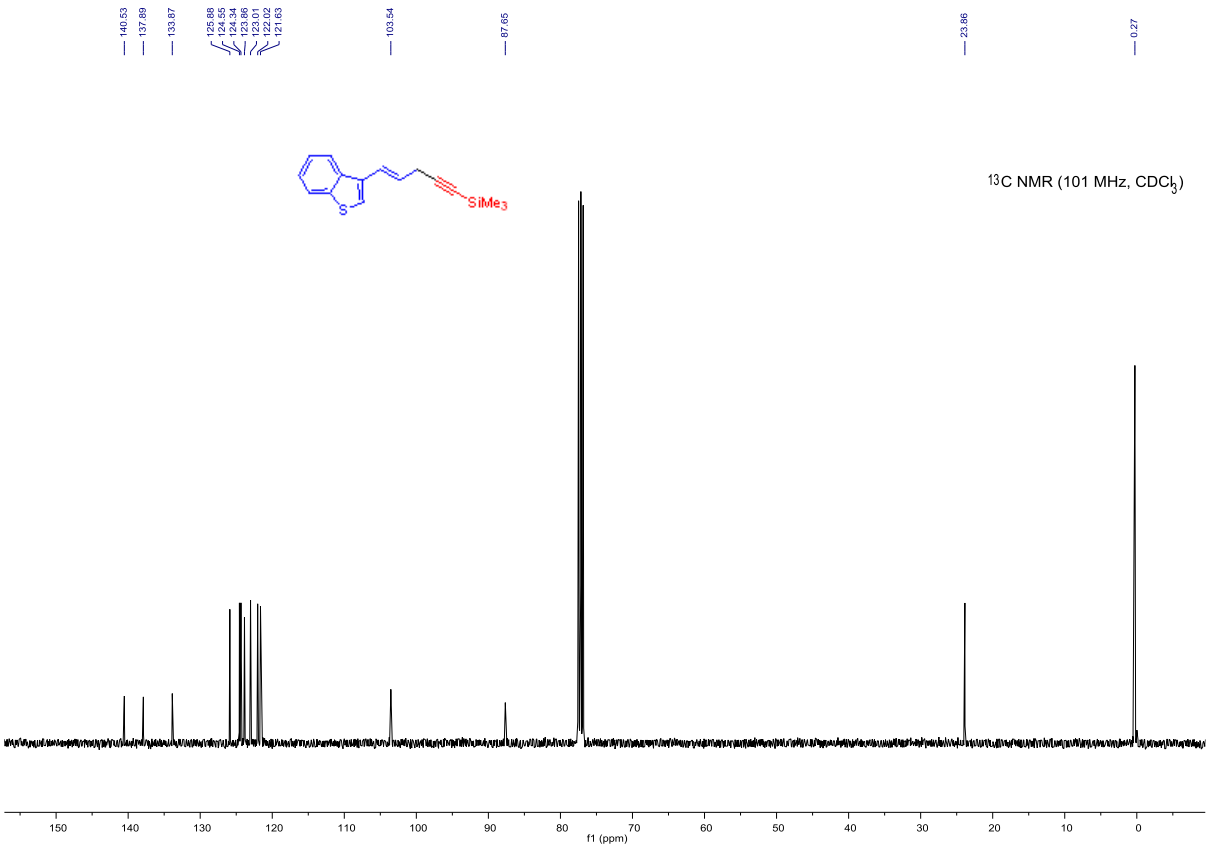
(23) (*E*)-trimethyl(5-(naphthalen-1-yl)pent-4-en-1-yn-1-yl)silane (**3nb**)



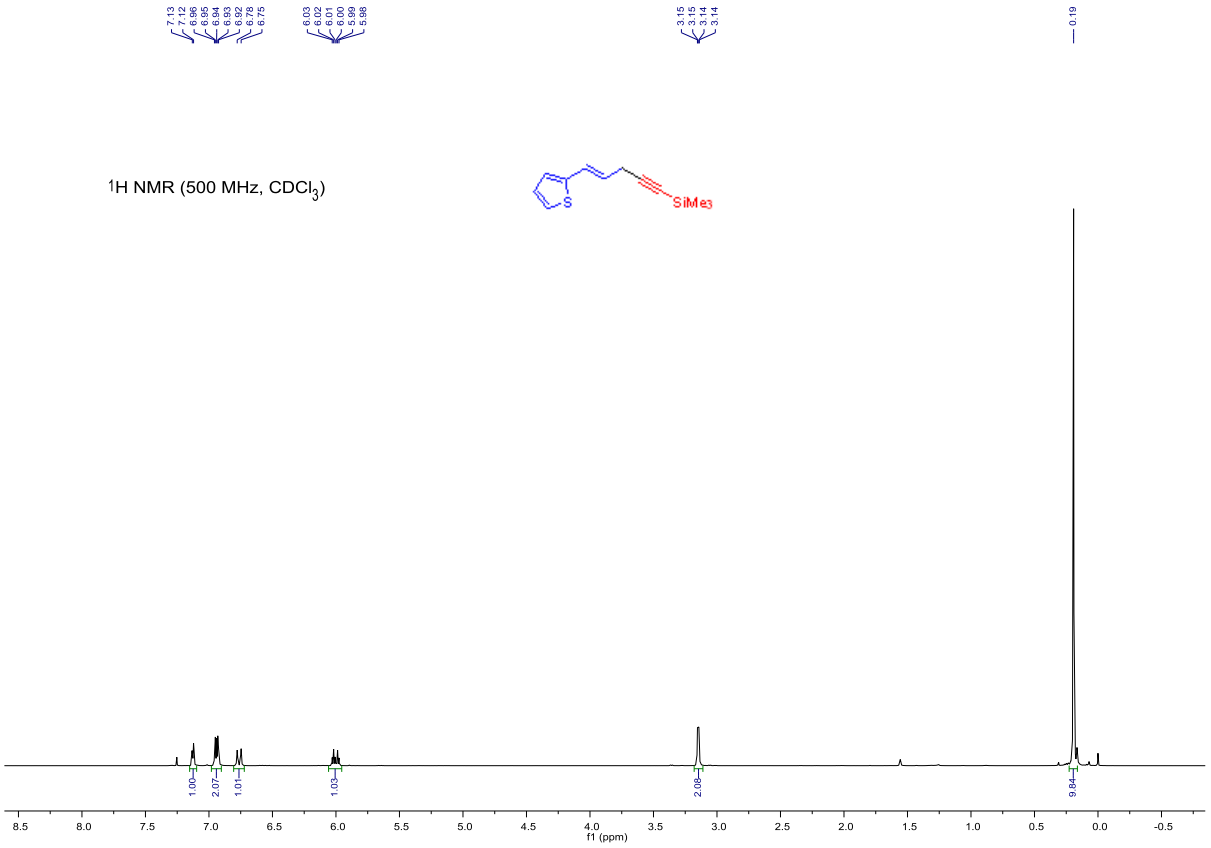


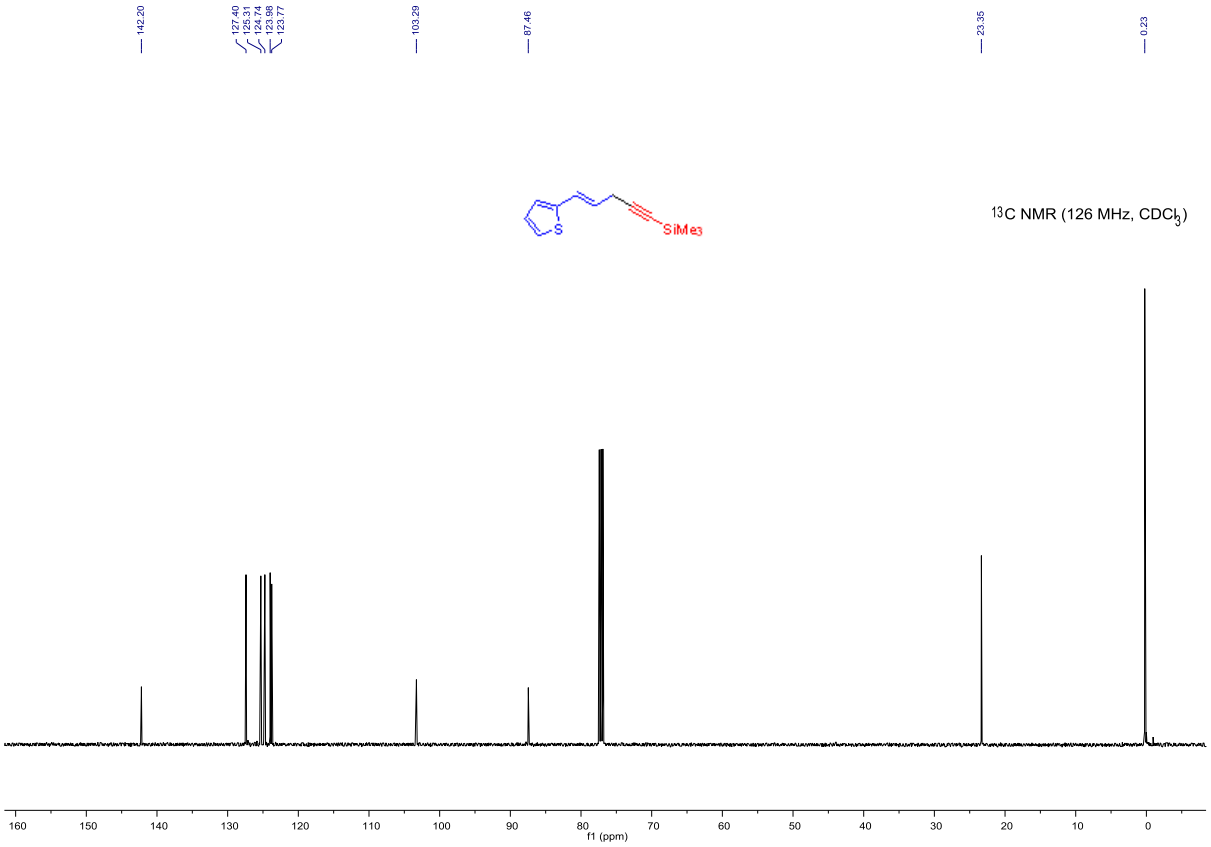
(24) (*E*)-(5-(benzo[b]thiophen-3-yl)pent-4-en-1-yn-1-yl)trimethylsilane (**3o**)



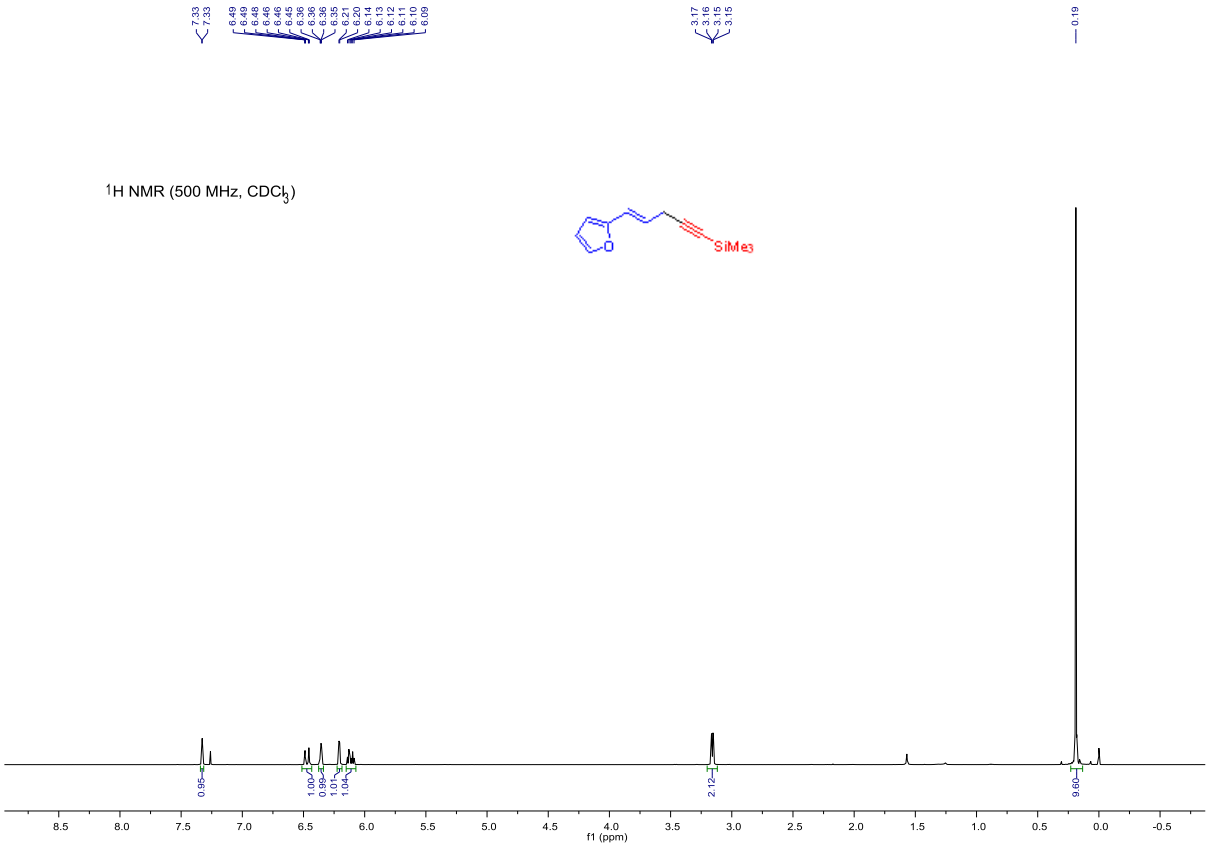


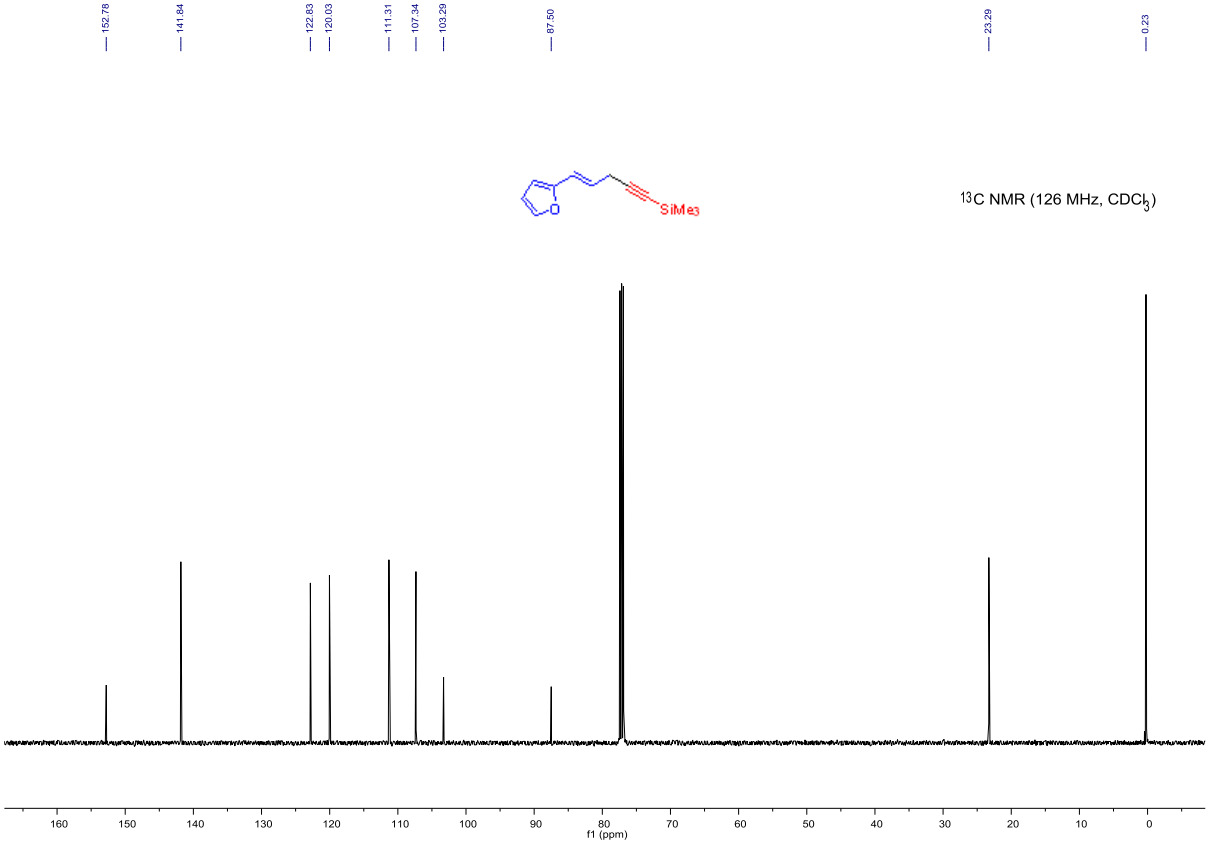
(25) (*E*)-trimethyl(5-(thiophen-2-yl)pent-4-en-1-yn-1-yl)silane (**3p**)



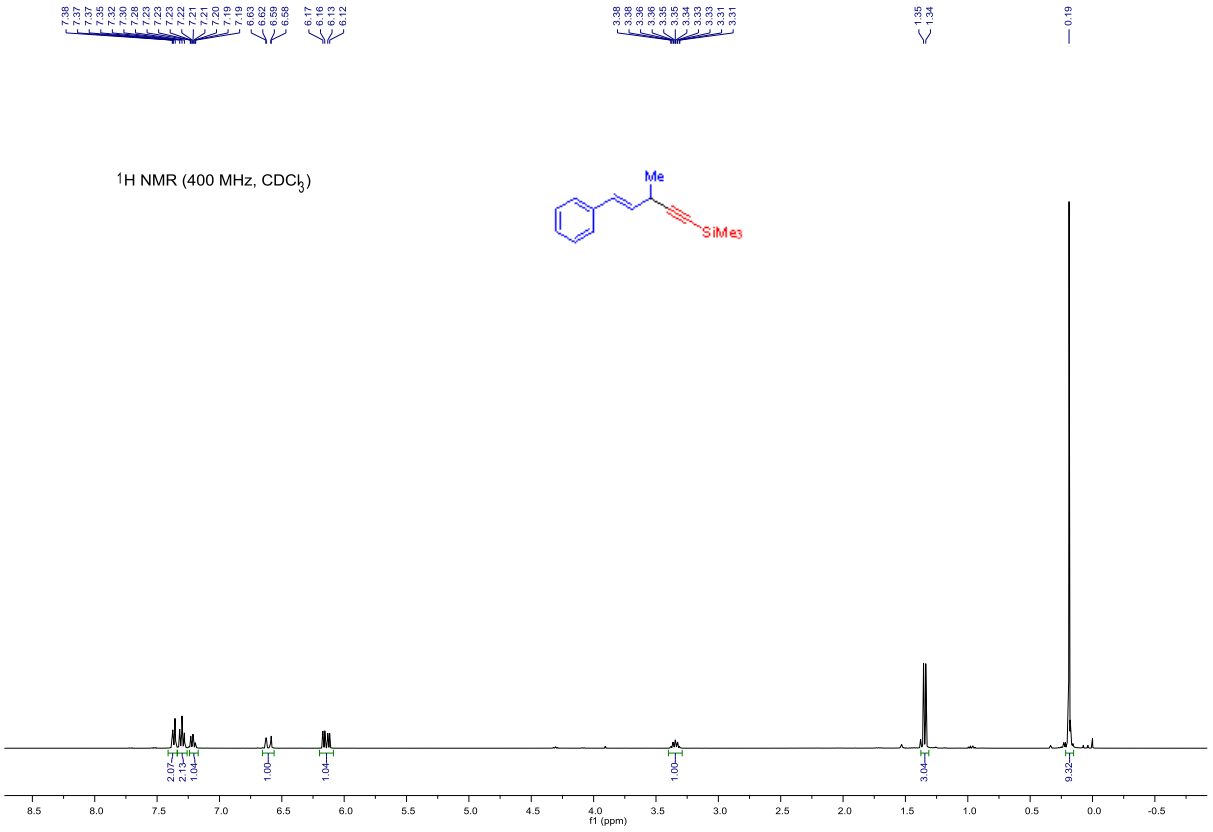


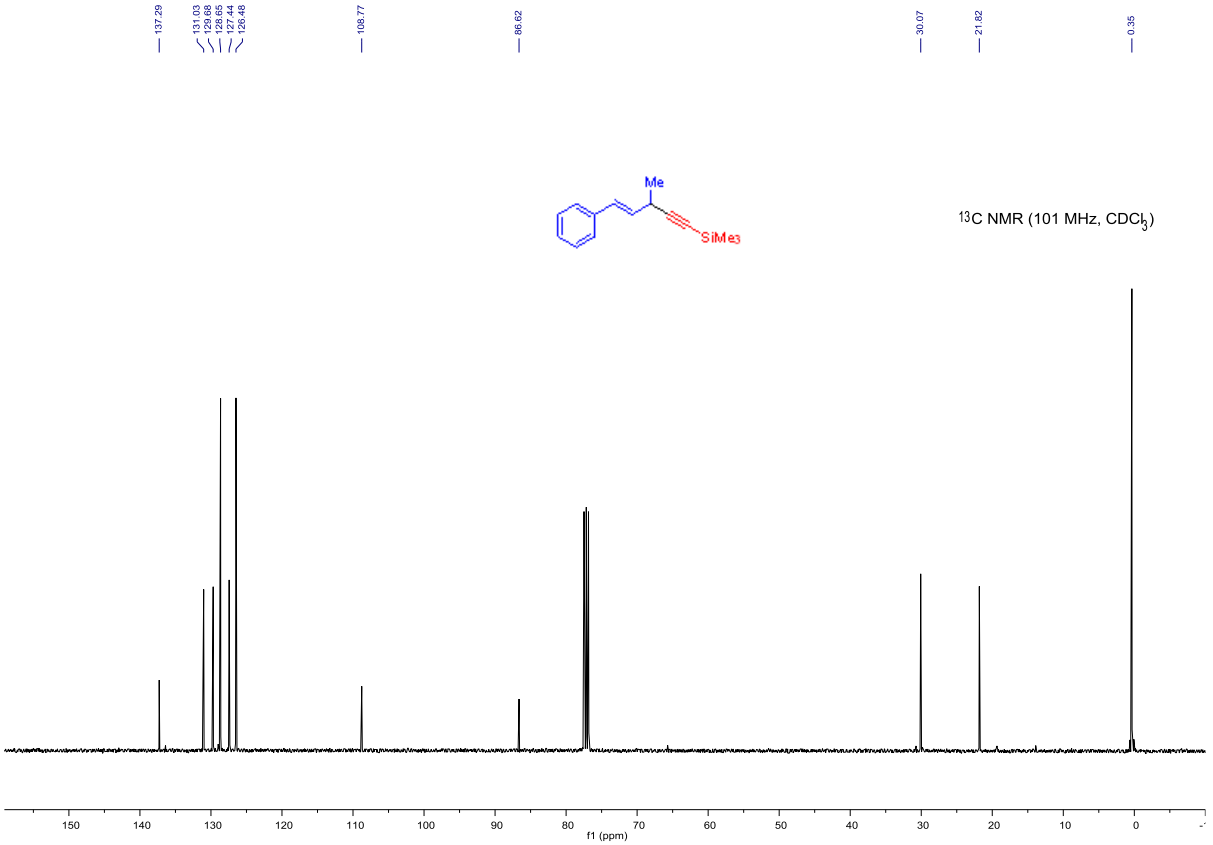
(26) (*E*)-(5-(furan-2-yl)pent-4-en-1-yn-1-yl)trimethylsilane (**3q**)



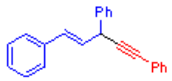


(27) (*E*)-trimethyl(3-methyl-5-phenylpent-4-en-1-yn-1-yl)silane (**3r**)

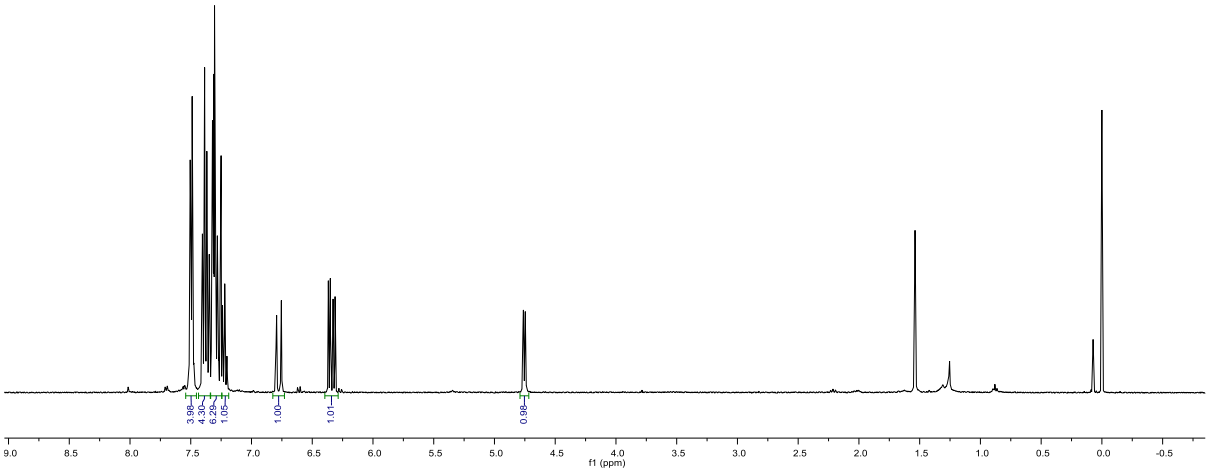


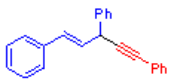


(28) (*E*)-pent-1-en-4-yne-1,3,5-triyltribenzene (**3sa**)



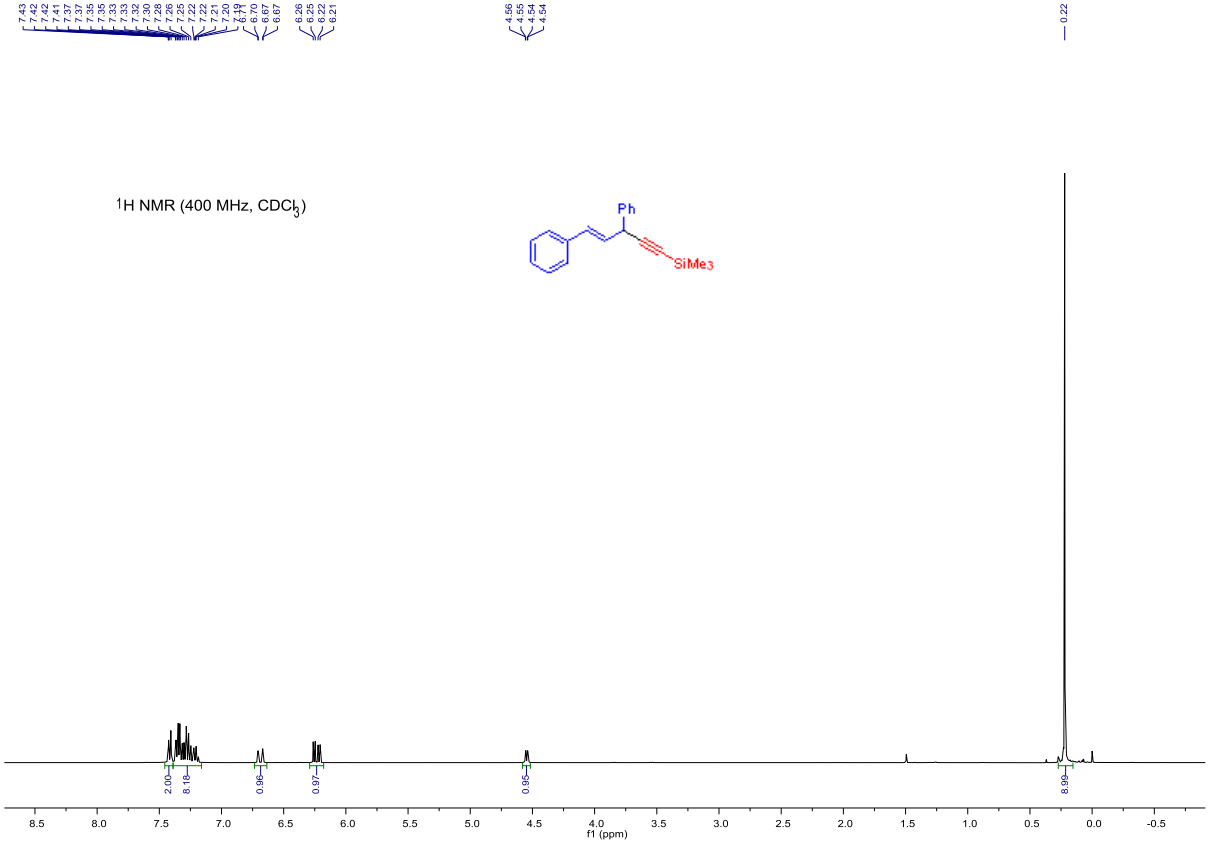
^{1}H NMR (400 MHz, $CDCl_3$)

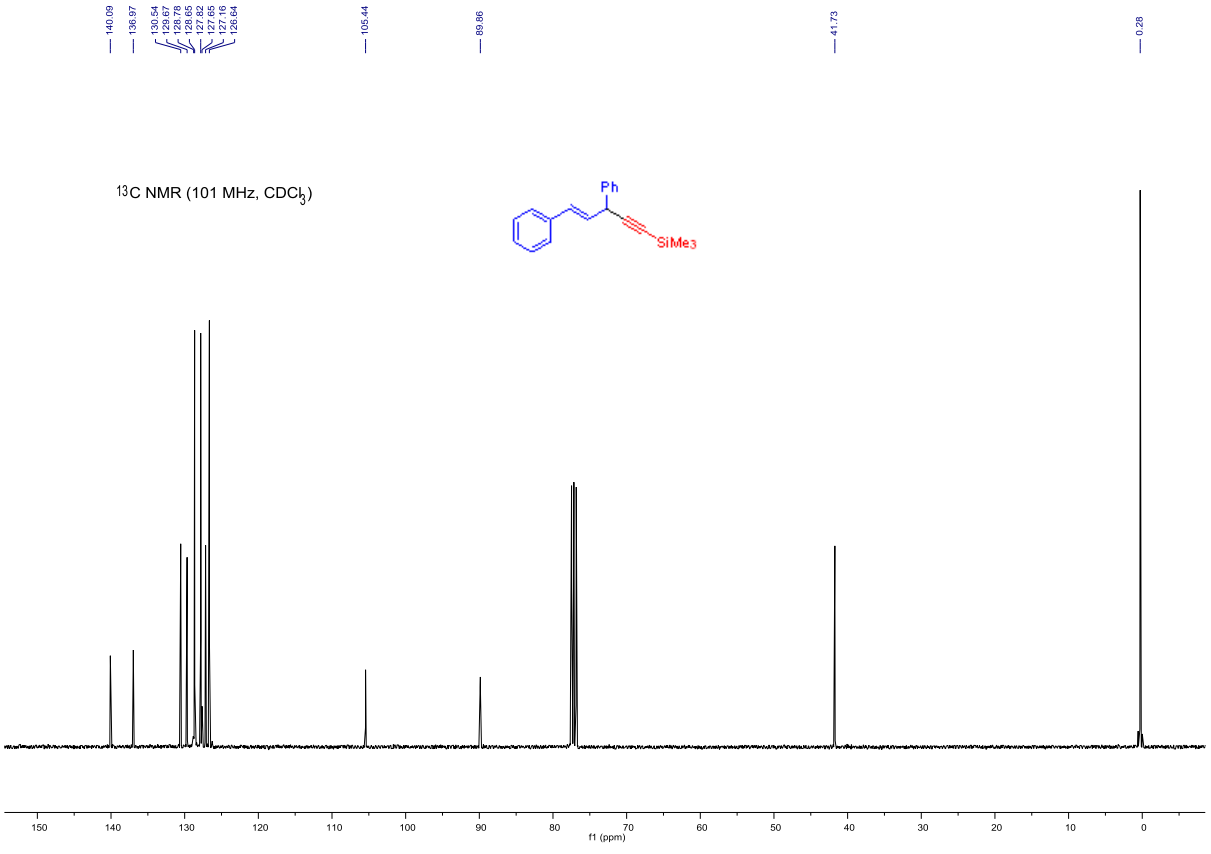




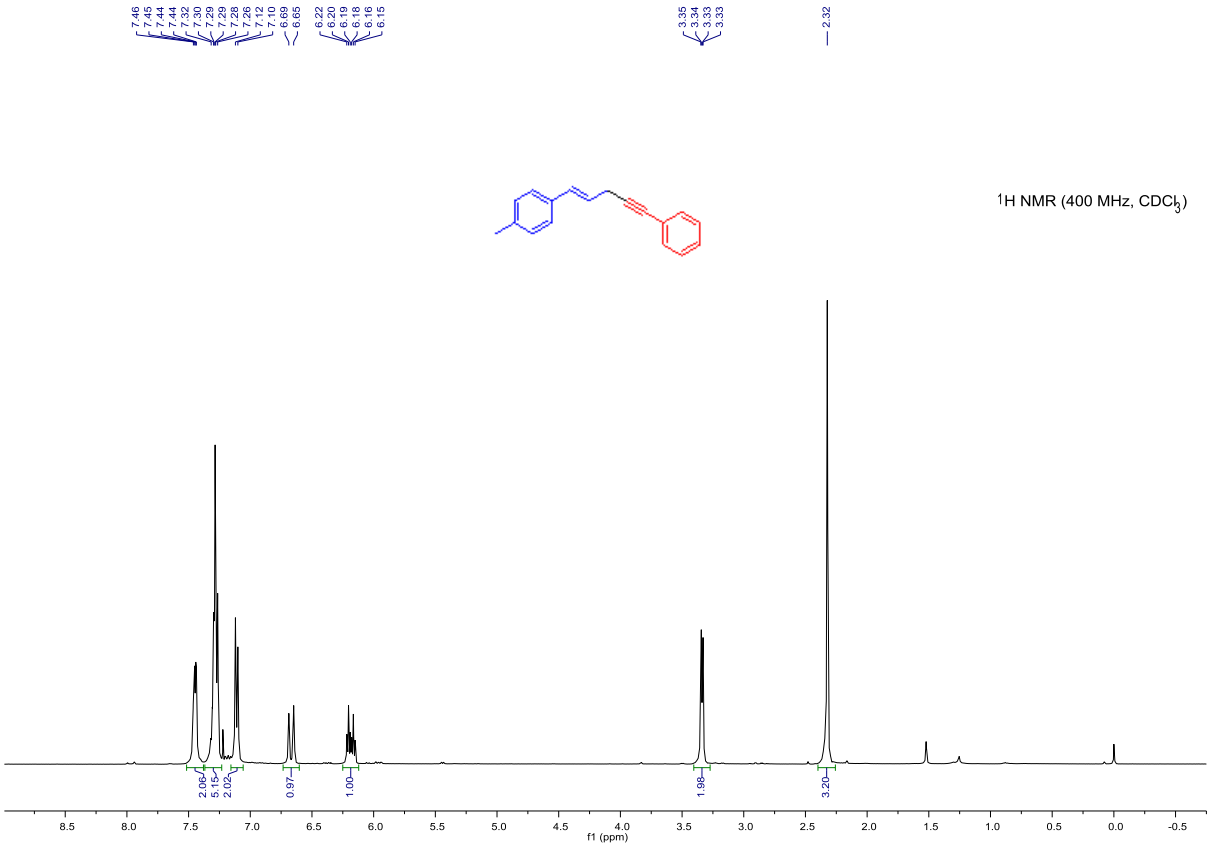
^{13}C NMR (101 MHz, $CDCl_3$)

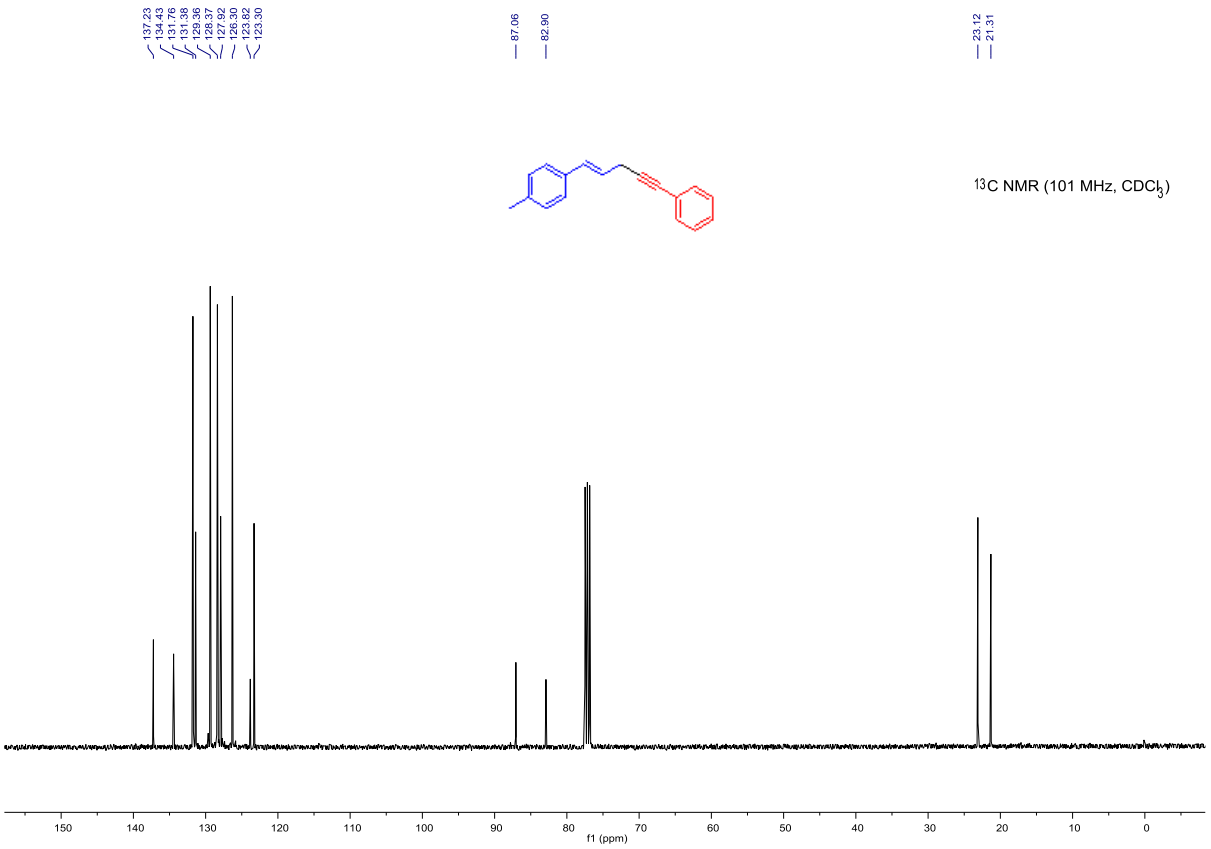
(29) (*E*)-(3,5-diphenylpent-4-en-1-yn-1-yl)trimethylsilane (**3sb**)



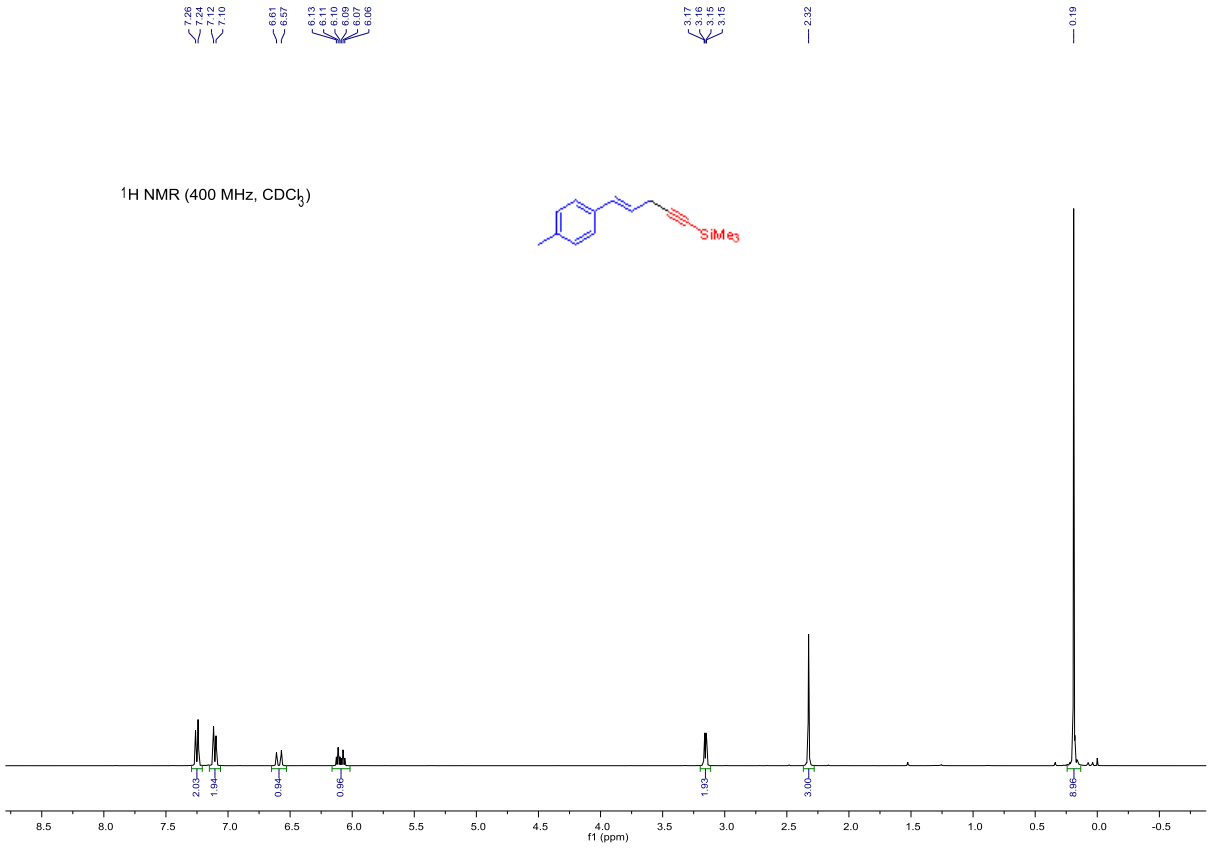


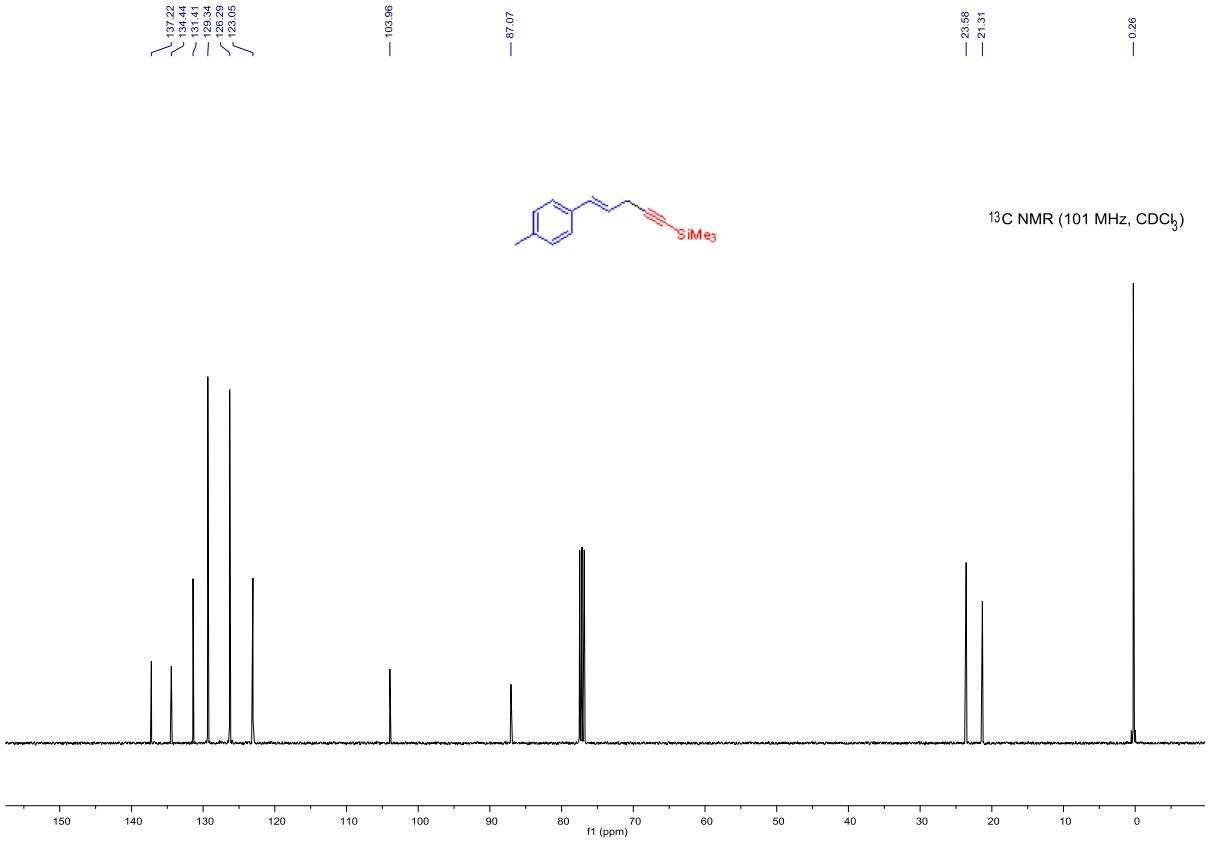
(30) (*E*)-1-methyl-4-(5-phenylpent-1-en-4-yn-1-yl)benzene (**3ta**)



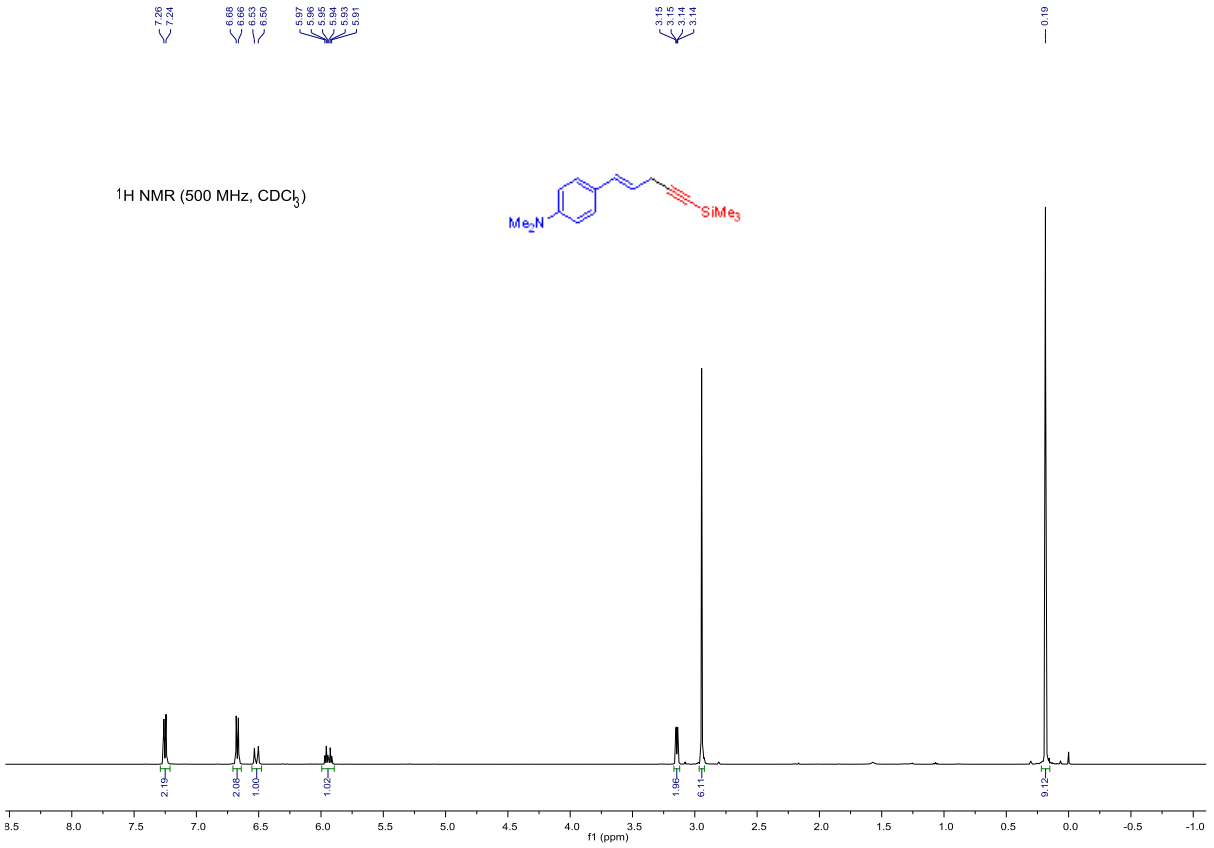


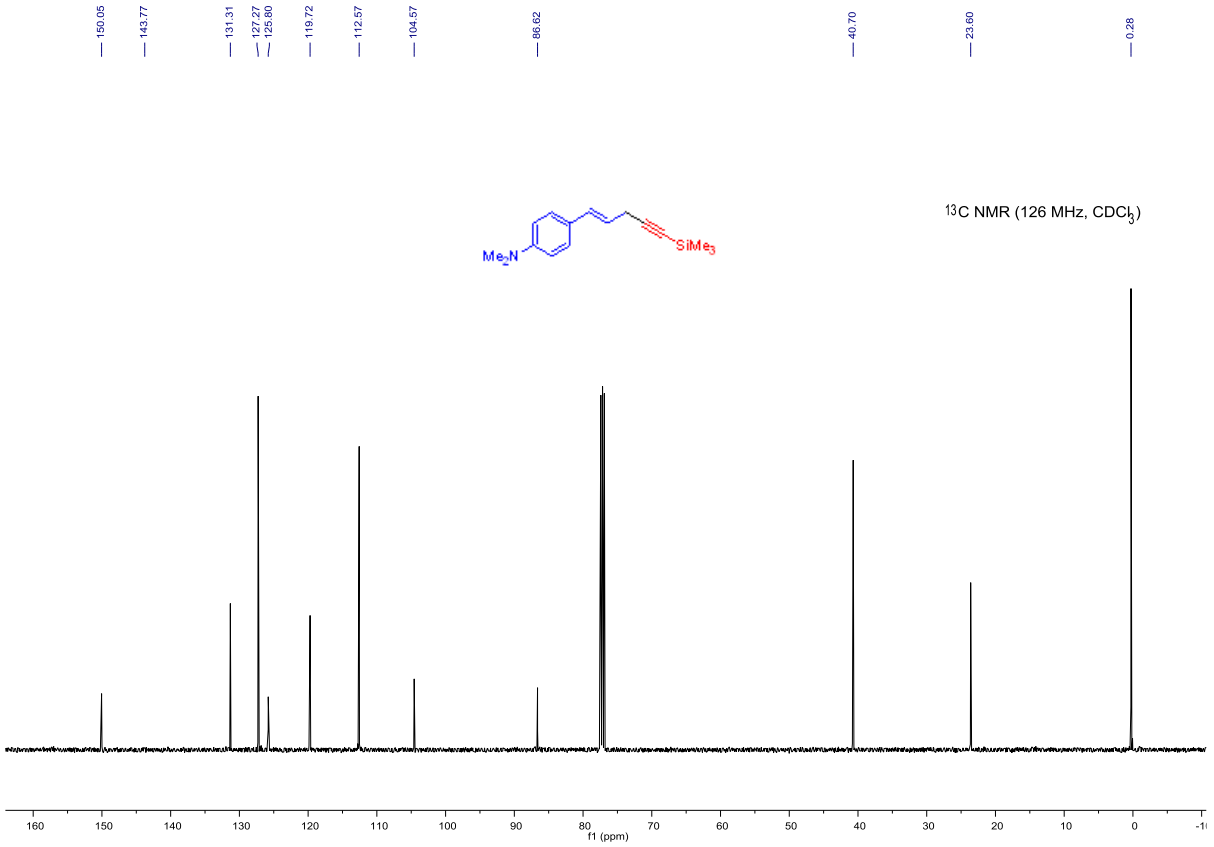
(31) (*E*)-trimethyl(5-(*p*-tolyl)pent-4-en-1-yn-1-yl)silane (**3tb**)



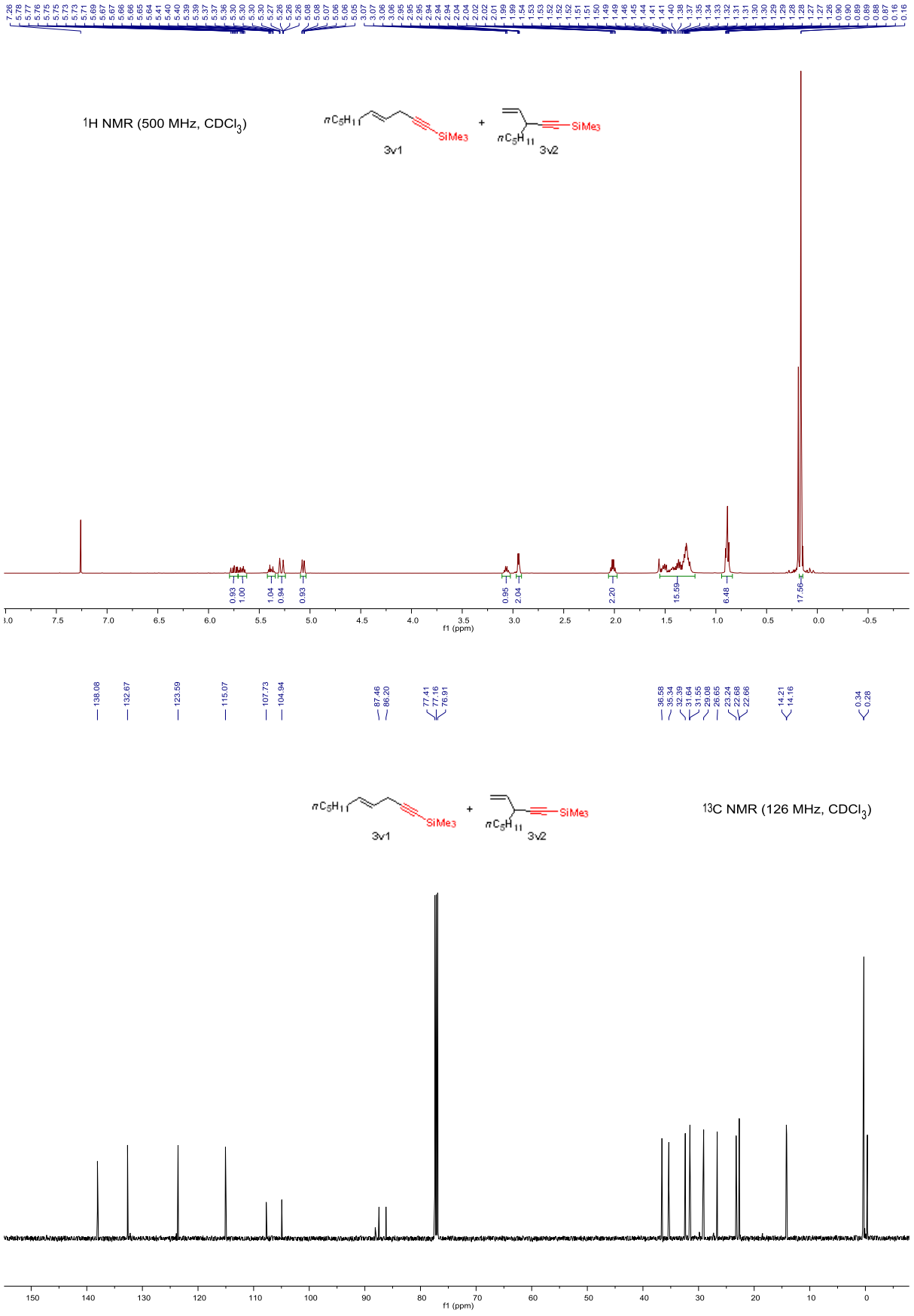


(32) (*E*)-N,N-dimethyl-4-(5-(trimethylsilyl)pent-1-en-4-yn-1-yl)aniline (**3u**)

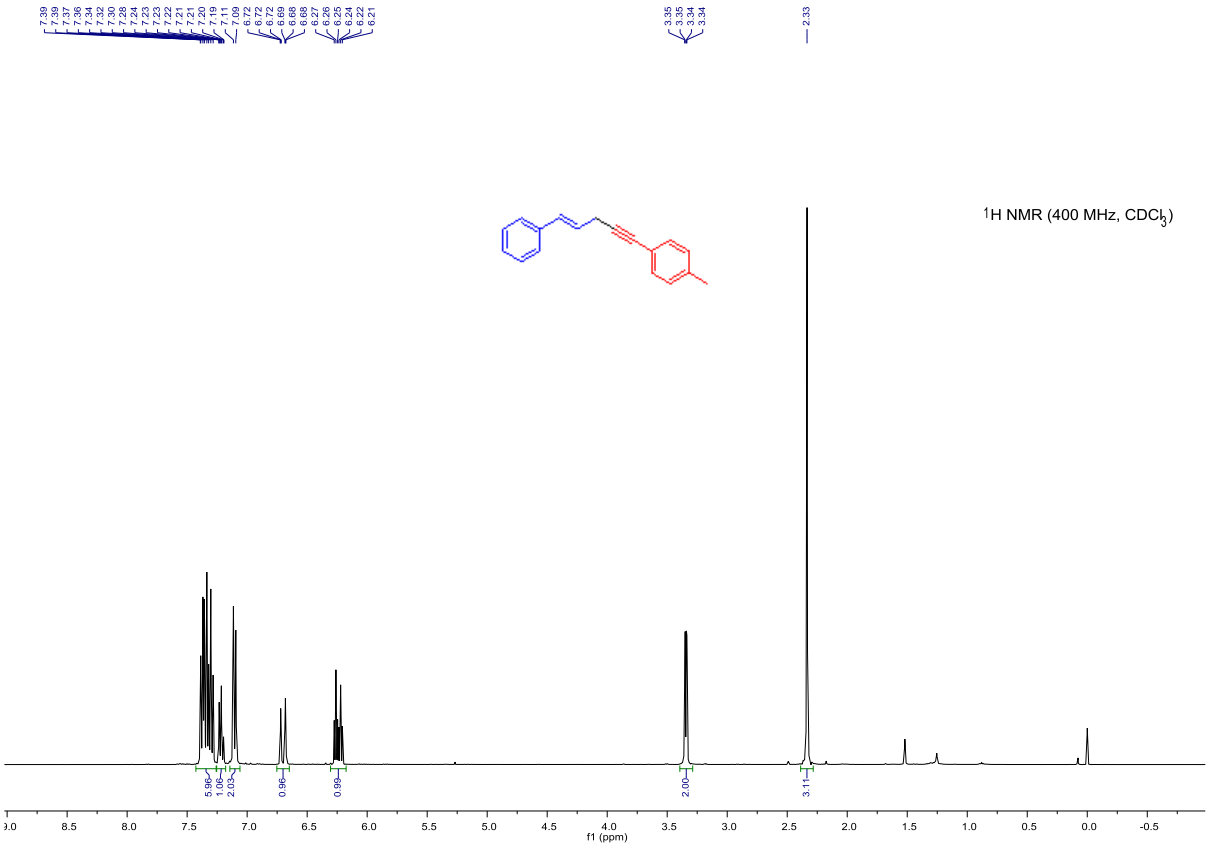


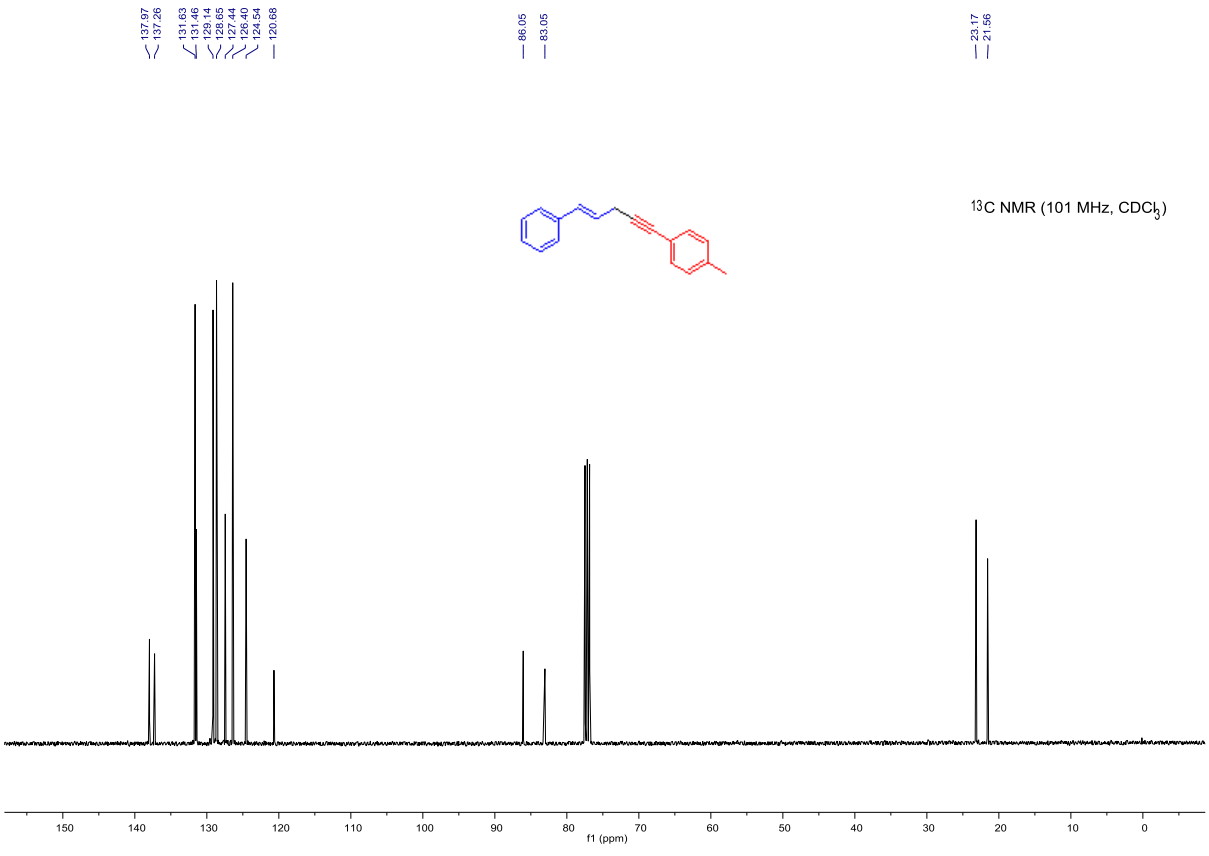


(33) mixture of (*E*)-dec-4-en-1-ynyltrimethylsilane (**3v1**) and trimethyl(3-vinyloct-1-ynyl) silane (**3v2**)

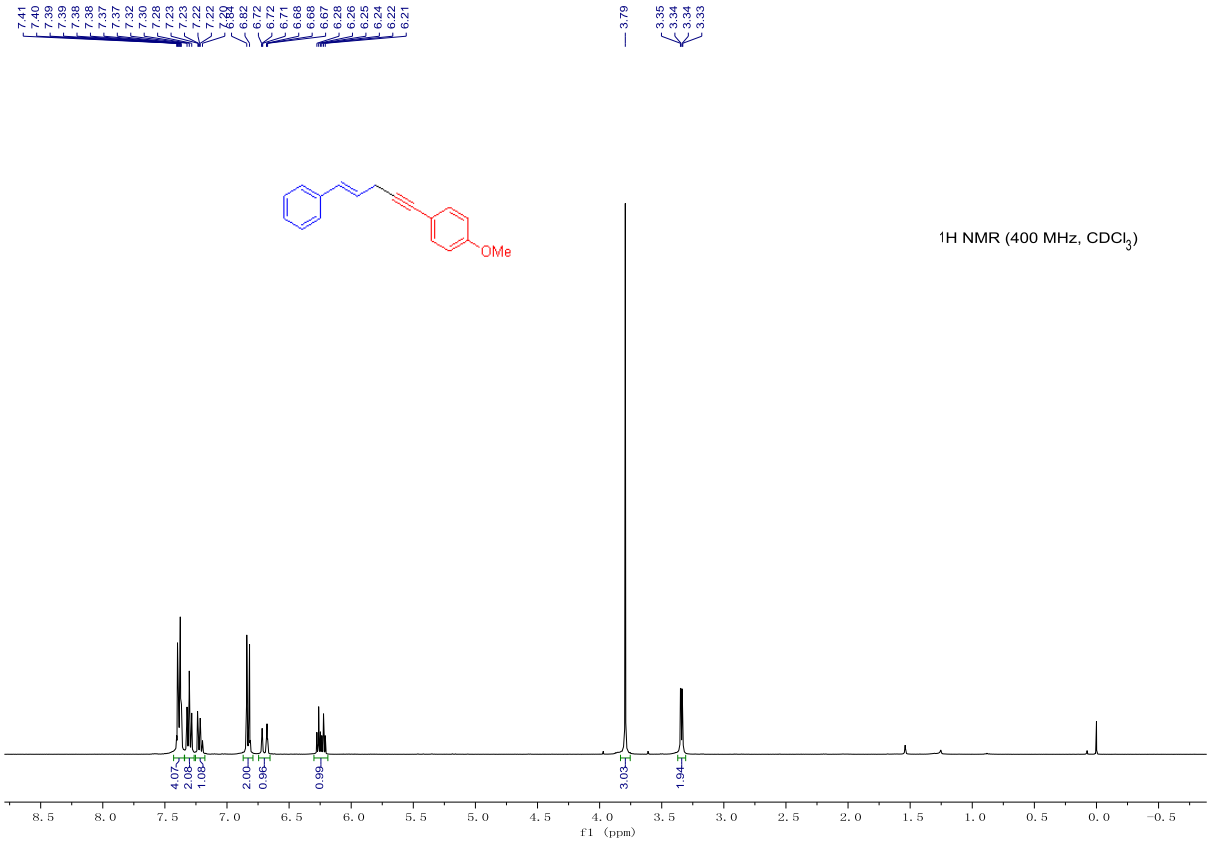


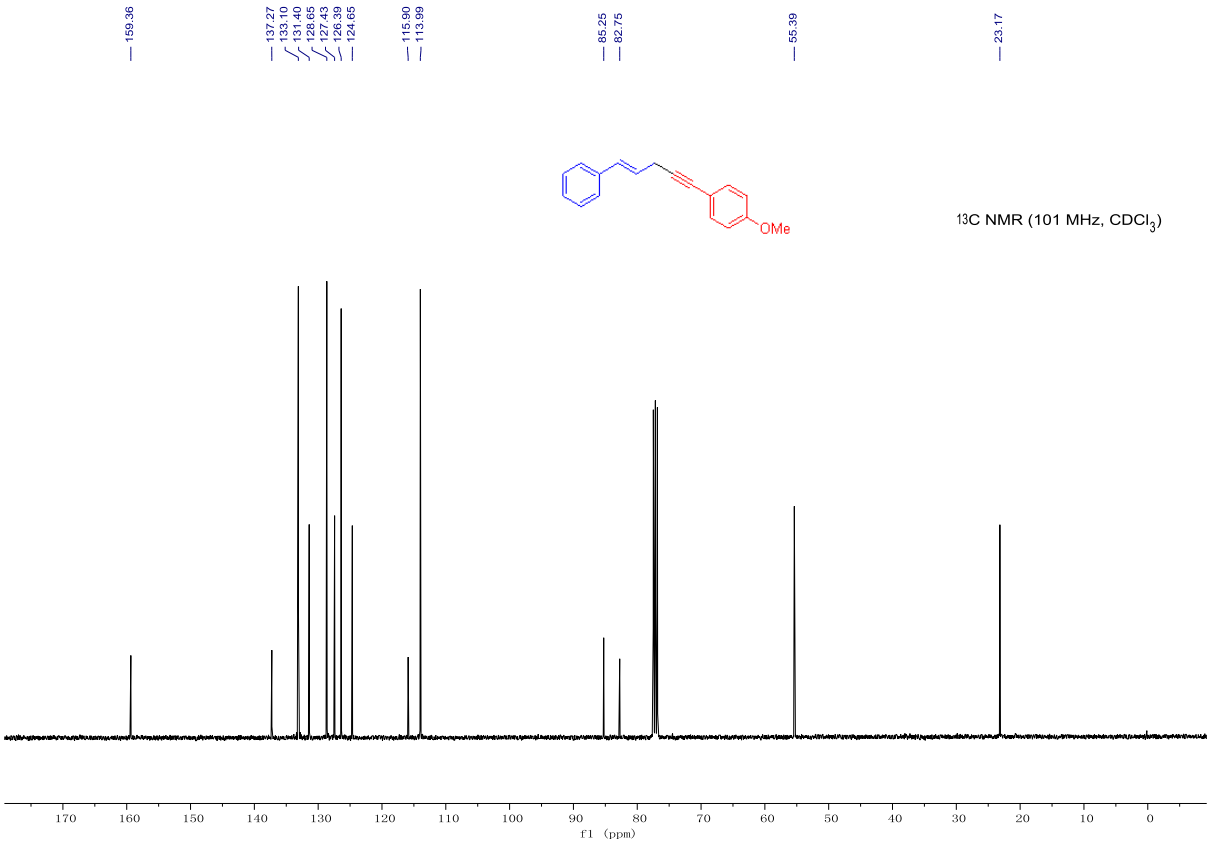
(34) (*E*)-1-methyl-4-(5-phenylpent-4-en-1-yn-1-yl)benzene (**3ac**)



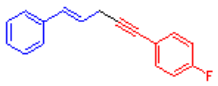


(35) (*E*)-1-methoxy-4-(5-phenylpent-4-en-1-yn-1-yl)benzene (**3ad**)

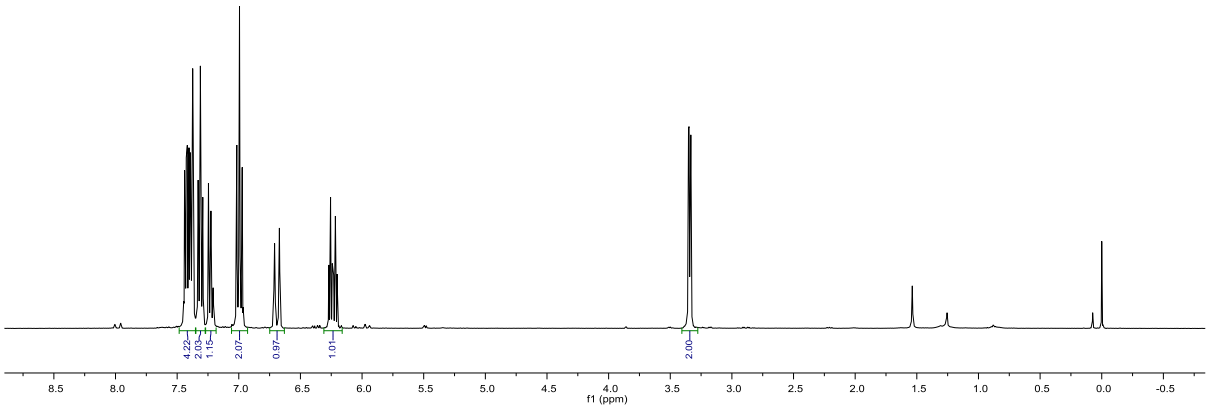


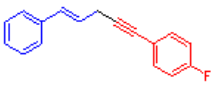


(36) (*E*)-1-fluoro-4-(5-phenylpent-4-en-1-yn-1-yl)benzene (**3ae**)

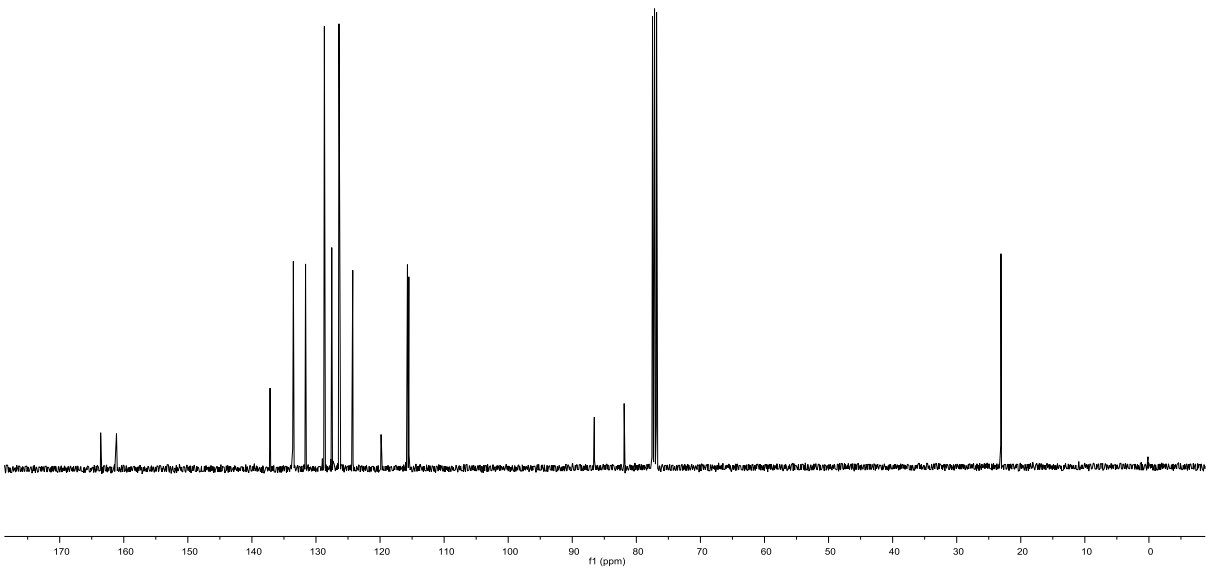


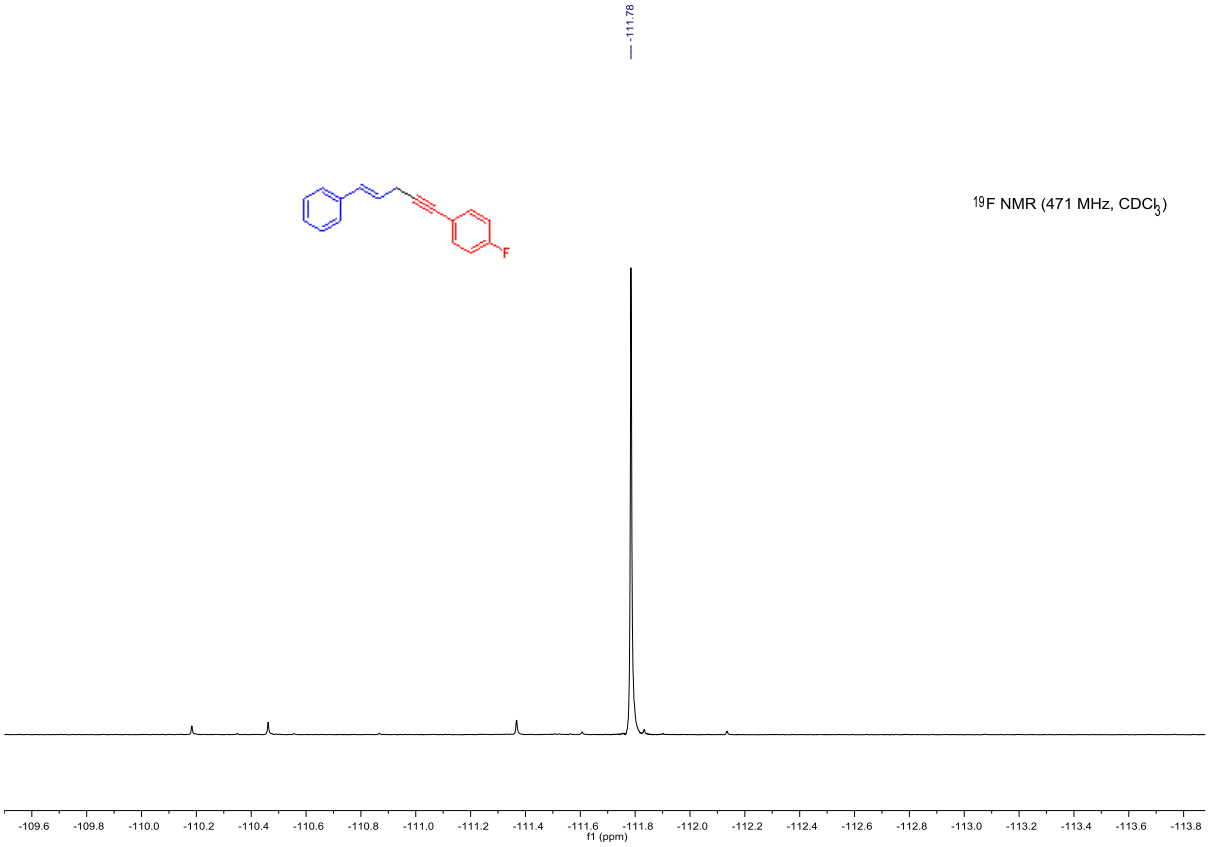
^{1}H NMR (400 MHz, $CDCl_3$)



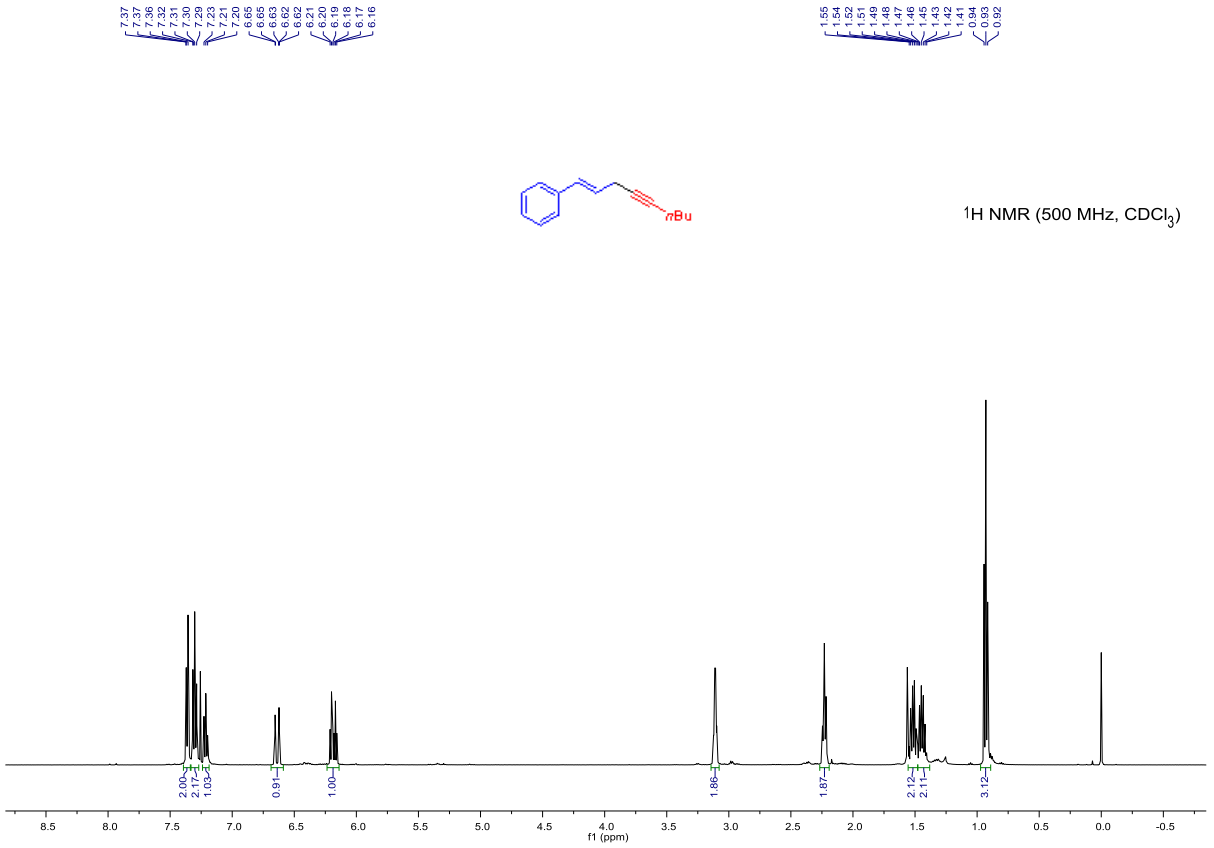


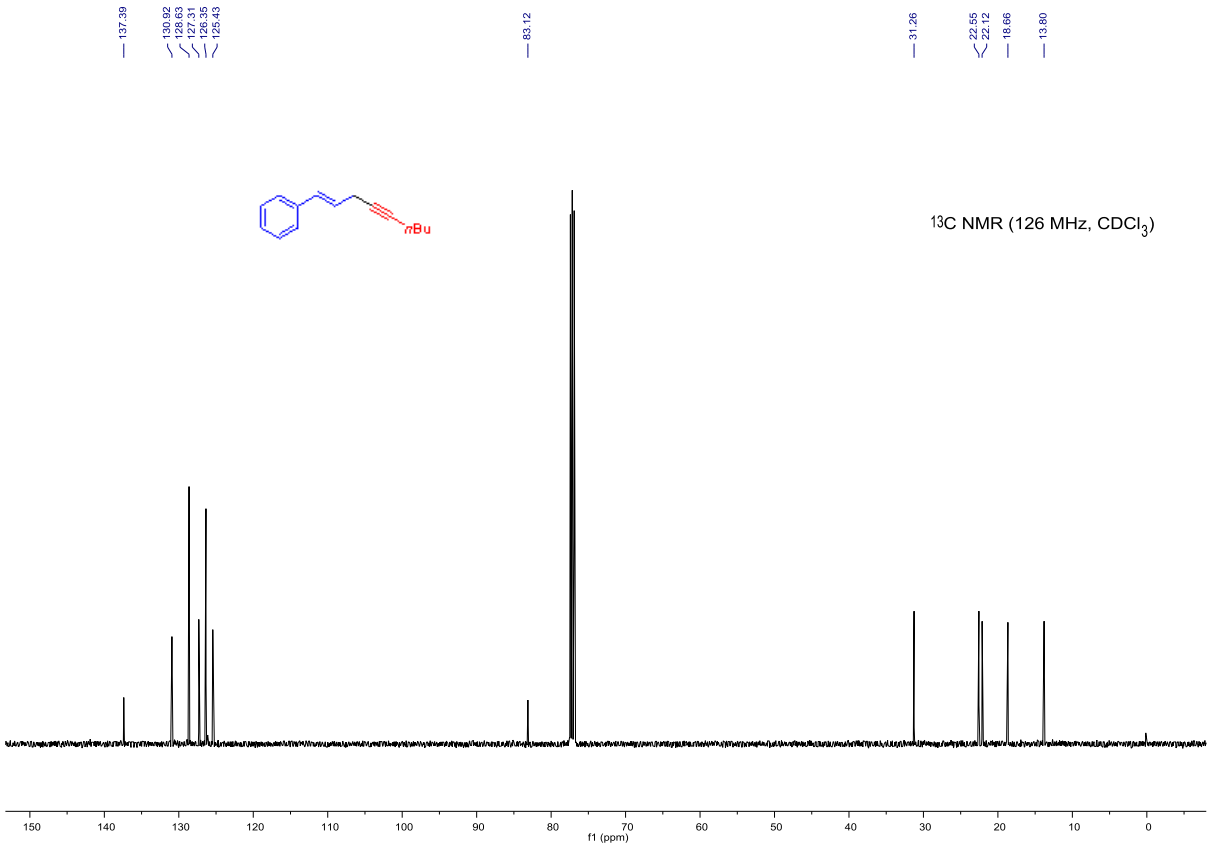
^{13}C NMR (101 MHz, $CDCl_3$)



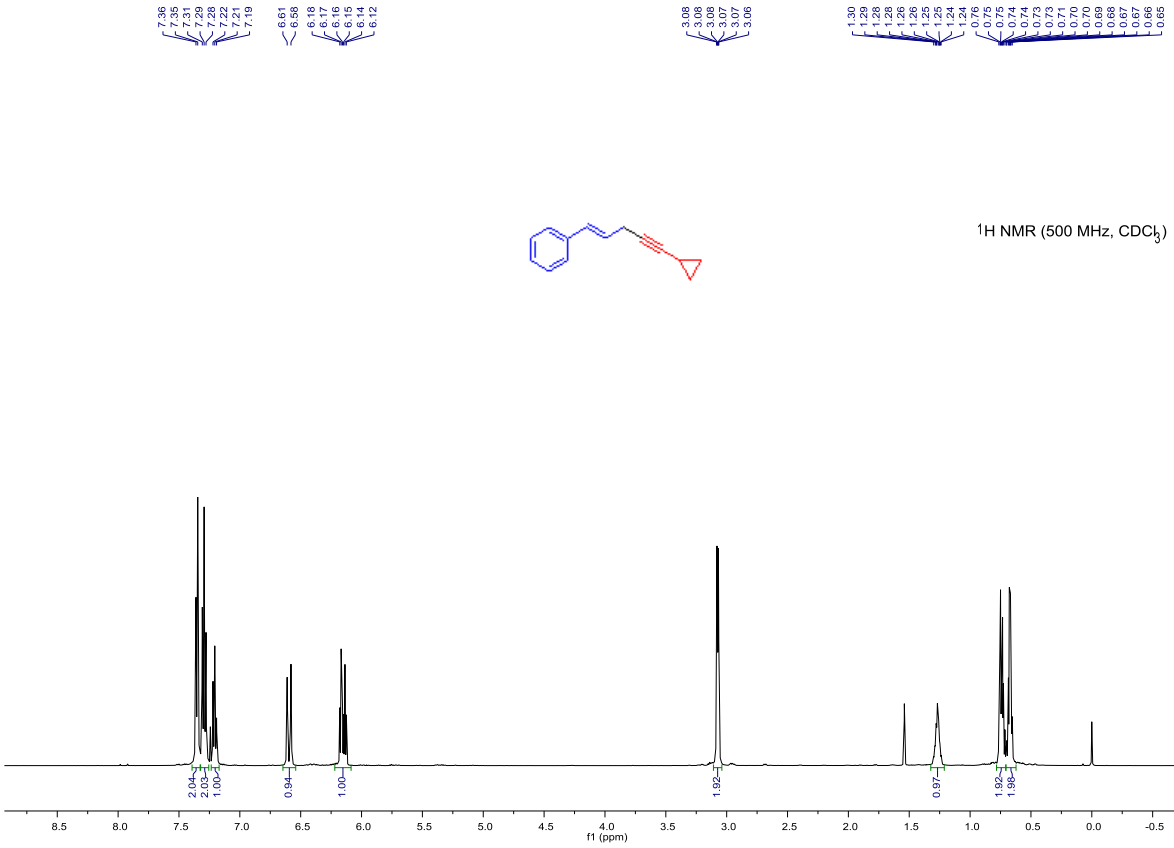

-111.78
F
^{19}F NMR (471 MHz, $CDCl_3$)
-109.6
-109.8
-110.0
-110.2
-110.4
-110.6
-110.8
-111.0
-111.2
-111.4
-111.6
-111.8
-112.0
-112.2
-112.4
-112.6
-112.8
-113.0
-113.2
-113.4
-113.6
-113.8
f1 (ppm)

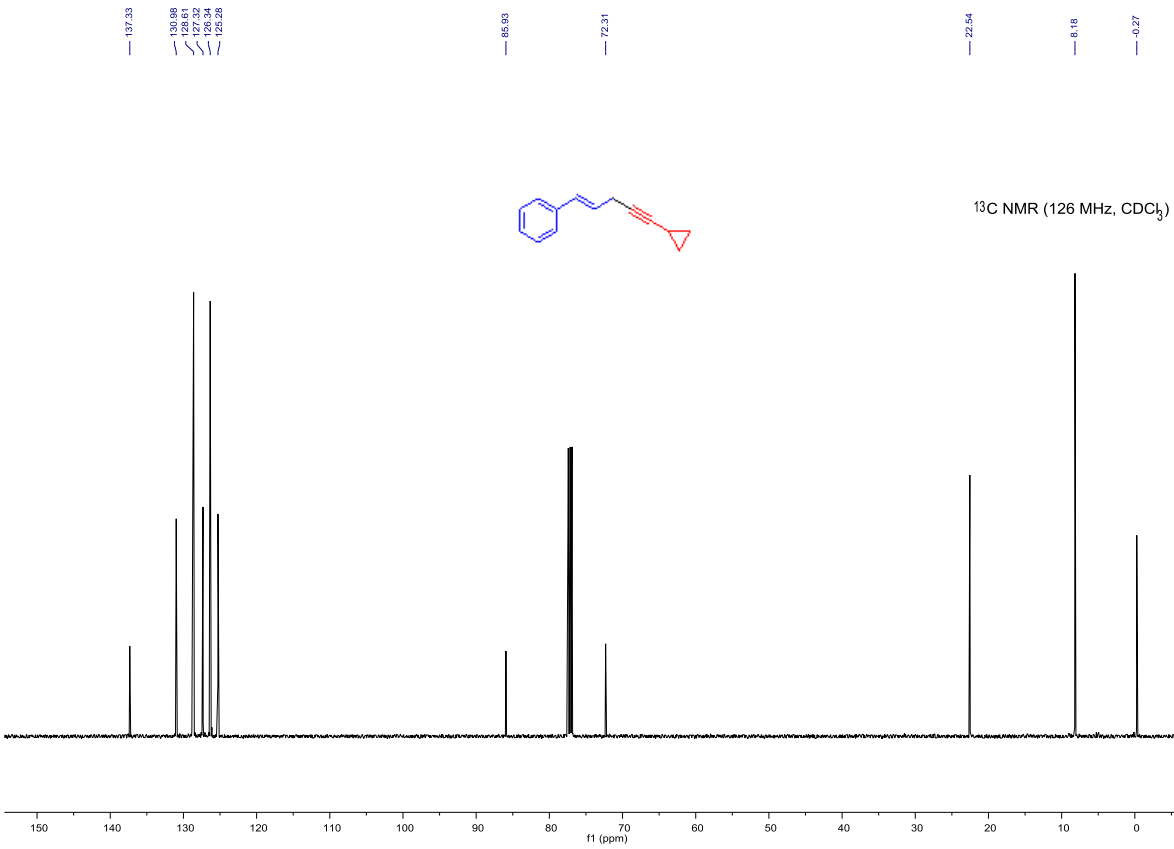
(37) (*E*)-non-1-en-4-yn-1-ylbenzene (**3af**)



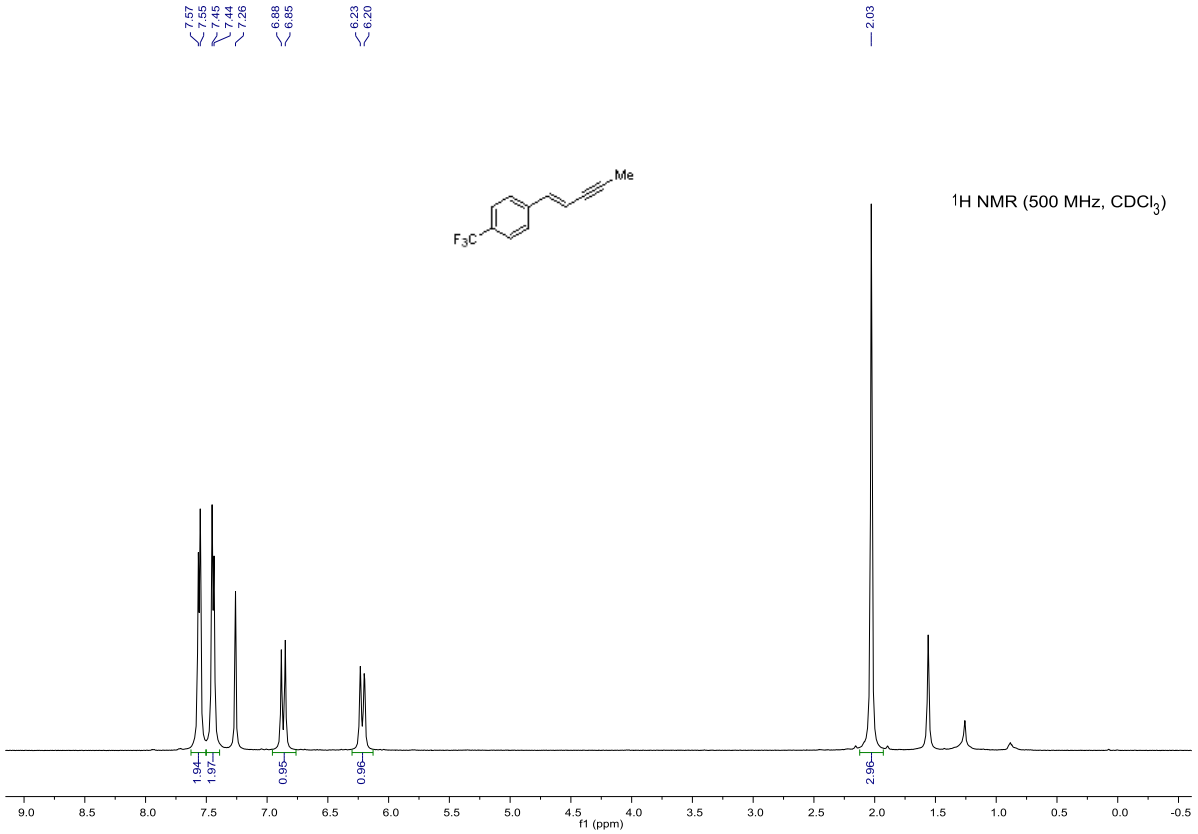


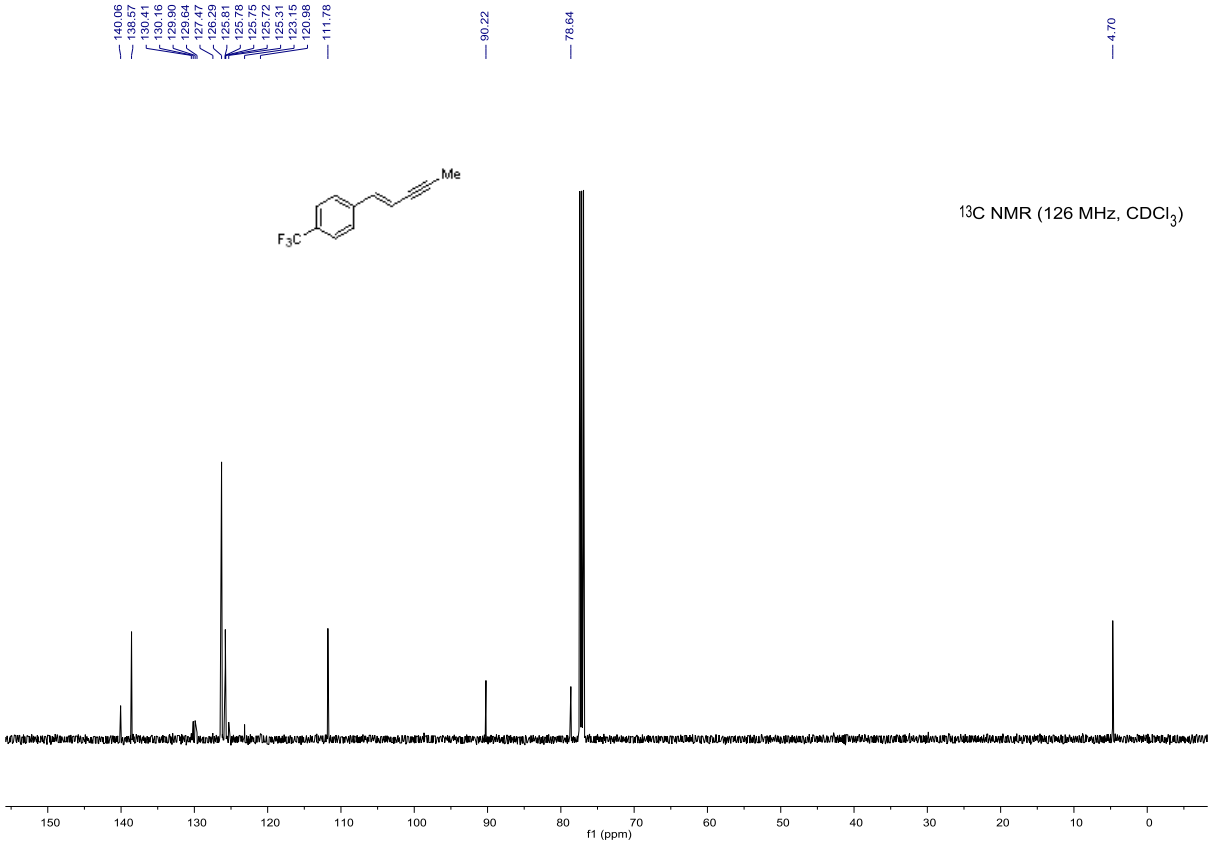
(38) (*E*)-(5-cyclopropylpent-1-en-4-yn-1-yl)benzene (**3ag**)

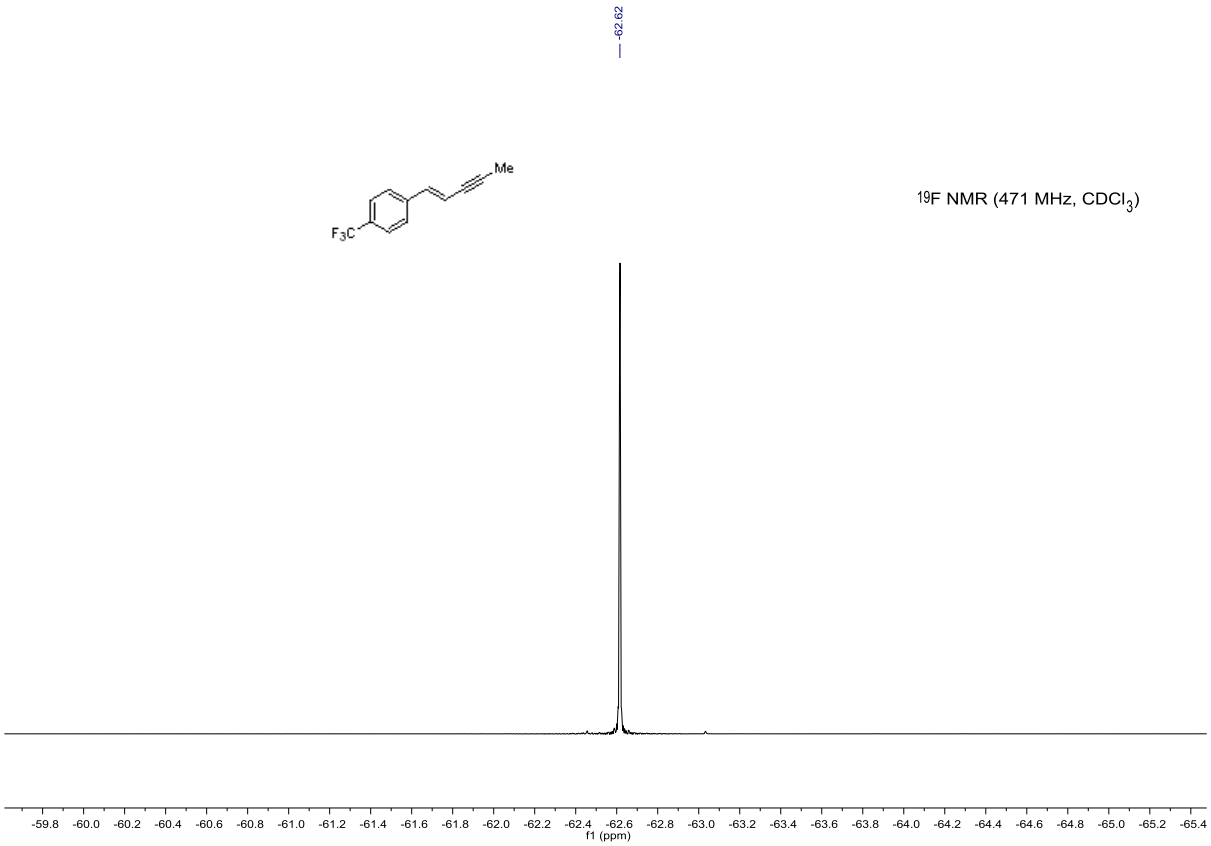




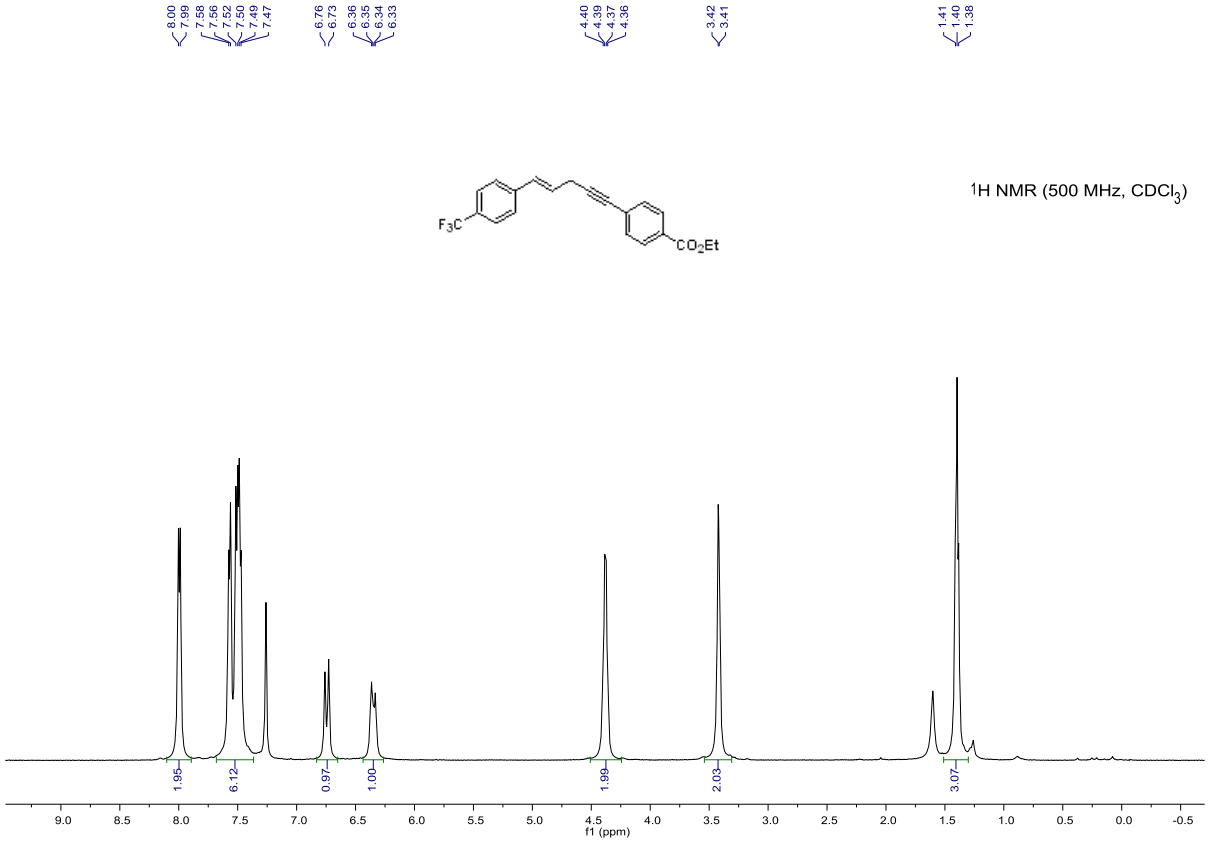
(39) (*E*)-1-(pent-1-en-3-yn-1-yl)-4-(trifluoromethyl)benzene (**4**)

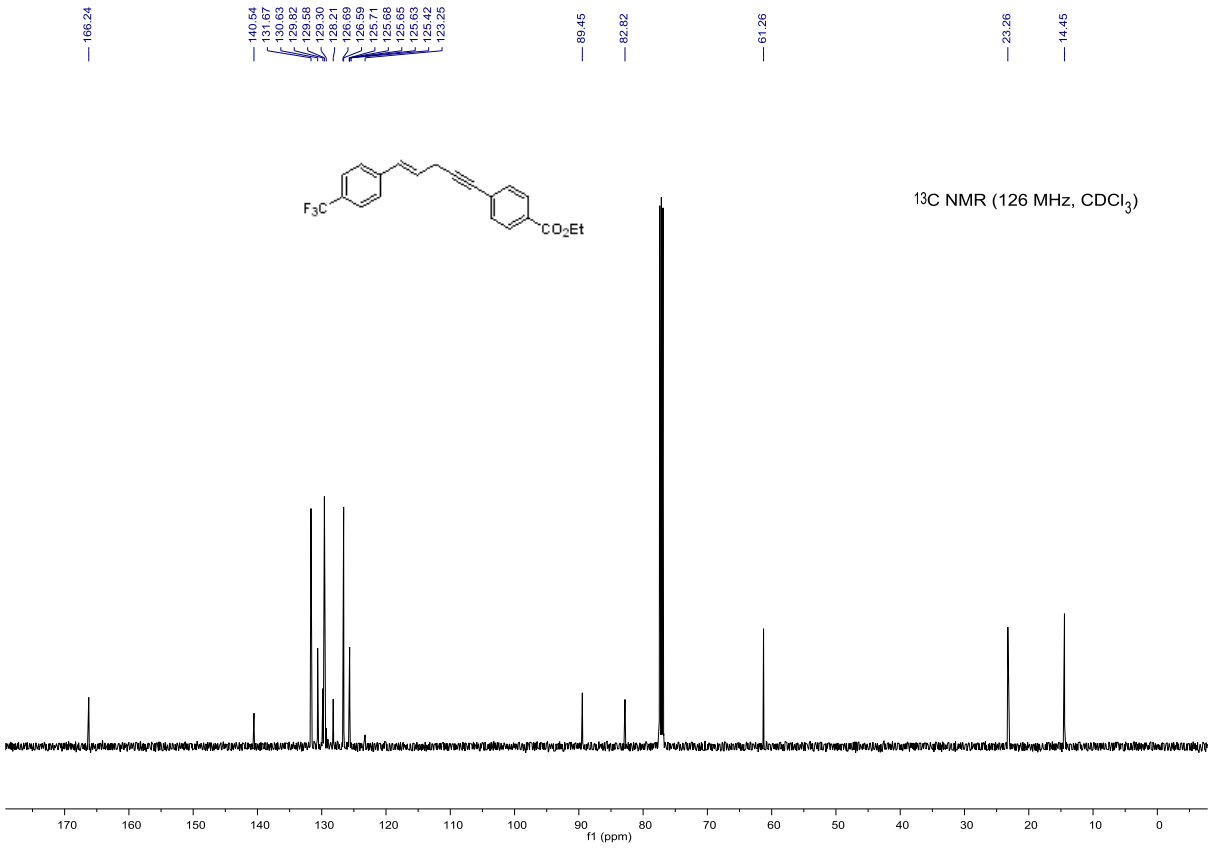


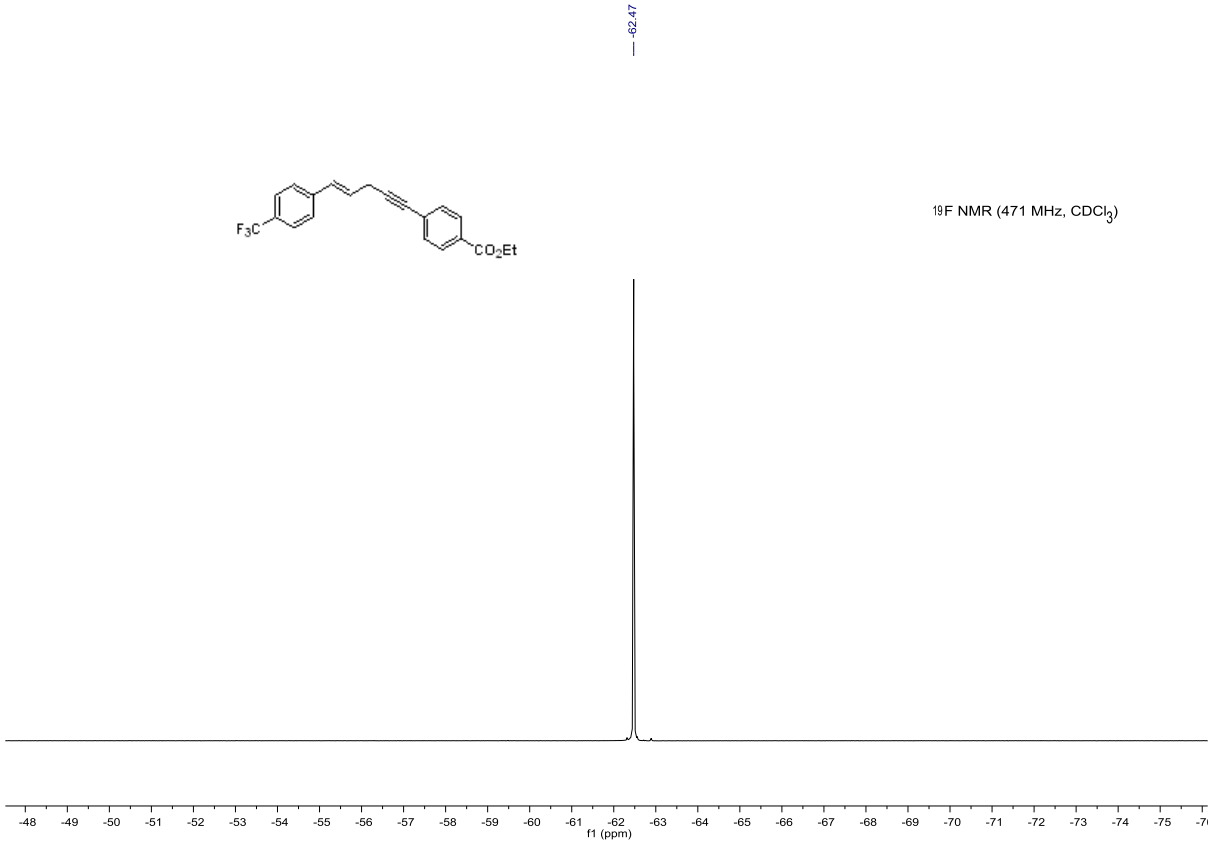



-62.62
Me
F3C
19F NMR (471 MHz, CDCl3)
-59.8 -60.0 -60.2 -60.4 -60.6 -60.8 -61.0 -61.2 -61.4 -61.6 -61.8 -62.0 -62.2 -62.4 -62.6 -62.8 -63.0 -63.2 -63.4 -63.6 -63.8 -64.0 -64.2 -64.4 -64.6 -64.8 -65.0 -65.2 -65.4
f1 (ppm)

(40) ethyl (*E*)-4-(5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yn-1-yl)benzoate (**5**)






-62.47
F3C
CO2Et
19F NMR (471 MHz, CDCl3)
-48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75
f1 (ppm)