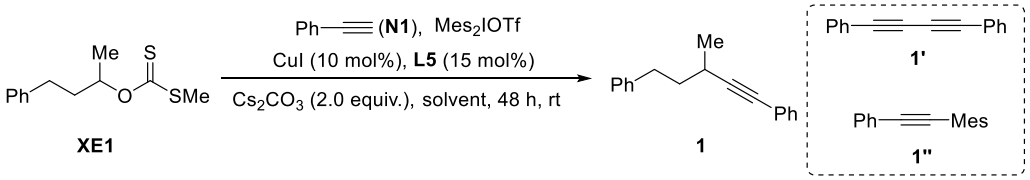
Supporting Information

Contents

General Information

Most of reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. CuI was purchased from Alfa Aesar and Bide. Anhydrous benzene (PhH) was purchased from J&K Scientific. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm), iodine, basic $KMnO_4$, or phosphomolybdic acid indicator. NMR spectra were recorded on Bruker DRX-400 spectrometers at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR, and Bruker DRX-600 spectrometers at 600 MHz for ^1H NMR, 150 MHz for ^{13}C NMR respectively, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS.

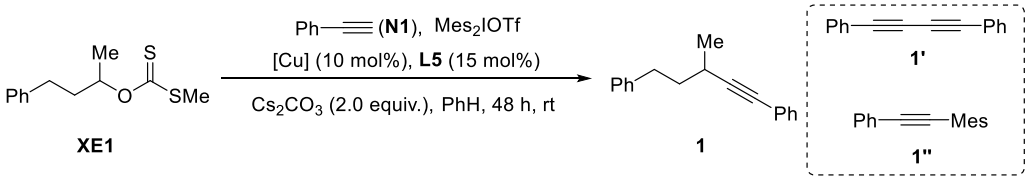
Table S1. Reaction condition optimization: screening of different solvents



Entry	solvent	Conv. (%)	Yield (%)		
			1	**1'**	**1''**
1	PhH	95	85	8	6
2	CyH	54	25	12	8
3	EA	78	47	14	0
4	$PhCH_3$	56	50	32	20
5	*p*-xylene	43	42	42	24
6	Et_2O	49	23	34	28
7	MTBE	76	52	24	18
8	$^{i}Pr_2O$	66	61	18	14
9	$PhCF_3$	76	48	11	7
10	CyH	54	25	12	8

Reaction conditions: **XE1** (1.0 equiv., 0.10 mmol), **N1** (1.2 equiv., 0.12 mmol), Mes_2IOTf (1.5 equiv., 0.15 mmol), CuI (10 mol%), **L5** (15 mol%), Cs_2CO_3 (2.0 equiv., 0.2 mmol) in solvent (1.0 mL) under argon at room temperature for 48 h; Yield was determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard based on **XE1**.

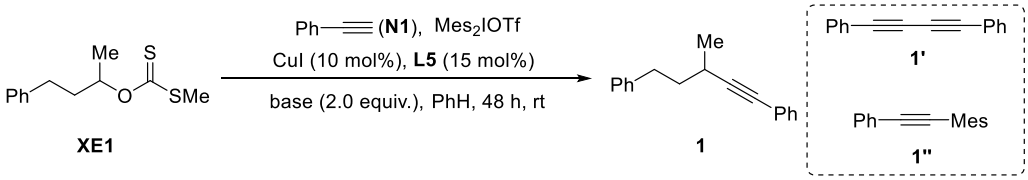
Table S2. Reaction condition optimization: screening of different copper salts



Entry	[Cu]	Conv. (%)	Yield (%)		
			1	**1'**	**1''**
1	CuBr	77	68	11	11
2	$CuBr.SMe_2$	94	68	10	6
3	CuCN	89	63	16	10
4	CuTc	91	71	9	12
5	$Cu(CN)_4PF_6$	96	71	17	6
6	CuI	95	85	8	6

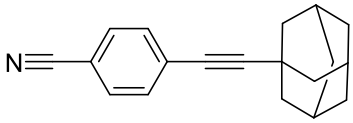
Reaction conditions: **XE1** (1.0 equiv., 0.10 mmol), **N1** (1.2 equiv., 0.12 mmol), Mes_2IOTf (1.5 equiv., 0.15 mmol), [Cu] (10 mol%), **L5** (15 mol%), Cs_2CO_3 (2.0 equiv., 0.2 mmol) in PhH (1.0 mL) under argon at room temperature for 48 h; Yield was determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard based on **XE1**.

Table S3. Reaction condition optimization: screening of different base



Entry	base	Conv. (%)	Yield (%)		
			1	**1'**	**1''**
1	Cs_2CO_3	95	85	8	6
2	K_2CO_3	78	57	10	6
3	DBU	68	65	25	20

Reaction conditions: **XE1** (1.0 equiv., 0.10 mmol), **N1** (1.2 equiv., 0.12 mmol), Mes_2IOTf (1.5 equiv., 0.15 mmol), CuI (10 mol%), **L5** (15 mol%), base (2.0 equiv., 0.2 mmol) in PhH (1.0 mL) under argon at room temperature for 48 h; Yield was determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard based on **XE1**.



50

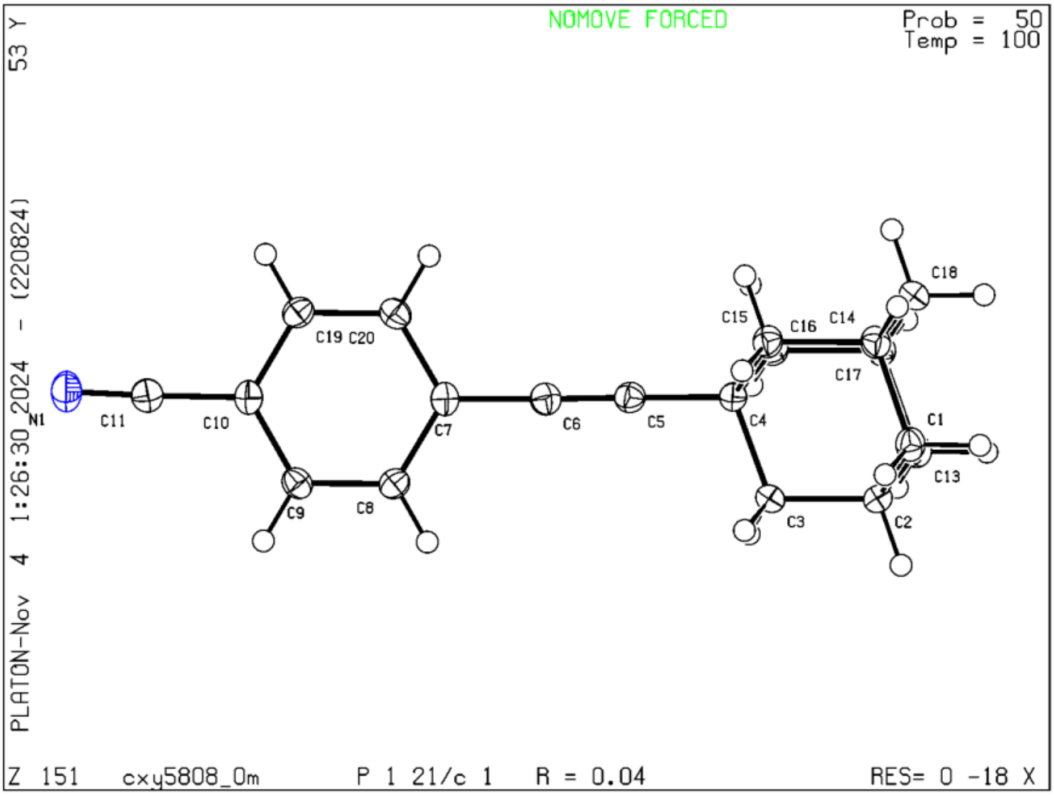
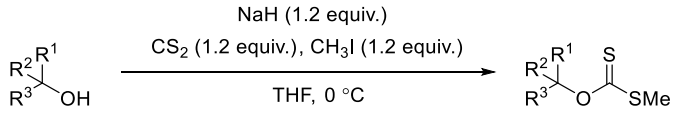


Figure S1. The X-ray structure of **50**

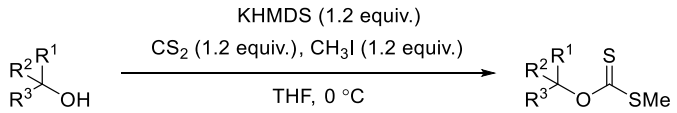
The synthesis of oxidants, ligands, and alkynes

Ox1[1], **Ox2**[1], and **Ox4**[2] were synthesized following previously reported procedures, and their characterization data were consistent with literature values. **Ox3** was commercially obtained from Bide Pharm. Ltd. **L1** and **L2** were commercially obtained from Bide Pharm. **L3** to **L6** were synthesized following previously reported procedures,[3] and their characterization data were consistent with literature values. Most alkynes were purchased from commercial sources. Others were synthesized according to the reported literature.[4] All the characterization data are consistent with those in the reported literature.

The synthesis substrates of xanthate esters

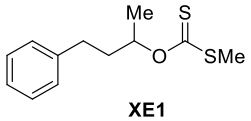


General procedure 1: An oven-dried round bottom flask was charged with a Teflon-coated magnetic stir bar, and NaH (60% in mineral oil, 1.2 equiv.) was added under an argon atmosphere followed by dry THF (0.3 M). The alcohol (1.0 equiv.) was slowly added via syringe(oil) or slowly added (solid) to the stirring solution at 0 ºC. The reaction was capped under argon and allowed to stir for 1 h at 0 ºC. Carbon disulfide (CS_2, 1.2 equiv.) was then added via syringe at 0 ºC, stirred for 1 h, and the reaction was quenched with methyl iodiode (1.2 equiv.), and stirred for an additional 1 h. The reaction was diluted with Et_2O, carefully quenched with sat. NH_4Cl solution, and diluted with H_2O. The mixture was transferred to a separatory funnel and the organics were washed with H_2O and then brine. The organics were dried with Na_2SO_4, filtered, and concentrated to a yellow oil or light-yellow solid which often contained analytically pure xanthate ester to be employed directly in the next step. When needed, the resulting xanthate can be purified by column chromatography on silica gel, eluting with PE and EtOAc, to obtain products in pure form.



General procedure 2: An oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was charged with the alcohol (1.0 equiv.) dissolved in dry THF. KHMDS (1.0 M in THF) was then added dropwise at 0 °C. After stirring at room temperature for 1 h, CS_2 (1.2 equiv.) was added to the mixture, which was stirred at room temperature for 20 min before adding MeI (1.2 equiv.). Following 1 h of stirring at room temperature, the reaction was quenched with saturated aqueous NH_4Cl at 0 °C and extracted three times with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford yellow oil, which often contained analytically pure xanthate ester to be employed directly in the next step.

***S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate (XE1)**



XE1

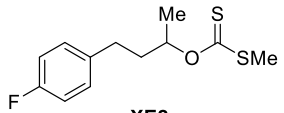
According to General Procedure 1 with 4-phenylbutan-2-ol (1.5 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE1** as a yellow oil (2.35 g, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 5.81 – 5.71 (m, 1H), 2.82 – 2.66 (m, 2H), 2.59 (s, 3H), 2.30 – 2.13 (m, 1H), 2.03 – 1.95 (m, 1H), 1.43 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.4, 141.2, 128.5, 128.4, 126.1, 80.7, 37.5, 31.7, 19.4, 18.9.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{16}OS_2$ $[M + Na]^+$ 265.0535, found 265.0538.

O-(4-(4-Fluorophenyl)butan-2-yl) *S*-methyl carbonodithioate (XE2)



XE2

According to General Procedure 1 with 4-(4-fluorophenyl)butan-2-ol (0.50 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE2** as a yellow oil (0.74 g, 96% yield).

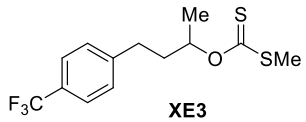
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.09 (m, 2H), 7.04 – 6.90 (m, 2H), 5.86 – 5.63 (m, 1H), 2.89 – 2.62 (m, 2H), 2.58 (s, 3H), 2.21 – 2.09 (m, 1H), 1.99 – 1.88 (m, 1H), 1.41 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.5, 161.4 (d, *J* = 243.8 Hz), 136.8 (d, *J* = 3.2 Hz), 129.7 (d, *J* = 7.9 Hz), 115.2 (d, *J* = 21.1 Hz), 80.4, 37.5, 30.9, 19.3, 18.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.31 – -117.54 (m, 1F).

HRMS (ESI) *m/z* calcd. for $C_{12}H_{15}FOS_2$ $[M + Na]^+$ 281.0441, found 281.0445.

O-(4-(4-Fluorophenyl)butan-2-yl) *S*-methyl carbonodithioate (XE3)



XE3

According to General Procedure 1 with 4-(4-(trifluoromethyl)phenyl)butan-2-ol (0.65 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE3** as a yellow oil (0.88 g, 95% yield).

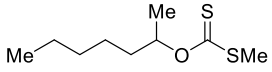
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.82 – 5.70 (m, 1H), 2.88 – 2.70 (m, 2H), 2.58 (s, 3H), 2.26 – 2.12 (m, 1H), 2.04 – 1.93 (m, 1H), 1.42 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.5, 145.3, 128.7, 125.4 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 270.2 Hz), 79.6, 36.4, 32.5, 21.6, 18.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.35 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{13}H_{15}F_3OS_2$ $[M + H]^+$ 309.0589, found 309.0591.

O-(Heptan-2-yl) *S*-methyl carbonodithioate (XE4)



XE4

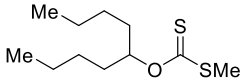
According to General Procedure 1 with heptan-2-ol (0.58 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE4** as a yellow oil (0.76 g, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 – 5.64 (m, 1H), 2.56 (s, 3H), 1.87 – 1.75 (m, 1H), 1.69 – 1.58 (m, 1H), 1.43 – 1.25 (m, 9H), 0.94 – 0.84 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.5, 81.5, 35.6, 31.6, 25.0, 22.5, 19.3, 18.8, 14.0.

HRMS (ESI) *m/z* calcd. for $C_9H_{18}OS_2$ $[M + H]^+$ 207.0872, found 207.0878.

S-Methyl *O*-(nonan-5-yl) carbonodithioate (XE5)



XE5

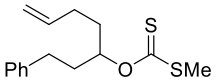
According to General Procedure 1 with nonan-5-ol (0.72 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE5** as a yellow oil (0.93 g, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (tt, J = 7.2, 5.2 Hz, 1H), 2.57 (s, 3H), 1.83 – 1.61 (m, 4H), 1.44 – 1.22 (m, 8H), 0.95 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.9, 85.0, 33.4, 27.3, 22.7, 18.8, 14.0.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{22}OS_2$ $[M + H]^+$ 235.1185, found 235.1184.

S-Methyl *O*-(1-phenylhept-6-en-3-yl) carbonodithioate (XE6)



XE6

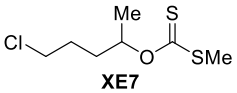
According to General Procedure 1 with 1-phenylhept-6-en-3-ol (0.95 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE6** as a yellow oil (1.3 g, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.27 – 7.19 (m, 3H), 5.90 – 5.78 (m, 2H), 5.12 – 4.98 (m, 2H), 2.83 – 2.64 (m, 2H), 2.60 (s, 3H), 2.25 – 1.78 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.8, 141.3, 137.5, 128.5, 128.4, 126.1, 115.3, 83.6, 35.5, 33.0, 31.6, 29.4, 19.0.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}OS_2$ $[M + H]^+$ 281.1028, found 281.1031.

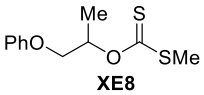
O-(5-Chloropentan-2-yl) *S*-methyl carbonodithioate (XE7)



XE7

According to General Procedure 1 with 5-chloropentan-2-ol (0.61 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 100/1 to yield the product **XE7** as a yellow oil (0.42 g, 40% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.71 (m, 1H), 3.62 – 5.54 (m, 2H), 2.57 (s, 3H), 1.96 – 1.82 (m, 4H), 1.40 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.6, 80.2, 44.7, 33.0, 28.4, 19.4, 18.9.
HRMS (ESI) *m/z* calcd. for $C_7H_{13}ClOS_2$ $[M + H]^+$ 213.0169, found 213.0164.

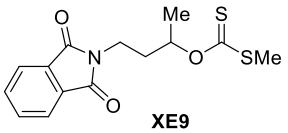
S-Methyl *O*-(1-phenoxypropan-2-yl) carbonodithioate (XE8)



XE8

According to General Procedure 1 with 1-phenoxypropan-2-ol (0.76 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 50/1 to yield the product **XE8** as a yellow oil (1.13 g, 93% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.07 – 6.90 (m, 3H), 6.23 – 5.91 (m, 1H), 4.30 – 4.08 (m, 2H), 2.59 (s, 3H), 1.56 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.6, 158.5, 129.6, 121.3, 114.8, 78.3, 69.4, 19.0, 16.2.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}O_2S_2$ $[M + H]^+$ 243.0508, found 243.0508.

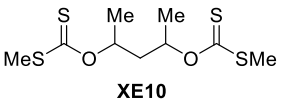
O-(4-(1,3-Dioxoisoindolin-2-yl)butan-2-yl) *S*-methyl carbonodithioate (XE9)



XE9

The 2-(3-hydroxybutyl)isoindoline-1,3-dione was synthesized with the reported procedure.[5] According to General Procedure 1 with 2-(3-hydroxybutyl)isoindoline-1,3-dione (0.66 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 5/1 to yield the product **XE9** as a yellow oil (0.86 g, 93% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.72 – 7.69 (m, 2H), 5.79 – 5.69 (m, 1H), 3.89 – 3.71 (m, 2H), 2.54 (s, 3H), 2.27 – 2.15 (m, 1H), 2.14 – 2.02 (m, 1H), 1.44 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.3, 168.2, 134.0, 132.1, 123.3, 78.4, 34.4, 34.2, 19.2, 18.9.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{15}NO_3S_2$ $[M + Na]^+$ 332.0386, found 332.0382.

S,S′-Dimethyl *O,O′*-(pentane-2,4-diyl) bis(carbonodithioate) (XE10)



XE10

According to General Procedure 1 with pentane-2,4-diol (0.52 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using

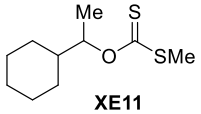
PE/EtOAc = 100/1 to yield the meso product **XE10** as a yellow oil (0.91 g, 64% yield, a meso product).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.74 (m, 4H), 2.56 (s, 6H), 2.54 (s, 6H), 2.46 – 2.35 (m, 1H), 2.14 (t, *J* = 6.4 Hz, 2H), 1.99 – 1.89 (m, 1H), 1.41 (d, *J* = 6.4 Hz, 6H), 1.40 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.1, 77.6, 77.2, 41.7, 40.9, 19.7, 19.5, 19.0, 18.9.

HRMS (ESI) *m/z* calcd. for $C_9H_{16}O_2S_4$ $[M + Na]^+$ 306.9925, found 306.9928.

O-(1-Cyclohexylethyl) *S*-methyl carbonodithioate (XE11)



XE11

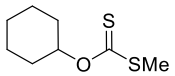
According to General Procedure 1 with 1-cyclohexylethan-1-ol (0.64 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE11** as a yellow oil (0.78 g, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 – 5.53 (m, 1H), 2.56 (s, 3H), 1.87 – 1.64 (m, 6H), 1.32 (d, *J* = 6.4 Hz, 3H), 1.29 – 0.98 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.6, 85.2, 42.6, 28.6, 28.5, 26.4, 25.98, 25.95, 18.8, 16.3.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{18}OS_2$ $[M + Na]^+$ 241.0691, found 241.0679.

O-Cyclohexyl *S*-methyl carbonodithioate (XE12)



XE12

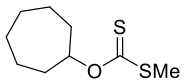
According to General Procedure 1 with cyclohexanol (0.50 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE12** as a yellow oil (0.74 g, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (tt, *J* = 8.8, 3.8 Hz, 1H), 2.56 (s, 3H), 2.05 – 1.94 (m, 2H), 1.83 – 1.73 (m, 2H), 1.70 – 1.54 (m, 3H), 1.51 – 1.30 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.0, 82.5, 30.9, 25.3, 23.6, 18.7.

HRMS (ESI) *m/z* calcd. for $C_8H_{14}OS_2$ $[M + H]^+$ 191.0559, found 191.0561.

O-Cycloheptyl *S*-methyl carbonodithioate (XE13)



XE13

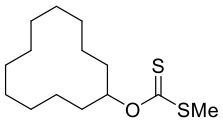
According to General Procedure 1 with cycloheptanol (0.57 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE13** as a yellow oil (0.89 g, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.64 (m, 1H), 2.55 (s, 3H), 2.11 – 2.01 (m, 2H), 1.93 – 1.78 (m, 2H), 1.77 – 1.65 (m, 2H), 1.63 – 1.52 (m, 4H), 1.55 – 1.44 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 214.9, 85.4, 33.2, 28.4, 22.9, 18.8.

HRMS (ESI) *m/z* calcd. for $C_9H_{16}OS_2$ $[M + H]^+$ 205.0715, found 205.0717.

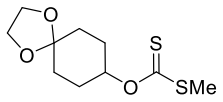
***O*-Cyclododecyl S-methyl carbonodithioate (XE14)**



XE14

According to General Procedure 1 with cyclododecanol (0.92 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE14** as a yellow oil (1.28 g, 93% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (tt, *J* = 7.1, 4.8 Hz, 1H), 2.56 (s, 3H), 1.91 – 1.80 (m, 2H), 1.77 – 1.67 (m, 2H), 1.54 – 1.27 (m, 18H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.4, 82.9, 28.7, 24.0, 23.7, 23.4, 23.2, 21.0, 18.7.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{26}OS_2$ $[M + Na]^+$ 293.1317, found 293.1318.

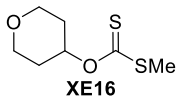
***S*-Methyl *O*-(1,4-dioxaspiro[4.5]decan-8-yl) carbonodithioate (XE15)**



XE15

According to General Procedure 1 with 1,4-dioxaspiro[4.5]decan-8-ol (0.79 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 50/1 to yield the product **XE15** as an orange solid (1.17 g, 94% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 – 5.61 (m, 1H), 4.00 – 3.90 (m, 4H), 2.54 (d, *J* = 2.7 Hz, 3H), 2.04 – 1.94 (m, 4H), 1.87 – 1.76 (m, 2H), 1.72 – 1.61 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.0, 107.8, 79.6, 64.41, 64.38, 31.2, 27.8, 18.8.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{16}O_3S_2$ $[M + Na]^+$ 271.0433, found 271.0435.

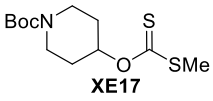
***S*-Methyl *O*-(tetrahydro-2*H*-pyran-4-yl) carbonodithioate (XE16)**



XE16

According to General Procedure 1 with tetrahydro-2*H*-pyran-4-ol (0.51 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 20/1 to yield the product **XE16** as a yellow oil (0.79 g, 82% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.56 (m, 1H), 4.09 – 3.88 (m, 2H), 3.68 – 3.52 (m, 2H), 2.59 – 2.53 (m, 3H), 2.19 – 1.98 (m, 2H), 1.92 – 1.80 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.9, 78.3, 65.2, 31.1, 19.0.
HRMS (ESI) *m/z* calcd. for $C_7H_{12}O_2S_2$ $[M + H]^+$ 193.0351, found 193.0354.

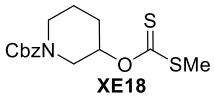
***tert*-Butyl 4-(((methylthio)carbonothioyl)oxy)piperidine-1-carboxylate (XE17)**



XE17

According to General Procedure 1 with *tert*-butyl 4-hydroxypiperidine-1-carboxylate (1.0 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 5/1 to yield the product **XE17** as a yellow oil (1.35 g, 93% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (tt, *J* = 7.6, 3.7 Hz, 1H), 3.73 – 3.63 (m, 2H), 3.41 – 3.31 (m, 2H), 2.57 (s, 3H), 2.04 – 1.93 (m, 2H), 1.88 – 1.77 (m, 2H), 1.48 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.0, 154.7, 79.8, 78.9, 41.0, 30.0, 28.4, 19.0.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{21}NO_3S_2$ $[M + Na]^+$ 314.0855, found 314.0857.

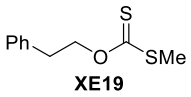
Benzyl 3-(((methylthio)carbonothioyl)oxy)piperidine-1-carboxylate (XE18)



XE18

According to General Procedure 1 with benzyl 3-hydroxypiperidine-1-carboxylate (0.71 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 5/1 to yield the product **XE18** as a yellow oil (0.89 g, 91% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 5.63 (s, 1H), 5.15 (s, 2H), 4.04 – 3.26 (m, 4H), 2.49 (s, 3H), 2.08 – 1.52 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.9, 155.4, 136.6, 128.5, 128.0, 127.8, 76.6, 67.3, 46.9, 44.1, 28.5, 21.6, 18.8.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{19}NO_3S_2$ $[M + H]^+$ 326.0879, found 326.0880.

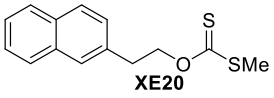
***S*-Methyl *O*-phenethyl carbonodithioate (XE19)**



XE19

According to General Procedure 1 with 2-phenylethan-1-ol (0.61 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE19** as a yellow oil (1.05 g, 99% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.03 (m, 5H), 4.85 (t, *J* = 7.1 Hz, 2H), 3.16 (t, *J* = 7.1 Hz, 2H), 2.57 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.7, 137.3, 129.0, 128.7, 126.8, 74.1, 34.7, 18.9.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{12}OS_2$ $[M + H]^+$ 213.0402, found 213.0404.

***S*-Methyl *O*-(2-(naphthalen-2-yl)ethyl) carbonodithioate (XE20)**

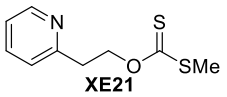


XE20

According to General Procedure 1 with 2-(naphthalen-2-yl)ethan-1-ol (0.86 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE20** as a yellow oil (1.3 g, 99% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 3H), 7.67 (s, 1H), 7.51 – 7.40 (m, 2H), 7.35 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.87 (t, *J* = 7.0 Hz, 2H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.50 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.8, 134.8, 133.6, 132.4, 128.3, 127.7, 127.6, 127.5, 127.3, 126.2, 125.7, 74.0, 34.8, 19.0.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{14}OS_2$ $[M + H]^+$ 263.0559, found 263.0566.

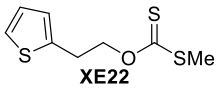
S-Methyl *O*-(2-(pyridin-2-yl)ethyl) carbonodithioate (XE21)



XE21

According to General Procedure 1 with 2-(pyridin-2-yl)ethan-1-ol (0.61 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 5/1 to yield the product **XE21** as a yellow oil (1.0 g, 94% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.8 Hz, 1H), 7.63 (td, *J* = 7.7, 1.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.14 (m, 1H), 4.99 (t, *J* = 6.7 Hz, 2H), 3.28 (t, *J* = 6.7 Hz, 2H), 2.50 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.6, 157.5, 149.6, 136.5, 123.5, 121.8, 72.7, 36.9, 18.9.
HRMS (ESI) *m/z* calcd. for $C_9H_{11}NOS_2$ $[M + H]^+$ 214.0355, found 214.0355.

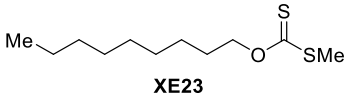
S-Methyl *O*-(2-(thiophen-2-yl)ethyl) carbonodithioate (XE22)



XE22

According to General Procedure 1 with 2-(thiophen-2-yl)ethan-1-ol (0.64 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 20/1 to yield the product **XE22** as a yellow oil (0.84 g, 77% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 1H), 6.99 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.94 – 6.90 (m, 1H), 4.84 (t, *J* = 6.7 Hz, 2H), 3.37 (t, *J* = 6.7 Hz, 2H), 2.59 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.6, 139.3, 127.0, 125.9, 124.3, 73.6, 28.9, 19.1.
HRMS (ESI) *m/z* calcd. for $C_8H_{10}OS_3$ $[M + Na]^+$ 240.9786, found 240.9788.

S-Methyl *O*-nonyl carbonodithioate (XE23)

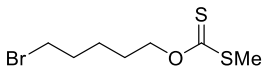


XE23

According to General Procedure 1 with nonan-1-ol (0.72 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE23** as a yellow oil (1.16 g, 99% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (t, *J* = 6.7 Hz, 2H), 2.58 (s, 3H), 1.95 – 1.73 (m, 2H), 1.45 – 1.23 (m, 12H), 0.94 – 0.86 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 74.3, 31.9, 29.5, 29.2, 28.3, 25.9, 22.7, 18.9, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{22}OS_2$ $[M + H]^+$ 235.1185, found 235.1188.

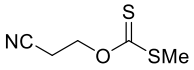
O-(5-Bromopentyl) *S*-methyl carbonodithioate (XE24)



XE24

According to General Procedure 1 with 5-bromopentan-1-ol (0.84 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE24** as a yellow oil (0.79 g, 62% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (t, *J* = 6.5 Hz, 2H), 3.45 (t, *J* = 6.7 Hz, 2H), 2.58 (s, 3H), 2.01 – 1.80 (m, 4H), 1.67 – 1.55 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 73.6, 33.5, 32.2, 27.5, 24.6, 19.0.
HRMS (ESI) *m/z* calcd. for $C_7H_{13}BrOS_2$ $[M + H]^+$ 256.9664, found 256.9667.

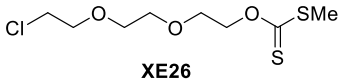
O-(2-Cyanoethyl) *S*-methyl carbonodithioate (XE25)



XE25

According to General Procedure 1 with 3-hydroxypropanenitrile (0.36 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 50/1 to yield the product **XE25** as a yellow oil (0.34 g, 42% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (t, *J* = 6.3 Hz, 2H), 2.89 (t, *J* = 6.3 Hz, 2H), 2.59 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.3, 116.6, 66.7, 19.3, 17.7.
HRMS (ESI) *m/z* calcd. for $C_5H_7NOS_2$ $[M + H]^+$ 162.0042, found 162.0044.

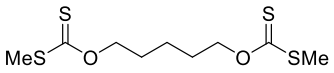
O-(2-(2-(2-Chloroethoxy)ethoxy)ethyl) *S*-methyl carbonodithioate (XE26)



XE26

According to General Procedure 1 with 2-(2-(2-chloroethoxy)ethoxy)ethan-1-ol (0.84 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 50/1 to yield the product **XE26** as a yellow oil (0.87 g, 67% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 – 4.69 (m, 2H), 3.93 – 3.83 (m, 2H), 3.76 (t, *J* = 5.8 Hz, 2H), 3.69 – 3.66 (m, 4H), 3.63 (t, *J* = 5.7 Hz, 2H), 2.56 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 72.7, 71.4, 70.74, 70.65, 68.6, 42.8, 19.1.
HRMS (ESI) *m/z* calcd. for $C_8H_{15}ClO_3S_2$ $[M + H]^+$ 259.0224, found 259.0219.

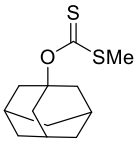
S,S′-Dimethyl *O,O′*-(pentane-1,5-diyl) bis(carbonodithioate) (XE27)



XE27

According to General Procedure 1 with pentane-1,5-diol (0.52 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 100/1 to yield the product **XE27** as a yellow oil (1.16 g, 82% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (t, *J* = 6.5 Hz, 4H), 2.58 (s, 6H), 2.02 – 1.78 (m, 4H), 1.68 – 1.50 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 73.7, 27.9, 22.5, 19.0.
HRMS (ESI) *m/z* calcd. for $C_9H_{16}O_2S_4$ $[M + Na]^+$ 306.9925, found 306.9929.

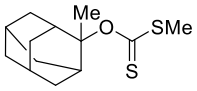
O-(Adamantan-1-yl) *S*-methyl carbonodithioate (XE28)



XE28

According to General Procedure 1 with adamantan-1-ol (0.76 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE28** as a white powder (0.70 g, 58% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 – 2.43 (m, 9H), 2.29 – 2.23 (m, 3H), 1.76 – 1.66 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 91.4, 41.1, 36.1, 31.4, 19.1.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}OS_2$ $[M + Na]^+$ 265.0691, found 265.0693.

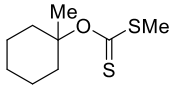
S-Methyl *O*-(2-methyladamantan-2-yl) carbonodithioate (XE29)



XE29

According to General Procedure 2 with 2-methyladamantan-2-ol (0.33 g, 2.0 mmol, 1.0 equiv.), the crude product **XE29** showed 78% purity by NMR and was directly used in the next step without purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 3H), 2.15 – 2.05 (m, 2H), 1.91 (s, 3H), 1.90 – 1.85 (m, 3H), 1.84 – 1.78 (m, 3H), 1.77 – 1.73 (m, 2H), 1.69 – 1.59 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 212.5, 98.4, 38.0, 36.5, 32.9, 27.3, 26.5, 21.7, 19.2.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{20}OS_2$ $[M + H]^+$ 257.1028, found 257.1030.

S-Methyl *O*-(1-methylcyclohexyl) carbonodithioate (XE30)

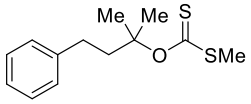


XE30

According to General Procedure 1 with 1-methylcyclohexan-1-ol (0.34 g, 3.0 mmol, 1.0 equiv.), the crude product **XE30** showed 81% purity by NMR and was directly used in the next step without purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3H), 1.76 (s, 3H), 1.61 – 1.50 (m, 8H), 1.33 – 1.24 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.0, 92.8, 36.7, 25.6, 25.1, 21.9, 19.1.
HRMS (ESI) *m/z* calcd. for $C_9H_{16}OS_2$ $[M + Na]^+$ 227.0535, found 227.0530.

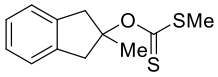
S-Methyl *O*-(2-methyl-4-phenylbutan-2-yl) carbonodithioate (XE31)



XE31

According to General Procedure 2 with 2-methyl-4-phenylbutan-2-ol (0.33 g, 2.0 mmol, 1.0 equiv.), the crude product **XE31** showed 75% purity by NMR and was directly used in the next step without purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 2.74 – 2.67 (m, 2H), 2.50 (s, 3H), 2.43 – 2.36 (m, 2H), 1.76 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.3, 141.8, 128.5, 128.4, 126.0, 92.5, 42.5, 30.2, 26.2, 19.3.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}OS_2$ $[M + H]^+$ 255.0872, found 255.0873.

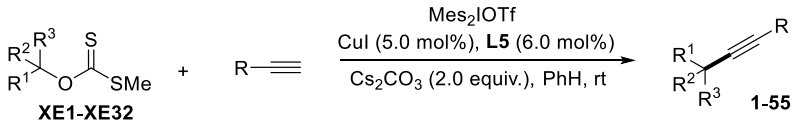
S-Methyl *O*-(2-methyl-2,3-dihydro-1*H*-inden-2-yl) carbonodithioate (XE32)



XE32

According to General Procedure 2 with 2-methyl-2,3-dihydro-1*H*-inden-2-ol (0.15 g, 1.0 mmol, 1.0 equiv.), the crude product **XE32** showed 65% purity by NMR and was directly used in the next step without purification.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 4H), 3.75 (d, J = 16.5 Hz, 2H), 3.34 (d, J = 16.6 Hz, 2H), 2.48 (s, 3H), 1.92 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.5, 139.9, 126.9, 124.6, 97.5, 46.3, 24.3, 19.3.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{14}OS_2$ $[M + H]^+$ 239.0559, found 239.0555.

The synthesis of product



XE1-XE32 **1-55**

General procedure A:

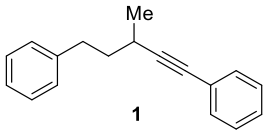
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L5** (3.0 mg, 0.012 mmol, 6.0 mol%), Mes_2IOTf (154.2 mg, 0.30 mmol, 1.5 equiv.), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous benzene (2.0 mL). Then, xanthate ester (0.24 mmol, 1.2 equiv.), and alkyne (0.20 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 24 to 48

h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure B:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L5** (3.0 mg, 0.012 mmol, 6.0 mol%), Mes_2IOTf (308.4 mg, 0.60 mmol, 3.0 equiv.), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous benzene (2.0 mL). Then, xanthate ester (0.20 mmol, 1.0 equiv.), and alkyne (0.44 mmol, 2.2 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 24 to 48 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

(3-Methylpent-1-yne-1,5-diyl)dibenzene (1)



1

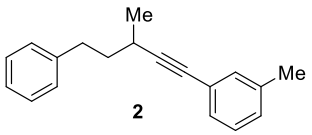
According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and ethynylbenzene **N1** (20.4 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **1** as a colorless oil (37.4 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.35 – 7.12 (m, 8H), 2.94 – 2.84 (m, 1H), 2.83 – 2.73 (m, 1H), 2.71 – 2.58 (m, 1H), 1.92 – 1.73 (m, 2H), 1.28 (d, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 131.6, 128.6, 128.4, 128.3, 127.6, 125.9, 124.0, 94.3, 81.4, 38.8, 33.8, 26.1, 21.1.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{18}$ $[M + H]^+$ 235.1481, found 235.1482.

1-Methyl-3-(3-methyl-5-phenylpent-1-yn-1-yl)benzene (2)

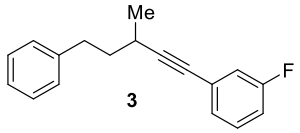


2

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 1-ethynyl-3-methylbenzene **N2** (23.2 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **2** as a colorless oil (40.2 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 8H), δ 7.16 – 7.11 (m, 1H), 3.00 – 2.89 (m, 1H), 2.88 – 2.78 (m, 1H), 2.75 – 2.63 (m, 1H), 2.37 (s, 3H), 1.95 – 1.79 (m, 2H), 1.32 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 137.9, 132.3, 128.7, 128.6, 128.5, 128.4, 128.2, 125.8, 123.8, 93.9, 81.5, 38.8, 33.8, 26.1, 21.3, 21.2.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{20}$ $[M + H]^+$ 249.1638, found 249.1638.

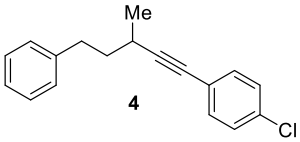
1-Fluoro-3-(3-methyl-5-phenylpent-1-yn-1-yl)benzene (3)



3

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 1-ethynyl-3-fluorobenzene **N3** (24.0 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **3** as a colorless oil (37.8 mg, 75% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.17 (m, 7H), 7.15 – 7.08 (m, 1H), δ 7.33 – 7.17 (m, 1H), 2.95 – 2.84 (m, 1H), 2.82 – 2.72 (m, 1H), 2.70 – 2.58 (m, 1H), 1.91 – 1.75 (m, 2H), 1.27 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.8 Hz), 142.0, 129.7 (d, *J* = 8.7 Hz), 128.6, 128.4, 127.5 (d, *J* = 2.9 Hz), 125.91, 125.89 (d, *J* = 9.3 Hz), 118.4 (d, *J* = 22.5 Hz), 114.9 (d, *J* = 21.2 Hz), 95.4, 80.3 (d, *J* = 3.4 Hz), 38.6, 33.8, 26.0, 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.29 – -113.41 (m, 1F).
HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}F$ $[M + H]^+$ 253.1387, found 253.1407.

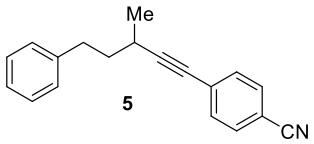
1-Chloro-4-(3-methyl-5-phenylpent-1-yn-1-yl)benzene (4)



4

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 1-chloro-4-ethynylbenzene **N4** (27.3 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **4** as a colorless oil (41.9 mg, 78% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.21 (m, 9H), 2.98 – 2.87 (m, 1H), 2.86 – 2.76 (m, 1H), 2.75 – 2.63 (m, 1H), 1.94 – 1.79 (m, 2H), 1.32 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 133.5, 132.9, 128.55, 128.54, 128.4, 125.9, 122.5, 95.3, 80.4, 38.6, 33.8, 26.1, 21.0.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}Cl$ $[M + H]^+$ 269.1092, found 269.1091.

4-(3-Methyl-5-phenylpent-1-yn-1-yl)benzonitrile (5)



5

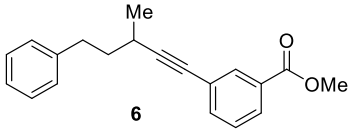
According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 4-ethynylbenzonitrile **N5** (25.4 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 50/1 to yield the product **5** as a colorless oil (36.3 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.27 – 7.17 (m, 3H), 2.92 – 2.82 (m, 1H), 2.82 – 2.73 (m, 1H), 2.73 – 2.63 (m, 1H), 1.93 – 1.76 (m, 2H), 1.29 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 132.2, 132.0, 129.0, 128.50, 128.45, 126.0, 118.7, 110.9, 99.4, 80.2, 38.4, 33.7, 26.2, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{17}N$ $[M + H]^+$ 260.1434, found 260.1439.

Methyl 3-(3-methyl-5-phenylpent-1-yn-1-yl)benzoate (6)



6

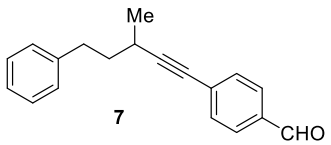
According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and methyl 3-ethynylbenzoate **N6** (32.0 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 50/1 to yield the product **6** as a colorless oil (45.0mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.31 – 7.21 (m, 3H), 3.96 (s, 3H), 2.98 – 2.89 (m, 1H), 2.88 – 2.79 (m, 1H), 2.77 – 2.66 (m, 1H), 1.97 – 1.80 (m, 2H), 1.34 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 142.0, 135.8, 132.8, 130.3, 128.61, 128.56, 128.42, 128.37, 125.9, 124.5, 95.3, 80.5, 52.3, 38.6, 33.8, 26.1, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{20}O_2$ $[M + H]^+$ 293.1536, found 293.1538.

4-(3-Methyl-5-phenylpent-1-yn-1-yl)benzaldehyde (7)

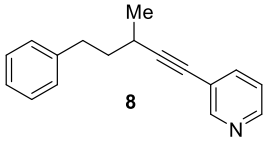


7

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 4-ethynylbenzaldehyde **N7** (26.0 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **7** as a colorless oil (33.0 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.13 (m, 5H), 2.96 – 2.87 (m, 1H), 2.85 – 2.78 (m, 1H), 2.77 – 2.67 (m, 1H), 1.92 – 1.84 (m, 2H), 1.33 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 141.8, 135.0, 132.2, 130.5, 129.5, 128.52, 128.45, 126.0, 99.0, 80.9, 38.5, 33.8, 26.2, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{18}O$ $[M + H]^+$ 263.1430, found 263.1433.

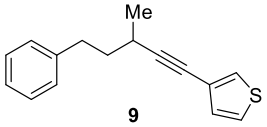
3-(3-Methyl-5-phenylpent-1-yn-1-yl)pyridine (8)



8

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 3-ethynylpyridine **N8** (20.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 2/1 to yield the product **8** as a colorless oil (37.2 mg, 79% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 1.3 Hz, 1H), 8.52 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.72 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.36 – 7.19 (m, 6H), 2.95 – 2.86 (m, 1H), 2.85 – 2.76 (m, 1H), 2.75 – 2.64 (m, 1H), 1.96 – 1.80 (m, 2H), 1.32 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 148.0, 141.8, 138.5, 128.5, 128.4, 125.9, 122.9, 121.1, 97.9, 78.2, 38.5, 33.7, 26.1, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}N$ $[M + H]^+$ 236.1434, found 236.1435.

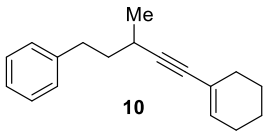
3-(3-Methyl-5-phenylpent-1-yn-1-yl)thiophene (9)



9

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 3-ethynylthiophene **N1** (21.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **9** as a colorless oil (30.3 mg, 63% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 2.9 Hz, 1H), 7.32 – 7.15 (m, 6H), 7.09 (d, *J* = 5.0 Hz, 1H), 2.92 – 2.82 (m, 1H), 2.82 – 2.71 (m, 1H), 2.68 – 2.58 (m, 1H), 1.90 – 1.73 (m, 2H), 1.26 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 130.1, 128.6, 128.4, 127.6, 125.9, 125.1, 123.0, 93.7, 76.4, 38.7, 33.8, 26.1, 21.1.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}S$ $[M + H]^+$ 241.1045, found 241.1045.

(5-(Cyclohex-1-en-1-yl)-3-methylpent-4-yn-1-yl)benzene (10)



10

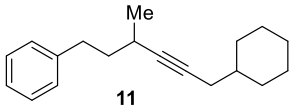
According to General Procedure *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **A** with **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 1-ethynylcyclohex-1-ene **N10** (21.2 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **10** as a colorless oil (36.2 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.24 – 7.12 (m, 3H), 6.08 – 6.00 (m, 1H), 2.87 – 2.77 (m, 1H), 2.76 – 2.65 (m, 1H), 2.60 – 2.48 (m, 1H), 2.17 – 2.11 (m, 2H), 2.10 – 2.05 (m, 2H), 1.78 – 1.70 (m, 2H), 1.67 – 1.51 (m, 4H), 1.19 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 133.3, 128.6, 128.3, 125.8, 121.0, 91.4, 83.1, 38.9, 33.8, 29.8, 26.0, 25.6, 22.5, 21.7, 21.3.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}$ $[M + H]^+$ 239.1794, found 239.1794.

(6-Cyclohexyl-3-methylhex-4-yn-1-yl)benzene (11)



11

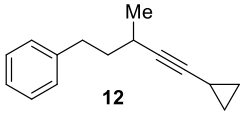
According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-ylcyclohexane **N11** (24.4 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **11** as a colorless oil (33.1 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.24 – 7.14 (m, 3H), 2.89 – 2.77 (m, 1H), 2.74 – 2.63 (m, 1H), 2.47 – 2.35 (m, 1H), 2.09 (dd, *J* = 6.6, 2.0 Hz, 2H), 1.82 (d, *J* = 13.0 Hz, 2H), 1.77 – 1.61 (m, 5H), 1.50 – 1.38 (m, 1H), 1.33 – 1.10 (m, 6H), 1.01 (qd, *J* = 12.4, 2.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 128.5, 128.3, 125.7, 85.3, 79.8, 39.3, 37.8, 33.9, 32.8, 26.7, 26.4, 26.3, 25.6, 21.6.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{26}$ $[M + H]^+$ 255.2107, found 255.2106.

(5-Cyclopropyl-3-methylpent-4-yn-1-yl)benzene (12)

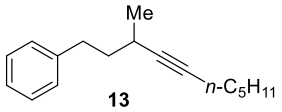


12

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and ethynylcyclopropane **N12** (13.2 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **12** as a colorless oil (28.2 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.12 (m, 3H), 2.84 – 2.72 (m, 1H), 2.71 – 2.60 (m, 1H), 2.47 – 2.28 (m, 1H), 1.74 – 1.61 (m, 2H), 1.29 – 1.19 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 3H), 0.76 – 0.70 (m, 2H), 0.65 – 0.59 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 128.9, 128.7, 126.1, 84.5, 80.1, 39.4, 34.2, 25.9, 21.9, 8.7, 8.6, 0.00.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{18}$ $[M + H]^+$ 199.1481, found 199.1485.

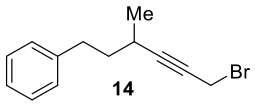
(3-Methyldec-4-yn-1-yl)benzene (13)



13

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and hept-1-yne **N13** (19.2 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **13** as a colorless oil (35.2 mg, 77% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 5H), 2.94 – 2.82 (m, 1H), 2.82 – 2.69 (m, 1H), 2.52 – 2.40 (m, 1H), 2.29 – 2.20 (m, 2H), 1.81 – 1.71 (m, 2H), 1.61 – 1.53 (m, 2H), 1.50 – 1.34 (m, 4H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.01 – 0.91 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 128.5, 128.3, 125.7, 84.4, 81.1, 39.2, 33.8, 31.1, 29.0, 25.6, 22.3, 21.6, 18.8, 14.1.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{24}$ $[M + H]^+$ 229.1951, found 229.1956.

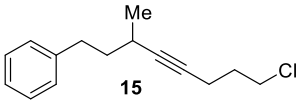
(6-Bromo-3-methylhex-4-yn-1-yl)benzene (14)



14

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 3-bromoprop-1-yne **N14** (23.8 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **14** as a colorless oil (25.1 mg, 50% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.24 – 7.13 (m, 3H), 3.97 (d, *J* = 2.1 Hz, 2H), 2.90 – 2.75 (m, 1H), 2.74 – 2.62 (m, 1H), 2.54 – 2.44 (m, 1H), 1.81 – 1.68 (m, 2H), 1.18 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 128.5, 128.4, 125.9, 92.1, 76.2, 38.4, 33.6, 25.6, 20.7, 15.8.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{15}Br$ $[M + H]^+$ 251.0430, found 251.0417.

(8-Chloro-3-methyloct-4-yn-1-yl)benzene (15)



15

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl)

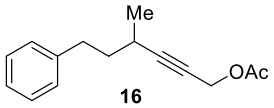
carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 5-chloropent-1-yne **N15** (20.5 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **15** as a colorless oil (35.2 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.89 – 2.79 (m, 1H), 2.76 – 2.66 (m, 1H), 2.46 – 2.40 (m, 3H), 1.99 (p, *J* = 6.6 Hz, 2H), 1.79 – 1.66 (m, 2H), 1.19 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 128.5, 128.4, 125.8, 85.6, 78.8, 43.8, 39.0, 33.8, 31.9, 25.5, 21.5, 16.3.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{19}Cl$ $[M + H]^+$ 235.1248, found 235.1240.

4-Methyl-6-phenylhex-2-yn-1-yl acetate (16)



16

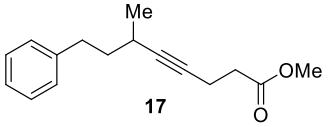
According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 2/1 to yield the product **16** as a colorless oil (38.2 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.23 – 7.13 (m, 3H), 4.70 (d, *J* = 2.0 Hz, 2H), 2.85 – 2.74 (m, 1H), 2.73 – 2.63 (m, 1H), 2.53 – 2.41 (m, 1H), 2.10 (s, 3H), 1.82 – 1.65 (m, 2H), 1.19 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 141.9, 128.5, 128.4, 125.9, 91.5, 74.7, 52.9, 38.4, 33.6, 25.5, 20.9, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{18}O_2$ $[M + H]^+$ 231.1380, found 231.1383.

Methyl 6-methyl-8-phenyloct-4-ynoate (17)



17

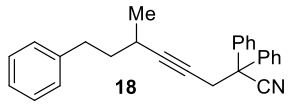
According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and methyl pent-4-ynoate **N17** (22.4 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 2/1 to yield the product **17** as a colorless oil (40.1 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), δ 7.22 – 7.12 (m, 3H), 3.69 (s, 3H), 2.84 – 2.73 (m, 1H), 2.72 – 2.61 (m, 1H), 2.58 – 2.47 (m, 4H), 2.43 – 2.30 (m, 1H), 1.72 – 1.62 (m, 2H), 1.14 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 142.2, 128.5, 128.3, 125.8, 85.3, 78.9, 51.7, 38.9, 34.1, 33.7, 25.4, 21.3, 14.9.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{20}O_2$ $[M + H]^+$ 245.1536, found 245.1544.

6-Methyl-2,2,8-triphenyloct-4-ynenitrile (18)



18

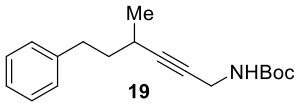
According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and 2,2-diphenylpent-4-ynenitrile **N18** (46.2 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **18** as a colorless oil (40.0 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 4H), 7.39 – 7.27 (m, 6H), 7.26 – 7.18 (m, 2H), 7.16 – 7.13 (m, 1H), 7.12 – 7.02 (m, 2H), 3.25 (d, *J* = 2.0 Hz, 2H), 2.67 – 2.55 (m, 1H), 2.53 – 2.44 (m, 1H), 2.35 – 2.25 (m, 1H), 1.58 (q, *J* = 8.0 Hz, 2H), 1.06 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 139.34, 139.32, 128.8, 128.6, 128.3, 128.2, 127.2, 125.7, 122.1, 89.6, 75.2, 51.9, 38.7, 33.4, 31.4, 25.4, 21.1.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{25}N$ $[M + H]^+$ 364.2060, found 364.2061.

***tert*-Butyl (4-methyl-6-phenylhex-2-yn-1-yl)carbamate (19)**



19

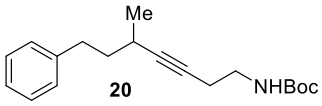
According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and *tert*-butyl prop-2-yn-1-ylcarbamate **N19** (31.0 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/3 to yield the product **19** as a colorless oil (37.9 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.23 – 7.15 (m, 3H), 4.69 (s, 1H), 3.92 (s, 2H), 2.85 – 2.73 (m, 1H), 2.72 – 2.62 (m, 1H), 2.46 – 2.35 (m, 1H), 1.75 – 1.67 (m, 2H), 1.45 (s, 9H), 1.16 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 142.0, 128.5, 128.4, 125.8, 87.6, 79.8, 76.8, 38.5, 33.7, 30.9, 28.4, 25.4, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{25}NO_2$ $[M + H]^+$ 288.1958, found 288.1963.

***tert*-Butyl (5-methyl-7-phenylhept-3-yn-1-yl)carbamate (20)**

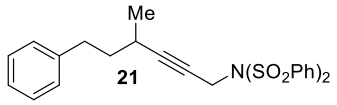


20

According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and *tert*-butyl but-3-yn-1-ylcarbamate **N20** (33.8 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/3 to yield the product **20** as a colorless oil (42.2 mg, 70% yield).

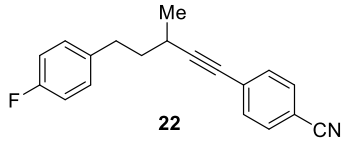
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.12 (m, 3H), 4.83 (s, 1H), 3.32 – 3.18 (m, 2H), 2.85 – 2.75 (m, 1H), 2.72 – 2.62 (m, 1H), 2.44 – 2.35 (m, 3H), 1.75 – 1.65 (m, 2H), 1.44 (s, 9H), 1.16 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 142.1, 128.5, 128.3, 125.8, 86.2, 79.4, 77.8, 39.9, 38.9, 33.8, 28.4, 25.5, 21.4, 20.3.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{27}NO_2$ $[M + H]^+$ 302.2115, found 302.2119.

_N_-(4-Methyl-6-phenylhex-2-yn-1-yl)-N-(phenylsulfonyl)benzenesulfonamide (21)



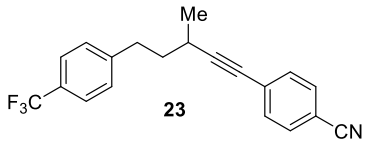
According to General Procedure **A** with *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), and *N*-(phenylsulfonyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide **N21** (67.1 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/1 to yield the product **21** as a colorless oil (72.0 mg, 77% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.07 (m, 4H), 7.68 – 7.61 (m, 2H), 7.68 – 7.61 (m, 4H), 7.35 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 4.62 (d, *J* = 1.8 Hz, 2H), 2.75 – 2.64 (m, 1H), 2.63 – 2.54 (m, 1H), 2.34 – 2.25 (m, 1H), 1.74 – 1.53 (m, 2H), 1.06 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 139.8, 134.0, 129.0, 128.6, 128.4, 125.9, 89.9, 74.6, 38.9, 38.3, 33.5, 25.3, 20.5.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{25}NO_4S_2$ $[M + H]^+$ 468.1298, found 468.1304.

4-(5-(4-Fluorophenyl)-3-methylpent-1-yn-1-yl)benzonitrile (22)



According to General Procedure **A** with *O*-(4-(4-fluorophenyl)butan-2-yl) *S*-methyl carbonodithioate **XE2** (62.0 mg, 0.24 mmol, 1.2 equiv.), and 4-ethynylbenzonitrile **N5** (25.4 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 10/1 to yield the product **22** as a colorless oil (38.3 mg, 69% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.12 (m, 2H), 7.02 – 6.92 (m, 2H), 2.88 – 2.61 (m, 3H), 1.89 – 1.74 (m, 2H), 1.29 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, *J* = 243.6 Hz), 137.3 (d, *J* = 3.0 Hz), 132.2, 132.0, 129.8 (d, *J* = 7.8 Hz), 128.9, 118.7, 115.2 (d, *J* = 21.1 Hz), 110.9, 99.1, 80.3, 38.5, 32.9, 26.1, 20.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.41 – -117.57 (m, 1F).
HRMS (ESI) *m/z* calcd. for $C_{19}H_{16}FN$ $[M + H]^+$ 278.1340, found 278.1344.

4-(3-Methyl-5-(4-(trifluoromethyl)phenyl)pent-1-yn-1-yl)benzonitrile (23)



According to General Procedure **A** with *S*-methyl *O*-(4-(4-(trifluoromethyl)phenyl)butan-2-yl) carbonodithioate **XE3** (74.0 mg, 0.24 mmol, 1.2 equiv.), and 4-ethynylbenzonitrile **N5** (25.4 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 10/1 to yield the product **23** as a colorless oil (45.8mg, 70% yield).

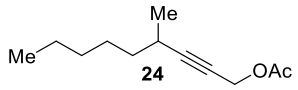
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.98 – 2.77 (m, 2H), 2.73 – 2.62 (m, 1H), 1.92 – 1.81 (m, 2H), 1.30 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 132.2, 132.0, 128.8, 128.5, 128.2, 125.4 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 271.7 Hz), 118.6, 111.0, 98.8, 80.5, 38.0, 33.6, 26.2, 20.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.28 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{20}H_{16}F_3N$ $[M + H]^+$ 328.1308, found 328.1305.

4-Methylnon-2-yn-1-yl acetate (24)



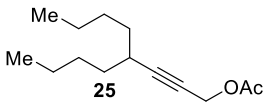
According to General Procedure **A** with *O*-(heptan-2-yl) *S*-methyl carbonodithioate **XE4** (49.5 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **24** as a colorless oil (31.4 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 2.0 Hz, 2H), 2.55 – 2.41 (m, 1H), 2.10 (s, 3H), 1.50 – 1.25 (m, 8H), 1.16 (d, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 92.1, 73.9, 52.9, 36.6, 31.6, 27.0, 25.9, 22.6, 20.9, 20.8, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{20}O_2$ $[M + H]^+$ 197.1536, found 197.1540.

4-Butyloct-2-yn-1-yl acetate (25)

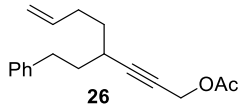


According to General Procedure **A** with *S*-methyl *O*-(nonan-5-yl) carbonodithioate **XE5** (56.3 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **25** as a colorless oil (34.1 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 1.8 Hz, 2H), 2.40 – 2.28 (m, 1H), 2.09 (s, 3H), 1.51 – 1.23 (m, 12H), 0.90 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 91.2, 74.8, 53.0, 34.6, 31.7, 29.5, 22.6, 20.9, 14.0.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{24}O_2$ $[M + H]^+$ 225.1849, found 225.1851.

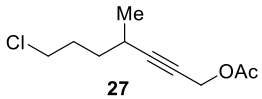
4-Phenethyloct-7-en-2-yn-1-yl acetate (26)



26

According to General Procedure **A** with *S*-methyl *O*-(1-phenylhept-6-en-3-yl) carbonodithioate **XE6** (67.3 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **26** as a colorless oil (40.0 mg, 74% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.08 – 4.89 (m, 2H), 4.72 (d, *J* = 2.0 Hz, 2H), 2.89 – 2.76 (m, 1H), 2.74 – 2.62 (m, 1H), 2.46 – 2.36 (m, 1H), 2.30 – 2.18 (m, 1H), 2.17 – 2.07 (m, 4H), 1.81 – 1.70 (m, 2H), 1.59 – 1.51 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 141.9, 138.1, 128.5, 128.4, 125.9, 115.0, 90.0, 76.0, 52.9, 36.6, 34.0, 33.6, 31.5, 30.8, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}O_2$ $[M + H]^+$ 271.1693, found 271.1693.

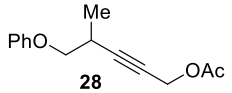
7-Chloro-4-methylhept-2-yn-1-yl acetate (27)



27

According to General Procedure **A** with *O*-(5-chloropentan-2-yl) *S*-methyl carbonodithioate **XE7** (51.1 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **27** as a colorless oil (24.3 mg, 60% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (d, *J* = 2.0 Hz, 2H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.56 – 2.47 (m, 1H), 2.10 (s, 3H), 2.03 – 1.80 (m, 2H), 1.68 – 1.48 (m, 2H), 1.19 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 91.0, 74.7, 52.8, 44.9, 33.8, 30.4, 25.5, 20.9, 20.8.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{15}ClO_2$ $[M + H]^+$ 203.0833, found 203.0831.

4-Methyl-5-phenoxypent-2-yn-1-yl acetate (28)



28

According to General Procedure **A** with *S*-methyl *O*-(1-phenoxypropan-2-yl) carbonodithioate **XE8** (58.2 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by

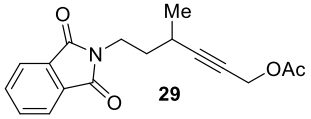
column chromatography on silica gel using PE/DCM = 1/1 to yield the product **28** as a colorless oil (36.2 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H), 6.98 – 6.93 (m, 1H), 6.92 – 6.87 (m, 2H), 4.68 (d, *J* = 2.0 Hz, 2H), 4.04 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.82 (dd, *J* = 8.8, 7.9 Hz, 1H), 3.06 – 2.86 (m, 1H), 2.09 (s, 3H), 1.31 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 158.6, 129.5, 121.0, 114.7, 88.3, 75.4, 71.2, 52.7, 26.5, 20.9, 17.5.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{16}O_3$ $[M + H]^+$ 233.1172, found 233.1172.

6-(1,3-Dioxoisoindolin-2-yl)-4-methylhex-2-yn-1-yl acetate (29)



29

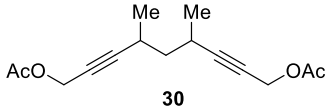
According to General Procedure **A** with *O*-(4-(1,3-dioxoisoindolin-2-yl)butan-2-yl) *S*-methyl carbonodithioate **XE9** (74.2 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/3 to yield the product **29** as a colorless oil (37.7 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.80 (m, 2H), 7.78 – 7.66 (m, 2H), 4.53 (d, *J* = 2.0 Hz, 2H), 3.93 – 3.70 (m, 2H), 2.64 – 2.49 (m, 1H), 2.08 (s, 3H), 1.92 – 1.77 (m, 2H), 1.23 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 168.3, 133.9, 132.2, 123.2, 90.4, 74.9, 52.6, 36.2, 34.8, 24.0, 20.8, 20.7.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}NO_4$ $[M + Na]^+$ 322.1050, found 322.1045.

4,6-Dimethylnona-2,7-diyne-1,9-diyl diacetate (30)



30

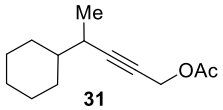
According to General Procedure **B** with *S*,*S'*-dimethyl *O*,*O'*-(pentane-2,4-diyl) bis(carbonodithioate) **XE10** (56.9 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (43.2 mg, 0.44 mmol, 2.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/1 to yield the product **30** as a colorless oil (14.8 mg, 28% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (t, *J* = 2.4 Hz, 4H), 2.79 – 2.60 (m, 2H), 2.10 (s, 6H), 1.53 – 1.40 (m, 2H), 1.20 – 1.15 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 91.1, 91.0, 74.7, 74.5, 52.83, 52.79, 44.0, 43.1, 24.7, 23.7, 21.2, 20.9, 20.2.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}O_4$ $[M + H]^+$ 265.1434, found 265.1434.

4-Cyclohexylpent-2-yn-1-yl acetate (31)



31

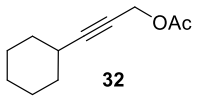
According to General Procedure **A** with *O*-(1-cyclohexylethyl) *S*-methyl carbonodithioate **XE11** (52.4 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 5/1 to yield the product **31** as a colorless oil (31.2 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 1.9 Hz, 2H), 2.37 – 2.30 (m, 1H), 2.10 (s, 3H), 1.88 – 1.60 (m, 5H), 1.32 – 1.16 (m, 4H), 1.14 (d, *J* = 7.1 Hz, 3H), 1.11 – 1.01 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 91.1, 74.8, 53.0, 42.5, 31.9, 30.9, 29.5, 26.4, 26.4, 26.3, 20.9, 18.0.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{20}O_2$ $[M + H]^+$ 209.1536, found 209.1538.

3-Cyclohexylprop-2-yn-1-yl acetate (32)



32

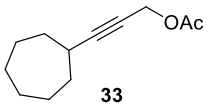
According to General Procedure **A** with *O*-cyclohexyl *S*-methyl carbonodithioate **XE12** (45.7 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 8/1 to yield the product **32** as a colorless oil (25.9 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 2.0 Hz, 2H), 2.44 – 2.34 (m, 1H), 2.09 (s, 3H), 1.85 – 1.75 (m, 2H), 1.74 – 1.64 (m, 2H), 1.56 – 1.48 (m, 1H), 1.47 – 1.38 (m, 2H), 1.34 – 1.23 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 91.7, 73.7, 53.0, 32.4, 29.1, 25.8, 24.9, 20.9.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{16}O_2$ $[M + H]^+$ 181.1223, found 181.1226.

3-Cycloheptylprop-2-yn-1-yl acetate (33)



33

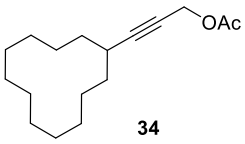
According to General Procedure **A** with *O*-cycloheptyl *S*-methyl carbonodithioate **XE13** (49.0 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 6/1 to yield the product **33** as a colorless oil (24.9 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 2.0 Hz, 2H), 2.67 – 2.56 (m, 1H), 2.09 (s, 3H), 1.89 – 1.79 (m, 2H), 1.74 – 1.62 (m, 4H), 1.59 – 1.41 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 92.5, 73.9, 53.0, 34.4, 31.1, 27.9, 25.6, 20.9.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}O_2$ $[M + H]^+$ 195.1380, found 195.1382.

3-Cyclododecylprop-2-yn-1-yl acetate (34)



34

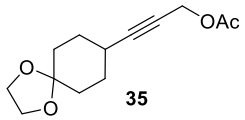
According to General Procedure **A** with *O*-cyclododecyl *S*-methyl carbonodithioate **XE14** (65.9 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 2/1 to yield the product **34** as a colorless oil (44.9 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (d, *J* = 2.0 Hz, 2H), 2.57 – 2.45 (m, 1H), 2.09 (s, 3H), 1.66 – 1.55 (m, 2H), 1.54 – 1.43 (m, 4H), 1.42 – 1.20 (m, 16H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 92.2, 73.4, 53.0, 29.6, 26.8, 23.8, 23.7, 23.4, 23.3, 22.1, 20.9.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{28}O_2$ $[M + Na]^+$ 287.1982, found 287.1982.

3-(1,4-Dioxaspiro[4.5]decan-8-yl)prop-2-yn-1-yl acetate (35)



35

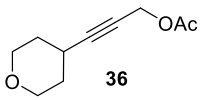
According to General Procedure **A** with *S*-methyl *O*-(1,4-dioxaspiro[4.5]decan-8-yl) carbonodithioate **XE15** (59.6 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/3 to yield the product **35** as a yellow oil (33.3 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (d, *J* = 1.8 Hz, 2H), 3.95 (s, 4H), 2.56 – 2.46 (m, 1H), 2.10 (s, 3H), 1.91 – 1.79 (m, 4H), 1.77 – 1.62 (m, 2H), 1.61 – 1.51 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 108.1, 90.1, 74.1, 64.3, 52.8, 32.9, 29.4, 27.4, 20.9.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}O_4$ $[M + H]^+$ 239.1278, found 239.1277.

3-(tetrahydro-*2H*-Pyran-4-yl)prop-2-yn-1-yl acetate (36)



36

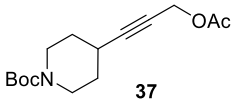
According to General Procedure **A** with *S*-methyl *O*-(tetrahydro-2H-pyran-4-yl) carbonodithioate **XE16** (46.2 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/8 to yield the product **36** as a colorless oil (20.0 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (d, *J* = 1.9 Hz, 2H), 3.97 – 3.74 (m, 2H), 3.55 – 3.43 (m, 2H), 2.72 – 2.60 (m, 1H), 2.10 (s, 3H), 1.87 – 1.78 (m, 2H), 1.74 – 1.57 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 89.5, 75.0, 66.3, 52.7, 31.9, 26.3, 20.9.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{14}O_3$ $[M + H]^+$ 183.1016, found 183.1017.

***tert*-Butyl 4-(3-acetoxyprop-1-yn-1-yl)piperidine-1-carboxylate (37)**



37

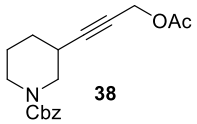
According to General Procedure **A** with *tert*-butyl 4-(((methylthio)carbonothioyl)oxy)piperidine-1-carboxylate **XE17** (69.9 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/5 to yield the product **37** as a colorless oil (46.1 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (d, *J* = 2.0 Hz, 2H), 3.75 – 3.60 (m, 2H), 3.19 – 3.10 (m, 2H), 2.65 – 2.54 (m, 1H), 2.08 (s, 3H), 1.80 – 1.70 (m, 2H), 1.60 – 1.50 (m, 2H), 1.44 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 154.7, 89.1, 79.5, 52.6, 41.9, 31.1, 28.4, 27.0, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{23}NO_4$ $[M + H]^+$ 282.1700, found 282.1703.

Benzyl 3-(3-acetoxyprop-1-yn-1-yl)piperidine-1-carboxylate (38)



38

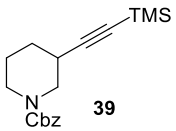
According to General Procedure **A** with benzyl 3-(((methylthio)carbonothioyl)oxy)piperidine-1-carboxylate **XE18** (78.0 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/8 to yield the product **38** as a colorless oil (39.7 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 5.22 – 5.05 (m, 2H), 4.65 – 4.65 (m, 2H), 4.11 – 3.75 (m, 2H), 3.28 – 2.87 (m, 2H), 2.57 – 2.46 (m, 1H), 2.10 (s, 3H), 2.03 – 1.93 (m, 1H), 1.82 – 1.39 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 155.1, 136.8, 128.5, 128.0, 127.9, 87.6, 75.6, 67.2, 52.6, 48.6, 44.2, 30.6, 28.5, 23.7, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}NO_4$ $[M + H]^+$ 316.1543, found 316.1540.

Benzyl 3-((trimethylsilyl)ethynyl)piperidine-1-carboxylate (39)

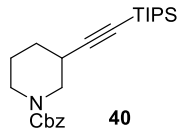


39

According to General Procedure **A** with benzyl 3-(((methylthio)carbonothioyl)oxy)piperidine-1-carboxylate **XE18** (78.0 mg, 0.24 mmol, 1.2 equiv.), and ethynyltrimethylsilane **N22** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/3 to yield the product **39** as a colorless oil (49.2 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 5H), 5.14 (s, 2H), 4.21 – 3.72 (m, 2H), 3.29 – 2.73 (m, 2H), 2.48 (tt, *J* = 9.6, 3.9 Hz, 1H), 2.07 – 1.90 (m, 1H), 1.81 – 1.20 (m, 3H), 0.15 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 136.7, 128.4, 127.9, 127.8, 107.1, 85.8, 67.0, 48.7, 44.1, 30.8, 29.3, 24.2, 23.6, 0.0.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{25}NO_2Si$ $[M + H]^+$ 316.1727, found 316.1723.

Benzyl 3-((triisopropylsilyl)ethynyl)piperidine-1-carboxylate (40)

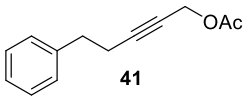


40

According to General Procedure **A** with benzyl 3-(((methylthio)carbonothioyl)oxy)piperidine-1-carboxylate **XE18** (78.0 mg, 0.24 mmol, 1.2 equiv.), and ethynyltriisopropylsilane **N23** (36.5 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/3 to yield the product **40** as a colorless oil (63.9 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 5H), 5.11 (s, 2H), 4.13 – 3.54 (m, 2H), 3.32 – 3.00 (m, 2H), 2.52 (tt, *J* = 8.5, 3.8 Hz, 1H), 2.03 – 1.88 (m, 1H), 1.85 – 1.38 (m, 3H), 1.15 – 0.95 (m, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 136.9, 128.5, 128.0, 127.9, 109.1, 81.8, 67.1, 48.9, 44.2, 31.1, 29.4, 24.1, 23.5, 18.6, 11.8.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{37}NO_2Si$ $[M + H]^+$ 400.2666, found 400.2667.

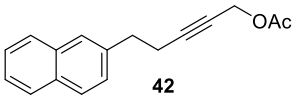
5-Phenylpent-2-yn-1-yl acetate (41)



41

According to General Procedure **A** with *O*-cyclohexyl *S*-methyl carbonodithioate **XE19** (45.7 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **41** as a colorless oil (21.0 mg, 52% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 4.65 (t, *J* = 2.1 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.51 (tt, *J* = 7.6, 2.1 Hz, 2H), 2.09 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 140.4, 128.4, 126.4, 86.8, 74.7, 52.8, 34.8, 21.0, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{14}O_2$ $[M + H]^+$ 203.1067, found 203.1068.

5-(Naphthalen-2-yl)pent-2-yn-1-yl acetate (42)



42

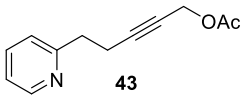
According to General Procedure **A** with *S*-methyl *O*-(2-(naphthalen-2-yl)ethyl) carbonodithioate **XE20** (62.9 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **42** as a colorless oil (26.2 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 3H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.38 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.69 (t, *J* = 2.2 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H), 2.65 (tt, *J* = 7.5, 2.2 Hz, 2H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 137.9, 133.6, 132.2, 128.0, 127.7, 127.6, 127.1, 126.7, 126.0, 125.4, 86.8, 74.9, 52.8, 34.9, 21.0, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}O_2$ $[M + H]^+$ 253.1223, found 253.1222.

5-(Pyridin-2-yl)pent-2-yn-1-yl acetate (43)



43

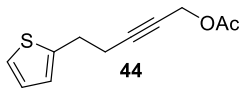
According to General Procedure **A** with *S*-methyl *O*-(2-(pyridin-2-yl)ethyl) carbonodithioate **XE21** (51.1 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using DCM/MeOH = 100/1 to yield the product **43** as a colorless oil (21.5 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.44 (m, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.17 – 7.11 (m, 1H), 4.63 (t, *J* = 2.2 Hz, 2H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.68 (td, *J* = 7.4, 6.3, 3.7 Hz, 2H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 159.8, 149.4, 136.4, 123.1, 121.5, 86.6, 74.7, 52.8, 36.9, 20.8, 18.9.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{13}NO_2$ $[M + H]^+$ 204.1019, found 204.1016.

5-(Thiophen-2-yl)pent-2-yn-1-yl acetate (44)



44

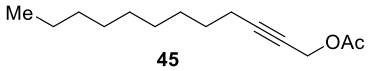
According to General Procedure **A** with *S*-methyl *O*-(2-(thiophen-2-yl)ethyl) carbonodithioate **XE22** (52.4 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **44** as a colorless oil (20.8 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.95 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.90 – 6.78 (m, 1H), 4.69 (t, *J* = 2.2 Hz, 2H), 3.20 – 2.91 (m, 2H), 2.59 (tt, *J* = 7.5, 2.2 Hz, 2H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 142.9, 126.8, 124.8, 123.6, 86.2, 75.2, 52.7, 29.1, 21.5, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}O_2S$ $[M + H]^+$ 209.0631, found 209.0633.

Dodec-2-yn-1-yl acetate (45)



45

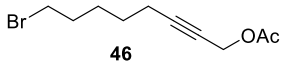
According to General Procedure **A** with *S*-methyl *O*-nonyl carbonodithioate **XE23** (56.3 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 10/1 to yield the product **45** as a colorless oil (22.9 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (t, *J* = 2.2 Hz, 2H), 2.27 – 2.18 (m, 2H), 2.11 (s, 3H), 1.60 – 1.47 (m, 2H), 1.42 – 1.32 (m, 2H), 1.31 – 1.22 (m, 10H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 87.8, 73.8, 52.9, 31.9, 29.5, 29.3, 29.1, 28.9, 28.4, 22.7, 20.9, 18.8, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{24}O_2$ $[M + Na]^+$ 247.1669, found 247.1670.

8-Bromooct-2-yn-1-yl acetate (46)



46

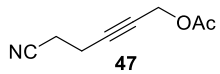
According to General Procedure **A** with *O*-(5-bromopentyl) *S*-methyl carbonodithioate **XE24** (61.7 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 2/1 to yield the product **46** as a colorless oil (20.3 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (t, *J* = 2.2 Hz, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 2.33 – 2.22 (m, 2H), 2.11 (s, 3H), 1.97 – 1.83 (m, 2H), 1.61 – 1.49 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 87.1, 74.3, 52.8, 33.6, 32.3, 27.5, 27.4, 20.9, 18.6.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{15}BrO_2$ $[M + Na]^+$ 269.0148, found 269.0148.

5-Cyanopent-2-yn-1-yl acetate (47)



47

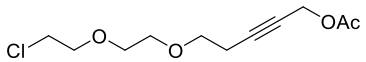
According to General Procedure **A** with *O*-(2-cyanoethyl) *S*-methyl carbonodithioate **XE25** (38.7 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/3 to yield the product **47** as a colorless oil (15.7 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (t, *J* = 2.0 Hz, 2H), 2.69 – 2.52 (m, 4H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 118.1, 82.6, 77.0, 52.3, 20.8, 17.3, 16.1.

HRMS (ESI) *m/z* calcd. for $C_8H_9NO_2$ $[M + H]^+$ 152.0706, found 152.0707.

5-(2-(2-Chloroethoxy)ethoxy)pent-2-yn-1-yl acetate (48)



48

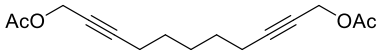
According to General Procedure **A** with *O*-(2-(2-(2-chloroethoxy)ethoxy)ethyl) *S*-methyl carbonodithioate **XE26** (62.1 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using DCM/MeOH = 400/1 to yield the product **48** as a colorless oil (24.9 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (t, *J* = 2.2 Hz, 2H), 3.77 (t, *J* = 5.9 Hz, 2H), 3.70 – 3.59 (m, 8H), 2.53 (tt, *J* = 7.0, 2.2 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 84.2, 75.1, 71.4, 70.6, 70.3, 69.3, 52.7, 42.7, 20.8, 20.1.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{17}ClO_4$ $[M + H]^+$ 249.0888, found 249.0886.

Undeca-2,9-diyne-1,11-diyl diacetate (49)



49

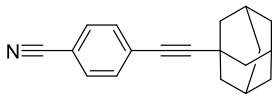
According to General Procedure **B** with *S*,*S'*-dimethyl *O*,*O'*-(pentane-1,5-diyl) bis(carbonodithioate) **XE27** (56.9 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (43.2 mg, 0.44 mmol, 2.2 equiv.) after 48 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/3 to yield the product **49** as a colorless oil (20.1 mg, 38% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (t, *J* = 2.3 Hz, 4H), 2.27 – 2.19 (m, 4H), 2.10 (s, 6H), 1.57 – 1.44 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 87.4, 74.1, 52.9, 28.0, 27.9, 20.9, 18.7.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}O_4$ $[M + H]^+$ 265.1434, found 265.1433.

4-(Adamantan-1-ylethynyl)benzonitrile (50)



50

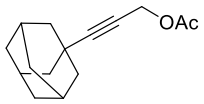
According to General Procedure **A** with *O*-(adamantan-1-yl) *S*-methyl carbonodithioate **XE28** (58.2 mg, 0.24 mmol, 1.2 equiv.), and 4-ethynylbenzonitrile **N5** (25.4 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **50** as a colorless oil (26.1 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.47 – 7.42 (m, 2H), 2.03 – 1.98 (m, 3H), 1.97 – 1.91 (m, 6H), 1.75 – 1.69 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2, 131.9, 129.3, 118.8, 110.6, 103.3, 78.4, 42.5, 36.3, 30.3, 27.9.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{19}N$ $[M + H]^+$ 262.1590, found 262.1595.

3-(Adamantan-1-yl)prop-2-yn-1-yl acetate (51)



51

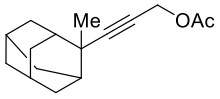
According to General Procedure **A** with *O*-(adamantan-1-yl) *S*-methyl carbonodithioate **XE28** (58.2 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 4/1 to yield the product **51** as a colorless oil (24 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (s, 2H), 2.09 (s, 3H), 1.98 – 1.93 (m, 3H), 1.88 – 1.83 (m, 6H), 1.70 – 1.64 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 95.6, 72.7, 53.0, 42.6, 36.3, 29.6, 27.9, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}O_2$ $[M + Na]^+$ 255.1356, found 229.1353.

3-(2-Methyladamantan-2-yl)prop-2-yn-1-yl acetate (52)



52

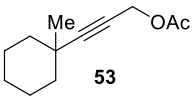
According to General Procedure **A** with *S*-methyl *O*-(2-methyladamantan-2-yl) carbonodithioate **XE29** (78.8 mg, 78% pure, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 4/1 to yield the product **52** as a colorless oil (26 mg, 53% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.71 (s, 2H), 2.39 – 2.26 (m, 2H), 2.09 (s, 3H), 1.98 – 1.94 (m, 2H), 1.86 – 1.81 (m, 1H), 1.80 – 1.76 (m, 1H), 1.70 – 1.67 (m, 3H), 1.66 – 1.65 (m, 1H), 1.64 – 1.62 (m, 1H), 1.61 – 1.59 (m, 2H), 1.59 – 1.57 (m, 1H), 1.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 95.8, 75.6, 53.1, 38.5, 38.2, 36.8, 35.2, 31.7, 27.32, 27.30, 25.7, 20.9.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{22}O_2$ $[M + Na]^+$ 269.1512, found 269.1510.

3-(1-Methylcyclohexyl)prop-2-yn-1-yl acetate (53)



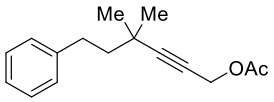
53

According to General Procedure **A** with crude *S*-methyl *O*-(1-methylcyclohexyl) carbonodithioate **XE30** (49.0 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 20/1 to yield the product **53** as a colorless oil (20.2 mg, 52% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.69 (s, 2H), 2.09 (s, 3H), 1.75 – 1.68 (m, 2H), 1.66 – 1.59 (m, 3H), 1.59 – 1.52 (m, 3H), 1.19 (s, 3H), 1.17 – 1.10 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 93.9, 75.0, 53.0, 39.2, 32.7, 29.7, 25.8, 23.2, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}O_2$ $[M + H]^+$ 195.1380, found 195.1382.

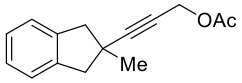
4,4-Dimethyl-6-phenylhex-2-yn-1-yl acetate (54)



54

According to General Procedure **A** with *S*-Methyl *O*-(2-methyl-4-phenylbutan-2-yl) carbonodithioate **XE31** (81.3 mg, 75% pure, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 4/1 to yield the product **54** as a colorless oil (26 mg, 53% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 4.70 (s, 2H), 2.86 – 2.67 (m, 2H), 2.10 (s, 3H), 1.73 – 1.66 (m, 2H), 1.26 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 142.6, 128.4, 128.4, 125.7, 94.1, 74.3, 52.9, 45.2, 31.9, 31.4, 29.0, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{20}O_2$ $[M + Na]^+$ 267.1356, found 267.1353.

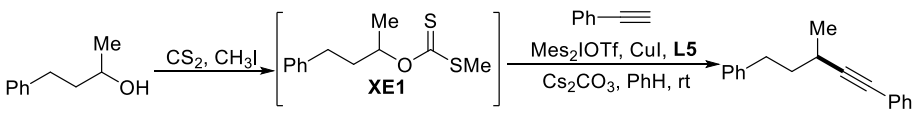
3-(2-Methyl-2,3-dihydro-1*H*-inden-2-yl)prop-2-yn-1-yl acetate (55)



55

According to General Procedure **A** with *S*-2-methyl-2,3-dihydro-1*H*-inden-2-ol **XE32** (87.8 mg, 65% pure, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 4/1 to yield the product **55** as a colorless oil (26 mg, 53% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 4H), 4.67 (s, 2H), 3.28 (d, *J* = 15.5 Hz, 2H), 2.91 (d, *J* = 15.5 Hz, 2H), 2.09 (s, 3H), 1.36 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 141.4, 126.5, 124.7, 94.5, 73.3, 52.9, 47.8, 37.5, 27.7, 20.9.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}O_2$ $[M + Na]^+$ 251.1043, found 251.1040.

One-pot large scale process



6.0 mmol

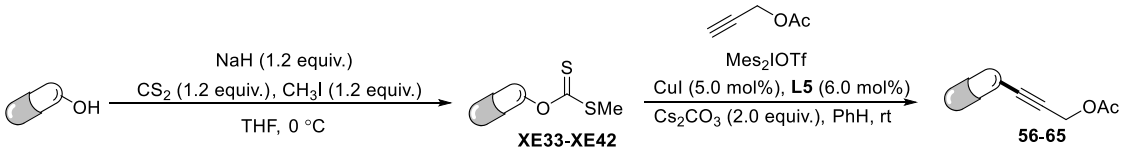
1, 70% yield

An oven-dried round bottom flask was charged with a Teflon-coated magnetic stir bar, and NaH (0.29 g, 60% in mineral oil, 7.2mmol, 1.2 equiv.) was added under an argon

atmosphere followed by dry THF (20 mL, 0.3 M). The 4-phenylbutan-2-ol (0.9 g, 1.0 equiv.) in THF was slowly added via syringe the stirring solution at 0 ºC. The reaction was capped under argon and allowed to stir for 1 h at 0 ºC. Carbon disulfide (CS_2, 0.43 mL, 7.2mmol, 1.2 equiv.) was then added via syringe at 0 ºC, stirred for 1 h, and the reaction was quenched with methyl iodiode (1.2 equiv., 0.45 mL, 7.2mmol,), and stirred for an additional 1 h. The reaction was diluted with Et_2O, carefully quenched with sat. NH_4Cl solution, and diluted with H_2O. The mixture was transferred to a separatory funnel and the organics were washed with H_2O and then brine. The organics were dried with Na_2SO_4, filtered, and concentrated to the crude product.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (47.5 mg, 0.25 mmol, 5.0 mol%), **L5** (74.7 mg, 0.3 mmol, 6.0 mol%), Mes_2IOTf (1.15 g, 7.5 mmol, 1.5 equiv.), Cs_2CO_3 (3.26 g, 10 mmol, 2.0 equiv.), and anhydrous benzene (10 mL). Then, crude **XE1**, and **N1** (0.51 g, 5.0 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 48 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **1** as a colorless oil (0.82 g, 70% yield).

Late-stage cross-coupling of bioactive molecules

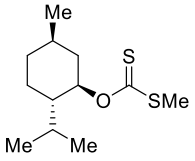


General procedure step A: An oven-dried round bottom flask was charged with a Teflon-coated magnetic stir bar, and NaH (60% in mineral oil, 1.2 equiv.) was added under an argon atmosphere followed by dry THF (0.3 M). The alcohol from bioactive molecules (1.0 equiv.) was slowly added via syringe(oil) or slowly added (solid) to the stirring solution at 0 ºC. The reaction was capped under argon and allowed to stir for 1 h at 0 ºC or room temperature. Carbon disulfide (CS_2, 1.2 equiv.) was then added via syringe at 0 ºC, stirred for 1 h, and the reaction was quenched with methyl iodiode (1.2 equiv.), and stirred for an additional 1 h. The reaction was diluted with Et_2O, carefully quenched with sat. NH_4Cl solution, and diluted with H_2O. The mixture was transferred to a separatory funnel and the organics were washed with H_2O and then brine. The organics were dried with Na_2SO_4, filtered, and concentrated to a yellow oil or light-yellow solid, the resulting xanthate can be purified by column chromatography on silica gel, eluting with PE and EtOAc, to obtain products in pure form.

General procedure step B: Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L5** (3.0 mg, 0.012 mmol, 6.0 mol%), Mes_2IOTf (154.2 mg, 0.30 mmol, 1.5 equiv.), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous benzene (2.0 mL).

Then, xanthate ester (0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 24 to 48 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

***O*-((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl) *S*-methyl carbonodithioate (XE33)**



XE33

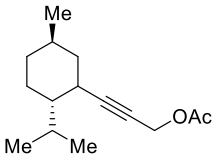
According to General Procedure step A with L-Menthol (0.78 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE to yield the product **XE33** as a yellow oil (1.12 g, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (td, *J* = 10.8, 4.5 Hz, 1H), 2.57 (s, 3H), 2.28 – 2.20 (m, 1H), 1.96 – 1.83 (m, 1H), 1.79 – 1.62 (m, 3H), 1.57 – 1.48 (m, 1H), 1.22 – 0.90 (m, 9H), 0.82 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.4, 84.5, 47.3, 39.6, 34.2, 31.4, 26.6, 23.8, 22.0, 20.6, 18.8, 17.0.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{22}OS_2$ $[M + H]^+$ 247.1185, found 247.1196.

3-((2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)prop-2-yn-1-yl acetate (56)



56

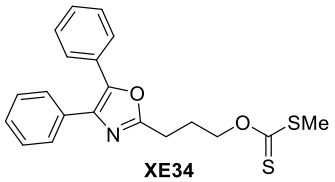
According to General Procedure step B with *O*-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) *S*-methyl carbonodithioate **XE33** (49.3 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 3/1 to yield the product **56** as a colorless oil (34.0 mg, 72% yield, dr = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 – 4.64 (m, 2H), 2.26 – 2.13 (m, 2H), 2.09 (s, 3H), 1.99 – 1.93 (m, 1H), 1.75 – 1.56 (m, 3H), 1.40 – 1.04 (m, 4H), 0.93 – 0.86 (m, 6.6H), 0.77 (d, *J* = 6.9 Hz, 2.4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 90.8, 88.9, 76.3, 74.7, 53.0, 47.1, 42.1, 40.1, 35.2, 34.7, 33.4, 32.4, 30.8, 30.7, 28.6, 27.7, 26.3, 24.1, 22.2, 21.3, 20.9, 20.9, 20.8, 15.7.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{24}O_2$ $[M + Na]^+$ 259.1669, found 259.1669.

***O*-(3-(4,5-Diphenyloxazol-2-yl)propyl) *S*-methyl carbonodithioate (XE34)**



XE34

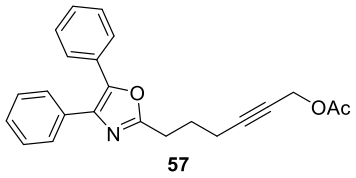
The 3-(4,5-diphenyloxazol-2-yl)propan-1-ol was synthesized according to the reported procedure from oxaprozin.[6] According to General Procedure step A with 3-(4,5-diphenyloxazol-2-yl)propan-1-ol (0.28 g, 1.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 20/1 to yield the product **XE34** as a yellow oil (0.19 g, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.61 – 7.51 (m, 2H), 7.41 – 7.27 (m, 6H), 4.76 (t, *J* = 6.1 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.53 (s, 3H), 2.45 – 2.33 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 162.2, 145.4, 135.2, 132.5, 129.0, 128.7, 128.6, 128.5, 128.1, 127.9, 126.5, 72.8, 25.9, 25.0, 19.1.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}NO_2S_2$ $[M + H]^+$ 370.0930, found 370.0926.

6-(4,5-Diphenyloxazol-2-yl)hex-2-yn-1-yl acetate (57)



57

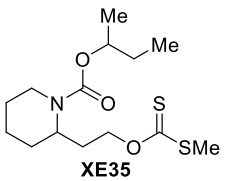
According to General Procedure step B with *O*-(3-(4,5-diphenyloxazol-2-yl)propyl) *S*-methyl carbonodithioate **XE34** (73.9 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using PE/DCM = 1/3 to yield the product **53** as a colorless oil (23.7 mg, 33% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.4 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.40 – 7.27 (m, 6H), 4.66 (t, *J* = 2.3 Hz, 2H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.60 – 2.40 (m, 2H), 2.14 – 2.02 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 162.7, 145.3, 135.1, 132.5, 129.0, 128.7, 128.6, 128.4, 128.1, 127.9, 126.4, 86.3, 75.0, 52.8, 27.2, 25.8, 20.8, 18.4.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{21}NO_3$ $[M + H]^+$ 360.1594, found 360.1590.

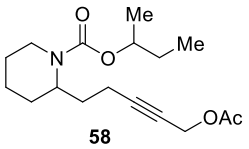
***sec*-Butyl 2-(2-(((methylthio)carbonothioyl)oxy)ethyl)piperidine-1-carboxylate (XE35)**



XE35

According to General Procedure step A with Lcaridin (1.14 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 5/1 to yield the product **XE35** as a yellow oil (0.98 g, 62% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 – 4.67 (m, 1H), 4.62 – 4.52 (m, 2H), 4.50 – 4.38 (m, 1H), 4.15 – 3.97 (m, 1H), 2.89 – 2.74 (m, 1H), 2.54 (s, 3H), 2.29 – 2.18 (m, 1H), 1.98 – 1.83 (m, 1H), 1.71 – 1.34 (m, 8H), 1.24 – 1.12 (m, 3H), 0.93 – 0.84 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.7, 155.5, 73.1, 73.0, 71.51, 71.49, 47.8, 47.7, 39.0, 29.1, 28.7, 28.4, 25.5, 19.8, 19.3, 19.1, 19.0, 9.84, 9.77.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{25}NO_3S_2$ $[M + Na]^+$ 342.1168, found 342.1164.

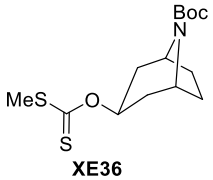
***sec*-Butyl 2-(5-acetoxypent-3-yn-1-yl)piperidine-1-carboxylate (58)**



58

According to General Procedure step B with *sec*-butyl 2-(2-(((methylthio)carbonothioyl)oxy)ethyl)piperidine-1-carboxylate **XE35** (63.9 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using DCM/MeOH = 100/1 to yield the product **58** as a colorless oil (29.7 mg, 48% yield, dr = 1:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 – 4.70 (m, 1H), 4.65 (t, *J* = 2.2 Hz, 2H), 4.48 – 3.87 (m, 3H), 2.87 – 2.69 (m, 1H), 2.23 – 2.16 (m, 2H), 2.09 (s, 3H), 2.03 – 1.94 (m, 1H), 1.73 – 1.43 (m, 8H), 1.25 – 1.12 (m, 3H), 0.95 – 0.85 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 155.6, 87.11, 87.05, 73.98, 73.97, 72.91, 72.85, 52.8, 50.01, 49.96, 38.9, 29.11, 29.08, 28.9, 28.8, 25.54, 25.49, 20.8, 19.82, 19.77, 19.1, 16.03, 15.98, 9.8, 9.7.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{27}NO_4$ $[M + H]^+$ 310.2013, found 310.2009.

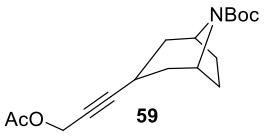
***tert*-Butyl (1*R*,3*s*,5*S*)-3-(((methylthio)carbonothioyl)oxy)-8-azabicyclo[3.2.1]octane-8-carboxylate (XE36)**



XE36

According to General Procedure step A with *N*-Boc-Nortropine (0.68 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 5/1 to yield the product **XE36** as a yellow oil (0.69 g, 72% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (t, *J* = 5.0 Hz, 1H), 4.39 – 4.07 (m, 2H), 2.58 (s, 3H), 2.28 – 2.08 (m, 2H), 2.07 – 1.95 (m, 6H), 1.47 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.9, 153.3, 79.5, 78.1, 52.5, 51.7, 35.3, 34.7, 28.5, 28.3, 27.7, 18.9.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{23}NO_3S_2$ $[M + Na]^+$ 340.1012, found 340.1008.

***tert*-Butyl (1*R*,5*S*)-3-(3-acetoxyprop-1-yn-1-yl)-8-azabicyclo[3.2.1]octane-8-carboxylate (59)**



59

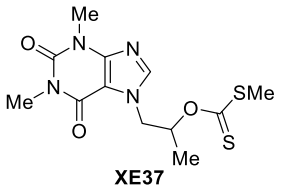
According to General Procedure step B with *tert*-butyl (1*R*,3*s*,5*S*)-3-(((methylthio)carbonothioyl)oxy)-8-azabicyclo[3.2.1]octane-8-carboxylate **XE36** (63.5 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using DCM/MeOH = 100/1 to yield the product **59** as a colorless oil (36.9 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (d, *J* = 1.8 Hz, 2H), 4.32 – 4.04 (m, 2H), 2.93 – 2.74 (m, 1H), 2.08 (s, 3H), 2.02 – 1.89 (m, 2H), 1.83 – 1.70 (m, 4H), 1.64 – 1.56 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 153.2, 89.8, 79.3, 74.1, 53.3, 52.7, 52.5, 37.3, 36.6, 28.5, 28.2, 27.5, 21.3, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{25}NO_4$ $[M + Na]^+$ 330.1676, found 3330.1672.

***O*-(1-(1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-7*H*-purin-7-yl)propan-2-yl) *S*-methyl carbonodithioate (XE37)**



XE37

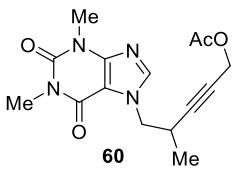
According to General Procedure step A with Proxyphylline (0.71 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 5/1 to yield the product **XE37** as a yellow solid (0.69 g, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 6.17 – 5.97 (m, 1H), 4.74 (dd, *J* = 14.5, 2.7 Hz, 1H), 4.49 (dd, *J* = 14.5, 7.8 Hz, 1H), 3.59 (s, 3H), 3.41 (s, 3H), 2.53 (s, 3H), 1.46 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.1, 155.3, 151.6, 148.7, 141.8, 107.0, 77.9, 50.3, 29.8, 28.0, 19.3, 16.7.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{16}N_4O_3S_2$ $[M + H]^+$ 329.0737, found 329.0733.

5-(1,3-Dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-7*H*-purin-7-yl)-4-methylpent-2-yn-1-yl acetate (60)



60

According to General Procedure step B with *O*-(1-(1,3-dimethyl-2,6-dioxo-1,2,3,6-

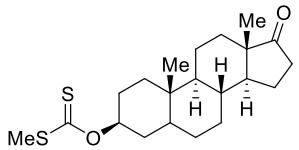
tetrahydro-7*H*-purin-7-yl)propan-2-yl) *S*-methyl carbonodithioate **XE37** (65.7 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel using DCM/MeOH = 100/1 to yield the product **60** as a colorless oil (33.7 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 4.63 – 4.53 (d, *J* = 1.6 Hz, 2H), 4.43 (dd, *J* = 13.2, 5.1 Hz, 1H), 4.08 (dd, *J* = 13.2, 9.2 Hz, 1H), 3.58 (s, 3H), 3.39 (s, 3H), 3.13 (q, *J* = 7.2 Hz, 1H), 2.08 (s, 3H), 1.25 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 155.2, 151.6, 149.0, 141.9, 106.7, 87.2, 77.4, 52.2, 51.7, 29.8, 28.3, 28.0, 20.8, 17.7.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{18}N_4O_4$ $[M + H]^+$ 319.1401, found 319.1398.

O-((3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl) *S*-methyl carbonodithioate (XE38)



XE38

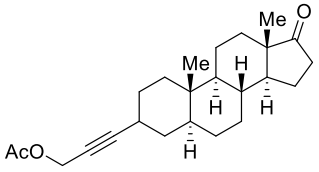
According to General Procedure step A with Epiandrosterone (0.58 g, 2.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 10/1 to yield the product **XE38** as a white solid (0.31 g, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 – 5.44 (m, 1H), 2.54 (s, 3H), 2.49 – 2.39 (m, 1H), 2.14 – 2.00 (m, 2H), 1.98 – 1.88 (m, 1H), 1.87 – 1.75 (m, 4H), 1.71 – 1.62 (m, 3H), 1.62 – 1.47 (m, 2H), 1.40 – 1.18 (m, 6H), 1.14 – 0.94 (m, 2H), 0.88 (d, *J* = 9.9 Hz, 6H), 0.78 – 0.69 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 221.3, 215.3, 83.3, 54.3, 51.3, 47.8, 44.6, 36.6, 35.9, 35.7, 35.0, 33.2, 31.5, 30.8, 28.3, 26.8, 21.8, 20.5, 18.9, 13.8, 12.3.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{32}O_2S_2$ $[M + Na]^+$ 403.1736, found 403.1734.

3-((5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)prop-2-yn-1-yl acetate (61)

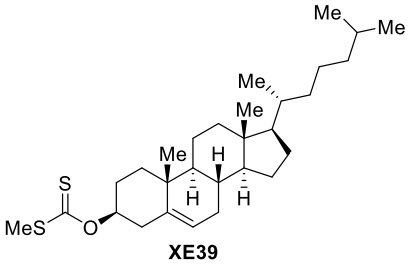


61

According to General Procedure step B with *O*-((3*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl) *S*-methyl carbonodithioate **XE38** (76.1 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel PE/DCM = 1/3 to yield the product **61** as a colorless oil (40.0 mg, 54% yield, dr = 2.4:1. NMR is a major diastereomer).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (d, *J* = 2.1 Hz, 2H), 2.95 – 2.80 (m, 1H), 2.61 – 2.36 (m, 1H), 2.11 (s, 3H), 2.00 – 1.93 (m, 1H), 1.86 – 1.76 (m, 2H), 1.73 – 1.62 (m, 4H), 1.60 – 1.46 (m, 4H), 1.42 – 1.18 (m, 9H), 1.12 – 1.00 (m, 1H), 0.87 (s, 3H), 0.81 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 221.6, 170.4, 91.3, 74.4, 54.3, 53.0, 51.5, 47.8, 41.5, 36.3, 35.9, 35.0, 34.0, 32.8, 31.6, 30.7, 28.2, 27.2, 26.4, 21.8, 20.9, 20.1, 13.8, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{34}O_3$ $[M + Na]^+$ 393.2400, found 393.2400.

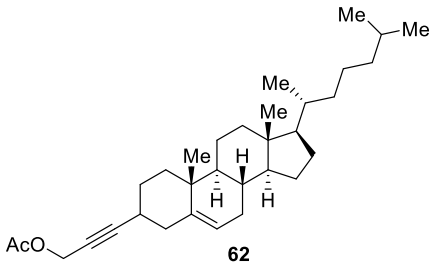
O-((3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) S-methyl carbonodithioate (XE39)



XE39

According to General Procedure step A with Cholesterol (1.93 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 20/1 to yield the product **XE39** as a white solid (2.07 g, 87% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 – 5.34 (m, 2H), 2.63 – 2.43 (m, 5H), 2.22 – 1.70 (m, 6H), 1.63 – 1.44 (m, 6H), 1.44 – 1.11 (m, 11H), 1.07 (s, 3H), 1.05 – 0.96 (m, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 1.9 Hz, 3H), 0.88 (d, *J* = 1.9 Hz, 3H), 0.70 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.1, 139.2, 123.3, 83.6, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 37.4, 36.9, 36.7, 36.2, 35.8, 31.94, 31.86, 28.3, 28.0, 27.2, 24.3, 23.8, 22.9, 22.6, 21.1, 19.3, 18.9, 18.7, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{48}OS_2$ $[M + H]^+$ 477.3219, found 477.3229.

3-((8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)prop-2-yn-1-yl acetate (62)



62

According to General Procedure step B with *O*-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl) *S*-methyl carbonodithioate **XE39** (95.4 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on

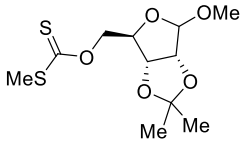
silica gel PE/DCM = 1/3 to yield the product **62** as a colorless oil (59.7 mg, 64% yield, dr = 1.2:1, a mixture of diastereomer).

^{1}H NMR (400 MHz, $CDCl_3$) 5.36 – 5.28 (m, 1H), 4.68 (d, *J* = 1.8 Hz, 0.92H), 4.66 (d, *J* = 2.0 Hz, 1.02H), 2.53 – 2.18 (m, 3H), 2.09 (s, 1.43H), 2.08 (s, 1.63H), 2.04 – 1.03 (m, 26H), 0.99 (s, 1.41H), 0.97 (s, 1.62H), 0.94 – 0.90 (m, 3H), 0.87 (d, *J* = 1.6 Hz, 3.19H), 0.86 (d, *J* = 1.6 Hz, 2.72H), 0.68 (s, 1.69H), 0.67 (s, 1.31H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.40, 170.35, 141.1, 139.2, 122.0, 121.0, 91.4, 90.2, 75.3, 73.8, 56.79, 56.77, 56.2, 56.1, 53.0, 52.9, 50.2, 50.1, 42.30, 42.28, 39.80, 39.75, 39.5, 38.8, 38.7, 37.2, 37.0, 36.7, 36.2, 35.9, 35.8, 35.1, 31.9, 31.83, 31.78, 31.77, 31.1, 28.9, 28.7, 28.28, 28.25, 28.0, 26.8, 24.3, 23.9, 23.8, 22.9, 22.6, 20.93, 20.89, 20.83, 20.76, 19.3, 19.2, 18.7, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{32}H_{50}O_2$ $[M + Na]^+$ 489.3703, found 489.3710.

O-(((3a*R*,4*R*,6a*R*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl) *S*-methyl carbonodithioate (XE40)



XE40

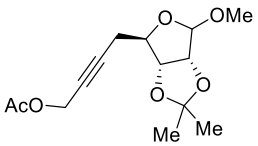
According to General Procedure step A with methyl-2,3-*O*-isopropylidene-D-ribofuranoside (0.61 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 20/1 to yield the product **XE40** as a yellow oil (0.72 g, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (s, 1H), 4.72 (d, *J* = 5.9 Hz, 1H), 4.65 – 4.57 (m, 3H), 4.58 – 4.52 (m, 1H), 3.34 (s, 3H), 2.58 (s, 3H), 1.50 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 215.7, 112.7, 109.4, 85.1, 83.6, 81.8, 73.1, 55.0, 26.4, 25.0, 19.2.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{18}O_5S_2$ $[M + Na]^+$ 317.0488, found 317.0486.

4-((3a*R*,4*R*,6a*R*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)but-2-yn-1-yl acetate (63)

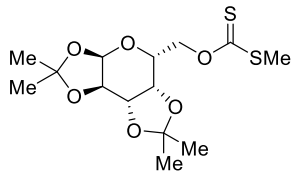


63

According to General Procedure step B with *O*-(((3a*R*,4*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl) *S*-methyl carbonodithioate **XE40** (58.9 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel DCM/MeOH = 300/1 to yield the product **63** as a colorless oil (30.1 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96 (s, 1H), 4.72 – 4.66 (m, 3H), 4.61 (d, *J* = 5.9 Hz, 1H), 4.31 (dd, *J* = 9.2, 6.6 Hz, 1H), 3.33 (s, 3H), 2.64 – 2.42 (m, 2H), 2.09 (s, 3H), 1.48 (s, 3H), 1.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 112.5, 109.7, 85.3, 85.0, 83.3, 83.1, 75.9, 54.9, 52.6, 26.4, 24.99, 24.96, 20.8.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{20}O_6$ $[M + Na]^+$ 307.1152, found 307.1149.

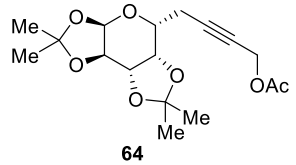
_S_-methyl _O_-(((3a_R_,5_R_,5a_S_,8a_S_,8b_R_)-2,2,7,7-tetramethyltetrahydro-5_H_-bis([1,3]dioxolo)[4,5-_b_:4',5'-_d_]pyran-5-yl)methyl) carbonodithioate (XE41)



XE41

According to General Procedure step A with 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose (0.78 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 20/1 to yield the product **XE41** as a yellow oil (0.79 g, 75% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (d, *J* = 4.9 Hz, 1H), 4.83 (dd, *J* = 11.4, 4.7 Hz, 1H), 4.72 – 4.60 (m, 2H), 4.34 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.28 (dd, *J* = 7.9, 2.0 Hz, 1H), 4.26 – 4.20 (m, 1H), 2.56 (s, 3H), 1.52 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.7, 109.7, 108.9, 96.3, 72.0, 71.0, 70.7, 70.5, 65.6, 26.04, 25.95, 25.0, 24.5, 19.0.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{22}O_6S_2$ $[M + Na]^+$ 373.0750, found 373.0747.

4-((3a_R_,5_R_,5a_S_,8a_S_,8b_R_)-2,2,7,7-Tetramethyltetrahydro-5_H_-bis([1,3]dioxolo)[4,5-_b_:4',5'-_d_]pyran-5-yl)but-2-yn-1-yl acetate (64)

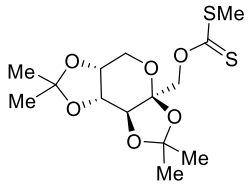


64

According to General Procedure step B with *S*-methyl *O*-(((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl) carbonodithioate **XE41** (70.1 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel DCM/MeOH = 300/1 to yield the product **64** as a colorless oil (19.7 mg, 29% yield,).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (d, *J* = 5.0 Hz, 1H), 4.67 (t, *J* = 2.2 Hz, 2H), 4.63 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.36 – 4.26 (m, 2H), 3.94 – 3.86 (m, 1H), 2.68 – 2.49 (m, 2H), 2.09 (s, 3H), 1.55 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 109.3, 108.7, 96.5, 83.2, 75.5, 71.3, 70.8, 70.5, 66.5, 52.8, 26.1, 26.0, 24.9, 24.5, 20.8, 20.7.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{24}O_7$ [M + Na]$^+$ 363.1414, found 363.1408.

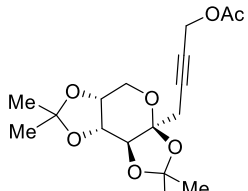
S-Methyl *O*-(((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl) carbonodithioate (XE42)



XE42

According to General Procedure step A with Diacetonefructose (0.78 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel using PE/EtOAc = 20/1 to yield the product **XE42** as a yellow oil (1.01 g, 96% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (d, *J* = 11.4 Hz, 1H), 4.62 (dd, *J* = 7.9, 2.7 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 2.7 Hz, 1H), 4.25 (d, *J* = 7.9 Hz, 1H), 3.93 (dd, *J* = 12.9, 1.9 Hz, 1H), 3.77 (d, *J* = 12.9 Hz, 1H), 2.59 (s, 3H), 1.55 (s, 3H), 1.48 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.6, 109.14, 109.07, 101.3, 72.9, 70.7, 70.4, 70.0, 61.3, 26.6, 25.9, 25.3, 24.1, 19.5.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{22}O_6S_2$ [M + Na]$^+$ 373.0750, found 373.0747.

4-((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)but-2-yn-1-yl acetate (65)

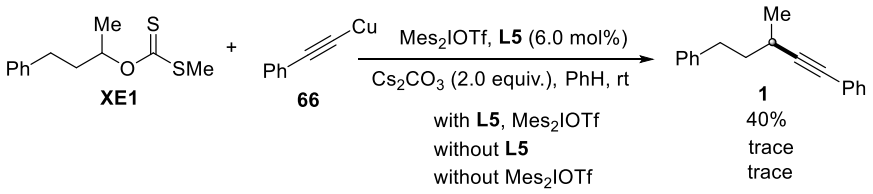


65

According to General Procedure step B with *S*-methyl *O*-(((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl) carbonodithioate **XE42** (70.1 mg, 0.20 mmol, 1.0 equiv.), and prop-2-yn-1-yl acetate **N16** (23.5 mg, 0.24 mmol, 1.2 equiv.) after 24 h, the reaction mixture was purified by column chromatography on silica gel DCM/MeOH = 300/1 to yield the product **65** as a colorless oil (25.2 mg, 37% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 2H), 4.62 (dd, *J* = 7.9, 2.7 Hz, 1H), 4.38 (d, *J* = 2.7 Hz, 1H), 4.23 (dd, *J* = 7.9, 1.8 Hz, 1H), 3.91 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.74 (d, *J* = 13.0 Hz, 1H), 2.94 (dt, *J* = 17.1, 2.3 Hz, 1H), 2.73 (dt, *J* = 17.1, 2.2 Hz, 1H), 2.08 (s, 3H), 1.55 (s, 3H), 1.48 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 109.1, 108.7, 102.1, 82.4, 76.6, 71.6, 70.8, 70.3, 61.7, 52.6, 29.7, 26.7, 25.9, 25.5, 24.0, 20.7.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{24}O_7$ [M + Na]$^+$ 363.1414, found 363.1410.

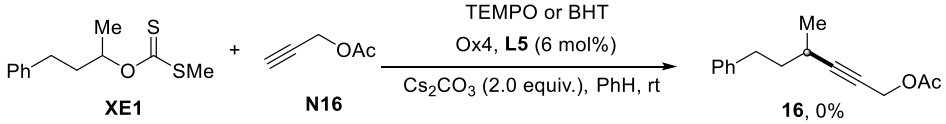
Mechanistic study

Control experiment with copper phenylacetylide



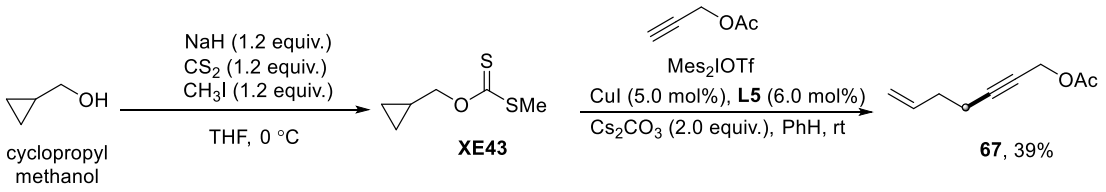
The (phenylethynyl)copper was synthesized according to a reported procedure.[7]
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **L5** (3.0 mg, 0.012 mmol, 6.0 mol%), Mes_2IOTf (154.2 mg, 0.30 mmol, 1.5 equiv.), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous benzene (2.0 mL). Then, *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), (phenylethynyl)copper **66** (32.9 mg, 0.2 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 24 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel using PE to afford **1** (18.7 mg, 40% yield).
The procedure for the reaction without **L5** and without Mes_2IOTf were the same with that described above except that **L5** and Mes_2IOTf were not added. Trace product **1** was observed in both experiments.

Control experiment with TEMPO and BHT



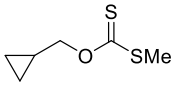
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L5** (3.0 mg, 0.012 mmol, 6.0 mol%), Mes_2IOTf (154.2 mg, 0.30 mmol, 1.5 equiv.), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous benzene (2.0 mL). Then, *S*-Methyl *O*-(4-phenylbutan-2-yl) carbonodithioate **XE1** (57.6 mg, 0.24 mmol, 1.2 equiv.), prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.), and 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (46.8 mg, 0.30 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was monitored by TLC. There was no product **16** observed.
The procedure for the reaction with BHT (butylated hydroxytoluene) (66.0 mg, 0.30 mmol, 1.5 equiv.) was the same with that described above. Trace product **16** was observed.

Control experiment with a clock substrate



An oven-dried round bottom flask was charged with a Teflon-coated magnetic stir bar, and NaH (60% in mineral oil, 120 mg, 3.6 mmol, 1,2 equiv.) was added under an argon atmosphere followed by dry THF (9.0 mL, 0.3 M). The cyclopropylmethanol (0.22 g, 3.0 mmol, 1.0 equiv.) was slowly added via syringe(oil) to the stirring solution at 0 ºC. The reaction was capped under argon and allowed to stir for 0.5 h at room temperature. Carbon disulfide (CS_2, 0.22 mL, 1.2 equiv.) was then added via syringe at 0 ºC, stirred for 0.5 h, and the reaction was quenched with methyl iodiode (0.23 mL,1.2 equiv.), and stirred for an additional 0.5 h. The reaction was diluted with Et_2O, carefully quenched with sat. NH_4Cl solution, and diluted with H_2O. The mixture was transferred to a separatory funnel and the organics were washed with H_2O and then brine. The organics were dried with Na_2SO_4, filtered, and concentrated to a yellow oil. The crude xanthate was purified by column chromatography on silica gel using PE to obtain **XE43** (0.31 g, 64% yield) as a slight yellow oil.

O-(Cyclopropylmethyl) *S*-methyl carbonodithioate (XE43)

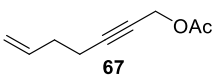


XE43

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.43 (d, *J* = 7.4 Hz, 2H), 2.57 (s, 3H), 1.41 – 1.18 (m, 1H), 0.71 – 0.59 (m, 2H), 0.43 – 0.27 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 216.1, 79.1, 19.0, 9.4, 3.5.
HRMS (ESI) *m/z* calcd. for $C_6H_{10}OS_2$ $[M + Na]^+$ 185.0065, found 185.0066.

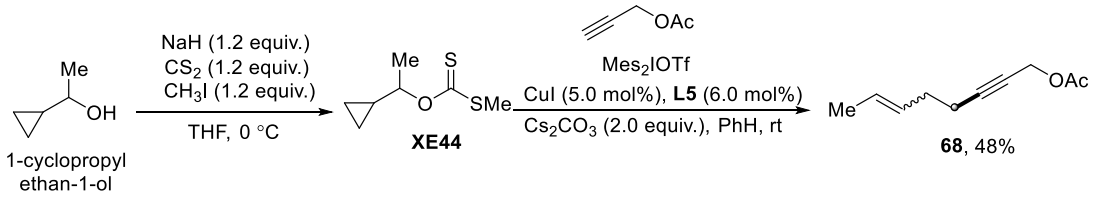
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L5** (3.0 mg, 0.012 mmol, 6.0 mol%), Mes_2IOTf (154.2 mg, 0.30 mmol, 1.5 equiv.), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous benzene (2.0 mL). Then, *O*-(cyclopropylmethyl) *S*-methyl carbonodithioate **XE43** (38.9 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 24 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel using PE/DCM = 3/1 to afford **67** (11.9 mg, 39% yield) as a colorless oil. the desired product.

Hept-6-en-2-yn-1-yl acetate (67)



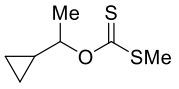
67

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 – 5.77 (m, 1H), 5.17 – 4.96 (m, 2H), 4.67 (t, *J* = 2.1 Hz, 2H), 2.36 – 2.20 (m, 4H), 2.10 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 136.7, 115.8, 86.9, 74.4, 52.8, 32.5, 20.9, 18.6.
HRMS (ESI) *m/z* calcd. for $C_9H_{12}O_2$ $[M + Na]^+$ 175.0730, found 175.0732.



An oven-dried round bottom flask was charged with a Teflon-coated magnetic stir bar, and NaH (60% in mineral oil, 120 mg, 3.6 mmol, 1,2 equiv.) was added under an argon atmosphere followed by dry THF (9.0 mL, 0.3 M). The 1-cyclopropylethan-1-ol (0.26 g, 3.0 mmol, 1.0 equiv.) was slowly added via syringe(oil) to the stirring solution at 0 ºC. The reaction was capped under argon and allowed to stir for 0.5 h at room temperature. Carbon disulfide (CS_2, 0.22 mL, 1.2 equiv.) was then added via syringe at 0 ºC, stirred for 0.5 h, and the reaction was quenched with methyl iodiode (0.23 mL,1.2 equiv.), and stirred for an additional 0.5 h. The reaction was diluted with Et_2O, carefully quenched with sat. NH_4Cl solution, and diluted with H_2O. The mixture was transferred to a separatory funnel and the organics were washed with H_2O and then brine. The organics were dried with Na_2SO_4, filtered, and concentrated to a yellow oil for the crude **XE44** (0.33 g, 64% crude yield), which was used for the next step without further purification.

O-(1-Cyclopropylethyl) *S*-methyl carbonodithioate (XE44)



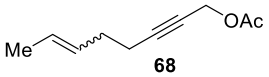
XE44

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 – 5.13 (m, 1H), 2.54 (s, 3H), 1.41 (d, *J* = 6.3 Hz, 3H), 1.22 – 1.12 (m, 1H), 0.61 – 0.52 (m, 2H), 0.50 – 0.41 (m, 1H), 0.37 – 0.28 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 215.7, 85.6, 19.1, 18.9, 16.1, 3.9, 2.7.
HRMS (ESI) *m/z* calcd. for $C_7H_{12}OS_2$ $[M + H]^+$ 177.0402, found 177.0405.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.010 mmol, 5.0 mol%), **L5** (3.0 mg, 0.012 mmol, 6.0 mol%), Mes_2IOTf (154.2 mg, 0.30 mmol, 1.5 equiv.), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous benzene (2.0 mL). Then, *O*-(1-cyclopropylethyl) *S*-methyl carbonodithioate **XE44** (42.3 mg, 0.24 mmol, 1.2 equiv.), and prop-2-yn-1-yl acetate **N16** (19.6 mg, 0.20 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 24 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column

chromatography on silica gel using PE/DCM = 3/1 to afford **68** (15.9 mg, 48% yield, a *Z* and *E* mixture) as a colorless oil. the desired product.

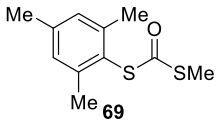
Oct-6-en-2-yn-1-yl acetate (68)



68

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 – 5.26 (m, 2H), 4.66 (t, *J* = 2.1 Hz, 2H), 2.38 – 2.15 (m, 4H), 2.10 (s, 3H), 1.75 – 1.43 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 129.2, 128.4, 126.4, 125.5, 87.2, 74.2, 74.0, 52.9, 52.8, 31.5, 25.9, 20.9, 19.3, 19.0, 17.9, 12.9.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{14}O_2$ $[M + Na]^+$ 189.0886, found 189.0886.

***S*-Mesityl *S*-methyl carbonodithioate (69)**



69

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 2H), 2.40 (s, 6H), 2.32 (s, 3H), 2.31 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 143.7, 141.0, 129.5, 123.2, 21.9, 21.3, 13.4.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}OS_2$ $[M + H]^+$ 227.0559, found 227.0560.

Reference

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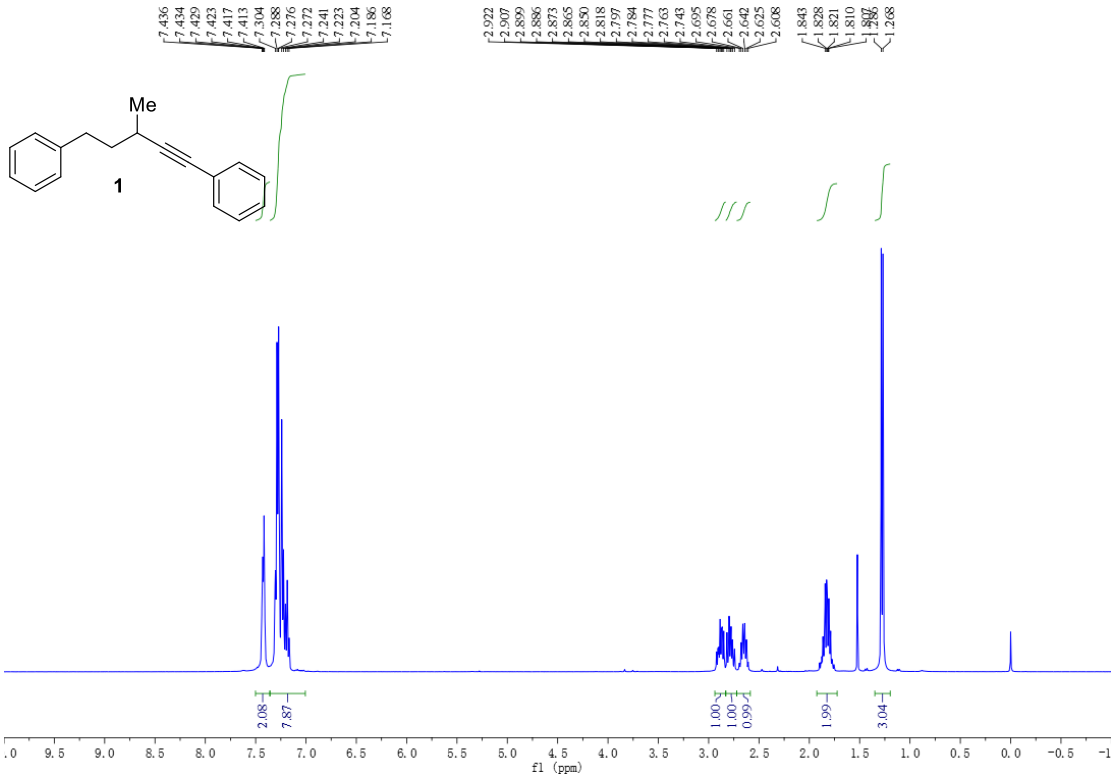
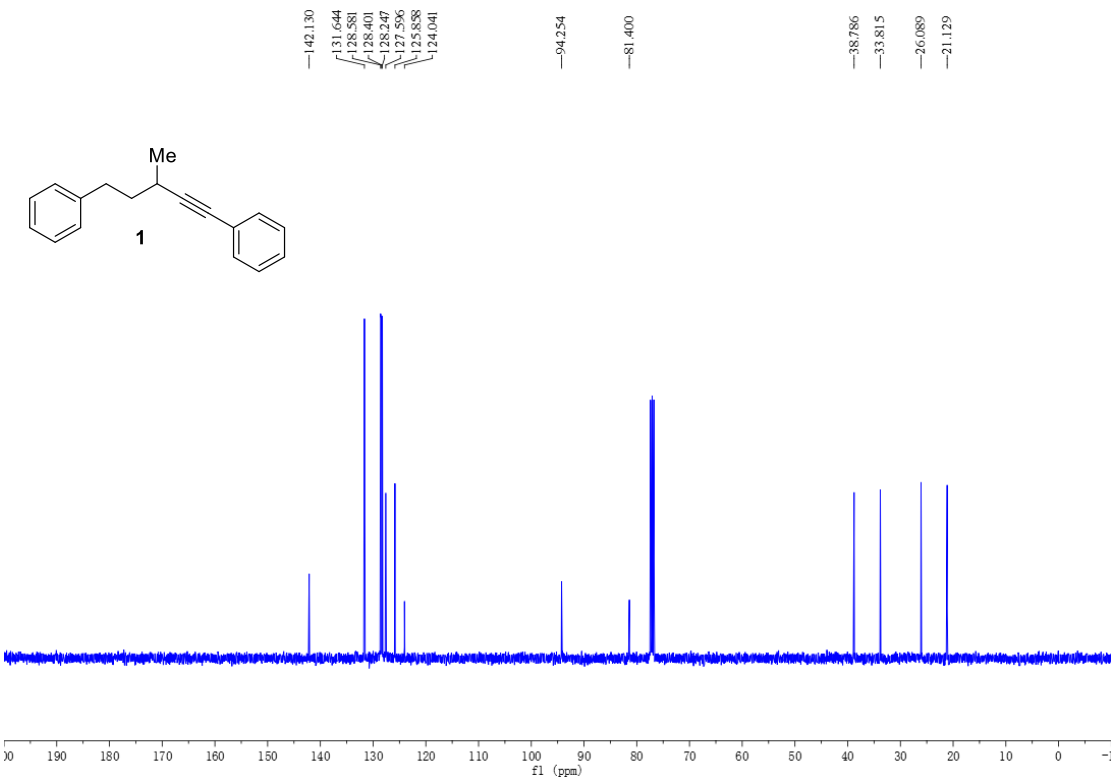
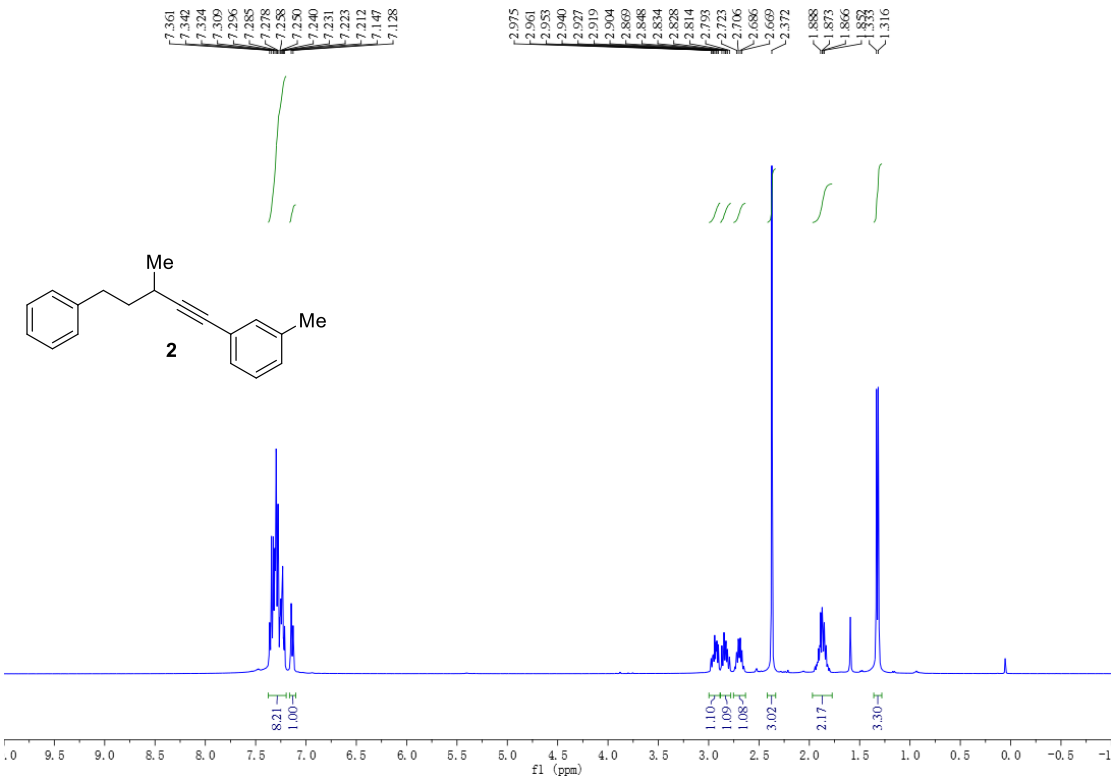
[7]. A. Sagadevan, A. Ragupathi, K. C. Hwang, P, *Angew. Chem. Int. Ed.* **2015**, *54*, 13896–13901.

NMR spectrum



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7.309
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7.285
7.278
7.258
7.250
7.240
7.231
7.223
7.212
7.147
7.128
2.975
2.961
2.953
2.940
2.927
2.919
2.904
2.869
2.848
2.834
2.828
2.814
2.793
2.723
2.706
2.686
2.669
2.372
1.888
1.873
1.866
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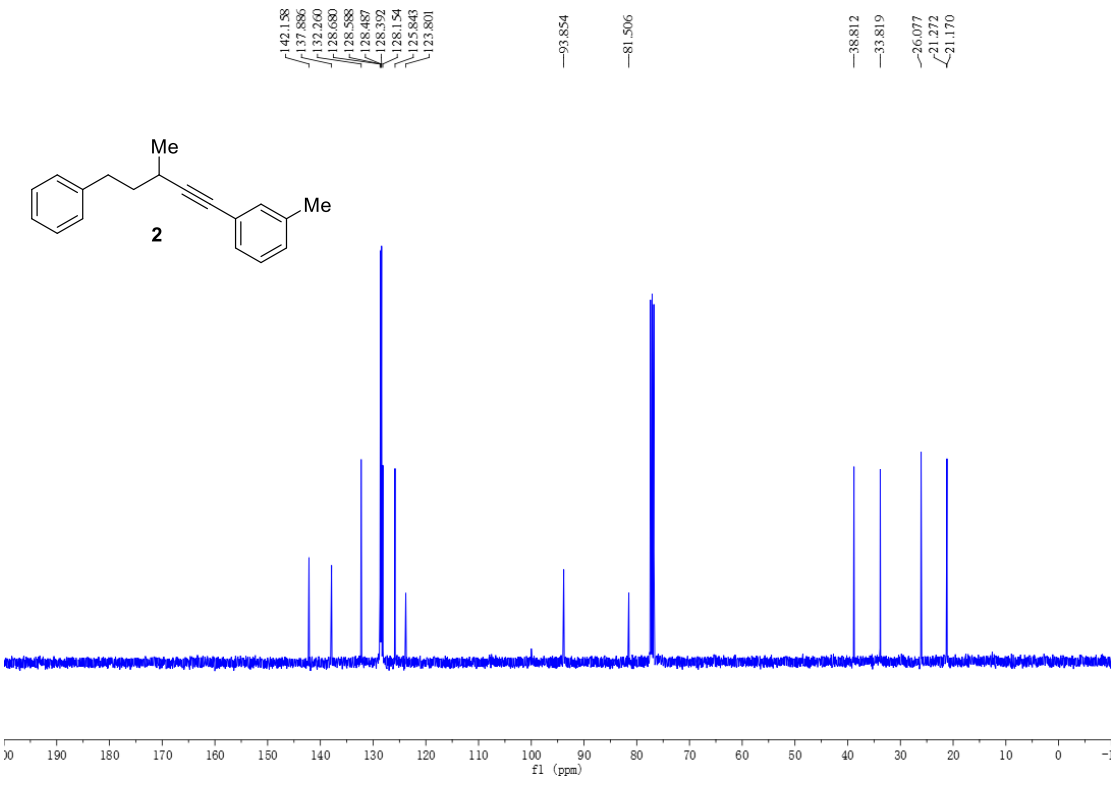
Me
Me
2
8.21
1.00
1.10
1.09
1.08
3.02
2.17
3.30
f1 (ppm)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137.886
132.260
128.680
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128.487
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128.154
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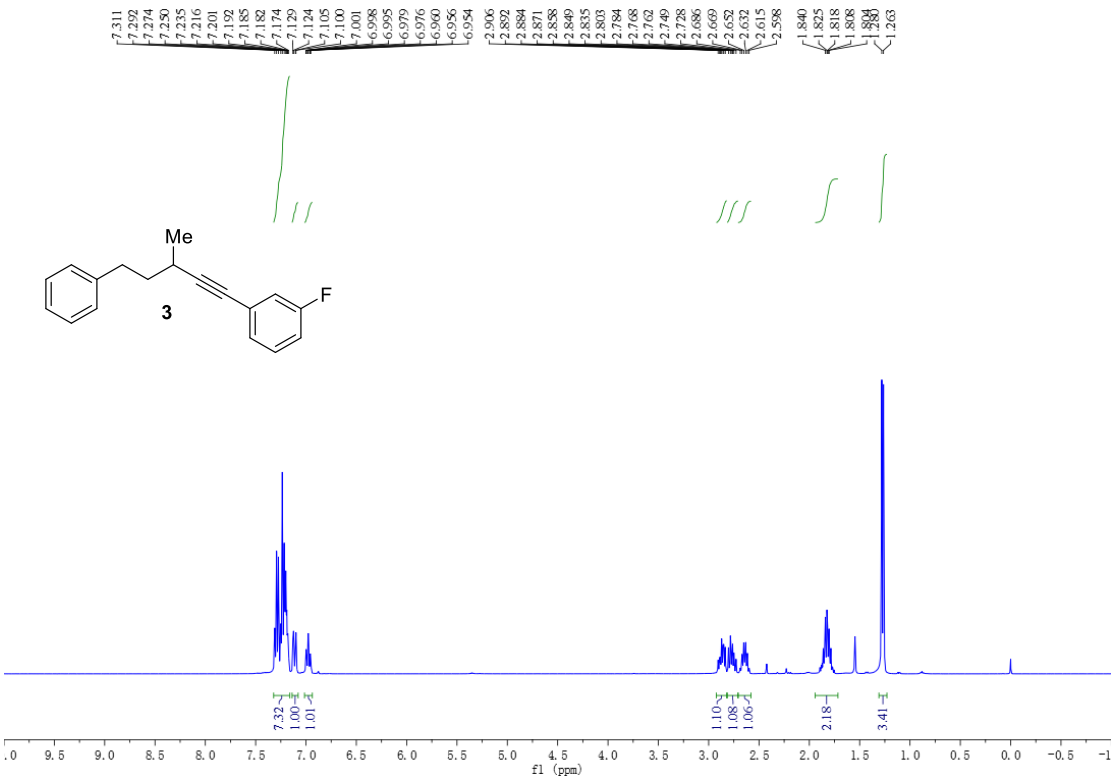
33.819
26.077
21.272
21.170
Me
Me
2
f1 (ppm)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7.250
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7.216
7.201
7.192
7.185
7.182
7.174
7.129
7.124
7.105
7.100
7.001
6.998
6.995
6.979
6.976
6.960
6.956
6.954
2.906
2.892
2.884
2.871
2.858
2.849
2.835
2.803
2.784
2.768
2.762
2.749
2.728
2.686
2.669
2.652
2.632
2.615
2.598
1.840
1.825
1.818
1.808
1.804
1.280
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1.01
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1.08
1.06
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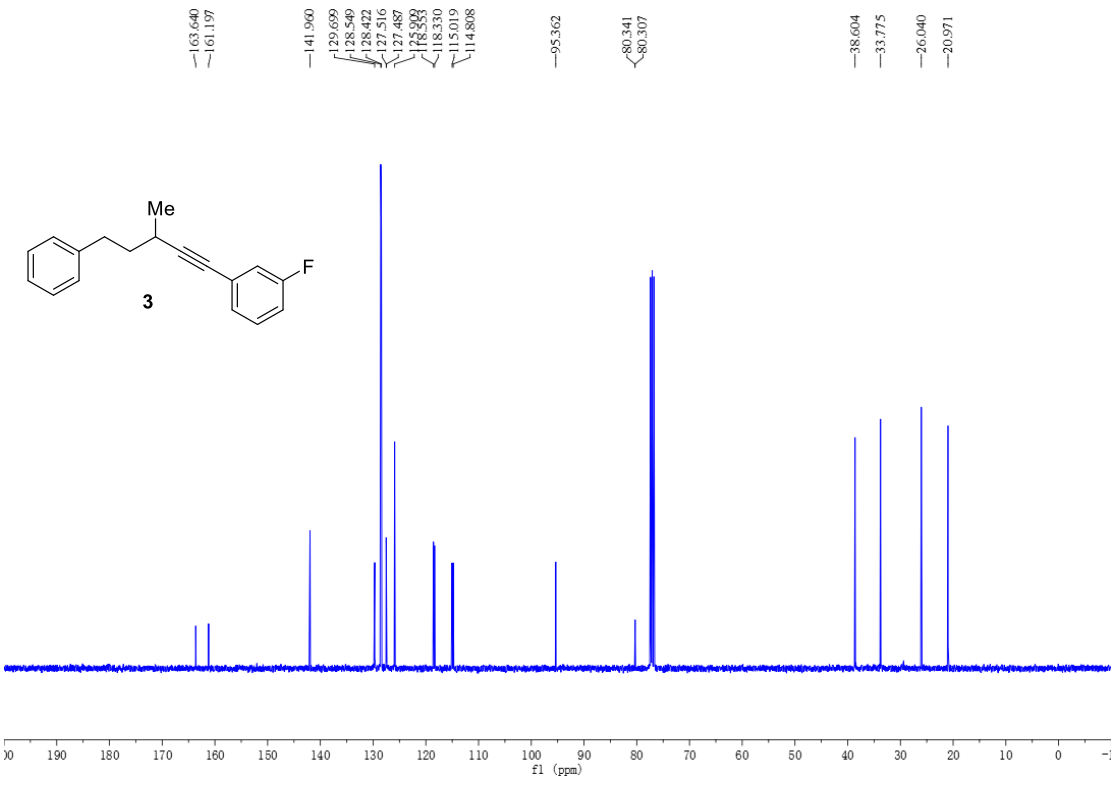
3.41
f1 (ppm)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161.197
141.960
129.699
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128.422
127.516
127.487
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115.019
114.808
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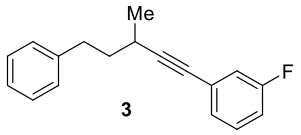
80.341
80.307
38.604
33.775
26.040
20.971
Me
F
3
f1 (ppm)


Me
F

3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-113.349
-113.364
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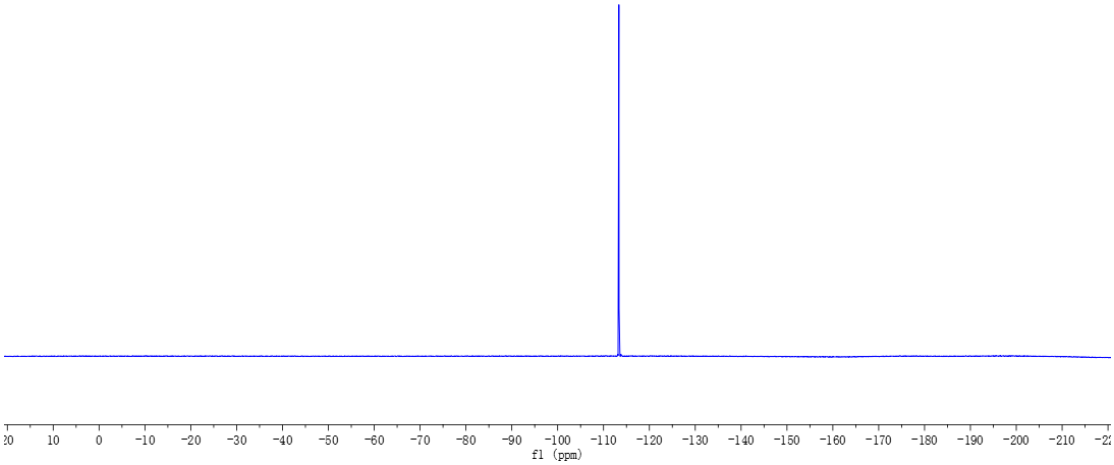
-113.389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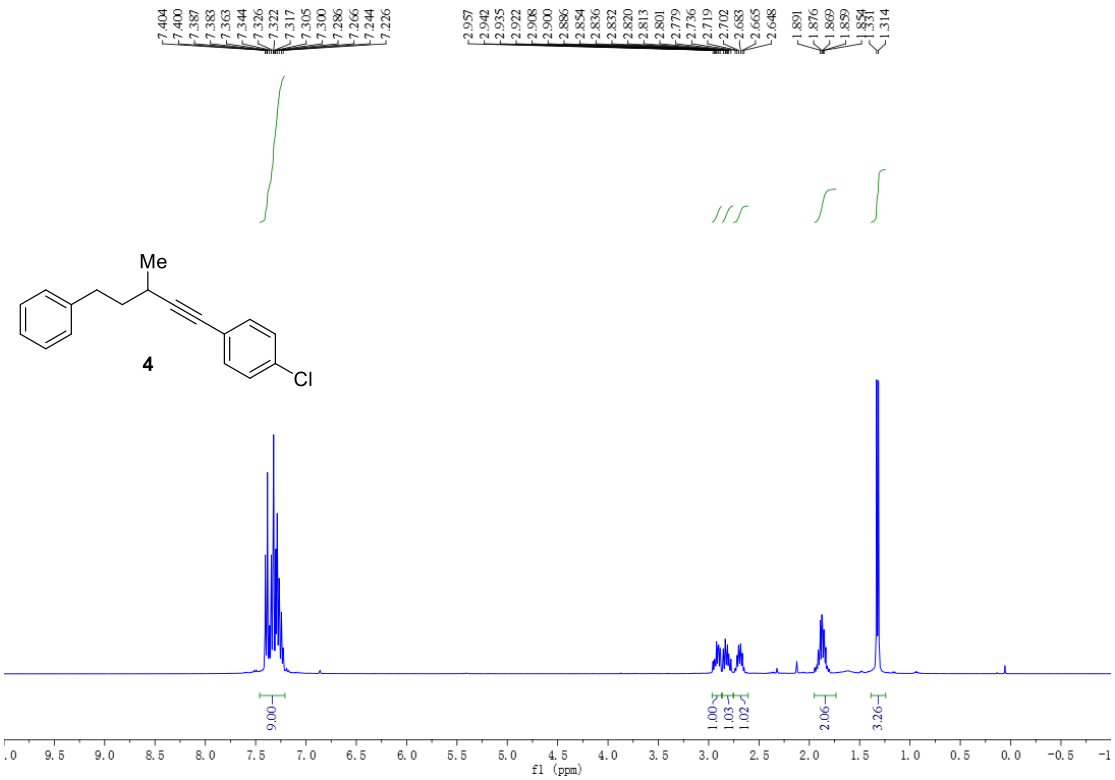
f1 (ppm)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7.226
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2.935
2.922
2.908
2.900
2.886
2.854
2.836
2.832
2.820
2.813
2.801
2.779
2.736
2.719
2.702
2.683
2.665
2.648
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1.876
1.869
1.859
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1.314
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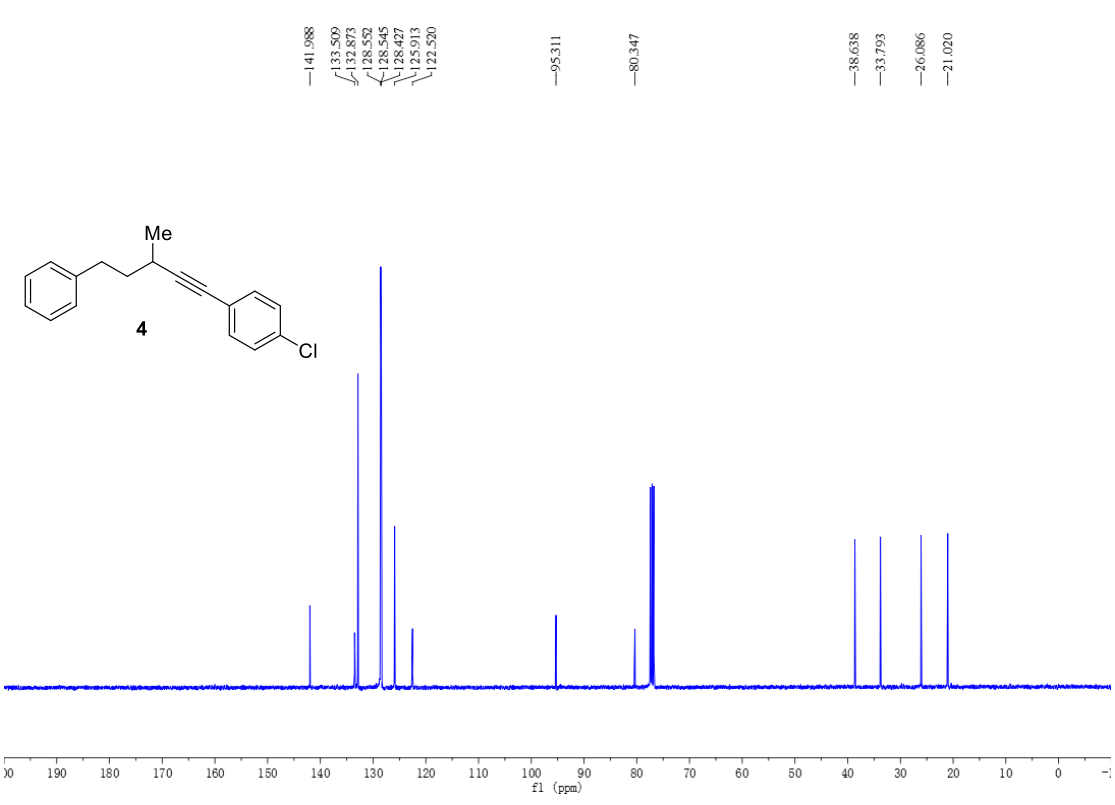
1.02
2.06
3.26
f1 (ppm)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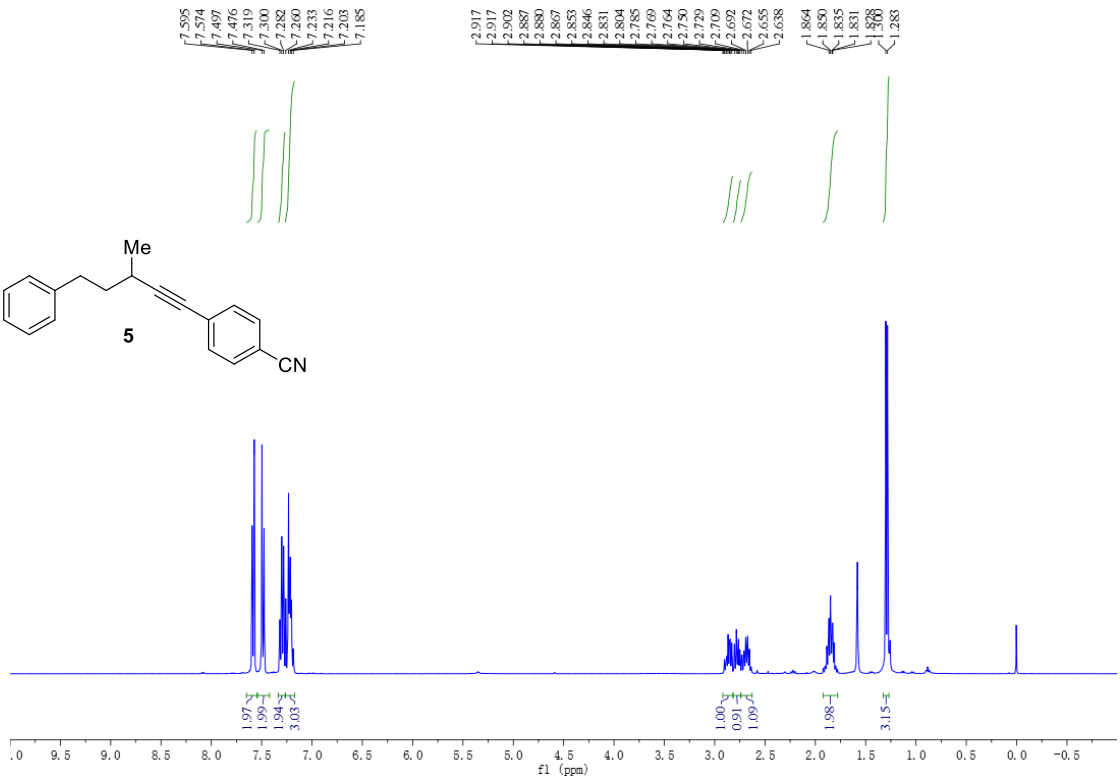
26.086
21.020
Me
4
Cl
f1 (ppm)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7.216
7.203
7.185
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2.917
2.902
2.887
2.880
2.867
2.853
2.846
2.831
2.804
2.785
2.769
2.764
2.750
2.729
2.709
2.692
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2.655
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1.864
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1.831
1.828
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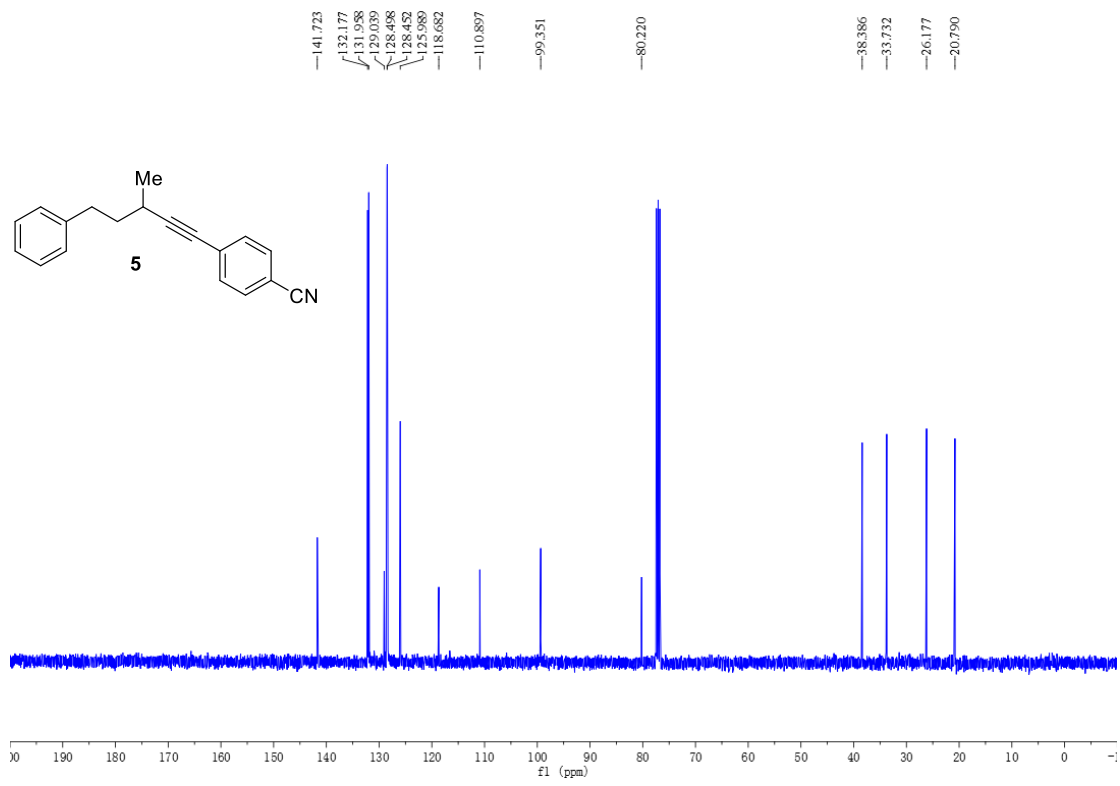
f1 (ppm)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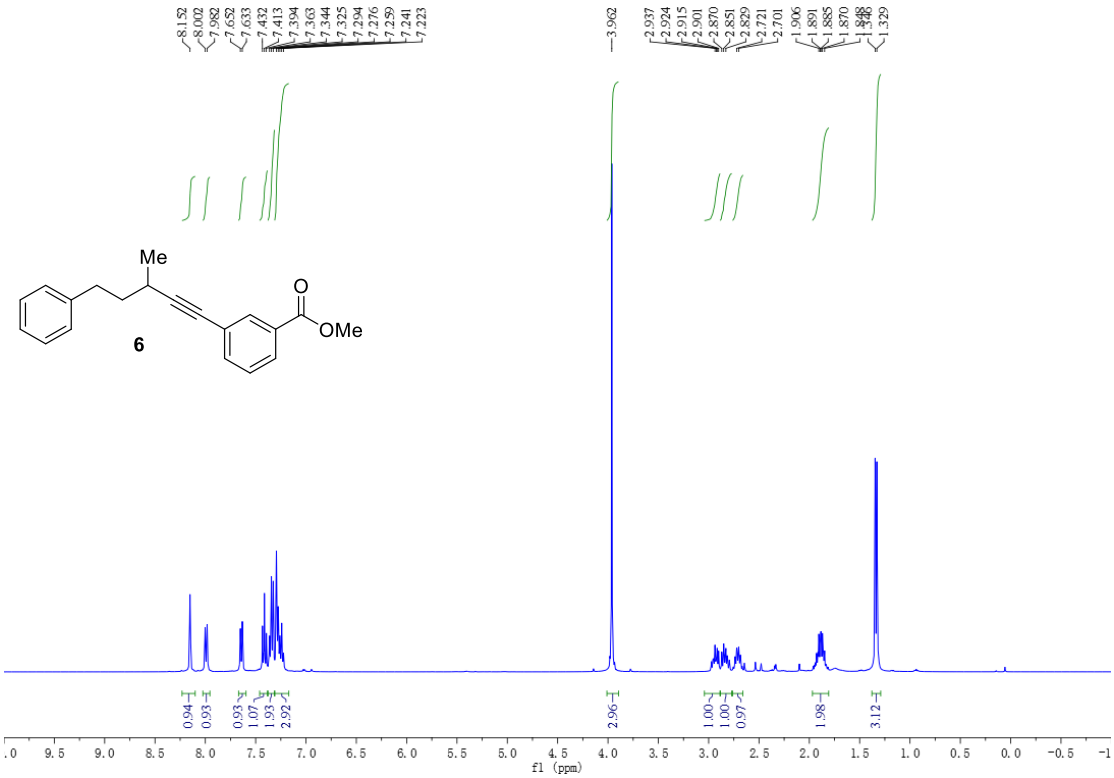
Me
5
CN
f1 (ppm)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2.937
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2.870
2.851
2.829
2.721
2.701
1.906
1.891
1.885
1.870
1.329
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O
OMe
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2.96
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1.00
0.97
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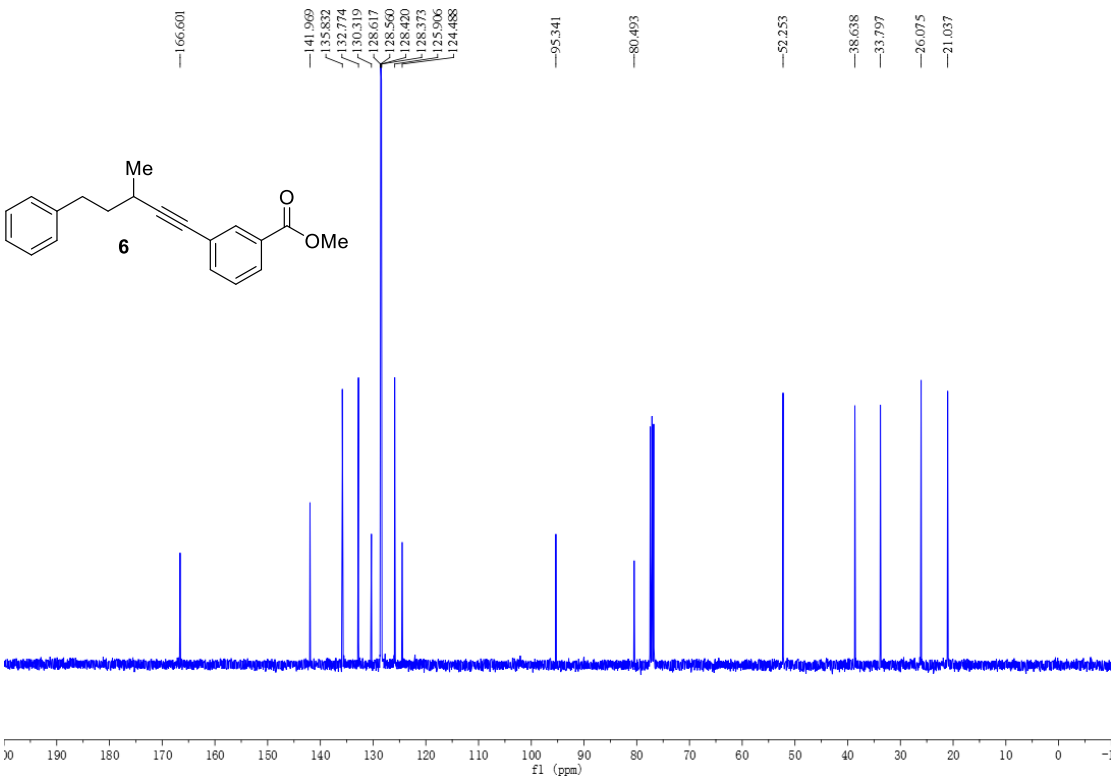
f1 (ppm)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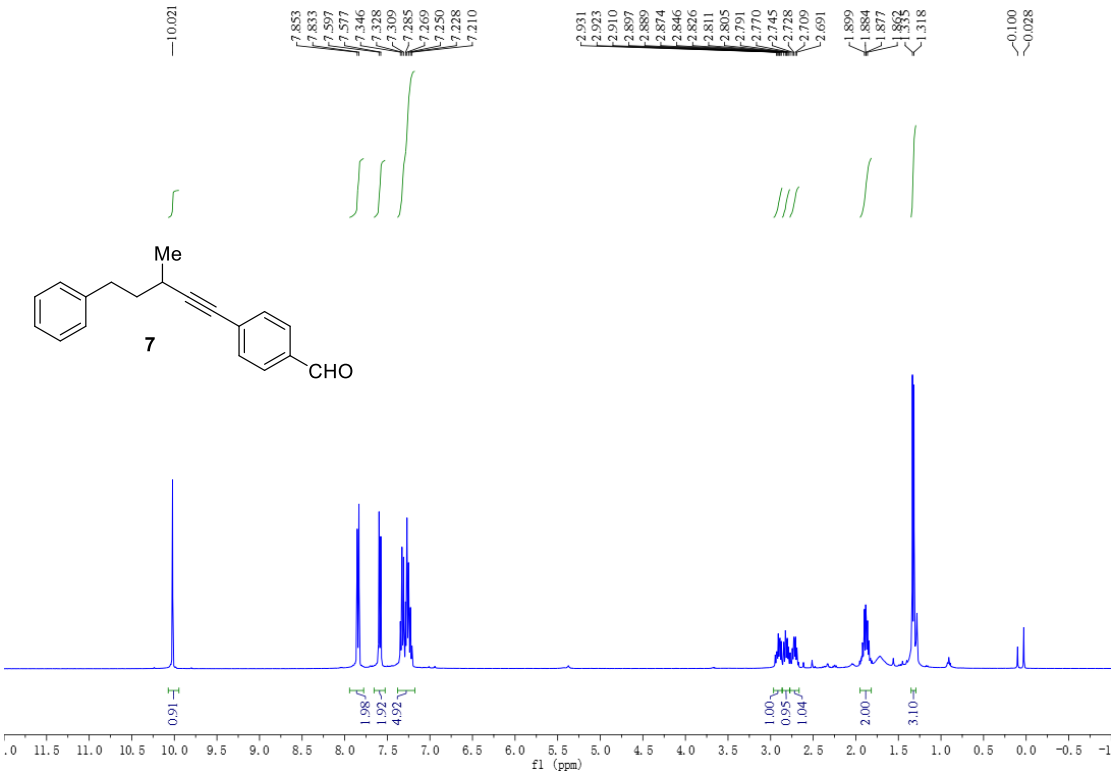
Me
O
OMe
6
f1 (ppm)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7.210
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2.923
2.910
2.897
2.889
2.874
2.846
2.826
2.811
2.805
2.791
2.770
2.745
2.728
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1.877
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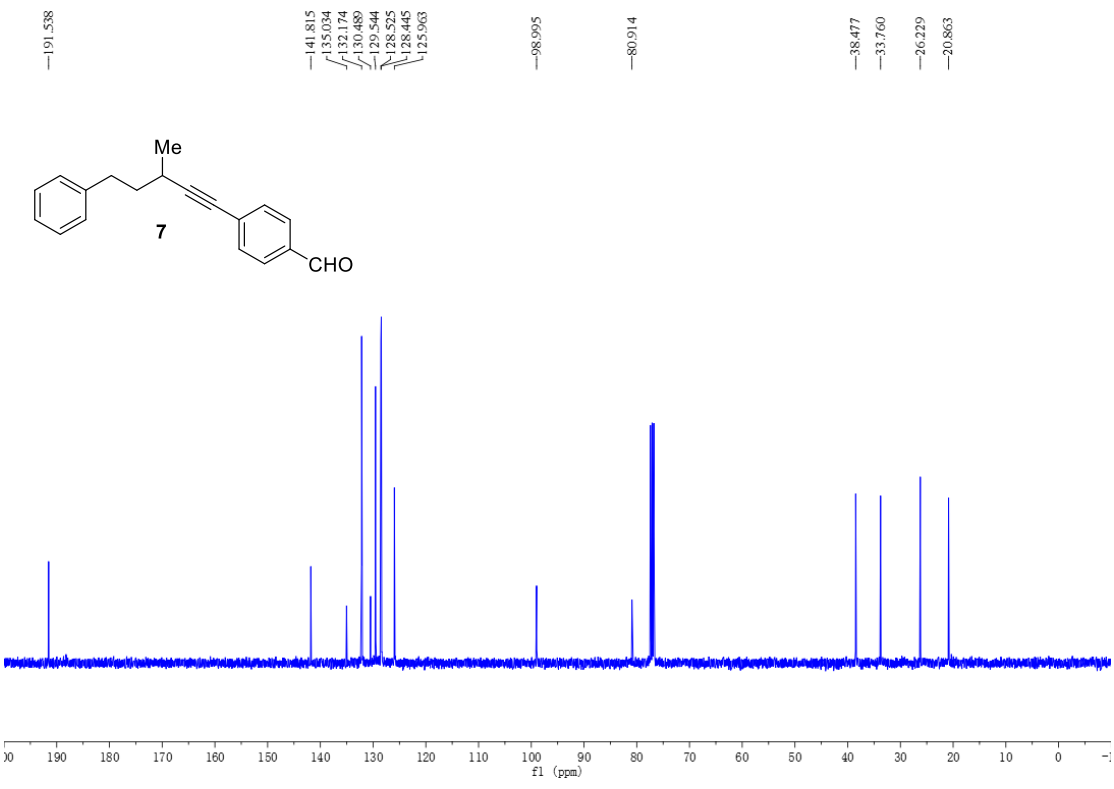
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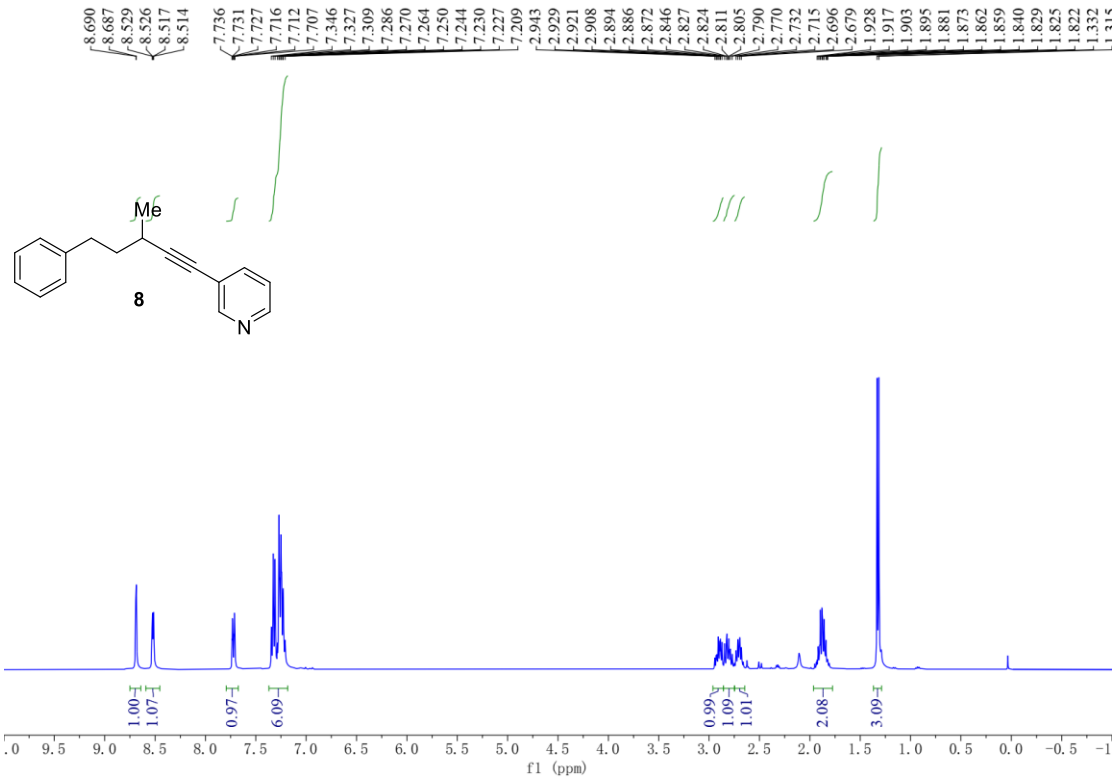
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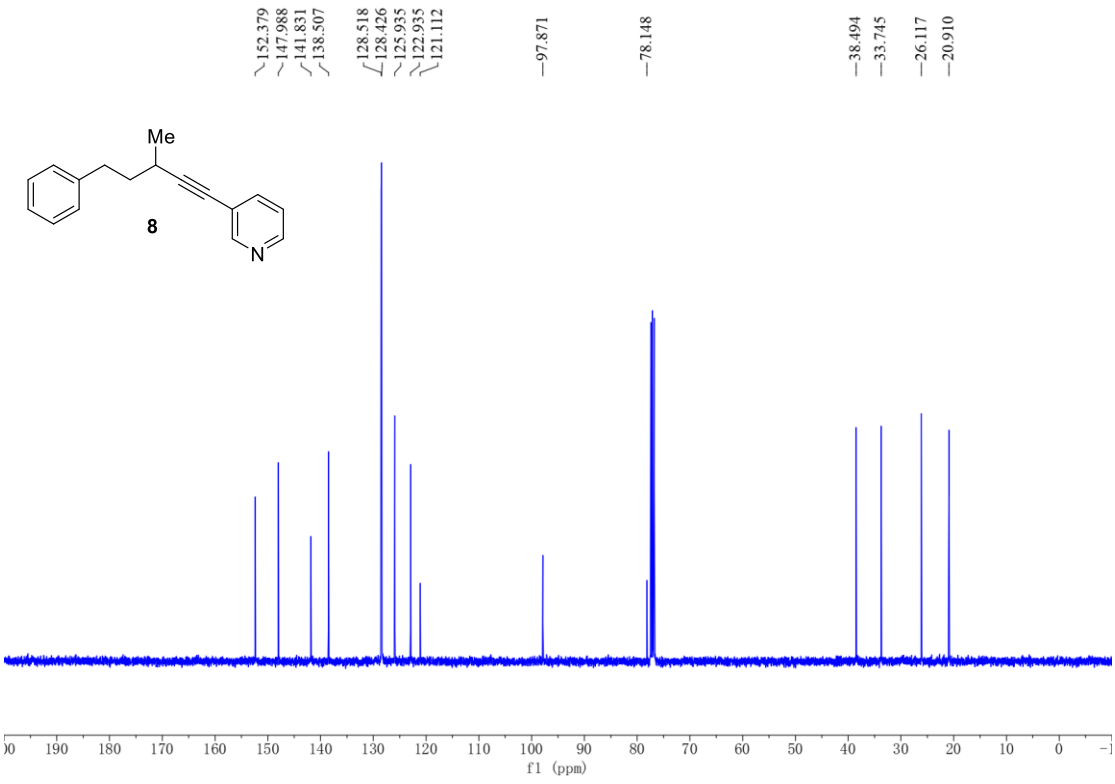
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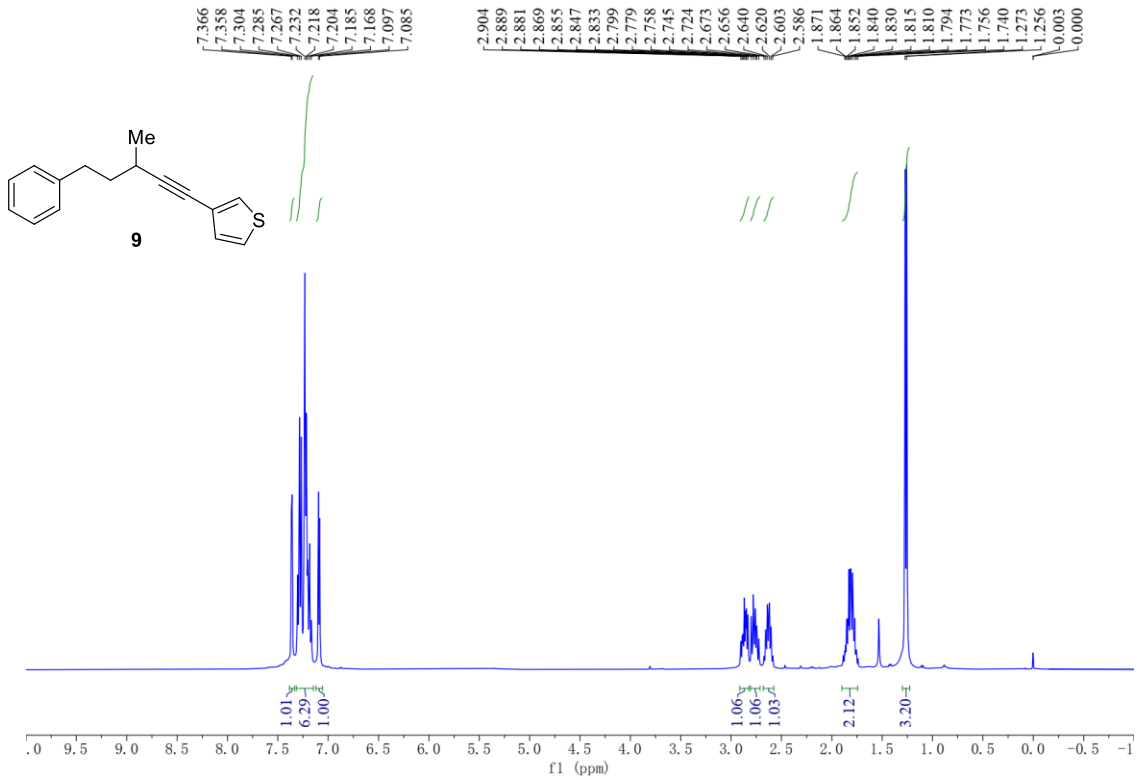
Me
8
N
f1 (ppm)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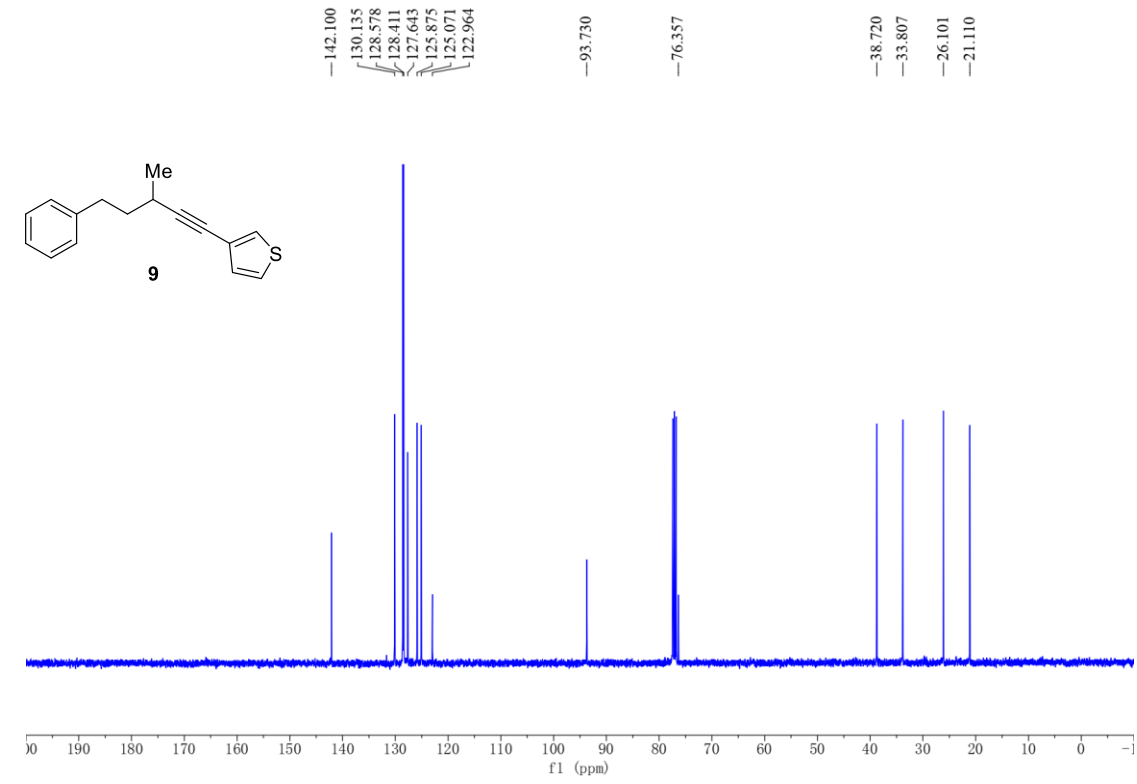
3.20
f1 (ppm)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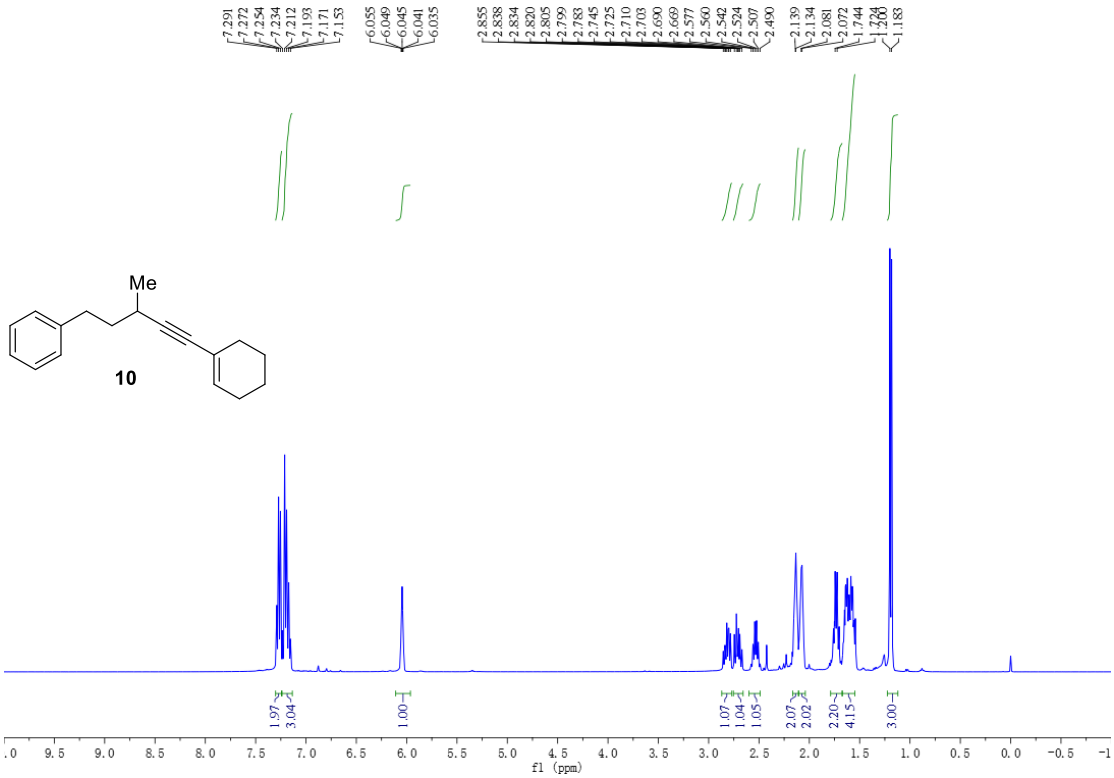
Me
S
9
f1 (ppm)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2.725
2.710
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2.669
2.577
2.560
2.542
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2.490
2.139
2.134
2.081
2.072
1.744
1.183
Me
10
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1.07
1.04
1.05
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2.20
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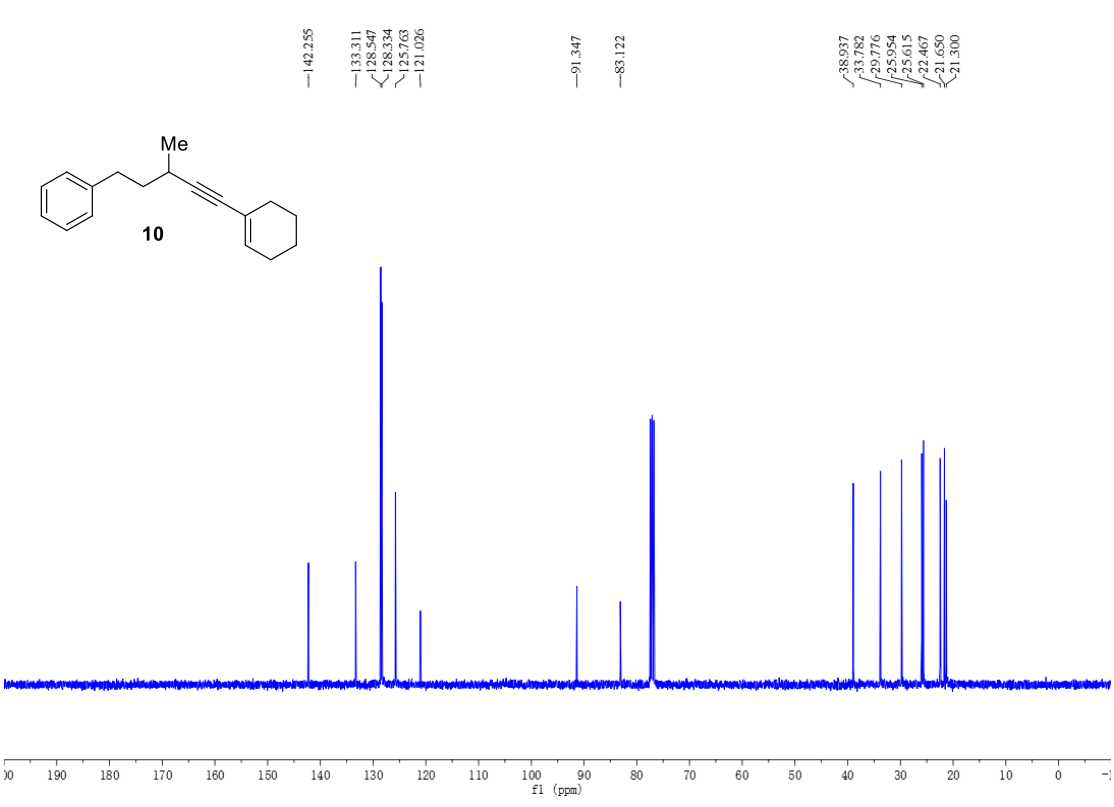
3.00
f1 (ppm)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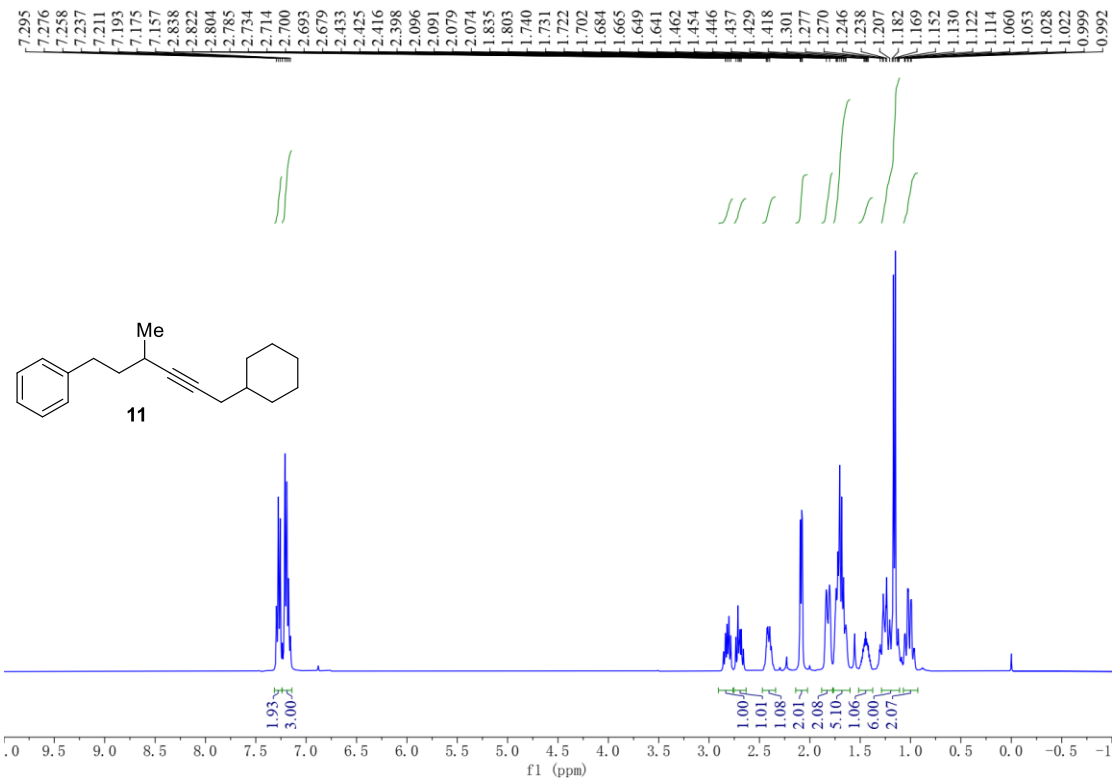
21.650
21.300
Me
10
f1 (ppm)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2.714
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2.074
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1.731
1.722
1.702
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1.649
1.641
1.462
1.454
1.446
1.437
1.429
1.418
1.301
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1.270
1.246
1.238
1.207
1.182
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1.130
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1.114
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1.028
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0.992
Me
11
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2.01
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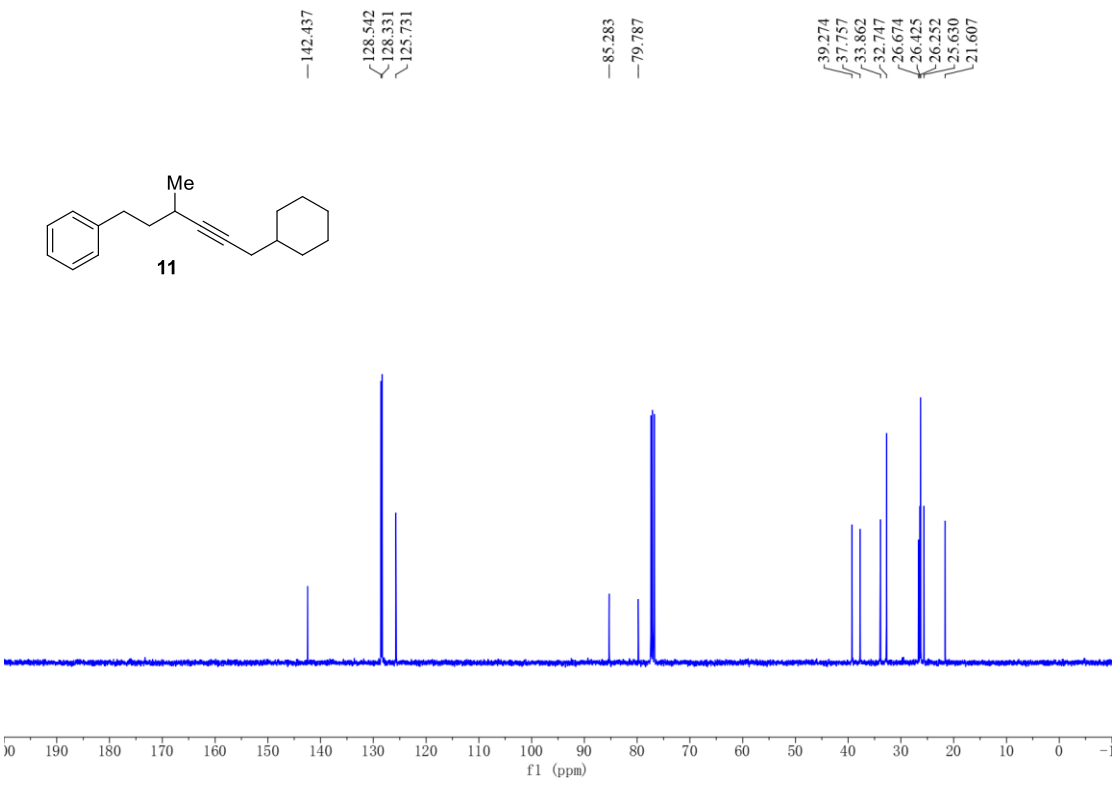
f1 (ppm)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37.757
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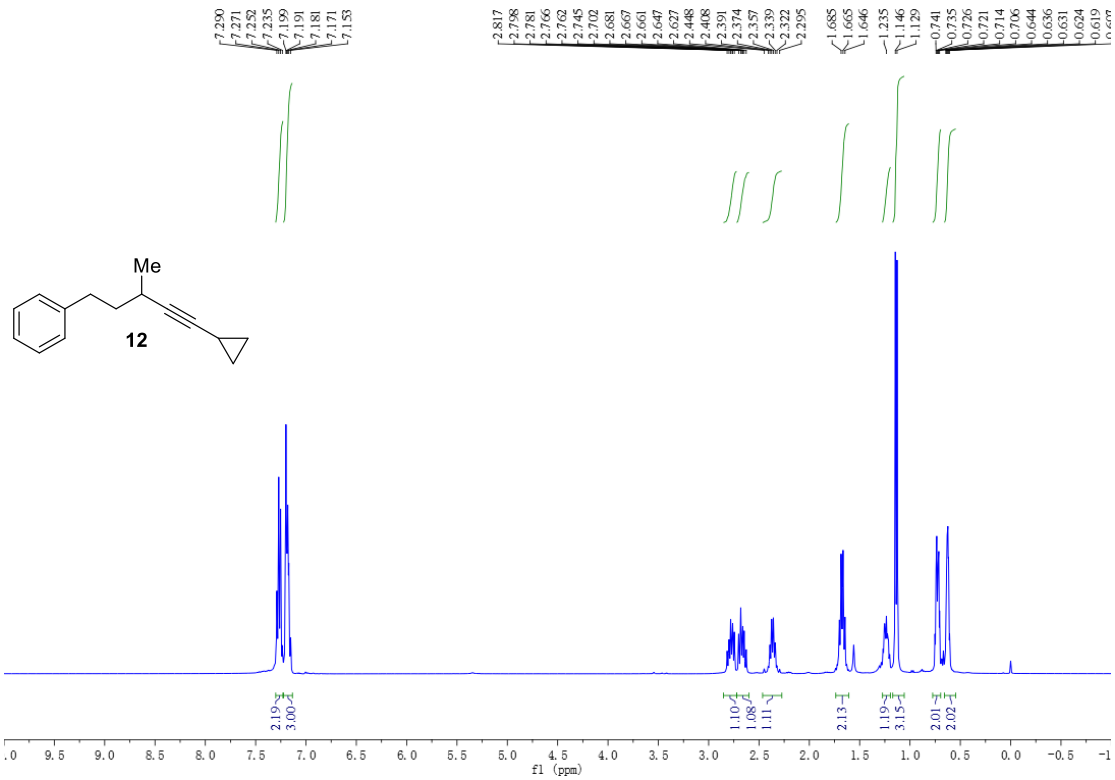
32.747
26.674
26.425
26.252
25.630
21.607
Me
11
f1 (ppm)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2.762
2.745
2.702
2.681
2.667
2.661
2.647
2.627
2.448
2.408
2.391
2.374
2.357
2.339
2.322
2.295
1.685
1.665
1.646
1.235
1.146
1.129
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0.735
0.726
0.721
0.714
0.706
0.644
0.636
0.631
0.624
0.619
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1.11
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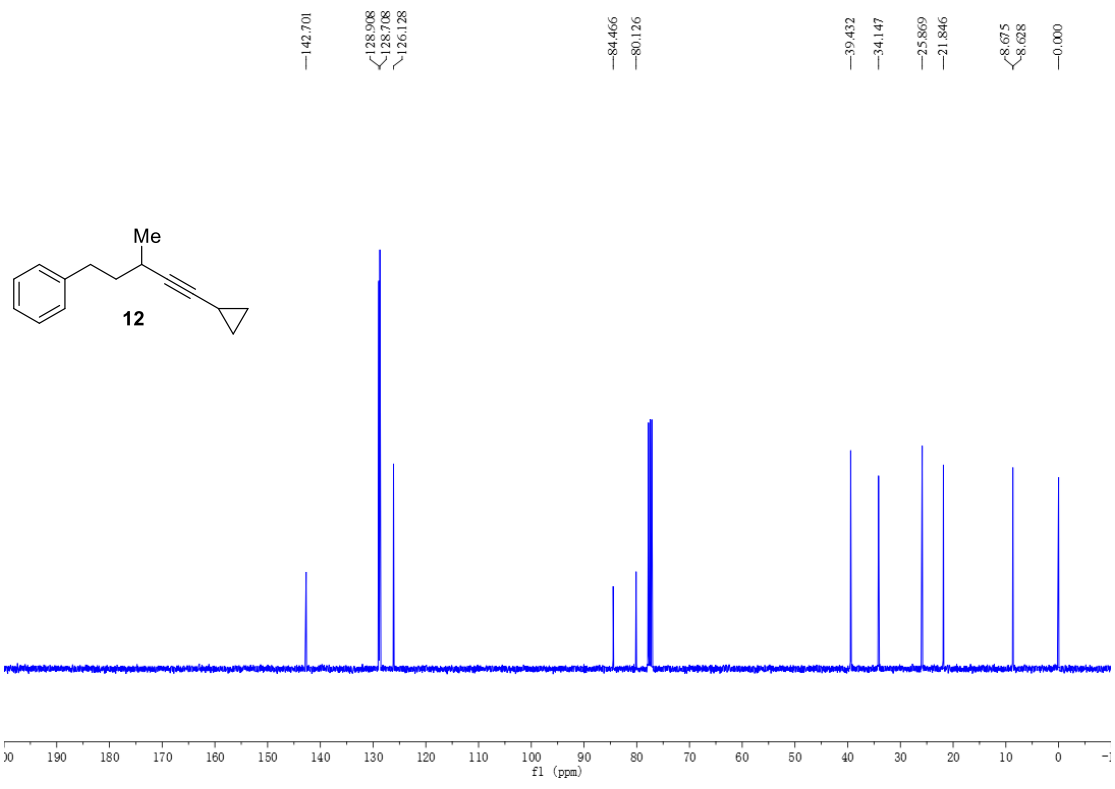
1.19
3.15
2.01
2.02
f1 (ppm)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34.147
25.869
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8.628
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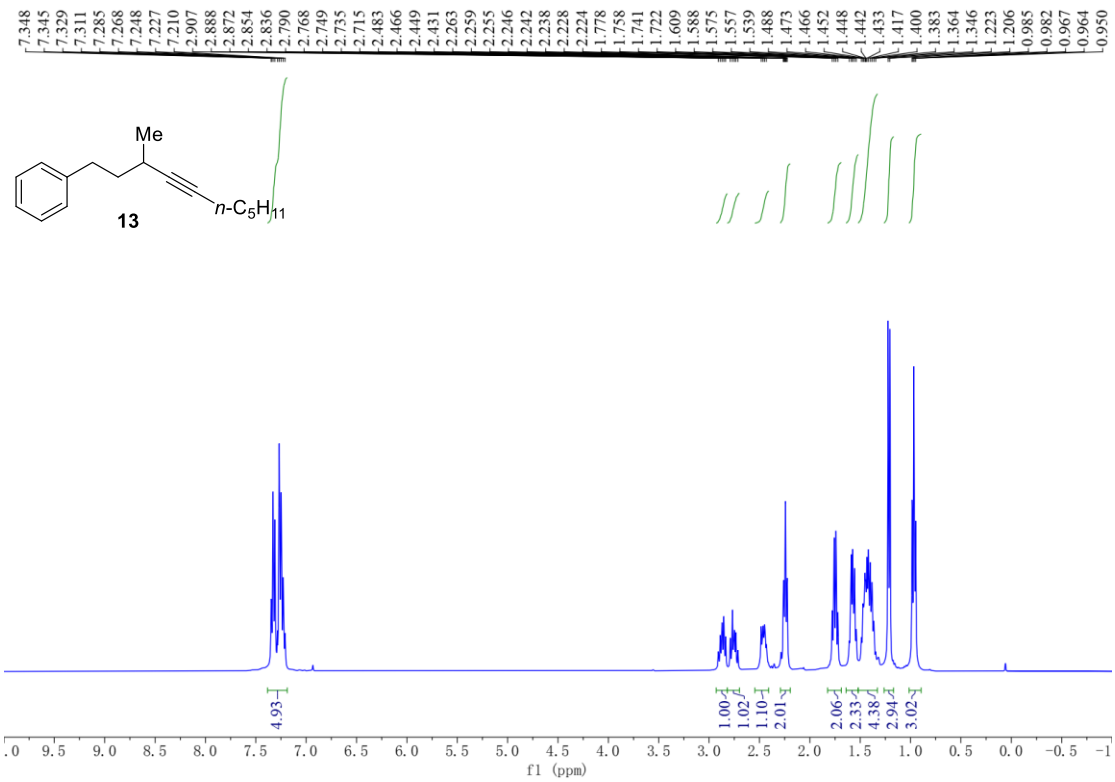
Me
12
f1 (ppm)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2.768
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2.715
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2.449
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2.259
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2.246
2.242
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2.228
2.224
1.778
1.758
1.741
1.722
1.609
1.588
1.575
1.557
1.539
1.488
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1.466
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1.448
1.442
1.433
1.417
1.400
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1.364
1.346
1.223
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0.967
0.964
0.950
Me
n-C5H11
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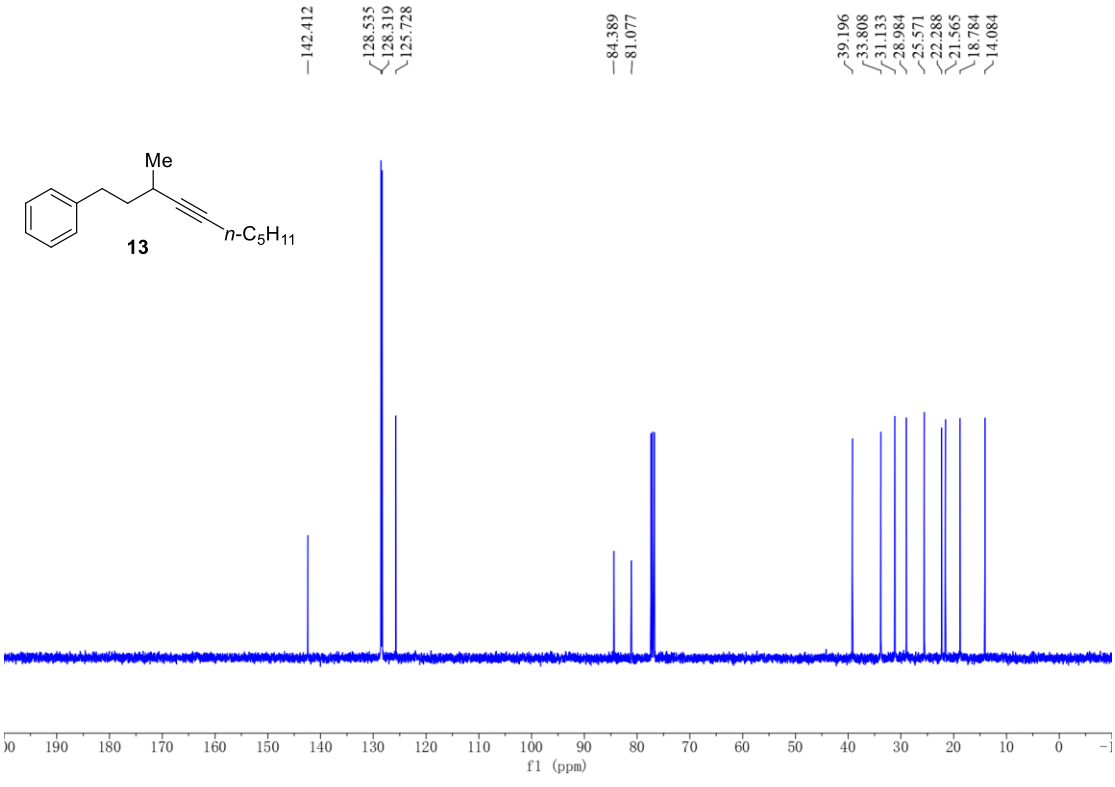
f1 (ppm)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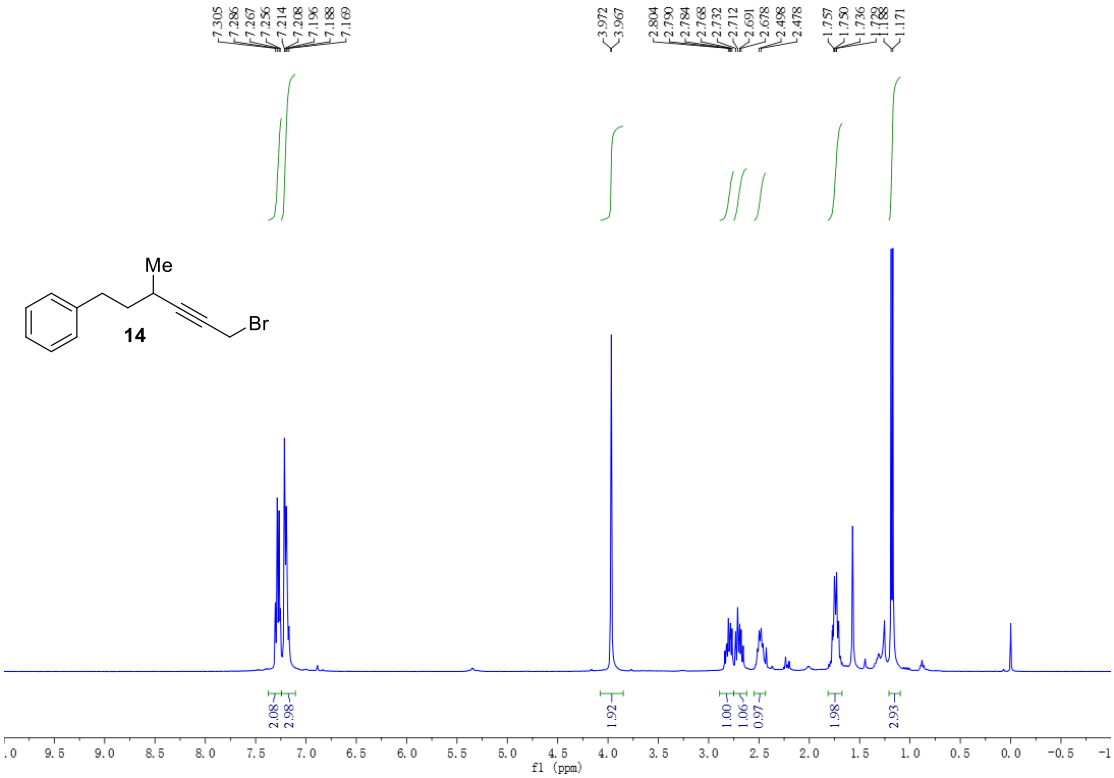
21.565
18.784
14.084
Me
n-C5H11
13
f1 (ppm)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7.208
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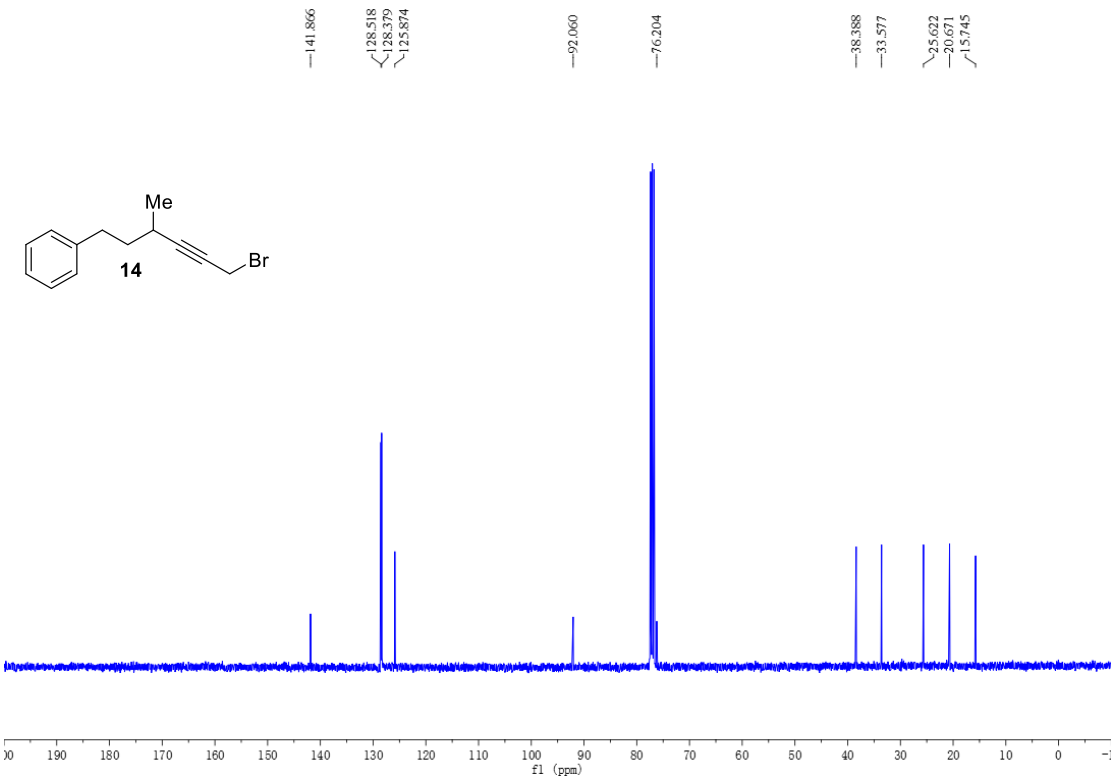
7.188
7.169
3.972
3.967
2.804
2.790
2.784
2.768
2.732
2.712
2.691
2.678
2.498
2.478
1.757
1.750
1.736
1.171
Me
Br
14
2.08
2.98
1.92
1.00
1.06
0.97
1.98
2.93
f1 (ppm)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33.577
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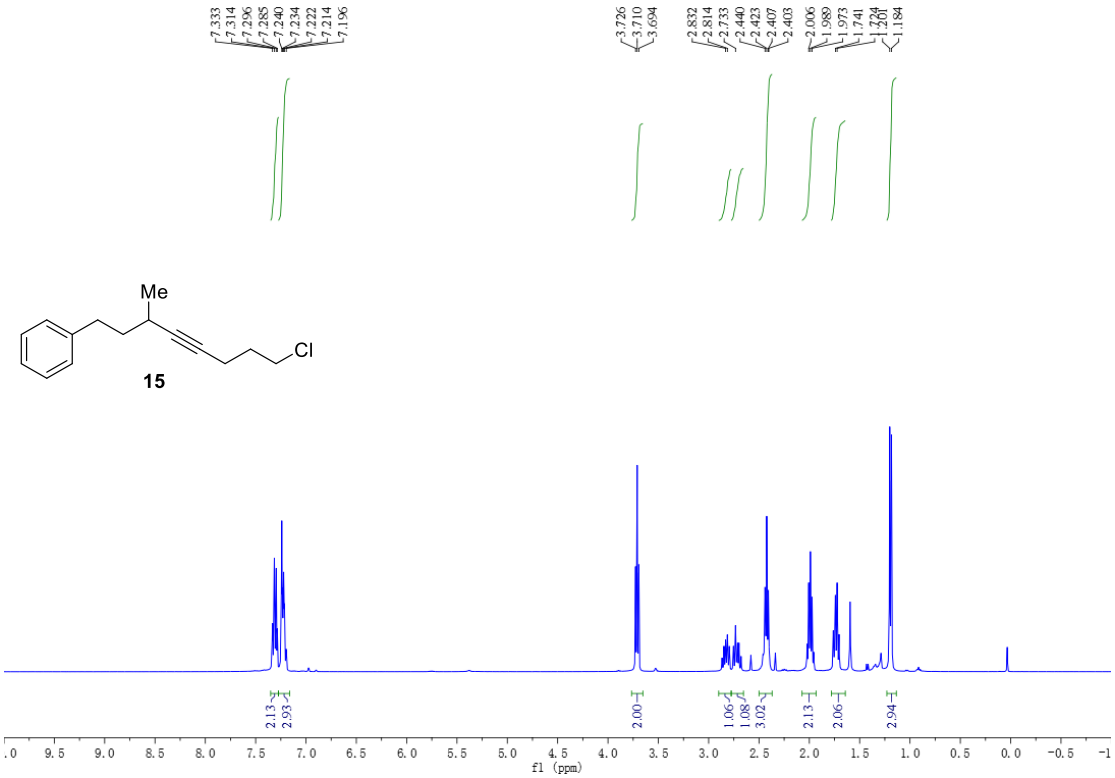
15.745
Me
Br
14
f1 (ppm)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7.240
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7.222
7.214
7.196
3.726
3.710
3.694
2.832
2.814
2.733
2.440
2.423
2.407
2.403
2.006
1.989
1.973
1.741
1.724
1.701
1.184
Me
Cl
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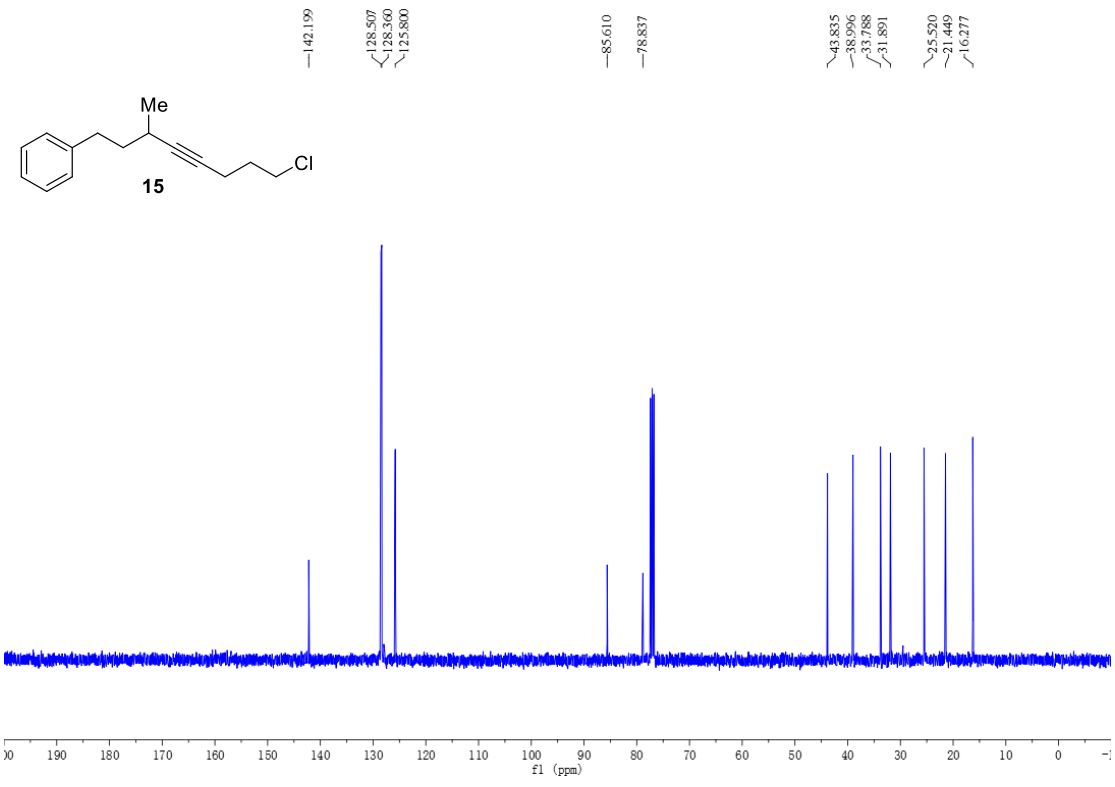
2.93
2.00
1.06
1.08
3.02
2.13
2.06
2.94
f1 (ppm)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85.610
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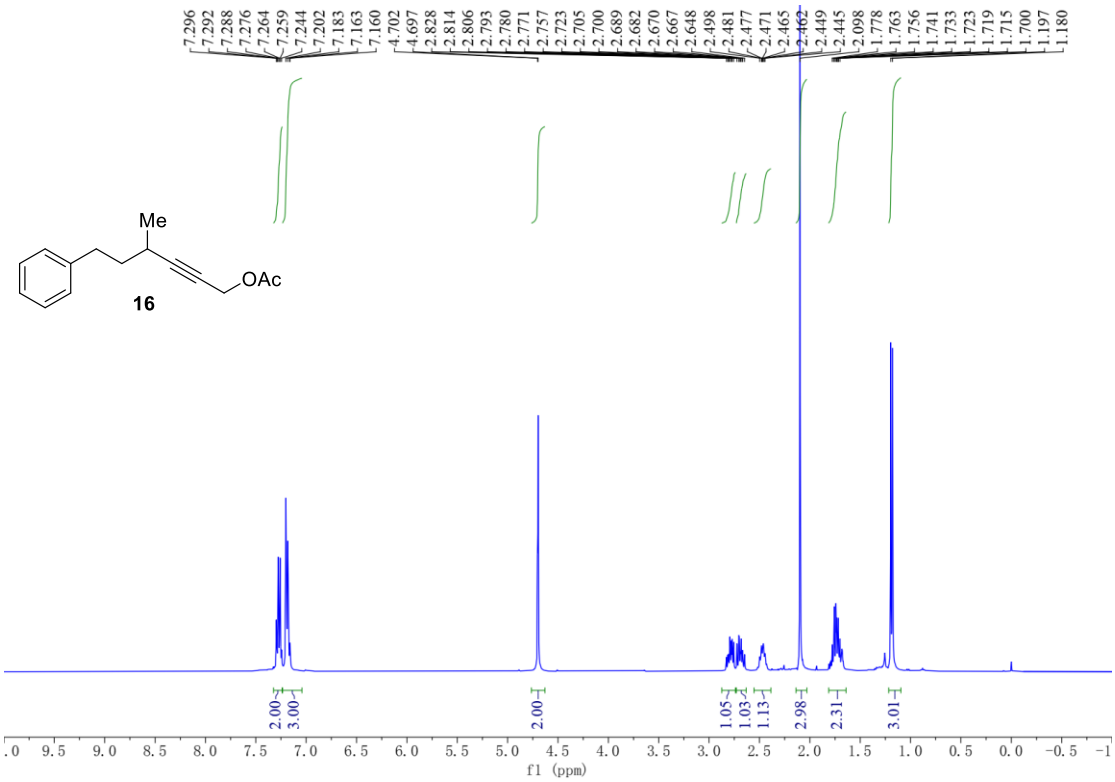
21.449
16.277
Me
Cl
15
f1 (ppm)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7.276
7.264
7.259
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7.202
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7.163
7.160
4.702
4.697
2.828
2.814
2.806
2.793
2.780
2.771
2.757
2.723
2.705
2.700
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2.682
2.670
2.667
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2.481
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2.471
2.465
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2.449
2.445
2.098
1.778
1.763
1.756
1.741
1.733
1.723
1.719
1.715
1.700
1.197
1.180
Me
OAc
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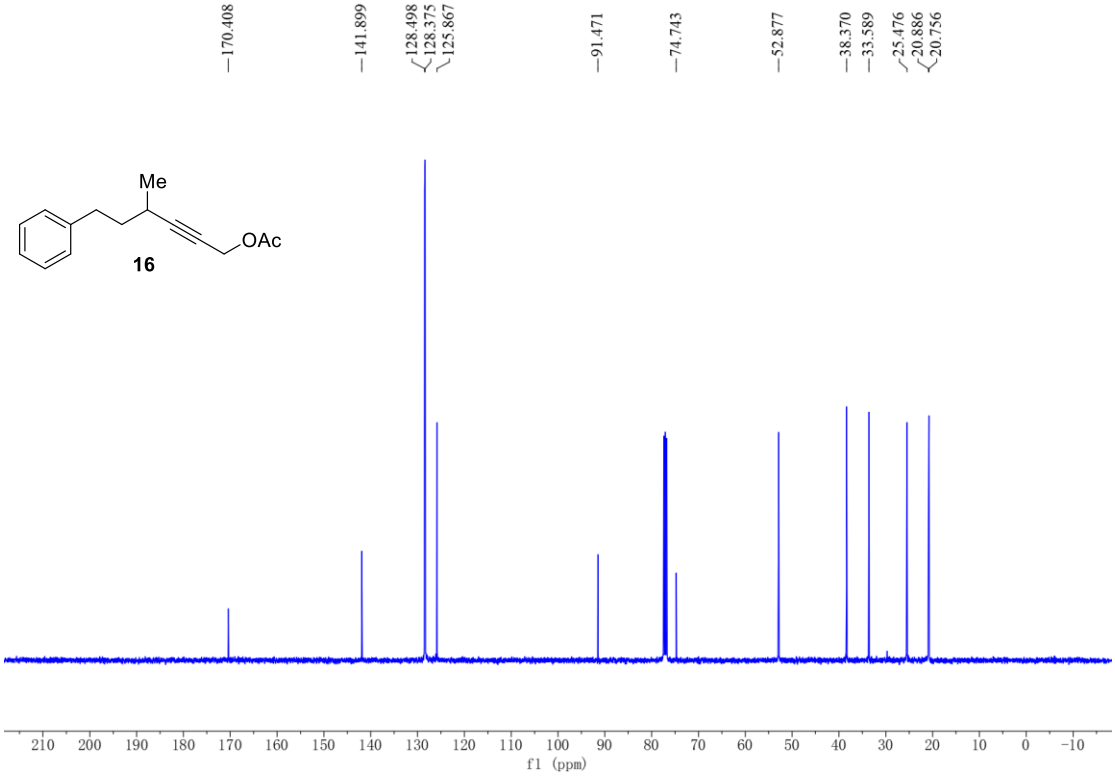
2.00
1.05
1.03
1.13
2.98
2.31
3.01
f1 (ppm)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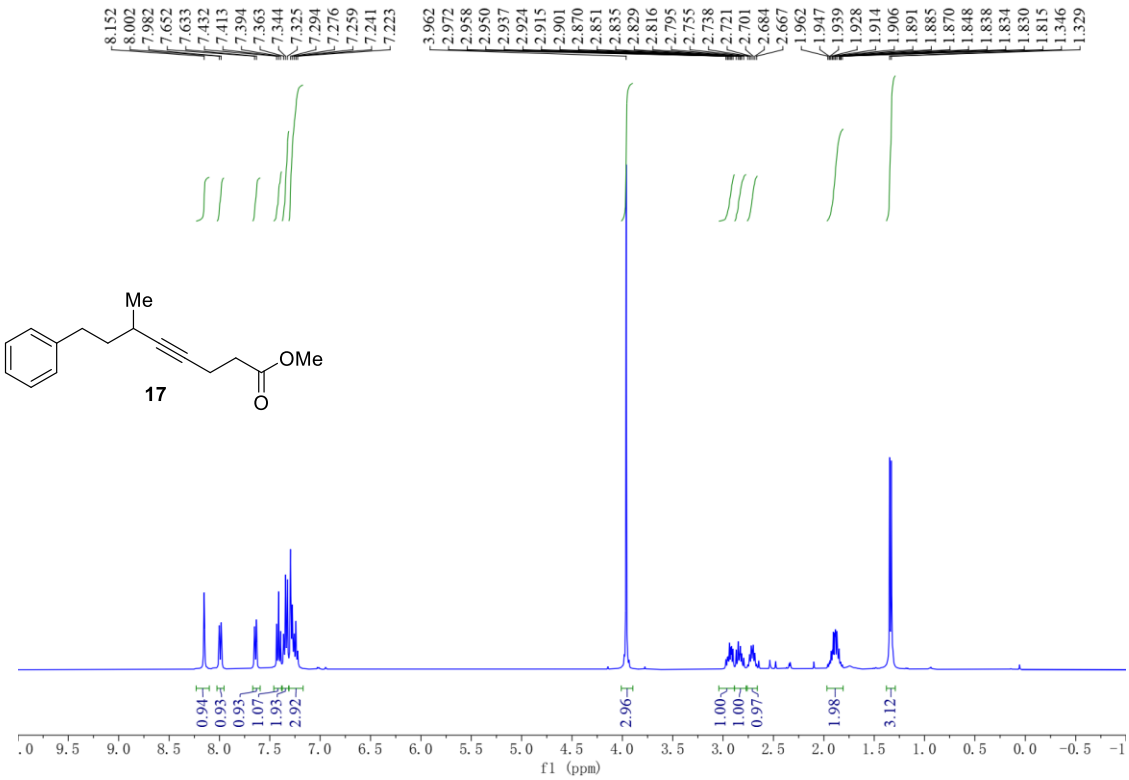
OAc
16
f1 (ppm)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7.413
7.394
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7.344
7.325
7.294
7.276
7.259
7.241
7.223
3.962
2.972
2.958
2.950
2.937
2.924
2.915
2.901
2.870
2.851
2.835
2.829
2.816
2.795
2.755
2.738
2.721
2.701
2.684
2.667
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1.947
1.939
1.928
1.914
1.906
1.891
1.885
1.870
1.848
1.838
1.834
1.830
1.815
1.346
1.329
Me
OMe
O
17
0.94
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0.93
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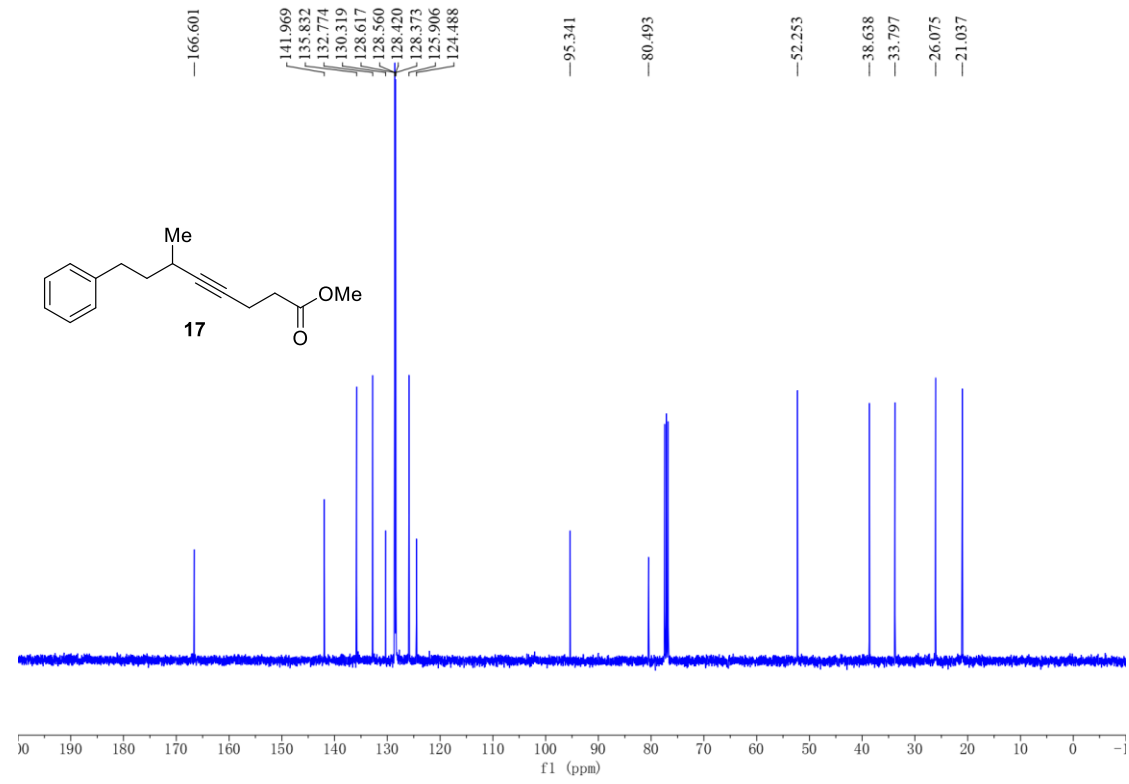
1.93
2.92
2.96
1.00
1.00
0.97
1.98
3.12
f1 (ppm)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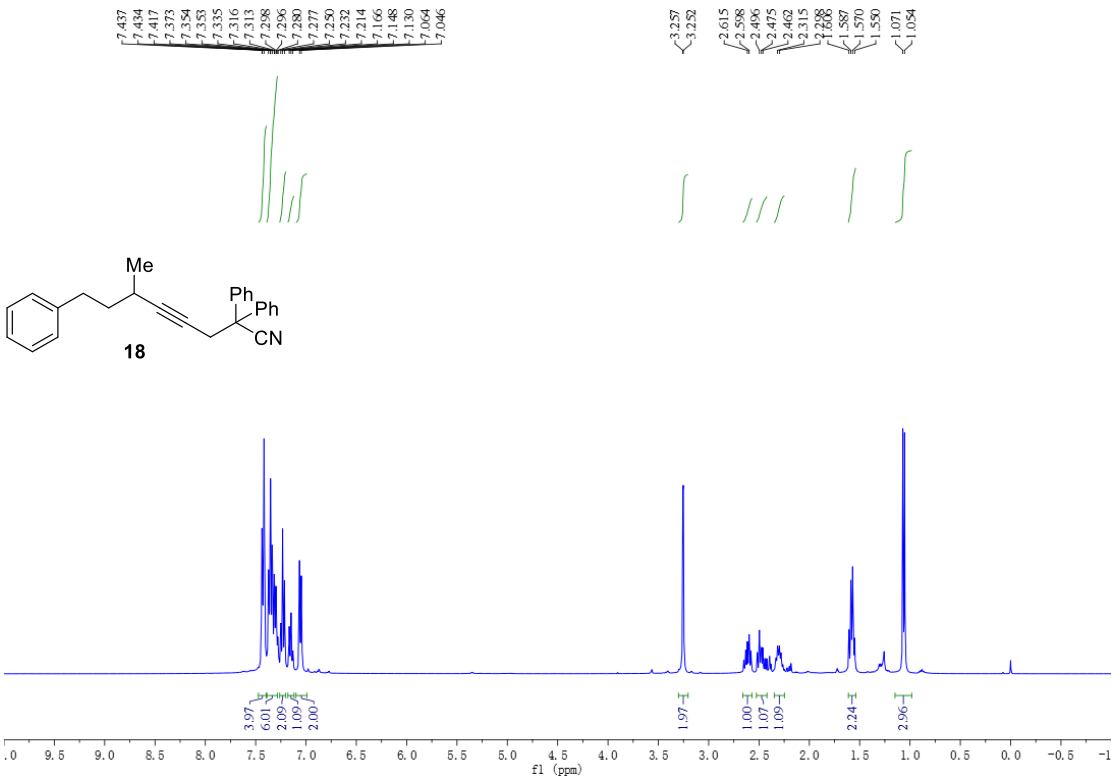
21.037
Me
OMe
O
17
f1 (ppm)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7.277
7.250
7.232
7.214
7.166
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7.130
7.064
7.046
3.257
3.252
2.615
2.598
2.496
2.475
2.462
2.315
2.208
2.008
1.587
1.570
1.550
1.071
1.054
Me
Ph
Ph
CN
18
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6.01
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1.09
2.00
1.97
1.00
1.07
1.09
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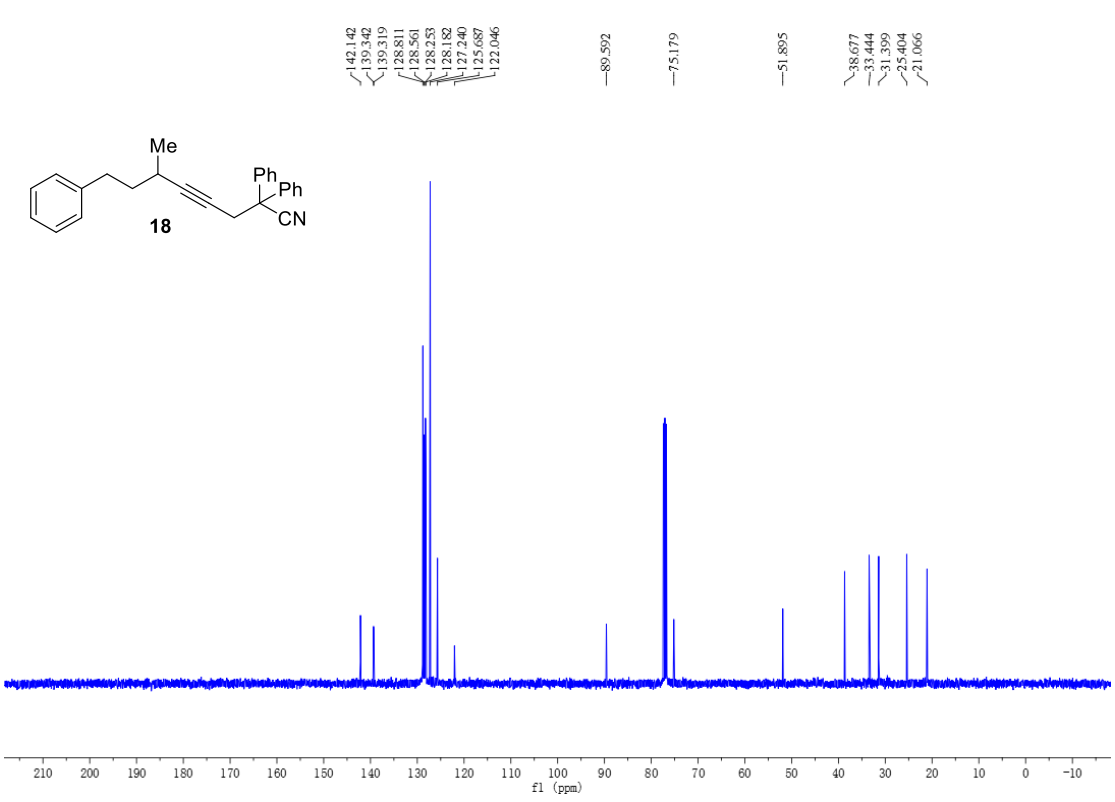
2.96
f1 (ppm)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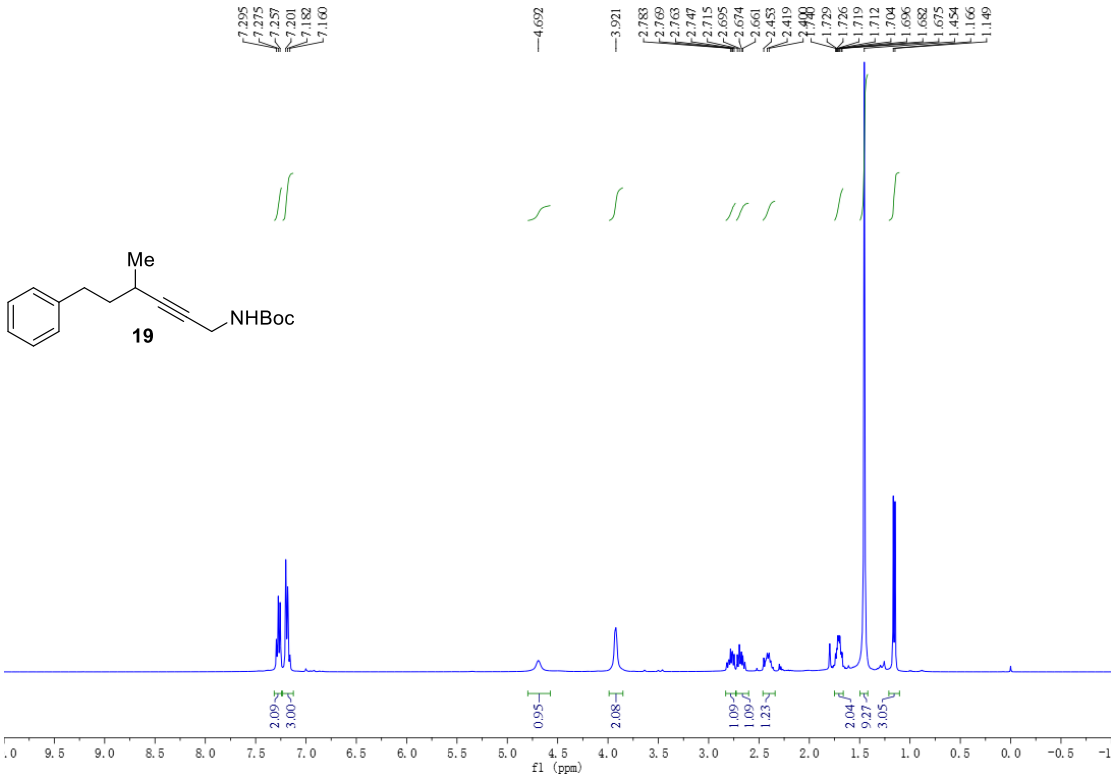
Me
Ph
Ph
CN
18
f1 (ppm)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7.201
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3.921
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2.769
2.763
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2.715
2.695
2.674
2.661
2.453
2.419
1.729
1.726
1.719
1.712
1.704
1.696
1.682
1.675
1.454
1.166
1.149
Me
NHBoc
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1.09
1.09
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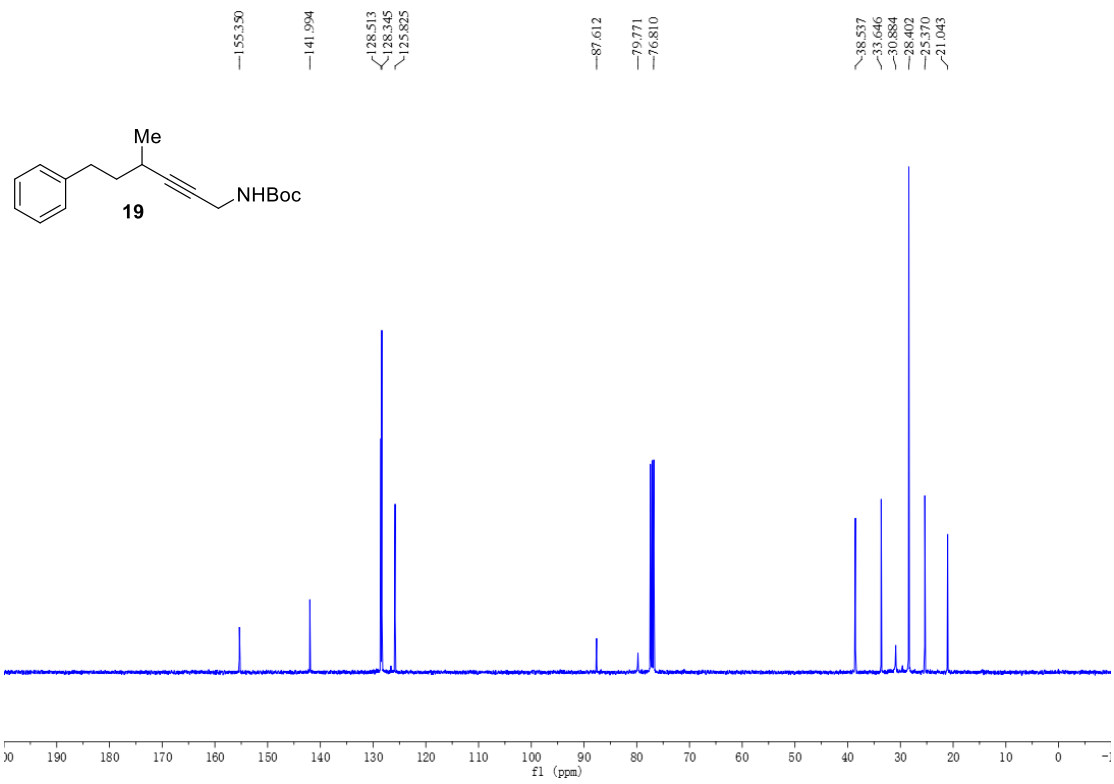
2.04
9.27
3.05
f1 (ppm)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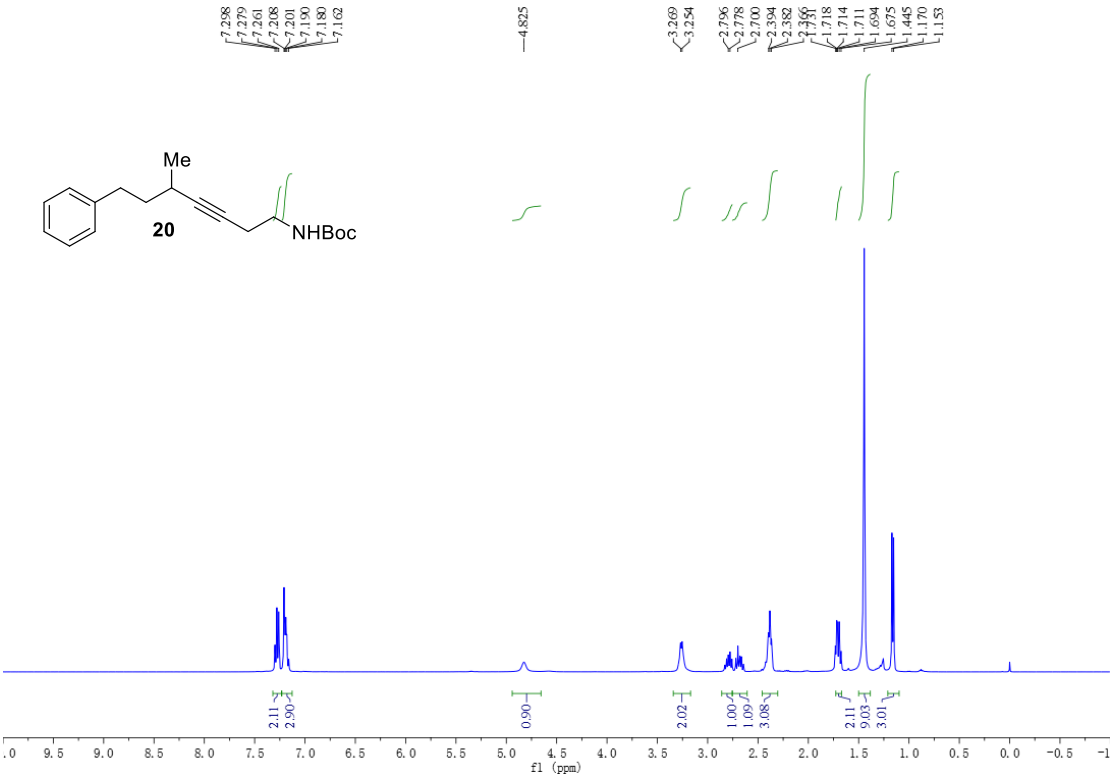
21.043
Me
NHBoc
19
f1 (ppm)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3.269
3.254
2.796
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2.700
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2.382
1.718
1.714
1.711
1.694
1.675
1.445
1.170
1.153
Me
20
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1.09
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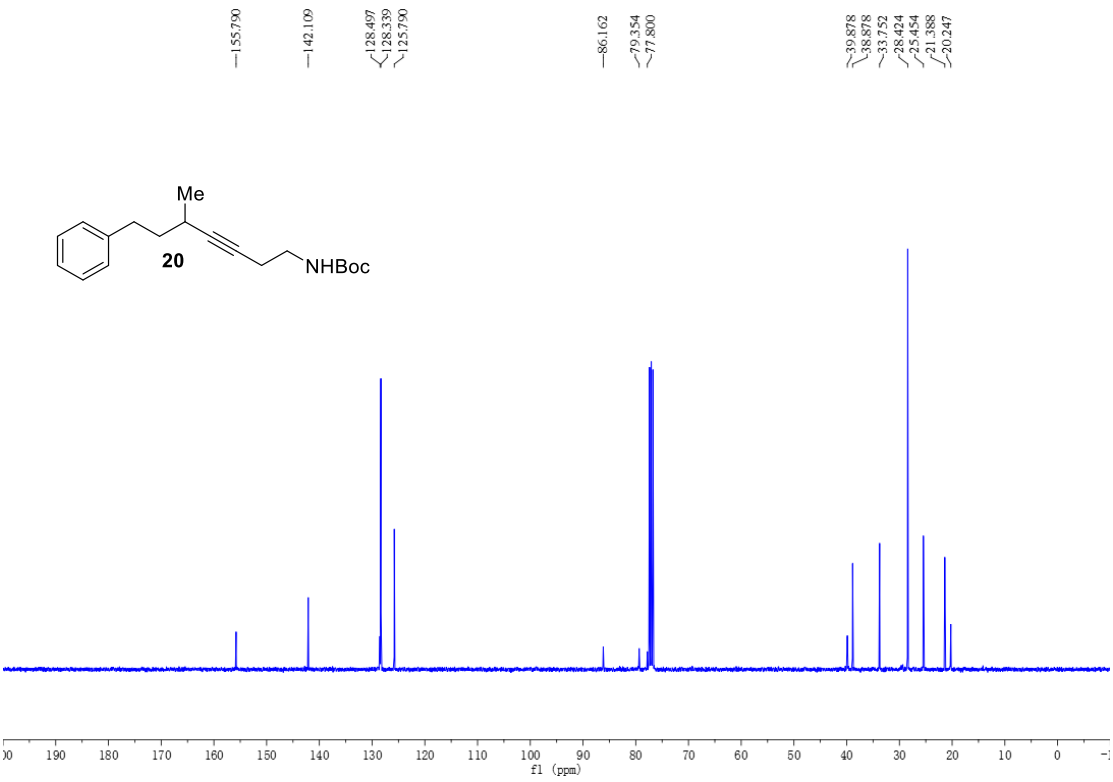
2.11
9.03
3.01
f1 (ppm)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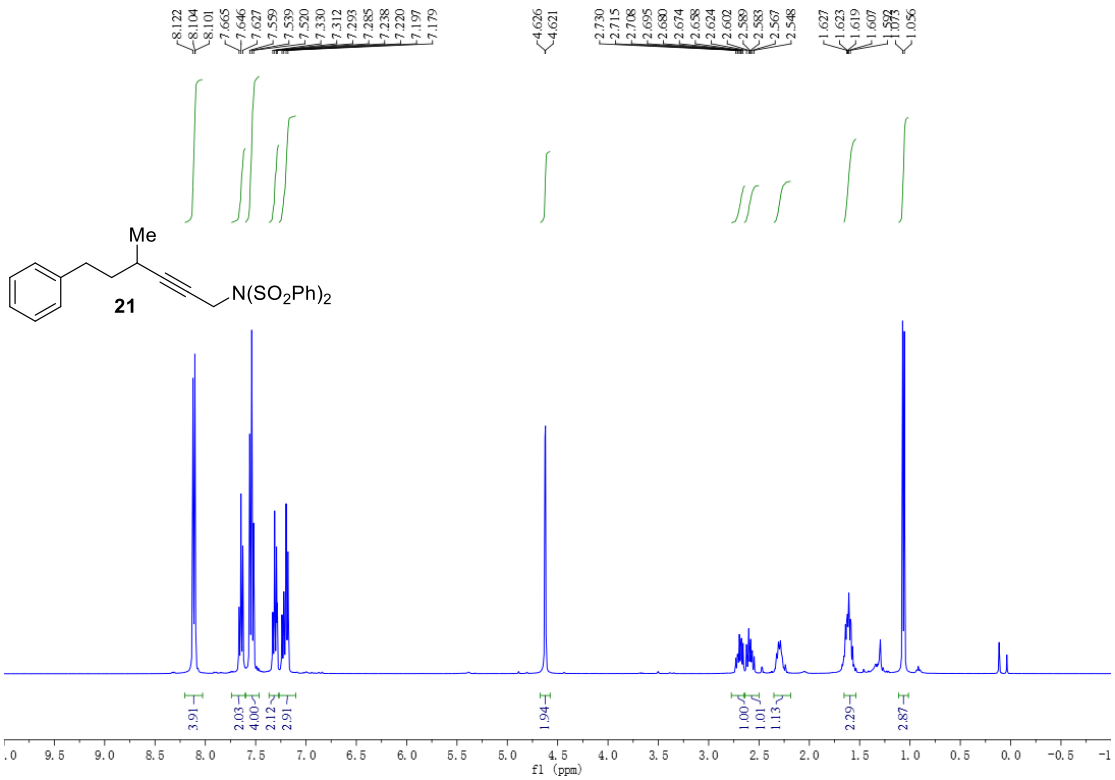
Me
20
NHBoc
f1 (ppm)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7.330
7.312
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7.285
7.238
7.220
7.197
7.179
4.626
4.621
2.730
2.715
2.708
2.695
2.680
2.674
2.658
2.624
2.602
2.589
2.583
2.567
2.548
1.627
1.623
1.619
1.607
1.056
Me
N(SO2Ph)2
21
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1.94
1.00
1.01
1.13
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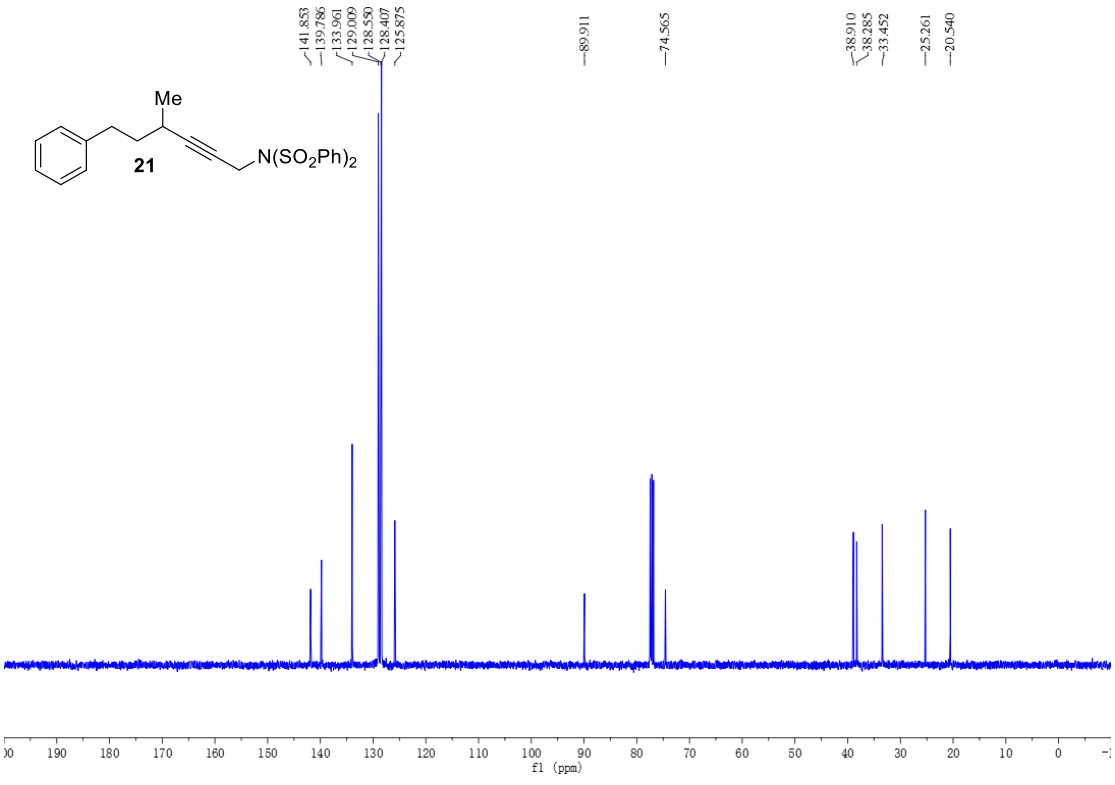
2.87
f1 (ppm)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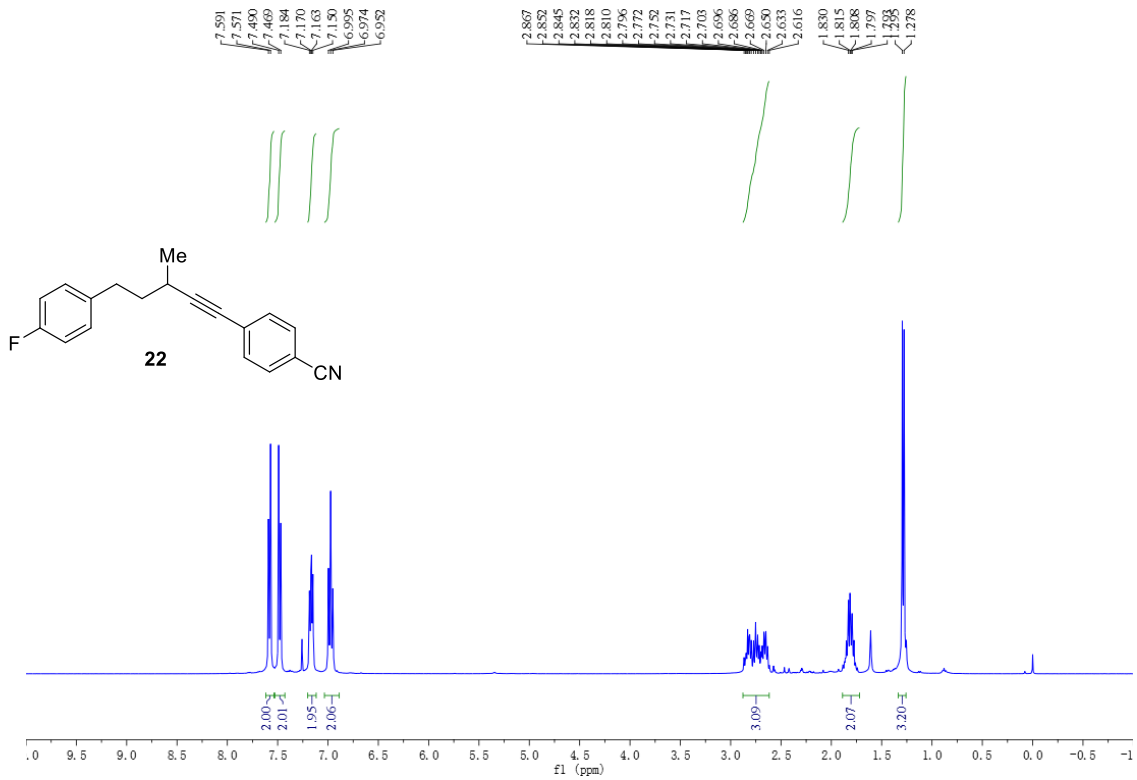
Me
N(SO2Ph)2
21
f1 (ppm)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2.650
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2.616
1.830
1.815
1.808
1.797
1.295
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F
22
CN
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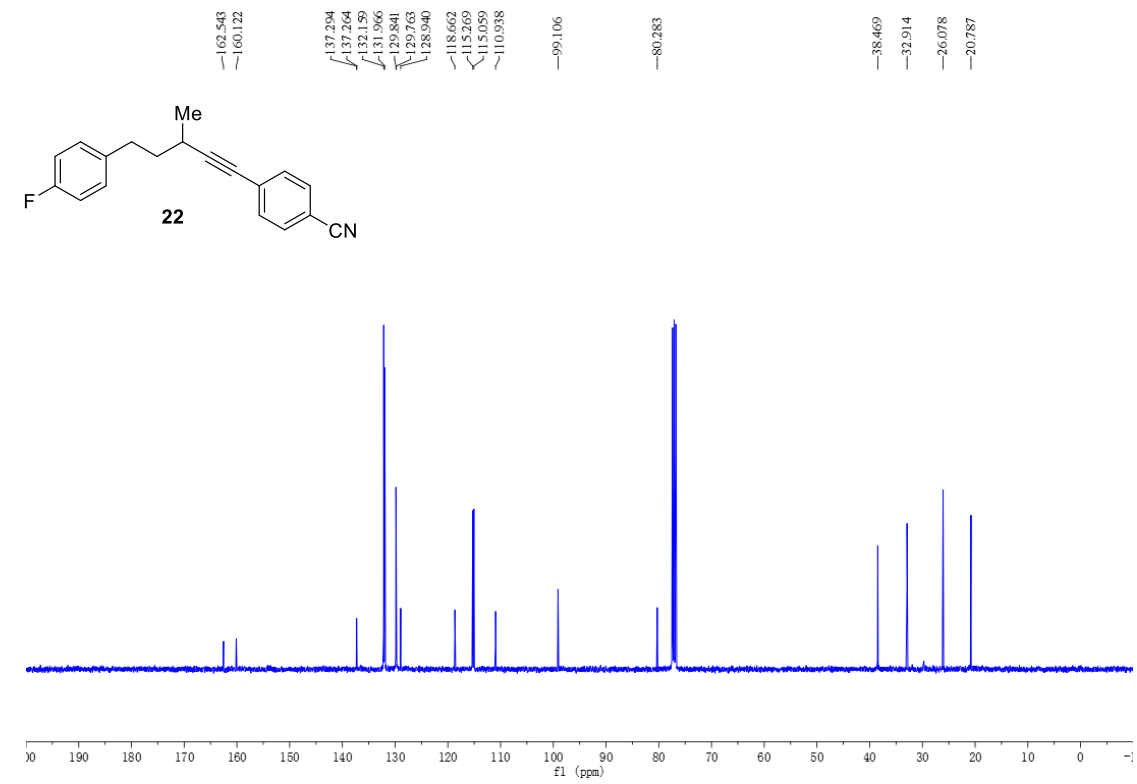
2.01
1.95
2.06
3.09
2.07
3.20
f1 (ppm)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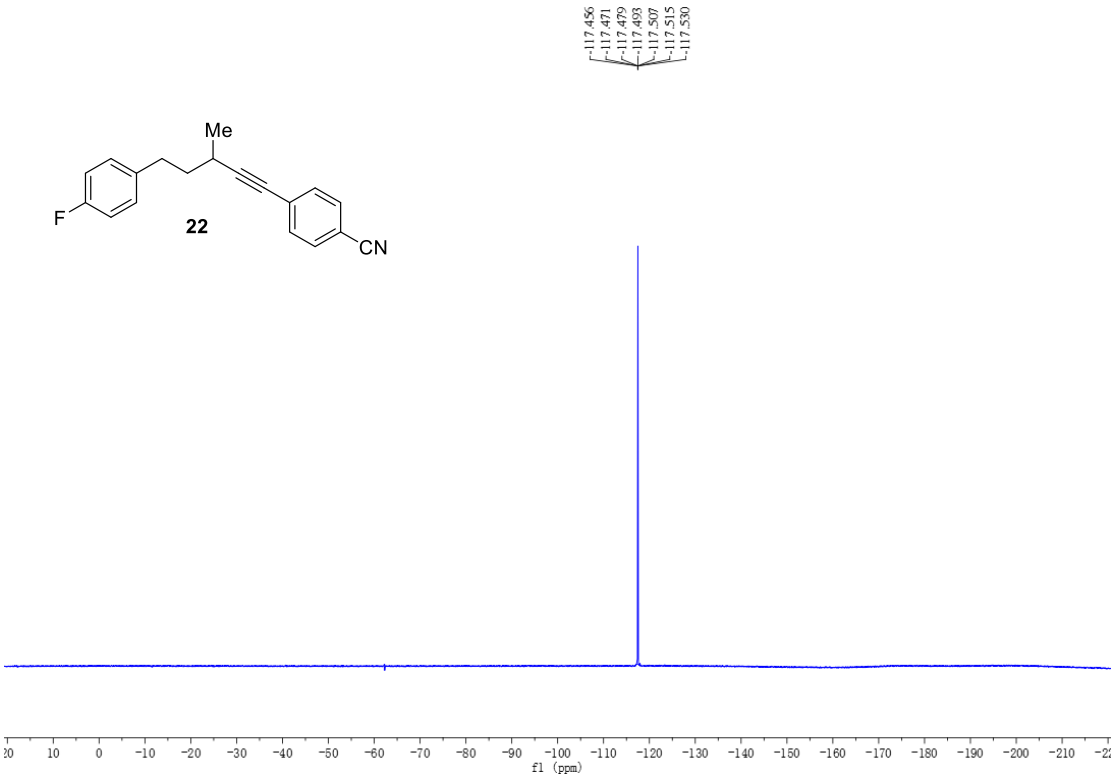
80.283
38.469
32.914
26.078
20.787
Me
F
22
CN
f1 (ppm)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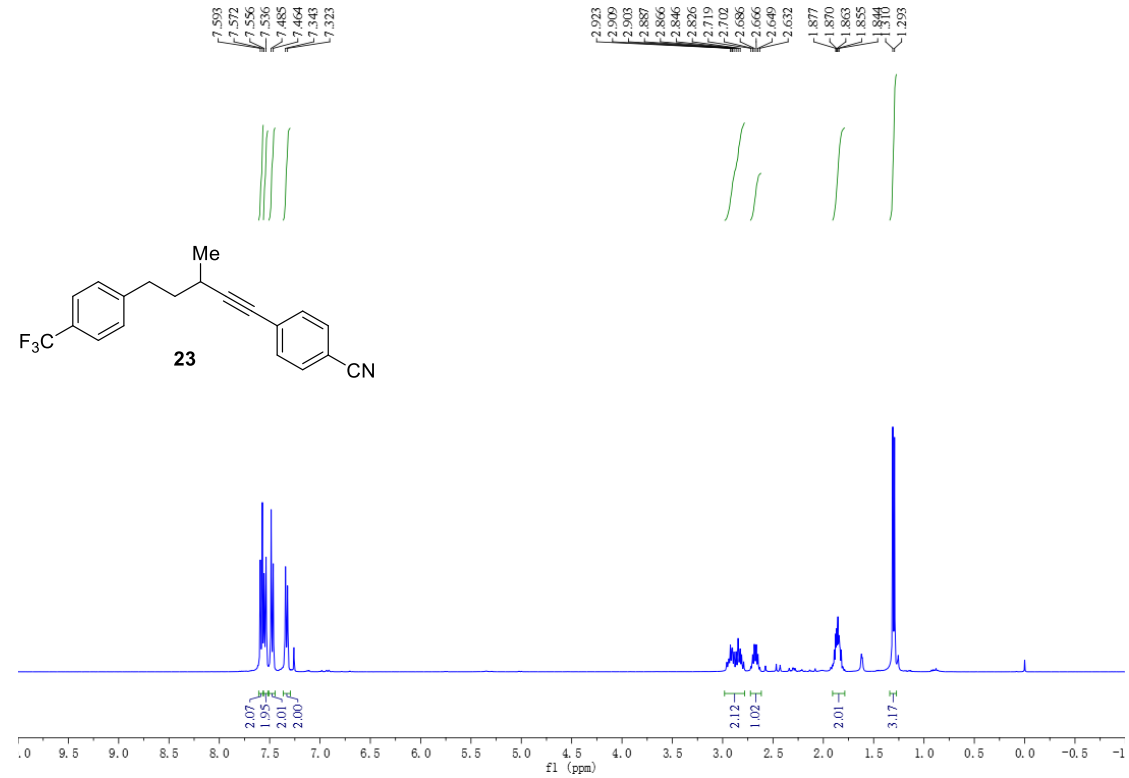
F
CN
22
f1 (ppm)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7.572
7.556
7.536
7.485
7.464
7.343
7.323
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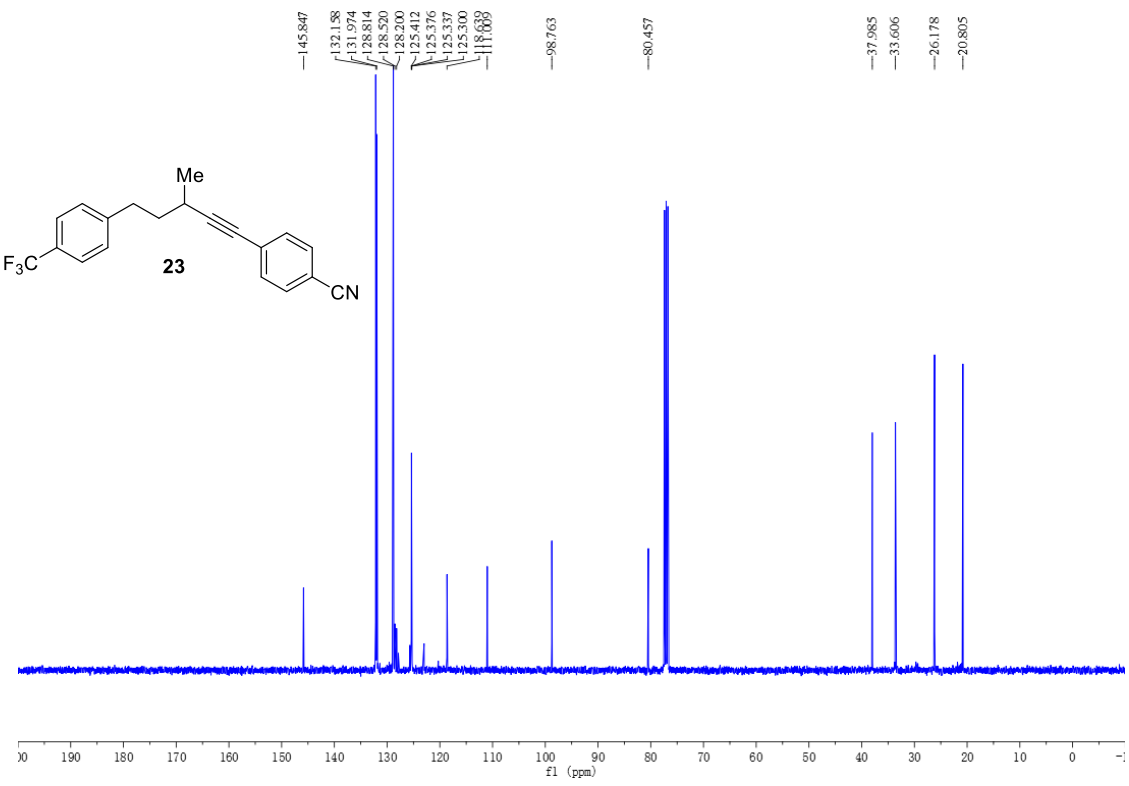
2.909
2.903
2.887
2.866
2.846
2.826
2.719
2.702
2.686
2.666
2.649
2.632
1.877
1.870
1.863
1.855
1.844
1.310
1.293
Me
F3C
CN
23
2.07
1.95
2.01
2.00
2.12
1.02
2.01
3.17
f1 (ppm)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129.814
128.520
128.200
125.412
125.376
125.337
125.300
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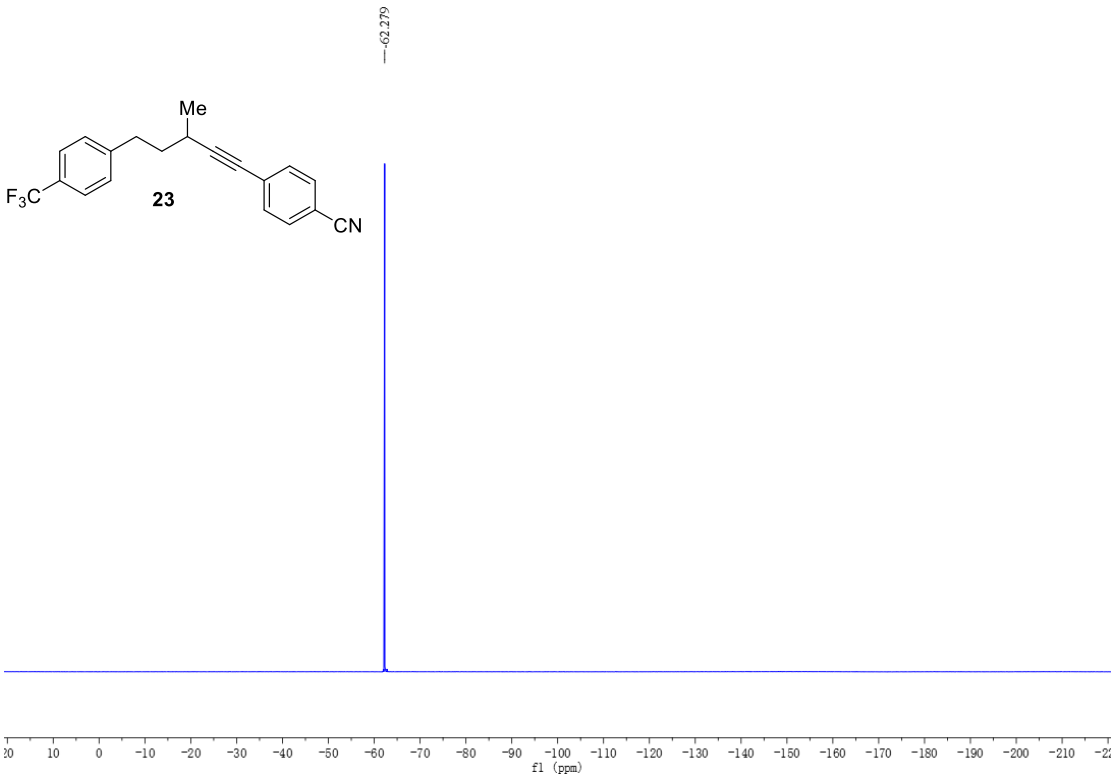
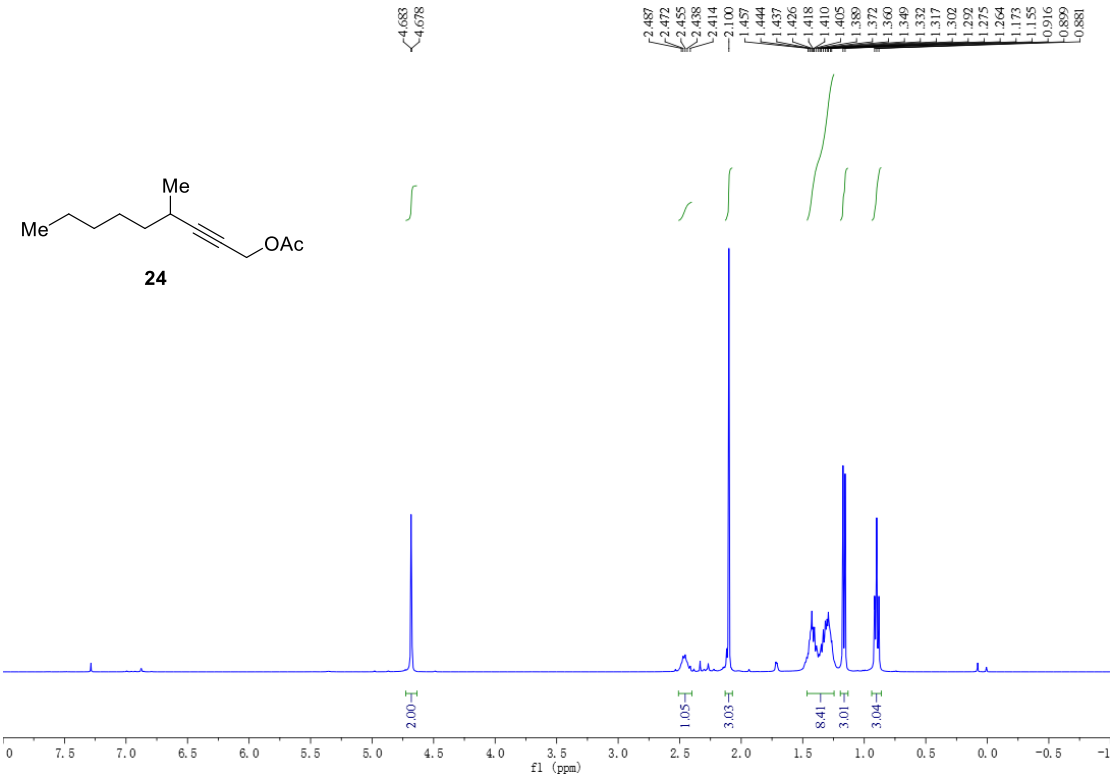
98.763
80.457
37.985
33.606
26.178
20.805
Me
F3C
CN
23
f1 (ppm)


-62.279
Me
F3C
23
CN
f1 (ppm)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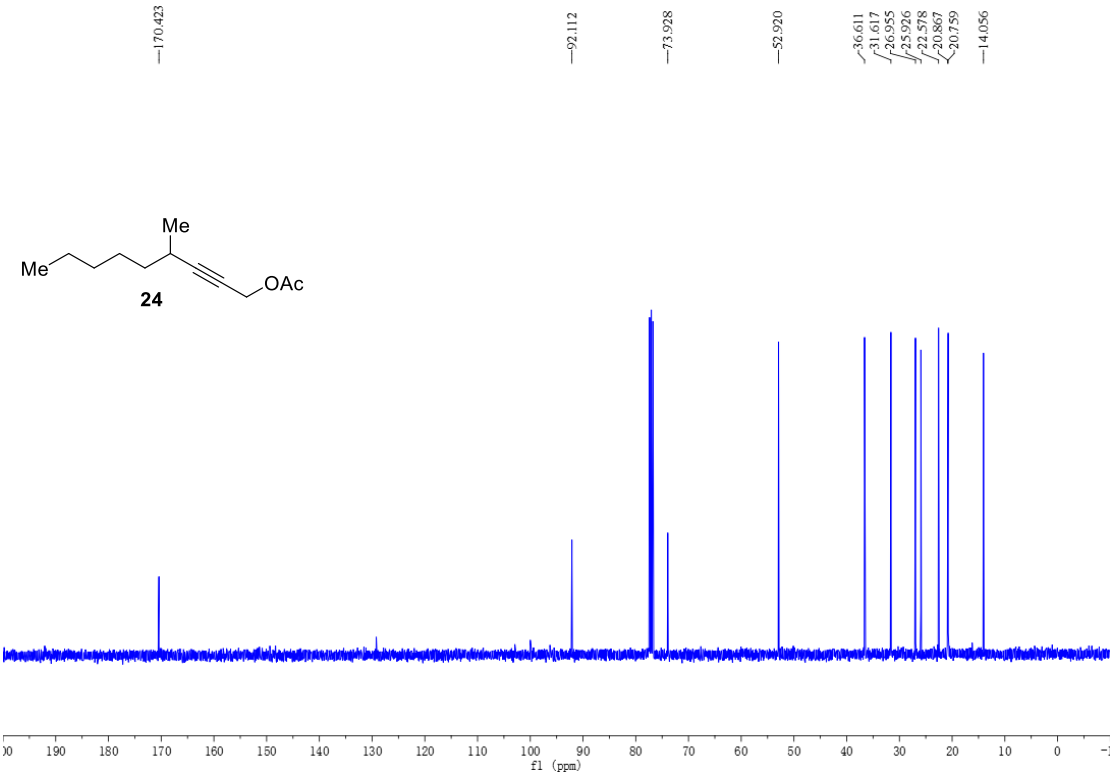
2.472
2.455
2.438
2.414
2.100
1.457
1.444
1.437
1.426
1.418
1.410
1.405
1.389
1.372
1.360
1.349
1.332
1.317
1.302
1.292
1.275
1.264
1.173
1.155
0.916
0.899
0.881
Me
Me
OAc
24
2.00
1.05
3.03
8.41
3.01
3.04
f1 (ppm)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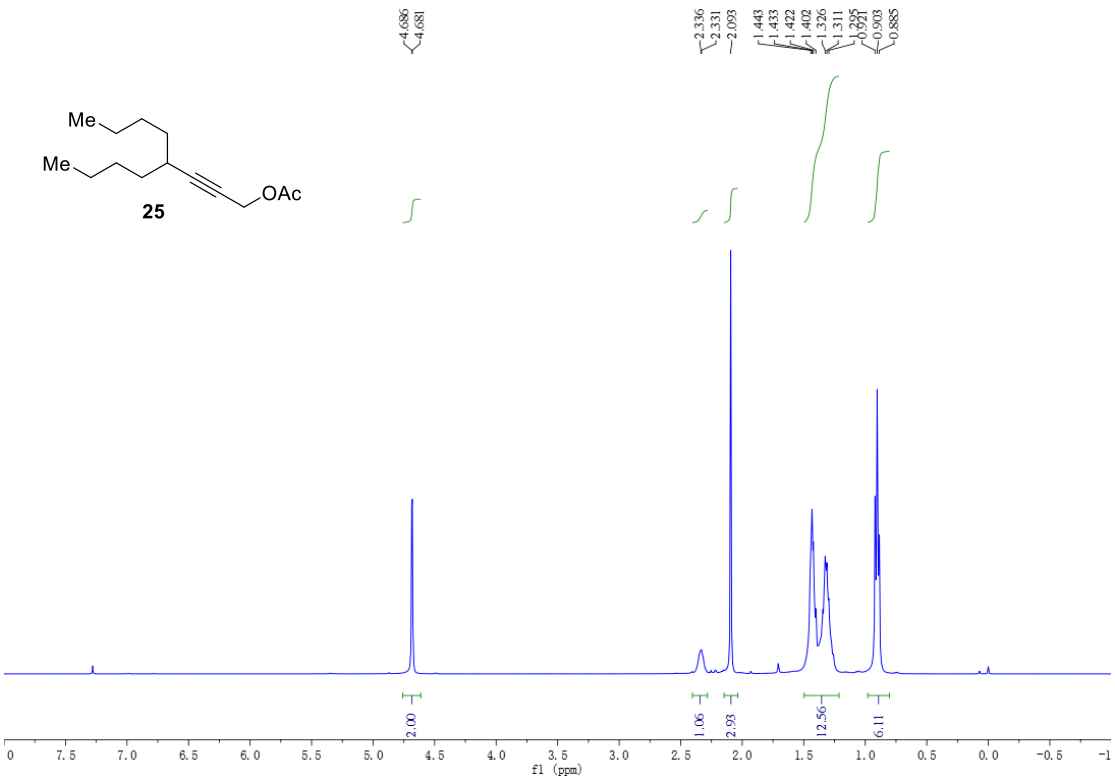
92.112
73.928
52.920
36.611
31.617
26.955
25.926
22.578
20.867
20.759
14.056
Me
Me
OAc
24
f1 (ppm)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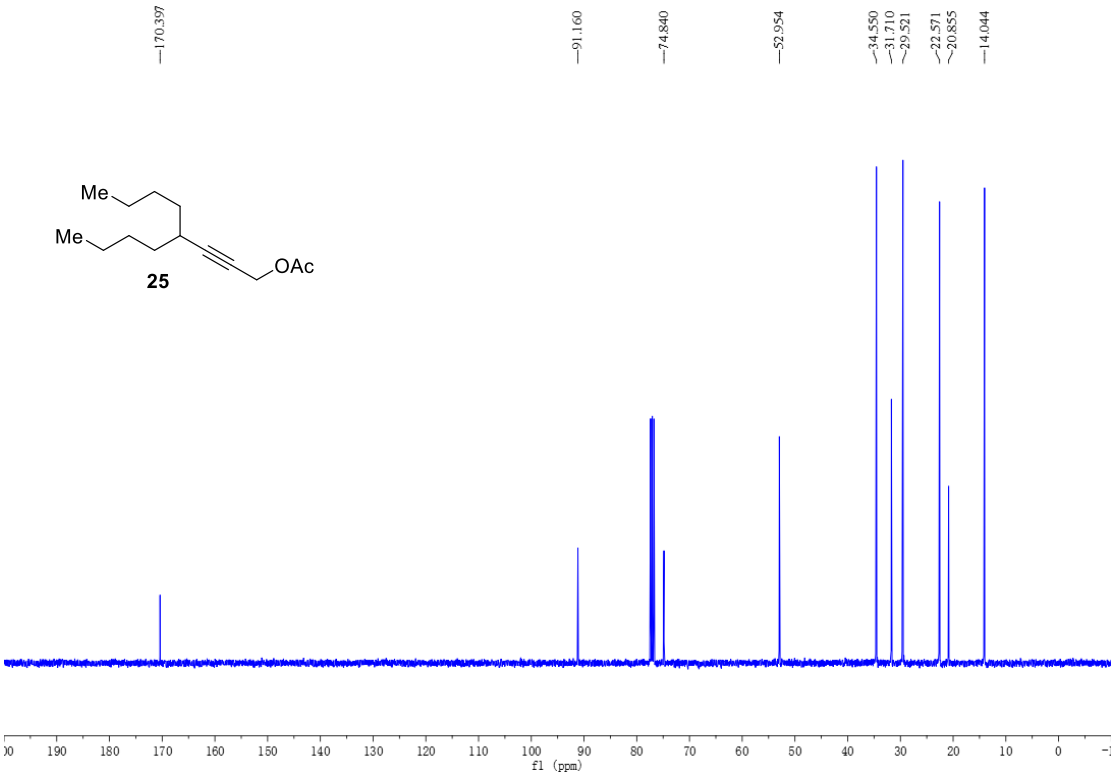
4.681
2.336
2.331
2.093
1.443
1.433
1.422
1.402
1.326
1.311
1.295
0.921
0.903
0.885
Me
Me
OAc
25
2.00
1.06
2.93
12.56
6.11
f1 (ppm)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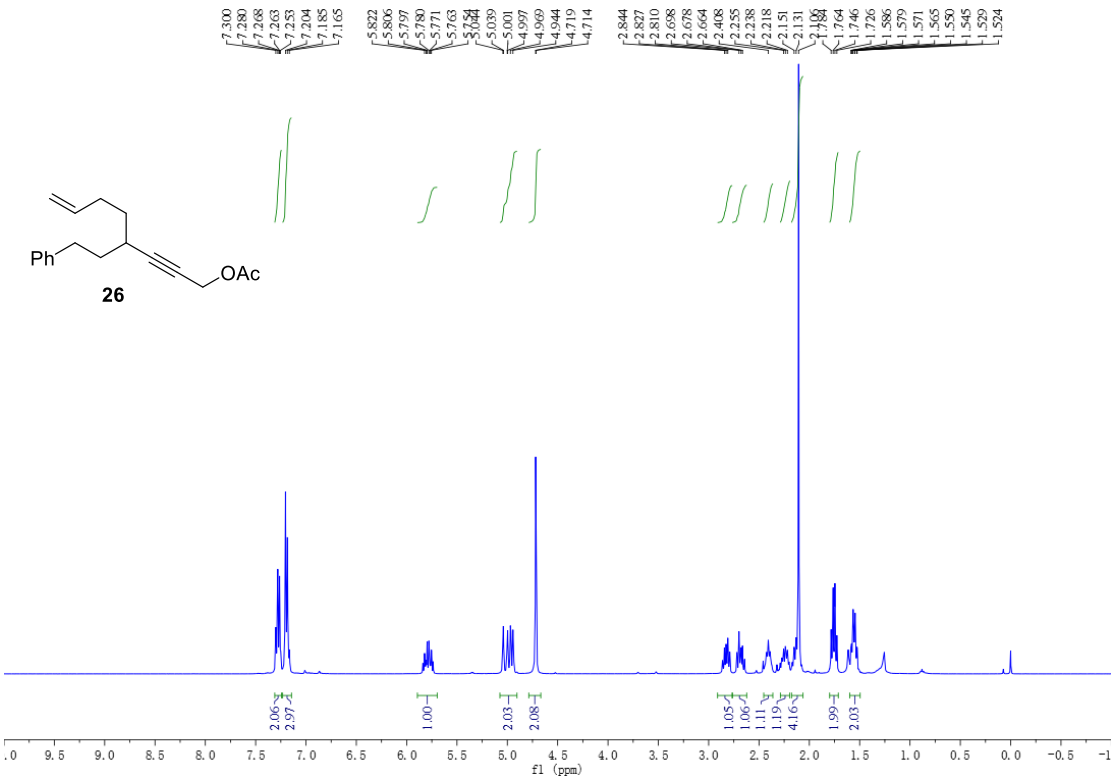
91.160
74.840
52.954
34.550
31.710
29.521
22.571
20.855
14.044
Me
Me
OAc
25
f1 (ppm)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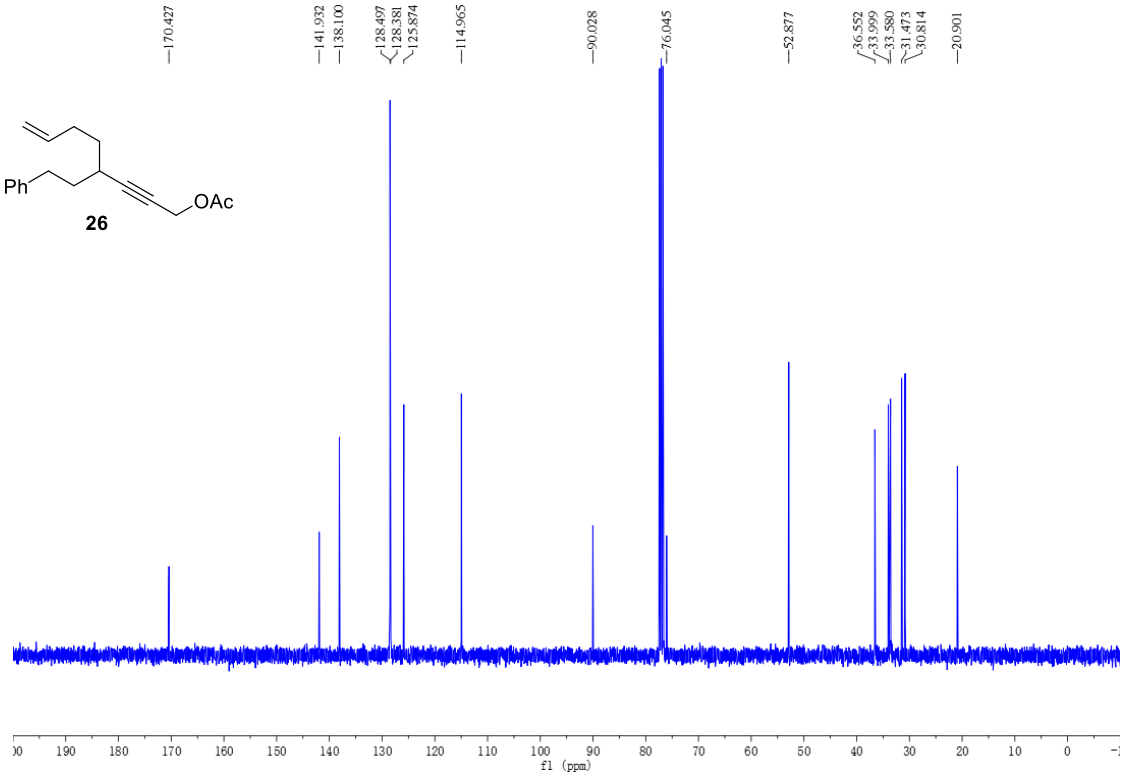
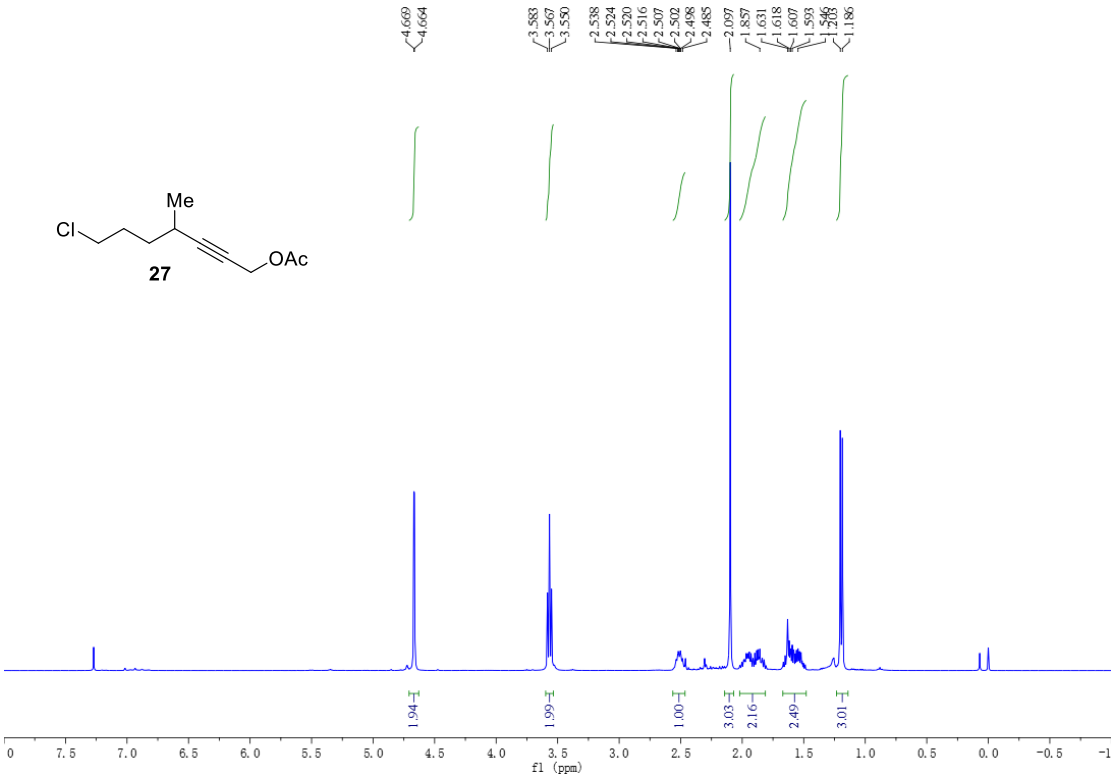
7.280
7.268
7.263
7.253
7.204
7.185
7.165
5.822
5.806
5.797
5.780
5.771
5.763
5.039
5.001
4.997
4.969
4.944
4.719
4.714
2.844
2.827
2.810
2.698
2.678
2.664
2.408
2.255
2.238
2.218
2.151
2.131
1.764
1.746
1.726
1.586
1.579
1.571
1.565
1.550
1.545
1.529
1.524
Ph
OAc
26
2.06
2.97
1.00
2.03
2.08
1.05
1.06
1.11
1.19
4.16
1.99
2.03
f1 (ppm)


170.427
141.932
138.100
128.497
128.381
125.874
114.965
90.028
76.045
52.877
36.552
33.999
33.580
31.473
30.814
20.901
Ph
OAc
26
f1 (ppm)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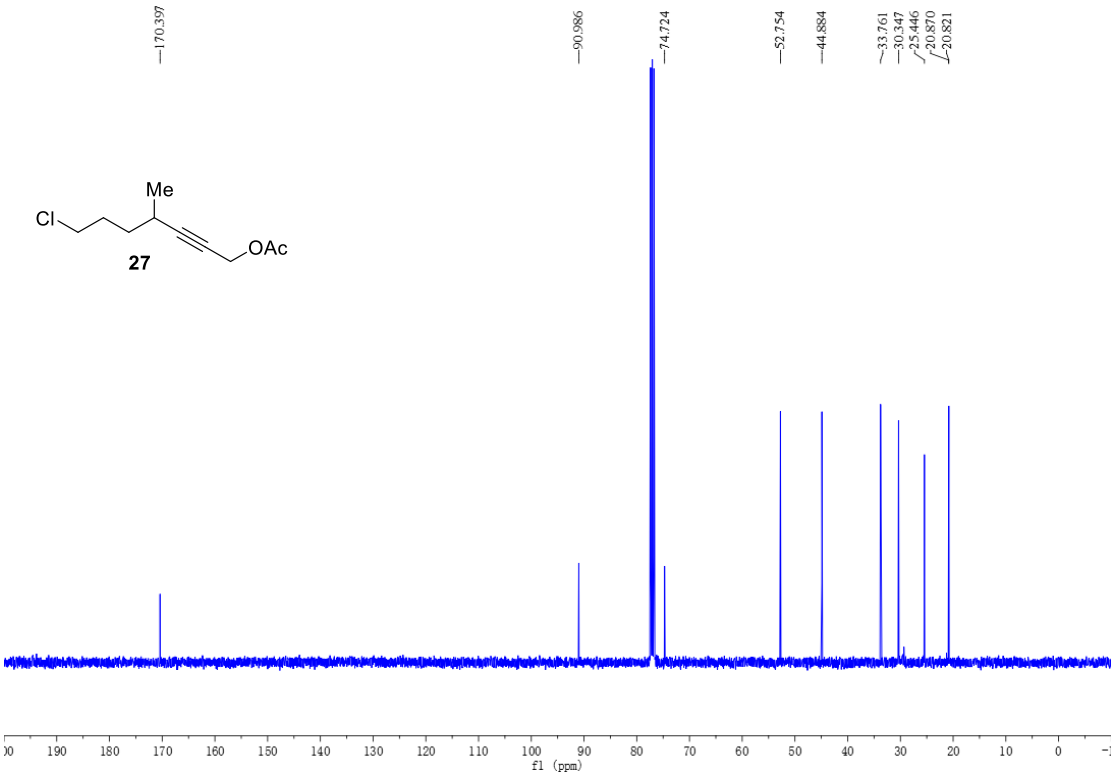
4.664
3.583
3.567
3.550
2.538
2.524
2.520
2.516
2.507
2.502
2.498
2.485
2.097
1.857
1.631
1.618
1.607
1.593
1.546
1.203
1.186
Me
Cl
OAc
27
1.94
1.99
1.00
3.03
2.16
2.49
3.01
f1 (ppm)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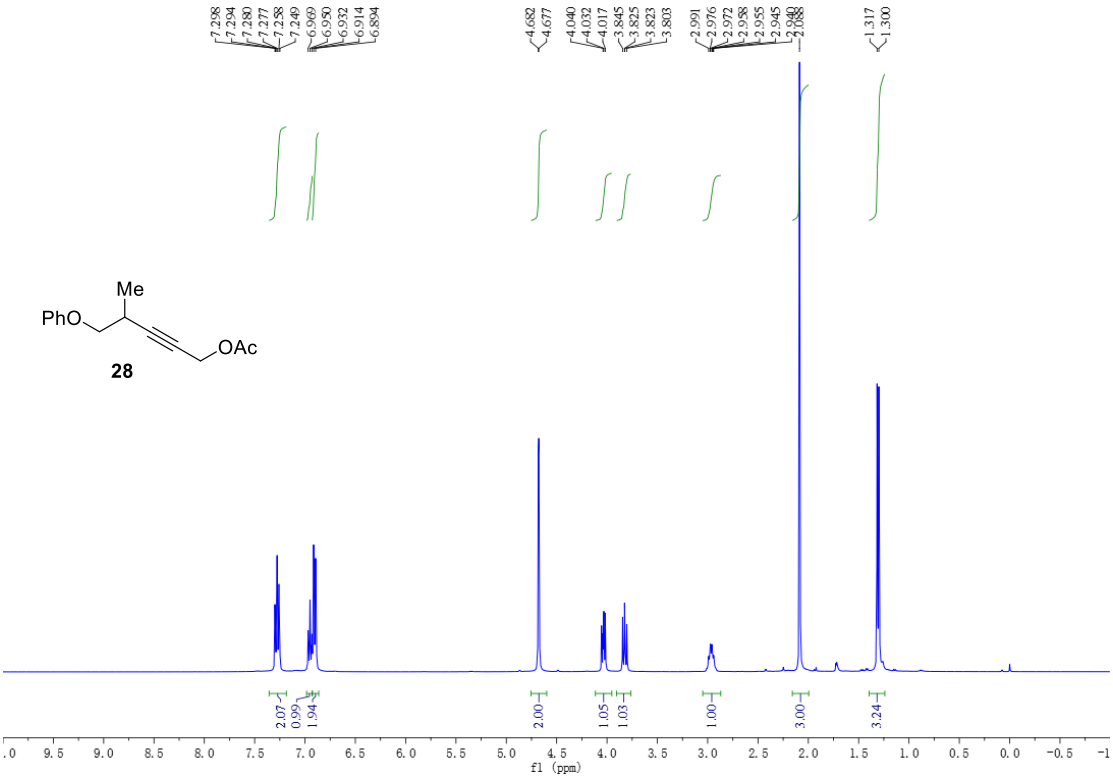
25.446
20.870
20.821
Me
Cl
OAc
27
f1 (ppm)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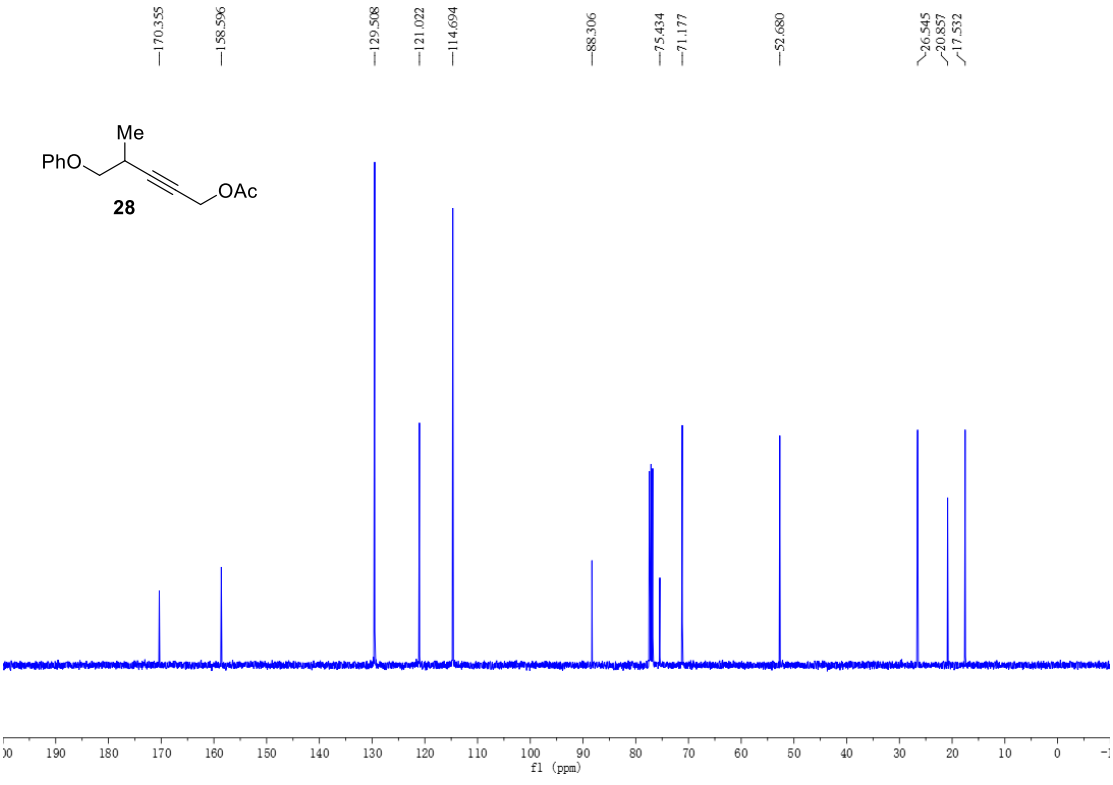
7.294
7.280
7.277
7.258
7.249
6.969
6.950
6.932
6.914
6.894
4.682
4.677
4.040
4.032
4.017
3.845
3.825
3.823
3.803
2.991
2.976
2.972
2.958
2.955
2.945
2.088
1.317
1.300
Me
PhO
OAc
28
2.07
0.99
1.94
2.00
1.05
1.03
1.00
3.00
3.24
f1 (ppm)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158.596
129.508
121.022
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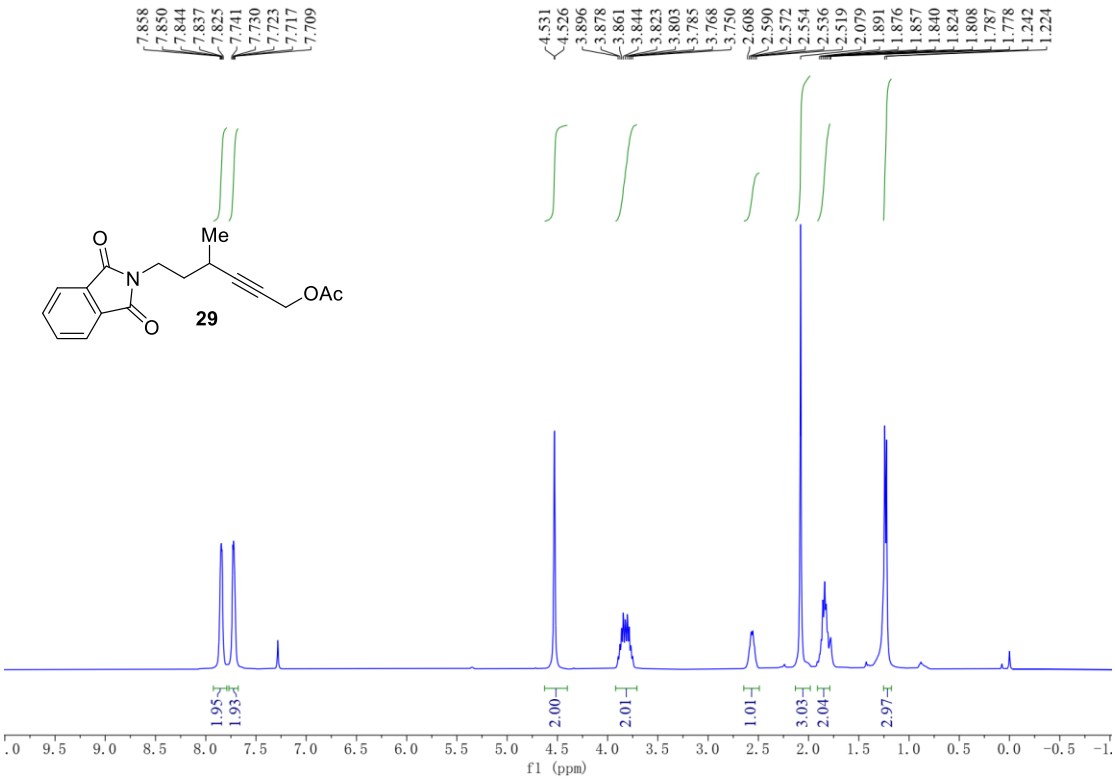
71.177
52.680
26.545
20.857
17.532
Me
PhO
OAc
28
f1 (ppm)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7.850
7.844
7.837
7.825
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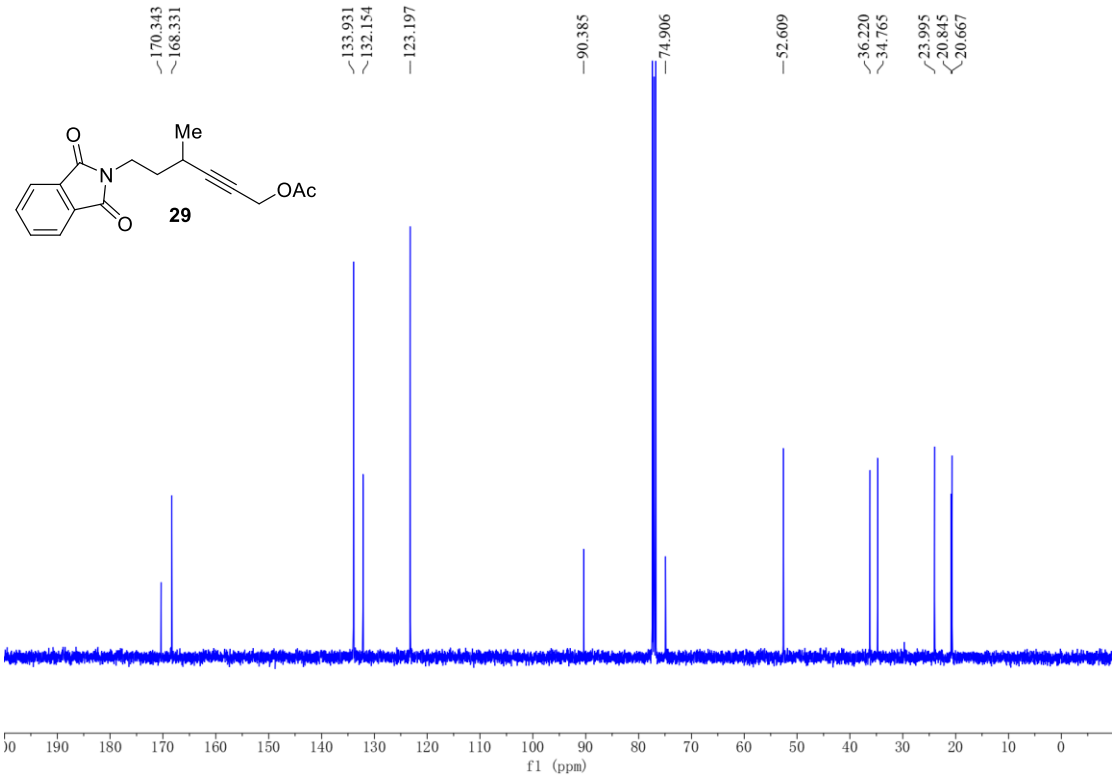
7.730
7.723
7.717
7.709
4.531
4.526
3.896
3.878
3.861
3.844
3.823
3.803
3.785
3.768
3.750
2.608
2.590
2.572
2.554
2.536
2.519
2.079
1.891
1.876
1.857
1.840
1.824
1.808
1.787
1.778
1.242
1.224
Me
OAc
O
N
O
29
1.95
1.93
2.00
2.01
1.01
3.03
2.04
2.97
f1 (ppm)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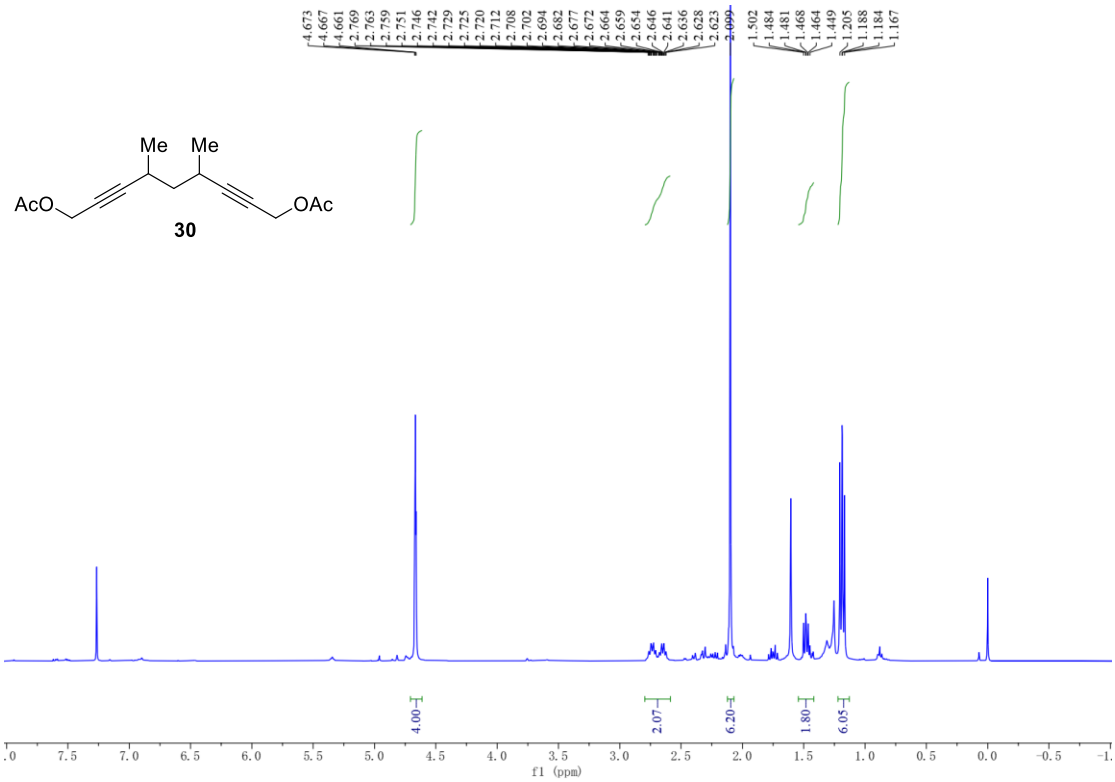
168.331
133.931
132.154
123.197
90.385
74.906
52.609
36.220
34.765
23.995
20.845
20.667
Me
OAc
O
N
O
29
f1 (ppm)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4.661
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2.763
2.759
2.751
2.746
2.742
2.729
2.725
2.720
2.712
2.708
2.702
2.694
2.682
2.677
2.672
2.664
2.659
2.654
2.646
2.641
2.636
2.628
2.623
2.000
1.502
1.484
1.481
1.468
1.464
1.449
1.205
1.188
1.184
1.167
Me
Me
AcO
OAc
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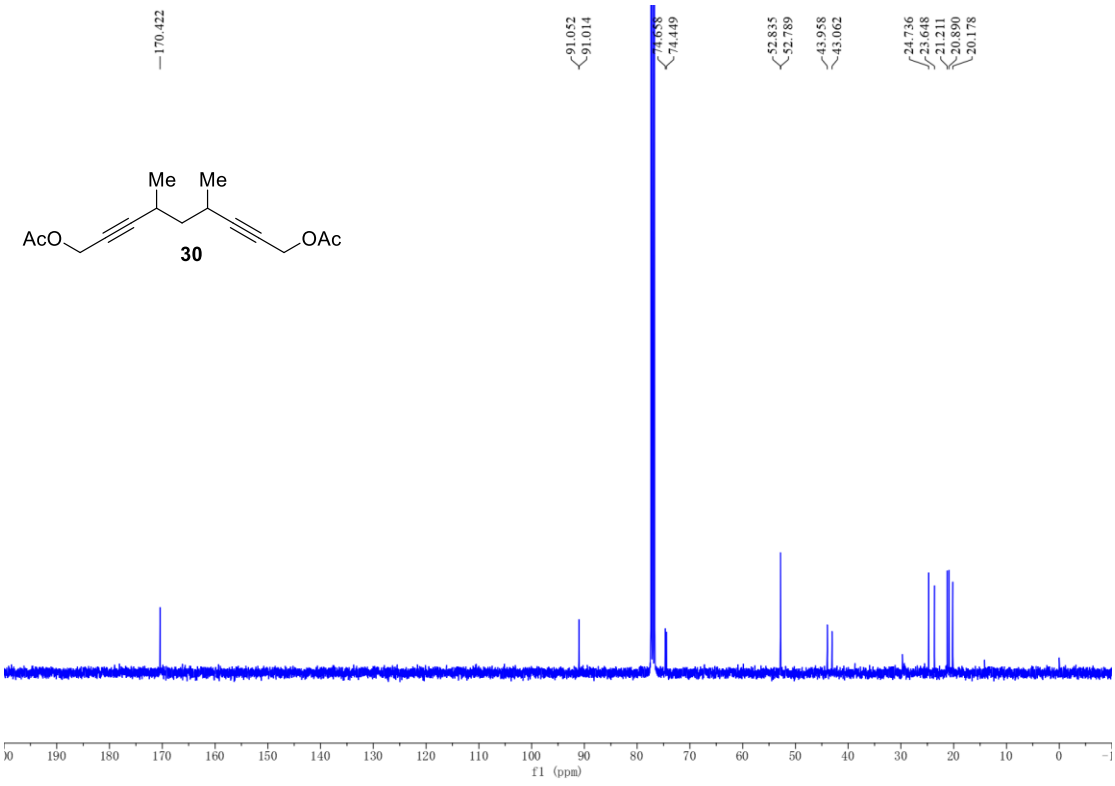
4.00
2.07
6.20
1.80
6.05
f1 (ppm)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91.014
74.658
74.449
52.835
52.789
43.958
43.062
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23.648
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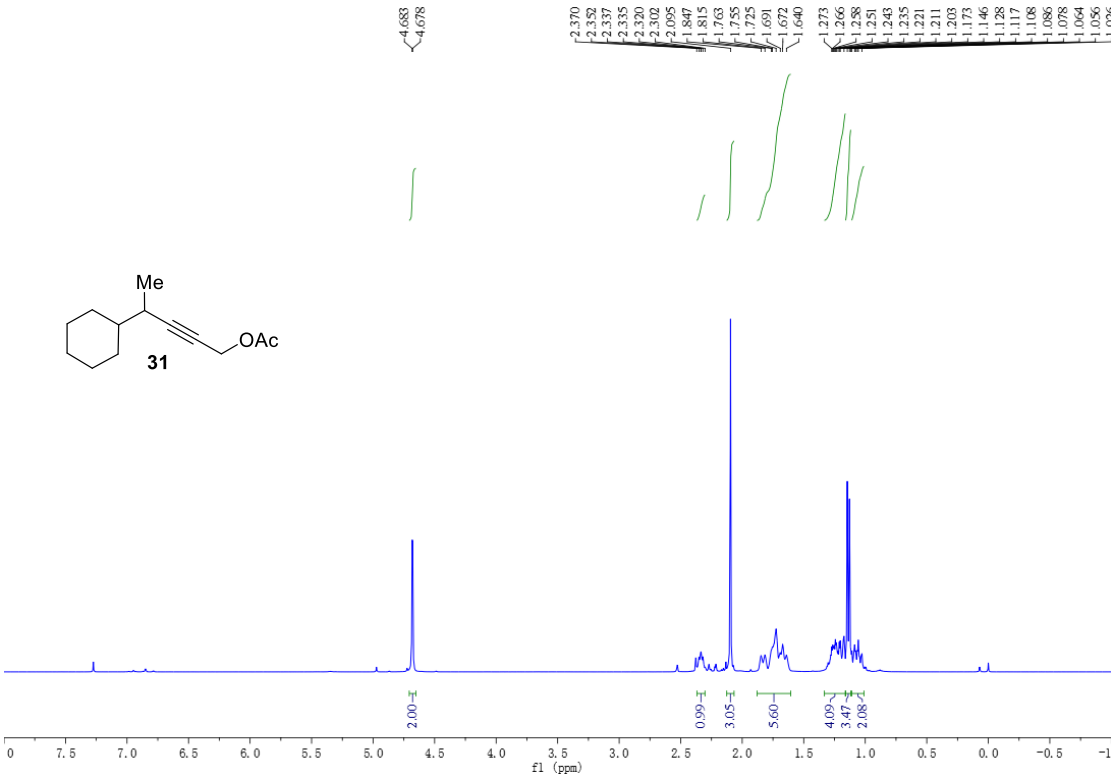
20.178
Me
Me
AcO
OAc
30
f1 (ppm)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4.678
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2.335
2.320
2.302
2.095
1.847
1.815
1.763
1.755
1.725
1.691
1.672
1.640
1.273
1.266
1.258
1.251
1.243
1.235
1.221
1.211
1.203
1.173
1.146
1.128
1.117
1.108
1.086
1.078
1.064
1.056
Me
OAc
31
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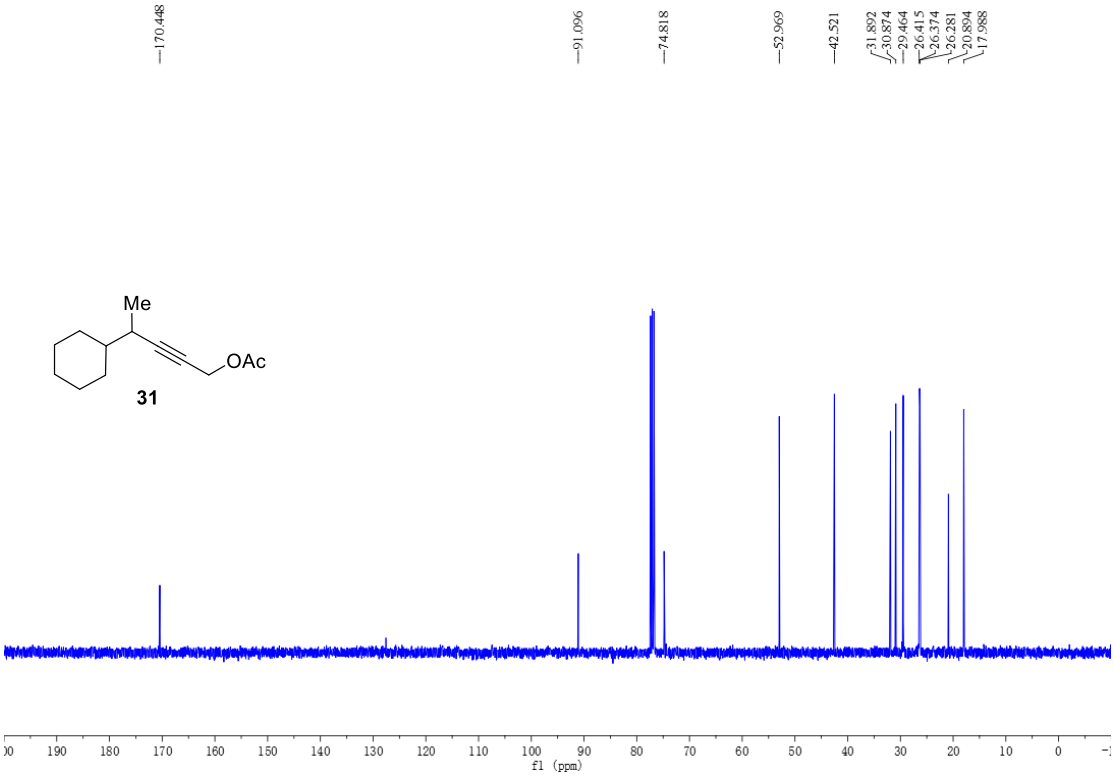
0.99
3.05
5.60
4.09
3.47
2.08
f1 (ppm)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26.281
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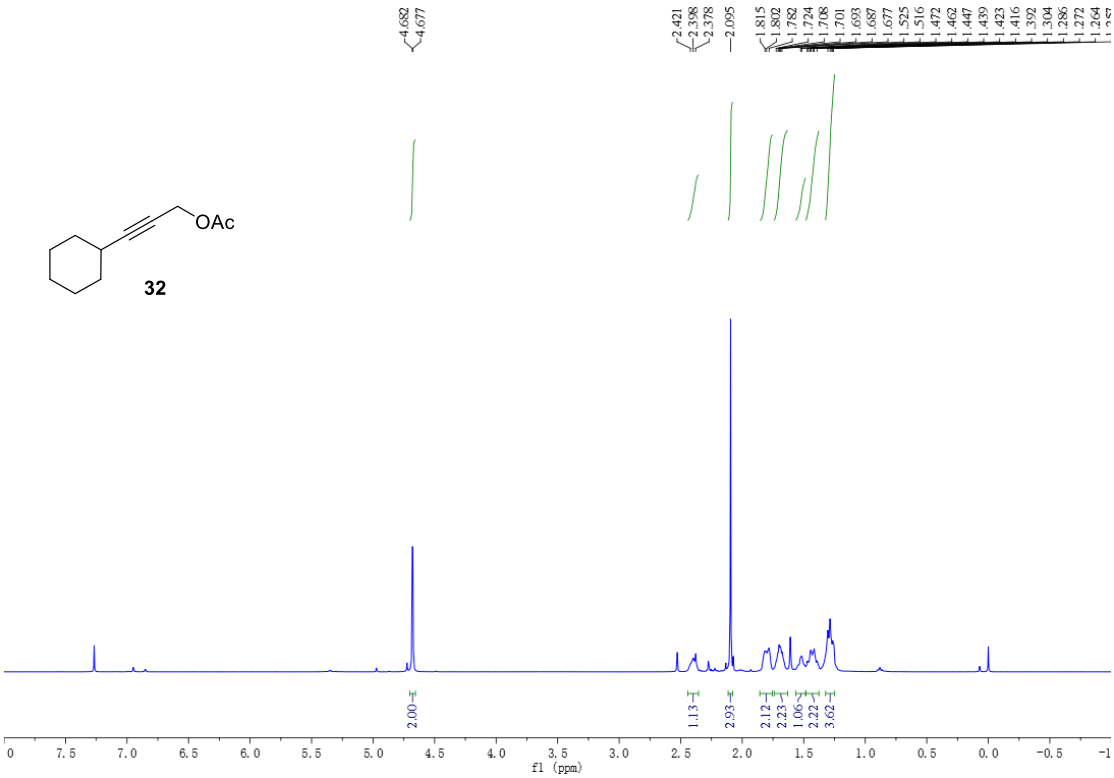
17.988
Me
OAc
31
f1 (ppm)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2.095
1.815
1.802
1.782
1.724
1.708
1.701
1.693
1.687
1.677
1.525
1.516
1.472
1.462
1.447
1.439
1.423
1.416
1.392
1.304
1.286
1.272
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OAc
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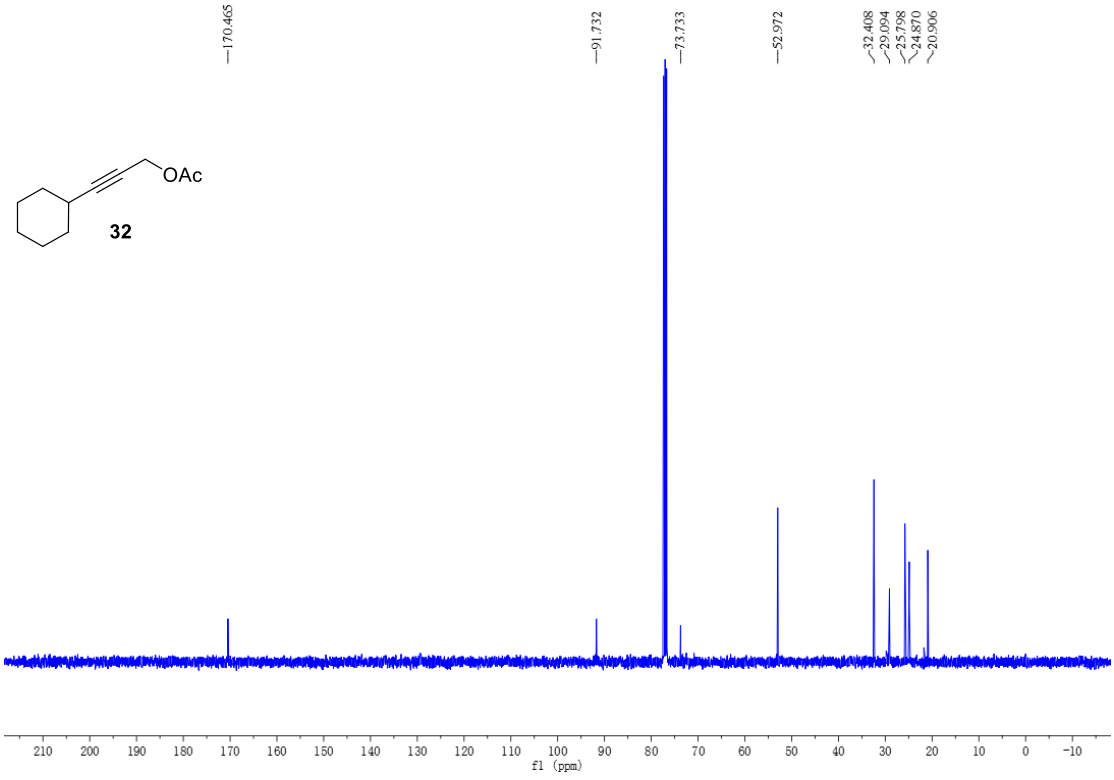
2.93
2.12
2.23
1.06
2.22
3.62
f1 (ppm)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32.408
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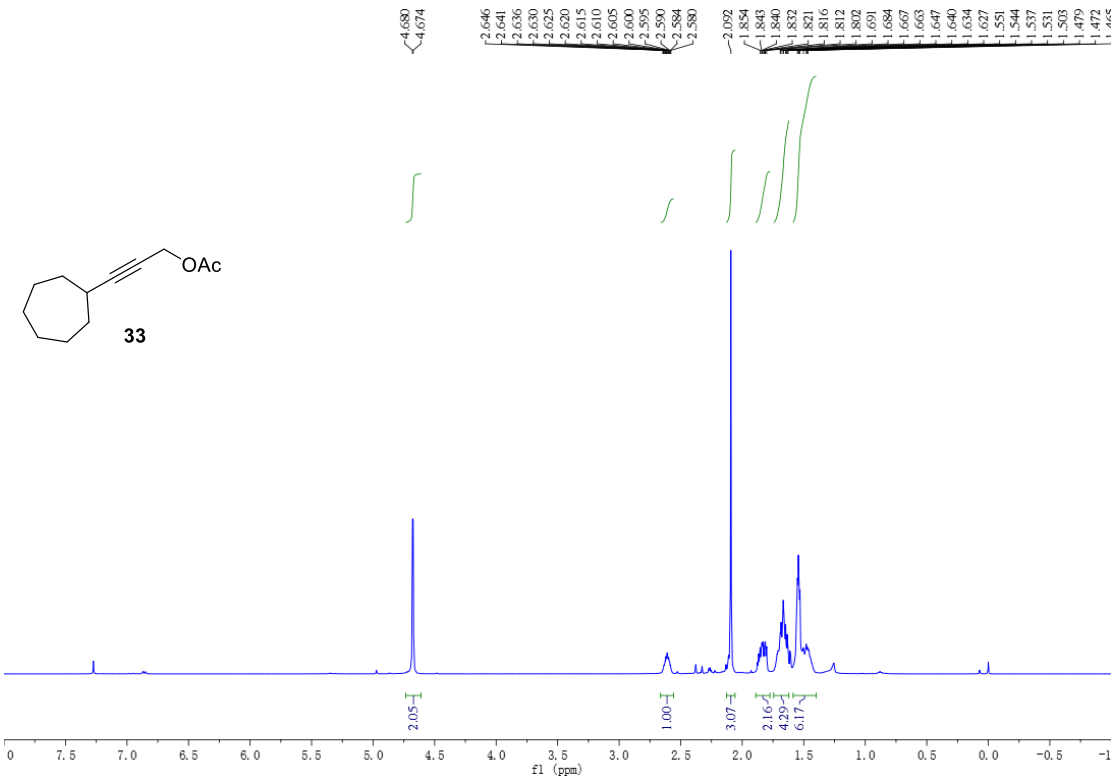
25.798
24.870
20.906
OAc
32
f1 (ppm)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4.674
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2.620
2.615
2.610
2.605
2.600
2.595
2.590
2.584
2.580
2.092
1.854
1.843
1.840
1.832
1.821
1.816
1.812
1.802
1.691
1.684
1.667
1.663
1.647
1.640
1.634
1.627
1.551
1.544
1.537
1.531
1.503
1.479
1.472
OAc
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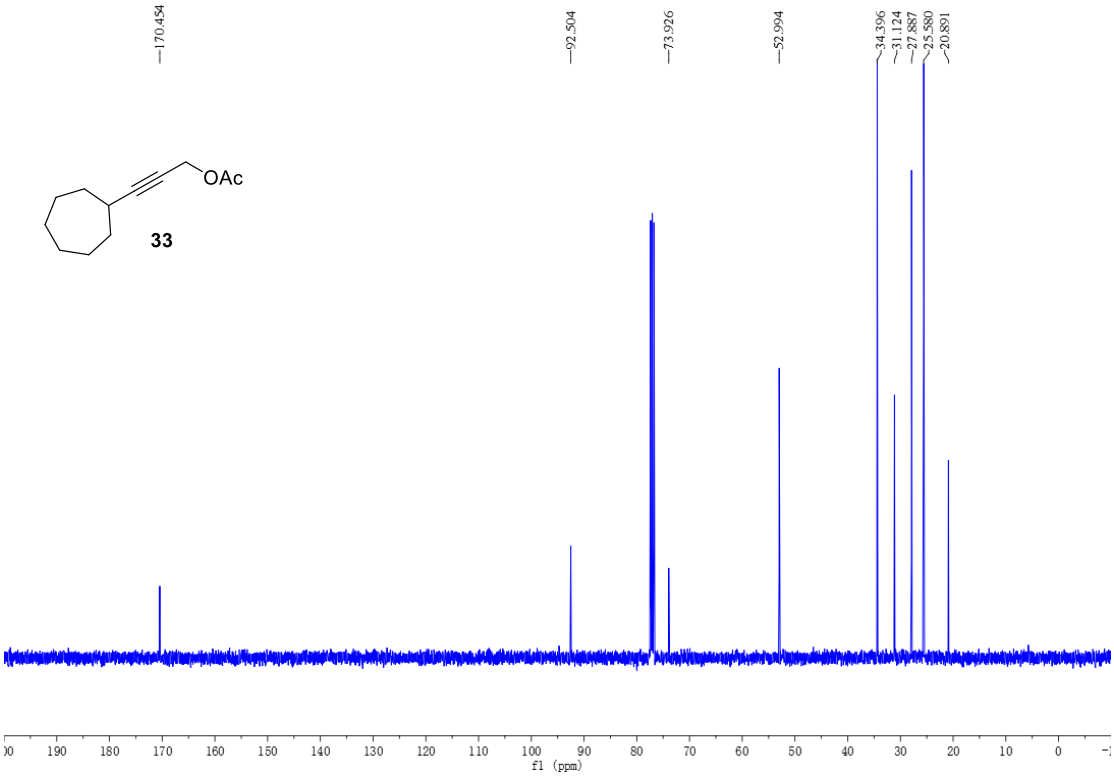
2.05
1.00
3.07
2.16
4.29
6.17
f1 (ppm)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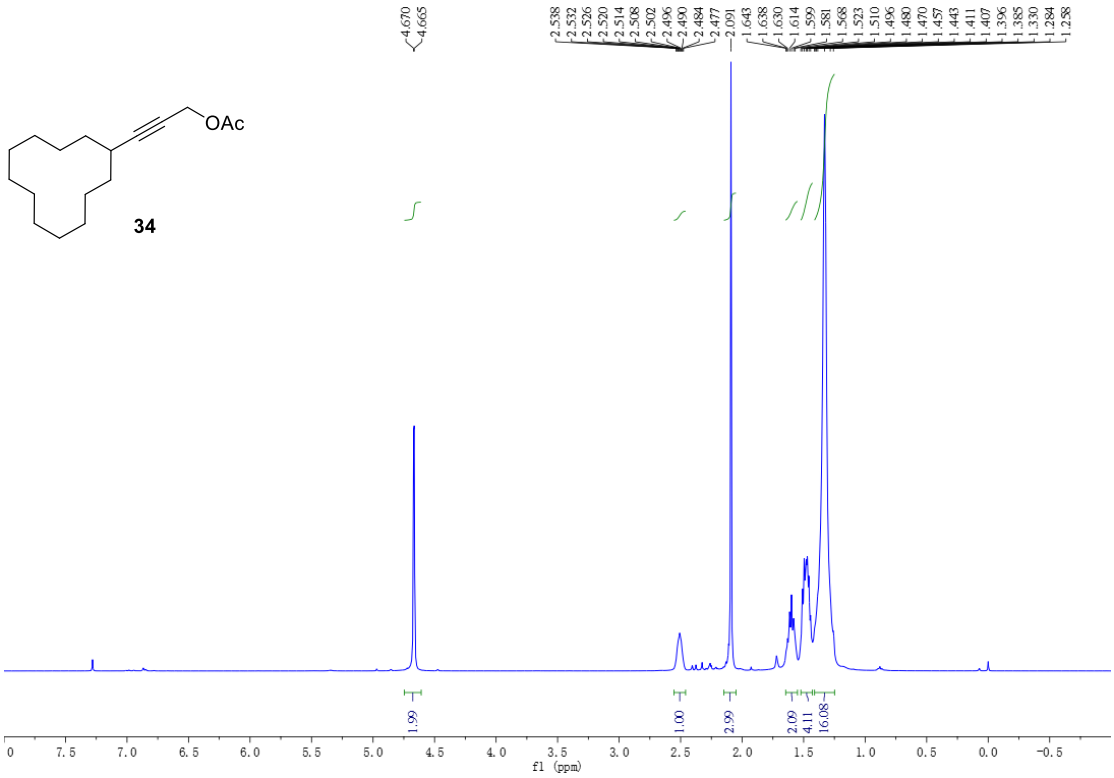
27.887
25.580
20.891
OAc
33
f1 (ppm)


OAc
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2.502
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2.490
2.484
2.477
2.091
1.643
1.638
1.630
1.614
1.599
1.581
1.568
1.523
1.510
1.496
1.480
1.470
1.457
1.443
1.411
1.407
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1.385
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1.238
1.99
1.00
2.99
2.09
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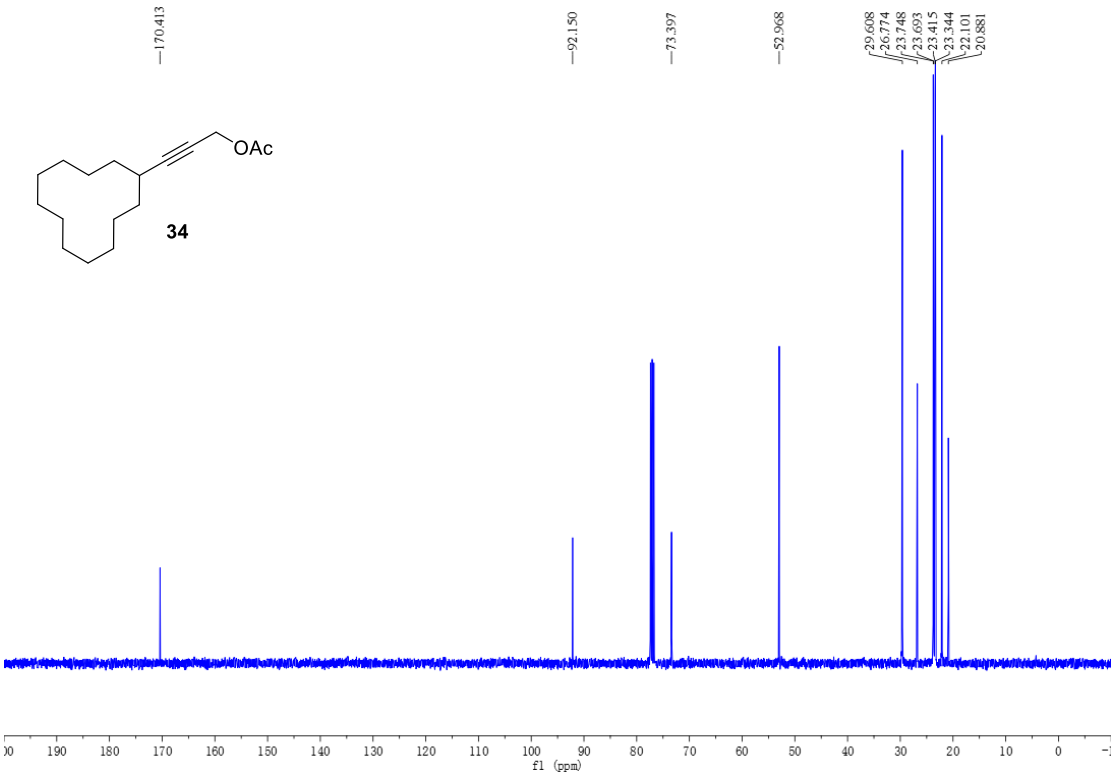
16.08
f1 (ppm)


OAc
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23.344
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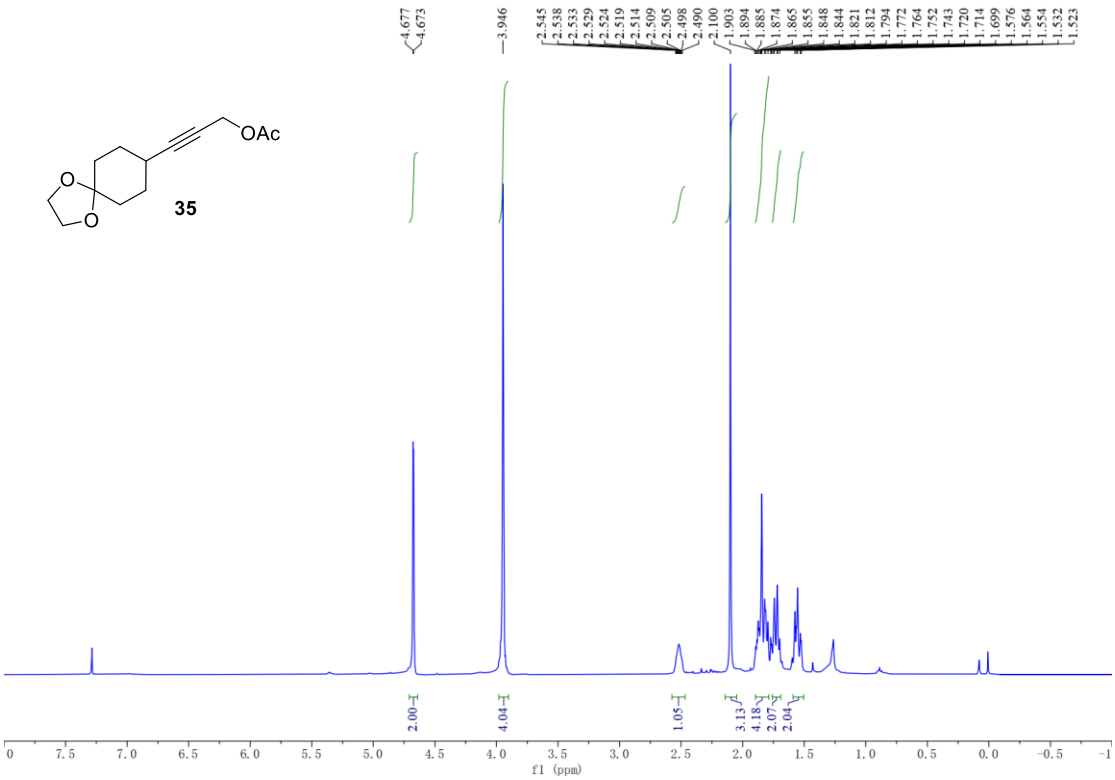
20.881
f1 (ppm)


OAc
O
O
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3.946
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2.529
2.524
2.519
2.514
2.509
2.505
2.498
2.490
2.100
1.903
1.894
1.885
1.874
1.865
1.855
1.848
1.844
1.821
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1.794
1.772
1.764
1.752
1.743
1.720
1.714
1.699
1.576
1.564
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1.523
2.00
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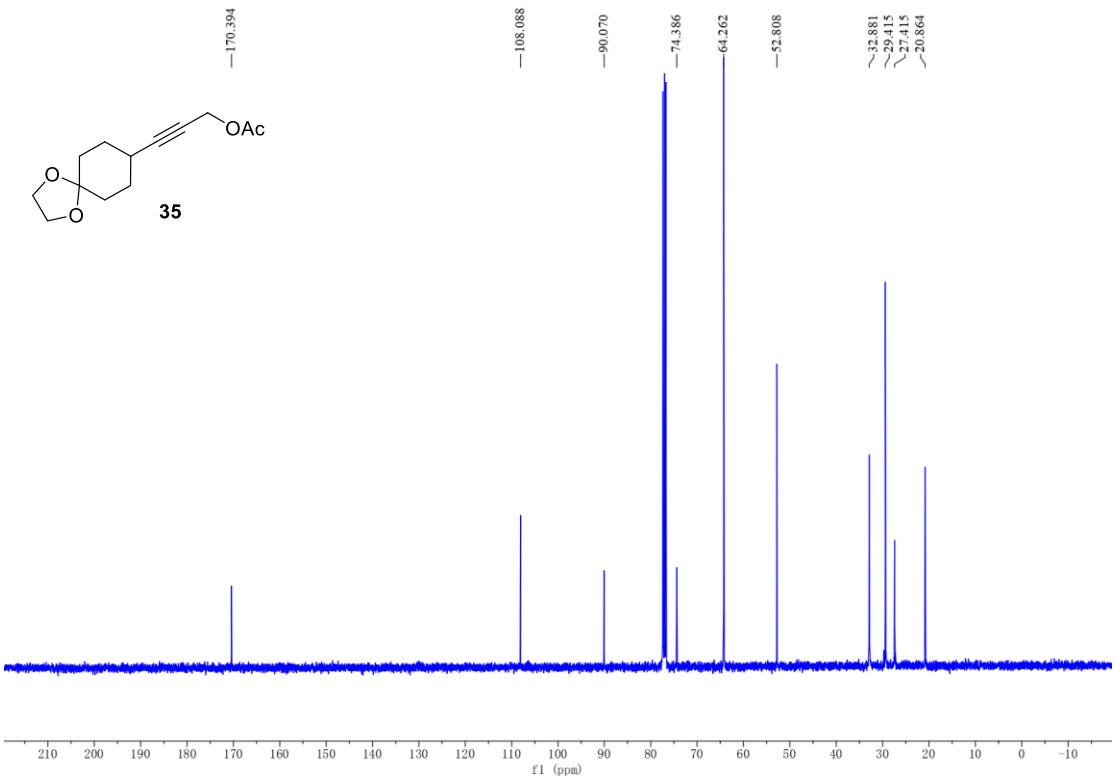
1.05
3.13
4.18
2.07
2.04
f1 (ppm)


OAc
O
O
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90.070
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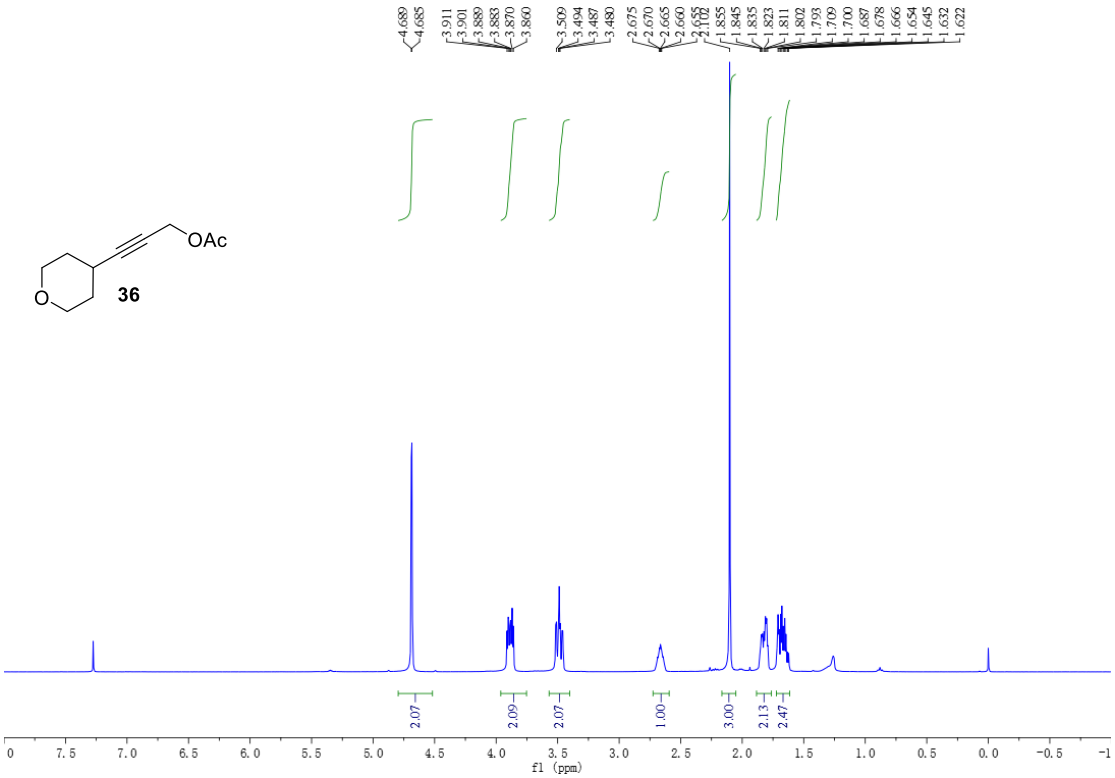
52.808
32.881
29.415
27.415
20.864
f1 (ppm)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2.670
2.665
2.660
2.655
2.102
1.855
1.845
1.835
1.823
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1.802
1.793
1.709
1.700
1.687
1.678
1.666
1.654
1.645
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1.622
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1.00
3.00
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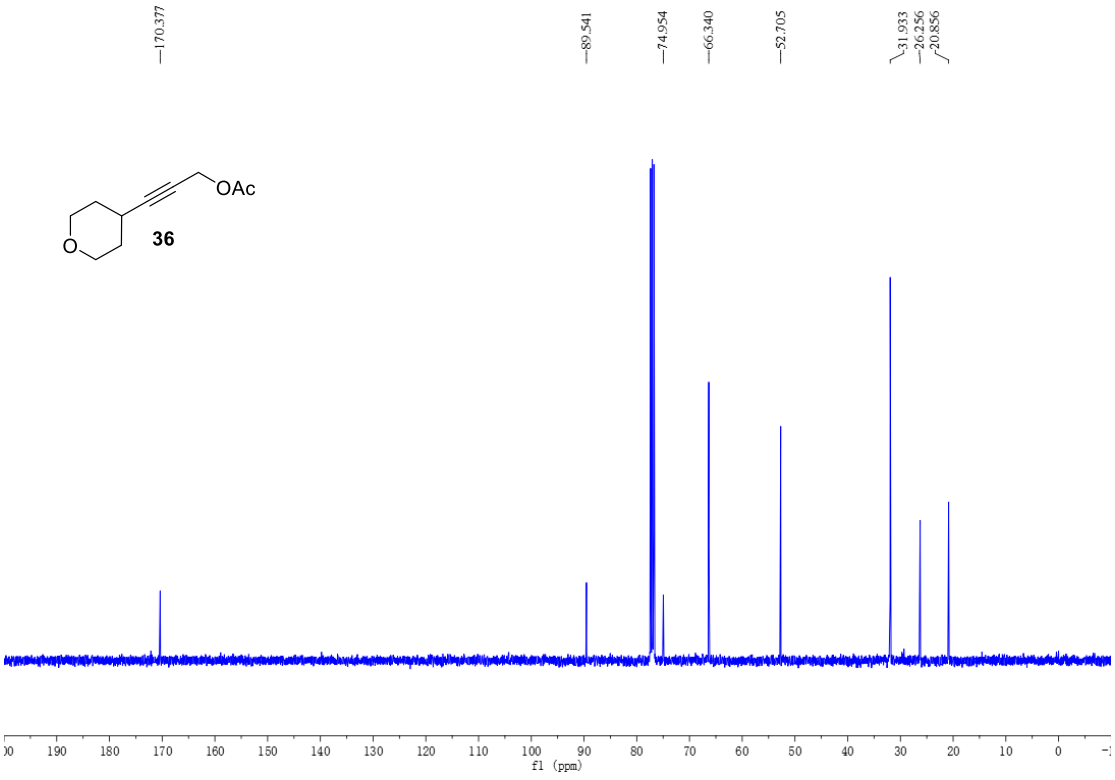
2.47
f1 (ppm)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66.340
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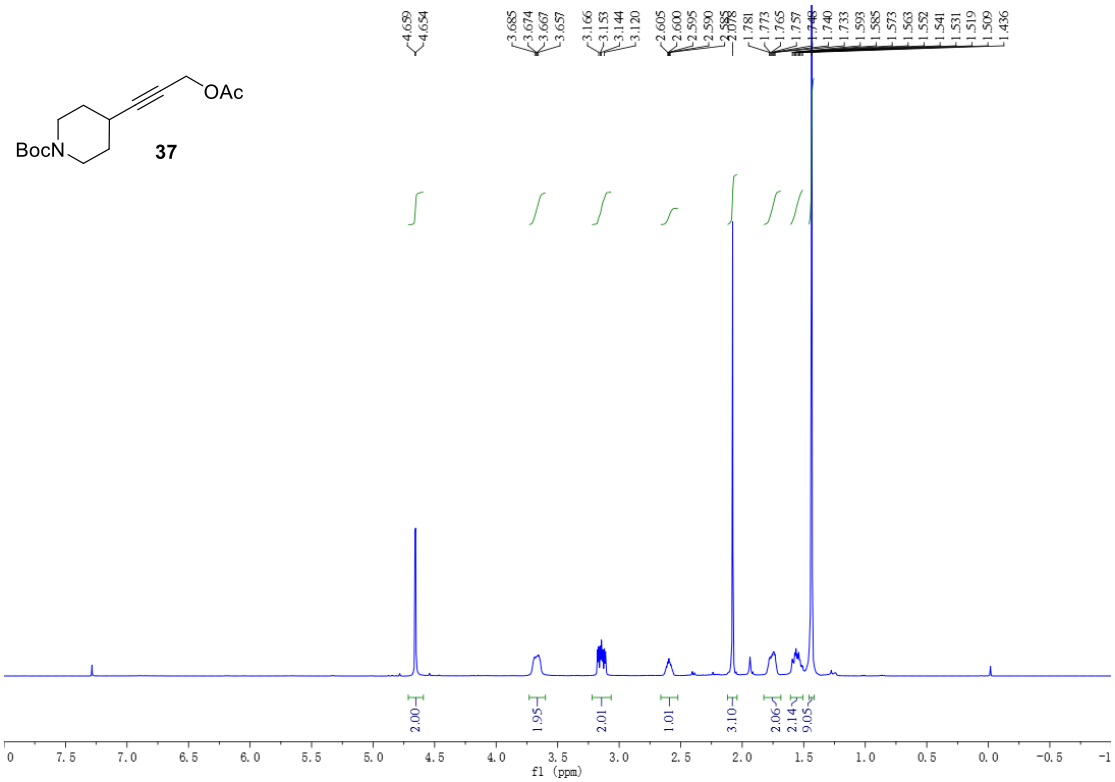
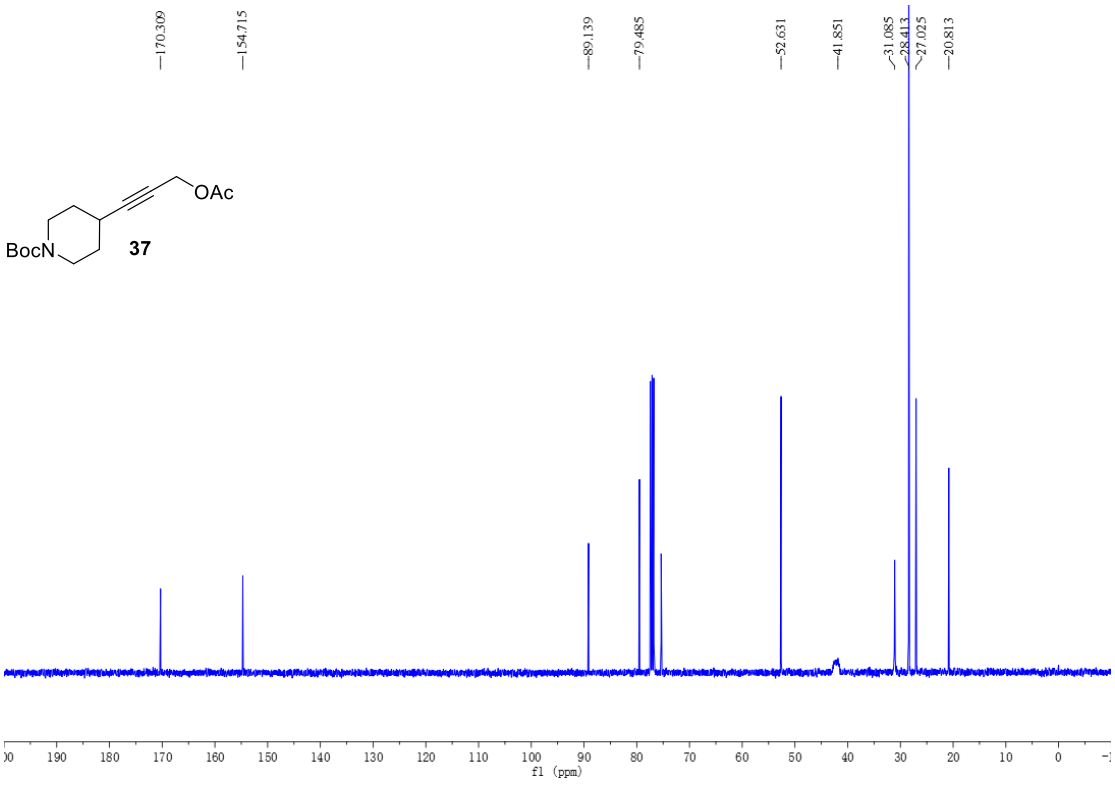
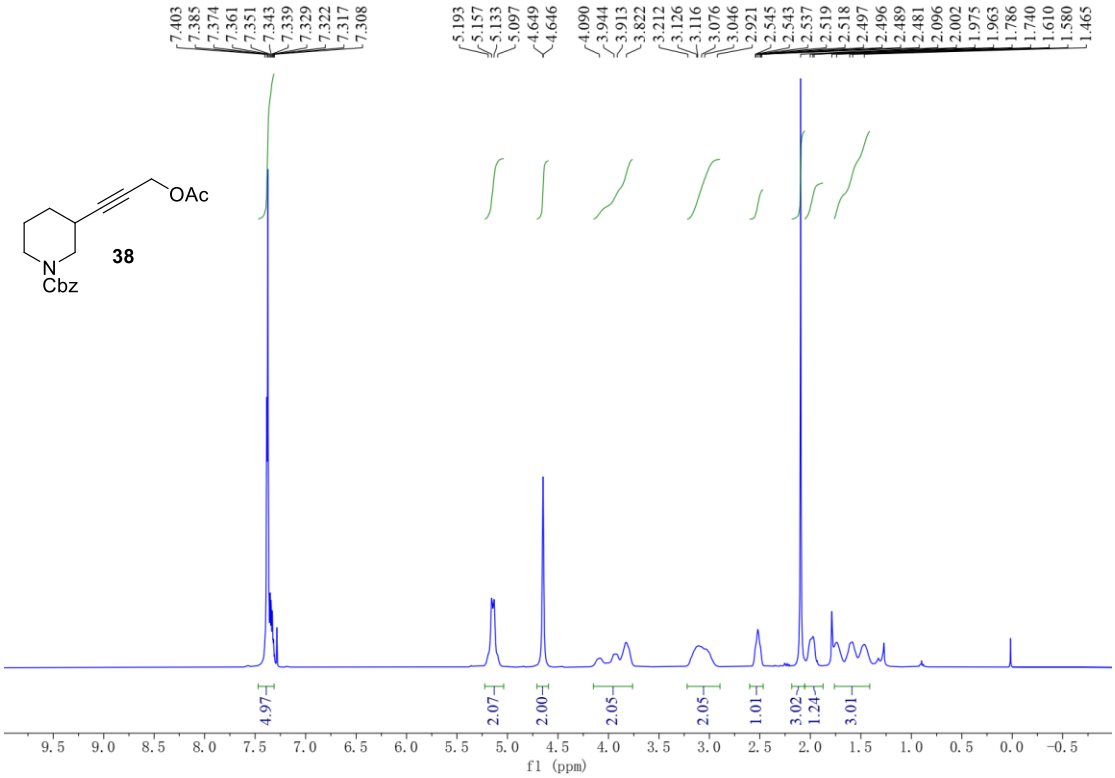
31.933
26.256
20.856
OAc
O
36
f1 (ppm)


OAc
BocN
37
4.659
4.654
3.685
3.674
3.667
3.657
3.166
3.153
3.144
3.120
2.605
2.600
2.595
2.590
2.078
1.781
1.773
1.765
1.757
1.740
1.733
1.593
1.585
1.573
1.563
1.552
1.541
1.531
1.519
1.509
1.436
2.00
1.95
2.01
1.01
3.10
2.06
2.14
9.05
f1 (ppm)


OAc
BocN
37
170.309
154.715
89.139
79.485
52.631
41.851
31.085
28.413
27.025
20.813
f1 (ppm)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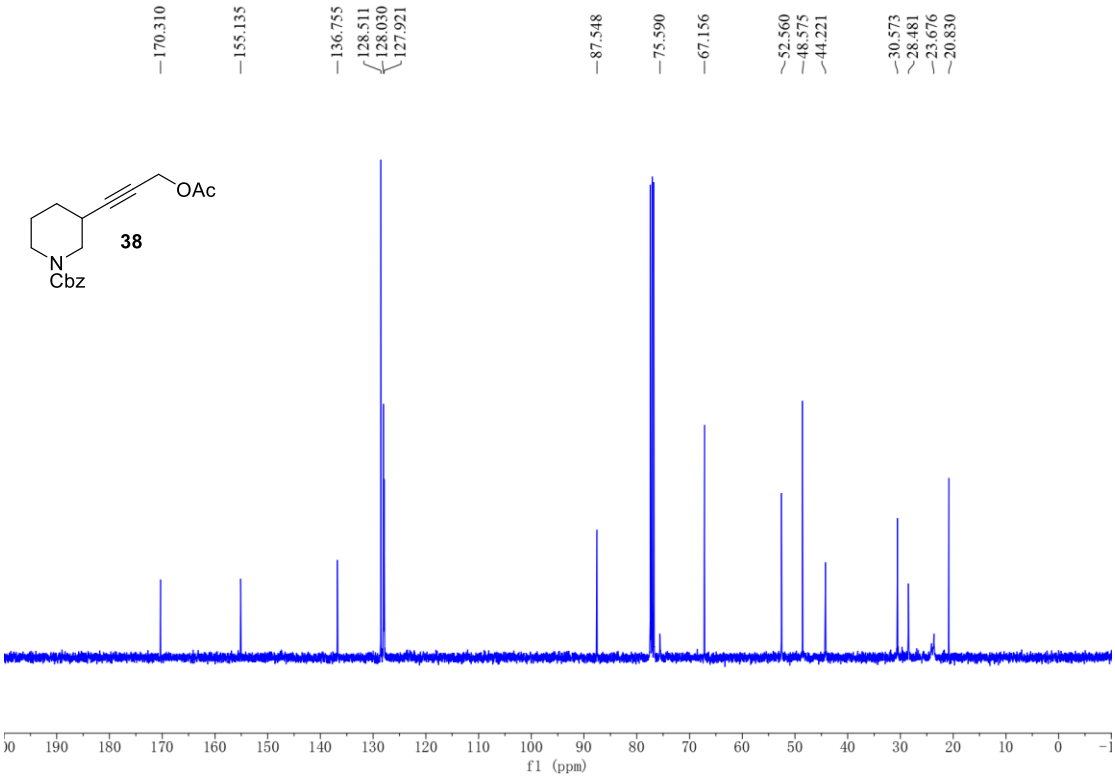
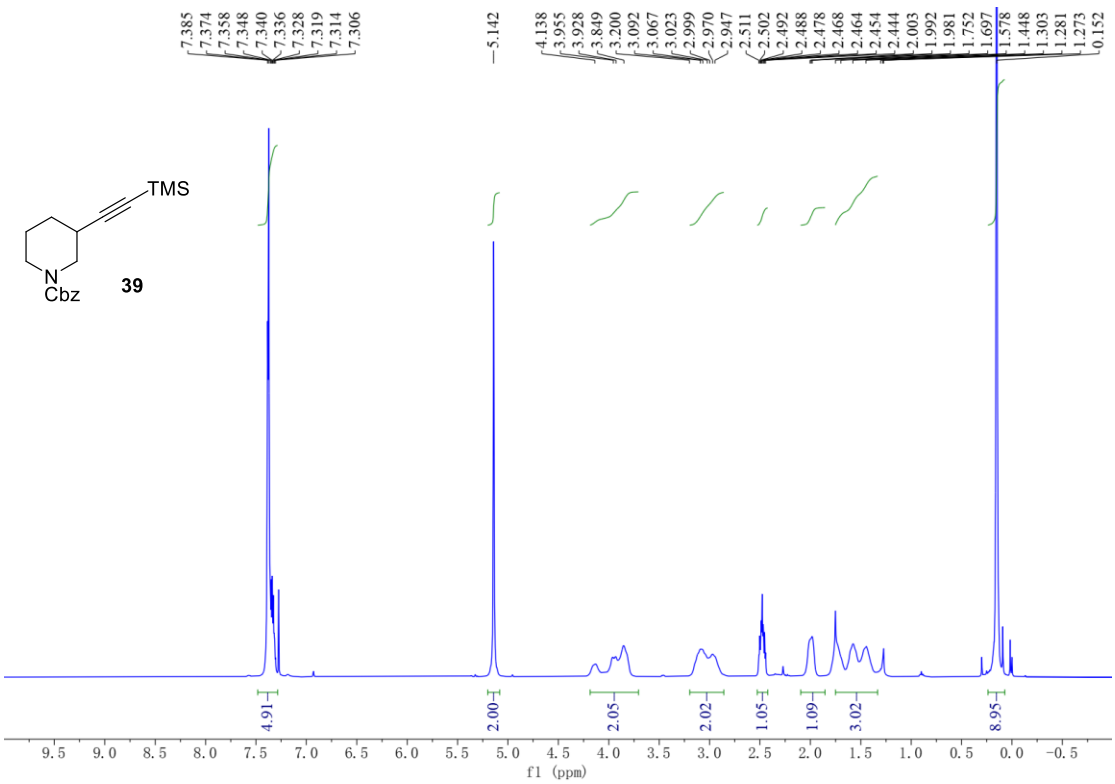
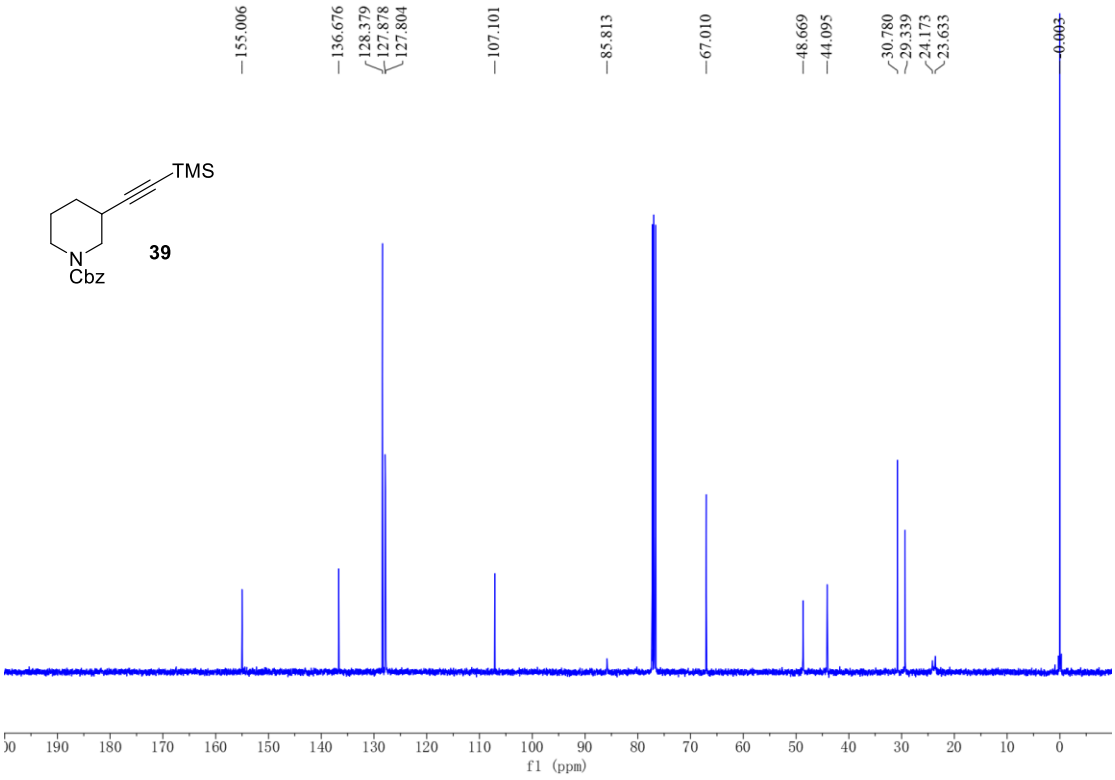
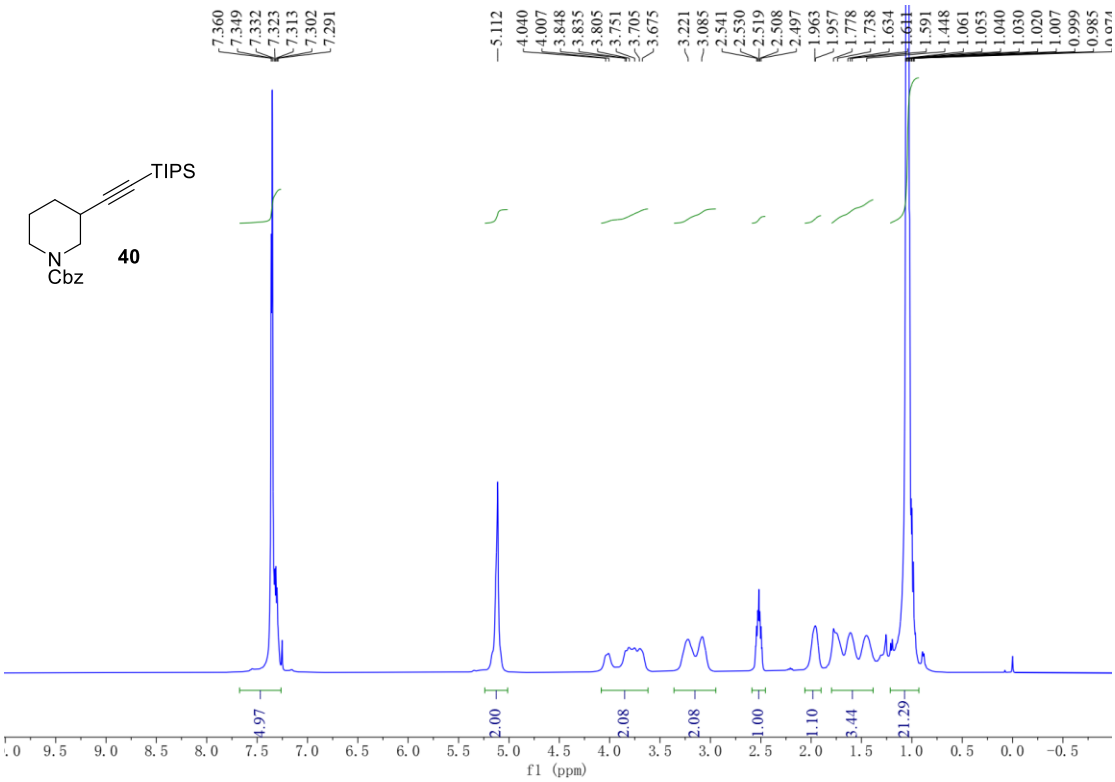
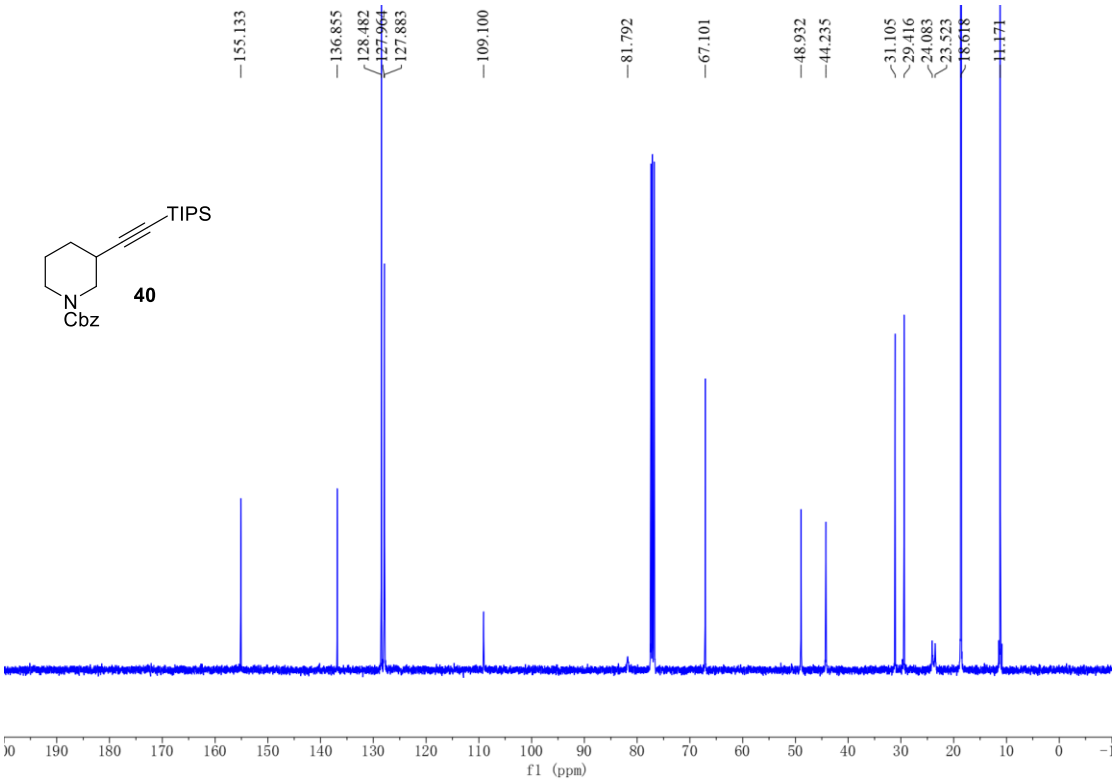
7.385
7.374
7.361
7.351
7.343
7.339
7.329
7.322
7.317
7.308
5.193
5.157
5.133
5.097
4.649
4.646
4.090
3.944
3.913
3.822
3.212
3.126
3.116
3.076
3.046
2.921
2.545
2.543
2.537
2.519
2.518
2.497
2.496
2.489
2.481
2.096
2.002
1.975
1.963
1.786
1.740
1.610
1.580
1.465
OAc
38
N
Cbz
4.97
2.07
2.00
2.05
2.05
1.01
3.02
1.24
3.01
f1 (ppm)

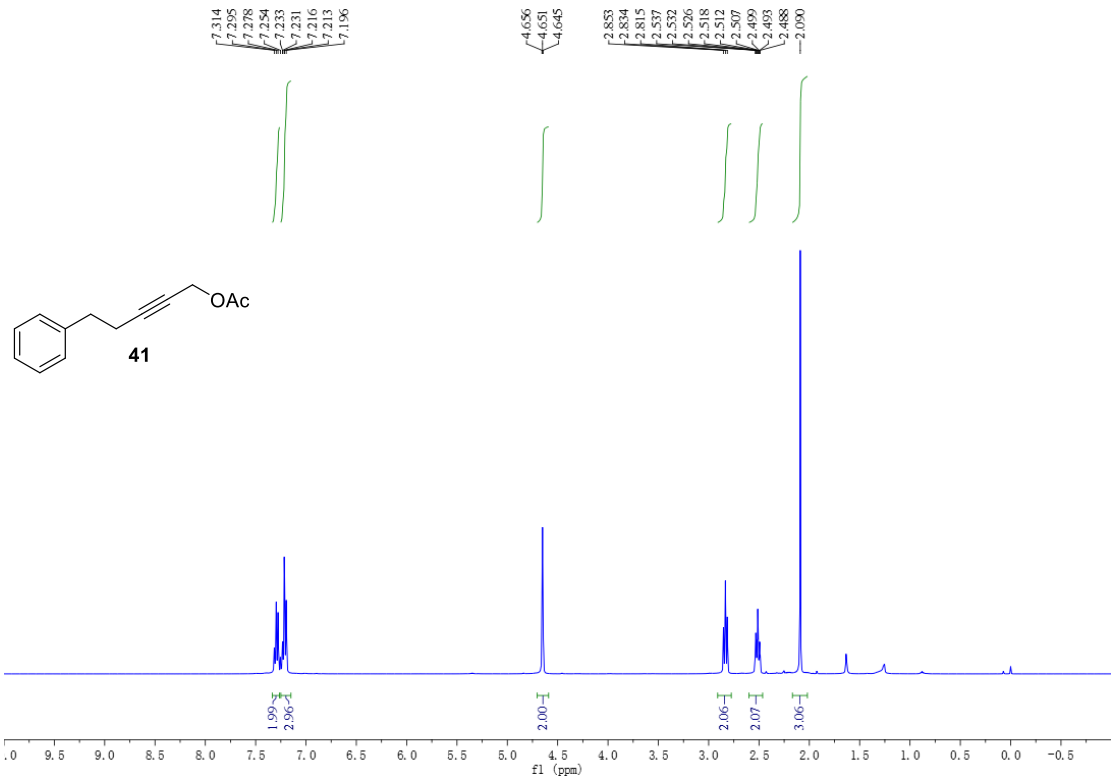

170.310
155.135
136.755
128.511
128.030
127.921
87.548
75.590
67.156
52.560
48.575
44.221
30.573
28.481
23.676
20.830
OAc
38
N
Cbz
f1 (ppm)

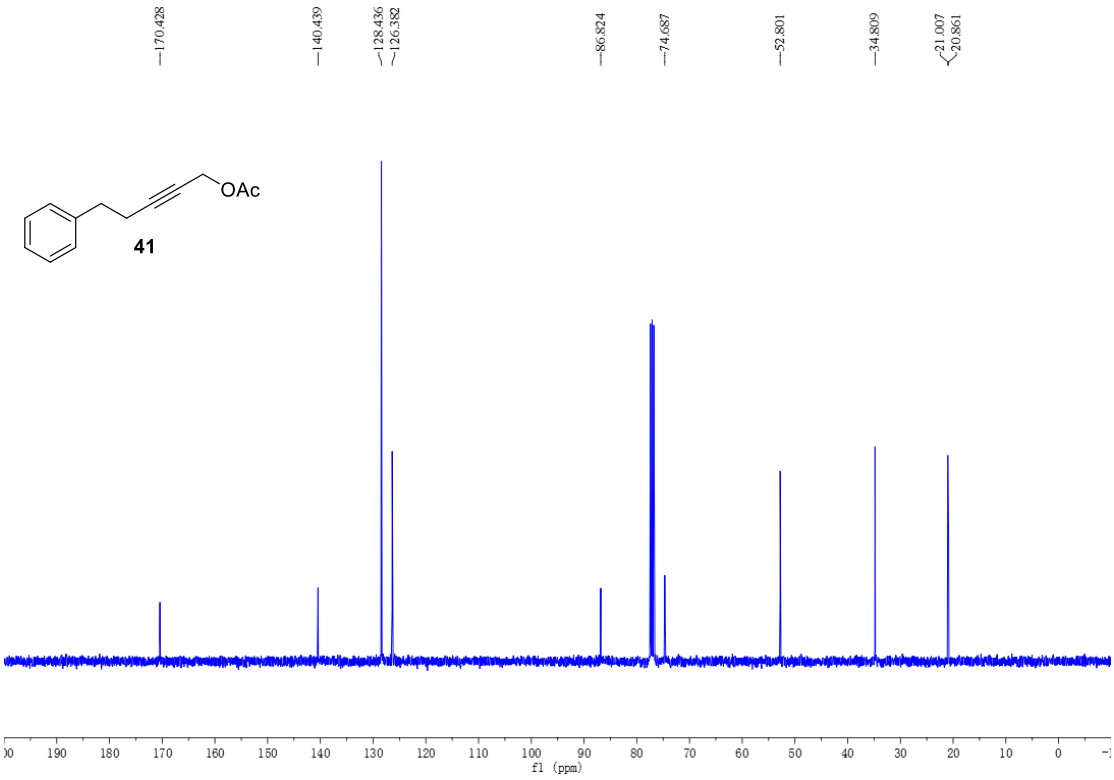

7.385
7.374
7.358
7.348
7.340
7.336
7.328
7.319
7.314
7.306
5.142
4.138
3.955
3.928
3.849
3.200
3.092
3.067
3.023
2.999
2.970
2.947
2.511
2.502
2.492
2.488
2.478
2.468
2.464
2.454
2.444
2.003
1.992
1.981
1.752
1.697
1.578
1.448
1.303
1.281
1.273
0.152
TMS
N
Cbz
39
4.91
2.00
2.05
2.02
1.05
1.09
3.02
8.95
f1 (ppm)

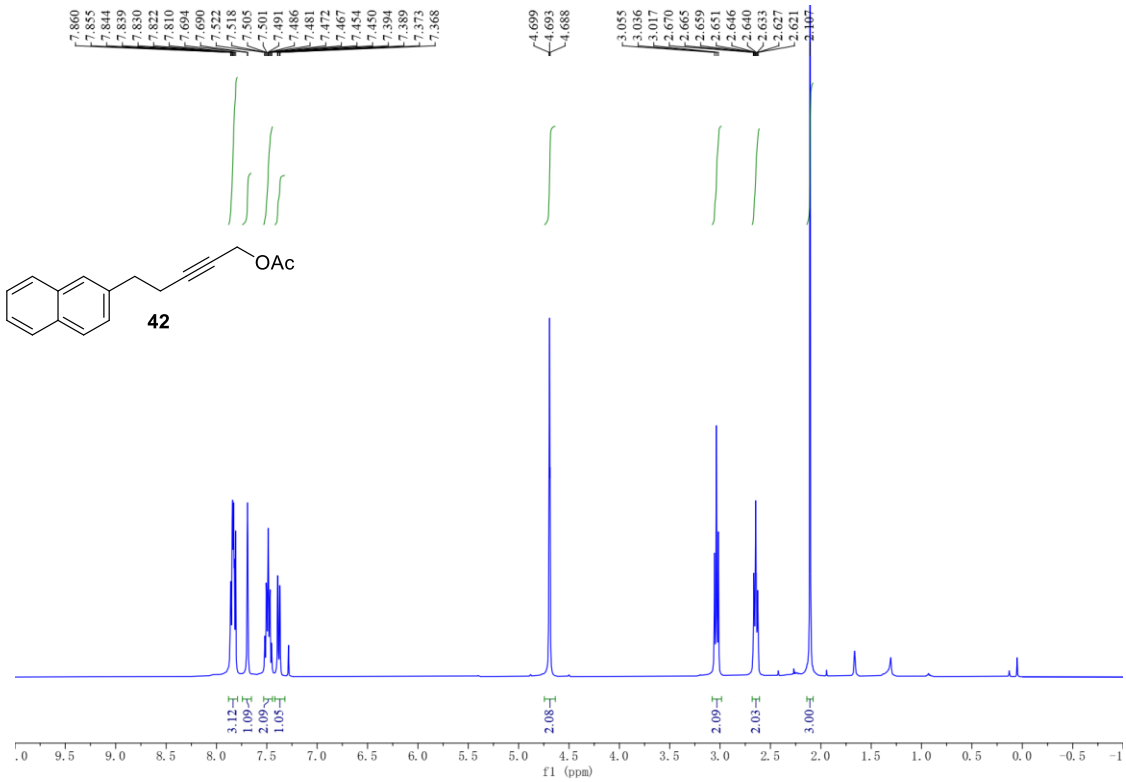

155.006
136.676
128.379
127.878
127.804
107.101
85.813
67.010
48.669
44.095
30.780
29.339
24.173
23.633
0.003
TMS
N
Cbz
39
f1 (ppm)

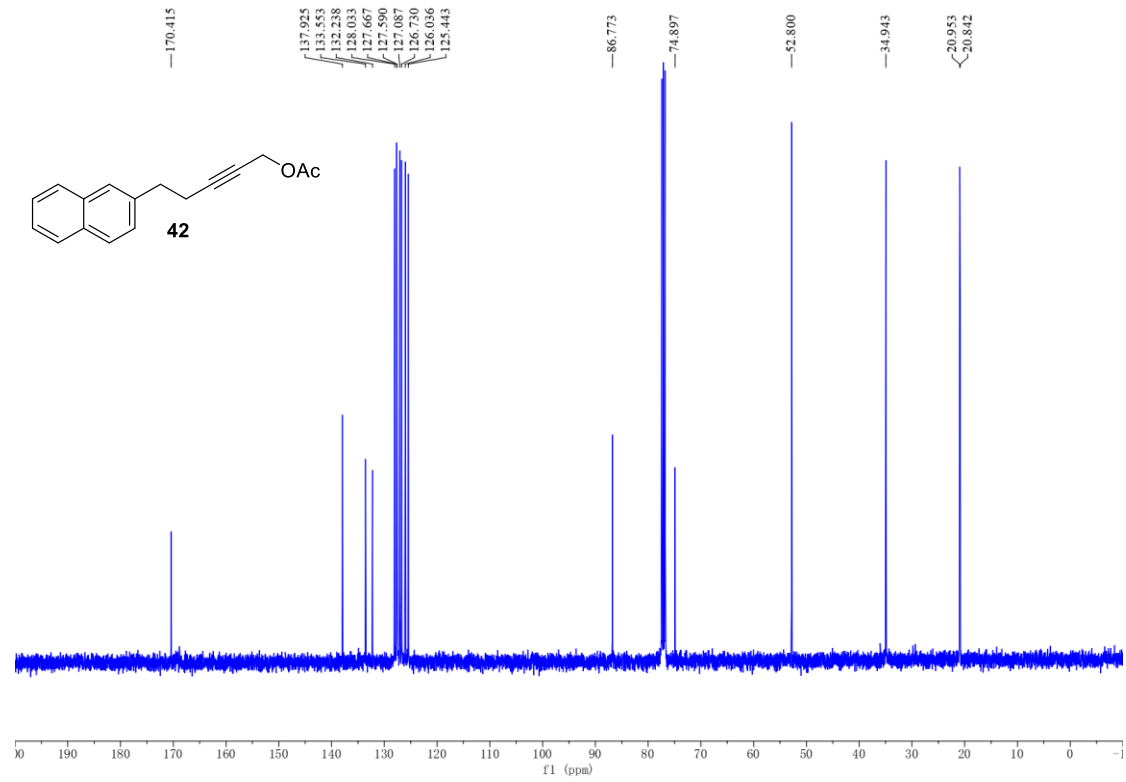

TIPS
N
Cbz
40
7.360
7.349
7.332
7.323
7.313
7.302
7.291
5.112
4.040
4.007
3.848
3.835
3.805
3.751
3.705
3.675
3.221
3.085
2.541
2.530
2.519
2.508
2.497
1.963
1.957
1.778
1.738
1.634
1.611
1.591
1.448
1.061
1.053
1.040
1.030
1.020
1.007
0.999
0.985
4.97
2.00
2.08
2.08
1.00
1.10
3.44
21.29
f1 (ppm)

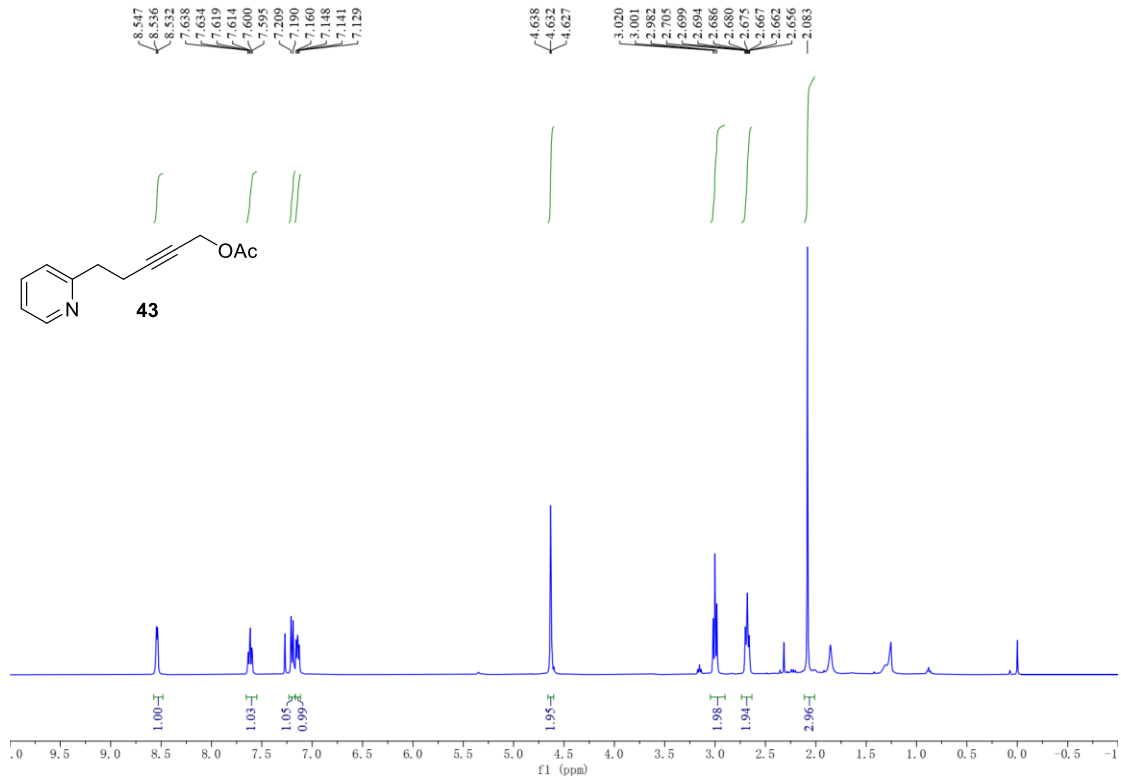

TIPS
N
Cbz
40
155.133
136.855
128.482
127.964
127.883
109.100
81.792
67.101
48.932
44.235
31.105
29.416
24.083
23.523
18.618
11.171
f1 (ppm)

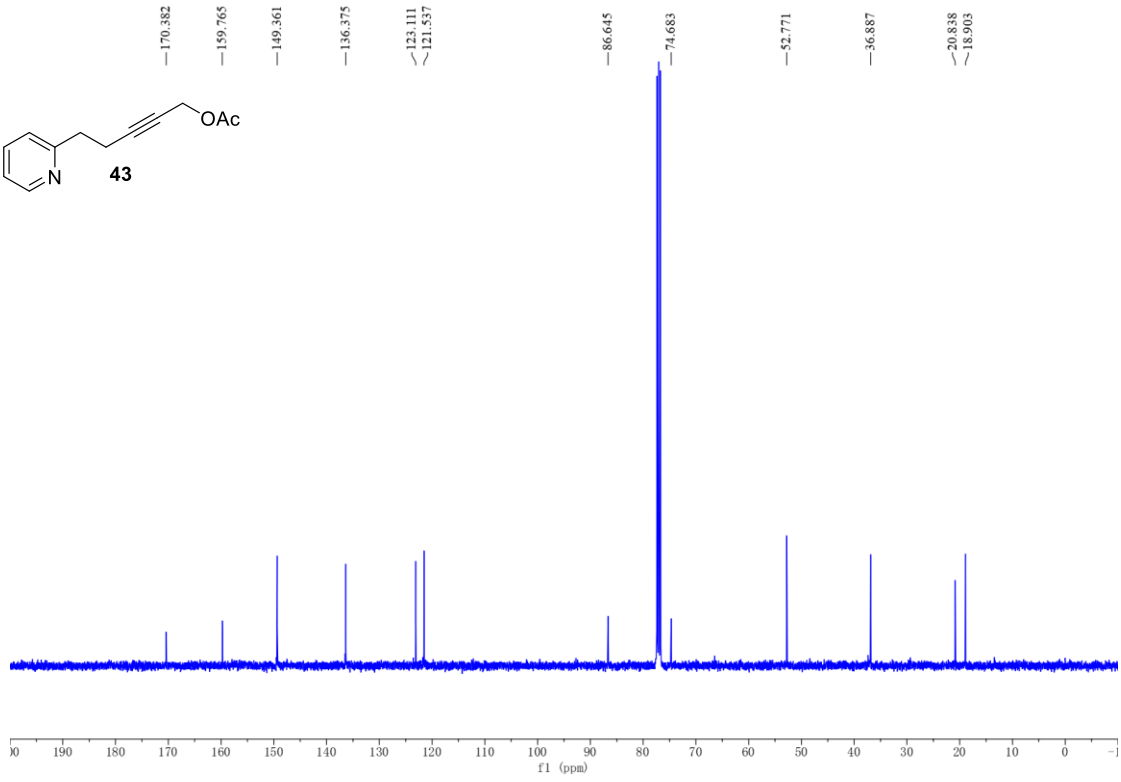

7.314
7.295
7.278
7.254
7.233
7.231
7.216
7.213
7.196
4.656
4.651
4.645
2.853
2.834
2.815
2.537
2.532
2.526
2.518
2.512
2.507
2.499
2.493
2.488
2.090
OAc
41
1.99
2.96
2.00
2.06
2.07
3.06
f1 (ppm)

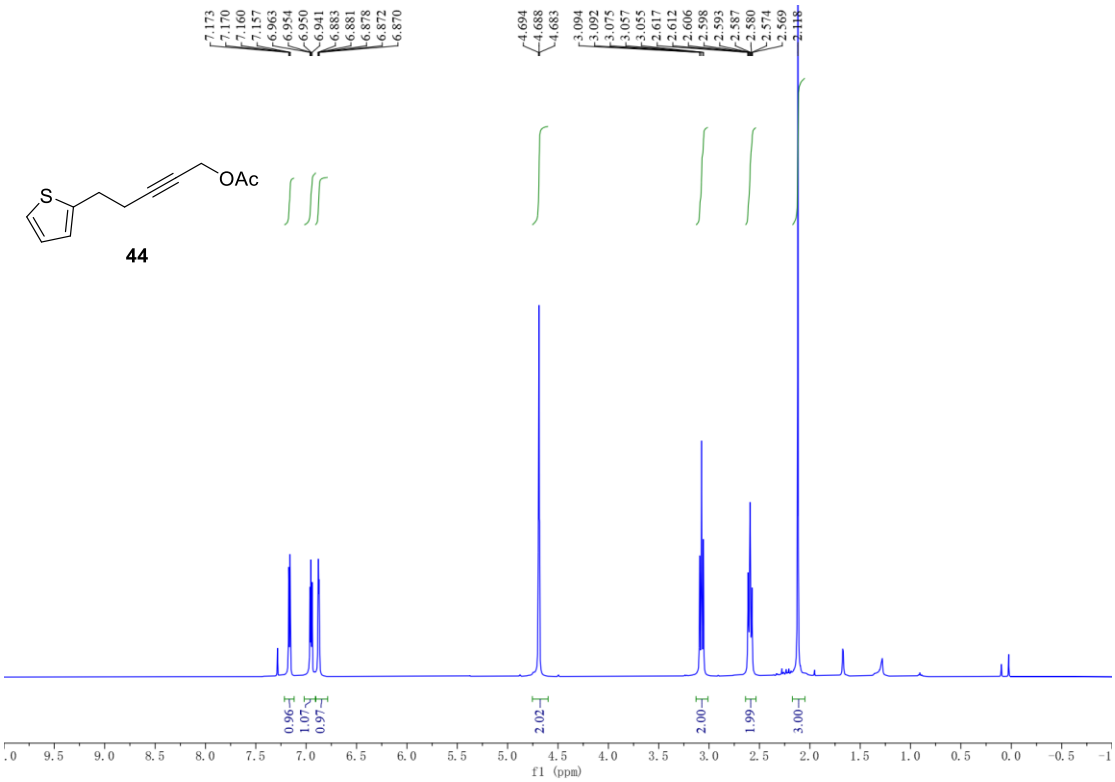

170.428
140.439
128.436
126.382
86.824
74.687
52.801
34.809
21.007
20.861
OAc
41
f1 (ppm)

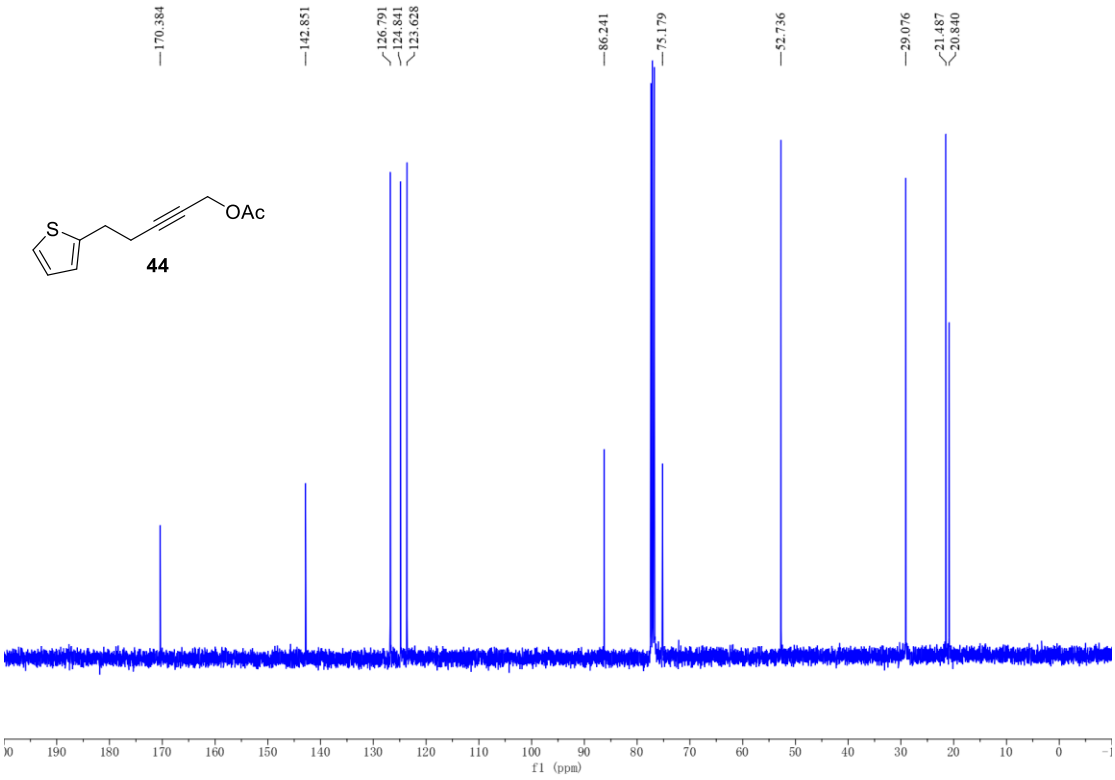

7.860
7.855
7.844
7.839
7.830
7.822
7.810
7.694
7.690
7.522
7.518
7.505
7.501
7.491
7.486
7.481
7.472
7.467
7.454
7.450
7.394
7.389
7.373
7.368
4.699
4.693
4.688
3.055
3.036
3.017
2.670
2.665
2.659
2.651
2.646
2.640
2.633
2.627
2.621
2.107
OAc
42
3.12
1.09
2.09
1.05
2.08
2.09
2.03
3.00
f1 (ppm)

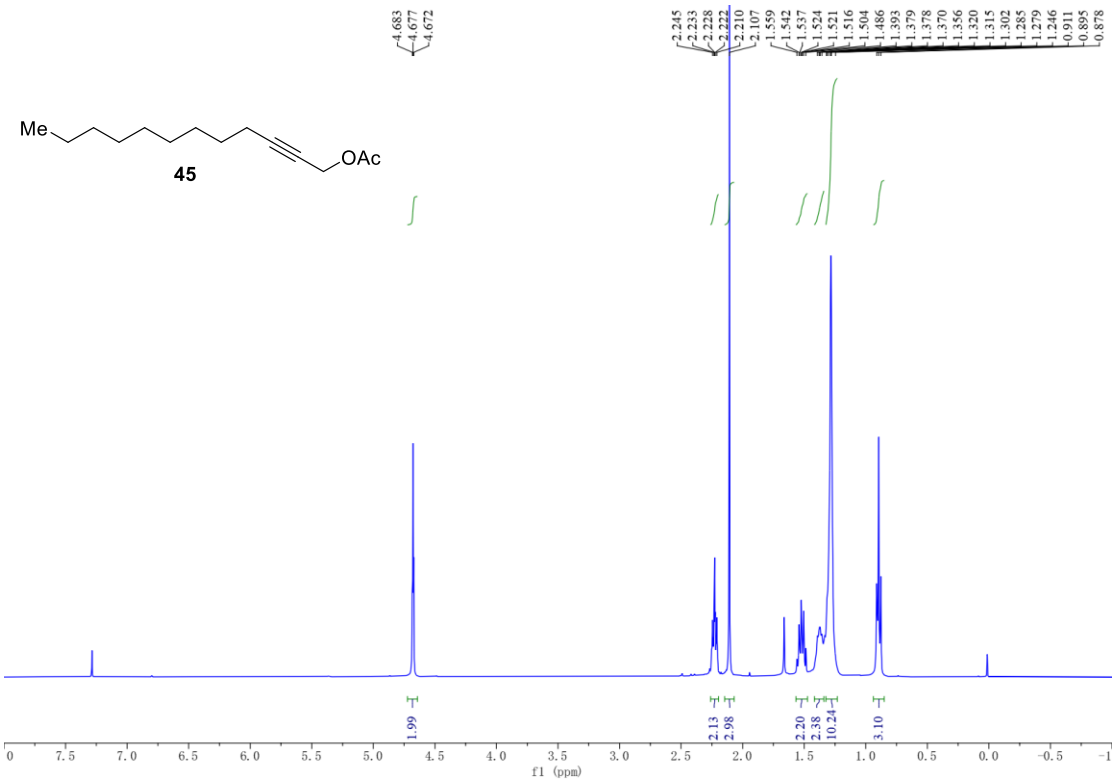

170.415
137.925
133.553
132.238
128.033
127.667
127.590
127.087
126.730
126.036
125.443
86.773
74.897
52.800
34.943
20.953
20.842
OAc
42
f1 (ppm)

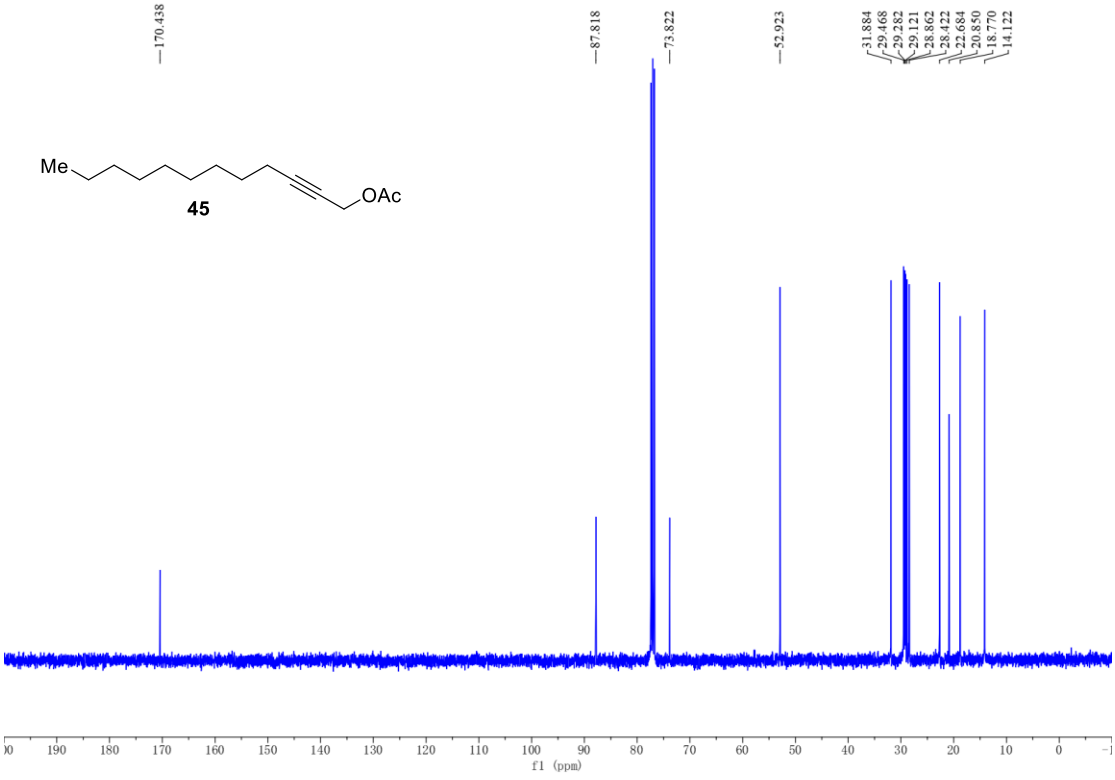

8.547
8.536
8.532
7.638
7.634
7.619
7.614
7.600
7.595
7.209
7.190
7.160
7.148
7.141
7.129
4.638
4.632
4.627
3.020
3.001
2.982
2.705
2.699
2.694
2.686
2.680
2.675
2.667
2.662
2.656
2.083
OAc
N
43
1.00
1.03
1.05
0.99
1.95
1.98
1.94
2.96
f1 (ppm)

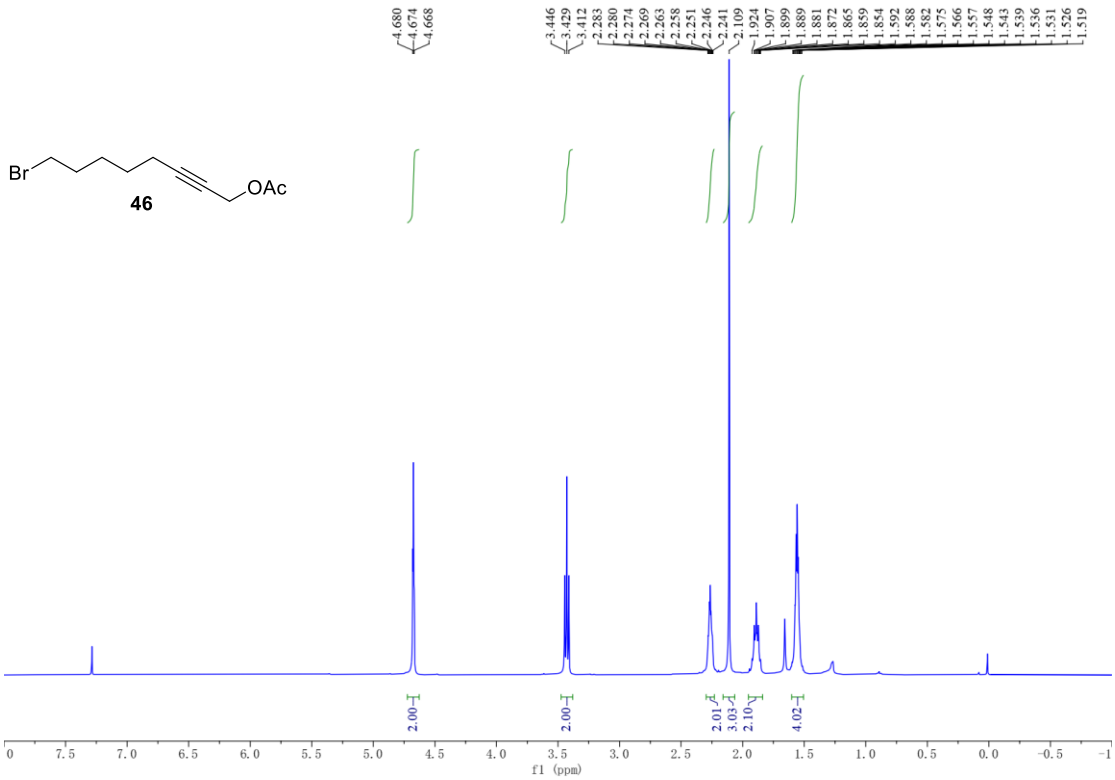

170.382
159.765
149.361
136.375
123.111
121.537
86.645
74.683
52.771
36.887
20.838
18.903
OAc
N
43
f1 (ppm)


7.173
7.170
7.160
7.157
6.963
6.954
6.950
6.941
6.883
6.881
6.878
6.872
6.870
4.694
4.688
4.683
3.094
3.092
3.075
3.057
3.055
2.617
2.612
2.606
2.598
2.593
2.587
2.580
2.574
2.569
2.118
S
OAc
44
0.96
1.07
0.97
2.02
2.00
1.99
3.00
f1 (ppm)


170.384
142.851
126.791
124.841
123.628
86.241
75.179
52.736
29.076
21.487
20.840
S
OAc
44
f1 (ppm)


Me
OAc
45
4.683
4.677
4.672
2.245
2.233
2.228
2.222
2.210
2.107
1.559
1.542
1.537
1.524
1.521
1.516
1.504
1.486
1.393
1.379
1.378
1.370
1.356
1.320
1.315
1.302
1.285
1.279
1.246
0.911
0.895
0.878
1.99
2.13
2.98
2.20
2.38
10.24
3.10
f1 (ppm)


Me
OAc
45
170.438
87.818
73.822
52.923
31.884
29.468
29.282
29.121
28.862
28.422
22.684
20.850
18.770
14.122
f1 (ppm)


Br
OAc
46
4.680
4.674
4.668
3.446
3.429
3.412
2.283
2.280
2.274
2.269
2.263
2.258
2.251
2.246
2.241
2.109
1.924
1.907
1.899
1.889
1.881
1.872
1.865
1.859
1.854
1.592
1.588
1.582
1.575
1.566
1.557
1.548
1.543
1.539
1.536
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1.519
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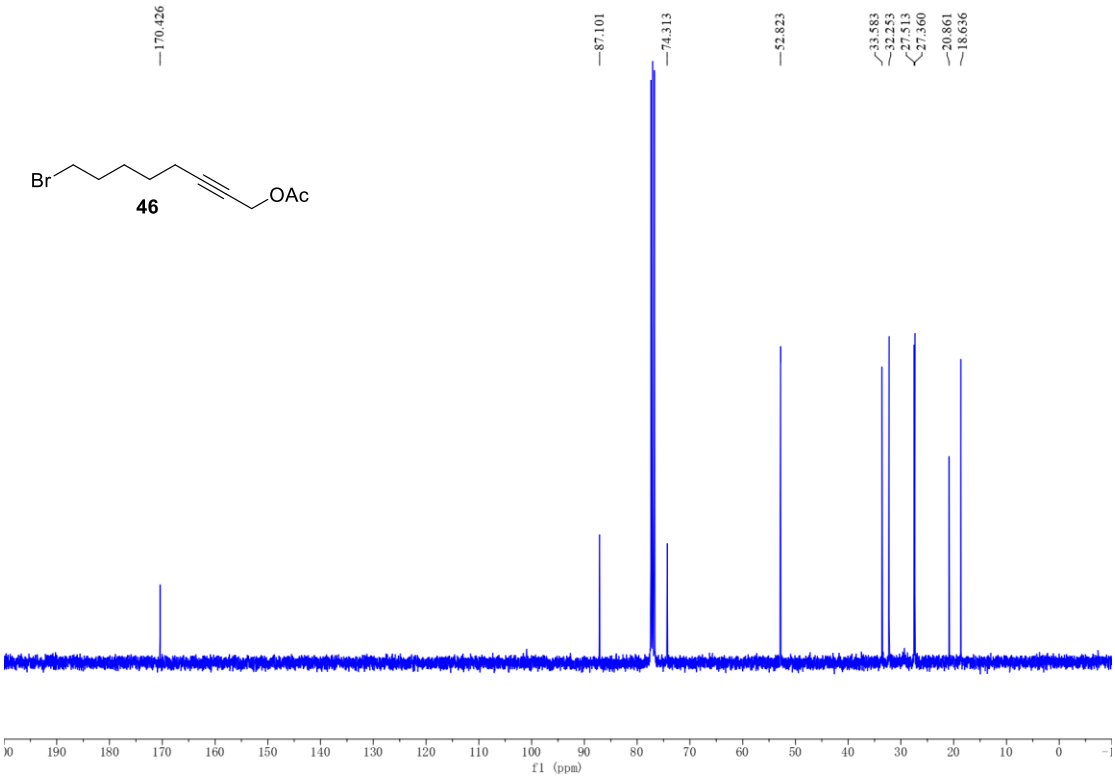
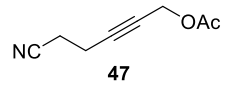
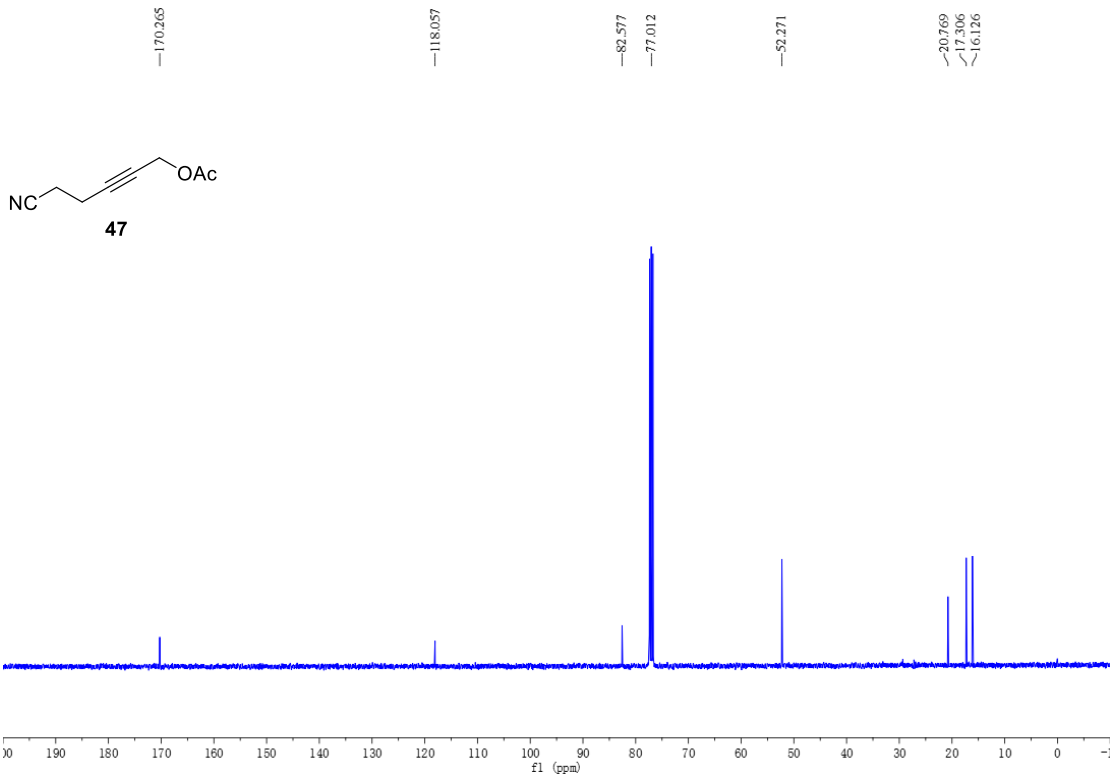
2.01
3.03
2.10
4.02
f1 (ppm)


Br
OAc
46
170.426
87.101
74.313
52.823
33.583
32.253
27.513
27.360
20.861
18.636
f1 (ppm)


NC
OAc

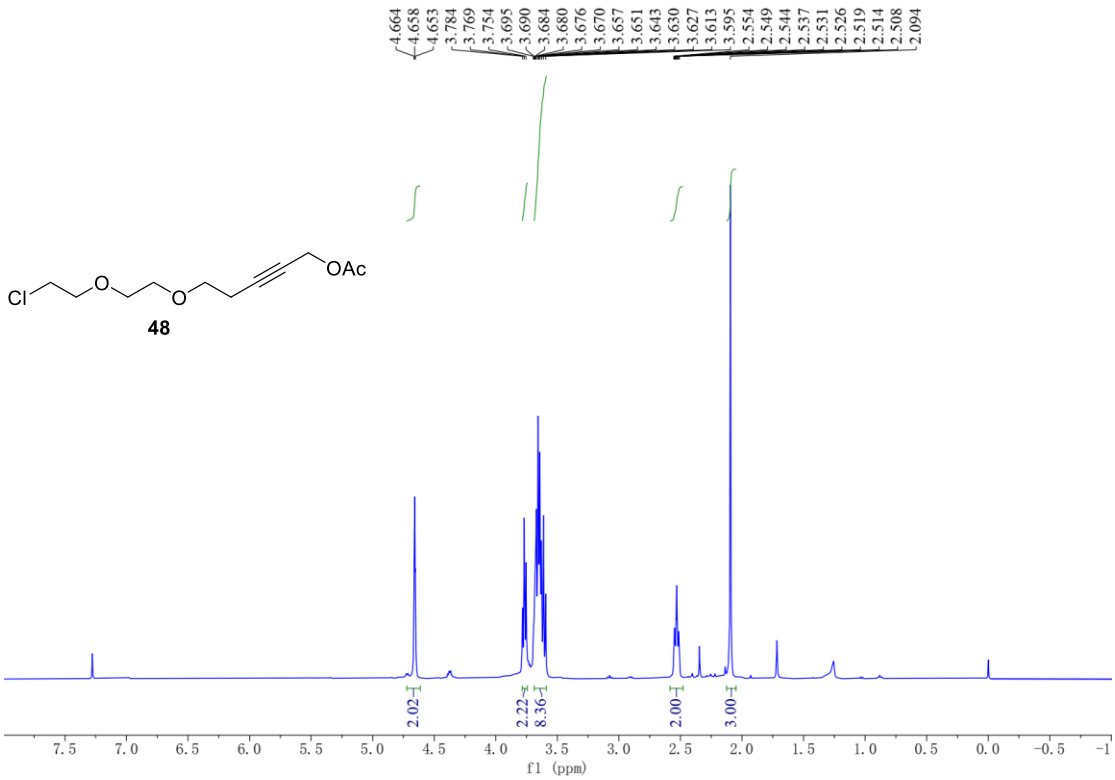
47

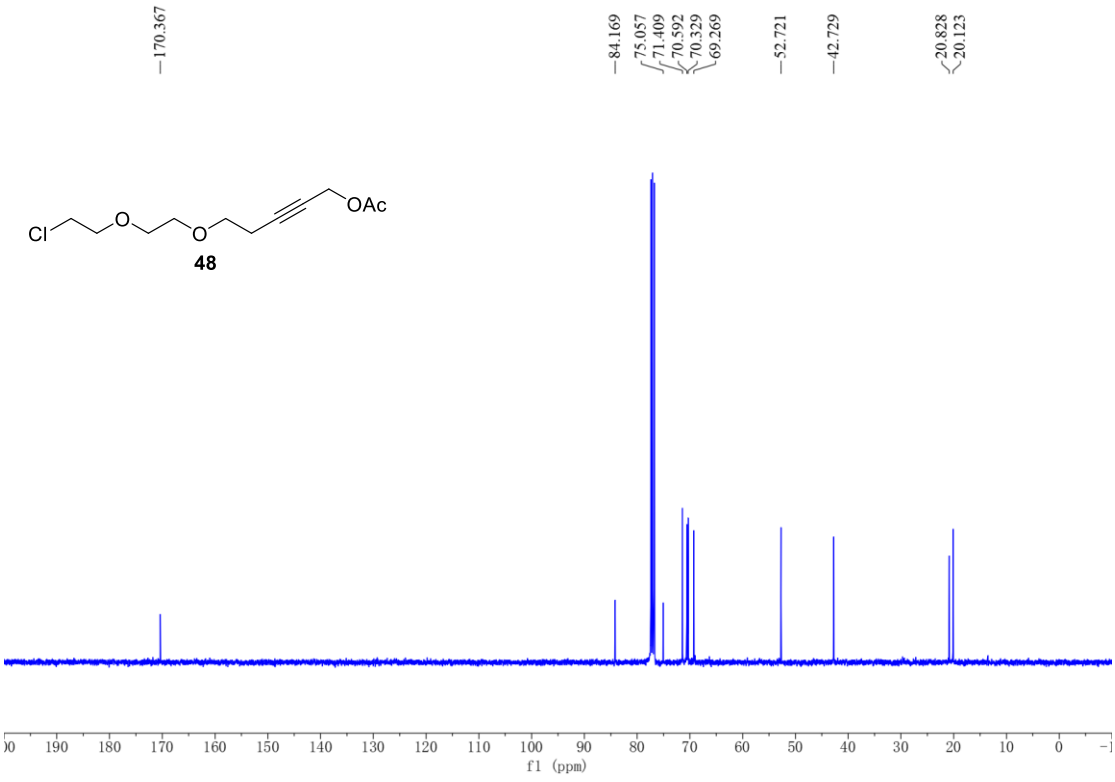
4.693
4.688
4.683
2.647
2.638
2.632
2.627
2.622
2.618
2.615
2.607
2.595
2.582
2.578
2.570
2.120
2.00
4.03
3.09
f1 (ppm)

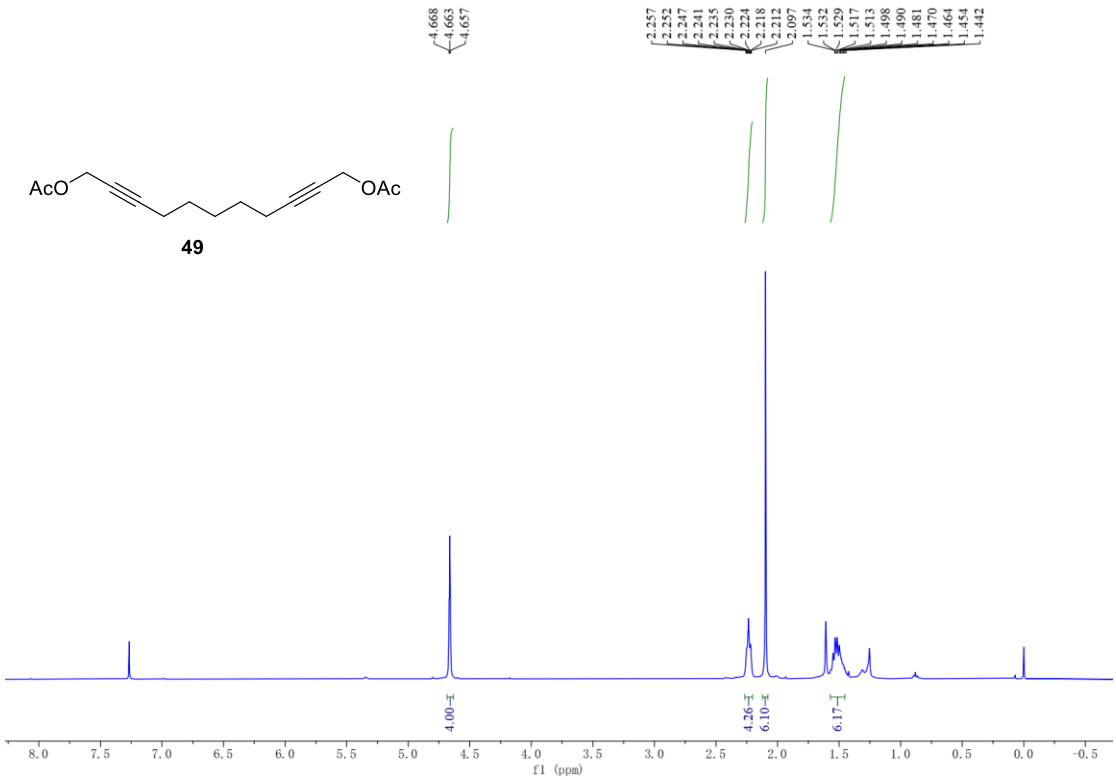

170.265
118.057
82.577
77.012
52.271
20.769
17.306
16.126
f1 (ppm)

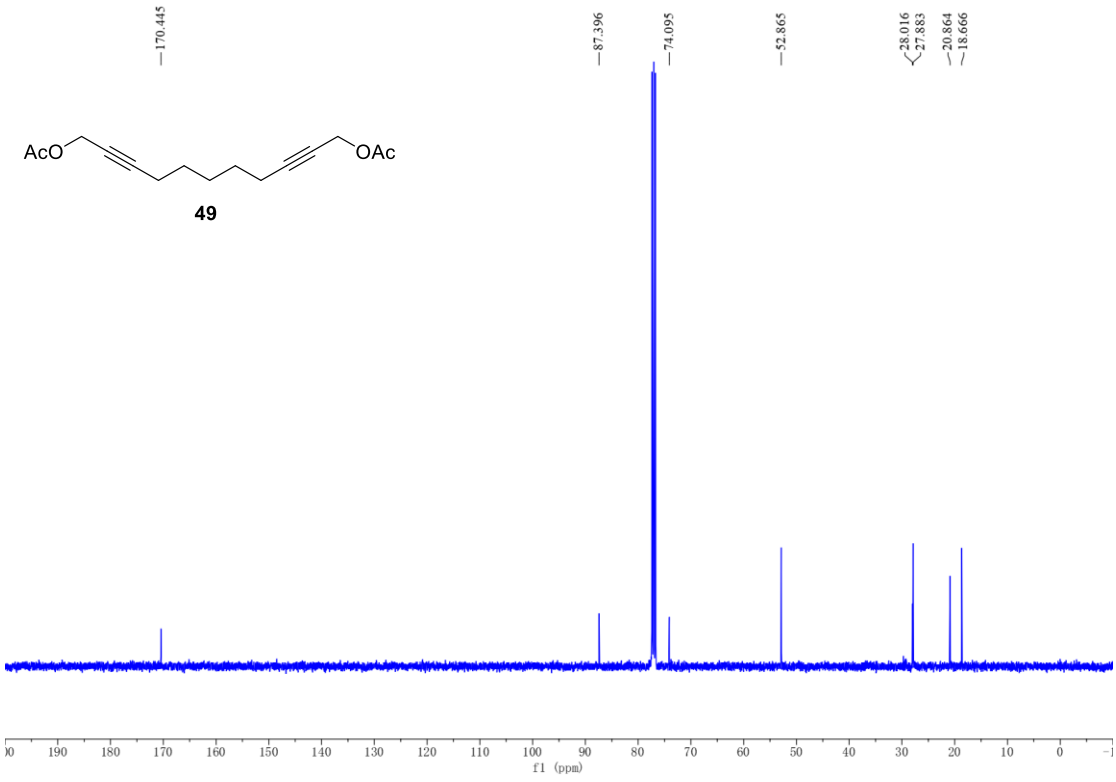
NC
OAc

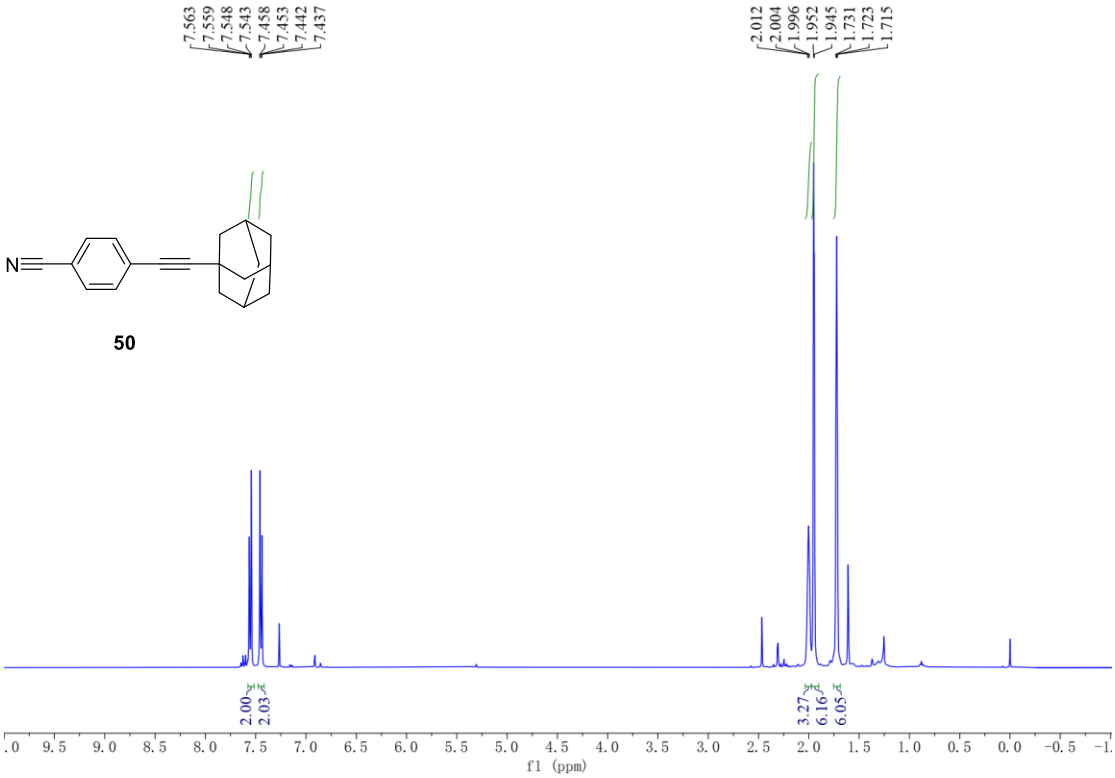
47


4.664
4.658
4.653
3.784
3.769
3.754
3.695
3.690
3.684
3.680
3.676
3.670
3.657
3.651
3.643
3.630
3.627
3.613
3.595
2.554
2.549
2.544
2.537
2.531
2.526
2.519
2.514
2.508
2.094
Cl
O
O
OAc
48
2.02
2.22
8.36
2.00
3.00
f1 (ppm)

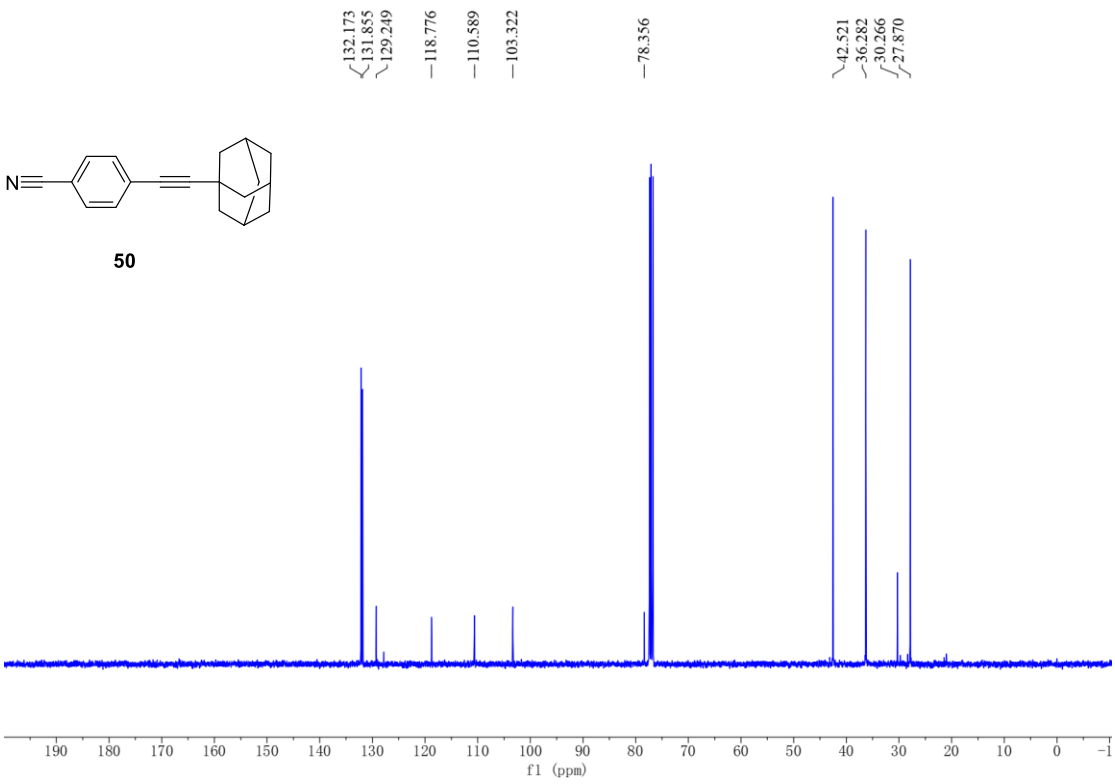

170.367
84.169
75.057
71.409
70.592
70.329
69.269
52.721
42.729
20.828
20.123
Cl
O
O
OAc
48
f1 (ppm)


4.668
4.663
4.657
2.257
2.252
2.247
2.241
2.235
2.230
2.224
2.218
2.212
2.097
1.534
1.532
1.529
1.517
1.513
1.498
1.490
1.481
1.470
1.464
1.454
1.442
AcO
OAc
49
4.00
4.26
6.10
6.17
f1 (ppm)

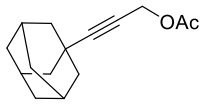

170.445
87.396
74.095
52.865
28.016
27.883
20.864
18.666
AcO
OAc
49
f1 (ppm)


7.563
7.559
7.548
7.543
7.458
7.453
7.442
7.437
2.012
2.004
1.996
1.952
1.945
1.731
1.723
1.715
N
2.00
2.03
3.27
6.16
6.05
f1 (ppm)

50


132.173
131.855
129.249
118.776
110.589
103.322
78.356
42.521
36.282
30.266
27.870
N
f1 (ppm)

50


OAc

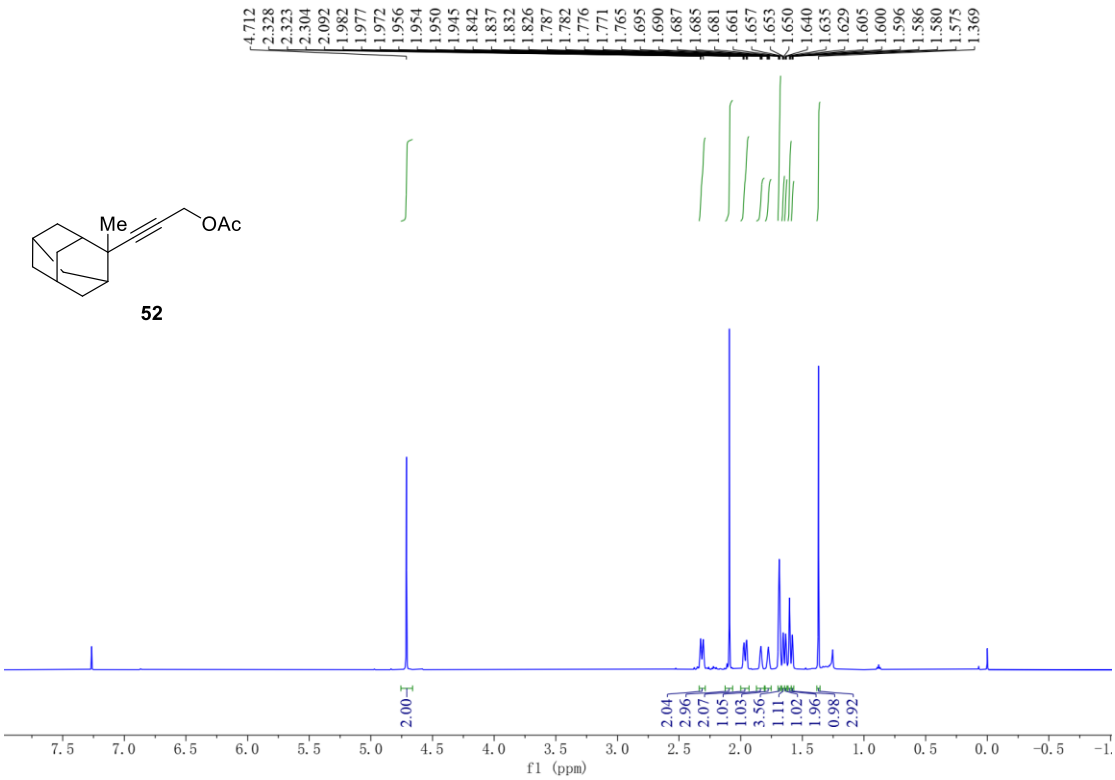
51

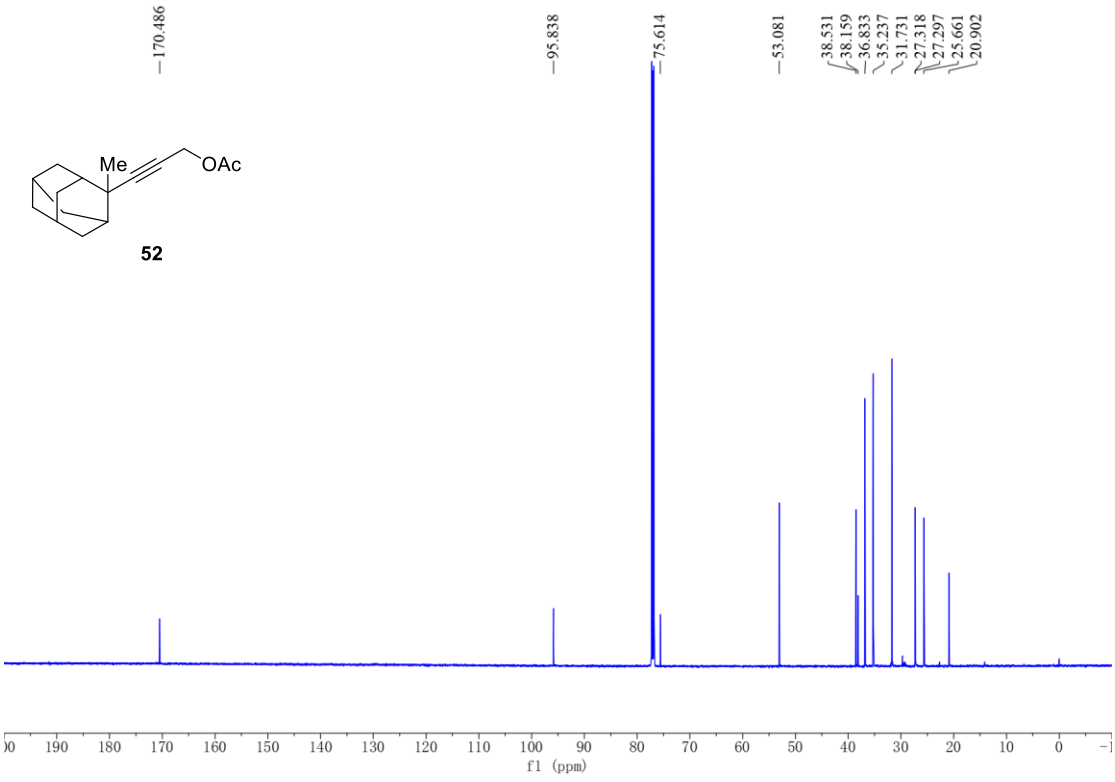
4.674
2.091
1.960
1.952
1.943
1.866
1.857
1.686
1.678
1.670
2.00
2.95
3.10
5.99
5.98
f1 (ppm)

OAc

51

170.477
95.552
72.681
53.016
42.552
36.286
29.559
27.873
20.953
f1 (ppm)


4.712
2.328
2.323
2.304
2.092
1.982
1.977
1.972
1.956
1.954
1.950
1.945
1.842
1.837
1.832
1.826
1.787
1.782
1.776
1.771
1.765
1.695
1.690
1.687
1.685
1.681
1.661
1.657
1.653
1.650
1.640
1.635
1.629
1.605
1.600
1.596
1.586
1.580
1.575
1.369
Me
OAc
52
2.00
2.04
2.96
2.07
1.05
1.03
3.56
1.11
1.02
1.96
0.98
2.92
f1 (ppm)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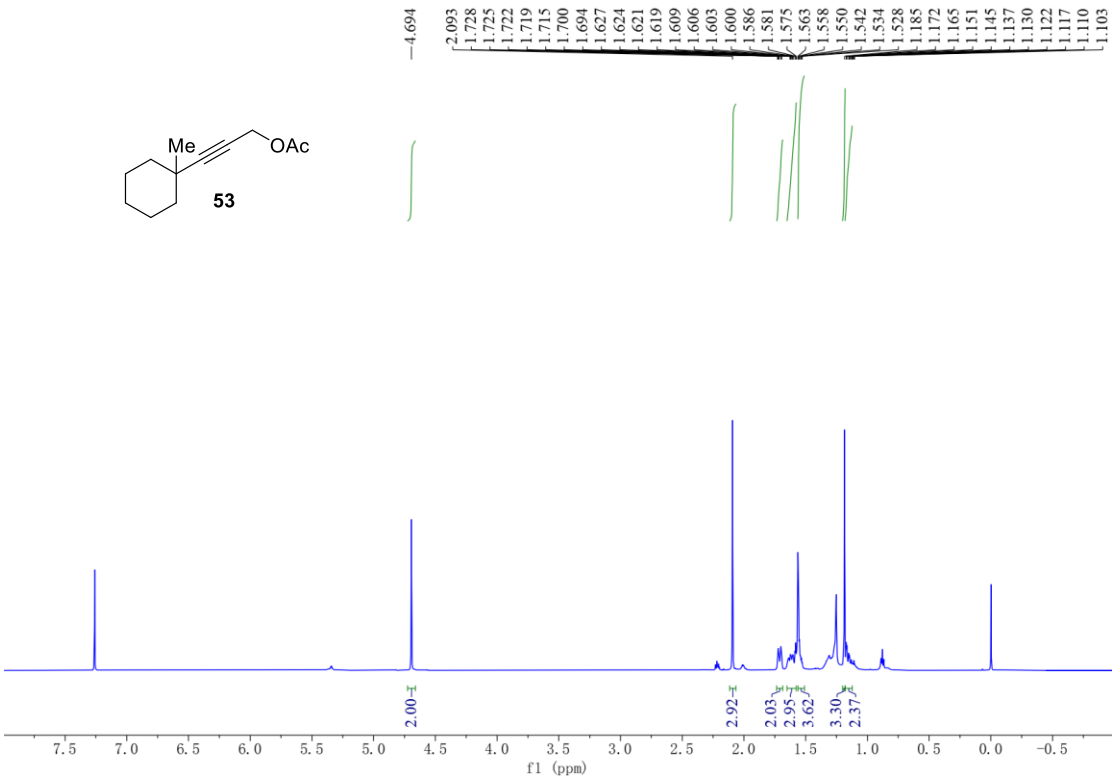
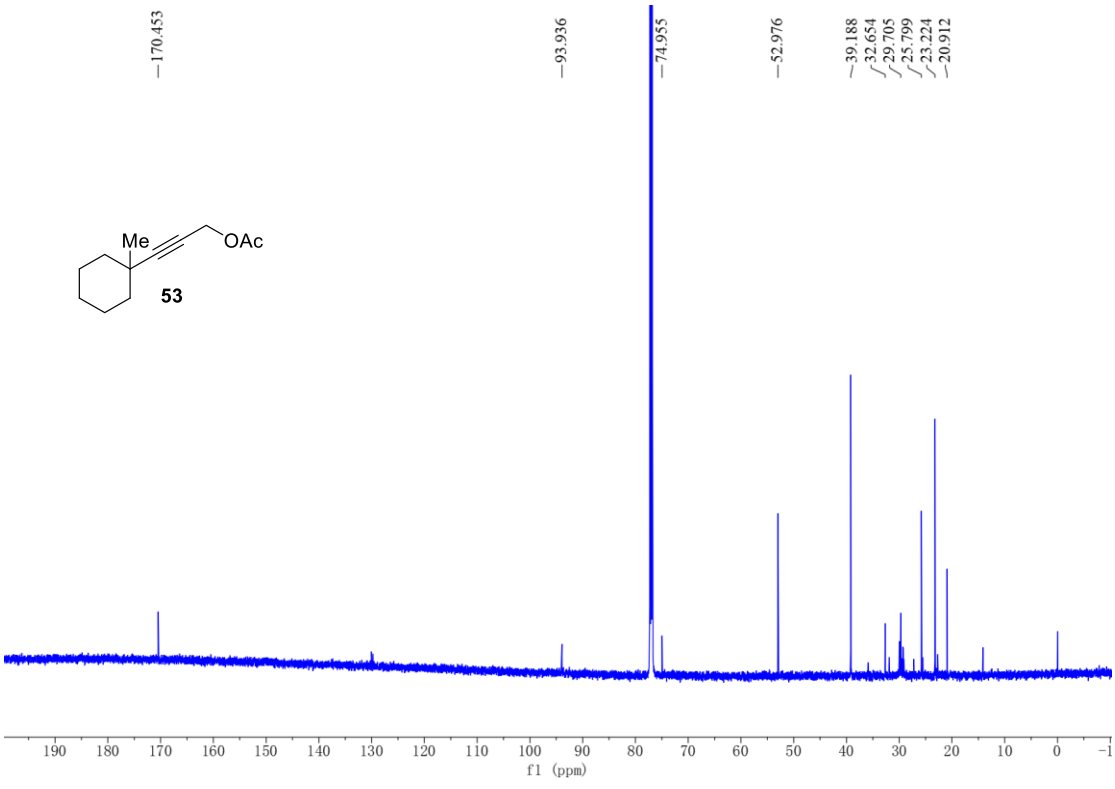
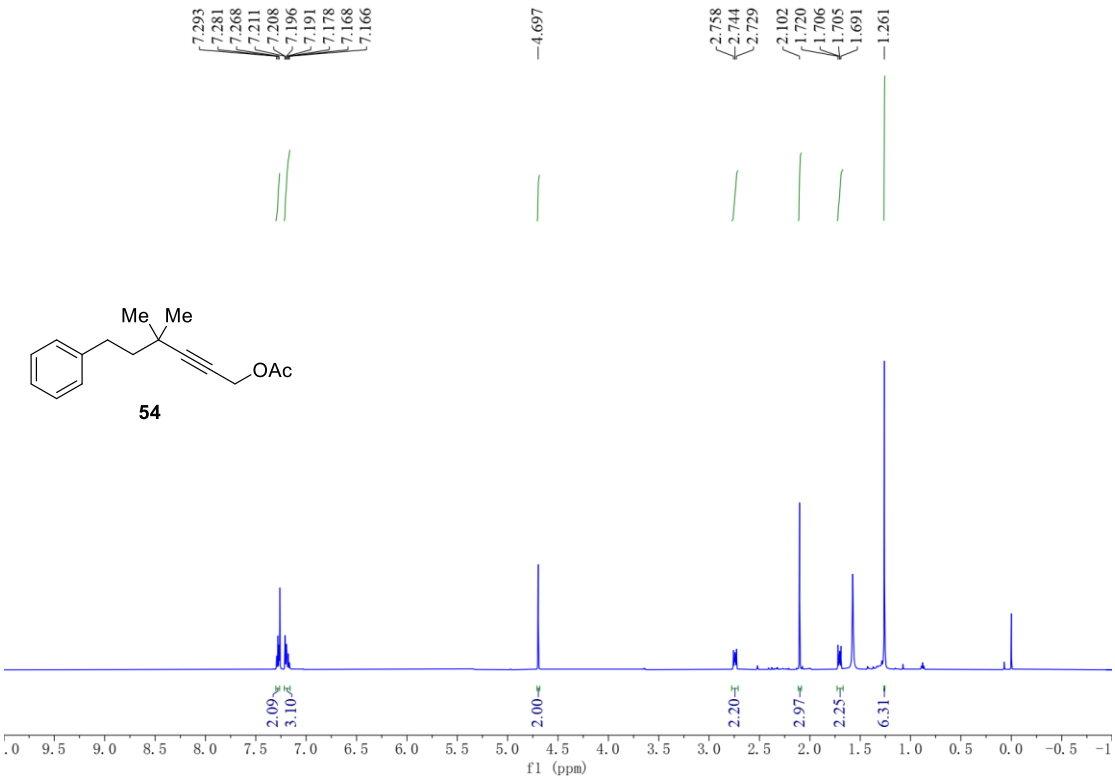
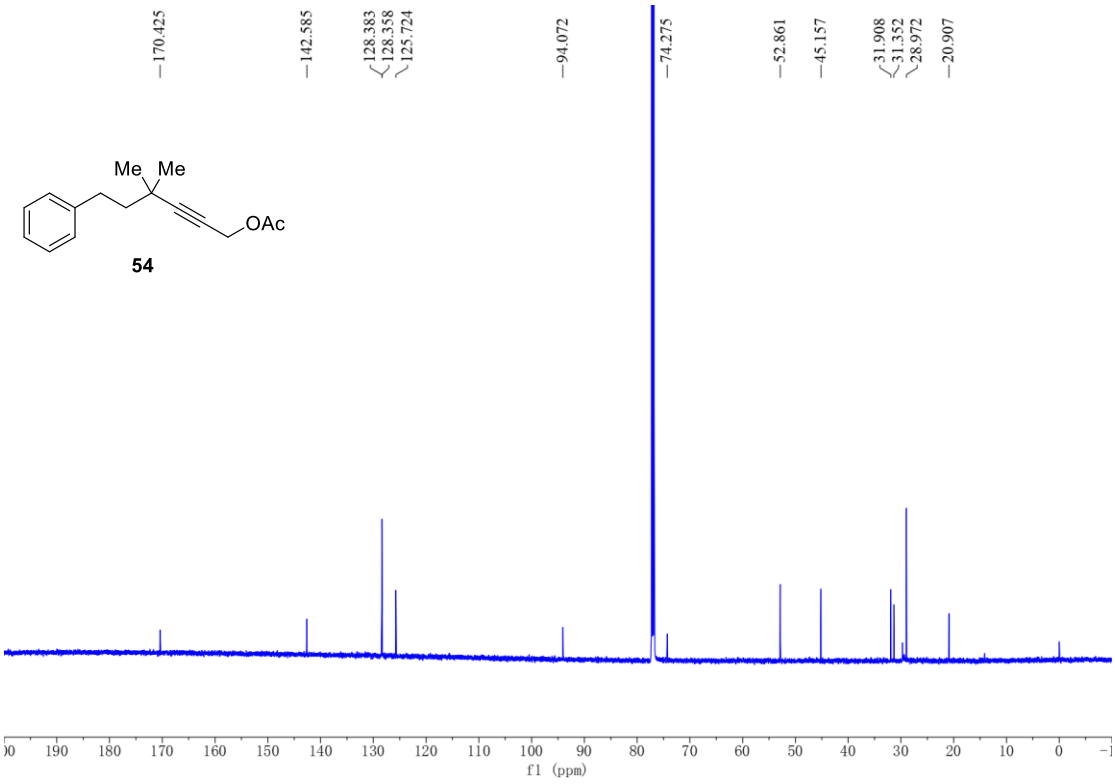
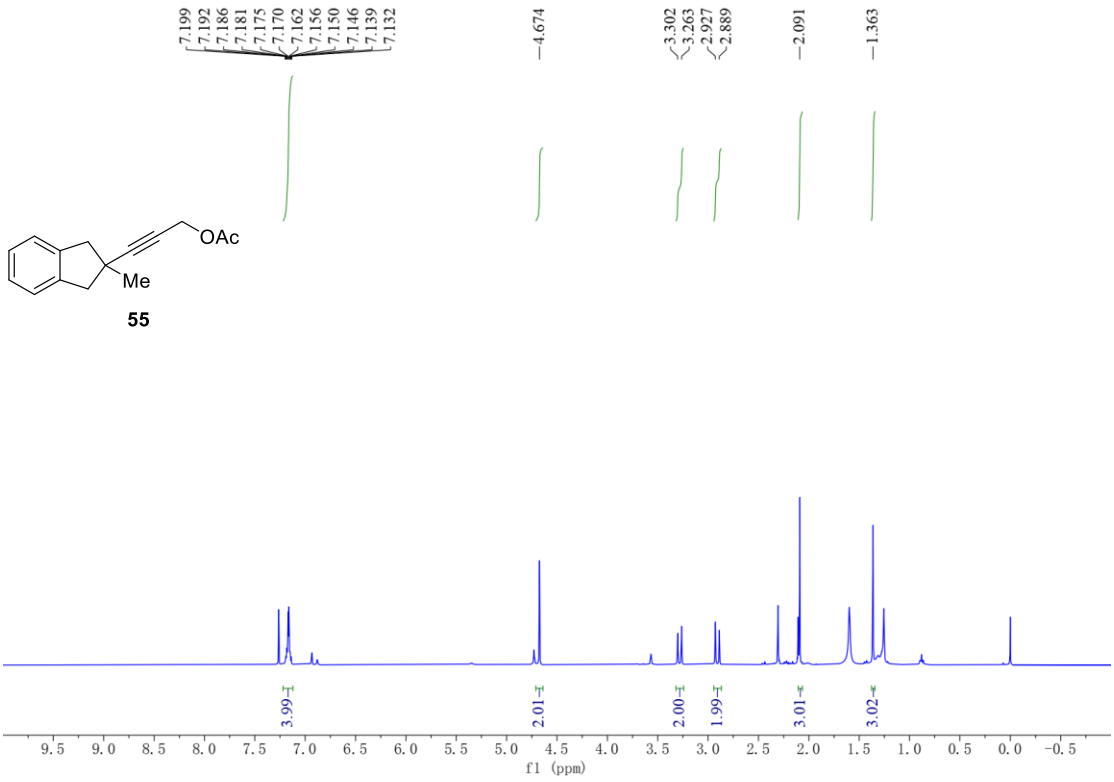
95.838
75.614
53.081
38.531
38.159
36.833
35.237
31.731
27.318
27.297
25.661
20.902
Me
OAc
52
f1 (ppm)


4.694
2.093
1.728
1.725
1.722
1.719
1.715
1.700
1.694
1.627
1.624
1.621
1.619
1.609
1.606
1.603
1.600
1.586
1.581
1.575
1.563
1.558
1.550
1.542
1.534
1.528
1.185
1.172
1.165
1.151
1.145
1.137
1.130
1.122
1.117
1.110
1.103
Me
OAc
53
2.00
2.92
2.03
2.95
3.62
3.30
2.37
f1 (ppm)

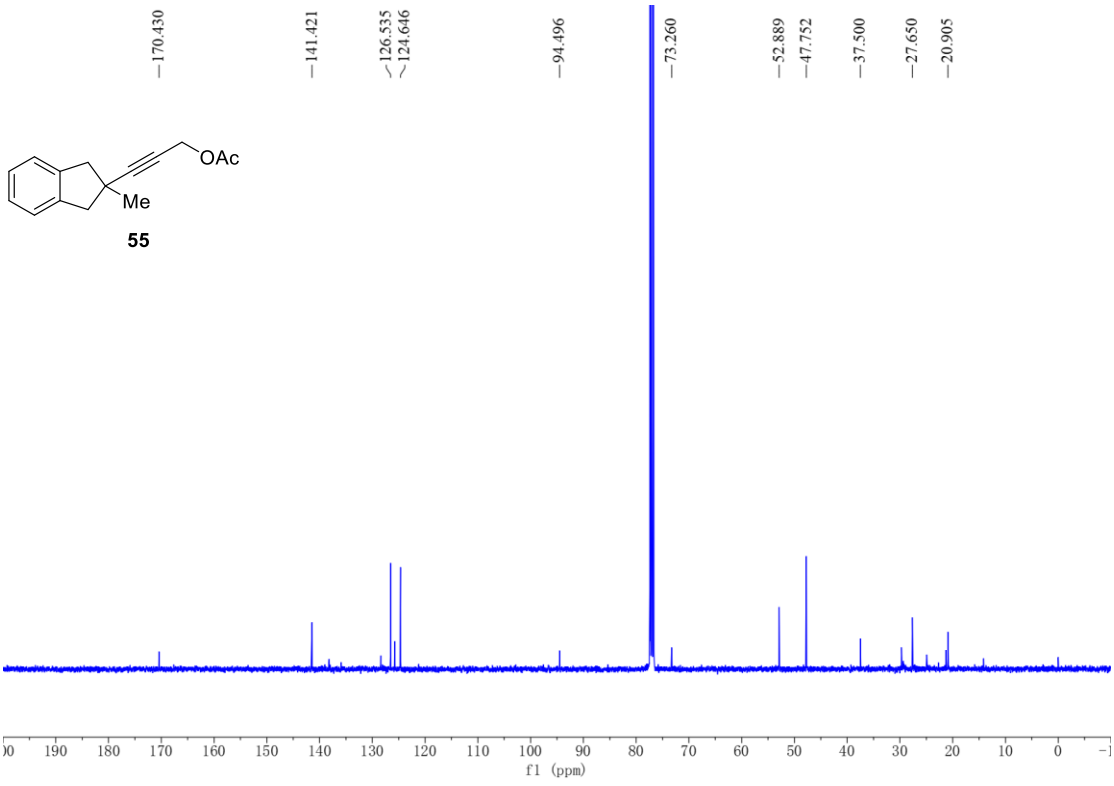

170.453
93.936
74.955
52.976
39.188
32.654
29.705
25.799
23.224
20.912
Me
OAc
53
f1 (ppm)


7.293
7.281
7.268
7.211
7.208
7.196
7.191
7.178
7.168
7.166
4.697
2.758
2.744
2.729
2.102
1.720
1.706
1.705
1.691
1.261
Me Me
OAc
54
2.09
3.10
2.00
2.20
2.97
2.25
6.31
f1 (ppm)

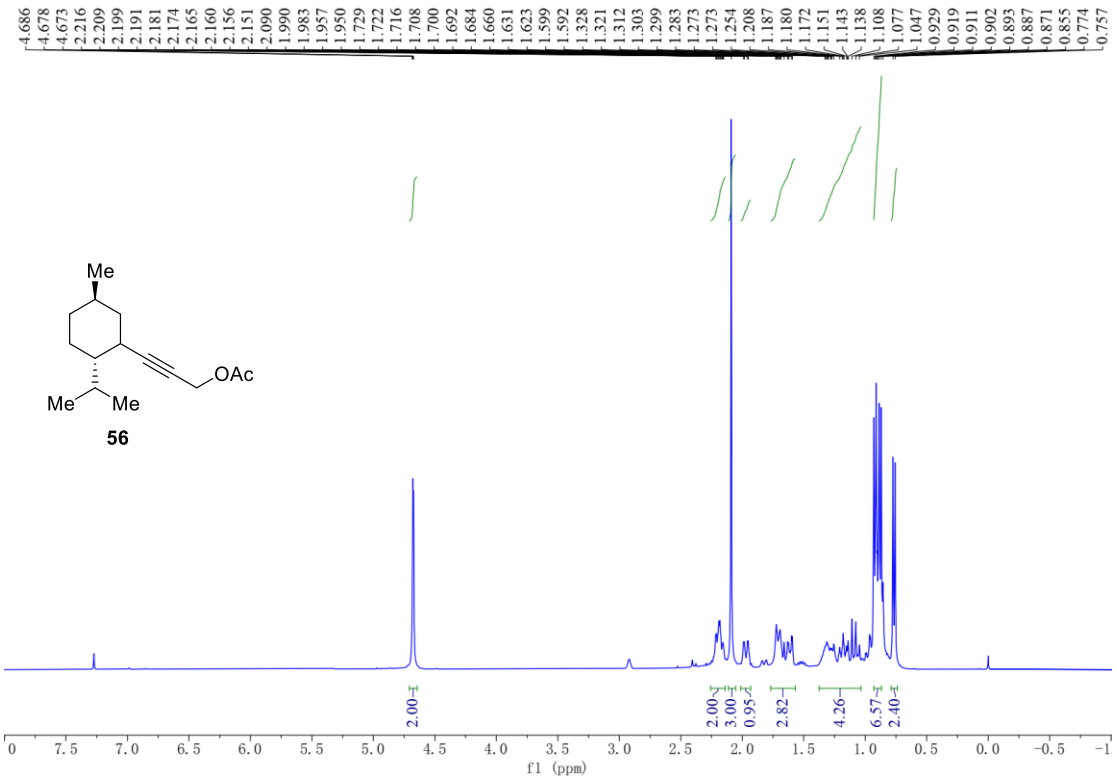

170.425
142.585
128.383
128.358
125.724
94.072
74.275
52.861
45.157
31.908
31.352
28.972
20.907
Me Me
OAc
54
f1 (ppm)


7.199
7.192
7.186
7.181
7.175
7.170
7.162
7.156
7.150
7.146
7.139
7.132
4.674
3.302
3.263
2.927
2.889
2.091
1.363
OAc
Me
3.99
2.01
2.00
1.99
3.01
3.02
f1 (ppm)

55


170.430
141.421
126.535
124.646
94.496
73.260
52.889
47.752
37.500
27.650
20.905
OAc
Me
f1 (ppm)

55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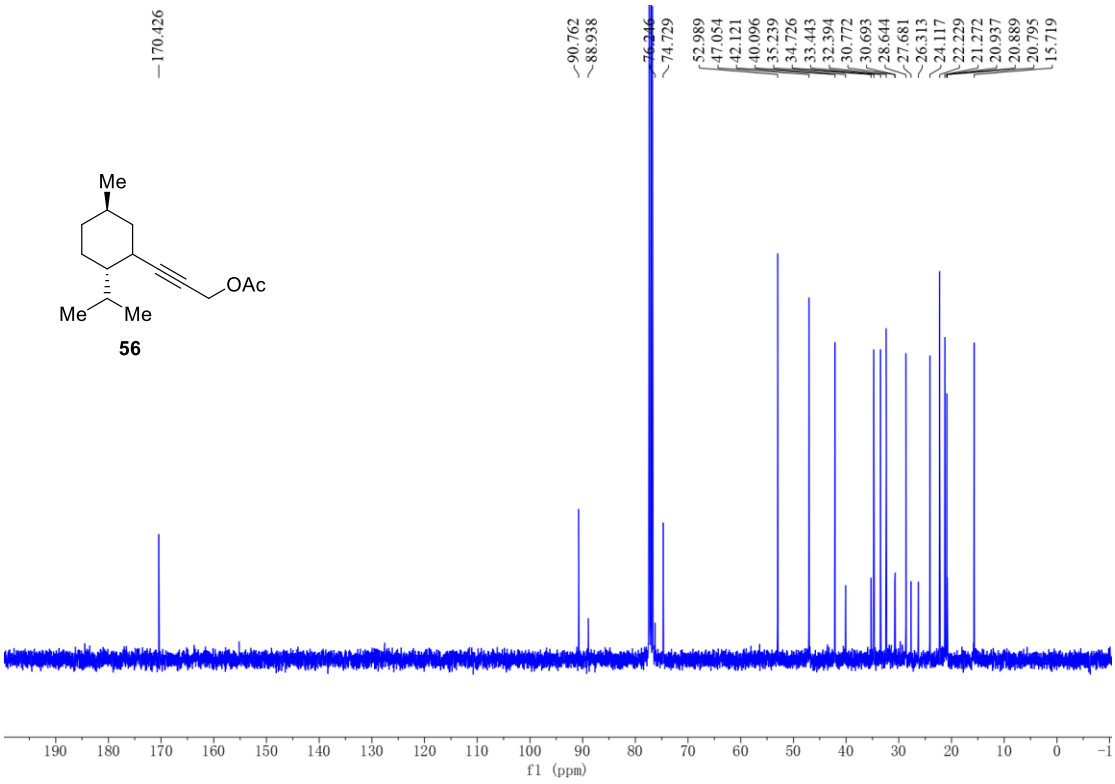
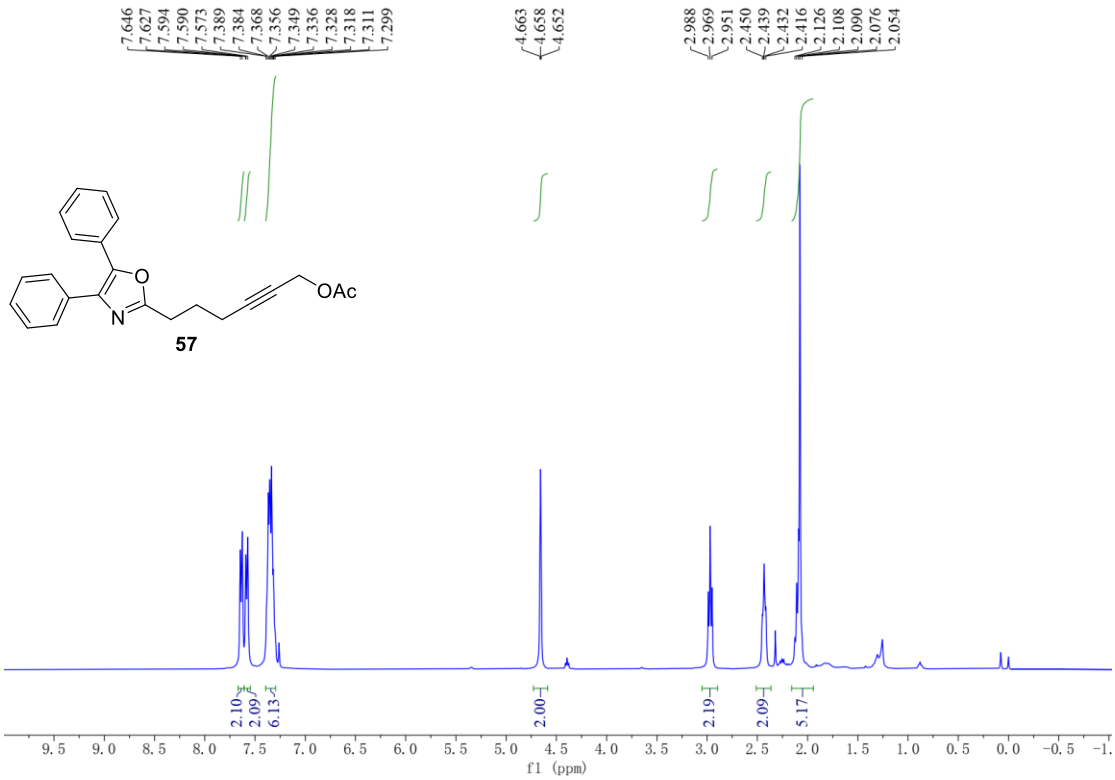
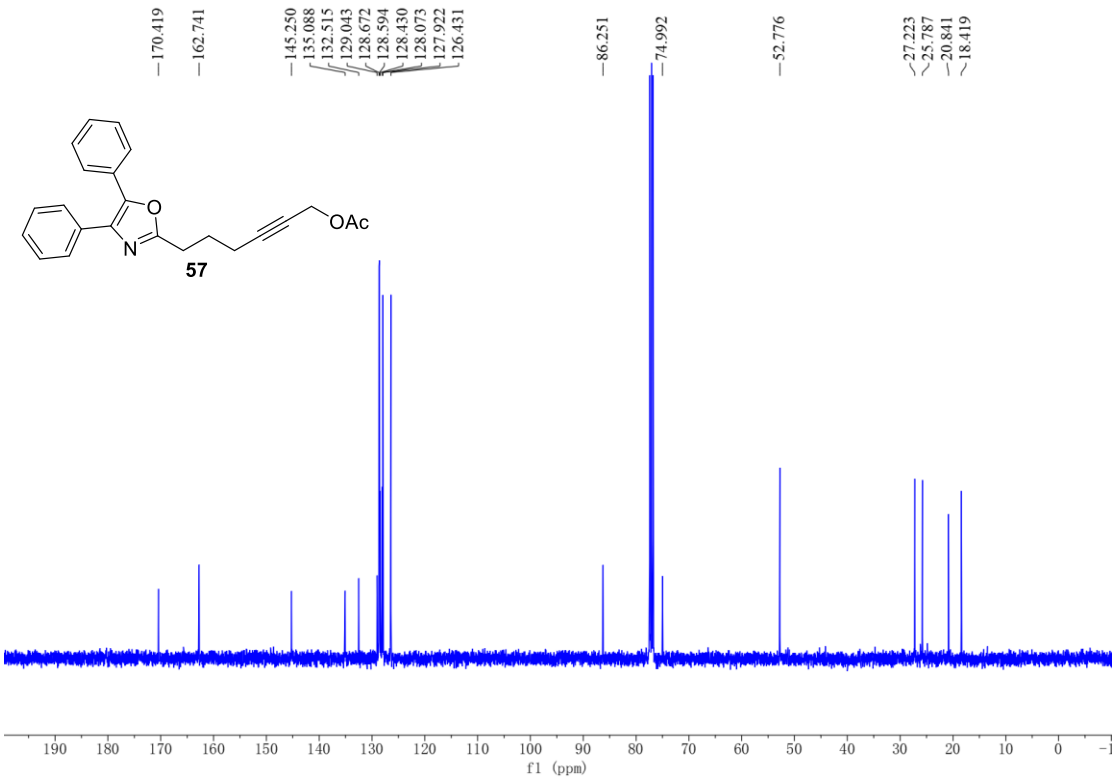
4.678
4.673
2.216
2.209
2.199
2.191
2.181
2.174
2.165
2.160
2.156
2.151
2.090
1.990
1.983
1.957
1.950
1.729
1.722
1.716
1.708
1.700
1.692
1.684
1.660
1.631
1.623
1.599
1.592
1.328
1.321
1.312
1.303
1.299
1.283
1.273
1.273
1.254
1.208
1.187
1.180
1.172
1.151
1.143
1.138
1.108
1.077
1.047
0.929
0.919
0.911
0.902
0.893
0.887
0.871
0.855
0.774
0.757
Me
OAc
Me
Me
56
2.00
2.00
3.00
0.95
2.82
4.26
6.57
2.40
f1 (ppm)


170.426
90.762
88.938
76.346
74.729
52.989
47.054
42.121
40.096
35.239
34.726
33.443
32.394
30.772
30.693
28.644
27.681
26.313
24.117
22.229
21.272
20.937
20.889
20.795
15.719
Me
OAc
Me
Me
56
f1 (ppm)


7.646
7.627
7.594
7.590
7.573
7.389
7.384
7.368
7.356
7.349
7.336
7.328
7.318
7.311
7.299
4.663
4.658
4.652
2.988
2.969
2.951
2.450
2.439
2.432
2.416
2.126
2.108
2.090
2.076
2.054
O
N
OAc
57
2.10
2.09
6.13
2.00
2.19
2.09
5.17
f1 (ppm)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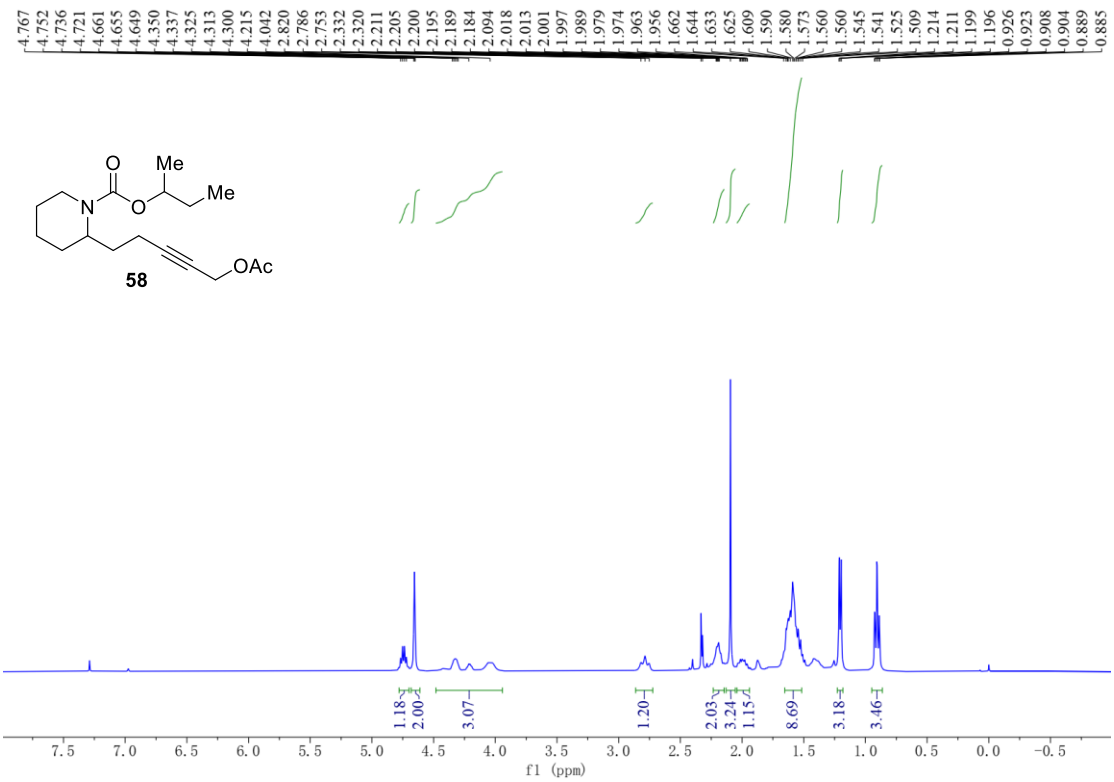
162.741
145.250
135.088
132.515
129.043
128.672
128.594
128.430
128.073
127.922
126.431
86.251
74.992
52.776
27.223
25.787
20.841
18.419
O
N
OAc
57
f1 (ppm)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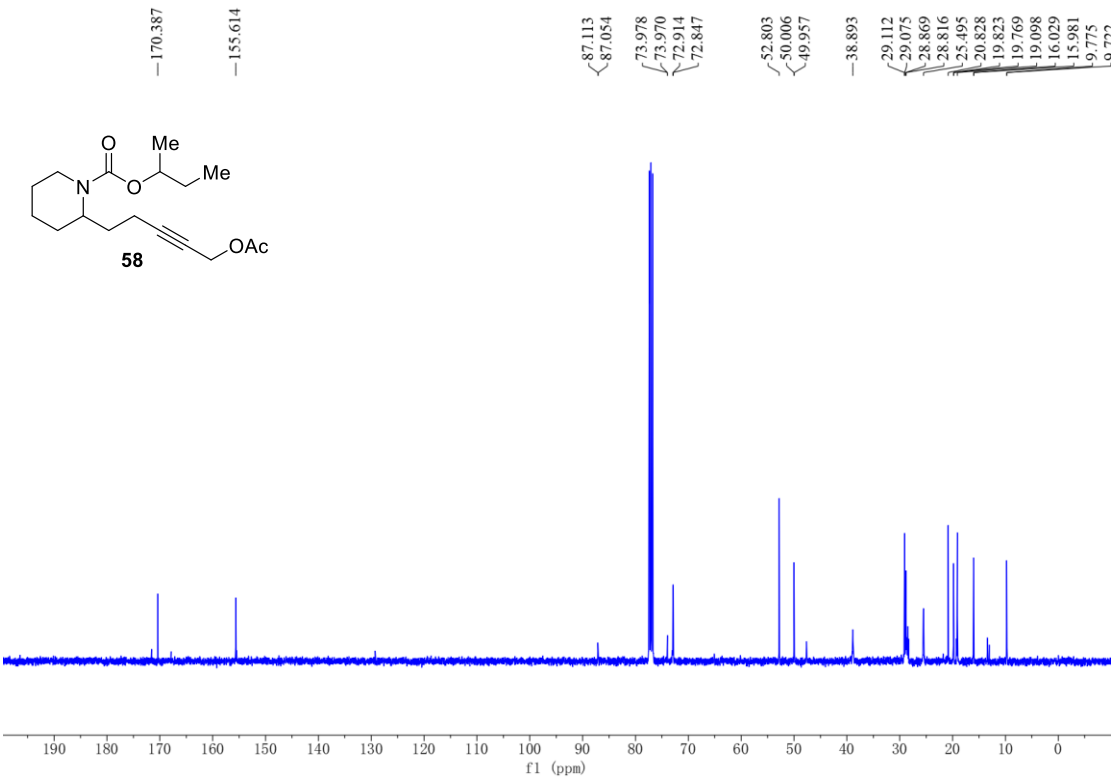
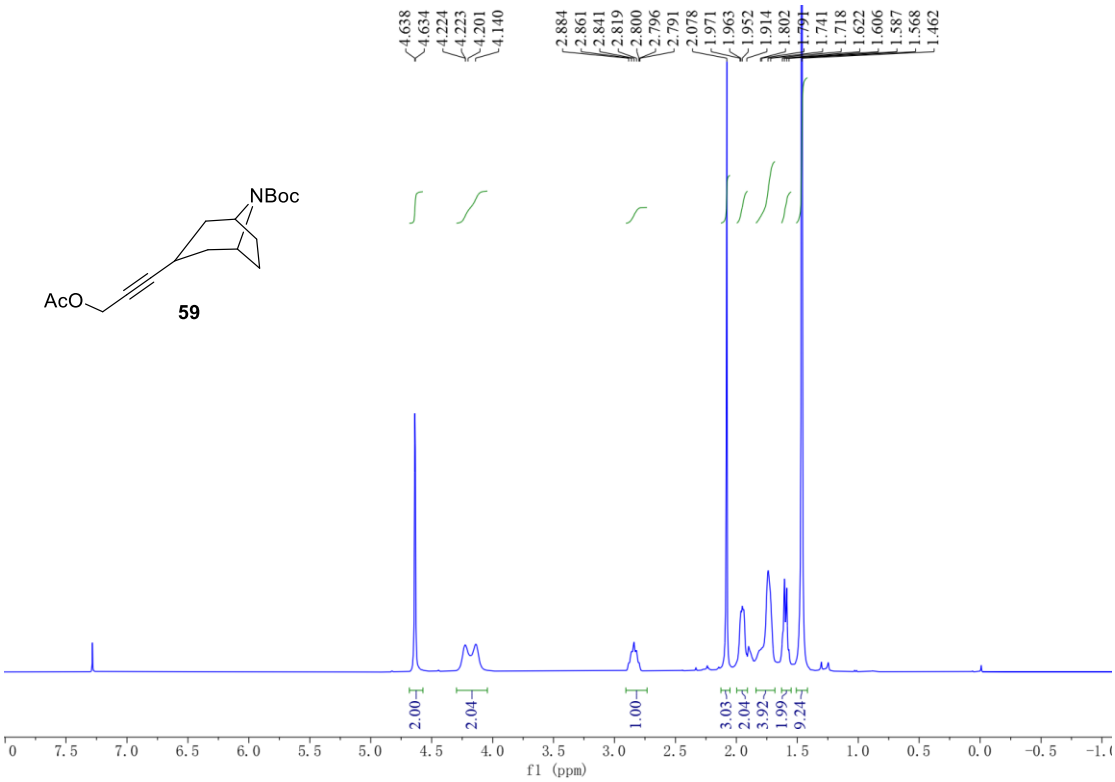
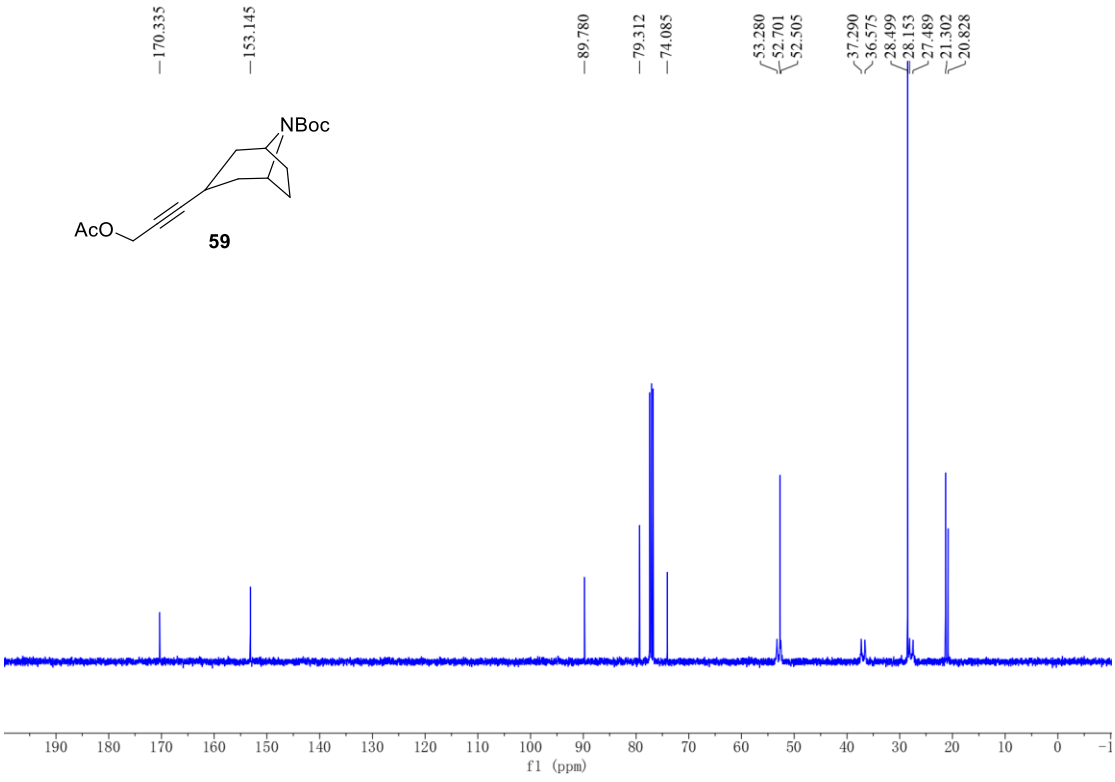
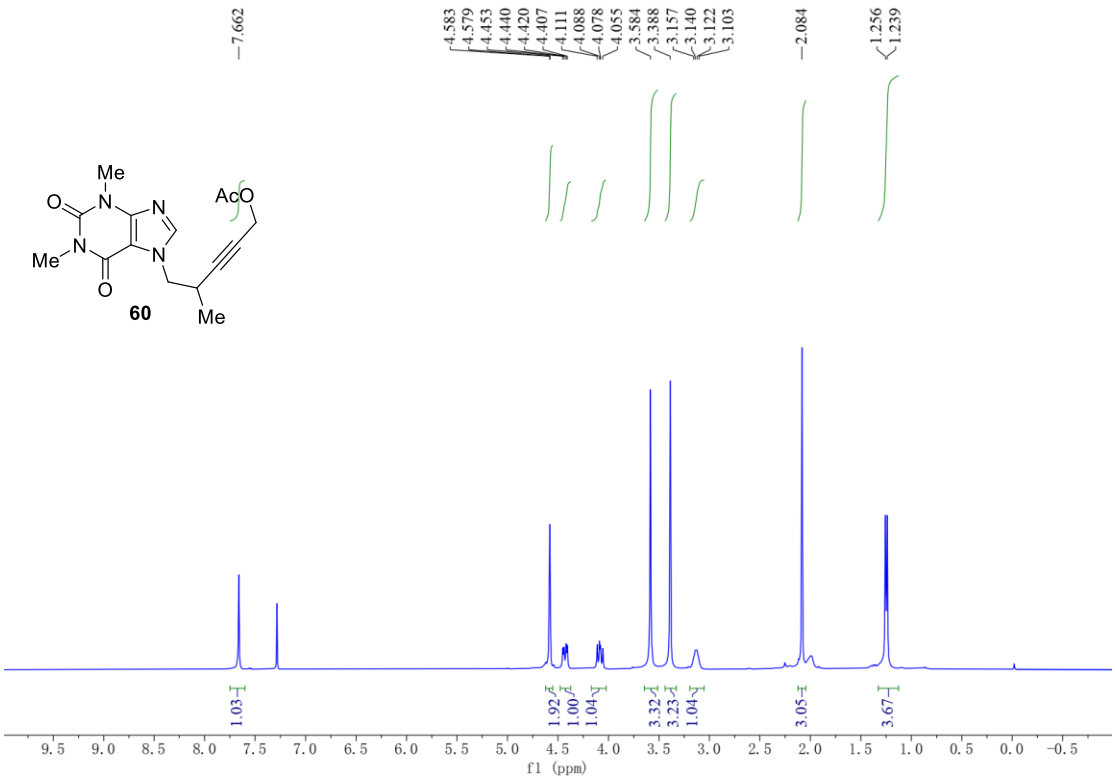
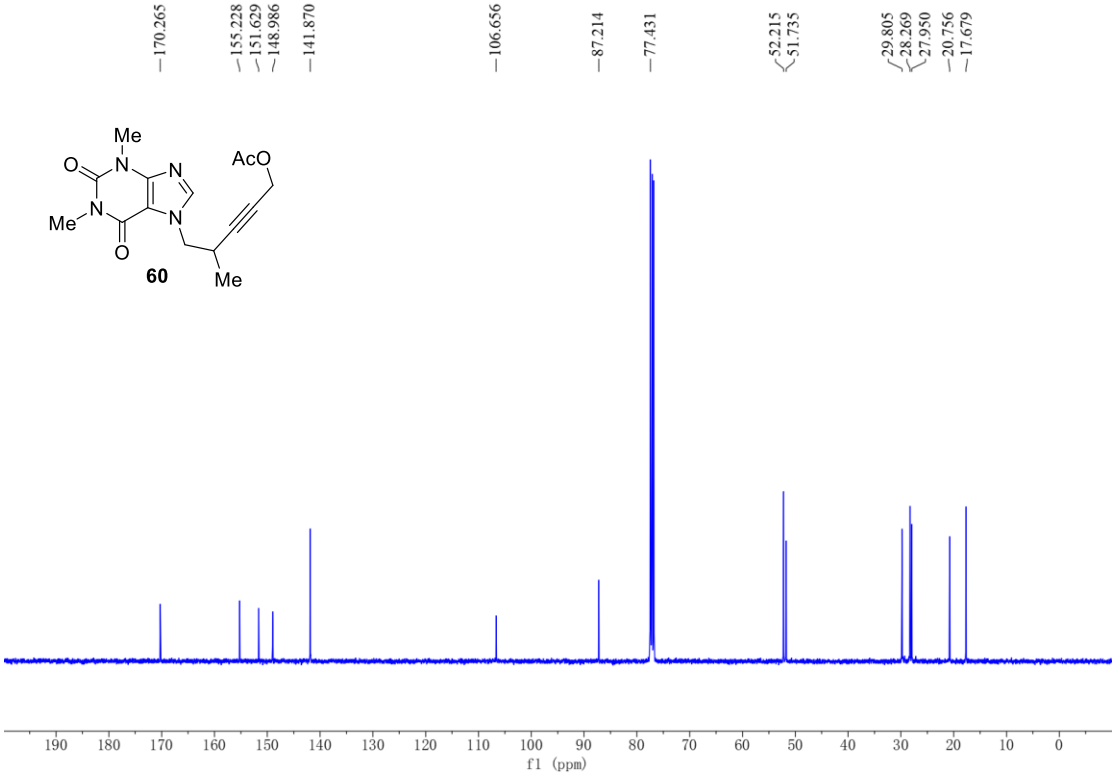
4.752
4.736
4.721
4.661
4.655
4.649
4.350
4.337
4.325
4.313
4.300
4.215
4.042
2.820
2.786
2.753
2.332
2.320
2.211
2.205
2.200
2.195
2.189
2.184
2.094
2.018
2.013
2.001
1.997
1.989
1.979
1.974
1.963
1.956
1.662
1.644
1.633
1.625
1.609
1.590
1.580
1.573
1.560
1.560
1.545
1.541
1.525
1.509
1.214
1.211
1.199
1.196
0.926
0.923
0.908
0.904
0.889
0.885
O
Me
N
O
Me
OAc
58
1.18
2.00
3.07
1.20
2.03
3.24
1.15
8.69
3.18
3.46
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


170.387
155.614
87.113
87.054
73.978
73.970
72.914
72.847
52.803
50.006
49.957
38.893
29.112
29.075
28.869
28.816
25.495
20.828
19.823
19.769
19.098
16.029
15.981
9.775
O
Me
N
O
Me
OAc
58
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4.638
4.634
4.224
4.223
4.201
4.140
2.884
2.861
2.841
2.819
2.800
2.796
2.791
2.078
1.971
1.963
1.952
1.914
1.802
1.791
1.741
1.718
1.622
1.606
1.587
1.568
1.462
NBoc
AcO
59
2.00
2.04
1.00
3.03
2.04
3.92
1.99
9.24
f1 (ppm)


170.335
153.145
89.780
79.312
74.085
53.280
52.701
52.505
37.290
36.575
28.499
28.153
27.489
21.302
20.828
NBoc
AcO
59
f1 (ppm)


7.662
4.583
4.579
4.453
4.440
4.420
4.407
4.111
4.088
4.078
4.055
3.584
3.388
3.157
3.140
3.122
3.103
2.084
1.256
1.239
Me
O
N
N
Me
N
O
AcO
Me
60
1.03
1.92
1.00
1.04
3.32
3.23
1.04
3.05
3.67
f1 (ppm)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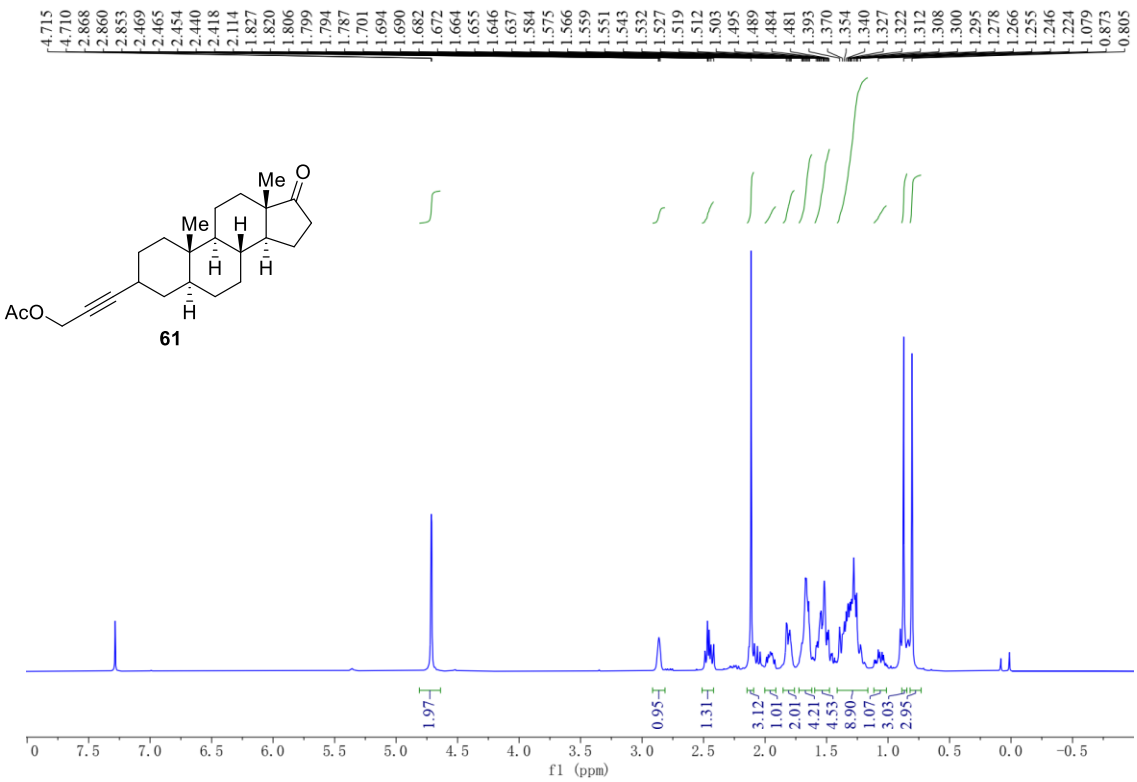
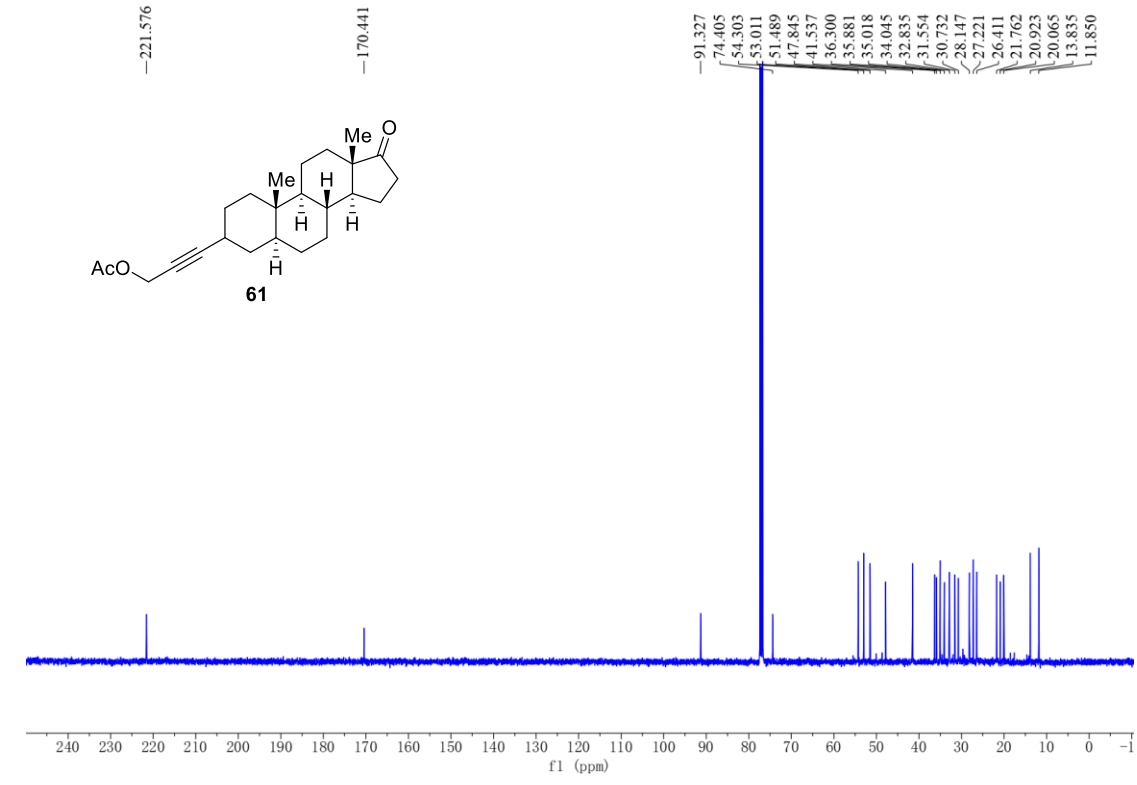
155.228
151.629
148.986
141.870
106.656
87.214
77.431
52.215
51.735
29.805
28.269
27.950
20.756
17.679
Me
O
N
N
Me
N
O
AcO
Me
60
f1 (ppm)


4.715
4.710
2.868
2.860
2.853
2.469
2.465
2.454
2.440
2.418
2.114
1.827
1.820
1.806
1.799
1.794
1.787
1.701
1.694
1.690
1.682
1.672
1.664
1.655
1.646
1.637
1.584
1.575
1.566
1.559
1.551
1.543
1.532
1.527
1.519
1.512
1.503
1.495
1.489
1.484
1.481
1.393
1.370
1.354
1.340
1.327
1.322
1.312
1.308
1.300
1.295
1.278
1.266
1.255
1.246
1.224
1.079
0.873
0.805
Me
O
Me
H
H
H
H
AcO
61
1.97
0.95
1.31
3.12
1.01
2.01
4.21
4.53
8.90
1.07
3.03
2.95
f1 (ppm)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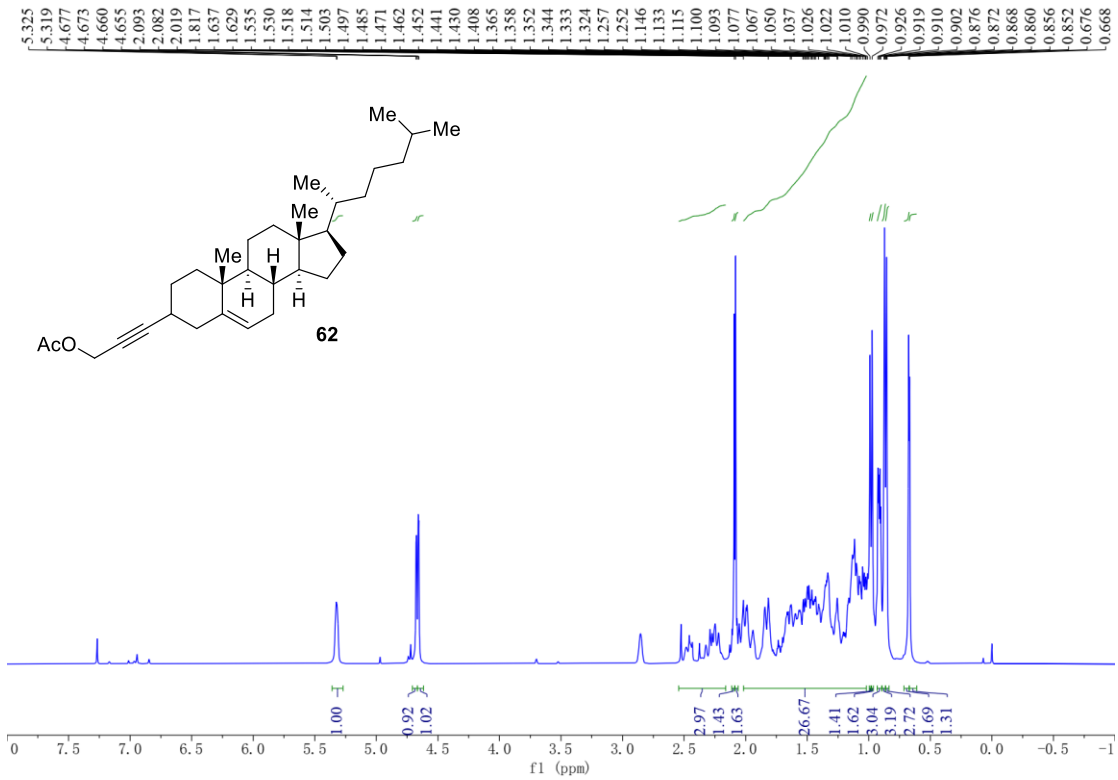
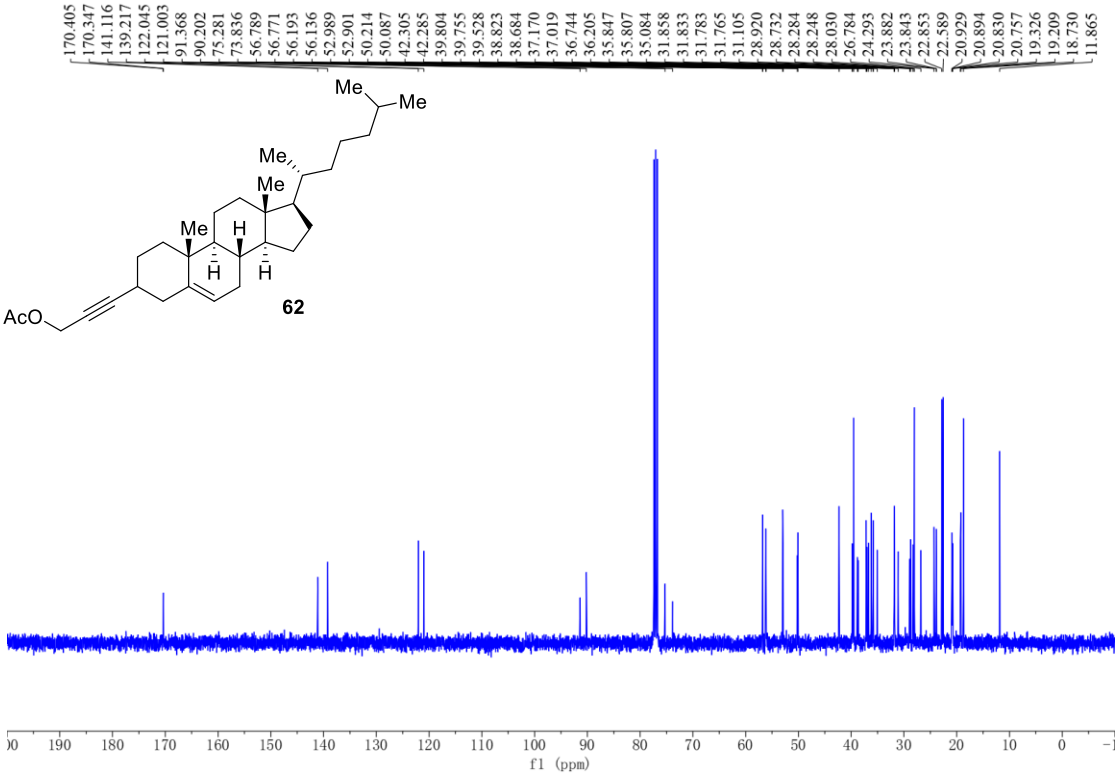
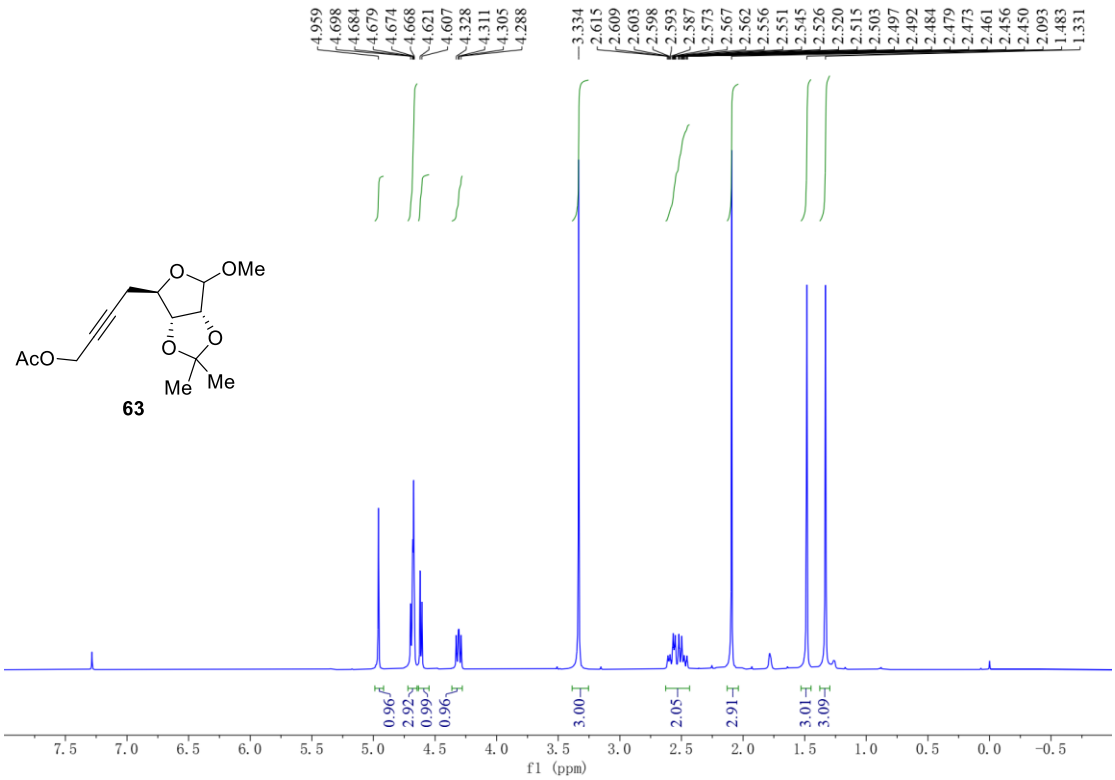
170.441
91.327
74.405
54.303
53.011
51.489
47.845
41.537
36.300
35.881
35.018
34.045
32.835
31.554
30.732
28.147
27.221
26.411
21.762
20.923
20.065
13.835
11.850
Me
O
Me
H
H
H
H
AcO
61
f1 (ppm)


5.325 5.319 4.677 4.673 4.660 4.655 2.093 2.082 2.019 1.817 1.637 1.629 1.535 1.530 1.518 1.514 1.503 1.497 1.485 1.471 1.462 1.452 1.441 1.430 1.408 1.365 1.358 1.352 1.344 1.333 1.324 1.257 1.252 1.146 1.133 1.115 1.100 1.093 1.077 1.067 1.050 1.037 1.026 1.022 1.010 0.990 0.972 0.926 0.919 0.910 0.902 0.876 0.872 0.868 0.860 0.856 0.852 0.676 0.668
Me
Me
Me
Me
H
H
H
AcO
62
1.00 0.92 1.02 2.97 1.43 1.63 26.67 1.41 1.62 3.04 3.19 2.72 1.69 1.31
f1 (ppm)


170.405 170.347 141.116 139.217 122.045 121.003 91.368 90.202 75.281 73.836 56.789 56.771 56.193 56.136 52.989 52.901 50.214 50.087 42.305 42.285 39.804 39.755 39.528 38.823 38.684 37.170 37.019 36.744 36.205 35.847 35.807 35.084 31.858 31.833 31.783 31.765 31.105 28.920 28.732 28.284 28.248 28.030 26.784 24.293 23.882 23.843 22.853 22.589 20.929 20.894 20.830 20.757 19.326 19.209 18.730 11.865
Me
Me
Me
Me
H
H
H
AcO
62
f1 (ppm)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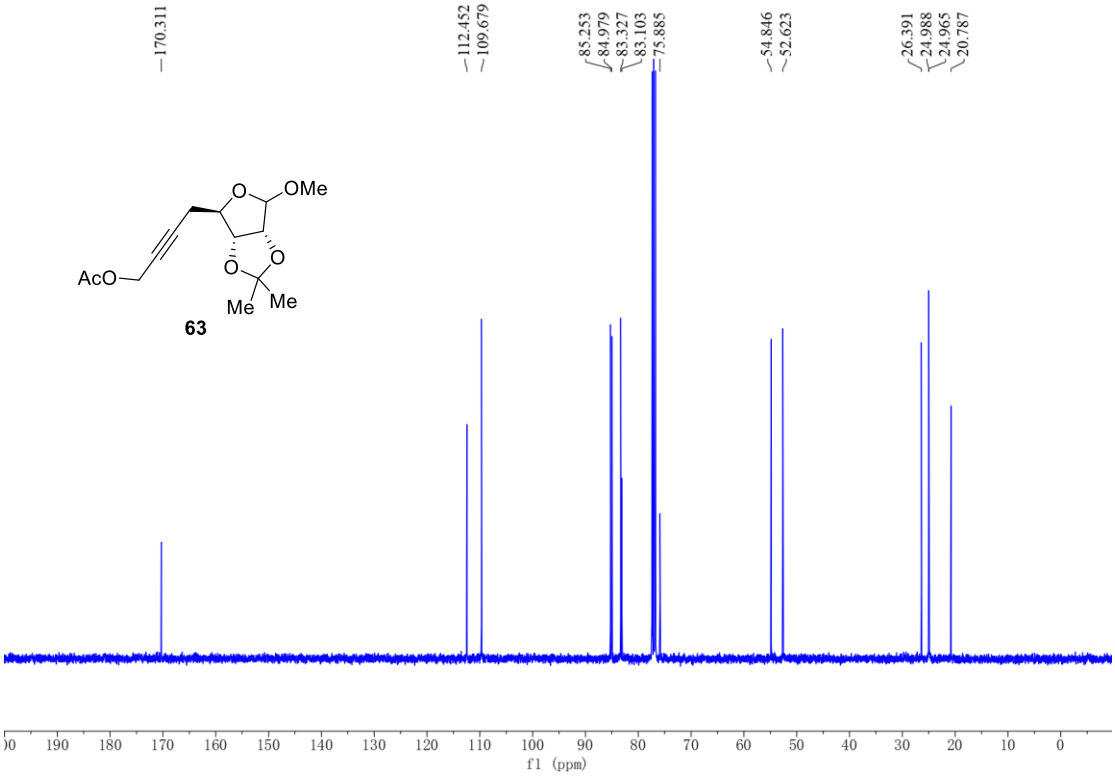
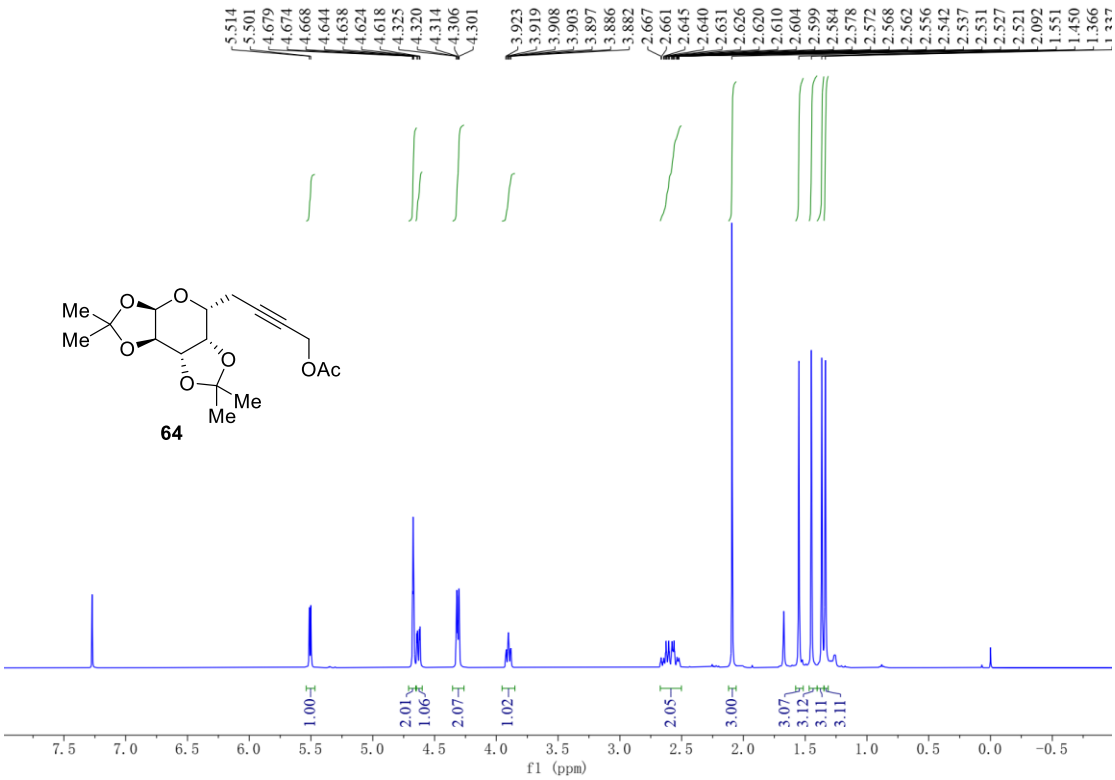
4.684
4.679
4.674
4.668
4.621
4.607
4.328
4.311
4.305
4.288
3.334
2.615
2.609
2.603
2.598
2.593
2.587
2.573
2.567
2.562
2.556
2.551
2.545
2.526
2.520
2.515
2.503
2.497
2.492
2.484
2.479
2.473
2.461
2.456
2.450
2.093
1.483
1.331
OMe
O
O
O
AcO
Me
Me
63
0.96
2.92
0.99
0.96
3.00
2.05
2.91
3.01
3.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


170.311
112.452
109.679
85.253
84.979
83.327
83.103
75.885
54.846
52.623
26.391
24.988
24.965
20.787
OMe
O
O
O
AcO
Me
Me
63
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


5.514
5.501
4.679
4.674
4.668
4.644
4.638
4.624
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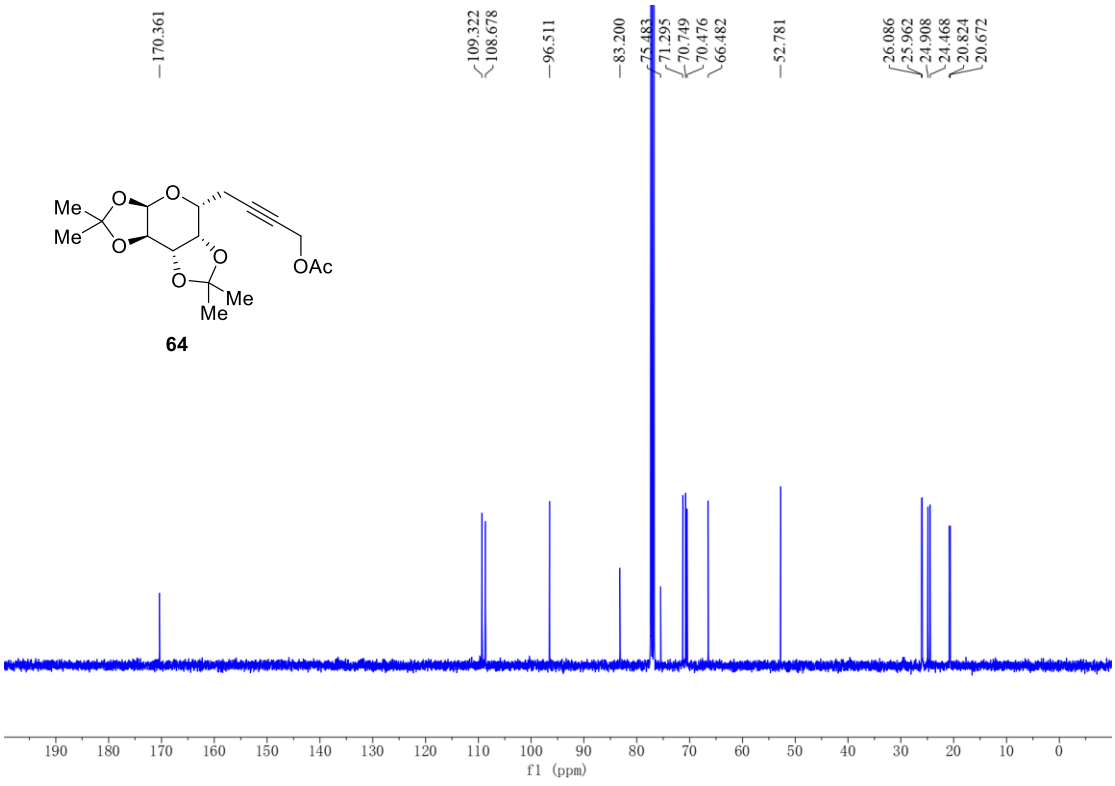
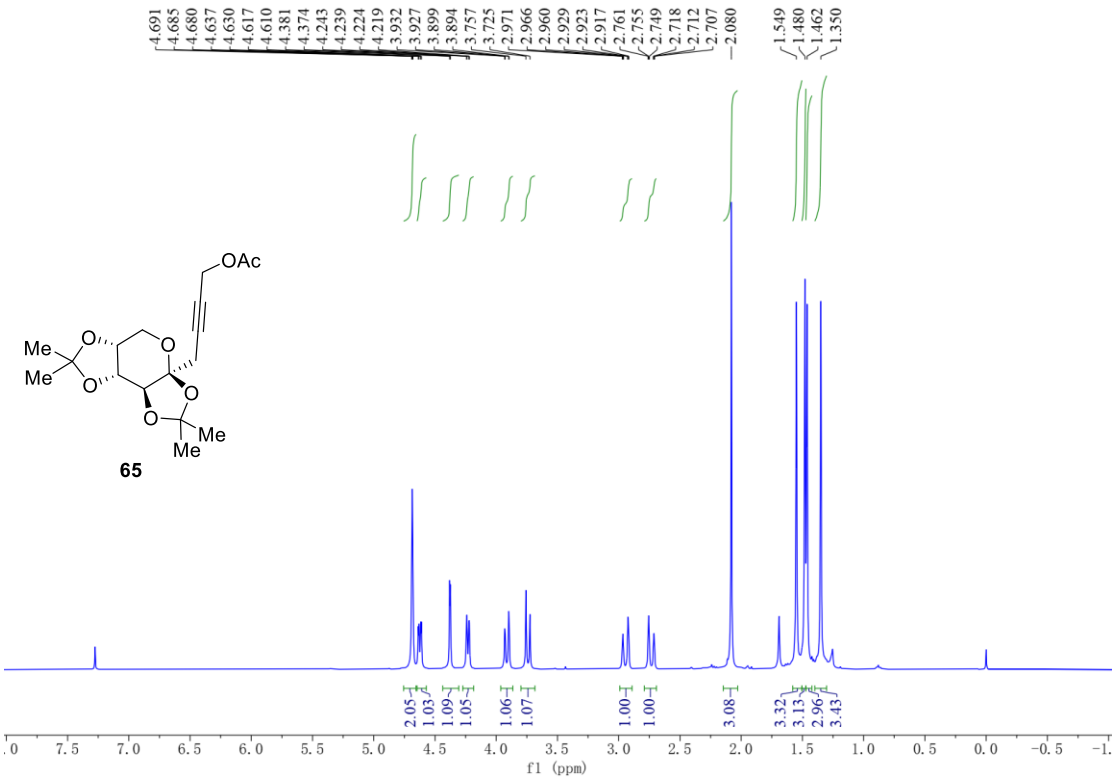
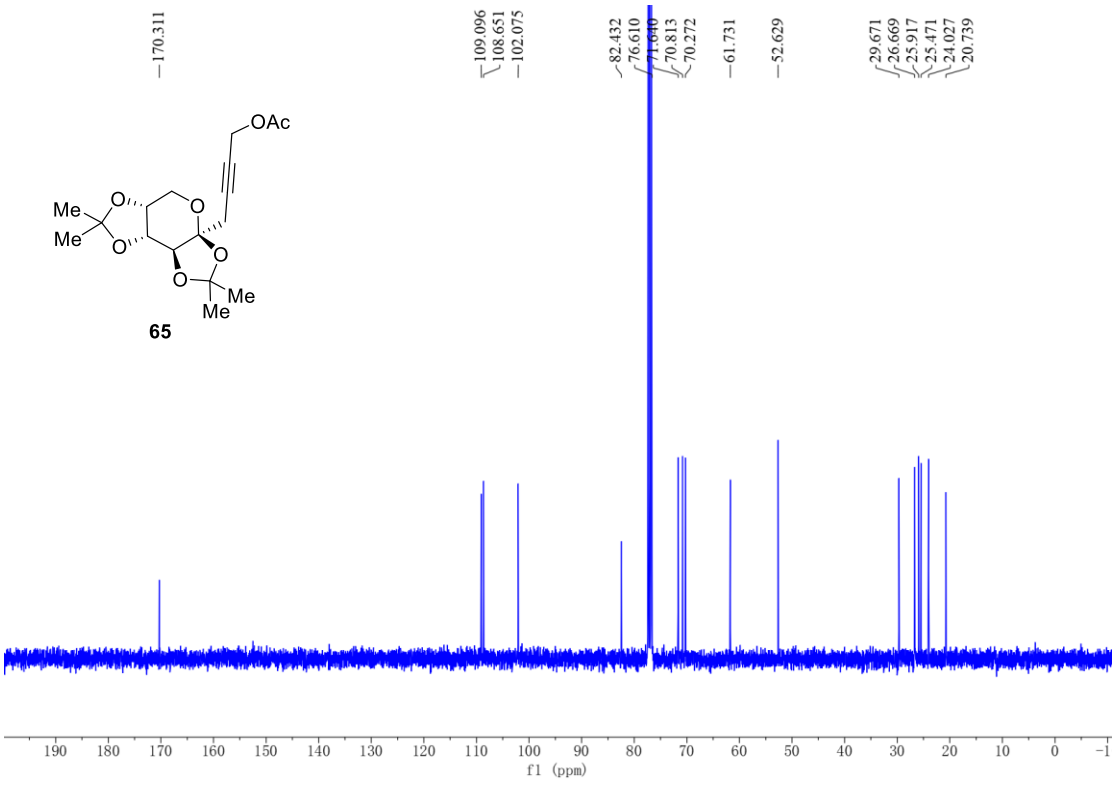
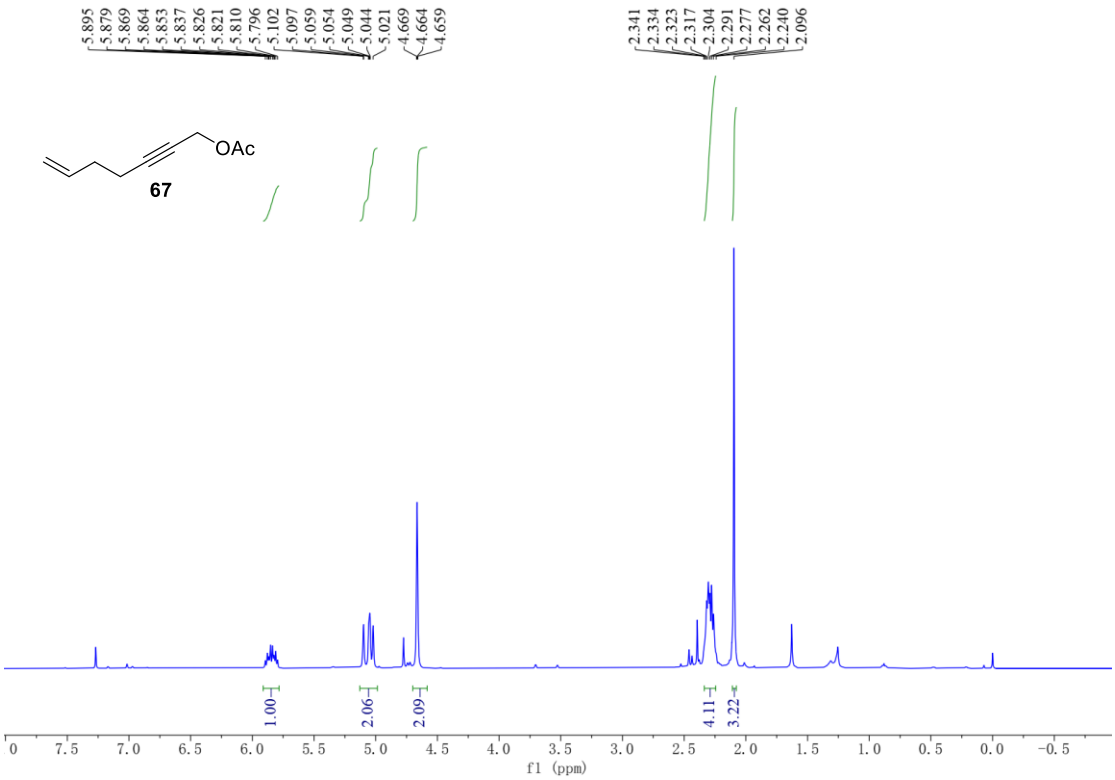
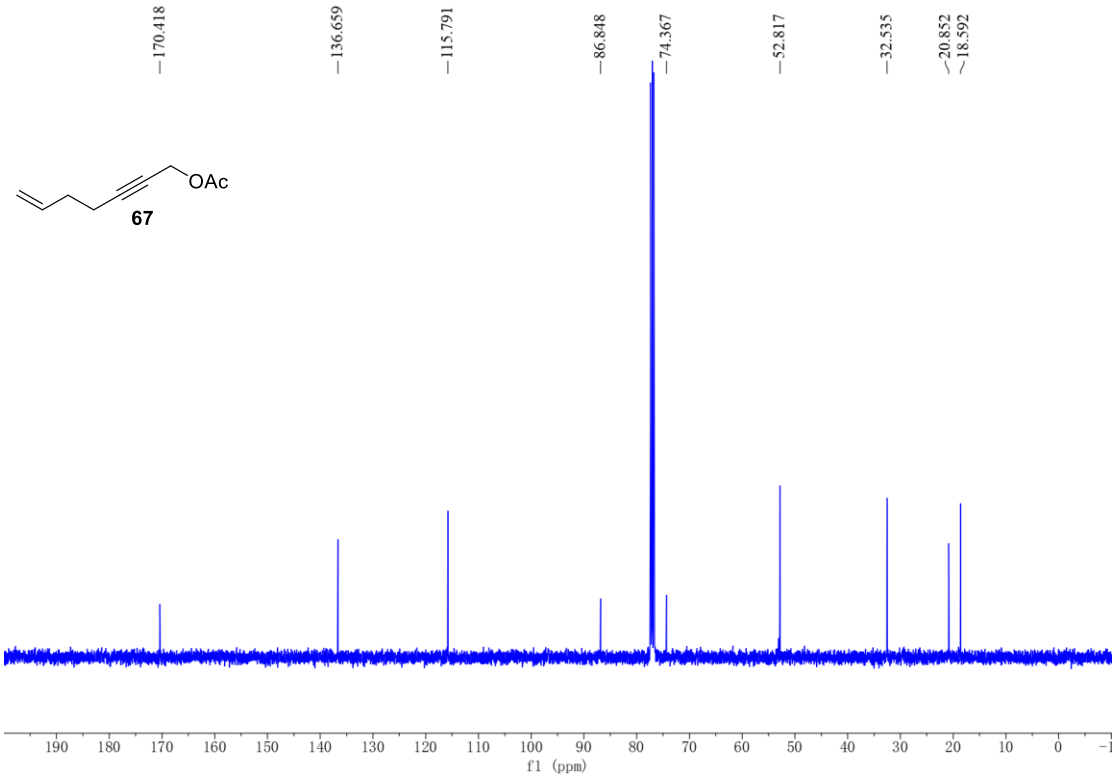
4.325
4.320
4.314
4.306
4.301
3.923
3.919
3.908
3.903
3.897
3.886
3.882
2.667
2.661
2.645
2.640
2.631
2.626
2.620
2.610
2.604
2.599
2.584
2.578
2.572
2.568
2.562
2.556
2.542
2.537
2.531
2.527
2.521
2.092
1.551
1.450
1.366
Me
Me
O
O
O
O
O
Me
Me
OAc
64
1.00
2.01
1.06
2.07
1.02
2.05
3.00
3.07
3.12
3.11
3.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


170.361
109.322
108.678
96.511
83.200
75.483
71.295
70.749
70.476
66.482
52.781
26.086
25.962
24.908
24.468
20.824
20.672
Me
Me
O
O
O
O
O
Me
Me
OAc
64
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4.691
4.685
4.680
4.637
4.630
4.617
4.610
4.381
4.374
4.243
4.239
4.224
4.219
3.932
3.927
3.899
3.894
3.757
3.725
2.971
2.966
2.960
2.929
2.923
2.917
2.761
2.755
2.749
2.718
2.712
2.707
2.080
1.549
1.480
1.462
1.350
OAc
Me
Me
O
O
O
O
O
Me
Me
65
2.05
1.03
1.09
1.05
1.06
1.07
1.00
1.00
3.08
3.32
3.13
2.96
3.43
f1 (ppm)


170.311
109.096
108.651
102.075
82.432
76.610
71.840
70.813
70.272
61.731
52.629
29.671
26.669
25.917
25.471
24.027
20.739
OAc
Me
Me
O
O
O
O
O
Me
Me
65
f1 (ppm)


5.895
5.879
5.869
5.864
5.853
5.837
5.826
5.821
5.810
5.796
5.102
5.097
5.059
5.054
5.049
5.044
5.021
4.669
4.664
4.659
2.341
2.334
2.323
2.317
2.304
2.291
2.277
2.262
2.240
2.096
OAc
67
1.00
2.06
2.09
4.11
3.22
f1 (ppm)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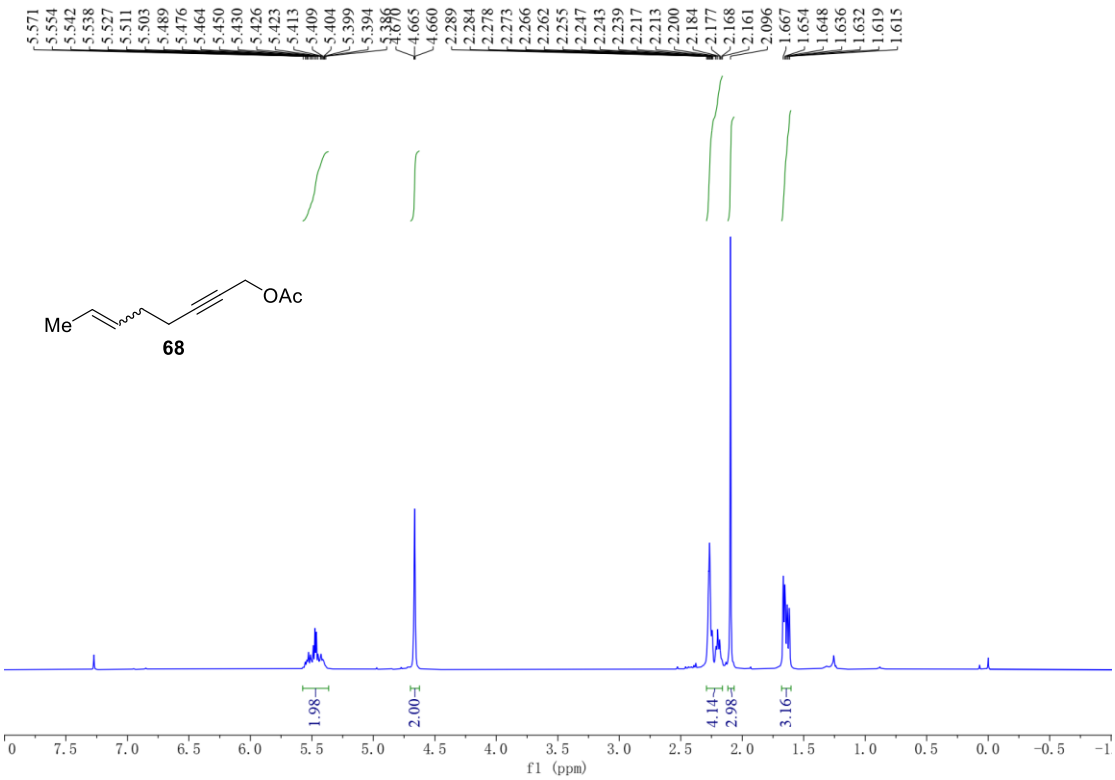
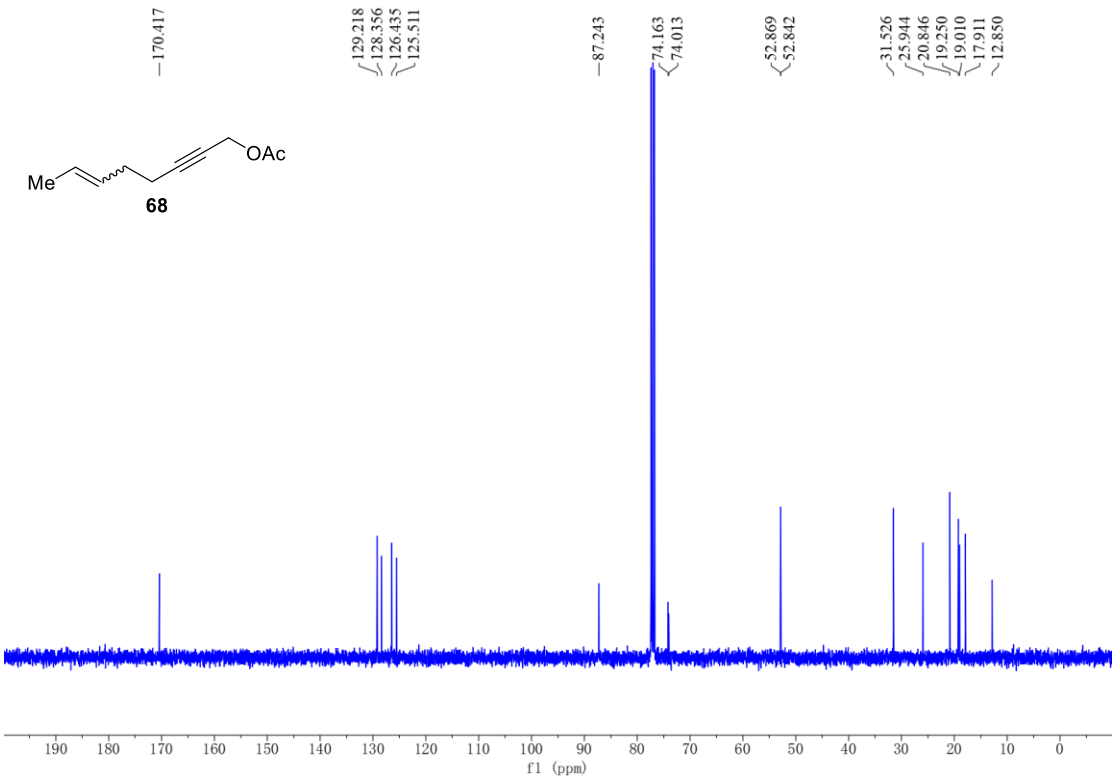
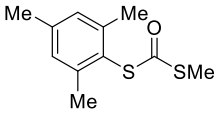
136.659
115.791
86.848
74.367
52.817
32.535
20.852
18.592
OAc
67
f1 (ppm)

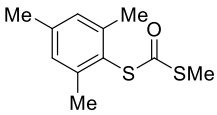

5.571
5.554
5.542
5.538
5.527
5.511
5.503
5.489
5.476
5.464
5.450
5.430
5.426
5.423
5.413
5.409
5.404
5.399
5.394
4.670
4.665
4.660
2.289
2.284
2.278
2.273
2.266
2.262
2.255
2.247
2.243
2.239
2.217
2.213
2.200
2.184
2.177
2.168
2.161
2.096
1.667
1.654
1.648
1.636
1.632
1.619
1.615
Me
OAc
68
1.98
2.00
4.14
2.98
3.16
f1 (ppm)


170.417
129.218
128.356
126.435
125.511
87.243
74.163
74.013
52.869
52.842
31.526
25.944
20.846
19.250
19.010
17.911
12.850
Me
OAc
68
f1 (ppm)


Me
Me
O
S
SMe
Me

69

7.001
2.403
2.321
2.309
2.00
6.16
3.02
3.01
f1 (ppm)


Me
Me
O
S
SMe
Me

69

190.405
143.648
141.036
129.474
123.169
21.868
21.287
13.442
f1 (ppm)