Supporting Information for

α,β-Alkynone Accelerated PPM Level Pd-Catalyzed Sonogashira Coupling Reaction

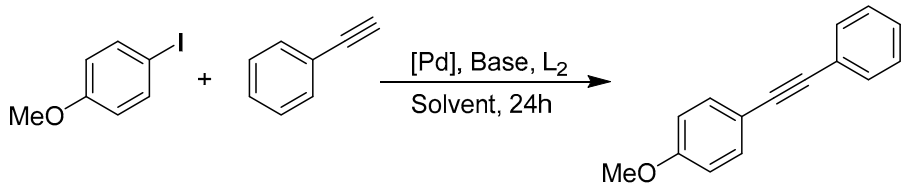
Meng Guo [1], Zhen Wei[1], Jianming Yang[2], Zunyuan Xie* [1] and Weiqiang Zhang [1,*]

[1] Key Laboratory of Applied Surface and Colloid Chemistry MOE, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, China
[2] Xi'an Modern Chemistry Research Institute, Xi'an 710065, China
* Correspondence: zyxie123@snnu.edu.cn, zwq@snnu.edu.cn

Table of Contents

1. Optimization of Reaction Conditions

Table S1 Trace-Pd catalyzed Sonogashira coupling reaction [ab]



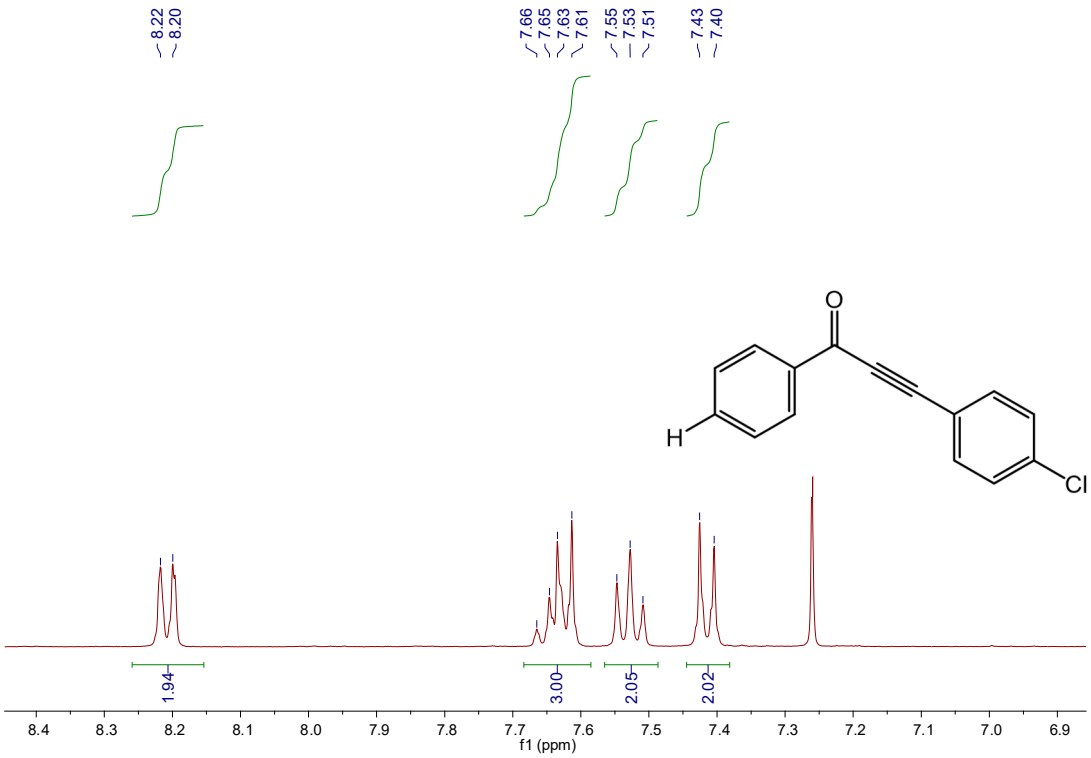
Entry [a]	$PdCl_2$ (ppm)	Base (eq.)	Solvent	T (℃)	Yields (%)[b]
1	0.1	K_2CO_3	EtOH	80	N.D
2	2	K_2CO_3	EtOH	80	8
3	5	K_2CO_3	EtOH	80	32
4	10	K_2CO_3	EtOH	80	31
5	5	Cs_2CO_3	EtOH	80	trace
6	5	Na_2CO_3	EtOH	80	N.D
7	5	Na_2OAc	EtOH	80	N.D
8	5	NaOH	EtOH	80	N.D
9	5	KOH	EtOH	80	N.D
10	5	Et_3N	EtOH	80	trace
11	5	K_2CO_3	EtOH	90	59
12	5	K_2CO_3	EtOH	95	60
13	5	K_2CO_3	MeCN	90	N.D
14	5	K_2CO_3	DMF	90	N.D
15	5	K_2CO_3	DMSO	90	N.D
16	5	K_2CO_3	Water	90	trace
17	5	K_2CO_3	Water/ EtOH(v/v=1/1)	90	trace
18	5	K_2CO_3	MeOH	90	trace
19	5	K_2CO_3	IPA	90	trace
20	5	K_2CO_3	*t*-Butanol	90	N.D
21	5	K_2CO_3	EG	90	20

[a] Reaction conditions: 4-Iodoanisole (0.5 mmol), Phenylacetylene (0.6 mmol), L_2 (5 mol%), 24h, under air.

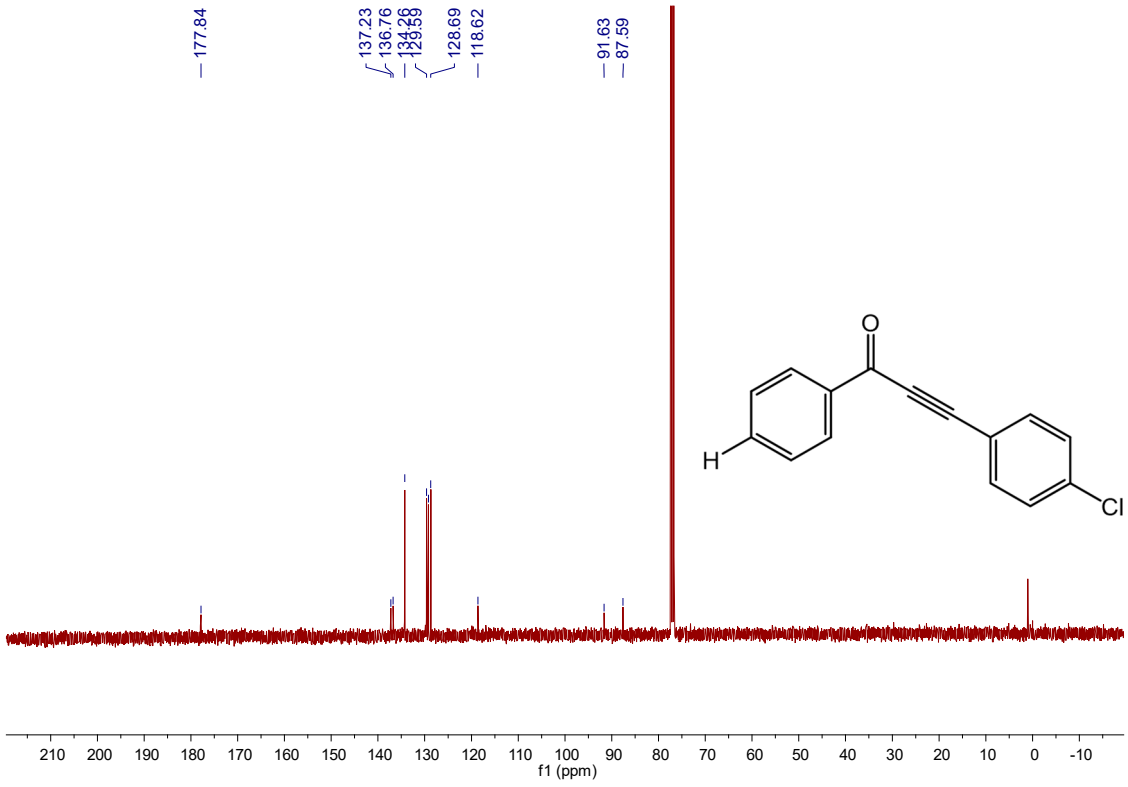
[b] Determined by ^{1}H NMR.

2. ^{1}H and ^{13}C-NMR Spectra for Ligands

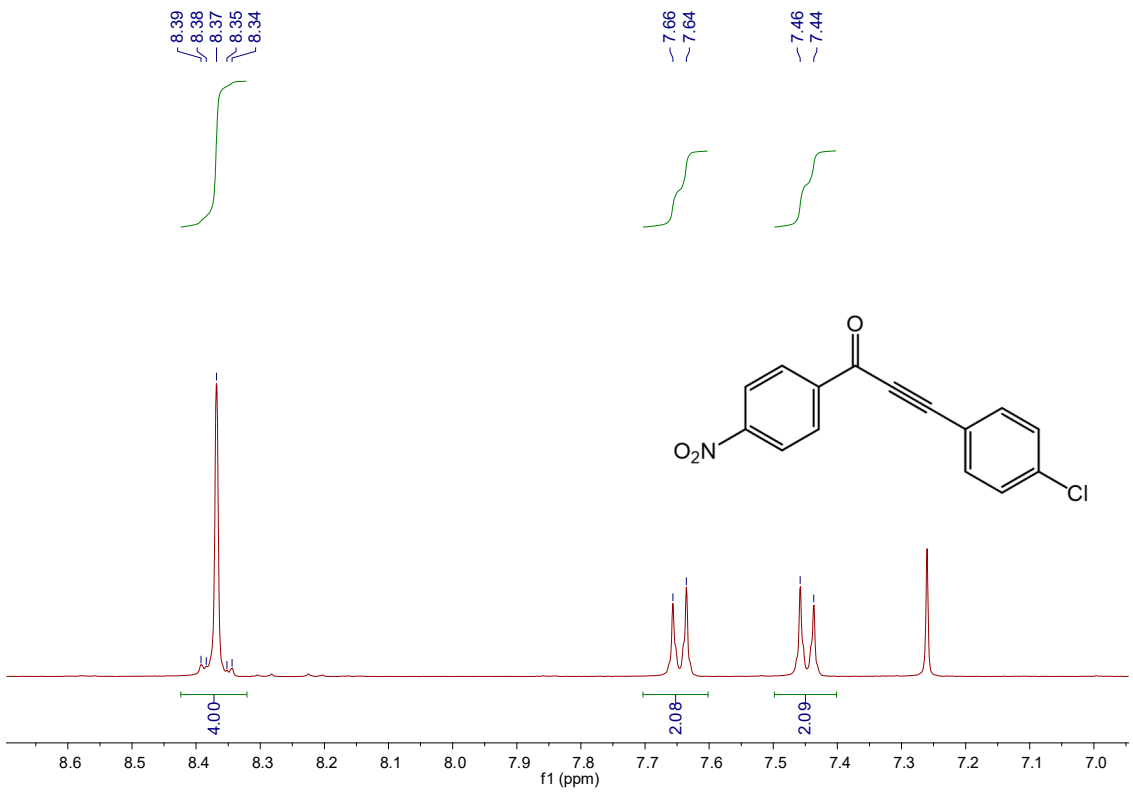
3-(4-chlorophenyl)-1-phenylprop-2-yn-1-one ^{1}H-NMR



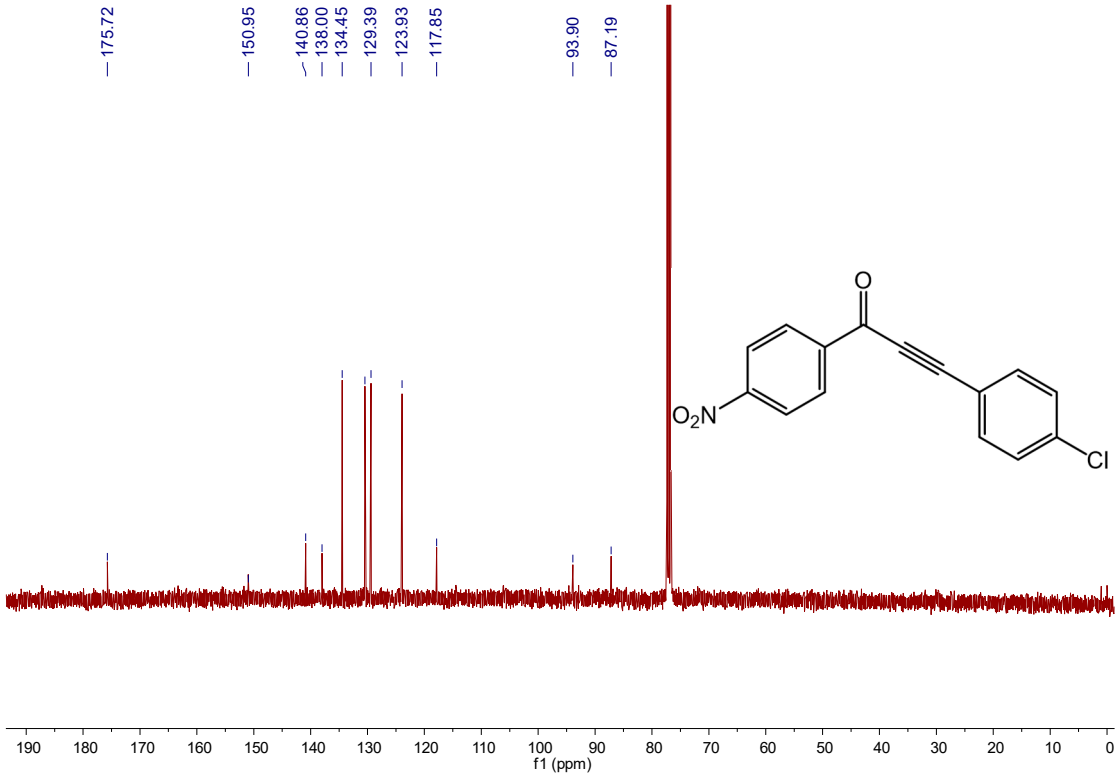
3-(4-chlorophenyl)-1-phenylprop-2-yn-1-one ^{13}C-NMR



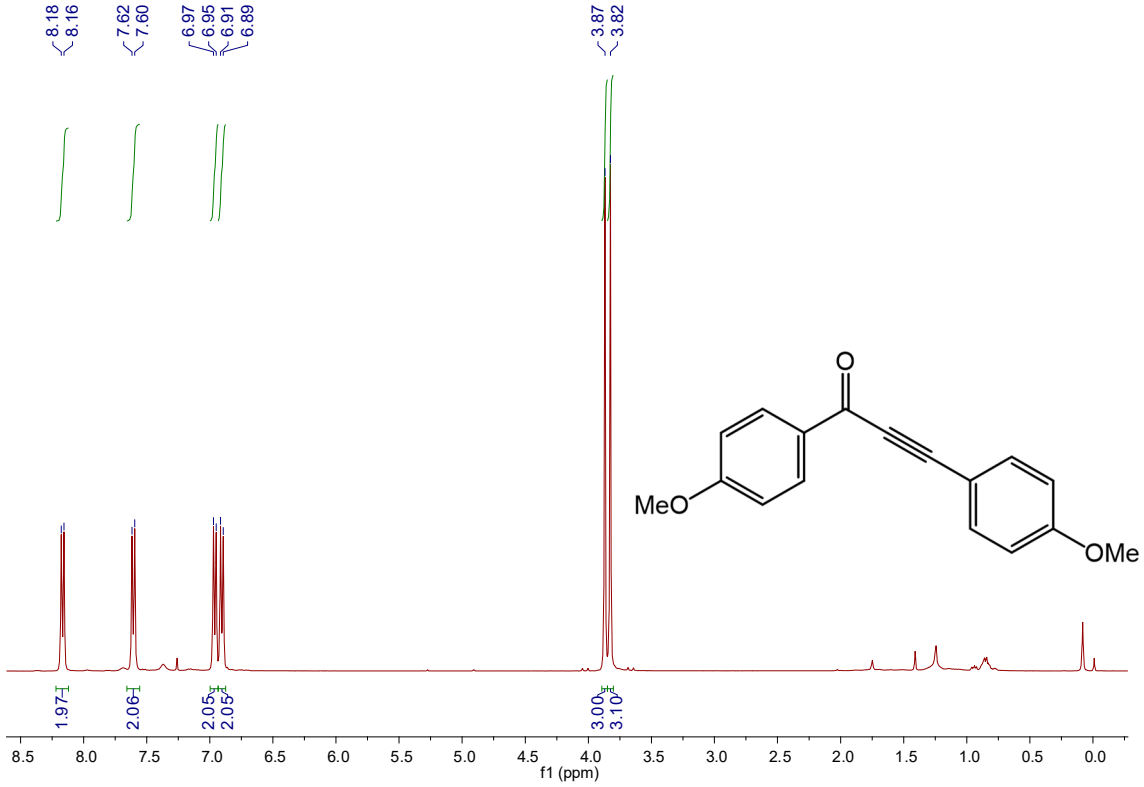
3-(4-chlorophenyl)-1-(4-nitrophenyl)prop-2-yn-1-one ^{1}H-NMR



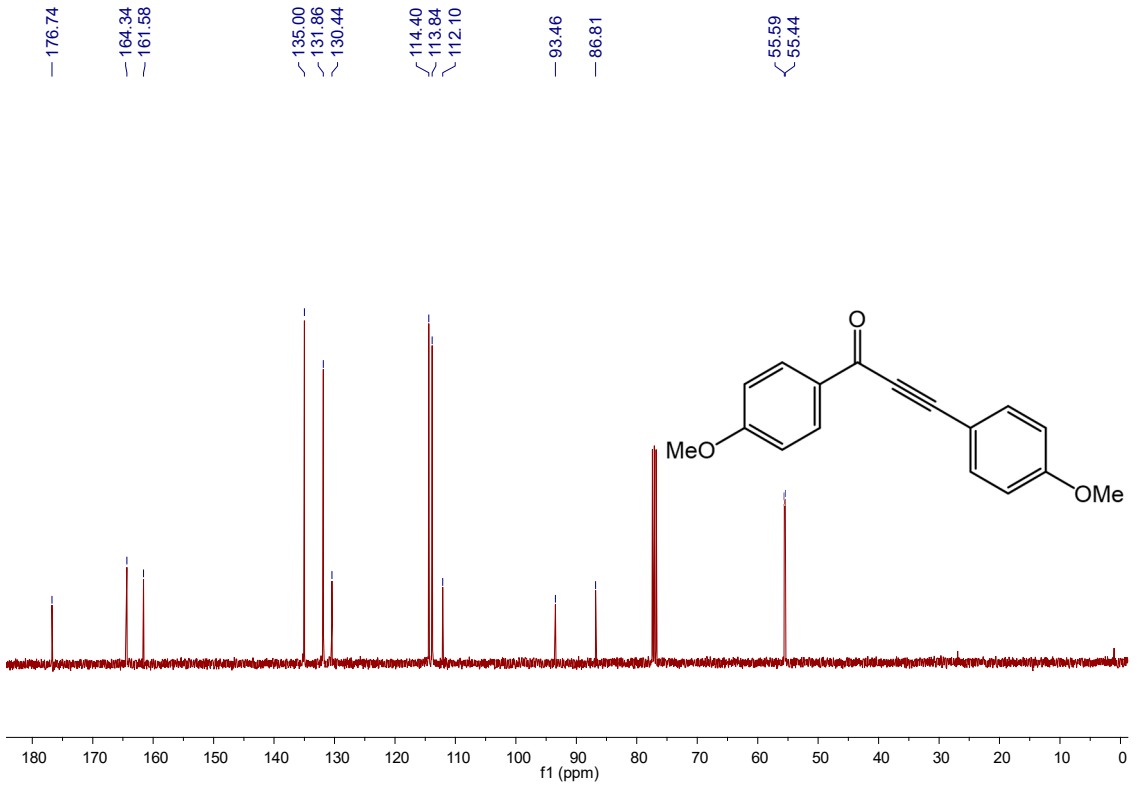
3-(4-chlorophenyl)-1-(4-nitrophenyl)prop-2-yn-1-one ^{13}C-NMR



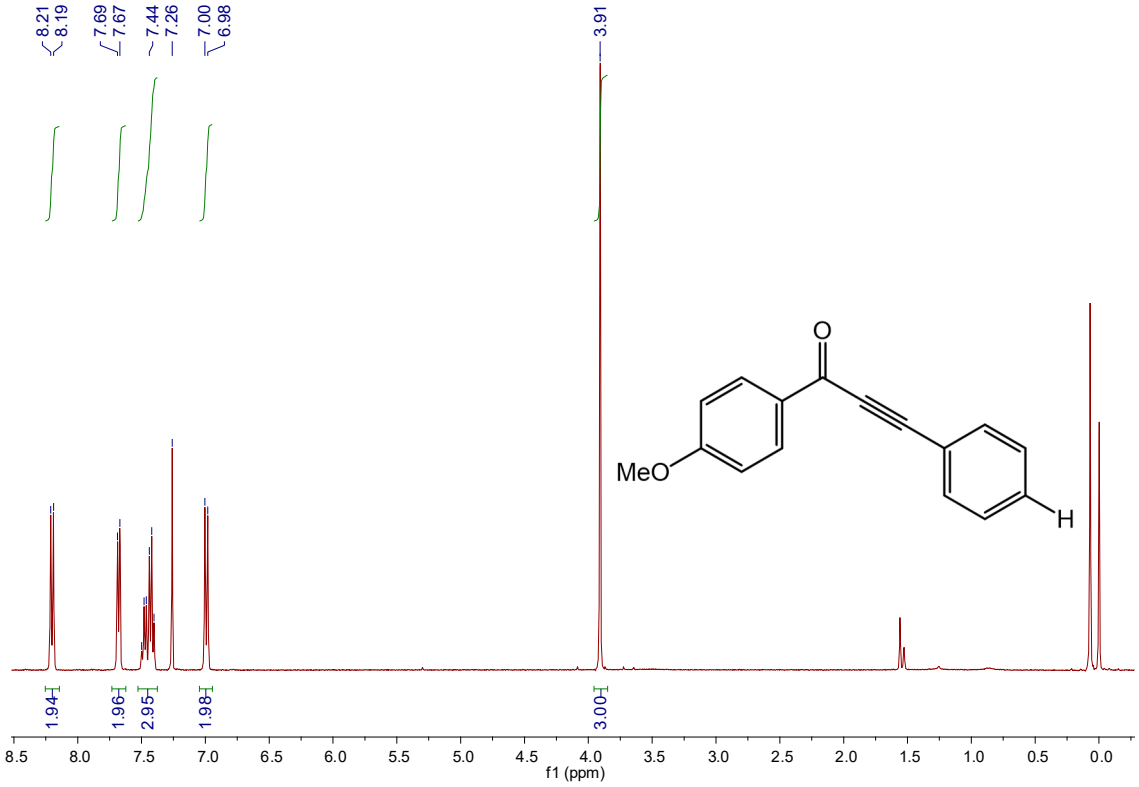
1,3-bis(4-methoxyphenyl)prop-2-yn-1-one ^{1}H-NMR



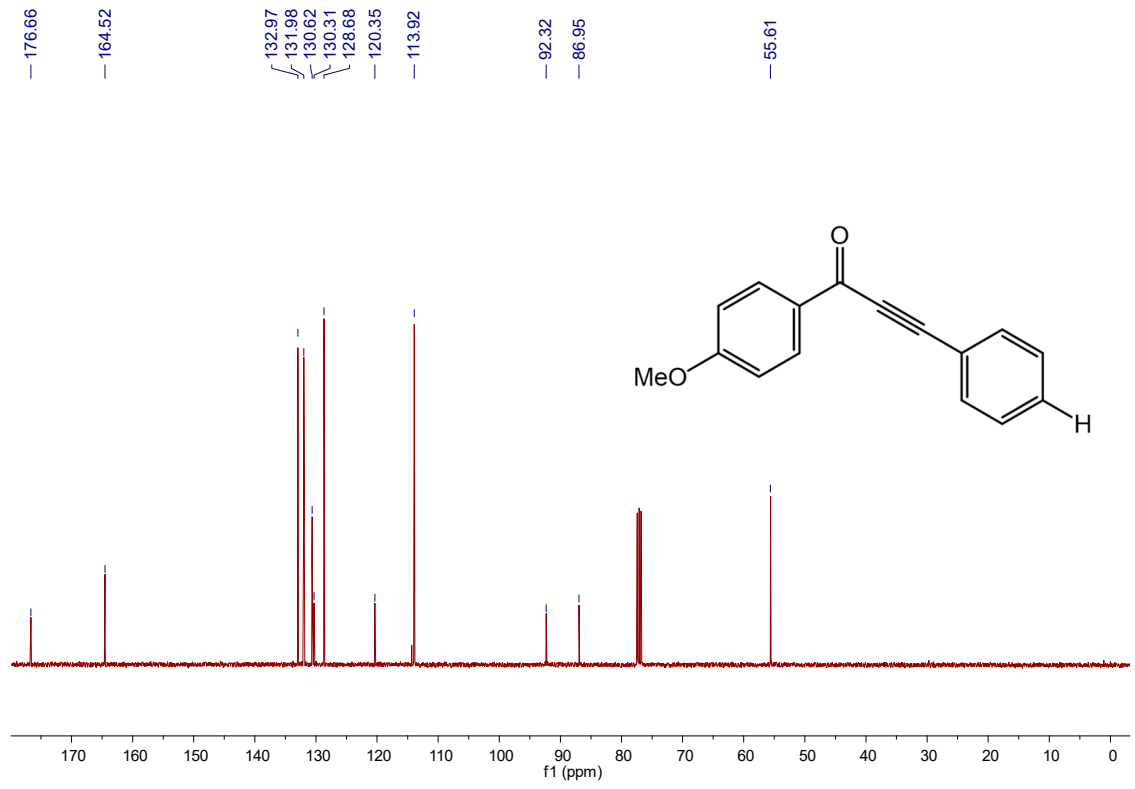
1,3-bis(4-methoxyphenyl)prop-2-yn-1-one ^{13}C-NMR



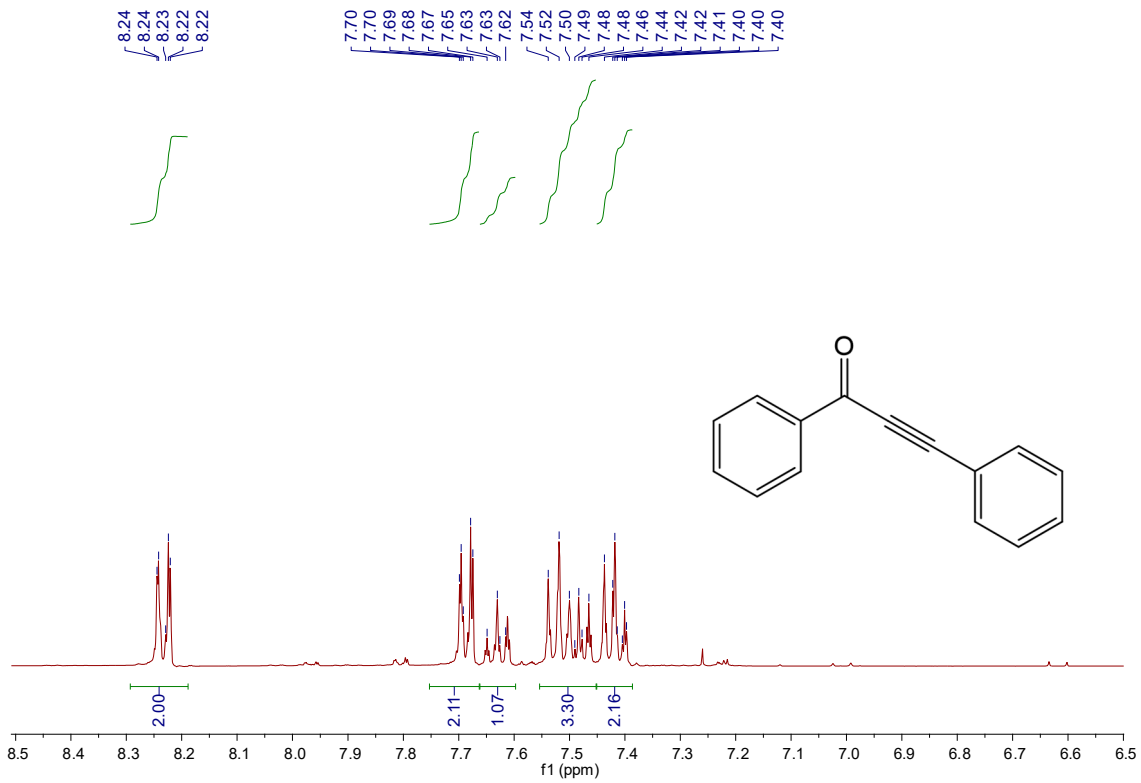
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one ^{1}H-NMR



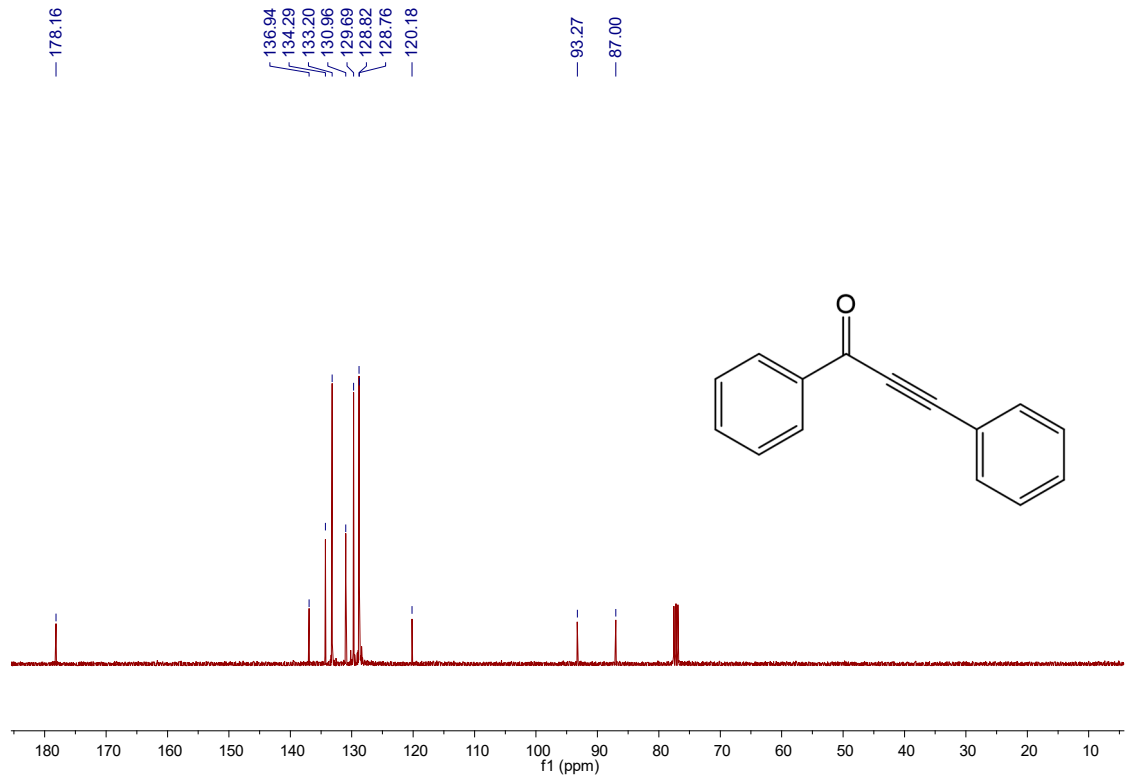
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one ^{13}C-NMR



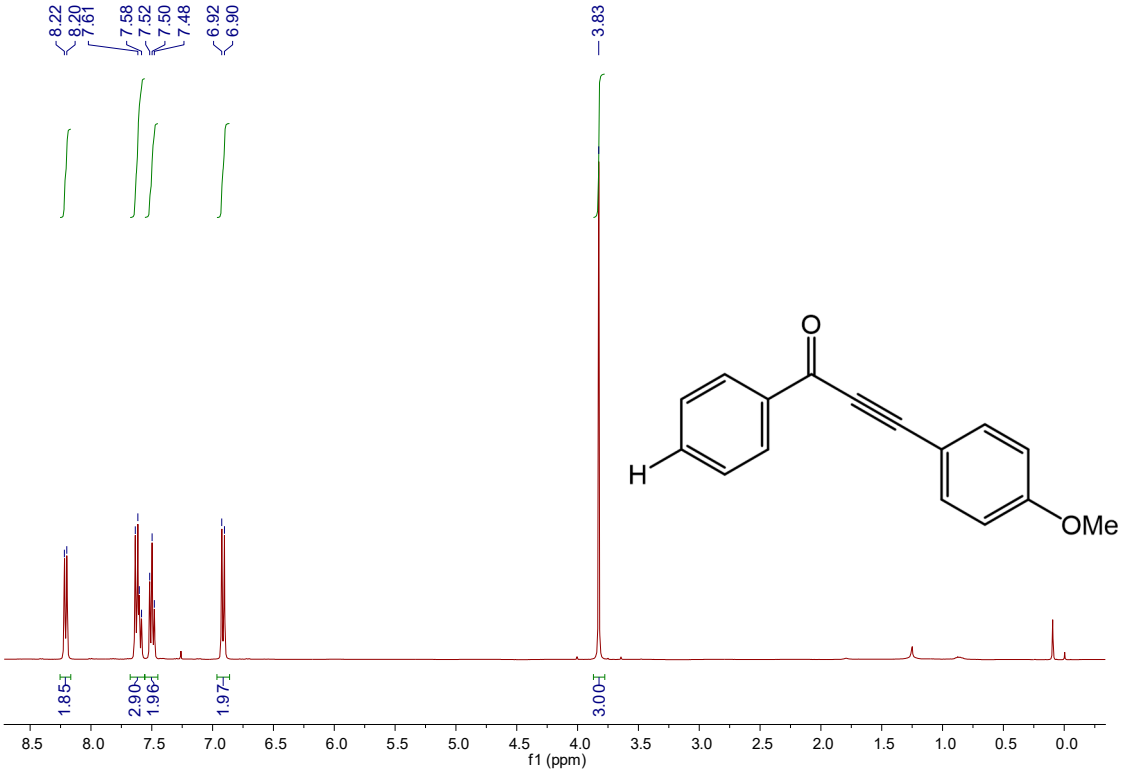
1,3-diphenylprop-2-yn-1-one ^{1}H-NMR



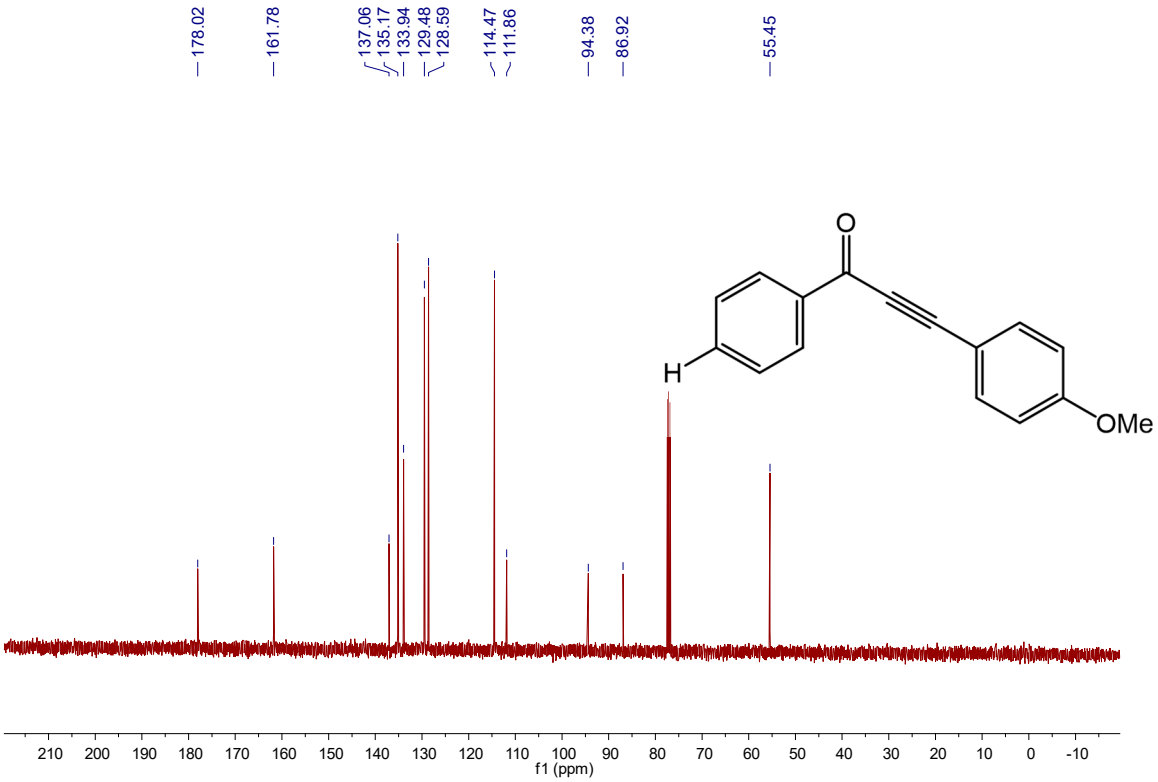
1,3-diphenylprop-2-yn-1-one ^{13}C-NMR



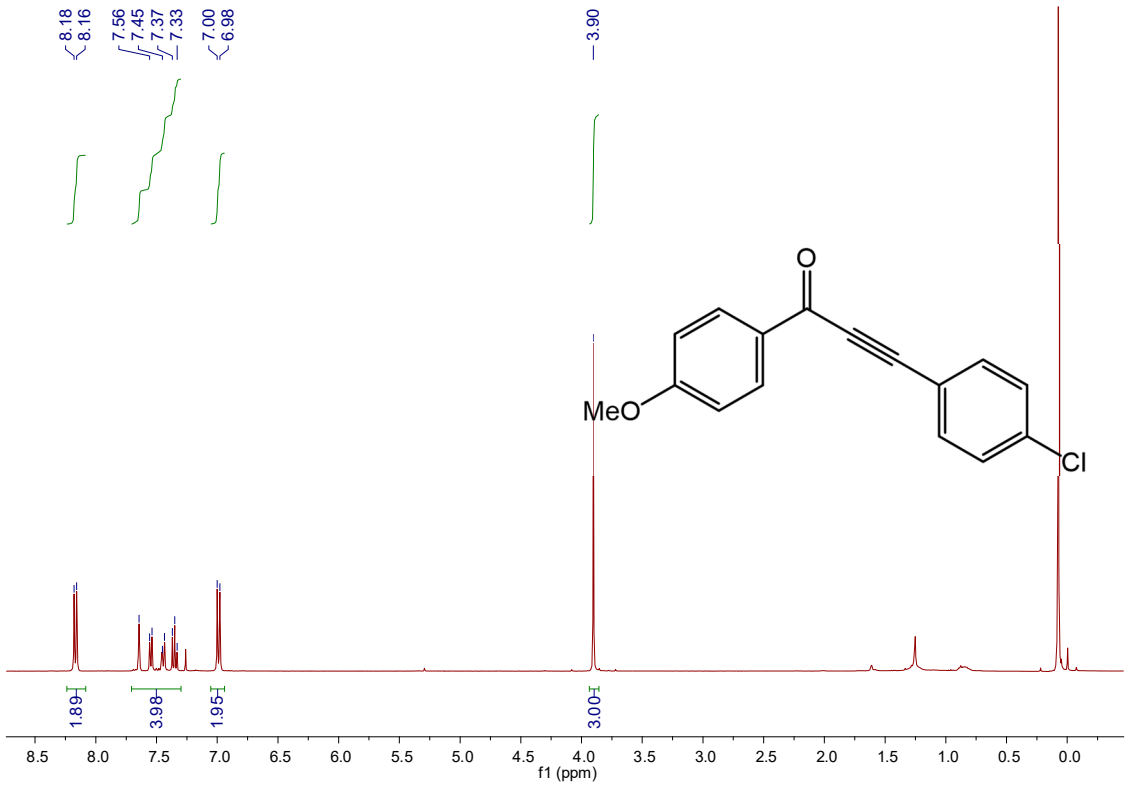
3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one ^{1}H-NMR



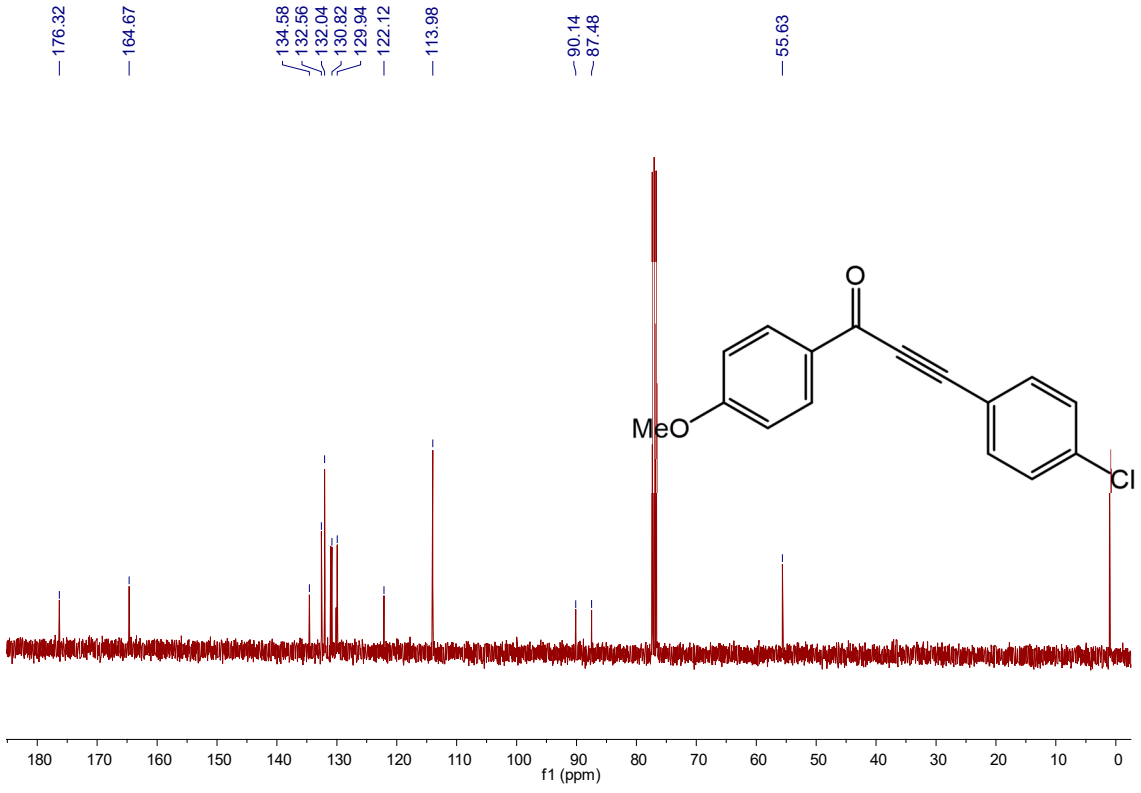
3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one ^{13}C-NMR



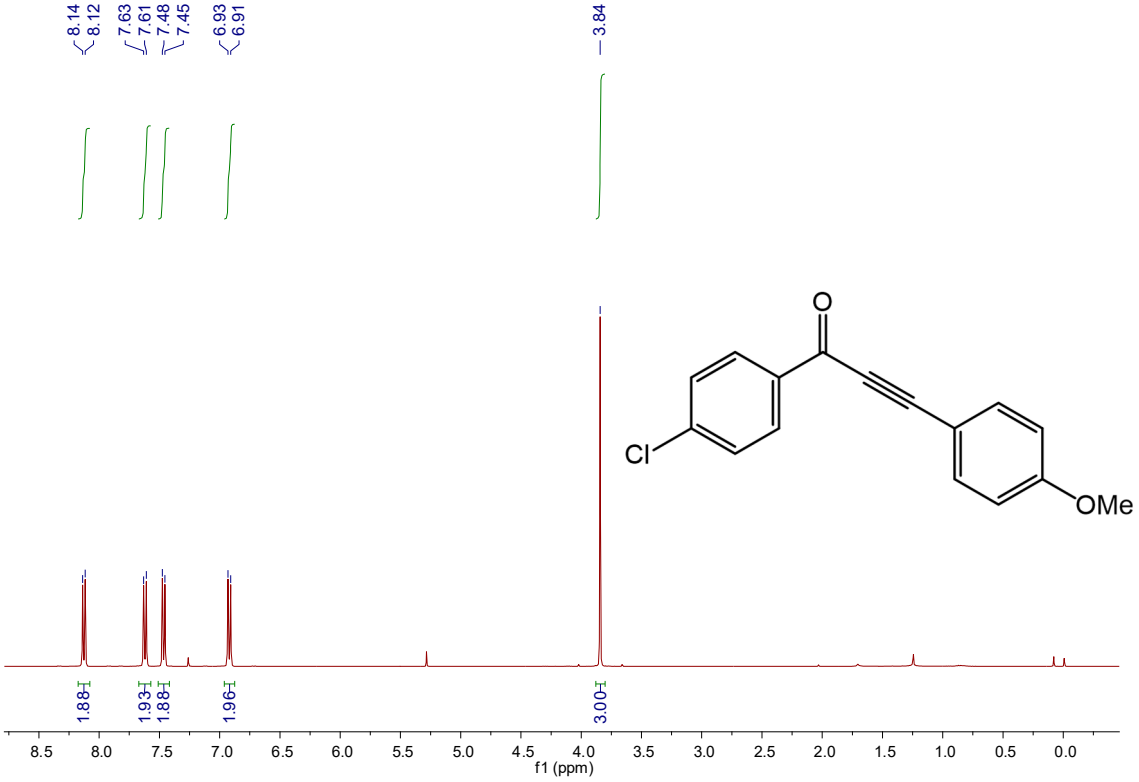
3-(4-chlorophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-one ^{1}H-NMR



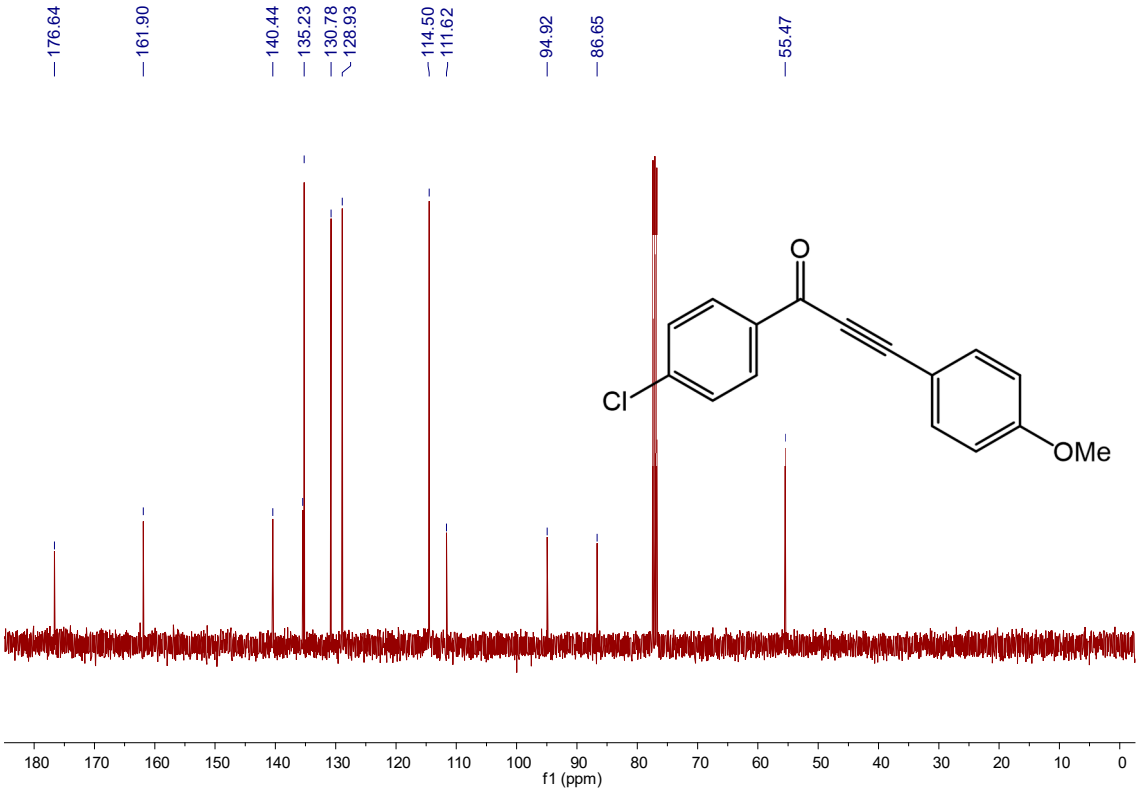
3-(4-chlorophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-one ^{13}C-NMR



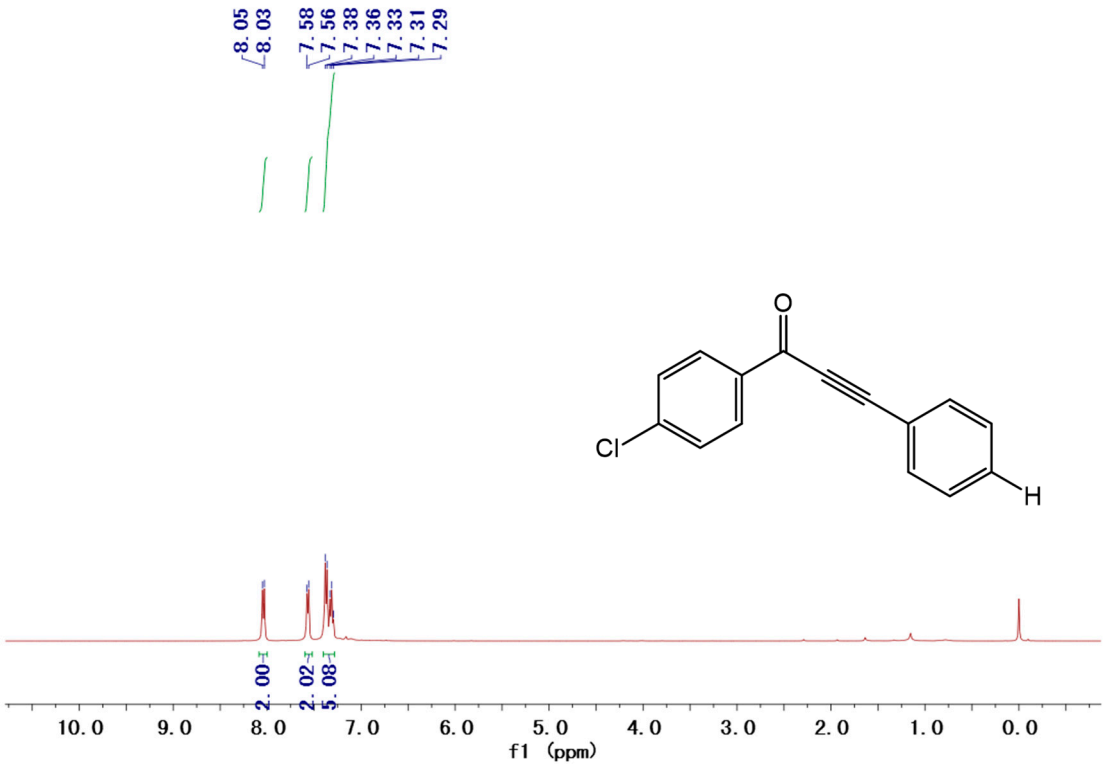
1-(4-chlorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one ^{1}H-NMR



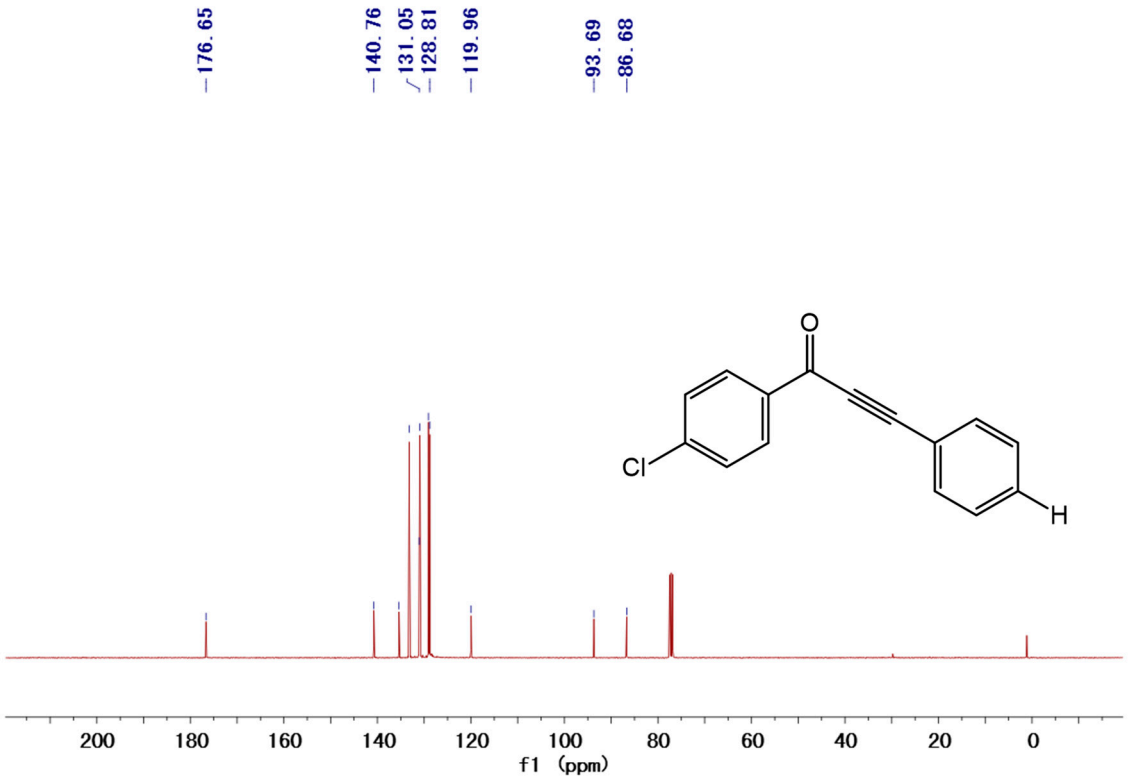
1-(4-chlorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one ^{13}C-NMR



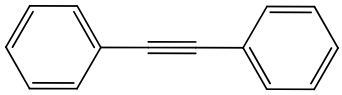
1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one ^{1}H-NMR



1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one ^{13}C-NMR

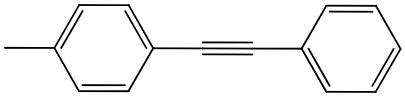


3. Spectroscopic Data for Sonogashira Cross-Coupling Products



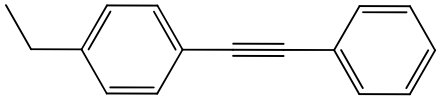
1,2-diphenylethyne

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.55 (m, 4H), 7.36 (m, 6H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 133.05, 129.78, 129.69, 124.73, 90.81.



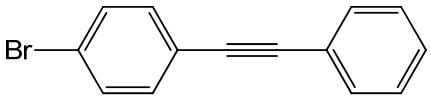
1-methyl-4-(phenylethynyl)benzene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.55-7.53 (m, 2H), 7.45 (d, 2H), 7.35 (d, 3H), 7.17 (d, 2H), 2.38 (s, 3H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 139.82, 132.99, 132.94, 130.56, 129.75, 129.51, 124.93, 121.64, 91.00, 90.16, 22.94.



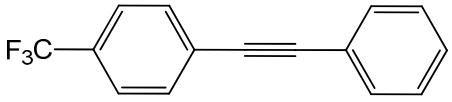
1-ethyl-4-(phenylethynyl)benzene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.65-7.57 (m, 2H), 7.52 (d, 2H), 7.38 (d, 3H), 7.23 (d, 2H), 2.71 (q, 2H), 1.30 (t, 3H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 146.16, 133.10, 133.05,129.81, 129.56, 129.42, 125.02, 121.95, 91.13, 90.25, 30.33, 16.83.



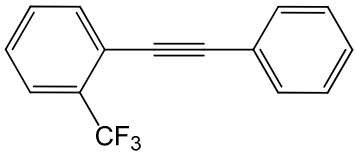
1-bromo-4-(phenylethynyl)benzene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.52 (dd, 2.9 Hz, 2H), 7.48 (d, 2H), 7.39 (d, 2H), 7.37-7.33 (m, 3H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 133.03, 132.52, 131.63, 131.61, 129.21, 128.52, 128.45, 128.41, 122.95, 121.83, 90.53, 88.32.



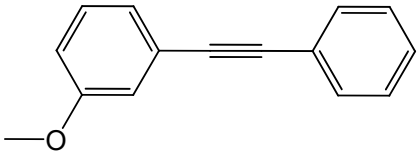
1-(phenylethynyl)-4-(trifluoromethyl)benzene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.67-7.62 (q, 4H), 7.59-7.56 (m, 2H), 7.40-7.39 (m, 3H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 134.66, 131.75, 128.89, 128.78, 128.48, 124.74, 124.34, 122.68, 90.98, 87.85.



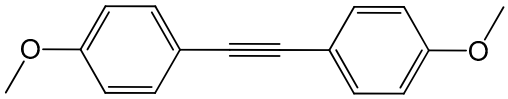
1-(phenylethynyl)-2-(trifluoromethyl)benzene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.64 (t, 2H), 7.58-7.51 (m, 2H), 7.46 (t, 1H), 7.37 (d, 1H), 7.35-7.30 (m, 3H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 133.76, 131.75, 131.43, 128.87, 128.46, 127.96, 125.95, 125.90, 125.86, 122.82, 122.37, 121.65, 95.03, 85.45.



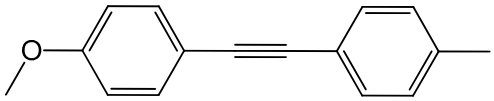
1-methoxy-3-(phenylethynyl)benzene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ7.60-7.53 (m, 2H), 7.42-7.35 (m, 3H), 7.32-7.25 (m, 2H), 7.16 (d, 1H), 7.09 (s, 1H), 6.92 (dd, 2.3 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR spectrum (400 MHz, $CDCl_3$) δ 160.84, 133.06, 130.83, 129.77, 129.72, 125.69, 125.66, 117.77, 116.38, 90.79, 90.59, 56.73.



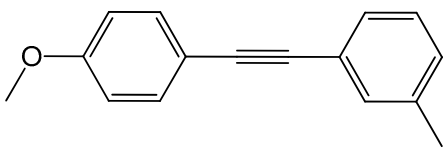
1,2-bis(4-methoxyphenyl)ethyne

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.46 (d, 4H), 6.87 (d, 4H), 3.82 (s, 6H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 159.41, 132.89, 124.40, 115.74, 113.98, 87.97, 55.29.



1-methoxy-4-(*p*-tolylethynyl)benzene

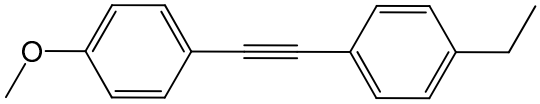
^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.48-7.46 (d, 2H), 7.43-7.41 (d, 2H), 7.16-7.14 (d, 2H), 6.89-6.87 (d, 2H), 3.83 (s, 3H), 2.37 (s, 3H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 159.51, 138.03, 132.99, 131.36, 129.10, 120.53, 115.62, 113.99, 88.68, 88.22, 55.30, 21.49.



1-((4-methoxyphenyl)ethynyl)-3-methylbenzene

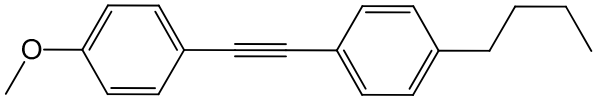
^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.53-7.51 (d, 2H), 7.40-7.37 (d, 2H), 7.27-7.26 (m, 1H),

7.18-7.16 (d, 1H), 3.85 (s, 3H), 2.40 (s, 3H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 159.58, 137.97, 133.04, 132.05, 128.85, 128.53, 128.22, 123.41, 115.52, 114.00, 89.03, 88.25, 55.30, 21.25.



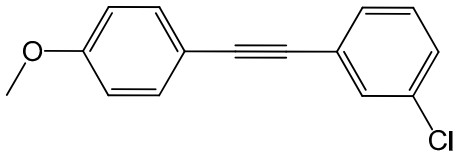
1-ethyl-4-((4-methoxyphenyl)ethynyl)benzene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.48-7.43 (m, 4H), 7.19-7.17 (d, 2H), 6.98-6.87 (d, 2H), 3.83 (s, 3H), 2.69-2.64 (q, 2H), 1.27-1.23 (t, 3H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 159.50, 148.96, 144.34, 132.99, 131.44, 127.89, 120.77, 115.65, 113.98, 88.66, 88.24, 55.30, 28.82, 15.36.



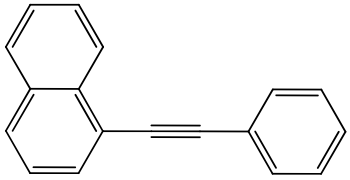
1-butyl-4-((4-methoxyphenyl)ethynyl)benzene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.46 (d, 2H), 7.42 (d, 2H), 7.15 (d, 2H), 6.87 (d, 2H), 3.83 (s, 3H), 2.67-2.57 (m, 2H), 1.59 (dd, 2H), 1.36 (dd, 2H), 0.93 (t, 3H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 159.49, 143.04, 132.98, 131.35, 128.43, 120.71, 115.66, 113.97, 88.65, 88.24, 55.3, 35.58, 33.41, 22.31, 13.93.



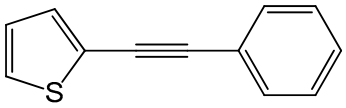
1-chloro-3-((4-methoxyphenyl)ethynyl)benzene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.50-7.48 (d, 2H), 7.42-7.40 (m, 1H), 7.31-7.28 (m, 2H), 6.92-6.90 (d, 2H), 3.85 (s, 3H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 159.90, 134.15, 133.18, 131.29, 129.55, 129.53, 128.15, 125.39, 114.86, 114.09, 90.67, 86.75, 55.32.



1-(phenylethynyl)naphthalene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 8.52 (m, 1H), 7.91-7.83 (m, 3H), 7.71-7.58 (m, 4H), 7.50-7.43 (m, 4H). ^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 133.35, 133.30, 131.75, 130.45, 128.85, 128.52, 128.47, 128.40, 126.86, 126.51, 126.30, 125.36, 123.49, 120.98, 94.42, 87.65.



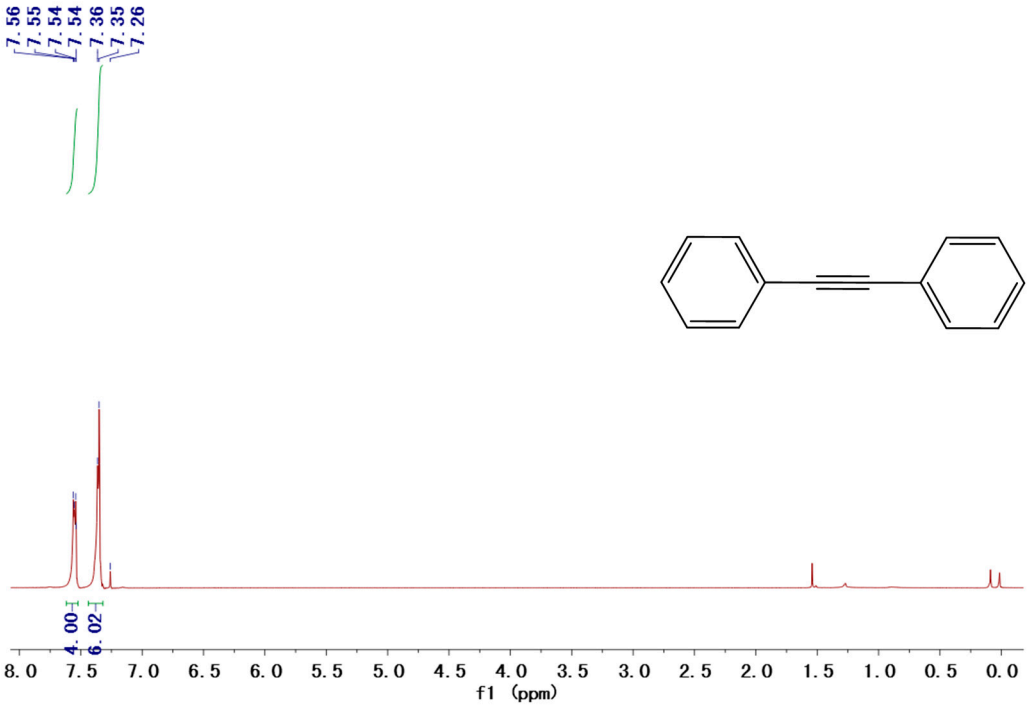
2-(phenylethynyl)thiophene

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.38-7.30 (m, 5H), 7.04-7.02 (m, 2H).

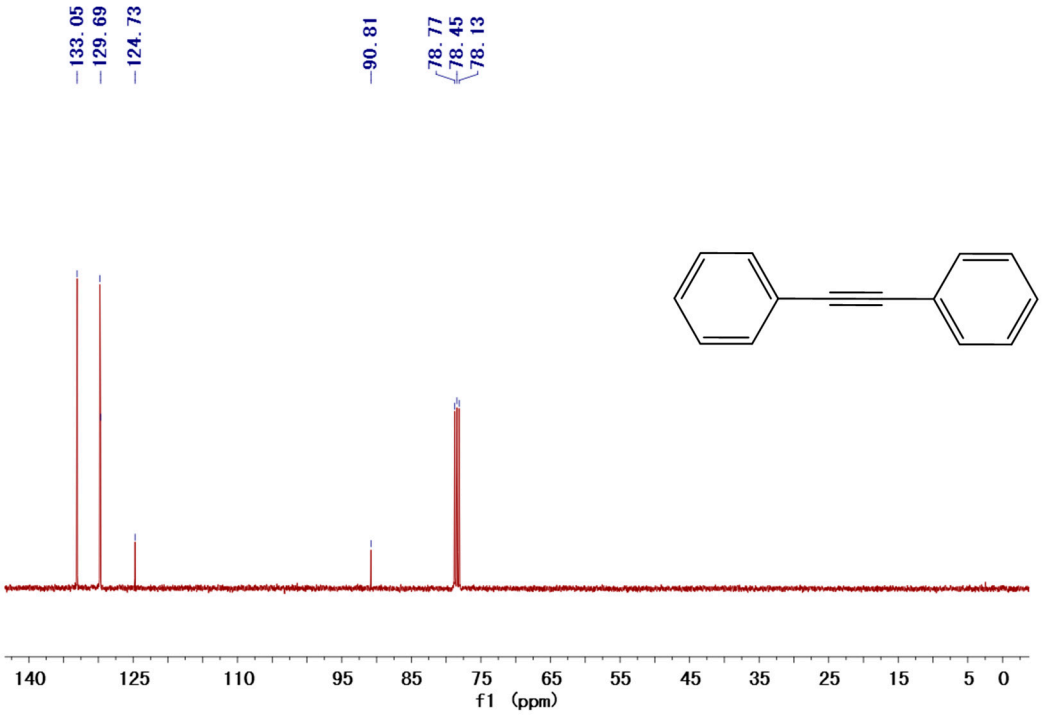
^{13}C-NMR spectrum (400 MHz, $CDCl_3$) δ 133.24, 131.79, 130.58, 127.67, 127.46, 127.37, 121.91, 120.77, 89.29, 87.21.

4. ^{1}H- and ^{13}C-NMR Spectra for Sonogashira Cross-Coupling Products

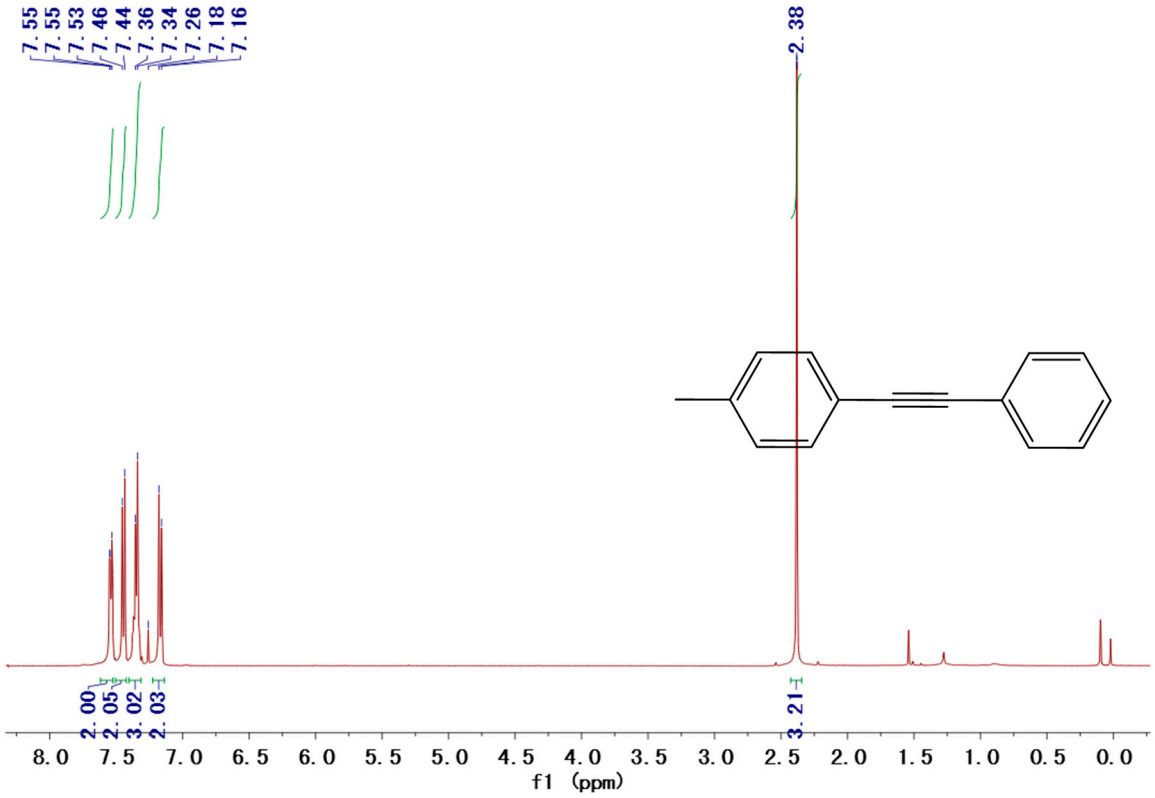
1,2-diphenylethyne ^{1}H-NMR



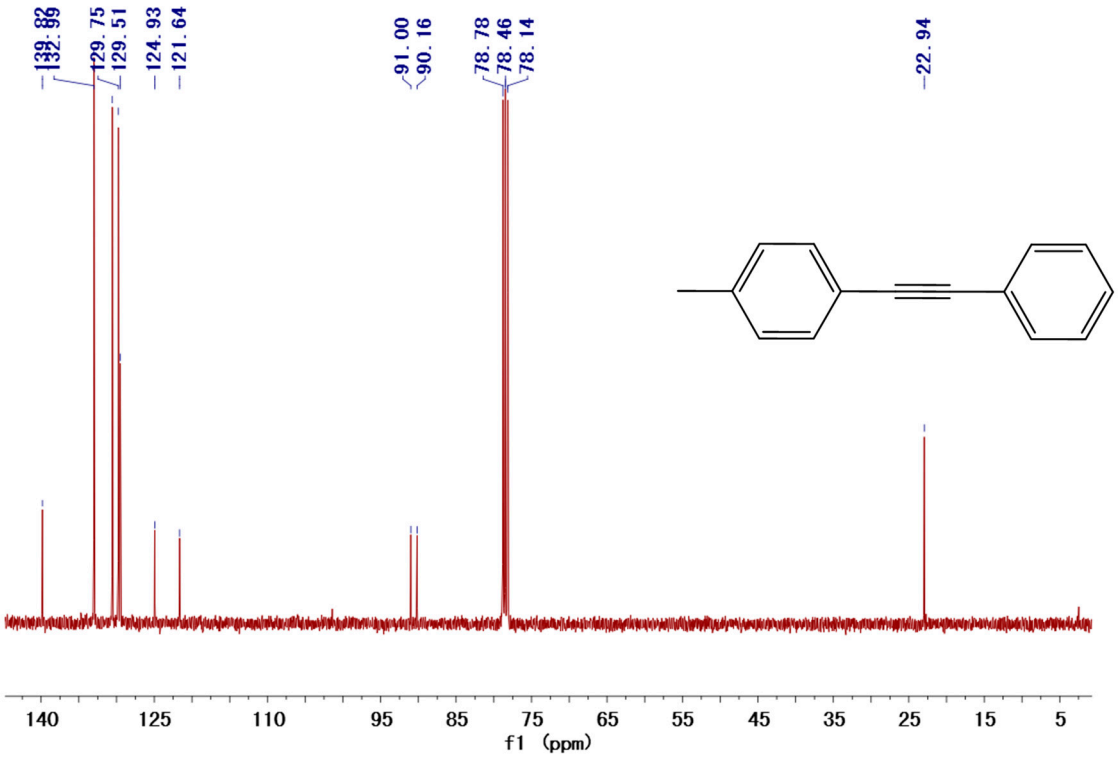
1,2-diphenylethyne ^{13}C-NMR



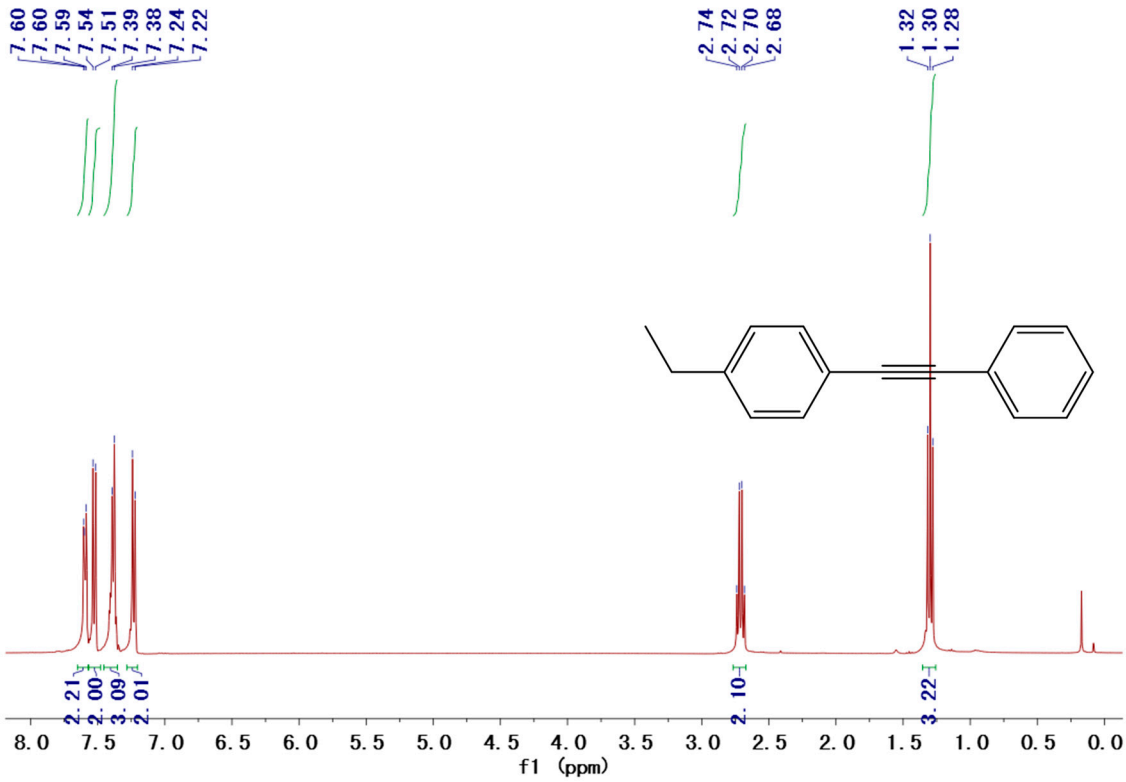
1-methyl-4-(phenylethynyl)benzene ^{1}H-NMR



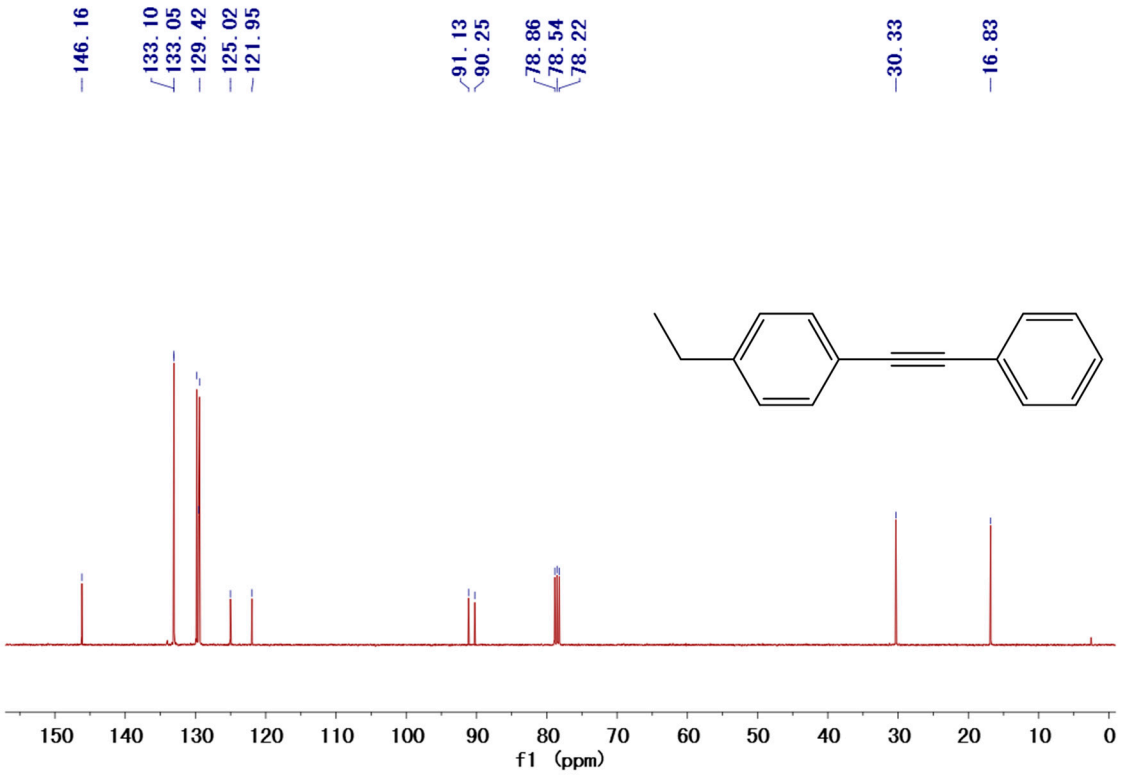
1-methyl-4-(phenylethynyl)benzene ^{13}C-NMR



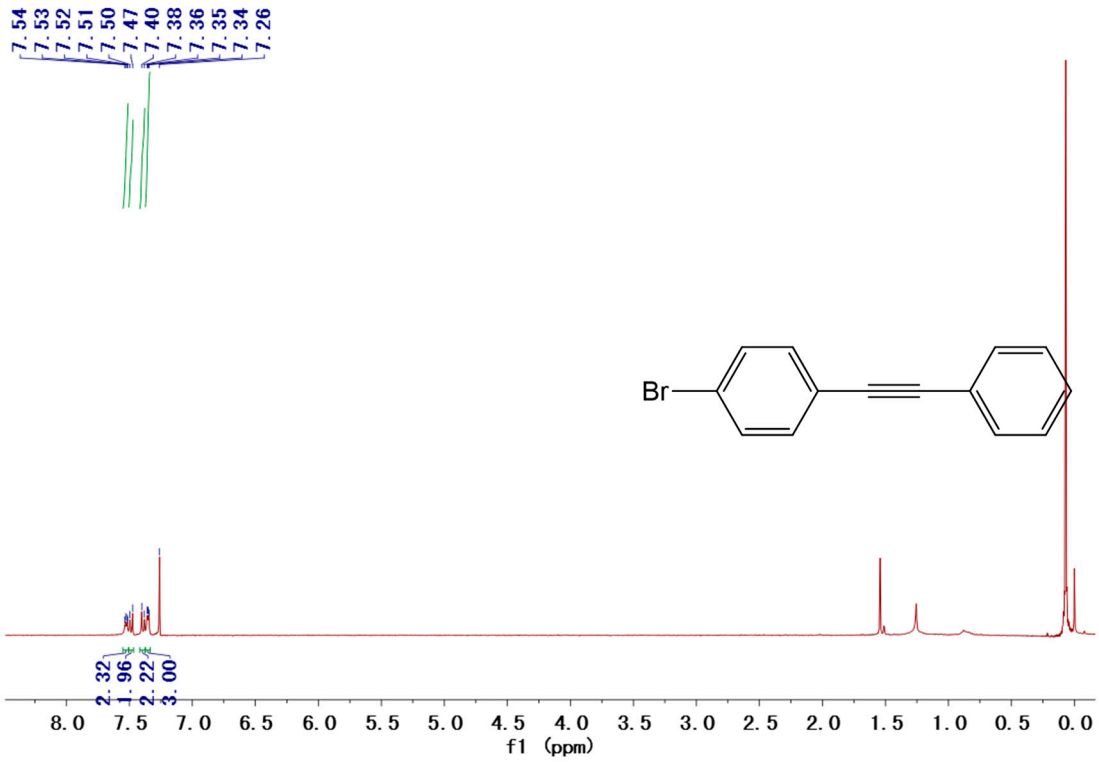
1-ethyl-4-(phenylethynyl)benzene ^{1}H-NMR



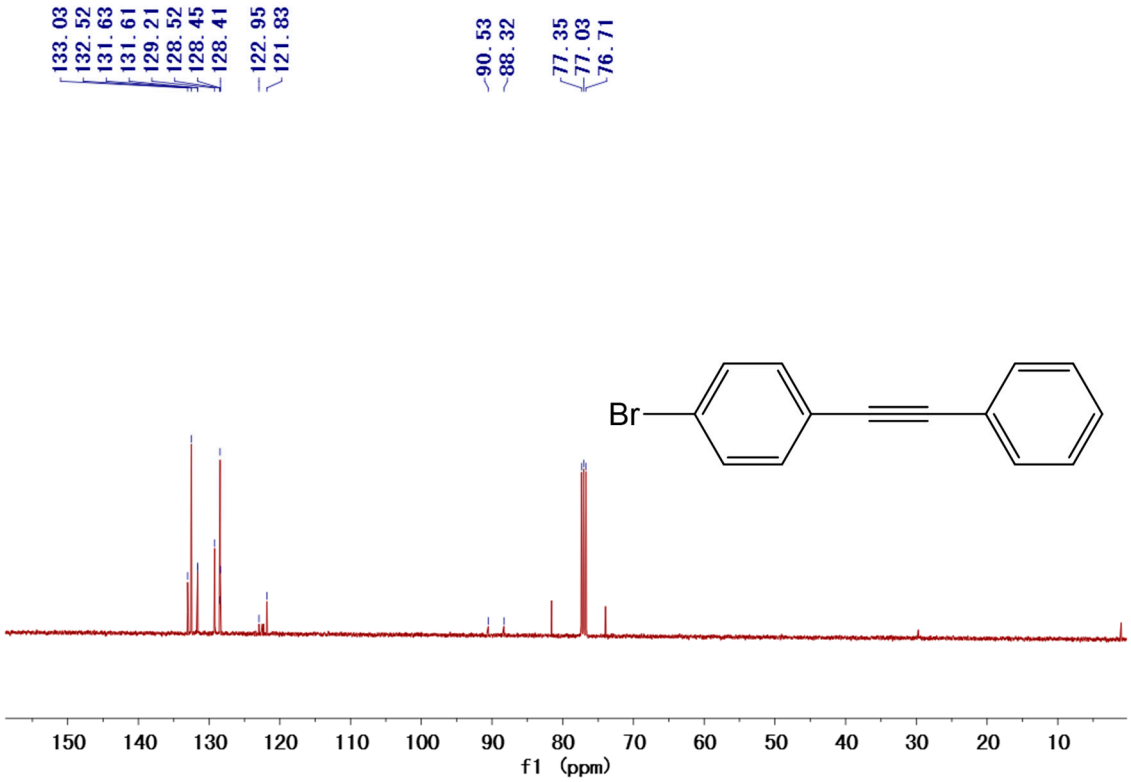
1-ethyl-4-(phenylethynyl)benzene ^{13}C-NMR



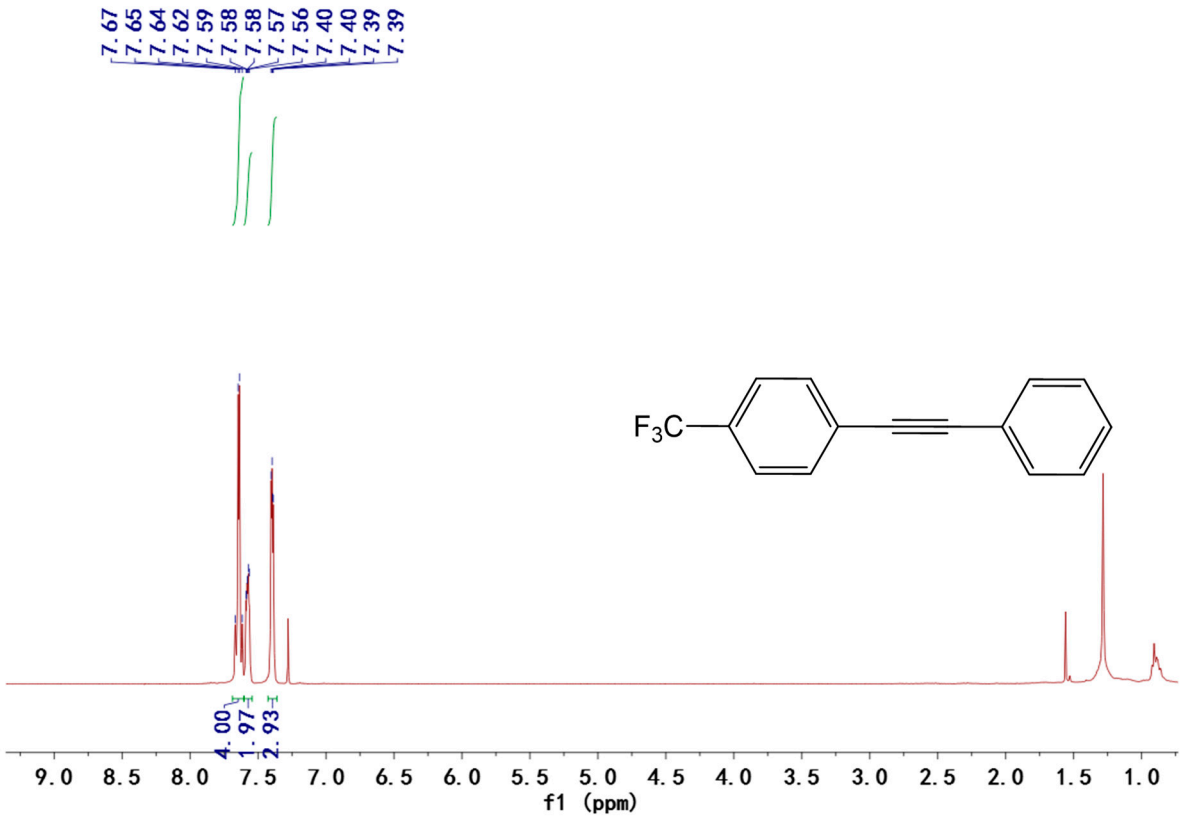
1-bromo-4-(phenylethynyl)benzene ^{1}H-NMR



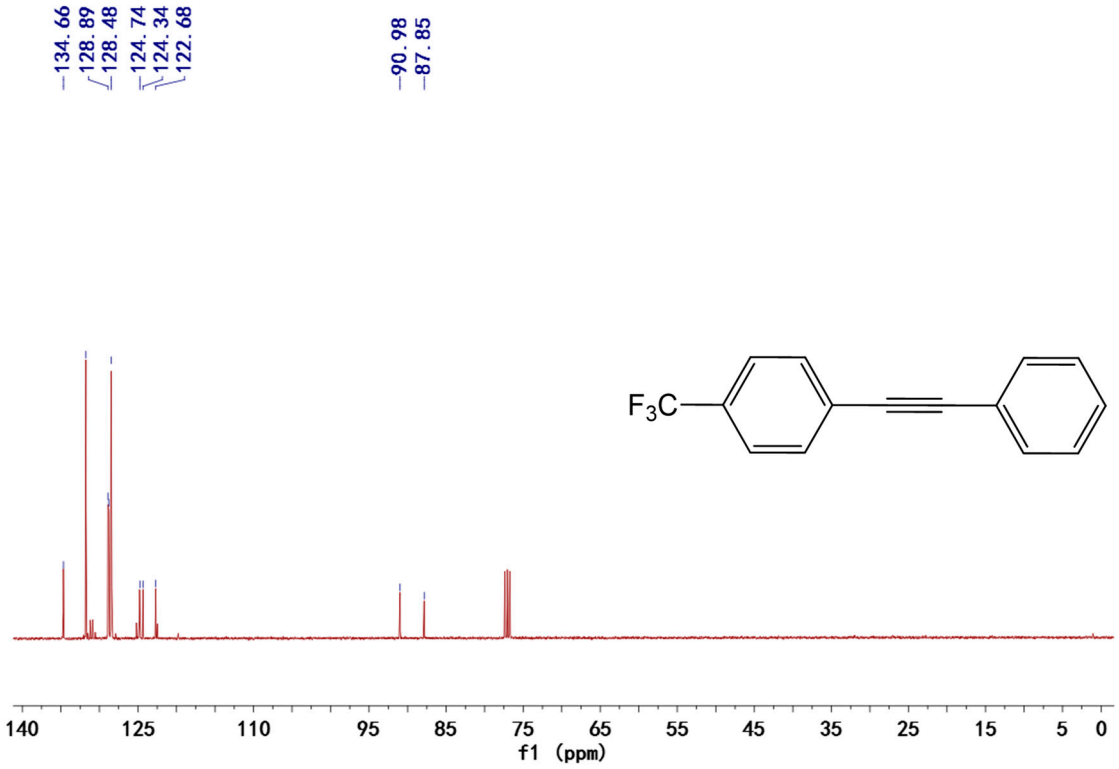
1-bromo-4-(phenylethynyl)benzene ^{13}C-NMR



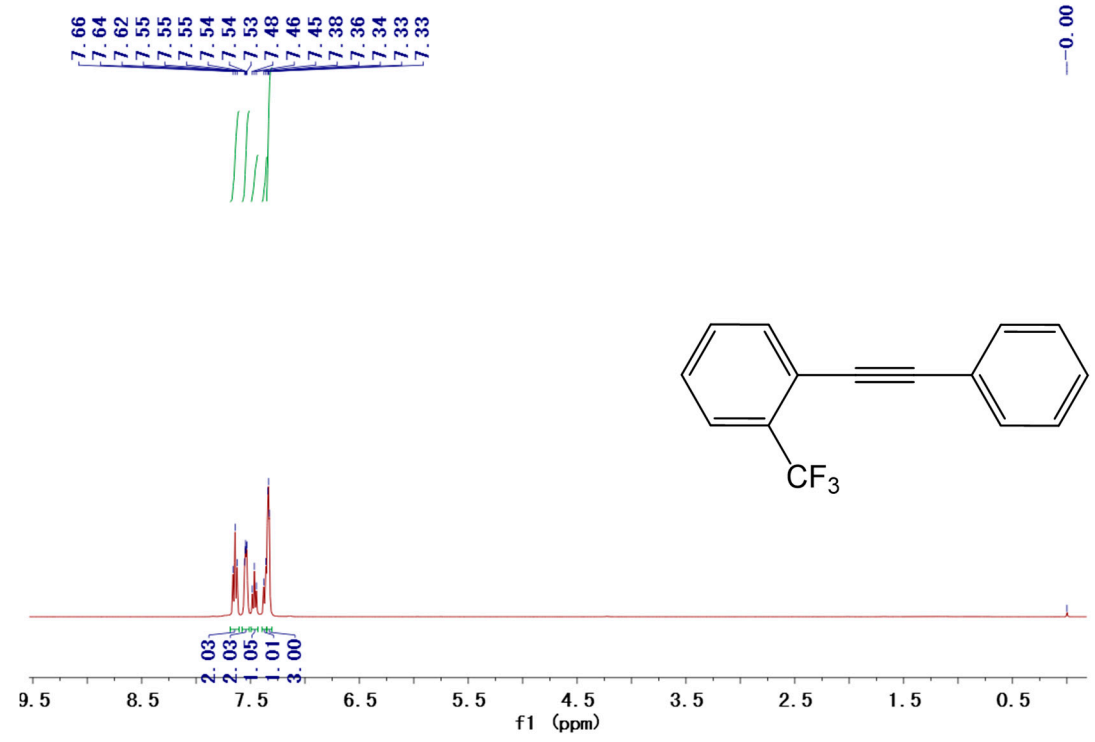
1-(phenylethynyl)-4-(trifluoromethyl)benzene ^{1}H-NMR



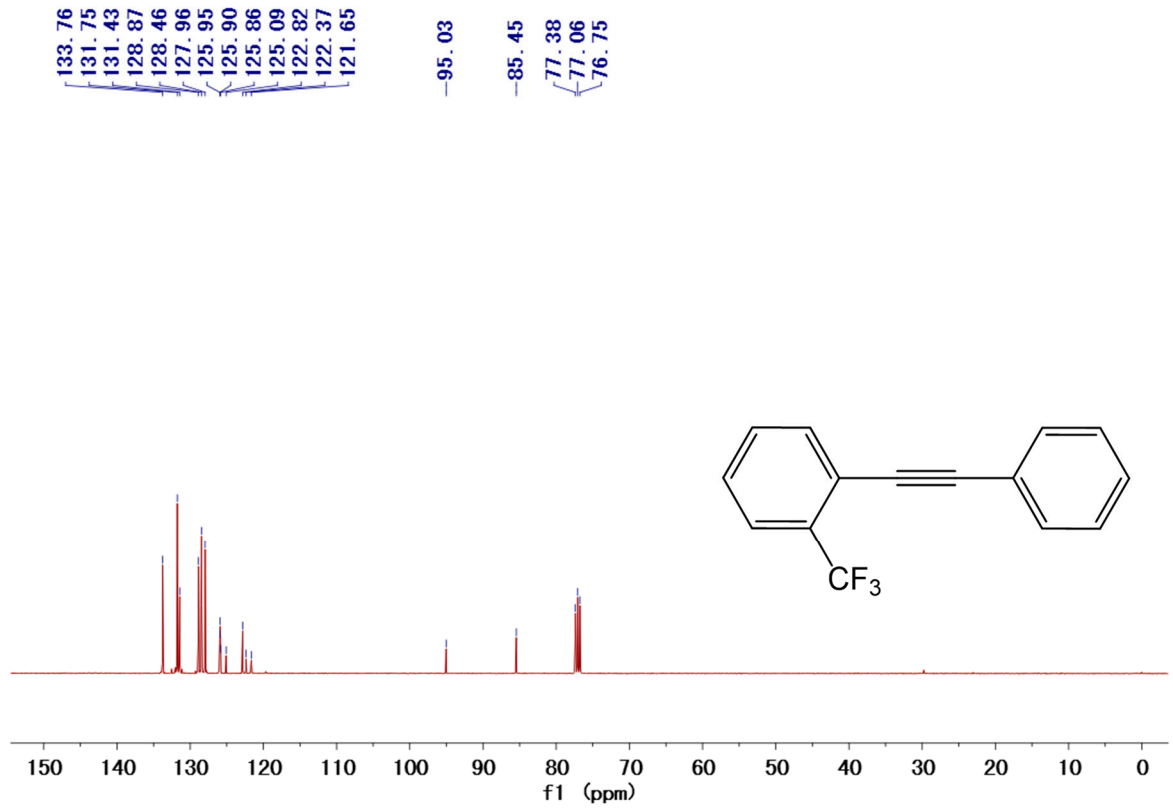
1-(phenylethynyl)-4-(trifluoromethyl)benzene ^{13}C-NMR



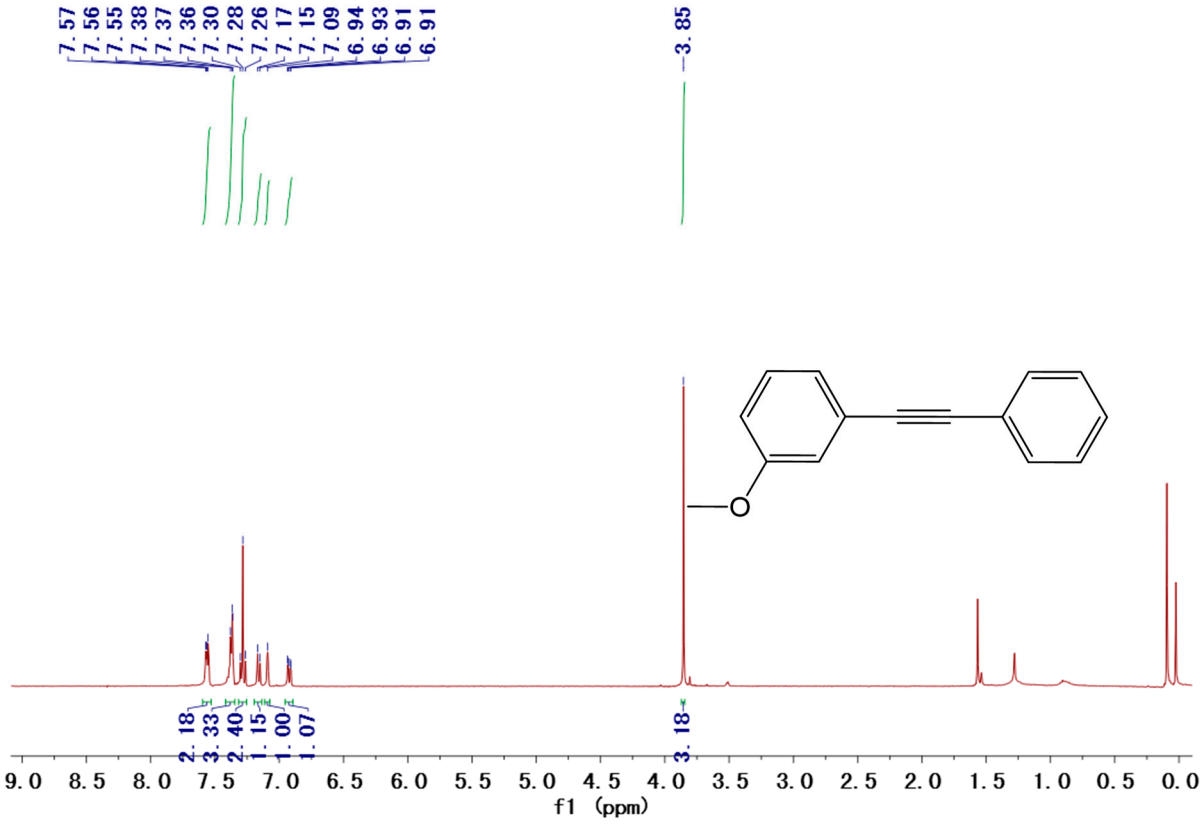
1-(phenylethynyl)-2-(trifluoromethyl)benzene ^{1}H-NMR



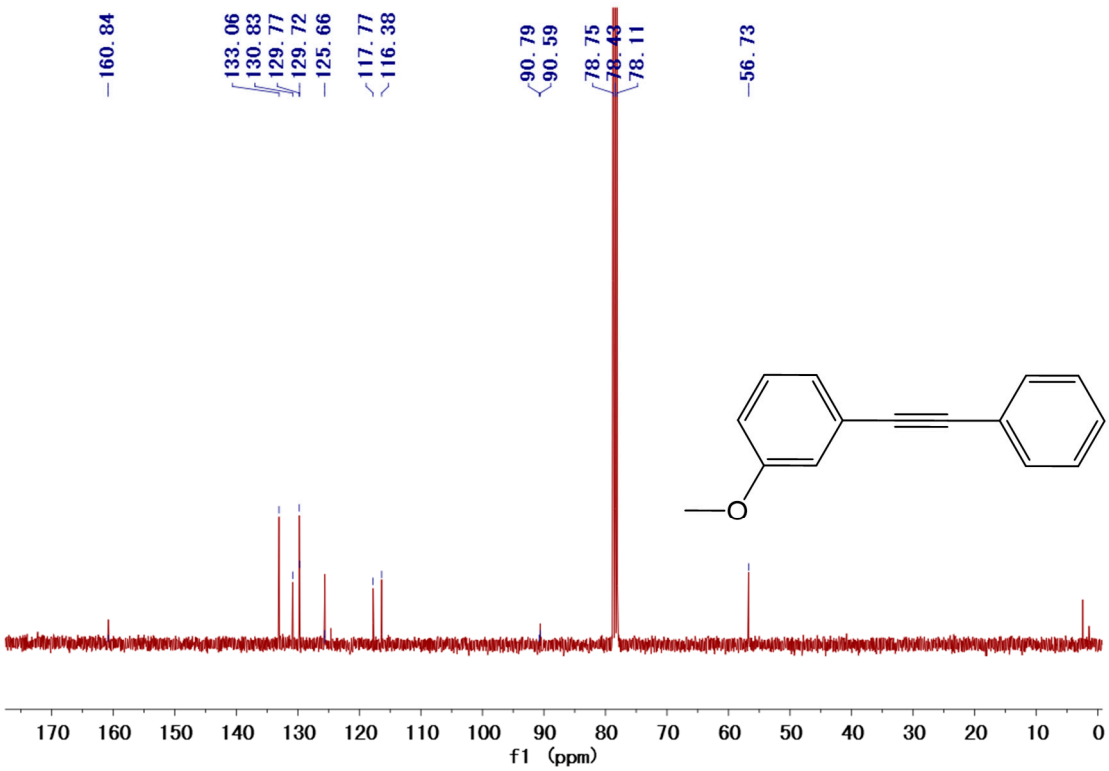
1-(phenylethynyl)-2-(trifluoromethyl)benzene ^{13}C-NMR



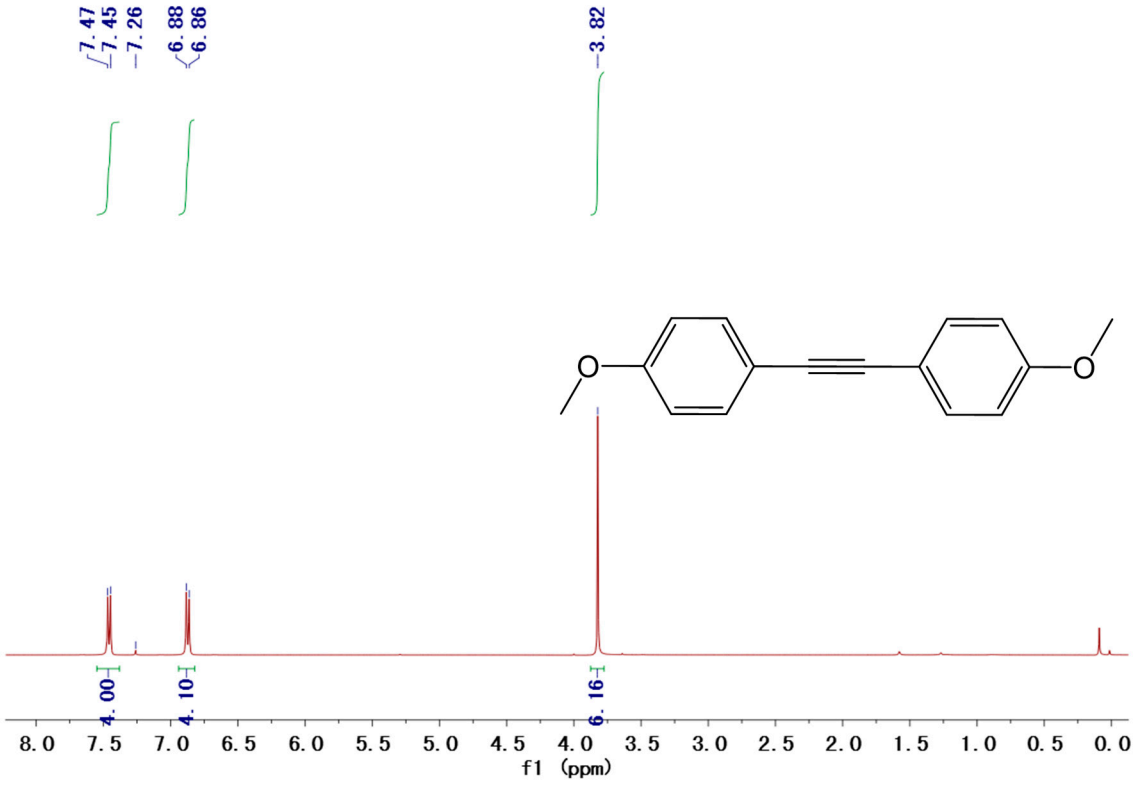
1-methoxy-3-(phenylethynyl)benzene ^{1}H-NMR



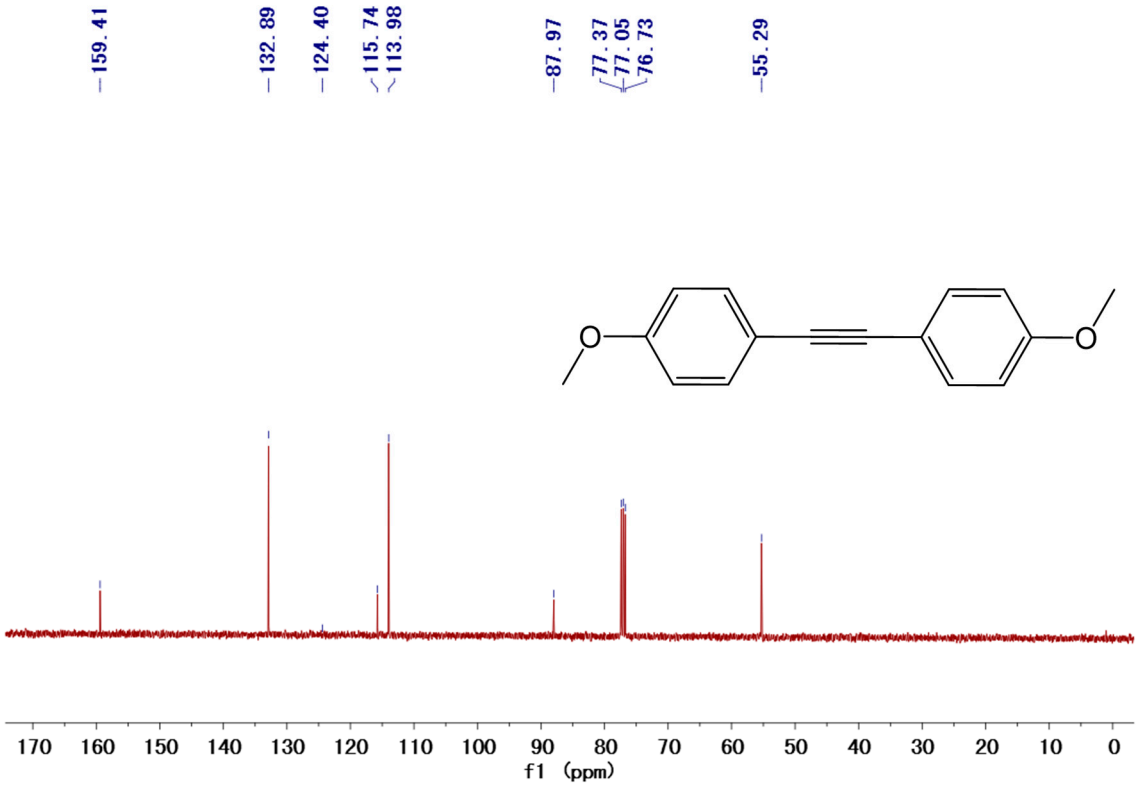
1-methoxy-3-(phenylethynyl)benzene ^{13}C-NMR



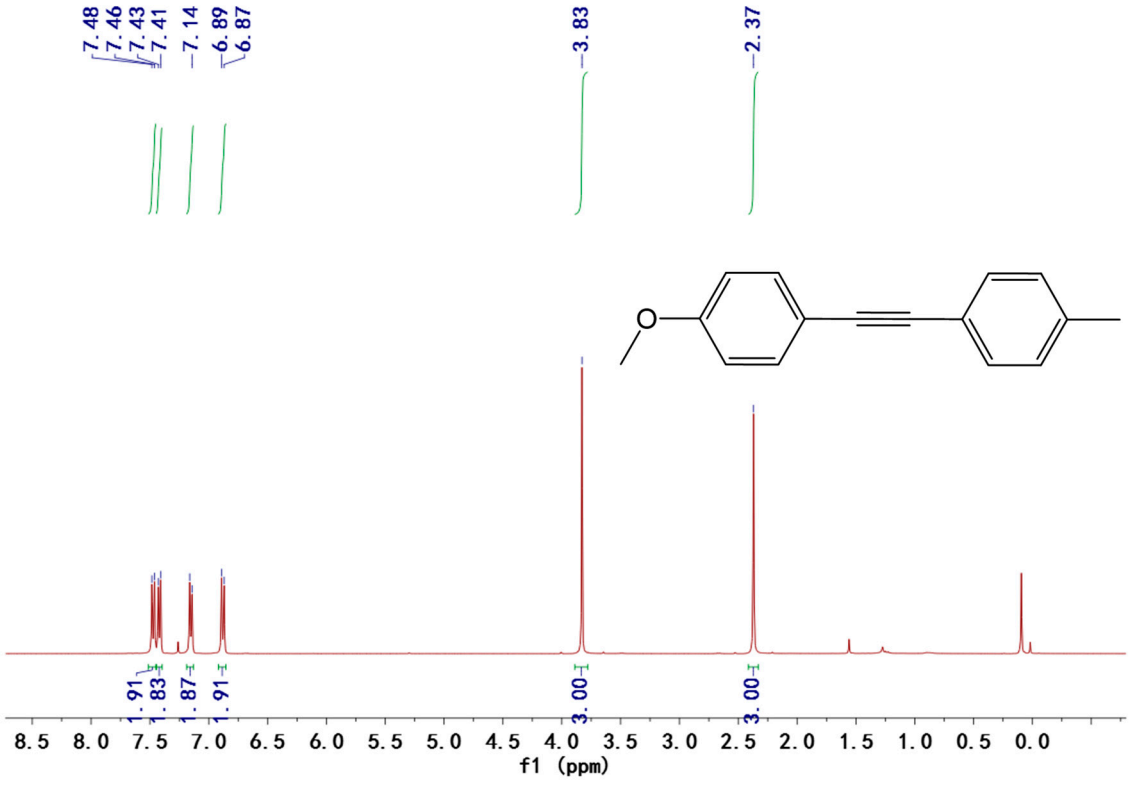
1,2-bis(4-methoxyphenyl)ethyne ^{1}H-NMR



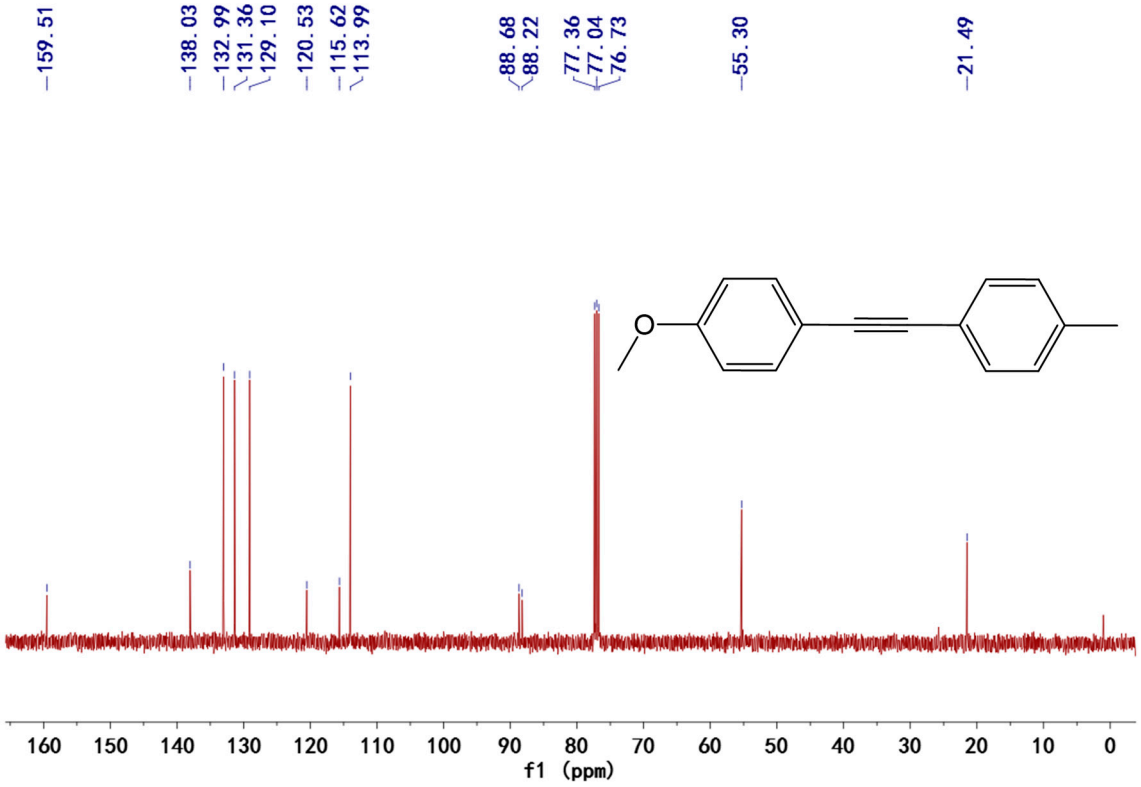
1,2-bis(4-methoxyphenyl)ethyne ^{13}C-NMR



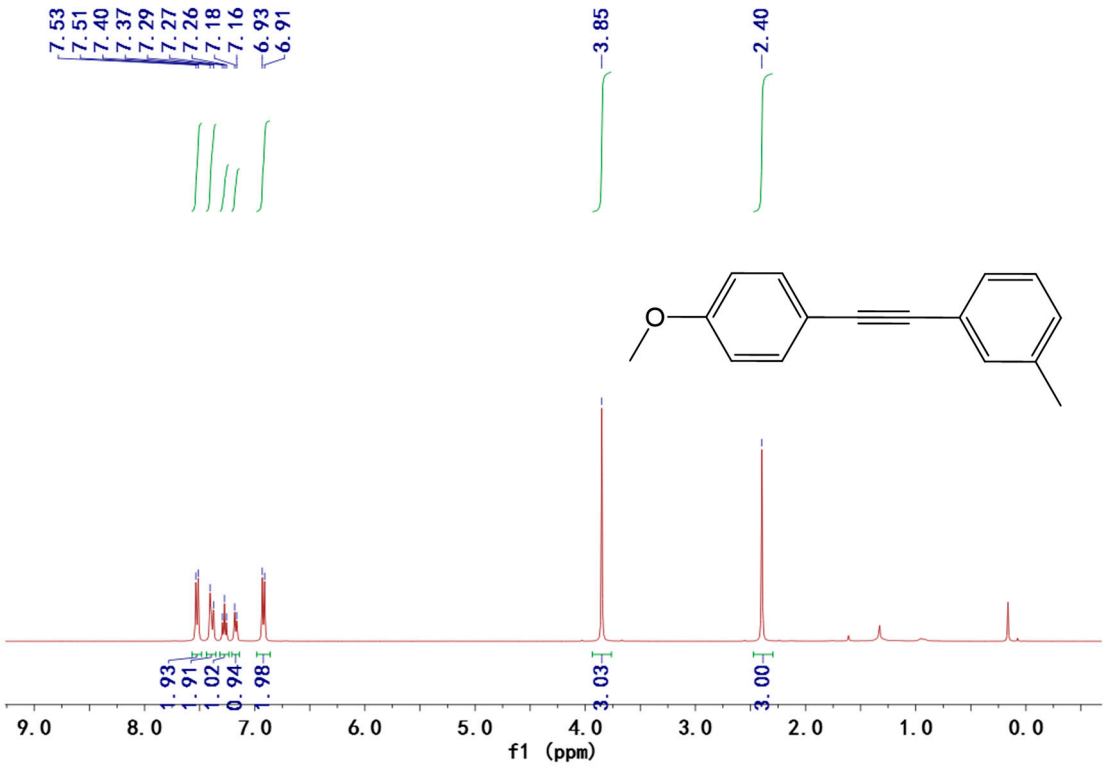
1-methoxy-4-(*p*-tolylethynyl)benzene ^{1}H-NMR



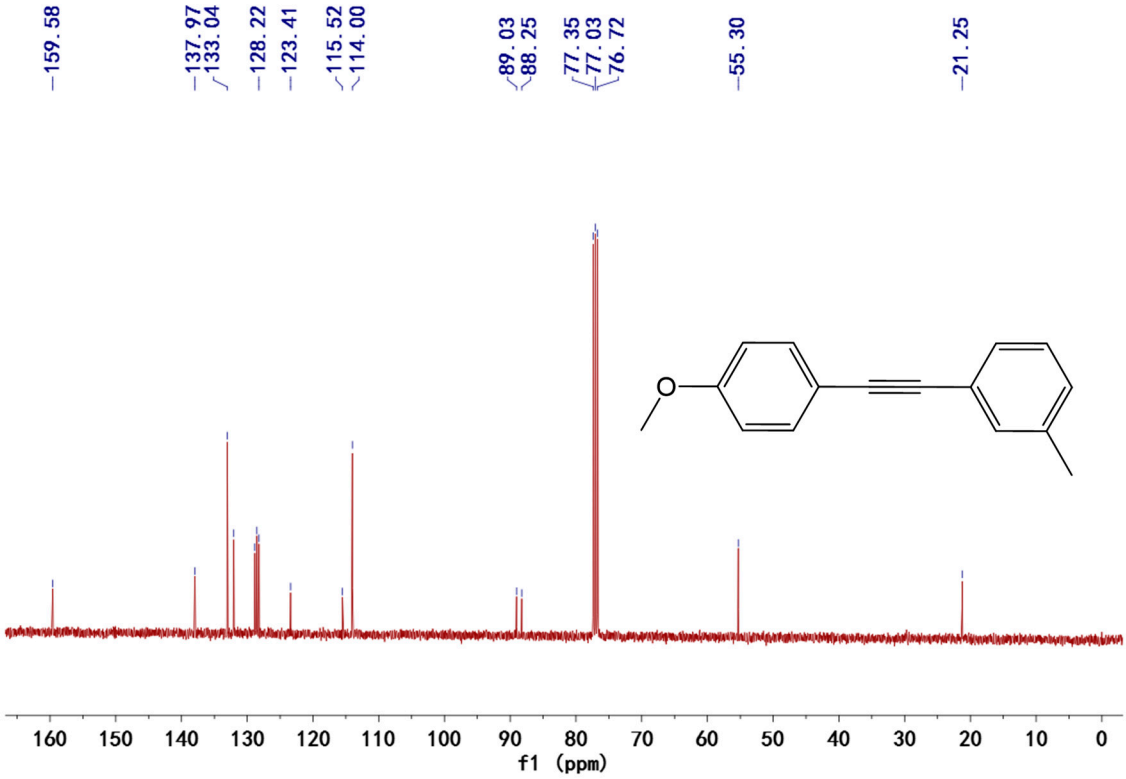
1-methoxy-4-(*p*-tolylethynyl)benzene ^{13}C-NMR



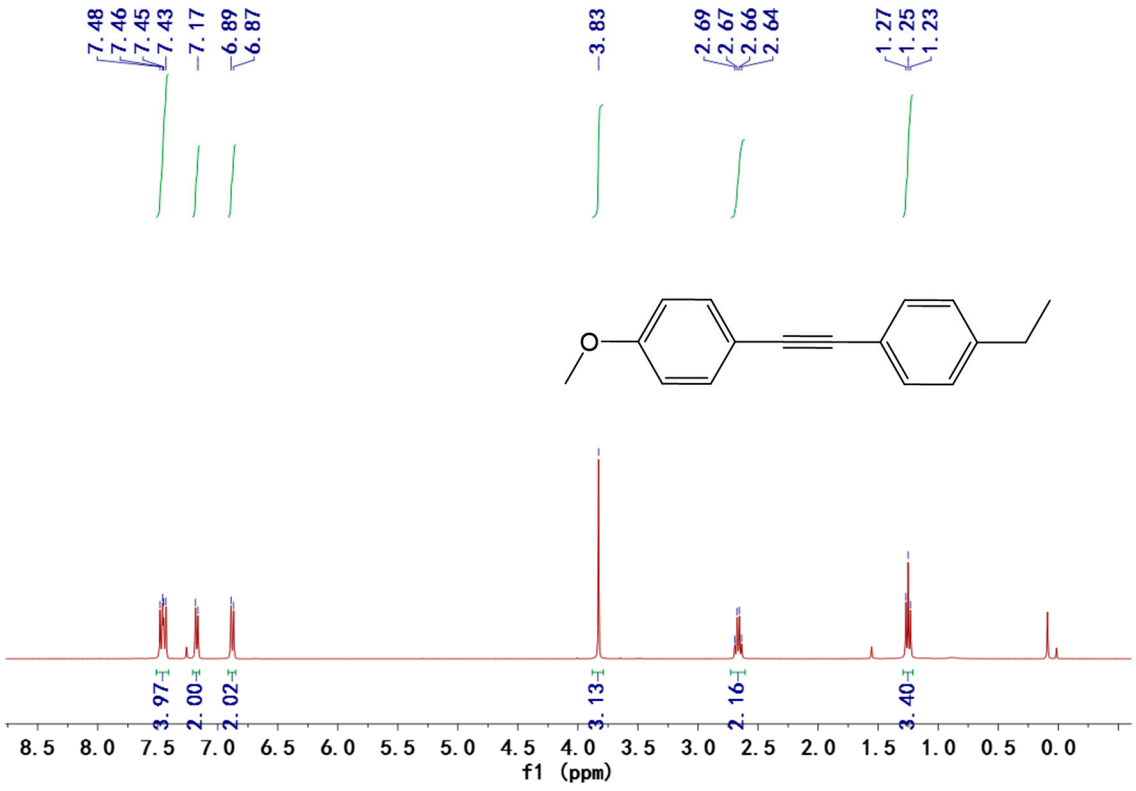
1-((4-methoxyphenyl)ethynyl)-3-methylbenzene ^{1}H-NMR



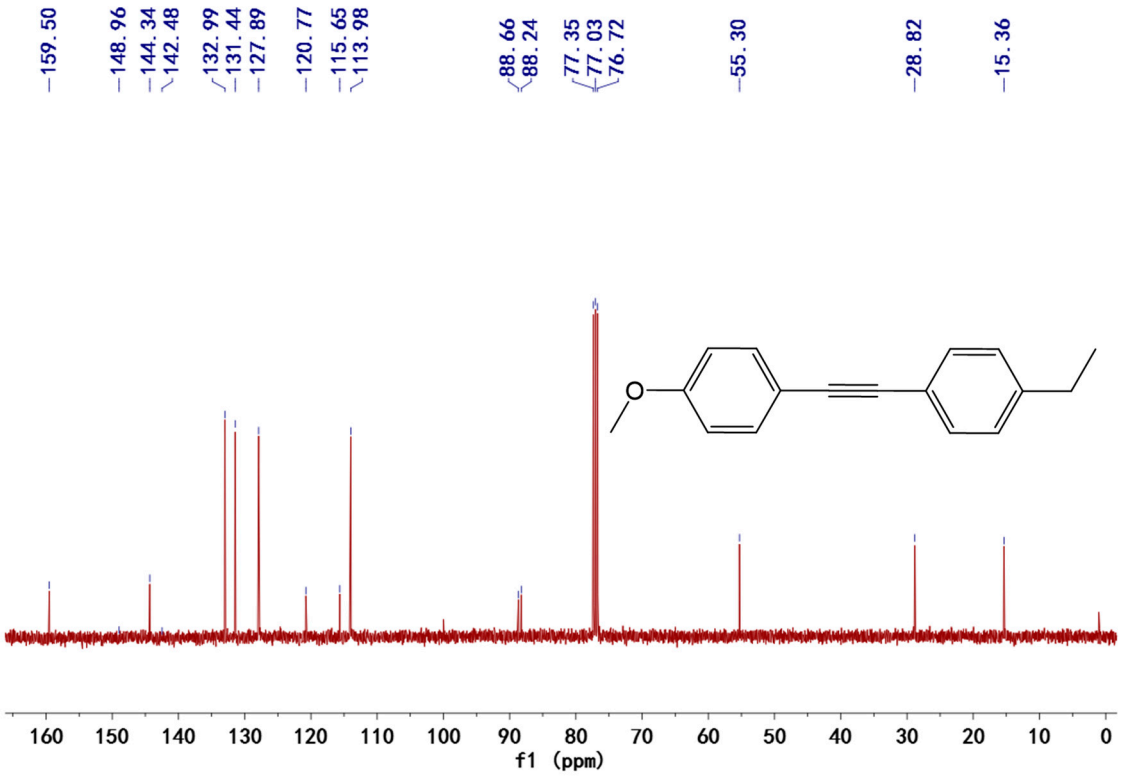
1-((4-methoxyphenyl)ethynyl)-3-methylbenzene ^{13}C-NMR



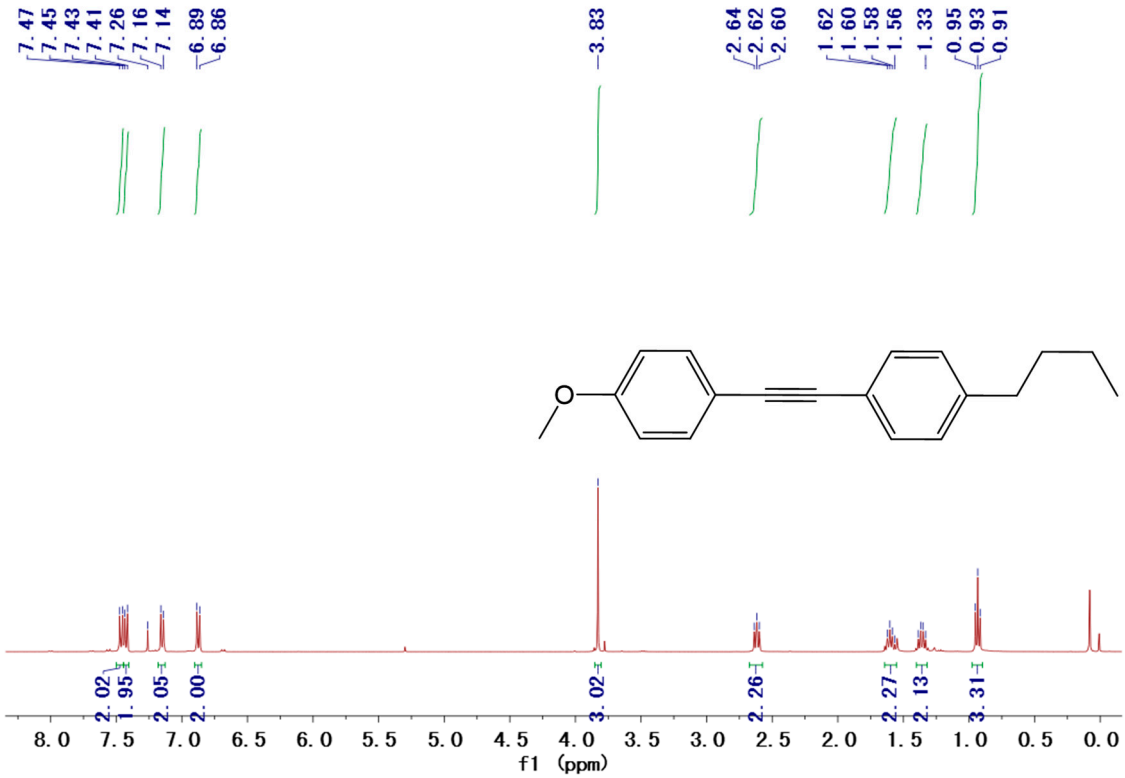
1-ethyl-4-((4-methoxyphenyl)ethynyl)benzene ^{1}H-NMR



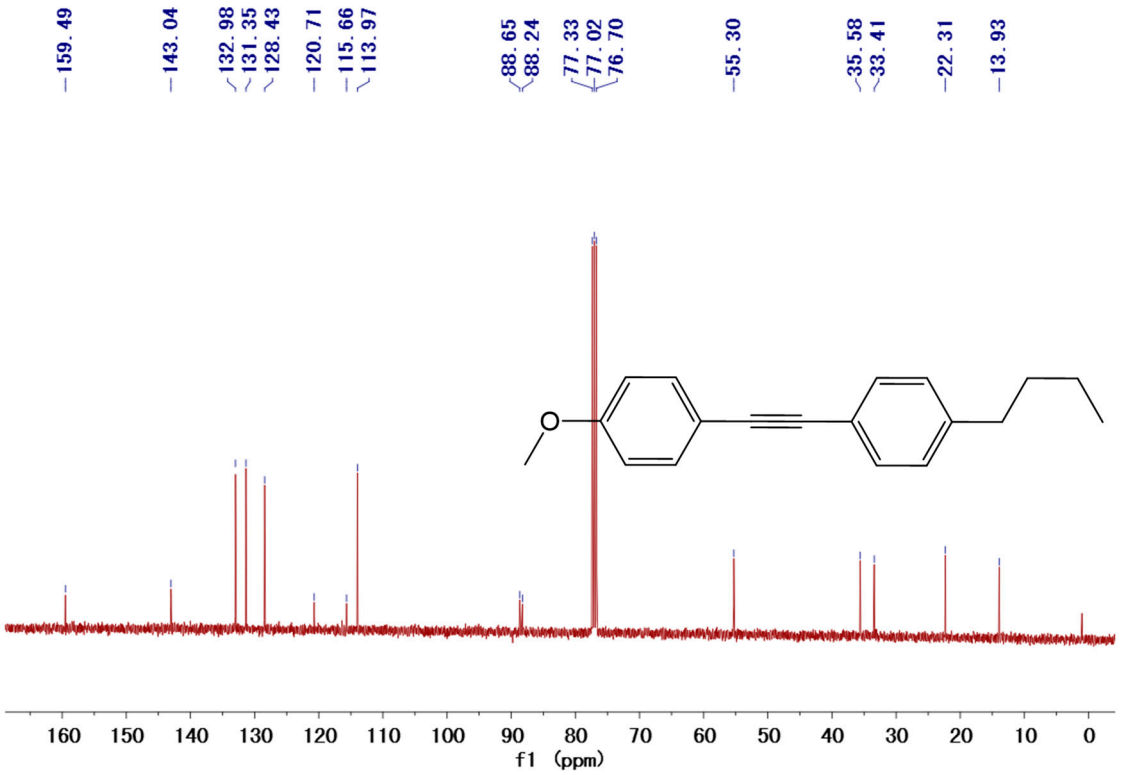
1-ethyl-4-((4-methoxyphenyl)ethynyl)benzene ^{13}C-NMR



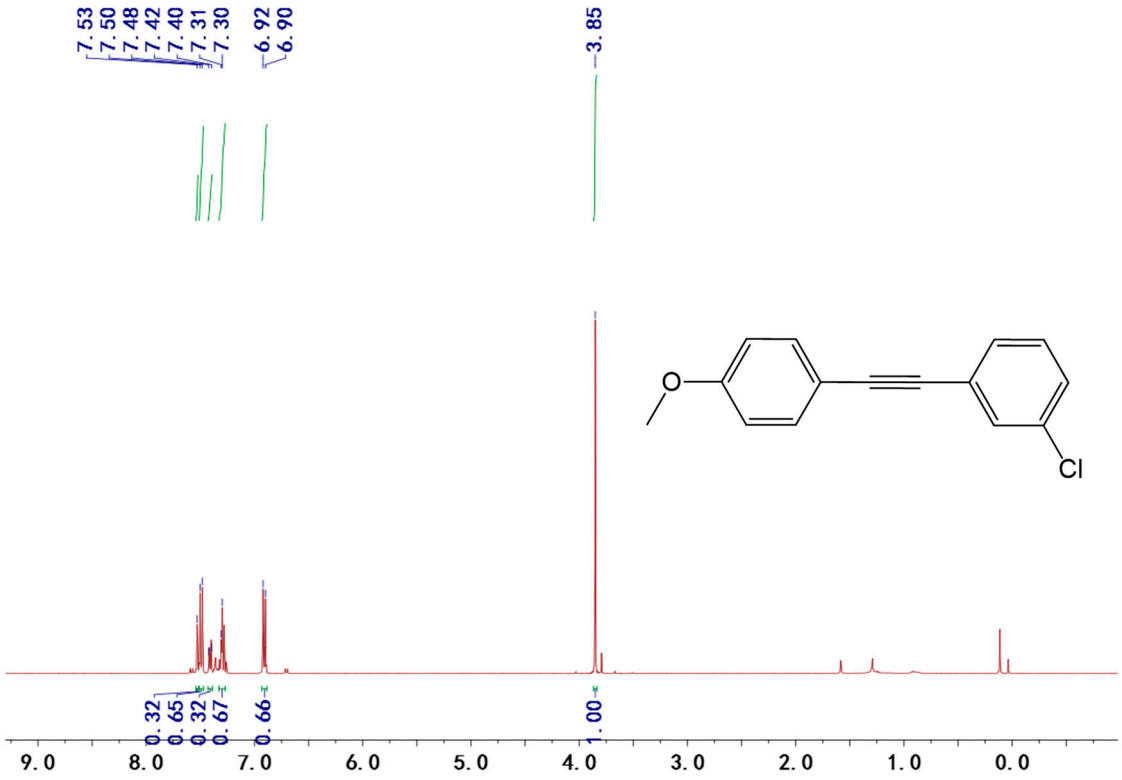
1-butyl-4-((4-methoxyphenyl)ethynyl)benzene ^{1}H-NMR



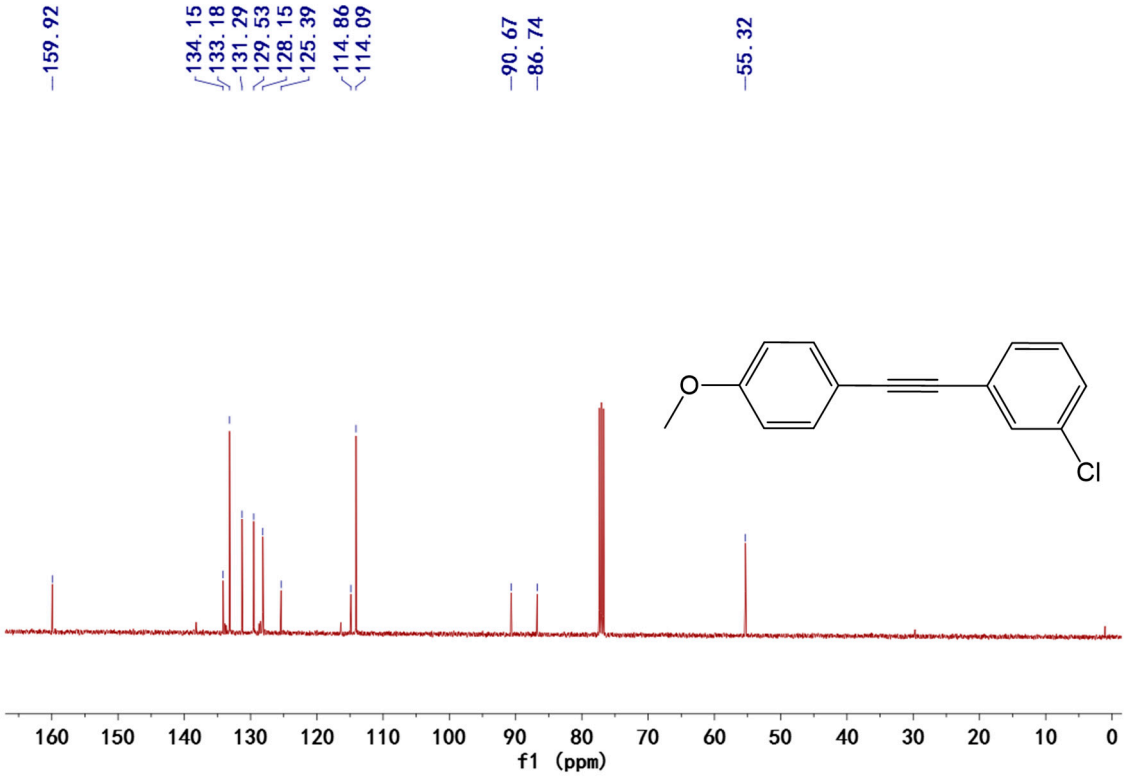
1-butyl-4-((4-methoxyphenyl)ethynyl)benzene ^{13}C-NMR



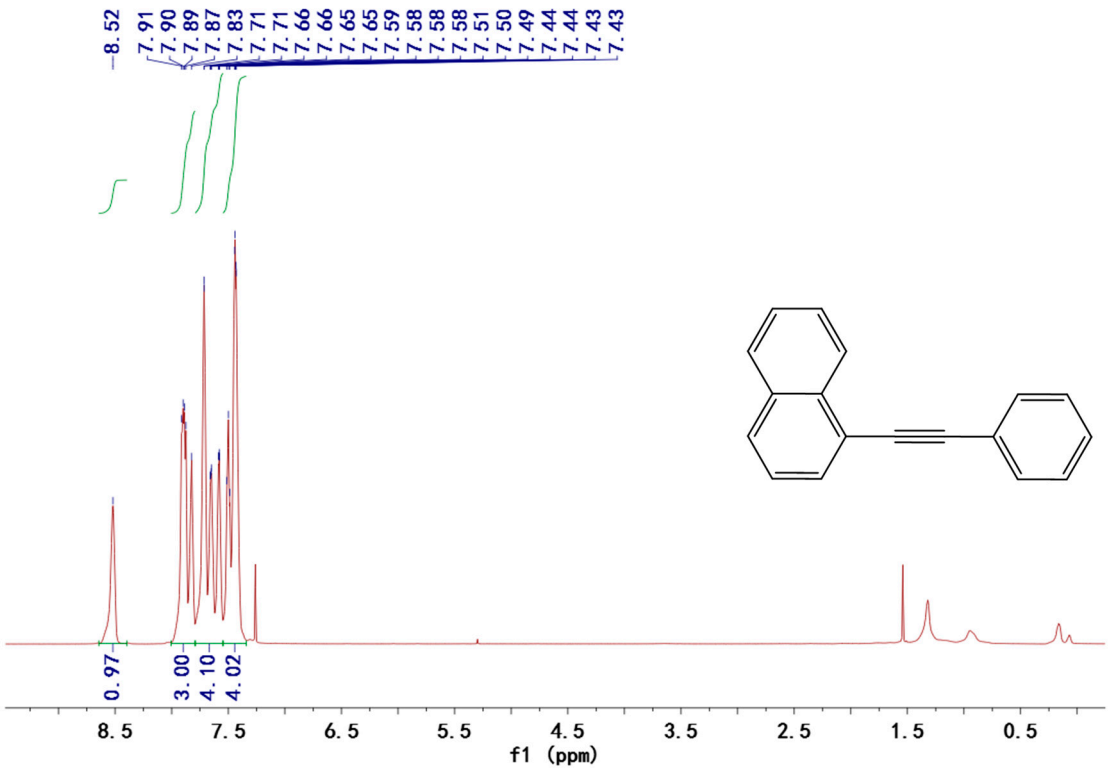
1-chloro-3-((4-methoxyphenyl)ethynyl)benzene ^{1}H-NMR



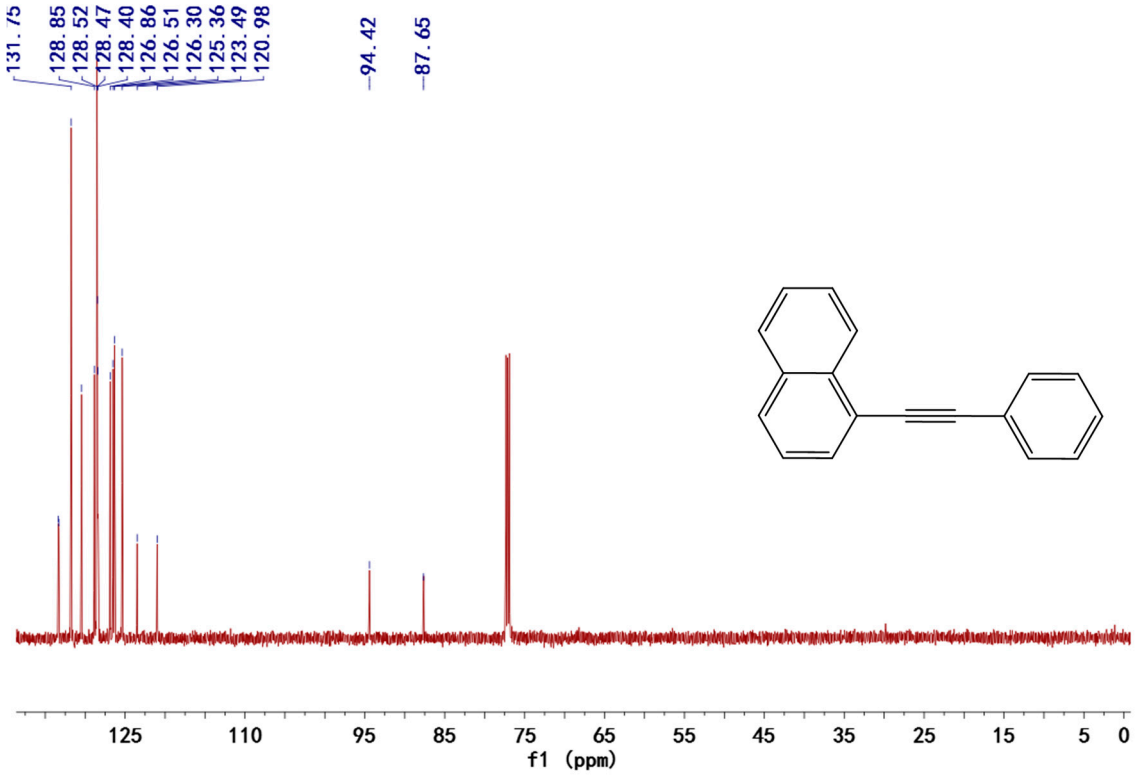
1-chloro-3-((4-methoxyphenyl)ethynyl)benzene ^{13}C-NMR



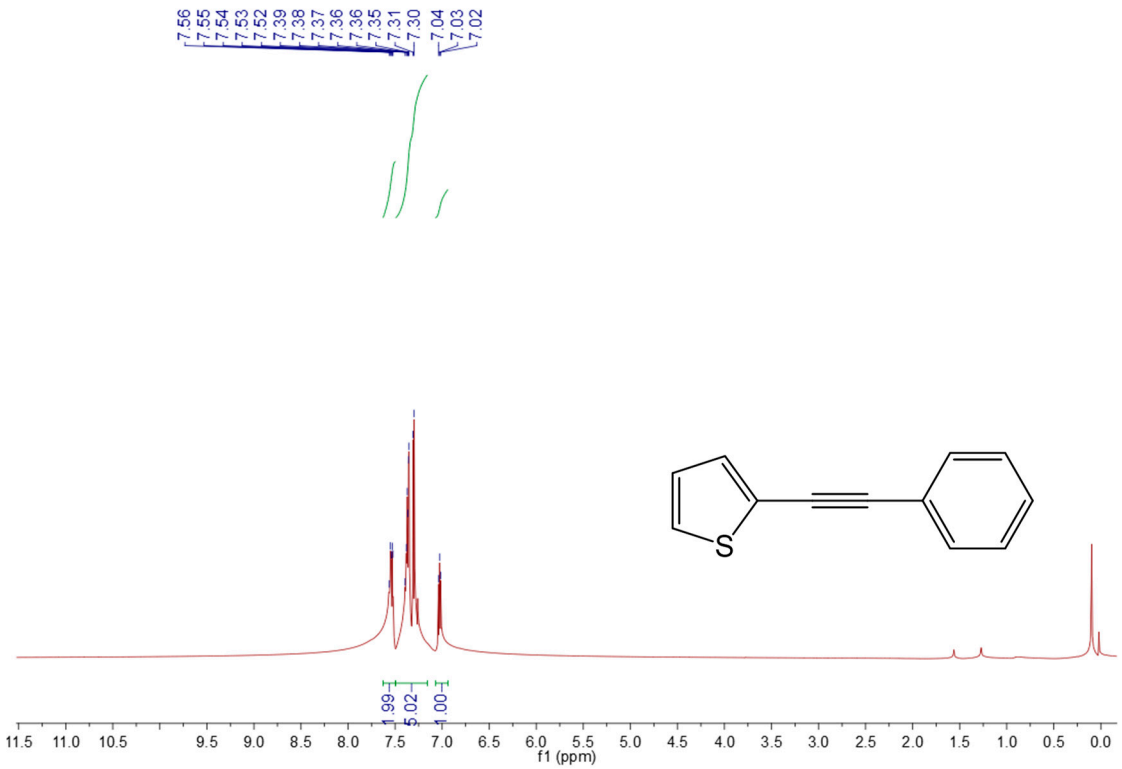
1-(phenylethynyl)naphthalene ^{1}H-NMR



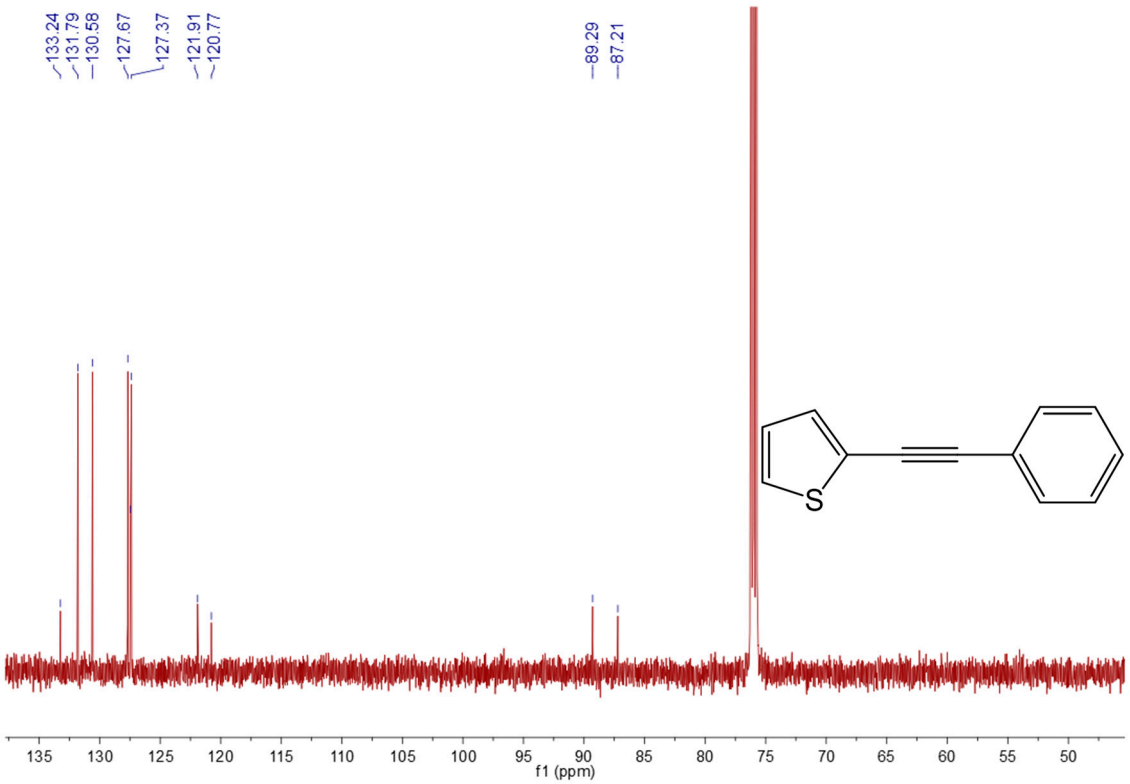
1-(phenylethynyl)naphthalene ^{13}C-NMR



2-(phenylethynyl)thiophene ^{1}H-NMR



2-(phenylethynyl)thiophene ^{13}C-NMR


133.24
131.79
130.58
127.67
127.37
121.91
120.77
89.29
87.21
S
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
f1 (ppm)