Copper Catalyzed, Aerobic Oxidative Cross-Coupling of Alkynes with Arylboronic Acids : Remarkable Selectivity in 2,6-lutidine Media

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Electronic Supplementary Information

Contens

1. General

- JEOL JMN-LA400, 500 or 600 spectrometers were used for NMR measurement. Chloroform (δ= 7.24) was used as an internal standard for ^{1}H NMR and $CDCl_3$ (δ = 77.0) for ^{13}C NMR. Structures of known compounds were confirmed by comparison with commercially available compounds or data shown in literature.
- IR spectra were measured on a JASCO FT/IR-610 spectrometer.
- ICP analysis was performed on Shimadzu ICPS-7510 equipment.
- GC analysis. was performed on Shimadzu GC-2010 apparatus (**Condition A :** Column = GL Science, TCWAX, 0.25 mm ID, 0.25 μm, 60.0 m; Gas pressure: 214.2 kPa; Total flow: 90.6 mL/min; Column flow: 1.86 mL/min; Velocity: 30.8 cm/sec; Purge flow: 3.0 mL/min; Sprit ratio: 46.0; Injector: 250 ˚C, FID: 250 ˚C; Column program: starting from 50.0 ˚C, 10 min hold, 10 ˚C/min to 220 ˚C, 15 min hold) (**Condition B :** column = J & W SCIENTIFIC DB-1 0.25 mm ID, 0.25 μm, 60.0 m; Gas pressure: 157.5 kPa, Total flow: 41.3 mL/min, Column folw: 0.93 mL/min, Velocity: 21.1 cm/sec; Purge flow: 3.0 mL/min; Sprit ratio: 40.1; Injector: 300 °C, FID: 300 °C; Column program: starting from 100 ˚C, 10 ˚C/min to 300 ˚C, 10 min hold). Structures of known compounds were confirmed by comparison with commercially available compounds or literature data.
- MeOH was purchased from Wako Pure Chemical Company. Purchased MeOH was distilled over Na and dried over MS 3A.

- 2,6-Lutidine was purchased from Wako Pure Chemical Company. Purchased 2,6-Lutidine was distilled over KOH and dried over MS 5A.
- Other solvents were purchased in dried grade from Wako Pure Chemical Company and used without further purification.
- Various alkynes (**1c**, **1f**, **1i**, **1k**) were synthesized by reported method (Ref 1)
- The other alkynes were purchased from Wako Pure Chemical Company.

1-ethynyl-2-methylbenzene[2] (**1c**) : ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.49 (s, 3H), 3.30 (s, 1H), 7.17 (t, 1H, J = 7.2 Hz), 7.23 (d, 1H, J = 6.9 Hz), 7.26-7.29 (m, 1H), 7.49 (d, 1H, J = 7.6 Hz).

1-ethynyl-2-methoxybenzene[3] (**1f**) : ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 3.29 (s, 1H), 3.89 (s, 3H), 6.86-6.91 (m, 2H), 7.29-7.32 (m, 1H), 7.45 (dd, 1H, J = 1.7, 7.4 Hz).

1-bromo-4-ethynylbenzene[4] (**1i**) : ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 3.10 (s, 1H), 7.33 (d, 2H, J = 8.5 Hz), 7.44 (d, 2H, J = 8.5 Hz).

4-ethynylpyridine[5] (**1k**) : ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 3.27 (s, 1H), 7.33 (d, 2H, J = 4.5 Hz), 8.57 (d, 2H, J = 4.5 Hz).

2. Cross-coupling reaction catalyzed by copper salt

2-1. A typical procedure for preparation of a copper salt solution: Copper bromide (I) (2.7 mg, 0.0188 mmol) was dissolved in methanol (0.5 mL) and 2,6-lutidine (0.5 mL). This *CuBr solution* was used for coupling reactions.

2-2. A typical procedure for the cross-coupling reaction between alkyne (1a) and arylboronic acid (2b) catalyzed by CuBr, (Table 3, entry 2): Phenylacetylene (**1a**, 12.8 mg, 0.125 mmol), *o*-tolylboronic acid (**2b**, 32.3 mg, 0.238 mmol), methanol (0.115 mL) and 2,6-lutidine (0.28 mL) were combined in a round-bottomed flask. After the *CuBr solution* (0.1 mL) was added to the reaction mixture, it was stirred for 16 h under O_2 atmosphere at 45 ^{o}C. 1 M HCl aq. (10 mL) was added and the whole aqueous layer was extracted with dichloromethane (30~40 mL). The organic layer was dried over Na_2SO_4. The conversion of the alkyne and the yields of side products were determined by GC analysis, with reference to an internal standard (IS = ethylbenzene or methyl benzoate) using condition B for 1,4-diphenylbuta-1,3-diyne and condition A for the other compounds. The solvent was removed *in vacuo* and the residue was purified by

preparative TLC to afford 1-methyl-2-(phenylethynyl)benzene (85% yield). The structure of product was confirmed by ^{1}H NMR and ^{13}C NMR analysis. **1-Methyl-2-(phenylethynyl)benzene[6] (3ab, 3ca)**: ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.53 (s, 3H), 7.18 (m, 1H), 7.25 (m, 2H), 7.34-7.38 (m, 3H), 7.51 (d, 1H, J = 7.6 Hz), 7.55 (dd, 2H, J = 1.7, 7.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 20.7, 88.3, 93.3, 123.0, 123.5, 125.6, 128.2, 128.3, 128.3, 129.4, 131.5, 131.8, 140.2.

1,3-Dimethyl-5-(phenylethynyl)benzene[7] (3ac): ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.30 (s, 6H), 6.96 (s, 1H), 7.16 (s, 2H), 7.31-7.35 (m, 3H), 7.50-7.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 21.1, 88.7, 89.7, 122.8, 123.4, 128.1, 128.3, 129.3, 130.2, 131.5, 137.9.

1-Fluoro-4-(phenylethynyl)benzene[6] (3ad): ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 7.03 (dd, 2H, J = 8.3 Hz), 7.33-7.34 (m, 3H), 7.49-7.51 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 88.3, 89.0, 115.6 (d, J = 23.1 Hz), 119.3, 123.1, 128.3 (d, J = 5.8 Hz, 131.5, 133.5 (d, J = 8.7 Hz), 161.7, 163.3.

1-(Phenylethynyl)-3-(trifluoromethyl)benzene[8] (3ae): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.35 (m, 3H), 7.46 (t, 1H, J = 7.9 Hz), 7.52-7.57 (m, 3H), 7.68 (d, 1H, J = 7.4 Hz), 7.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 87.8, 90.9, 122.6, 123.7 (q, J = 271.7 Hz), 124.3, 124.7, 128.4, 128.7, 128.8, 129.5, 131.0 (q, J = 32.6 Hz), 131.7, 134.6.

1-Methoxy-4-(phenylethynyl)benzene[6] (3af): ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 3.81 s, 3H), 6.86 (d, 2H, J = 8.2 Hz), 7.29-7.33 (m, 3H), 7.45-7.50 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 55.3, 88.0, 89.3, 114.0, 115.3, 123.5, 127.9, 128.3, 131.4, 133.0, 159.6.

2-(Phenylethynyl)naphthalene[6] (3ag): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.35 (m, 3H), 7.48 (m, 2H), 7.57 (m, 3H), 7.80 (m, 3H), 8.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 89.7, 89.8, 120.5, 123.2, 126.5, 126.7, 127.76, 127.78, 128.0, 128.30, 128.38, 128.41, 131.4, 131.6, 132.8, 133.0.

Methyl 3-phenylpropiolate[9] (3ba): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 3.82 (s, 3H), 7.36 (t, 2H, J = 7.7 Hz), 7.43 (t, 1H, J = 7.4 Hz), 7.57 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 52.8, 80.3, 86.5, 119.5, 128.6, 130.7, 133.0, 154.5.

Methyl 3-(4-fluorophenyl)propiolate[10] (3bd): ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 3.82 (s,

3H), 7.06 (t, 2H, J = 8.6 Hz), 7.56-7.58 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 52.8, 80.2, 85.4, 115.6 (d, 1C, J = 4.3 Hz), 116.1 (d, 2C, J = 21.7 Hz), 135.3 (d, 2C, J = 10.1 Hz), 154.3, 163.9 (d, 1C, J = 253 Hz)

Methyl 3-(3-(trifluoromethyl)phenyl)propiolate (3be):Colorless oil, ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 3.84 (s, 3H), 7.51 (t, 1H, J = 7.6 Hz), 7.69 (d, 1H, J = 8.2 Hz), 7.74 (d, 1H, J = 7.6 Hz), 7.83 (s, 1H) ; ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 53.0, 81.3, 84.2, 120.6, 123.31 (d, J = 273.1 Hz), 127.2, 129.2, 129.7, 131.4 (q, J = 33.2 Hz), 135.9, 154.0; IR (neat): 2957, 2229, 1718, 1438, 1335, 903, 805, 747, 694 cm^{-1}; DART-MS (m/z) calcd. for C11H9F3O2 (MH^+): 229.04764, found: 229.04675.

Methyl 3-(*o*-tolyl)propiolate[11] (3bb): ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.47 (s, 3H), 3.82 (s, 3H), 7.17 (t, 1H, J = 7.6Hz), 7.22 (d, 1H, J = 7.6 Hz), 7.32 (t, 1H, J = 7.9 Hz), 7.52 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 20.5, 52.8, 84.0, 85.5, 119.3, 125.8, 129.7, 130.6, 133.4, 142.2, 154.6.

Methyl 3-(3,5-dimethylphenyl)propiolate[9] (3bc): ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.28 (s, 6H), 3.81 (s, 3H), 7.06 (s, 1H), 7.19 (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 21.0, 52.7, 79.7, 87.1, 119.1, 130.7, 132.7, 138.2, 154.6.

1-Methyl-3-(phenylethynyl)benzene[12] (3da): ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 2.37 (s, 3H), 7.16 (d, 1H, J = 7.6 Hz), 7.26 (t, 1H, J = 7.6 Hz), 7.34-7.38 (m, 5H), 7.54 (dd, 2H, J = 2.1 Hz, 7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 21.2, 89.0, 89.5, 123.0, 123.4, 128.16, 128.22, 128.3, 128.7, 129.2, 131.6, 132.2, 138.0.

1-Methyl-4-(phenylethynyl)benzene[6] (3ea): ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 2.36 (s, 3H), 7.14 (d, 2H, J = 7.6 Hz), 7.31-7.34 (m, 3H), 7.42 (d, 2H, J = 8.2 Hz), 7.51 (dd, 2H, J = 1.7 , 7.9 Hz) ; ^{13}C NMR ($CDCl_3$, 125 MHz)δ= 21.5, 88.7, 89.5, 120.1, 123.4, 128.1, 128.3, 129.1, 131.5, 131.5, 138.4.

1-Methoxy-2-(phenylethynyl)benzene[13] (3fa): ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 3.90 (s, 3H), 6.89 (d, 1H, J = 8.2 Hz), 6.92 (t, 1H, J = 7.6 Hz), 7.28-7.33 (m, 4H), 7.48 (d, 1H, J = 7.6 Hz), 7.54 (d, 2H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ= 55.8, 85.7, 93.4, 110.7, 112.4, 120.5, 123.5, 128.1, 128.2, 129.7, 131.6, 133.6, 159.9.

1-Bromo-4-(phenylethynyl)benzene[13] (3ia): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.32-7.39 (m, 5H), 7.45-7.52 (m,. 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 88.3, 90.5, 122.2, 122.5, 122.9, 128.4, 128.5, 131.58, 131.60, 133.0.

4-(Phenylethynyl)-1,1'-biphenyl[12] (3ja): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.32-7.37 (m, 4H), 7.43-7.46 (m, 2H), 7.53-7.61 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 89.3, 90.0, 122.2, 123.3, 127.0, 127.6, 128.3, 128.4, 128.8, 131.6, 132.0, 140.3, 140.9.

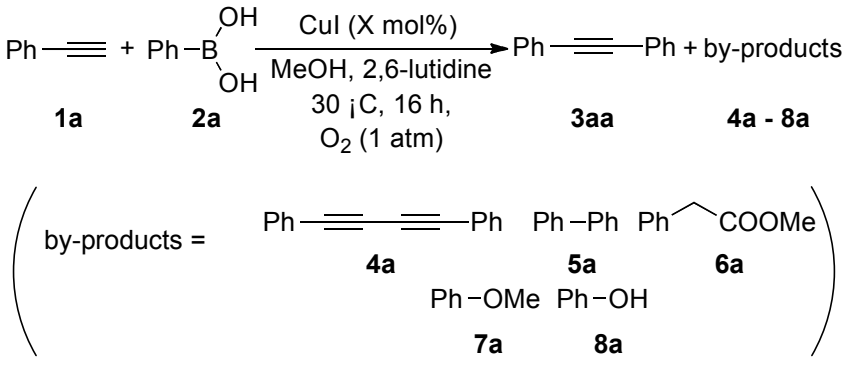
4-(Phenylethynyl)pyridine[14] (3ka): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.34-7.38 (m, 5H), 7.53-7.54 (m, 2H), 8.58 (d, 2H, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 86.6, 94.0, 122.1, 125.5, 128.5, 129.2, 131.5, 131.9, 149.8.

Dodec-1-yn-1-ylbenzene (3la):Colorless oil, ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.86 (t, 3H, J = 7.1 Hz), 1.22-1.28 (m, 12H), 1.39-1.45 (m, 2H), 1.55-1.61 (m, 2H), 2.38 (t, 2H, J = 7.4 Hz), 7.25 (m, 3H), 7.36-7.38 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 14.1, 19.4, 22.7, 28.8, 28.9, 29.2, 29.3, 29.5, 29.6, 31.9, 80.5, 90.5, 124.1, 127.4, 128.1, 131.5; IR (neat): 2926, 2854, 2232, 755, 722 cm^{-1}; DART-MS (m/z) calcd. for C18H27(MH^+): 243.21128, found: 243.21101

1-(Phenylethynyl)cyclohexanol[6] (3ma): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.25 (m, 1H), 1.55-1.75 (m, 7H), 1.98-2.05 (m, 3H), 7.27-7.30 (m, 3H), 7.40-7.43 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 23.4, 25.2, 40.1, 69.1, 84.4, 92.8, 122.9, 128.1, 128.2, 131.7.

The mixture of diastereomers of 4-ethyl-1-phenyloct-1-yn-3-ol (3na):Colorless oil, ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.89-0.97 (m, 6H), 1.32-1.58 (m, 8H), 1.80-1.81 (m, 1H), 4.61 (d, 1H, J = 4.5 Hz), 7.27-7.29 (m, 3H), 7.40-7.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 11.6, 11.7, 14.06, 14.08, 22.4, 22.7, 23.0, 23.1, 28.9, 29.2, 29.4, 29.5, 46.0, 65.4, 65.5, 85.6, 89.4, 122.8, 128.26, 128.28, 131.7; IR (neat): 3361, 2958, 2929, 2870, 2225, 1027, 756, 691 cm^{-1}; DART-MS (m/z) calcd. for C16H21 ([M-OH]$^+$): 213.16433, found: 213.16504

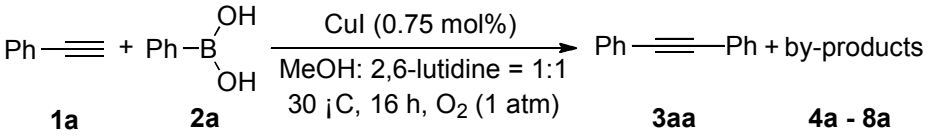
Table S-1. Effect of the amounts of the catalyst[a]



entry	CuI (mol%)	conv. **1a** (%)[b]	yield (%)[b]					
			3aa	**4a**	**5a**[c]	**6a**	**7a**[c]	**8a**[c]
1	0.15	26	21	1	1	0	3	3
2	0.3	29	23	trace	1	0	3	4
3	0.45	46	41	2	1	0	6	6
4	0.75	59	50	2	1	0	8	8
5[d]	0.75	79	69	3	3	1	11	11
6	1.2	52	46	2	1	0	7	6
7	3	24	17	2	trace	0	2	2
8[d]	3	98	67	24	4	2	12	9

[a] Reaction conditions: 30 ˚C, alkyne (0.25 mmol), boronic acid (0.5 mmol), methanol (0.5 ml), 2,6-lutidine (0.5 ml). [b] Determined by GC analysis. [c] Yield was determined based on used **2a**. [d] Reaction temperature was 60 ˚C.

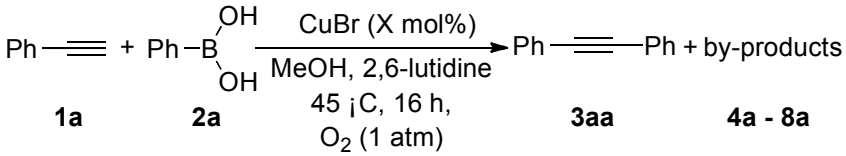
Table S-2. Effect of concentrations[a]



entry	conc. (M)	conv. **1a** (%)[b]	yield (%)[b]					
			3aa	**4a**	**5a**[c]	**6a**	**7a**[c]	**8a**[c]
1[d]	1.25	27	14	1	2	0	3	3
2	0.417	52	41	2	trace	0	6	6
3	0.3125	57	49	4	1	0	7	7
4	0.25	59	50	2	1	0	8	8
5	0.2083	56	50	2	1	0	8	7
6	0.167	56	48	3	1	0	8	7

[a] Reaction conditions: 30 ˚C, alkyne (0.25 mmol), boronic acid (0.5 mmol). [b] Determined by GC analysis. [c] Yield was determined based on used **2a**. [d] Reaction temperature was 60 ˚C.

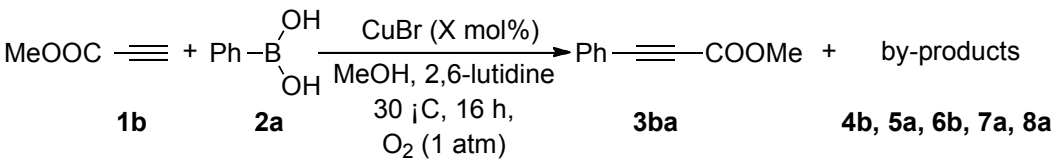
Table S-3. Optimization of reaction conditions using 1.5 equiv of phenylboronic acid[a]

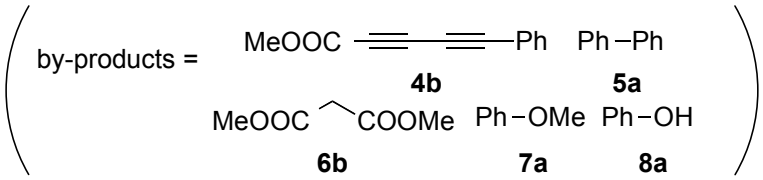


entry	**2a** (equiv)	X (mol%)	MeOH (ml)	lutidine (ml)	conv. **1a** (%)[b]	yield (%)[b] **3aa**	**4a**	**5a**[c]	**6a**	**7a**[c]	**8a**[c]
1	2.0	1.5	0.33	0.66	97	83	5	1	0	14	13
2	1.9	1.5	0.33	0.66	94	85	5	1	1	15	13
3	1.8	1.5	0.33	0.66	95	83	5	1	1	15	13
4	1.7	1.5	0.33	0.66	93	81	6	1	1	16	13
5	1.6	1.5	0.33	0.66	92	79	6	1	1	16	16
6	1.5	1.5	0.33	0.66	89	76	9	1	1	17	12
7[d]	1.5	1.5	0.33	0.66	92	75	8	1	1	16	12
8	1.5	2.25	0.33	0.66	92	76	9	1	1	16	13
9	1.5	3	0.33	0.66	92	76	10	trace	1	16	13
10	1.5	1.5	0.25	0.75	86	75	<12	1	1	14	12
11	1.5	2.25	0.25	0.75	89	75	9	1	1	14	12
12	1.5	3	0.25	0.75	88	73	9	trace	1	13	12
13	1.5	1.5	0.2	0.8	81	68	5	1	1	11	12
14	1.5	2.25	0.2	0.8	81	69	6	trace	1	11	12
15	1.5	3	0.2	0.8	84	70	7	trace	1	11	11
16	1.5	1.5	0.4	0.6	86	72	7	1	1	16	12
17	1.5	1.5	0.5	0.5	81	69	6	2	1	16	11
18	1.5	1.5	0.6	0.4	76	64	4	2	1	15	10
19[e]	1.5	1.5	0.33	0.66	91	74	13	1	1	16	12

[a] Reaction conditions: 45 ˚C, alkyne (0.25 mmol), boronic acid (0.375 mmol). [b] Determined by GC analysis. [c] Yield was determined based on used **2a**. [d] Reaction time was 36 h. [e] Reaction temperature was 50 ˚C.

Table S-4. Optimization of reaction conditions using methyl propiolate (1)[a]

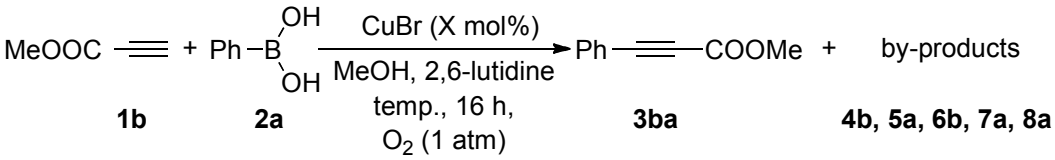




entry	X (mol%)	Y (equiv)	MeOH (ml)	lutidine (ml)	conv. **1b** (%)[b]	yield (%)[b] **3ba**	**5a**[c]	**7a**[c]	**8a**[c]
1	0.75	1.5	0.5	0.5	95	20	0	11	0
2	0.75	1.5	0.9	0.1	95	54	trace	1	7
3	0.75	1.1	0.9	0.1	87	41	8	1	0
4	0.75	1.1	0.95	0.05	59	27	5	trace	trace
5	0.75	1.1	1.4	0.1	92	48	8	2	0
6	1.5	1.1	0.9	0.1	88	40	8	1	0
7	1.5	1.1	1.4	0.1	80	45	0	0	7
8	1.5	1.5	1.4	0.1	92	62	2	0	7
9	1.5	1.1	1.3	0.2	92	48	0	1	9
10	1.5	1.1	1.2	0.3	96	44	0	1	10

[a] Reaction conditions: 30 ˚C, alkyne (0.25 mmol). [b] Determined by GC analysis. [c] Yield was determined based on used **2a**.

Table S-5. Optimization of reaction conditions using methyl propiolate part (2)[a]

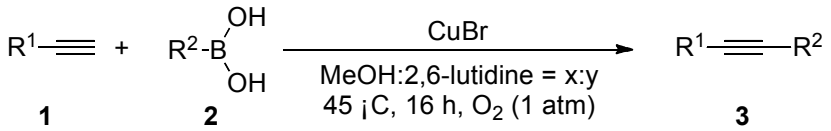


entry	X (mol%)	Y (equiv)	temp. (˚C)	MeOH (ml)	lutidine (ml)	conv. **1b** (%)[b]	yield (%)[b] **3ba**	**5a**[c]	**7a**[c]	**8a**[c]
11	0.75	1.1	45	1.4	0.1	100	48	0	4	11
12	0.75	1.1	0	1.4	0.1	9	0	0	0	0
13	0.9	1.1	30	1.3	0.2	86	45	0	1	8
14	0.75	1.1	30	1.3	0.2	85	47	0	1	8
15	0.6	1.1	30	1.3	0.2	80	44	0	1	8
16	0.45	1.1	30	1.3	0.2	71	41	0	1	7
17	0.3	1.1	30	1.3	0.2	69	38	0	1	6
18	0.75	1.1	30	1.8	0.2	89	57	0	2	8
19	0.75	1.1	30	1.85	0.15	87	58	0	2	8

20	0.75	1.1	30	1.9	0.15	85	58	0	2	7
21	0.75	1.1	30	2.3	0.2	89	64	0	2	8
22	0.75	1.1	30	2.8	0.2	89	64	0	2	8
23	0.75	1.3	30	2.3	0.2	100	68	0	4	8
24	0.75	1.5	30	2.3	0.2	100	75	1	4	7
25	0.75	1.7	30	2.3	0.2	100	75	1	4	7
26	0.75	1.9	30	2.3	0.2	100	74	1	4	6
27	0.75	1.5	20	2.3	0.2	93	71	0	2	7
28	0.75	1.5	25	2.3	0.2	96	75	0	3	6
29	0.75	1.5	45	2.3	0.2	100	68	1	6	10
30	0.75	1.5	30	2.4	0.1	100	77	1	5	7
31	0.75	1.5	30	2.8	0.2	100	77	1	5	7
32	0.75	1.5	30	2.9	0.1	99	79	1	6	7
33	0.75	1.5	30	3.8	0.2	100	79	1	6	7
34	1.5	1.5	30	3.9	0.1	97	82	1	6	6
35	0.75	1.5	30	3.9	0.1	95	75	1	6	6

[a] Reaction conditions: 30 ˚C, alkyne (0.25 mmol). [b] Determined by GC analysis. [c] Yield was determined based on used **2a**.

Table S-6. Optimization of reaction conditions using various substrates[a]



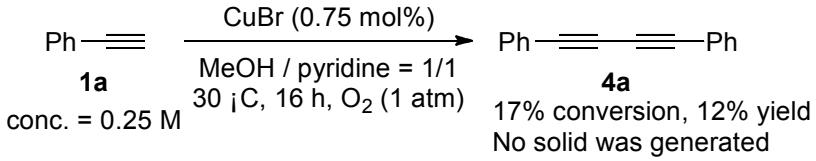
1 **2** **3**

entry	**1**	**2** (equiv.)	x:y	CuBr (mol%)	conc. (M)	product	yield (%)[b]
1	**1g**	**2a** (1.9)	1.4	1.5	0.125	**3ga**	54
2	**1g**	**2a** (1.9)	1:4	0.75	0.125	**3ga**	76
3	**1h**	**2a** (1.9)	1:2	1.5	0.125	**3ha**	67
4	**1h**	**2a** (1.9)	1:2	0.75	0.125	**3ha**	74
5	**1j**	**2a** (1.9)	1:2	1.5	0.25	**3ja**	35
6	**1j**	**2a** (1.9)	1:2	0.75	0.125	**3ja**	62
7[c]	**1j**	**2a** (1.9)	1:2	0.75	0.125	**3ja**	71
8	**1a**	**2g** (1.9)	1:2	1.5	0.25	**3ag**	26
9[d]	**1a**	**2g** (1.9)	1:2	0.75	0.125	**3ag**	86
10	**1k**	**2a** (1.9)	1:2	0.3	0.125	**3ka**	Tr
11	**1k**	**2a** (3.0)	1:2	0.15	0.25	**3ka**	23

12[c]	**1k**	**2a** (3.0)	1:2	0.15	0.125	**3ka**	34
13[c]	**1k**	**2a** (3.0)	1:4	0.15	0.125	**3ka**	36
14[c, e]	**1k**	**2a** (3.0)	1:4	0.15	0.125	**3ka**	44
15[c, e]	**1k**	**2a** (3.0)	1:4	0.45	0.125	**3ka**	12
16[c]	**1k**	**2a** (3.0)	1:4	0.75	0.125	**3ka**	13
17[c, e]	**1k**	**2a** (3.0)	1:4	0.75	0.125	**3ka**	30
18[c, e]	**1k**	**2a** (3.0)	1:4	0.45	0.0625	**3ka**	38

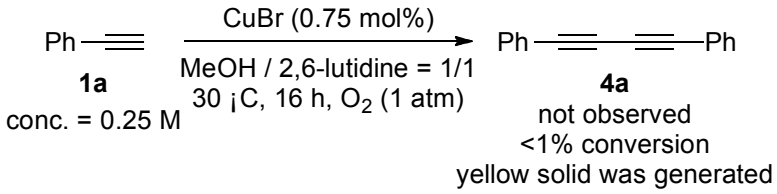
[a] All reactions were conducted on a 0.125 mmol scale as an alkynes. [b] Isolated yield.
[c] Reaction time was 36 h. [d] Reaction time was 30 h. [e] Reaction temperature was 60 °C.

2-3. A procedure for the homocoupling reaction of phenyl acetylene (1a) catalyzed by CuBr in pyridine media (Scheme S-1): Phenylacetylene (**1a**, 25.6 mg, 0.25 mmol), methanol (0.45 mL) and pyridine (0.45 mL) were combined in a round-bottomed flask. After a *CuBr solution* (0.1 mL), which was prepared from methanol, pyridine and copper bromide, was added to the reaction mixture, it was stirred for 16 h under O_2 atmosphere at 30 °C. 1 M HCl aq. (10 mL) was added and the whole aqueous layer was extracted with dichloromethane (30~40 mL). The organic layer was dried over Na_2SO_4. The conversion of the alkyne and the yields of products were determined by GC analysis, with reference to an internal standard (IS = methyl benzoate) using condition B.



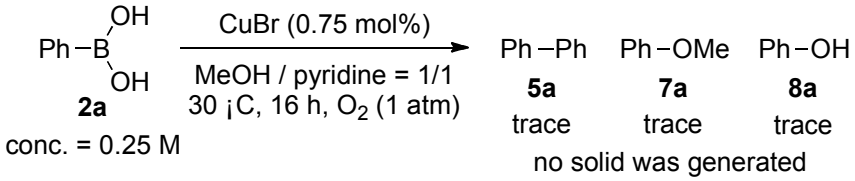
Scheme S-1. Homocoupling of an alkyne in pyridine media

2-4. A procedure for homocoupling reaction of phenyl acetylene (1a) catalyzed by CuBr in 2,6-lutidine media (Scheme S-2): Phenylacetylene (25.6 mg, 0.25 mmol), methanol (0.45 mL) and 2,6-lutidine (0.45 mL) were combined in a round-bottomed flask. After the *CuBr solution* (0.1 mL) was added to the reaction mixture, it was stirred for 16 h under O_2 atmosphere at 30 °C. 1 M HCl aq. (10 mL) was added and the whole aqueous layer was extracted with dichloromethane (30~40 mL). The organic layer was dried over Na_2SO_4. The conversion of the alkyne and the yields of products were determined by GC analysis, with reference to an internal standard (IS = ethylbenzene or methyl benzoate) using condition B.



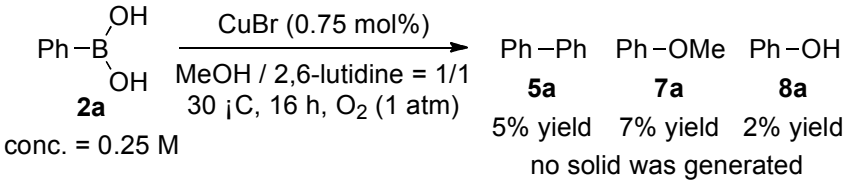
Scheme S-2. Homocoupling of an alkyne in 2,6-lutidine media

2-5. A procedure for homocoupling reaction of phenylboronic acid (2a) catalyzed by CuBr in pyridine media (Scheme S-3): Phenylboronic acid (**2a**, 30.5 mg, 0.25 mmol), methanol (0.45 mL) and pyridine (0.45 mL) were combined in a round-bottomed flask. After a *CuBr solution* (0.1 mL), which was prepared from methanol, pyridine and copper bromide, was added to the reaction mixture, it was stirred for 16 h under O_2 atmosphere at 30 ^{o}C. 1 M HCl aq. (10 mL) was added and the whole aqueous layer was extracted with dichloromethane (30~40 mL). The organic layer was dried over Na_2SO_4. The yields of products were determined by GC analysis, with reference to an internal standard (IS = methyl benzoate) using condition A.



Scheme S-3. Homocoupling of a boronic acid in pyridine media

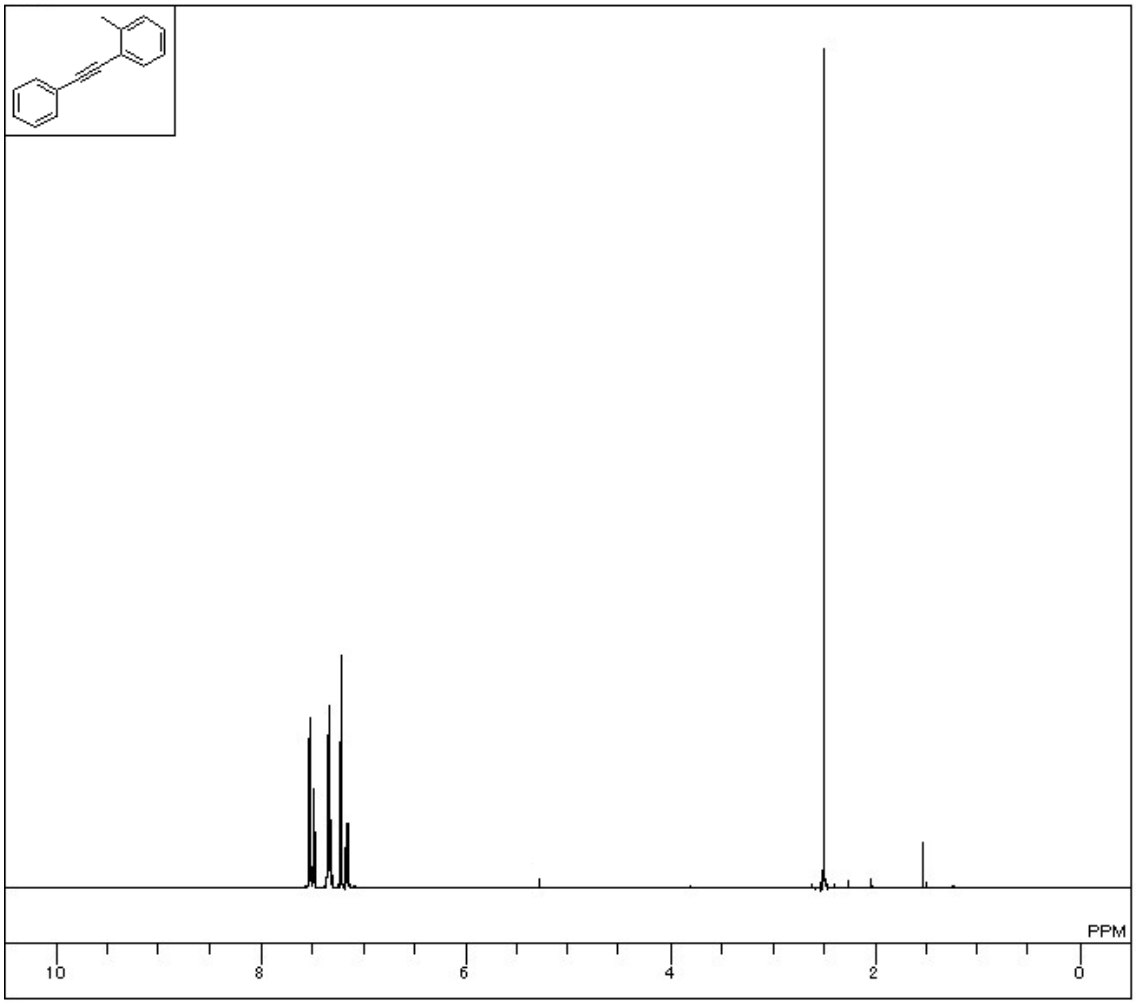
2-6. A procedure for homocoupling reaction of phenylboronic acid (2a) catalyzed by CuBr in 2,6-lutidine media (Scheme S-4): Phenylboronic acid (**2a**, 30.5 mg, 0.25 mmol), methanol (0.45 mL) and 2,6-lutidine (0.45 mL) were combined in a round-bottomed flask. After the *CuBr solution* (0.1 mL) was added to the reaction mixture, it was stirred for 16 h under O_2 atmosphere at 30 ^{o}C. 1 M HCl aq. (10 mL) was added and the whole aqueous layer was extracted with dichloromethane (30~40 mL). The organic layer was dried over Na_2SO_4. The yields of products were determined by GC analysis, with reference to an internal standard (IS = ethylbenzene or methyl benzoate) using condition A for the other compounds.

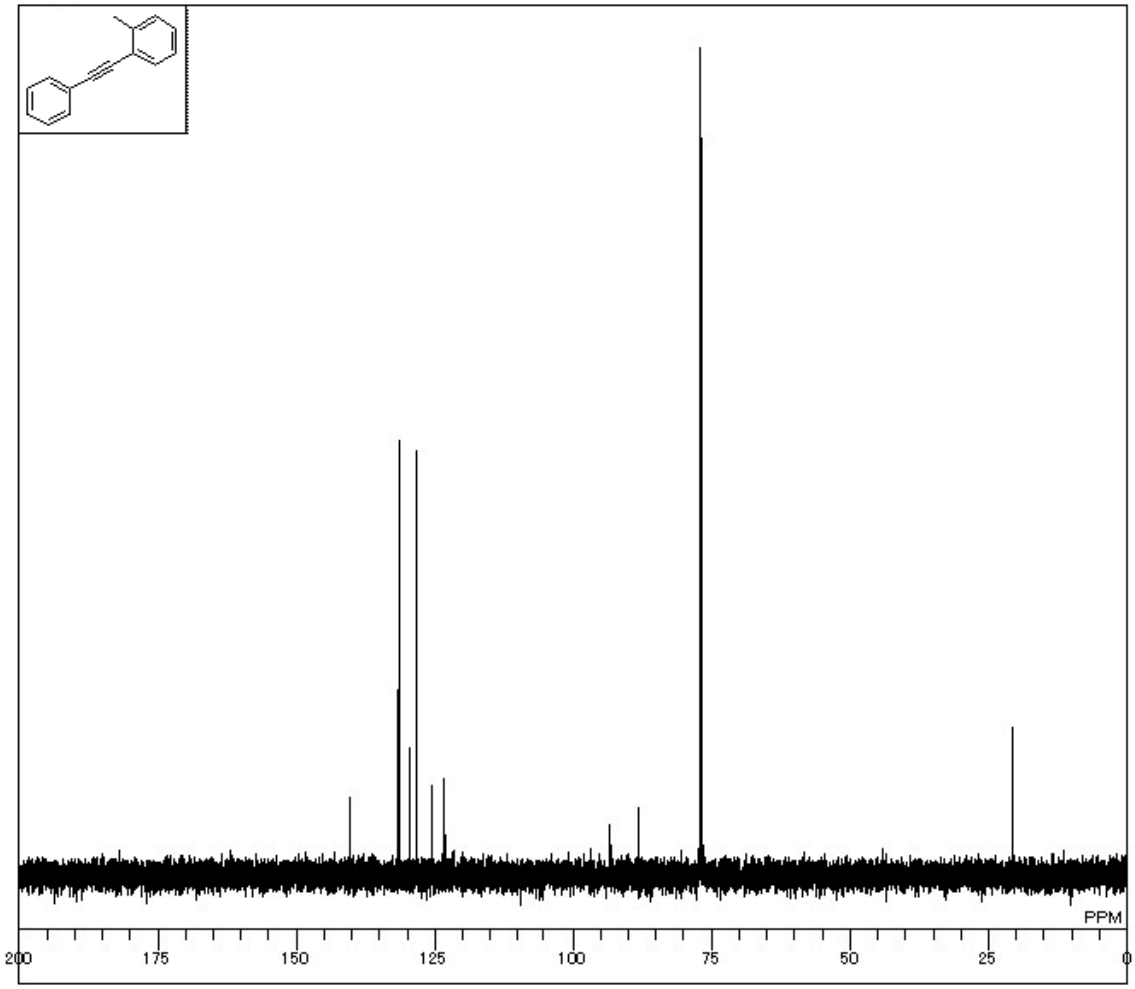


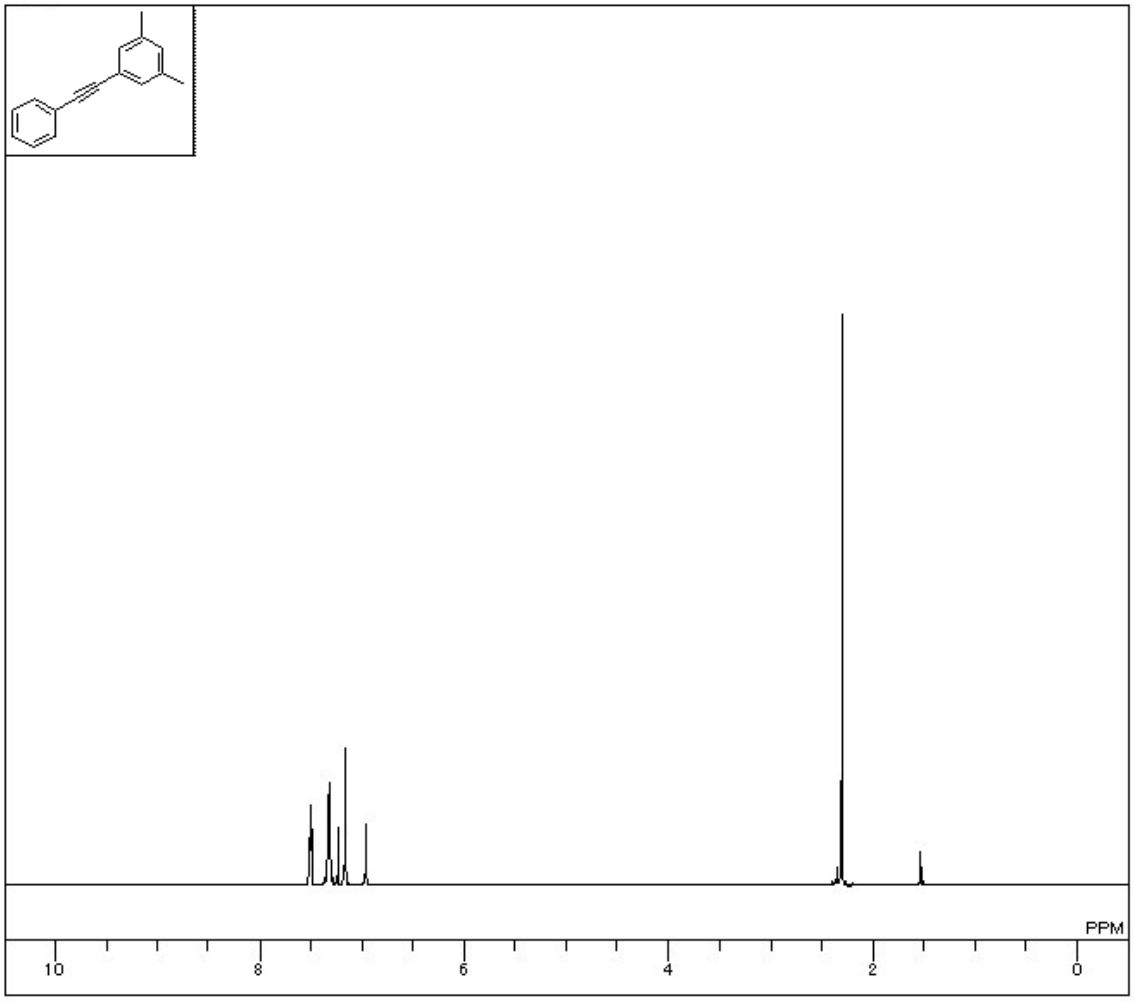
Scheme S-4. Homocoupling of a boronic acid in 2,6-lutidine media

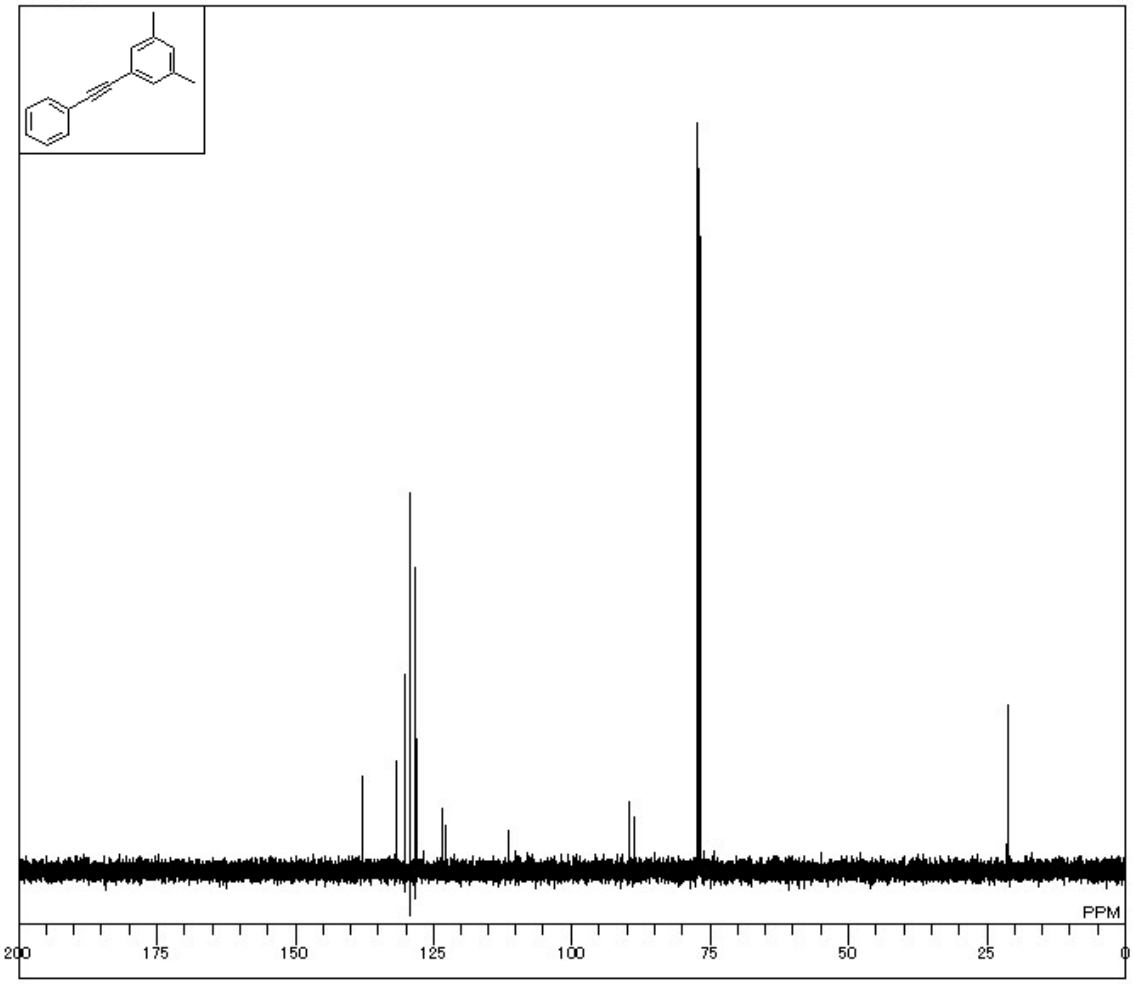
2-7. A procedure for quantification of palladium in CuBr by ICP analysis : CuBr (100 mg) was dissolved in mixture of sulfuric acid (1 ml) and aqua regia (1 ml). Pure water was added to this solution until total volume became 50 ml. The amount of palladium in the resulting solution was measured by ICP analysis and found under detection limit.

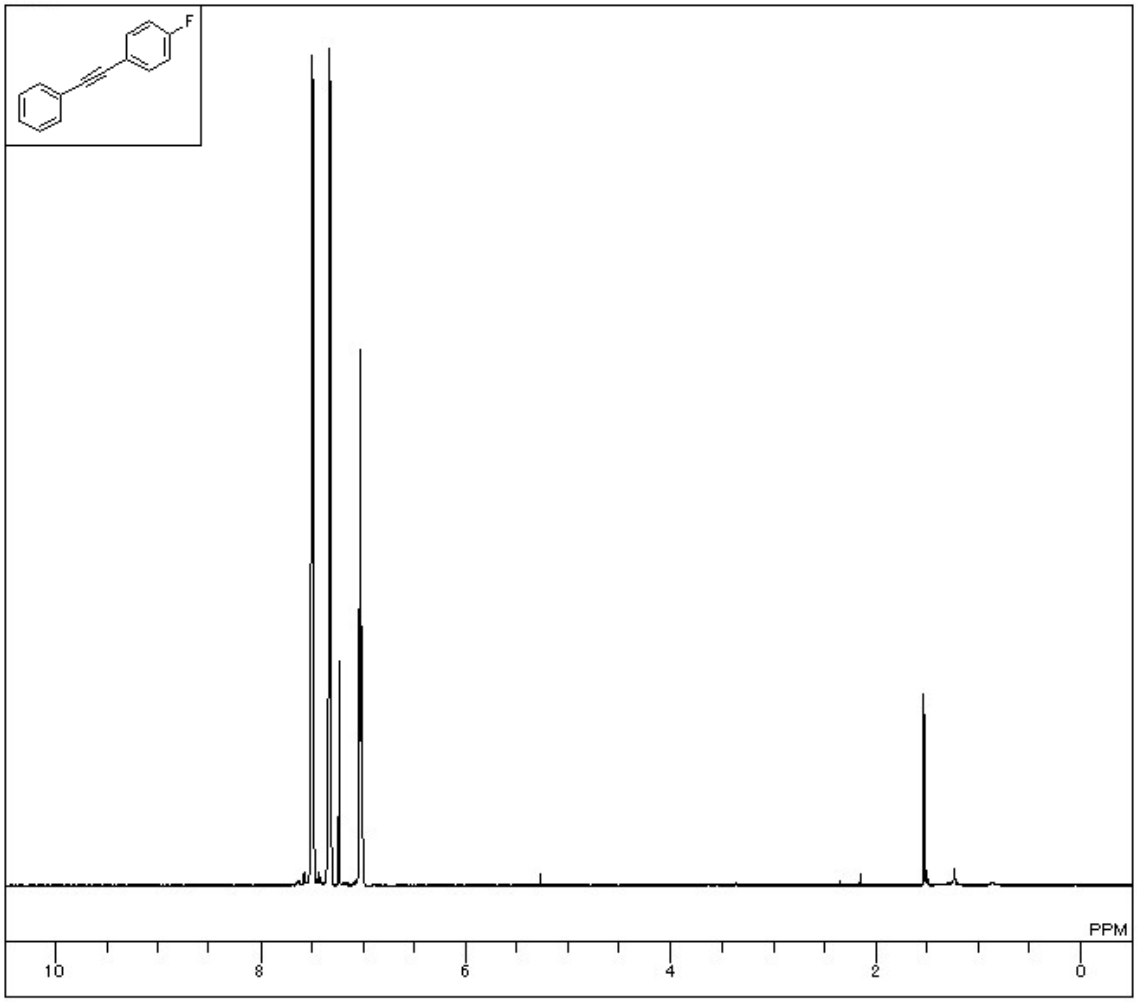
3. NMR charts

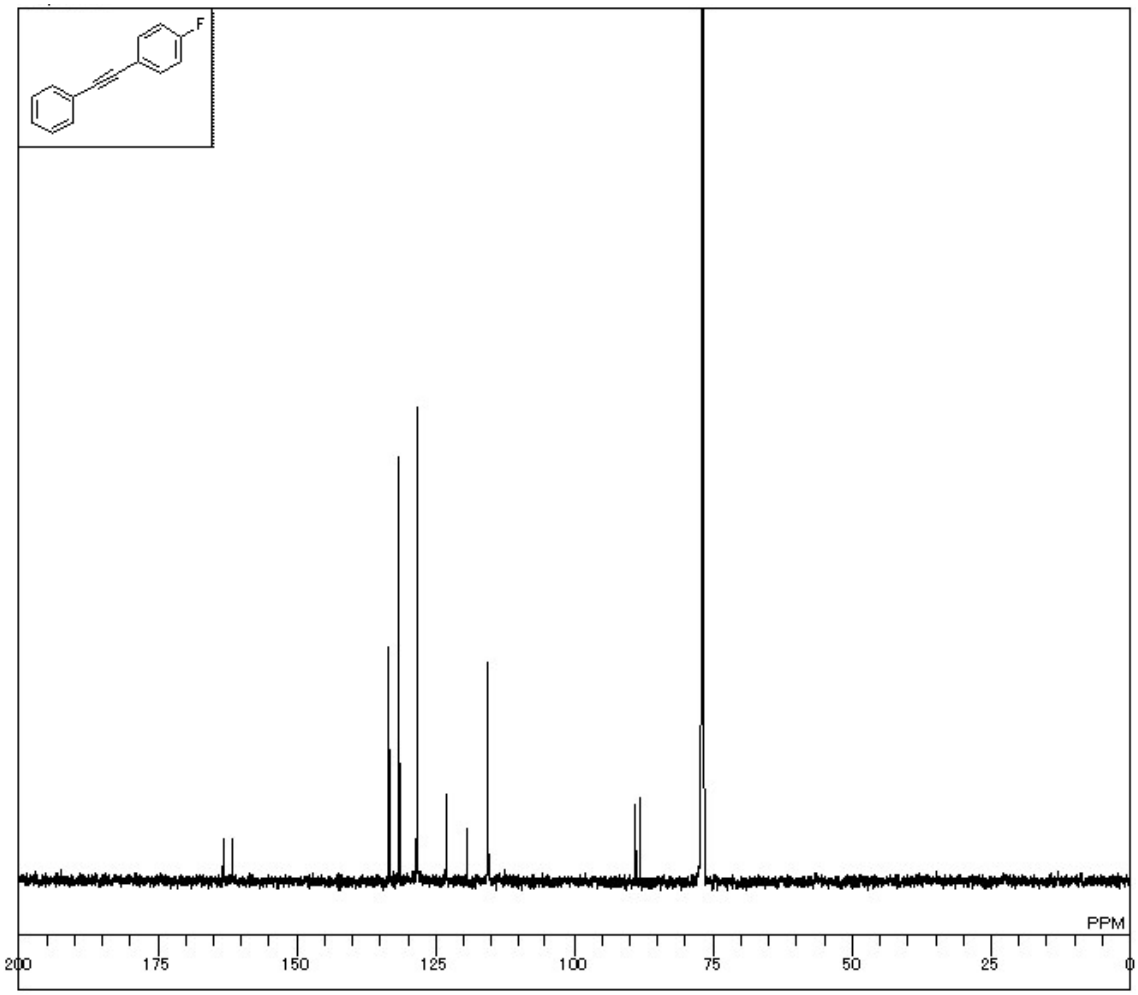


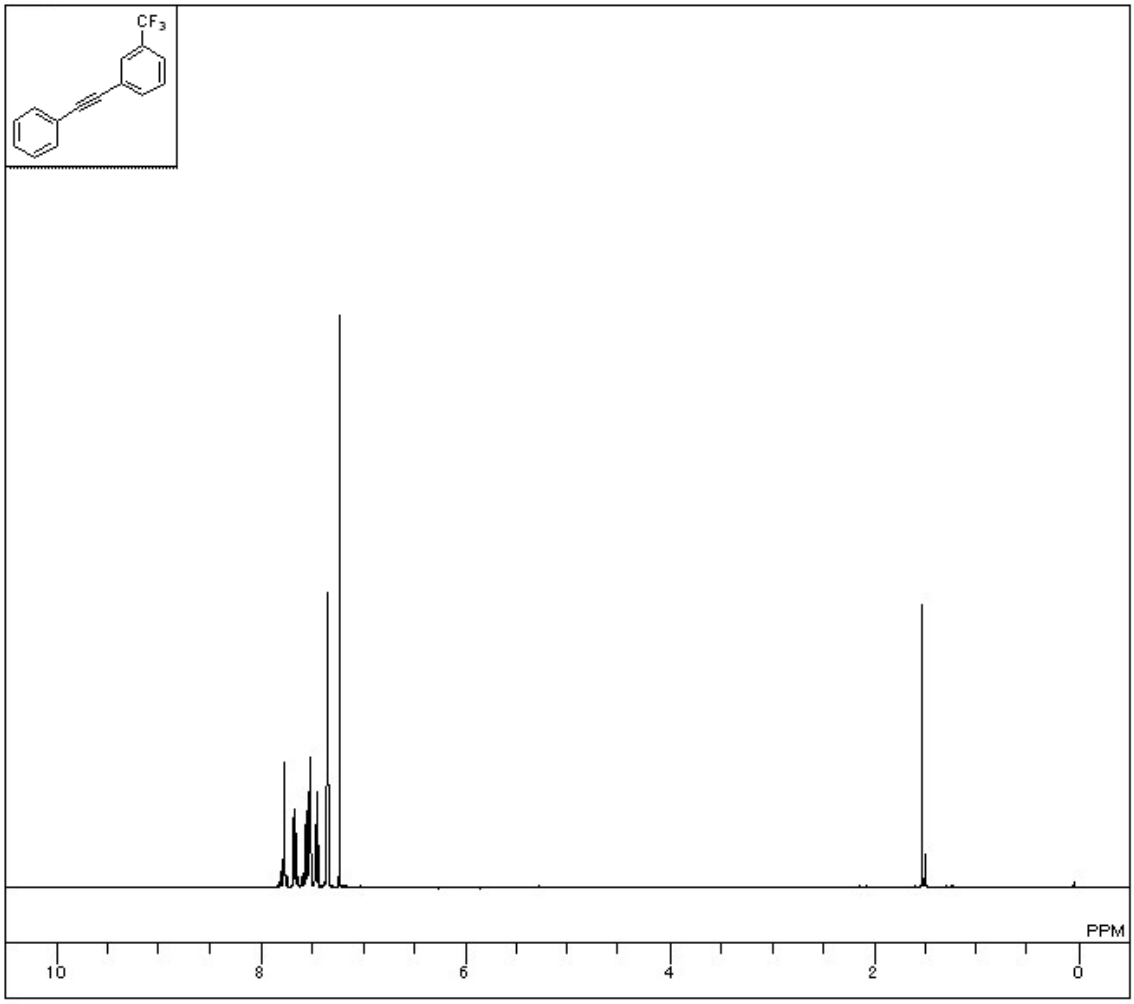


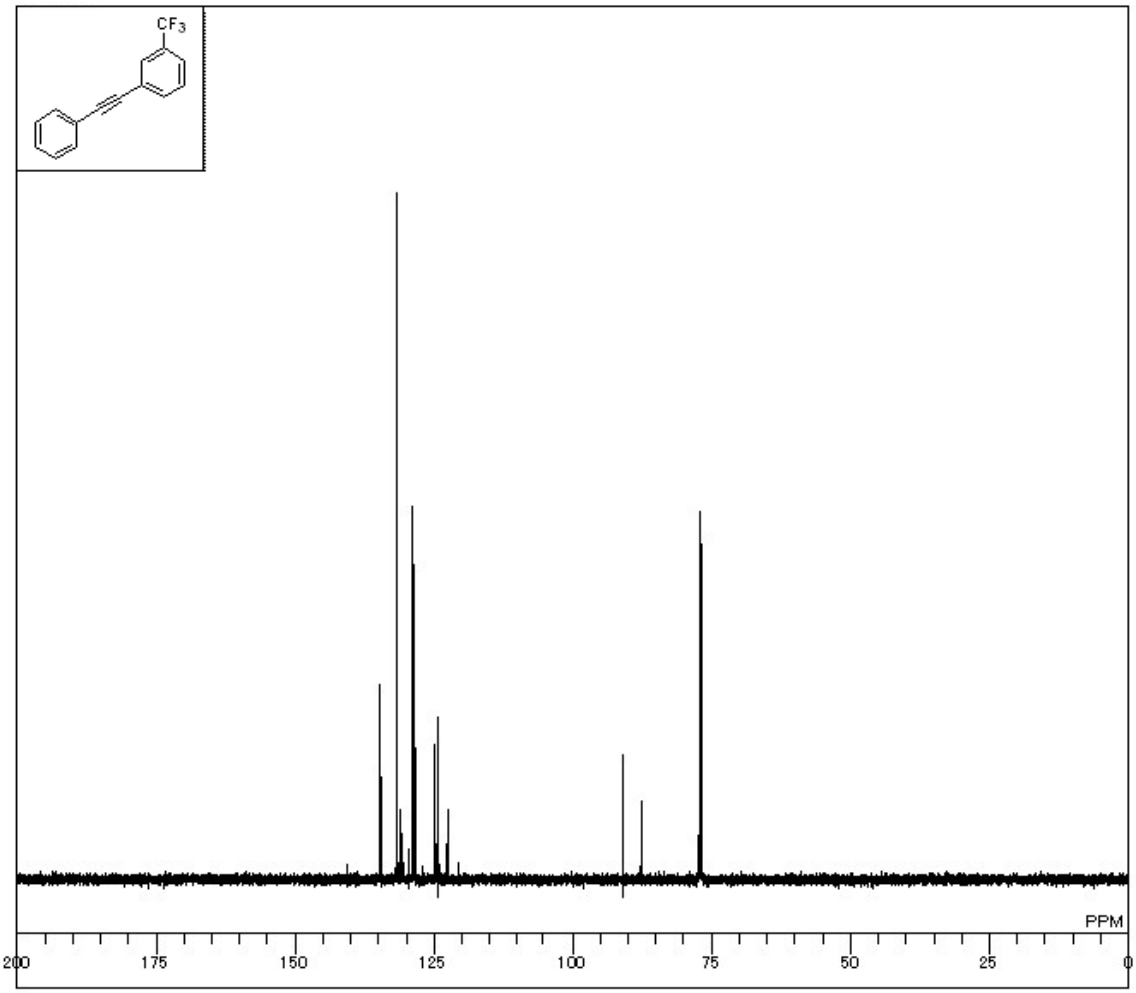


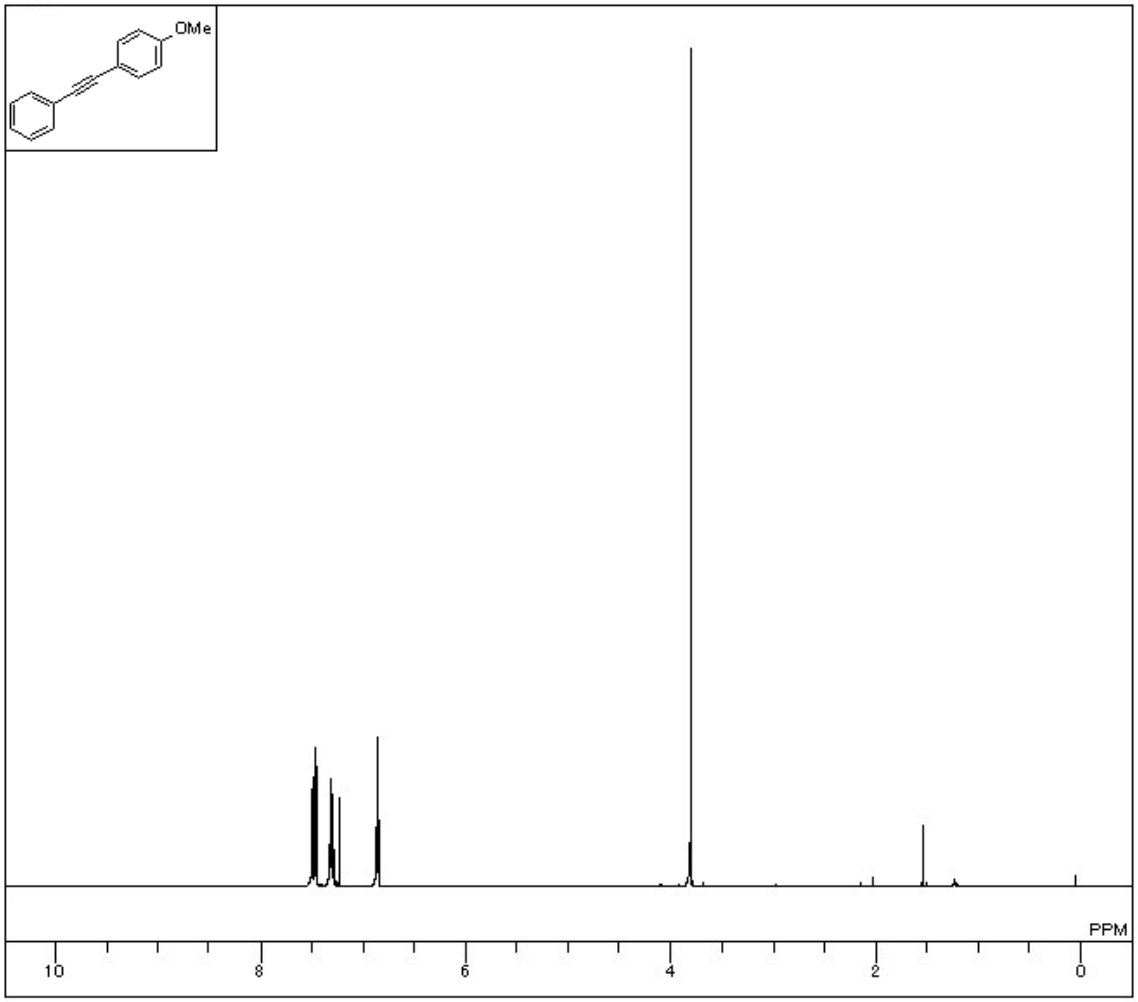


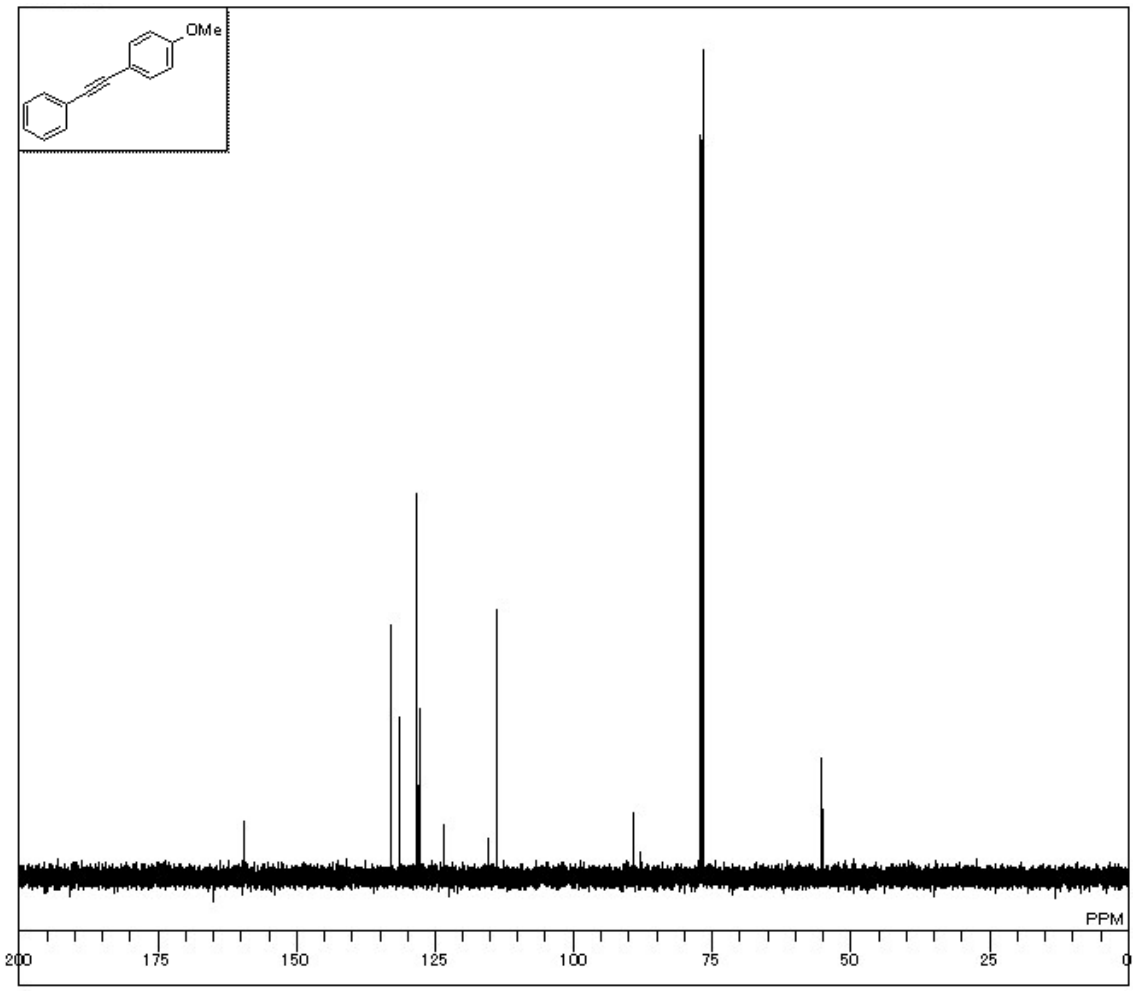


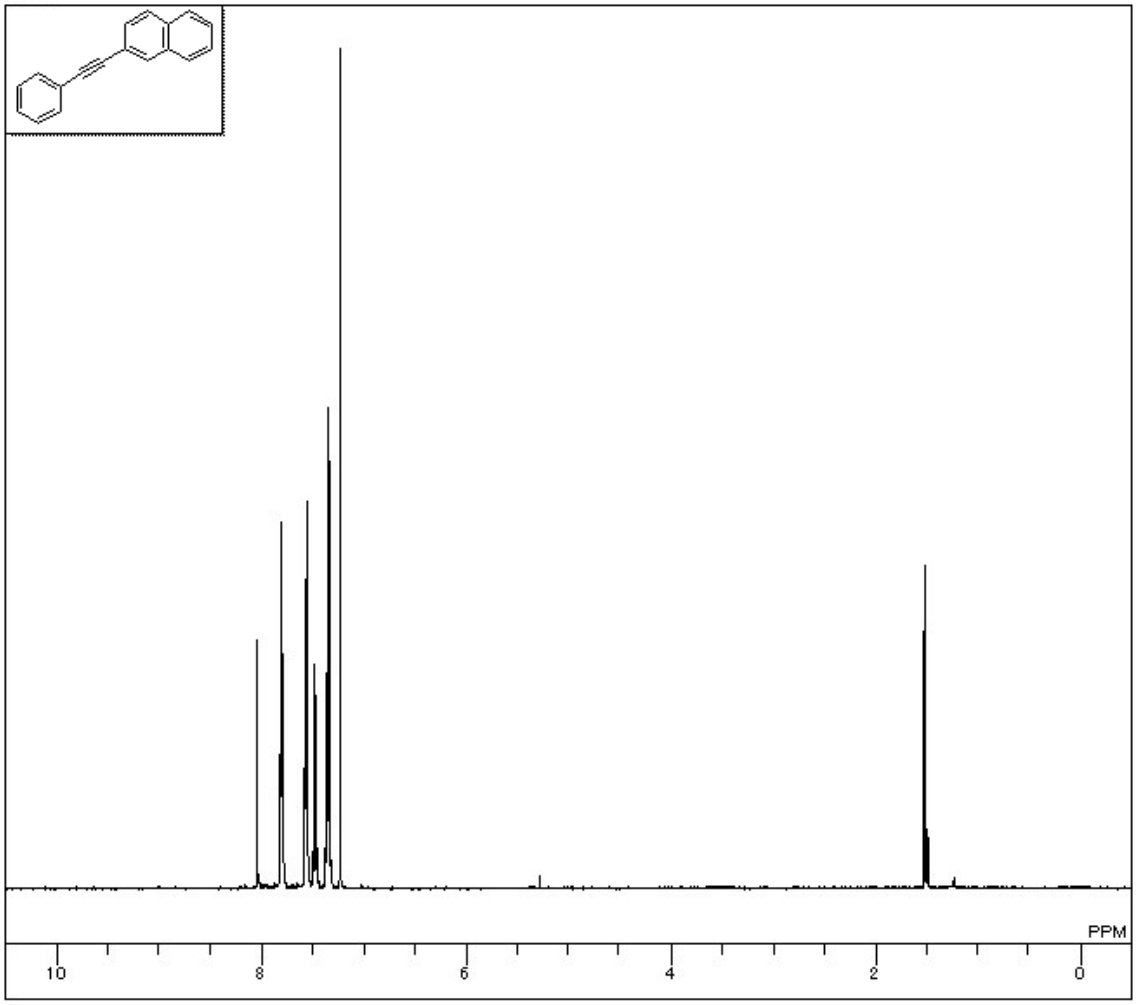








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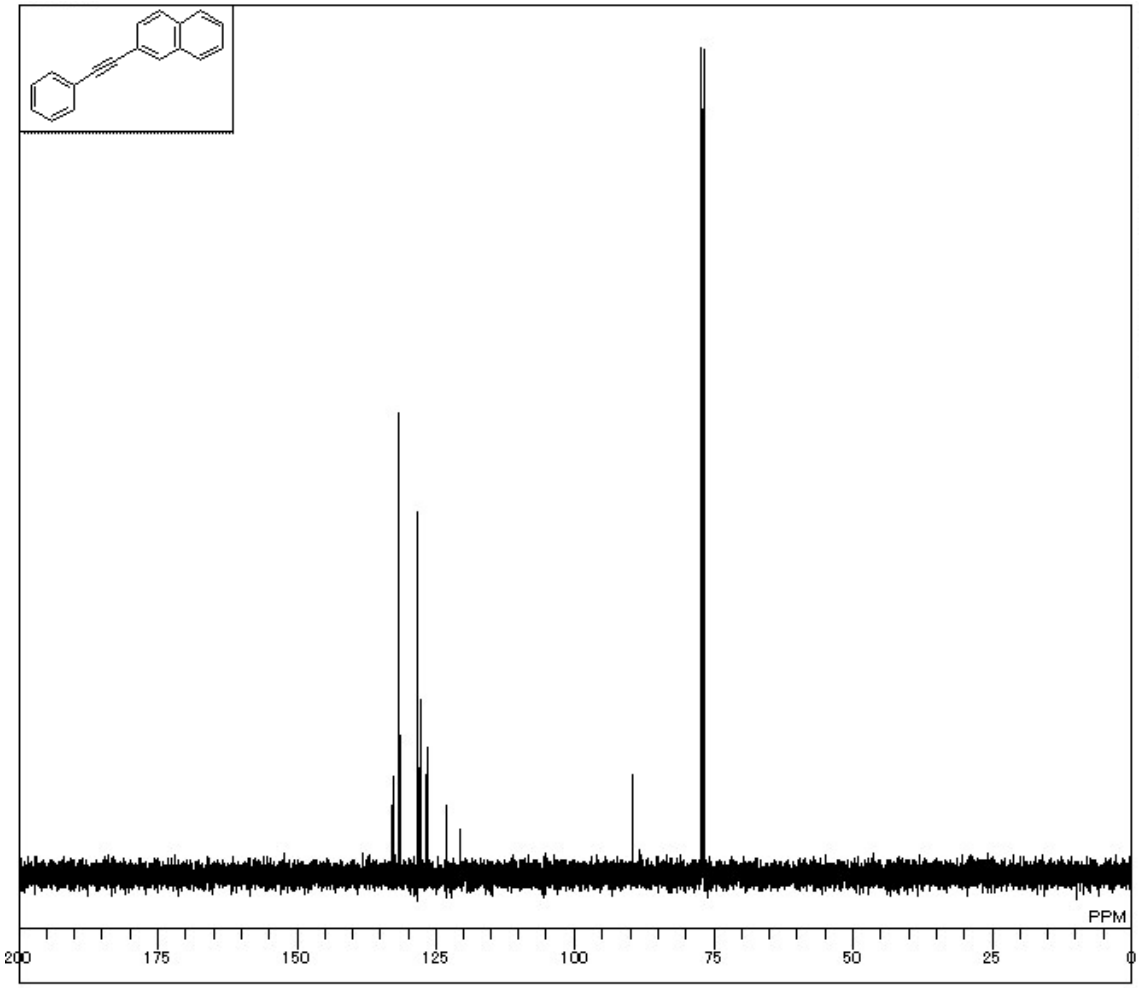
2
0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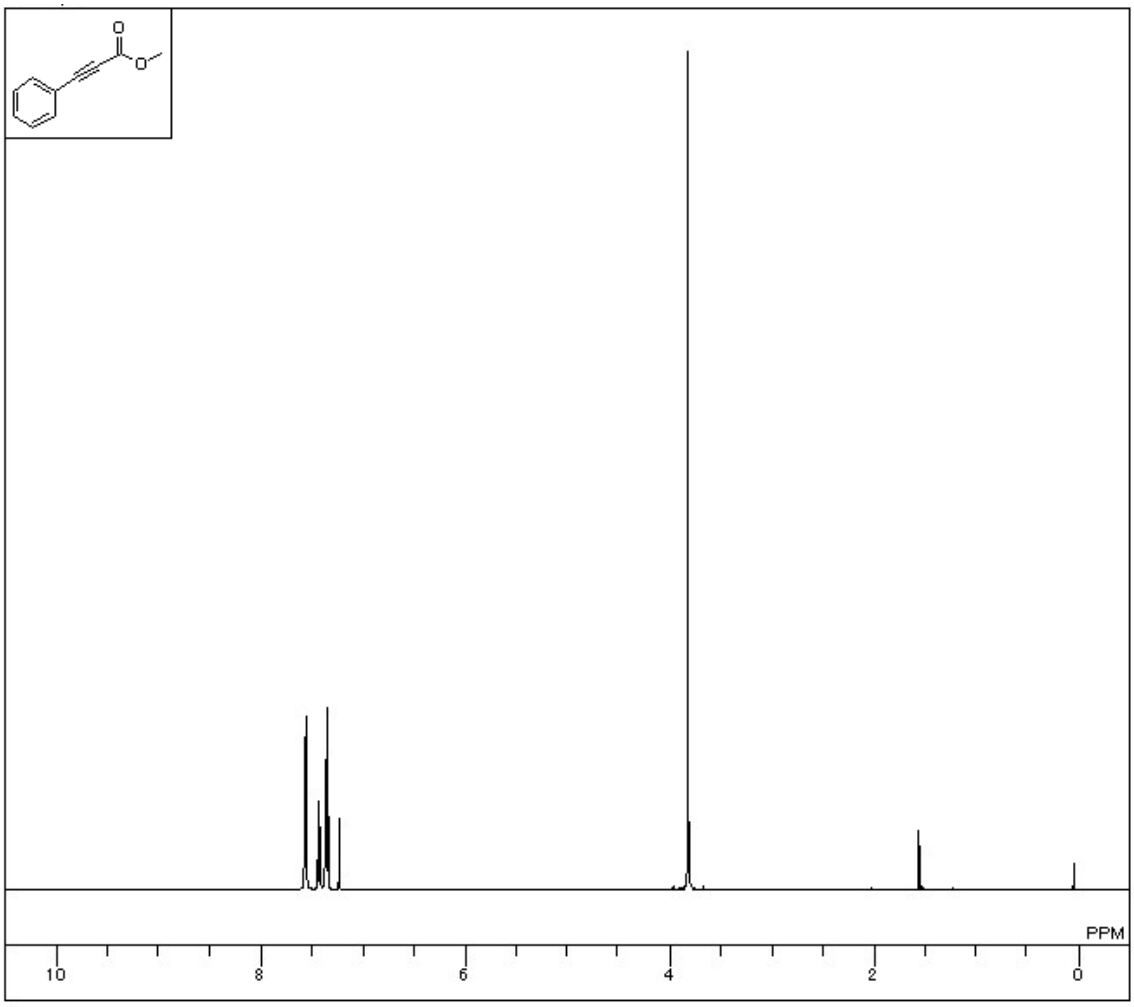
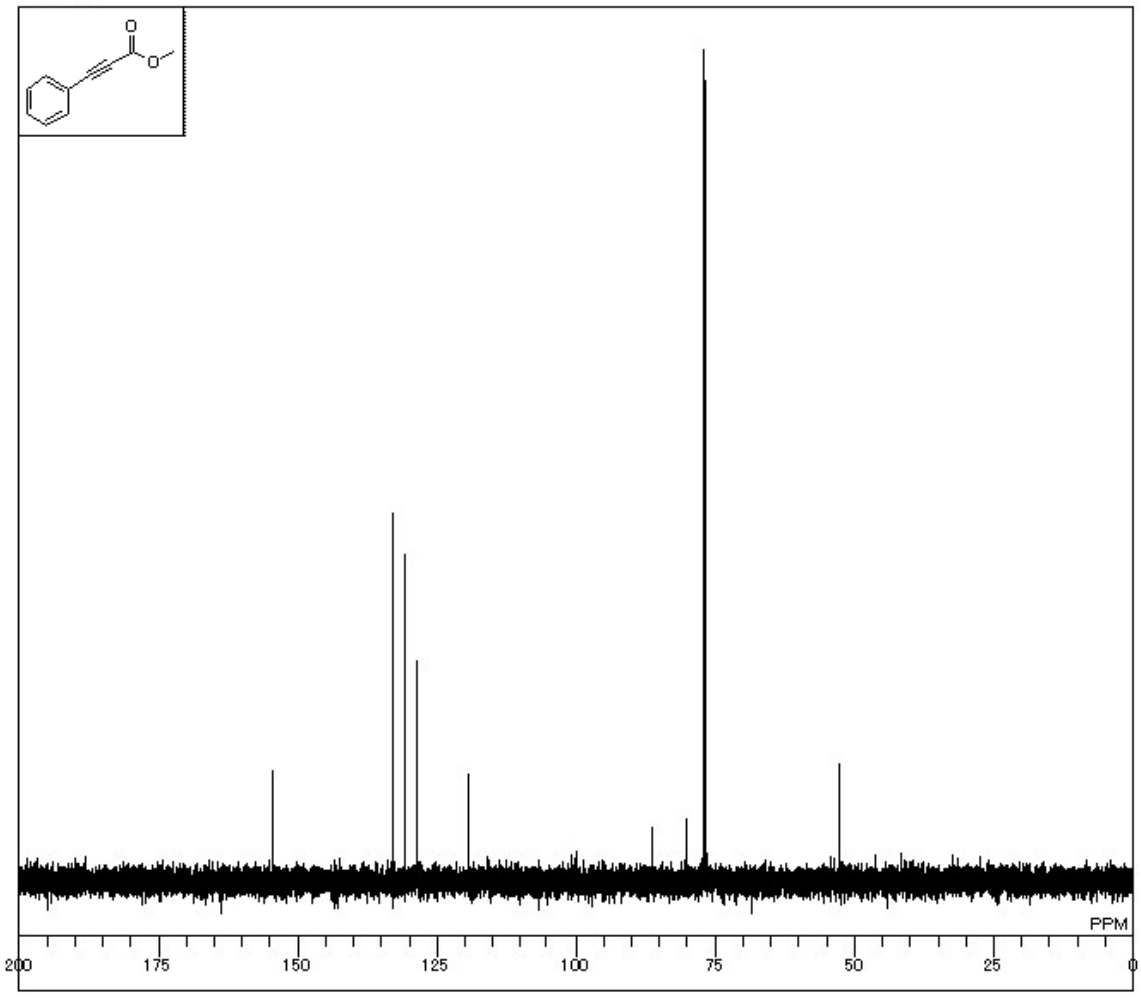
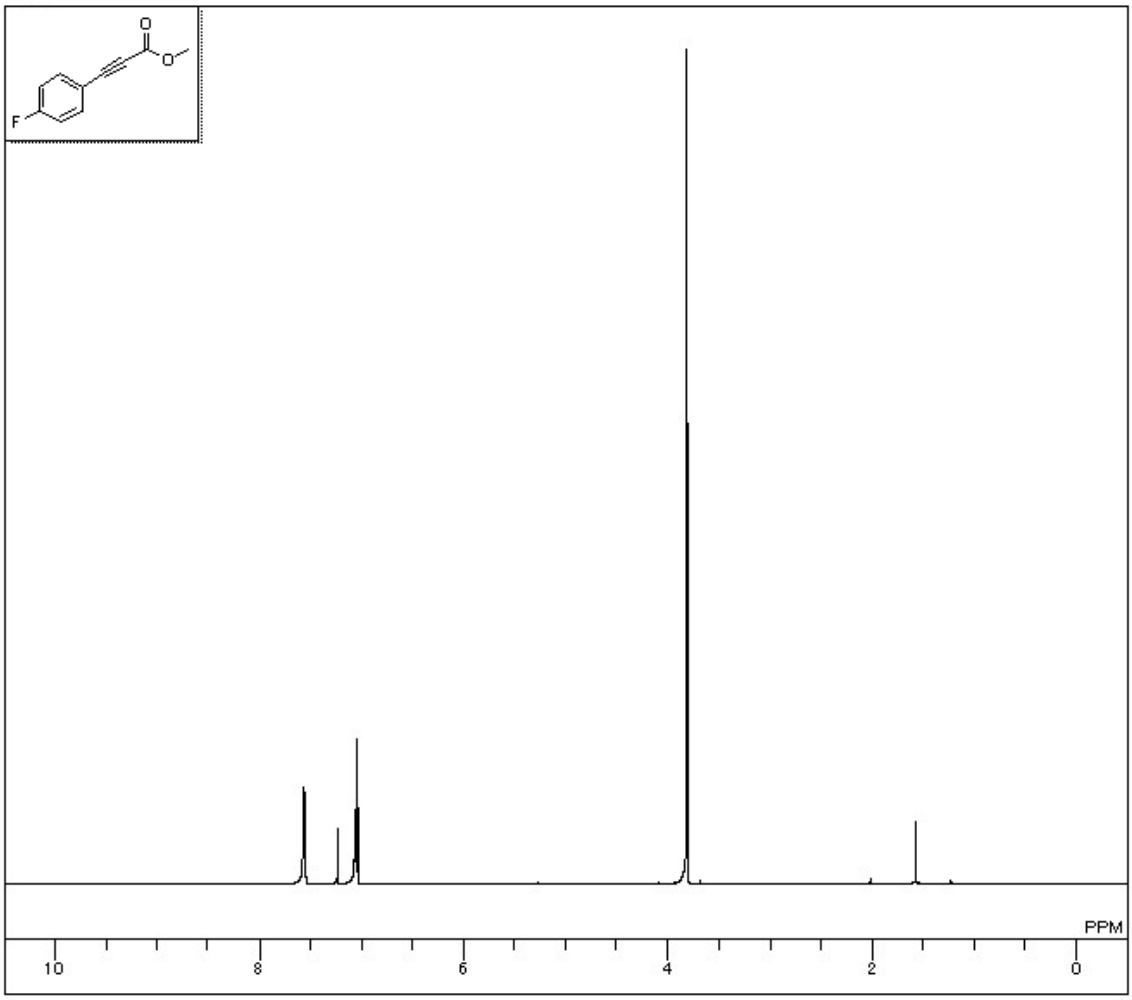
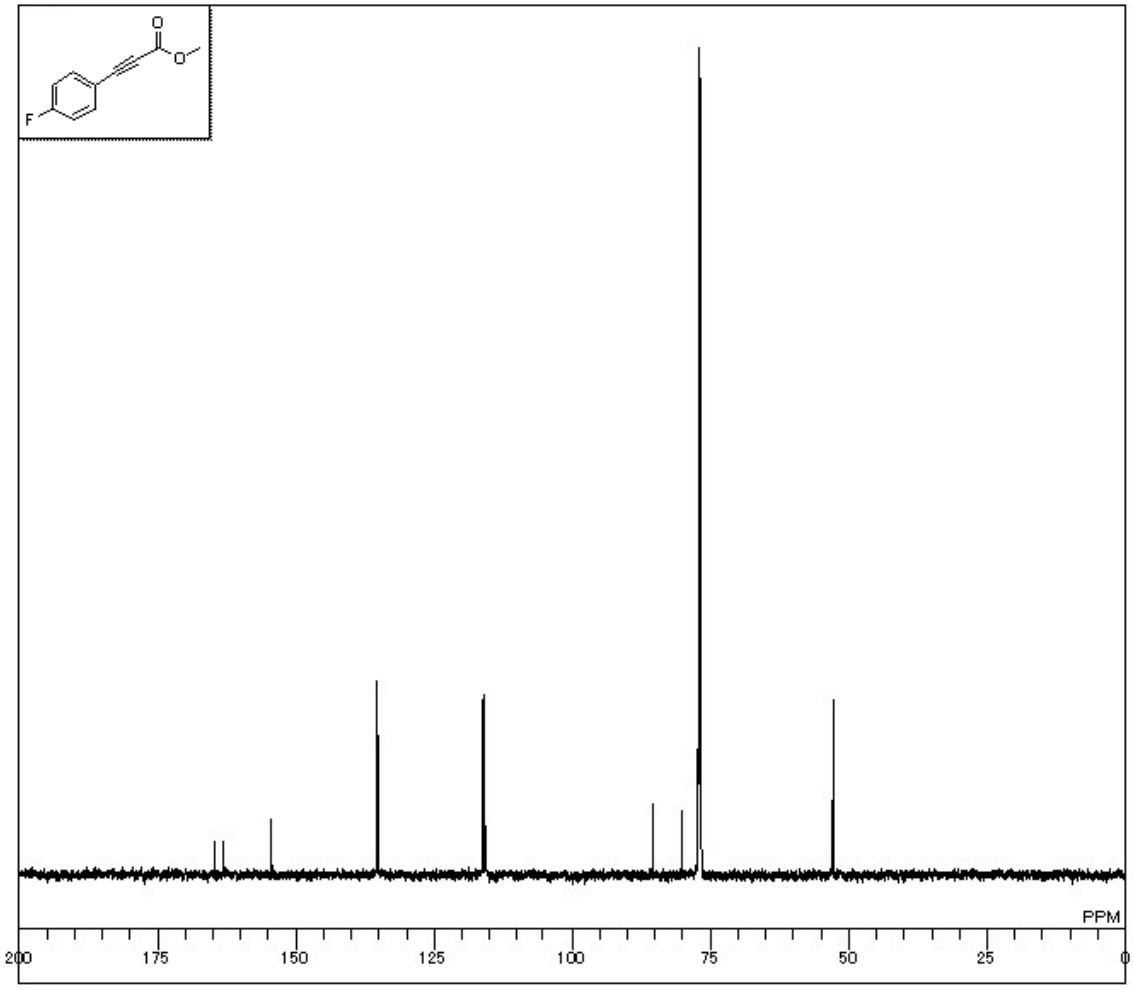
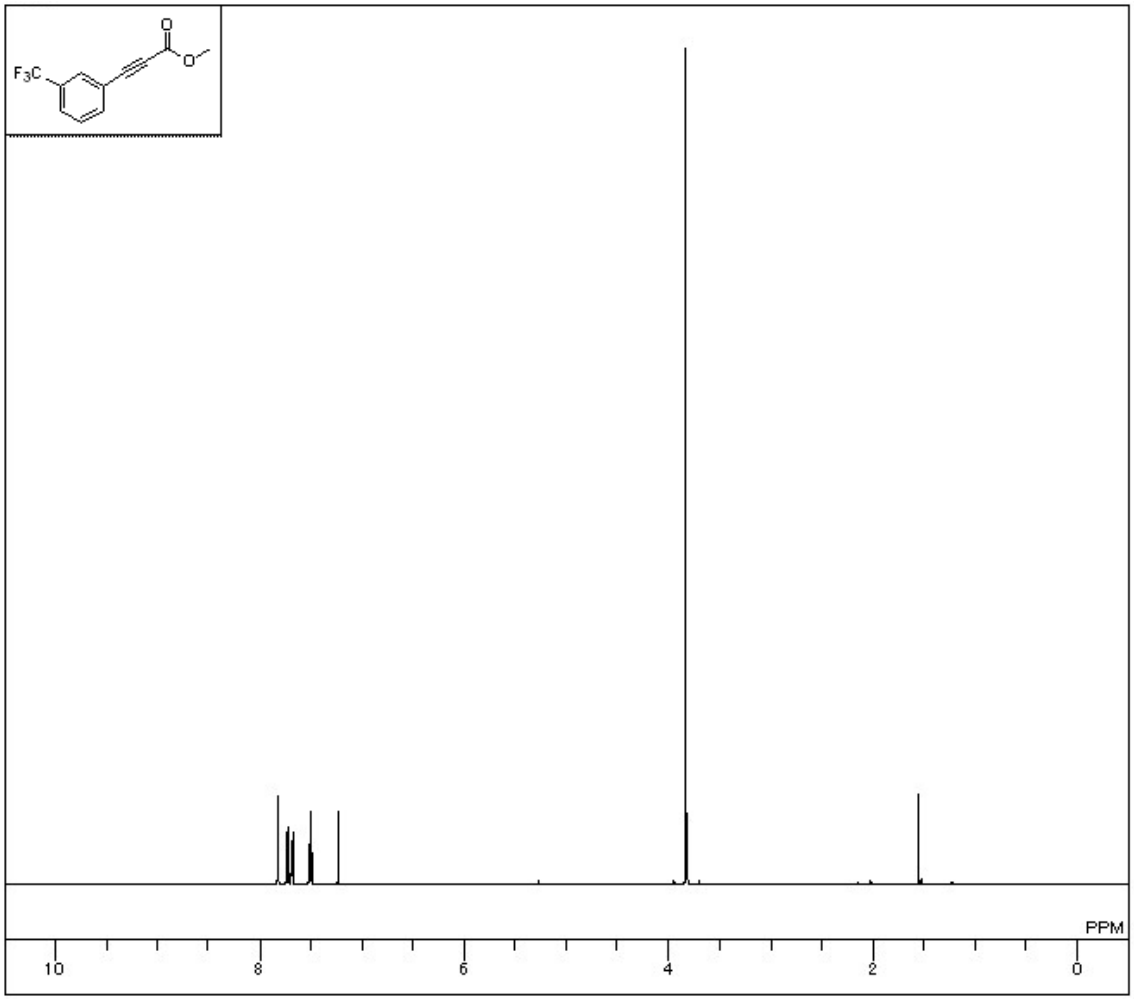
150
125
100
75
50
25
0

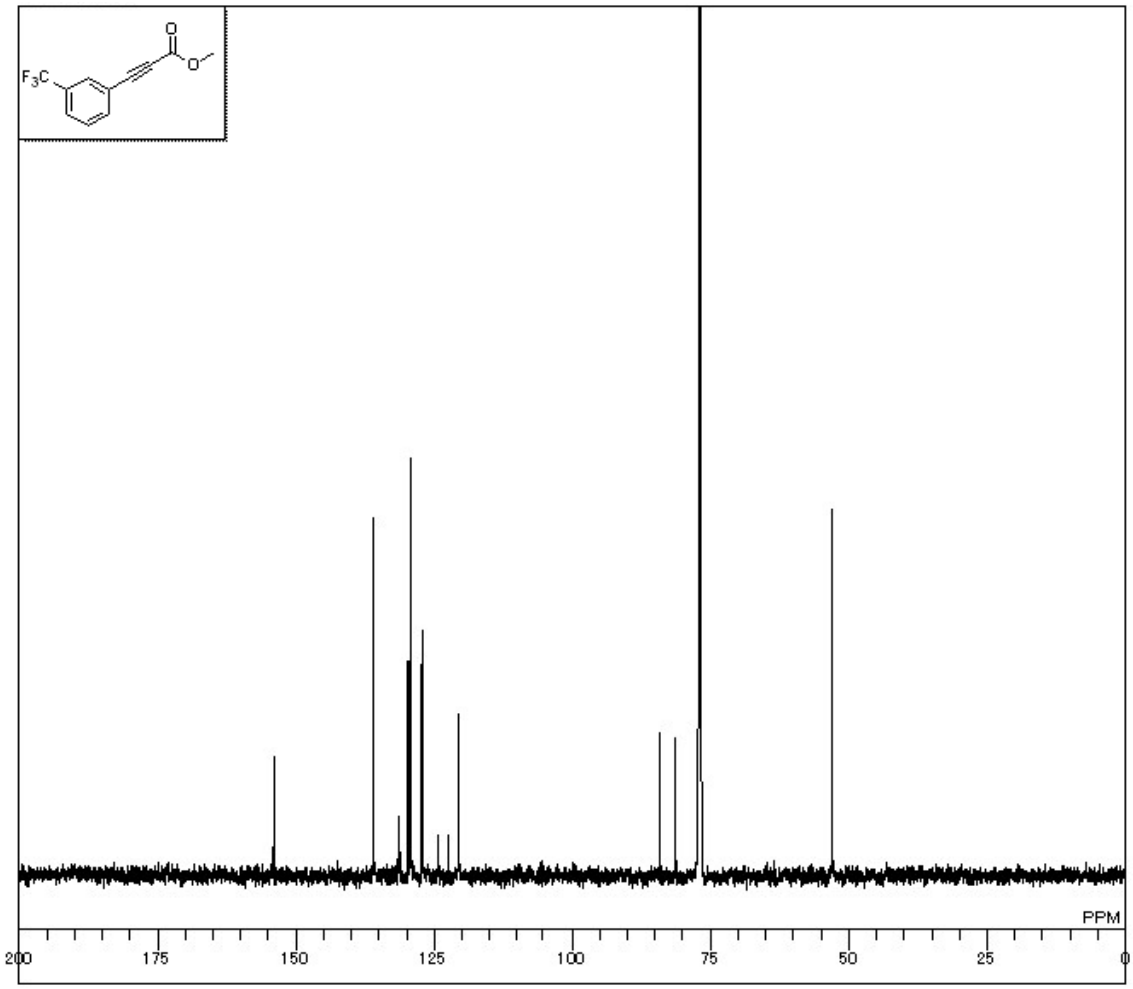


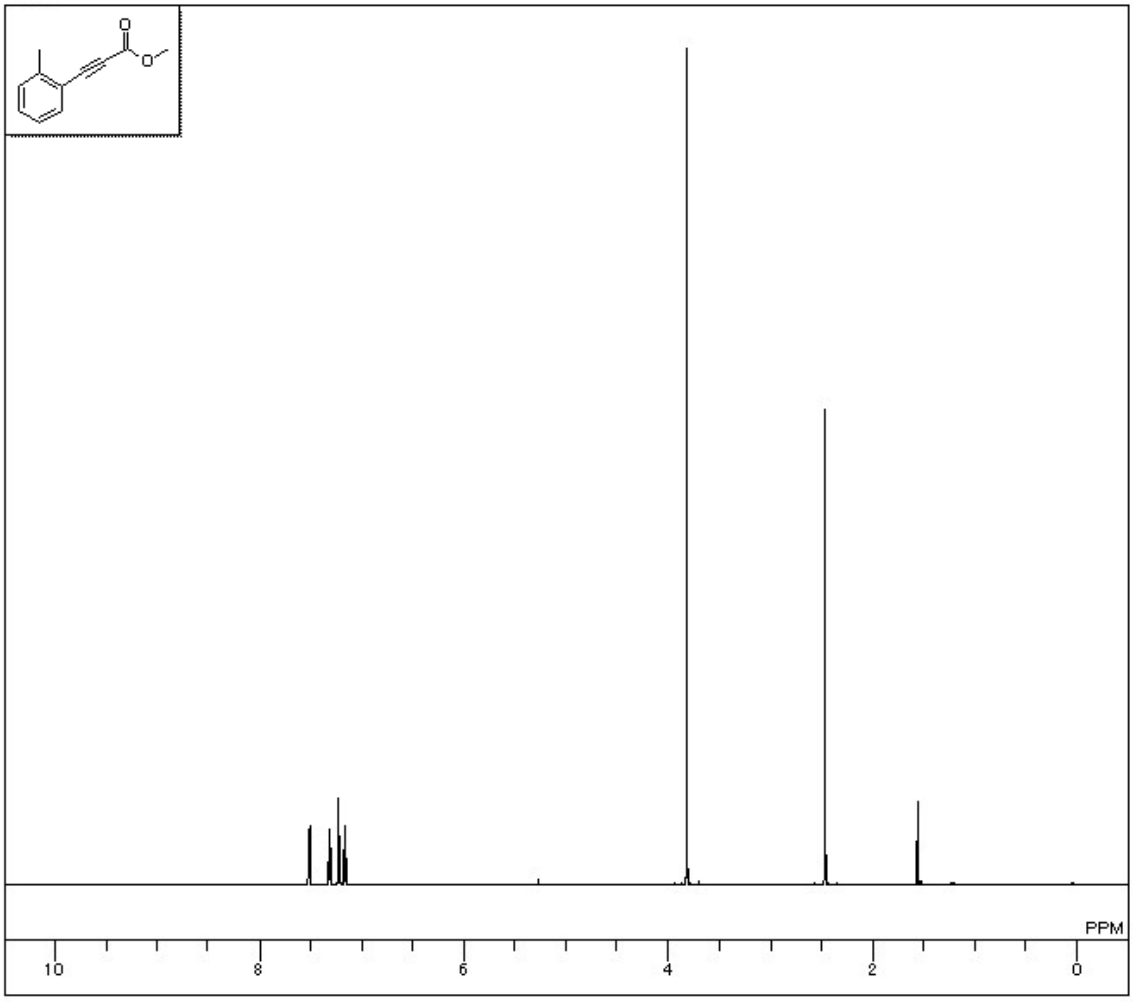


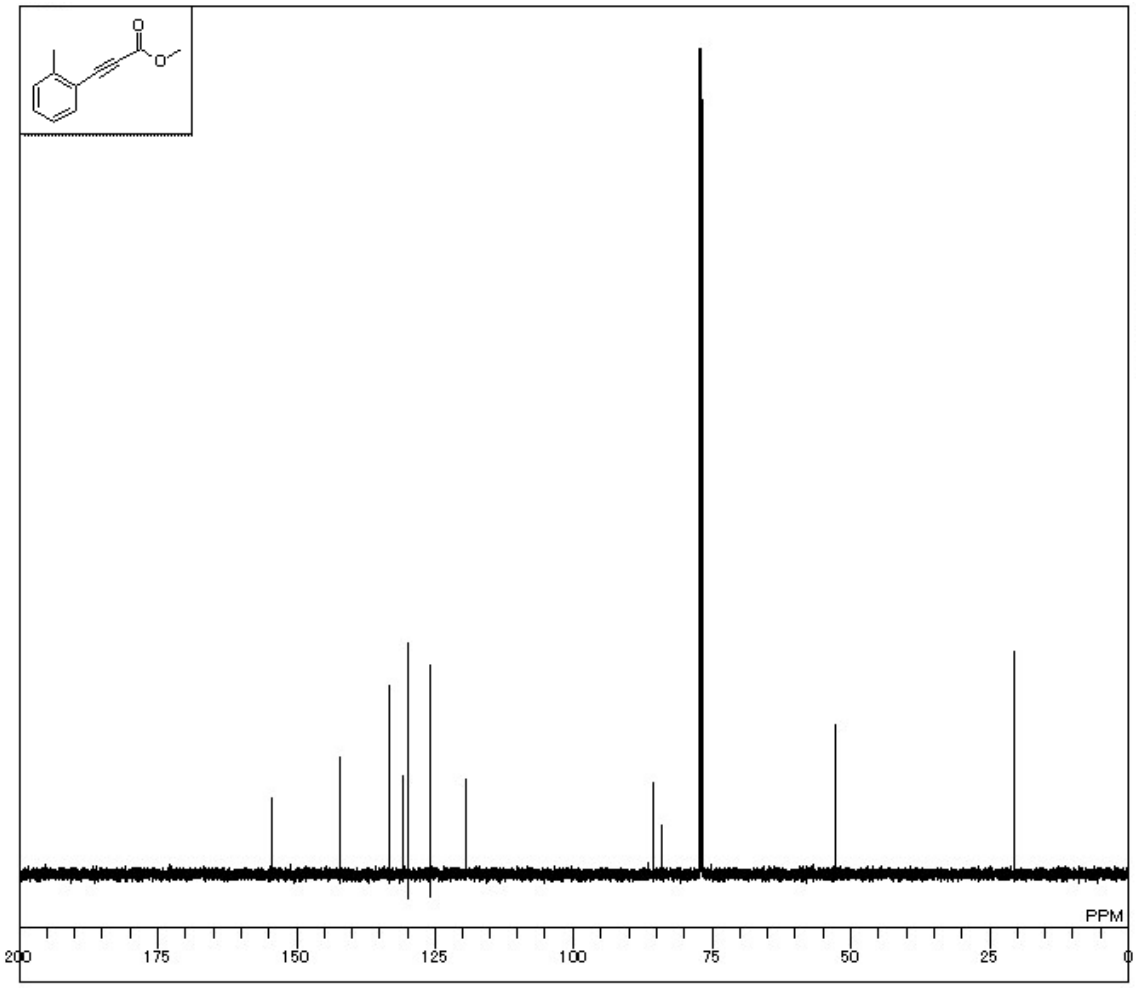


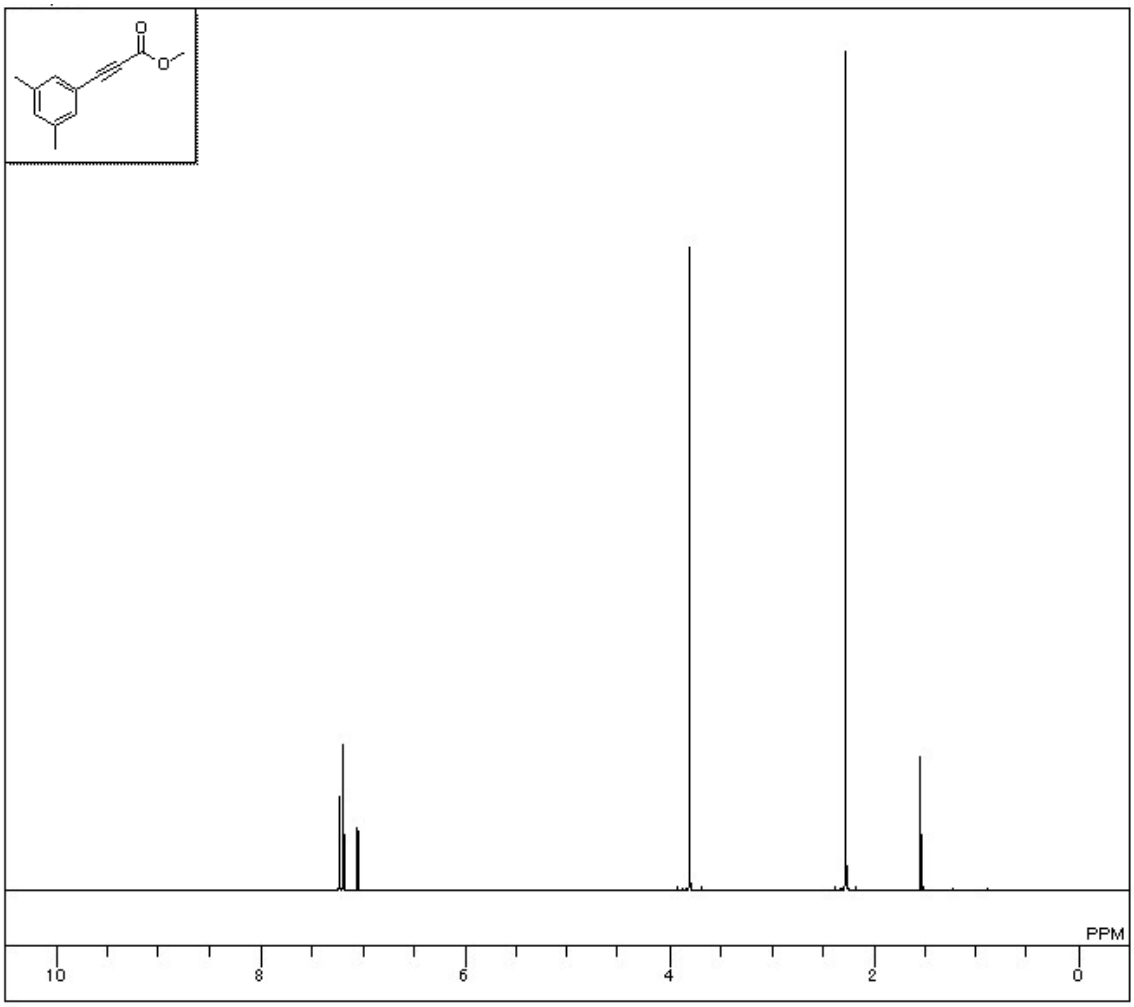


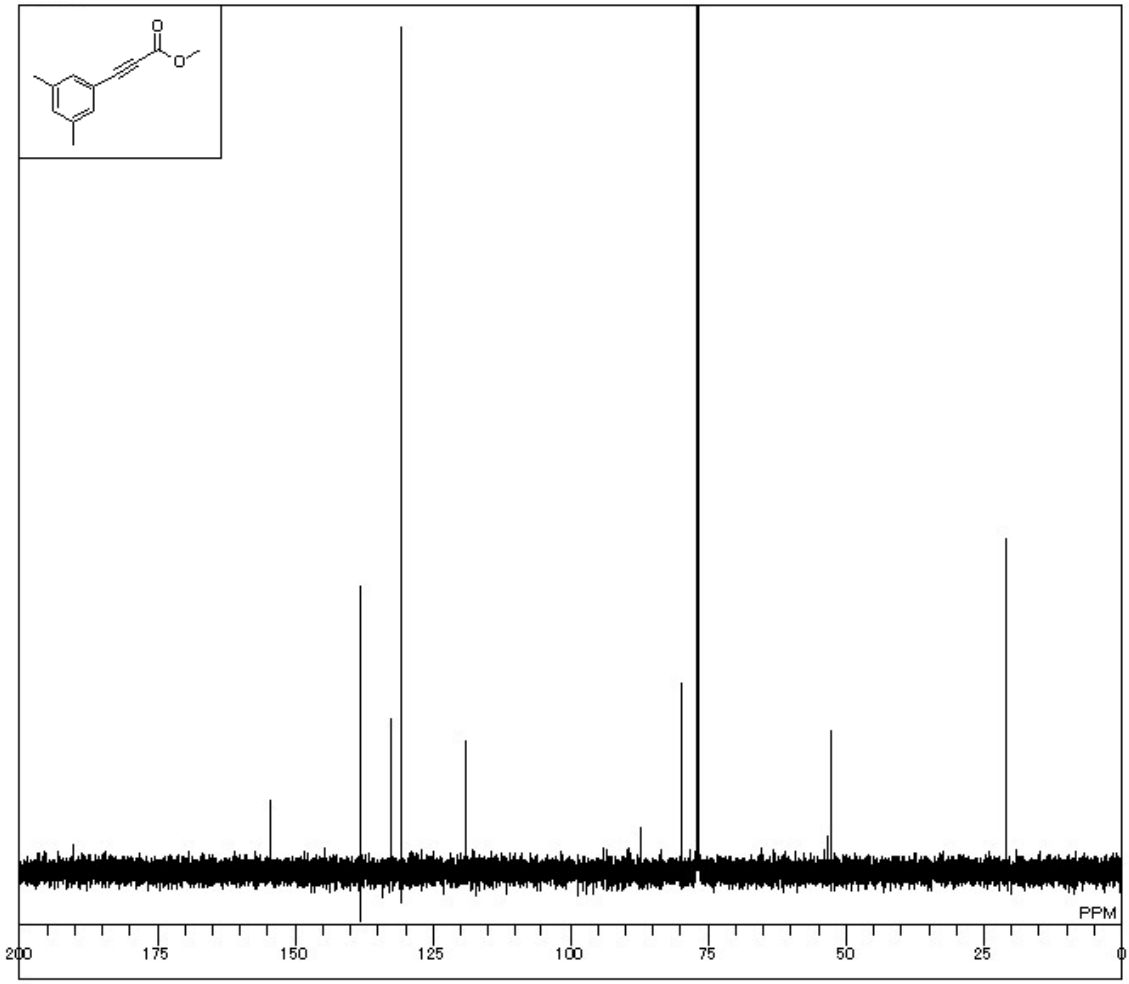


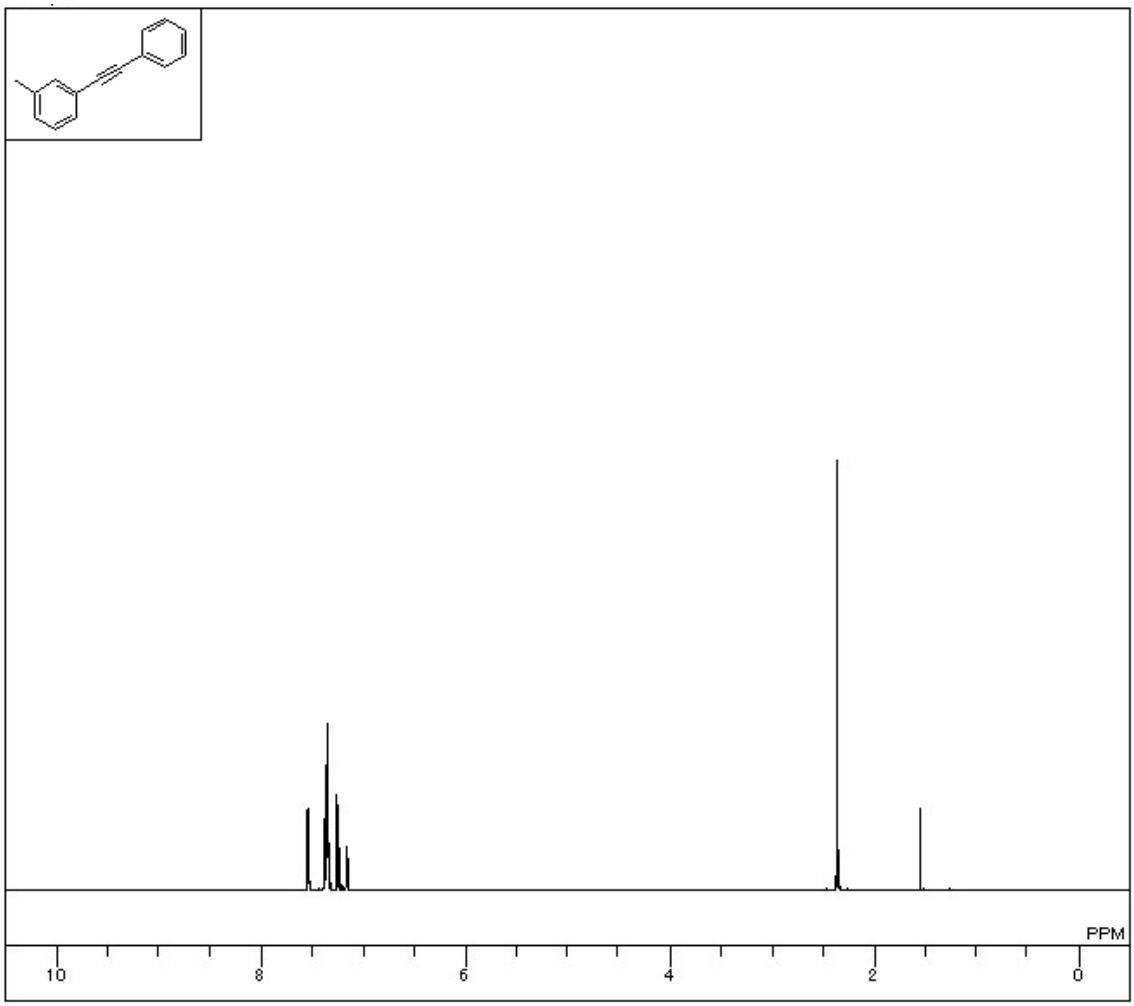


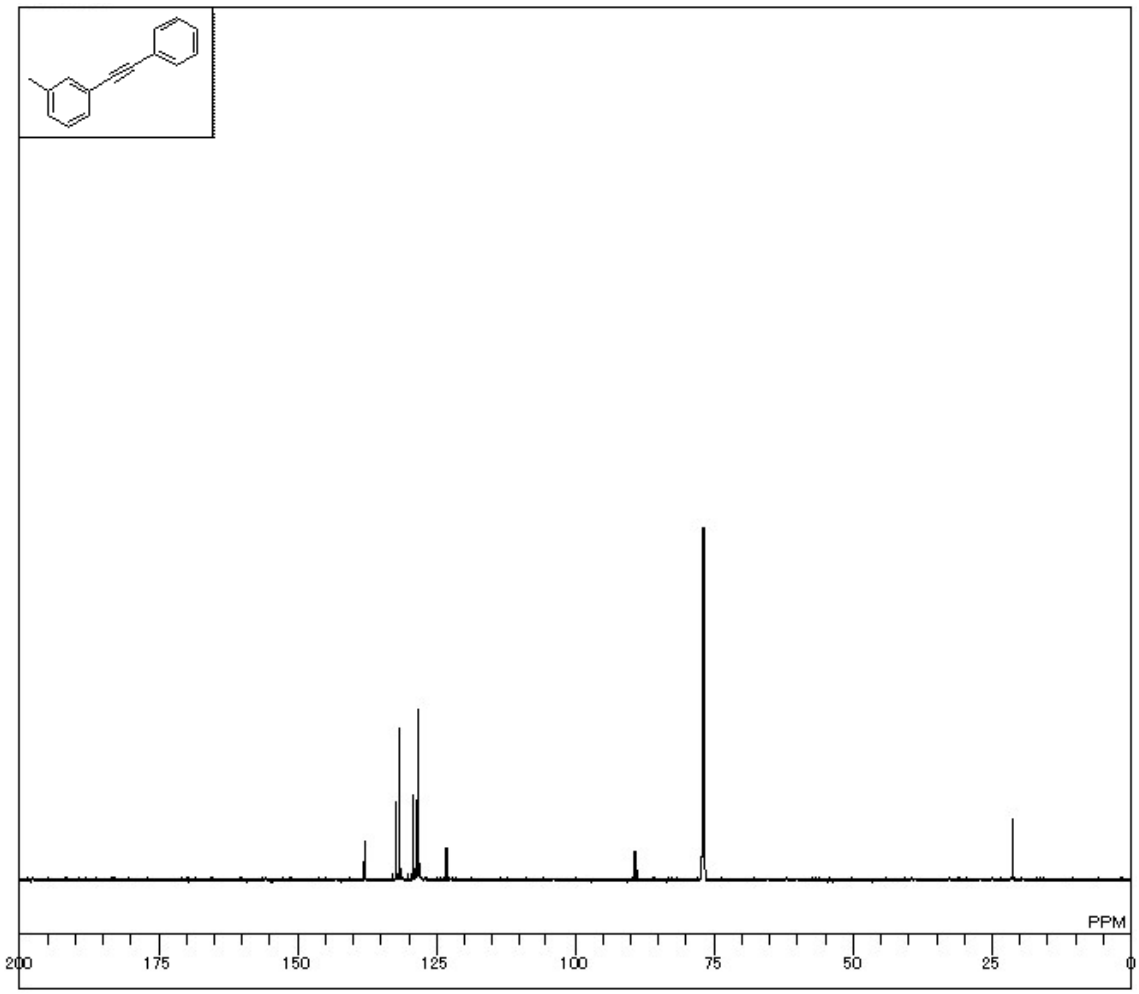


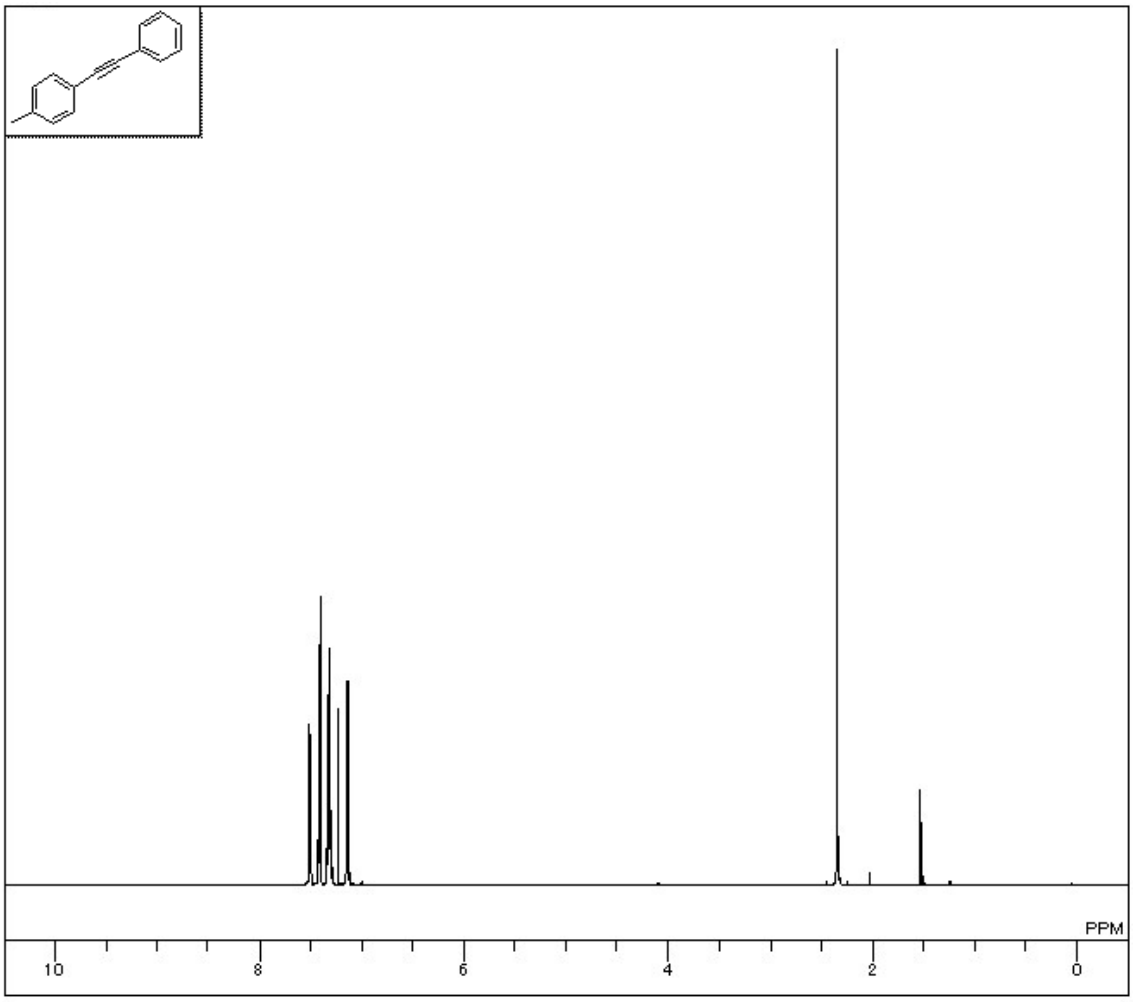


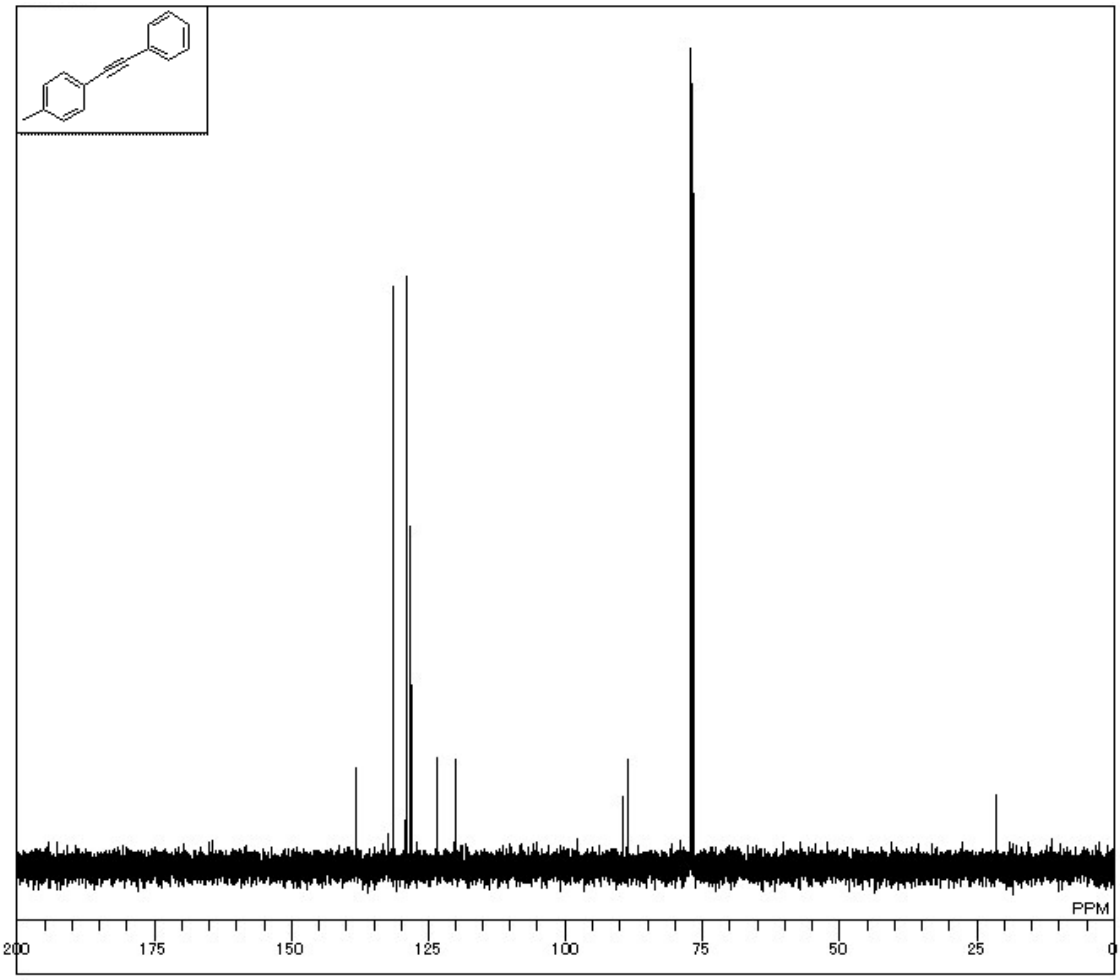


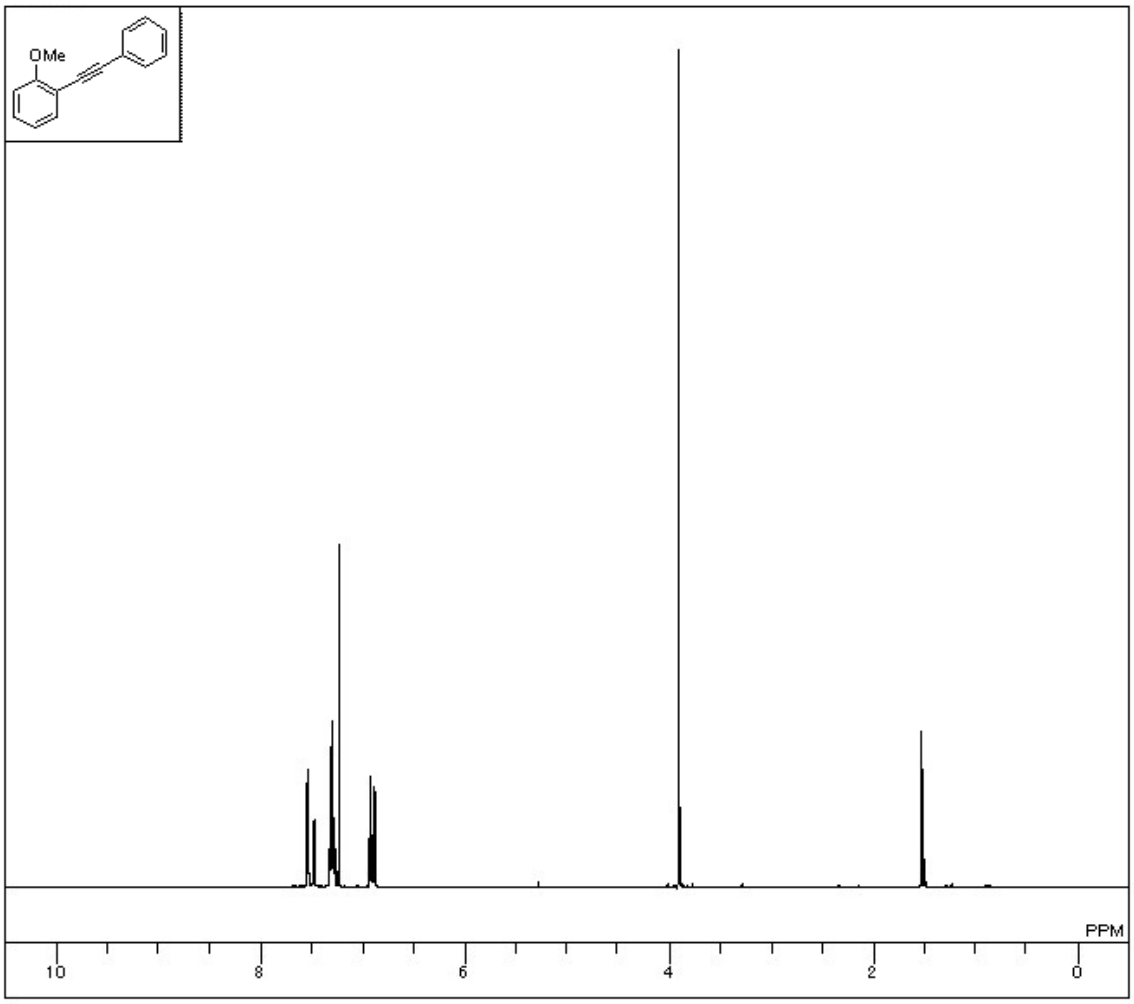


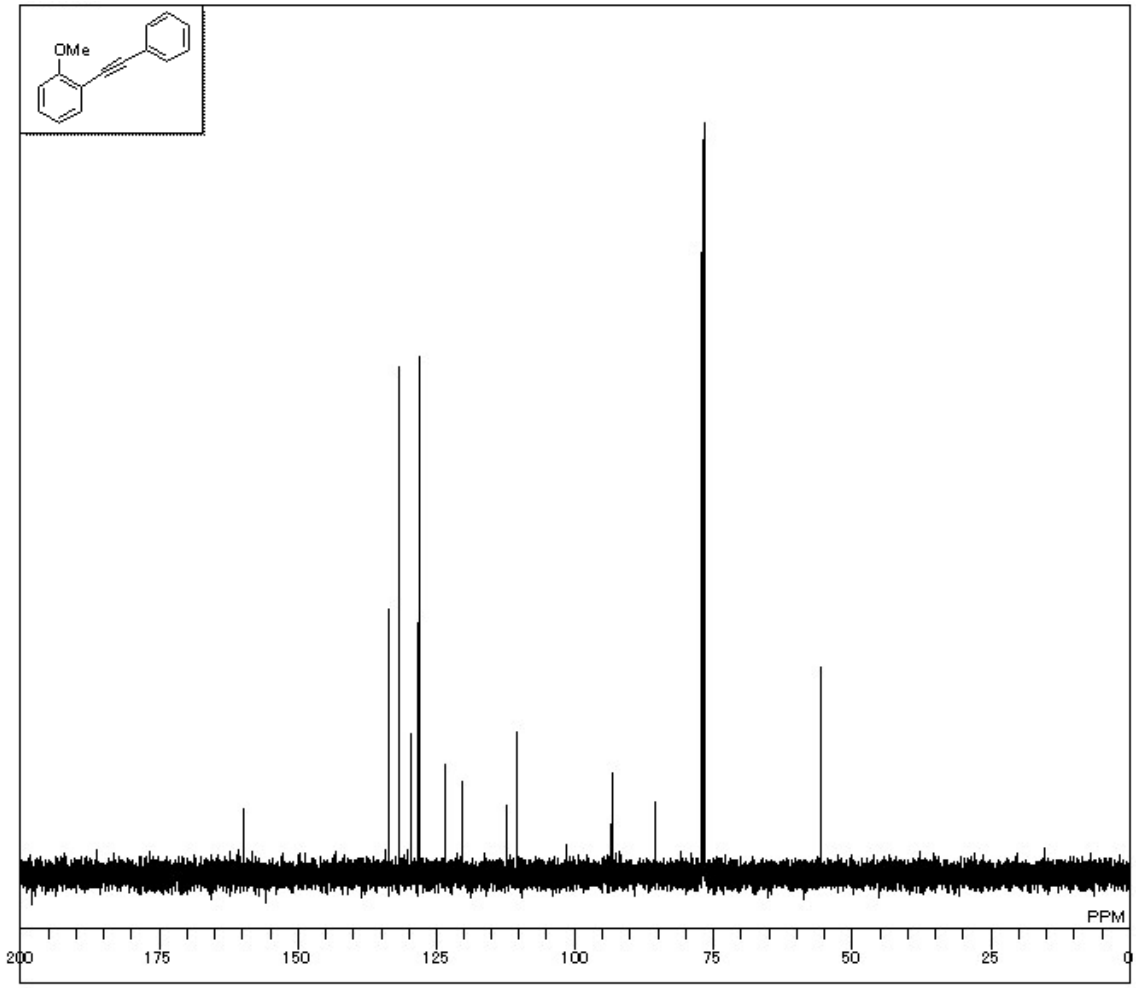


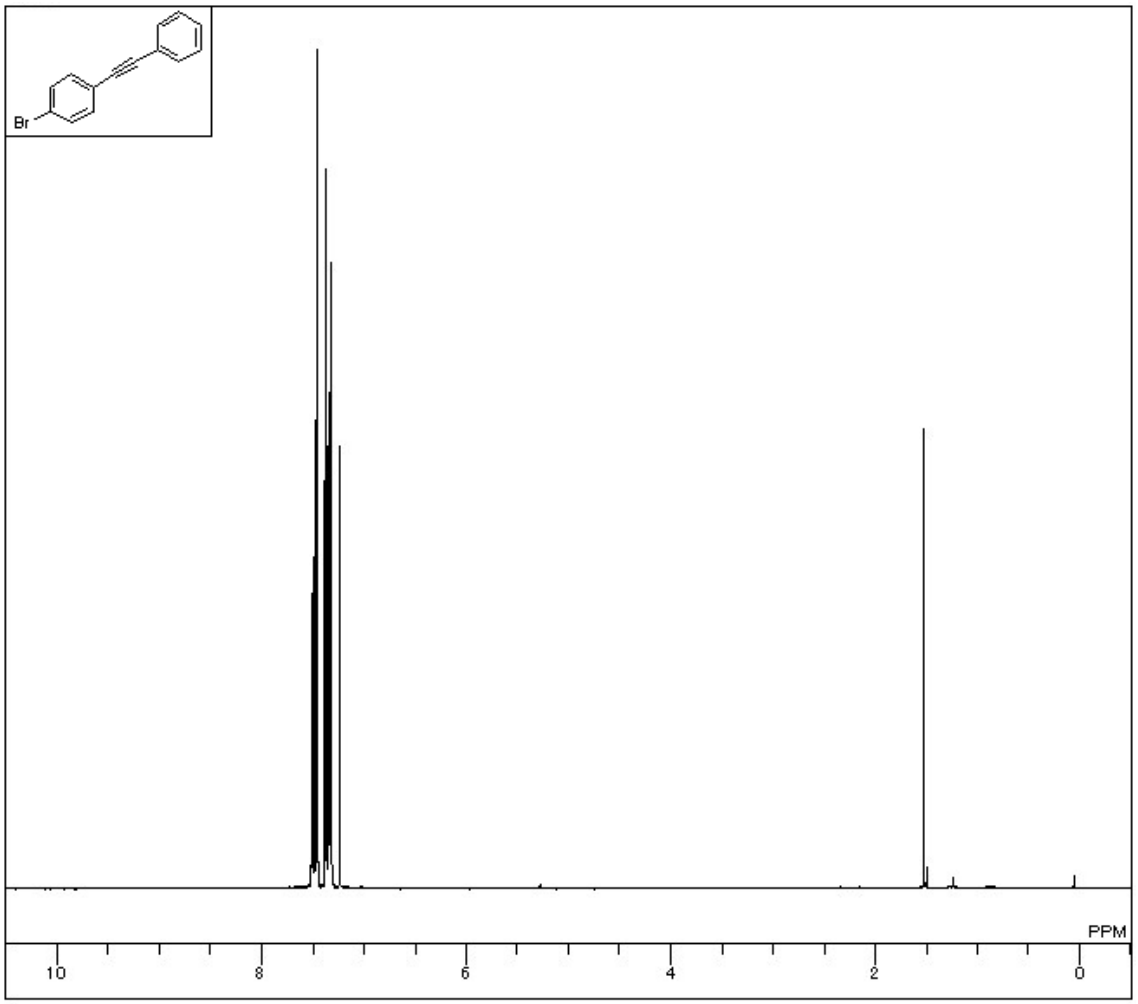


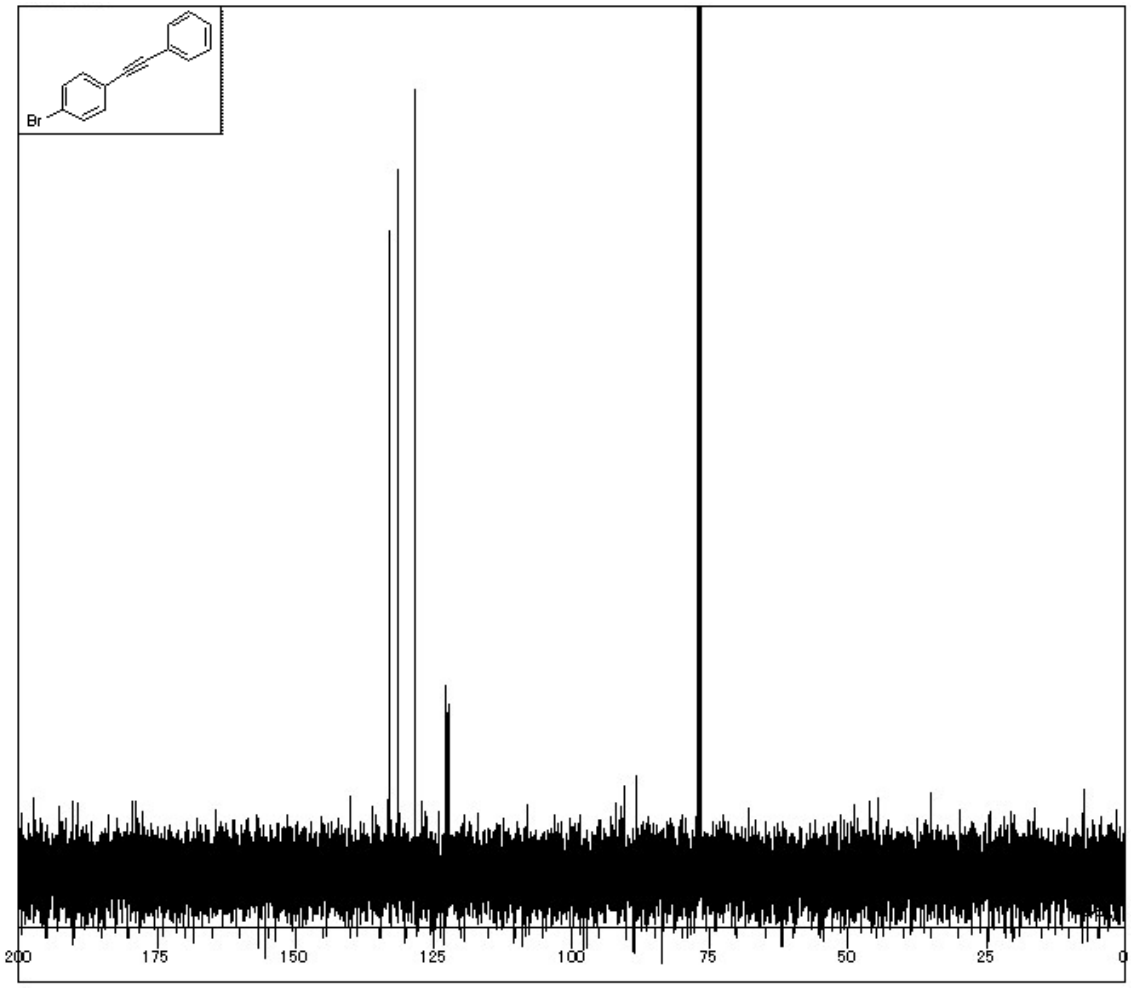


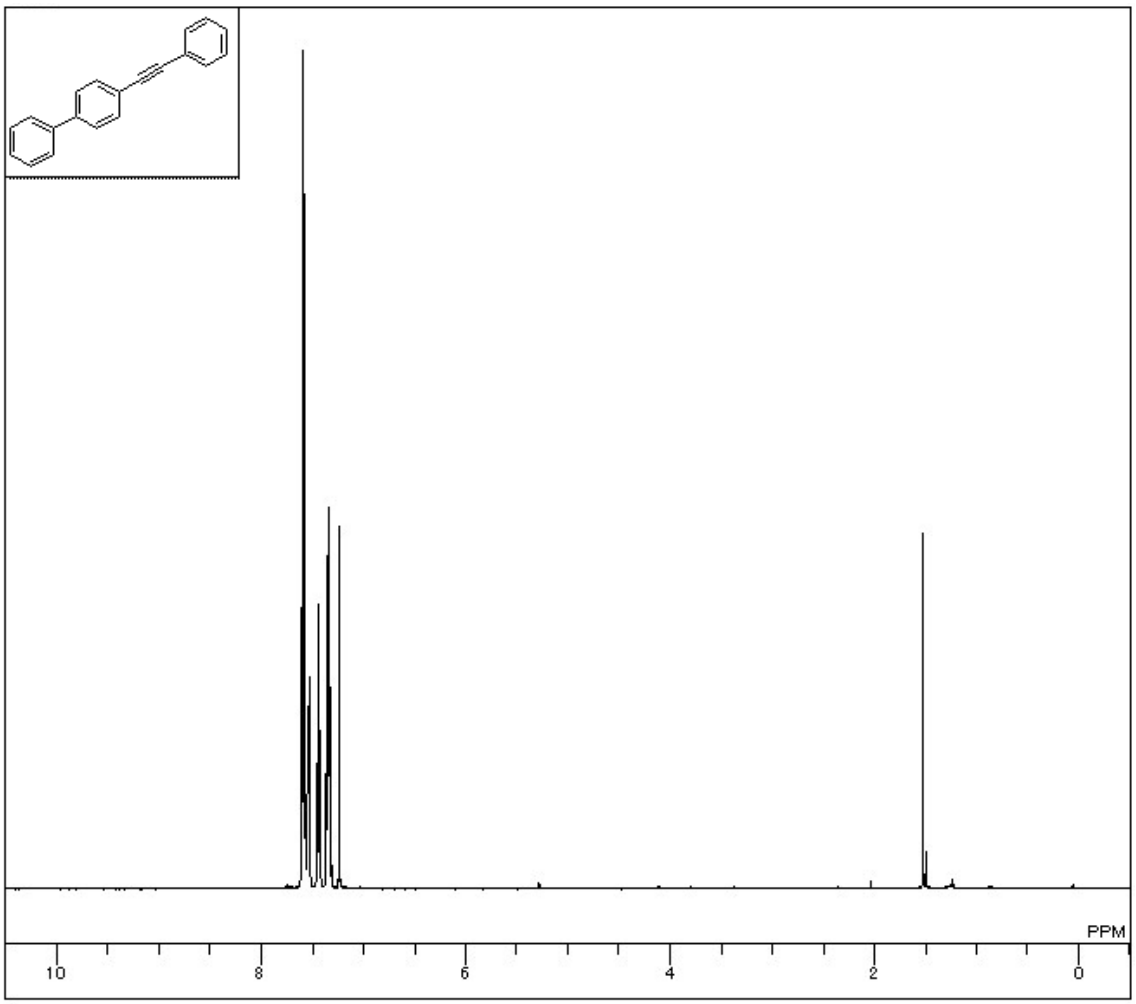


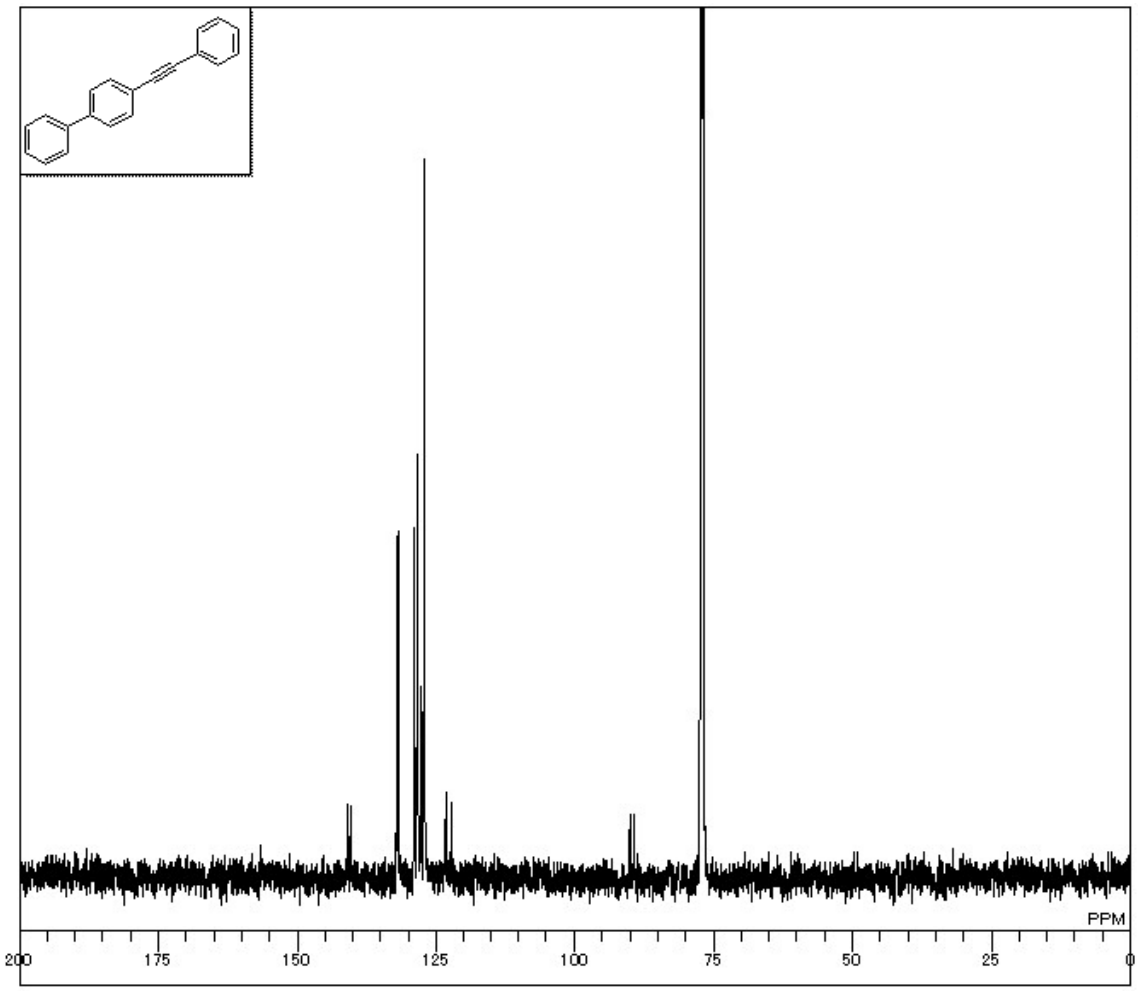


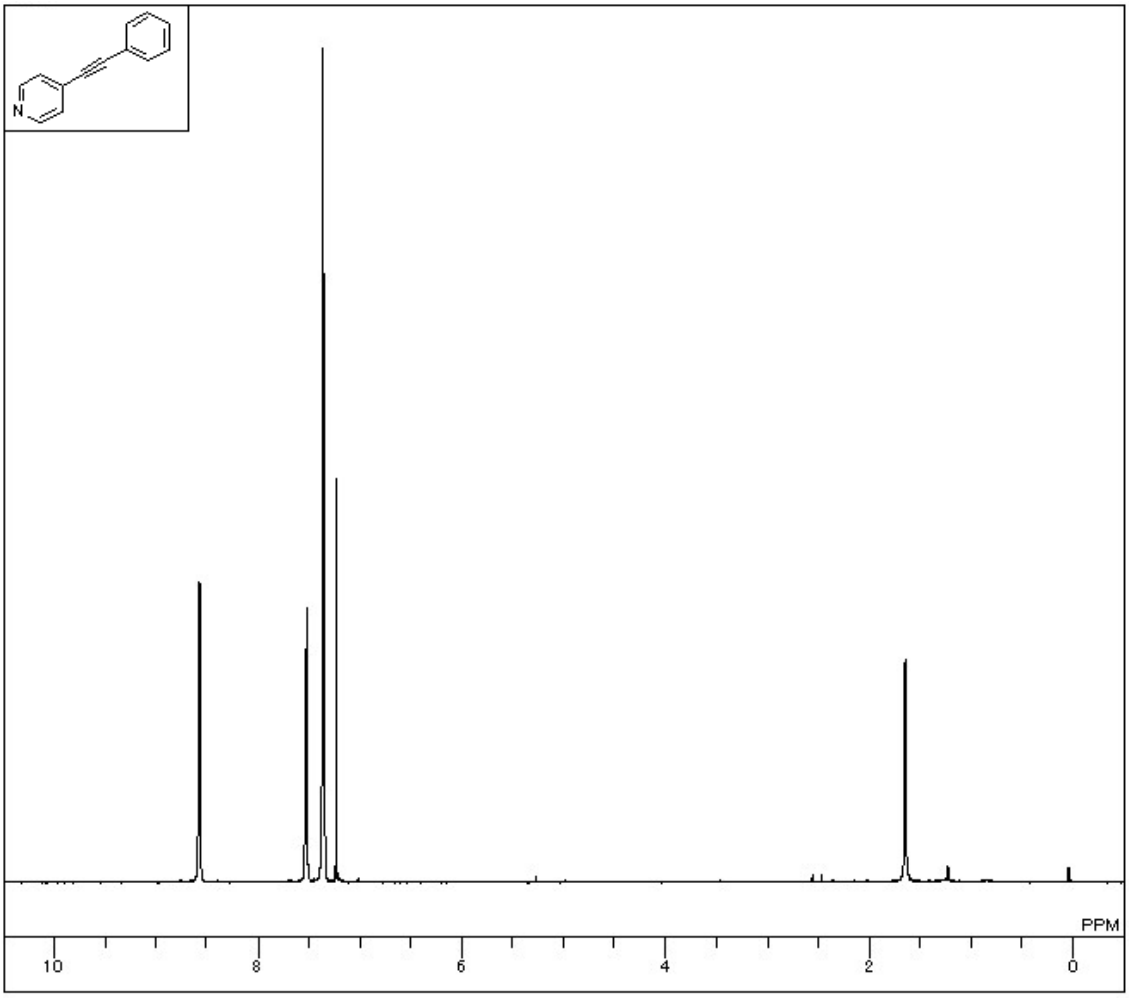


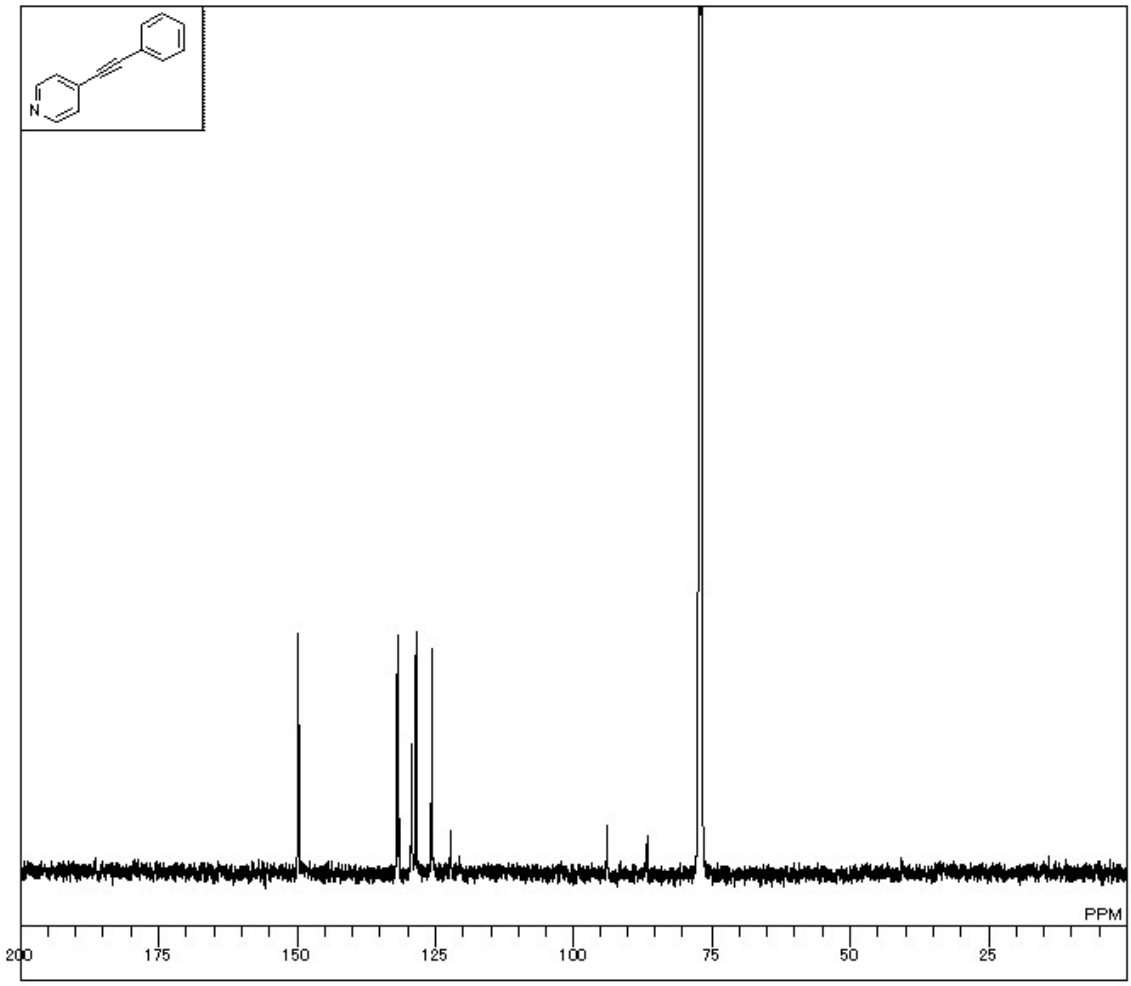


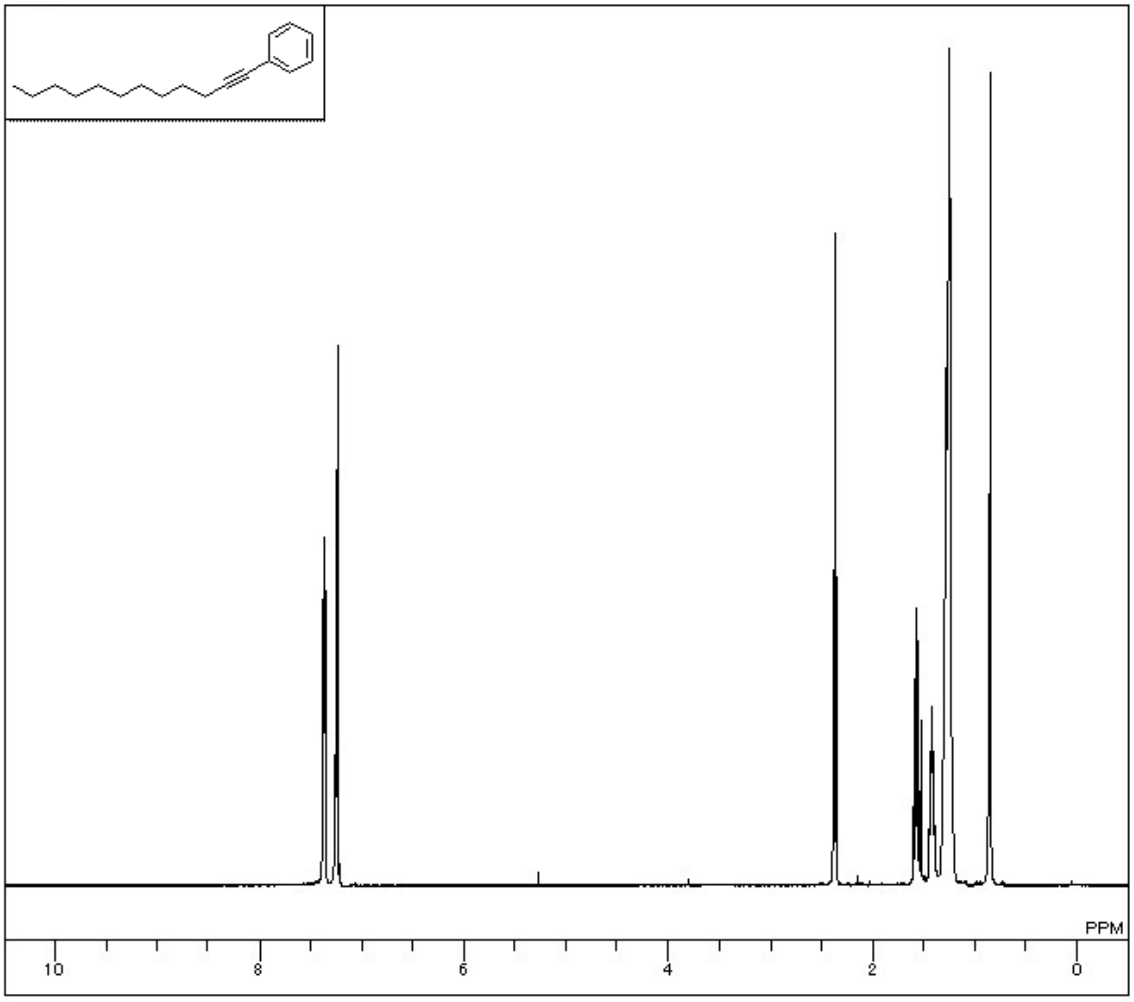


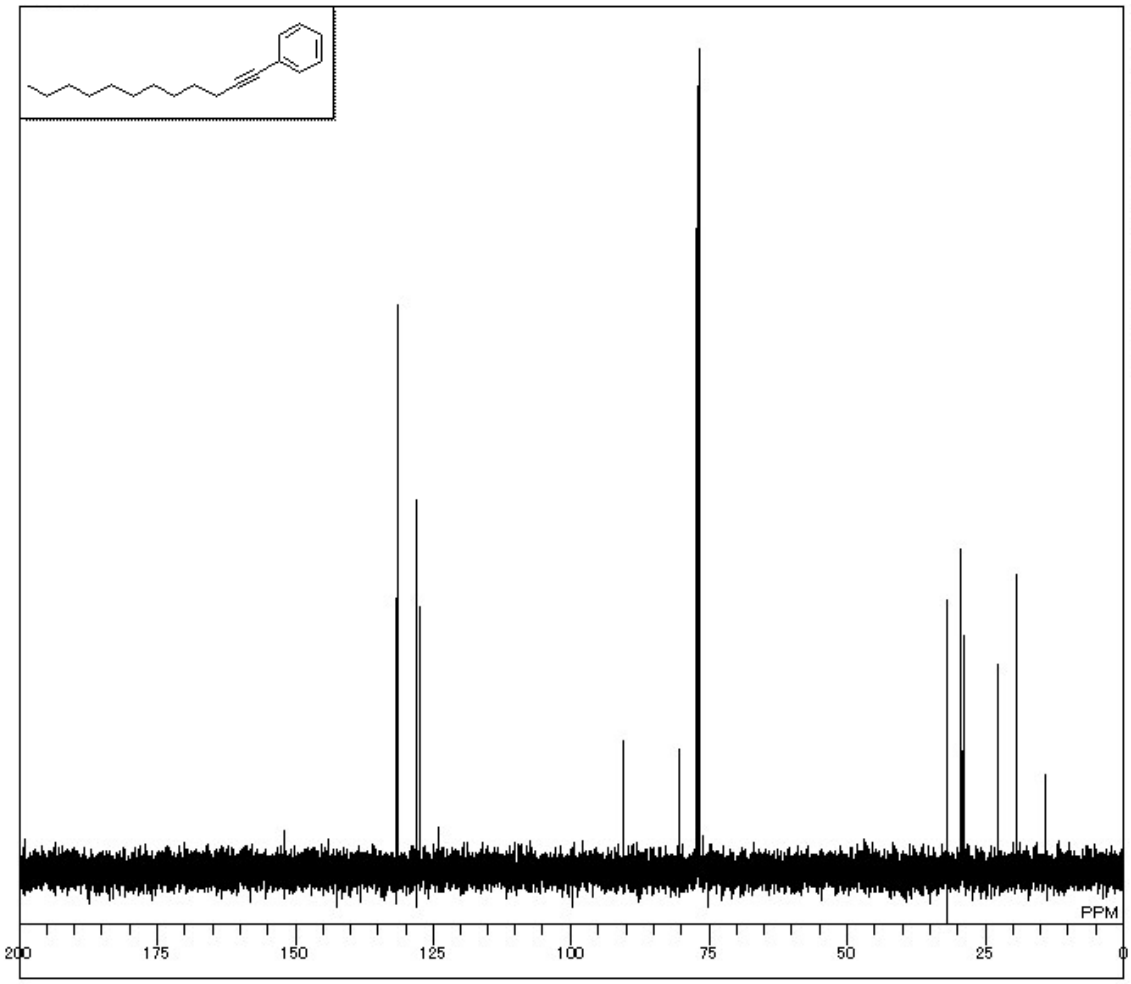


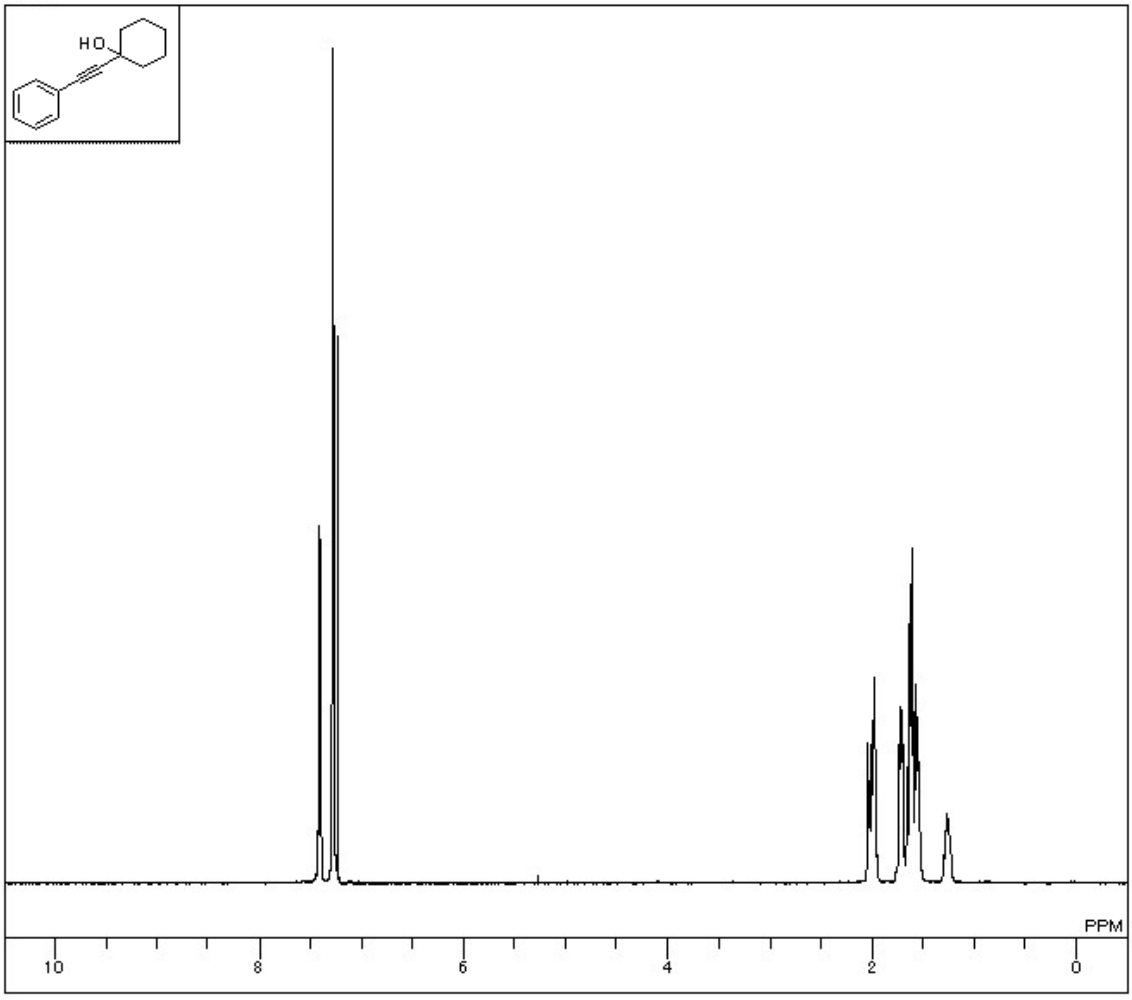


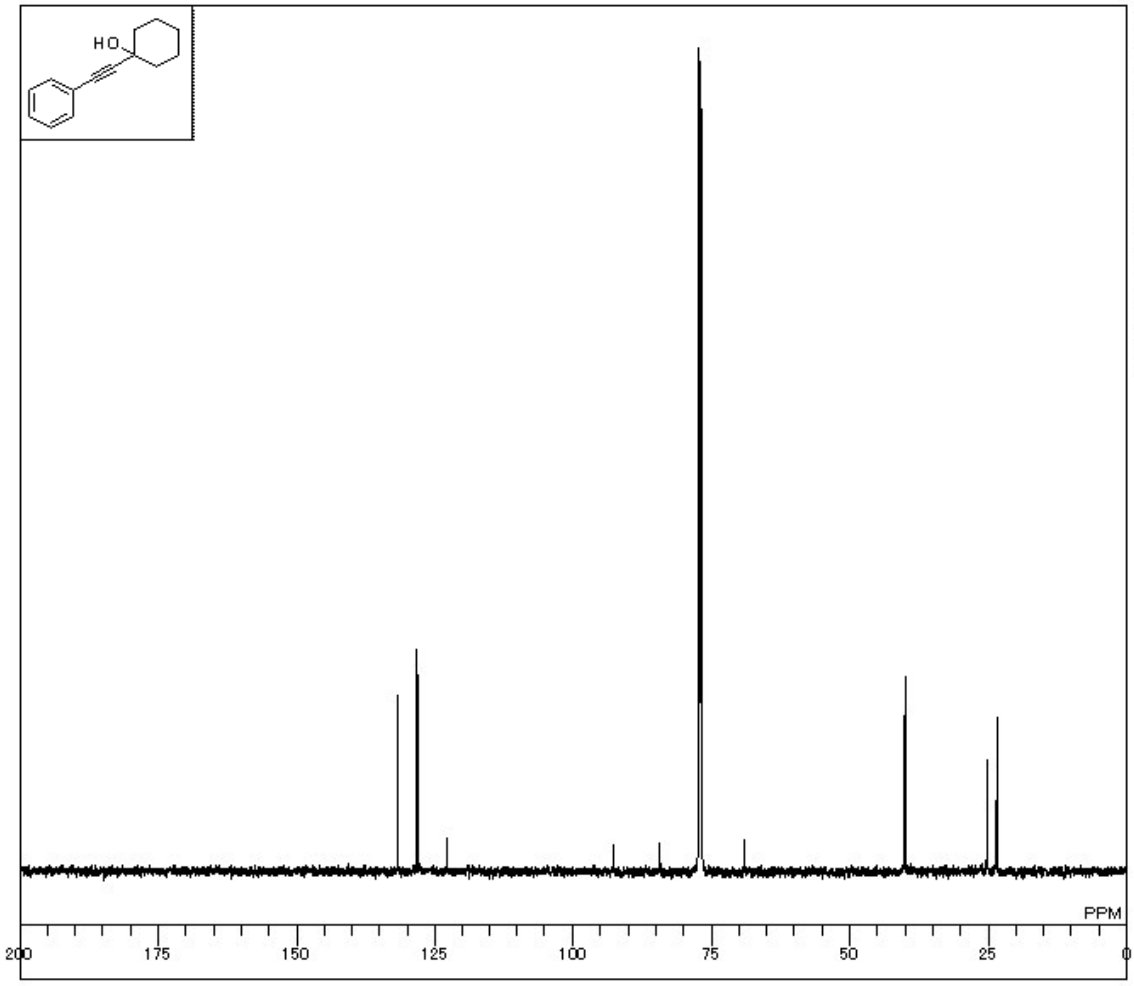


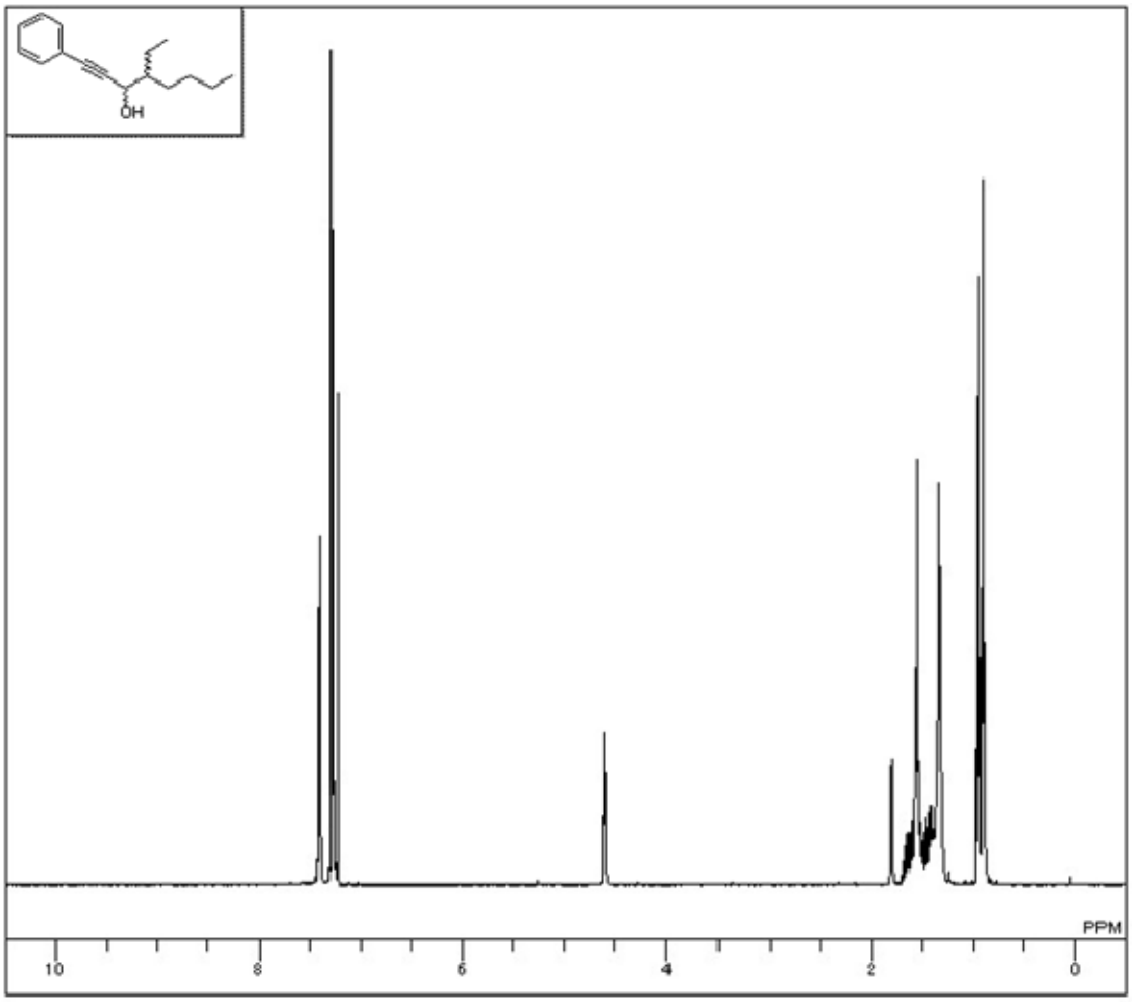


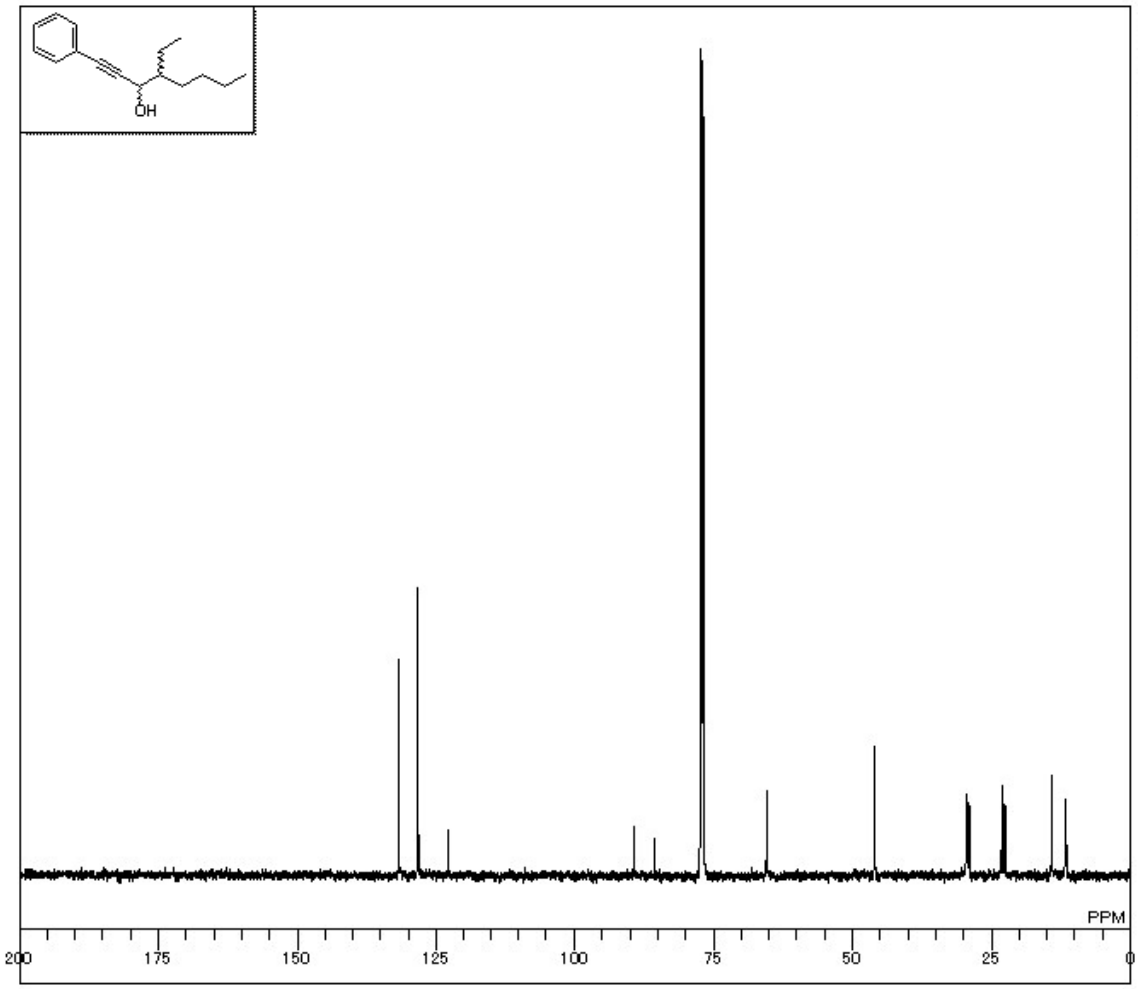












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