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Pd-catalyzed decarboxylative alkynylation of alkynyl carboxylic acids with arylsulfonyl hydrazides via desulfinative process

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Supporting Materials

Content

General

Reagents and solvents were used as it is obtained from commercial vendors. All reactions were performed in a 100 mL autoclave. Products were purified by column chromatography on silica gel (200–300) mesh. ^{1}H and ^{13}C NMR spectra were obtained on Bruker–400 MHz spectrometers using tetramethylsilane as internal standard in $CDCl_3$. Chemical shifts of ^{1}H NMR and ^{13}C NMR are reported as δ values relative to TMS and $CDCl_3$ respectively. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad resonances (br). HRMS (EI) data were collected on High Resolution mass spectrometer. All products are known compounds and are in accord with characterization in literature.

Preparation and Characterization of Starting Materials

General procedure for preparation of alkynyl carboxylic acids:

Step 1 : Triphenylphosphine (20 mmol) was added to a well-stirred solution of carbon tetrabromide (10 mmol) in dry dichloromethane (50 mL). Upon addition of aldehyde (5 mmol), the solution slowly faded away. The reaction mixture was stirred at ambient temperature for 6 hours till completion (TLC monitoring). After removal of solvent, the residue was repeatedly triturated with hexane (5 x 25 mL) and hexane solution was concentrated. This cycle was continued three times. Finally the mixture was subjected to column chromatography (silica gel 60-120 mesh, eluent hexane) to afford the (2,2-dibromovinyl)arene.

Step 2 : A solution of (2,2-dibromovinyl)arene (6 mmol) in 10 mL of dry THF at –78 ^{o}C was treated with a solution of *n*-BuLi in hexane (1.6 M, 7.5 mL, 12 mmol) under Nitrogen atmosphere. After stirring for 1h at –78 ^{o}C, the reaction mixture was warmed to 25 ^{o}C during 1 h, and again cooled to –60 ^{o}C. Solid carbon dioxide (5 g) was added to the above solution at –60 ^{o}C and the mixture was allowed to warm gradually to room temperature. The mixture was poured into water, and ethyl acetate was added. The aqueous layer was separated and washed further with ethyl acetate. The aqueous part was acidified with 6(N) HCl and extracted with ethyl acetate (3 x 50 mL). The organic layer was washed with brine

and dried over anhydrous magnesium sulfate. Evaporation of solvent afforded pure arylpropiolic acid.

Typical procedure for the product

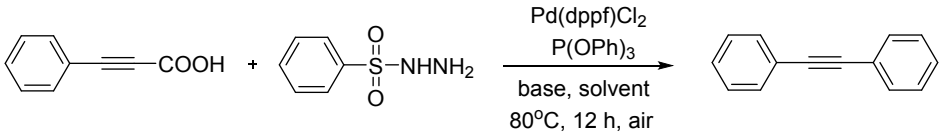
Cross-coupling of alkynyl carboxylic acids and arylsulfonyl hydrazides:

A mixture of alkynyl carboxylic acids (1.0 mmol), arylsulfonyl hydrazides (1.1 mmol), $Pd(dppf)Cl_2$ (5 mol%), $P(OPh)_3$ (0.1 mmol), K_2CO_3 (1.5 mmol) in DMA (1 mL) was stirred at 80 ^oC for 12 h under air. Afterward, the mixture was cooled to room temperature, filtered through a pad of celite after the addition of water (1 mL). The reaction mixture was extracted by Et_2O (2 mL) for three times. And then the organic phase was combined and evaporated under reduced pressure, and the residue was subjected to flash column chromatography to obtain the desired product.

Optimization table of bases, solvents, etc

Then, a series of commercially available bases (e.g., KOAc, Cs_2CO_3, K_2CO_3, Et_3N, and Na_2CO_3) were checked, and the product could be obtained in a good yield of 88% by using K_2CO_3 as the base (Table SI, entries 1–5). Solvent screening showed that DMA was superior to DMSO and DMF (Table SI, entries 6−7). On the contrary, other solvents such as DME and DCE were found to be ineffective (Table SI, entries 8−9). Finally, the efficiency of palladium-catalyzed coupling was reduced under 0.1 M concentration (Table SI, entry 10). The reaction A temperature screening suggested that the transformation at 80^oC delivered the coupling product in the highest isolated yield (Table SI, entries 11−13).

Table SI. Bases and solvent selection of palladium-catalyzed coupling of phenylsulfonyl hydrazide and phenylpropiolic acid [a]



entry	base	solvent	Temperature (°C)	yield (%) [b]
1	**K_2CO_3**	**DMA**	**80**	**88**
2	KOAc	DMA	80	81
3	Cs_2CO_3	DMA	80	72
4	Et_3N	DMA	80	55
5	Na_2CO_3	DMA	80	78
6	K_2CO_3	DMSO	80	85
7	K_2CO_3	DMF	80	80
8	K_2CO_3	DME	80	38
9	K_2CO_3	DCE	80	35
10	K_2CO_3	DMA	80	46 [c]
11	K_2CO_3	DMA	60	22
12	K_2CO_3	DMA	70	57
13	K_2CO_3	DMA	90	87

[a] Reaction conditions: phenylpropiolic acid (1.0 mmol), phenylsulfonyl hydrazide (1.1 mmol), $Pd(dppf)Cl_2$ (0.05 mmol), $P(OPh)_3$ (0.1 mmol), base (1.5 mmol), solvent (1 mL), 80 °C, 12 h, under air. [b] Isolated yields. [c] solvent (10 mL).

Characterization data of the product

1,2-bis(4-methoxyphenyl)ethyne (2a): White solid, mp:146−149 °C (ref [1] 147−148 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 4H), 6.86 (d, *J* = 8.8 Hz, 4H), 3.81 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 132.9, 124.4, 115.7, 114.0, 88.0, 55.3. HRMS (EI) Calcd for $C_{16}H_{15}O_2$ $[M+H]^+$, 239.1067; found, 239.1076.

1-methoxy-4-(p-tolylethynyl)benzene (2b): White solid, mp:126−128 °C (ref [2] 126−130 °C). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.89–6.86 (m, 2H), 3.84 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 138.0, 133.1, 131.4, 129.2, 120.6, 115.6, 114.0, 88.6, 88.2, 55.4, 21.5. HRMS (EI) Calcd for $C_{16}H_{15}O$ $[M+H]^+$, 223.1117; found, 223.1111.

(4-ethyl-methoxyphenyl)ethynyl)benzene (2c): White solid, mp:116−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 12.4, 8.4 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 145.8, 134.4, 132.9, 129.3, 122.2, 117.1, 115.4, 90.1, 89.6, 56.7, 30.2, 16.8. HRMS (EI) Calcd for $C_{17}H_{17}O$ $[M+H]^+$, 237.1274; found, 237.1266.

1-butyl-4-((4-methoxyphenyl)ethynyl)benzene (2d): White solid, mp:105−107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 2.66 – 2.57 (m, 2H), 1.58 (dd, *J* = 15.2, 7.6 Hz, 2H), 1.37 (dd, *J* = 14.8, 7.6 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 143.0, 133.0, 131.4, 128.4, 120.7, 115.7, 114.0, 88.7, 88.2, 55.3, 35.6, 33.4, 22.3, 13.9. HRMS (EI) Calcd for $C_{19}H_{21}O$ $[M+H]^+$, 265.1587; found, 265.1579.

1-Methoxy-4-((4-nitrophenyl)ethynyl)benzene (2e): Yellow solid, mp:122−123 °C (ref [3] 121 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 147.0, 133.9, 132.4, 131.2, 124.0, 114.6, 95.6, 87.0, 78.1, 55.7. HRMS (EI) Calcd for $C_{15}H_{12}NO_3$ $[M+H]^+$, 254.0812; found, 254.0819.

1-methoxy-4-(m-tolylethynyl)benzene (2f): White solid, mp:42−44 °C (ref [4] 43−44°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.28 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 138.0, 133.0, 132.0, 128.8, 128.5, 128.2, 123.5, 115.5, 114.0, 89.0, 88.2, 55.3, 21.2. HRMS (EI) Calcd for $C_{16}H_{15}O$ $[M+H]^+$, 223.1117; found, 223.1125.

1-methoxy-4-(m-bromoethynyl)benzene (2g): White solid, mp:67−69 °C (ref [15] 65−67°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.90–6.83 (m, 3H), 6.65 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 147.7, 134.5, 130.7, 125.7, 123.4, 119.2, 116.9, 116.5, 115.4, 90.2, 89.7, 56.7. HRMS (EI) Calcd for $C_{15}H_{12}ClO$ $[M+H]^+$, 243.0571; found, 243.0562.

2-((4-methoxyphenyl)ethynyl)naphthalene (2h) : White solid, mp:120−122 °C (ref [5] 122−124 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.80–7.77 (m, 3H), 7.56–7.46 (m, 5H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 133.3, 133.1, 132.7, 131.2, 128.5, 128.1, 127.8, 127.7, 126.4, 121.0, 115.3, 114.1, 89.7, 88.5, 55.2. HRMS (EI) Calcd for $C_{19}H_{15}O$ $[M+H]^+$, 259.1117; found, 259.1109.

2-(4-Methoxyphenyl)benzofuran (2i): White crystals, mp:140−143 °C (ref [6] 143−144 °C). ^{1} H NMR (400 MHz, $CDCl_3$) δ 7.70 (td, *J* = 10, 2.4 Hz, 2H), 7.49−7.37 (m, 3H), 7.21− 7.06 (m, 2H), 6.88 (td, *J* = 32, 2.0 Hz, 2H), 6.78 (d, *J* = 0.8 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 156.3, 154.8, 129.6, 126.6, 123.9, 123.6, 123.0, 120.8, 114.4, 111.1, 99.9, 55.5. HRMS (EI) Calcd for $C_{17}H_{13}O_2$ $[M+H]^+$, 249.0910; found, 249.0916.

1-(hex-1-ynyl)-4-methoxybenzene (2j): Colorless liquid. ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.38 (dd, *J* = 8.8, 5.2, 2H), 1.62–1.54 (m, 2H), 1.51–1.41 (m, 2H), 0.93 (dd, *J* = 15.6, 8.4, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 131.8, 115.4, 112.8, 87.6, 79.2, 54.3, 30.9, 21.1, 18.4, 13.2. HRMS (EI) Calcd for $C_{13}H_{17}O$ $[M+H]^+$, 189.1274; found, 189.1269.

1-(hept-1-ynyl)-4-methoxybenzene (2k): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 2H), 2.41 (t, *J* = 7.2 Hz, 1H), 1.69 – 1.56 (m,

1H), 1.43 (dddt, J = 28.8, 21.6, 14.4, 7.2 Hz, 2H), 0.95 (t, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 132.9, 116.4, 113.8, 88.8, 80.3, 55.2, 31.2, 28.6, 22.3, 19.4, 14.0. HRMS (EI) Calcd for $C_{14}H_{19}O$ $[M+H]^+$, 203.1430; found, 203.1440.

1-(oct-1-ynyl)-4-methoxybenzene (2l): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.37 (t, J = 7.2 Hz, 2H), 1.57 (dd, J = 12.4, 4.8, 2H), 1.49–1.40 (m, 2H), 1.34–1.30 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 132.9, 116.5, 113.8, 88.9, 80.3, 55.2, 31.4, 28.8, 28.5, 22.6, 19.5, 14.1. HRMS (EI) Calcd for $C_{15}H_{21}O$ $[M+H]^+$, 217.1587; found, 217.1579.

1-(3, 3-dimethyl-1-butynyl)-4-methoxybenzene (2m): A pale yellow powder, mp:37−38 °C (ref [7] 39 °C).[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.27 (m, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 132.9, 116.4, 113.7, 96.8, 78.7, 55.4, 31.2, 27.8. HRMS (EI) Calcd for $C_{13}H_{17}O$ $[M+H]^+$, 189.1274; found, 189.1266.

1-methyl-4-(phenylethynyl)benzene (3a): White powder, mp:74−75 °C (ref [8] 72−73 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.53 (m, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 6.4 Hz, 3H), 7.17 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 139.8, 133.0, 132.9, 130.6, 129.8, 129.5, 124.9, 121.6, 91.0, 90.2, 22.9. HRMS (EI) Calcd for $C_{15}H_{13}$ $[M+H]^+$, 193.1012; found, 193.1020.

1-ethyl-4-(phenylethynyl)benzene (3b): White powder, mp:30−33 °C (ref [8] 32−33°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 6.8 Hz, 3H), 7.22 (d, J = 8.0 Hz, 2H), 2.72 (q, J = 7.6 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 133.1, 133.1, 129.8, 129.6, 129.4, 125.0, 122.0, 91.1, 90.3, 30.3, 16.8. HRMS (EI) Calcd for $C_{16}H_{15}$ $[M+H]^+$, 207.1168; found, 207.1162.

2-diphenylethyne (3c): White powder, mp:59−60 °C (ref [8] 58−59 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.2, 2.0 Hz, 4H), 7.35 (d, J = 5.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1, 129.8, 129.7, 124.7, 90.8. HRMS (EI) Calcd for $C_{14}H_{11}$ $[M+H]^+$, 179.0855; found, 179.0851.

1-methoxy-4-(phenylethynyl)benzene (3d): White solid, mp:56−58 °C (ref [8] 57−59 °C) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 133.1, 131.4, 128.3, 127.8, 123.7, 115.4, 114.0, 89.5, 88.1, 55.4. HRMS (EI) Calcd for $C_{15}H_{13}O$ $[M+H]^+$, 209.0961; found, 209.0966.

1-nitro-4-phenylethynylbenzene (3e): White solid, mp:121−124 °C (ref [9] 121−122 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.56 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.38 (dd, *J* = 5.2, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 133.7, 133.3, 131.7, 130.7, 130.0, 125.1, 123.5, 96.2, 89.0. HRMS (EI) Calcd for $C_{14}H_{10}NO_2$ $[M+H]^+$, 224.0706; found, 224.0713.

1-chloro-4-(phenylethynyl)benzene (3f): White solid, mp:83−85 °C (ref [8] 83−84 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.28 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8, 132.5, 131.6, 129.3, 128.7, 128.5, 128.4, 128.5, 121.8, 81.6. HRMS (EI) Calcd for $C_{14}H_{10}Cl$ $[M+H]^+$, 213.0466; found, 213.0461.

1-(phenylethynyl)-4-(trifluoromethyl)benzene (3g): White solid, mp:102−105 °C (ref [10] 103−104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.54 (dd, *J* = 6.0, 3.6 Hz, 2H), 7.42–7.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2, 133.2, 130.3, 129.9, 126.7, 126.7, 124.0, 124.0, 93.2, 89.4. HRMS (EI) Calcd for $C_{15}H_{10}F_3$ $[M+H]^+$, 247.0729; found, 247.0722.

1-(4-(phenylethynyl)phenyl)ethanone (3h): White solid, mp:97−99 °C (ref [11] 98−99 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.58–7.52 (m, 2H), 7.42–7.34 (m, 3H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 137.6, 133.2, 133.1, 130.3, 129.9, 129.7, 129.6, 124.1, 94.2, 90.1, 28.1. HRMS (EI) Calcd for $C_{16}H_{13}O$ $[M+H]^+$, 221.0961; found, 221.0953.

1-ethyl-4-(phenylethynyl)benzoate (3i): White solid, mp:77−79 °C (ref [11] 78−79 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.54 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.40–7.33 (m, 3H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 150.3, 134.5, 133.9, 133.1, 130.6, 130.0, 129.8, 124.3,123.5, 122.3, 91.6, 89.3, 54.8, 15.6. HRMS (EI) Calcd for $C_{17}H_{15}O_2$ $[M+H]^+$, 251.1067; found, 251.1061.

1-(phenylethynyl)-4-(trifluoromethoxy)benzene (3j): White solid, mp:69−71 °C (ref [12] 68−70 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.8 Hz, 2H), 7.55 – 7.51 (m, 2H), 7.39 – 7.34 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 134.5, 133.1, 130.0, 129.8, 124.3, 123.5, 122.3 , 91.6, 89.3. HRMS (EI) Calcd for $C_{15}H_{10}F_3O$ $[M+H]^+$, 263.0678; found, 263.0673.

1-bromo-4-(phenylethynyl)benzene (3k): White solid, mp:84−85 °C (ref [13] 82−83 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0, 132.5, 131.7, 131.6, 129.2, 128.5, 128.4, 128.3, 123.0, 121.8, 90.5, 88.3. HRMS (EI) Calcd for $C_{14}H_{10}Br$ $[M+H]^+$, 256.9960; found, 256.9963.

1-methoxy-3-(phenylethynyl)benzene (3l): White solid, mp:79−80 °C (ref [8] 77−78 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.53 (m, 2H), 7.43 – 7.35 (m, 3H), 7.32 – 7.26 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.08 (s, 1H), 6.91 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 133.6, 130.8, 129.8, 129.7, 125.7, 125.6, 117.8, 116.4, 90.8, 90.6, 56.7. HRMS (EI) Calcd for $C_{15}H_{13}O$ $[M+H]^+$, 209.0961; found, 209.0955.

1-methyl-3-(phenylethynyl)benzene (3m): White solid, mp:70−72 °C (ref [4] 71−73 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.42 (dd, *J* = 11.6, 8.8 Hz, 5H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 133.7, 133.1, 130.7, 130.2, 129.8, 129.8, 129.7, 124.9, 124.6, 91.1, 90.6, 22.7. HRMS (EI) Calcd for $C_{15}H_{13}$ $[M+H]^+$, 193.1012; found, 193.1008.

1-(phenylethynyl)-3-(trifluoromethyl)benzene (3n): White solid, mp:105−108 °C (ref [14] 105-106 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.52 (m, 3H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 133.1, 130.3, 130.2, 129.9, 126.2, 126.2, 125.7, 124.0, 92.3, 89.2. HRMS (EI) Calcd for $C_{15}H_{10}F_3O$ $[M+H]^+$, 263.0678; found, 263.0670.

1-iodo-3-(phenylethynyl)benzene (3o): White solid, mp:44−47 °C (ref [15] 45−47 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.39 – 7.33 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 138.7, 133.1, 132.1, 131.3, 130.0, 129.8, 126.8, 124.2, 95.1, 92.1, 89.1. HRMS (EI) Calcd for $C_{14}H_{10}I$ $[M+H]^+$, 304.9822; found, 304.9805.

1-methoxy-2-(phenylethynyl)benzene (3p): White solid, mp:139−142 °C (ref [16] 138−140 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.51 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.39 – 7.27 (m, 4H), 6.92 (dd, *J* = 17.2, 8.0 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 133.6, 131.7, 129.7, 128.2, 128.1, 123.6, 120.4, 112.5, 110.8, 93.5, 85.7, 55.9. HRMS (EI) Calcd for $C_{15}H_{13}O$ $[M+H]^+$, 209.0961; found, 209.0969.

1-methyl-2-(phenylethynyl)benzene (3q): White solid, 28−29°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.8 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 6.4 Hz, 3H), 7.28 (d, *J* = 4.4 Hz, 2H), 7.22 (dt, *J* = 8.4, 4.4 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 131.8, 131.5, 129.5, 128.4, 128.3, 128.2, 125.6, 123.6, 123.1, 93.4, 88.4, 20.7. HRMS (EI) Calcd for $C_{15}H_{13}$ $[M+H]^+$, 193.1012; found, 193.1017.

1-chloro-2-(phenylethynyl)benzene (3r): White solid, 33−34°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (td, *J* = 8.0, 3.6 Hz, 3H), 7.49 – 7.43 (m, 1H), 7.40 (dd, *J* = 4.8, 1.6 Hz, 3H), 7.30 – 7.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 133.2, 132.5, 131.8, 129.3, 129.3, 128.7, 128.5, 128.4, 126.5, 123.3, 123.0, 95.1, 89.1. HRMS (EI) Calcd for $C_{14}H_{10}Cl$ $[M+H]^+$, 213.0466; found, 213.0471.

1-trifluoromethyl-2-(phenylethynyl)benzene (3s): White solid, 26−28°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 8.4 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.54 – 7.50 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9, 131.9, 131.6, 129.0, 128.6, 128.1, 126.2, 126.1, 126.0, 124.9, 122.9, 122.7, 121.8, 95.2, 85.6. HRMS (EI) Calcd for $C_{15}H_{10}F_3O$ $[M+H]^+$, 263.0678; found, 263.0685.

2-(phenylethynyl)naphthalene (3t): White solid, mp:106−107 °C (ref [14] 105−106 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.76–

7.68 (m, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.44 (d, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3, 133.2, 131.7, 130.4, 128.8, 128.5, 128.4, 128.3, 126.8, 126.5, 126.2, 125.3, 123.5, 120.9, 94.4, 87.6. HRMS (EI) Calcd for $C_{18}H_{13}$ $[M+H]^+$, 229.1012; found, 229.1019.

4-(phenylethynyl)pyridine (3u): White solid, mp:95−97 °C (ref [17] 94−94.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.49 (m, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 7.0, 3H), 7.14 (d, J = 8.0 Hz, 2H), 2.66–2.54 (m, 2H), 1.65–1.54 (m, 2H), 1.31 (dd, J = 6.4, 3.2 Hz, 4H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 131.6, 131.5, 128.5, 128.3, 128.1, 123.6, 120.5, 89.7, 88.8. HRMS (EI) Calcd for $C_{13}H_{10}N$ $[M+H]^+$, 180.0808; found, 180.0813.

1,3-bis(phenylethynyl)benzene (3v): White solid, mp:106−108 °C (ref [2] 104−105 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.56 (d, J = 4.4 Hz, 2H), 7.54 (d, J = 2.0 Hz, 2H), 7.51 (d, J = 1.6 Hz, 1H), 7.48 (d, J = 1.6 Hz, 1H), 7.37 – 7.32 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 133.1, 132.7, 130.0, 129.9, 129.8, 125.1, 124.5, 91.4, 90.0. HRMS (EI) Calcd for $C_{22}H_{15}$ $[M+H]^+$, 279.1168; found, 279.1160.

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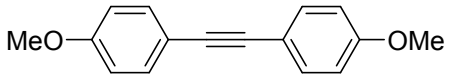
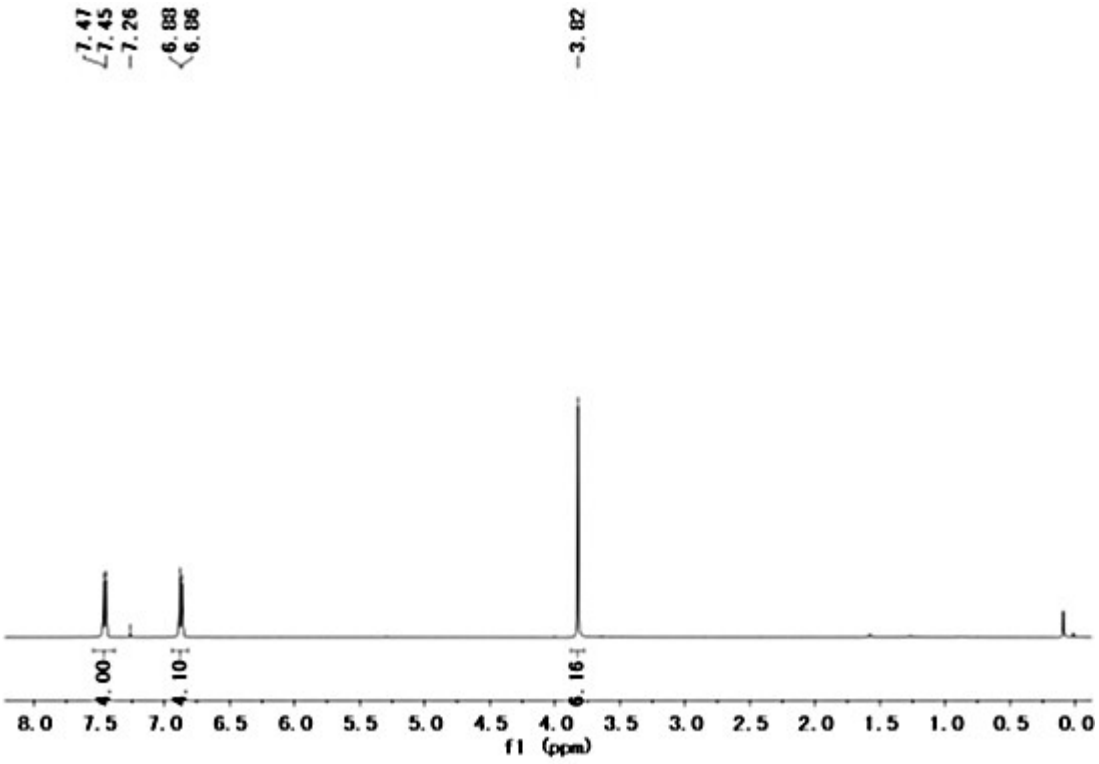
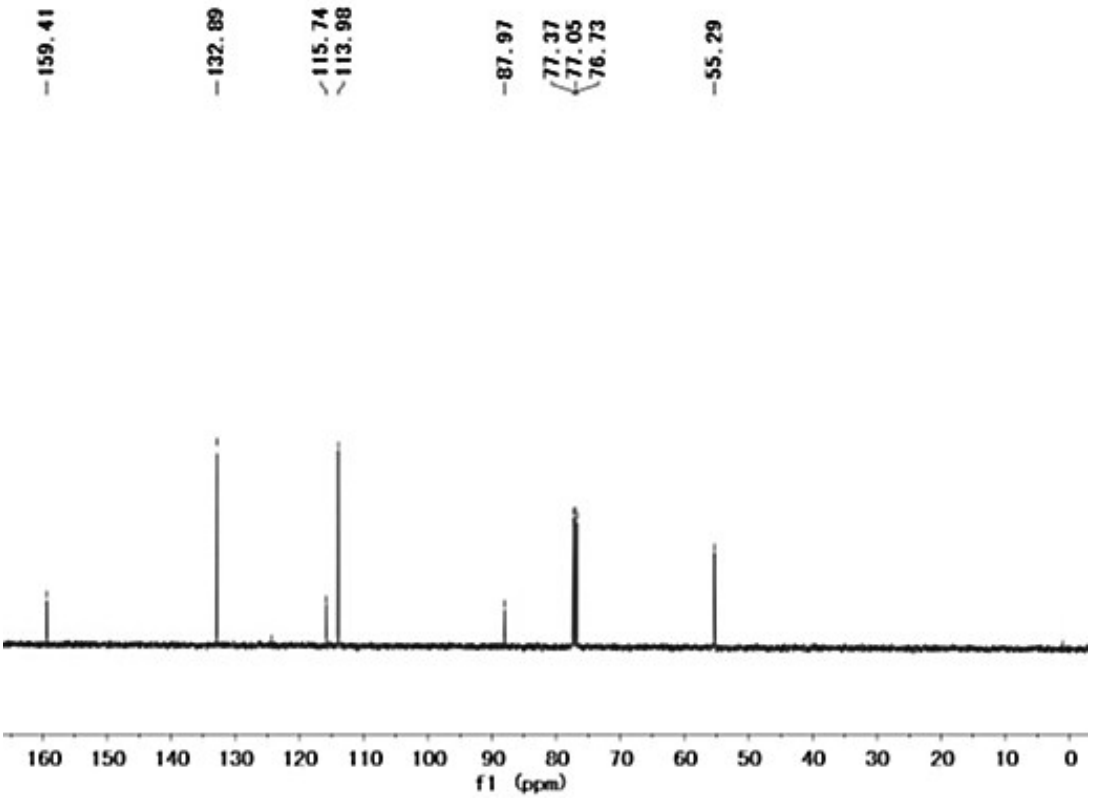
Copies of NMR Spectra

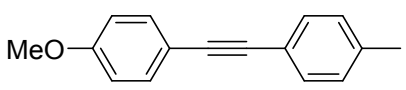
(1) 1,2-bis(4-methoxyphenyl)ethyne (2a)

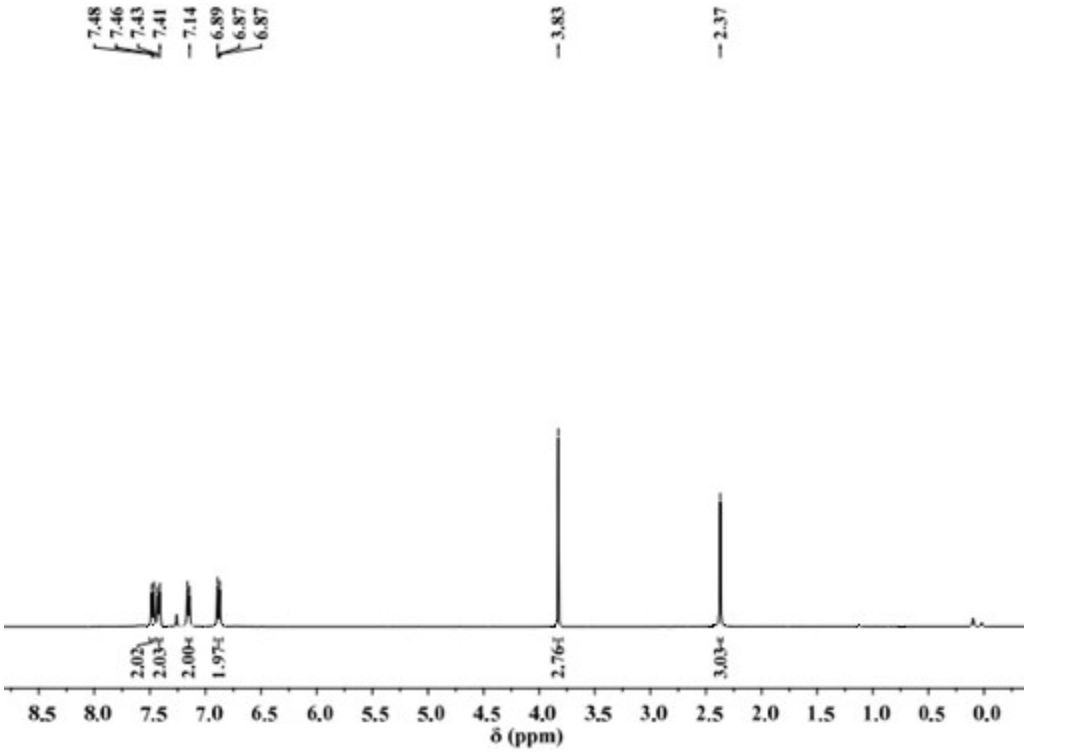


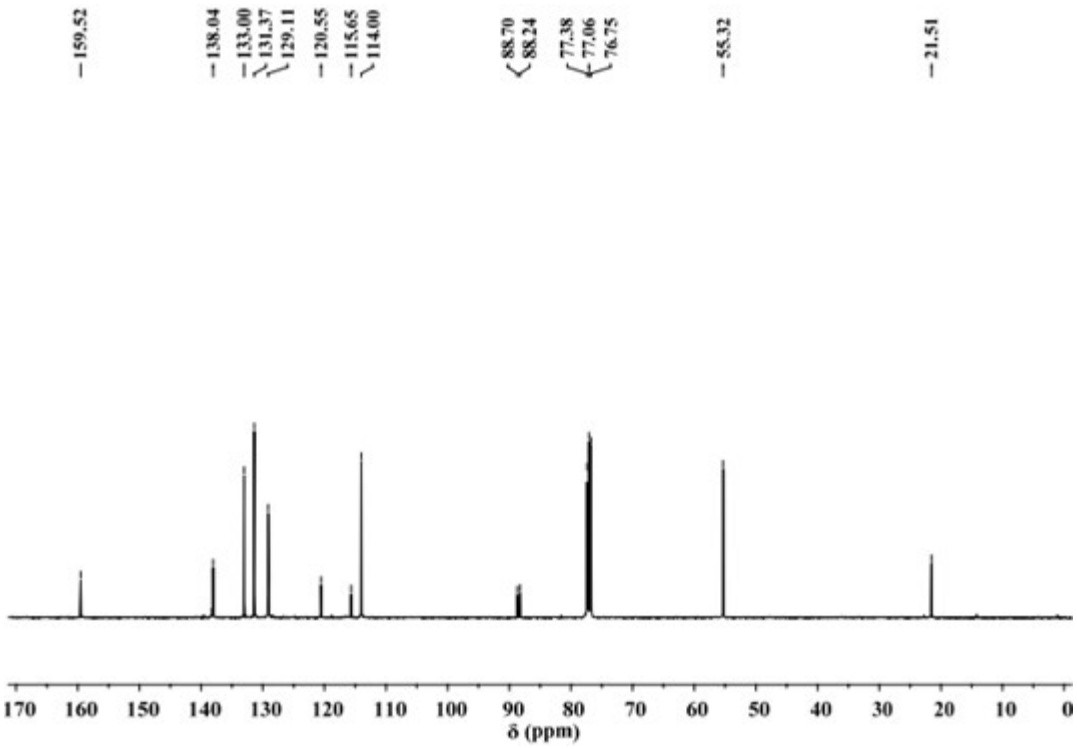




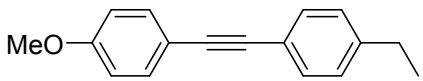
(2) 1-methoxy-4-(p-tolylethynyl)benzene (2b)

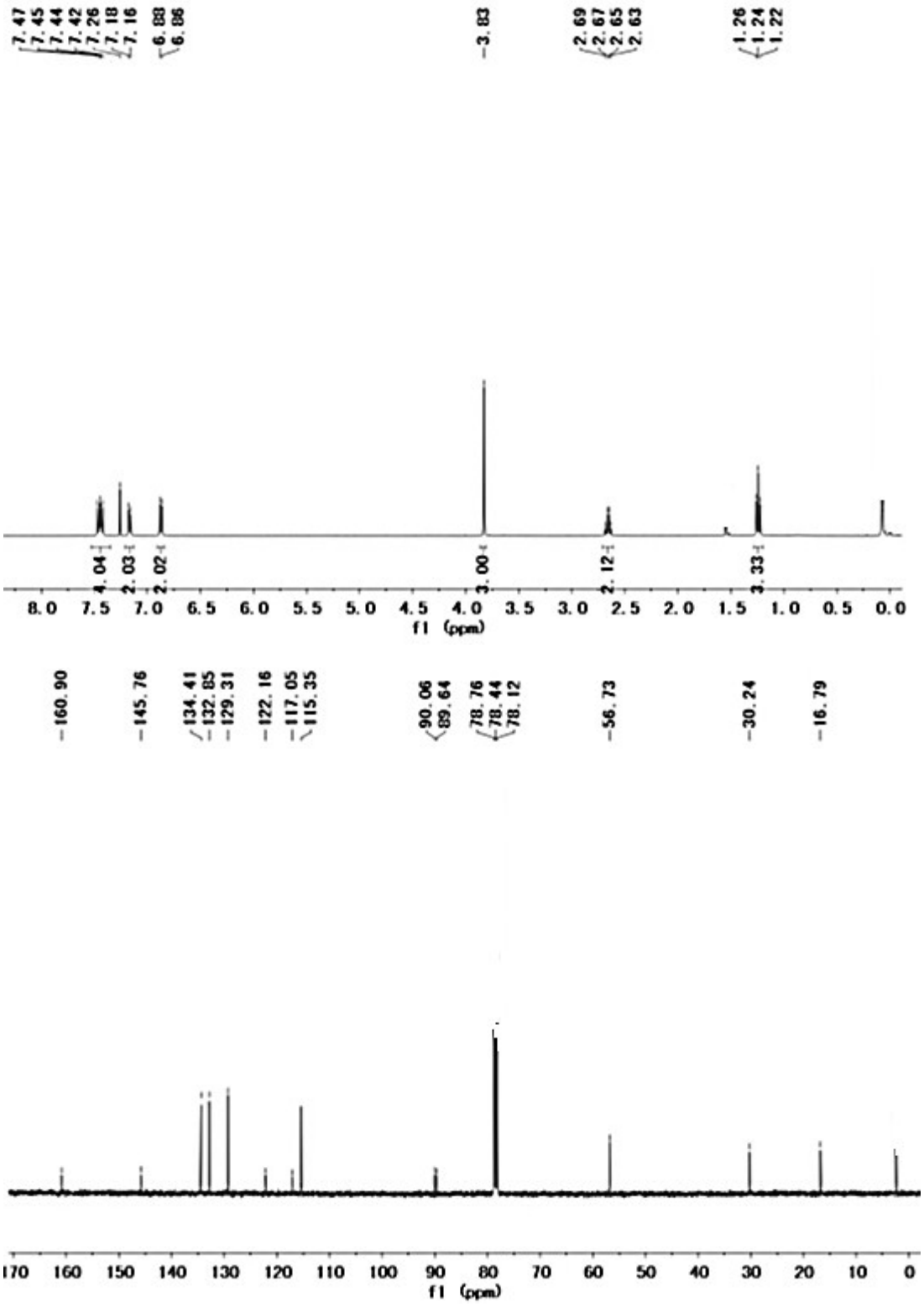






(3) 1-ethyl-4-((4-methoxyphenyl)ethynyl)benzene (2c)





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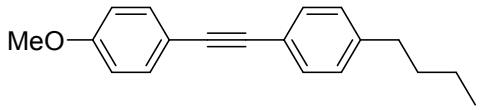
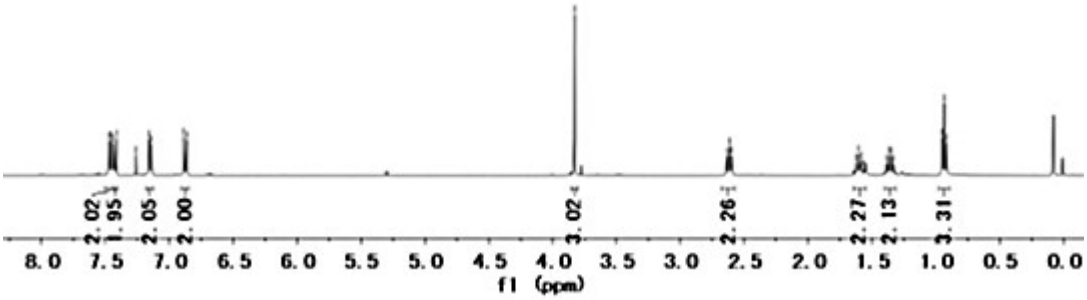
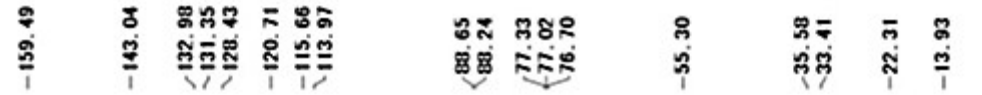
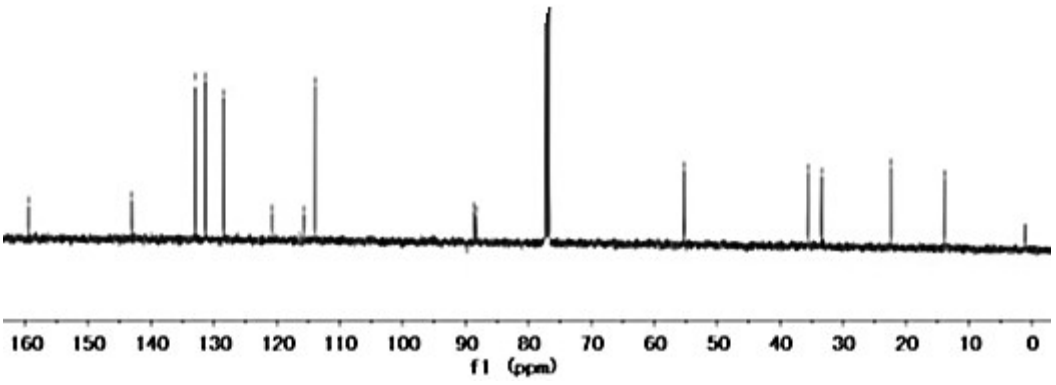
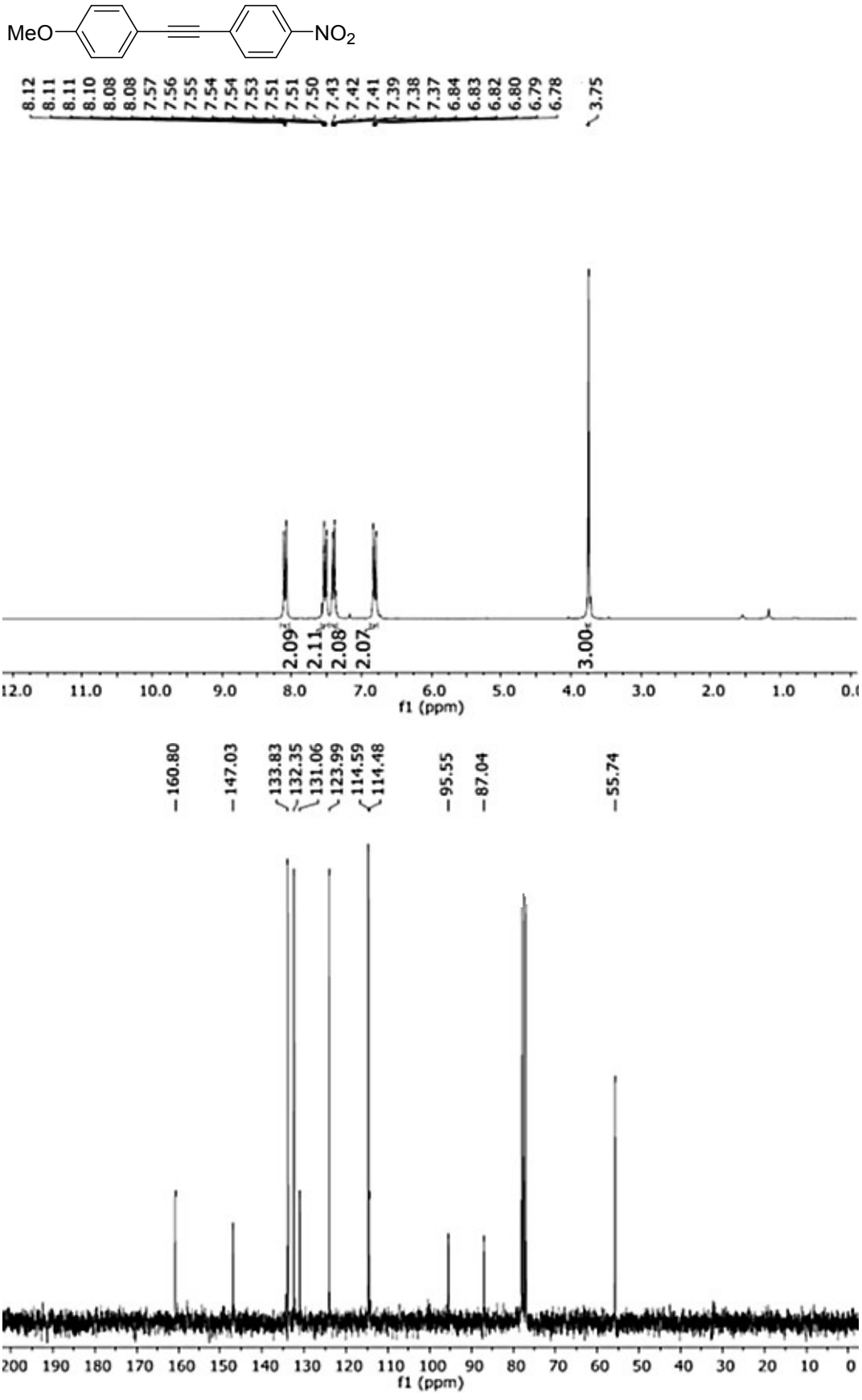




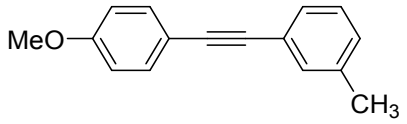


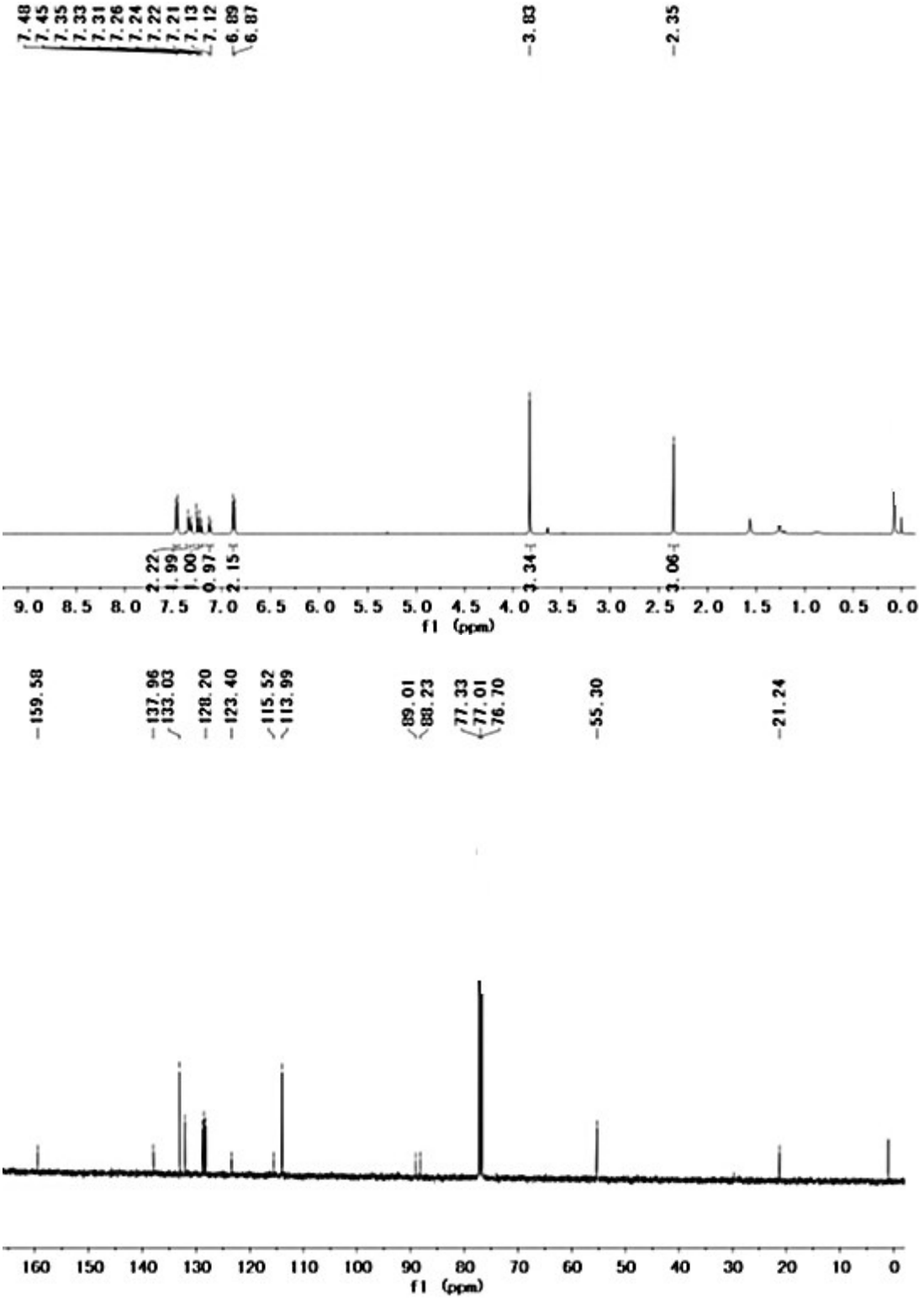


(5) 1-Methoxy-4-((4-nitrophenyl)ethynyl)benzene (2e)

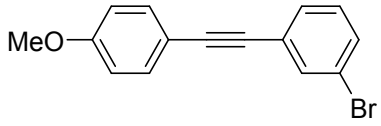


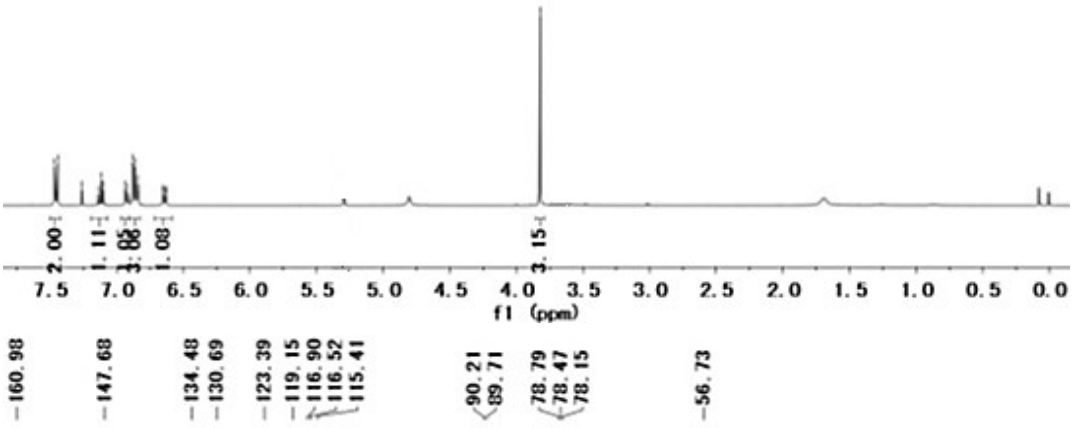
(6) 1-methoxy-4-(m-tolylethynyl)benzene (2f)

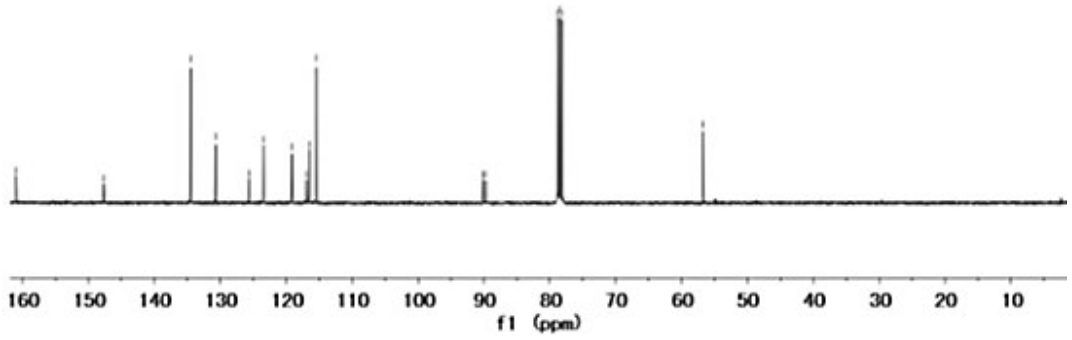




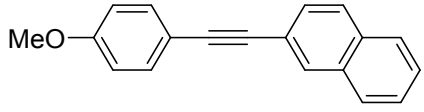
(7) 1-methoxy-4-(m-bromoethynyl)benzene (2g)

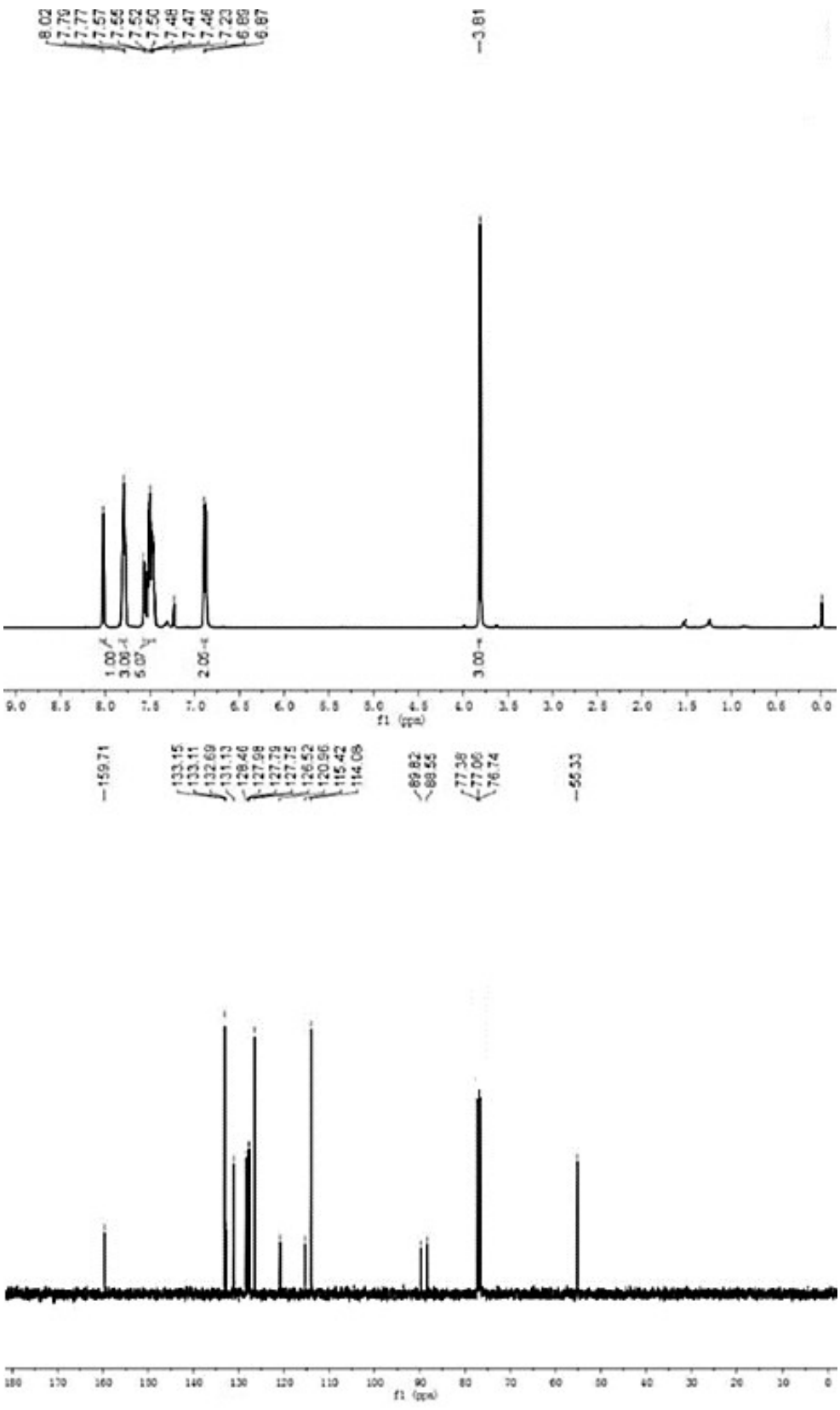




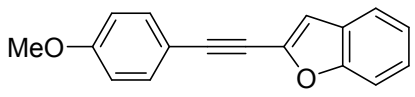


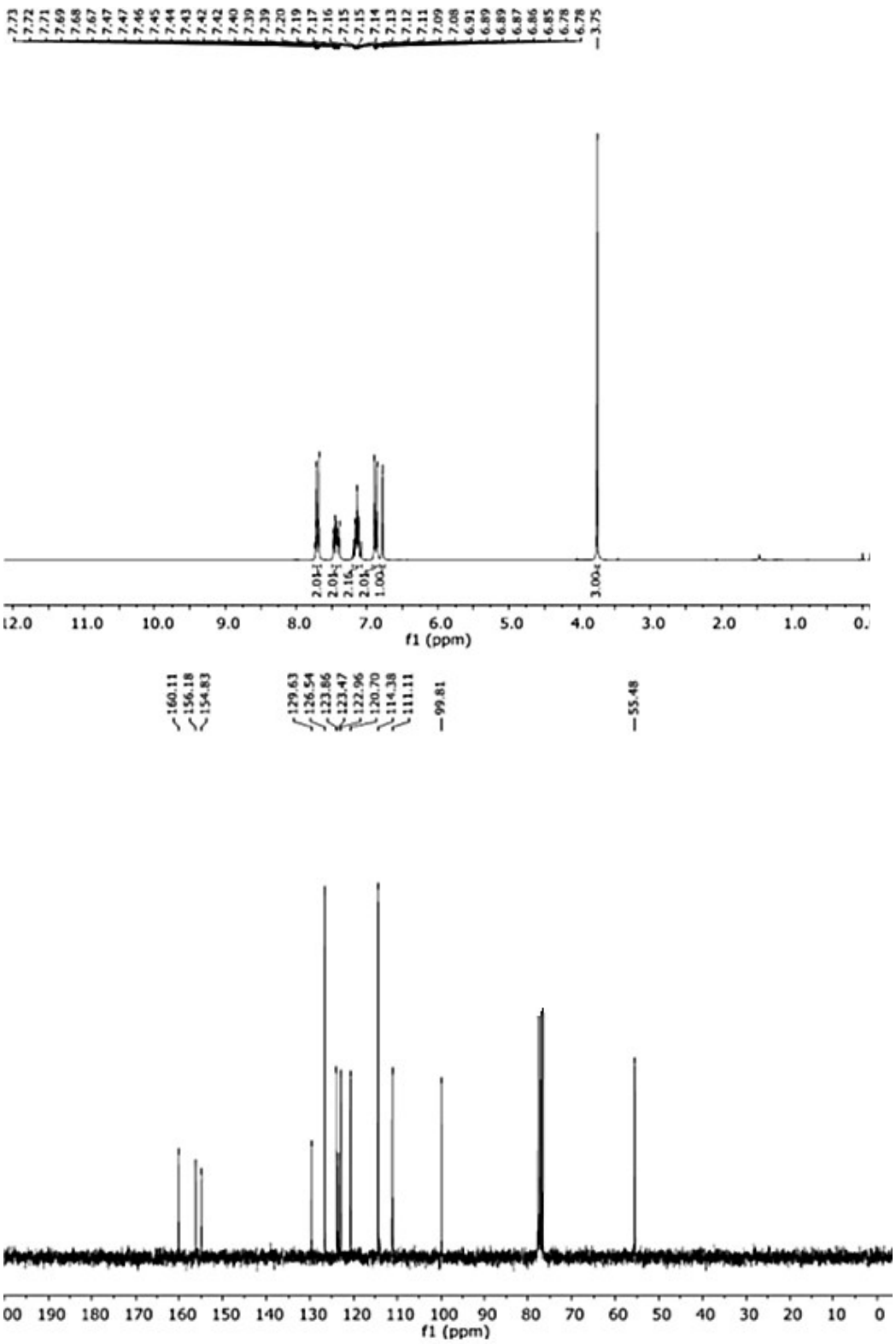
(8) 2-((4-methoxyphenyl)ethynyl)naphthalene (2h)



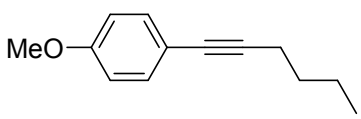


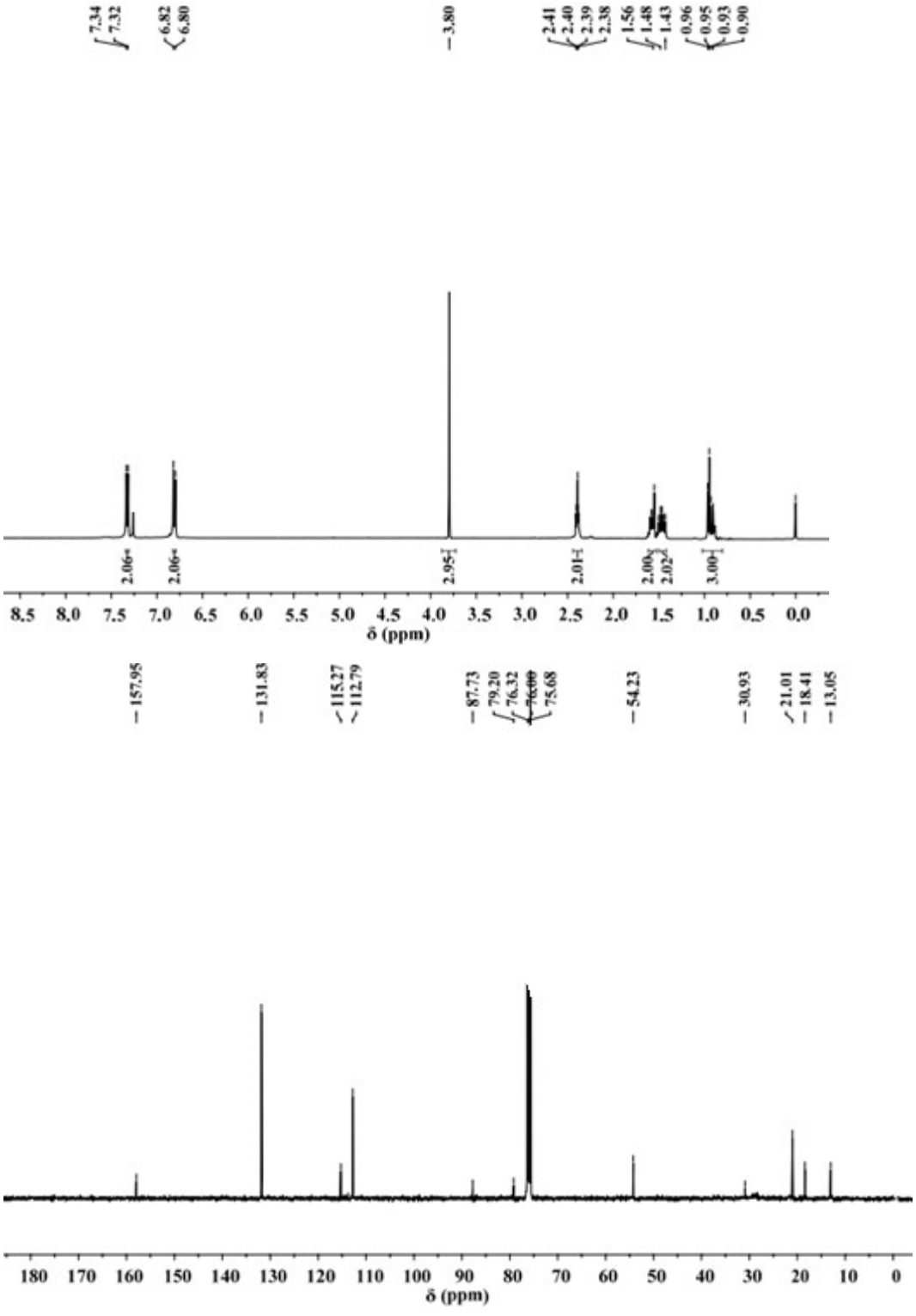
(9) 2-(4-Methoxyphenyl)benzofuran (2i)



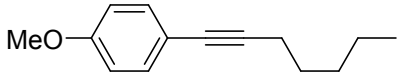


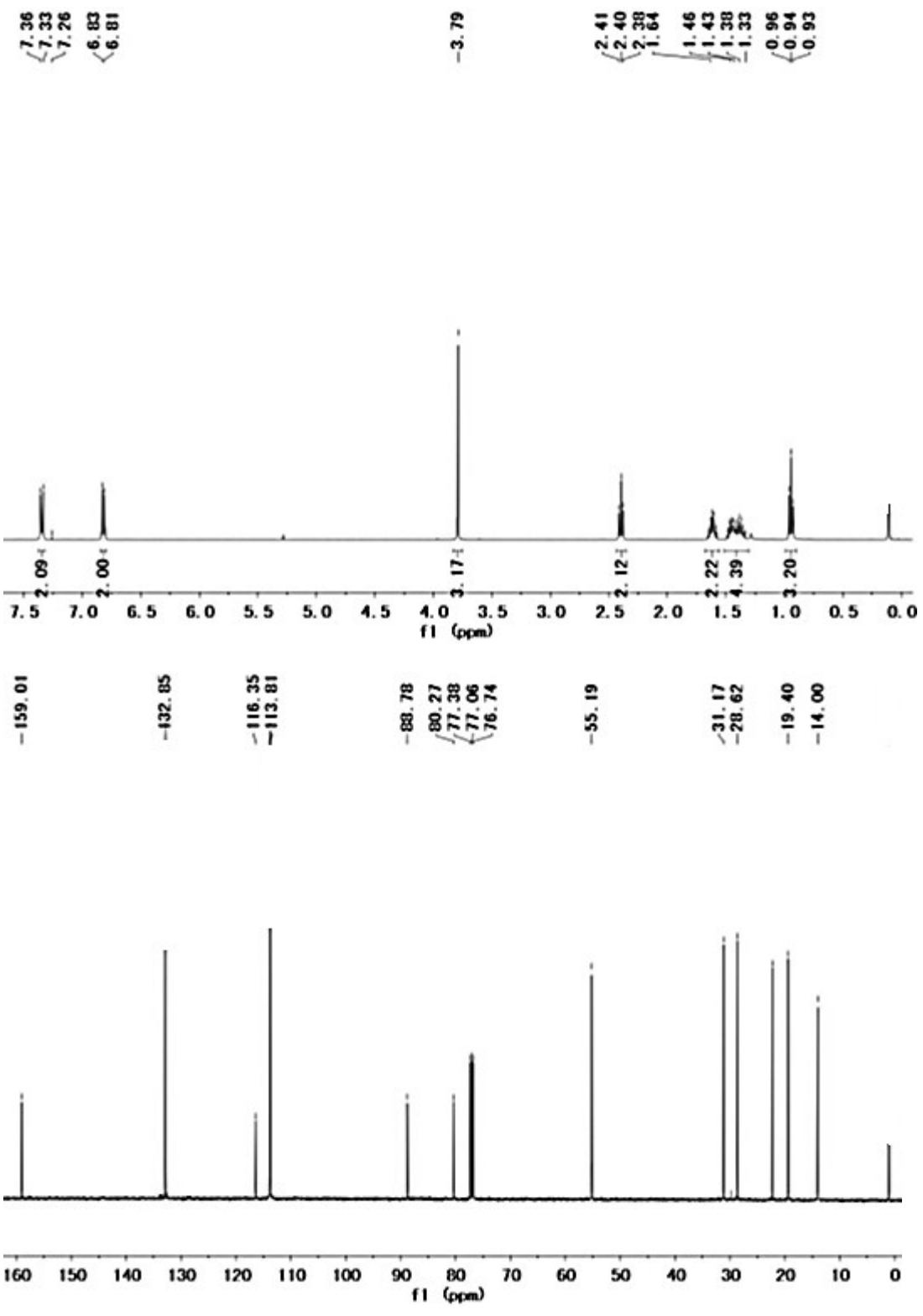
(10) 1-(hex-1-ynyl)-4-methoxybenzene (2j)



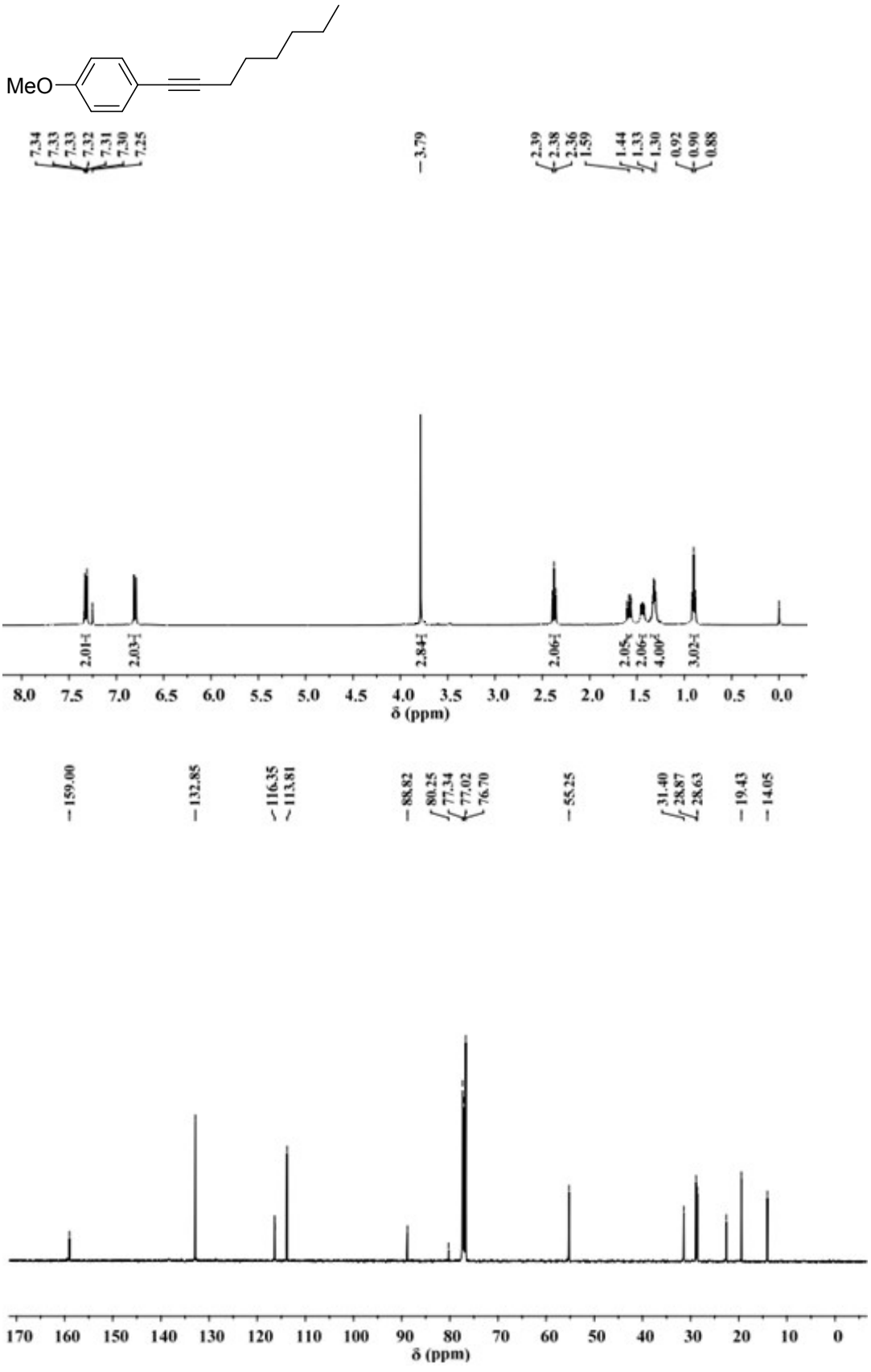


(11) 1-(hept-1-ynyl)-4-methoxybenzene (2k)

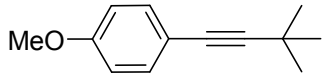




(12) 1-(oct-1-ynyl)-4-methoxybenzene (2l)



(13) 1-(3, 3-Dimethyl-1-butynyl)-4-methoxybenzene (2m):



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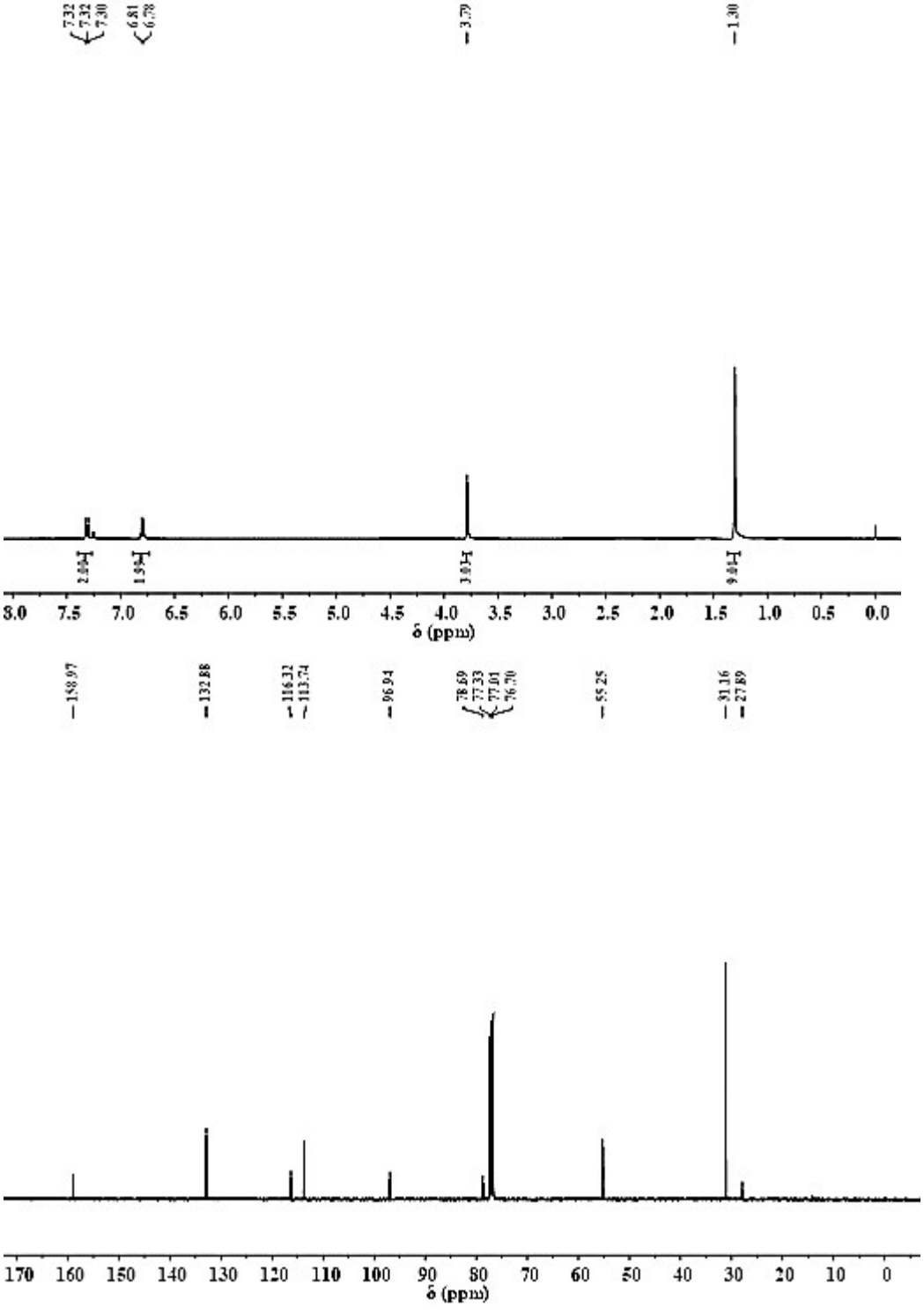
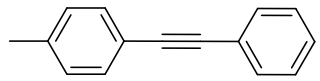
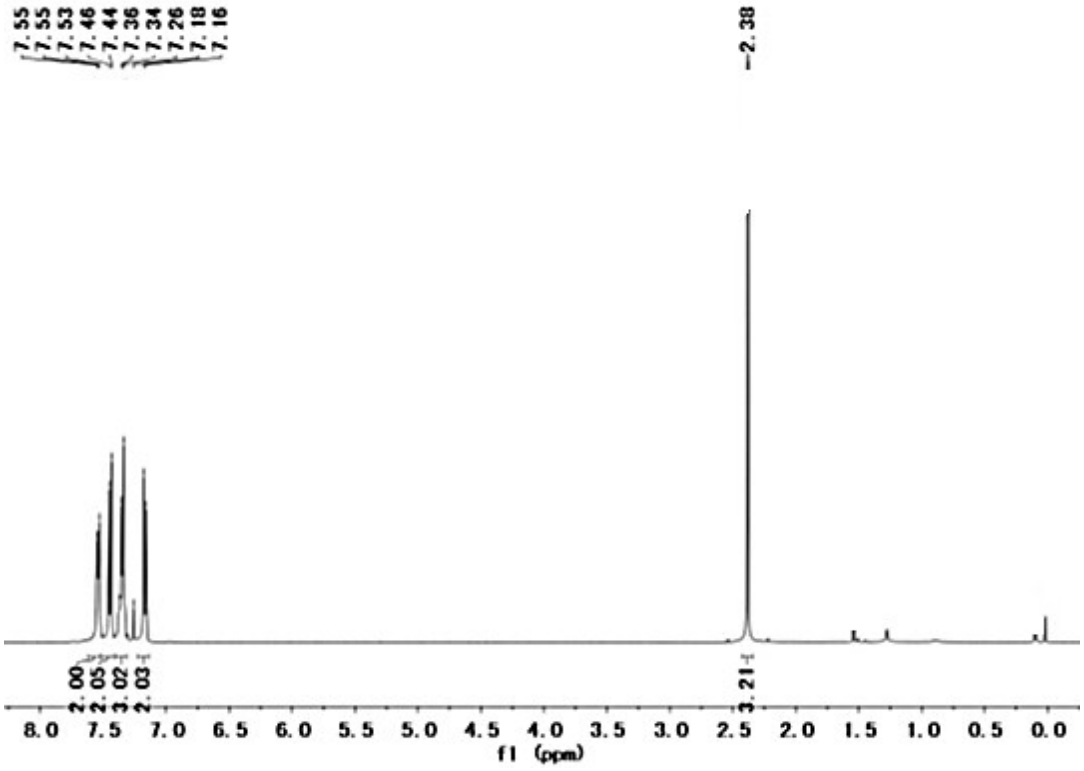
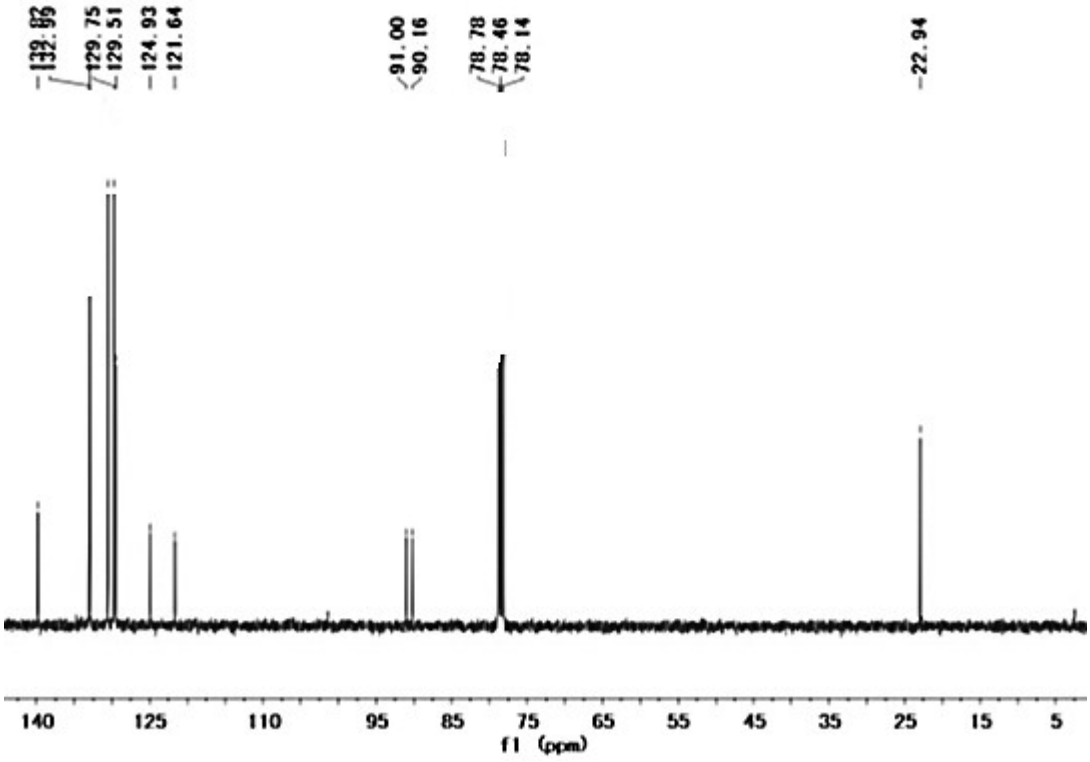


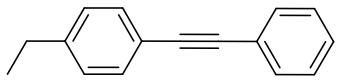
(14) 1-methyl-4-(phenylethynyl)benzene (3a):

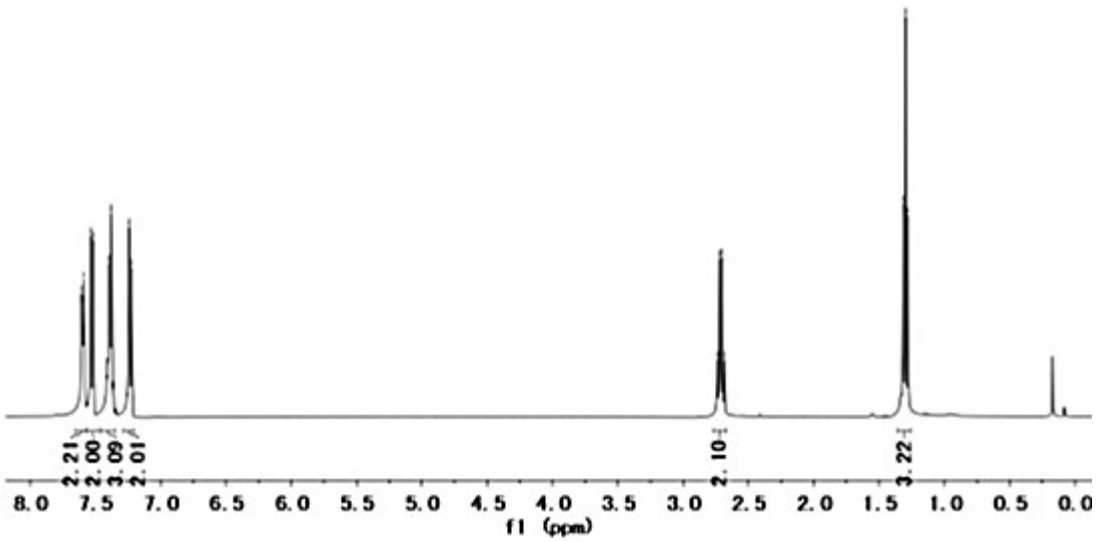


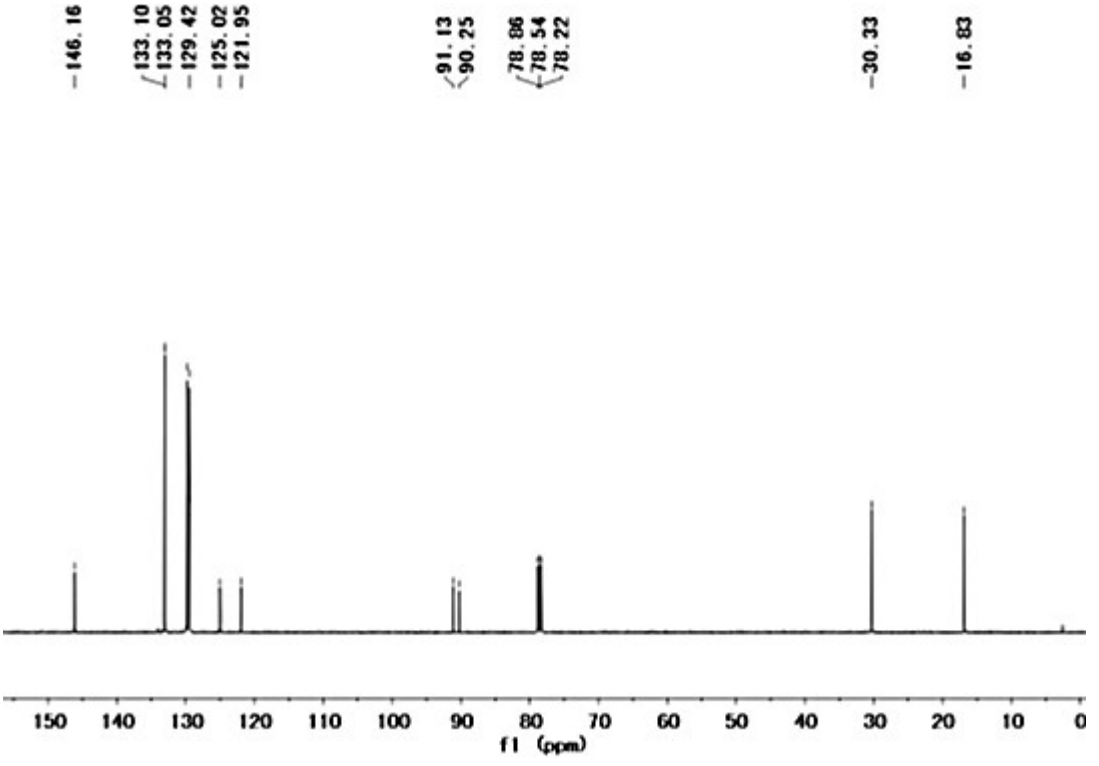




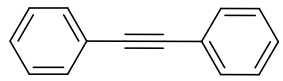
(15) 1-ethyl-4-(phenylethynyl)benzene (2b):

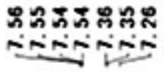


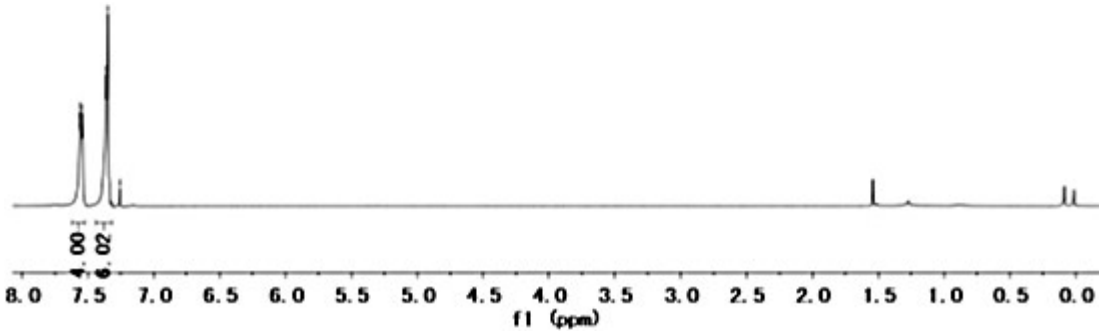


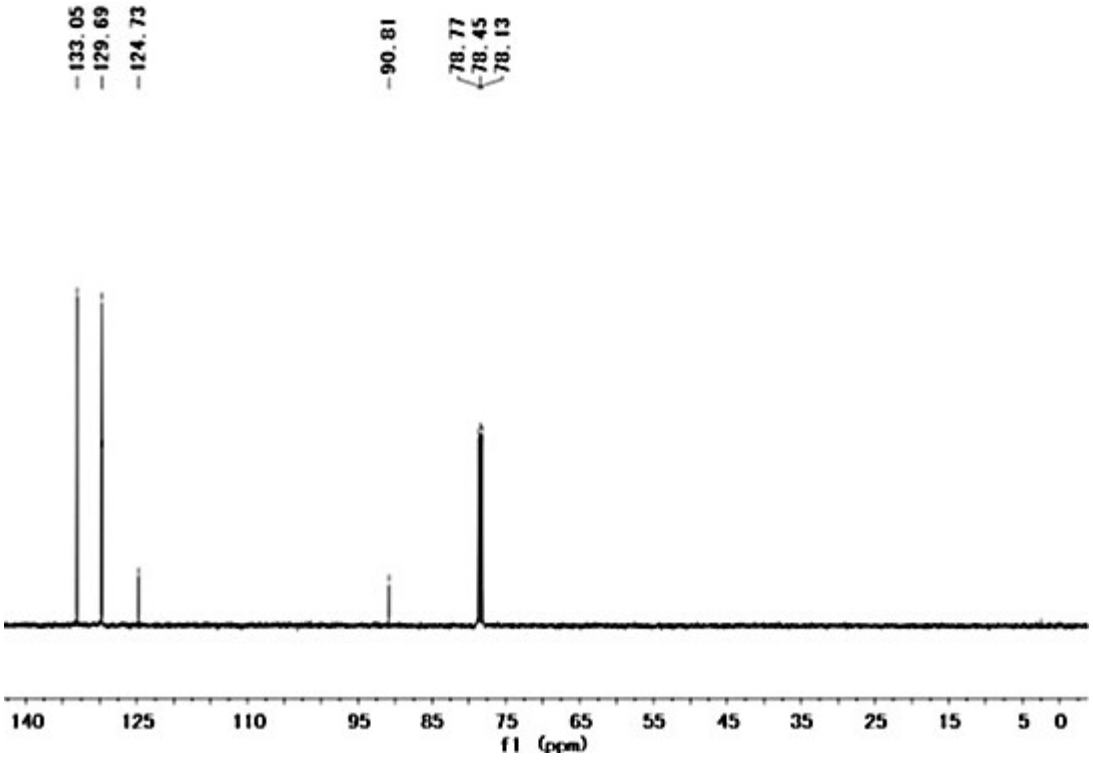


(16) 2-diphenylethyne (3c):

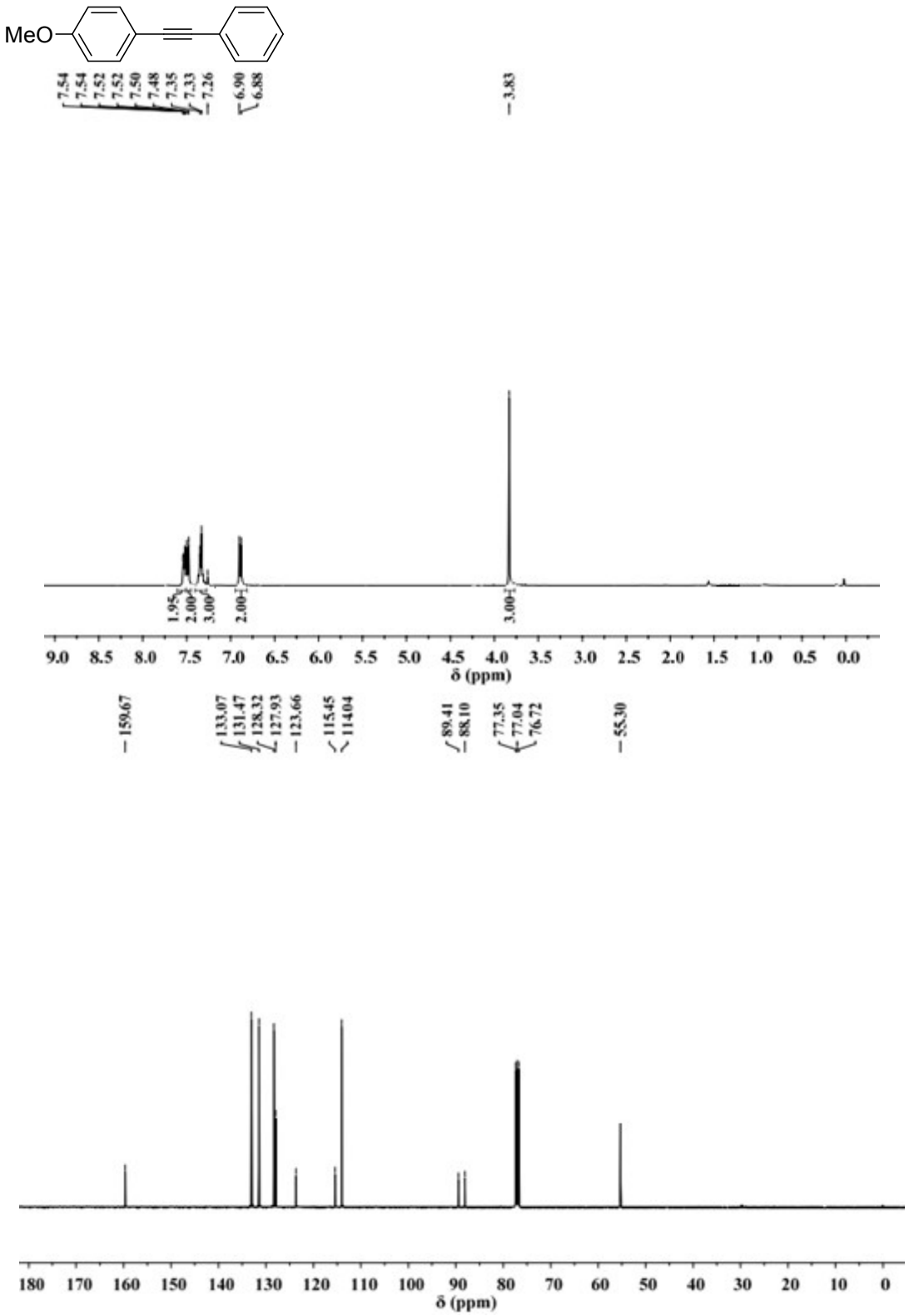




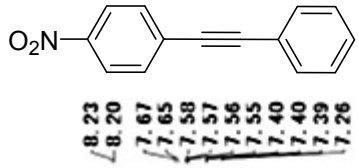


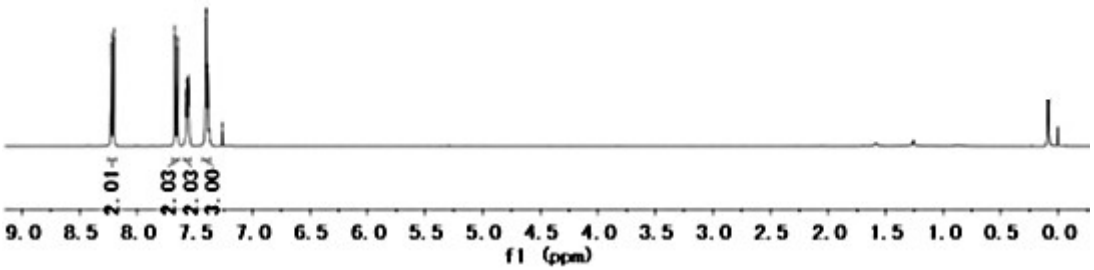


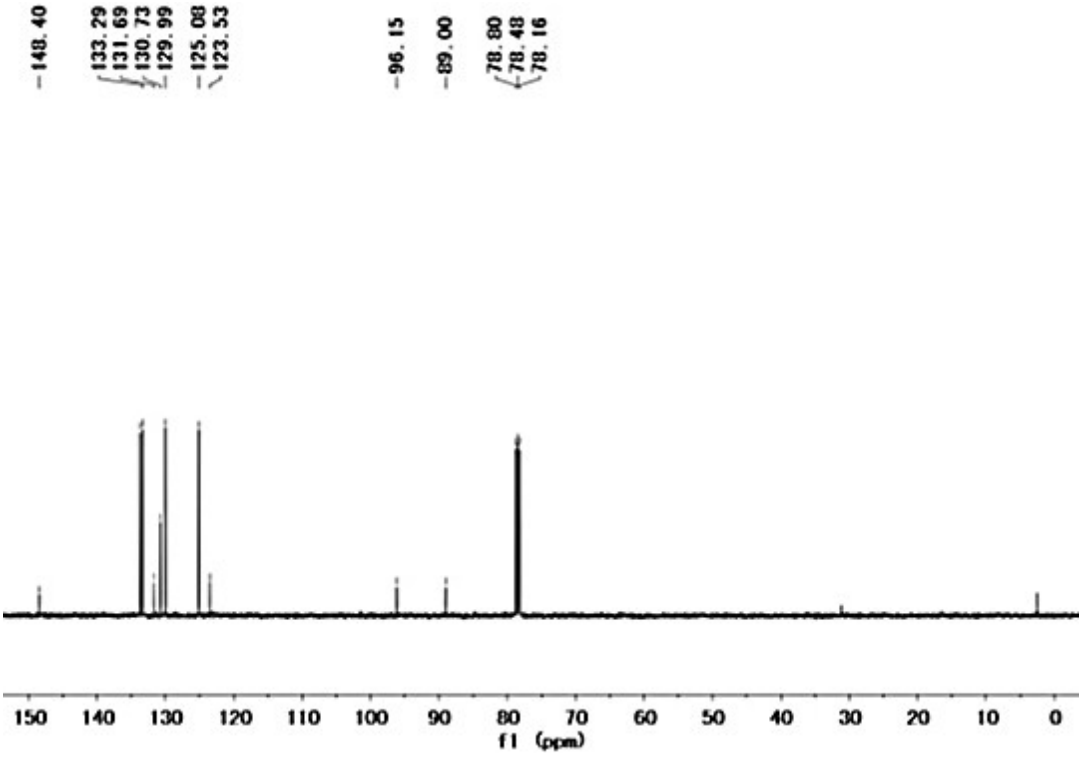
(17) 1-methoxy-4-(phenylethynyl)benzene (3d):



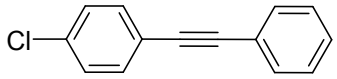
(18) 1-nitro-4-phenylethynylbenzene (3e):

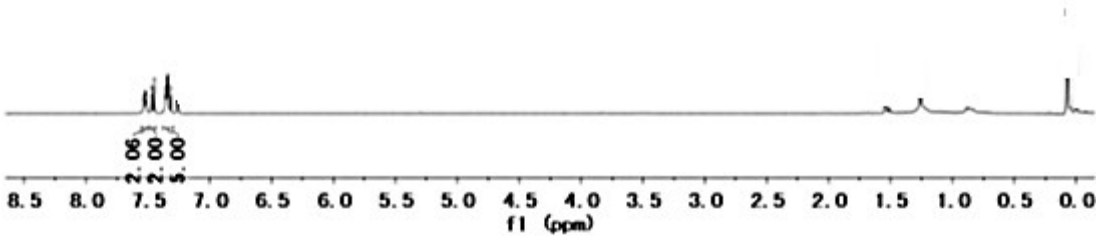


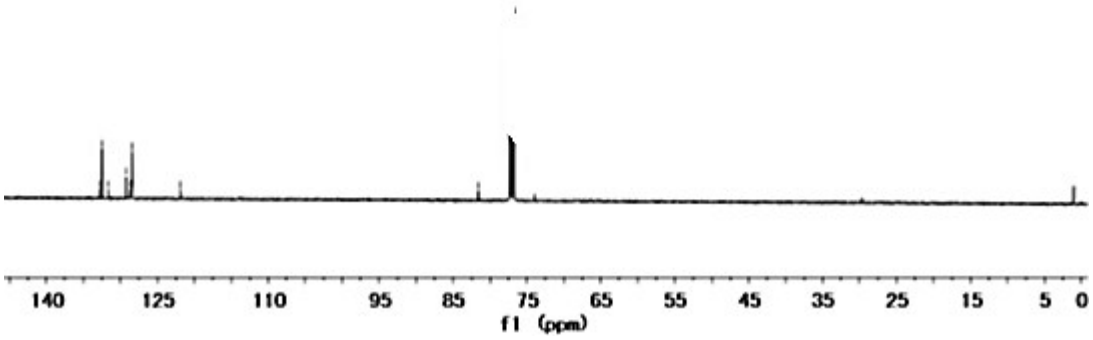




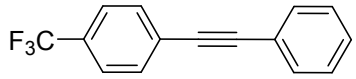
(19) 1-chloro-4-(phenylethynyl)benzene (3f)

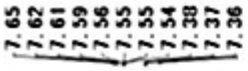


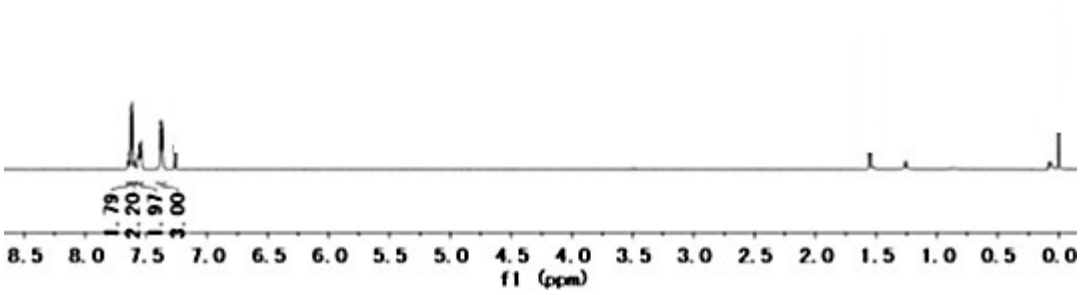


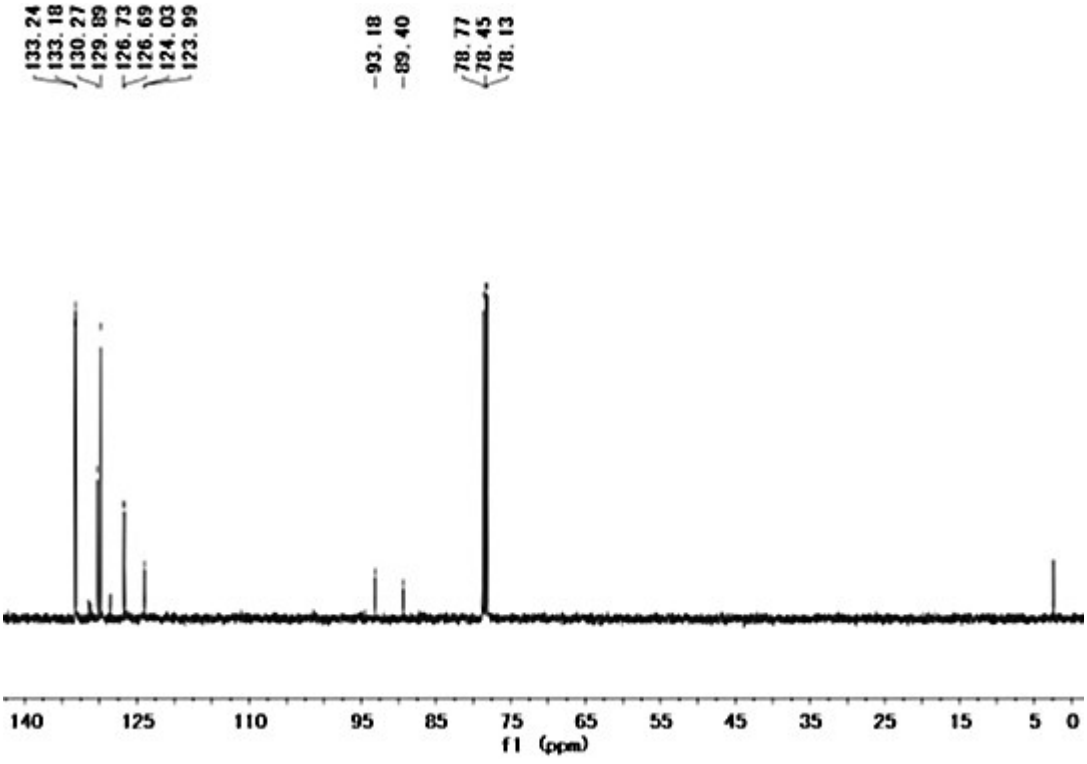


(20) 1-(phenylethynyl)-4-(trifluoromethyl)benzene (3g):

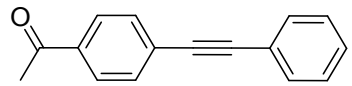


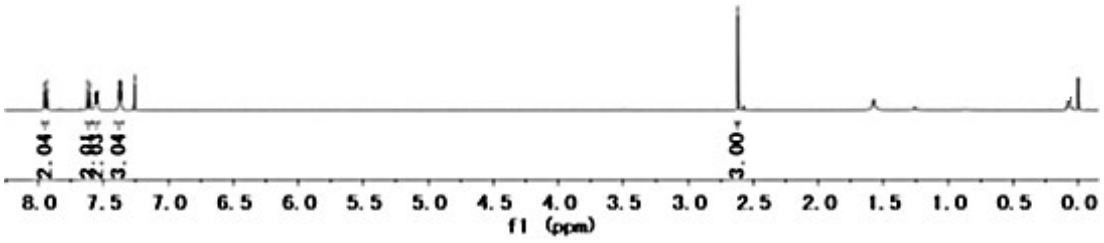


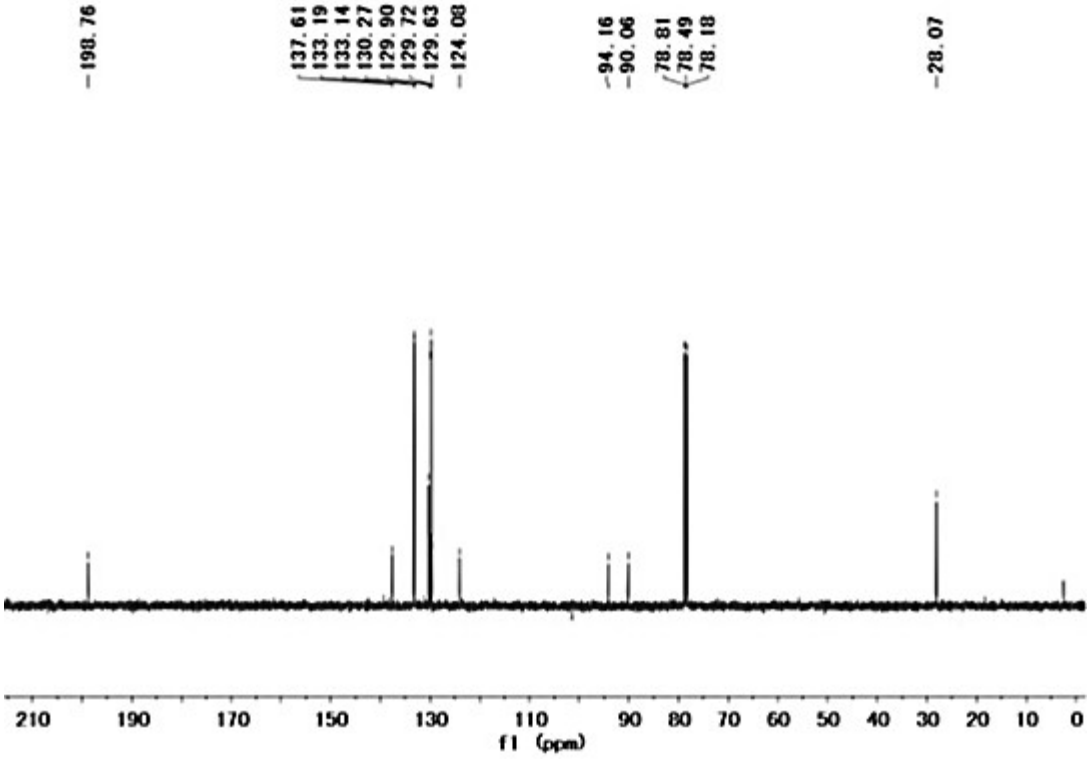




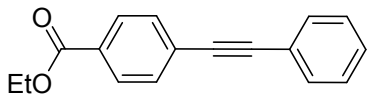
(21) 1-(4-(phenylethynyl)phenyl)ethanone (3h):

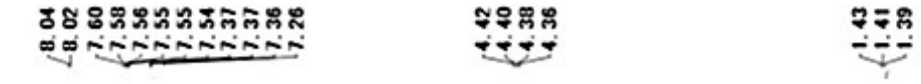


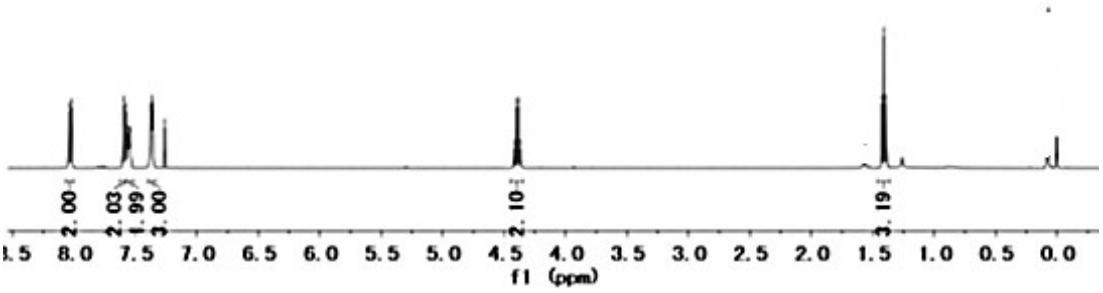


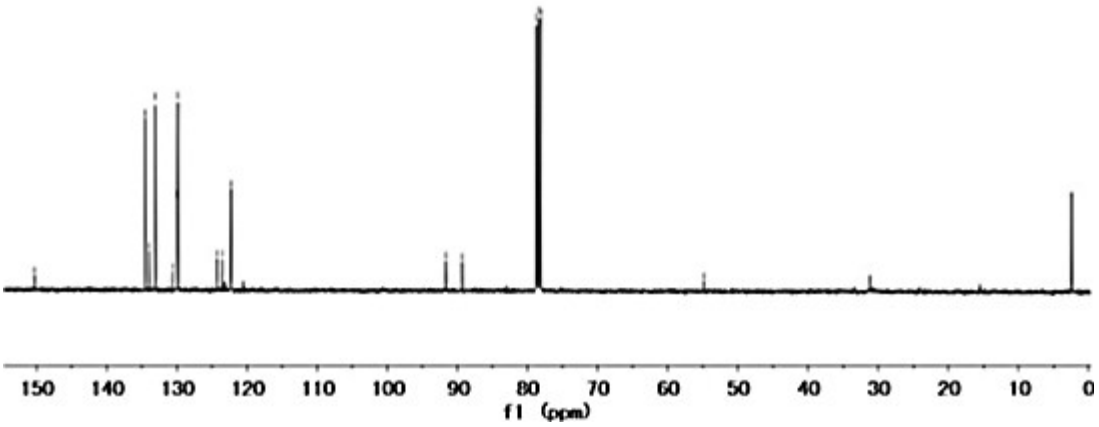


(22) 1-ethyl-4-(phenylethynyl)benzoate (3i):

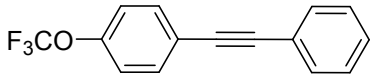


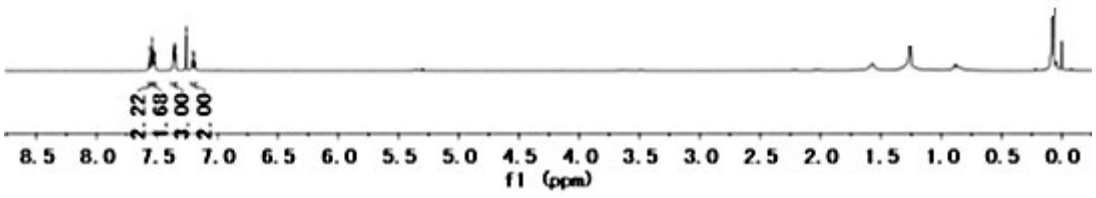


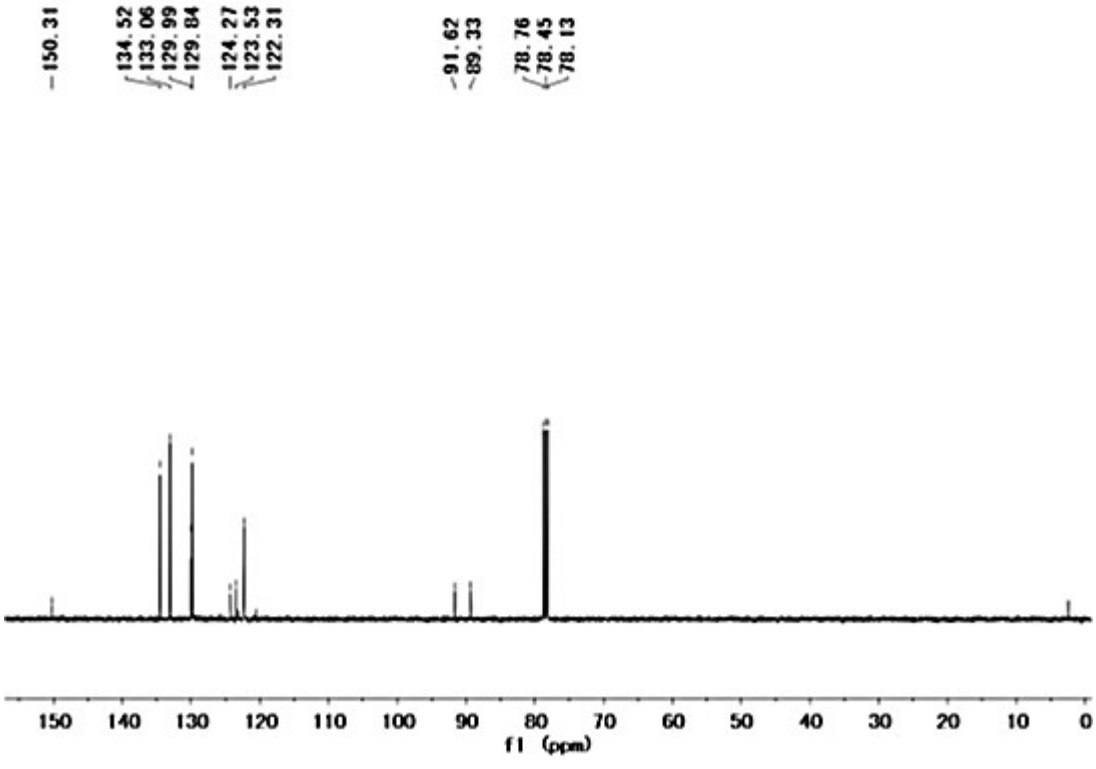




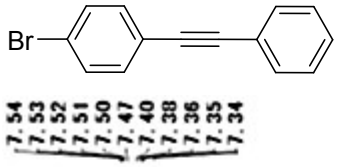
(23) 1-(phenylethynyl)-4-(trifluoromethoxy)benzene (3j):

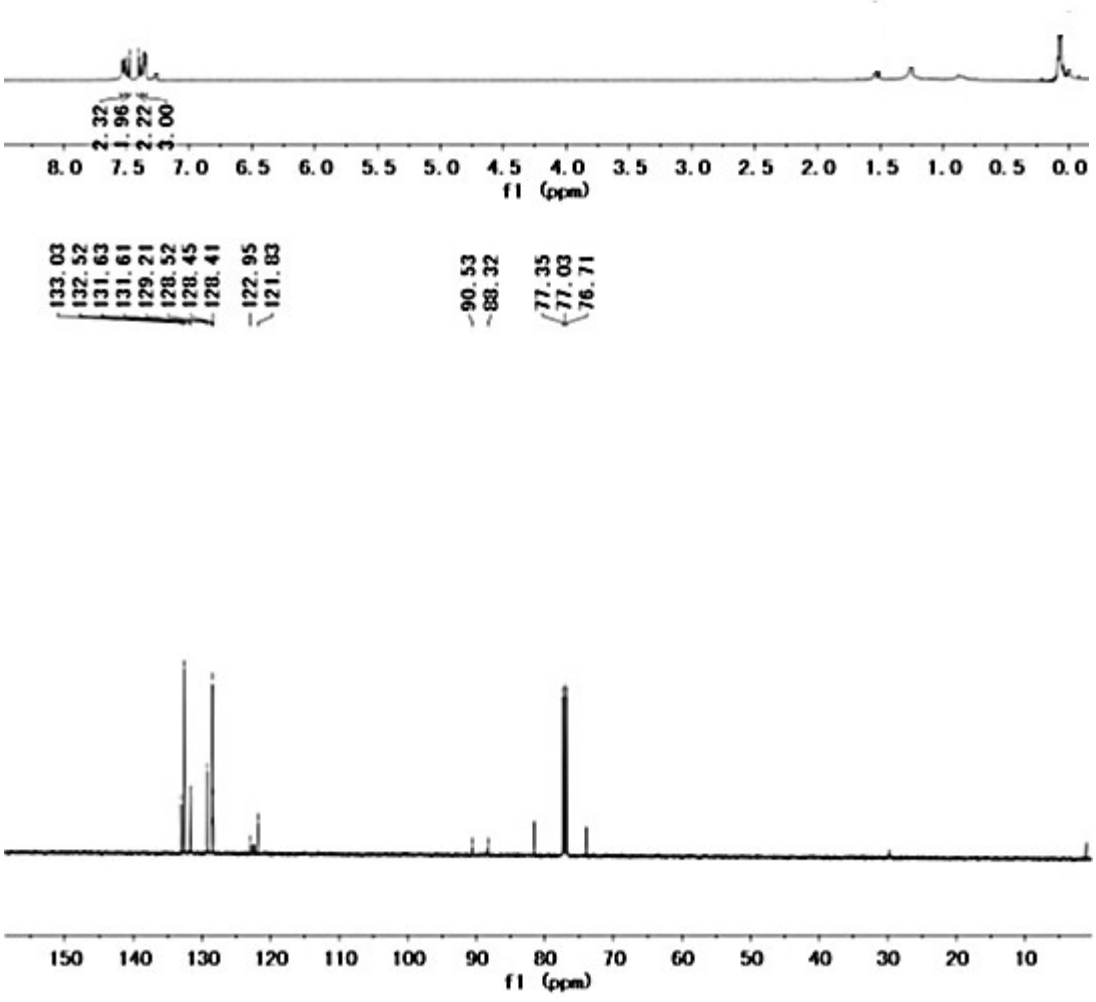




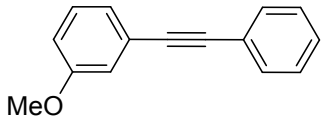


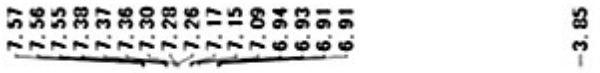
(24) 1-bromo-4-(phenylethynyl)benzene (3k):

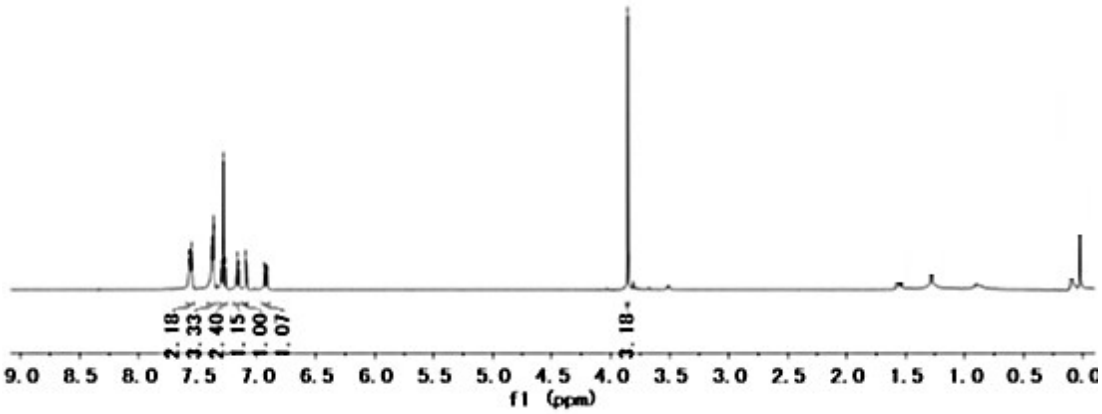


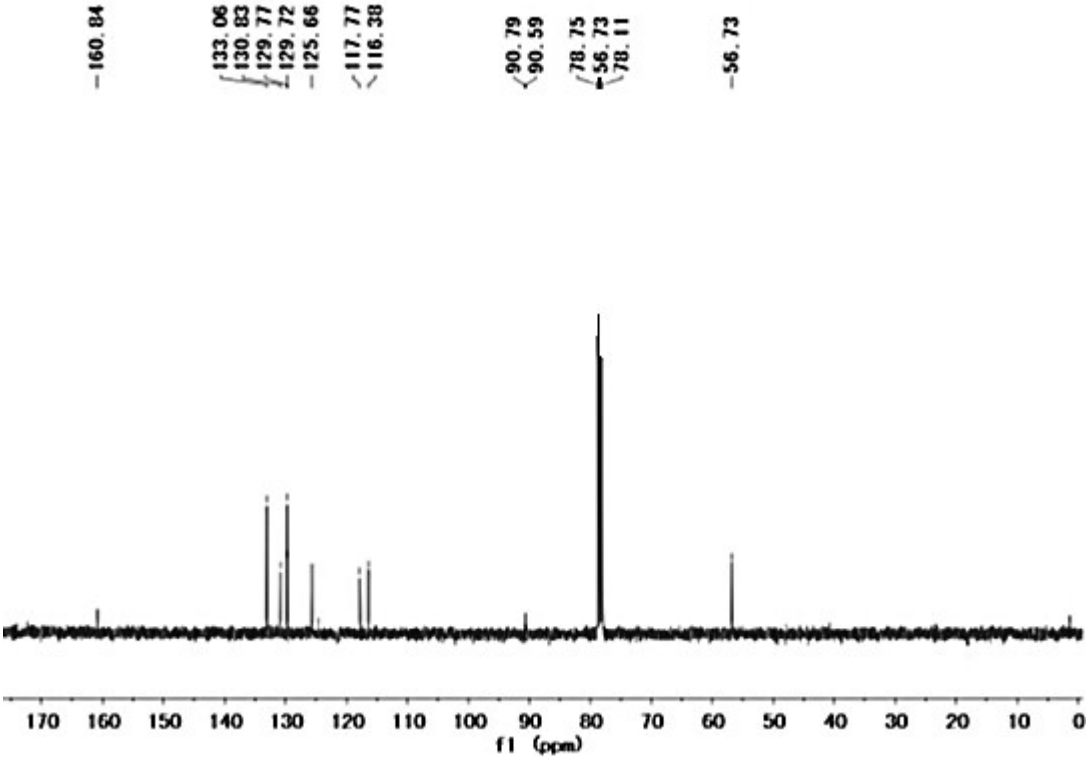


(25) 1-methoxy-3-(phenylethynyl)benzene (3l):

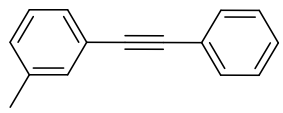


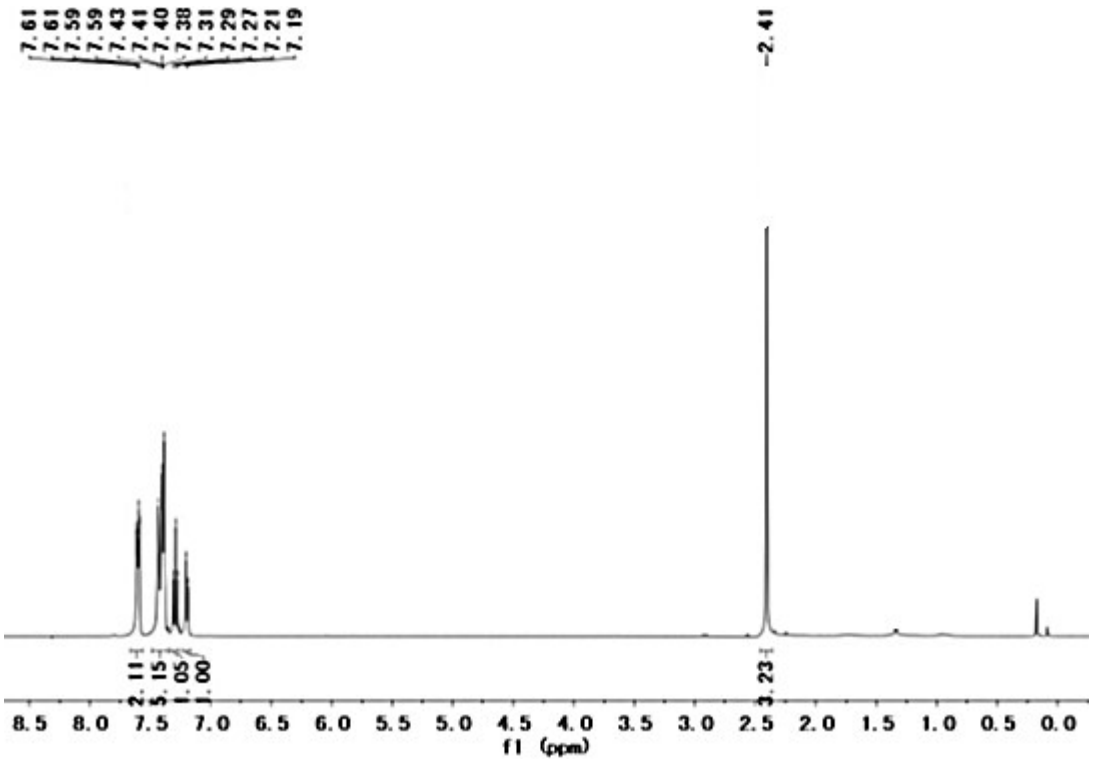


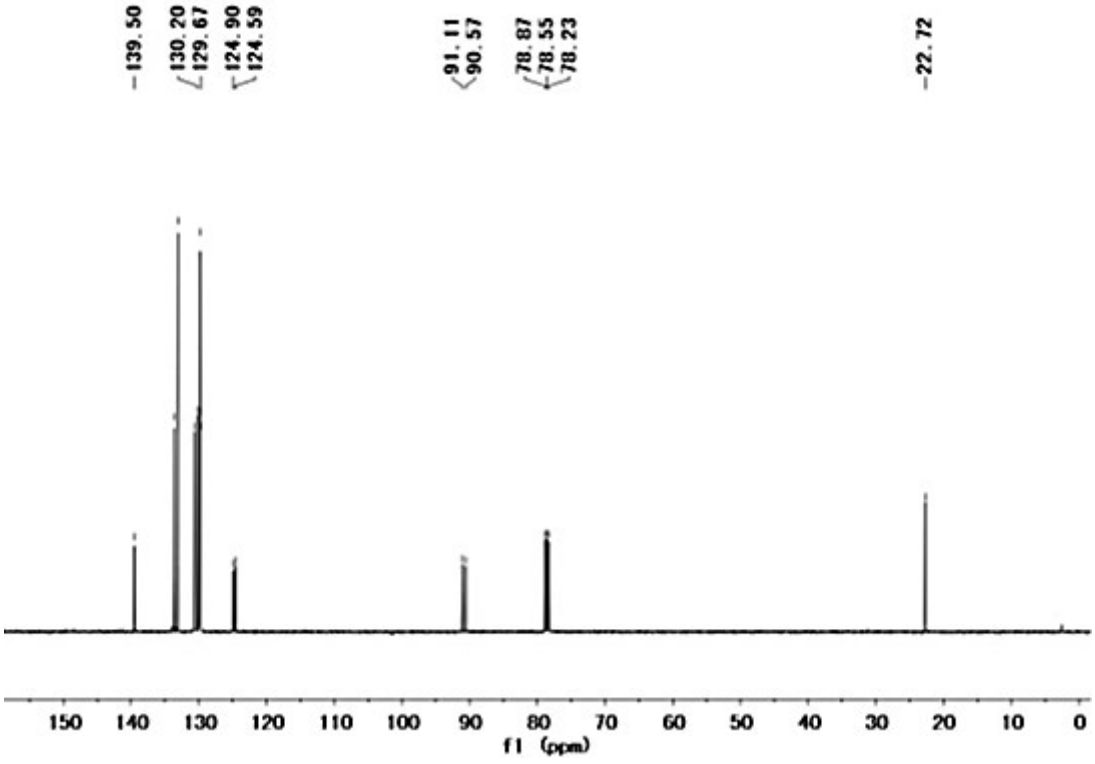




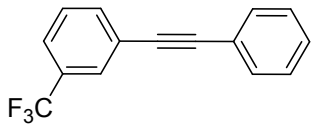
(26) 1-methyl-3-(phenylethynyl)benzene (3m):

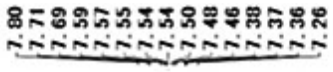


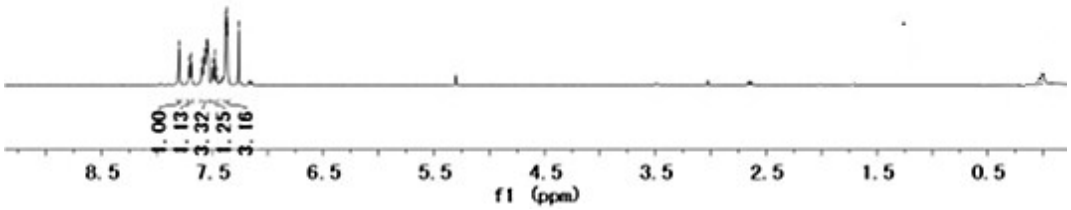


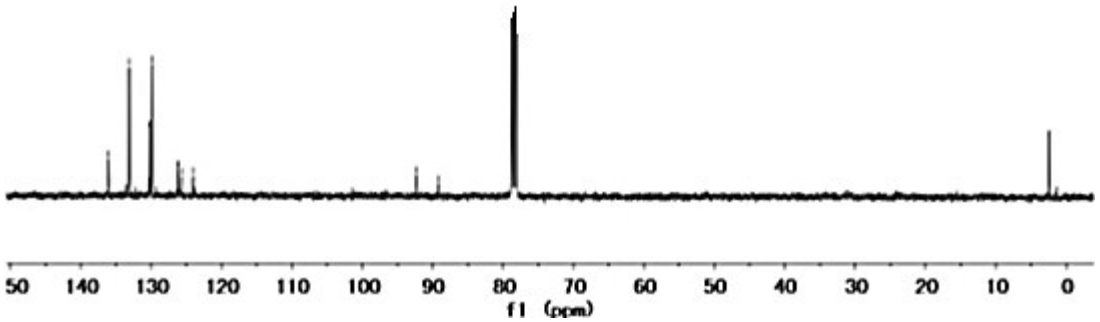


(27) 1-(phenylethynyl)-3- (trifluoromethyl)benzene (3n):

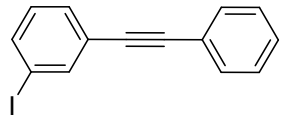


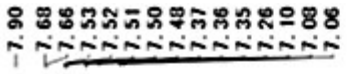


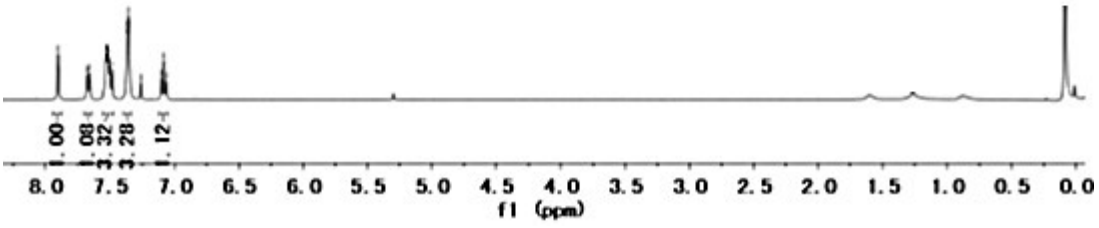


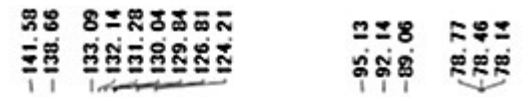


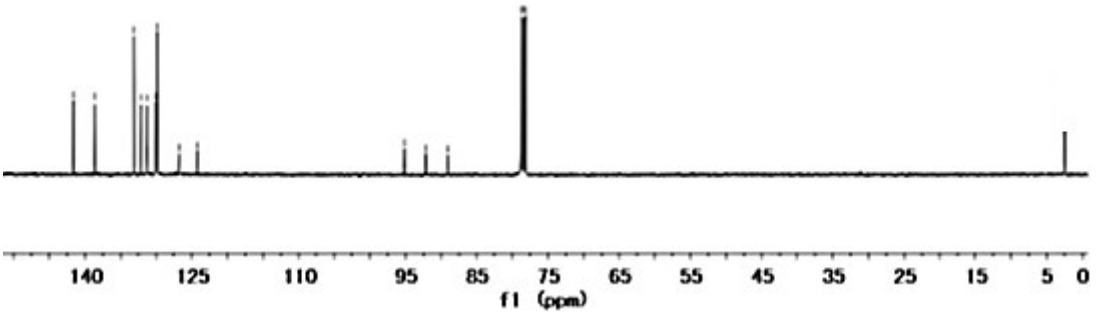
(28) 1-iodo-3-(phenylethynyl)benzene (3o):



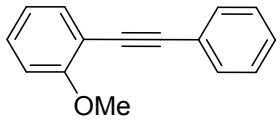


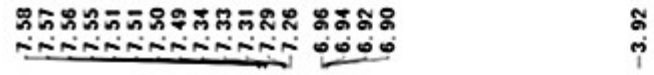


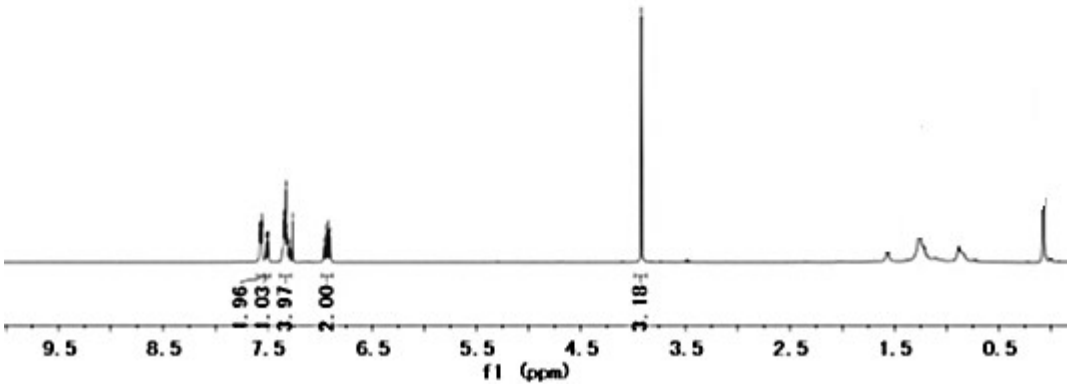


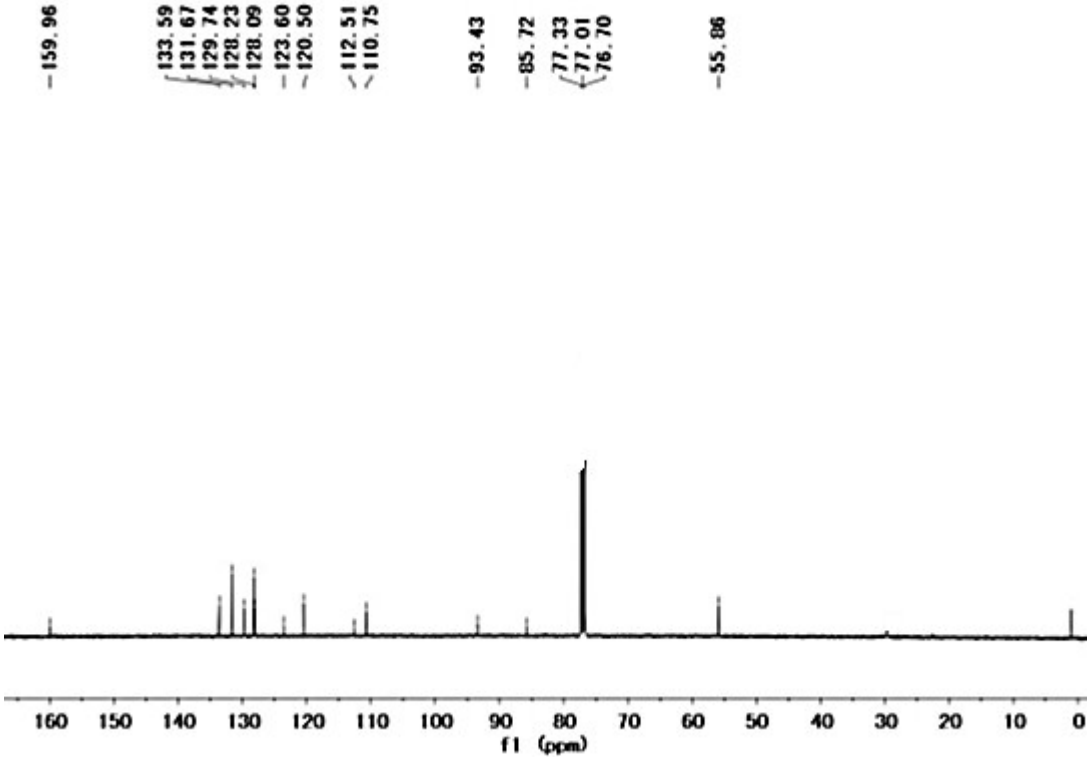


(29) 1-methoxy-2-(phenylethynyl)benzene (3p):

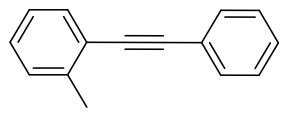


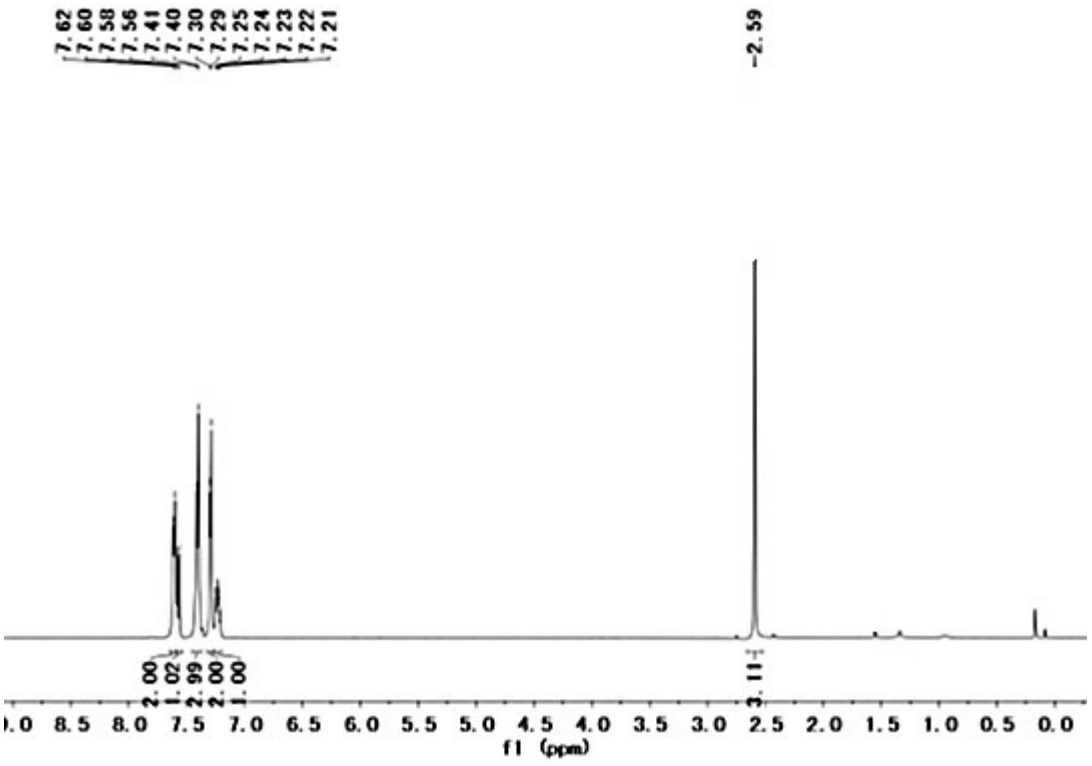


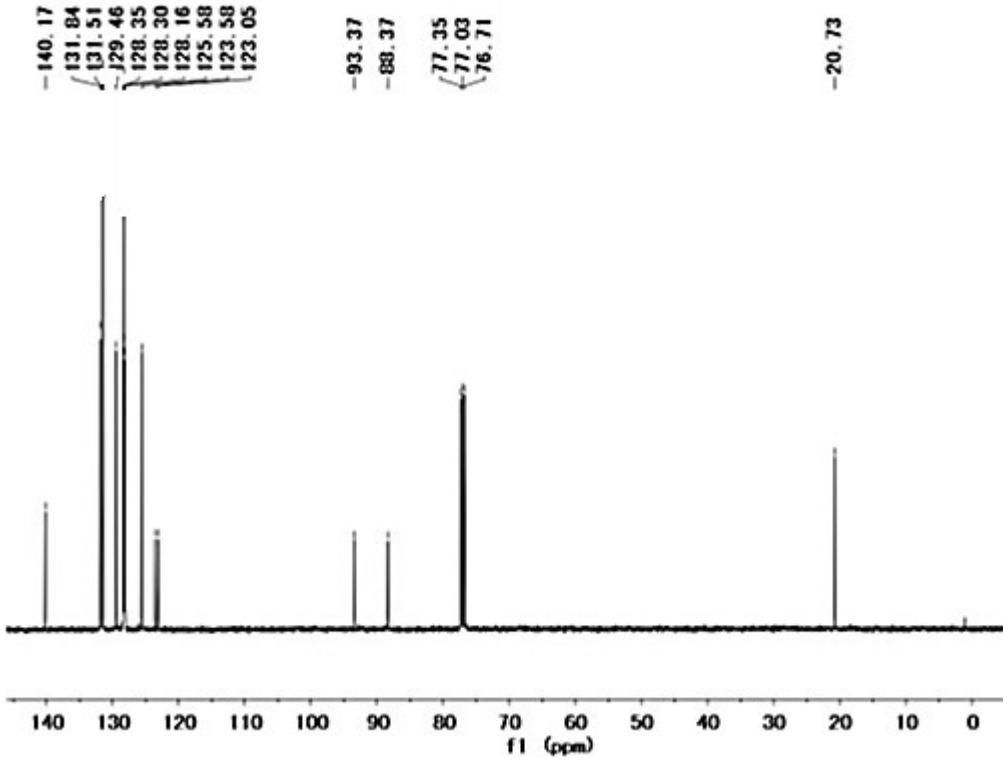




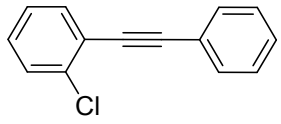
(30) 1-methyl-2-(phenylethynyl)benzene (3q):

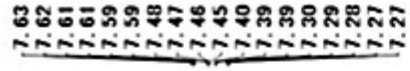


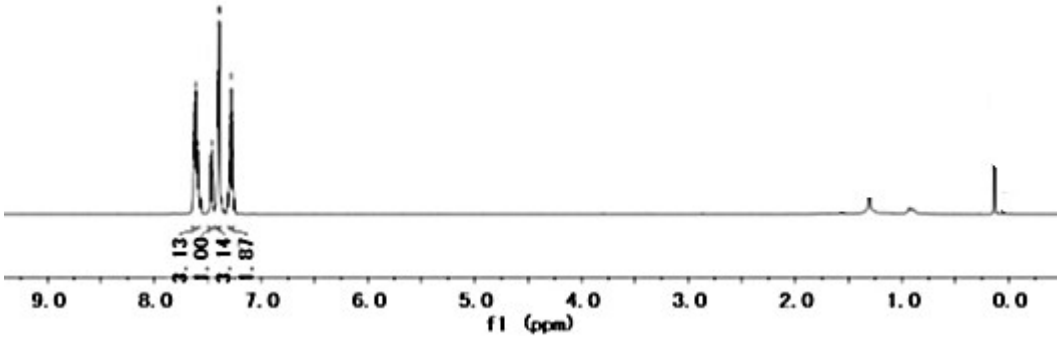


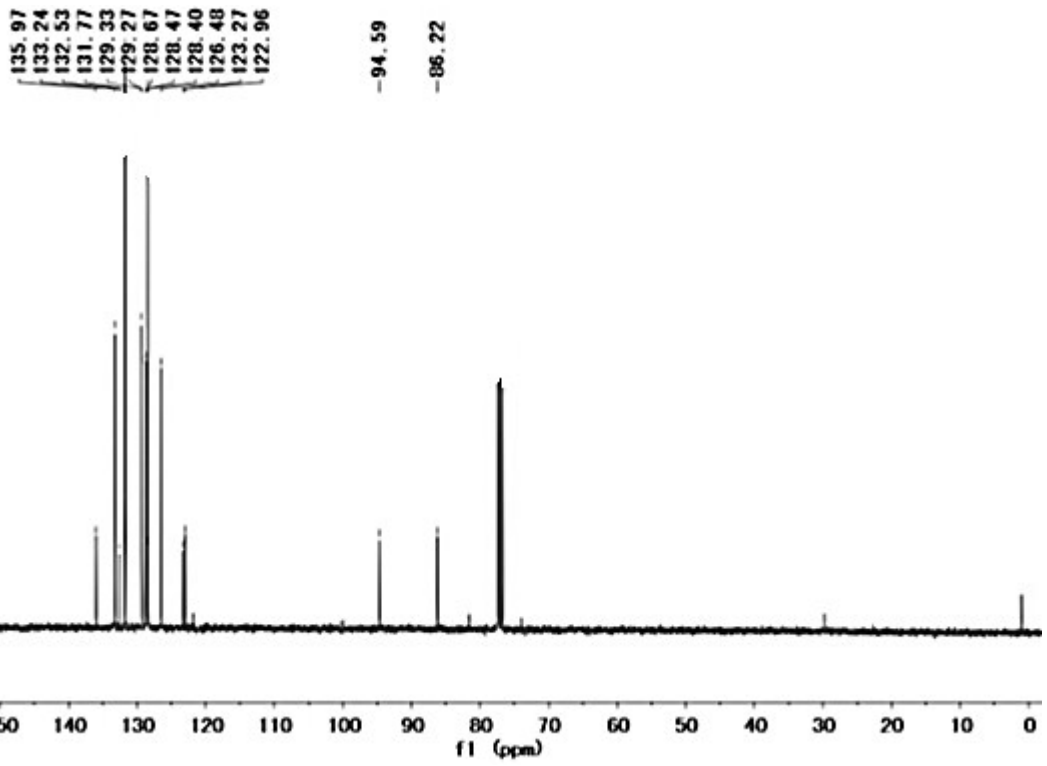


(31) 1-chloro-2-(phenylethynyl)benzene (3r):

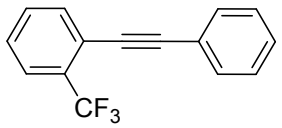


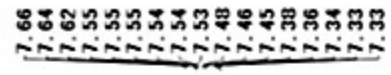


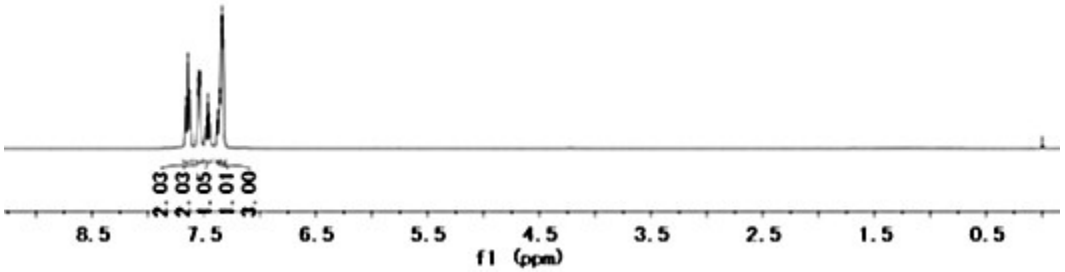


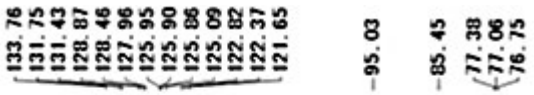


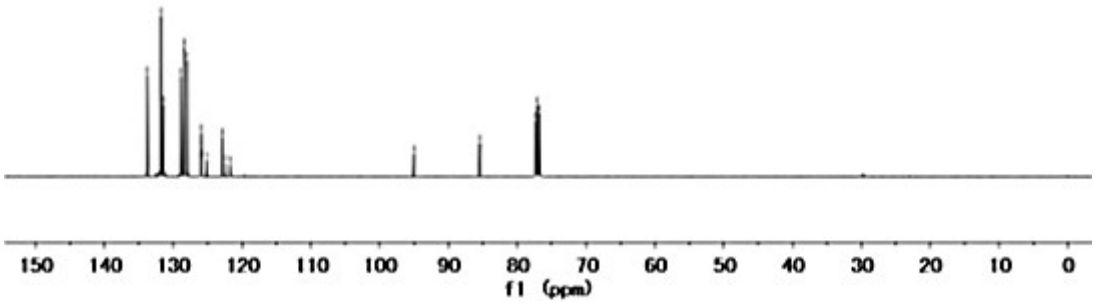
(32) 1-trifluoromethyl -2-(phenylethynyl)benzene (3s):



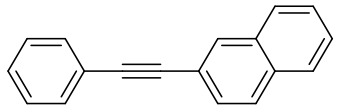


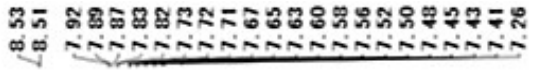


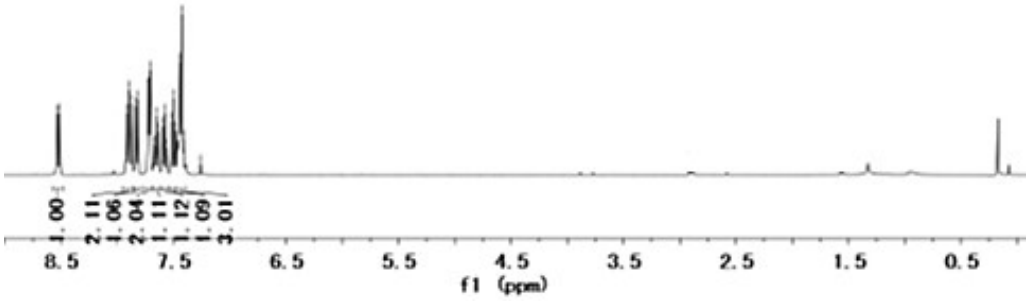


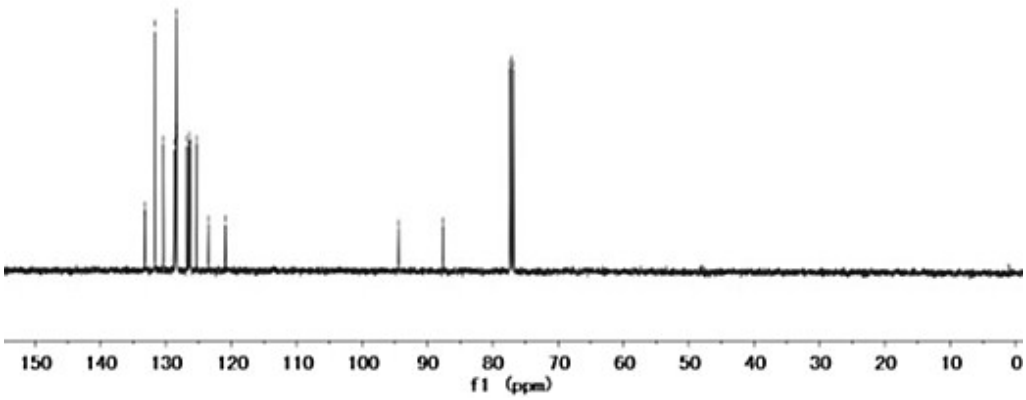


(33) 2-(phenylethynyl)naphthalene (3t):

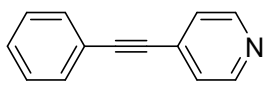


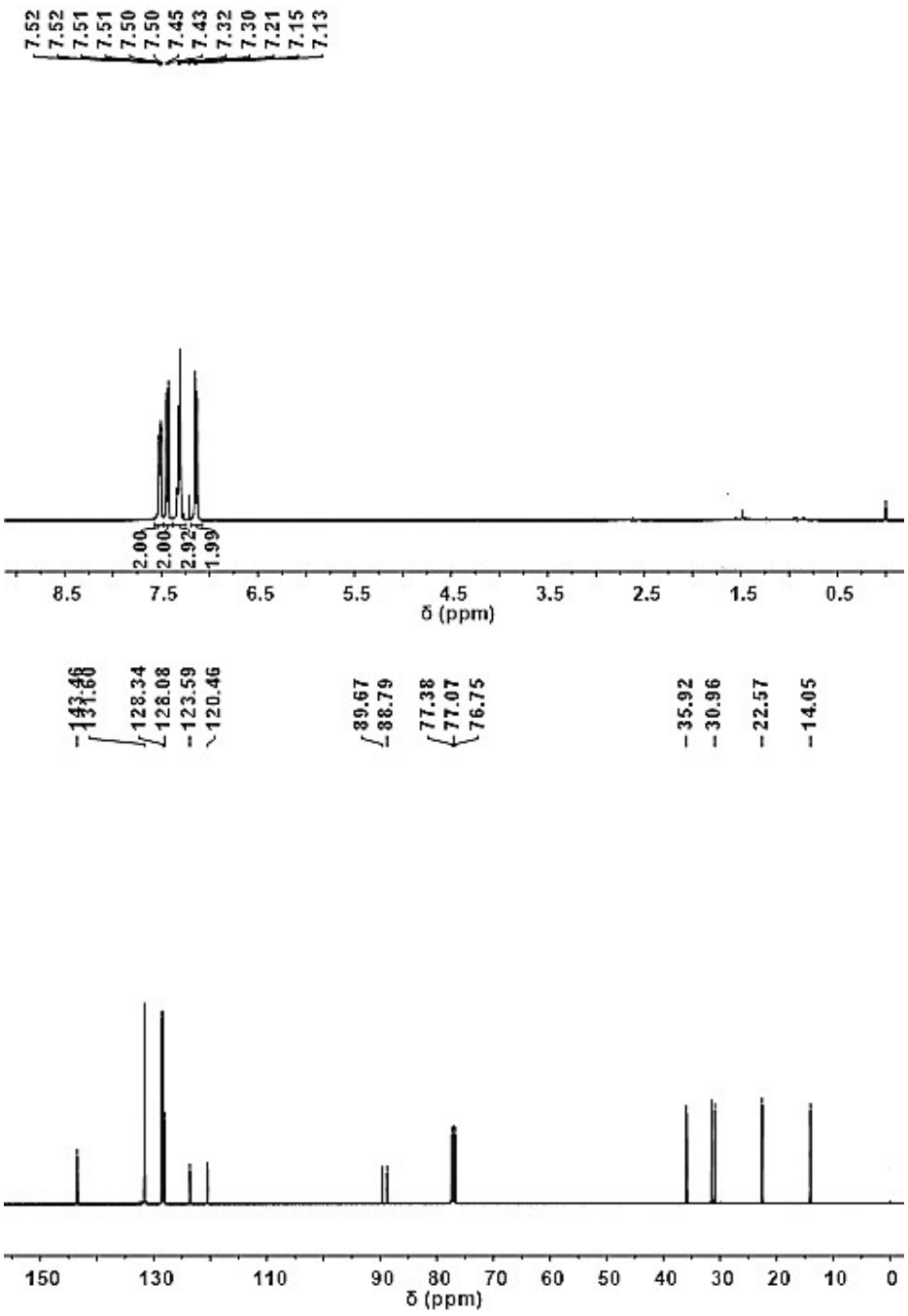




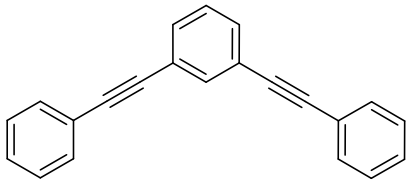


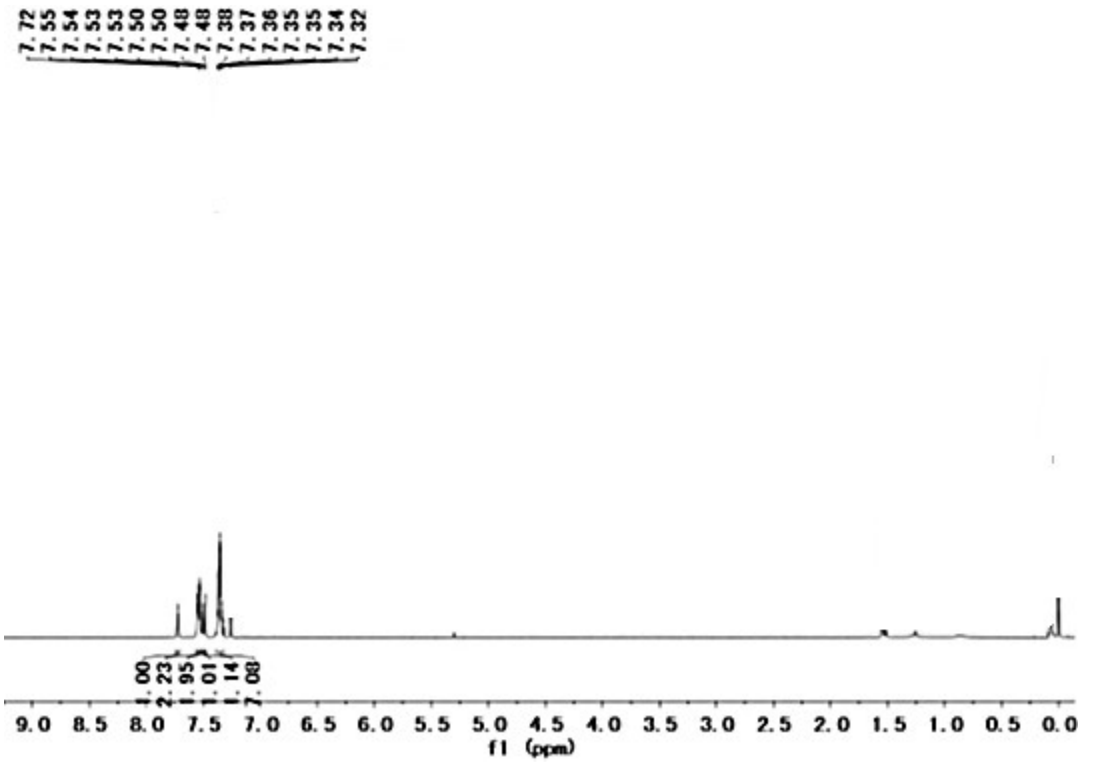
(34) 1-pentyl-4-(phenylethynyl)benzene (3u):

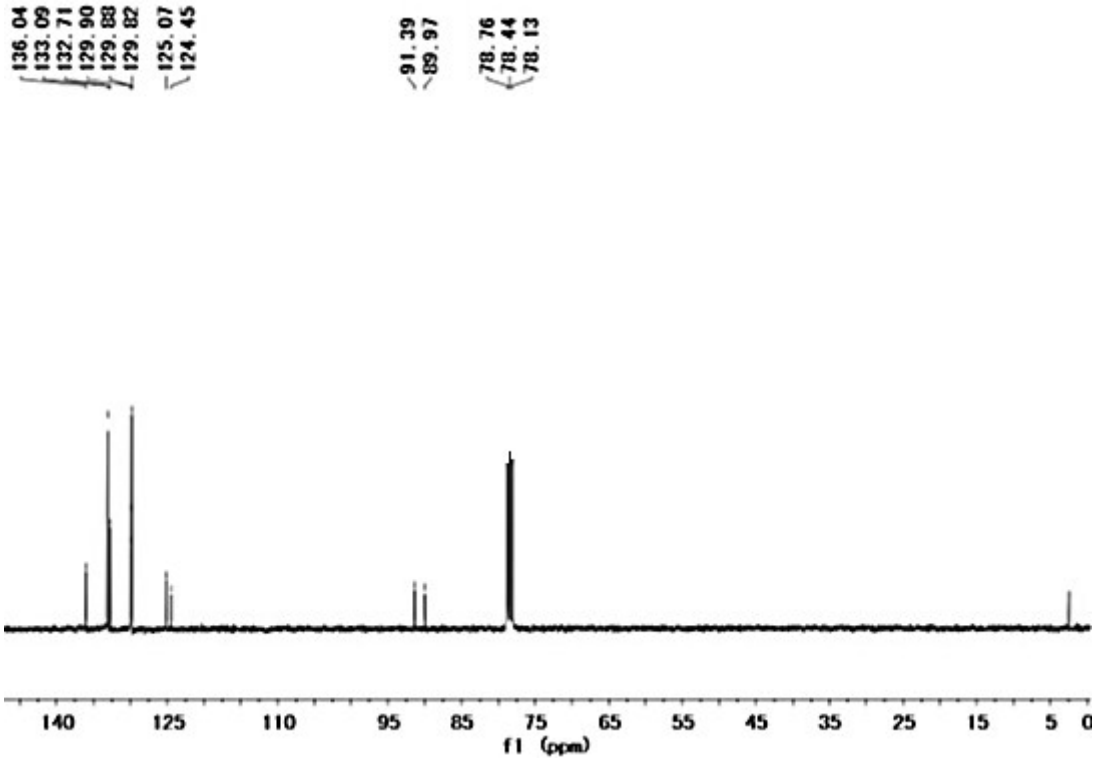




(35) 1,3-bis(phenylethynyl)benzene (3v):




7.72
7.55
7.54
7.53
7.53
7.50
7.50
7.48
7.48
7.38
7.37
7.36
7.35
7.35
7.34
7.32
1.00
2.23
1.95
1.01
1.14
2.08
9.0 8.5 8.0 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
f1 (ppm)


136.04
133.09
132.71
129.90
129.88
129.82
125.07
124.45
91.39
89.97
78.76
78.44
78.13
140 125 110 95 85 75 65 55 45 35 25 15 5 0
f1 (ppm)