Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Efficient Copper-free Sonogashira Coupling of Aryl Chlorides with Palladium on Charcoal

Anna Komáromi and Zoltán Novák *

Department of Organic Chemistry, Institute of Chemistry, Eötvös Loránd University, Pázmány Péter s. 1/A, H-1117 Budapest, Hungary

novakz@chem.elte.hu

General

Unless otherwise indicated, all starting materials were obtained from commercial suppliers, and were used without further purification. As a heterogeneous palladium source commercially available Selcat Q6 (10% palladium on charcoal) was used. All reactions were performed under an atmosphere of argon. Analytical thin-layer chromatography (TLC) was performed on Merck DC pre coated TLC plates with 0.25 mm Kieselgel 60 F_{254}. Visualization was performed with a 254 nm UV lamp. Silica gel column chromatography was carried out with Flash silica gel (0.040-0.063 mm), using n-hexane as eluent or n-hexane - ethyl-acetate eluent mixture. The ^{1}H and ^{13}C NMR spectra were recorded on a Brucker DRX-250 spectrometer in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards (δ 7.26 for ^{1}H, δ 77.0 for ^{13}C). Coupling constants (*J*) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), m (multiplet). Combination gas chromatography and low resolution mass spectrometry was obtained on an Agilent 6890N Gas Chromatograph (30 m x 0.25 mm column with 0.25 μm HP-5MS coating, He carrier gas) and Agilent 5973 Mass Spectrometer (Ion source: EI+, 70eV, 230°C; interface: 300°C). IR spectra were obtained on a Bruker IFS55 spectrometer on a single-reflection diamond ATR unit. All melting points were measured on Büchi 501 apparatus and are uncorrected.

Optimization of reaction conditions

Ligand screening: A dry 4ml screw capped vial with septa was charged with the appropriate amount of 10 % Pd/C (5mmol), 1 equivalent of Ligand (5 mmol) and 97 mg K_2CO_3 (0.75 mmol). The vial was purged with argon, then 0.5 ml of the DMA was added followed by 51 μl (56.8 mg, 0.5 mmol) of chlorobenzene and 87 μl (76.6 mg, 0.75 mmol) of phenylacetylene. The reaction mixture was placed into a 110 °C oilbath and it was stirred for 12 hours. Conversions were determined by the GC analysis of samples taken from the reaction mixture

Entry	Phosphane	conversion [%]
1	Ph_3P	1
2	$(1\text{-Naftyl})_3P$	0
3	$(o\text{-Tolyl})_3P$	0
4	$(2\text{-Furyl})_3P$	0
5	$(\text{Mesityl})_3P$	0
6	$(4\text{-Fluorophenyl})_3P$	2
7	$(4\text{-Methoxyphenyl})_3P$	5
8	$(3,5\text{-Bis-trifluoromethyl})_3P$	4
9	$^{t}Bu_3P$	0
10	Cy_3P	20
11	Dppe	2
12	Dppp	5
13	Dppb	16
14	Dppf	37
15	Xantphos	1
16	BINAP	11
17	Cyclohexyl JohnPhos[a]	31
18	XPhos[b]	96
19	*tert*-Butyl XPhos [c]	95

[a] 2-(Dicyclohexylphosphino)-biphenyl. [b] 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl. [c] 2-Di-tert-butylphosphino-2',4',6'-triisopropylbiphenyl.

Examination of the solvent effect: A dry 4ml screw capped vial with septa was charged with 25 mg of 10 % Pd/C (0.025mmol), 13.9 mg of XPhos (0.025 mmol) and 97 mg K_2CO_3 (0.75mmol). The vial was purged with argon, then 0.5 ml of the solvent was added followed by 51 μl (56.8 mg, 0.5mmol) of chlorobenzene and 87 μl (76.6 mg, 0.75mmol) of phenylacetylene. The reaction mixture was placed into a 110 °C oilbath and it was stirred for the appropriate reaction time. Conversions were determined by the GC analysis of samples taken from the reaction mixture.

Solvent	T (°C)	t (h)	Conversion (%)
Toluene	110	2	62
DMF	110	2	100
Dioxane	110	2	90
Acetonitrile	110	2	0
DMSO	110	2	100

Effect of the catalyst's amount: A dry 4ml screw capped vial with septa was charged with the appropriate amount of 10 % Pd/C , 1 equivalent of XPhos and 97 mg K_2CO_3 (0.75 mmol). The vial was purged with argon, then 0.5 ml of the solvent was added followed by 51 μl (56.8 mg, 0.5 mmol) of chlorobenzene and 87 μl (76.6 mg, 0.75 mmol) of phenylacetylene. The reaction mixture was placed into a 110 °C oilbath and it was stirred for 2 hours. Conversions were determined by the GC analysis of samples taken from the reaction mixture.

Solvent	Catalyst [Pd] (%)	Conversion (%)
DMA	3	100
DMA	1	100
DMA	0,5	100
DMF	3	100
DMF	1	95
DMSO	3	100
DMSO	1	100

Bases: A dry 4ml screw capped vial with septa was charged with 5 mg of 10 % Pd/C (0.005 mmol, 1% Pd), 2.4 mg of XPhos (0.005 mmol, 1%) and 0.75mmol of the base. The vial was purged with argon, then 0.25 ml of DMA was added followed by 51 μl (56.8 mg, 0.5 mmol) of chlorobenzene and 87 μl (76.6 mg, 0.75 mmol) of phenylacetylene. The reaction mixture was placed into a 110 °C oilbath and it was stirred for the appropriate reaction time. Conversions were determined by the GC analysis of samples taken from the reaction mixture.

Base	T (°C)	t (h)	Conversion (%)
Li_2CO_3	110	12	0
Na_2CO_3	110	12	96
K_2CO_3	110	12	100
K-O^{t}Bu	110	12	decomp.
NaO^{t}Bu	110	12	decomp.
NaOMe	110	12	decomp.
KOH	110	12	decomp.
NaOH	110	12	decomp.
DIPA	110	12	0
$MeNCy_2$	110	12	0

Palladium:ligand ratio: A dry 4ml screw capped vial with septa was charged with 5 mg of 10 % Pd/C (0.005 mmol), 0.5, 1, 2, 3 equivalent of XPhos and 97 mg K_2CO_3 (0.75 mmol). The vial was purged with argon, then 0.25 ml of DMA by 51 μl (56.8 mg, 0.5 mmol) of chlorobenzene and 87 μl (76.6 mg, 0.75 mmol) of phenylacetylene. The reaction mixture was placed into a 110 °C oilbath and it was stirred for the appropriate reaction time. Conversions were determined by the GC analysis of samples taken from the reaction mixture.

Catalyst:Ligand	time(h)	Conversion (%)
0.5	1	23
	3	46
1	1	71
	3	100
2	1	72
	3	100
3	1	73
	3	100

Temperature dependence: A dry 4ml screw capped vial with septa was charged with the appropriate amount of 10 % Pd/C , 1 equivalent of XPhos to Pd and 97 mg K_2CO_3 (0.75 mmol). The vial was purged with argon, then 0.5 ml of the solvent was added followed by 51 μl (56.8 mg, 0.5 mmol) of chlorobenzene and 87 μl (76.6 mg, 0.75 mmol) of phenylacetylene. The reaction mixture was placed into a 80 °C oilbath and it was stirred for the appropriate reaction time. Conversions were determined by the GC analysis of samples taken from the reaction mixture.

Catalyst [Pd] (%)	Solvent	T (°C)	time (h)	Conversion (%)
3	DMA	80	2	24
		80	18	89
		90	2	92
		100	2	99
1	DMA	80	2	3
		80	18	4
		90	2	46
		100	2	77
3	DMF	80	2	26
		80	18	83
1	DMF	80	2	7
		80	18	26
3	DMSO	80	2	61
		80	18	72
		90	2	90
		100	2	95
1	DMSO	80	2	5
		80	18	65
		90	2	71
		100	2	83

Copper effect: A dry 4ml screw capped vial with septa was charged with 5 mg of 10 % Pd/C (0.005 mmol, 1% Pd) , 2.4 mg XPhos (0.005 mmol, 1%), appropriate amount of CuI and 97 mg K_2CO_3 (0.75 mmol). The vial was purged with argon, then 0.25 ml of DMA was added followed by by 51 μl (56.8 mg, 0.5 mmol) of chlorobenzene and 87 μl (76.6 mg, 0.75 mmol) phenylacetylene. The reaction mixture was placed into an 80 °C oil bath and it was stirred for the appropriate reaction time. Conversions were determined by the GC analysis of samples taken from the reaction mixture.

CuI (%)	Conversion (%)
0	98
0.5	0
1	0
2	0
3	0
5	0

Pd/C catalyst recycling.

A dry 4ml screw capped vial with septa was charged with 100 mg of 10 % Pd/C (0.1 mmol, 1% Pd), 48 mg of XPhos (0.1 mmol, 1%) and 1.94 g K_2CO_3 (15 mmol). The vial was purged with argon, then 5 mL DMA was added followed by 1.02 mL (1.136g, 10 mmol) chlorobenzene and 1.74 mL (1.532 g, 15 mmol) of the phenylacetylene. The reaction mixture was placed

into a 110 °C oil bath and it was stirred for the appropriate reaction time. After the mixture was cooled to ambient temperature, the charcoal was filtered off and washed with water, acetone and DCM. Then the catalyst was dried at 110°C in oven before the next run. The following table summarizes the required reaction time for complete conversion of the chlorobenzene. It was necessary to add 0.1 mmol XPhos to the catalyst in every repeated run.

Run	Time (h)
1st	2
2nd	12
3rd	16
4th	18
5th	20
6th	24

Comparative study of commercially available Palladium on Charcoal catalysts

A dry 4ml screw capped vial with septa was charged with 5 mg of 10 % Pd/C (0.005mmol, 1% Pd), 2.4 mg of XPhos (0.005 mmol, 1%) and 97 mg K_2CO_3 (0.75 mmol). The vial was purged with argon, then 0.25 mL DMA was added followed by 0.5 mmol of the aryl chloride and 0.75 mmol of the acetylene. The reaction mixture was placed into a 110 °C oil bath and it was stirred for 1 hour, than sample was taken and the conversion was determined by GC analysis. 1.5 hour reaction time was optimal for comparison of catalytic activities.

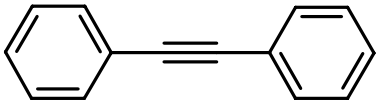
Catalyst	Conversion (%)
Degussa E196 KP/D	0
Degussa E1702 CB/D	33
Degussa E196 WN/D	52
Hereaus K0218 (old batch)	8
Hereaus K0218 (new batch)	70
Dutral	72
Panreac	42
Fluka (purchased from Sigma-Aldrich)	39
Selcat H6	72
Selcat A6	80
Selcat Q6 (old batch)	87
Selcat Q6 (new batch)	***88***
Norit A*	13

* the catalyst was prepared[1] in our laboratory using Norit A as solid support.

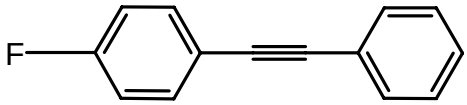
General procedure for the Pd/C-catalyzed Sonogashira coupling of aryl chlorides.

A dry 4ml screw capped vial with septa was charged with 5 mg of 10 % Pd/C (0.005mmol, 1% Pd), 2.4 mg of XPhos (0.005 mmol, 1%) and 97 mg K_2CO_3 (0.75 mmol). The vial was purged with argon, then 0.25 mL DMA was added followed by 0.5 mmol of the aryl chloride and 0.75 mmol of the acetylene. The reaction mixture was placed into a 110 ^oC oil bath and it was stirred for the appropriate reaction time. After the mixture was cooled to ambient temperature, the charcoal was filtered off and water was added to the reaction mixture. The aqueous phase was extracted with ether, and the combined organic phases were dried over magnesium sulphate. After the removal of the solvent in vacuum, the crude products were purified by column chromathography using pure hexane or hexane-ethylacetate mixtures as eluent.

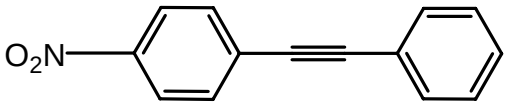
Compounds which were prepared using this procedure:



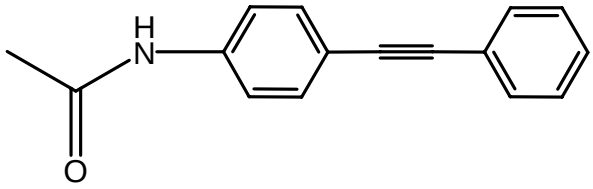
Diphenylacetylene (3aa)[2]: White solid, 82 mg (0.46 mmol, 92% yield), mp.: 54-55^oC. R_f (hexane) = 0.68; ^1H NMR ($CDCl_3$; 250MHz): δ 7.60–7.56 (m, 4H), 7.41-7.36 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 131.6, 128.3, 128.2, 123.2, 89.4; MS (EI, 70eV) m/z (% relative intensity, ion): 178(100, [M^+]), 152(10), 76(10).



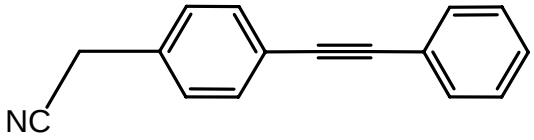
4-Phenylethynyl-fluorobenzene (3ba)[2] Pale yellow solid, 80 mg (0.41 mmol, 82% yield). mp.: 109-110^oC. R_f (hexane – ethylacetate 10:1) = 0.78; ^1H NMR ($CDCl_3$; 250MHz): δ 7.57-7.50 (m, 4H) 7.39-7.34 (m, 3H), 7.06 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 164.4, 160.5, 133.4 (d, *J* = 8.7 Hz), 131.5, 128.3, 126.6, 121.4 (d, *J* = 3.7 Hz), 115.6 (d, *J* = 22.1 Hz), 89.0, 88.3. MS (EI, 70eV) m/z (% relative intensity, ion): 196(100, [M^+]), 170(11), 98(15).



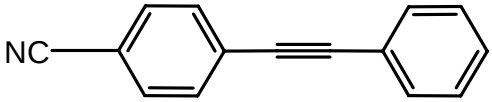
4-Phenylethylnyl-nitrobenzene (3ca)[3] Yellow solid, 111 mg (0.49 mmol, 99% yield). mp.: 120-121^oC. R_f (hexane – ethylacetate 10:1) = 0.68; ^1H NMR ($CDCl_3$; 250MHz): δ 8.21 (d, 2H, *J* = 7.7 Hz), 7.66 (d, 2H, *J* = 8.0 Hz) 7.58-7.54 (m, 2H), 7.41-7.38 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 147.3, 132.7, 132.3, 130.6, 129.7, 129.0, 124.0, 122.5, 95.1, 88.0. MS (EI, 70eV) m/z (% relative intensity, ion): 223(100, [M^+]), 193(25), 176(85), 165(25), 151(30).



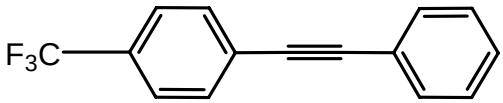
4-Phenylethylnyl-acetanilide (3da) Pale yellow solid, 94 mg (0.40 mmol, 80% yield). mp.: 179-180°C. R_f (hexane – ethylacetate 10:1) = 0.11; ^{1}H NMR (DMSO; 250MHz): δ 10.14 (s, 1H) 7.67-7.62 (m, 2H), 7.55-7.41 (m, 7H), 2.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 168.9, 140.1, 132.4, 131.6, 129.1, 128.9, 122.9, 119.2, 116.7, 89.9, 88.8, 24.5. MS (EI, 70eV) m/z (% relative intensity, ion): 235(37, [M^+]), 193(100), 165(20). IR: ν [cm^{-1}] 3302, 2210, 1664, 1591, 1526, 1510, 1322. HRMS (ESI): calculated for $C_{16}H_{14}NO$ $(M+H)^+$ 236.1070 found 236.1070.



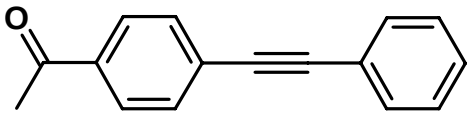
4-Phenylethynyl-benzylnitrile (3ea) Pale yellow solid, 101 mg (0.46 mmol, 93% yield). mp.: 83-84°C. R_f (hexane – ethylacetate 10:1) = 0.15; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.57-7.53 (m, 4H), 7.38-7.26 (m, 5H), 3.75 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 132.7, 132.0, 130.3, 128.9, 128.8, 128.4, 123.7, 123.3, 117.9, 90.7, 88.9, 23.9. MS (EI, 70eV) m/z (% relative intensity, ion): 217(100, [M^+]), 189(32), 94(13). IR: ν [cm^{-1}] 3052, 2922, 2246, 1975, 1595, 1508, 1402. HRMS (ESI): calculated for $C_{16}H_{11}N$ [M^+] 217.0891 found 217.0887.



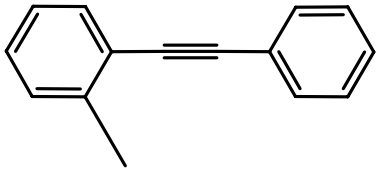
4-Phenylnethynyl-benzonitrile (3fa)[2] Pale yellow solid, 96 mg (0.48 mmol, 95% yield). mp.: 108-110°C. R_f (hexane – ethylacetate 10:1) = 0.32; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.65-7.53 (m, 6H), 7.40-7.26 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 132.5, 132.4, 132.2, 129.6, 128.9, 128.6, 122.6, 119.0, 111.8, 94.2, 88.2. MS (EI, 70eV) m/z (% relative intensity, ion): 203(100, [M^+]), 176(15), 151(10), 101(15).



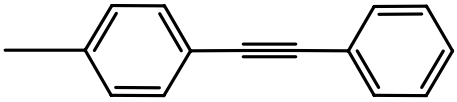
(4'-Trifluormethylphenyl-ethynyl)benzene (3ga)[2] White solid, 116 mg (0.47 mmol, 95% yield). Mp.: 102-104°C. R_f (hexane – ethylacetate 10:1) = 0.78; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.63-7.56 (m, 6H), 7.40-7.38 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 131.8, 131.7, 128.8, 128.4, 125.34, 125.28, 125.21, 125.1, 123.0, 91.7, 88.0. MS (EI, 70eV) m/z (% relative intensity, ion): 246(100, [M^+]), 176(16), 98(10).



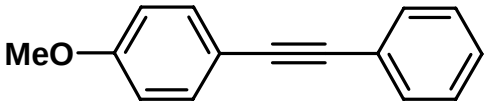
4-Phenylethynyl-acetophenone (3ha)[2]: Pale yellow solid, 101 mg (0.46 mmol, 92% yield). mp.: 95-96°C. R_f (hexane – ethylacetate 10:1) = 0.25; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.83 (d, 2H, *J*= 8.7 Hz), 7.52-7.44 (m, 4H), 7.28-7.24 (m, 3H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 197.2, 136.1, 131.7, 131.6, 128.7, 128.4, 128.2, 128.1, 122.5, 92.6, 88.6, 26.5. MS (EI, 70eV) m/z (% relative intensity, ion): 220(70, [M^+]), 205(100), 176(75), 151(20), 102(15), 88(20).



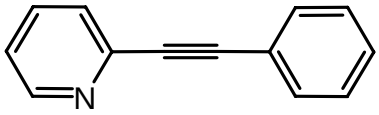
2-Phenylethynyl-toluene (3ia)[3] White solid, 79 mg (0.41 mmol, 82% yield). mp.: 69-70°C. R_f (hexane) = 0.60; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.55-7.48 (m, 3H), 7.36-7.30 (m, 3H), 7.22- 7.14 (m, 3H), 2.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 140.1, 131.8, 131.5, 129.4, 128.31, 128.26, 128.1, 125.6, 123.5, 123.0, 93.5, 88.3, 20.7. MS (EI, 70eV) m/z (% relative intensity, ion): 192(100, [M^+]), 165(25), 115 (20).



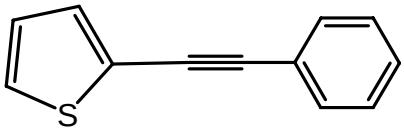
4-Phenylethynyl-toluene (3ja)[3] White solid, 78 mg (0.40 mmol, 81% yield). mp.: 70-72 °C. R_f (hexane) = 0.60; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.44-7.40 (m, 2H), 7.35-7.31 (m, 2H), 7.23-7.20 (m, 3H), 7.05-7.01 (m, 2H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 138.3, 131.5, 131.4, 129.1, 128.3, 128.0, 123.4, 120.1, 89.5, 88.7, 21.4. MS (EI, 70eV) m/z (% relative intensity, ion): 192(100, [M^+]), 165(25), 115 (20).



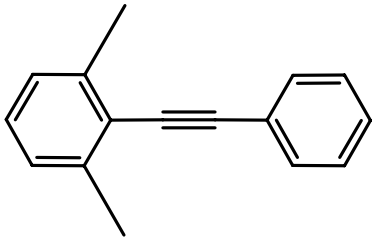
4-Phenylethynyl-anisole (3ka)[3]: Pale yellow solid, 97 mg (0.47 mmol, 93% yield). mp.: 59-60°C. R_f (hexane – ethylacetate 10:1) = 0.23; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.45-7.37 (m, 4H), 7.25-7.22 (m, 3H), 6.79 (d, 2H, *J*= 8.9 Hz), 3.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.3, 113.9, 89.4, 88.0, 55.2.



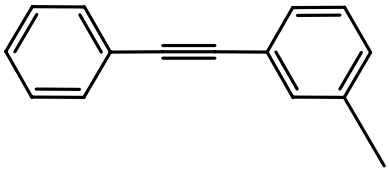
2-Phenylethynyl-pyridine (3la)[2] yellow oil, 90 mg (0.50 mmol, 99% yield). R_f (hexane – ethylacetate 10:1) = 0.19; ^{1}H NMR ($CDCl_3$; 250MHz): δ 8.62 (d, 1H, *J* = 4.1 Hz), 7.68-7.54 (m, 3H), 7.50 (d, 1H, *J* = 7.7 Hz), 7.39-7.31 (m, 3H), 7.25-7.17 (m, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 149.9, 143.3, 136.0, 131.9, 128.8, 128.2, 127.0, 122.6, 122.1, 89.1, 88.5. MS (EI, 70eV) m/z (% relative intensity, ion): 179(100, [M^+]), 151 (20), 126 (20), 76 (25).



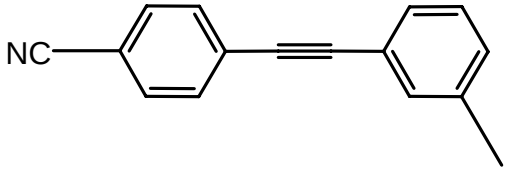
2-Phenylethynyl-thiophene (3ma)[3] Colorless oil, 72 mg (0.39 mmol, 78% yield). R_f (hexane – ethylacetate 10:1) = 0.82; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.45- 7.41 (m, 2H), 7.26-7.21 (m, 3H), 7.20-7.16 (m, 2H), 6.93 (dd, 1H, *J* = 8.8 Hz, *J* = 3.6 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 131.9, 131.4, 128.4, 128.3, 127.2, 127.1, 123.1, 122.9, 93.0, 82.6. MS (EI, 70eV) m/z (% relative intensity, ion): 184(100, [M^+]), 152(22), 139 (30).



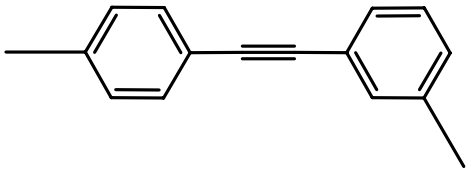
2-Phenylethynyl-toluene (3na)[4] Colorless oil, 80 mg (0.39 mmol, 78% yield). R_f (hexane) = 0.34; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.46-7.42 (m, 2H), 7.26-7.20 (m, 3H), 7.00- 6.93 (m, 3H), 2.41 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 140.2, 131.3, 128.3, 128.0, 127.7, 126.6, 123.8, 122.9, 97.8, 87.1, 21.1. MS (EI, 70eV) m/z (% relative intensity, ion): 206(100, [M^+]), 191(95), 165(25), 128(20).



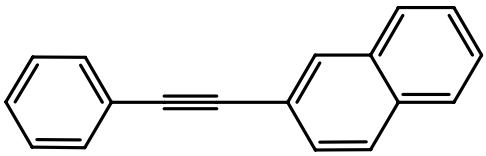
1-(3'-Tolylethynyl)benzene (3ab)[5] White solid, 92 mg (0.48 mmol, 96% yield). mp.: 71-73°C. R_f (hexane) = 0.70; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.54-7.50 (m, 2H), 7.40-7.31 (m, 5H), 7.21 (d, 1H, *J*= 7.4 Hz), 7.12 (d, 1H, *J*= 7.4 Hz), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 138.0, 132.2, 131.6, 129.1, 128.6, 128.3, 128.2, 128.1, 123.3, 123.0, 89.5, 89.0, 21.2. MS (EI, 70eV) m/z (% relative intensity, ion): 192(100, [M^+]), 165(25), 115 (20).



4-(3'-Tolylethynyl)benzonitrile (3fb) Pale yellow solid, 102 mg (0.47 mmol, 94% yield). mp.: 106-107°C. R_f (hexane – ethylacetate 10:1) = 0.53; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.57-7.49 (m, 4H), 7.29-7.10 (m, 4H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 138.2, 132.3, 132.0, 130.0, 128.8, 128.4, 128.3, 122.0, 118.5, 111.3, 94.0, 87.4, 21.2. MS (EI, 70eV) m/z (% relative intensity, ion): 217(100, [M^+]), 190(15), 115 (12), 108(12), 94(15). IR: ν [cm^{-1}] 3058, 2228, 2205, 1601, 1500. HRMS (ESI): calculated for $C_{16}H_{11}N$ [M^+] 217.0891 found 217.0887.

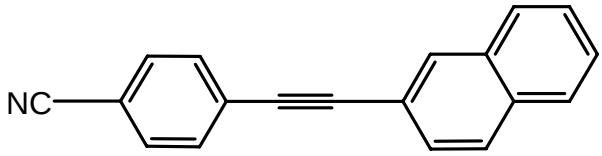


3-(4'-Tolylethynyl)-toluene (3jb) Pale yellow solid, 99 mg (0.48 mmol, 96% yield). mp.: 83-84°C. R_f (hexane) = 0.51; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.44 (d, 2H, *J* = 8.2 Hz), 7.37 (d, 2H, *J* = 8.1 Hz), 7.26- 7.14 (m, 4H), 2.36 (s, 3H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 138.7, 138.4, 132.6, 131.9, 129.5, 129.4, 129.1, 128.7, 123.7, 120.7, 89.7, 89.4, 21.9, 21.7 MS (EI, 70eV) m/z (% relative intensity, ion): 206 (100, [M^+]), 189(25), 101(15), 89(15). IR: ν [cm^{-1}] 2919, 2850, 1594, 1509, 814. HRMS (ESI): calculated for $C_{16}H_{14}$ [M^+] 206.1096 found 206.1089.

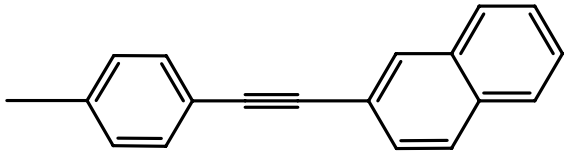


2-Phenylethynyl-naphthalene (3ac)[6]: White solid, 96 mg (0.40 mmol, 80% yield). mp.: 114-116°C. R_f (hexane) = 0.38. ^{1}H NMR ($CDCl_3$; 250MHz): δ 8.11 (s, 1H), 7.87-7.82 (m, 3H), 7.63-7.60 (m, 3H), 7.54-7.50 (m, 2H), 7.44-7.38 (m, 3H);

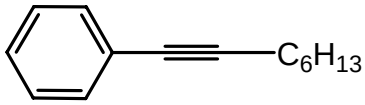
^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 133.0, 132.8, 131.6, 131.4, 128.4, 128.4, 128.3, 128.0, 127.8, 127.8, 126.6, 126.5, 123.3, 120.5, 89.8, 89.7. MS (EI, 70eV) m/z (% relative intensity, ion): 228(100, [M^+]), 114(35), 101 (20).



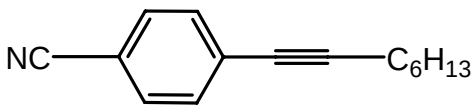
2-(4'-Cyanophenyl)ethynyl-naphthalene (3fc) Pale yellow solid, 120 mg (0.47 mmol, 95% yield). mp.: 123-124°C. R_f (hexane – ethylacetate 10:1) = 0.43. ^{1}H NMR ($CDCl_3$; 250MHz): δ 8.09 (s, 1H), 7.86-7.82 (m, 3H), 7.63-7.51 (m, 7H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 133.1, 132.8, 132.1, 132.0, 128.2, 128.1, 127.9, 127.8, 127.2, 126.8, 119.4, 118.5, 111.4, 94.2, 88.0. MS (EI, 70eV) m/z (% relative intensity, ion): 253(100, [M^+]), 126(20), 112(15), 110(10). IR: ν [cm^{-1}] 3500, 3055, 2928, 2227, 2033, 1975, 1600, 1500. HRMS (ESI): calculated for $C_{19}H_{11}N$ [M^+] 253.0891 found 253.0884.



2-(4'-Tolylethynyl)-naphthalene (3jc) White solid, 112 mg (0.46 mmol, 93% yield). mp.: 131-133°C. R_f (hexane) = 0.41. ^{1}H NMR ($CDCl_3$; 250MHz): δ 8.09 (s, 1H), 7.86-7.82 (m, 3H), 7.65 (dd, 1H, *J* = 1.75 Hz, *J* = 8.50 Hz), 7.54-7.50 (m, 4H), 7.22 (d, 2H, *J* = 7.74 Hz), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 138.4, 133.0, 131.7, 131.5, 131.2, 129.1, 128.4, 127.9, 127.7, 126.5, 126.4, 120.7, 120.1, 90.0, 89.1, 21.5. MS (EI, 70eV) m/z (% relative intensity, ion): 253 (100, [M^+]), 126(16). IR: ν [cm^{-1}] 3055, 3023, 2919, 2851, 1991, 1912, 1592, 1506. HRMS (ESI): calculated for $C_{19}H_{14}$ [M^+] 242.1096 found 242.1093.

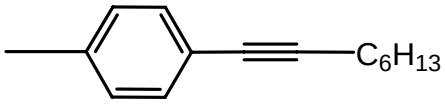


1-(Octyn-1-yl)benzene (3ad)[7] Colorless oil, 67 mg (0.36 mmol, 72% yield). R_f (hexane) = 0.22. ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.33-7.29 (m, 2H), 7.21-7.16 (m, 3H), 2.32 (t, 2H, *J* = 6.79 Hz), 1.56-1.21 (m, 8H), 0.83 (t, 3H, *J* = 6.95 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 131.5, 128.1, 127.4, 124.1, 90.4, 80.5, 31.4, 28.7, 28.6, 22.6, 19.4, 14.0. MS (EI, 70eV) m/z (% relative intensity, ion): 186(28, [M^+]), 143 (57), 129 (60), 115 (100), 102 (22), 91 (20).

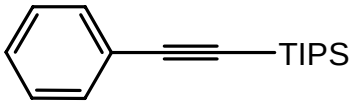


4-(Octyn-1-yl)benzonitrile (3fd)[3] Pale yellow oil, 78 mg (0.34 mmol, 74% yield). R_f (hexane – ethylacetate 10:1) = 0.71; ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.57 (d, 2H, *J* = 8.69 Hz), 7.45 (d, 2H, *J* = 8.69 Hz), 2.41 (t, 2H, *J* = 6.79 Hz), 1.63-1.57 (m, 2H), 1.46-1.24 (m, 6H), 0.89 (t, 3H, *J* = 6.95 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 132.0, 131.8, 129.1, 118.5, 110.7, 95.6,

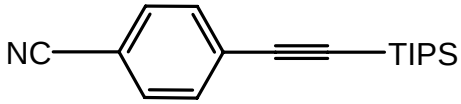
79.3, 31.2, 28.5, 28.3, 22.4, 19.4, 14.0. MS (EI, 70eV) m/z (% relative intensity, ion): 211(20, [M^+]), 182(50), 168 (80), 154 (70), 140 (100), 127 (50), 120 (45), 118 (30).



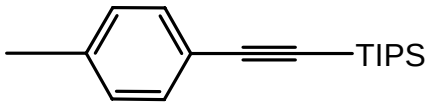
1-Methyl-4-(octyn-1-yl)benzene (3jd)[8] Yellow oil, 69 mg (0.36 mmol, 72% yield). R_f (hexane) = 0.15. ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.33 (d, 2H, *J* = 8.41 Hz), 7.12 (d, 2H, *J* = 8.53 Hz), 2.42 (t, 2H, *J* = 6.83 Hz), 2.35 (s, 3H), 1.66-1.31 (m, 8H), 0.93 (t, 3H, *J* = 6.95 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 137.3, 131.4, 128.9, 121.0, 89.6, 80.5, 31.4, 28.8, 28.6, 22.6, 21.3, 19.4, 14.0. MS (EI, 70eV) m/z (% relative intensity, ion): 200(25, [M^+]), 171(15), 157 (45), 143(50), 129(100), 115(40), 105(15), 91(15).



Triisoprolysilylethynyl-benzene (3ae)[9] Pale yellow oil, 1978 mg (0.47 mmol, 93% yield). R_f (hexane) = 0.80. ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.53-7.49 (m, 2H), 7.34-7.31 (m, 3H), 1.17 (s, 21H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 132.0, 128.3, 128.2, 123.6, 107.1, 90.4, 18.7, 11.3. MS (EI, 70eV) m/z (% relative intensity, ion): 258(4, [M^+]), 215(60), 187 (25), 173 (30), 159 (70), 145 (100), 129 (40), 105 (20).

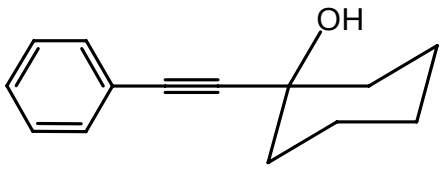


4-Triisoprolysilylethynyl-benzonitrile (3fe)[9] Colorless oil, 122 mg (0.43 mmol, 86% yield). R_f (hexane – ethylacetate 10:1) = 0.78. ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.52-7.43 (m, 4H), 1.04 (s, 21H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 132.4, 131.8, 128.1, 118.3, 111.5, 104.9, 96.1, 18.5, 11.1. MS (EI, 70eV) m/z (% relative intensity, ion): 283(5, [M^+]), 240 (50), 212 (20), 198 (25), 184 (80), 170 (100), 154 (40), 130 (20).

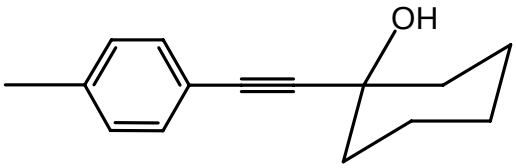


4-Triisoprolysilylethynyl-toluene (3je) Colorless oil, 115 mg (0.42 mmol, 84% yield). R_f (hexane) = 0.77. ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.43 (d, 2H, *J* = 8.24 Hz), 7.15 (d, 2H, *J* = 8.85 Hz), 2.37 (s, 3H), 1.17 (s, 21H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 138.3, 131.9, 128.9, 120.6, 107.3, 89.4, 21.5, 18.7, 11.4. MS (EI, 70eV) m/z (% relative intensity, ion): 272(5, [M^+]),

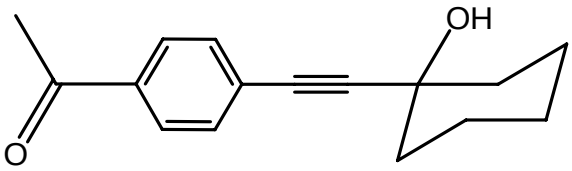
229 (50), 201 (20), 187 (25), 173 (80), 159 (100), 143 (40), 119 (20), 86 (22). IR: ν [cm^{-1}] 2940, 2890, 2863, 2153, 1507, 1461. HRMS (ESI): calculated for $C_{18}H_{28}Si$ [M^+] 272.1960 found 272.1958.



1-Phenylethynylcyclohexan-1-ol (3af)[10] Pale yellow solid, 89 mg (0.45 mmol, 89% yield). M.p.: 57-59°C. R_f (hexane – ethylacetate 10:1) = 0.28. ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.45-7.41 (m, 2H), 7.32-7.26 (m, 3H), 2.27 (s, 1H), 2.04-1.98 (m, 2H), 1.77-1.56 (m, 7H), 1.30-1.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 131.6, 128.2, 128.1, 122.9, 92.8, 84.3, 69.0, 40.0, 25.2, 23.4. MS (EI, 70eV) m/z (% relative intensity, ion): 199(40, [M^+]), 182 (90), 167 (60), 157 (95), 155 (65), 141 (30), 129 (70), 115 (100), 102 (65), 91 (35), 77 (40), 63 (30), 55 (55).



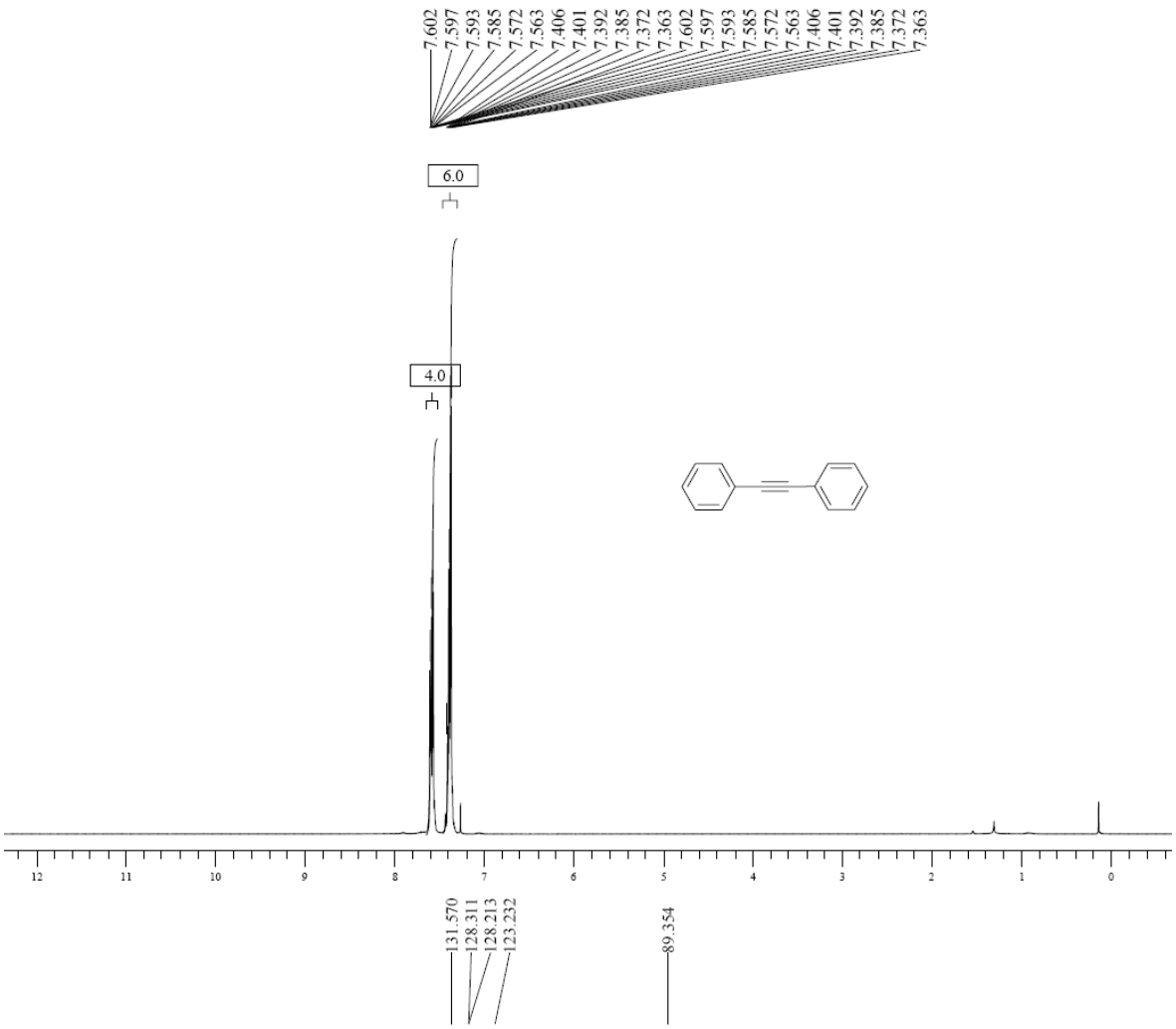
1-(4'-Tolylethynyl)cyclohexan-1-ol (3ff)[10] yellow solid (82 mg, 0.39 mmol, 77% yield). M.p.: 83-84°C. R_f (hexane – ethylacetate 10:1) = 0.25. ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.34 (d, 2H, *J* = 8.84 Hz), 7.12 (d, 2H, *J* = 8.25 Hz), 2.34-2.28 (m, 4H), 2.03-1.94 (m, 2H), 1.79-1.55 (m, 7H), 1.33-1.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 138.2, 131.5, 128.9, 119.8, 92.1, 84.4, 69.0, 40.0, 25.2, 23.4, 21.4. MS (EI, 70eV) m/z (% relative intensity, ion): 214(10, [M^+]), 196 (85), 171 (70), 158 (10), 143 (40), 128 (38), 115 (100), 89 (30), 55 (20).

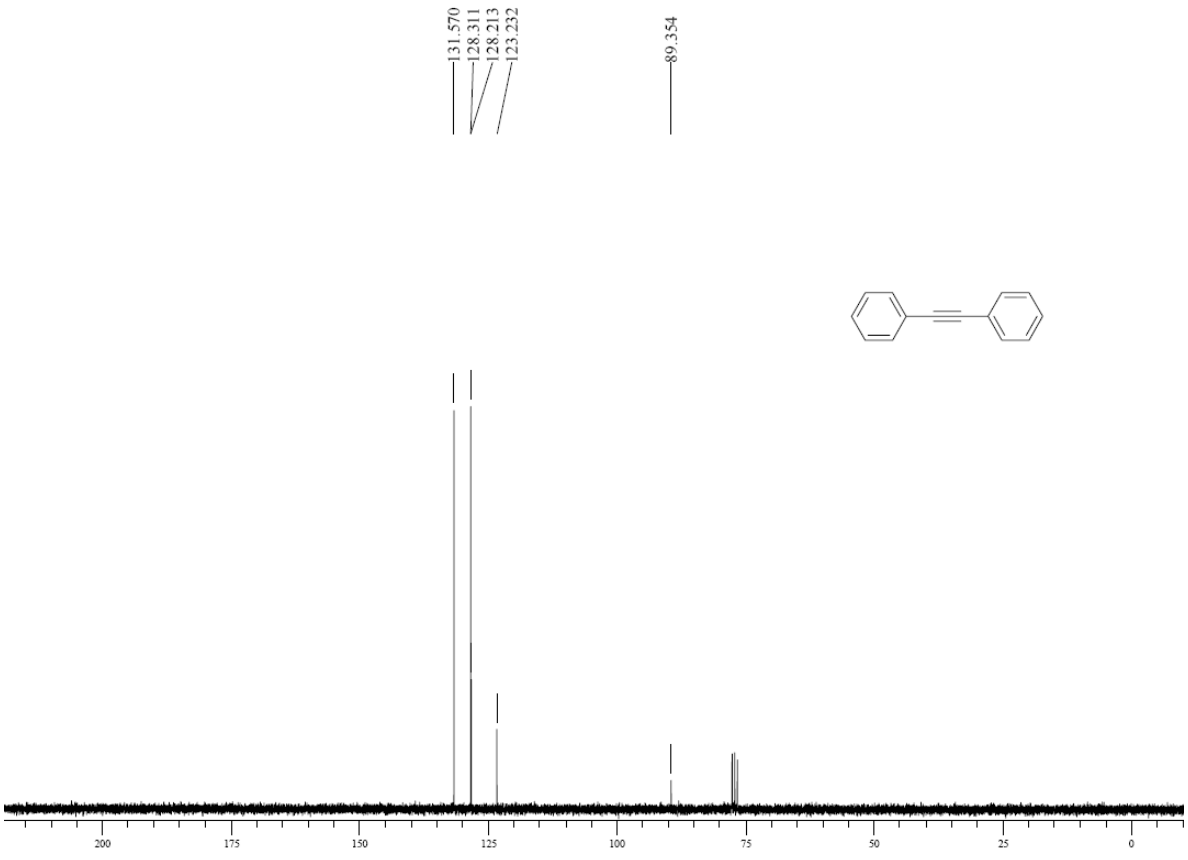


1-(4'-Acetylphenyl)ethynylcyclohexan-1-ol (3hf)[11]: Pale yellow solid (99 mg, 0.41 mmol, 82 % yield). mp.:80-81°C ^{1}H NMR ($CDCl_3$; 250MHz): δ 7.87 (d, 2H, *J*= 8.5 Hz), 7.48 (d, 2H, *J*= 8.5 Hz), 2.58 (s, 1H), 2.57 (s, 3H), 2.03-1.97 (m, 2H), 1.76-1.52 (m, 7H), 1.29-1.20 (m, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 197.4, 136.1, 131.7, 128.1, 127.8, 96.3, 83.5, 69.0, 39.8, 26.5, 25.1, 23.3; MS (EI, 70eV) m/z (% relative intensity, ion): 242(34, [M^+]), 199(100), 171(50), 143(19), 129(23), 115(21), 55(47).

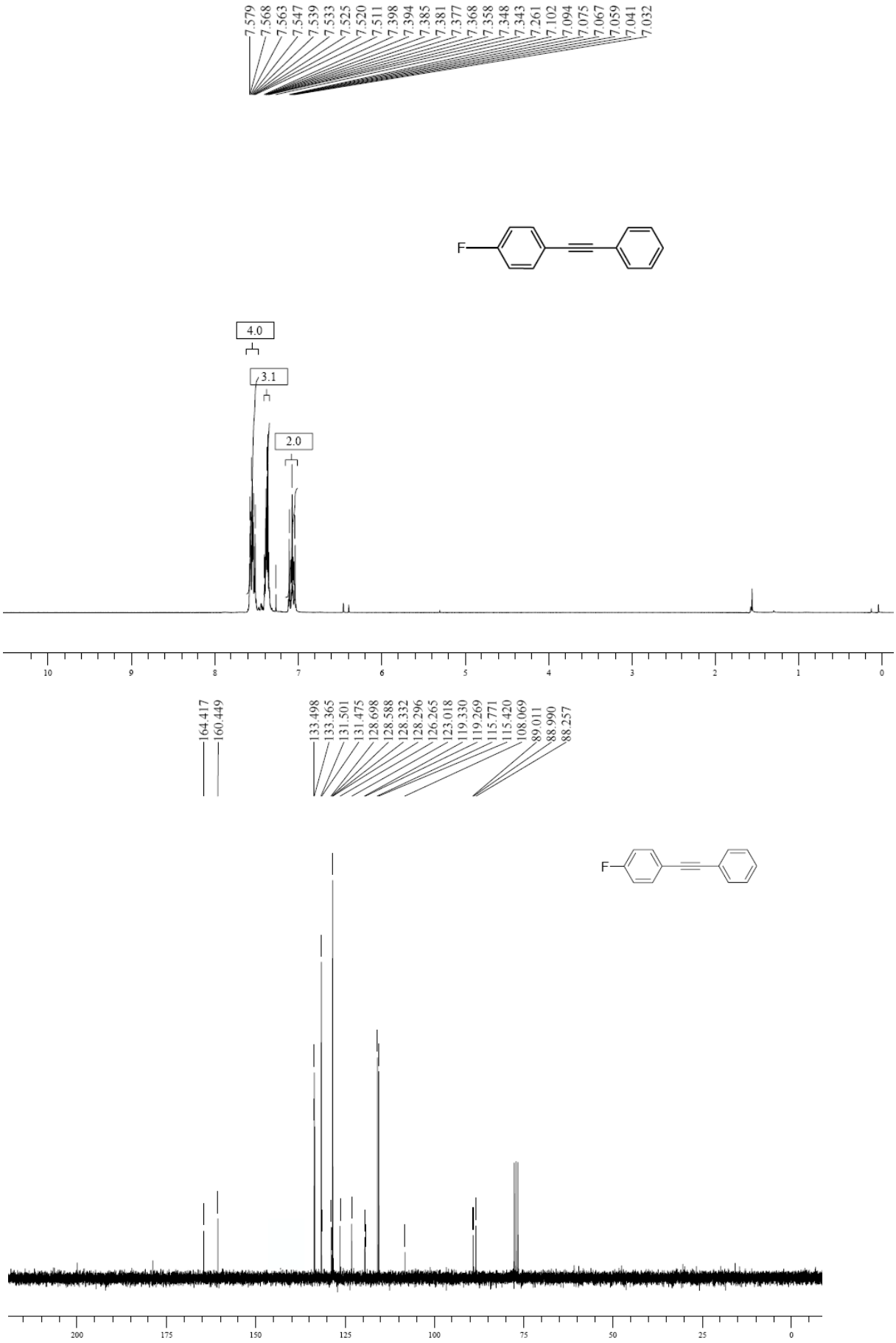
NMR spectra of the prepared compounds

Diphenylacetylene (3aa)

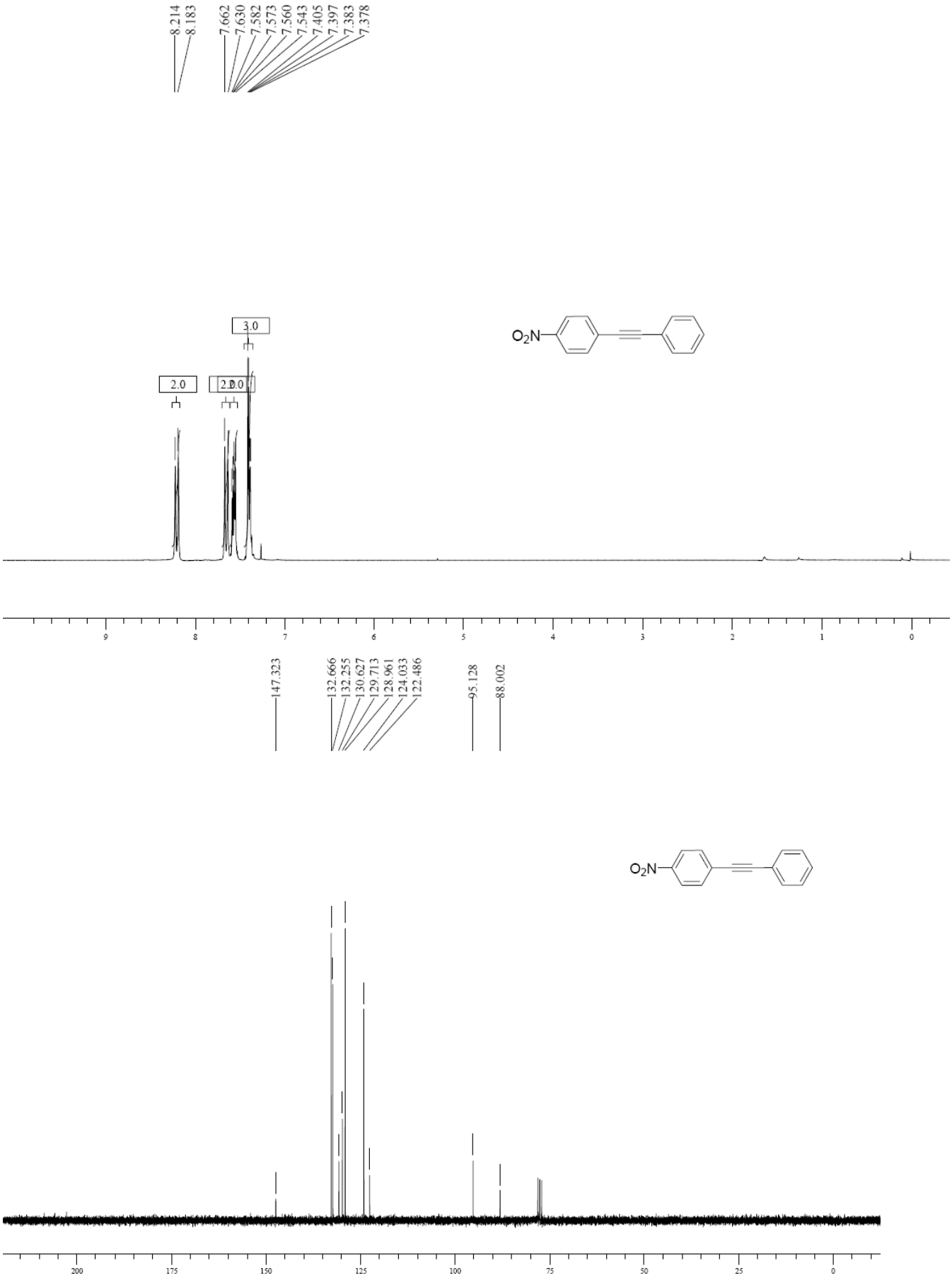




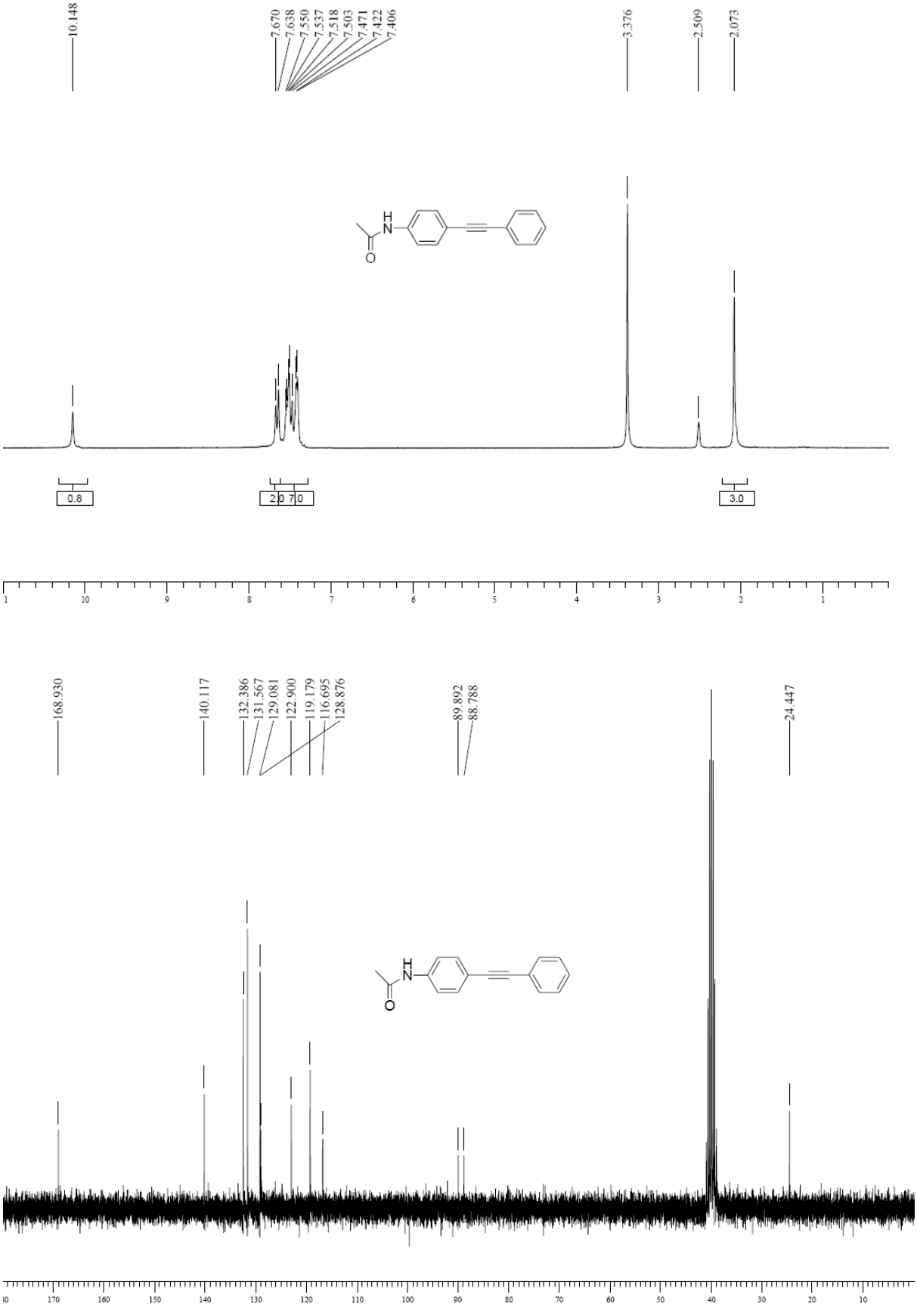
4-Phenylethynyl-fluorobenzene (3ba)



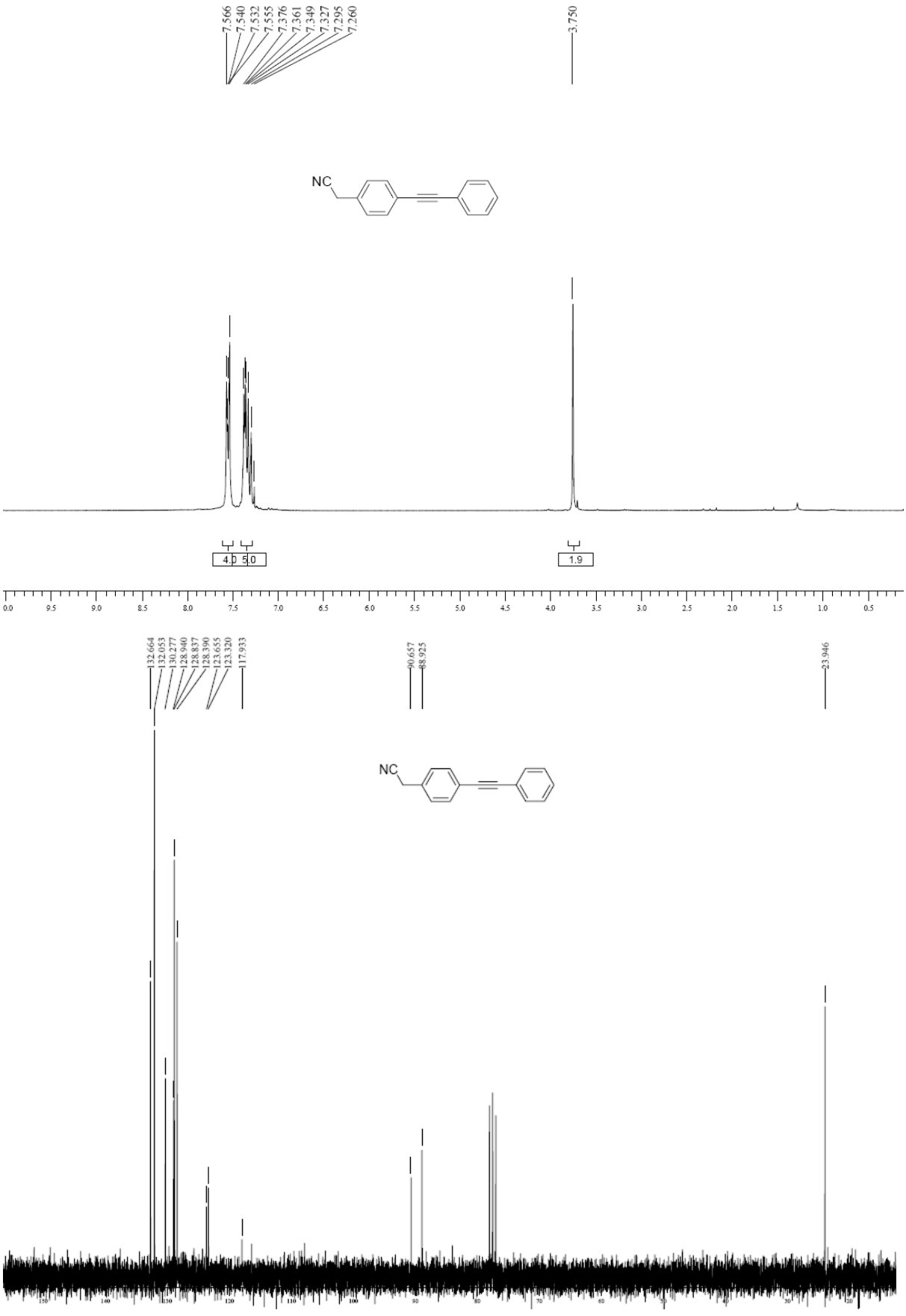
4-Phenylethylnyl-nitrobenzene (3ca)



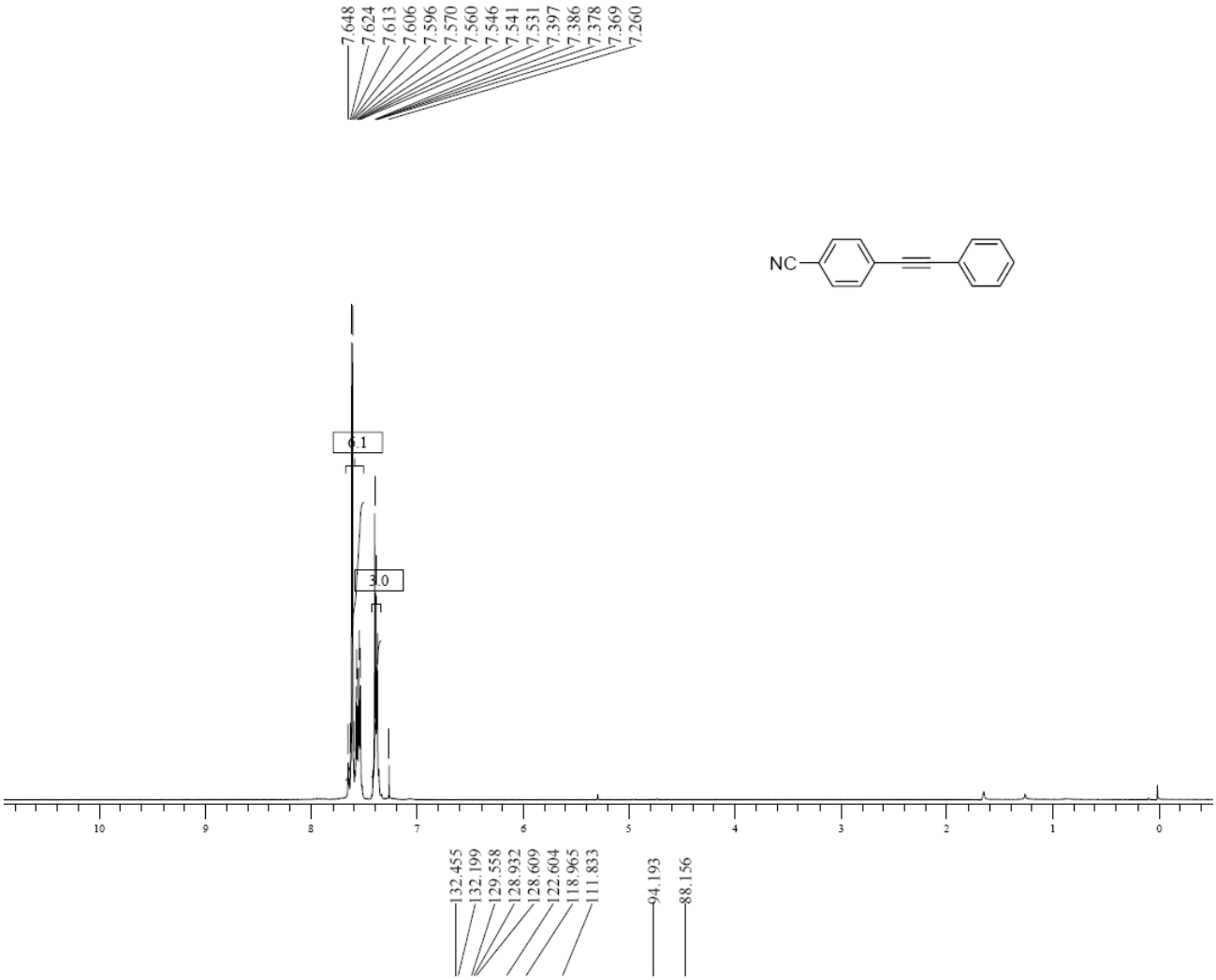
4-Phenylethylnyl-acetanilide (3da)

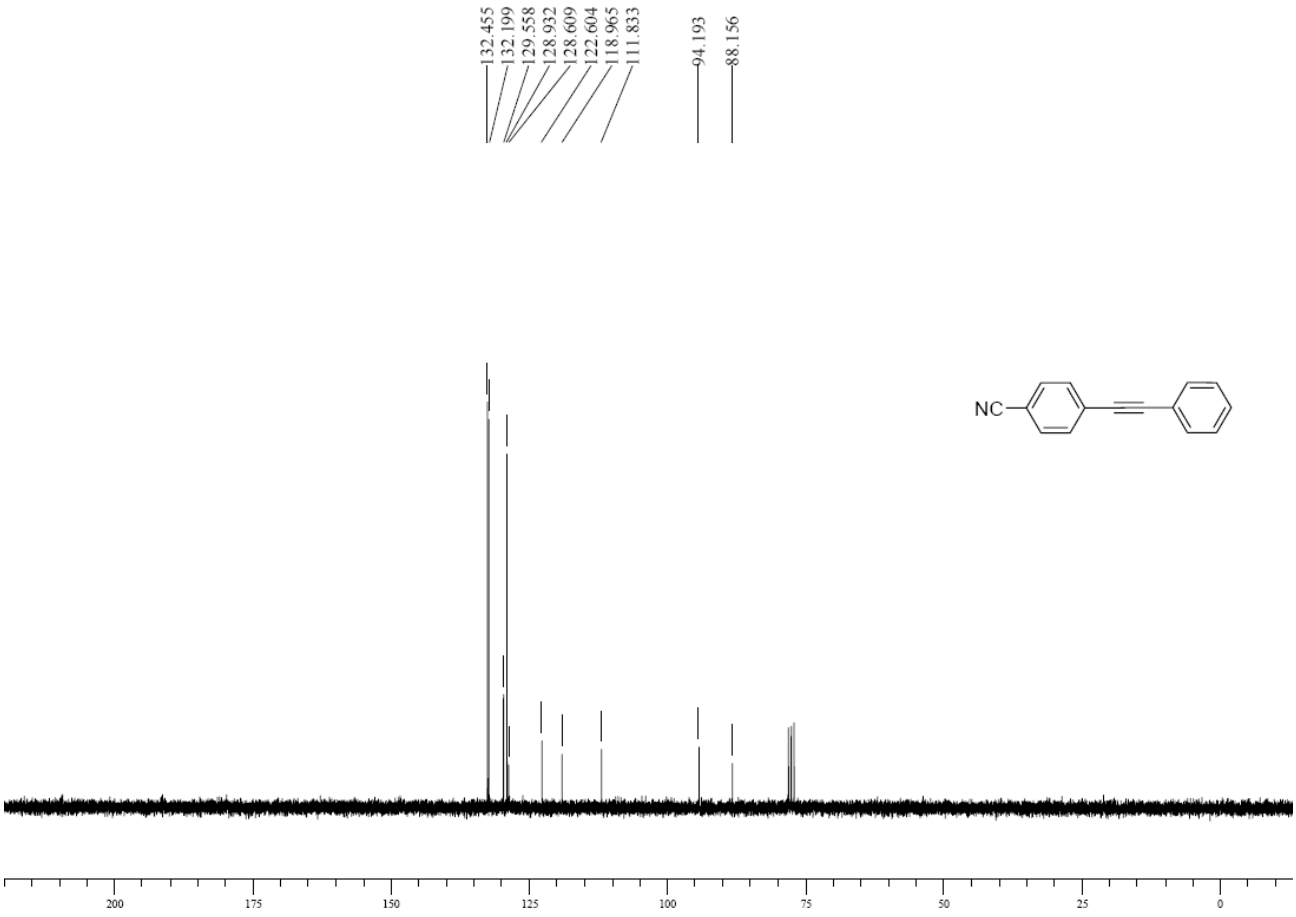


4-Phenylethynyl-benzylnitrile (3ea)

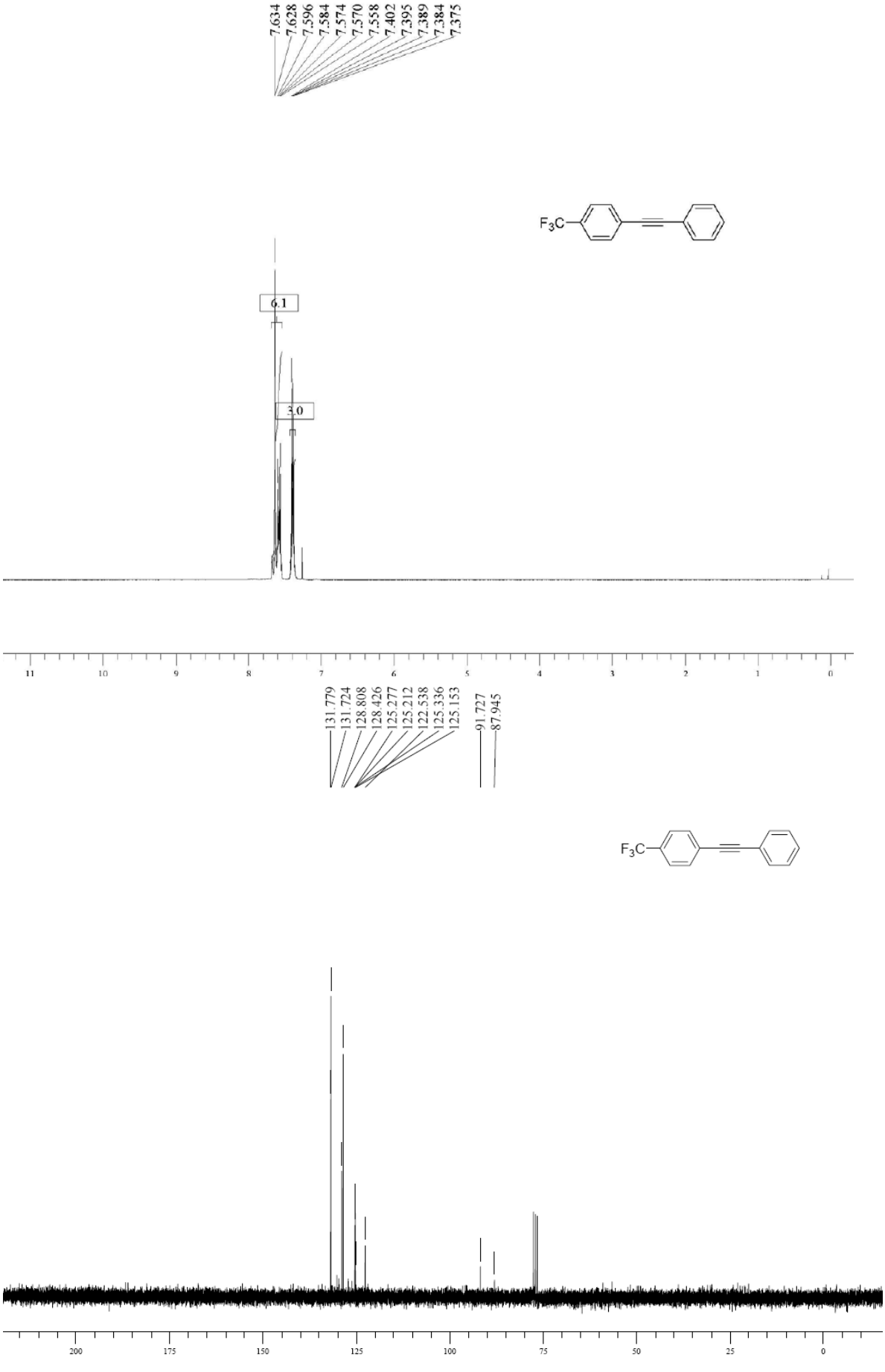


4-Phenylnethynyl-benzonitrile (3fa)

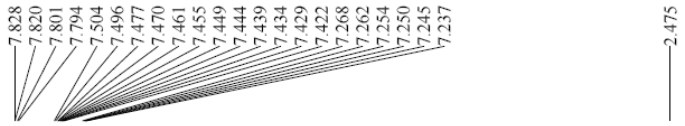


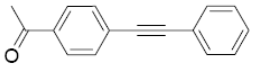


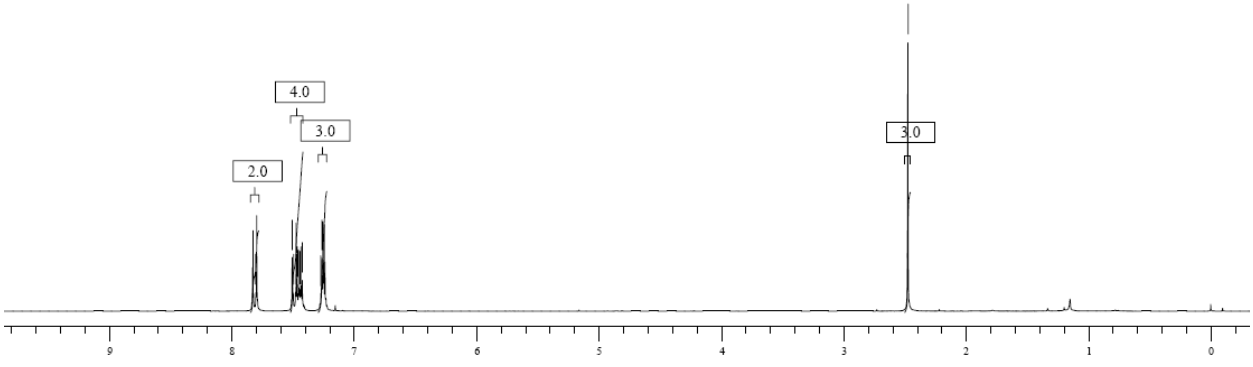
(4'-Trifluormethylphenyl-ethynyl)benzene (3ga)

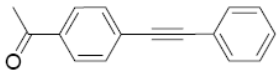


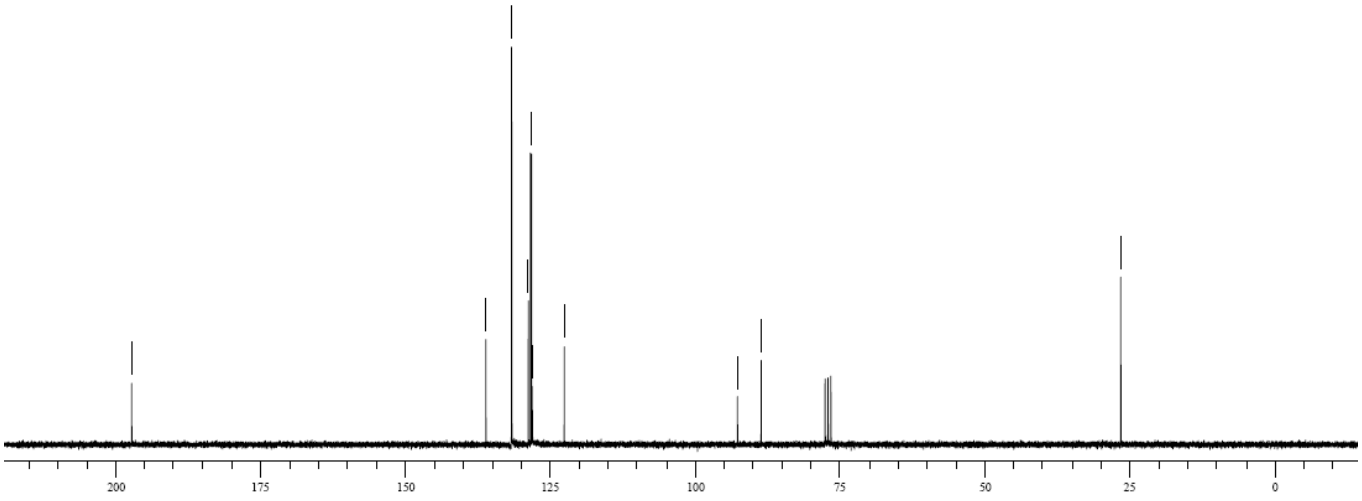
4-Phenylethynyl-acetophenone (3ha)



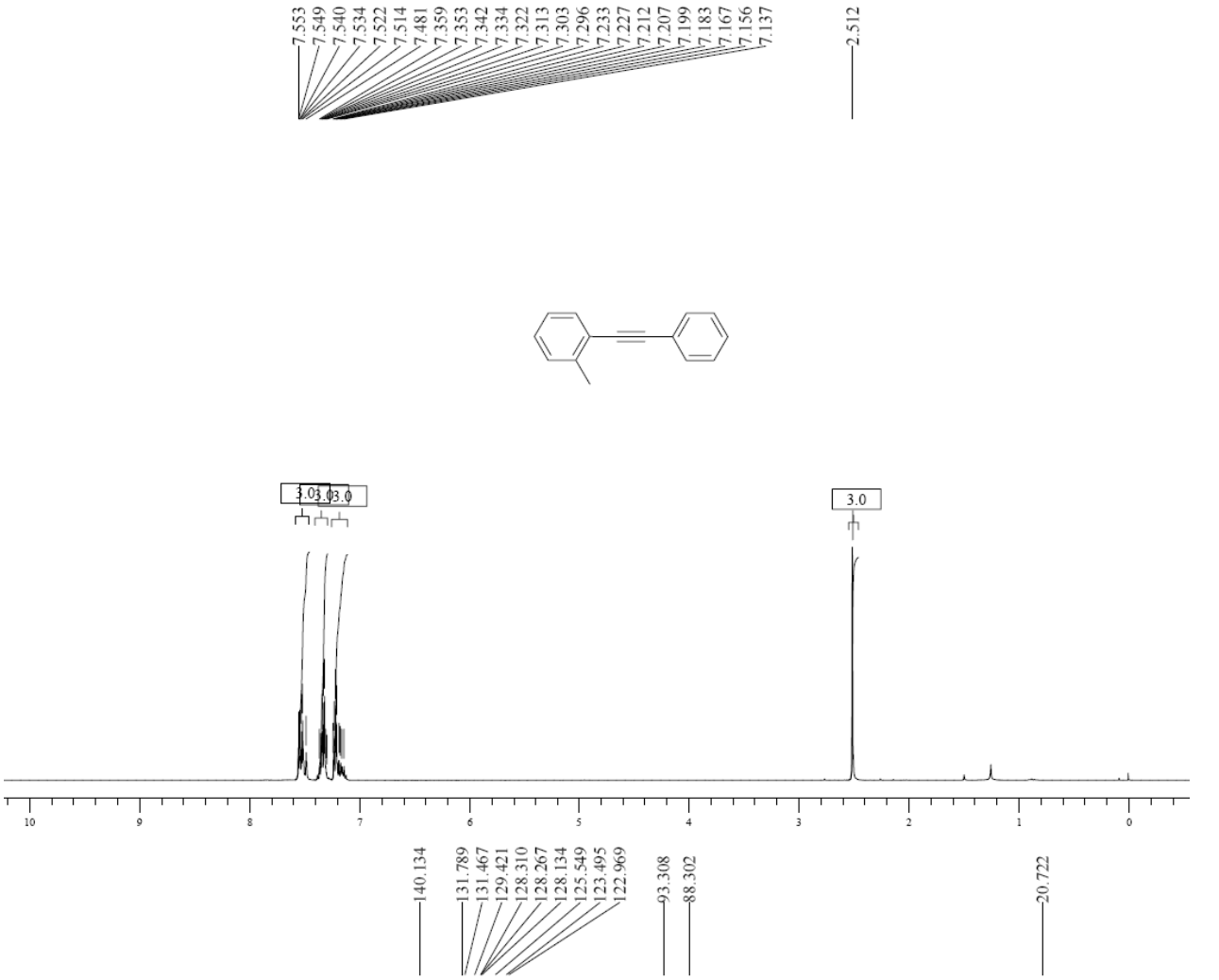




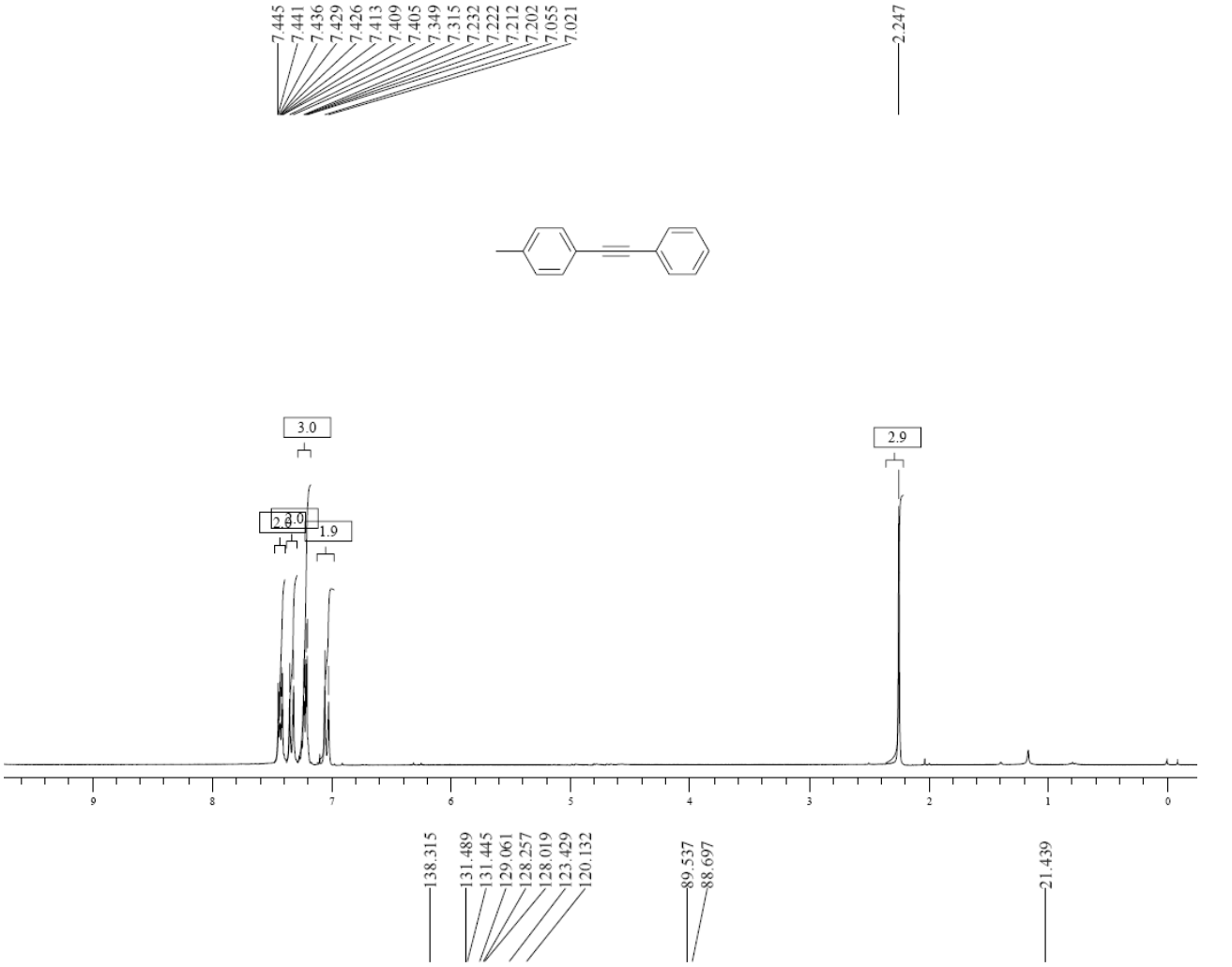


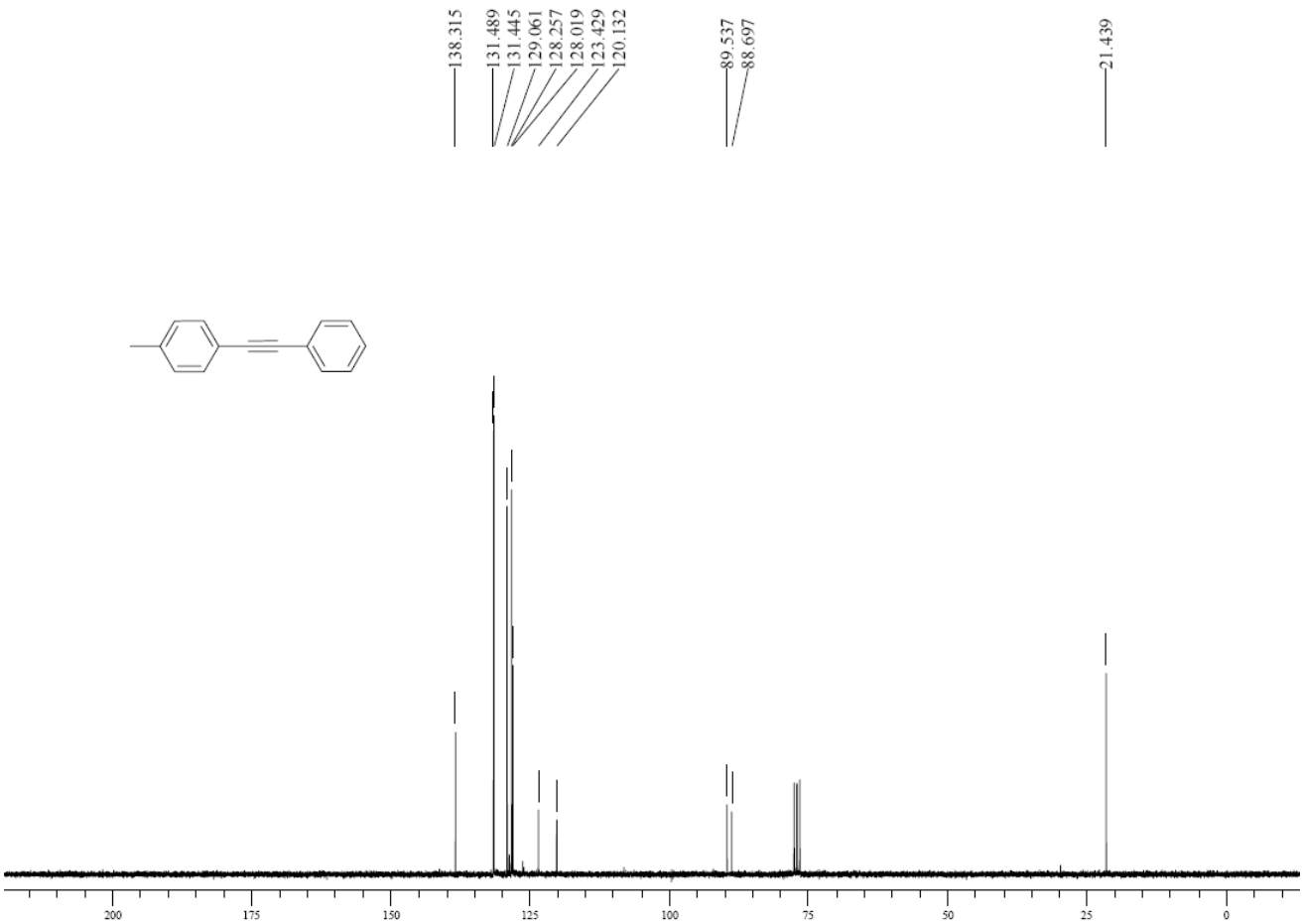


2-Phenylethynyl-toluene (3ia)

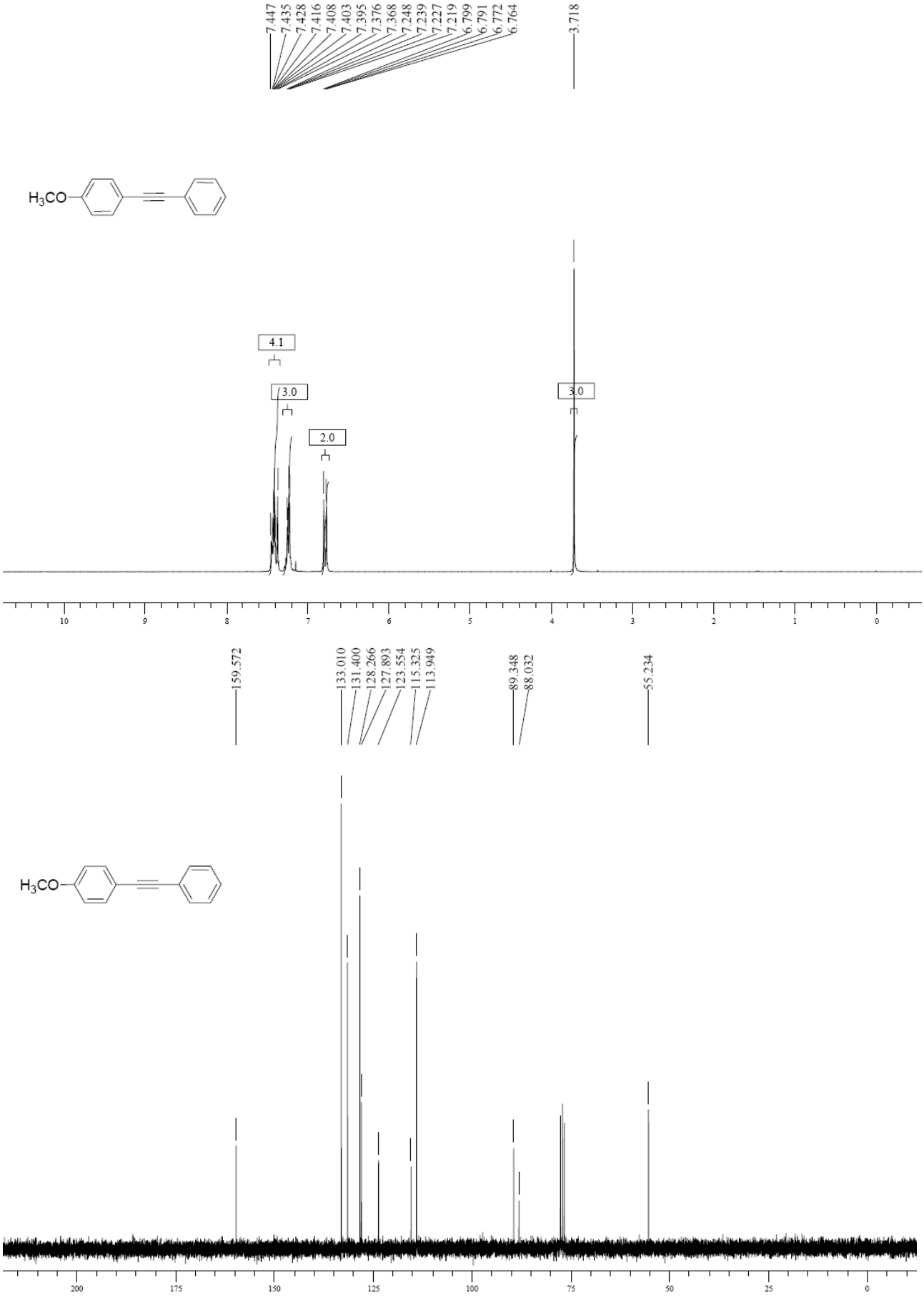


4-Phenylethynyl-toluene (3ja)

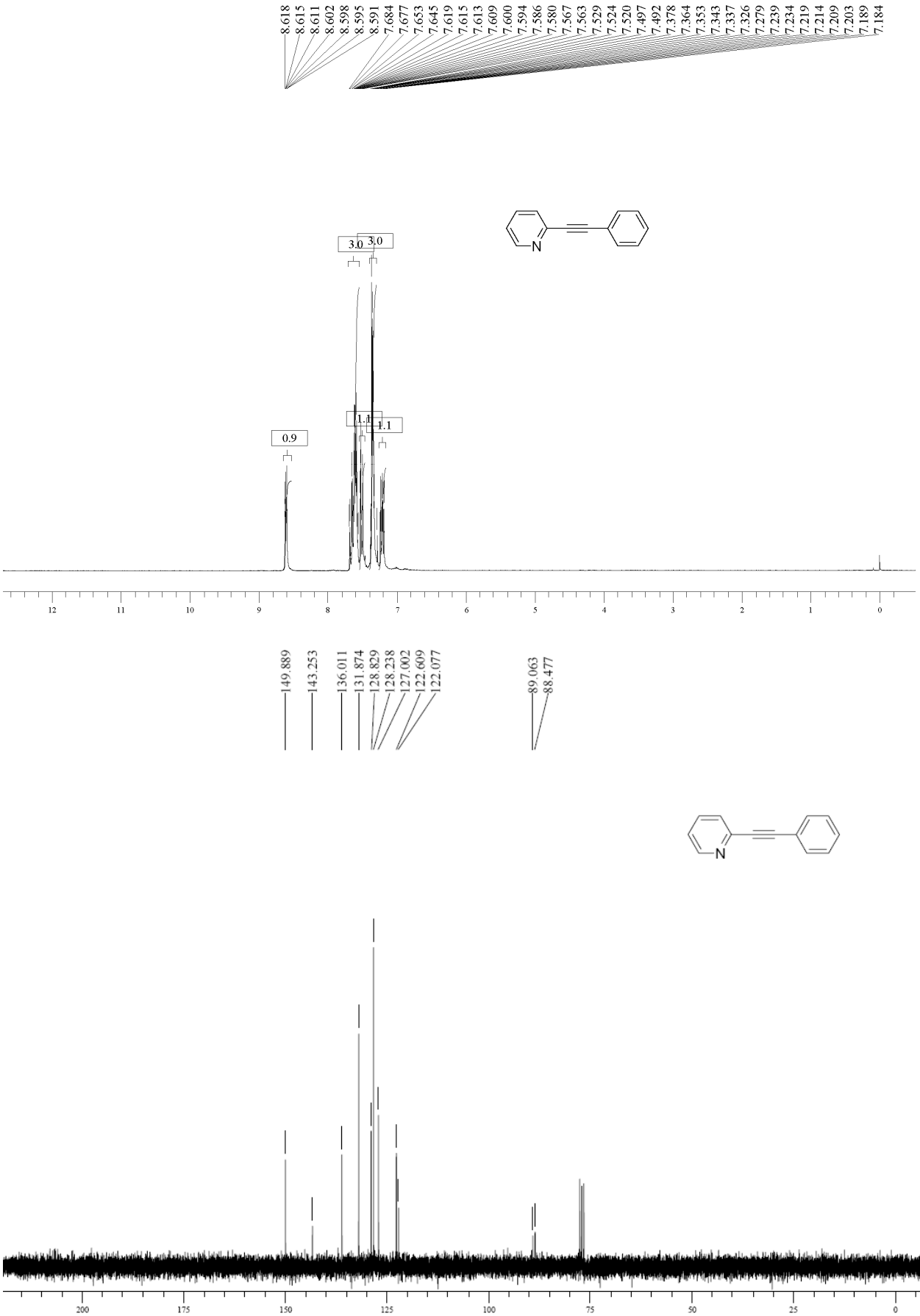




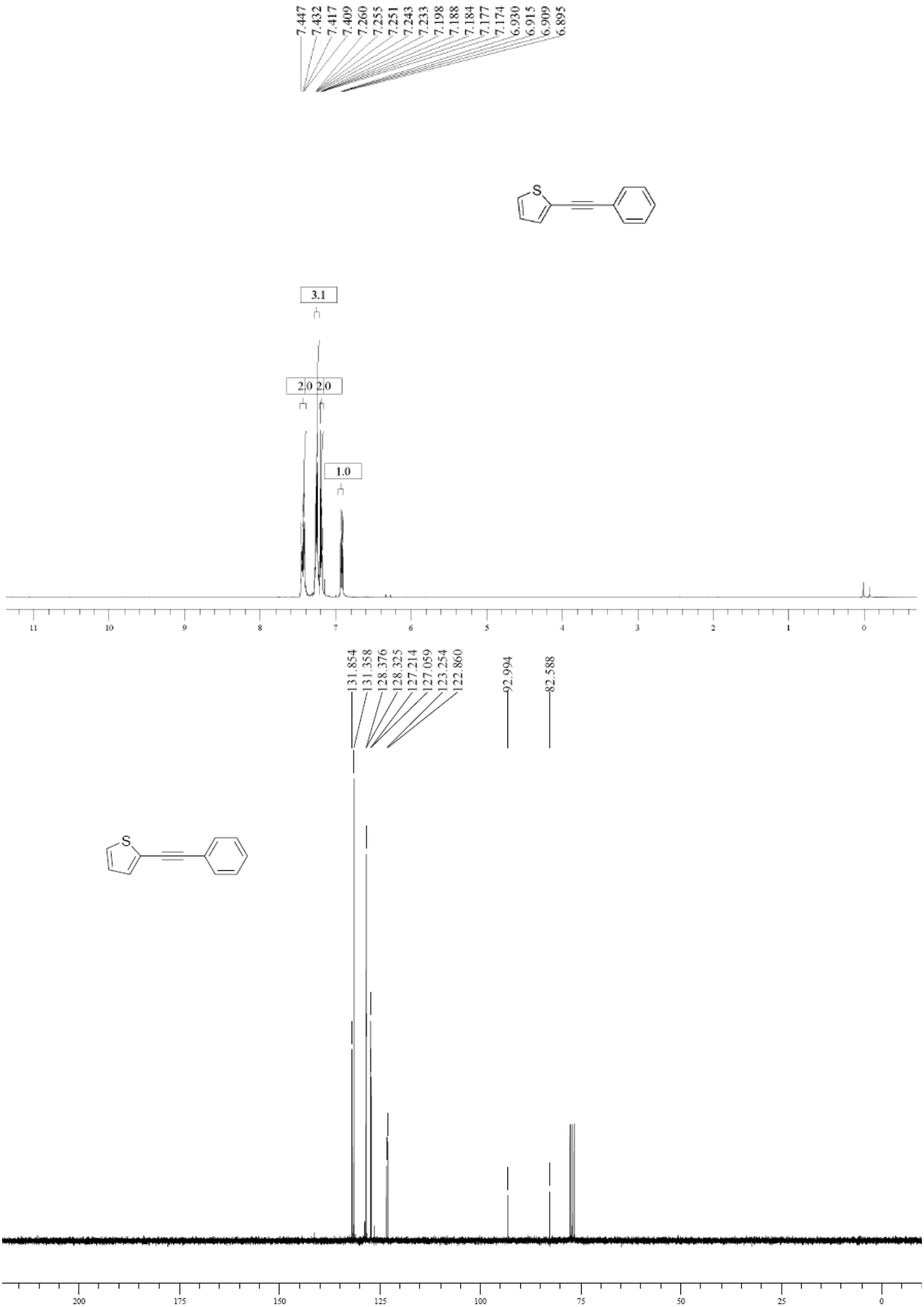
4-Phenylethynyl-anisole (3ka)



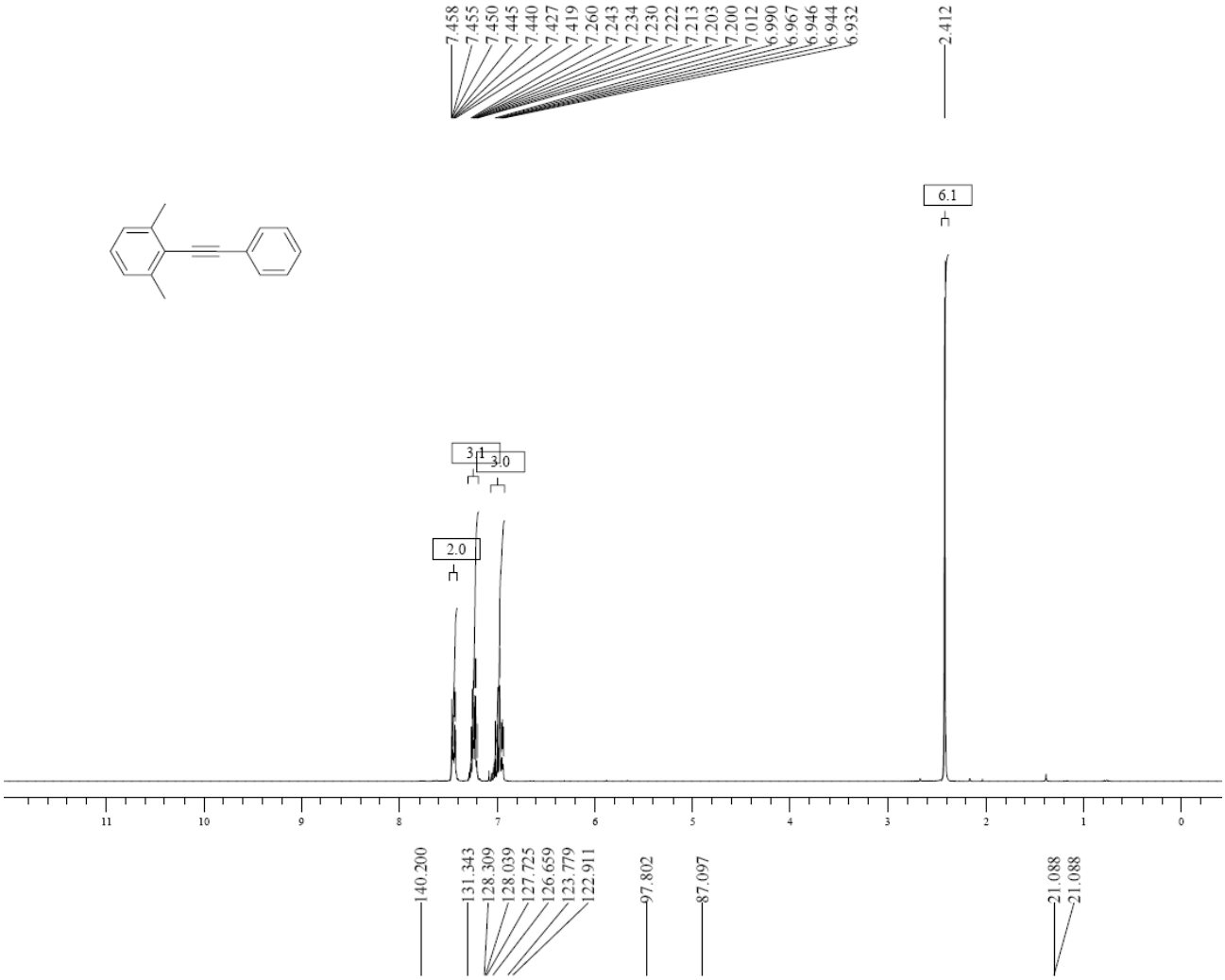
2-Phenylethynyl-pyridine (3la)

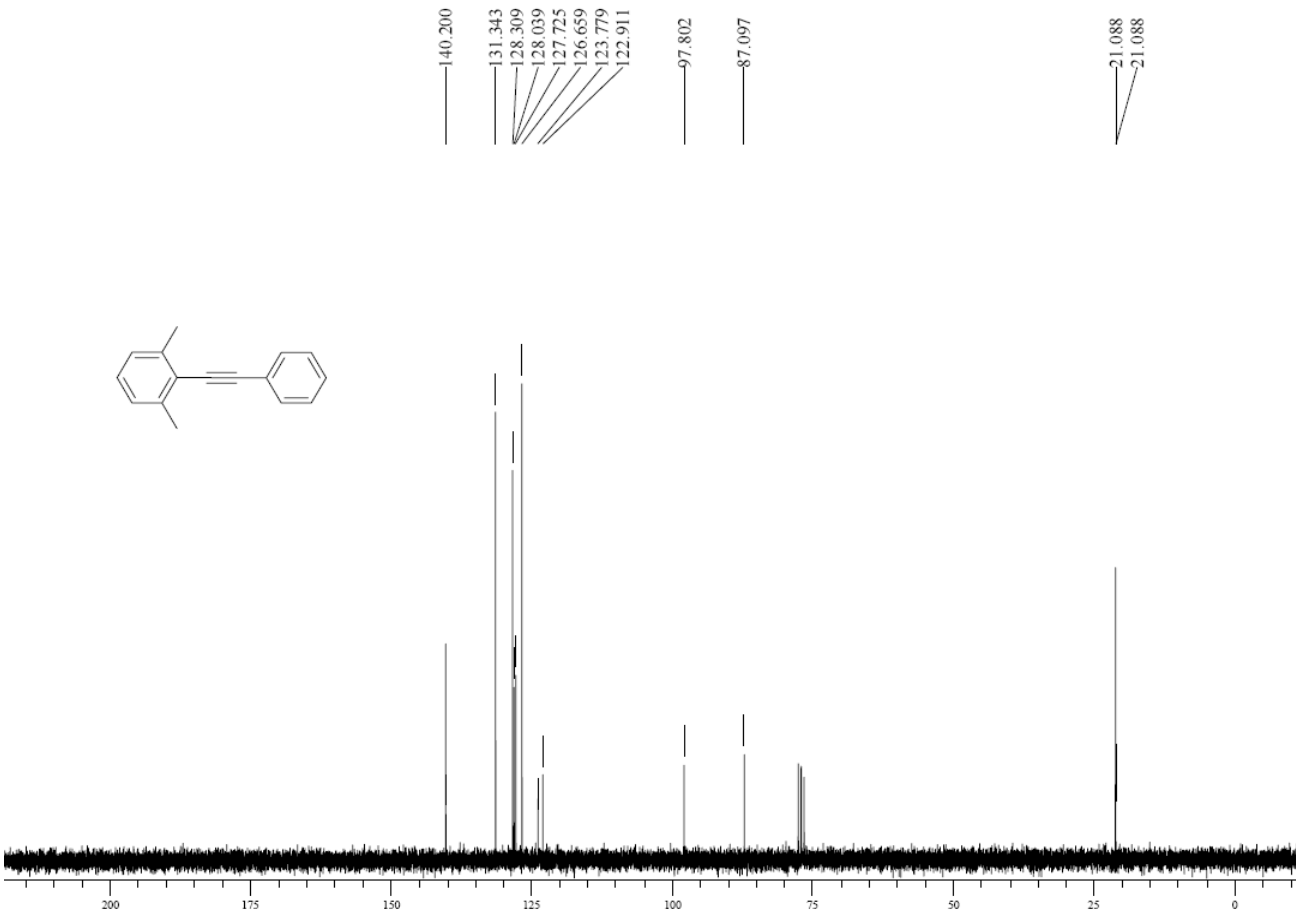


2-Phenylethynyl-thiophene (3ma)

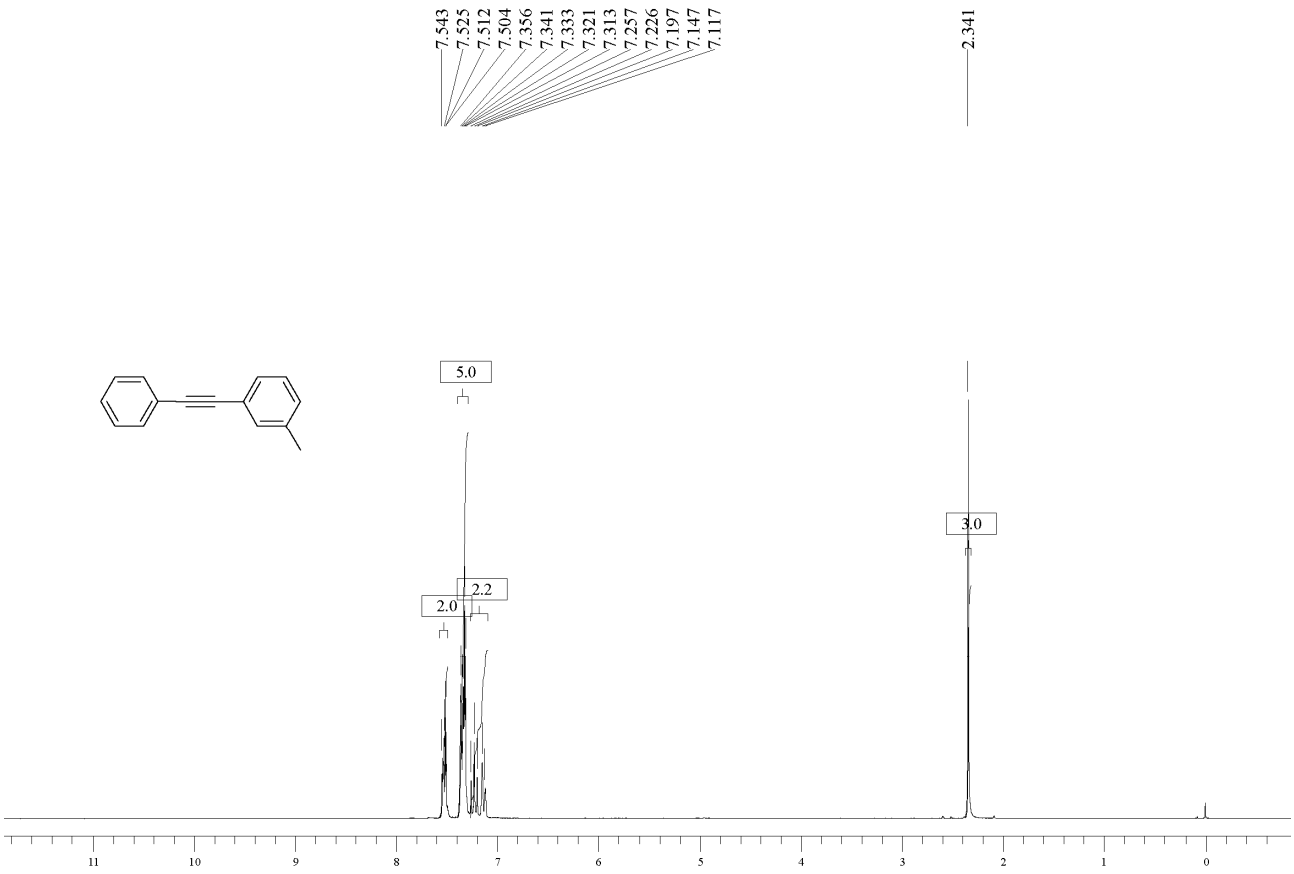

7.447
7.432
7.417
7.409
7.260
7.255
7.251
7.243
7.233
7.198
7.188
7.184
7.177
7.174
6.930
6.915
6.909
6.895
S
3.1
2.0
2.0
1.0
11
10
9
8
7
6
5
4
3
2
1
0
131.854
131.358
128.376
128.325
127.214
127.059
123.254
122.860
92.994
82.588
S
200
175
150
125
100
75
50
25
0

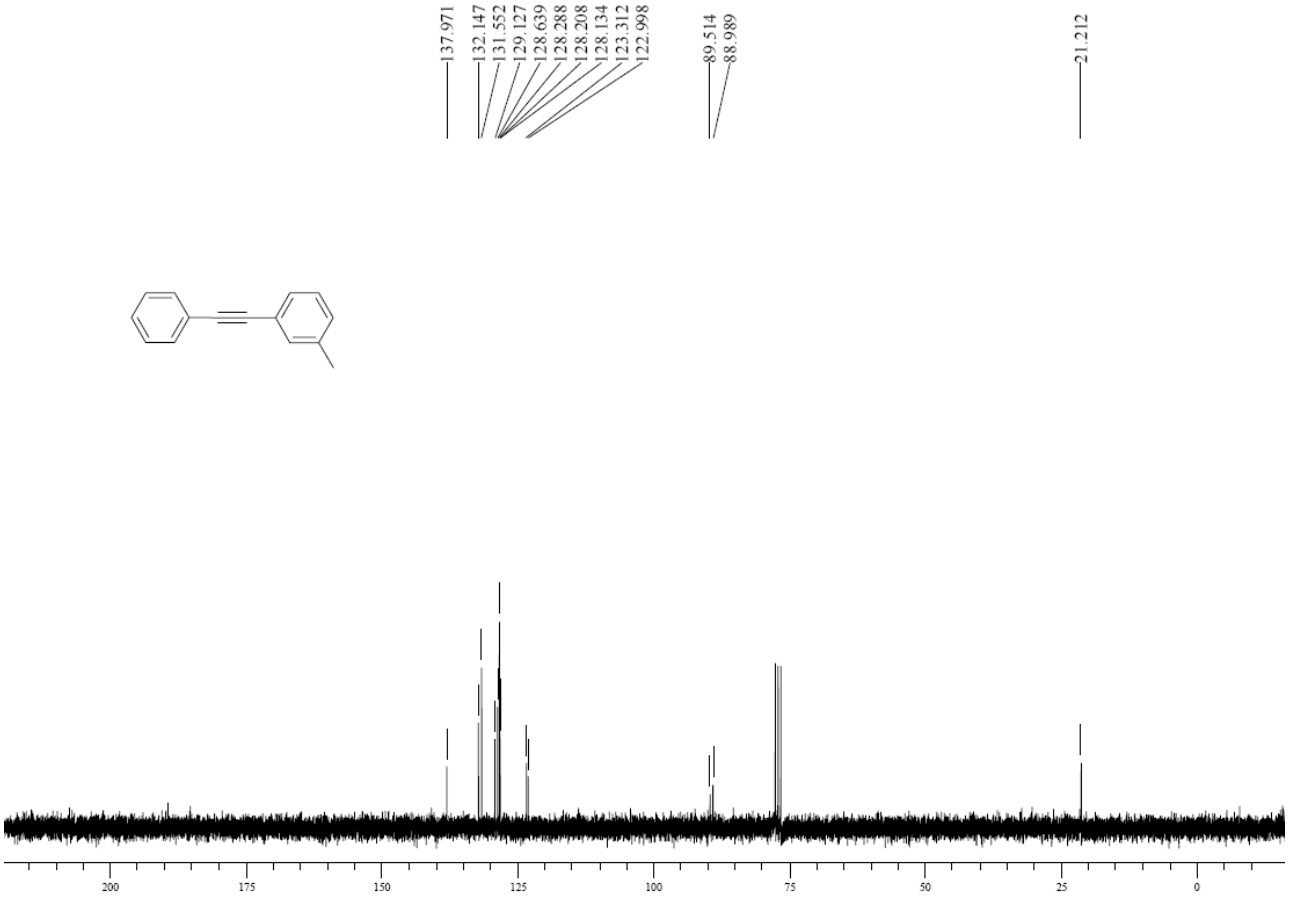
2-Phenylethynyl-toluene (3na)



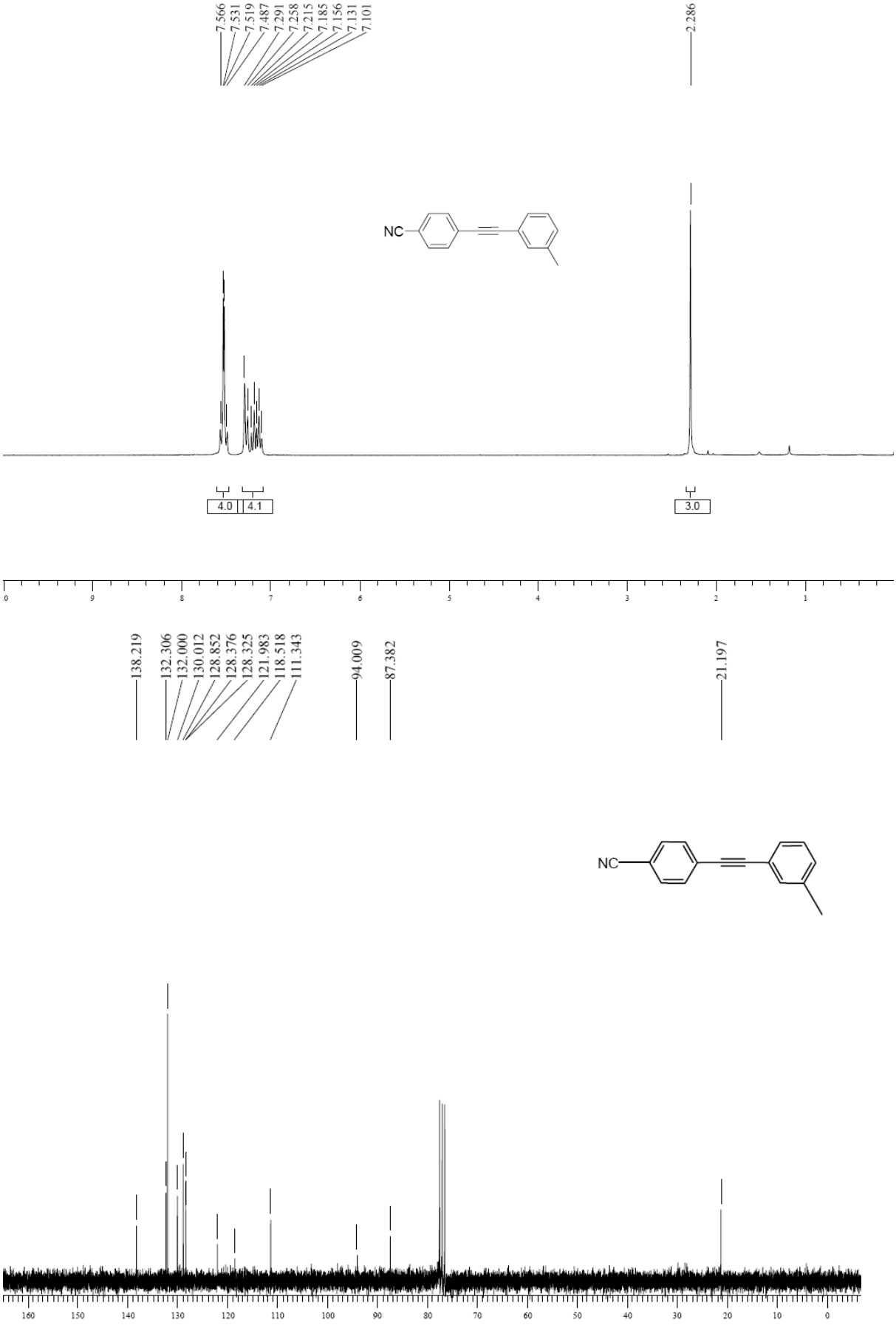


1-(3'-Tolylethynyl)benzene (3ab)

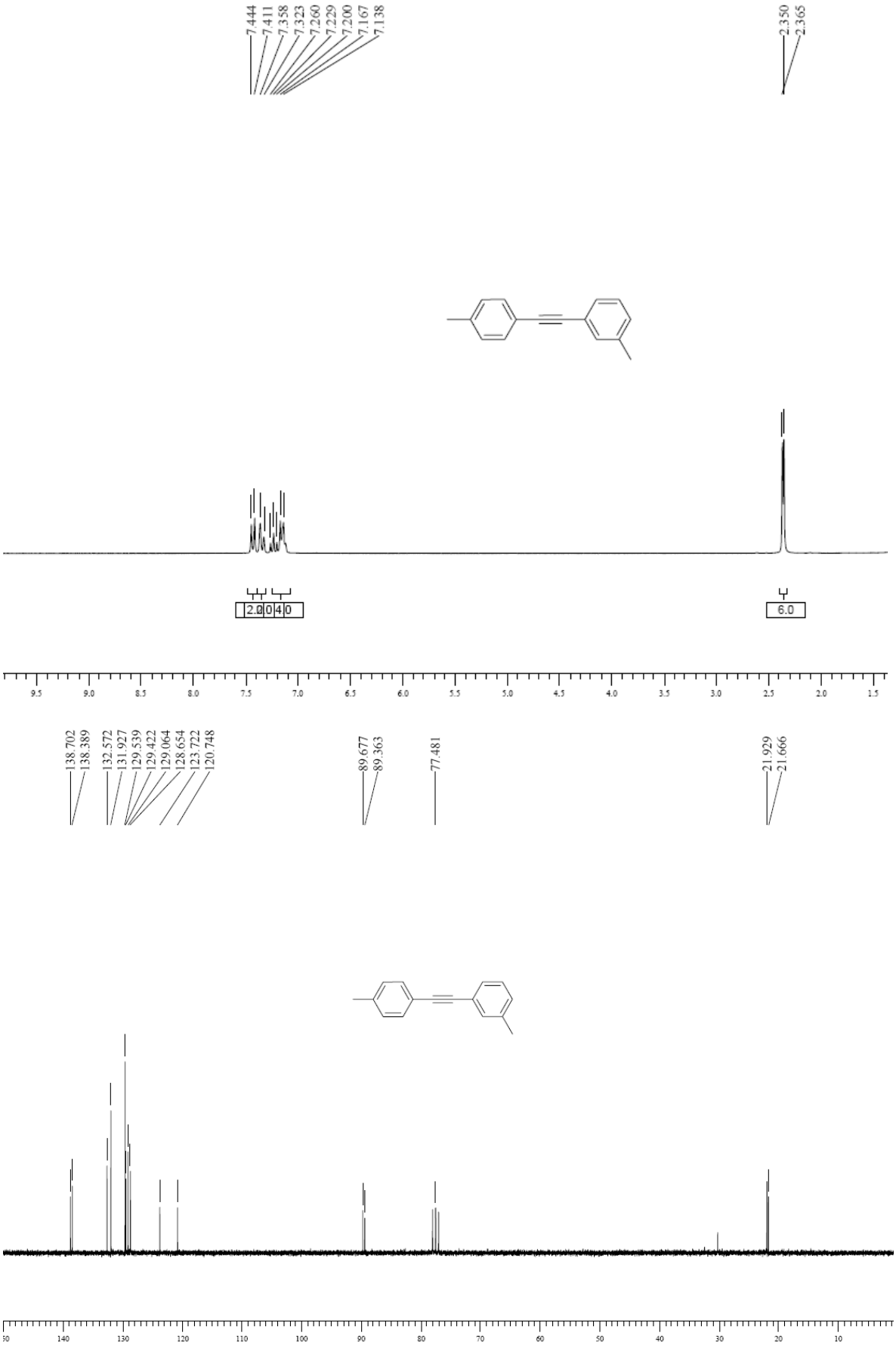




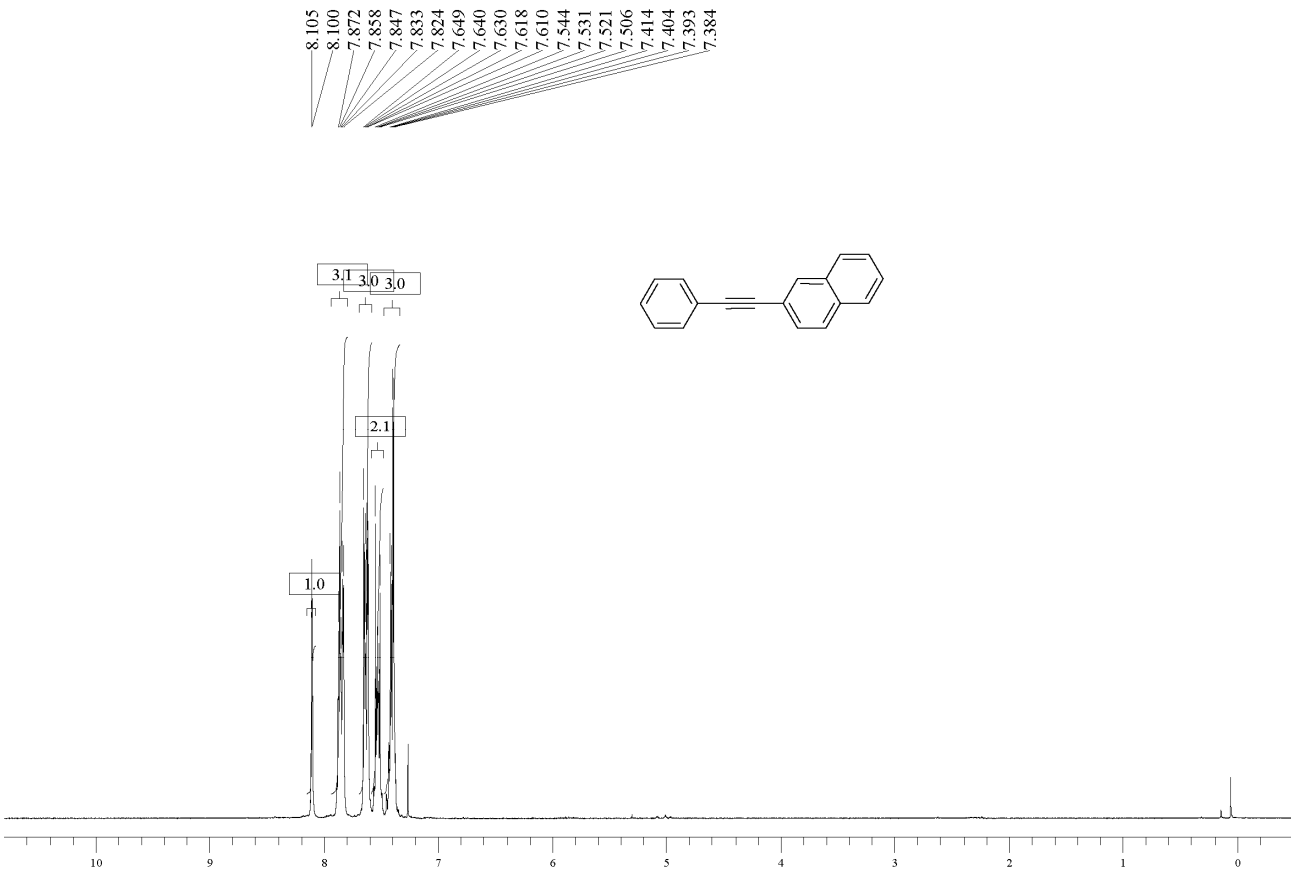
4-(3'-Tolylethynyl)benzonitrile (3fb)

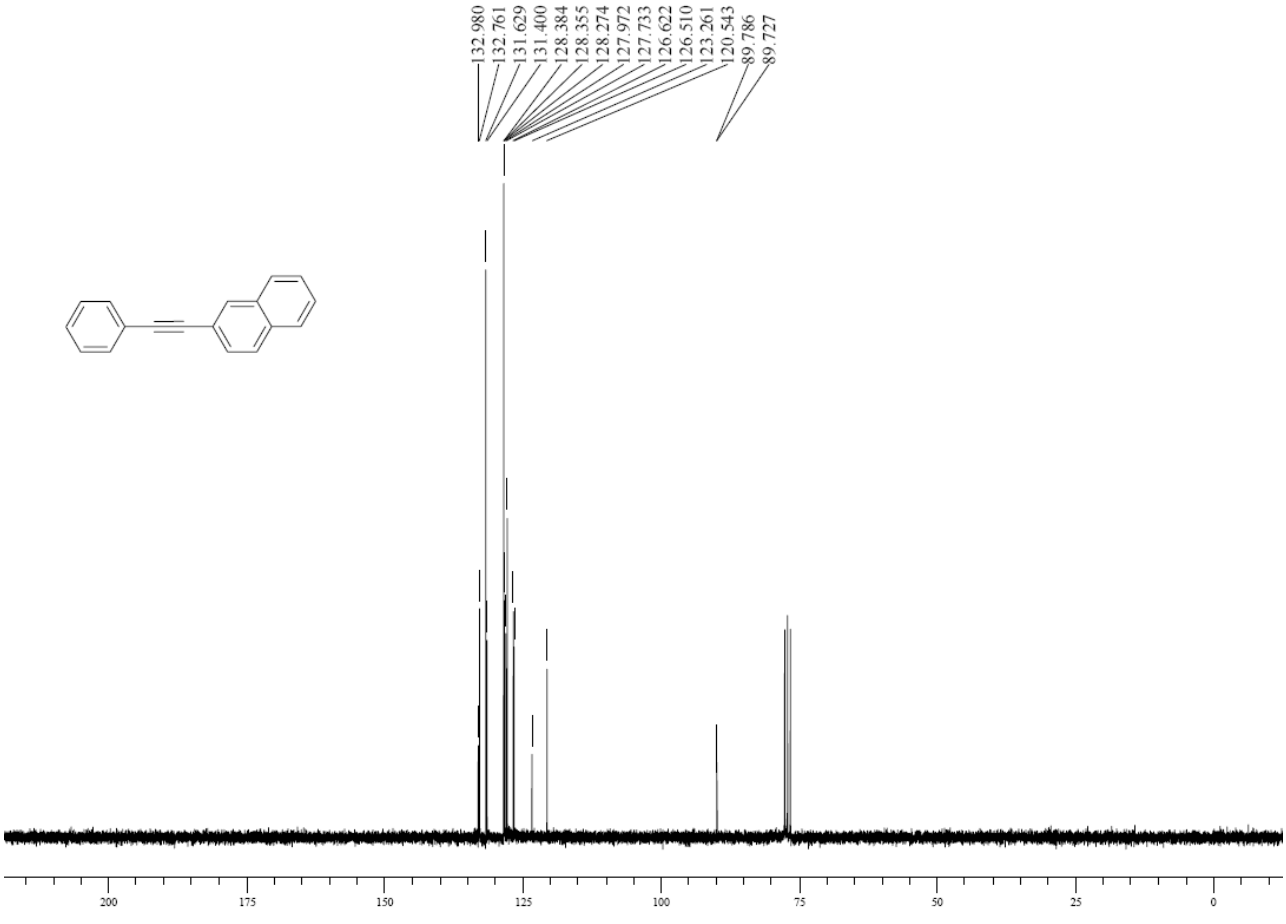


3-(4'-Tolylethynyl)-toluene **(3jb)**

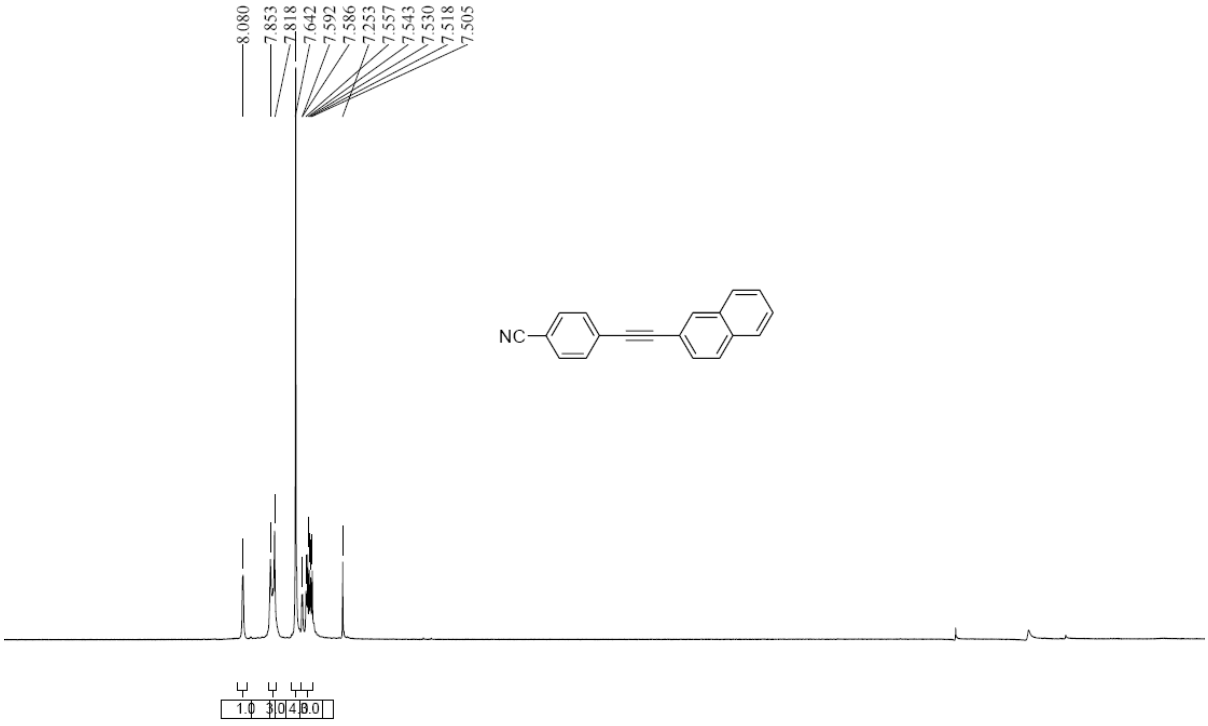


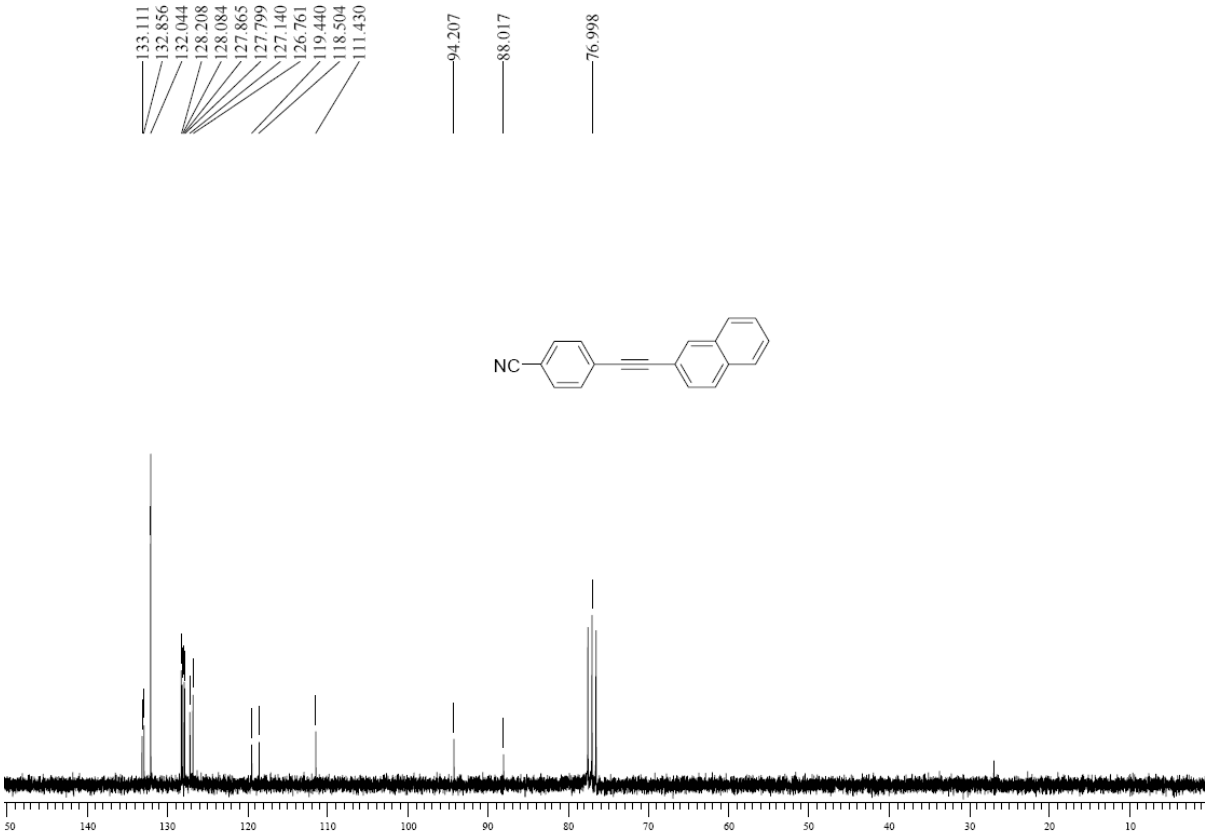
2-Phenylethynyl-naphthalene (3ac)


8.105
8.100
7.872
7.858
7.847
7.833
7.824
7.649
7.640
7.630
7.618
7.610
7.544
7.531
7.521
7.506
7.414
7.404
7.393
7.384
3.1
3.0
3.0
2.1
1.0
10
9
8
7
6
5
4
3
2
1
0

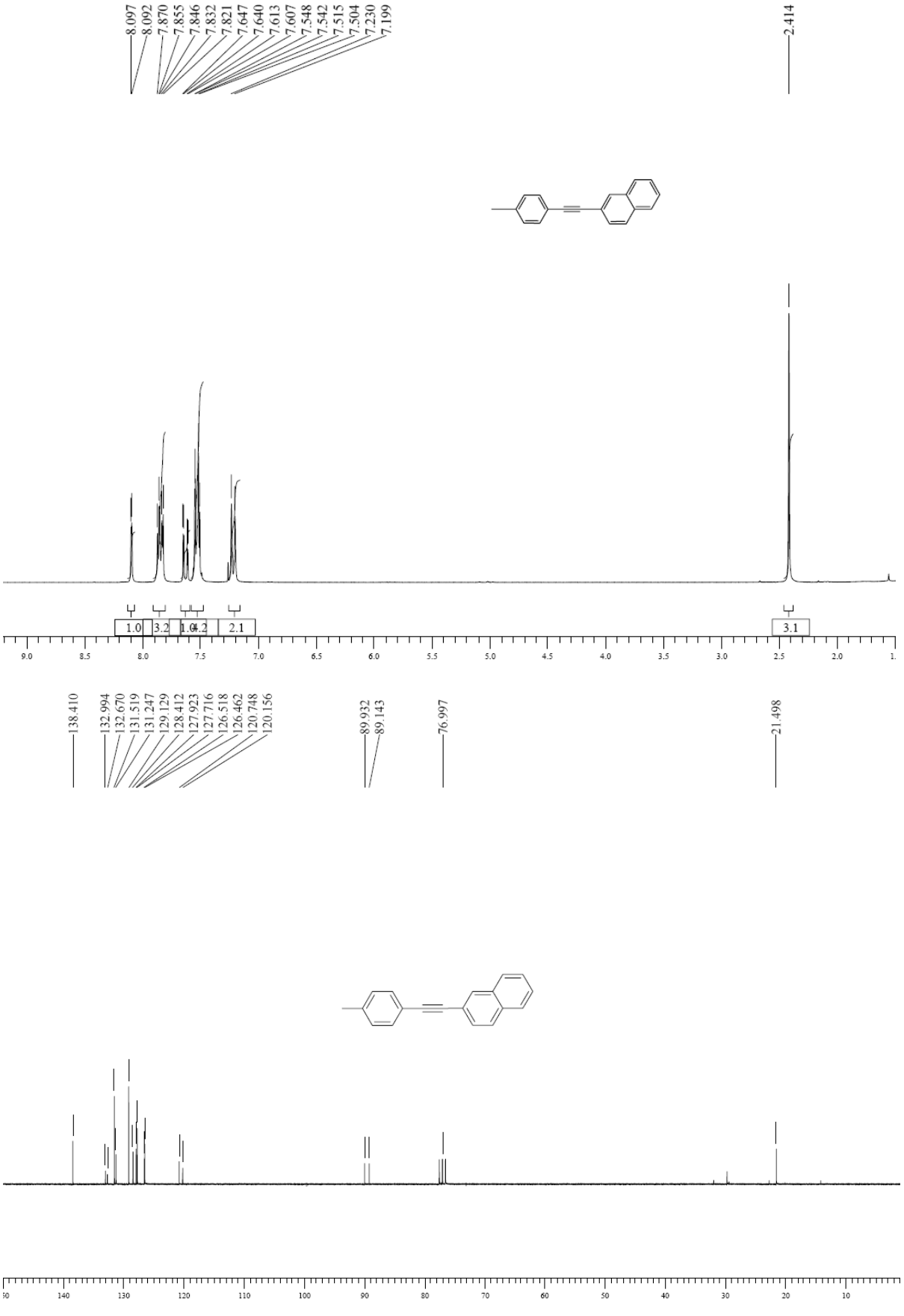

132.980
132.761
131.629
131.400
128.384
128.355
128.274
127.972
127.733
126.622
126.510
123.261
120.543
89.786
89.727
200
175
150
125
100
75
50
25
0

2-(4'-Cyanophenyl)ethynyl-naphthalene (3fc)

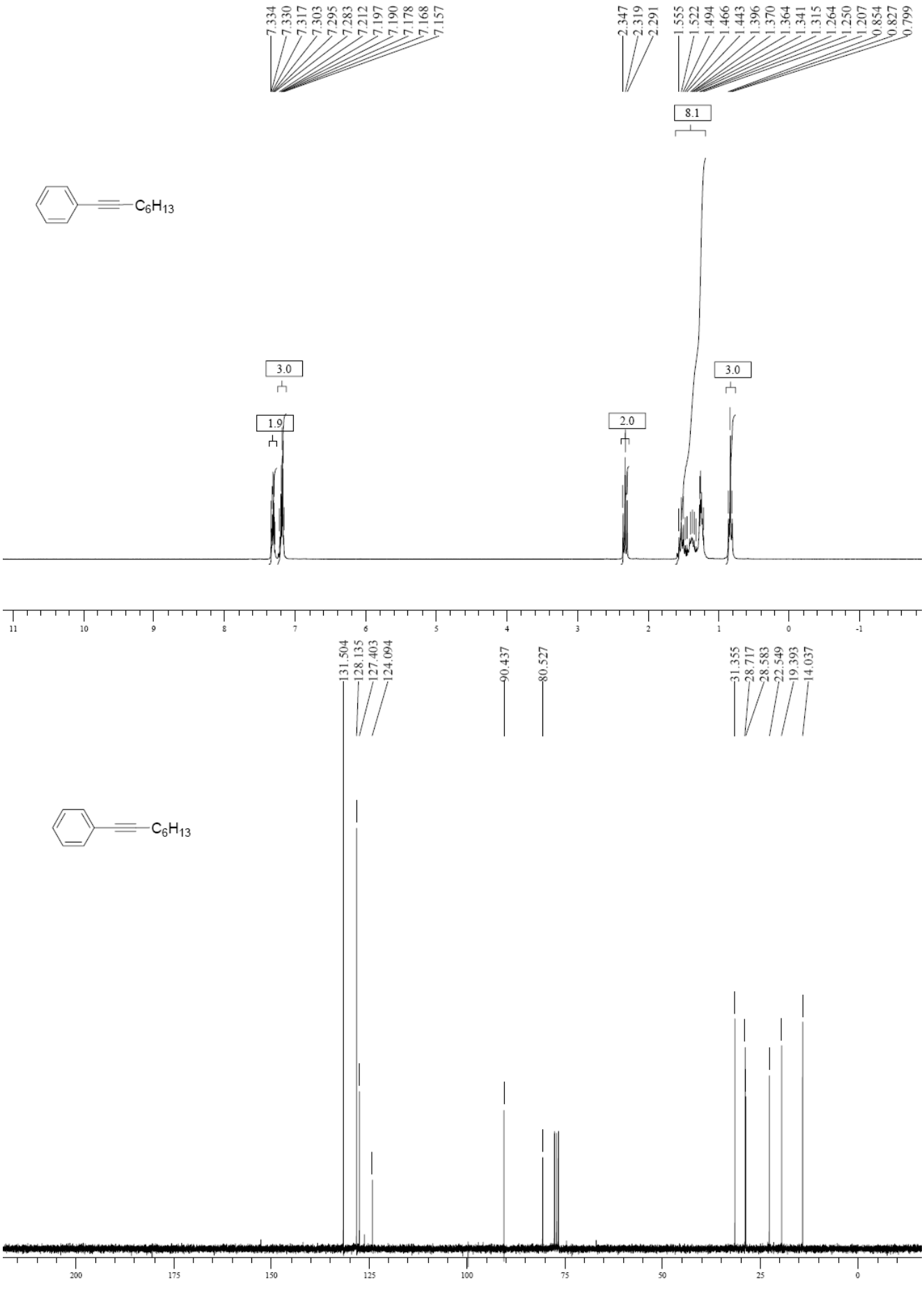




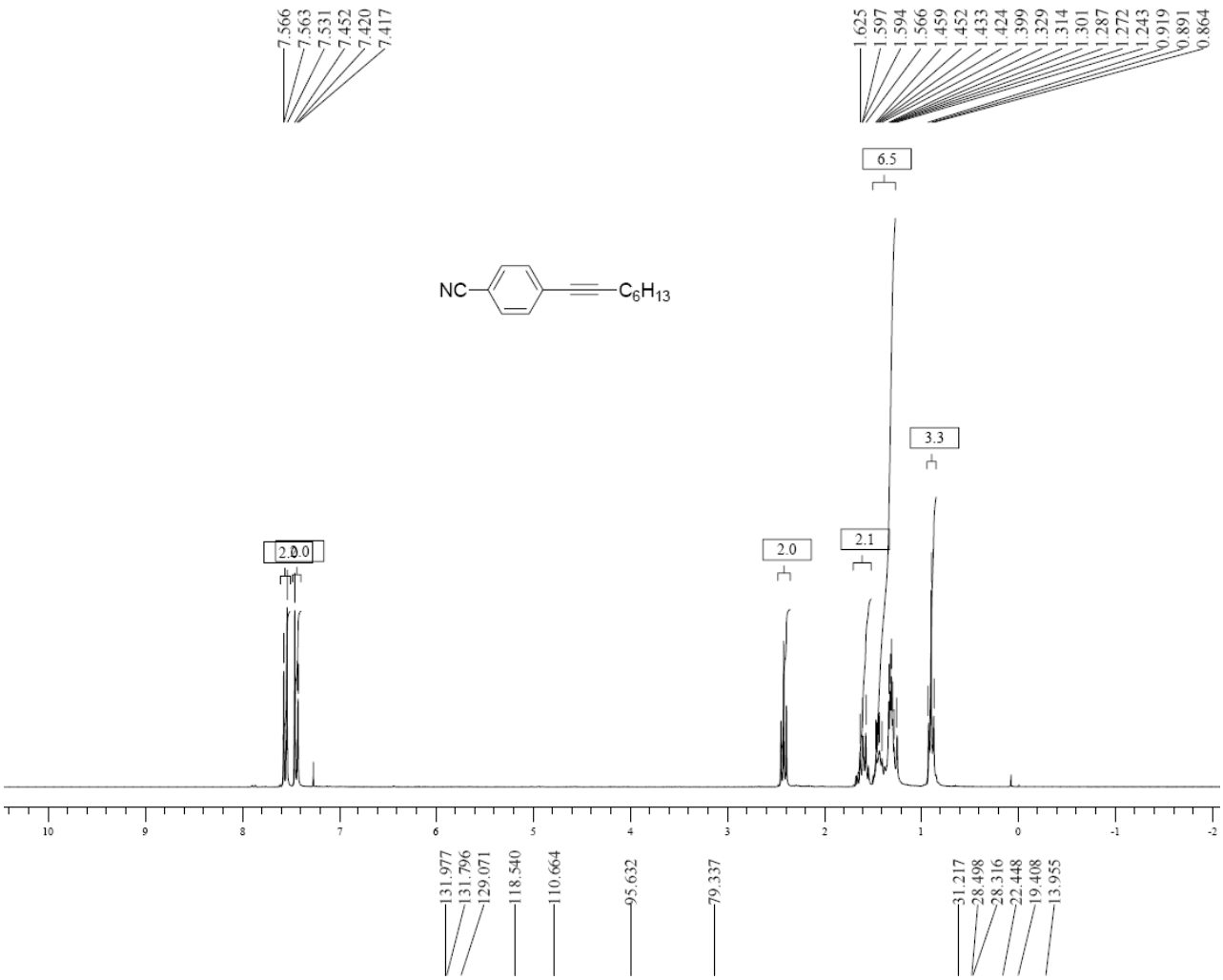
2-(4'-Tolylethynyl)-naphthalene **(3jc)**

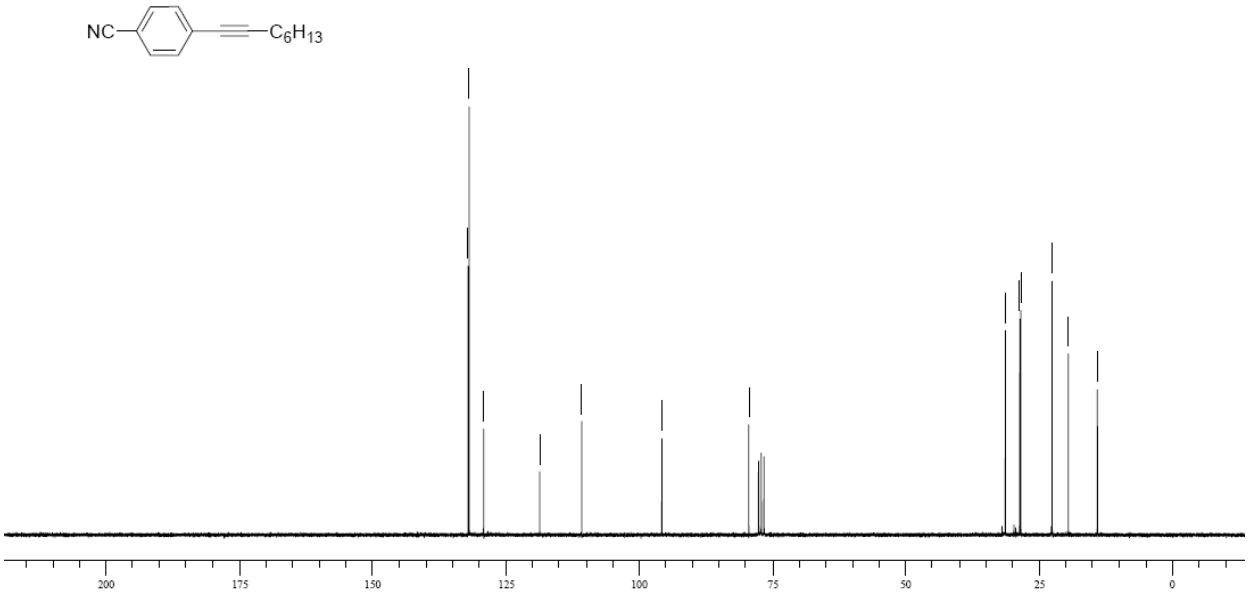


1-(Octyn-1-yl)benzene (3ad)

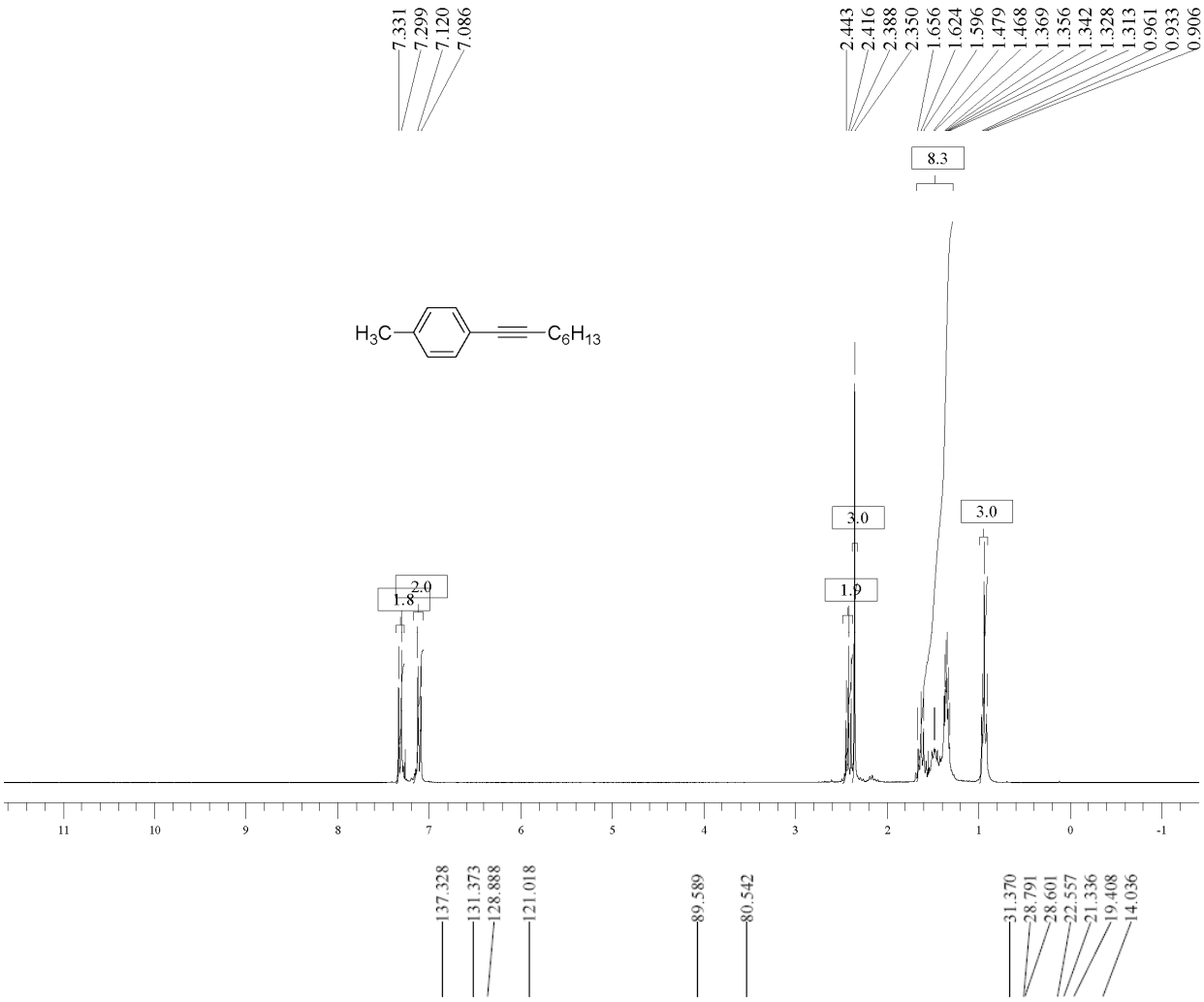


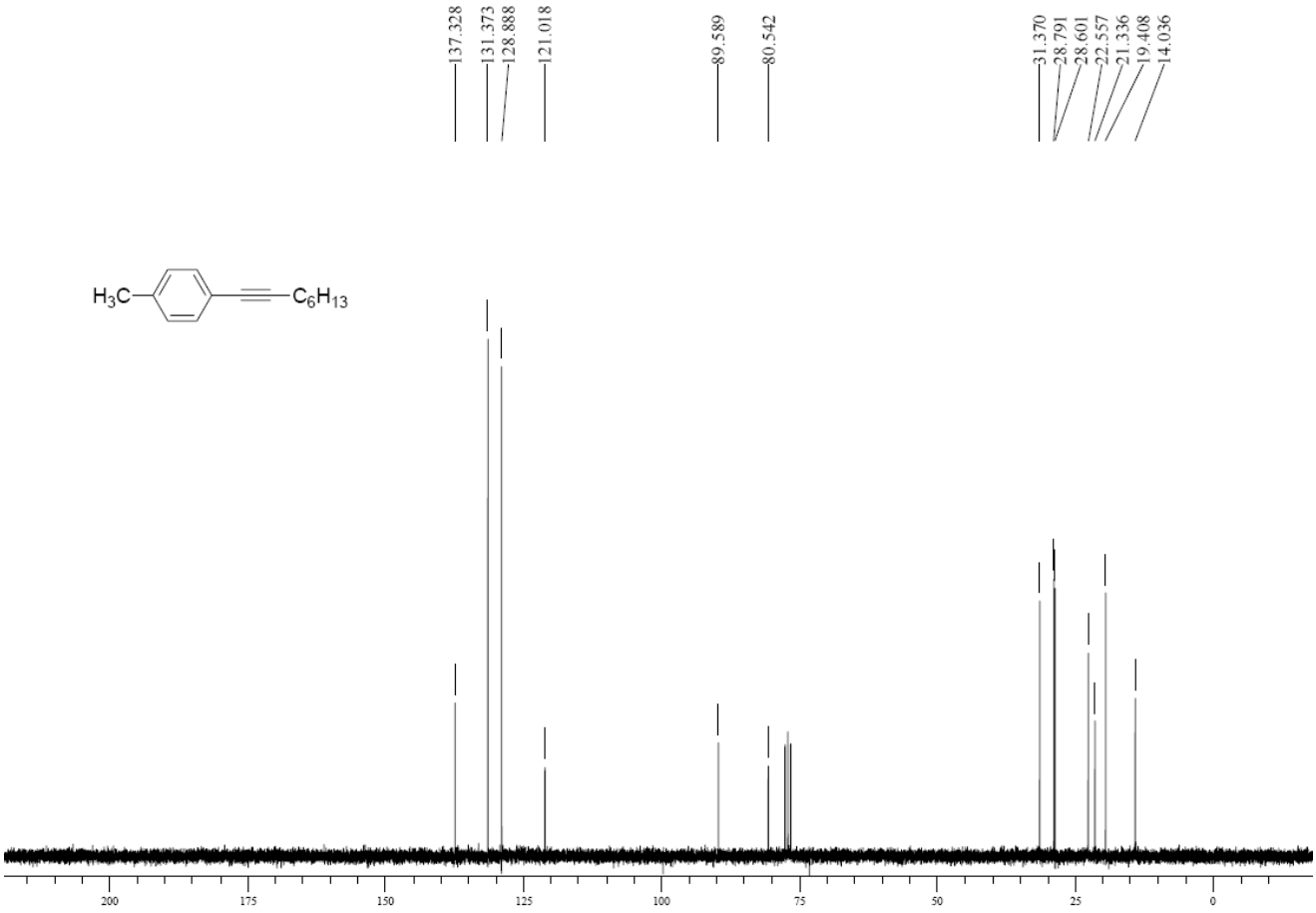
4-(Octyn-1-yl)benzonitrile (3fd)



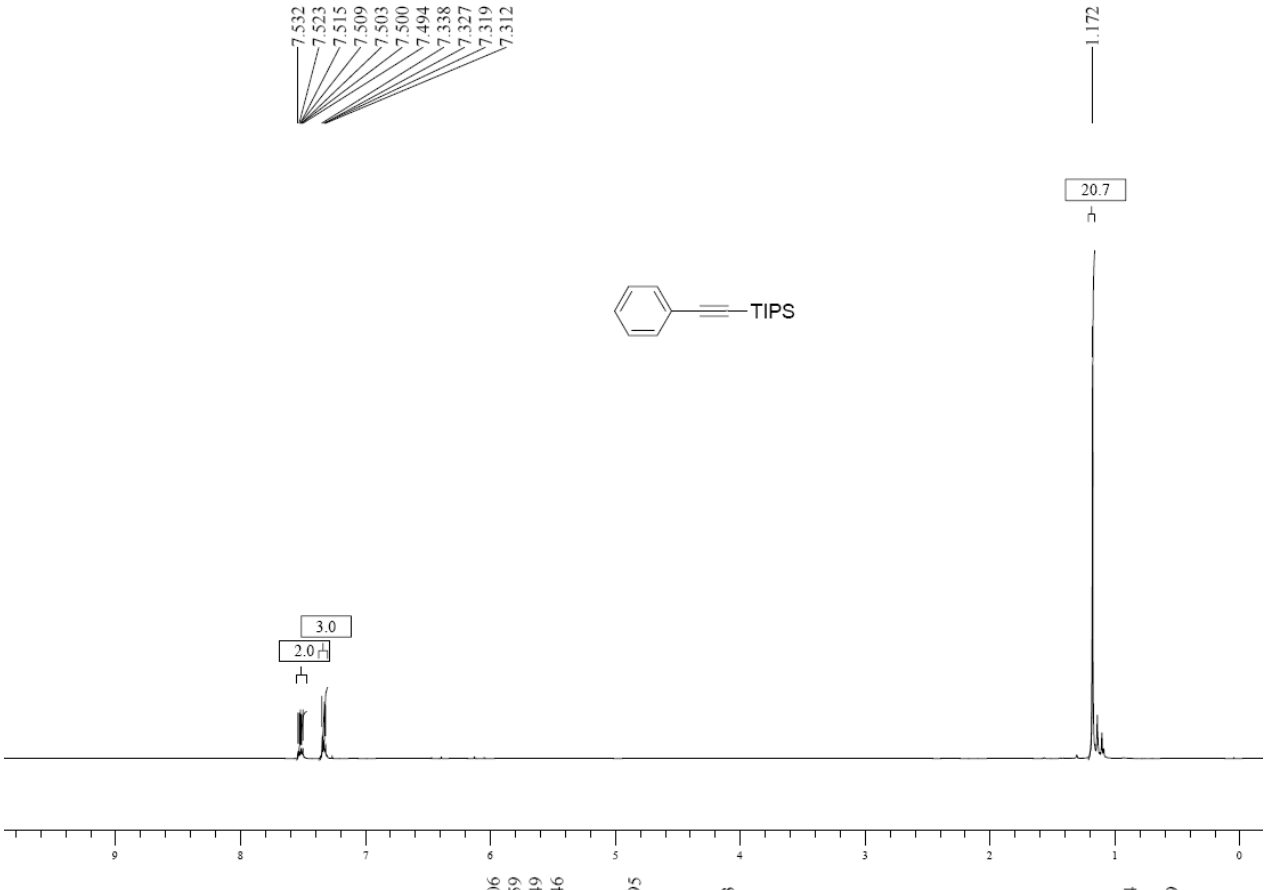


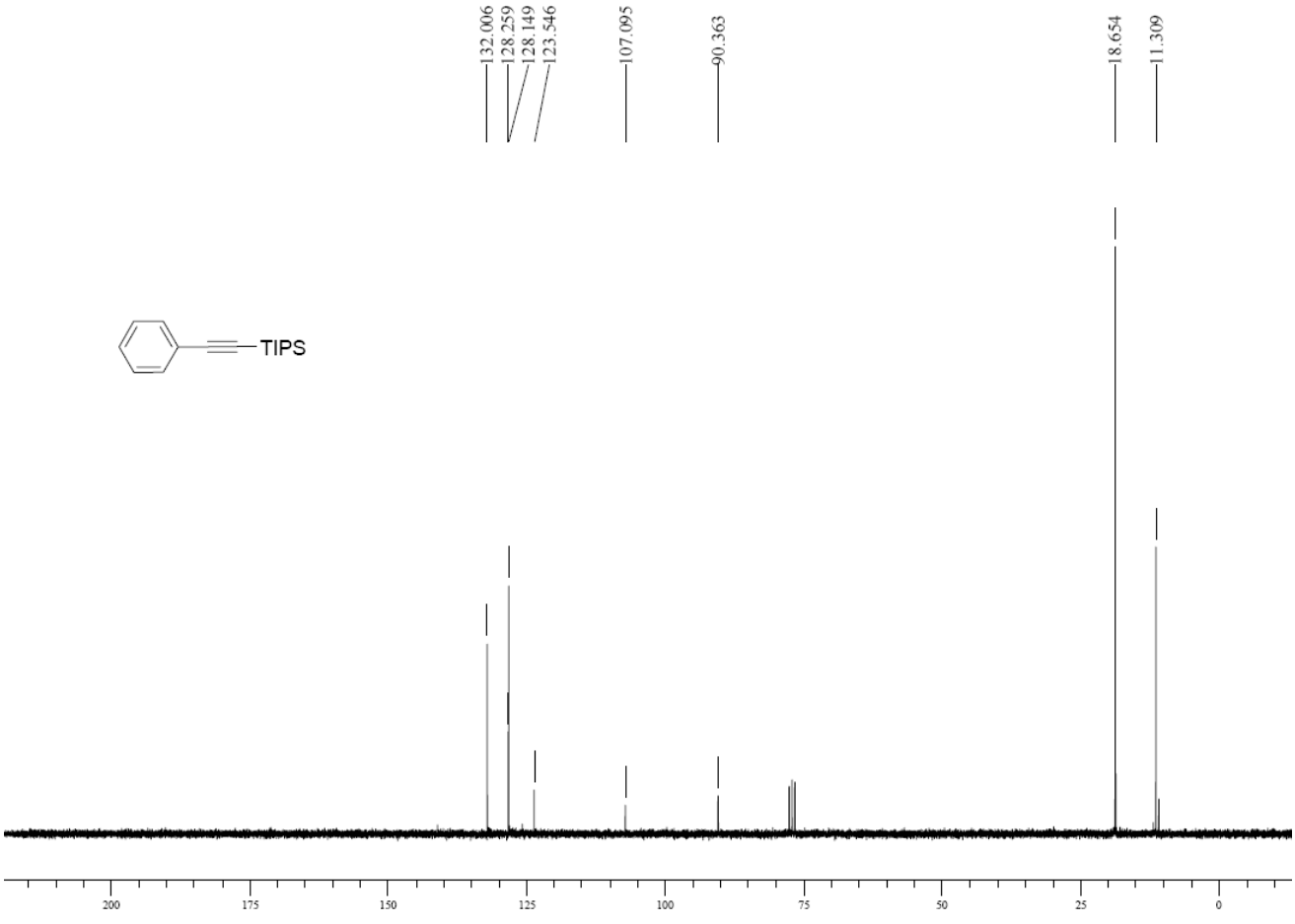
1-Methyl-4-(octyn-1-yl)benzene (3jd)



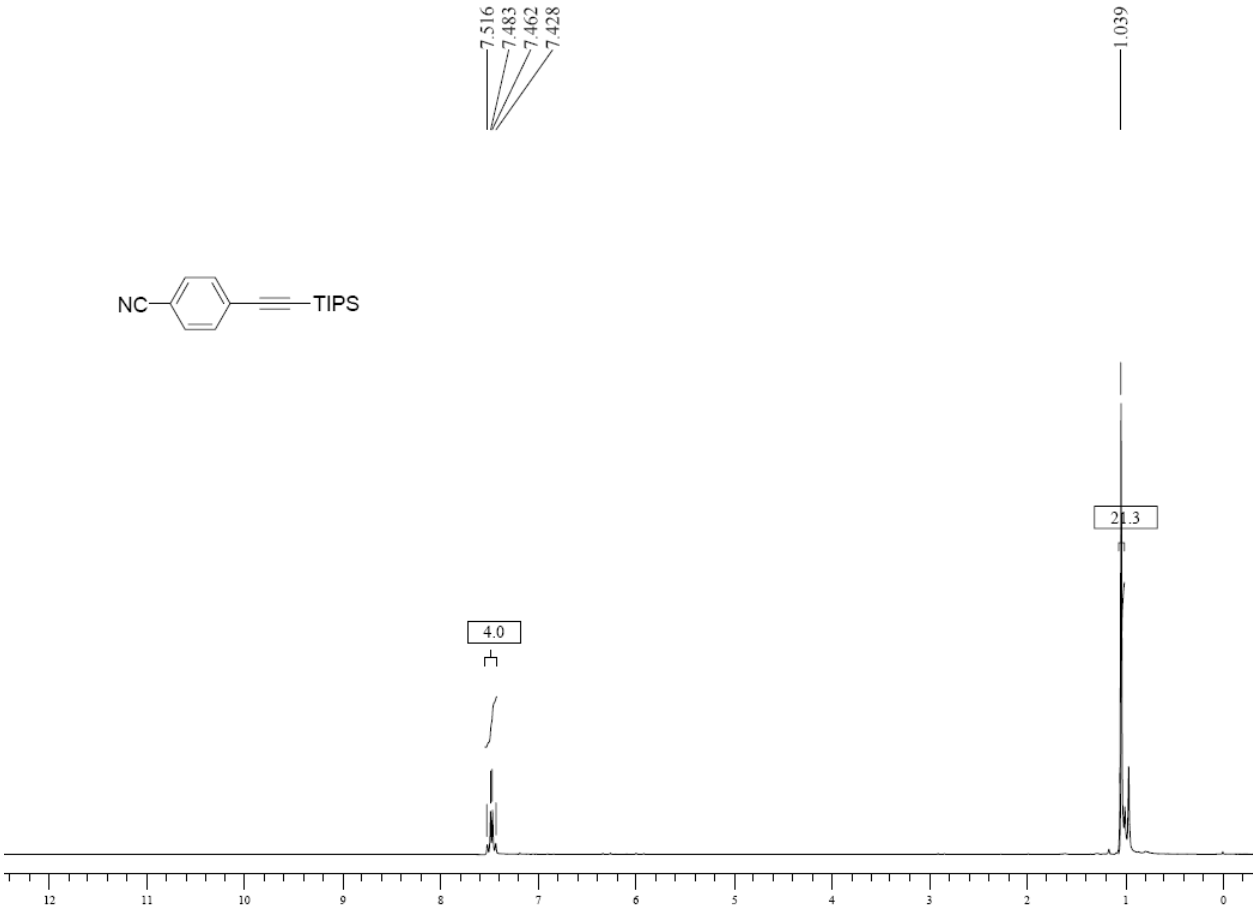


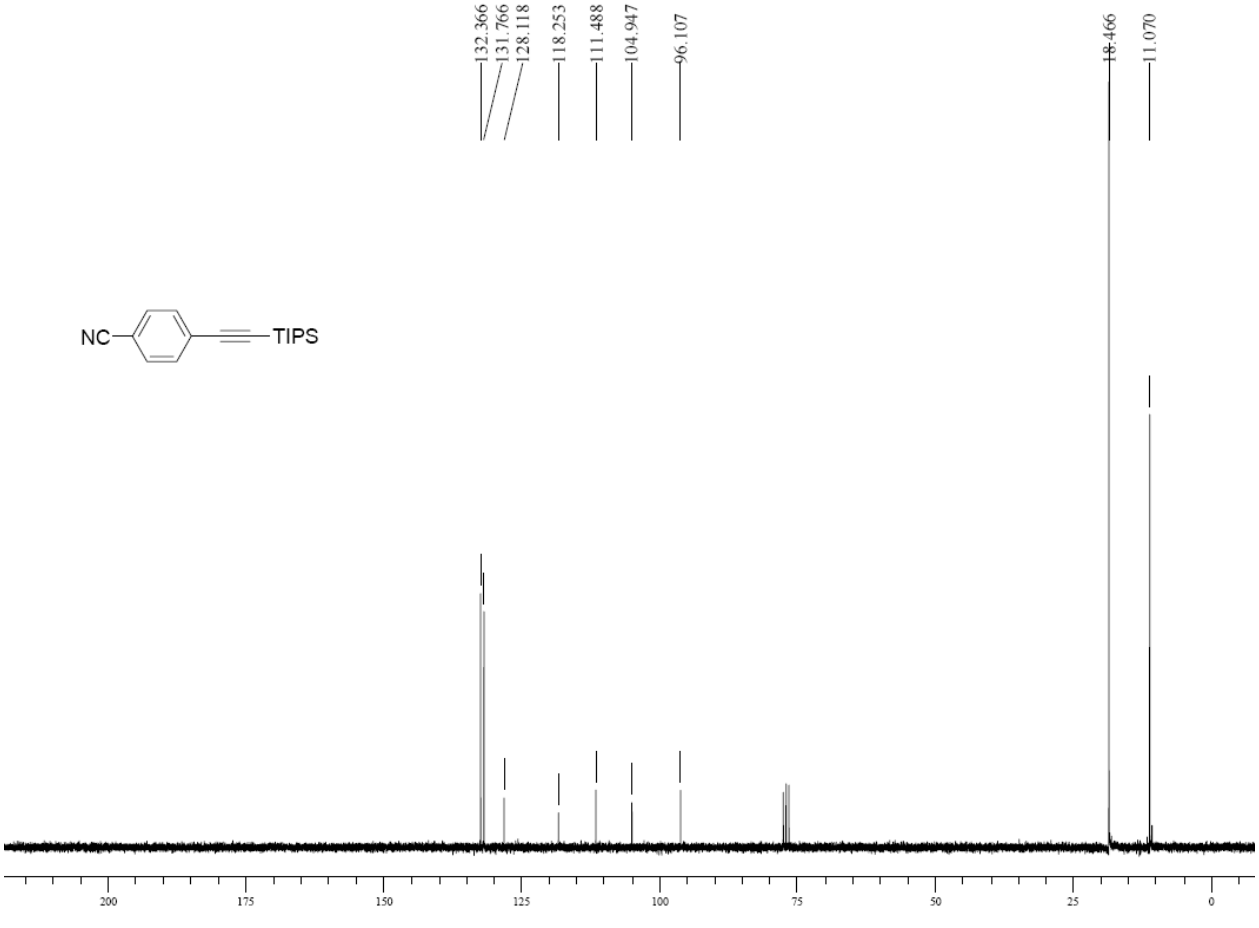
Triisoprolysilylethynyl-benzene (3ae)



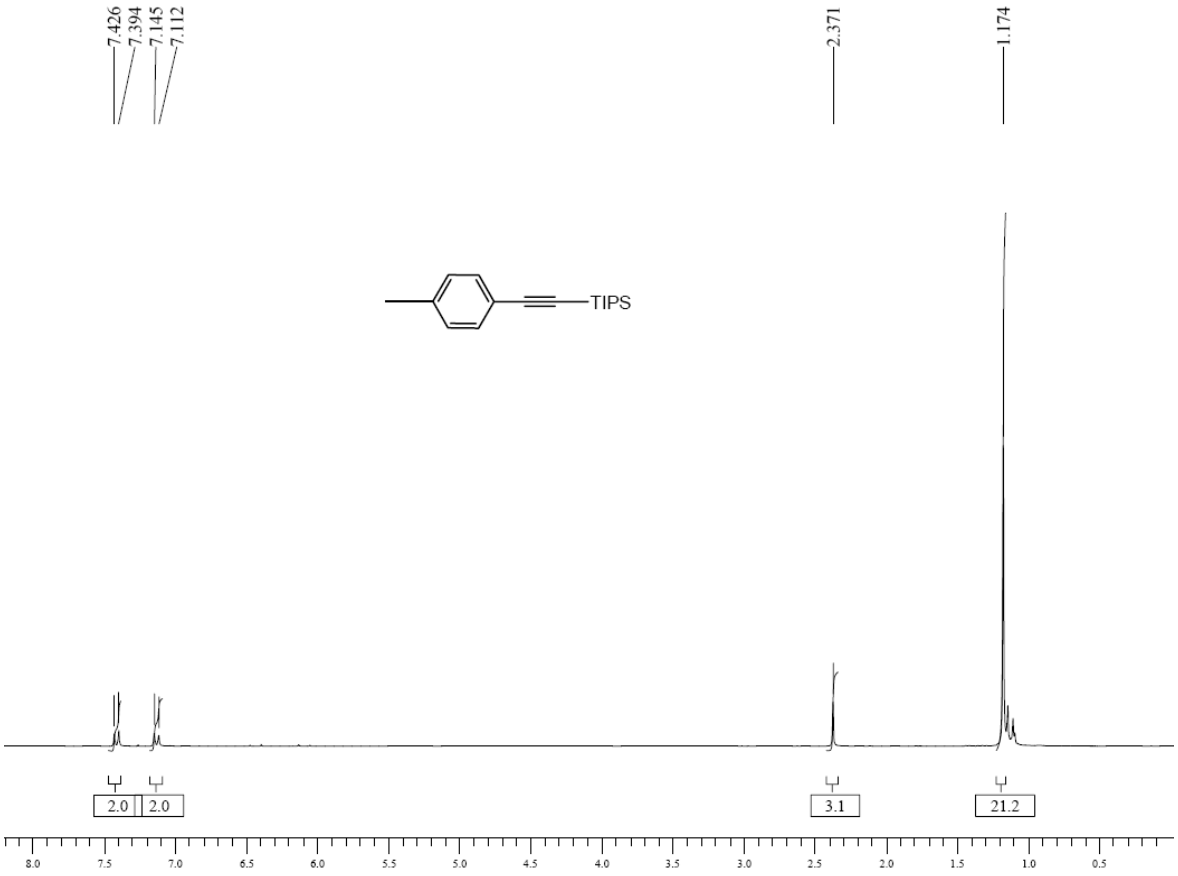


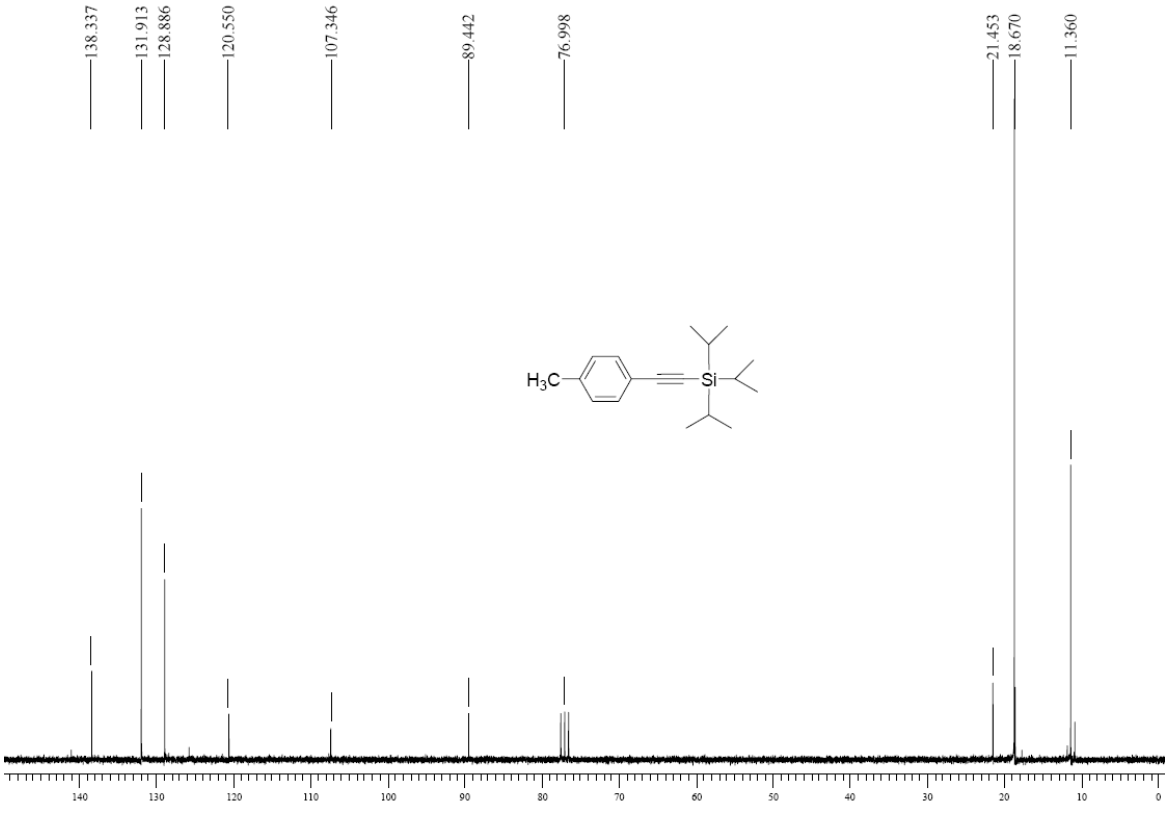
4-Triisoprolysilylethynyl-benzonitrile (3fe)



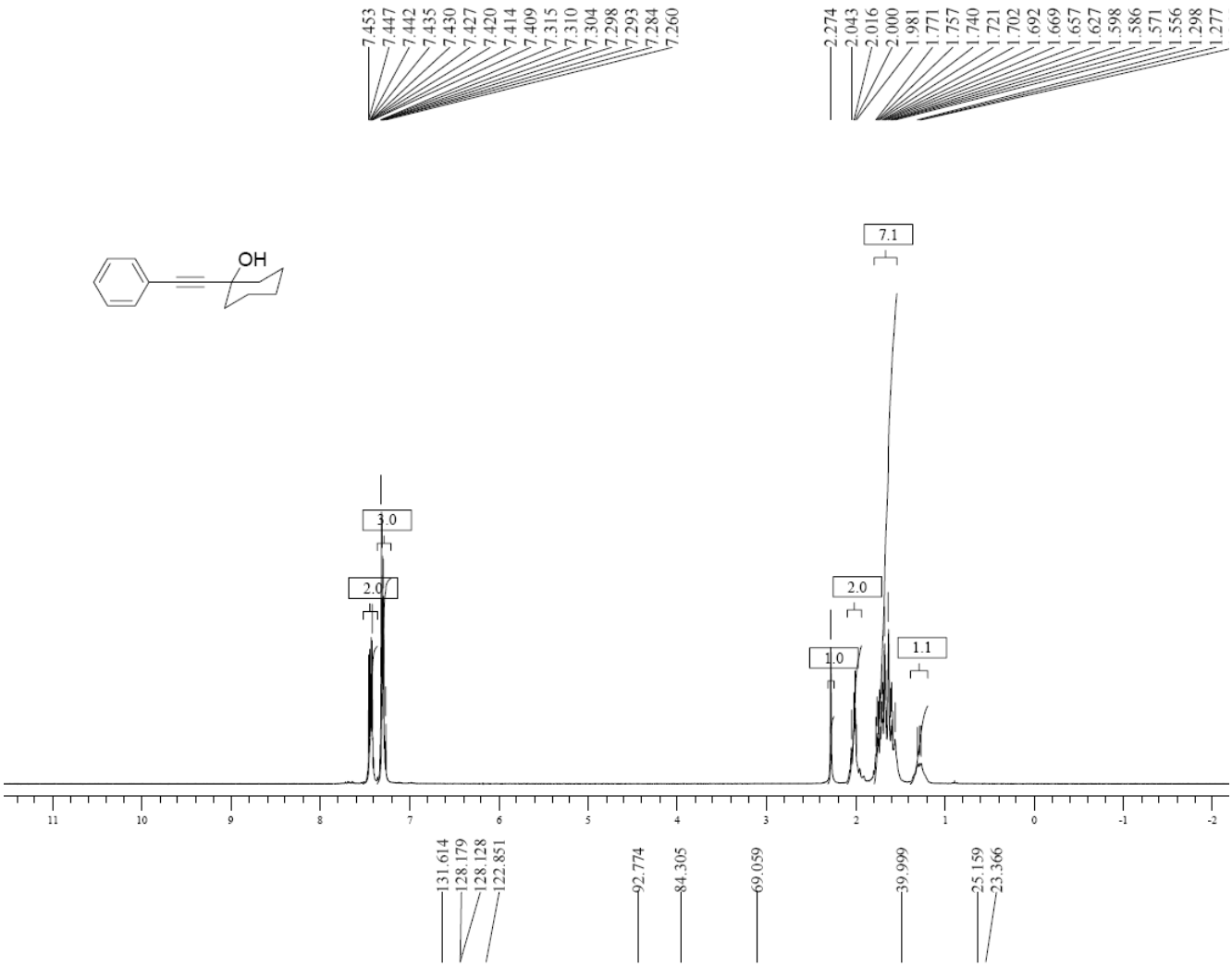


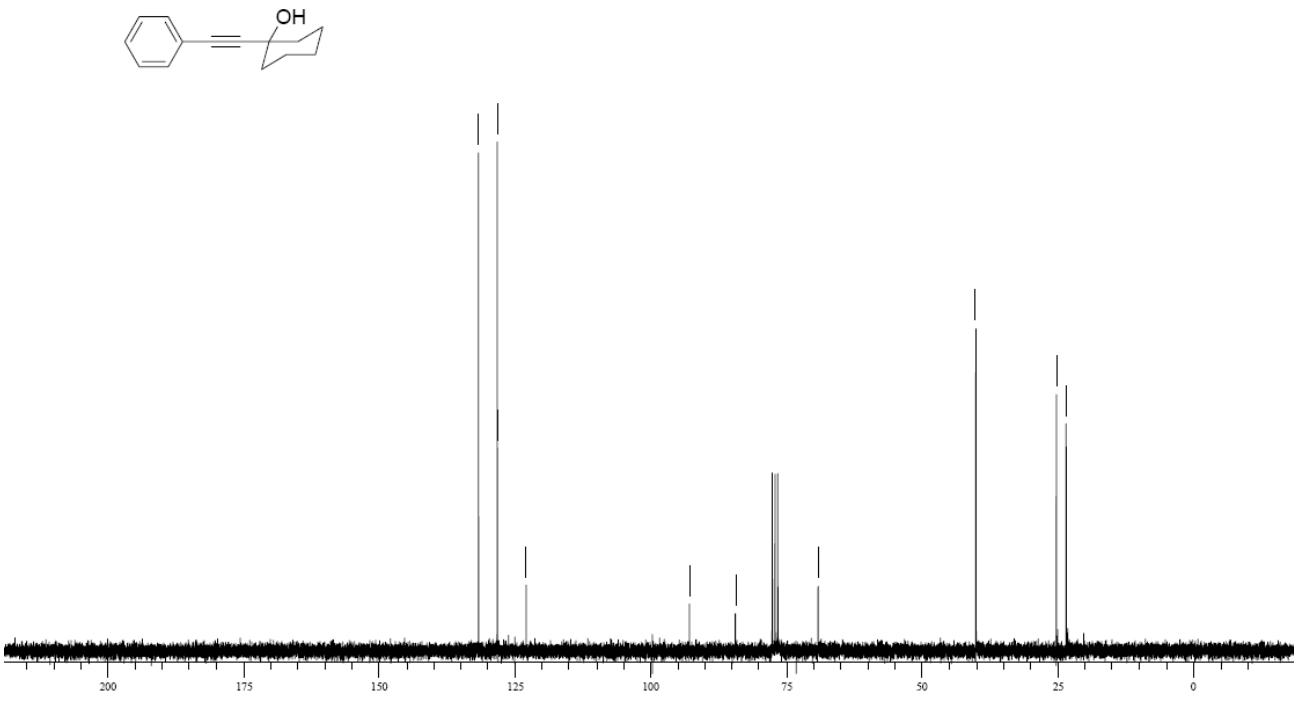
4-Triisoprolysilylethynyl-toluene (3je)



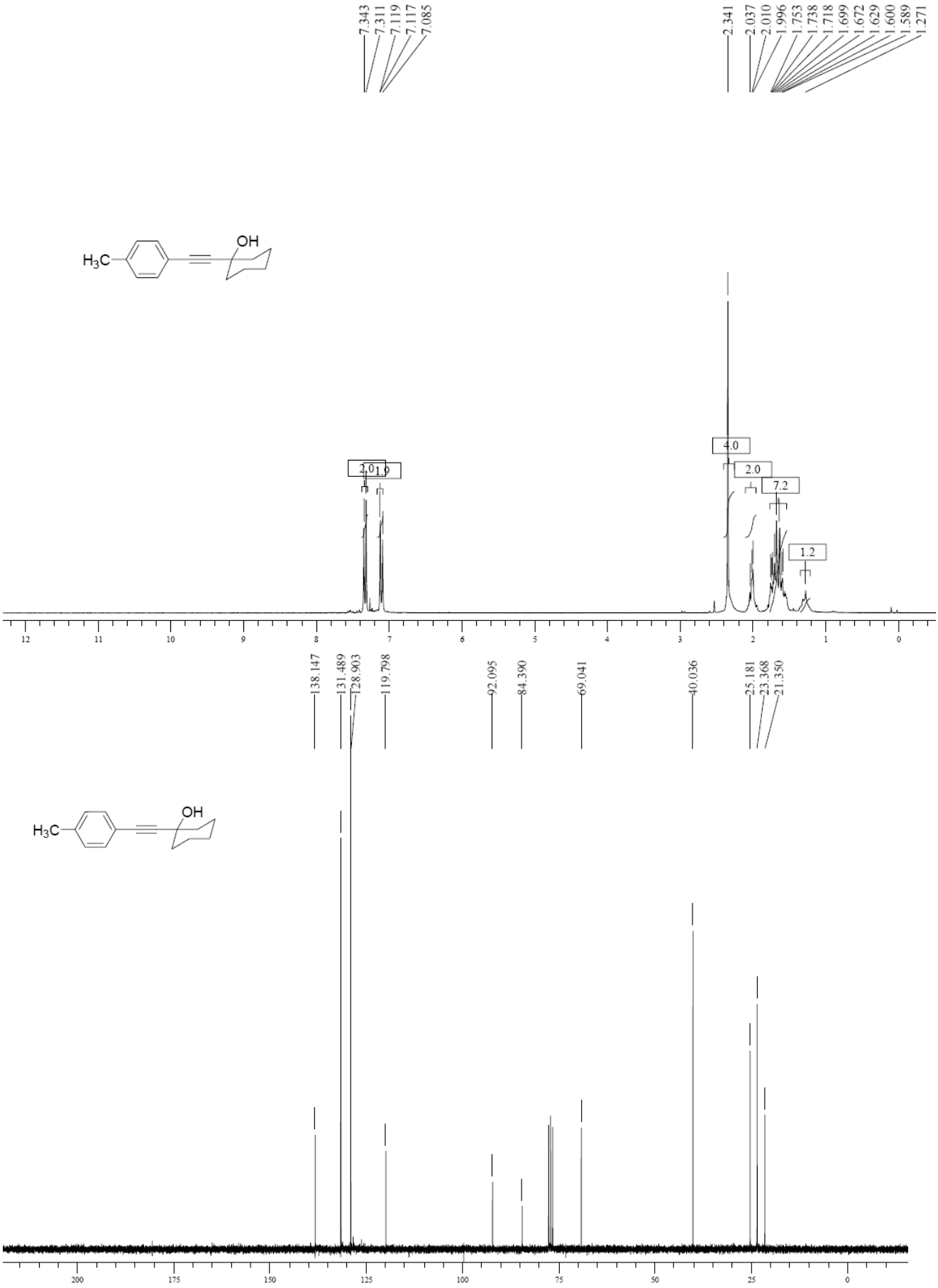


1-Phenylethynyl-1-cyclohexanol (3af)

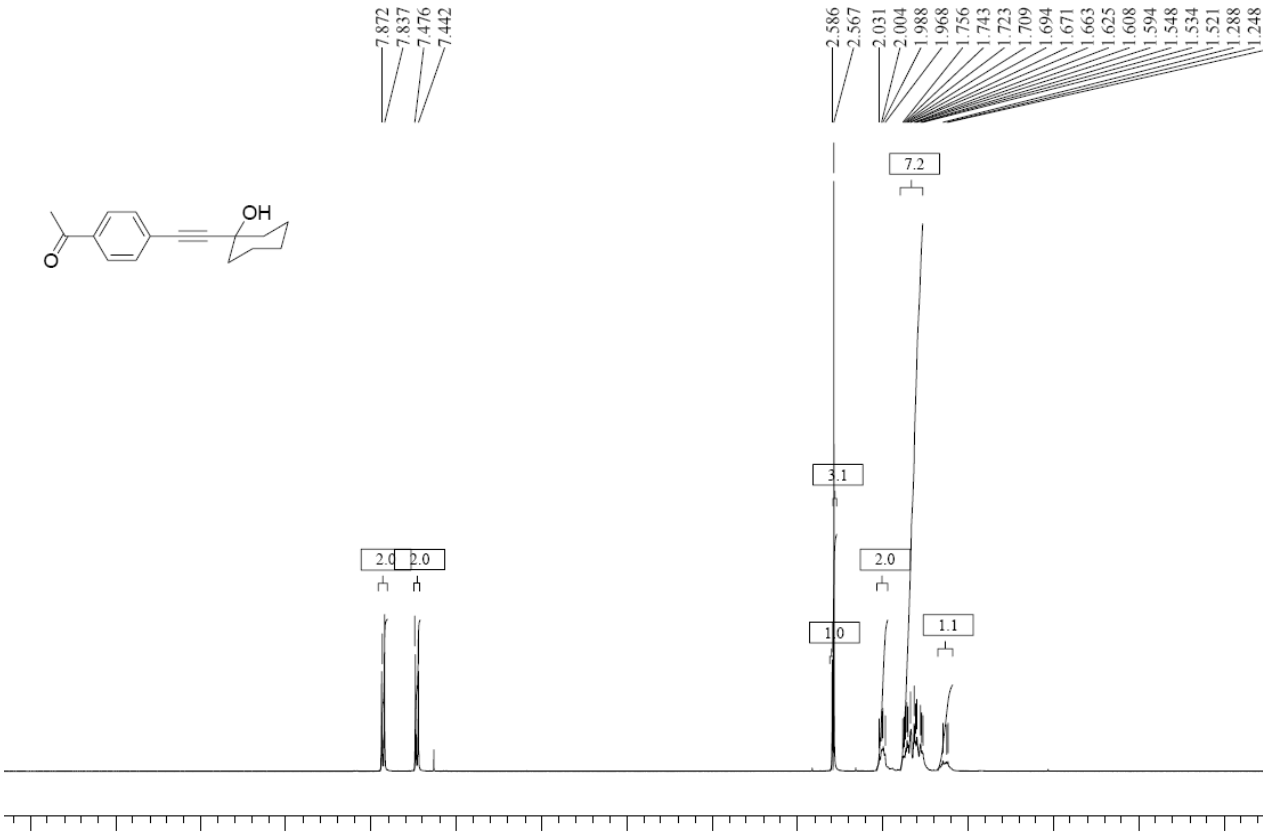


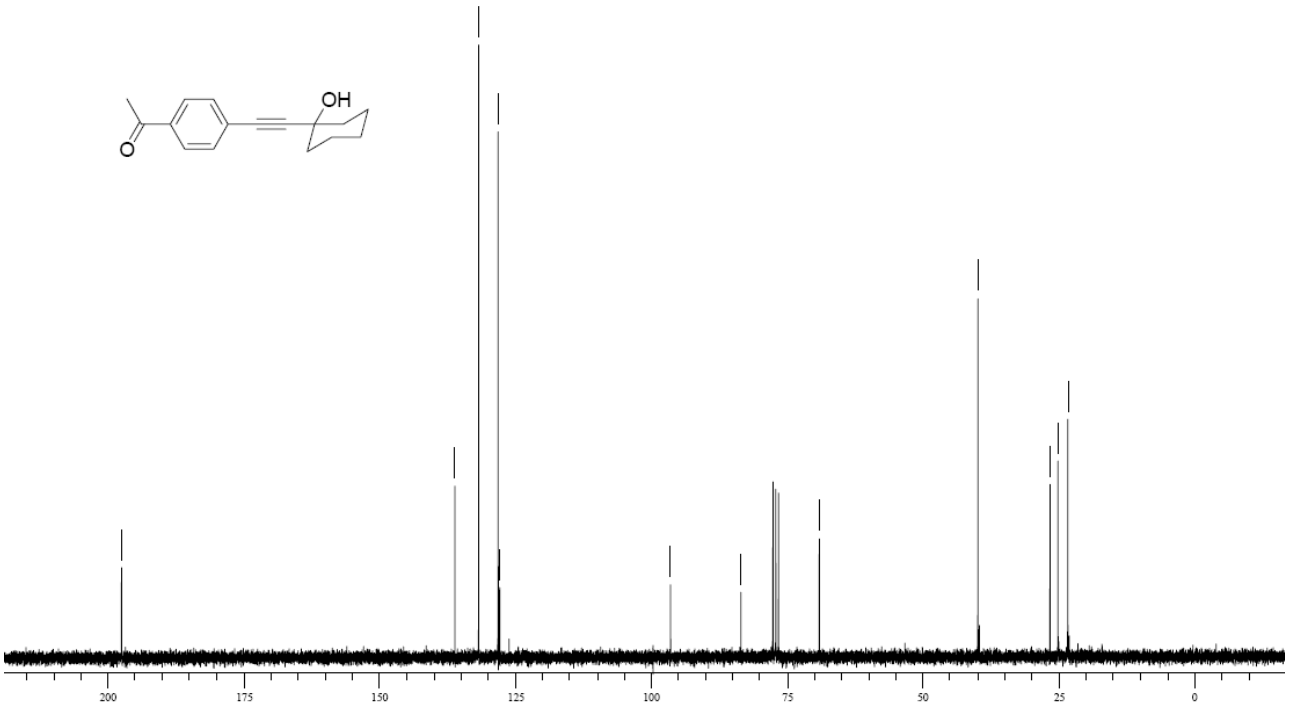


1-(4'-Tolylethynyl)-1-cyclohexanol (3ff)



1-(4'-Acetylphenyl)ethynyl-1-cyclohexanol (3hf)





REFERENCES

[1] Mathé, T.; Tungler, A.; Petro, J. U. S. Patent 4 361 500;.
[2] Pinhua L.; Lei W.; Hongji L.; *Tetrahedron* **2005,** *61,* 8633-8640.
3 Sakai, N.; Annaka, K.; Konakahara, T.; *Org. Lett.* **2004,** *6,* 1527-1530.
4 Cheng, J.; Sun, Y.; Wang, F.; Guo, M.; Xu, J-H.; Pan, Y.; Zhang, Z.; *J. Org. Chem.***2004,** *69,* 5428-5432.
5 Novák, Z.; Nemes, P.; Kotschy, A.; *Org. Lett.* **2004,** *6,* 4917-4920.
[6] Ranu, B. C.; Jana, R. *J. Org. Chem.* **2005,** *70,* 8621-8624.
7 Torres, G. H.; Choppin, S.; Colobert, F.; *Eur. J. Org. Chem.* **2006,** 1450-1454.
8 Sweis R. F.; Scramm, M. P.; Kozmin, S. A.; *J. Am. Chem. Soc.* **2004,** *126,* 7442-7443.
9 Urganokar, S.; Verkade J. G.; *J. Org. Chem.***2004,** *69,* 5752-5755.
10 Maifeld, S. V.; Lee, D.;*Org. Lett.*, **2005**, *7,*4995-4998.
[11] Golap, A. R.; Venkatesan, K.; Pasricha, R.; Daniel, T.; Lahoti, R. J.; Srinivasan, K. V. *J. Org. Chem.* **2005,** *70,* 4869-4872.