Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Microwave-assisted Palladium-catalyzed Highly Regio- and Stereoselective Head to Head Dimerization of Terminal Aryl Alkynes in Water

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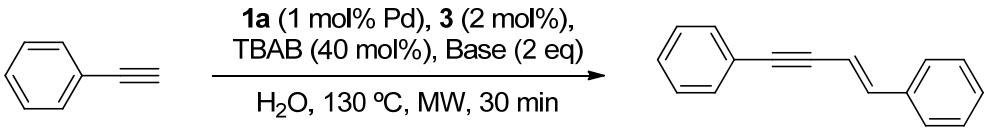
1. General

Unless otherwise noted, all commercial reagents and solvents were used without further purification. All the employed surfactants: tetra-*n*-butylammonium bromide (TBAB, Alfa Aesar), hexadecyltrimethylammonium bromide (CTAB, Alfa Aesar), polyoxyethanyl-α-tocopheryl sebacate (PTS, Sigma-Aldrich), and sodium dodecylbenzenesulfonate (SDBS, Sigma-Aldrich) were commercially available and were used without further purification. All ligands and palladium catalysts were commercially available (Sigma-Aldrich). Ligands **6-9**[1] were provided by Dr. Isidro M. Pastor, from Alicante University. Melting points were determined with a Reichert Thermovar hot plate apparatus and were not corrected. IR spectra were recorded on a Nicolet 510 P-FT apparatus. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were obtained on a Bruker AC-300, using $CDCl_3$ as solvent and TMS as internal standard, unless otherwise stated. Proton and carbon chemical shifts are given in ppm and coupling constants in Hz. Low-resolution electron impact (EI) mass spectra were obtained at 70 EV on an Agilent 5973 Network Mass selective detector. High-resolution mass spectra were obtained either with an electron impact (EI, 70 eV) Agilent 7200 QTOF apparatus or with a Waters LCT Premier XE apparatus (ESI, TOF).

Analytical TLC was performed on Merck aluminium sheets with silica gel 60 F_{254}. Silica gel 60, (0.04-0.06 mm) was employed for flash chromatography. Silica gel 60 F_{254} containing gypsum was employed for preparative layer chromatography. Microwave reactions were performed with a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC) with a continuous focused microwave power delivery system in glass vessels (10 ml) sealed with a septum under magnetic stirring. The temperature of the reaction mixture inside the vessel was monitored using a calibrated infrared temperature control under the reaction vessel.

2. Base optimization



Entry	Base	Conversion (%)[a]	Yield (%)[b]
1	Pyrrolidine	84	69
2	KOH	47	39
3	Cs_2CO_3	76	41
4	K_2CO_3	76	45
5	Et_3N	99	82
6	$^{i}Pr_2NH$	99	75
7	Piperidine	99	55

[a] Determined by GC. [b] Isolated yield after preparative thin layer chromatography.

3. Mercury poisoning experiment

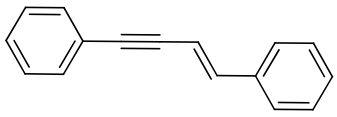
A 10 mL MW vessel was charged with phenylacetylene (55 μL, 0.5 mmol, 1 equiv), TEA (140 μL, 1 mmol, 2 equiv), TBAB (64.5 mg, 0.2 mmol, 40 mol%) catalyst **1a** (1.2 mg, 1 mol% Pd), ligand **3** (4.3 mg, 2 mol%) and H_2O (1 mL). The vessel was sealed with a pressure lock, and the mixture was heated in air at 130 ºC for 5 min with the aid of an initial 40 W MW irradiation in a CEM Discover MW reactor. After this time, Hg (175 mg, 0.875 mmol, 350 equiv) was added and the reaction was heated again at 130 ºC for 30 min under the above mentioned conditions. Then, the reaction mixture was cooled to room temperature and extracted with EtOAc (3 x 10 mL), and the organic layers were washed with H_2O (3 x 10 mL), dried over $MgSO_4$, filtered over Celite, and concentrated under reduced pressure. The reaction conversion was checked after 1 minute without Hg (70%) and after 30 minutes in the presence of excess

of Hg (full conversion), demonstrating that Pd nanoparticles were not the active species in the dimerization process.

4. Typical procedure for the alkyne dimerization in water under MW irradiation conditions

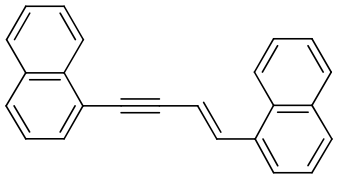
A 10 mL MW vessel was charged with phenylacetylene (55 μL, 0.5 mmol, 1 equiv), TEA (140 μL, 1 mmol, 2 equiv), TBAB (64.5 mg, 0.2 mmol, 40 mol%) catalyst **1a** (1.2 mg, 1 mol% Pd), ligand **3** (4.3 mg, 2 mol%) and H_2O (1 mL). The vessel was sealed with a pressure lock, and the mixture was heated in air at 130 ºC for 30 min with the aid of an initial 40 W MW irradiation in a CEM Discover MW reactor. After this time, the reaction mixture was extracted with EtOAc (3 x 10 mL), and the organic layers were washed with H_2O (3 x 10 mL), dried over $MgSO_4$, filtered over Celite, and concentrated under reduced pressure. The crude mixture was purified by preparative thin layer chromatography, obtaining **2a** in an 82% isolated yield.

5. Physical and spectroscopic data



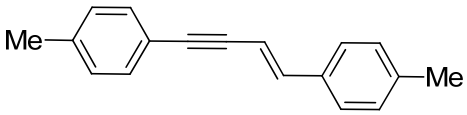
(*E*)-but-1-en-3-yne-1,4-diyldibenzene (2a**).**[2]

^{1}H NMR: δ = 7.54-7.45 (4H, m), 7.41-7.33 (6H, m), 7.09 (1H, d, *J* = 16.3), 6.43 (1H, d, *J* = 16.2); ^{13}C-NMR (101 MHz): δ = 141.3, 136.3, 131.5, 128.8, 128.6, 128.4, 128.2, 126.3, 123.4, 108.1, 91.8, 88.9; MS (*m/z*) = 205 (M^++1, 14), 204 (M^+, 100), 203 (95), 202 (87), 201 (14), 200 (10).



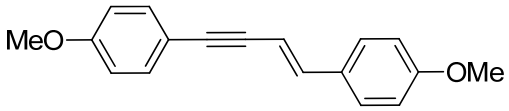
(*E*)-1,1'-(but-1-en-3-yne-1,4-diyl)dinaphthalene (2b**).**[3]

^{1}H NMR: δ = 8.44 (1H, d, *J* = 8.3), 8.23 (1H, d, *J* = 8.2), 7.95 (1H, d, *J* = 16.0), 7.86 (4H, t, *J* = 8.5), 7.78-7.72 (2H, m), 7.65-7.44 (7H, m), 6.62 (1H, d, *J* = 16.0); ^{13}C-NMR: δ = 138.4, 133.8, 133.7, 133.2, 130.9, 130.5, 129.1, 128.8, 128.6, 128.3, 126.8, 126.5, 126.3, 126.0, 125.6, 125.3, 123.6, 123.5, 121.0, 110.9, 94.1, 89.8; MS (*m/z*) = 305 (M^++1, 11), 304 (M^+, 54), 303 (100), 302 (82), 301 (13), 300 (24), 151 (24), 150 (17).



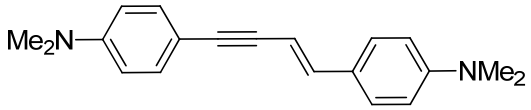
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)bis(methylbenzene) (2c**).**[2]

^{1}H NMR: δ = 7.37-7.30 (4H, m), 7.15-7.11 (4H, m), 6.99 (1H, d, *J* = 16.2), 6.32 (1H, d, *J* = 16.2), 2.35 (6H, s); ^{13}C-NMR (101 MHz): δ = 140.9, 138.6, 138.2, 133.7, 131.4, 129.5, 129.1, 126.2, 120.4, 107.2, 91.6, 88.5, 21.5, 21.3; MS (*m/z*) = 233 (M^++1, 20), 232 (M^+, 100), 231 (27), 217 (44), 216 (32), 215 (45), 203 (11), 202 (51).



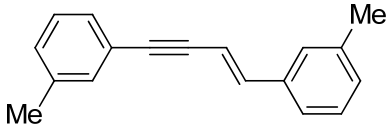
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)bis(methoxybenzene) (2d**).**[2]

^{1}H NMR: δ = 7.44-7.36 (8H, m), 6.98 (1H, d, *J* = 16.2), 6.89 (1H, d, *J* = 16.2), 3.84 (6H); ^{13}C-NMR (101 MHz): δ = 159.9, 159.4, 140.1, 132.9, 129.4, 127.5, 115.7, 114.2, 144.0, 106.0, 91.0, 87.9, 55.3, 55.3; MS (*m/z*) = 265 (M^++1, 20), 264 (M^+, 100), 249 (26), 221 (12), 206 (11), 189 (13), 178 (17).



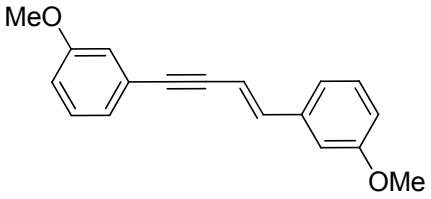
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)bis(*N,N*-dimethylaniline) (2e**).**[2]

^{1}H NMR: δ = 7.35-7.29 (4H, m), 6.90 (1H, d, *J* = 16.2), 6.68-6.62 (4H, m), 6.17 (1H, d, *J* = 16.2), 2.97 (12H, s); ^{13}C-NMR (101 MHz): δ = 150.4, 149.8, 139.8, 132.5, 127.3, 125.2, 112.2, 111.9, 110.8, 103.8, 91.6, 87.8, 40.4, 40.3; MS (*m/z*) = 291 (M^++1, 22), 290 (M^+, 100), 289 (12), 274 (11), 202 (10), 145 (11), 144 (15).



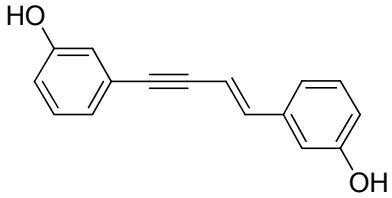
(*E*)-3,3'-(but-1-en-3-yne-1,4-diyl)bis(methylbenzene) (2f**).**[2]

^{1}H NMR: δ = 7.30-7.18 (6H, m), 7.13-7.08 (2H, m), 6.99 (1H, d, *J* = 16.2), 6.36 (1H, d, *J* = 16.2), 2.35 (3H, s), 2.33 (3H, s); ^{13}C-NMR (101 MHz): δ = 141.3, 138.3, 138.0, 136.3, 132.1, 129.4, 129.1, 128.6, 128.6, 128.2, 127.0, 123.5, 123.3, 108.0, 91.8, 88.7, 21.4 21.2; MS (*m/z*) = 233 (M^++1, 19), 232 (M^+, 100), 231 (42), 218 (15), 217 (85), 216 (52), 215 (80), 203 (17), 202 (71), 189 (11).



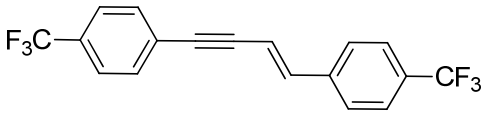
(*E*)-3,3'-(But-1-en-3-yne-1,4-diyl)bis(methoxybenzene) (2g**).**[2]

^{1}H-RMN: δ = 7.29-7.19 (2H, m), 7.09-6.94 (5H, m), 6.90-6.81 (2H, m), 6.37 (1H, d, *J* = 16.2), 3.82 (3H, s), 3.80 (3H, s); ^{13}C-RMN (101 MHz): δ = 159.9, 159.3, 141.3, 137.7, 129.7, 129.4, 124.4, 124.1, 119.0, 116.3, 114.9, 114.3, 111.6, 108.4, 91.9, 88.7, 55.3; MS (*m/z*) = 265 (M^++1, 19), 264 (M^+, 100), 233, (10), 221 (29), 218 (11), 205 (12), 202 (12), 190 (12), 189 (28), 178 (20), 176 (14).



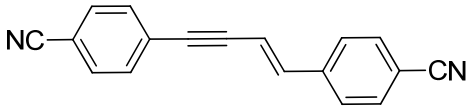
(*E*)-3,3'-(But-1-en-3-yne-1,4-diyl)diphenol (2h**).**

White solid, Mp.132-134 (EtOAc/Hexane); IR: ν (cm^{-1}) = 3249, 2922, 2853, 1584, 1446, 776, 680; ^{1}H-RMN: δ = 7.21-7.14 (2H, m), 6.99-6.90 (5H, m), 6.79 (2H, t, *J* = 7.4), 6.33 (1H, d, *J* = 16.2); ^{13}C-RMN (101 MHz): δ = 156.9, 156.5, 141.2, 137.7, 129.7, 129.4, 124.2, 123.2, 118.2, 118.0, 115.8, 112.7, 108.0, 91.7, 88.4; MS (*m/z*) = 237 (M^++1, 15), 236 (M^+, 100), 235 (36), 219 (13), 208 (12), 207 (40), 189 (22), 179 (13), 178 (20), 165 (11), 152 (12); HRMS calcd. for $C_{16}H_{12}O_2$ 236.0837, found 236.0831.



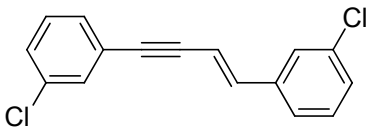
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)bis[(trifluoromethyl)benzene] (2i**).**[2]

^{1}H NMR: δ = 7.62-7.51 (8H, m), 7.10 (1H, d, *J* = 16.3), 6.47 (1H, d, *J* = 16.3); ^{13}C-NMR (101 MHz): δ = 140.7, 139.3, 131.8, 130.5 (q, *J* = 32.7), 130.1 (q, *J* = 32.5), 126.8, 126.5, 125.8 (q, *J* = 3.3), 125.3 (q, *J* = 3.5), 123.9 (q, *J* = 272.0), 123.8 (q, *J* = 272.0), 110.2, 91.5, 90.5; MS (*m/z*) = 341 (M^++1, 20), 340 (M^+, 100), 321 (16), 271, (21), 270 (19), 251 (20), 202 (32).



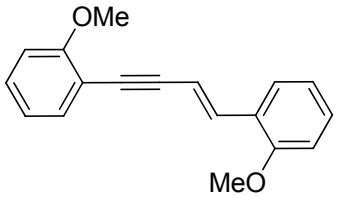
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)dibenzonitrile (2j**).**[3]

^{1}H NMR: δ = 7.67-7.63 (4H, m), 7.57-7.51 (4H, m), 7.08 (1H, d, *J* = 16.3), 6.49 (1H, d, *J* = 16.2); ^{13}C-NMR (101 MHz): δ = 140.7, 140.1, 132.6, 132.1, 132.1, 127.8, 126.9, 118.6, 118.4, 112.2, 111.9, 111.2, 92.2, 92.0; MS (*m/z*) = 255 (M^{+}+1, 19), 254 (M^{+}, 100), 253 (62), 252 (24), 227 (18), 226 (24), 225 (10).



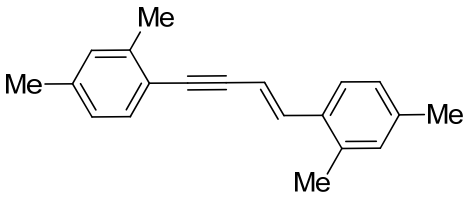
(*E*)-3,3'-(but-1-en-3-yne-1,4-diyl)bis(chlorobenzene) (2k**).**[4]

Colorless oil; ^{1}H NMR: δ = 7.46-7.45 (1H, m), 7.40-7.39 (1H, m), 7.34 (1H, dt, *J* = 7.0, 1.6), 7.32-7.25 (5H, m), 6.97 (1H, d, *J* = 16.2), 6.36 (1H, d, *J* = 16.2); ^{13}C-NMR (101 MHz): δ = 140.4, 137.9, 134.8, 134.2, 131.4, 130.0, 129.7, 129.6, 128.7, 128.6, 126.2, 124.9, 124.6, 109.3, 91.0, 89.5; MS (*m/z*) = 276 (M^{+}+4, 5), 274 (M^{+}+2, 26), 272 (M^{+}, 40), 236 (11), 203 (17), 202 (100), 201 (17), 200 (19); HRMS calcd. for $C_{16}H_{10}Cl_2$ 272.0158, found 272.0154.



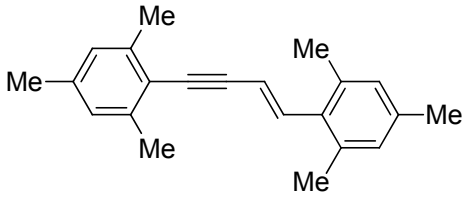
(*E*)-2,2'-(But-1-en-3-yne-1,4-diyl)bis(methoxybenzene) (2l**).**[2]

^{1}H-RMN (400 MHz): δ = 7.44 (2H, dt, *J* = 7.7, 2.0), 7.36 (1H, d, *J* = 16.4), 7.31-7.20 (2H, m), 6.96-6.84 (4H, m), 6.53 (1H, d, *J* = 16.4), 3.90 (3H, s), 3.85 (3H, s); ^{13}C-RMN (101 MHz): δ = 159.8, 157.0, 136.4, 133.5, 129.5, 126.9, 125.5, 120.7, 120.5, 112.8, 111.0, 110.6, 109.1, 93.8, 87.6, 55.8, 55.5; MS (*m/z*) = 265 (M^{+}+1, 20), 264 (M^{+}, 100), 218 (16), 205 (18), 202 (12), 178 (10), 131 (14), 119 (14), 91 (17).



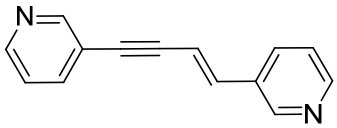
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)bis(1,3-dimethylbenzene) (2m**).**

White solid, Mp. 96-98 ºC (EtOAc/Hexane); IR (film): ν (cm^{-1}) = 2916, 1607, 1488, 956, 812, 805; ^{1}H NMR: δ = 7.45 (1H, d, *J* =8.5), 7.38 (1H, d, *J* = 7.8), 7.26 (1H, d, *J* = 16.1), 7.07-6.98 (4H, m), 6.34 (1H, d, *J* = 16.1), 2.48 (3H, s), 2.40 (3H, s), 2.36 (3H, s), 2.35 (3H, s); ^{13}C-NMR: δ = 139.9, 138.3, 138.22, 138.18, 135.6, 132.6, 131.7, 131.3, 130.3, 127.0, 126.4, 124.8, 120.2, 108.4, 92.5, 90.3, 21.4, 21.2, 20.7, 19.7; MS (*m/z*) = 261 (M^++1, 22), 260 (M^+, 100), 259 (13), 245 (39), 244 (18), 230 (56), 229 (46), 228 (15), 115 (11), 114 (11); HRMS calcd. for $C_{20}H_{20}$ 260.1565, found 260.1561.



(*E*)-2,2'-(but-1-en-3-yne-1,4-diyl)bis(1,3,5-trimethylbenzene) (2n**).**[2]

^{1}H NMR: δ = 7.09 (1H, d, *J* = 16.5), 6.92 (4H, d, *J* = 3.0), 6.05 (1H, d, *J* = 16.5), 2.48 (6H, s), 2.39 (6H, s), 2.32 (6H, s); ^{13}C-NMR: δ = 140.0, 138.6, 137.6, 136.9, 136.1, 133.0, 128.9, 127.6, 120.2, 113.8, 96.4, 88.7, 21.3, 21.1, 21.0, 21.0; MS (*m/z*) = 289 (M^++1, 20), 288 (M^+, 100), 274 (12), 273 (35), 259 (20), 258 (61), 257 (22), 244 (14), 243 (57), 241 (12), 238 (16), 227 (12), 132 (14), 129 (12), 128 (24), 115 (12).



(*E*)-3,3'-(but-1-en-3-yne-1,4-diyl)dipyridine (2o**).**[2]

^{1}H NMR: δ = 8.69 (2H, dd, *J* = 17.8, 1.7), 8.56-8.53 (2H, m), 7.76 (2H, dt, *J* = 7.9, 1.9 Hz), 7.32-7.26 (2H, m), 7.07 (1H, d, *J* = 16.3), 6.46 (1H, d, *J* = 16.3); ^{13}C-NMR (101 MHz): δ = 152.2, 149.8, 148.7, 148.3, 138.5, 138.4, 132.5, 131.7, 123.6, 123.1, 120.3, 109.8, 91.4, 89.2; MS (*m/z*) = 207 (M^++1, 10), 206 (M^+, 70), 205 (100), 178 (18).

6. References

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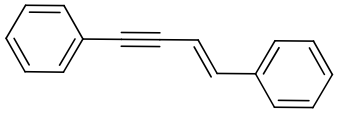
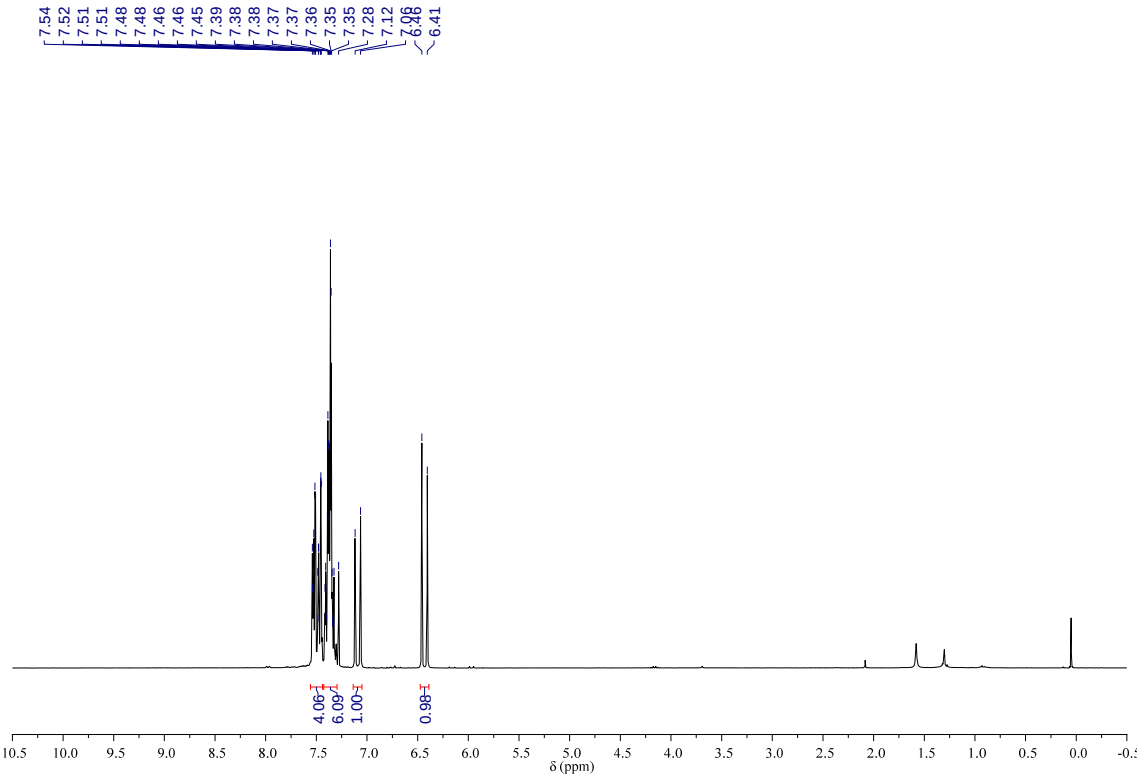
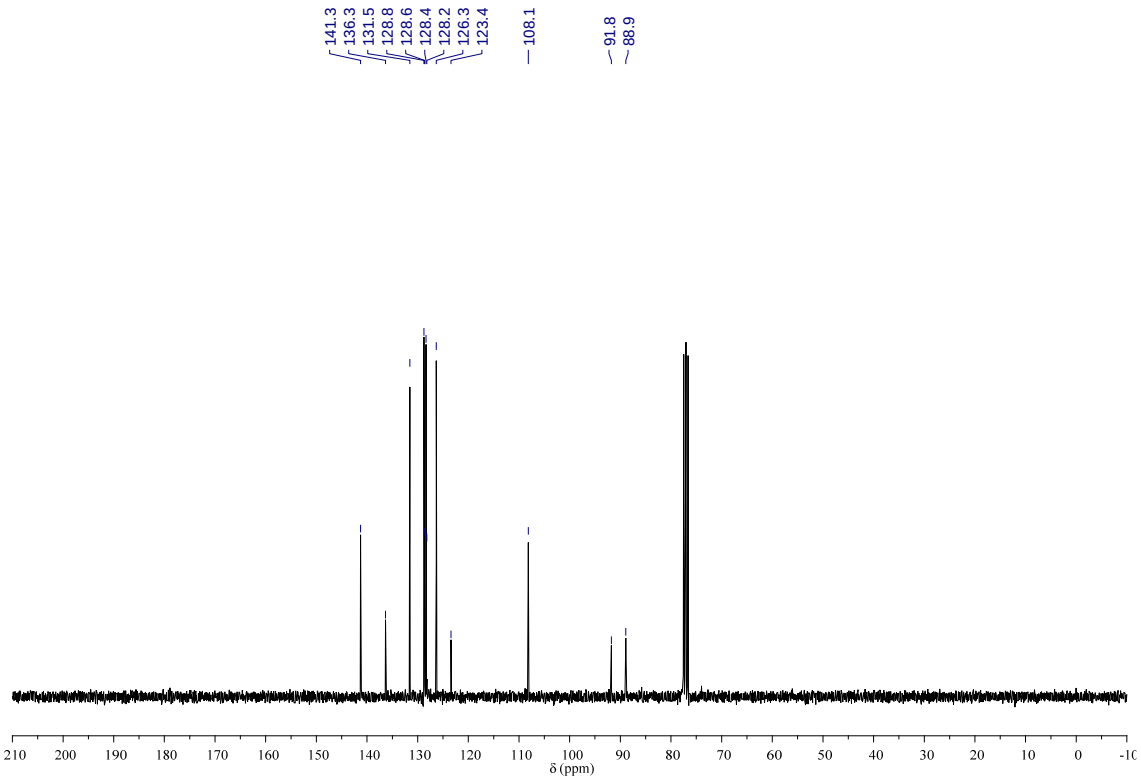
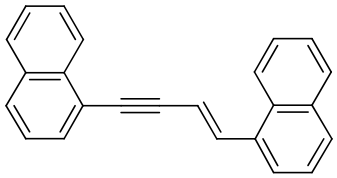
7. ^{1}H-NMR and ^{13}C-NMR spectra



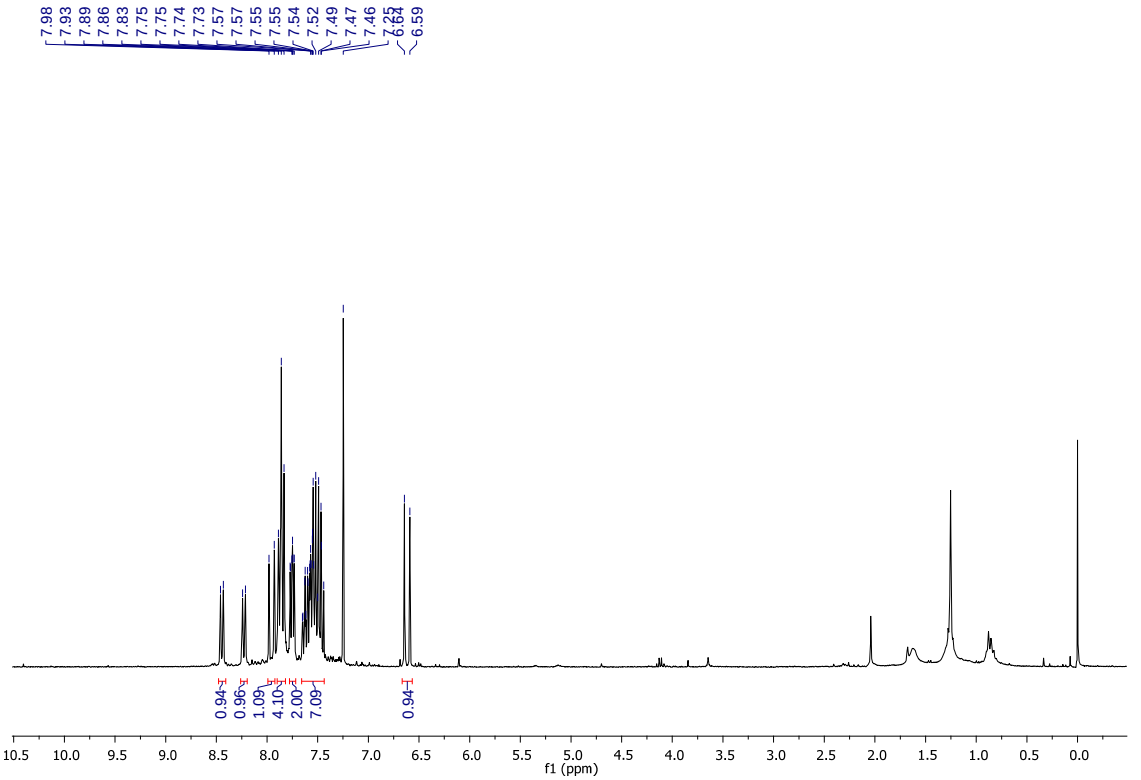
(*E*)-but-1-en-3-yne-1,4-diyldibenzene (2a**).**

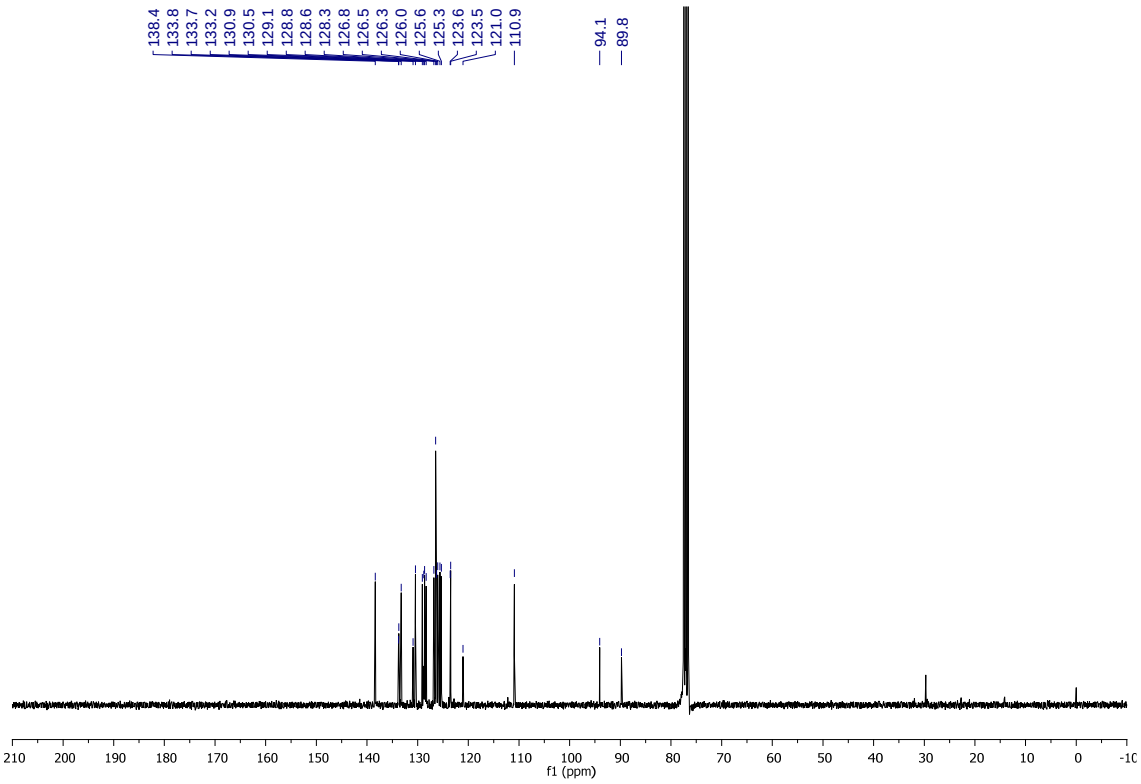


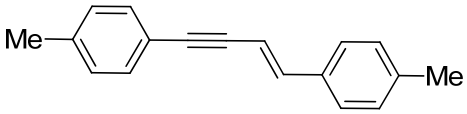




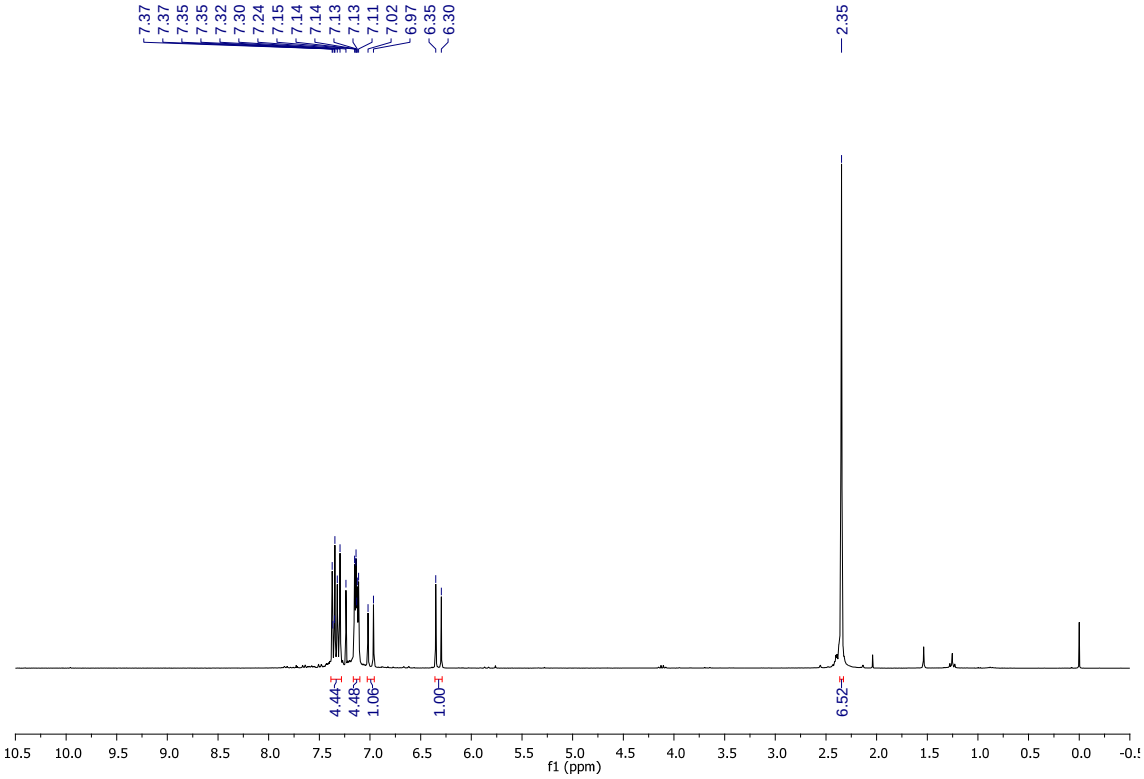
(*E*)-1,1'-(but-1-en-3-yne-1,4-diyl)dinaphthalene (2b**).**

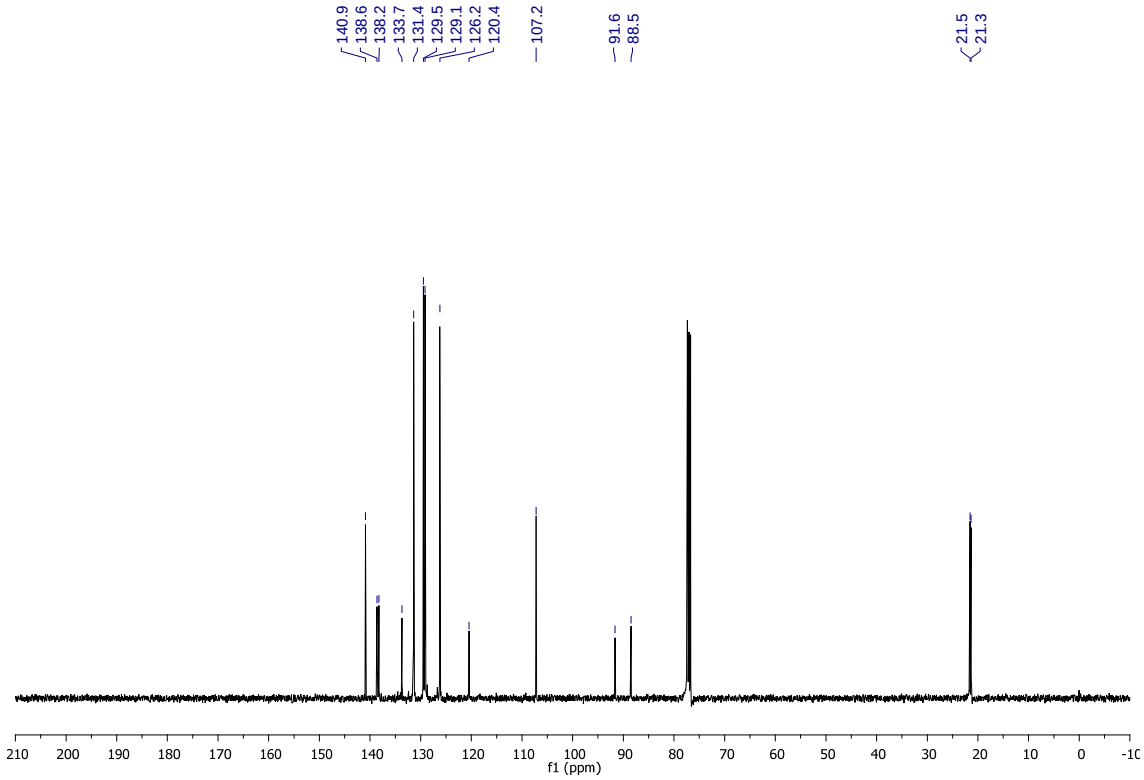


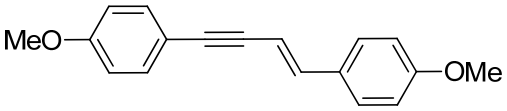




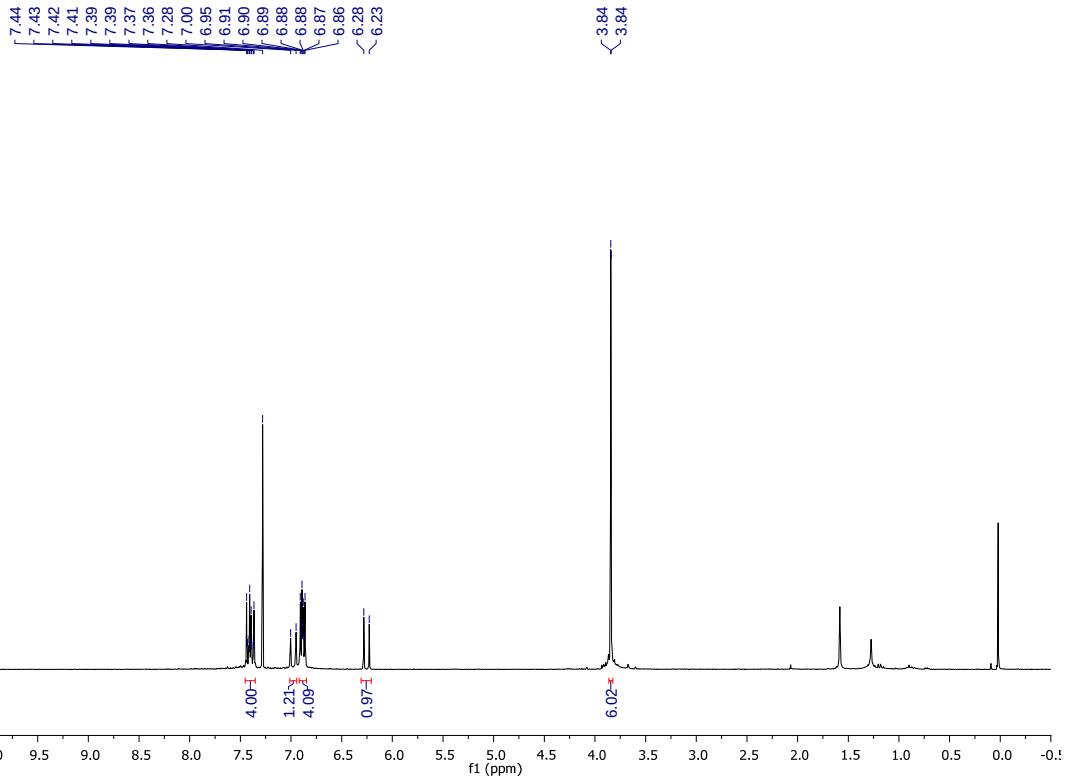
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)bis(methylbenzene) (2c).

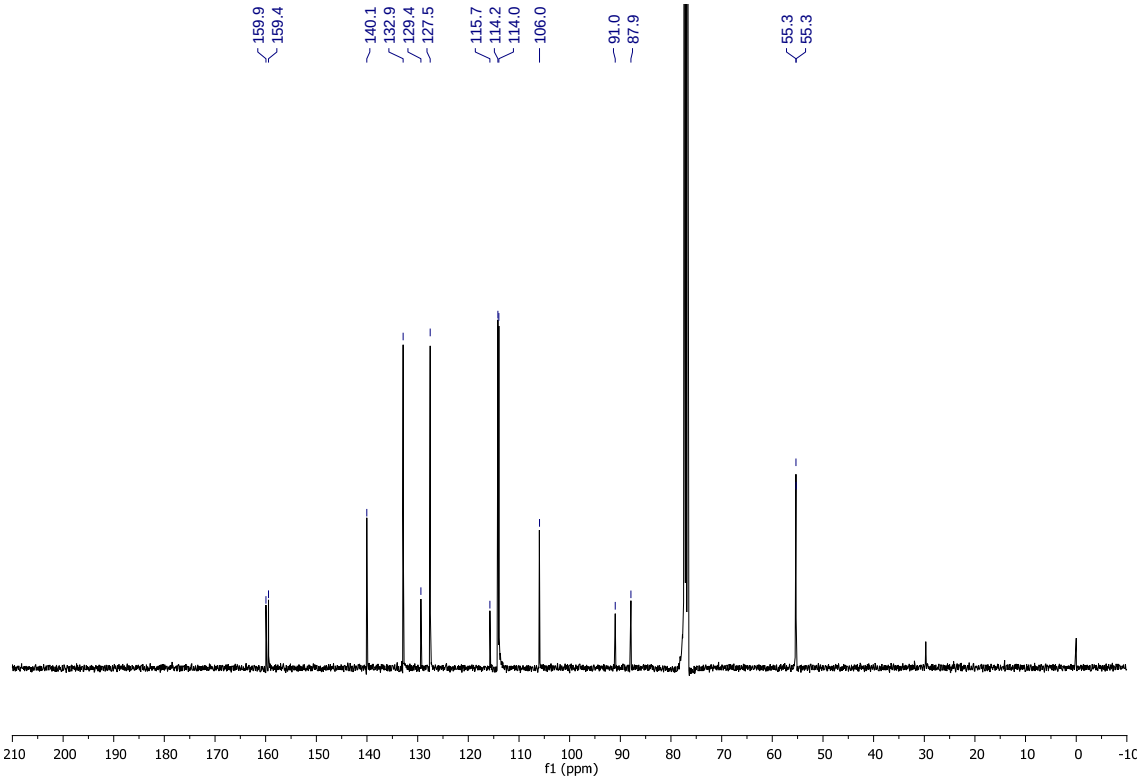


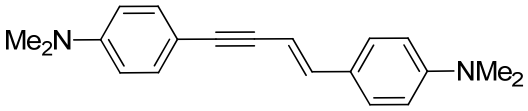




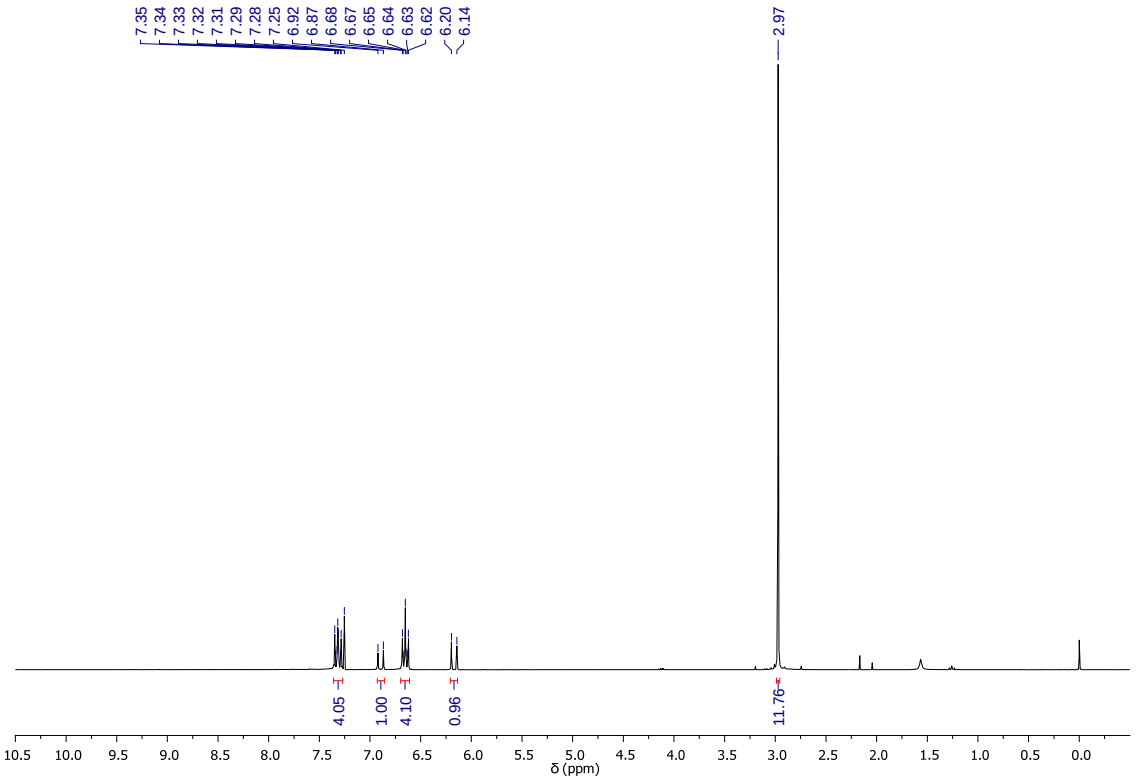
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)bis(methoxybenzene) (2d**).**

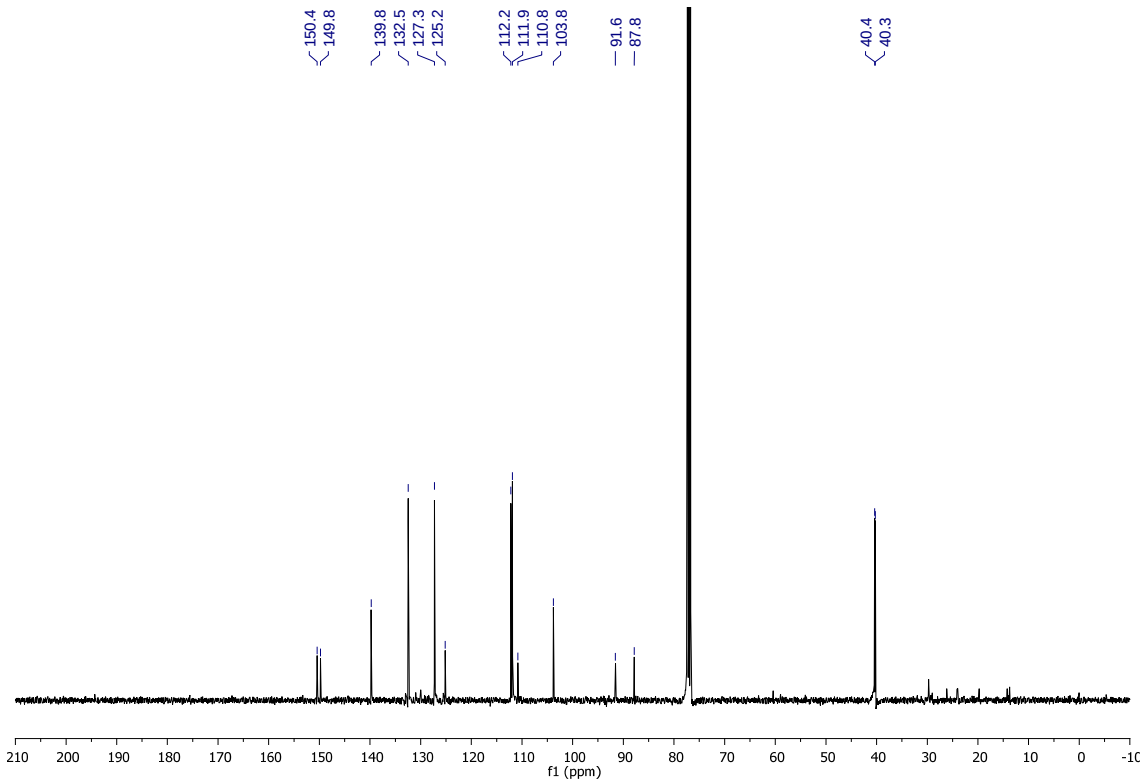


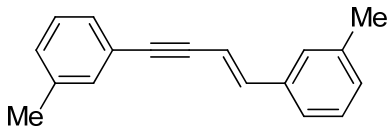




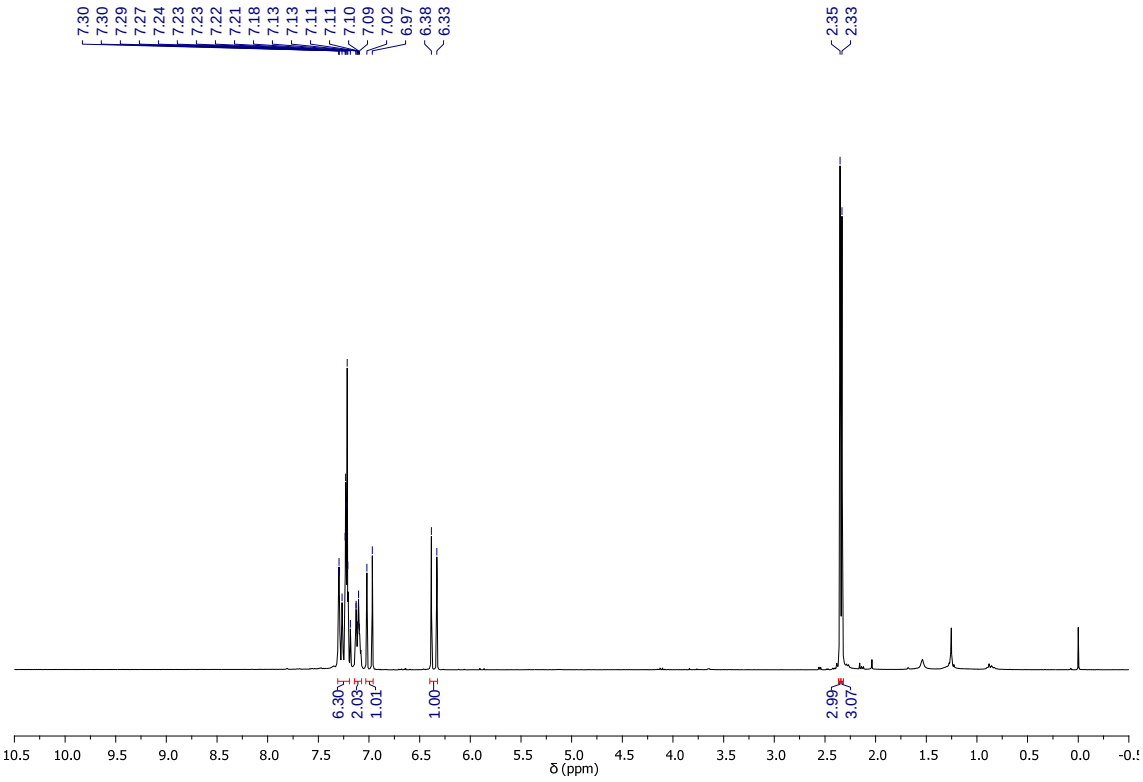
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)bis(*N*,*N*-dimethylaniline) (2e**).**

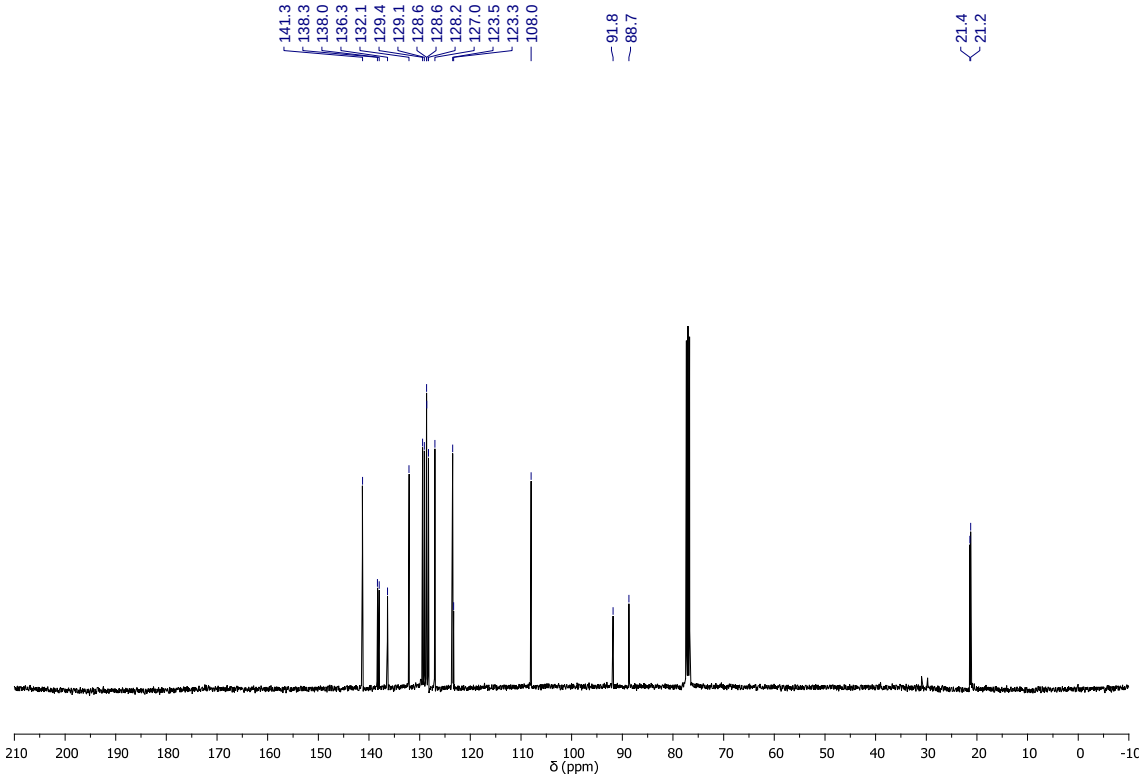


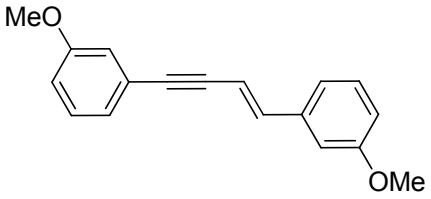




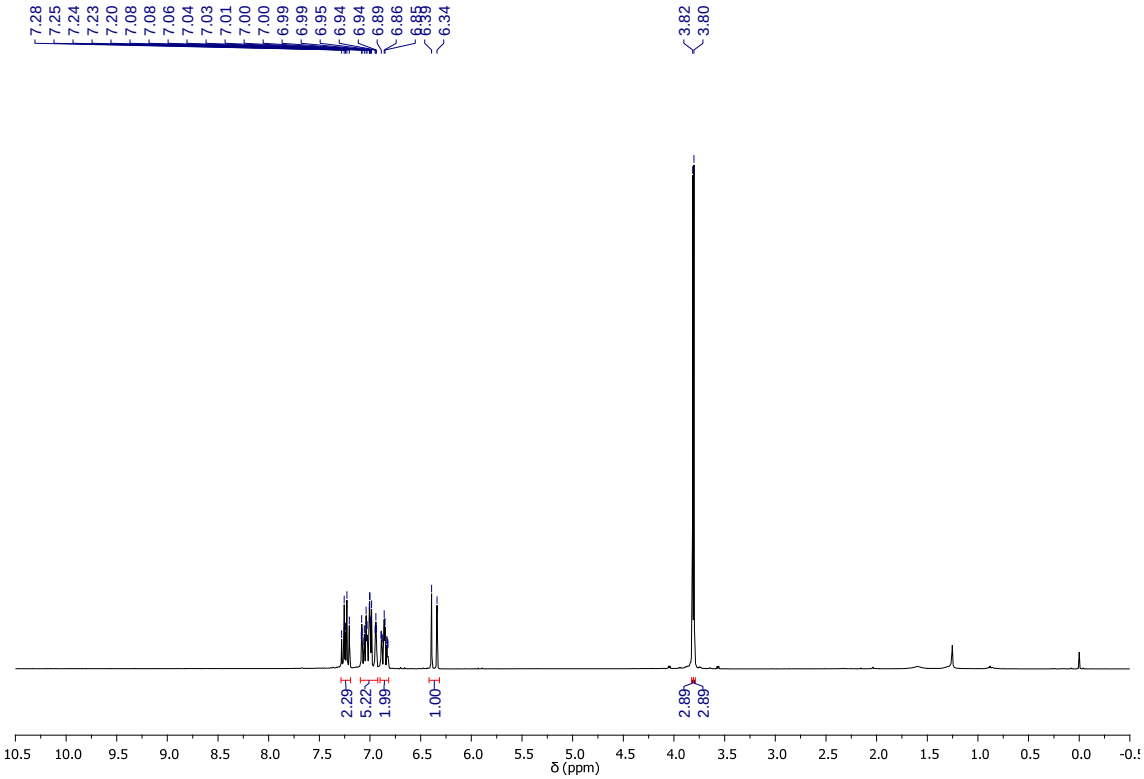
(*E*)-3,3'-(but-1-en-3-yne-1,4-diyl)bis(methylbenzene) (2f).

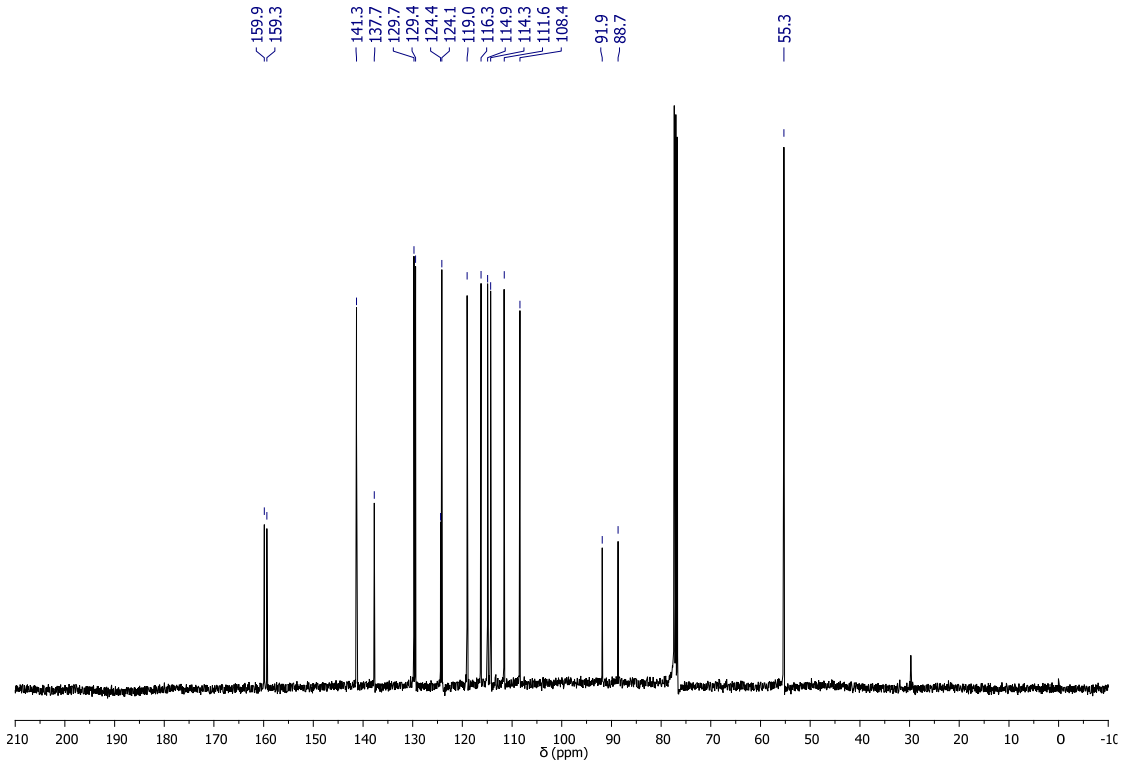


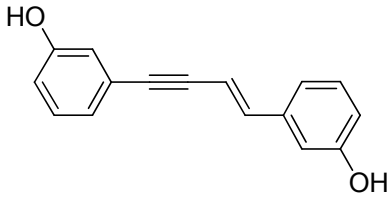




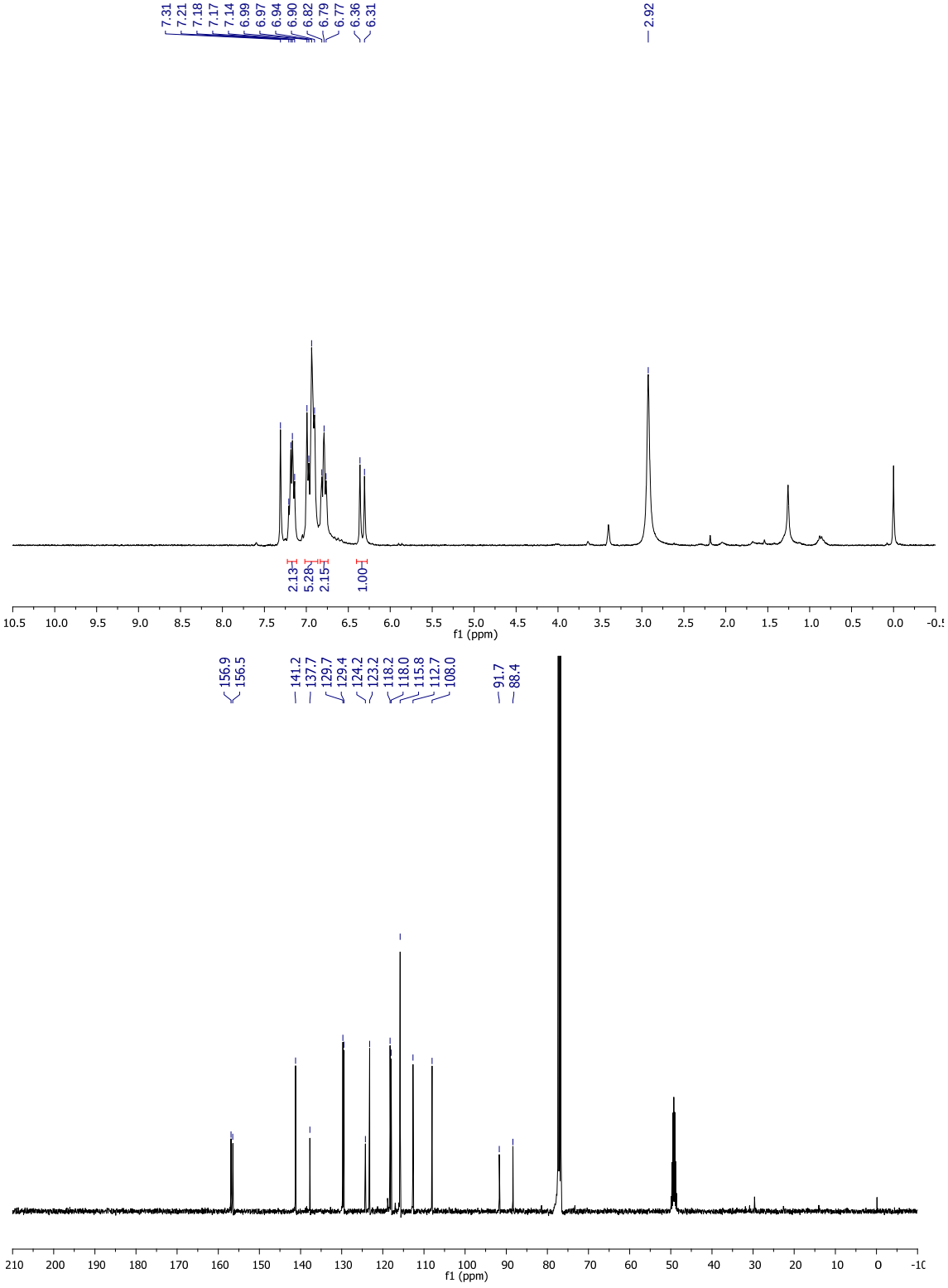
(*E*)-3,3'-(But-1-en-3-yne-1,4-diyl)bis(methoxybenzene) (2g**).**

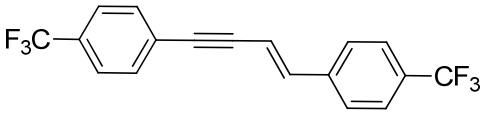




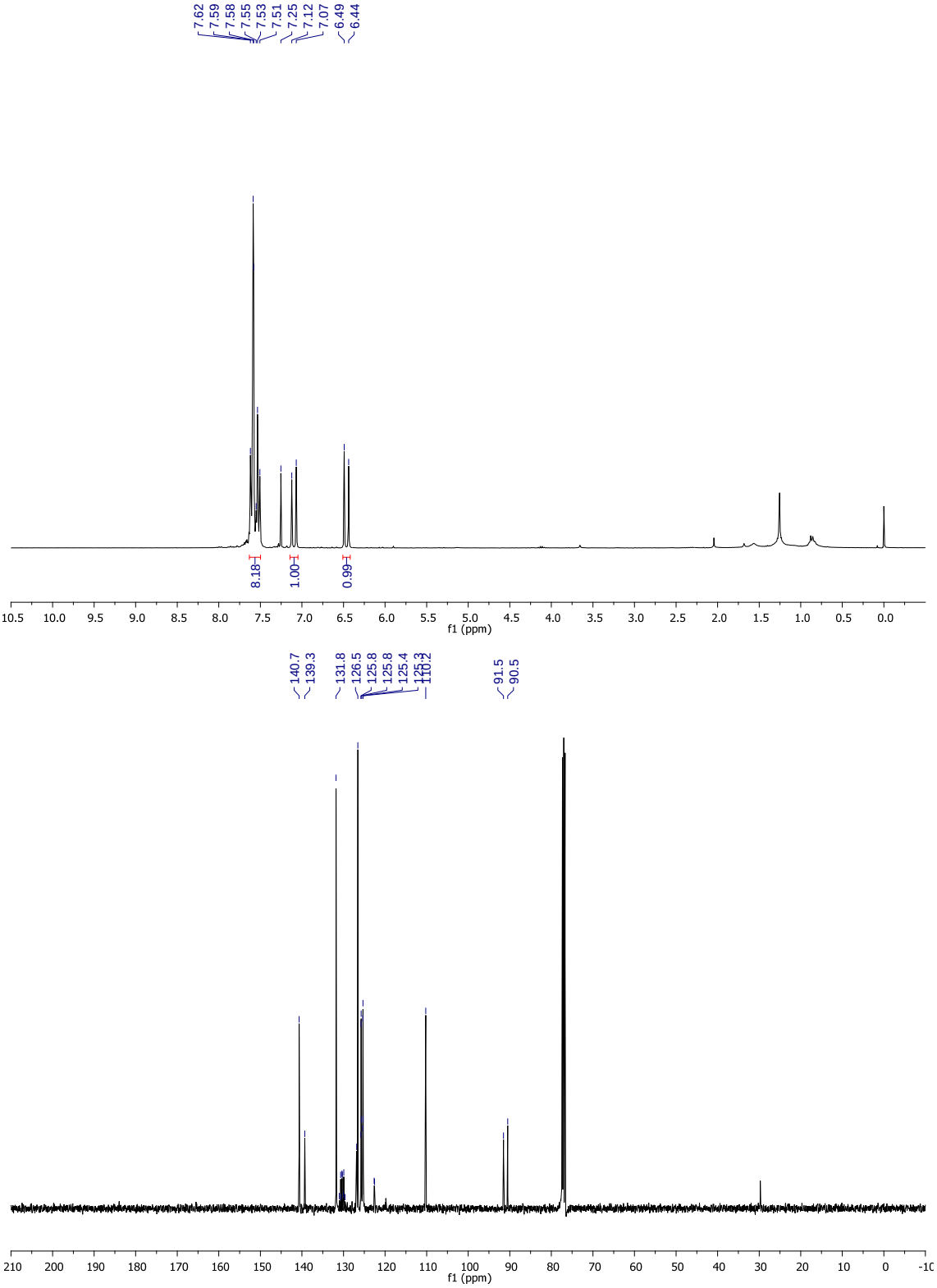


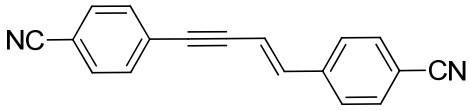
(*E*)-3,3'-(But-1-en-3-yne-1,4-diyl)diphenol (2h**).**



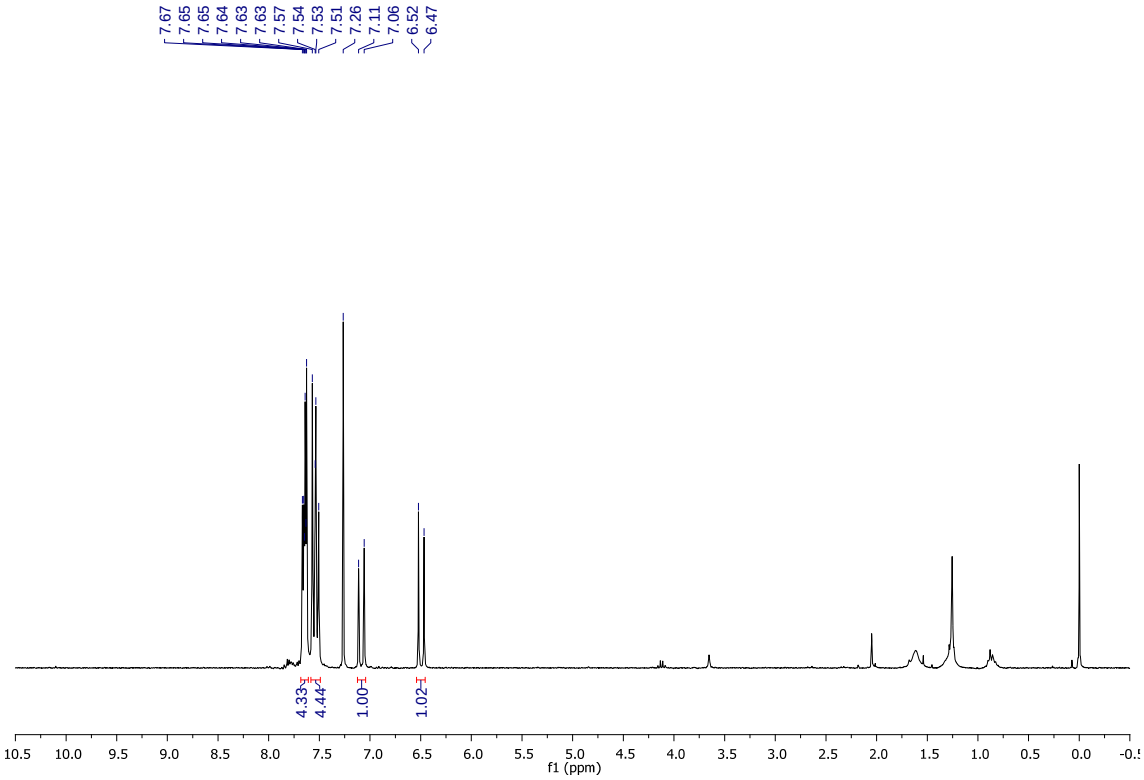


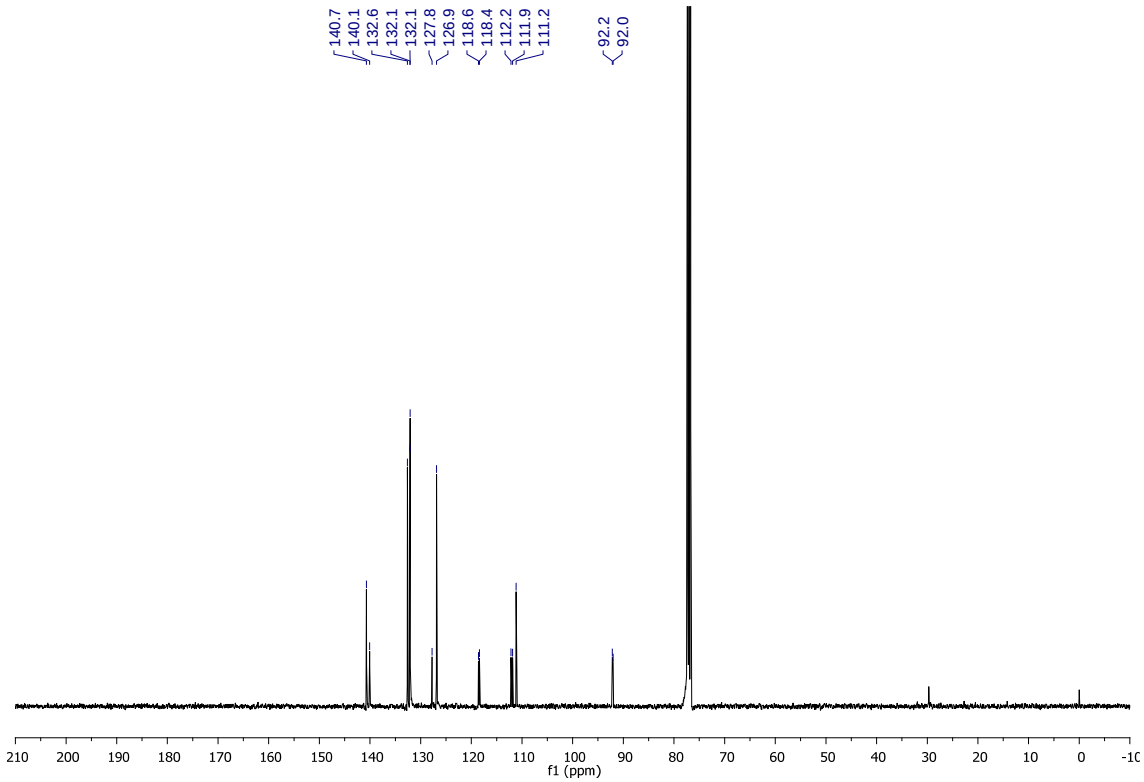
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)bis[(trifluoromethyl)benzene] (2i**).**

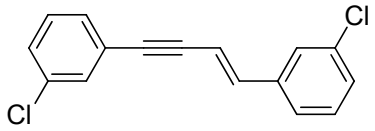




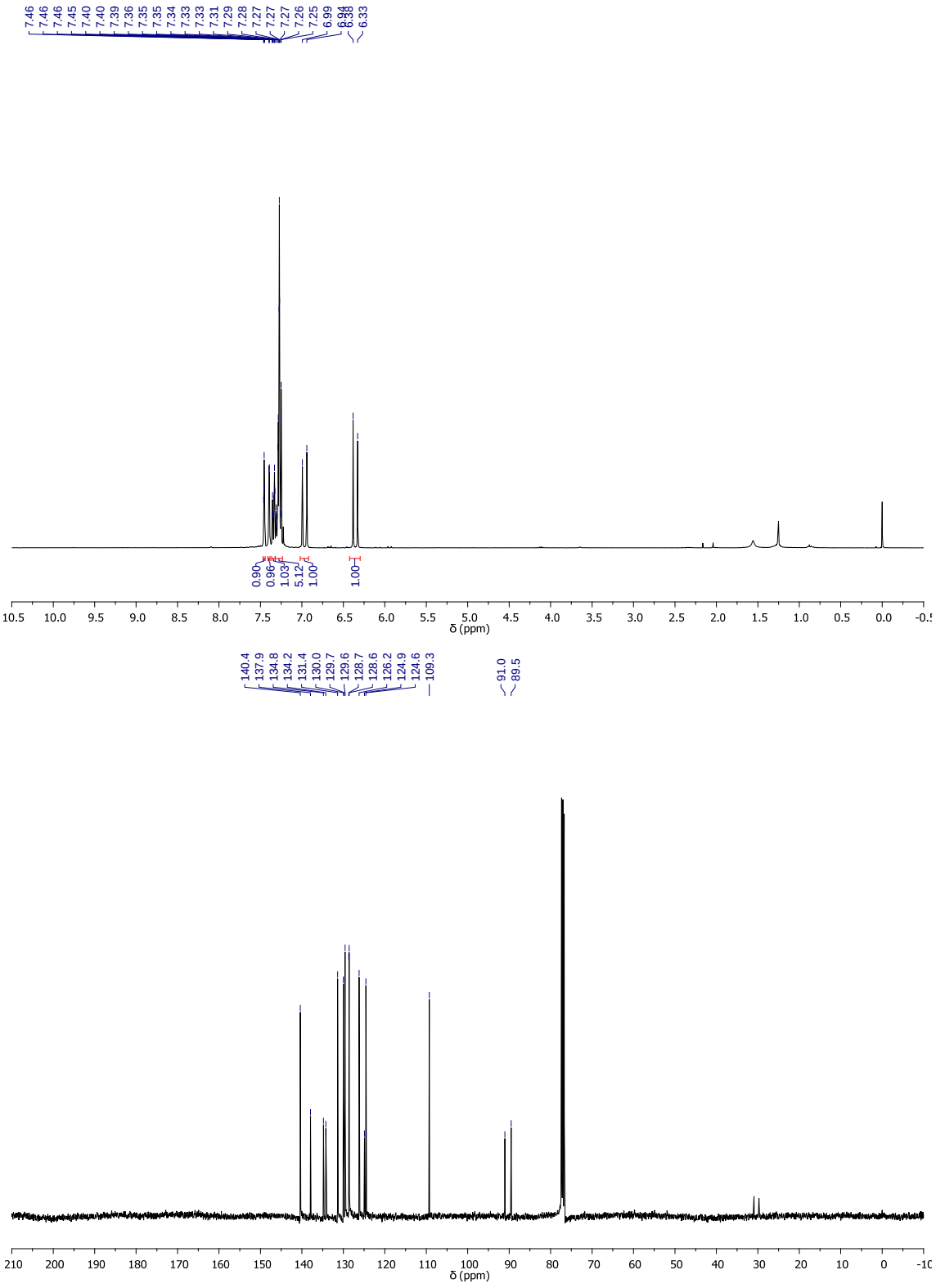
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)dibenzonitrile (2j).

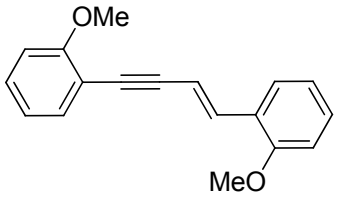




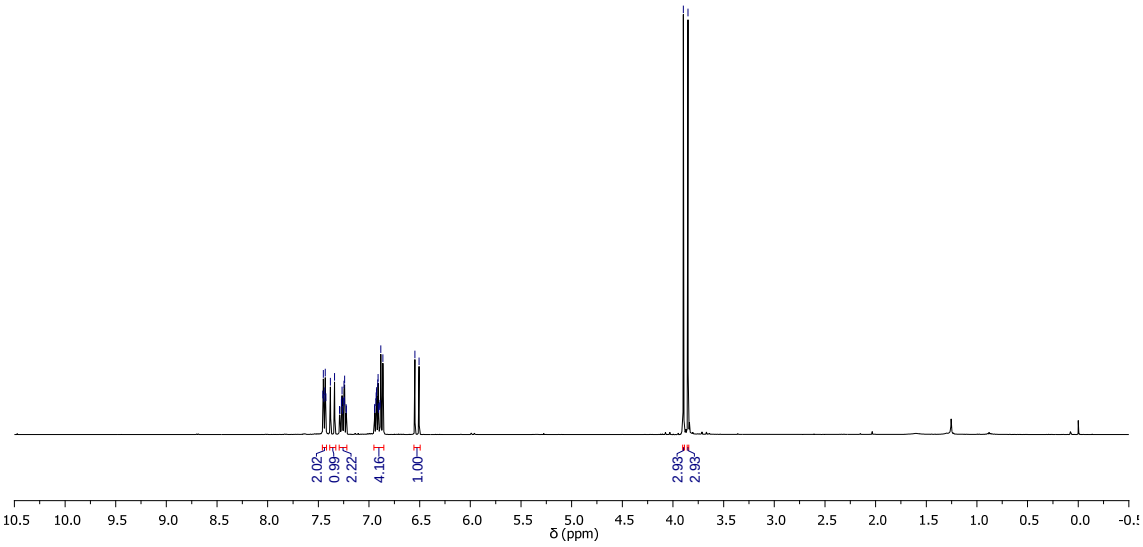


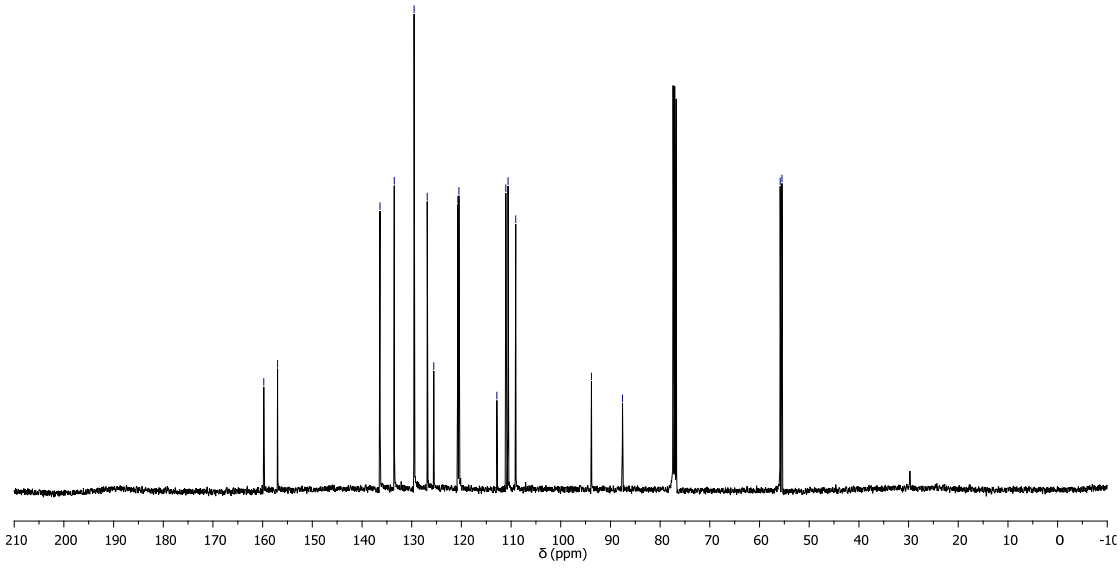
(*E*)-3,3'-(but-1-en-3-yne-1,4-diyl)bis(chlorobenzene) (2k**).**

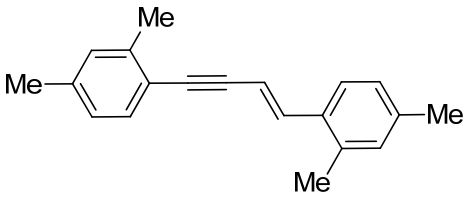




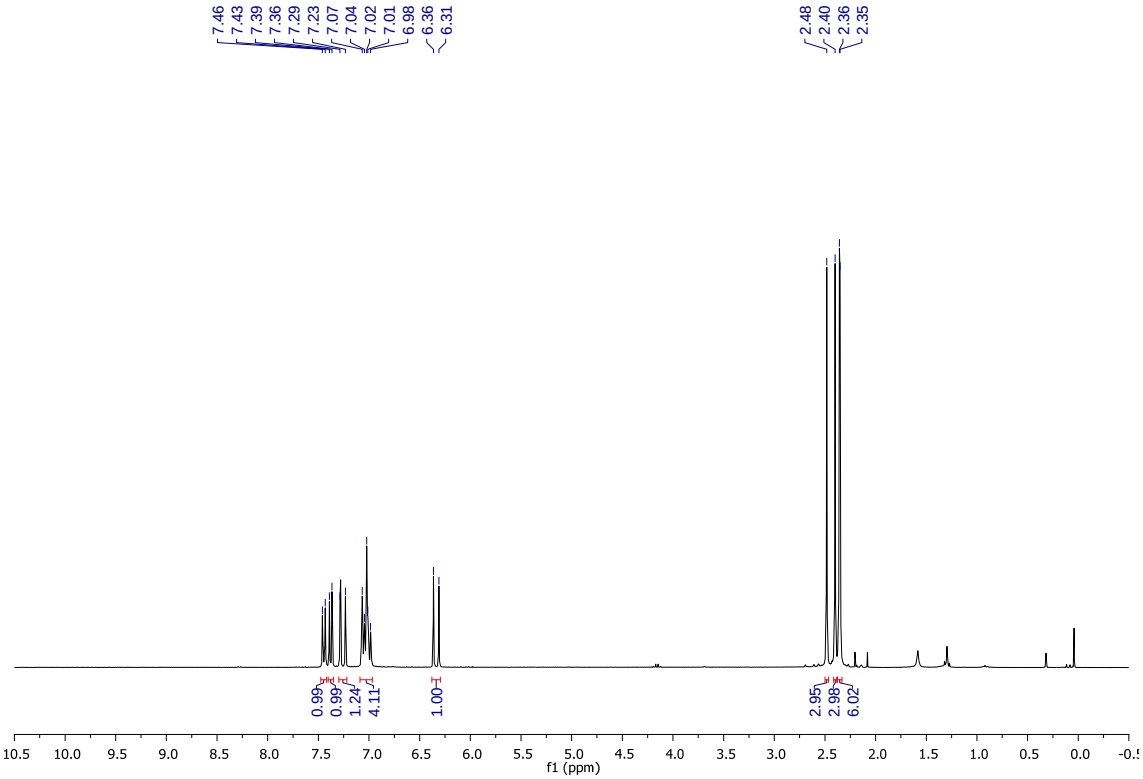
(*E*)-2,2'-(But-1-en-3-yne-1,4-diyl)bis(methoxybenzene) (2l).

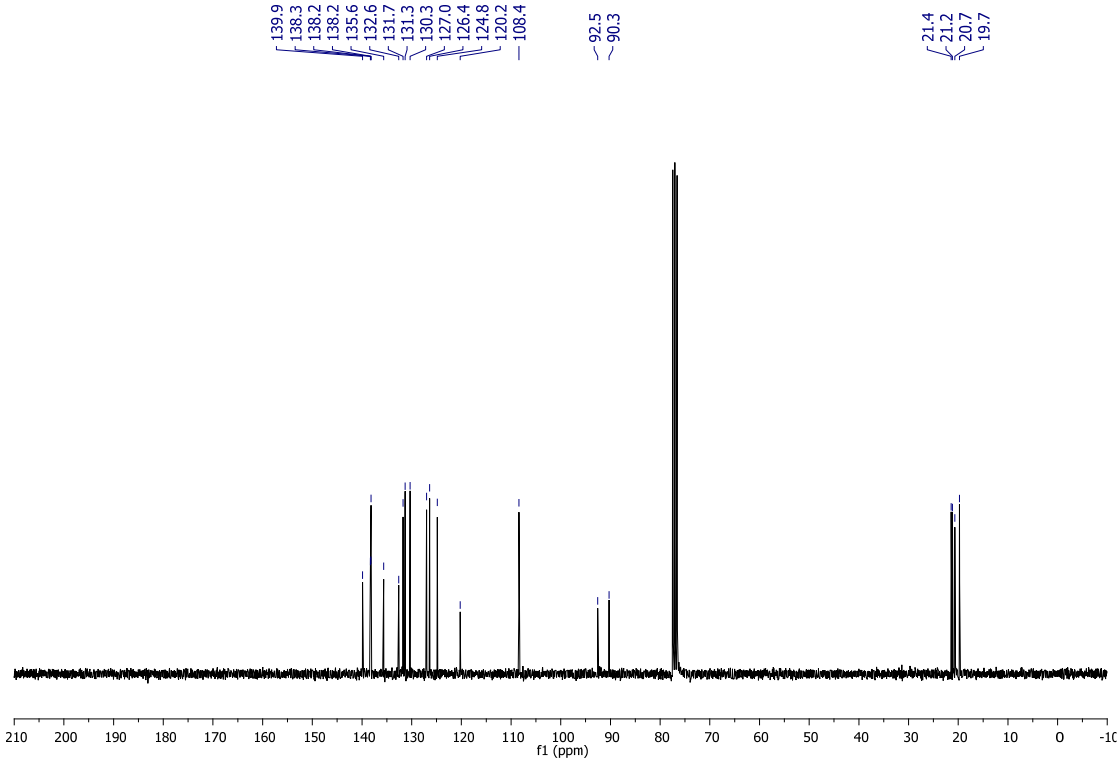


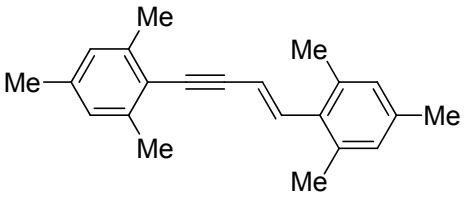




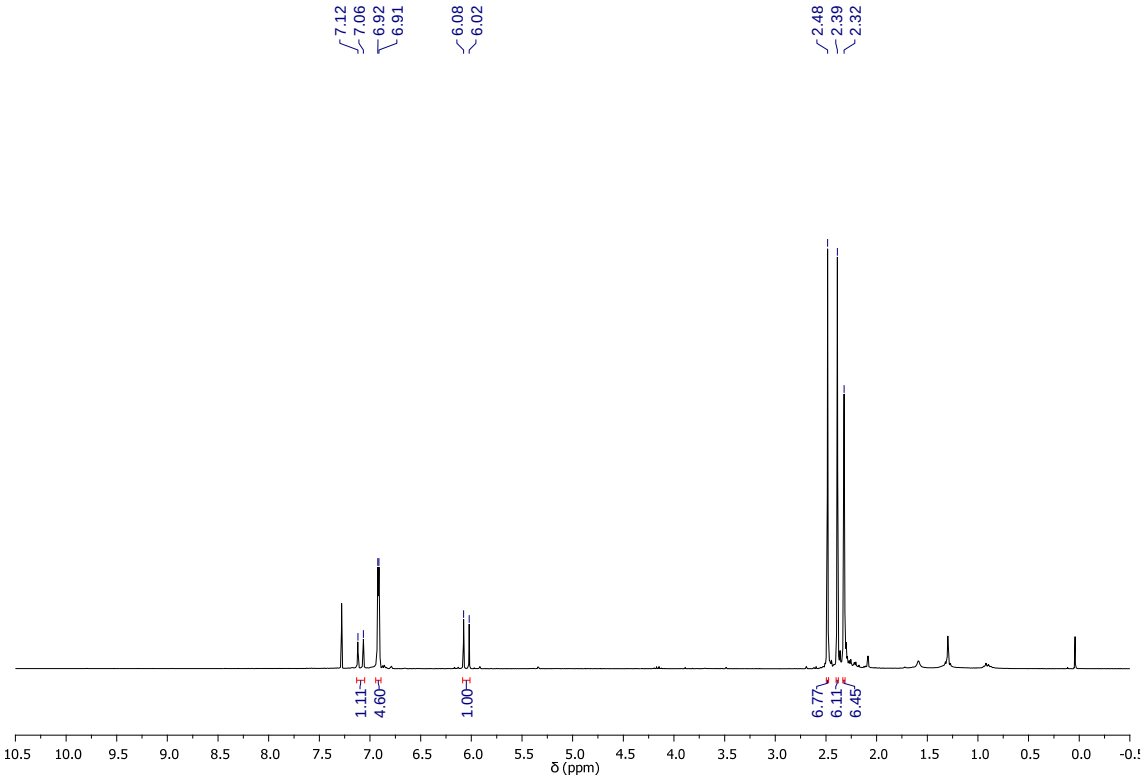
(*E*)-4,4'-(but-1-en-3-yne-1,4-diyl)bis(1,3-dimethylbenzene) (2m**).**

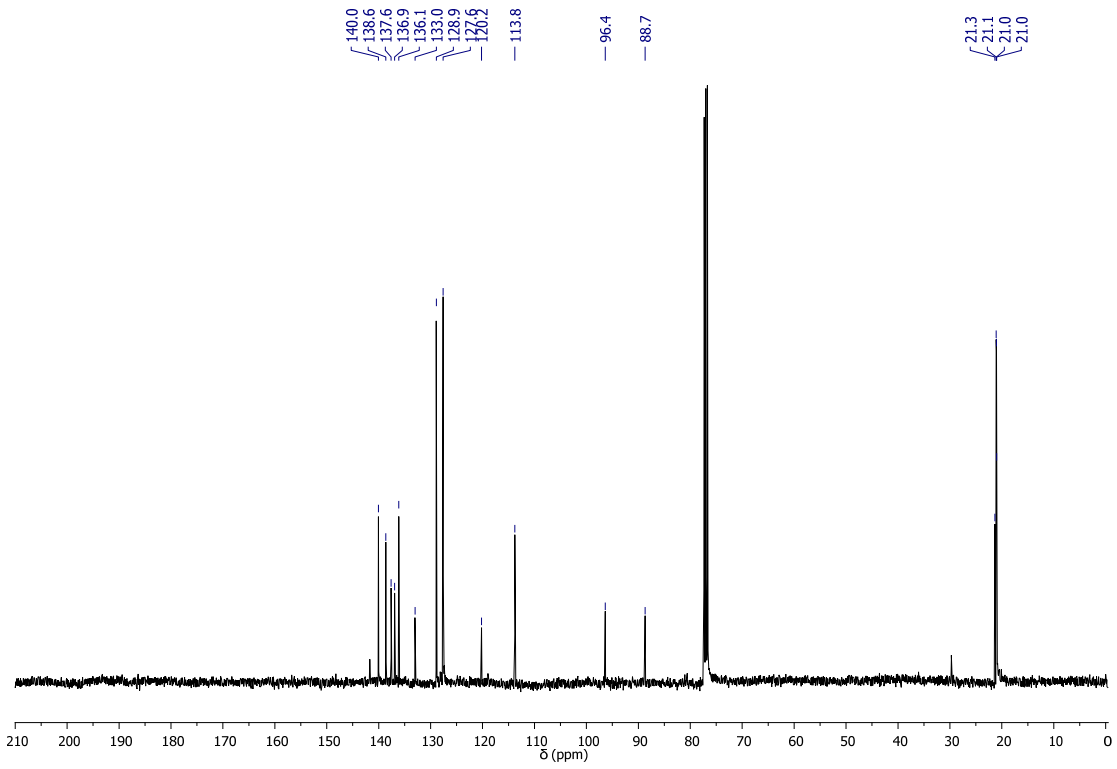


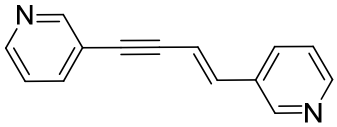




(*E*)-2,2'-(but-1-en-3-yne-1,4-diyl)bis(1,3,5-trimethylbenzene) (2n**).**







(*E*)-3,3'-(but-1-en-3-yne-1,4-diyl)dipyridine (2o).