

Supporting Information

Rapid access to unsymmetrical tolans and alkynones by sequentially palladium-catalyzed one-pot processes

Alissa C. Götzinger, Thomas J. J. Müller*

**Institut für Organische Chemie und Makromolekulare Chemie, Heinrich-Heine-Universität
Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany*

Fax: (+) 49 (0)211 8114324

E-Mail: ThomasJJ.Mueller@uni-duesseldorf.de

Table of Contents

1. General Considerations.....	2
2. General Procedure for the synthesis of alkynones 4	3
2.1 Analytical data for alkynones 4	4
3. General procedure for the synthesis of diarylalkynes 6 and 8	12
3.1 Analytical data for diarylalkynes 6 and 8	13
4. NMR spectra of compounds 4 , 6 , and 8	22

1. General Considerations

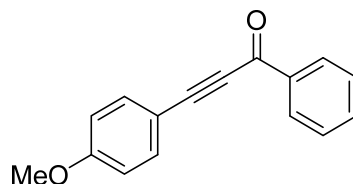
All reactions were performed in flame dried Schlenk tubes or microwave vials under a nitrogen atmosphere. Reaction progress was monitored qualitatively by thin layer chromatography using silica gel layered aluminium foil (60 F254 Merck, Darmstadt). For detection, UV light of wavelengths 254 and 366 was employed. All chemicals that were not synthesised were purchased from Sigma Aldrich, Alfa Aesar, Fluorochem, and ACROS and were used as received without any further purification. Ethynyl magnesium bromide solution was purchased from ACROS or Sigma Aldrich. ^1H and ^{13}C NMR spectra were measured on a Bruker Avance III-300 spectrometer. Chemical shifts are given in ppm (δ) and were referenced to the internal solvent signal: CDCl_3 (^1H δ 7.26, ^{13}C δ 77.2) or DMSO-d_6 (^1H δ 2.50, ^{13}C δ 39.5). Multiplicities are stated as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), td (triplet of doublet), m (multiplet). Coupling constants (J) are given in Hz. The assignment of primary (CH_3), secondary (CH_2), tertiary (CH) and quaternary carbon nuclei (C_{quat}) was made using DEPT-135 spectra. Mass-spectrometric investigations were carried out in the Department of Mass Spectrometry of the Institute of Inorganic Chemistry and Structural Chemistry, Heinrich Heine University Düsseldorf. IR spectra were recorded using a Shimadzu IRAffinity-1. The intensities of the IR bands are abbreviated as w (weak), m (medium), s (strong). Melting points (uncorrected) were measured using a Büchi Melting Point B-540. Combustion analyses were measured on a Perkin Elmer Series II Analyser 2400 in the Institute of Pharmaceutical and Medicinal Chemistry, Heinrich Heine University, Düsseldorf.

2. General Procedure for the synthesis of alkynones 4

Bis(triphenylphosphane)palladium(II)dichloride (35.1 mg, 50.0 μ mol, 5.00 mol%) and aryl iodide **1** (1.00 mmol, 1.00 equiv, if solid) were placed in a flame-dried 10 mL Schlenk tube under a nitrogen atmosphere and the Schlenk tube was evacuated and flushed with nitrogen two more times. A solution of ethynyl magnesium bromide (**2**) in THF (2.40 mL, 0.500 M, 1.20 mmol) was added, as was aryl iodide **1**, if liquid. The resulting yellow solution was stirred at 45 °C until completion of the reaction (ca. 30 min, TLC control). Towards the end of the reaction the mixture turned turbid. It was cooled to room temp, triethylamine hydrochloride (41.3 mg, 0.300 mmol, 0.300 equiv) was added and stirred for several minutes before the addition of triethylamine (106 mg, 1.05 mmol, 1.05 equiv), aryl chloride **3** (1.40 mmol, 1.40 equiv) and copper(I) iodide (9.50 mg, 50.0 μ mol, 5.00 mol%), upon which the reaction mixture darkened to brown. The reaction was stirred for ca. 1 h at 45 °C (TLC control). Brine was added and the aqueous phase was extracted with EtOAc (5 \times 10 mL). The combined organic phases were washed with brine, dried with anhydrous MgSO₄, filtered, and the crude product was adsorbed onto Celite®. For purification, chromatography on silica gel was performed using a Biotage SP4 flash purification system or manual flash technique with eluents consisting of *n*-hexane und EtOAc, acetone, or DCM.

2.1 Analytical data for alkynes 4

3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-one (4a)



According to the general procedure using 4-iodoanisole and benzoyl chloride, and after chromatography on the flash purification system (*n*-hexane/EtOAc 19:1 → 4:1) 183 mg (0.775 mmol, 77%) of **4a** were obtained as a light yellow solid, Mp 79 °C (lit.¹ 79-80 °C).

¹H NMR (CDCl₃, 300 MHz): δ 3.86 (s, 3 H, OCH₃), 6.91–6.96 (m, 2 H, CH_{Ar}), 7.49–7.54 (m, 2 H, CH_{Ar}), 7.59–7.67 (m, 3 H, CH_{Ar}), 8.20–8.24 (m, 2 H, CH_{Ar}).

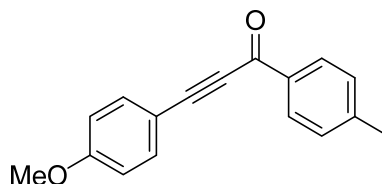
¹³C NMR (CDCl₃, 75 MHz): δ 55.6 (CH₃), 87.0 (C_{quat}), 94.5 (C_{quat}), 112.1 (C_{quat}), 114.6 (CH), 128.7 (CH), 129.6 (CH), 134.0 (CH), 135.3 (CH), 137.2 (C_{quat}), 161.9 (C_{quat}), 178.2 (C_{quat}).

EI + MS (*m/z* (%)): 236 (87) [M⁺], 208 (39), 193 (50), 165 (37), 164 (11), 160 (11), 159 (100) [C₁₀H₇O₂⁺], 144(16) [C₉H₄O₂⁺], 116 (12) [C₈H₄O⁺].

IR: $\tilde{\nu}$ [cm⁻¹] = 606 (m), 644 (m), 673 (s), 696 (s), 764 (w), 795 (m), 826 (m), 835 (s), 947 (w), 964 (w), 997 (s), 1030 (s), 1070 (w), 1094 (w), 1115 (w), 1155 (m), 1166 (s), 1188 (m), 1209 (s), 1252 (s), 1292 (m), 1315 (m), 1441 (m), 1460 (m), 1491 (w), 1508 (s), 1597 (s), 1624 (m), 2019 (w), 2085 (w), 2183 (s), 2423 (w), 2554 (w), 2594 (w), 2768 (w), 2843 (w), 2941 (w), 978 (w), 3200 (w).

Anal. calcd. for C₁₆H₁₂O₂ (236.1): C 81.34, H 5.12; Found: C 81.33, H 5.18.

3-(4-Methoxyphenyl)-1-(*p*-tolyl)prop-2-yn-1-one (4b)



According to the general procedure using 4-iodoanisole and *p*-toluoyl chloride, and after chromatography on the flash purification system (*n*-hexane/EtOAc 19:1 → 4:1) 199 mg (0.795 mmol, 80%) of **4b** were obtained as a colorless solid, Mp 99 °C (lit.² 93-94 °C).

^1H NMR (CDCl_3 , 300 MHz): δ 2.45 (s, 3 H, CH_3), 3.86 (s, 3 H, OCH_3), 6.91–6.96 (m, 2 H, CH_{Ar}), 7.29–7.32 (m, 2 H, CH_{Ar}), 7.62–7.66 (m, 2 H, CH_{Ar}), 8.10–8.12 (m, 2 H, CH_{Ar}).

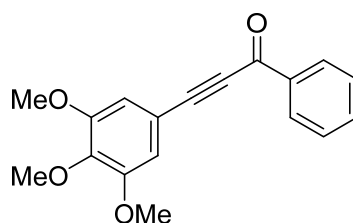
^{13}C NMR (CDCl_3 , 75 MHz): δ 22.0 (CH_3), 55.6 (CH_3), 87.1 (C_{quat}), 93.9 (C_{quat}), 112.1 (C_{quat}), 114.5 (CH), 129.4 (CH), 129.8 (CH), 134.9 (C_{quat}), 135.2 (CH), 145.1 (C_{quat}), 161.8 (C_{quat}), 177.9 (C_{quat}).

EI + MS (m/z (%)): 250 (100) [M^+], 222 (59) [$\text{C}_{15}\text{H}_{10}\text{O}_2^+$], 207 (65) [$\text{C}_{15}\text{H}_{11}\text{O}^+$], 179 (27), 159 (69) [$\text{C}_{10}\text{H}_7\text{O}_2^+$], 144 (13) [$\text{C}_9\text{H}_4\text{O}_2^+$].

IR: $\tilde{\nu}$ [cm^{-1}] = 739 (s), 799 (m), 831 (s), 947 (w), 1005 (m), 1208 (s), 1076 (w), 1113 (w), 1167 (s), 1188 (m), 1209 (m), 1254 (s), 1292 (m), 1312 (w), 1406 (w), 1441 (m), 1460 (w), 1512 (m), 1558 (w), 1568 (w), 1597 (s), 1622 (m), 1911 (w), 2843 (w), 2901 (w), 2970 (w), 2986 (w).

Anal. calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_2$ (250.3): C 81.58, H 5.64; Found: C 81.37, H 5.46.

1-Phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-yn-1-one (4c)



According to the general procedure using 5-iodo-1,2,3-trimethoxybenzene and benzoyl chloride, 201 mg (0.678 mmol, 68%) of **4c** were obtained as a colorless solid. Purification was performed using the flash purification system (*n*-hexane/EtOAc 5:1 \rightarrow 1:1), Mp 161 °C (lit.³ 158–160 °C).

^1H NMR (CDCl_3 , 300 MHz): δ 3.90 (s, 6 H, OCH_3), 3.91 (s, 3 H, OCH_3), 6.92 (s, 2 H, CH_{Ar}), 7.50–7.56 (m, 2 H, CH_{Ar}), 7.61–7.67 (m, 1 H, CH_{Ar}), 8.20–8.24 (m, 2 H, CH_{Ar}).

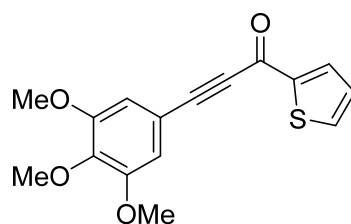
^{13}C NMR (CDCl_3 , 75 MHz): δ 56.5 (CH_3), 61.2 (CH_3), 86.5 (C_{quat}), 93.7 (C_{quat}), 110.6 (CH), 114.9 (C_{quat}), 128.8 (CH), 129.7 (CH), 134.2 (CH), 137.0 (C_{quat}), 141.2 (C_{quat}), 153.4 (C_{quat}), 178.1 (C_{quat}).

EI + MS (m/z (%)): 296 (100) [M^+], 281 (48) [$\text{C}_{17}\text{H}_{13}\text{O}_4^+$], 253 (17), 225 (19), 210 (12), 139 (11), 105 (13) [$\text{C}_7\text{H}_5\text{O}^+$], 77 (11) [C_6H_5^+].

IR: $\tilde{\nu}$ [cm^{-1}] = 631 (m), 696 (s), 783 (w), 824 (m), 833 (m), 918 (w), 939 (w), 997 (m), 1022 (m), 1053 (m), 1125 (s), 1157 (w), 1177 (w), 1234 (m), 1248 (m), 1261 (m), 1312 (m), 1354 (w), 1408 (m), 1431 (m), 1464 (w), 1499 (m), 1574 (m), 1597 (w), 1636 (m), 2189 (m), 2833 (w), 2943 (w), 2980 (w), 3003 (w).

Anal. calcd. for C₁₈H₁₆O₄ (296.3): C 72.96, H 5.44; Found C 72.79, H 5.34.

1-(Thiophen-2-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-yn-1-one (4d)



According to the general procedure using 5-iodo-1,2,3-trimethoxybenzene and 2-thiophenecarbonyl chloride, 230 mg (0.760 mmol, 76%) of **4d** were obtained as a yellow solid. Purification was performed using manual flash technique (*n*-hexane/acetone 10:1 → 5:1 → 1:1), Mp 166 °C.

¹H NMR (CDCl₃, 600 MHz): δ 3.89 (s, 6 H, OCH₃), 3.90 (s, 3 H, OCH₃), 6.89 (s, 2 H, CH_{Ar}), 7.19 (dd, 1 H, CH_{Ar}, ³J_H = 4.9, 3.8 Hz), 7.73 (dd, 1 H, CH_{Ar}, ³J_H = 4.9 Hz, ⁴J_H = 1.2 Hz), 8.00 (dd, 1 H, CH_{Ar}, ³J_H = 3.8 Hz, ⁴J_H = 1.3 Hz).

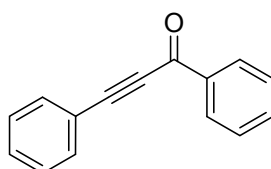
¹³C NMR (CDCl₃, 150 MHz): δ 56.4 (CH₃), 61.2 (CH₃), 86.1 (C_{quat}), 92.3 (C_{quat}), 110.5 (CH), 114.7 (C_{quat}), 128.5 (CH), 135.1 (CH), 135.3 (CH), 141.3 (C_{quat}), 145.0 (C_{quat}), 153.4 (C_{quat}), 169.8 (C_{quat}).

EI + MS (*m/z* (%)): 302 (3) [M⁺], 262 (100) [C₁₃H₁₀O₄S⁺], 183 (58), 108 (24).

IR: $\tilde{\nu}$ [cm⁻¹] = 675 (w), 704 (m), 721 (s), 745 (s), 779 (w), 804 (w), 821 (m), 833 (s), 856 (w), 901 (m), 997 (s), 1011 (s), 1057 (s), 1094 (m), 1125 (s), 1161 (w), 1180 (w), 1231 (s), 1277 (s), 1290 (w), 1354 (w), 1408 (s), 1433 (m), 1445 (w), 1468 (w), 1501 (s), 1574 (m), 1609 (m), 1734 (w), 2189 (m), 2833 (w), 2945 (w), 2982 (w), 3075 (w).

HRMS (ESI) (*m/z*) calcd. for [C₁₆H₁₅O₄S]⁺: 303.0686; Found: 303.0684.

1,3-Diphenylprop-2-yn-1-one (4e)



According to the general procedure using iodobenzene and benzoyl chloride, 177 mg (0.858 mmol, 86%) of **4e** were obtained as a yellow oil. Purification was performed using the flash purification system (*n*-hexane/EtOAc 19:1 → 4:1).

^1H NMR (CDCl_3 , 300 MHz): δ 7.39–7.55 (m, 5 H, CH_{Ar}), 7.60–7.71 (m, 3 H, CH_{Ar}), 8.22–8.25 (m, 2 H, CH_{Ar}).

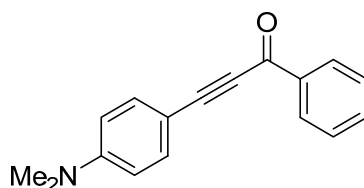
^{13}C NMR (CDCl_3 , 75 MHz): δ 87.0 (C_{quat}), 93.2 (C_{quat}), 120.2 (C_{quat}), 128.7 (CH), 128.8 (CH), 129.7 (CH), 130.9 (CH), 133.2 (CH), 134.2 (CH), 137.0 (C_{quat}), 178.1 (C_{quat}).

EI + MS (m/z (%)): 206 (71) [M^+], 178 (100), 129 (80) [$\text{C}_9\text{H}_5\text{O}^+$], 105 (23) [$\text{C}_7\text{H}_9\text{O}^+$], 77 (17) [C_6H_5^+], 51 (12).

IR: $\tilde{\nu}$ [cm^{-1}] = 619 (m), 687 (s), 756 (w), 814 (w), 845 (w), 920 (w), 995 (s), 1011 (s), 1032 (m), 1070 (w), 1098 (w), 1113 (w), 1159 (w), 1171 (m), 1207 (s), 1240 (w), 1285 (s), 1315 (m), 1391 (w), 1445 (w), 1489 (m), 1551 (w), 1581 (w), 1597 (m), 1636 (s), 1719 (w), 1904 (w), 2102 (w), 2162 (w), 2195 (m), 2320 (w), 2474 (w), 2805 (w), 3034 (w), 3059 (w).

HRMS (ESI) (m/z) calcd. for [$\text{C}_{15}\text{H}_{11}\text{O}$] $^+$: 207.0804; Found: 207.0804.

3-(4-(Dimethylamino)phenyl)-1-phenylprop-2-yn-1-one (4f)



According to the general procedure using 4-iodo-*N,N*-dimethylaniline and benzoyl chloride, 197 mg (0.790 mmol, 79%) of **4f** were obtained as a yellow solid. Purification was performed using manual flash technique (*n*-hexane/EtOAc 10:1), Mp 127 °C.

^1H NMR (CDCl_3 , 300 MHz): δ 3.04 (s, 6 H, $\text{N}(\text{CH}_3)_2$), 6.63–6.68 (m, 2 H, CH_{Ar}), 7.74–7.53 (m, 2 H, CH_{Ar}), 7.55–7.61 (m, 3 H, CH_{Ar}), 8.21–8.25 (m, 2 H, CH_{Ar}).

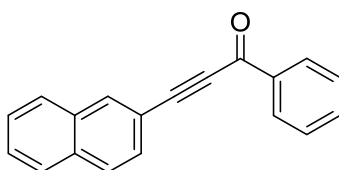
^{13}C NMR (CDCl_3 , 75 MHz): δ 40.1 (CH_3), 88.0 (C_{quat}), 97.7 (C_{quat}), 105.7 (C_{quat}), 111.7 (CH), 128.6 (CH), 129.5 (CH), 133.6 (CH), 135.3 (CH), 137.5 (C_{quat}), 151.9 (C_{quat}), 178.1 (C_{quat}).

EI + MS (m/z (%)): 249 (100) [M^+], 220 (23) [$\text{C}_{15}\text{H}_{10}\text{NO}^+$], 172 (45) [$\text{C}_{10}\text{H}_{11}\text{NO}^+$], 110 (17).

IR: $\tilde{\nu}$ [cm^{-1}] = 629 (m), 664 (m), 681 (s), 752 (m), 806 (m), 820 (m), 839 (m), 924 (w), 995 (m), 1011 (m), 1030 (s), 1069 (w), 1111 (m), 1159 (m), 1188 (m), 1213 (m), 1260 (m), 1288 (m), 1306 (m), 1368 (w), 1422 (m), 1441 (w), 1489 (m), 1508 (m), 1558 (m), 1570 (m), 1593 (m), 1628 (m), 2195 (m).

Anal. calcd. for $\text{C}_{17}\text{H}_{15}\text{NO}$ (249.3): C 81.90, H 6.06, N 5.62; Found: C 81.90, H 6.06, N 5.61.

3-(Naphthalen-2-yl)-1-phenylprop-2-yn-1-one (4g)



According to the general procedure using 1-iodonaphthalene and benzoyl chloride, 211 mg (0.823 mmol, 82%) of **4g** were obtained as a light yellow solid. Purification was performed using manual flash technique (*n*-hexane/EtOAc 80:1→ 50:1), a sample was recrystallized from *n*-hexane/EtOAc for analytical purposes, Mp 97 °C.

¹H NMR (CDCl₃, 300 MHz): δ 3.90 (s, 3 H, OCH₃), 6.96–7.01 (m, 2 H, CH_{Ar}), 7.38–7.50 (m, 3 H, CH_{Ar}), 7.66–7.69 (m, 2 H, CH_{Ar}), 8.17–8.22 (m, 2 H, CH_{Ar}).

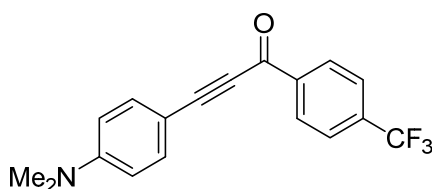
¹³C-NMR (CDCl₃, 75 MHz): δ 87.3 (C_{quat}), 93.8 (C_{quat}), 117.4 (C_{quat}), 127.2 (CH), 128.1 (CH), 128.2 (CH), 128.4 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 129.7 (CH), 132.8 (C_{quat}), 134.1 (C_{quat}), 134.3 (CH), 134.5 (CH), 137.1 (C_{quat}), 178.1 (C_{quat}).

EI + MS (*m/z* (%)): 334 (100) [M⁺], 306 (28) [C₂₄H₁₈⁺], 278 (52), 176 (11), 257 (51) [C₁₈H₉O₂₉⁺], 229 (46) [C₁₇H₉O⁺], 200 (26), 139 (16), 105 (16) [C₇H₅O⁺], 77 (17) [C₆H₅⁺].

IR: $\tilde{\nu}$ [cm⁻¹] = 662 (s), 694 (s), 787 (m), 839 (m), 937 (w), 999 (m), 1011 (s), 1032 (m), 1171 (m), 1209 (m), 1231 (w), 1277 (m), 1288 (s), 1314 (m), 1449 (m), 1497 (w), 1580 (m), 1599 (w), 1630 (s), 2195 (m), 3028 (w).

HRMS (ESI) (*m/z*) calcd. for [C₁₅H₁₁O]⁺: 257.0961; Found: 257.0963.

3-(4-(Dimethylamino)phenyl)-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (4h)



According to the general procedure using 4-iodo-*N,N*-dimethylaniline and 4-trifluoromethylbenzoyl chloride, 233 mg (0.734 mmol, 73%) of **4h** were obtained as a dark orange solid. Purification was performed using manual flash technique (*n*-hexane/EtOAc 10:1), Mp 124 °C.

¹H NMR (CDCl₃, 300 MHz): δ 3.05 (s, 6 H, N(CH₃)₂), 6.64–6.69 (m, 2 H, CH_{Ar}), 7.55–7.60 (m, 2 H, CH_{Ar}), 7.75–7.78 (m, 2 H, CH_{Ar}), 8.30–8.33 (m, 2 H, CH_{Ar}).

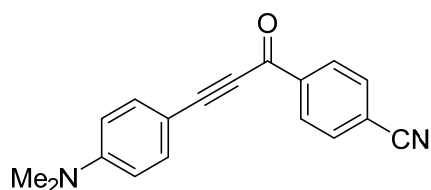
^{13}C NMR (CDCl_3 , 75 MHz): δ 40.1 (CH_3), 88.2 (C_{quat}), 99.5 (C_{quat}), 105.1 (C_{quat}), 111.7 (CH), 125.6 (q, CH , $^3J_{\text{F}} = 4$ Hz), 129.7 (CH), 134.7 (q, C_{quat} , $^2J_{\text{F}} = 33$ Hz), 135.5 (CH), 140.1 (C_{quat}), 152.1 (C_{quat}), 176.6 (C_{quat}). The quaternary C resonance of CF_3 is missing due to signal overlap.

EI + MS (m/z (%)): 317 (100) [M^+], 288 (16) [$\text{C}_{16}\text{H}_9\text{F}_3\text{NO}^+$], 172 (41) [$\text{C}_8\text{H}_3\text{F}_3\text{O}^+$], 144 (23) [$\text{C}_7\text{H}_3\text{F}_3^+$].

IR: $\tilde{\nu}$ [cm^{-1}] = 635 (w), 683 (s), 729 (m), 762 (s), 775 (m), 806 (m), 814 (s), 853 (m), 943 (m), 999 (m), 1011 (s), 1026 (m), 1065 (s), 1105 (s), 1119 (s), 1167 (s), 1221 (m), 1317 (s), 1371 (m), 1410 (w), 1443 (w), 1526 (m), 1574 (m), 1597 (s), 1628 (m), 1674 (w), 2174 (m), 2623 (w), 2857 (w).

Anal. calcd. for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{NO}$ (317.3): C 68.13, H 4.45, N 4.41; Found C 67.88, H 4.71, N 4.23.

4-(3-(4-(Dimethylamino)phenyl)propioloyl)benzonitrile (4i)



According to the general procedure using 4-iodo-*N,N*-dimethylaniline and 4-cyanobenzoyl chloride, 207 mg (0.755 mmol, 76%) of **4i** were obtained as an orange solid. Purification was performed using the flash purification system twice (*n*-hexane/acetone 9:1), Mp 187 °C.

^1H NMR (CDCl_3 , 300 MHz): δ 3.06 (s, 6 H, $\text{N}(\text{CH}_3)_2$), 6.63–6.68 (m, 2 H, CH_{Ar}), 7.54–7.59 (m, 2 H, CH_{Ar}), 7.77–7.81 (m, 2 H, CH_{Ar}), 8.26–8.30 (m, 2 H, CH_{Ar}).

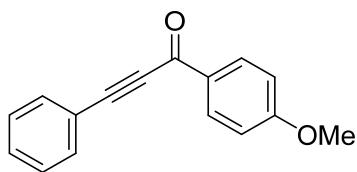
^{13}C -NMR (CDCl_3 , 75 MHz): δ 40.1 (CH_3), 88.3 (C_{quat}), 100.4 (C_{quat}), 104.8 (C_{quat}), 111.7 (CH), 116.5 (C_{quat}), 118.2 (C_{quat}), 129.7 (CH), 132.4 (CH), 135.6 (CH), 140.5 (C_{quat}), 152.2 (C_{quat}), 175.9 (C_{quat}).

EI + MS (m/z (%)): 274 (100) [M^+], 245 (17) [$\text{C}_{16}\text{H}_9\text{N}_2\text{O}^+$], 172 (47) [$\text{C}_{11}\text{H}_{10}\text{NO}^+$], 144 (17) [$\text{C}_{10}\text{H}_{10}\text{N}^+$], 123 (17), 102 (10) [$\text{C}_7\text{H}_4\text{N}^+$].

FT-IR: $\tilde{\nu}$ [cm^{-1}] = 646 (w), 673 (s), 712 (m), 752 (s), 795 (w), 814 (s), 853 (m), 977 (m), 958 (m), 997 (s), 1013 (s), 1028 (s), 1067 (m), 1125 (w), 1167 (s), 1184 (s), 1217 (m), 1294 (m), 1321 (s), 1371 (m), 1447 (m), 1489 (w), 1526 (s), 1560 (s), 1593 (s), 1618 (s), 2145 (m), 2168 (s), 2330 (w), 2394 (m), 2361 (w), 2826 (w), 2907 (w), 3084 (w), 3177 (w).

HRMS (ESI) (m/z) calcd. for [$\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}$] $^+$: 275.1179; Found: 275.1180.

1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (4j)



According to the general procedure using iodobenzene and 4-methoxybenzoyl chloride, 139 mg (0.588 mmol, 59%) of **4j** were obtained as a colorless solid. Purification was performed using the flash purification system (*n*-hexane/EtOAc 19:1→ 4:1), Mp 100 °C (lit.¹ 97 - 99 °C).

¹H NMR (CDCl₃, 300 MHz): δ 3.90 (s, 3 H, OCH₃), 6.96–7.01 (m, 2 H, CH_{Ar}), 7.38–7.50 (m, 3 H, CH_{Ar}), 7.66–7.69 (m, 2 H, CH_{Ar}), 8.17–8.22 (m, 2 H, CH_{Ar}).

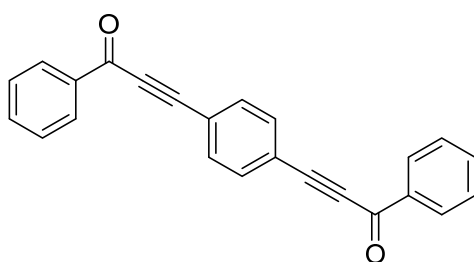
¹³C NMR (CDCl₃, 75 MHz): δ 55.7 (CH₃), 87.1 (C_{quat}), 92.4 (C_{quat}), 114.0 (CH), 120.5 (C_{quat}), 128.8 (CH), 130.5 (C_{quat}), 130.7 (CH), 132.1 (CH), 133.1 (CH), 164.6 (C_{quat}), 176.8 (C_{quat}).

EI + MS (*m/z* (%)): 236 (100) [M⁺], 208 (87), 193 (62), 165 (33), 135 (18) [C₈H₇O₂⁺], 129 (41) [C₉H₅O⁺].

IR: $\tilde{\nu}$ [cm⁻¹] = 669 (m), 681 (s), 752 (s), 777 (w), 822 (m), 839 (s), 922 (w), 995 (m), 1011 (m), 1069 (w), 1111 (m), 1157 (m), 1172 (m), 1188 (w), 1213 (m), 1258 (m), 1288 (m), 1306 (m), 1333 (w), 1422 (m), 1441 (w), 1456 (w), 1489 (m), 1508 (m), 1570 (m), 1593 (s), 1628 (s), 1892 (w), 1989 (w), 2195 (m), 2847 (w), 2901 (w), 2959 (w), 3011 (w).

HRMS (ESI) (*m/z*) calcd. for [C₁₆H₁₃O₂]⁺: 237.0910; Found: 237.0912.

1,1'-(1,4-Phenylene)bis(3-phenylprop-2-yn-1-one) (4k)



In deviation from the general procedure, 1.00 equiv of 1,4-diiodobenzene were used as aryl iodide **1** while the amount of all other reactants was doubled. With benzoyl chloride as aroyl chloride component, 199 mg (0.595 mmol, 60%) of **4k** were obtained as a yellow solid. Purification was performed using the flash purification system (*n*-hexane/DCM 4:1 → 1:1 → 0:1), Mp 185 °C (lit.⁴ 191 °C).

^1H NMR (CDCl_3 , 300 MHz): δ 7.51–7.57 (m, 4 H, CH_{Ar}), 7.63–7.69 (m, 2 H, CH_{Ar}), 7.73 (s, 4 H, CH_{Ar}), 8.20–8.24 (m, 4 H, CH_{Ar}).

^{13}C NMR (CDCl_3 , 75 MHz): δ 89.0 (C_{quat}), 91.3 (C_{quat}), 122.6 (C_{quat}), 128.9 (CH), 129.8 (CH), 133.2 (CH), 134.6 (CH), 136.8 (C_{quat}), 177.8 (C_{quat}).

EI + MS (m/z (%)): 334 (100) [M^+], 306 (28) [$\text{C}_{24}\text{H}_{18}^+$], 278 (52), 176 (11), 257 (51) [$\text{C}_{18}\text{H}_9\text{O}_{29}^+$], 229 (46) [$\text{C}_{17}\text{H}_9\text{O}^+$], 200 (26), 139 (16), 105 (16) [$\text{C}_7\text{H}_5\text{O}^+$], 77 (17) [C_6H_5^+].

IR: $\tilde{\nu}$ [cm^{-1}] = 662 (s), 694 (s), 787 (m), 839 (m), 937 (w), 999 (m), 1011 (s), 1032 (m), 1171 (m), 1209 (m), 1231 (w), 1277 (m), 1288 (s), 1314 (m), 1449 (m), 1497 (w), 1580 (m), 1599 (w), 1630 (s), 2195 (m), 3028 (w).

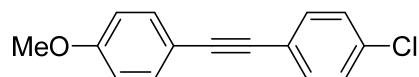
HRMS (ESI) (m/z) calcd. for [$\text{C}_{24}\text{H}_{15}\text{O}_2$] $^+$: 335.1067; Found: 335.1065.

3. General procedure for the synthesis of diarylalkynes **6** and **8**

Bis(triphenylphosphane)palladium(II)dichloride (35.1 mg, 50.0 μmol , 5.00 mol%) and aryl iodide **1** (1.00 mmol, 1.00 equiv, if solid) were placed in a flame-dried 10 mL Schlenk tube under a nitrogen atmosphere and the Schlenk tube was evacuated and flushed with nitrogen two more times. A solution of ethynyl magnesium bromide (**2**) in THF (2.40 mL, 0.500 M, 1.20 mmol) was added, as was aryl iodide **1**, if liquid. The resulting yellow solution was stirred at 45 °C until completion of the reaction (ca. 30 min, TLC control). Towards the end of the reaction the mixture turned turbid. It was cooled to rt, triethylamine hydrochloride (41.3 mg, 0.300 mmol, 0.300 equiv) was added and stirred for several minutes before the addition of triethylamine (106 mg, 1.05 mmol, 1.05 equiv), aryl iodide or aryl bromide **5** (1.10 mmol, 1.10 equiv) and copper(I) iodide (9.50 mg, 50.0 μmol , 5.00 mol%), upon which the reaction mixture darkened to brown. The reaction was stirred at room temp for ca. 1.5 h (for aryl iodides) or at 60 °C for 4.5 h (for aryl bromides) (TLC control). Brine was added and the aqueous phase was extracted with EtOAc (5 \times 10 mL). The combined organic phases were washed with brine, dried with anhydrous MgSO_4 , filtered, and the crude product was adsorbed onto Celite®. For purification, chromatography on silica gel was performed using a Biotage *SP4* flash purification system or manual flash technique with eluents consisting of *n*-hexane und EtOAc or DCM.

3.1 Analytical data for diarylalkynes **6** and **8**

1-Chloro-4-((4-methoxyphenyl)ethynyl)benzene (**6a**)



According to the general procedure using 4-iodoanisole (aryl iodide **1**) and 1-chloro-4-iodobenzene (aryl iodide **2**), 196 mg (0.808 mmol, 81%) of **6a** were obtained as a light yellow solid. Purification was performed using the flash purification system (*n*-hexane/EtOAc 19:1 → 9:1), Mp 123 °C (lit.⁵ 122-124 °C).

¹H NMR (CDCl₃, 300 MHz): δ 3.83 (s, 3 H, OCH₃), 6.86–6.91 (m, 2 H, CH_{Ar}), 7.29–7.33 (m, 2 H, CH_{Ar}), 7.41–7.49 (m, 4 H, CH_{Ar}).

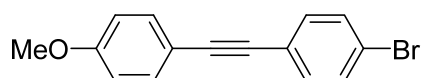
¹³C NMR (CDCl₃, 75 MHz): δ 55.4 (CH₃), 87.1 (C_{quat}), 90.5 (C_{quat}), 114.2 (CH), 115.1 (C_{quat}), 122.3 (C_{quat}), 128.8 (CH), 132.8 (CH), 133.2 (CH), 134.0 (C_{quat}), 159.9 (C_{quat}).

EI + MS (*m/z* (%)): 244 (34) [M⁺, ³⁹Cl], 242 (100) [M⁺, ³⁷Cl], 229 (21) [C₁₄H₈³⁹ClO⁺], 227 (60) [C₁₄H₈³⁷ClO⁺], 201 (11) [C₁₃H₈³⁹Cl⁺], 199 (35) [C₁₃H₈³⁷Cl⁺], 163 (32).

FT-IR: $\tilde{\nu}$ [cm⁻¹] = 698 (m), 719 (w), 783 (w), 820 (m), 829 (s), 1013 (m), 1028 (m), 1084 (m), 1099 (m), 1138 (m), 1173 (m), 1248 (m), 1287 (m), 1317 (w), 1396 (w), 1441 (w), 1485 (m), 1506 (m), 1605 (m), 1908 (w), 2216 (w), 2841 (w), 2916 (w), 2938 (w), 2965 (w), 3015 (w).

Anal. calcd. for C₁₅H₁₁ClO (242.1): C 74.23, H 4.57; Found: C 74.01, H 4.60.

1-Bromo-4-((4-methoxyphenyl)ethynyl)benzene (**6b**)



According to the general procedure using 4-iodoanisole (aryl iodide **1**) and 1-bromo-4-iodobenzene (aryl iodide **2**), 226 mg (0.787 mmol, 79%) of **6b** were obtained as a beige solid. Purification was performed using the flash purification system (*n*-hexane/EtOAc 19:1 → 9:1), Mp 153 °C (lit.⁶ 153-154 °C).

¹H NMR (CDCl₃, 300 MHz): δ 3.83 (s, 3 H, OCH₃), 6.86–6.90 (m, 2 H, CH_{Ar}), 7.34–7.39 (m, 2 H, CH_{Ar}), 7.44–7.50 (m, 4 H, CH).

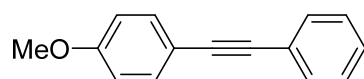
¹³C NMR (CDCl₃, 75 MHz): δ 55.4 (OCH₃), 87.2 (C_{quat}), 90.7 (C_{quat}), 114.2 (CH), 115.1 (C_{quat}), 122.2 (C_{quat}), 122.7 (C_{quat}), 131.7 (CH), 133.0 (CH), 133.2 (CH), 159.9 (C_{quat}).

EI + MS (m/z (%)): 288 (100) [M^+ , ^{81}Br], 286 (100) [M^+ , ^{79}Br], 245 (20) [$\text{C}_{13}\text{H}_8^{81}\text{Br}^+$], 243 (22) [$\text{C}_{13}\text{H}_8^{79}\text{Br}^+$], 164 (45) [$\text{C}_{13}\text{H}_8^+$], 163 (57) [$\text{C}_{13}\text{H}_7^+$].

FT-IR: $\tilde{\nu}$ [cm^{-1}] = 681 (m), 781 (w), 824 (s), 1009 (m), 1030 (m), 1069 (m), 1109 (m), 1175 (m), 1250 (s), 1287 (m), 1393 (m), 1441 (m), 1481 (m), 1506 (m), 1605 (m), 2216 (w), 2839 (w), 2901 (w), 2938 (w), 2965 (w), 3011 (w).

Anal. calcd. for $\text{C}_{15}\text{H}_{11}\text{BrO}$ (287.2): C 62.47, H 3.86; Found: C 62.55, H 3.62.

1-Methoxy-4-(phenylethynyl)benzene (6c)



According to the general procedure using 4-iodoanisole (aryl iodide 1) and iodobenzene (224 mg, aryl iodide 2), 163 mg (0.783 mmol, 78%) of **6c** were obtained as beige solid. Purification was performed using the flash purification system (*n*-hexane/EtOAc 19:1 → 9:1), Mp 60 °C (lit.⁷ 60-61 °C).

^1H NMR (CDCl_3 , 300 MHz): δ 3.83 (s, 3 H, OCH_3), 6.86–6.91 (m, 2 H, CH_{Ar}), 7.30–7.38 (m, 3 H, CH_{Ar}), 7.44–7.55 (m, 4 H, CH_{Ar}).

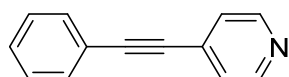
^{13}C NMR (CDCl_3 , 75 MHz): δ 55.4 (CH_3), 88.2 (C_{quat}), 89.5 (C_{quat}), 114.1 (CH), 115.5 (C_{quat}), 123.7 (C_{quat}), 128.1 (CH), 128.4 (CH), 131.6 (CH), 133.2 (CH), 159.7 (C_{quat}).

EI + MS (m/z (%)): 208 (100) [M^+], 193 (65) [$\text{C}_{14}\text{H}_9\text{O}^+$], 165 (53) [$\text{C}_{13}\text{H}_9^+$].

FT-IR: $\tilde{\nu}$ [cm^{-1}] = 689 (s), 752 (s), 779 (m), 812 (m), 835 (s), 914 (w), 1026 (s), 1069 (m), 1107 (m), 1138 (m), 1173 (m), 1246 (s), 1287 (m), 1439 (m), 1456 (m), 1489 (m), 1508 (s), 1593 (m), 1605 (m), 2241 (w), 2533 (w), 2839 (w), 2901 (w), 3011 (w), 3051 (w).

Anal. calcd. for $\text{C}_{15}\text{H}_{12}\text{O}$ (208.3): C 86.15, H 5.81; Found: C 86.26, H 5.64.

4-(Phenylethynyl)pyridine (6d)



According to the general procedure using iodobenzene (aryl iodide 1) and 4-iodopyridine (aryl iodide 2), 142 mg (0.798 mmol, 80%) of **6d** were obtained as a beige solid. Purification was performed using the flash purification system (*n*-hexane/EtOAc 19:1 → 2:1), Mp 93 °C (lit.⁸ 92-

93 °C).

^1H NMR (CDCl_3 , 300 MHz): δ 7.33–7.43 (m, 5 H, CH_{Ar}), 7.51–5.59 (m, 2 H, CH_{Ar}), 8.57–8.63 (m, 2 H, CH_{Ar}).

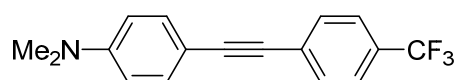
^{13}C NMR (CDCl_3 , 75 MHz): δ 86.8 (C_{quat}), 94.1 (C_{quat}), 122.2 (C_{quat}), 125.7 (CH), 128.6 (CH), 129.3 (CH), 131.6 (C_{quat}), 132.0 (CH), 149.9 (CH).

EI + MS (m/z (%)): 179 (100) [M^+], 151 (16).

FT-IR: $\tilde{\nu}$ [cm^{-1}] = 667 (m), 691 (s), 758 (s), 827 (s), 854 (m), 910 (w), 922 (m), 972 (w), 987 (m), 1026 (m), 1963 (w), 1105 (w), 1121 (w), 1215 (m), 1260 (w), 1412 (m), 1441 (m), 1537 (m), 1587 (m), 1599 (m), 2222 (m), 2336 (w), 2924 (w), 3022 (w), 3061 (w), 3075 (w), 3836 (w).

HRMS (ESI) (m/z) calcd. for [$\text{C}_{13}\text{H}_9\text{N-H}$] $^+$: 180.0808; Found: 180.0809.

***N,N*-Dimethyl-4-((4-(trifluoromethyl)phenyl)ethynyl)aniline (6e)**



According to the general procedure using 4-iodo-*N,N*-dimethylaniline (aryl iodide 1) and 4-iodobenzotrifluoride (aryl iodide 2), 239 mg (0.826 mmol, 83%) of **6e** were obtained as an orange solid. Purification was performed using manual flash technique (*n*-hexane/EtOAc 20:1), Mp 165 °C.

^1H NMR (CDCl_3 , 300 MHz): δ 3.01 (s, 6 H, $\text{N}(\text{CH}_3)_2$), 6.63–6.71 (m, 2 H, CH_{Ar}), 7.39–7.47 (m, 2 H, CH_{Ar}), 7.55–7.61 (m, 4 H, CH_{Ar}).

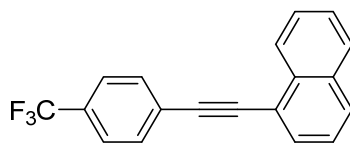
^{13}C NMR (CDCl_3 , 75 MHz): δ 40.3 ($\text{N}(\text{CH}_3)_2$), 84.6 (C_{quat}), 93.6 (C_{quat}), 109.2 (C_{quat}), 111.9 (CH), 124.2 (q, C_{quat} , $^1\text{J}_{\text{F}} = 272$ Hz), 125.3 (q, CH, $^3\text{J}_{\text{F}} = 4$ Hz), 128.2 (q, C_{quat} , $^5\text{J}_{\text{F}} = 2$ Hz), 129.1 (q, C_{quat} , $^2\text{J}_{\text{F}} = 33$ Hz), 131.5 (CH), 133.1 (CH), 150.6 (C_{quat}).

EI + MS (m/z (%)): 289 (100) [M^+], 273 (20), 144 (16) [$\text{C}_{10}\text{H}_{10}\text{N}^+$].

FT-IR: $\tilde{\nu}$ 660 (m), 735 (m), 818 (s), 945 (m), 1003 (m), 1065 (m), 1099 (s), 1157 (m), 1184 (w), 1200 (w), 1227 (m), 1312 (m), 1362 (w), 1460 (w), 1445 (w), 1481 (w), 1508 (w), 1526 (m), 1597 (m), 1892 (w), 2168 (w), 2208 (w), 2812 (w), 2966 (w), 2901 (w), 2990 (w).

Anal. calcd. for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{N}$ (289.3): C 70.58, H 4.88; Found: C 70.33, H 4.71.

1-((4-(Trifluoromethyl)phenyl)ethynyl)naphthalene (6f)



According to the general procedure using 4-iodobenzotrifluoride (aryl iodide 1) and 1-iodonaphthalene (aryl iodide 2), 195 mg (0.658 mmol, 66%) of **6f** were obtained as a light yellow solid. Purification was performed using manual flash technique (*n*-hexane), Mp 58 °C.

¹H NMR (CDCl₃, 300 MHz): δ 7.46–7.51 (m, 1 H, CH_{Ar}), 7.53–7.67 (m, 4 H, CH_{Ar}), 7.74–7.81 (m, 3 H, CH_{Ar}), 7.88–7.90 (m, 2 H, CH_{Ar}), 8.40–8.43 (m, 1 H, CH_{Ar}).

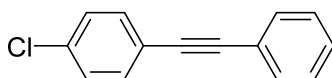
¹³C NMR (CDCl₃, 75 MHz): δ 90.1 (C_{quat}), 93.0 (C_{quat}), 120.3 (C_{quat}), 125.4 (CH), 125.5 (q, CH, ³J_F = 4 Hz), 126.1 (CH), 126.7 (CH), 127.2 (CH), 127.4 (q, C_{quat}, ⁵J_F = 1 Hz), 128.6 (CH), 129.5 (CH), 130.2 (q, C_{quat}, ²J_F = 33 Hz), 130.9 (CH), 132.0 (CH), 133.4 (C_{quat}). Probably due to overlap, the signal for one C_{quat} and the CF₃ group are not visible.

EI + MS (*m/z* (%)): 296 (100) [M⁺], 226 (31) [C₁₈H₁₀⁺].

FT-IR: $\tilde{\nu}$ [cm⁻¹] = 681 (w), 735 (w), 746 (w), 770 (s), 795 (m), 843 (s), 907 (w), 957 (w), 1011 (w), 1065 (m), 1103 (s), 1115 (s), 1155 (m), 1184 (w), 1321 (m), 1406 (w), 1504 (w), 1612 (w), 1684 (w), 1929 (w), 2208 (w), 2928 (w), 3046 (w), 3055 (w).

Anal. calcd. for C₁₇H₁₄F₃N (296.3): C 77.02, H 3.74; Found: C 76.82, H 3.54.

1-Chloro-4-(phenylethynyl)benzene (6g)



According to the general procedure using 1-chloro-4-iodobenzene (aryl iodide 1) and iodobenzene (aryl iodide 2), 142 mg (0.668 mmol, 67%) of **6g** were obtained as a light yellow solid. Purification was performed using manual flash technique (*n*-hexane), Mp 85 °C (lit.⁹ 82–84 °C).

¹H NMR (CDCl₃, 300 MHz): δ 7.31–7.32 (m, 1 H, CH_{Ar}), 7.34–7.38 (m, 4 H, CH_{Ar}), 7.44–7.49 (m, 2 H, CH_{Ar}), 7.50–7.56 (m, 2 H, CH_{Ar}).

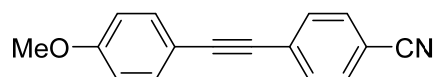
¹³C NMR (CDCl₃, 75 MHz): δ 88.4 (C_{quat}), 90.5 (C_{quat}), 121.9 (C_{quat}), 123.0 (C_{quat}), 128.5 (CH), 128.6 (CH), 128.8 (CH), 131.7 (CH), 132.9 (CH), 134.4 (C_{quat}).

EI + MS (m/z (%)): 214 (33) [M^+ , ^{37}Cl], 212 (100) [M^+ , ^{35}Cl], 176 (46) [$\text{C}_{14}\text{H}_8^+$], 151 (11).

FT-IR: $\tilde{\nu}$ [cm^{-1}] = 685 (s), 731 (m), 750 (s), 797 (w), 824 (s), 910 (w), 1011 (s), 1028 (w), 1090 (s), 1180 (w), 1261 (w), 1398 (w), 1495 (s), 1585 (w), 1911 (w), 3049 (w).

Anal. calcd. for $\text{C}_{14}\text{H}_9\text{Cl}$ (212.7): C 79.07, H 4.27; Found: C 78.91, H 4.27.

4-((4-Methoxyphenyl)ethynyl)benzonitrile (**6h**)



According to the general procedure using 4-iodoanisole (aryl iodide **1**) and 4-iodobenzonitrile (aryl iodide **2**), 149 mg (0.639 mmol, 64%) of **6h** were obtained as a light yellow solid. Purification was performed using the flash purification system (*n*-hexane/EtOAc 19:1 → 4:1), Mp 120 °C (lit.¹⁰ 120-122 °C).

^1H NMR (CDCl_3 , 300 MHz): δ 3.84 (s, 3 H, OCH_3), 6.89–6.91 (m, 2 H, CH_{Ar}), 7.47–7.49 (m, 2 H, CH_{Ar}), 7.56–7.62 (m, 4 H, CH_{Ar}).

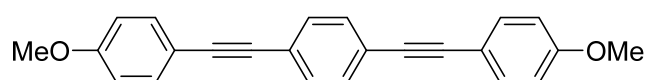
^{13}C NMR (CDCl_3 , 75 MHz): δ 55.5 (CH_3), 86.9 (C_{quat}), 94.2 (C_{quat}), 111.1 (C_{quat}), 114.3 (CH), 114.4 (C_{quat}), 118.8 (C_{quat}), 128.8 (C_{quat}), 132.0 (CH), 132.1 (CH), 133.5 (CH), 160.4 (CN).

EI + MS (m/z (%)): 233 (100) [M^+], 218 (46) [$\text{C}_{15}\text{H}_8\text{NO}^+$], 190 (47) [$\text{C}_{14}\text{H}_8\text{N}^+$], 163 (16).

FT-IR: $\tilde{\nu}$ [cm^{-1}] = 644 (w), 729 (w), 793 (w), 826 (m), 833 (s), 1026 (m), 1109 (m), 1134 (m), 1173 (w), 1250 (m), 1290 (w), 1445 (w), 1504 (m), 1595 (w), 2210 (w), 2226 (w), 2544 (w), 2847 (w), 2941 (w), 3086 (w).

Anal. calcd. for $\text{C}_{16}\text{H}_{11}\text{NO}$ (233.3): C 82.38, H 5.36, N 6.00; Found: C 82.11, H 4.84, N 5.70.

1,4-Bis((4-methoxyphenyl)ethynyl)benzene (**6i**)



In deviation from the general procedure, 0.500 equiv of 1,4-diiodobenzene were used as aryl iodide **1**. With 4-iodoanisole (aryl iodide **5**), 115 mg (0.680 mmol, 68%) of **6i** were obtained as a light yellow solid. Purification was performed using the flash purification system (*n*-hexane/DCM 9:1 → 2:1), a sample was recrystallized from *n*-hexane for analytical purposes, Mp >210 °C (dec.) (lit.¹¹ 216-218 °C).

^1H NMR (CDCl_3 , 600 MHz, 60 °C): δ 3.81 (s, 6 H, OCH_3), 6.99 (d, 4 H, CH_{Ar} , $^3J_{\text{H}} = 8.1$ Hz), 7.50 (d, 4 H, CH_{Ar} , $^3J_{\text{H}} = 7.9$ Hz), 7.53 (s, 4 H, CH_{Ar}).

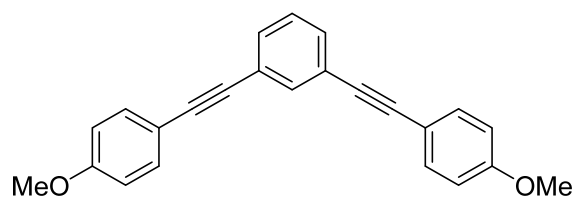
^{13}C NMR (CDCl_3 , 150 MHz, 60 °C): δ 55.1 (OCH_3), 87.5 (C_{quat}), 91.3 (C_{quat}), 113.9 (C_{quat}), 114.3 (CH), 122.4 (C_{quat}), 131.1 (CH), 132.8 (CH), 159.6 (C_{quat}).

EI + MS (m/z (%)): 338 (100) [M^+], 323 (42) [$\text{C}_{23}\text{H}_{15}\text{O}_2^+$], 280 (10) [$\text{C}_{21}\text{H}_{12}\text{O}^+$], 252 (11) [$\text{C}_{20}\text{H}_{12}^+$], 169 (14), 126 (13).

FT-IR: $\tilde{\nu}$ [cm^{-1}] = 760 (m), 818 (m), 835 (s), 1028 (m), 1074 (m), 1107 (m), 1134 (w), 1148 (m), 1175 (m), 1242 (s), 1287 (m), 1406 (w), 1441 (m), 1491 (m), 1518 (s), 1568 (w), 1603 (m), 2210 (w), 2841 (w), 2901 (w), 2967 (w).

Anal. calcd. for $\text{C}_{24}\text{H}_{18}\text{O}_2$ (338.4): C 85.18, H 5.36; Found: C 84.90, H 5.43.

1,3-Bis((4-methoxyphenyl)ethynyl)benzene (**6j**)



In deviation from the general procedure, 0.500 equiv of 1,3-diiodobenzene were used as aryl iodide **1**. With 4-iodoanisole (aryl iodide **5**), 149 mg (0.441 mmol, 88%) of **6j** were obtained as a light yellow solid. Purification was performed using the flash purification system (*n*-hexane/DCM 9:1 \rightarrow 2:1), a sample was recrystallized from *n*-hexane/EtOAc for analytical purposes, Mp 125–136 °C.

^1H NMR (CDCl_3 , 300 MHz): δ 3.83 (s, 6 H, OCH_3), 6.86–6.91 (m, 4 H, CH_{Ar}), 7.28–7.34 (m, 1 H, CH_{Ar}), 7.43–7.50 (m, 6 H, CH_{Ar}), 7.67–7.71 (m, 1 H, CH_{Ar}).

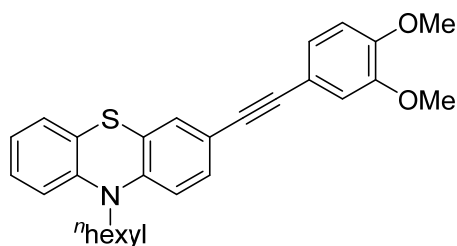
^{13}C NMR (CDCl_3 , 75 MHz): δ 55.5 (CH_3), 87.5 (C_{quat}), 90.1 (C_{quat}), 114.2 (CH), 115.3 (C_{quat}), 124.0 (C_{quat}), 128.5 (CH), 130.9 (CH), 133.3 (CH), 134.4 (CH), 159.9 (C_{quat}).

EI + MS (m/z (%)): 338 (100) [M^+], 323 (26) [$\text{C}_{23}\text{H}_{15}\text{O}_2^+$], 238 (16), 223 (11), 169 (12) [$\text{C}_{12}\text{H}_9\text{O}^+$].

FT-IR: $\tilde{\nu}$ [cm^{-1}] = 640 (w), 685 (s), 762 (w), 797 (s), 820 (s), 835 (s), 897 (m), 930 (w), 1028 (s), 1088 (w), 1105 (m), 1155 (w), 1173 (s), 1244 (s), 1279 (m), 1288 (m), 1434 (w), 1441 (m), 1456 (m), 1508 (s), 1557 (m), 1589 (m), 1605 (m), 1896 (w), 2210 (w), 2536 (w), 2839 (w), 2934 (w), 2965 (m), 3003 (w), 3661 (w).

Anal. calcd. for C₂₄H₁₈O₂ (338.4): C 85.18, H 5.36; Found: C 84.43, H 5.38.

3-((3,4-Dimethoxyphenyl)ethynyl)-10-hexyl-10H-phenothiazine (6k)



Using 3-iodo-10-hexyl-10H-phenothiazine (aryl iodide **1**) and 4-iodo-1,2-dimethoxybenzene (aryl iodide **5**), 307 mg (0.692 mmol, 69%) of **6k** were obtained as a yellow resin that crystallised slowly. Purification was performed using the flash purification system (*n*-hexane/acetone 19:1 → 4:1), Mp 77 °C.

¹H NMR (CDCl₃, 300 MHz): δ 0.85–0.90 (m, 3 H, CH₃), 1.26–1.34 (m, 4 H, CH₂), 1.38–1.48 (m, 2 H, CH₂), 1.74–1.84 (m, 2 H, CH₂), 3.80 – 3.87 (m, 2 H, NCH₂), 3.898 (s, 3 H, OCH₃), 3.901 (s, 3 H, OCH₃), 6.77–6.86 (m, 3 H, CH_{Ar}), 6.91 (t, 1 H, CH_{Ar}, ³J_H = 7.9 Hz), 7.01 (d, 1 H, ⁴J_H = 1.8 Hz), 7.09–7.17 (m, 3 H, CH_{Ar}), 7.27–7.30 (m, 2 H, CH_{Ar}).

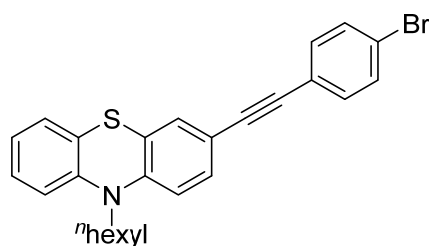
¹³C NMR (CDCl₃, 75 MHz): δ 14.0 (CH₃), 22.6 (CH₂), 26.6 (CH₂), 26.8 (CH₂), 31.4 (CH₂), 47.6 (NCH₂), 55.9 (2 OCH₃), 87.4 (C_{quat}), 89.2 (C_{quat}), 111.0 (CH), 114.1 (CH), 115.0 (CH), 115.5 (CH), 115.7 (C_{quat}), 117.1 (C_{quat}), 126.6 (CH), 124.2 (C_{quat}), 124.7 (CH), 124.8 (C_{quat}), 127.3 (CH), 127.5 (CH), 130.0 (CH), 130.6 (CH), 144.7 (C_{quat}), 145.1 (C_{quat}), 148.6 (C_{quat}), 149.3 (C_{quat}).

EI + MS (*m/z* (%)): 443 (72) [M⁺], 358 (100) [C₂₂H₁₈NO₂S⁺], 340 (13), 314 (17), 149 (15).

FT-IR: $\tilde{\nu}$ [cm⁻¹] = 617 (w), 638 (w), 683 (w), 716 (w), 735 (m), 743 (s), 762 (w), 800 (s), 818 (m), 872 (m), 949 (w), 1022 (s), 1036 (w), 1053 (w), 1103 (w), 1126 (m), 1180 (m), 1194 (w), 1223 (s), 1256 (m), 1296 (w), 1325 (m), 1337 (m), 1369 (w), 1398 (w), 1442 (w), 1441 (m), 1456 (s), 1495 (w), 1516 (m), 1574 (w), 1599 (w), 2841 (w), 2857 (w), 2868 (w), 2922 (w), 2954 (w), 2968 (w), 2999 (w), 3061 (w).

HRMS (ESI) (*m/z*) calcd. for [C₂₈H₂₉NO₂S]⁺: 443.1916; Found: 443.1914.

3-((4-Bromophenyl)ethynyl)-10-hexyl-10H-phenothiazine (6I)



Departing from the general procedure, the reaction was performed on a 0.880 mmol scale. Using 3-iodo-10-hexyl-10H-phenothiazine (aryl iodide **1**) and 1-bromo-4-iodobenzene (aryl iodide **5**), 199 mg (0.430 mmol, 49%) of **6I** were obtained as a yellow resin. Purification was performed using manual flash technique (*n*-hexane).

^1H NMR (CDCl_3 , 300 MHz): δ 0.86–0.90 (m, 3 H, CH_3), 1.26–1.38 (m, 4 H, CH_2), 1.34–1.38 (m, 2 H, CH_2), 1.75–1.85 (m, 2 H, CH_2), 3.81–3.86 (m, 3 H, NCH_2), 6.79 (d, 1 H, CH_{Ar} , $^3J_{\text{H}} = 8.3$ Hz), 6.85 (dd, 1 H, CH_{Ar} , $^3J_{\text{H}} = 8.2$ Hz, $^4J_{\text{H}} = 1.2$ Hz), 6.92 (td, 1 H, CH_{Ar} , $^3J_{\text{H}} = 7.5$ Hz, $^4J_{\text{H}} = 1.2$ Hz), 7.10–7.18 (m, 2 H, CH_{Ar}), 7.26–7.31 (m, 2 H, CH_{Ar}), 7.33–7.37 (m, 2 H, CH_{Ar}), 7.44–7.48 (m, 2 H, CH_{Ar}).

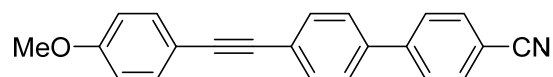
^{13}C NMR (CDCl_3 , 75 MHz): δ 14.1 (CH_3), 22.7 (CH_2), 26.7 (CH_2), 26.9 (CH_2), 31.6 (CH_2), 47.7 (NCH_2), 88.3 (C_{quat}), 90.2 (C_{quat}), 115.1 (CH), 115.7 (CH), 116.7 (C_{quat}), 122.3 (C_{quat}), 122.6 (C_{quat}), 122.9 (CH), 124.3 (C_{quat}), 125.0 (C_{quat}), 127.5 (CH), 127.6 (CH), 130.3 (CH), 130.9 (CH), 131.7 (CH), 133.0 (CH), 144.7 (C_{quat}), 145.7 (C_{quat}).

EI + MS (m/z (%)): 463 (80) [M^+ , ^{81}Br], 461 (81) [M^+ , ^{79}Br], 392 (40) [$\text{C}_{21}\text{H}_{13}^{81}\text{BrNS}^+$], 390 (39) [$\text{C}_{21}\text{H}_{13}^{79}\text{BrNS}^+$], 378 (100) [$\text{C}_{20}\text{H}_{11}^{81}\text{BrNS}^+$], 376 (93) [$\text{C}_{20}\text{H}_{11}^{79}\text{BrNS}^+$], 358 (15), 339 (10) [$\text{C}_{23}\text{H}_{17}\text{NS}^+$], 297 (22) [$\text{C}_{20}\text{H}_{11}\text{NS}^+$], 296 (23), 254 (12) [$\text{C}_{16}\text{H}_{16}\text{NS}^+$], 248 (10) [$\text{C}_{16}\text{H}_{10}\text{NS}^+$], 139 (14), 43 (11) [C_3H_7^+].

FT-IR: $\tilde{\nu}$ [cm^{-1}] = 627 (w), 671 (w), 704 (m), 745 (s), 773 (w), 820 (s), 854 (w), 880 (m), 923 (w), 1009 (s), 1040 (m), 1069 (m), 1103 (m), 1142 (m), 1153 (m), 1194 (m), 1236 (m), 1250 (m), 1267 (m), 1285 (m), 1333 (m), 1362 (m), 1393 (m), 1443 (s), 1456 (s), 1483 (m), 1497 (s), 1545 (w), 1574 (w), 1599 (w), 2201 (w), 2855 (w), 2924 (m), 2953 (w), 3061 (w).

Anal. calcd. for $\text{C}_{26}\text{H}_{24}\text{BrNS}$ (462.5): C 67.53, H 5.23, N 3.03, S 6.93; Found: H 67.52, H 5.23, N 2.69, S 6.67.

4'-((4-Methoxyphenyl)ethynyl)-[1,1'-biphenyl]-4-carbonitrile (**8**)



In deviation from the general procedure, the reaction was performed in a 10 mL microwave vial using 4-iodoanisole (aryl iodide **1**) and 1-bromo-4-iodobenzene (aryl iodide **5**). After completion of the second step (TLC control), cesium carbonate (978 mg, 3.00 mmol, in 1.00 mL distilled H₂O), 4-cyanophenylboronic acid pinacolyl ester (354 mg, 1.50 mmol), and triphenylphosphane (52.5 mg, 0.200 mmol) were added and the reaction mixture was heated to 120 °C (microwave irradiation) for 1 h. Brine was added and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic phases were washed with saturated aqueous NH₄Cl solution and brine, dried with anhydrous MgSO₄, filtered, and the crude product was adsorbed onto Celite®. Purification using manual flash technique (*n*-hexane/DCM 2:1 → 1:1) gave 143 mg (0.462 mmol, 46%) of **8** as a beige solid, Mp 198 °C (lit.¹² 202 °C).

¹H NMR (CDCl₃, 300 MHz): δ 3.84 (s, 3 H, OCH₃), 6.87–6.92 (m, 2 H, CH_{Ar}), 7.74–7.52 (m, 2 H, CH_{Ar}), 7.55–7.63 (m, 4 H, CH_{Ar}), 7.67–7.75 (m, 4 H, CH_{Ar}).

¹³C NMR (CDCl₃, 75 MHz): δ 55.5 (CH₃), 87.7 (C_{quat}), 91.3 (C_{quat}), 111.2 (C_{quat}), 114.2 (CH), 115.2 (C_{quat}), 119.0 (C_{quat}), 124.3 (C_{quat}), 127.2 (CH), 127.7 (CH), 132.2 (CH), 132.8 (CH), 133.3 (CH), 138.5 (C_{quat}), 144.9 (C_{quat}), 160.0 (C_{quat}).

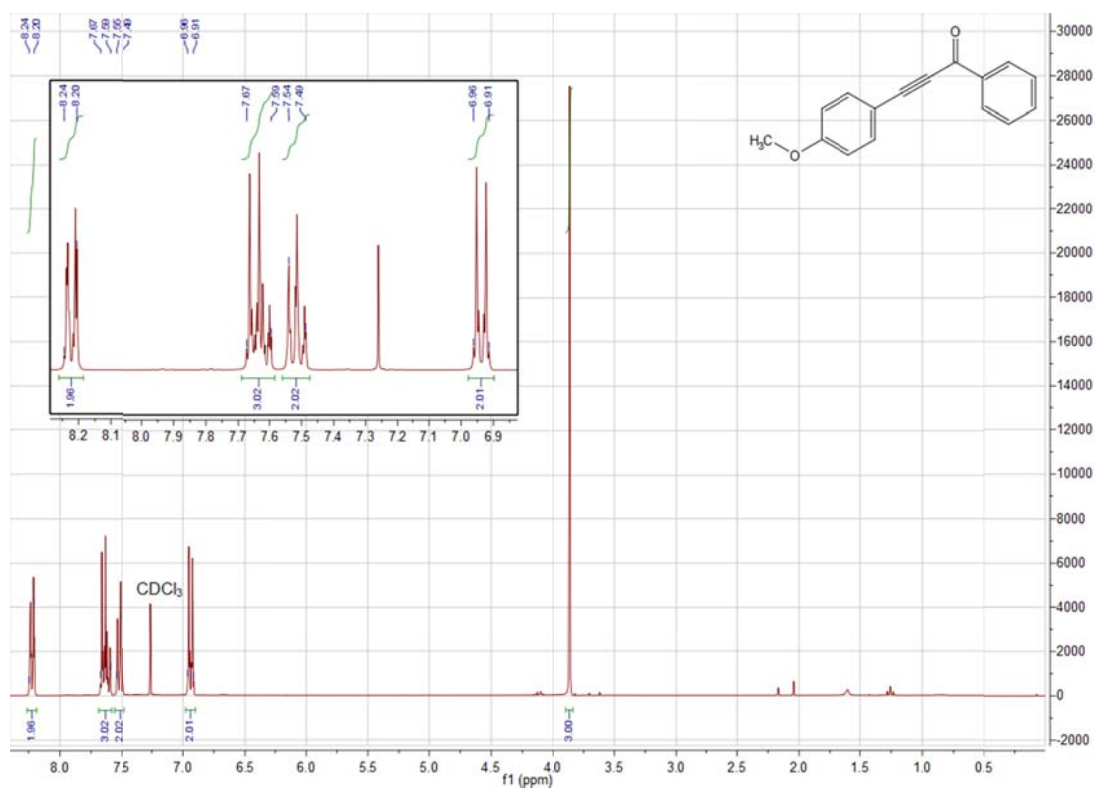
EI + MS (*m/z* (%)): 309 (100) [M⁺], 294 (32) [C₂₁H₁₂NO⁺], 266 (16), 264 (17), 155 (13).

FT-IR: $\tilde{\nu}$ [cm⁻¹] = 638 (w), 691 (m), 716 (w), 739 (w), 793 (m), 808 (s), 822 (s), 856 (w), 953 (w), 1003 (m), 1022 (s), 1107 (m), 1138 (m), 1173 (s), 1248 (s), 1288 (m), 1395 (w), 1445 (m), 1506 (s), 1568 (w), 1597 (m), 1867 (w), 1917 (w), 2212 (w), 2226 (m), 2538 (w), 2839 (w), 2916 (w), 2957 (w), 3036 (w), 3065 (w).

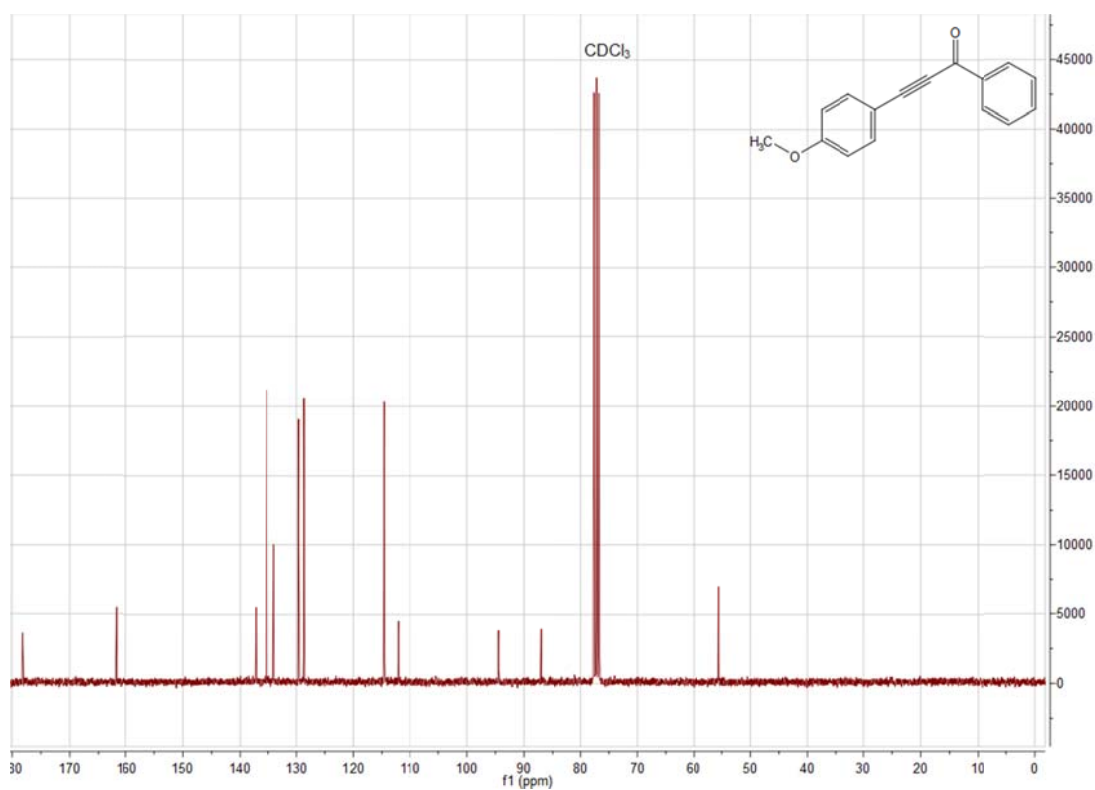
HRMS (ESI) (*m/z*) calcd. for [C₂₂H₁₅NO-H]⁺: 310.1126; found: 310.1129.

4. NMR spectra of compounds 4, 6, and 8

^1H NMR of 3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (4a) (CDCl_3 , 300 MHz, $T = 298$ K)



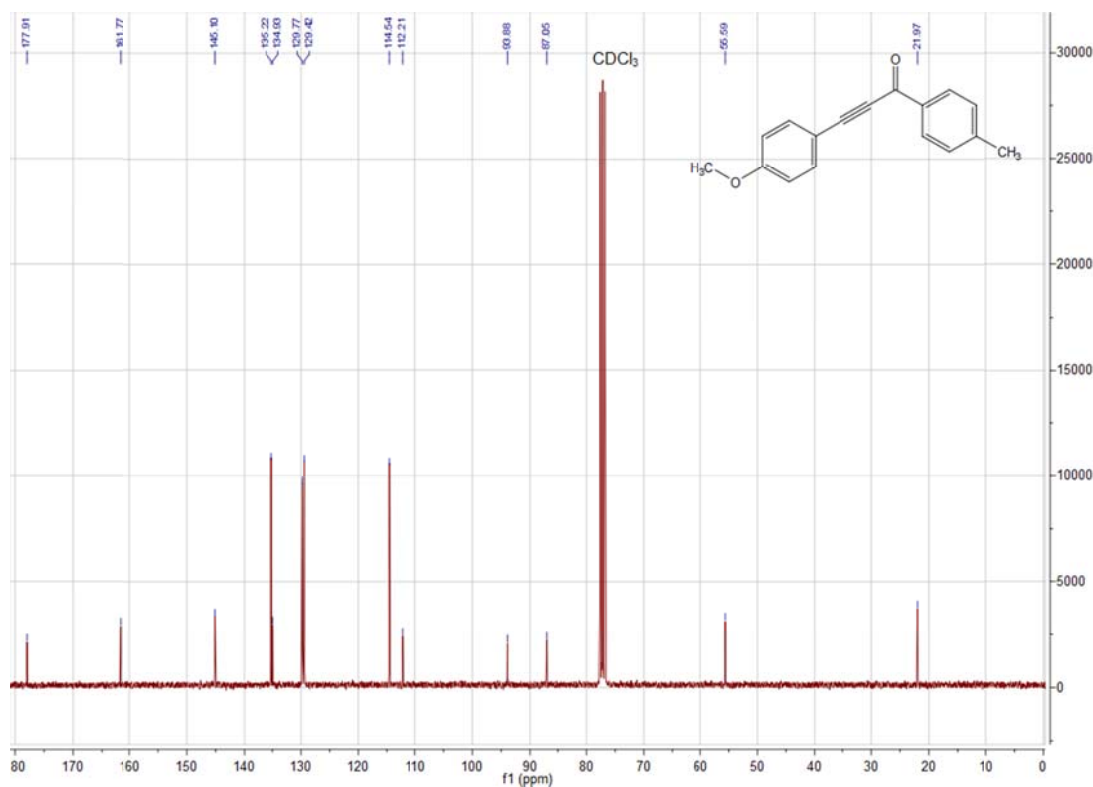
^{13}C NMR of 3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (4a) (CDCl_3 , 75 MHz, $T = 298$ K)



¹H NMR of 3-(4-methoxyphenyl)-1-(*p*-tolyl)prop-2-yn-1-one (4b) (CDCl₃, 300 MHz, T = 298 K)

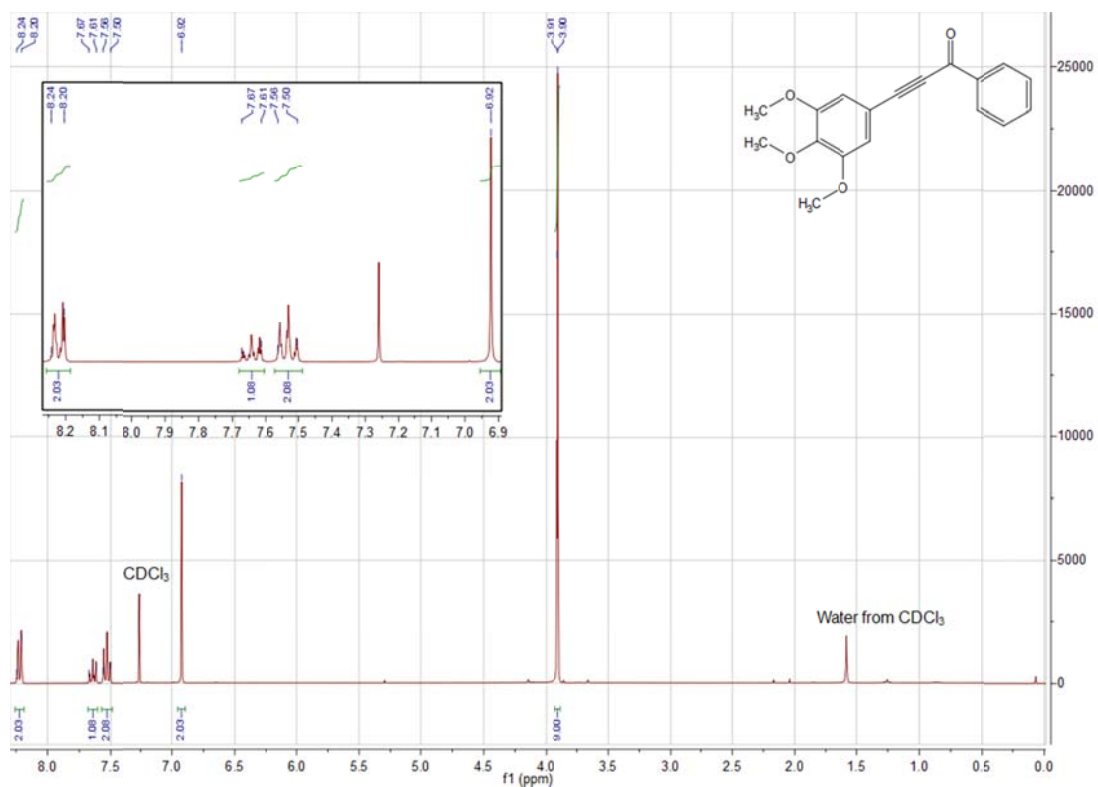


¹³C NMR of 3-(4-methoxyphenyl)-1-(*p*-tolyl)prop-2-yn-1-one (4b) (CDCl₃, 75 MHz, T = 298 K)



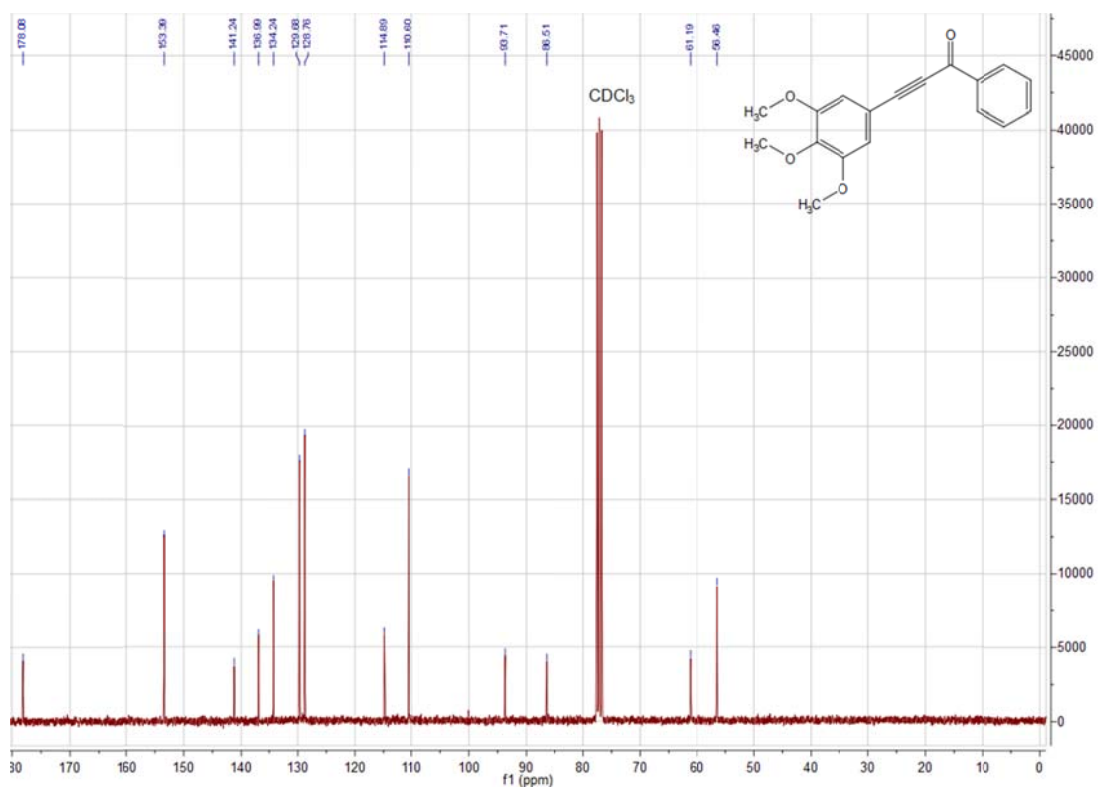
^1H NMR of 1-phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-yn-1-one (4c) (CDCl_3 , 300 MHz, $T = 298$

K)

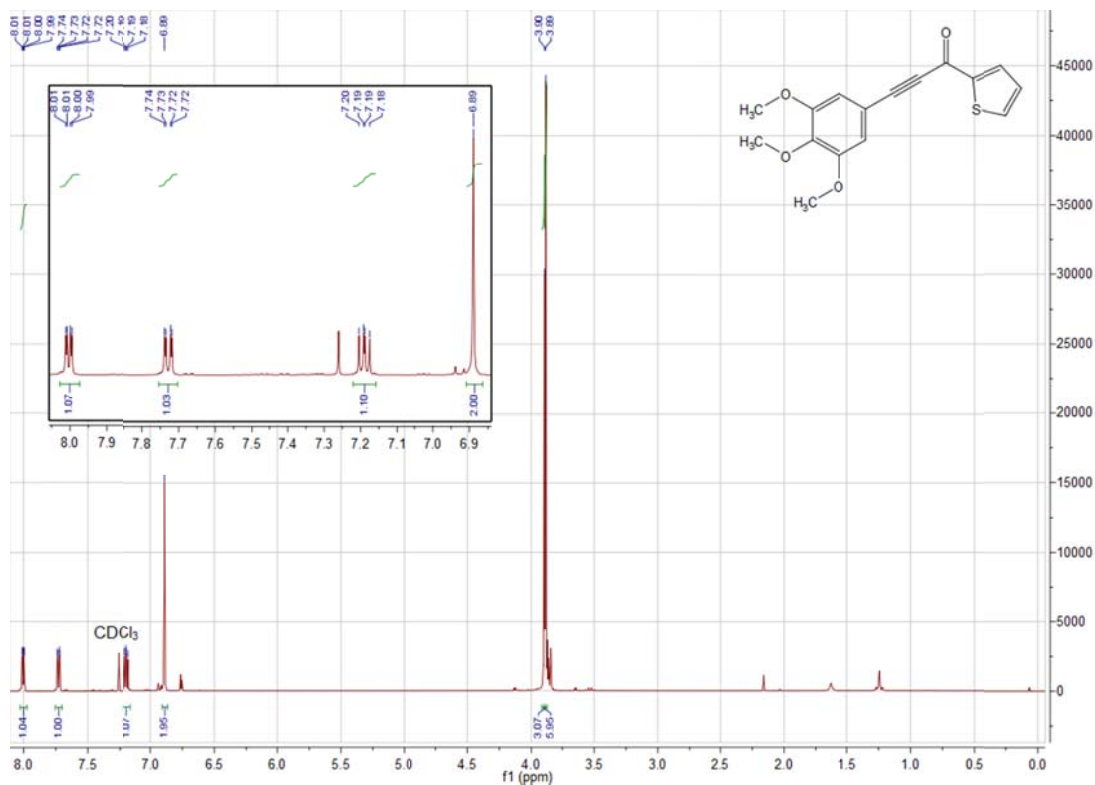


^{13}C NMR of 1-phenyl-3-(3,4,5-trimethoxyphenyl)prop-2-yn-1-one (4c) (CDCl_3 , 75 MHz, $T = 298$

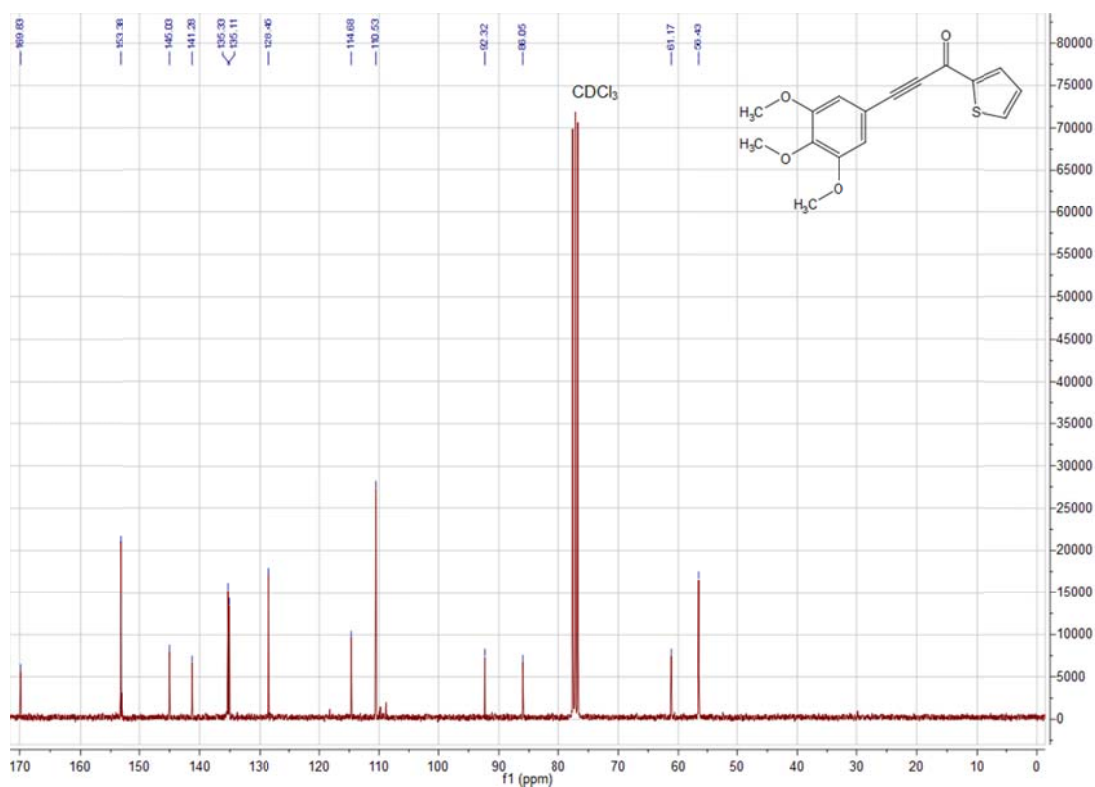
K)



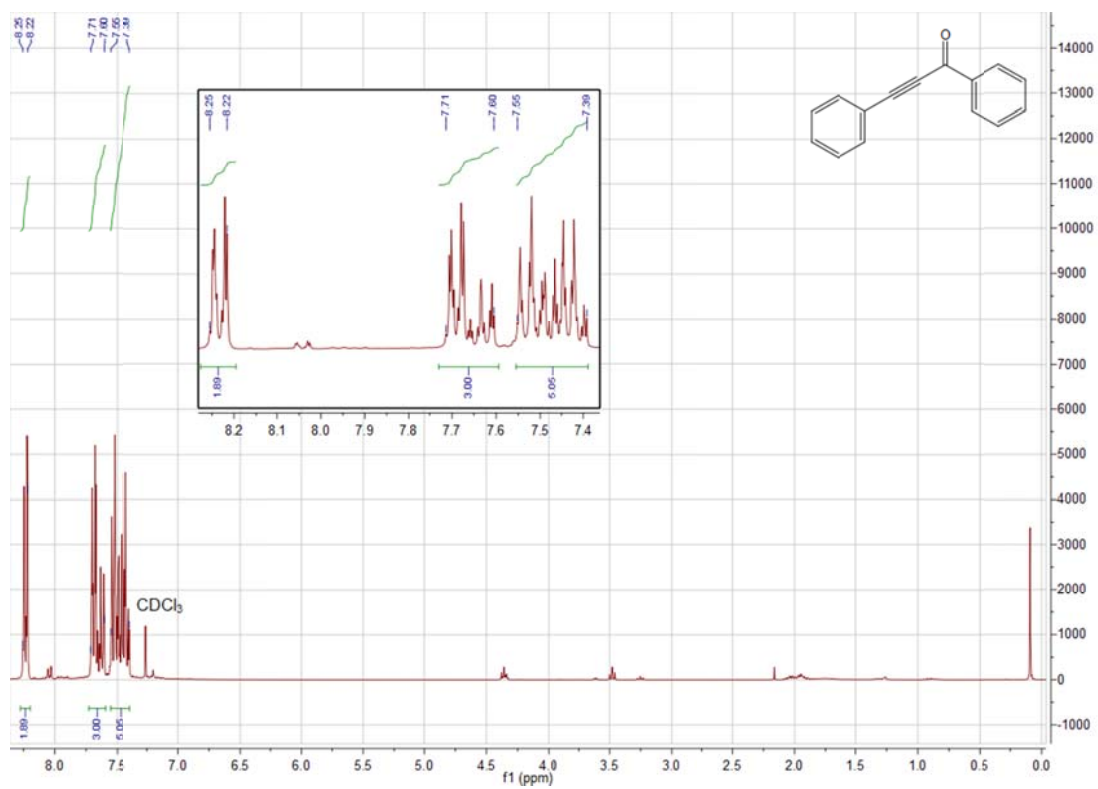
^1H NMR of 1-(thiophen-2-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-yn-1-one (4d) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



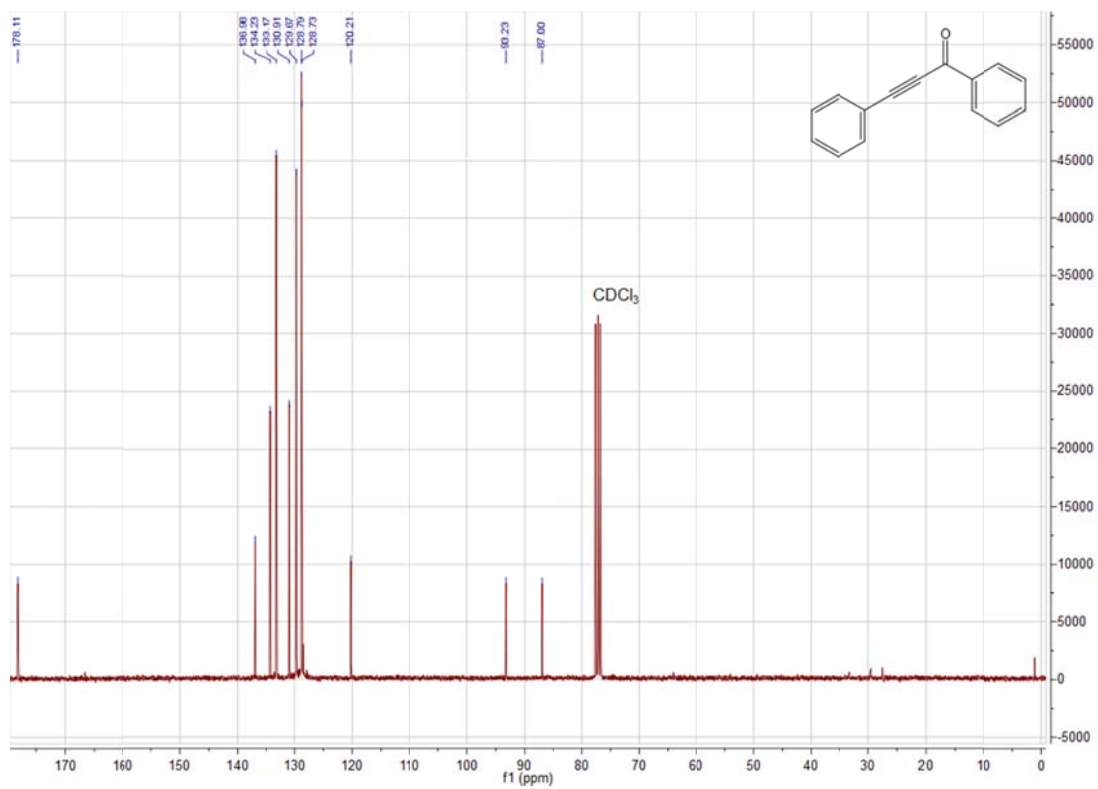
^{13}C NMR of 1-(thiophen-2-yl)-3-(3,4,5-trimethoxyphenyl)prop-2-yn-1-one (4d) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



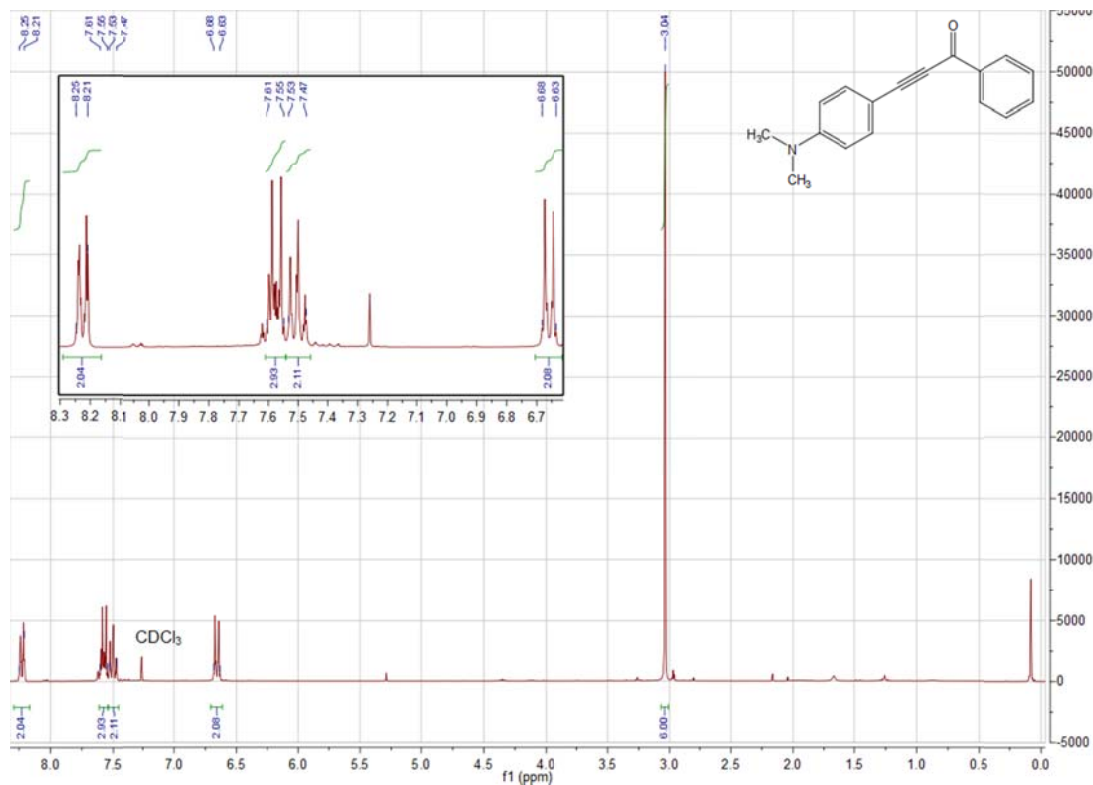
^1H NMR of 1,3-diphenylprop-2-yn-1-one (4e) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



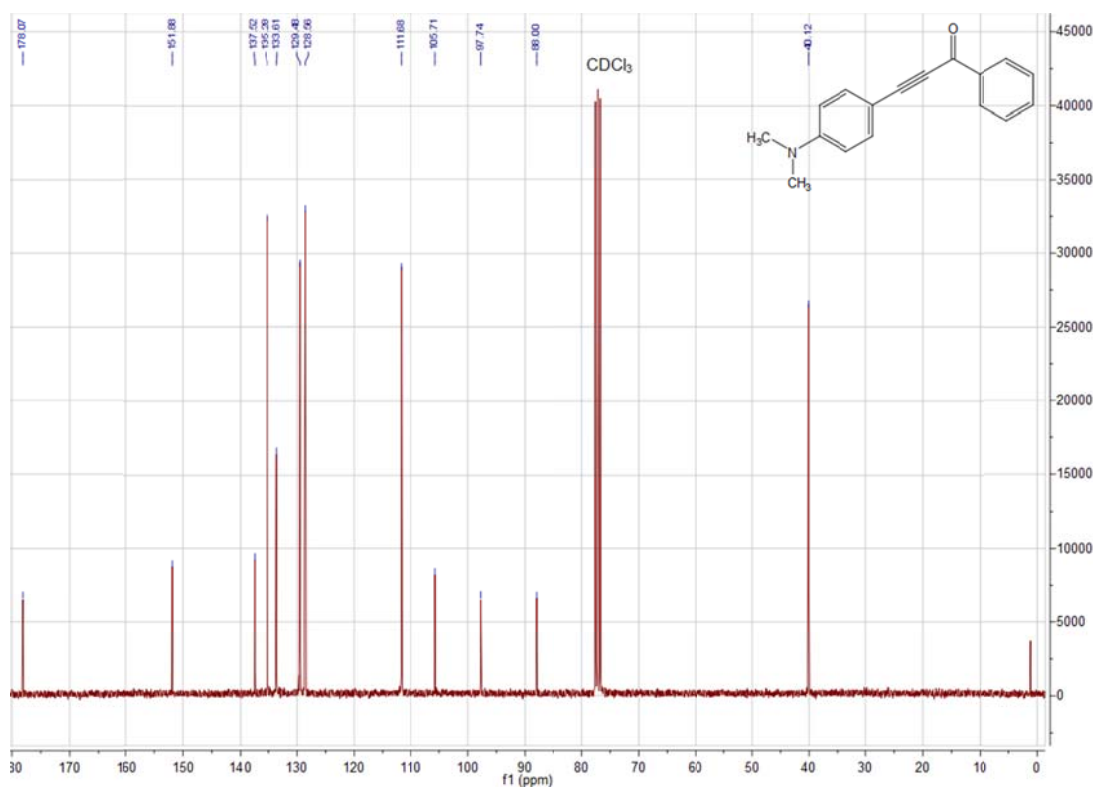
^{13}C NMR of 1,3-diphenylprop-2-yn-1-one (4e) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



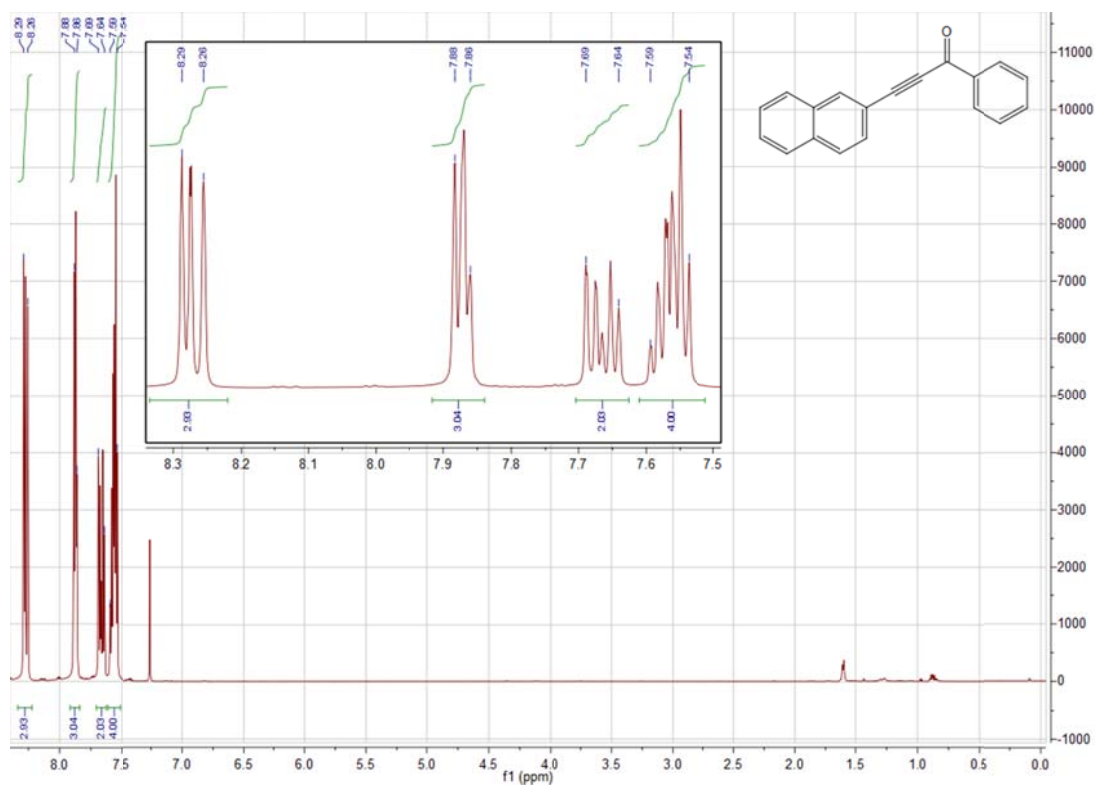
^1H NMR of 3-(4-(dimethylamino)phenyl)-1-phenylprop-2-yn-1-one (4f) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



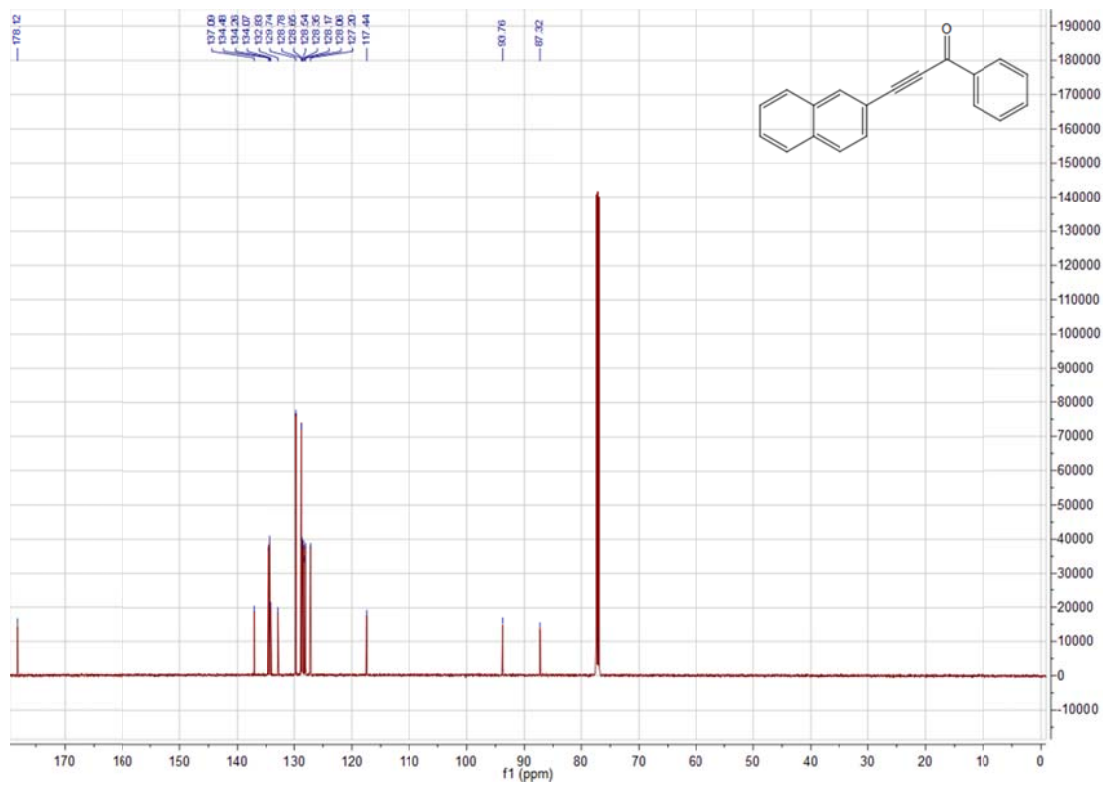
^{13}C NMR of 3-(4-(dimethylamino)phenyl)-1-phenylprop-2-yn-1-one (4f) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



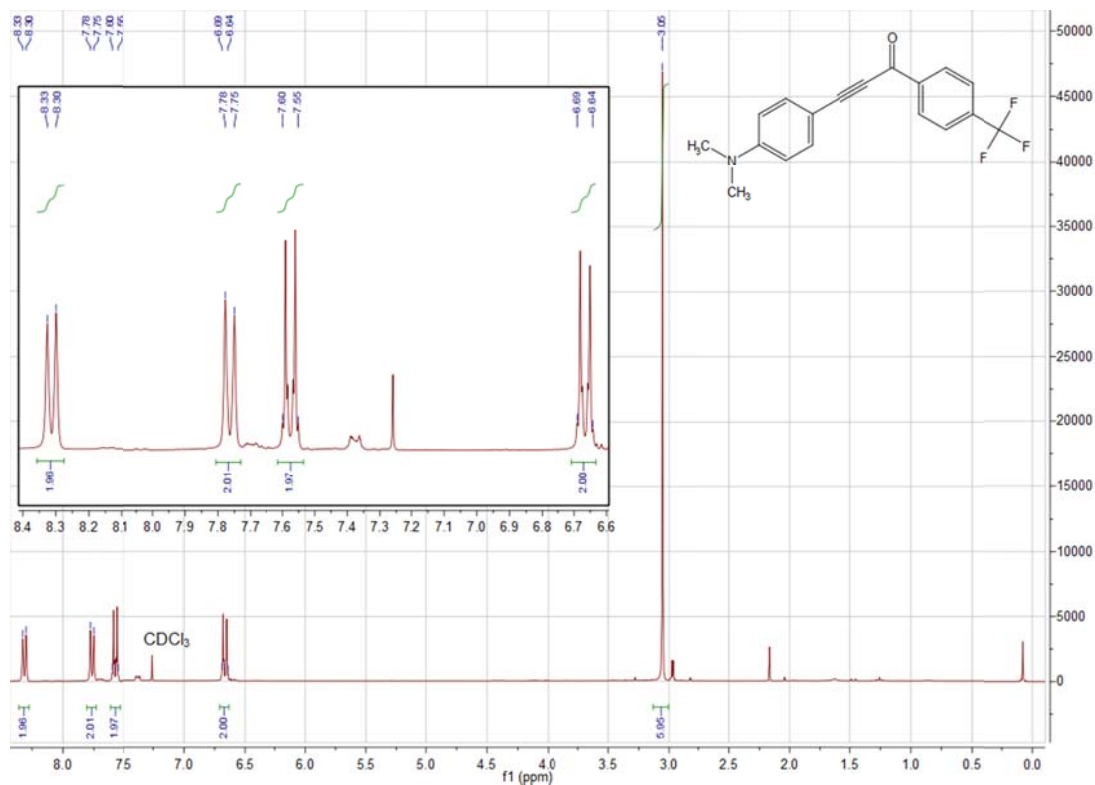
¹H NMR of 3-(naphthalen-2-yl)-1-phenylprop-2-yn-1-one (4g, T = 298 K)



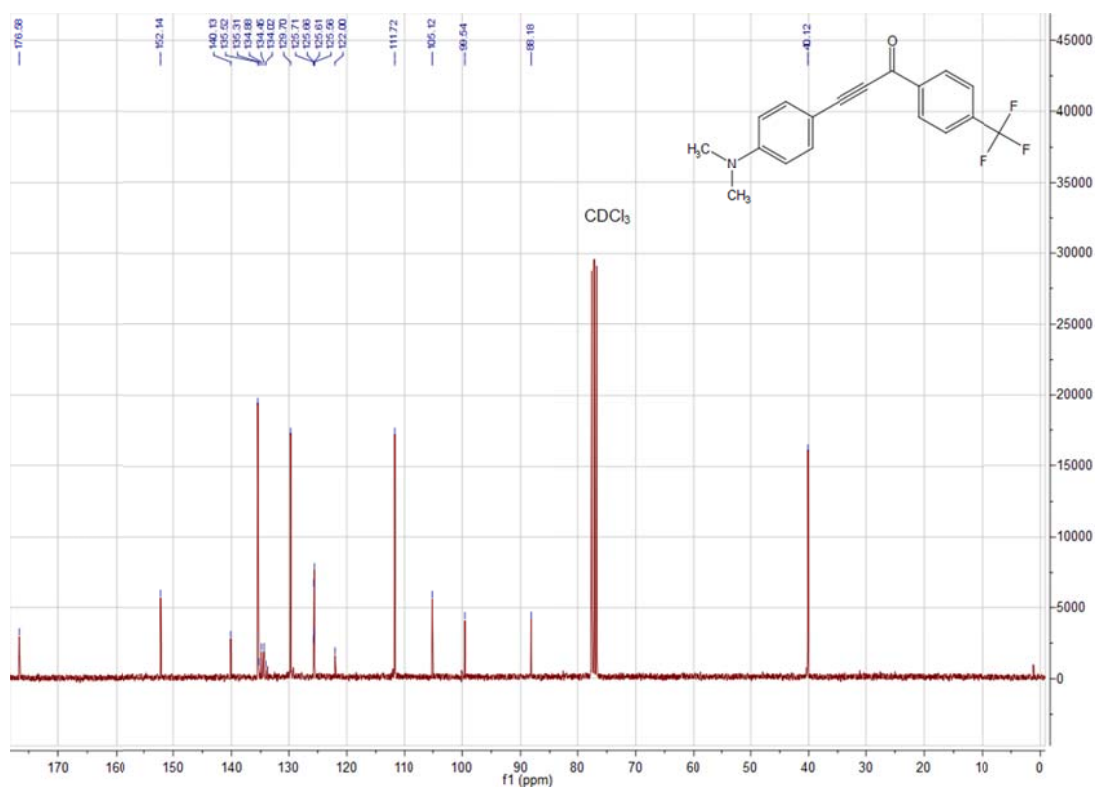
¹³C NMR of 3-(naphthalen-2-yl)-1-phenylprop-2-yn-1-one (4g, T = 298 K)



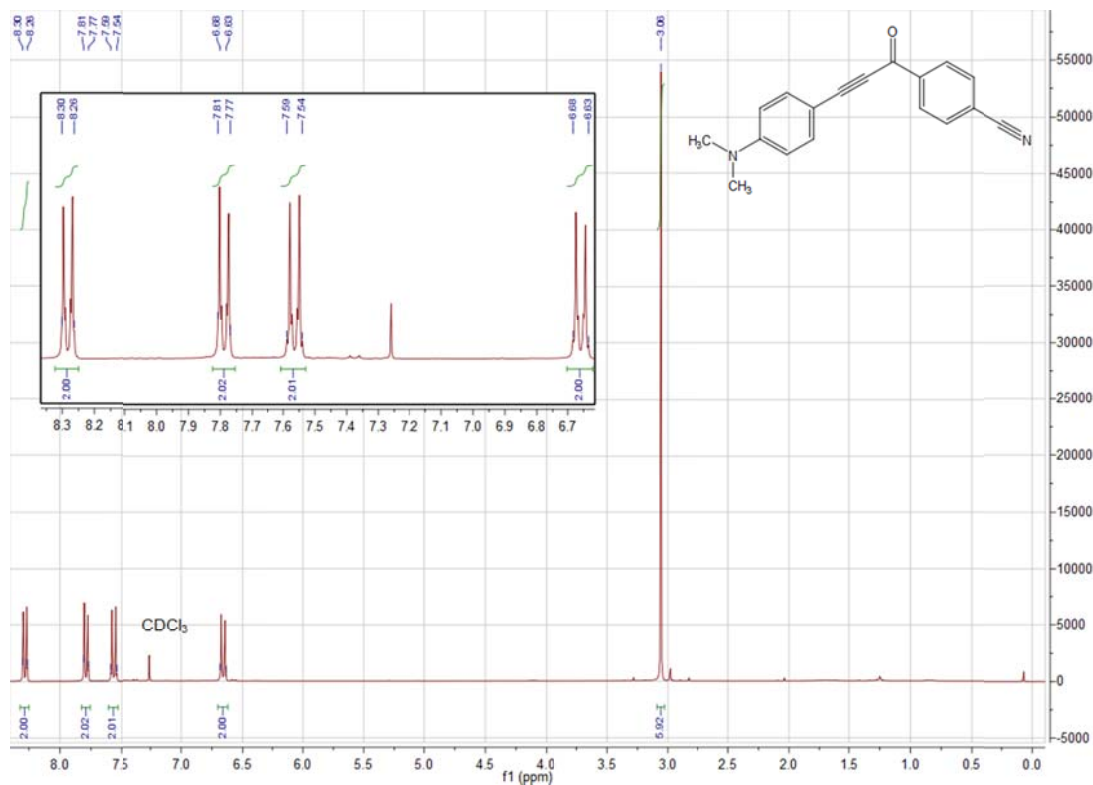
¹H NMR of 3-(4-(dimethylamino)phenyl)-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (4h)
(CDCl₃, 300 MHz, T = 298 K)



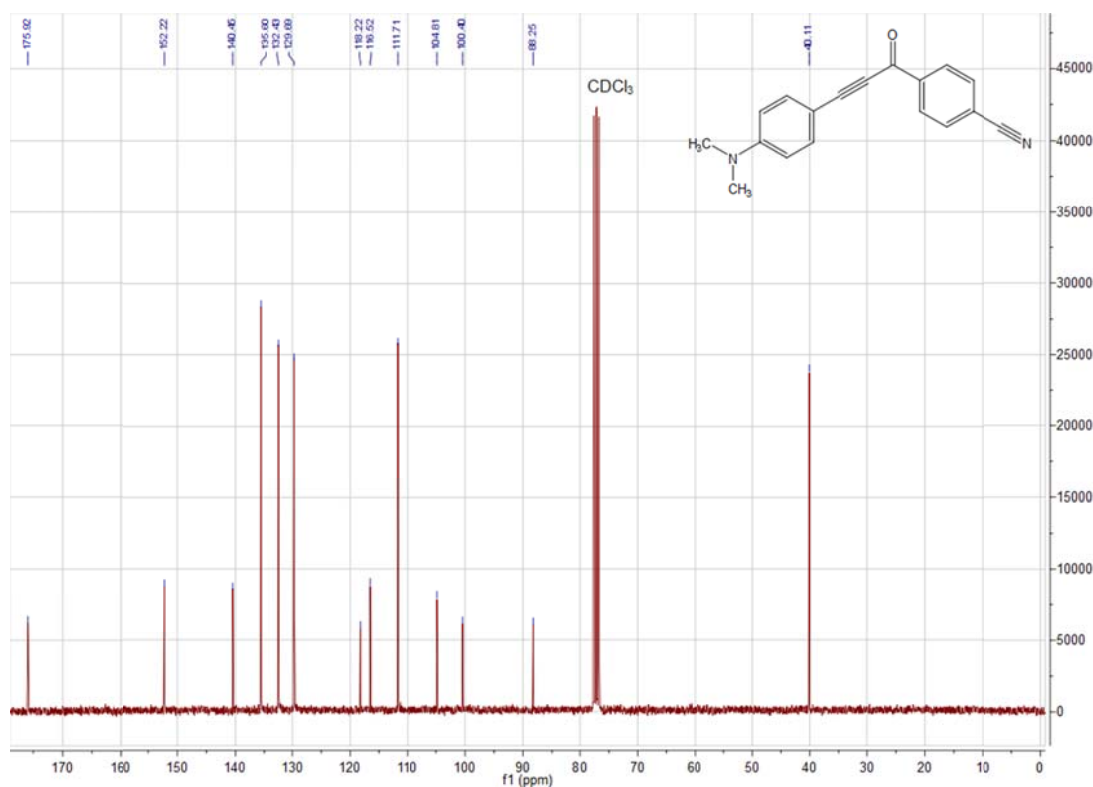
¹³C NMR of 3-(4-(dimethylamino)phenyl)-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (4h)
(CDCl₃, 75 MHz, T = 298 K)



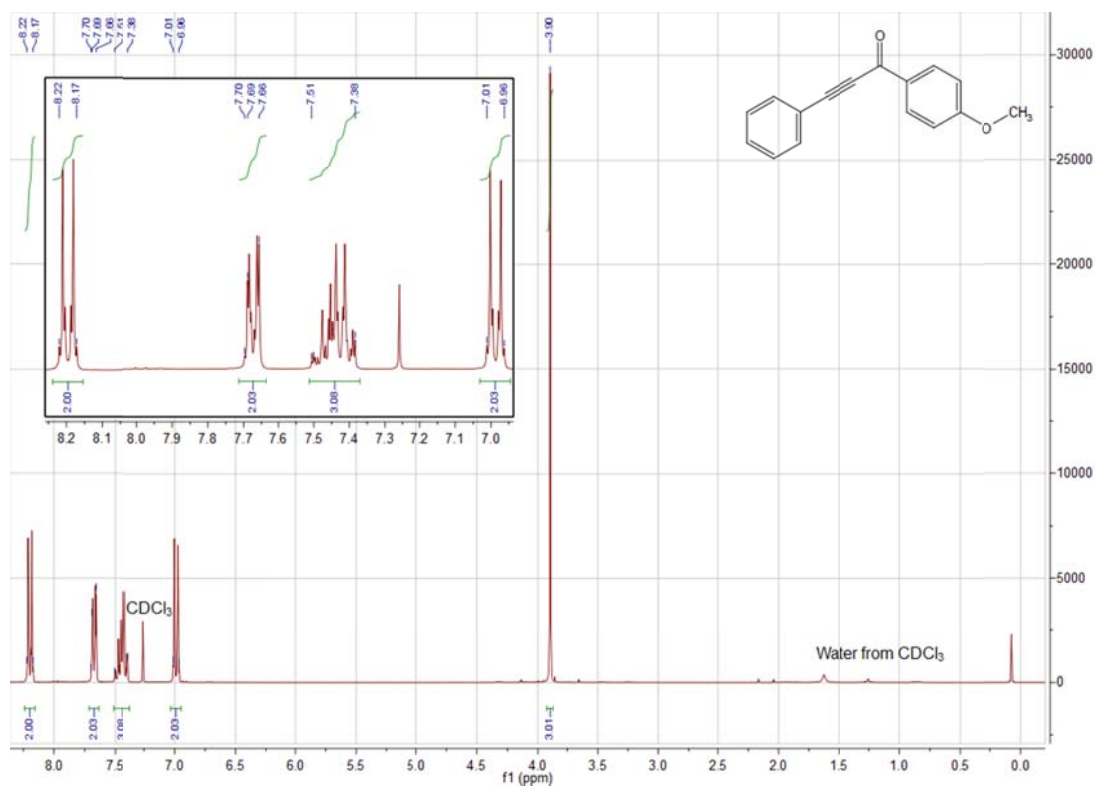
^1H NMR of 4-(3-(4-(dimethylamino)phenyl)propioloyl)benzonitrile (4i) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



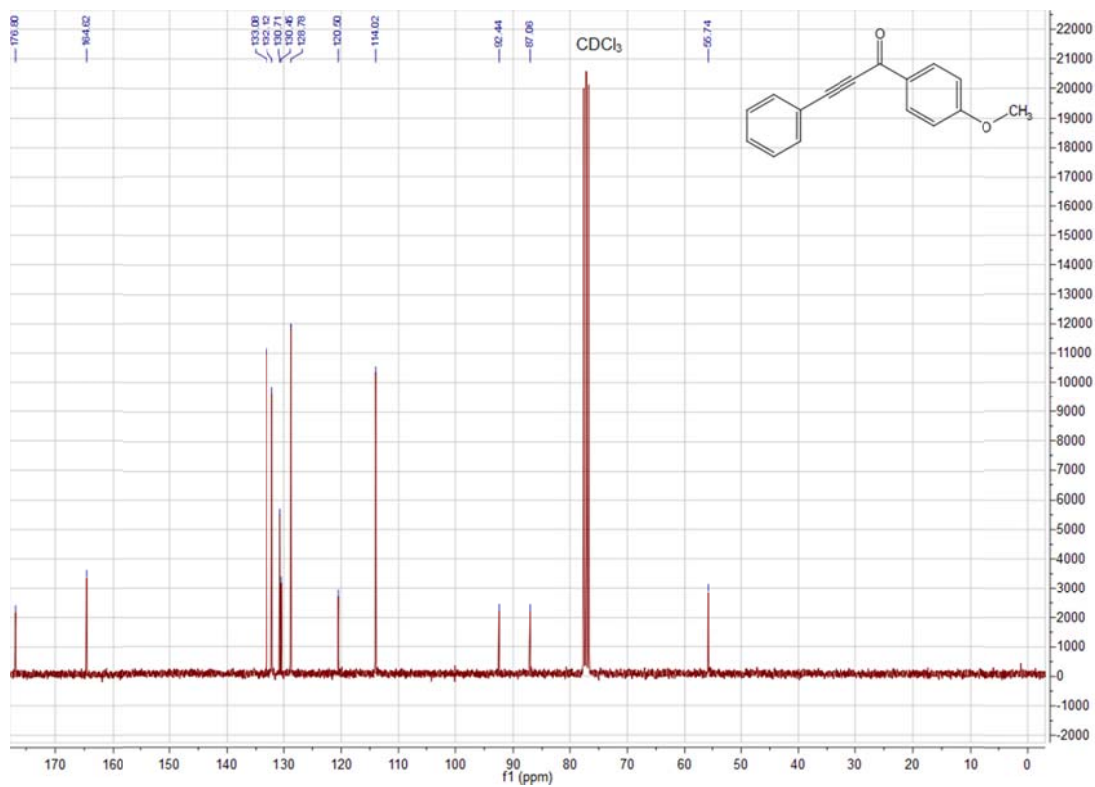
^{13}C NMR of 4-(3-(4-(dimethylamino)phenyl)propioloyl)benzonitrile (4i) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



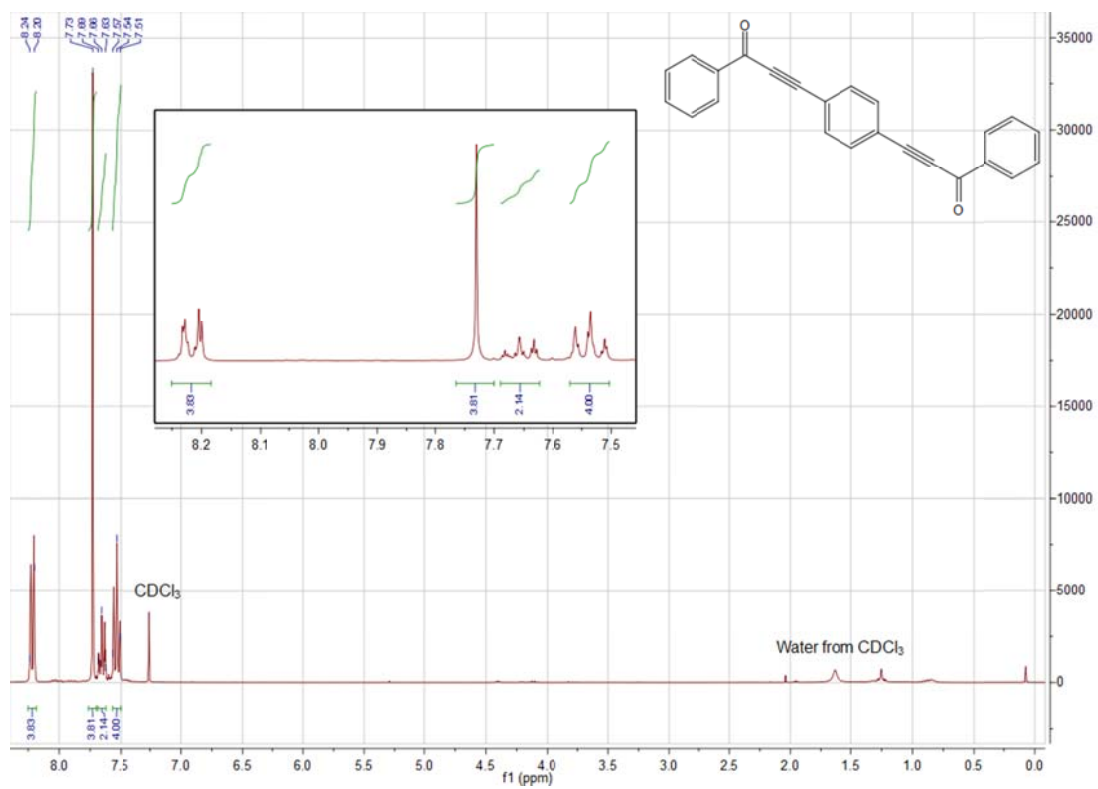
¹H NMR of 1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (4j) (CDCl₃, 300 MHz, T = 298 K)



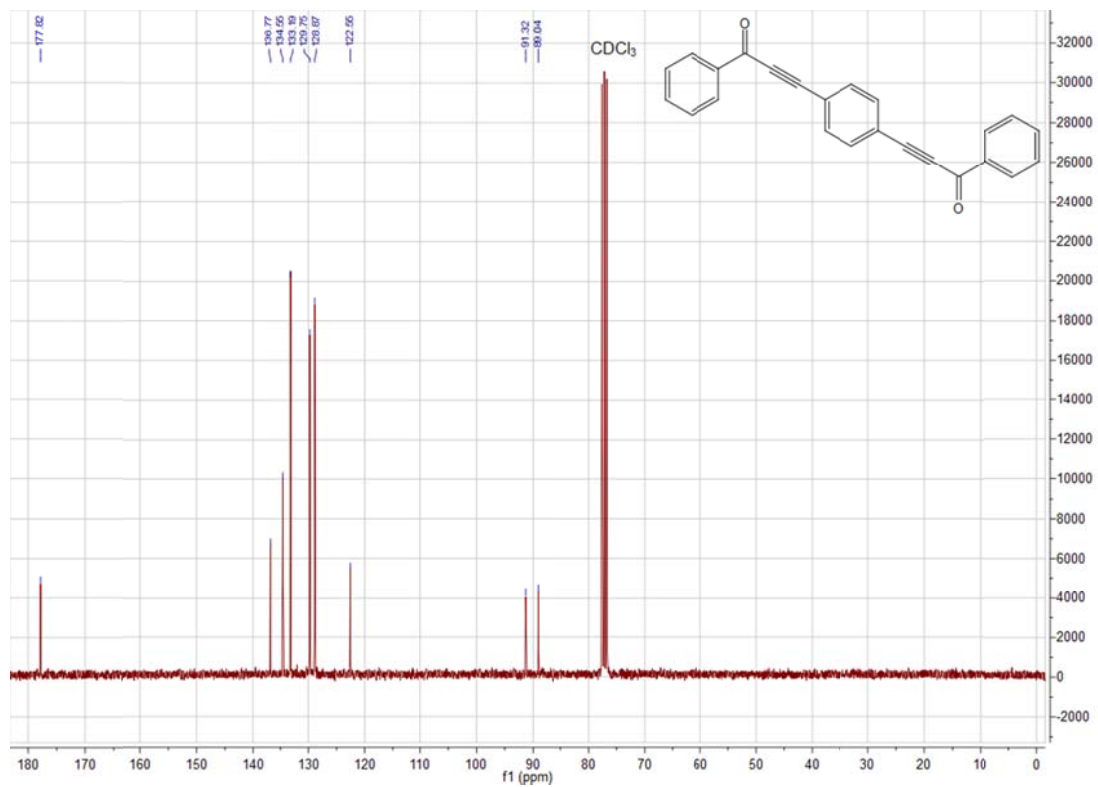
¹³C NMR of 1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (4j) (CDCl₃, 75 MHz, T = 298 K)



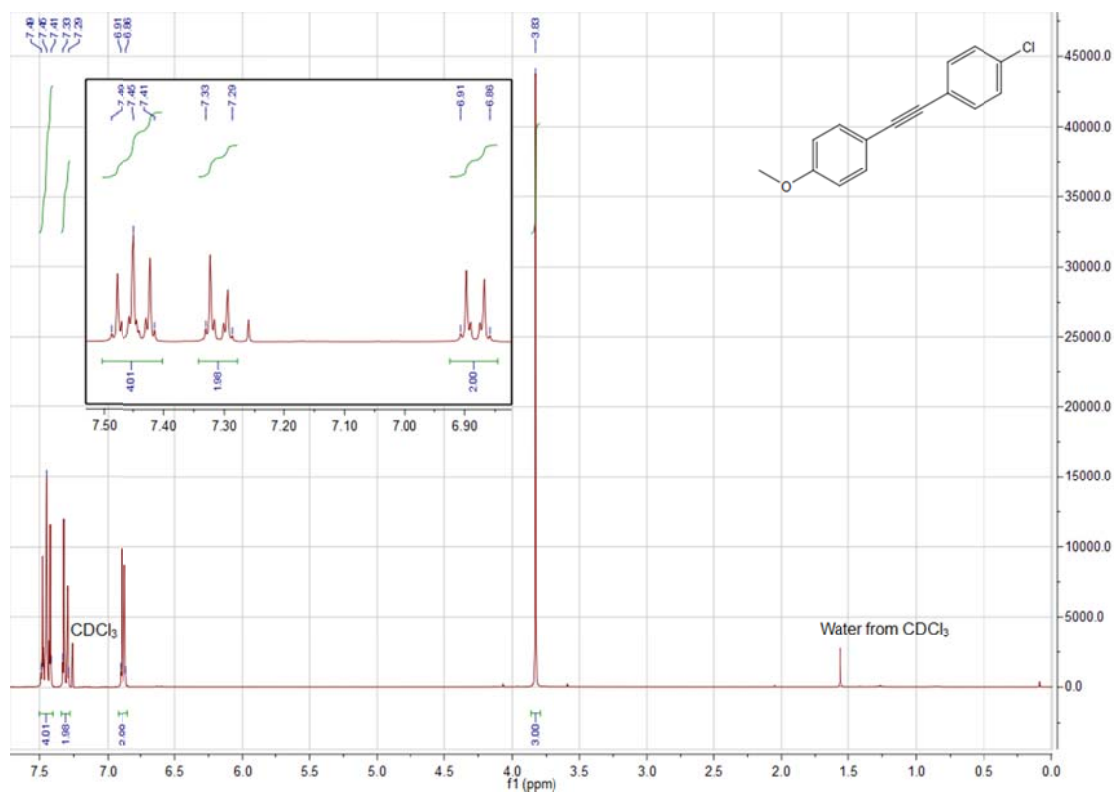
^1H NMR of 1,1'-(1,4-phenylene)bis(3-phenylprop-2-yn-1-one) (4k) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



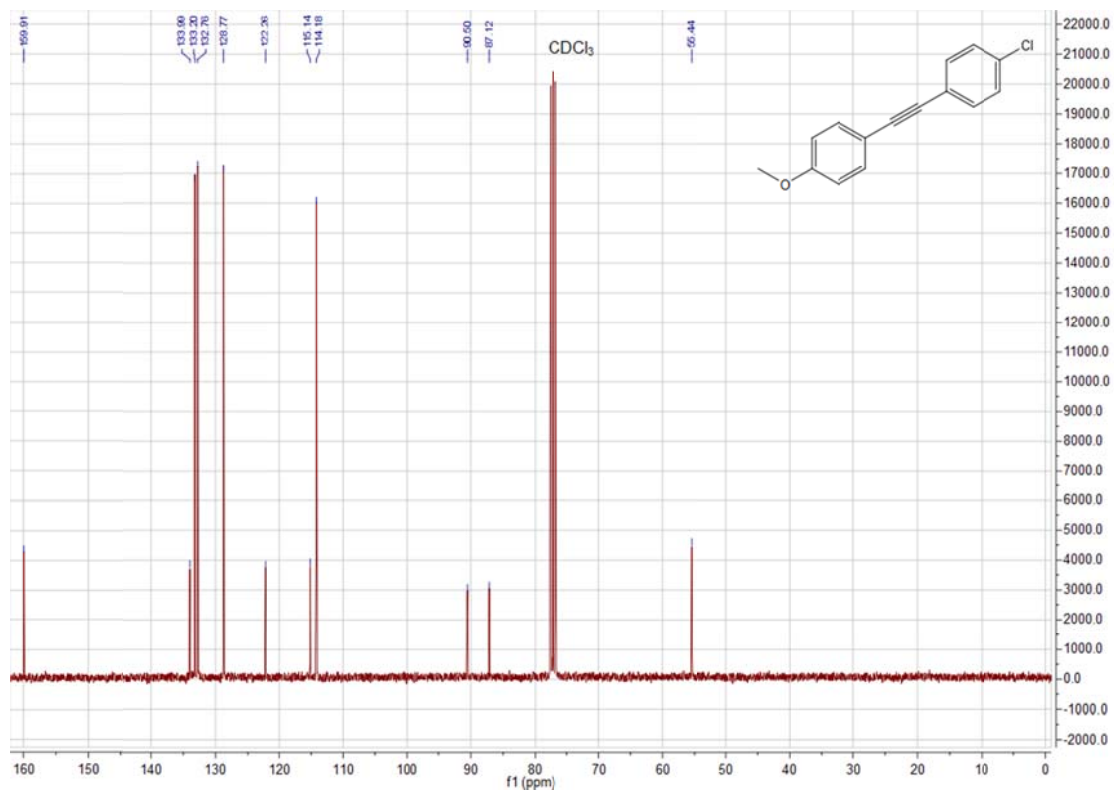
^{13}C NMR of 1,1'-(1,4-phenylene)bis(3-phenylprop-2-yn-1-one) (4k) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



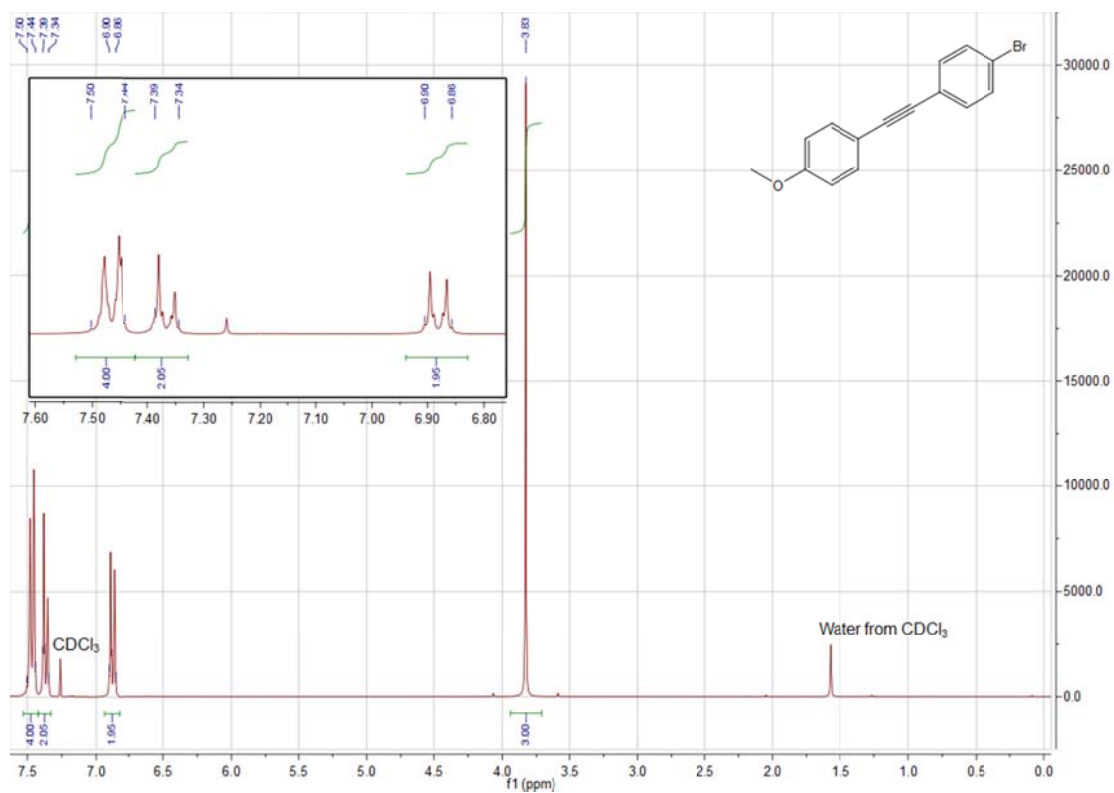
^1H NMR of 1-chloro-4-((4-methoxyphenyl)ethynyl)benzene (6a) (CDCl_3 , 300 MHz, $T = 298$ K)



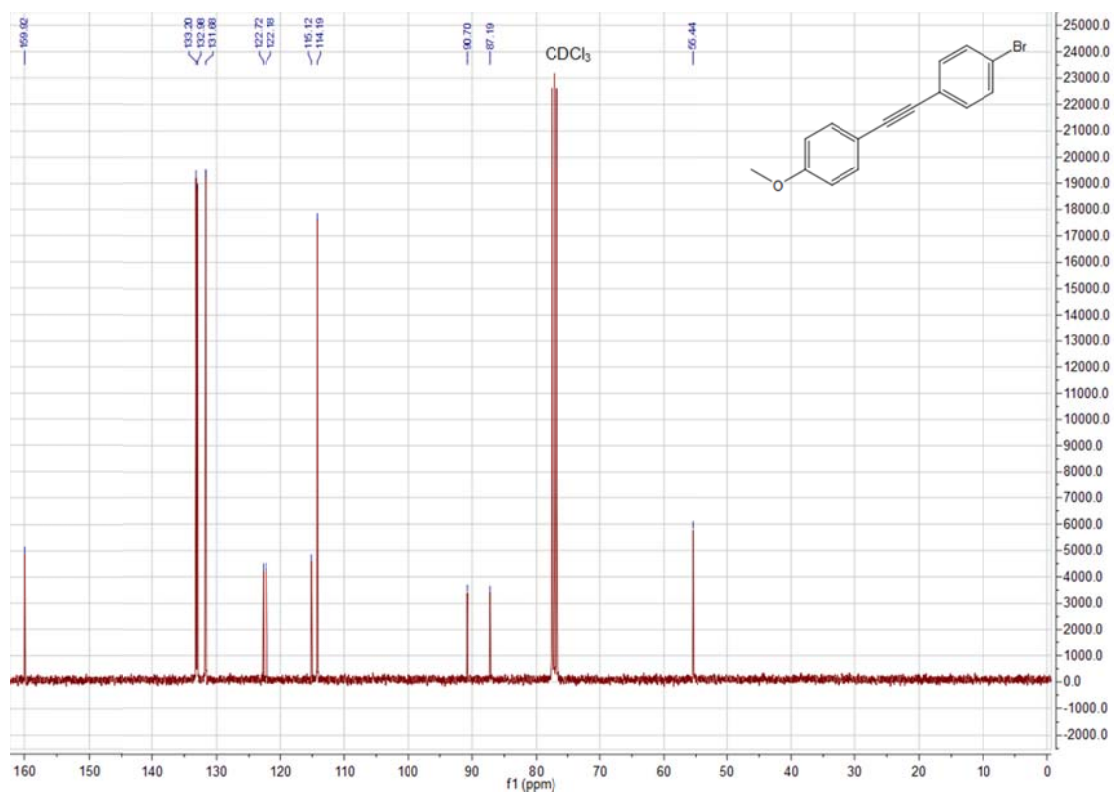
^{13}C NMR of 1-chloro-4-((4-methoxyphenyl)ethynyl)benzene (6a) (CDCl_3 , 75 MHz, $T = 298$ K)



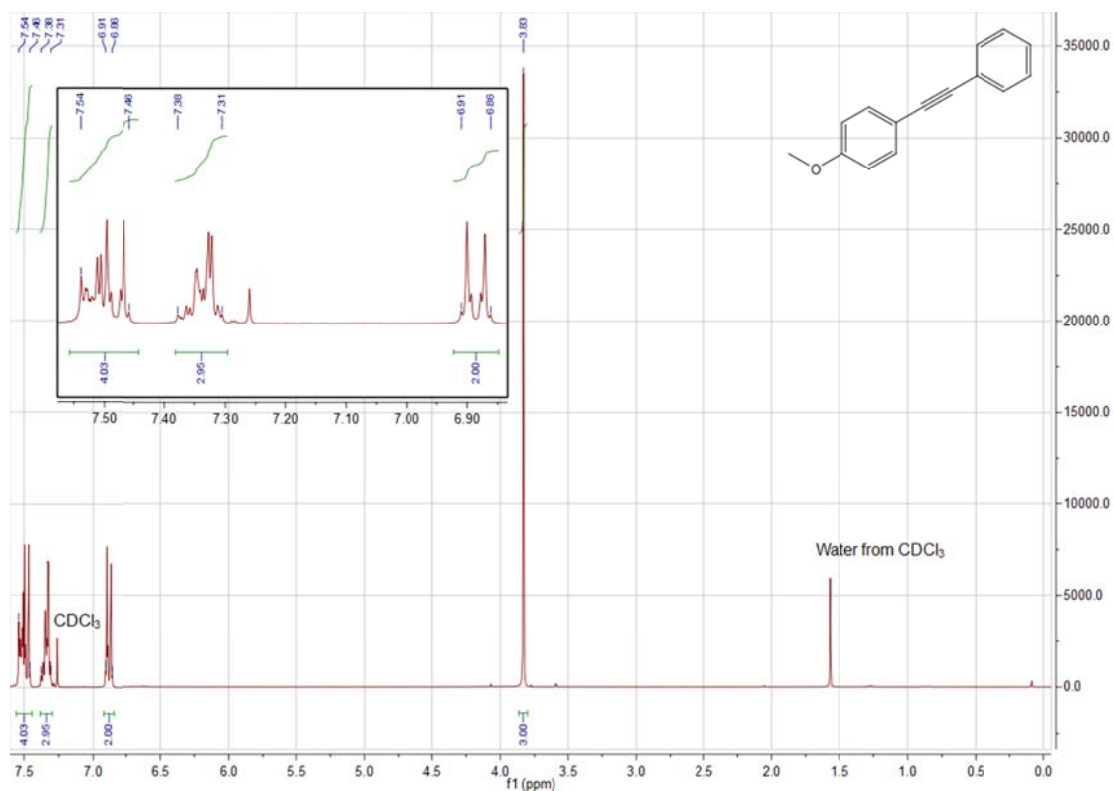
^1H NMR of 1-bromo-4-((4-methoxyphenyl)ethynyl)benzene (6b) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



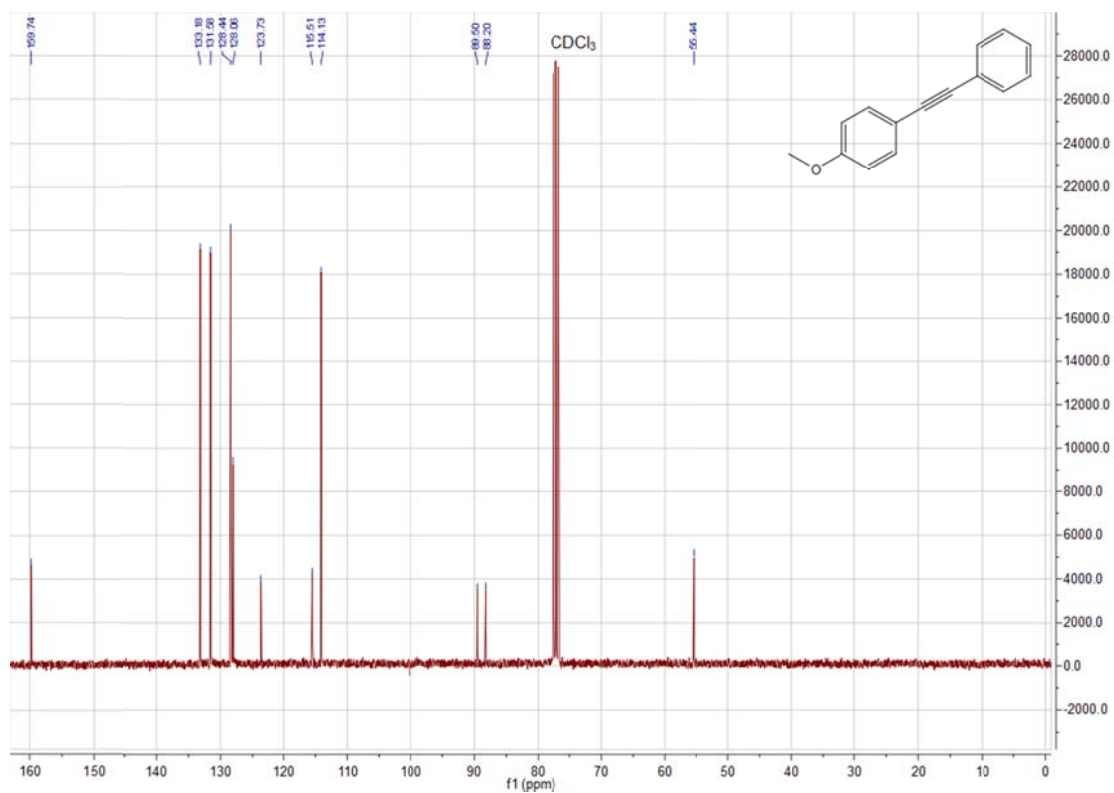
^{13}C NMR of 1-bromo-4-((4-methoxyphenyl)ethynyl)benzene (6b) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



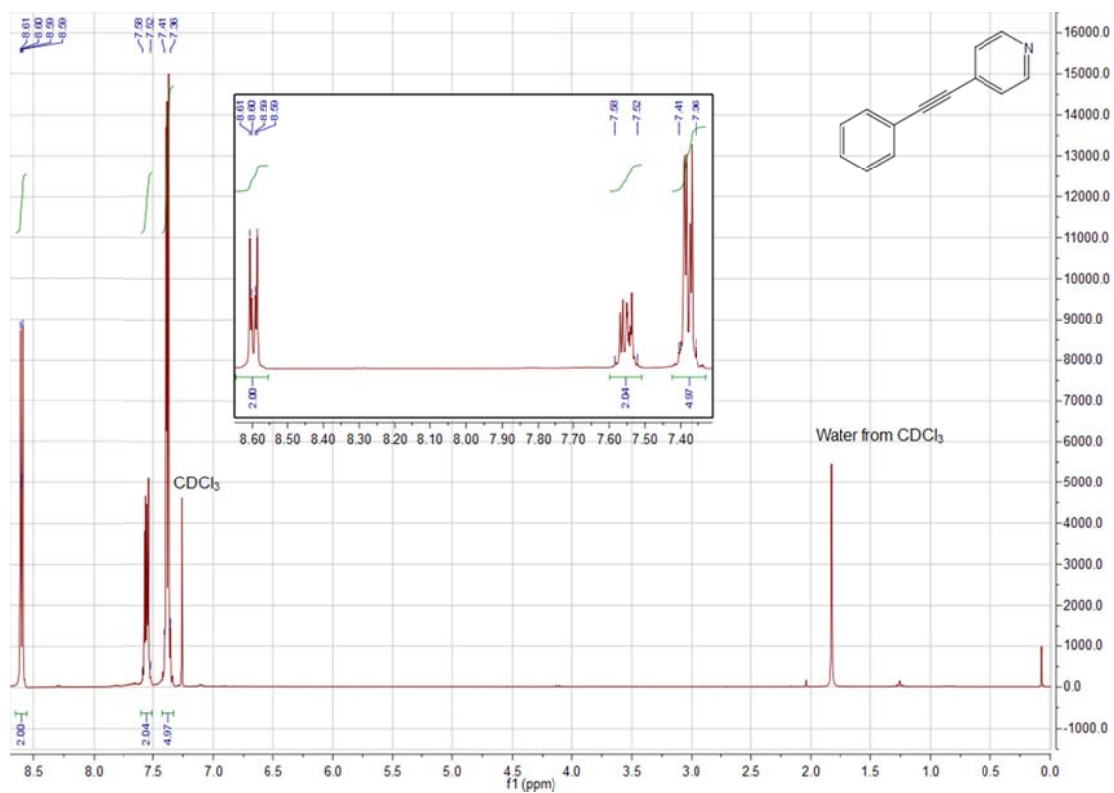
¹H NMR of 1-methoxy-4-(phenylethynyl)benzene (6c) (CDCl₃, 300 MHz, T = 298 K)



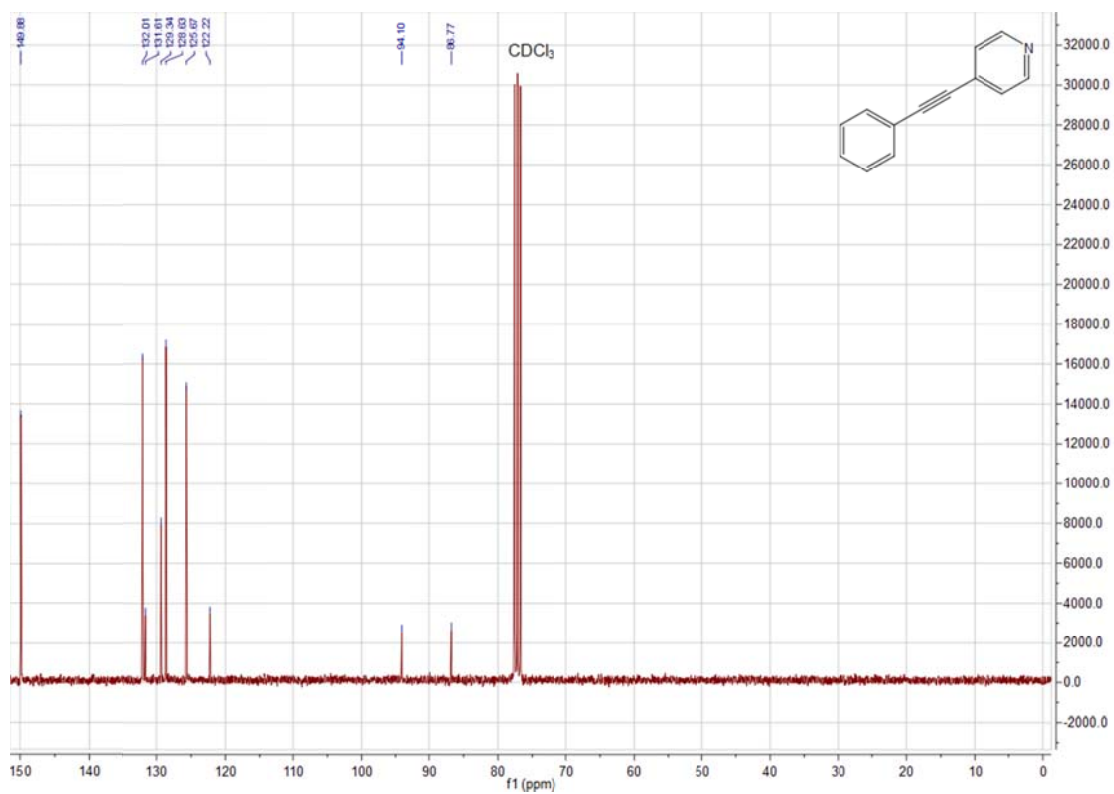
¹³C NMR of 1-methoxy-4-(phenylethynyl)benzene (6c) (CDCl₃, 75 MHz, T = 298 K)



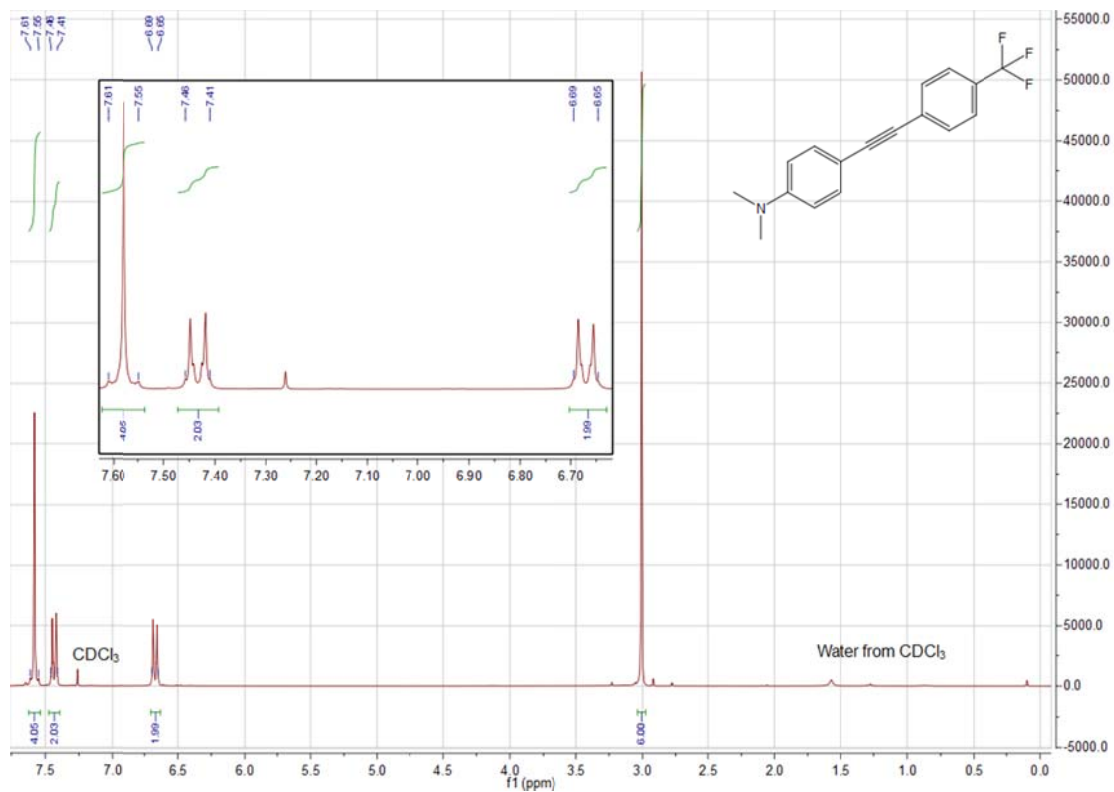
¹H NMR of 4-(phenylethynyl)pyridine (6d) (CDCl₃, 300 MHz, T = 298 K)



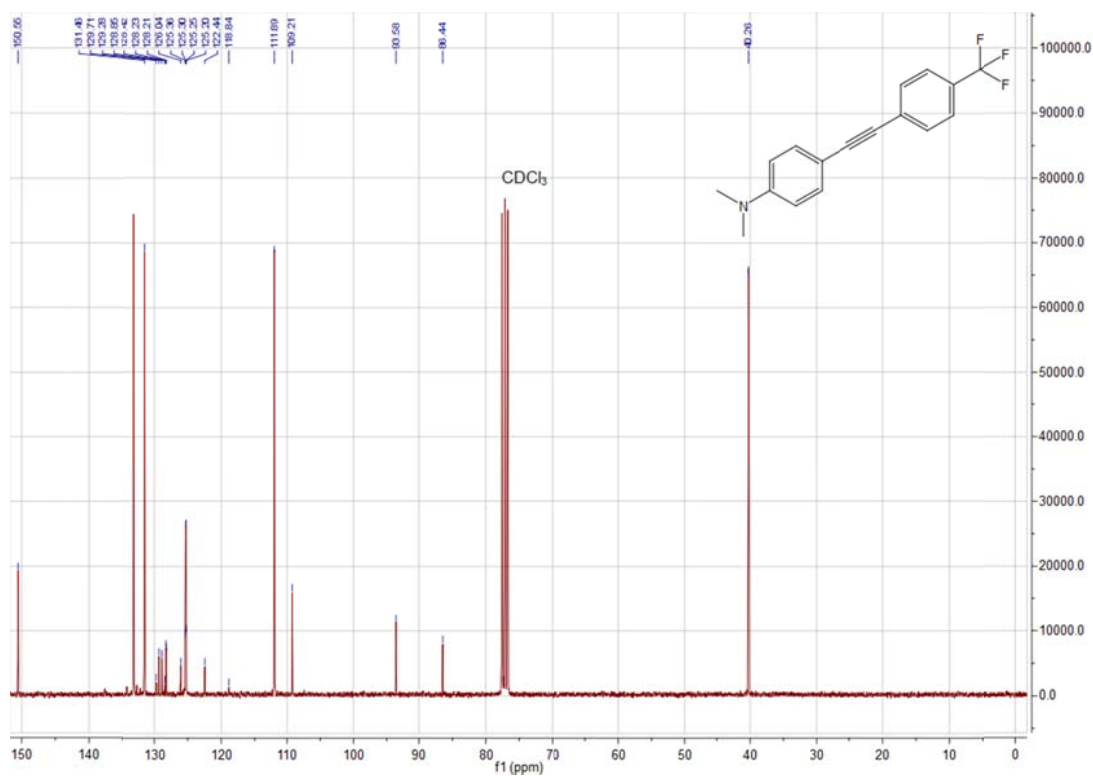
¹³C NMR of 4-(phenylethynyl)pyridine (6d) (CDCl₃, 75 MHz, T = 298 K)



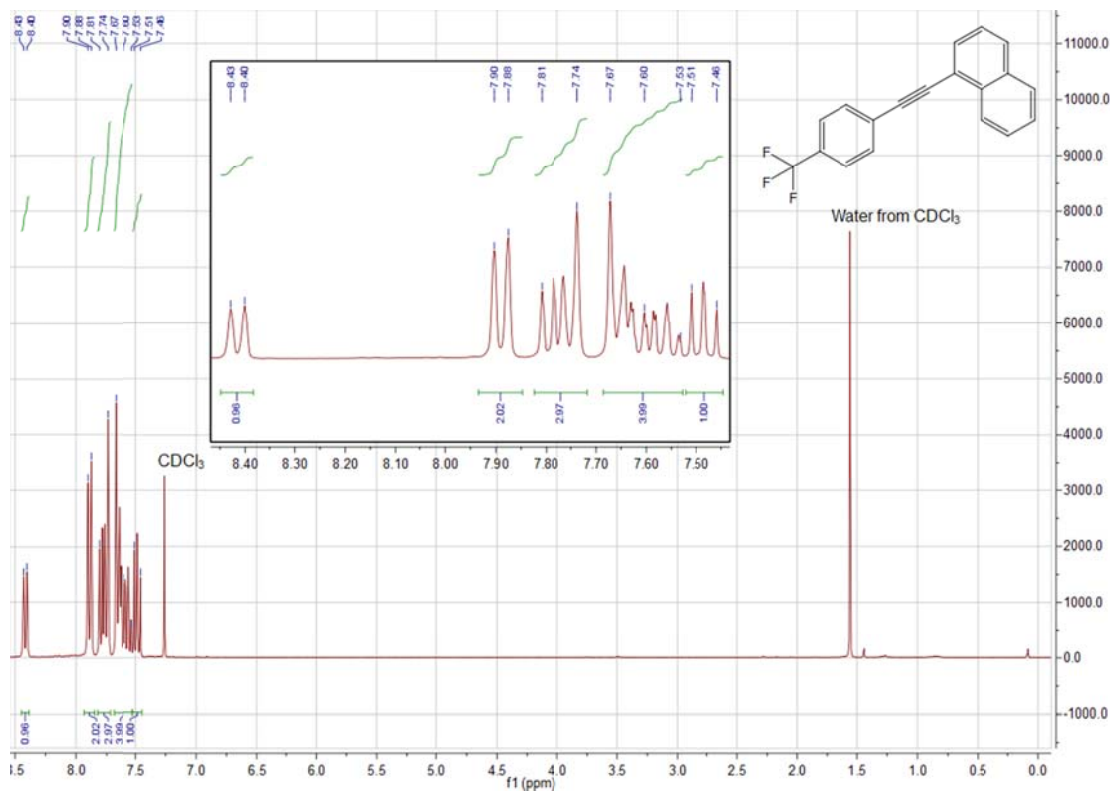
^1H NMR of *N,N*-dimethyl-4-((4-(trifluoromethyl)phenyl)ethynyl)aniline (6e) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



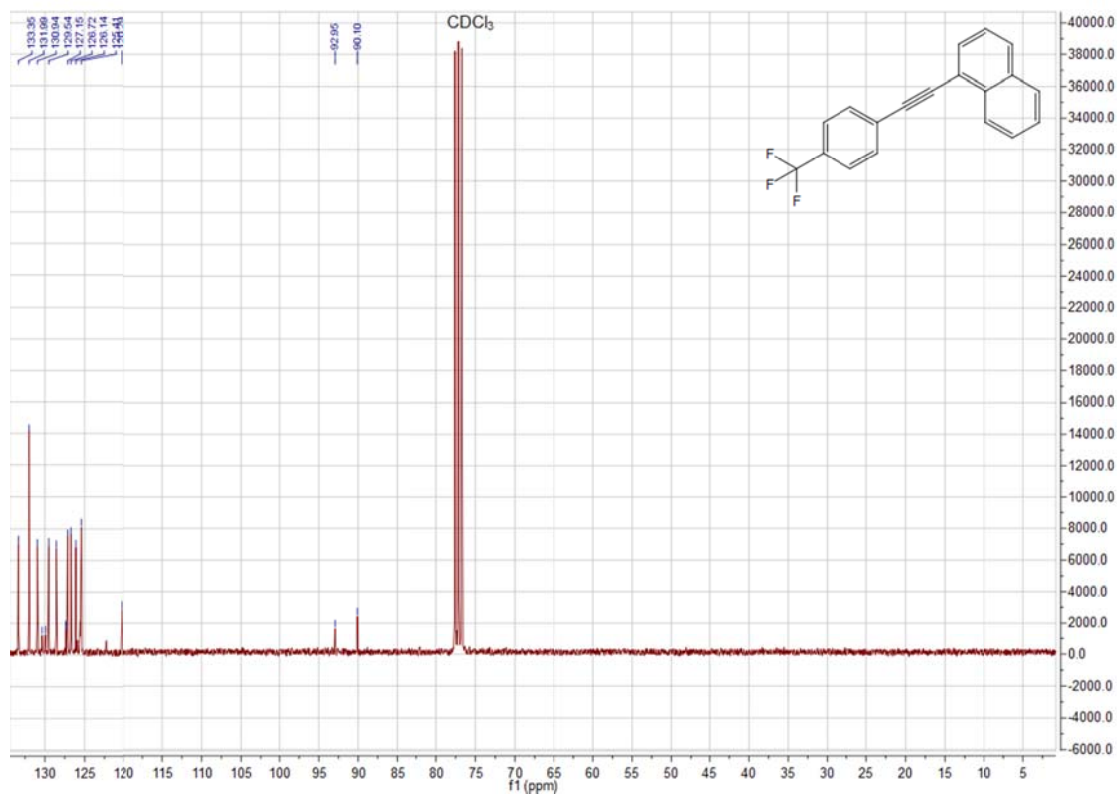
^{13}C NMR of *N,N*-dimethyl-4-((4-(trifluoromethyl)phenyl)ethynyl)aniline (6e) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



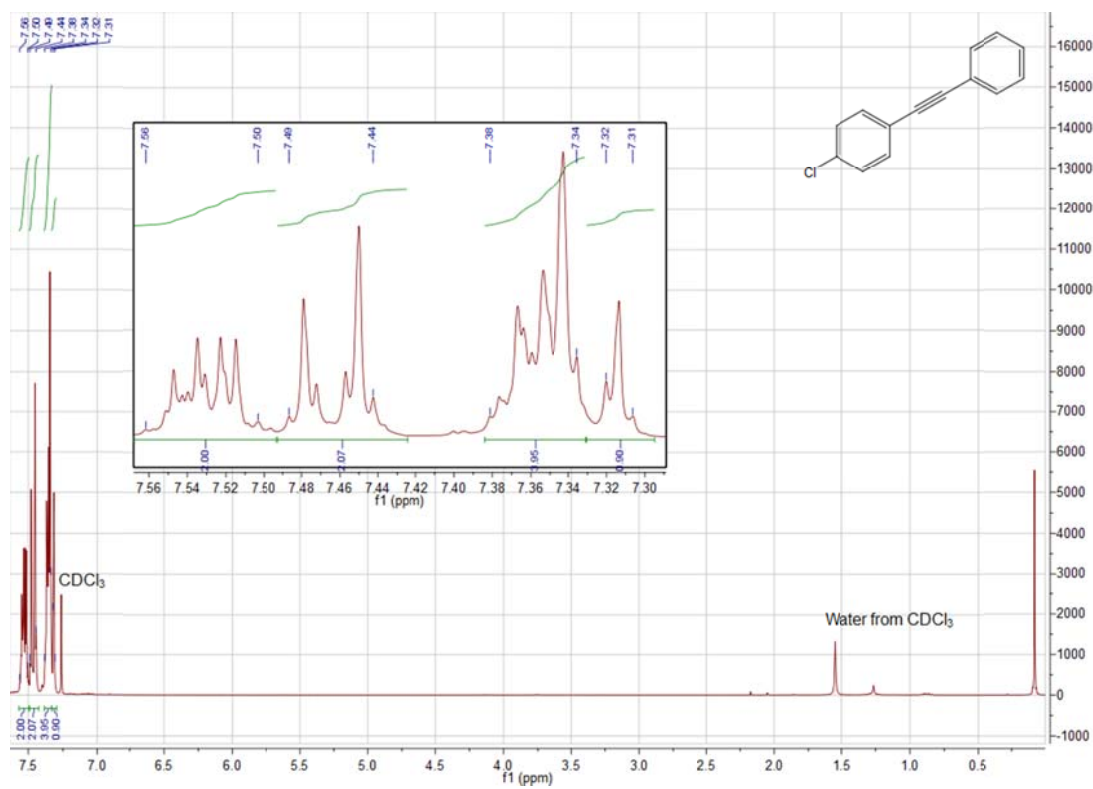
^1H NMR of 1-((4-(trifluoromethyl)phenyl)ethynyl)naphthalene (6f) (CDCl_3 , 300 MHz, $T = 298$ K)



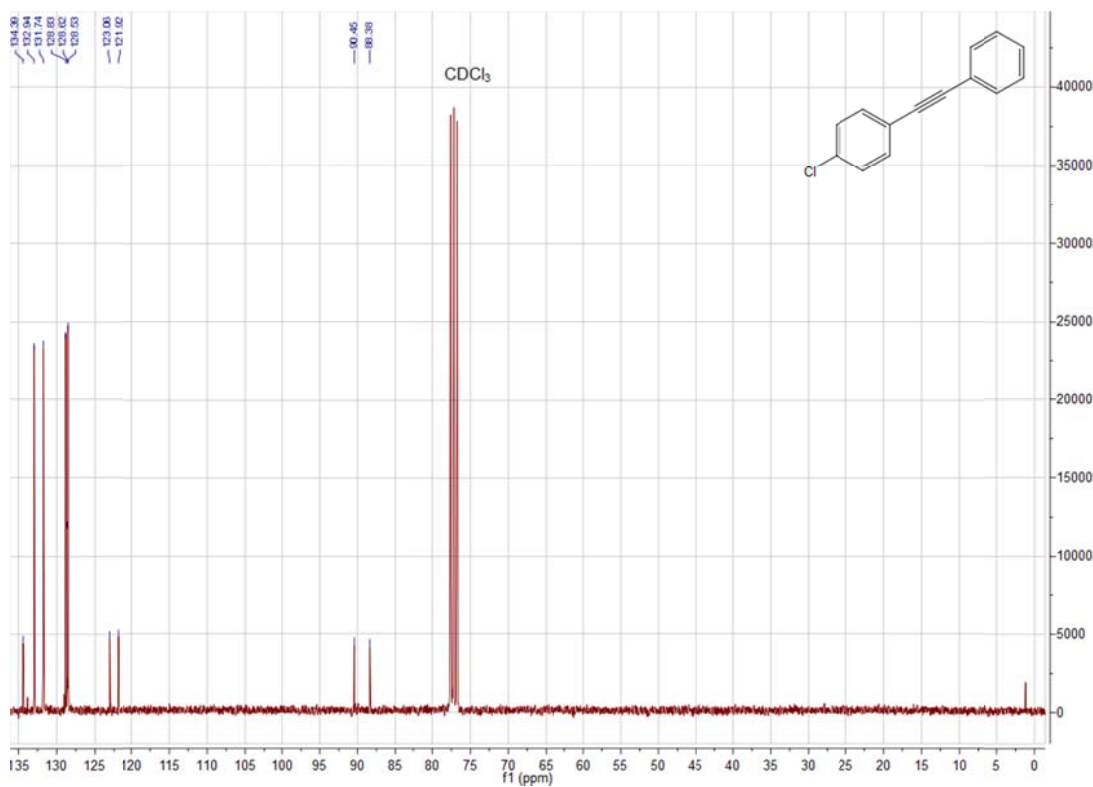
^{13}C NMR of 1-((4-(trifluoromethyl)phenyl)ethynyl)naphthalene (6f) (CDCl_3 , 75 MHz, $T = 298$ K)



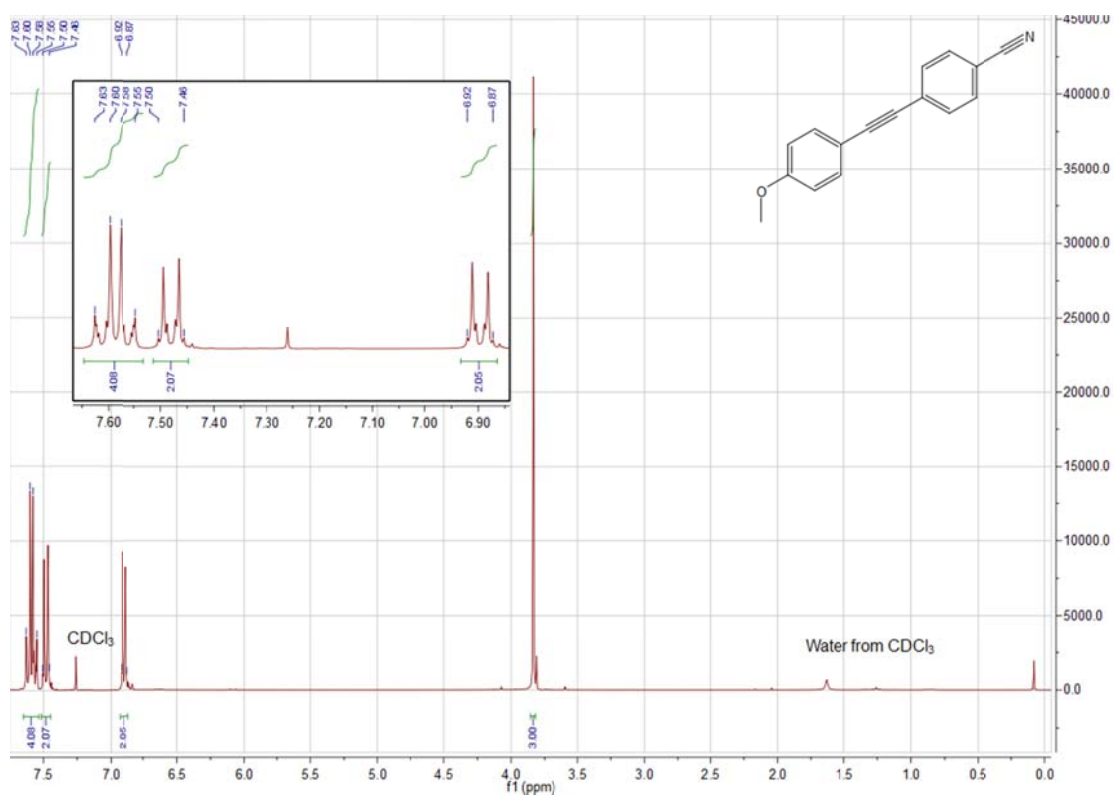
^1H NMR of 1-chloro-4-(phenylethynyl)benzene (6g) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



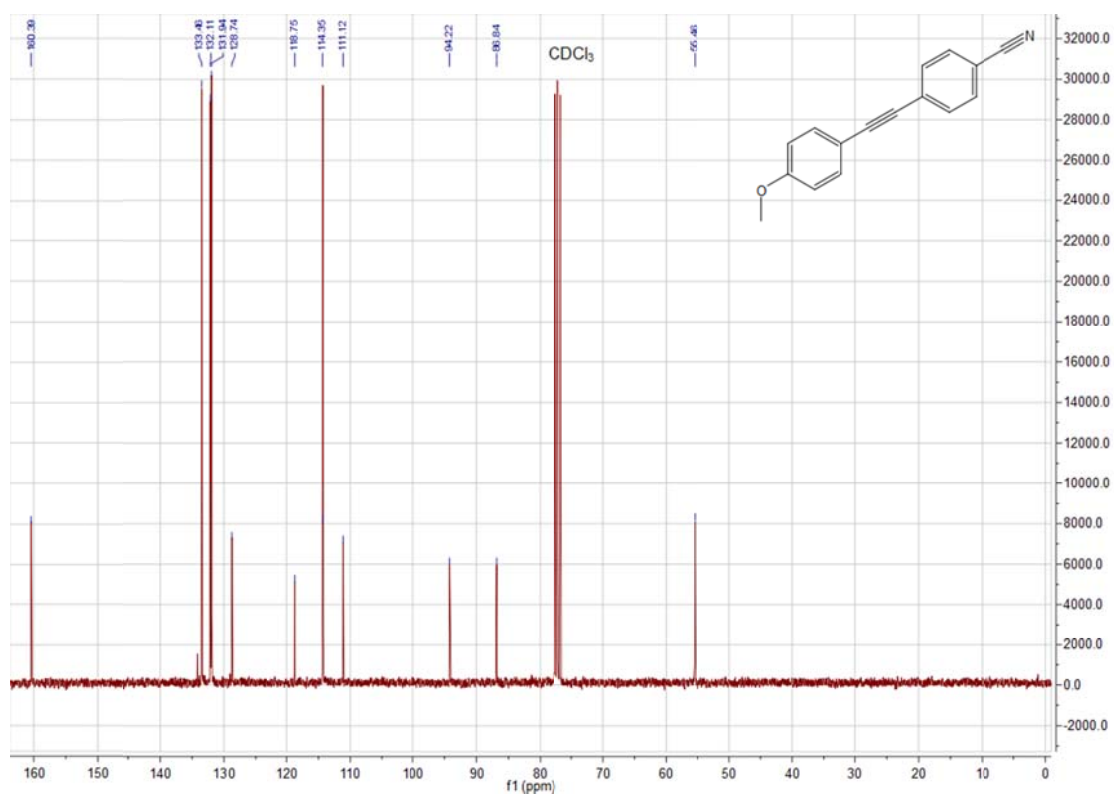
^{13}C NMR of 1-chloro-4-(phenylethynyl)benzene (6g) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



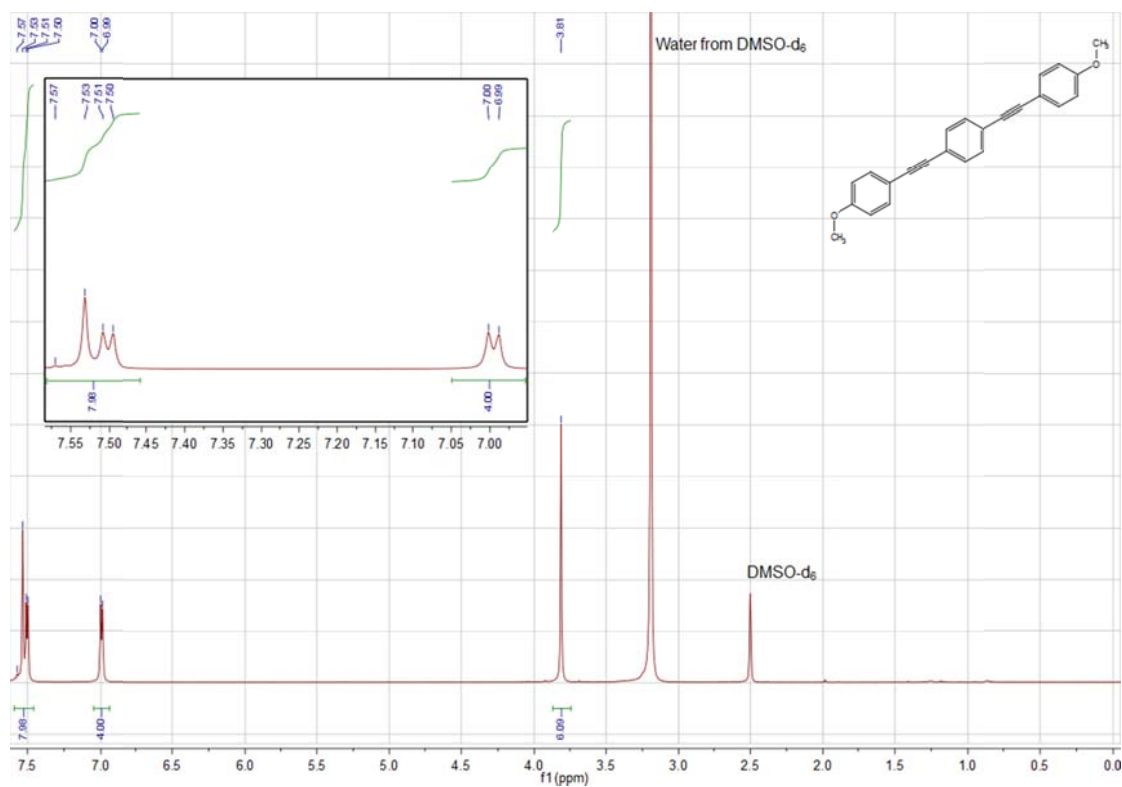
^1H NMR of 4-((4-methoxyphenyl)ethynyl)benzonitrile (6h) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



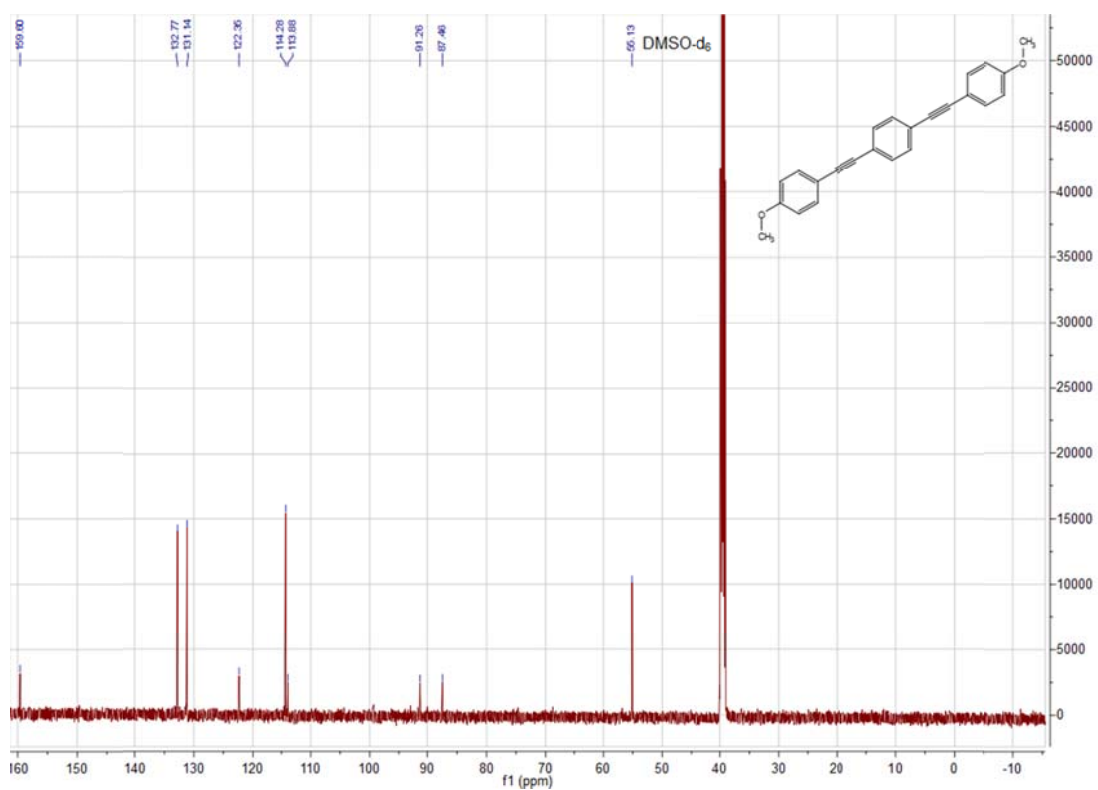
^{13}C NMR of 4-((4-methoxyphenyl)ethynyl)benzonitrile (6h) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



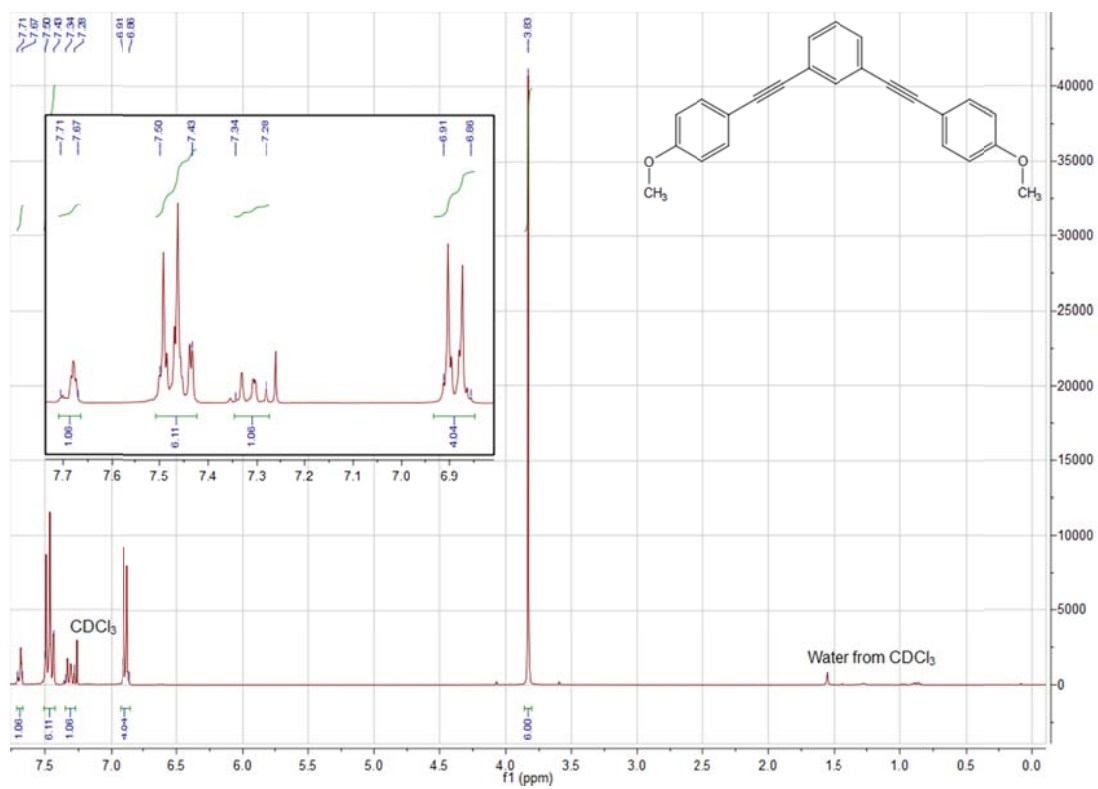
^1H NMR of 1,4-bis((4-methoxyphenyl)ethynyl)benzene (6i) (CDCl_3 , 600 MHz, $T = 333$ K)



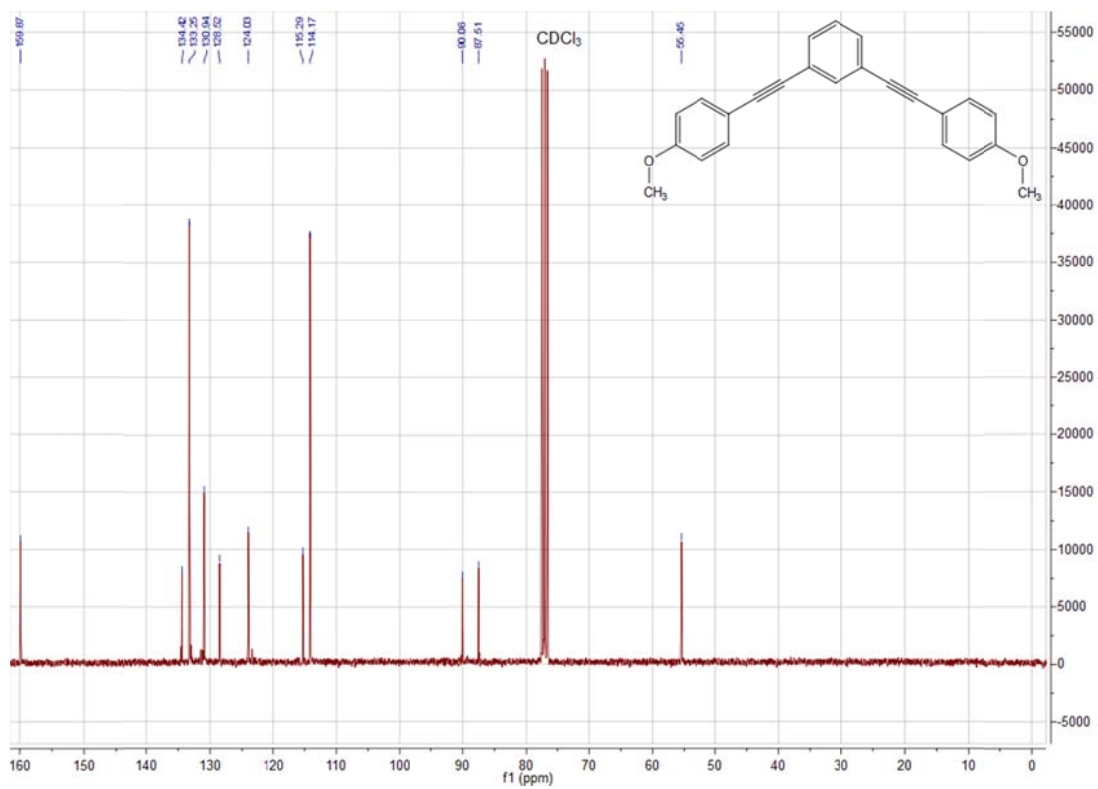
^{13}C NMR of 1,4-bis((4-methoxyphenyl)ethynyl)benzene (6i) (CDCl_3 , 150 MHz, $T = 333$ K)



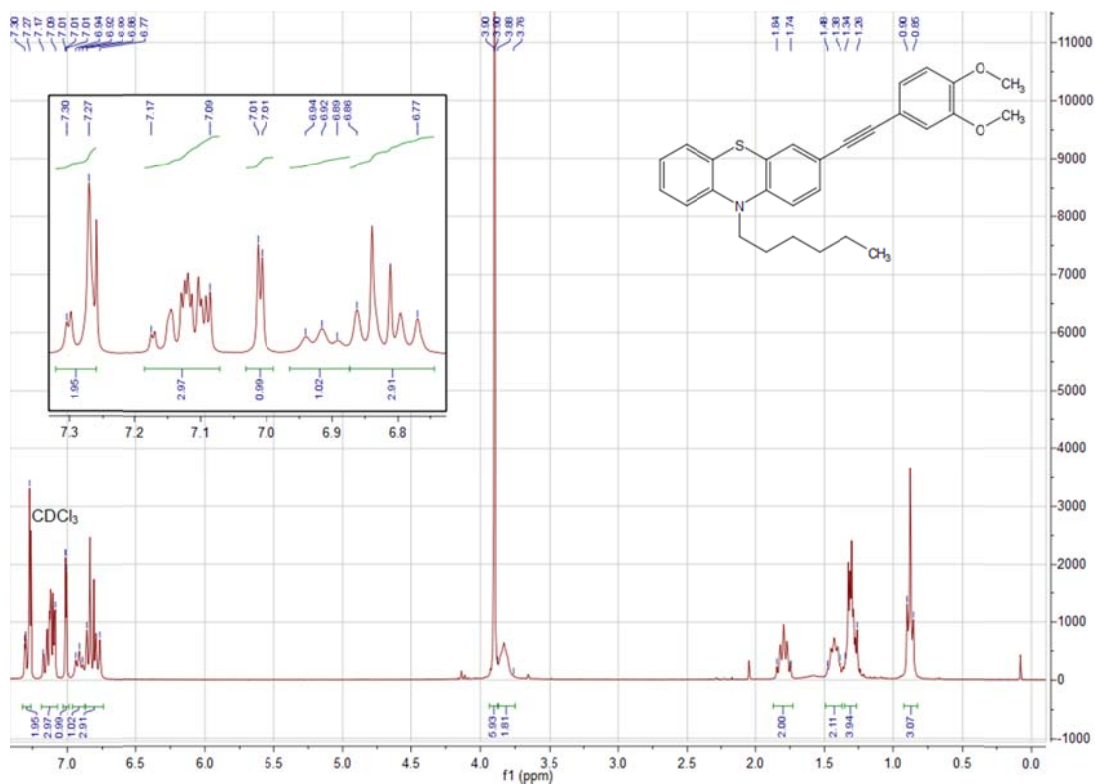
^1H NMR of 1,3-bis((4-methoxyphenyl)ethynyl)benzene (6j) (CDCl_3 , 300 MHz, $T = 298$ K)



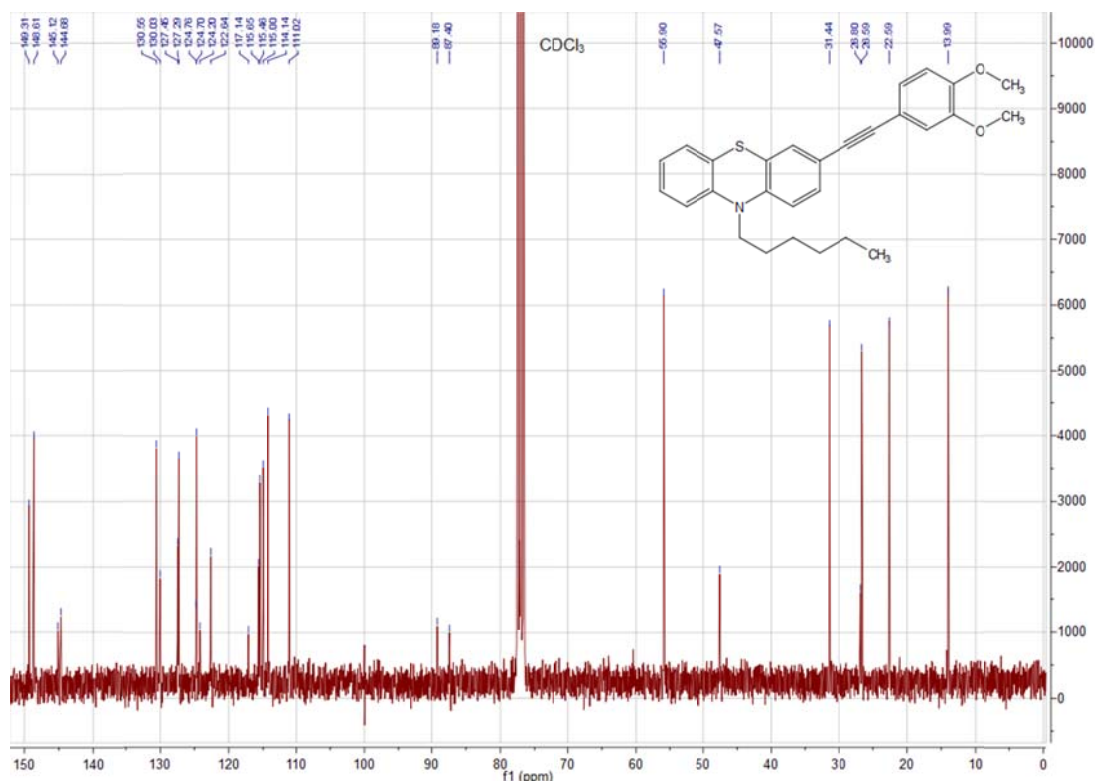
^{13}C NMR of 1,3-bis((4-methoxyphenyl)ethynyl)benzene (6j) (CDCl_3 , 300 MHz, $T = 298$ K)



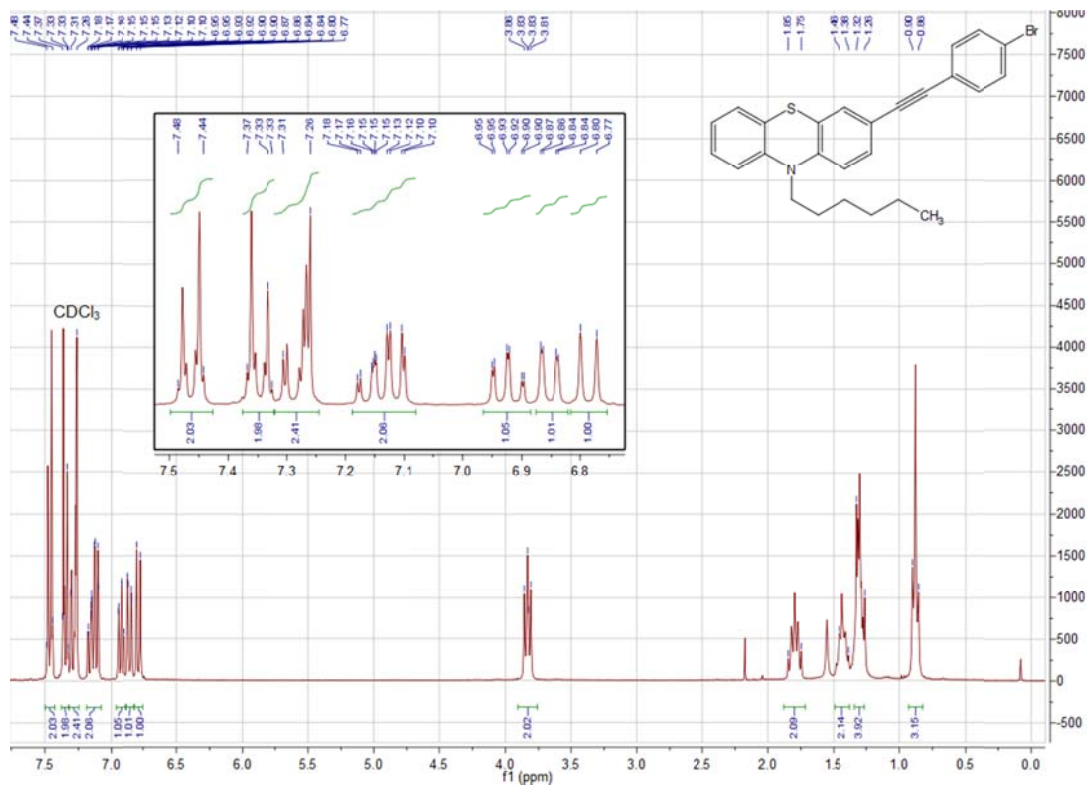
^1H NMR of 3-((3,4-dimethoxyphenyl)ethynyl)-10-hexyl-10H-phenothiazine (6k) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



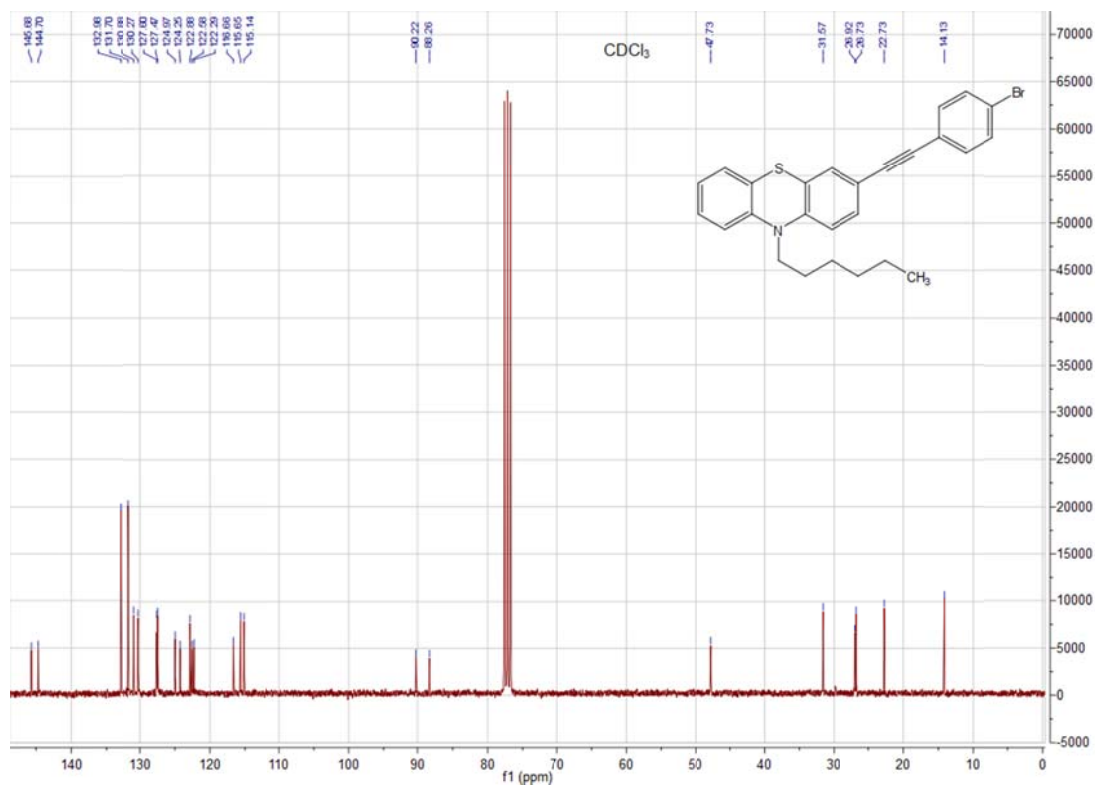
^{13}C NMR of 3-((3,4-dimethoxyphenyl)ethynyl)-10-hexyl-10H-phenothiazine (6k) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



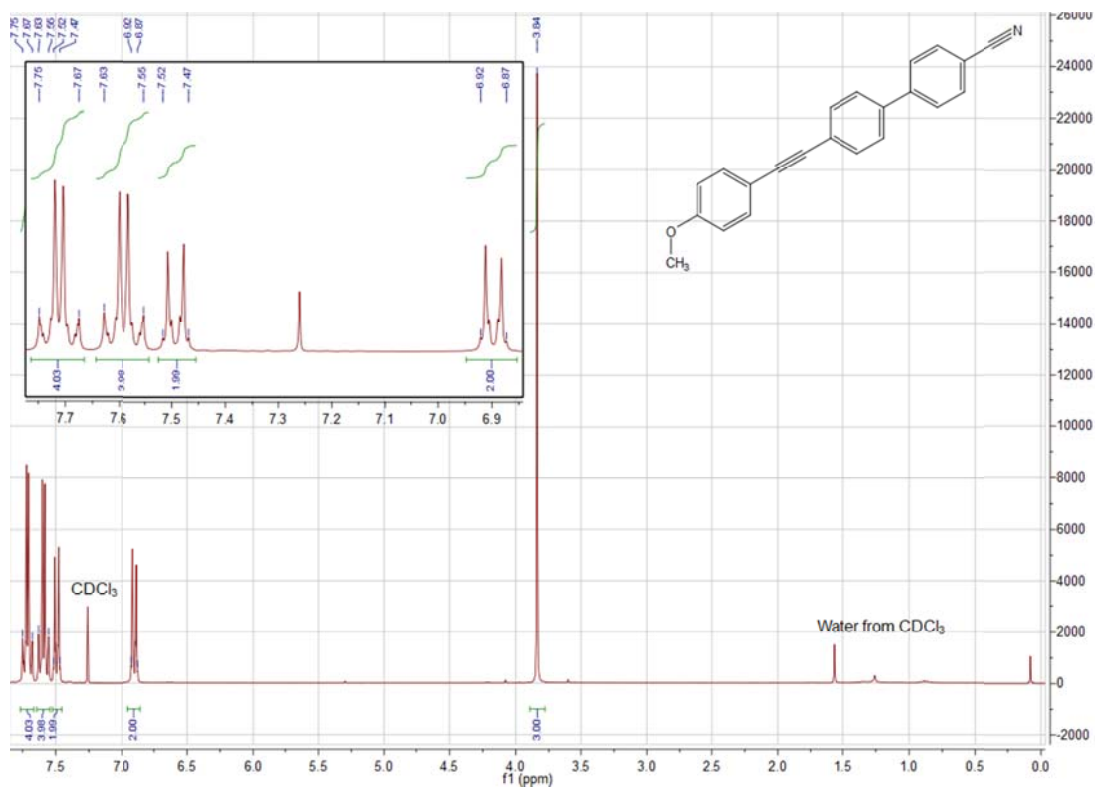
^1H NMR of 3-((4-bromophenyl)ethynyl)-10-hexyl-10H-phenothiazine (6I) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



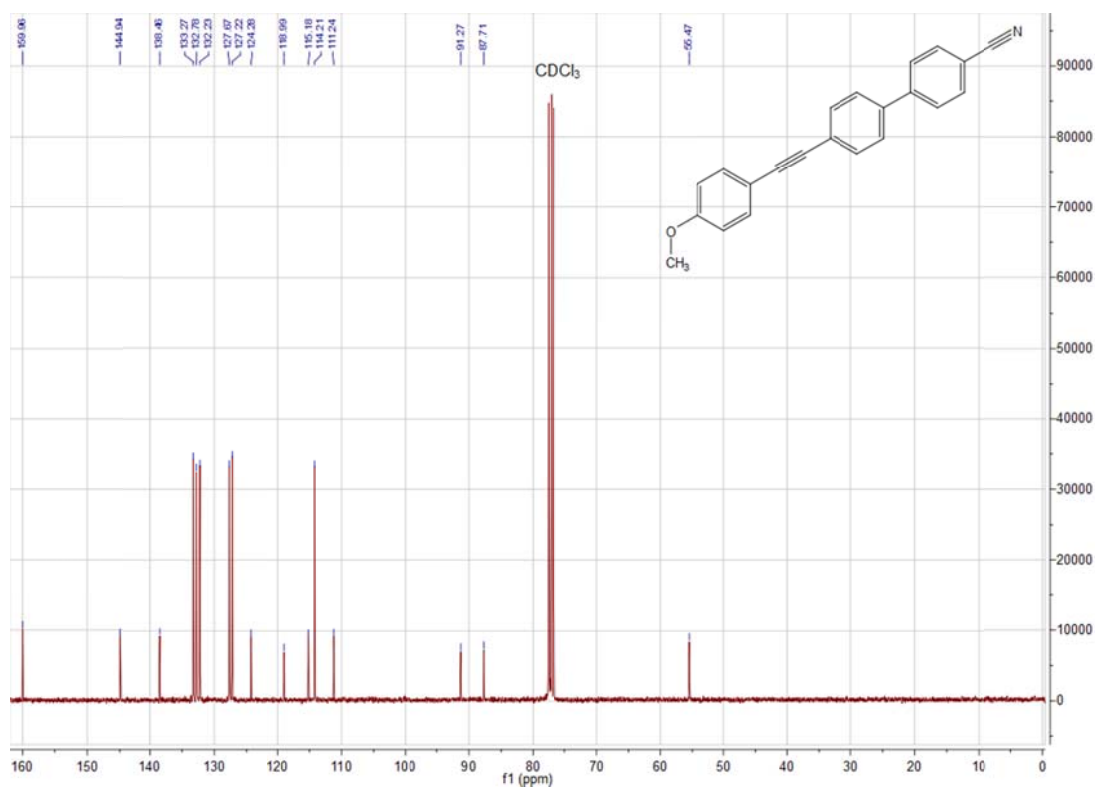
^{13}C NMR of 3-((4-bromophenyl)ethynyl)-10-hexyl-10H-phenothiazine (6I) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



^1H NMR of 4'-((4-methoxyphenyl)ethynyl)-[1,1'-biphenyl]-4-carbonitrile (**8**) (CDCl_3 , 300 MHz, $T = 298\text{ K}$)



^{13}C NMR of 4'-((4-methoxyphenyl)ethynyl)-[1,1'-biphenyl]-4-carbonitrile (**8**) (CDCl_3 , 75 MHz, $T = 298\text{ K}$)



-
- ¹ Y. Ogiwara, M. Kubota, K. Kurogi, T. Konakahara and N. Sakai, *Chem. Eur. J.*, 2015, **21**, 18598-18600.
- ² J.-Y. Chen, T.-C. Lin, S.-C. Chen, A.-J. Chen, C.-Y. Mou and F.-Y. Tsai, *Tetrahedron*, 2009, **65**, 10134-10141.
- ³ Merrell Dow Pharmaceuticals Inc., Patent: US5248825 A1, 1993.
- ⁴ S. I. Shergina, I. E. Sokolov, A. S. Zanina and I. L. Kotlyarevskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 639-641.
- ⁵ A. P. Rudenko and A. V. Vasil'ev, *Russ. J. Org. Chem.*, 1995, **31**, 1360-1379.
- ⁶ Y. Xu, J. Zhao, X. Tang, W. Wu and H. Jiang, *Adv. Synth. Catal.*, 2014, **356**, 2029-2039.
- ⁷ M. Barbero, S. Cadamuro and S. Dughera, *Eur. J. Org. Chem.*, 2014, 598-605.
- ⁸ J. Okubo, H. Shinozaki, T. Koitabashi and R. Yomura, *Bull. Chem. Soc. Japan*, 1998, **71**, 329-335.
- ⁹ Z.-W. Chen, Y.-Z. Zhu, J.-W. Ou, Y.-P. Wang and J.-Y. Zheng, *J. Org. Chem.*, 2014, **79**, 10988-10998.
- ¹⁰ A. V. Vasil'ev and A. P. Rudenko, *Russ. J. Org. Chem.*, 1997, **33**, 1555-1584.
- ¹¹ S. Nakatsuji, K. Matsuda, Y. Uesugi, K. Nakashima, S. Akiyama and W. Fabian, *J. Chem. Soc., Perkin Trans. 1*, 1992, 755-758.
- ¹² G.-X. He, F. Wada, K. Kikukawa, S. Shinkai and T. Matsuda, *J. Org. Chem.*, 1990, **55**, 541-548.