Supporting Information

Synthesis of Fused Chromenes by Indium(III)-Catalyzed Cascade Hydroarylation/Cycloisomerization Reactions of Polyyne-Type Aryl Propargyl Ethers

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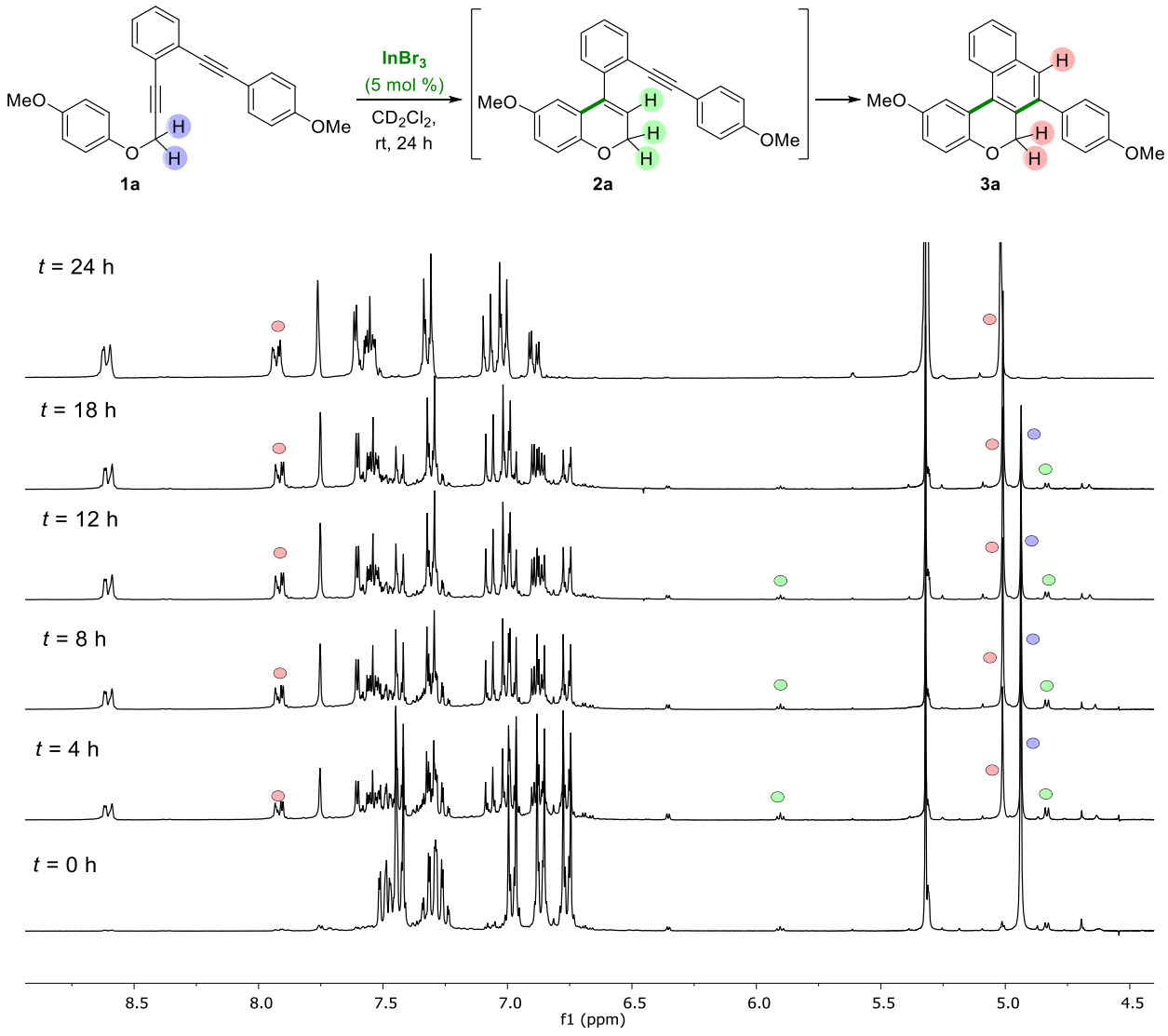
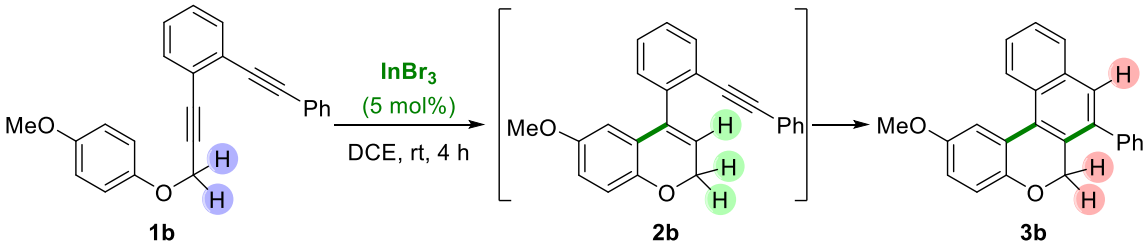
Reaction of 1a with $InBr_3$ monitorized by ^1H NMR measurements.

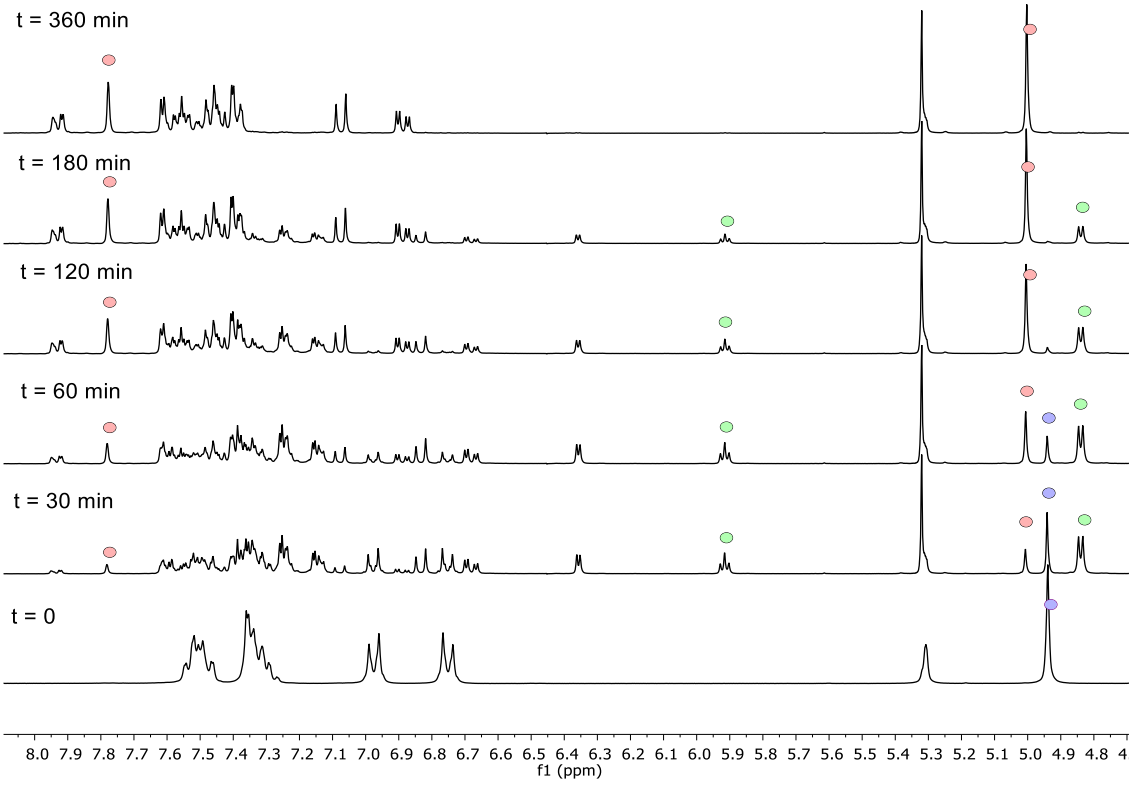
The reaction of **1a** (20 mg, 0.054 mmol) with $InBr_3$ (0.082 mL, 0.0027 mmol, 5 mol %) in CD_2Cl_2 (0.5 mL) was monitored by analysis of the ^1H NMR spectra at different time intervals (4 h, 8 h, 12 h, 18 h and 24 h).



Reaction of 1b with $InBr_3$ monitorized by ^1H NMR measurements.

Monitoring of the reaction of **1b** (22.6 mg, 0.067 mmol) with $InBr_3$ (0.100 mL, 0.0033 mmol, 5 mol %) in CD_2Cl_2 (0.5 mL) was carried out by analysis of the ^1H NMR spectra at different time intervals (30 min, 60 min, 120 min, 180 min and 360 min).



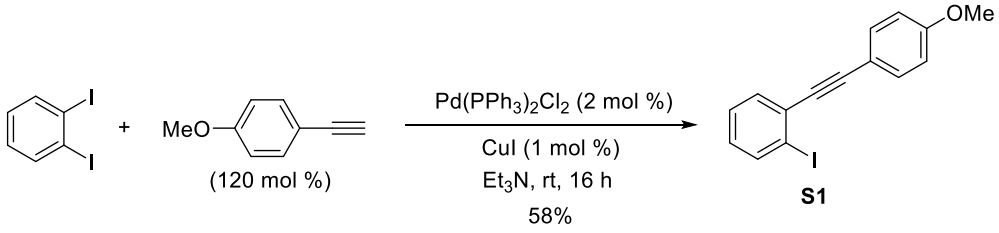


General methods.

All reactions were carried out in flame-dried glassware, under argon atmosphere, using standard gastight syringes, cannulae and septa. Toluene and THF were distilled from sodium/benzophenone. Dry MeOH, DCE, Et_3N, piperidine and other commercially available reagents were used as received. Reaction temperatures refer to external bath temperatures. Butyllithium was titrated prior to use. Indium(III) iodide (99.998%), indium(III) bromide (99.999%), were purchased from Aldrich and used as received under argon. 1-Methoxy-4-(prop-1-yn-1-iloxy)benzene (**S6**) was prepared according to previous reported method.[1] Reactions were monitored by TLC using pre-coated silica gel plates (Alugram® Xtra SIL G/UV_{254}, 0.20 mm thick), UV light as the visualizing agent and ethanolic phosphomolybdic acid as the developing agent. Flash column chromatography was performed with 230–400 mesh silica gel packed in glass columns. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 MHz and 75 MHz, respectively, in a Bruker Avance 300 spectrometer at ambient temperature, and calibrated to the solvent peak. DEPT data were used to assign carbon types. The low resolution EIMS were measured on a Thermo Finnigan Trace MS spectrometer at 70 eV. The HRMS were measured on a Thermo Finnigan MAT 95XP spectrometer or in a QSTAR LC/MS Turbo Spray. Melting points were measured in a Stuart Scientific melting point apparatus SMP3 and are uncorrected.

Preparation of compounds S1–5.

1-Iodo-2-((4-methoxyphenyl)ethynyl)benzene (S1).[2]



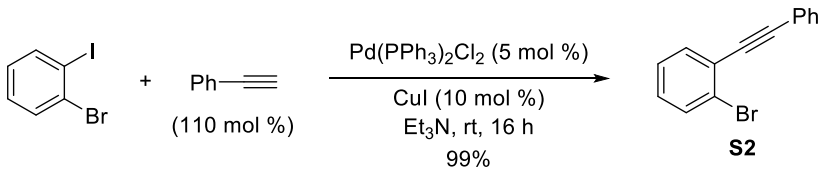
To a room temperature solution of 4-methoxyphenylacetylene (485 mg, 3.67 mmol, 120 mol %) in Et_3N (8 mL), $Pd(PPh_3)_2Cl_2$ (42.8 mg, 0.061 mmol, 2 mol %), CuI (5.9 mg, 0.031 mmol, 1 mol %) and 1,2-diiodobenzene (1.0 g, 3.06 mmol) were added and the resulting mixture was stirred overnight. After the reaction was completed, the mixture was diluted with EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL) and

1 S. Orbisaglia, B. Jacques, P. Braustein, D. Hueber, P. Pale, A. Blanc and P. Frémont, *Organometallics,* 2013, **32**, 4153–4164.

2 A. K. Verma, M. Joshi and V. P. Singh, *Org. Lett.,* 2011, **13**, 1630–1633.

the combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95–10:90) to afford **S1** (594 mg, 58%) as a white solid. R_f = 0.38 (EtOAc/hexane 10:90); mp 108–110 °C (lit.,[2] 86–87 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.87 (dd, J = 8.0, 1.0 Hz, 1H), 7.55 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 7.7 Hz, 1H), 7.32 (td, J = 7.6, 1.1 Hz, 1H), 6.98 (td, J = 7.7, 1.7 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.0 (C), 138.7 (CH), 133.1 (2 × CH), 132.1 (CH), 130.1 (C), 129.0 (CH), 127.8 (CH), 115.1 (C), 114.1 (2 × CH), 101.0 (C), 93.2 (C), 90.5 (C), 55.3 (CH_3) ppm; MS (EI) *m/z* (%) 335 [M, ^{128}I]$^+$ (10), 335 [M, ^{127}I]$^+$ (100), 319 [M – CH_3]$^+$ (20). HRMS (EI) calcd for $C_{15}H_{11}IO$ [M]$^+$ 333.9849, found 333.9850.

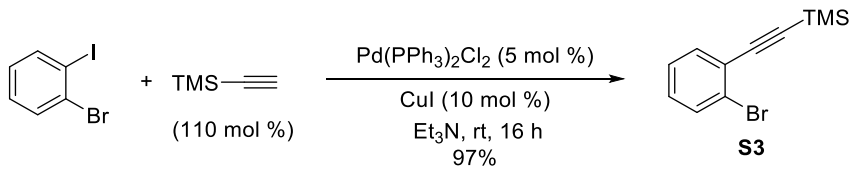
1-Bromo-(2-phenylethynyl)benzene (S2).[3]



To a room temperature solution of 2-bromoiodobenzene (0.7 mL, 5.45 mmol) in Et_3N (12 mL), $Pd(PPh_3)_2Cl_2$ (0.191 mg, 0.272 mmol, 5 mol %), CuI (0.104 mg, 0.545 mmol, 10 mol %) and phenylacetylene (0.660 mL 6.00 mmol, 110 mol %) were added and the resulting mixture was stirred overnight. After the reaction was completed, the mixture was diluted with EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 2:98) to afford **S2** (1.58 g, 99%) as a yellow oil. R_f = 0.41, (EtOAc/hexane 2:98); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64–7.55 (m, 4H), 7.39–7.36 (m, 3H), 7.30 (td, J = 7.5, 1.7 Hz, 1H), 7.19 (td, J = 7.7, 1.7 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 133.2 (CH), 132.4 (CH), 131.7 (2 × CH), 129.4 (CH), 128.6 (CH), 128.4 (2 × CH), 127.0 (CH), 125.6 (C), 125.4 (C), 122.9 (C), 93.9 (C), 88.0 (C) ppm; MS (EI) *m/z* (%) 258 [M, ^{81}Br]$^+$ (98), 256 [M, ^{79}Br]$^+$ (100); HRMS (EI) calcd for $C_{14}H_9Br$ [M]$^+$ 255.9882, found 255.9888.

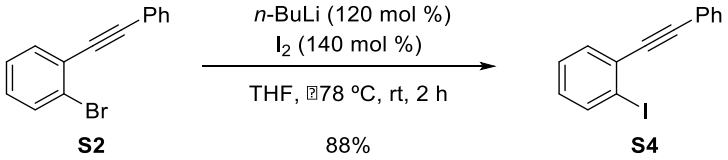
3 A. Orita, N. Yoshioka, P. Struwe, A. Braier, A. Beckmann and J. Otera, *Chem. Eur. J.*, 1999, **5**, 1355–1363.

((2-Bromophenyl)ethynyl)trimethylsilane (S3).[4]



To a solution of 2-bromoiodobenzene (1.0 mL, 7.79 mmol) in Et_3N (15 mL), $Pd(PPh_3)_2Cl_2$ (0.273 mg, 0.389 mmol, 5 mol %), CuI (0.148 mg, 0.778 mmol, 10 mol %) and ethynyltrimethylsilane (1.20 mL 8.57 mmol, 110 mol %) were added and the resulting mixture was stirred at room temperature overnight. After the reaction was completed, the mixture was diluted with EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 2:98) to afford **S3** (1.92 g, 97%) as a yellow oil. R_f = 0.50, EtOAc/hexane (2:98); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58 (d, J = 7.9 Hz, 1H), 7.50 (dd, J = 7.6 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.17 (td, J = 7.7, 1.5 Hz, 1H), 0.29 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 133.6 (CH), 132.3 (CH), 129.5 (CH), 126.9 (CH), 125.8 (C), 125.2 (C), 103.0 (C), 99.6 (C), –0.17 (3 × CH_3) ppm; MS (EI) *m/z* (%) 254 [M, ^{81}Br]$^+$ (22), 252 [M, ^{79}Br]$^+$ (21), 239 [M – CH_3, ^{81}Br]$^+$ (100), 237 [M – CH_3, ^{79}Br]$^+$ (98); HRMS (EI) calcd for $C_{11}H_{13}BrSi$ [M]$^+$ 251.9964, found 251.9971.

1-Iodo-2-(phenylethynyl)benzene (S4).[5]



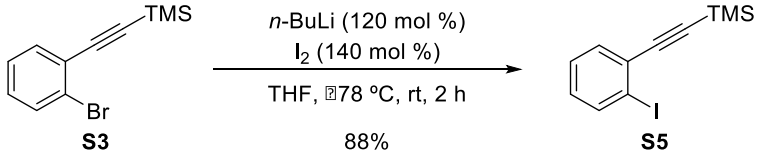
To a –78 °C solution of **S2** (1.58 g, 6.15 mmol) in dry THF (30 mL), *n*-BuLi (3.10 mL, 7.37 mmol, 120 mol %) was added dropwise, and the resulting mixture was stirred 30 minutes. Then I_2 (2.18 g, 8.60 mmol, 140 mol %) was added in one portion and the mixture was stirred for 2 hours and warmed to room temperature. The reaction was quenched by the addition H_2O (10 mL) and poured into a sepratory funnel over $Na_2S_2O_3$ (50 mL) and the aqueous layer was extracted with EtOAc (3 × 40 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 2:98) to afford **S4** (1.62 g, 88%) as a yellow oil. R_f = 0.50

4 J. S. Swenton, A. Callinan and S. Wang, *J. Org. Chem.,* 1992, **57**, 78–84.

5 C.-J. F. Du and H. Hart, *J. Org. Chem.,* 1987, **52**, 4311–4314.

(EtOAc/hexane 2:98); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90 (d, J = 8.4 Hz, 1H), 7.64–7.60 (m, 2H), 7.55 (dd, J = 7.7, 1.4 Hz, 1H), 7.39–7.32 (m, 4H), 7.03 (dt, J = 7.7, 1.4 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.7 (CH), 132.4 (CH), 131.6 (2 × CH), 129.8 (C), 129.3 (CH), 128.6 (CH), 128.4 (2 × CH), 127.8 (CH), 122.9 (C), 101.2 (C), 93.0 (C), 91.6 (C) ppm; MS (EI) *m/z* (%) 305 [M, ^{128}I]$^+$ (15), 304 [M, ^{127}I]$^+$ (100); HRMS (EI) calcd for $C_{14}H_9I$ [M]$^+$ 303.9743, found 303.9774.

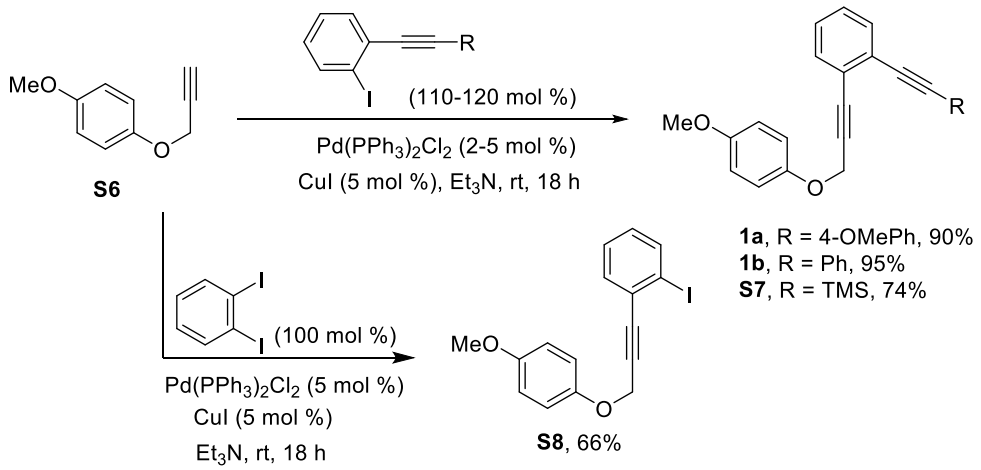
((2-Iodophenyl)ethynyl)trimethylsilane (S5).[6]



According to the known procedure,[6] to a solution of **S3** (1.92 g, 7.58 mmol) in dry THF (40 mL) at –78 °C, *n*-BuLi (3.90 mL, 9.10 mmol, 120 mol %) was added dropwise, and the resulting mixture was stirred for 30 minutes. Then I_2 (2.70 g, 10.6 mmol, 140 mol %) was added in one portion and the mixture was stirred for 2 hours at –78 °C and warmed to room temperature. The reaction was quenched by the addition H_2O (10 mL) and poured into a sepratory funnel over $Na_2S_2O_3$ (50 mL) and the aqueous layer was extracted with EtOAc (3 × 40 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure The crude was purified by flash chromatography (EtOAc/hexane 2:98) to afford **S5** (2.01 g, 88%) as a yellow oil. R_f = 0.36 (hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84 (dd, J = 8.0, 1.0 Hz, 1H), 7.47 (dd, J = 7.7, 1.6 Hz, 1H), 7.28 (dt, J = 7.6, 1.1 Hz, 1H), 6.98 (dt, J = 7.7, 1.7 Hz, 1H), 0.29 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.7 (CH), 132.7 (CH), 129.6 (C), 129.5 (CH), 127.7 (CH), 106.5 (C), 101.2 (C), 98.8 (C), –0.20 (3 × CH_3) ppm; MS (EI) *m/z* (%) 301 [M, ^{128}I]$^+$ (6), 300 [M, ^{127}I]$^+$ (37), 285 [M – CH_3]$^+$ (100); HRMS (EI) calcd for $C_{11}H_{13}ISi$ [M]$^+$ 299.9826, found 299.9826.

6 H. Kinoshita, N. Hirai and K. Miura, *J. Org. Chem.,* 2014, **79**, 8171–8181.

Preparation of diynes 1a–b, S7 and compound S8.



1-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)-2-((4-methoxyphenyl)ethynyl)benzene (1a).

To a solution of **S6** (291 mg, 1.80 mmol) in Et_3N (3 mL), $Pd(PPh_3)_2Cl_2$ (52.5 mg, 0.075 mmol, 5 mol %), CuI (14.3 mg, 0.075 mmol, 5 mol %) and a solution of **S1** (720 mg, 2.16 mmol, 120 mol %) in Et_3N (2 mL) were added and the resulting mixture was stirred at room temperature overnight. the mixture was diluted with EtOAc (10 mL) and saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford **1a** (596 mg, 90%) as a brown solid. R_f = 0.12 (EtOAc/hexane 5:95); mp 86–88 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.51–7.43 (m, 4H), 7.42–7.21 (m, 2H), 7.01 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 6.77 (d, J = 9.1 Hz, 2H), 4.95 (s, 2H), 3.84 (s, 3H), 3.73 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.8 (C), 154.3 (C), 152.1 (C), 133.2 (2 × CH), 132.1 (CH), 131.5 (CH), 128.3 (CH), 127.5 (CH), 126.4 (C), 124.6 (C), 116.2 (2 × CH), 115.3 (C), 114.6 (2 × CH), 114.0 (2 × CH), 93.6 (C), 88.2 (C), 86.8 (C), 85.8 (C), 57.6 (CH_2), 55.6 (CH_3), 55.3 (CH_3) ppm; MS (EI) *m/z* (%) 368 $[M]^+$ (137), 245 $[M - C_7H_7O_2]^+$ (61), 230 $[M - C_8H_9O_2]^+$ (52), 202 $[M - C_9H_{11}O_3]^+$ (100); HRMS (EI) calcd for $C_{25}H_{20}O_3$ $[M]^+$ 368.1407, found 368.1401.

1-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)-2-(phenylethynyl)benzene (1b).

To a solution of **S6** (291 mg, 1.80 mmol) in Et_3N (3 mL), $Pd(PPh_3)_2Cl_2$ (52.5 mg, 0.075 mmol, 5 mol%), CuI (14.3 mg, 0.075 mmol, 5 mol%) and a solution of **S3** (656 mg, 2.16 mmol, 120 mol%), in Et_3N (2 mL) were added and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc (10 mL) and saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash

chromatography (EtOAc/hexane 2:98) to afford **1b** (577 mg, 95%) as a brown solid. R_f = 0.20 (EtOAc/hexane 2:98); mp 66–68 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55–7.47 (m, 4H), 7.36–7.28 (m, 5H), 7.02 (d, J = 9.1 Hz, 2H), 6.77 (d, J = 9.1 Hz, 2H), 4.95 (s, 2H), 3.73 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.3 (C), 152.1 (C), 132.2 (CH), 131.8 (3 × CH), 128.4 (CH), 128.3 (3 × CH), 127.9 (CH), 126.0 (C), 124.8 (C), 123.1 (C), 116.2 (2 × CH), 114.6 (2 × CH), 93.5 (C), 88.4 (C), 88.0 (C), 85.6 (C), 57.6 (CH_2), 55.6 (CH_3) ppm; MS (EI) *m/z* (%) 338 $[M]^+$ (32), 215 $[M - C_7H_7O_2]^+$ (100); HRMS (EI) calcd for $C_{24}H_{18}O_2$ $[M]^+$ 338.130, found 338.1300.

[(2-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)phenyl)ethynyl]trimethylsilane (S7).

To a solution of **S6** (500 mg, 3.08 mmol) in Et_3N (5 mL), $Pd(PPh_3)_2Cl_2$ (43.3 mg, 0.062 mmol, 2 mol %), CuI (23.4 mg, 0.123 mmol, 4 mol %) and a solution of **S5** (1.02, 3.39 mmol, 110 mol %), in Et_3N (2 mL) were added and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford **S7** (763 mg, 74%) as a viscose colorless oil. R_f = 0.22 (EtOAc/hexane 5:95); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48–7.41 (m, 2H), 7.27–7.24 (m, 2H), 7.02 (d, J = 9.1 Hz, 2H), 6.87 (d, J = 9.1 Hz, 2H), 4.91 (s, 2H), 3.79 (s, 3H), 0.27 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 152.1 (C), 132.1 (2 × CH), 128.2 (CH), 128.1 (CH), 125.8 (C), 125.3 (C), 116.3 (2 × CH), 114.6 (2 × CH), 103.2 (C), 98.4 (C), 88.2 (C), 85.5 (C), 57.6 (CH_2), 55.7 (CH_3), –0.06 (3 × CH_3) ppm; MS (EI) *m/z* (%) 334 $[M]^+$ (100), 211 $[M - C_7H_7O_2]^+$ (20); HRMS (EI) calcd for $C_{21}H_{22}O_2Si$ $[M]^+$ 334.1384, found 334.1376.

1-Iodo-2-[3-(4-methoxyphenoxy)prop-1-yn-yl]benzene (S8).

To a solution of **S6** (500 mg, 3.08 mmol) in Et_3N (6 mL), $Pd(PPh_3)_2Cl_2$ (108 mg, 0.154 mmol, 5 mol %), CuI (29.3 mg, 0.154 mmol, 5 mol %) and 1,2-diiodobenzene (0.405 mL, 3.08 mmol, 100 mol %) were added and the resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95–10:90) to afford **S8** (741 mg, 66%) as a yellow oil. R_f = 0.28 (EtOAc/hexane 5:95); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84 (d, J = 8.0 Hz, 1H), 7.44 (dd, J = 7.7, 1.2 Hz, 1H), 7.31–7.27 (m, 1H), 7.06–6.98 (m, 3H), 6.87 (d, J = 9.1 Hz, 2H), 4.93 (s, 2H), 3.79 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.5 (C), 151.9 (C), 138.7 (CH), 133.0 (CH), 129.8 (CH),

129.0 (C), 127.7 (CH), 116.4 (2 × CH), 114.6 (2 × CH), 100.7 (C), 88.8 (C), 88.2 (C), 57.4 (CH_2), 55.7 (CH_3) ppm; MS (EI) *m/z* (%) 364 [M, $^{127}I]^+$ (32), 365 [M, $^{128}I]^+$ (5), 241 [M – $C_7H_7O_2]^+$ (96), 123 [M – $C_9H_6I]^+$ (48); HRMS (EI) calcd for $C_{16}H_{13}O_2I$ [M]$^+$ 363.9955, found 363.9952.

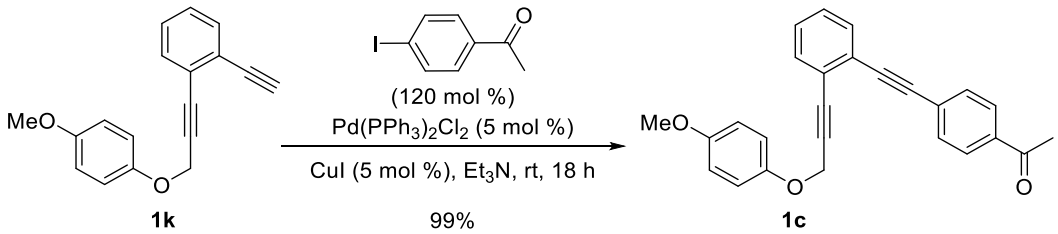
4-(2-Iodophenyl)-6-methoxy-2*H*-chromene (S9).

S8 **S9**

To a solution of **S8** (98.0 mg, 0.269 mmol) in dry DCE (3 mL) placed in a Schlenk tube, $InBr_3$ (0.410 mL, 0.013 mmol, 0.033M in DCE) was added and the reaction was stirred at room temperature for 16 h. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (EtOAc/hexane 5:95) to afford **S9** (88.1 mg, 90%) as a colorless oil. R*f* = 0.35 (EtOAc/hexane 5:95); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 6.3 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.71 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.17 (d, *J* = 2.6 Hz, 1H), 5.74 (t, *J* = 3.5 Hz, 1H), 4.96 – 4.81 (m, 2H), 3.65 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.0 (C), 148.0 (C), 142.9 (C), 139.42 (C), 139.40 (CH), 130.3 (CH), 129.3 (CH), 128.3 (CH), 123.7 (C), 122.5 (CH), 116.4 (CH), 113.9 (CH), 111.7 (CH), 99.5 (C), 65.2 (CH_2), 55.7 (CH_3) ppm; MS (EI) *m/z* (%) 364 [M]$^+$ (100); HRMS (EI) calcd for $C_{16}H_{13}O_2$ [M]$^+$ 363.9955, found 363.9939.

Preparation of diynes 1c–k.

1-[4-((2-(3-(4-Methoxyphenoxy)prop-1-yn-yl)phenyl)ethynyl)phenyl]ethan-1-one (1c).

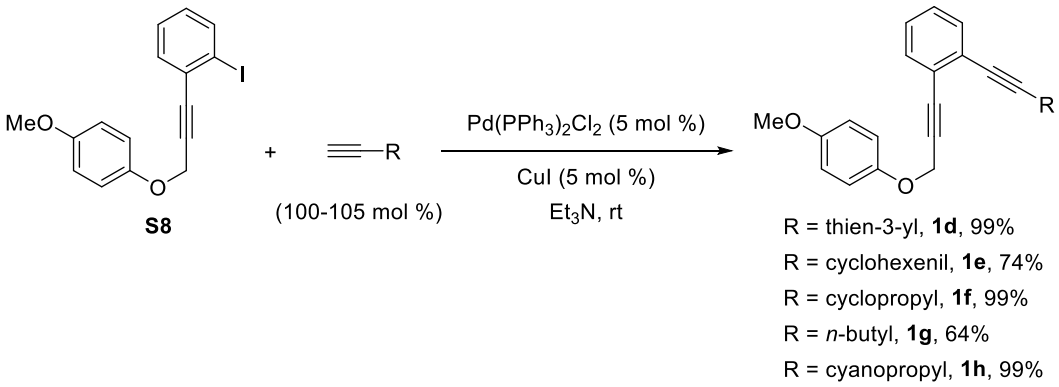


1k **1c**

To a solution of diine **1k** (200 mg 0.762 mmol) in Et_3N (2 mL), $Pd(PPh_3)_2Cl_2$ (26.8 mg, 0.038 mmol, 5 mol %) and CuI (7.2 mg, 0.038 mmol, 5 mol %) were added. Then a solution of 4-iodoacetophenone (225 mg, 0.914 mmol, 120 mol %) in Et_3N (2 mL) was added and the mixture was stirred at room temperature overnight. The reaction was quenched by adition of saturated

aqueous NH_4Cl (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layes were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 10:90) to afford **1c** (287 mg, 99%) as a brown solid. R_f = 0.13, 10% EtOAc/hexane; mp 73–75 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 3H), 7.50–7.47 (m, 1H), 7.32–7.27 (m, 2H), 7.01 (d, J = 9.1 Hz, 2H), 6.78 (d, J = 9.1 Hz, 2H), 4.94 (s, 2H), 3.70 (s, 3H), 2.59 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz)δ 197.2 (C), 154.4 (C), 152.0 (C), 136.3 (C), 132.2 (CH), 131.9 (CH), 131.8 (2 × CH), 128.5 (CH), 128.4 (CH), 128.2 (2 × CH), 127.9 (C), 125.3 (C), 125.1 (C), 116.1 (2 × CH), 114.6 (2 × CH), 92.6 (C), 91.2 (C), 88.8 (C), 85.5 (C), 57.5 (CH_2), 55.5 (CH_3), 26.6 (CH_3) ppm; MS (EI) *m/z* (%) 380 $[M]^+$ (100); HRMS (EI) calcd for $C_{26}H_{20}O_3$ $[M]^+$ 380.1407, found 380.1408.

General Procedure for diynes 1d–h.



To a solution of aryl propargyl ether (0.419 mmol) in Et_3N (2 mL), $Pd(PPh_3)_2Cl_2$ (0.021 mmol, 5 mol %), CuI (0.021 mmol, 5 mol %) and the alkyne (0.419 mmol, 100 mol %) were added at room temperature and the resulting mixture was stirred for 18 hours. The mixture was diluted with EtOAc (10 mL) and saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane) to afford the corresponding diyne.

3-[(2-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)phenyl)ethynyl]tiophene (1d).

Following the General Procedure, the reaction of aryl propargyl ether **S8** (150 mg, 0.419 mmol) in Et_3N (2 mL) with $Pd(PPh_3)_2Cl_2$ (14.7 mg, 0.021 mmol, 5 mol %), CuI (4.0 mg, 0.021 mmol, 5 mol %) and 3-ethynyltiophene (0.045 mL, 0.419 mmol, 100 mol %) afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound **1d** (143 mg, 99%) as a yellow viscose oil. R_f =

0.31 (EtOAc/hexane 10:90); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55–7.49 (m, 3H), 7.31–7.27 (m, 3H), 7.22 (d, J = 4.7 Hz, 1H), 7.05 (d, J = 8.9 Hz, 2H), 6.81 (d, J = 8.9 Hz, 2H), 4.96 (s, 2H), 3.75 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 152.1 (C), 132.2 (CH), 131.7 (CH), 130.0 (CH), 129.2 (CH), 128.4 (CH), 127.9 (CH), 126.0 (C), 125.4 (CH), 124.8 (C), 122.2 (C), 116.2 (2 × CH), 114.7 (2 × CH), 88.8 (C), 88.5 (C), 87.6 (C), 85.7 (C), 57.6 (CH_2), 55.6 (CH_3) ppm; MS (EI) *m/z* (%) 344 $[M]^+$ (35), 221 $[M - C_7H_7O_2]^+$ (100). HRMS (IE) calcd for $C_{22}H_{16}O_2S$ $[M]^+$ 344.0866, found 344.0854.

1-(Cyclohex-1-en-1-ylethynyl)-2-[3-(4-methoxyphenoxy)prop-1-yn-1-yl]benzene (1e).

Following the General Procedure, the reaction of aryl propargyl ether **S8** (275 mg, 0.755 mmol) in Et_3N (5 mL) with $Pd(PPh_3)_2Cl_2$ (26.5 mg, 0.038 mmol, 5 mol %), CuI (7.2 mg, 0.038 mmol, 5 mol %) and ethynylcyclohexene (0.093 mL, 0.793 mmol, 105 mol %) afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound **1e** (191 mg, 74%) as a yellow oil. R_f = 0.35 (EtOAc/hexane 10:90); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44 (d, J = 7.4 Hz, 2H), 7.26–7.21 (m, 2H), 7.04 (d, J = 9.4 Hz, 1H), 6.87 (d, J = 9.0 Hz, 2H), 6.22 (s, 1H), 4.92 (s, 2H), 3.78 (s, 3H), 2.25–2.16 (m, 4H), 1.68–1.64 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 152.2 (C), 135.8 (CH), 132.1 (CH), 131.6 (CH), 128.3 (CH), 127.4 (CH), 126.6 (C), 124.6 (C), 120.8 (CH), 116.2 (2 × CH), 114.6 (2 × CH), 95.6 (C), 88.1 (C), 85.8 (C), 85.5 (C), 57.6 (CH_2), 55.6 (CH_3), 29.2 (CH_2), 25.9 (CH_2), 22.4 (CH_2), 21.5 (CH_2) ppm; MS (EI) *m/z* (%) 342 $[M]^+$ (100); HRMS (EI) calcd for $C_{24}H_{22}O_2$ $[M]^+$ 342.1614, found 342.1618.

1-Cyclopropylethynyl-2-[3-(4-methoxyphenoxy)prop-1-yn-1-yl]benzene (1f).

Following the General Procedure, the reaction of aryl propargyl ether **S8** (275 mg, 0.755 mmol) in Et_3N (5 mL) with $Pd(PPh_3)_2Cl_2$ (26.5 mg, 0.038 mmol, 5 mol %), CuI (7.2 mg, 0.038 mmol, 5 mol %) and cyclopropylacetylene (0.067 mL, 0.793 mmol, 105 mol %) afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound **1f** (228 mg, 99%) as an orange oil. R_f = 0.33 (EtOAc/hexane 10:90); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.41 (d, J = 7.0 Hz, 2H), 7.21 (t, J = 6.3 Hz, 2H), 7.06 (d, J = 8.9 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 4.93 (s, 2H), 3.77 (s, 3H), 1.49–1.44 (m, 1H), 0.90–0.85 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 152.1 (C), 132.0 (CH), 131.8 (CH), 128.3 (CH), 127.1 (CH), 126.7 (C), 124.8 (C), 116.2 (2 × CH), 114.6 (2 × CH), 98.2 (C), 87.8 (C), 85.9 (C), 74.3 (C), 57.6 (CH_2), 55.7 (CH_3), 9.0 (2 × CH_2), 0.49 (CH) ppm; MS (EI) *m/z* (%) 302 $[M]^+$ (16), 192 $[M - C_7H_{10}O]^+$ (24), 178 $[M - C_8H_{12}O]^+$ (82), 69 $[M - C_{17}H_{13}O]^+$ (100); HRMS (EI) calcd for $C_{21}H_{18}O_2$ $[M]^+$ 302.1301, found 302.1306.

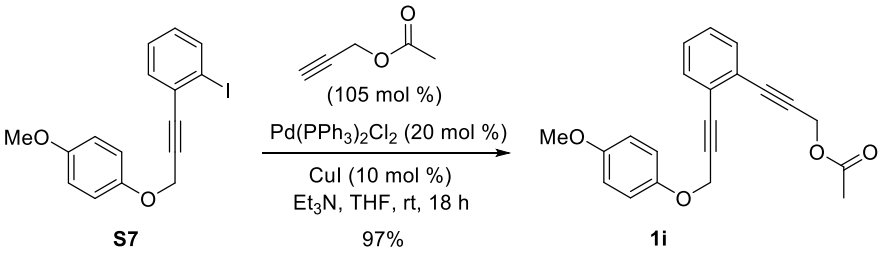
1-(Hex-1-yn-1-yl)-2-[3-(4-methoxyphenoxy)prop-1-yn-1-yl]benzene (1g).

Following the General Procedure, the reaction of propargyl ether **S8** (275 mg, 0.755 mmol) in Et_3N (5 mL) with $Pd(PPh_3)_2Cl_2$ (26.5 mg, 0.038 mmol, 5 mol %), CuI (7.2 mg, 0.038 mmol, 5 mol %) and hexyne (0.092 mL, 0.793 mmol, 105 mol %) afforded, after purification by flash chromatography (EtOAc/hexane 10:90) to afford **1g** (154 mg, 65%) as an orange viscous oil. R_f = 0.40 (EtOAc/hexane 10:90); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42 (d, J = 6.2 Hz, 2H), 7.27–7.18 (m, 2H), 7.04 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 4.92 (s, 2H), 3.78 (s, 3H), 2.43 (t, J = 6.6 Hz, 2H), 1.63–1.49 (m, 4H) ppm, 0.97 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 152.1 (C), 132.1 (CH), 131.8 (CH), 128.2 (CH), 127.1 (CH), 126.8 (C), 124.7 (C), 116.2 (2 × CH), 114.6 (2 × CH), 94.9 (C), 87.7 (C), 86.0 (C), 79.2 (C), 57.6 (CH_2), 55.7 (CH_3), 30.8 (CH_2), 22.0 (CH_2), 19.3 (CH_2), 13.7 (CH_3) ppm; MS (EI) *m/z* (%) 318 $[M]^+$ (42), 195 $[M - C_7H_7O_2]^+$ (50), 181 $[M - C_8H_9O_2]^+$ (60); HRMS (EI) calcd for $C_{22}H_{22}O_2$ $[M]^+$ 318.1614, found 318.1630.

6-[2-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)phenyl]hex-5-ynenitrile (1h).

Following a General Procedure, the reaction of aryl propargyl ether **S8** (275 mg, 0.755 mmol) in Et_3N (5 mL) with $Pd(PPh_3)_2Cl_2$ (26.5 mg, 0.038 mmol, 5 mol %), CuI (7.2 mg, 0.038 mmol, 5 mol %) and 5-hexynenitrile (0.085 mL, 0.793 mmol, 105 mol %) afforded, after purification by flash chromatography (EtOAc/hexane 20:80) compound **1h** (184 mg, 99%) as a yellow viscous oil. R_f = 0.16 (EtOAc/hexane 20:80); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45–7.38 (m, 2H), 7.25–7.23 (m, 2H), 7.02 (d, J = 9.0 Hz, 2H), 6.87 (d, J = 9.0 Hz, 2H), 4.92 (s, 2H), 3.75 (s, 3H), 2.54 (t, J = 6.5 Hz, 4H), 1.86 (t, J = 6.9 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 150.0 (C), 132.1 (CH), 131.8 (CH), 128.4 (CH), 127.7 (CH), 125.8 (C), 124.8 (C), 119.4 (C), 116.2 (2 × CH), 114.7 (2 × CH), 91.5 (C), 88.0 (C), 85.8 (C), 80.9 (C), 57.6 (CH_2), 55.7 (CH_3), 24.5 (CH_2), 18.6 (CH_2), 16.0 (CH_2) ppm; MS (EI) *m/z* (%) 239 $[M]^+$ (11), 277 $[M - C_4H_4]^+$ (42), 206 $[M - C_7H_7O_2]^+$ (63); HRMS (EI) calcd for $C_{22}H_{19}O_2$ $[M]^+$ 329.1410, found 329.1403.

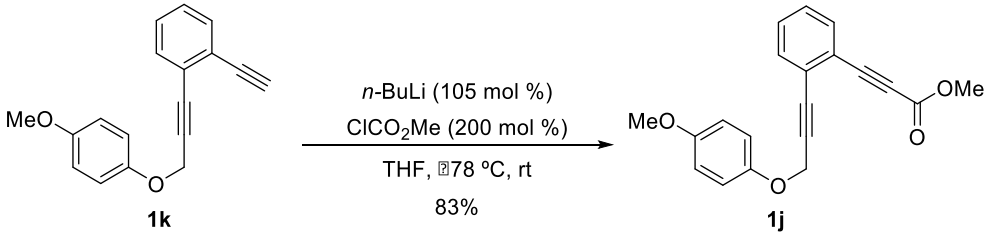
3-[2-(3-(4-Methoxyphenoxy)prop-1-yn-1-yl)phenyl]prop-2-yn-1-yl acetate (1i).



S7 **1i**

To a solution of the aryl propargyl ether **S7** (275 mg, 0.755 mmol) in Et_3N (5 mL) and THF (4 mL) $Pd(PPh_3)_2Cl_2$ (106 mg, 0.151 mmol, 20 mol %) and propargyl acetate (0.080 mL, 0.793 mmol, 105 mol %) were added at room temperature. The mixture was stirred for additional 5 minutes and CuI (14.4 mg, 0.076 mmol, 10 mol %) was added. The reaction mixture was stirred for 3 hours at room temperature and quenched by adition of saturated aqueous NH_4Cl (10 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic layes were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude was purified by flash chromatography (EtOAc/hexane 20:80) to afford **1i** (245 mg, 97%) as an orange oil. R_f = 0.30 (EtOAc/hexane 20:80); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46–7.41 (m, 2H), 7.27–7.24 (m, 2H), 7.03 (d, J = 9.1 Hz, 2H), 6.86 (d, J = 9.1 Hz, 2H), 4.92 (s, 2H), 4.83 (s, 2H), 3.76 (s, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.2 (C), 154.4 (C), 151.0 (C), 132.2 (CH), 132.1 (CH), 128.4 (CH), 128.3 (CH), 125.2 (C), 124.8 (C), 116.2 (2 × CH), 114.6 (2 × CH), 88.6 (C), 87.0 (C), 85.3 (C), 84.7 (C), 57.4 (CH_2), 55.6 (CH_3), 52.7 (CH_2), 20.7 (CH_3) ppm; MS (EI) *m/z* (%) 334 $[M]^+$ (10), 292 $[M - C_2H_3O + H]^+$ (47), 169 $[M - C_8H_{10}O_3 + H]^+$ (50), 85 $[M - C_{17}H_{14}O_2]^+$ (69); HRMS (EI) calcd for $C_{21}H_{18}O_4$ $[M]^+$ 334.1200, found 334.1189.

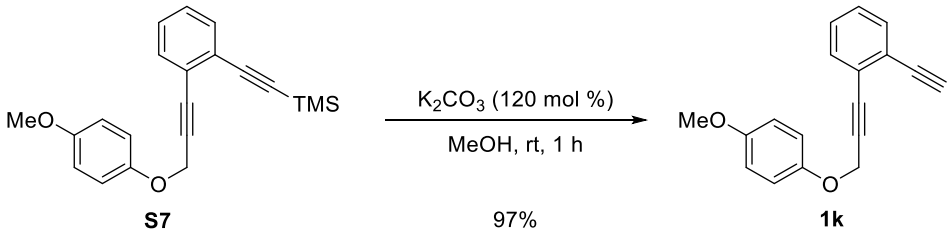
Methyl 3 -(2-(3-(4-methoxyphenoxy)prop-1-yn-1-yl)phenyl)propiolate (1j).



To a solution of diine **1k** (250 mg, 0.381 mmol) in dry THF (8 mL) at –78 °C *n*-BuLi (0.190 mL, 0.400 mmol, 105 mol %) was added dropwise. After 30 minutes, methyl cloroformate (0.150 mL, 1.91 mmol, 200 mol %) was added and the mixture was stirred at room temperature overnight. The solvent was concentrated under reduced pressure and the residue was redisolved in Et_2O (10 mL). The organic layer was washed with H_2O (5 mL), then dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude was purified by flash chromatography (EtOAc/hexane 10:90) to afford **1j** (102 mg, 83%) as a yellow oil. R_f = 0.13 (EtOAc/hexane 10:90); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (d, J = 7.5 Hz, 1H), 7.47 (d, J = 7.3 Hz, 1H), 7.39–7.27 (m, 2H), 7.03 (d, J = 9.0 Hz, 2H) 6.86 (d, J = 9.0 Hz, 2H), 4.95 (s, 2H), 3.85(s, 3H), 3.79 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 154.3 (C), 151.9 (C), 133.2 (CH), 132.4 (CH), 130.3 (CH), 128.5 (CH), 126.4 (C), 122.3 (C), 116.2 (2 × CH), 114.6 (2 × CH), 89.8 (C), 84.6 (C), 84.4 (C), 83.6 (C), 57.3 (CH_2), 55.6 (CH_3), 52.8

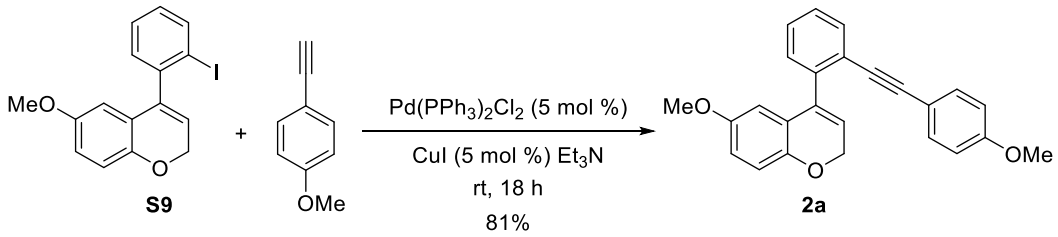
(CH_3) ppm; MS (EI) *m/z* (%) 320 $[M]^+$ (45), 261 $[M - C_2H_3O_2]^+$ (42) , 123 $[M - C_{13}H_9O_2]^+$ (100); HRMS (EI) calcd for $C_{20}H_{16}O_4$ $[M]^+$ 320.1043, found 320.1055.

1-Ethynyl-2-[3-(4-methoxyphenoxy)prop-1-yn-1-yl]benzene (1k).



To a solution of diyne **S7** (318 mg, 0.951 mmol) in MeOH (5 mL), K_2CO_3 (158 mg, 1.14 mmol, 120 mol %) was added and the mixture was stirred at room temperature for 1 hour. The reaction mixture was diluted with EtOAc (15 mL) and H_2O (15 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford **1k** (241 mg, 97%) as a viscose white oil. R_f = 0.15 (EtOAc/hexane 5:95); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.49–7.43 (m, 2H), 7.30–7.27 (m, 2H), 7.04 (d, J = 9.1 Hz, 2H), 6.87 (d, J = 9.1 Hz, 2H), 4.93 (s, 2H), 3.79 (s, 3H), 3.23 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 152.0 (C), 132.5 (CH), 132.2 (CH), 128.5 (CH), 128.3 (CH), 125.4 (C), 124.8 (C), 116.4 (2 × CH), 114.5 (2 × CH), 88.4 (C), 85.3 (C), 81.9 (C), 81.1 (CH), 57.4 (CH_2), 55.7 (CH_3) ppm; MS (EI) *m/z* (%) 262 $[M]^+$ (21), 139 $[M - C_7H_7O_2]^+$ (100); HRMS (EI) calcd for $C_{18}H_{14}O_2$ $[M]^+$ 262.0988, found 262.0970.

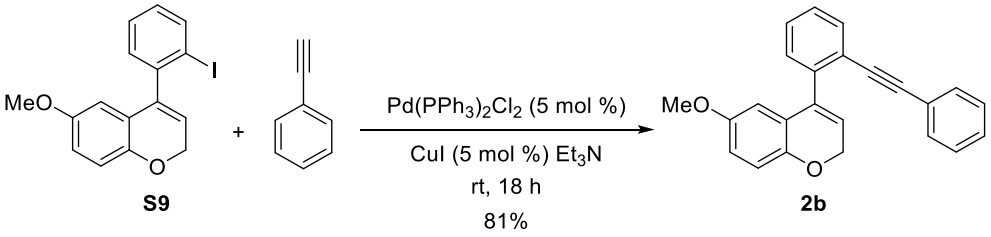
6-Methoxy-4-[2-(4-(methoxyphenyl)ethynyl]phenyl-2*H*-chromene (2a).



To a solution of **S9** (88.1 mg 0.242 mmol) in Et_3N (2 mL), $Pd(PPh_3)_2Cl_2$ (8.5 mg 0.012 mmol, 5 mol %), CuI (2.3 mg, 0.012 mmol, 5 mol %) and 4-methoxyphenylacetylene (0.040 mL, 0.290 mmol, 120 mol %) were added at room temperature and the resulting mixture was stirred for 18 hours. The reaction was diluted with EtOAc (10 mL) and satureated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with AcOEt (2 × 10 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford **2a** (72.2 mg, 81%) as a viscose orange oil. R*f* = 0.20 (EtOAc/hexane 5:95); ^{1}H NMR

($CDCl_3$, 300 MHz) δ 7.60 (d, J = 8.7 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.13 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.7 Hz, 1H), 6.79 (d, J = 8.8 Hz, 2H), 6.70 (dd, J = 8.7, 3.0 Hz, 1H), 6.44 (d, J = 3.0 Hz, 1H), 5.93 (t, J = 3.9 Hz, 1H), 4.89 (d, J = 3.9 Hz, 2H), 3.79 (s, 3H), 3.63 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.5 (C), 154.0 (C), 148.2 (C), 140.2 (C), 136.3 (CH), 132.9 (2 × CH), 132.0 (CH), 129.7 (CH), 128.0 (CH), 127.7 (CH), 124.5 (C), 123.3 (C), 122.5 (CH), 116.3 (CH), 115.4 (C), 114.0 (CH), 113.8 (2 × CH), 111.8 (CH), 93.8 (C), 87.2 (C), 65.3 (CH_2), 55.8 (CH_3), 55.2 (CH_3) ppm; MS (EI) *m/z* (%) 368 $[M]^+$ (100); HRMS (EI) calcd for $C_{25}H_{20}O_3$ $[M]^+$ 368.1407, found 368.1392.

6-Methoxy-4-[2-(4-(phenyl)ethynyl]phenyl-2*H*-chromene (2b).



To a solution of **S9** (103 mg 0.283 mmol) in Et_3N (2 mL), $Pd(PPh_3)_2Cl_2$ (9.9 mg 0.014 mmol, 5 mol %), CuI (2.3 mg, 0.014 mmol, 5 mol %) and phenylacetylene (0.032 mL, 0.339 mmol, 120 mol %) were added at room temperature and the resulting mixture was stirred for 18 hours. The reaction was diluted with EtOAc (10 mL) and satureated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with AcOEt (2 × 10 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford **2b** (39.4 mg, 41%) as a yellow oil. R*f* = 0.43 (EtOAc/hexane 10:90); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 – 7.61 (m, 1H), 7.39 – 7.35 (m, 3H), 7.27 – 7.19 (m, 5H), 6.88 (d, J = 8.7 Hz, 1H), 6.71 (dd, J = 8.8, 2.9 Hz, 2H), 6.43 (d, J = 2.8 Hz, 1H), 5.94 (t, J = 3.8 Hz, 1H), 4.89 (d, J = 3.8 Hz, 2H), 3.63 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.0 (C), 148.2 (C), 140.5 (C), 136.2 (C), 132.3 (CH), 131.4 (2 × CH), 129.7 (CH), 128.3 (CH), 128.1 (2 × CH), 128.09 (CH), 127.7 (CH), 124.5 (C), 123.2 (C), 122.9 (C), 122.5 (CH), 116.3 (CH), 114.0 (CH), 111.8 (CH), 93.6 (C), 88.5 (C), 65.3 (CH_2), 55.8 (CH_3) ppm.

General Procedure for indium(III)-catalyzed cascade cycloisomerizacion (3a–g).

1a-g 3a-g

To a solution of diyne (100 mg) in dry dichloroethane (3 mL) placed in an argon filled Schlenk tube, 5 mol % of a solution of $InBr_3$ in DCE 0.033M (5 mol %) was added, and the resulting mixture was stirred at the adecuate temperature until the starting material has been consumend. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (EtOAc/hexane) to afford the corresponding polycyclization product.

Synthesis of naphtho[*c*]chromenes 3a–g and 2*H*-chromenes 2h–k.

2-Methoxy-7-(4-methoxyphenyl)-6*H*-naphtho[*2,1-c*]chromene (3a).

Following the General Procedure, the reaction of **1a** (100 mg, 0.271 mmol) with $InBr_3$ (0.410 mL, 0.014 mmol, 5 mol %) at room temperature for 24 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound **3a** (84.7 mg, 85%) as a yellow solid. R_f = 0.20 (EtOAc/hexane 10:90); mp 142–144 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.63 (d, J = 9.2 Hz, 1H), 7.93–7.90 (m, 1H), 7.75 (s, 1H), 7.64 (d, J = 2.9 Hz, 1H), 7.58–7.51 (m, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 8.7 Hz, 2H), 6.90 (dd, J = 8.8, 2.9 Hz, 1H), 5.05 (s, 2H), 3.91 (s, 3H), 3.90 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.2 (C), 154.3 (C), 150.6 (C), 136.8 (C), 134.0 (C), 132.4 (C), 132.0 (C), 130.4 (2 × CH), 128.9 (CH), 128.6 (CH), 128.3 (C), 127.8 (C), 126.6 (CH), 125.9 (CH), 125.2 (C), 125.1 (CH), 117.8 (CH), 114.2 (CH), 113.9 (2 × CH), 113.8 (CH), 68.3 (CH_2), 55.9 (CH_3), 55.4 (CH_3) ppm; MS (EI) *m/z* (%) 368 $[M]^+$ (100); HRMS (EI) calcd for $C_{25}H_{20}O_2$ $[M]^+$ 368.1407, found 368.1403.

2-Methoxy-7-phenyl-6*H*-naphtho[*2,1-c*]chromene (3b).

Following the General Procedure, the reaction of **1b** (100 mg, 0.295 mmol) with $InBr_3$ (0.450 mL, 0.015 mmol, 5 mol %) at room temperature for 4 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90), compound **3b** (90.8 mg, 91%) as a beige solid. R_f = 0.41 (EtOAc/hexane 10:90); mp 150–152 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.64 (d, J = 7.7 Hz, 1H), 7.93 (dd, J = 6.8, 2.6 Hz, 1H), 7.78 (s, 1H), 7.63 (d, J = 2.9 Hz, 1H), 7.58–7.55 (m, 2H), 7.51–7.47 (m, 3H), 7.4 (d, J = 6.4 Hz, 2H), 7.11 (d, J = 8.8 Hz, 1H), 6.91 (dd, J = 8.8, 2.9 Hz, 1H), 5.04 (s, 2H), 3.91 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.3 (C), 150.6 (C), 139.7 (C), 137.1 (C), 133.9 (C), 132.1 (C), 129.3 (2 × CH), 129.0 (CH), 128.7 (CH), 128.5 (2 × CH), 128.4 (C), 127.9

(C), 127.7 (CH), 126.7 (CH), 126.0 (CH), 125.2 (C), 125.1 (CH), 117.8 (CH), 114.2 (CH), 113.9 (CH), 68.2 (CH_2), 56.0 (CH_3) ppm; MS (EI) *m/z* (%) 338 $[M]^+$ (30); HRMS (EI) calcd for $C_{24}H_{18}O_2$ $[M]^+$ 338.1301, found 338.1295.

1-[4-(2-Methoxy-6*H*-naphtho[*2,1-c*]chromen-7-yl)phenyl]ethan-1-one (3c).

Following the General Procedure, the reaction of **1c** (100 mg, 0.263 mmol) with $InBr_3$ (0.400 mL, 0.013 mmol, 5 mol %) at 80 ºC for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 20:80) compound **3c** (85.2 mg, 85%) as a red solid. R_f = 0.25 (EtOAc/hexane 20:80); mp 187–189 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.63 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.1 Hz, 2H), 7.91 (d, J = 7.1 Hz, 1H), 7.75 (s, 1H), 7.62 (d, J = 2.7 Hz, 1H), 7.56 (t, J = 6.6 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.8 Hz, 1H), 6.91 (dd, J = 8.7, 2.7 Hz, 1H), 5.01 (s, 2H), 3.91 (s, 3H), 2.69 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 197.6 (C), 154.4 (C), 150.5 (C), 144.5 (C), 136.3 (C), 135.9 (C), 133.8 (C), 131.6 (C), 129.5 (2 × CH), 129.0 (CH), 128.7 (CH), 128.6 (C), 128.5 (2 × CH), 128.2 (C), 127.1 (CH), 126.2 (CH), 125.2 (CH), 124.9 (CH), 117.8 (CH), 114.3 (CH), 114.0 (CH), 68.0 (CH_2), 55.9 (CH_3), 26.7 (CH_3) ppm; MS (EI) *m/z* (%) 380 $[M]^+$ (100), 322 $[M - C_3H_6O]^+$ (41); HRMS (EI) calcd for $C_{26}H_{20}O_3$ $[M]^+$ 380.1407, found 380.1406.

2-Methoxy-7-(thien-3-yl)-6*H*-naphtho[*2,1-c*]chromene (3d).

Following the General Procedure, the reaction of **1d** (100 mg, 0.290 mmol) with $InBr_3$ (0.440 mL, 0.015 mmol, 5 mol %) at room temperature for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound **3d** as a yellow solid (90.1 mg, 90%). R_f = 0.33 (EtOAc/hexane 10:90); mp 170–172 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.63 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.82 (s, 1H), 7.63 (d, J = 2.6 Hz, 1H), 7.59–7.51 (m, 2H), 7.45 (dd, J = 4.7, 3.0 Hz, 1H), 7.27 (d, J = 2.6 Hz, 1H), 7.18 (d, J = 4.2 Hz, 1H), 7.13 (dd, J = 8.8, 2.8 Hz, 1H), 6.91 (dd, J = 8.7, 2.8 Hz, 1H), 5.11 (s, 2H), 3.90 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.3 (C), 150.6 (C), 140.1 (C), 133.9 (C), 132.4 (C), 131.6 (C), 128.9 (CH), 128.8 (CH and C), 128.6 (CH), 128.5 (C), 127.9 (C), 126.8 (CH), 126.0 (CH), 125.9 (CH), 125.1 (CH), 123.5 (CH), 117.8 (CH), 114.2 (CH), 113.9 (CH), 68.1 (CH_2), 55.9 (CH_3) ppm; MS (EI) *m/z* (%) 344 $[M]^+$ (100); HRMS (EI) calcd for $C_{22}H_{16}O_2S$ $[M]^+$ 344.0866, found 344.0859.

7-(Cyclohex-1-en-1-yl)-2-methoxy-6*H*-naphtho[2,1-c]chromene (3e).

Following the General Procedure, the reaction of **1e** (100 mg, 0.292 mmol) with $InBr_3$ (0.440 mL, 0.015 mmol, 5 mol %) at room temperature for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound **3e** (87.4 mg, 87%) as a yellow oil. R_f = 0.40

(EtOAc/hexane 10:90); mp 148–150 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.62 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.64 (s, 2H), 7.53–7.51 (m, 2H), 7.15 (d, J = 8.7 Hz, 1H), 6.91 (dd, J = 8.7, 2.6 Hz, 1H), 5.70 (s, 1H), 5.10 (s, 2H), 3.90 (s, 3H), 2.33–2.25 (m, 4H), 1.86–1.76 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.3 (C), 150.6 (C), 139.5 (C), 136.7 (C), 134.0 (C), 132.3 (C), 128.7 (CH), 128.0 (C), 127.9 (CH), 127.4 (C), 126.9 (CH), 126.3 (CH), 125.7 (CH), 125.3 (C), 125.0 (CH), 117.7 (CH), 114.1 (CH), 113.7 (CH), 68.0 (CH_2), 55.9 (CH_3), 30.7 (CH_2), 25.5 (CH_2), 23.1 (CH_2), 22.1 (CH_2) ppm; MS (EI) *m/z* (%) 342 $[M]^+$ (34); HRMS (EI) calcd for $C_{24}H_{22}O_2$ $[M]^+$ 342.1614, found 342.1606.

7-Cyclopropyl-2-methoxy-6*H*-naphtho[*2,1-c*]chromene (3f).

Following the General Procedure, the reaction of **1f** (100 mg, 0.331 mmol) with $InBr_3$ (0.500 mL, 0.017 mmol, 5 mol %) at room temperature for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound **3f** (85.8 mg, 86%) as a yellow oil. R_f = 0.36 (EtOAc/hexane 10:90); mp 99–101 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.59 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.61 (d, J = 2.6 Hz, 1H), 7.55 (s, 1H), 7.50 (t, J = 3.7 Hz, 2H), 7.16 (d, J = 8.6 Hz, 1H), 6.90 (dd, J = 8.7, 2.8 Hz, 1H), 5.36 (s, 2H), 3.88 (s, 3H), 2.00–1.95 (m, 1H), 1.03 (d, J = 8.2 Hz, 2H), 0.81 (d, J = 4.6 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.3 (C), 150.4 (C), 135.9 (C), 134.7 (C), 134.1 (C), 128.5 (CH), 127.9 (C), 126.9 (C), 126.1 (CH), 125.7 (CH), 125.6 (CH), 125.1 (C), 125.0 (CH), 117.8 (CH), 114.1 (CH), 113.6 (CH), 67.0 (CH_2), 55.9 (CH_3), 13.1 (CH_2), 6.3 (2 × CH_2) ppm; MS (EI) *m/z* (%) 302 $[M]^+$ (100); HRMS (EI) calcd for $C_{21}H_{18}O_2$ $[M]^+$ 302.1301, found 302.1307.

7-Butyl-2-methoxy-6*H*-naphtho[*2,1-c*]chromene (3g).

Following the General Procedure, the reaction of **1g** (100 mg, 0.314 mmol) with $InBr_3$ (0.480 mL, 0.016 mmol, 5 mol %) at 80 ºC for 6 hours afforded, after purification by flash chromatography (EtOAc/hexane 10:90) compound **3g** (92.3 mg, 92%) as a yellow oil. R_f = 0.38 (EtOAc/hexane 10:90); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.61 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.63 (broad s, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.7 Hz, 1H), 6.91 (dd, J = 8.7, 2.6 Hz, 1H), 5.16 (s, 2H), 3.90 (s, 3H), 2.79 (t, J = 7.6 Hz, 2H), 1.69–1.64 (m, 2H), 1.67–1.42 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.3 (C), 150.4 (C), 135.6 (C), 134.1 (C), 133.1 (C), 128.3 (CH), 127.8 (C), 127.7 (CH), 127.3 (C), 125.9 (CH), 125.6 (CH), 125.2 (C), 125.1 (CH), 117.7 (CH), 114.1 (CH), 113.6 (CH), 67.0 (CH_2), 55.9 (CH_3), 32.9 (CH_2), 32.7 (CH_2), 22.6 (CH_2), 14.0 (CH_2) ppm; MS (EI) *m/z* (%) 318 $[M]^+$ (100); HRMS (EI) calcd for $C_{22}H_{22}O_2$ $[M]^+$ 318.1614, found 318.1612.

6-(2-(6-Methoxy-2*H*-chromen-4-yl)phenyl)hex-5-ynenitrile (2h).

Following the General Procedure, the reaction of **1h** (100 mg, 0.304 mmol) with $InBr_3$ (0.920 mL, 0.030 mmol, 10 mol %) at 80 ºC for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 20:80) compound **2h** (79.3 mg, 79%) as a red oil. R_f = 0.23 (EtOAc/hexane 20:80); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46 (d, J = 7.5 Hz, 1H), 7.36–7.26 (m, 3H), 6.85 (d, J = 8.7 Hz, 1H), 6.71 (dd, J = 8.7, 2.6 Hz, 1H), 6.29 (d, J = 2.7 Hz, 1H), 5.82 (t, J = 3.6 Hz, 1H), 4.85 (d, J = 3.5 Hz, 2H), 3.66 (s, 3H), 2.38 (t, J = 6.4 Hz, 2H), 2.17 (t, J = 7.2 Hz, 2H), 1.60 (t, J = 6.6 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.0 (C), 147.9 (C), 140.5 (C), 136.6 (C), 132.2 (CH), 129.7 (CH), 128.2 (CH), 127.8 (CH), 124.5 (C), 122.9 (C), 122.2 (CH), 119.4 (C), 116.4 (CH), 113.6 (CH), 111.9 (CH), 91.3 (C), 81.2 (C), 65.3 (CH_2), 55.7 (CH_3), 24.4 (CH_2), 18.5 (CH_2), 15.7 (CH_2) ppm; MS (EI) *m/z* (%) 329 $[M]^+$ (5), 83 $[M - C_{17}H_{10}O_2]^+$ (100); HRMS (EI) calcd for $C_{22}H_{19}O_2N$ $[M]^+$ 329.1410, found 329.1403.

3-(2-(6-Methoxy-2*H*-chromen-4-yl)phenyl)prop-2-yn-1-yl acetate (2i).

Following the General Procedure, the reaction of **1i** (100 mg, 0.300 mmol) with $InBr_3$ (0.450 mL, 0.015 mmol, 5 mol %) at room temperature for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 20:80) compound **2i** (64.8 mg, 65%) as a yellow oil. R_f = 0.25 (EtOAc/hexane 20:80); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54 (d, J = 8.0 Hz, 1H), 7.37–7.26 (m, 3H), 6.82 (d, J = 8.7 Hz, 1H), 6.69 (dd, J = 8.7, 2.8 Hz, 1H), 6.32 (d, J = 2.7 Hz, 1H), 5.87 (t, J = 3.8 Hz, 1H), 4.85 (d, J = 3.8 Hz, 2H), 4.69 (s, 2H), 3.65 (s, 3H), 2.04 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.1 (C), 153.9 (C), 148.2 (C), 140.7 (C), 135.5 (C), 132.7 (CH), 129.6 (CH), 128.7 (CH), 127.6 (CH), 124.4 (C), 122.7 (CH), 121.9 (C), 116.3 (CH), 113.9 (CH), 111.6 (CH), 86.8 (C), 85.2 (C), 65.2 (CH_2), 55.7 (CH_3), 52.6 (CH_2), 20.7 (CH_3) ppm; MS (EI) *m/z* (%) 334 $[M]^+$ (42), 274 $[M - C_2H_4O_2]^+$ (80) 243 $[M - C_3H_7O_2]^+$ (95); HRMS (EI) calcd for $C_{21}H_{18}O_4$ $[M]^+$ 334.1200, found 334.1187.

Methyl 3-[2-(6-methoxy-2*H*-chromen-4-yl)phenyl]propiolate (2j).

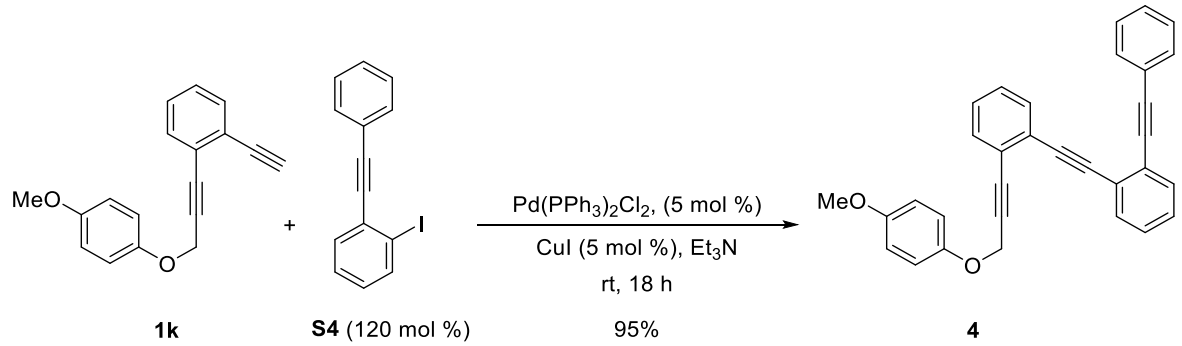
Following the General Procedure, the reaction of **1j** (100 mg, 0.312 mmol) with $InBr_3$ (0.470 mL, 0.016 mmol, 5 mol %) at room temperature for 48 hours afforded, after purification by flash chromatography (EtOAc/hexane 5:95) compound **2j** (71.3 mg, 71%) as a red oil. R_f = 0.33 (EtOAc/hexane 5:95); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.3 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 6.2 Hz, 1H), 6.85 (d, J = 8.7 Hz, 1H), 6.74 (dd, J = 8.7, 2.8 Hz, 1H), 6.28 (d, J = 2.7 Hz, 1H), 5.93 (t, J = 3.8 Hz, 1H), 4.87 (d, J = 3.8 Hz, 2H), 3.74 (s,

3H), 3.66 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.0 (2 × C), 148.3 (C), 142.0 (C), 134.5 (C), 134.1 (CH), 130.5 (CH), 129.8 (CH), 127.8 (CH), 124.2 (C), 123.6 (CH), 119.4 (C), 116.5 (CH), 114.0 (CH), 111.5 (CH), 85.4 (C), 83.4 (C), 65.1 (CH_2), 55.7 (CH_3), 52.6 (CH_3) ppm; MS (EI) *m/z* (%)320 $[M]^+$ (67), 305 $[M - CH_3]^+$ (100), 261 $[M - C_2H_3O]^+$ (54), 83 $[M - C_{16}H_{13}O_2]^+$ (100); HRMS (EI) calcd for $C_{20}H_{16}O_4$ $[M]^+$ 320.1043, found 320.1040.

4-(2-Ethynylphenyl)-6-methoxy-2*H*-chromene (2k).

Following the General Procedure, the reaction of **1k** (100 mg, 0.381 mmol) with $InBr_3$ (0.580 mL, 0.019 mmol, 5 mol %) at room temperature for 16 hours afforded, after purification by flash chromatography (EtOAc/hexane 5:95–10:90) compound **2k** (48.2 mg, 48%) as a yellow oil. R_f = 0.30 (EtOAc/hexane 10:90). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60 (d, J = 7.2 Hz, 1H), 7.41–7.26 (m, 3H), 6.84 (d, J = 8.7 Hz, 1H), 6.70 (dd, J = 8.5, 2.2 Hz, 1H), 6.32 (d, J = 2.0 Hz, 1H), 5.89 (t, J = 3.3 Hz, 1H), 4.87 (d, J = 3.4 Hz, 2H), 3.65 (s, 3H), 3.04 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.9 (C), 148.1 (C), 140.9 (C), 135.5 (C), 133.4 (CH), 129.6 (CH), 128.7 (CH), 127.6 (CH), 124.5 (C), 122.6 (CH), 121. (C), 116.3 (CH), 113.8 (CH), 111.6 (CH), 82.2 (C), 80.7 (CH), 65.3 (CH_2), 55.7 (CH_3) ppm. MS (EI) *m/z* (%) 262 $[M]^+$ (98), 261 $[M - H]^+$ (100). HRMS (EI) calcd for $C_{18}H_{14}O_2$ $[M]^+$ 262.0988, found 262.0984.

1-[3-(4-Methoxyphenoxy)prop-1-yn-1-yl)-2-((2-(phenylethynyl)phenyl)ethynyl]benzene (4).



1k **S4** (120 mol %) 95% **4**

To a solution of aryl diyne **1k** (471 mg, 1.80 mmol) in Et_3N (3 mL), $Pd(PPh_3)_2Cl_2$ (52.5 mg, 0.075 mmol, 5 mol %), CuI (14.3 mg, 0.075 mmol, 5 mol %) and a solution of **S4** (656 mg, 2.16 mmol, 120 mol %) in Et_3N (2 mL) were added and stirred at room temperature 18 h. The resulting mixture was quenched by addition of saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude was purified by flash chromatography (EtOAc/hexane 10:90) to afford **4** (577 mg, 95%) as a brown viscous oil. R_f = 0.19 (EtOAc/hexane 10:90); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63–7.50 (m,

6H), 7.37–7.30 (m, 7H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 2H), 4.78 (s, 2H), 3.70 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2 (C), 152.0 (C), 132.3 (CH), 132.2 (CH), 132.0 (CH), 131.9 (CH), 131.8 (2 × CH), 128.5 (CH), 128.4 (3 × CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 126.1 (C), 125.8 (C), 125.7 (C), 124.9 (C), 123.3 (C), 116.1 (2 × CH), 114.5 (2 × CH), 93.7 (C), 92.2 (C), 92.0 (C), 88.6 (C), 88.4 (C), 85.5 (C), 57.4 (CH_2), 55.6 (CH_3) ppm; MS (EI) *m/z* (%) 438 $[M]^+$ (21), 315 $[M - C_7H_7O_2]^+$ (97), 313 $[M - C_7H_9O_2]^+$ (100); HRMS (EI) calcd for $C_{32}H_{22}O_2$ $[M]^+$ 438.1614, found 438.1608.

2-Methoxy-7-[2-(phenylethynyl)phenyl]-6*H*-naphtho[*2,1-c*]chromene (6).

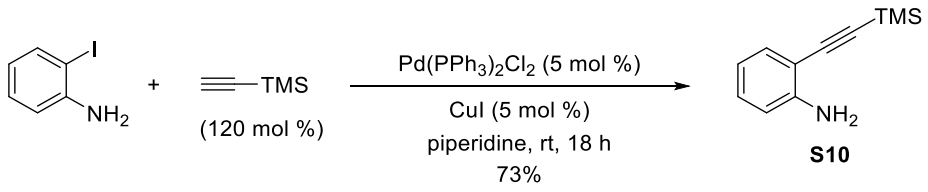
Following the General Procedure, the reaction of **4** (100 mg, 0.228 mmol) with $InBr_3$ (0.690 mL, 0.023 mmol, 10 mol %) at room temperature for 24 hours afforded, after purification by flash chromatography (EtOAc/hexane 5:95) componud **6** (71.4 mg, 70%) as a light green oil. R_f = 0.15 (EtOAc/hexane 5:95); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.69 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 1H), 7.81 (s, 1H), 7.69 (d, *J* = 2.6 Hz, 2H), 7.62–7.52 (m, 3H), 7.43–7.45 (m, 3H), 7.15–7.05 (m, 3H), 6.99 (d, *J* = 7.0 Hz, 2H), 6.91 (dd, *J* = 8.8, 2.8Hz, 1H), 5.11 (d, *J* = 13.7 Hz, 1H), 4.91 (d, *J* = 13.7 Hz, 1H), 3.92 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.3 (C), 150.8 (C), 142.2 (C), 135.7 (C), 133.8 (C), 133.2 (C), 131.9 (CH), 131.3 (2 × CH), 129.9 (CH), 129.1 (CH), 129.0 (CH), 128.6 (C), 128.4 (CH), 128.1 (3 × CH), 127.9 (CH), 127.3 (C), 126.8 (CH), 125.8 (CH), 125.2 (C), 125.1 (CH), 123.4 (C), 122.8 (C), 117.9 (CH), 114.1 (CH), 113.8 (CH), 93.2 (C), 88.5 (C), 68.3 (CH_2), 56.0 (CH_3) ppm; MS (EI) *m/z* (%) 438 $[M]^+$ (100); HRMS (EI) calcd for $C_{32}H_{22}O_2$ $[M]^+$ 438.1614, found 438.1599.

11-Methoxy-1-phenyl-7*H*-chryseno[*5,6-c*]chromene (7).

Following the General Procedure, the reaction of **4** (100 mg, 0.228 mmol) with $InBr_3$ (0.690 ml, 0.023 mmol, 10 mol %) at room temperature for 24 hours followed by 16 hours at 80 ºC afforded, after purification by flash chromatography (EtOAc/hexane 10%) compound **7** (60.2 mg, 60%) as a yellow solid. R_f = 0.20 (EtOAc/hexane 10:90); mp 88–90 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.71 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.85 (s, 1H), 7.68–7.60 (m, 3H), 7.50–7.43 (m, 6H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.74 (s, 2H), 3.93 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4 (C), 150.8 (C), 145.2 (C), 138.0 (C), 132.5 (C), 131.7 (C), 130.9 (CH), 130.6 (C), 129.9 (CH), 129.14 (2 × CH), 129.09 (C), 128.9 (2 × CH), 128.88 (C), 128.8 (2 × C), 128.4 (CH), 128.0 (C), 127.4 (CH), 127.0 (CH), 126.6 (CH), 126.1 (CH), 125.6 (CH), 125.4 (C), 125.0 (CH), 123.9 (CH),

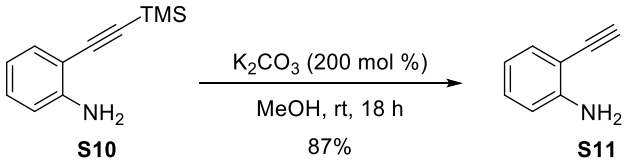
117.4 (CH), 114.6 (CH), 114.0 (CH), 70.9 (CH_2), 56.0 (CH_3) ppm; MS (EI) *m/z* (%) 438 $[M]^+$ (100); HRMS (EI) calcd for $C_{32}H_{22}O_2$ $[M]^+$ 438.1614, found 438.1605.

2-[(Trimethylsilyl)ethynyl]aniline (S10).[7]



According to the known procedure,[7] on a round-bottomed flask coupled with a Liebig refrigerant, 2-iodoaniline (1.50 g, 6.85 mmol), $Pd(PPh_3)_2Cl_2$ (0.240 g, 0.342 mmol, 5 mol %), CuI (0.065 g, 0.342 mmol, 5 mol %) and Et_3N (30 mL) were successively added. Then, trimethylsilylacetylene (1.20 mL, 8.22 mmol, 120 mol %) was added and the reaction mixture was heated to reflux for 5 hours. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and H_2O (30 mL) and the aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was purified by flash chromatography (EtOAc/hexane 5:95) to afford **S10** (1.19 g, 91%) as a yellow oil. R_f = 0.30 (EtOAc/hexane 5:95); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31 (d, J = 7.6 Hz, 1H), 7.13 (t, J = 7.1 Hz, 1H), 6.70 (d, J = 8.6 Hz, 2H), 4.24 (br s, 2H), 0.29 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.3 (C), 132.3 (CH), 130.0 (CH), 117.7 (CH), 114.2 (CH), 107.8 (C), 101.8 (C), 99.7 (C), 0.16 (3 × CH_3) ppm; MS (EI) *m/z* (%) 189 $[M]^+$ (82), 174 $[M - CH_3]^+$ (100); HRMS (EI) calcd for $C_{11}H_{15}NSi$ $[M]^+$ 189.0968, found 189.0971.

2-Ethynylaniline (S11).[7]

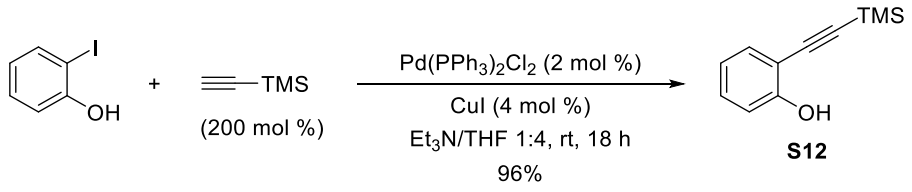


According to the known procedure,[7] to a solution of aniline **S10** (1.19 g, 6.27 mmol) in MeOH (15 mL), K_2CO_3 (1.74 g, 12.6 mmol, 200 mol %) was added and the mixture was stirred at room temperature for 30 minutes. The reaction mixture was diluted with EtOAc (30 mL) and H_2O (30 mL) and the aqueous player was extracted with EtOAc (2 × 30 mL). The combined organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified by

7 S. W. Youn and S. R. Lee, *Org. Biomol. Chem.,* 2015, **13**, 4652–4656.

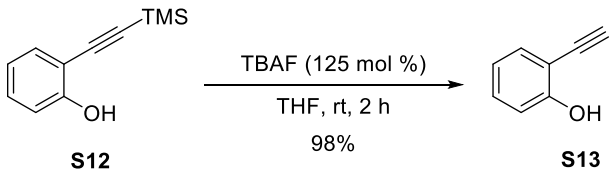
flash chromatography (EtOAc/hexane 10:90) to afford **S11** (735 mg, 99%) as a yellow oil. R_f = 0.25 (Et_2O/hexane 10:90); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.35 (d, J = 7.8 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 6.71 (d, J = 7.8 Hz, 2H), 4.26 (br s, 2H), 3.40 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.5 (C), 132.6 (CH), 130.1 (CH), 117.8 (CH), 114.3 (CH), 106.6 (C), 82.4 (CH), 80.6 (C) ppm; MS (EI) *m/z* (%) 117 $[M]^+$ (100); HRMS (EI) calcd for C_8H_7N $[M]^+$ 117.0573, found 117.0562.

2-[(Trimethylsilyl)ethynyl]phenol (S12).[8]



To a solution of 2-iodophenol (1.00 g, 4.54 mmol) in THF (40 mL) and Et_3N (10 mL), CuI (35 mg, 0.182 mmol, 4 mol %), $Pd(PPh_3)_2Cl_2$ (64 mg, 0.091 mmol, 2 mol %) and ethynyltrimethylsilane (1.28 mL, 9.09 mmol, 200 mol %) were added at room temperature and stirred 18 h. The resulting mixture was diluted with CH_2Cl_2 (30 mL) and saturated aqueous NH_4Cl (20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic layer was washed with H_2O (20 mL), dried ($MgSO_4$), filtrated, and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography with silica gel (EtOAc/hexane 5:95) to afford **S12** (830 mg, 96%) as an orange viscous oil. R_f = 0.25 (EtOAc/hexane 5:95); ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, J = 7.7, 1.6 Hz, 1H), 7.26 (dd, J = 7.4, 1.6 Hz, 1H), 6.95 (d, J = 8.3, 0.8 Hz, 1H), 6.87 (td, J = 7.5, 1.0 Hz, 1H), 5.85 (s, 1H), 0.30 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1 (C), 131.6 (CH), 130.6 (CH), 120.2 (CH), 114.5 (CH), 109.5 (C), 102.4 (C), 98.9 (C), -0.04 (3 × CH_3) ppm.

2-Ethynylphenol (S13).[9]



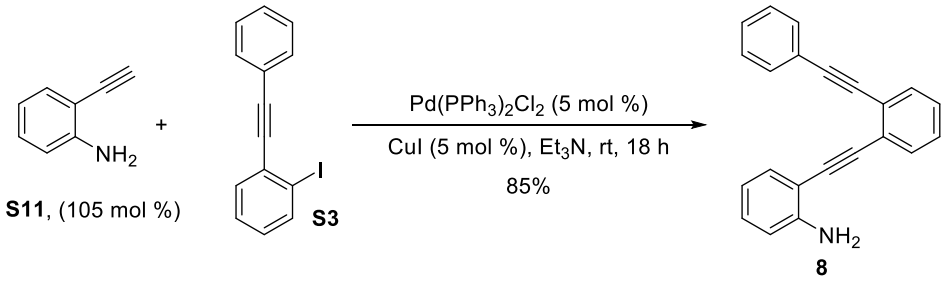
To a solution of **S12** (830 mg, 4.36 mmol) in dry THF (35 mL) a solution of TBAF (5.25 mL, 125 mol %, 1.0 M in THF) was added and the resulting mixture was stirred at room temperature for 2 hours. The reaction mixture was diluted with Et_2O (20 mL) and brine (20 mL) and the aqueous

8 T. Barton and B. L. Groh, *J. Org. Chem.,* 1985, **50**, 158–166.

9 M. Topolski, *J. Org. Chem.,* 1995, **60**, 5588–5594.

layer was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford, after purification by flash chromatography (Et_2O/hexane 20:80) compound **S13** (426 mg, 86%) as a brown oil. R_f = 0.26 (EtOAc/hexane 10:90); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.7, 1.6 Hz, 1H), 7.28 (td, J = 7.4, 1.7 Hz, 1H), 6.96 (dd, J = 8.3, 0.8 Hz, 1H), 6.88 (td, J = 7.5, 1.1 Hz, 1H), 5.80 (br s, 1H), 3.47 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4 (C), 132.0 (CH), 130.9 (CH), 120.3 (CH), 114.8 (CH), 108.2 (C), 84.3 (CH), 78.3 (C) ppm; MS (EI) *m/z* 118 $[M]^+$ (40); HRMS (EI) calcd for C_8H_6O $[M]^+$ 118.0413 found 118.0415.

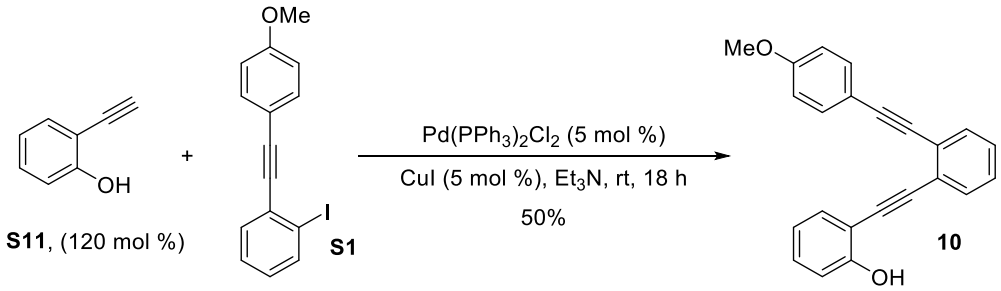
2-[(2-(Phenylethynyl)phenyl)ethynyl]aniline (8).[10]



In a round-bottom flask coupled with a Liebig refrigerant, compound **S3** (371 mg, 1.22 mmol), $Pd(PPh_3)_2Cl_2$ (42.8 mg, 0.061 mmol, 5 mol %), CuI (11.6 mg, 0.061 mmol, 5 mol %) and Et_3N (3 mL) were added at room temperature. After 5 minutes a solution of 2-ethynylaniline (**S11**, 150 mg, 1.28 mmol, 105 mol %) in THF (2 mL) was added at room temperature and the reaction mixture was heated at 80 °C during 18 hours. The reaction was quenched by addition of an aqueous saturated solution of NH_4Cl (10 mL) and was extracted with EtOAc (3 × 10 mL), dried with $MgSO_4$, filtered and concentrated *in vacuo* to afford, after purification by flash chromatography (EtOAc/hexane 10:90–20:80) compound **8** (304 mg, 85%) as a brown solid. R_f = 0.20 (EtOAc/hexane 2:98); mp 95–97 °C (lit.,[10] 90–91 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62–7.59 (m, 4H), 7.45–7.32 (m, 6H), 7.17 (dt, J = 7.8, 1.4 Hz, 1H), 6.75–6.68 (m, 2H), 4.40 (br s, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.2 (C), 132.1 (CH), 132.0 (C), 131.9 (2 × CH), 131.4 (CH), 130.0 (CH), 128.6 (CH), 128.4 (2 × CH), 128.2 (CH), 127.8 (CH), 125.9 (C), 125.0 (C), 123.0 (C), 117.6 (CH), 114.1 (C), 107.5 (C), 93.7 (C), 93.1 (C), 90.5 (C), 88.9 (C) ppm; MS (EI) *m/z* (%) 293 $[M]^+$ (100); HRMS (EI) calcd for $C_{22}H_{15}N$ $[M]^+$ 293.1199, found 293.1186.

10 K. Hirano, Y. Inaba. T. Watanabe, S. Oishi, N. Fujii and H. Ohno, *Adv. Synth. Catal.,* 2010, **352**, 368–372.

2-[(2-((4-Methoyphenyl)ethynyl)phenyl)ethynyl]phenol (10).



To a solution of **S1** (659 mg, 1.97 mmol) in Et_3N (4 mL), $Pd(PPh_3)_2Cl_2$ (69.2 mg, 0.098 mmol, 5 mol %), CuI (18.8 mg, 0.098 mmol, 5 mol %) and a solution of 2-ethynylphenol (**S11**, 280 mg, 2.37 mmol, 120 mol %) in Et_3N (3 mL) were added at room temperature, and the reaction mixture was stirred overnight. The reaction was quenched by addition of an aqueous saturated solution of NH_4Cl (10 mL) and was extracted with EtOAc (3 × 20 mL), dried with $MgSO_4$, filtered and concentrated under reduced pressure to afford, after purification by flash chromatography (EtOAc/hexane 5:95–10:90) compound **10** (230 mg, 50%) as a yellow solid. R_f = 0.15 (EtOAc/hexane 10:90); mp 87–89 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62–7.54 (m, 4H), 7.47 (dd, J = 7.7, 1.5 Hz, 1H), 7.36–7.26 (m, 3H), 7.02 (dd, J = 8.3, 0.8 Hz, 1H), 6.95–6.90 (m, 3H), 6.43 (s, 1H), 3.85 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.0 (C), 157.1 (C), 133.5 (2 × CH), 132.2 (CH), 131.3 (CH), 131.1 (CH), 130.6 (CH), 128.4 (CH), 127.9 (CH), 125.8 (C), 124.4 (C), 120.2 (CH), 114.8 (C), 114.6 (C), 114.1 (2 × CH), 109.5 (C), 95.7 (C), 94.2 (C), 87.4 (C), 87.1 (C), 55.3 (CH_3) ppm; MS (EI) *m/z* (%) 324 $[M]^+$ (100); HRMS (EI) calcd for $C_{23}H_{16}O_2$ $[M]^+$ 324.1145, found 324.1156.

General Procedure for indium(III)-catalyzed cascade cycloisomerization (9 and **11).**

To a solution of diyne (100 mg scale) in dry toluene or DCE (6 mL) placed in a Schlenk tube, 5 mol% of InX_3 was added, and the resulting mixture was stirred at the adecuate temperature until the starting material has been consumend. The mixture was concentrated under reduced pressure to remove the solvent and the residue was purified by flash chromatography (EtOAc/hexane) to afford the corresponding polycyclization product.

6-Phenyl-11*H*-benzo[*a*]carbazole (9).[10]

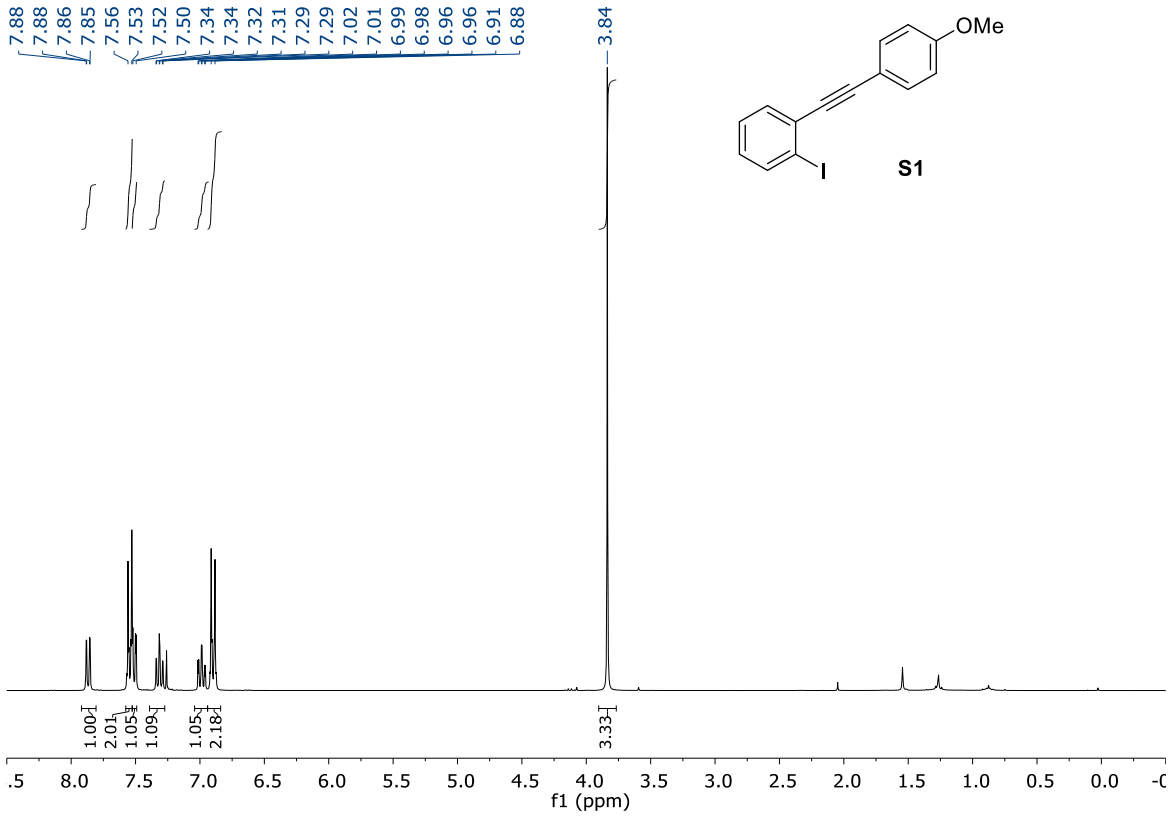
Following the General Procedure, the reaction of diyne **8** (90.4 mg, 0.308 mmol) with $InBr_3$ (5.3 mg, 0.015 mmol, 5 mol %) in toluene (4 mL) at 110 °C for 24 hours, afforded after purification by flash chromatography (EtOAc/hexane 20:80) compound **9** (73.2 mg, 81%) as an orange solid. R_f = 0.33 (EtOAc/hexane 20:80); mp 120–123 °C (lit.,[10] 164–165 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ

8.91 (s, 1H), 8.16 (d, J = 7.4 Hz, 1H), 8.03 (d, J = 6.9 Hz, 1H), 7.73 (d, J = 7.4 Hz, 2H), 7.60 – 7.55 (m, 6H), 7.48 (d, J = 8.1 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.3 (C), 138.7 (C), 136.6 (C), 135.3 (C), 132.1 (C), 129.4 (2 × CH), 128.9 (CH), 128.4 (2 × CH), 127.6 (CH), 125.7 (CH), 125.4 (CH), 124.7 (C), 123.9 (C), 122.1 (CH), 120.9 (CH), 120.4 (CH), 120.2 (C), 119.3 (CH), 116.8 (C), 111.0 (CH) ppm; MS (EI) *m/z* (%) 293 $[M]^+$ (100); HRMS (EI) calcd for $C_{22}H_{15}N$ $[M]^+$ 293.1199, found 293.1194.

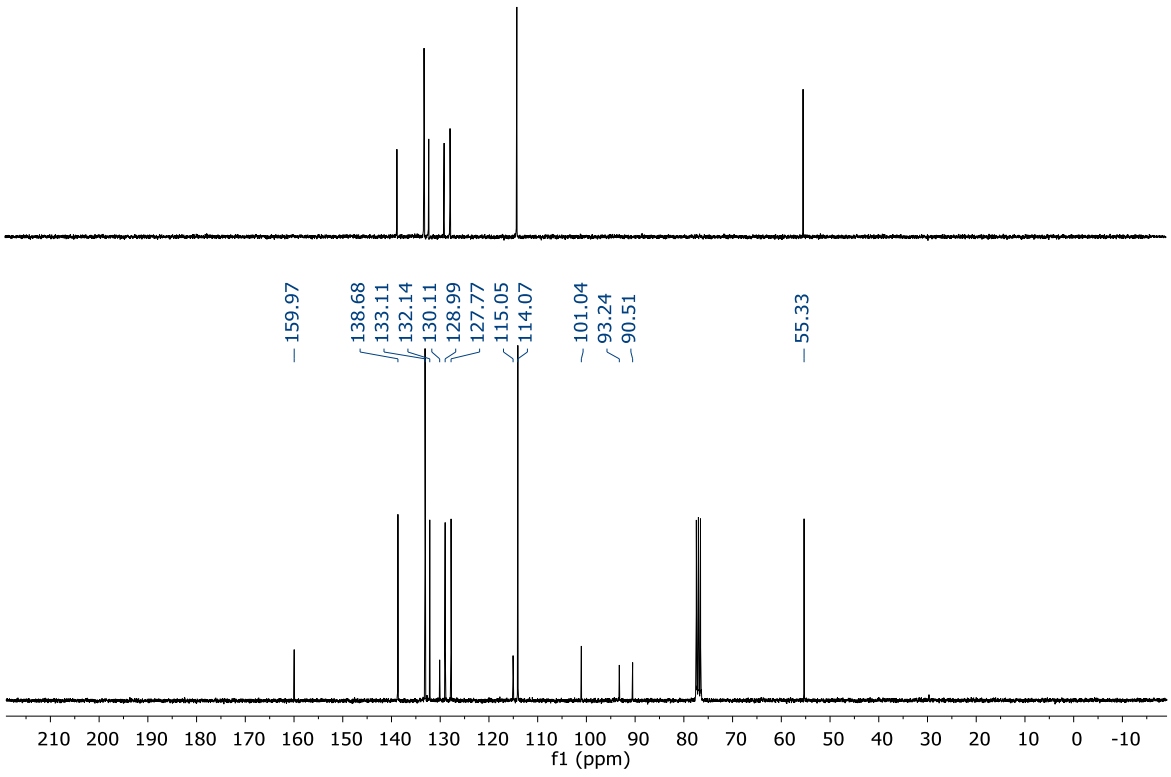
6-(4-Methoxyphenyl)indene[1,2-*c*]chromene (11).

Following the General Procedure, the reaction of diyne **10** (100 mg, 0.308 mmol) with InI_3 (7.6 mg, 0.015 mmol, 5 mol %) in DCE (4 mL) at 80 °C for 4 hours, afforded after purification by flash chromatography (EtOAc/hexane 5:95) compound **11** (67.8 mg, 68%) as a yellow solid. R_f = 0.30 (EtOAc/hexane 5:95); mp 143–145 °C; ^{1}H NMR δ 8.07 (dd, J = 7.1, 2.2 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 6.8 Hz, 2H), 7.51 (dd, J = 8.0, 1.5 Hz, 1H), 7.46–7.36 (m, 3H), 7.20 (s, 1H), 7.13 (d, J = 8.8 Hz, 3H), 3.96 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.4 (C), 152.8 (C), 149.7 (C), 143.3 (C), 131.1 (2 × CH), 130.7 (C), 129.7 (C), 127.9 (CH), 126.6 (CH), 126.0 (C), 124.7 (CH), 124.1 (CH), 122.2 (CH), 121.7 (CH), 120.5 (CH), 119.8 (C), 117.7 (CH), 116.9 (C), 114.1 (2 × CH), 106.9 (CH), 55.5 (CH_3) ppm; MS (EI) *m/z* (%) 324 $[M]^+$ (100); HRMS (EI) calcd for $C_{23}H_{16}O_2$ $[M]^+$ 324.1145, found 324.1148.

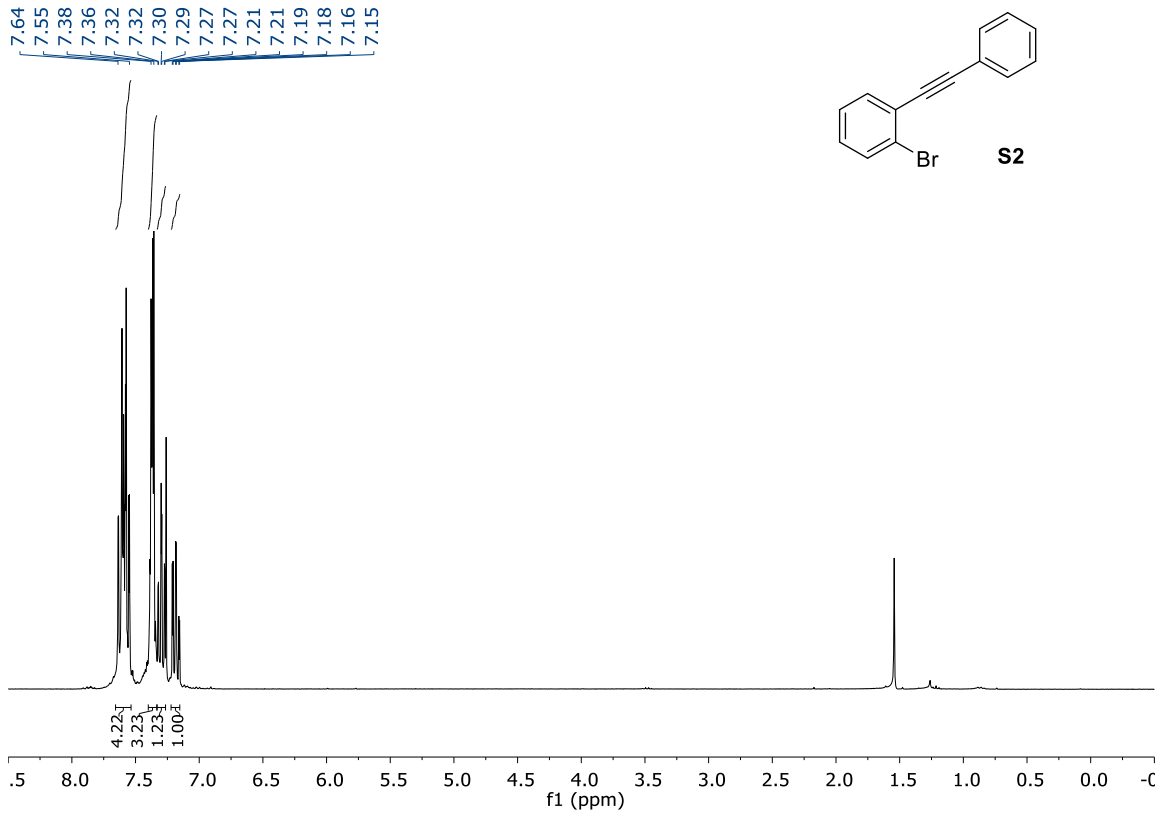
300 MHz ^{1}H NMR Spectrum of compound **S1** ($CDCl_3$, 300 K)



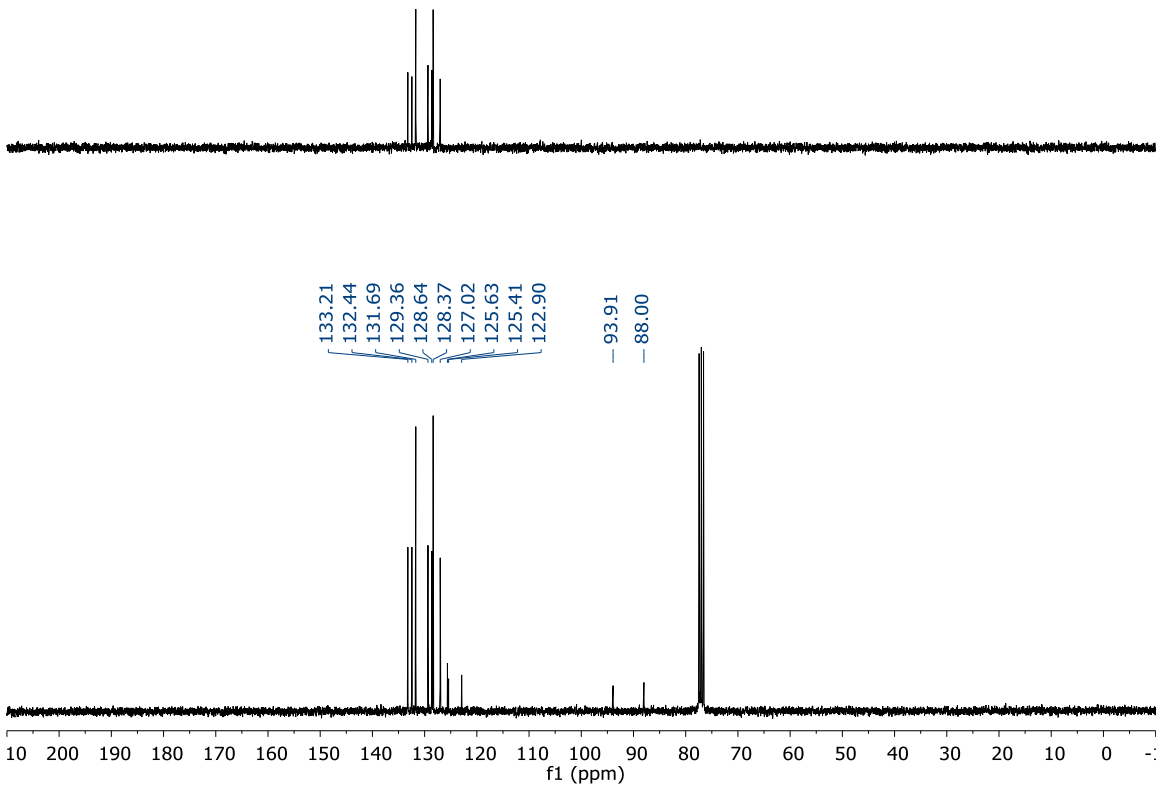
75 MHz ^{13}C NMR Spectrum of compound **S1** ($CDCl_3$, 300 K)



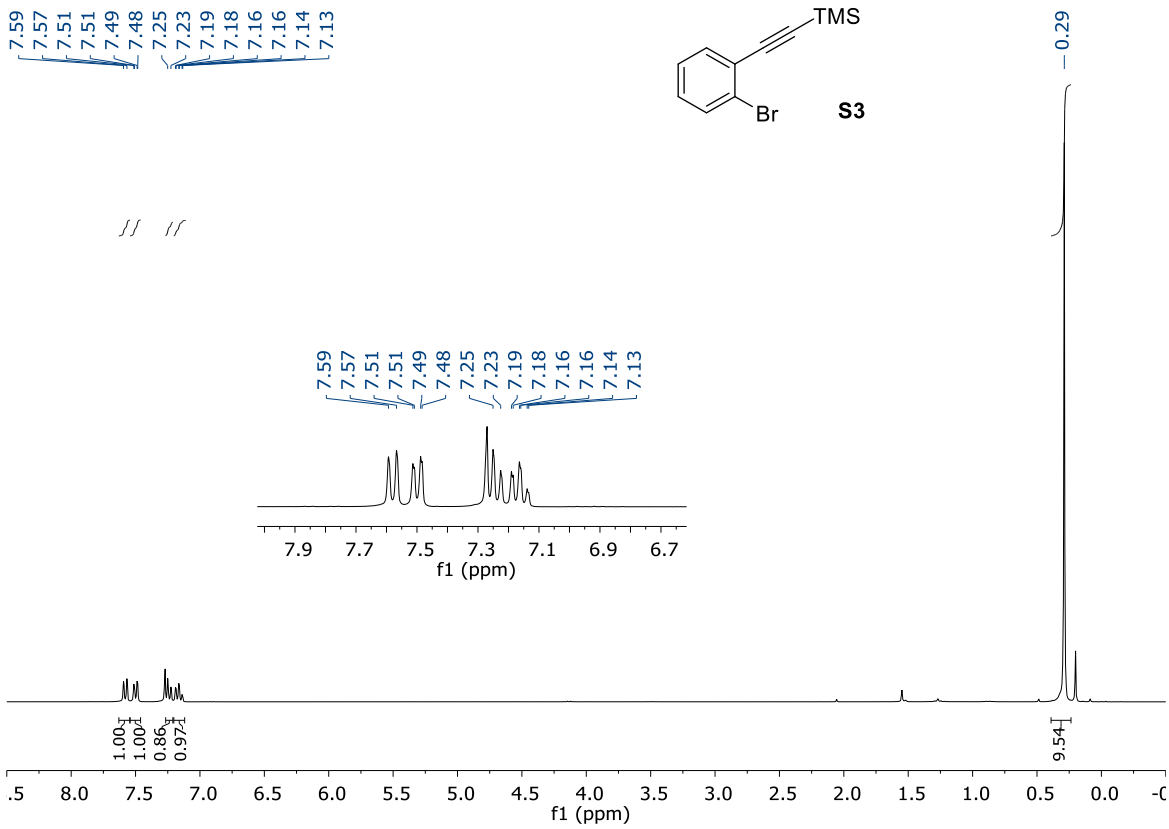
300 MHz ^{1}H NMR Spectrum of compound **S2** ($CDCl_3$, 300 K)



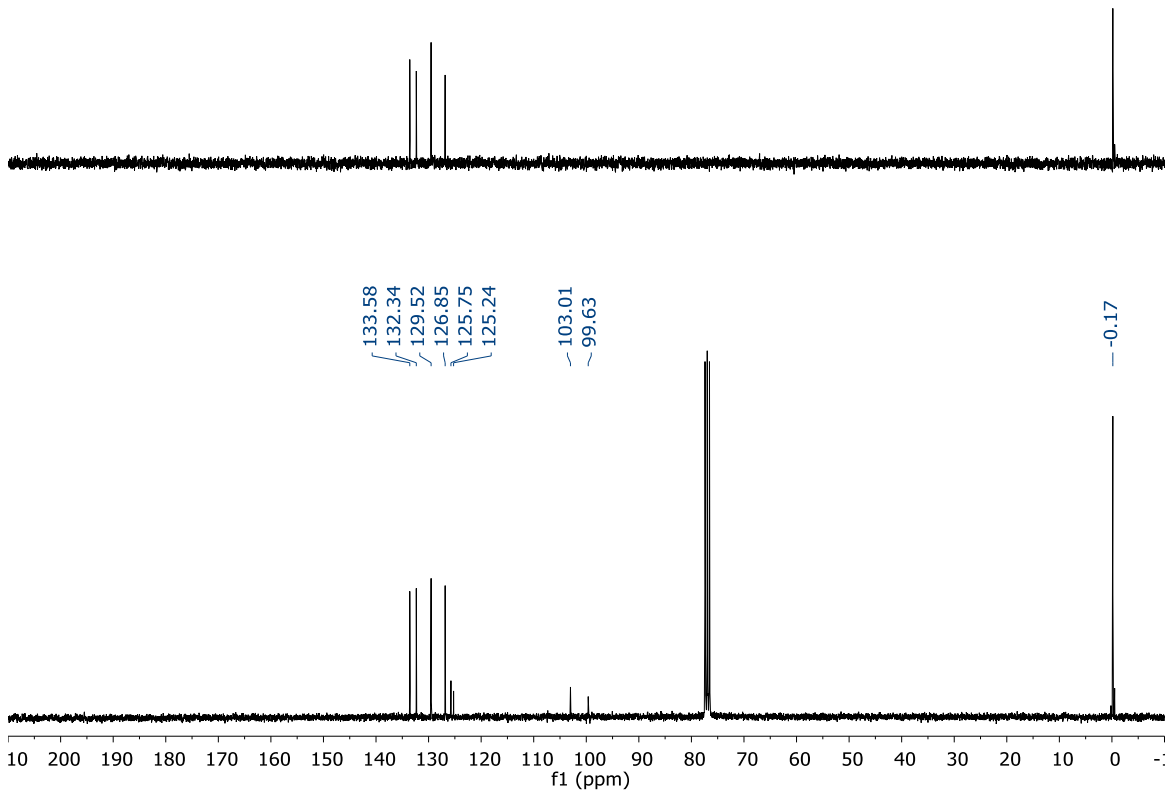
75 MHz ^{13}C NMR Spectrum of compound **S2** ($CDCl_3$, 300 K)



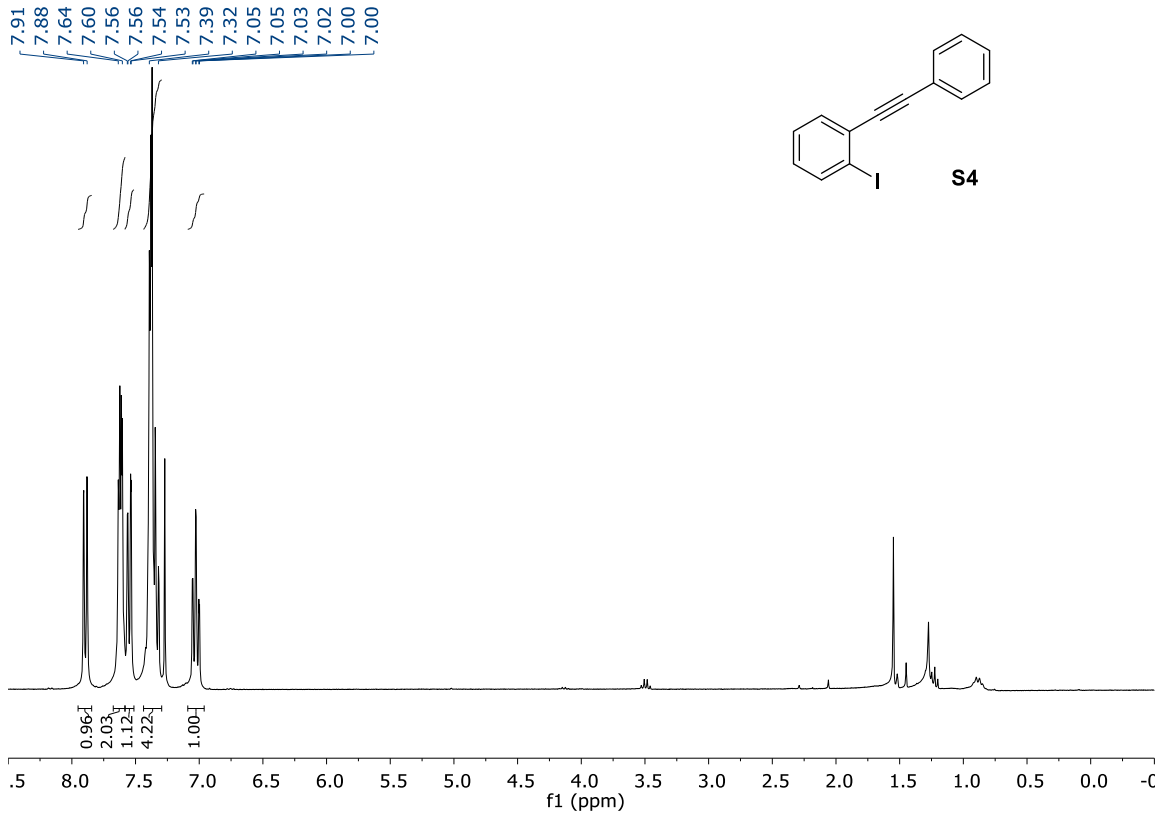
300 MHz ^{1}H NMR Spectrum of compound **S3** ($CDCl_3$, 300 K)



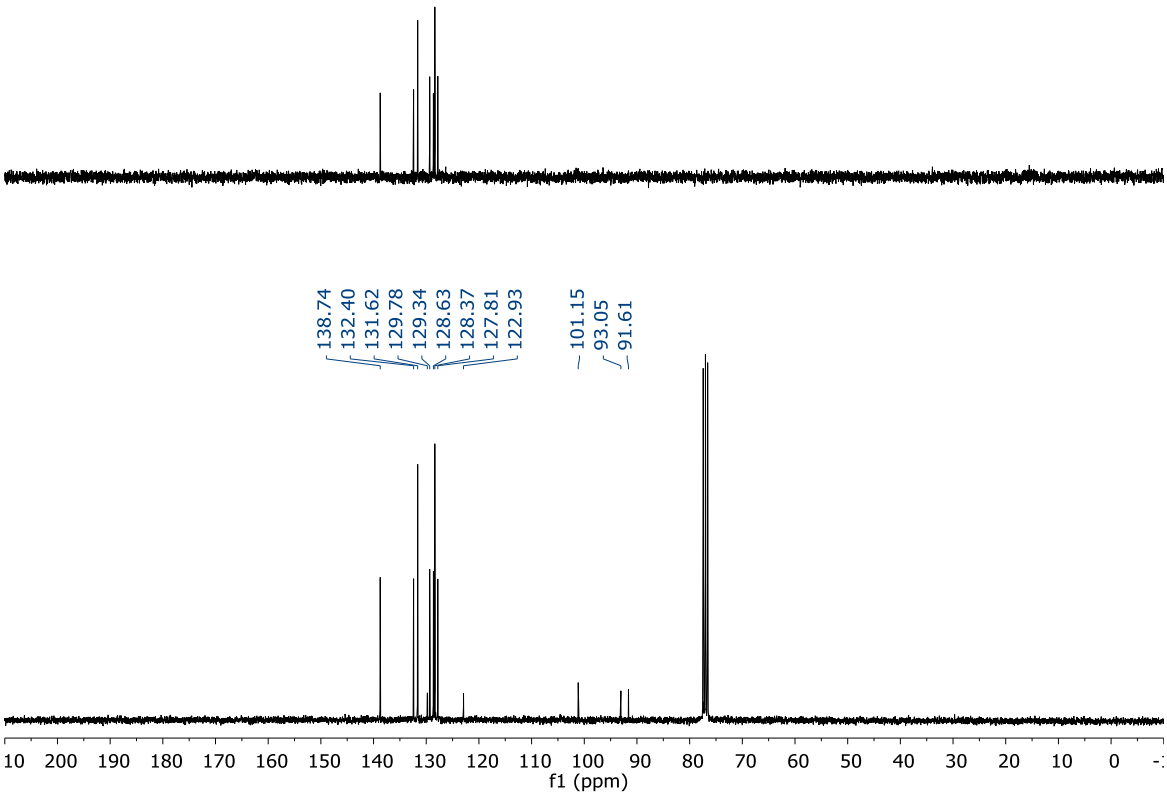
75 MHz ^{13}C NMR Spectrum of compound **S3** ($CDCl_3$, 300 K)



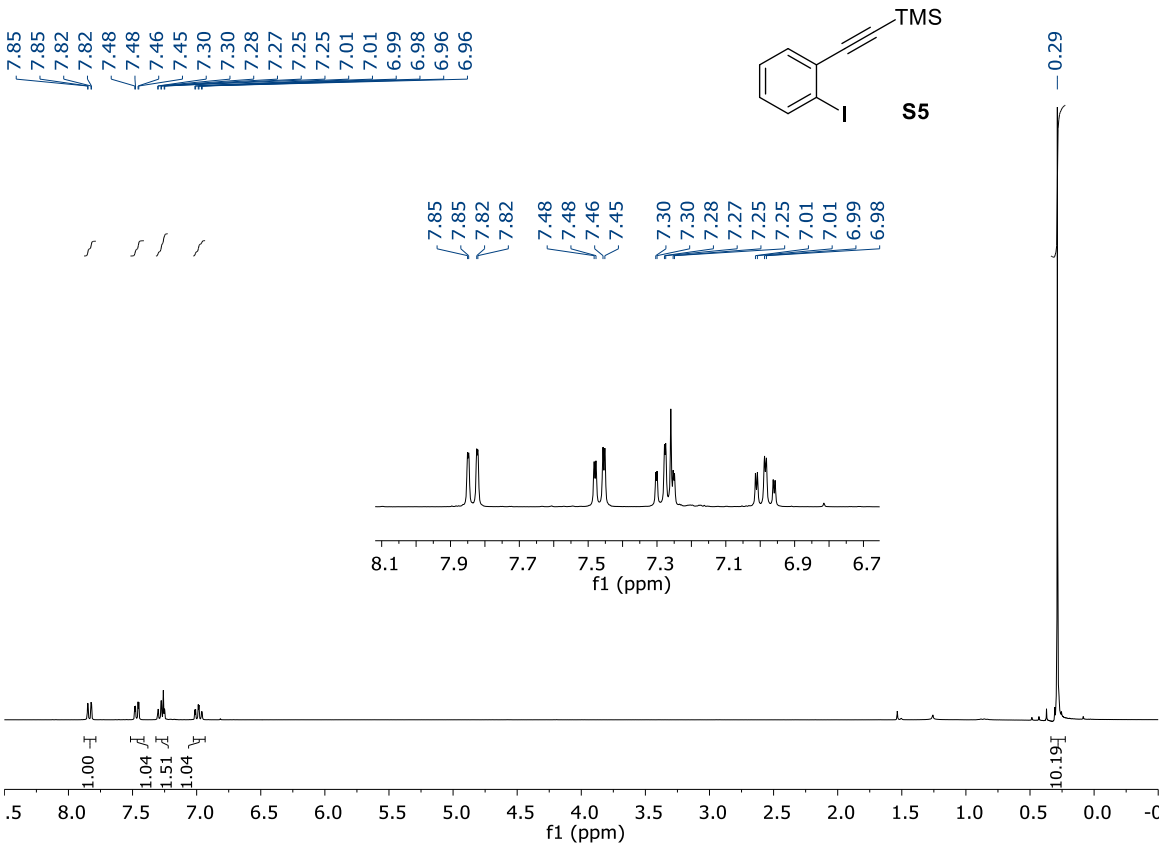
300 MHz ^{1}H NMR Spectrum of compound **S4** ($CDCl_3$, 300 K)



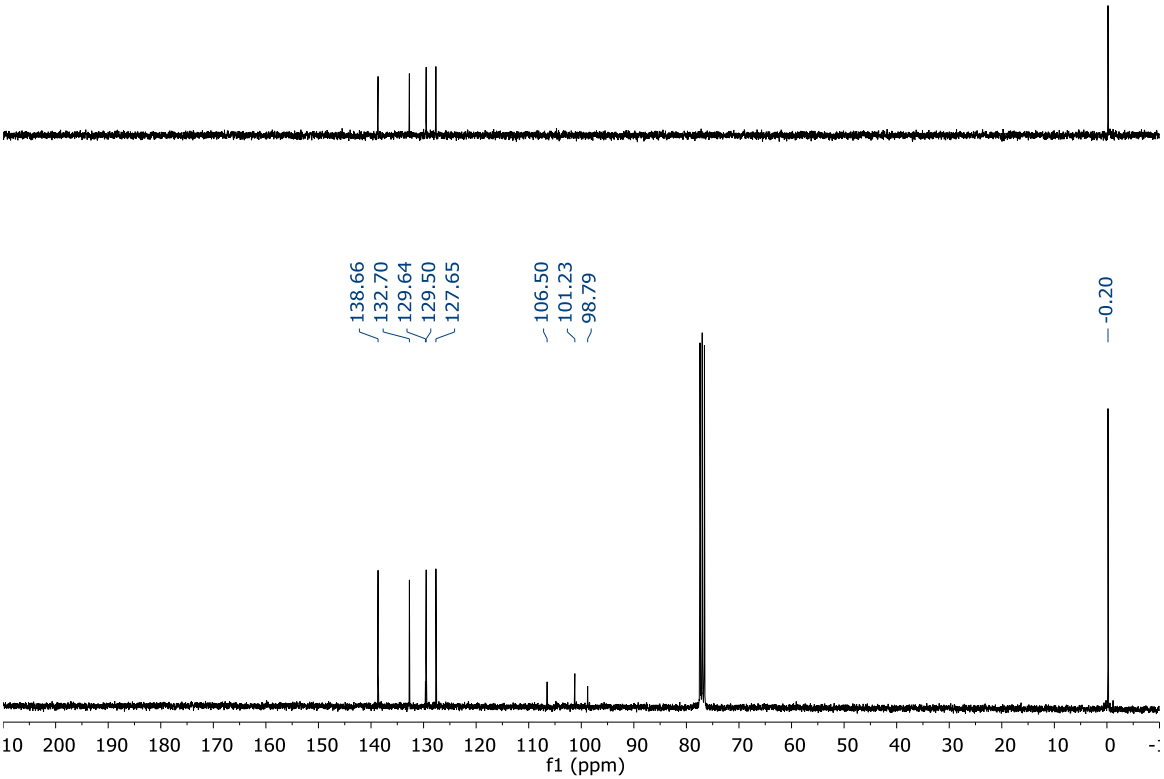
75 MHz ^{13}C NMR Spectrum of compound **S4** ($CDCl_3$, 300 K)



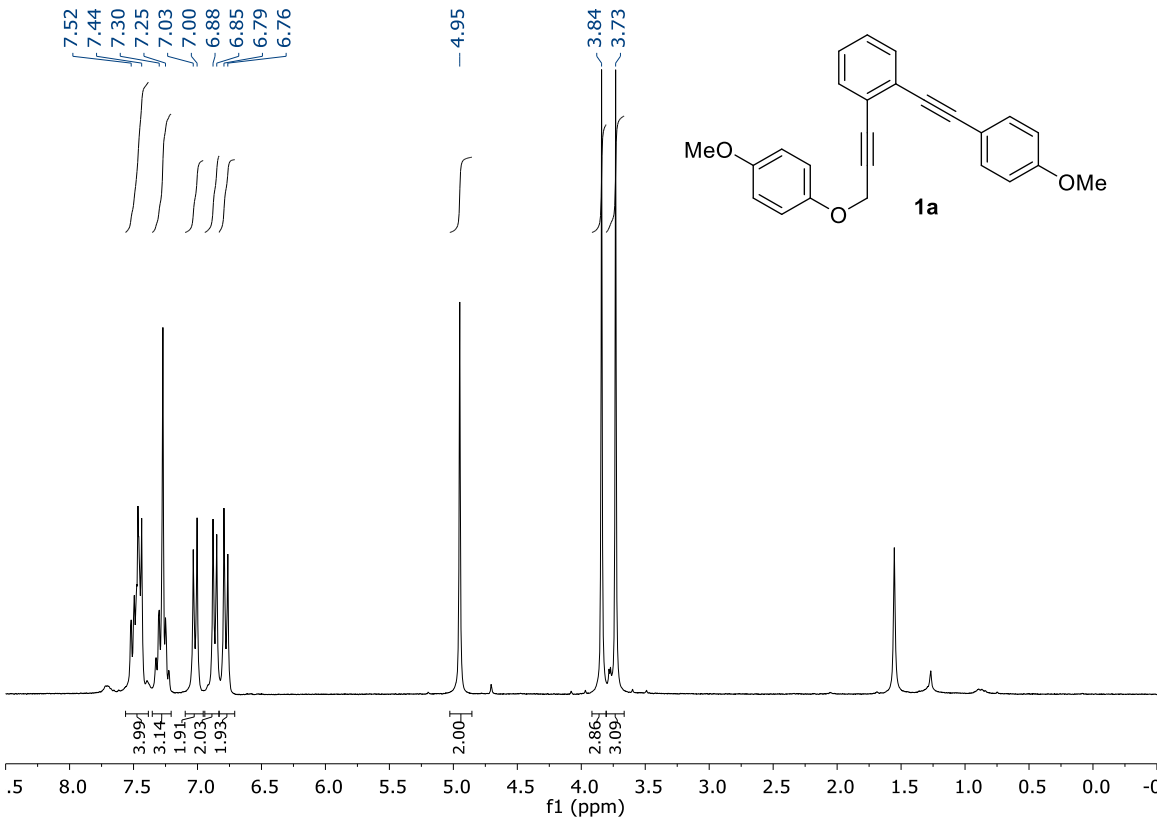
300 MHz ^{1}H NMR Spectrum of compound **S5** ($CDCl_3$, 300 K)



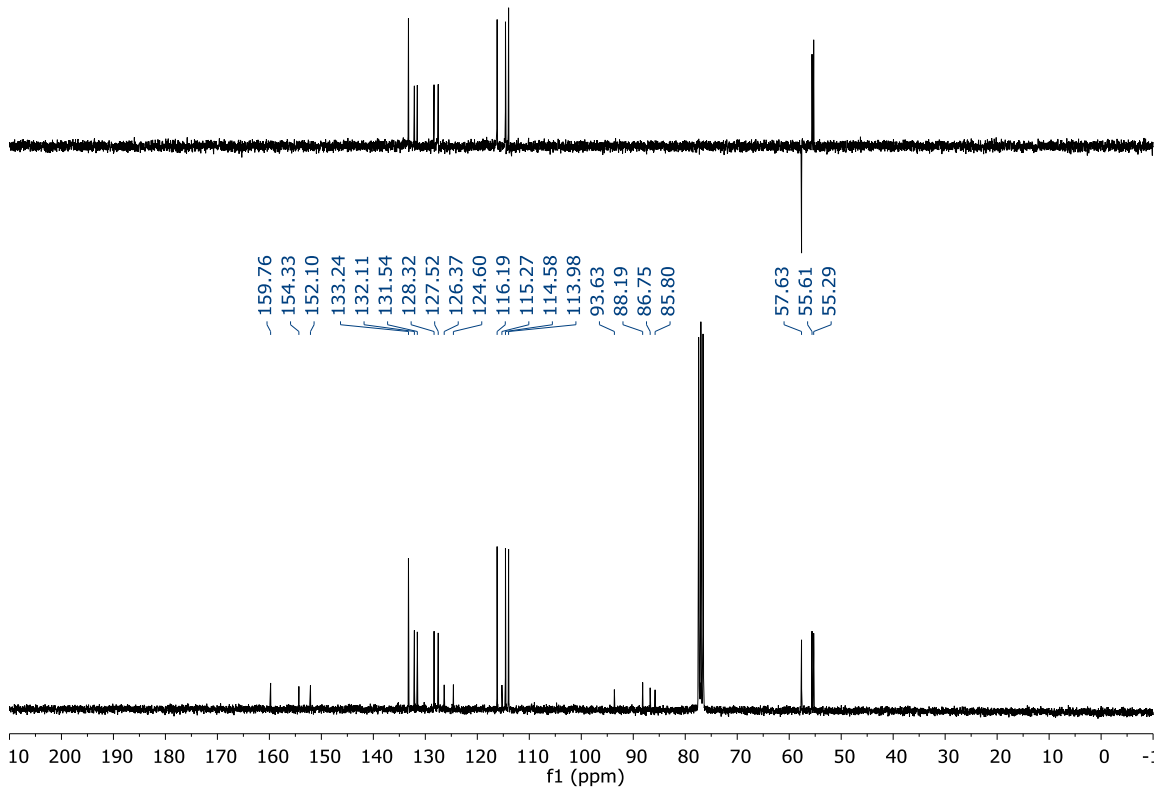
75 MHz ^{13}C NMR Spectrum of compound **S5** ($CDCl_3$, 300 K)



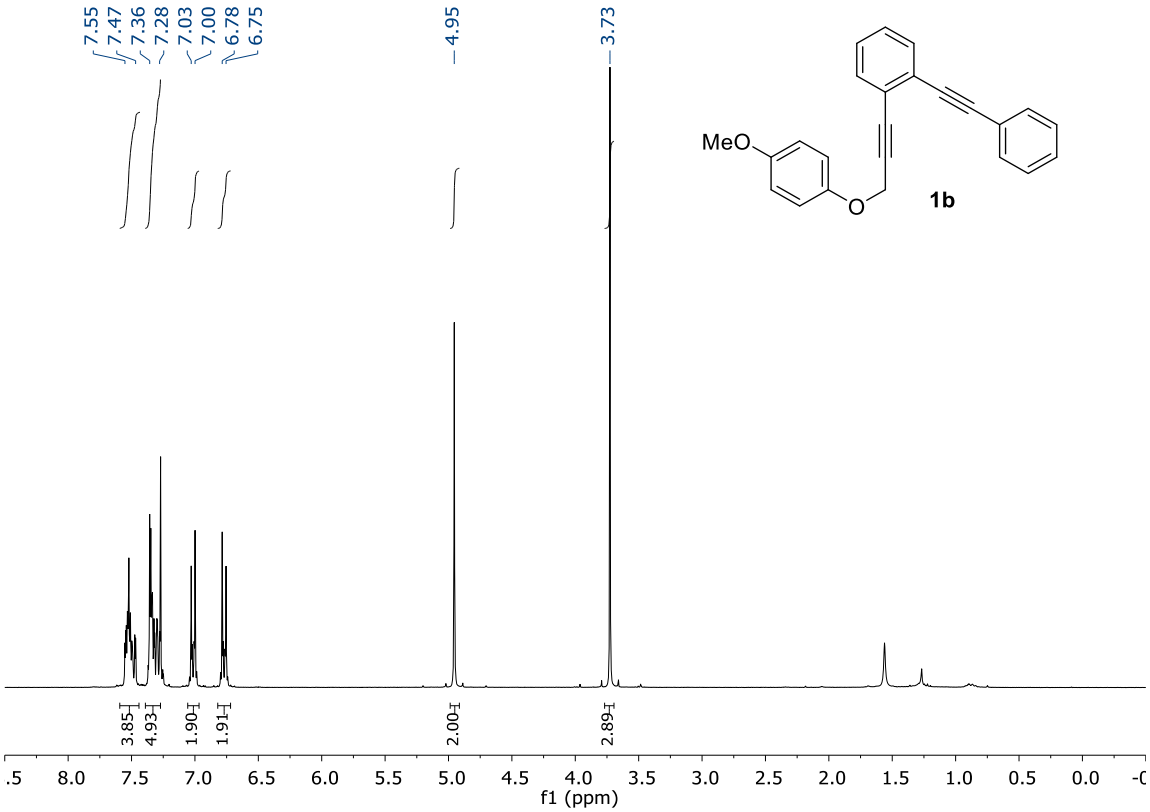
300 MHz ^{1}H NMR Spectrum of compound **1a** ($CDCl_3$, 300 K)



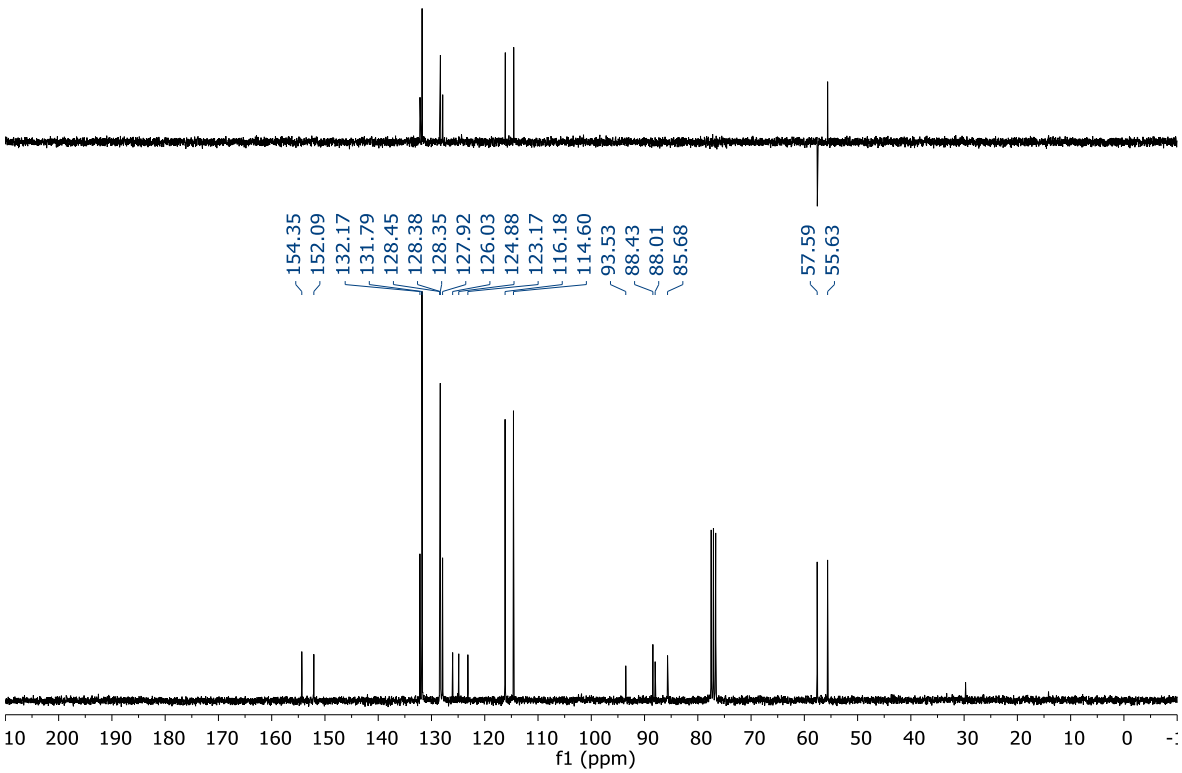
75 MHz ^{13}C NMR Spectrum of compound **1a** ($CDCl_3$, 300 K)



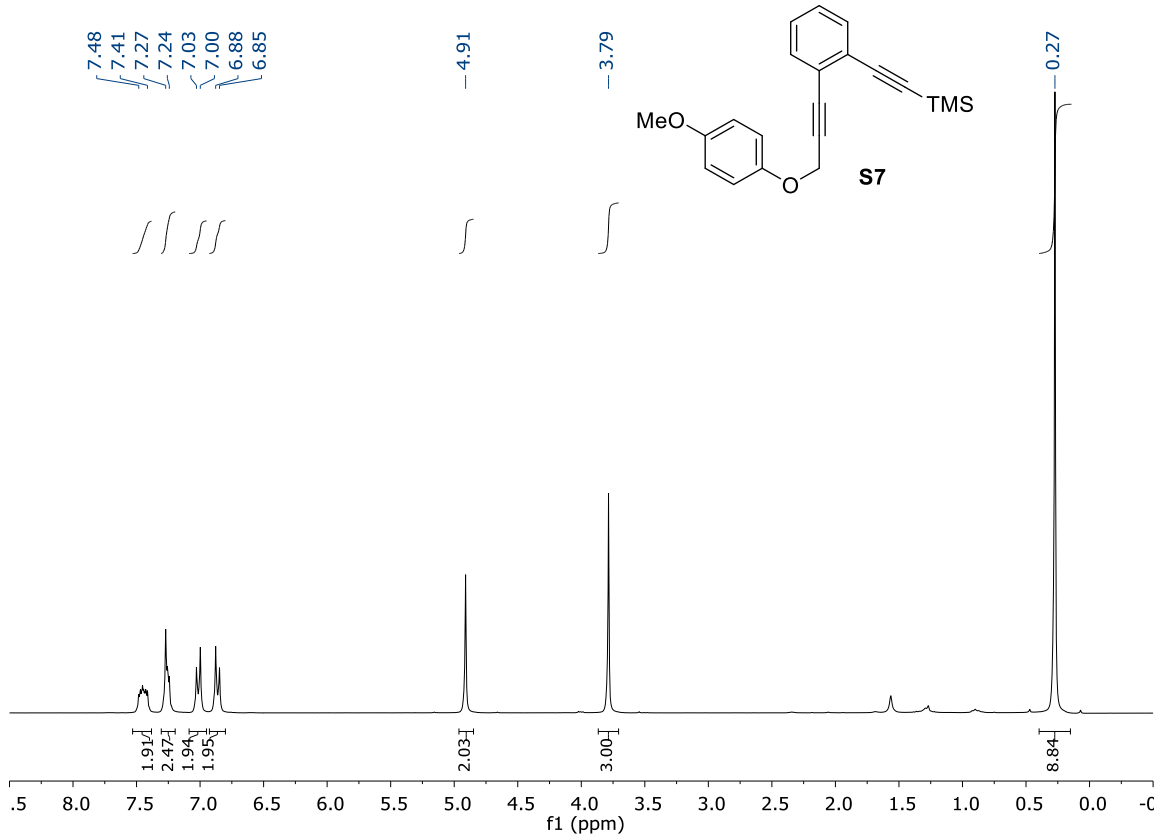
300 MHz ^{1}H NMR Spectrum of compound **1b** ($CDCl_3$, 300 K)



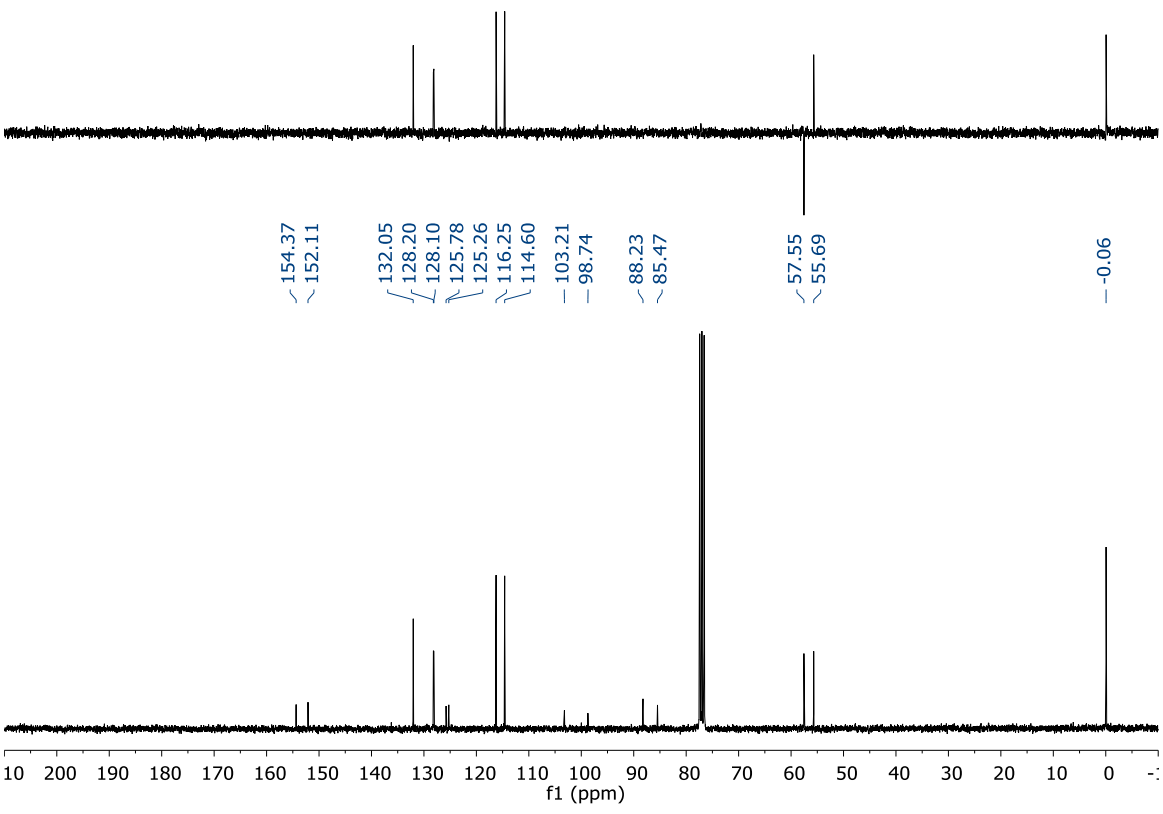
75 MHz ^{13}C NMR Spectrum of compound **1b** ($CDCl_3$, 300 K)



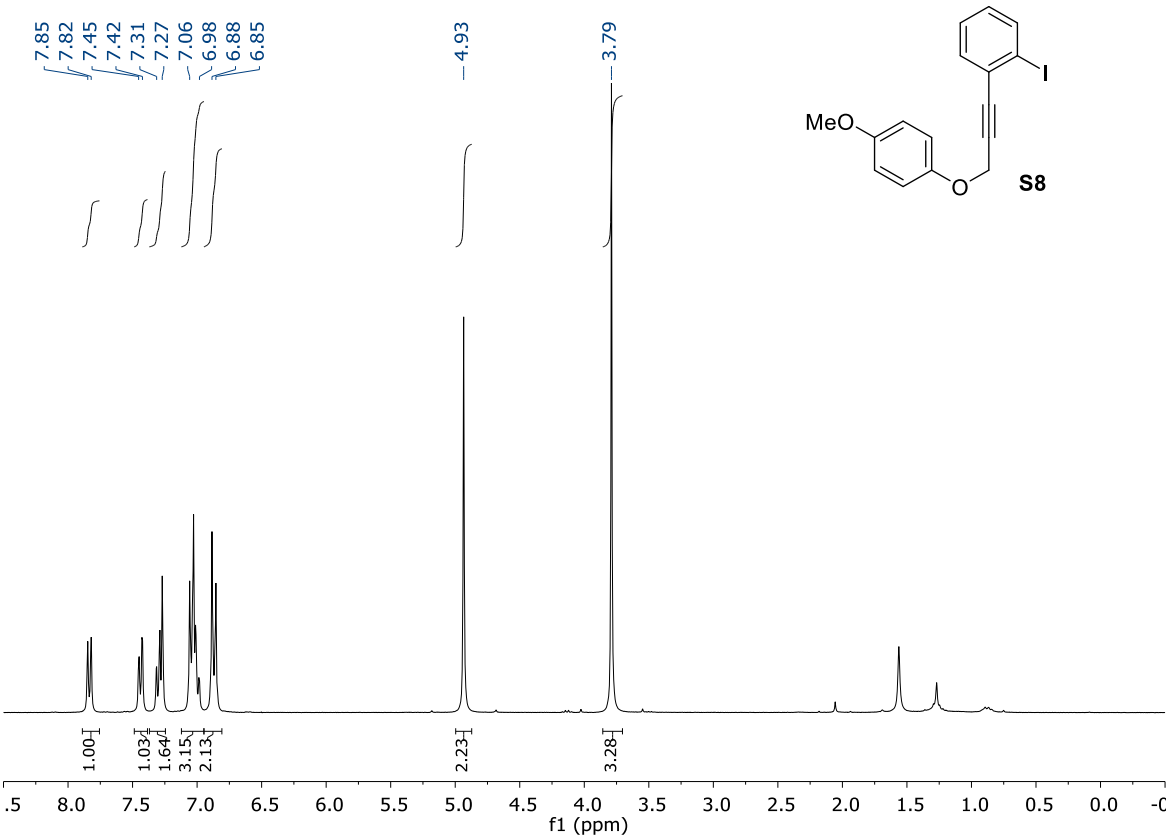
300 MHz ^{1}H NMR Spectrum of compound **S7** ($CDCl_3$, 300 K)



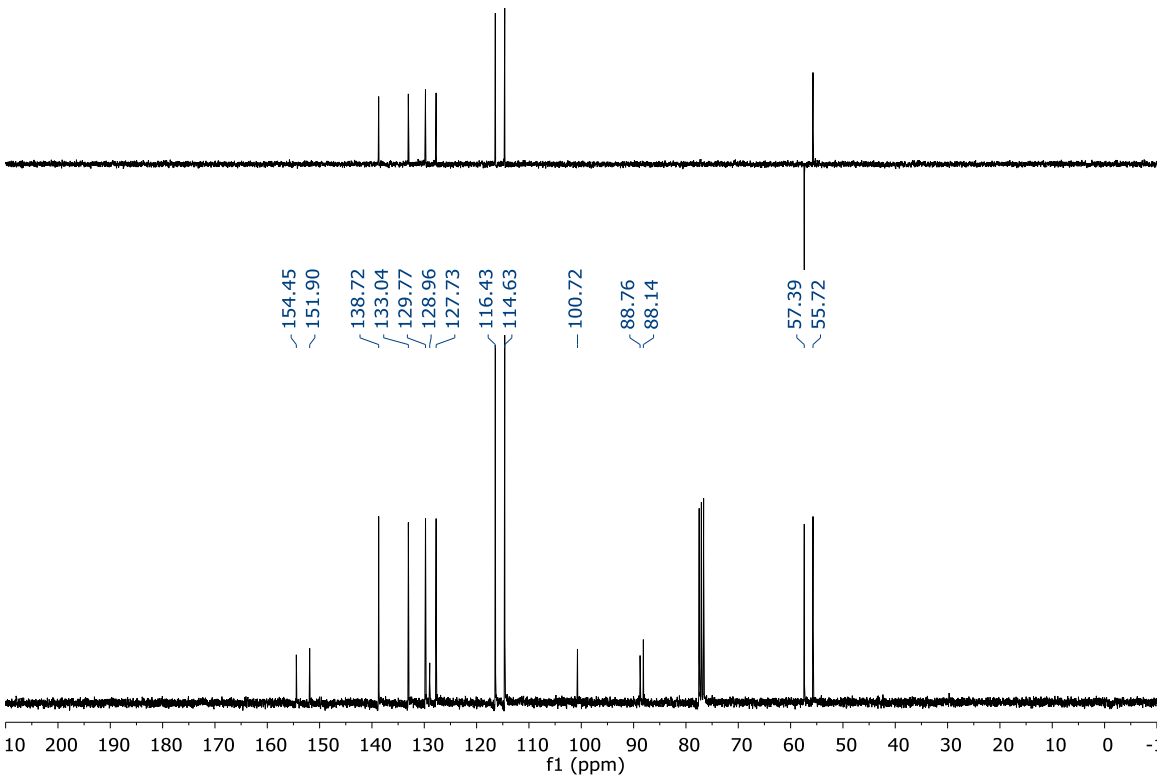
75 MHz ^{13}C NMR Spectrum of compound **S7** ($CDCl_3$, 300 K)



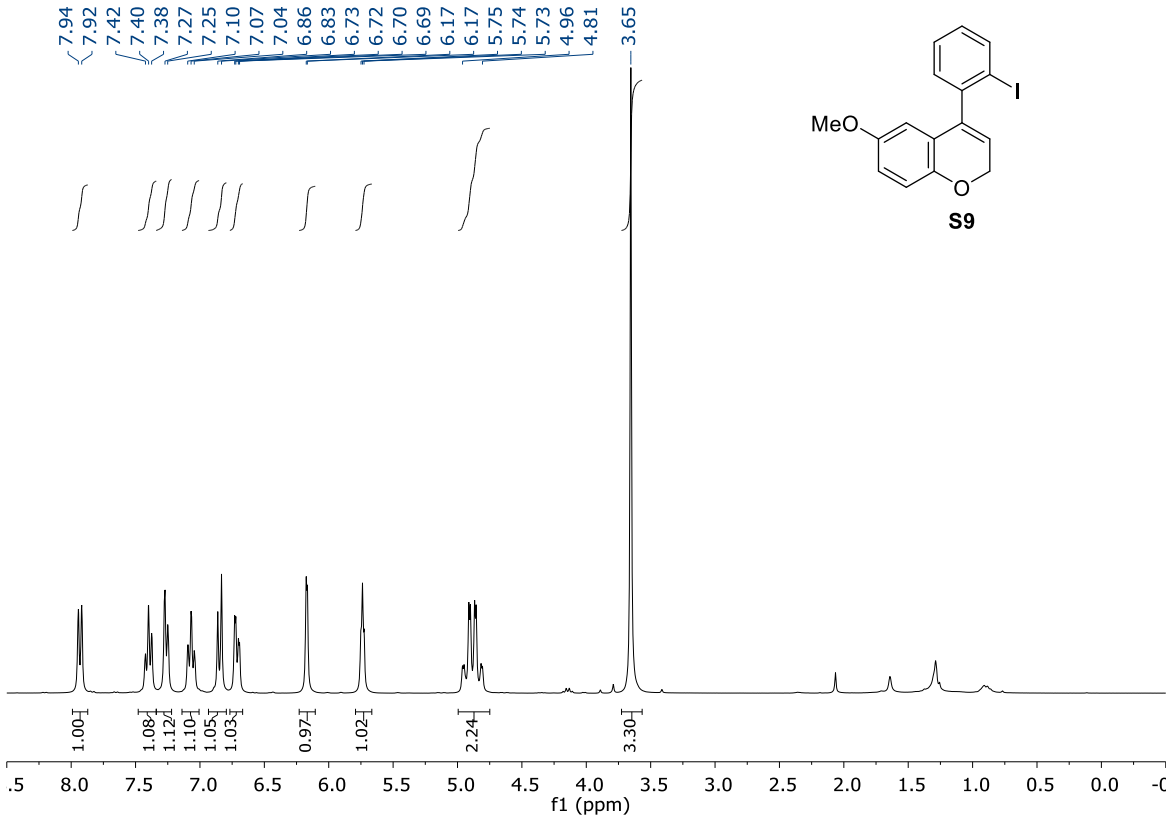
300 MHz ^{1}H NMR Spectrum of compound **S8** ($CDCl_3$, 300 K)



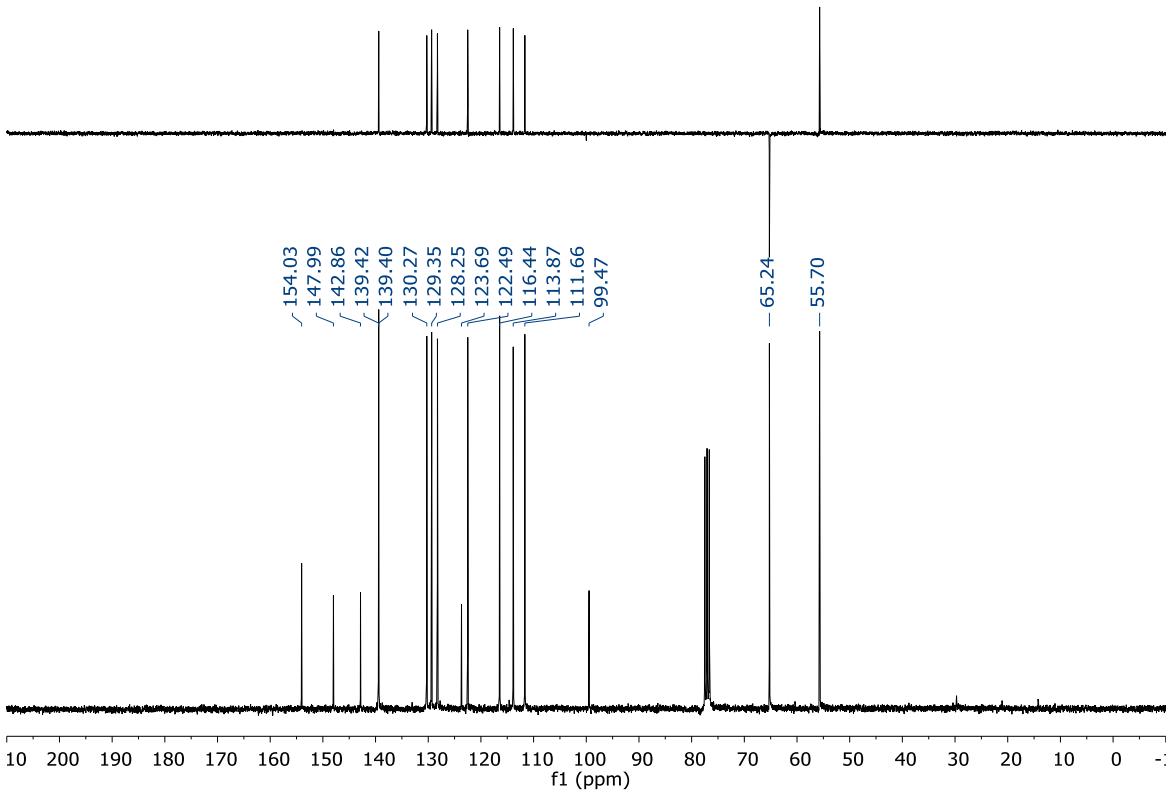
75 MHz ^{13}C NMR Spectrum of compound **S8** ($CDCl_3$, 300 K)



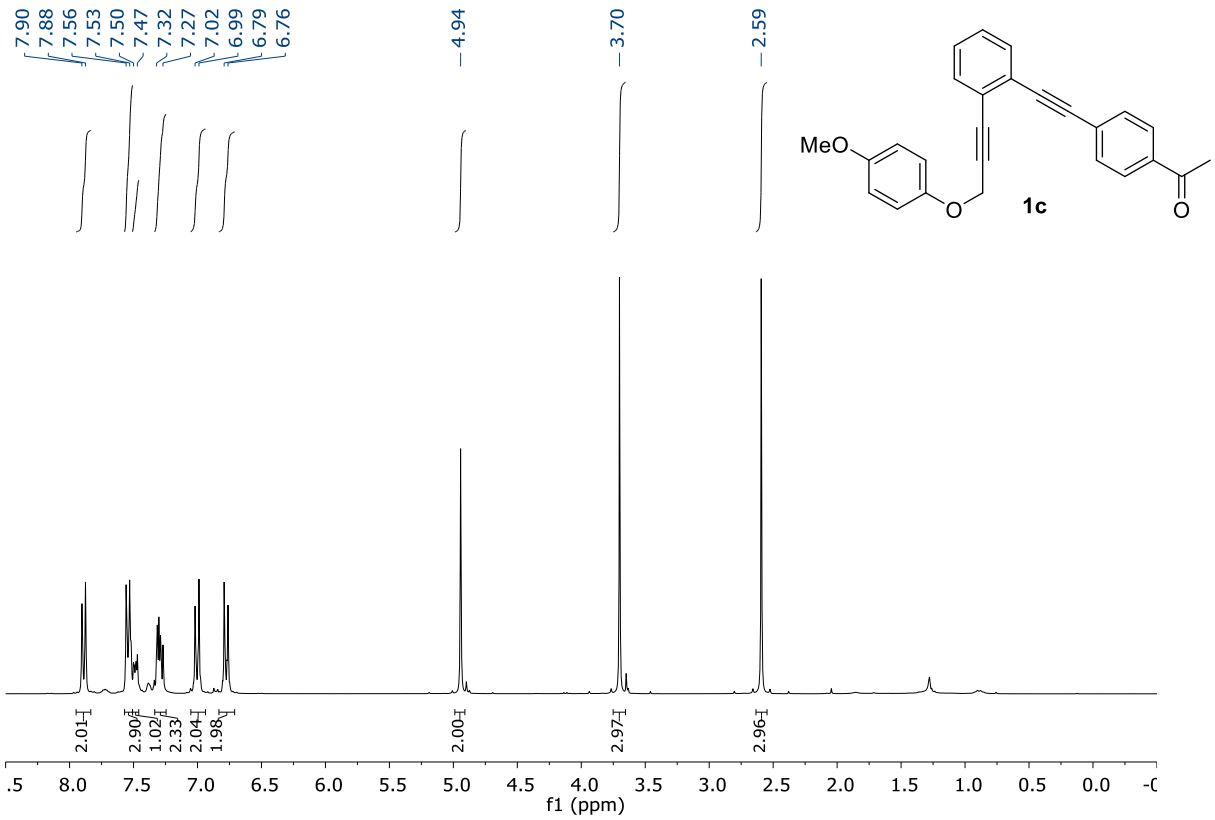
300 MHz ^{1}H NMR Spectrum of compound **S9** ($CDCl_3$, 300 K)



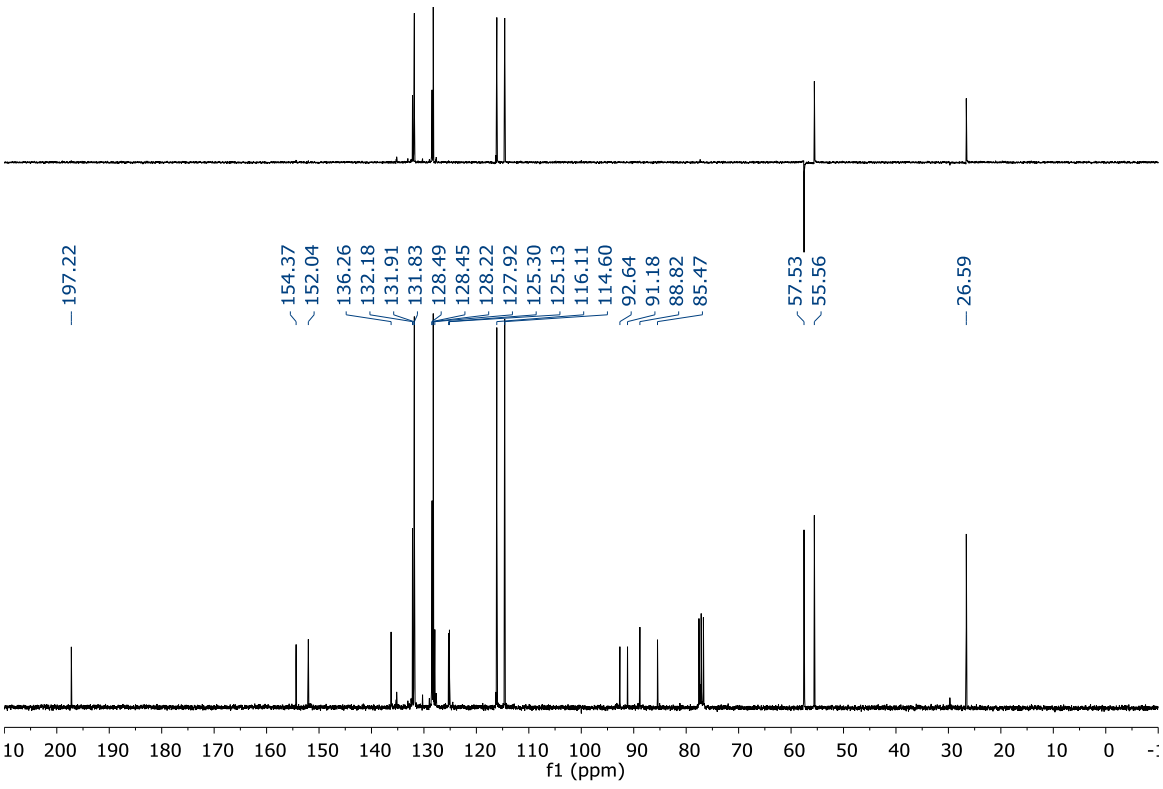
75 MHz ^{13}C NMR Spectrum of compound **S9** ($CDCl_3$, 300 K)



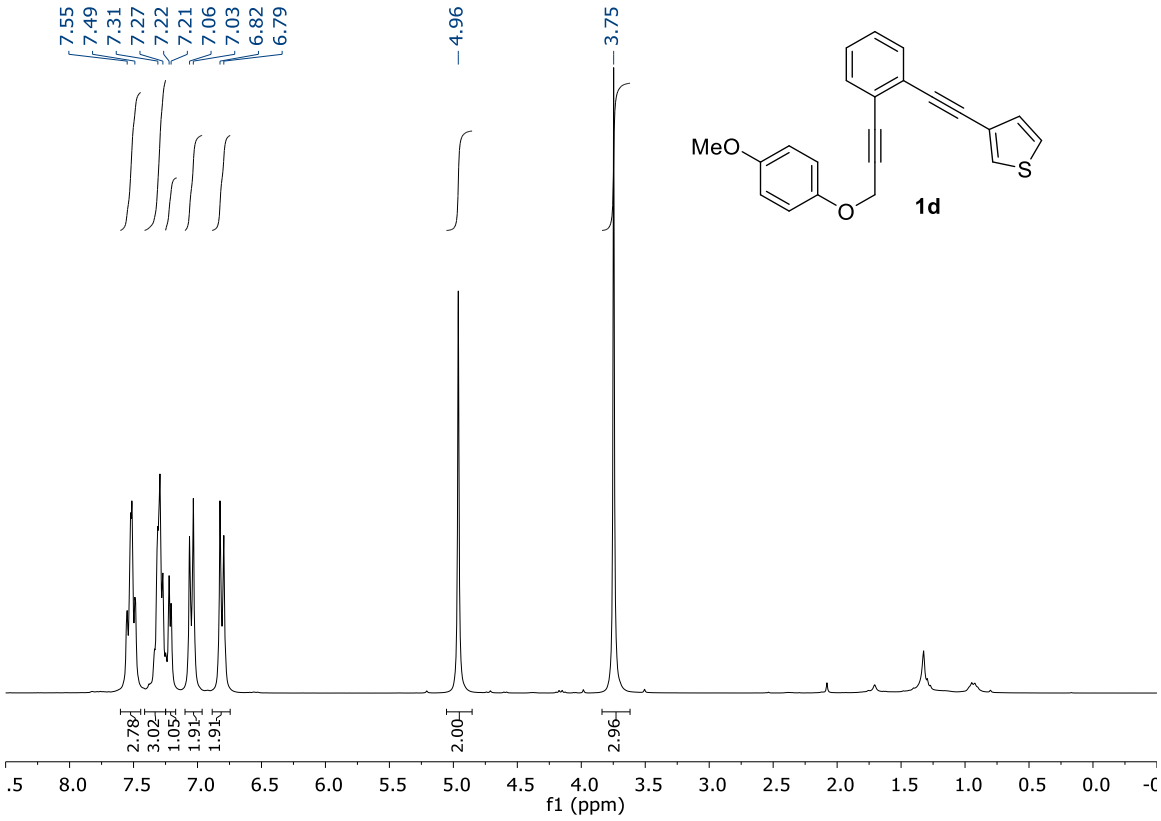
300 MHz ^{1}H NMR Spectrum of compound **1c** ($CDCl_3$, 300 K)



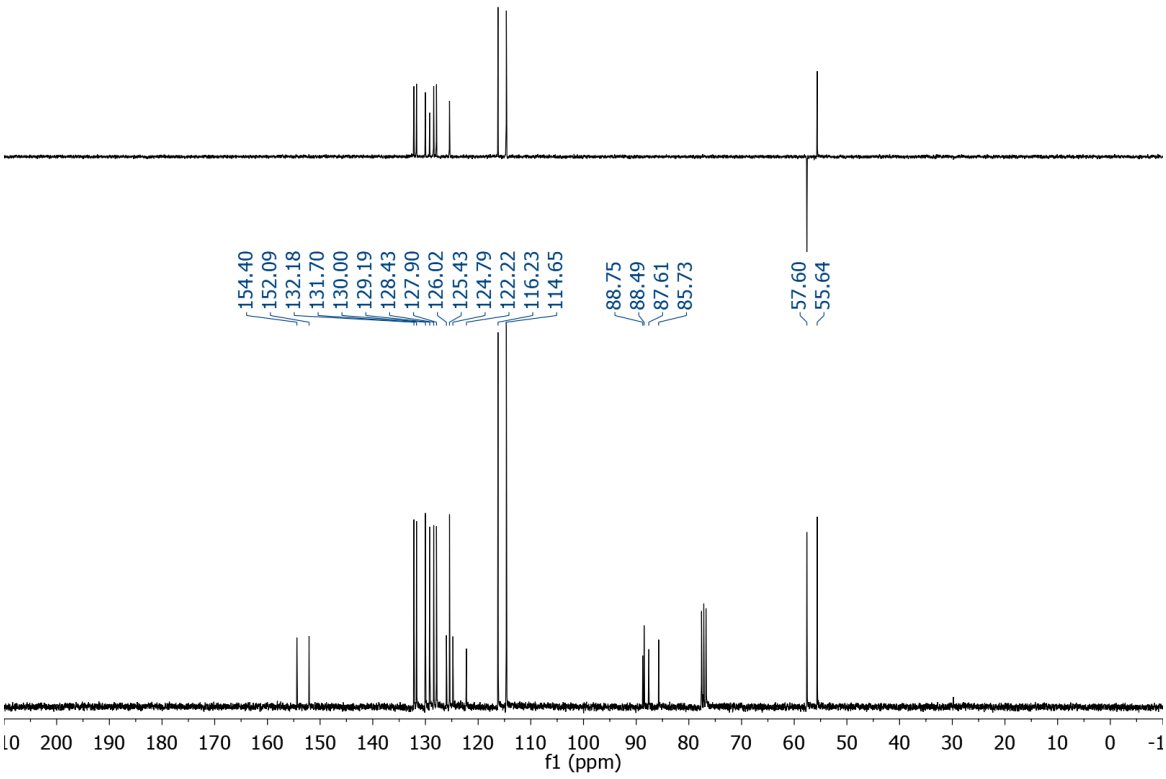
75 MHz ^{13}C NMR Spectrum of compound **1c** ($CDCl_3$, 300 K)



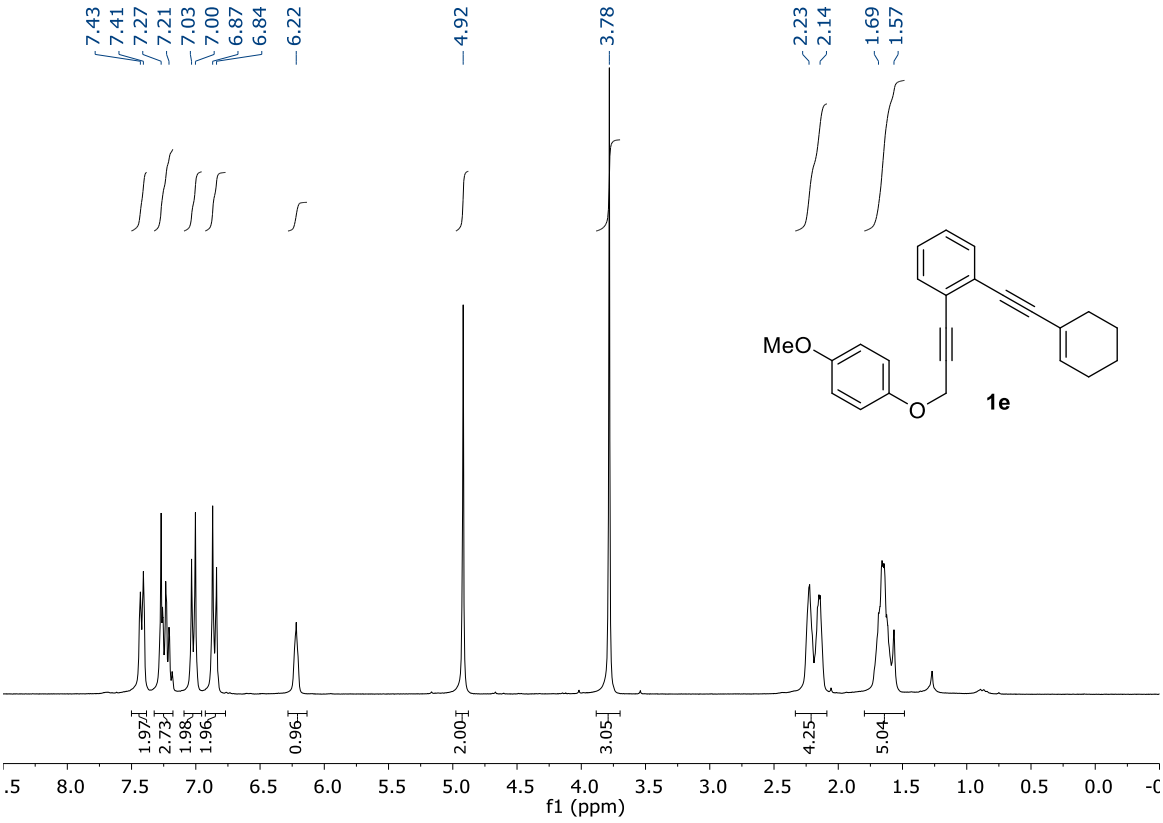
300 MHz ^{1}H NMR Spectrum of compound **1d** ($CDCl_3$, 300 K)



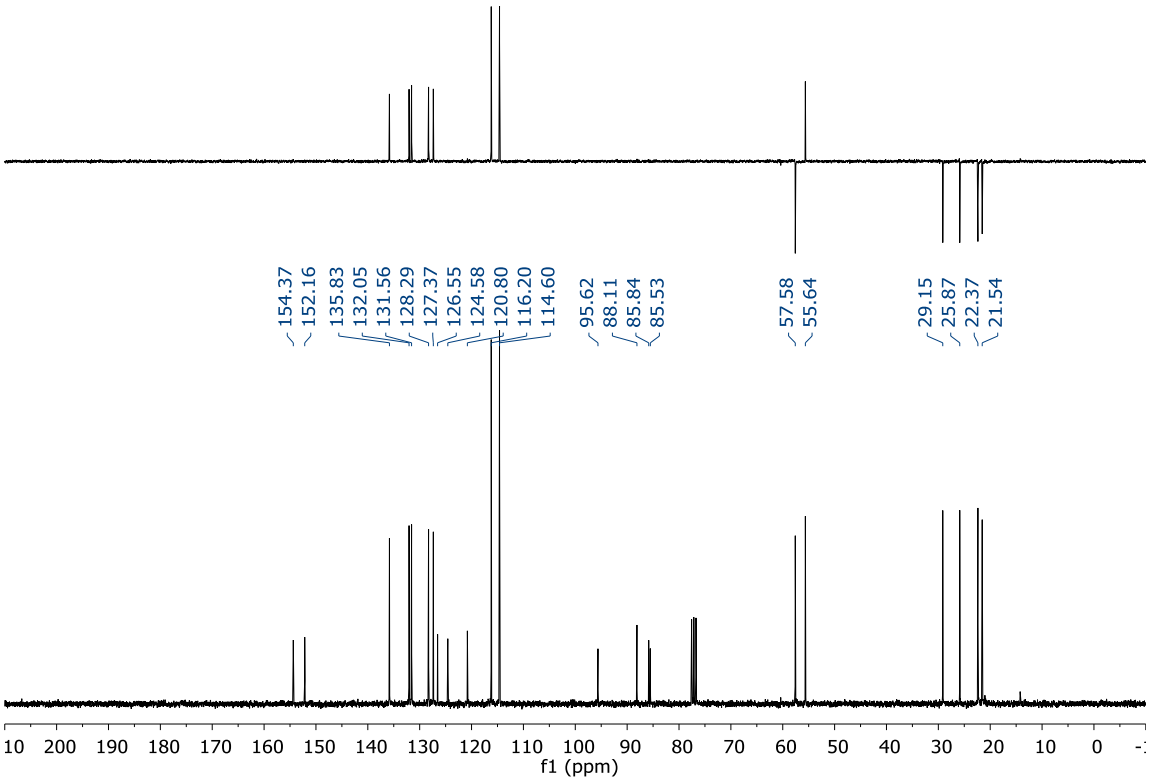
75 MHz ^{13}C NMR Spectrum of compound **1d** ($CDCl_3$, 300 K)



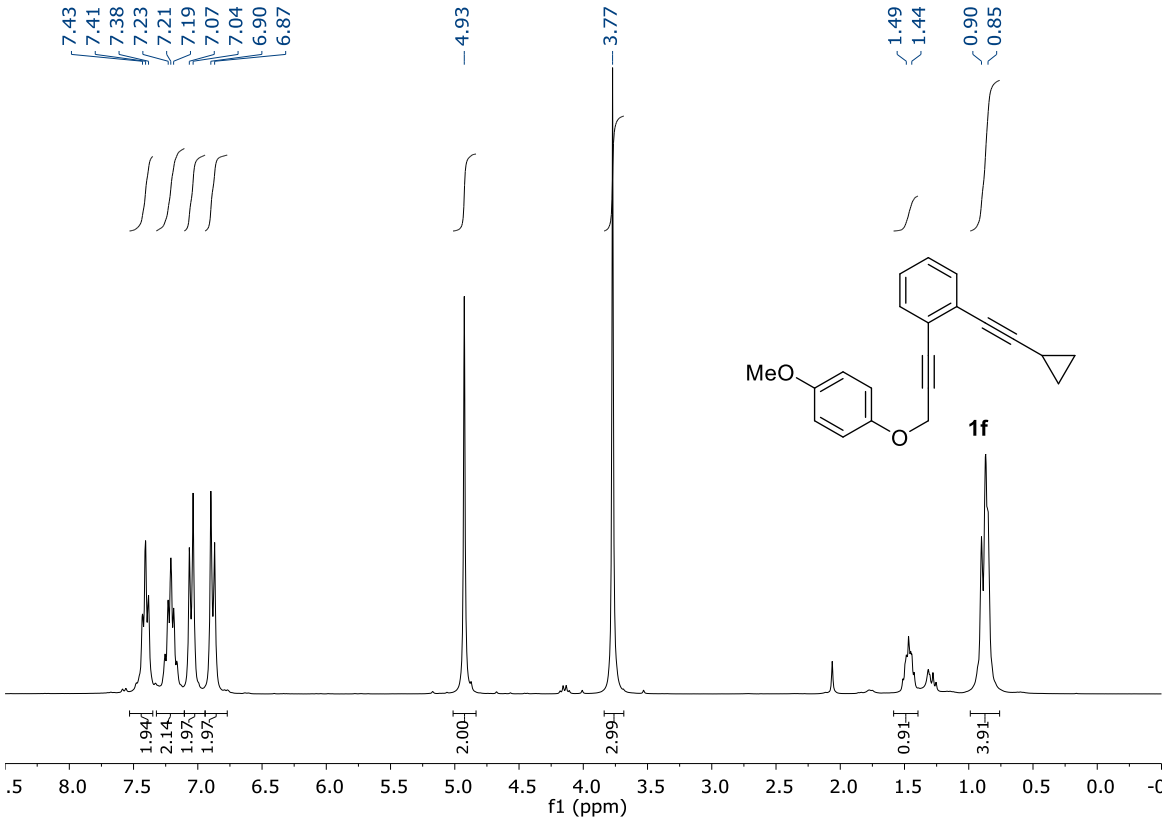
300 MHz ^{1}H NMR Spectrum of compound **1e** ($CDCl_3$, 300 K)



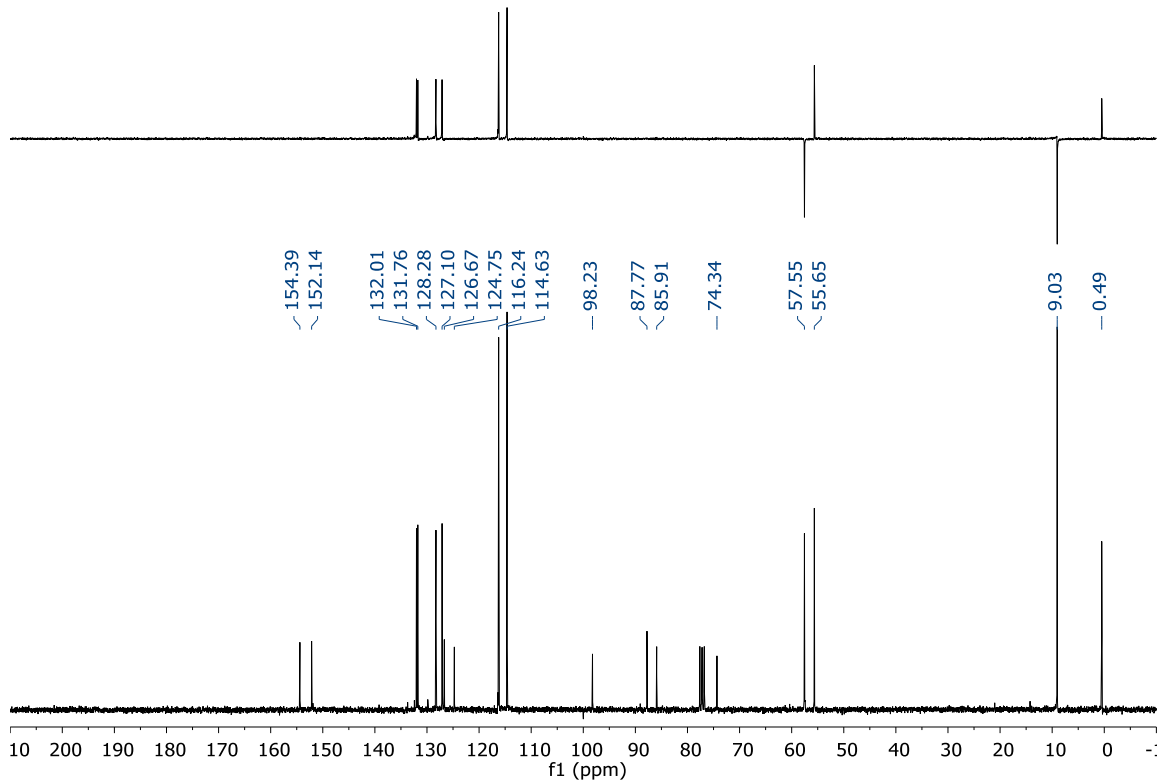
75 MHz ^{13}C NMR Spectrum of compound **1e** ($CDCl_3$, 300 K)



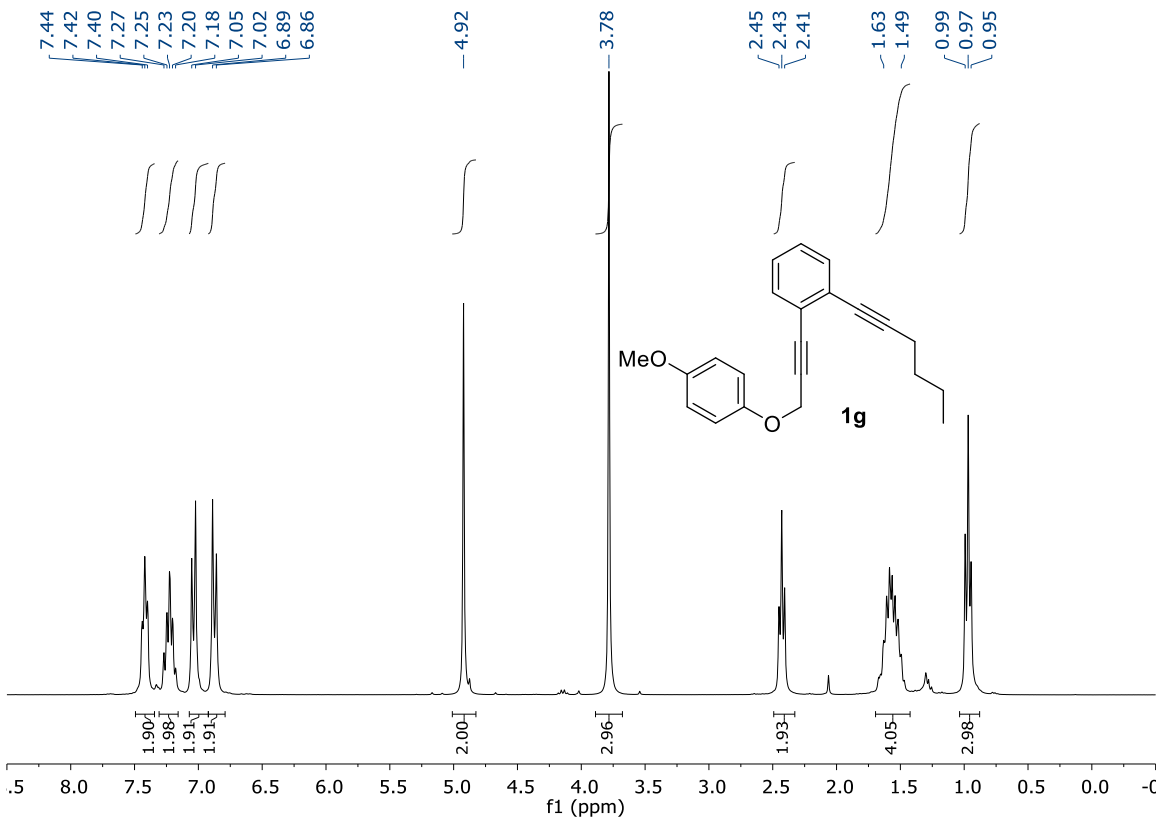
300 MHz ^{1}H NMR Spectrum of compound **1f** ($CDCl_3$, 300 K)



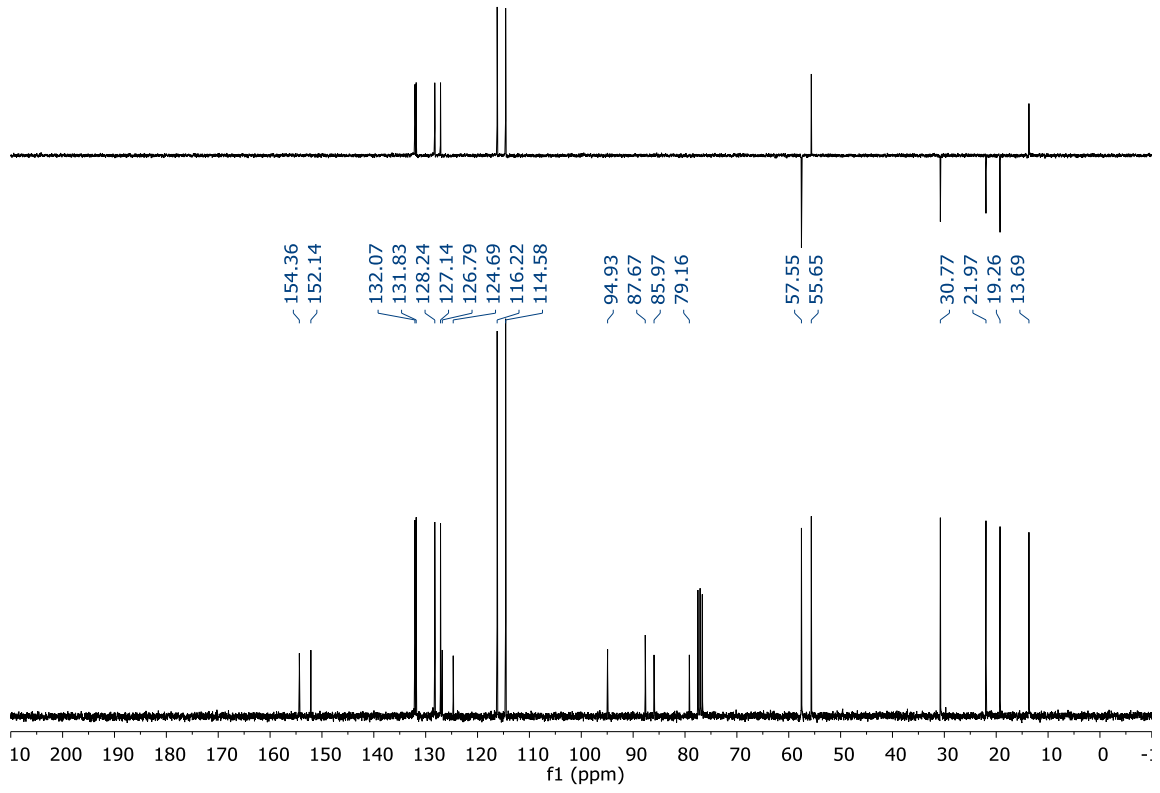
75 MHz ^{13}C NMR Spectrum of compound **1f** ($CDCl_3$, 300 K)



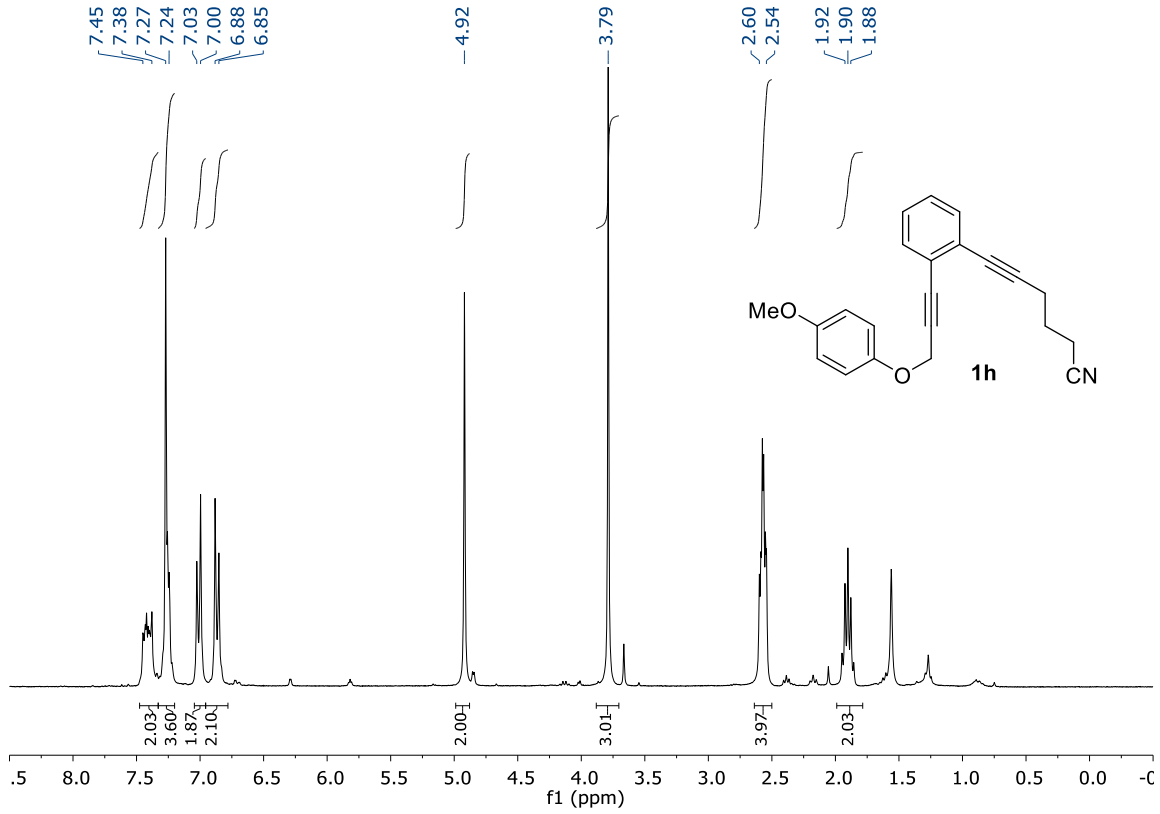
300 MHz ^{1}H NMR Spectrum of compound **1g** ($CDCl_3$, 300 K)



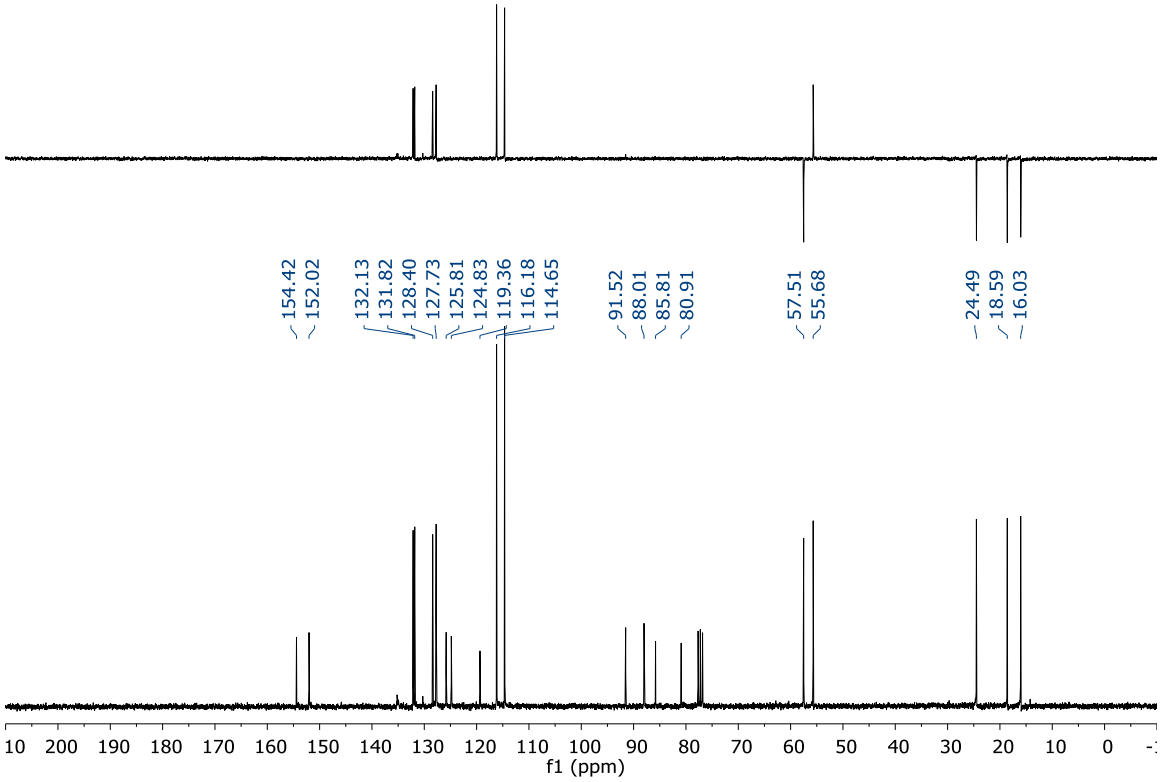
75 MHz ^{13}C NMR Spectrum of compound **1g** ($CDCl_3$, 300 K)



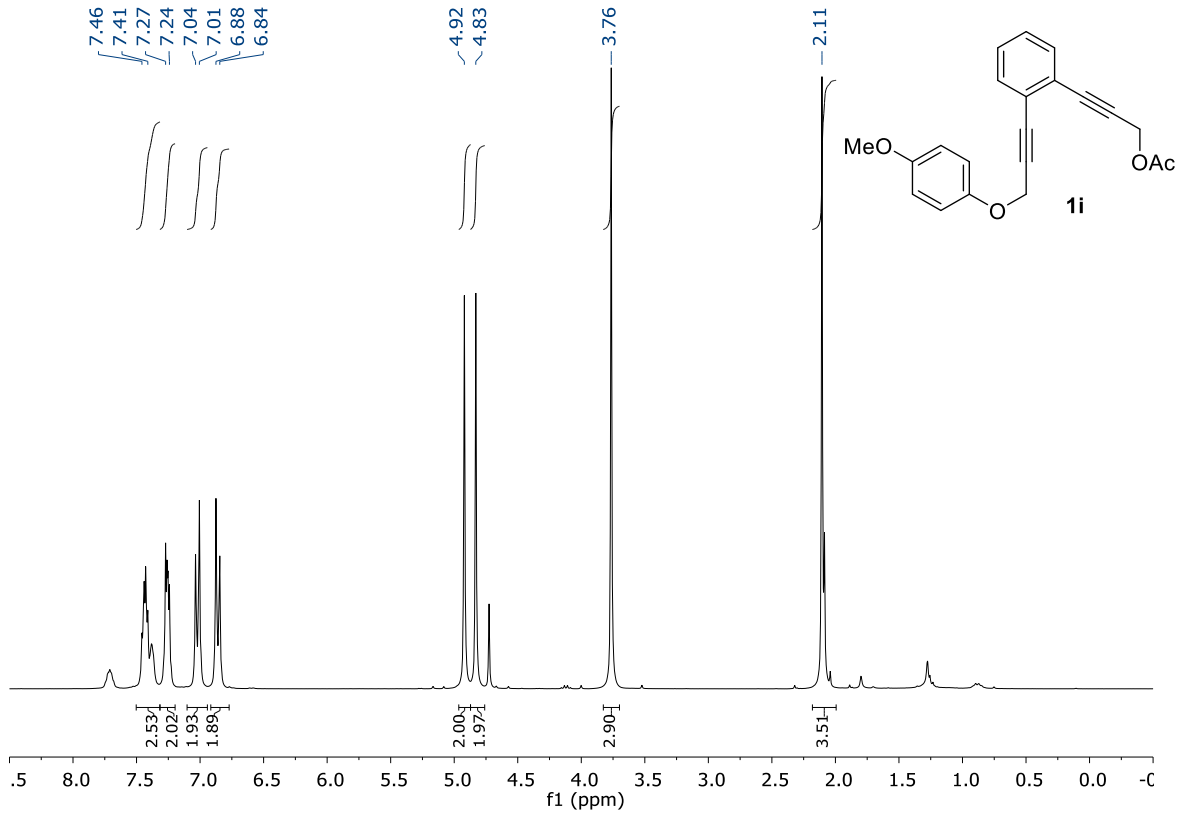
300 MHz ^{1}H NMR Spectrum of compound **1h** ($CDCl_3$, 300 K)



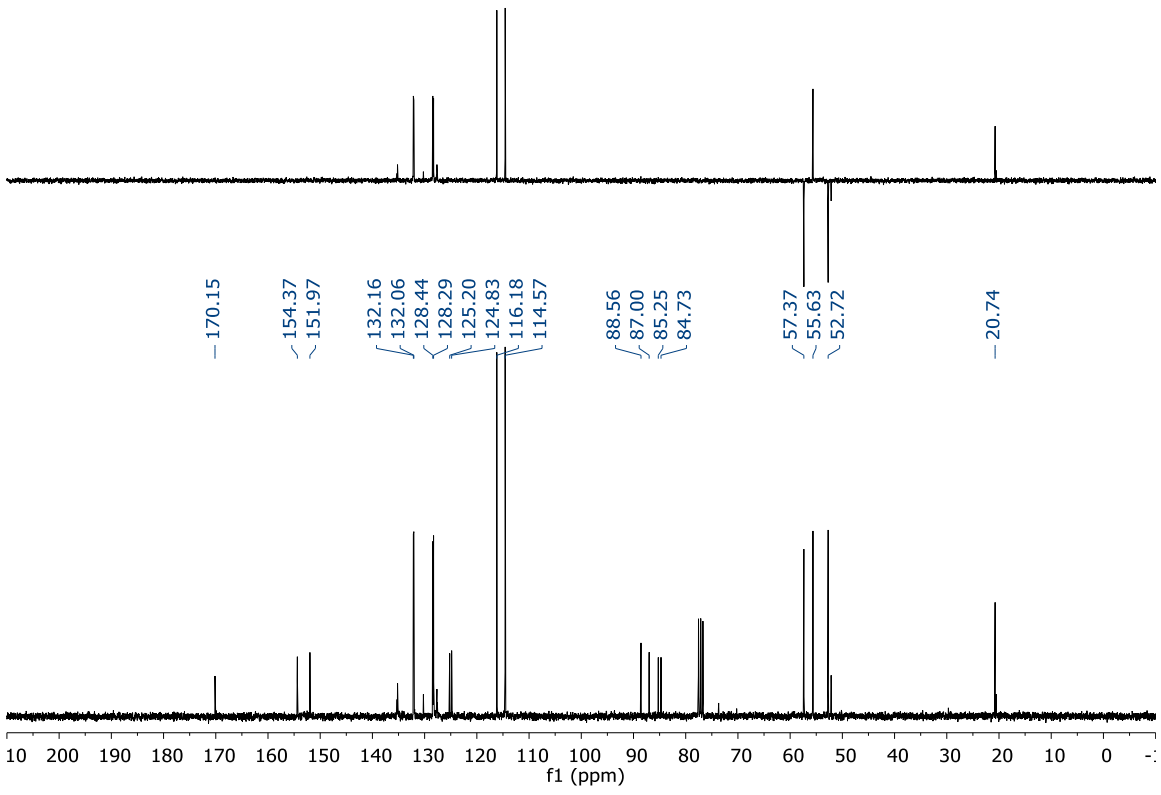
75 MHz ^{13}C NMR Spectrum of compound **1h** ($CDCl_3$, 300 K)



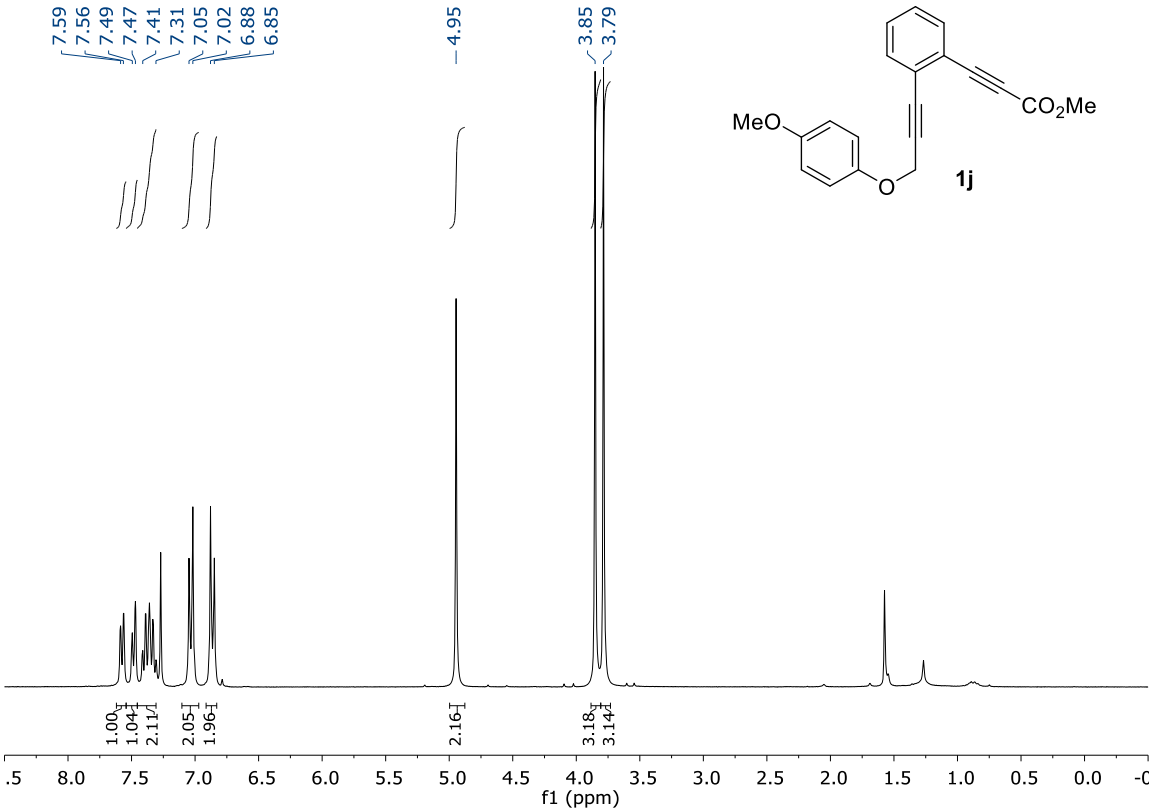
300 MHz ^{1}H NMR Spectrum of compound **1i** ($CDCl_3$, 300 K)



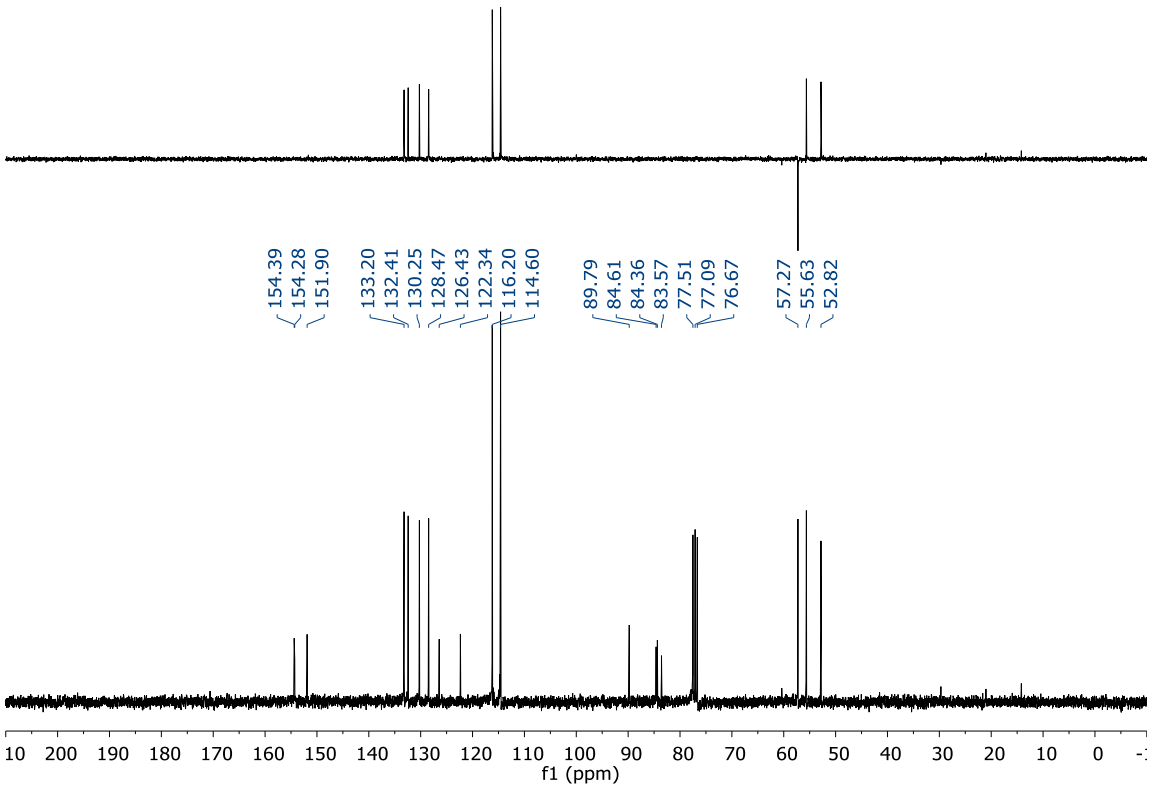
75 MHz ^{13}C NMR Spectrum of compound **1i** ($CDCl_3$, 300 K)



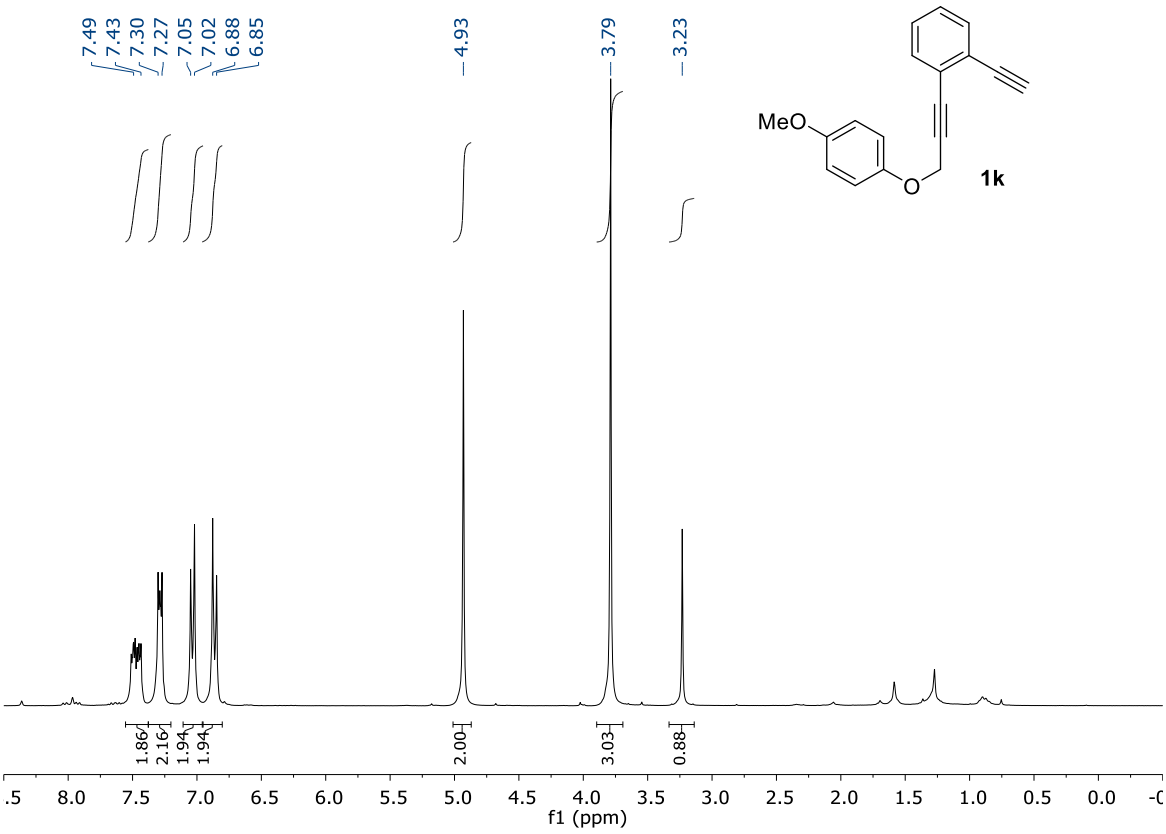
300 MHz ^{1}H NMR Spectrum of compound **1j** ($CDCl_3$, 300 K)



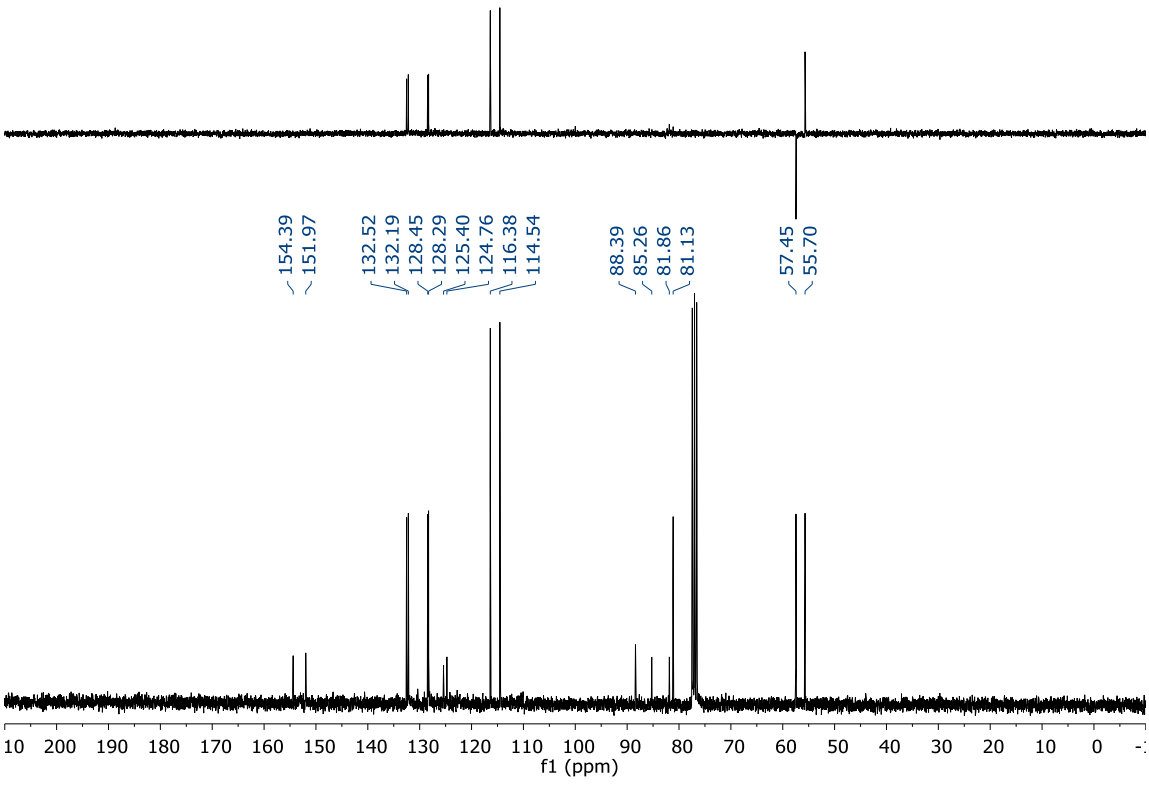
75 MHz ^{13}C NMR Spectrum of compound **1j** ($CDCl_3$, 300 K)



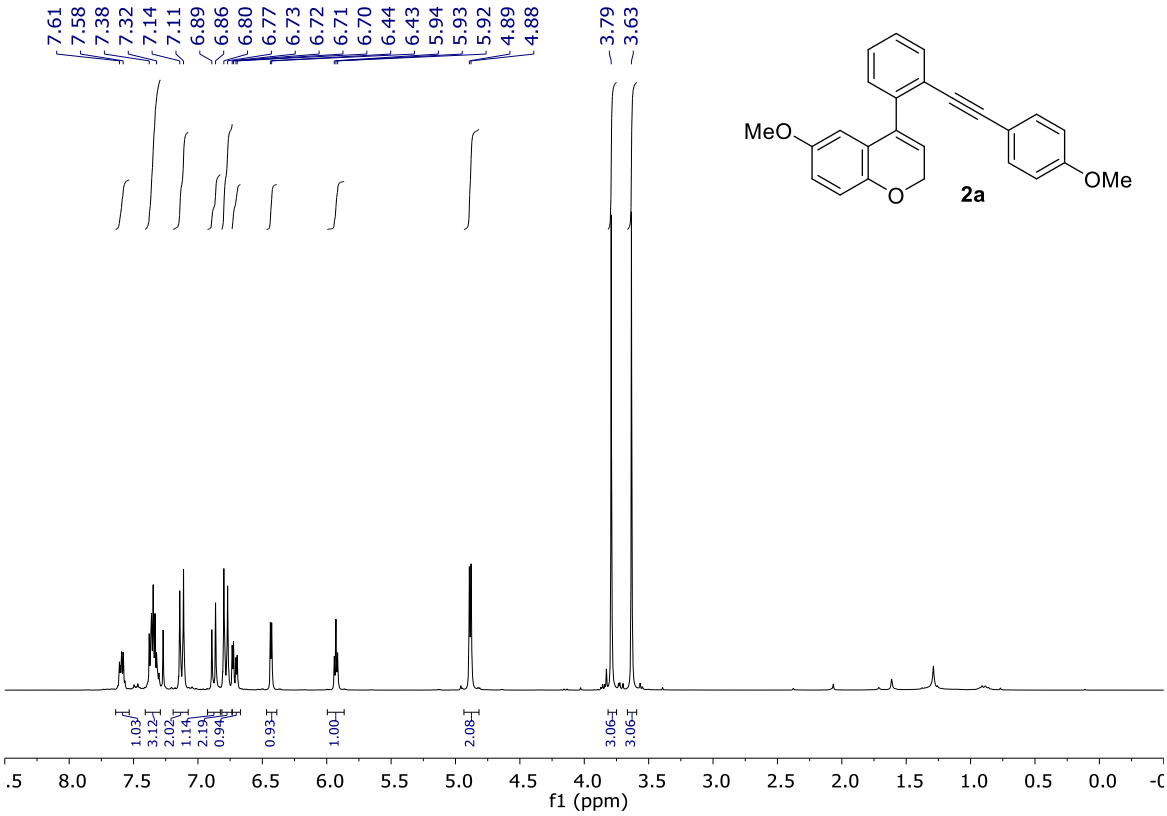
300 MHz ^{1}H NMR Spectrum of compound **1k** ($CDCl_3$, 300 K)



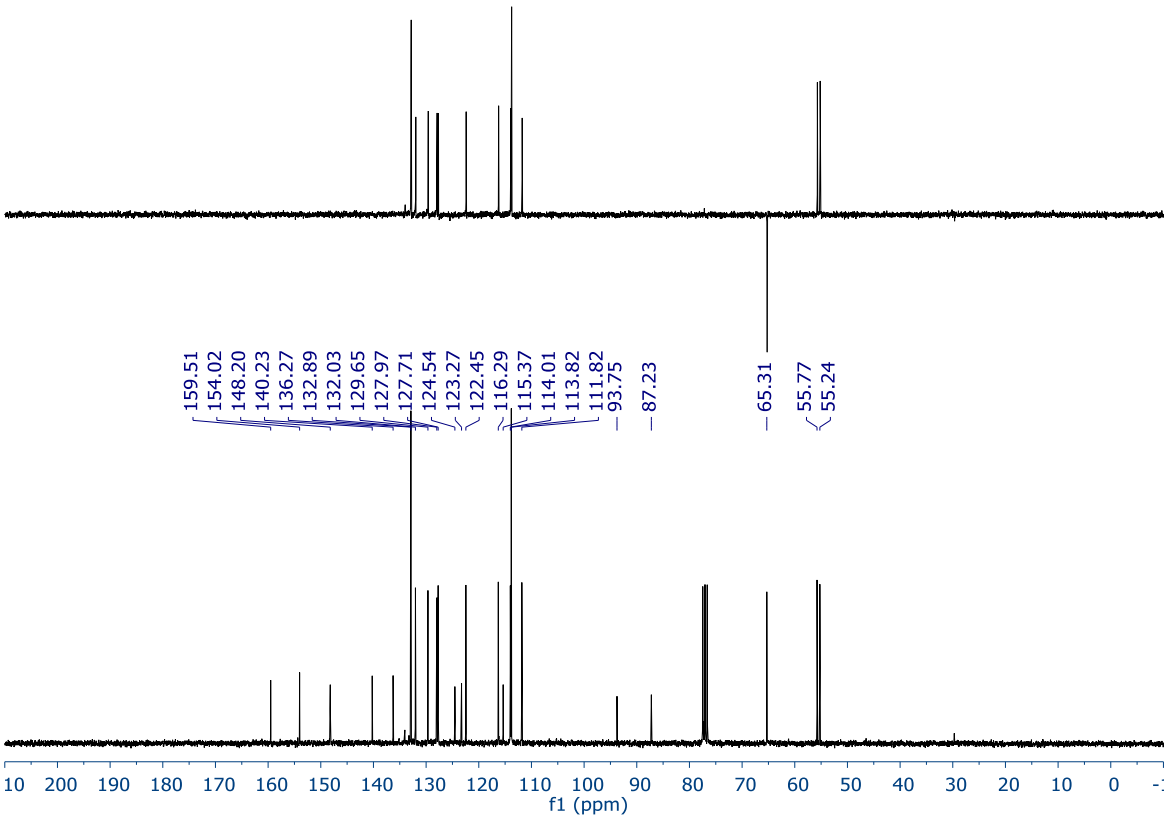
75 MHz ^{13}C NMR Spectrum of compound **1k** ($CDCl_3$, 300 K)



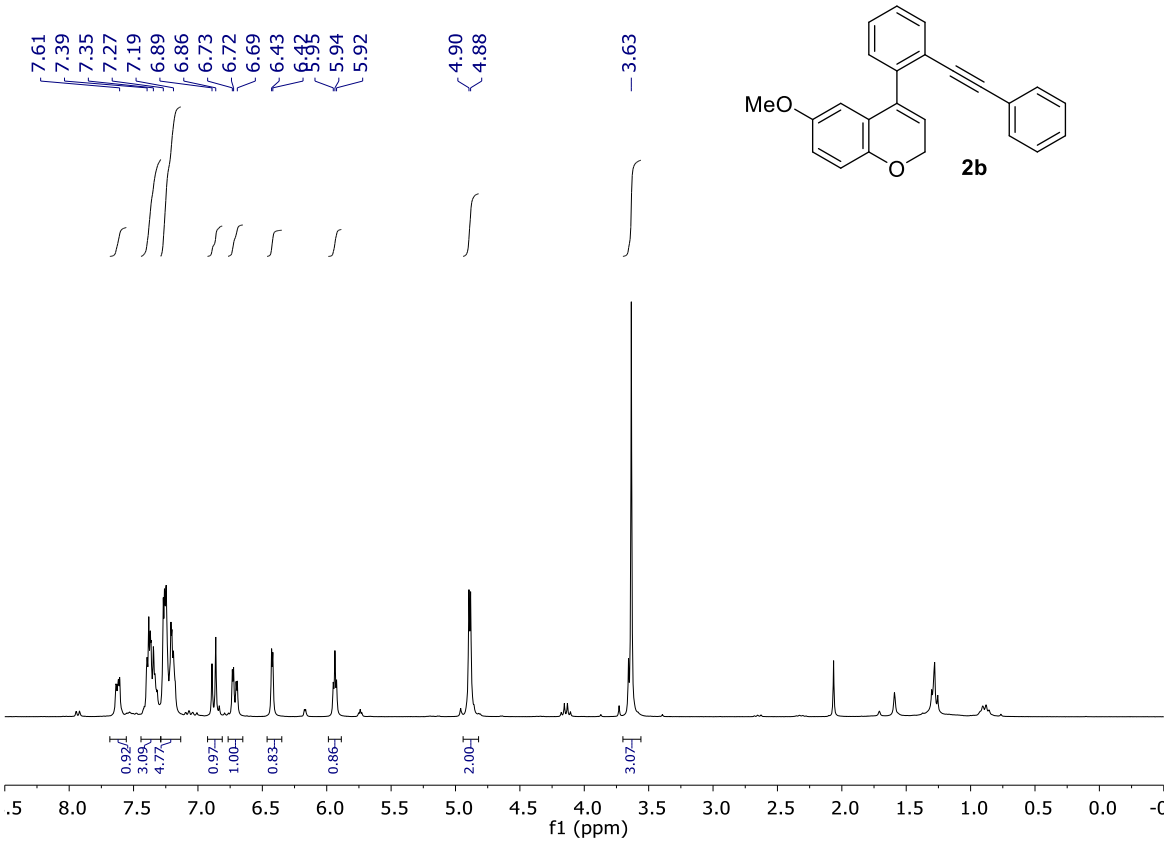
300 MHz ^{1}H NMR Spectrum of compound **2a** ($CDCl_3$, 300 K)



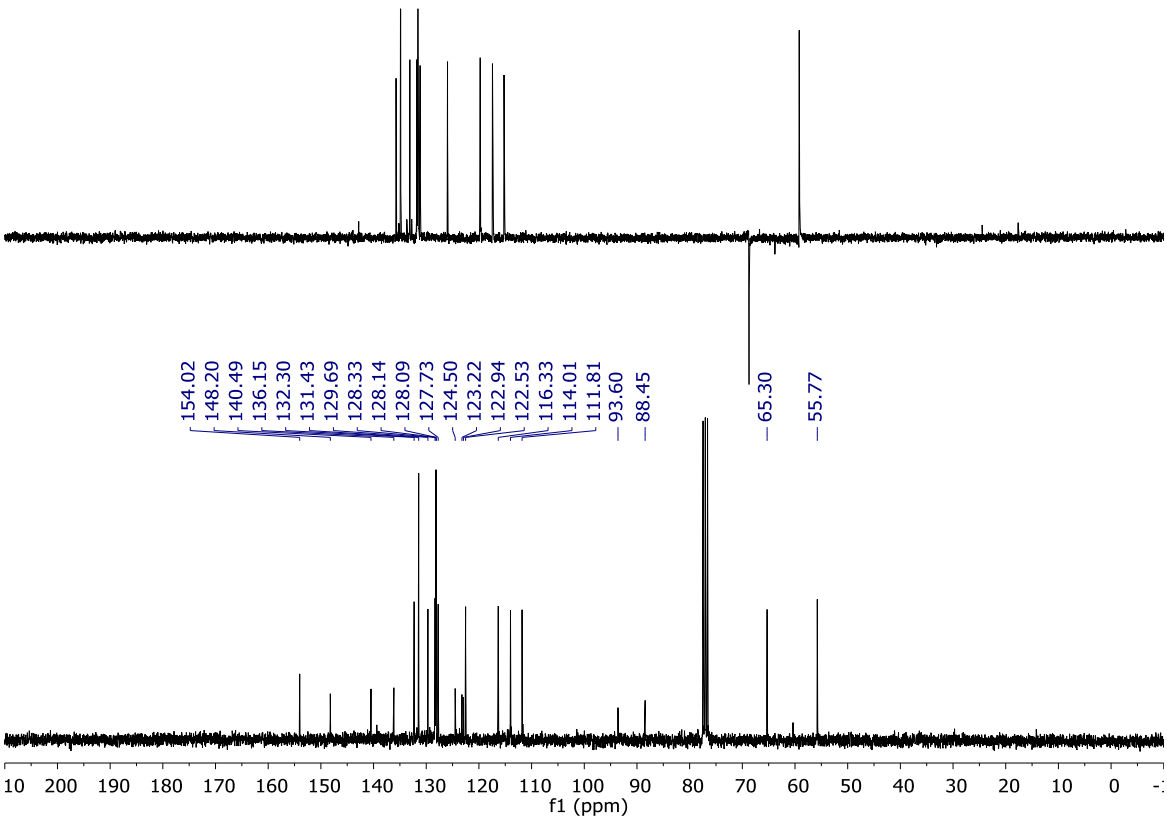
75 MHz ^{13}C NMR Spectrum of compound **2a** ($CDCl_3$, 300 K)



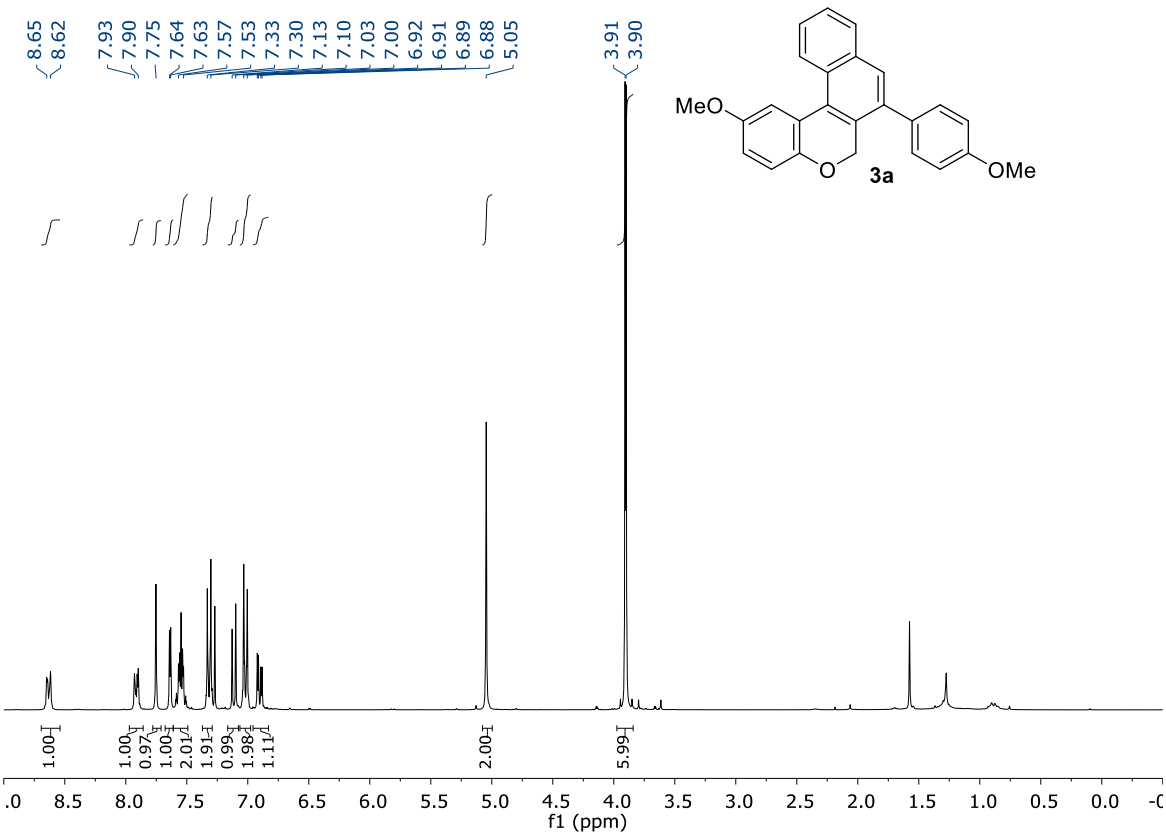
300 MHz ^{1}H NMR Spectrum of compound **2b** ($CDCl_3$, 300 K)



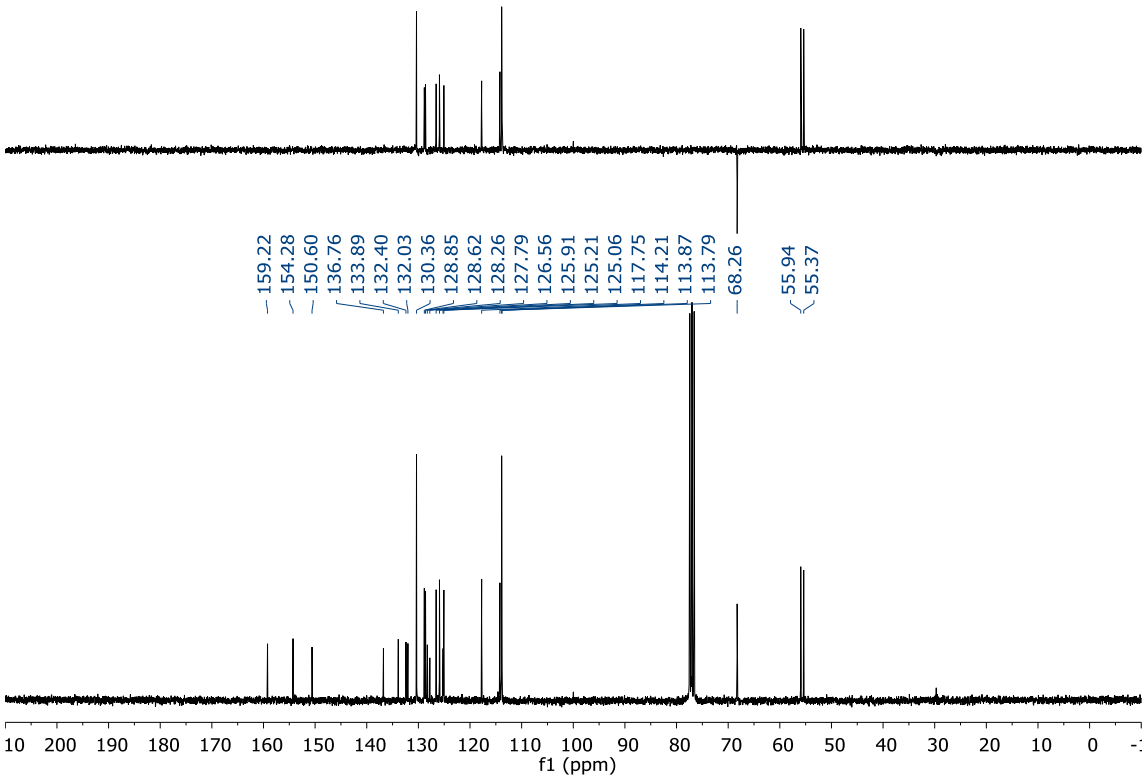
75 MHz ^{13}C NMR Spectrum of compound **2b** ($CDCl_3$, 300 K)



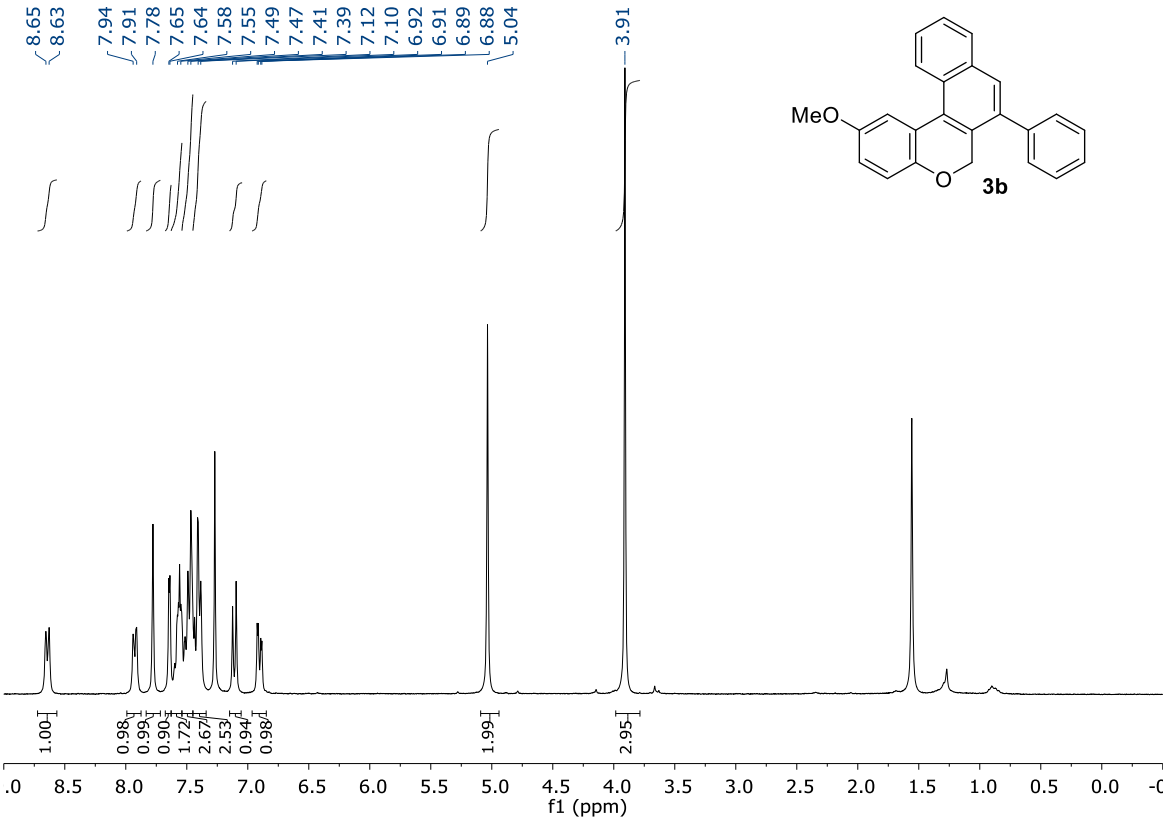
300 MHz ^{1}H NMR Spectrum of compound **3a** ($CDCl_3$, 300 K)



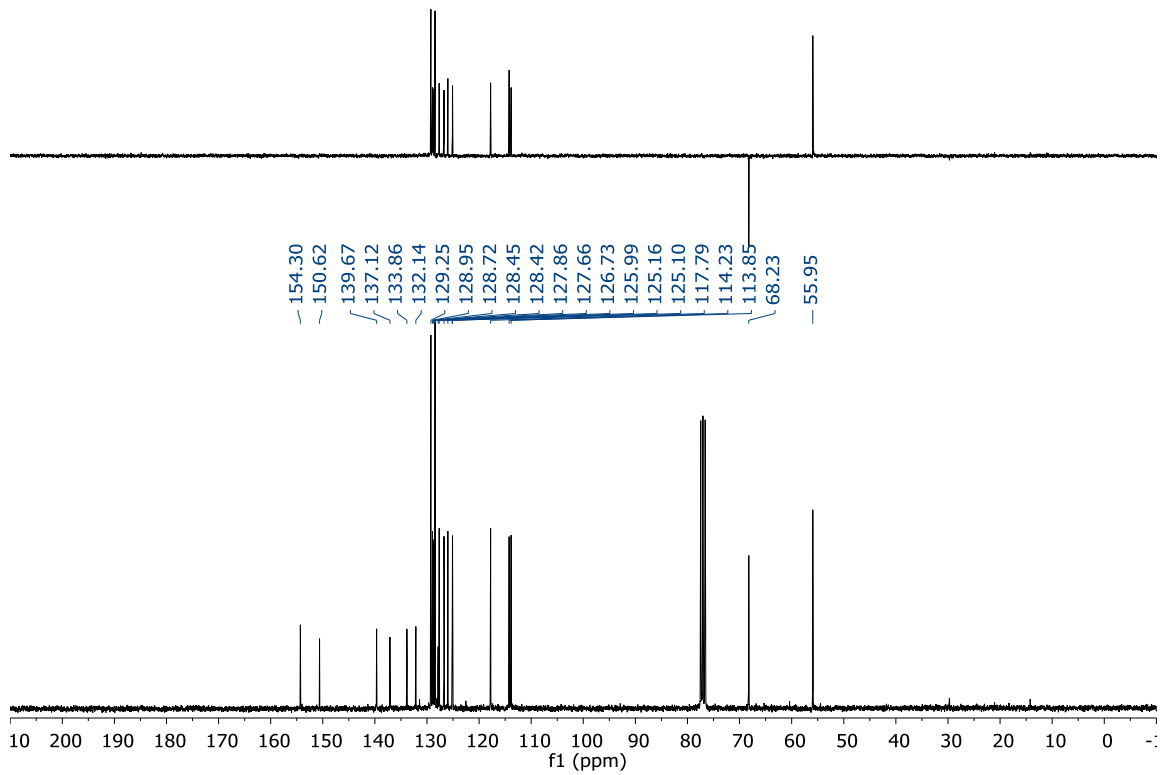
75 MHz ^{13}C NMR Spectrum of compound **3a** ($CDCl_3$, 300 K)



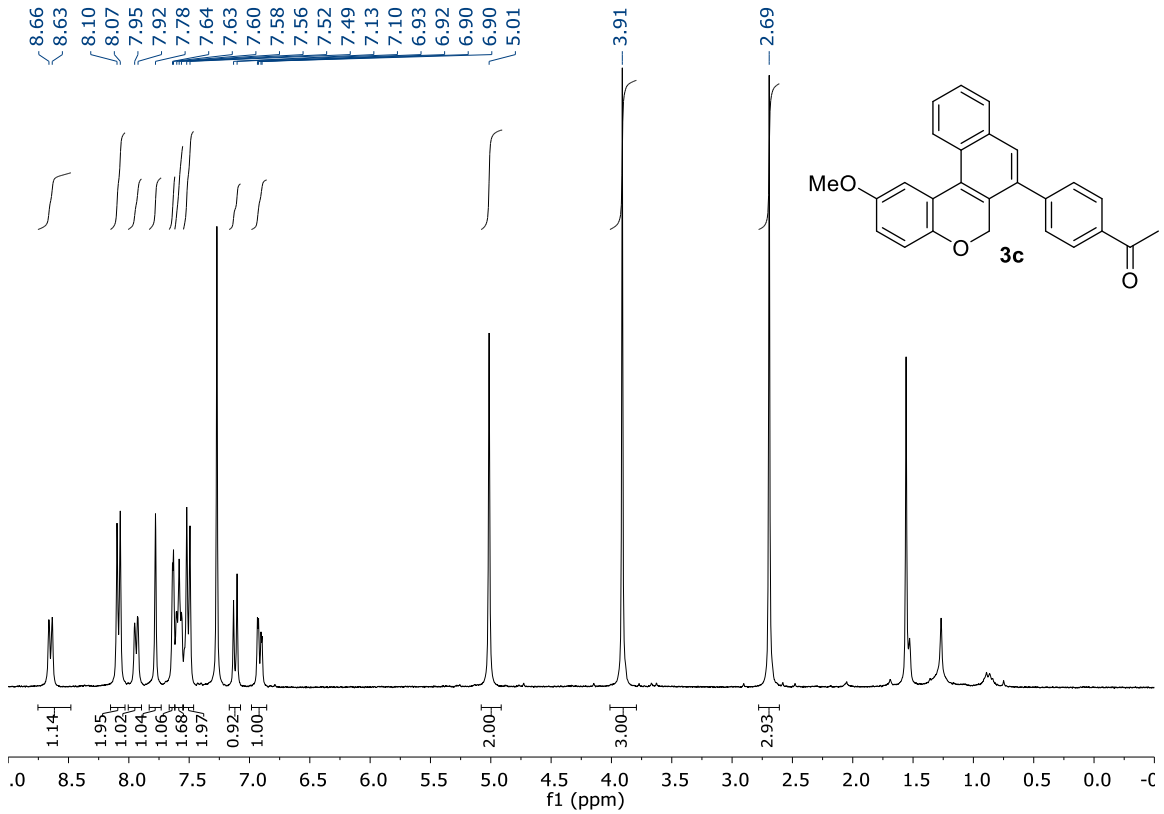
300 MHz ^{1}H NMR Spectrum of compound **3b** ($CDCl_3$, 300 K)



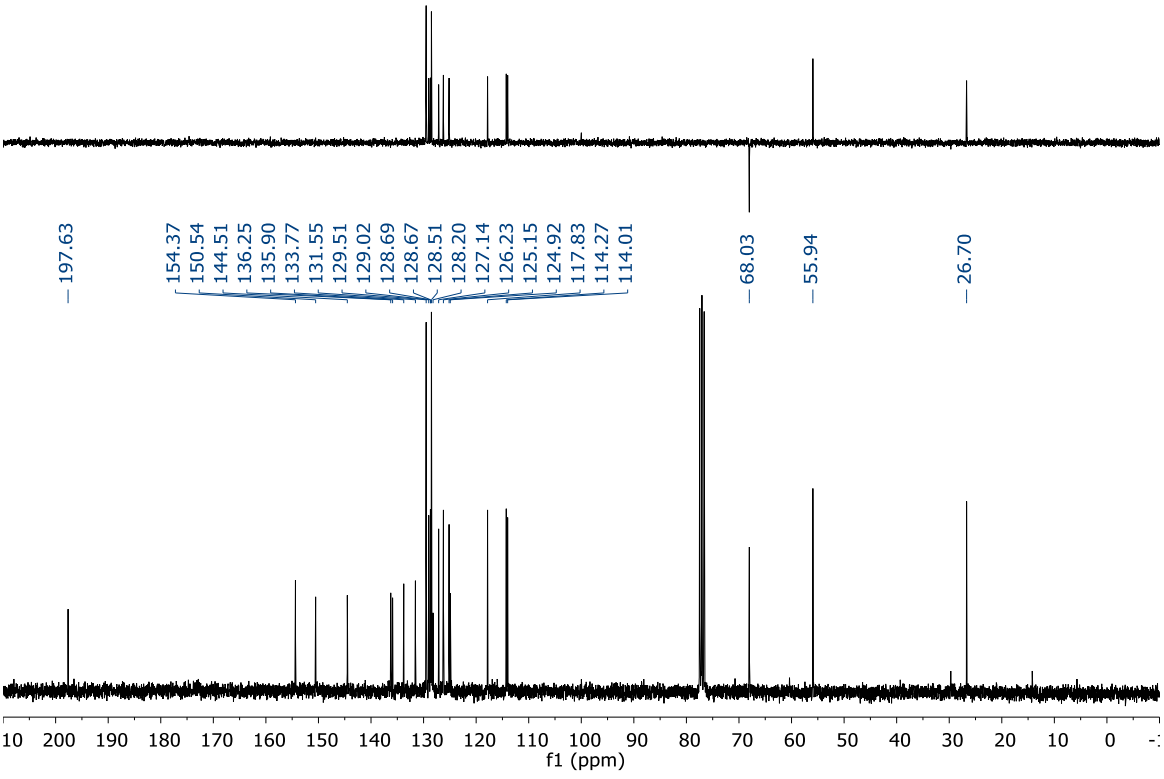
75 MHz ^{13}C NMR Spectrum of compound **3b** ($CDCl_3$, 300 K)



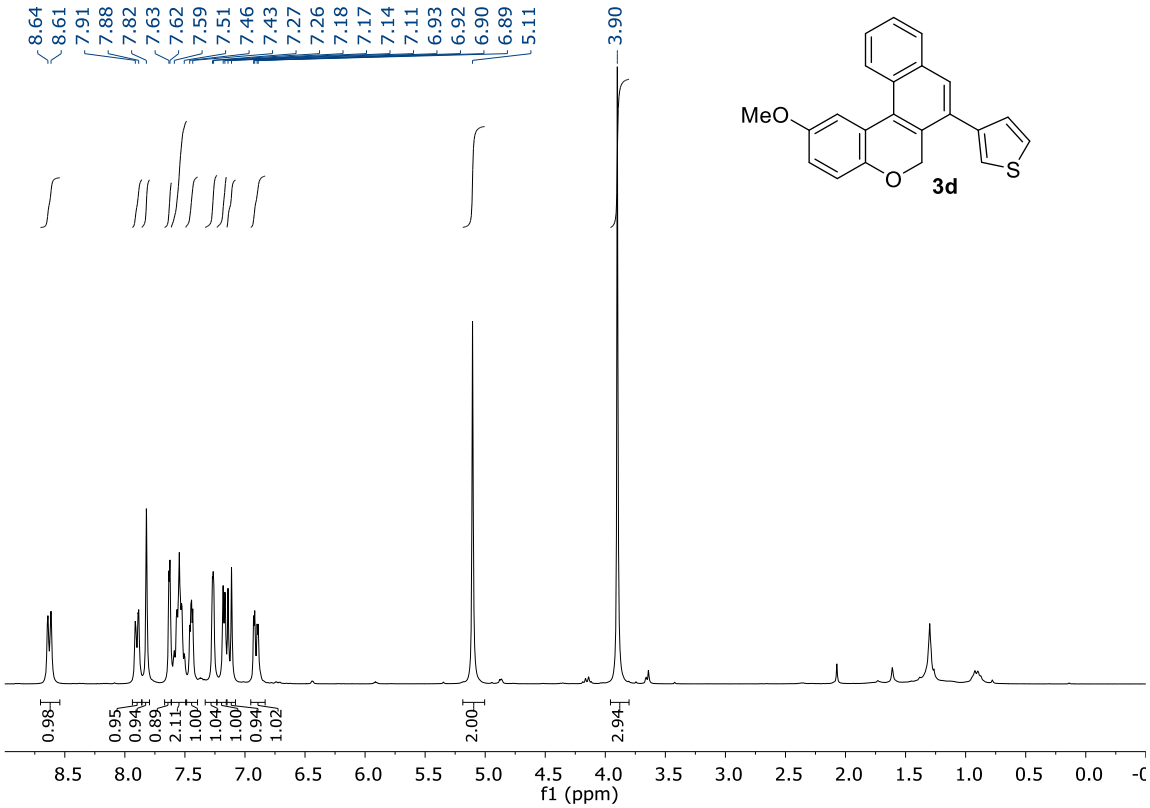
300 MHz ^{1}H NMR Spectrum of compound **3c** ($CDCl_3$, 300 K)



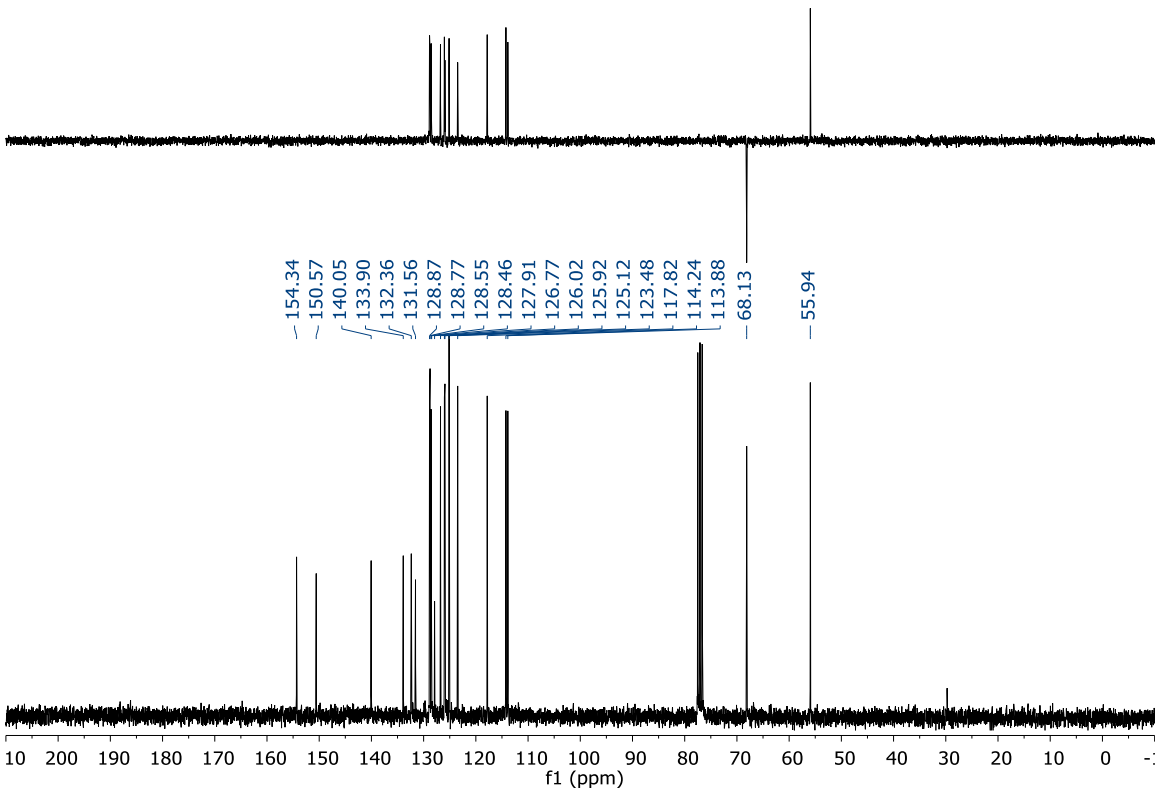
75 MHz ^{13}C NMR Spectrum of compound **3c** ($CDCl_3$, 300 K)



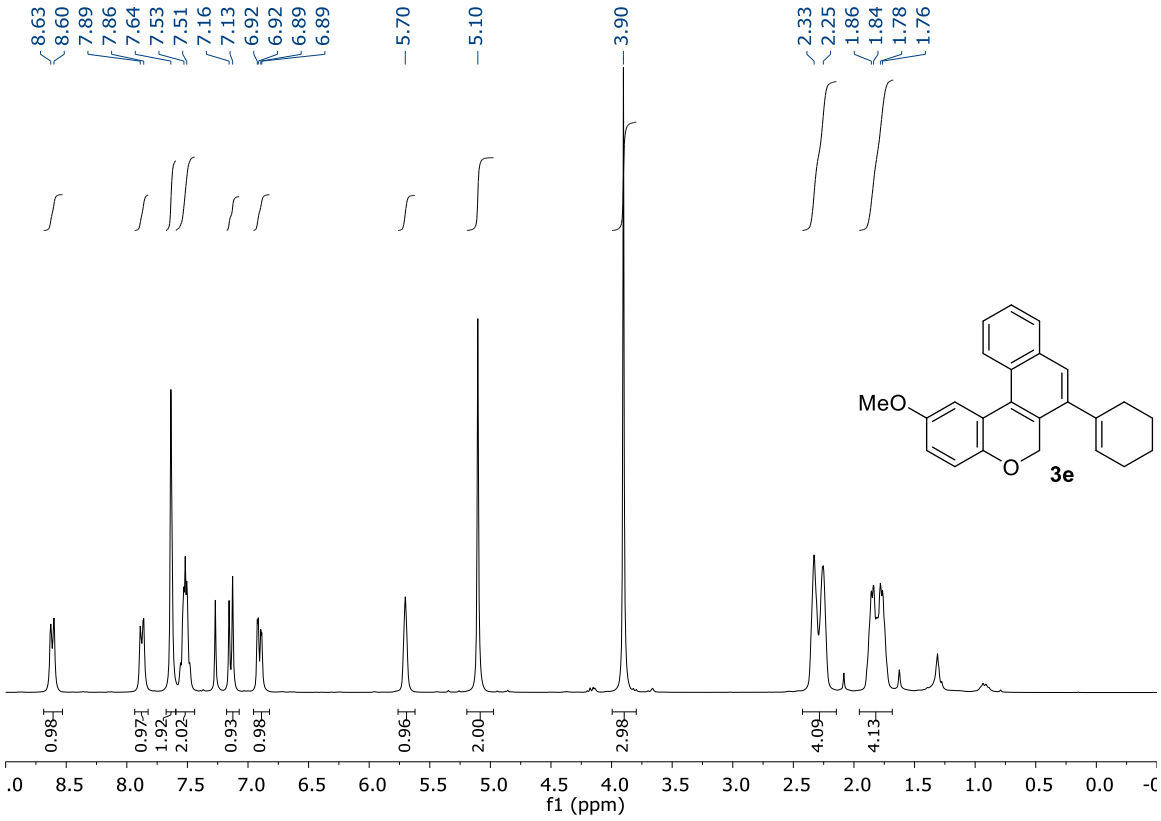
300 MHz ^{1}H NMR Spectrum of compound **3d** ($CDCl_3$, 300 K)



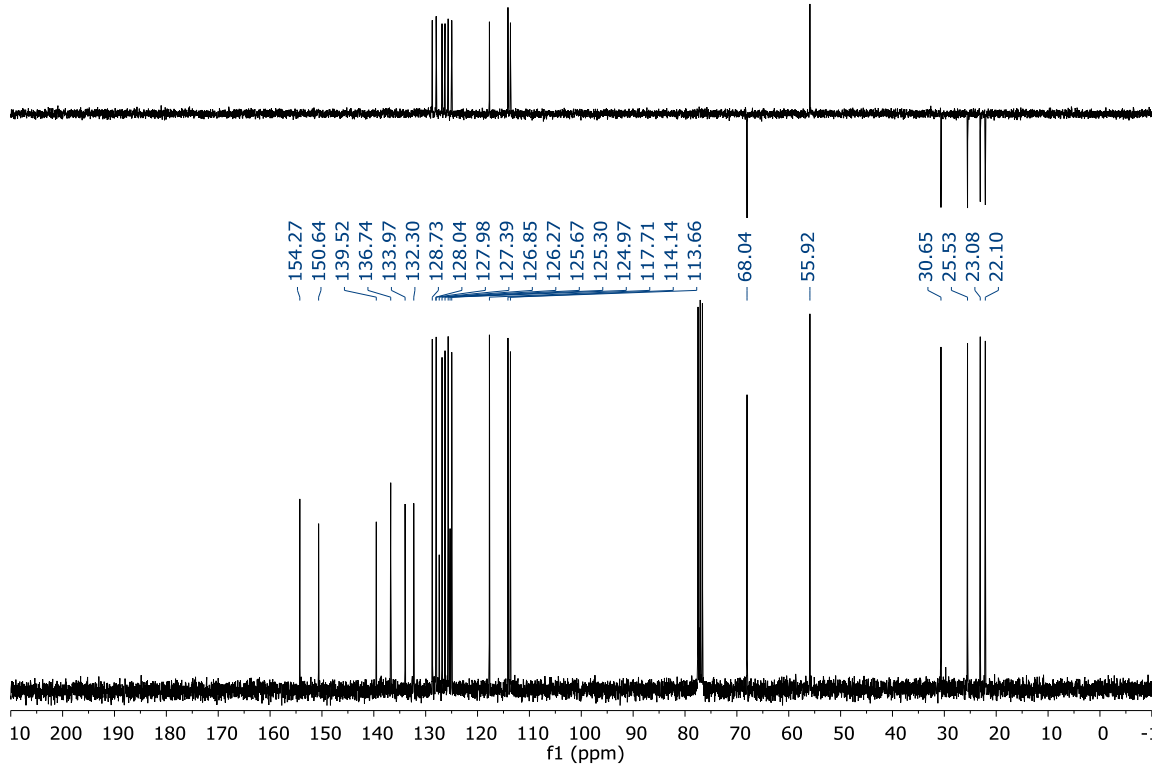
75 MHz ^{13}C NMR Spectrum of compound **3d** ($CDCl_3$, 300 K)



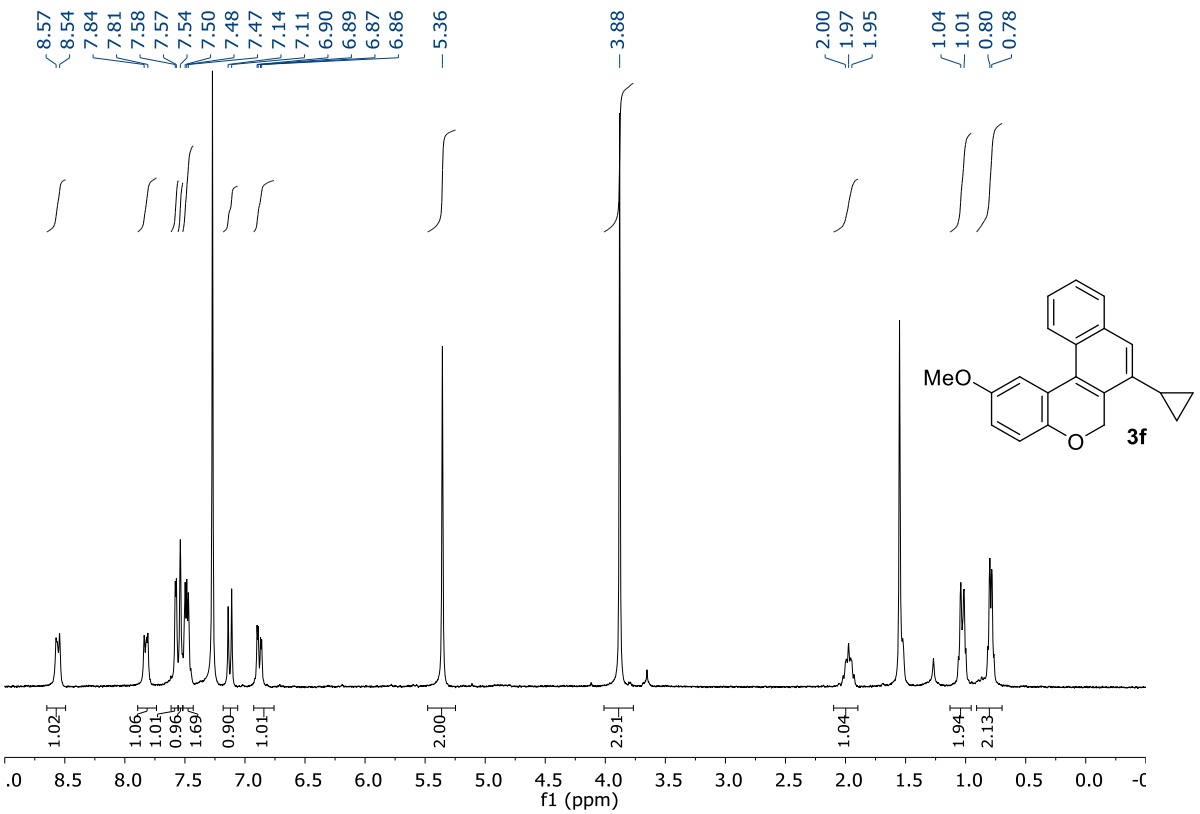
300 MHz ^{1}H NMR Spectrum of compound **3e** ($CDCl_3$, 300 K)



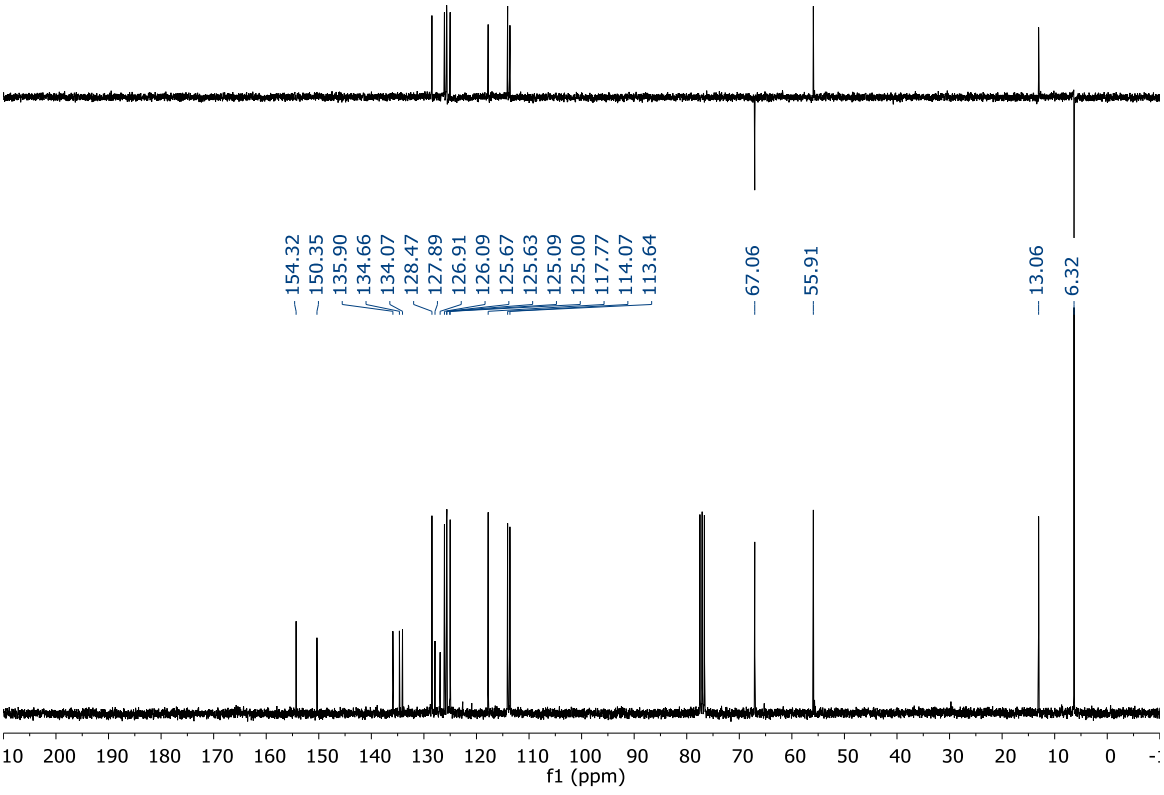
75 MHz ^{13}C NMR Spectrum of compound **3e** ($CDCl_3$, 300 K)



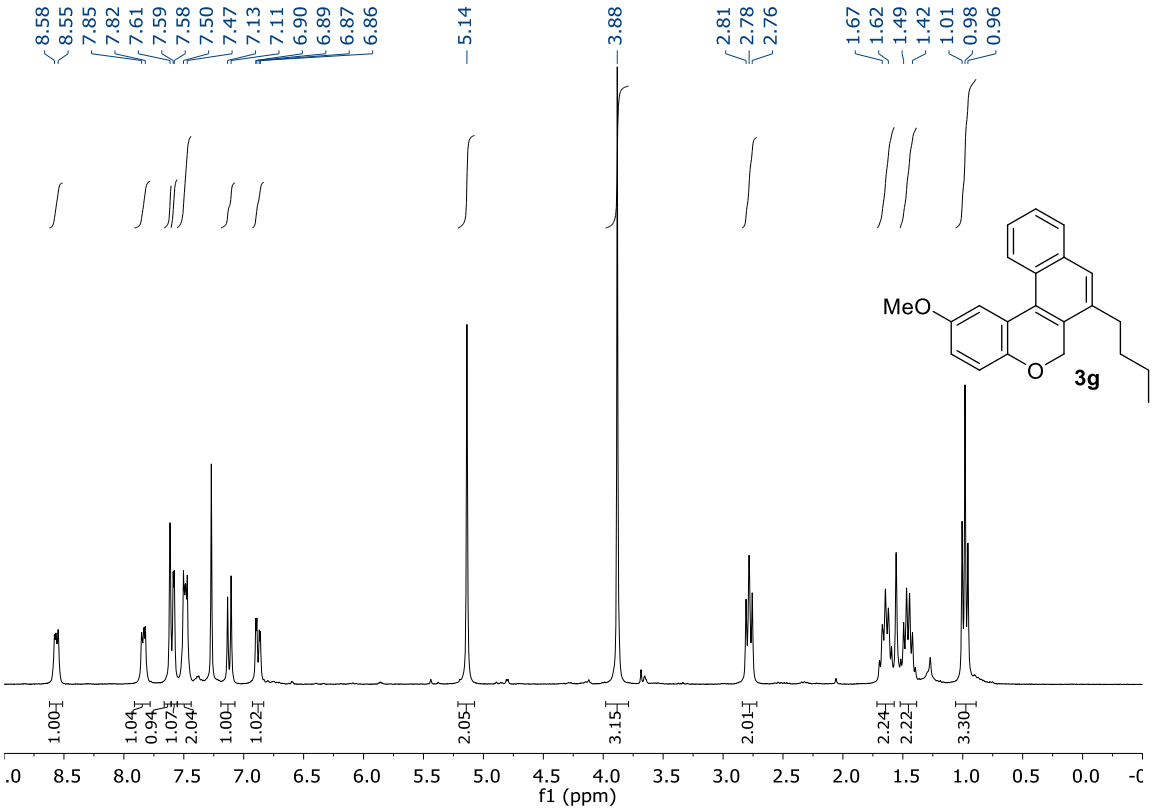
300 MHz ^{1}H NMR Spectrum of compound **3f** ($CDCl_3$, 300 K)



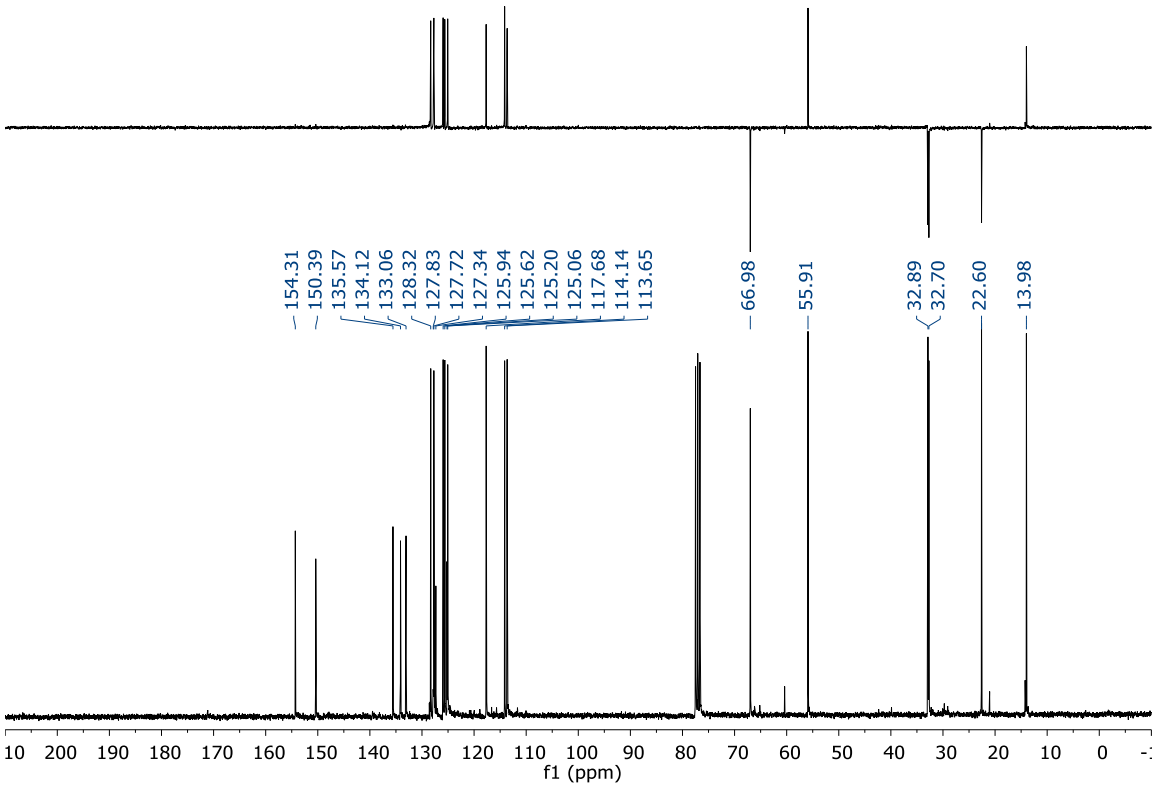
75 MHz ^{13}C NMR Spectrum of compound **3f** ($CDCl_3$, 300 K)



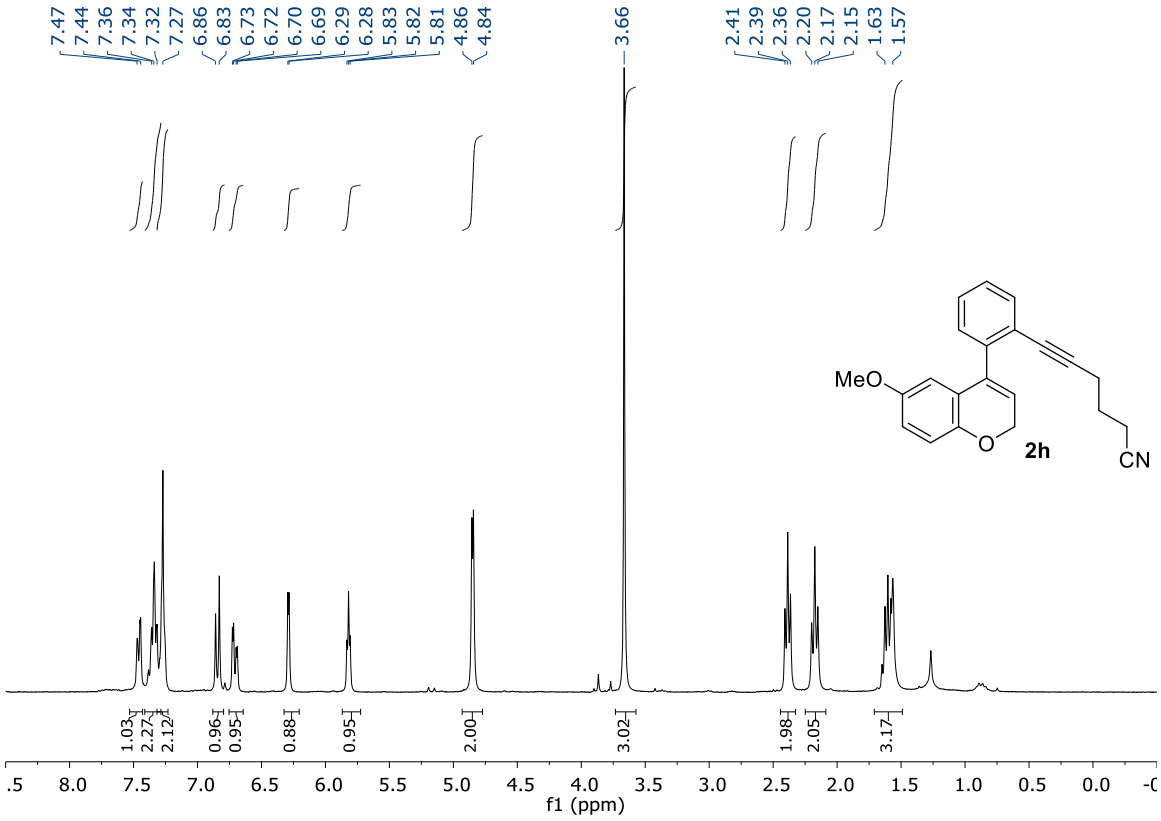
300 MHz ^{1}H NMR Spectrum of compound **3g** ($CDCl_3$, 300 K)



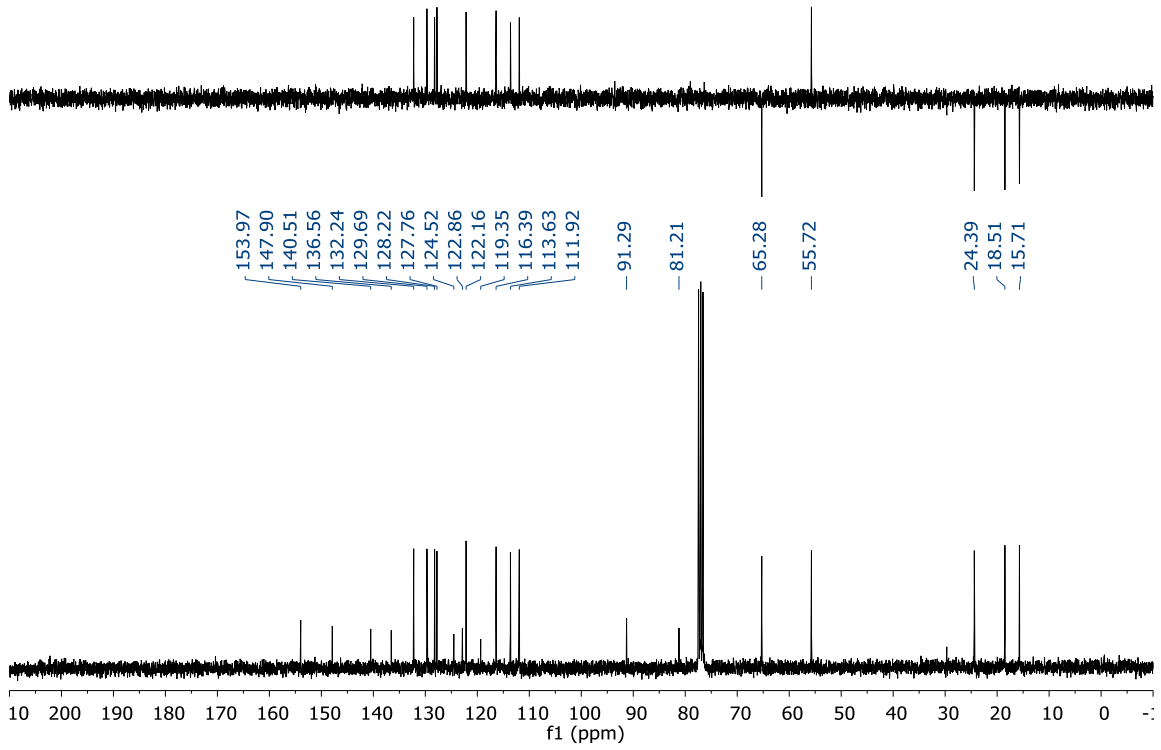
75 MHz ^{13}C NMR Spectrum of compound **3g** ($CDCl_3$, 300 K)



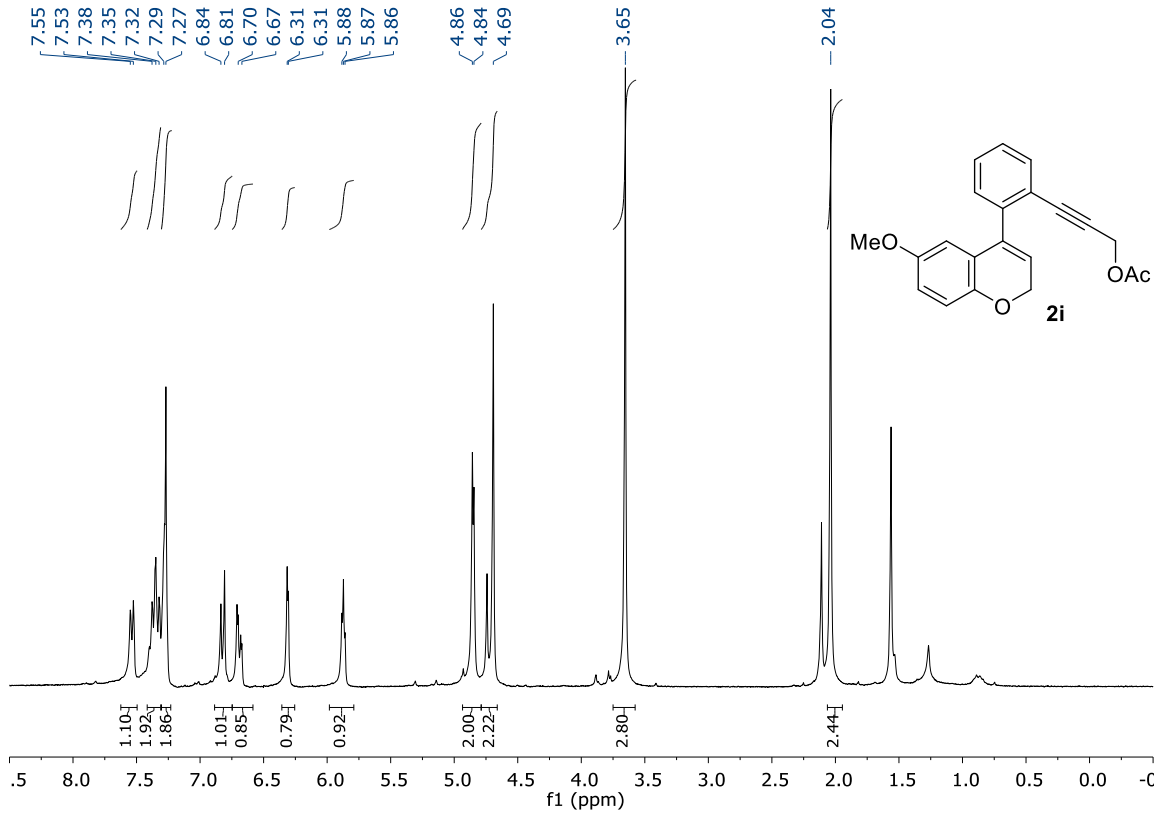
300 MHz ^{1}H NMR Spectrum of compound **2h** ($CDCl_3$, 300 K)



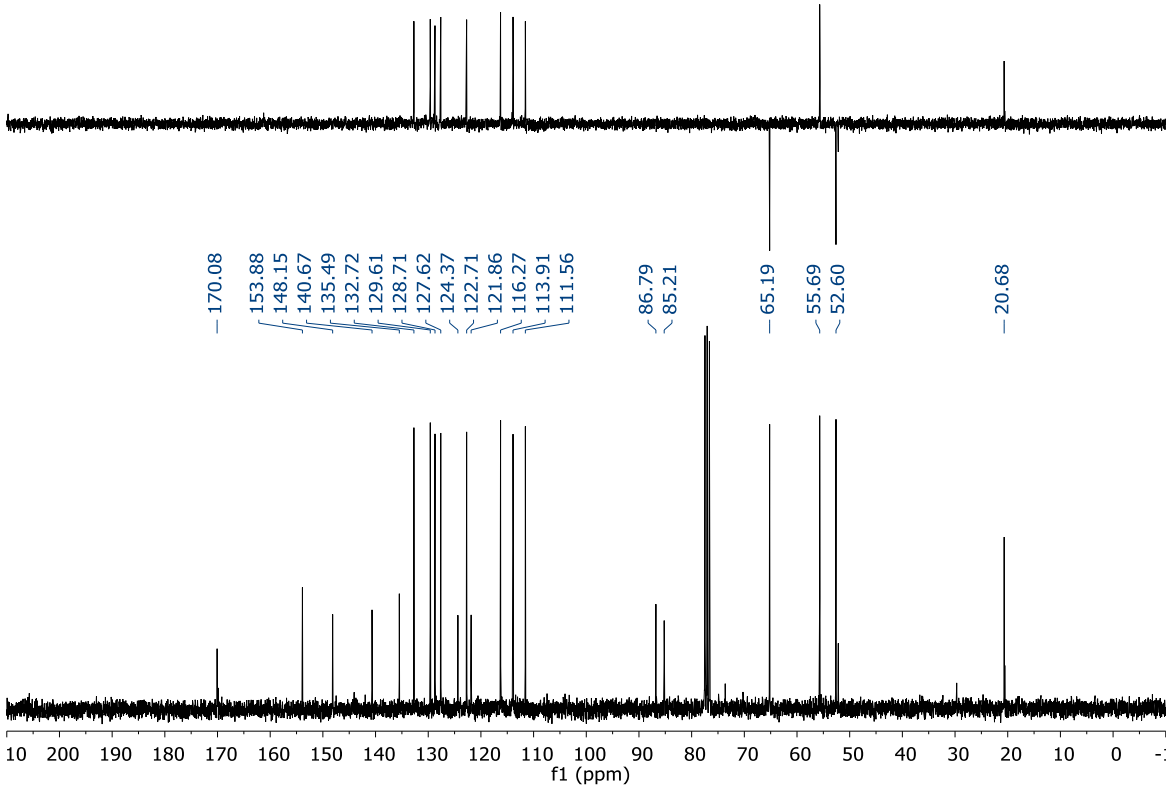
75 MHz ^{13}C NMR Spectrum of compound **2h** ($CDCl_3$, 300 K)



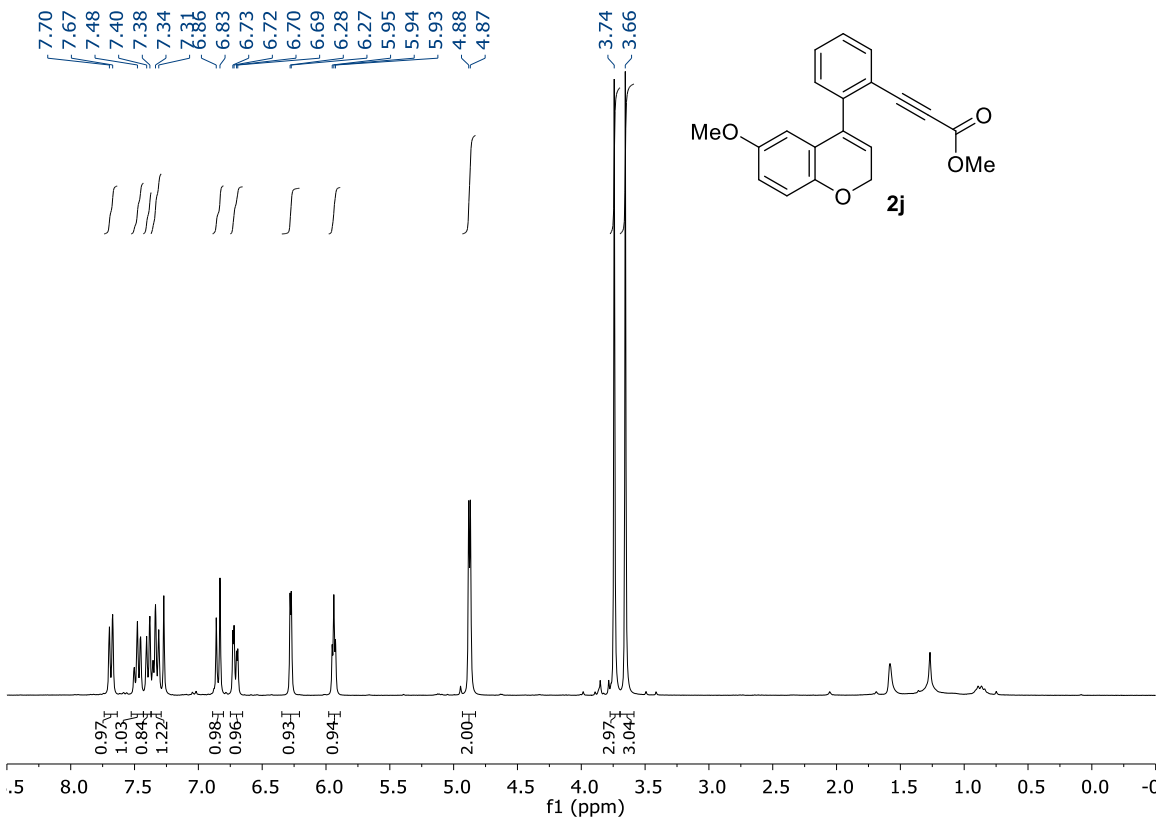
300 MHz ^{1}H NMR Spectrum of compound **2i** ($CDCl_3$, 300 K)



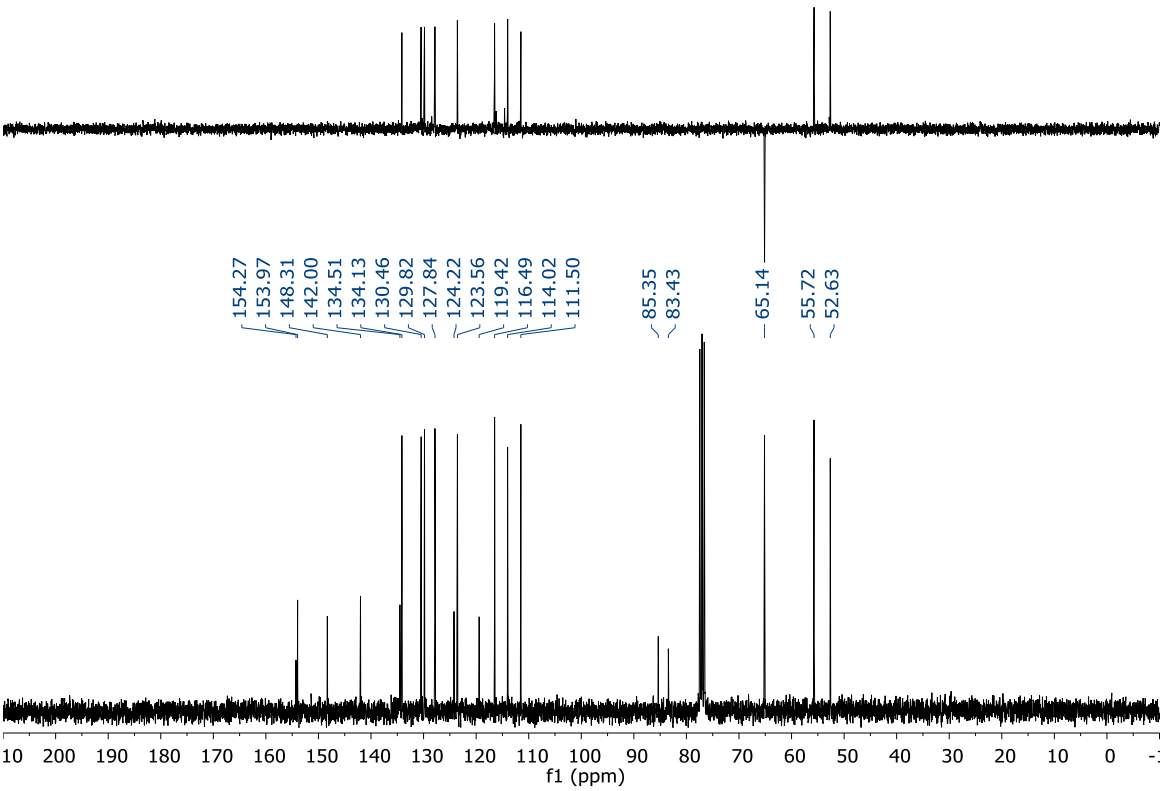
75 MHz ^{13}C NMR Spectrum of compound **2i** ($CDCl_3$, 300 K)



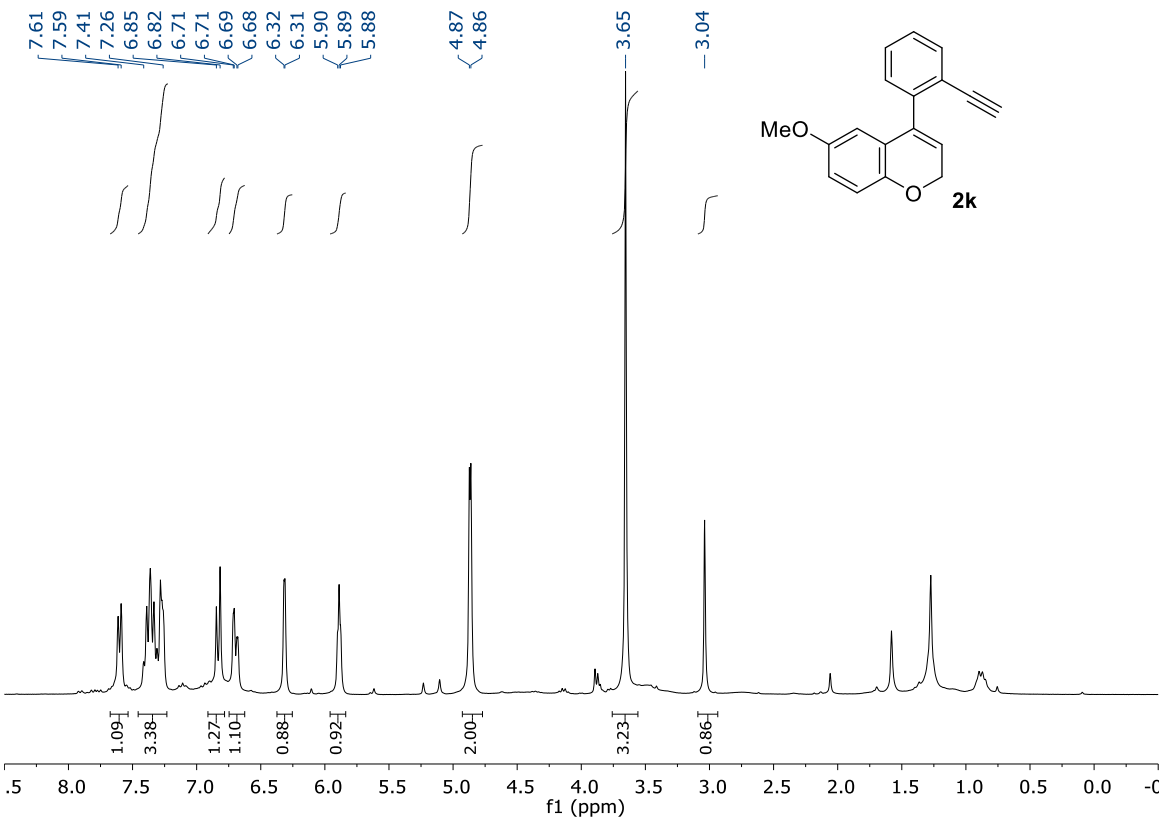
300 MHz ^{1}H NMR Spectrum of compound **2j** ($CDCl_3$, 300 K)



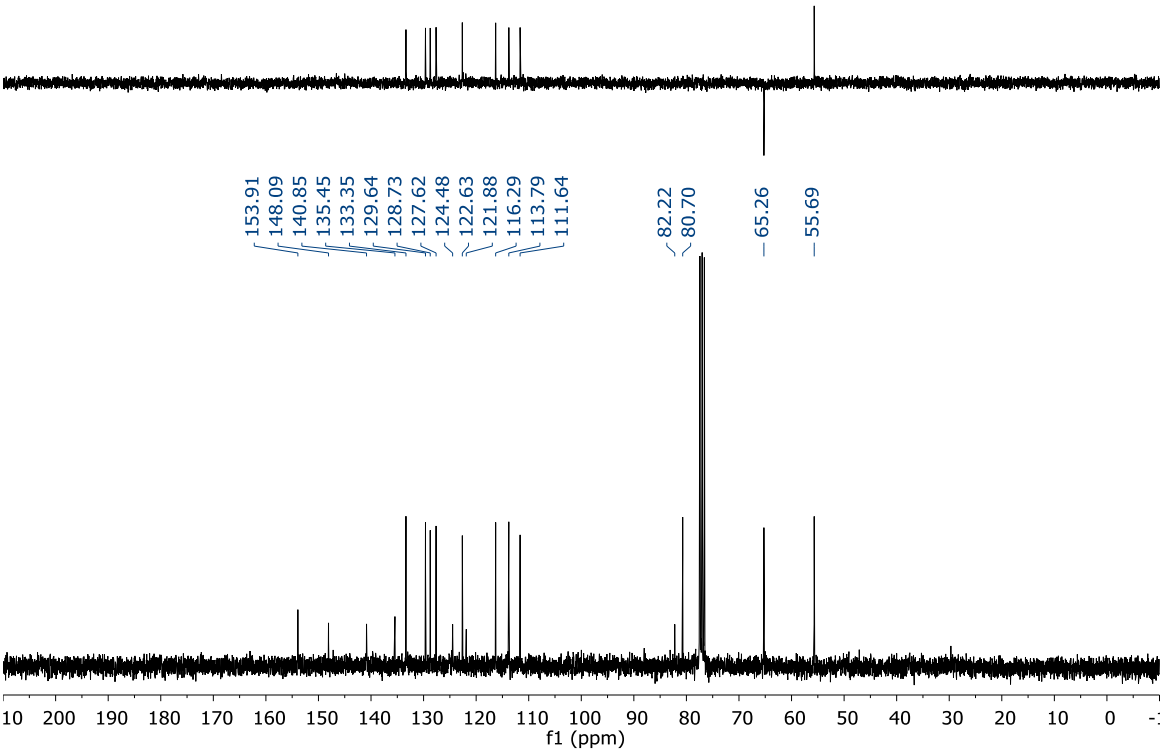
75 MHz ^{13}C NMR Spectrum of compound **2j** ($CDCl_3$, 300 K)



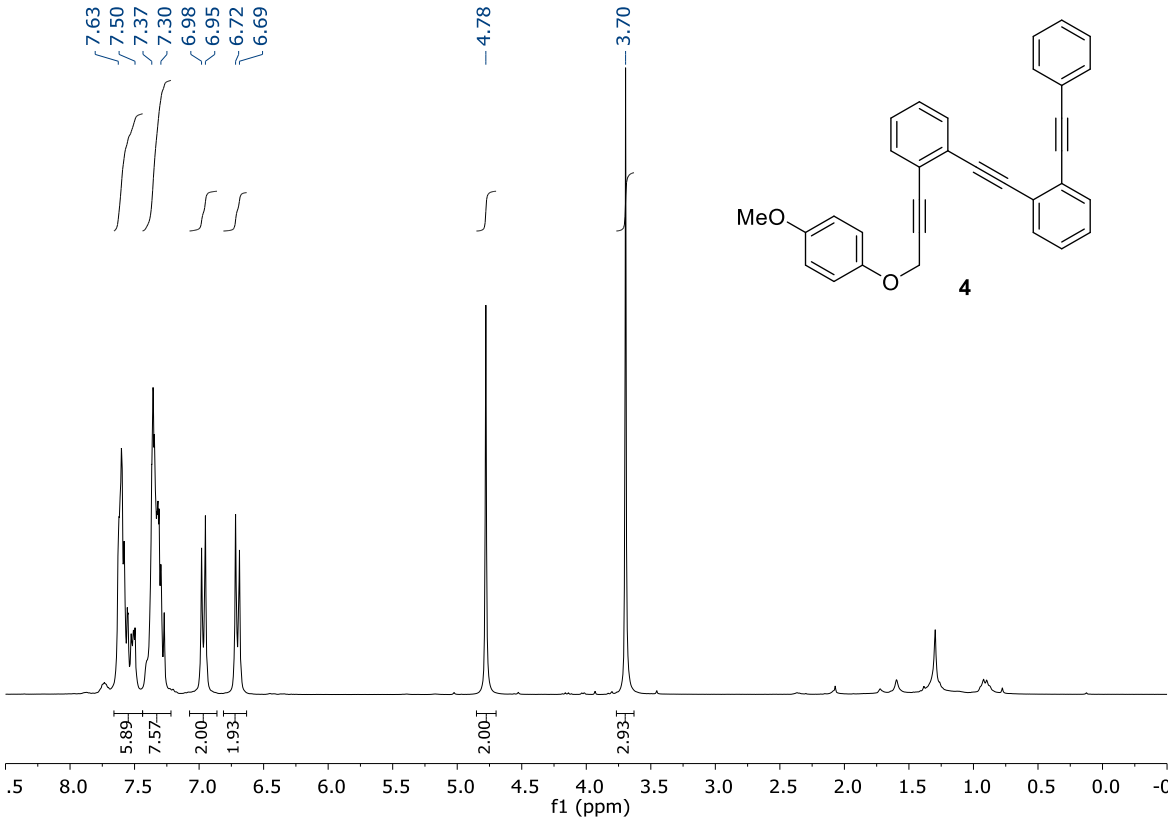
300 MHz ^{1}H NMR Spectrum of compound **2k** ($CDCl_3$, 300 K)



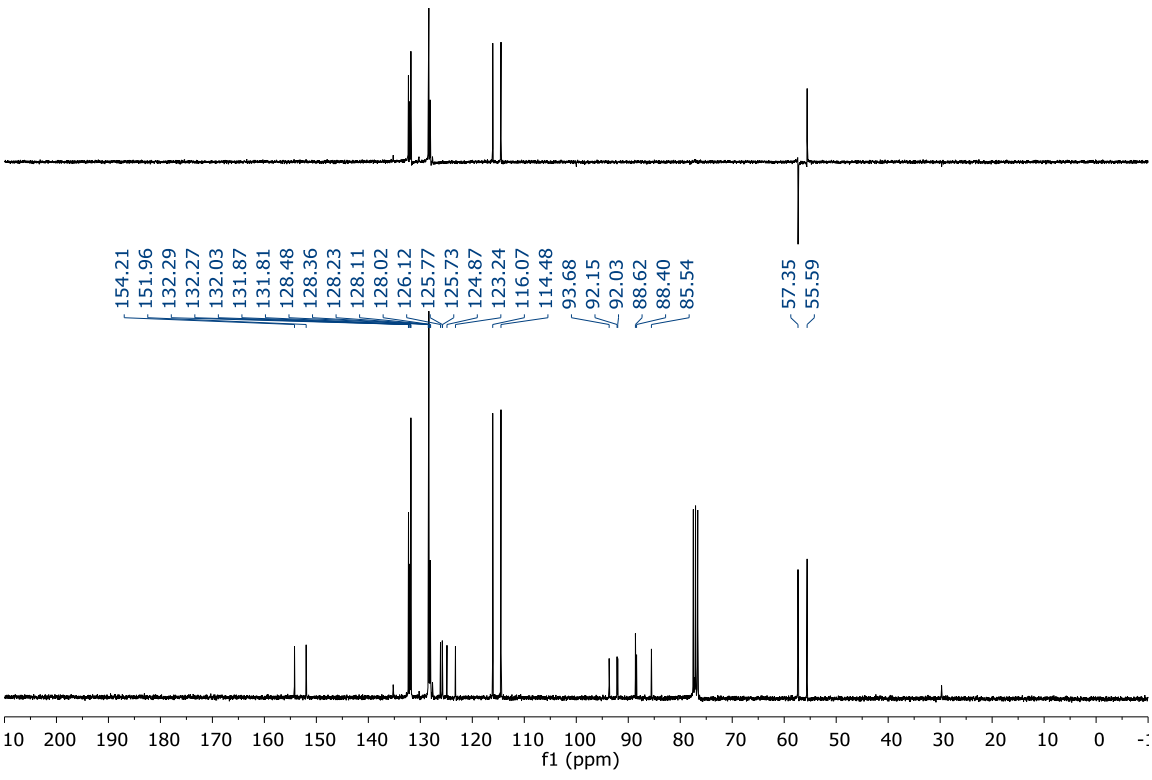
75 MHz ^{13}C NMR Spectrum of compound **2k** ($CDCl_3$, 300 K)



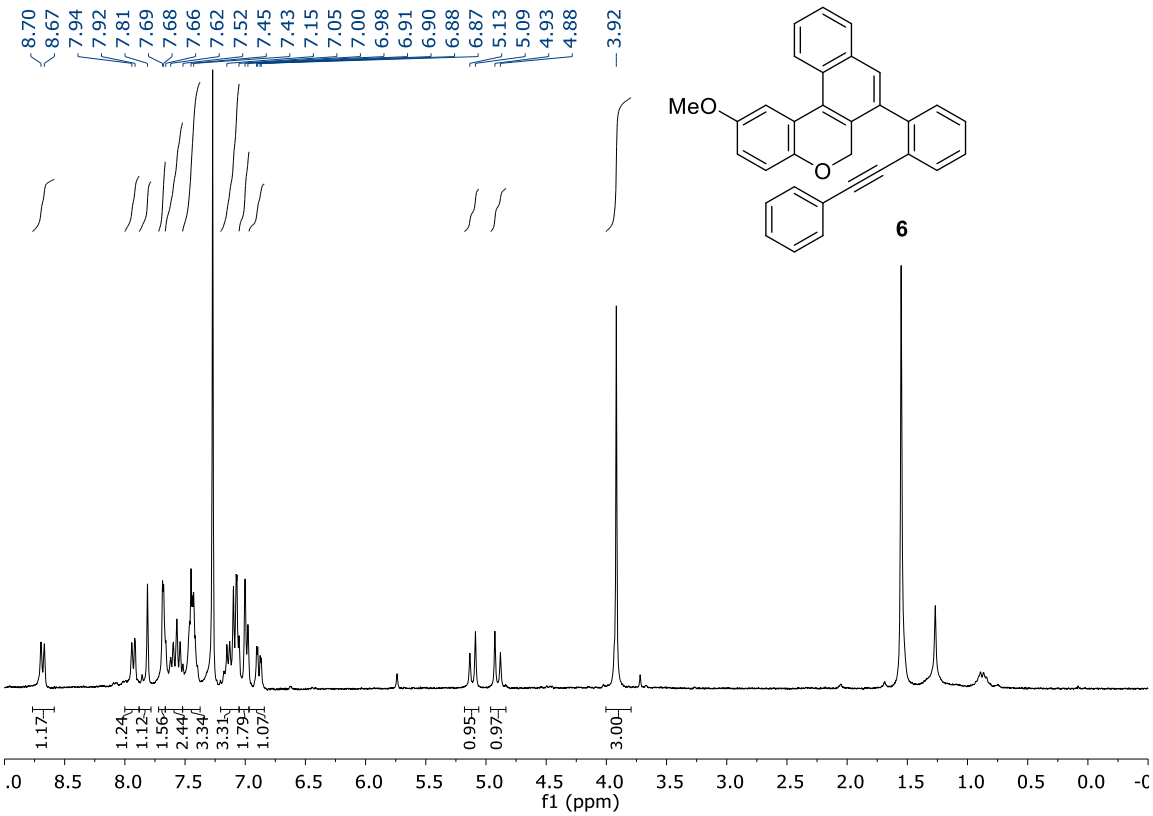
300 MHz ^{1}H NMR Spectrum of compound **4** ($CDCl_3$, 300 K)



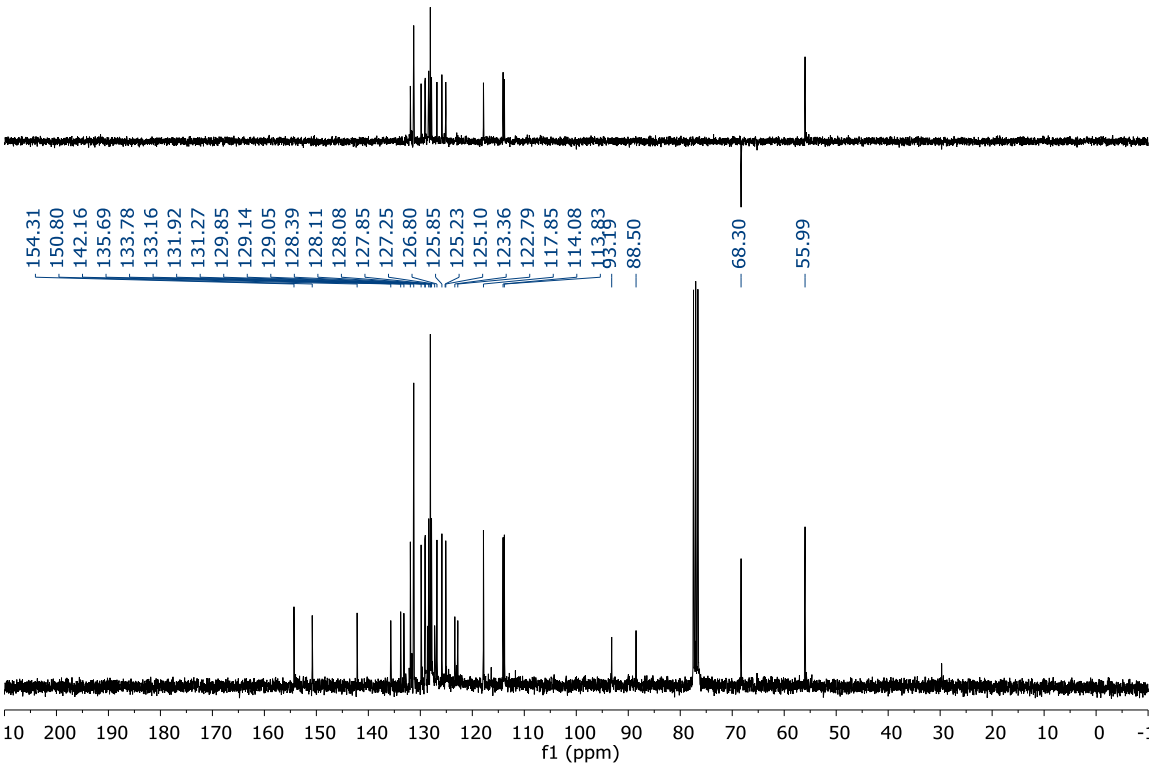
75 MHz ^{13}C NMR Spectrum of compound **4** ($CDCl_3$, 300 K)



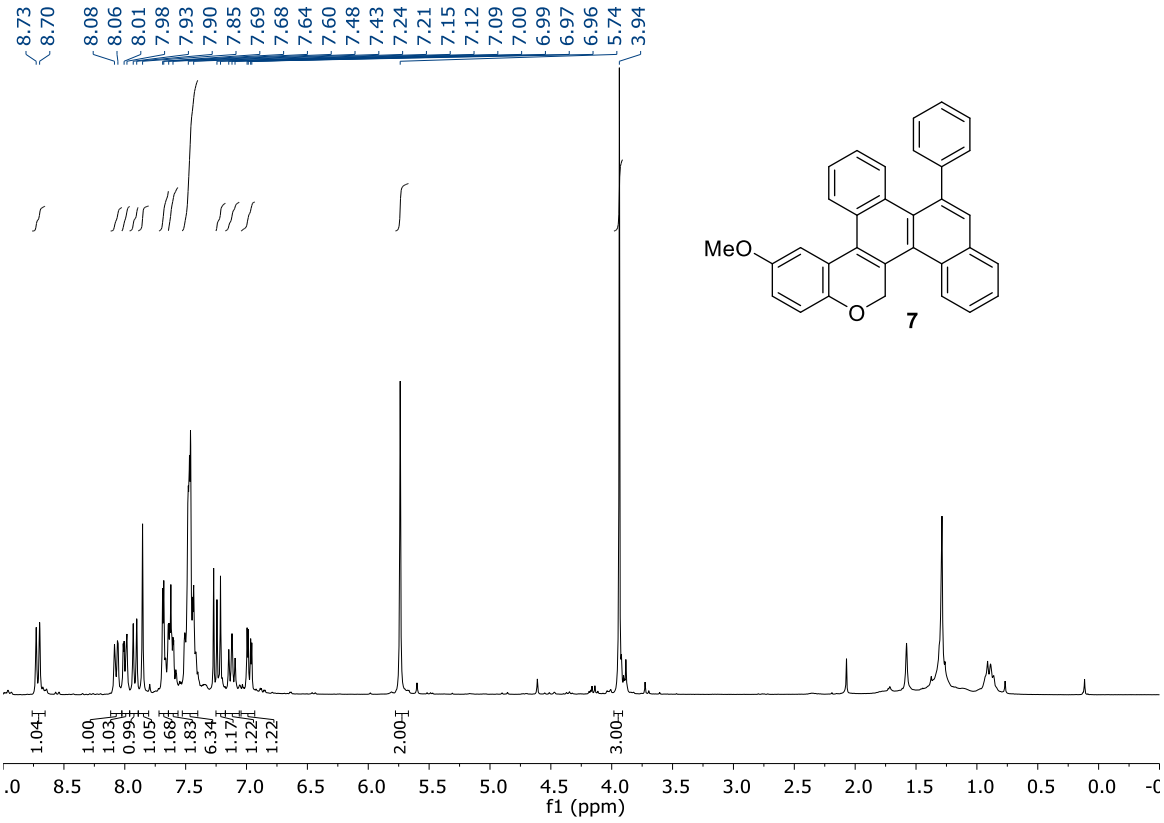
300 MHz ^{1}H NMR Spectrum of compound **6** ($CDCl_3$, 300 K)



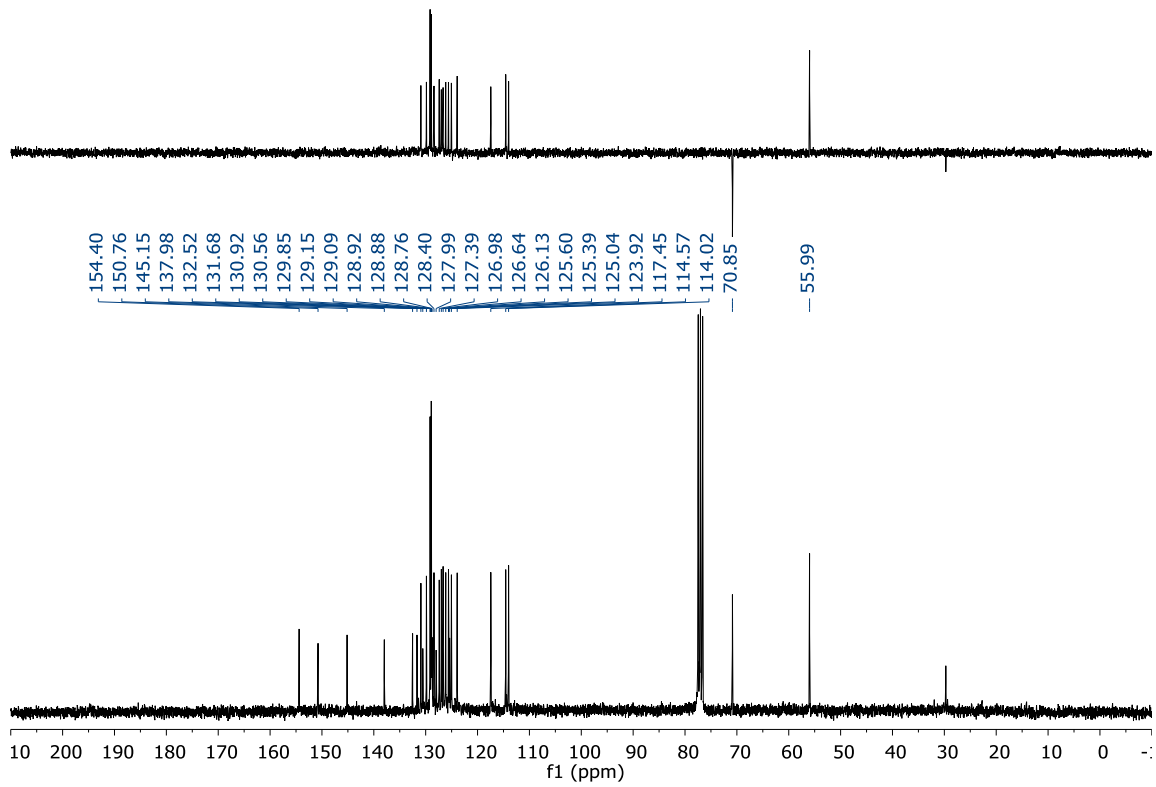
75 MHz ^{13}C NMR Spectrum of compound **6** ($CDCl_3$, 300 K)



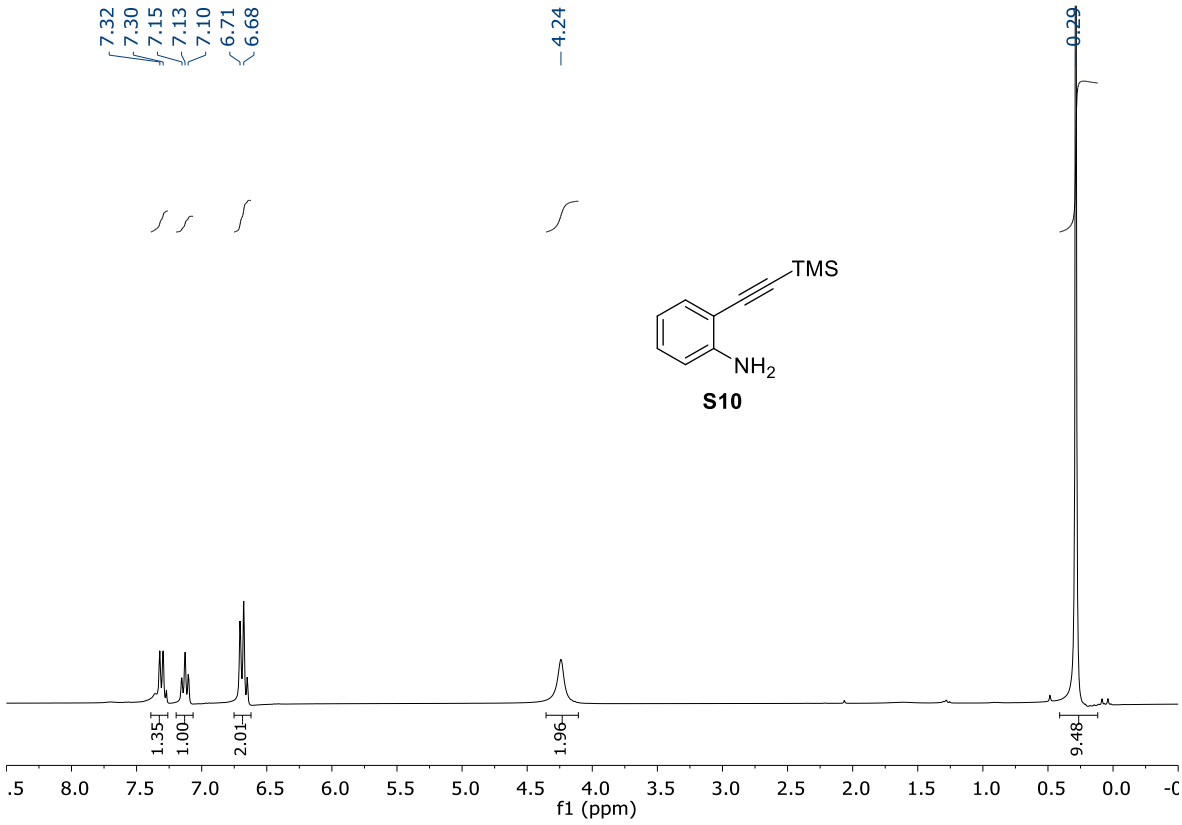
300 MHz ^{1}H NMR Spectrum of compound **7** ($CDCl_3$, 300 K)



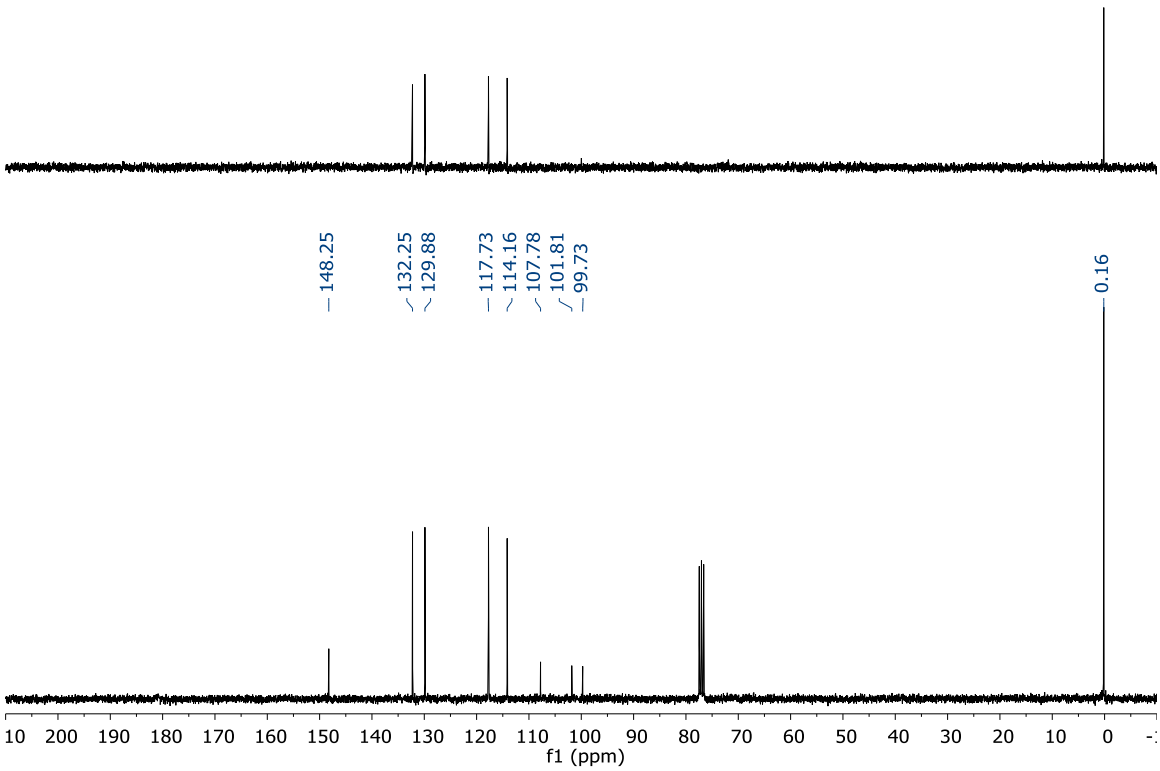
75 MHz ^{13}C NMR Spectrum of compound **7** ($CDCl_3$, 300 K)



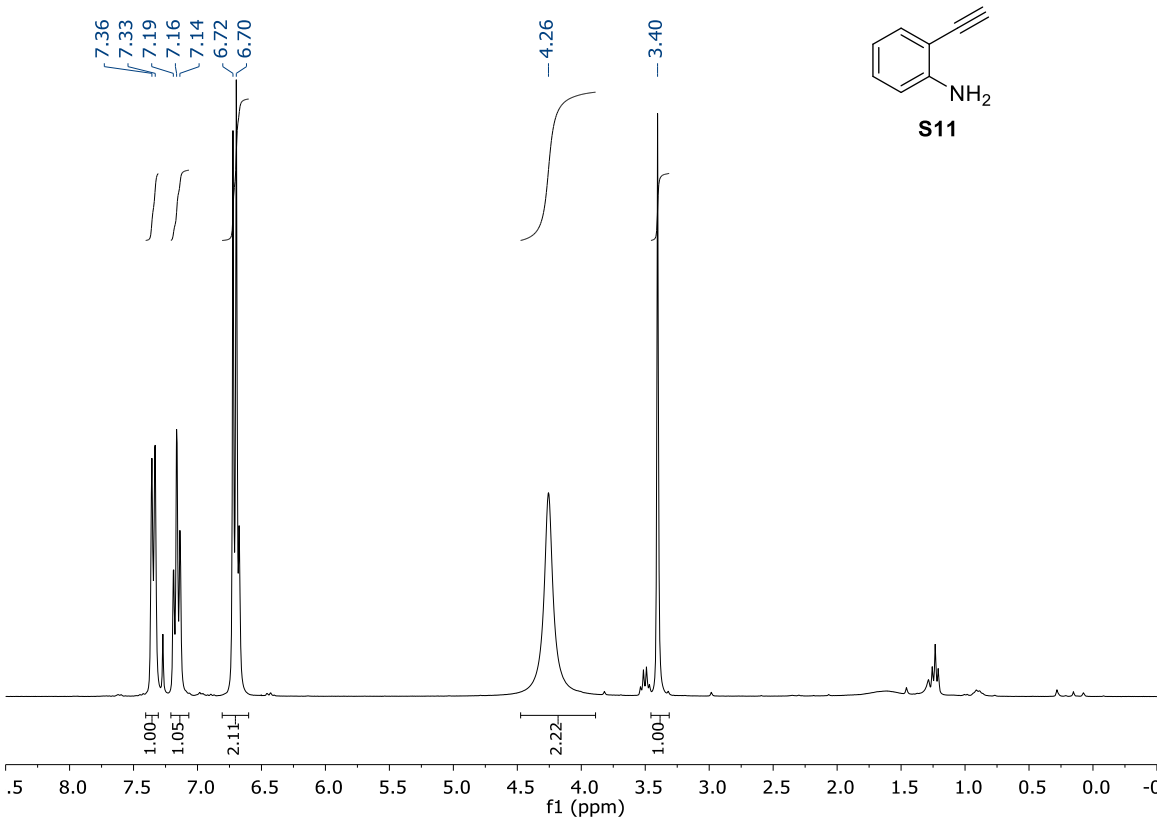
300 MHz ^{1}H NMR Spectrum of compound **S10** ($CDCl_3$, 300 K)



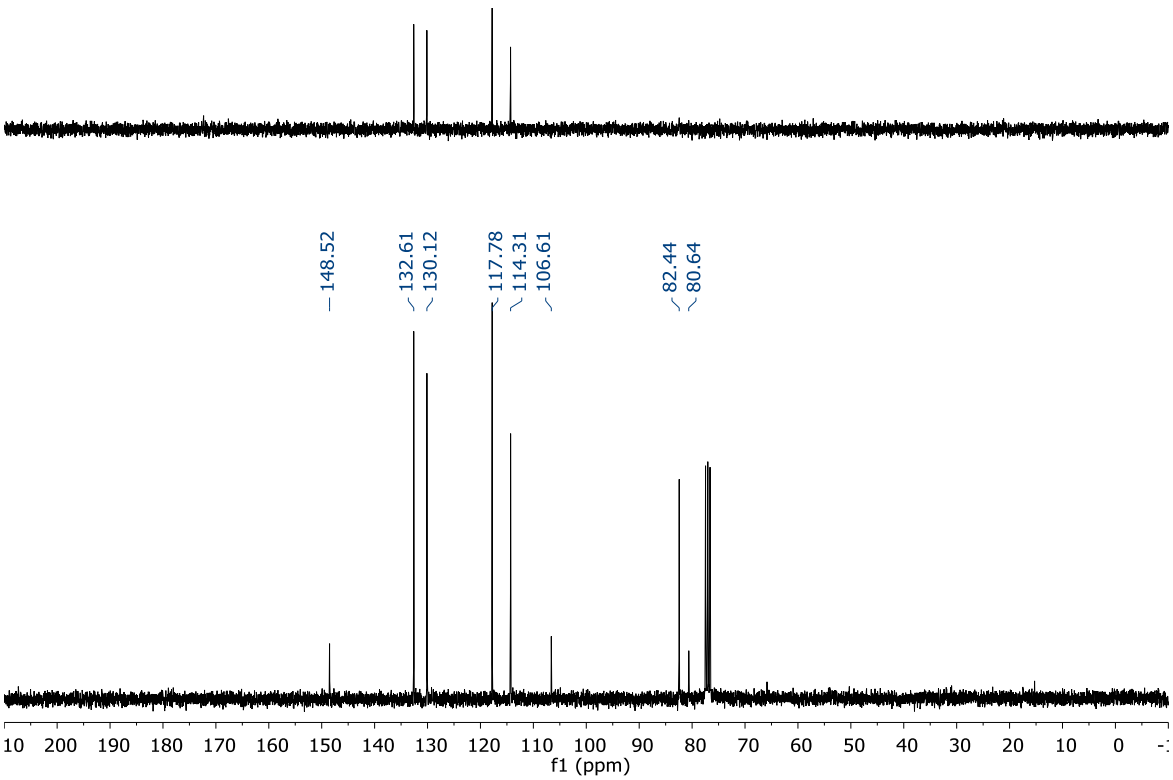
75 MHz ^{13}C NMR Spectrum of compound **S10** ($CDCl_3$, 300 K)



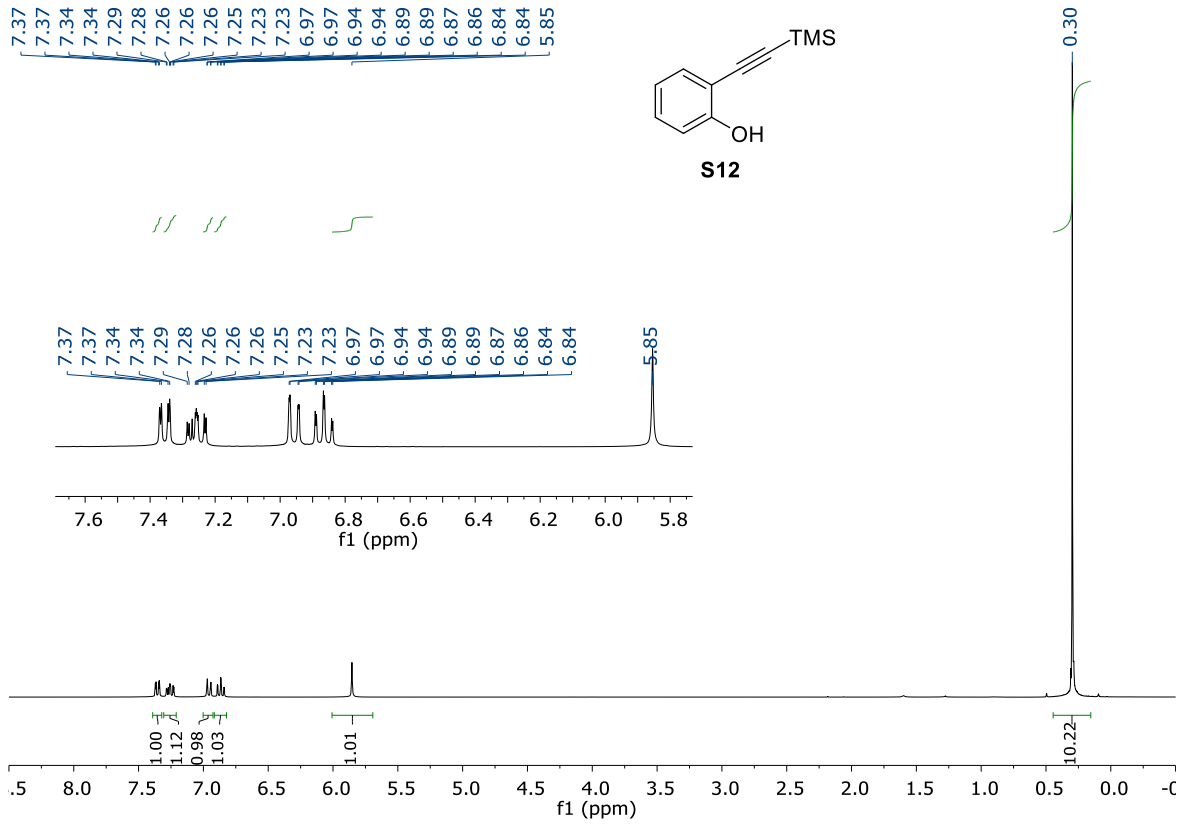
300 MHz ^{1}H NMR Spectrum of compound **S11** ($CDCl_3$, 300 K)



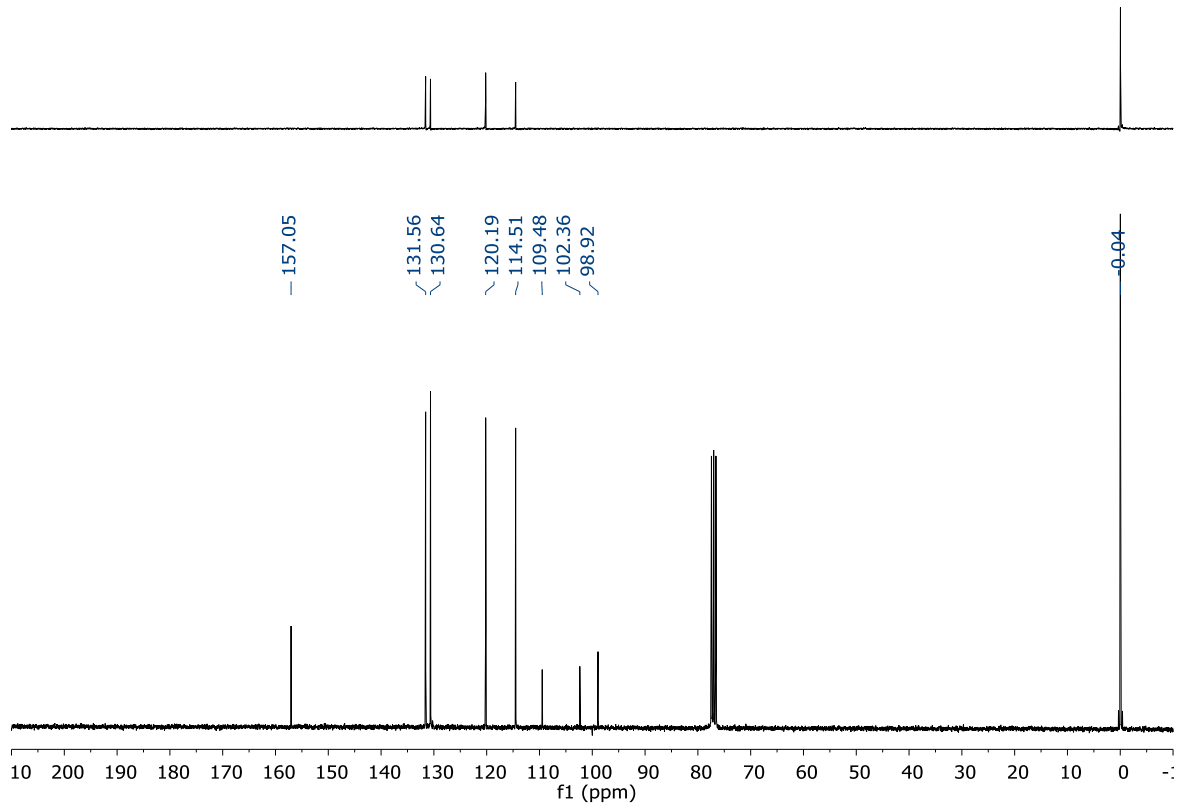
75 MHz ^{13}C NMR Spectrum of compound **S11** ($CDCl_3$, 300 K)



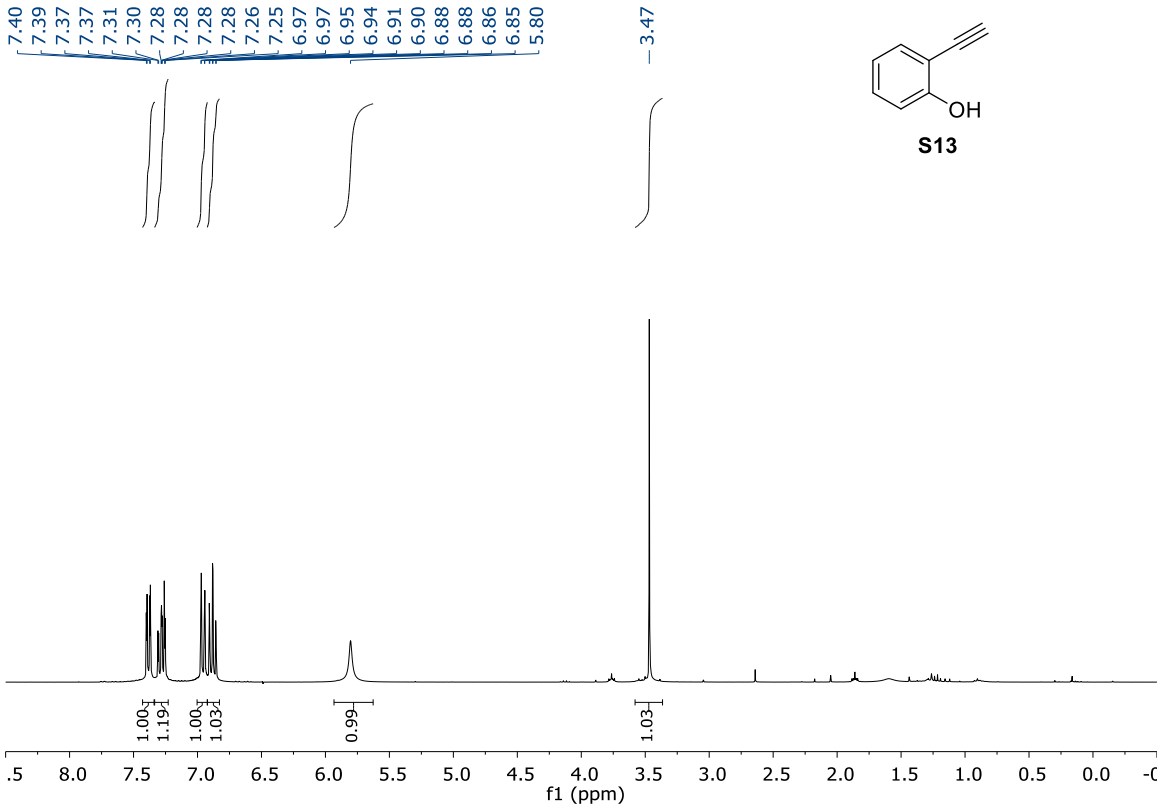
300 MHz ^{1}H NMR Spectrum of compound **S12** ($CDCl_3$, 300 K)



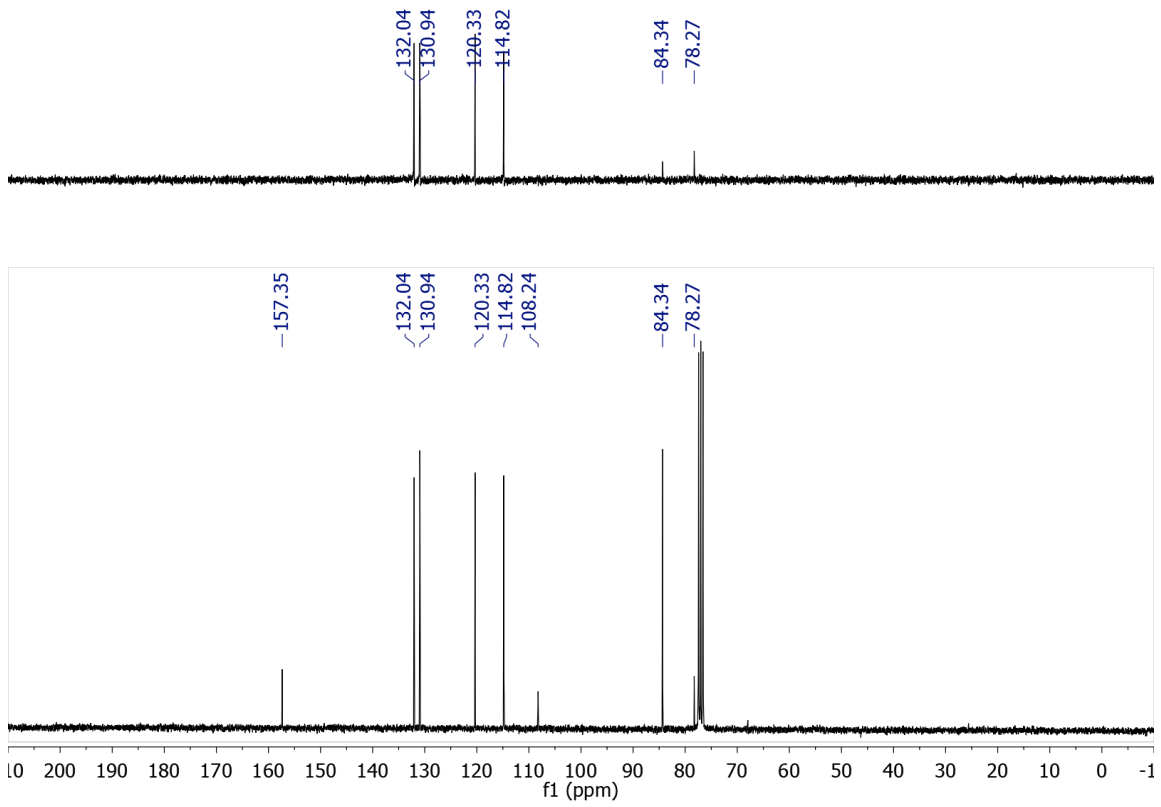
75 MHz ^{13}C NMR Spectrum of compound **S12** ($CDCl_3$, 300 K)



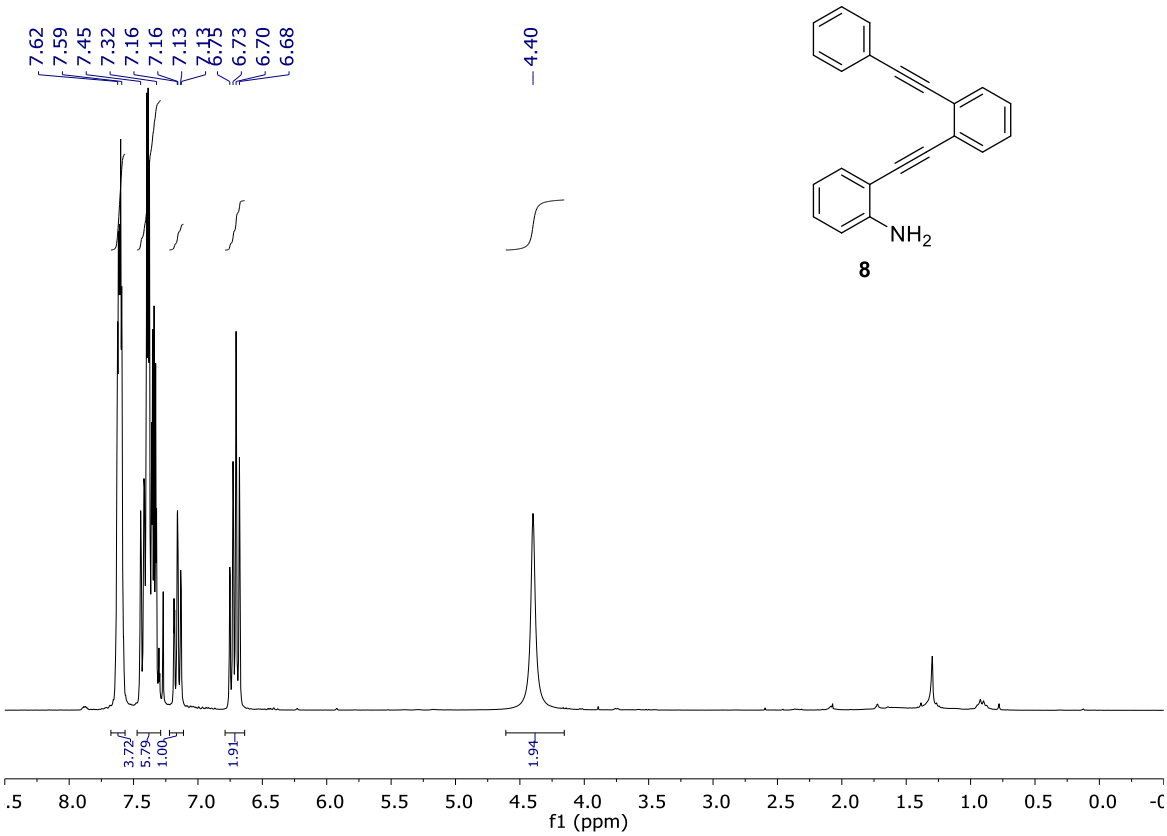
300 MHz ^{1}H NMR Spectrum of compound **S13** ($CDCl_3$, 300 K)



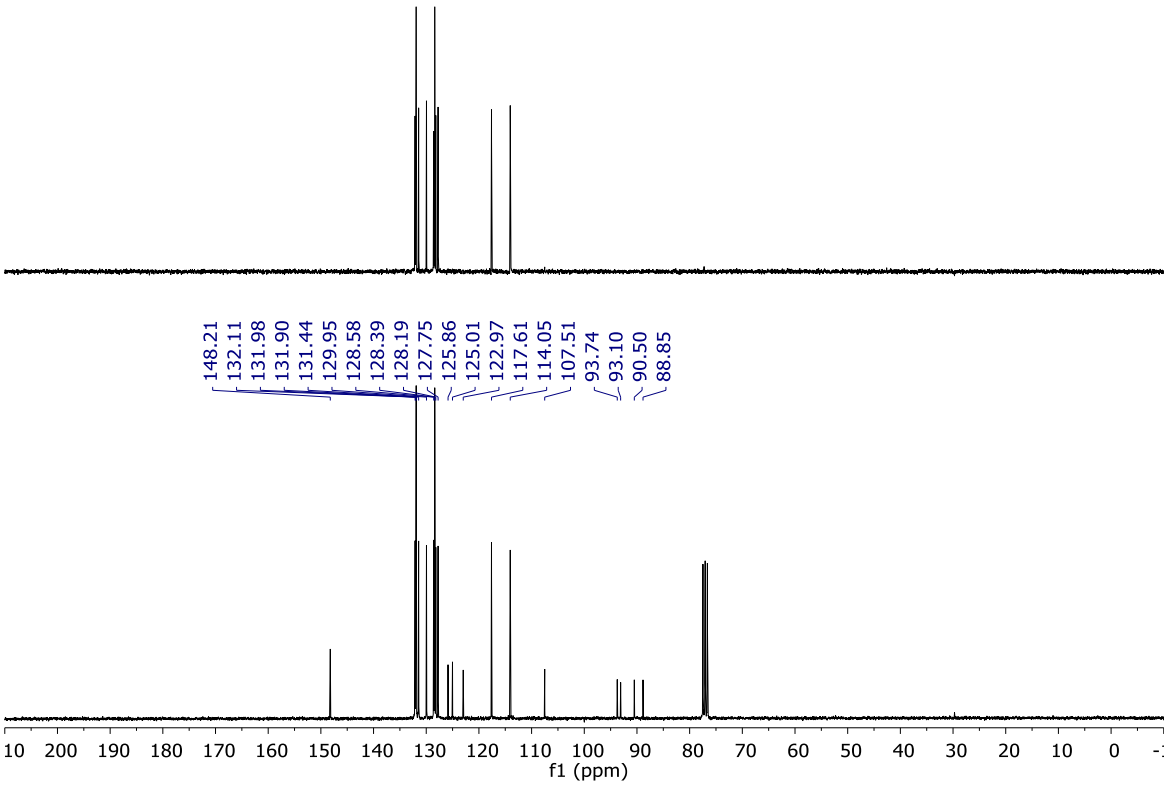
75 MHz ^{13}C NMR Spectrum of compound **S13** ($CDCl_3$, 300 K)



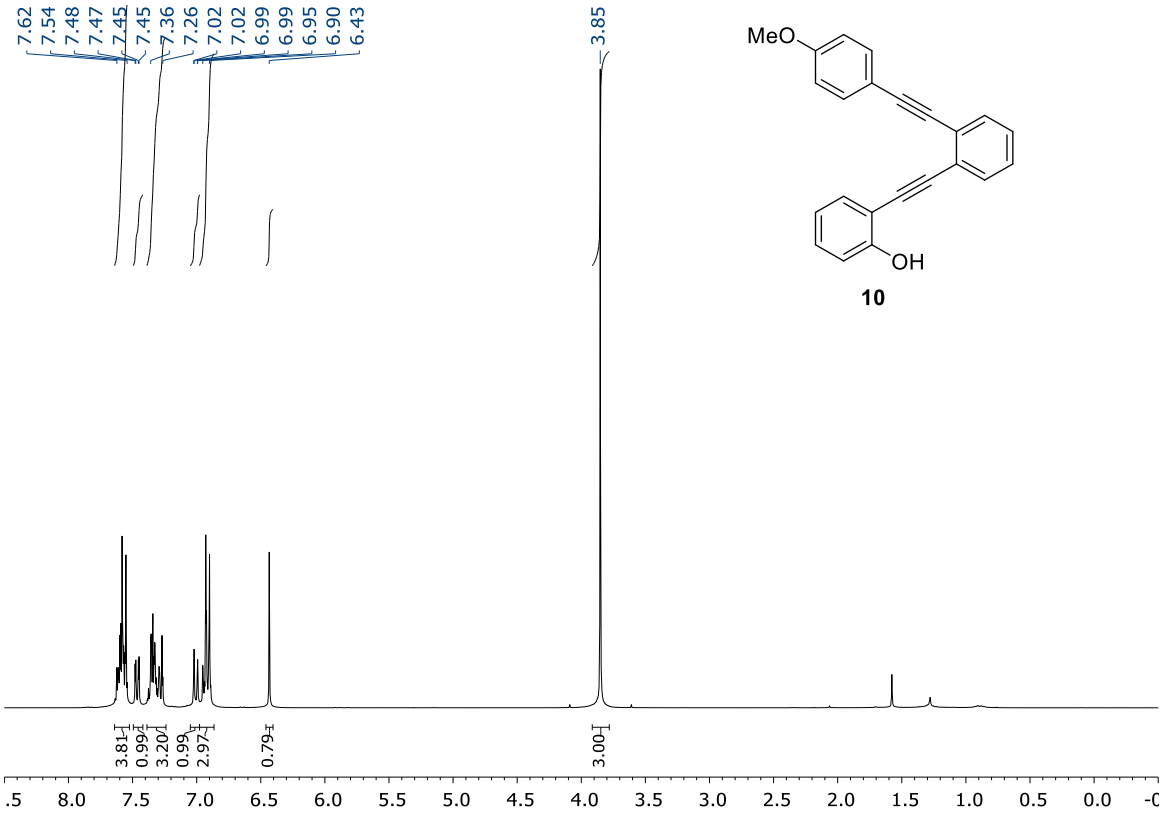
300 MHz ^{1}H NMR Spectrum of compound **8** ($CDCl_3$, 300 K)



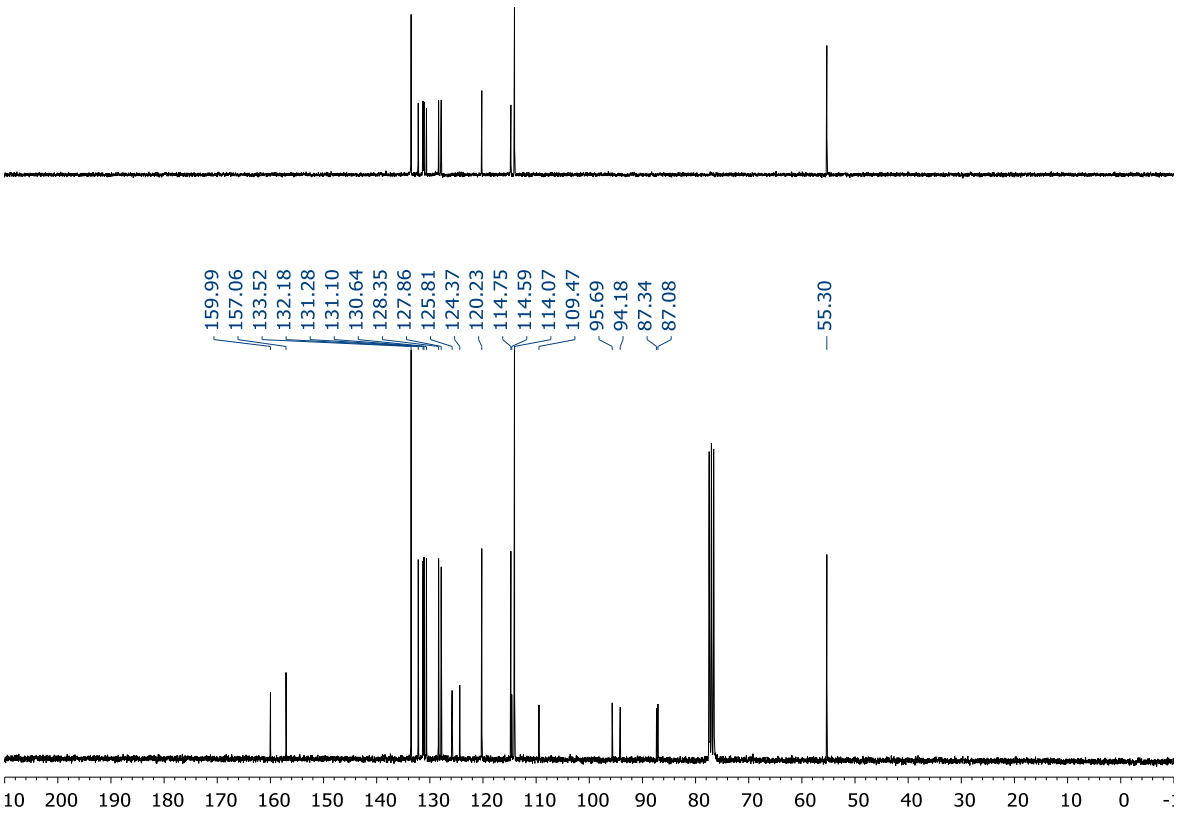
75 MHz ^{13}C NMR Spectrum of compound **8** ($CDCl_3$, 300 K)



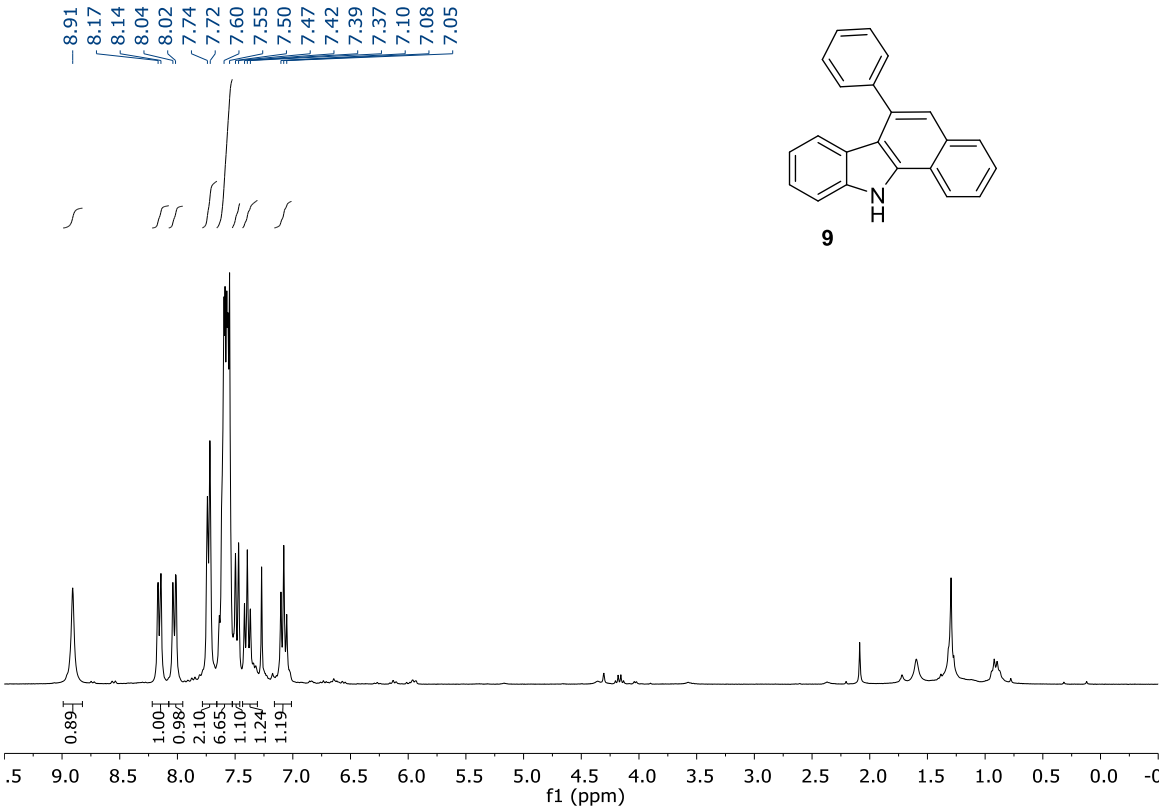
300 MHz ^{1}H NMR Spectrum of compound **10** ($CDCl_3$, 300 K)



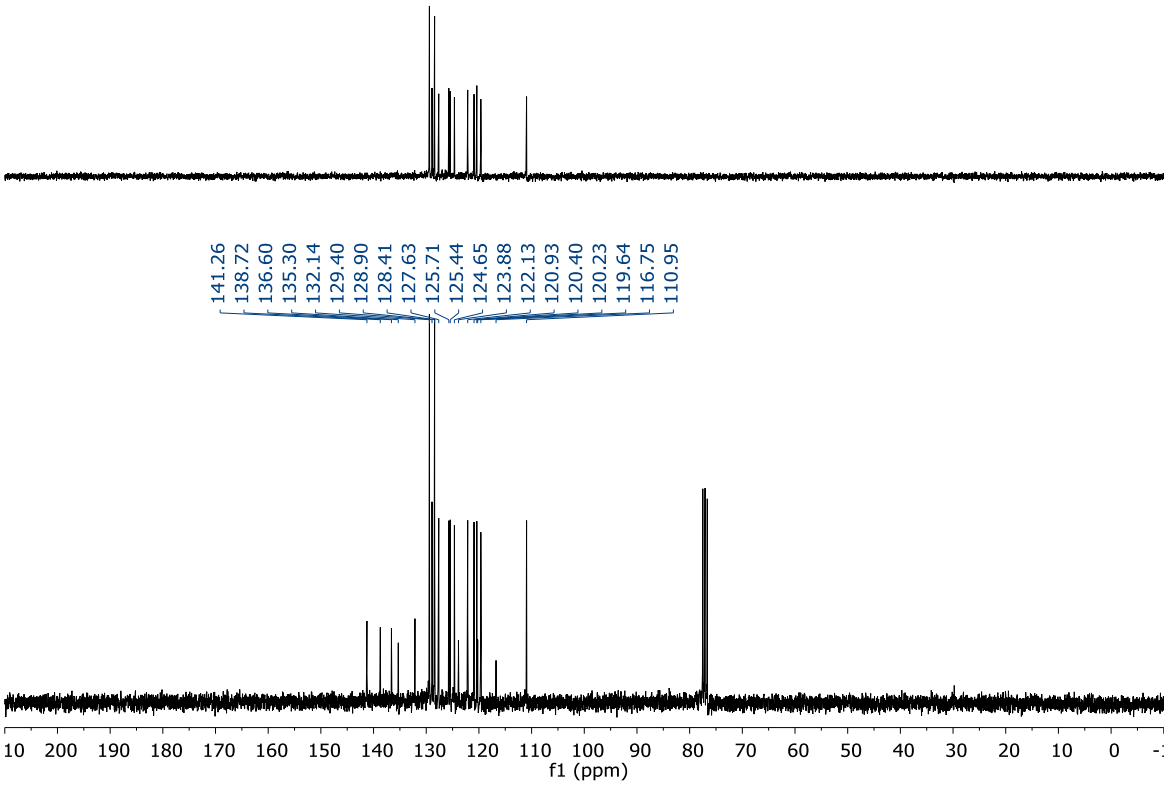
75 MHz ^{13}C NMR Spectrum of compound **10** ($CDCl_3$, 300 K)



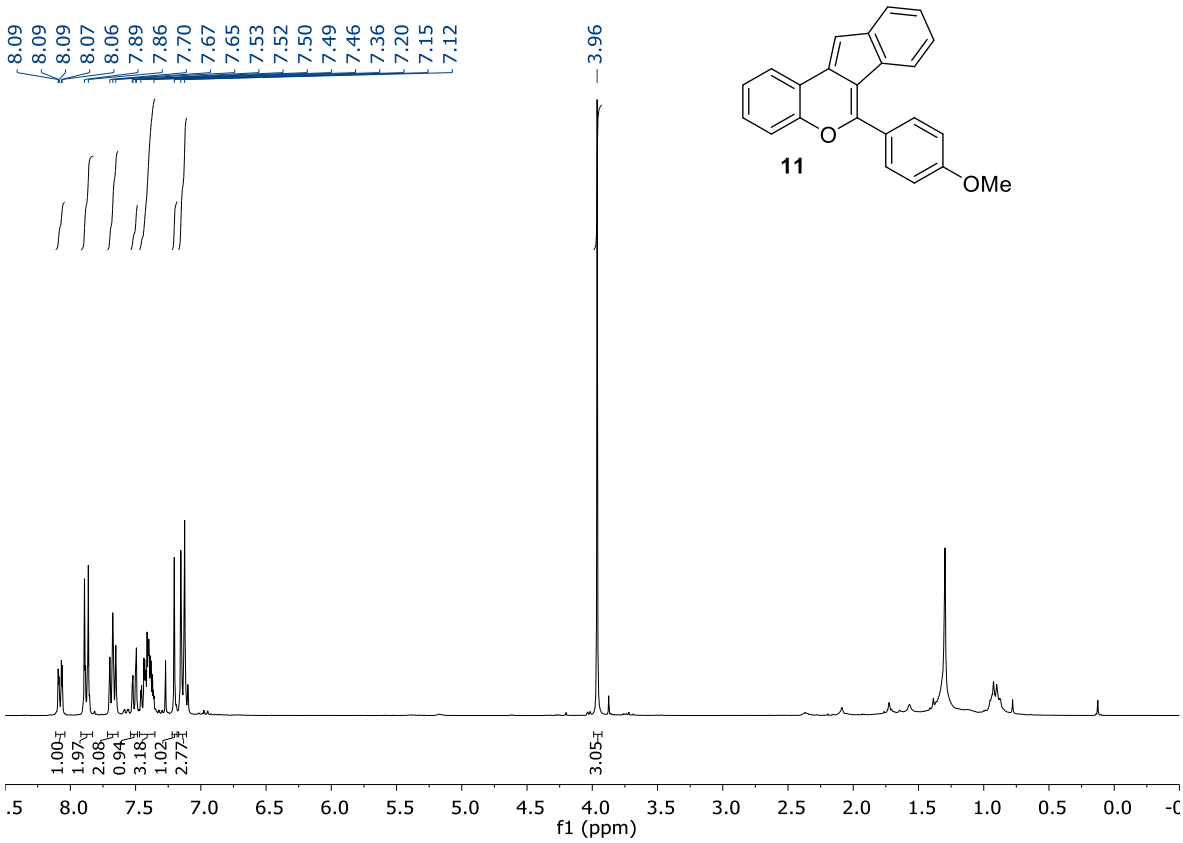
300 MHz ^{1}H NMR Spectrum of compound **9** ($CDCl_3$, 300 K)



75 MHz ^{13}C NMR Spectrum of compound **9** ($CDCl_3$, 300 K)



300 MHz ^{1}H NMR Spectrum of compound **11** ($CDCl_3$, 300 K)



75 MHz ^{13}C NMR Spectrum of compound **11** ($CDCl_3$, 300 K)