Supplementary Information (SI) for Organic & Biomolecular Chemistry.

SUPPLEMENTARY INFORMATION

Facile one-pot synthesis of 5-alkylidene-2,3,5,6,7,8-hexahydroimidazo[1,2-*a*]pyridines

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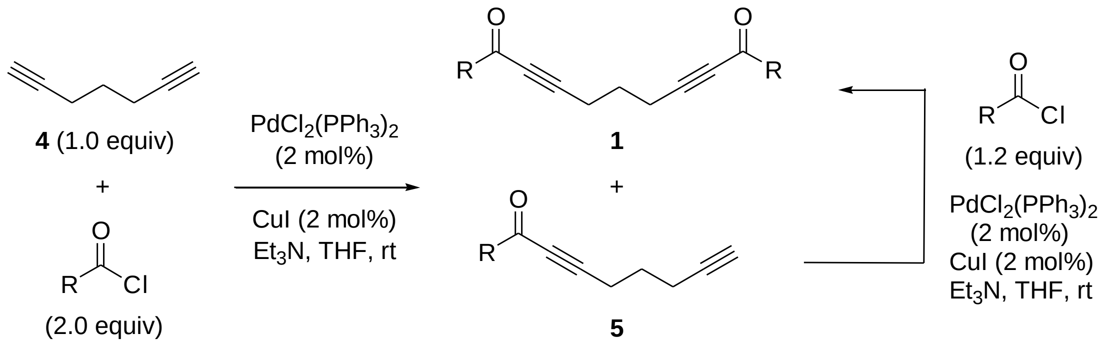
Experimental Section

General Information. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts were given in parts per million (ppm) relative to $CDCl_3$ (7.26 and 77.16 ppm in ^{1}H and ^{13}C NMR, respectively. Coupling constants (J) were given in hertz (Hz), and spin multiplicities were shown by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet) and m (multiplet). Infrared (IR) spectra were obtained using attenuated total reflection (ATR). Band positions were recorded in reciprocal centimeters (cm^{-1}). Mass spectra (MS) and high-resolution MS (HRMS) were obtained using electrospray ionization (ESI) with micro-Tof; m/z values are reported (for each measurement, the mass scale was recalibrated with sodium formate clusters, and samples were dissolved and measured in MeOH or CH_3CN). Flash chromatography was performed using thick-walled glass columns and “flash-grade” silica gel (230−400 mesh). Thin layer chromatography (TLC) was accomplished by using commercially prepared 0.25 mm silica gel plates. TLC plates were visualized by exposing them to UV light or iodine vapors. The relative proportions of solvents in chromatography solvent mixtures refer to the volume/volume ratio. All commercially available reagents were used directly without purification unless otherwise stated. All solvents used in reactions and chromatography were distilled and/or dried properly for purity. The inert atmosphere was created using slight positive pressure (ca. 0.1 psi) of argon. All glassware was dried in an oven prior to use.

Table S1. Synthesis of Symmetrical bis-α,β-Alkynic Ketones.[a]



Entry	R	Yield of 1 (%)	Yield of 5 (%)
1	C_6H_5	**1a** (47) [50][b]	**5a** (29)
2	*p*-Me-C_6H_4	**1b** (59)	**5b** (7)
3	*p*-Et-C_6H_4	**1c** (46)	**5c** (29)
4	*p*-CH_3-$(CH_2)_6$-C_6H_4	**1d** (37)	**5d** (11)
5	*o*-MeO-C_6H_4	**1e** (44)	**5e** (9)
6	*p*-MeO-C_6H_4	**1f** (63)	**5f** (11)
7	*p*-MeS-C_6H_4	**1g** (54)	**5g** (7)
8	*p*-Me_2N-C_6H_4	**1h** (46)	**5h** (6)
9	*o*-Br-C_6H_4	**1i** (33)	**5i** (47)
10	*m*-Br-C_6H_4	**1j** (35)	**5j** (17)
11	*p*-Br-C_6H_4	**1k** (64)	**5k** (25)
12	*m*-Cl-C_6H_4	**1l** (41)	**5l** (13)
13	*p*-Cl-C_6H_4	**1m** (64)	**5m** (6)
14	*o*-F-C_6H_4	**1n** (38)	**5n** (48)
15	*p*-F-C_6H_4	**1o** (34)	**5o** (28)
16	3,5-Cl_2-C_6H_3	**1p** (35)	**5p** (33)

[a] Isolated yields. [b] The yield of the product **1a** obtained from the reaction of **5a** with 1.2 equiv of benzoyl chloride is given in square parenthesis.

General Procedure 1. Synthesis of Symmetrical 1,9-Diarylnona-2,7-diyne-1,9-diones 1 (Table S1). To a stirred solution of the proper aryloyl chloride (3.0 mmol) in THF (12 mL) under argon was added $PdCl_2(PPh_3)_2$ (0.03 mmol) and Et_3N (1.8 mmol), and the resulting mixture was stirred for 10 min at room temperature and CuI (0.03 mmol) was added. After stirring the reaction mixture for another 10 min, 1,6-heptadiyne (**4**) (1.5 mmol) was added slowly, and the stirring at room temperature continued until the end of the reaction (The progress of the reaction was monitored by routine TLC analysis for the disappearance of 1,6-heptadiyne (**4**) using 9:1 hexane/ethyl acetate as the eluent). After the reaction was over, the solvent was removed on a rotary evaporator, and ethyl acetate (50 mL) and a saturated aqueous solution of NH_4Cl solution (50 mL) were added. After the layers were separated, the aqueous layer was extracted with ethyl acetate (2 x 50 mL). The combined organic layers were dried over $MgSO_4$ and evaporated on a rotary evaporator to give the crude product, which was purified by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as the eluent to afford the corresponding symmetrical 1,9-diarylnona-2,7-diyne-1,9-dione **1** and 1-arylocta-2,7-diyn-1-one **5**.

Synthesis of 1,9-Diphenylnona-2,7-diyne-1,9-dione (1a). Benzoyl chloride (458.4 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 92.6 mg (29%) of 1-phenylocta-2,7-diyne-1-one (**5a**) as a dark brownish orange oil (R_f = 0.62 in 4:1 hexane/ethyl acetate). Second fraction yielded 227.7 mg (47%) of the indicated product **1a** as an orange solid (R_f = 0.37 in 4:1 hexane/ethyl acetate; mp 55.5–58.2 ^{o}C).

1,9-Diphenylnona-2,7-diyne-1,9-dione (**1a**) was also synthesized from 1-phenylocta-2,7-diyne-1-one (**5a**) as summarized below:

Benzoyl chloride (158.9 mg, 1.13 mmol), $PdCl_2(PPh_3)_2$ (13.3 mg, 0.019 mmol), Et_3N (115.1 mg, 1.13 mmol), CuI (2.7 mg, 0.019 mmol) and 1-phenylocta-2,7-diyne-1-one (**5a**) (184.0 mg, 0.94 mmol) were employed to afford 141.2 mg (50%) of the indicated product **1a** as an orange solid (R_f = 0.37 in 4:1 hexane/ethyl acetate).

1a:[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.8, 1.2 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 4H), 2.70 (t, *J* = 7.0 Hz, 4H), 2.03 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8 (CO), 136.5 (C), 134.0 (CH), 129.4 (CH), 128.5 (CH), 94.3 (C), 80.3 (C), 25.9 (CH_2), 18.3 (CH_2); IR (neat): 3055, 2233, 2195, 1635, 1577, 1445, 1311, 1261, 1171, 1015, 921, 893, 793, 691, 615, 502, 425 cm^{-1}; MS (ESI, *m/z*): 301.12 [M+H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{17}O_2$: 301.1223 [M+H]$^+$, found: 301.1227.

5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–8.10 (m, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.50–7.43 (m, 2H), 2.65 (t, *J* = 7.1 Hz, 2H), 2.39 (td, *J* = 6.8, 2.3 Hz, 2H), 2.02 (t, *J* = 2.3 Hz, 1H), 1.89 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1 (CO), 136.7 (C), 134.0 (CH), 129.6 (CH), 128.6 (CH), 95.3 (C), 82.7 (C), 80.0 (C), 69.6 (CH), 26.6 (CH_2), 18.1 (CH_2), 17.7 (CH_2); IR (neat): 2922, 2853, 2236, 2198, 1686, 1642, 1604, 1570, 1457, 1414, 1309, 1264, 1176, 1114, 1018, 920, 851, 754, 694, 635, 549 cm^{-1}; MS (ESI, *m/z*): 197.09 [M+H]$^+$; HRMS (ESI) calcd. for $C_{14}H_{13}O$: 197.0961 [M+H]$^+$, found: 197.0960.

Synthesis of 1,9-Di-*p*-tolylnona-2,7-diyne-1,9-dione (1b). 4-Methylbenzoyl chloride (*p*-toluoyl chloride) (504 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 24.0 mg (7%) of 1-*p*-tolylocta-2,7-diyne-1-one (**5b**) as a brownish orange oil (*R*$_f$ = 0.64 in 4:1 hexane/ethyl acetate). Second fraction yielded 314.9 mg (59%) of the indicated product **1b** as an orange solid (*R*$_f$ = 0.37 in 4:1 hexane/ethyl acetate; mp 77.9–81.2 ^{o}C).

1b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.6 Hz, 4H), 7.26 (d, *J* = 7.4 Hz, 4H), 2.71 (t, *J* = 7.0 Hz, 4H), 2.41 (s, 6H), 2.04 (p, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7 (CO), 145.2 (C–Me), 134.4 (C), 129.6 (CH), 129.3 (CH), 93.8 (C), 80.4 (C), 26.0 (CH_2), 21.8 (CH_3), 18.4 (CH_2); IR (neat): 3742, 2919, 2242, 2202, 1744, 1631, 1603, 1571, 1404, 1267, 1168, 1111, 1013, 925, 894, 831, 793, 738, 677, 591, 521, 469, 418 cm^{-1}; MS (ESI, *m/z*): 329.15 [M+H]$^+$; HRMS (ESI) calcd. for $C_{23}H_{21}O_2$: 329.1536 [M+H]$^+$, found: 329.1538.

5b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.67 (t, *J* = 7.0 Hz, 2H), 2.46 (s, 5H), 2.05 (t, *J* = 2.4 Hz, 1H), 1.91 (p, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8 (CO), 162.6 (C), 145.6 (C), 130.6 (CH), 129.6 (CH), 94.7 (C), 82.8 (C), 80.1 (C), 69.6 (CH), 26.7 (CH_2), 21.9 (CH_3), 18.2 (CH_2), 17.7 (CH_2); IR (neat): 3290, 2935, 2235, 2195, 1781, 1717, 1637, 1603, 1571, 1540, 1507, 1455, 1430, 1309, 1266, 1221, 1174, 1110, 1038, 1003, 919, 834, 794, 741, 682, 634, 594, 517, 472, 445, 435, 425, 417 cm^{-1}. MS (ESI, *m/z*): 211.10 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{15}O$: 211.1117 [M+H]$^+$, found: 211.1077.

Synthesis of 1,9-Bis(4-ethylphenyl)nona-2,7-diyne-1,9-dione (1c). 4-Ethylbenzoyl chloride (549.7 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 106.7 mg (29%) of 1-(4-ethylphenyl)octa-2,7-diyne-1-one (**5c**) as an orange oil (R_f = 0.68 in 4:1 hexane/ethyl acetate). Second fraction yielded 265.9 mg (46%) of the indicated product **1c** as a brownish orange oil (R_f = 0.4 in 4:1 hexane/ethyl acetate).

1c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 4H), 7.20 (d, *J* = 8.1 Hz, 4H), 2.66-2.56 (m, 8H), 1.96 (p, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8 (CO), 151.4 (C–CH_2CH_3), 134.7 (C), 129.9 (CH), 128.2 (CH), 93.8 (C), 80.5 (C), 29.1 (CH_2), 26.1 (CH_2), 18.5 (CH_2), 15.2 (CH_3); IR (neat): 2965, 2933, 2872, 2235, 2196, 1637, 1602, 1568, 1414, 1308, 1262, 1175, 1112, 1050, 976, 919, 898, 876, 848, 753, 690, 629, 594, 518, 419 cm^{-1}; MS (ESI, *m/z*): 357.18 $[M+H]^+$; HRMS (ESI) calcd. for $C_{25}H_{25}O_2$: 357.1849 $[M+H]^+$, found: 357.1844.

5c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 2.75–2.58 (m, 4H), 2.46-2.27 (m, 2H), 2.04 (t, *J* = 2.6 Hz, 1H), 1.89 (p, *J* = 6.9 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7 (CO), 151.2 (C), 134.7 (C), 129.8 (CH), 128.1 (CH), 94.6 (C), 82.7 (C), 80.1 (C), 69.6 (CH), 29.0 (CH_2), 26.6 (CH_2), 18.1 (CH_2), 17.7 (CH_2), 15.2 (CH_3); IR (neat): 3298, 2965, 2934, 2235, 2197, 1717, 1686, 1638, 1603, 1569, 1541, 1507, 1456, 1415, 1309, 1264, 1176, 1110, 1051, 1017, 993, 905, 877, 849, 781, 753, 691, 631, 595, 518 cm^{-1}; MS (ESI, *m/z*): 225.12 $[M+H]^+$; HRMS (ESI) calcd. for $C_{16}H_{17}O$: 225.1274 $[M+H]^+$, found: 225.1279.

Synthesis of 1,9-Bis(4-heptylphenyl)nona-2,7-diyne-1,9-dione (1d). 4-Heptylbenzoyl chloride (778.3 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 53.7 mg (11%) of (4-heptylphenyl)octa-2,7-diyne-1-one (**5d**) as a dark orange oil (R_f = 0.82 in 4:1 hexane/ethyl acetate). Second fraction yielded 303.2 mg (37%) of the indicated product **1d** as a dark orange oil (R_f = 0.76 in 4:1 hexane/ethyl acetate).

1d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 4H), 7.29 (d, *J* = 8.2 Hz, 4H), 2.74–2.67 (m, 6H), 2.06 (p, *J* = 7.0 Hz, 2H), 1.71–1.56 (m, 6H), 1.35-1.26 (m, 16H), 0.89 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8 (CO), 150.2 (C), 134.6 (C), 129.8 (CH), 128.7 (CH), 93.8 (C), 80.5 (C), 36.2 (CH_2), 31.8 (CH_2), 31.1 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 18.5 (CH_2), 14.2 (CH_3); IR (neat): 2923, 2853, 2236, 2196, 1733, 1716, 1684, 1643, 1603, 1570, 1540, 1507, 1457, 1415, 1375, 1309, 1264, 1175, 1113, 1017, 975, 851, 802, 753, 722, 693, 634, 525, 470, 434 cm^{-1}; MS (ESI, *m/z*): 497.34 [M+H]$^+$; HRMS (ESI) calcd. for $C_{35}H_{45}O_2$: 497.3414 [M+H]$^+$, found: 497.3415.

5d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 10.4 Hz, 2H), 2.63 (m, 4H), 2.37 (td, *J* = 6.9, 2.6 Hz, 2H), 1.99 (t, *J* = 2.6 Hz, 1H), 1.87 (p, *J* = 7.0 Hz, 2H), 1.60 (m, 2H), 1.36–1.11 (m, 8H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0 (CO), 150.2 (C), 134.8 (C), 129.9 (CH), 128.8 (CH), 94.7 (C), 82.9 (C), 80.3 (C), 69.6 (CH), 36.3 (CH_2), 31.9 (CH_2), 31.2 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 26.8 (CH_2), 22.8 (CH_2), 18.3 (CH_2), 17.9 (CH_2), 14.2 (CH_3); IR (neat): 2925, 2854, 2235, 2202, 1772, 1717, 1684, 1642, 1603, 1569, 1521, 1507, 1457, 1414, 1309, 1265, 1174, 1111, 1038, 995, 876, 850, 753, 693, 628, 526 cm^{-1}; MS (ESI, *m/z*): 295.20 [M+H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{27}O$: 295.2056 [M+H]$^+$, found: 295.2058.

Synthesis of 1,9-Bis(2-methoxyphenyl)nona-2,7-diyne-1,9-dione (1e). 2-Methoxybenzoyl chloride (945 mg, 5.54 mmol), $PdCl_2(PPh_3)_2$ (39 mg, 0.055 mmol), Et_3N (363 mg, 3.56 mmol), CuI (11 mg, 0.055 mmol) and 1,6-heptadiyne (**4**) (255 mg, 2.77 mmol) were employed. Two fractions were isolated. First fraction afforded 58.8 mg (9%) of 1-(2-methoxyphenyl)octa-2,7-diyne-1-one (**5e**) as a yellow oil (R_f = 0.57 in 4:1 hexane/ethyl acetate). Second fraction yielded 437.6 mg (44%) of the indicated product **1e** as an orange oil (R_f = 0.34 in 4:1 hexane/ethyl acetate).

1e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 2H), 7.01–6.92 (m, 4H), 3.78 (s, 6H), 2.53 (t, *J* = 7.1 Hz, 4H), 2.01 (p, *J* = 8.4 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0 (CO), 158.4 (C–OMe), 130.9 (CH), 130.8 (C), 126.0 (CH), 121.0 (CH), 111.6 (CH), 83.4 (C), 69.4 (C), 55.8 (OCH_3), 25.9 (CH_2), 17.2 (CH_2); IR (neat): 2968, 2934, 2354, 2322, 1736, 1654, 1597, 1541, 1507, 1484, 1457, 1435, 1362, 1282, 1241, 1215, 1162, 1115, 1019, 867, 753, 630, 538 cm^{-1}; MS (ESI, *m/z*): 361.14 [M+H]$^+$; HRMS (ESI) calcd. for $C_{23}H_{21}O_4$: 361.1434 [M+H]$^+$, found: 361.1446.

5e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H), 3.08 (t, *J* = 7.5 Hz, 1H), 2.30 (td, *J* = 7.2, 2.4 Hz, 2H), 1.98 (t, *J* = 2.1 Hz, 2H), 1.91 (p, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9 (CO), 158.3 (C–OMe), 133.8 (CH), 130.8 (C), 128.5 (CH), 120.9 (CH), 111.7 (CH), 83.8 (2xC), 80.0 (C), 68.9 (CH), 55.8 (OCH_3), 35.7 (CH_2), 26.9 (CH_2), 17.9 (CH_2) (Note that two C peaks overlap on each other); IR (neat): 2941, 2354, 1735, 1654, 1597, 1558, 1540, 1520, 1507, 1485, 1457, 1434, 1363, 1282, 1241, 1215, 1180, 1162, 1116, 1077, 1020, 862, 753, 632, 527 cm^{-1}; MS (ESI, *m/z*): 227.10 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{15}O_2$: 227.1067 [M+H]$^+$, found: 227.1052.

Synthesis of 1,9-Bis(4-methoxyphenyl)nona-2,7-diyne-1,9-dione (1f). 4-Methoxybenzoyl chloride (556.1 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 42 mg (11%) of 1-(4-methoxyphenyl)octa-2,7-diyne-1-one (**5f**) as a brownish orange oil (R_f = 0.41 in 4:1 hexane/ethyl acetate). Second fraction yielded 369.3 mg (63%) of the indicated product **1f** as a brownish orange oil (R_f = 0.13 in 4:1 hexane/ethyl acetate).

1f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.9 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 4H), 3.86 (s, 6H), 2.69 (t, *J* = 7.0 Hz, 4H), 2.02 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8 (CO), 164.5 (C–OMe), 132.0 (CH), 130.1 (C), 113.9 (CH), 93.6 (C), 80.5 (C), 55.7 (OCH_3), 26.1 (CH_2), 18.5 (CH_2); IR (neat): 2915, 2849, 2237, 2197, 1735, 1594, 1571, 1507, 1458, 1420, 1252, 1164, 1110, 1021, 898, 842, 755, 685, 596, 507 cm^{-1}; MS (ESI, *m/z*): 361.14 [M+H]$^+$; HRMS (ESI) calcd. for $C_{23}H_{21}O_4$: 361.1434 [M+H]$^+$, found: 361.1439.

5f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 2.59 (t, *J* = 7.1 Hz, 2H), 2.34 (td, *J* = 6.9, 2.6 Hz, 2H), 1.99 (t, *J* = 2.6 Hz, 1H), 1.84 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7 (CO), 164.3 (C–OMe), 131.9 (CH), 130.1 (C), 113.8 (CH), 94.3 (C), 82.8 (C), 80.0 (C), 69.6 (C), 55.5 (OCH_3), 26.6 (CH_2), 18.1 (CH_2), 17.7 (CH_2); IR (neat): 2933, 2838, 2234, 2196, 1716, 1631, 1591, 1570, 1456, 1420, 1317, 1250, 1162, 1109, 1022, 915, 842, 756, 685, 595, 540, 507, 418 cm^{-1}; MS (ESI, *m/z*): 227.10 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{15}O_2$: 227.1067 [M+H]$^+$, found: 227.1069.

Synthesis of 1,9-Bis(4-(methylthio)phenyl)nona-2,7-diyne-1,9-dione (1g). 4-(Methylthio)benzoyl chloride (407 mg, 2.18 mmol), $PdCl_2(PPh_3)_2$ (15.4 mg, 0.022 mmol), Et_3N (133.5 mg, 1.31 mmol), CuI (4.2 mg, 0.022 mmol) and 1,6-heptadiyne (**4**) (100 mg, 1.09 mmol) were employed. Two fractions were isolated. First fraction afforded 18.5 mg (7%) of 1-(4-methylthiophenyl)octa-2,7-diyne-1-one (**5g**) as a dark brownish orange oil (R_f = 0.85 in 4:1 hexane/ethyl acetate). Second fraction yielded 230 mg (54%) of the indicated product **1g** as a light orange oil (R_f = 0.17 in 4:1 hexane/ethyl acetate).

1g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 4H), 7.20 (d, *J* = 10.7 Hz, 4H), 2.68 (t, *J* = 7.0 Hz, 4H), 2.46 (s, 6H), 2.00 (p, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8 (CO), 147.5 (C–SMe), 133.0 (C), 129.7 (CH), 124.5 (CH), 93.9 (C), 80.2 (C), 25.9 (CH_2), 18.3

(CH_2), 14.5 (CH_3); IR (neat): 2920, 2238, 2193, 1629, 1583, 1552, 1399, 1310, 1263, 1178, 1086, 969, 918, 898, 874, 834, 743, 679, 519, 476 cm^{-1}; MS (ESI, *m/z*): 393.09 [M+H]$^+$; HRMS (ESI) calcd. for $C_{23}H_{21}O_2S_2$: 393.0978 [M+H]$^+$, found: 393.0978.

5g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 3.8 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 2.81-2.72 (m, 3H), 2.65 (q, *J* = 7.5, 7.0 Hz, 2H), 2.55 (s, 3H), 2.09 (p, *J* = 7.09 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1 (CO), 130.0 (C–SMe), 129.2 (C), 125.1 (CH), 124.9 (CH), 94.3 (C), 94.0 (C), 80.6 (C), 80.5 (CH), 25.2 (CH_2), 18.5 (CH_2), 18.1 (CH_2), 14.8 (CH_3); IR (neat): 3289, 2922, 2238, 2194, 1771, 1715, 1684, 1635, 1586, 1556, 1507, 1488, 1433, 1400, 1362, 1311, 1265, 1219, 1177, 1111, 1088, 1034, 995, 905, 871, 835, 759, 745, 681, 645, 518, 476, 417 cm^{-1}; MS (ESI, *m/z*): 243.08 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{15}OS$: 243.0838 [M+H]$^+$, found: 243.0831.

Synthesis of 1,9-Bis(4-(dimethylamino)phenyl)nona-2,7-diyne-1,9-dione (1h). 4-(Dimethylamino)benzoyl chloride (598.6 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 286.8 mg (46%) of 1-(4-(dimethylamino)phenyl)octa-2,7-diyn-1-one (**5h**) as a brown solid (R_f = 0.38 in 1:1 methanol/ethyl acetate; mp 98.1–103.8 °C). Second fraction yielded 24.5 mg (6%) of the indicated product **1h** as a brownish orange solid (R_f = 0.35 in 4:1 hexane/ethyl acetate; mp 80.1–82.6 °C).

1h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.1 Hz, 4H), 6.60 (d, *J* = 9.1 Hz, 4H), 3.02 (s, 12H), 2.65 (t, *J* = 7.0 Hz, 4H), 1.98 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1 (CO), 154.1 (C–N(Me)$_2$), 132.0 (CH), 125.3 (C), 110.6 (CH), 92.3 (C), 80.7 (C), 40.0 (Me-N), 26.4 (CH_2), 18.4 (CH_2); IR (neat): 3742, 2813, 2231, 2193, 1743, 1583, 1527, 1436, 1371, 1282, 1229, 1180, 1156, 1009, 970, 941, 821, 754, 686, 584, 503, 457, 418 cm^{-1}; MS (ESI, *m/z*): 387.20 [M+H]$^+$; HRMS (ESI) calcd. for $C_{25}H_{27}N_2O_2$: 387.2067 [M+H]$^+$, found: 387.2060.

5h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 9.0 Hz, 2H), 3.05 (s, 6H), 2.60 (t, *J* = 7.0 Hz, 2H), 2.37 (td, *J* = 6.9, 2.6 Hz, 2H), 1.99 (t, *J* = 2.5 Hz, 1H), 1.86 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3 (CO), 154.1 (C), 132.0 (CH), 125.5 (C) 110.6 (CH), 92.9 (C), 83.0 (C), 80.4 (C), 69.4 (CH), 40.1 ($N(CH_3)_2$), 26.9 (CH_2), 18.2 (CH_2), 17.8 (CH_2); IR (neat): 3231, 2906, 2236, 2156, 1748, 1716, 1652, 1616, 1579, 1541, 1488, 1456, 1443, 1375, 1339, 1318, 1287, 1232, 1183, 1110, 1066, 1018, 942, 899, 823, 756, 689, 586, 540, 502, 469, 418 cm^{-1}; MS (ESI, *m/z*): 240.13 [M+H]$^+$; HRMS (ESI) calcd. for $C_{16}H_{18}NO$: 240.1383 [M+H]$^+$, found: 240.1379.

Synthesis of 1,9-Bis(2-bromophenyl)nona-2,7-diyne-1,9-dione (1i). 2-Bromobenzoyl chloride (715.5 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 209.9 mg (47%) of 1-(2-bromophenyl)octa-2,7-diyne-1-one (**5i**) as an orange oil (R_f = 0.57 in 4:1 hexane/ethyl acetate). Second fraction yielded 248.1 mg (33%) of the indicated product **1i** as a brownish orange oil (R_f = 0.42 in 4:1 hexane/ethyl acetate).

1i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.64 (dd, *J* = 7.9, 1.1 Hz, 2H), 7.43–7.31 (m, 4H), 2.66 (t, *J* = 7.0 Hz, 4H), 1.97 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5 (CO), 137.4 (C), 135.0 (CH), 133.4 (CH), 132.9 (CH), 127.4 (CH), 121.1 (C–Br), 95.6 (C), 81.5 (C), 25.7 (CH_2), 18.6 (CH_2); IR (neat): 3063, 2939, 2199, 1647, 1583, 1461, 1427, 1286, 1237, 1135, 1028, 974, 917, 875, 779, 735, 682, 648, 620, 555, 474, 448 cm^{-1}; MS (ESI, *m/z*): 456.94 $[M+H]^+$; HRMS (ESI) calcd. for $C_{21}H_{15}Br_2O_2$: 456.9433 $[M+H]^+$, found: 456.9423.

5i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.41-7.29 (m, 2H), 2.59 (t, *J* = 7.1 Hz, 2H), 2.33 (td, *J* = 6.9, 2.7 Hz, 2H), 1.99 (t, *J* = 2.7 Hz, 1H), 1.82 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4 (CO), 137.1 (C), 134.9 (CH), 133.3 (CH), 132.9 (CH), 127.3 (CH), 121.0 (C–Br), 96.5 (C), 82.7 (C), 81.0 (C), 69.7 (CH), 26.4 (CH_2), 18.2 (CH_2), 17.7 (CH_2); IR (neat): 3295, 2939, 2202, 1717, 1649, 1585, 1559, 1541, 1497, 1458, 1429, 1373, 1289, 1238, 1136, 1046, 1028, 991, 917, 905, 877, 779, 736, 636, 446 cm^{-1}; MS (ESI, *m/z*): 275.00 $[M+H]^+$; HRMS (ESI) calcd. for $C_{14}H_{12}BrO$: 275.0066 $[M+H]^+$, found: 275.0068.

Synthesis of 1,9-Bis(3-bromophenyl)nona-2,7-diyne-1,9-dione (1j). 3-Bromobenzoyl chloride (715,5 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 74.8 mg (17%) of 1-(3-bromophenyl)octa-2,7-diyne-1-one (**5j**) as a dark orange oil (R_f = 0.71 in 4:1 hexane/ethyl acetate). Second fraction yielded 263.9 mg (35%) of the indicated product **1j** as a brown solid (R_f = 0.48 in 4:1 hexane/ethyl acetate; mp 99.7–101.3 °C).

1j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.7 Hz, 2H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 5.0 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 2H), 2.66 (t, *J* = 7.0 Hz, 4H), 1.98 (p, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3 (CO), 138.3 (C), 136.9 (CH), 132.3 (CH), 130.2 (CH), 128.1 (CH), 122.9 (C–Br), 95.2 (C), 80.1 (C), 25.9 (CH_2), 18.5 (CH_2); IR (neat): 3062, 2940, 2235, 2199, 1788, 1725, 1638, 1563, 1459, 1419, 1242, 1197, 1064, 1017, 994, 914, 897, 799, 726, 661, 615, 481, 431 cm^{-1}; MS (ESI, *m/z*): 456.94 [M+H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{15}Br_2O_2$: 456.9433 [M+H]$^+$, found: 456.9440.

5j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.18 (m, 1H), 8.04–8.00 (m, 1H), 7.71–7.67 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 2.72 (t, *J* = 7.0 Hz, 2H), 2.09-2.00 (m, 3H), 1.83 (p, *J* = 3.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6 (CO), 138.6 (C), 136.9 (CH), 132.5 (CH), 130.3 (CH), 128.2 (CH), 123.0 (C–Br), 96.5 (C), 96.3 (C), 79.94 (C), 79.91 (CH), 29.8 (CH_2), 18.6 (CH_2), 18.4 (CH_2); IR (neat): 3308, 2955, 2204, 1735, 1653, 1586, 1568, 1540, 1521, 1471, 1464, 1431, 1363, 1289, 1231, 1216, 1028, 739, 648, 507 cm^{-1}; MS (ESI, *m/z*): 275.00 [M+H]$^+$; HRMS (ESI) calcd. for $C_{14}H_{12}BrO$: 275.0066 [M+H]$^+$, found: 275.0061.

Synthesis of 1,9-Bis(4-bromophenyl)nona-2,7-diyne-1,9-dione (1k). 4-Bromobenzoyl chloride (715.5 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 112 mg (25%) of 1-(4-bromophenyl)octa-2,7-diyne-1-one (**5k**) as a yellow solid (R_f = 0.78 in 4:1 hexane/ethyl acetate; mp 106–108.2 ^{o}C). Second fraction yielded 480.4 mg (64%) of the indicated product **1k** as a brown solid (R_f = 0.31 in 4:1 hexane/ethyl acetate; mp 111.3–115.1 ^{o}C).

1k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 4H), 7.62 (d, *J* = 8.5 Hz, 4H), 2.72 (t, *J* = 7.0 Hz, 4H), 2.05 (p, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8 (CO), 135.5 (C), 132.0 (CH), 130.9 (CH), 129.6 (C–Br), 94.9 (C), 80.2 (C), 25.9 (CH_2), 18.5 (CH_2); IR (neat): 3744, 2942, 2231, 2193, 1786, 1730, 1640, 1567, 1394, 1262, 1230, 1065, 1007, 974, 874, 839, 740, 672, 628, 535, 466, 420 cm^{-1}; MS (ESI, *m/z*): 456.94 [M+H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{15}Br_2O_2$: 456.9433 [M+H]$^+$, found: 456.9428.

5k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 2.63 (t, *J* = 7.1 Hz, 2H), 2.36 (td, *J* = 6.9, 2.6 Hz, 2H), 2.01 (t, *J* = 2.6 Hz, 1H), 1.87 (p, *J* = 7.0 Hz, 2H); IR (neat): 3301, 2954, 2235, 2196, 1674, 1646, 1584, 1541, 1521, 1507, 1480, 1456, 1429, 1396, 1363, 1262, 1229, 1200, 1172, 1111, 1067, 1009, 919, 871, 841, 756, 741, 717, 703, 675, 642, 626, 538, 466, 437, 418 cm^{-1}; MS (ESI, *m/z*): 275.00 [M+H]$^+$; HRMS (ESI) calcd. for $C_{14}H_{12}BrO$: 275.0066 [M+H]$^+$, found: 275.0060.

Synthesis of 1,9-Bis(3-chlorophenyl)nona-2,7-diyne-1,9-dione (1l). 3-Chlorobenzoyl chloride (570.5 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed.

Two fractions were isolated. First fraction afforded 47.3 mg (13%) of 1-(3-chlorophenyl)octa-2,7-diyne-1-one (**5l**) as a brown solid (R_f = 0.63 in 4:1 hexane/ethyl acetate; mp 91-93.7 °C). Second fraction yielded 243.6 mg (41%) of the indicated product **1l** as a brown solid (R_f = 0.52 in 4:1 hexane/ethyl acetate; mp 92.1–93.6 °C).

1l: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.07 (m, 2H), 8.01 (d, *J* = 6.5 Hz, 2H), 7.57 (d, *J* = 7.1 Hz, 2H), 7.43 (t, *J* = 7.9 Hz, 2H), 2.74 (t, *J* = 7.0 Hz, 4H), 2.07 (p, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6 (CO), 138.3 (C), 135.0 (C–Cl), 134.2 (CH), 130.1 (CH), 129.6 (CH), 127.8 (CH), 95.2 (C), 80.2 (C), 26.0 (CH_2), 18.6 (CH_2); IR (neat): 3742, 2970, 2165, 1737, 1688, 1640, 1568, 1421, 1298, 1247, 1230, 1138, 1072, 913, 896, 849, 802, 747, 719, 652, 546, 493, 418 cm^{-1}; MS (ESI, *m/z*): 369.04 [M+H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{15}Cl_2O_2$: 369.0444 [M+H]$^+$, found: 369.0441.

5l: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.40–7.27 (m, 3H), 2.53 (t, *J* = 6.8 Hz, 2H), 2.26 (td, *J* = 6.6, 2.4 Hz, 2H), 1.93 (t, *J* = 2.2 Hz, 1H), 1.76 (p, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2 (CO), 138.1 (C), 134.5 (CH), 133.7 (CH), 130.2 (CH), 128.5 (CH), 127.5 (C–Br), 96.2 (C), 82.5 (C), 79.5 (C), 69.7 (CH), 26.4 (CH_2), 18.0 (CH_2), 17.6 (CH_2); IR (neat): 3297, 3073, 2969, 2204, 1789, 1731, 1697, 1646, 1594, 1572, 1541, 1521, 1507, 1472, 1419, 1373, 1288, 1252, 1196, 1143, 1061, 996, 895, 847, 798, 730, 718, 685, 665, 651, 611, 543, 492, 467, 417 cm^{-1}; MS (ESI, *m/z*): 231.05 [M+H]$^+$; HRMS (ESI) calcd. for $C_{14}H_{12}ClO$: 231.0571 [M+H]$^+$, found: 231.0552.

Synthesis of 1,9-Bis(4-chlorophenyl)nona-2,7-diyne-1,9-dione (1m). 4-Chlorobenzoyl chloride (570.5 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 21 mg (6%) of 1-(4-chlorophenyl)octa-2,7-diyne-1-one (**5m**) as a brownish orange oil (R_f = 0.83 in 4:1 hexane/ethyl acetate). Second fraction yielded 382.7 mg (64%) of the indicated product **1m** as a brown solid (R_f = 0.37 in 4:1 hexane/ethyl acetate; mp 135.0–137.0 °C).

1m: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 4H), 7.41 (d, *J* = 8.5 Hz, 4H), 2.70 (t, *J* = 7.0 Hz, 4H), 2.03 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6 (CO), 140.7 (C–Cl), 135.0 (C), 130.9 (CH), 129.0 (CH), 94.8 (C), 80.2 (C), 25.9 (CH_2), 18.5 (CH_2); IR (neat): 2234, 2195, 1786, 1639, 1587, 1483, 1398, 1260, 1223, 1171, 1088, 1008, 924, 897, 843, 743, 674, 629, 523, 471 cm^{-1}; MS (ESI, *m/z*): 369.04 [M+H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{15}Cl_2O_2$: 369.0444 [M+H]$^+$, found: 369.0454.

5m: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 2.64 (t, *J* = 6.8 Hz, 2H), 2.37 (td, *J* = 6.9, 2.2 Hz, 2H), 2.02 (t, *J* = 2.7 Hz, 1H), 1.88 (p, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 176.8 (CO), 140.6 (C–Cl) 135.2 (C), 130.9 (CH), 129.0 (CH), 95.9 (C), 82.7 (C), 79.8 (C), 69.8 (C), 26.6 (CH$_2$), 18.2 (CH$_2$), 17.8 (CH$_2$); IR (neat): 3300, 2939, 2235, 2198, 1736, 1644, 1586, 1485, 1399, 1260, 1170, 1089, 1011, 844, 745, 674, 632, 524, 474 cm^{-1}; MS (ESI, *m/z*): 231.05 [M+H]$^+$; HRMS (ESI) calcd. for $C_{14}H_{12}ClO$: 231.0571 [M+H]$^+$, found: 231.0574.

Synthesis of 1,9-Bis(2-fluorophenyl)nona-2,7-diyne-1,9-dione (1n). 2-Fluorobenzoyl chloride (942 mg, 5.94 mmol), PdCl$_2$(PPh$_3$)$_2$ (41 mg, 0.059 mmol), Et$_3$N (363 mg, 3.56 mmol), CuI (11 mg, 0.059 mmol) and 1,6-heptadiyne (**4**) (274 mg, 2.97 mmol) were employed. Two fractions were isolated. First fraction afforded 305.5 mg (48%) of 1-(2-fluorophenyl)octa-2,7-diyne-1-one (**5n**) as a dark brown oil (R_f = 0.64 in 4:1 hexane/ethyl acetate). Second fraction yielded 376.9 mg (38%) of the indicated product **1n** as a brown solid (R_f = 0.36 in 4:1 hexane/ethyl acetate; mp 45.3–46.7 °C).

1n:[2] ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (td, *J* = 7.7, 1.8 Hz, 2H), 7.61–7.55 (m, 2H), 7.29–7.24 (m, 2H), 7.16 (dd, *J* = 10.9, 8.7 Hz, 2H), 2.72 (t, *J* = 6.9 Hz, 4H), 2.03 (p, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 174.4 (CO), 162.2 (d, ^1J = 261.7 Hz, C–F), 135.7 (d, ^3J = 8.9 Hz, CH), 132.1 (CH), 125.6 (d, ^2J = 7.6 Hz, C), 124.3 (d, ^4J = 3.9 Hz, CH), 117.2 (d, ^2J = 21.8 Hz, CH), 94.6 (C), 82.0 (C), 25.8 (CH$_2$), 18.5 (CH$_2$); IR (neat): 2969, 2228, 1736, 1717, 1647, 1637, 1606, 1558, 1541, 1507, 1478, 1455, 1419, 1364, 1291, 1217, 1155, 1088, 1032, 1016, 978, 959, 922, 900, 807, 779, 749, 676, 650, 614, 570, 545, 518 cm^{-1}; MS (ESI, *m/z*): 337.10 [M+H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{15}F_2O_2$: 337.1035 [M+H]$^+$, found: 337.1047.

5n: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00–7.94 (m, 1H), 7.58–7.54 (m, 1H), 7.27-7.00 (m, 2H), 2.55 (t, *J* = 7.0 Hz, 2H), 2.29 (td, *J* = 6.9, 2.6 Hz, 2H), 1.93 (t, *J* = 2.6 Hz, 1H), 1.78 (p, *J* = 6.9 Hz, 2H);^{13}C NMR (100 MHz, CDCl$_3$) δ 174.4 (d, ^3J = 1.3 Hz, CO), 162.0 (d, ^1J = 261.6 Hz, C–F), 137.1 (d, ^3J = 9.5 Hz, CH), 135.5 (d, ^5J = 9.3 Hz, CH), 125.5 (d, ^2J = 7.8 Hz, C), 124.6 (d, ^4J = 3.9 Hz, CH), 117.3 (d, ^2J = 21.3 Hz, CH), 95.4 (d, ^4J = 2.6 Hz, C), 82.8 (C), 81.5 (C), 69.6 (CH), 26.5 (CH$_2$), 18.2 (CH$_2$), 17.6 (CH$_2$); IR (neat): 3304, 2969, 2207, 1868, 1783, 1735, 1683, 1652, 1635, 1606, 1576, 1558, 1540, 1520, 1507, 1481, 1454, 1364, 1291, 1272, 1231, 1195, 1156, 1116, 1022, 995, 881, 792, 752, 734, 643, 540, 515 cm^{-1}; MS (ESI, *m/z*): 215.08 [M+H]$^+$; HRMS (ESI) calcd. for $C_{14}H_{12}FO$: 215.0867 [M+H]$^+$, found: 215.0846.

Synthesis of 1,9-Bis(4-fluorophenyl)nona-2,7-diyne-1,9-dione (1o). 4-Fluorobenzoyl chloride (942 mg, 5.94 mmol), $PdCl_2(PPh_3)_2$ (41 mg, 0.059 mmol), Et_3N (363 mg, 3.56 mmol), CuI (11 mg, 0.059 mmol) and 1,6-heptadiyne (**4**) (274 mg, 2.97 mmol) were employed. Two fractions were isolated. First fraction afforded 175 mg (28%) of 1-(4-fluorophenyl)octa-2,7-diyne-1-one (**5o**) as a dark brownish orange oil (R_f = 0.69 in 4:1 hexane/ethyl acetate). Second fraction yielded 343.8 mg (34%) of the indicated product **1o** as a brownish orange solid (R_f = 0.61 in 4:1 hexane/ethyl acetate; mp 103.4–104.5 °C).

1o: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 7.9, 6.0 Hz, 4H), 7.11 (t, J = 8.4 Hz, 4H), 2.69 (t, J = 7.0 Hz, 4H), 2.02 (p, J = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3 (CO), 166.4 (d, ^1J = 256.6 Hz, C–F), 133.2 (d, ^4J = 2.2 Hz, C), 132.2 (d, ^3J = 9.6 Hz, CH), 115.8 (d, ^2J = 22.1 Hz, CH), 94.6 (C), 80.2 (C), 25.9 (CH_2), 18.4 (CH_2); IR (neat): 2969, 2239, 2199, 1736, 1683, 1635, 1591, 1558, 1541, 1489, 1456, 1409, 1364, 1263, 1217, 1145, 1103, 1011, 924, 897, 845, 813, 768, 751, 676, 654, 610, 589, 547, 518, 498, 424 cm^{-1}; MS (ESI, *m/z*): 337.10 $[M+H]^+$; HRMS (ESI) calcd. for $C_{21}H_{15}F_2O_2$: 337.1035 $[M+H]^+$, found: 337.1041.

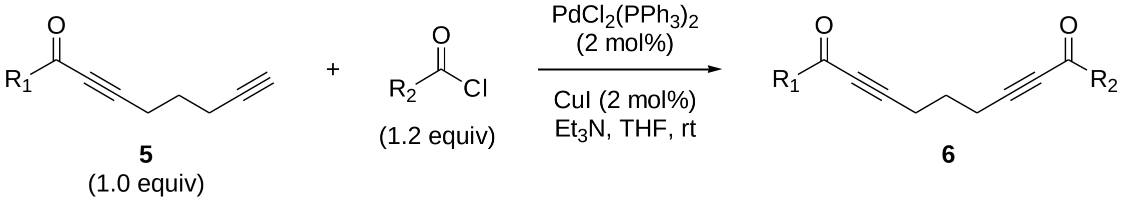
5o: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 7.2, 1.6 Hz, 2H), 7.14 (t, J = 8.6 Hz, 2H), 2.65 (t, J = 7.1 Hz, 2H), 2.39 (td, J = 6.9, 2.6 Hz, 2H), 2.02 (t, J = 2.6 Hz, 1H), 1.89 (p, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5 (CO), 166.4 (d, ^1J = 256.4 Hz, C–F), 133.3 (d, ^4J = 9.6 Hz, C), 132.2 (d, ^3J = 9.6 Hz, CH), 116.3 (d, ^2J = 22.4 Hz, CH), 95.5 (C), 82.7 (C), 79.8 (C), 69.6 (CH), 26.6 (CH_2), 18.1 (CH_2), 17.7 (CH_2); IR (neat): 3304, 2969, 2942, 2236, 2197, 1718, 1683, 1646, 1593, 1558, 1540, 1473, 1456, 1410, 1364, 1264, 1227, 1150, 1108, 1090, 1032, 1004, 918, 879, 846, 753, 676, 632, 592, 571, 497 cm^{-1}; MS (ESI, *m/z*): 215.08 $[M+H]^+$; HRMS (ESI) calcd. for $C_{14}H_{12}FO$: 215.0867 $[M+H]^+$, found: 215.0853.

Synthesis of 1,9-Bis(3,5-dichlorophenyl)nona-2,7-diyne-1,9-dione (1p). 3,5-Dichlorobenzoyl chloride (683 mg, 3.26 mmol), $PdCl_2(PPh_3)_2$ (23.2 mg, 0.033 mmol), Et_3N (199.7 mg, 1.96 mmol), CuI (6.3 mg, 0.033 mmol) and 1,6-heptadiyne (**4**) (150 mg, 1.63 mmol) were employed. Two fractions were isolated. First fraction afforded 144 mg (33%) of 1-(3,5-dichlorophenyl)octa-2,7-diyne-1-one (**5p**) as a dark orange oil (R_f = 0.88 in 4:1 hexane/ethyl acetate). Second fraction yielded 251.9 mg (35%) of the indicated product **1p** as a light brown solid (R_f = 0.57 in 4:1 hexane/ethyl acetate; mp 90.1–92.6 °C).

1p: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 1.7 Hz, 4H), 7.53 (s, 2H), 2.74 (t, J = 7.0 Hz, 4H), 2.06 (p, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0 (CO), 139.0 (C), 135.7 (C–Cl), 133.7 (CH), 127.8 (CH), 95.9 (C), 79.8 (C), 25.8 (CH_2), 18.6 (CH_2); IR (neat): 3742, 3067, 2208, 1646, 1563, 1426, 1398, 1248, 1138, 1100, 987, 953, 877, 802, 774, 738, 656, 631, 474 cm^{-1}; MS (ESI, *m/z*): 436.96 [M+H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{13}Cl_4O_2$: 436.9664 [M+H]$^+$, found: 436.9659.

5p: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.9 Hz, 2H), 7.55 (s, 1H), 2.67 (t, *J* = 7.1 Hz, 2H), 2.39 (td, *J* = 6.8, 2.7 Hz, 2H), 2.03 (t, *J* = 2.6 Hz, 1H), 1.89 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2 (CO), 139.2 (C), 135.7 (C–Cl), 133.6 (CH), 127.8 (CH), 97.2 (C), 82.6 (C), 79.5 (C), 69.9 (CH), 26.5 (CH_2), 18.3 (CH_2), 17.8 (CH_2); IR (neat): 3305, 3067, 2945, 2211, 1793, 1732, 1683, 1652, 1565, 1541, 1521, 1507, 1488, 1473, 1456, 1428, 1251, 1203, 1105, 1039, 992, 865, 802, 743, 658, 630 cm^{-1}; MS (ESI, *m/z*): 265.01 [M+H]$^+$; HRMS (ESI) calcd. for $C_{14}H_{11}Cl_2O$: 265.0182 [M+H]$^+$, found: 265.0179.

Table S2. Synthesis of Unsymmetrical bis-α,β-Alkynic Ketones.[a]



Entry	R_1	R_2	Yield of 6 (%)
1	*p*-Et-C_6H_4	Ph	**6a** (40)
2	Ph	*p*-Me_2N-C_6H_4	**6b** (64)
3	Ph	*p*-Br-C_6H_4	**6c** (72)

[a] Isolated yields.

General Procedure 2. Synthesis of Unsymmetrical 1,9-Diarylnona-2,7-diyne-1,9-diones 6 (Table S2). To a stirred solution of the proper aryloyl chloride (1.2 mmol) in THF (8 mL) under argon was added $PdCl_2(PPh_3)_2$ (0.02 mmol) and Et_3N (1.2 mmol), and the resulting mixture was stirred for 10 min at room temperature and CuI (0.02 mmol) was added. After stirring the reaction mixture for another 10 min, 1-arylocta-2,7-diyne-1-one **5** (1.0 mmol) was added slowly, and the stirring at room temperature continued until the end of the reaction (The progress of the reaction was monitored by routine TLC analysis for the disappearance of 1-arylocta-2,7-diyne-1-one **5** using 9:1 hexane/ethyl acetate as the eluent). After the reaction was over, the solvent was removed on a rotary evaporator, and ethyl acetate (50 mL) and a saturated aqueous solution of NH_4Cl solution (50 mL) were added. After the layers were separated, the aqueous layer was extracted with ethyl acetate (2 x 50 mL). The combined organic layers were dried over $MgSO_4$ and evaporated on a rotary evaporator to give the crude product, which was purified by flash chromatography on silica gel using 9:1 hexane/ethyl acetate as the eluent to afford the corresponding unsymmetrical 1,9-diarylnona-2,7-diyne-1,9-dione **6**.

Synthesis of 1-(4-Ethylphenyl)-9-phenylnona-2,7-diyne-1,9-dione (6a). Benzoyl chloride (87.2 mg, 0.62 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol), Et_3N (63.2 mg, 0.62 mmol), CuI (1,9 mg, 0.01 mmol) and 1-(4-ethylphenyl)octa-2,7-diyne-1-one (**5c**) (116.6 mg, 0.52 mmol) were employed to afford 67.9 mg (40%) of the indicated product **6a** as a brownish orange oil (R_f = 0.47 in 4:1 hexane/ethyl acetate).

6a: ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.1 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 2.67-2.59 (m, 6H), 1.97 (p, J

= 7.0 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0 (CO), 177.8 (CO), 151.4 (C–CH_2CH_3), 136.7 (C), 134.7 (C), 134.2 (CH), 129.9 (CH), 129.6 (CH), 128.7 (CH), 128.2 (CH), 94.4 (C), 93.8 (C), 80.6 (C), 80.5 (C), 29.1 (CH_2), 26.1 (CH_2), 18.5 (CH_2), 15.2 (CH_2) (Note that two CH_2 peaks overlap on each other); IR (neat): 2965, 2932, 2235, 2197, 1687, 1639, 1602, 1449, 1415, 1311, 1262, 1175, 1109, 975, 920, 849, 700, 595, 518,418 cm^{-1}; MS (ESI, m/z): 329.15 [M+H]$^+$; HRMS (ESI) calcd. for $C_{23}H_{21}O_2$: 329.1536 [M+H]$^+$, found: 329.1529.

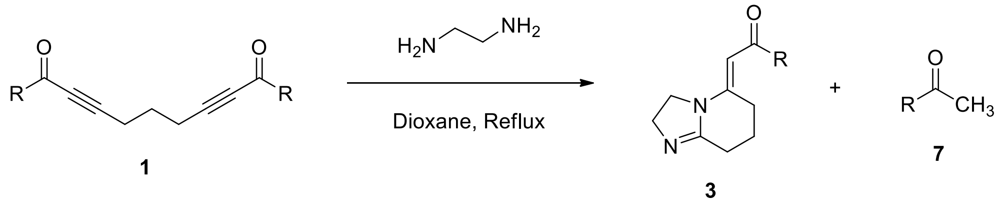
Synthesis of 1-(4-(Dimethylamino)phenyl)-9-phenylnona-2,7-diyne-1,9-dione (6b). 4-(Dimethylamino)benzoyl chloride (156.1 mg, 0.85 mmol), $PdCl_2(PPh_3)_2$ (9.8 mg, 0.014 mmol), Et_3N (86.6 mg, 0.85 mmol), CuI (2.7 mg, 0.014 mmol) and 1-phenylocta-2,7-diyne-1-one (**5a**) (139.3 mg, 0.71 mmol) were employed to afford 155 mg (64%) of the indicated product **6b** as a dark brown solid (R_f = 0.19 in 4:1 hexane/ethyl acetate; mp 52.1–54.8 °C).

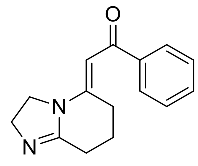
6b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.10 (m, 3H), 8.00 (t, *J* = 8.0 Hz, 1H), 7.49-7.43 (m, 3H), 6.63 (d, *J* = 9.0 Hz, 2H), 3.06 (s, 6H), 2.70 (dt, *J* = 13.6, 7.0 Hz, 4H), 2.02 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2 (CO), 176.2 (CO), 154.2 (C–N(Me)$_2$), 133.8 (C), 132.1 (C), 130.2 (CH), 129.6 (CH), 128.7 (CH), 128.5 (CH), 110.7 (CH), 94.8 (C), 92.2 (C), 80.9 (C), 80.4 (C), 40.1 (NMe_2), 26.3 (CH_2), 18.53 (CH_2), 18.50 (CH_2); IR (neat): 3069, 2821, 2235, 2196, 1682, 1643, 1618, 1580, 1541, 1451, 1417, 1374, 1321, 1285, 1264, 1182, 1126, 1070, 1025, 999, 921, 878, 824, 805, 756, 701, 666, 589, 550, 506, 417 cm^{-1}; MS (ESI, m/z): 344.16 [M+H]$^+$; HRMS (ESI) calcd. for $C_{23}H_{22}NO_2$: 344.1645 [M+H]$^+$, found: 344.1654.

Synthesis of 1-(4-Bromophenyl)-9-phenylnona-2,7-diyne-1,9-dione (6c). 4-Bromobenzoyl chloride (261 mg, 1.19 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), Et_3N (121.3 mg, 1.19 mmol), CuI (4 mg, 0.02 mmol) and 1-phenylocta-2,7-diyne-1-one (**5a**) (194 mg, 0.99 mmol) were employed to afford 269.3 mg (72%) of the indicated product **6c** as a dark brownish orange oil (R_f = 0.36 in 4:1 hexane/ethyl acetate).

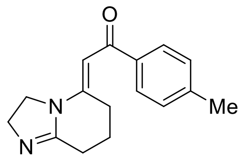
6c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18–8.12 (m, 3H), 8.01–7.97 (m, 2H), 7.63–7.61 (m, 2H), 7.53–7.48 (m, 2H), 2.73 (td, *J* = 7.0, 3.1 Hz, 4H), 2.06 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0 (CO), 177.4 (CO), 134.9 (CH), 134.2 (CH), 133.4 (C), 132.9 (C), 129.6 (CH), 128.6 (CH), 127.4 (CH), 121.0 (C–Br), 95.6 (C), 94.3 (C), 81.4 (C), 80.4 (C), 25.8 (CH_2), 18.5 (CH_2), 18.4 (CH_2); IR (neat): 3059, 2936, 2200, 1638, 1579, 1464, 1448, 1429, 1311, 1263, 1240, 1173, 1118, 1026, 974, 872, 811, 739, 700, 639, 555, 448, 425 cm^{-1}; MS (ESI, m/z): 379.03 [M+H]$^+$; HRMS (ESI) calcd. for $C_{21}H_{16}BrO_2$: 379.0328 [M+H]$^+$, found: 379.0333.

Table S3. Synthesis of 5-Alkylidene-2,3,5,6,7,8-hexahydroimidazo[1,2-*a*]pyridines **3**.[a,b,c,d]

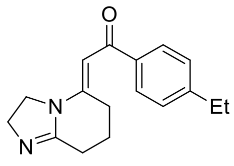




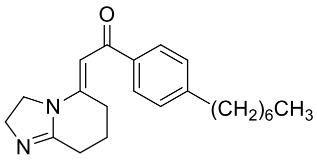
3a (54%) (43%)[d]
7a (41%) (33%)[d]



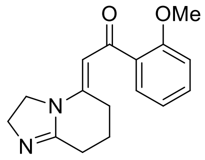
3b (42%)
7b (52%)



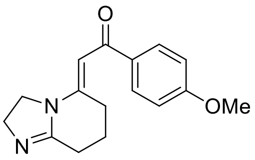
3c (50%)
7c (39%)



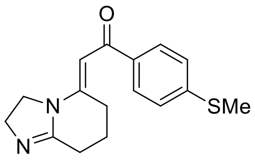
3d (17%)
7d (44%)



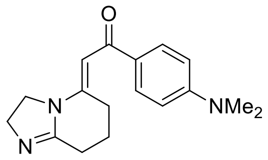
3e (43%)
7e (37%)



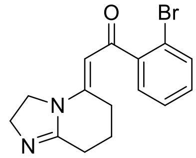
3f (32%)
7f (48%)



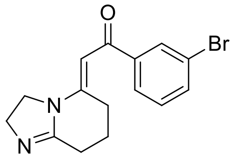
3g (46%)
7g (*n.d.*)



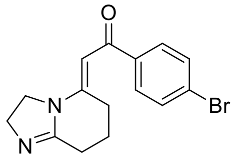
3h (22%)
7h (32%)



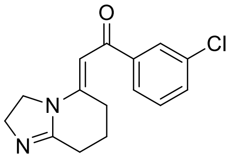
3i (56%)
7i (*n.d.*)



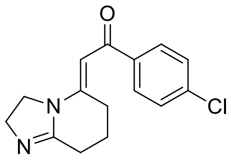
3j (46%)
7j (*n.d.*)



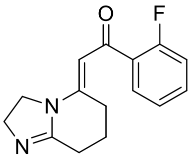
3k (28%)
7k (60%)



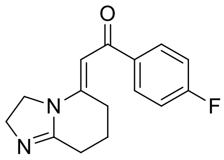
3l (29%)
7l (15%)



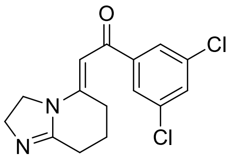
3m (32%)
7m (27%)



3n (48%)
7n (*n.d.*)



3o (55%)
7o (*n.d.*)



3p (21%)
7p (33%)

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[a] Isolated yields. [b] For the identities of the corresponding aryl methyl ketones **7**, see Experimental part. [c] *n.d.* = Yield not determined. [d] Yield of the product obtained from the reaction performed on a 2.40 mmol scale of bis-α,β-alkynic ketones **1a** (see Experimental part).

General Procedure 3. Synthesis of 1-Aryl-2-(2,3,7,8-tetrahydroimidazo[1,2-a] pyridin-5(6*H*)-ylidene)ethanones 3 (Table S3). To a stirred solution of the proper 1,9-diarylnona-2,7-diyne-1,9-dione **1** (0.25 mmol) in dioxane (5.0 mL) under argon was added ethylenediamine (0.50 mmol), and the resulting mixture was refluxed until the end of the reaction (The progress of the reaction was monitored by routine TLC analysis for the disappearance of bis-α,β-alkynic ketone **1** using 4:1 hexane/ethyl acetate as the eluent). After the reaction was over, the solvent was removed on a rotary evaporator, and the resulting crude product was purified by flash chromatography on silica gel using 4:1 hexane/ethyl acetate, followed by 1:1 methanol/ethyl acetate, as the eluent to afford the corresponding 1-aryl-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone **3** and aryl methyl ketone **7**.

Synthesis of 1-Phenyl-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3a). 1,9-Diphenylnona-2,7-diyne-1,9-dione (**1a**) (86.9 mg, 0.29 mmol) and ethylenediamine (34.8 mg, 0.58 mmol) were employed. Two fractions were isolated. First fraction afforded 14.2 mg (41%) of acetophenone (**7a**) as a brownish orange oil (R_f = 0.72 in 4:1 hexane/ethyl acetate). Second fraction yielded 37.3 mg (54%) of the indicated product **3a** as an orange solid (R_f = 0.53 in 1:1 methanol/ethyl acetate; mp 125.9–129.7 °C).

This reaction was also performed on a larger scale as summarized below: 1,9-Diphenylnona-2,7-diyne-1,9-dione (**1a**) (721.2 mg, 2.40 mmol) and ethylenediamine (288.5 mg, 4.80 mmol) were employed in 10 ml dioxane. Two fractions were isolated. First fraction afforded 94.3 mg (33%) of acetophenone (**7a**) as a brownish orange oil (R_f = 0.72 in 4:1 hexane/ethyl acetate). Second fraction yielded 248.3 mg (43%) of the indicated product **3a** as an orange solid (R_f = 0.53 in 1:1 methanol/ethyl acetate).

3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 6.9 Hz, 2H), 7.49-7.38 (m, 3H), 5.84 (s, 1H), 3.94 (t, J = 8.7 Hz, 2H), 3.70 (t, J = 8.9 Hz, 2H), 3.33 (t, J = 6.0 Hz, 2H), 2.62 (t, J = 6.2 Hz, 2H), 1.83 (p, J = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2 (CO), 158.3 (C=N), 155.6 (C), 141.2 (C), 131.5 (CH), 128.4 (CH), 127.6 (CH), 96.7 (CH), 52.6 (CH_2), 46.3 (CH_2), 26.7 (CH_2), 26.0 (CH_2), 18.7 (CH_2); IR (neat): 2939, 2871, 1649, 1624, 1540, 1399, 1358, 1295, 1262, 1215, 1180, 1041, 988, 875, 766, 706, 671, 572, 496, 415 cm^{-1}; MS (ESI, m/z): 241.13 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{17}N_2O$: 241.1335 [M+H]$^+$, found: 241.1336.

7a: ^{1}H NMR (400 MHz, $CDCI_3$) δ 7.97–7.95 (m, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.46 (d, J = 7.4 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCI_3$) δ 198.3 (CO), 137.2 (C), 133.2 (CH), 128.7 (CH), 128.4 (CH), 26.8 (CH_3). The spectral data are in agreement with those reported previously for this compound.[3-8]

Synthesis of 2-(2,3,7,8-Tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)-1-(p-tolyl)ethanone (3b). 1,9-Di-*p*-tolylnona-2,7-diyne-1,9-dione (**1b**) (70.8 mg, 0.22 mmol) and ethylenediamine (26.4 mg, 0.44 mmol) were employed. Two fractions were isolated. First fraction afforded 15.3 mg (52%) of 4′-methylacetophenone (1-(4-methylphenyl)ethanone) (**7b**) as a dark orange oil (R_f = 0.67 in 4:1 hexane/ethyl acetate). Second fraction yielded 23.7 mg (42%) of the indicated product **3b** as a light orange solid (R_f = 0.22 in 1:1 methanol/ethyl acetate; mp 197.1–199.6 °C).

3b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 5.85 (s, 1H), 3.95 (t, *J* = 8.9 Hz, 2H), 3.71 (t, *J* = 8.8 Hz, 2H), 3.34 (t, *J* = 6.0 Hz, 2H), 2.63 (t, *J* = 5.7 Hz, 2H), 2.39 (s, 3H), 1.84 (p, *J* = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9 (CO), 158.3 (C=N), 155.4 (C), 142.0 (C–CH_3), 138.6 (C), 129.1 (CH), 127.7 (CH), 96.6 (CH), 52.7 (CH_2), 46.3 (CH_2), 26.7 (CH_2), 26.1 (CH_2), 21.6 (CH_3), 18.8 (CH_2); IR (neat): 2948, 2876, 2369, 1651, 1603, 1536, 1428, 1356, 1295, 1260, 1227, 1181, 1043, 986, 877, 776, 668, 634, 571, 499, 471, 418 cm^{-1}; MS (ESI, m/z): 255.14 $[M+H]^+$; HRMS (ESI) calcd. for $C_{16}H_{19}N_2O$: 255.1492 $[M+H]^+$, found: 255.1486.

7b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 2.51 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1 (CO), 144.0 (C), 134.8 (C), 129.4 (CH), 128.6 (CH), 26.7 (CH_3), 21.8 (CH_3). The spectral data are in agreement with those reported previously for this compound.[3-8]

Synthesis of 1-(4-Ethylphenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3c). 1,9-Bis(4-ethylphenyl)nona-2,7-diyne-1,9-dione (**1c**) (107 mg, 0.30 mmol) and ethylenediamine (36.1 mg, 0.60 mmol) were employed. Two fractions were isolated. First fraction afforded 17.2 mg (39%) of 4′-ethylacetophenone (1-(4-ethylphenyl)ethanone) (**7c**) as a dark orange oil (R_f = 0.68 in 4:1 hexane/ethyl acetate). Second fraction yielded 40.1 mg (50%) of the indicated product **3c** as a light yellow solid (R_f = 0.53 in 1:1 methanol/ethyl acetate; mp 131.7–134.4 °C).

3c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 5.88 (s, 1H), 3.97 (t, *J* = 8.8 Hz, 2H), 3.73 (t, *J* = 8.3 Hz, 2H), 3.36 (t, *J* = 6.0 Hz, 2H), 2.74 – 2.62 (m, 4H), 1.86 (p, *J* = 6.3 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0 (CO), 158.3 (C=N), 155.3 (C), 148.3 (C–CH_2CH_3), 138.8 (C), 127.9 (CH), 127.8 (CH), 96.7 (CH), 52.7 (CH_2), 46.3 (CH_2), 28.9 (CH_2), 26.7 (CH_2), 26.1 (CH_2), 18.7 (CH_2), 15.5 (CH_3); IR (neat): 2939, 2874, 1738, 1654, 1603, 1536, 1474, 1431, 1396, 1356, 1295, 1260, 1220, 1181, 1105, 1042, 987, 877, 833, 769, 694, 669, 635, 581, 564, 527, 468, 418 cm^{-1}; MS (ESI, m/z): 269.16 $[M+H]^+$; HRMS (ESI) calcd. for $C_{17}H_{21}N_2O$: 269.1648 $[M+H]^+$, found: 269.1646.

7c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 2.58 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0

(CO), 150.2 (C), 135.1 (C), 128.7 (CH), 128.2 (CH), 29.1 (CH_2), 26.7 (CH_3), 15.3 (CH_3). The spectral data are in agreement with those reported previously for this compound.[4,7]

Synthesis of 1-(4-Heptylphenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3d). 1,9-Bis(4-heptylphenyl)nona-2,7-diyne-1,9-dione (**1d**) (101.8 mg, 0.20 mmol) and ethylenediamine (24 mg, 0.40 mmol) were employed. Two fractions were isolated. First fraction afforded 19.3 mg (44%) of 4′-heptylacetophenone (1-(4-heptylphenyl)ethanone) (**7d**) as an orange oil (R_f = 0.74 in 4:1 hexane/ethyl acetate). Second fraction yielded to 11.2 mg (17%) of the indicated product **3d** as a light yellow solid (R_f = 0.65 in 1:1 methanol/ethyl acetate; mp 141.4–144.2 °C).

3d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 6.14 (s, 1H), 4.17–4.01 (m, 2H), 3.32 (t, *J* = 6.1 Hz, 1H), 3.01 (t, *J* = 5.9 Hz, 1H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.91 (p, *J* = 6.0 Hz, 2H), 1.62 (t, *J* = 7.0 Hz, 2H), 1.29 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6 (CO), 171.0 (C=N), 149.3 (C), 148.5 (C), 137.3 (C), 130.3 (CH), 128.6 (CH), 102.7 (CH), 46.7 (CH_2), 36.2 (CH_2), 36.1 (CH_2), 31.9 (CH_2), 31.32 (CH_2), 31.28 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 25.8 (CH_2), 24.5 (CH_2), 22.8 (CH_2), 14.2 (CH_3); IR (neat): 2920, 2852, 1691, 1648, 1634, 1605, 1572, 1521, 1466, 1416, 1394, 1224, 1177, 1119, 1041, 947, 829, 748, 696, 622, 572, 522, 485 cm^{-1}; MS (ESI, m/z): 339.24 $[M+H]^+$; HRMS (ESI) calcd. for $C_{22}H_{31}N_2O$: 339.2431 $[M+H]^+$, found: 339.2422.

7d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 3.0 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 2.57 (s, 3H), 1.61 (p, *J* = 7.3 Hz, 2H), 1.31–1.24 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0 (CO), 149.0 (C), 135.0 (C), 128.7 (CH), 128.6 (CH), 36.1 (CH_2), 31.9 (CH_2), 31.3 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 26.7 (CH_3), 22.8 (CH_2), 14.2 (CH_3). The spectral data are in agreement with those reported previously for this compound.[9]

Synthesis of 1-(2-Methoxyphenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3e). 1,9-Bis(2-methoxyphenyl)nona-2,7-diyne-1,9-dione (**1e**) (66.4 mg, 0.18 mmol) and ethylenediamine (21.6 mg, 0.36 mmol) were employed. Two fractions were isolated. First fraction afforded 10 mg (37%) of 2′-methoxyacetophenone (1-(2-methoxyphenyl)ethanone) (**7e**) as an orange oil (R_f = 0.57 in 4:1 hexane/ethyl acetate). Second fraction yielded 20.8 mg (43%) of the indicated product **3e** as an orange oil (R_f = 0.65 in 1:1 methanol/ethyl acetate).

3e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.41–7.33 (m, 1H), 7.00–6.91 (m, 2H), 5.79 (s, 1H), 3.91 (t, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.63 (t, *J* = 9.0 Hz, 2H), 3.33 (t, *J*

= 6.2 Hz, 2H), 2.61 (t, *J* = 6.2 Hz, 2H), 1.84 (p, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2 (CO), 158.4 (C–OMe), 157.0 (C=N), 154.3 (C), 132.6 (CH), 131.6 (C), 129.8 (CH), 120.8 (CH), 111.6 (CH), 101.7 (CH), 55.8 (OCH_3), 52.7 (CH_2), 46.3 (CH_2), 26.8 (CH_2), 26.1 (CH_2), 18.7 (CH_2); IR (neat): 2942, 2877, 2495, 1649, 1593, 1524, 1480, 1434, 1396, 1357, 1278, 1239, 1181, 1114, 1038, 1018, 988, 879, 754, 674, 635, 581, 540, 508 cm^{-1}; MS (ESI, m/z): 271.14 $[M+H]^+$; HRMS (ESI) calcd. for $C_{16}H_{19}N_2O_2$: 271.1441 $[M+H]^+$, found: 271.1449.

7e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.49–7.44 (m, 1H), 7.02–6.94 (m, 2H), 3.91 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1 (CO), 167.9 (C–OMe), 132.6 (CH), 131.0 (CH), 130.5 (C), 129.0 (CH), 124.1 (CH), 55.6 (OCH_3), 30.5 (CH_3). The spectral data are in agreement with those reported previously for this compound.[3,5,8]

Synthesis of 1-(4-Methoxyphenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3f). 1,9-Bis(4-methoxyphenyl)nona-2,7-diyne-1,9-dione (**1f**) (121 mg, 0.34 mmol) and ethylenediamine (40.8 mg, 0.68 mmol) were employed. Two fractions were isolated. First fraction afforded 24.5 mg (48%) of 4′-methoxyacetophenone (1-(4-methoxyphenyl)ethanone) (**7f**) as a dark orange oil (R_f = 0.48 in 4:1 hexane/ethyl acetate). Second fraction yielded 29 mg (32%) of the indicated product **3f** as a brown solid (R_f = 0.17 in 1:1 methanol/ethyl acetate; mp 116.3–118.6 °C).

3f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.86 (s, 1H), 3.96 (t, *J* = 9.0 Hz, 2H), 3.84 (s, 3H), 3.73 (t, *J* = 8.5 Hz, 2H), 3.32 (t, *J* = 6.1 Hz, 2H), 2.65 (t, *J* = 6.2 Hz, 2H), 1.84 (p, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0 (CO), 162.5 (C-OMe), 158.7 (C=N), 154.8 (C), 133.8 (C), 129.7 (CH), 113.6 (CH), 96.8 (CH), 55.5 (OCH_3), 52.3 (CH_2), 46.3 (CH_2), 26.6 (CH_2), 26.0 (CH_2), 18.7 (CH_2); IR (neat): 2950, 2874, 2831, 1648, 1542, 1506, 1397, 1359, 1298, 1255, 1219, 1169, 1024, 987, 879, 844, 778, 689, 667, 631, 602, 575, 510, 462, 419 cm^{-1}; MS (ESI, m/z): 271.14 $[M+H]^+$; HRMS (ESI) calcd. for $C_{16}H_{19}N_2O_2$: 271.1441 $[M+H]^+$, found: 271.1441.

7f: ^{1}H NMR (400 MHz, $CDCI_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCI_3$) δ 196.7 (CO), 163.5 (C), 130.6 (CH), 130.3 (C), 113.6 (CH), 55.4 (OCH_3), 26.3 (CH_3). The spectral data are in agreement with those reported previously for this compound.[3-8]

Synthesis of 1-(4-(Methylthio)phenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3g). 1,9-Bis(4-(methylthio)phenyl)nona-2,7-diyne-1,9-dione (**1g**)

(137.3 mg, 0.35 mmol) and ethylenediamine (42.1 mg, 0.70 mmol) were employed. One fraction was isolated, which afforded 45.8 mg (46%) of the indicated product **3g** as an orange solid (R_f = 0.17 in 1:1 methanol/ethyl acetate; mp 173.0–175.3 °C). The fraction containing 4′-(methylthio)acetophenone (1-(4-(methylthio)phenyl)ethanone) (**7g**) was not isolated.

3g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.81 (s, 1H), 3.94 (t, *J* = 8.9 Hz, 2H), 3.70 (t, *J* = 8.9 Hz, 2H), 3.32 (t, *J* = 6.1 Hz, 2H), 2.62 (t, *J* = 6.3 Hz, 2H), 2.49 (s, 3H), 1.83 (p, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1 (CO), 158.3 (C=N), 155.5 (C), 143.5 (C–SMe), 137.5 (C), 128.1 (CH), 125.2 (CH), 96.3 (CH), 52.6 (CH_2), 46.3 (CH_2), 26.7 (CH_2), 26.0 (CH_2), 18.7 (CH_2), 15.1 (CH_3); IR (neat): 2915, 2870, 1733, 1657, 1619, 1589, 1529, 1465, 1392, 1356, 1305, 1259, 1216, 1180, 1087, 1041, 983, 878, 842, 828, 782, 674, 575, 462 cm^{-1}; MS (ESI, m/z): 287.12 $[M+H]^+$; HRMS (ESI) calcd. for $C_{16}H_{19}N_2OS$: 287.1213 $[M+H]^+$, found: 287.1211.

Synthesis of 1-(4-(Dimethylamino)phenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3h). 1,9-Bis(4-(dimethylamino)phenyl)nona-2,7-diyne-1,9-dione (**1h**) (100.5 mg, 0.26 mmol) and ethylenediamine (31.3 mg, 0.52 mmol) were employed. Two fractions were isolated. First fraction afforded 13.6 mg (32%) of 4′-(dimethylamino)acetophenone (1-(4-(dimethylamino)phenyl)ethanone) (**7h**) as a yellow solid (R_f = 0.38 in 4:1 hexane/ethyl acetate; mp 92.6–94.3 °C). Second fraction yielded 16.1 mg (22%) of the indicated product **3h** as a yellow solid (R_f = 0.17 in 1:1 methanol/ethyl acetate; mp 153.3–155.4 °C).

3h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 5.89 (s, 1H), 3.94 (t, *J* = 8.8 Hz, 2H), 3.72 (t, *J* = 10.5 Hz, 2H), 3.33 (t, *J* = 6.0 Hz, 2H), 3.04 (s, 6H), 2.63 (t, *J* = 6.2 Hz, 2H), 1.83 (p, *J* = 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9 (CO), 159.1 (C=N), 153.6 (C–N(Me)$_2$), 152.8 (C), 129.7 (CH), 128.7 (C), 110.9 (CH), 97.1 (CH), 52.2 (CH_2), 46.3 (CH_2), 40.2 (N-CH_3), 26.6 (CH_2), 26.0 (CH_2), 18.8 (CH_2); IR (neat): 2946, 2830, 1736, 1646, 1584, 1559, 1524, 1475, 1399, 1372, 1269, 1245, 1166, 1041, 997, 942, 881, 843, 788, 750, 578, 540, 493, 458, 417 cm^{-1}; MS (ESI, m/z): 284.17 $[M+H]^+$; HRMS (ESI) calcd. for $C_{17}H_{22}N_3O$: 284.1757 $[M+H]^+$, found: 284.1755

7h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.1 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 3.05 (s, 6H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5 (CO), 153.5 (C), 130.7 (CH), 125.5 (C), 110.8 (CH), 40.2 ($N(CH_3)_2$), 26.1 (CH_3). The spectral data are in agreement with those reported previously for this compound.[6]

Synthesis of 1-(2-Bromophenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3i). 1,9-Bis(2-bromophenyl)nona-2,7-diyne-1,9-dione (**1i**) (61 mg, 0.13 mmol) and ethylenediamine (15.6 mg, 0.26 mmol) were employed. One fraction was isolated, which afforded 23.4 mg (56%) of 2′-bromoacetophenone (1-(2-bromophenyl)ethanone) (**7i**) as an orange oil (R_f = 0.26 in 1:1 methanol/ethyl acetate). The fraction containing 2′-bromoacetophenone (1-(2-bromophenyl)ethanone) (**7i**) was not isolated. **3i:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.36-7.14 (m, 3H), 5.43 (s, 1H), 3.88 (t, *J* = 8.6, 2H), 3.63–3.56 (m, 2H), 3.29 (t, *J* = 6.2, 2H), 2.58 (t, *J* = 6.2 Hz, 2H), 1.83 (p, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1 (CO), 157.9 (C=N), 155.7 (C), 144.9 (C), 133.4 (CH), 130.5 (CH), 128.8 (CH), 127.5 (CH), 119.0 (C–Br), 100.1 (CH), 52.8 (CH_2), 46.3 (CH_2), 26.7 (CH_2), 26.0 (CH_2), 18.6 (CH_2); IR (neat): 2954, 2929, 2871, 1650, 1616, 1584, 1528, 1474, 1401, 1333, 1302, 1261, 1210, 1182, 1113, 1093, 1034, 986, 882, 748, 677, 583, 529, 444 cm^{-1}; MS (ESI, m/z): 319.04 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{16}BrN_2O$: 319.0441 [M+H]$^+$, found: 319.0438.

Synthesis of 1-(3-Bromophenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3j). 1,9-Bis(3-bromophenyl)nona-2,7-diyne-1,9-dione (**1j**) (73.6 mg, 0.16 mmol) and ethylenediamine (19.2 mg, 0.32 mmol) were employed. One fraction was isolated, which afforded 23.7 mg (46%) of 3′-bromoacetophenone (1-(3-bromophenyl)ethanone) (**7j**) as a dark orange oil (R_f = 0.54 in 1:1 methanol/ethyl acetate). The fraction containing 3′-bromoacetophenone (1-(3-bromophenyl)ethanone) (**7j**) was not isolated. **3j:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 5.77 (s, 1H), 3.98 (t, *J* = 8.9 Hz, 2H), 3.74 (t, *J* = 7.5 Hz, 2H), 3.33 (t, *J* = 6.1 Hz, 2H), 2.66 (t, *J* = 6.0 Hz, 2H), 1.86 (p, *J* = 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5 (CO), 158.3 (C=N), 156.6 (C), 143.2 (C), 134.3 (CH), 130.7 (CH), 130.1 (CH), 126.2 (CH), 122.7 (C–Br), 96.3 (CH), 52.6 (CH_2), 46.4 (CH_2), 26.8 (CH_2), 25.9 (CH_2), 18.6 (CH_2); IR (neat): 2929, 2875, 1648, 1630, 1526, 1469, 1396, 1357, 1303, 1263, 1206, 1180, 1041, 990, 882, 781, 718, 672, 578, 517, 439 cm^{-1}; MS (ESI, m/z): 319.04 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{16}BrN_2O$: 319.0441 [M+H]$^+$, found: 319.0439.

Synthesis of 1-(4-Bromophenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3k). 1,9-Bis(4-bromophenyl)nona-2,7-diyne-1,9-dione (**1k**) (102.7 mg, 0.22 mmol) and ethylenediamine (26.4 mg, 0.44 mmol) were employed. Two fractions were isolated. First fraction afforded 26.3 mg (60%) of 4′-bromoacetophenone (1-(4-

bromophenyl)ethanone) (**7k**) as a dark orange oil (R_f = 0.64 in 4:1 hexane/ethyl acetate). Second fraction yielded 20.2 mg (28%) of the indicated product **3k** as an orange solid (R_f = 0.56 in 1:1 methanol/ethyl acetate; mp 172.8–174.4 °C).

3k: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, *J* = 7.1 Hz, 2H), 7.55 (d, *J* = 7.1 Hz, 2H), 5.82 (s, 1H), 3.99 (t, *J* = 8.6 Hz, 2H), 3.76 (t, *J* = 9.1 Hz, 2H), 3.33 (t, *J* = 6.0 Hz, 2H), 2.69 (t, *J* = 5.6 Hz, 2H), 1.87 (p, *J* = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 188.9 (CO), 158.9 (C=N), 155.9 (C), 139.8 (C), 131.7 (CH), 129.3 (CH), 126.4 (C–Br), 96.8 (CH), 52.1 (CH$_2$), 46.4 (CH$_2$), 26.7 (CH$_2$), 25.9 (CH$_2$), 18.5 (CH$_2$); IR (neat): 2937, 2874, 1744, 1661, 1616, 1582, 1535, 1400, 1355, 1259, 1214, 1180, 1069, 1044, 989, 862, 772, 676, 624, 571, 473, 458, 420 cm^{-1}; MS (ESI, m/z): 319.04 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{16}BrN_2O$: 319.0441 [M+H]$^+$, found: 319.0439.

7k: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.1 (CO), 131.9 (C), 129.9 (CH), 129.8 (CH), 128.9 (C–Br), 26.6 (CH$_3$). The spectral data are in agreement with those reported previously for this compound.[3-8]

Synthesis of 1-(3-Chlorophenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3l). 1,9-Bis(3-chlorophenyl)nona-2,7-diyne-1,9-dione (**1l**) (97.6 mg, 0.26 mmol) and ethylenediamine (31.3 mg, 0.52 mmol) were employed. Two fractions were isolated. First fraction afforded 6 mg (15%) of 3′-chloroacetophenone (1-(3-chlorophenyl)ethanone) (**7l**) as a brownish orange oil (R_f = 0.64 in 4:1 hexane/ethyl acetate). Second fraction yielded 20.6 mg (29%) of the indicated product **3l** as a brownish orange solid (R_f = 0.22 in 1:1 methanol/ethyl acetate; mp 92.1–93.5 °C).

3l: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.82 (s, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 9.9 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 5.79 (s, 1H), 3.99 (t, *J* = 8.7 Hz, 2H), 3.75 (t, *J* = 7.2 Hz, 2H), 3.34 (t, *J* = 6.2 Hz, 2H), 2.67 (t, *J* = 6.2 Hz, 2H), 1.87 (p, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 188.6 (CO), 158.5 (C=N), 156.5 (C), 142.9 (C), 134.6 (C–Cl), 131.4 (CH), 129.8 (CH), 127.8 (CH), 125.7 (CH), 96.4 (CH), 52.5 (CH$_2$), 46.4 (CH$_2$), 26.8 (CH$_2$), 25.9 (CH$_2$), 18.6 (CH$_2$); IR (neat): 3063, 2922, 2851, 1632, 1529, 1424, 1396, 1361, 1302, 1263, 1208, 1182, 1040, 991, 887, 787, 756, 730, 646, 582, 495, 414 cm^{-1}; MS (ESI, m/z): 275.09 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{16}ClN_2O$: 275.0946 [M+H]$^+$, found: 275.0941.

7l: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 2.60 (s, 3H). The spectral data are in agreement with those reported previously for this compound.[6-8]

Synthesis of 1-(4-Chlorophenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3m). 1,9-Bis(4-chlorophenyl)nona-2,7-diyne-1,9-dione (**1m**) (103 mg, 0.28 mmol) and ethylenediamine (33.6 mg, 0.56 mmol) were employed. Two fractions were isolated. First fraction afforded 11.5 mg (27%) of 4′-chloroacetophenone (1-(4-chlorophenyl)ethanone) (**7m**) as a brownish orange oil (R_f = 0.64 in 4:1 hexane/ethyl acetate). Second fraction yielded 24.3 mg (32%) of the indicated product **3m** as an orange solid (R_f = 0.81 in 1:1 methanol/ethyl acetate; mp 150.3–153.5 °C).

3m: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 5.79 (s, 1H), 3.97 (t, *J* = 8.8 Hz, 2H), 3.72 (t, *J* = 9.0 Hz, 2H), 3.33 (t, *J* = 6.1 Hz, 2H), 2.65 (t, *J* = 6.3 Hz, 2H), 1.86 (p, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8 (CO), 155.9 (C=N), 139.3 (C), 137.9 (C–Cl), 131.5 (C), 129.1 (CH), 128.7 (CH), 97.0 (CH), 46.4 (CH_2), 29.8 (CH_2), 26.7 (CH_2), 25.7 (CH_2), 18.5 (CH_2); IR (neat): 3069, 2948, 2542, 1680, 1588, 1539, 1400, 1279, 1215, 1174, 1089, 1043, 1013, 927, 849, 761, 683, 524, 471, 437, 409 cm^{-1}; MS (ESI, m/z): 275.09 $[M+H]^+$; HRMS (ESI) calcd. for $C_{15}H_{16}ClN_2O$: 275.0946 $[M+H]^+$, found: 275.0943.

7m: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 2.59 (s, 3H). The spectral data are in agreement with those reported previously for this compound.[3-6]

Synthesis of 1-(2-Fluorophenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3n). 1,9-Bis(2-fluorophenyl)nona-2,7-diyne-1,9-dione (**1n**) (102 mg, 0.30 mmol) and ethylenediamine (36.1 mg, 0.60 mmol) were employed. One fraction was isolated, which afforded 37.2 mg (48%) of the indicated product **3n** as a brownish orange solid (R_f = 0.76 in 1:1 methanol/ethyl acetate; mp 130.9–132.1 °C). The fraction containing 2′-fluoroacetophenone (1-(2-fluorophenyl)ethanone) (**7n**) was not isolated.

3n: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.68 (m, 1H), 7.42–7.36 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.06 (dd, *J* = 10.8, 8.4 Hz, 1H), 5.76 (s, 1H), 3.92 (t, *J* = 8.8 Hz, 2H), 3.66 (t, *J* = 8.9 Hz, 2H), 3.32 (t, *J* = 6.1 Hz, 2H), 2.62 (t, *J* = 6.3 Hz, 2H), 1.85 (p, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6 (d, ^3J = 2.8 Hz, CO), 160.3 (d, ^1J = 250.3 Hz, C–F), 157.9 (C=N), 155.7 (C), 132.4 (d, ^3J = 8.7 Hz, CH), 130.6 (d, ^3J = 2.8 Hz, CH), 130.0 (d, ^2J = 13.7 Hz, C), 124.3 (d, ^4J = 3.3 Hz, CH), 116.2 (d, ^2J = 23.8 Hz, CH), 100.6 (d, ^4J = 7.3 Hz, CH), 52.7 (CH_2), 46.2 (CH_2), 26.9 (CH_2), 25.9 (CH_2), 18.5 (CH_2); IR (neat): 2969, 2945, 2365, 1737, 1651, 1574, 1540, 1521, 1497, 1473, 1456, 1419, 1397, 1362, 1301, 1264, 1229, 1216, 1180, 1100, 1033, 989, 876, 777, 751, 685, 670, 624, 577, 518 cm^{-1}; MS (ESI, m/z): 259.12 $[M+H]^+$; HRMS (ESI) calcd. for $C_{15}H_{16}FN_2O$: 259.1241 $[M+H]^+$, found: 259.1246.

Synthesis of 1-(4-Fluorophenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3o). 1,9-Bis(4-fluorophenyl)nona-2,7-diyne-1,9-dione (**1o**) (92 mg, 0.27 mmol) and ethylenediamine (32.5 mg, 0.54 mmol) were employed. One fraction was isolated, which afforded 38.4 mg (55%) of the indicated product **3o** as a yellow solid (R_f = 0.69 in 1:1 methanol/ethyl acetate; mp 155.2–156.6 °C). The fraction containing 4′-fluoroacetophenone (1-(4-fluorophenyl)ethanone) (**7o**) was not isolated.

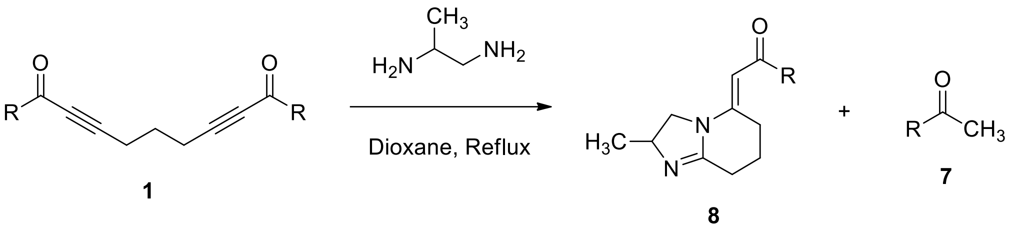
3o: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 5.79 (s, 1H), 3.96 (t, *J* = 8.8 Hz, 2H), 3.70 (t, *J* = 4.3 Hz, 2H), 3.32 (t, *J* = 6.1 Hz, 2H), 2.63 (t, *J* = 6.4 Hz, 2H), 1.84 (p, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6 (CO), 164.8 (d, ^1J = 251.8 Hz, C–F), 158.2 (C=N), 156.0 (C), 137.4 (d, ^4J = 3.0 Hz, C), 130.0 (d, ^3J = 9.0 Hz, CH), 115.3 (d, ^2J = 21.6 Hz, CH), 96.2 (CH), 52.7 (CH_2), 46.3 (CH_2), 26.8 (CH_2), 26.0 (CH_2), 18.7 (CH_2); IR (neat): 2954, 2356, 2323, 1737, 1683, 1653, 1635, 1617, 1585, 1541, 1505, 1474, 1457, 1435, 1356, 1304, 1260, 1216, 1182, 1161, 1104, 1045, 988, 879, 856, 777, 669, 630, 602, 574, 508 cm^{-1}; MS (ESI, m/z): 259.12 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{16}FN_2O$: 259.1241 [M+H]$^+$, found: 259.1246.

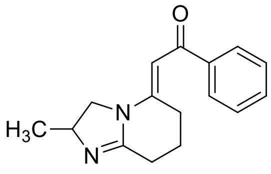
Synthesis of 1-(3,5-Dichlorophenyl)-2-(2,3,7,8-tetrahydroimidazo[1,2-a]pyridin-5(6*H*)-ylidene)ethanone (3p). 1,9-Bis(3,5-dichlorophenyl)nona-2,7-diyne-1,9-dione (**1p**) (88.5 mg, 0.202 mmol) and ethylenediamine (24.3 mg, 0.404 mmol) were employed. Two fractions were isolated. First fraction afforded 12.6 mg (33%) of 3′,5′-dichloroacetophenone (1-(3,5-dichlorophenyl)ethanone) (**7p**) as a brownish orange oil (R_f = 0.64 in 4:1 hexane/ethyl acetate). Second fraction yielded 12.8 mg (21%) of the indicated product **3p** as an orange oil (R_f = 0.63 in 1:1 methanol/ethyl acetate).

3p: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.6 Hz, 2H), 7.48 (s, 1H), 5.82 (s, 1H), 4.06 (t, *J* = 8.8 Hz, 2H), 3.88 (t, *J* = 9.0 Hz, 2H), 3.33 (t, *J* = 6.1 Hz, 2H), 2.81 (t, *J* = 6.0 Hz, 2H), 1.90 (p, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9 (CO), 156.7 (C=N), 143.7 (C), 135.4 (C and C–Cl), 131.3 (CH), 126.2 (CH), 96.7 (CH), 51.9 (CH_2), 46.5 (CH_2), 26.8 (CH_2), 25.7 (CH_2), 18.4 (CH_2) (Note that two C peaks overlap on each other); IR (neat): 3070, 2918, 2875, 1732, 1651, 1524, 1470, 1395, 1357, 1303, 1260, 1205, 1180, 1122, 1046, 991, 859, 790, 729, 658, 577, 518, 427 cm^{-1}; MS (ESI, m/z): 309.05 [M+H]$^+$; HRMS (ESI) calcd. for $C_{15}H_{15}Cl_2N_2O$: 309.0556 [M+H]$^+$, found: 309.0557.

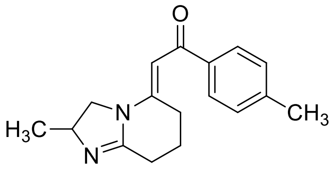
7p: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.9 Hz, 2H), 7.57 (t, *J* = 1.9 Hz, 1H), 2.61 (s, 3H). The spectral data are in agreement with those reported previously for this compound.[8]

Table S4. Synthesis of 2-Methyl-Substituted 5-Alkylidene-2,3,5,6,7,8-hexahydroimidazo[1,2-*a*]pyridines **8**.[a,b]

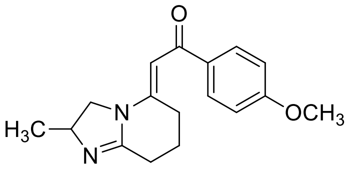




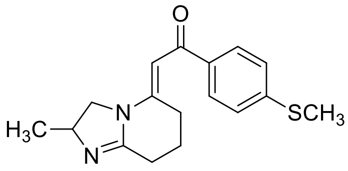
8a (45%)
7a (8%)



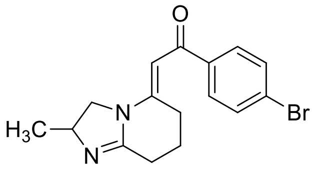
8b (29%)
7b (44%)



8f (30%)
7f (65%)



8g (23%)
7g (65%)



8k (29%)
7k (32%)

[a] Isolated yields. [b] For the identities of the corresponding aryl methyl ketones **7**, see Experimental part.

General Procedure 4. Synthesis of 2-Methyl-Substituted 5-Alkylidene-2,3,5,6,7,8-hexahydroimidazo[1,2-*a*]pyridines 8 (Table S4). To a stirred solution of the proper 1,9-diarylnona-2,7-diyne-1,9-dione **1** (0.25 mmol) in dioxane (5.0 mL) under argon was added 1,2-propylenediamine (1,2-diaminopropane) (0.50 mmol), and the resulting mixture was refluxed until the end of the reaction (The progress of the reaction was monitored by routine TLC analysis for the disappearance of bis-α,β-alkynic ketone **1** using 4:1 hexane/ethyl acetate as the eluent). After the reaction was over, the solvent was removed on a rotary evaporator, and the resulting crude product was purified by flash chromatography on silica gel using 4:1 hexane/ethyl acetate, followed by 1:1 methanol/ethyl acetate, as the eluent to afford the corresponding 2-(2-methyl-2,3,7,8-tetrahydroimidazo[1,2-*a*]pyridin-5(6*H*)-ylidene)-1-arylethanone **8** and aryl methyl ketone **7**.

Synthesis of 2-(2-methyl-2,3,7,8-tetrahydroimidazo[1,2-*a*]pyridin-5(6*H*)-ylidene)-1-phenylethanone (8a). 1,9-Diphenylnona-2,7-diyne-1,9-dione (**1a**) (120 mg, 0.40 mmol) and 1,2-diaminopropane (59.3 mg, 0.80 mmol) were employed. Two fractions were isolated. First fraction afforded 4 mg (8%) of acetophenone (**7a**) as a brownish orange oil (R_f = 0.72 in 4:1 hexane/ethyl acetate). Second fraction yielded 45.6 mg (45%) of the indicated product **8a** as a yellow solid (R_f = 0.67 in 1:1 methanol/ethyl acetate; mp 92.0-95.2 °C).

8a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.9 Hz, 2H), 7.46–7.40 (m, 3H), 5.86 (s, 1H), 4.29–4.22 (m, 1H), 3.86 (t, *J* = 10.1 Hz, 1H), 3.34–3.26 (m, 3H), 2.66 (t, *J* = 6.4 Hz, 2H), 1.87–1.82 (m, 2H), 1.35 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1 (CO), 157.6 (C=N), 155.4 (C), 141.0 (C), 131.6 (CH), 128.4 (CH), 127.6 (CH), 97.2 (CH), 59.1 (CH), 53.4 (CH_2), 26.6 (CH_2), 25.7 (CH_2), 22.3 (CH_2), 18.6 (CH_3); IR (neat): 2963, 2924, 1655, 1542, 1397, 1350, 1310, 1258, 1214, 1179, 1042, 928, 880, 772, 707, 573, 502 cm^{-1}; MS (ESI, m/z): 255.14 $[M+H]^+$; HRMS (ESI) calcd. for $C_{16}H_{19}N_2O$: 255.1492 $[M+H]^+$, found: 255.1488

7a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.95 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3 (CO), 137.2 (C), 133.2 (CH), 128.7 (CH), 128.4 (CH), 26.8 (CH_3). The spectral data are in agreement with those reported previously for this compound.[3-8]

Synthesis of 2-(2-methyl-2,3,7,8-tetrahydroimidazo[1,2-*a*]pyridin-5(6*H*)-ylidene)-1-(p-tolyl)ethanone (8b). 1,9-Di-*p*-tolylnona-2,7-diyne-1,9-dione (**1b**) (110.8 mg, 0.34 mmol) and 1,2-diaminopropane (50.4 mg, 0.68 mmol) were employed. Two fractions were isolated. First fraction afforded 19.9 mg (44%) of 4′-methylacetophenone (1-(4-methylphenyl)ethanone) (**7b**) as a dark orange oil (R_f = 0.67 in 4:1 hexane/ethyl acetate). Second fraction yielded 26.1 mg (29%) of the indicated product **8b** as a yellowish brown solid (R_f = 0.63 in 1:1 methanol/ethyl acetate; mp 132.1–135.3 °C).

8b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 5.88 (s, 1H), 4.30-4.19 (m, 1H), 3.88 (t, *J* = 10.1 Hz, 1H), 3.34–3.24 (m, 3H), 2.66 (t, *J* = 6.3 Hz, 2H), 2.38 (s, 3H), 1.88–1.80 (m, 2H), 1.35 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7 (CO), 158.1 (C=N), 154.6 (C), 142.3 (C–CH_3), 138.2 (C), 129.1 (CH), 127.7 (CH), 97.8 (CH), 58.7 (CH), 53.4 (CH_2), 26.5 (CH_2), 25.7 (CH_2), 22.3 (CH_2), 21.6 (CH_3), 18.5 (CH_3); IR (neat): 2964, 2928, 1654, 1604, 1541, 1398, 1349, 1312, 1259, 1225, 1181, 1043, 929, 881, 782, 735, 682, 636, 565, 504 cm^{-1}; MS (ESI, m/z): 269.16 $[M+H]^+$; HRMS (ESI) calcd. for $C_{17}H_{21}N_2O$: 269.1648 $[M+H]^+$, found: 269.1632

7b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 2.51 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1 (CO), 144.0 (C), 134.8 (C), 129.4 (CH), 128.6 (CH), 26.7 (CH_3), 21.8 (CH_3). The spectral data are in agreement with those reported previously for this compound.[3-8]

Synthesis of 1-(4-methoxyphenyl)-2-(2-methyl-2,3,7,8-tetrahydroimidazo[1,2-*a*]pyridin-5(6*H*)-ylidene)ethanone (8f). 1,9-Bis(4-methoxyphenyl)nona-2,7-diyne-1,9-dione (**1f**) (221.5 mg, 0.61 mmol) and 1,2-diaminopropane (90 mg, 1.22 mmol) were employed. Two fractions were isolated. First fraction afforded 60 mg (65%) of 4′-methoxyacetophenone (1-(4-methoxyphenyl)ethanone) (**7f**) as a dark orange oil (R_f = 0.48 in 4:1 hexane/ethyl acetate). Second fraction yielded 51.5 mg (30%) of the indicated product **8f** as a yellowish brown solid (R_f = 0.52 in 1:1 methanol/ethyl acetate; mp 106.1–109.0 °C).

8f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.85 (s, 1H), 4.28-4.17 (m, 1H), 3.89-3.83 (m, 4H), 3.34-3.23 (m, 3H), 2.63 (t, *J* = 6.4 Hz, 2H), 1.87–1.79 (m, 2H), 1.34 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9 (CO), 162.4 (C-OMe), 157.4 (C=N), 154.8 (C), 133.7 (C), 129.7 (CH), 113.6 (CH), 96.9 (CH), 59.2 (CH), 55.5 (OCH_3), 53.4 (CH_2), 26.6 (CH_2), 25.9 (CH_2), 22.4 (CH_2), 18.7 (CH_3); IR (neat): 2962, 2925, 1649, 1595, 1569, 1544, 1506, 1431, 1397, 1355, 1302, 1259, 1220, 1168, 1027, 930, 882, 848, 785, 687, 630, 596, 508 cm^{-1}; MS (ESI, m/z): 285.15 $[M+H]^+$; HRMS (ESI) calcd. for $C_{17}H_{21}N_2O_2$: 285.1598 $[M+H]^+$, found: 285.1591.

7f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7 (CO), 163.5 (C), 130.6 (CH), 130.3 (C), 113.6 (CH), 55.4 (OCH_3), 26.3 (CH_3). The spectral data are in agreement with those reported previously for this compound.[3-8]

Synthesis of 2-(2-methyl-2,3,7,8-tetrahydroimidazo[1,2-*a*]pyridin-5(6*H*)-ylidene)-1-(4-(methylthio)phenyl)ethanone (8g). 1,9-Bis(4-(methylthio)phenyl)nona-2,7-diyne-1,9-dione (**1g**) (117.7 mg, 0.30 mmol) and 1,2-diaminopropane (44.5 mg, 0.60 mmol) were employed. Two fractions were isolated. First fraction afforded 32.6 mg (65%) of 4′-(methylthio)acetophenone (1-(4-(methylthio)phenyl)ethanone) (**7g**) as a brown solid (R_f = 0.46 in 4:1 hexane/ethyl acetate). Second fraction yielded 20.9 mg (23%) of the indicated product **8g** as a light yellowish orange solid (R_f = 0.79 in 1:1 methanol/ethyl acetate; mp 138.8–140.2 °C).

8g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 9.0 Hz, 2H), 5.99 (s, 1H), 4.43-4.32 (m, 1H), 4.05 (t, *J* = 10.4 Hz, 1H), 3.44 (dd, *J* = 10.4, 7.1 Hz, 1H), 3.26 (q, *J* = 6.1 Hz, 2H), 2.84 (t, *J* = 8.0 Hz, 2H), 2.46 (s, 3H), 1.87–1.81 (m, 2H), 1.43 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7 (CO), 161.8 (C=N), 152.3 (C), 145.0 (C–SMe), 136.2 (C), 128.3 (CH), 125.2 (CH), 101.1 (CH), 56.1 (CH), 53.6 (CH_2), 26.0 (CH_2), 24.7 (CH_2), 21.8 (CH_2), 17.8 (CH_3), 15.0 (CH_3); IR (neat): 2956, 2921, 1650, 1586, 1521, 1384, 1352, 1279, 1217, 1178, 1091, 1039, 880, 811, 658, 568, 420 cm^{-1}; MS (ESI, m/z): 301.13 $[M+H]^+$; HRMS (ESI) calcd. for $C_{17}H_{21}N_2OS$: 301.1369 $[M+H]^+$, found: 301.1364.

7g: ^{1}H NMR (400 MHz, $CDCI_3$) δ δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 2.50 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCI_3$) δ 197.2 (CO), 146.0 (C-SMe), 133.5 (C), 128.8 (CH), 125.0 (CH), 26.5 (CH_3), 14.8 (SCH_3). The spectral data are in agreement with those reported previously for this compound.[10-13]

Synthesis of 1-(4-bromophenyl)-2-(2-methyl-2,3,7,8-tetrahydroimidazo[1,2-*a*]pyridin-5(6*H*)-ylidene)ethanone (8k). 1,9-Bis(4-bromophenyl)nona-2,7-diyne-1,9-dione (**1k**) (241.3 mg, 0.53 mmol) and 1,2-diaminopropane (78.6 mg, 1.06 mmol) were employed. Two fractions were isolated. First fraction afforded 34 mg (32%) of 4′-bromoacetophenone (1-(4-bromophenyl)ethanone) (**7k**) as a dark orange oil (R_f = 0.64 in 4:1 hexane/ethyl acetate). Second fraction yielded 52 mg (29%) of the indicated product **8k** as a brownish orange solid (R_f = 0.63 in 1:1 methanol/ethyl acetate; mp 120.4–123.0 °C).

8k: ^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 5.83 (s, 1H), 4.34-4.23 (m, 1H), 3.92 (t, *J* = 10.2 Hz, 1H), 3.36–3.25 (m, 3H), 2.70 (t, *J* = 6.4 Hz, 2H), 1.90–1.81 (m, 2H), 1.37 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7 (CO), 158.2 (C=N), 155.4 (C), 139.6 (C), 131.7 (CH), 129.2 (CH), 126.5 (C–Br), 97.5 (CH), 58.6 (CH), 53.4 (CH_2), 26.5 (CH_2), 25.6 (CH_2), 22.2 (CH_2), 18.3 (CH_3); IR (neat): 2932, 2862, 1655, 1616, 1534, 1403, 1351, 1304, 1258, 1213, 1184, 1070, 1042, 1008, 989, 933, 879, 851, 826, 776, 739, 681, 625, 568, 500, 457, 416 cm^{-1}; MS (ESI, m/z): 333.05 $[M+H]^+$; HRMS (ESI) calcd. for $C_{16}H_{18}BrN_2O$: 333.0597 $[M+H]^+$, found: 333.0587.

7k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1 (CO), 131.9 (C), 129.9 (CH), 129.8 (CH), 128.9 (C–Br), 26.6 (CH_3). The spectral data are in agreement with those reported previously for this compound.[3-8]

Copies of ^{1}H and ^{13}C{^{1}H} NMR Spectra for Starting Materials 1, 5 and 6

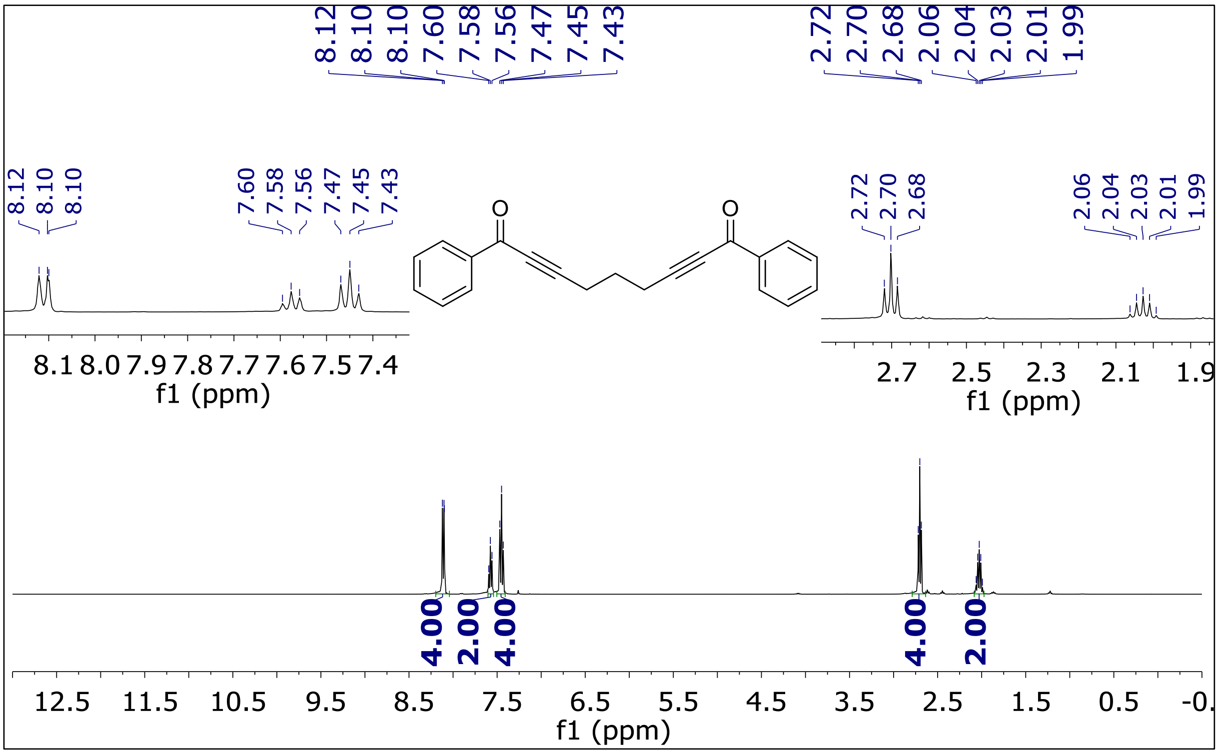


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1a**.

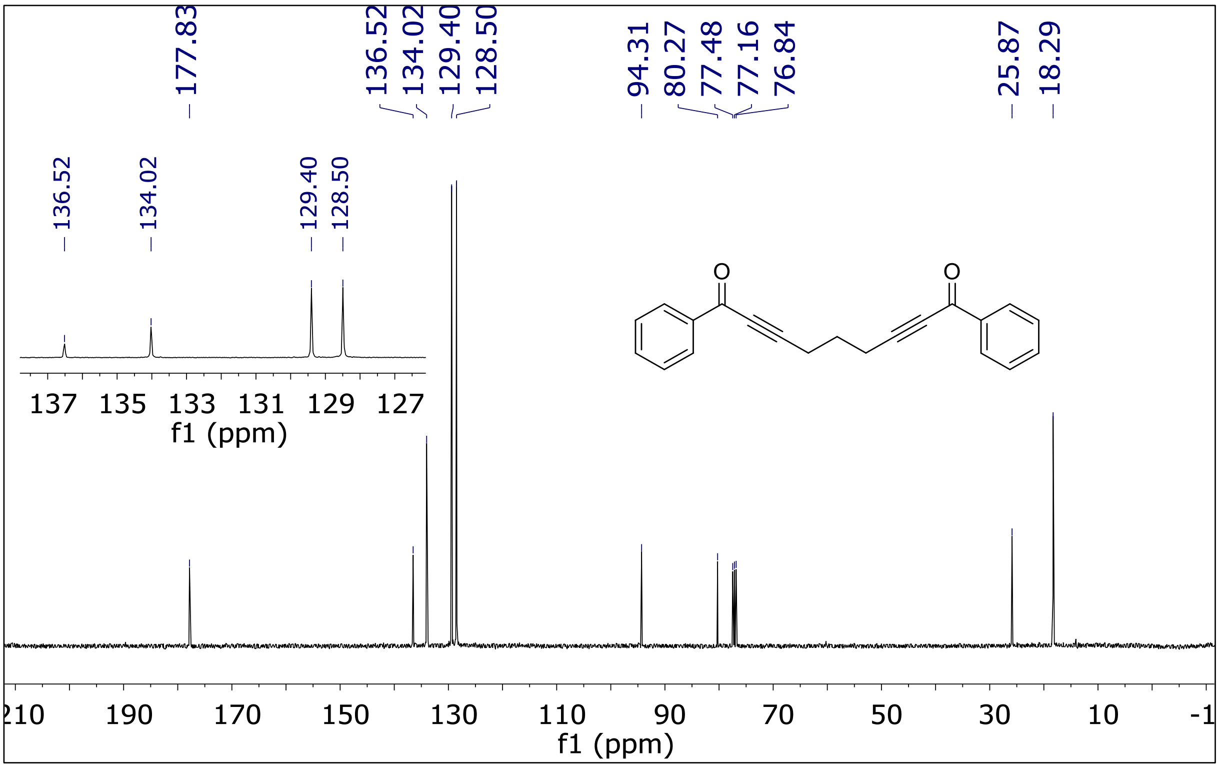


Figure S2. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of compound **1a**.

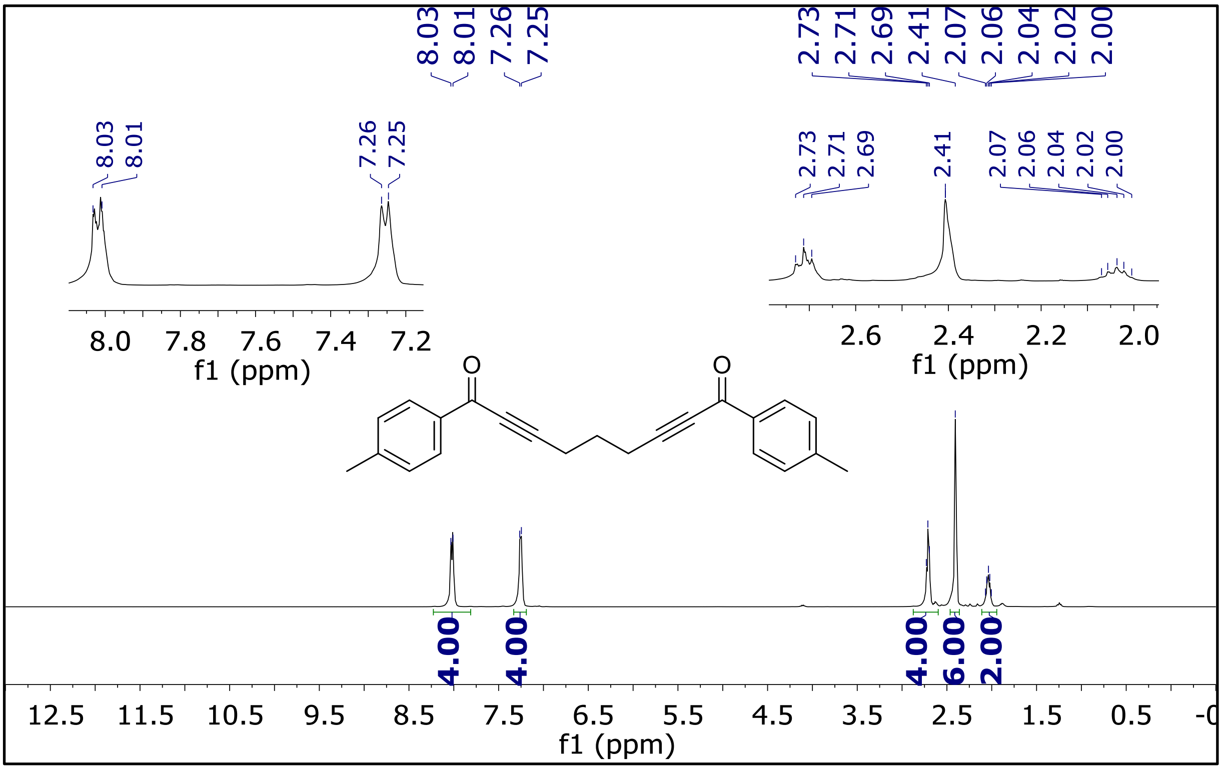


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1b**.

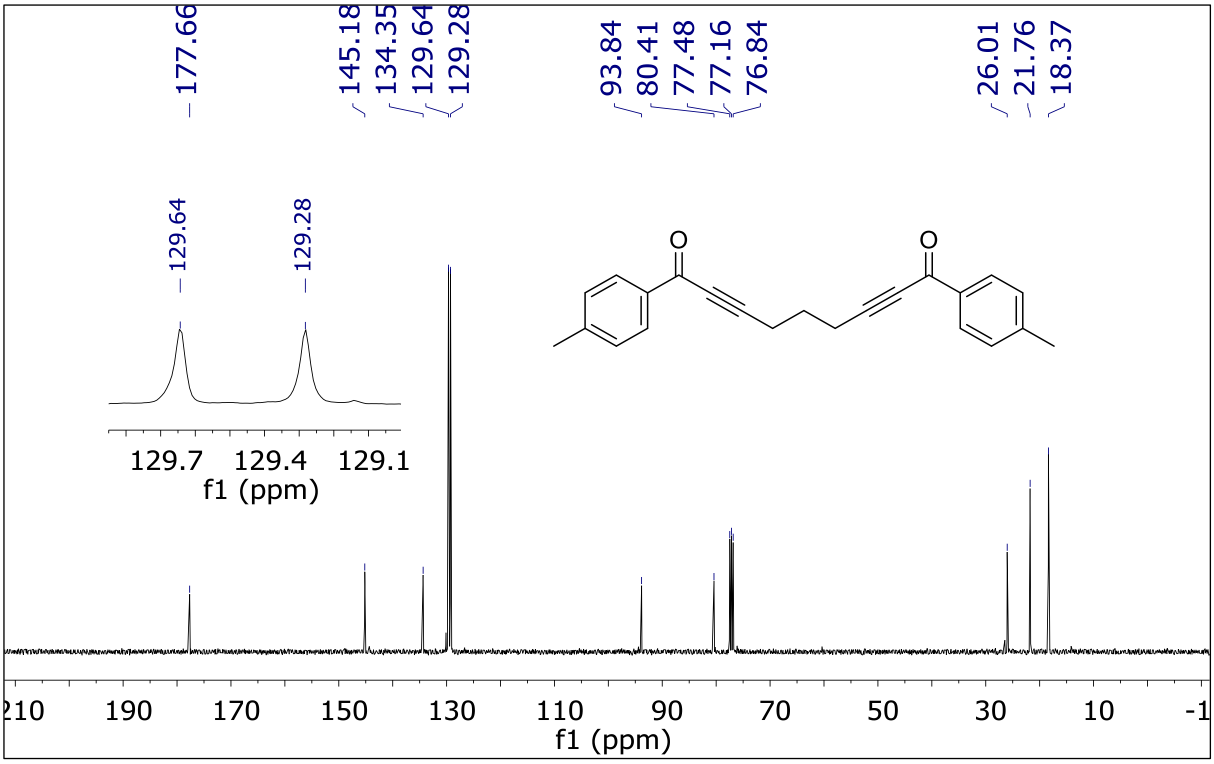


Figure S4. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1b**.

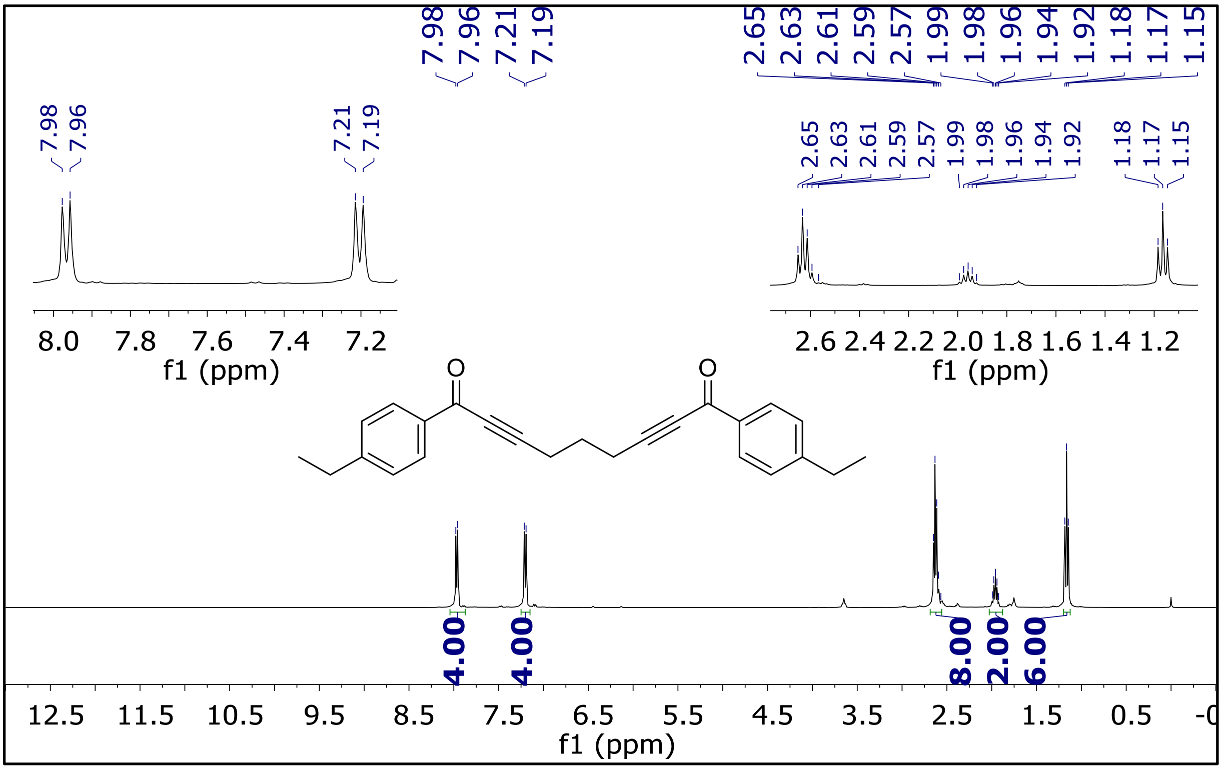


Figure S5. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1c**.

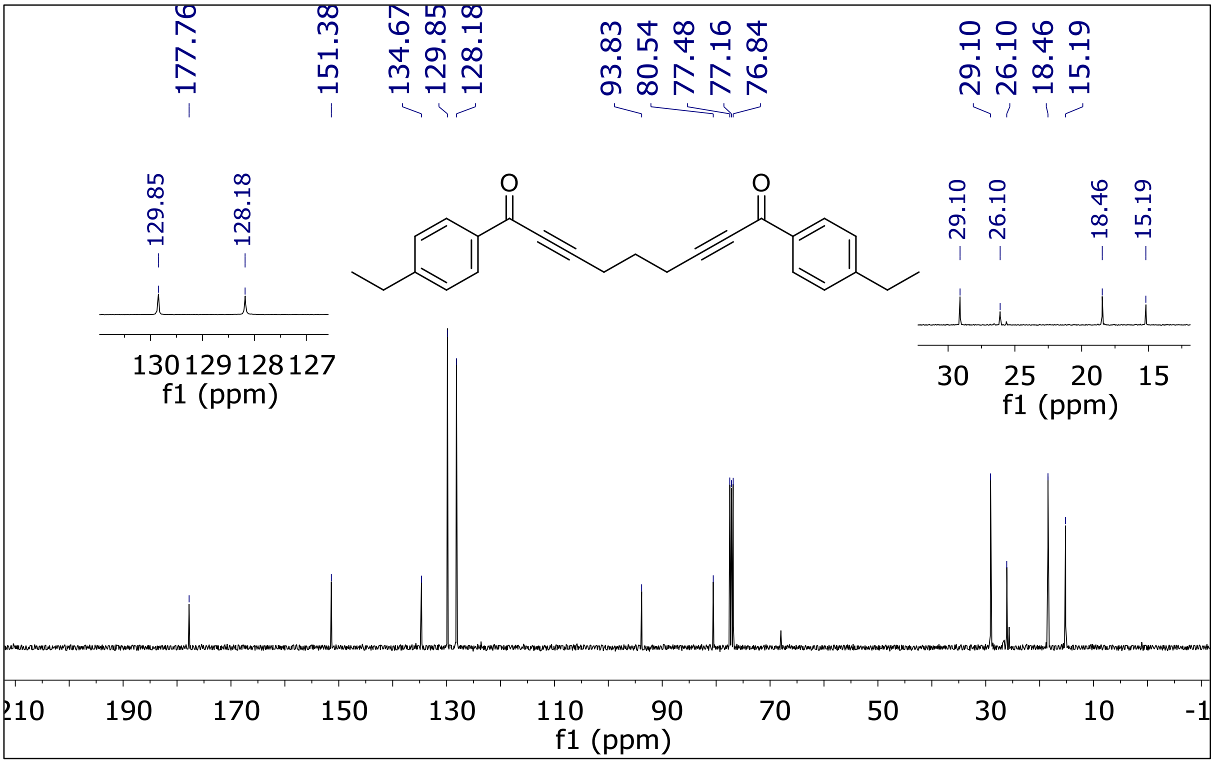


Figure S6. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1c**.

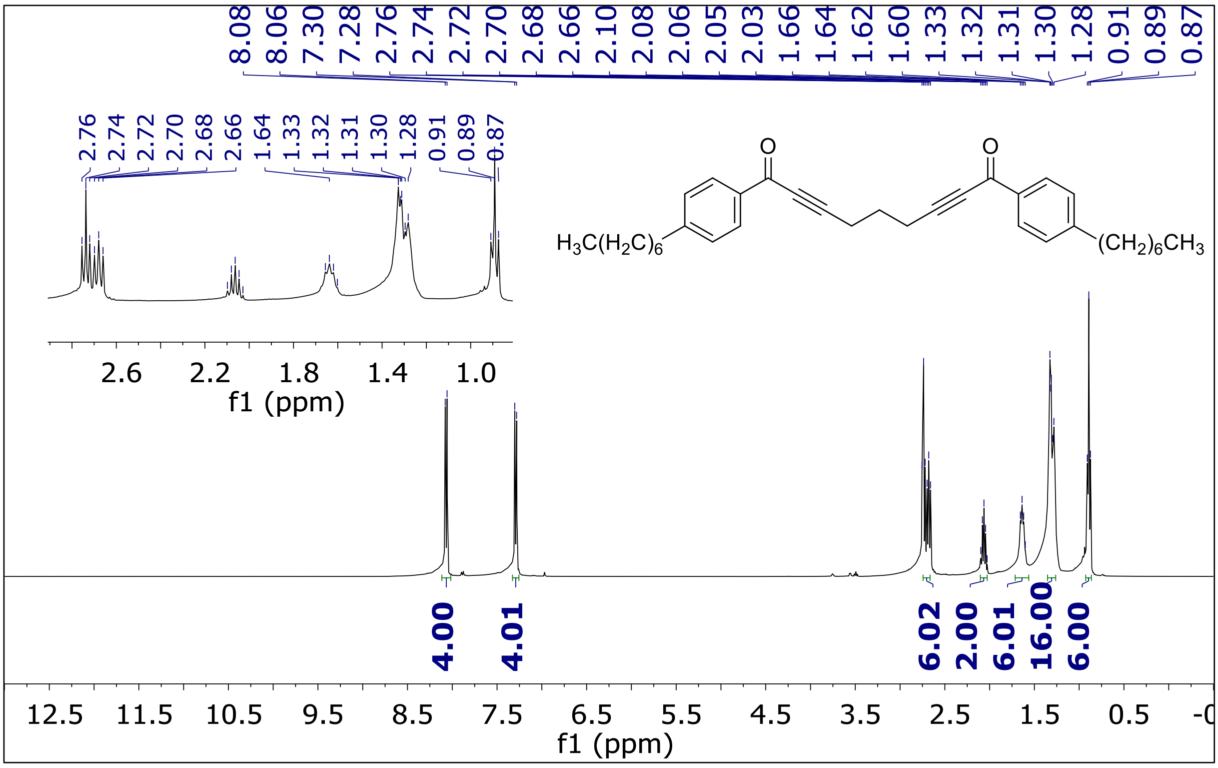


Figure S7. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1d**.

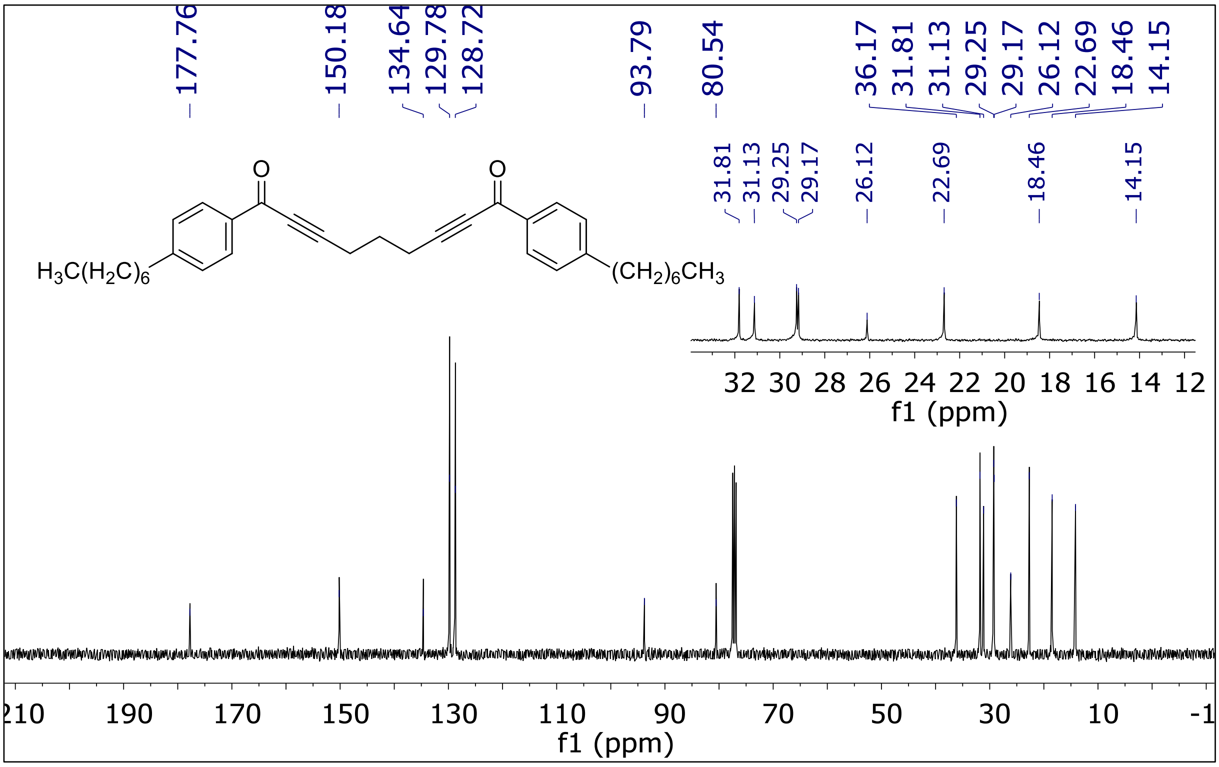


Figure S8. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1d**.

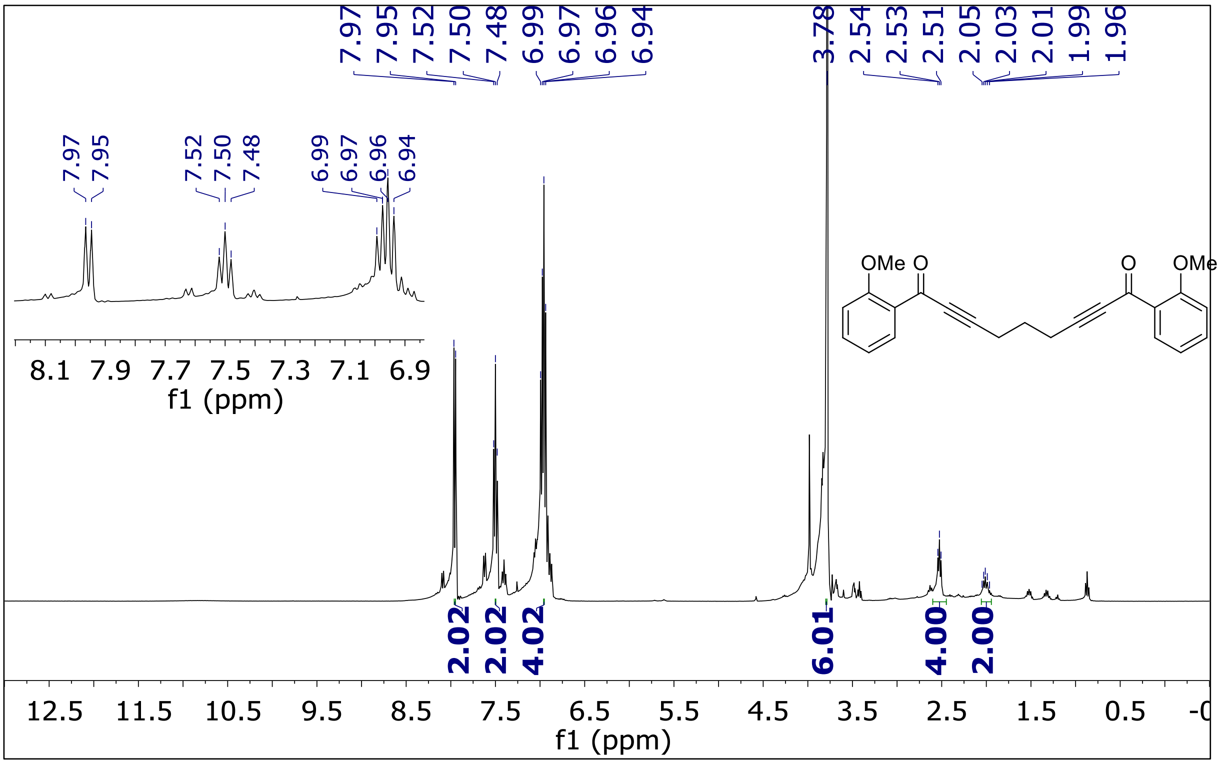


Figure S9. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1e**.

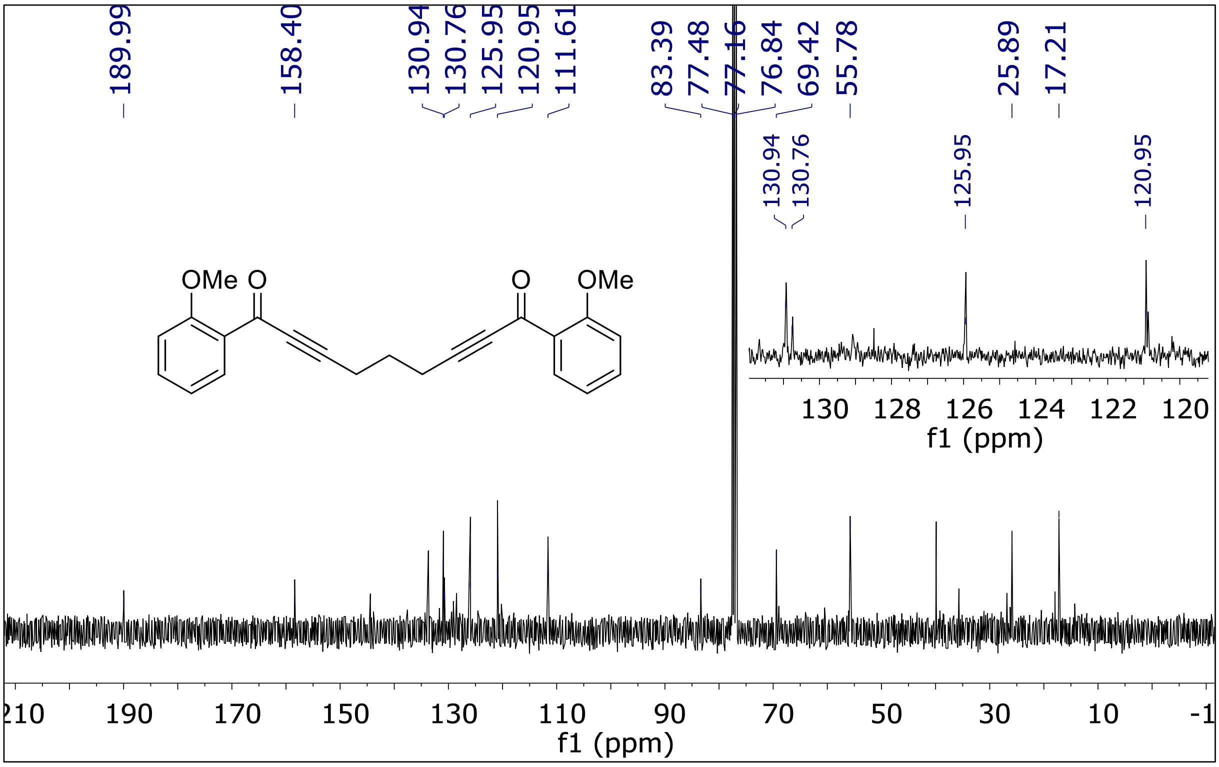


Figure S10. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1e**.

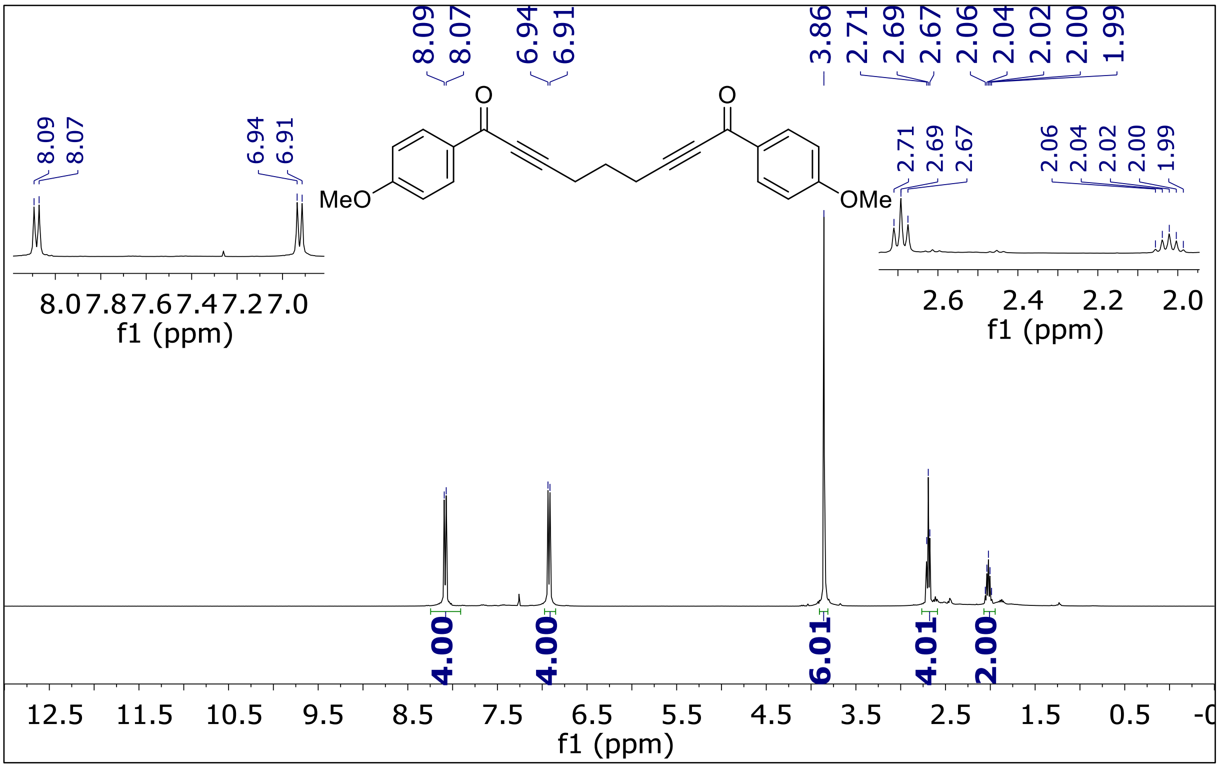


Figure S11. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1f**.

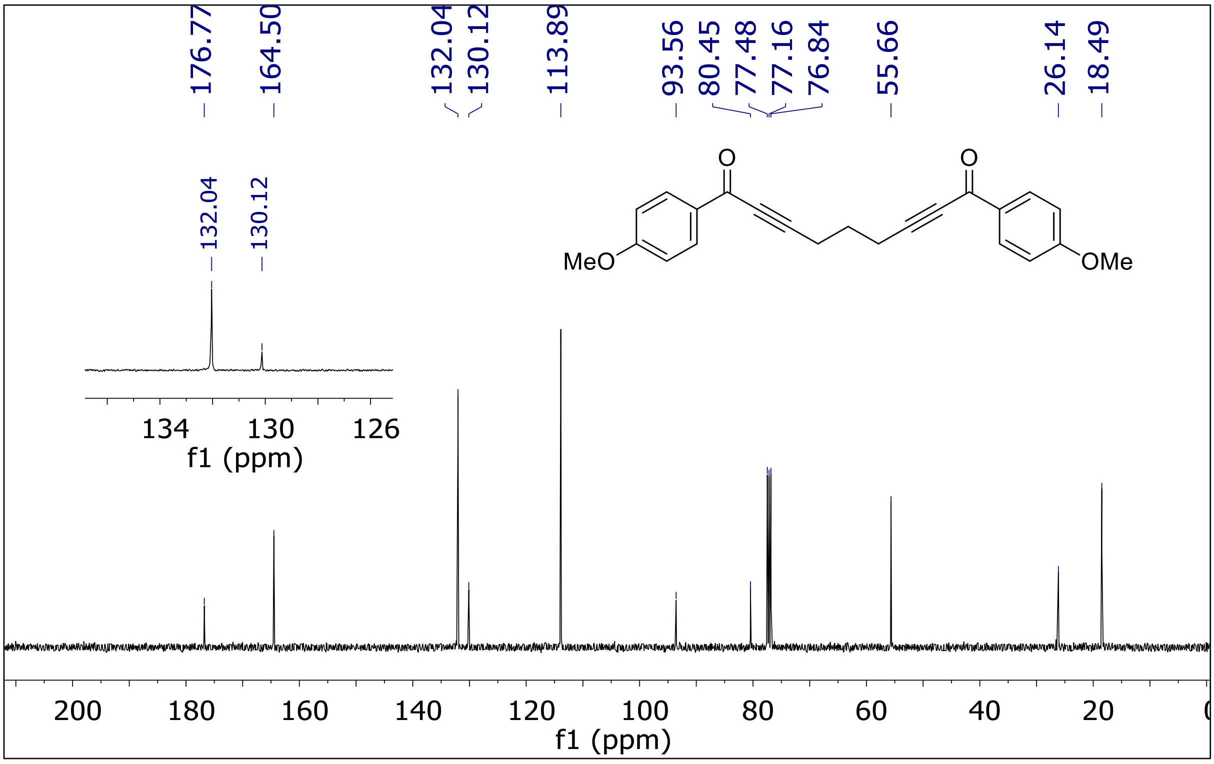


Figure S12. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1f**.

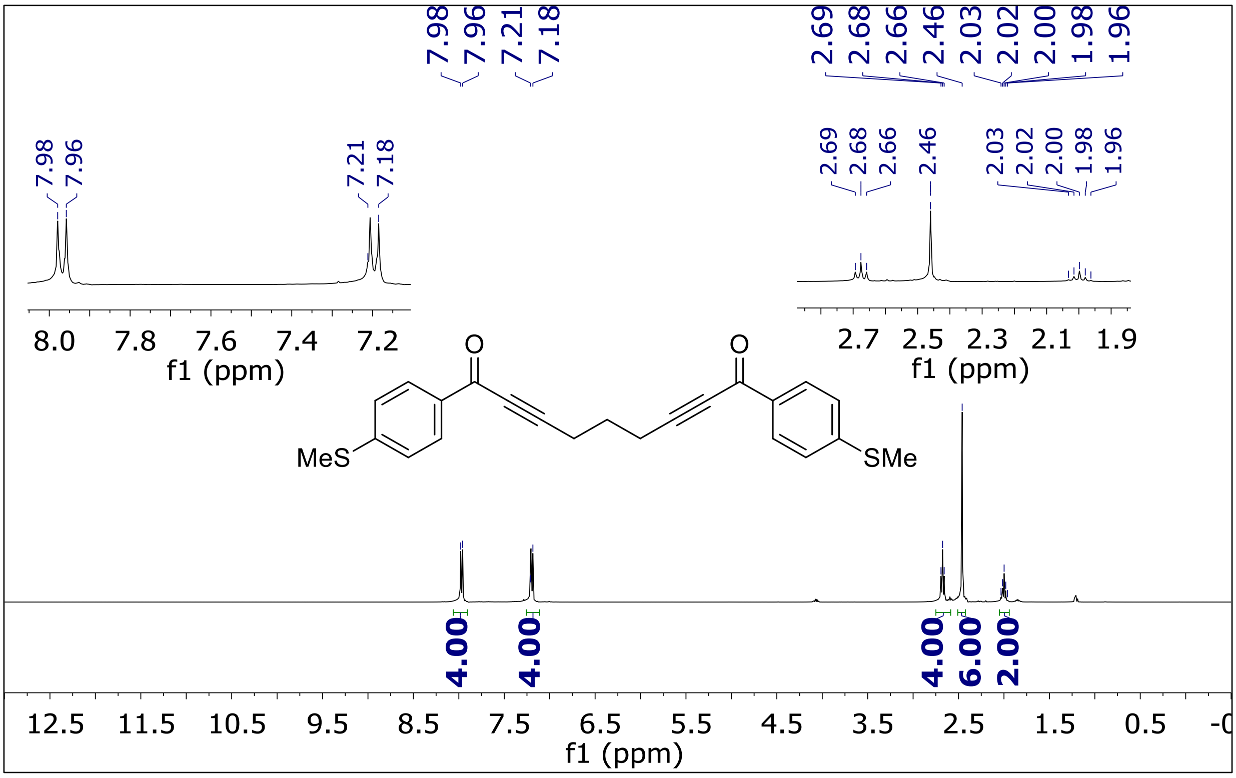


Figure S13. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1g**.

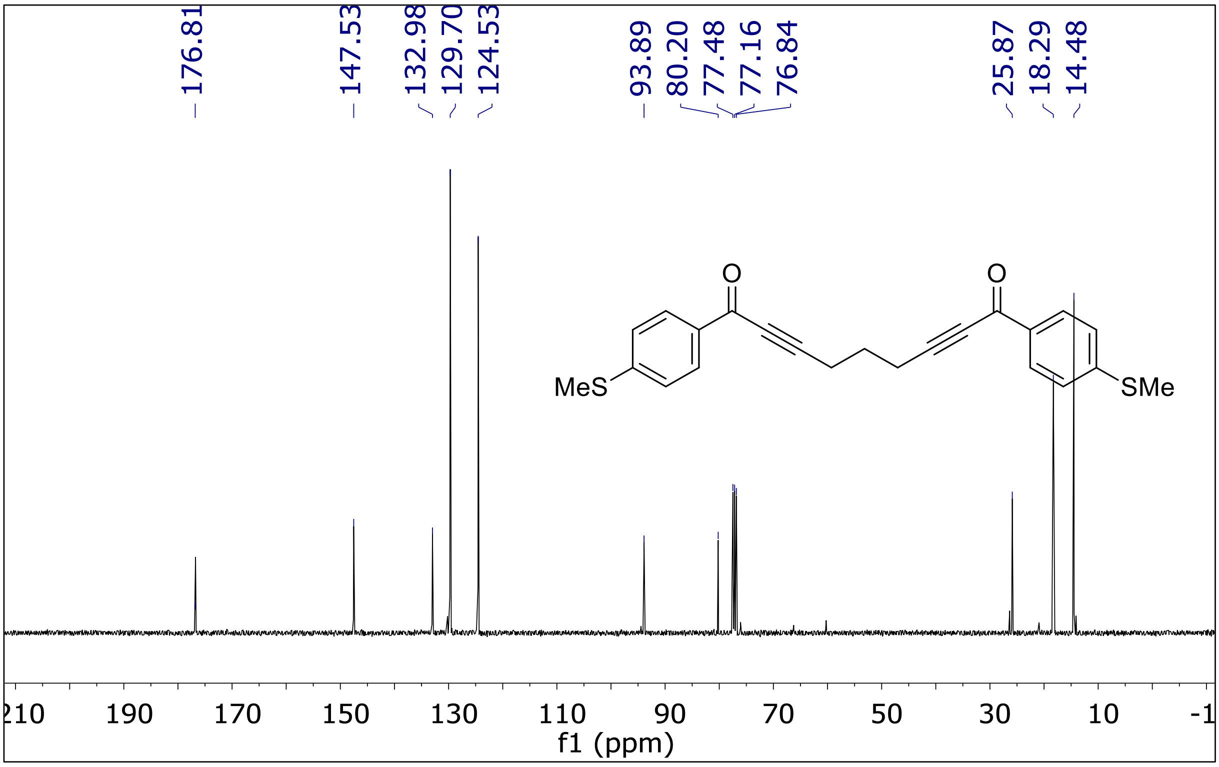


Figure S14. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1g**.

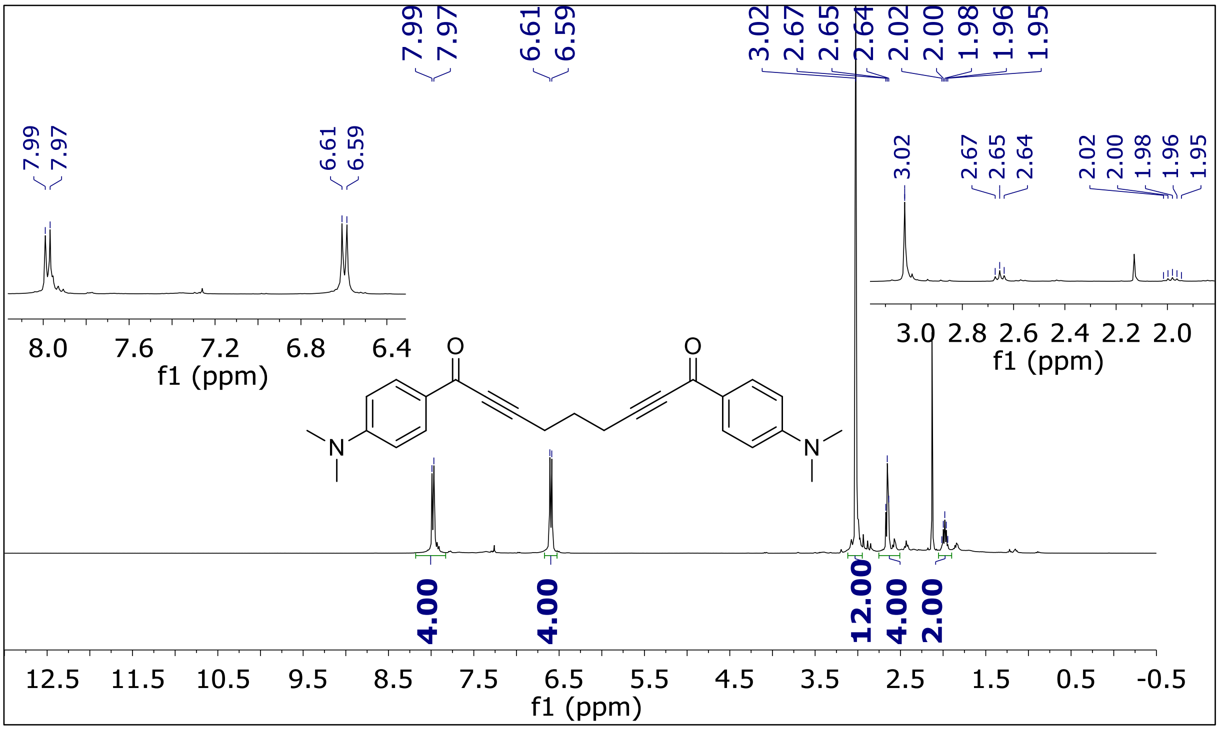


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1h**.

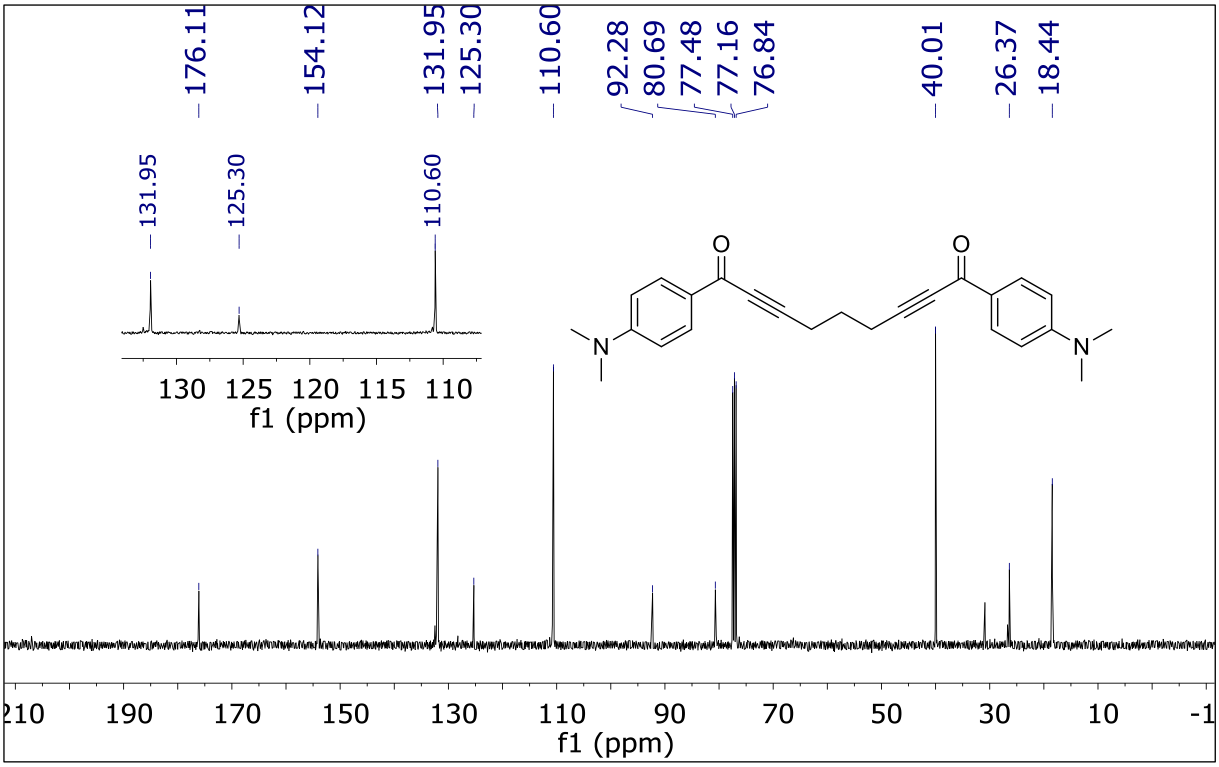


Figure S16. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **1h**.

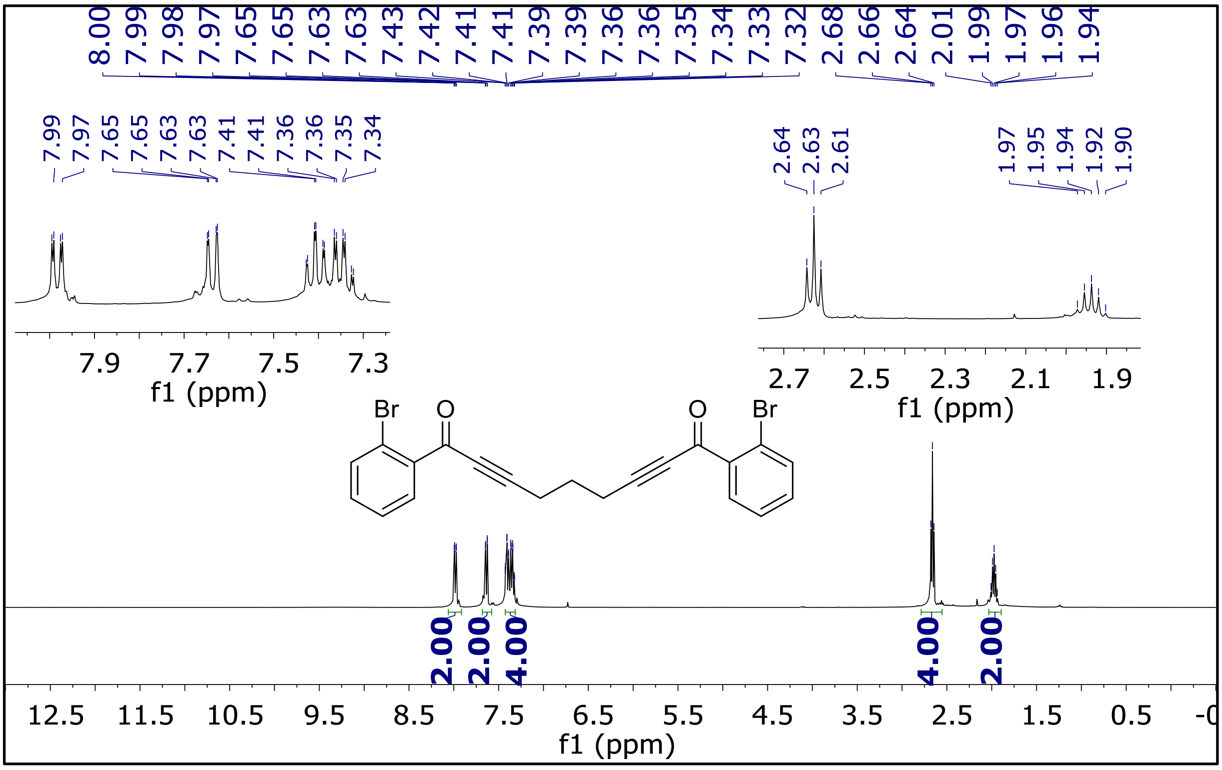


Figure S17. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1i**.

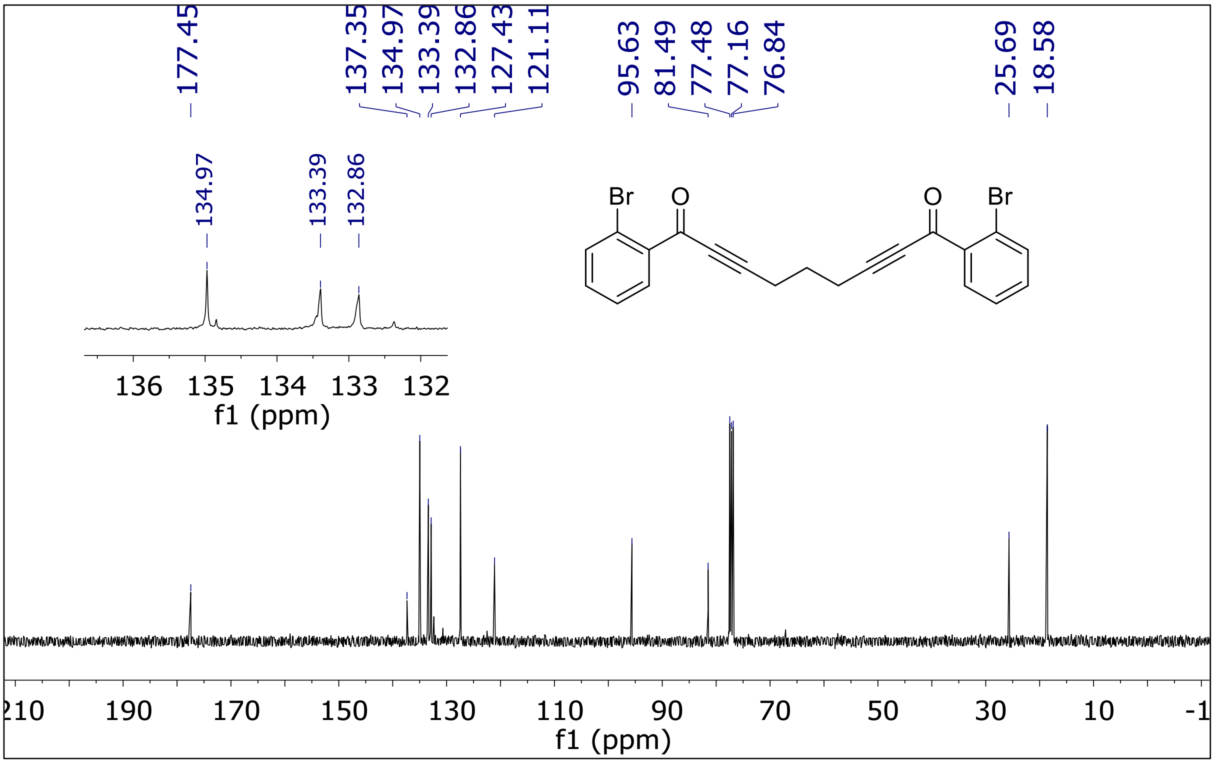


Figure S18. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1i**.

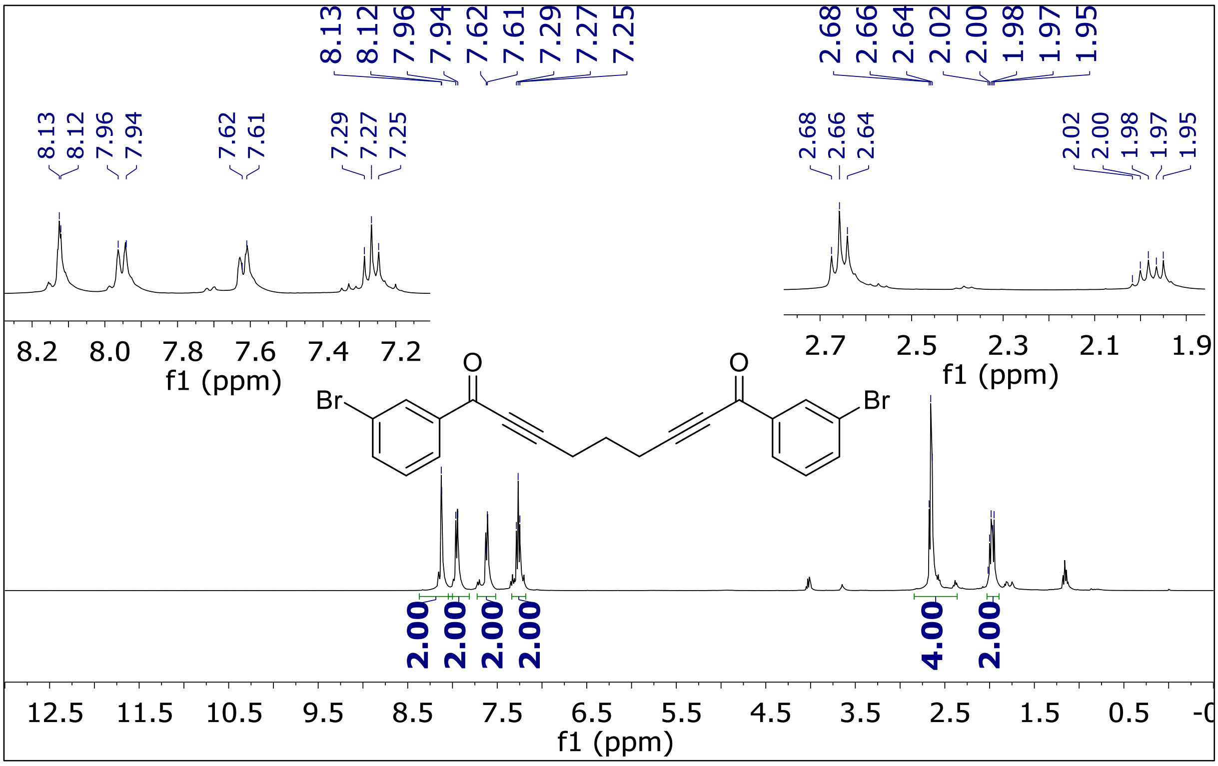


Figure S19. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1j**.

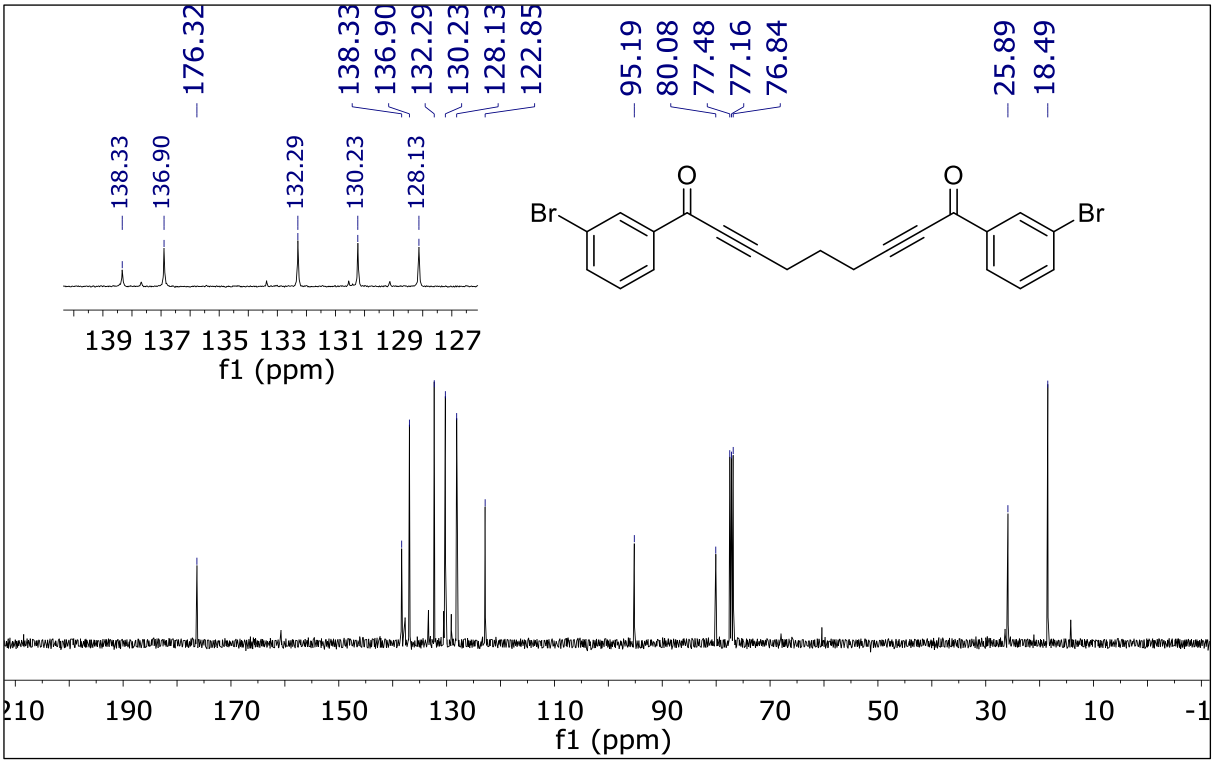


Figure S20. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1j**.

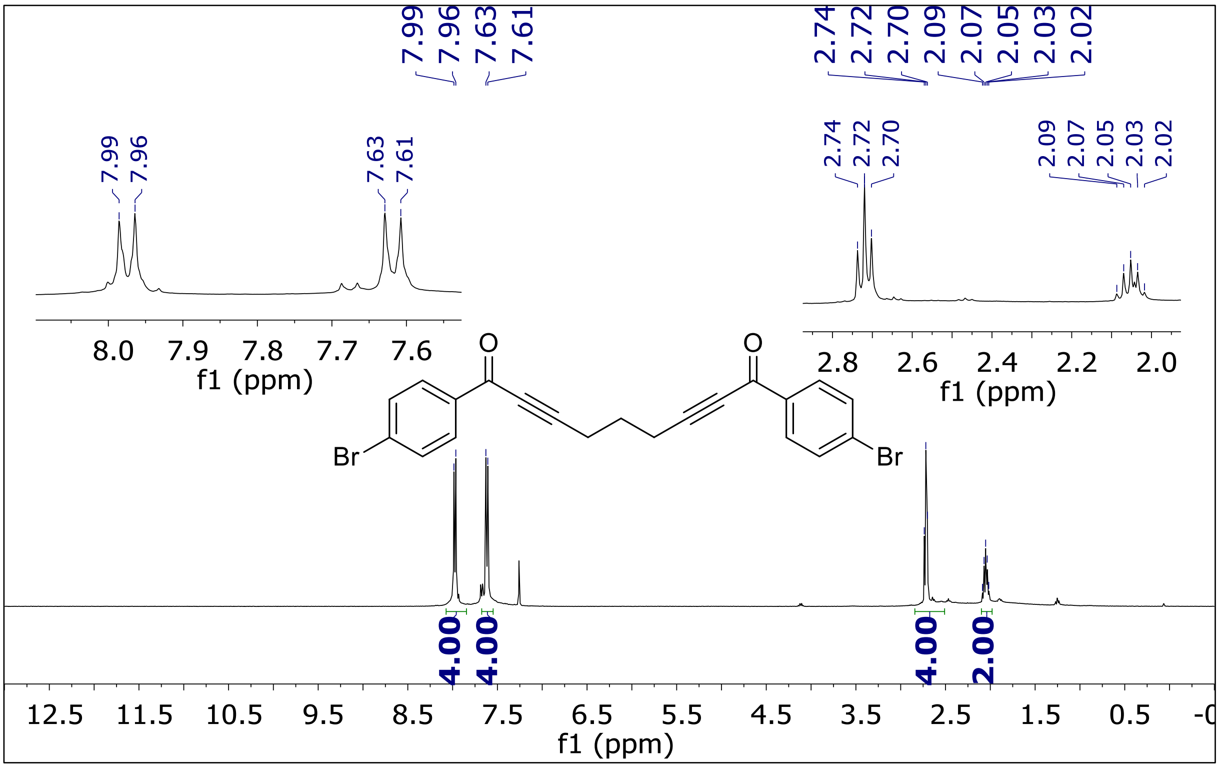


Figure S21. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1k**.

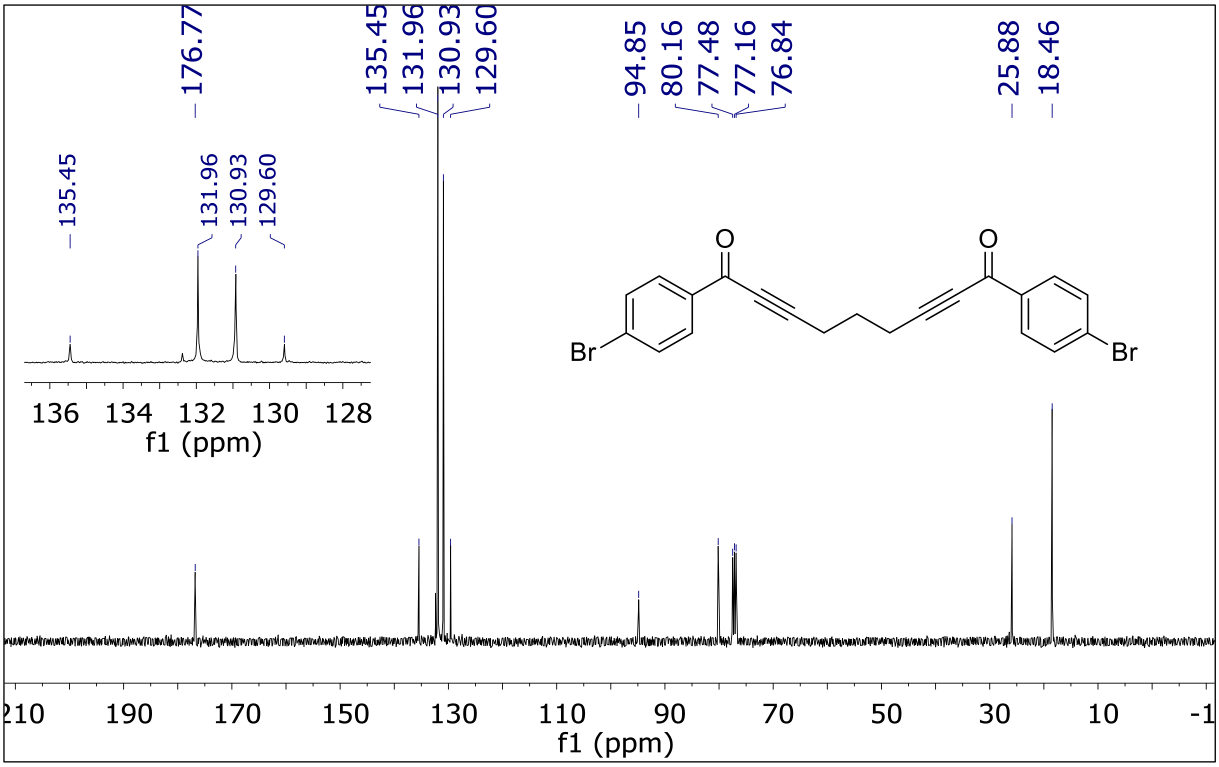


Figure S22. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1k**.

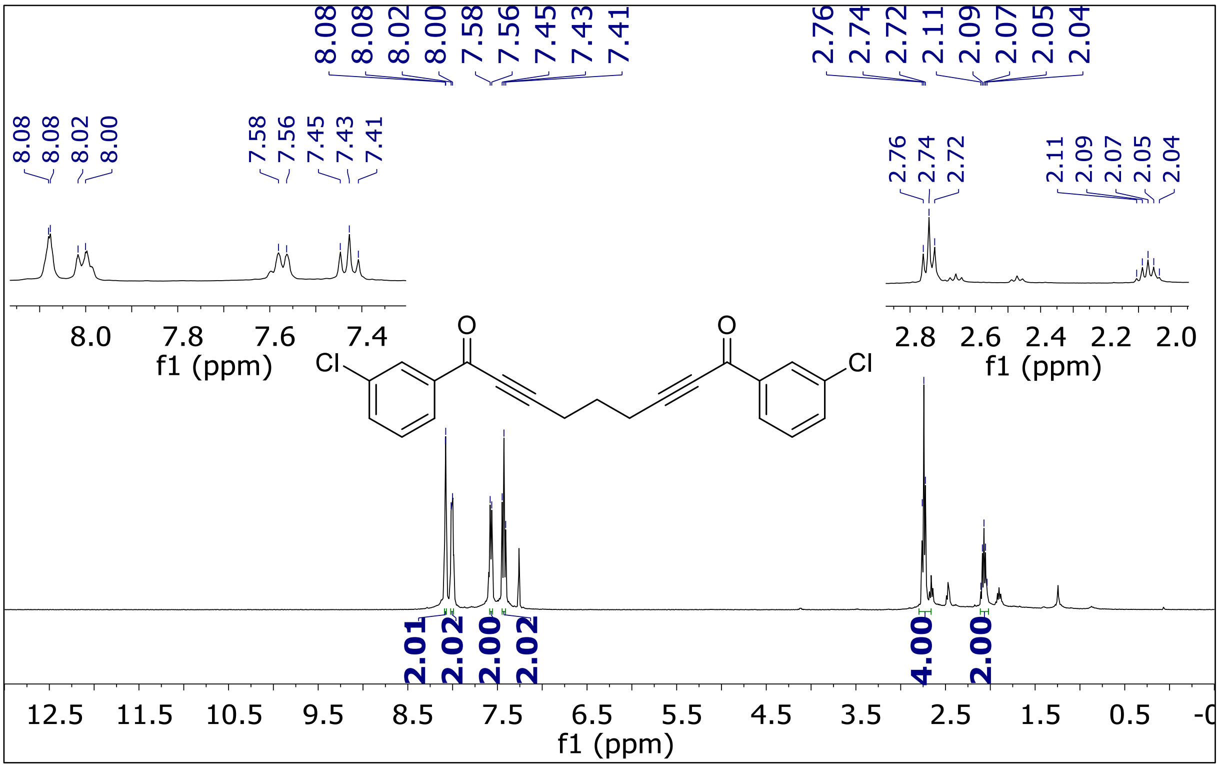


Figure S23. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1l**.

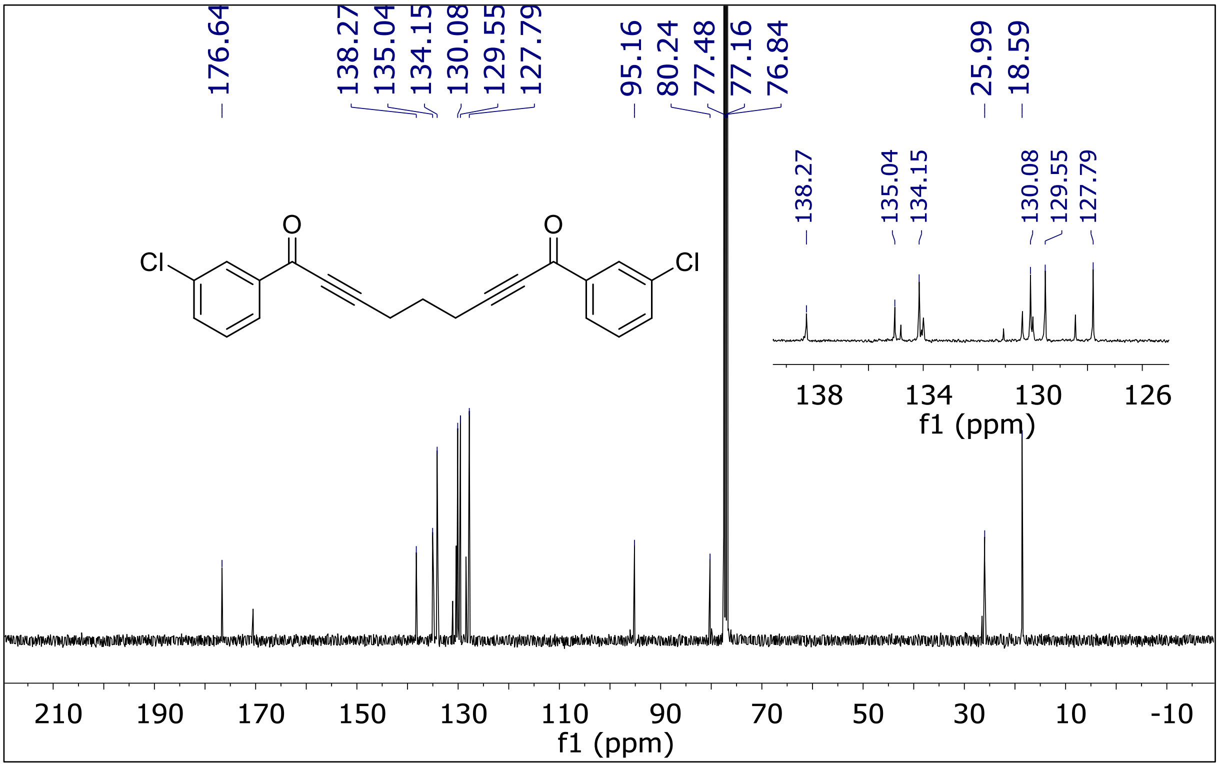


Figure S24. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1l**.

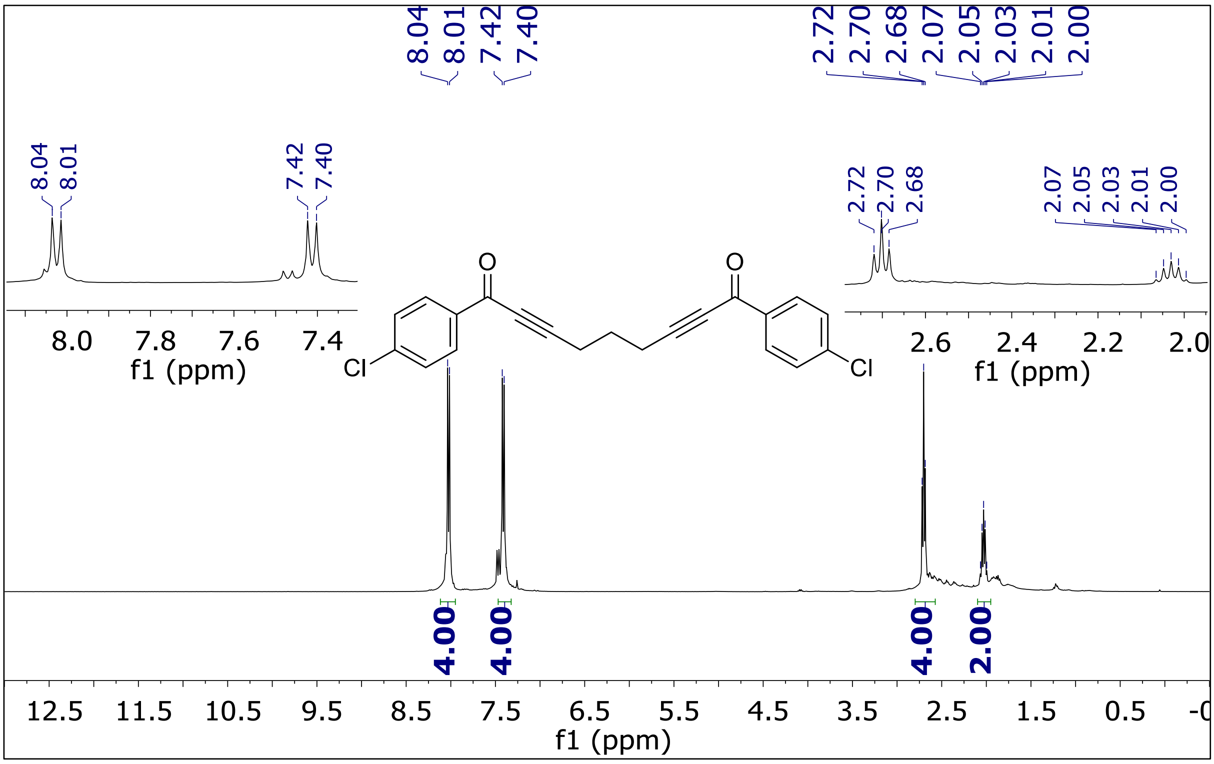


Figure S25. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1m**.

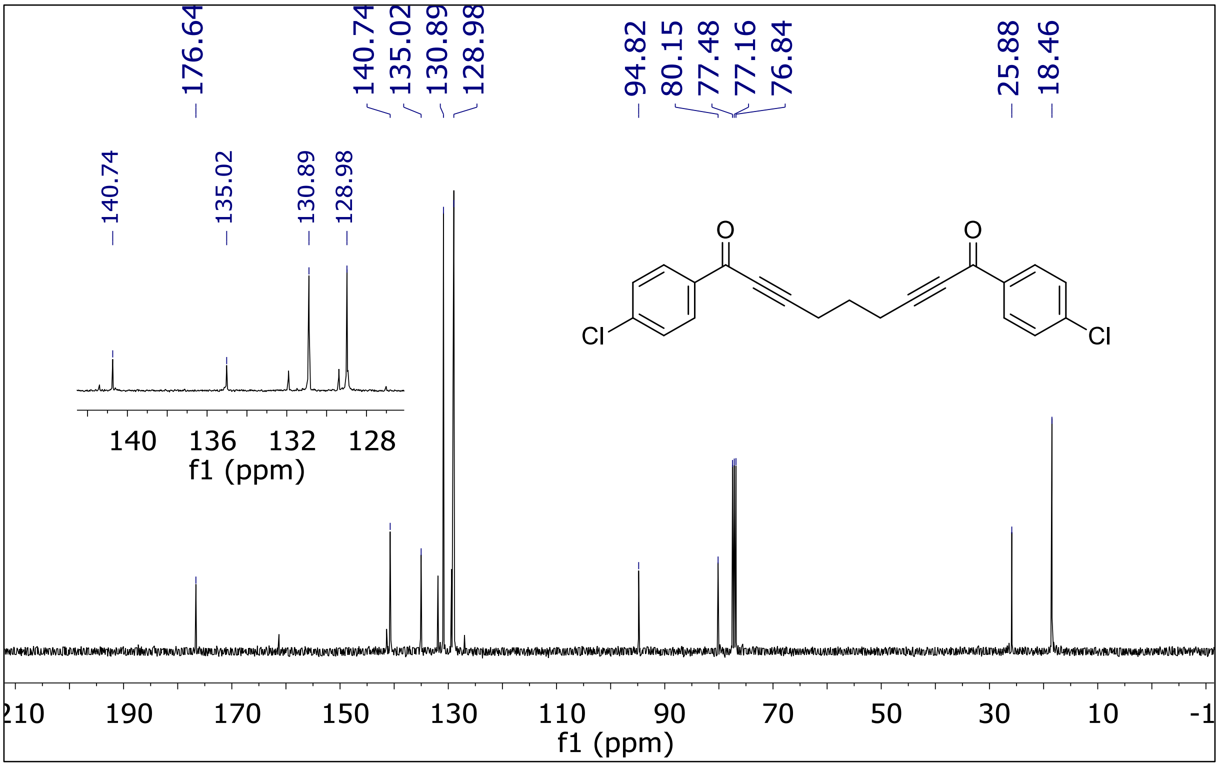


Figure S26. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1m**.

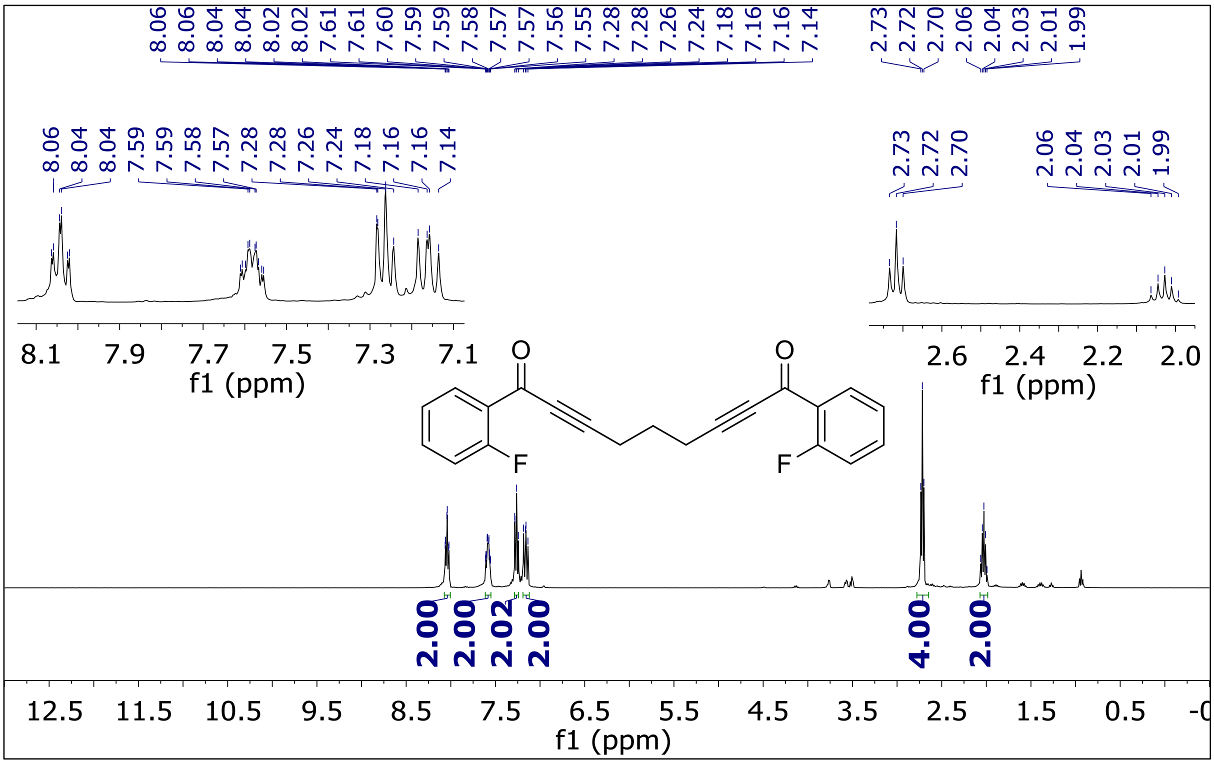


Figure S27. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1n**.

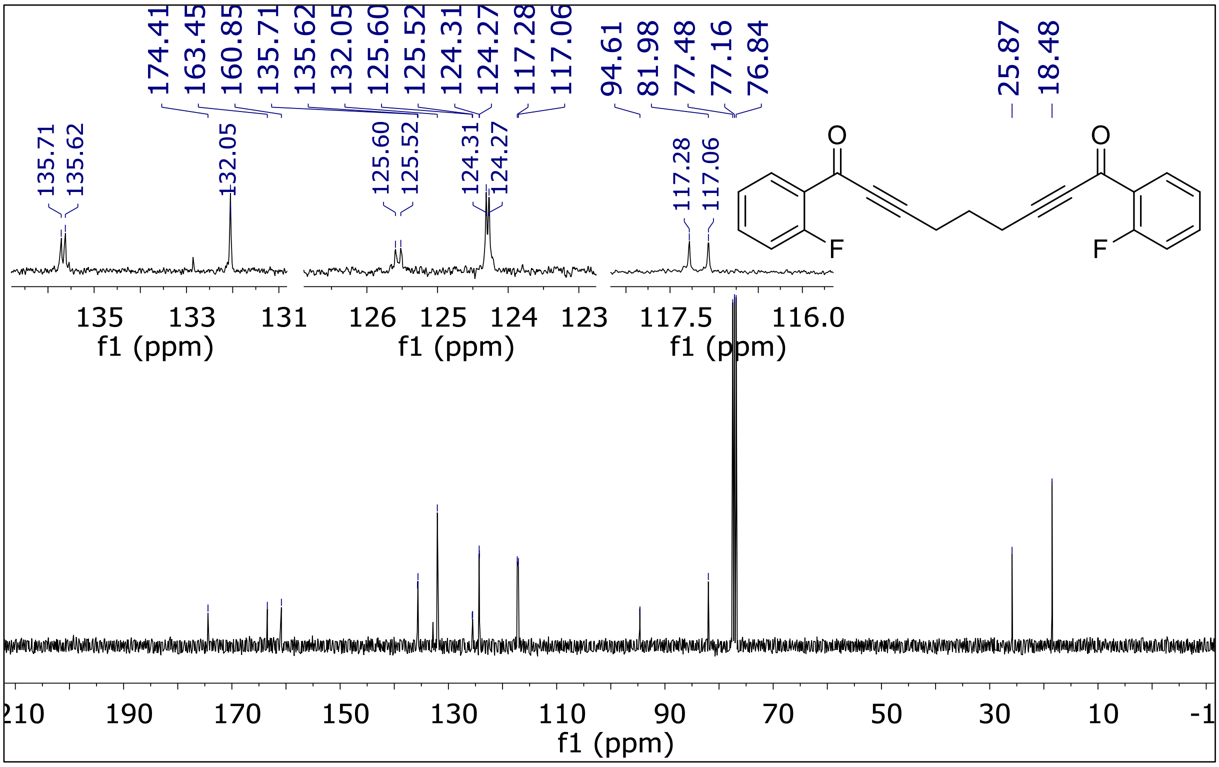


Figure S28. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1n**.

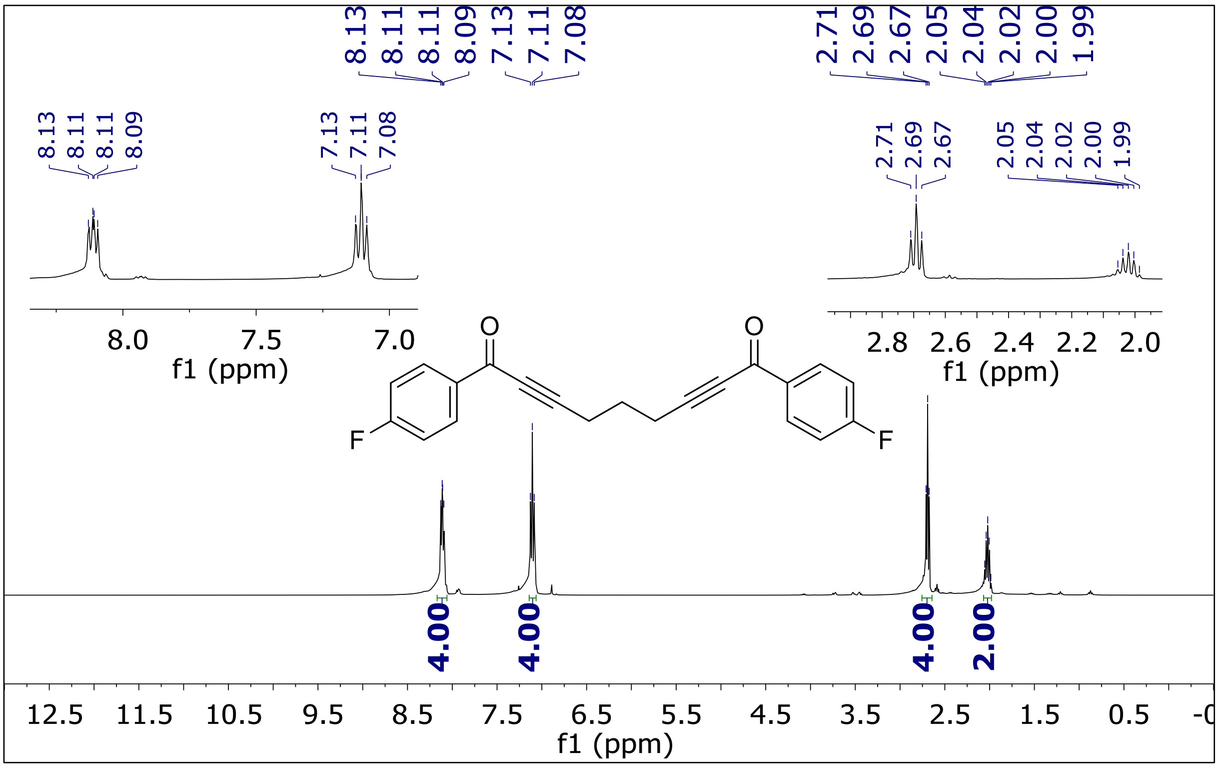


Figure S29. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1o**.

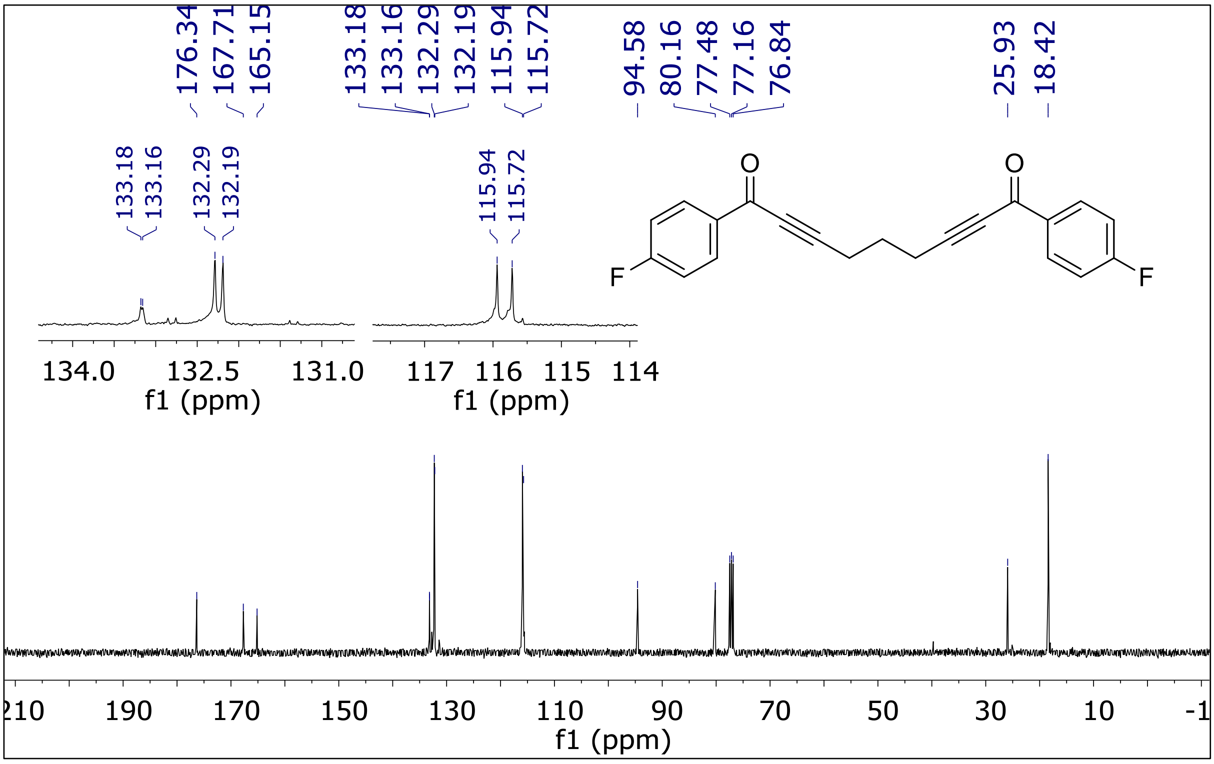


Figure S30. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1o**.

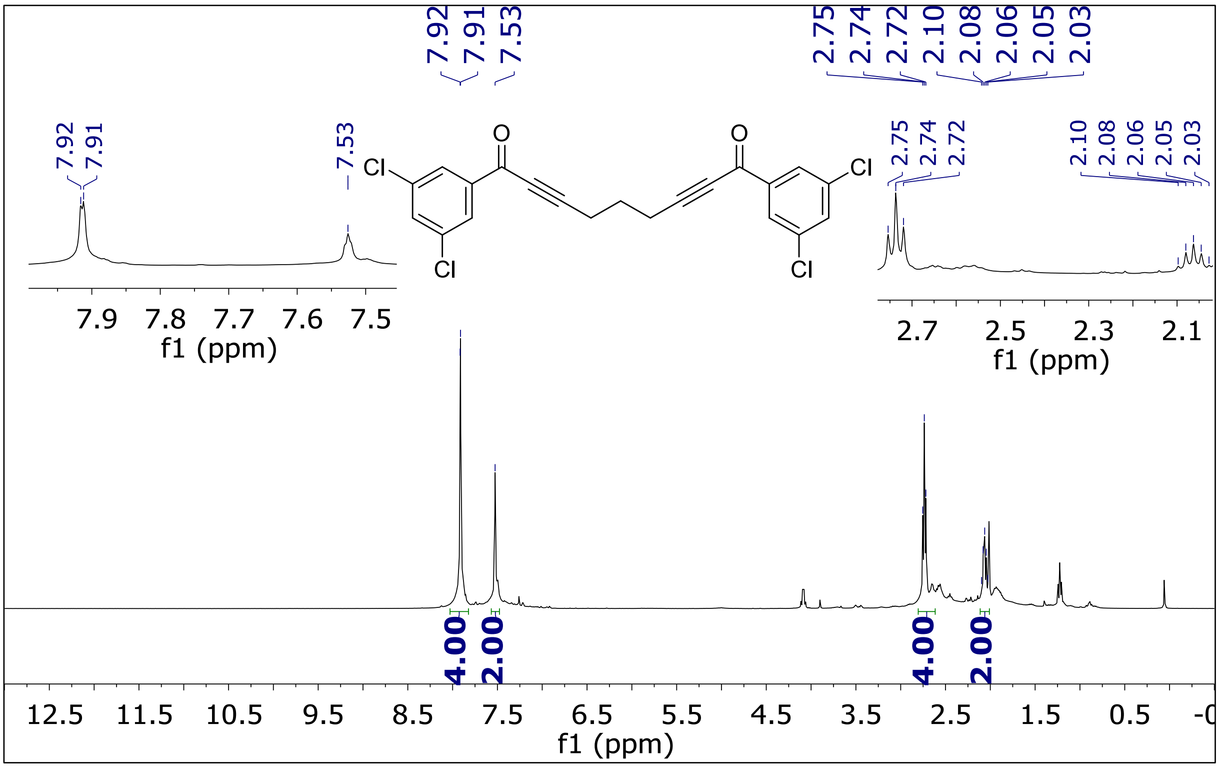


Figure S31. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **1p**.

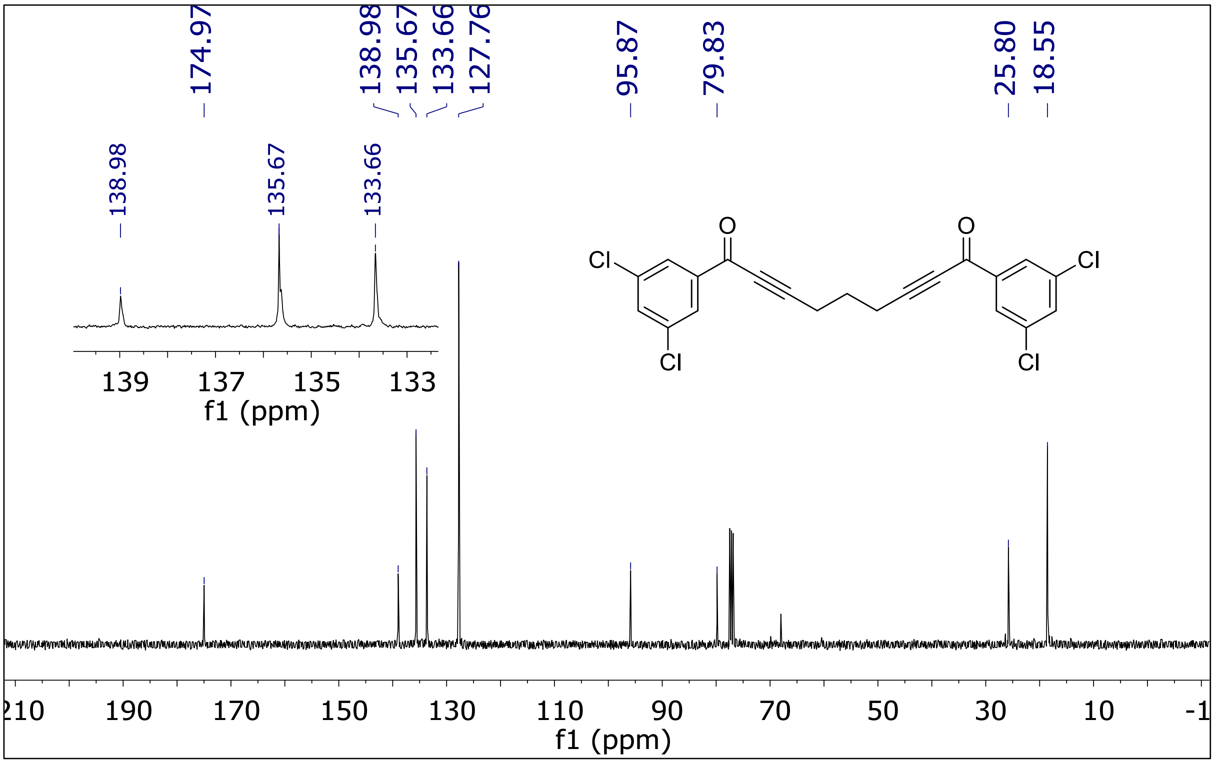


Figure S32. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **1p**.

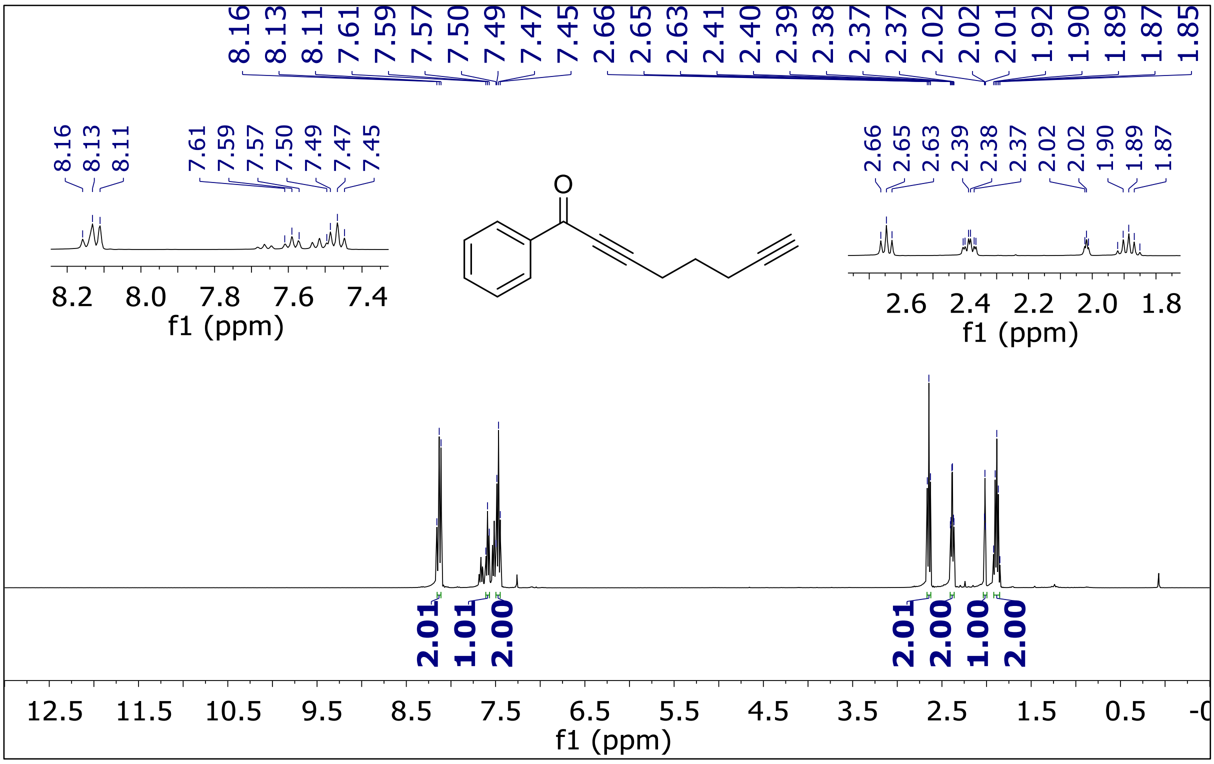


Figure S33. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **5a**.

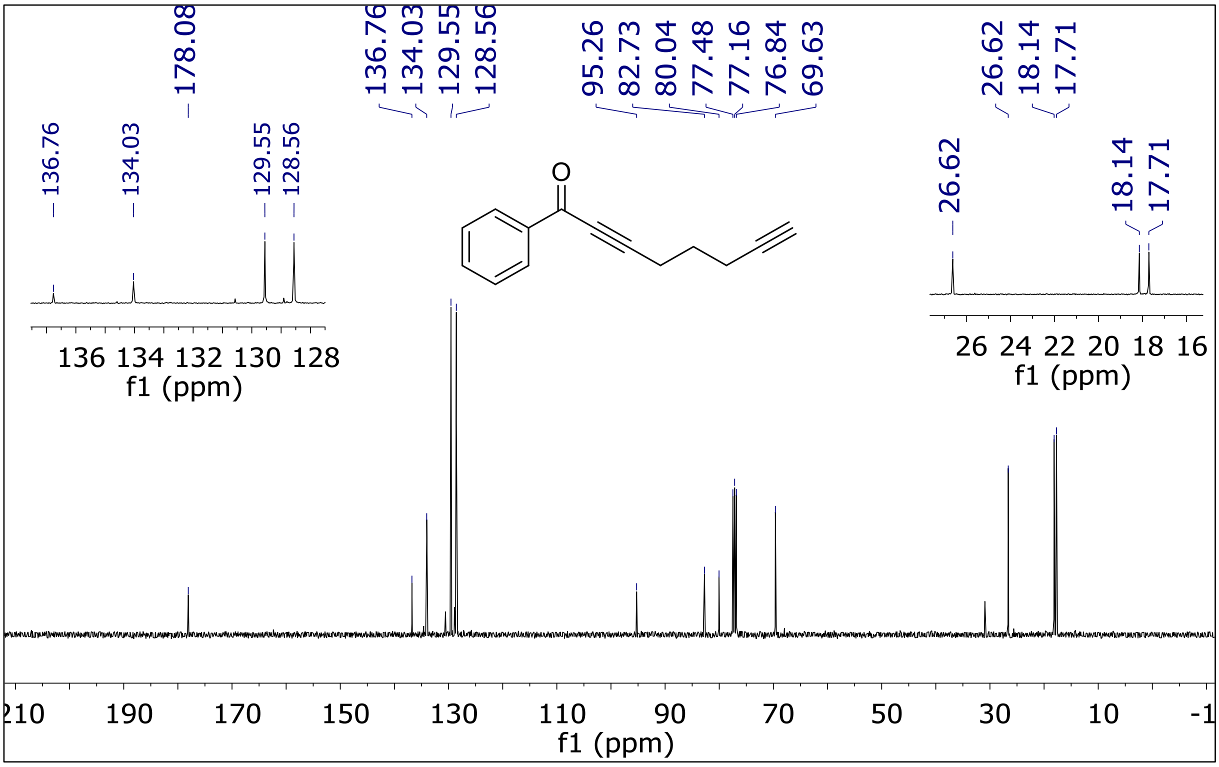


Figure S34. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **5a**.

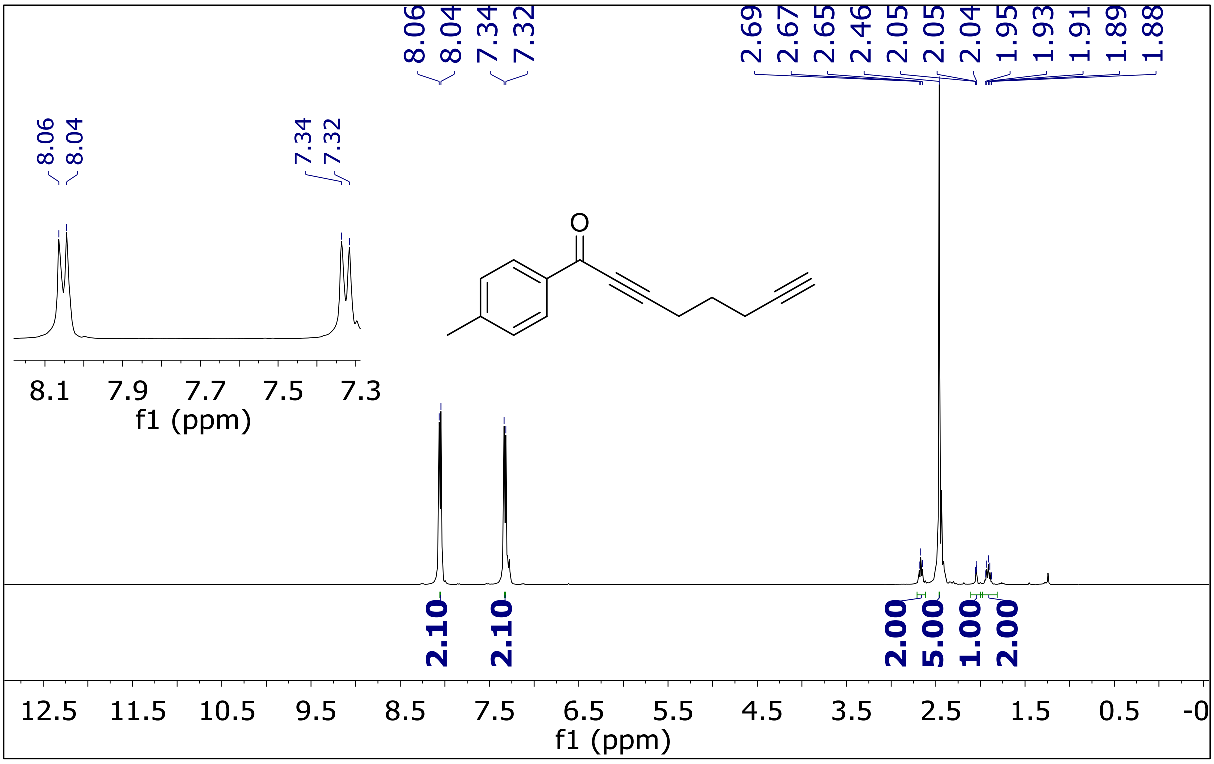


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5b**.

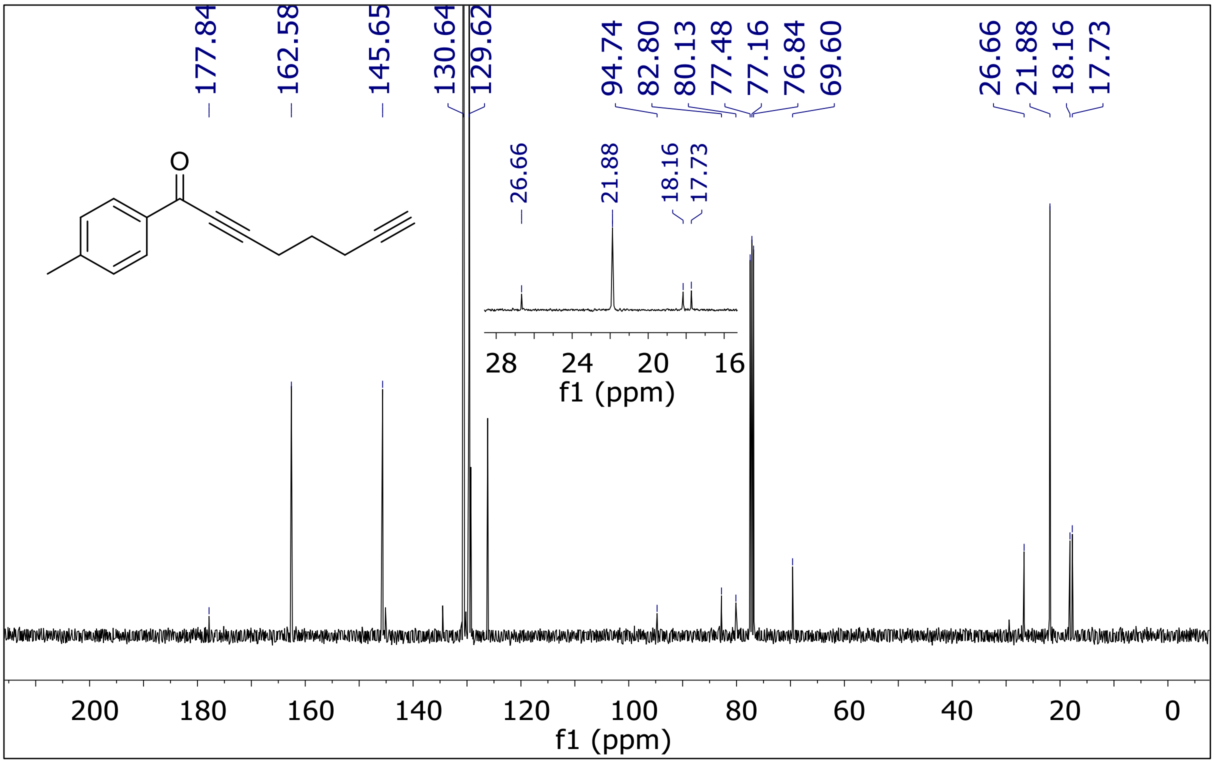


Figure S36. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **5b**.

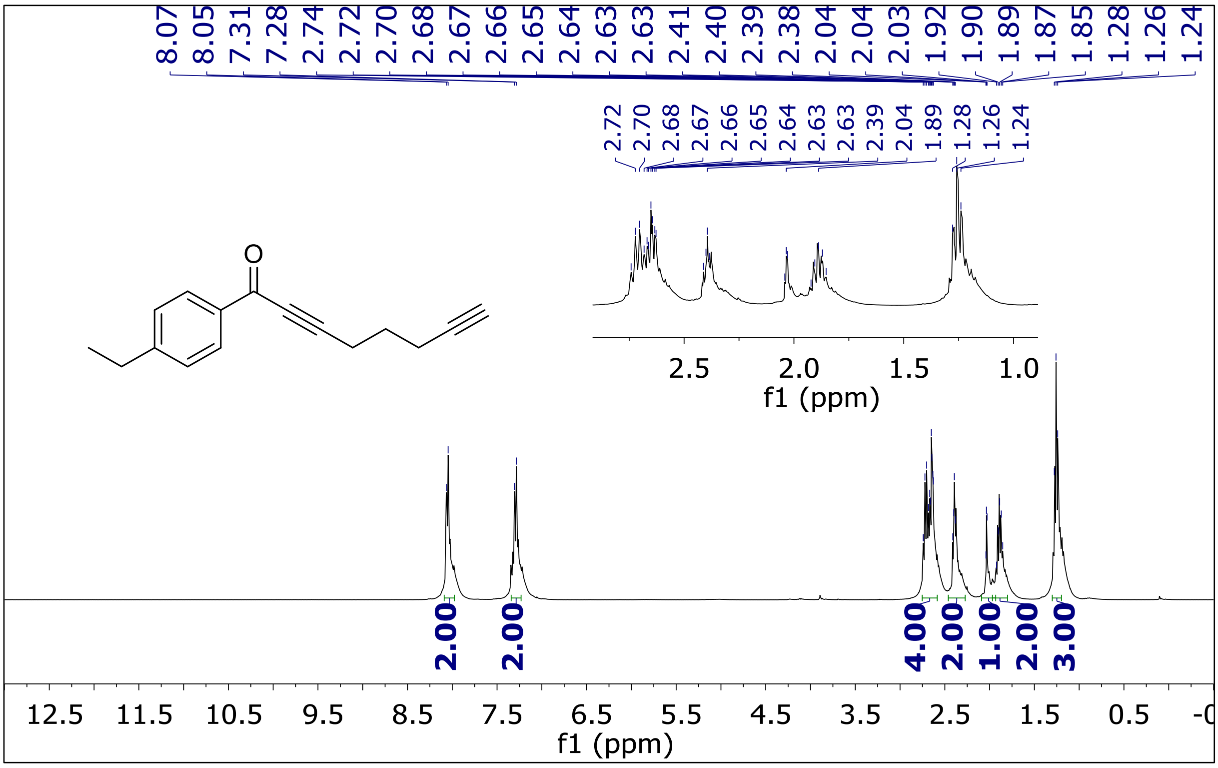


Figure S37. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **5c**.

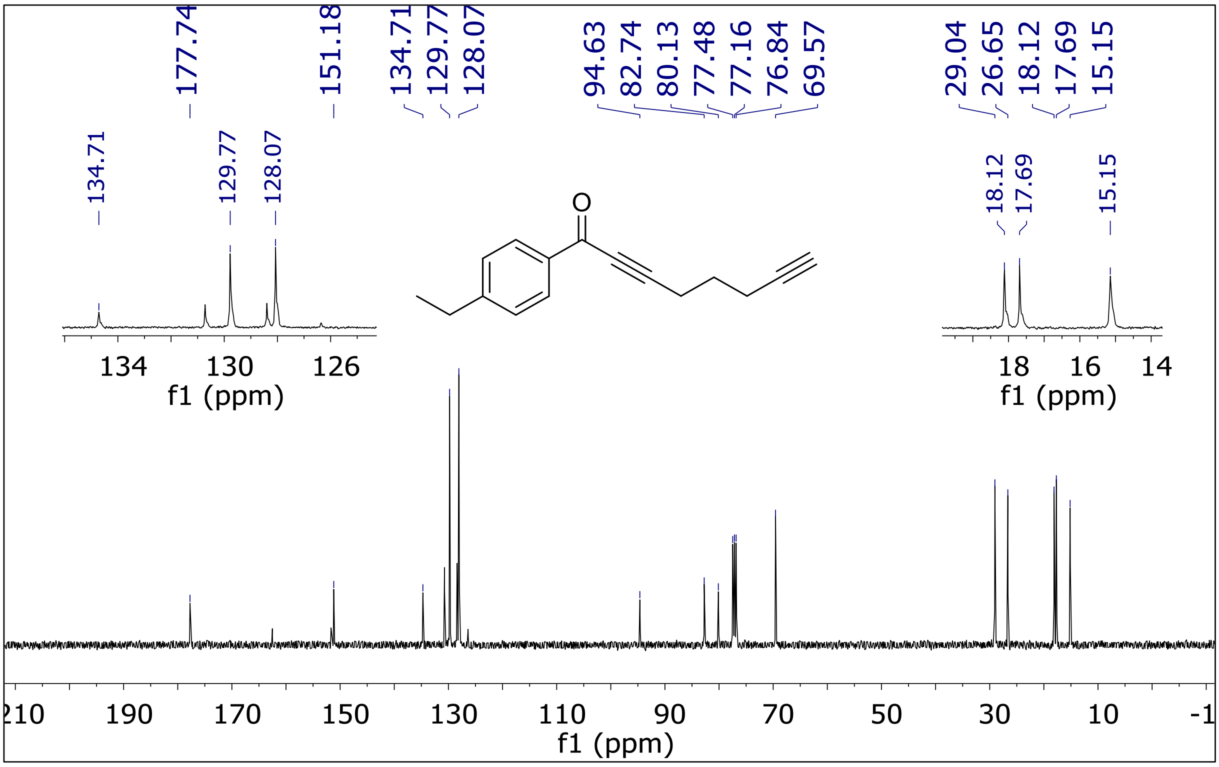


Figure S38. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **5c**.

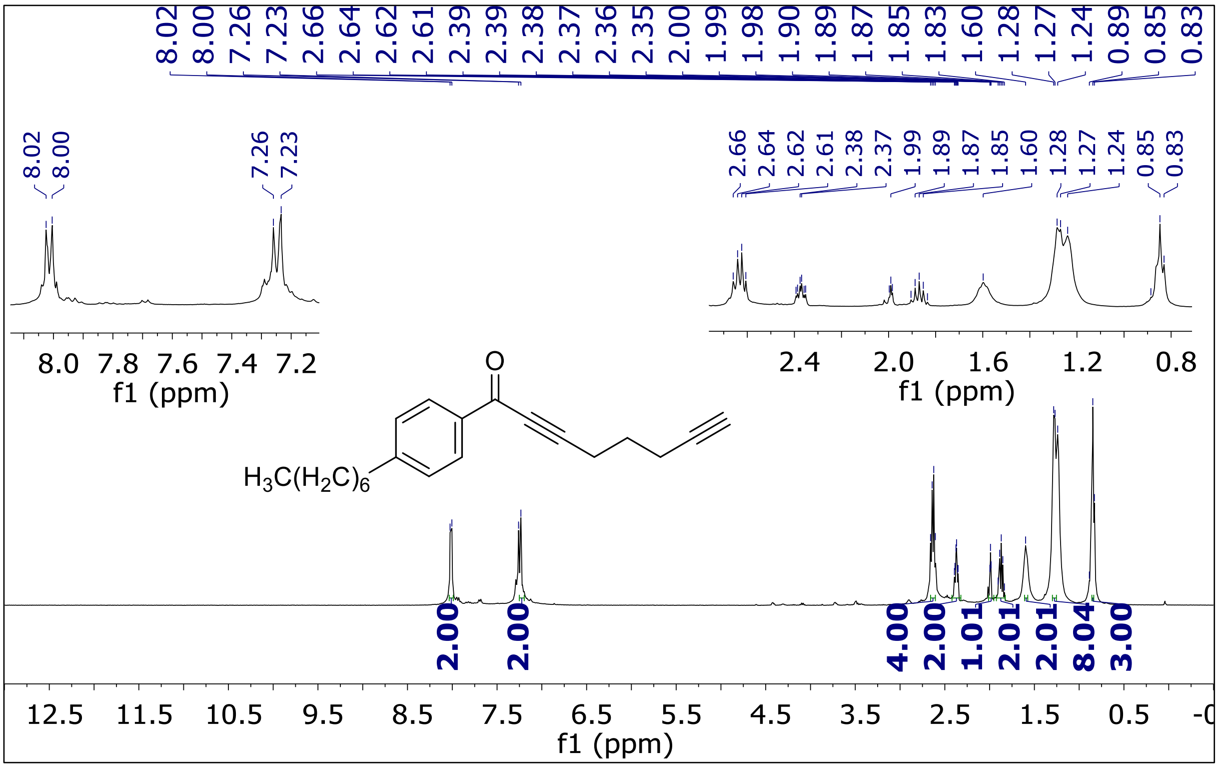


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5d**.

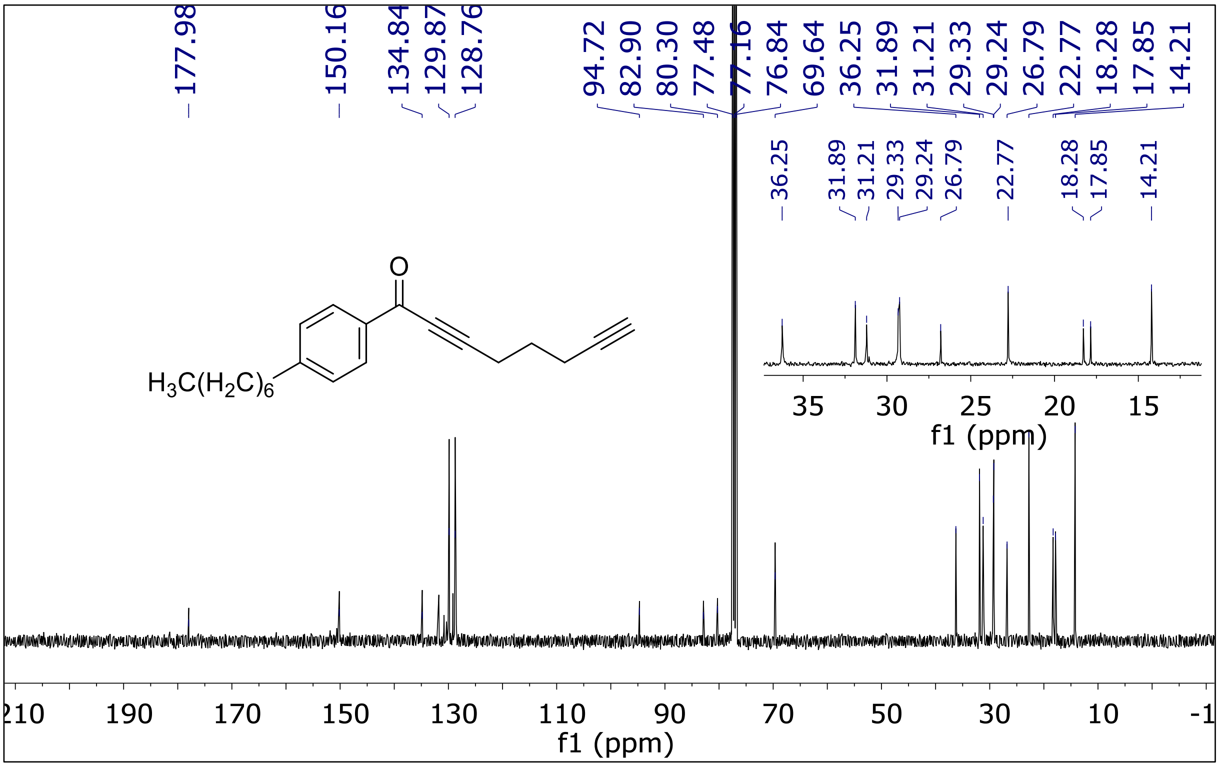


Figure S40. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **5d**.

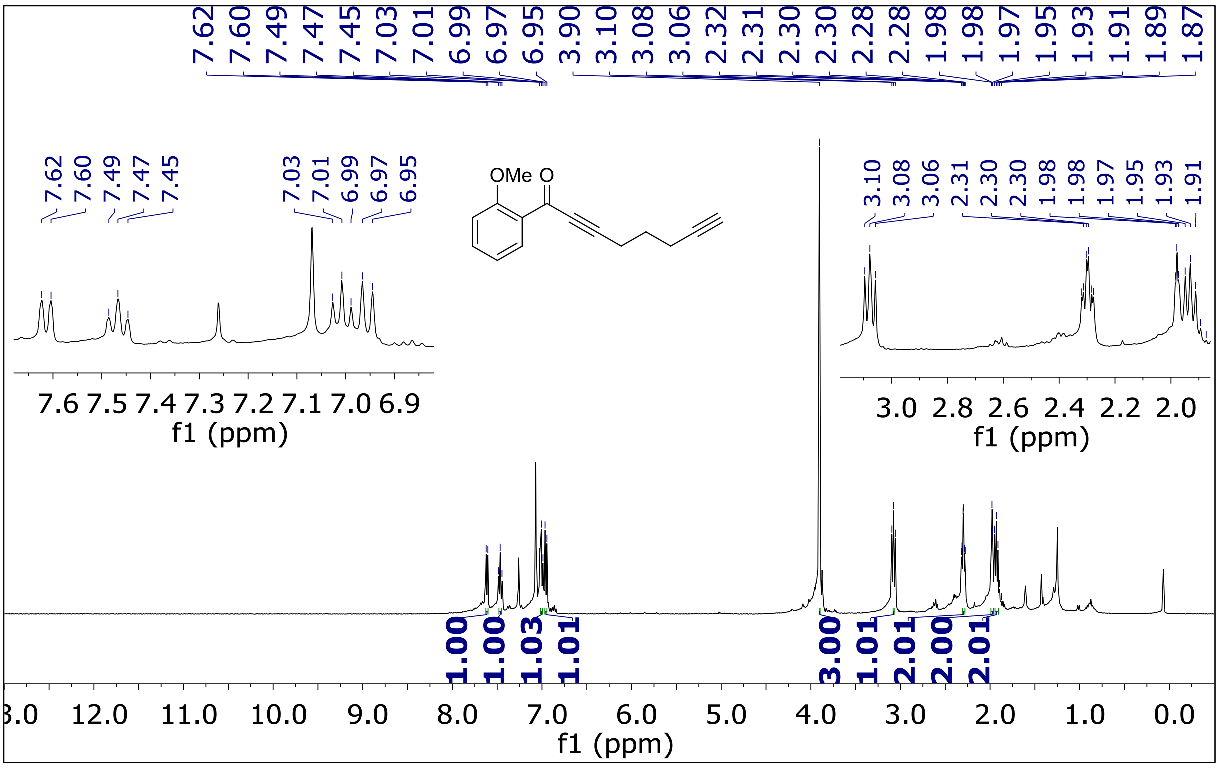


Figure S41. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **5e**.

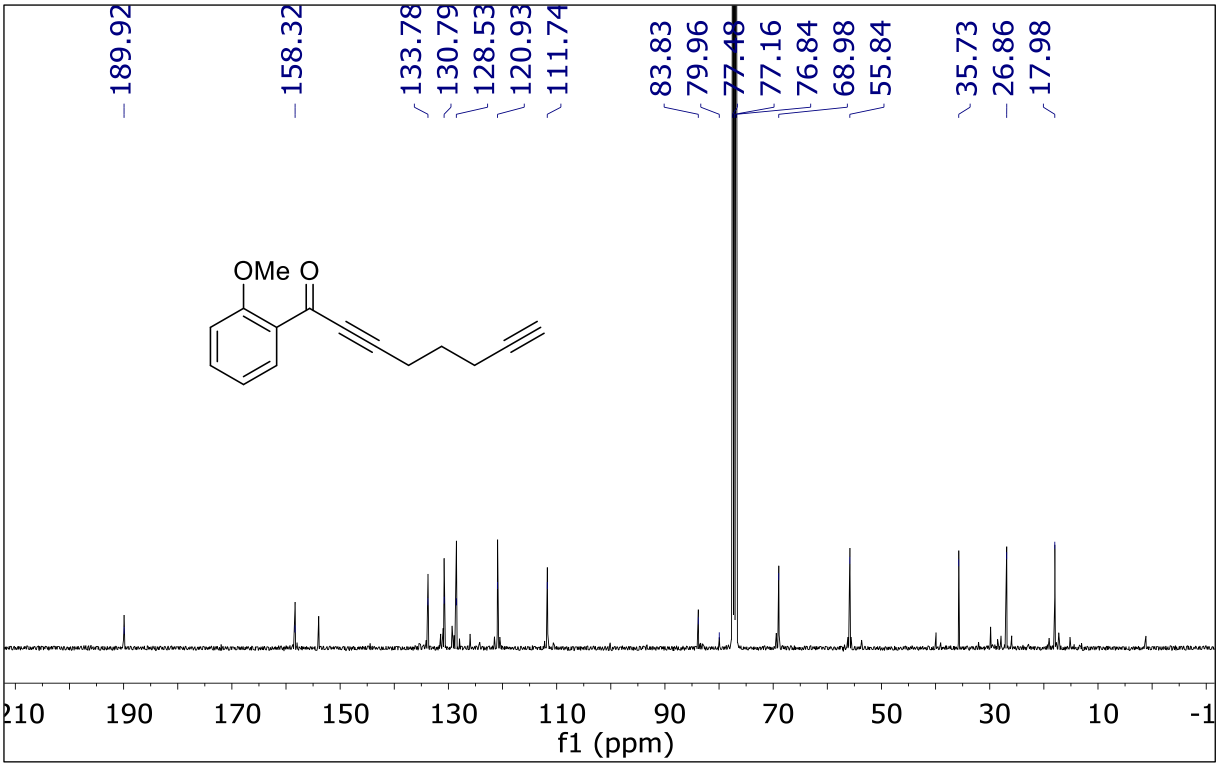


Figure S42. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **5e**.

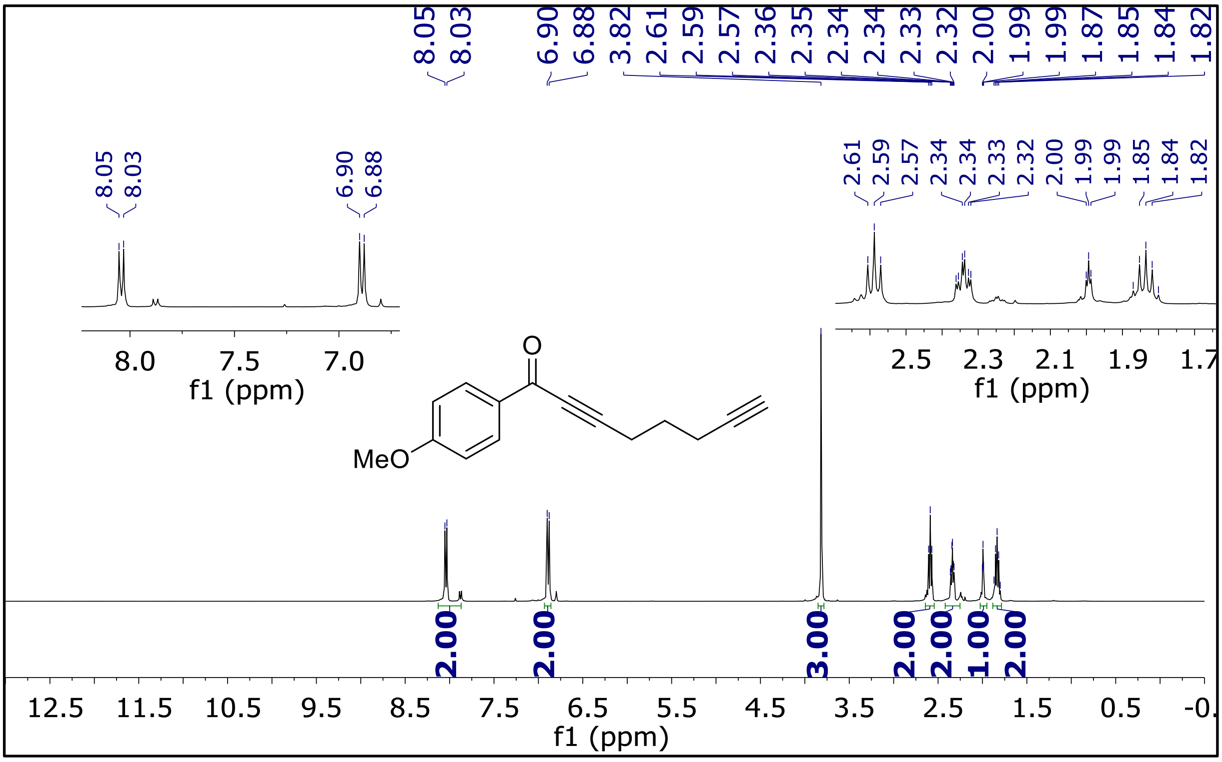


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5f**.

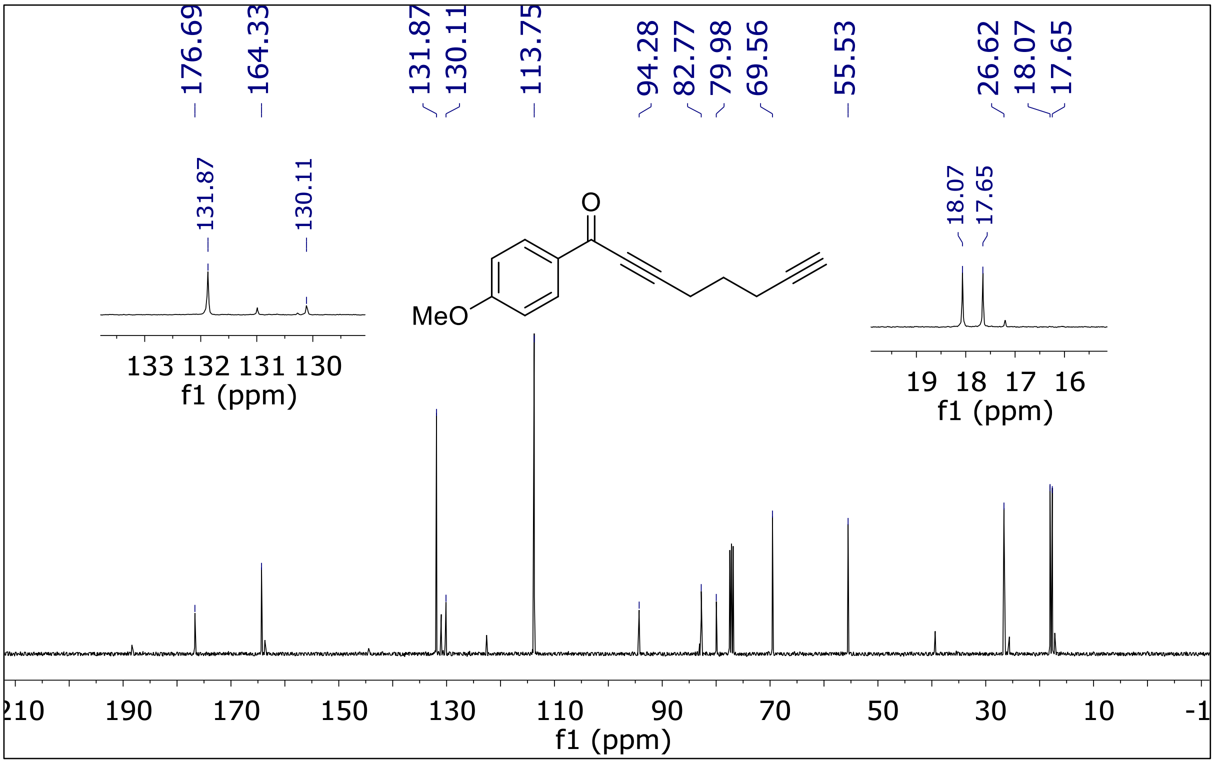


Figure S44. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **5f**.

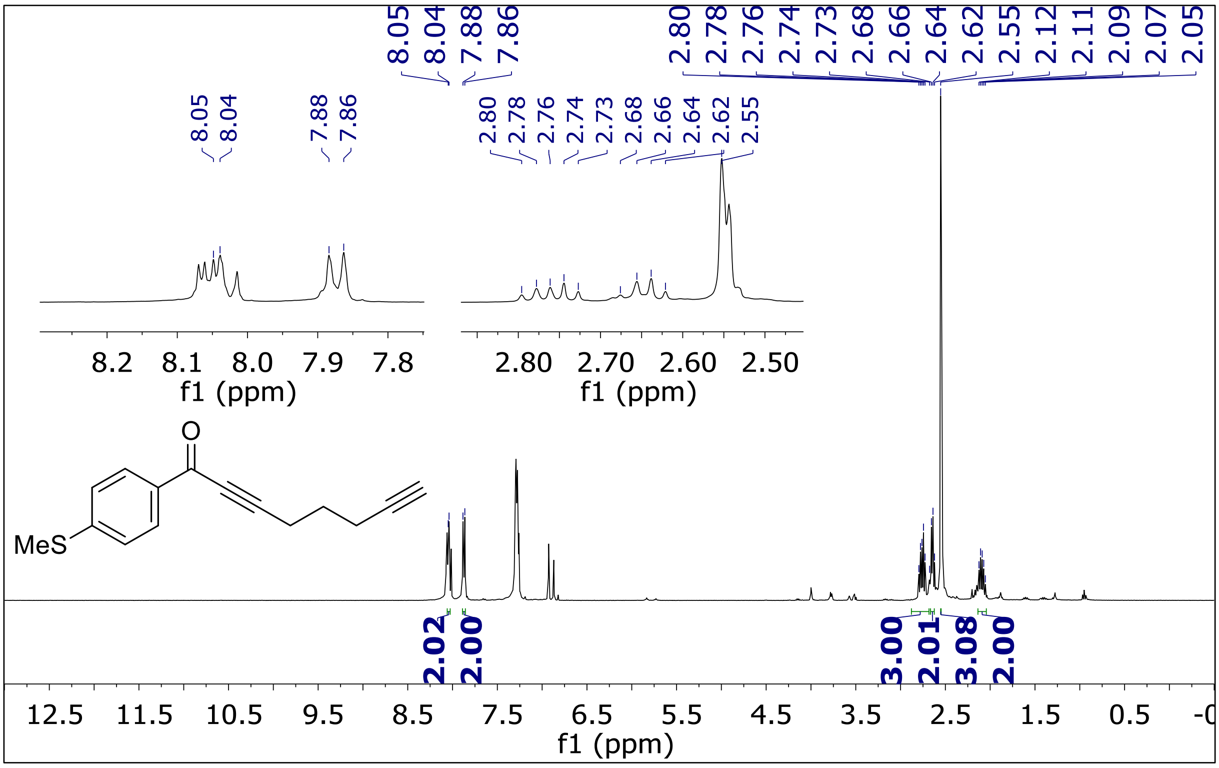


Figure S45. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **5g**.

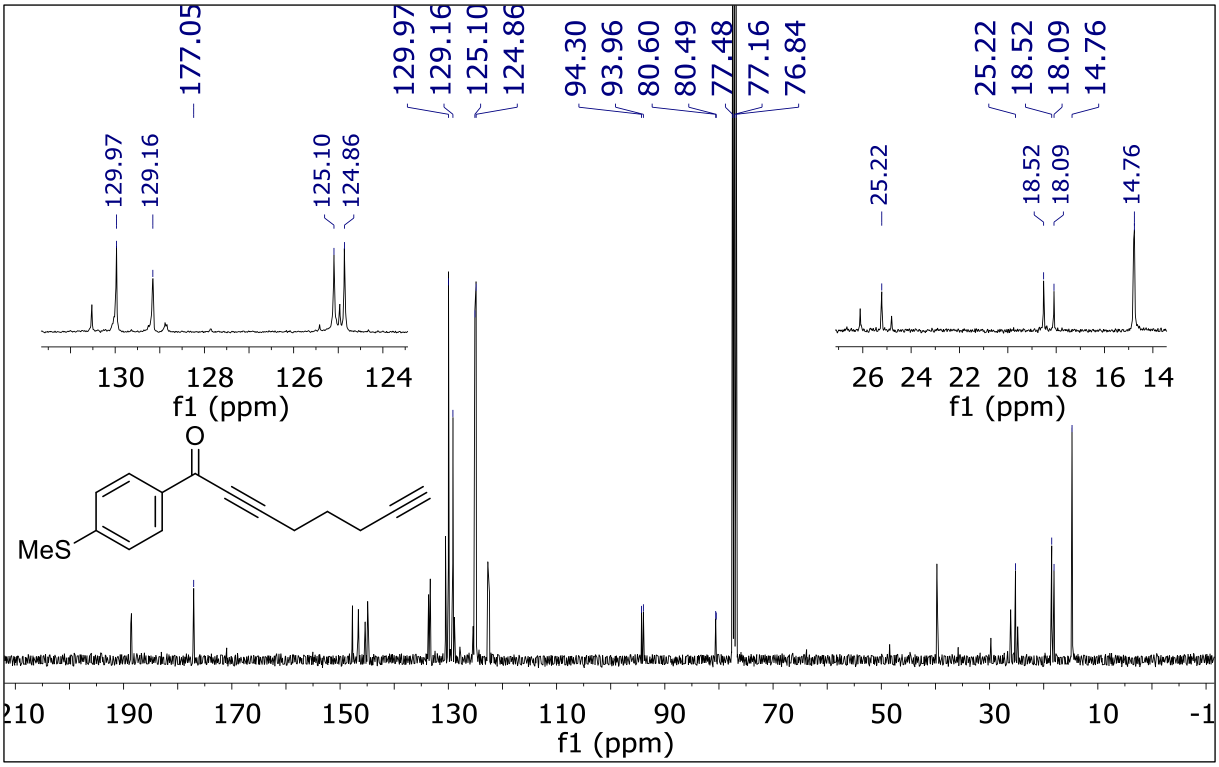


Figure S46. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **5g**.

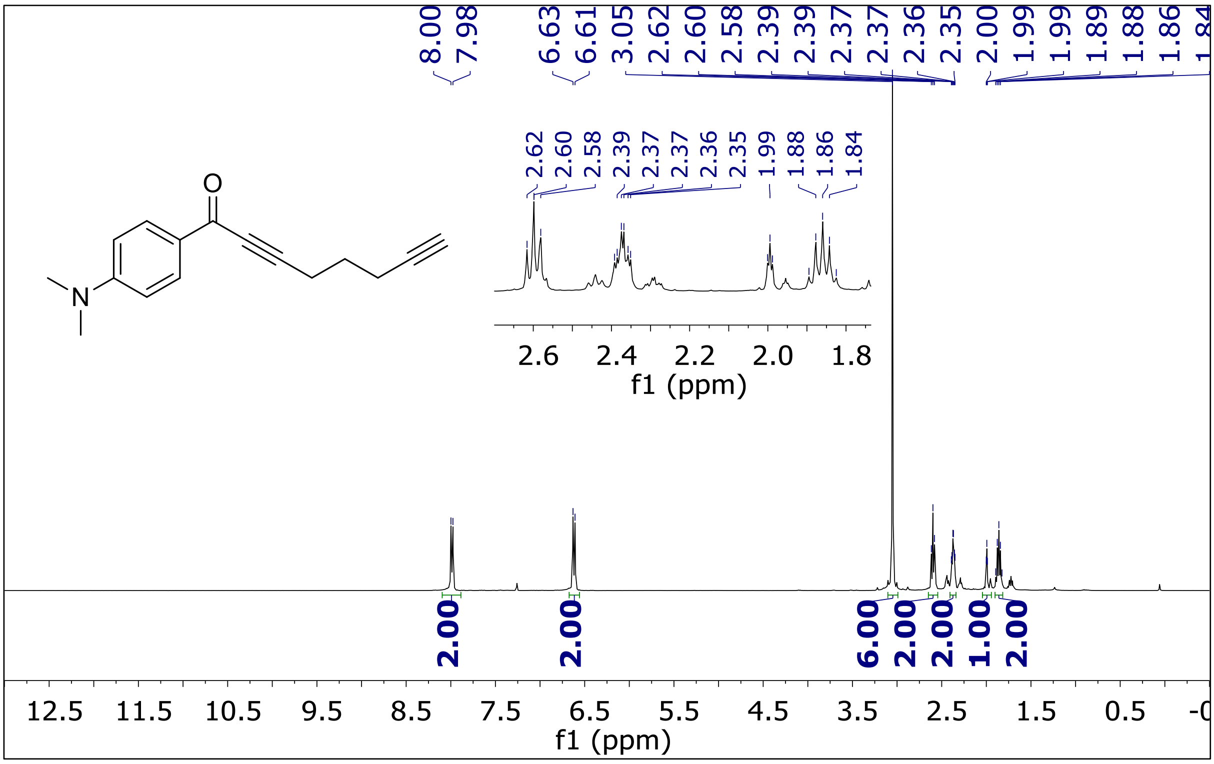


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5h**.

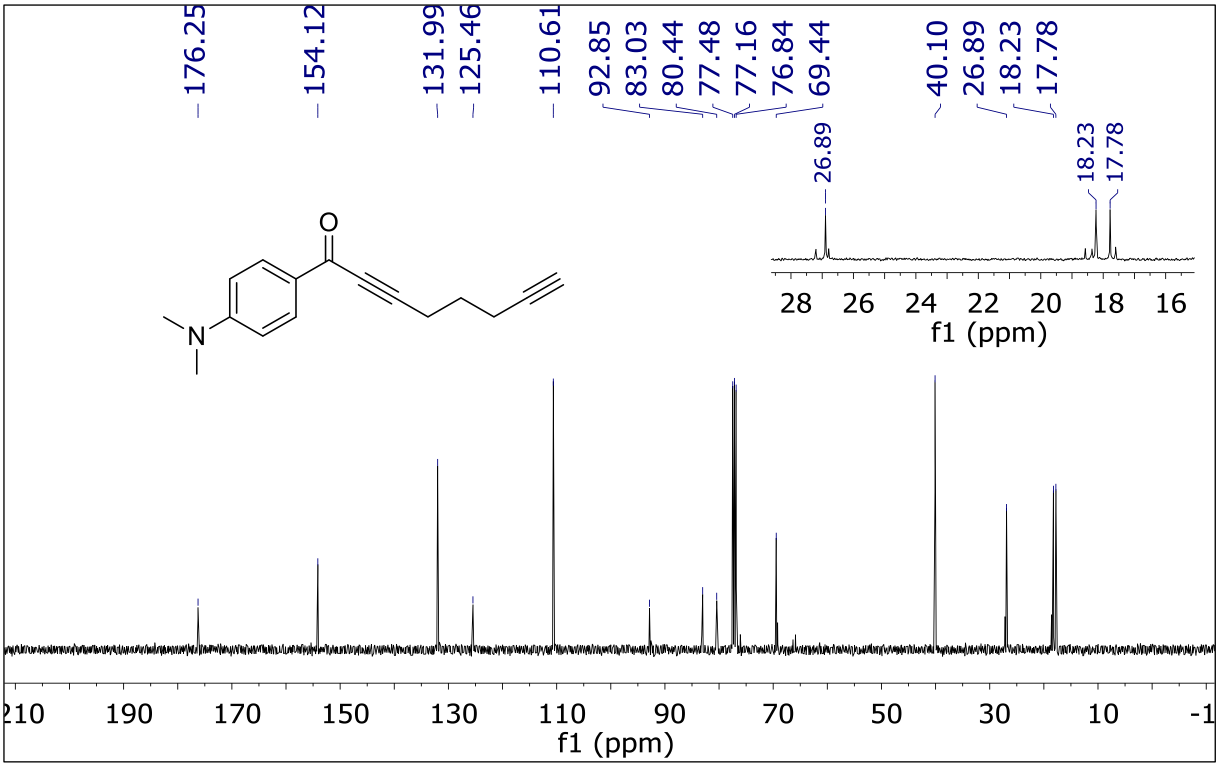


Figure S48. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of compound **5h**.

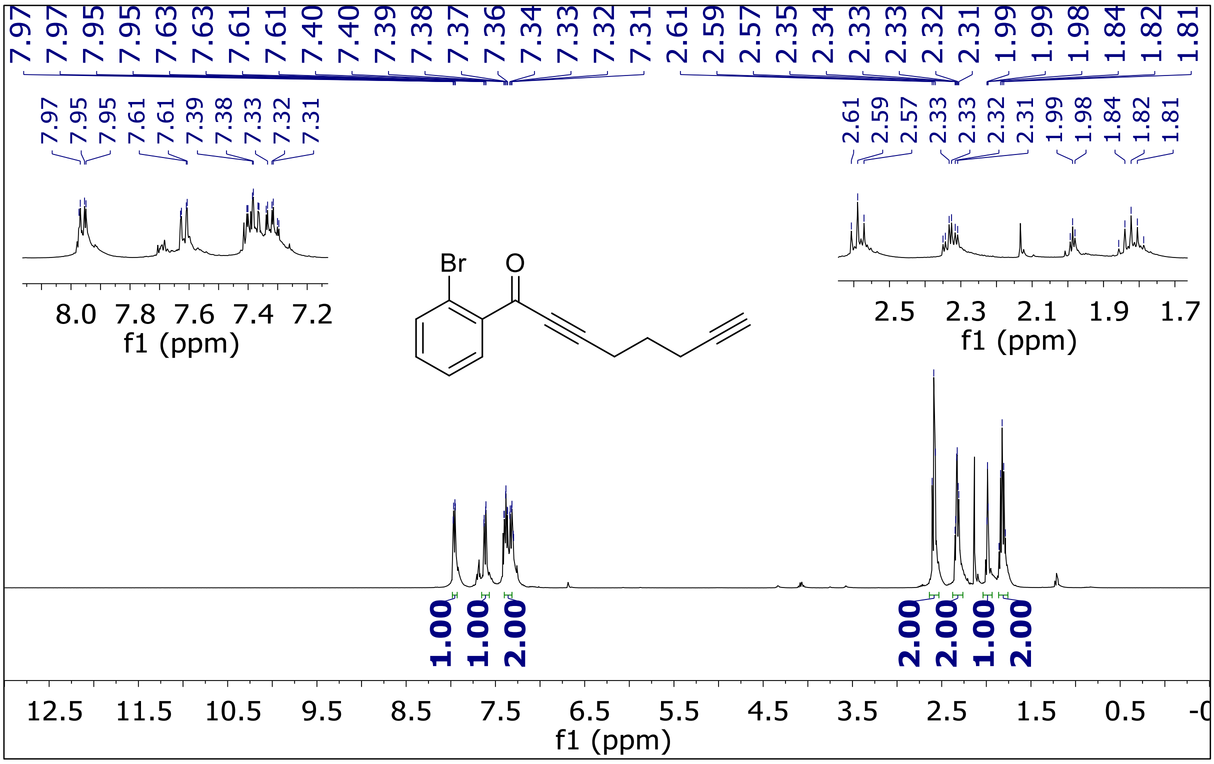


Figure S49. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **5i**.

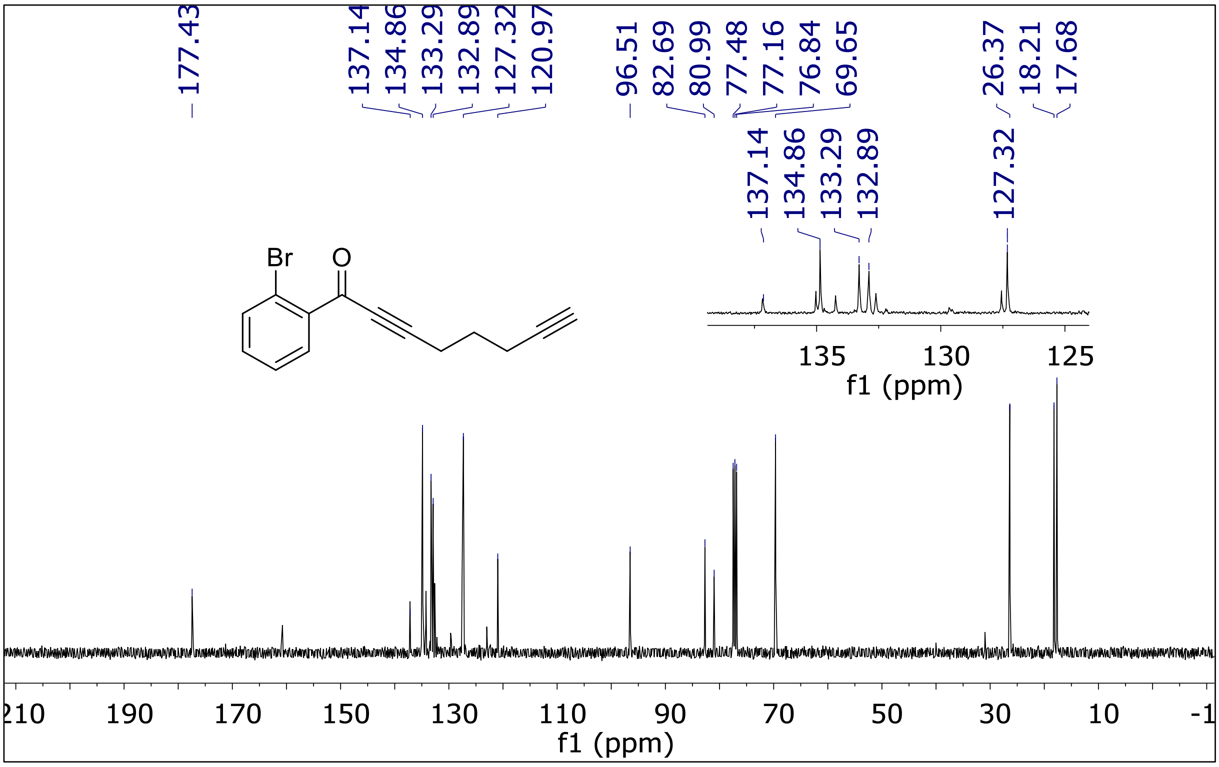


Figure S50. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **5i**.

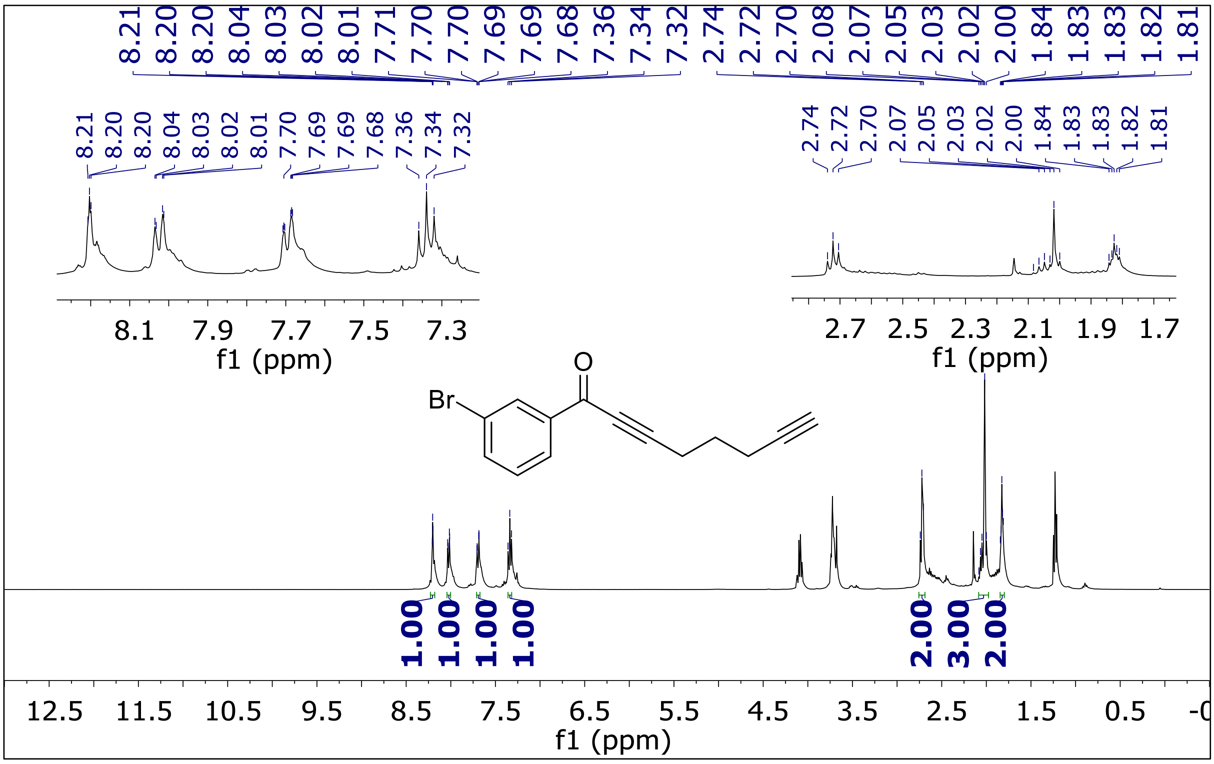


Figure S51. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **5j**.

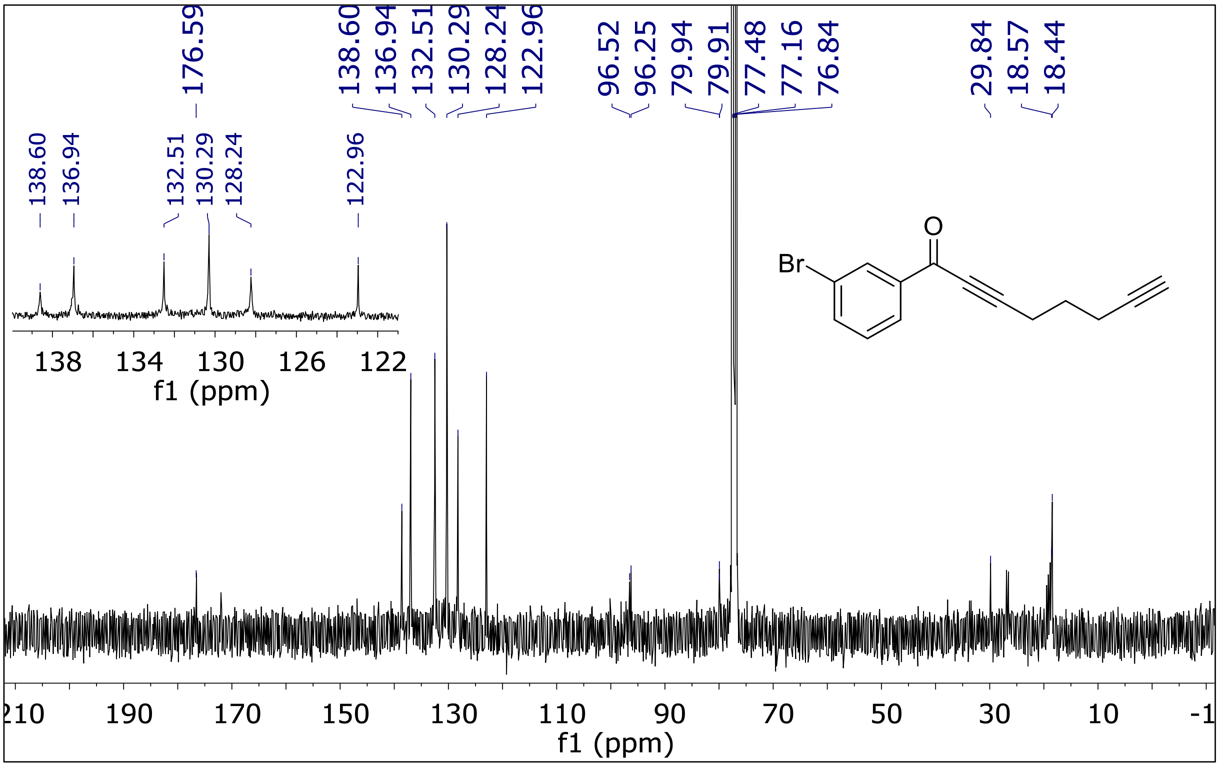


Figure S52. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **5j**.

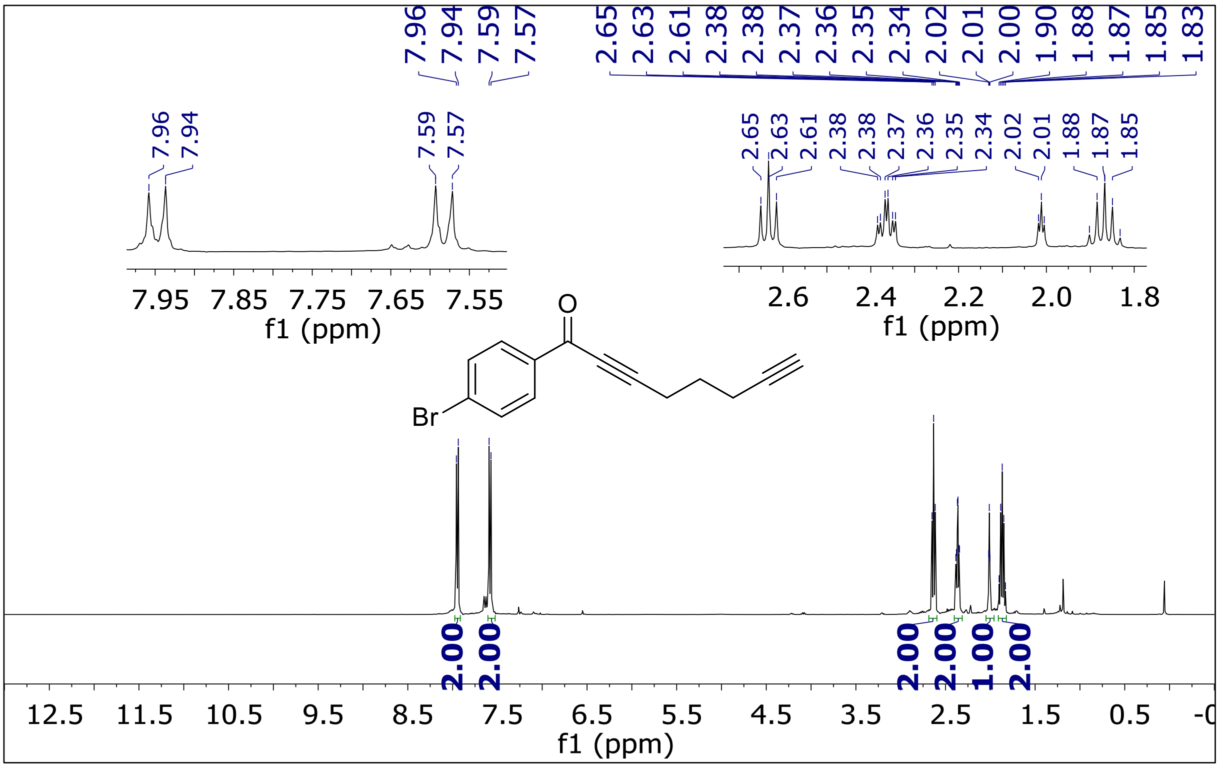


Figure S53. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **5k**.

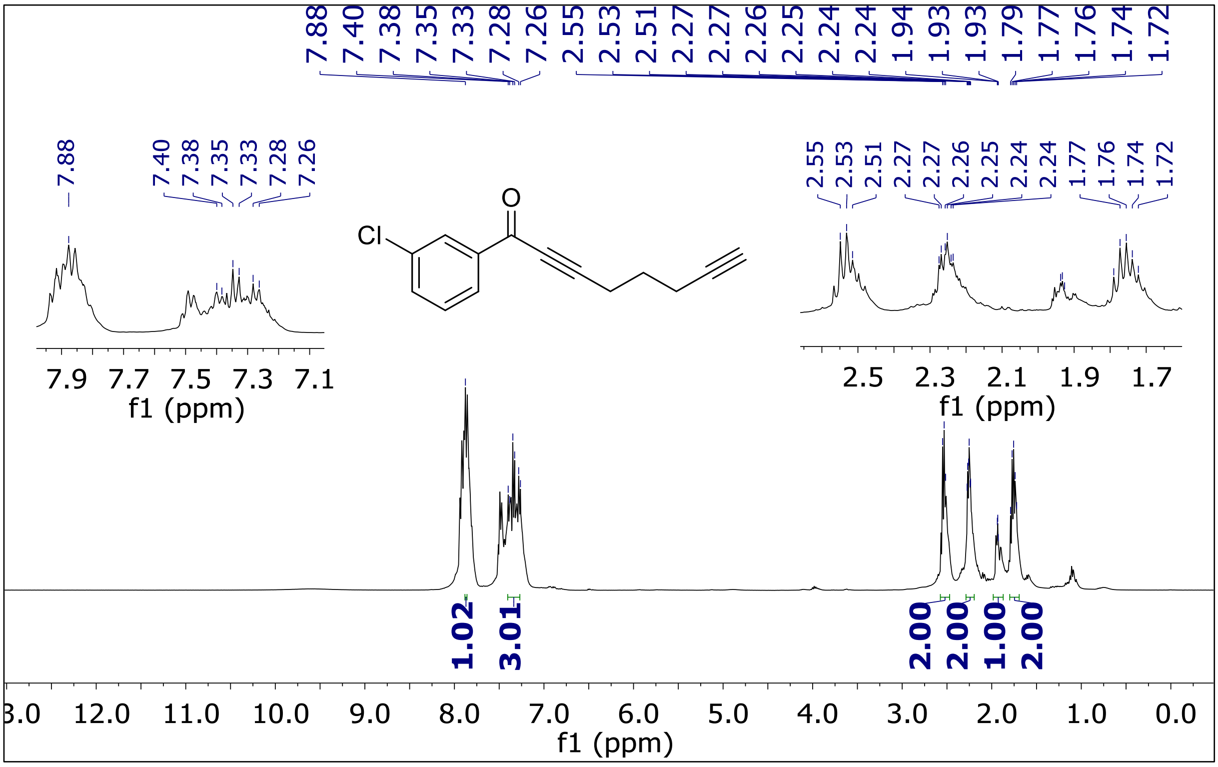


Figure S54. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **5l**.

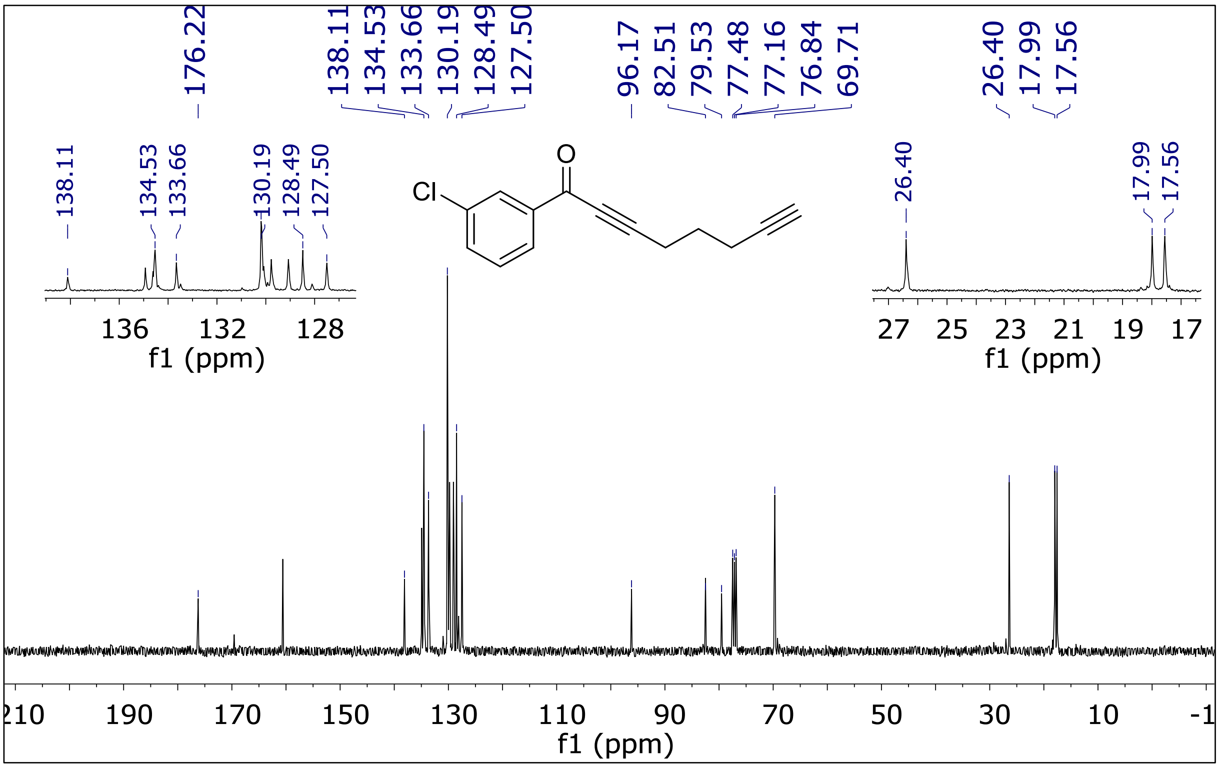


Figure S55. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **5l**.

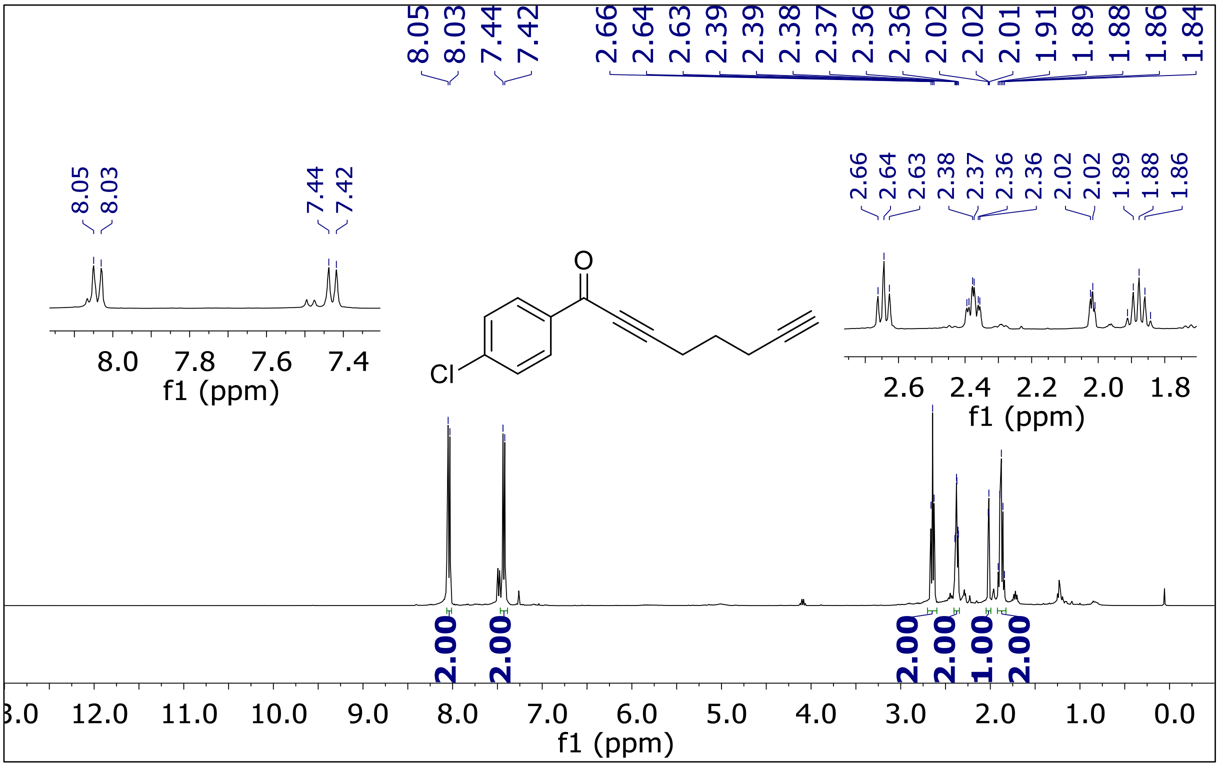


Figure S56. ^1H NMR (400 MHz, $CDCl_3$) spectrum of compound **5m**.

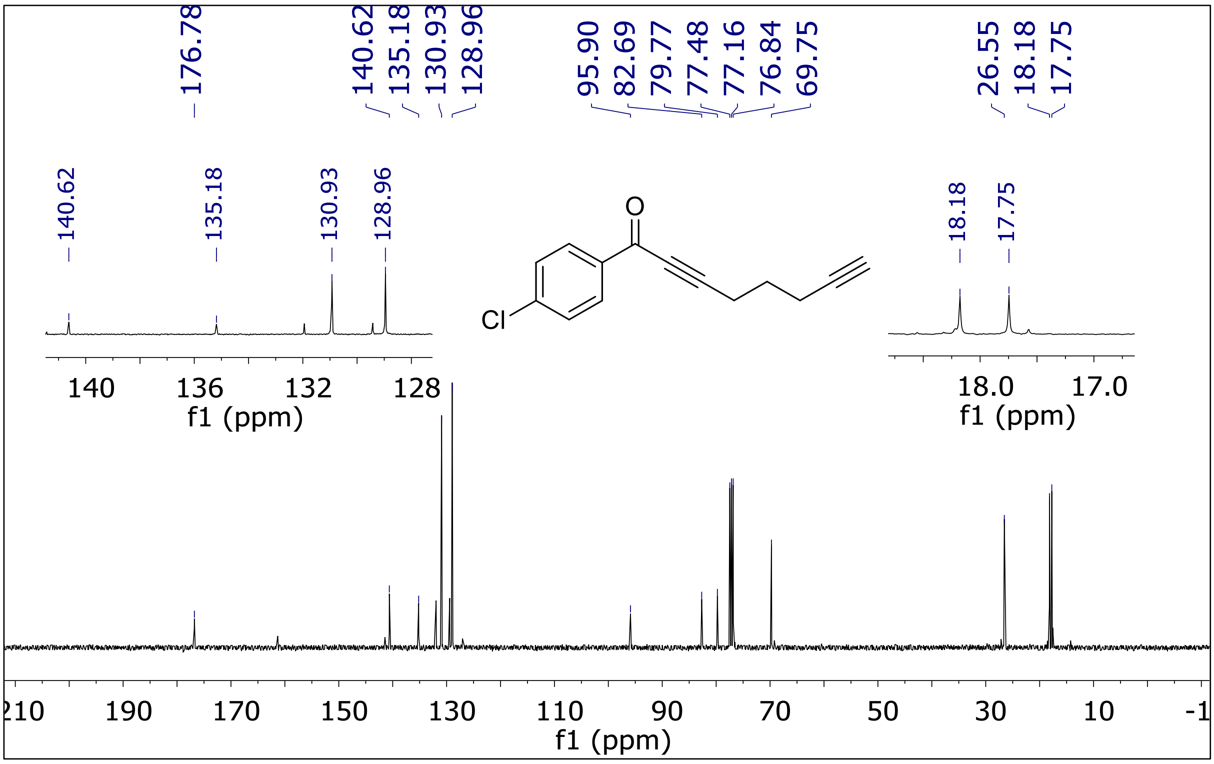


Figure S57. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **5m**.

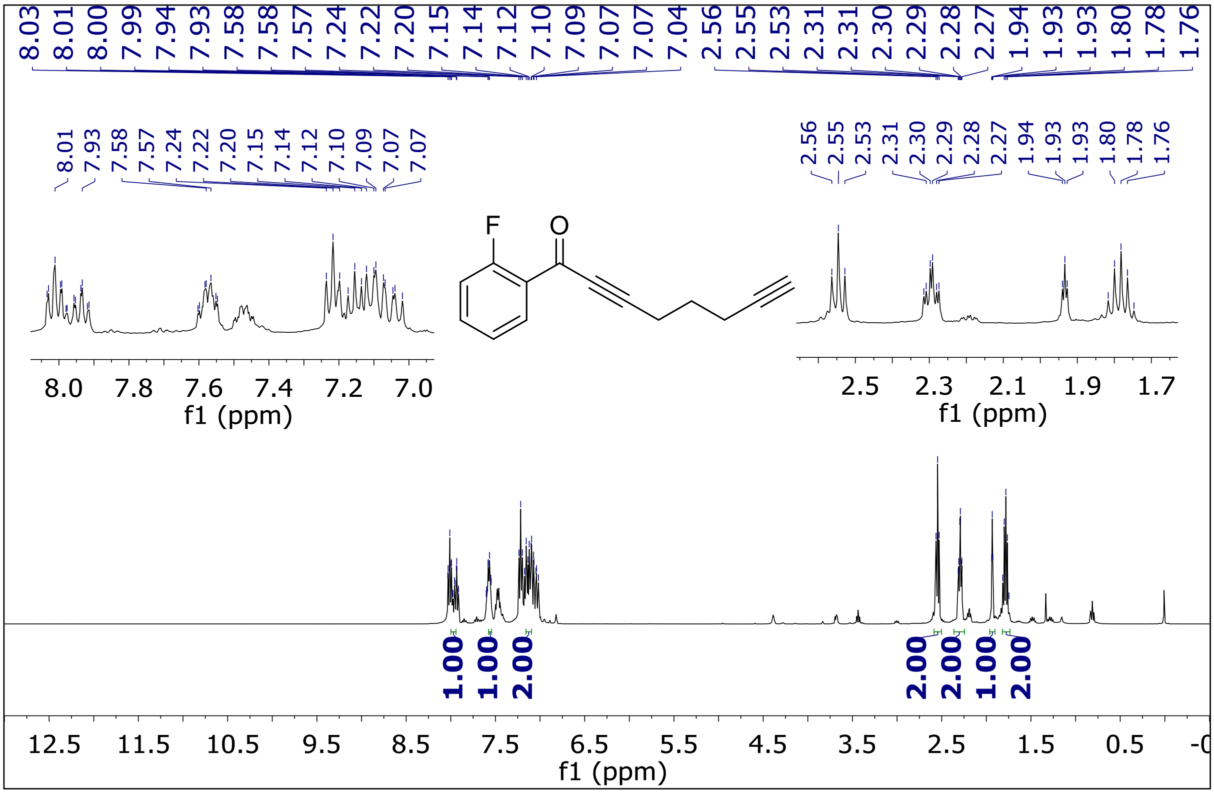


Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5n**.

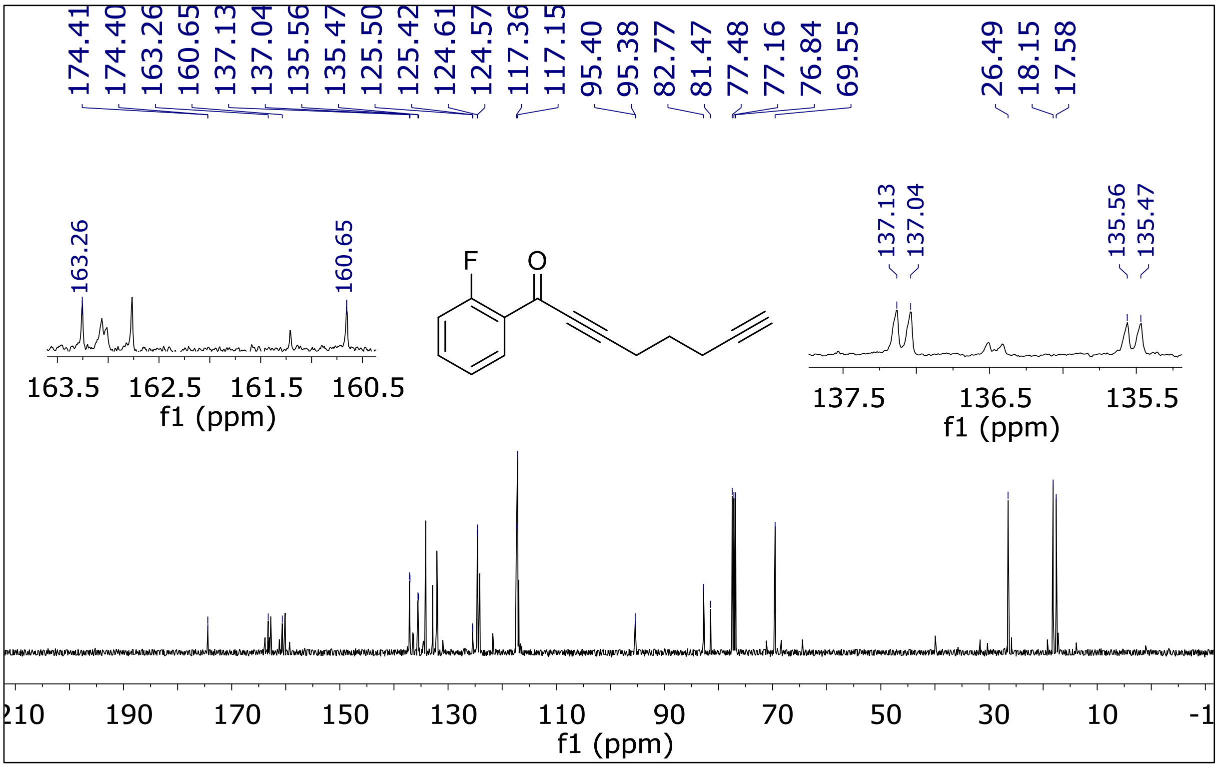


Figure S59. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **5n**.

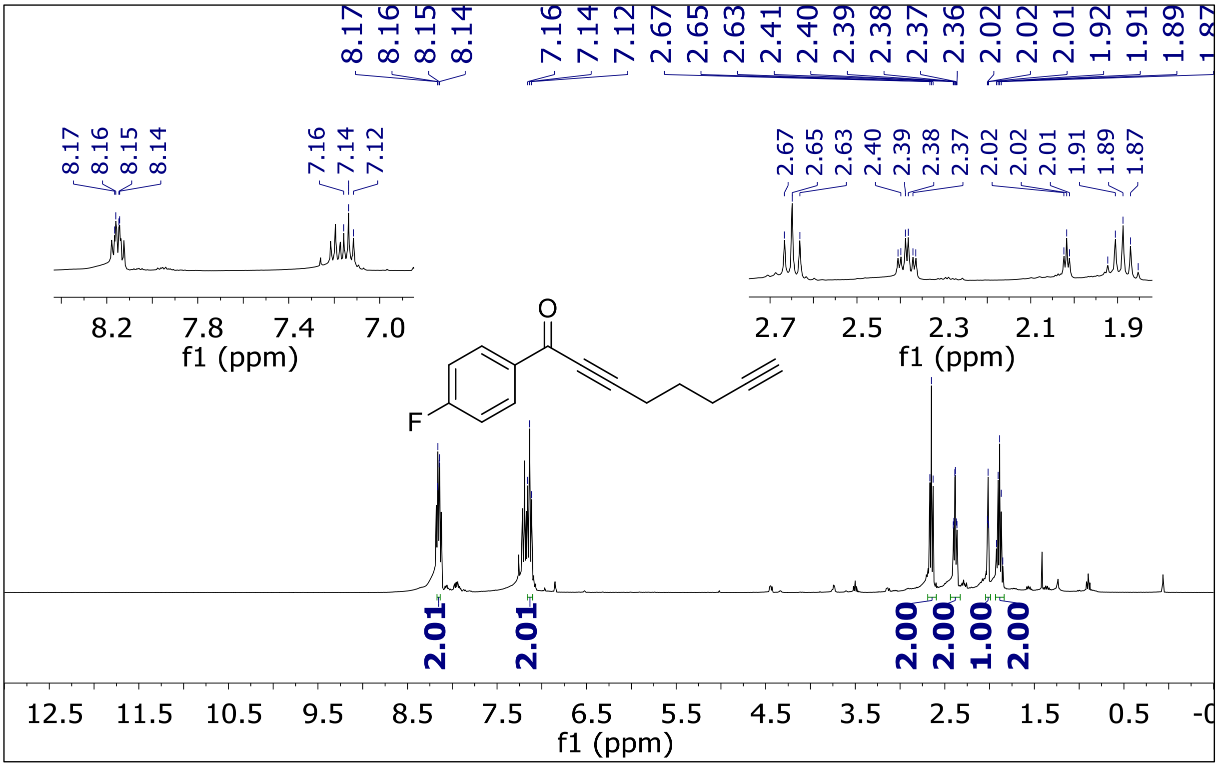


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5o**.

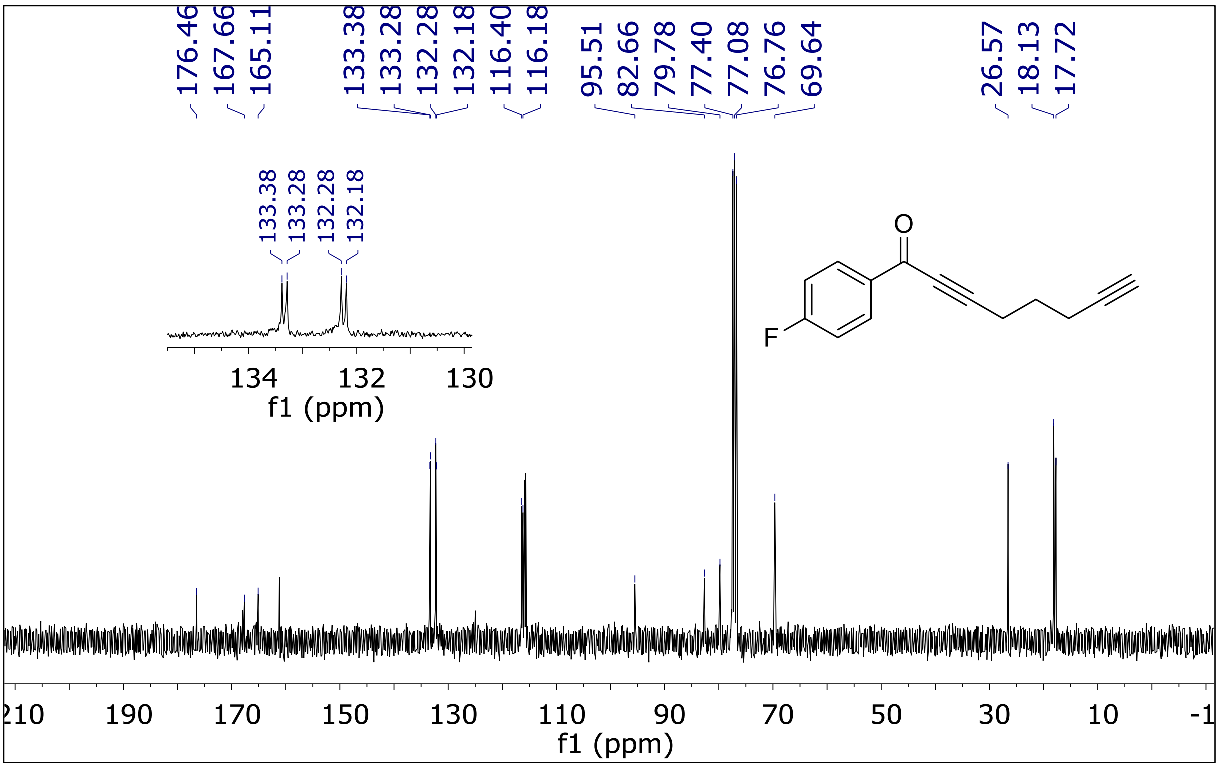


Figure S61. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **5o**.

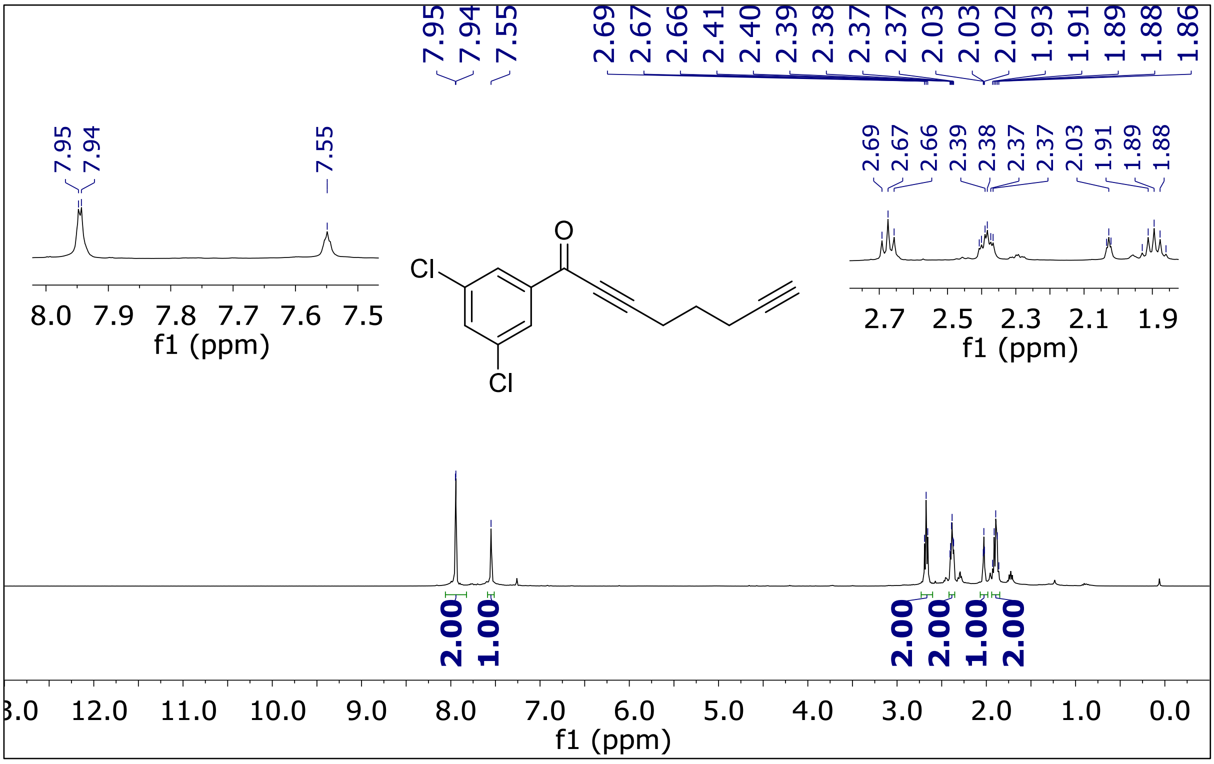


Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5p**.

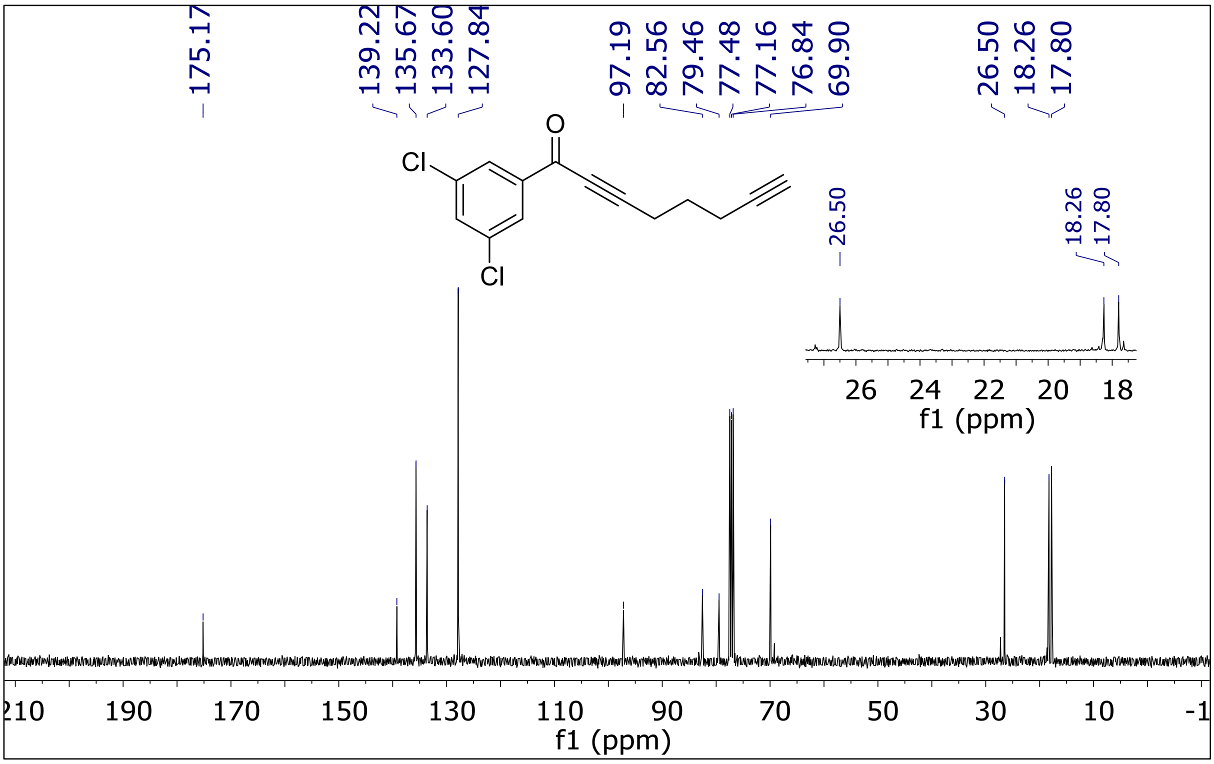


Figure S63. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **5p**.

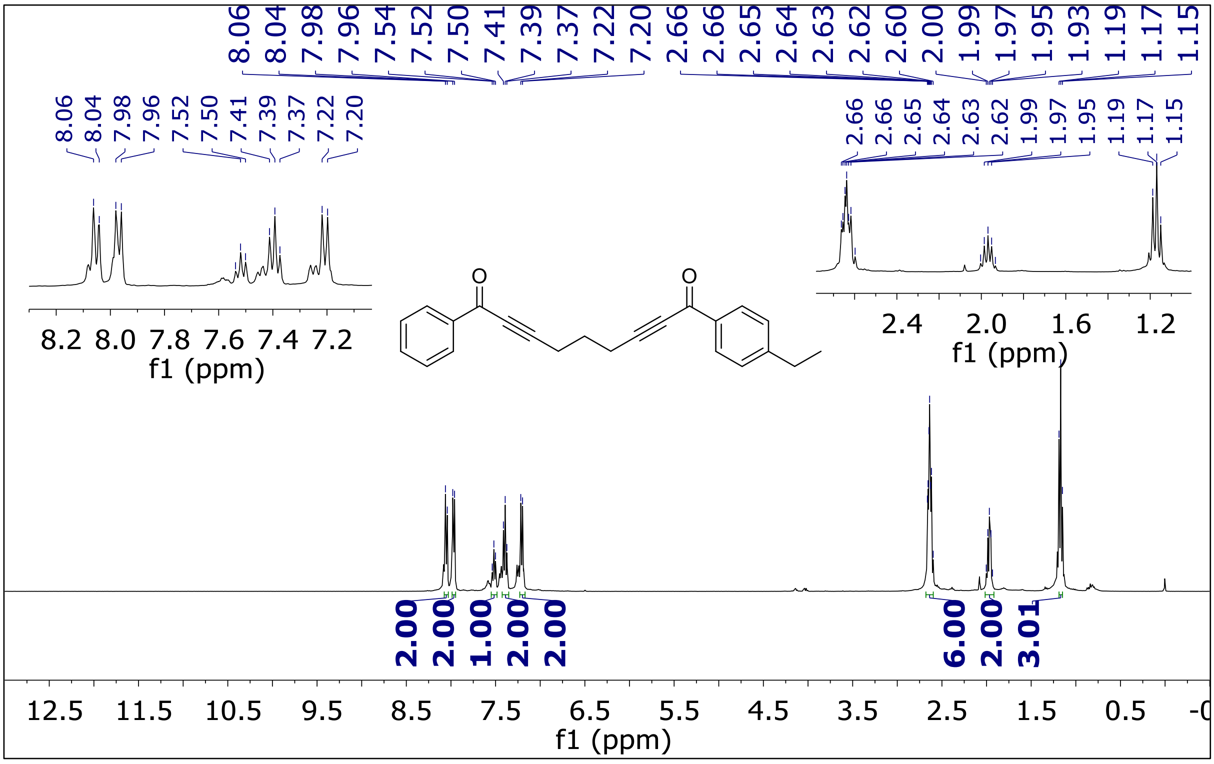


Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6a**.

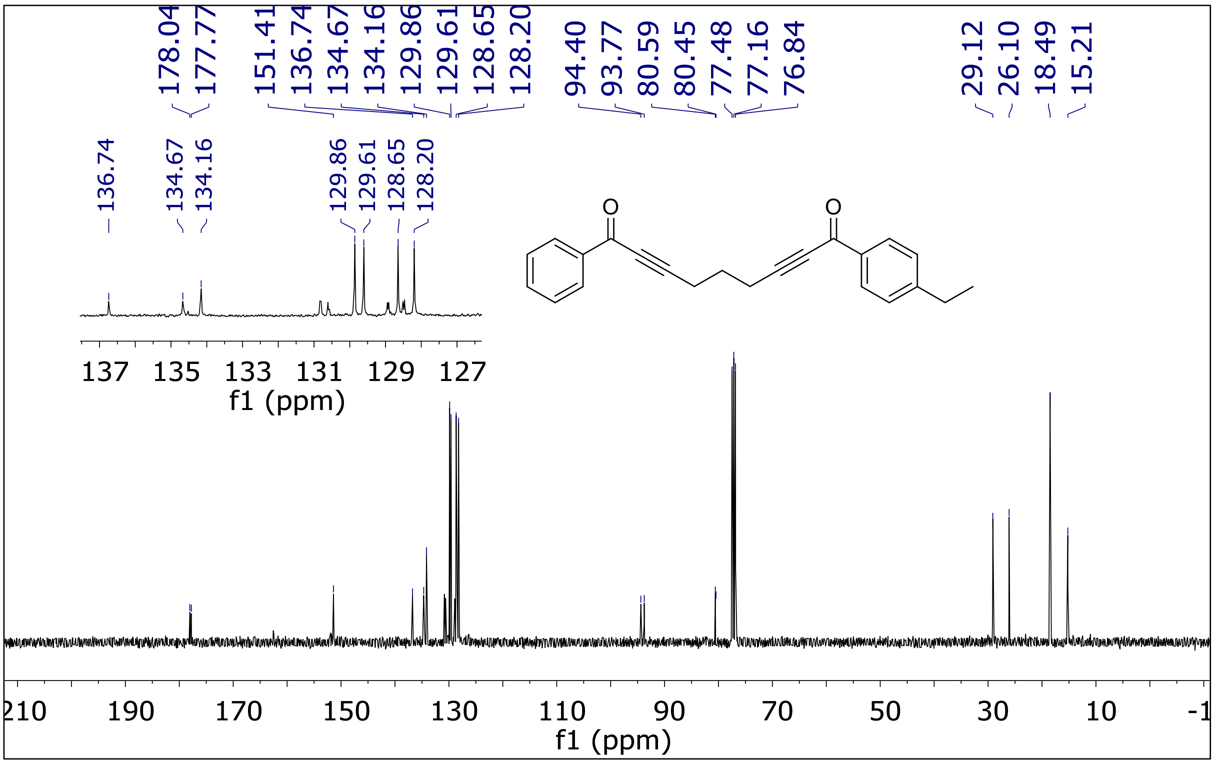


Figure S65. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **6a**.

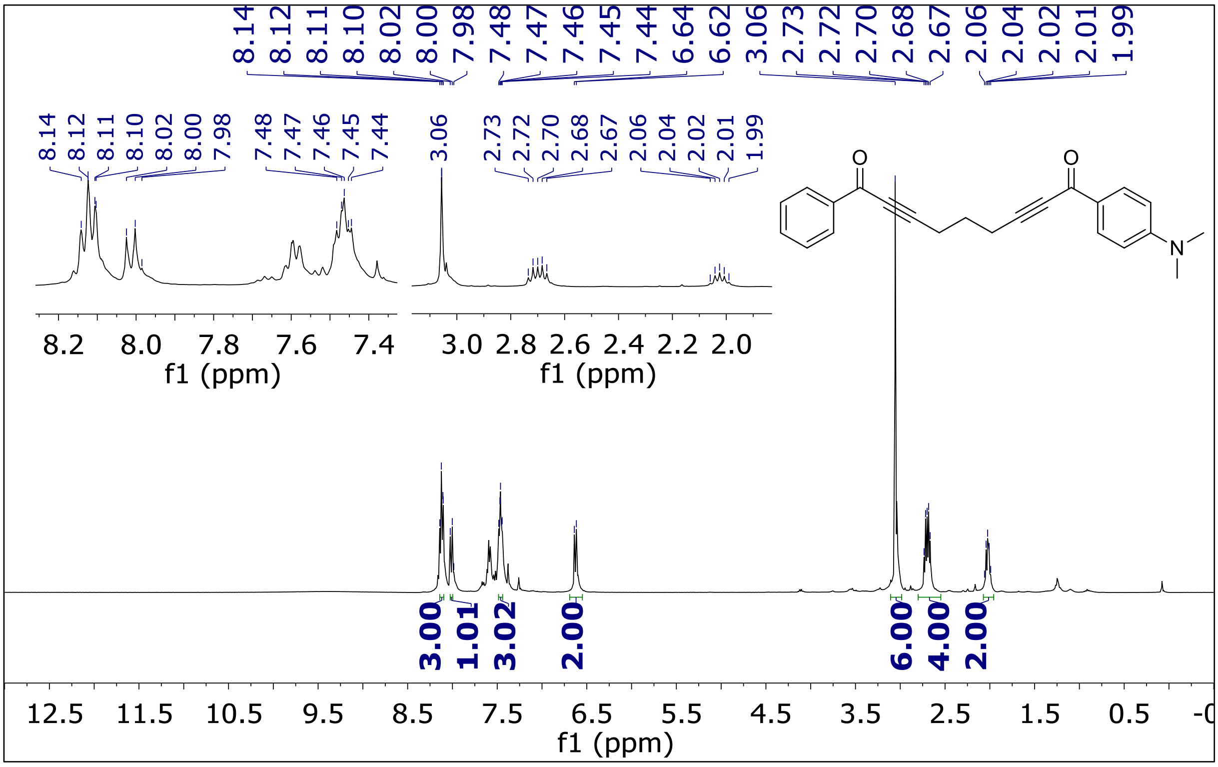


Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6b**.

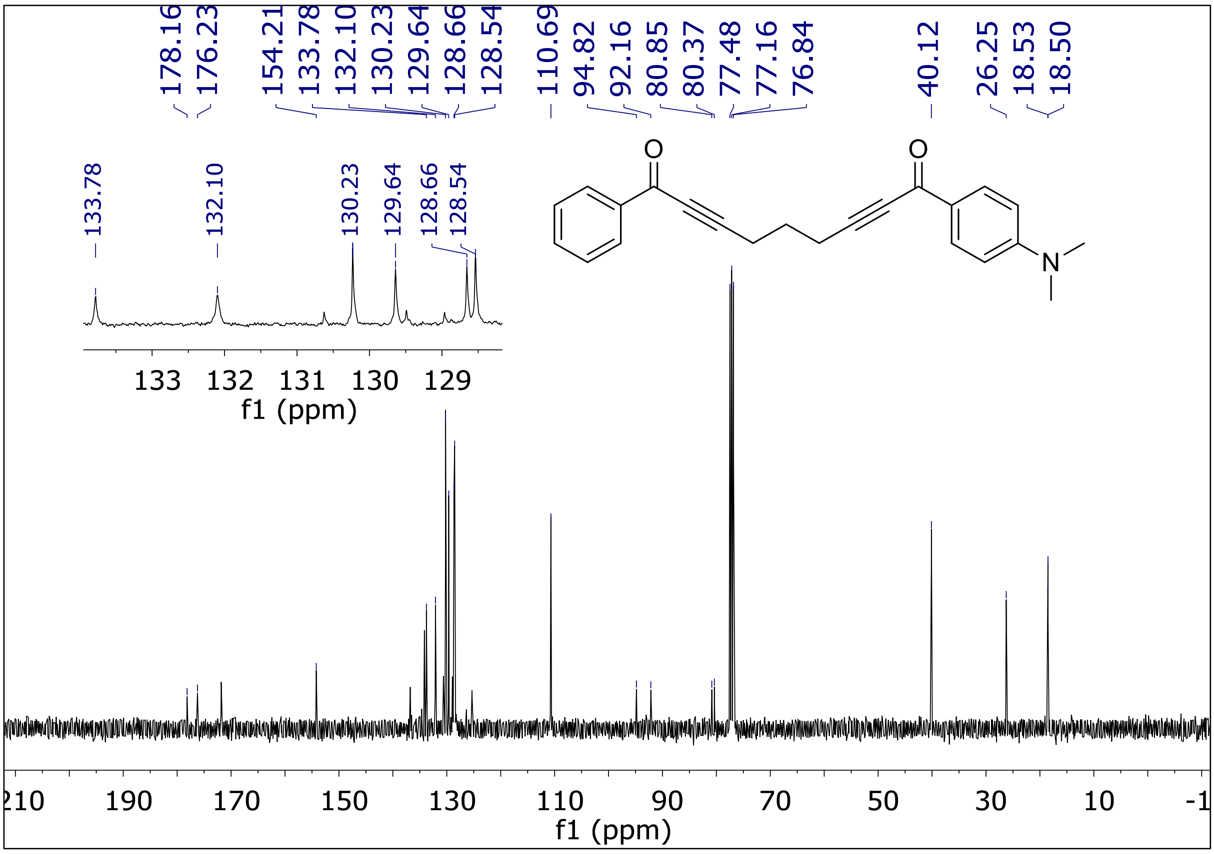


Figure S67. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **6b**.

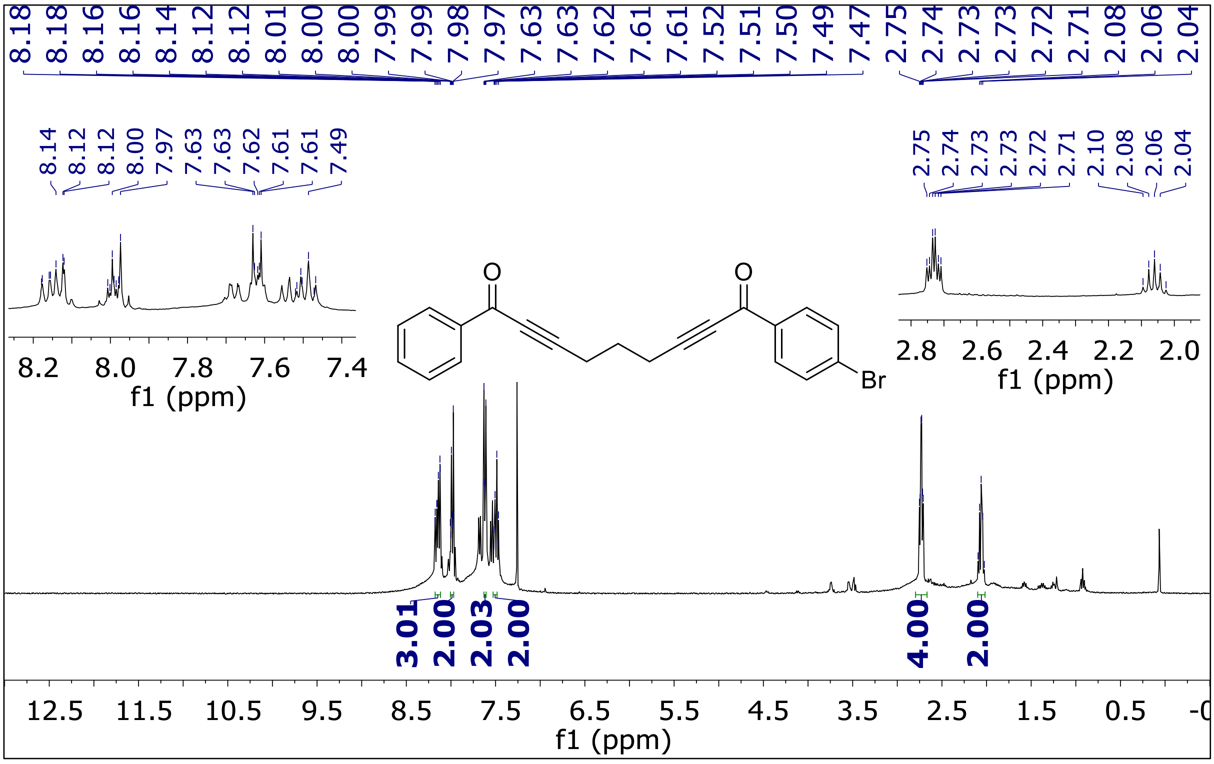


Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6c**.

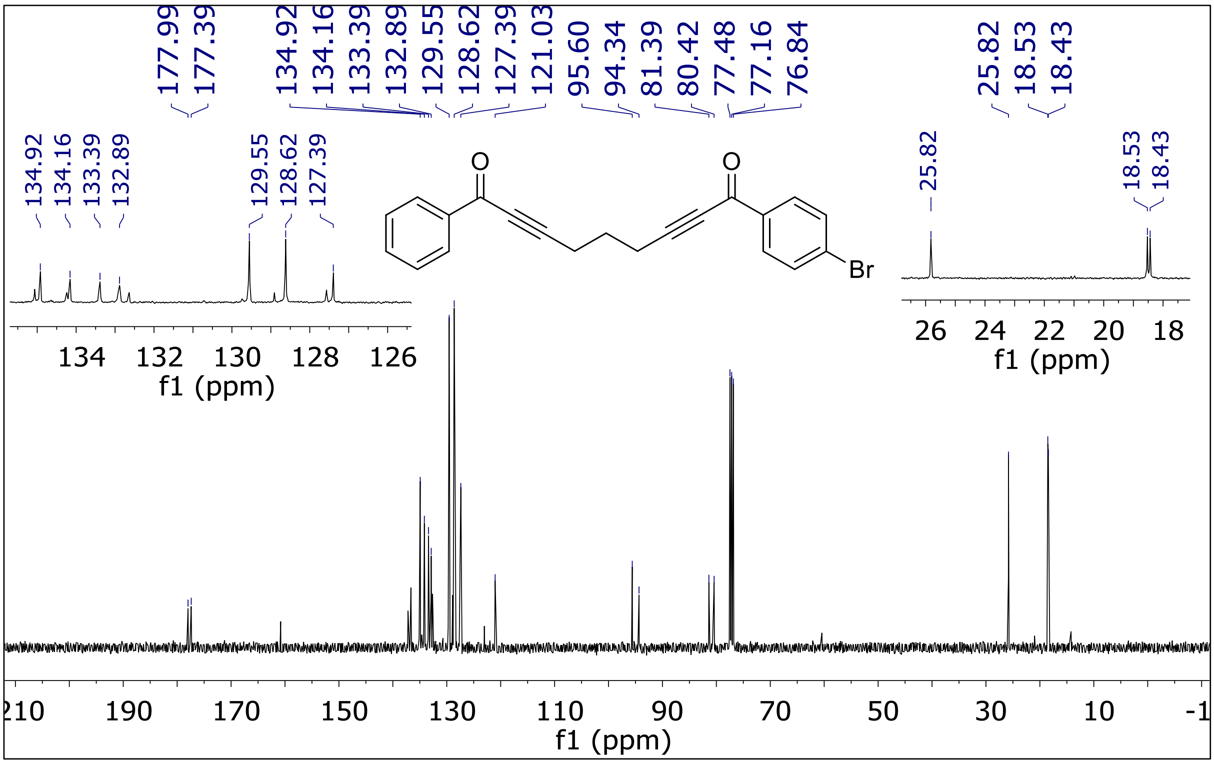


Figure S69. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **6c**.

Copies of ^{1}H and ^{13}C{^{1}H} NMR Spectra for Products 3, 7 and 8

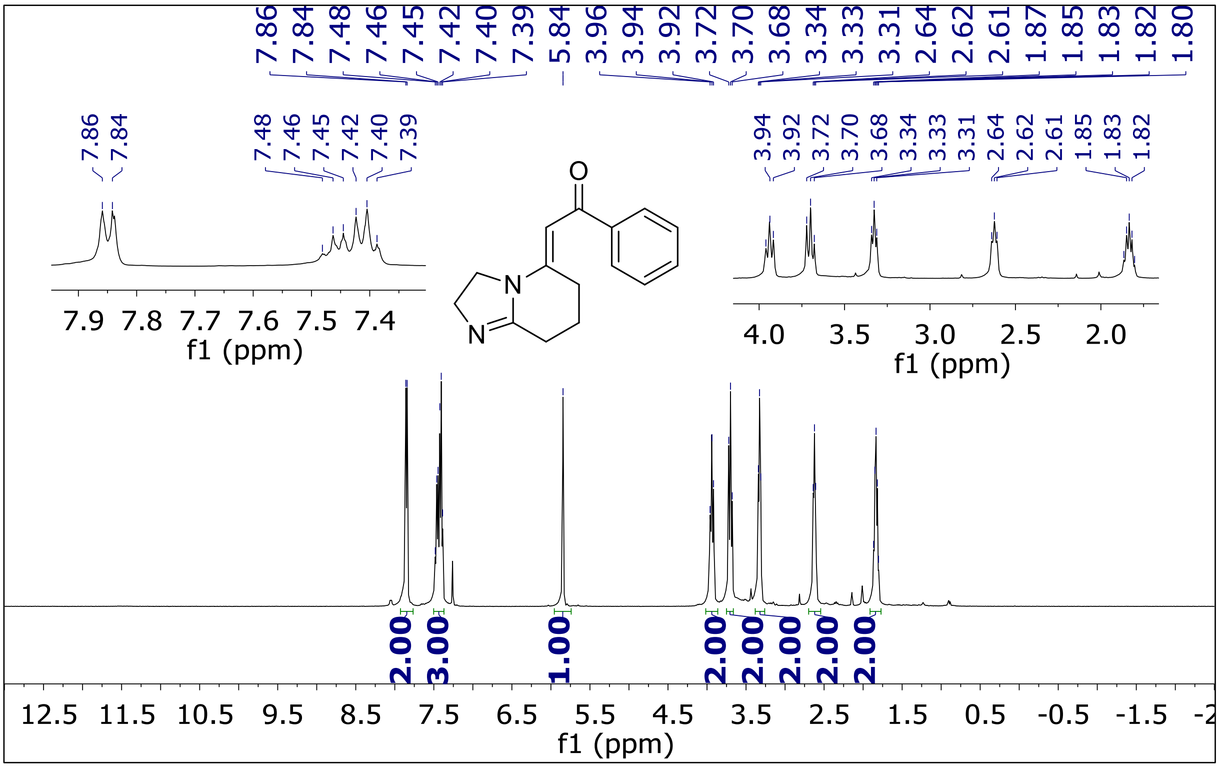


Figure S70. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **3a**.

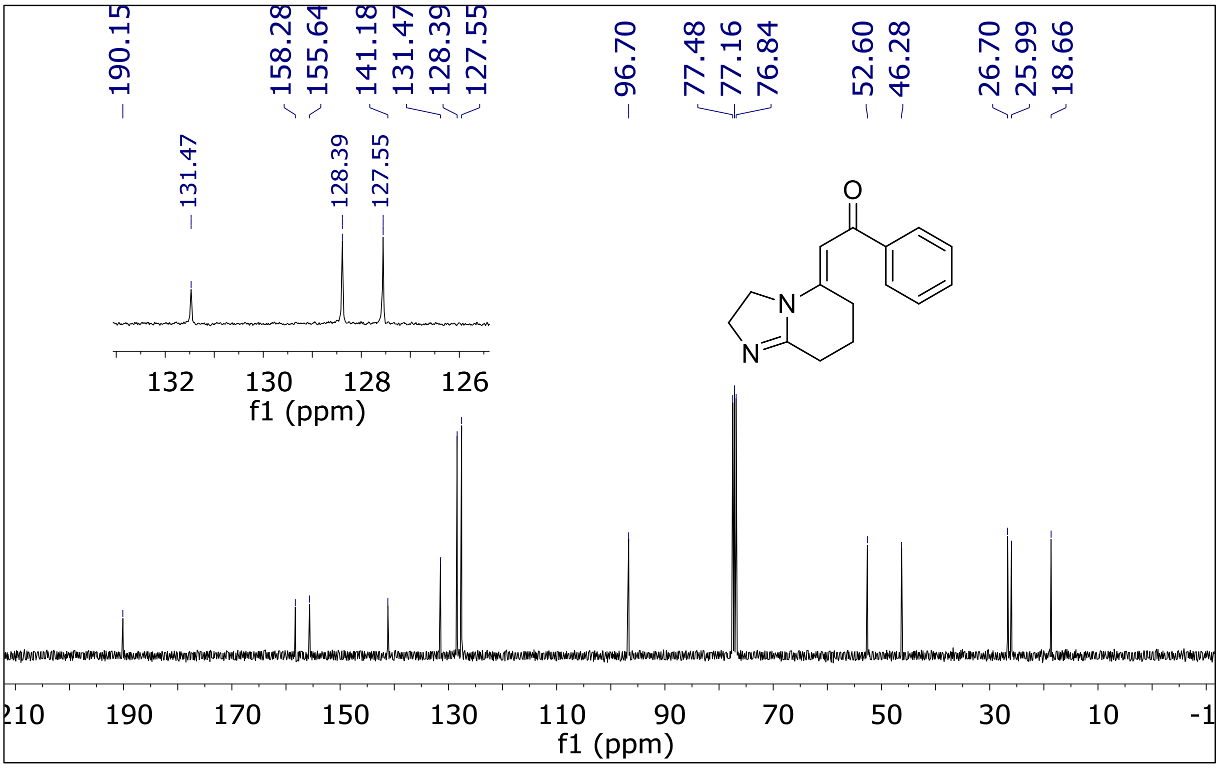


Figure S71. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **3a**.

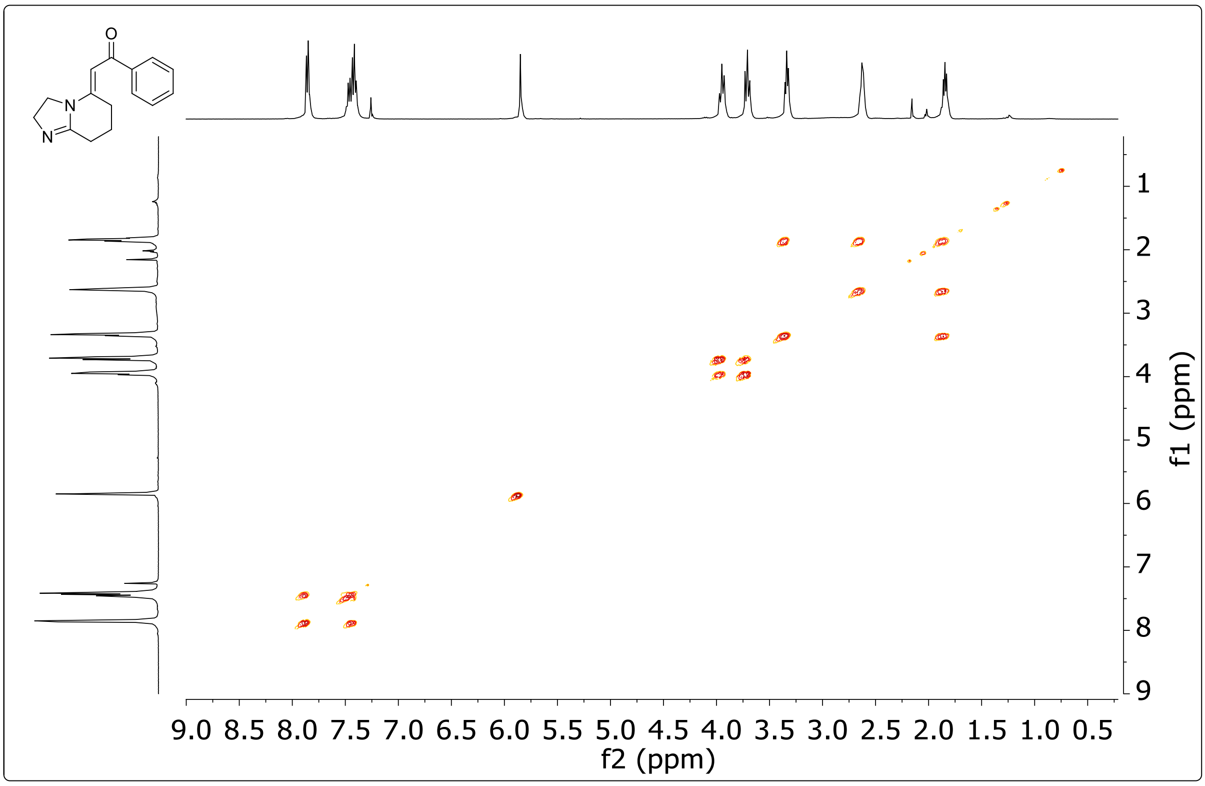


Figure S72. ^{1}H/^{1}H COSY (400/400 MHz, CDCl$_3$) spectrum of compound **3a**.

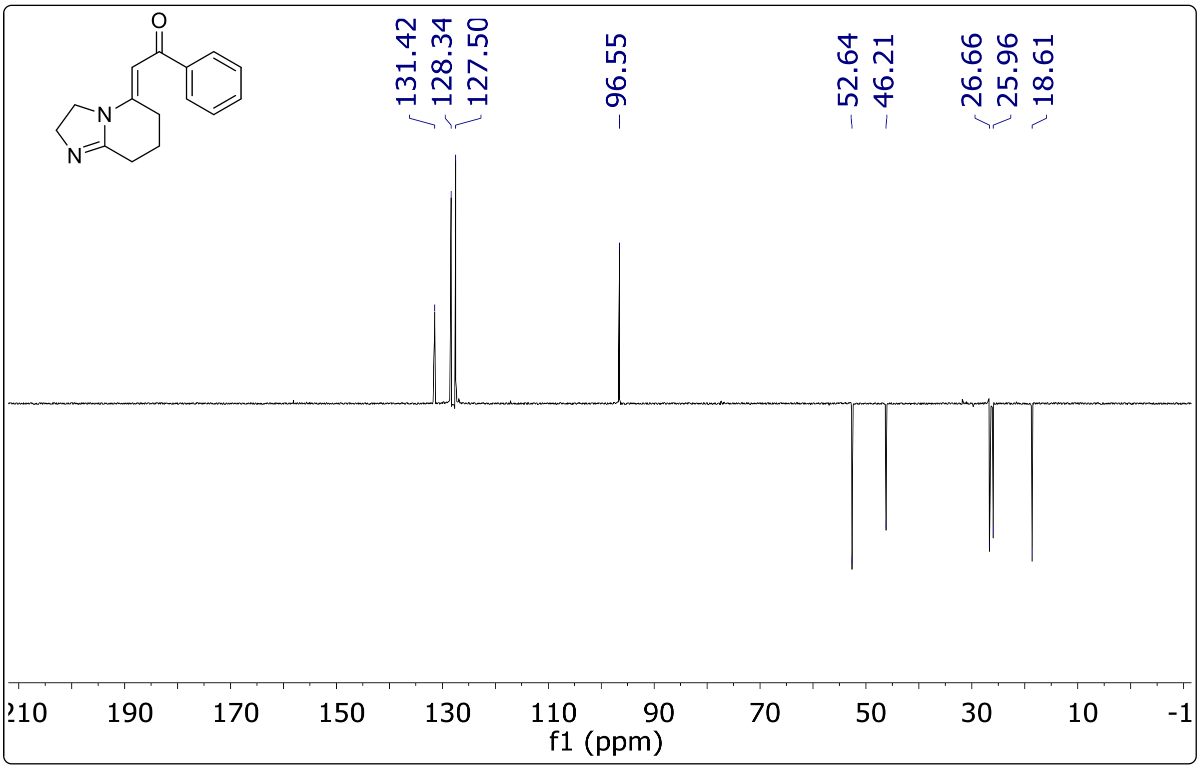


Figure S73. ^{13}C{^{1}H} DEPT–135 (100 MHz, CDCl$_3$) spectrum of compound **3a**.

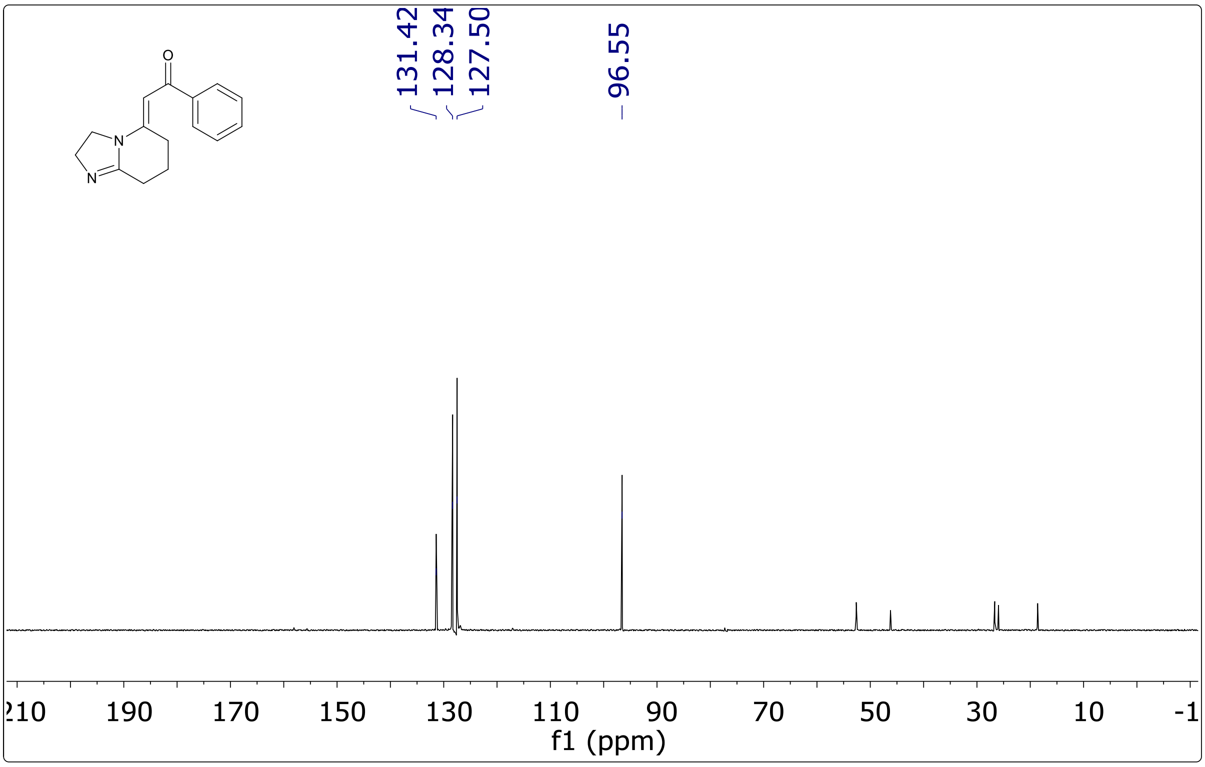


Figure S74. $^{13}C\{^1H\}$ DEPT–90 (100 MHz, CDCl$_3$) spectrum of compound **3a**.

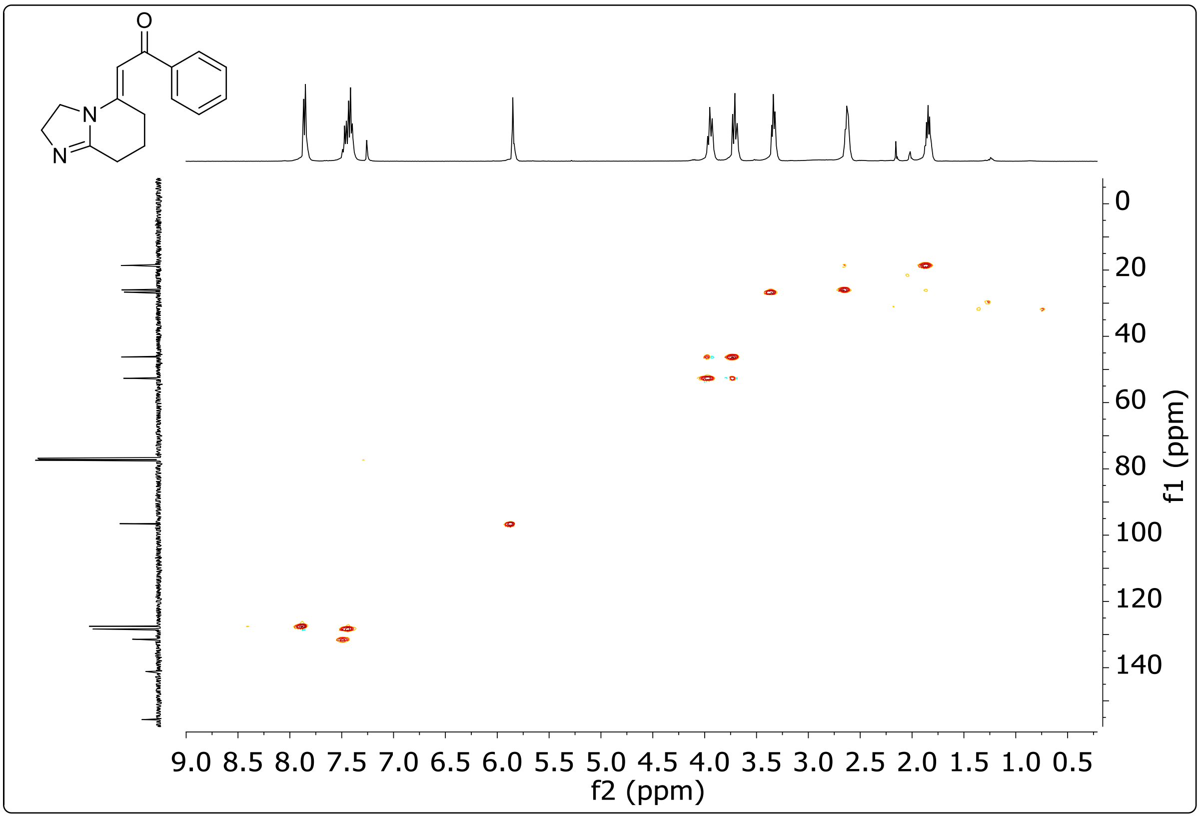


Figure S75. $^1H/^{13}C$ HSQC (400/100 MHz, CDCl$_3$) spectrum of compound **3a**.

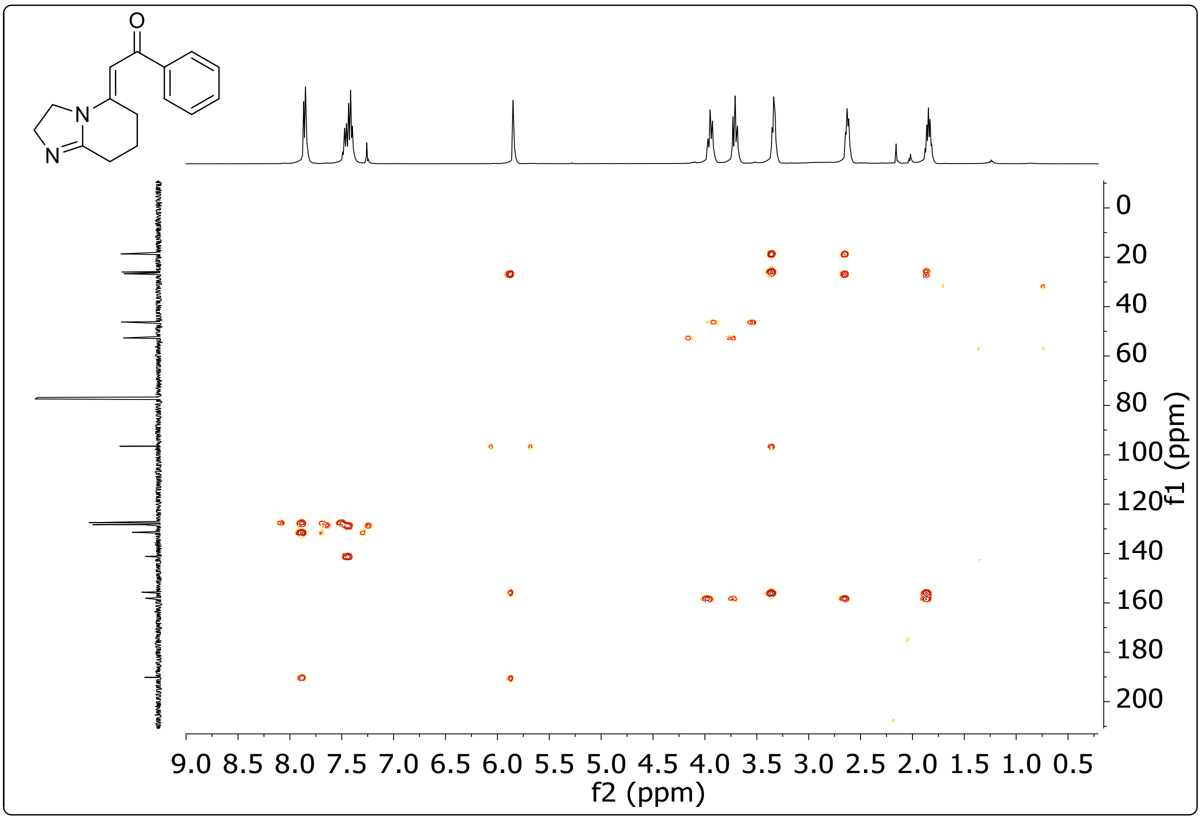


Figure S76. ^{1}H/^{13}C HMBC (400/100 MHz, CDCl$_3$) spectrum of compound **3a**.

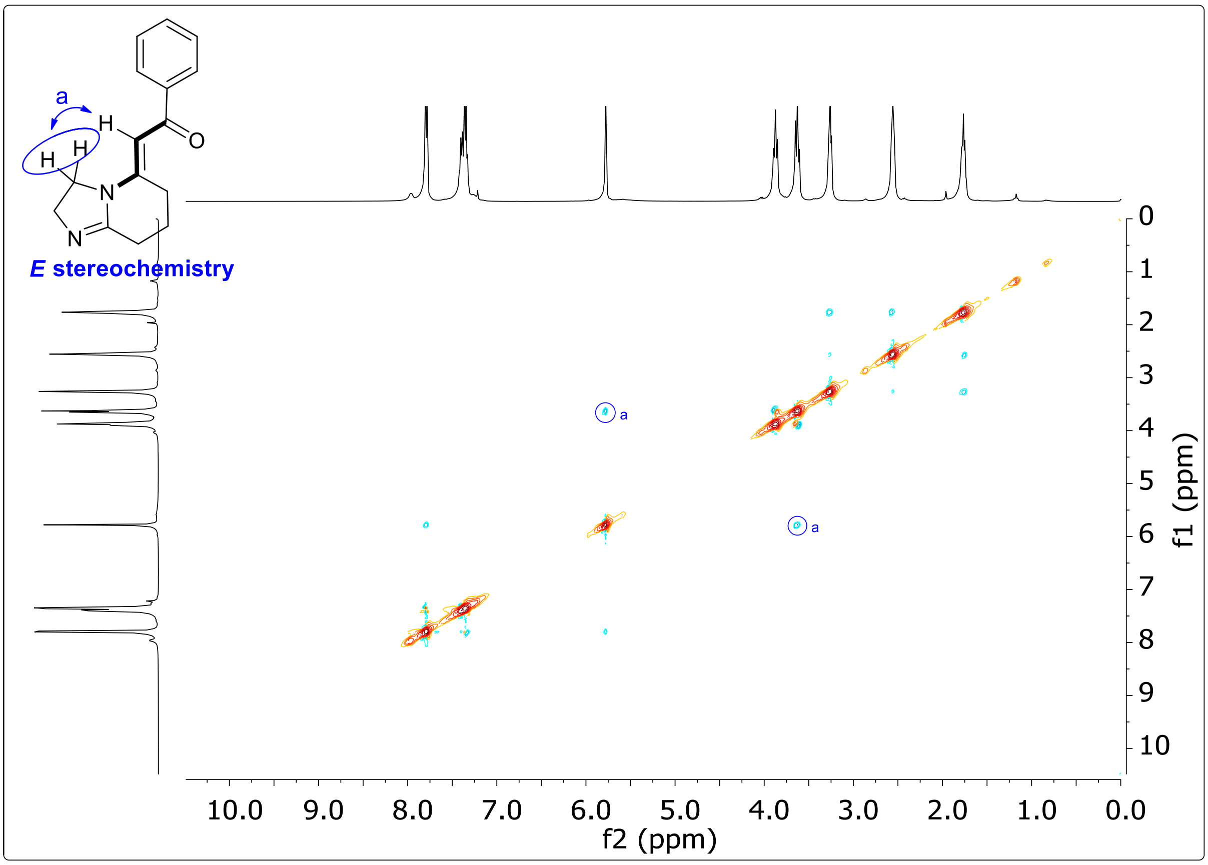


Figure S77. ^{1}H/^{1}H NOESY (400/400 MHz, CDCl$_3$) spectrum of compound **3a**.

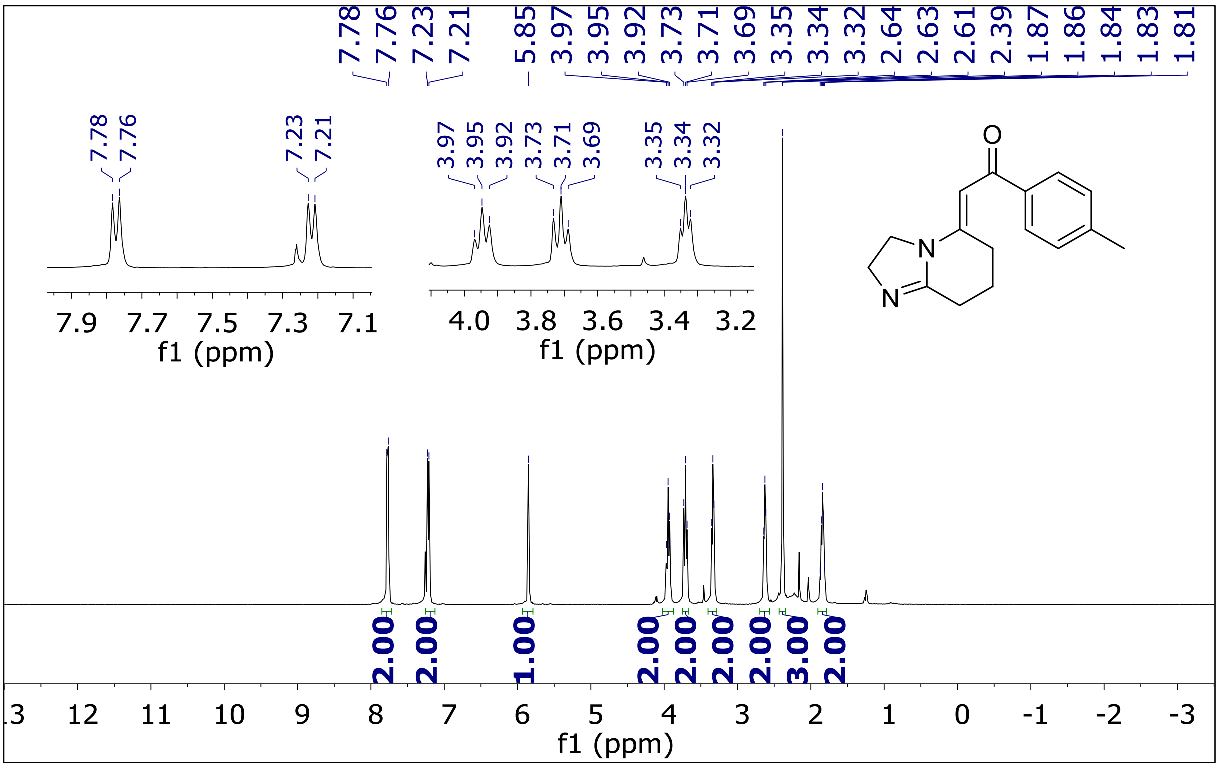


Figure S78. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **3b**.

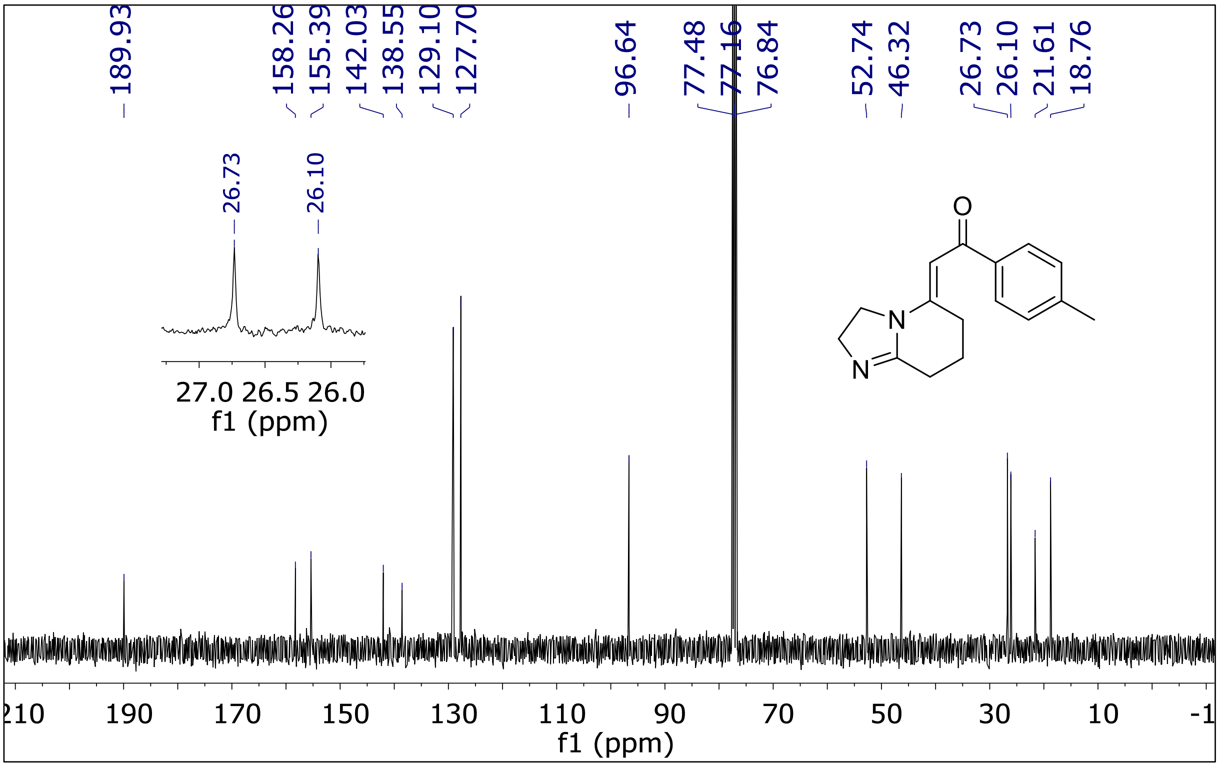


Figure S79. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **3b**.

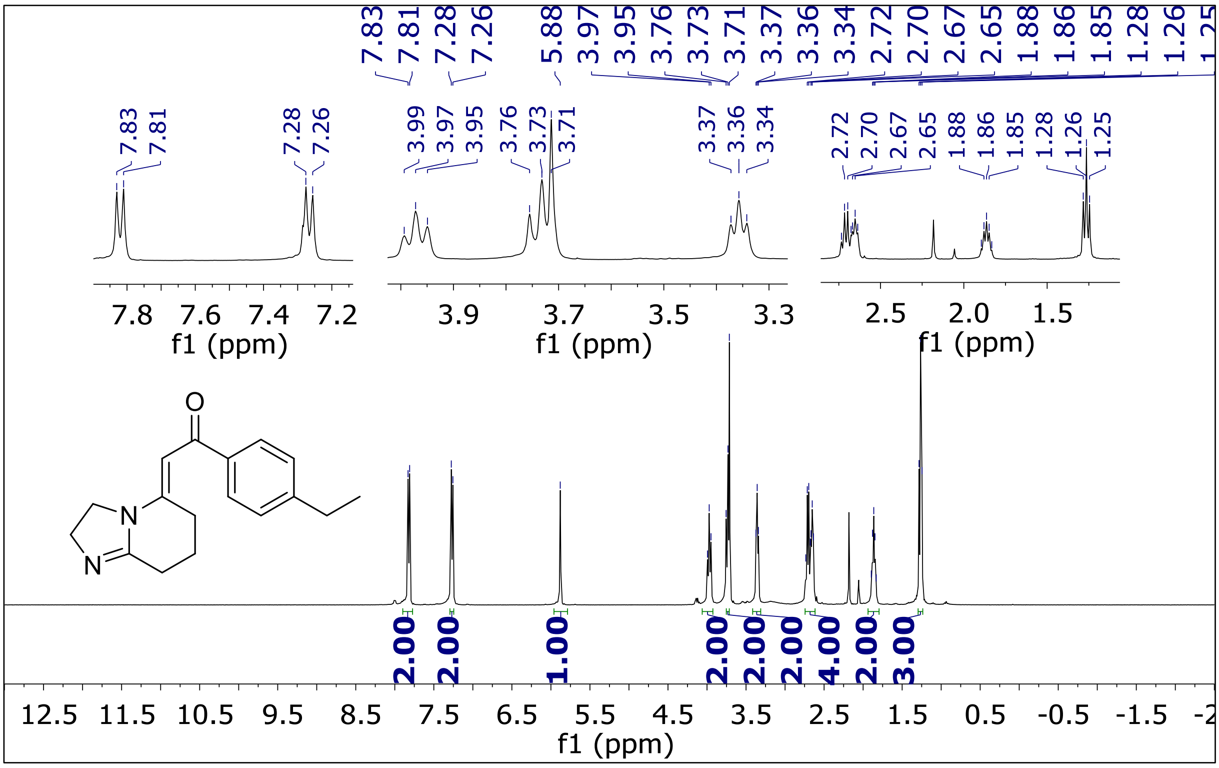


Figure S80. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **3c**.

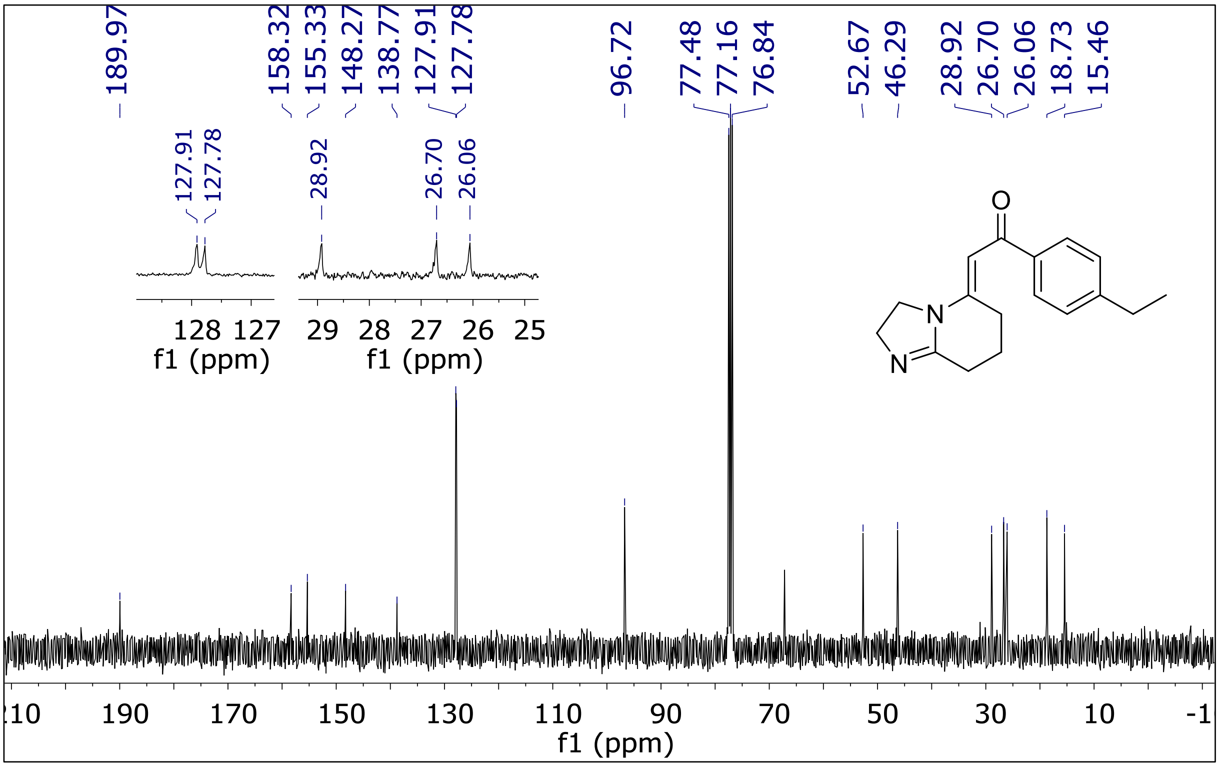


Figure S81. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **3c**.

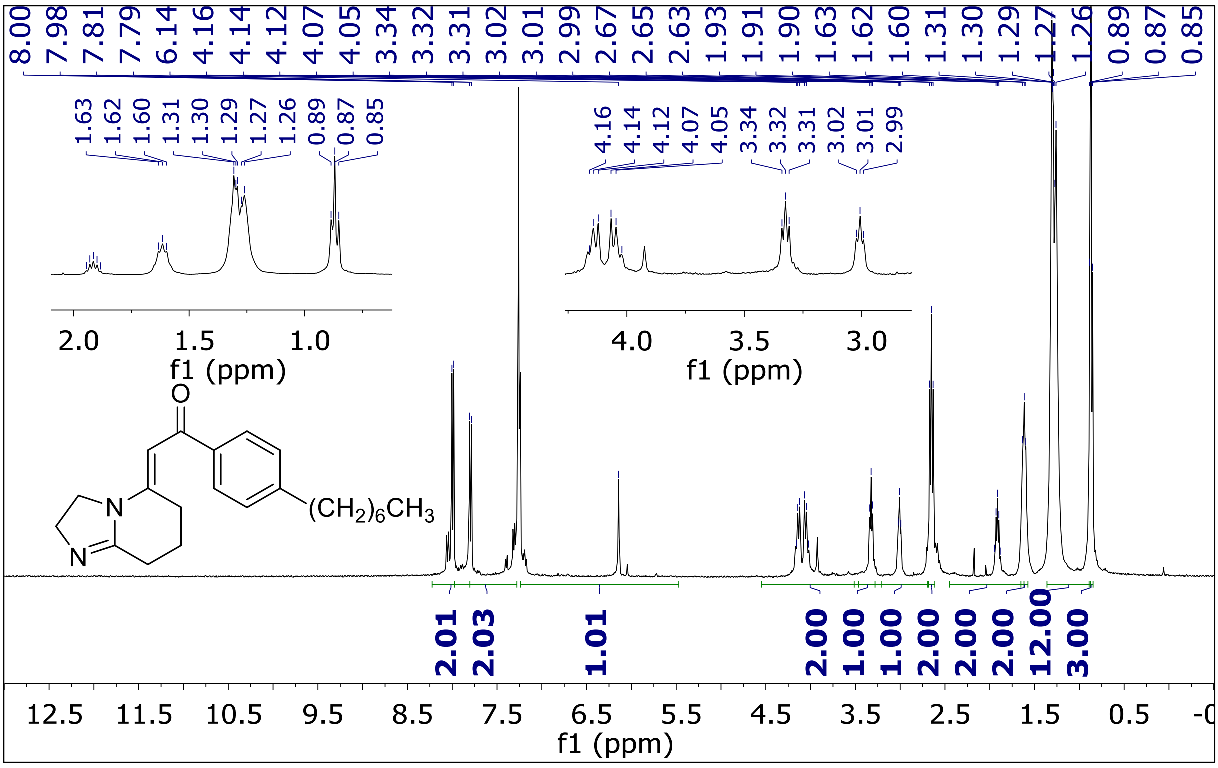


Figure S82. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**.

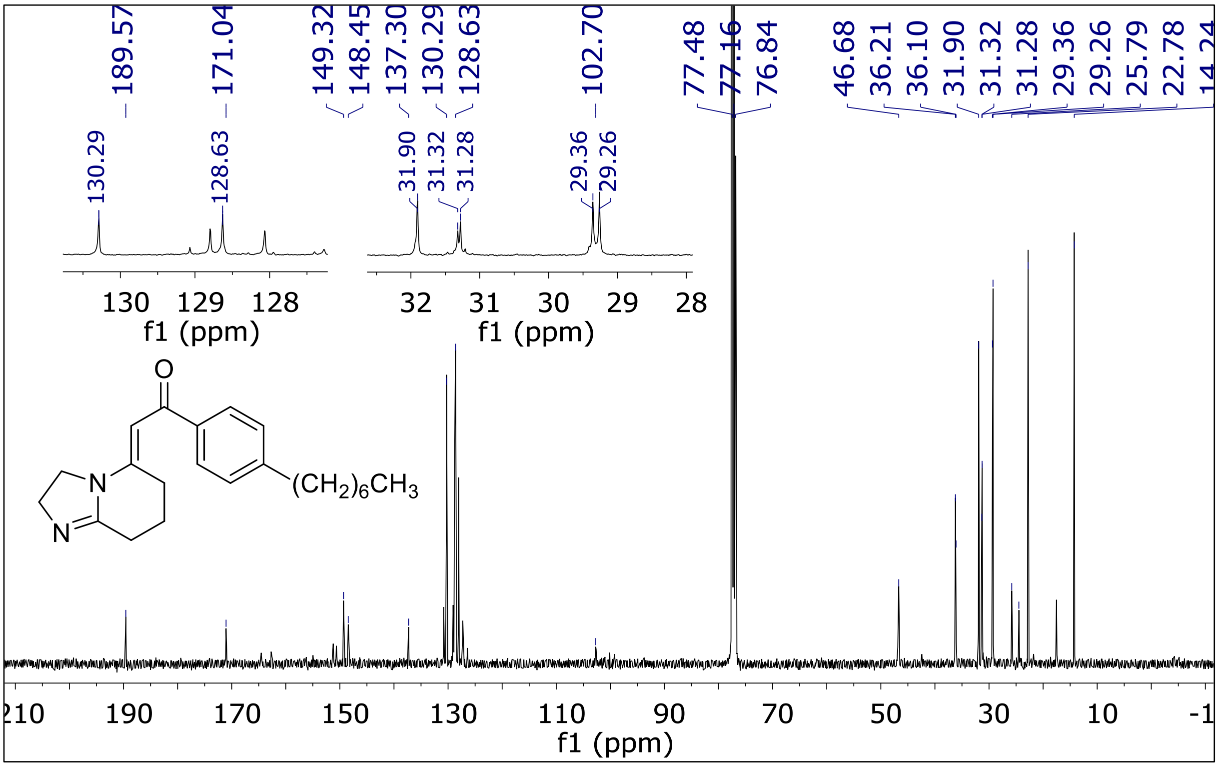


Figure S83. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3d**.

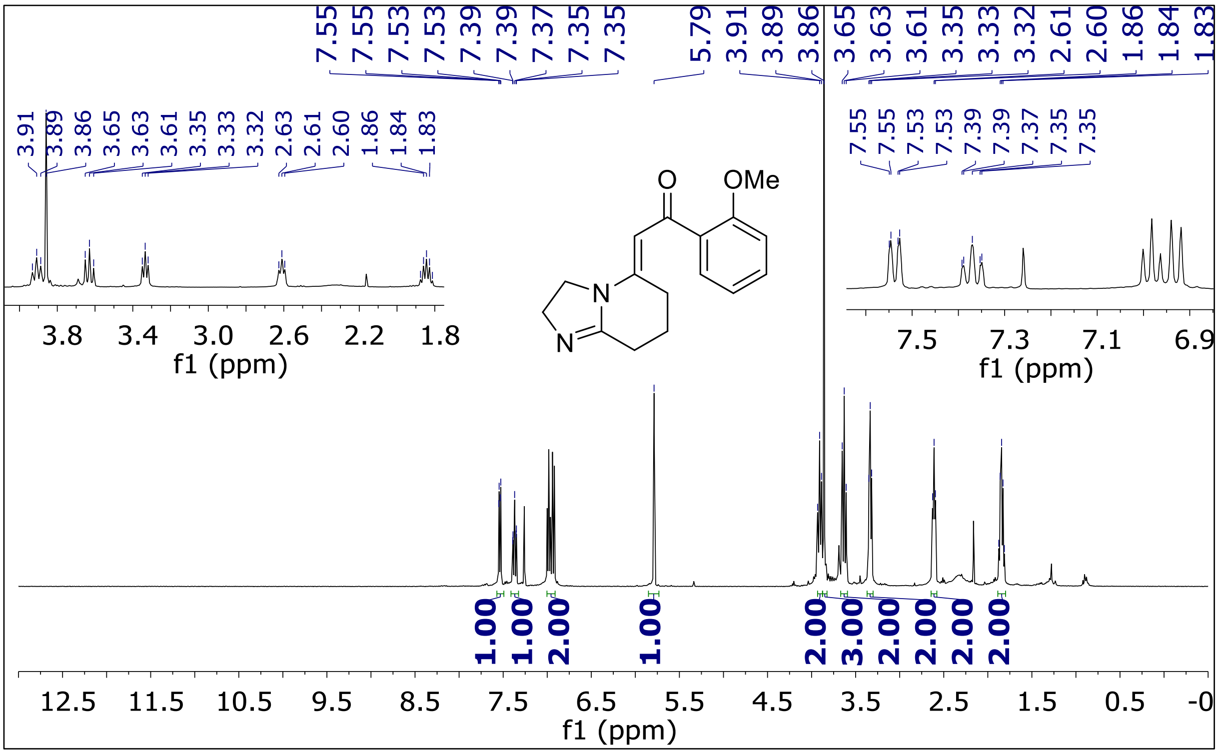


Figure S84. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **3e**.

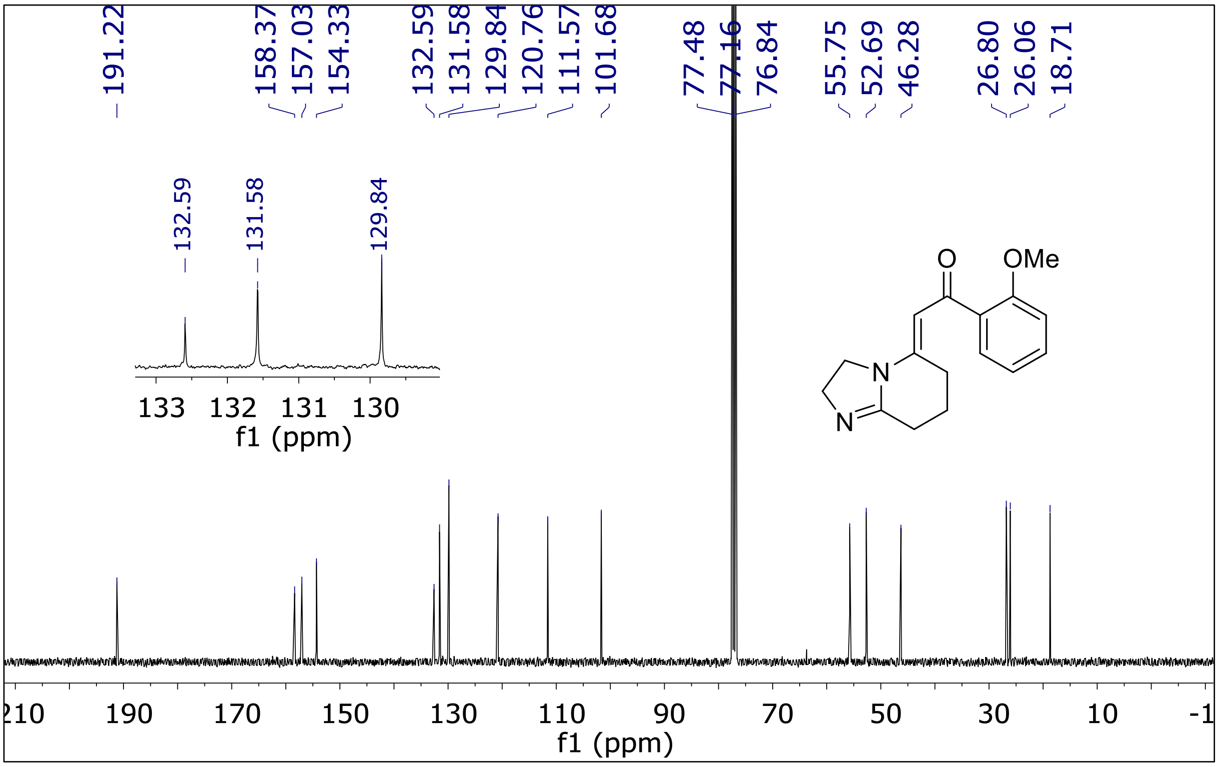


Figure S85. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **3e**.

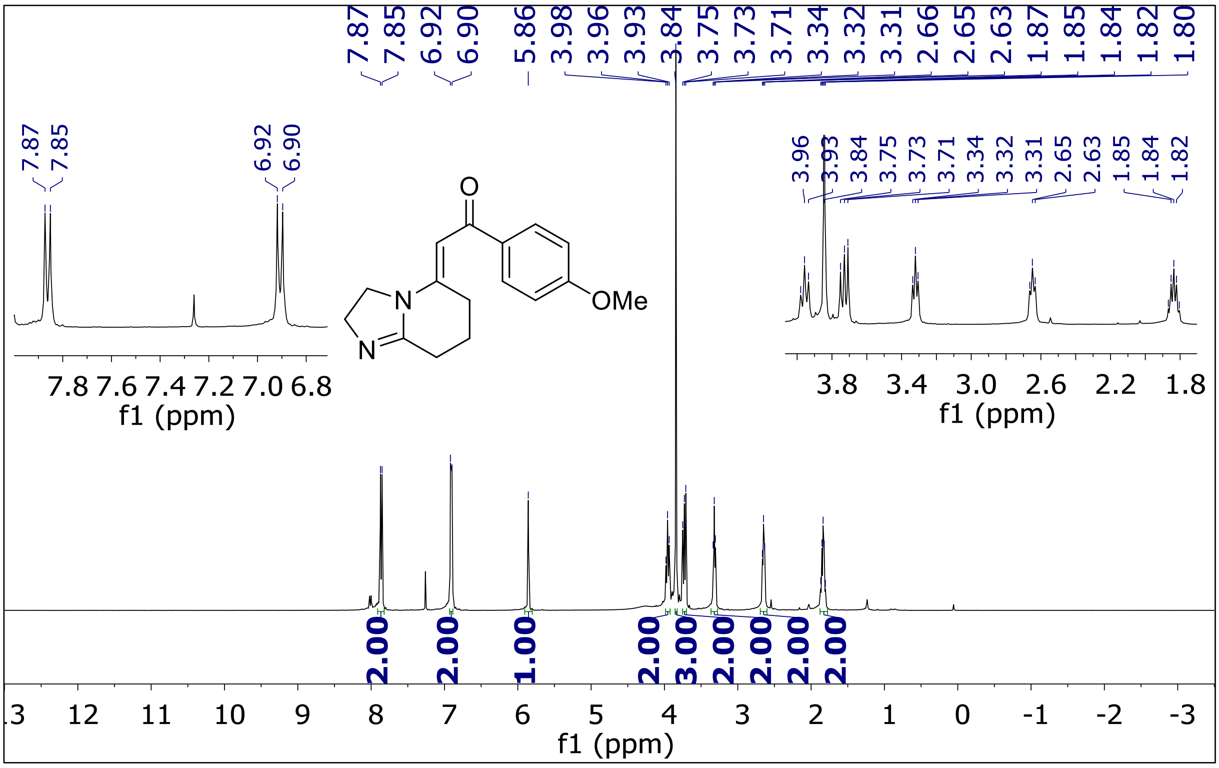


Figure S86. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **3f**.

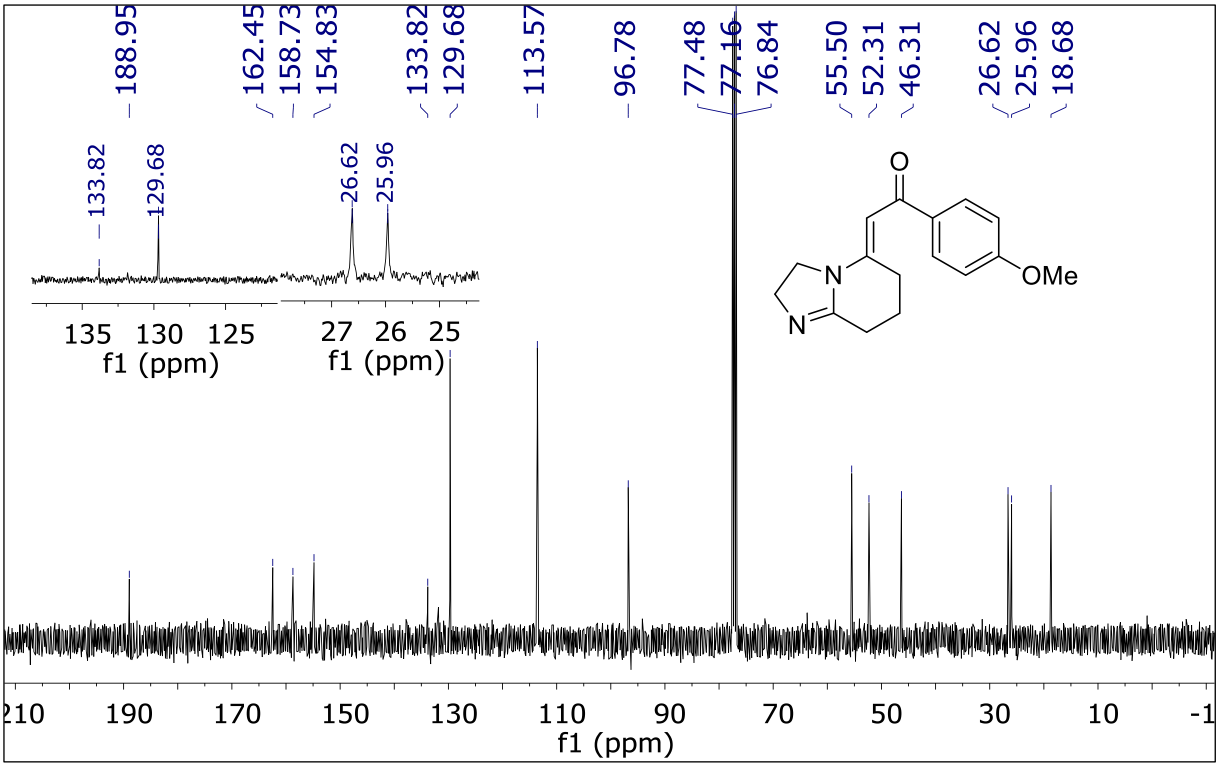


Figure S87. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **3f**.

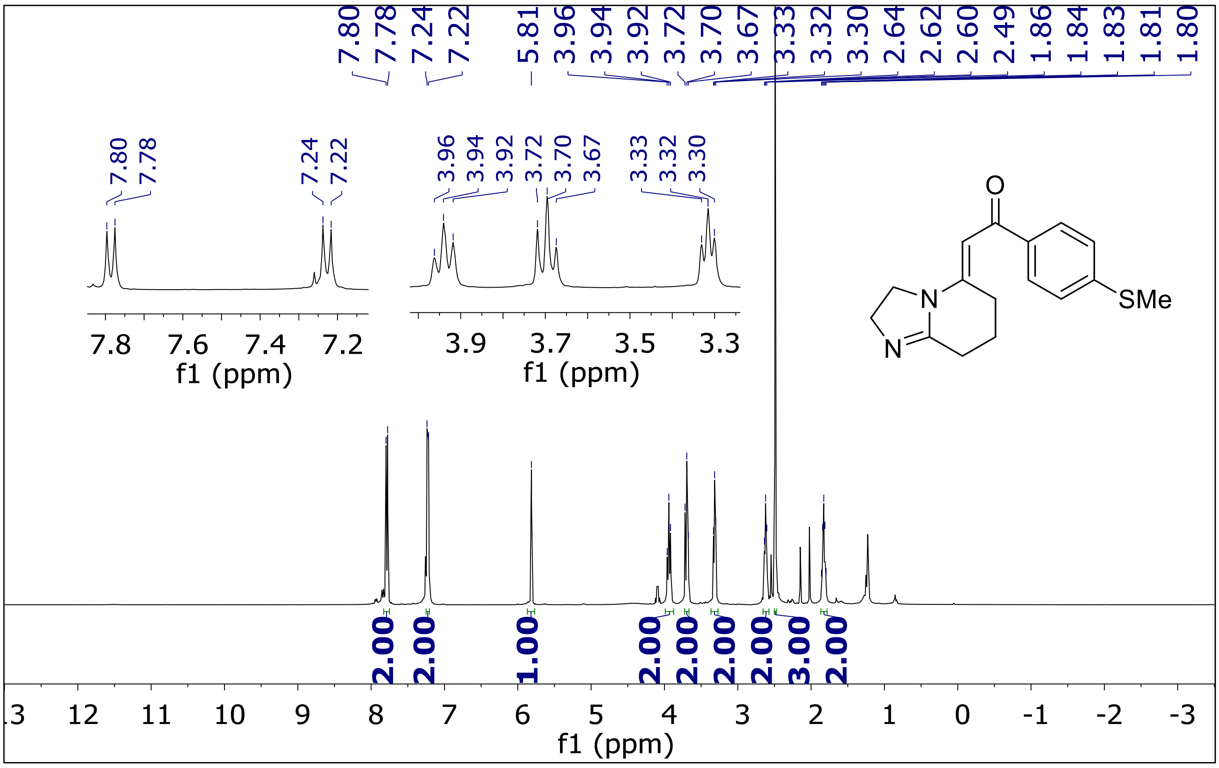


Figure S88. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **3g**.

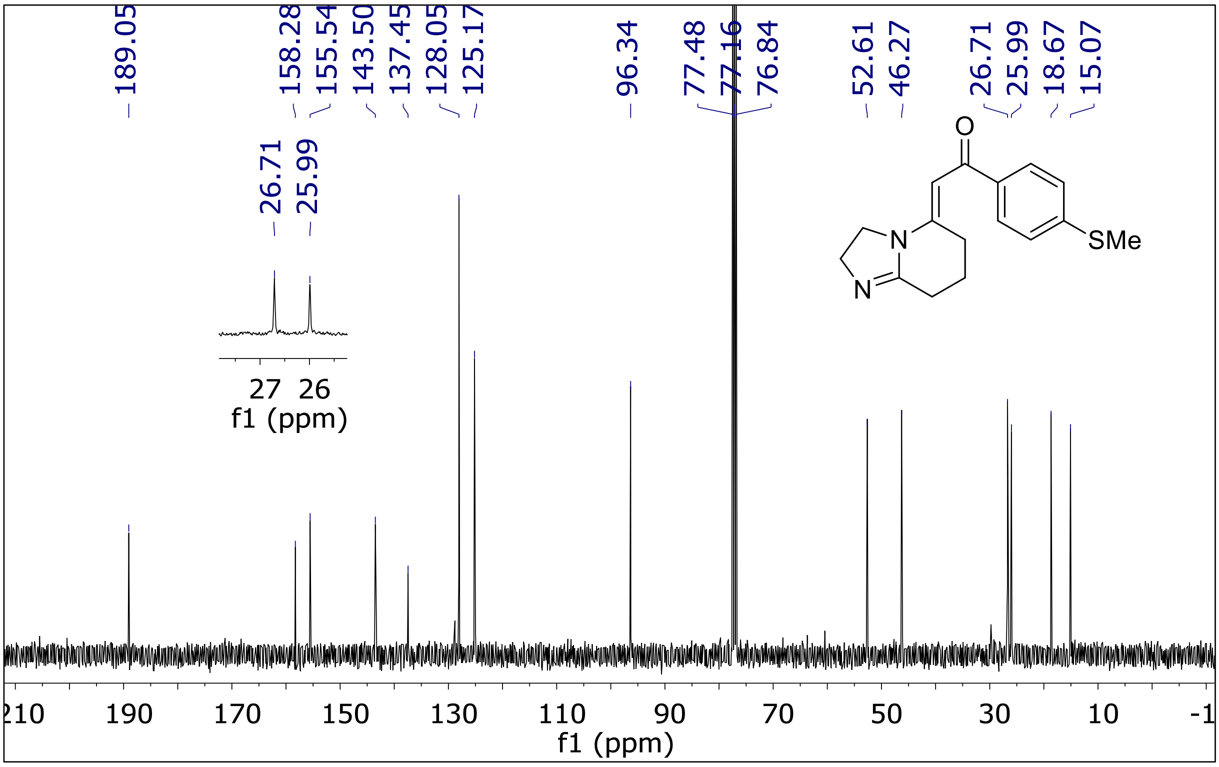


Figure S89. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **3g**.

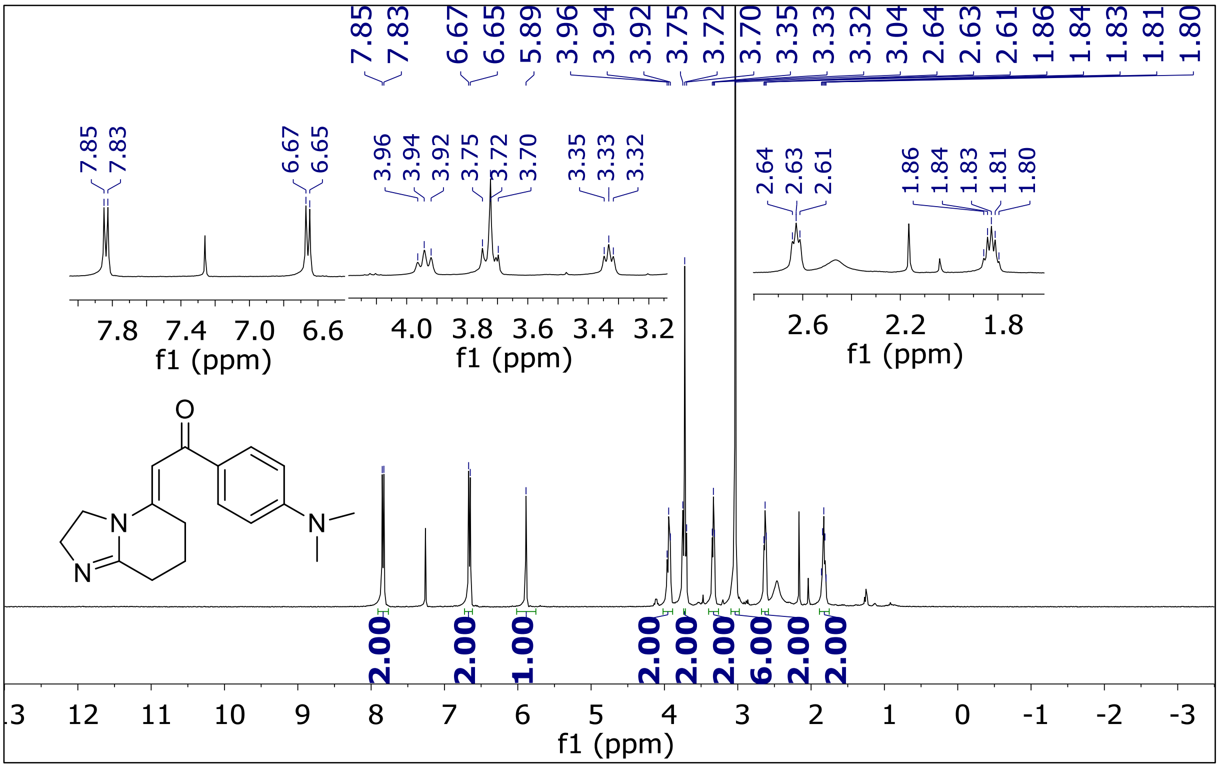


Figure S90. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **3h**.

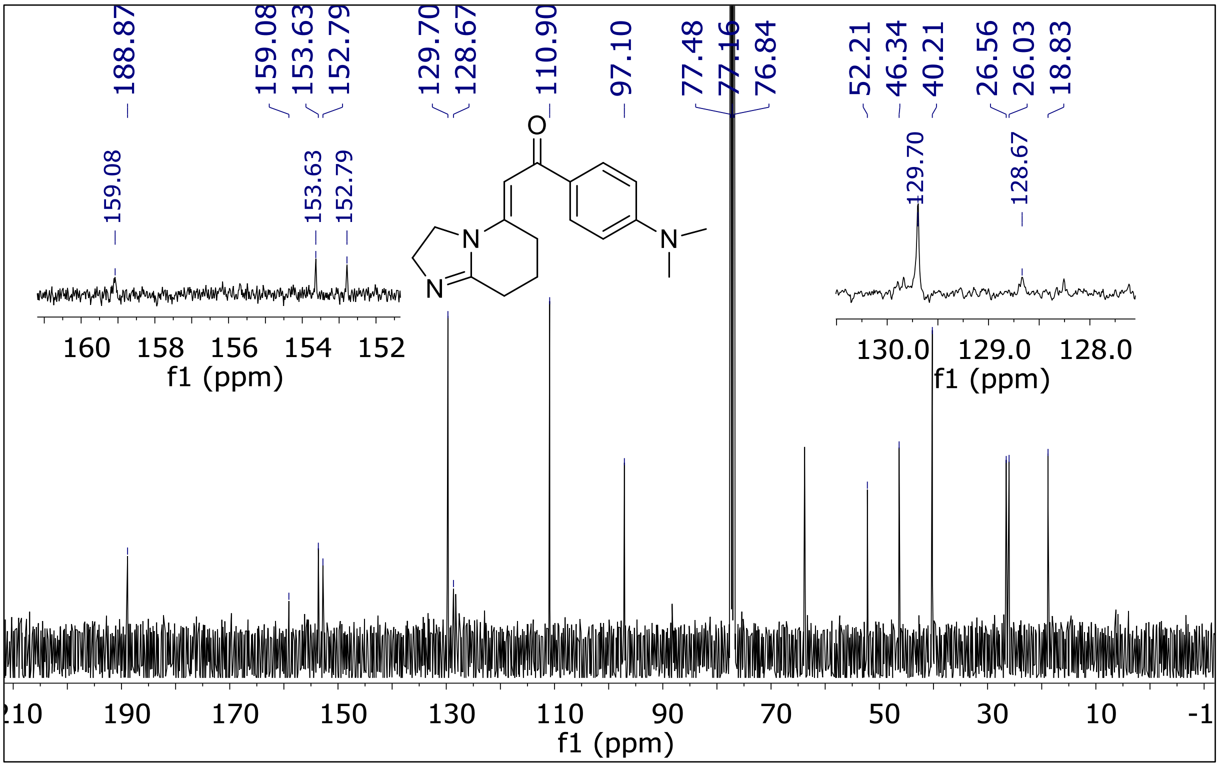


Figure S91. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **3h**.

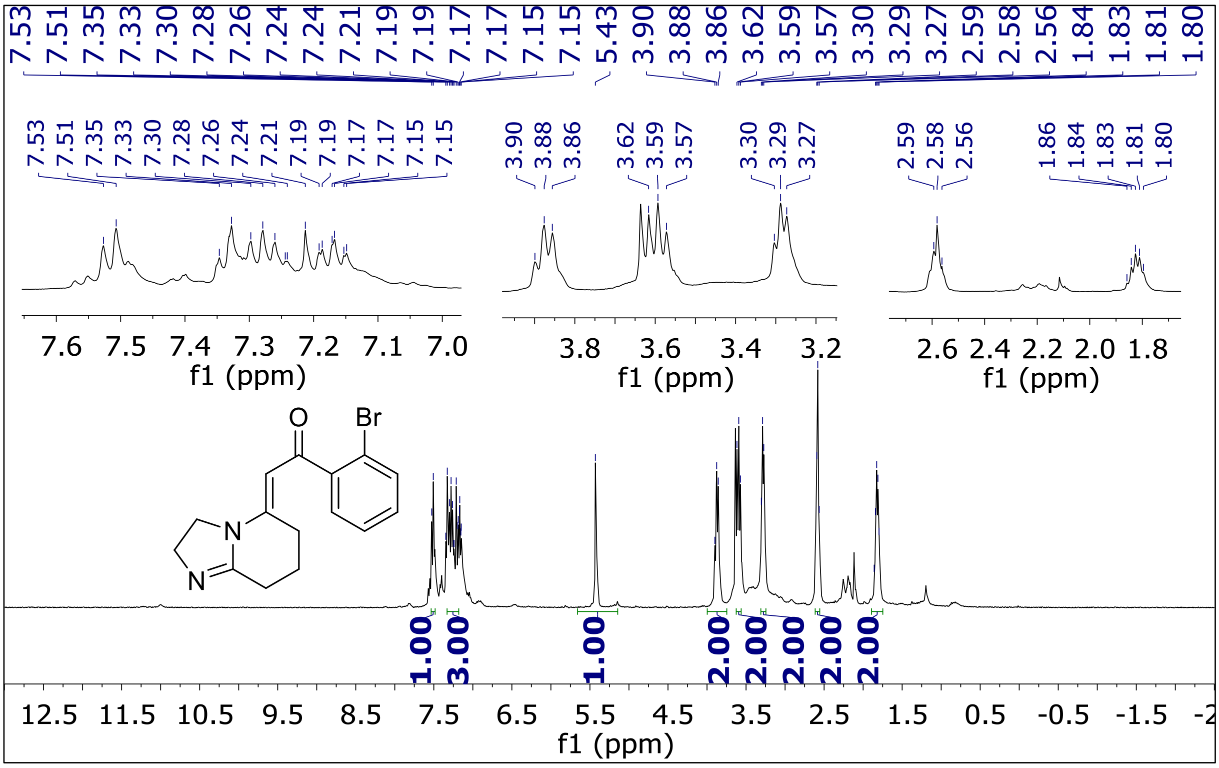


Figure S92. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**.

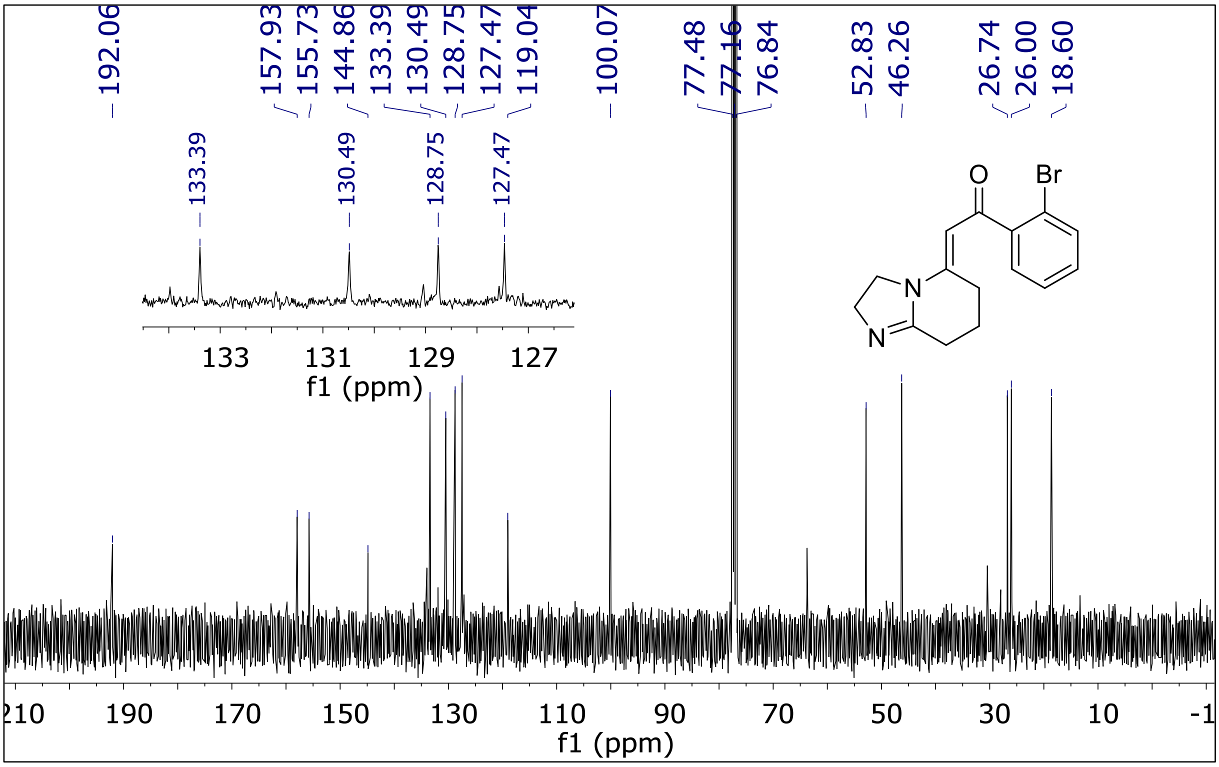


Figure S93. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3i**.

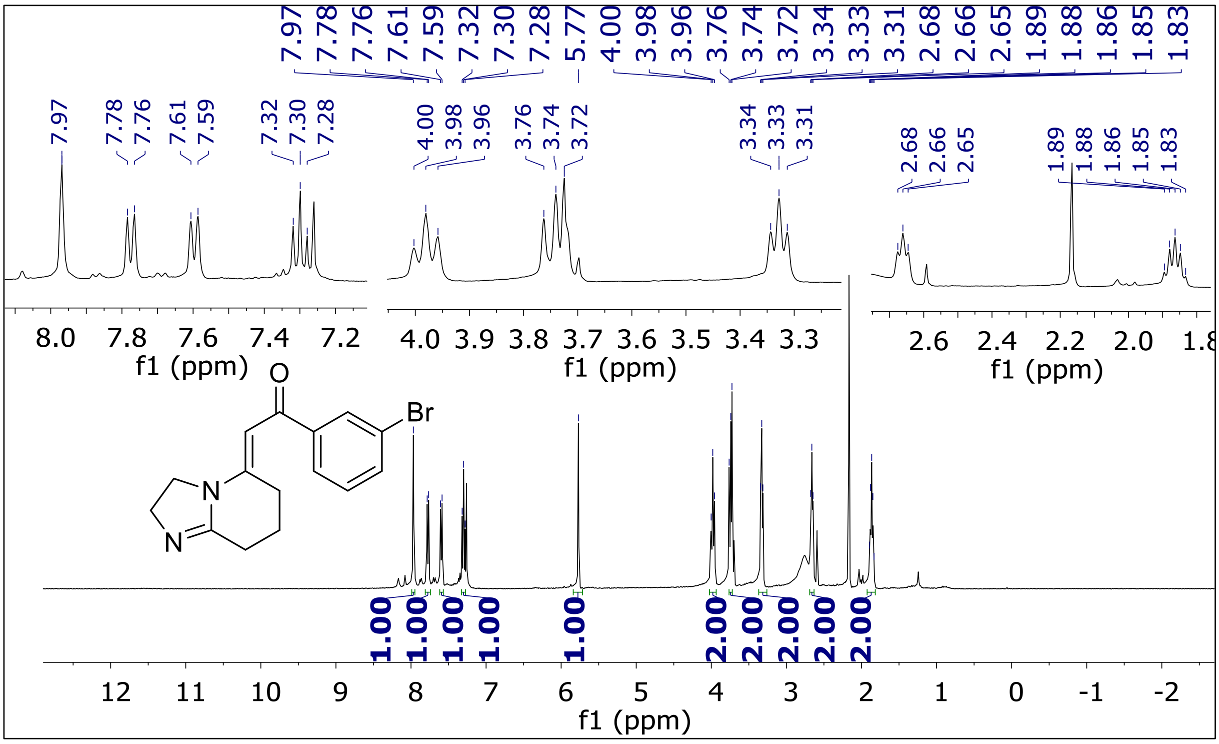


Figure S94. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**.

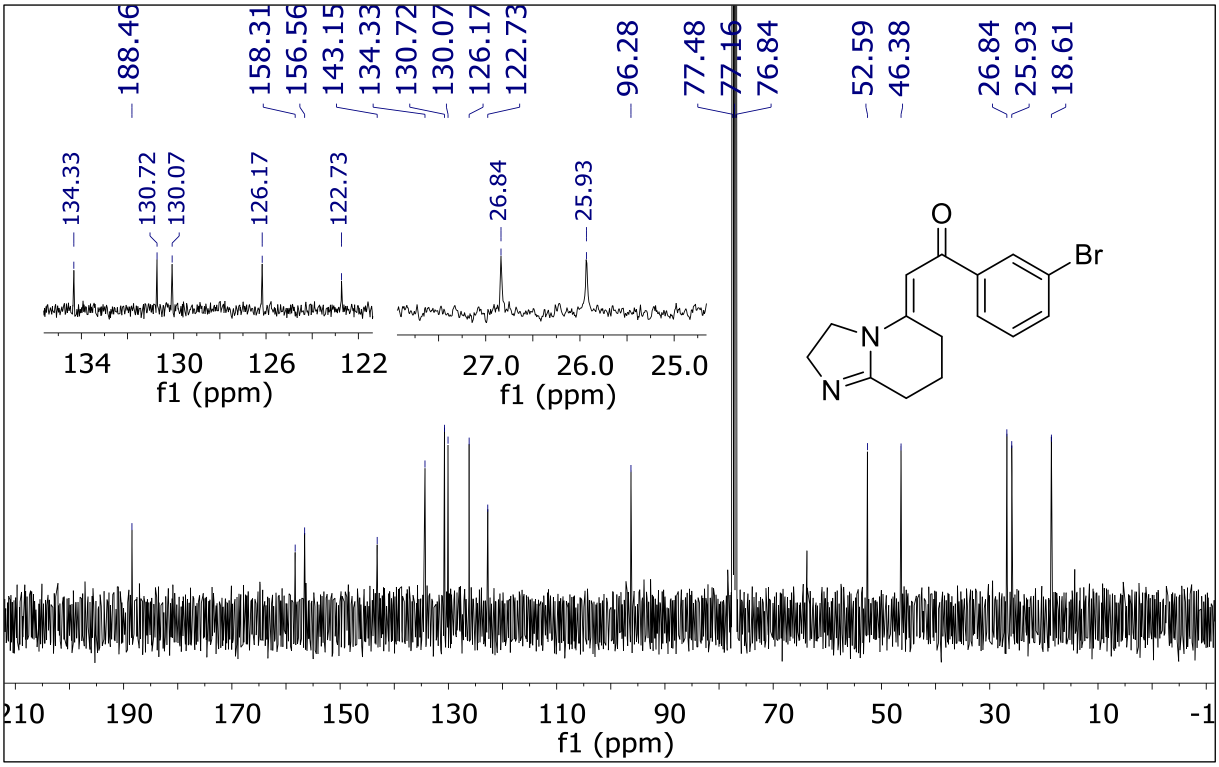


Figure S95. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3j**.

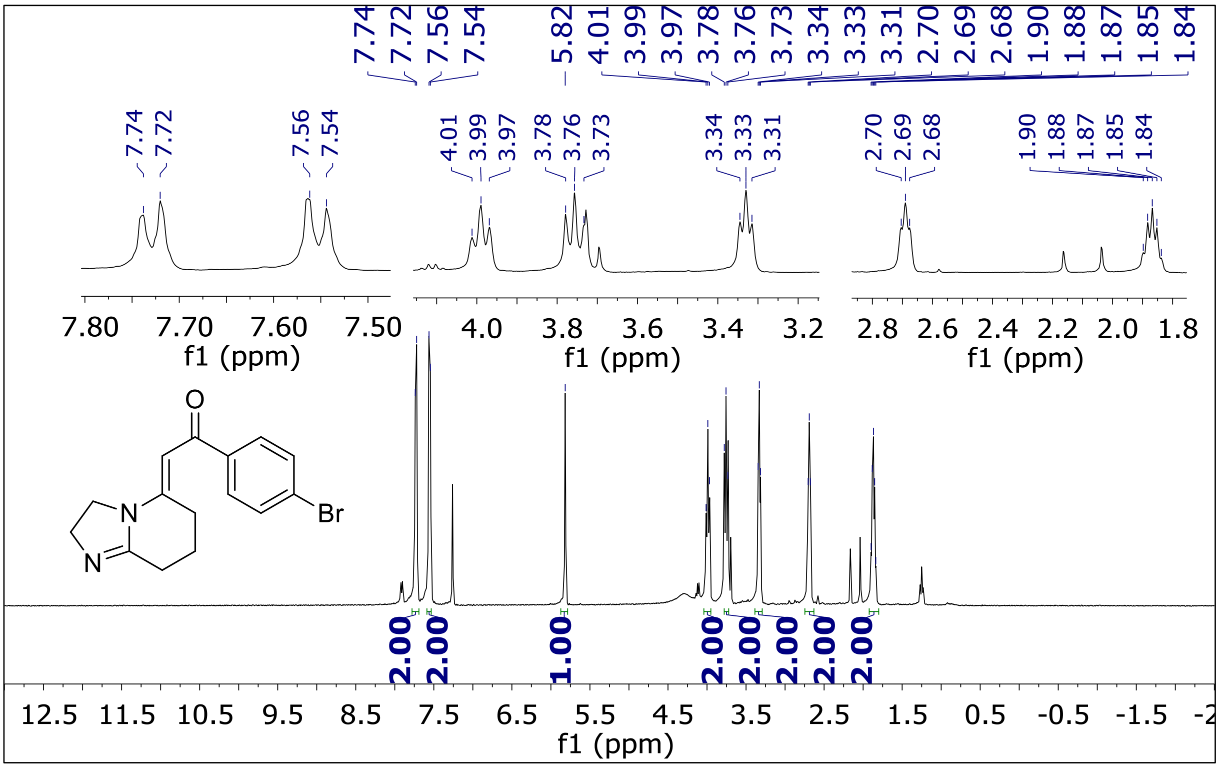


Figure S96. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **3k**.

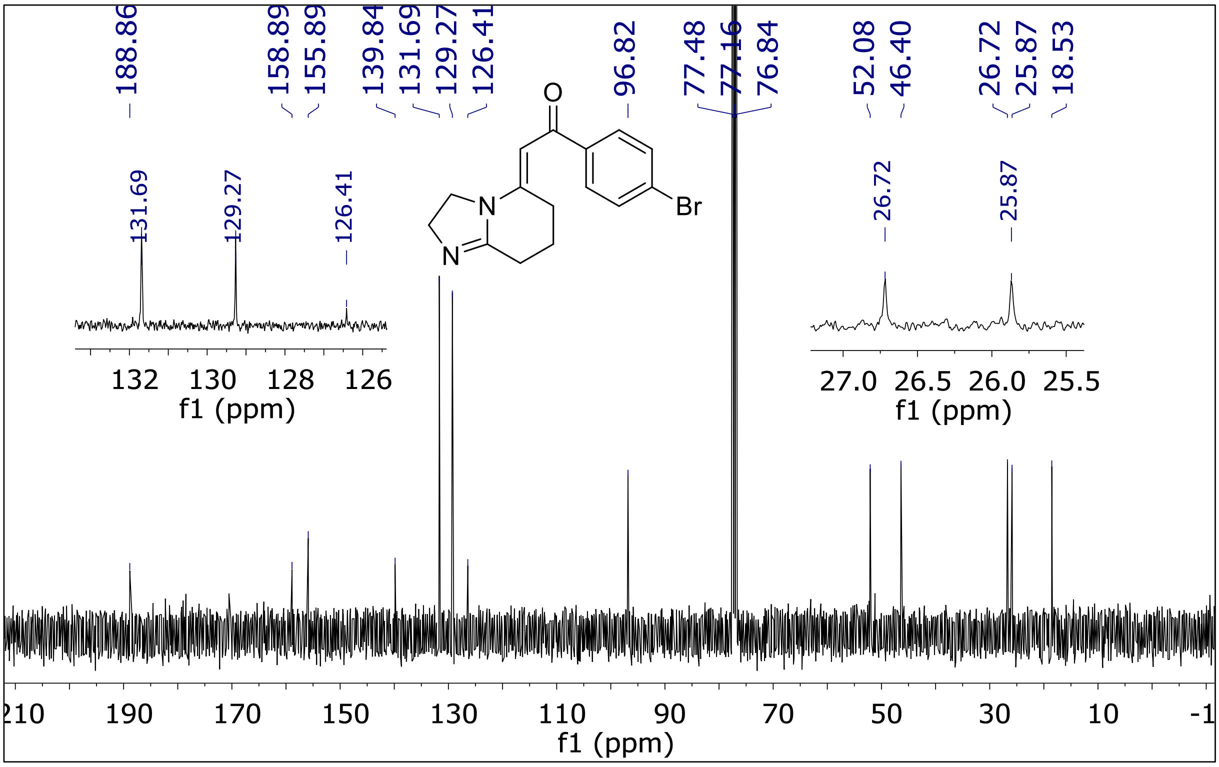


Figure S97. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **3k**.

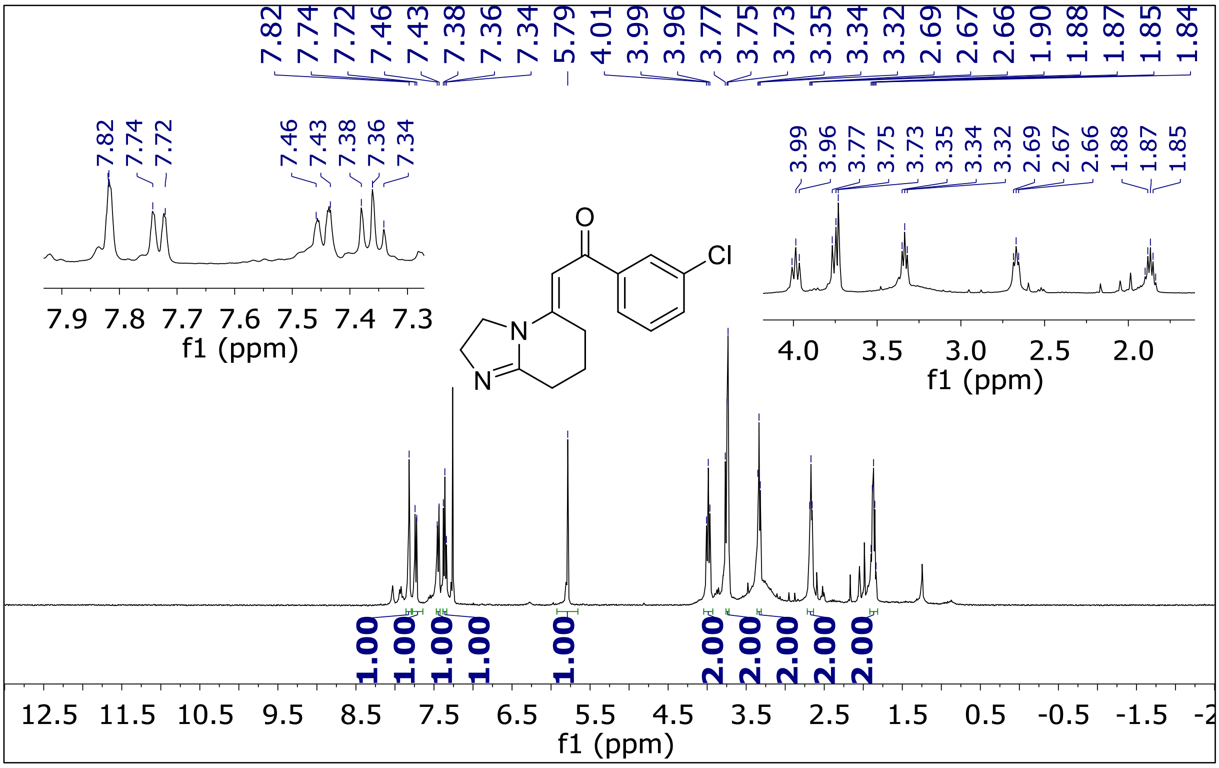


Figure S98. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**.

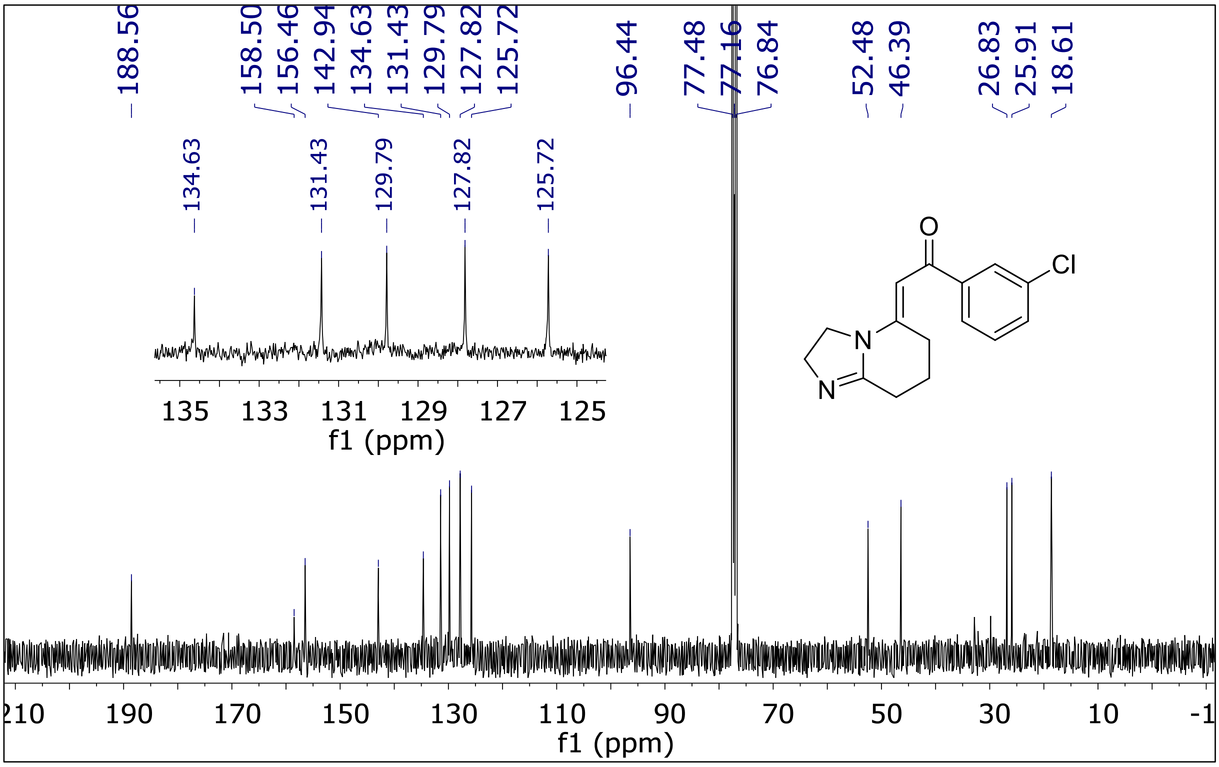


Figure S99. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3l**.

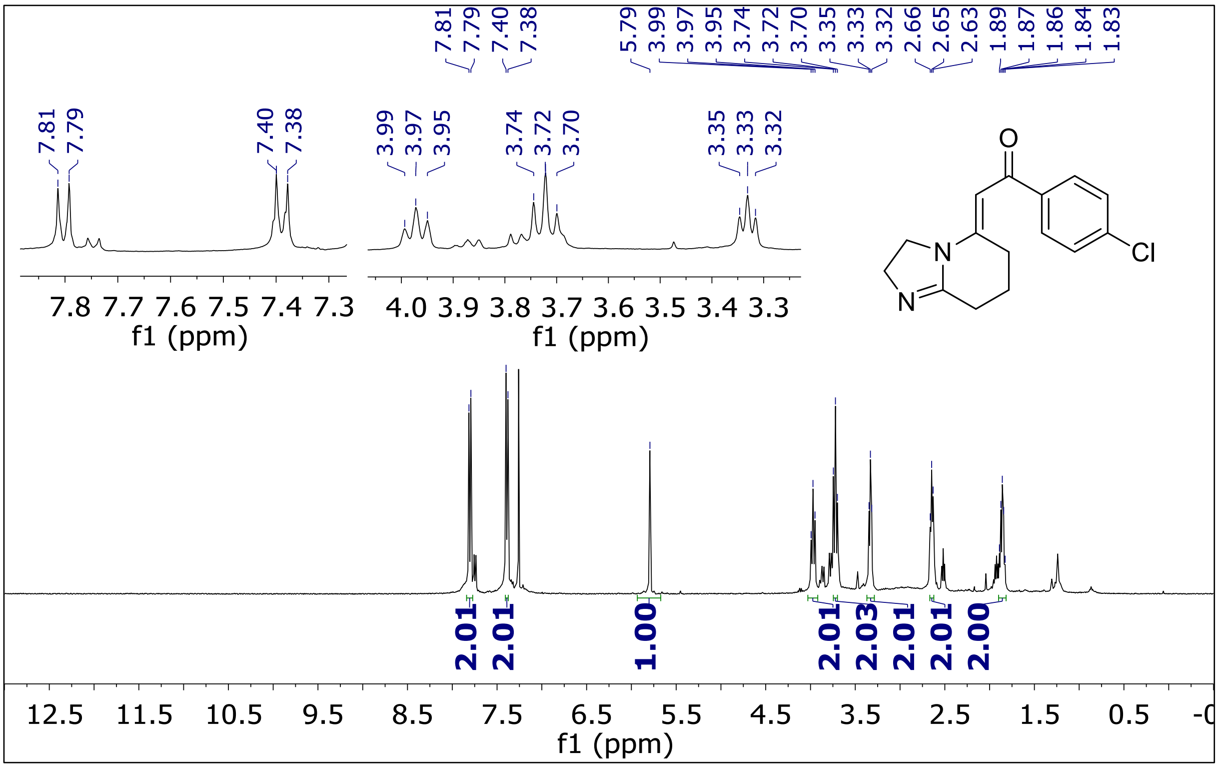


Figure S100. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**.

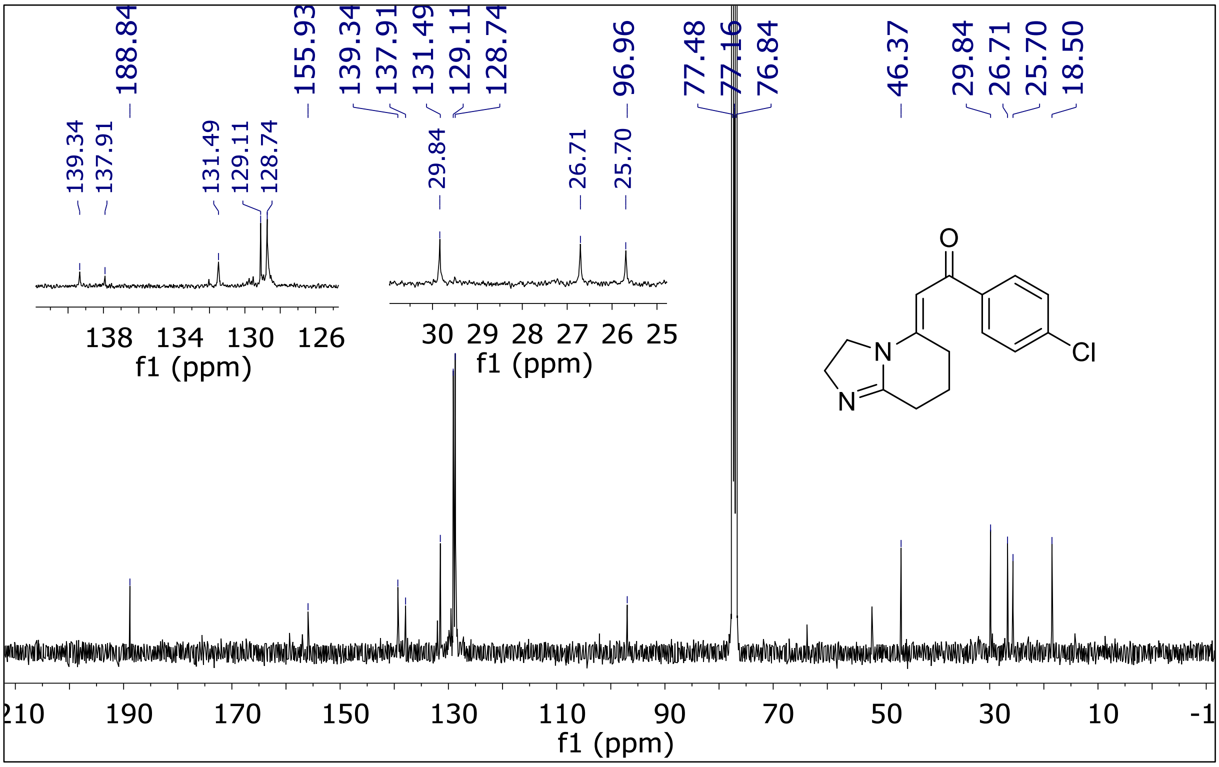


Figure S101. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3m**.

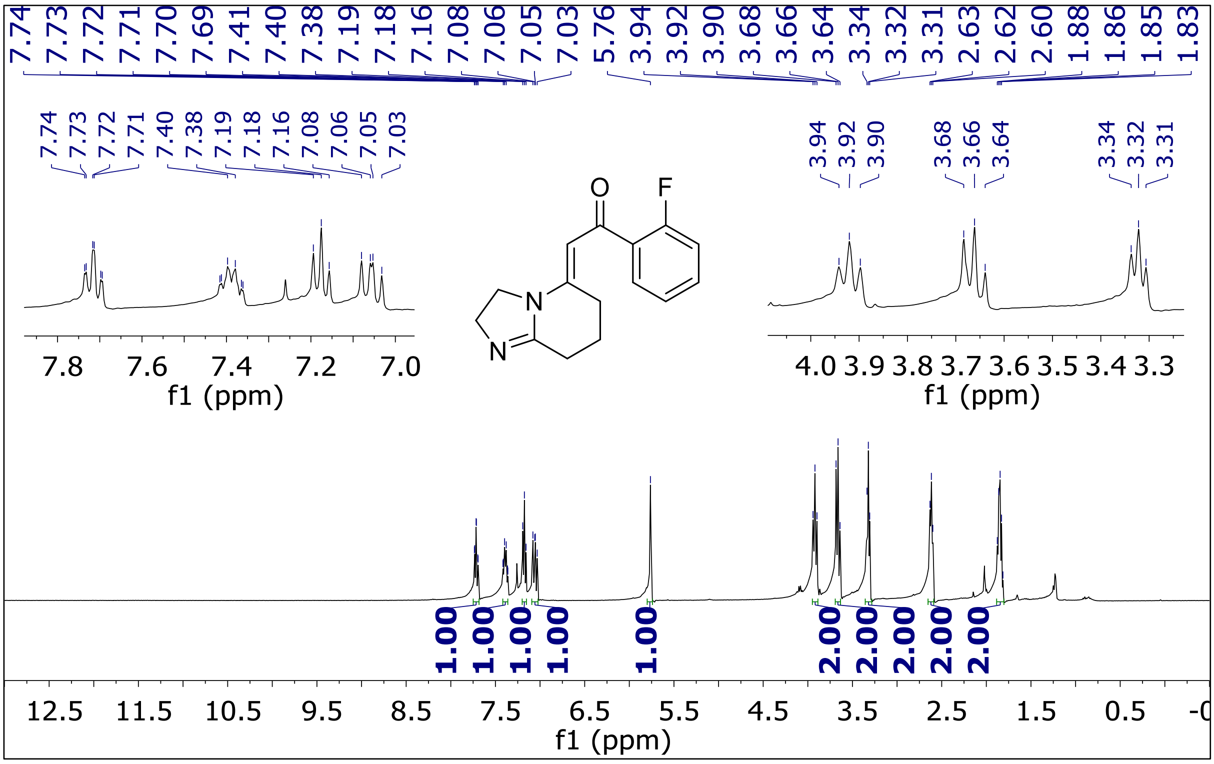


Figure S102. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**.

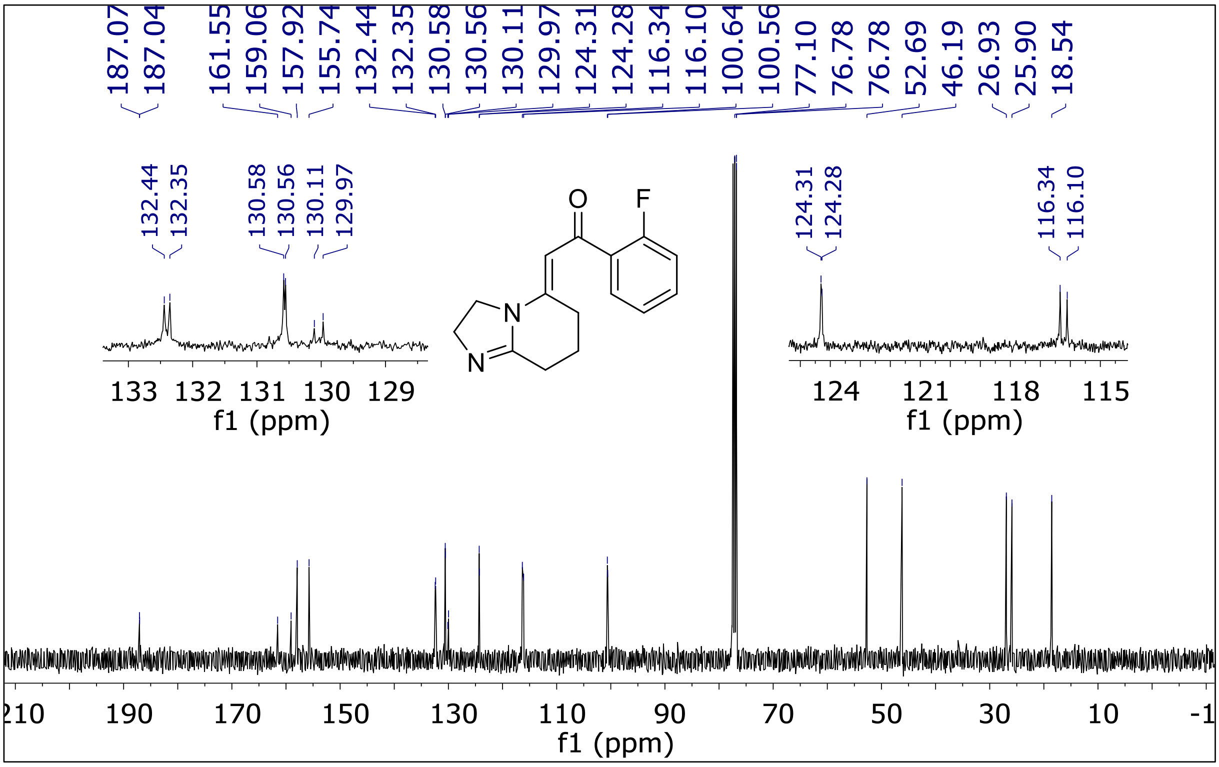


Figure S103. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3n**.

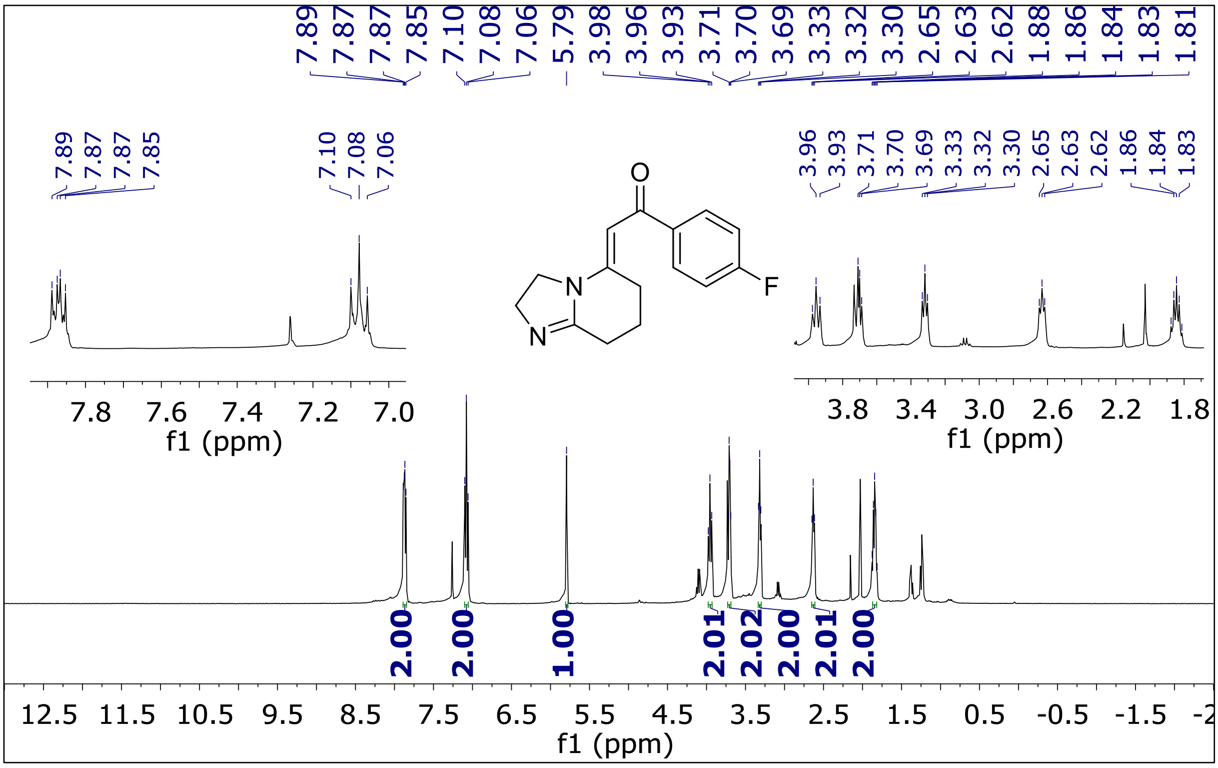


Figure S104. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**.

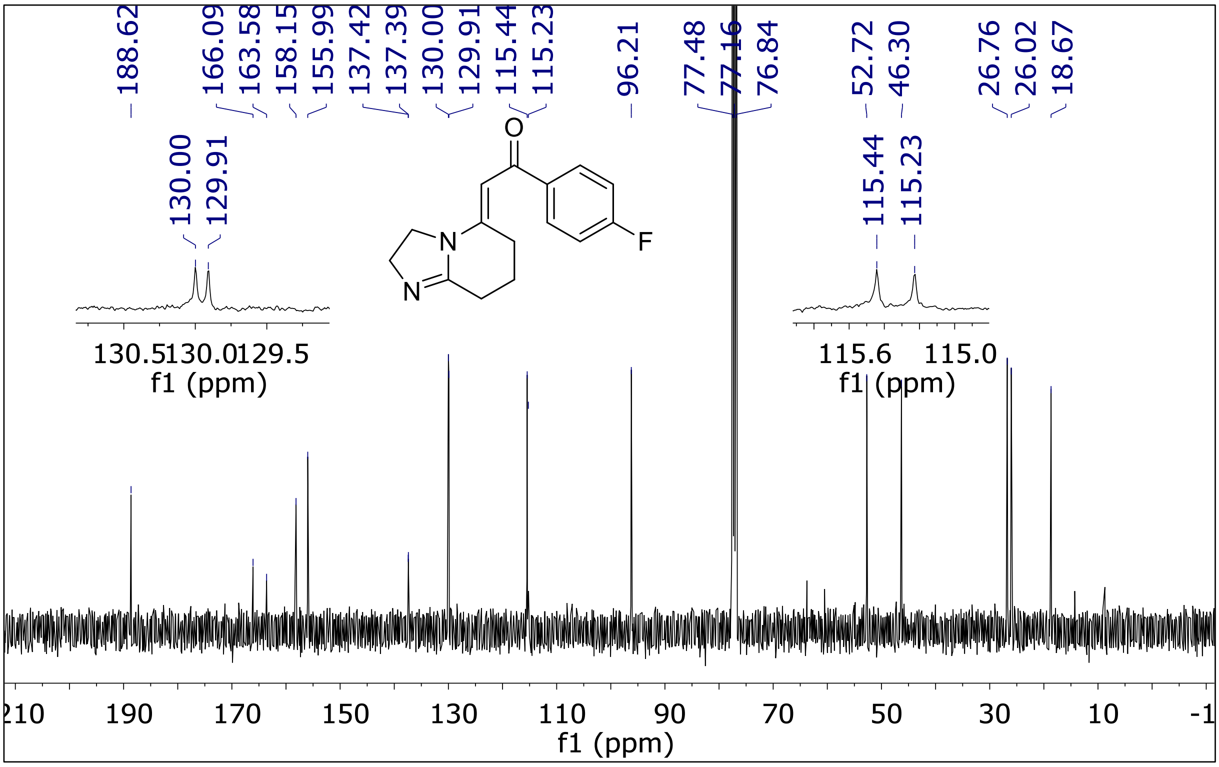


Figure S105. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **3o**.

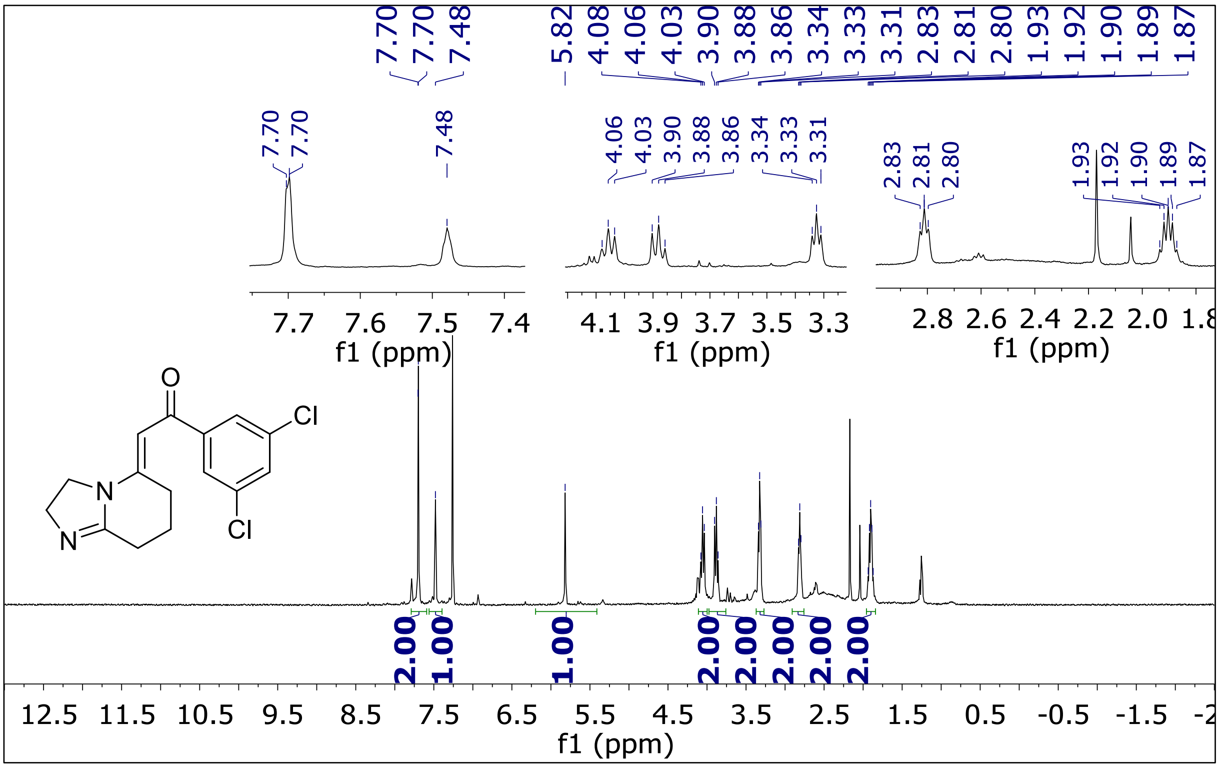


Figure S106. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **3p**.

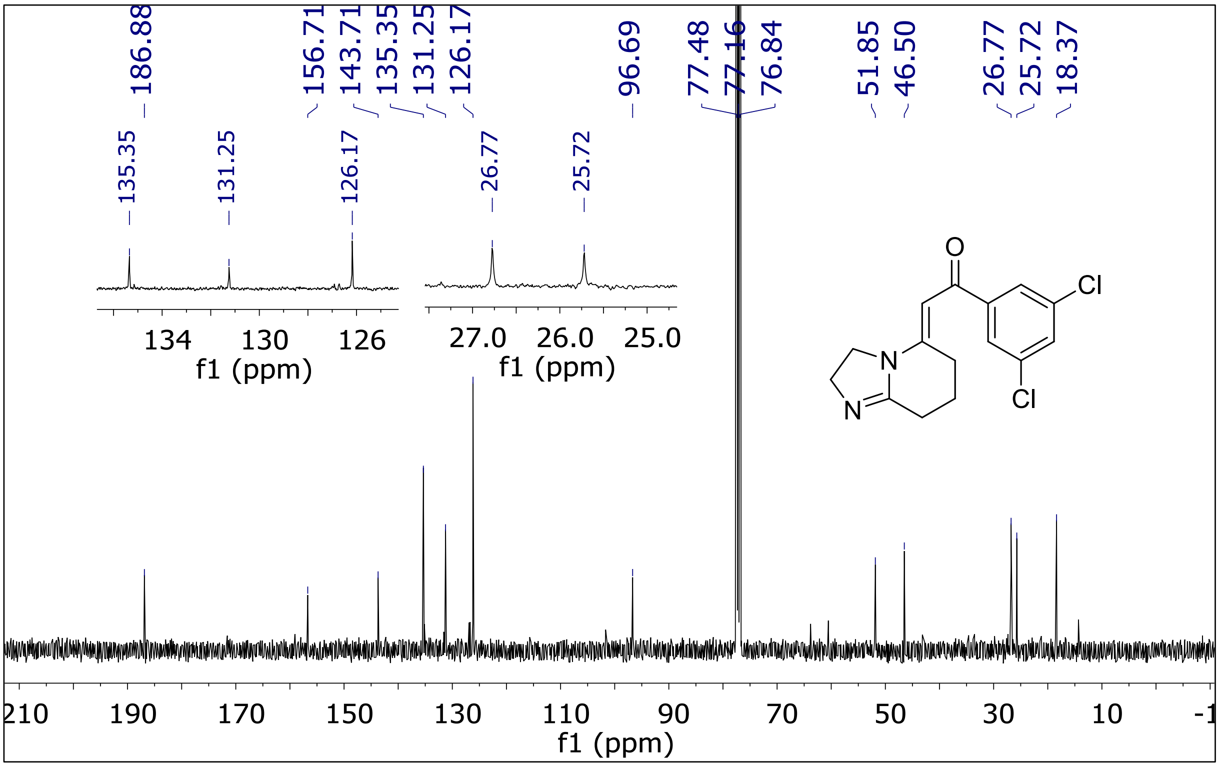


Figure S107. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **3p**.

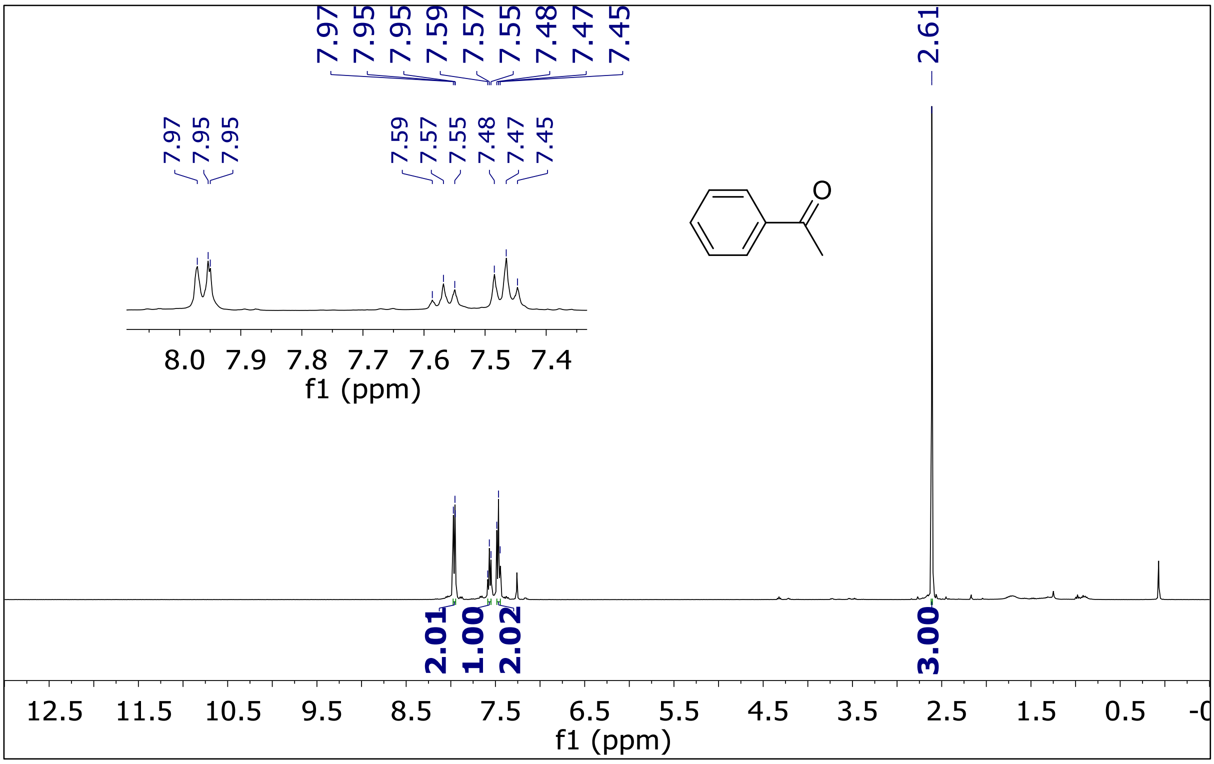


Figure S108. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **7a**.

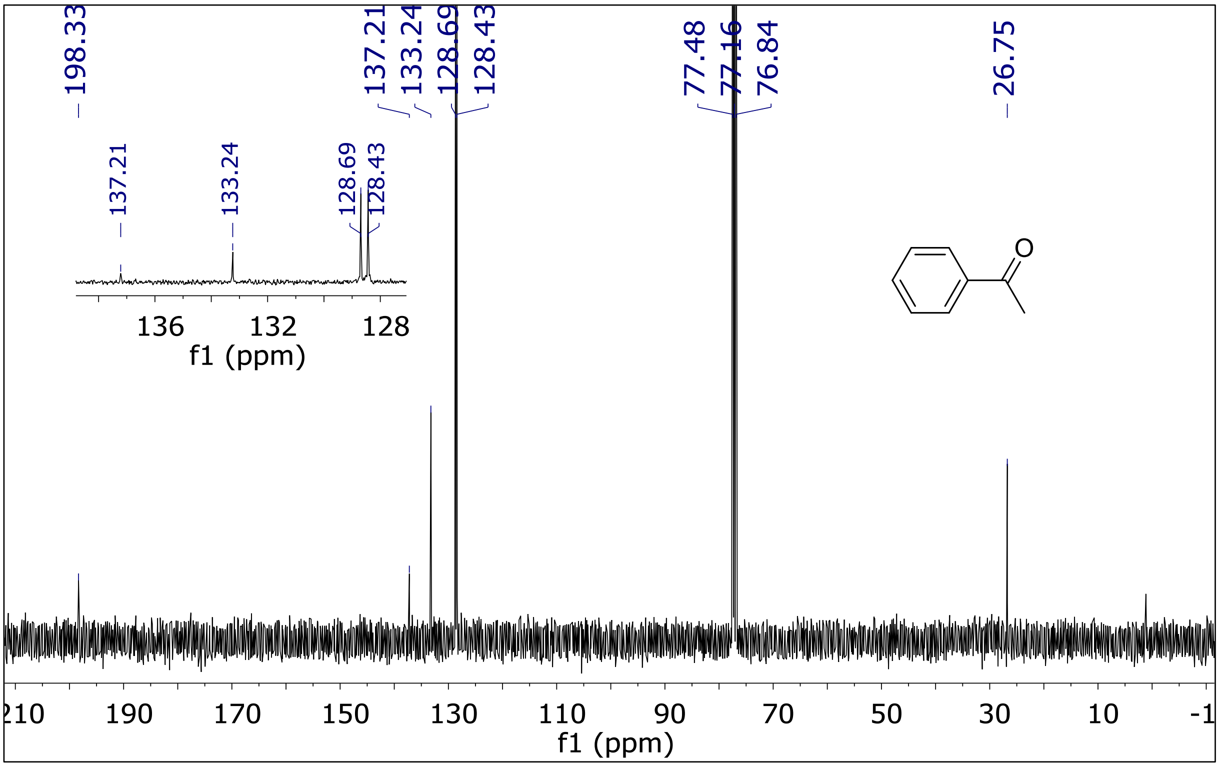


Figure S109. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **7a**.

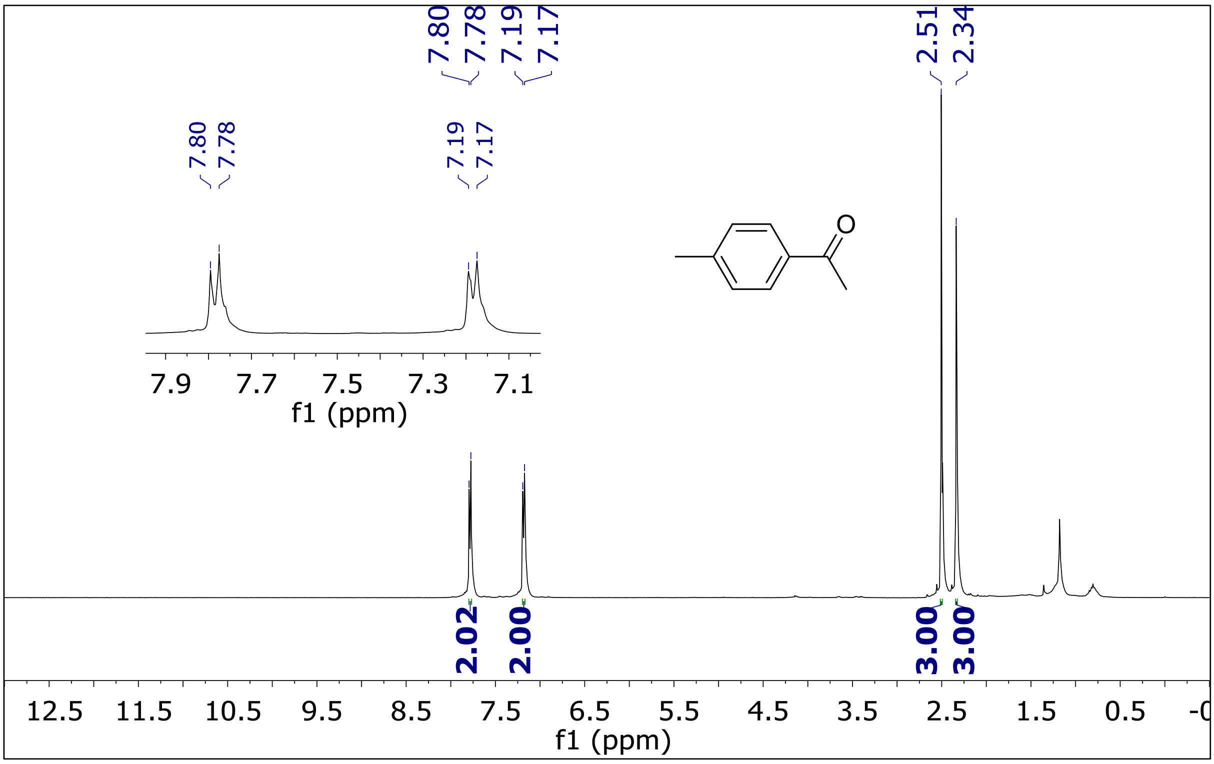


Figure S110. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **7b**.

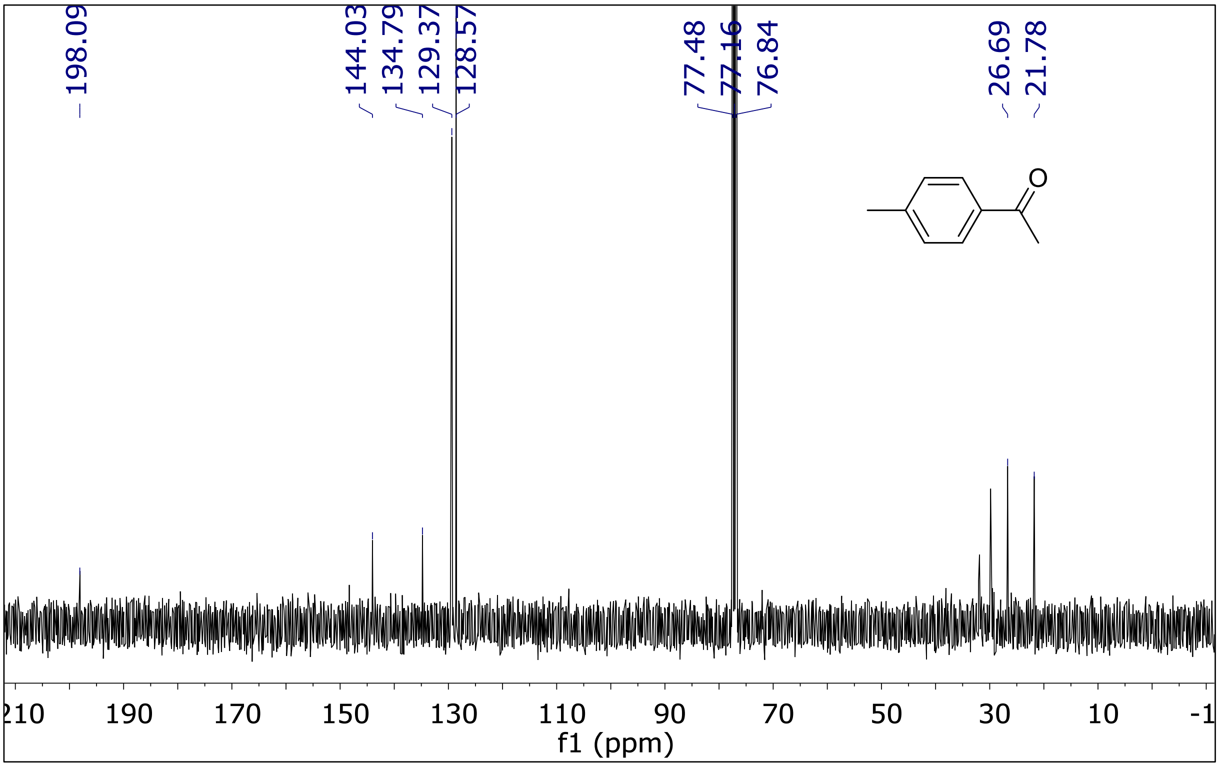


Figure S111. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **7b**.

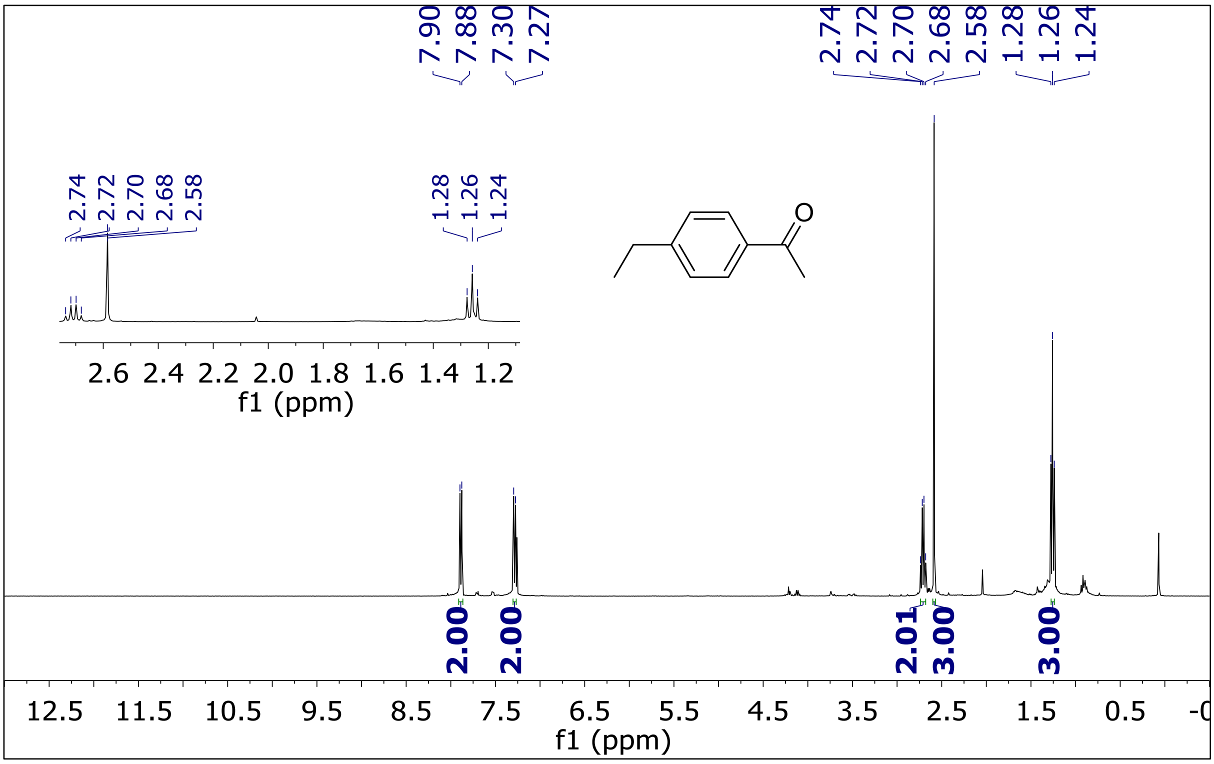


Figure S112. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **7c**.

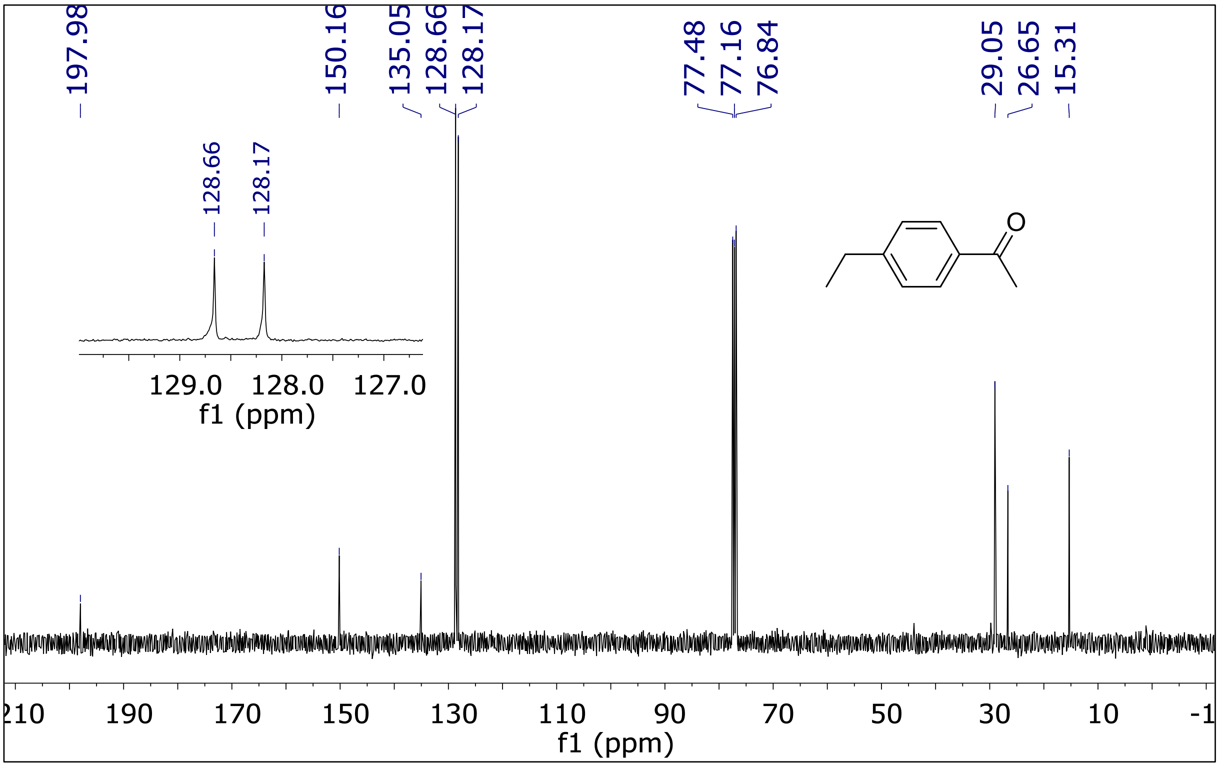


Figure S113. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **7c**.

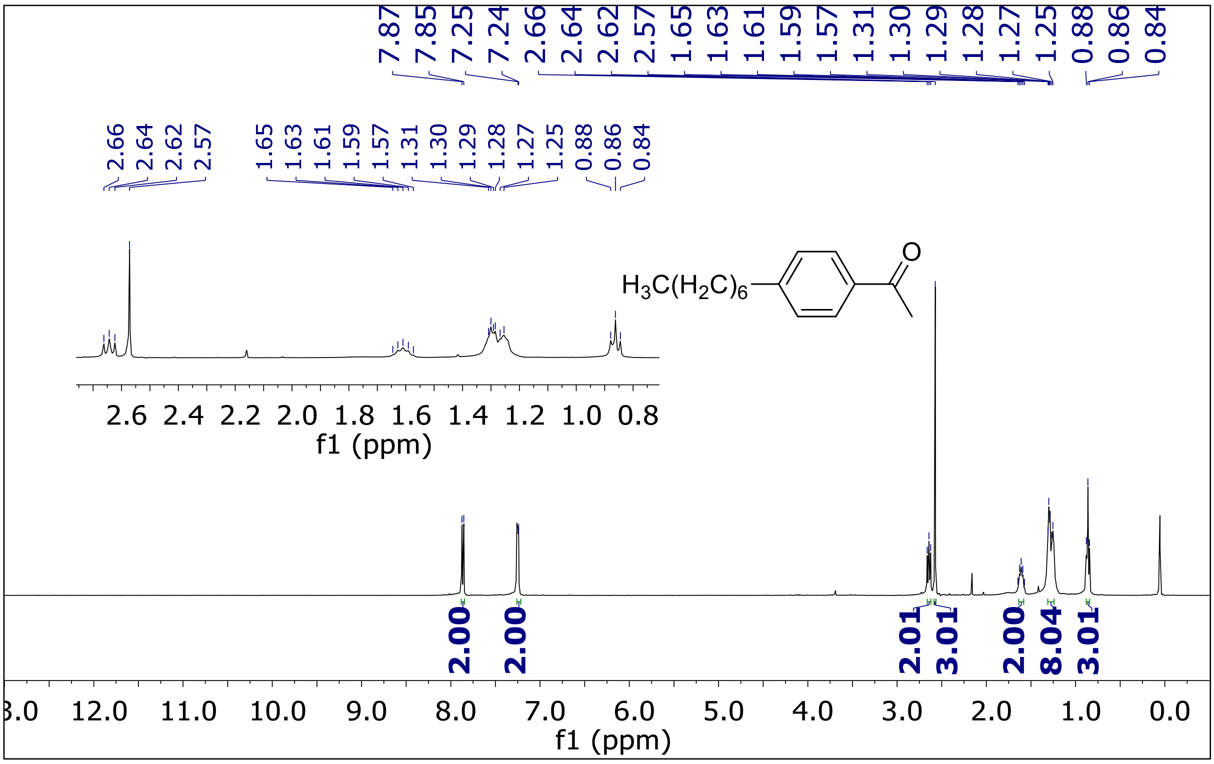


Figure S114. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7d**.

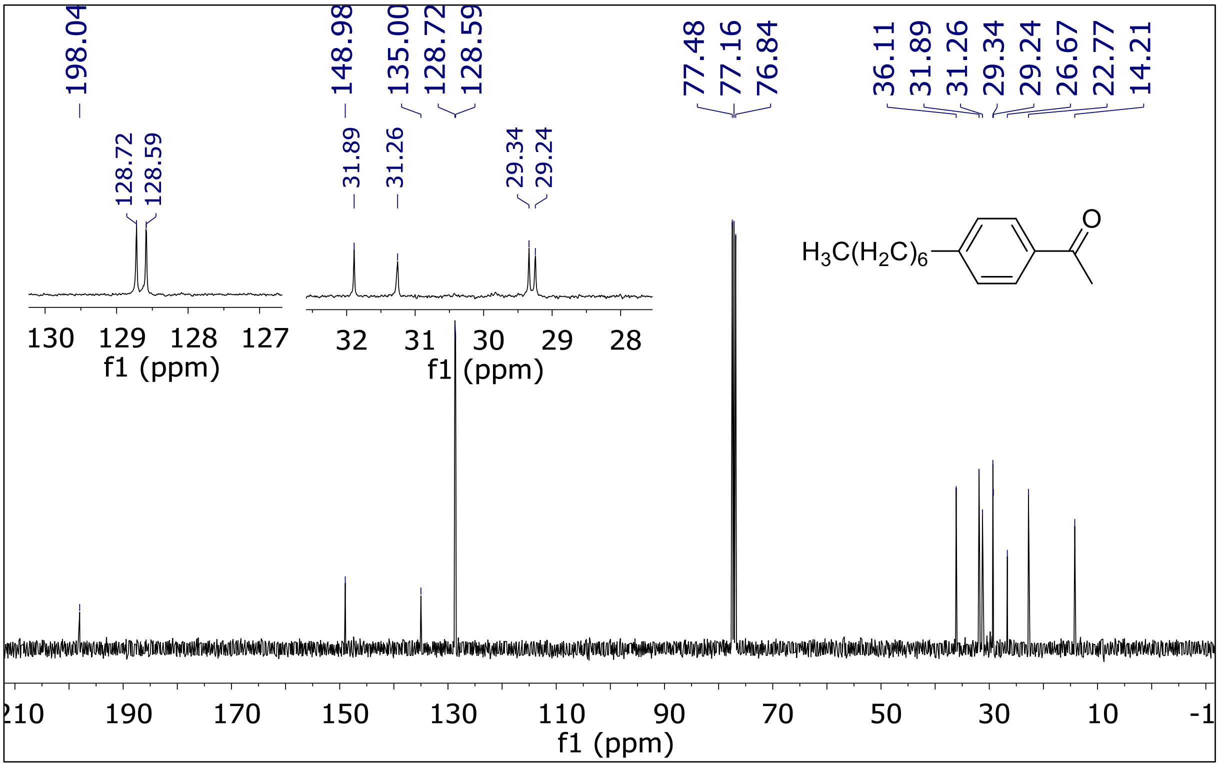


Figure S115. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of compound **7d**.

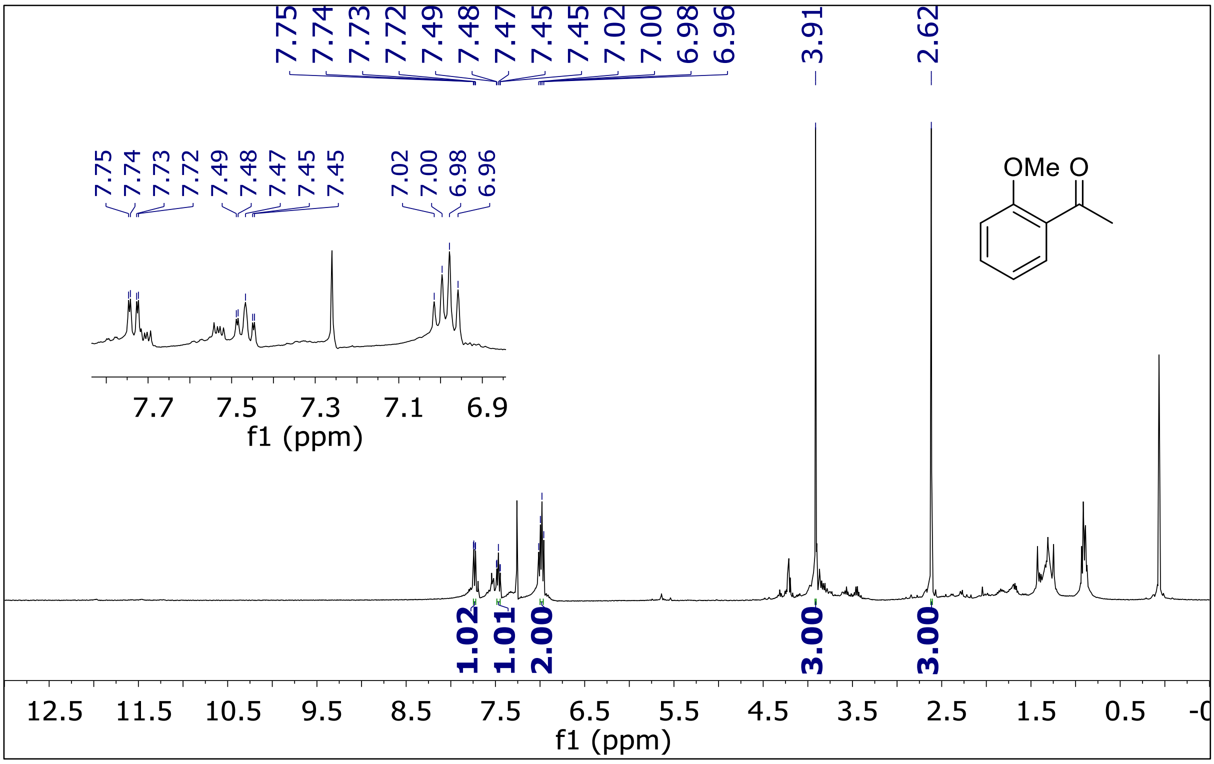


Figure S116. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **7e**.

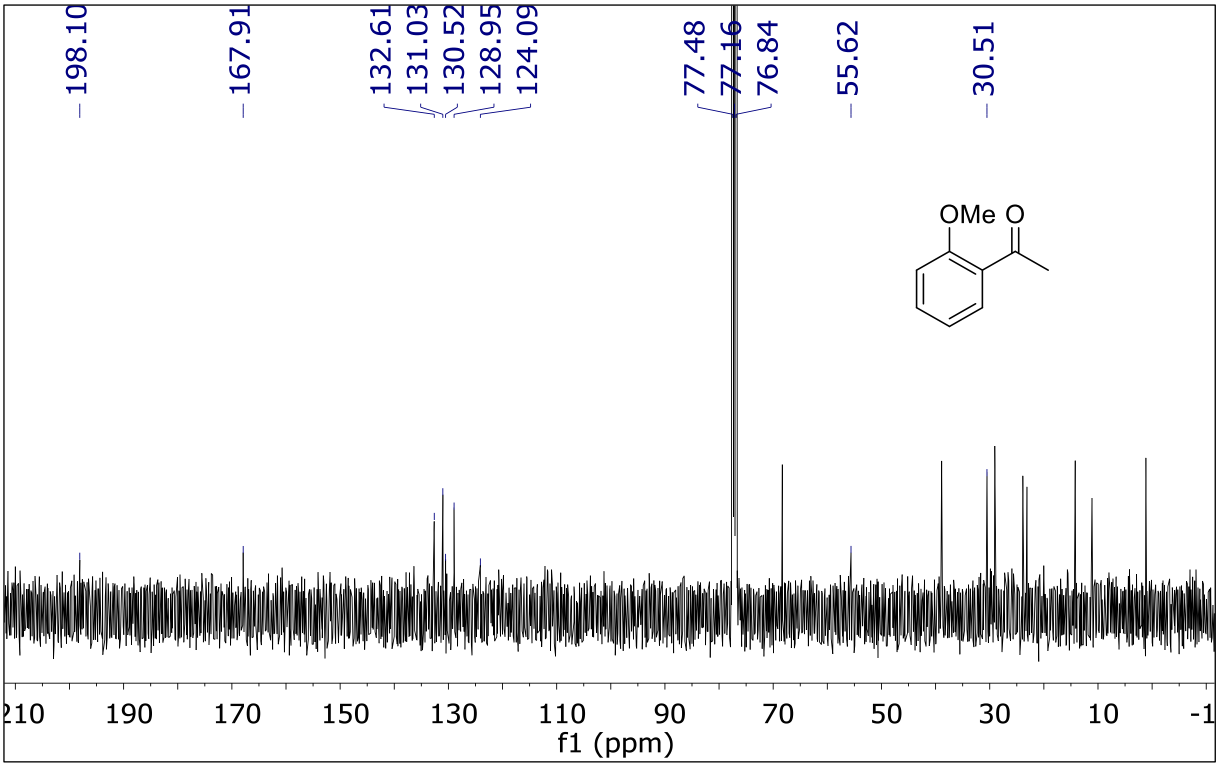


Figure S117. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **7e**.

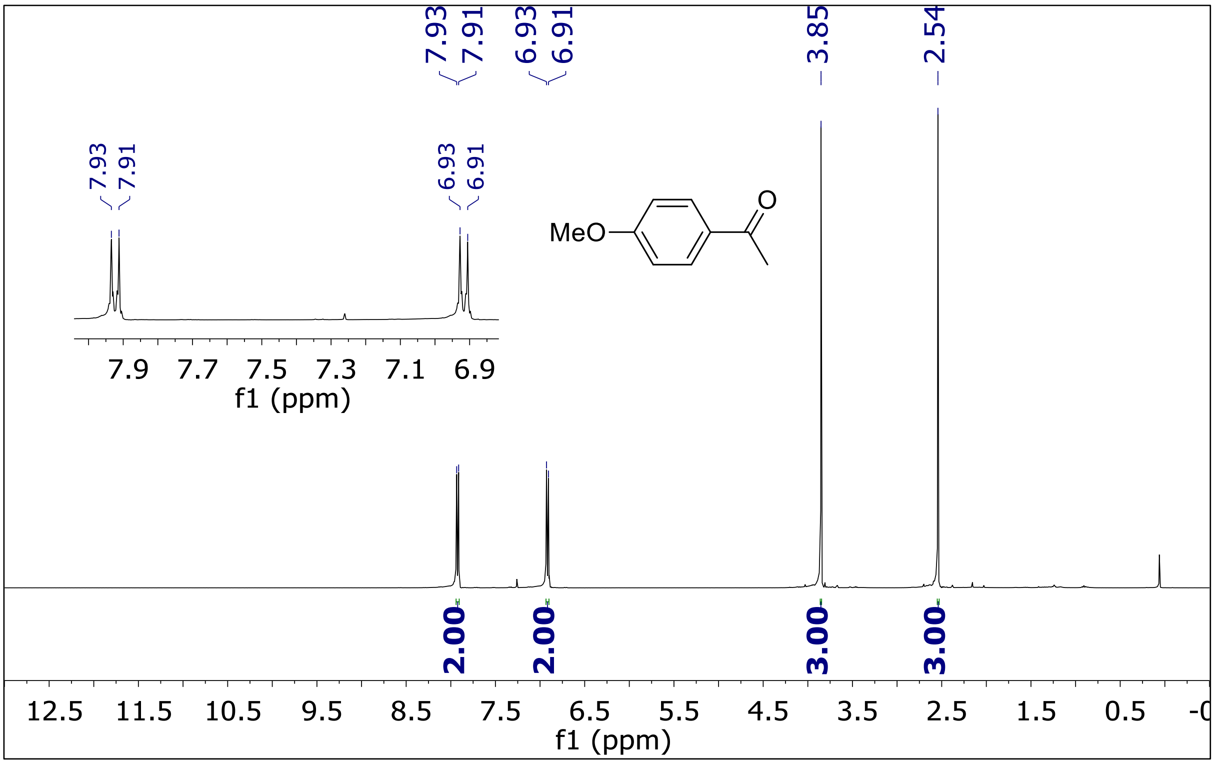


Figure S118. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7f**.

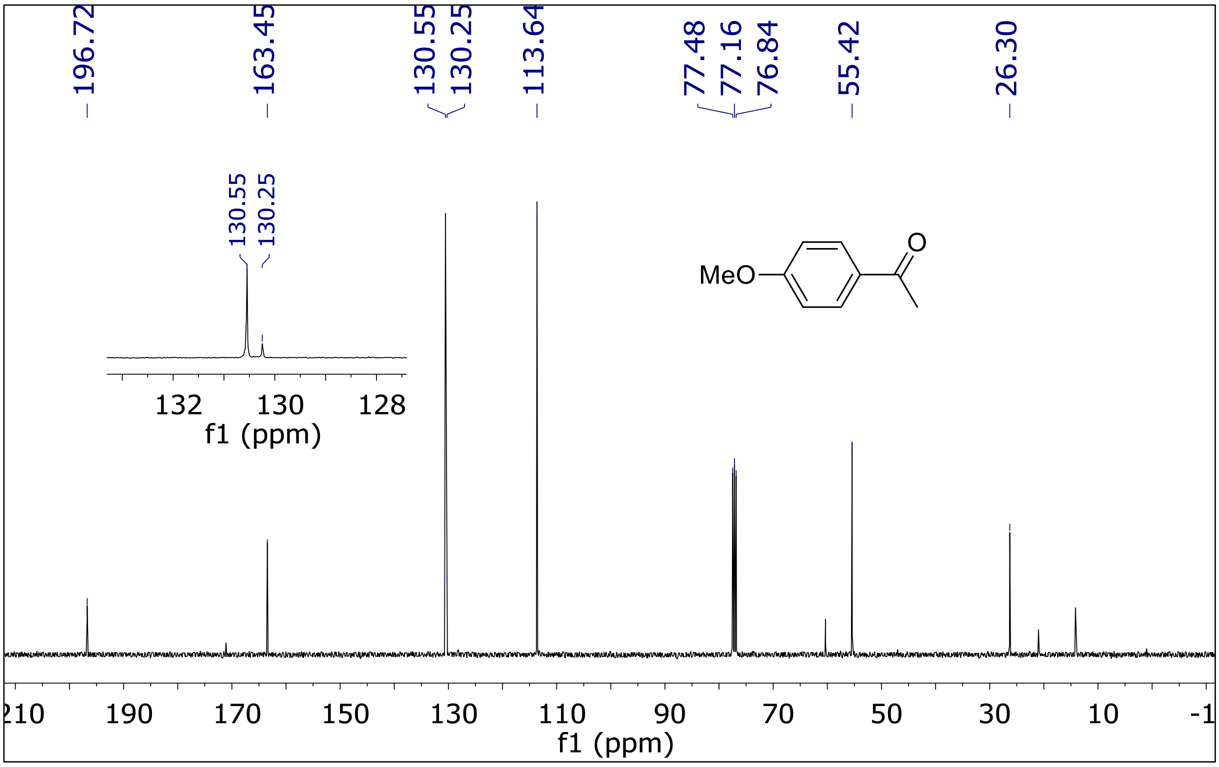


Figure S119. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **7f**.

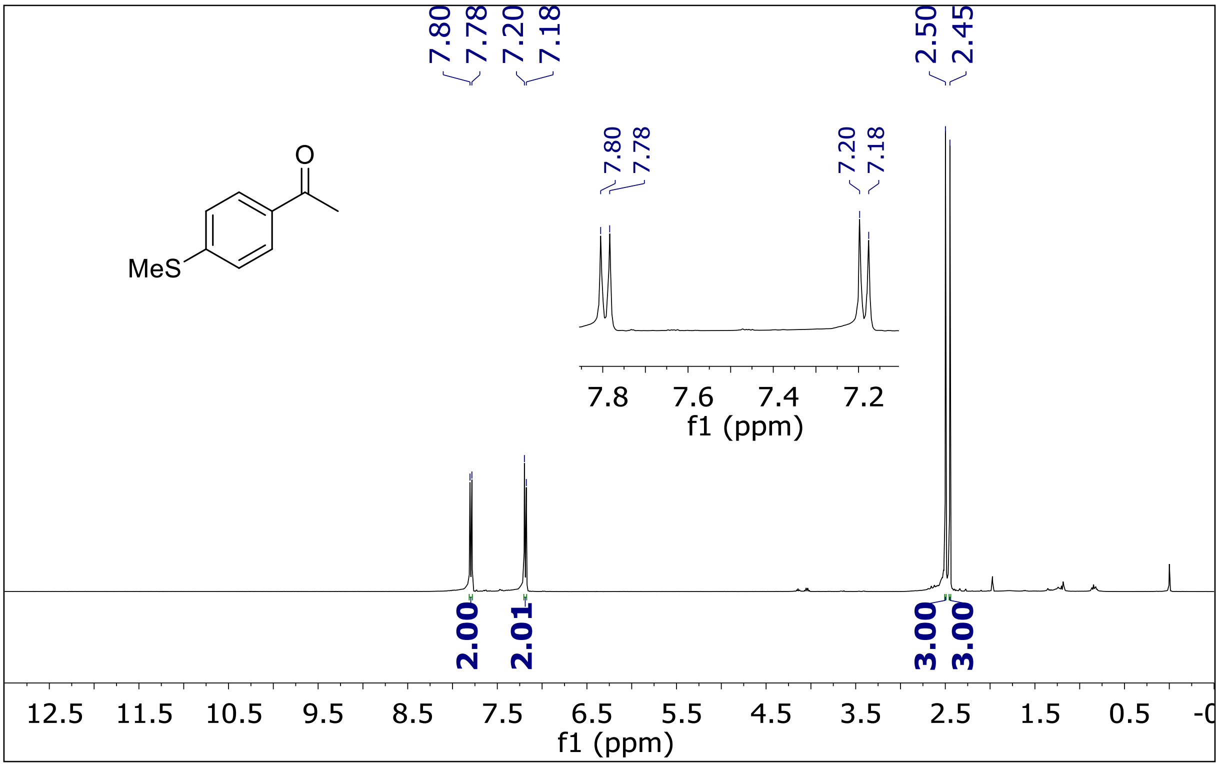


Figure S120. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **7g**.

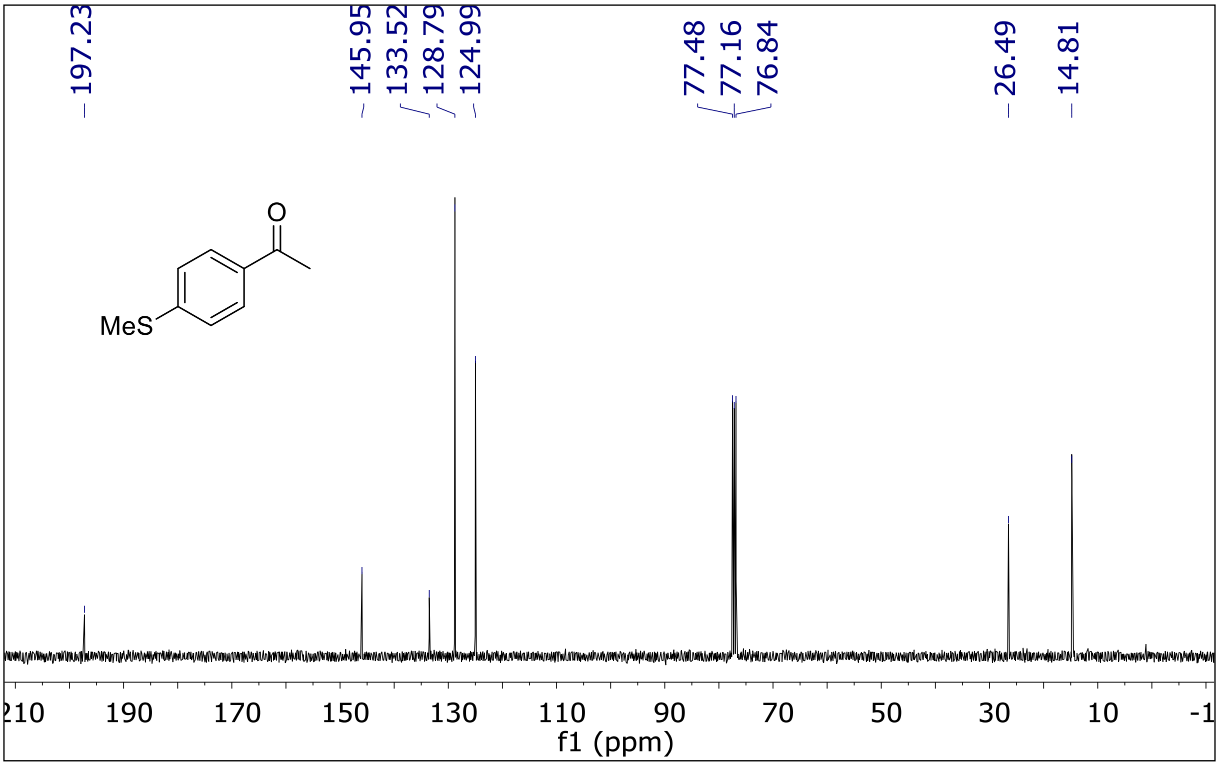


Figure S121. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **7g**.

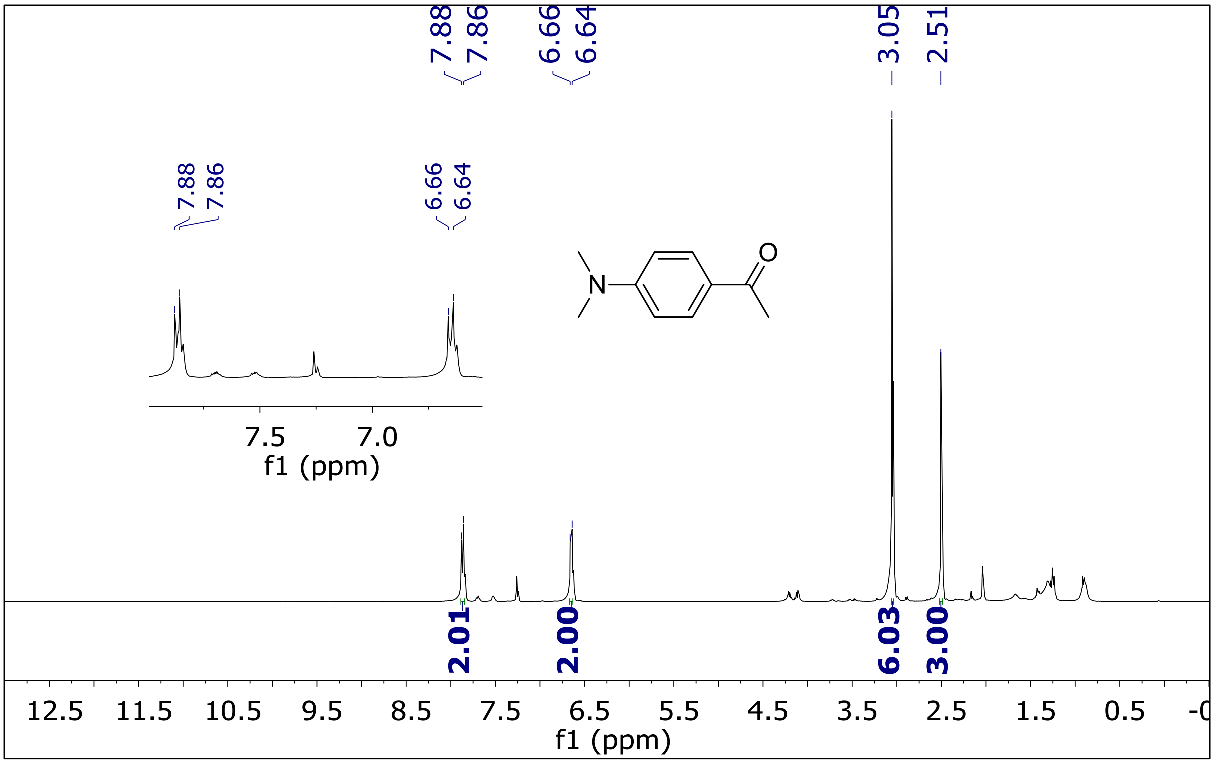


Figure S122. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7h**.

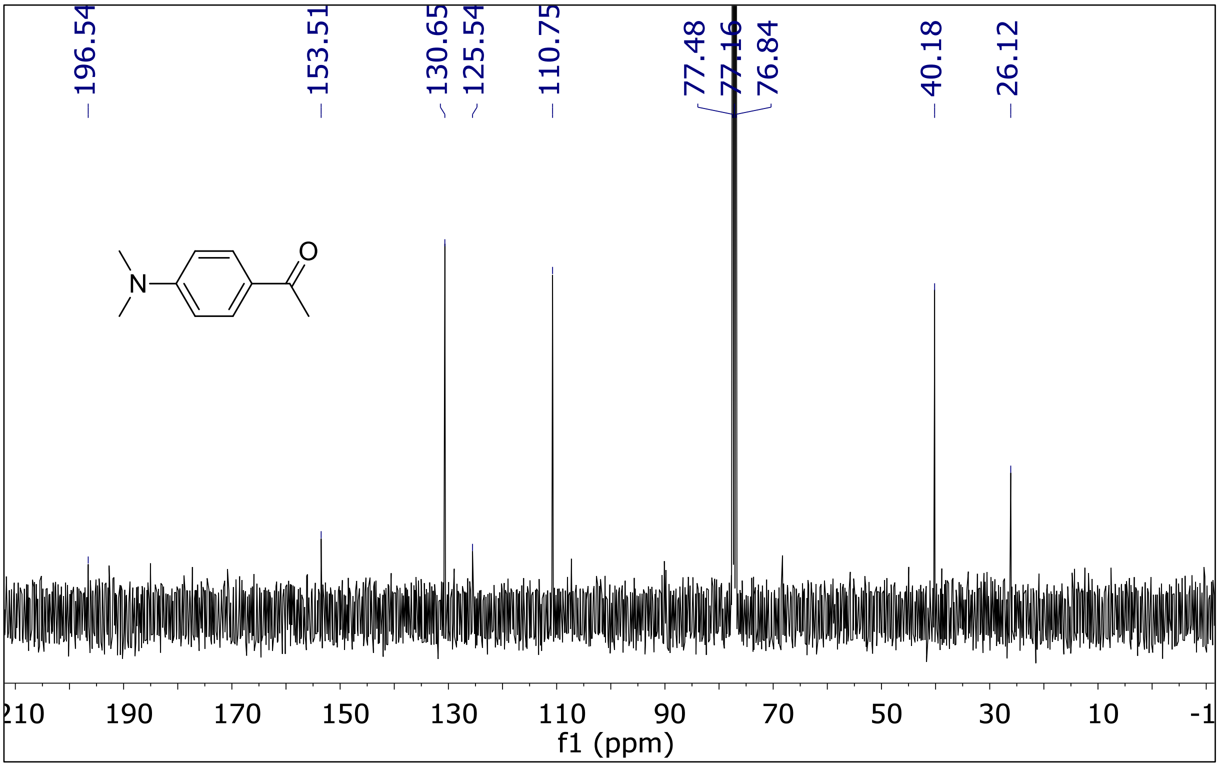


Figure S123. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **7h**.

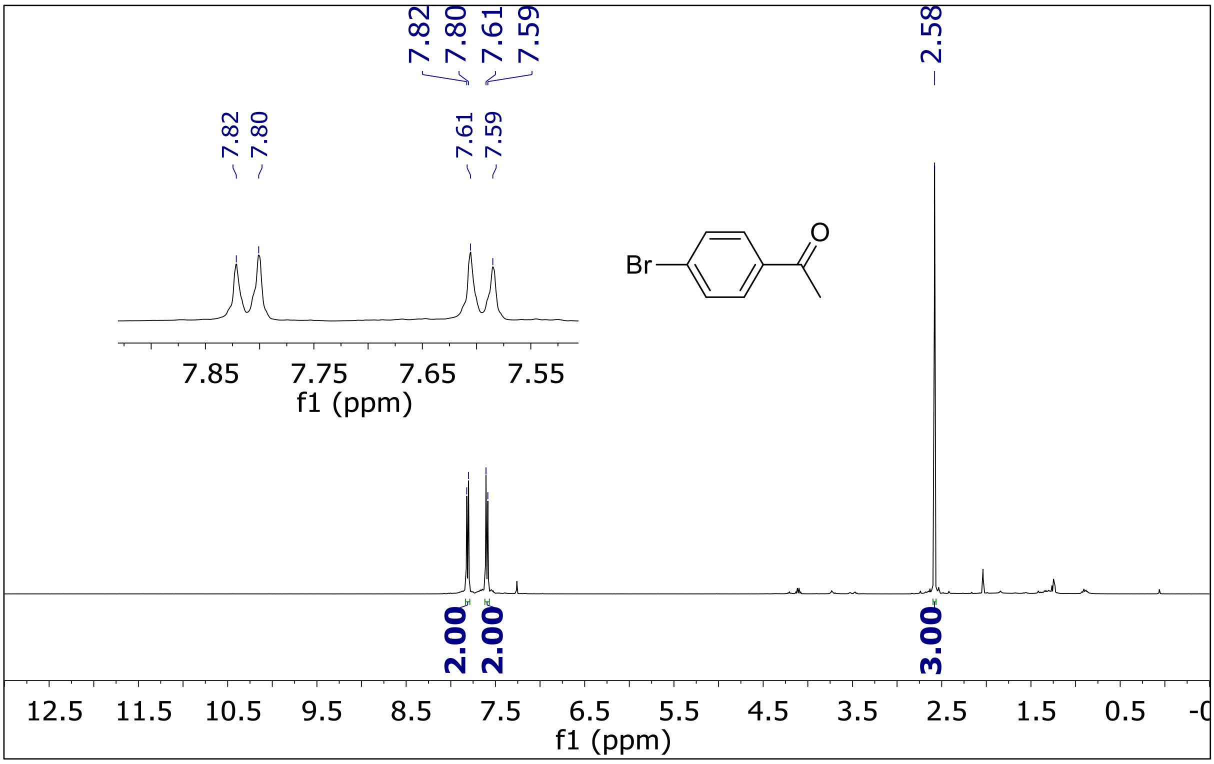


Figure S124. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **7k**.

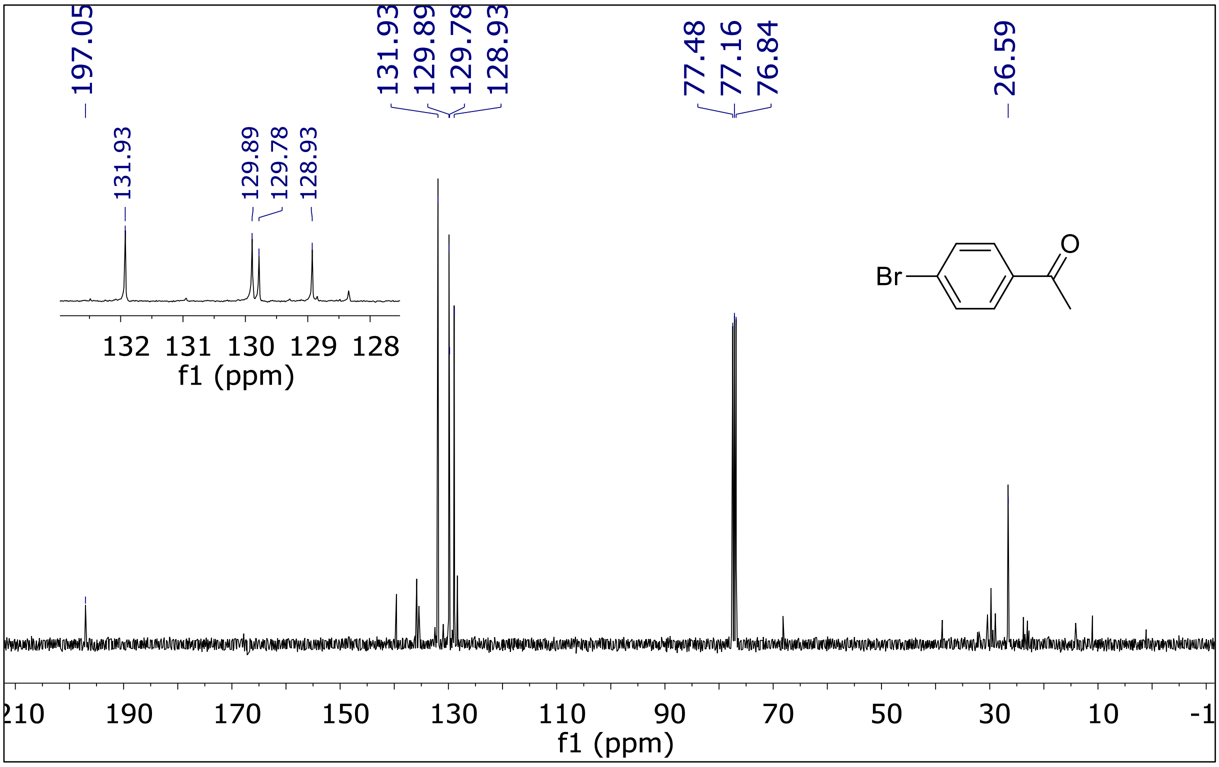


Figure S125. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **7k**.

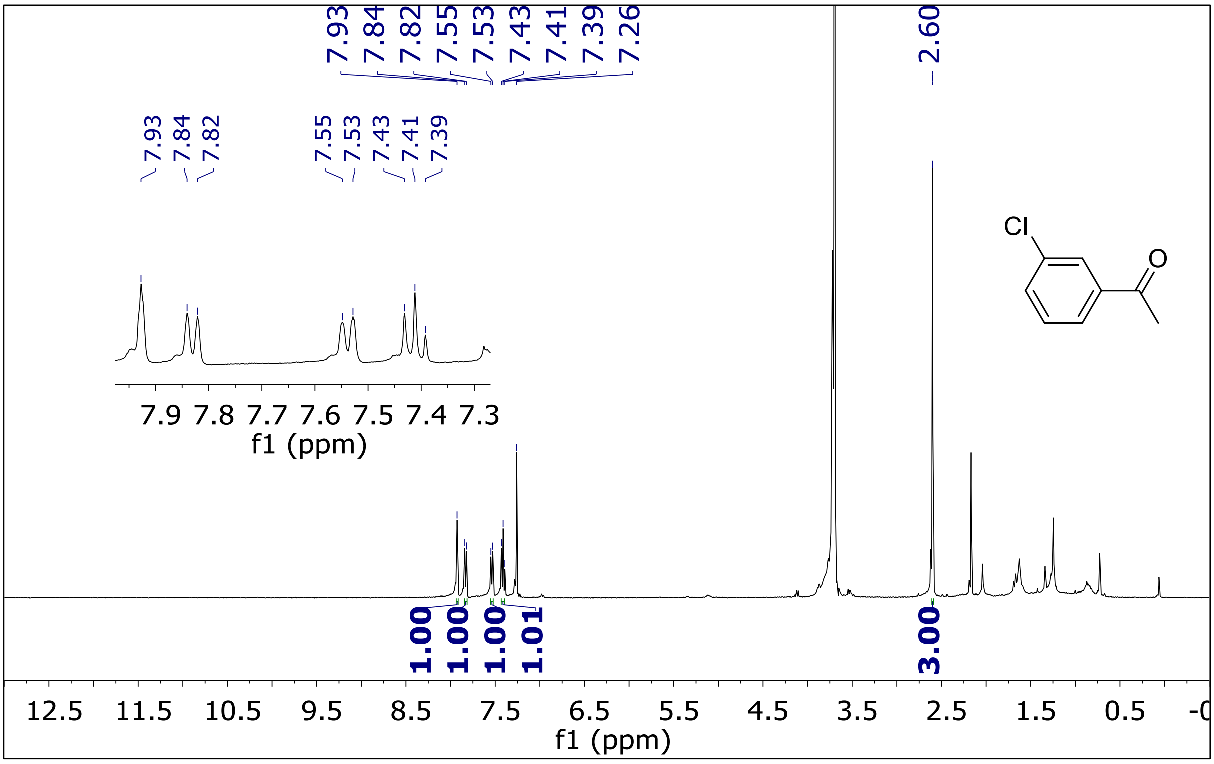


Figure S126. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **7l**.

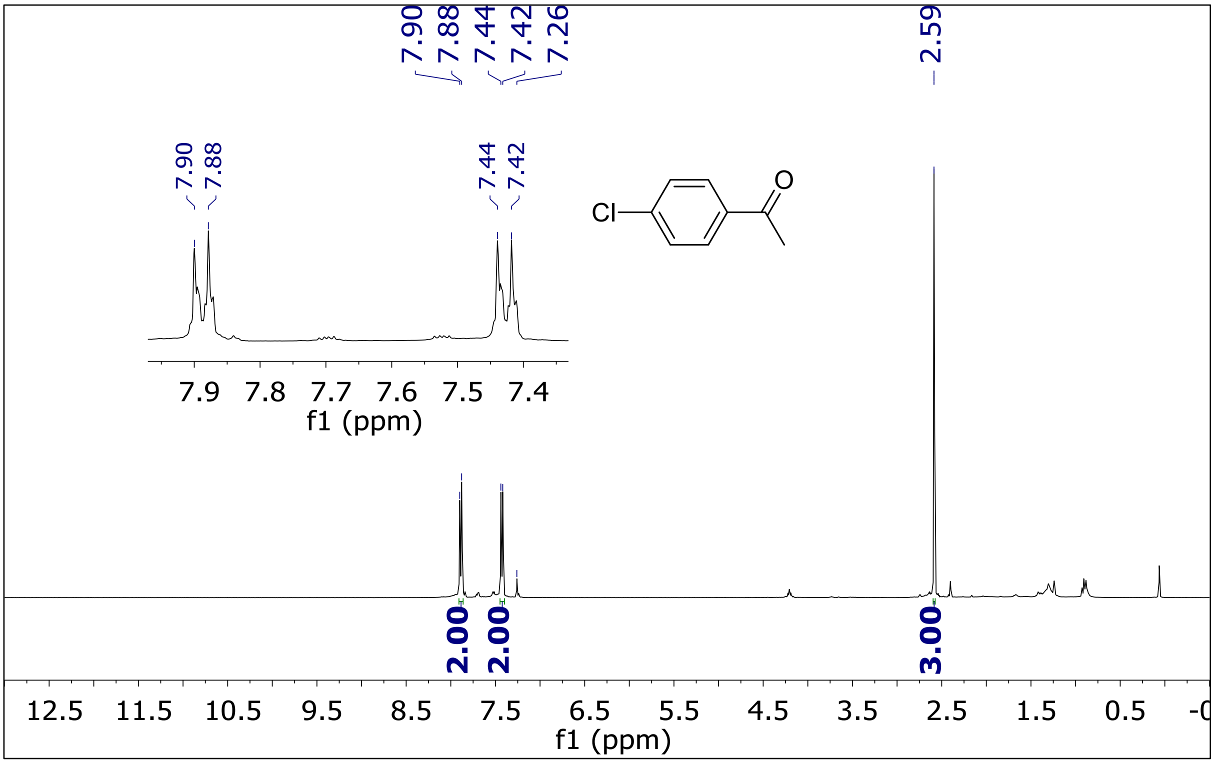


Figure S127. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **7m**.

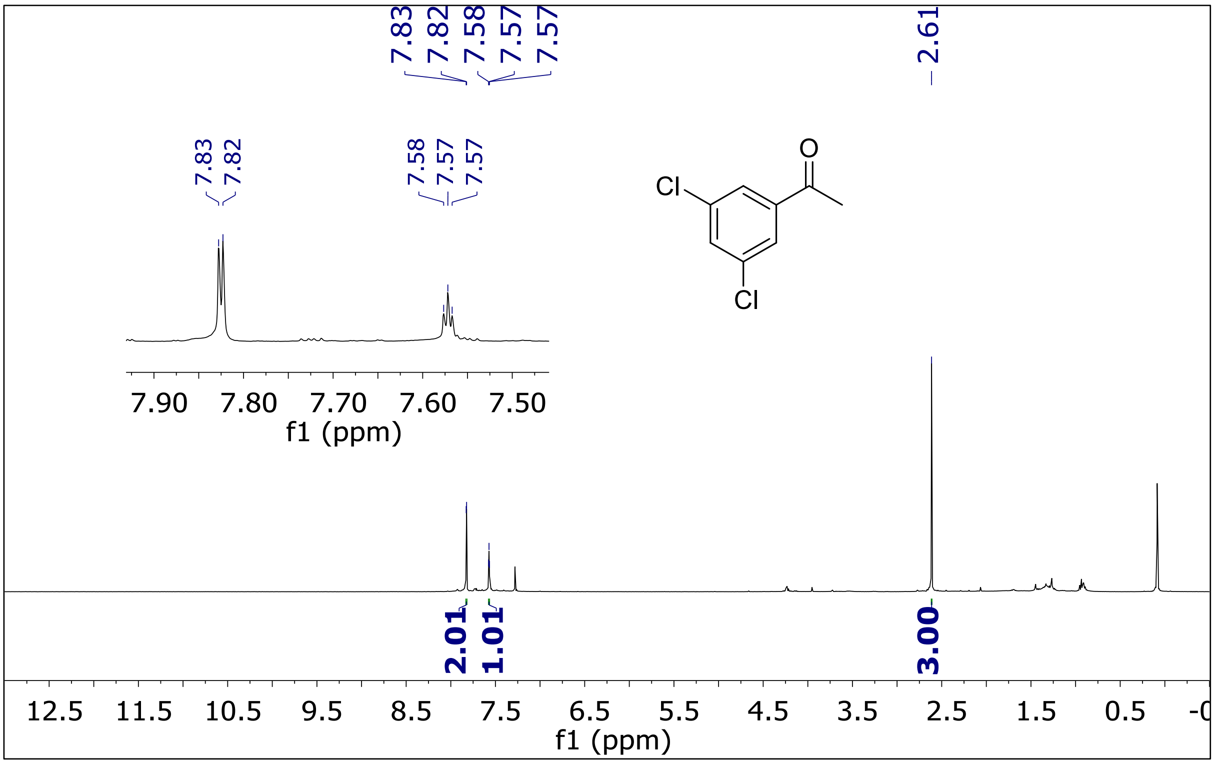


Figure S128. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7p**.

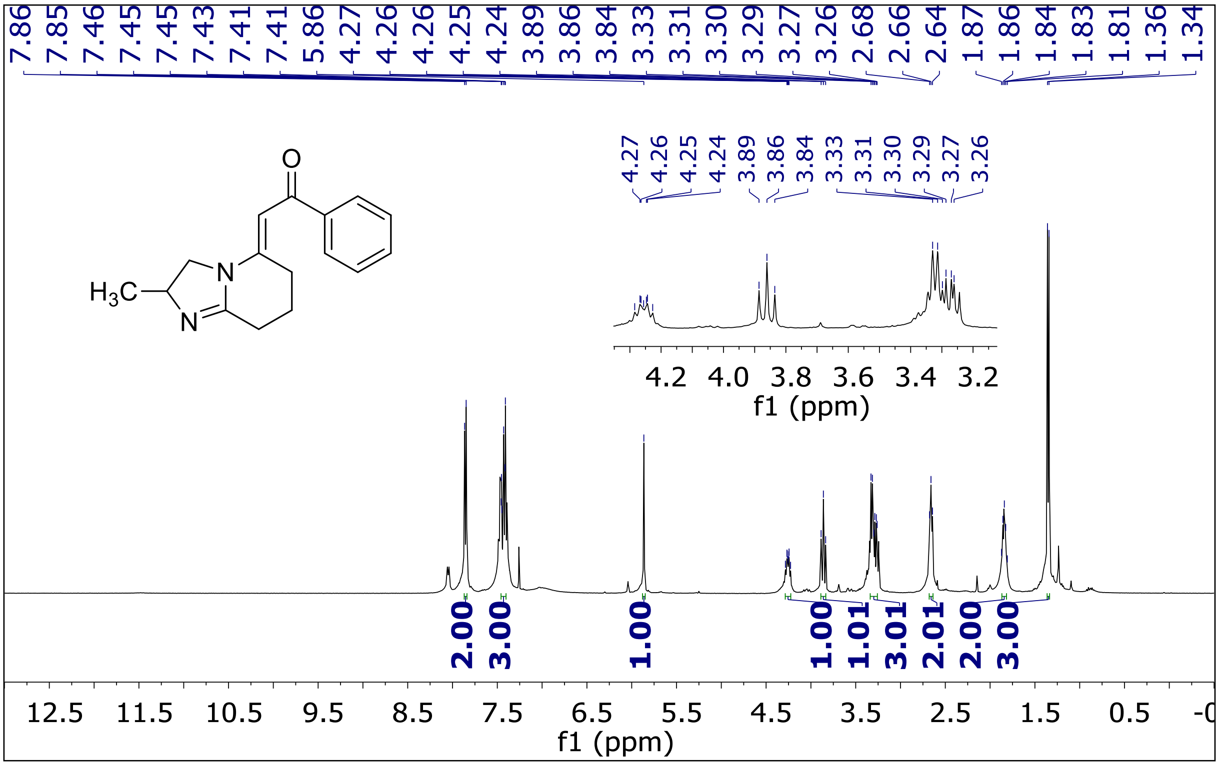


Figure S129. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8a**.

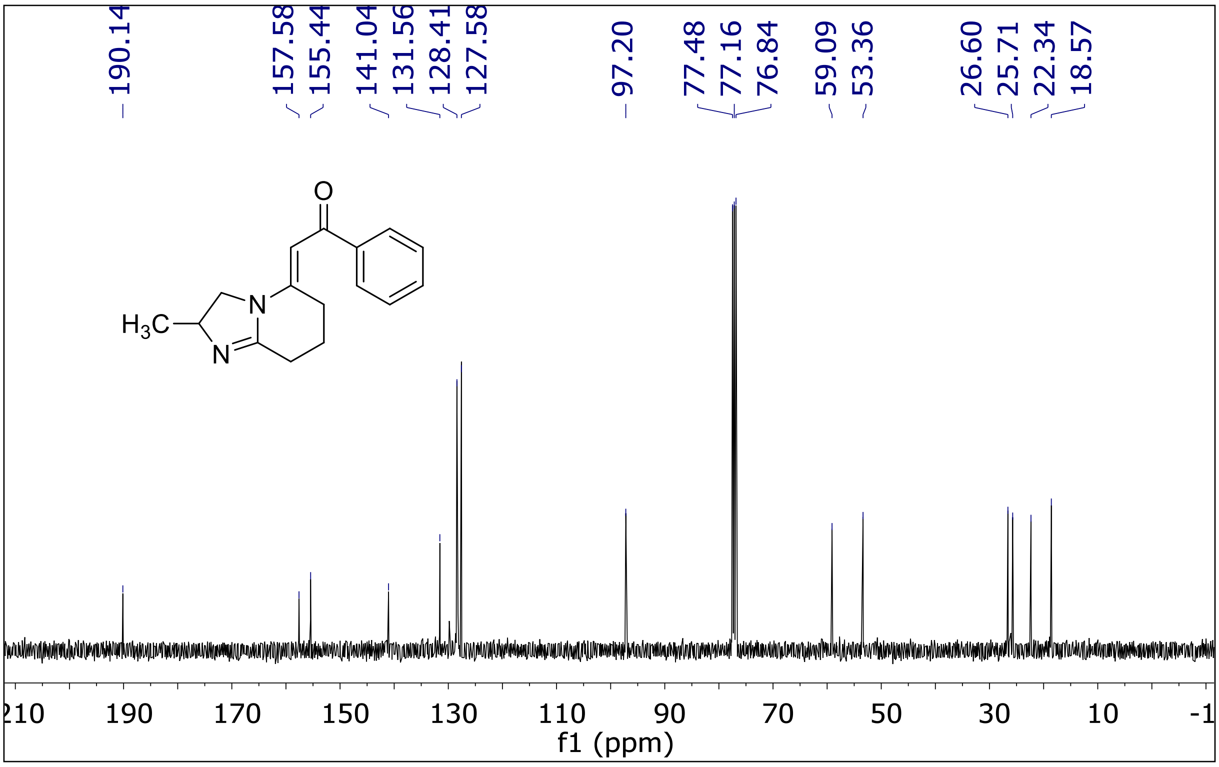


Figure S130. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **8a**.

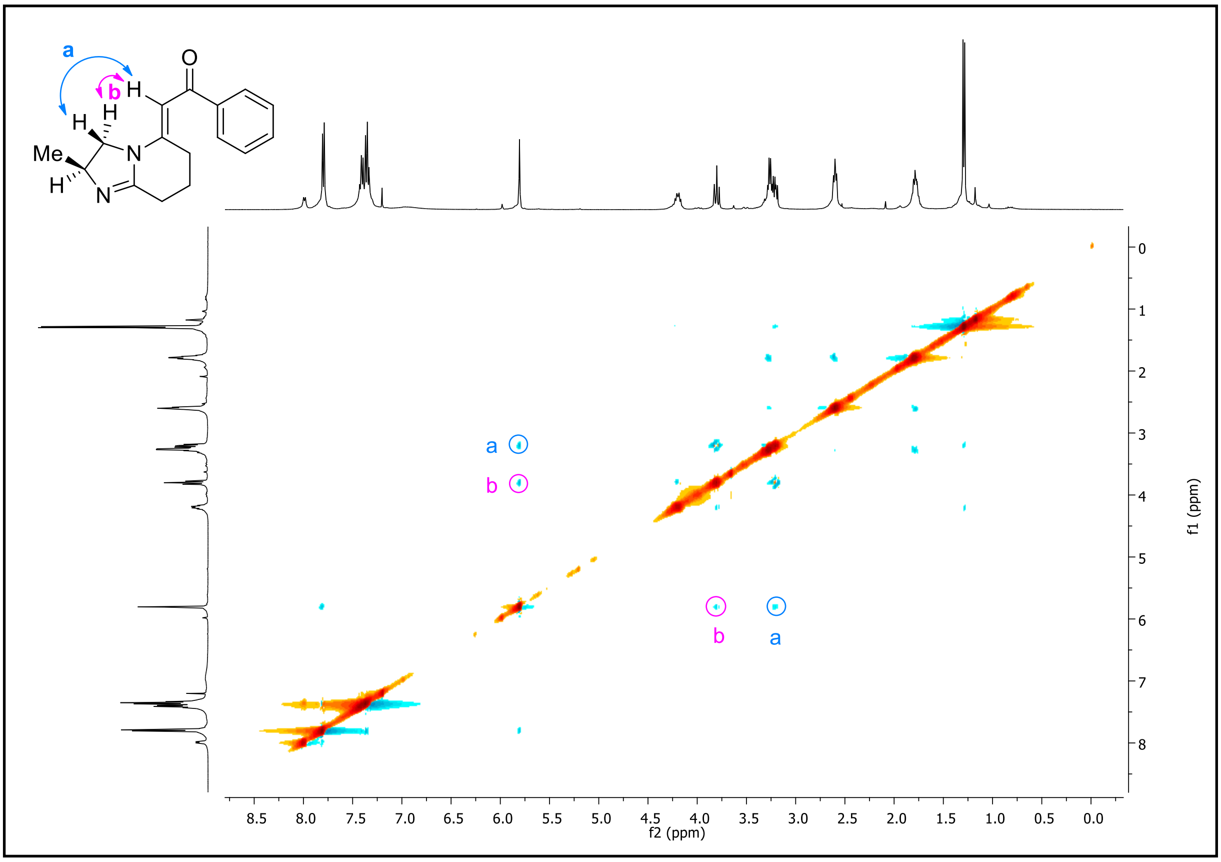


Figure S131. $^{1}H/^{1}H$ NOESY (400/400 MHz, $CDCl_3$) spectrum of compound **8a**.

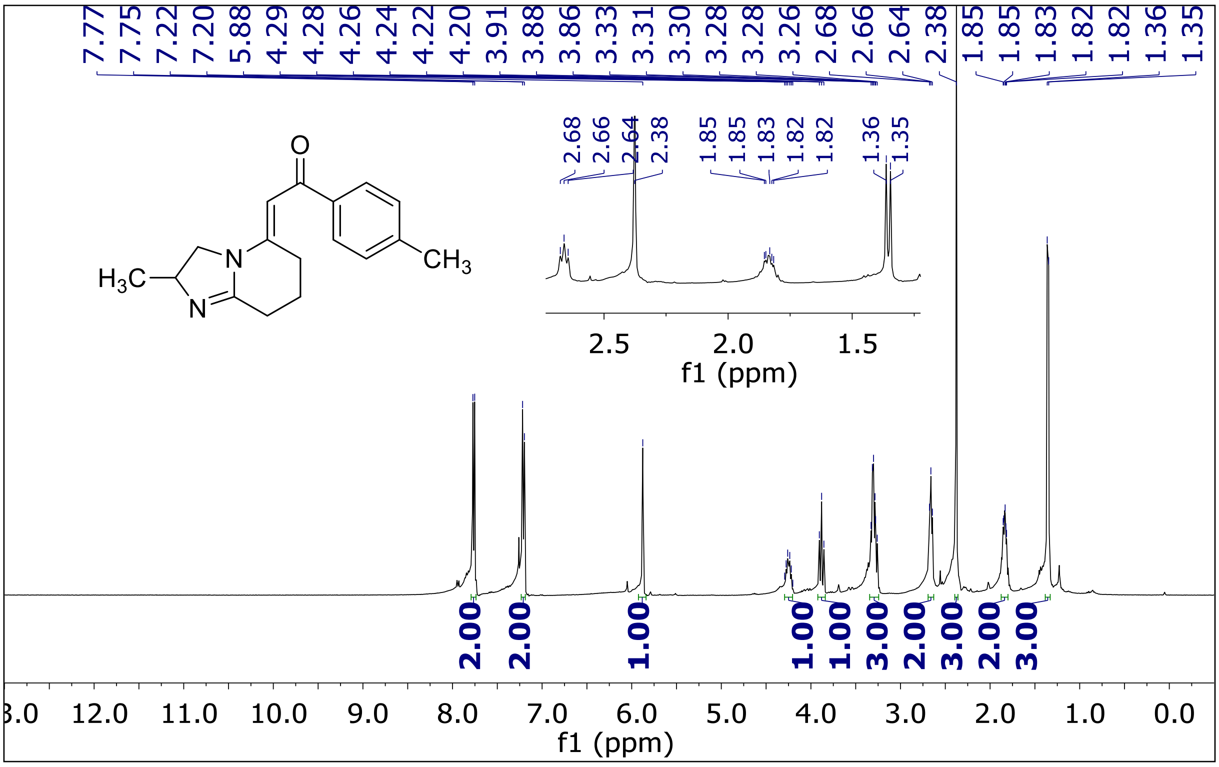


Figure S132. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **8b**.

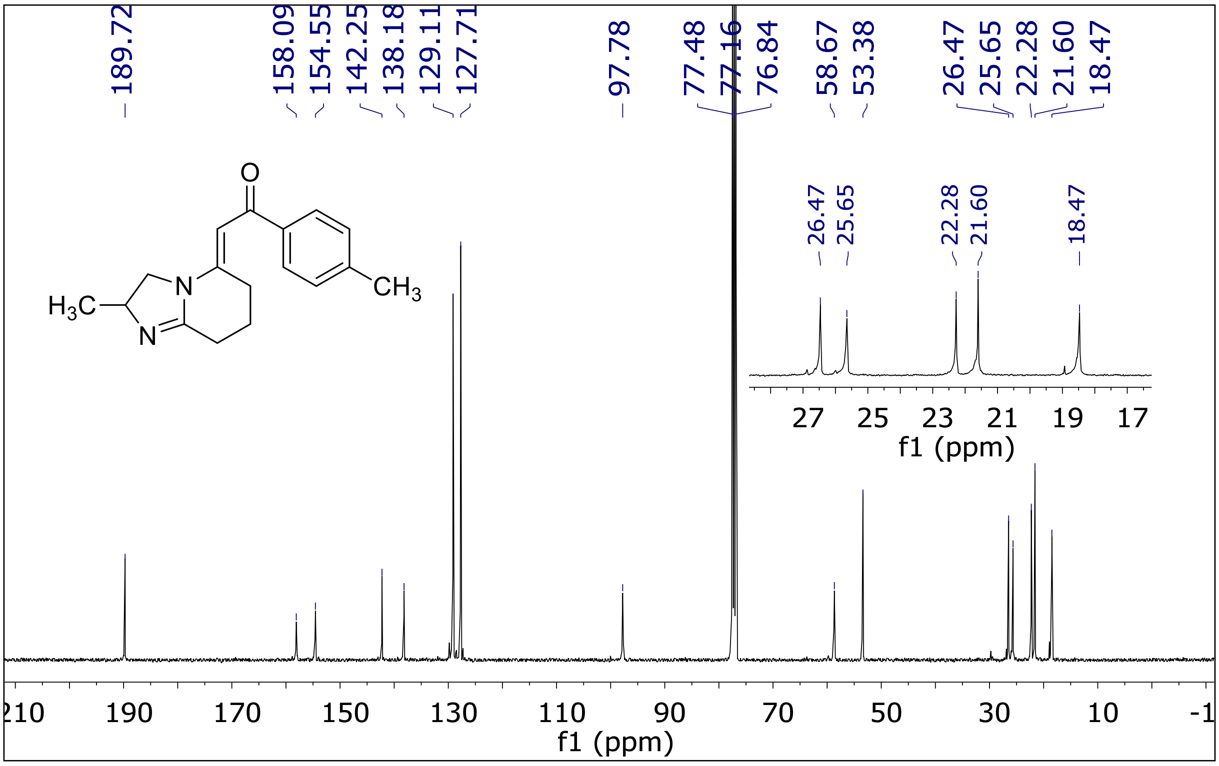


Figure S133. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **8b**.

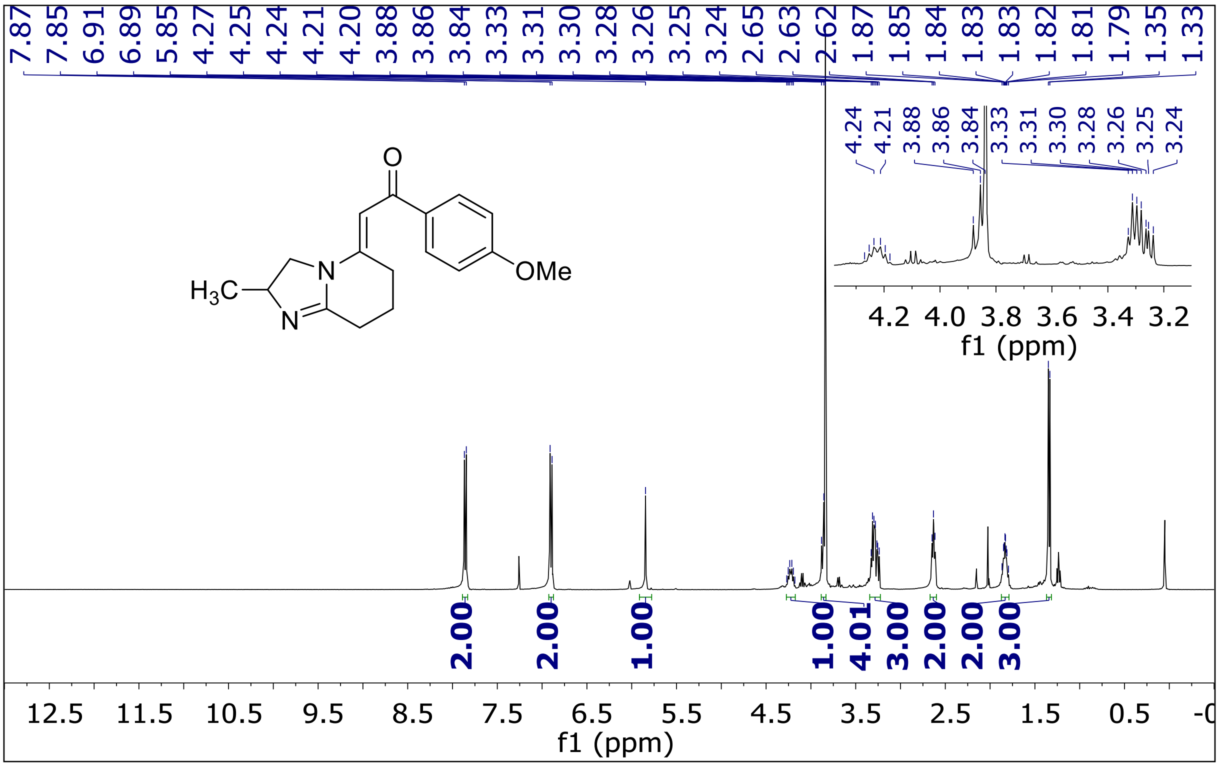


Figure S134. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **8f**.

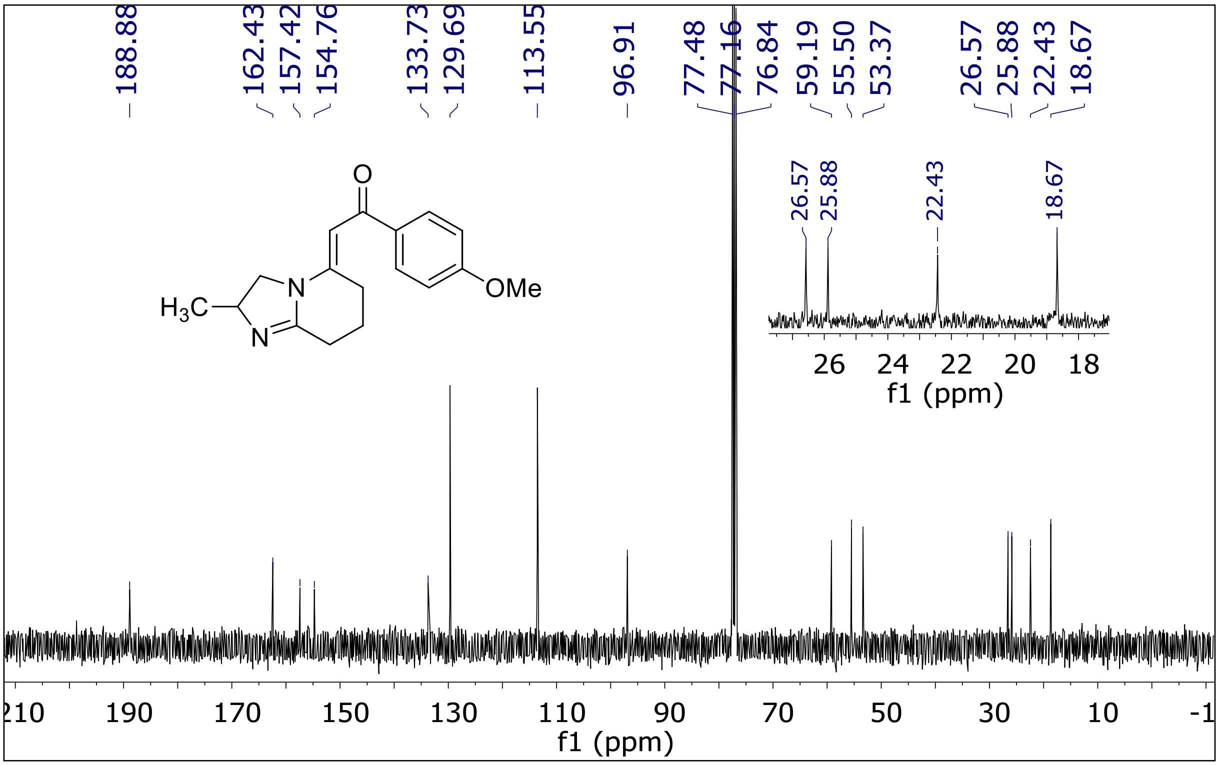


Figure S135. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **8f**.

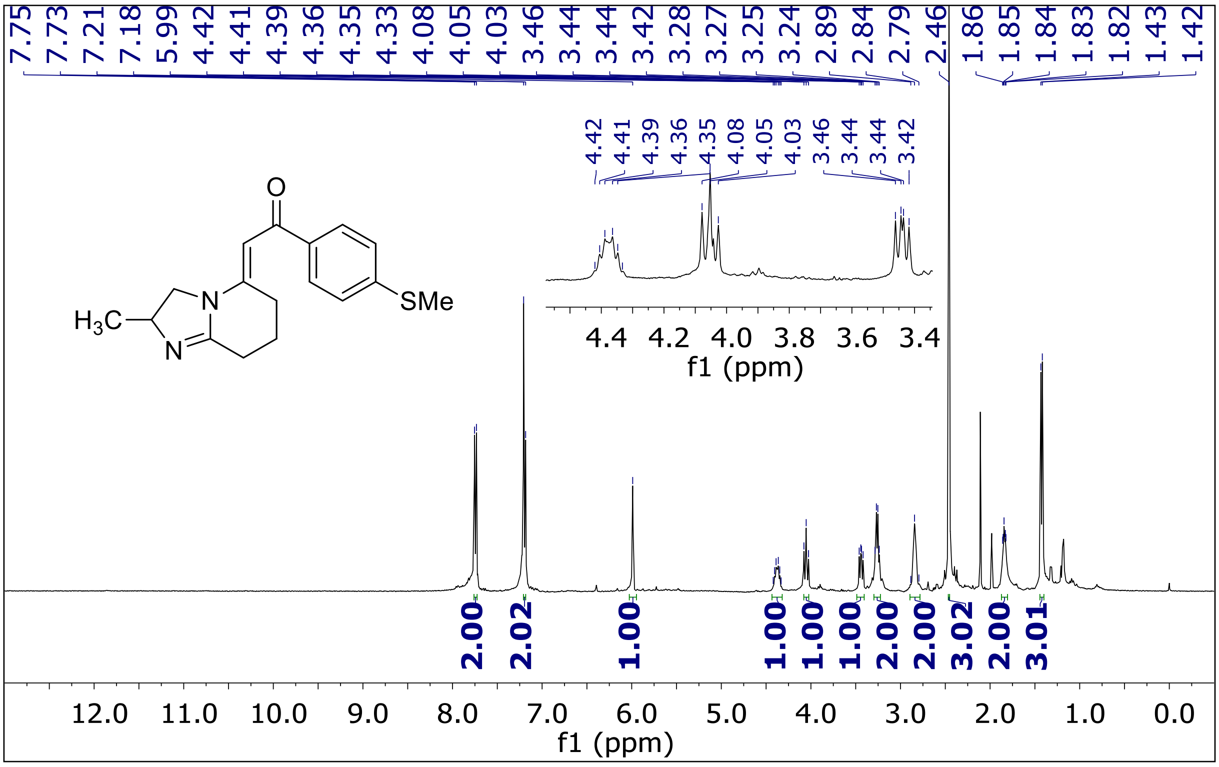


Figure S136. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8g**.

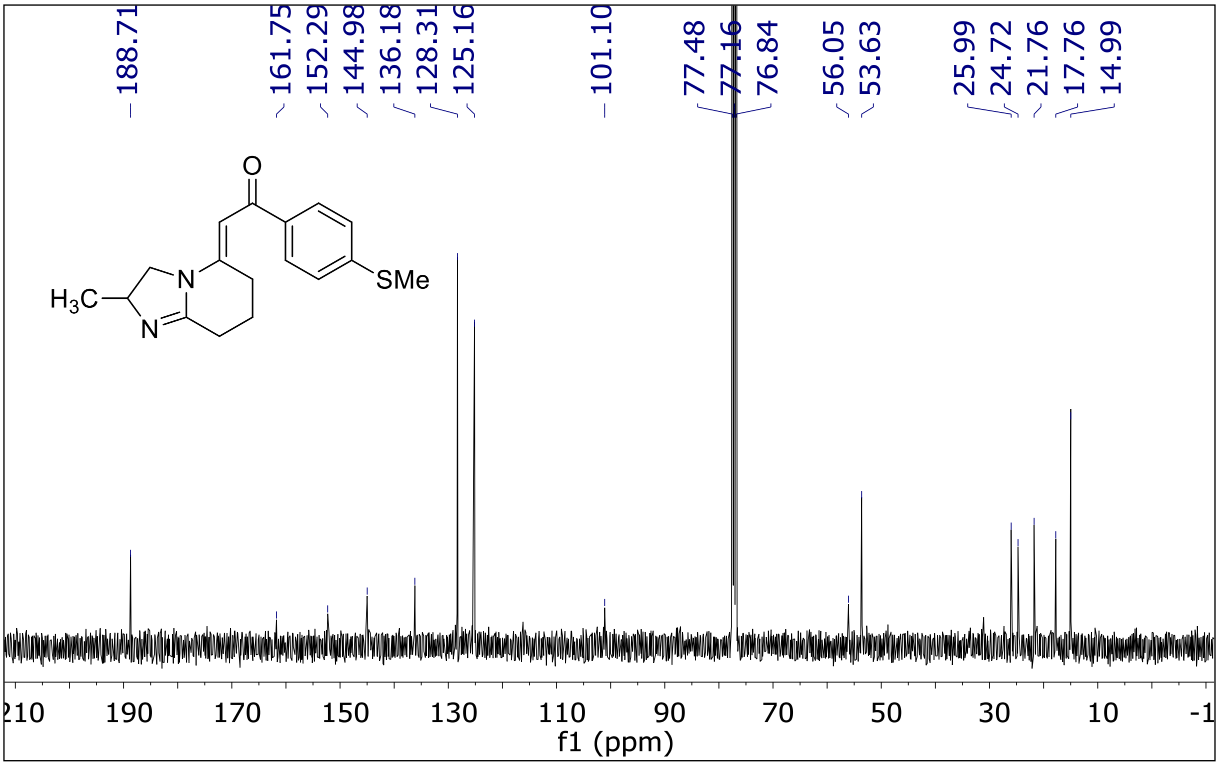


Figure S137. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of compound **8g**.

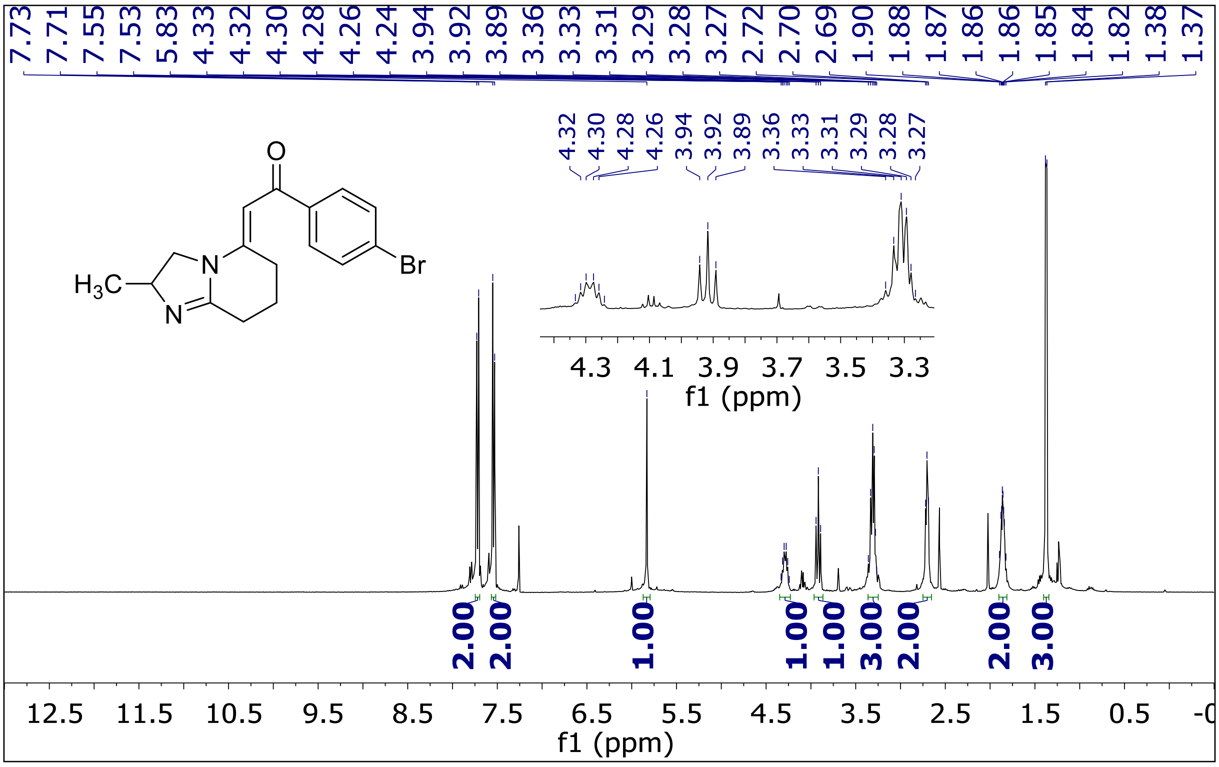


Figure S138. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of compound **8k**.

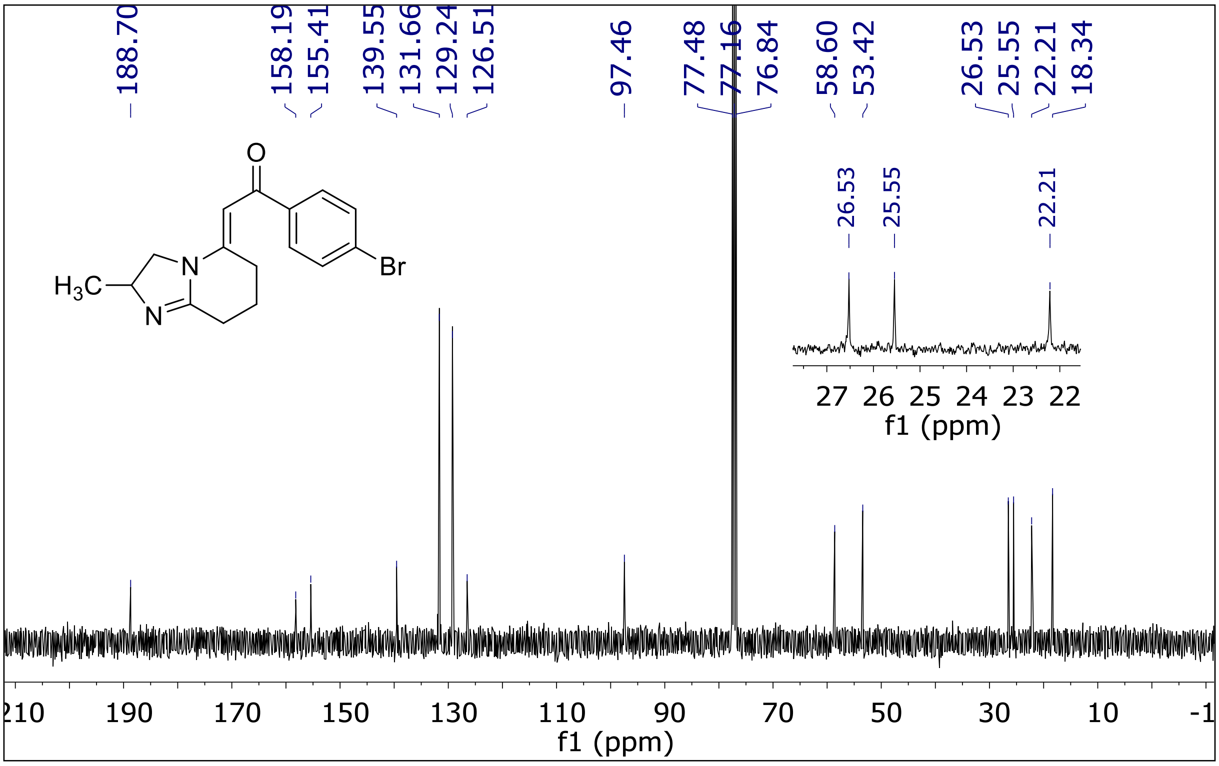


Figure S139. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of compound **8k**.

REFERENCES

1. Compound **1a** was previously synthesized from 1,9-diphenylnona-2,7-diyne-1,9-diol by oxidation and characterized by elemental analysis. No any spectroscopic data related to this compound was reported. See: W. Parkerr, A. Raphael and D. I. Wilkinson, Acetylenic Routes to Tropinone, pseudoPelletierine, and Lobelanine, *J. Chem. Soc.,* 1959, **438**, 2433–2437.

2. Compound **1n** was previously prepared by a similar coupling reaction and used in the next step without purification. No any spectroscopic data related to this compound was given. See: W. Zambach, L. Quaranta, C. Massolfrieh, S. Trah, D. Stierli, M. Pouliot and K. Nebel, Novel Microbiocides, WO 2013/026866 A2.

3. G. Zhang, X. Xie, Y. Wang, X. Wen, Y. Zhao and C. Ding, Highly selective Wacker reaction of styrene derivatives: a green and efficient aerobic oxidative process promoted by benzoquinone/$NaNO_2$/$HClO_4$ under mild conditions, *Org. Biomol. Chem.*, 2013, **11**, 2947–2950.

4. H. Liu, Y. Wei and C. Cai, A Combination System of p-Toluenesulfonic Acid and Acetic Acid for the Hydration of Alkynes, *Synlett,* 2016, **27**, 2378–2383.

5. S. Xu, Z. Yun, Y. Fen, Ting Tang, Z. Fang and Tiandi Tang, Zeolite Y nanoparticle assemblies with high activity in the direct hydration of terminal alkynes, *RSC Adv.*, 2016, **6**, 69822−69827.

6. (a) D. W. Tan, H. X. Li, M. J. Zhang, J. L. Yao and J. P. Lang, Acceptorless Dehydrogenation of Alcohols Catalyzed by CuI *N*-Heterocycle Thiolate Complexes, *ChemCatChem,* 2017, **9**, 1113–1118; (b) T. Shimbayashi, H. Ito, M. Shimizu, H. Sano, S. Sakaki and K. Fujita, Effect of Substituents in Functional Bipyridonate Ligands on Ruthenium-Catalyzed Dehydrogenative Oxidation of Alcohols: An Experimental and Computational Study, *ChemCatChem,* 2022, **14**, No. e202200280.

7. Y. Li, Y. Dong, J. L. Kan, X. Wu and Y. B. Dong, Synthesis and Catalytic Properties of Metal−*N*-Heterocyclic-Carbene-Decorated Covalent Organic Framework, *Org. Lett.*, 2020, **22**, 7363−7368.

8. Y. M. Yang, W. Yan, H. W. Hu, Y. Luo, Z. Y. Tang and Z. Luo, Photoinduced Acetylation of Anilines under Aqueous and Catalyst-Free Conditions, *J. Org. Chem.,* 2021, **86**, 12344−12353.

9. (a) P. H. J. Kouwer, W. F. Jager, W. J. Mijs and S. J. Picken, Specific interactions in discotic liquid crystals, *J. Mater. Chem.*, 2003, **13**, 458–469; (b) A. Krasovskiy, C. Duplais and B. H. Lipshutz, Zn-Mediated, Pd-Catalyzed Cross-Couplings in Water at Room Temperature Without Prior Formation of Organozinc Reagents, *J. Am. Chem. Soc.*, 2009, **131**, 15592–15593.

10. M. Meng, L. Yang, K. Cheng and C. Qi, Pd (II)-catalyzed denitrogenative and desulfinative addition of arylsulfonyl hydrazides with nitriles, *J. Org. Chem.*, 2018, **83**, 3275–3284.

11. S. Li, Y. Shi, P. Li and J. Xu, Nucleophilic organic base DABCO-mediated chemospecific meinwald rearrangement of terminal epoxides into methyl ketones, *J. Org. Chem.*, 2019, **84**, 4443–4450.

12. J. Zhang, J. Chen, J. Chen, Y. Luo and Y. Xia, Solvent as photoreductant for dehalogenation of α-haloketones under catalyst-free conditions, *Tetrahedron Lett.*, 2022, ***98,*** 153835.

13. X. Zhang, G. Jin, Q. Zhang, C. Sun, Y. Han, C. Dou and D. Shen, Flavoenzyme-inspired Reductive Dehalogenation of α-Br and α-Cl Carbonyl Compounds with Riboflavin Tetraacetate as Photocatalyst, *Asian J. Org. Chem.*, 2025, **14**, e202400709.