Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Rhodium Catalysed Intramolecular Benzannulation for the Formation of Tetracyclic Carbazoles

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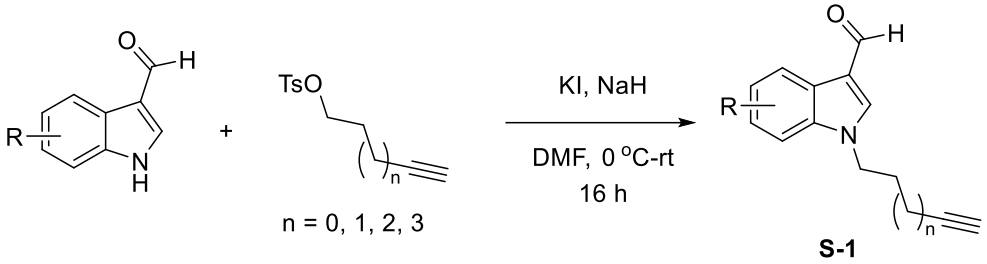
I. General details

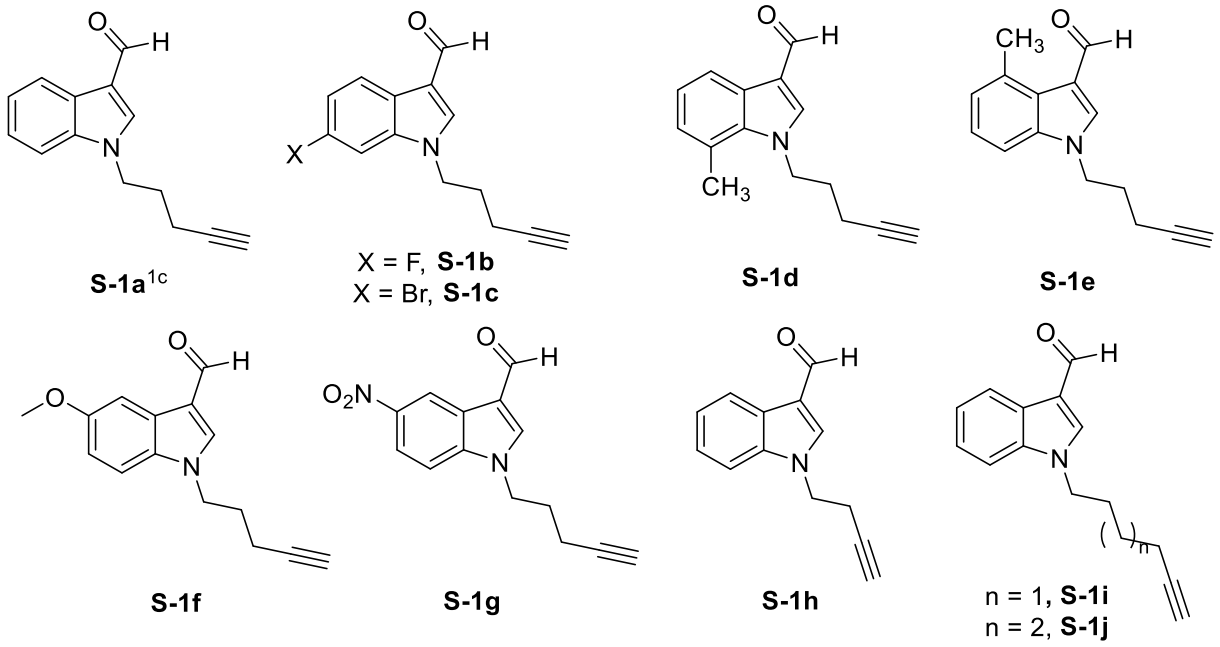
General information: Unless otherwise noted, all reagents were used as received from commercial suppliers. All nonaqueous reactions were performed under an atmosphere of nitrogen using an oven-dried glassware. All solvents were dried before use, following the standard procedures. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm), iodine treatment or using *p*-anisaldehyde stain. Column chromatography was carried out using silica gel (100-200 mesh) packed in glass columns. NMR spectra were recorded at 300, 400, 500 MHz (H) and at 75, 101, 126 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.16 ppm) as internal standard, and coupling constants (*J*) are given in Hz. High-resolution mass spectrometry (HRMS) was recorded using electrospray ionization (ESI)−Time-of-light techniques.

II. Experimental procedures and analytical data

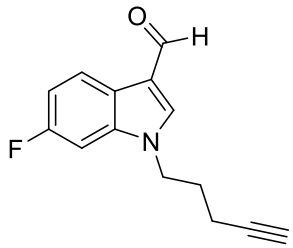
A. General procedure for SN_2 reaction[1]



To a suspension of corresponding indole (6.89 mmol, 1.0 equiv.) in DMF (20 mL) was added NaH (13.78 mmol, 2 equiv.) and potassium iodide (13.78 mmol, 2 equiv.) at 0 °C. At the same temperature, alkynyl sulphonate (6.89 mmol, 1.0 equiv.) in DMF (5 mL) was added drop wise and stirred at room temperature for 16 h. Then, the reaction mixture was quenched with saturated NH_4Cl solution (30 mL), extracted with ethyl acetate (2 x 30 mL). The combined organic phase was washed with cold water (2 x 30 mL), brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexanes).

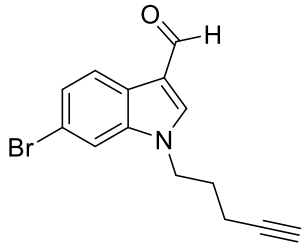


6-Fluoro-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-1b)



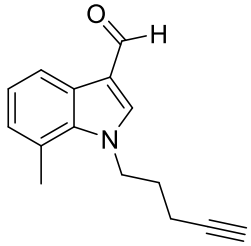
Prepared according to general procedure A using 6-fluoro-1*H*-indole-3-carbaldehyde (500 mg, 3.06 mmol, 1.0 equiv.) and pent-4-yn-1-yl-4-methylbenzenesulfonate (730 mg, 3.06 mmol, 1.0 equiv.). Pale Red solid (688 mg, 98% yield); R_f = 0.2 (30% EtOAc/hexane); mp = 104−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (d, *J* = 2.1 Hz, 1H), 8.26 (dd, *J* = 8.6, 5.5 Hz, 1H), 7.75 (s, 1H), 7.12 − 7.04 (m, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 2.24 – 2.20 (m, 2H), 2.14 (t, *J* = 2.6 Hz, 1H), 2.08 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.4, 160.7 (d, $^1J_{C\text{-}F}$ = 242 Hz), 138.9, 137.3 (d, $^3J_{C\text{-}F}$ = 12 Hz), 123.4 (d, $^3J_{C\text{-}F}$ = 10 Hz), 121.8, 118.3, 111.6 (d, $^2J_{C\text{-}F}$ = 24 Hz), 96.8 (d, $^2J_{C\text{-}F}$ = 25 Hz), 82.0, 70.6, 45.6, 27.9, 15.6; HRMS (ESI) calcd for $C_{14}H_{13}FNO$ $[M+H]^+$: 230.0976; found: 230.0994.

6-Bromo-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-1c)



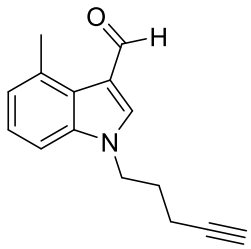
Prepared according to general procedure A using 6-bromo-1*H*-indole-3-carbaldehyde (500 mg, 2.24 mmol, 1.0 equiv.) and pent-4-yn-1-yl-4-methylbenzenesulfonate (531 mg, 2.23 mmol, 1.0 equiv.). Yellow solid (466 mg, 72% yield); R_f = 0.2 (30% EtOAc/hexane); mp = 105−107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (d, *J* = 2.2 Hz, 1H), 8.18 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.74 (d, *J* = 1.5 Hz, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.42 (dt, *J* = 8.4, 1.6 Hz, 1H), 4.33 (td, *J* = 6.7, 2.1 Hz, 2H), 2.23 – 2.19 (m, 2H), 2.14 (t, *J* = 2.6 Hz, 1H), 2.11 – 2.05 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 138.8, 137.9, 126.3, 124.3, 123.6, 118.2, 117.7, 113.2, 82.0, 70.7, 45.6, 27.9, 15.6; HRMS (ESI) calcd for $C_{14}H_{13}BrNO$ $[M+H]^+$: 290.0175; found: 290.0184.

7-Methyl-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-1d)



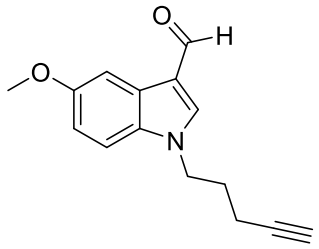
Prepared according to general procedure A using 7-methyl-1*H*-indole-3-carbaldehyde (500 mg, 3.14 mmol, 1.0 equiv.) and pent-4-yn-1-yl-4-methylbenzenesulfonate (748 mg, 3.14 mmol, 1.0 equiv.). Light brown solid (580 mg, 82% yield); R_f = 0.2 (30% EtOAc/hexane); mp = 138−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.20 (d, *J* = 7.7 Hz, 1H), 7.71 (s, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 4.53 (t, *J* = 7.0 Hz, 2H), 2.73 (s, 3H), 2.24 (td, *J* = 6.6, 2.6 Hz, 2H), 2.12 (t, *J* = 2.6 Hz, 1H), 2.05 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 140.1, 135.7, 127.2, 126.7, 123.1, 121.3, 120.2, 118.0, 82.2, 70.5, 48.0, 30.3, 19.7, 15.5; HRMS (ESI) calcd for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1232; found: 226.1237.

4-Methyl-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-1e)



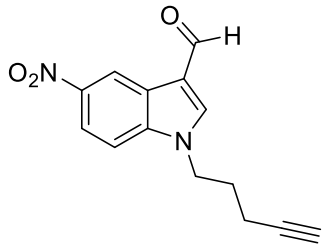
Prepared according to general procedure A using 4-methyl-1*H*-indole-3-carbaldehyde (500 mg, 3.14 mmol, 1.0 equiv.) and pent-4-yn-1-yl-4-methylbenzenesulfonate (748 mg, 3.14 mmol, 1.0 equiv.). Brown liquid (509 mg, 72% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.89 (s, 1H), 7.27 – 7.20 (m, 2H), 7.09 (d, *J* = 6.9 Hz, 1H), 4.34 (t, *J* = 6.8 Hz, 2H), 2.84 (s, 3H), 2.20 (td, *J* = 6.5, 2.7 Hz, 2H), 2.13 – 2.04 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.8, 137.6, 137.5, 132.5, 125.3, 124.3, 123.6, 119.7, 107.9, 82.2, 70.4, 45.6, 28.0, 22.6, 15.7; HRMS (ESI) calcd for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1232; found: 226.1255.

5-Methoxy-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-1f)



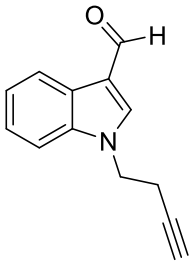
Prepared according to general procedure A using 5-methoxy-1*H*-indole-3-carbaldehyde (500 mg, 2.85 mmol, 1.0 equiv.) and pent-4-yn-1-yl-4-methylbenzenesulfonate (680 mg, 2.85 mmol, 1.0 equiv.). Brown solid (440 mg, 64% yield); R_f = 0.4 (50% EtOAc/hexane); mp = 83−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 – 9.94 (m, 1H), 7.80 (s, 1H), 7.71 – 7.69 (m, 1H), 7.31 – 7.26 (m, 1H), 6.97 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.35 – 4.29 (m, 2H), 3.91 – 3.88 (m, 3H), 2.19 (dt, *J* = 6.9, 3.4 Hz, 2H), 2.12 (t, *J* = 2.6 Hz, 1H), 2.07 (dd, *J* = 8.7, 4.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 156.7, 138.6, 131.9, 126.3, 118.0, 114.6, 110.9, 103.5, 82.2, 70.4, 55.9, 45.7, 28.1, 15.6; HRMS (ESI) calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$: 242.1176; found: 242.1186.

5-Nitro-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-1g)



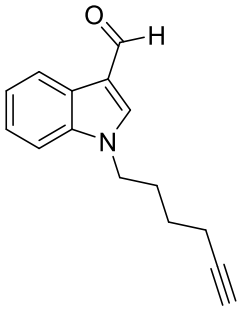
Prepared according to general procedure A using 5-nitro-1*H*-indole-3-carbaldehyde (500 mg, 2.63 mmol, 1.0 equiv.) and pent-4-yn-1-yl-4-methylbenzenesulfonate (626 mg, 2.62 mmol, 1.0 equiv.). Light red solid (552 mg, 82% yield); R_f = 0.4 (50% EtOAc/hexane); mp = 163−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 – 10.05 (m, 1H), 9.23 – 9.18 (m, 1H), 8.26 – 8.21 (m, 1H), 7.93 (s, 1H), 7.50 (dd, *J* = 9.1, 3.3 Hz, 1H), 4.44 (t, *J* = 6.7 Hz, 2H), 2.26 – 2.22 (m, 2H), 2.16 – 2.09 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.1, 144.0, 140.6, 139.8, 124.8, 119.6, 119.5, 119.1, 110.3, 81.8, 70.9, 45.9, 28.1, 15.6; HRMS (ESI) calcd for $C_{14}H_{13}N_2O_3$ $[M+H]^+$: 257.0921; found: 257.0921.

1-(But-3-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-1h)



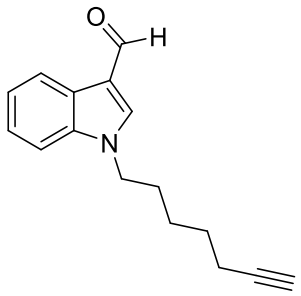
Prepared according to general procedure A using 1*H*-indole-3-carbaldehyde (500 mg, 3.45 mmol, 1.0 equiv.) and but-3-yn-1-yl-4-methylbenzenesulfonate (772 mg, 3.45 mmol, 1.0 equiv.). White solid (414 mg, 61% yield); R_f = 0.6 (50% EtOAc/hexane); mp = 95−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (d, *J* = 2.1 Hz, 1H), 8.34 – 8.30 (m, 1H), 7.80 (s, 1H), 7.38 – 7.30 (m, 3H), 4.36 – 4.31 (m, 2H), 2.77 – 2.72 (m, 2H), 2.08 (t, *J* = 2.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.7, 138.7, 136.8, 125.5, 124.1, 123.1, 122.3, 118.3, 109.7, 79.8, 71.8, 45.8, 20.1; HRMS (ESI) calcd for $C_{13}H_{12}NO$ $[M+H]^+$: 198.0913; found: 198.0915.

1-(Hex-5-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-1i)



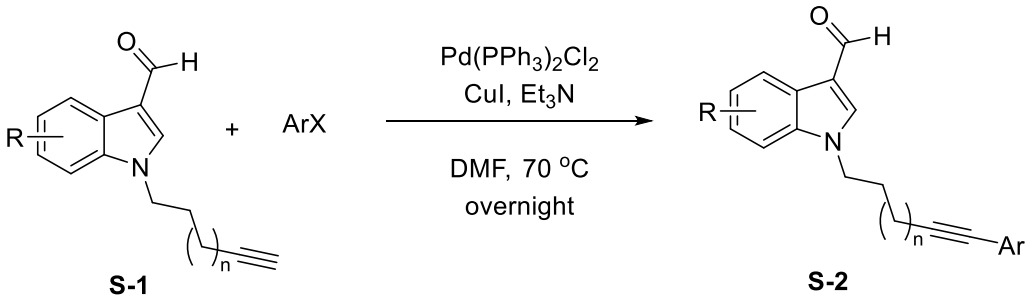
Prepared according to general procedure A using 1*H*-indole-3-carbaldehyde (500 mg, 3.45 mmol, 1.0 equiv.) and hex-5-yn-1-yl-4-methylbenzenesulfonate (869 mg, 3.45 mmol, 1.0 equiv.). Red colour liquid (582 mg, 75% yield); R_f = 0.7 (50% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.32 – 8.30 (m, 1H), 7.74 (s, 1H), 7.41 – 7.38 (m, 1H), 7.36 – 7.30 (m, 2H), 4.23 (t, *J* = 7.2 Hz, 2H), 2.26 (td, *J* = 6.9, 2.7 Hz, 2H), 2.09 – 2.03 (m, 2H), 1.99 (t, *J* = 2.7 Hz, 1H), 1.61 – 1.55 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5, 138.1, 137.2, 125.5, 124.0, 123.0, 122.2, 118.2, 110.0, 83.3, 69.4, 46.8, 28.8, 25.5, 18.0; HRMS (ESI) calcd for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1226; found: 226.1239.

1-(Hept-6-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-1j)



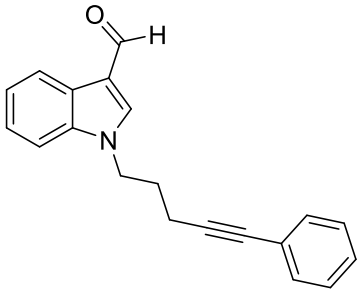
Prepared according to general procedure A using 1*H*-indole-3-carbaldehyde (500 mg, 3.45 mmol, 1.0 equiv.) and hept-6-yn-1-yl-4-methylbenzenesulfonate (917 mg, 3.45 mmol, 1.0 equiv.). Colourless liquid (461 mg, 56% yield); R_f = 0.8 (50% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.33 – 8.30 (m, 1H), 7.73 (s, 1H), 7.40 – 7.30 (m, 3H), 4.20 (t, *J* = 7.2 Hz, 2H), 2.20 (td, *J* = 6.8, 2.6 Hz, 2H), 1.97 – 1.90 (m, 3H), 1.61 – 1.57 (m, 2H), 1.52 – 1.47 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 138.1, 137.2, 125.5, 124.0, 122.9, 122.2, 118.1, 110.0, 83.8, 68.8, 47.2, 29.3, 27.8, 25.9, 18.2; HRMS (ESI) calcd for $C_{16}H_{18}NO$ $[M+H]^+$: 240.1383; found: 240.1394.

B. General procedure for sonogashira reaction[2]



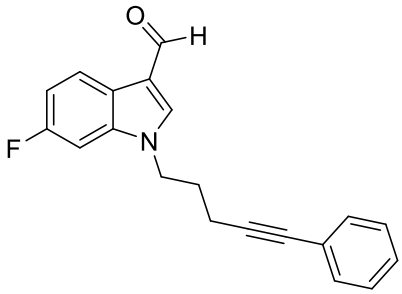
A mixture of halo substituted compound (1.0 equiv.), CuI (5 mol%), $Pd(PPh_3)_2Cl_2$ (5 mol%), Et_3N (8 mL) was added successively under N_2 and then corresponding alkyne (2.37 mmol, 1.0 equiv.) in DMF (5 mL) was added drop wise via syringe. The mixture was stirred for overnight at 70 °C. Upon completion, the reaction mixture diluted with cold water (20 mL) and extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4 and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (EtOAc/Hexane).

1-(5-Phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde[2e] **(S-2a)**



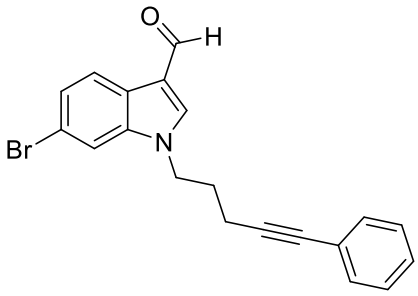
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) and bromobenzene (372 mg, 2.37 mmol, 1.0 equiv.). Black colour liquid (394 mg, 58% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.35 – 8.30 (m, 1H), 7.79 (s, 1H), 7.47 – 7.41 (m, 3H), 7.36 – 7.31 (m, 5H), 4.42 (t, *J* = 6.8 Hz, 2H), 2.44 (t, *J* = 6.6 Hz, 2H), 2.18 (p, *J* = 6.7 Hz, 2H).

6-Fluoro-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2b)



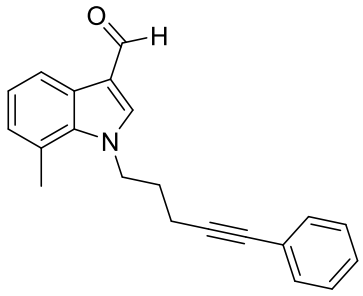
Prepared according to general procedure B using 6-fluoro-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.18 mmol, 1.0 equiv.) and bromobenzene (342 mg, 2.18 mmol, 1.0 equiv.). Black colour liquid (386 mg, 58% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.25 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.77 (s, 1H), 7.45 – 7.43 (m, 2H), 7.34 – 7.31 (m, 3H), 7.14 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.07 (td, *J* = 8.8, 2.2 Hz, 1H), 4.36 (t, *J* = 6.7 Hz, 2H), 2.44 (t, *J* = 6.6 Hz, 2H), 2.16 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 160.7 (d, $^1J_{C\text{-}F}$ = 242 Hz), 138.9, 137.4 (d, $^3J_{C\text{-}F}$ = 12 Hz), 131.6, 128.4, 128.2, 123.4 (d, $^3J_{C\text{-}F}$ = 10 Hz), 123.2, 121.8, 118.4, 111.6 (d, $^2J_{C\text{-}F}$ = 24 Hz), 96.9 (d, $^2J_{C\text{-}F}$ = 26 Hz), 87.4, 82.7, 45.9, 28.3, 16.7; HRMS (ESI) calcd for $C_{20}H_{17}FNO$ $[M+H]^+$: 306.1289; found: 306.1304.

6-Bromo-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2c)



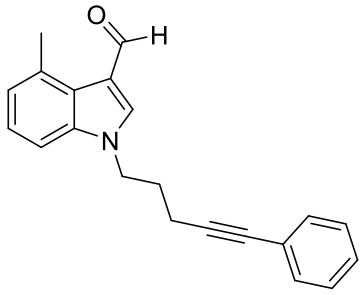
Prepared according to general procedure B using 6-bromo-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (400 mg, 1.38 mmol, 1.0 equiv.) and bromobenzene (216 mg, 1.37 mmol, 1.0 equiv.). Black colour liquid (312 mg, 62% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.76 (s, 1H), 7.63 (d, *J* = 1.5 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.35 – 7.32 (m, 3H), 4.38 (t, *J* = 6.7 Hz, 2H), 2.44 (t, *J* = 6.6 Hz, 2H), 2.17 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.4, 138.8, 138.0, 131.7, 128.4, 128.2, 126.3, 124.3, 123.6, 123.1, 118.3, 117.7, 113.2, 87.3, 82.8, 45.8, 28.4, 16.7; HRMS (ESI) calcd for $C_{20}H_{17}BrNO$ $[M+H]^+$: 366.0488; found: 366.0493.

7-Methyl-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2d)



Prepared according to general procedure B using 7-methyl-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.21 mmol, 1.0 equiv.) and bromobenzene (348 mg, 2.21 mmol, 1.0 equiv.). Dark brown solid (401 mg, 60% yield); R_f = 0.2 (30% EtOAc/hexane); mp = 90−92 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.73 (s, 1H), 7.45 – 7.39 (m, 2H), 7.35 – 7.29 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 4.59 (t, *J* = 7.1 Hz, 2H), 2.76 (s, 3H), 2.48 (t, *J* = 6.6 Hz, 2H), 2.17 – 2.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 140.1, 135.8, 131.6, 128.4, 128.1, 127.3, 126.7, 123.2, 123.1, 121.3, 120.2, 118.0, 87.6, 82.6, 48.4, 30.8, 19.8, 16.6; HRMS (ESI) calcd for $C_{21}H_{20}NO$ $[M+H]^+$: 302.1545; found: 302.1540.

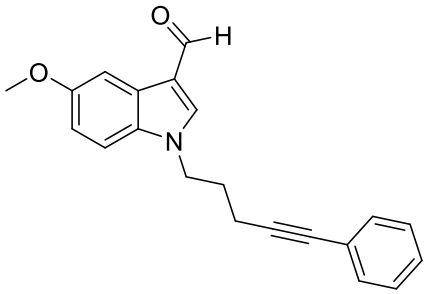
4-Methyl-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2e)



Prepared according to general procedure B using 4-methyl-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.21 mmol, 1.0 equiv.) and bromobenzene (348 mg, 2.21 mmol, 1.0 equiv.). Black colour liquid (387 mg, 58% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.90 (s, 1H), 7.44 – 7.39 (m, 2H), 7.33 – 7.27 (m, 4H), 7.24 – 7.19

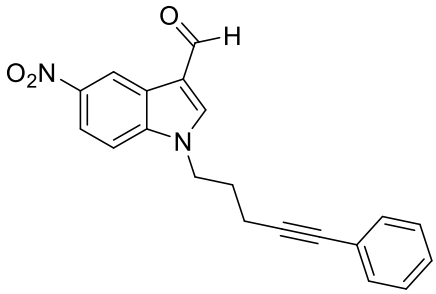
(m, 1H), 7.08 (d, *J* = 7.1 Hz, 1H), 4.37 (t, *J* = 6.8 Hz, 2H), 2.83 (s, 3H), 2.41 (t, *J* = 6.6 Hz, 2H), 2.14 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.8, 137.7, 137.6, 132.5, 131.6, 128.4, 128.1, 125.3, 124.3, 123.6, 123.3, 119.8, 108.0, 87.6, 82.4, 45.9, 28.4, 22.6, 16.7; HRMS (ESI) calcd for $C_{21}H_{20}NO$ $[M+H]^+$: 302.1545; found: 302.1549.

5-Methoxy-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2f)



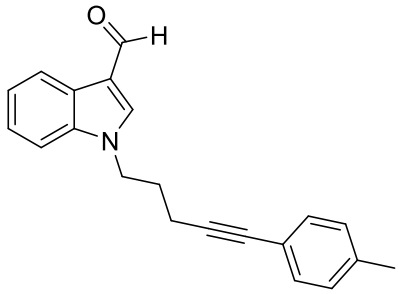
Prepared according to general procedure B using 5-methoxy-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (400 mg, 1.66 mmol, 1.0 equiv.) and bromobenzene (260 mg, 1.66 mmol, 1.0 equiv.). Black colour liquid (342 mg, 65% yield); R_f = 0.4 (50% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.80 (d, *J* = 2.5 Hz, 1H), 7.72 (s, 1H), 7.44 – 7.41 (m, 2H), 7.34 – 7.30 (m, 4H), 6.97 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.36 (t, *J* = 6.7 Hz, 2H), 3.89 (s, 3H), 2.42 (t, *J* = 6.5 Hz, 2H), 2.15 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5, 156.8, 138.7, 132.0, 131.6, 128.4, 128.1, 126.3, 123.3, 118.0, 114.6, 110.9, 103.5, 87.6, 82.5, 55.9, 45.9, 28.5, 16.7; HRMS (ESI) calcd for $C_{21}H_{20}NO_2$ $[M+H]^+$: 318.1489; found: 318.1489.

5-Nitro-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2g)



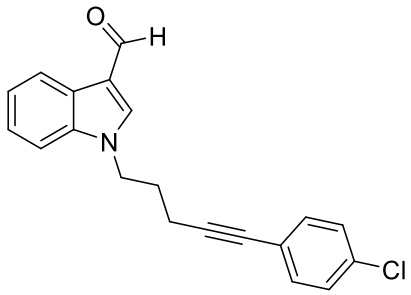
Prepared according to general procedure B using 5-nitro-1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (400 mg, 1.56 mmol, 1.0 equiv.) and bromobenzene (245 mg, 1.56 mmol, 1.0 equiv.). Yellow solid (316 mg, 61% yield); R_f = 0.4 (50% EtOAc/hexane); mp = 145−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 9.21 (d, *J* = 1.9 Hz, 1H), 8.23 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.96 (s, 1H), 7.53 (d, *J* = 9.1 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.36 – 7.32 (m, 3H), 4.49 (t, *J* = 6.8 Hz, 2H), 2.48 (t, *J* = 6.5 Hz, 2H), 2.25 – 2.17 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.1, 144.1, 140.5, 139.9, 131.6, 128.5, 128.3, 124.9, 123.0, 119.6, 119.5, 119.1, 110.3, 87.0, 82.9, 46.2, 28.4, 16.7; HRMS (ESI) calcd for $C_{20}H_{17}N_2O_3$ $[M+H]^+$: 333.1234; found: 333.1243.

1-(5-(*p*-Tolyl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2h)



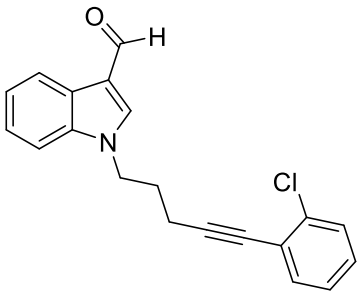
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) and 1-bromo-4-methylbenzene (404 mg, 2.37 mmol, 1.0 equiv.). Black colour liquid (363 mg, 51% yield); R_f = 0.6 (50% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.33 – 8.30 (m, 1H), 7.79 (s, 1H), 7.46 – 7.44 (m, 1H), 7.36 – 7.30 (m, 4H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.41 (t, *J* = 6.8 Hz, 2H), 2.42 (t, *J* = 6.6 Hz, 2H), 2.36 (s, 3H), 2.19 – 2.13 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 138.6, 138.2, 137.2, 131.5, 129.2, 125.6, 124.1, 123.0, 122.3, 120.2, 118.3, 110.1, 86.8, 82.6, 45.8, 28.5, 21.5, 16.7; HRMS (ESI) calcd for $C_{21}H_{20}NO$ $[M+H]^+$: 302.1539; found: 302.1541.

1-(5-(4-Chlorophenyl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2i)



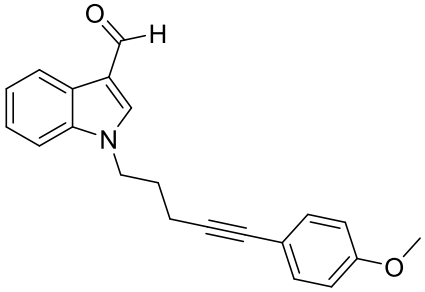
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) and 1-chloro-4-iodobenzene (564 mg, 2.37 mmol, 1.0 equiv.). Black colour liquid (441 mg, 58% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.34 – 8.29 (m, 1H), 7.76 (s, 1H), 7.46 – 7.41 (m, 1H), 7.37 – 7.27 (m, 6H), 4.38 (t, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 6.7 Hz, 2H), 2.17 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 138.4, 137.2, 134.1, 132.8, 128.7, 125.6, 124.1, 123.0, 122.3, 121.8, 118.3, 110.0, 88.7, 81.4, 45.8, 28.4, 16.8; HRMS (ESI) calcd for $C_{20}H_{17}ClNO$ $[M+H]^+$: 322.0993; found: 322.1025.

1-(5-(2-Chlorophenyl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2j)



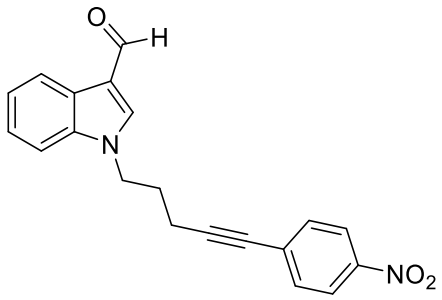
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) and 1-chloro-2-iodobenzene (564 mg, 2.37 mmol, 1.0 equiv.). Grey colour liquid (517 mg, 68% yield); R_f = 0.25 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.34 – 8.30 (m, 1H), 7.86 (s, 1H), 7.48 – 7.45 (m, 2H), 7.44 – 7.41 (m, 1H), 7.37 – 7.30 (m, 2H), 7.29 – 7.20 (m, 2H), 4.49 (t, *J* = 6.7 Hz, 2H), 2.48 (t, *J* = 6.5 Hz, 2H), 2.19 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 138.9, 137.1, 135.9, 133.3, 129.3, 129.2, 126.7, 125.6, 124.1, 123.1, 123.0, 122.3, 118.3, 110.1, 93.2, 79.6, 45.6, 28.2, 16.8; HRMS (ESI) calcd for $C_{20}H_{17}ClNO$ $[M+H]^+$: 322.0993; found: 322.1003.

1-(5-(4-Methoxyphenyl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2k)



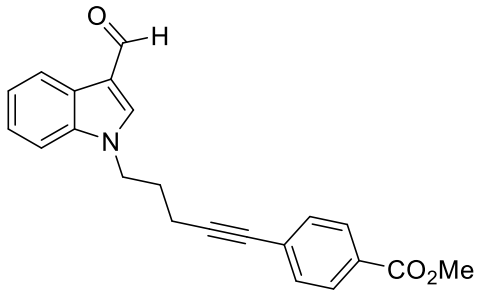
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) and 1-bromo-4-methoxybenzene (442 mg, 2.37 mmol, 1.0 equiv.). Black colour liquid (360 mg, 48% yield); R_f = 0.15 (30% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.35 – 8.32 (m, 1H), 7.80 (s, 1H), 7.46 (dd, *J* = 6.5, 2.0 Hz, 1H), 7.39 – 7.33 (m, 4H), 6.88 – 6.85 (m, 2H), 4.42 (t, *J* = 6.8 Hz, 2H), 3.83 (s, 3H), 2.43 (t, *J* = 6.6 Hz, 2H), 2.20 – 2.14 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 159.5, 138.6, 137.2, 133.0, 125.6, 124.1, 123.0, 122.3, 118.2, 115.4, 114.0, 110.1, 86.0, 82.3, 55.4, 45.8, 28.5, 16.7; HRMS (ESI) calcd for $C_{21}H_{20}NO_2$ $[M+H]^+$: 318.1489; found: 318.1496.

1-(5-(4-Nitrophenyl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2l)



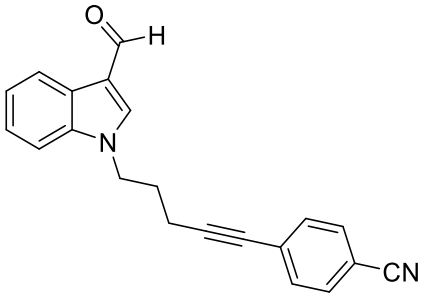
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) and 1-bromo-4-nitrobenzene (478 mg, 2.37 mmol, 1.0 equiv.). Black colour liquid (488 mg, 62% yield); R_f = 0.1 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.33 – 8.29 (m, 1H), 8.19 – 8.15 (m, 2H), 7.77 (s, 1H), 7.53 – 7.49 (m, 2H), 7.43 (dd, *J* = 6.4, 2.2 Hz, 1H), 7.38 – 7.30 (m, 2H), 4.40 (t, *J* = 6.7 Hz, 2H), 2.50 (t, *J* = 6.7 Hz, 2H), 2.23 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.5, 145.9, 137.1, 136.1, 131.3, 129.2, 124.6, 123.1, 122.6, 122.5, 122.1, 121.3, 117.4, 108.9, 92.5, 79.8, 44.9, 27.2, 15.9; HRMS (ESI) calcd for $C_{20}H_{17}N_2O_3$ $[M+H]^+$: 333.1234; found: 333.1266.

Methyl 4-(5-(3-formyl-1*H*-indol-1-yl)pent-1-yn-1-yl)benzoate (S-2m)



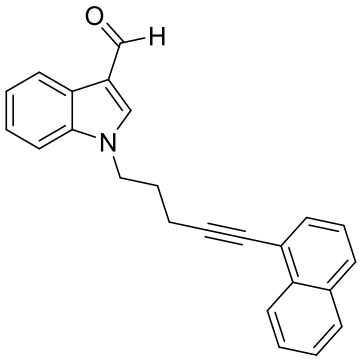
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol 1.0 equiv.) and methyl 4-bromobenzoate (508 mg, 2.37 mmol, 1.0 equiv.). Black colour liquid (531 mg, 65% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.34 – 8.29 (m, 1H), 8.01 – 7.98 (m, 2H), 7.78 (s, 1H), 7.48 – 7.43 (m, 3H), 7.37 – 7.30 (m, 2H), 4.40 (t, *J* = 6.7 Hz, 2H), 3.92 (s, 3H), 2.47 (t, *J* = 6.7 Hz, 2H), 2.20 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5, 166.5, 138.2, 137.2, 131.5, 129.6, 129.5, 128.0, 125.6, 124.1, 123.0, 122.3, 118.4, 110.0, 90.9, 81.9, 52.2, 45.8, 28.3, 16.9; HRMS (ESI) calcd for $C_{22}H_{20}NO_3$ $[M+H]^+$: 346.1438; found: 346.1447.

4-(5-(3-Formyl-1*H*-indol-1-yl)pent-1-yn-1-yl)benzonitrile (S-2n)



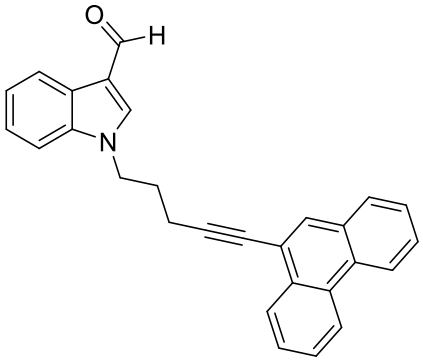
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) and 4-bromobenzonitrile (430 mg, 2.37 mmol, 1.0 equiv.). Black colour liquid (407 mg, 55% yield); R_f = 0.1 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.25 – 8.19 (m, 1H), 7.67 (s, 1H), 7.51 – 7.45 (m, 2H), 7.39 – 7.31 (m, 3H), 7.29 – 7.17 (m, 2H), 4.29 (t, *J* = 6.7 Hz, 2H), 2.39 (t, *J* = 6.7 Hz, 2H), 2.11 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.5, 137.3, 136.1, 131.1, 131.0, 127.2, 124.5, 123.1, 122.0, 121.2, 117.5, 117.3, 110.4, 109.0, 91.6, 79.9, 44.8, 27.2, 15.9; HRMS (ESI) calcd for $C_{21}H_{17}N_2O$ $[M+H]^+$: 313.1335; found: 313.1336.

1-(5-(Naphthalen-1-yl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2o)



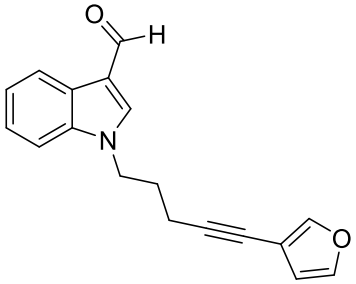
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol 1.0 equiv.) and 1-bromonaphthalene (490 mg, 2.37 mmol, 1.0 equiv.). Black colour liquid (383 mg, 48% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.35 – 8.29 (m, 2H), 7.88 – 7.81 (m, 2H), 7.79 (s, 1H), 7.66 (dd, *J* = 7.1, 1.0 Hz, 1H), 7.59 – 7.57 (m, 1H), 7.54 – 7.51 (m, 1H), 7.48 – 7.40 (m, 2H), 7.35 – 7.29 (m, 2H), 4.46 (t, *J* = 6.8 Hz, 2H), 2.58 (t, *J* = 6.6 Hz, 2H), 2.26 (p, *J* = 6.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.6, 138.6, 137.2, 133.4, 133.3, 130.4, 128.6, 128.5, 126.8, 126.5, 126.0, 125.6, 125.3, 124.1, 123.1, 122.3, 121.0, 118.3, 110.1, 92.6, 80.6, 45.9, 28.7, 17.0; HRMS (ESI) calcd for $C_{24}H_{20}NO$ $[M+H]^+$: 338.1539; found: 338.1541.

1-(5-(Phenanthren-9-yl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2p)



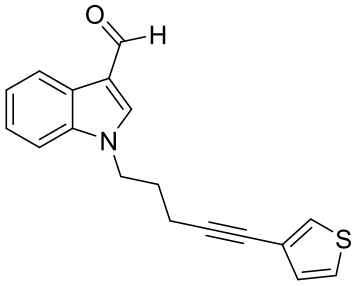
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) and 9-bromophenanthrene (608 mg, 2.37 mmol, 1.0 equiv.). Yellow colour liquid (623 mg, 68% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.73 – 8.65 (m, 2H), 8.45 – 8.41 (m, 1H), 8.35 – 8.32 (m, 1H), 7.98 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.83 (s, 1H), 7.74 – 7.65 (m, 3H), 7.64 – 7.59 (m, 1H), 7.51 – 7.48 (m, 1H), 7.37 – 7.31 (m, 2H), 4.51 (t, *J* = 6.8 Hz, 2H), 2.63 (t, *J* = 6.6 Hz, 2H), 2.31 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 138.6, 137.2, 131.8, 131.3, 131.2, 130.2, 128.5, 127.5, 127.1, 127.1, 126.7, 125.6, 124.1, 123.1, 122.9, 122.7, 122.3, 119.6, 118.4, 110.1, 92.2, 80.7, 45.9, 28.6, 17.0; HRMS (ESI) calcd for $C_{28}H_{22}NO$ $[M+H]^+$: 388.1696; found: 388.1701.

1-(5-(Furan-3-yl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2q)



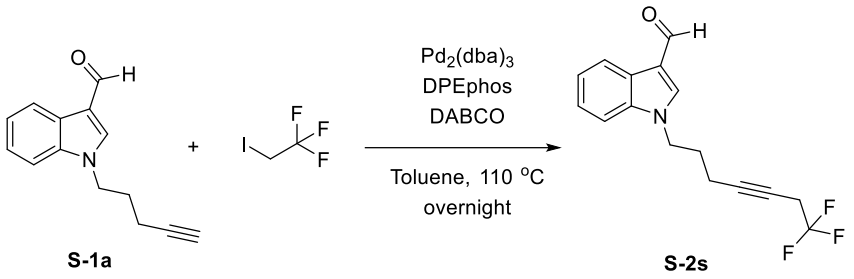
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) and 3-bromofuran (347 mg, 2.37 mmol, 1.0 equiv.). Black colour liquid (361 mg, 55% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.32 (dd, *J* = 6.0, 2.9 Hz, 1H), 7.77 (s, 1H), 7.59 (s, 1H), 7.43 (dd, *J* = 6.3, 2.5 Hz, 1H), 7.38 (t, *J* = 1.6 Hz, 1H), 7.37 – 7.30 (m, 2H), 6.43 (d, *J* = 1.5 Hz, 1H), 4.38 (t, *J* = 6.8 Hz, 2H), 2.40 (t, *J* = 6.6 Hz, 2H), 2.19 – 2.11 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 145.4, 142.9, 138.5, 137.2, 125.6, 124.1, 123.0, 122.3, 118.3, 112.6, 110.1, 89.3, 76.8, 73.4, 45.8, 28.3, 16.8; HRMS (ESI) calcd for $C_{18}H_{16}NO_2$ $[M+H]^+$: 278.1176; found: 278.1193.

1-(5-(Thiophen-3-yl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2r)



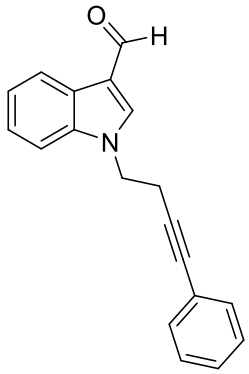
Prepared according to general procedure B using 1-(pent-4-yn-1-yl)-1H-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) and 3-bromothiophene (385 mg, 2.37 mmol, 1.0 equiv.). Black colour liquid (402 mg, 58% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.32 (dd, *J* = 6.4, 2.2 Hz, 1H), 7.77 (s, 1H), 7.44 (dd, *J* = 6.8, 1.9 Hz, 1H), 7.40 (d, *J* = 2.9 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.29 – 7.25 (m, 1H), 7.10 (dd, *J* = 5.0, 0.9 Hz, 1H), 4.39 (t, *J* = 6.8 Hz, 2H), 2.41 (t, *J* = 6.6 Hz, 2H), 2.16 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 138.5, 137.2, 129.9, 128.3, 125.6, 125.4, 124.1, 123.0, 122.3, 118.3, 110.1, 87.2, 45.8, 28.4, 16.7; HRMS (ESI) calcd for $C_{18}H_{16}NOS$ $[M+H]^+$: 294.0947; found: 294.0963.

1-(7,7,7-Trifluorohept-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2s)



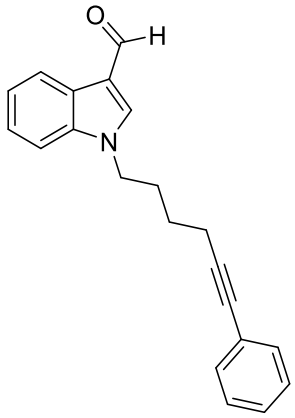
A screw-cap vial equipped with magnetic stir bar was charged with $Pd_2(dba)_3$ (108 mg, 0.12 mmol, 0.05 equiv.), DPEphos (253 mg, 0.47 mmol, 0.2 equiv.), DABCO (530 mg, 4.74 mmol, 2.0 equiv.).[2d] Under nitrogen atmosphere, 1,1,1-trifluoro-2-iodoethane (992 mg, 4.74 mmol, 2.0 equiv.) and 1-(pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (500 mg, 2.37 mmol, 1.0 equiv.) in toluene (5mL) was added by syringe and the vial was closed and stir it for overnight at 110 °C. Then the reaction mixture was cool to room temperature, diluted with ethyl acetate (20 mL), and washed with water (10 mL). The organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/ hexane) to afford compound **S-2s** as a yellow colour liquid (472 mg, 68%yield); R_f = 0.5 (40% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.32 (dd, *J* = 6.5, 2.0 Hz, 1H), 7.73 (s, 1H), 7.40 (dd, *J* = 6.8, 1.8 Hz, 1H), 7.36 – 7.30 (m, 2H), 4.34 (t, *J* = 6.7 Hz, 2H), 3.10 –3.03 (m, 2H), 2.22 – 2.19 (m, 2H), 2.08 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 138.5, 137.1, 125.5, 124.4 (q, $^1J_{C\text{-}F}$ = 277 Hz), 124.1, 123.0, 122.3, 118.3, 110.0, 82.7, 70.5 (q, $^3J_{C\text{-}F}$ = 5 Hz), 45.6, 29.7, 28.0, 26.3 (q, $^2J_{C\text{-}F}$ = 34 Hz), 15.8; HRMS (ESI) calcd for $C_{16}H_{15}F_3NO$ $[M+H]^+$: 294.1101; found: 294.1140.

1-(4-Phenyl-but-3-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2t)



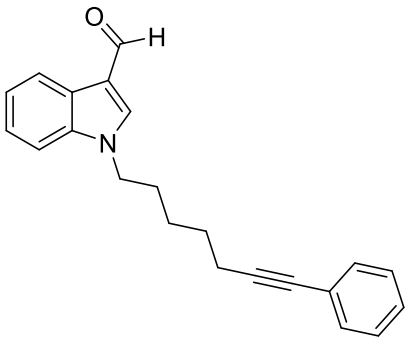
Prepared according to general procedure B using 1-(but-3-yn-1-yl)-1*H*-indole-3-carbaldehyde (400 mg, 2.03 mmol, 1.0 equiv.) and bromobenzene (318 mg, 2.03 mmol, 1.0 equiv.). Black colour liquid (288 mg, 52% yield); R_f = 0.2 (30% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.35 – 8.33 (m, 1H), 7.85 (s, 1H), 7.45 – 7.43 (m, 1H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 5H), 4.43 (t, *J* = 6.7 Hz, 2H), 2.97 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 138.7, 137.0, 131.5, 128.4, 128.3, 125.5, 124.2, 123.1, 122.7, 122.4, 118.5, 109.8, 85.2, 83.8, 46.1, 21.2; HRMS (ESI) calcd for $C_{19}H_{16}NO$ $[M+H]^+$: 274.1226; found: 274.1230.

1-(6-Phenylhex-5-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2u)



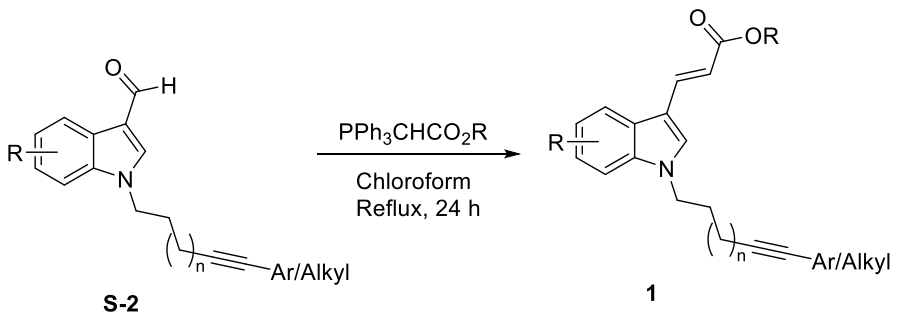
Prepared according to general procedure B using 1-(hex-5-yn-1-yl)-1*H*-indole-3-carbaldehyde (400 mg, 1.78 mmol, 1.0 equiv.) and bromobenzene (278 mg, 1.78 mmol, 1.0 equiv.). Black colour liquid (326 mg, 61% yield); R_f = 0.15 (30% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.34 – 8.30 (m, 1H), 7.75 (s, 1H), 7.43 – 7.40 (m, 1H), 7.38 – 7.35 (m, 2H), 7.33 – 7.31 (m, 2H), 7.30 – 7.27 (m, 3H), 4.26 (t, *J* = 7.1 Hz, 2H), 2.48 (t, *J* = 6.8 Hz, 2H), 2.15 – 2.09 (m, 2H), 1.69 – 1.63 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 138.1, 137.2, 131.6, 128.3, 127.9, 125.5, 124.0, 123.5, 123.0, 122.2, 118.2, 110.1, 88.8, 81.7, 46.9, 28.9, 25.7, 19.0; HRMS (ESI) calcd for $C_{21}H_{20}NO$ $[M+H]^+$: 302.1539; found: 302.1538.

1-(7-Phenylhept-6-yn-1-yl)-1*H*-indole-3-carbaldehyde (S-2v)



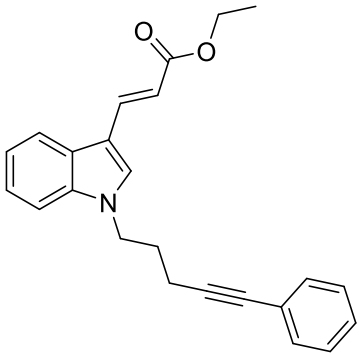
Prepared according to general procedure B using 1-(hept-6-yn-1-yl)-1*H*-indole-3-carbaldehyde (400 mg, 1.67 mmol, 1.0 equiv.) and bromobenzene (262 mg, 1.67 mmol, 1.0 equiv.). Black colour liquid (327 mg, 62% yield); R_f = 0.25 (30% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.32 – 8.30 (m, 1H), 7.72 (d, *J* = 1.2 Hz, 1H), 7.40 – 7.38 (m, 1H), 7.36 – 7.31 (m, 4H), 7.30 – 7.26 (m, 3H), 4.23 – 4.19 (m, 2H), 2.42 (t, *J* = 6.8 Hz, 2H), 2.00 – 1.93 (m, 2H), 1.69 – 1.62 (m, 2H), 1.57 – 1.51 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5, 138.2, 137.2, 131.5, 128.3, 127.7, 125.5, 124.0, 123.8, 122.9, 122.2, 118.1, 110.1, 89.4, 81.2, 47.2, 29.4, 28.1, 26.1, 19.2; HRMS (ESI) calcd for $C_{22}H_{22}NO$ $[M+H]^+$: 316.1696; found: 316.1696.

C. General procedure for witting reaction[3]



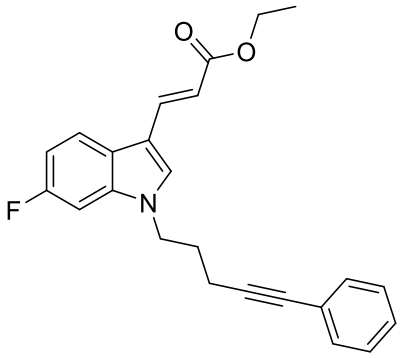
To a stirred solution of corresponding aldehyde (0.69 mmol, 1.0 equiv.) in $CHCl_3$ (20 mL) was added ethyl(triphenylphosphoranylidene)acetate (1.39 mmol, 2.0 equiv.) and the resulting solution was reflux for 16 h. The solvent was evaporated, and the resulting residue was purified by column chromatography on silica gel (EtOAc/ Hexane) to get the corresponding product **1**.

Ethyl (*E*)-3-(1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1a)



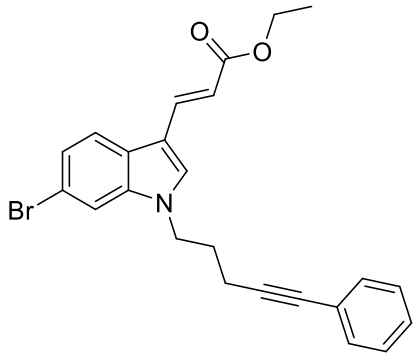
Prepared according to general procedure C using 1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.69 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (484 mg, 1.39 mmol, 2.0 equiv.). Light yellow solid (236 mg, 95% yield); R_f = 0.6 (20% EtOAc/hexane); mp = 100−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.45 – 7.40 (m, 4H), 7.34 – 7.23 (m, 5H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.35 (t, *J* = 6.7 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.40 (t, *J* = 6.6 Hz, 2H), 2.13 (p, *J* = 6.7 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 138.0, 137.4, 132.4, 131.6, 128.4, 128.0, 126.3, 123.4, 123.0, 121.3, 120.8, 112.8, 112.4, 110.1, 88.0, 82.3, 60.1, 45.2, 28.7, 16.7, 14.5; HRMS (ESI) calcd for $C_{24}H_{24}NO_2$ $[M+H]^+$: 358.1802; found: 358.1802.

Ethyl (*E*)-3-(6-fluoro-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1b)



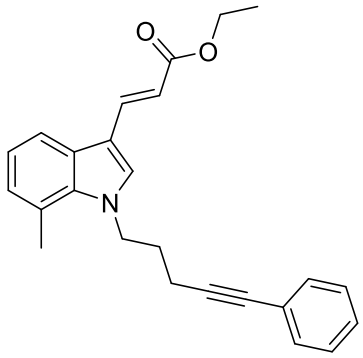
Prepared according to general procedure C using 6-fluoro-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.65 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene) acetate (456 mg, 1.30 mmol, 2.0 equiv.). White solid (216 mg, 88% yield); R_f = 0.6 (20% EtOAc/hexane); mp = 98−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.45 – 7.42 (m, 3H), 7.34 – 7.30 (m, 3H), 7.12 (dd, *J* = 9.5, 2.3 Hz, 1H), 7.03 – 6.97 (m, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.31 – 4.23 (m, 4H), 2.41 (t, *J* = 6.6 Hz, 2H), 2.11 (p, *J* = 6.7 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 160.2 (d, $^1J_{C\text{-}F}$ = 241 Hz), 137.6 (d, $^3J_{C\text{-}F}$ = 11 Hz), 137.5, 132.6, 131.6, 128.4, 128.1, 123.3, 122.7, 121.6 (d, $^3J_{C\text{-}F}$ = 10 Hz), 113.3, 112.6, 109.9 (d, $^2J_{C\text{-}F}$ = 24 Hz), 96.9 (d, $^2J_{C\text{-}F}$ = 26 Hz), 87.7, 82.4, 60.1, 45.3, 28.5, 16.7, 14.5; HRMS (ESI) calcd for $C_{24}H_{23}FNO_2$ $[M+H]^+$: 376.1707; found: 376.1719

Ethyl (*E*)-3-(6-bromo-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1c)



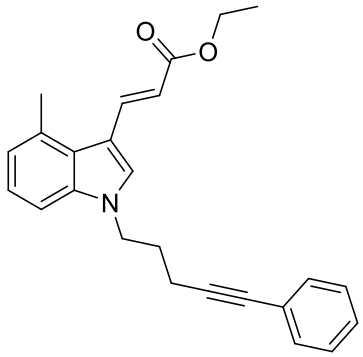
Prepared according to general procedure C using 6-bromo-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.55 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene) acetate (380 mg, 1.09 mmol, 2.0 equiv.). White solid (219 mg, 92% yield); R_f = 0.6 (20% EtOAc/hexane); mp = 100−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 1.6 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.42 (s, 1H), 7.34 – 7.31 (m, 4H), 6.37 (d, *J* = 16.0 Hz, 1H), 4.33 – 4.24 (m, 4H), 2.41 (t, *J* = 6.6 Hz, 2H), 2.12 (p, *J* = 6.6 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 138.2, 137.3, 132.5, 131.7, 128.4, 128.1, 125.1, 124.5, 123.3, 121.9, 116.7, 113.7, 113.3, 112.5, 87.6, 82.5, 60.2, 45.2, 28.6, 16.7, 14.5; HRMS (ESI) calcd for $C_{24}H_{23}BrNO_2$ $[M+H]^+$: 436.0907; found: 436.0910.

Ethyl (*E*)-3-(7-methyl-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1d)



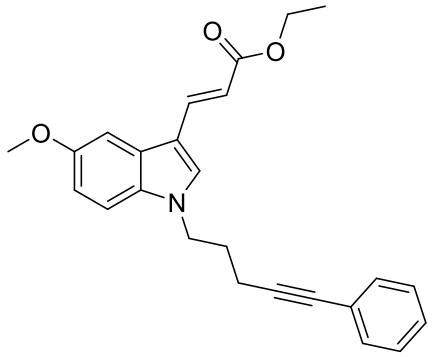
Prepared according to general procedure C using 7-methyl-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.66 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene) acetate (462 mg, 1.32 mmol, 2.0 equiv.). White solid (226 mg, 92% yield); R_f = 0.7 (20% EtOAc/hexane); mp = 106−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.40 (m, 3H), 7.34 – 7.30 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.53 (t, *J* = 7.1 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 3H), 2.44 (t, *J* = 6.6 Hz, 2H), 2.09 (p, *J* = 6.8 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 137.8, 135.9, 133.7, 131.6, 128.4, 128.0, 127.6, 126.2, 123.4, 121.5, 121.4, 118.6, 112.8, 112.2, 87.9, 82.4, 60.1, 47.9, 30.9, 20.0, 16.6, 14.5; HRMS (ESI) calcd for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1964; found: 372.1966.

Ethyl (*E*)-3-(4-methyl-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1e)



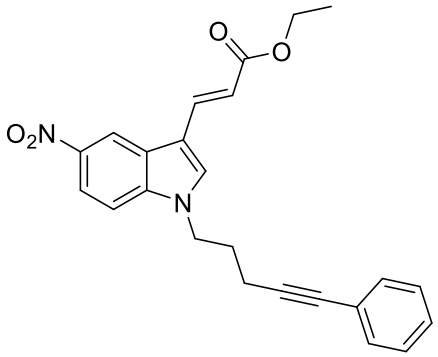
Prepared according to general procedure C using 4-methyl-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.66 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene) acetate (462 mg, 1.32 mmol, 2.0 equiv.). Yellow colour solid (201 mg, 89% yield); R_f = 0.7 (20% EtOAc/hexane); mp = 75−77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 15.7 Hz, 1H), 7.58 (s, 1H), 7.46 – 7.41 (m, 2H), 7.34 – 7.24 (m, 4H), 7.16 – 7.11 (m, 1H), 6.95 (d, *J* = 7.1 Hz, 1H), 6.20 (d, *J* = 15.7 Hz, 1H), 4.34 (t, *J* = 6.7 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.76 (s, 3H), 2.41 (t, *J* = 6.7 Hz, 2H), 2.13 (p, *J* = 6.7 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 139.0, 136.8, 131.6, 128.4, 128.0, 127.6, 125.9, 123.4, 122.9, 122.5, 113.4, 113.0, 108.0, 88.0, 82.2, 60.0, 45.4, 28.7, 21.2, 16.8, 14.5; HRMS (ESI) calcd for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1964; found: 372.1956.

Ethyl (*E*)-3-(5-methoxy-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1f)



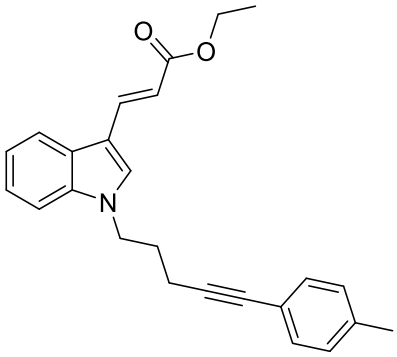
Prepared according to general procedure C using 5-methoxy-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.63 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene) acetate (439 mg, 1.26 mmol, 2.0 equiv.). Yellow solid (193 mg, 79% yield); R_f = 0.3 (20% EtOAc/hexane); mp = 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 15.9 Hz, 1H), 7.44 – 7.41 (m, 3H), 7.34 – 7.31 (m, 5H), 6.94 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 4.33 – 4.24 (m, 4H), 3.90 (s, 3H), 2.39 (t, *J* = 6.7 Hz, 2H), 2.11 (p, *J* = 6.6 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 155.5, 138.1, 132.5, 132.4, 131.6, 128.4, 128.0, 126.9, 123.4, 113.0, 112.1, 111.9, 110.9, 102.7, 87.9, 82.3, 60.1, 56.0, 45.4, 28.7, 16.7, 14.5; HRMS (ESI) calcd for $C_{25}H_{26}NO_3$ $[M+H]^+$: 388.1907; found: 388.1909.

Ethyl (*E*)-3-(5-nitro-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1g)



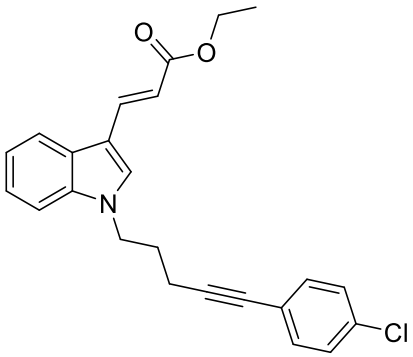
Prepared according to general procedure C using 5-nitro-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.60 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (419 mg, 1.20 mmol, 2.0 equiv.). Light Brown solid (194 mg, 80% yield); R_f = 0.4 (20% EtOAc/hexane); mp = 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.19 (dd, *J* = 9.1, 1.4 Hz, 1H), 7.85 (d, *J* = 16.1 Hz, 1H), 7.59 (s, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 7.42 – 7.40 (m, 2H), 7.35 – 7.32 (m, 2H), 6.48 (d, *J* = 16.1 Hz, 1H), 4.42 (t, *J* = 6.7 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.44 (t, *J* = 6.5 Hz, 2H), 2.16 (p, *J* = 6.6 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 142.8, 140.1, 135.8, 134.1, 131.6, 128.5, 128.2, 125.6, 123.1, 118.5, 117.6, 115.6, 114.5, 110.2, 87.3, 82.7, 60.5, 45.7, 28.7, 16.7, 14.5; HRMS (ESI) calcd for $C_{24}H_{23}N_2O_4$ $[M+H]^+$: 403.1652; found: 403.1649.

Ethyl (*E*)-3-(1-(5-(p-tolyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1h)



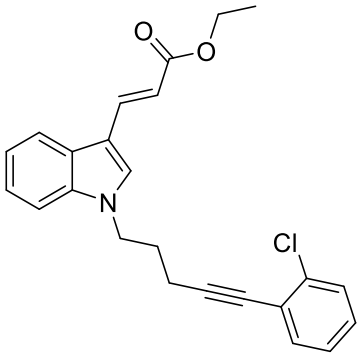
Prepared according to general procedure C using 1-(5-(*p*-tolyl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.66 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (462 mg, 1.32 mmol, 2.0 equiv.). Light yellow solid (197 mg, 80% yield); R_f = 0.5 (20% EtOAc/hexane); mp = 92−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.46 – 7.42 (m, 2H), 7.34 – 7.23 (m, 4H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.42 (d, *J* = 15.9 Hz, 1H), 4.35 (t, *J* = 6.7 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.39 (t, *J* = 6.6 Hz, 2H), 2.36 (s, 3H), 2.12 (p, *J* = 6.6 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 138.1, 138.0, 137.4, 132.4, 131.5, 129.1, 126.3, 123.0, 121.3, 120.8, 120.3, 112.8, 112.3, 110.2, 87.1, 82.4, 60.1, 45.2, 28.7, 21.5, 16.8, 14.5; HRMS (ESI) calcd for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1958; found: 372.1959.

Ethyl (*E*)-3-(1-(5-(4-chlorophenyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1i)



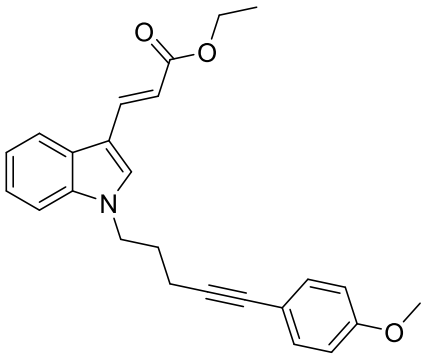
Prepared according to general procedure C using 1-(5-(4-chlorophenyl)pent-4-yn-1-yl)-1H-indole-3-carbaldehyde (200 mg, 0.62 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene) acetate (433 mg, 1.24 mmol, 2.0 equiv.). Light yellow solid (194 mg, 80% yield); R_f = 0.5 (20% EtOAc/hexane); mp = 92−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.37 – 7.33 (m, 2H), 7.28 – 7.16 (m, 6H), 6.34 (d, *J* = 15.9 Hz, 1H), 4.26 (t, *J* = 6.7 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.32 (t, *J* = 6.7 Hz, 2H), 2.06 (p, *J* = 6.7 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 136.9, 136.3, 133.0, 131.8, 131.3, 127.7, 125.3, 122.0, 120.1, 120.3, 119.8, 111.9, 111.4, 109.1, 88.0, 80.1, 59.1, 44.2, 27.5, 15.8, 13.5; HRMS (ESI) calcd for $C_{24}H_{23}ClNO_2$ $[M+H]^+$: 392.1412; found: 392.1432.

Ethyl (*E*)-3-(1-(5-(2-chlorophenyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1j)



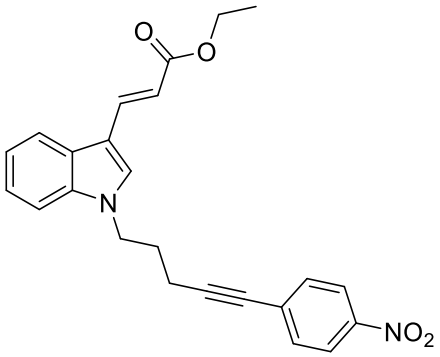
Prepared according to general procedure C using 1-(5-(2-chlorophenyl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.62 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene) acetate (433 mg, 1.24 mmol, 2.0 equiv.). Yellow solid (194 mg, 80% yield); R_f = 0.5 (20% EtOAc/hexane); mp = 83−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.51 (s, 1H), 7.47 – 7.40 (m, 3H), 7.32 – 7.19 (m, 4H), 6.42 (d, *J* = 15.9 Hz, 1H), 4.41 (t, *J* = 6.7 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.45 (t, *J* = 6.5 Hz, 2H), 2.14 (p, *J* = 6.6 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 138.0, 137.3, 135.9, 133.3, 132.6, 129.3, 129.1, 126.6, 126.3, 123.3, 123.0, 121.3, 120.8, 112.8, 112.3, 110.2, 93.6, 79.3, 60.1, 45.1, 28.5, 16.9, 14.5; HRMS (ESI) calcd for $C_{24}H_{23}ClNO_2$ $[M+H]^+$: 392.1412; found: 392.1419.

Ethyl (*E*)-3-(1-(5-(4-methoxyphenyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1k)



Prepared according to general procedure C using 1-(5-(4-methoxyphenyl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.63 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene) acetate (439 mg, 1.26 mmol, 2.0 equiv.). Yellow solid (176 mg, 72% yield); R_f = 0.5 (20% EtOAc/hexane); mp = 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.88 (m, 2H), 7.47 – 7.43 (m, 2H), 7.40 – 7.38 (m, 1H), 7.38 – 7.35 (m, 2H), 7.33 – 7.24 (m, 2H), 6.43 (d, *J* = 15.9 Hz, 1H), 4.36 (t, *J* = 6.7 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 2.40 (t, *J* = 6.6 Hz, 2H), 2.13 (p, *J* = 6.7 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 159.4, 138.0, 137.4, 133.0, 132.5, 126.3, 123.0, 121.3, 120.8, 114.0, 112.8, 112.3, 110.2, 86.3, 82.1, 60.1, 55.3, 45.2, 28.7, 16.8, 14.5; HRMS (ESI) calcd for $C_{25}H_{26}NO_3$ $[M+H]^+$: 388.1907; found: 388.1915.

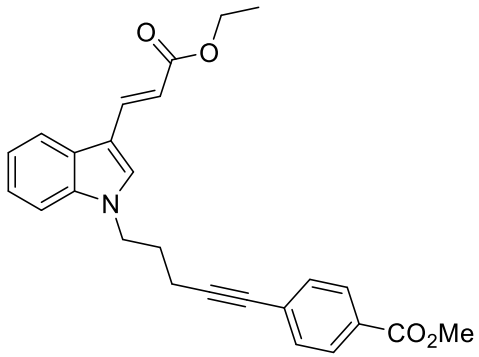
Ethyl (*E*)-3-(1-(5-(4-nitrophenyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1l)



Prepared according to general procedure C using 1-(5-(4-nitrophenyl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.60 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (419 mg, 1.20 mmol, 2.0 equiv.). Light yellow solid (203 mg, 84% yield); R_f = 0.3 (20% EtOAc/hexane); mp = 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 2H), 7.92 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.88 (d, *J* = 16.0 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.43 – 7.40 (m, 2H), 7.33 – 7.24 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.34 (t, *J* = 6.6 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.46 (t, *J* = 6.7 Hz, 2H), 2.18 (p, *J* = 6.7 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 146.9, 137.8, 137.3, 132.4, 132.2, 130.3, 126.3, 123.6, 123.1, 121.4, 120.9, 113.1, 112.5,

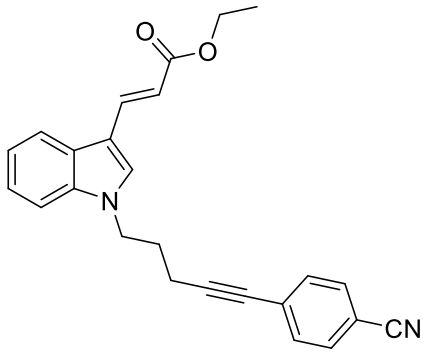
110.0, 93.9, 80.6, 60.1, 45.3, 28.4, 17.0, 14.5; HRMS (ESI) calcd for $C_{24}H_{23}N_2O_4$ $[M+H]^+$: 403.1652; found: 403.1672.

Methyl (*E*)-4-(5-(3-(3-ethoxy-3-oxoprop-1-en-1-yl)-1*H*-indol-1-yl)pent-1-yn-1-yl)benzoate (1m)



Prepared according to general procedure C using methyl 4-(5-(3-formyl-1*H*-indol-1-yl)pent-1-yn-1-yl)benzoate (200 mg, 0.58 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (403 mg, 1.15 mmol, 2.0 equiv.). Light yellow solid (202 mg, 84% yield); R_f = 0.3 (20% EtOAc/hexane); mp = 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.98 (m, 2H), 7.94 – 7.87 (m, 2H), 7.48 – 7.41 (m, 4H), 7.32 – 7.23 (m, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.34 (t, *J* = 6.7 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 2.43 (t, *J* = 6.7 Hz, 2H), 2.15 (p, *J* = 6.7 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 166.6, 137.9, 137.4, 132.3, 131.6, 129.6, 129.4, 128.1, 126.3, 123.0, 121.4, 120.8, 113.0, 112.5, 110.1, 91.3, 81.6, 60.1, 52.3, 45.2, 28.5, 16.9, 14.5; HRMS (ESI) calcd for $C_{26}H_{26}NO_4$ $[M+H]^+$: 416.1856; found: 416.1860.

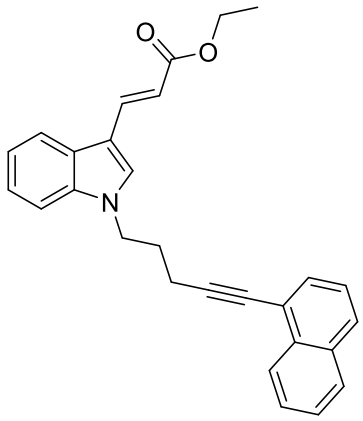
Ethyl (*E*)-3-(1-(5-(4-cyanophenyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1n)



Prepared according to general procedure C using 4-(5-(3-formyl-1*H*-indol-1-yl)pent-1-yn-1-yl)benzonitrile (200 mg, 0.64 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (446 mg, 1.24 mmol, 2.0 equiv.). Light yellow solid (205 mg, 84% yield); R_f = 0.2 (20% EtOAc/hexane); mp = 102−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.47 – 7.40 (m, 4H), 7.32 – 7.23 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.33 (t, *J* = 6.6 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.44 (t, *J* = 6.7 Hz, 2H), 2.16 (p, *J* = 6.7 Hz, 2H), 1.35 (t, *J*

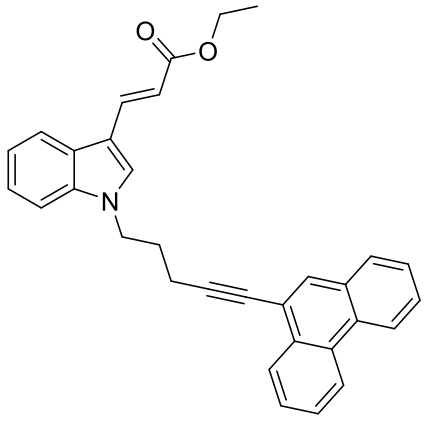
= 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 137.8, 137.3, 132.2, 132.1, 128.6, 128.5, 128.3, 126.3, 123.1, 121.4, 120.9, 118.5, 113.0, 112.5, 111.4, 110.0, 92.9, 80.8, 60.1, 45.3, 28.4, 16.9, 14.5; HRMS (ESI) calcd for $C_{25}H_{23}N_2O_2$ $[M+H]^+$: 383.1754; found: 383.1752.

Ethyl (*E*)-3-(1-(5-(naphthalen-1-yl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1o)



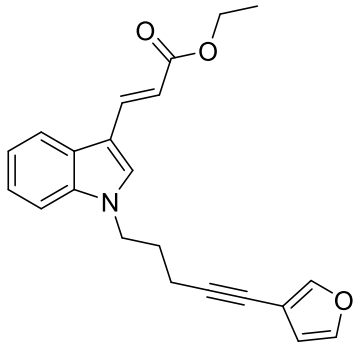
Prepared according to general procedure C using 1-(5-(naphthalen-1-yl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.59 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene) acetate (412 mg, 1.18 mmol, 2.0 equiv.). Light yellow solid (193 mg, 80% yield); R_f = 0.4 (20% EtOAc/hexane); mp = 113−115 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.59 (dd, *J* = 7.1, 1.0 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.47 – 7.44 (m, 1H), 7.42 (s, 1H), 7.40 – 7.35 (m, 2H), 7.25 – 7.14 (m, 3H), 6.35 (d, *J* = 15.9 Hz, 1H), 4.35 (t, *J* = 6.7 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.49 (t, *J* = 6.7 Hz, 2H), 2.16 (p, *J* = 6.7 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 138.0, 137.4, 133.5, 133.3, 132.4, 130.4, 128.5, 128.4, 126.8, 126.4, 126.3, 126.0, 125.3, 123.0, 121.4, 121.1, 120.8, 112.9, 112.4, 110.2, 92.9, 80.3, 60.1, 45.3, 28.9, 17.0, 14.5; HRMS (ESI) calcd for $C_{28}H_{26}NO_2$ $[M+H]^+$: 408.1958; found: 408.1956.

Ethyl (*E*)-3-(1-(5-(phenanthren-9-yl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1p)



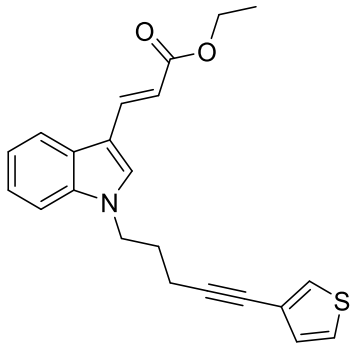
Prepared according to general procedure C using 1-(5-(phenanthren-9-yl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.51 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene) acetate (359 mg, 1.03 mmol, 2.0 equiv.). Light yellow solid (184 mg, 78% yield); R_f = 0.4 (20% EtOAc/hexane); mp = 142−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.65 (m, 2H), 8.46 – 8.42 (m, 1H), 7.97 – 7.85 (m, 4H), 7.75 – 7.59 (m, 4H), 7.52 – 7.47 (m, 2H), 7.33 – 7.24 (m, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.44 (t, *J* = 6.6 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.60 (t, *J* = 6.6 Hz, 2H), 2.26 (p, *J* = 6.6 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 137.9, 137.4, 132.3, 131.7, 131.3, 131.3, 130.2, 128.4, 127.4, 127.1, 127.0, 126.8, 126.3, 123.0, 122.9, 122.6, 121.4, 120.8, 119.8, 112.9, 112.4, 110.2, 92.6, 80.5, 60.1, 45.4, 28.9, 17.1, 14.5; HRMS (ESI) calcd for $C_{32}H_{28}NO_2$ $[M+H]^+$: 458.2115; found: 458.2120.

Ethyl (*E*)-3-(1-(5-(furan-3-yl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1q)



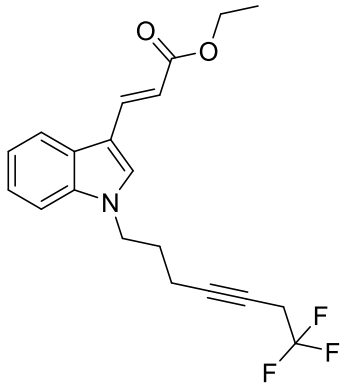
Prepared according to general procedure C using 1-(5-(furan-3-yl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.72 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (502 mg, 1.45 mmol, 2.0 equiv.). Brown solid (188 mg, 75% yield); R_f = 0.4 (20% EtOAc/hexane); mp = 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.59 (d, *J* = 0.7 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.39 – 7.37 (m, 1H), 7.32 – 7.23 (m, 2H), 6.44 – 6.40 (m, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.37 (t, *J* = 6.7 Hz, 2H), 2.11 (p, *J* = 6.7 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 145.3, 142.8, 138.0, 137.4, 132.3, 126.3, 123.0, 121.3, 120.8, 112.9, 112.6, 112.4, 110.1, 89.6, 73.1, 60.1, 45.2, 28.6, 16.8, 14.5; HRMS (ESI) calcd for $C_{22}H_{22}NO_3$ $[M+H]^+$: 348.1594; found: 348.1606.

Ethyl (*E*)-3-(1-(5-(thiophen-3-yl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1r)



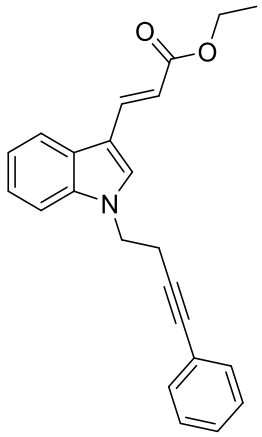
Prepared according to general procedure D using 1-(5-(thiophen-3-yl)pent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.68 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (474 mg, 1.37 mmol, 2.0 equiv.). White solid (203 mg, 82% yield); R_f = 0.4 (20% EtOAc/hexane); mp = 82−84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.44 – 7.39 (m, 3H), 7.30 – 7.25 (m, 3H), 7.09 (dd, *J* = 5.0, 1.1 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.32 (t, *J* = 6.7 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.37 (t, *J* = 6.7 Hz, 2H), 2.11 (p, *J* = 6.7 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 138.0, 137.4, 132.4, 129.9, 128.2, 126.3, 125.3, 123.0, 122.4, 121.3, 120.8, 112.9, 112.4, 110.2, 87.5, 60.1, 45.2, 28.6, 16.8, 14.5; HRMS (ESI) calcd for $C_{22}H_{22}NO_2S$ $[M+H]^+$: 364.1366; found: 364.1375.

Ethyl (*E*)-3-(1-(7,7,7-trifluorohept-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1s)



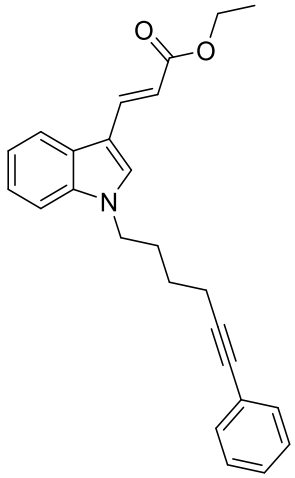
Prepared according to general procedure C using 1-(7,7,7-trifluorohept-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.68 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (475 mg, 1.36 mmol, 2.0 equiv.). Yellow solid (218 mg, 88% yield); R_f = 0.4 (20% EtOAc/hexane); mp = 83−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.41 – 7.38 (m, 2H), 7.32 – 7.23 (m, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.30 – 4.24 (m, 4H), 3.10 – 3.02 (m, 2H), 2.20 – 2.15 (m, 2H), 2.04 (p, *J* = 6.6 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 137.9, 137.3, 132.3, 126.3, 124.4 (q, $^1J_{C-F}$ = 278 Hz), 123.0, 121.3, 120.8, 112.9, 112.4, 110.1, 83.0, 70.2 (q, $^3J_{C-F}$ = 5 Hz), 60.1, 45.0, 28.3, 26.2 (q, $^2J_{C-F}$ = 34 Hz), 15.9, 14.5; HRMS (ESI) calcd for $C_{20}H_{21}F_3NO_2$ $[M+H]^+$: 364.1519; found: 364.1550.

Ethyl (*E*)-3-(1-(4-phenylbut-3-yn-1-yl)-1*H*-indol-3-yl)acrylate (1t)



Prepared according to general procedure C using 1-(4-phenylbut-3-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.73 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (509 mg, 1.46 mmol, 2.0 equiv.). Light yellow solid (213 mg, 85% yield); R_f = 0.4 (20% EtOAc/hexane); mp = 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.49 (s, 1H), 7.45 – 7.42 (m, 1H), 7.34 – 7.25 (m, 7H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.39 (t, *J* = 6.8 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.93 (t, *J* = 6.8 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 137.9, 137.2, 132.3, 131.6, 128.3, 128.2, 126.4, 123.1, 122.9, 121.4, 120.9, 113.1, 112.6, 110.0, 85.6, 83.5, 60.1, 45.7, 21.4, 14.5; HRMS (ESI) calcd for $C_{23}H_{22}NO_2$ $[M+H]^+$: 344.1645; found: 344.1646.

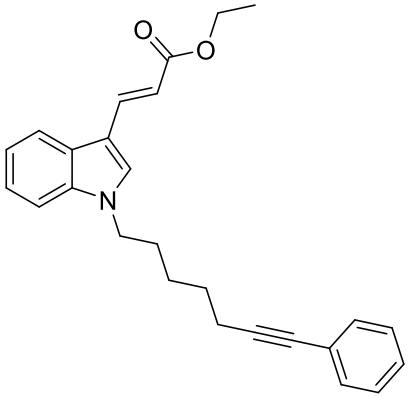
Ethyl (*E*)-3-(1-(6-phenylhex-5-yn-1-yl)-1*H*-indol-3-yl)acrylate (1u)



Prepared according to general procedure C using 1-(6-phenylhex-5-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.66 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (462 mg, 1.32 mmol, 2.0 equiv.). White solid (150 mg, 61% yield); R_f = 0.4 (20% EtOAc/hexane); mp = 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.40 (s, 1H), 7.39 – 7.35 (m, 2H), 7.30 – 7.22 (m, 5H), 6.41 (d, *J* = 15.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.20 (t, *J* = 7.1 Hz, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 2.10 – 2.02 (m, 2H), 1.67 – 1.59 (m, 2H),

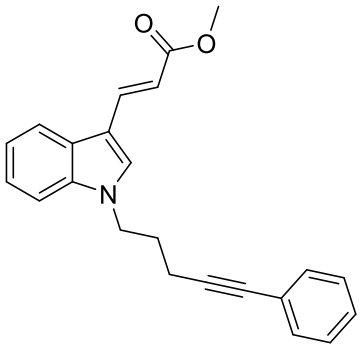
1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 138.0, 137.4, 132.1, 131.6, 128.3, 127.8, 126.3, 123.6, 122.9, 121.3, 120.8, 112.7, 112.3, 110.2, 89.0, 81.5, 60.1, 46.3, 29.1, 25.8, 19.0, 14.5; HRMS (ESI) calcd for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1958; found: 372.1956.

Ethyl (*E*)-3-(1-(7-phenylhept-6-yn-1-yl)-1*H*-indol-3-yl)acrylate (1v)



Prepared according to general procedure C using 1-(7-phenylhept-6-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.63 mmol, 1.0 equiv.) and ethyl(triphenylphosphoranylidene)acetate (441 mg, 1.26 mmol, 2.0 equiv.). White solid (195 mg, 80% yield); R_f = 0.4 (20% EtOAc/hexane); mp = 90−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.39 – 7.32 (m, 4H), 7.31 – 7.22 (m, 5H), 6.41 (d, *J* = 15.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.15 (t, *J* = 7.1 Hz, 2H), 2.40 (t, *J* = 6.9 Hz, 2H), 1.95 – 1.87 (m, 2H), 1.65 – 1.61 (m, 2H), 1.55 – 1.47 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 138.0, 137.4, 132.2, 131.5, 128.3, 127.7, 126.2, 123.8, 122.9, 121.2, 120.7, 112.7, 112.2, 110.1, 89.5, 81.1, 60.0, 46.7, 29.6, 28.2, 26.2, 19.3, 14.5; HRMS (ESI) calcd for $C_{26}H_{28}NO_2$ $[M+H]^+$: 386.2115; found: 386.2116.

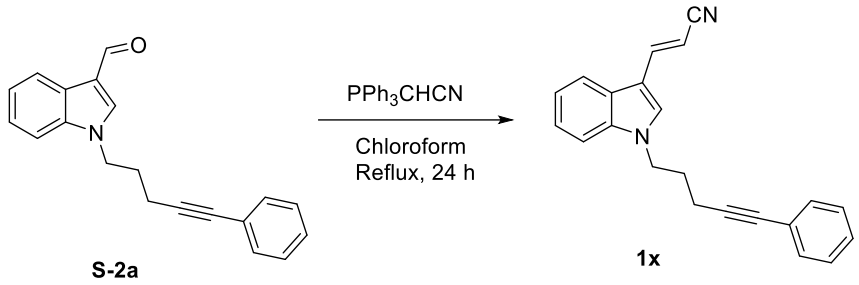
Methyl (*E*)-3-(1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (1w)



Prepared according to general procedure C using 1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.69 mmol, 1.0 equiv.) and methyl(triphenylphosphoranylidene)acetate (465 mg, 1.39 mmol, 2.0 equiv.). Colourless liquid (186 mg, 78% yield); R_f = 0.6 (20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.46 – 7.41 (m, 4H), 7.35 – 7.23 (m, 5H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.35 (t, *J* = 6.7 Hz, 2H), 3.80 (s, 3H), 2.40 (t, *J* = 6.6 Hz,

2H), 2.13 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 138.3, 137.4, 132.5, 131.6, 128.4, 128.0, 126.3, 123.4, 123.0, 121.4, 120.8, 112.3, 112.3, 110.2, 87.9, 82.3, 51.4, 45.2, 28.6, 16.8; HRMS (ESI) calcd for $C_{23}H_{22}NO_2$ $[M+H]^+$: 344.1651; found: 344.1653.

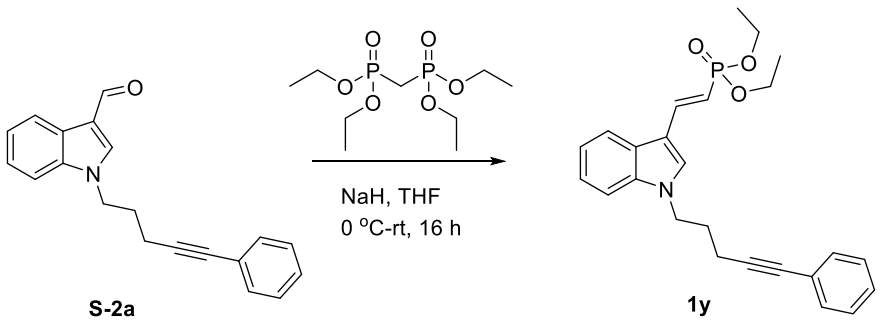
(*E*)-3-(1-(5-Phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylonitrile (1x)



S-2a 1x

Prepared according to general procedure C using 1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.69 mmol, 1.0 equiv.) and 2-(triphenylphosphoranylidene)acetonitrile (419 mg, 1.39 mmol, 2.0 equiv.). Colourless liquid (205 mg, 95% yield); R_f = 0.4 (20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 16.5 Hz, 1H), 7.48 – 7.41 (m, 4H), 7.36 – 7.26 (m, 5H), 5.74 (d, *J* = 16.5 Hz, 1H), 4.36 (t, *J* = 6.7 Hz, 2H), 2.42 (t, *J* = 6.6 Hz, 2H), 2.14 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 137.4, 132.3, 131.6, 128.4, 128.1, 125.7, 123.4, 123.4, 121.9, 120.3, 120.1, 112.1, 110.5, 89.8, 87.8, 82.4, 45.4, 28.6, 16.8; HRMS (ESI) calcd for $C_{22}H_{19}N_2$ $[M+H]^+$: 311.1543; found: 311.1544.

Diethyl (*E*)-(2-(1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)vinyl)phosphonate (1y)

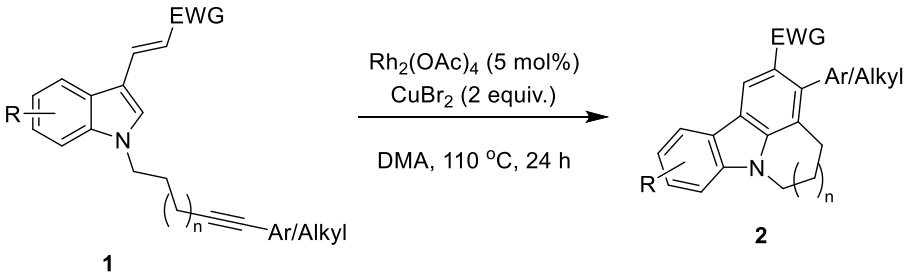


S-2a 1y

To a suspension of NaH (33 mg, 0.84 mmol, 1.2 equiv.) in THF (7 mL) was added tetraethyl methylenediphosphonate (240 mg, 0.84 mmol, 1.2 equiv.) in THF (1 mL) at 0 °C. A solution of 1-(5-phenylpent-4-yn-1-yl)-1*H*-indole-3-carbaldehyde (200 mg, 0.69 mmol 1.0 equiv.) in THF (10 mL) was added at the same temperature and the reaction was allowed to stir for overnight at room temperature. Then, the reaction was diluted with ethyl acetate (25 mL) and washed with water (15 mL), followed by brine solution (15 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (EtOAc/hexane) to get the title compound as a yellow colour liquid

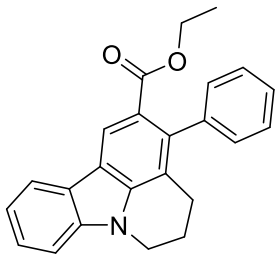
(228 mg, 78% yield). R_f = 0.4 (50% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.69 (dd, *J* = 23.3, 17.5 Hz, 1H), 7.45 – 7.41 (m, 4H), 7.34 – 7.22 (m, 5H), 6.10 (dd, *J* = 18.6, 17.6 Hz, 1H), 4.35 (t, *J* = 6.7 Hz, 2H), 4.18 – 4.09 (m, 4H), 2.40 (t, *J* = 6.6 Hz, 2H), 2.13 (p, *J* = 6.7 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4 (d, J_{C-P} = 7 Hz), 137.3, 131.9, 131.6, 128.4, 128.0, 126.1, 123.4, 122.9, 121.3, 120.5, 113.0 (d, J_{C-P} = 26 Hz), 110.2, 108.1, 106.1, 87.9, 82.3, 61.6 (d, J_{C-P} = 6 Hz), 45.2, 28.7, 16.7, 16.5 (d, J_{C-P} = 6 Hz); HRMS (ESI) calcd for $C_{25}H_{29}NO_3P$ $[M+H]^+$: 422.1880; found: 422.1877.

D. General procedure for intramolecular benzannulation reaction:



A screw-cap vial equipped with magnetic stir bar was charged with compound **1** (50 mg, 0.14 mmol, 1.0 equiv.), $CuBr_2$ (62 mg, 0.28 mmol, 2 equiv.), $Rh_2(OAc)_4$ (5 mol%) in Dry DMA (1 mL) under nitrogen atmosphere. The reaction mixture was stirred at 110 °C using an oil bath for 24 h. Then the reaction mixture was cooled to room temperature, diluted with saturated NH_4Cl solution (10 mL) and extracted with ethyl acetate (2 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/ hexane) to afford compound **2**.

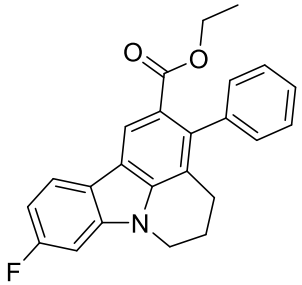
Ethyl 3-phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2a)



Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.14 mmol, 1.0 equiv.). White solid (37 mg, 75% yield); R_f = 0.2 (10% EtOAc/hexane); mp = 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.44 – 7.39 (m, 3H), 7.38 – 7.33 (m, 1H), 7.28 (m, 2H), 7.26-7.25 (m, 1H), 4.21 (t, *J* = 6.4 Hz, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 6.2 Hz, 2H), 2.25 – 2.17 (m, 2H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 140.7, 140.6, 139.6, 137.6, 129.1, 127.7, 126.6, 126.0, 122.9, 122.4, 121.3, 121.1, 119.6, 119.5, 119.3, 108.7,

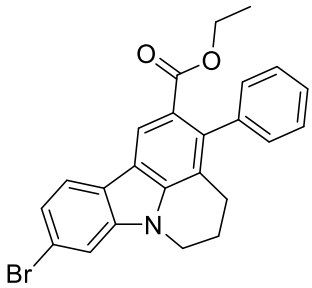
60.4, 40.9, 23.8, 22.3, 13.8; HRMS (ESI) calcd for $C_{24}H_{22}NO_2$ $[M+H]^+$: 356.1645; found: 356.1645.

Ethyl 9-fluoro-3-phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2b)



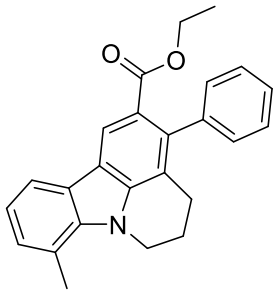
Prepared according to general procedure D using ethyl (*E*)-3-(6-fluoro-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol 1.0 equiv.). Brown solid (34 mg, 68% yield); R_f = 0.5 (10% EtOAc/hexane); mp = 166−168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.04 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.44 – 7.34 (m, 3H), 7.26 – 7.24 (m, 2H), 7.07 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.01 – 6.98 (m, 1H), 4.15 (t, *J* = 6.5 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.76 (t, *J* = 6.2 Hz, 2H), 2.23 – 2.17 (m, 2H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 163.2 (d, $^1J_{C-F}$ = 243 Hz), 141.4 (d, $^3J_{C-F}$ = 12 Hz), 140.4, 140.1, 137.4, 129.1, 127.8, 126.7, 122.9, 122.0 (d, $^3J_{C-F}$ = 10 Hz), 120.8, 119.6, 119.1 (d, $^4J_{C-F}$ = 11 Hz), 107.7 (d, $^2J_{C-F}$ = 24 Hz), 95.7 (d, $^2J_{C-F}$ = 26 Hz), 60.5, 41.1, 23.7, 22.2, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.43; HRMS (ESI) calcd for $C_{24}H_{21}FNO_2$ $[M+H]^+$: 374.1551; found: 374.1563.

Ethyl 9-bromo-3-phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2c)



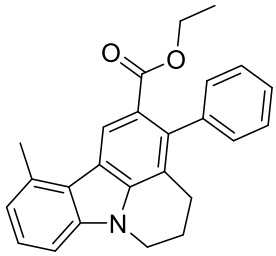
Prepared according to general procedure D using ethyl (*E*)-3-(6-bromo-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.11 mmol, 1.0 equiv.). White solid (29 mg, 58% yield); R_f = 0.5 (10% EtOAc/hexane); mp = 140−142 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.44 – 7.35 (m, 5H), 7.25 – 7.24 (m, 1H), 4.17 (t, *J* = 6.2 Hz, 2H), 4.07 – 4.02 (m, 2H), 2.78 – 2.75 (m, 2H), 2.23 – 2.18 (m, 2H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 141.5, 140.3, 139.7, 138.1, 129.1, 127.8, 126.7, 123.1, 122.8, 122.2, 121.8, 121.2, 119.8, 119.6, 118.9, 111.9, 60.5, 41.0, 23.7, 22.2, 13.8; HRMS (ESI) calcd for $C_{24}H_{21}BrNO_2$ $[M+H]^+$: 434.0750; found: 434.0742.

Ethyl 8-methyl-3-phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2d)



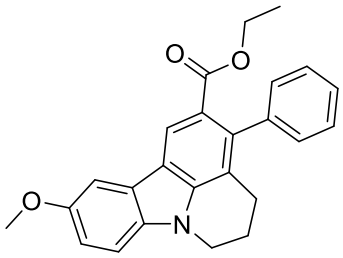
Prepared according to general procedure D using ethyl (*E*)-3-(7-methyl-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol, 1.0 equiv.). Brown solid (36 mg, 72% yield); R_f = 0.5 (10% EtOAc/hexane); mp = 187−189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.99 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.44 – 7.33 (m, 3H), 7.27 – 7.24 (m, 2H), 7.21 – 7.13 (m, 2H), 4.63 (t, *J* = 7.1 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.83 (s, 3H), 2.74 – 2.69 (m, 2H), 2.22 – 2.15 (m, 2H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 140.7, 139.8, 139.7, 137.4, 129.2, 128.8, 127.7, 126.6, 123.3, 122.3, 120.9, 120.6, 119.8, 119.7, 118.8, 60.4, 44.4, 23.7, 23.2, 20.0, 13.8; HRMS (ESI) calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1807; found: 370.1813.

Ethyl 11-methyl-3-phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2e)



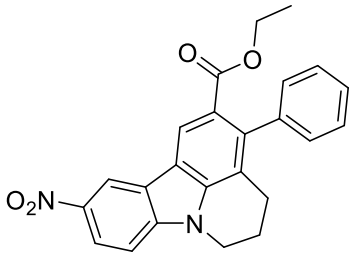
Prepared according to general procedure D using ethyl (*E*)-3-(4-methyl-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol, 1.0 equiv.). Colourless liquid (33 mg, 68% yield); R_f = 0.5 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.44 – 7.33 (m, 4H), 7.29 – 7.24 (m, 3H), 7.06 (d, *J* = 7.3 Hz, 1H), 4.22 – 4.17 (m, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.93 (s, 3H), 2.78 (t, *J* = 6.2 Hz, 2H), 2.23 – 2.15 (m, 2H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 140.8, 140.6, 139.4, 137.0, 134.0, 129.2, 127.7, 126.6, 125.9, 123.1, 122.5, 121.5, 121.0, 119.9, 119.2, 106.2, 60.4, 40.9, 23.9, 22.2, 20.6, 13.7; HRMS (ESI) calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1807; found: 370.1824.

Ethyl 10-methoxy-3-phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2f)



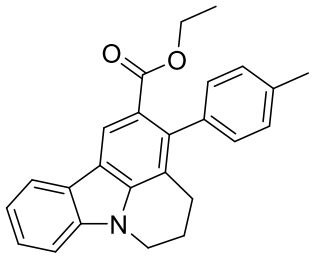
Prepared according to general procedure D using ethyl (*E*)-3-(5-methoxy-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol, 1.0 equiv.). White solid (30 mg, 61% yield); R_f = 0.4 (10% EtOAc/hexane); mp = 138-140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.64 (d, *J* = 2.4 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.38 – 7.34 (m, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.14 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.18 (t, *J* = 6.2 Hz, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 2.75 (t, *J* = 6.2 Hz, 2H), 2.22 – 2.17 (m, 2H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 154.1, 140.7, 140.0, 137.5, 135.8, 129.1, 127.7, 126.6, 123.2, 121.8, 121.4, 119.5, 119.1, 115.3, 109.3, 104.0, 60.4, 56.1, 40.9, 23.7, 22.3, 13.8; HRMS (ESI) calcd for $C_{25}H_{24}NO_3$ $[M+H]^+$: 386.1751; found: 386.1747.

Ethyl 10-nitro-3-phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2g)



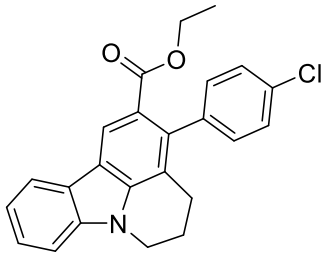
Prepared according to general procedure D using ethyl (*E*)-3-(5-nitro-1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.12 mmol, 1.0 equiv.). Light Yellow solid (26 mg, 52% yield); R_f = 0.2 (10% EtOAc/hexane); mp = 178−180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 2.2 Hz, 1H), 8.60 (s, 1H), 8.41 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.46 – 7.38 (m, 5H), 7.27 – 7.24 (m, 1H), 4.27 (t, *J* = 6.4 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.79 (t, *J* = 6.1 Hz, 2H), 2.28 – 2.22 (m, 2H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 143.7, 141.2, 140.7, 139.7, 139.3, 128.9, 127.9, 127.1, 124.6, 122.6, 122.0, 121.5, 120.8, 119.5, 118.0, 108.3, 60.8, 41.5, 23.5, 22.1, 13.8; HRMS (ESI) calcd for $C_{24}H_{21}N_2O_4$ $[M+H]^+$: 401.1496; found: 401.1498.

Ethyl 3-(*p*-tolyl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2h)



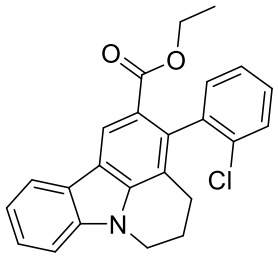
Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-(*p*-tolyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol, 1.0 equiv.). Colourless liquid (31 mg, 62% yield); R_f = 0.5 (10% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.28 (m, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.16 – 7.14 (m, 2H), 4.23 – 4.20 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.78 (t, *J* = 6.6 Hz, 2H), 2.43 (s, 3H), 2.23 – 2.18 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 140.7, 139.6, 137.7, 137.4, 136.1, 129.0, 128.5, 125.9, 122.9, 122.5, 121.2, 121.1, 119.5, 119.2, 108.6, 60.4, 40.9, 23.8, 22.3, 21.3, 13.9; HRMS (ESI) calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802; found: 370.1802.

Ethyl 3-(4-chlorophenyl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2i)



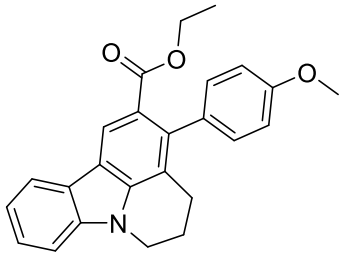
Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-(4-chlorophenyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol, 1.0 equiv.). Grey colour liquid (32 mg, 64% yield); R_f = 0.5 (10% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.44 – 7.38 (m, 3H), 7.32 – 7.28 (m, 1H), 7.21 – 7.18 (m, 2H), 4.24 – 4.20 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 6.2 Hz, 2H), 2.25 – 2.19 (m, 2H), 1.07 (t, *J* = 7.1 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 139.7, 138.5, 138.1, 135.4, 131.6, 129.5, 126.9, 125.1, 121.8, 120.8, 120.6, 120.1, 118.7, 118.5, 107.7, 59.5, 39.8, 22.7, 21.2, 12.9; HRMS (ESI) calcd for $C_{24}H_{21}ClNO_2$ $[M+H]^+$: 390.1255; found: 390.1281.

Ethyl 3-(2-chlorophenyl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2j)



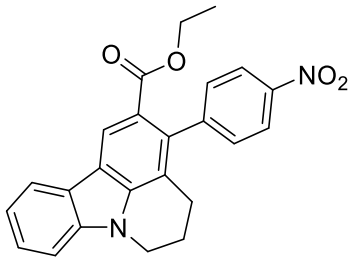
Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-(2-chlorophenyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol, 1.0 equiv.). Colourless liquid (32 mg, 65% yield); R_f = 0.5 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.23 – 7.20 (m, 1H), 4.25 – 4.20 (m, 2H), 4.11 (qd, *J* = 7.1, 1.9 Hz, 2H), 2.73 – 2.59 (m, 2H), 2.28 – 2.21 (m, 2H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 139.7, 138.8, 138.7, 134.0, 132.5, 129.5, 127.9, 127.2, 125.3, 125.1, 121.9, 120.9, 120.2, 118.8, 118.7, 107.7, 59.3, 39.8, 22.2, 21.2, 12.8; HRMS (ESI) calcd for $C_{24}H_{21}ClNO_2$ $[M+H]^+$: 390.1255; found: 390.1265.

Ethyl 3-(4-methoxyphenyl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2k)



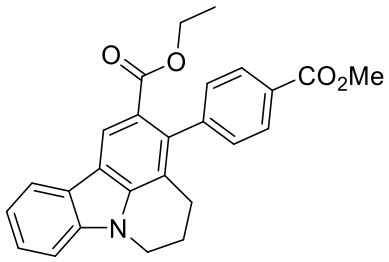
Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-(4-methoxyphenyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol, 1.0 equiv.). Colourless liquid (19 mg, 38% yield); R_f = 0.4 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.29 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.20 – 7.16 (m, 2H), 6.98 – 6.94 (m, 2H), 4.23 – 4.19 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 2.79 (t, *J* = 6.2 Hz, 2H), 2.24 – 2.18 (m, 2H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 158.4, 140.7, 139.5, 137.3, 132.7, 130.2, 125.9, 122.9, 122.7, 121.2, 121.1, 119.8, 119.5, 119.1, 113.2, 108.6, 60.4, 55.3, 40.9, 23.9, 22.3, 14.0; HRMS (ESI) calcd for $C_{25}H_{24}NO_3$ $[M+H]^+$: 386.1751; found: 386.1751.

Ethyl 3-(4-nitrophenyl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2l)



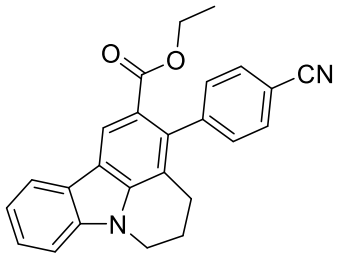
Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-(4-nitrophenyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.12 mmol, 1.0 equiv.). White solid (37 mg, 75% yield); R_f = 0.4 (10% EtOAc/hexane); mp = 198-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.32 – 8.28 (m, 2H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.46 – 7.42 (m, 3H), 7.35 – 7.30 (m, 1H), 4.26 – 4.21 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.69 (t, *J* = 6.1 Hz, 2H), 2.27 – 2.20 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 148.4, 146.8, 140.9, 139.6, 135.7, 130.1, 126.5, 123.1, 122.7, 122.1, 121.3, 120.8, 120.0, 119.2, 108.9, 60.6, 40.8, 23.7, 22.2, 14.0; HRMS (ESI) calcd for $C_{24}H_{21}N_2O_4$ $[M+H]^+$: 401.1496; found: 401.1519.

Ethyl 3-(4-(methoxycarbonyl)phenyl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2m)



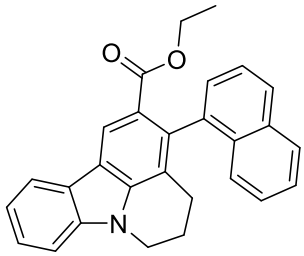
Prepared according to general procedure D using methyl (*E*)-4-(5-(3-(3-ethoxy-3-oxoprop-1-en-1-yl)-1*H*-indol-1-yl)pent-1-yn-1-yl)benzoate (50 mg, 0.12 mmol, 1.0 equiv.). Grey colour liquid (36 mg, 72% yield); R_f = 0.3 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.12 – 8.19 (m, 2H), 7.54 – 7.50 (m, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 4.24 – 4.20 (m, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 2.71 (t, *J* = 6.1 Hz, 2H), 2.25 – 2.18 (m, 2H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 166.2, 145.0, 139.7, 138.5, 135.7, 128.2, 128.1, 127.4, 125.2, 121.7, 120.7, 120.5, 120.2, 118.7, 118.6, 118.2, 107.7, 59.5, 51.1, 39.8, 22.7, 21.2, 12.9; HRMS (ESI) calcd for $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1700; found: 414.1710.

Ethyl 3-(4-cyanophenyl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2n)



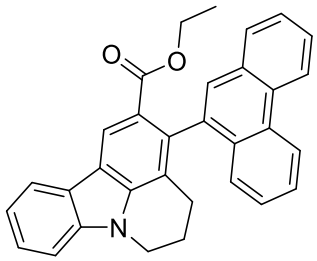
Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-(4-cyanophenyl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol, 1.0 equiv.). Light yellow solid (35 mg, 70% yield); R_f = 0.5 (10% EtOAc/hexane); mp = 200–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.71 (m, 2H), 7.56 – 7.51 (m, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.34 – 7.29 (m, 1H), 4.25 – 4.21 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.68 (t, *J* = 6.1 Hz, 2H), 2.27 – 2.20 (m, 2H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 146.2, 140.8, 139.6, 135.9, 131.6, 130.0, 126.4, 122.7, 122.0, 121.3, 121.0, 120.0, 119.9, 119.2, 110.5, 108.8, 60.6, 40.8, 23.7, 22.2, 14.0; HRMS (ESI) calcd for $C_{25}H_{21}N_2O_2$ $[M+H]^+$: 381.1598; found: 381.1599.

Ethyl 3-(naphthalen-1-yl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2o)



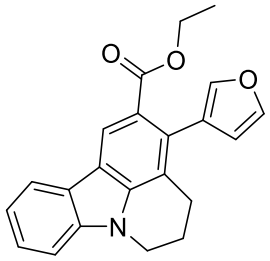
Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-(naphthalen-1-yl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.12 mmol, 1.0 equiv.). Colourless liquid (32 mg, 65% yield); R_f = 0.5 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.55 – 7.50 (m, 2H), 7.47 – 7.40 (m, 3H), 7.34 – 7.29 (m, 3H), 4.24 – 4.20 (m, 2H), 3.85 – 3.77 (m, 2H), 2.68 – 2.60 (m, 1H), 2.49 – 2.42 (m, 1H), 2.21 – 2.11 (m, 2H), 0.58 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 140.8, 139.8, 138.7, 135.8, 133.4, 132.8, 128.1, 127.1, 126.2, 126.1, 125.9, 125.5, 125.2, 123.0, 122.8, 121.8, 121.2, 120.5, 119.7, 119.6, 108.7, 60.1, 40.9, 23.4, 22.3, 13.3; HRMS (ESI) calcd for $C_{28}H_{24}NO_2$ $[M+H]^+$: 406.1802; found: 406.1822.

Ethyl 3-(phenanthren-9-yl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2p)



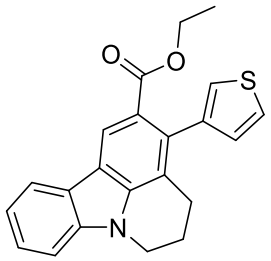
Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-(phenanthren-9-yl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.11 mmol, 1.0 equiv.). Yellow solid (33 mg, 67% yield); R_f = 0.5 (10% EtOAc/hexane); mp = 218–220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 – 8.74 (m, 3H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.70 – 7.41 (m, 8H), 7.35 – 7.30 (m, 1H), 4.25 – 4.18 (m, 2H), 3.81 – 3.76 (m, 2H), 2.76 – 2.69 (m, 1H), 2.54 – 2.46 (m, 1H), 2.21 – 2.10 (m, 2H), 0.46 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 140.8, 139.9, 137.4, 135.8, 132.4, 131.8, 130.1, 130.0, 128.5, 126.7, 126.6, 126.4, 126.3, 126.2, 126.1, 123.0, 122.8, 122.8, 122.6, 121.9, 121.3, 120.7, 119.8, 119.7, 108.8, 60.2, 40.9, 23.5, 22.3, 13.2; HRMS (ESI) calcd for $C_{32}H_{26}NO_2$ $[M+H]^+$: 456.1958; found: 456.1965.

Ethyl 3-(furan-3-yl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2q)



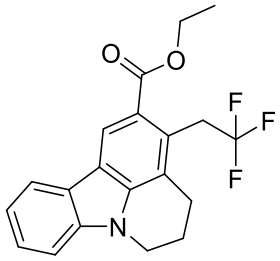
Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-(furan-3-yl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.14 mmol, 1.0 equiv.). Light yellow solid (27 mg, 54% yield); R_f = 0.4 (10% EtOAc/hexane); mp = 115−117 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.15 – 8.12 (m, 1H), 7.53 (t, *J* = 1.7 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.43 – 7.38 (m, 2H), 7.29 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.47 (dd, *J* = 1.7, 0.8 Hz, 1H), 4.24 – 4.18 (m, 4H), 2.92 (t, *J* = 6.2 Hz, 2H), 2.28 – 2.22 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 142.2, 140.7, 139.9, 139.4, 127.6, 126.0, 123.3, 123.1, 122.8, 121.2, 121.0, 120.6, 119.6, 119.4, 113.0, 108.7, 60.7, 40.8, 23.9, 22.3, 14.0; HRMS (ESI) calcd for $C_{22}H_{20}NO_3$ $[M+H]^+$: 346.1438; found: 346.1447.

Ethyl 3-(thiophen-3-yl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2r)



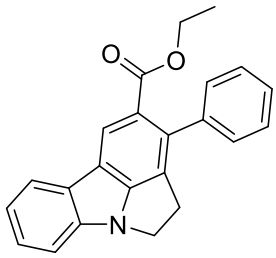
Prepared according to general procedure D using ethyl (*E*)-3-(1-(5-(thiophen-3-yl)pent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.14 mmol, 1.0 equiv.). Brown solid (26 mg, 52% yield); R_f = 0.4 (10% EtOAc/hexane); mp = 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.15 – 8.13 (m, 1H), 7.52 – 7.48 (m, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.38 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.10 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.07 (dd, *J* = 4.9, 1.3 Hz, 1H), 4.23 – 4.19 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.84 (t, *J* = 6.2 Hz, 2H), 2.27 – 2.20 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 140.7, 140.0, 139.5, 132.1, 129.6, 126.0, 124.3, 123.0, 122.1, 121.2, 120.2, 119.6, 119.4, 108.7, 60.6, 40.9, 23.8, 22.3, 13.9; HRMS (ESI) calcd for $C_{22}H_{20}NO_2S$ $[M+H]^+$: 362.1209; found: 362.1220.

Ethyl 3-(2,2,2-trifluoroethyl)-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2s)



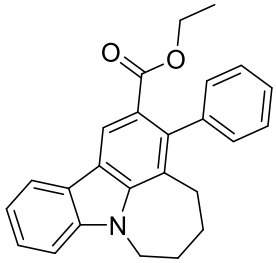
Prepared according to general procedure G using ethyl (*E*)-3-(1-(7,7,7-trifluorohept-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.14 mmol, 1.0 equiv.). Colourless liquid (32 mg, 65% yield); R_f = 0.5 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.18 (m, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.25 (q, *J* = 9.2 Hz, 2H), 4.16 – 4.12 (m, 2H), 3.06 – 3.02 (m, 2H), 2.31 – 2.24 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 139.5, 138.6, 125.5 (q, $^1J_{C\text{-}F}$ = 278 Hz), 125.2, 123.6, 121.6, 121.4, 121.2, 121.0, 120.1, 118.7, 118.6, 107.7, 59.8, 39.6, 30.1 (q, $^2J_{C\text{-}F}$ = 31 Hz), 22.1, 21.2, 13.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.25; HRMS (ESI) calcd for $C_{20}H_{19}F_3NO_2$ $[M+H]^+$: 362.1362; found: 362.1392.

Ethyl 3-phenyl-4,5-dihydropyrrolo[3,2,1-*jk*]carbazole-2-carboxylate (2t)



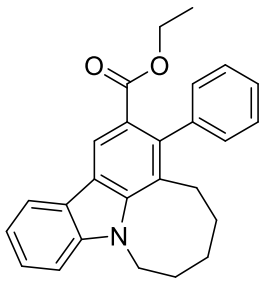
Prepared according to general procedure D using ethyl (*E*)-3-(1-(4-phenylbut-3-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.15 mmol, 1.0 equiv.). Light yellow liquid (32 mg, 65% yield); R_f = 0.5 (10% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.32 (m, 7H), 7.28 – 7.25 (m, 1H), 4.55 (t, *J* = 7.4 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.75 (t, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 153.6, 140.9, 140.4, 135.7, 128.6, 128.0, 127.8, 126.8, 125.6, 124.3, 123.9, 123.3, 122.7, 119.6, 113.9, 110.6, 60.6, 48.8, 33.8, 13.8; HRMS (ESI) calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$: 342.1489; found: 342.1490.

Ethyl 3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-*jk*]carbazole-2-carboxylate (2u)



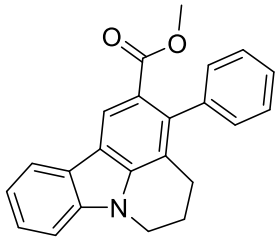
Prepared according to general procedure D using ethyl (*E*)-3-(1-(6-phenylhex-5-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol, 1.0 equiv.). Colourless liquid (34 mg, 69% yield); R_f = 0.6 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.11 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.43 – 7.34 (m, 4H), 7.29 – 7.24 (m, 3H), 4.46 – 4.42 (m, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.95 – 2.91 (m, 2H), 2.25 – 2.19 (m, 2H), 2.07 – 2.00 (m, 2H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 143.6, 142.4, 141.4, 139.0, 129.5, 127.7, 126.6, 126.1, 124.8, 123.6, 123.2, 122.0, 120.7, 120.5, 119.7, 109.3, 60.5, 44.3, 27.9, 27.8, 26.6, 13.8; HRMS (ESI) calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802; found: 370.1801.

Ethyl 3-phenyl-5,6,7,8-tetrahydro-4*H*-azocino[3,2,1-*jk*]carbazole-2-carboxylate (2v)



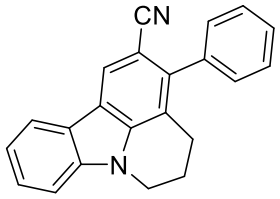
Prepared according to general procedure D using ethyl (*E*)-3-(1-(7-phenylhept-6-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.13 mmol, 1.0 equiv.). Light yellow solid (31 mg, 62% yield); R_f = 0.65 (10% EtOAc/hexane); mp = 128−130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.43 – 7.36 (m, 4H), 7.30 – 7.26 (m, 1H), 7.25 – 7.22 (m, 2H), 4.78 (bs, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.12 (bs, 2H), 2.07 – 2.00 (m, 2H), 1.79 – 1.73 (m, 2H), 1.42 (bs, 2H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 143.3, 141.5, 141.3, 140.3, 129.4, 127.5, 126.6, 126.0, 123.3, 122.7, 121.2, 120.8, 120.4, 119.6, 108.4, 60.4, 43.1, 30.2, 29.2, 27.5, 21.4, 13.8; HRMS (ESI) calcd for $C_{26}H_{26}NO_2$ $[M+H]^+$: 384.1958; found: 384.1954.

Methyl 3-phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carboxylate (2w)



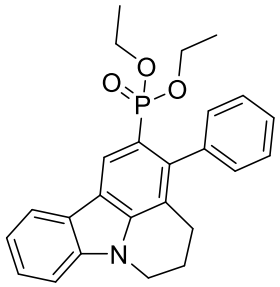
Prepared according to general procedure D using methyl (*E*)-3-(1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (50 mg, 0.14 mmol, 1.0 equiv.). Colourless liquid (35 mg, 71% yield); R_f = 0.4 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.45 – 7.34 (m, 4H), 7.31 – 7.23 (m, 3H), 4.23 – 4.16 (m, 2H), 3.62 (s, 3H), 2.75 (t, *J* = 6.2 Hz, 2H), 2.24 – 2.15 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 140.8, 140.4, 139.6, 138.0, 129.0, 127.8, 126.7, 126.0, 122.9, 121.7, 121.4, 121.1, 119.7, 119.2, 108.7, 51.7, 40.9, 23.8, 22.3; HRMS (ESI) calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$: 342.1494; found: 342.1507.

3-Phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole-2-carbonitrile (2x)



Prepared according to general procedure D using (*E*)-3-(1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylonitrile (50 mg, 0.16 mmol, 1.0 equiv.). White solid (30 mg, 60% yield); R_f = 0.4 (10% EtOAc/hexane); mp = 240−242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.46 – 7.40 (m, 4H), 7.35 – 7.31 (m, 1H), 4.24 – 4.20 (m, 2H), 2.88 – 2.85 (m, 2H), 2.24 – 2.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 139.7, 139.2, 137.0, 129.8, 128.4, 128.2, 126.7, 124.3, 121.9, 121.2, 120.1, 120.2, 119.8, 119.7, 108.9, 102.6, 40.9, 23.8, 22.0; HRMS (ESI) calcd for $C_{22}H_{17}N_2$ $[M+H]^+$: 309.1386; found: 309.1388.

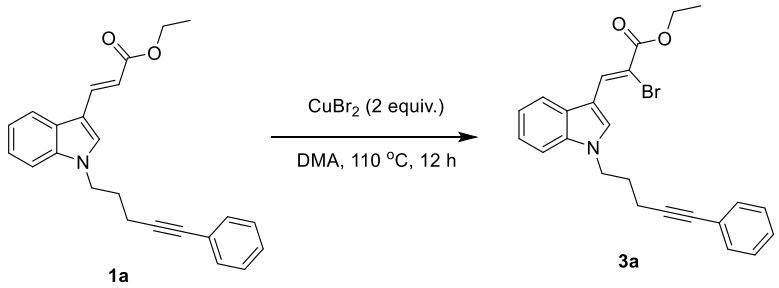
Diethyl (3-phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazol-2-yl)phosphonate (2y)



Prepared according to general procedure D using diethyl (*E*)-(2-(1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)vinyl)phosphonate (50 mg, 0.12 mmol, 1.0 equiv.). Yellow colour liquid (32 mg, 65% yield); R_f = 0.5 (30% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 15.1 Hz, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.49 (m, 1H), 7.43 – 7.38 (m, 4H), 7.33 – 7.28 (m, 3H), 4.22 – 4.19 (m, 2H), 3.96 – 3.81 (m, 4H), 2.67 (t, *J* = 6.2 Hz, 2H), 2.24 – 2.18 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 139.9, 139.6 (d, J_{C-P} = 12 Hz), 139.1, 130.1, 128.7, 127.3, 127.2, 126.0, 125.7 (d, J_{C-P} = 11 Hz), 122.7, 121.2, 120.5 (d, J_{C-P} = 16 Hz), 119.8, 119.2 (d, J_{C-P} = 18 Hz), 117.5, 115.6, 108.7, 61.5 (d, J_{C-P} = 6 Hz),, 40.9, 23.8, 22.3, 16.2 (d, J_{C-P} = 7 Hz); HRMS (ESI) calcd for $C_{25}H_{27}NO_3P$ $[M+H]^+$: 420.1723; found: 420.1721.

E. Mechanism study experiments:

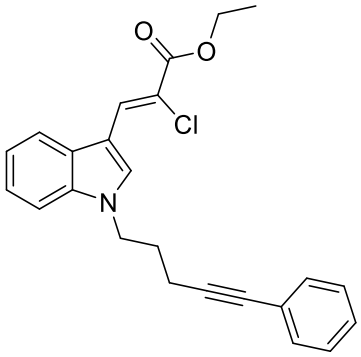
Ethyl (*Z*)-2-bromo-3-(1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (3a)



A screw-cap vial equipped with magnetic stir bar was charged with compound **1a** (50 mg, 0.14 mmol, 1.0 equiv.), $CuBr_2$ (62 mg, 0.28 mmol, 2 equiv.) in Dry DMA (1 mL) under nitrogen atmosphere. The reaction mixture was stirred at 110 °C using an oil bath for 12 h. Then the reaction mixture was cooled to room temperature, diluted with saturated NH_4Cl solution (10 mL) and extracted with ethyl acetate (2 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/ hexane) to afford compound **3a** as a yellow colour liquid (38 mg, 62% yield); R_f = 0.2 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.53 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.36 – 7.23 (m, 5H), 4.42 (t, *J* = 6.7 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.42 (t, *J* = 6.6 Hz, 2H), 2.23 – 2.12 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 135.7, 132.3, 131.7, 131.6, 128.9, 128.4, 128.0, 123.4, 123.2, 121.2, 118.7, 110.3, 110.1, 107.3, 87.9,

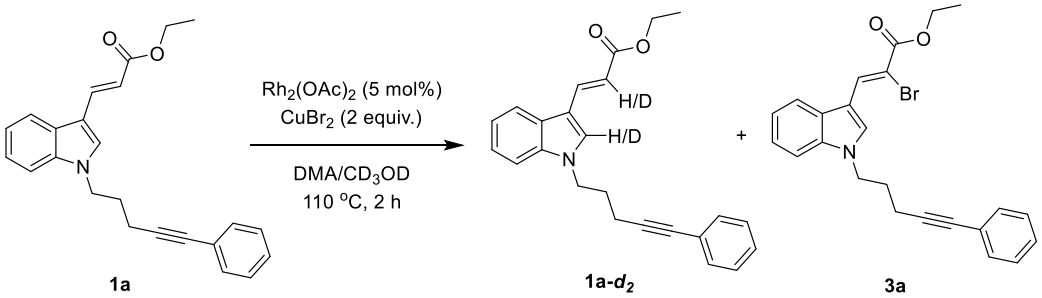
82.4, 62.3, 45.7, 28.5, 16.8, 14.4; HRMS (ESI) calcd for $C_{24}H_{23}NO_2Br$ $[M+H]^+$: 436.0912; found: 436.0892.

Ethyl (*Z*)-2-chloro-3-(1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)acrylate (3b)

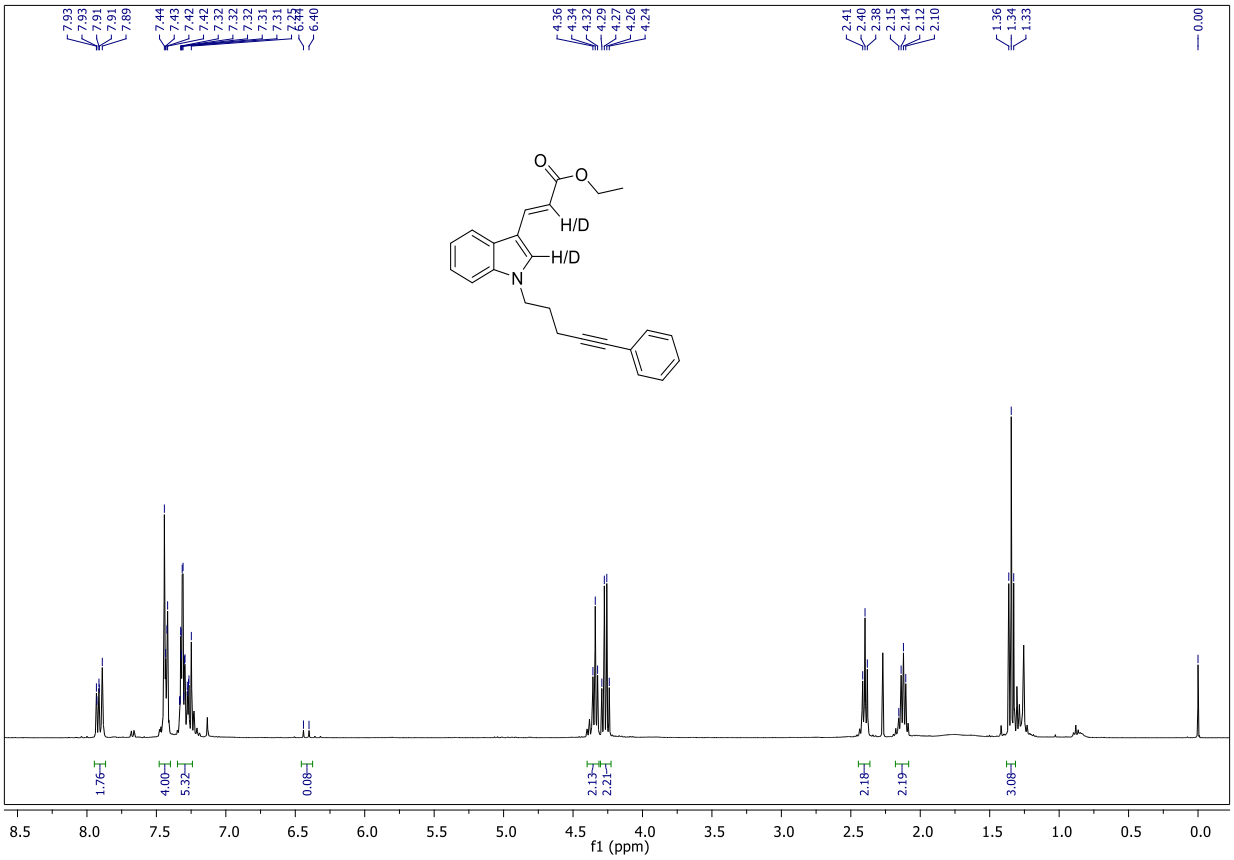


Prepared according to above procedure using $CuCl_2$ instead of $CuBr_2$. Yellow colour liquid (36 mg, 66% yield); R_f = 0.2 (10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.27 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.35 – 7.23 (m, 5H), 4.41 (t, *J* = 6.7 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.41 (t, *J* = 6.6 Hz, 2H), 2.21 – 2.12 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 135.7, 132.2, 131.6, 128.7, 128.7, 128.4, 128.0, 123.4, 123.1, 121.2, 118.7, 116.7, 110.1, 109.6, 87.9, 82.4, 62.1, 45.6, 28.6, 16.8, 14.4; HRMS (ESI) calcd for $C_{24}H_{23}NO_2Cl$ $[M+H]^+$: 392.1417; found: 392.1429.

F. H/D Exchange Reaction



A screw-cap vial equipped with magnetic stir bar was charged with compound **1** (50 mg, 0.14 mmol, 1.0 equiv.), $CuBr_2$ (62 mg, 0.28 mmol, 2 equiv.), $Rh_2(OAc)_4$ (5 mol%) in Dry DMA (1 mL) and CD_3OD (0.2 mL) under nitrogen atmosphere. The reaction mixture was stirred at 110 ^oC using an oil bath for 2 h. Then the reaction mixture was cooled to room temperature, diluted with saturated NH_4Cl solution (10 mL), and extracted with ethyl acetate (2 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/ hexane) to afford compound **1a-*d*$_2$** (26 mg, 52%) along with bromo intermediate **3a** (18 mg, 30%).



III. X-ray crystallographic data

X-ray data for the compound **2p** was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[4] The structure was solved using the intrinsic phasing method [2] and further refined with the SHELXL[5] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(C)$ for other H atoms]. Atoms C17/C18/O1/O2 were disordered over two positions and their site-occupational factors were refined to 0.51(2) and 0.46(2), respectively.

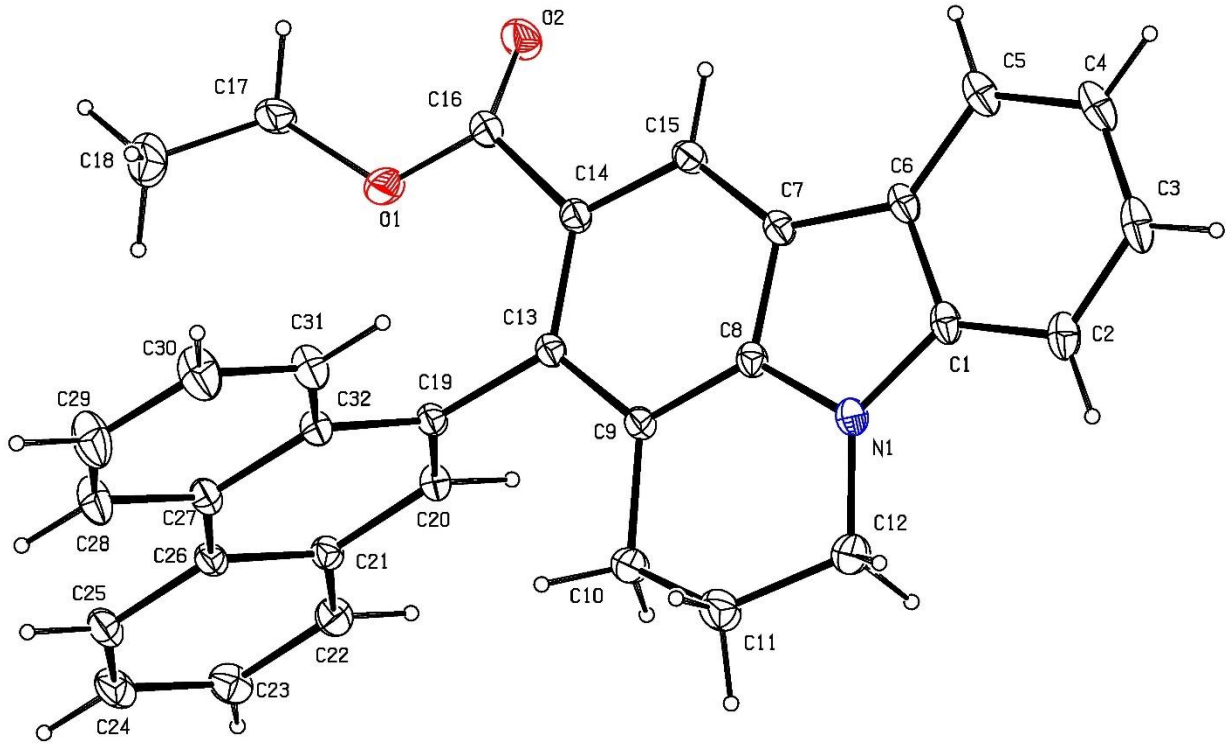


Figure 1. A view of **2p**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii. The minor disordered component atoms were omitted for clarity.

Crystal structure determination of 2p

Crystal Data for $C_{32}H_{25}NO_2$ (M =455.53 g/mol): triclinic, space group P-1 (no. 2), a = 8.2394(4) Å, b = 10.0790(6) Å, c = 15.9028(8) Å, α = 79.577(2)°, β = 77.886(2)°, γ = 69.796(2)°, V = 1203.30(11) Å^3, Z = 2, T = 294.15 K, μ(MoKα) = 0.078 mm^{-1}, *Dcalc* = 1.257 g/cm^3, 23411 reflections measured (4.336° ≤ 2Θ ≤ 56.68°), 5977 unique (R_{int} = 0.0646, R_{sigma} = 0.0882) which were used in all calculations. The final R_1 was 0.0597 (I > 2σ(I)) and wR_2 was 0.1979 (all data). CCDC 2195417 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

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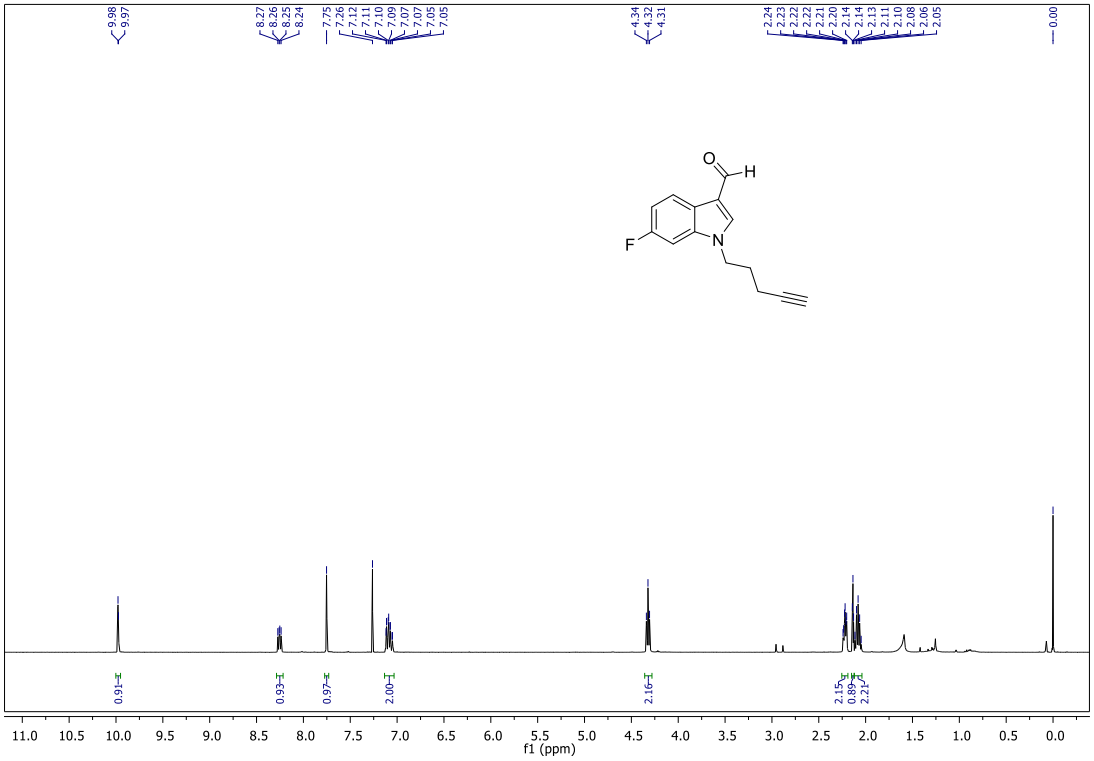
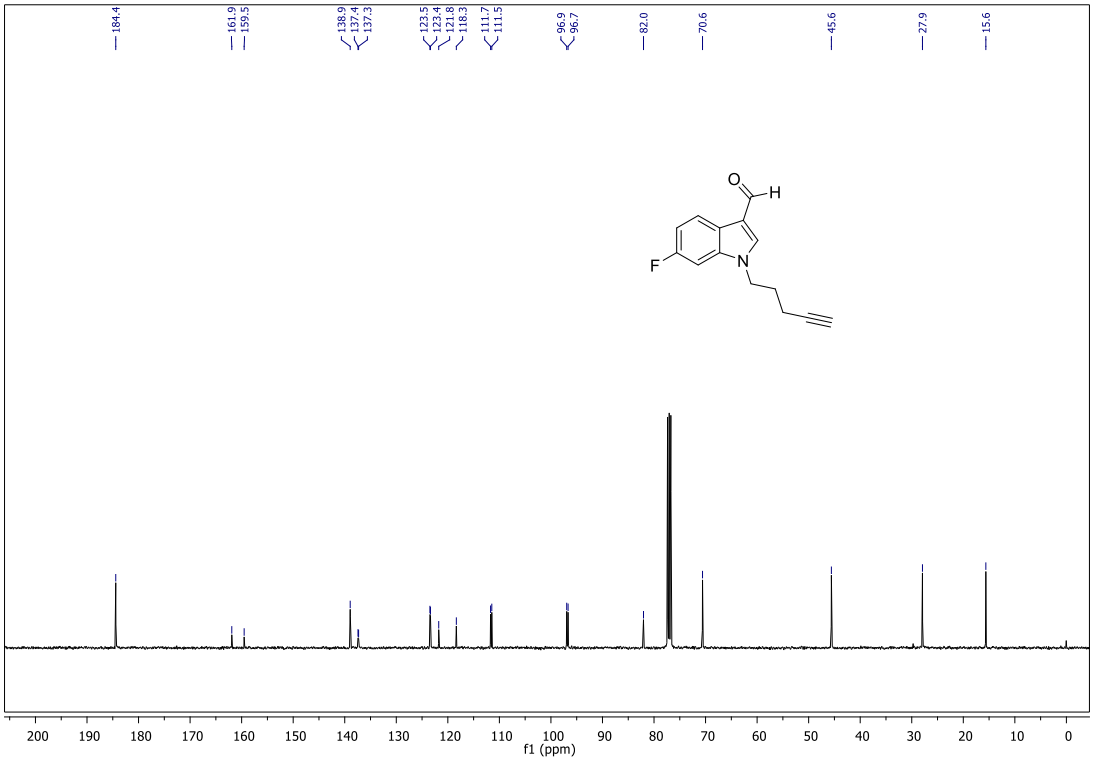
5. G. M. Sheldrick. *Acta Cryst.* **2015**, *C71*, 3.

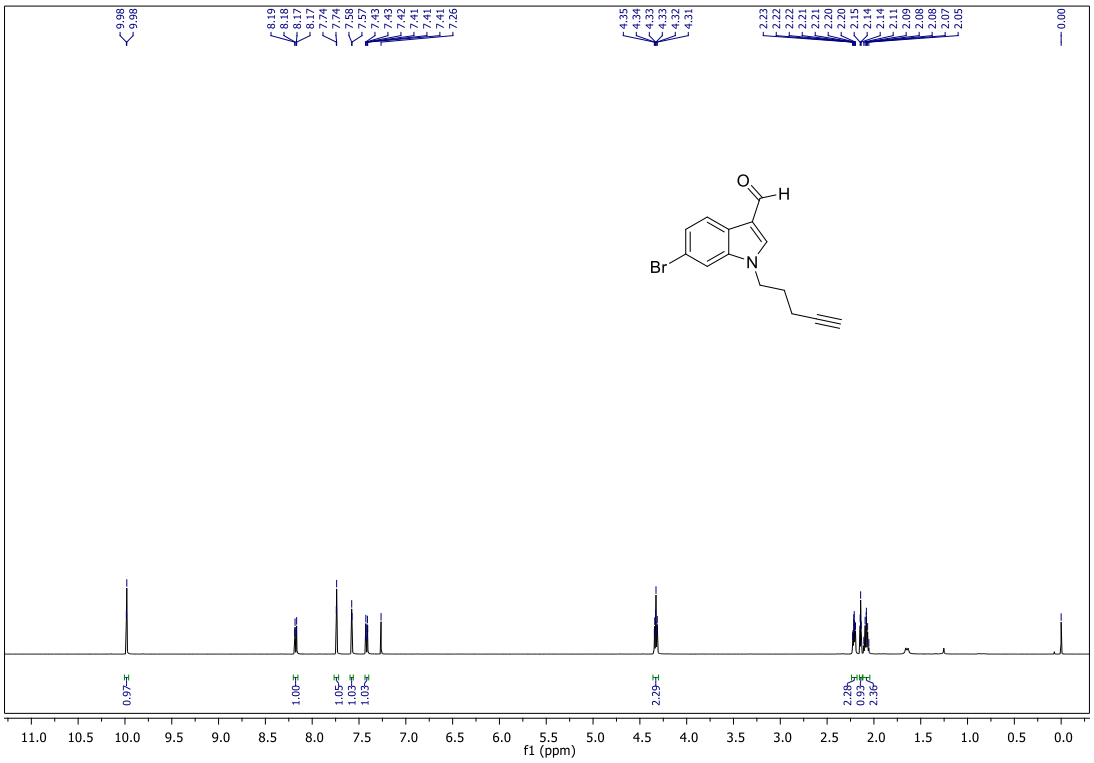
NMR spectra



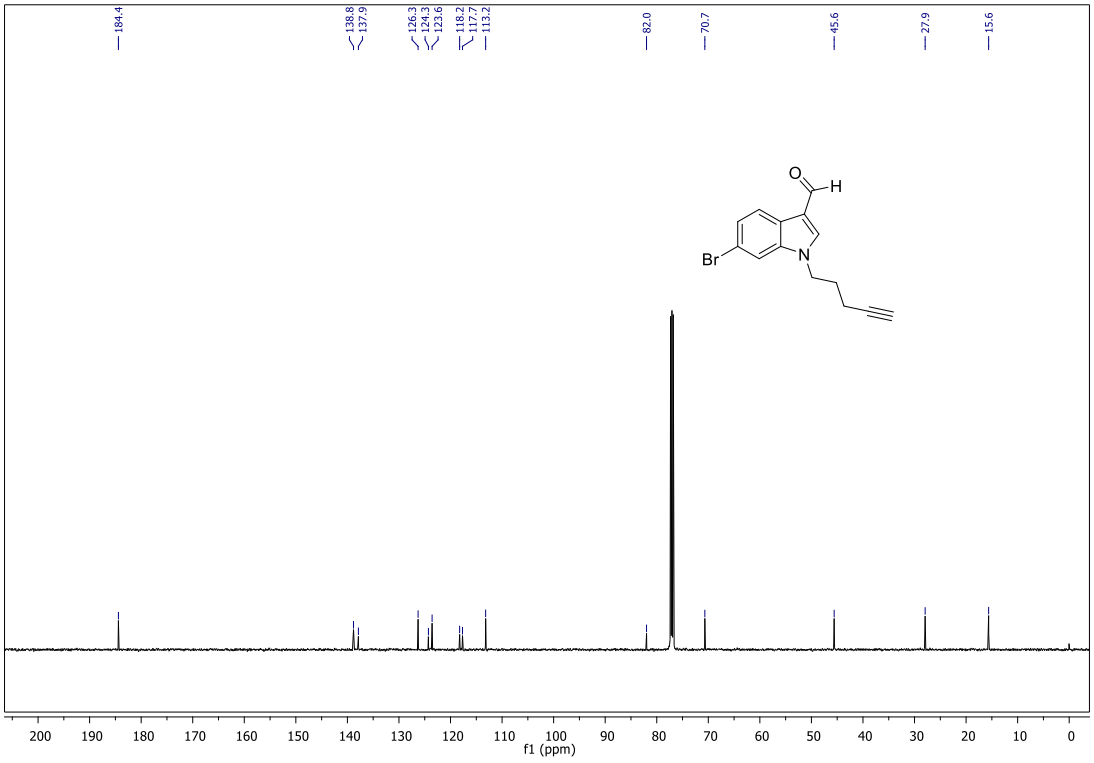
^{1}H NMR of compound **S-1b** in $CDCl_3$ (400 MHz)



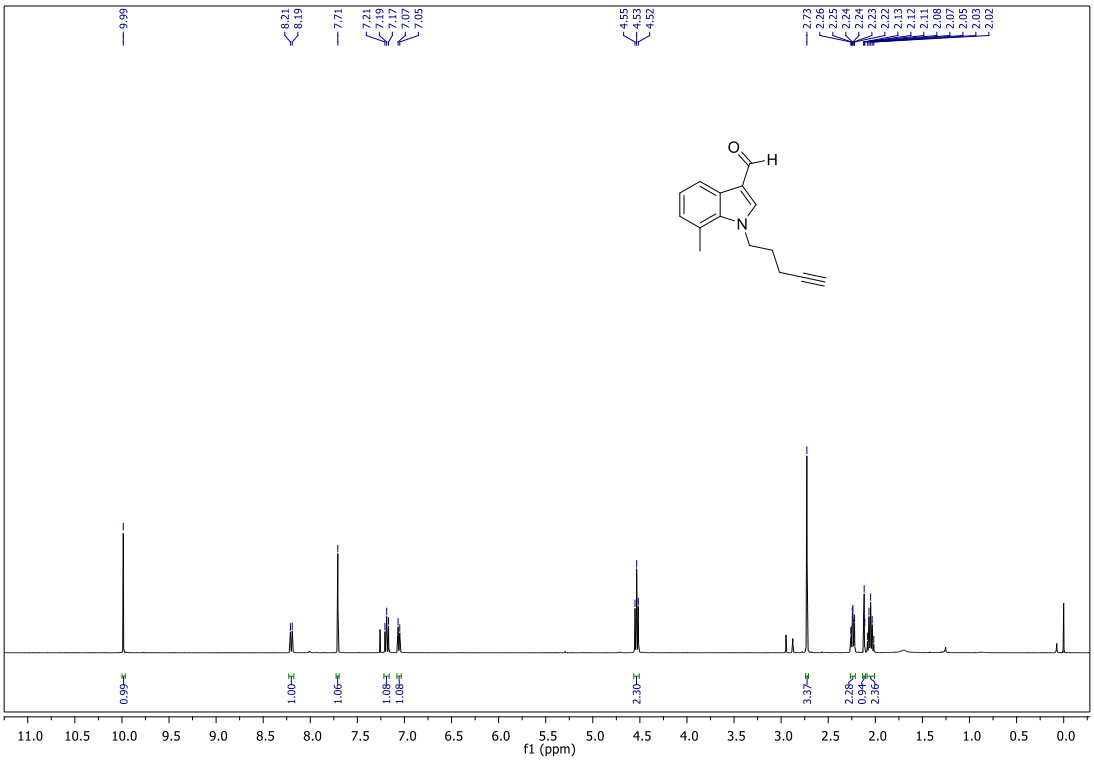
^{13}C NMR of compound **S-1b** in $CDCl_3$ (101 MHz)



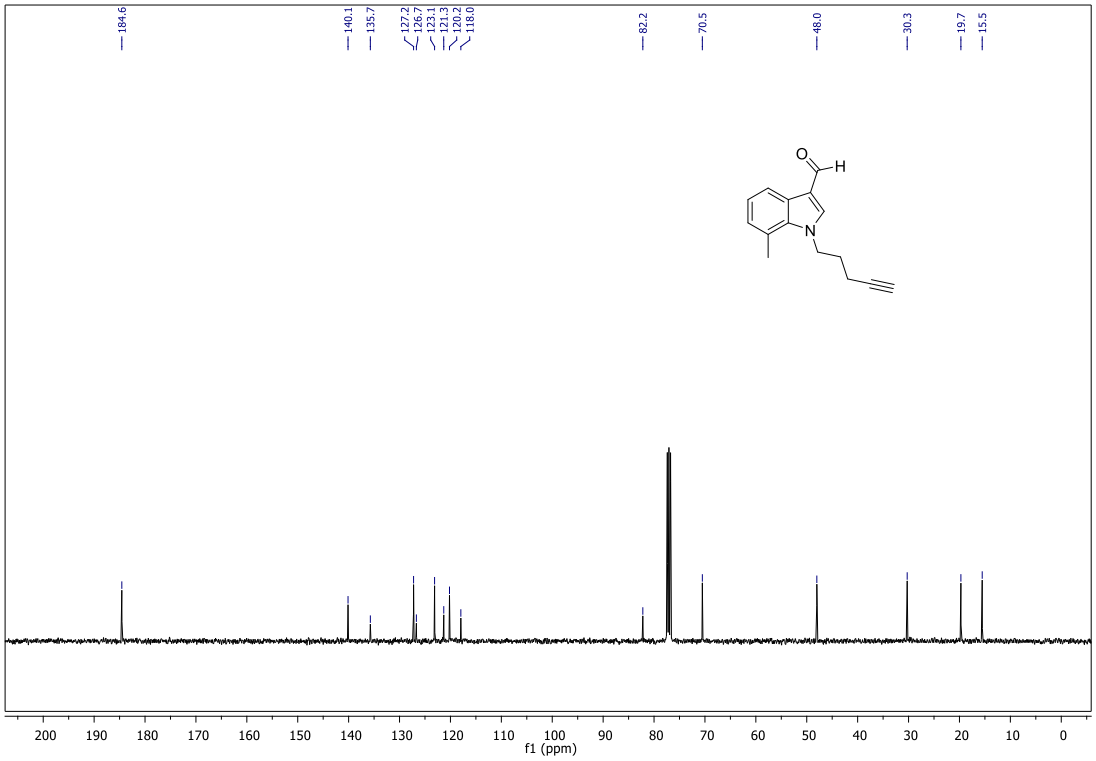
^{1}H NMR of compound **S-1c** in $CDCl_3$ (500 MHz)



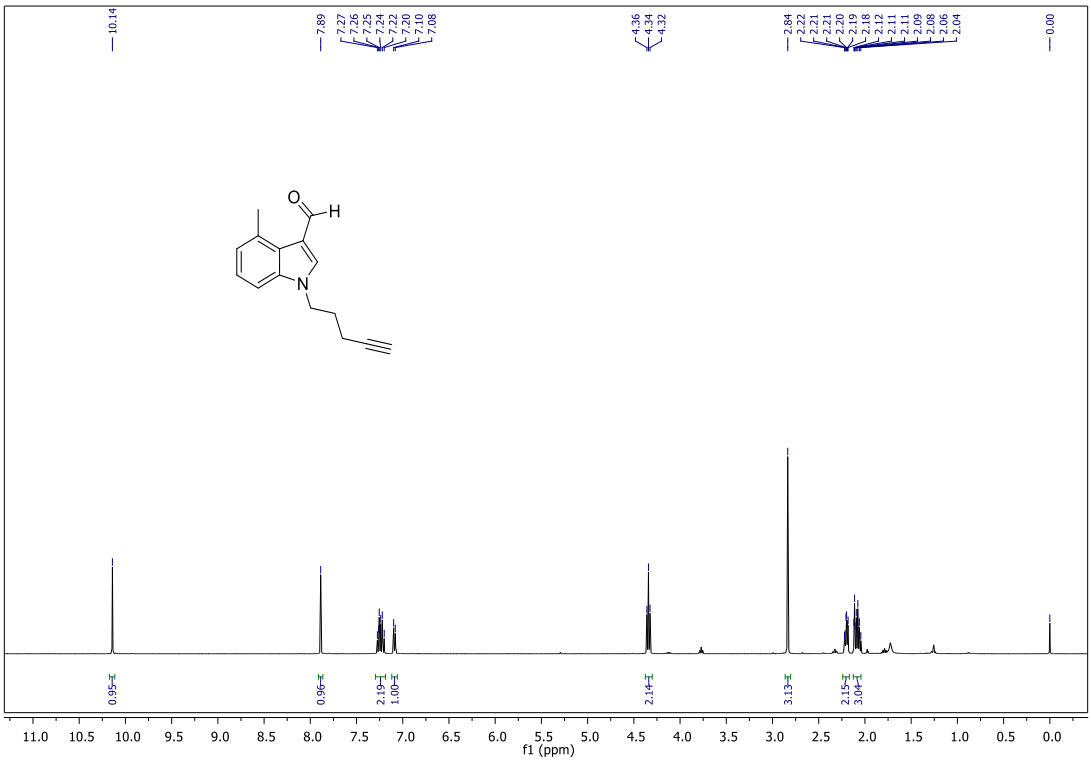
^{13}C NMR of compound **S-1c** in $CDCl_3$ (126 MHz)



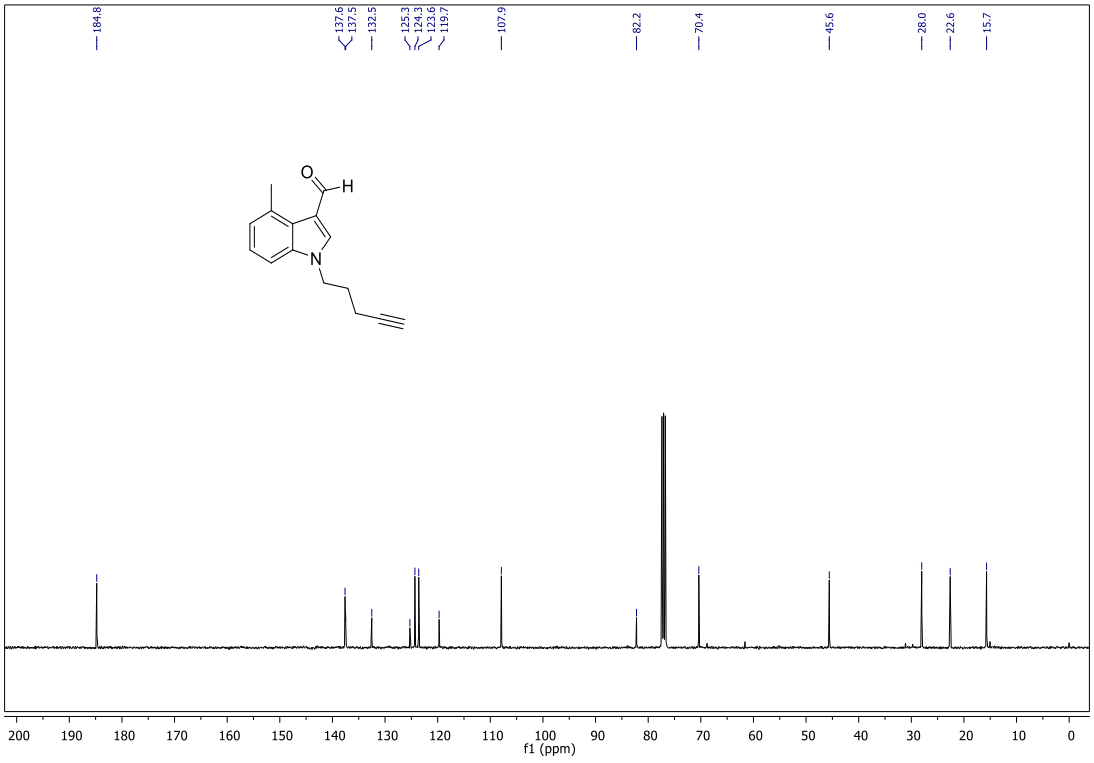
^{1}H NMR of compound **S-1d** in $CDCl_3$ (400 MHz)



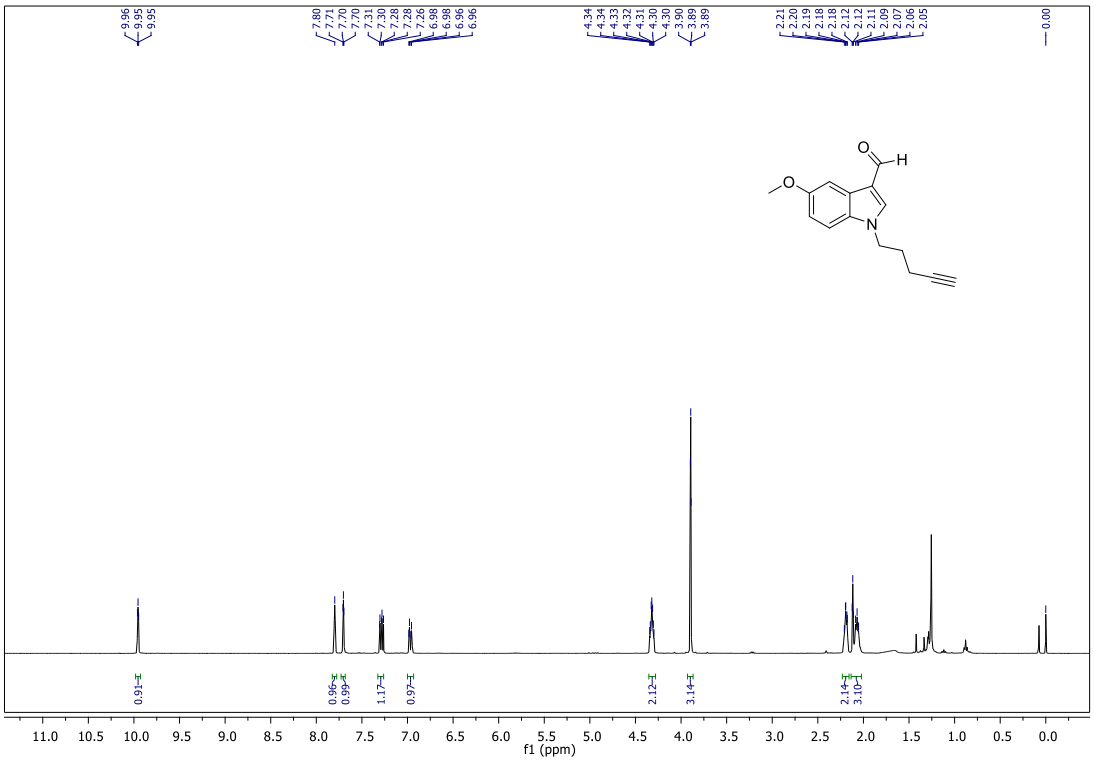
^{13}C NMR of compound **S-1d** in $CDCl_3$ (101 MHz)



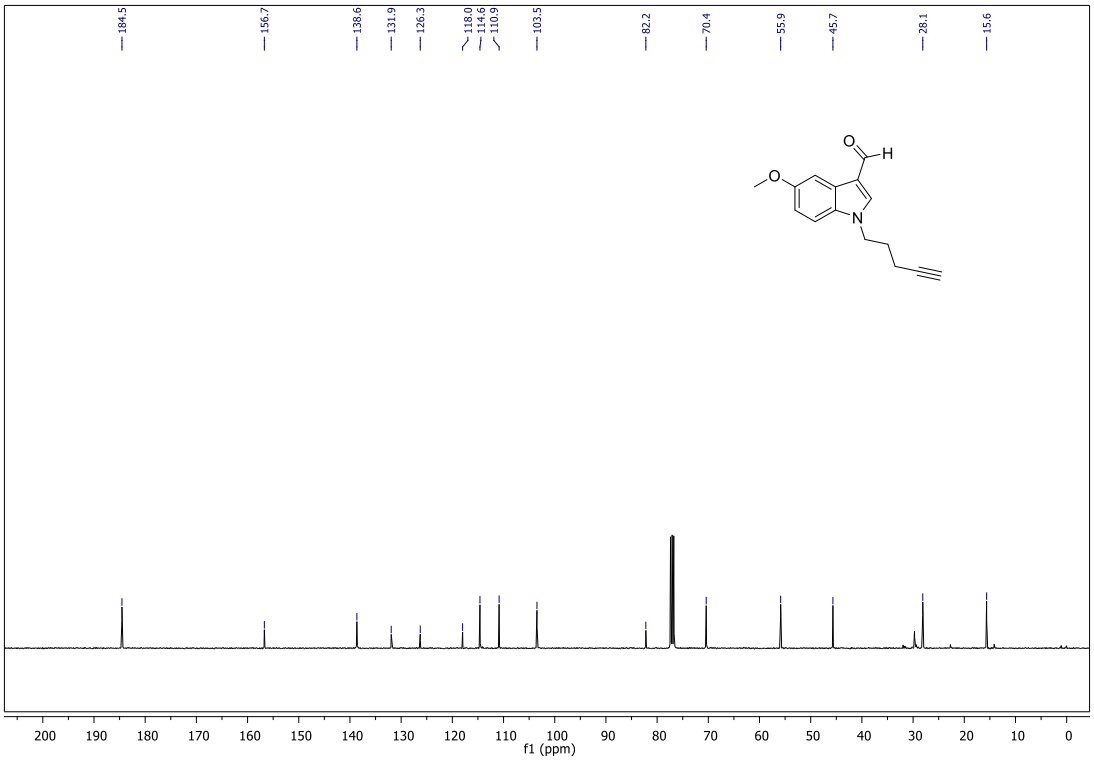
^{1}H NMR of compound **S-1e** in $CDCl_3$ (400 MHz)



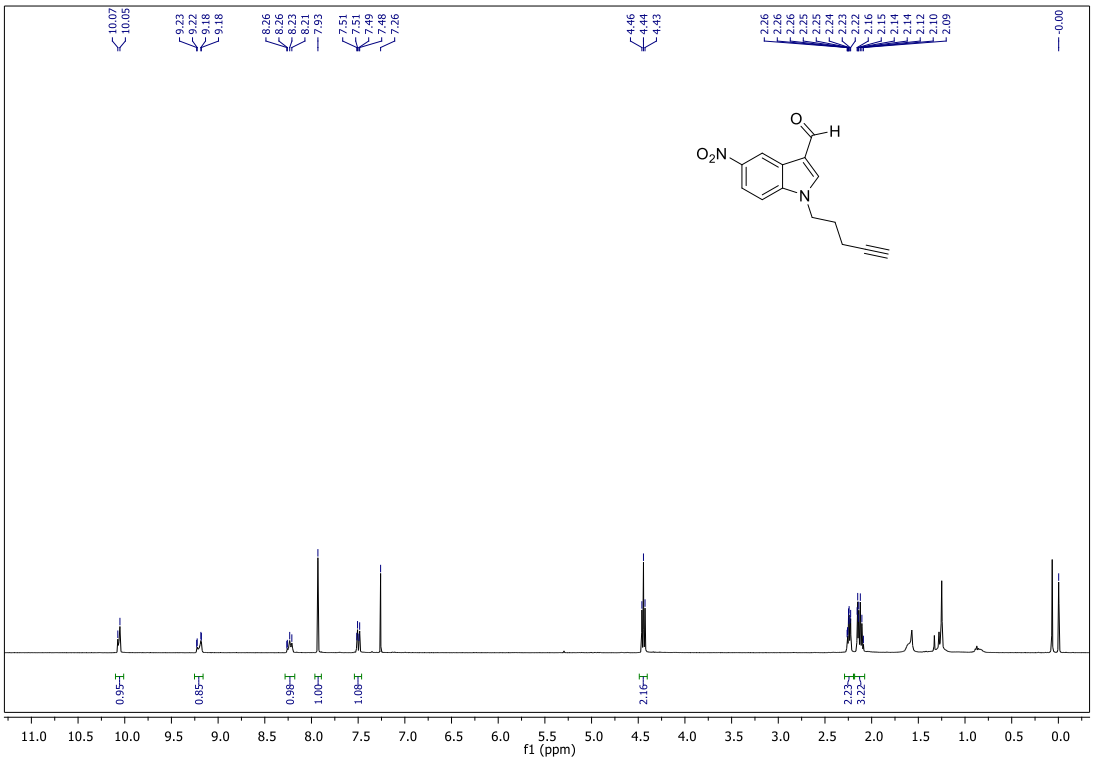
^{13}C NMR of compound **S-1e** in $CDCl_3$ (101 MHz)



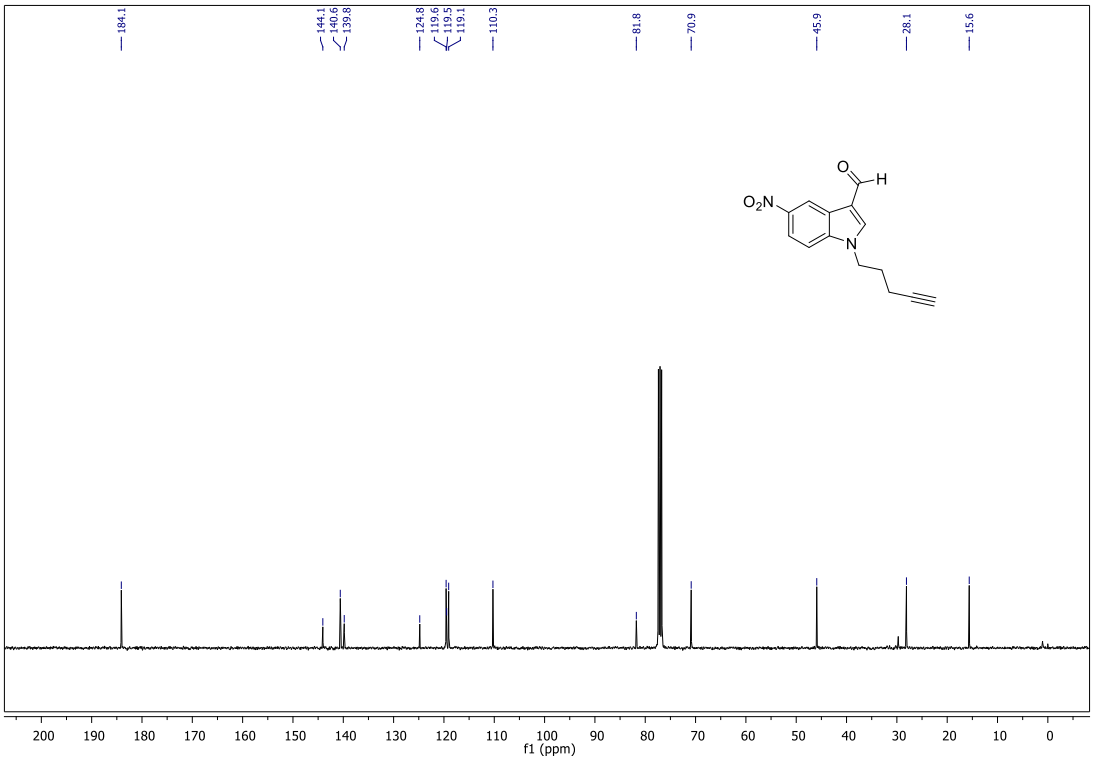
^{1}H NMR of compound **S-1f** in $CDCl_3$ (400 MHz)



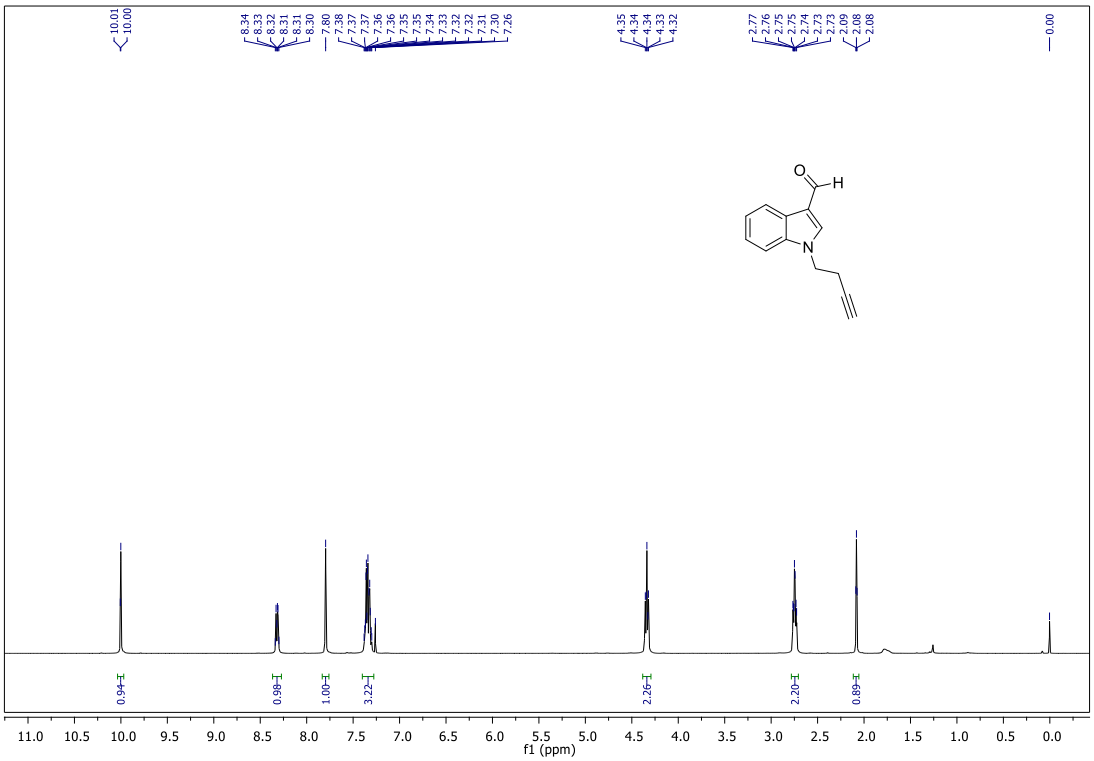
^{13}C NMR of compound **S-1f** in $CDCl_3$ (101 MHz)



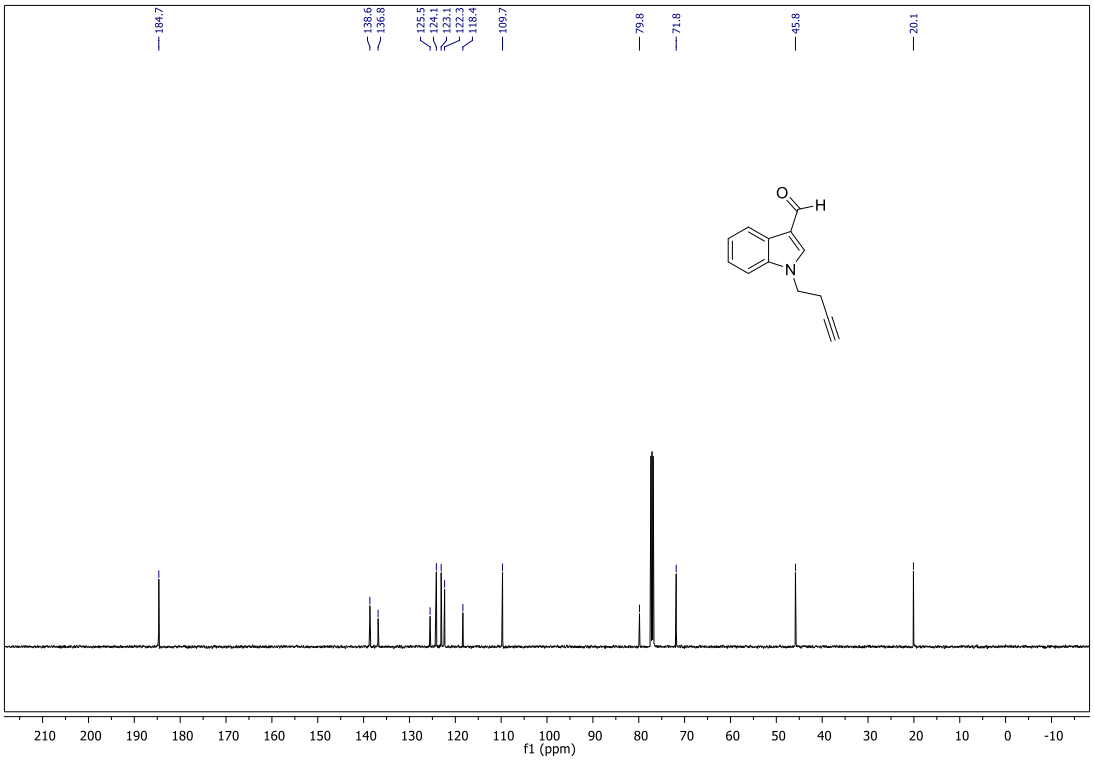
^{1}H NMR of compound **S-1g** in $CDCl_3$ (400 MHz)



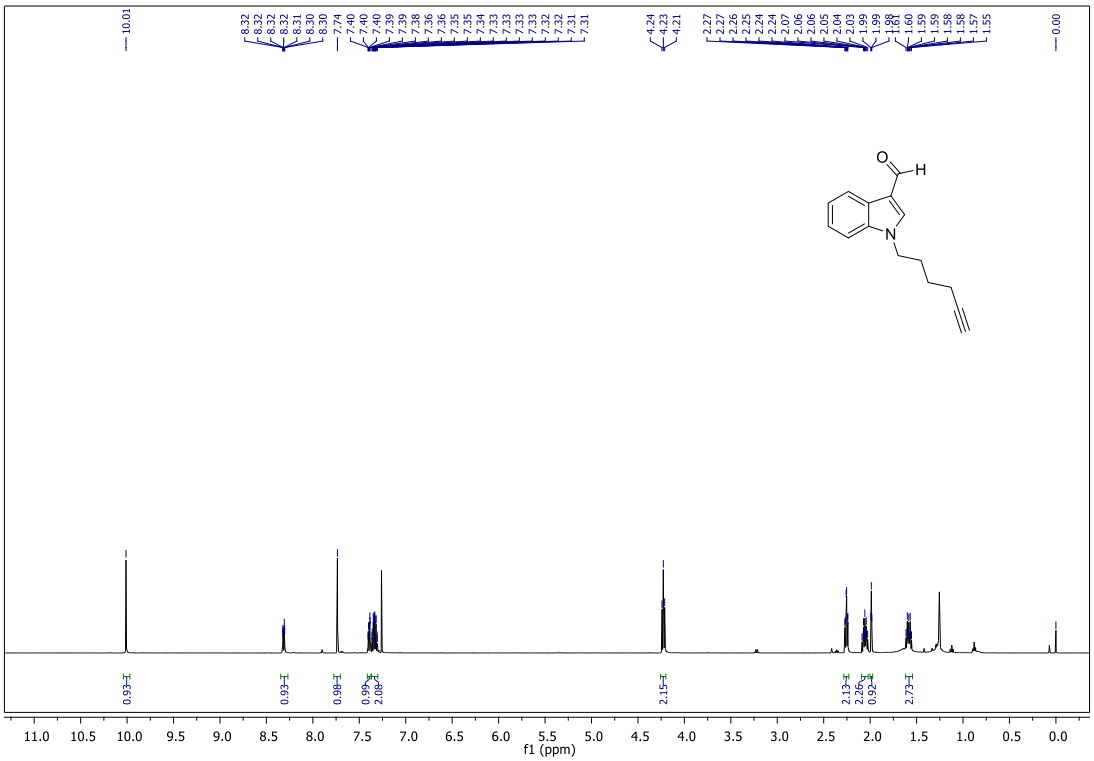
^{13}C NMR of compound **S-1g** in $CDCl_3$ (101 MHz)



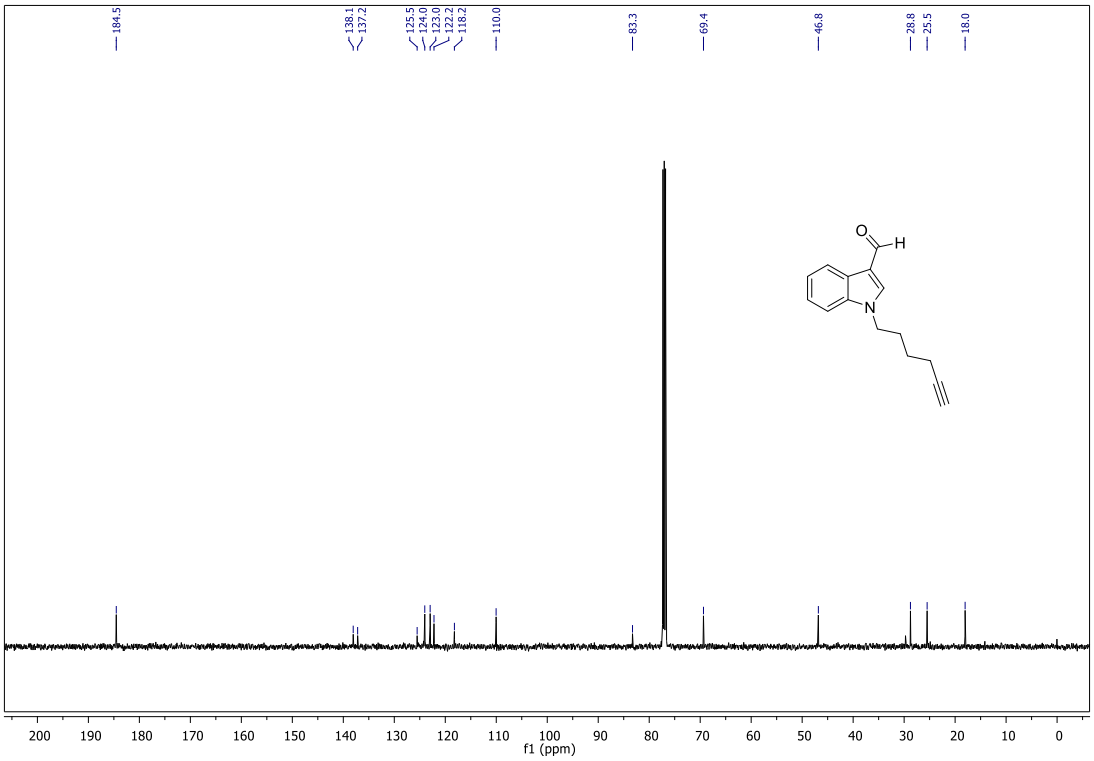
^{1}H NMR of compound **S-1h** in $CDCl_3$ (400 MHz)



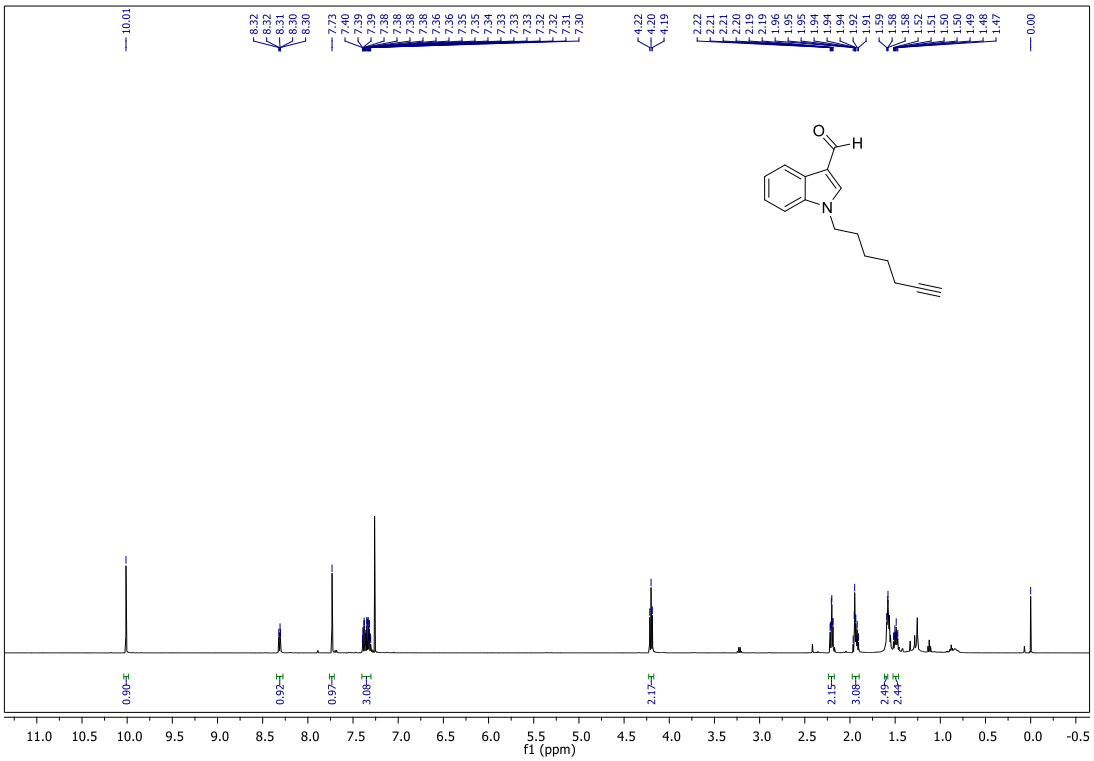
^{13}C NMR of compound **S-1h** in $CDCl_3$ (126 MHz)



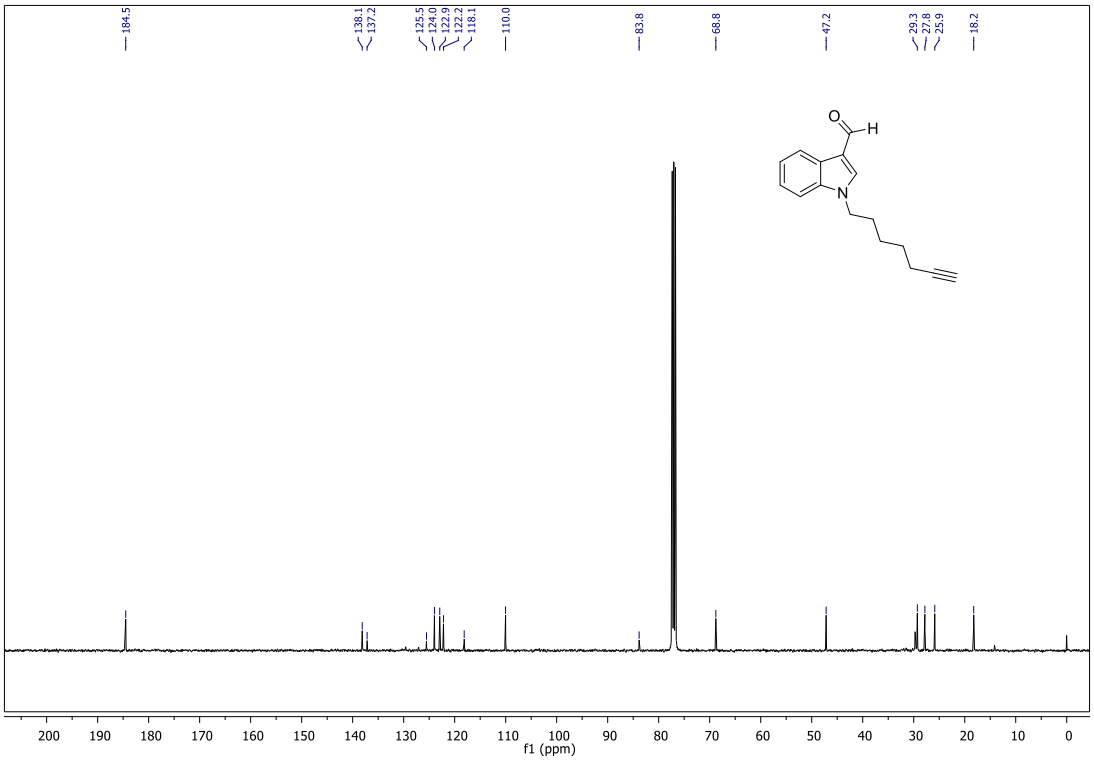
^{1}H NMR of compound **S-1i** in $CDCl_3$ (500 MHz)



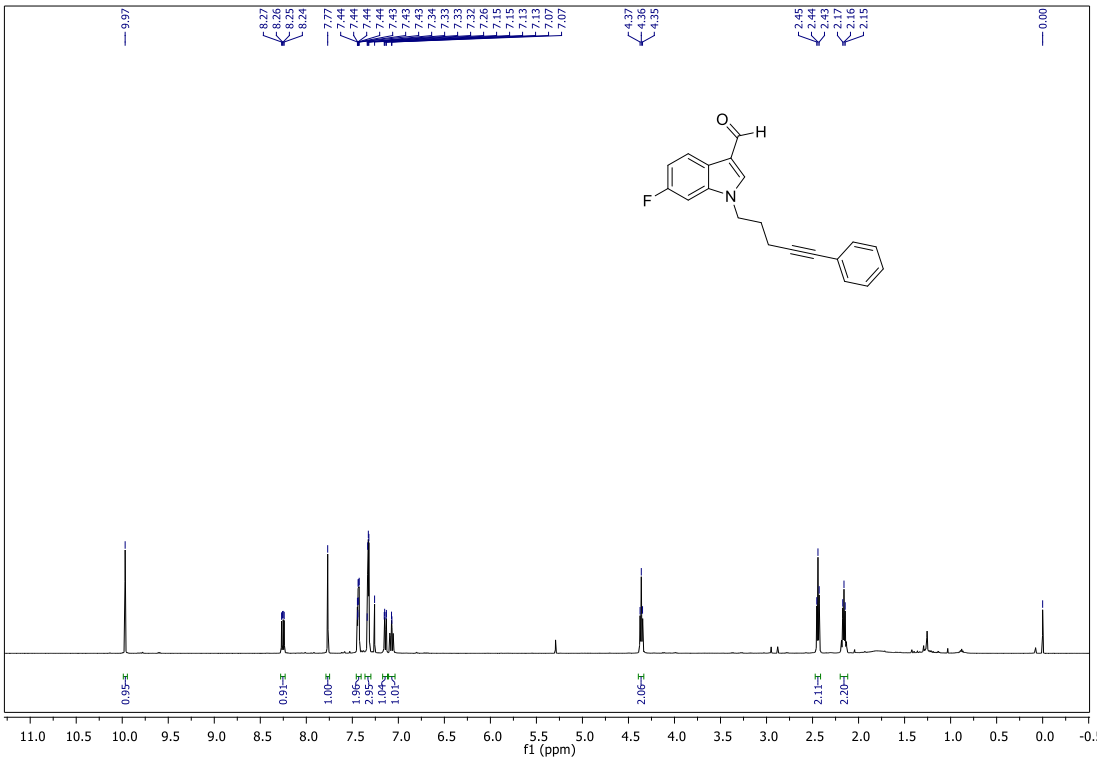
^{13}C NMR of compound **S-1i** in $CDCl_3$ (126 MHz)



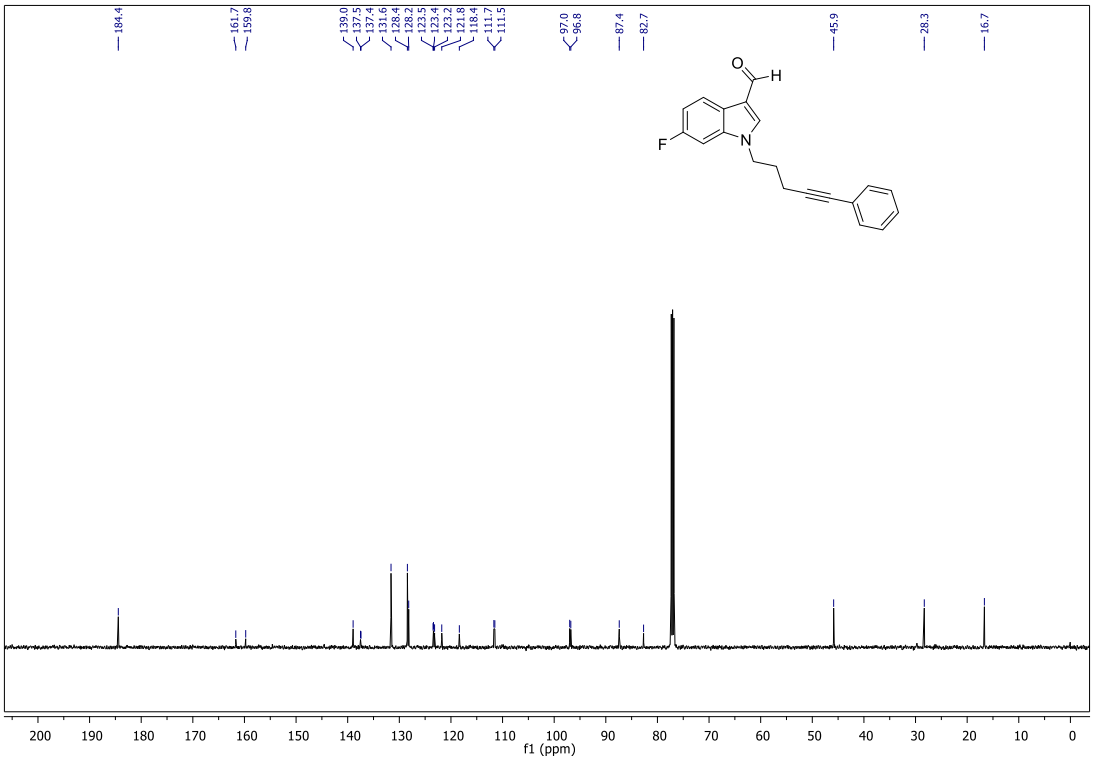
^{1}H NMR of compound **S-1j** in $CDCl_3$ (500 MHz)



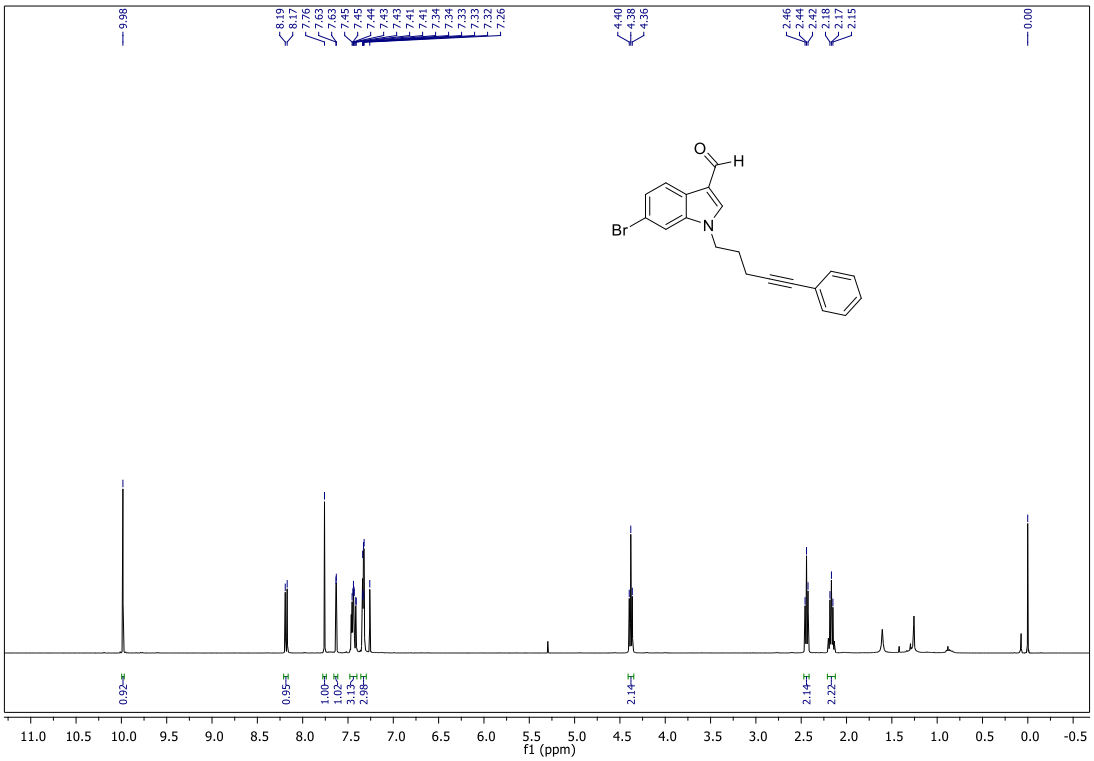
^{13}C NMR of compound **S-1j** in $CDCl_3$ (101 MHz)



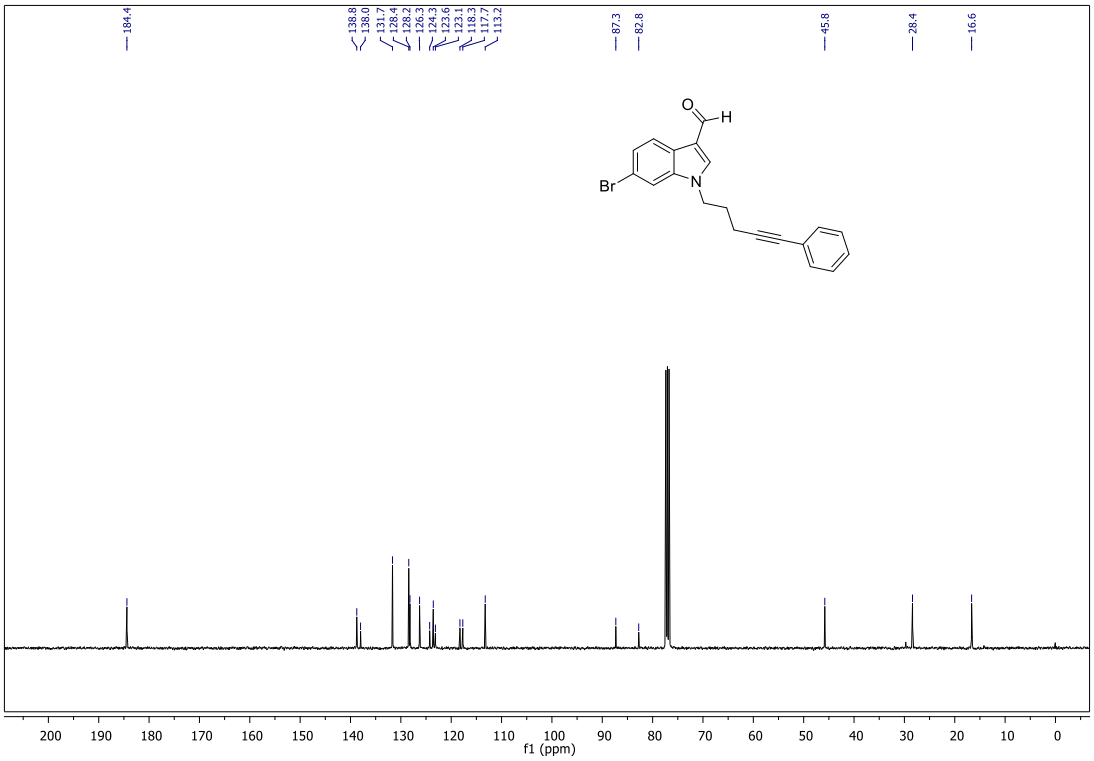
^{1}H NMR of compound **S-2b** in $CDCl_3$ (500 MHz)



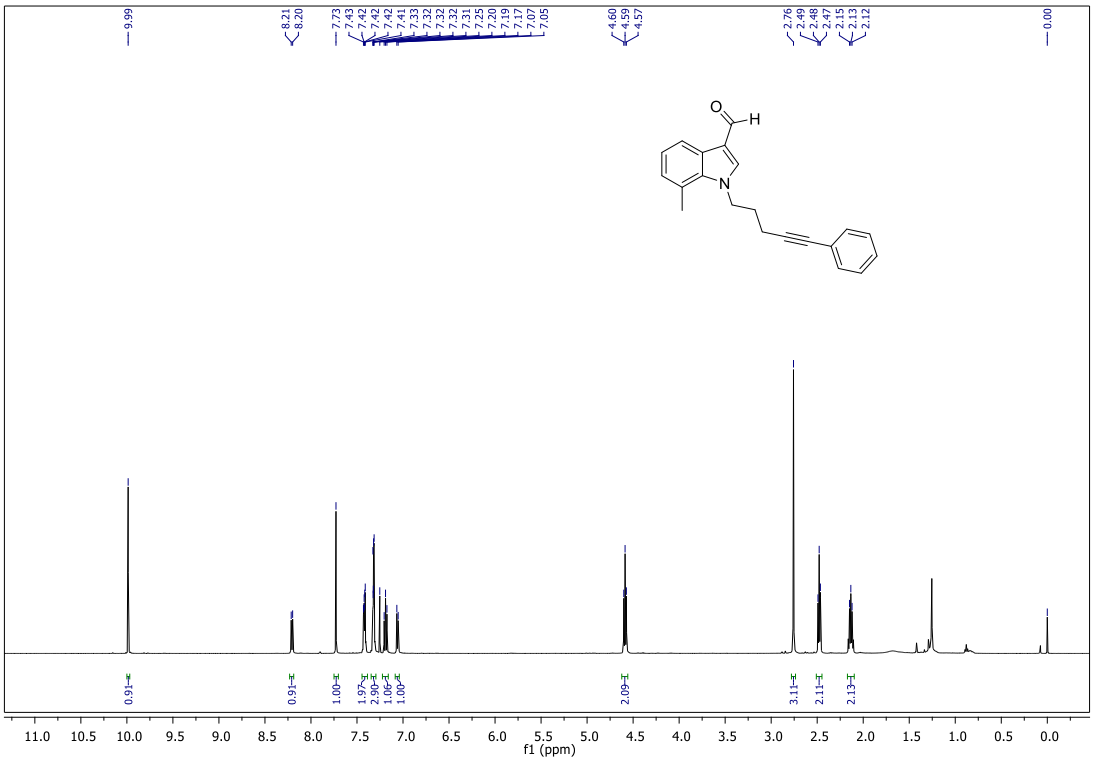
^{13}C NMR of compound **S-2b** in $CDCl_3$ (126 MHz)



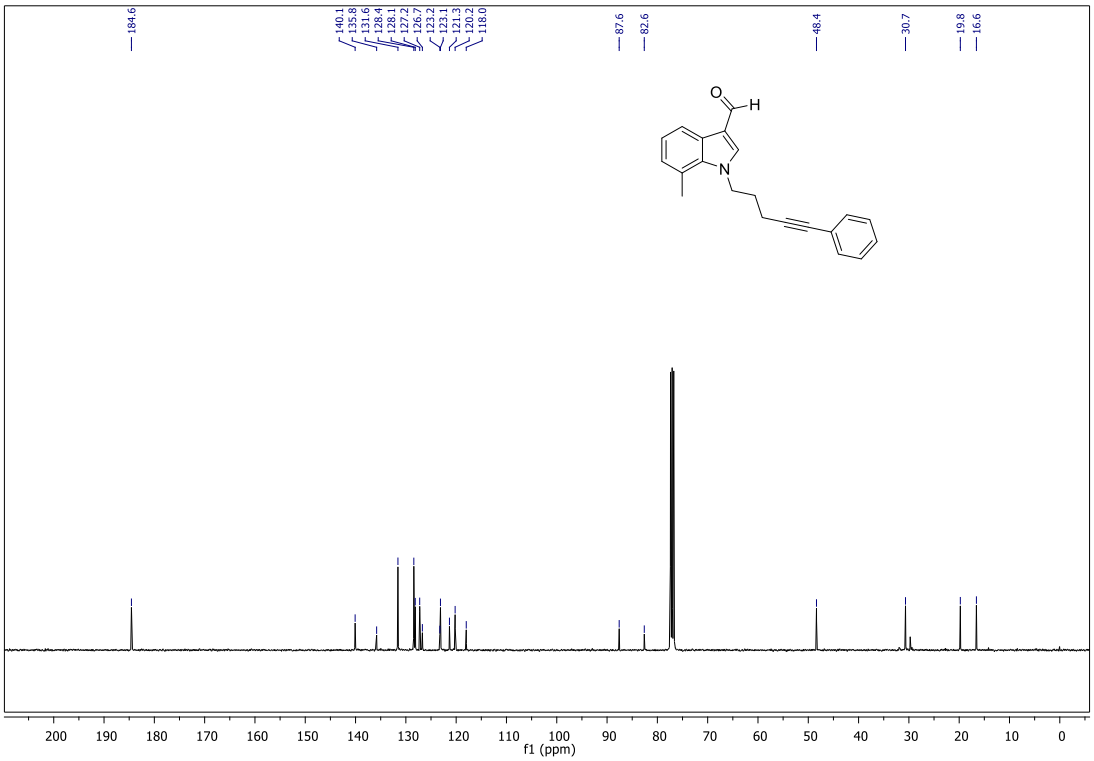
^{1}H NMR of compound **S-2c** in $CDCl_3$ (400 MHz)



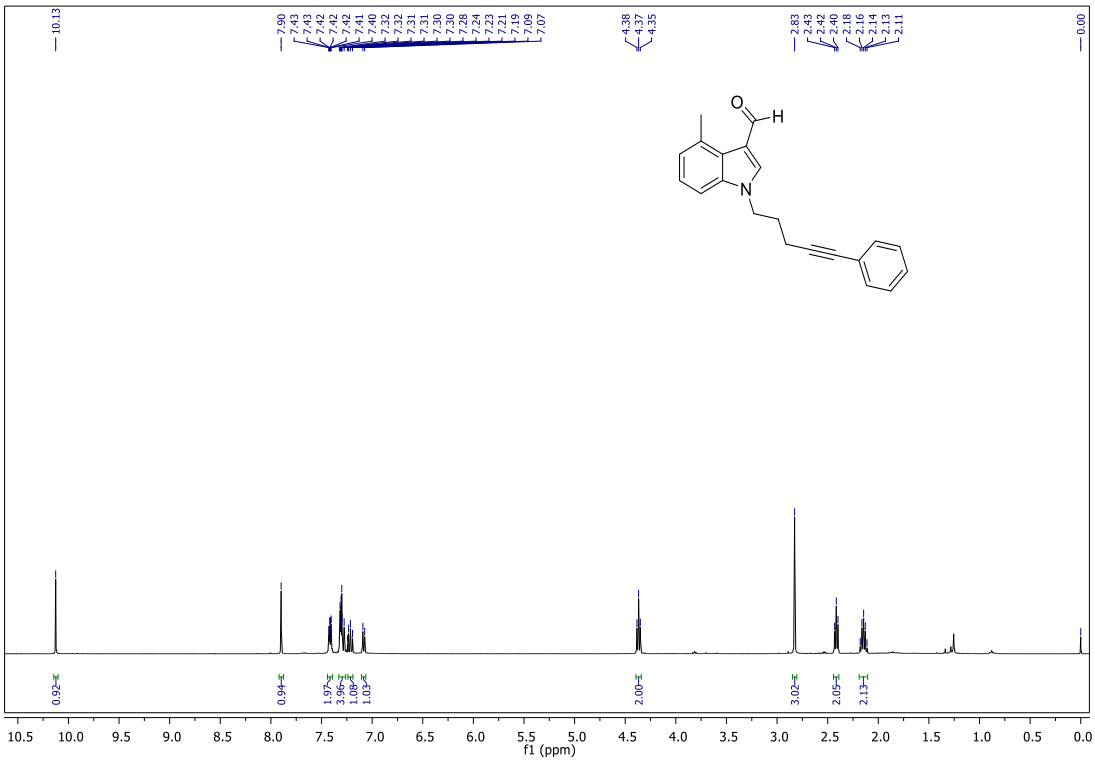
^{13}C NMR of compound **S-2c** in $CDCl_3$ (101 MHz)



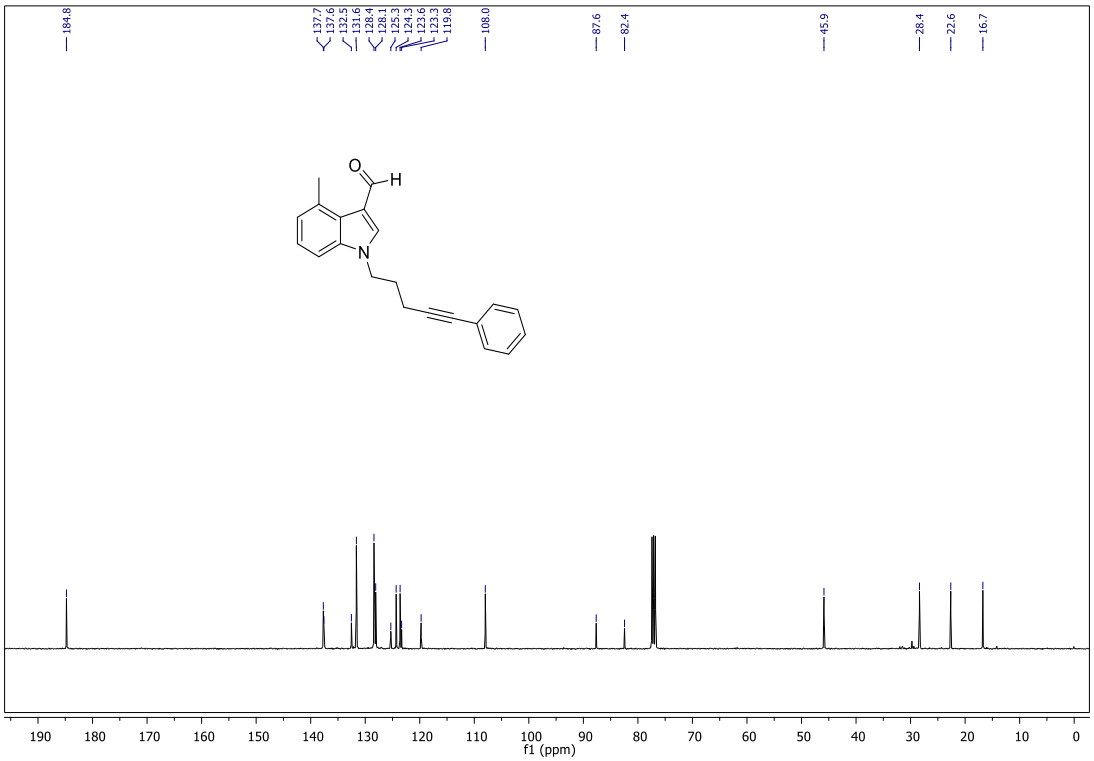
^{1}H NMR of compound **S-2d** in $CDCl_3$ (500 MHz)



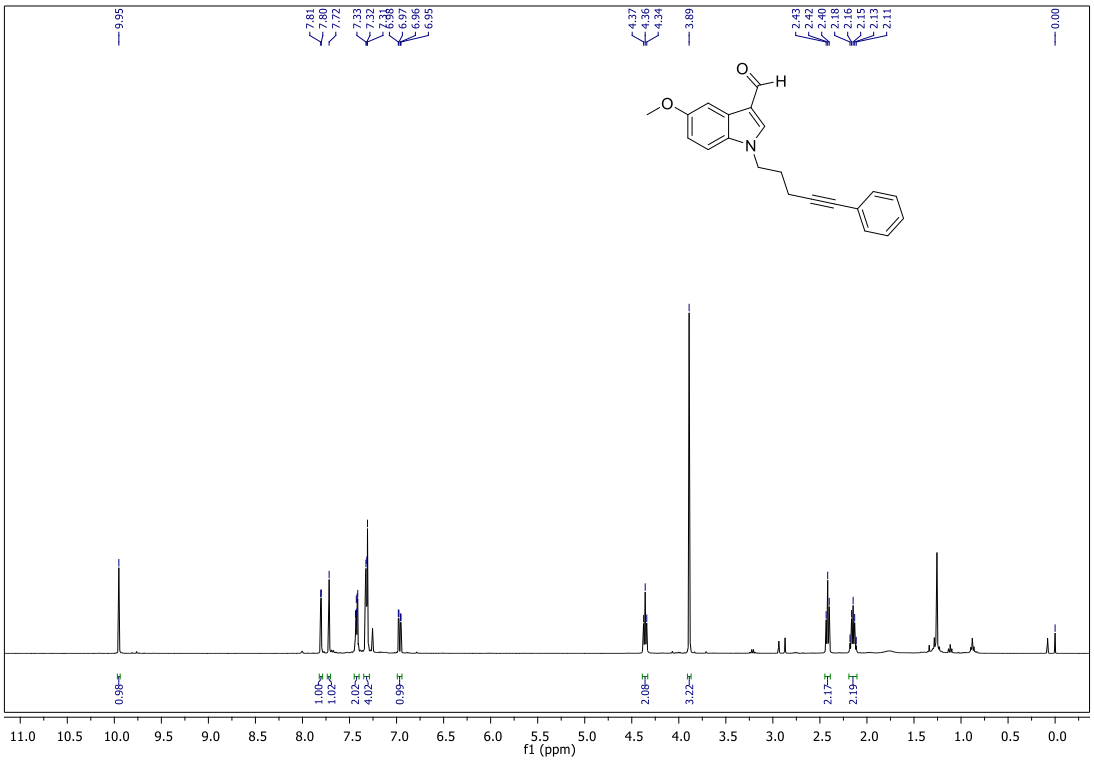
^{13}C NMR of compound **S-2d** in $CDCl_3$ (101 MHz)



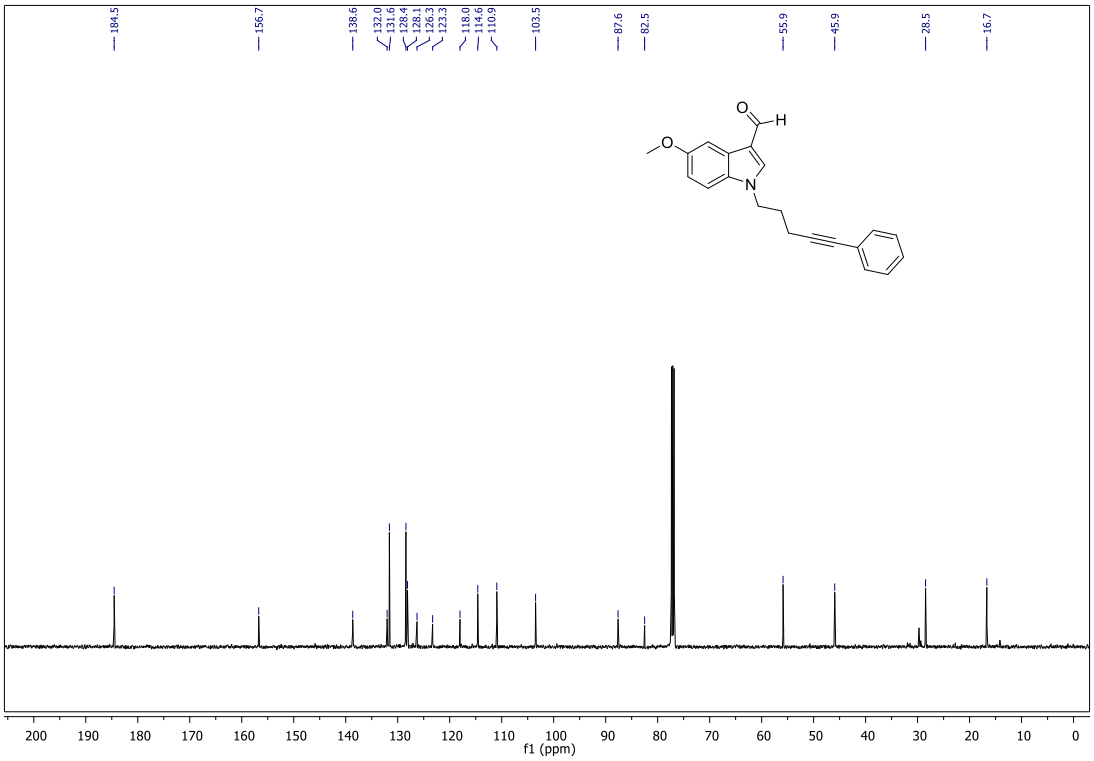
^{1}H NMR of compound **S-2e** in $CDCl_3$ (400 MHz)



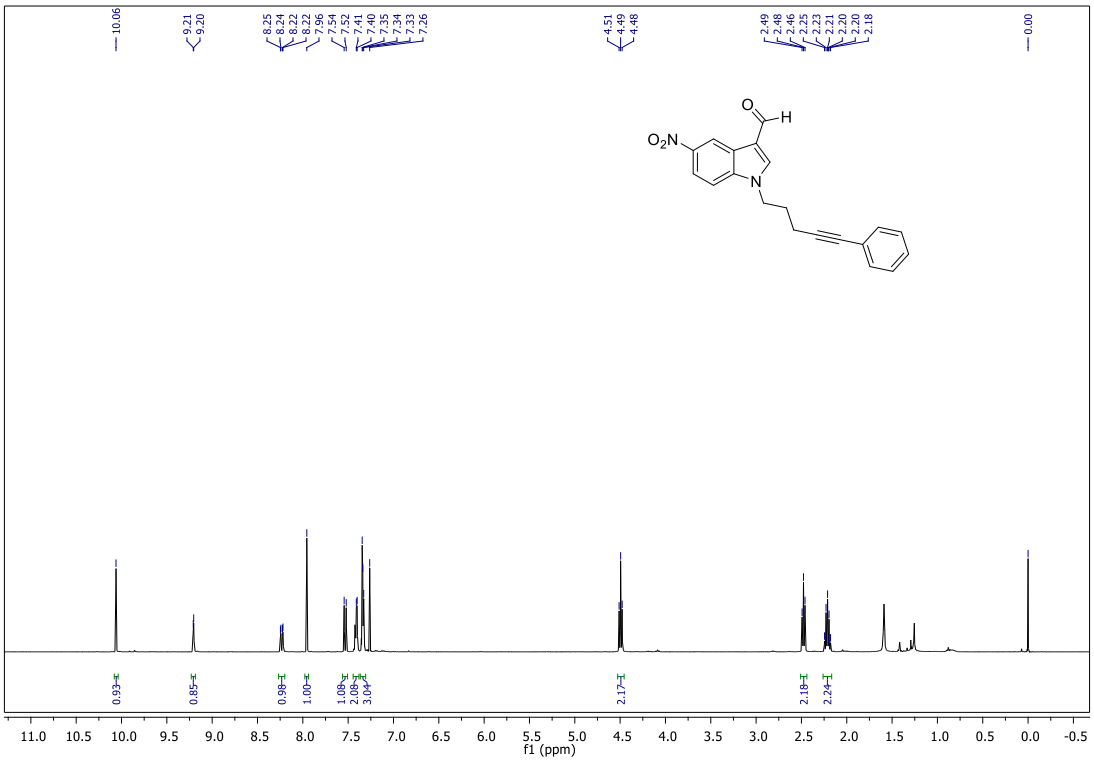
^{13}C NMR of compound **S-2e** in $CDCl_3$ (101 MHz)



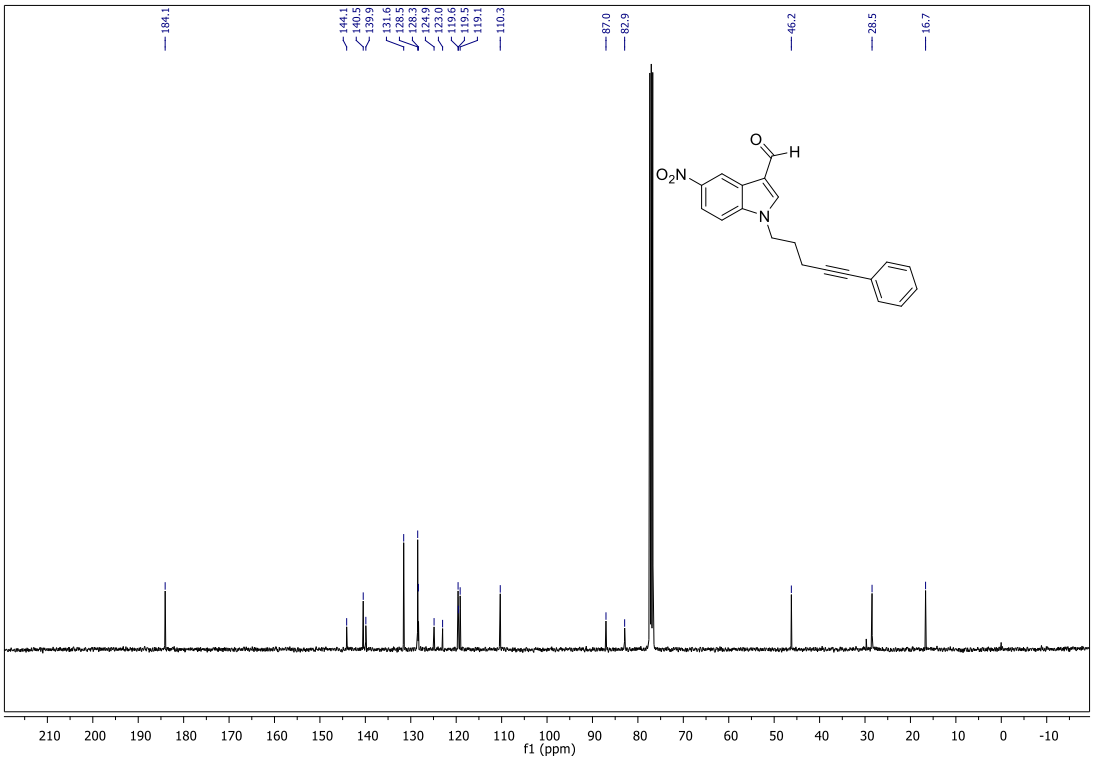
^{1}H NMR of compound **S-2f** in $CDCl_3$ (400 MHz)



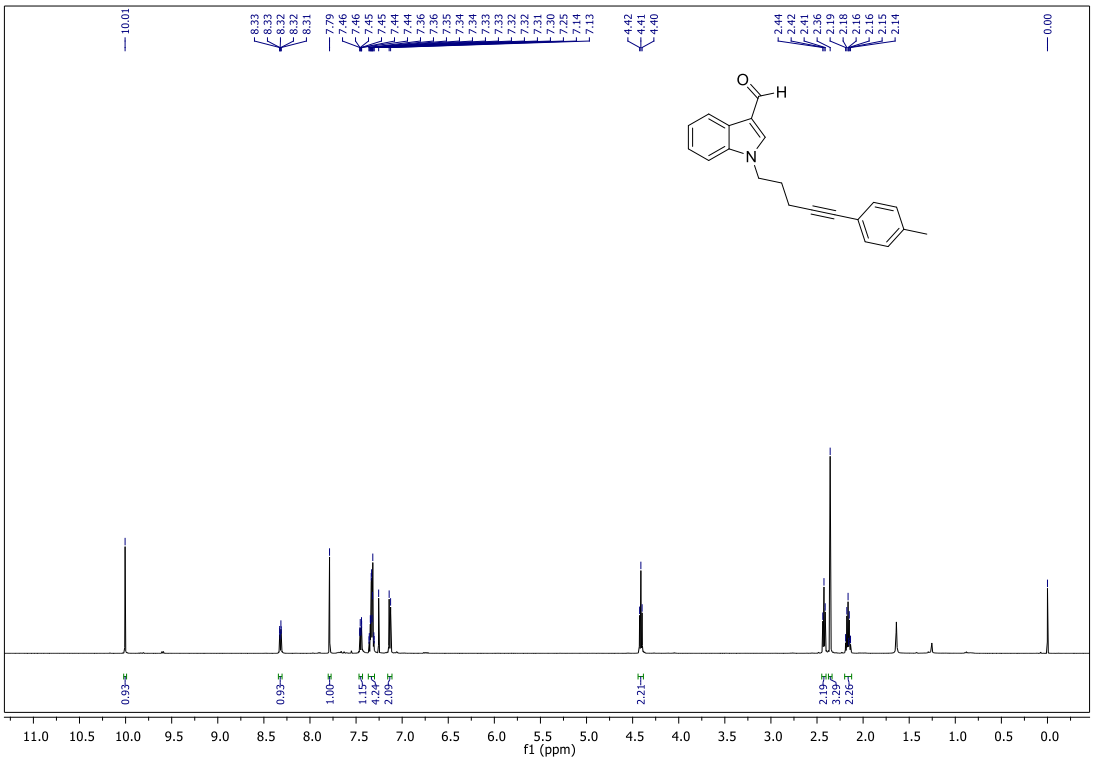
^{13}C NMR of compound **S-2f** in $CDCl_3$ (126 MHz)



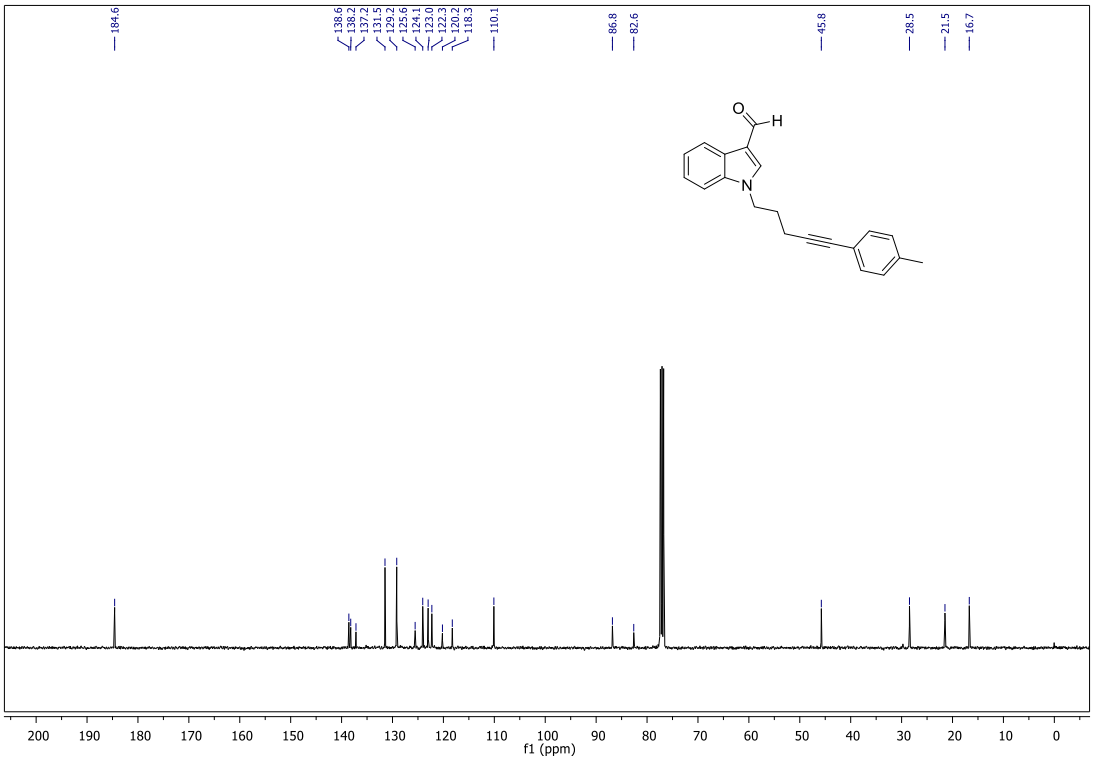
^{1}H NMR of compound **S-2g** in $CDCl_3$ (400 MHz)



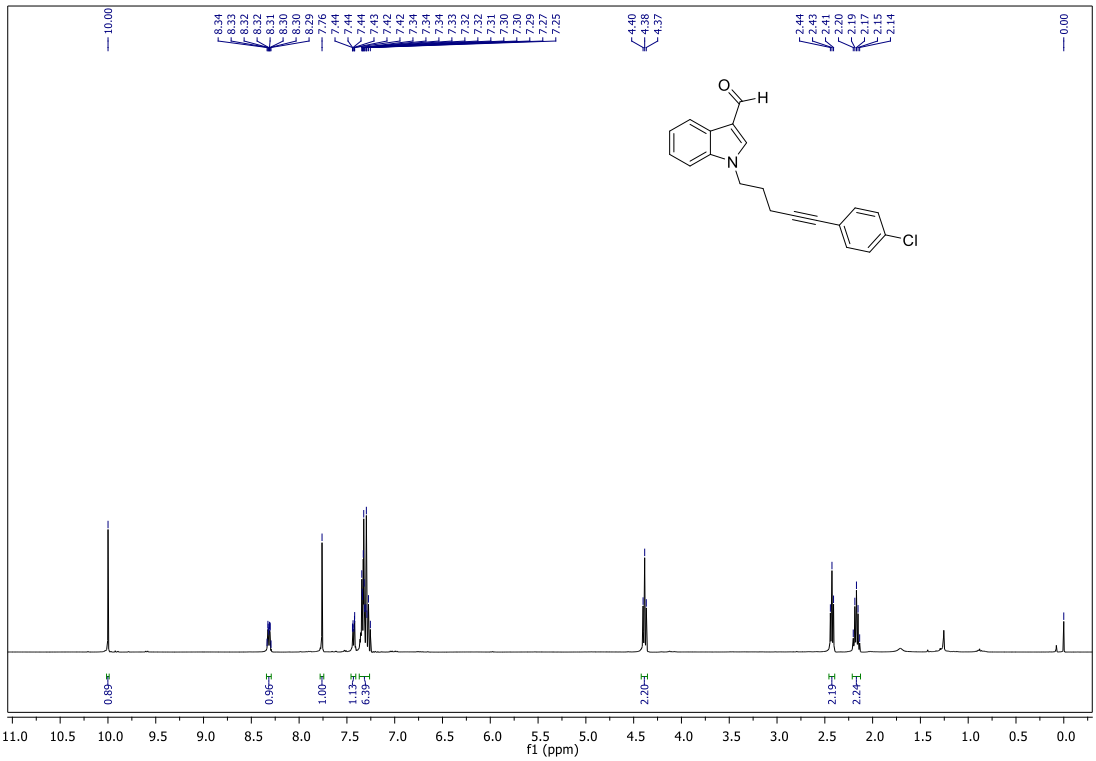
^{13}C NMR of compound **S-2g** in $CDCl_3$ (101 MHz)



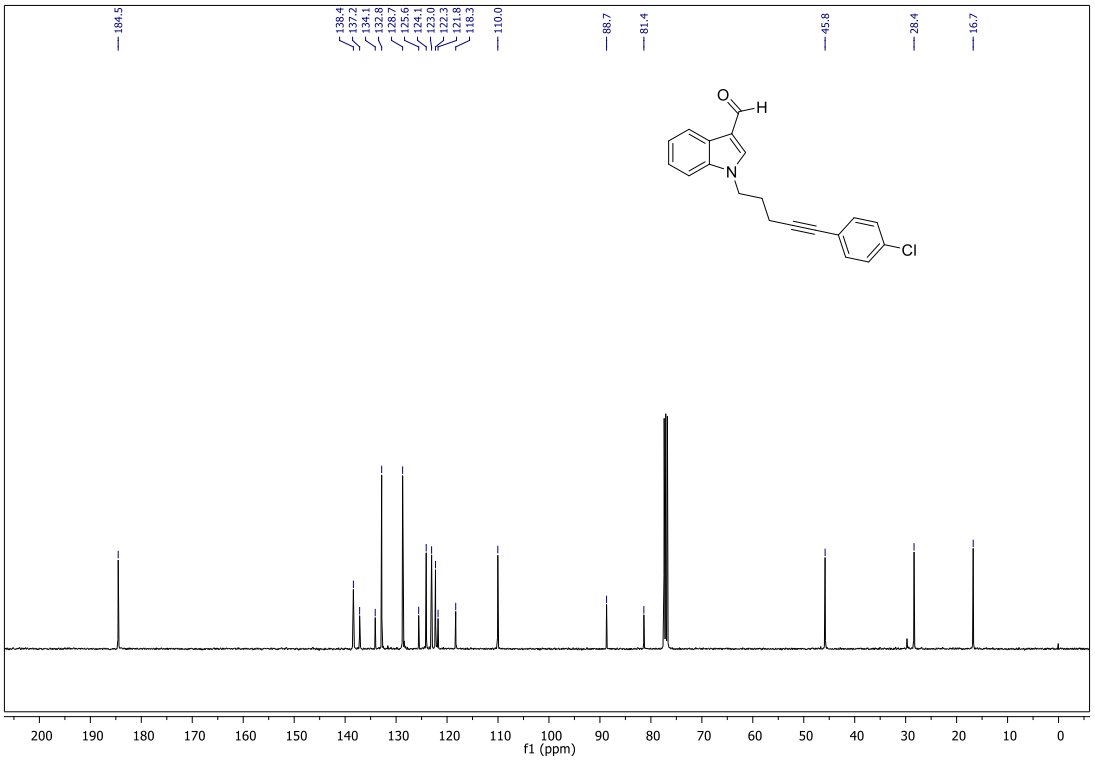
^{1}H NMR of compound **S-2h** in $CDCl_3$ (500 MHz)



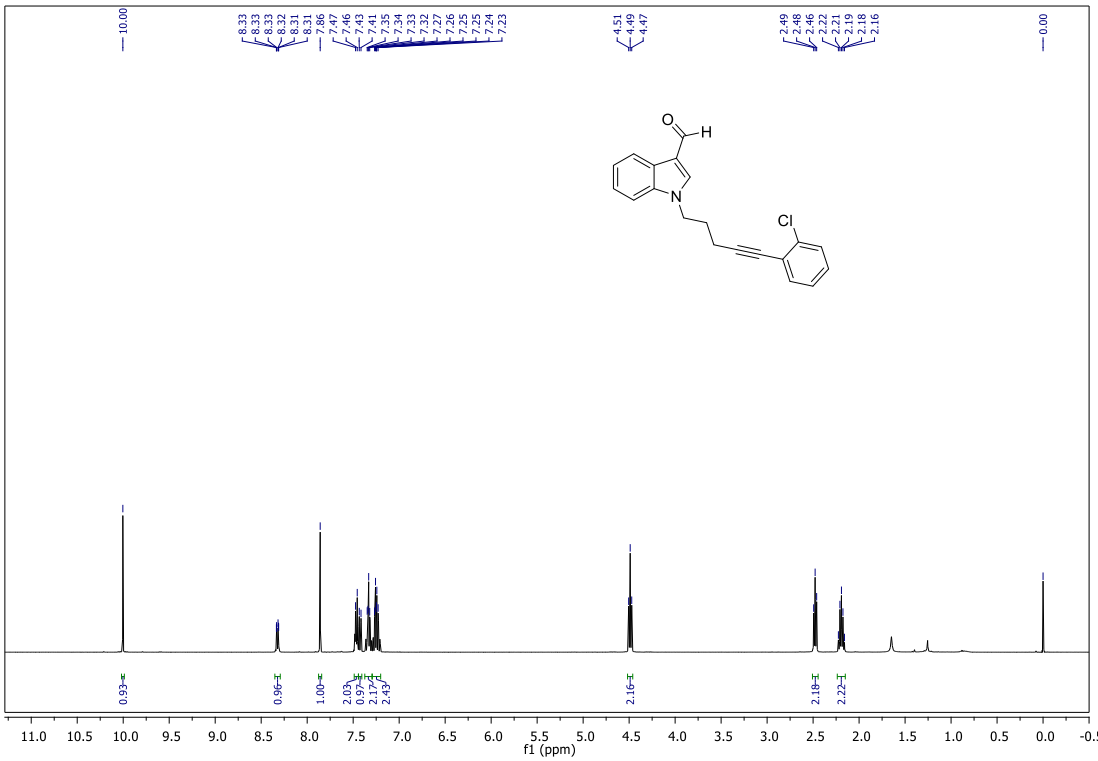
^{13}C NMR of compound **S-2h** in $CDCl_3$ (101 MHz)



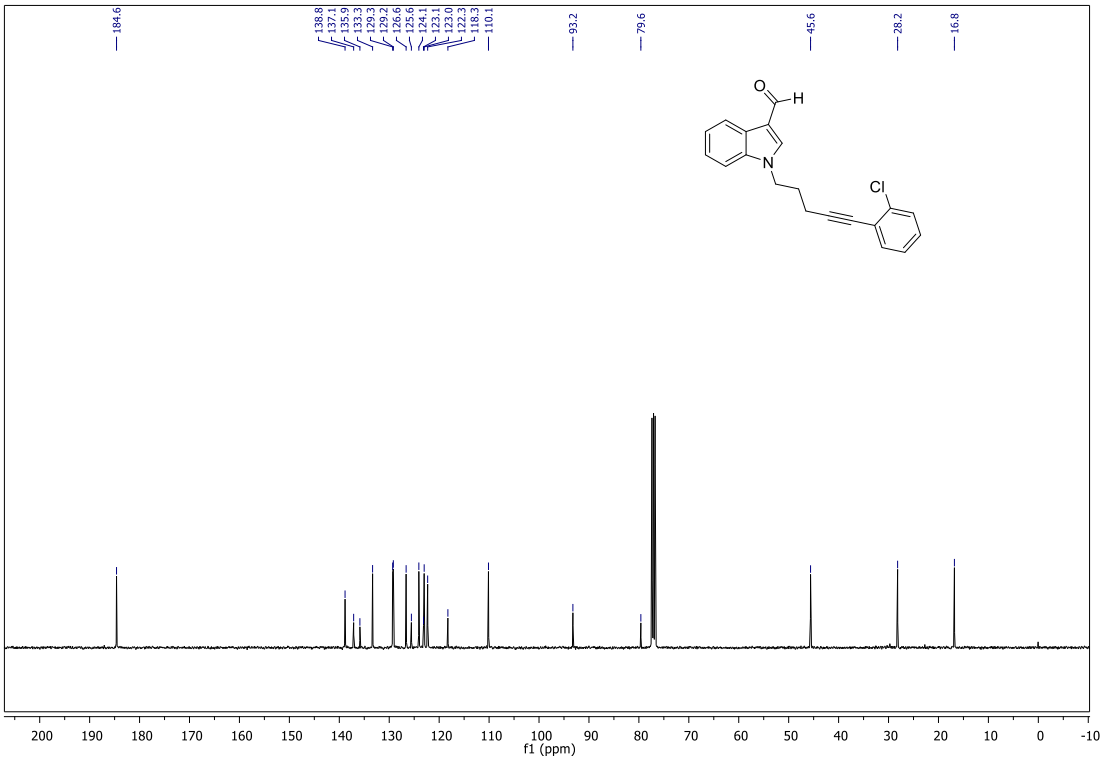
^{1}H NMR of compound **S-2i** in $CDCl_3$ (400 MHz)



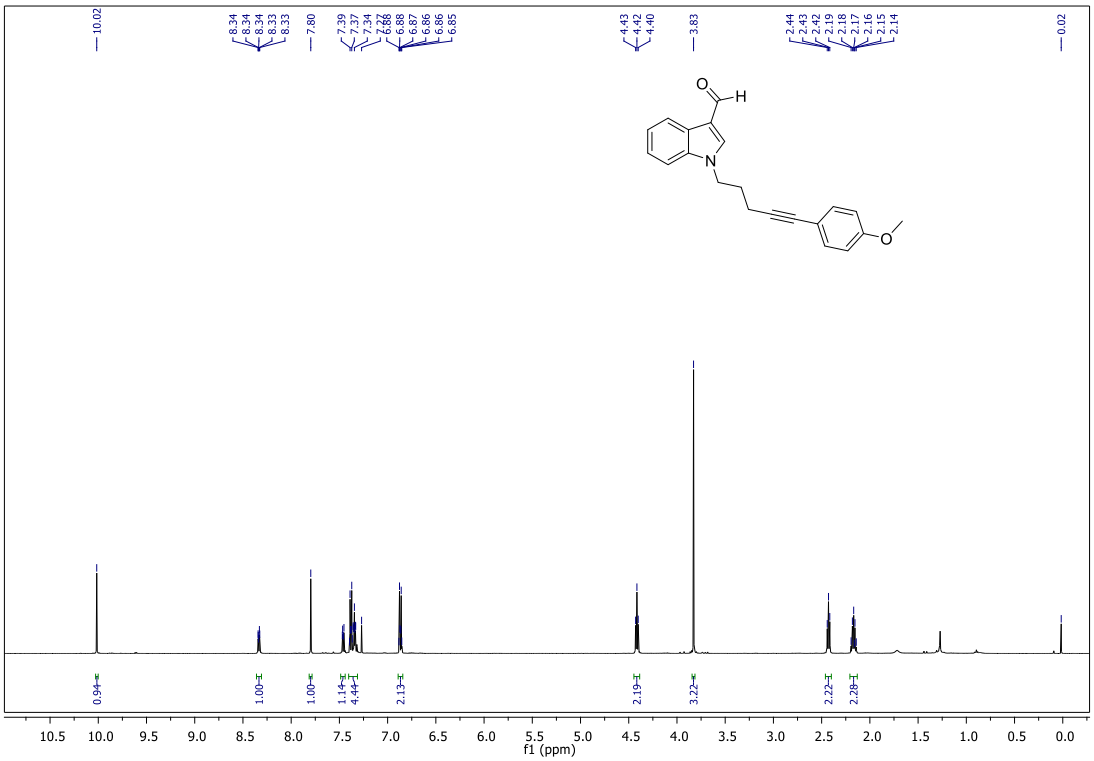
^{13}C NMR of compound **S-2i** in $CDCl_3$ (101 MHz)



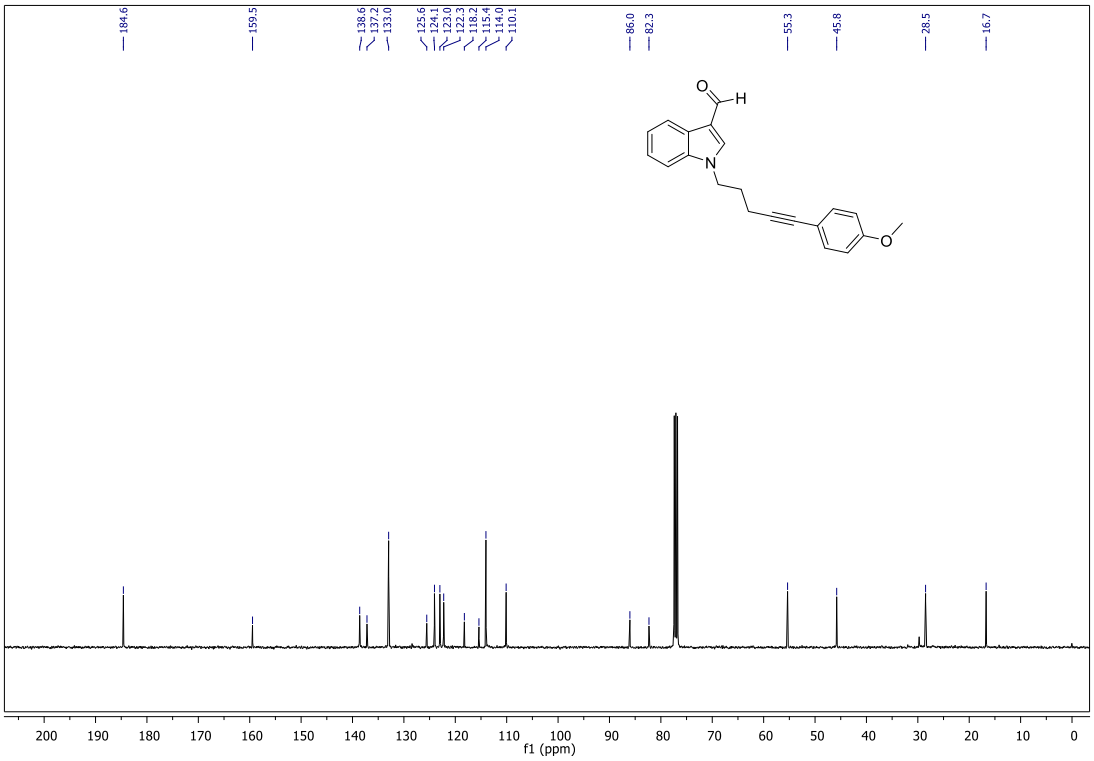
^{1}H NMR of compound **S-2j** in $CDCl_3$ (400 MHz)



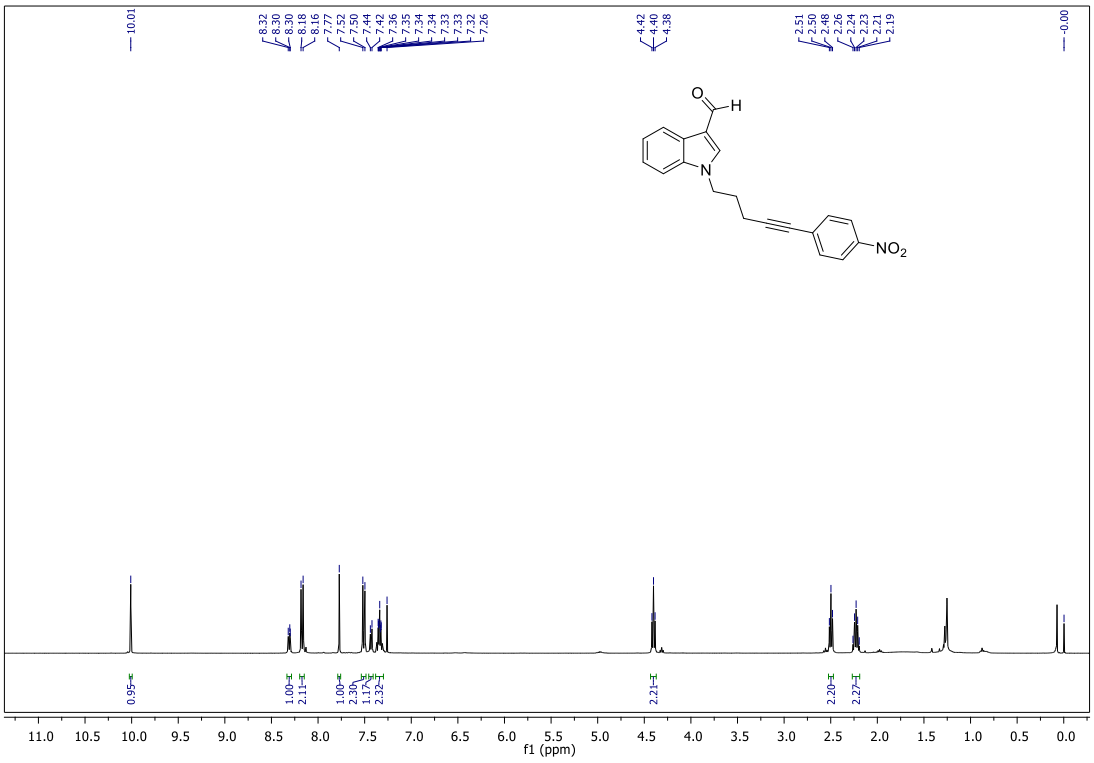
^{13}C NMR of compound **S-2j** in $CDCl_3$ (101 MHz)



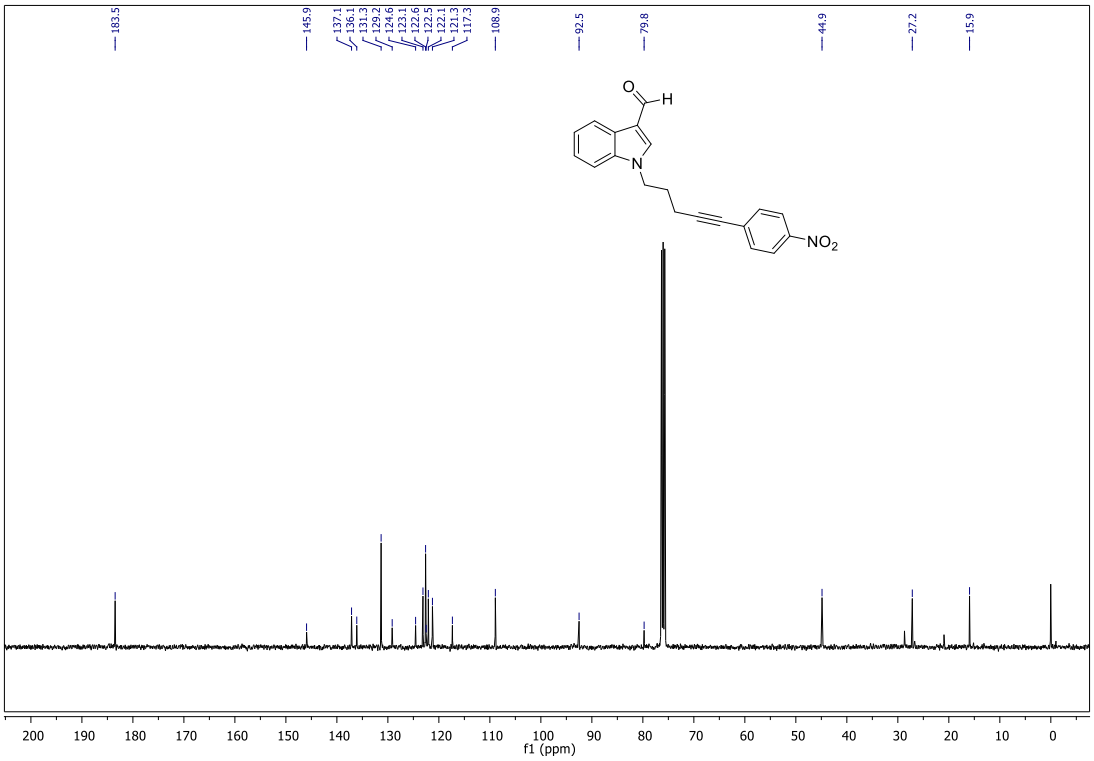
^{1}H NMR of compound **S-2k** in $CDCl_3$ (500 MHz)



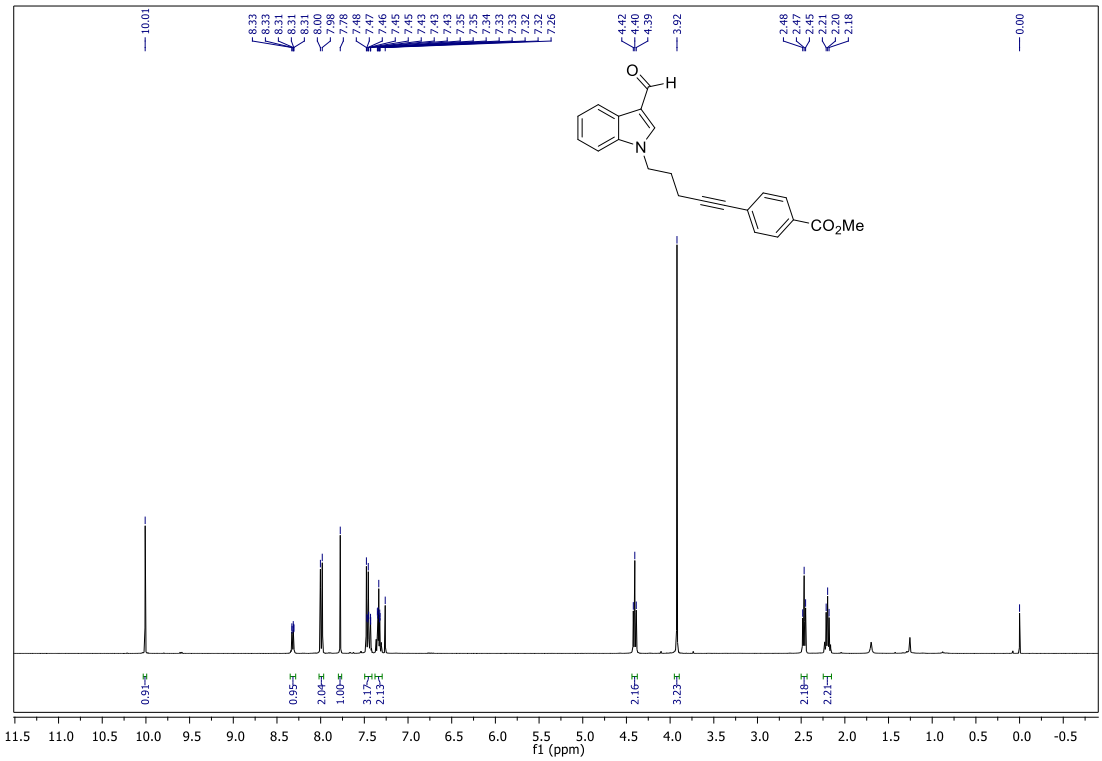
^{13}C NMR of compound **S-2k** in $CDCl_3$ (101 MHz)



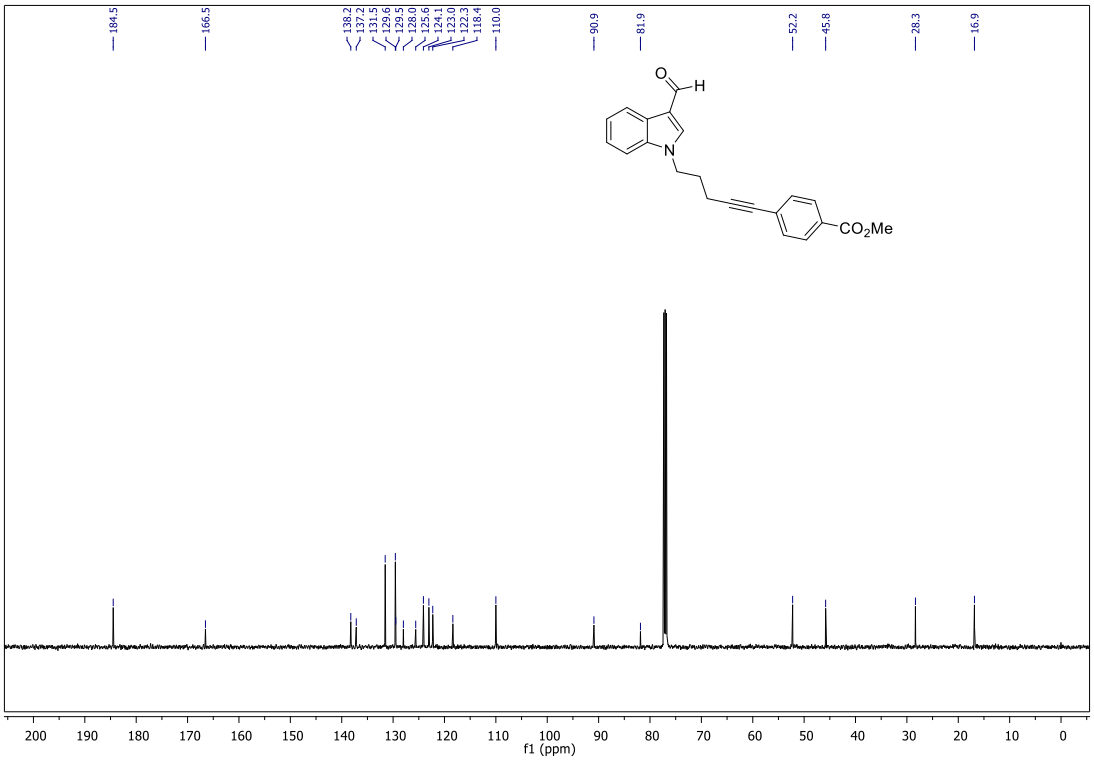
^{1}H NMR of compound **S-2l** in $CDCl_3$ (400 MHz)



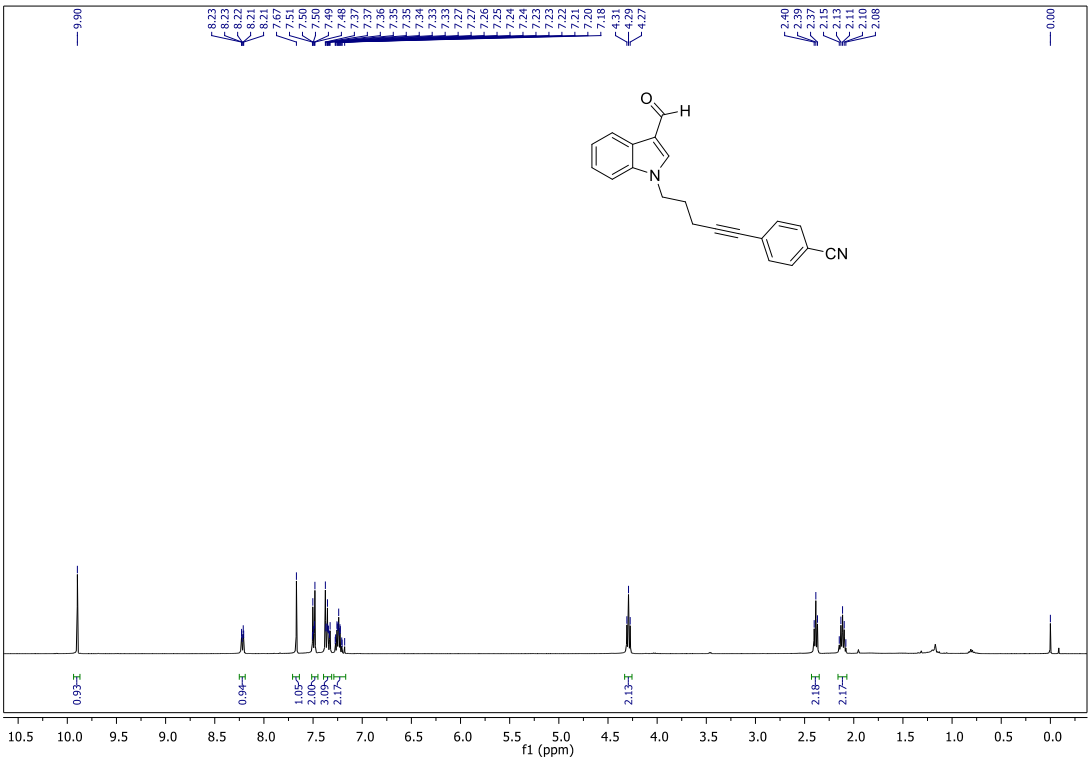
^{13}C NMR of compound **S-2l** in $CDCl_3$ (101 MHz)



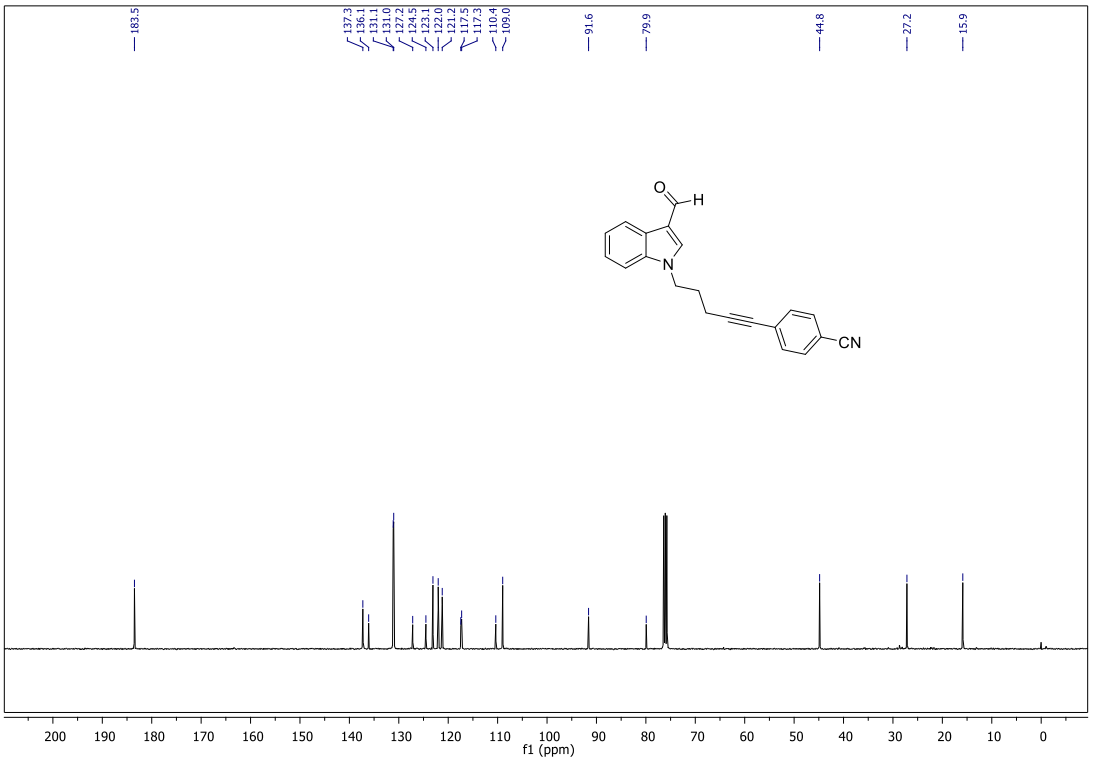
^{1}H NMR of compound **S-2m** in $CDCl_3$ (400 MHz)



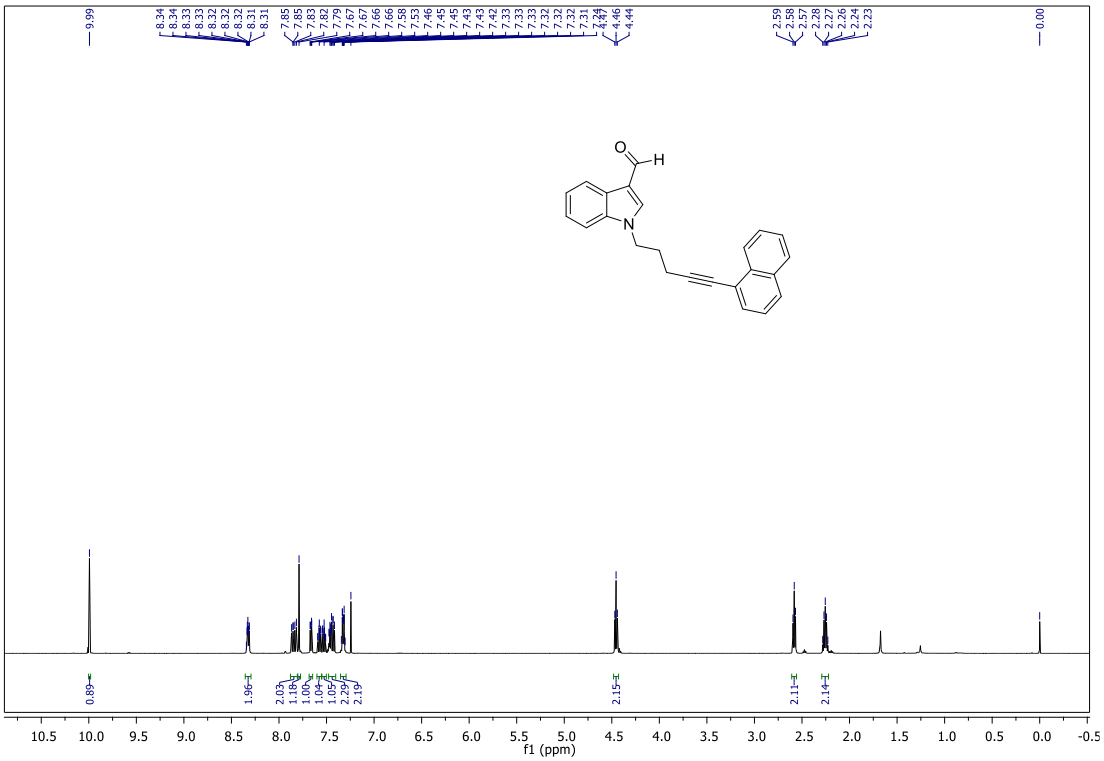
^{13}C NMR of compound **S-2m** in $CDCl_3$ (126 MHz)



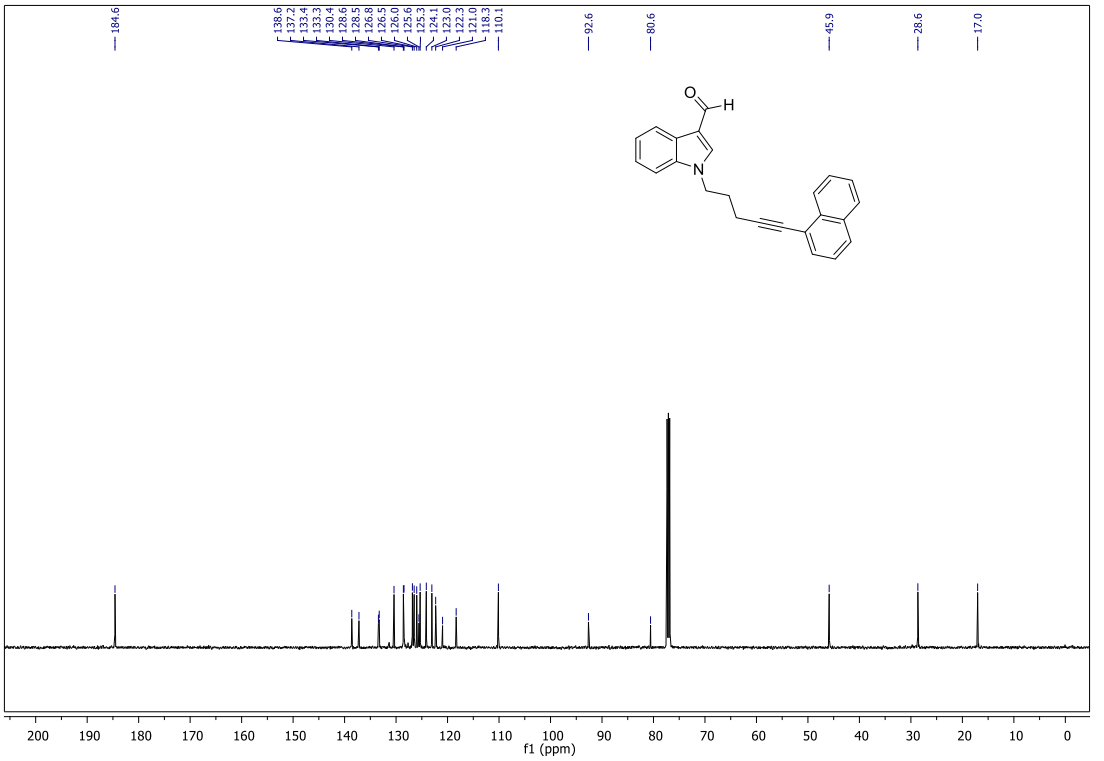
^{1}H NMR of compound **S-2n** in $CDCl_3$ (400 MHz)



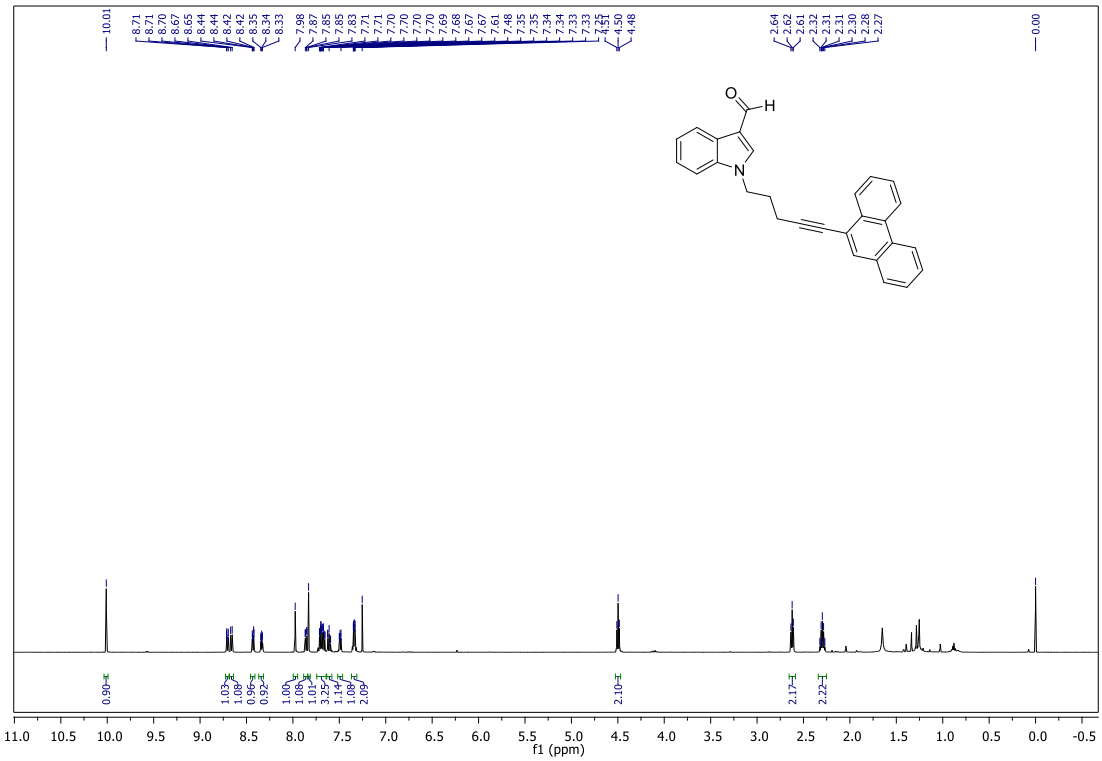
^{13}C NMR of compound **S-2n** in $CDCl_3$ (101 MHz)



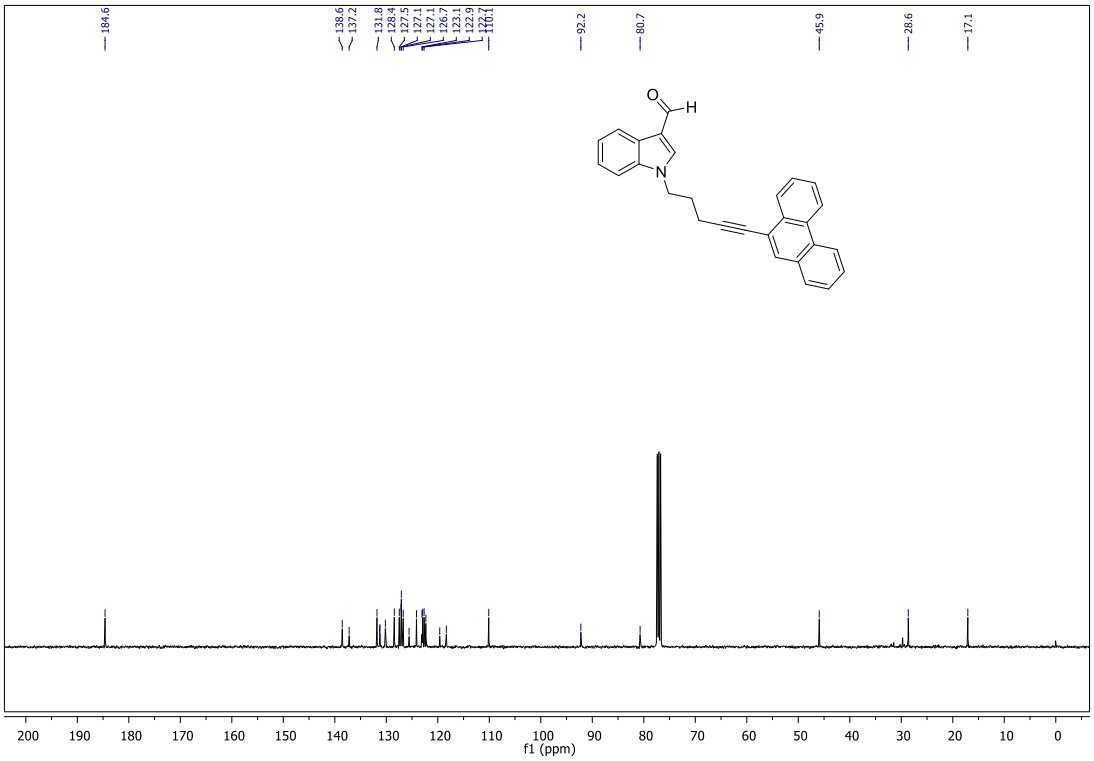
^{1}H NMR of compound **S-2o** in $CDCl_3$ (500 MHz)



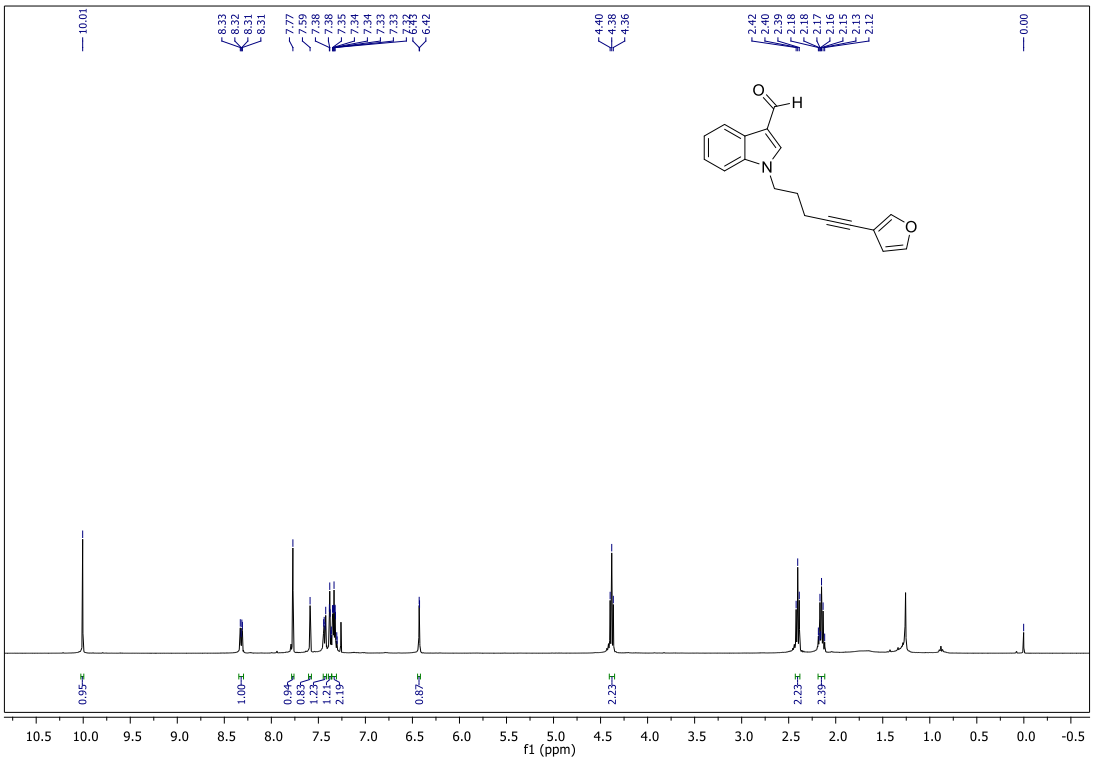
^{13}C NMR of compound **S-2o** in $CDCl_3$ (126 MHz)



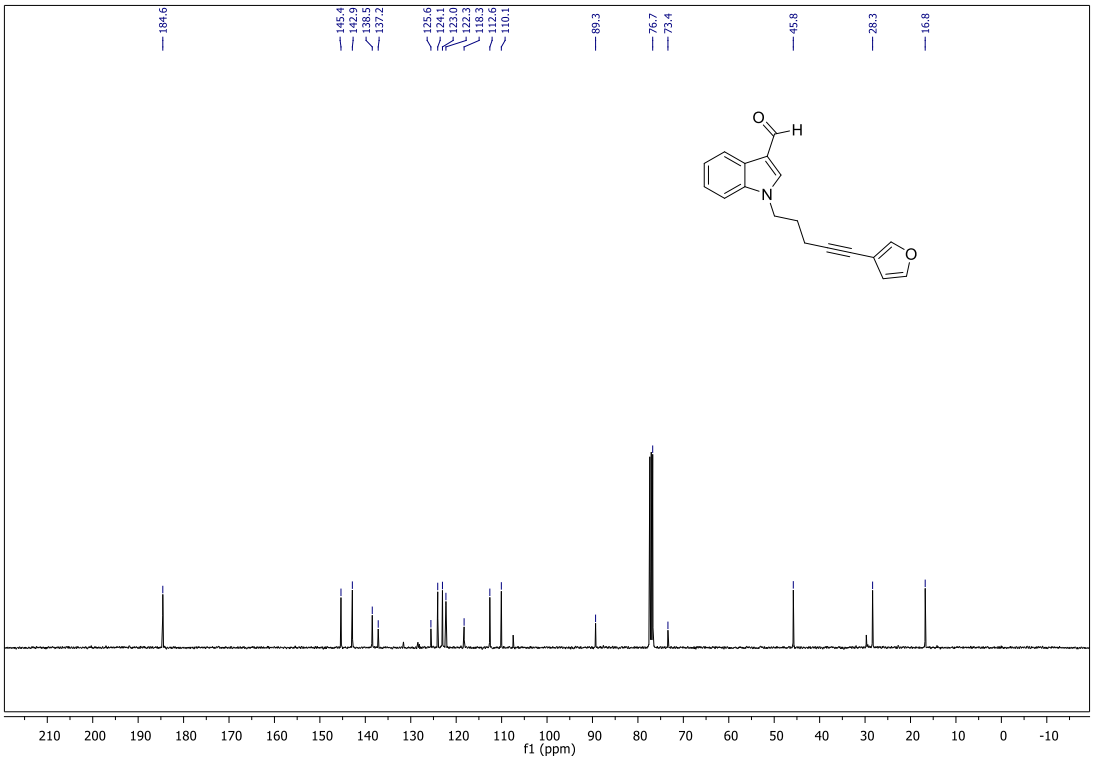
^{1}H NMR of compound **S-2p** in $CDCl_3$ (400 MHz)



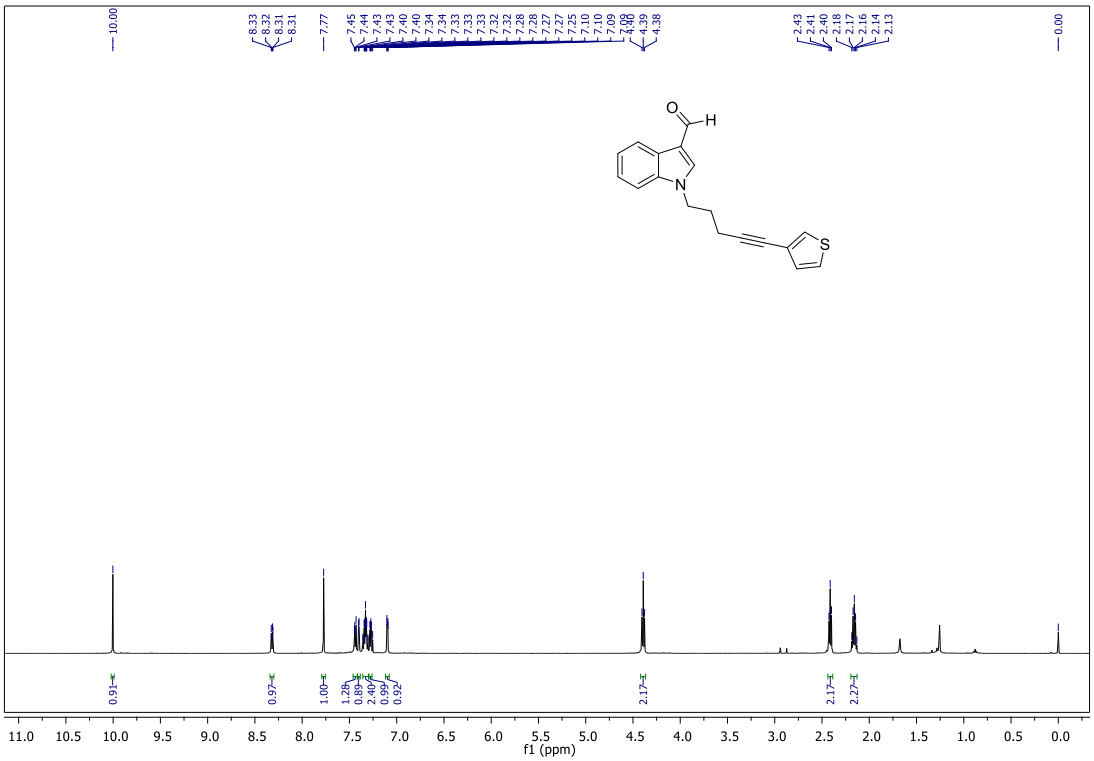
^{13}C NMR of compound **S-2p** in $CDCl_3$ (101 MHz)



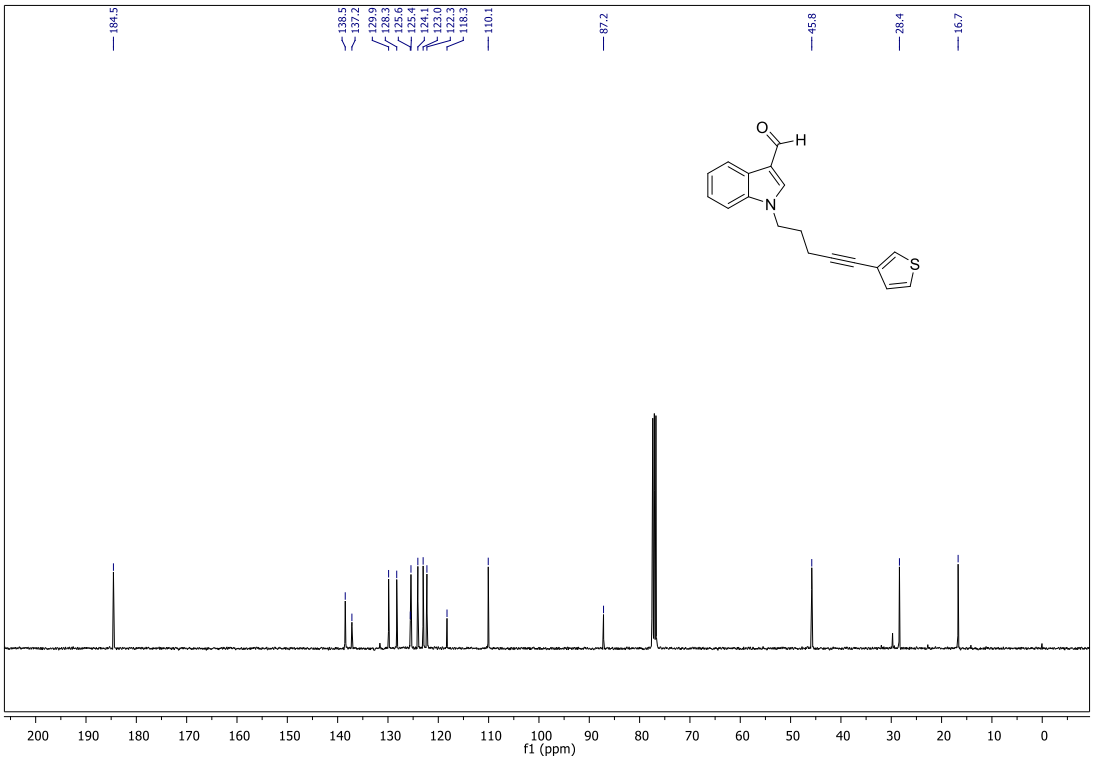
^{1}H NMR of compound **S-2q** in $CDCl_3$ (400 MHz)



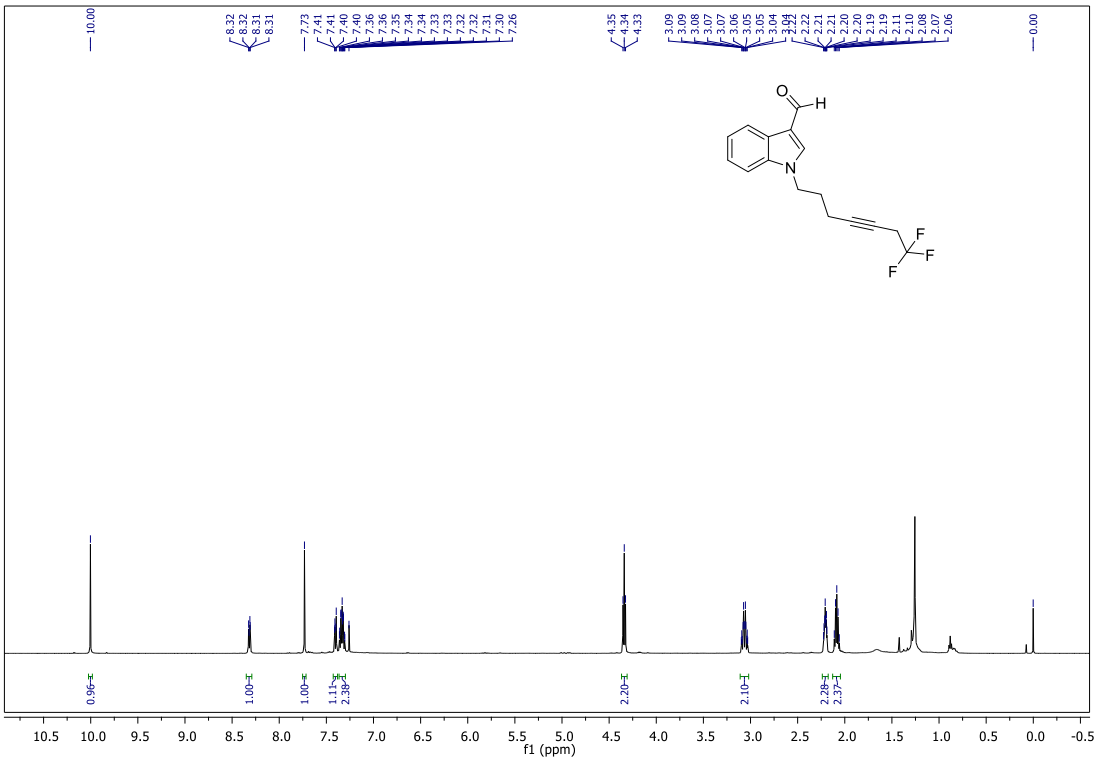
^{13}C NMR of compound **S-2q** in $CDCl_3$ (101 MHz)



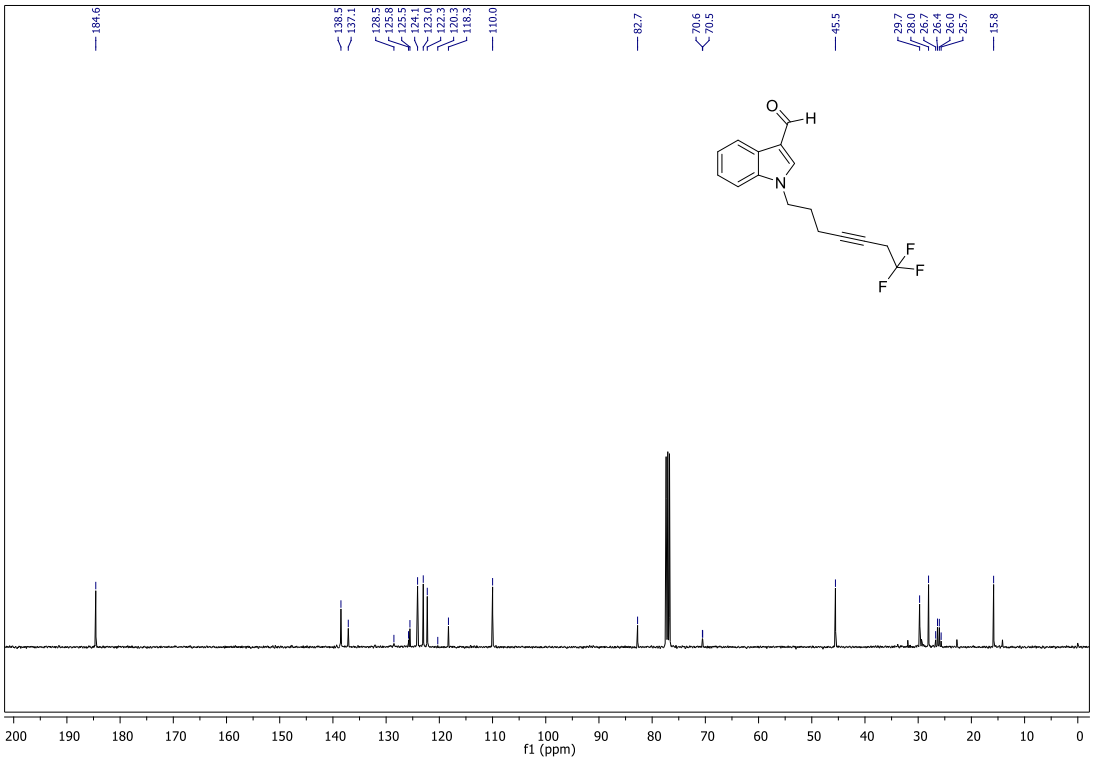
^{1}H NMR of compound **S-2r** in $CDCl_3$ (500 MHz)



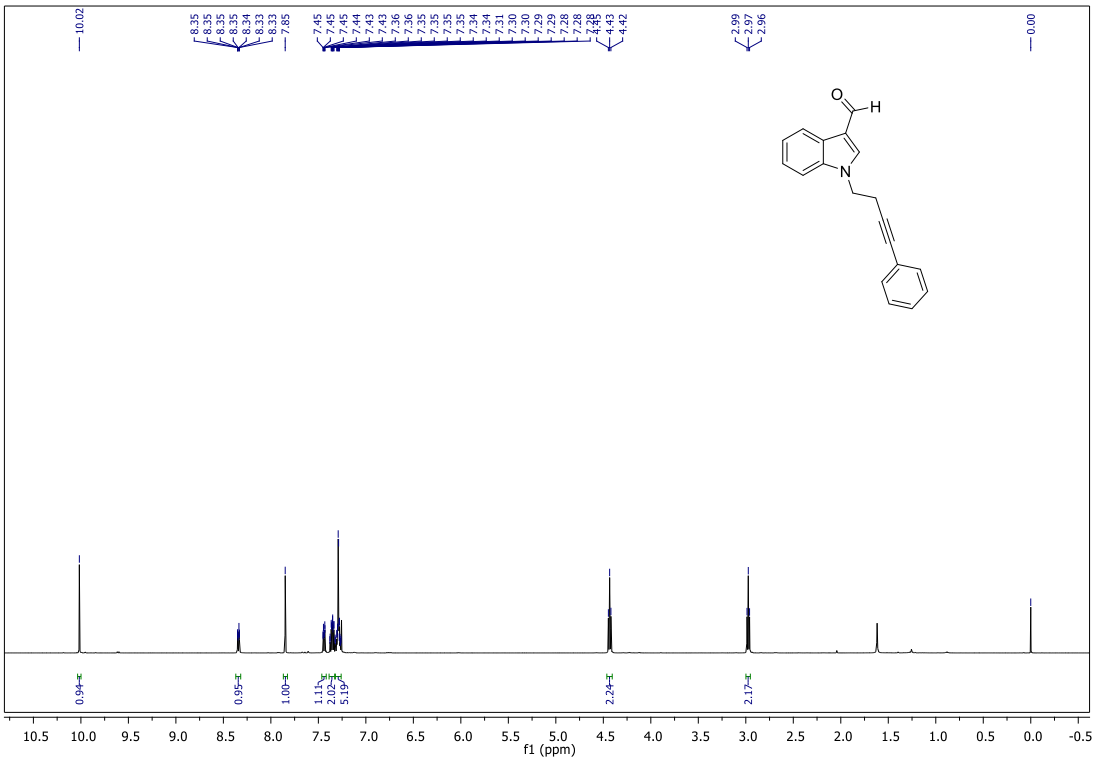
^{13}C NMR of compound **S-2r** in $CDCl_3$ (101 MHz)



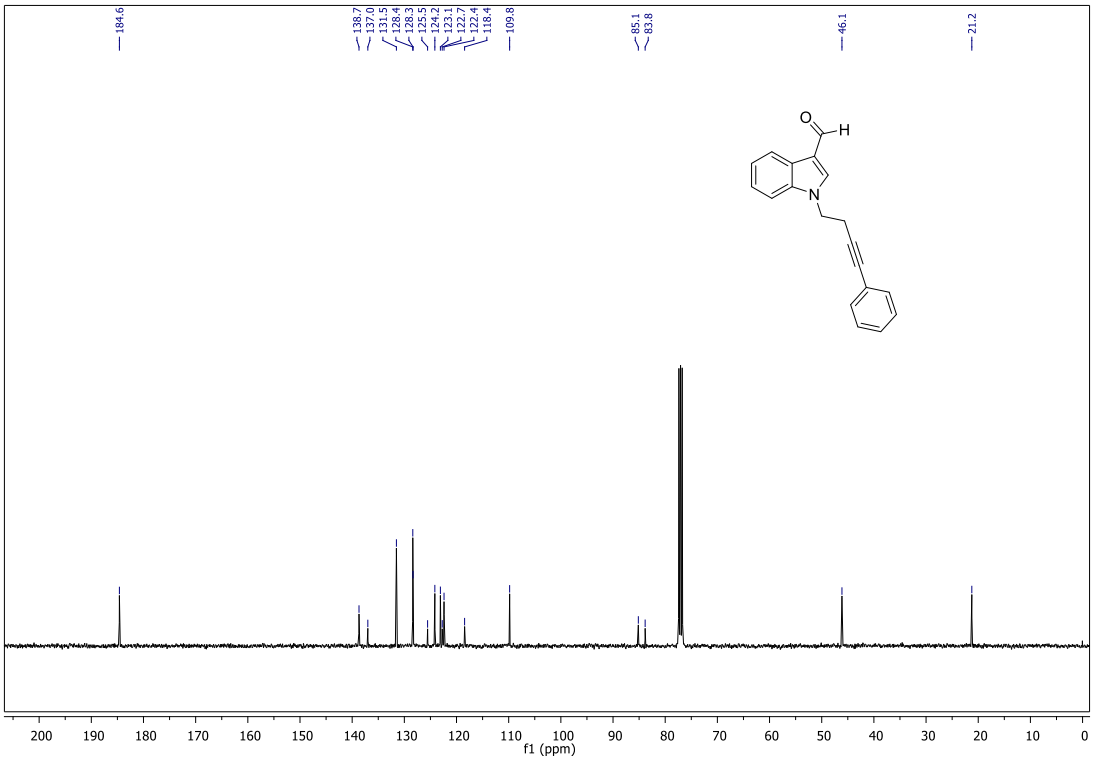
^{1}H NMR of compound **S-2s** in $CDCl_3$ (500 MHz)



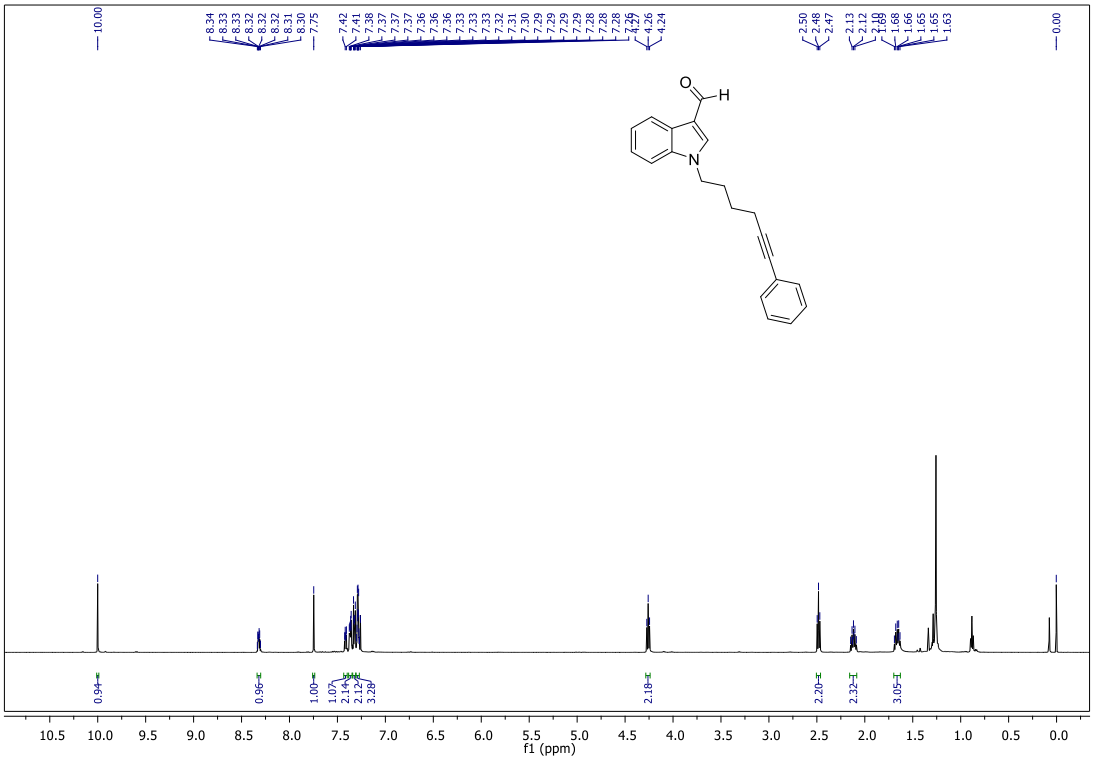
^{13}C NMR of compound **S-2s** in $CDCl_3$ (101 MHz)



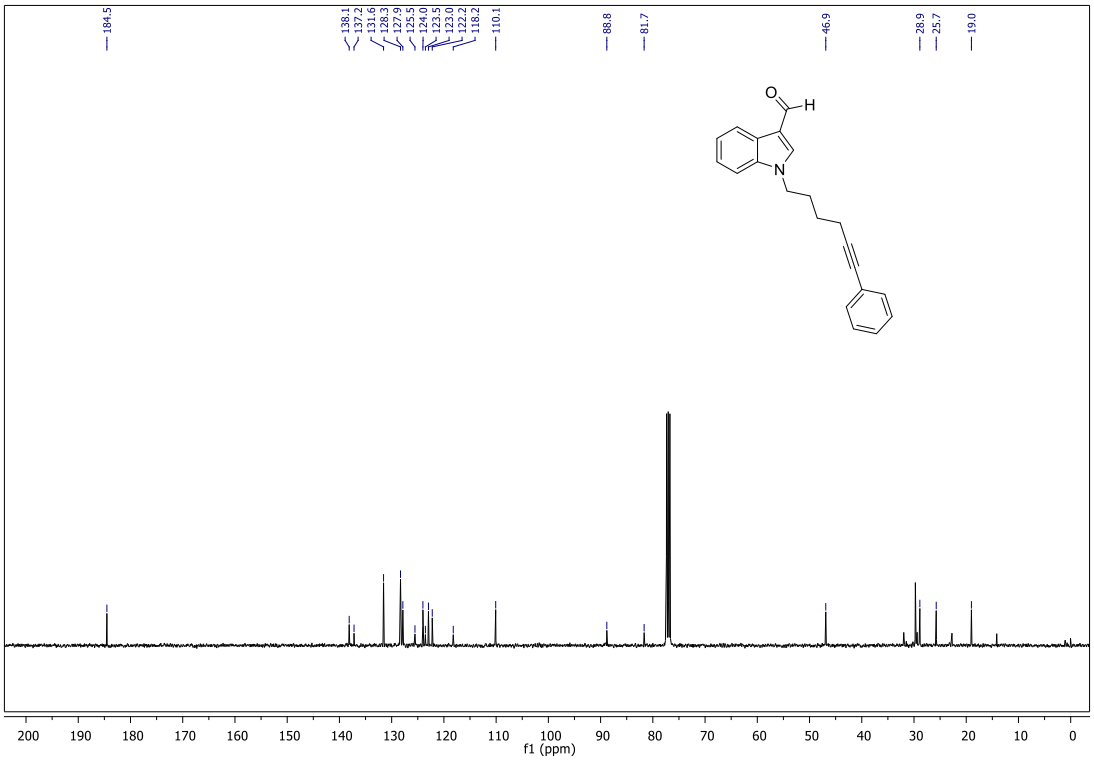
^{1}H NMR of compound **S-2t** in $CDCl_3$ (500 MHz)



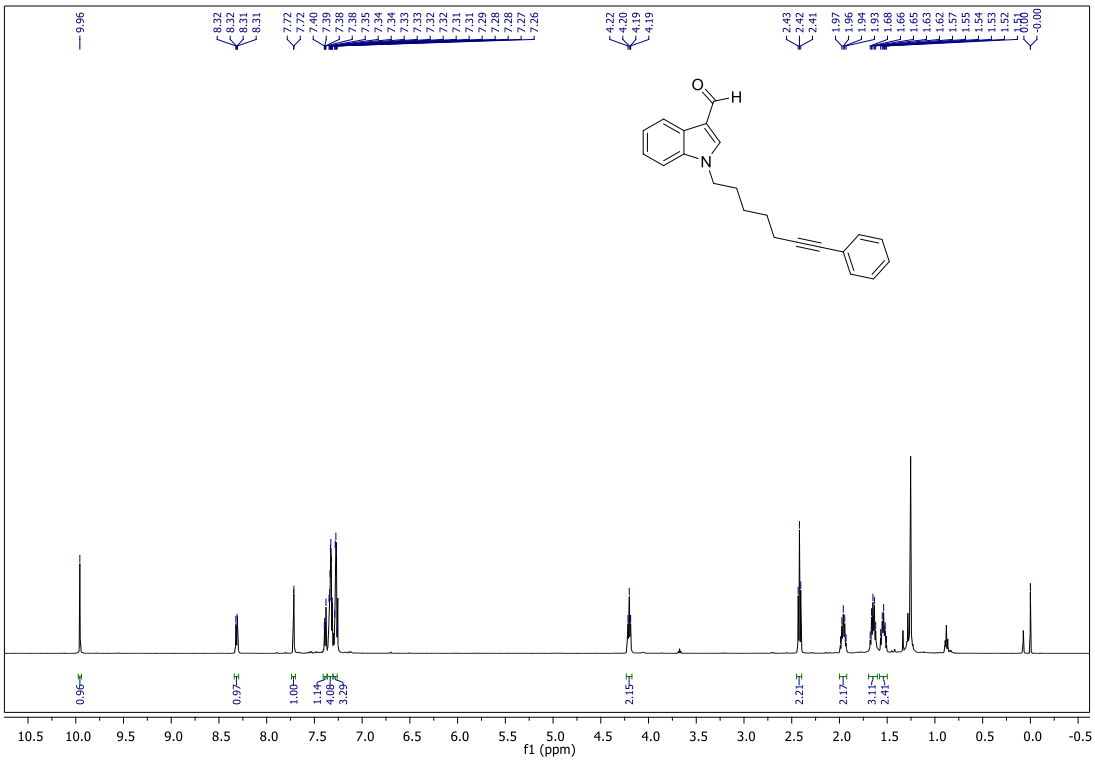
^{13}C NMR of compound **S-2t** in $CDCl_3$ (101 MHz)



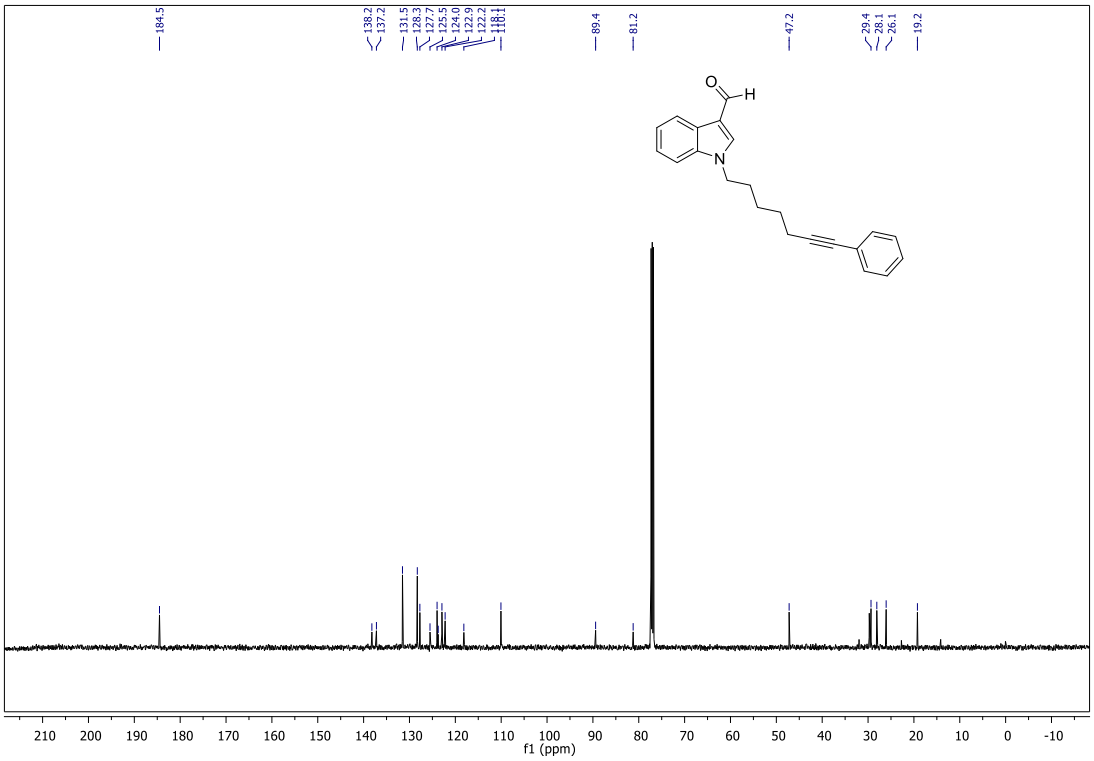
^{1}H NMR of compound **S-2u** in $CDCl_3$ (500 MHz)



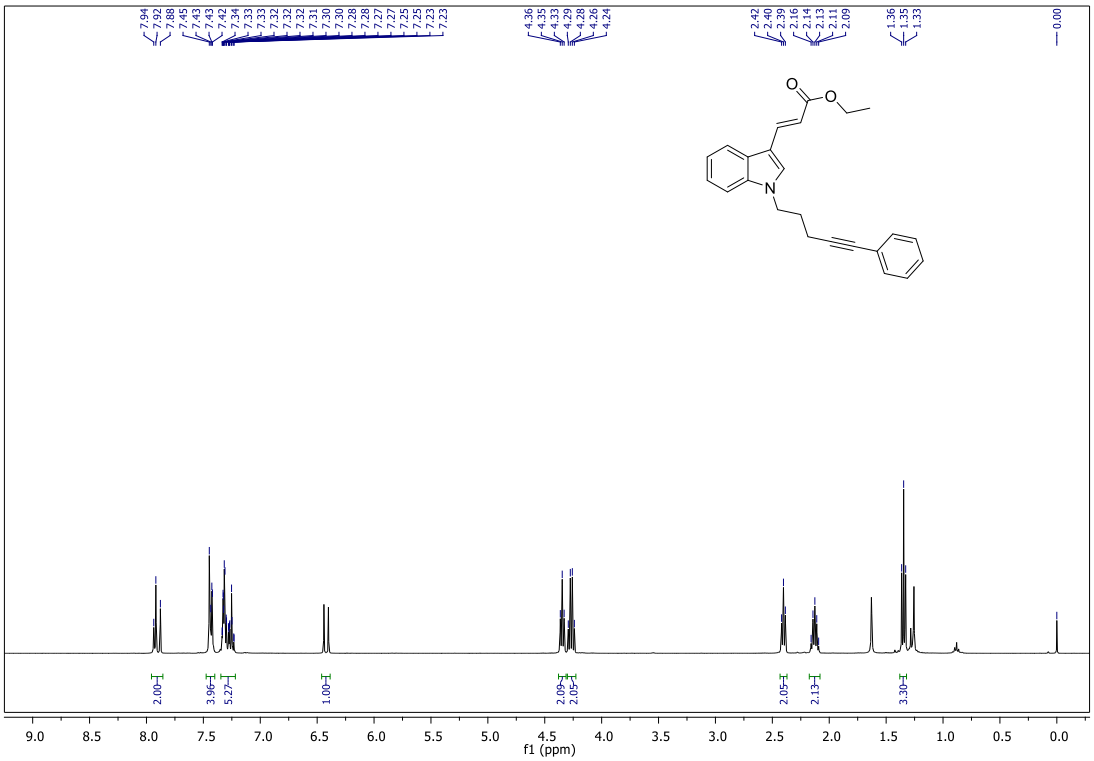
^{13}C NMR of compound **S-2u** in $CDCl_3$ (101 MHz)



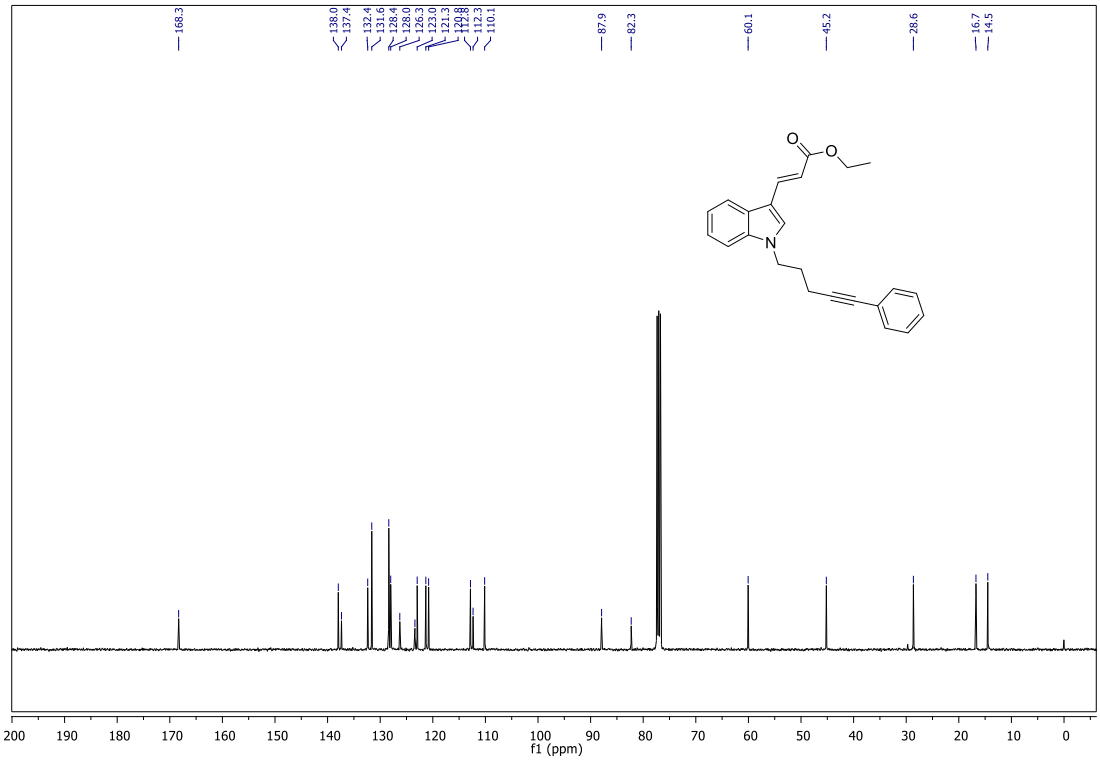
^{1}H NMR of compound **S-2v** in $CDCl_3$ (500 MHz)



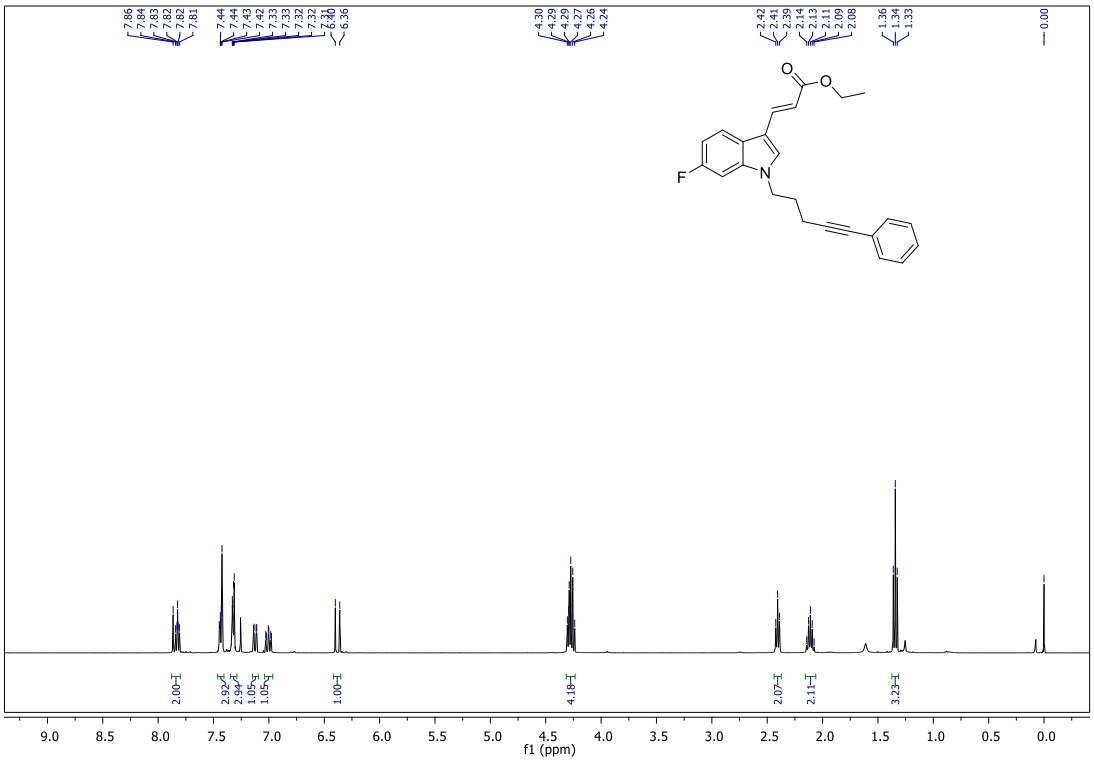
^{13}C NMR of compound **S-2v** in $CDCl_3$ (126 MHz)



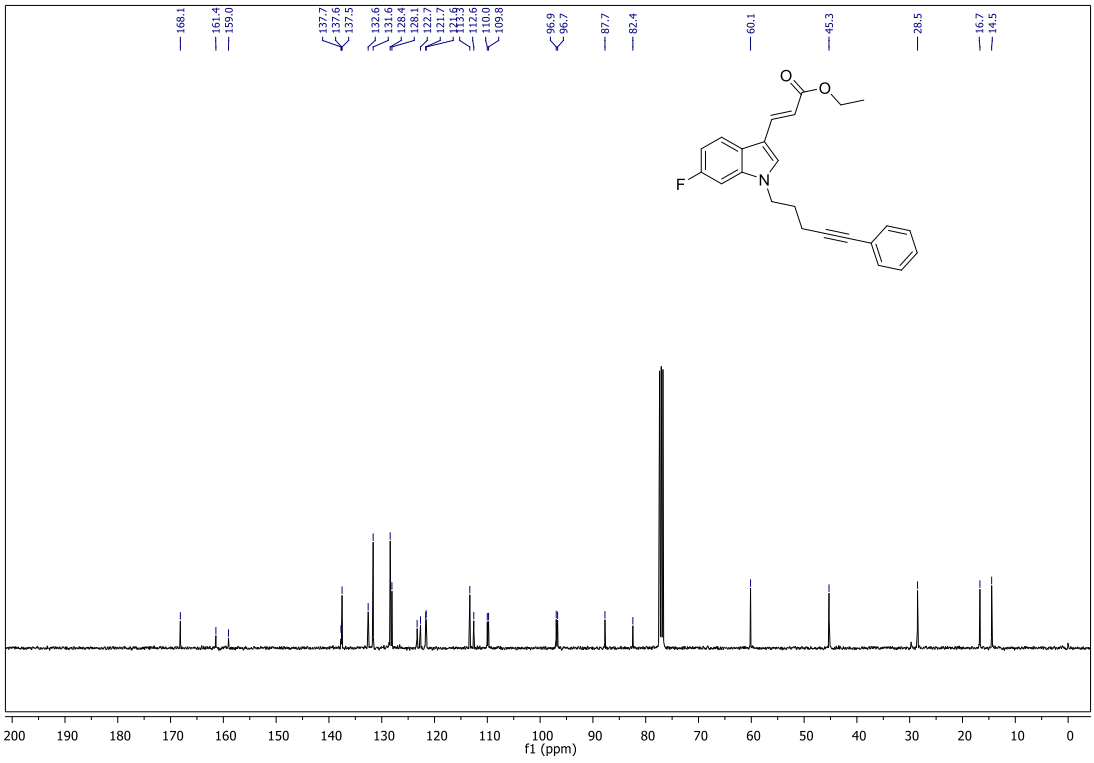
^{1}H NMR of compound **1a** in $CDCl_3$ (400 MHz)



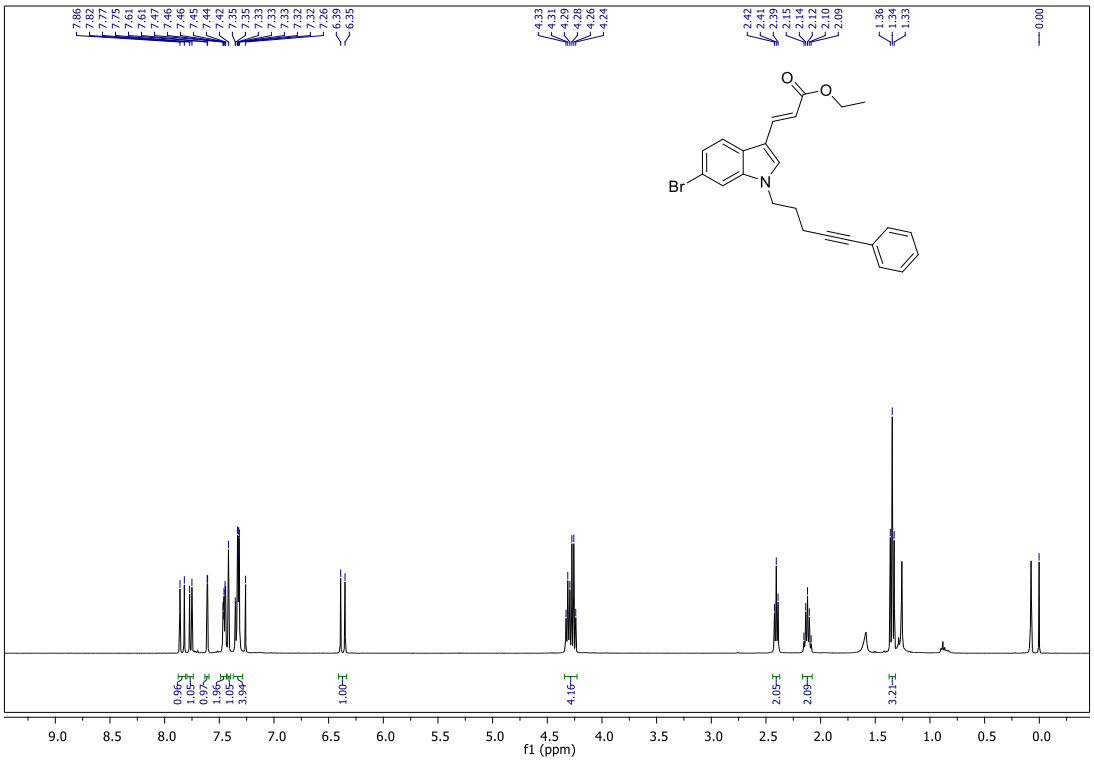
^{13}C NMR of compound **1a** in $CDCl_3$ (101 MHz)



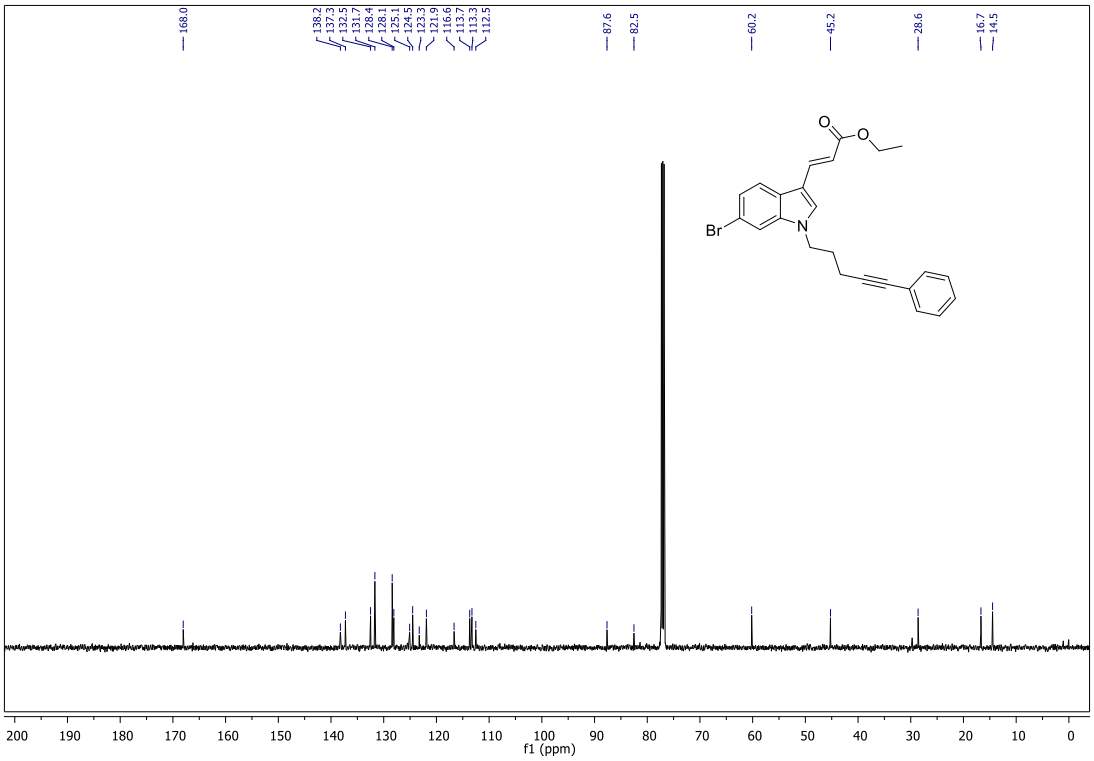
^{1}H NMR of compound **1b** in $CDCl_3$ (400 MHz)



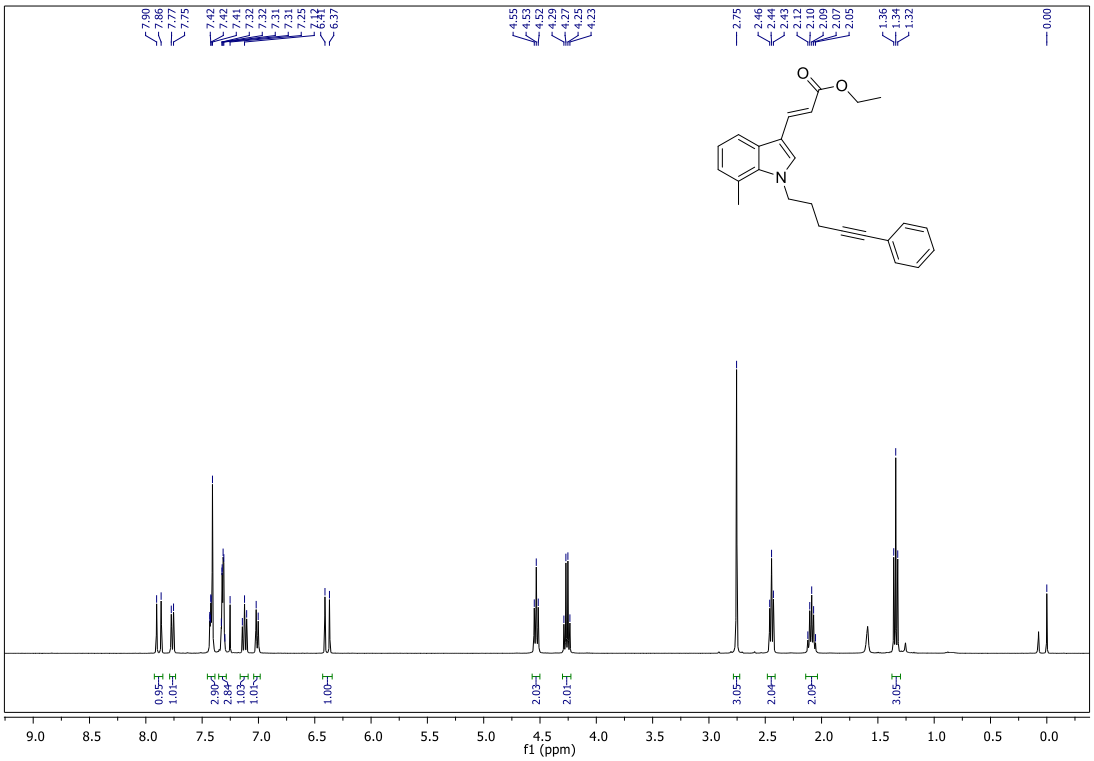
^{13}C NMR of compound **1b** in $CDCl_3$ (101 MHz)



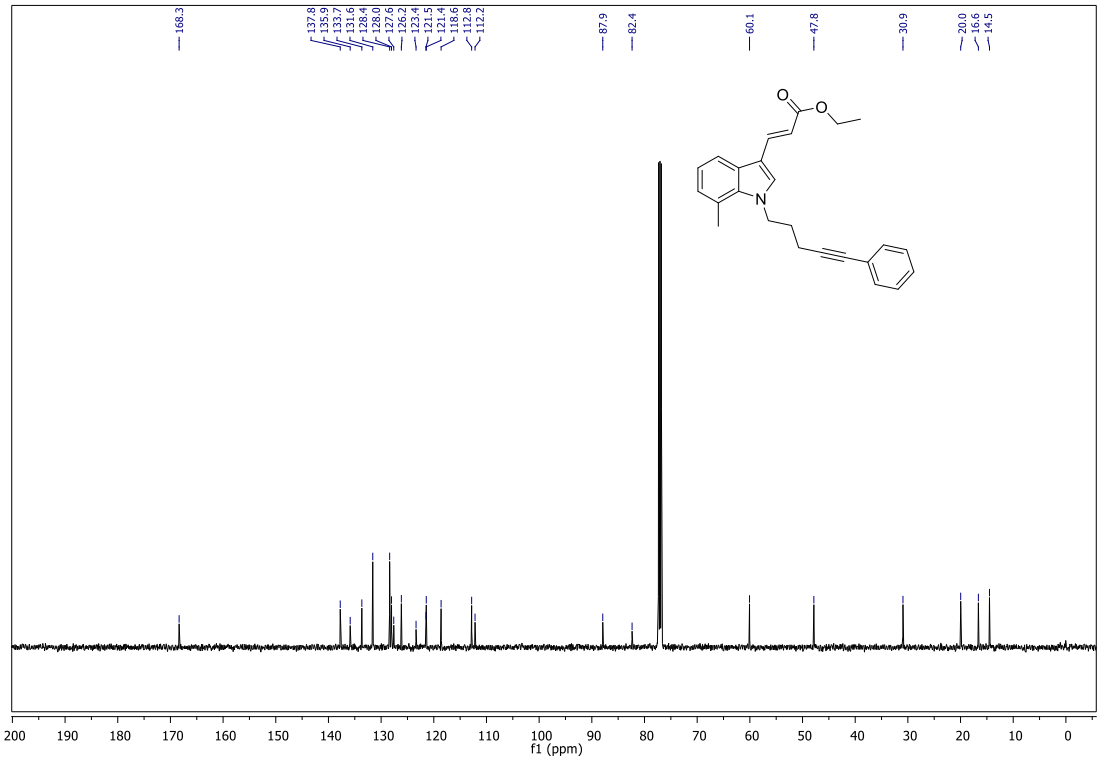
^{1}H NMR of compound **1c** in $CDCl_3$ (400 MHz)



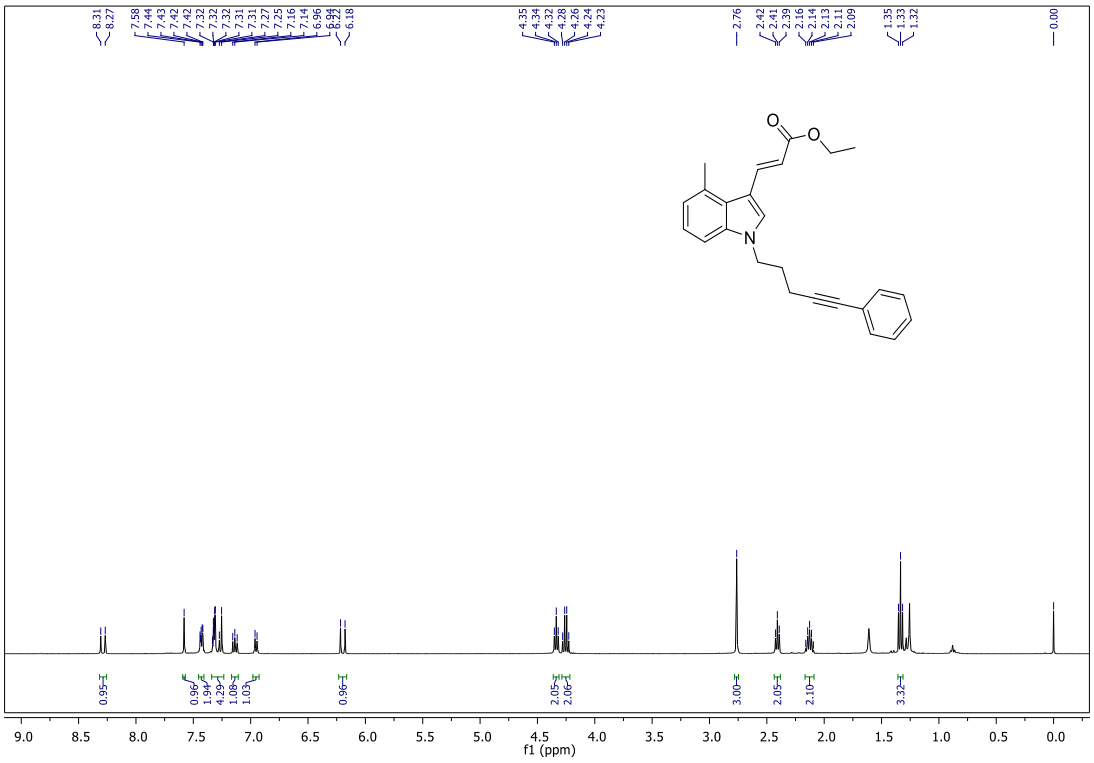
^{13}C NMR of compound **1c** in $CDCl_3$ (126 MHz)



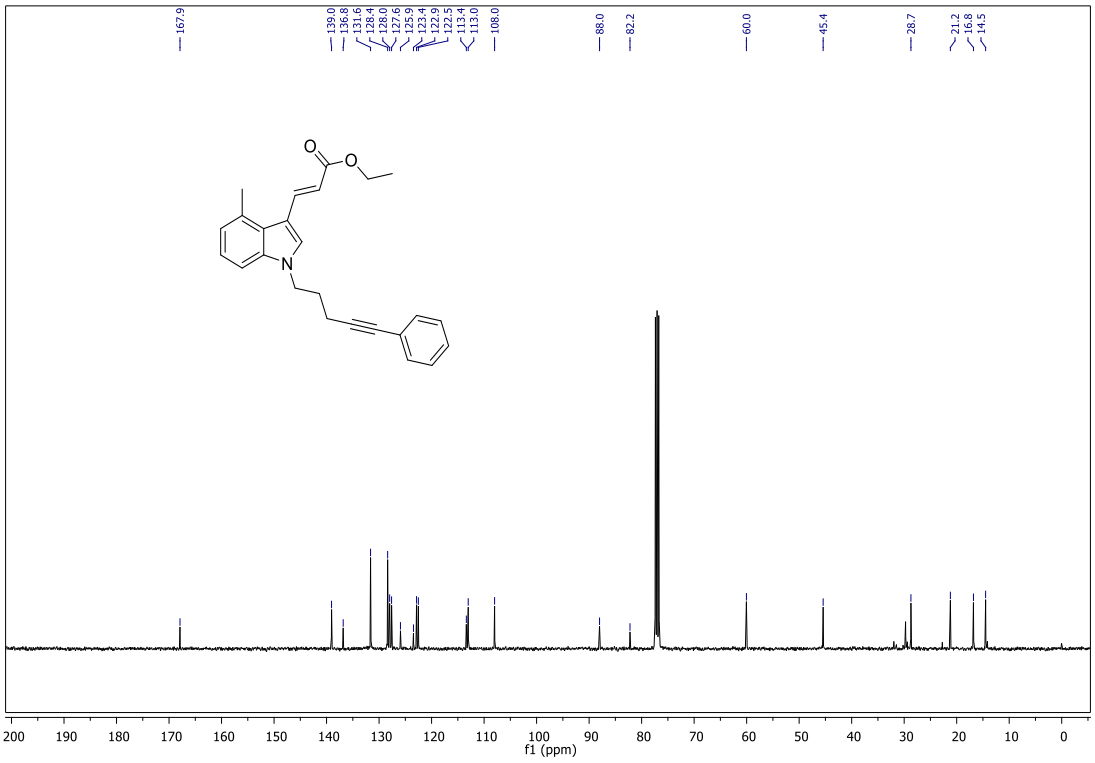
^{1}H NMR of compound **1d** in $CDCl_3$ (400 MHz)



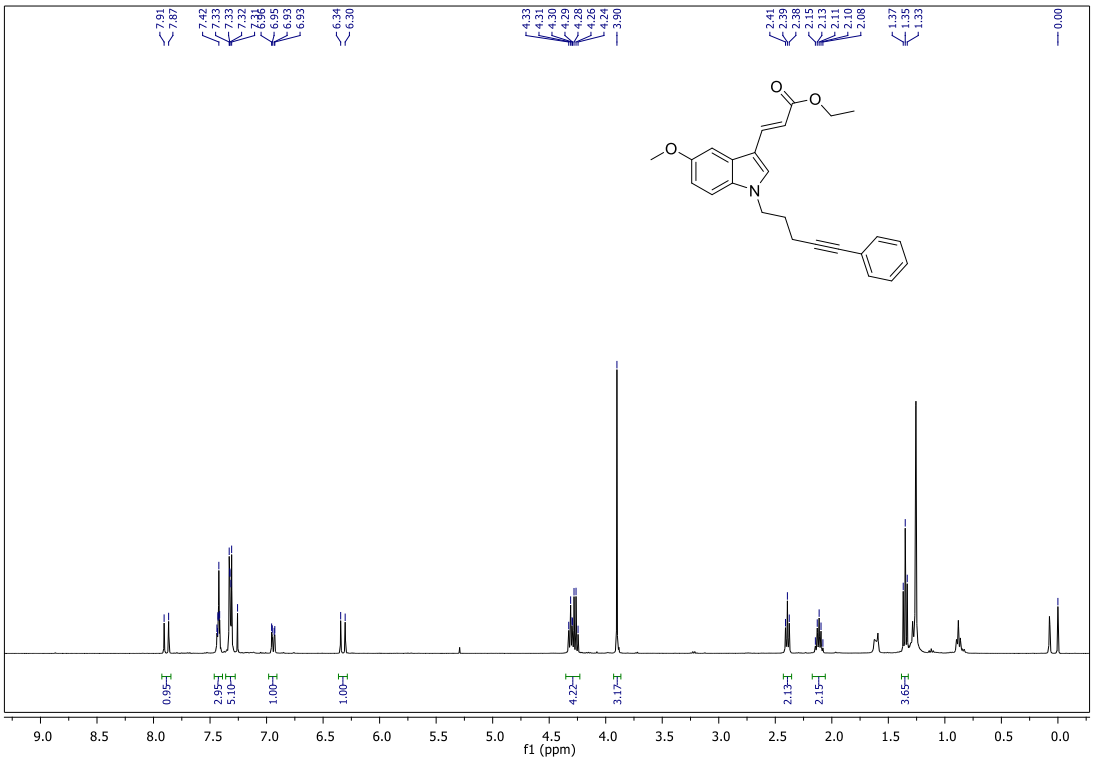
^{13}C NMR of compound **1d** in $CDCl_3$ (126 MHz)



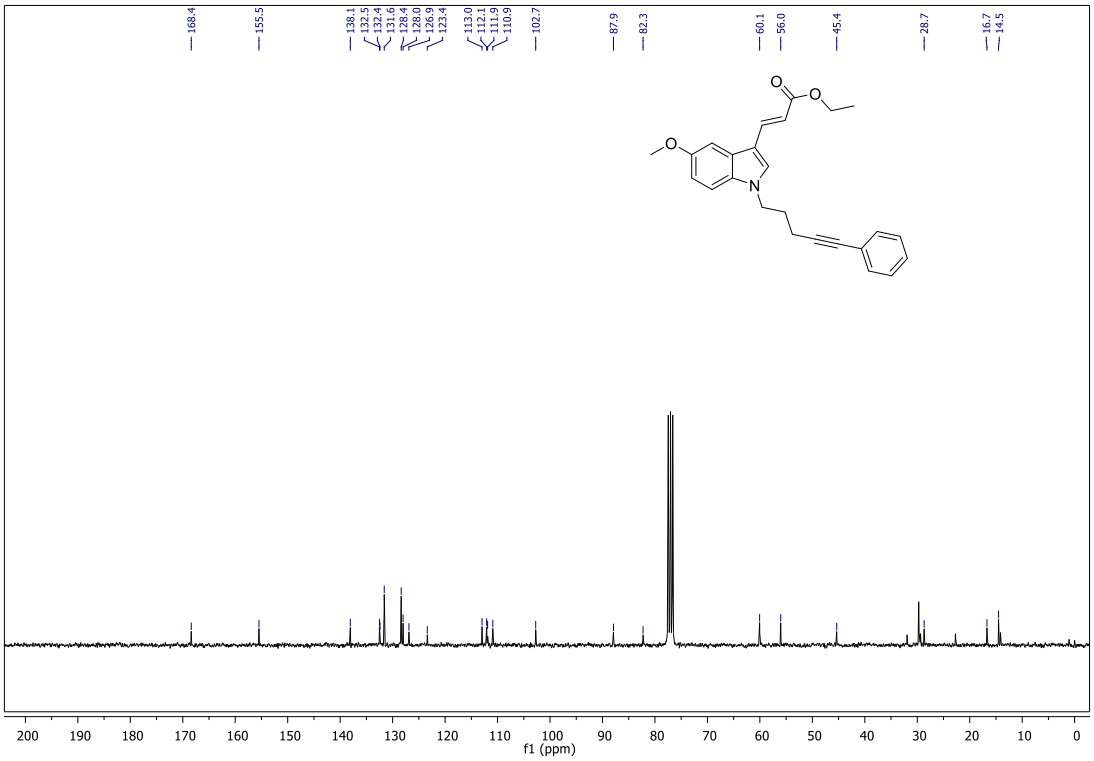
^{1}H NMR of compound **1e** in $CDCl_3$ (400 MHz)



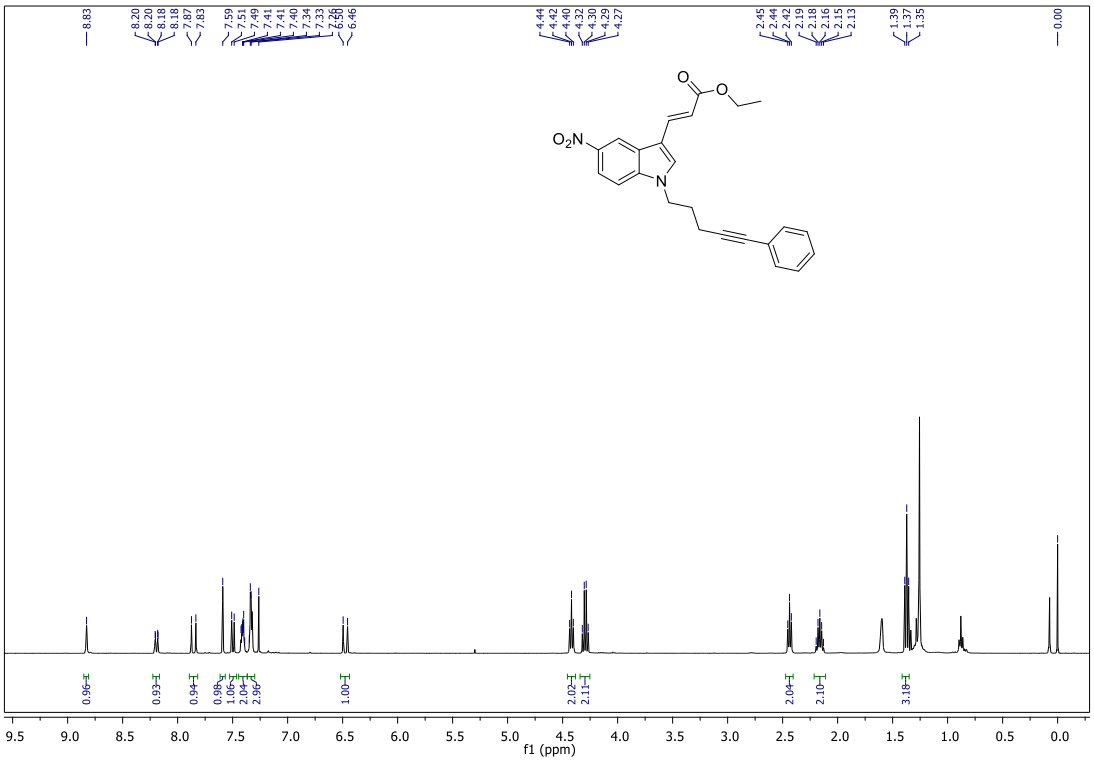
^{13}C NMR of compound **1e** in $CDCl_3$ (101 MHz)



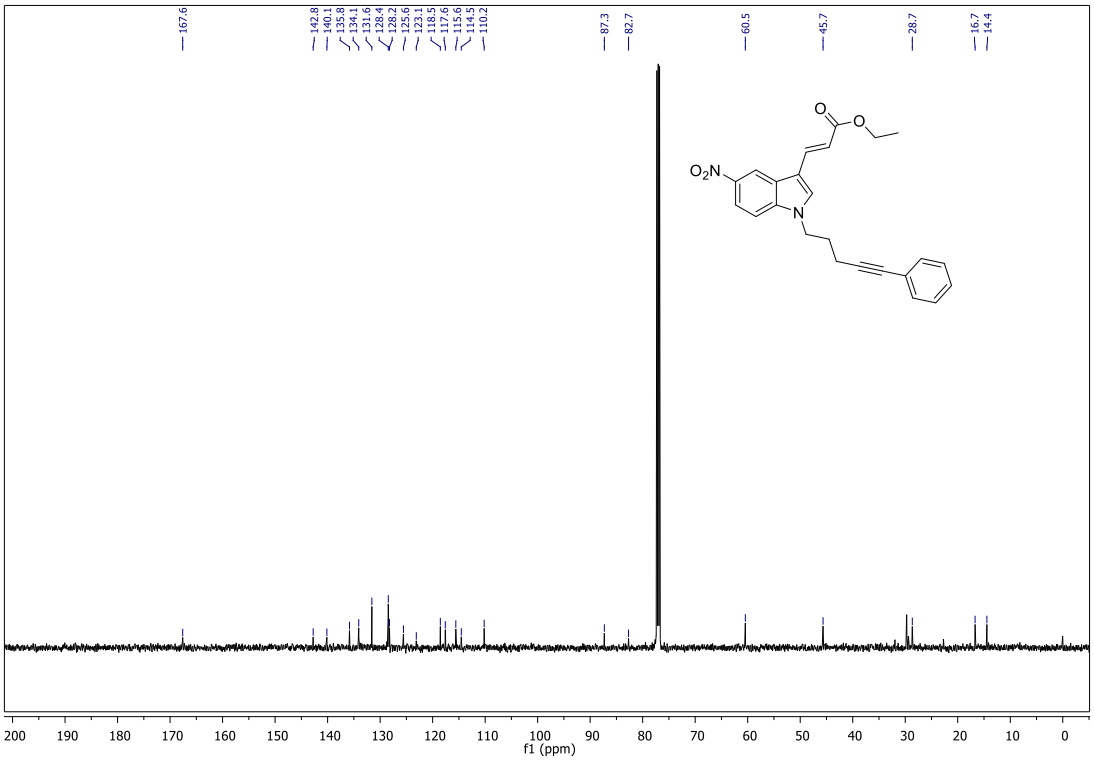
^{1}H NMR of compound **1f** in $CDCl_3$ (400 MHz)



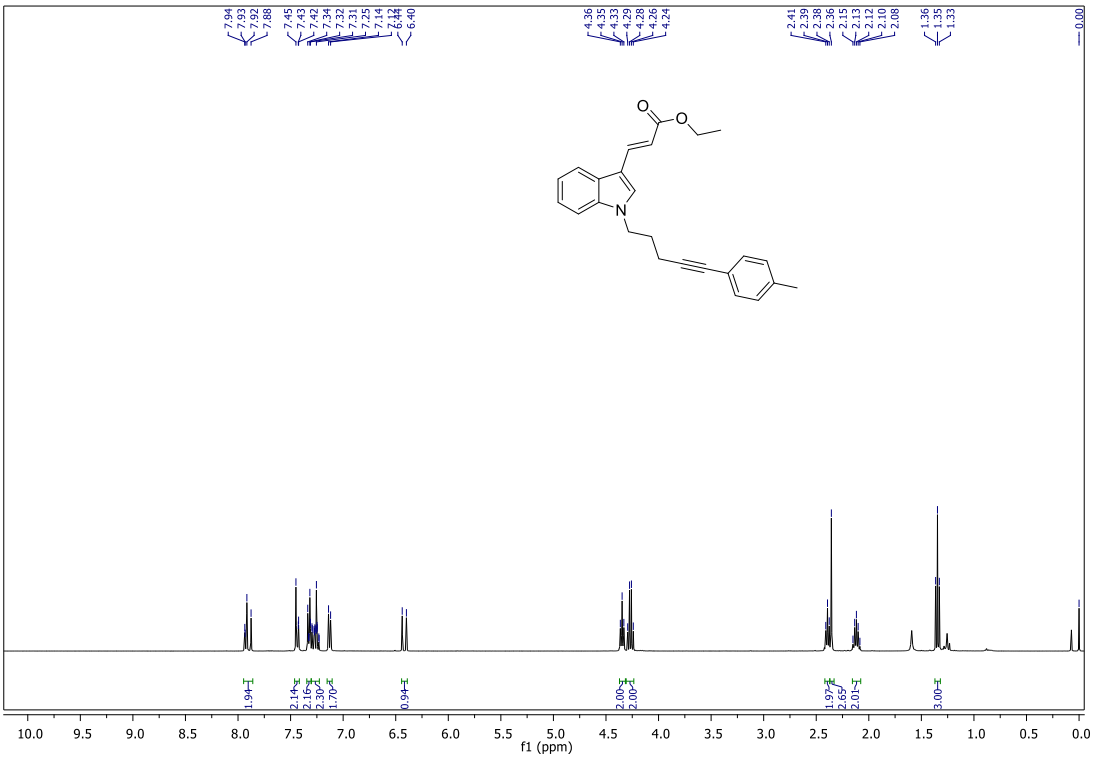
^{13}C NMR of compound **1f** in $CDCl_3$ (75 MHz)



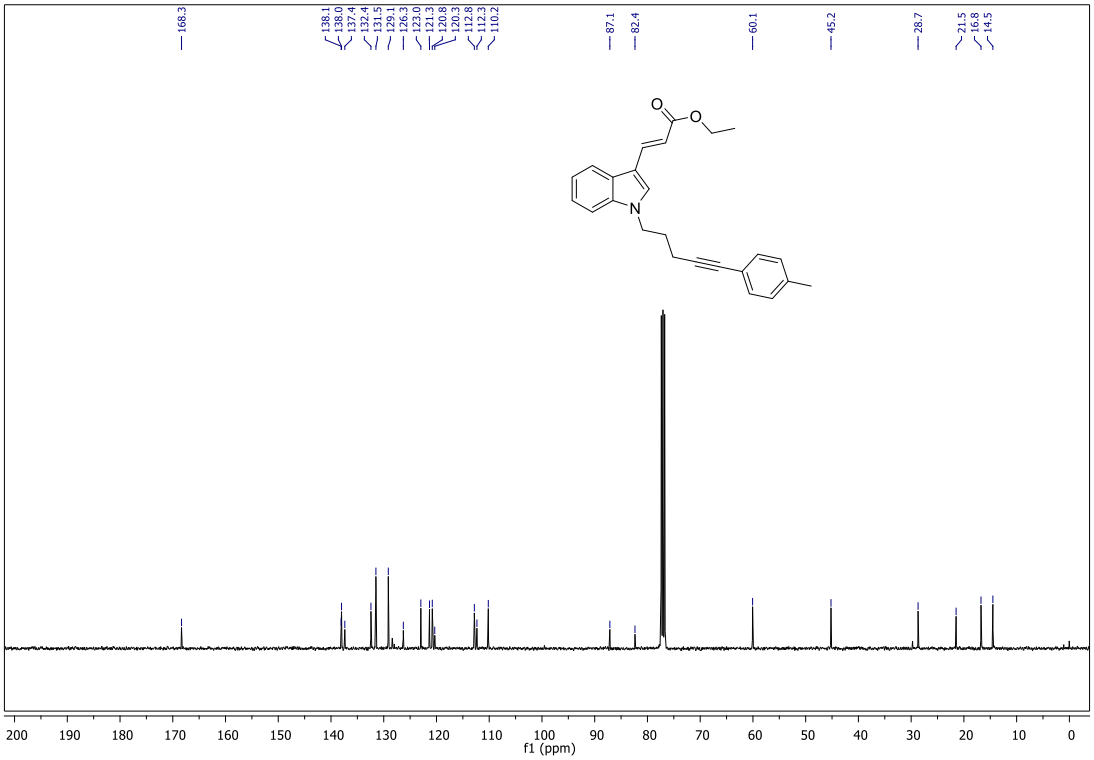
^{1}H NMR of compound **1g** in $CDCl_3$ (400 MHz)



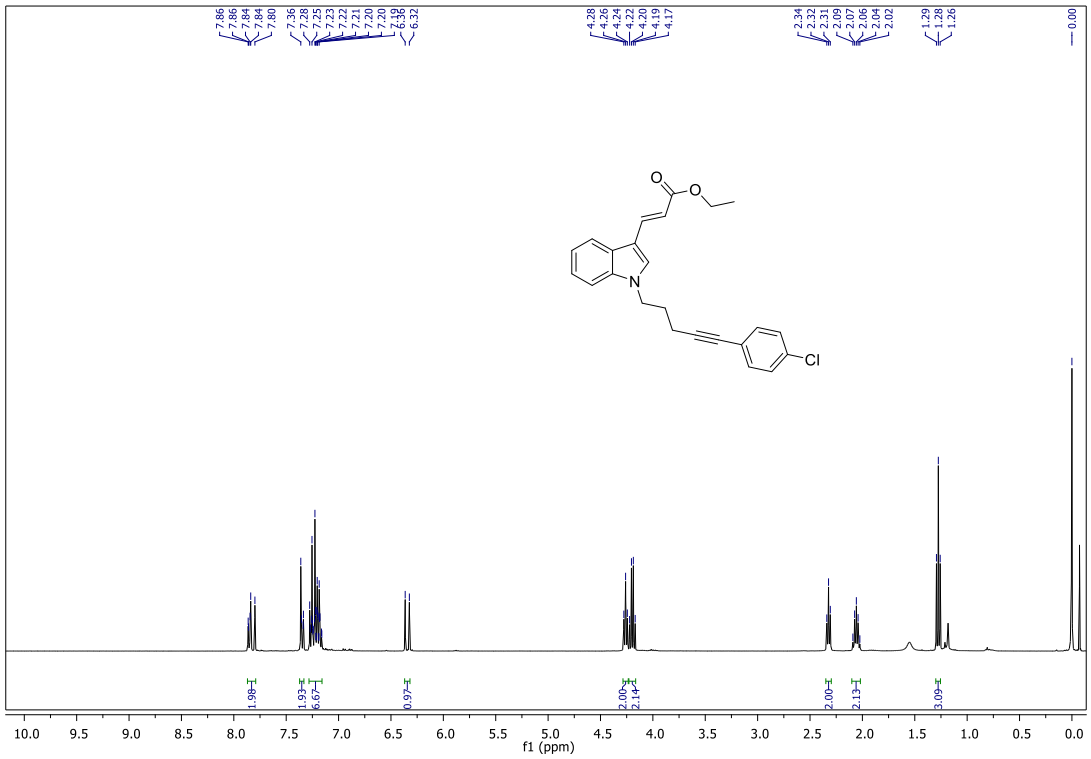
^{13}C NMR of compound **1g** in $CDCl_3$ (126 MHz)



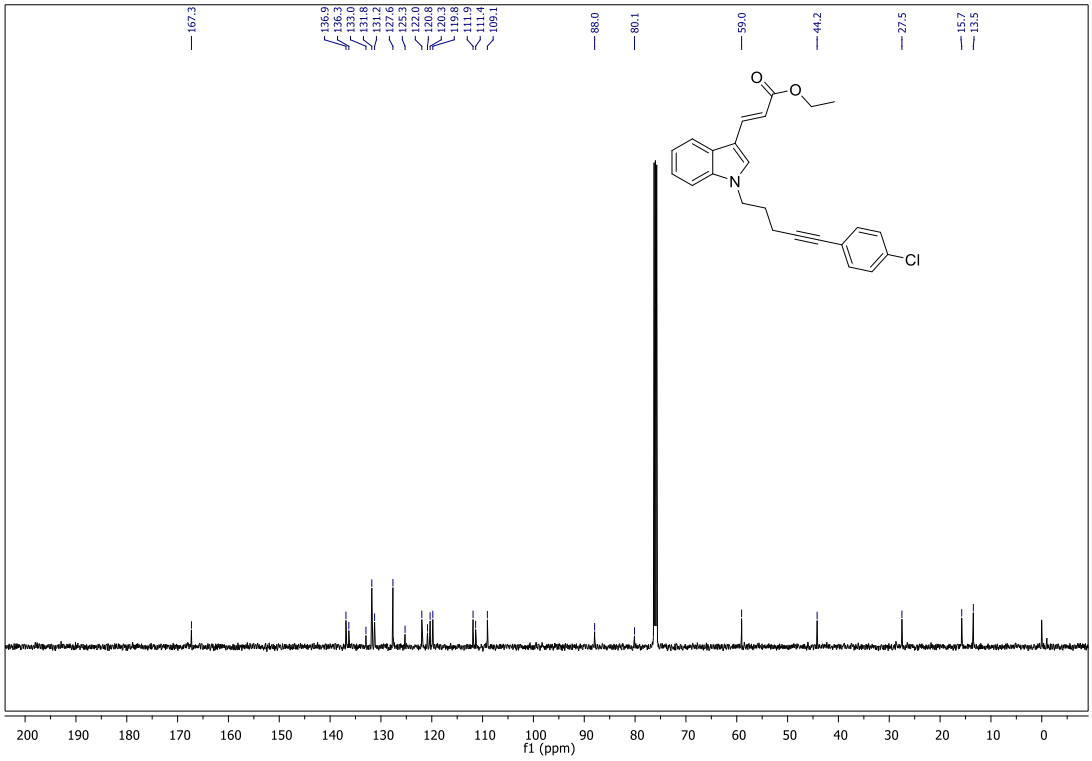
^{1}H NMR of compound **1h** in $CDCl_3$ (400 MHz)



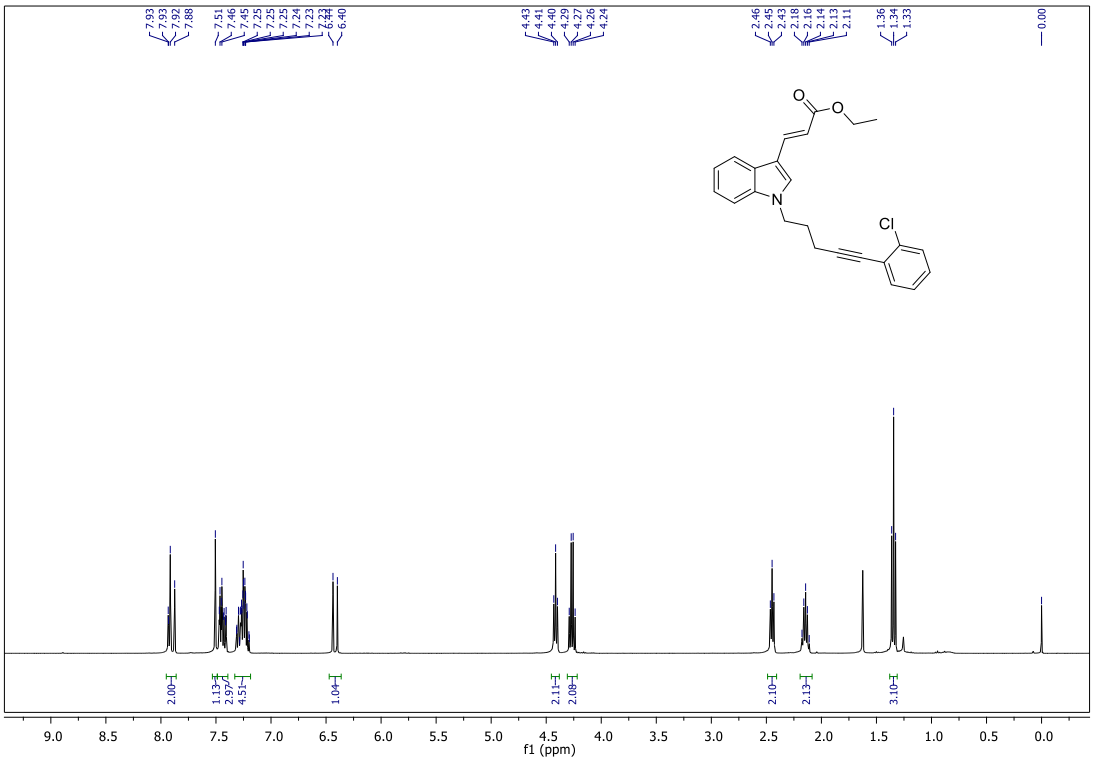
^{13}C NMR of compound **1h** in $CDCl_3$ (101 MHz)



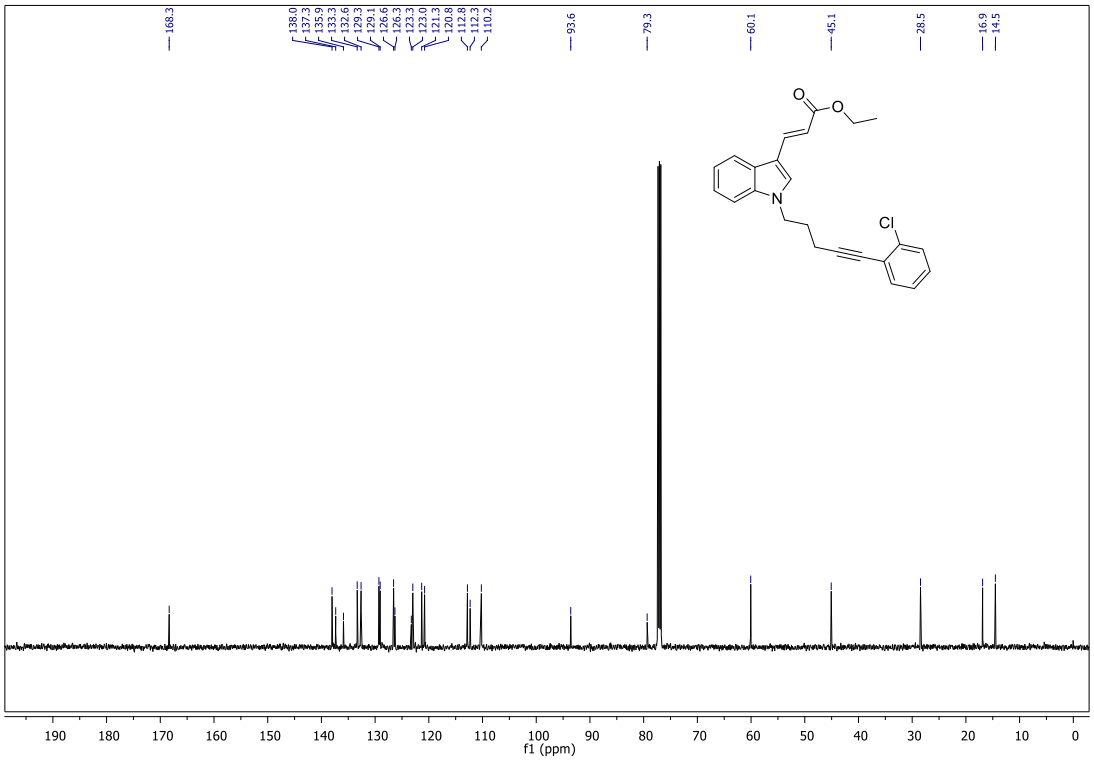
^{1}H NMR of compound **1i** in $CDCl_3$ (400 MHz)



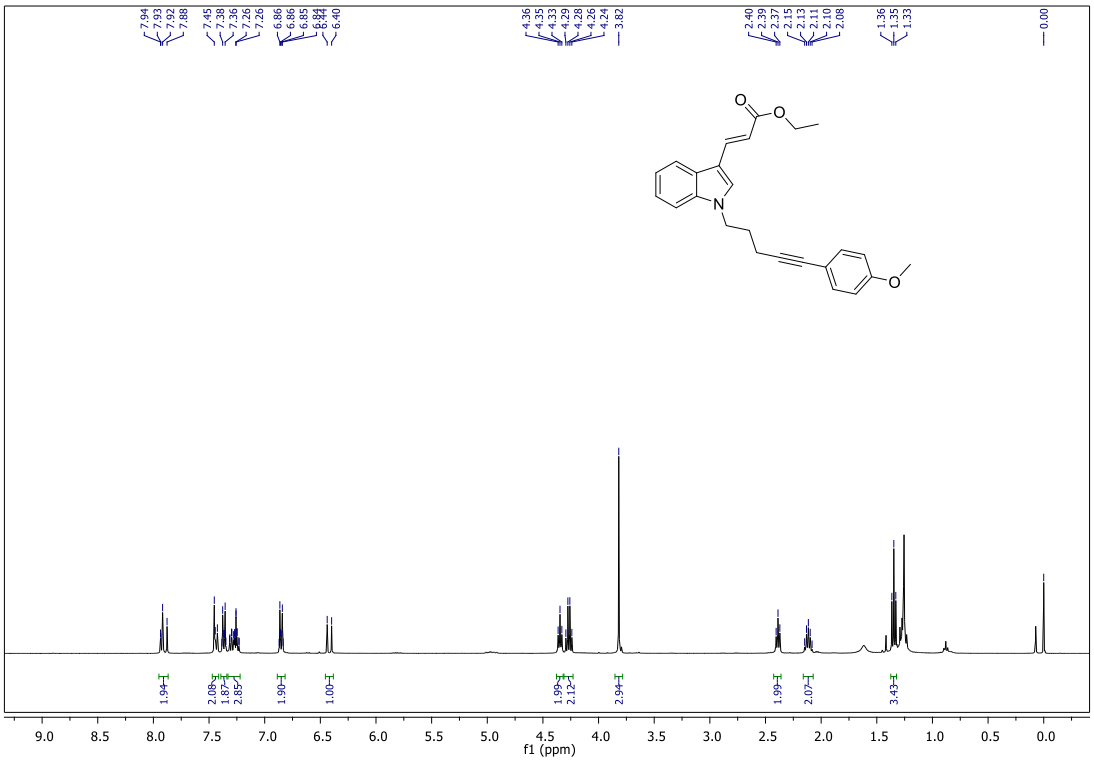
^{13}C NMR of compound **1i** in $CDCl_3$ (126 MHz)



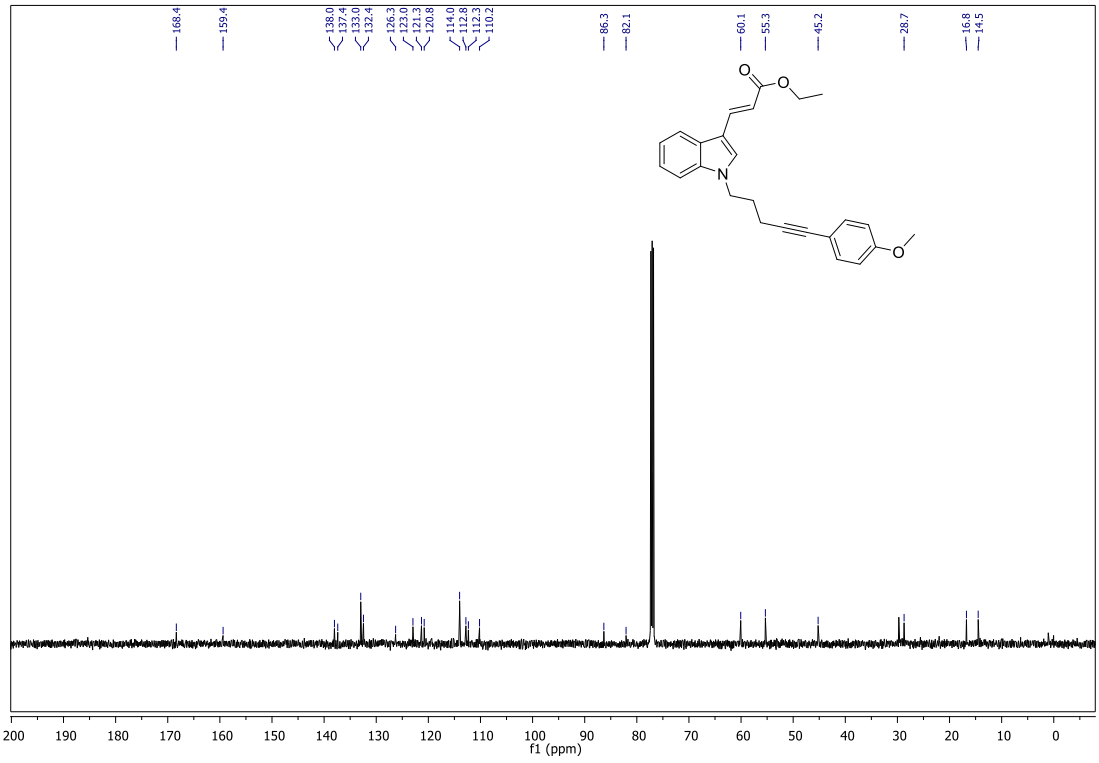
^{1}H NMR of compound **1j** in $CDCl_3$ (400 MHz)



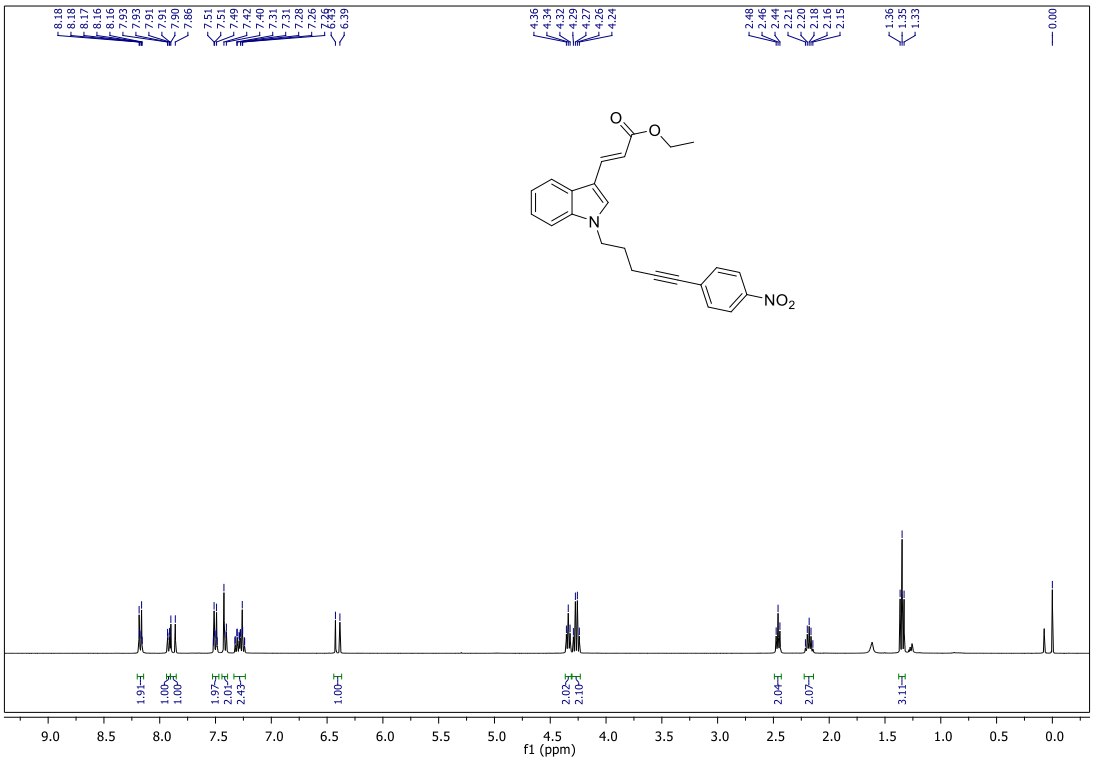
^{13}C NMR of compound **1j** in $CDCl_3$ (126 MHz)



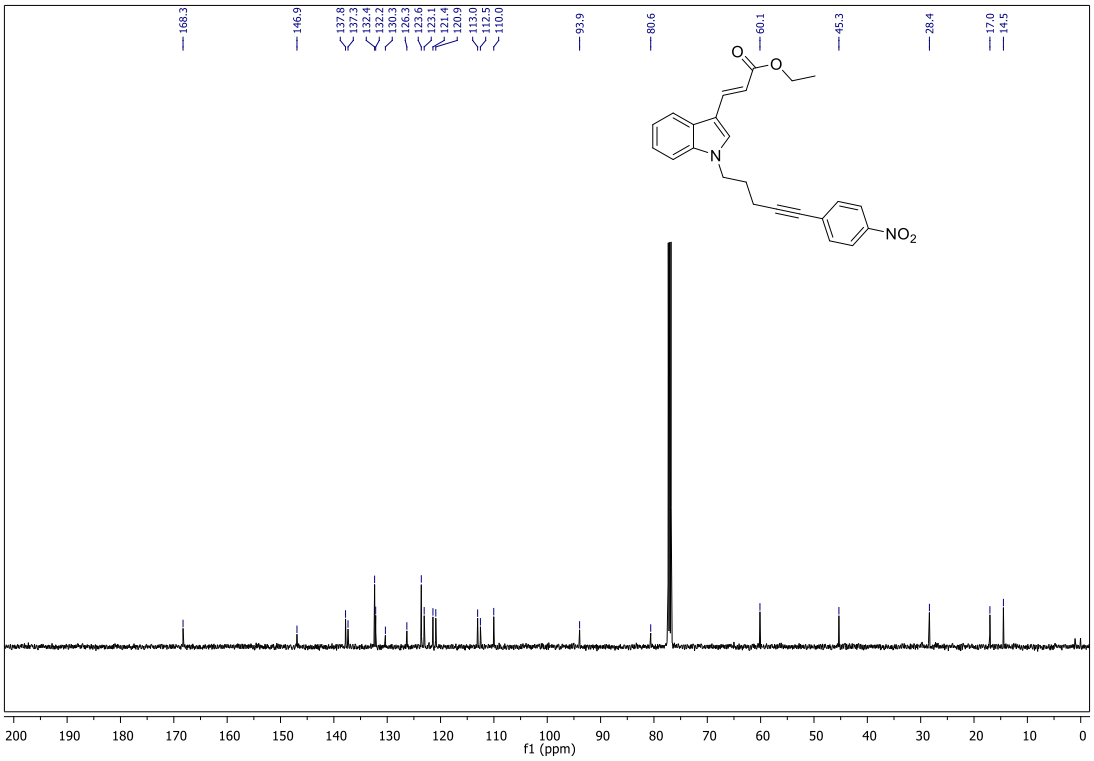
^{1}H NMR of compound **1k** in $CDCl_3$ (400 MHz)



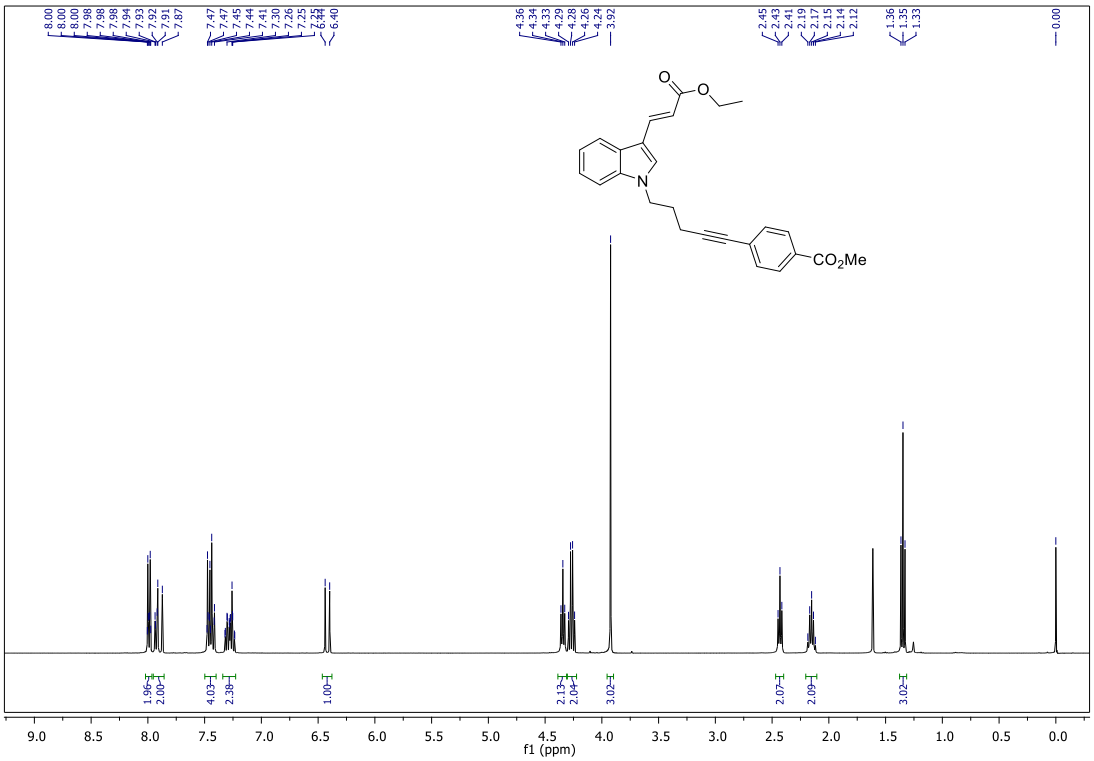
^{13}C NMR of compound **1k** in $CDCl_3$ (126 MHz)



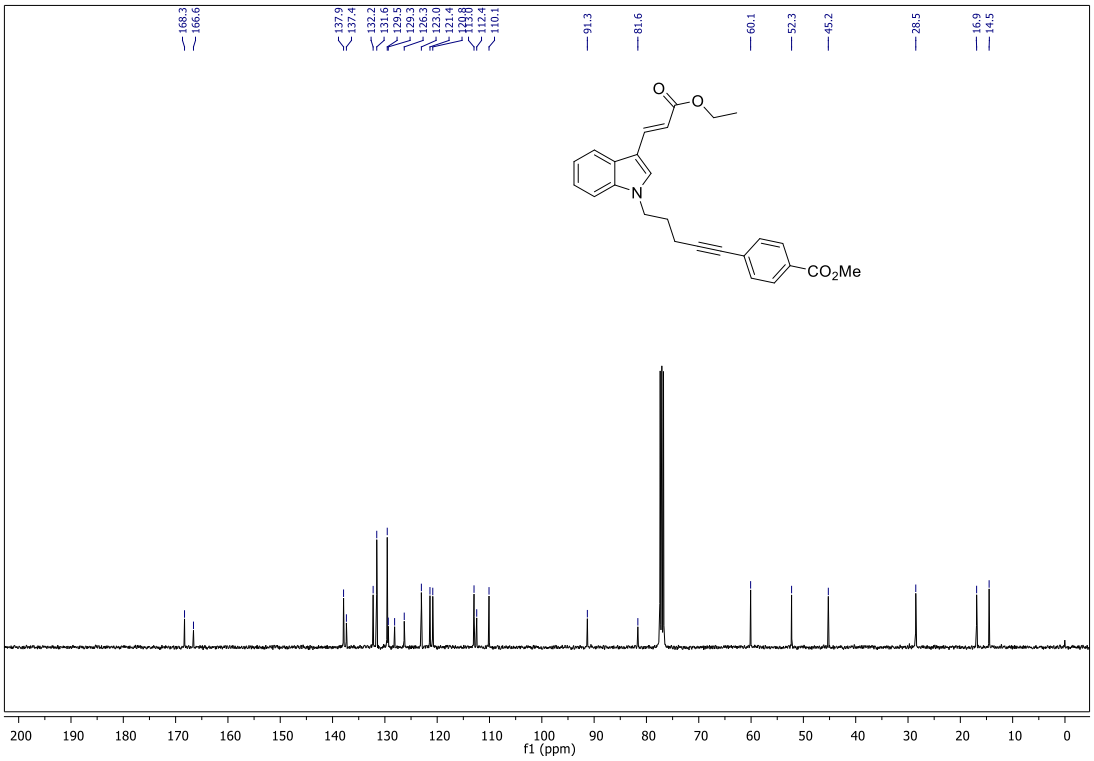
^{1}H NMR of compound **1l** in $CDCl_3$ (400 MHz)



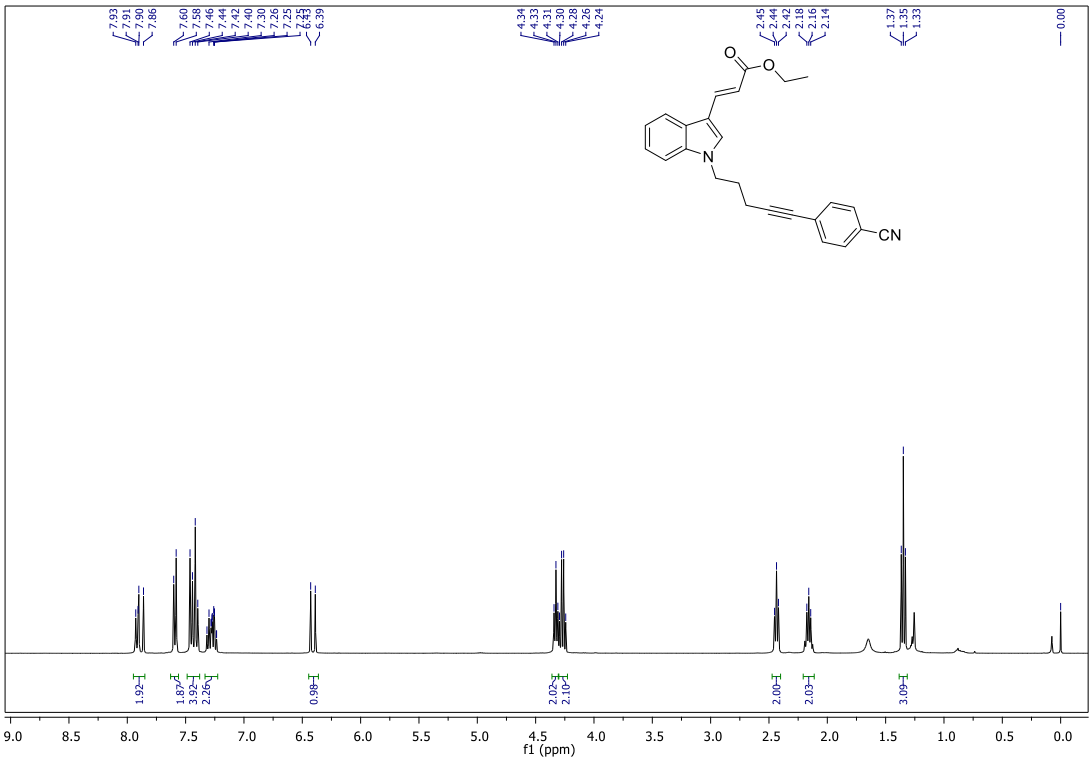
^{13}C NMR of compound **1l** in $CDCl_3$ (126 MHz)



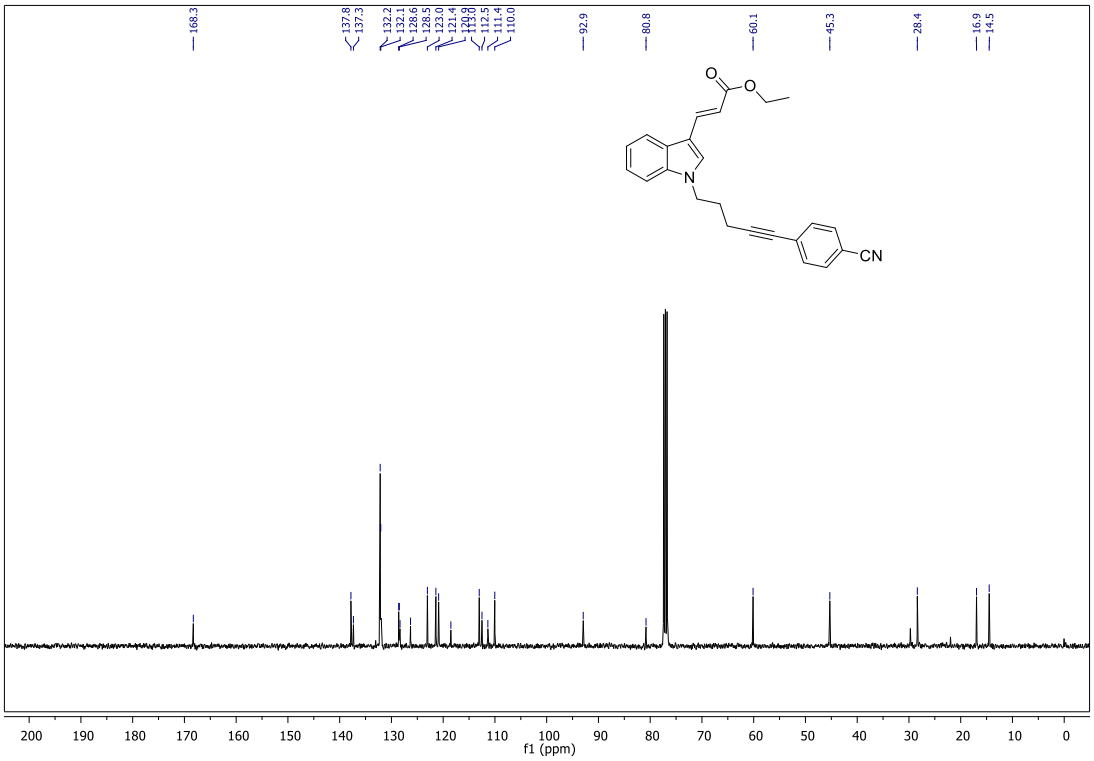
^{1}H NMR of compound **1m** in $CDCl_3$ (400 MHz)



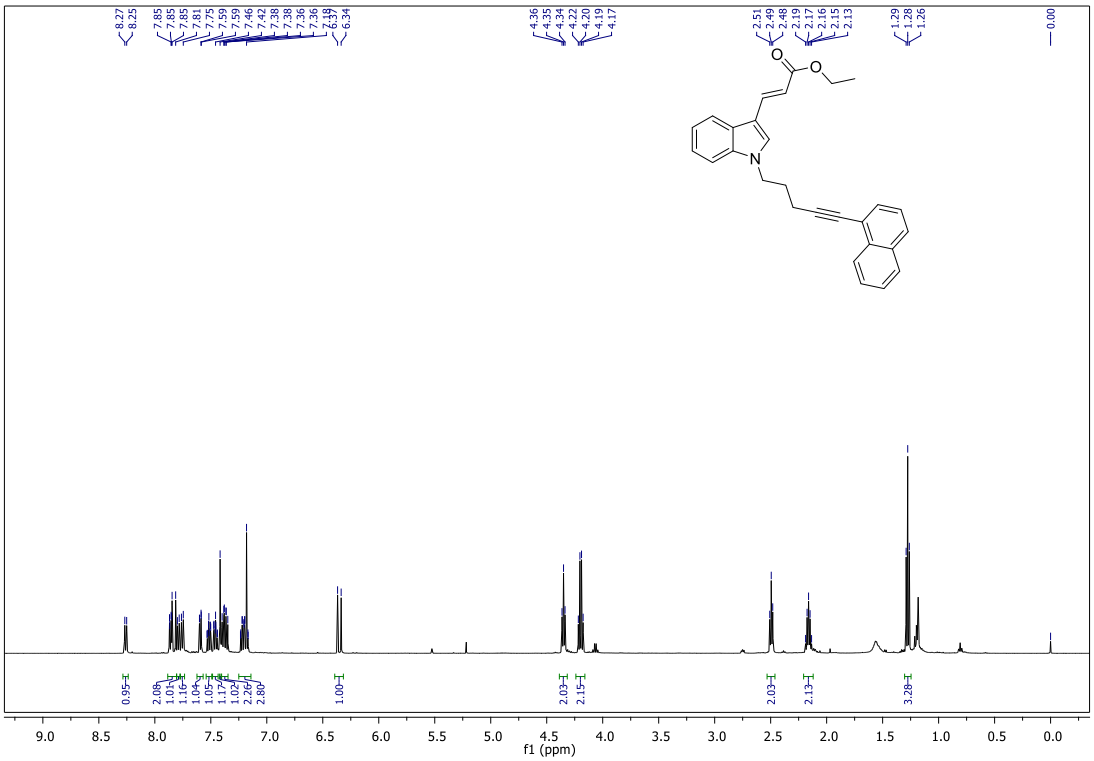
^{13}C NMR of compound **1m** in $CDCl_3$ (101 MHz)



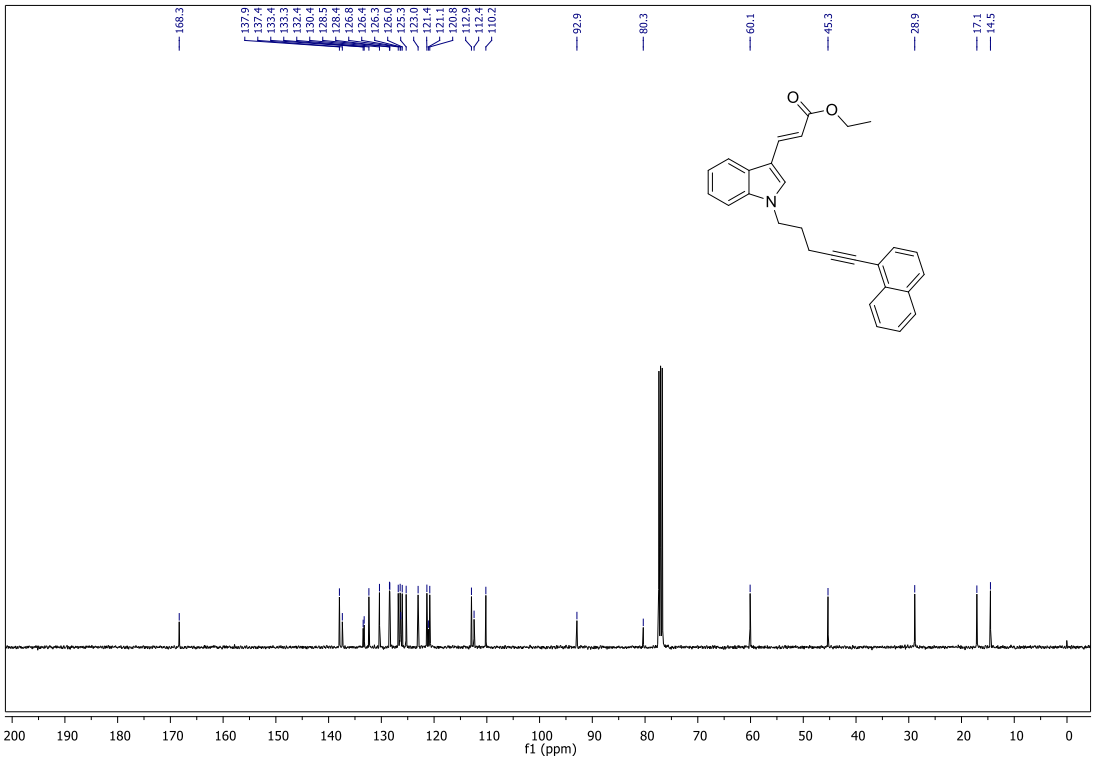
^{1}H NMR of compound **1n** in $CDCl_3$ (400 MHz)



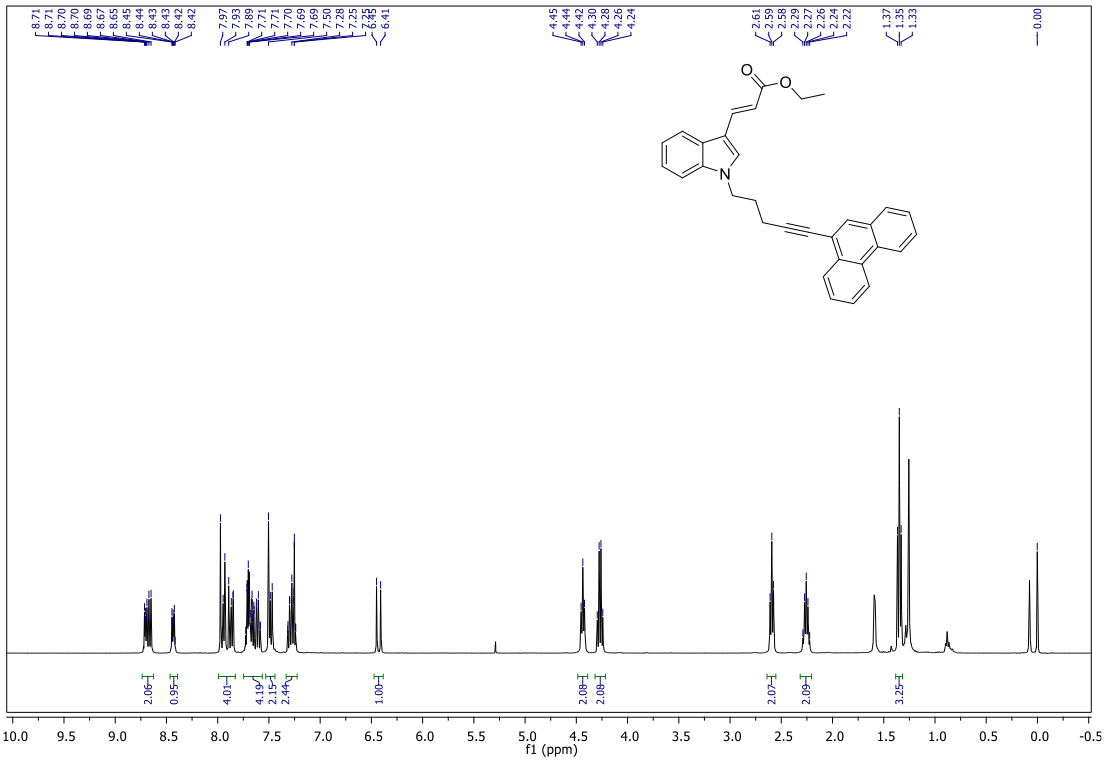
^{13}C NMR of compound **1n** in $CDCl_3$ (101 MHz)



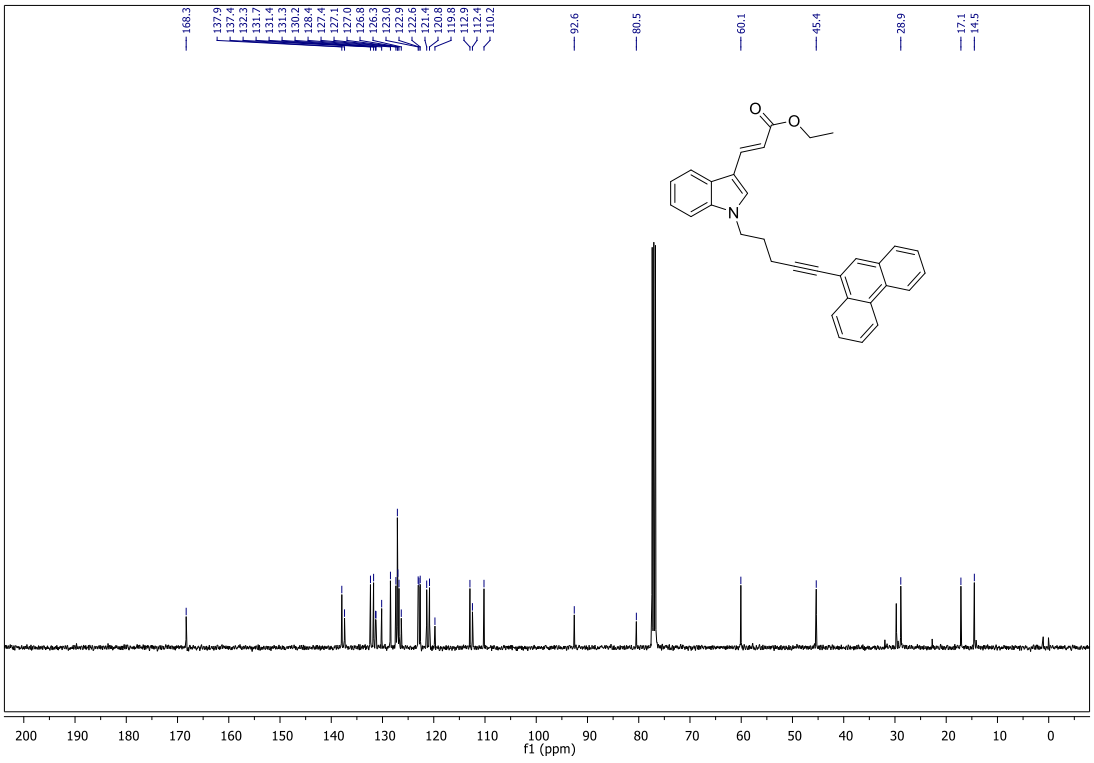
^{1}H NMR of compound **1o** in $CDCl_3$ (500 MHz)



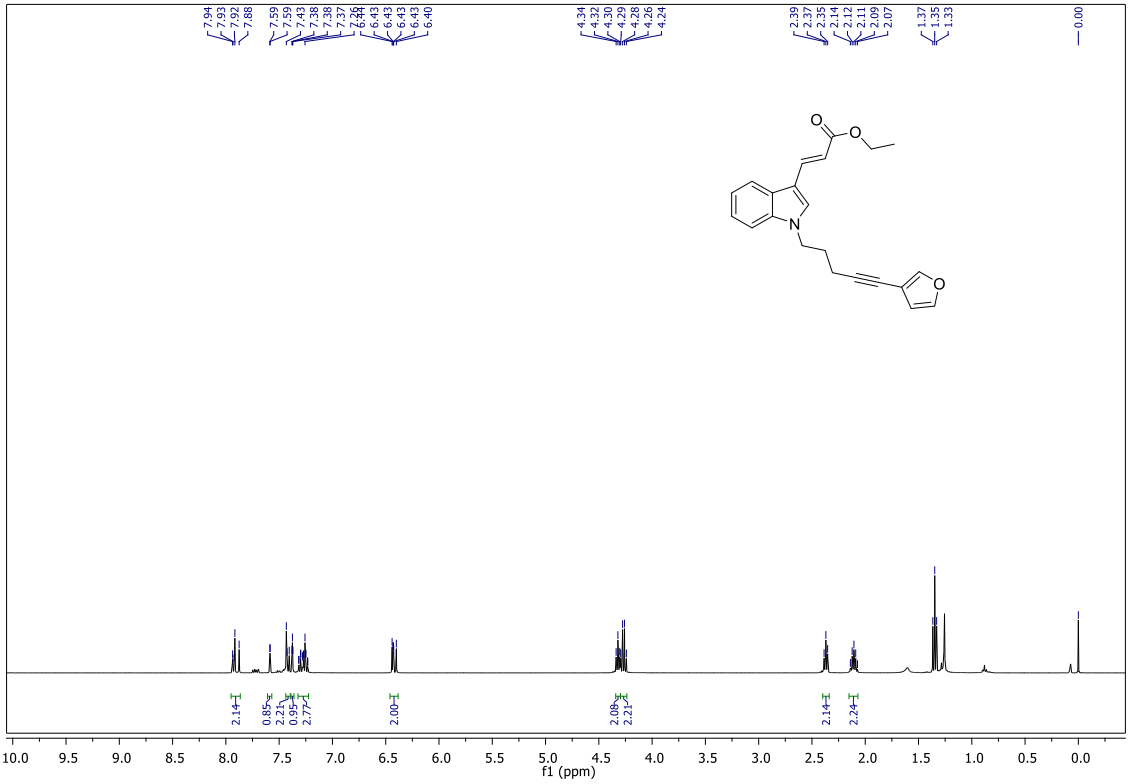
^{13}C NMR of compound **1o** in $CDCl_3$ (101 MHz)



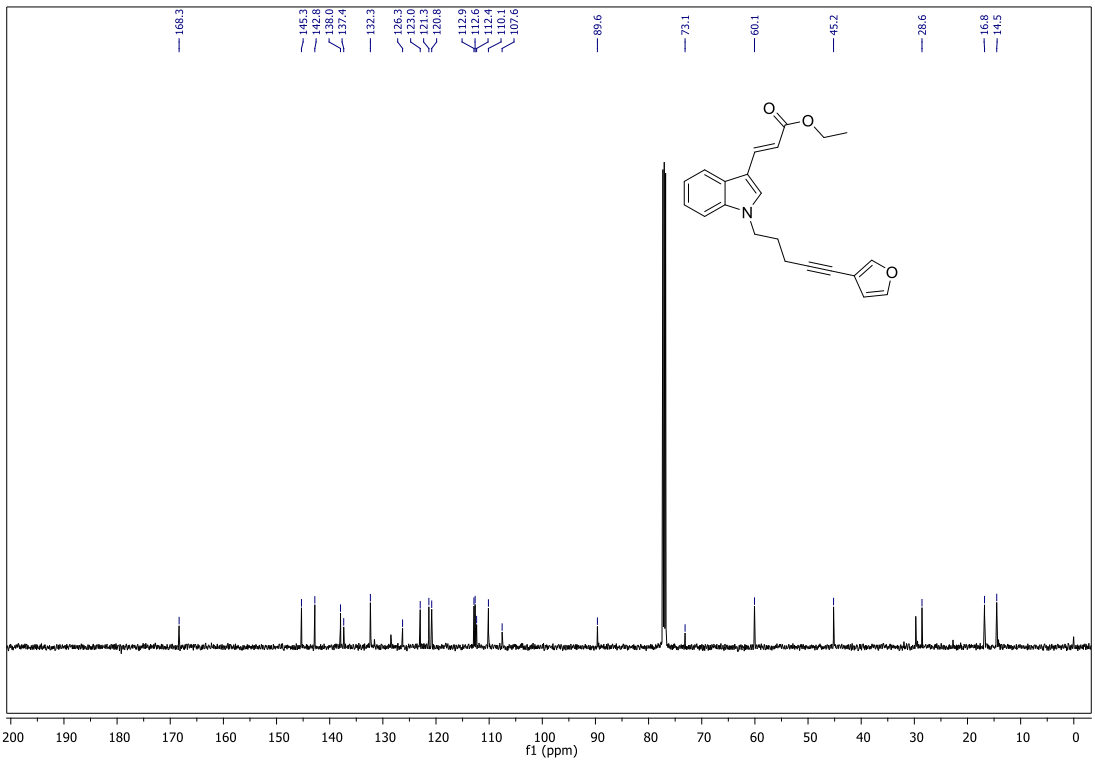
^{1}H NMR of compound **1p** in $CDCl_3$ (400 MHz)



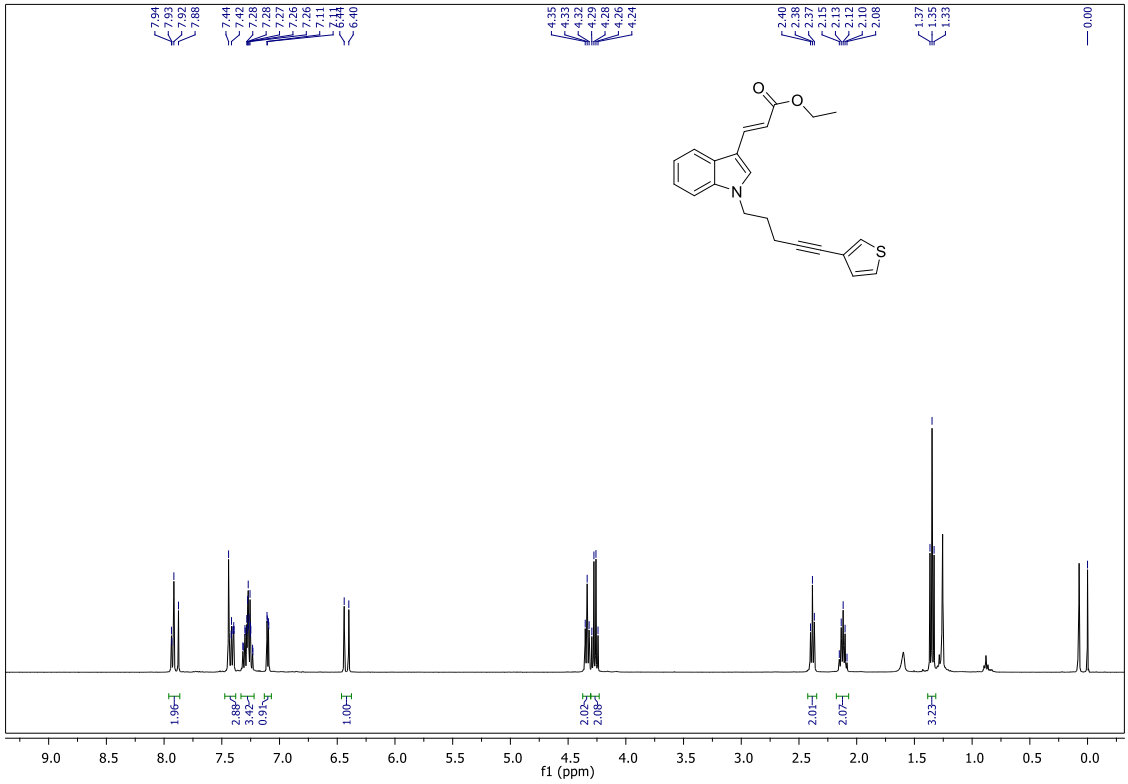
^{13}C NMR of compound **1p** in $CDCl_3$ (101 MHz)



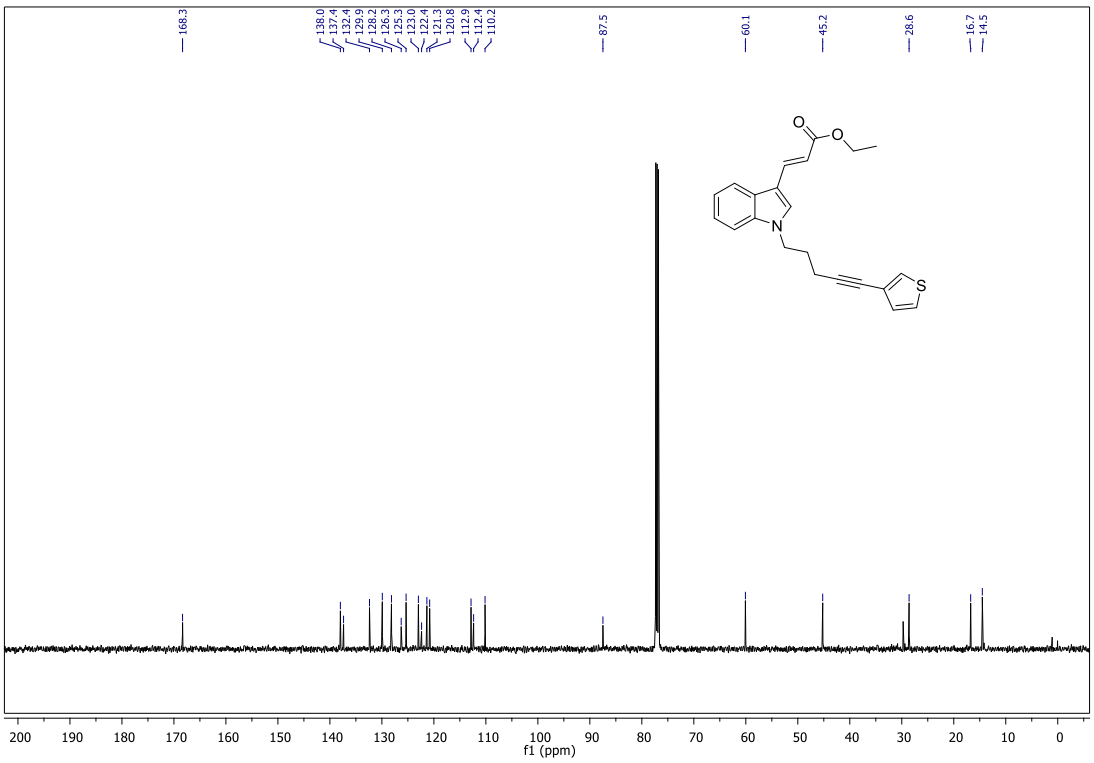
^{1}H NMR of compound **1q** in $CDCl_3$ (400 MHz)



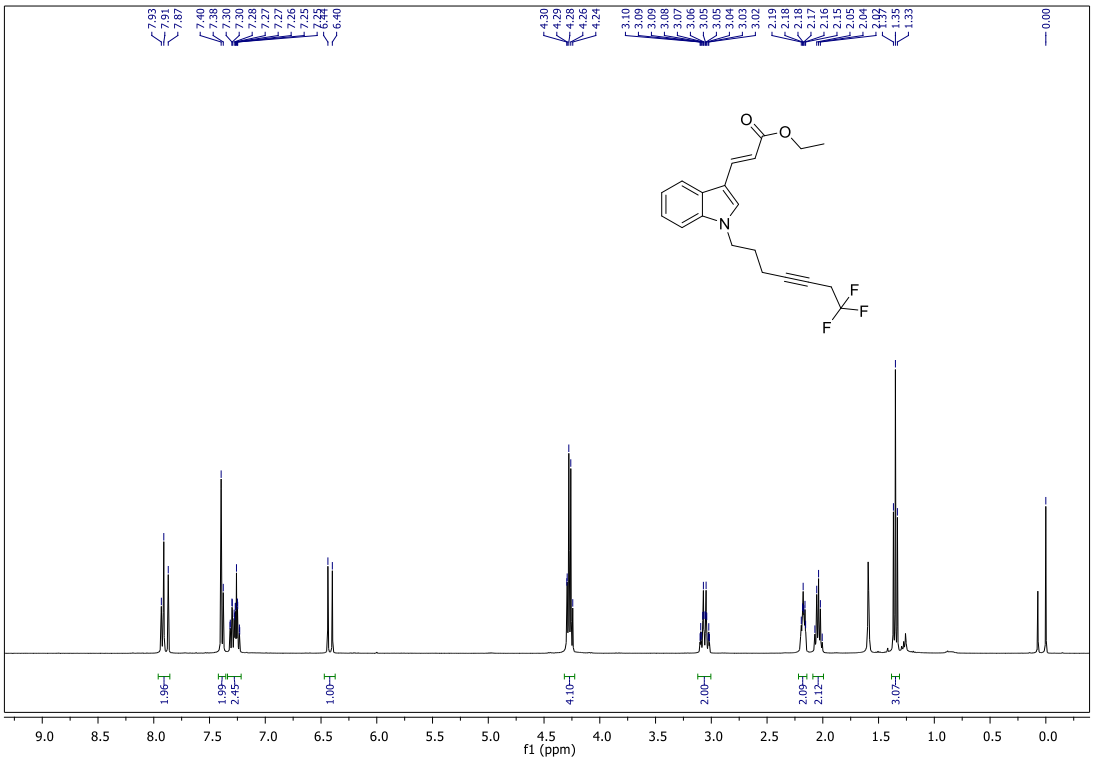
^{13}C NMR of compound **1q** in $CDCl_3$ (126 MHz)



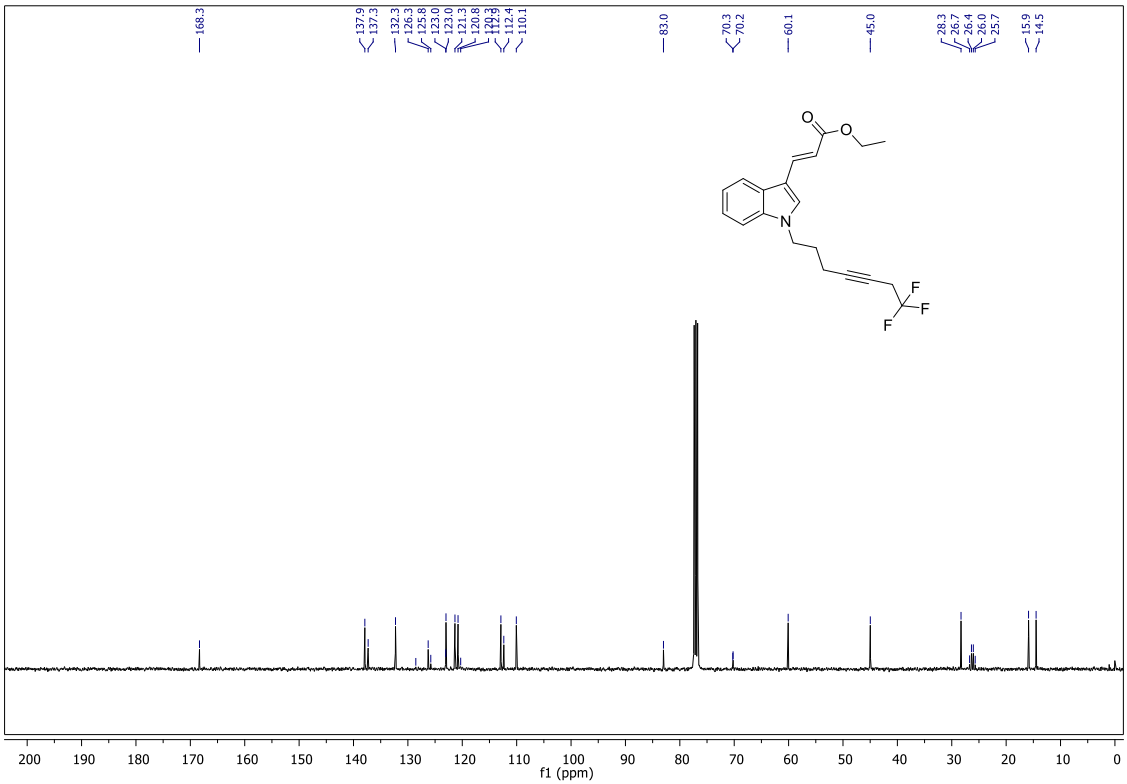
^{1}H NMR of compound **1r** in $CDCl_3$ (400 MHz)



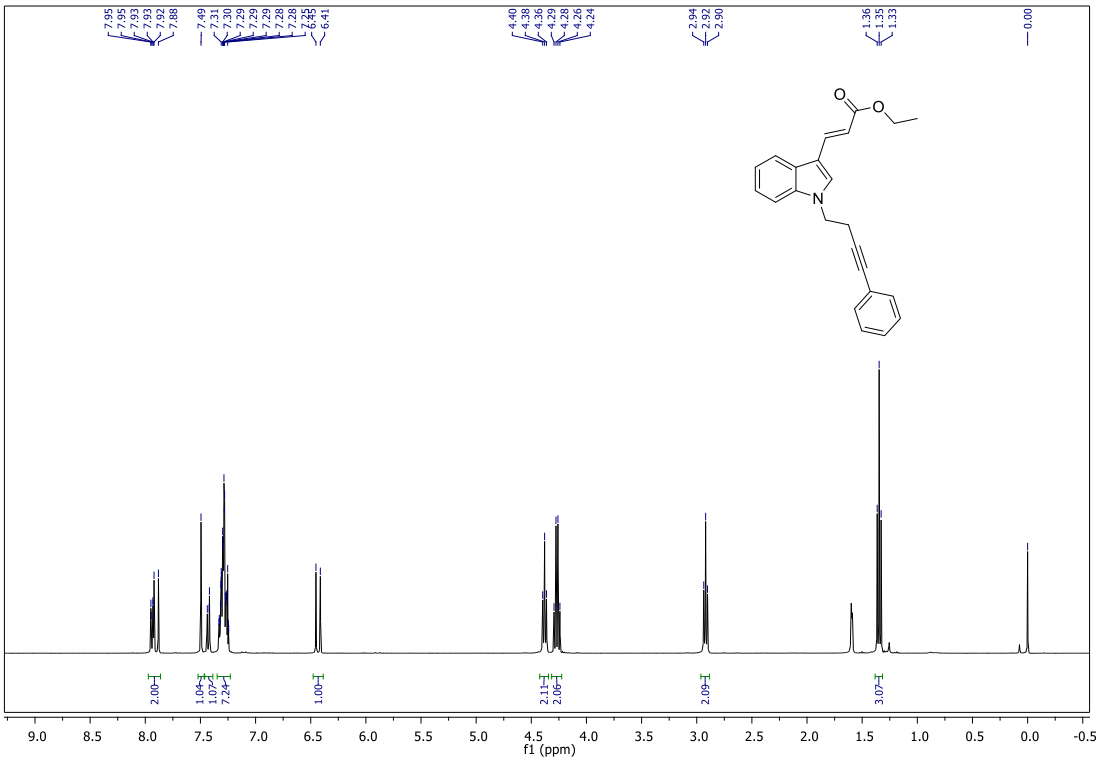
^{13}C NMR of compound **1r** in $CDCl_3$ (126 MHz)



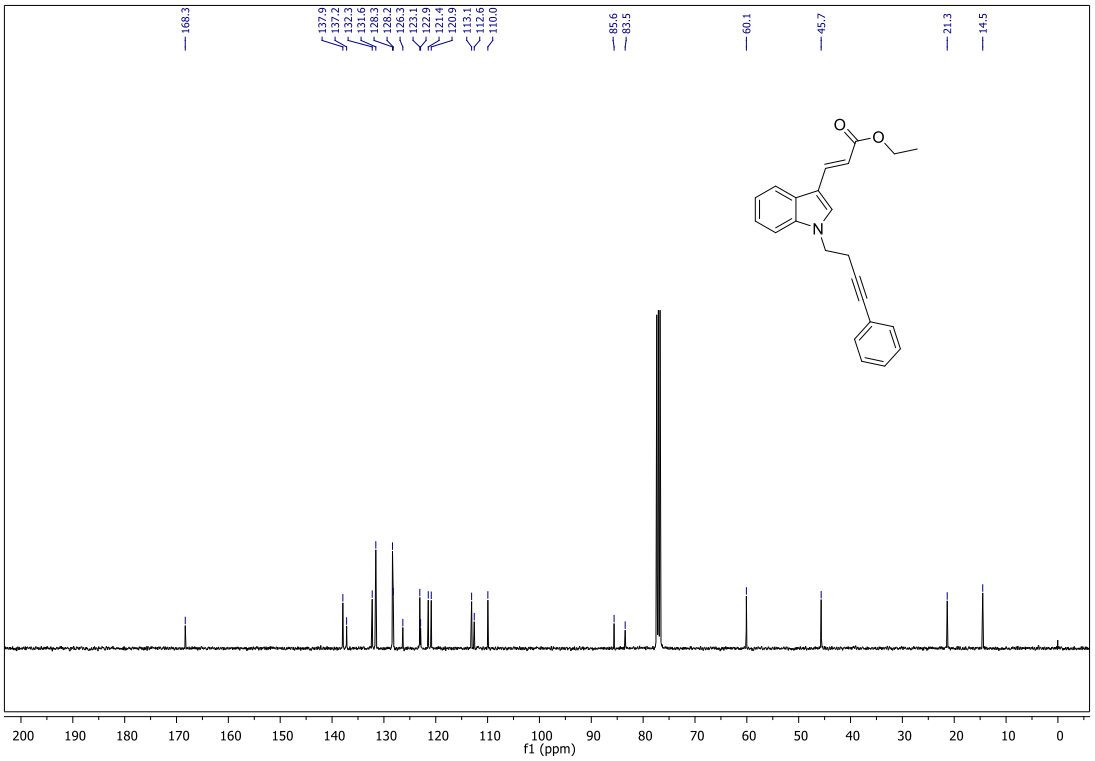
^{1}H NMR of compound **1s** in $CDCl_3$ (400 MHz)



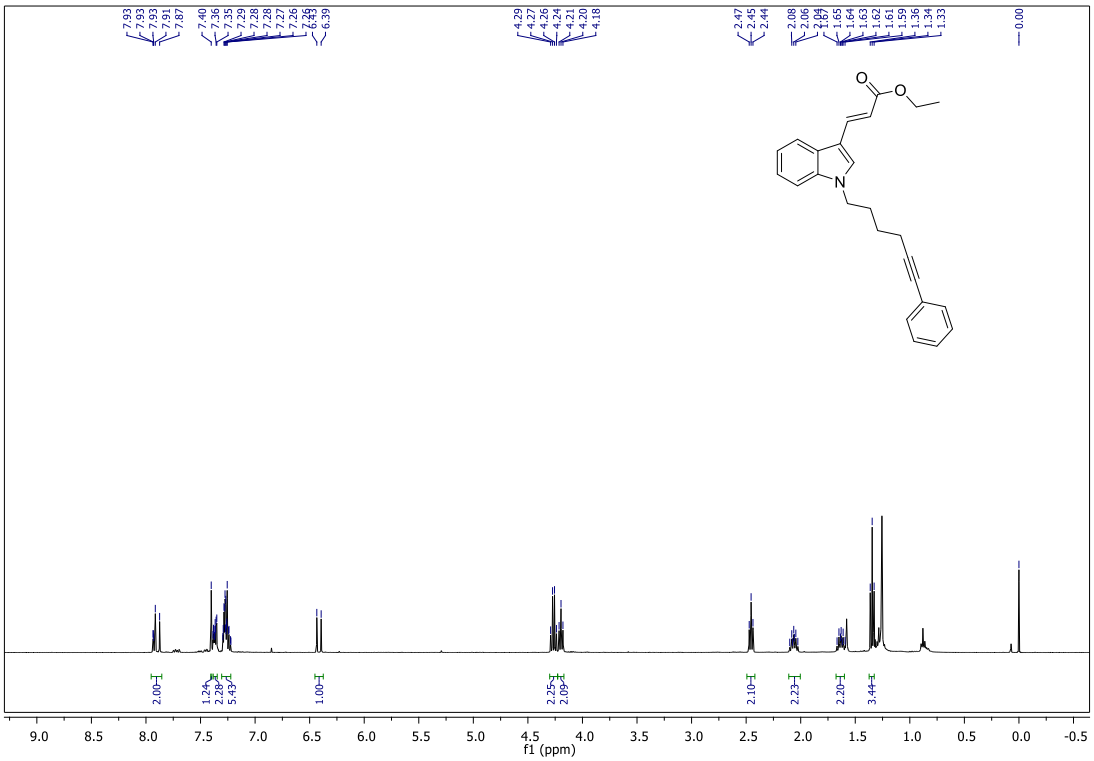
^{13}C NMR of compound **1s** in $CDCl_3$ (101 MHz)



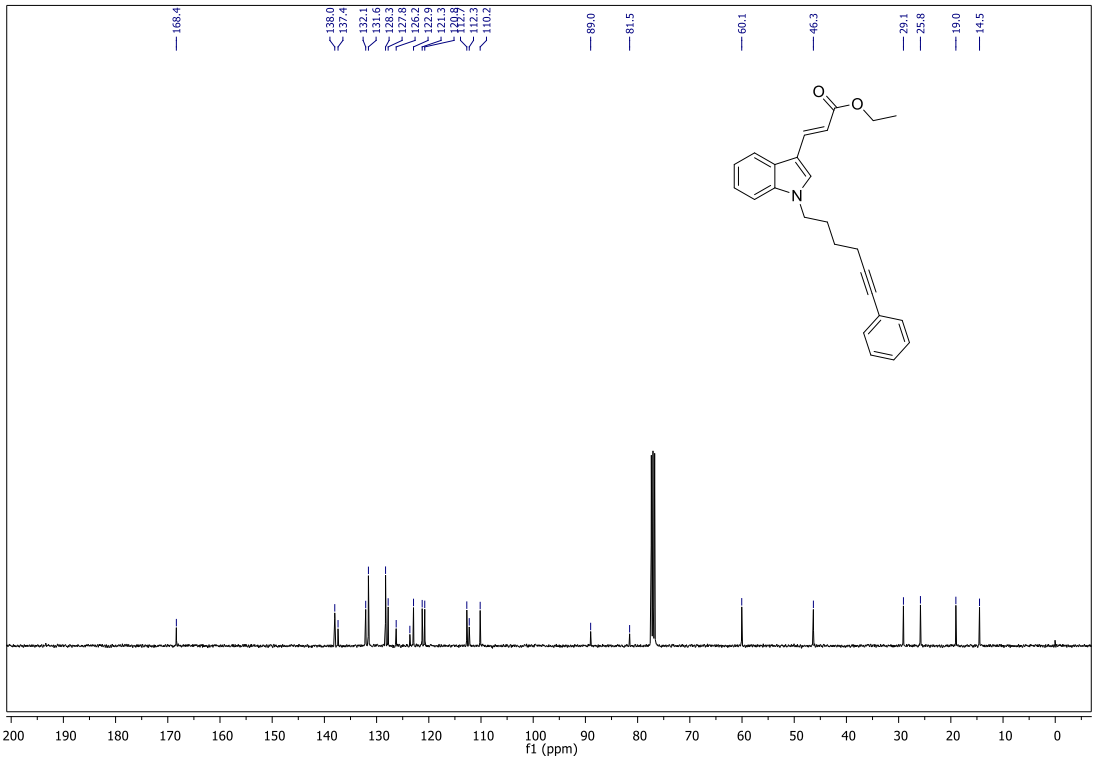
^{1}H NMR of compound **1t** in $CDCl_3$ (400 MHz)



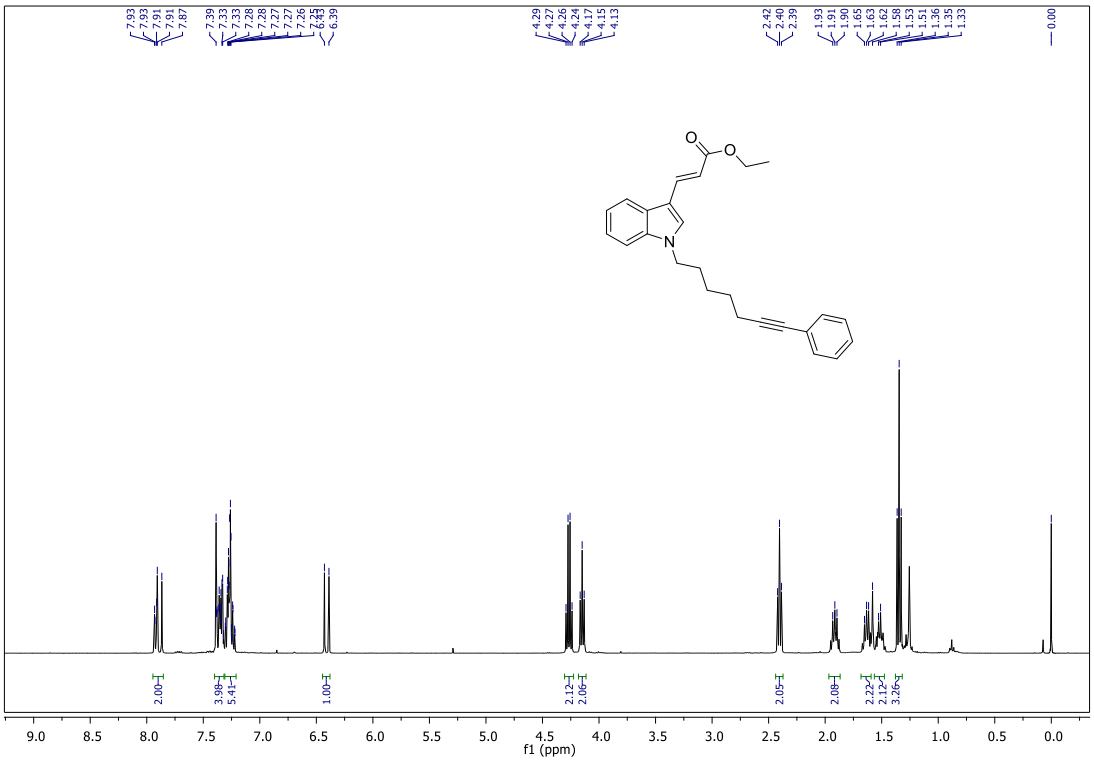
^{13}C NMR of compound **1t** in $CDCl_3$ (101 MHz)



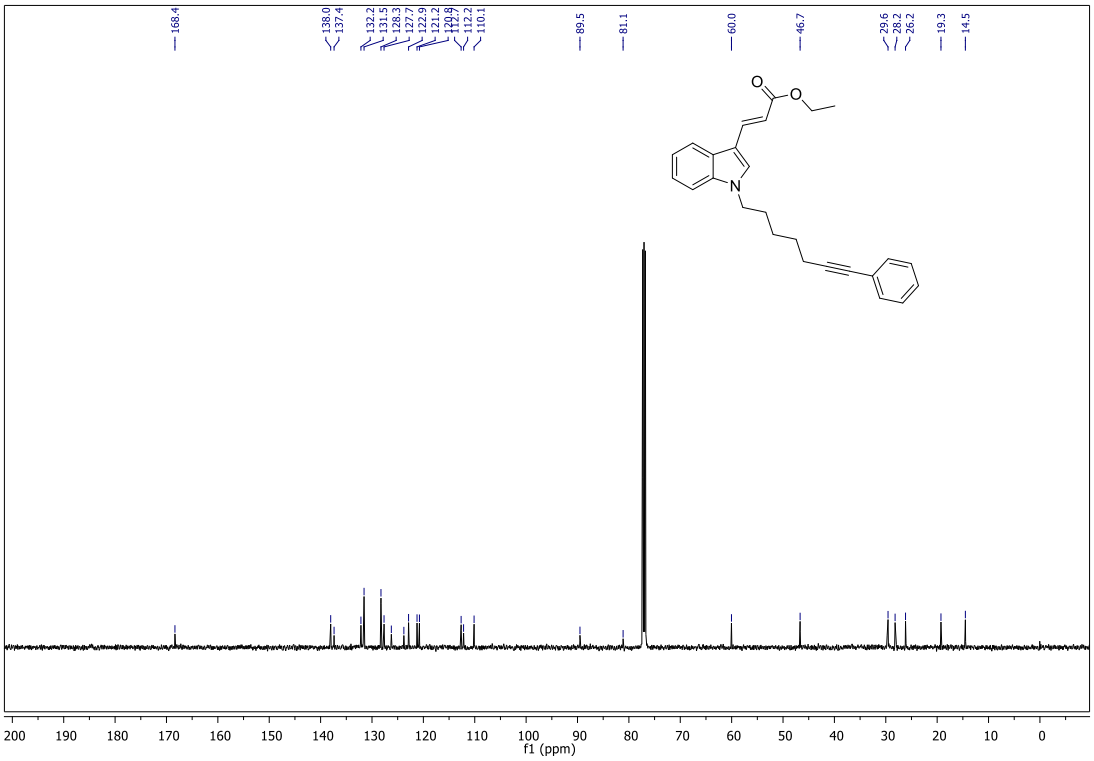
^{1}H NMR of compound **1u** in $CDCl_3$ (400 MHz)



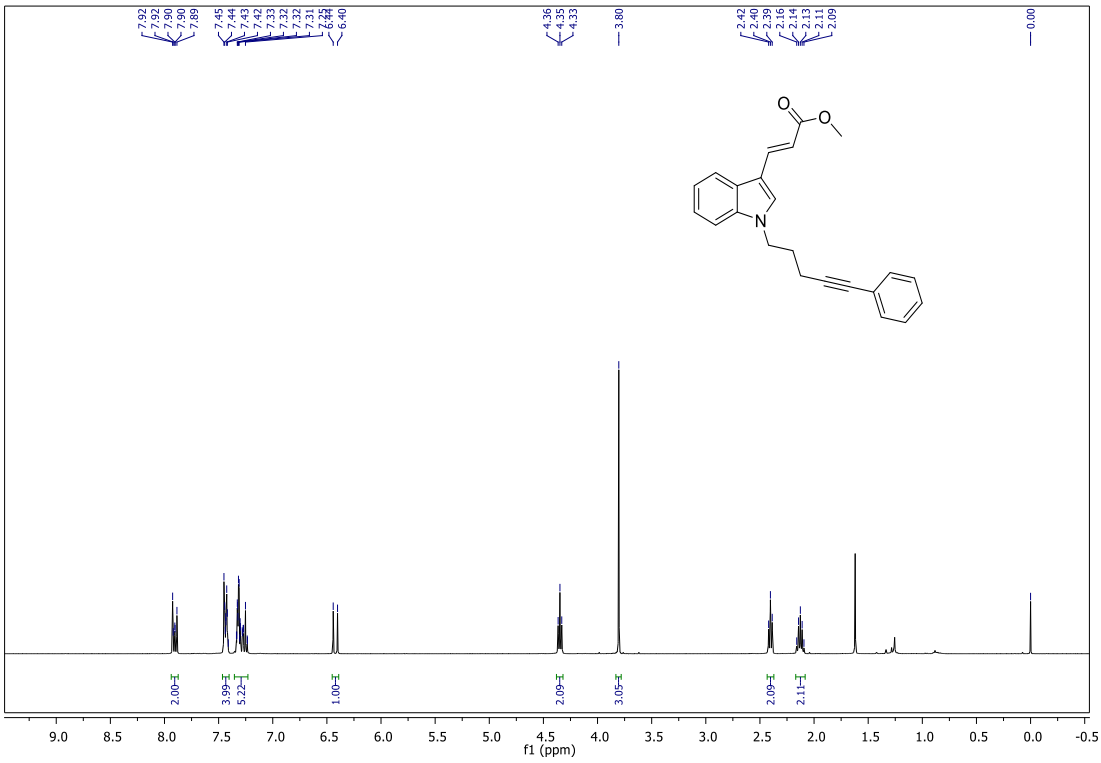
^{13}C NMR of compound **1u** in $CDCl_3$ (101 MHz)



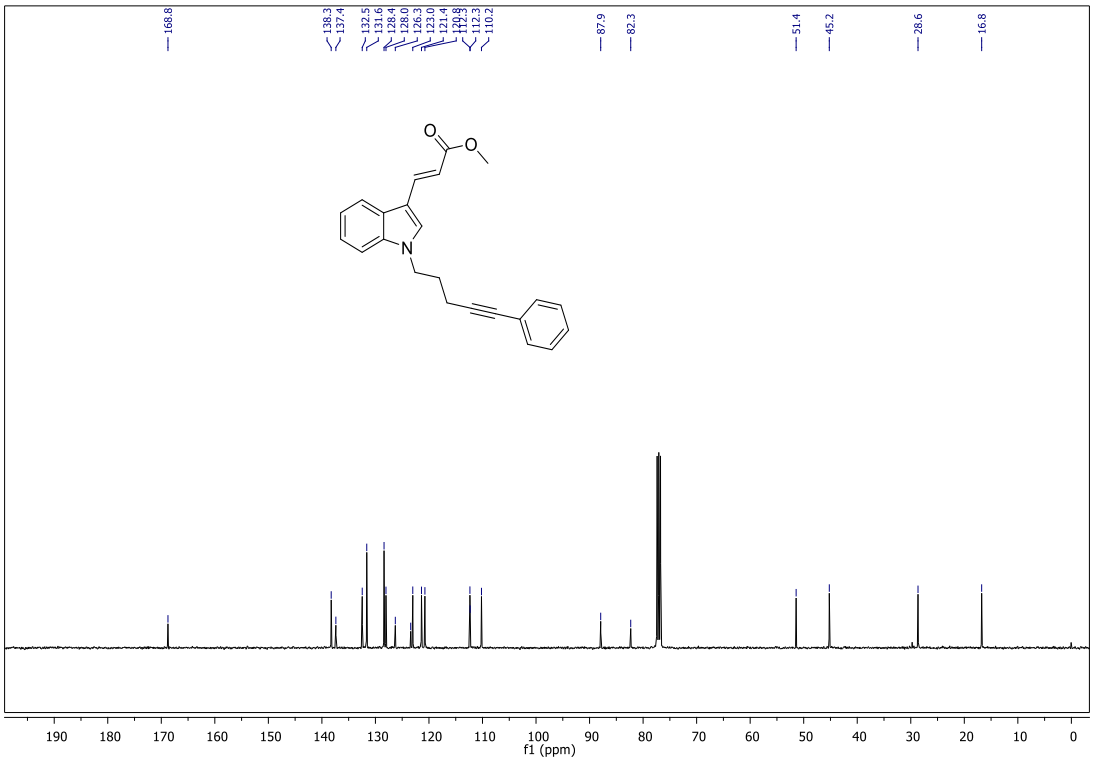
^{1}H NMR of compound **1v** in $CDCl_3$ (400 MHz)



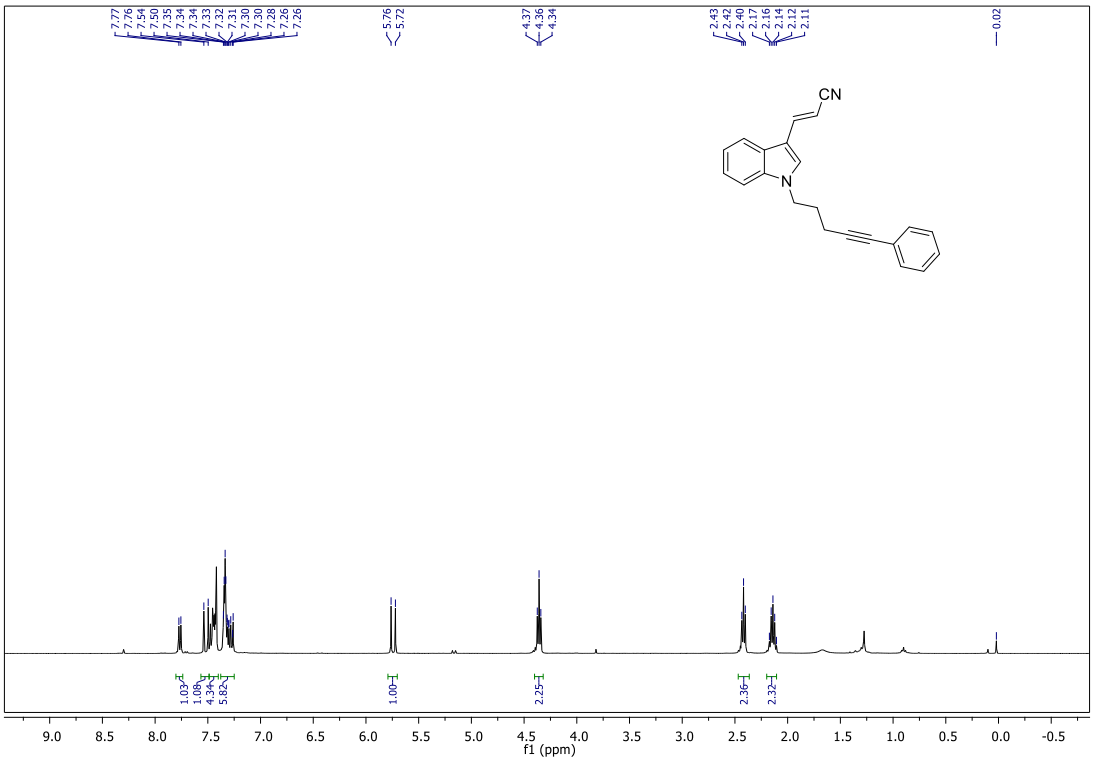
^{13}C NMR of compound **1v** in $CDCl_3$ (126 MHz)



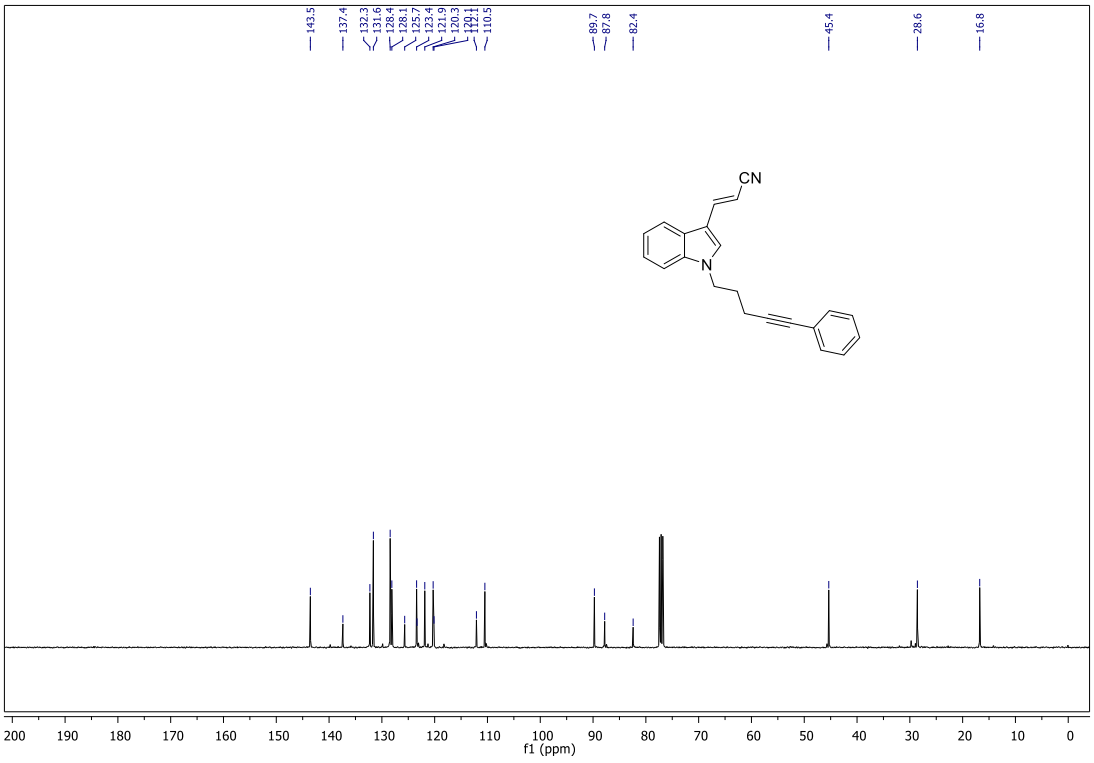
^{1}H NMR of compound **1w** in $CDCl_3$ (400 MHz)



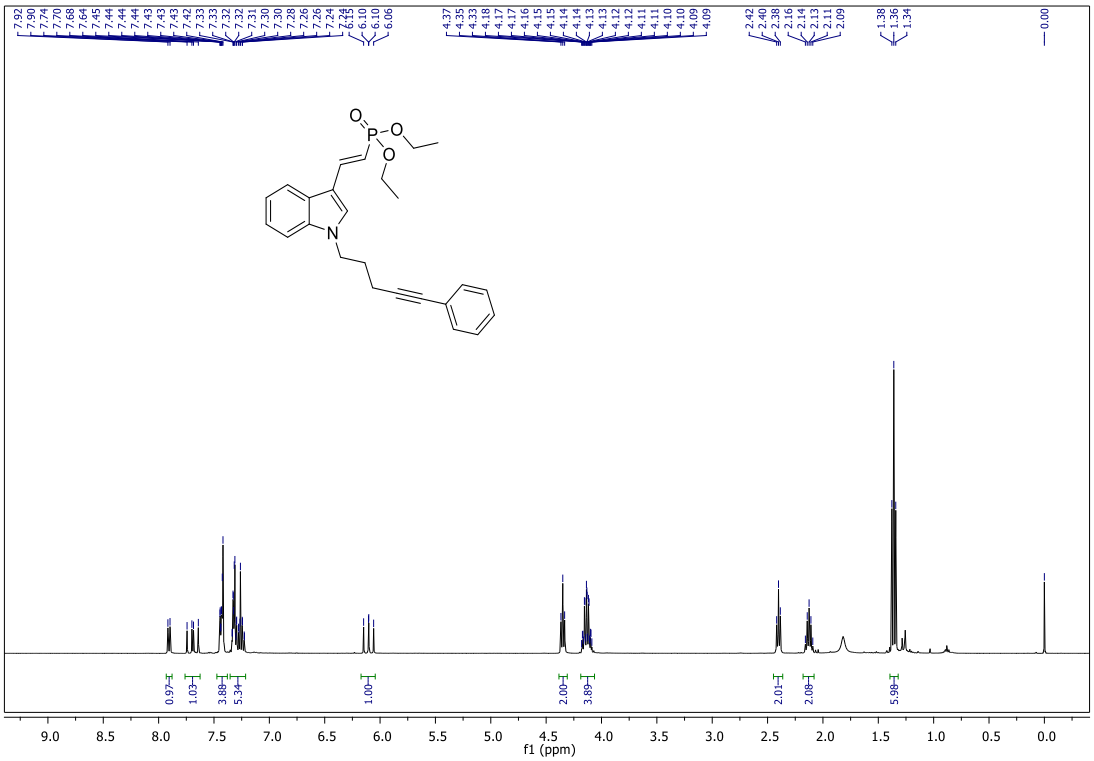
^{13}C NMR of compound **1w** in $CDCl_3$ (101 MHz)



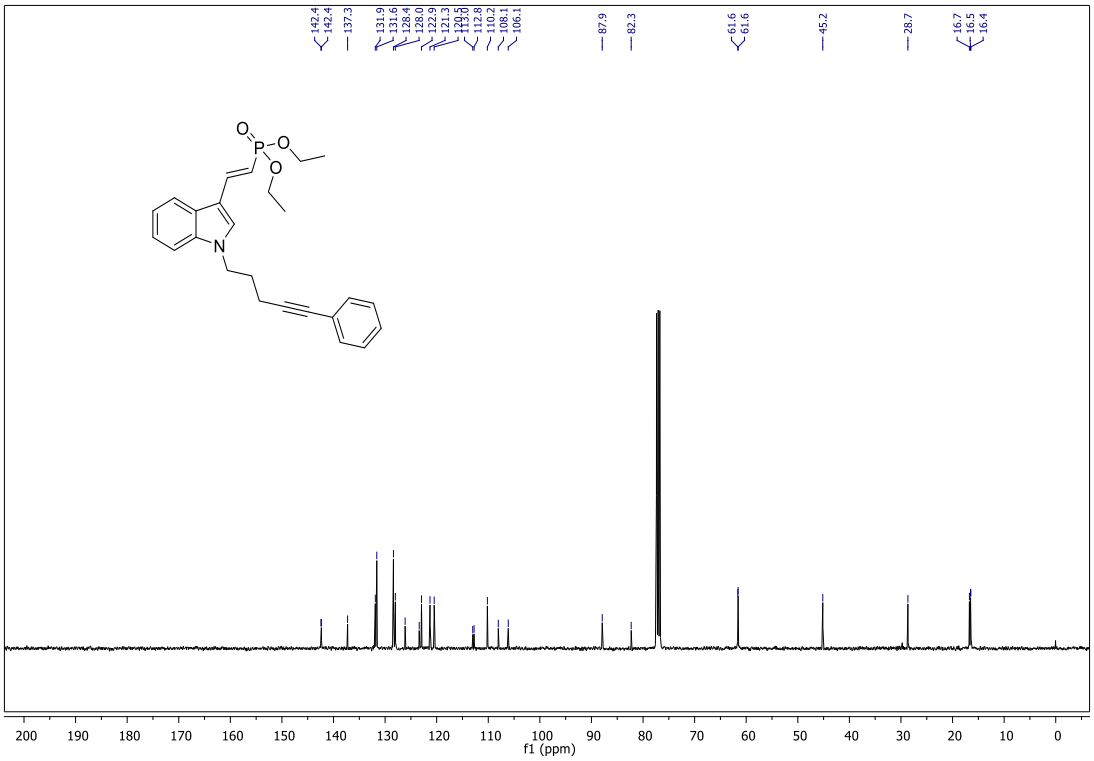
^{1}H NMR of compound **1x** in $CDCl_3$ (400 MHz)



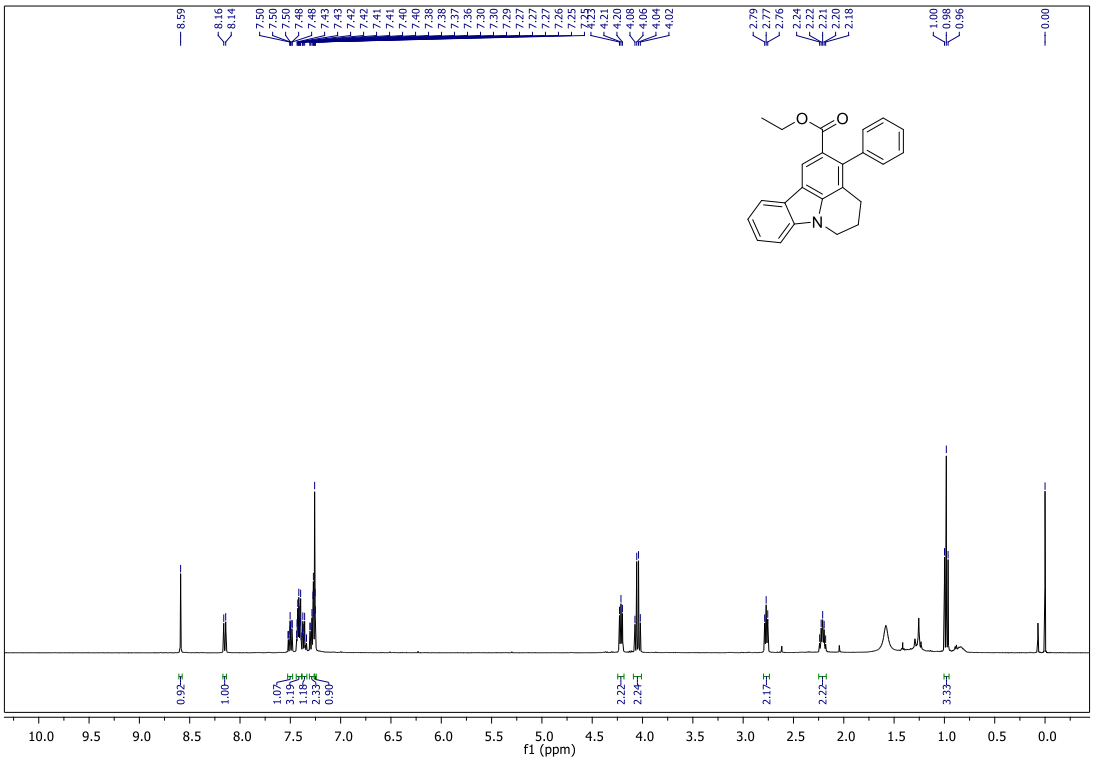
^{13}C NMR of compound **1x** in $CDCl_3$ (101 MHz)



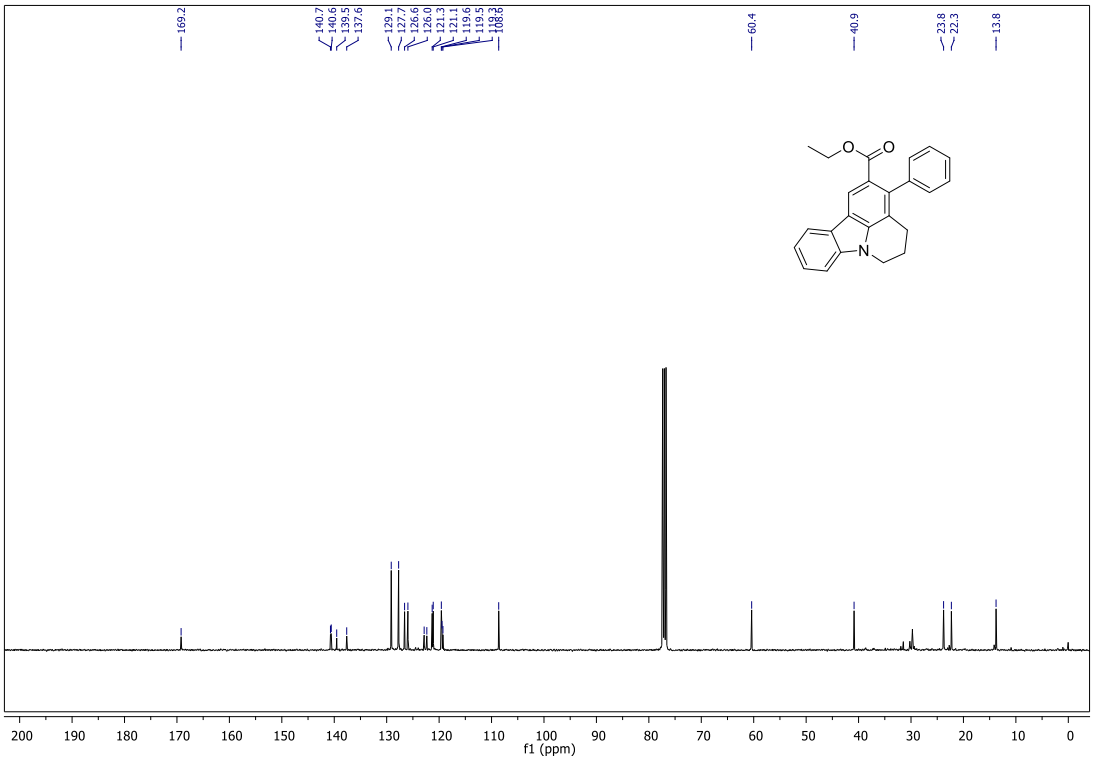
^{1}H NMR of compound **1y** in $CDCl_3$ (400 MHz)



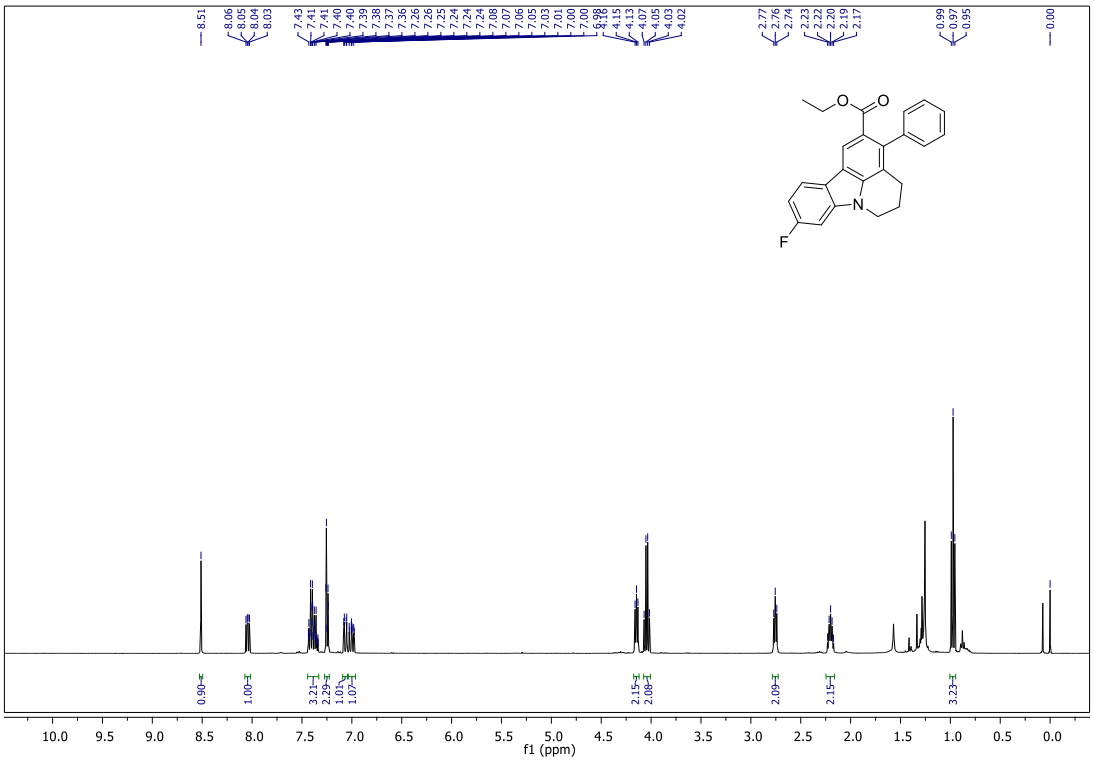
^{13}C NMR of compound **1y** in $CDCl_3$ (101 MHz)



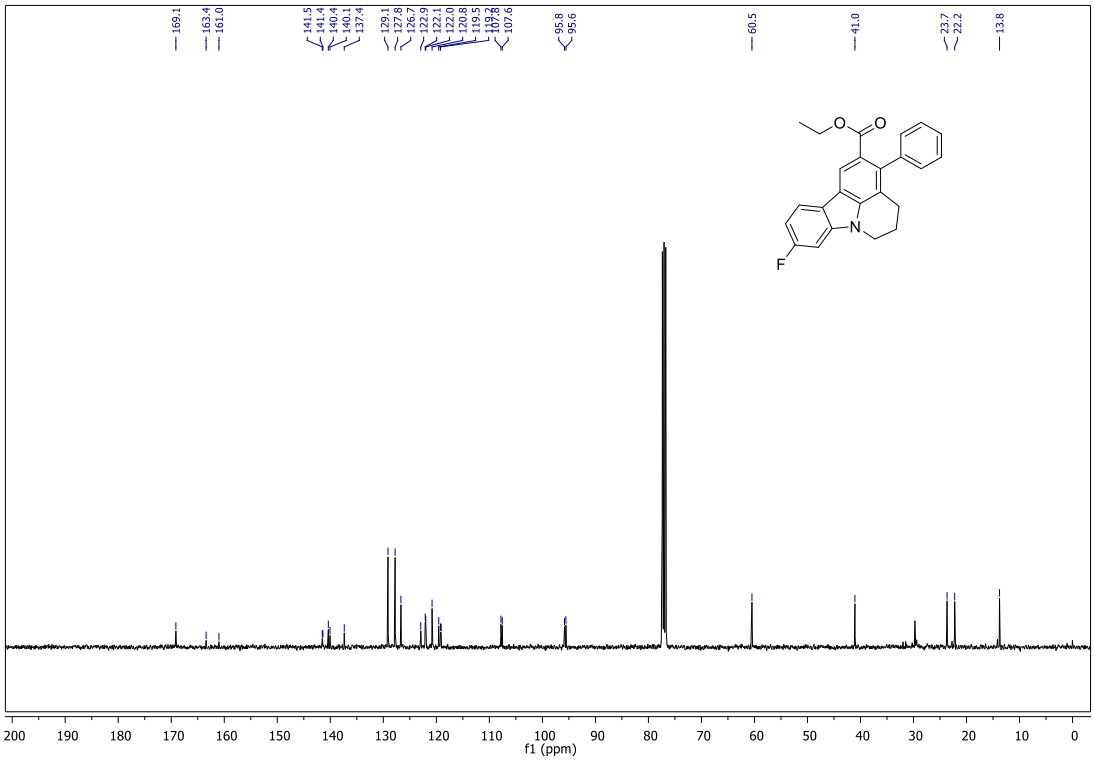
^{1}H NMR of compound **2a** in $CDCl_3$ (400 MHz)



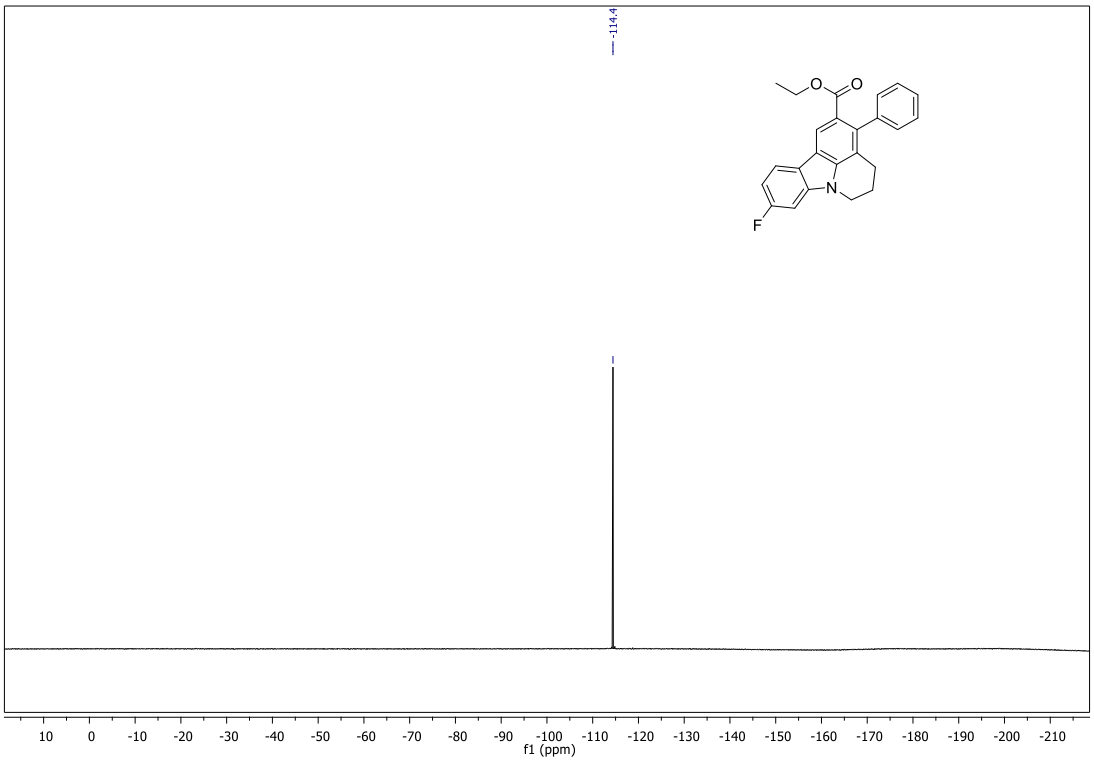
^{13}C NMR of compound **2a** in $CDCl_3$ (101 MHz)



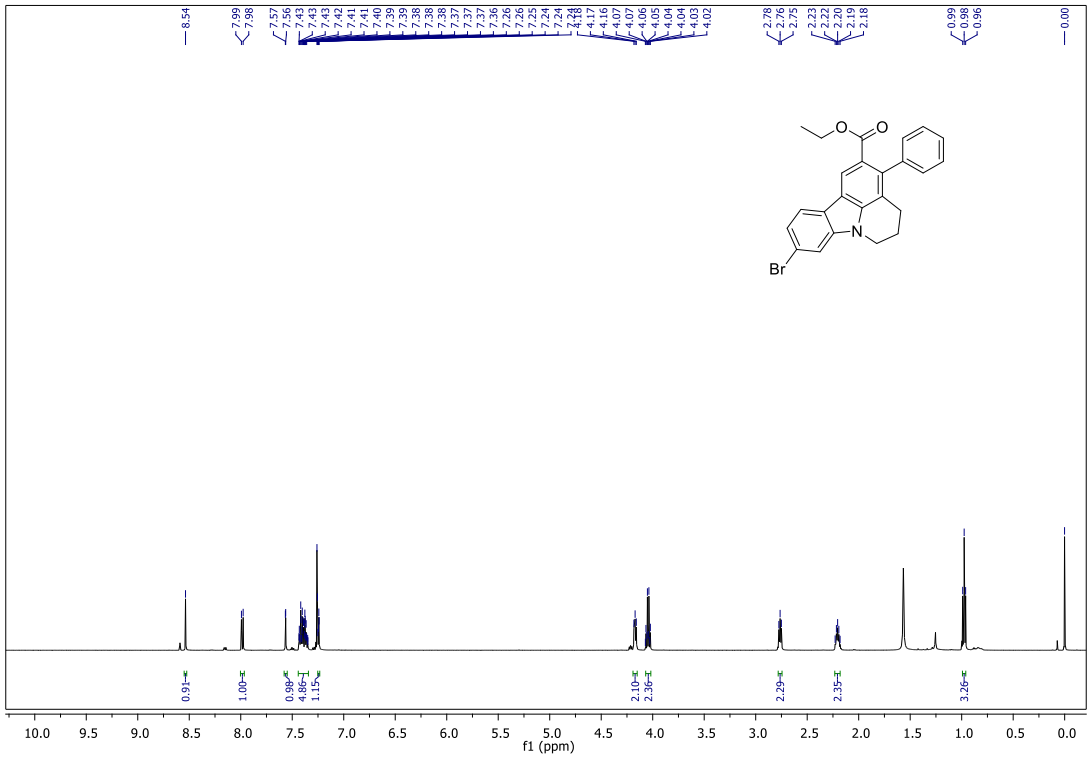
^{1}H NMR of compound **2b** in $CDCl_3$ (400 MHz)



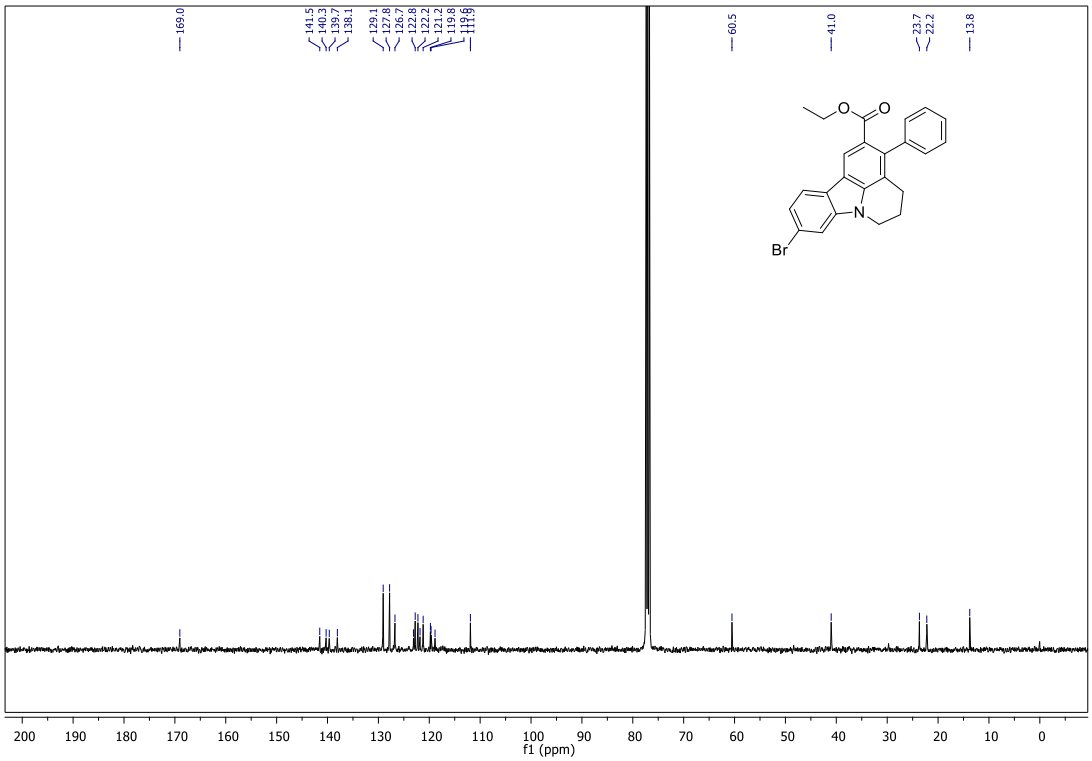
^{13}C NMR of compound **2b** in $CDCl_3$ (101 MHz)



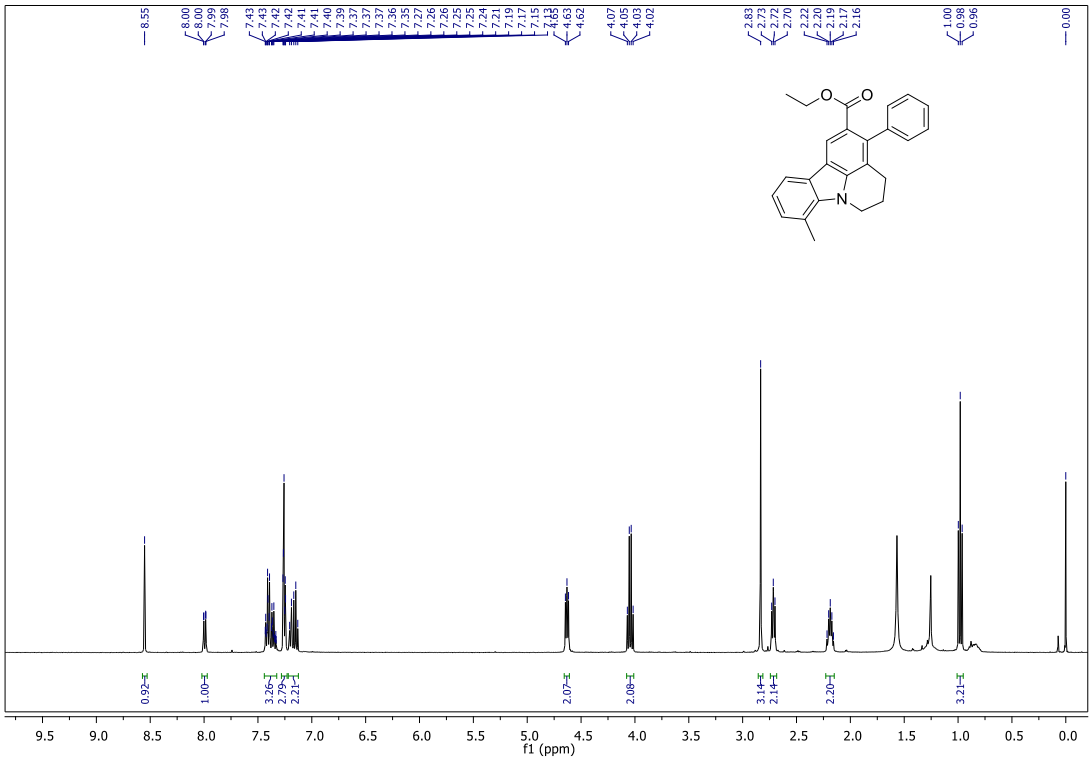
^{19}F NMR of compound **2b** in $CDCl_3$ (376 MHz)



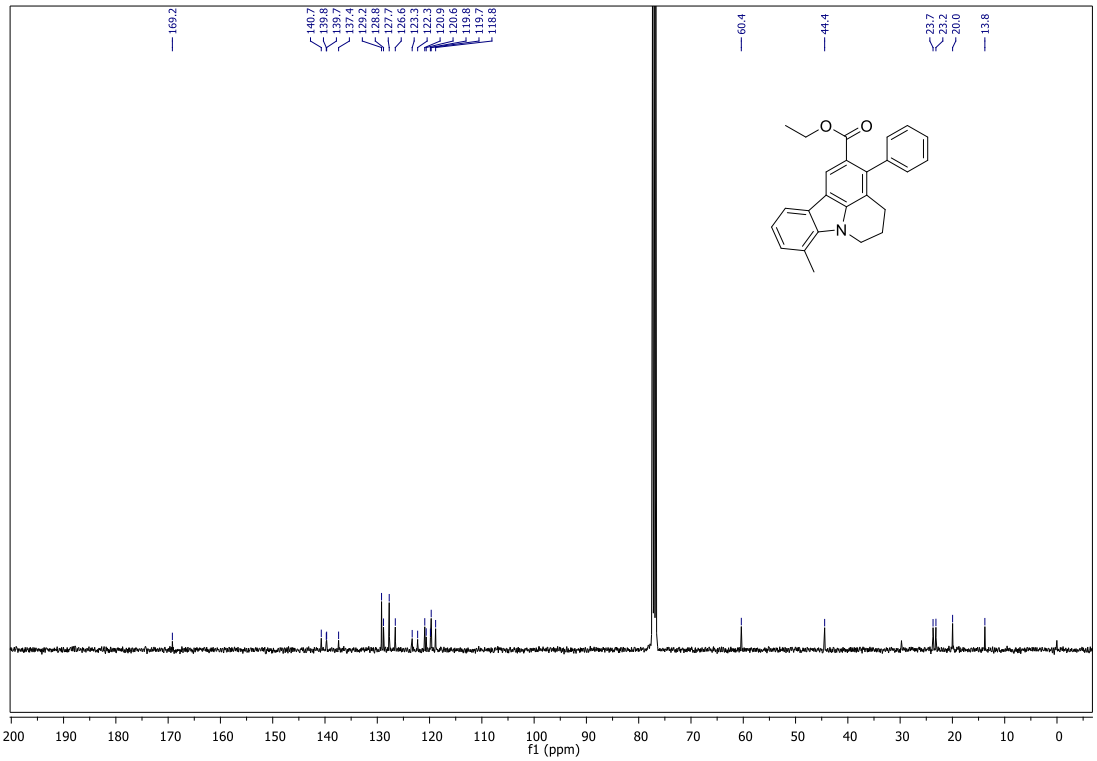
^{1}H NMR of compound **2c** in $CDCl_3$ (500 MHz)



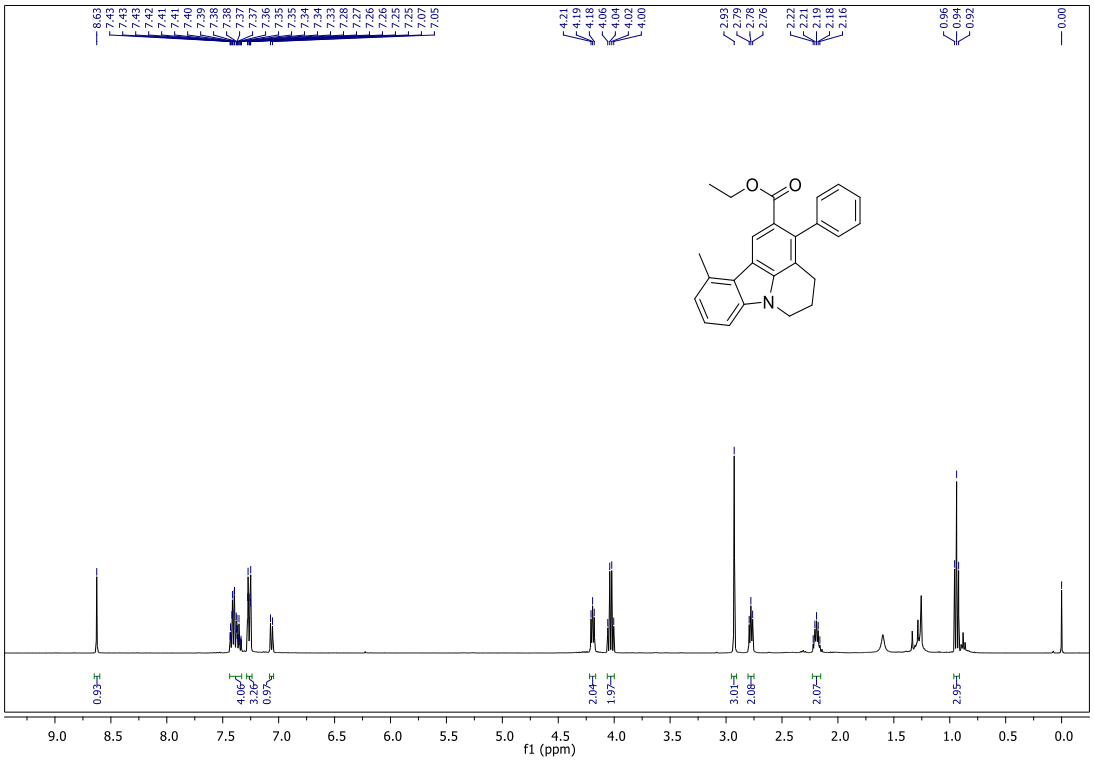
^{13}C NMR of compound **2c** in $CDCl_3$ (101 MHz)



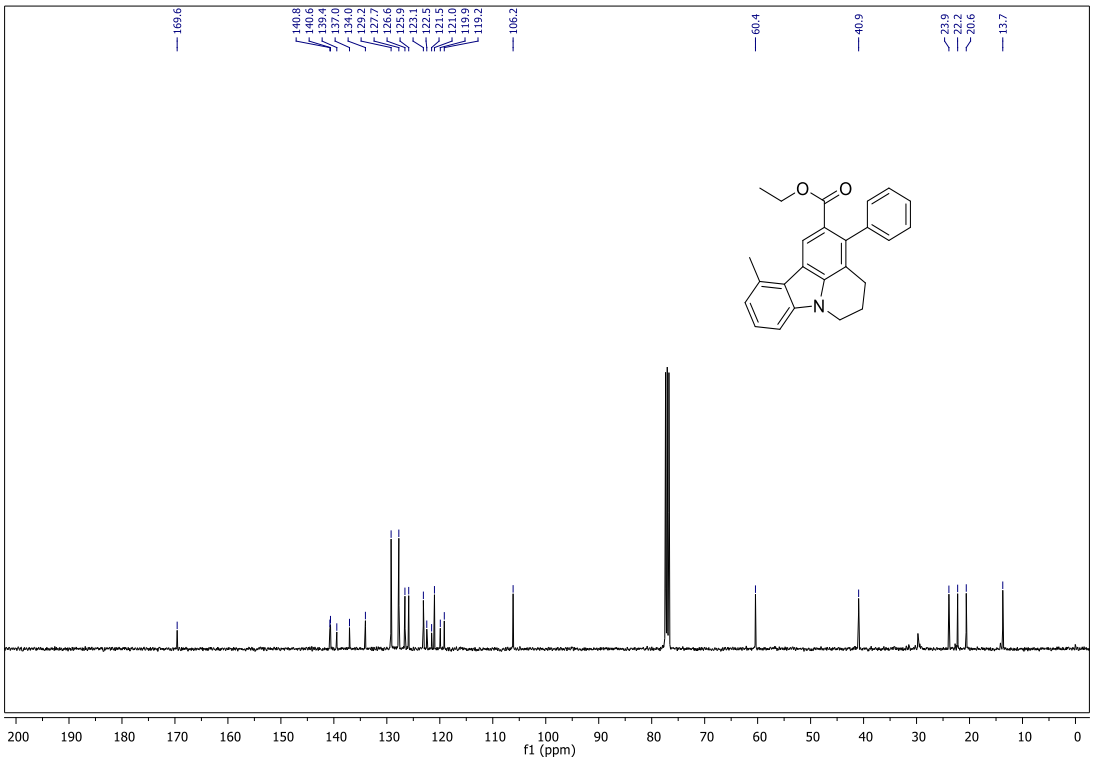
^{1}H NMR of compound **2d** in $CDCl_3$ (400 MHz)



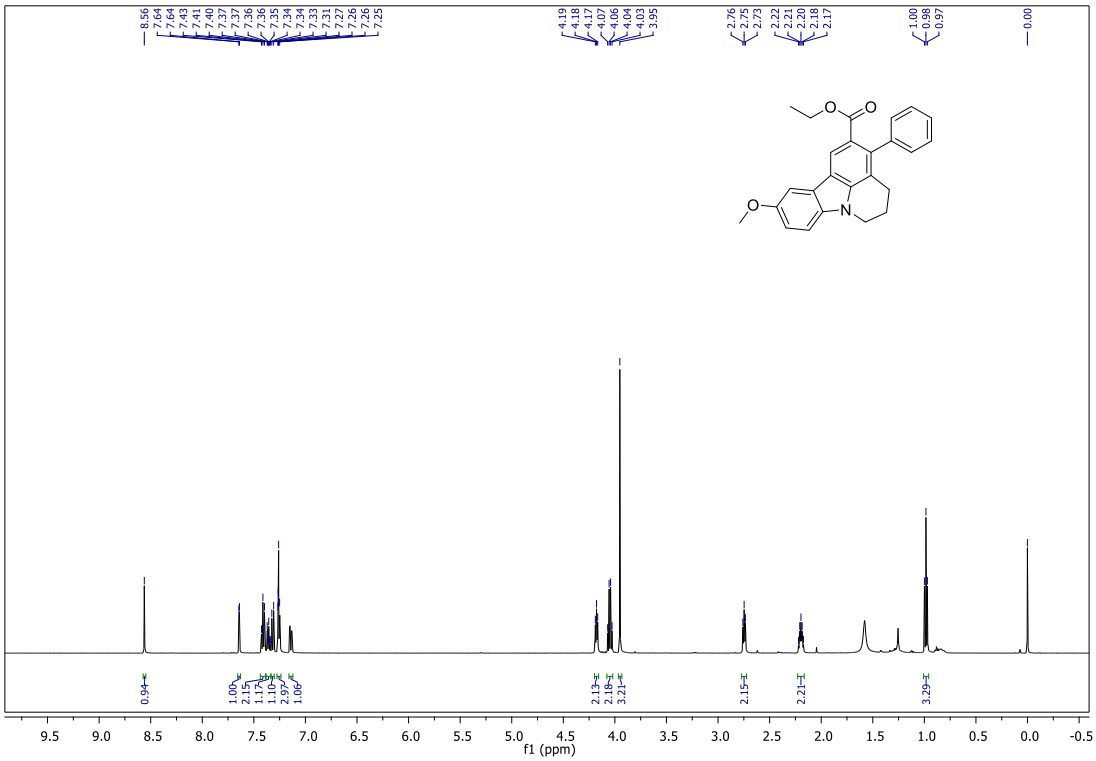
^{13}C NMR of compound **2d** in $CDCl_3$ (101 MHz)



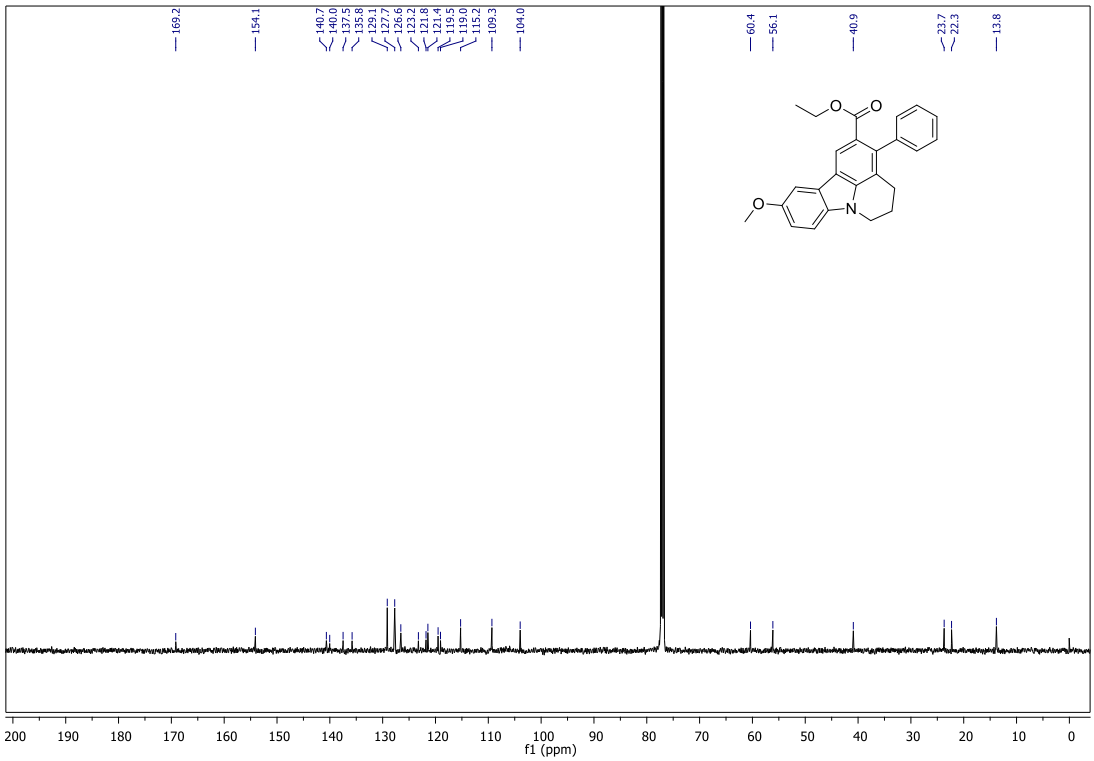
^{1}H NMR of compound **2e** in $CDCl_3$ (400 MHz)



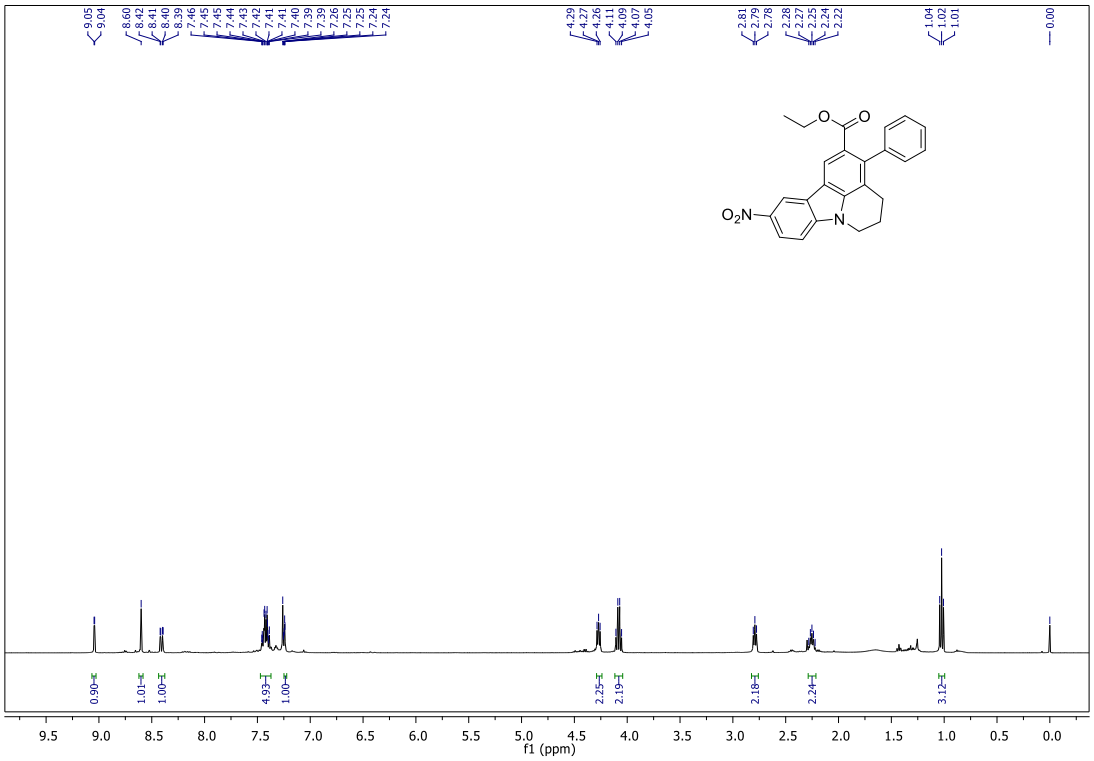
^{13}C NMR of compound **2e** in $CDCl_3$ (101 MHz)



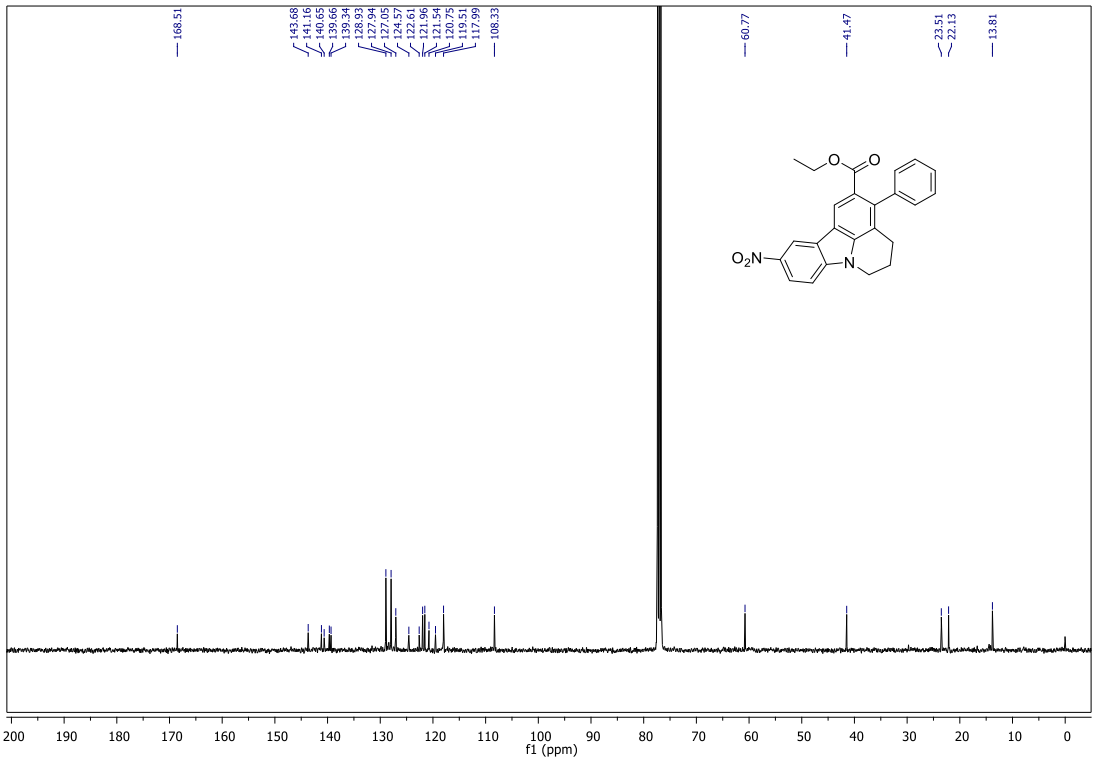
^{1}H NMR of compound **2f** in $CDCl_3$ (500 MHz)



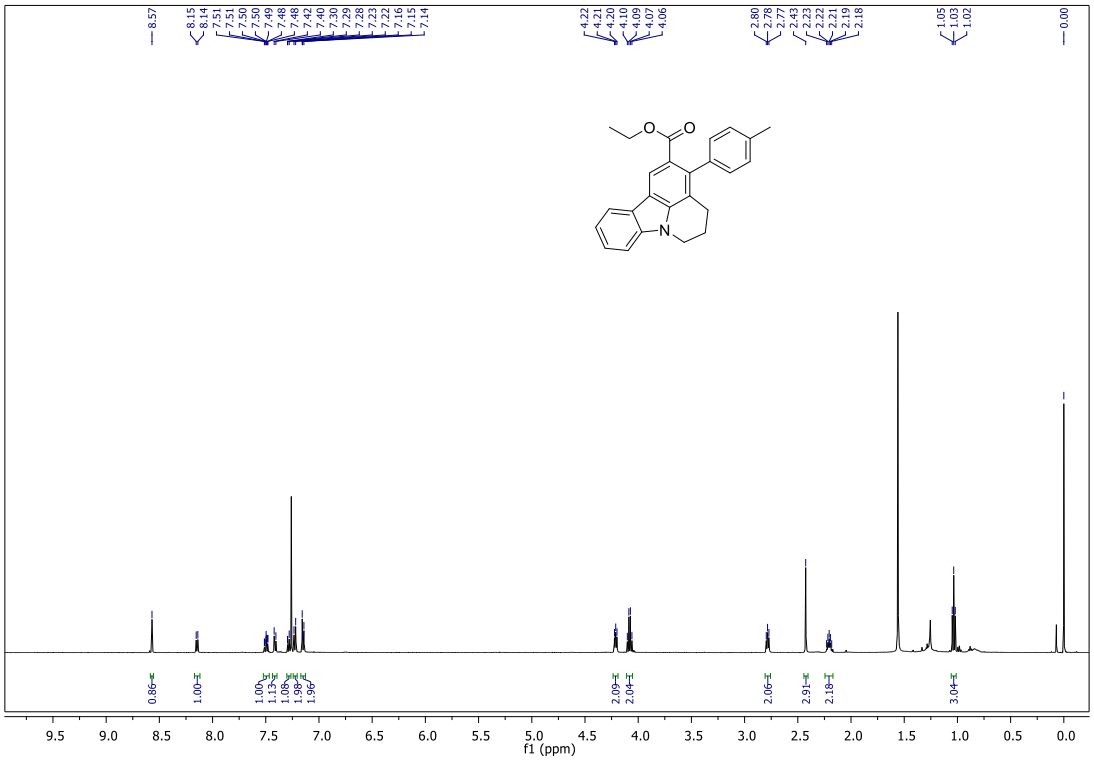
^{13}C NMR of compound **2f** in $CDCl_3$ (126 MHz)



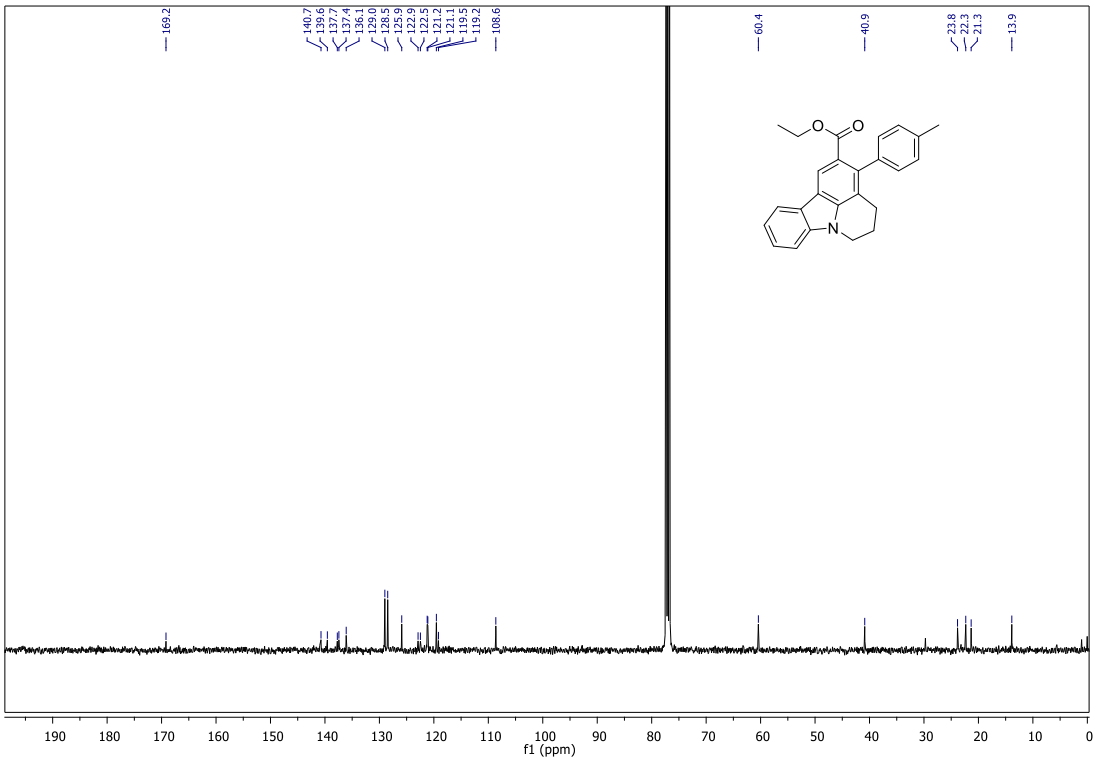
^{1}H NMR of compound **2g** in $CDCl_3$ (400 MHz)



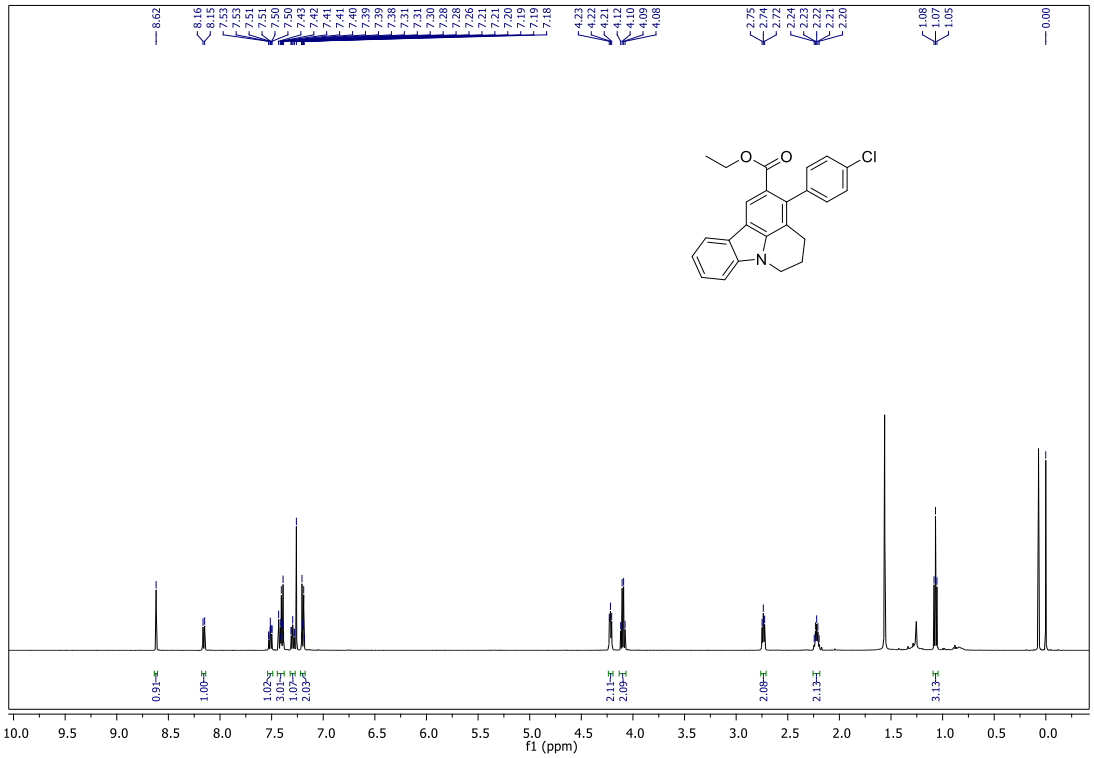
^{13}C NMR of compound **2g** in $CDCl_3$ (101 MHz)



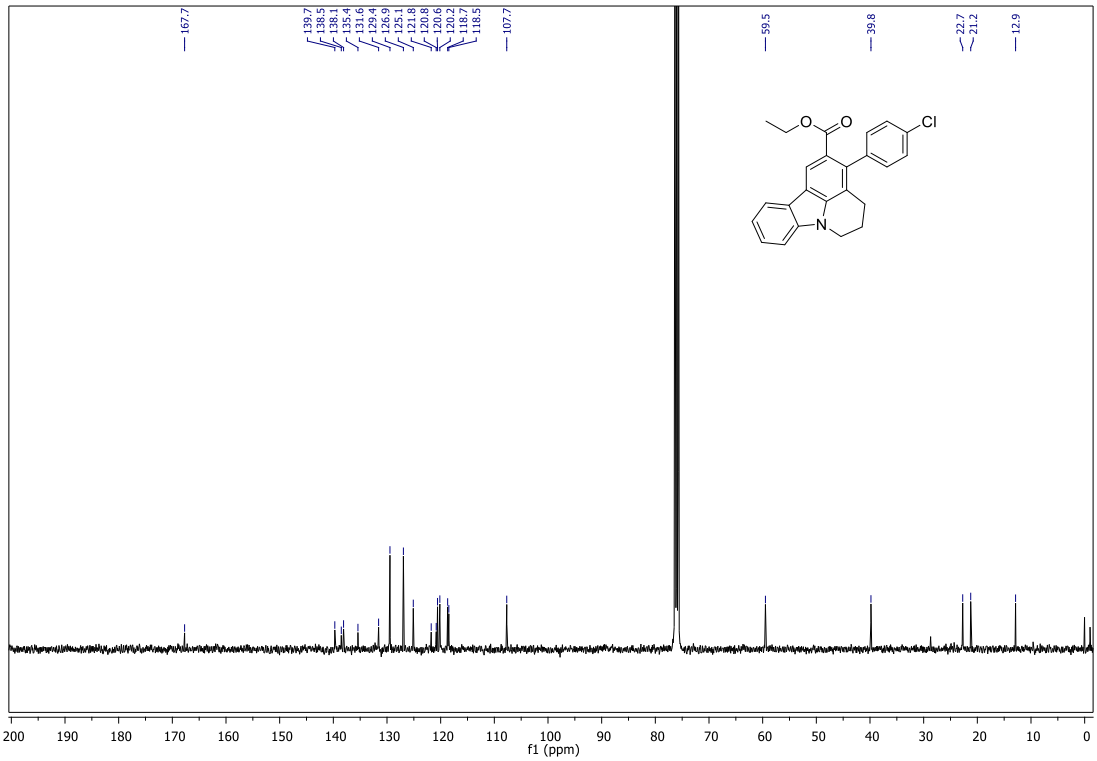
^{1}H NMR of compound **2h** in $CDCl_3$ (500 MHz)



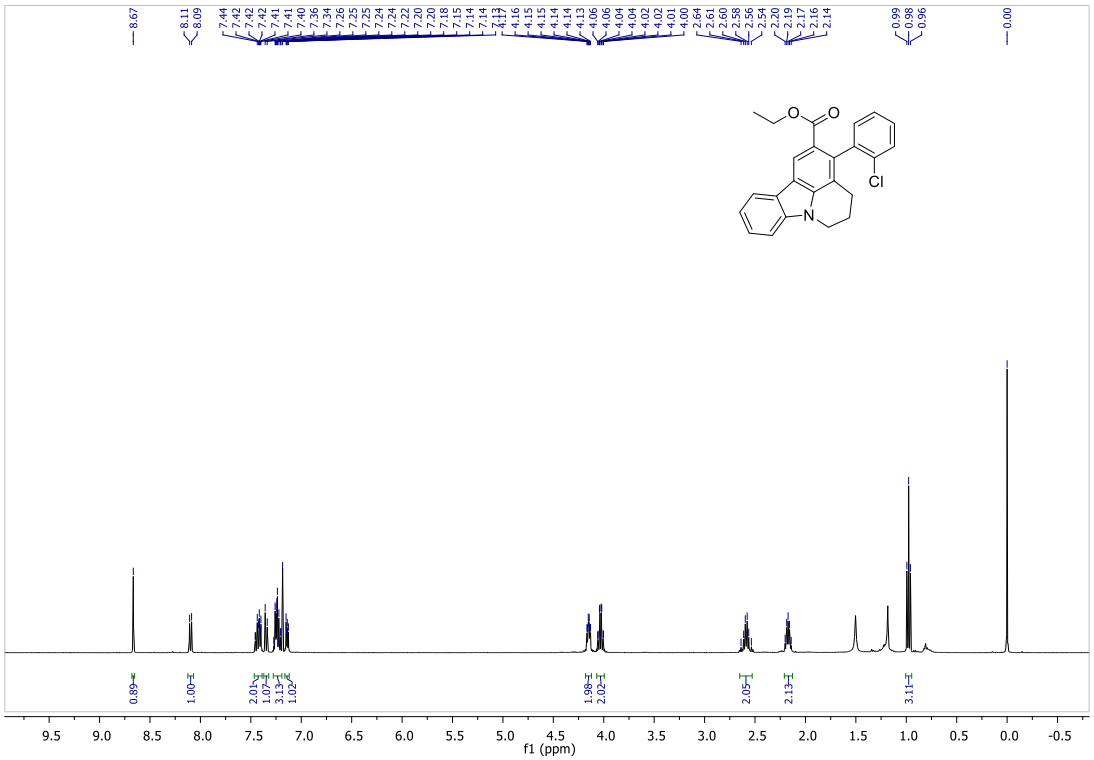
^{13}C NMR of compound **2h** in $CDCl_3$ (101 MHz)



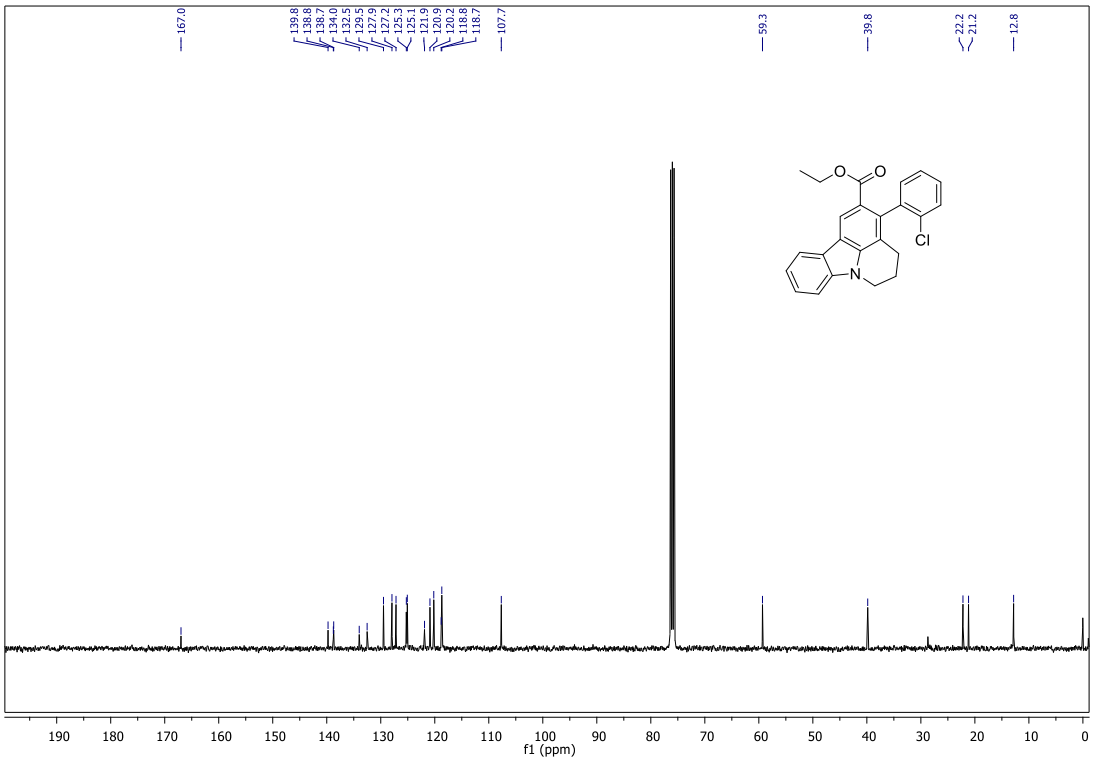
^{1}H NMR of compound **2i** in $CDCl_3$ (500 MHz)



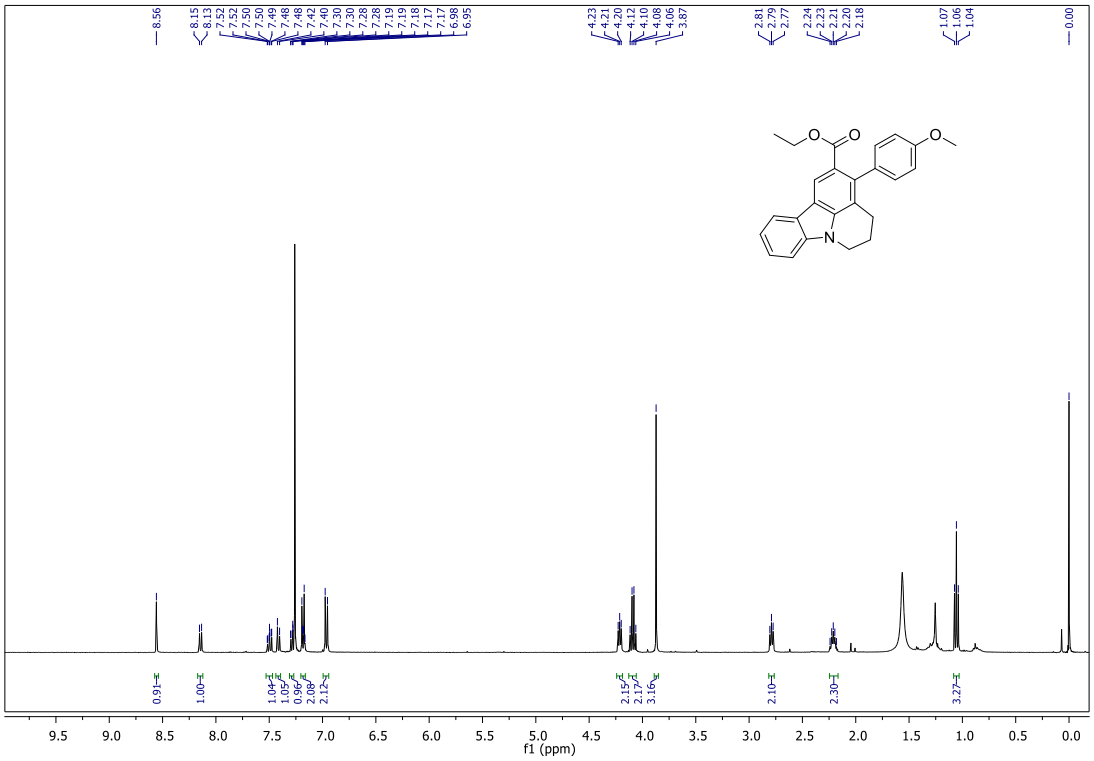
^{13}C NMR of compound **2i** in $CDCl_3$ (101 MHz)



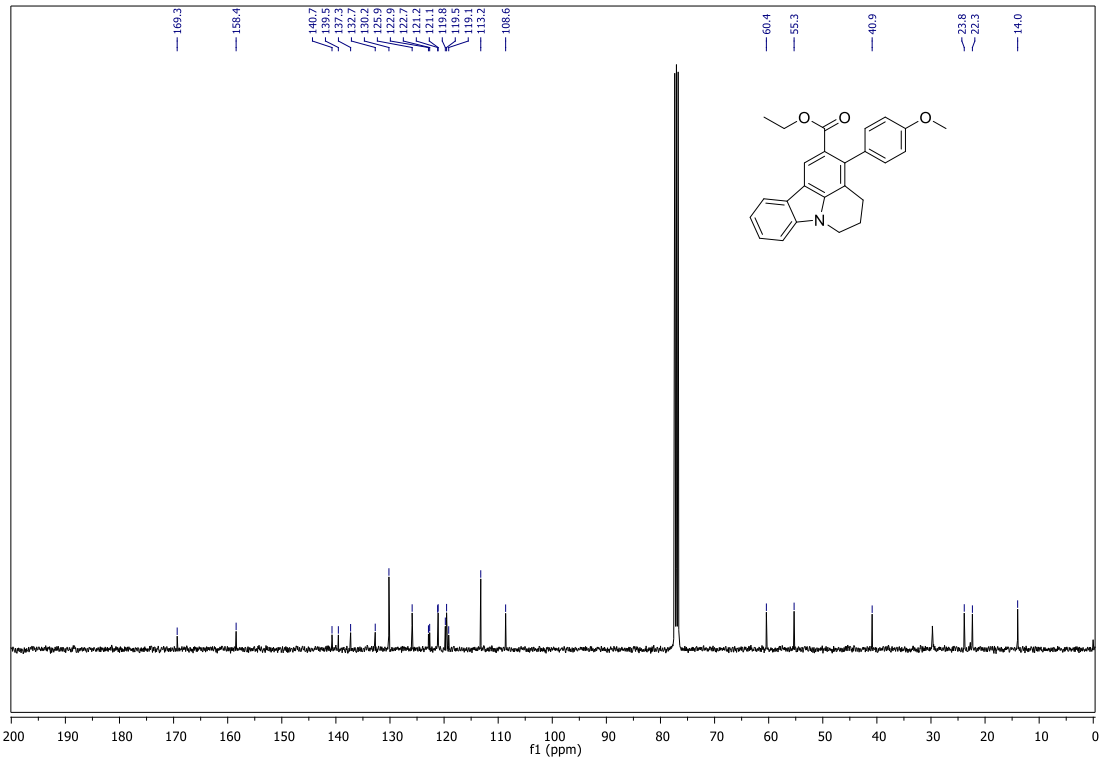
^{1}H NMR of compound **2j** in $CDCl_3$ (400 MHz)



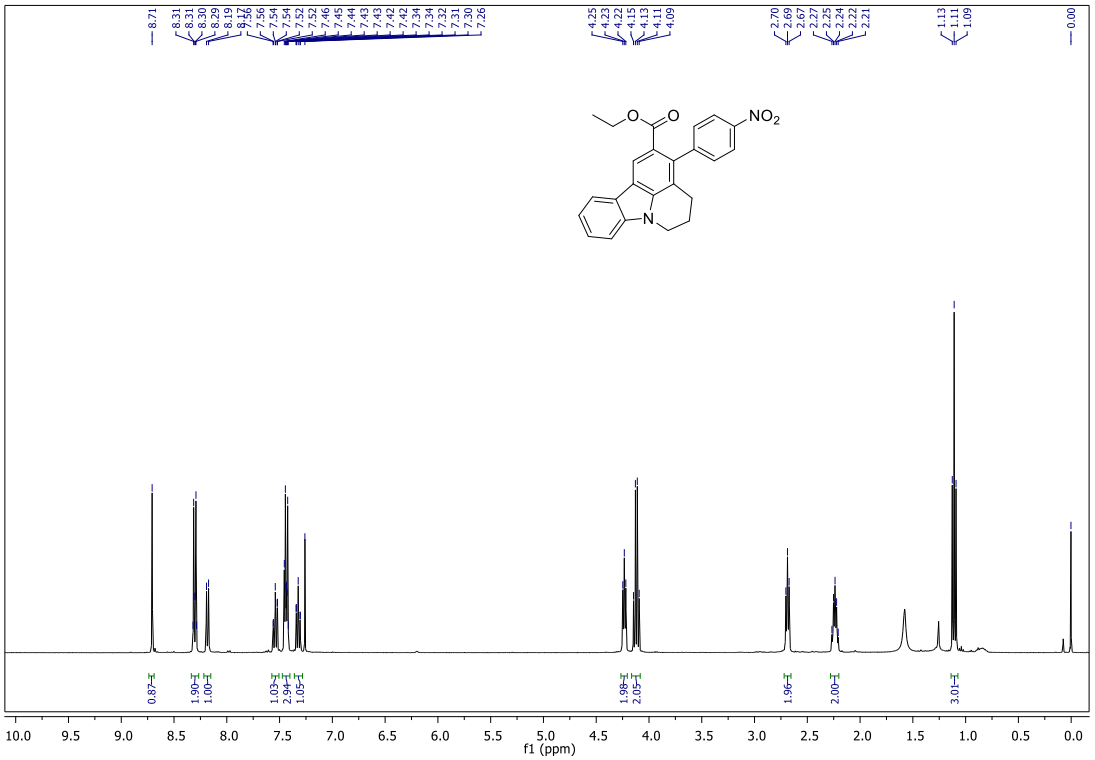
^{13}C NMR of compound **2j** in $CDCl_3$ (101 MHz)



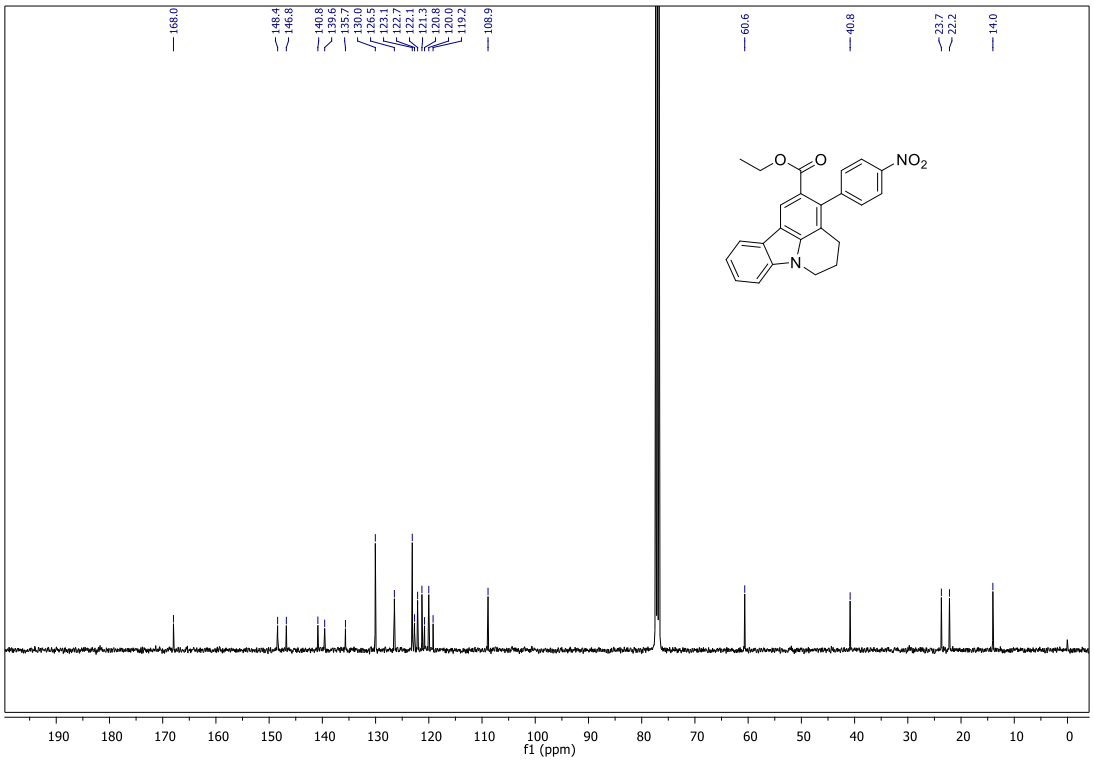
^{1}H NMR of compound **2k** in $CDCl_3$ (400 MHz)



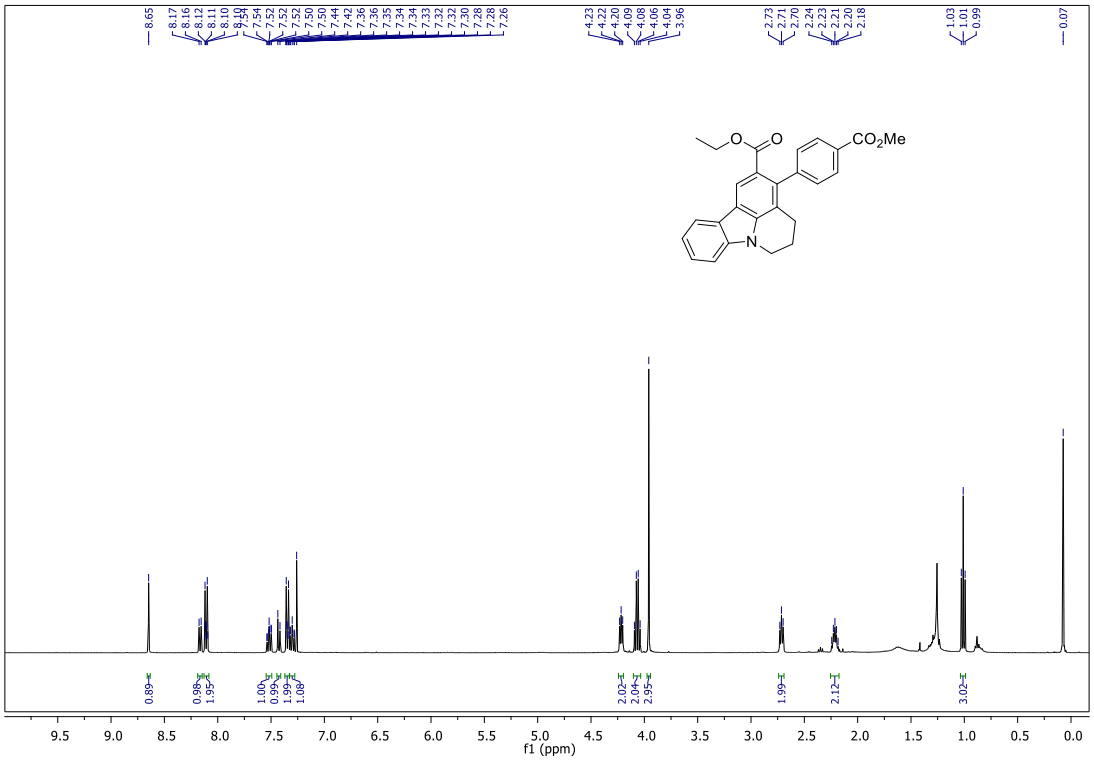
^{13}C NMR of compound **2k** in $CDCl_3$ (101 MHz)



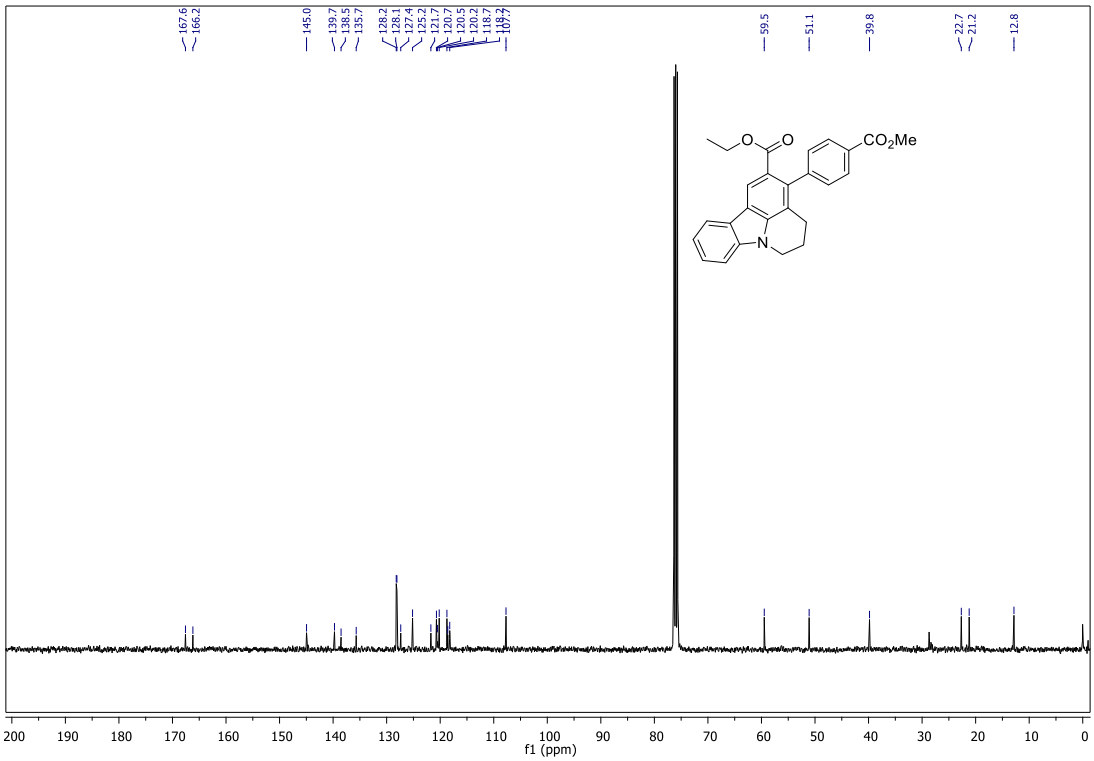
^{1}H NMR of compound **2l** in $CDCl_3$ (400 MHz)



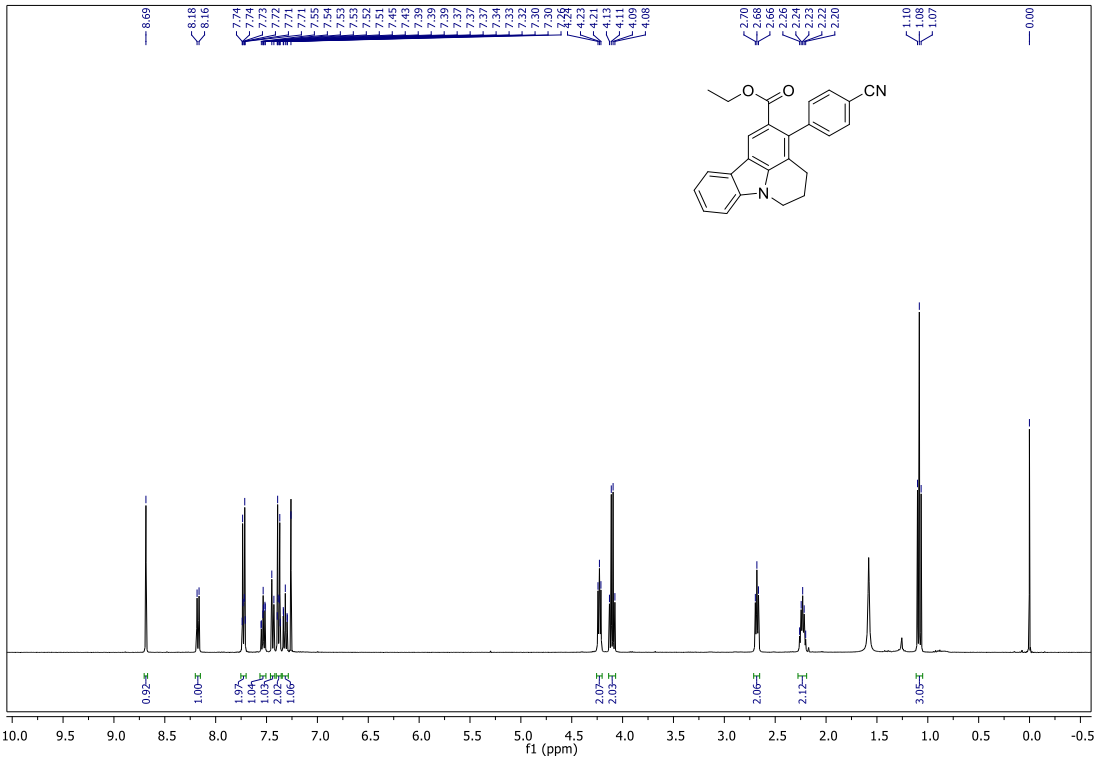
^{13}C NMR of compound **2l** in $CDCl_3$ (101 MHz)



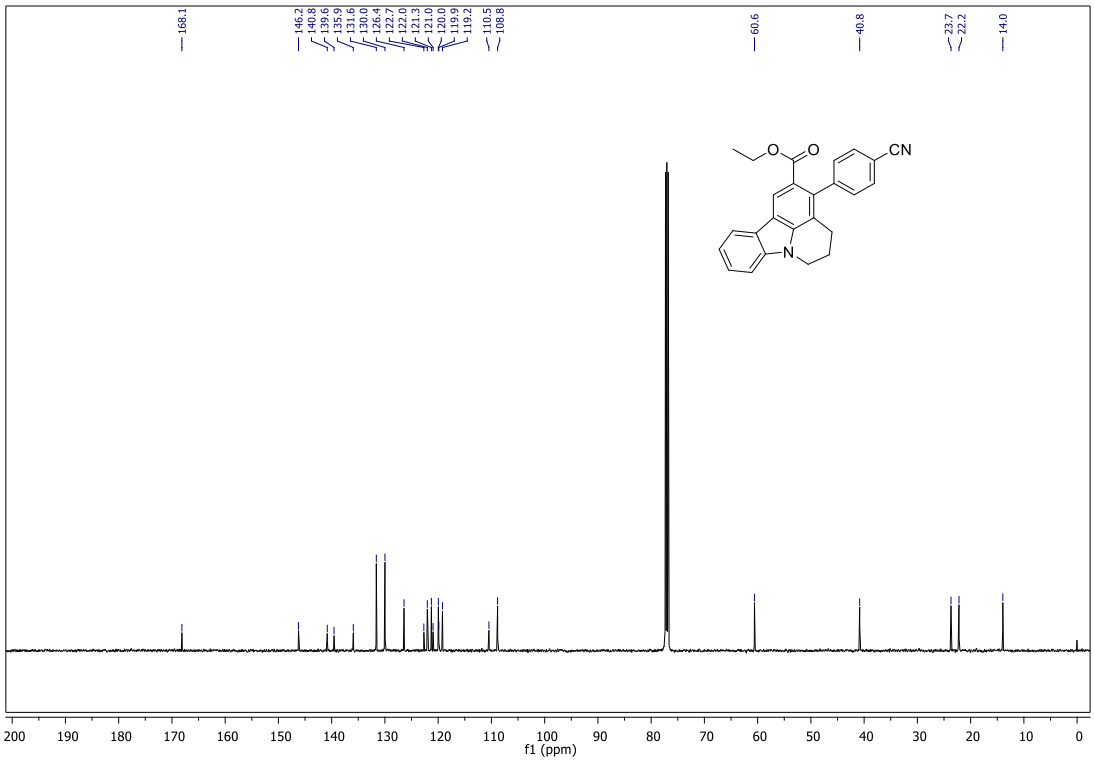
^{1}H NMR of compound **2m** in $CDCl_3$ (400 MHz)



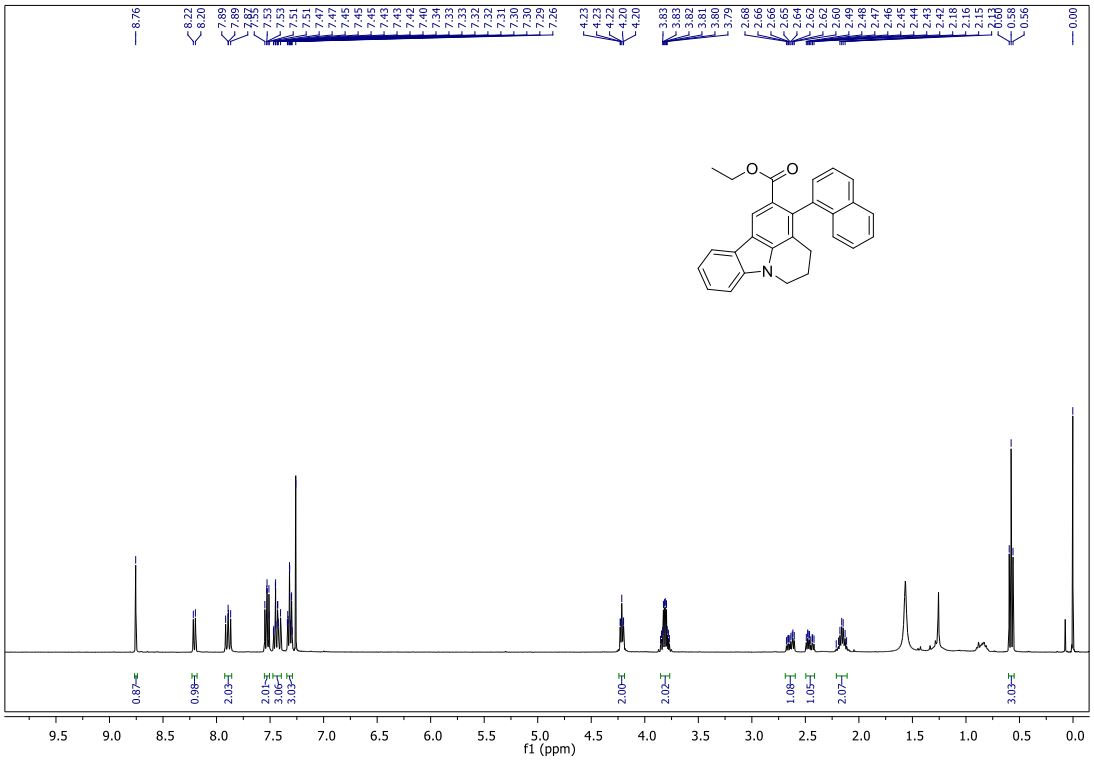
^{13}C NMR of compound **2m** in $CDCl_3$ (101 MHz)



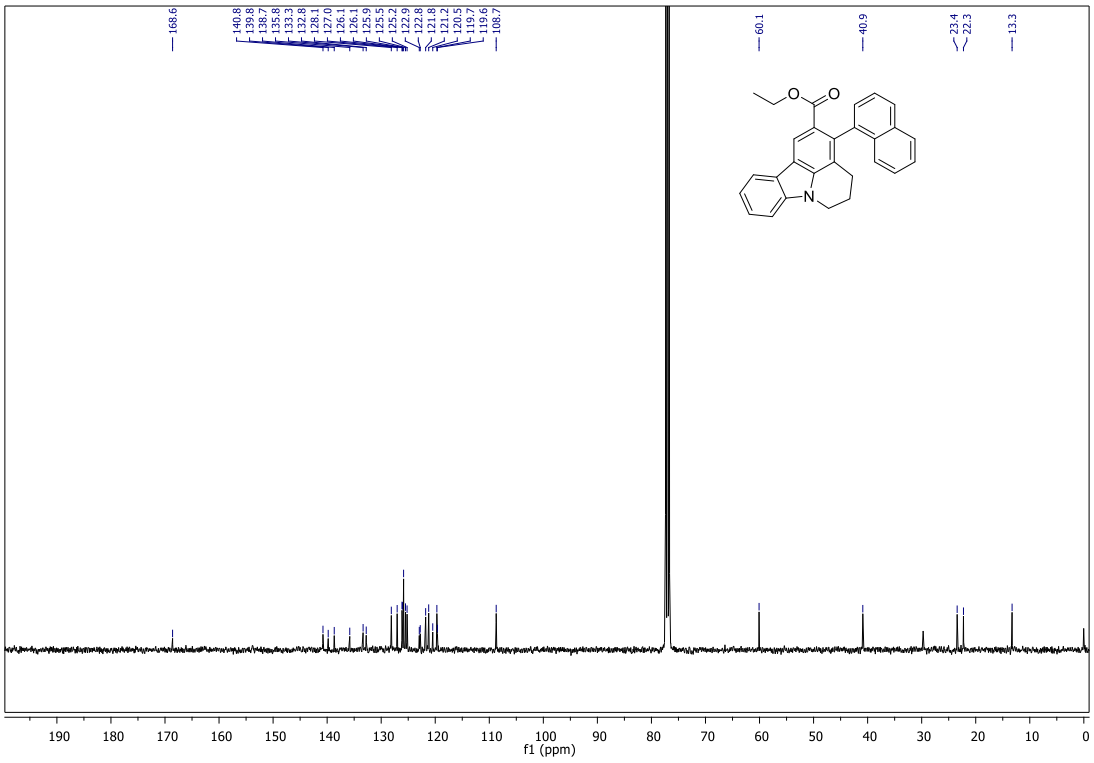
^{1}H NMR of compound **2n** in $CDCl_3$ (400 MHz)



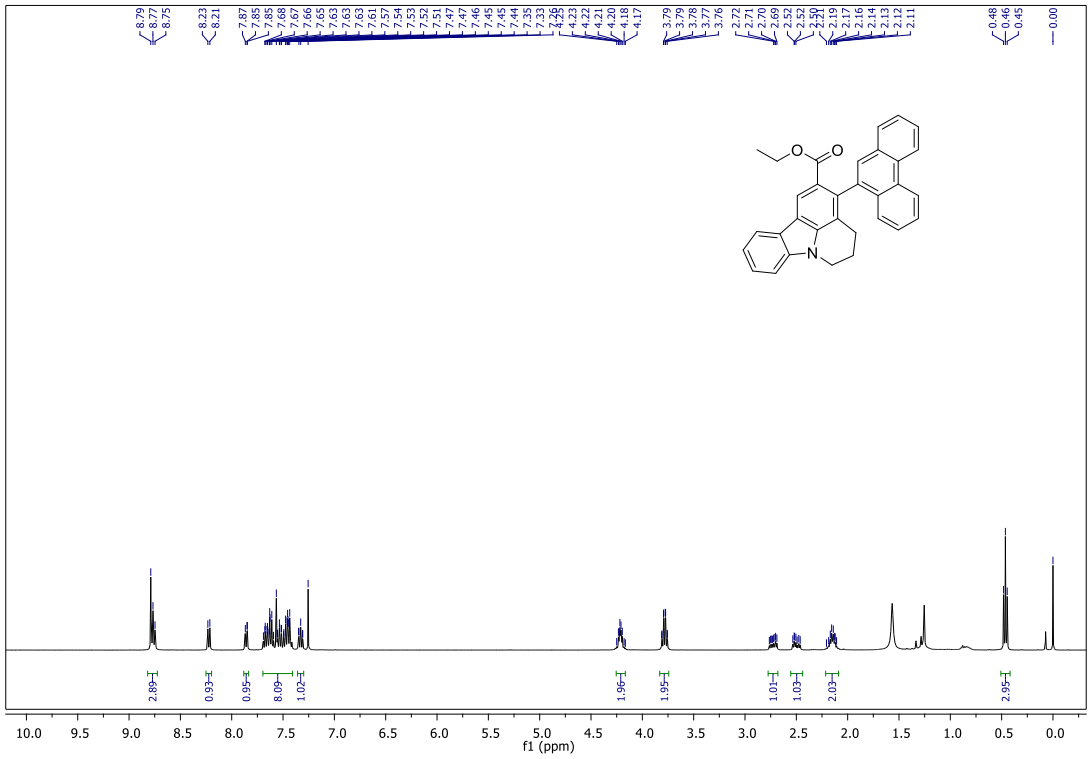
^{13}C NMR of compound **2n** in $CDCl_3$ (126 MHz)



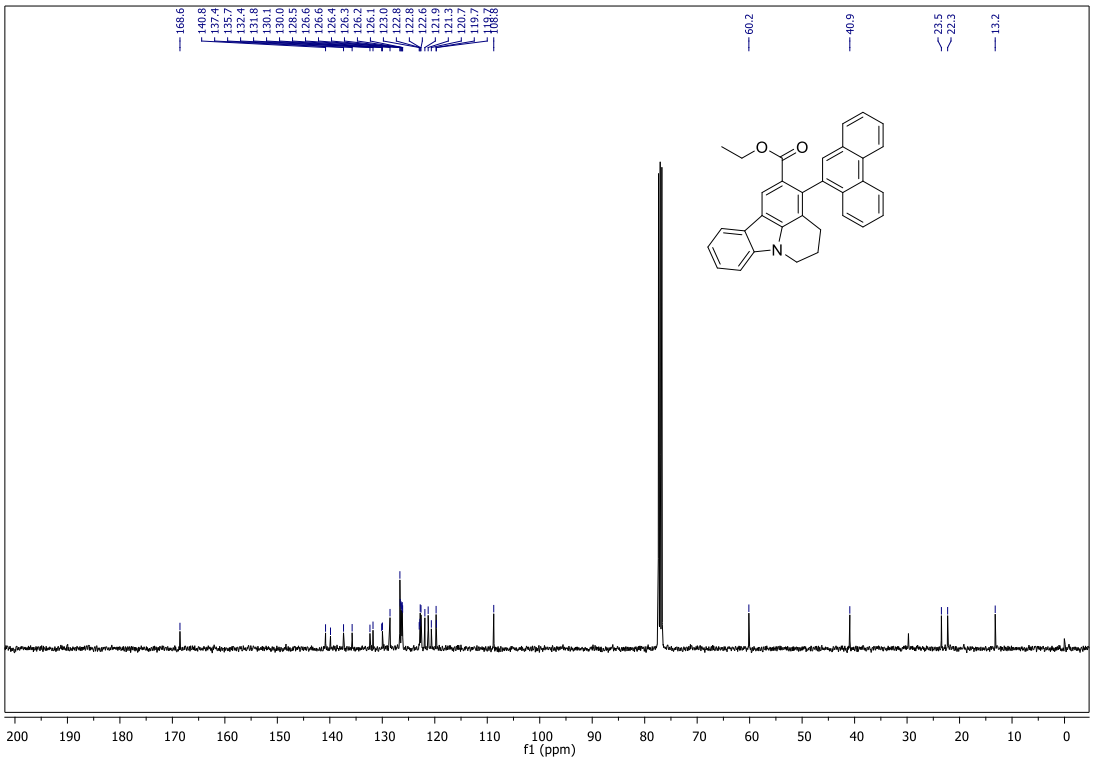
^{1}H NMR of compound **2o** in $CDCl_3$ (400 MHz)



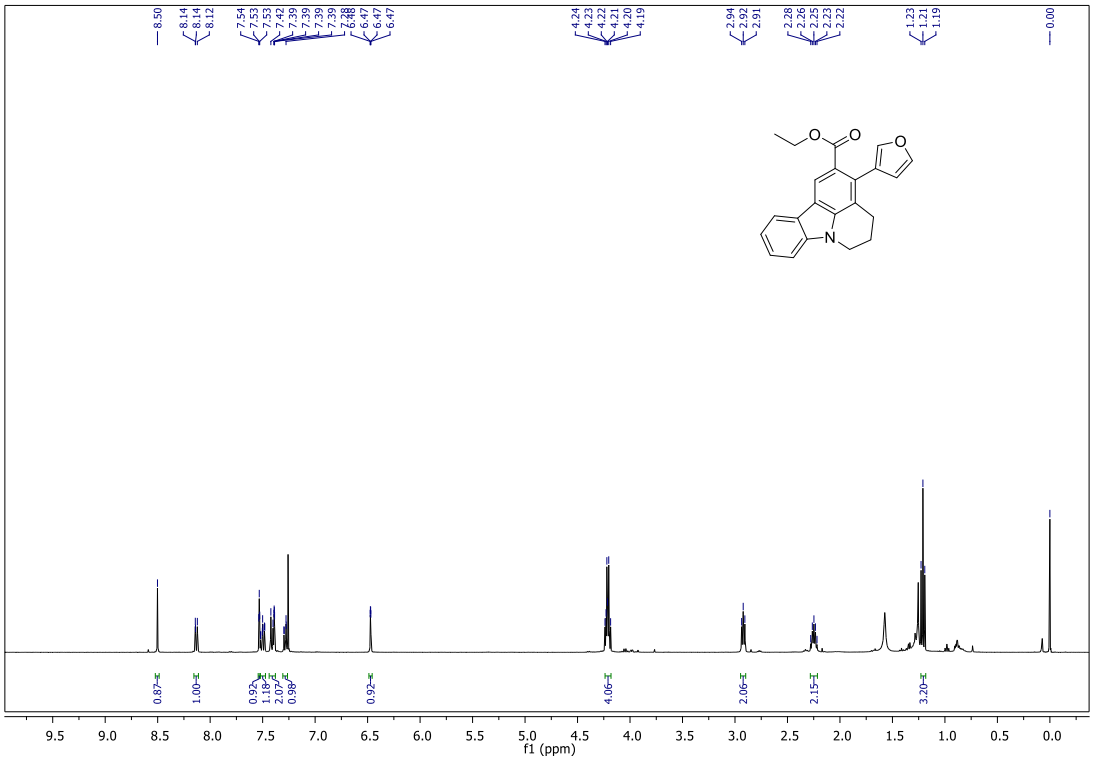
^{13}C NMR of compound **2o** in $CDCl_3$ (101 MHz)



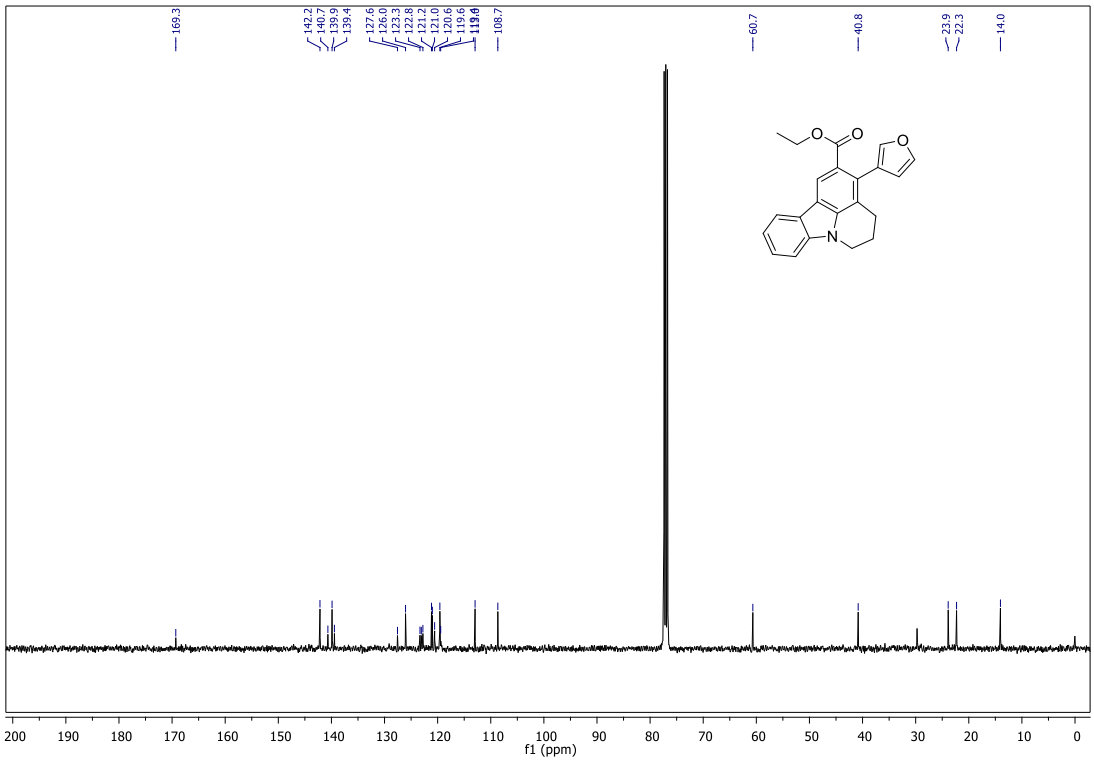
^{1}H NMR of compound **2p** in $CDCl_3$ (400 MHz)



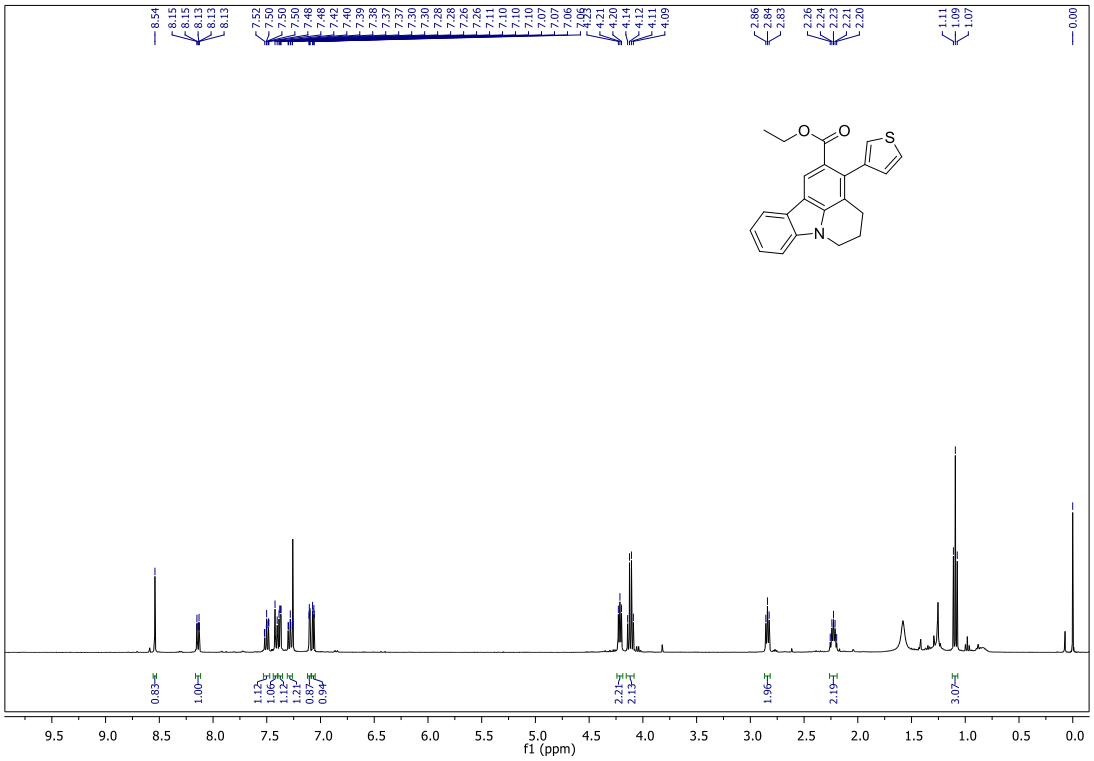
^{13}C NMR of compound **2p** in $CDCl_3$ (101 MHz)



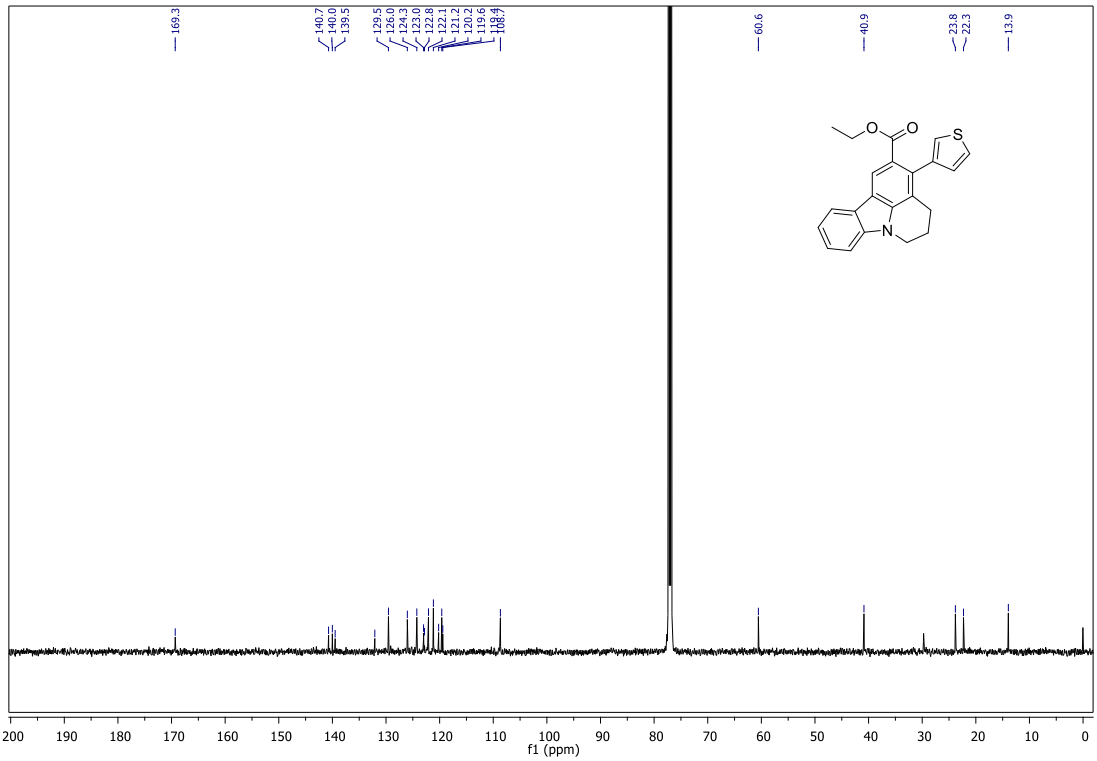
^{1}H NMR of compound **2q** in $CDCl_3$ (400 MHz)



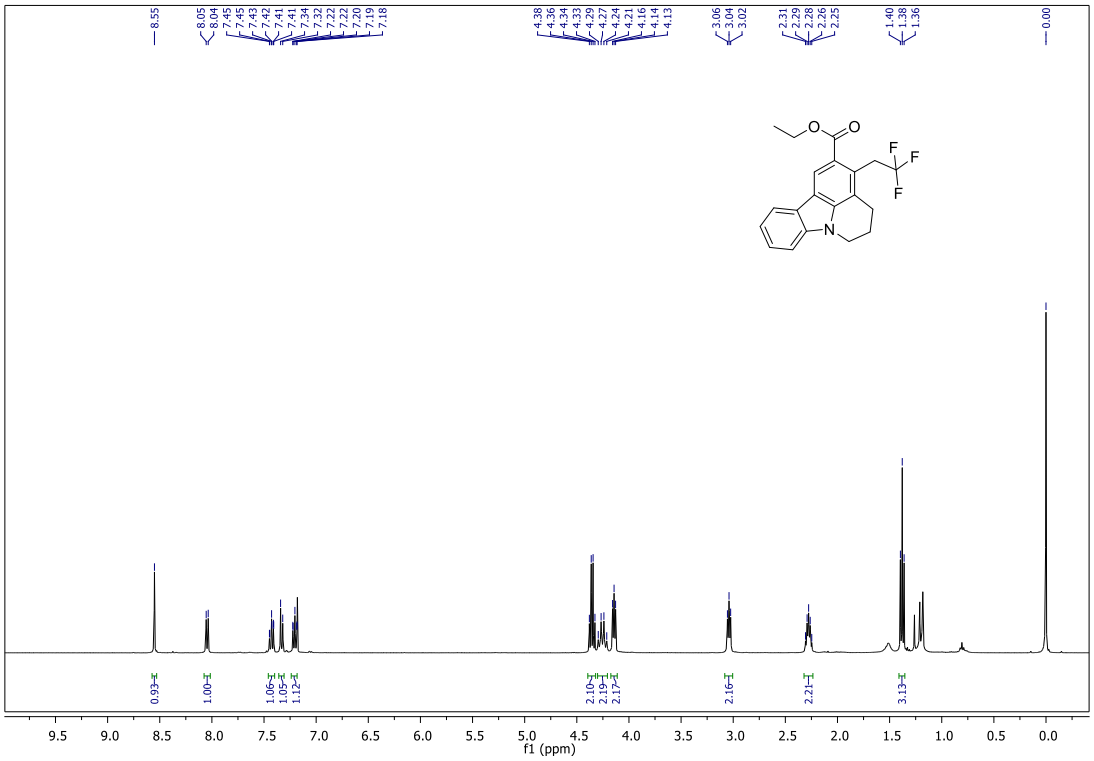
^{13}C NMR of compound **2q** in $CDCl_3$ (101 MHz)



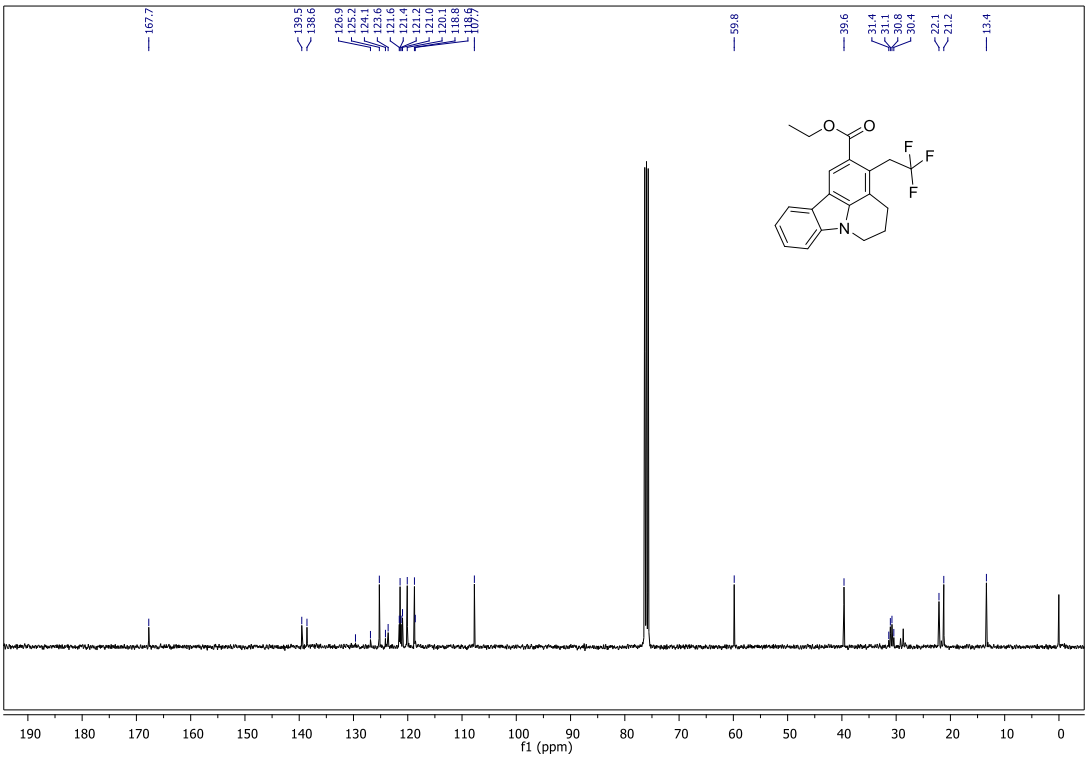
^{1}H NMR of compound **2r** in $CDCl_3$ (400 MHz)



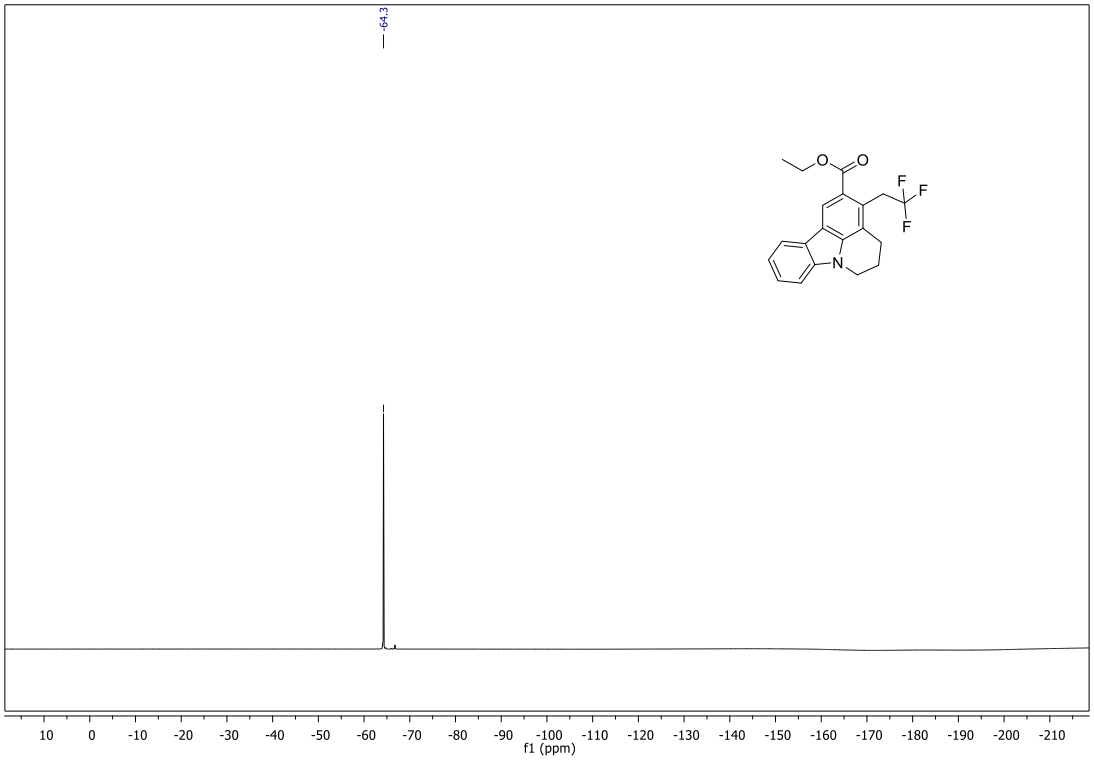
^{13}C NMR of compound **2r** in $CDCl_3$ (126 MHz)



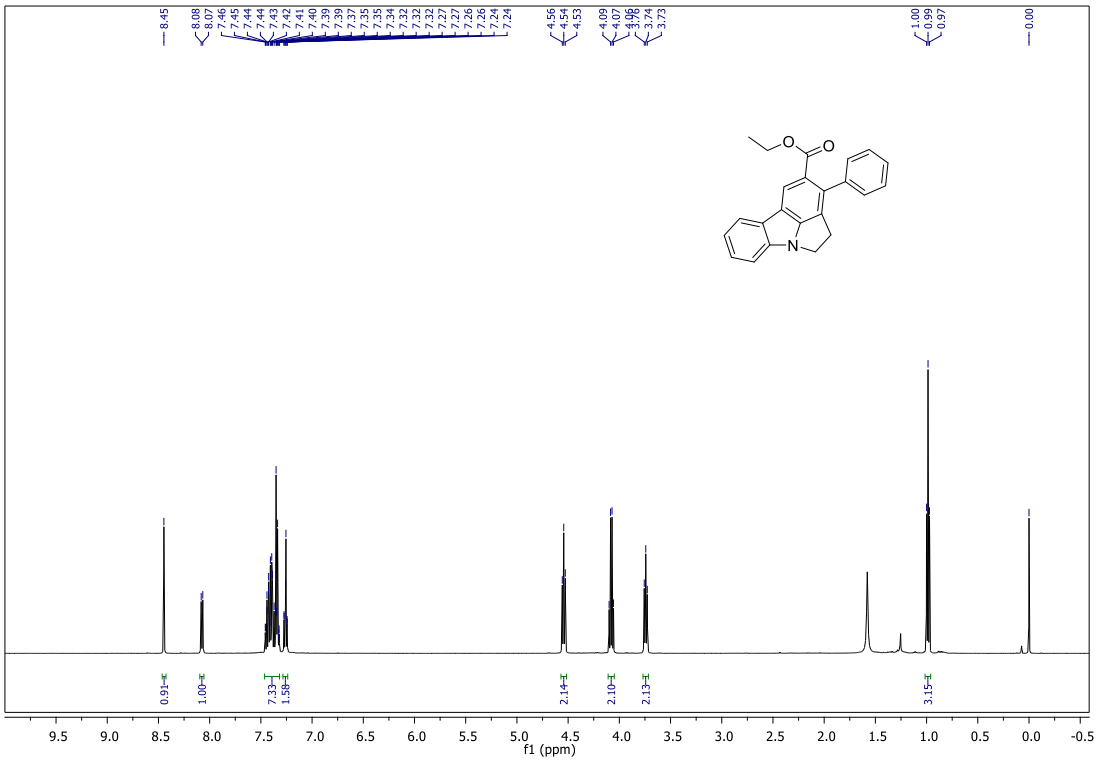
^{1}H NMR of compound **2s** in $CDCl_3$ (400 MHz)



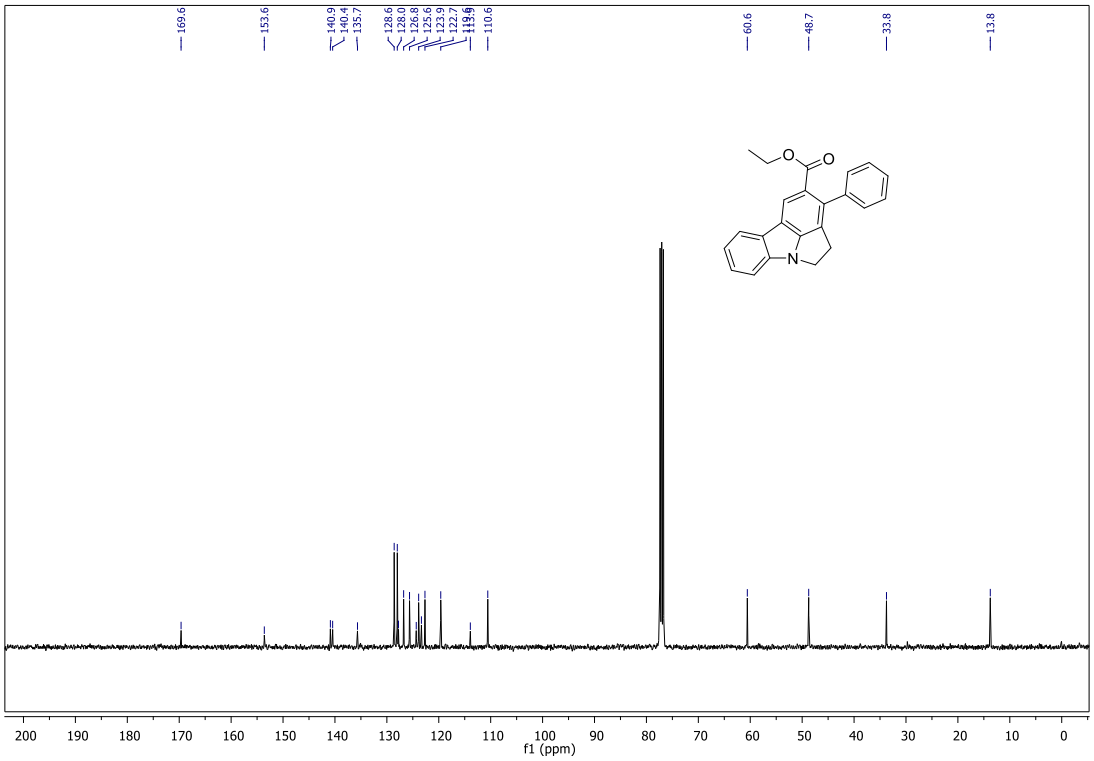
^{13}C NMR of compound **2s** in $CDCl_3$ (101 MHz)



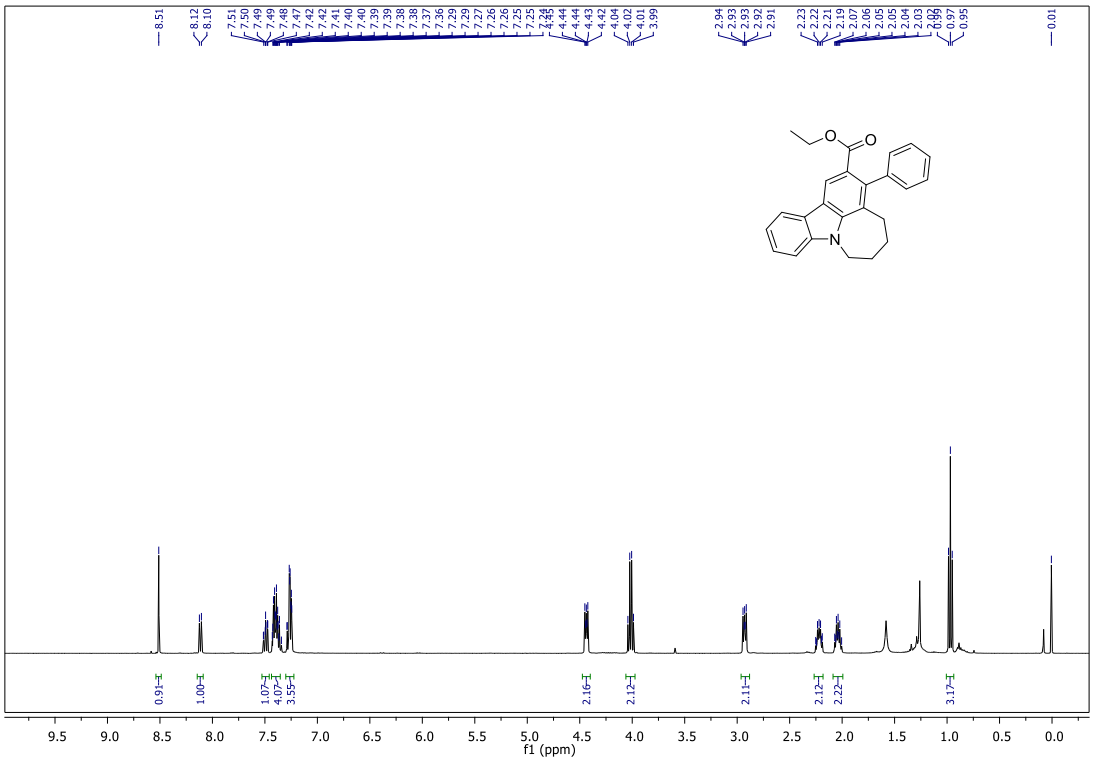
^{19}F NMR of compound **2s** in $CDCl_3$ (376 MHz)



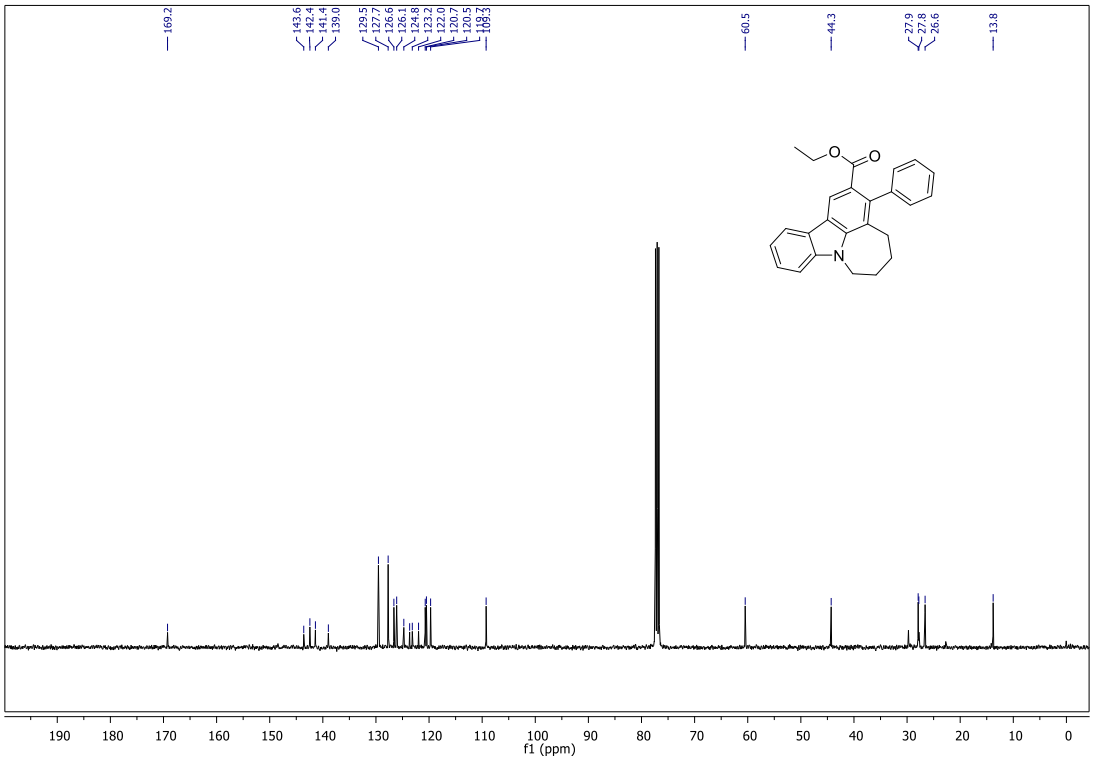
^{1}H NMR of compound **2t** in $CDCl_3$ (500 MHz)



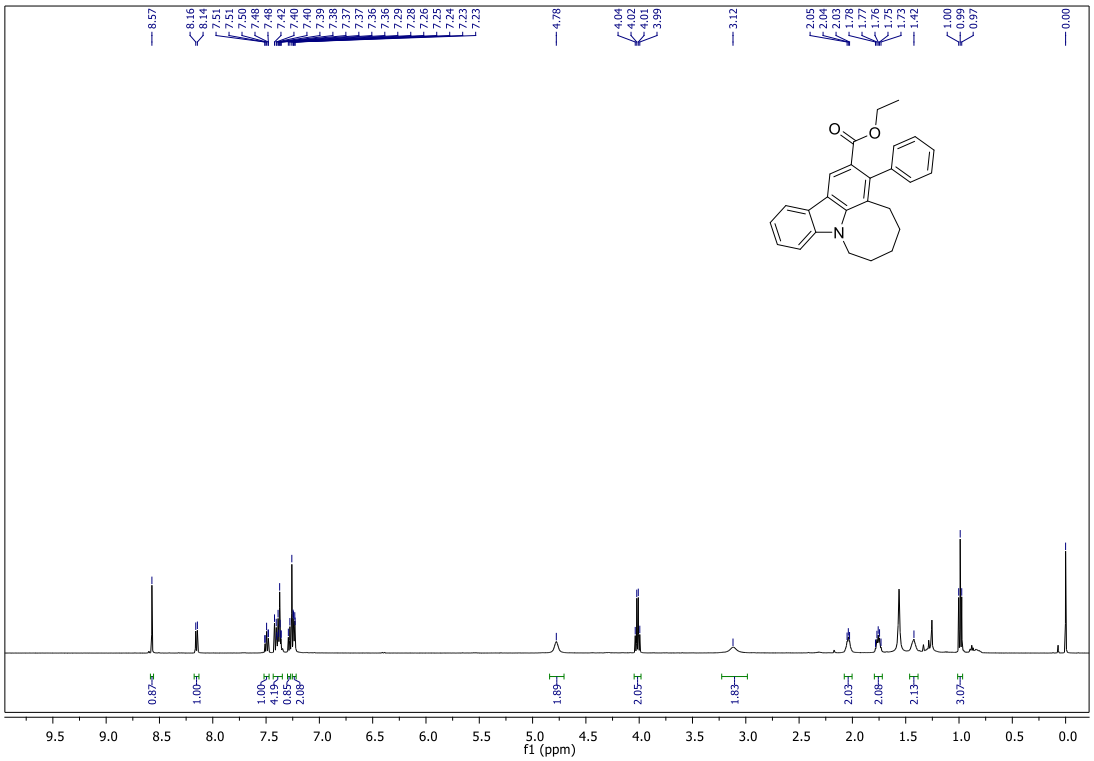
^{13}C NMR of compound **2t** in $CDCl_3$ (101 MHz)



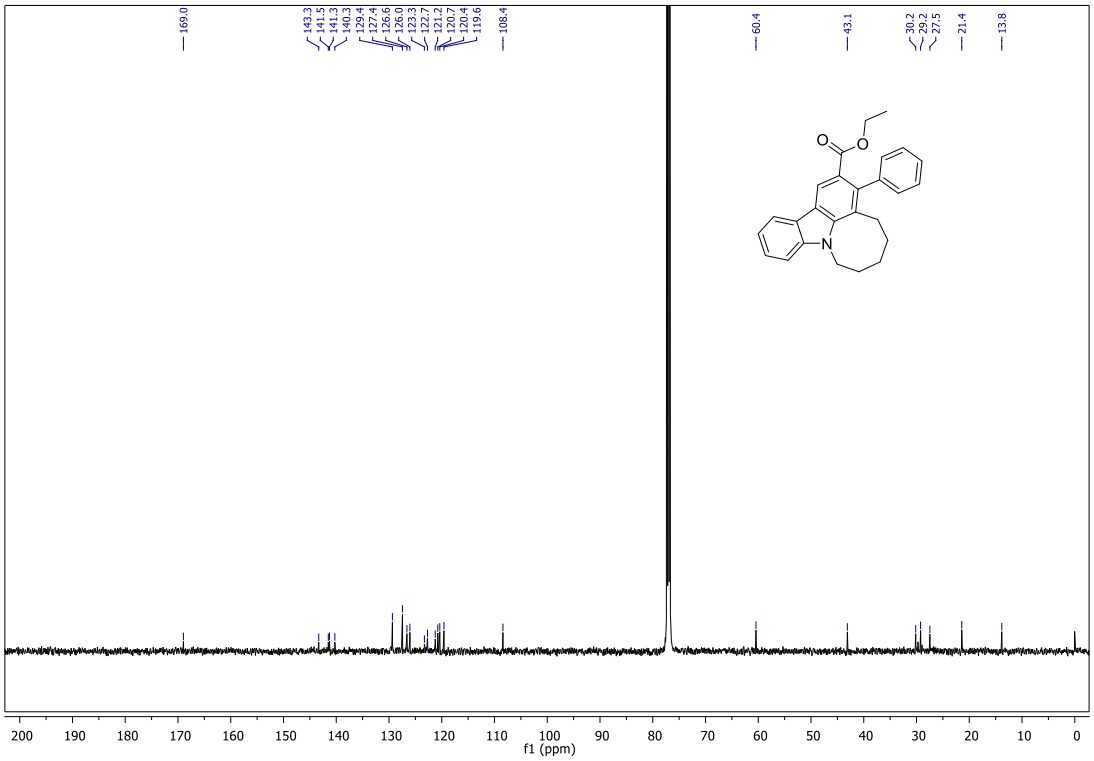
^{1}H NMR of compound **2u** in $CDCl_3$ (400 MHz)



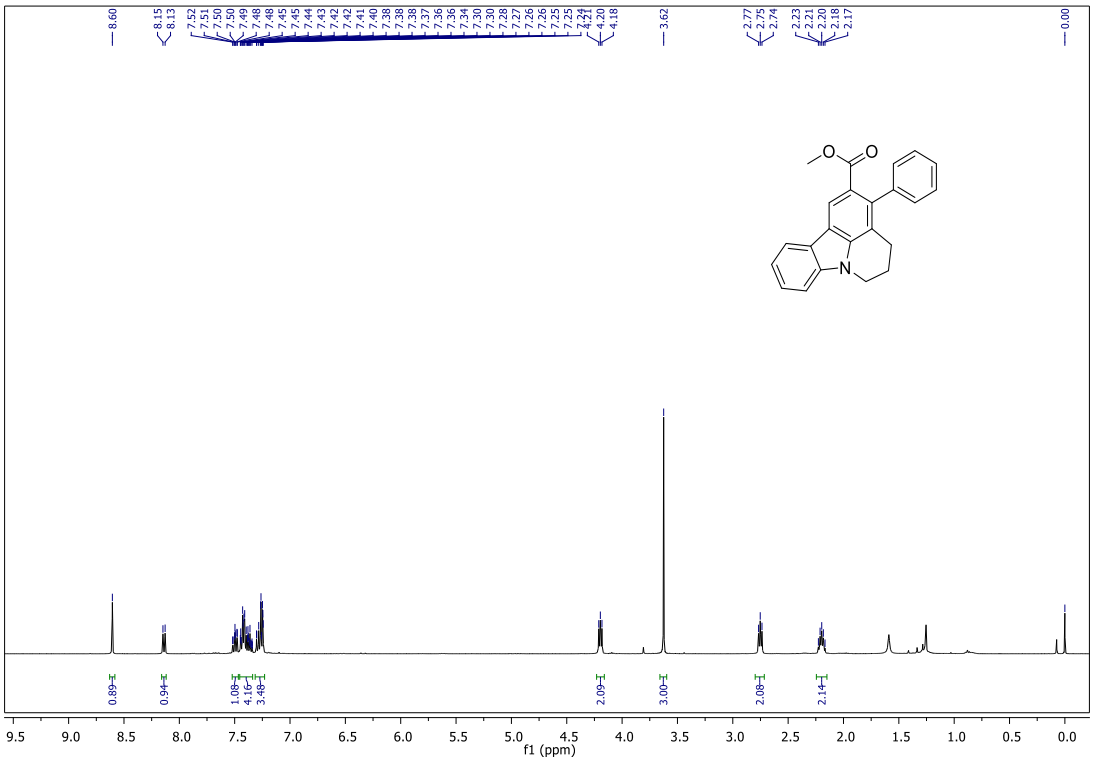
^{13}C NMR of compound **2u** in $CDCl_3$ (101 MHz)



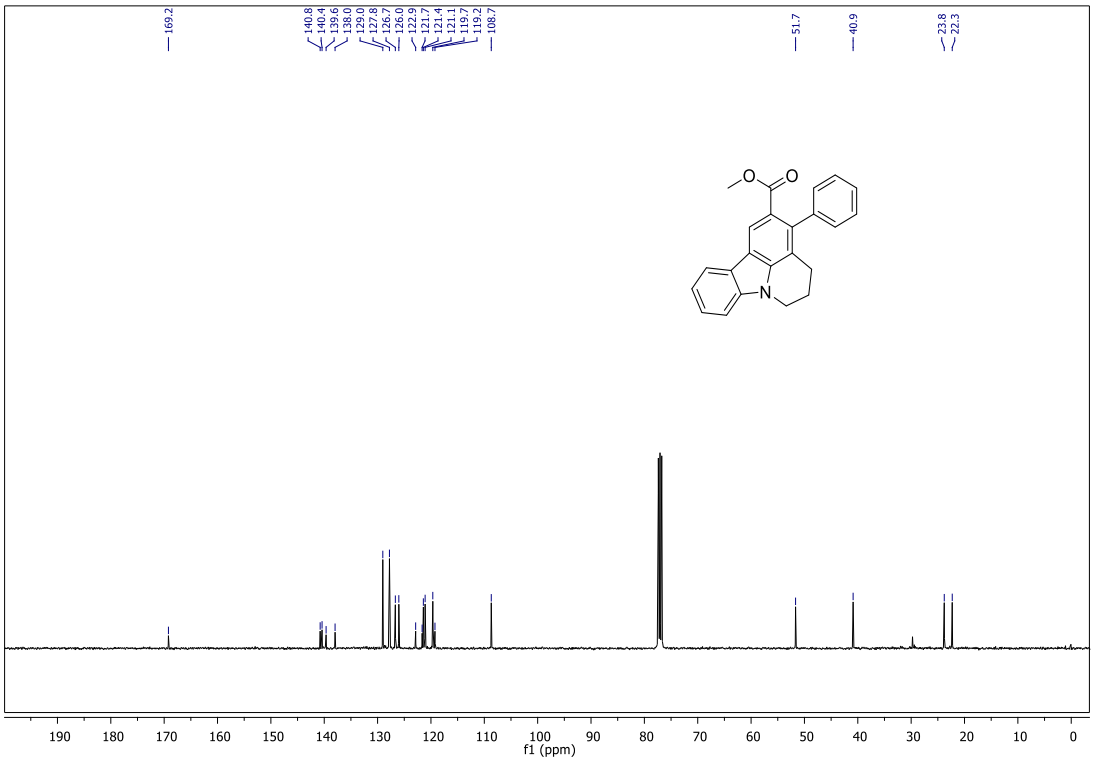
^{1}H NMR of compound **2v** in $CDCl_3$ (500 MHz)



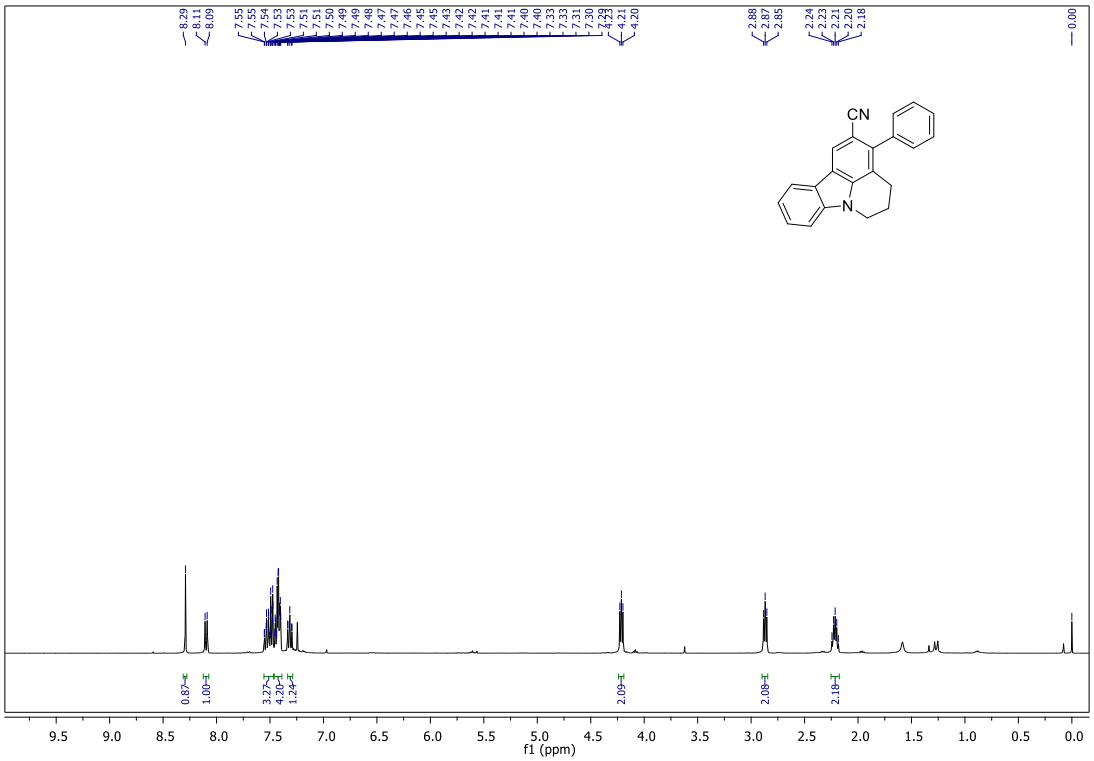
^{13}C NMR of compound **2v** in $CDCl_3$ (126 MHz)



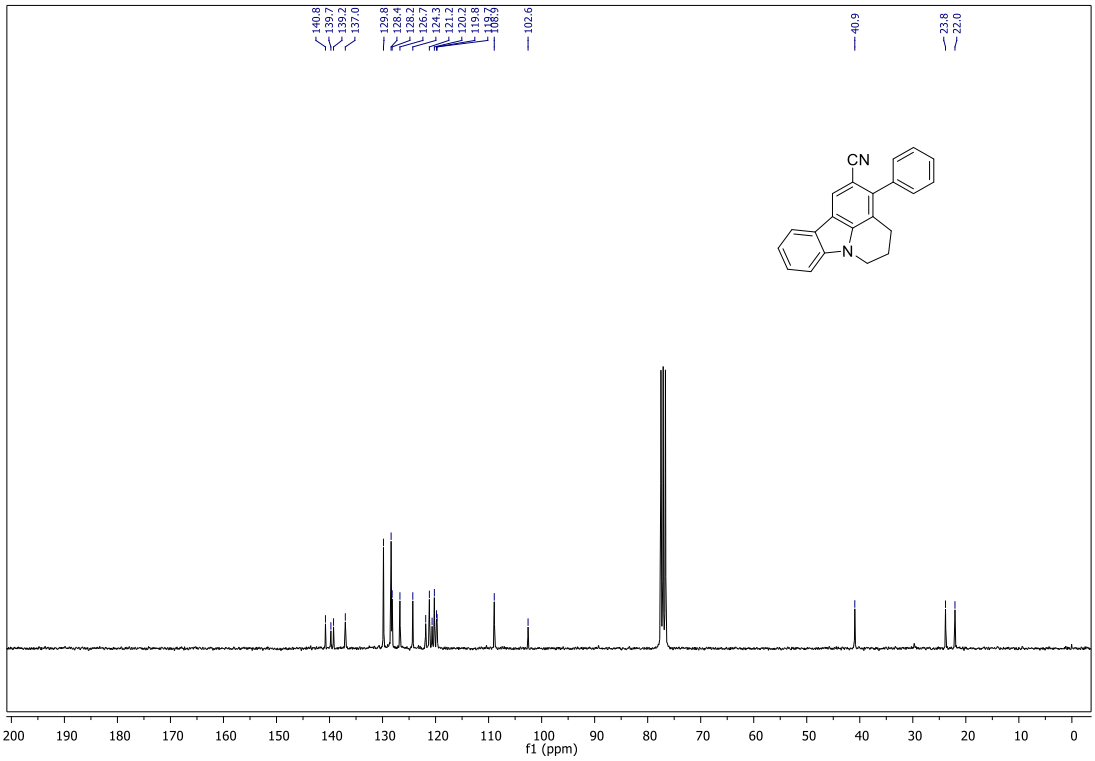
^{1}H NMR of compound **2w** in $CDCl_3$ (400 MHz)



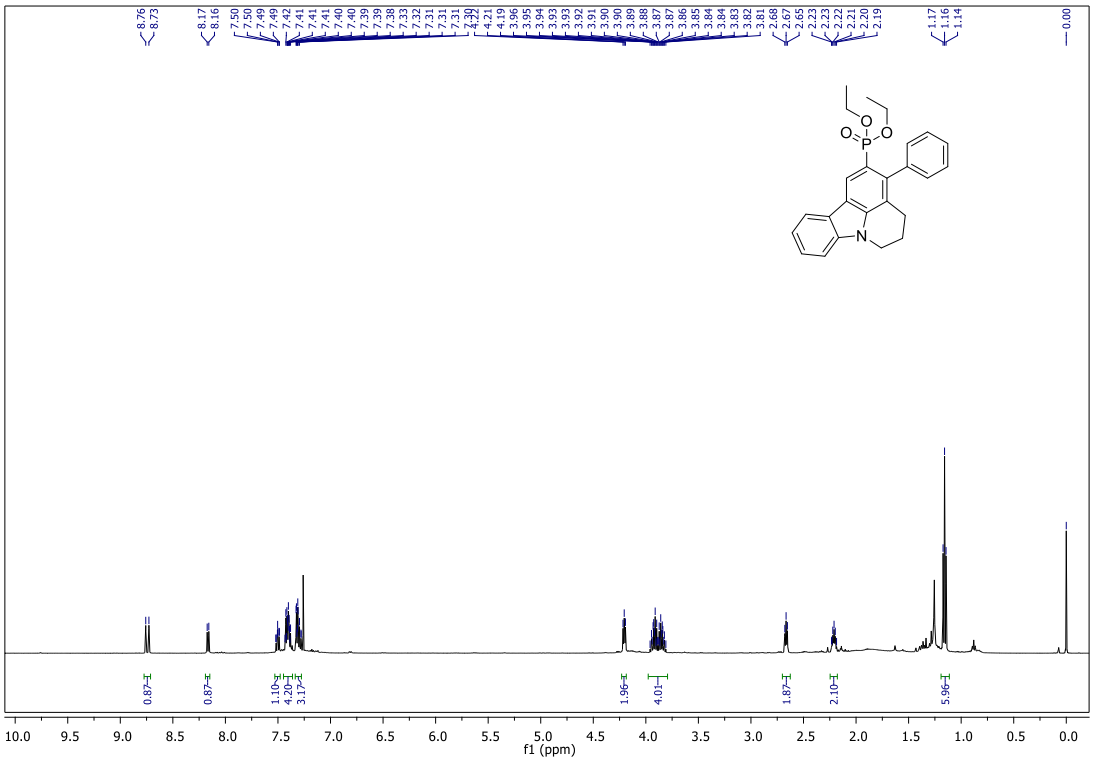
^{13}C NMR of compound **2w** in $CDCl_3$ (101 MHz)



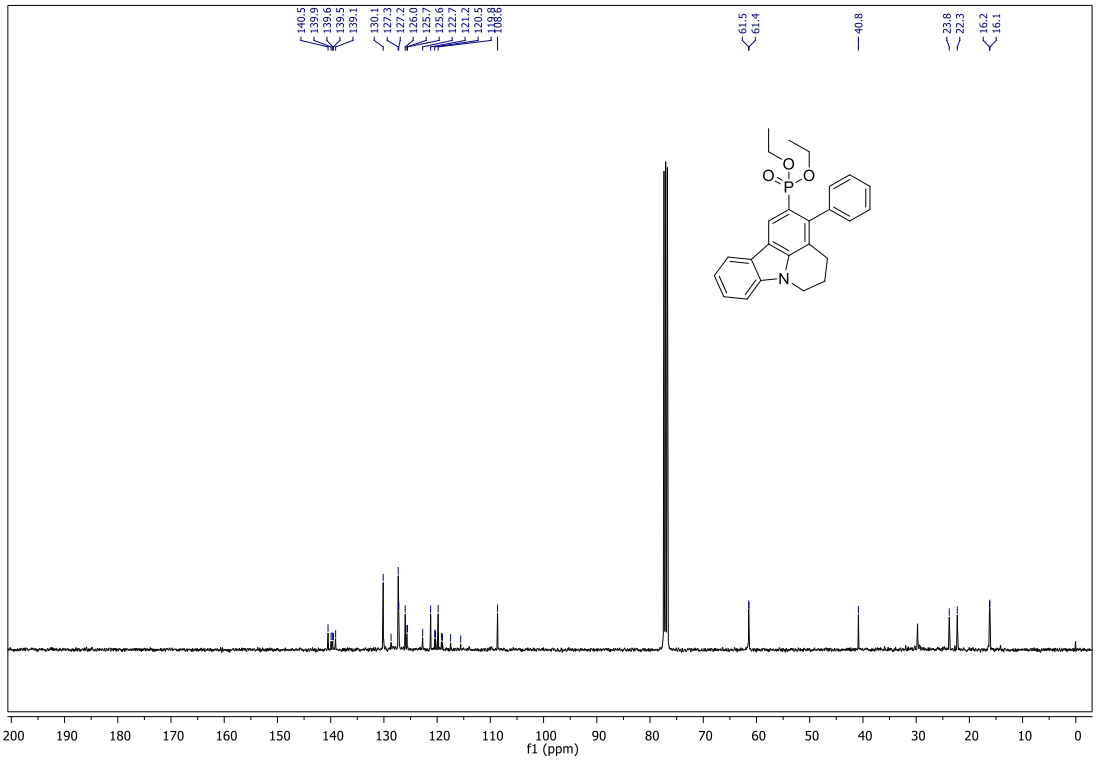
^{1}H NMR of compound **2x** in $CDCl_3$ (400 MHz)



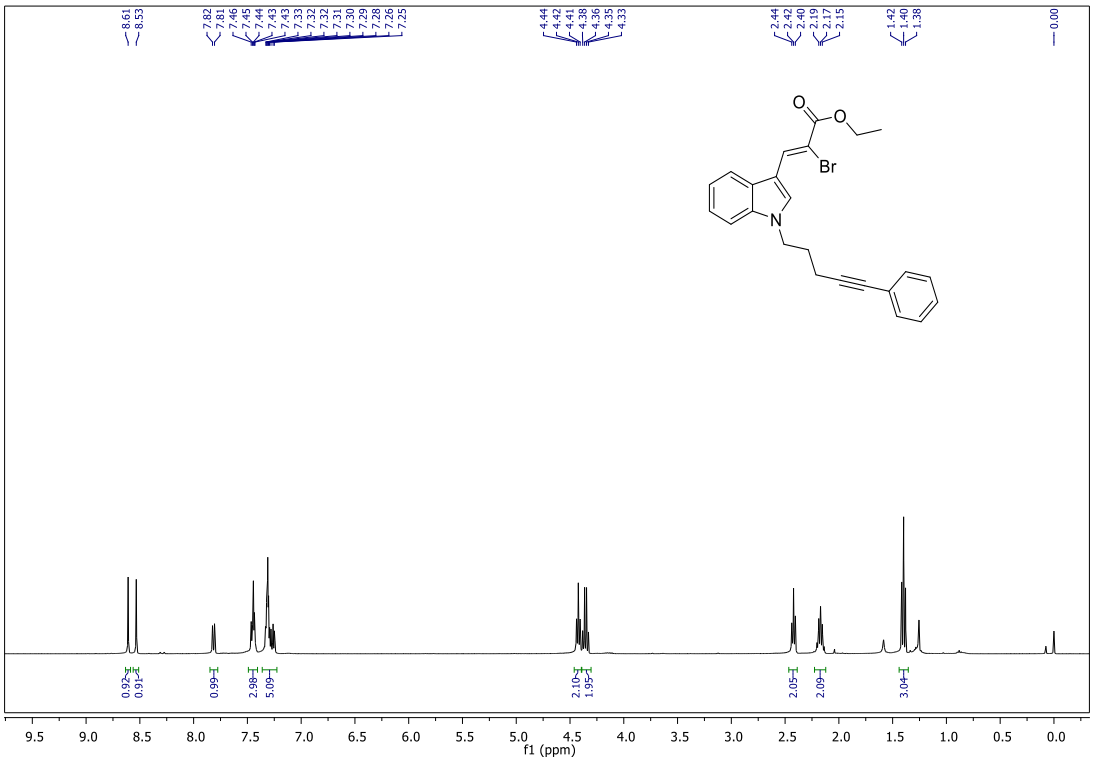
^{13}C NMR of compound **2x** in $CDCl_3$ (75 MHz)



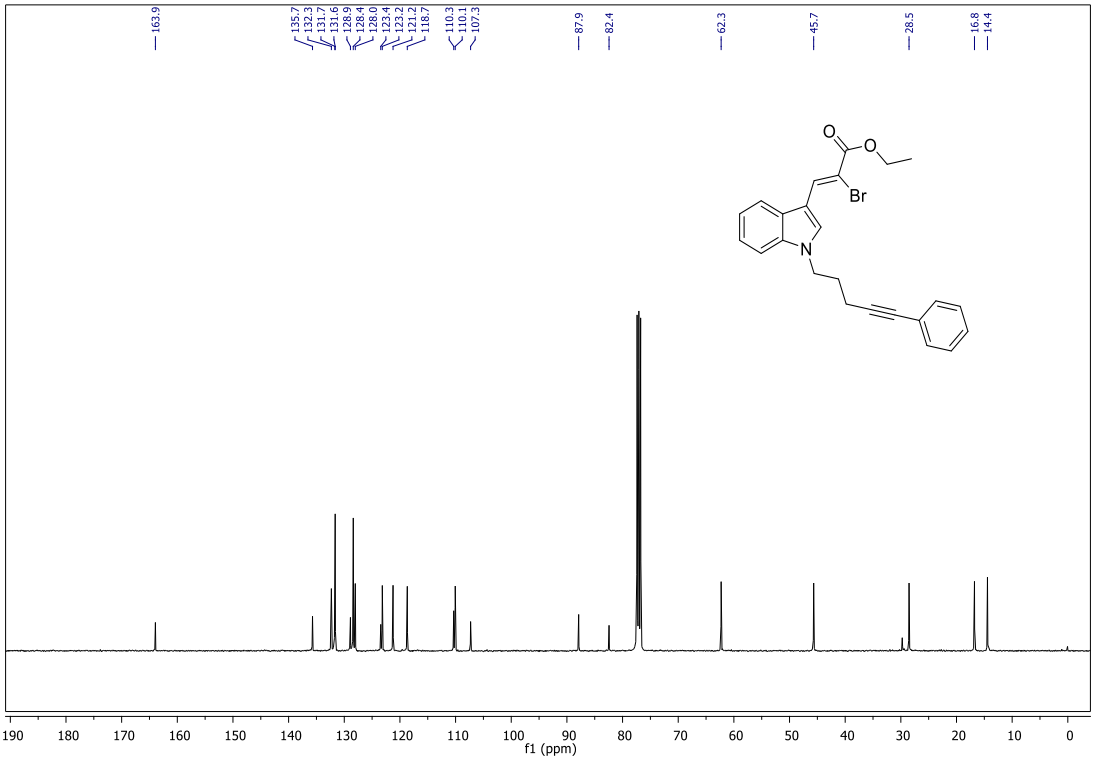
^{1}H NMR of compound **2y** in $CDCl_3$ (500 MHz)



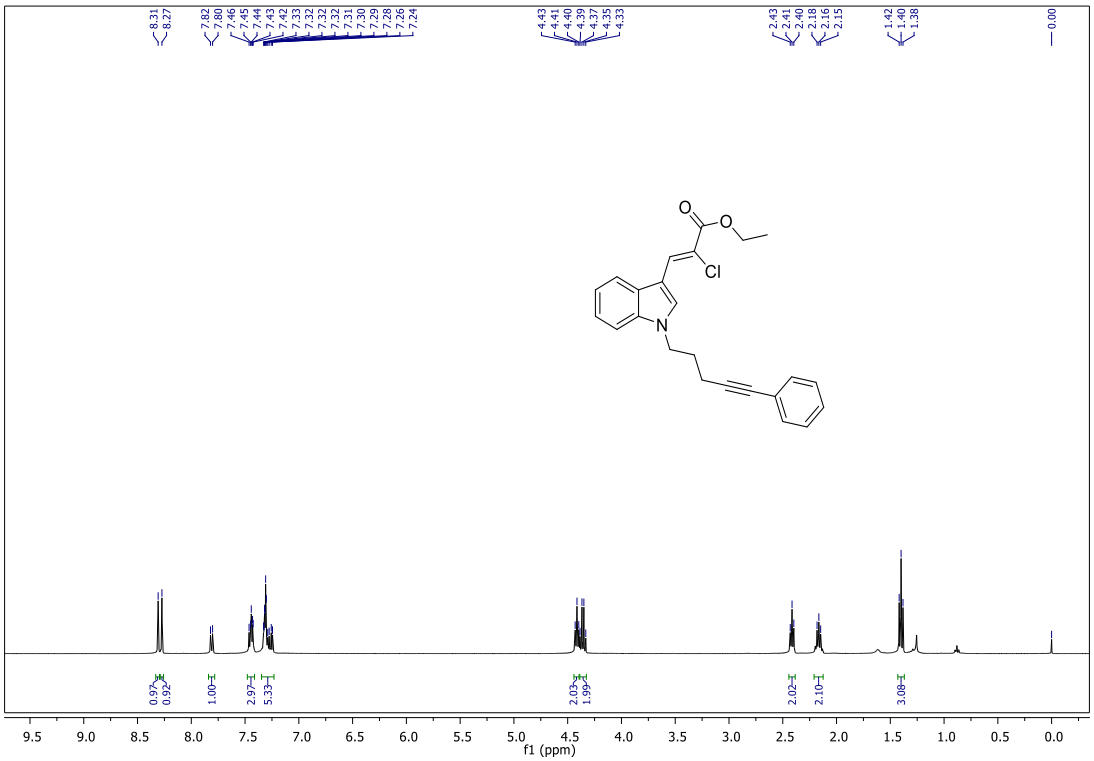
^{13}C NMR of compound **2y** in $CDCl_3$ (101 MHz)



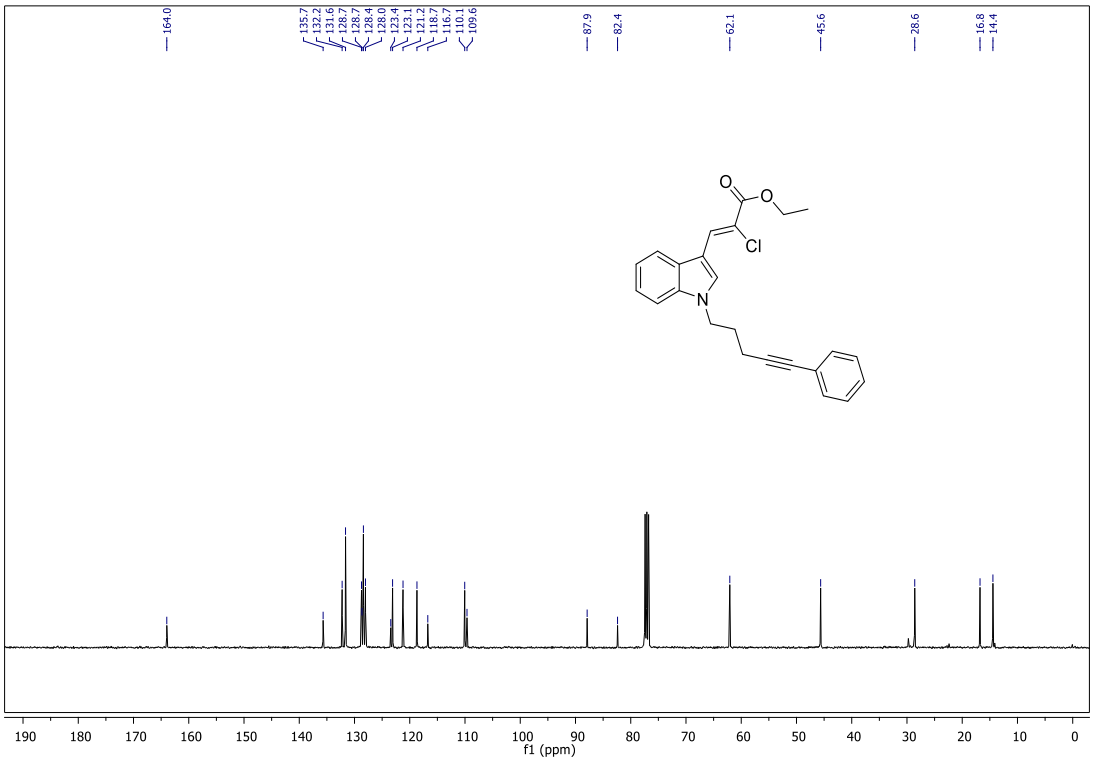
^{1}H NMR of compound **3a** in $CDCl_3$ (400 MHz)



^{13}C NMR of compound **3a** in $CDCl_3$ (101 MHz)



^{1}H NMR of compound **3b** in $CDCl_3$ (400 MHz)



^{13}C NMR of compound **3b** in $CDCl_3$ (101 MHz)