Enantioselective synthesis of 3-hydroxy- and 3-amino-3-alkynyl-2-oxindoles by dimethylzinc-mediated addition of terminal alkynes to isatins and isatin-derived ketimines

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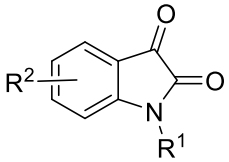
1. General experimental procedures

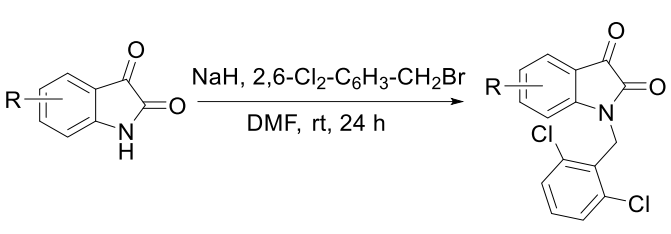
All reactions were carried out in anhydrous solvents under nitrogen atmosphere in dried glassware by means of Schlenk techniques. ^{1}H NMR (400 or 500 MHz) and ^{13}C NMR (100 or 126 MHz) spectra were recorded in $CDCl_3$ or DMSO-d_6. Chemical shifts for protons are reported in ppm from tetramethylsilane with the residual $CHCl_3$ or DMSO-d_6 resonance as internal reference. Chemical shifts for carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants in Hertz, and integration. Specific rotations were measured using a 5 mL cell with a 1 dm path length, and a sodium lamp, and concentration is given in g per 100 mL High resolution mass spectrometry analysis (HRMS) was performed by a quadrupole spectrometer with TOF analyzer Flash chromatography was carried out using silica gel (230–240 mesh). TLC analysis was performed on glass-backed plates coated with silica gel 60 and an F254 indicator and visualized by either UV irradiation or by staining with I_2 or phosphomolybdic acid solution. Chemical yields refer to pure isolated substances. Chiral HPLC analysis was performed using a Phenomenex Lux Cellulose-1, Phenomenex Lux Cellulose-2, Phenomenex Lux i-Amylose-1, Phenomenex Lux i-Amylose-2, Phenomenex Lux i-Amylose-3, Chiralpak AD-H or Chiralpak AS-H columns. UV detection was monitored at 210, 220 or 254 nm. Dimethylzinc (1.2 M solution in toluene) was purchased from Acros Organics.

2. Synthesis and Characterization Data of N-substituted Isatins.



1a, R^1 = Me, R^2 = H
1b, R^1 = Bn, R^2 = H
1c, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 = H
1d, R^1 = CPh_3, R^2 = H
1e, R^1 = Ac, R^2 = H
1f, R^1 =Ts, R^2 = H
1g, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 = 5-F
1h, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 = 5-Cl
1i, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 = 5-Br
1j, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 = 5-Me
1k, R^1 =2,6-Cl_2-C_6H_3-CH_2, R^2 = 5-OMe
1l, R^1 =2,6-Cl_2-C_6H_3-CH_2, R^2 = 5-NO_2
1m, R^1 =2,6-Cl_2-C_6H_3-CH_2, R^2 = 7-Me
1n, R^1 = MOM, R^2 = H
1o, R^1 = H, R^2 = H

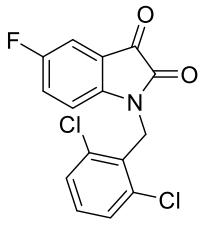
Isatins **1a**,[1] **1b**,[2] **1c**,[3] **1d**[4], **1e**[5], **1f**[6] and **1n**[7] were synthesized following described procedures and characterization data were in concordance to those reported in the literature.



1g, R = 5-F
1h, R = 5-Cl
1i, R = 5-Br
1j, R = 5-Me
1k, R^1 = 5-OMe
1l, R = 5-NO_2
1m, R = 7-Me

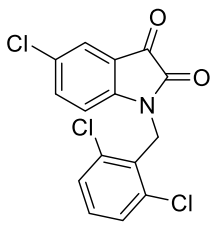
To a suspension of NaH (60% in mineral oil, 5.1 mmol, 204 mg) in anhydrous DMF (10 mL) at 0°C was added the N-unprotected isatin (3.4 mmol) and the mixture was stirred at 0°C for 15 min. Then, 2,6-dichlorobenzyl bromide (1.2 mmol, 1,32 g) was added and the reaction was stirred at rt for 24 h. Ice water was added to the mixture until precipitation of the N-protected isatin. The precipitate was filtrated and washed with water and the solid was recrystallized from ethyl acetate to afford the pure product.

5-Fluoro-1-(2,6-dichlorobenzyl)indoline-2,3-dione (1g). This compound was obtained from the



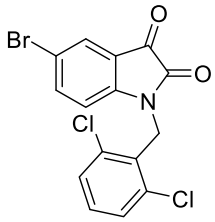
N-unprotected isatin (3.4 mmol, 560 mg). Red solid, yield: 951 mg, 82%; m.p. 170-171 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.24 (s, 2H), 6.69 (dd, *J* = 8.7, 3.6 Hz, 1H), 7.16 (m, 1H), 7.26 (m, 1H), 7.30 (dd, *J* = 6.5, 2.7 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.2, 112.3 (d, *J* = 7.1 Hz), 112.4 (d, *J* =24.3 Hz) , 118.6 (d, *J* = 7.1 Hz), 124.7(d, *J* =24.1 Hz), 128.8, 129.2, 130.4, 136.3, 146.5(d, *J* = 2.1Hz), 157.6, 159.2 (d, *J* = 246 Hz), 182.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ -118.1. IR (neat) ν 1730, 1616, 1482, 1432, 764 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_9Cl_2FNO_2$ $[M+H]^+$ 323.9989, found 323.9999.

5-Chloro-1-(2,6-dichlorobenzyl)indoline-2,3-dione (1h). This compound was obtained from the



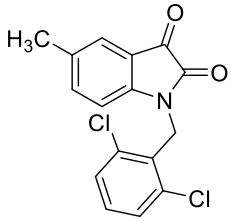
N-unprotected isatin (4.0 mmol, 725 mg). Orange solid, yield: 612 mg, 45%; m.p. 225-227 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.24 (s, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.40 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.28, 112.4, 118.7, 125.2, 128.7, 129.1, 129.5, 130.4, 136.2, 137.6, 148.6, 157.7, 181.8; IR (neat) ν 1733, 1613, 1428, 1324, 778, 721 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{15}H_9Cl_3NO_2$ $[M+H]^+$ 339.9693, found 339.9702.

5-Bromo-1-(2,6-dichlorobenzyl)indoline-2,3-dione (1i). This compound was obtained from the



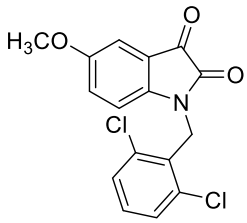
N-unprotected isatin (3.4 mmol, 768 mg). Orange solid, yield: 550 mg, 42%; m.p. 210-212 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.11 (s, 2H), 6.94 (d, *J* = 8.5 Hz, 1H), 7.41 (m, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 2.1 Hz, 1H), 7.89 (dd, *J* = 8.5, 2.1 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 113.4, 115.6, 119.8, 127.4, 129.5, 130.0, 131.2, 135.8, 140.6, 150.0, 157.8, 181.9; IR (neat) ν 1733, 1599, 1425, 778 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_9BrCl_2NO_2$ $[M+H]^+$ 383.9188, found 383.9195.

1-(2,6-Dichlorobenzyl)-5-methylindoline-2,3-dione (1j). This compound was obtained from the



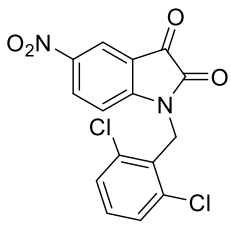
N-unprotected isatin (3.5 mmol, 565 mg). Red solid, yield: 763 mg, 68%; m.p. 179-182 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.27 (s, 3H), 5.21 (s, 2H), 6.61 (d, *J* = 8.1 Hz, 1H), 7.22-7.26 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.5, 40.1, 110.9, 117.9, 125.6, 129.0, 129.2, 130.1, 133.4, 136.3, 138.7, 148.2, 157.9, 183.1; IR (neat) ν 1737, 1623, 1495, 1435, 1328, 781 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{12}Cl_2NO_2$ $[M+H]^+$ 320.0240, found 320.0249.

1-(2,6-Dichlorobenzyl)-5-methoxyindoline-2,3-dione (1k). This compound was obtained from



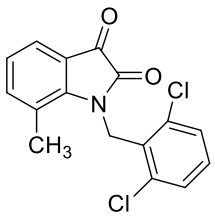
the N-unprotected isatin (3.4 mmol,550 mg). Brown solid, yield: 580 mg, 53%; m.p. 154-156 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 3H), 5.20 (s, 2H), 6.63 (d, *J* = 8.7 Hz, 1H), 6.98 (dd, *J* = 8.7, 2.8 Hz, 1H), 7.12 (d, *J* = 2.8 Hz, 1H), 7.24 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.1, 55.8, 109.5, 112.1, 118.3, 124.6, 129.1, 129.2, 130.2, 136.3, 144.3, 156.2, 157.9, 183.2; IR (neat) ν 1733, 1482, 1435, 1281, 1016, 791, 761 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{12}Cl_2NO_3$ $[M+H]^+$ 336.0189, found 336.0202.

1-(2,6-Dichlorobenzyl)-5-nitroindoline-2,3-dione (1l). This compound was obtained from the N-



unprotected isatin (4,0 mmol, 765 mg). Yellow solid, yield: 615 mg, 44%; m.p. 215-216 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (s, 2H), 6.89 (d, *J* = 8.8 Hz, 1H), 7.30 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 8.39 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.46 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.6, 111.3, 117.9, 120.8, 128.1, 129.3, 130.8, 133.5, 136.2, 144.0, 154.4, 157.3, 180.7; IR (neat) ν 1753, 1613, 1334, 1314, 1271, 795 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_9Cl_2N_2O_4$ $[M+H]^+$ 350.9934, found 350.9935.

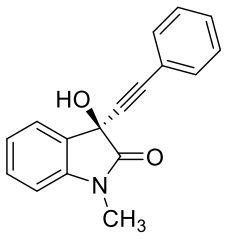
1-(2,6-Dichlorobenzyl)-7-methylindoline-2,3-dione (1m). This compound was obtained from the N-unprotected isatin (6.8 mmol,1.10 g). Red-orange solid, yield: 1,42 g, 65%; m.p. 209-211 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.39 (s, 3H), 5.42 (s, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.29-7.31 (m, 3H), 7.50 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.1, 43.2, 119.1, 121.8, 123.6, 123.8, 129.1, 129.4, 130.7, 135.4, 142.4, 149.2, 159.5, 183.1; IR (neat) ν 1727, 1593, 1435, 1321, 1244, 1043, 788, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{12}Cl_2NO_2$ $[M+H]^+$ 320.0240, found 320.0249.



3. General Procedure for the Catalytic Enantioselective Alkynylation of Isatins 1a-m and Characterization Data of Compounds 2a-f, 3a-p, 4a-k and 5a-b.

To a solution 1.2 M of $ZnMe_2$ in toluene (0.33 mL, 0.4 mmol) under nitrogen atmosphere was added the corresponding alkyne (0.4 mmol) and the mixture was stirred for 35 min at room temperature. Then, a solution 0.1 M of ligand **L2** in toluene (0.2 mL, 0.02 mmol) was added and the mixture was stirred at room temperature for 25 min whereupon the mixture was cooled to -20 °C. A solution of the isatin **1a-m** (0.1 mmol) in anhydrous CH_2Cl_2 (1.5 mL) was finally added dropwise. After stirring at -20 °C for 22 h, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl, diluted with CH_2Cl_2 and directly dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using mixtures of ethyl acetate-hexanes as eluent.

(*R*)-3-hydroxy-1-methyl-3-(phenylethynyl)indolin-2-one (2a). This compound was obtained from the isatin **1a** (0.12 mmol, 20 mg). White solid, yield: 24 mg, 72%; m.p. 141-143 ºC; $[\alpha]_D^{25}$ = -6.6 (*c* 0.3, CH_2Cl_2, 88% ee); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.25 (s, 3H), 3.53 (s, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 7.17 (td, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H), 7.26-7.33 (m, 3H), 7.39 (td, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.43-7.45 (m, 2H), 7.61 (ddd, J_1 = 7.4 Hz, J_2 = 1.3 Hz, J_3 = 0.6 Hz, 1H).;^{13}C-NMR (126 MHz, $CDCl_3$) δ 26.6, 69.5, 85.5, 86.3, 108.9, 121.6, 123.8, 124.7, 128.2, 128.9, 129.0, 130.5, 132.1, 143.1, 173.9; IR (neat) ν 3347, 2925, 2224, 1698, 1092, 756, 691 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{13}NO_2$ $[M+H]^+$ 264.1019, found 264.1025; HPLC (Chiralpak AS-H, hexane:isopropanol = 95:5 , 1 mL min^{-1}, λ = 254 nm): t_R (major) = 23.1 min, t_R (minor) = 29.5 min.

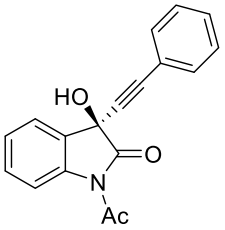


(*R*)-1-benzyl-3-hydroxy-3-(phenylethynyl)indolin-2-one (2b). This compound was obtained from the isatin **1b** (0.10 mmol, 24 mg).White solid, yield: 23 mg, 68%; m.p**.** 131-133 °C; $[\alpha]_D^{25}$ = -9.1 (*c* 0.3, CH_2Cl_2, 66% ee); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.69 (s, 1H), 4.93 (s, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 7.12 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 7.23-7.375 (m, 9H), 7.45-7.47 (m, 2H), 7.62 (d, *J* = 7.4 Hz, 1H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 44.1, 69.6, 85.4, 86.6, 109.9, 123.8, 124.8, 127.2, 127.8, 128.2, 128.9, 129.0, 130.4, 132.1, 135.0, 142.2, 174.1; IR (neat) ν 3310, 2925, 2218, 1709, 1171, 749, 691 cm^{-1}. HRMS (ESI-TOF) calcd for $C_{23}H_7NO_2$ $[M+H]^+$ 340.1332, found 340.1344; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 10.9 min, t_R (minor) = 15.2 min.

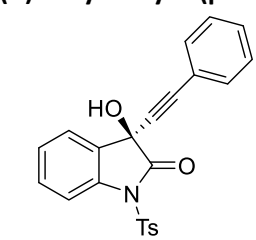
(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(phenylethynyl)indolin-2-one (2c). This compound was obtained from the isatin **1c** (0.10 mmol, 31 mg). White solid, yield: 32 mg, 78%; m.p. 162-164 °C; $[\alpha]_D^{25}$ = -107.4 (*c* 0.4, CH_2Cl_2, 92% ee). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.40 (s, 1H), 5.18 (d, 1H, *J* = 15.2 Hz), 5.33 (d, *J* = 15.3 H, 1H z), 6.69 (d, *J* = 7.9 Hz, 1H), 7.08 (td, *J* = 7.6, 1.0 Hz, 1H), 7.18-7.23 (m, 2H), 7.27-7.32 (m, 3H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.42-7.44 (m, 2H), 7.58 (ddd, *J* = 7.5 Hz, *J* = 1.3 Hz, *J* = 0.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.4, 69.4, 85.6, 86.4, 109.9, 121.7, 123.6, 124.7, 128.2, 128.8, 128.9, 129.0, 129.8, 130.0, 130.4, 132.0, 136.4, 141.8, 173.3; IR (neat) ν 3383, 2925, 2218, 1716, 1489, 1168, 976, 749 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{15}Cl_2NO_2$ $[M+H]^+$: 408.0553, found: 408.0564. HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 12.1 min, t_R (minor) = 15.1 min

(*R*)-3-hydroxy-3-(phenylethynyl)-1-tritylindolin-2-one (2d). This compound was obtained from the isatin **1d** (0.10 mmol, 40 mg). White solid, yield: 34 mg, 67%; m.p. 92-94 °C; $[\alpha]_D^{25}$ = +12.9 (*c* 0.3, CH_2Cl_2, 84% ee);. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.37 (s, 1H), 6.29 (d, *J* = 8.1 Hz, 1H), 6.95 (t, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 7.5 H, 1 H z), 7.20-7.36 (m, 12H), 7.47-7.50 (m, 8H), 7.55 (d, *J* = 7.5 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 69.7, 74.3, 85.9, 86.2, 116.2, 121.8, 123.1, 123.9, 127.1, 127.8, 128.3, 128.8, 128.9, 129.0, 129.2, 132.1, 141.6, 142.7, 175.6; IR (neat) ν 3387, 2925, 2221, 1723, 1468, 742, 699 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{35}H_{25}NO_2$ $[M+H]^+$: 492.1958, found: 492.1964. HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30 , 1 mL min^{-1}, λ = 254 nm): t_R (major) = 5.4 min, t_R (minor) = 17.1 min.

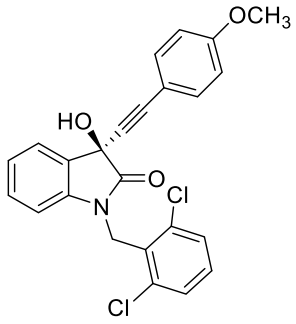
(*R*)-1-acetyl-3-hydroxy-3-(phenylethynyl)indolin-2-one (2e). This compound was obtained from the isatin **1e** (0.11 mmol, 21 mg). White solid, yield: 22 mg, 68%; m.p. 104-106 °C; $[\alpha]_D^{25}$ = +5.1 (*c* 0.4, CH_2Cl_2, 86% ee); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.72 (s, 3H), 3.47 (s, 1H), 7.28-7.37 (m, 4H), 7.42-7.45 (m, 3H), 7.66 (d, *J* = 7.5 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 26.5, 69.7, 84.7, 87.9, 117.1, 121.0, 124.6, 126.2, 127.8, 128.3, 129.4, 130.9, 132.0, 139.6, 170.5, 174.3; IR (neat) ν 3401, 2932, 2232, 1756, 1716, 1261, 753 cm^{-1}; HRMS (MALDI-TOF) calcd for $C_{18}H_{13}NO_3$ $[M+Na]^+$ 314.0788, found: 314.0802; HPLC (Chiralpak AS-H, hexane:isopropanol = 90:10 , 1 mL min^{-1}, λ = 254 nm): t_R (major) = 10.2 min, t_R (minor) = 13.1 min.



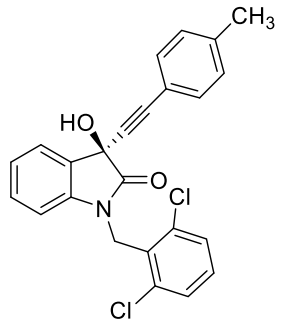
(*R*)-3-hydroxy-3-(phenylethynyl)-1-tosylindolin-2-one (2f). This compound was obtained from the isatin **1e** (0.12 mmol, 35 mg). Colorless oil, yield: 24 mg, 52%. $[\alpha]_D^{25}$ = +35.0 (*c* 0.2, CH_2Cl_2, 66% ee); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.38 (s, 1H), 7.26-7.39 (m, 8H), 7.44 (td, *J* = 7.9 Hz, *J* = 1.5 Hz, 1H), 7.59 (dd, J_1 = 7.5, J_2 = 1.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 21.7, 69.4, 84.0, 87.9, 114.1, 125.1, 125.8, 127.7, 127.9, 128.3, 129.4, 129.9, 131.1, 132.0, 134.5, 138.5, 146.0, 171.9; IR (neat) ν 3462, 2921, 2225, 1770, 1081, 756, 565 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{17}NO_4S$ $[M+H]^+$ 404.0951, found: 404.0957; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30 , 1 mL min^{-1}, λ = 254 nm): t_R (major) = 12.2 min, t_R (minor) = 22.2 min



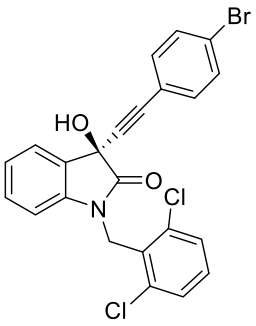
(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-((4-methoxyphenyl)ethynyl)indolin-2-one (3a). This compound was obtained from the isatin **1c** (0.11 mmol, 33 mg). White solid, yield: 32 mg, 67%; mg; m.p. 174-176 °C; $[\alpha]_D^{25}$ = -66.2 (*c* 0.2, CH_2Cl_2, 98% ee); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.52 (s, 1H), 3.79 (s, 3H), 5.17 (d, *J* = 15.3 Hz, 1H), 5.33 (d, *J* = 15.3 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 8.6 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.17-7.22 (m, 2H), 7.33-7.38 (m, 4H), 7.58 (d, *J* = 7.3 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.4, 55.2, 69.4, 84.4, 86.5, 109.9, 113.7, 113.9, 123.5, 124.7, 129.0, 129.8, 129.9, 130.3, 133.6, 136.4, 141.8, 160.1, 173.4; IR (neat) ν 3329, 2925, 2225, 1712, 1250, 976, 749 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{17}Cl_2NO_3$ $[M+H]^+$: 438.0658, found: 438.0670; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 13.5 min, t_R (minor) = 19.1 min.



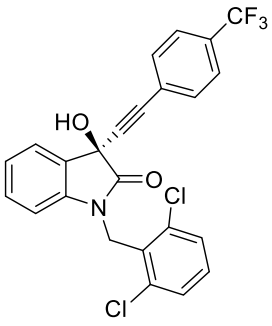
(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(p-tolylethynyl)indolin-2-one (3b). This compound was obtained from the isatin **1c** (0.11 mmol, 35 mg). White solid, yield: 32 mg, 67%.; m.p. 121-123 °C; $[\alpha]_D^{25}$ = -101.1 (*c* 0.4, CH_2Cl_2, 96% ee); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 6H), 3.49 (s, 1H), 5.17 (d, *J* = 15.3 Hz, 1H), 5.33 (d, *J* = 15.3 Hz, 1H), 6.68 (d, *J* = 7.8 H, 1H z), 7.06-7.09 (m, 3H), 7.17-7.21 (m, 2H), 7.33 (t, *J* = 8.2 Hz, 4H), 7.58 (d, *J* = 7.5 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.5, 40.4, 69.4, 85.0, 86.7, 109.8, 118.6, 123.5, 124.7, 129.0, 129.8, 129.9, 130.3, 131.9, 136.4, 139.1, 141.8, 173.4; IR (neat) ν 3350, 2924, 225, 1716, 976, 811, 749, 525 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{17}Cl_2NO_2$ $[M+H]^+$ 422.0709, found 422.0723; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 12.3 min, t_R (minor) = 18.1 min



(*R*)-3-((4-bromophenyl)ethynyl)-1-(2,6-dichlorobenzyl)-3-hydroxyindolin-2-one (3c). This compound was obtained from the isatin **1c** (0.11 mmol, 35 mg). White solid, yield: 41 mg, 74%; $[\alpha]_D^{25}$ = -97.2 (*c* 0.3, CH_2Cl_2, 96% ee); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.71 (s, 1H), 5.16 (d, *J* = 15.3 Hz, 1H), 5.32 (d, *J* = 15.2 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 7.08 (tt, J_1 = 7.6, J_2 = 0.9 Hz, 1H), 7.18-7.22 (m, 2H), 7.25-7.28 (m, 2H), 7.34 (d *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.57 (dd, J_1 = 7.4 Hz, J_2 = 1.3 Hz, 1H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 40.4, 69.4, 85.3, 86.8, 110.0, 120.6, 123.4, 123.6, 124.7, 128.6, 129.0, 129.7, 130.5, 131.5, 133.4, 136.4, 141.8, 173.2K IR (neat) ν 3322, 2221, 1709, 976, 749 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{14}BrCl_2NO_2$ $[M+H]^+$ 485.9658, found 485.9657; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 11.5 min, t_R (minor) = 23.2 min

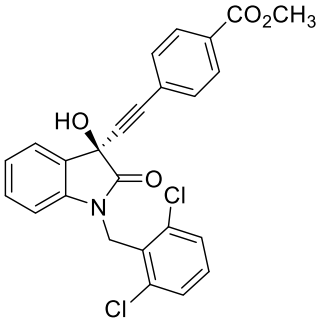


(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-((4-(trifluoromethyl)phenyl)ethynyl)indolin-2-one (3d). This compound was obtained from the isatin **1c** (0.11 mmol, 33 mg).White solid, yield: 37 mg 73%; m.p. 156-158 °C; $[\alpha]_D^{25}$ = -90.6 (*c* 0.5, CH_2Cl_2, 92% ee); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 1H), 5.18 (d, *J* = 15.2 Hz, 1H), 5.34 (d, *J* = 15.5 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.53 (s, 4H), 7.58 (d, *J* = 7.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 40.5, 69.3, 84.8, 88.1, 110.1, 123.7, 123.9 (q, *J* = 272.5 Hz), 124.7 , 125.2 (q, *J* = 3.8 Hz), 125.5 (q, *J* = 1.5 Hz), 128.4, 129.1, 129.6, 130.0, 130.6, 130.7 (q, *J* = 32.8 Hz), 132.2, 136.4, 141.8, 173.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0; IR (neat) ν 3343, 2921, 1724, 1324, 1063, 838, 743 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{14}Cl_2F_3NO_2$ $[M+H]^+$ 476.0426, found 476.0440; HPLC (Chiralpak



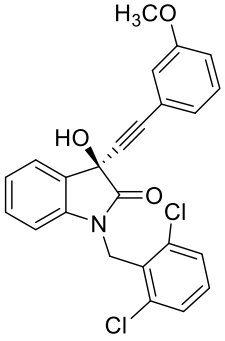
AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 8.6 min, t_R (minor) = 19.1 min

Methyl (*R*)-4-((1-(2,6-dichlorobenzyl)-3-hydroxy-2-oxoindolin-3-yl)ethynyl)benzoate (3e). This



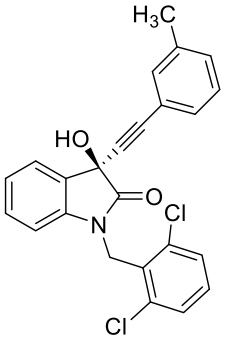
compound was obtained from the isatin **1c** (0.10 mmol, 32 mg). White solid, yield: 38 mg, 78%; m.p. 193-195 °C; $[\alpha]_D^{25}$ = -106.5 (*c* 0.5, CH_2Cl_2, 94% ee); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 1H), 3.91 (s, 3H), 5.17 (d, *J* = 15.1 Hz, 1H), 5.34 (d, *J* = 15.3 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.35 (dd, J_1 = 8.0 Hz, J_2 = 1.7 Hz, 2H), 7.47 (dd, J_1 = 8.1 Hz, J_2 = 1.6 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.94 (dd, J_1 = 8.1 Hz, J_2 = 1.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.5, 52.3, 69.4, 85.4, 88.5, 110.0, 123.6, 124.8, 126.3, 128.5, 129.1, 129.4, 129.7, 130.0, 130.1, 130.5, 131.9, 136.4, 141.8, 166.4 173.2; IR (neat) ν 3401, 3074, 2921, 1713, 1277, 10,51, 769, 751 cm^{-1}; L HRMS (ESI-TOF) calcd for $C_{25}H_{17}Cl_2NO_4$ $[M+H]^+$ 466.0607, found 466.0615; HPLC (Phenomenex Lux-Cellulose-1, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 10.4 min, t_R (minor) = 13.9 min.

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-((3-methoxyphenyl)ethynyl)indolin-2-one (3f). This



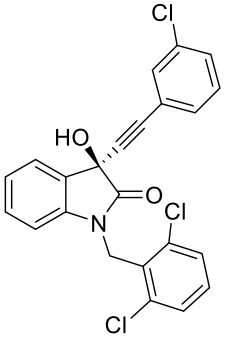
compound was obtained from the isatin **1c** (0.11 mmol, 35 mg). White solid, yield: 36 mg, 71%; m.p. 146-148 °C; $[\alpha]_D^{25}$ = -74.0 (*c* 0.25, CH_2Cl_2, 92% ee); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.54 (s, 1H), 3.77 (s, 3H), 5.17 (d, *J* = 15.2 Hz, 1H), 5.33 (d, *J* = 15.3 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.87 (ddd, J_1 = 8.4 Hz, J_2 = 2.6 Hz, J_3 = 0.9 Hz, 1H), 6.95 (dd, J_1 = 2.7, J_2 = 1.4 Hz, 1H), 7.02 (dt, J_1 = 7.6 Hz, J_2 = 1.3 Hz, 1H), 7.08 (td, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1H), 7.17-7.22 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.58 (dd, 1H, J_1 = 7.40 Hz, J_2 = 0.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.4, 55.3, 69.4, 85.4, 86.3, 109.9, 115.8, 116.6, 122.6, 123.6, 124.7, 128.8, 129.0, 129.3, 129.7, 130.0, 130.4, 136.4, 141.8, 159.2, 173.3; IR (neat) ν 3361, 2946, 1709, 1171, 980, 763 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{17}Cl_2NO_3$ $[M+H]^+$: 438.0658, found: 438.0653; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 11.8 min, t_R (minor) = 14.9 min.

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(m-tolylethynyl)indolin-2-one (3g). This compound was



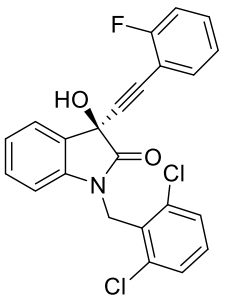
obtained from the isatin **1c** (0.11 mmol, 35 mg). White solid, yield: 37 mg, 77%; m.p. 99-101 °C; $[\alpha]_D^{25}$ = -116.7 (*c* 0.4, CH_2Cl_2, 98% ee); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.29 (s, 6H), 3.57 (s, 1H), 5.17 (d, *J* = 15.3 Hz, 1H), 5.33 (d, *J* = 15.3 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.11-7.26 (m, 6H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.1, 40.4, 69.4, 85.3, 86.6, 109.9, 121.5, 123.5, 124.7, 128.1, 128.9, 129.0, 129.1, 129.7, 129.8, 129.9, 130.4, 132.6, 136.4, 137.9, 141.8, 173.4; IR (neat) ν 3368, 2925, 2225, 1716, 1438, 980, 749, 688 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{17}Cl_2NO_2$ $[M+H]^+$ 422.0709, found 422.0717; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 19.3 min, t_R (minor) = 22.9 min.

(*R*)-3-((3-chlorophenyl)ethynyl)-1-(2,6-dichlorobenzyl)-3-hydroxyindolin-2-one (3h). This



compound was obtained from the isatin **1c** (0.10 mmol, 32 mg). White solid, yield: 37 mg, 80%; m.p. 198-200 °C.; $[\alpha]_D^{25}$ = -127.2 (*c* 0.4, CH_2Cl_2, 98% ee); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.50 (s, 1H), 5.17 (d, *J* = 15.3 Hz, 1H), 5.33 (d, *J* = 15.3 Hz, 1H), 6.70 (dt, J_1 = 7.9 Hz, J_2 = 0.8 Hz, 1H), 7.09 (td, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H), 7.19-7.24 (m, 3H), 7.28-7.33 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.40-7.43 (m, 1H), 7.57 (ddd, J_1 = 7.4 Hz, J_2 = 1.4 Hz, J_3 = 0.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.5, 69.3, 84.9, 86.9, 110.0, 123.4, 123.6, 124.7, 128.5, 129.1, 129.3, 129.5, 129.7, 130.0, 130.1, 130.6, 131.8, 134.1, 136.4, 141.8, 173.1; IR (neat) ν 3333, 1939, 1709, 976, 753 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{14}Cl_3NO_2$ $[M+H]^+$ 442.0163, found 442.0175; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min-1, λ = 254 nm): t_R (major) = 9.6 min, t_R (minor) = 12.0 min.

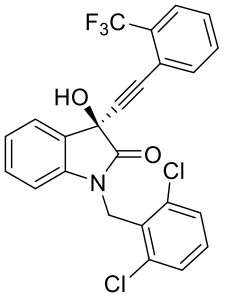
(*R*)-1-(2,6-dichlorobenzyl)-3-((2-fluorophenyl)ethynyl)-3-hydroxyindolin-2-one (3i). This



compound was obtained from the isatin **1c** (0.10 mmol, 30 mg). White solid, yield: 34 mg, 81%; m.p. 139-141 °C; $[\alpha]_D^{25}$ = -97.8 (*c* 0.3, CH_2Cl_2, 99% ee); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.69 (s, 1H), 5.17 (d, *J* = 15.3 Hz, 1H), 5.33 (d, *J* = 15.3 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 7.00-7.09 (m, 3H), 7.17-7.21 (m, 2H), 7.27-7.31 (m, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.41 (td, *J* = 7.3 Hz, *J* = 1.8 Hz, 1H), 7.59 (dd, J_1 = 7.5 Hz, J_2 = 1.3 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.4, 69.4, 79.9, 90.7, 109.9, 110.4 (d, *J* =15.5 Hz), 115.5 (d, *J* = 20.6 Hz), 123.6, 123.8 (d, *J* = 3.7 Hz), 124.8, 128.5, 129.0, 129.7, 130.0, 130.5, 130.7 (d, *J* = 7.9 Hz), 133.8, 136.4, 141.8, 162.9 (d, *J* = 253.3 Hz), 173.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ -108.9; IR (neat) ν 3333, 2928, 1712, 976, 753 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{14}Cl_2FNO_2$ $[M+H]^+$ 426.0458, found 426.0466; HPLC (Chiralpak

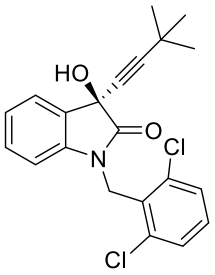
AD-H, hexane:isopropanol = 80:20, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 17.1 min, t_R (minor) = 20.4 min.

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-((2-(trifluoromethyl)phenyl)ethynyl)indolin-2-one (3j).



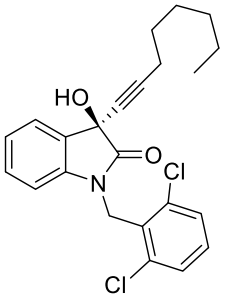
This compound was obtained from the isatin **1c** (0.12 mmol, 36 mg). White solid, yield: 41 mg, 74%; m.p. 151-153 °C; $[\alpha]_D^{25}$ = -86.7 (*c* 0.5, CH_2Cl_2, 98% ee); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 1H), 5.16 (d, *J* = 15.3 Hz, 1H), 5.31 (d, *J* = 15.3 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.33 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 2H), 7.38-7.46 (m, 2H), 7.57-7.62 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.5, 69.3, 82.2, 91.0, 109.9, 119.9 (q, *J* = 2.2 Hz), 123.2 (q, *J* = 273.6 Hz), 123.6, 124.9, 125.8 (q, *J* = 5.0 Hz), 128.3, 128.7, 129.0, 129.7, 129.9, 130.5, 131.3, 132.0 (q, *J* = 30.3 Hz), 134.34, 136.4, 141.8, 172.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.1; IR (neat) ν 3368, 1712, 1168, 1128, 763, 749 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{14}Cl_2F_3NO_2$ $[M+H]^+$ 476.0426, found 476.0415; HPLC (Chiralpak AD-H, hexane:isopropanol = 80:20, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 14.9 min, t_R (minor) = 20.4 min.

(*R*)-1-(2,6-dichlorobenzyl)-3-(3,3-dimethylbut-1-yn-1-yl)-3-hydroxyindolin-2-one (3k). This



compound was obtained from the isatin **1c** (0.11 mmol, 33 mg). White oil, yield: 16 mg, 38%; $[\alpha]_D^{25}$ = -88.1 (*c* 0.3, CH_2Cl_2, 84% ee); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 9H), 3.27 (s, 1H), 5.12 (d, *J* = 15.2 Hz, 1H), 5.31 (d, *J* = 15.2 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 7.18 (dt, J_1 = 15.5 Hz, J_3 = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.5, 30.6, 40.3, 68.9, 75.6, 95.8, 109.7, 123.4, 129.0, 129.4, 129.9, 130.0, 136.4, 141.7, 173.7; IR (neat) ν 3382, 2921, 1716, 988, 773, 747 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{19}Cl_2NO_2$ $[M+H]^+$ 388.0866, found 388.0880; HPLC (Phenomenex Lux-Cellulose-1, hexane:isopropanol = 90:10, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 9.0 min, t_R (minor)= 11.5 min.

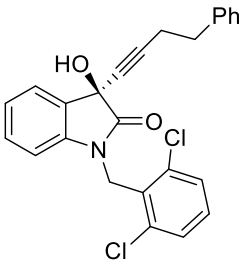
(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(oct-1-yn-1-yl)indolin-2-one (3l). This compound was



obtained from the isatin **1c** (0.11 mmol, 35 mg). Colorless oil, yield: 30 mg, 64%; $[\alpha]_D^{25}$ = -60.9 (*c* 0.3, CH_2Cl_2, 62% ee);^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.21-1.36 (m, 6H), 1.48 (quint, *J* = 7.0 Hz, 2H), 2.20 (t, *J* = 7.1 Hz, 2H), 3.31 (s, 1H), 5.14 (d, *J* = 14.7 Hz, 1H), 5.29 (d, *J* = 15.8 H, 1H z), 6.64 (d, *J* = 7.9 Hz, 1H), 7.04 (t, *J* = 7.6 H, 1H z), 7.14-7.21 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 1H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 14.0,

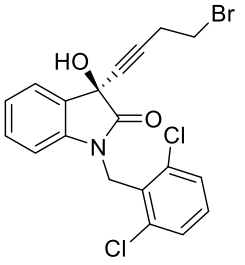
18.9, 22.5, 28.1, 28.5, 31.2, 67.0, 77.0, 88.1, 109.8, 123.4, 124.5, 129.0, 129.3, 129.8, 129.9, 130.1, 141.7, 173.6; IR (neat) ν 3383, 2928, 2236, 1716, 1467, 749 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{23}Cl_2NO_2$ $[M+H]^+$ 416.1179, found: 416.1191; HPLC (Chiralpak AD-H, hexane:isopropanol = 80:20, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 9.4, t_R (minor) = 12.0 min.

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(4-phenylbut-1-yn-1-yl)indolin-2-one (3m). This



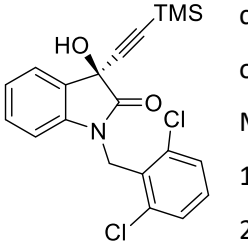
compound was obtained from the isatin **1c** (0.11 mmol, 35 mg). Colorless oil, yield: 33 mg , 66%; $[\alpha]_D^{25}$ = -30.0 (*c* 0.2, CH_2Cl_2, 64% ee). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.50 (t, *J* = 7.5 Hz, 2H), 2.80 (t *J* = 7.5 Hz, 2H,) 3.29 (s, 1H), 5.15 (d, *J* = 15.3 Hz, 1H), 5.27 (d, *J* = 15.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.15-7.20 (m, 5H), 7.23 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 1H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ 21.2, 34.6, 40.4, 69.0, 77.8, 87.2, 109.8, 123.4, 124.6, 126.3, 128.4, 128.5, 129.0, 129.1, 129.8, 129.9, 130.2, 136.4, 140.3, 141.7, 173.5; IR (neat) ν 3367, 2926, 2232, 1715, 1437, 750, 699 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{25}H_{19}Cl_2NO_2$ $[M+H]^+$ 436.0866, found 436.0877; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30 , 1 mL min^{-1}, λ = 254 nm): t_R (major) = 12.0 min, t_R (minor) = 17.2 min.

(*R*)-3-(4-bromobut-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-hydroxyindolin-2-one (3n). This



compound was obtained from the isatin **1c** (0.11 mmol, 34 mg). White solid, yield: 30 mg, 62%; m.p. 166-168 °C; $[\alpha]_D^{25}$ = -65.3 (*c* 0.2, CH_2Cl_2, 98% ee); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.79 (td, J_1 = 7.4 Hz, J_2 = 2.0 Hz, 2H), 3.40 (td, J_1 = 7.4 Hz, J_2 = 1.9 H, 2H z) 3.45 (s, 1H), 5.14 (d, *J* = 15.2 Hz, 1H), 5.29 (d, *J* = 15.2 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.16-7.23 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 23.3, 28.6, 40.4, 68.9, 79.1, 84.2, 109.9, 123.5, 124.6, 128.7, 129.0, 129.1, 129.7, 130.0, 130.4, 136.4, 141.8, 173.3; IR (neat) ν 3356, 2940, 2242, 1711, 1165, 753 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{14}BrCl_2NO_2$ $[M+H]^+$ 437.9658, found 437.9672; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30 , 1 mL min^{-1}, λ = 254 nm): t_R (major) = 10.1 min, t_R (minor) = 13.8 min.

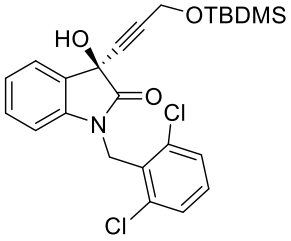
(*S*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-((trimethylsilyl)ethynyl)indolin-2-one (3o). This



compound was obtained from the isatin **1c** (0.12 mmol, 37 mg). Colorless oil, yield: 28 mg, 57%. $[\alpha]_D^{25}$ = -73.3 (*c* 0.4, CH_2Cl_2, 90% ee); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 9H), 3.28 (s, 1H), 5.13 (d, *J* = 15.2 Hz, 1H), 5.31 (d, *J* = 15.4 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.16-7.22 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ -0.4, 40.4, 69.2, 92.2, 101.1, 109.8, 123.5, 124.7, 128.6, 129.0, 129.7, 129.9, 130.4,

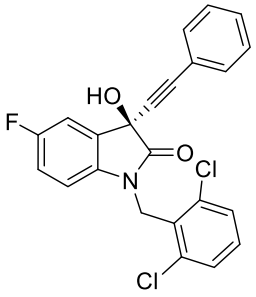
136.4, 141.9, 173.1; IR (neat) ν 3370, 2955, 2160, 1714, 981, 844, 753 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{19}Cl_2NO_2Si$ $[M+H]^+$ 404.0635, found 404.0636; HPLC (Phenomenex Lux-Cellulose-1, hexane:isopropanol = 95:5 , 1 mL min^{-1}, λ = 254 nm): t_R (major) = 12.1 min, t_R (minor) = 18.2 min.

(*R*)-3-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-hydroxyindolin-2-one (3p). This compound was obtained from the isatin **1c** (0.11 mmol, 33 mg).



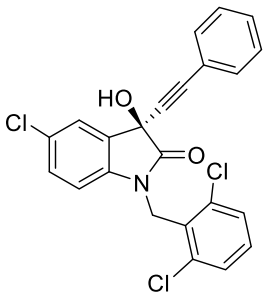
Yellowish oil, yield: 29 mg, 56%. $[\alpha]_D^{25}$ = -37.8 (*c* 0.5, CH_2Cl_2, 70% ee); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 6H), 0.86 (s, 9H), 3.42 (s, 1H), 5.14 (d, *J* = 15.2 Hz, 1H), 5.27 (d, *J* = 15.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.16-7.22 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 5.2, 18.2, 25.7, 40.4, 51.7, 68.9, 81.3, 85.5, 109.8, 123.4, 124.7, 128.5, 129.0, 129.7, 129.9, 130.4, 136.4, 141.8, 173.1; IR (neat) ν 3389, 2929, 1722, 1089, 996, 836, 778 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{27}Cl_2NO_3Si$ $[M+H]^+$ 476.1210, found 476.1187; HPLC (Phenomenex Lux-Cellulose-1, hexane:isopropanol = 90:10, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 11.8 min, t_R (minor) = 18.0 min.

(*R*)-1-(2,6-dichlorobenzyl)-5-fluoro-3-hydroxy-3-(phenylethynyl)indolin-2-one (4a). This compound was obtained from the isatin **1g** (0.10 mmol, 34 mg).



White solid, yield: 34 mg, 76%; m.p. 204-206 °C; $[\alpha]_D^{25}$ = −24.5 (*c* 0.8, CH_2Cl_2, 96% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (s, 1H), 5.16 (d, *J* = 15.3 Hz, 1H), 5.32 (d, *J* = 15.6 Hz, 1H), 6.61 (dd, J_1 = 8.7 Hz, J_2 = 4.0 Hz, 1H), 6.90 (td, J_1 = 8.9 Hz, J_2 = 2.7 Hz, 1H), 7.22 (dd, J_1 = 8.6 Hz, J_2 = 7.4 Hz, 1H), 7.27-7.36 (m, 6H), 7.42-7.45 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 40.5, 68.9, 85.2, 87.5, 110.7 (d, *J* = 8.5 Hz), 112.7 (d, *J* = 24.9 Hz), 116.6, 116.8, 121.5, 129.2, 129.6, 129.7, 130.2, 131.2, 131.9, 132.4 (d, J = 7.7 Hz), 135.8, 138.1, 159.0 (d, *J* = 239.8 Hz), 172.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.9; IR (neat) ν 3340, 2924, 1713, 1489, 1442, 1264, 1137, 764, 695, 579 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{15}Cl_2FNO_2$ $[M+H]^+$ 426.0458, found 426.0470; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 10.8 min, t_R (minor) = 12.6 min.

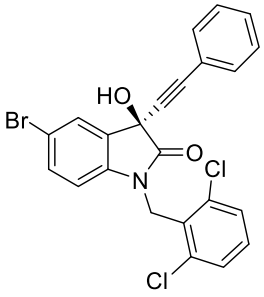
(*R*)-5-chloro-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(phenylethynyl)indolin-2-one (4b). This compound was obtained from the isatin **1h** (0.10 mmol, 35 mg).



White solid, yield: 30 mg, 66%; m.p. 224-226 °C; $[\alpha]_D^{25}$ = −92.6 (*c* 0.3, CH_2Cl_2, 84% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.45 (s, 1H), 5.16 (d, *J* = 15.3 Hz, 1H), 5.32 (d, *J* = 15.6 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 7.17 (dd, J_1 = 8.5 Hz, J_2 = 2.2 Hz, 1H), 7.22 (dd, J_1 = 8.6 Hz, J_2 = 7.6 Hz, 1H), 7.28-7.32 (m,

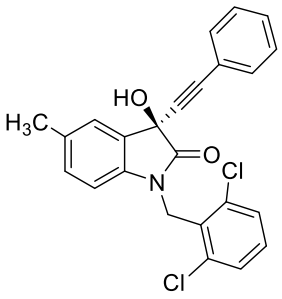
3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.43-7.45 (m, 2H), 7.55 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 40.6, 68.7, 85.3, 87.3, 111.3, 121.4, 124.8, 127.6, 129.2, 129.6, 129.7, 130.1, 130.2, 131.2, 131.9, 132.6, 135.8, 140.7, 172.6; IR (neat) ν 3347, 2924, 1721, 1438, 1170, 978, 753, 688 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{23}H_{15}Cl_3NO_2$ $[M+H]^+$: 442.0163, found: 442.0169. HPLC (Chiralpak AD-H, hexane:isopropanol = 85:15, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 20.1 min, t_R (minor) = 22.7 min.

(*R*)-5-bromo-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(phenylethynyl)indolin-2-one (4c). This



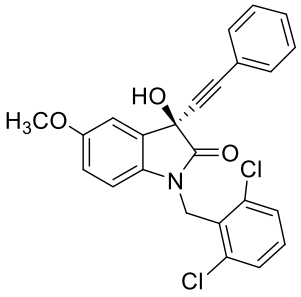
compound was obtained from the isatin **1i** (0.10 mmol, 50 mg). Colorless oil, yield: 23 mg, 45%; $[\alpha]_D^{25}$ = −120.5 (*c* 0.4, CH_2Cl_2, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.44 (s, 1H), 5.15 (d , *J* = 15.3 Hz, 1H), 5.31 (d, *J* = 15.6 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 7.22 (dd, J_1 = 8.6 Hz, J_2 = 7.5 Hz, 1H), 7.27-7.32 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.43-7.46 (m, 2H), 7.68 (d, *J* = 2.1 Hz*, 1H*); ^{13}C NMR (100 MHz, DMSO-d_6) δ 40.6, 68.7, 85.3, 87.3, 111.8, 115.2, 121.4, 127.5, 127.6, 129.2, 129.6, 129.7, 130.1, 131.2, 131.9, 132.9, 133.1, 135.8, 141.2, 172.4; IR (neat) ν 3337, 1717, 1601, 1485, 1434, 1329, 166, 981, 757, 692 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{15}BrCl_2NO_2$ $[M+H]^+$ 485.9658, found 485.9669; HPLC (Chiralpak AD-H, hexane:isopropanol = 85:15, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 19.3 min, t_R (minor) = 22.3 min.

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-5-methyl-3-(phenylethynyl)indolin-2-one (4d). This



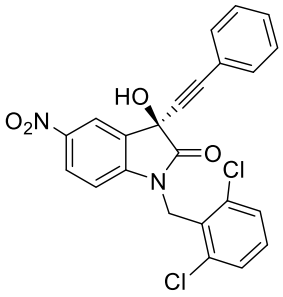
compound was obtained from the isatin **1j** (0.10 mmol,34 mg). White solid, yield: 26 mg, 58%; m.p. 220-222 °C; $[\alpha]_D^{25}$ = −168.8 (*c* 0.6, CH_2Cl_2, 94% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.42 (s, 1H), 5.15 (d, *J* = 15.3 Hz, 1H), 5.31 (d, *J* = 15.6 Hz, 1H), 6.57 (d, *J* = 8.1 Hz, 1H), 6.99 (ddt, J_1 = 8.1 Hz, J_2 = 1.8 Hz, J_3 = 0.7 Hz, 1H), 7.20 (dd, J_1 = 8.6 Hz, J_2 = 7.4 Hz, 1H), 7.27-7.32 (m, 3H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.40 (m, 1H), 7.42-7.46 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.9, 39.3, 69.0, 84.7, 88.3, 109.3, 121.7, 125.4, 129.2, 129.5, 130.4, 130.5, 130.7, 131.1, 131.8, 132.7, 135.8, 139.4, 173.0; IR (neat) ν 3376, 3076, 1699, 1492, 1434, 1340, 1061, 760, 695 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{18}Cl_2NO_2$ $[M+H]^+$ 422.0709, found 422.0716; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 11.7 min, t_R (minor) = 15.2 min.

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-5-methoxy-3-(phenylethynyl)indolin-2-one (4e). This



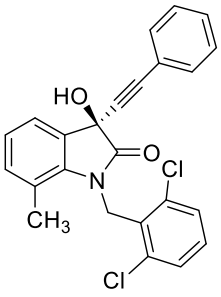
compound was obtained from the isatin **1k** (0.10 mmol, 35 mg). White solid, yield: 32 mg, 71%; m.p. 206-209 °C; $[\alpha]_D^{25}$ = −141.5 (*c* 0.6, CH_2Cl_2, 96% ee); ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.68 (s, 3H), 5.00 (d, *J* = 15.4 H, 1H z), 5.18 (d, *J* = 15.4 Hz, 1H), 6.59 (d, *J* = 8.6 Hz, 1H), 6.82 (dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz, 1H), 7.09 (d, *J* = 2.7 Hz, 1H), 7.22 (s, 1H), 7.35-7.38 (m, 6H), 7.50 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 40.5, 55.9, 69.2, 84.8, 88.2, 110.1, 111.7, 114.7, 121.7, 129.2, 129.6, 130.4, 131.1, 131.2, 131.8, 131.9, 134.9, 135.9, 156.2, 172.7; IR (neat) ν 3304, 2927, 1706, 1489, 1442, 985, 757, 684 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{18}Cl_2NO_3$ $[M+H]^+$ 438.0658, found 438.0671; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 14.9 min, t_R (minor) = 21.6 min

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-5-nitro-3-(phenylethynyl)indolin-2-one (4f). This



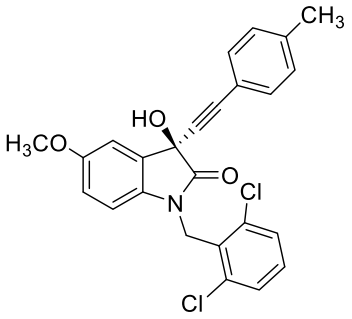
compound was obtained from the isatin **1l** (0.11 mmol, 38 mg). Yellow oil, yield: 23 mg, 47%. $[\alpha]_D^{25}$ = −76.3 (*c* 0.6, CH_2Cl_2, 96% ee); ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.18 (d, *J* = 15.5 Hz, 1H), 5.29 (d, *J* = 15.5 Hz, 1H), 7.04 (d, *J* = 9.5 Hz, 1H), 7.37-7.41 (m, 6H), 7.55 (dd, J_1 = 8.1 Hz, J_2 = 0.6 Hz, 2H), 7.64 (s, 1H), 8.27-8.30 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 41.2, 68.2, 85.7, 86.5, 110.3, 120.0, 121.2, 127.5, 129.2, 129.6, 129.8, 129.9, 131.3, 131.4, 131.5, 132.0, 135.8, 143.5, 147.7, 173.1; IR (neat) ν 3387, 1735, 1612, 1485, 1431, 1337, 1079, 750, 695 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{14}Cl_2N_2NaO_4$ $[M+Na]^+$ 475.0223, found 475.0234; HPLC (Phenomenex Lux Amylose-2, hexane:isopropanol = 80:20, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 34.0 min, t_R (minor) = 42.2 min.

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-7-methyl-3-(phenylethynyl)indolin-2-one (4g). This



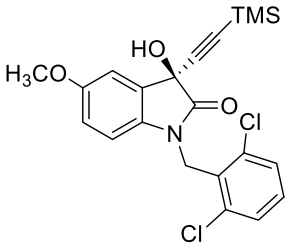
compound was obtained from the isatin **1m** (0.11 mmol, 36 mg). Yellow oil, yield: 37 mg, 77%; $[\alpha]_D^{25}$ = +71.5 (*c* 0.5, CH_2Cl_2, 90% ee); ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.37 (s, 3H), 5.34 (d, *J* = 3.2 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 7.08 (ddd, J_1 = 7.7 Hz, J_2 = 1.5 Hz, J_3 = 0.8 Hz, 1H), 7.11 (s, 1H), 7.29-7.38 (m, 7H), 7.44 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.2, 43.4, 68.3, 84.7, 88.3, 120.5, 121.8, 122.8, 123.5, 129.2, 129.5, 130.2, 130.3, 131.5, 131.7, 132.0, 134.1, 135.1, 140.6, 174.0; IR (neat) ν 3380, 2971, 1713, 1449, 1366, 1116, 949, 750, 688 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{18}Cl_2NO_2$ $[M+H]^+$ 422.0709, found: 422.0714; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 11.8 min, t_R (minor) = 18.4 min.

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-5-methoxy-3-(p-tolylethynyl)indolin-2-one (4h). This



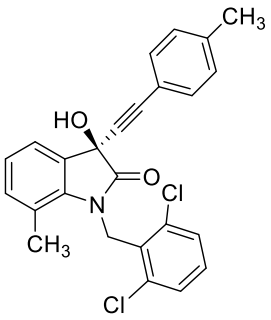
compound was obtained from the isatin **1k** (0.10 mmol, 35 mg). White solid, yield: 35 mg, 75%; m.p. 227-228 °C; $[\alpha]_D^{25}$ = -308.1 (*c* 0.5, CH_2Cl_2, 99% ee); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.28 (s, 3H), 3.69 (s, 3H), 5.00 (d, *J* = 15.4, 1H), 5.18 (d, *J* = 15.4, 1H), 6.59 (d, *J* = 8.6 Hz, 1H), 6.82 (dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz, 1H), 7.08 (d, *J* = 2.6 Hz, 1H), 7.16 (s, 1H), 7.18 (d, *J* = 4.6 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.4, 40.5, 56.0, 69.2, 85.0, 87.5, 110.1, 111.7, 114.7, 118.7, 129.5, 129.8, 130.4, 131.1, 131.8, 132.0, 134.9, 135.9, 139.4, 156.1, 172.8; IR (neat) ν 3329, 1710, 1496, 1188, 1155, 807, 692 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{25}H_{20}Cl_2NO_3$ $[M+H]^+$ 452.0815, found 452.0823; HPLC (Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 12.4 min, t_R (minor) = 20.1 min.

(*S*)-1-(2,6-dichlorobenzyl)-3-hydroxy-5-methoxy-3-((trimethylsilyl)ethynyl)indolin-2-one (4i).



This compound was obtained from the isatin **1k** (0.11 mmol, 36 mg).Colorless oil, yield, 23 mg 50%; $[\alpha]_D^{25}$ = -119.7 (*c* 0.3, CH_2Cl_2, 88% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 9H), 3.37 (s, 1H), 3.76 (s, 3H), 5.11 (d, *J* = 14.8 Hz, 1H), 5.28 (d, *J* = 14.8 Hz, 1H), 6.55 (dd, J_1 = 8.6 Hz, J_2 = 0.7 Hz, 1H), 6.70 (ddt, J_1 = 8.5 Hz, J_2 = 2.5 Hz, J_3 = 0.5 Hz, 1H), 7.11 (dd, J_1 = 2.7 Hz, J_2 = 0.7 Hz, 1H), 7.20 (ddd, J_1 = 8.5 Hz, J_2 = 7.4 Hz, J_3 = 0.9 Hz, 1H), 7.33 (dd, J_1 = 8.1 Hz, J_2 = 0.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.37, 40.4, 55.7, 69.5, 92.3, 101.1, 110.4, 111.3, 115.2, 128.9, 129.7, 129.8, 129.9, 135.0, 136.4, 156.4, 172.9. IR (neat): ν = 3405, 1717, 1485, 1431, 1213, 1036, 807, 601 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{22}Cl_2NO_3Si$ $[M+H]^+$ 434.0741, found 434.0756; HPLC (Phenomenex Lux Cellulose-1, hexane:isopropanol = 95:5, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 13.5 min, t_R (minor) = 16.0 min

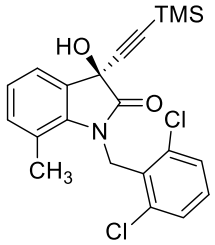
(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-7-methyl-3-(p-tolylethynyl)indolin-2-one (4j). This



compound was obtained from the isatin **1m** (0.11 mmol, 35 mg). White solid, yield: 36 mg, 75%; m.p. 182-183 °C; $[\alpha]_D^{25}$ = +86.5 (*c* 0.5, CH_2Cl_2, 94% ee); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.28 (s, 3H), 2.36 (s, 3H), 5.34 (d, J = 2.1 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 7.07-7.09 (m, 2H), 7.15-7.23 (m, 4H), 7.29-7.35 (m, 4H), 7.44 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.2, 21.4, 43.4, 68.3, 84.8, 87.6, 118.7, 120.5, 122.8, 123.4, 129.5, 129.8, 130.2, 131.6, 131.7, 132.0, 134.1, 135.0, 139.3, 140.6, 174.1; IR (neat) ν 3286, 176, 1362, 1195, 1112, 1018, 811, 775, 742 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{25}H_{20}Cl_2NO_2$

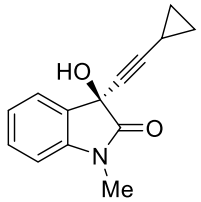
$[M+H]^+$ 436.0866, found 436.0879; HPLC (Chiralpak AD-H, hexane:isopropanol=70:30, 1 mL min^{-1}, λ = 254 nm) t_R (major) = 10.5 min, t_R (minor) = 17.7 min.

(*S*)-1-(2,6-dichlorobenzyl)-3-hydroxy-7-methyl-3-((trimethylsilyl)ethynyl)indolin-2-one (4k).



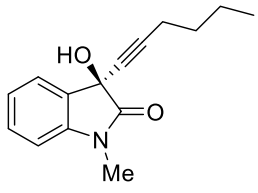
This compound was obtained from the isatin **1m** (0.12 mmol, 40 mg).Colorless oil, yield: 32 mg, 61%; $[\alpha]_D^{25}$ = +83.0 (*c* 0.3, CH_2Cl_2, 90% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 9H), 2.33 (s, 3H), 3.18 (s, 1H), 5.37 (d, *J* = 16.4 Hz, 1H), 5.46 (d, *J* = 16.4 Hz, 1H), 7.00-7.06 (m, 2H), 7.14-7.18 (m, 1H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.39-7.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.39, 18.9, 43.4, 68.6, 92.0, 101.9, 120.3, 122.8, 123.6, 129.0, 129.4, 131.3, 134.3, 135.3, 140.7, 174.3; IR (neat) ν 3351, 1699, 1358, 1155, 775, 739, 576 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{22}Cl_2NO_2Si$ $[M+H]^+$ 418.0791, found: 418.0801; HPLC (Phenomenex Lux Cellulose-1, hexane:isopropanol = 95:5, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 13.4 min, t_R (minor) = 19.0 min.

(*R*)-3-(cyclopropylethynyl)-3-hydroxy-1-methylindolin-2-one (5a). This compound was



obtained from the isatin **1a** (0.19 mmol, 30 mg). Yellow solid, yield: 30 mg, 70%; m.p. 177-180 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.67-0.77 (4H), 1.24 (m, 1H), 3.19 (s, 3H), 3.68 (s, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 7.10 (dd, J_1 = 11.0 Hz, J_2 = 4.1 Hz, 2H), 7.33 (, J = 7.8 Hz t, 1H), 7.49 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.43, 8.41, 8.44, 26.5, 69.1, 72.0, 90.8, 108.6, 123.5, 124.4, 129.3, 130.1, 142.9, 174.1; IR (neat) ν 3277, 2232, 1703, 1609, 1468, 1374, 1348, 1088, 1014, 919, 765, 648 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{13}NO_2$ $[M+Na]^+$ 250.0838, found 250.0842; HPLC (Phenomenex Lux i-Amylose-3, hexane:isopropanol = 90:10, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 21.3 min, t_R (minor) = 24.0 min. $[\alpha]_D^{25}$ = -22.0 (*c = 0.5*, CH_2Cl_2, 96% ee).

(*R*)-3-(hex-1-yn-1-yl)-3-hydroxy-1-methylindolin-2-one (5b). This compound was obtained



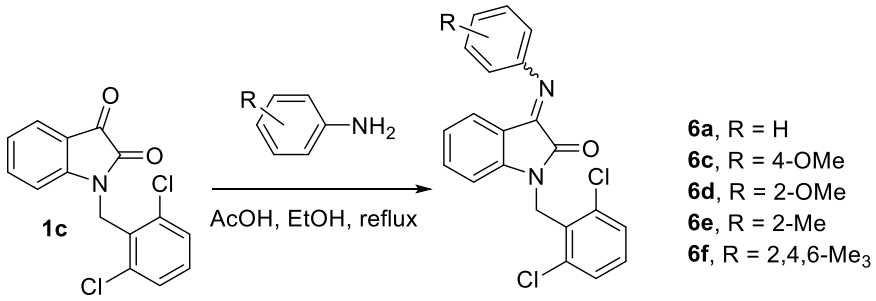
from the isatin **1a** (0.17 mmol, 28 mg). Colorless oil, yield: 25 mg, 60%; $[\alpha]_D^{25}$ = -16.1 (*c* 0.5, CH_2Cl_2, 74% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 7.3 Hz, 3H), 1.35 (m, 2H), 1.46 (m, 2H), 2.20 (dd, *J* = 10.7, 3.8 Hz, 2H), 3.20 (s, 3H), 3.63 (s, 1H), 6.82 (d, J = 7.8 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.33 (dd, J_1 = 11.4 Hz, J_2 = 4.1 Hz, 1H), 7.51 (dd, J_1 = 7.4 Hz, J_2 = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 18.5, 21.8, 26.5, 30.2, 69.1, 76.8, 87.5, 108.6, 123.5, 124.4, 129.3, 130.2, 142.9, 174.2; IR (neat) ν 3311, 1713, 1606, 1459, 1363, 1090, 1017, 751, 740, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{17}NO_2$ $[M+Na]^+$ 266.1151, found 266.1158; HPLC (Phenomenex Lux i-Amylose-3, hexane:isopropanol = 90:10, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 15.5 min, t_R (minor) = 17.7 min.

4. General procedure for the synthesis of racemic 3-alkynyl-3-hydroxyoxindoles.

To a solution of $ZnMe_2$ in toluene (1.2 M, 0.4 mmol) under nitrogen atmosphere was added the corresponding alkyne (0.4 mmol) and the mixture was stirred at rt for 1 h. Then, a solution of the isatin (0.1 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise and the reaction stirred at rt for 24 h. The reaction was quenched with NH_4Cl, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated. Purification by silica gel column chromatography afforded the pure racemic product.

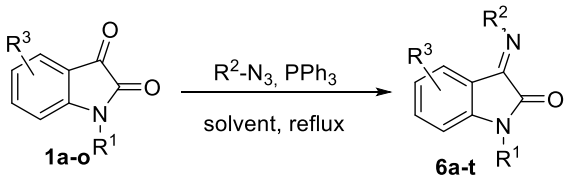
5. Synthesis and characterization data of isatin ketimines

5.1. Synthesis of isatin ketimines 6a and 6c-f.[8]



To a solution of isatin **1c** (1.6 mmol) and the corresponding aniline (1.6 mmol) in ethanol (45 mL) was added acetic acid (0.05 mL) and the reaction was refluxed until consumption of the starting materials (typically between 2-5 h, only **6d** was refluxed for 15 h). The mixture was allowed to cool to rt and 2/3 of the solvent were removed under vacuo. The resulting solid was filtrated and recrystallized from ethanol to afford the pure product.

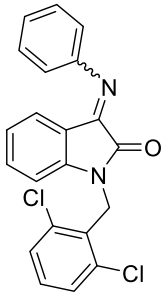
5.2. Synthesis a of Isatin Ketimines 6b and 6g-t.[9]



6b, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 =4-CF_3-C_6H_4, R^3 = H
6g, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 =3,5-Cl_2-C_6H_3, R^3 = H
6h, R^1 = Bn, R^2 =3,5-Cl_2-C_6H_3, R^3 = H
6i, R^1 = CH_3, R^2 =3,5-Cl_2-C_6H_3, R^3 = H
6j, R^1 = MOM, R^2 =3,5-Cl_2-C_6H_3, R^3 = H
6k, R^1 =CPh_3, R^2 =3,5-Cl_2-C_6H_3, R^3 = H
6l, R^1 =Ac, R^2 =3,5-Cl_2-C_6H_3, R^3 = H
6m, R^1 =H, R^2 =3,5-Cl_2-C_6H_3, R^3 = H
6n, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 =3,5-Cl_2-C_6H_3, R^3 =5-F
6o, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 =3,5-Cl_2-C_6H_3, R^3 =5-Cl
6p, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 =3,5-Cl_2-C_6H_3, R^3 =5-Br
6q, R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 =3,5-Cl_2-C_6H_3, R^3 =5-CH_3
6r,R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 =3,5-Cl_2-C_6H_3, R^3 =5-OCH_3
6s,R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 =3,5-Cl_2-C_6H_3, R^3 = 5-NO_2
6t,R^1 = 2,6-Cl_2-C_6H_3-CH_2, R^2 =3,5-Cl_2-C_6H_3, R^3 =7-Me

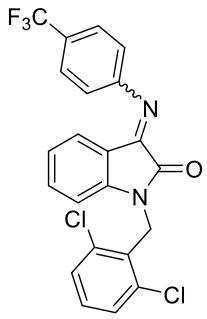
To a solution of the corresponding azide (1.3 mmol), prepared according described procedures,[10] in ethanol (35 mL) at rt, was added PPh_3 (1.3 mmol) and the reaction mixture was stirred for 15 min, whereupon the corresponding isatin (1.3 mmol) was added and the mixture refluxed until consumption of the starting materials (typically between 2-5 h). The mixture was allowed to cool to rt and 2/3 of the solvent were removed under vacuo. The resulting solid was filtrated and recrystallized from ethanol or ethyl acetate to afford the pure product. For synthesis of isatin ketimines **6l**, **6n-p** and **6s** solvent was changed to 1,4-dioxane.

1-(2,6-Dichlorobenzyl)-3-(phenylimino)indolin-2-one (6a). This compound was obtained from



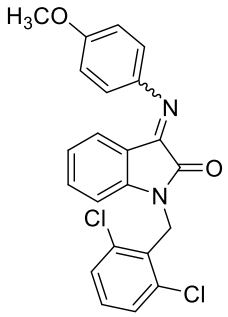
1c (1.6 mmol, 490 mg) Yellow solid, yield: 531g, 87%; m.p. 207-210 °C; two diastereomers *E*/*Z* 90:10;^{1}H NMR (500 MHz, $CDCl_3$,) (*E*)-**6a** δ 5.33 (s, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 2H), 7.0 (d, *J* = 7.4 Hz, 2H), 7.18 (td, J_1 = 7.9 Hz, J_2 =1.0 Hz, 1H), 7.23 (m, 2H), 7.36 (d, 2H), 7.42 (t , *J* = 7.8 Hz, 2H); (*Z*)-**6a** δ 5.16 (s, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.66 (m, 1H), 7.06 (m, 3H), 7.19-7.23 (m, 3H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.33 (m, 2H), 7.71 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.1, 110.3, 115.9, 117.7, 119.1, 122.4, 122.9, 123.0, 125.2, 125.3, 126.1, 128.5, 129.0, 129.3, 129.7, 129.9, 129.9, 133.9, 136.3, 146.8, 150.3, 153.8, 162.8; IR (neat): ν 1736, 1605, 1467, 1349, 765 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{15}Cl_2N_2O$ $[M+H]^+$ 381.0556, found. 381.0560.

1-(2,6-Dichlorobenzyl)-3-((4-(trifluoromethyl)phenyl)imino)indolin-2-one (6b). This compound



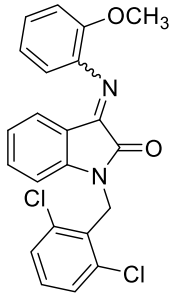
was obtained from **1c** (1.31 mmol, 400 mg) Yellow solid, yield: 351 mg, 60%, m.p. 209-211 °C.; two diastereomers *E*/*Z* 80:20; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6b** δ 5.33 (s, 2H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.21-7.26 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H); (*Z*)-**6b** δ 5.15 (s, 2H), 6.65 (d, *J* = 7.9 Hz, 1H), 6.73 (m, 1H), 7.05-7.08 (m, 3H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.34 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.71 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.7, 40.2, 110.0, 110.6, 115.5, 117.8, 118.6, 122.6, 123.3, 123.4, 126.0 (q, *J* = 4.0 Hz), 126.2, 126.8 (q, *J* = 4.0 Hz), 127.2 (q, *J* = 33.8 Hz), 129.0, 129.5, 130.1, 134.3, 134.6, 136.3, 147.2, 153.2, 154.3, 162.4; ^{19}F NMR (470 MHz, $CDCl_3$) (*E*)-**6b** δ -61.9; (*Z*)-**6b** δ -61.9;. IR (neat) ν 1729, 1675, 1605, 1467, 1323, 1108, 751 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{14}Cl_2F_3N_2O$ $[M+H]^+$ 449.0430, found 449.0440.

1-(2,6-Dichlorobenzyl)-3-((4-methoxyphenyl)imino)indolin-2-one (6c). This compound was



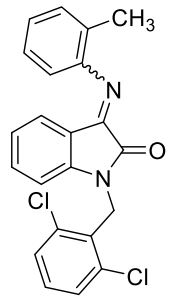
obtained from **1c** (1.6 mmol, 490 mg). Red solid, yield: 382 mg, 58%; m.p. 185-186 °C; two diastereomers *E*/*Z* 85:15; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6c** δ 3.86 (s, 3H), 5.33 (s, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.71 (td, J_1 = 7.7 Hz, J_2 = 0.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 8.9 Hz, 2H), 7.18 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H); (*Z*)-**6c** δ 3.84 (s, 3H), 5.19 (s, 2H), 6.61 (d, *J* = 7.9 Hz, 1H), 6.93 (m, 2H), 6.96 (m, 2H), 7.04 (m, 2H), 7.21 (m, 1H), 7.28 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.7, 40.1, 55.3, 55.4, 109.6, 110.3, 113.6, 114.5, 116.0, 120.1, 122.3, 122.5, 122.9, 123.2, 125.5, 129.0, 129.1, 129.8, 129.8, 129.9, 132.9, 133.7, 136.2, 136.3, 141.1, 143.0, 144.7, 146.7, 153.2, 157.2, 157.7, 158.5, 163.0; IR (neat) ν 1719, 1608, 1504, 139, 1239, 1034, 758 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{22}H_{17}Cl_2N_2O_2$ $[M+H]^+$ 411.0662, found. 411.0677.

1-(2,6-Dichlorobenzyl)-3-((2-methoxyphenyl)imino)indolin-2-one (6d). This compound was



obtained from **1c** (1.62 mmol, 495 mg). Orange solid, yield: 400 mg, 60%; m.p. 190-192 °C; two diastereomers *E*/*Z* 80:20; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6d** δ 3.73 (s, 3H), 5.33 (s, 2H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.67-6.71 (m, 2H), 6.97-7.02 (m, 3H), 7.15-7.23 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 2H); (*Z*)-**6c** δ 3.77 (s, 3H), 5.14 (s, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.97-7.02 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.13 (m, 1H), 7.15-7.23 (m, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.33 (m, 1H), 7.78 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.6, 40.1, 55.5, 55.7, 109.6, 110.1, 111.0, 111.8, 116.8, 119.3, 119.9, 120.5, 121.0, 121.5, 122.5, 122.8, 123.1, 125.6, 125.9, 126.2, 128.9, 129.0, 129.8, 129.9, 133.5, 133.7, 136.2, 136.3, 139.2, 146.5, 148.0, 154.6, 162.7; IR (neat) ν 1729, 1605, 1457, 1430, 1249, 741 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{17}Cl_2N_2O_2$ $[M+H]^+$ 411.0662, found. 411.0672.

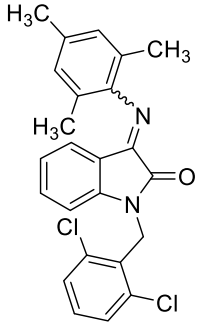
1-(2,6-Dichlorobenzyl)-3-(o-tolylimino)indolin-2-one (6e). This compound was obtained from



1c (1.6 mmol, 490 mg). Yellow solid, yield: 297 mg, 47%; m.p. 164-166 °C; two diastereomers *E*/*Z* 90:10; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6e** δ 2.12 (s, 3H), 5.34 (s, 2H), 6.45 (d, *J* = 7.0 Hz, 1H), 6.67 (d, *J* = 7.3 Hz, 2H), 6.83 (d, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.26 (t, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H); (*Z*)-**6e** δ 2.18 (s, 3H), 5.16 (s, 2H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.69 (m, 1H), 7.04-7.12 (m, 2H), 7.19-7.26 (m, 5H), 7.33 (m, 1H), 7.75 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.6, 40.1, 110.3, 116.3, 116.6, 117.1, 122.6, 122.9, 123.0, 125.0, 125.7, 125.8, 126.7, 129.0, 129.7, 129.9, 130.2, 130.8, 133.6, 133.9,

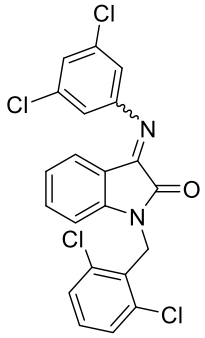
136.2, 136.3, 146.5, 149.3, 153.9, 162.7; IR (neat) ν 1736, 1642, 1598, 1470, 1353, 762, 731 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{17}Cl_2N_2O$ $[M+H]^+$ 395.0712, found 395.0713.

1-(2,6-Dichlorobenzyl)-3-(mesitylimino)indolin-2-one (6f). This compound was obtained from



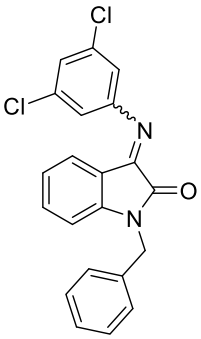
1c (1.61 mmol, 492 mg). Orange solid, yield: 395 mg, 58%; m.p. 201-204 °C; two diastereomers *E*/*Z* 95:5; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6f** δ 1.99 (s, 6H), 2.32 (s, 3H), 5.35 (s, 2H), 6.39 (d, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.91 (s, 2H), 7.16 (td, *J* = 7.8, 1.1 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H); (*Z*)-**6f** δ 2.02 (s, 6H), 2.28 (s, 3H), 5.15 (s, 2H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.88 (m, 3H), 7.04-7.09 (m, 3H), 7.43 (t, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.7, 17.9, 18.4, 20.8, 40.0, 110.1, 116.8, 123.0, 123.9, 125.0, 128.5, 129.0, 129.1, 129.7, 129.9, 133.6, 133.8, 136.2, 145.7, 145.9, 154.6, 162.7; IR (neat) ν 1732, 1648, 1601, 1467, 1440, 1348, 751 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{21}Cl_2N_2O$ $[M+H]^+$ 423.1025, found. 423.1033.

1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)imino)indolin-2-one (6g). This compound was



obtained from **1c** (1.3 mmol, 398 mg). Yellow solid, yield: 468 mg, 80%; m.p. 190-193 °C; two diastereomers *E*/*Z* 80:20; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6g** δ 5.31 (s, 2H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.91 (s, 2H), 7.22-7.26 (m, 3H), 7.37 (d, *J* = 7.9 Hz, 2H); (*Z*)-**6g** δ 5.15 (s, 2H), 6.87 (s, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.14 (s, 1H), 7.22-7.26 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.8, 40.2, 110.1, 110.7, 115.3, 116.3, 117.2, 122.8, 123.2, 123.4, 124.5, 124.9, 126.3, 129.0, 129.4, 130.0, 130.1, 134.5, 134.8, 134.9, 135.8, 136.2, 136.3, 147.2, 151.1, 152.0, 155.0, 156.7, 162.2; IR (neat) ν 1726, 1655, 1558, 1467, 1343, 748, 667 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{13}Cl_4N_2O$ $[M+H]^+$ 448.9777, found 448.9775.

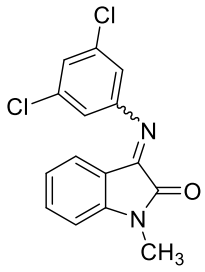
1-Benzyl-3-((3,5-dichlorophenyl)imino)indolin-2-one (6h). This compound was obtained from



1b (1.3 mmol, 308 mg). Yellow solid, yield: 273 mg, 55%; m.p. 124-127 °C; two diastereomers *E*/*Z* 80:20; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6h** δ 5.00 (s, 2H), 6.68 (dd, *J* = 7.7, 0.6 Hz, 1H), 6.77 (d , *J* = 8.0 Hz, 1H), 6.81 (td, *J* = 7.7, 0.8 Hz, 1H), 6.93 (d, *J* = 1.8 Hz, 2H), 7.24 (t, *J* = 1.8 Hz, 1H), 7.28-7.40 (m, 6H); (*Z*)-**6h** δ 4.84 (s, 2H), 6.75 (d, *J* = 8.8 Hz, 1H), 6.90 (d, *J* = 1.8 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 1.8 Hz, 1H), 7.28-7.40 (m, 2H), 7.47 (dd, *J* = 7.1, 2.3 Hz, 2H), 7.54 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 43.7, 44.0, 109.9, 110.6, 115.2, 116.3, 117.2, 120.7,

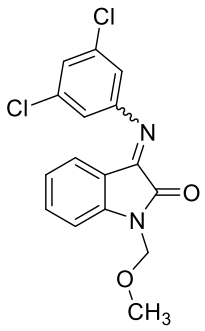
123.0, 123.4, 123.5, 124.5, 125.0, 126.4, 127.4, 127.5, 127.9, 128.0, 128.4, 128.5, 128.9, 128.9, 131.9, 132.0, 132.1, 134.5, 134.7, 134.8, 134.9, 135.9, 146.3, 147.5, 151.0, 152.0, 155.4, 157.1, 162.7; IR (neat) ν 1729, 1658, 1554, 1356, 1101, 923, 802, 698, 667 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{21}H_{15}Cl_2N_2O$ $[M+H]^+$: 381.0556, found: 381.0567.

3-((3,5-Dichlorophenyl)imino)-1-methylindolin-2-one (6i). This compound was obtained from



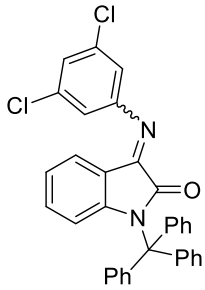
1a (1.3 mmol, 210 mg) Orange solid, yield: 243 mg, 61%; m. p. 191-193 °C; two diastereomers *E*/*Z* 80:20; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6i** δ 3.30 (s, 3H), 6.67 (d, *J* = 8.3 Hz, 1H), 6.85 (m, 2H), 6.87-6.89 (m, 2H), 7.23 (t, *J* = 1.8 Hz, 1H), 7.42 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H); (*Z*)-**6i** δ 3.16 (s, 3H), 6.83-6.89 (m, 3H), 7.12 (t, *J* = 1.8 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.50 (td, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1H), 7.67 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.9, 26.4, 108.9, 109.5, 115.0, 116.3, 117.0, 120.5, 123.0, 123.4, 124.4, 124.9, 126.3, 128.4, 131.8, 132.0, 134.6, 134.8, 135.0, 135.8, 138.3, 147.0, 148.3, 151.2, 152.0, 155.5, 162.6; IR (neat) ν 1726, 1655, 1558, 1376, 1101, 926, 795, 762 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{11}Cl_2N_2O$ $[M+H]^+$ 305.0243, found 305.0257.

3-((3,5-Dichlorophenyl)imino)-1-(methoxymethyl)indolin-2-one (6j). This compound was



obtained from **1n** (1.31 mmol, 250 mg). Orange solid, yield: 290 mg, 66%; m.p. 156-158 °C; two diastereomers *E*/*Z* 80:20; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6j** δ 3.41 (s, 3H), 5.22 (s, 2H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.88-6.92 (3H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 1.8 Hz, 1H), 7.43 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H); (*Z*)-**6j** δ 3.33 (s, 3H), 5.06 (s, 2H), 6.86 (d, *J* = 1.8 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 1.8 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.51 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.72 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.6, 56.7, 71.4, 71.6, 110.4, 111.2, 115.1, 116.2, 117.0, 118.8, 120.4, 123.5, 123.6, 123.9, 124.5, 125.0, 126.3, 128.4, 132.0, 134.8, 134.9, 135.2, 135.9, 145.5, 146.8, 151.0, 151.9, 153.0, 155.2, 157.3, 162.4, 163.0; IR (neat) ν 1736, 1658, 1558, 1353, 1067, 802, 758 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{13}Cl_2N_2O_2$ $[M+H]^+$ 335.0349, found 335.0355.

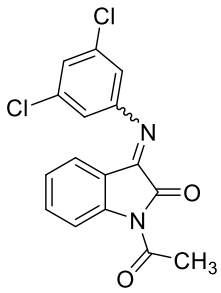
3-((3,5-Dichlorophenyl)imino)-1-tritylindolin-2-one (6k). This compound was obtained from **1d**



(1.3 mmol, 505 mg). Orange solid, yield: 485 mg, 70%; m.p. 260-262 °C; two diastereomers *E*/*Z* 80:20; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6k** δ 6.38 (d, *J* = 8.3 Hz, 1H), 6.66 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 1.8 Hz, 1H), 7.02 (m, 1H), 7.19-7.30 (m, 11H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.48-7.50 (m, 5H); (*Z*)-**6k** δ 6.29 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 1.8 Hz, 1H), 6.92 (d, *J* =

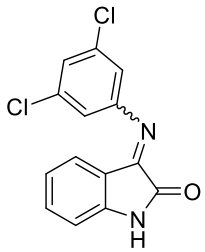
1.8 Hz, 2H), 6.99-7.04 (m, 2H), 7.11 (t, *J* = 8.6 Hz, 1H), 7.19-7.30 (m, 7H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.48-7.50 (m, 5H), 7.64 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 75.1, 116.2, 116.3, 117.2, 117.3, 122.3, 124.6, 125.6, 127.0, 127.1, 127.8, 127.9, 129.0, 129.2, 133.2, 134.8, 135.8, 141.3, 148.6, 152.3, 155.1, 163.5; IR (neat) ν 1736, 1672, 1558, 1454, 692 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{33}H_{23}Cl_2N_2O$ $[M+H]^+$ 533.1182, found 533.1197.

1-Acetyl-3-((3,5-dichlorophenyl)imino)indolin-2-one (6l). This compound was obtained from **1e**



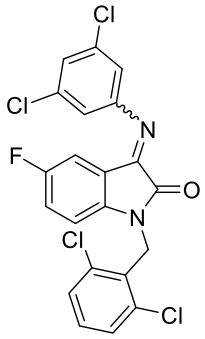
(1.3 mmol, 245 mg). Orange solid, yield: 246 mg, 57%; m.p. 191-193 °C; two diastereomers *E*/*Z* 75:25; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6l** δ 2.79 (s, 3H), 6.85 (d, *J* = 8.6 Hz, 1H), 6.89 (d, *J* = 1.8 Hz, 2H), 7.04 (t, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 1.7 Hz, 1H), 7.52 (t, *J* = 8.6 Hz, 1H), 8.41 (d, *J* = 8.3 Hz, 1H); (*Z*)-**6l** δ 2.61 (s, 3H), 6.83 (d, *J* = 1.8 Hz, 2H), 7.16 (t, *J* = 1.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 8.31 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.6, 26.8, 115.9, 116.4, 116.5, 117.3, 117.9, 123.2, 124.6, 125.2, 125.4, 125.8, 125.9, 135.1, 135.2, 135.4, 136.1, 143.9, 144.9, 151.0, 151.5, 153.5, 162.5, 170.0, 170.1; IR (neat) ν 1769, 1702, 1558, 1276, 795, 762 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{10}Cl_2N_2NaO_2$ $[M+H]^+$ 355.0012, found 355.0019.

3-((3,5-Dichlorophenyl)imino)indolin-2-one (6m). This compound was obtained from **1o** (1.3



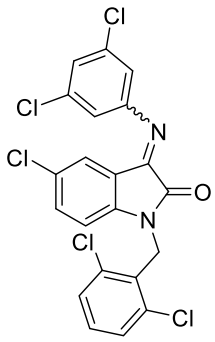
mmol, 190 mg). Orange solid, yield: 285, mg, 76%; m.p. 221-223 °C; two diastereomers *E*/*Z* 75:25; ^{1}H NMR (500 MHz, DMSO-d_6) (*E*)-**6m** δ 6.40 (d, *J* = 7.2 Hz, 1H), 6.80 (td, *J* = 7.7, 0.9 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 7.05 (m, 1H), 7.12 (d, *J* = 1.9 Hz, 1H), 7.37 (td, J_1 = 7.7Hz, J_2 = 1.2 Hz, 1H), 7.46 (m, 1H), 11.0 (s broad, 1H); (*Z*)-**6m** δ 6.86 (d, *J* = 7.8 Hz, 1H), 7.05 (m, 1H), 7.12 (d, *J* = 1.9 Hz, 1H), 7.25 (td, J_1 = 1.9 Hz, 1H), 7.46 (m, 1H), 7.52-7.62 (2H), 10.9 (s broad, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 111.4, 112.2, 115.9, 116.7, 117.7, 121.1, 122.5, 122.8, 123.4, 123.8, 124.5, 126.0, 129.1, 129.2, 131.8, 131.9, 134.1, 135.4, 135.5, 135.6, 146.7, 147.7, 152.5, 153.3, 155.1, 156.6, 158.9, 163.5; IR (neat) ν 1709, 1611, 1561, 795, 661 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_9Cl_2N_2O$ $[M+H]^+$ 291.0086, found 291.0093.

1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)imino)-5-fluoroindolin-2-one (6n). This



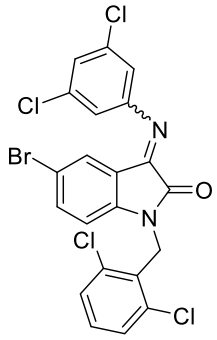
compound was obtained from **1g** (1.3 mmol, 420 mg).Yellow solid, yield: 340 mg, 56%; m.p. 205-207 °C; two diastereomers *E*/*Z* 70:30; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6n** δ 5.31 (s, 2H), 6.38 (dd, J_1 = 7.7 Hz, J_2 = 2.6 Hz, 1H), 6.66 (dd, J_1 = 8.8 Hz, J_2 = 4.0 Hz, 1H), 6.90 (m, 2H), 6.98 (td, J_1 = 8.7 Hz, J_2 = 2.7 Hz, 1H), 7.25 (m, 2H), 7.37 (m, 2H); (*Z*)-**1n** δ 5.15 (s, 2H), 6.60 (dd, J_1 = 8.7, J_2 = 3.8 Hz, 1H), 6.90 (m, 2H), 7.03 (td, J_1 = 8.8, J_2 = 2.7 Hz, 1H), 7.16 (t, *J* = 1.8 Hz, 1H), 7.25 (m, 2H), 7.37 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.9, 40.3, 110.9 (d, *J* = 25.1 Hz), 111.1 (d, *J* = 7.6 Hz) , 111.7(d, *J* = 7.6Hz), 113.7 (d, *J* = 26.9 Hz), 115.7 (d, *J* =8.1 Hz), 116.0, 117.3, 120.8 (d, *J* = 24.1 Hz), 121.4 (d, *J* = 23.9 Hz), 124.9, 125.3, 129.1, 129.3, 130.2, 130.3, 134.9, 136.0, 136.2, 136.3, 141.9 (d, *J* = 1.9 Hz), 143.4 (d, *J* = 2.0 Hz), 150.5, 151.4, 152.5(d, *J* = 2.9 Hz), 154.4(d, *J* = 2.5 Hz), 156.6, 157.1, 159.0, 159.2 (d, *J* = 243.8 Hz) 159.6 ((d, *J* = 243.7 Hz), 162.1; ^{19}F NMR (470 MHz, $CDCl_3$) (*E*)-**6n** δ -118.5; (*Z*)-**6n** δ = -119.0; IR (neat) ν 1730, 1666, 1559, 1479, 1328, 818, 768 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{12}Cl_4FN_2O$ $[M+H]^+$: 466.9682, found 466.9692.

5-Chloro-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)imino)indolin-2-one (6o). This



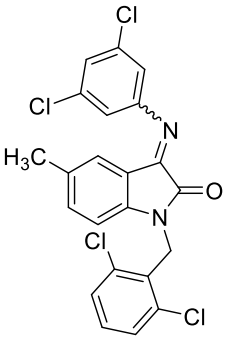
compound was obtained from **1h** (1.31 mmol, 445 mg) Yellow solid, yield: 538 mg, 85%; m.p. 199-200 °C; two diastereomers *E*/*Z* 65:35; ^{1}H NMR (500 MHz, $CDCl_3$)(*E*)-**6o** δ 5.31 (s, 2H), 6.65 (dd, J_1 = 7.4 Hz, J_2 = 3.5 Hz, 2H), 6.90 (m, 2H), 7.22-7.29 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H); (Z)-**6o** δ 5.15 (s, 2H), 6.60 (d, *J* = 8.5 Hz, 1H), 6.90 (m, 2H), 7.16 (s, 1H), 7.22-7.29 (m, 2H), 7.46 (td, J_1 = = 7.5 Hz, J_2 = 2.7 Hz, 2H), 7.54 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.9, 40.3, 111.2, 111.8, 116.1, 116.2, 117.3, 122.2, 123.5, 124.9, 125.4, 126.1, 128.2, 128.4, 128.5, 129.0, 129.1, 129.2, 130.2, 130.3, 131.8, 131.9, 132.0, 132.1, 132.1, 132.9, 134.0, 134.5, 134.9, 136.0, 136.2, 136.3, 144.1, 145.6, 150.5, 151.3, 152.0, 153.8, 156.3, 161.8; IR (neat) ν 1730, 1676, 1559, 1472, 1435, 670 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{21}H_{12}Cl_5N_2O$ $[M+H]^+$ 482.9387, found 482.9398.

5-Bromo-1-(2,6-dichlorobenzyl)indoline-2,3-dione (6p). This compound was obtained from **1i**



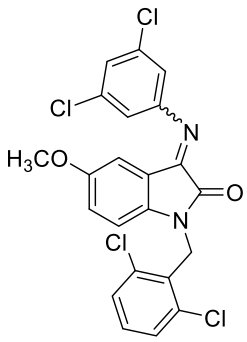
(1.31 mmol, 445 mg) Orange solid, yield: 502 mg, 73%; m.p. 171-173 °C; two diastereomers *E*/*Z* 65:35; ^{1}H NMR (500 MHz, $CDCl_3$): (*E*)-**6p** δ 5.30 (s, 2H), 6.61 (d, *J* = 8.5 Hz, 1H), 6.91 (d, *J* = 1.9 Hz, 2H), 7.23-7.27 (m, 2H), 7.36 (m, 4H); (*Z*)-**6p** δ 5.14 (s, 2H), 6.55 (d, J = 8.4 Hz, 1H), 6.79 (d, *J* = 2.0 Hz, 2H), 6.88 (d, *J* = 1.8 Hz, 2H), 7.16 (t, *J* = 1.8 Hz, 1H), 7.25 (m, 1H), 7.43 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 1H), 7.78 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.9, 40.3, 111.7, 112.2, 115.3, 116.2, 116.3, 116.6, 117.3, 122.5, 125.0, 125.4, 126.4, 129.0, 129.0, 129.1, 129.2, 130.3, 130.3, 134.9, 136.0, 136.2, 136.3, 136.9, 137.4, 144.6, 146.0, 150.4, 151.2, 151.8, 153.7, 156.2, 161.7; IR (neat) ν 1727, 1562, 1472, 1422, 808, 774, 677 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{12}BrCl_4N_2O$ $[M+H]^+$: 526.8882, found 526.8901.

1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)imino)-5-methylindolin-2-one (6q). This



compound was obtained from **1j** (1.3 mmol, 415 mg) Orange solid, yield:530 mg, 88%; m.p. 194-195 °C. (from EtOH); two diastereomers *E*/*Z* 75:25; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6q** δ 2.07 (s, 3H), 5.29 (s, 2H), 6.46 (s, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 1.7 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.20-7.24 (2H), 7.36 (d, *J* = 8.0 Hz, 2H); (*Z*)-**6q** δ 2.29 (s, 3H), 5.12 (s, 2H), 6.54 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 1.7 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.20-7.24 (m, 1H), 7.34 (d, *J* = 6.9 Hz, 2H), 7.48 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.7, 20.8, 39.8, 40.2, 109.9, 110.5, 115.3, 116.4, 117.2, 120.8, 123.9, 124.4, 124.8, 126.8, 129.0, 129.5, 129.7, 130.0, 132.3, 132.9, 134.8, 135.0, 135.3, 135.7, 136.2, 136.3, 143.6, 145.0, 151.2, 152.0, 153.2, 155.1, 162.3; IR (neat) ν 1732, 1564, 1484, 1333, 798 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{15}Cl_4N_2O$ $[M+H]^+$ 462.9933, found 462.9948.

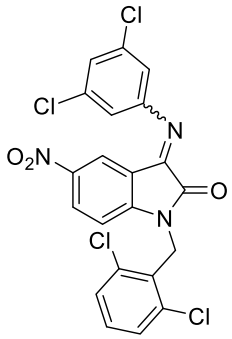
1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)imino)-5-methoxyindolin-2-one (6r). This



compound was obtained from **1k** (1.3 mmol, 437 mg) Red solid, yield: 363 mg 58%; m.p. 179-182 °C; two diastereomers *E*/*Z* 75:25; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6r** δ 3.51 (s, 3H), 5.28 (s, 2H), 6.22 (d, *J* = 2.6 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 1H), 6.79 (dd, J_1 = 8.7 Hz, J_2 = 2.7 Hz, 1H), 6.88 (d, *J* = 1.9 Hz, 1H), 6.93 (d, *J* = 1.8 Hz, 1H), 7.21-7.25 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H); (*Z*)-**6r** δ 3.78 (s, 3H), 5.12 (s, 2H), 6.56 (d, *J* = 8.6 Hz, 1H), 6.86 (d, *J* = 2.7 Hz, 2H), 6.93 (d, *J* = 1.8 Hz, 1H), 7.14 (t, *J* = 1.8 Hz, 1H), 7.21-7.25 (m, 2H), 7.35 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 39.8, 40.2, 55.4, 55.8, 108.2, 111.0, 111.4, 112.0, 115.8, 116.4, 117.2, 120.3, 120.8, 124.6, 124.9, 129.0, 129.5, 130.0, 135.8, 136.2, 136.3, 139.6,

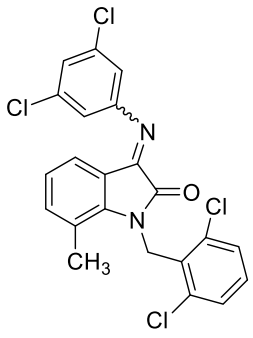
140.9, 151.0, 151.8, 153.3, 155.1, 155.3, 156.1, 156.9, 162.3; IR (neat) ν 1726, 1561, 1487, 1027, 795, 770 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{15}Cl_4N_2O_2$ $[M+H]^+$ 478.9882, found 478.9897.

1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)imino)-5-nitroindolin-2-one (6s). This



compound was obtained from **1l** (1.3 mmol, 455 mg) orange solid, yield: 520 mg, 81%, m.p. 144-146 °C; two diastereomers *E*/*Z* 55:45; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6s** δ 5.39 (s, 2H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.94 (t, *J* = 1.8 Hz, 3H), 7.28 (m, 1H), 7.38-7.41 (m, 3H), 8.21 (dd, J_1 = 8.8 Hz, J_2 = 2.3 Hz, 1H), (*Z*)-**6s** δ 5.23 (s, 2H), 6.79 (d, *J* = 8.8 Hz, 1H), 7.21 (t, *J* = 1.8 Hz, 1H), 7.28 (m, 2H), 7.34 (t, *J* = 1.8 Hz, 1H), 7.40 (m, 1H), 7.58 (d, *J* = 2.3 Hz, 1H), 8.28 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 8.54 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.2, 40.6, 110.0, 110.6, 114.9, 116.0, 117.6, 119.1, 121.3, 121.6, 125.6, 126.0, 128.5, 128.6, 129.2, 130.1, 130.5, 130.6, 130.7, 135.0, 136.2, 136.2, 136.3, 143.0, 143.9, 149.8, 150.0, 150.7, 150.8, 151.5, 152.9 156.4, 162.0; IR (neat) ν 1757, 1740, 1673, 1606, 1559, 1338, 1318, 791 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{12}Cl_4N_3O_3$ $[M+H]^+$ 493.9627, found. 493.9642

1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)imino)-7-methylindolin-2-one (6t). This



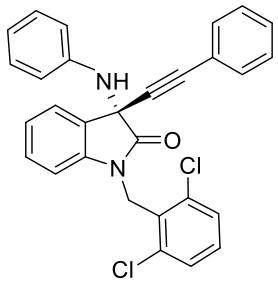
compound was obtained from **1m** (1.3 mmol, 416 mg) Yellow solid, yield: 500 mg, 83%, two diastereomers *E*/*Z* 70:30; m.p. 172-174 °C; ^{1}H NMR (500 MHz, $CDCl_3$) (*E*)-**6t** δ 2.38 (s, 3H), 5.50 (s, 2H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.73 (td, *J* = 7.7, 0.9 Hz, 1H), 6.86 (dd, J_1 = 1.9 Hz, J_2 = 0.9 Hz, 2H), 7.10 (m, 1H), 7.14-7.20 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 2H)); (*Z*)-**6t** δ 2.34 (s, 3H), 5.35 (s, 2H), 6.82 (dd, J_1 = 1.9 Hz, J_2 = 0.9 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.09 (m, 1H), 7.14-7.20 (m, 1H), 7.26-7.30 (m, 3H), 7.58 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.9, 19.4, 42.7, 43.3, 116.0, 116.3, 117.3, 120.7, 121.5, 121.6, 121.9, 122.9, 123.4, 124.4, 124.6, 124.7, 129.1, 129.2, 131.0, 134.7, 134.9, 135.3, 135.8, 138.6, 139.0, 144.7, 146.2, 151.2, 152.2, 152.9, 154.8, 164.0; IR (neat) ν 1728, 1655, 1558, 1442, 1326, 1213, 1058, 851, 800, 731 cm^{-1};. HRMS (ESI-TOF) calcd for $C_{22}H_{15}Cl_4N_2O$ $[M+H]^+$ 462.9933, found 462.9936.

6. General procedure for the catalytic enantioselective alkynylation of isatin-derived ketimines and characterization data of compounds 7a-k, 8a-o and 9a-m.

To a solution 1.2 M of $ZnMe_2$ in toluene (0.4 mmol, 0.33 mL) under nitrogen atmosphere, was added the corresponding alkyne (0.4 mmol) and the mixture was stirred at rt for 1 h. Then, a

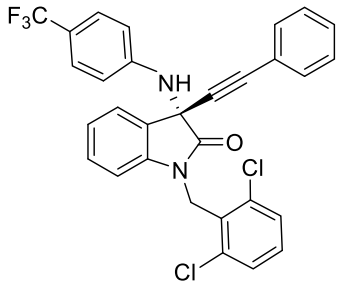
solution 0.1 M of ligand **L2** in toluene (0.02 mmol, 0.20 mL) was added and the reaction stirred for another 30 min, whereupon a solution of the imine (0.1 mmol) in DCM (1 mL) was added dropwise and the reaction stirred at rt for 18 h. The reaction was quenched with NH_4Cl, extracted with DCM, dried over $MgSO_4$, filtered and concentrated. Purification in column chromatography (hexane/DCM 3:1 to 1:2) afforded the pure product.

(*S*)-1-(2,6-Dichlorobenzyl)-3-(phenylamino)-3-(phenylethynyl)indolin-2-one (7a). This



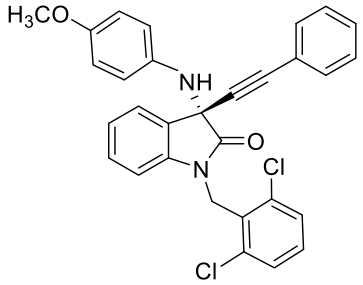
compound was obtained from **6a** (0.1 mmol, 38 mg). White solid, yield: 45 mg, 92%; m.p. 203-204 °C; $[\alpha]_D^{25}$ = +132.5 (*c* 0.8, CH_2Cl_2, 98% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.66 (s, 1H), 5.15 (d, *J* = 15.2 Hz, 1H), 5.40 (d, *J* = 15.2 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 2H), 6.79 (m, 2H), 7.04-7.12 (m, 3H), 7.21 (m, 2H), 7.26-7.32 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.41 (dd, J_1 = 7.6 Hz, J_2 = 1.7 Hz, 2H), 7.52 (dd, J_1 = 8.0 Hz, J_2 = 0.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.6, 59.3, 85.2, 85.7, 109.9, 116.8, 120.2, 121.9, 123.4, 124.5, 128.1, 12.87, 128.9, 129.0, 129.8, 129.9, 130.0, 131.9, 136.4, 141.5, 144.1, 172.6; IR (neat) ν 3368, 1716, 1601, 1487, 1433, 1343, 751, 688 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{21}Cl_2N_2O$ $[M+H]^+$ 483.1025, found 483.1036; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 8.5 min, t_R (minor) = 13.1 min.

(*S*)-1-(2,6-Dichlorobenzyl)-3-(phenylethynyl)-3-((4-(trifluoromethyl)phenyl)amino)indolin-2-one (7b). This compound was obtained from **6b** (0.1 mmol, 46 mg). White solid, yield: 53 mg,



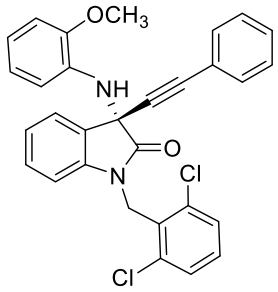
95%; m.p. 231-233 °C; $[\alpha]_D^{25}$ = +53.1 (*c* 0.6, CH_2Cl_2, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.94 (s, 1H), 5.20 (d, *J* = 15.2 Hz, 1H), 5.40 (d, *J* = 15.2 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 1H), 7.09 (td, J_1 = 7.6 Hz, J_2 = 0.6 Hz, 1H), 7.22 (m, 1H), 7.25 (m, 1H), 7.28-7.36 (m, 7H), 7.41 (dd, J_1 = 8.1 Hz, J_2 =1.5 Hz, 2H), 7.51 (dd, *J* = 7.5, 1.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.7, 58.6, 84.8, 85.8, 110.1, 114.9, 121.2 (q, *J* = 32.7 Hz), 123.6, 124.2, 126.3 (q, *J* = 3.8 Hz), 126.8 (q, *J* = 271.0 Hz) 128.3, 128.4, 128.9, 129.8, 130.0, 130.2, 131.9, 136.4, 141.4, 146.9, 172.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.4; IR (neat) ν 3345, 1719, 1611, 1487, 1323, 1104, 1064, 758, 751 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{20}Cl_2F_3N_2O$ $[M+H]^+$ 551.0899, found: 551.0906; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 6.4 min, t_R (minor) = 16.1 min.

(*S*)-1-(2,6-Dichlorobenzyl)-3-((4-methoxyphenyl)amino)-3-(phenylethynyl)indolin-2-one (7c).



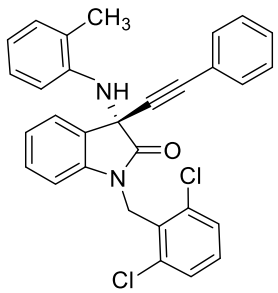
This compound was obtained from **6c** (0.1 mmol, 42 mg). White solid, yield: 37 mg, 71%; m.p. 194-195 °C; $[\alpha]_D^{25}$ = +20.8 (*c* 0.6, CH_2Cl_2, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 (s, 3H), 4.33 (s, 1H), 5.11 (d, *J* = 15.2 Hz, 1H), 5.33 (d, *J* = 15.2 Hz, 1H), 6.68 (d, *J* = 9.0 Hz, 2H), 6.73 (m, 1H), 6.73 (d, *J* = 8.9 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 8.2 Hz, 2H), 7.26-7.30 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.41 (dd, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.5, 55.4, 60.4, 85.3, 86.0, 109.8, 114.1, 121.9, 122.0, 123.1, 125.0, 128.1, 128.6, 128.9, 129.0, 129.7, 129.8, 130.0, 131.9, 136.4, 137.1, 141.8, 155.0, 172.9; IR (neat) ν 3331, 1729, 1608, 1511, 1228, 1168, 755 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{22}Cl_2N_2NaO_2$ $[M+H]^+$ 535.0951, found 535.0968; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 10.9 min, t_R (minor) = 22.3 min.

(*S*)-1-(2,6-Dichlorobenzyl)-3-((2-methoxyphenyl)amino)-3-(phenylethynyl)indolin-2-one (7d).



This compound was obtained from **6d** (0.1 mmol, 41 mg). White solid, yield: 44 mg, 85%; m.p. 168-171 °C; $[\alpha]_D^{25}$ = +22.7 (*c* 0.8, CH_2Cl_2, 30% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3H), 5.16 (d, *J* = 15.2 Hz, 1H), 5.34 (s, 1H), 5.44 (d, *J* = 15.2 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.73 (7, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.26-7.31 (3H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.6, 55.5, 58.9, 85.1, 85.8, 109.8, 109.9, 113.7, 119.0, 120.7, 122.0, 123.4, 124.3, 128.1, 128.7, 128.9, 129.3, 129.7, 129.8, 130.1, 131.9, 134.0, 136.4, 141.5, 147.7, 172.7; IR (neat) ν 3412, 1739, 1601, 1433, 1336, 1239, 751, 728 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{23}Cl_2N_2O_2$ $[M+H]^+$ 513.1131, found 513.1147; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 93:7, 0.7 mL/min, λ = 254 nm, t_R (major) = 27.5 min, t_R (minor) = 31.4 min.

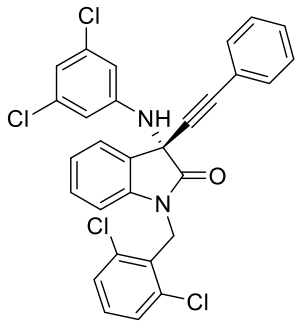
(*S*)-1-(2,6-Dichlorobenzyl)-3-(phenylethynyl)-3-(o-tolylamino)indolin-2-one (7e). This



compound was obtained from **6e** (0.1 mmol, 40 mg). White solid, yield: 19 mg, 38%; m.p. 146-148 °C; $[\alpha]_D^{25}$ = +33.5 (*c* 0.4, CH_2Cl_2, 90% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.27 (s, 3H), 4.50 (s, 1H), 5.18 (d, *J* = 15.2 Hz, 1H), 5.43 (d, *J* = 15.2 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.93 (t, *J* = 8.4 Hz, 1H), 7.03-7.07 m, (m, 2H), 7.19-7.24 (m, 2H), 7.26-7.32 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.42

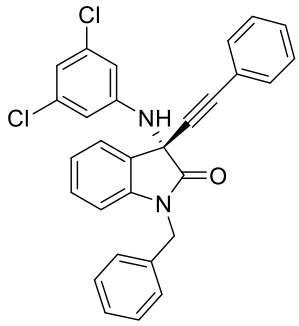
(dd, J_1 = 7.9 Hz, J_2 = 1.6 Hz, 2H), 7.48 (dd, J_1 = 7.7 Hz, J_2 = 0.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.8, 40.7, 59.2, 85.1, 85.9, 109.9, 114.4, 119.6, 121.9, 123.4, 124.3, 124.6, 124.7, 126.6, 128.1, 128.7, 128.9, 129.2, 129.7, 129.8, 130.0, 130.3, 131.9, 136.4, 141.5, 142.3, 172.7; IR (neat) ν 3425, 1729, 1601, 1487, 1437, 1336, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{23}Cl_2N_2O$ $[M+H]^+$ 497.1182, found 497.1198; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 7.9 min, t_R (minor) = 9.1 min.

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(phenylethynyl)indolin-2-one (7g). This compound was obtained from **6g** (0.1 mmol, 45 mg). White solid, yield: 54 mg, 98%;



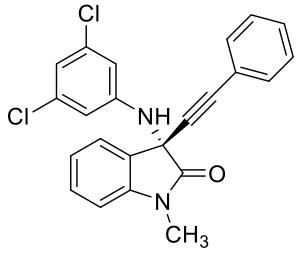
m.p. 225-227 °C; $[\alpha]_D^{25}$ = +29.9 (*c* 0.7, CH_2Cl_2, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (s, 1H), 5.21 (d, *J* = 15.2 Hz, 1H), 5.35 (d, *J* = 15.2 Hz, 1H), 6.65 (d, *J* = 1.7 Hz, 2H), 6.77 (t, *J* = 1.7 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 7.10 (td, *J* = 7.6, 0.8 Hz, 1H), 7.20-7.33 (m, 5H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.1, 1.6 Hz, 2H), 7.50 (dd, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.6, 58.6, 84.4, 86.4, 110.2, 114.5, 119.6, 121.5, 123.7, 124.2, 128.2, 129.0, 129.8, 130.0, 130.4, 131.9, 135.0, 136.4, 141.5, 145.9, 171.8.); IR (neat) ν 3335, 1712, 1591, 1437, 1343, 1084, 990, 758 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{19}Cl_4N_2O$ $[M+H]^+$ 551.0246, found. 551.0243; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 6.1 min, t_R (minor) = 11.7 min.

(*S*)-1-Benzyl-3-((3,5-dichlorophenyl)amino)-3-(phenylethynyl)indolin-2-one (7h). This



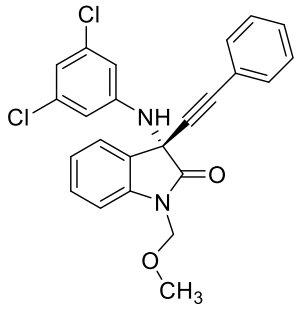
compound was obtained from **6h** (0.1 mmol, 38 mg). White solid, yield: 45 mg, 93%; m.p. 183-185 °C; $[\alpha]_D^{25}$ = −33.6 (*c* 0.6, CH_2Cl_2, 88% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (d, *J* = 15.7 Hz, 1H), 4.94 (s, 1H), 5.11 (d, *J* = 15.7 Hz, 1H), 6.51 (d, *J* = 1.0 Hz, 2H), 6.75 (m, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 7.13 (td, J_1 = 7.6 Hz, J_2 = 0.7 Hz, 1H), 7.26-7.35 (m, 9H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 44.6, 59.3, 84.5, 86.0, 110.3, 110.4, 114.3, 114.5, 119.8, 119.9, 121.3, 123.9, 124.2, 124.4, 127.1, 127.3, 128.0, 128.3, 129.1, 130.4, 131.9, 132.1, 134.9, 135.1, 141.7, 146.0, 172.7; IR (neat) ν 3311, 1716, 1595, 1454, 755, 688 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{21}Cl_2N_2O$ $[M+H]^+$ 483.1025, found 483.1040; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 7.0 min, t_R (minor) = 15.7 min.

(*S*)-3-((3,5-Dichlorophenyl)amino)-1-methyl-3-(phenylethynyl)indolin-2-one (7i). This



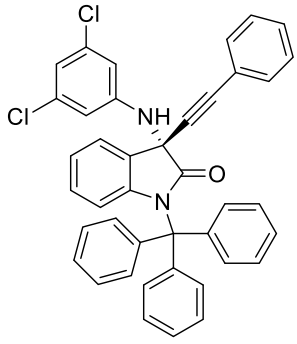
compound was obtained from **6i** (0.1 mmol, 32 mg). White solid, yield: 38 mg, 90%; m.p. 198-200 °C; $[\alpha]_D^{25}$ = −43.7 (*c* 0.7, CH_2Cl_2, 92% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30 (s, 3H), 4.75 (s, 1H), 6.54 (m, 2H), 6.75 (m, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.26-7.34 (m, 3H), 7.40-7.46 (m, 3H), 7.52 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.8, 58.9, 84.2, 86.1, 109.1, 114.2, 119.6, 121.3, 124.0, 124.3, 128.2, 129.1, 130.5, 132.0, 135.0, 142.6, 146.0, 172.4; IR (neat) ν 3294, 1709, 1581, 1447, 751, 684 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{17}Cl_2N_2O$ $[M+H]^+$ 407.0712, found 407.0726; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 6.3 min, t_R (minor) = 10.8 min.

(*S*)-3-((3,5-Dichlorophenyl)amino)-1-(methoxymethyl)-3-(phenylethynyl)indolin-2-one (7j).



This compound was obtained from **6j** (0.1 mmol, 35 mg). White solid, yield: 43 mg, 93%; m.p. 127-129 °C; $[\alpha]_D^{25}$ = −7.7 (*c* 0.9, CH_2Cl_2, 90% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35 (s, 3H), 4.84 (s, 1H), 5.17 (d, *J* = 11.0 Hz, 1H), 5.23 (d, *J* = 11.0 Hz, 1H), 6.50 (d, *J* = 1.6 Hz, 2H), 6.74 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.26-7.33 (m, 3H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.7, 59.4, 72.1, 84.3, 86.2, 110.8, 114.1, 119.8, 121.2, 124.3, 124.5, 127.6, 128.2, 129.1, 130.6, 132.0, 135.1, 140.8, 145.9, 173.1; IR (neat) ν 3304, 1719, 1591, 1454, 1084, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{19}Cl_2N_2O_2$ $[M+H]^+$: 437.0818, found 437.0834; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 6.4 min, t_R (minor) = 10.7 min.

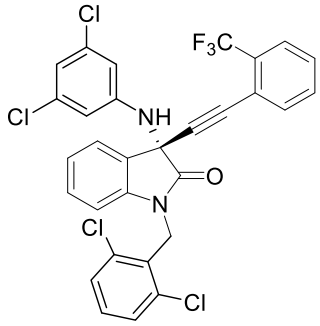
(*S*)-3-((3,5-Dichlorophenyl)amino)-3-(phenylethynyl)-1-tritylindolin-2-one (7k). This



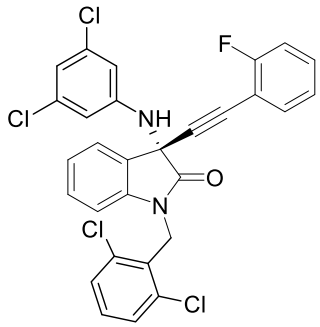
compound was obtained from **6k** (0.1 mmol, 55 mg). White solid, yield: 62 mg, 95%; m.p. 226-228 °C; $[\alpha]_D^{25}$ = +48.3 (*c* 0.6, CH_2Cl_2, 74% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.84 (s, 1H), 6.19 (d, *J* = 1.4 Hz, 2H), 6.42 (d, *J* = 8.8 Hz, 1H), 6.70 (m, 1H), 7.02 (m, 2H), 7.20-7.22 (m, 3H), 7.25-7.28 (m, 6H), 7.32-7.39 (m, 3H), 7.44-7.47 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 60.1, 74.4, 85.1, 85.3, 114.4, 114.5, 116.6, 119.7, 119.7, 121.5, 123.1, 123.4, 127.0, 127.8, 128.4, 128.7, 129.0, 129.1, 131.9, 134.9, 141.5, 142.7, 146.0, 173.9; IR (neat) ν 3332, 1727, 1593, 1448, 754, 704 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{41}H_{29}Cl_2N_2O$ $[M+H]^+$635.1651, found 635.1679; HPLC: Phenomenex Lux

Cellulose-1, hexane:2-propanol 83:17, 0.5 mL/min, λ = 254 nm, t_R (major) = 8.6 min, t_R (minor) = 21.4 min.

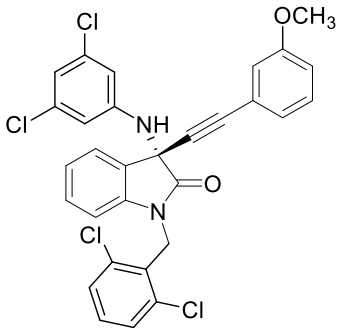
(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((2-(trifluoromethyl)phenyl)ethynyl)indolin-2-one (8a). This compound was obtained from **6g** (0.1 mmol, 45 mg) White solid, yield: 61 mg, 98%; m.p. 172-174 °C; $[\alpha]_D^{25}$ = −8.8 (*c* 0.6, CH_2Cl_2, 88% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.66 (s, 1H), 5.22 (d, *J* = 15.2 Hz, 1H), 5.33 (d, *J* = 15.2 Hz, 1H), 6.70 (m, 2H), 6.79 (d, *J* = 8.2 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.20-7.28 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.49 (dd, J_1 = 14.6 Hz, J_2 = 7.5 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.7, 58.6, 82.3, 89.7, 110.1, 114.6, 119.8,120.8 (q, *J* =275.0 Hz) 123.7, 124.4, 125.8 (q, *J* = 3.0 Hz), 127.8, 128.8, 128.9, 129.7, 130.0, 130.5, 131.3, 131.9 (q, *J* = 30.7 Hz), 134.2, 134.9, 136.4, 141.5, 145.7, 171.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.11; IR (neat) ν 3319, 1706, 1585, 1318, 1127, 751 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{30}H_{18}Cl_4F_3N_2O$ $[M+H]^+$ 619.0120, found 619.0154; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 5.8 min, t_R (minor) = 7.6 min.



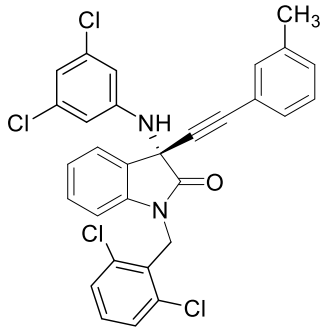
(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((2-fluorophenyl)ethynyl)indolin-2-one (8b). This compound was obtained from **6g** (0.1 mmol, 45 mg). White solid, yield: 55 mg, 97%; m.p. 212-213 °C; $[\alpha]_D^{25}$ = +20.0 (*c* 0.7, CH_2Cl_2, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (s, 1H), 5.21 (d, *J* = 15.2 Hz, 1H), 5.35 (d, *J* = 15.2 Hz, 1H), 6.68 (m, 2H), 6.78 (d, *J* = 9.2 Hz, 2H), 7.03-7.11 (m, 3H), 7.22 (t, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.31 (ddd, J_1 = 8.3 Hz, J_2 = 7.7 H, J_3 = 1.2 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.6, 58.7, 80.0, 89.4, 110.2, 110.3 (d, *J* = 15.7 Hz), 114.6, 115.5(d , *J* = 20.6 Hz) 119.7, 123.7, 123.9 (d, *J* = 3.8 Hz), 124.4, 128.1, 129.0, 129.7, 130.0, 130.5, 130.8 (d, *J* = 8.0 Hz), 133.7, 134.9, 136.4, 141.5, 145.8, 163.0 (d, *J* = 253.4 Hz), 171.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -108.8; IR (neat) ν 3289, 1717, 1593, 1452, 754 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{18}Cl_4FN_2O$ $[M+H]^+$ 569.0152, found 569.0173; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 8.4 min, t_R (minor) = 14.1 min.



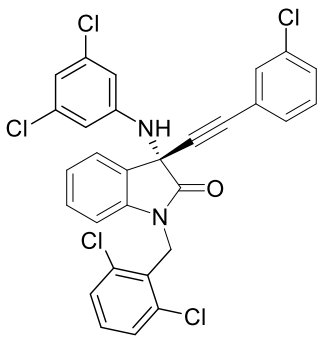
(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((3-methoxyphenyl)ethynyl)indolin-2-one (8c). This compound was obtained from **6g** (0.1 mmol, 45 mg). White solid, yield; 57 mg, 98%; m.p. 162-164 °C; $[\alpha]_D^{25}$ = +45.0 (*c* 0.8, CH_2Cl_2, 90% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.70 (s, 1H), 5.21 (d, *J* = 15.2 Hz, 1H), 5.35 (d, *J* = 15.2 Hz, 1H), 6.66 (d, *J* = 1.7 Hz, 2H), 6.77 (t, *J* = 1.7 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.88 (dd, J_1 = 7.9 Hz, J_2 = 3.0 Hz, 1H), 6.93 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.19 (dd, J_1 = 11.2 Hz, J_2 = 4.6 Hz, 1H), 7.22-7.27 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.50 (dd, J_1 = 7.4 Hz, J_2 = 0.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.6, 55.3, 58.6, 84.1, 86.4, 110.2, 114.5, 115.9, 116.4, 119.6, 122.4, 123.7, 124.3, 124.4, 128.2, 129.0, 129.3, 129.7, 130.0, 130.4, 134.9, 136.4, 141.5, 145.9, 159.2, 171.8; IR (neat) ν 3312, 1710, 1589, 1200, 781, 744 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{21}Cl_4N_2O_2$ $[M+H]^+$ 581.0352, found 581.0374. HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 11.1 min, t_R (minor) = 13.9 min.



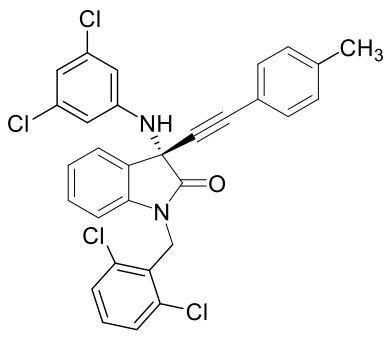
(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(m-tolylethynyl)indolin-2-one (8d). This compound was obtained from **6g** (0.1 mmol, 45 mg). White solid, yield: 55 mg, 97%; m.p. 185-186 °C; $[\alpha]_D^{25}$ = +22.2 (*c* 0.7, CH_2Cl_2, 86% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 4.71 (s, 1H), 5.21 (d, *J* = 15.8 Hz, 1H), 5.35 (d, *J* = 15.8 Hz, 1H), 6.65 (m, 2H), 6.76 (m, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.13-7.27 (m, 6H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.1, 40.6, 58.6, 84.0, 86.7, 110.1, 114.5, 119.6, 121.3, 123.7, 124.2, 128.1, 128.3, 128.9, 129.0, 129.8, 129.9, 129.9, 130.4, 132.5, 134.9, 136.4, 137.9, 141.5, 145.9, 171.8; IR (neat) ν 3319, 1723, 1582, 1442, 985, 751 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{21}Cl_4N_2O$ $[M+H]^+$ 565.0403, found 565.0420; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 9.2 min, t_R (minor) = 17.1 min.



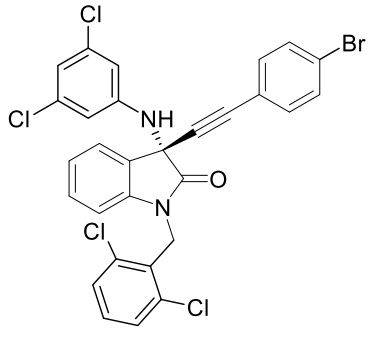
(*S*)-3-((3-Chlorophenyl)ethynyl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)indolin-2-one (8e). This compound was obtained from **6g** (0.1 mmol, 45 mg). White solid, yield: 57 mg, 97%; m.p. 170-173 °C; $[\alpha]_D^{25}$ = +23.9 (*c* 0.8, CH_2Cl_2, 92% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (s, 1H), 5.21 (d, *J* = 15.2 Hz, 1H), 5.35 (d, *J* = 15.2 Hz, 1H), 6.65 (d, *J* = 1.6 Hz, 2H), 6.77 (t, *J* = 1.4 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.23 (td, J_1 = 8.0 Hz, J_2 = 2.3 Hz, 2H), 7.26-7.31 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.39 (m, 1H), 7.49 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.7, 58.6, 85.0, 85.5, 110.2, 114.6, 119.8, 123.1, 123.7, 124.2, 128.0, 129.0, 129.3, 129.5, 129.7, 130.0, 130.6, 131.7, 134.1, 135.0, 136.4, 141.5, 145.7, 171.6; IR (neat) ν 3299, 1713, 1582, 1445, 748, 694 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{18}Cl_5N_2O$ $[M+H]^+$ 584.9856, found 584.9878; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 90:10, 1 mL/min, λ = 254 nm, t_R (major) = 13.3 min, t_R (minor) = 16.0 min.



(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(*p*-tolylethynyl)indolin-2-one (8f). This compound was obtained from **6g** (0.1 mmol, 46 mg). White solid, yield: 57 mg, 98%; m.p. 243-244 °C; $[\alpha]_D^{25}$ = +27.1 (*c* 0.8, CH_2Cl_2, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 4.70 (s, 1H), 5.21 (d, *J* = 15.2 Hz, 1H), 5.35 (d, *J* = 15.2 Hz, 1H), 6.63 (d, *J* = 1.7 Hz, 2H), 6.76 (t, *J* = 1.7 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 7.08-7.11 (m, 3H), 7.20-7.27 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.49 (dd, J_1 = 7.4 Hz, J_2 = 1.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5, 40.6, 58.7, 83.7, 86.6, 110.1, 114.4, 118.4, 119.5, 123.6, 124.2, 128.3, 129.0, 129.8, 129.9, 130.3, 131.8, 134.9, 136.4, 139.2, 141.5, 145.9, 171.9; IR (neat) ν 3339, 1710, 1586, 1432, 1344, 989, 825, 744 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{21}Cl_4N_2O$ $[M+H]^+$ 565.0403, found 565.0411; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 70:30, 1 mL/min, λ = 1 nm, t_R (major) = 6.6 min, t_R (minor) = 9.0 min.

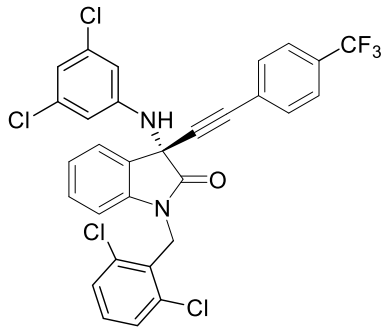


(*S*)-3-((4-Bromophenyl)ethynyl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)indolin-2-one (8g). This compound was obtained from **6g** (0.1 mmol, 46 mg). White solid, yield: 62 mg, 96%; m.p. 233-234 °C; $[\alpha]_D^{25}$ = +24.6 (*c* 0.4, CH_2Cl_2, 96% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.67 (s, 1H), 5.20 (d, *J* = 15.2 Hz, 1H), 5.35 (d, *J* = 15.2 Hz, 1H), 6.65 (d, *J* = 1.7 Hz, 2H), 6.77 (t, *J* = 1.7 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.23 (m, 1H), 7.25-7.29 (m, 3H),

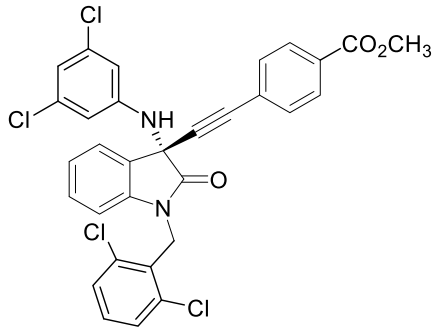


7.36 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.6, 58.6, 85.4, 85.5, 110.2, 114.6, 119.8, 120.4, 123.4, 123.7, 124.2, 128.0, 129.0, 129.7, 130.0, 130.5, 131.5, 133.3, 135.0, 136.3, 141.5, 145.8, 171.6; IR (neat) ν 3332, 1720, 1593, 1435, 1341, 982, 825, 744 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{17}BrCl_4N_2NaO$ $[M+Na]^+$ 650.9171, found 650.9173; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 90:10, 0.7 mL/min, λ = 254 nm, t_R (major) = 20.0 min, t_R (minor) = 17.9 min.

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((4-(trifluoromethyl)phenyl)ethynyl)indolin-2-one (8h). This compound was obtained from **6g** (0.1 mmol, 45 mg). White solid, yield: 61 mg, 98%; m.p. 200-202 °C; $[\alpha]_D^{25}$ = +14.3 (*c* 0.8, CH_2Cl_2, 98% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.72 (s, 1H), 5.21 (d, *J* = 15.2 Hz, 1H), 5.36 (d, *J* = 15.2 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 2H), 6.79 (t, *J* = 1.7 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 7.11 (td, J_1 = 7.6 Hz, J_2 = 0.9 Hz, 1H), 7.23 (m, 1H), 7.28 (td, *J* = 7.9, 1.3 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 3H), 7.55 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.7, 58.6, 85.0, 86.7, 110.3, 114.6, 119.8, 123.7 (q, *J* = 272.3 Hz), 123.8, 124.3, 125.2 (q, *J* = 3.0 Hz), 127.9, 129.0, 129.7, 130.1, 130.6, 130.7, 130.8, 132.1, 135.0, 136.4, 141.5, 145.7, 171.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.9; IR (neat) ν 3344, 1717, 1590, 1326, 1130, 1061, 989, 844, 746 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{17}Cl_4F_3N_2NaO$ $[M+Na]^+$ 640.9939, found 640.9948; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 90:10, 1 mL/min, λ = 254 nm, t_R (major) = 16.2 min, t_R (minor) = 11.0 min.

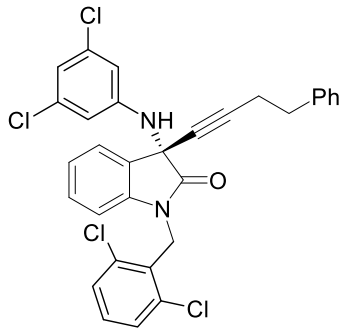


Methyl (*S*)-4-((1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-2-oxoindolin-3-yl)ethynyl)benzoate (8i). This compound was obtained from **6g** (0.1 mmol, 46 mg). White solid, yield: 59 mg, 96%; m.p. 181-182 °C; $[\alpha]_D^{25}$ = +21.1 (*c* 1.1, CH_2Cl_2, 96% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.91 (s, 3H), 4.75 (s, 1H), 5.21 (d, *J* = 15.2 Hz, 1H), 5.35 (d, *J* = 15.2 Hz, 1H), 6.66 (d, *J* = 1.7 Hz, 2H), 6.78 (t, *J* = 1.7 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 7.10 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.23 (m, 1H), 7.27 (td, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.50 (dd, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$); δ 40.7, 52.2, 58.7, 85.6, 87.2, 110.3, 112.8, 114.5, 118.6, 119.7, 122.9, 123.8, 124.3, 126.1, 127.9, 129.0, 129.4, 129.7, 130.0, 130.2, 130.6, 131.8, 135.0, 136.4, 141.5, 145.8, 166.3, 171.7. IR (neat) ν 3340, 1717, 1590,

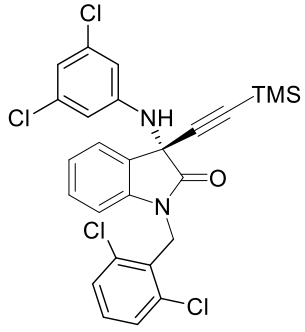


1434, 1275, 1090, 985, 750 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{20}Cl_4N_2NaO_3$ $[M+Na]^+$ 631.0120, found 631.0131; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 90:10, 1 mL/min, λ = 254 nm, t_R (major) = 24.1 min, t_R (minor) = 20.9 min.

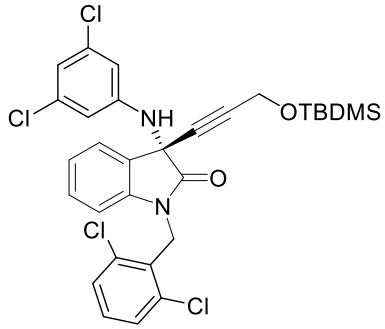
(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(4-phenylbut-1-yn-1-yl)indolin-2-one (8j). This compound was obtained from **6g** (0.1 mmol, 45 mg). White solid, yield: 56 mg, 96%; m.p. 166-169 °C (from AcOEt); $[\alpha]_D^{25}$ = −5.6 (*c* 1.2, CH_2Cl_2, 92% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.48 (t, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 4.59 (s, 1H), 5.19 (d, *J* = 15.2 Hz, 1H), 5.30 (d, *J* = 15.2 Hz, 1H), 6.51 (d, *J* = 1.2 Hz, 2H), 6.73 (t, *J* = 1.2 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.13 (m, 2H), 7.17-7.26 (m, 5H), 7.34-7.37 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.0, 34.4, 40.6, 58.2, 76.7, 86.8, 110.1, 114.2, 119.4, 123.5, 124.1, 126.3, 128.3, 128.4, 128.5, 128.9, 129.8, 129.9, 130.2, 134.9, 136.4, 140.1, 141.6, 145.9, 172.1; IR (neat) ν 3289, 1713, 1582, 1445, 748, 694 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{23}Cl_4N_2O$ $[M+H]^+$ 579.0559, found. 579.0587; HPLC: Phenomenex Lux Cellulose-2, hexane:2-propanol 95:5, 0.7 mL/min, λ = 254 nm, t_R (major) = 15.7 min, t_R (minor) = 19.9 min.



(*R*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((trimethylsilyl)ethynyl)indolin-2-one (8k). This compound was obtained from **6g** (0.1 mmol, 45 mg). White solid, yield: 52 mg, 95%; m.p. 157-158 °C; $[\alpha]_D^{25}$ = +2.9 (*c* 0.4, CH_2Cl_2, 90% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16 (s, 9H), 4.54 (s, 1H), 5.16 (d, *J* = 15.2 Hz, 1H), 5.33 (d, *J* = 15.2 Hz, 1H), 6.63 (d, *J* = 1.7 Hz, 2H), 6.74-6.76 (2H), 7.07 (td, J_1 = 7.6 Hz, J_2 = 0.9 Hz, 1H), 7.20-7.26 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ -0.42, 40.5, 58.6, 92.4, 99.5, 110.0, 114.5, 119.6, 123.6, 124.2, 128.2, 129.0, 129.7, 129.9, 130.3, 134.8, 136.4, 141.5, 145.8, 171.6; IR (neat) ν 3346, 1713, 1586, 989, 841, 751 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{26}H_{22}Cl_4N_2NaOSi$ $[M+Na]^+$ 569.0148, found 569.0149; HPLC: Phenomenex Lux i-Amylose-3, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 16.2 min, t_R (minor) = 18.2 min.

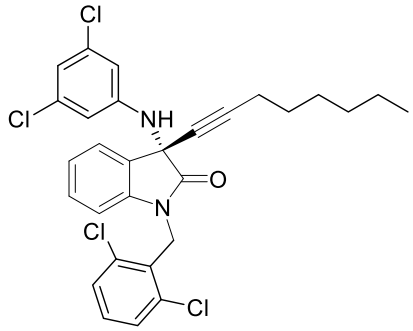


(*S*)-3-(3-((Tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)indolin-2-one (8l). This compound was obtained from **6g** (0.1 mmol, 43



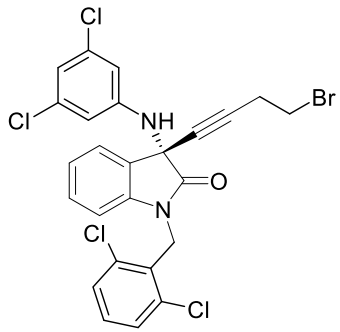
mg). White solid, yield: 56 mg, 95%; m.p. 134-136 °C; $[\alpha]_D^{25}$ = −17.4 (*c* 0.4, CH_2Cl_2, 96% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.04 (s, 3H), 0.05 (s, 3H), 0.85 (s, 9H), 4.32 (s, 2H), 4.64 (s, 1H), 5.19 (d, *J* = 15.1 Hz, 1H), 5.29 (d, *J* = 15.1 Hz, 1H), 6.51 (d, *J* = 1.7 Hz, 2H), 6.74 (t, *J* = 1.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 1.9 Hz, 1H), 7.20-7.26 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ -5.22, 18.1, 25.7, 40.7, 51.6, 58.2, 80.1, 85.1, 110.1, 114.3, 119.6, 123.6, 124.2, 127.9, 128.9, 129.8, 130.0, 130.4, 135.0, 136.4, 141.5, 145.8, 171.6; IR (neat) ν 3319, 1720, 1589, 1435, 1093, 835, 784, 744 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{30}Cl_4N_2NaO_2Si$ $[M+Na]^+$ 641.0723, found 641.0714; HPLC: Phenomenex Lux i-Amylose-3, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 23.8 min, t_R (minor) = 12.3 min.

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(oct-1-yn-1-yl)indolin-2-one (8m).



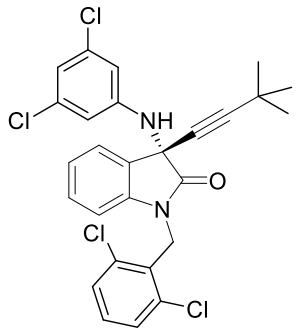
This compound was obtained from **6g** (0.1 mmol, 45 mg). Pale yellow solid, yield: 54 mg, 96%; m.p. 180-182 °C (from AcOEt); $[\alpha]_D^{25}$ = −5.2 (*c* 0.5, CH_2Cl_2, 88% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.20-1.34 (m, 6H), 1.48 (m, 2H), 2.18 (t, *J* = 7.2 Hz, 2H), 4.58 (s, 1H), 5.17 (d, *J* = 15.2 Hz, 1H), 5.31 (d, *J* = 15.2 Hz, 1H), 6.57 (d, *J* = 1.7 Hz, 2H), 6.73 (t, *J* = 1.7 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 7.06 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.20-7.24 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.41 (dd, J_1 = 7.4 Hz, J_2 =1.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.0, 18.8, 22.4, 28.1, 28.4, 31.2, 40.5, 58.2, 75.7, 87.9, 110.0, 114.3, 119.4, 123.5, 124.0, 128.8, 128.9, 129.9, 129.9, 130.1, 134.9, 136.4, 141.4, 146.0, 172.2; IR (neat) ν 3309, 1717, 1586, 1435, 751 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{29}H_{27}Cl_4N_2O$ $[M+H]^+$ 559.0872, found 559.0894; HPLC: Phenomenex Lux i-Amylose-1, hexane:2-propanol 70:30, 1 mL/min, λ = 254 nm, t_R (major) = 28.8 min, t_R (minor) = 14.6 min.

(*S*)-3-(4-Bromobut-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)indolin-2-one (8n). This compound was obtained from **6g** (0.1 mmol, 46 mg). White solid, yield: 58 mg, 97%; m.p. 154-155 °C (from AcOEt); $[\alpha]_D^{25}$ = −6.4 (*c* 0.9, CH_2Cl_2, 88% ee); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.77 (t, *J* = 7.2 Hz, 2H), 3.39 (t, *J* = 7.2 Hz, 2H), 4.57 (s, 1H), 5.18 (d, *J* = 15.2 Hz, 1H), 5.31 (d, *J* = 15.2 Hz, 1H), 6.59 (m, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.20-7.26 (m,

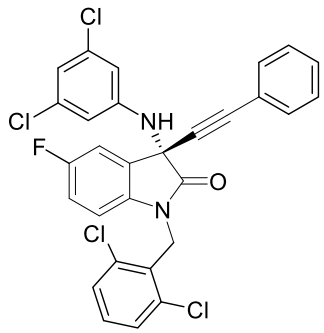


2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.2, 28.5, 40.6, 58.1, 77.8, 84.2, 110.1, 114.5, 119.7, 123.6, 124.1, 128.2, 129.0, 129.7, 130.0, 130.4, 134.9, 136.4, 141.4, 145.8, 171.8; IR (neat) ν 3312, 1720, 1586, 1435, 989, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{25}H_{18}BrCl_4N_2O$ $[M+H]^+$ 580.9351, found 580.9367; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 8.9 min, t_R (minor) = 10.9 min.

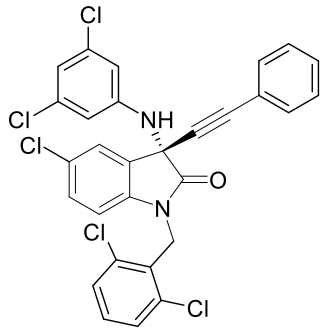
(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(3,3-dimethylbut-1-yn-1-yl)indolin-2-one (8o). This compound was obtained from **6g** (0.1 mmol, 44 mg). Colorless oil, yield: 50 mg, 94%; $[\alpha]_D^{25}$ = +12.6 (*c* 0.7, CH_2Cl_2, 78% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 9H), 4.48 (s, 1H), 5.14 (d, *J* = 15.2 Hz, 1H), 5.33 (d, *J* = 15.2 Hz, 1H), 6.66 (d, *J* = 1.7 Hz, 2H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.74 (t, *J* = 1.7 Hz, 1H), 7.06 (td, J_1 = 7.6 Hz, J_2 = 0.9 Hz, 1H), 7.21 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.40 (dd, J_1 = 7.5 Hz, J_2 = 0.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 27.5, 30.5, 40.4, 58.0, 74.1, 95.9, 109.9, 114.5, 119.3, 123.5, 124.0, 129.0, 129.1, 129.8, 129.9, 130.1, 134.8, 136.4, 141.4, 146.1, 172.2; IR (neat) ν 3344, 1710, 1579, 1456, 1351, 989, 757 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{27}H_{23}Cl_4N_2O$ $[M+H]^+$ 531.0559, found 531.0556; HPLC: Phenomenex Lux i-Amylose-1, hexane:2-propanol 90:10, 0.7 mL/min, λ = 254 nm, t_R (major) = 28.7 min, t_R (minor) = 25.1 min.



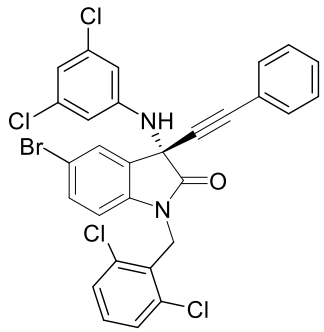
(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-5-fluoro-3-(phenylethynyl)indolin-2-one (9a). This compound was obtained from **6n** (0.1 mmol, 47 mg). White solid, yield: 56 mg, 98%; m.p. 221-222 °C; $[\alpha]_D^{25}$ = +40.3 (*c* 0.7, CH_2Cl_2, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.75 (s, 1H), 5.20 (d, *J* = 15.2 Hz, 1H), 5.36 (d, *J* = 15.2 Hz, 1H), 6.56 (d, *J* = 1.7 Hz, 2H), 6.75 (m, 1H), 6.79 (t, *J* = 1.7 Hz, 1H), 6.97 (td, J_1 = 8.8 Hz, J_2 = 2.7 Hz, 1H), 7.23-7.26 (2H), 7.29-7.35 (3H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.43 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.8, 58.9, 83.9, 86.6, 111.0 (d, *J* = 7.9 Hz), 112.4 (d, *J* = 25.0 Hz), 114.3, 116.9 (d, *J* =23.6 Hz), 119.9, 121.2, 128.3, 129.0, 129.2, 129.5, 129.7 (d, *J* = 7.7 Hz), 130.1, 131.9, 135.1, 136.4, 137.4 (d, *J* = 2.3 Hz), 145.6, 159.6 (d, *J* = 243.9 Hz), 171.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ -118.1; IR (neat) ν 3309, 1710, 1593, 1489, 959, 758 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{18}Cl_4FN_2O$ $[M+H]^+$ 569.0152, found 569.0167; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 8.4 min, t_R (minor) = 17.9 min.



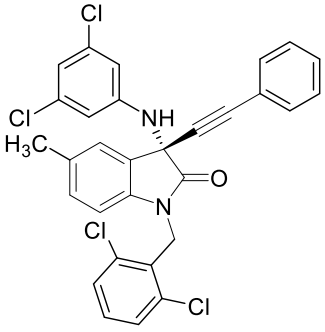
(*S*)-5-Chloro-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(phenylethynyl)indolin-2-one (9b). This compound was obtained from **6o** (0.1 mmol, 48 mg). White solid, yield: 56 mg, 96%; m.p. 197-198 °C; $[\alpha]_D^{25}$ = +66.5 (*c* 0.8, CH_2Cl_2, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.75 (s, 1H), 5.20 (d, *J* = 15.2 Hz, 1H), 5.36 (d, *J* = 15.2 Hz, 1H), 6.58 (d, *J* = 1.7 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.79 (t, *J* = 1.7 Hz, 1H), 7.22-7.26 (2H), 7.29-7.35 (3H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.42 (dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, 2H), 7.48 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.7, 58.6, 83.7, 86.8, 111.2, 114.3, 119.9, 121.9, 124.7, 128.3, 129.0, 129.2, 129.4, 129.8, 130.2, 130.4, 131.9, 135.1, 136.4, 139.9, 145.5, 171.4; IR (neat) ν 3306, 1706, 1586, 1438, 758, 677 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{18}Cl_5N_2O$ $[M+H]^+$ 584.9856, found 584.9868; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 9.1 min, t_R (minor) = 14.6 min.



(*S*)-5-Bromo-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(phenylethynyl)indolin-2-one (9c). This compound was obtained from **6p** (0.1 mmol, 53 mg). White solid, yield: 60 mg, 95%; m.p. 169-171 °C; $[\alpha]_D^{25}$ = +66.4 (*c* 0.5, CH_2Cl_2, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.73 (s, 1H), 5.19 (d, *J* = 15.2 Hz, 1H), 5.35 (d, *J* = 15.2 Hz, 1H), 6.59 (d, *J* = 1.7 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.79 (t, *J* = 1.7 Hz, 1H), 7.25 (m, 1H), 7.29-7.40 (6H), 7.43 (dd, J_1 = 8.2 Hz, J_2 = 1.4 Hz, 2H), 7.61 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.7, 58.6, 83.7, 86.9, 111.7, 114.3, 116.4, 119.9, 121.1, 127.4, 128.3, 129.0, 129.2, 129.4, 130.1, 130.2, 131.9, 133.3, 135.1, 136.3, 140.4, 145.5, 171.2; IR (neat) ν 3312, 1717, 1586, 1482, 1432, 761, 677, 533 cm^{-1}; HRMS (ESI-TOF): calcd for $C_{29}H_{18}BrCl_4N_2O$ $[M+H]^+$ 628.9351, found 628.9365; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 10.2 min, t_R (minor) = 14.9 min.

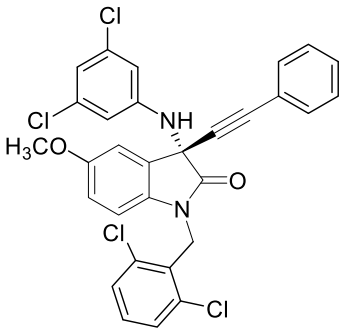


(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-5-methyl-3-(phenylethynyl)indolin-2-one (9d). This compound was obtained from **6q** (0.1 mmol, 45 mg). White solid, yield: 54 mg, 98%; m.p. 236-237 °C; $[\alpha]_D^{25}$ = +42.8 (*c* 0.5, CH_2Cl_2, 99% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (s, 3H), 4.72 (s, 1H), 5.19 (d, *J* = 15.2 Hz, 1H), 5.35 (d, *J* = 15.2 Hz, 1H), 6.64 (d, *J* = 1.8 Hz, 2H), 6.68 (d, *J* = 8.1 Hz, 1H), 6.76 (t, *J* = 1.8 Hz, 1H), 7.05 (dd, J_1 = 8.8 Hz, J_2 = 1.7 Hz, 1H), 7.22 (dd, J_1 = 8.5 Hz, J_2 =7.6 Hz, 1H),



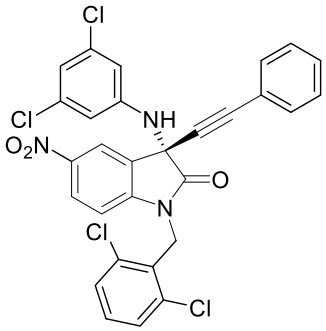
7.29-7.32 (m, 4H), 7.35 (d, J = 8.0 Hz, 2H), 7.42 (dd, J_1 = 8.1 Hz, J_2 =1.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.0, 40.6, 58.7, 84.5, 86.3, 109.9, 114.4, 119.5, 121.5, 124.9, 128.2, 128.9, 129.9, 129.9, 130.7, 133.4, 134.9, 136.4, 139.0, 146.0, 171.8; IR (neat) ν 3306, 1713, 1589, 1435, 1096, 989, 761 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{21}Cl_4N_2O$ $[M+H]^+$ 565.0403, found 565.0416; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 7.7 min, t_R (minor) = 12.7 min.

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-5-methoxy-3-(phenylethynyl)indolin-2-one (9e). This compound was obtained from **6r** (0.1 mmol, 48 mg).



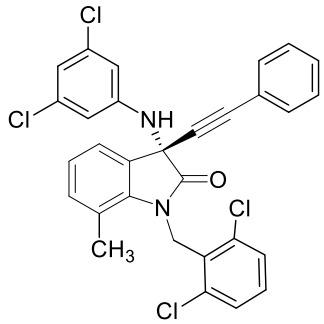
White solid, yield: 57 mg, 98%; m.p. 204-205 °C; $[\alpha]_D^{25}$ = +50.8 (*c* 0.6, CH_2Cl_2, 86% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.83 (s, 1H), 5.19 (d, J = 15.2 Hz, 1H), 5.35 (d, J = 15.2 Hz, 1H), 6.60 (d, J = 1.7 Hz, 2H), 6.71 (d, J = 8.6 Hz, 1H), 6.75 (t, J = 1.7 Hz, 1H), 6.78 (dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz, 1H), 7.10 (d, J = 2.6 Hz, 1H), 7.22 (dd, J_1 = 8.4 Hz, J_2 = 7.7 Hz, 1H), 7.28-7.33 (3H), 7.36 (d, J = 8.0 Hz, 2H), 7.41 (dd, J_1 = 8.2 Hz, J_2 = 1.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.7, 55.7, 59.0, 84.5, 86.3, 110.8, 111.3, 114.3, 115.0, 119.6, 121.4, 128.2, 129.0, 129.4, 129.8, 130.0, 131.9, 134.7, 135.0, 136.4, 145.9, 156.6, 171.9; IR (neat) ν 3312, 1710, 1586, 1492, 1435, 992, 751 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{21}Cl_4N_2O_2$ $[M+H]^+$: 581.0352, found 581.036; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mLmin, λ = 254 nm, t_R (major) = 9.6 min, t_R (minor) = 15.7 min.

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-5-nitro-3-(phenylethynyl)indolin-2-one (9f). This compound was obtained from **6s** (0.1 mmol, 50 mg). Pale yellow solid, yield: 56

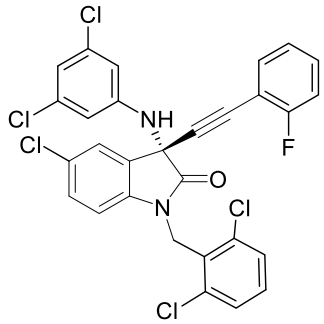


mg, 93%; m.p. 140-143 °C; $[\alpha]_D^{25}$ = +17.1 (*c* 0.6, CH_2Cl_2, 78% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.76 (s, 1H), 5.28 (d, J = 15.3 Hz, 1H), 5.42 (d, J = 15.3 Hz, 1H), 6.56 (d, J = 1.7 Hz, 2H), 6.82 (t, J = 1.7 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 7.28 (m, 1H), 7.31-7.37 (3H), 7.40 (d, J = 8.0 Hz, 2H), 7.43 (dd, J_1 = 8.3 Hz, J_2 = 1.4 Hz, 2H), 8.24 (dd, J_1 = 8.8 Hz, J_2 = 2.3 Hz, 1H), 8.38 (d, J = 2.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.0, 58.3, 82.9, 87.4, 110.0, 114.4, 120.1, 120.4, 120.7, 127.2, 128.4, 128.8, 129.2, 129.5, 130.5, 132.0, 135.2, 136.3, 144.0, 145.1, 146.8, 171.8; IR (neat) ν 3339, 1733, 1593, 1519, 1334, 764 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{18}Cl_4N_3O_3$ $[M+H]^+$ 596.0097, found 596.0105; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 70:30, 1 mL/min, λ = 254 nm, t_R (major) = 20.0 min, t_R (minor) = 16.0 min.

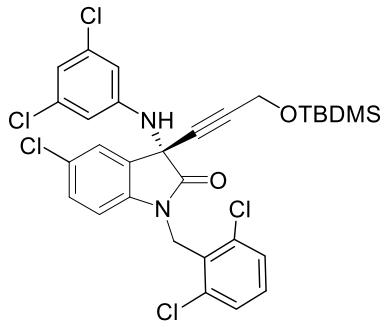
(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-7-methyl-3-(phenylethynyl)indolin-2-one (9g). This compound was obtained from **6t** (0.1 mmol, 45 mg). White solid, yield: 53 mg, 97%; m.p. 188-191 °C; $[\alpha]_D^{25}$ = −73.0 (*c* 0.7, CH_2Cl_2, 98% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46 (s, 3H), 4.54 (s, 1H), 5.41 (d, *J* = 16.0 Hz, 1H), 5.52 (d, *J* = 16.0 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 2H), 6.76 (t, *J* = 1.8 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.13 (m, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.26-7.29 (m, 4H), 7.31 (m, 1H), 7.37-7.41 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.4, 43.7, 58.2, 84.3, 86.5, 114.9, 119.8, 120.8, 121.6, 122.4, 123.7, 128.2, 128.9, 129.1, 131.2, 131.9, 134.4, 134.8, 135.4, 140.6, 145.9, 172.9; IR (neat) ν 3347, 1706, 1590, 1449, 1087, 753 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{21}Cl_4N_2O$ $[M+H]^+$ 565.0403, found: 565.0408; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 12.8 min, t_R (minor) = 26.0 min.



(*S*)-5-Chloro-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((2-fluorophenyl)ethynyl)indolin-2-one (9h). This compound was obtained from **6o** (0.1 mmol, 48 mg). White solid, yield: 58 mg, 97%; m.p. 214-217 °C; $[\alpha]_D^{25}$ = +39.0 (*c* 0.6, CH_2Cl_2, 98% ee); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.74 (s, 1H), 5.20 (d, *J* = 15.2 Hz, 1H), 5.36 (d, *J* = 15.2 Hz, 1H), 6.62 (d, *J* = 1.7 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 1H), 6.80 (t, *J* = 1.7 Hz, 1H), 7.06 (dd, J_1 = 13.4 Hz, J_2 = 5.0 Hz, 1H), 7.09 (td, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H), 7.24 (dd, J_1 = 8.5 Hz, J_2 = 2.1 Hz, 1H), 7.26 (d, *J* = 3.2 Hz, 1H), 7.33 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.40 (m, 1H), 7.49 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 40.8, 58.7, 80.5, 88.7, 109.9 (d, *J* = 15.6 Hz), 111.2, 114.5, 115.6 (d, *J* = 20.0 Hz), 120.1, 123.9 (d, *J* = 3.6 Hz), 124.8, 129.0, 129.2, 129.3, 129.6, 130.2, 130.5, 131.0 (d, *J* = 8.0 Hz), 133.7, 135.1, 136.4, 140.3, 145.5, 163.0 (d, *J* = 253.0 Hz), 171.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ -108.5; IR (neat) ν 3309, 1723, 1589, 1314, 1177, 811, 751 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{17}Cl_5FN_2O$ $[M+H]^+$ 602.9762, found 602.9768; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 11.2 min, t_R (minor) = 19.6 min.

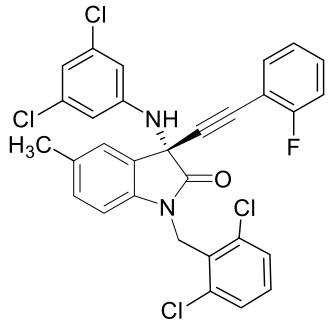


(*S*)-3-(3-((Tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-5-chloro-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)indolin-2-one (9i). This compound was obtained from **6o** (0.1 mmol, 50 mg). White solid, yield: 63 mg, 93%; m.p. 169-171 °C; $[\alpha]_D^{25}$ = −14.5 (*c* 0.8, CH_2Cl_2, 90% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.06 (s, 3H), 0.86 (s, 9H), 4.33 (s, 2H), 4.65 (s, 1H), 5.18 (d,



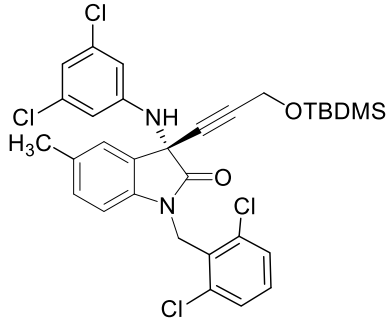
J = 15.2 Hz, 1H), 5.28 (d, *J* = 15.2 Hz, 1H), 6.46 (d, *J* = 1.7 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 1H), 6.76 (t, *J* = 1.7 Hz, 1H), 7.20-7.26 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ -5.2, -5.2, 25.7, 40.8, 51.6, 58.2, 79.6, 85.6, 111.2, 114.1, 119.9, 124.7, 129.0, 129.1, 129.4, 129.5, 130.2, 130.4, 135.1, 136.4, 139.9, 145.5, 171.2; IR (neat) ν 3306, 1720, 1593, 1257, 1070, 774 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{29}Cl_5N_2NaO_2Si$ $[M+Na]^+$ 675.0333, found 675.0331; HPLC: Phenomenex Lux i-Amylose-3, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 16.8 min, t_R (minor) = 10.5 min.

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((2-fluorophenyl)ethynyl)-5-methylindolin-2-one (9j). This compound was obtained from **6q** (0.1 mmol, 46 mg). White solid,



yield: 57 mg, 98%; m.p. 226-228 °C; $[\alpha]_D^{25}$ = +30.3 (*c* 0.6, CH_2Cl_2, 94% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (s, 3H), 4.70 (s, 1H), 5.19 (d, *J* = 15.2 Hz, 1H), 5.34 (d, *J* = 15.2 Hz, 1H), 6.66-6.68 (3H), 6.78 (t, *J* = 1.7 Hz, 1H), 7.04-7.09 (m, 3H), 7.22 (m, 1H), 7.29-7.34 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.40 (td, J_1 = 7.4 Hz, J_2 = 1.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.0, 40.7, 58.8, 79.9, 89.5, 110.0, 110.3 (d, *J* = 15.7 Hz), 114.5, 115.5 (d, *J* = 20.5 Hz), 119.7, 123.8, 125.0, 128.0, 128.8, 129.9 (d, *J* = 10.6 Hz), 130.7 (d, *J* = 8.0 Hz), 130.9, 133.5, 133.7, 135.0, 136.4, 139.1, 145.9, 163.0 (d, *J* = 253.0 Hz), 171.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -108.7; IR (neat) ν 3316, 1703, 1579, 1492, 1432, 1090, 986, 808, 751 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{20}Cl_4FN_2O$ $[M+H]^+$ 583.0308, found 583.0319; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 9.7 min, t_R (minor) = 16.4 min.

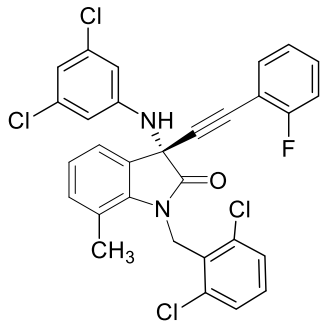
(*S*)-3-(3-((Tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-5-methylindolin-2-one (9k). This compound was obtained from **6q** (0.1



mmol, 45 mg). Colorless oil, yield: 59 mg, 96%; $[\alpha]_D^{25}$ = −19.3 (*c* 0.9, CH_2Cl_2, 98% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.06 (s, 3H), 0.86 (s, 9H), 2.28 (s, 3H), 4.33 (s, 2H), 4.64 (s, 1H), 5.17 (d, *J* = 15.1 Hz, 1H), 5.27 (d, *J* = 15.1 Hz, 1H), 6.52 (d, *J* = 1.7 Hz, 2H), 6.66 (d, *J* = 8.1 Hz, 1H), 6.74 (t, *J* = 1.7 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 1H), 7.20-7.23 (2H), 7.34 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ -5.2, -5.2, 18.1, 25.7, 40.7,

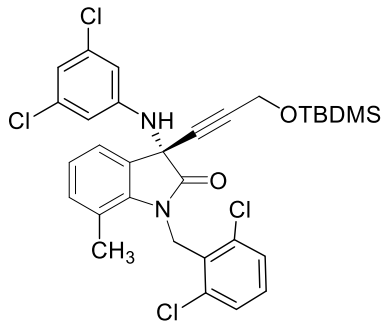
51.7, 58.3, 80.3, 85.0, 109.9, 114.2, 119.5, 124.9, 127.8, 128.9, 129.9, 130.7, 133.3, 135.0, 136.4, 139.0, 145.9, 171.6; IR (neat) ν 3319, 1720, 1586, 1499, 1442, 1257, 1086, 831, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{32}Cl_4N_2NaO_2Si$ $[M+Na]^+$ 655.0879, found 655.0873; HPLC: Phenomenex Lux i-Amylose-3, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 13.7 min, t_R (minor) = 23.8 min.

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((2-fluorophenyl)ethynyl)-7-methylindolin-2-one (4l). This compound was obtained from **1t** (0.1 mmol, 45 mg). White solid;



yield: 54 mg, 95%; m.p. 205-206 °C; $[\alpha]_D^{25}$ = −57.4 (*c* 0.7, CH_2Cl_2, 98% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.45 (s, 3H), 4.54 (s, 1H), 5.41 (d, *J* = 16.0 Hz, 1H), 5.52 (d, *J* = 16.0 Hz, 1H), 6.71 (d, *J* = 1.7 Hz, 2H), 6.77 (t, *J* = 1.7 Hz, 1H), 7.01-7.08 (3H), 7.13 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.28-7.32 (m, 3H), 7.36 (td, *J* = 7.5, 1.7 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.4, 43.7, 43.8, 58.3, 80.2, 89.3, 110.3 (d, *J* = 15.7 Hz), 115.1, 115.5 (d, *J* = 20.7 Hz), 119.9, 120.8, 122.5, 123.8, 123.9 (d, *J* = 3.8 Hz), 129.0, 129.1, 130.7 (d, *J* = 7.8 Hz), 131.2, 133.7, 134.5, 134.8, 135.4, 140.6, 145.8, 162.9 (d, *J* = 253.3 Hz), 172.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ -108.8; IR (neat) ν 3315, 1721, 1590, 1445, 782, 746, 739 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{20}Cl_4FN_2O$ $[M+H]^+$ 583.0308, found 583.0321; HPLC: Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 16.8 min, t_R (minor) = 19.4 min.

(*S*)-3-(3-((Tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-7-methylindolin-2-one (4m). This compound was obtained from **1t** (0.1



mmol, 46 mg). Colorless oil, yield: 60 mg, 95%; $[\alpha]_D^{25}$ = −13.2 (*c* 1.0, CH_2Cl_2, 90% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.85 (s, 9H), 2.47 (s, 3H), 4.29 (s, 2H), 4.46 (s, 1H), 5.37 (d, *J* = 15.8 Hz, 1H), 5.46 (d, *J* = 15.8 Hz, 1H), 6.55 (d, *J* = 1.8 Hz, 2H), 6.73 (t, *J* = 1.8 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 7.12 (m, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$)δ -5.2, 19.5, 25.7, 43.8, 51.6, 57.8, 80.0, 85.1, 114.8, 119.8, 120.7, 122.4, 123.6, 128.8, 128.9, 129.1, 131.2, 134.4, 134.8, 135.5, 140.5, 145.8, 172.7; IR (neat) ν 3312, 1718, 1590, 1306, 1251, 1076, 786, 771 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{32}Cl_4N_2NaO_2Si$ $[M+Na]^+$ 655.0879, found 655.0892. HPLC: Phenomenex Lux i-Amylose-3, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 16.1 min, t_R (minor) = 7.6 min.

7. Scaled-Up Version of the Reaction of Enantioselective Addition of Terminal Alkynes to Isatin-Derived Ketimines. To a solution 1.2 M of $ZnMe_2$ in toluene (10 mmol, 8.3 mL) under nitrogen atmosphere was added phenylacetylene (10 mmol, 1,1 mL) and the mixture was stirred at rt for 1 h. Then, a solution 0.1 M of ligand **L2** in toluene (0.5 mmol, 5 mL, 20 mol%) was added and the reaction stirred for another 30 min, whereupon a solution of the imine **6g** (1,13 g, 2.5 mmol) in CH_2Cl_2 (25 mL) was added dropwise and the reaction stirred at rt for 24 h. The reaction was quenched with NH_4Cl, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated. Purification in column chromatography (hexane/CH_2Cl_2 3:1 to 1:2) afforded the pure product **7g** (1.18 g, 85% yield) with an enantioselectivity of er = 98:2.

8. General Procedure for the Synthesis of Racemic 3-Alkynyl-3-Aminooxindoles . To a solution of $ZnMe_2$ in toluene (1.2 M, 0.4 mmol) under nitrogen atmosphere was added the corresponding alkyne (0.4 mmol) and the mixture was stirred at rt for 1 h. Then, a solution of the imine (0.1 mmol) in CH_2Cl_2 (1 mL) was added dropwise and the reaction stirred at rt for 48 h. The reaction was quenched with NH_4Cl, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated. Purification in column chromatography (hexane/ CH_2Cl_2 3/1 to 1/2) afforded the pure products.

9. References

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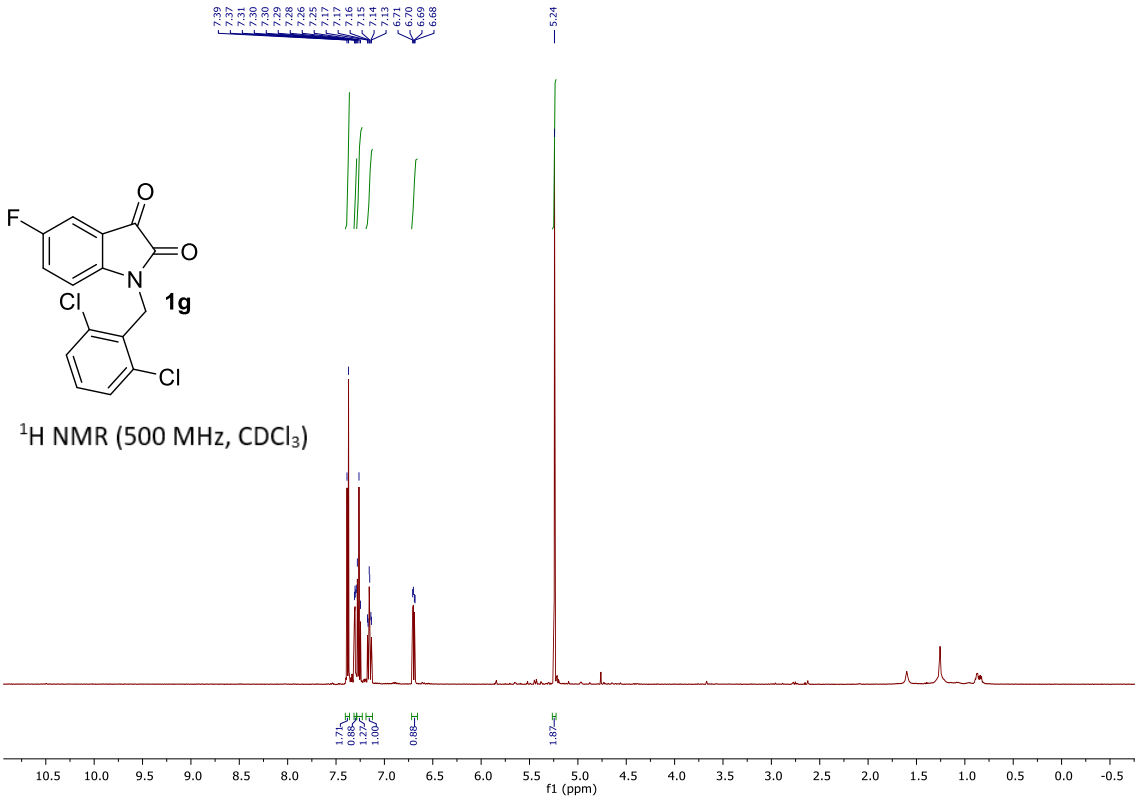
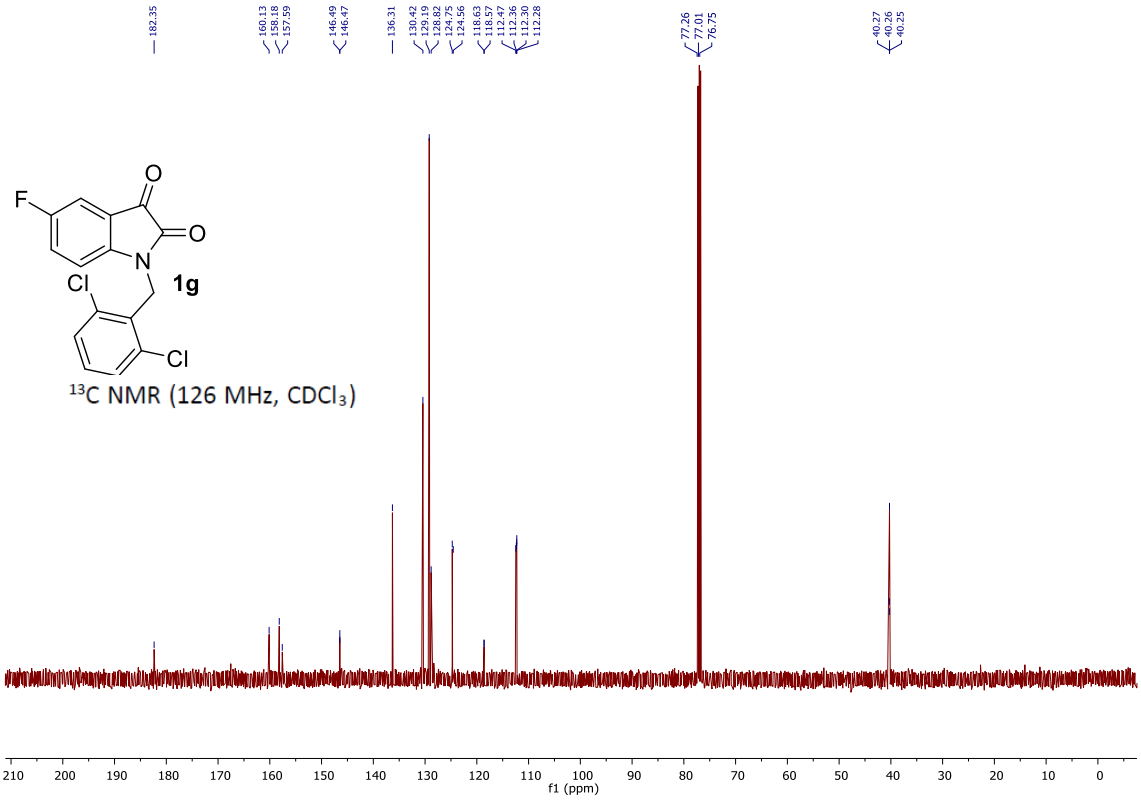
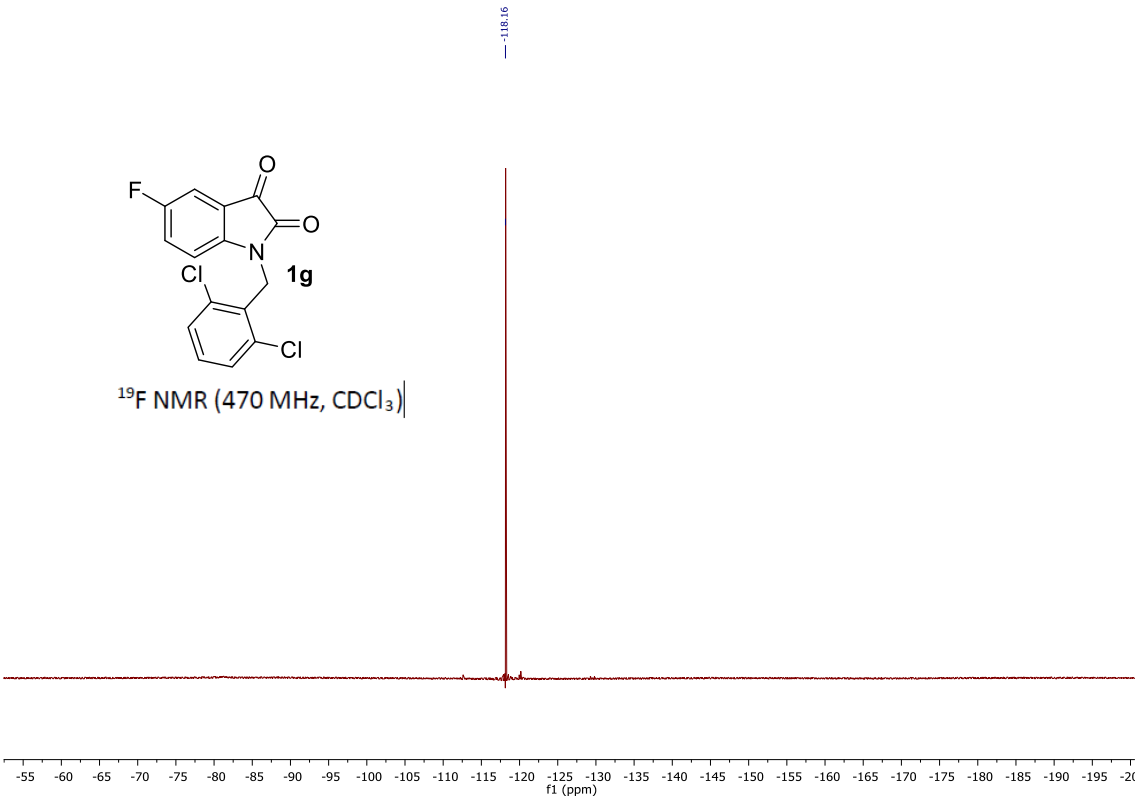
10. Copies of ^{1}H-NMR and ^{13}C-NMR Spectra.



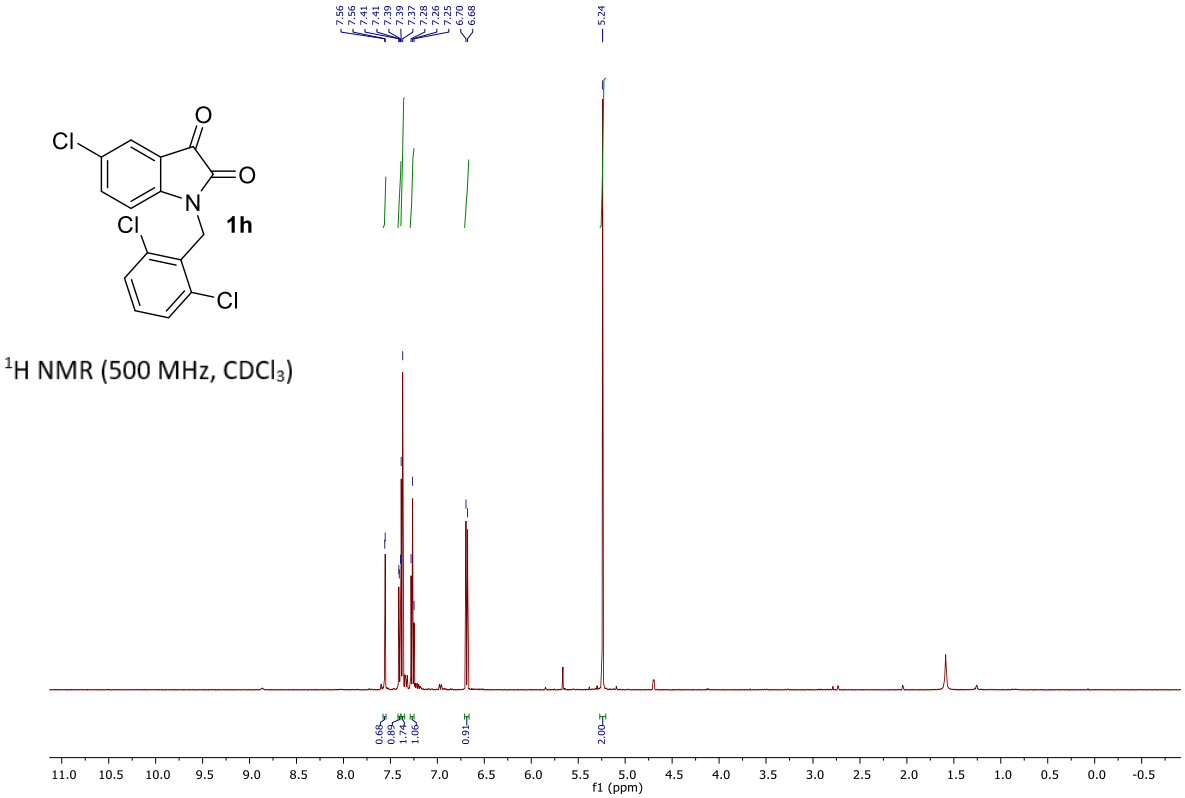
^{1}H NMR (500 MHz, $CDCl_3$)



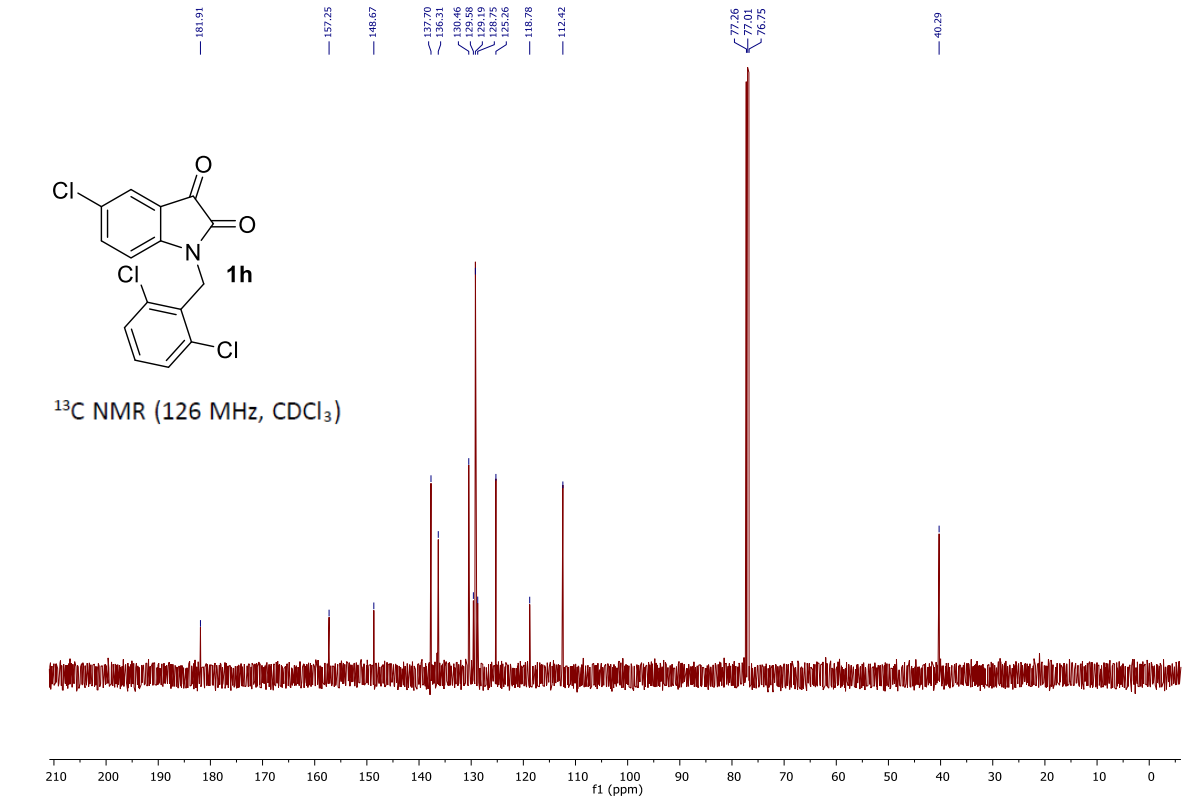
^{13}C NMR (126 MHz, $CDCl_3$)



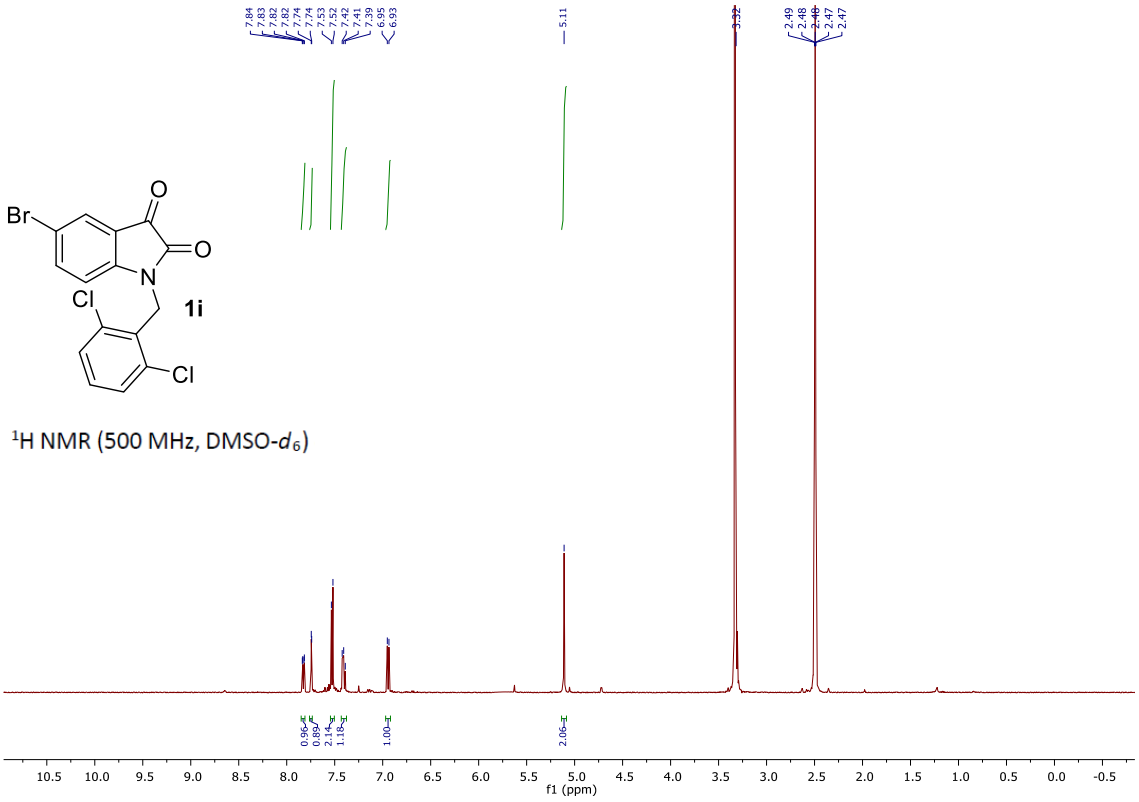
^{19}F NMR (470 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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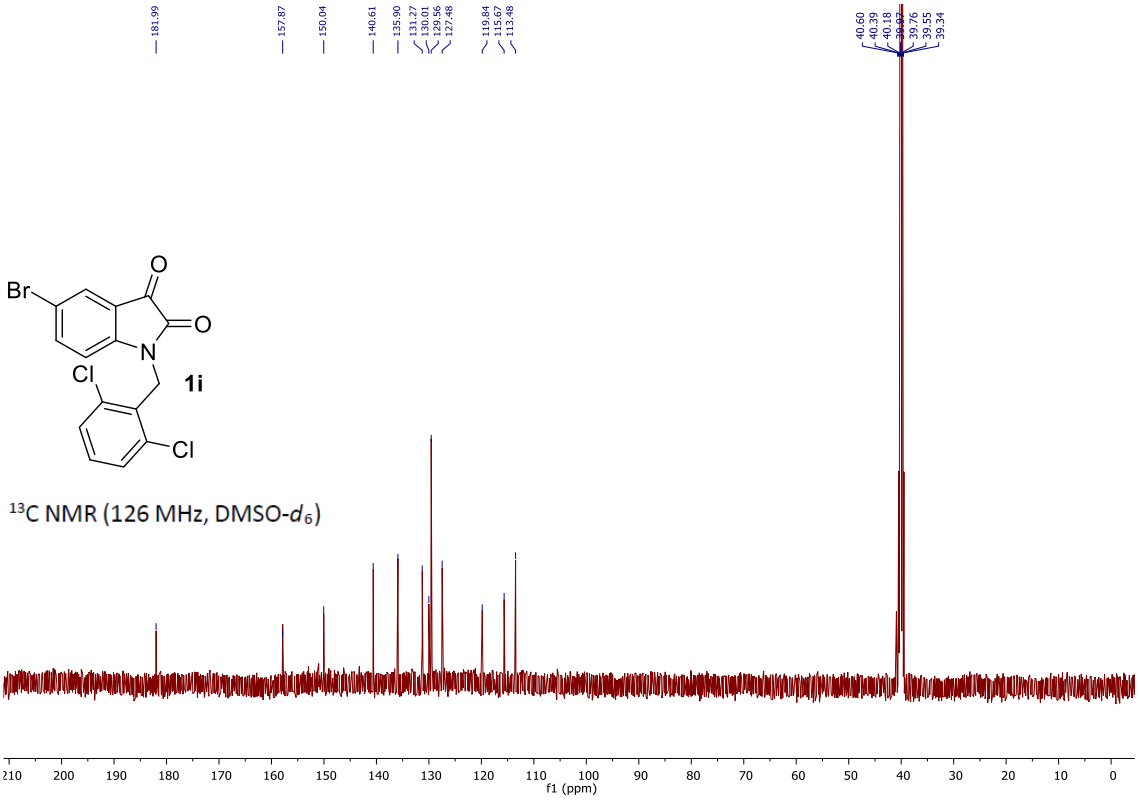

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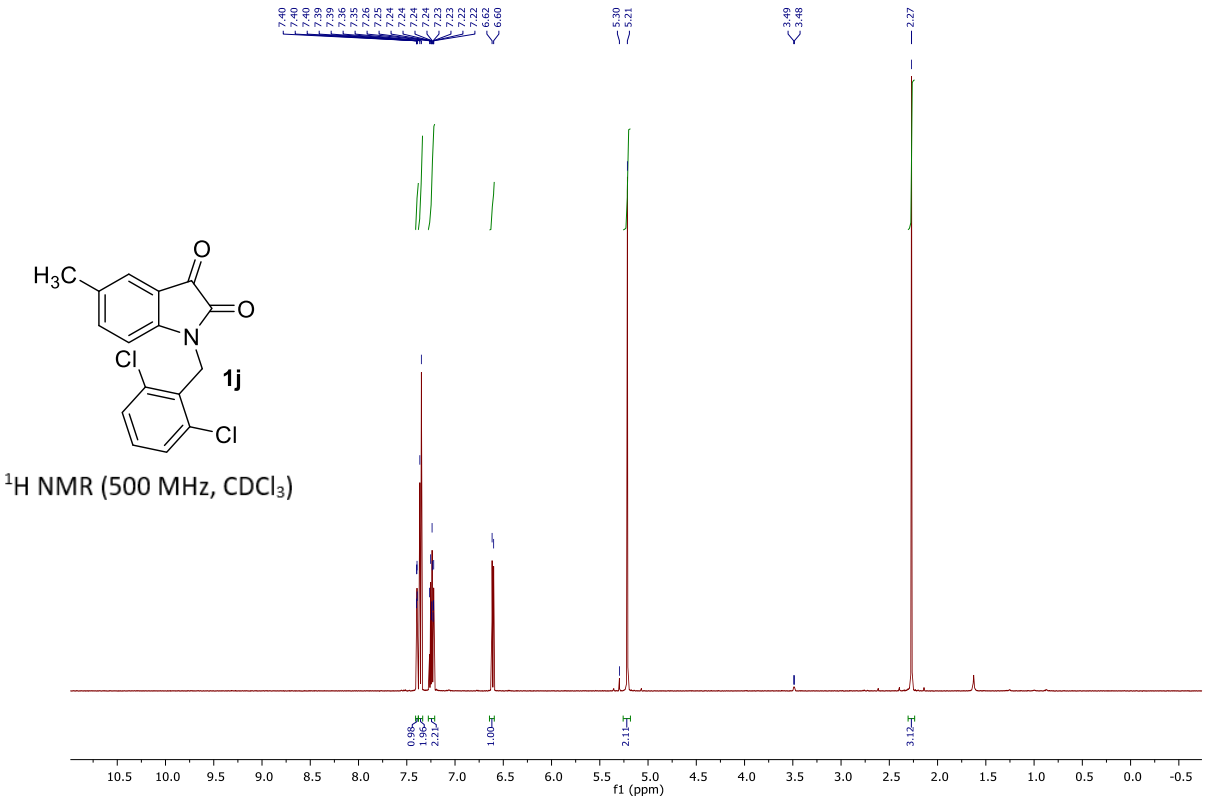

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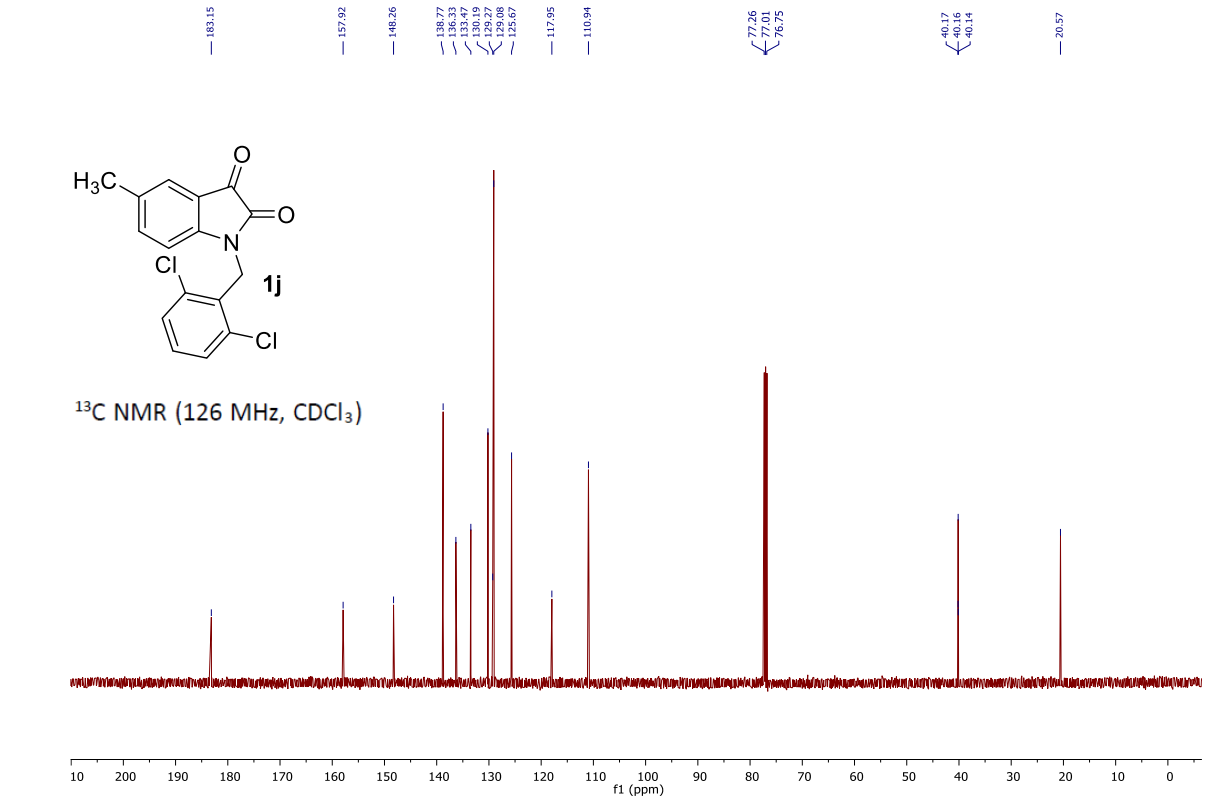

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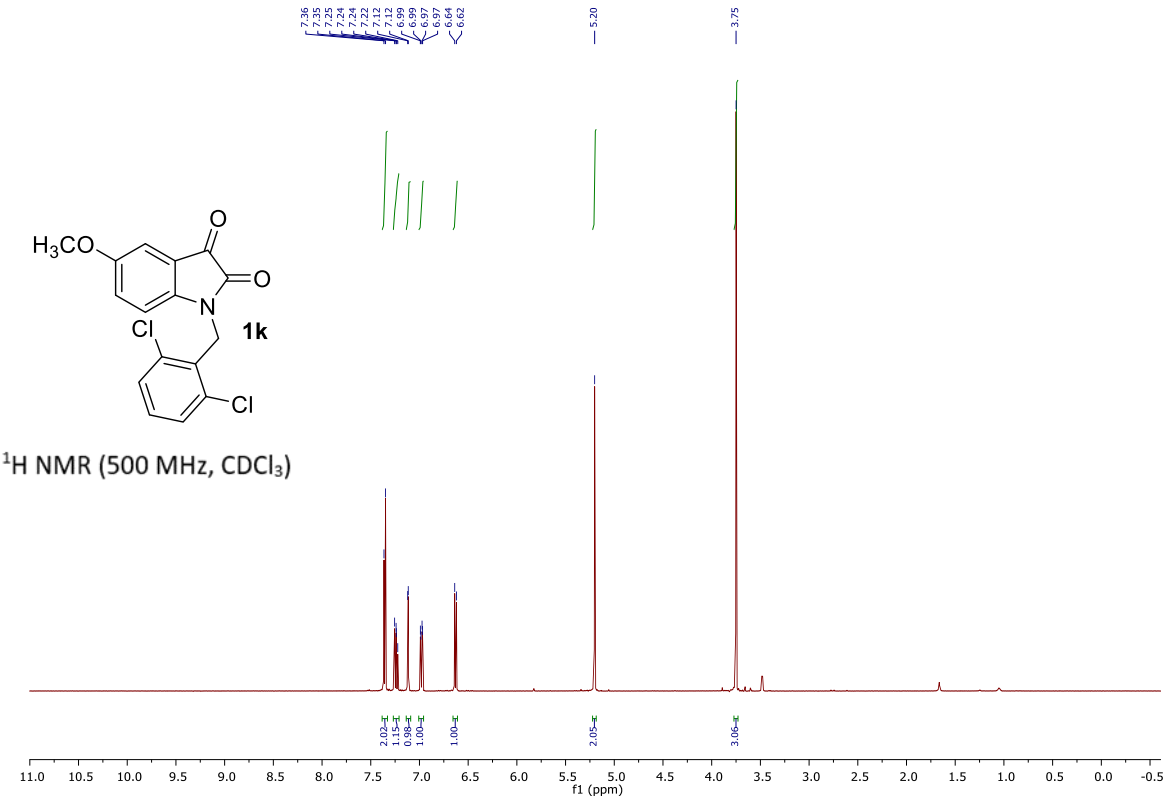

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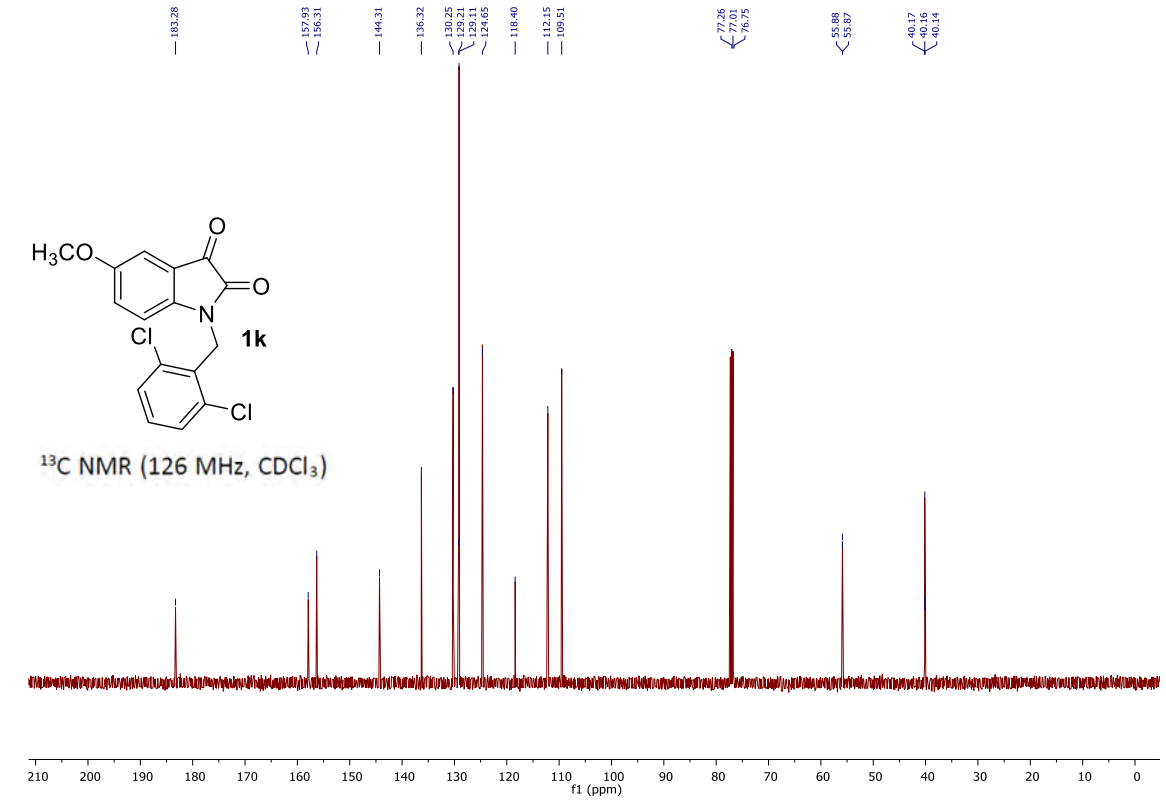

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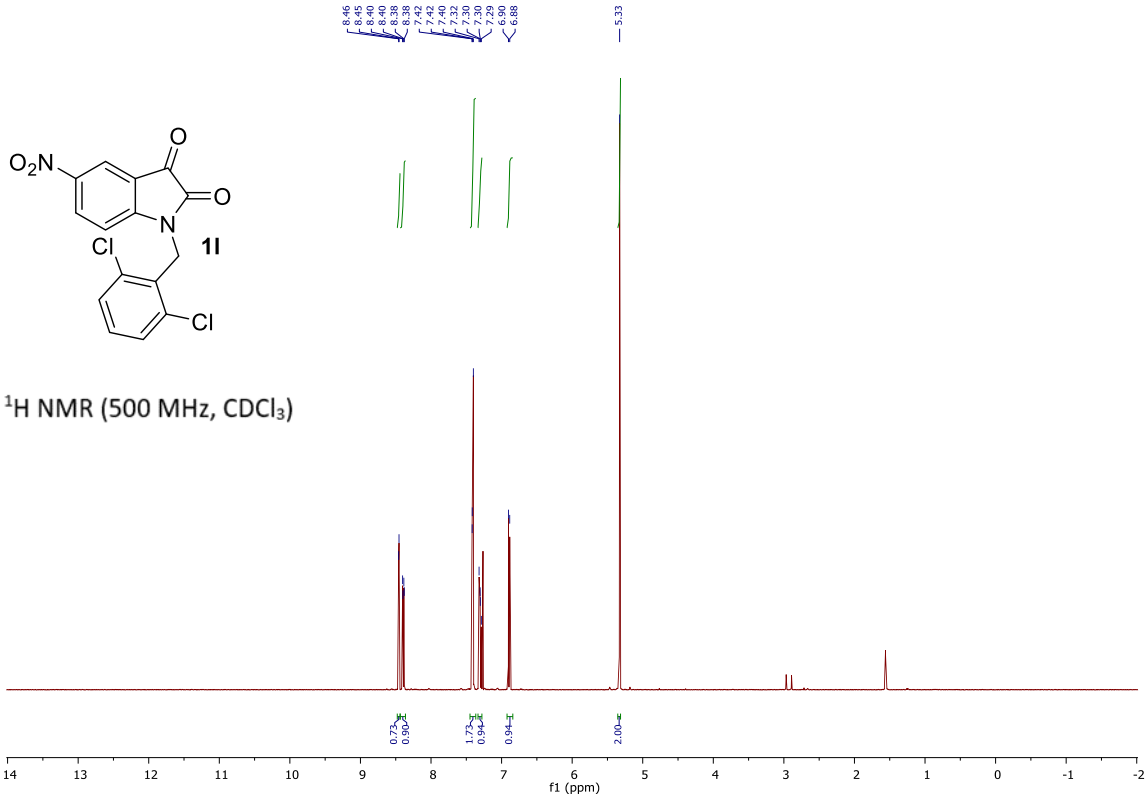

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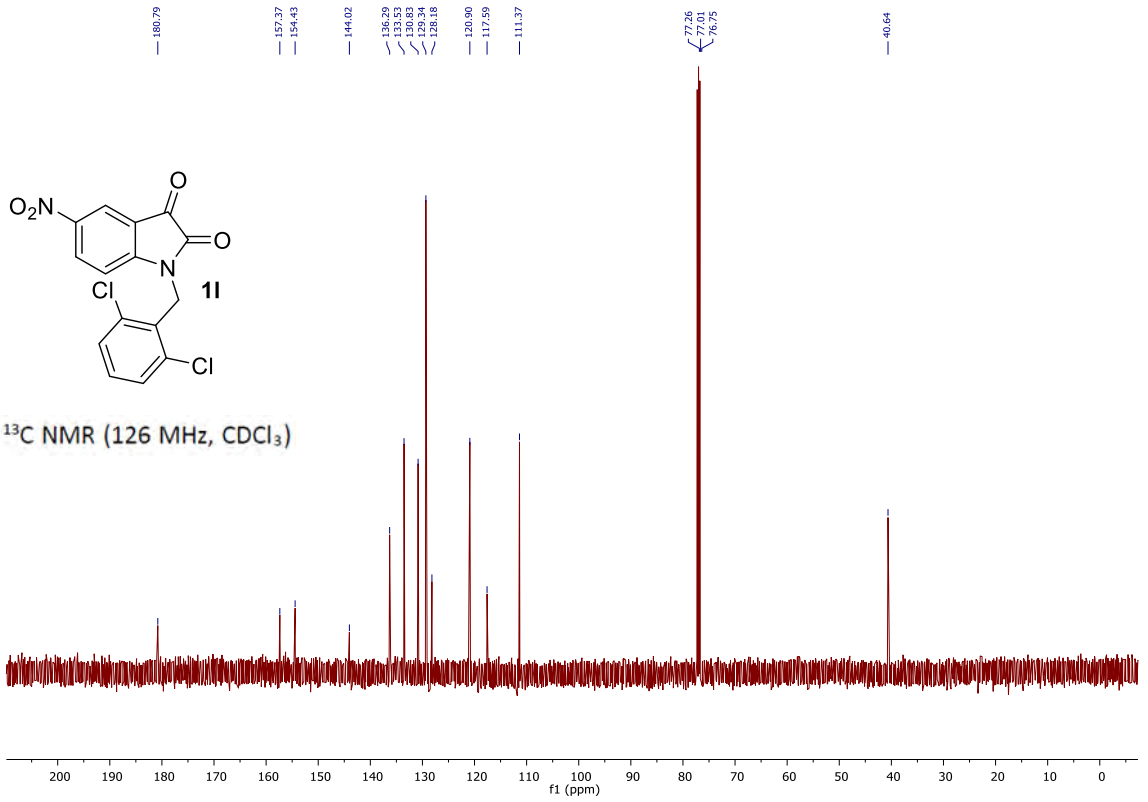

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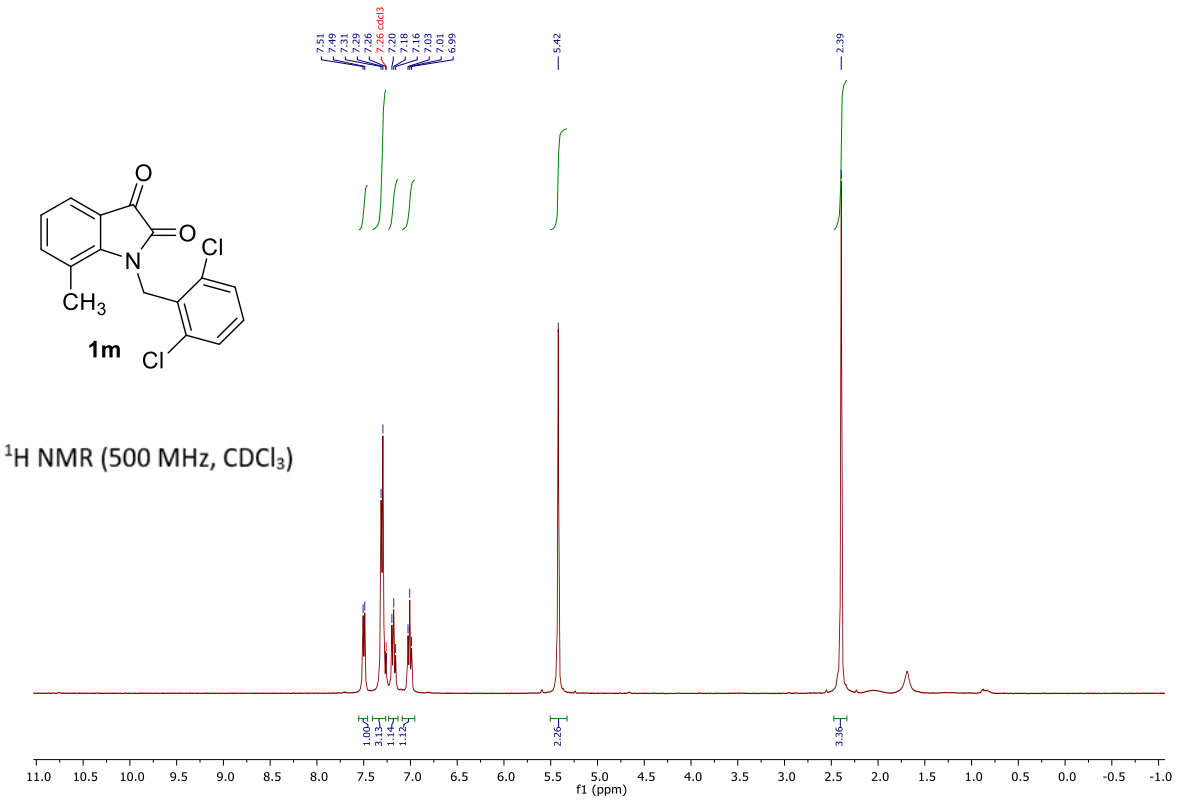
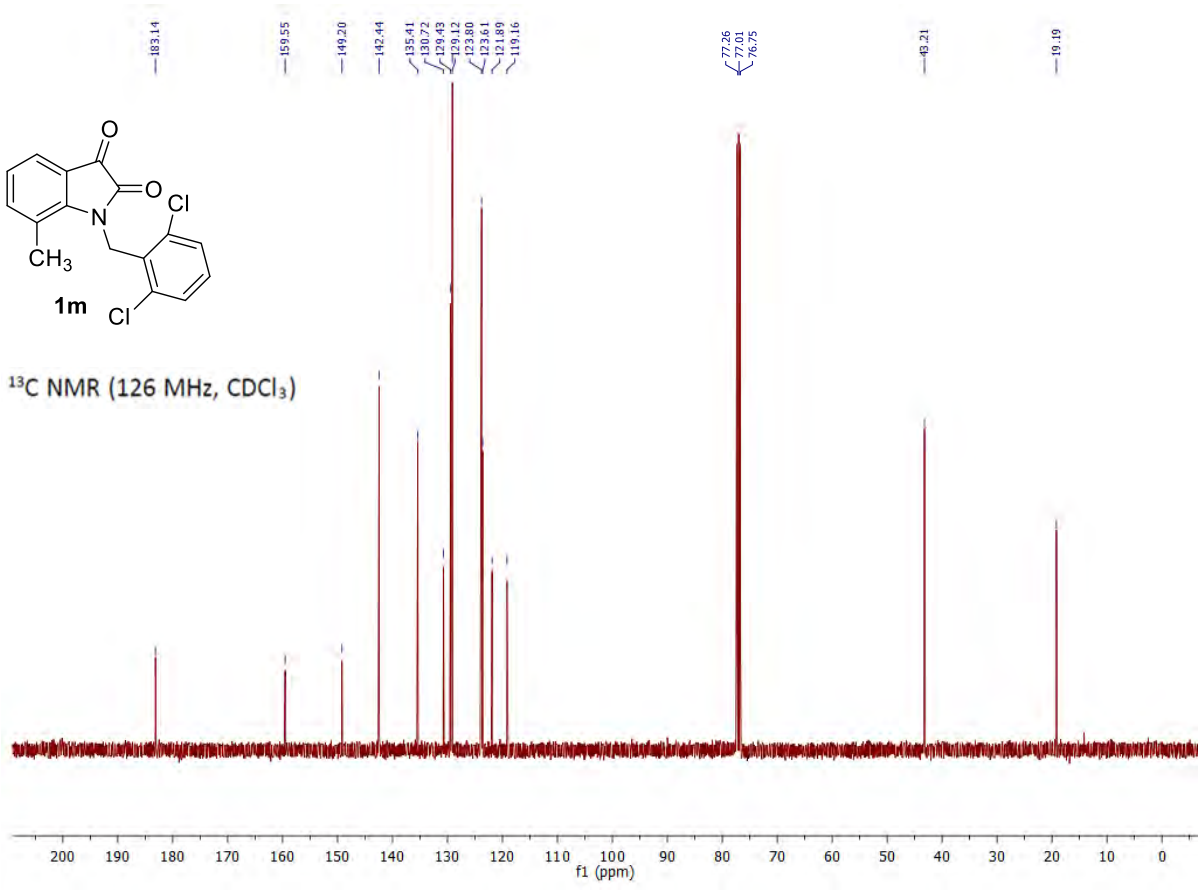
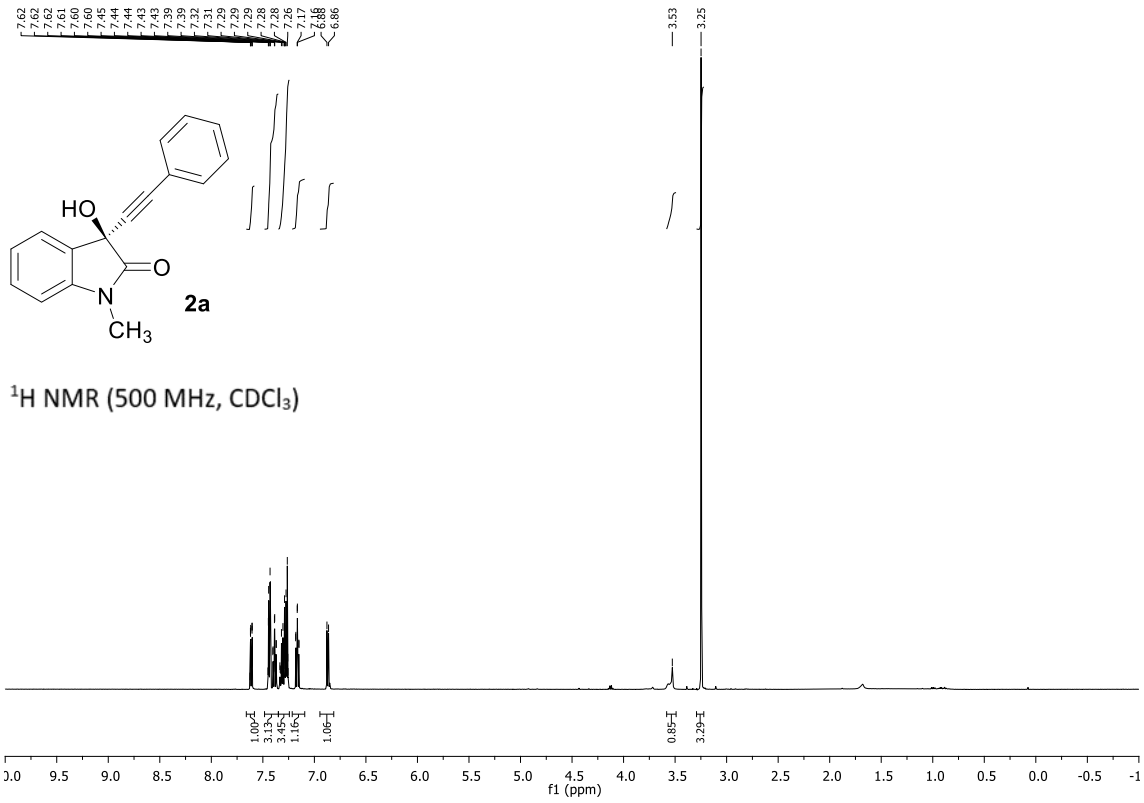

1m
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)


1m
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)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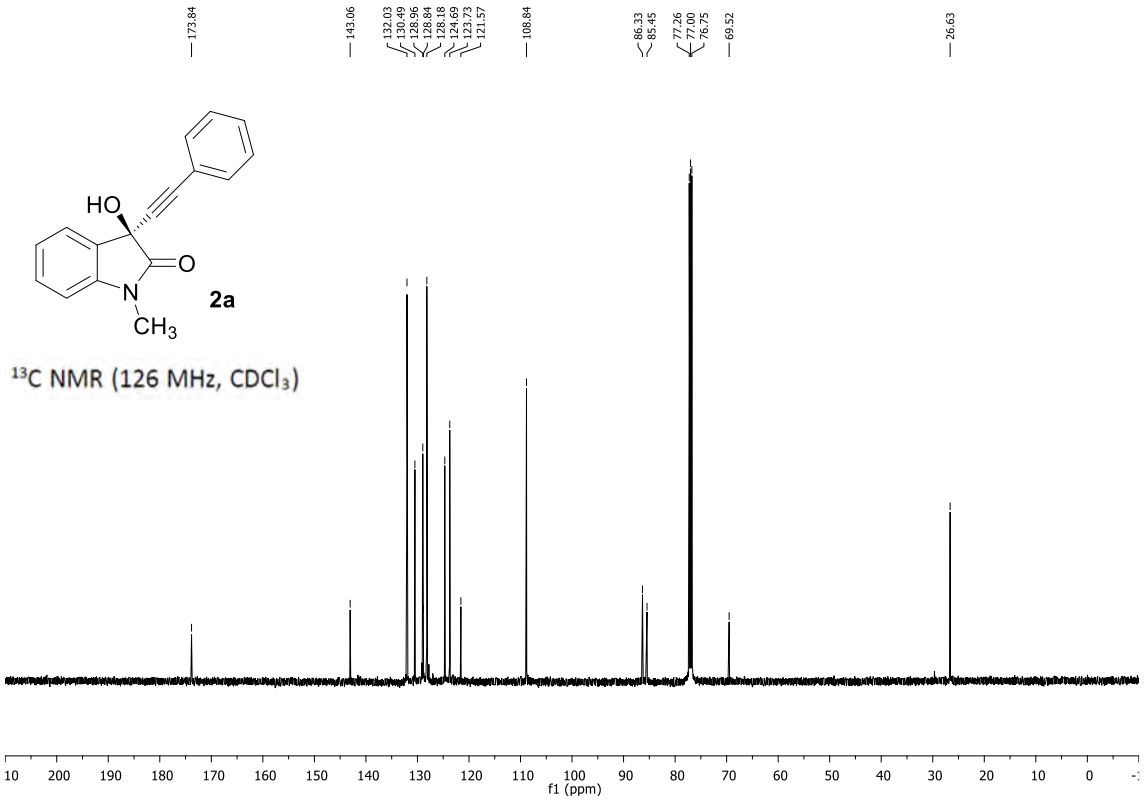
O
N
CH3
2a
1H NMR (500 MHz, CDCl3)
f1 (ppm)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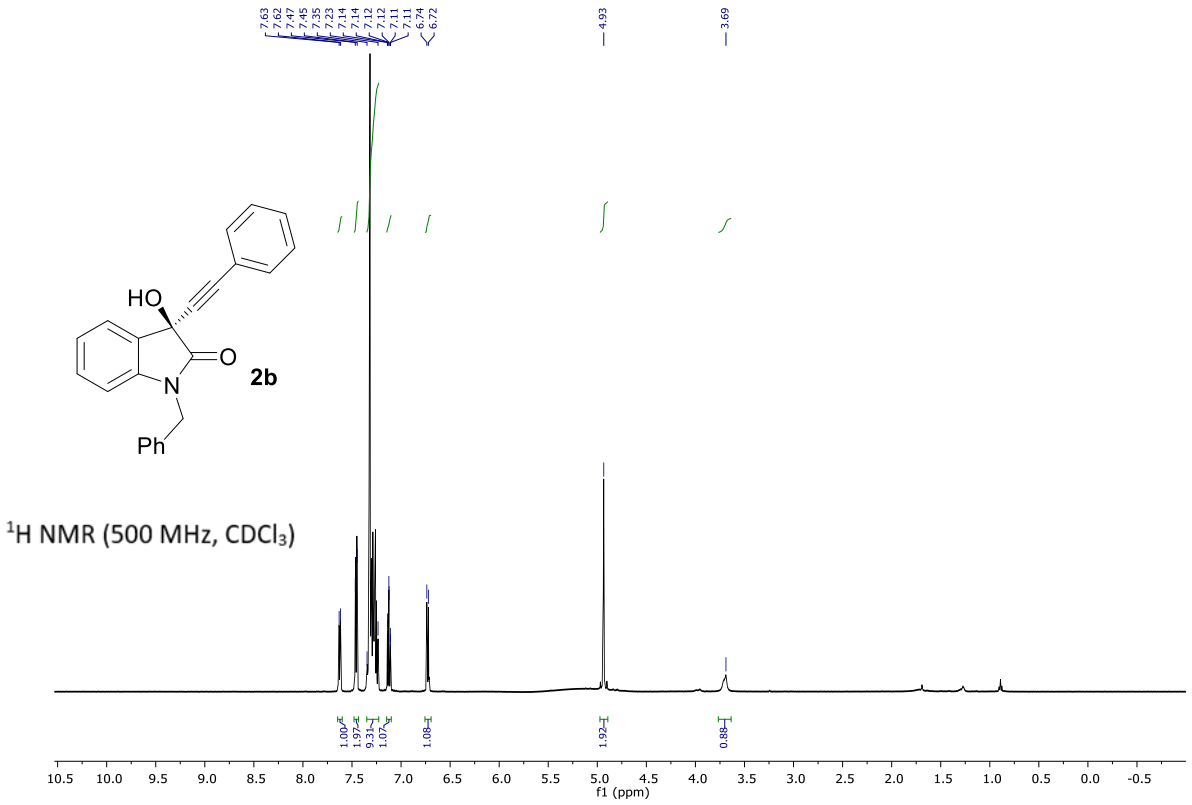
O
N
CH3
2a
13C NMR (126 MHz, CDCl3)
f1 (ppm)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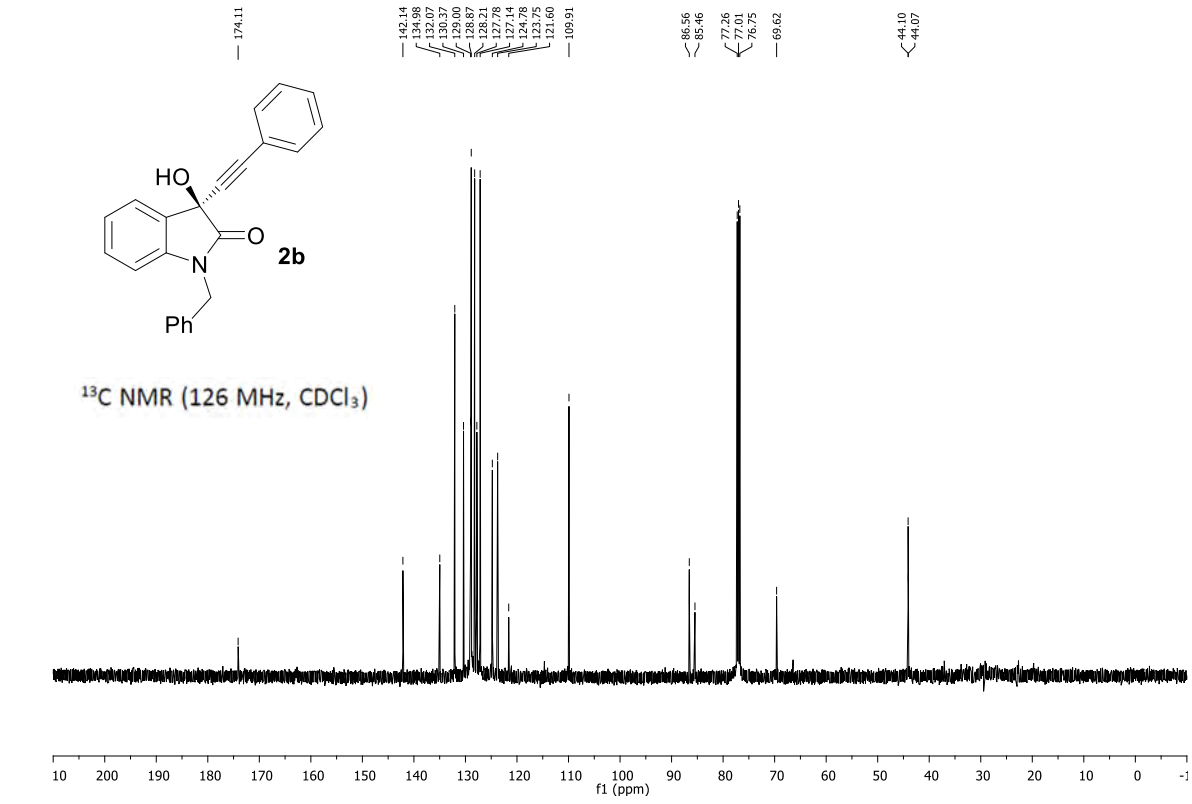
7.14
7.12
7.12
7.11
7.11
6.74
6.72
4.93
3.69
HO
O
N
Ph
2b
1H NMR (500 MHz, CDCl3)
1.00
1.97
9.31
1.07
1.08
1.92
0.88
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


174.11
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129.00
128.57
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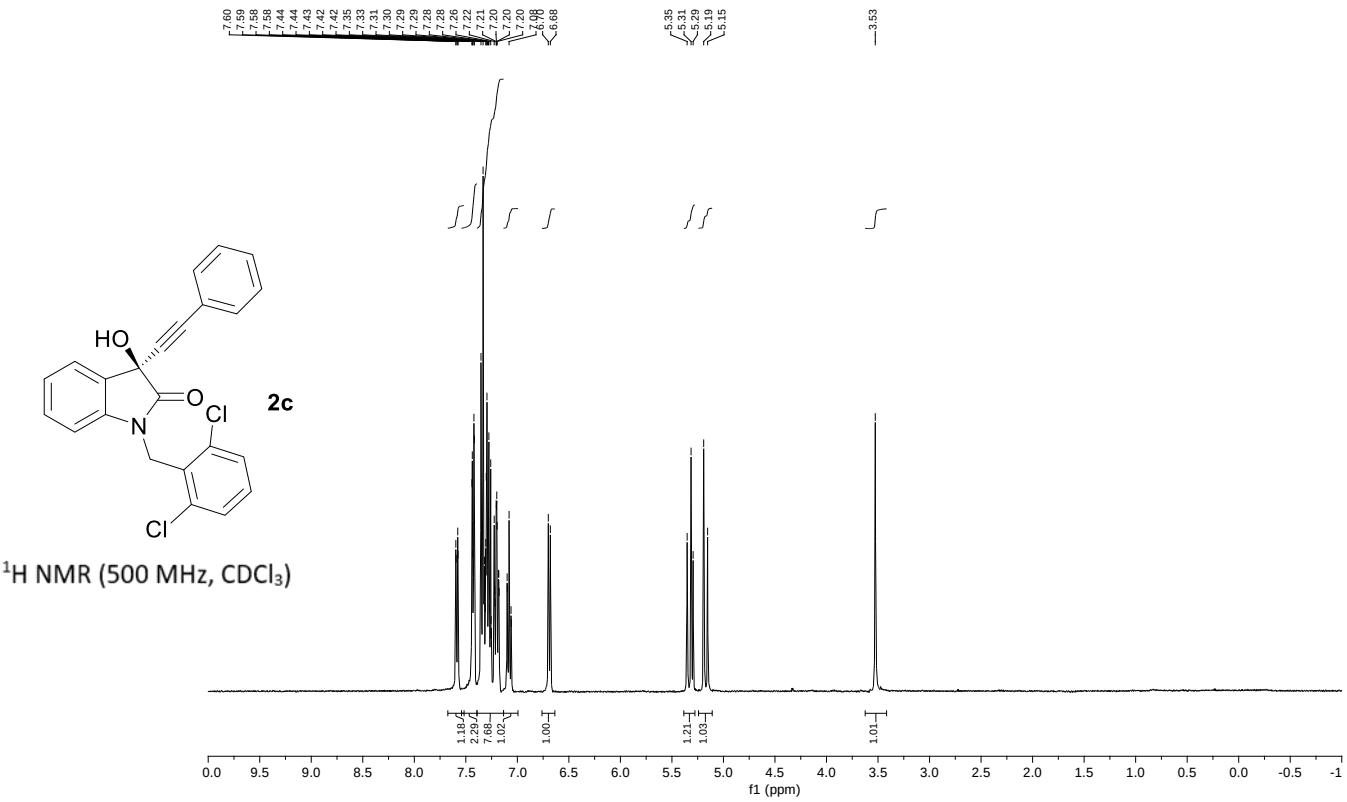
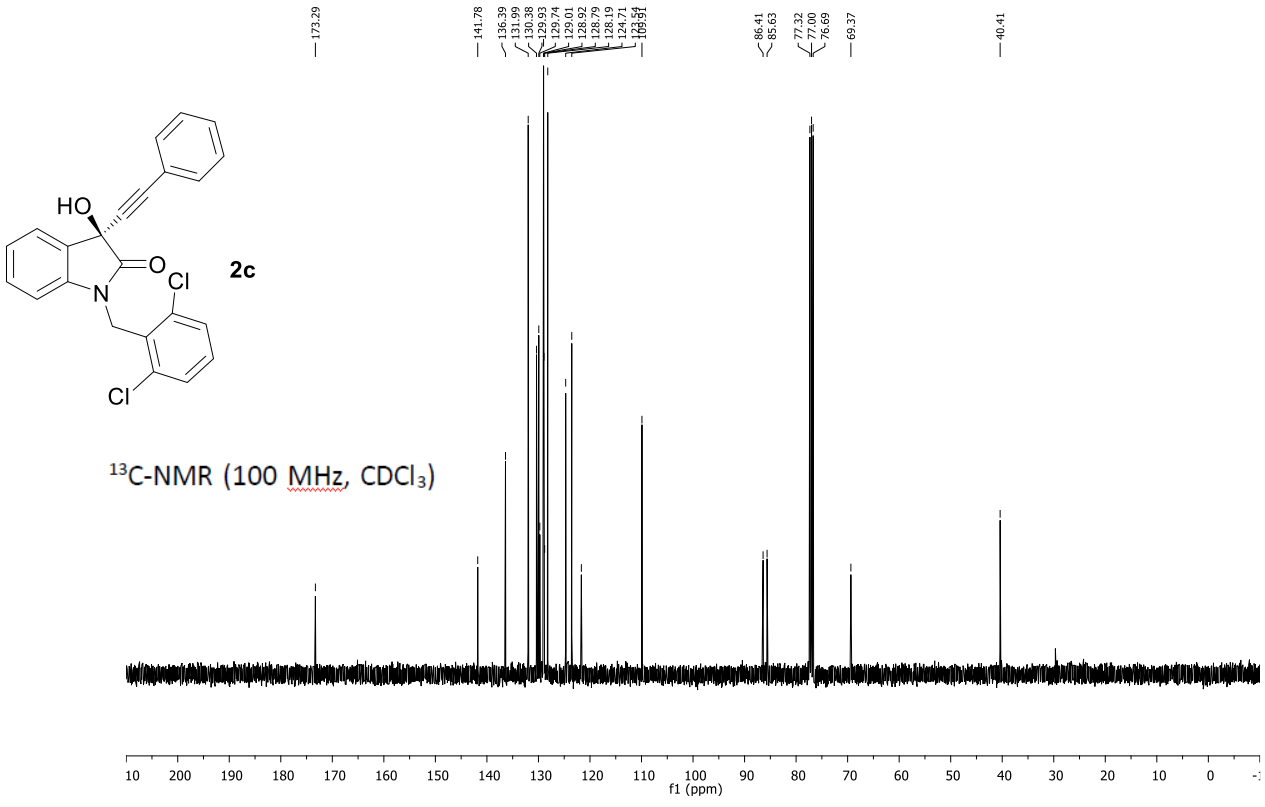
127.78
127.14
124.78
123.75
121.60
109.91
86.56
85.46
77.26
77.01
76.75
69.62
44.10
44.07
HO
O
N
Ph
2b
13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


HO
O
N
Cl
Cl
2c
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)


HO
O
N
Cl
Cl
2c
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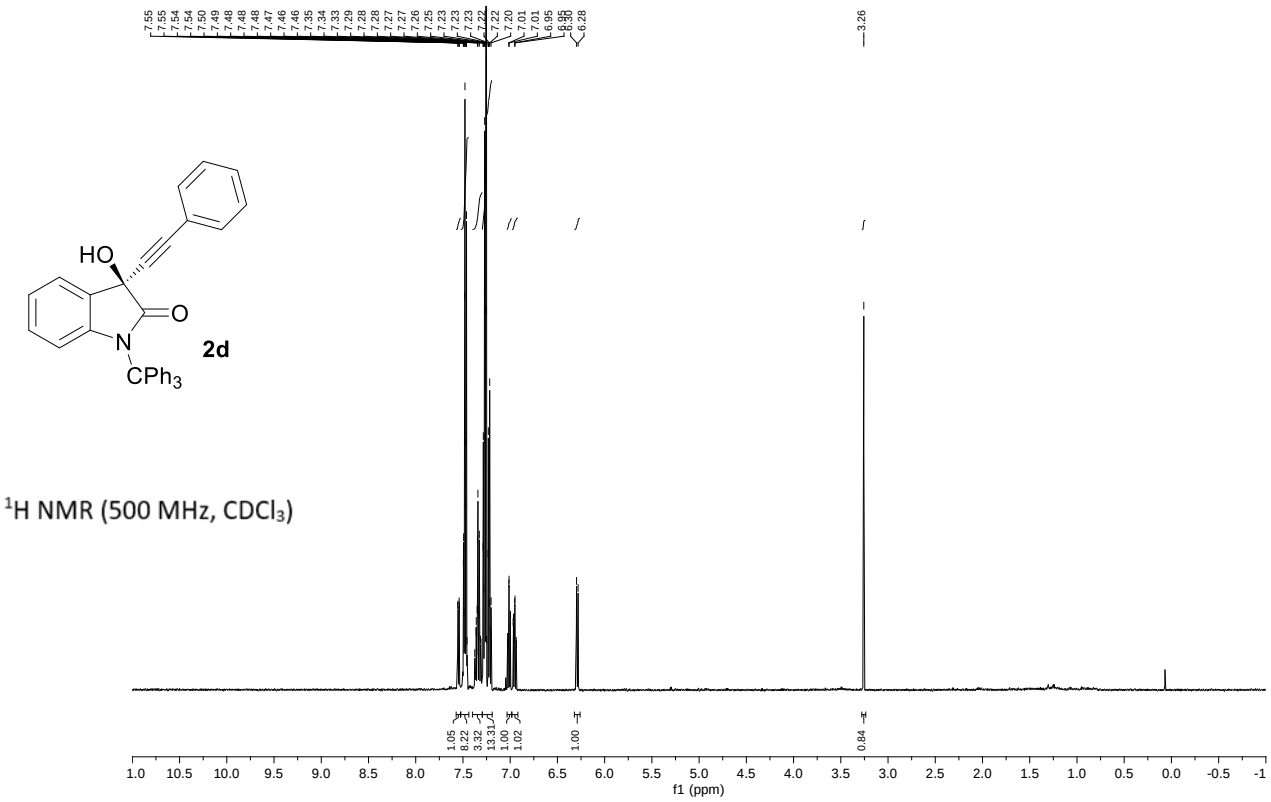
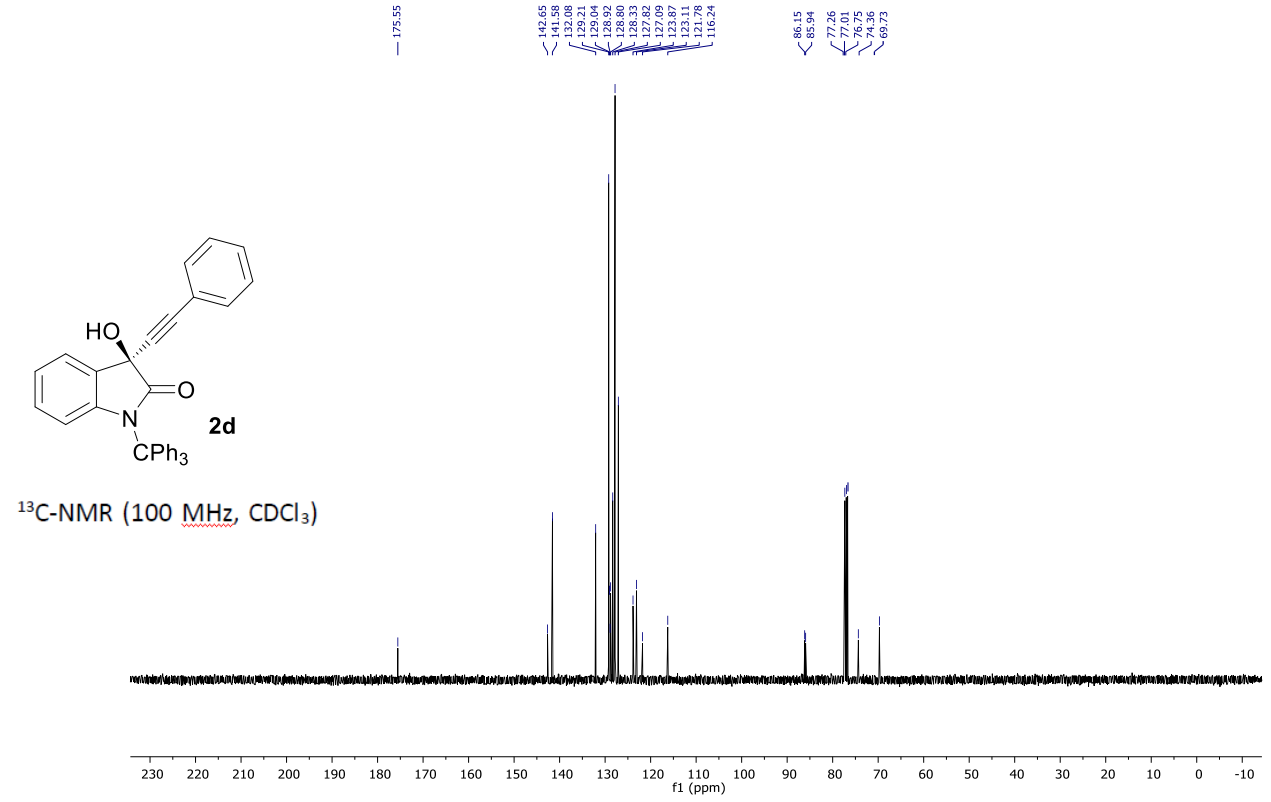
f1 (ppm)



^{1}H NMR (500 MHz, $CDCl_3$)



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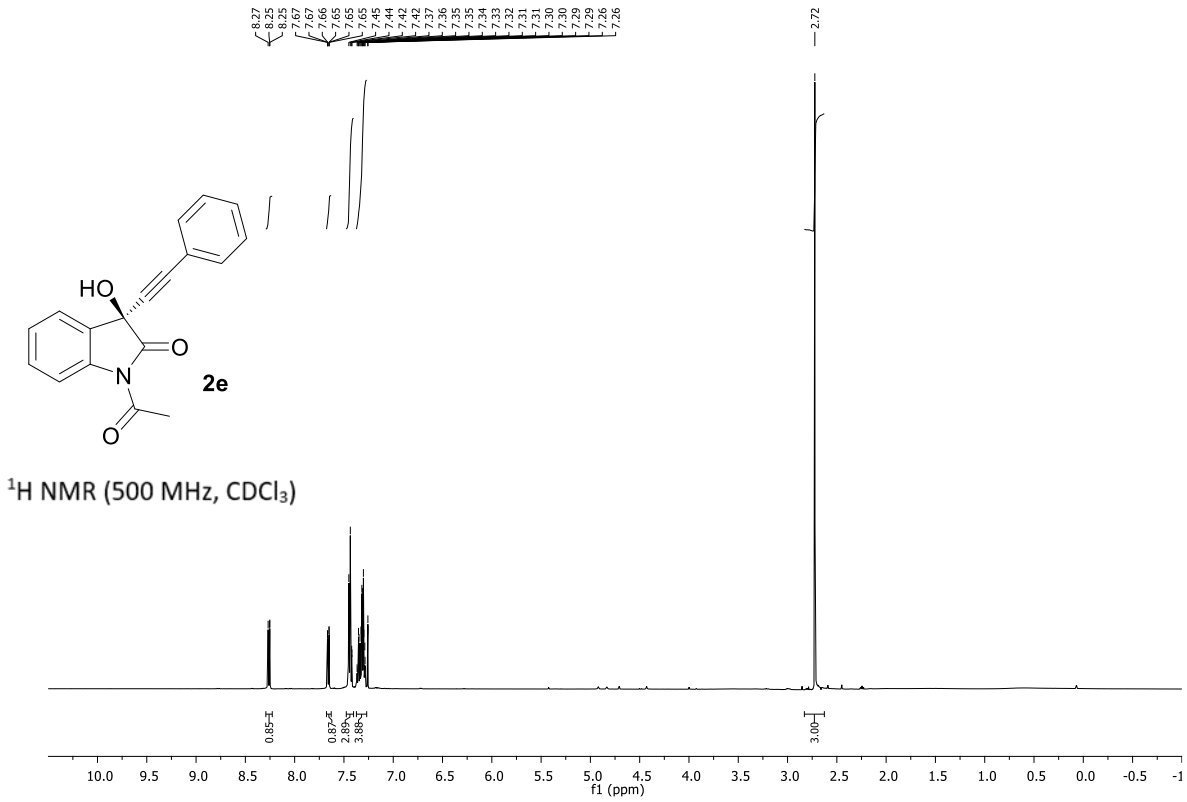

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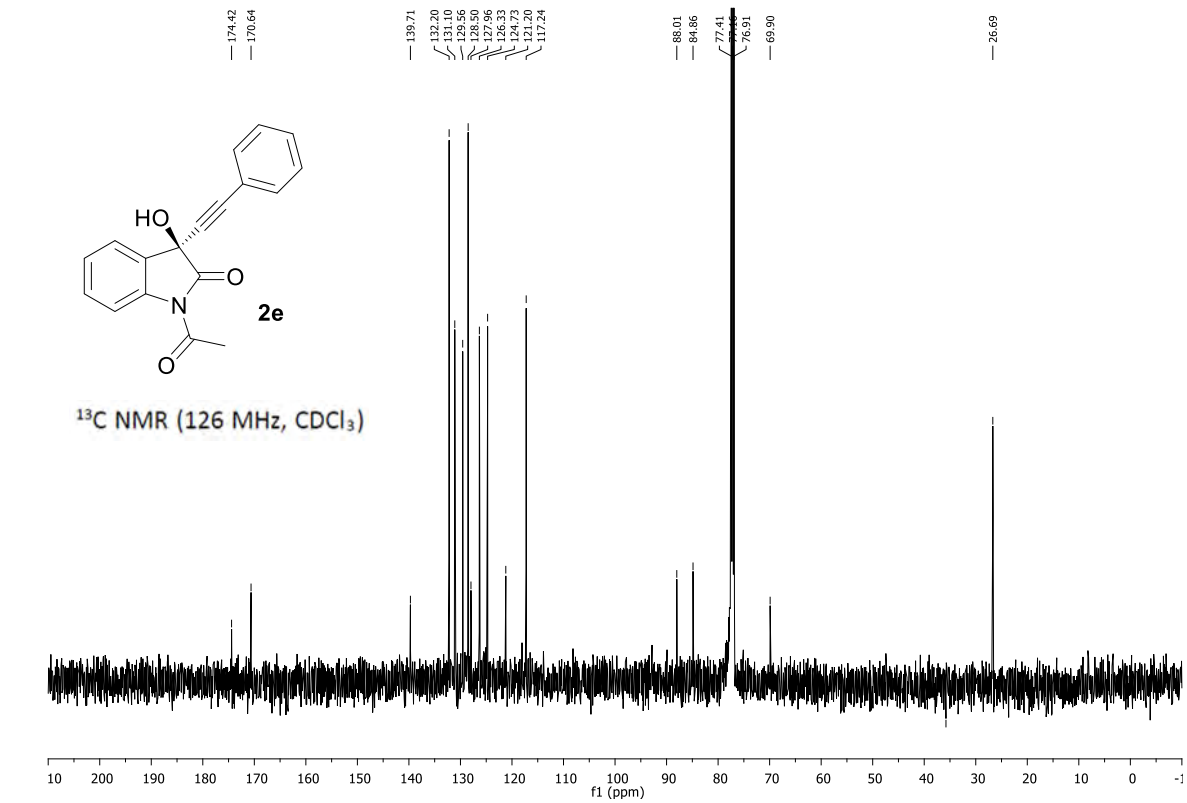

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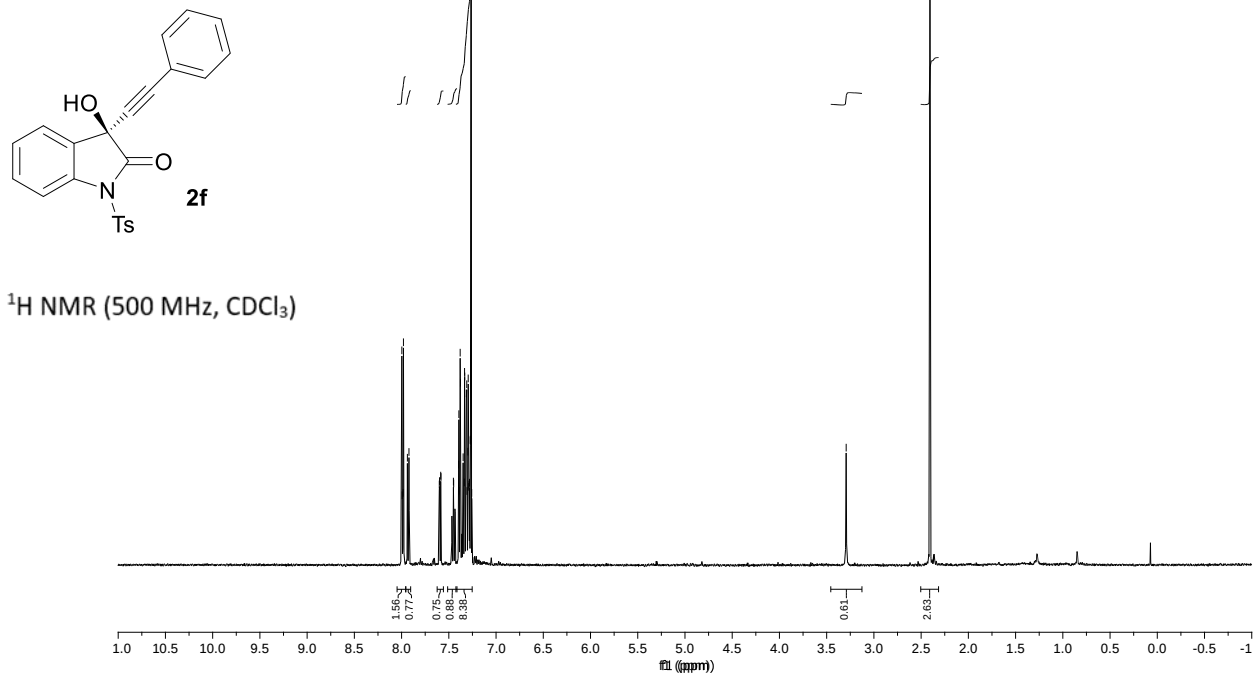
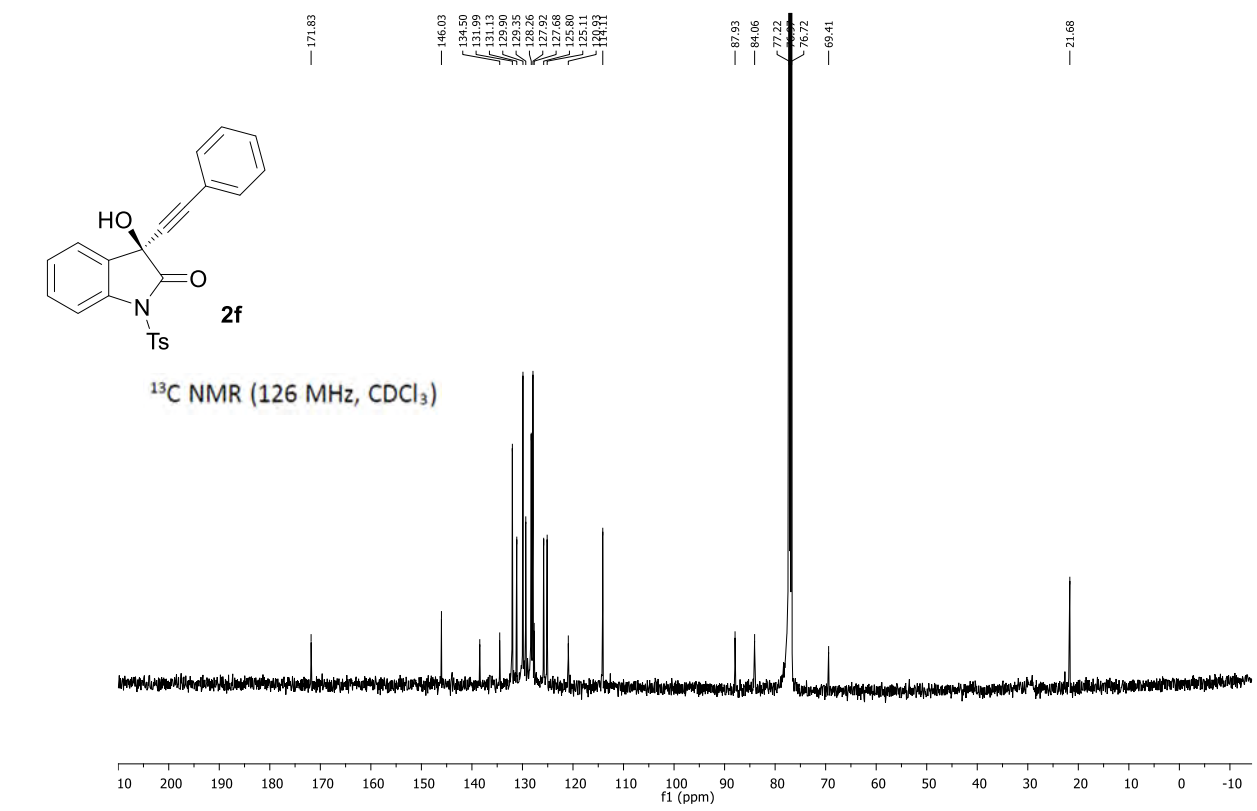
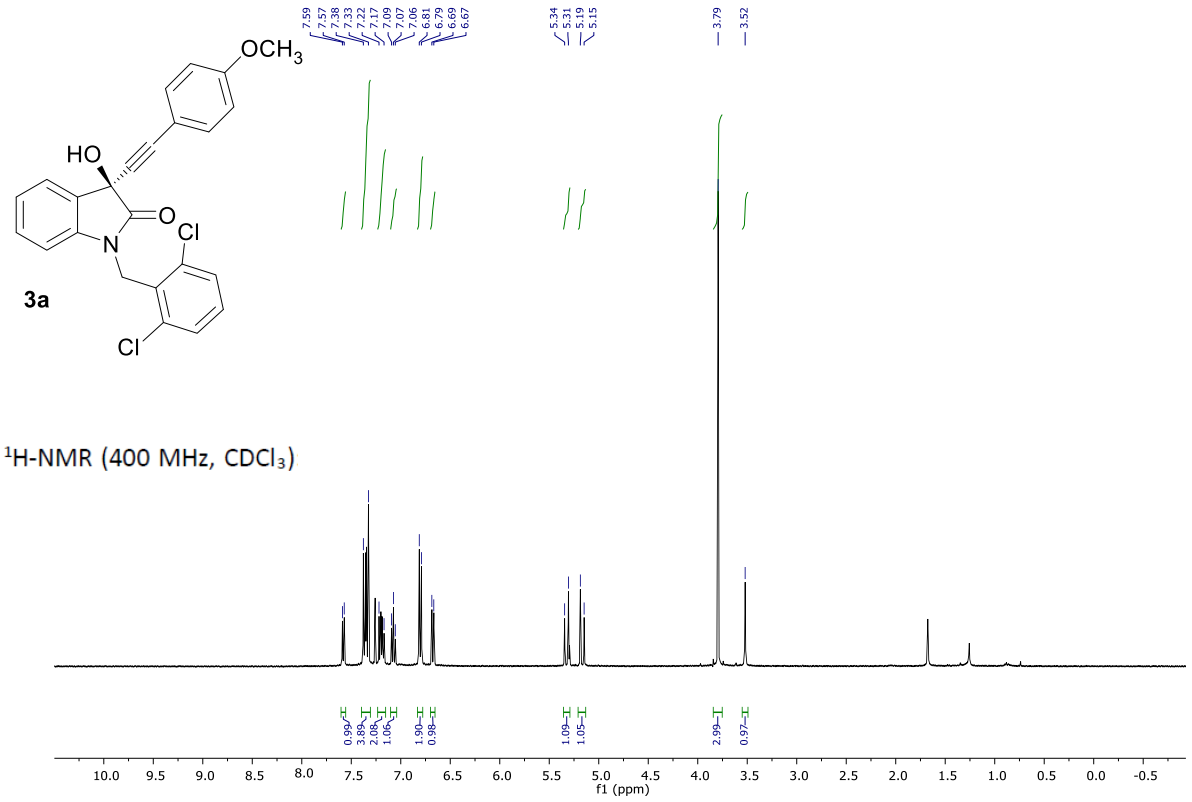
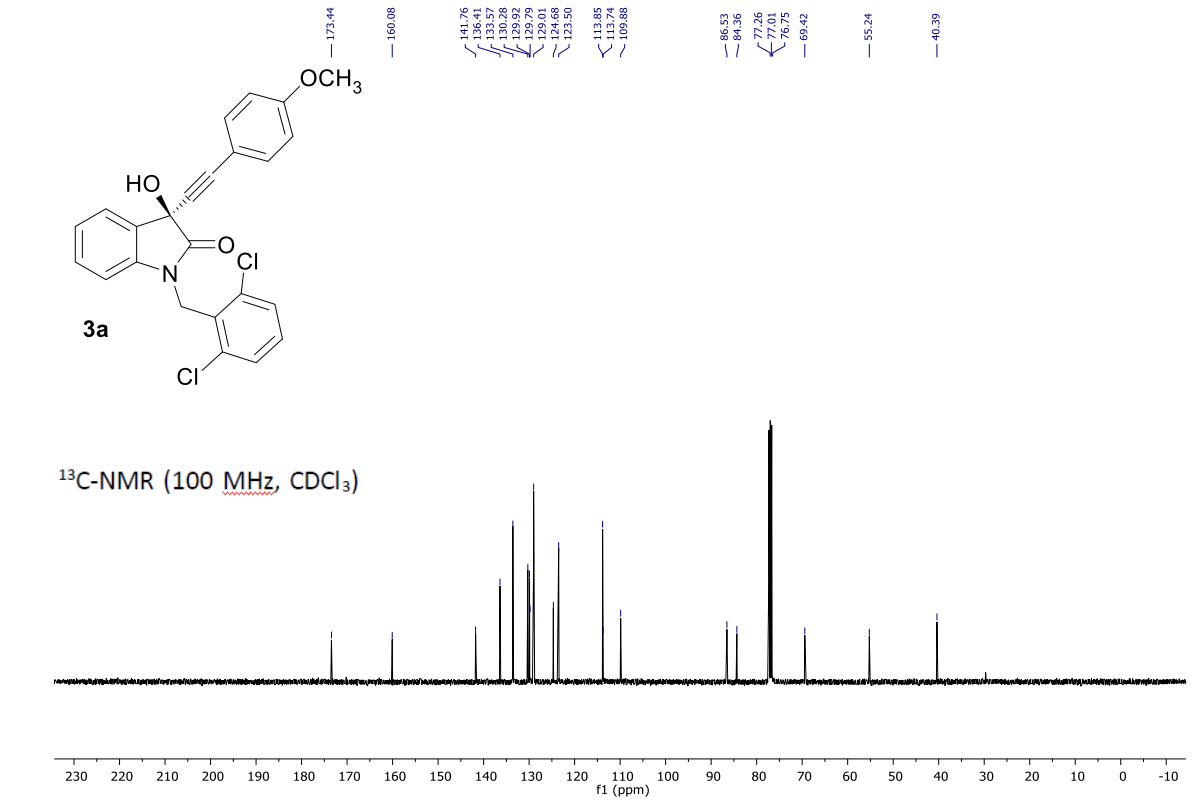


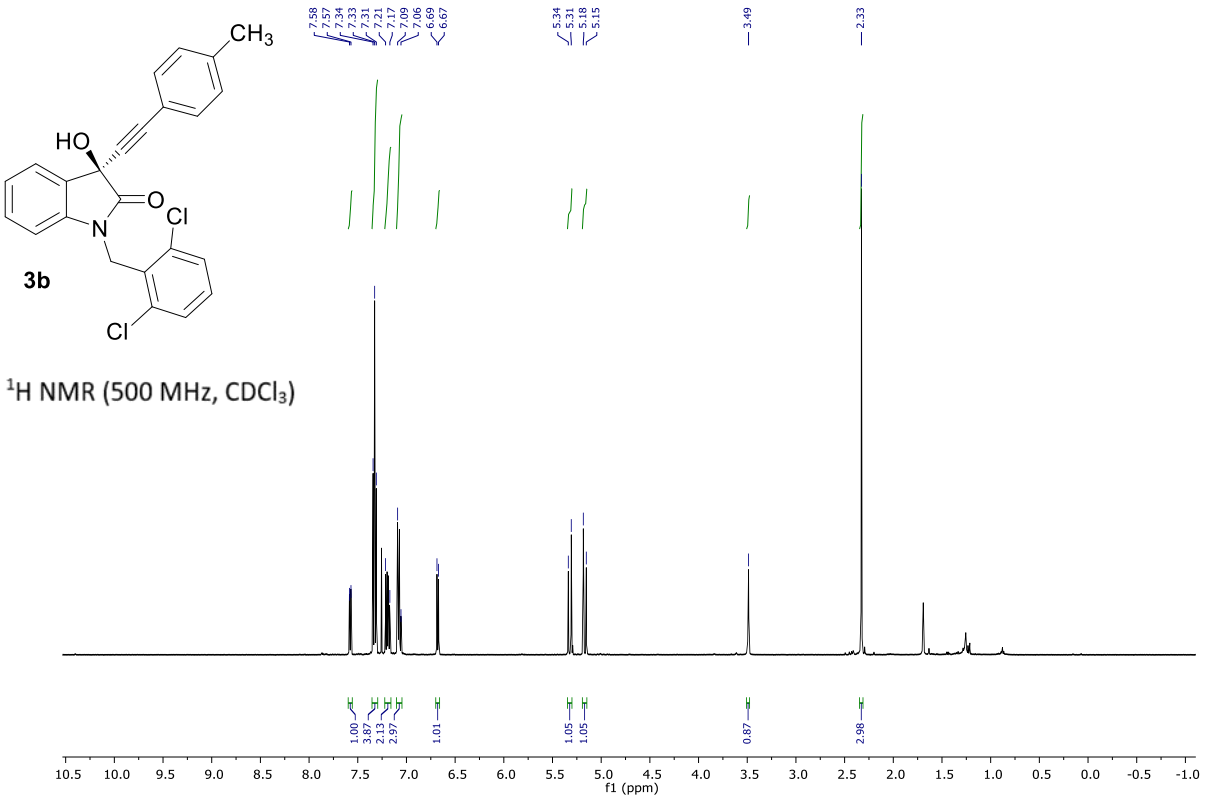
^{1}H NMR (500 MHz, $CDCl_3$)



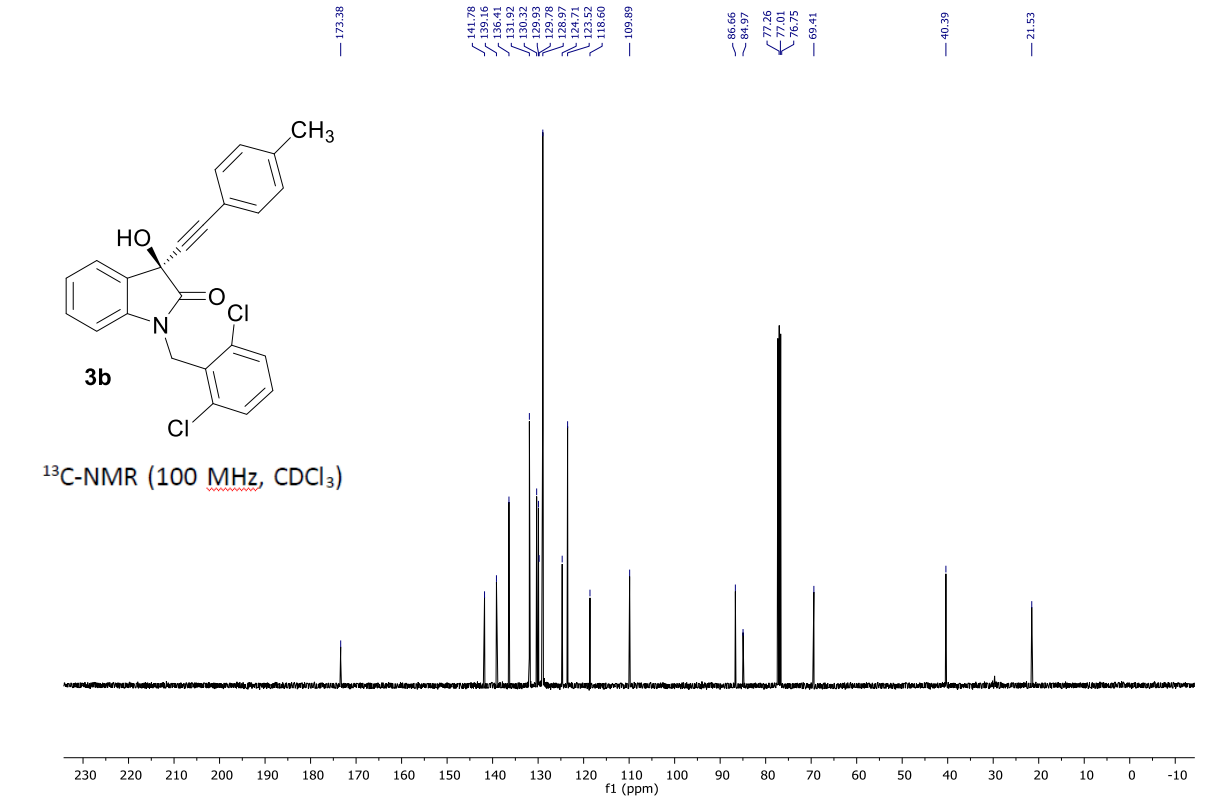
^{13}C NMR (126 MHz, $CDCl_3$)


OCH3
HO
O
N
Cl
Cl
3a
7.59
7.57
7.38
7.33
7.22
7.17
7.09
7.07
7.06
6.81
6.79
6.69
6.67
5.34
5.31
5.19
5.15
3.79
3.52
1H-NMR (400 MHz, CDCl3)
0.99
3.89
2.08
1.06
1.90
0.98
1.09
1.05
2.99
0.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

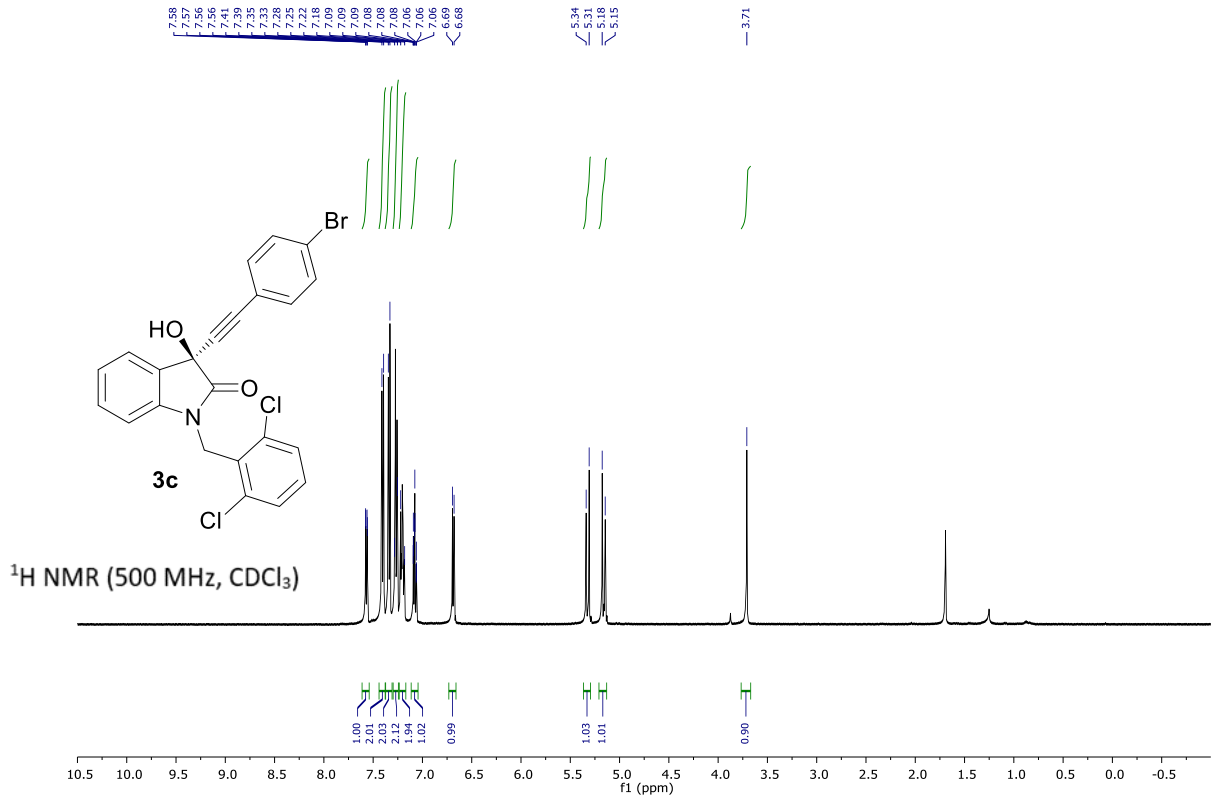

OCH3
HO
O
N
Cl
Cl
3a
173.44
160.08
141.76
136.41
133.57
130.28
129.92
129.79
129.01
124.68
123.50
113.85
113.74
109.88
86.53
84.36
77.26
77.01
76.75
69.42
55.24
40.39
13C-NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

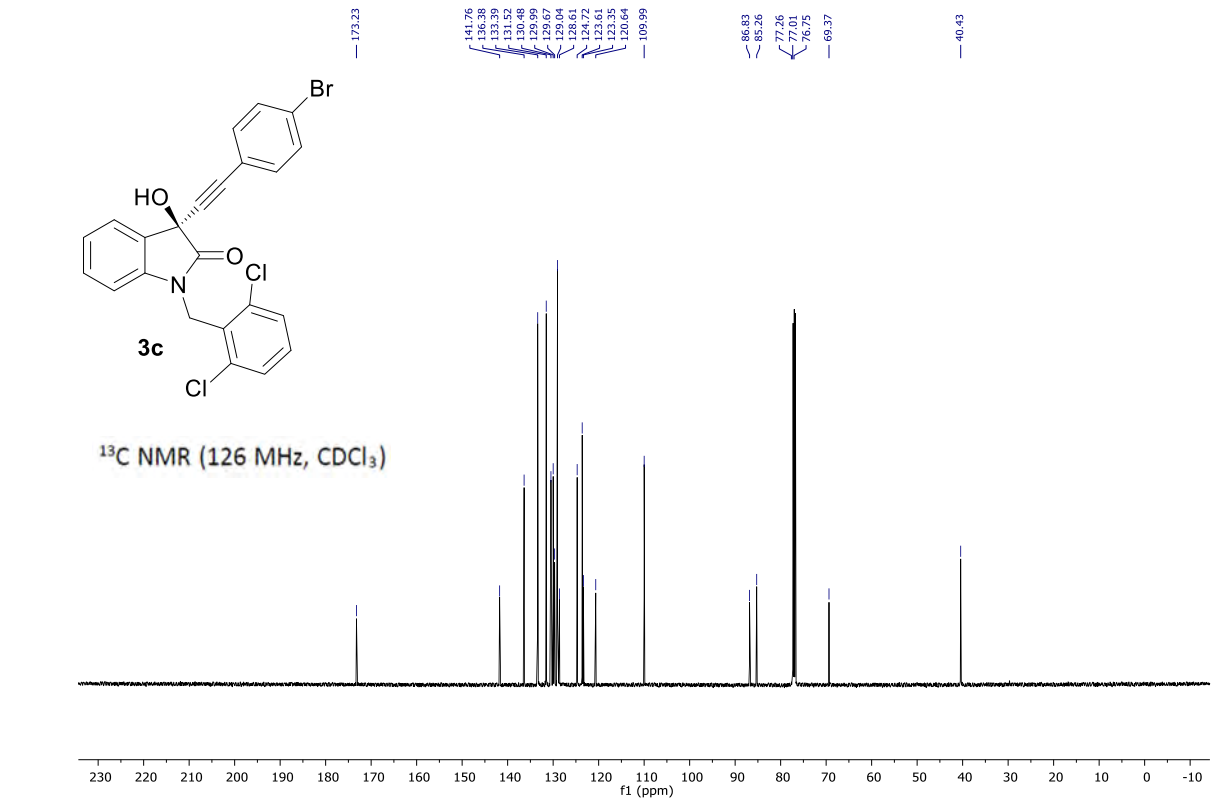


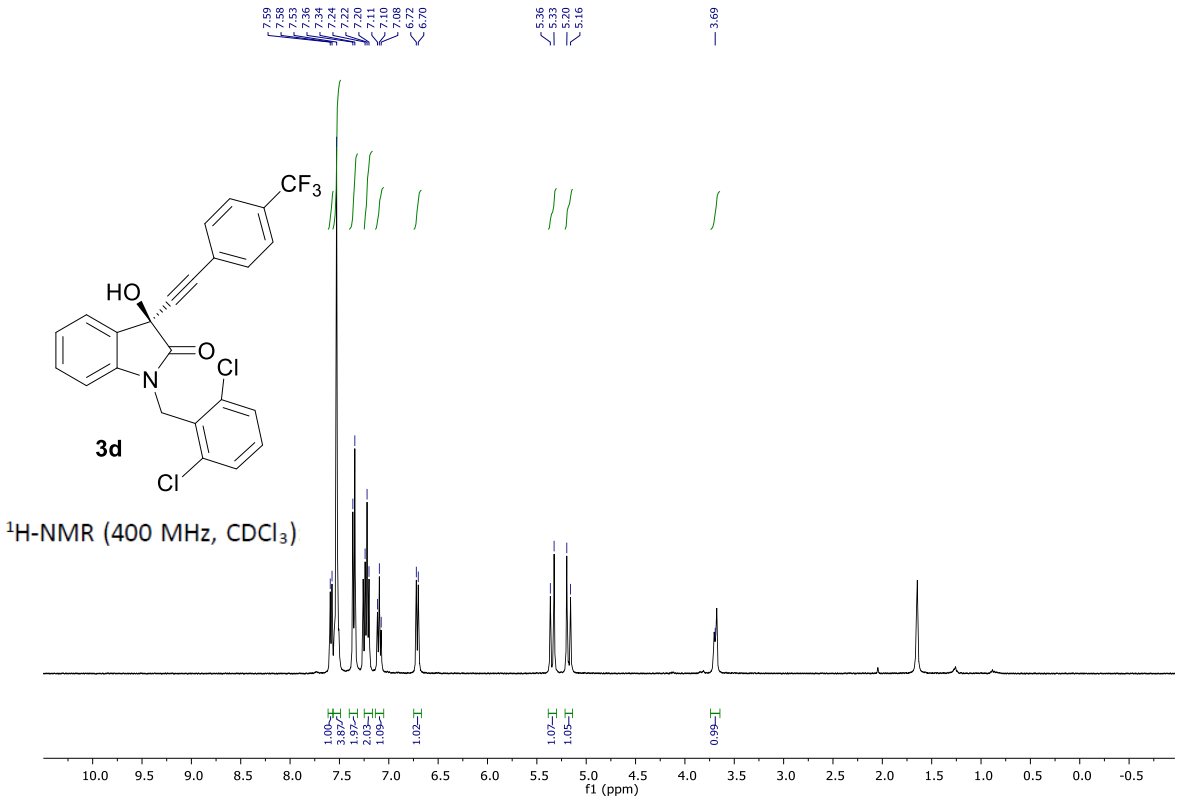
^{1}H NMR (500 MHz, $CDCl_3$)

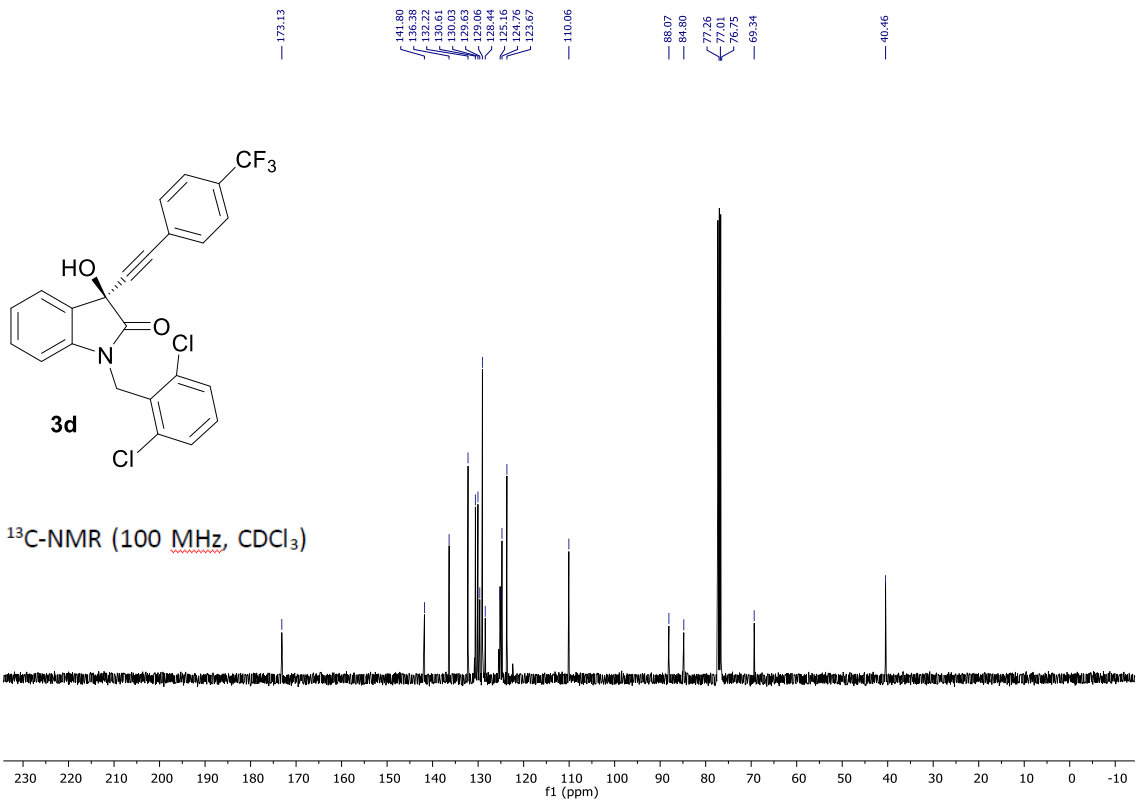


^{13}C-NMR (100 MHz, $CDCl_3$)

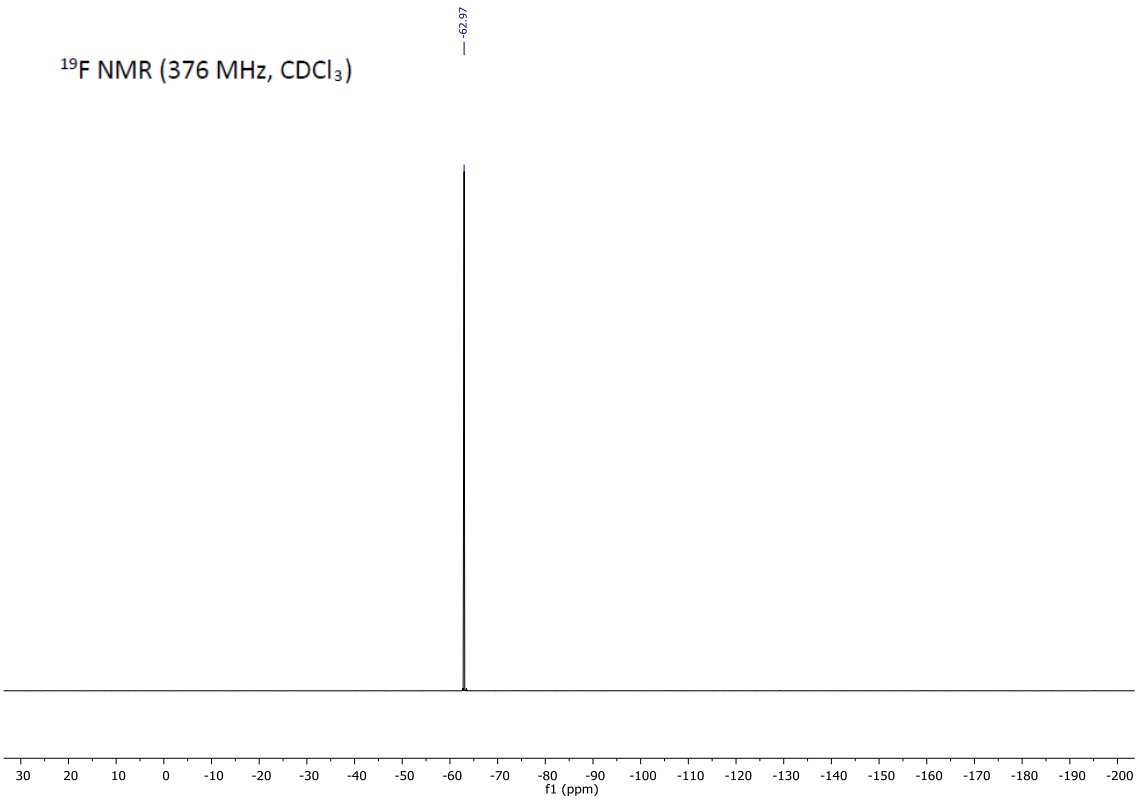

Br
HO
O
N
Cl
Cl
3c
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

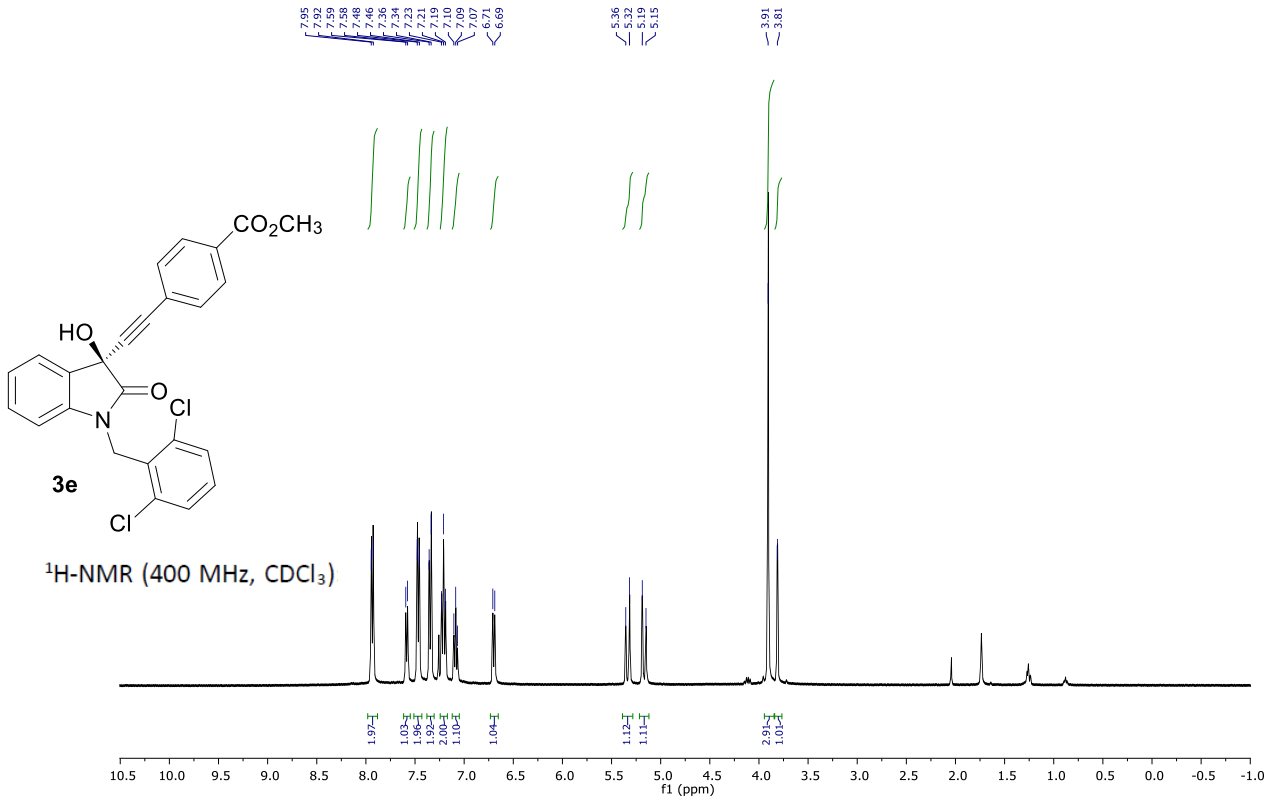

Br
HO
O
N
Cl
Cl
3c
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

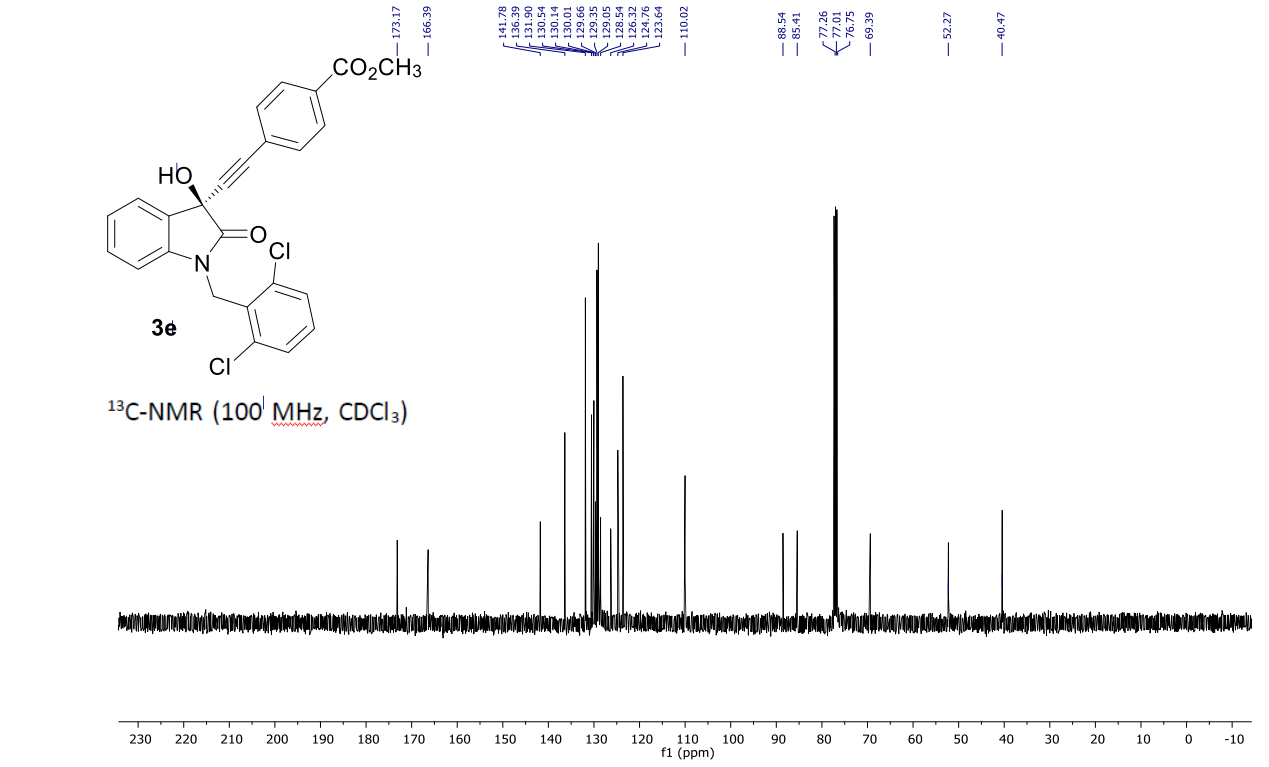

7.59
7.58
7.53
7.36
7.34
7.24
7.22
7.20
7.11
7.10
7.08
6.72
6.70
5.36
5.33
5.20
5.16
3.69
CF3
HO
O
Cl
N
Cl
3d
1H-NMR (400 MHz, CDCl3)
1.00
3.87
1.97
2.03
1.09
1.02
1.07
1.05
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

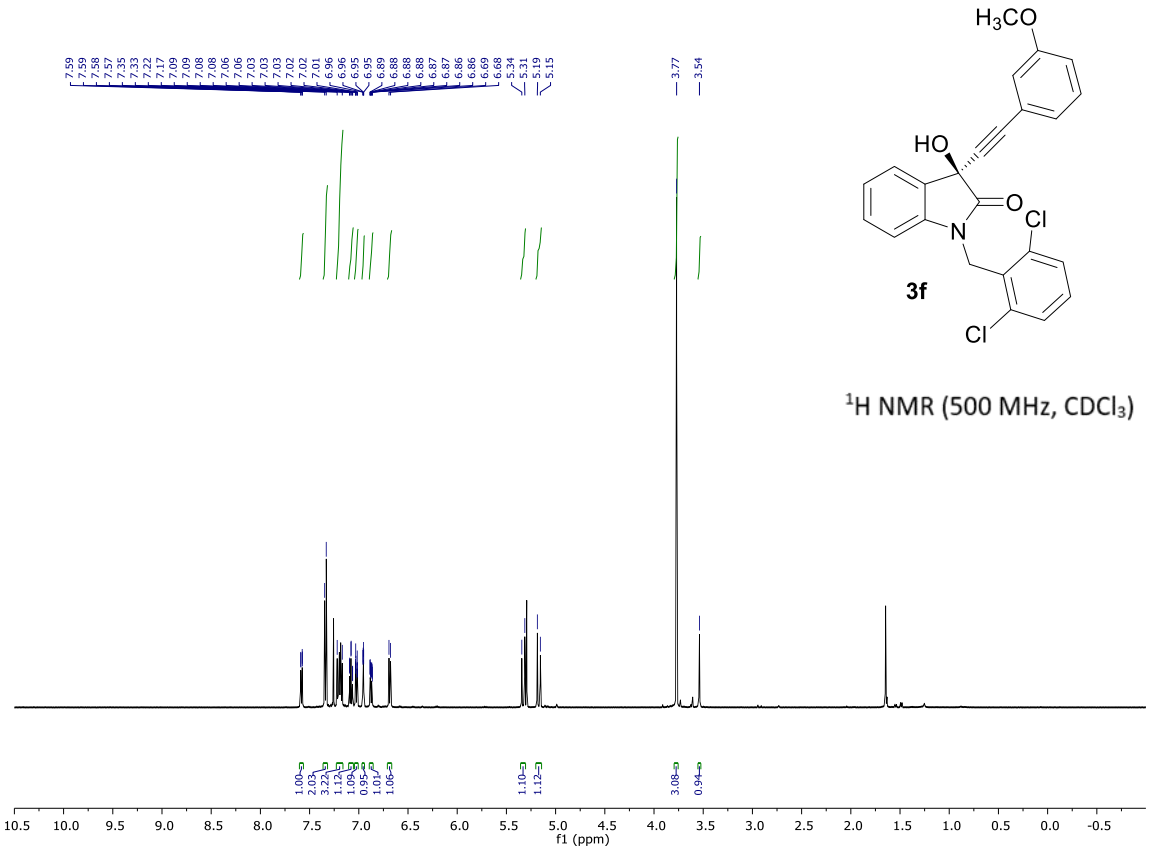

173.13
141.80
136.38
132.22
130.61
130.03
129.63
129.06
128.44
125.16
123.76
123.67
110.06
88.07
84.80
77.26
77.01
76.75
69.34
40.46
CF3
HO
O
Cl
N
Cl
3d
13C-NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

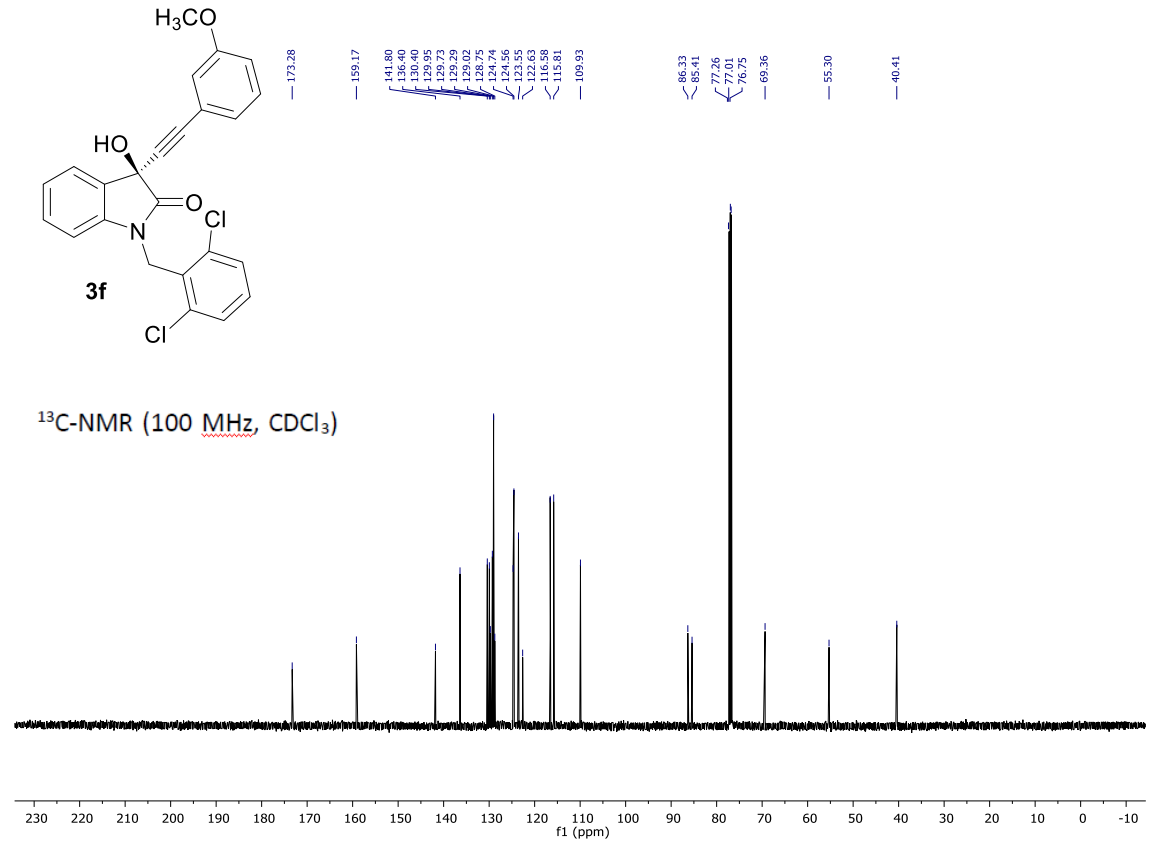
^{19}F NMR (376 MHz, $CDCl_3$)

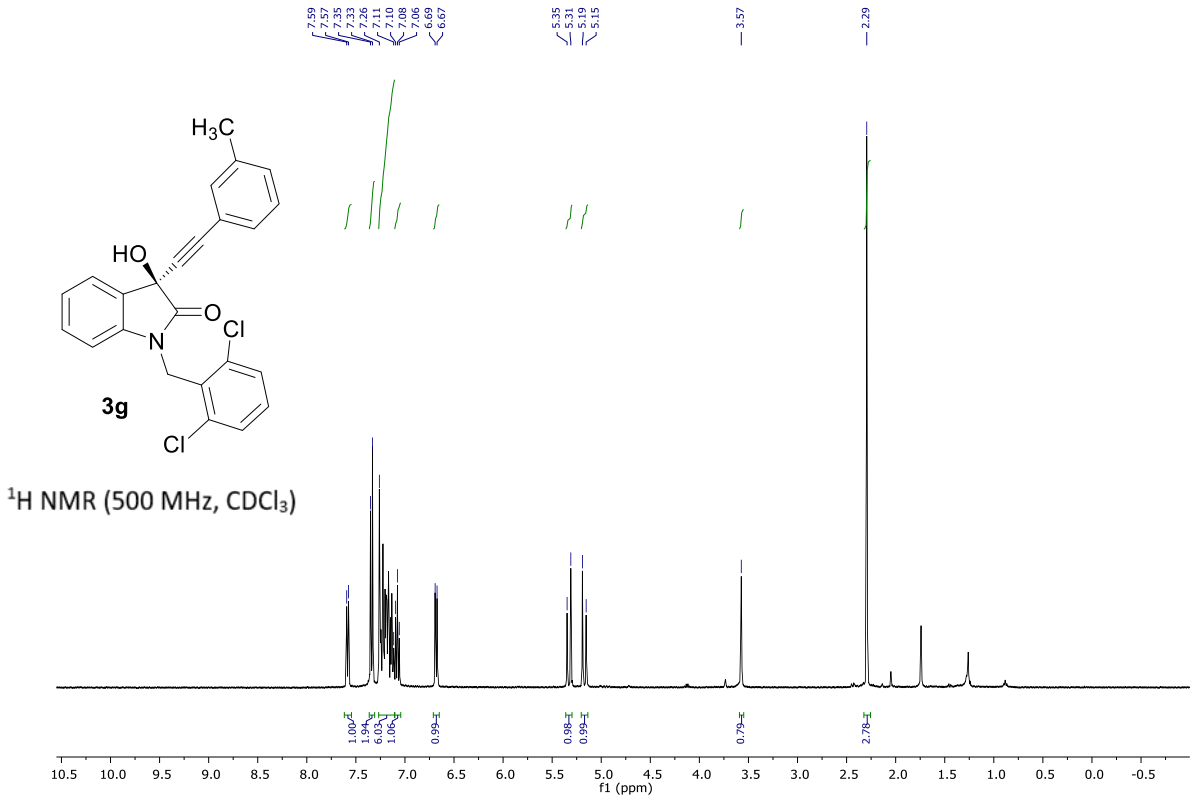


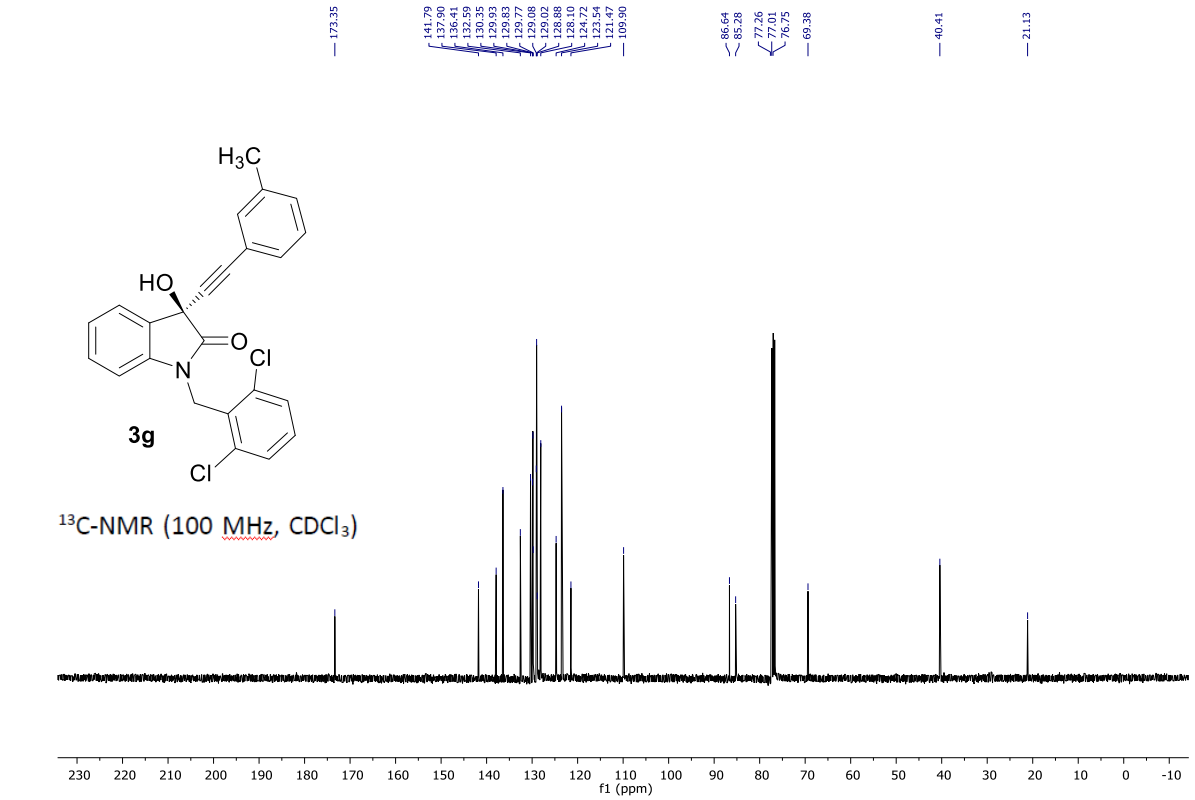

7.95
7.92
7.59
7.58
7.48
7.46
7.36
7.34
7.23
7.21
7.19
7.10
7.09
7.07
6.71
6.69
5.36
5.32
5.19
5.15
3.91
3.81
CO2CH3
HO
O
N
Cl
Cl
3e
1H-NMR (400 MHz, CDCl3)
1.97
1.03
1.96
1.92
2.00
1.10
1.04
1.12
1.11
2.91
1.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

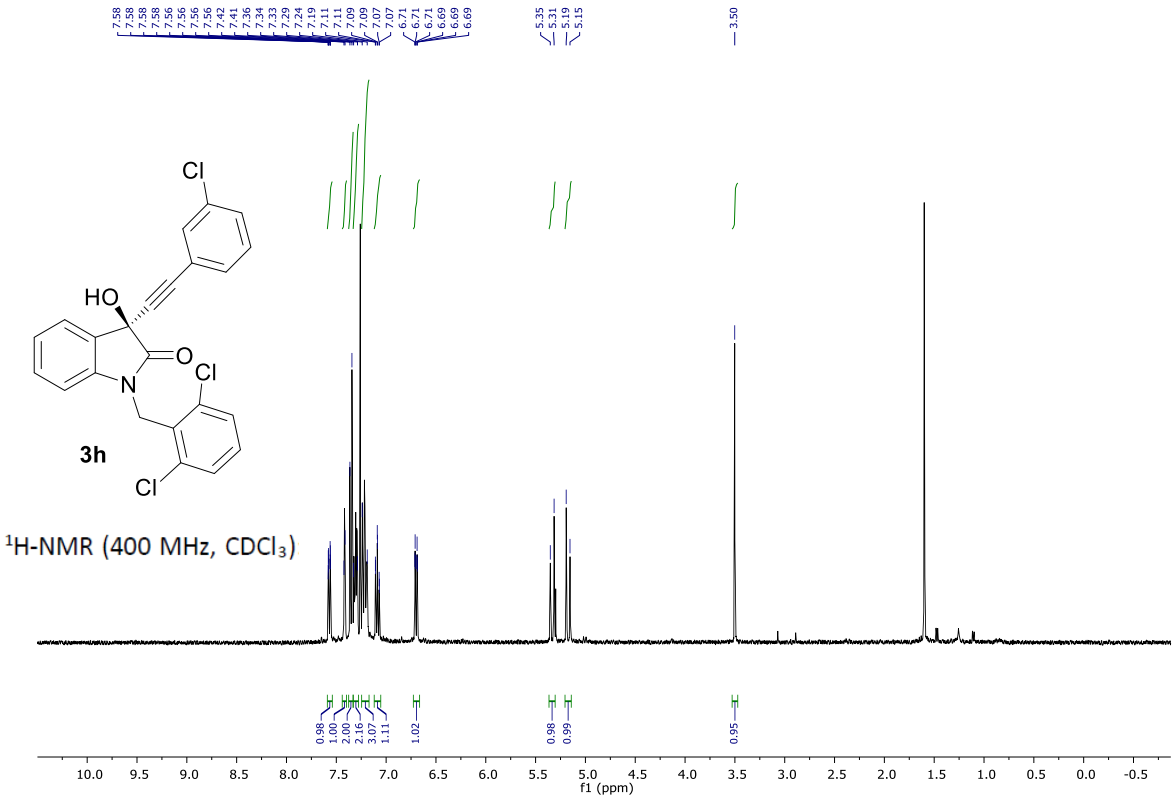

173.17
166.39
141.78
136.39
131.90
130.54
130.14
130.01
129.66
129.35
129.05
128.54
126.32
124.76
123.64
110.02
88.54
85.41
77.26
77.01
76.75
69.39
52.27
40.47
CO2CH3
HO
O
N
Cl
Cl
3e
13C-NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

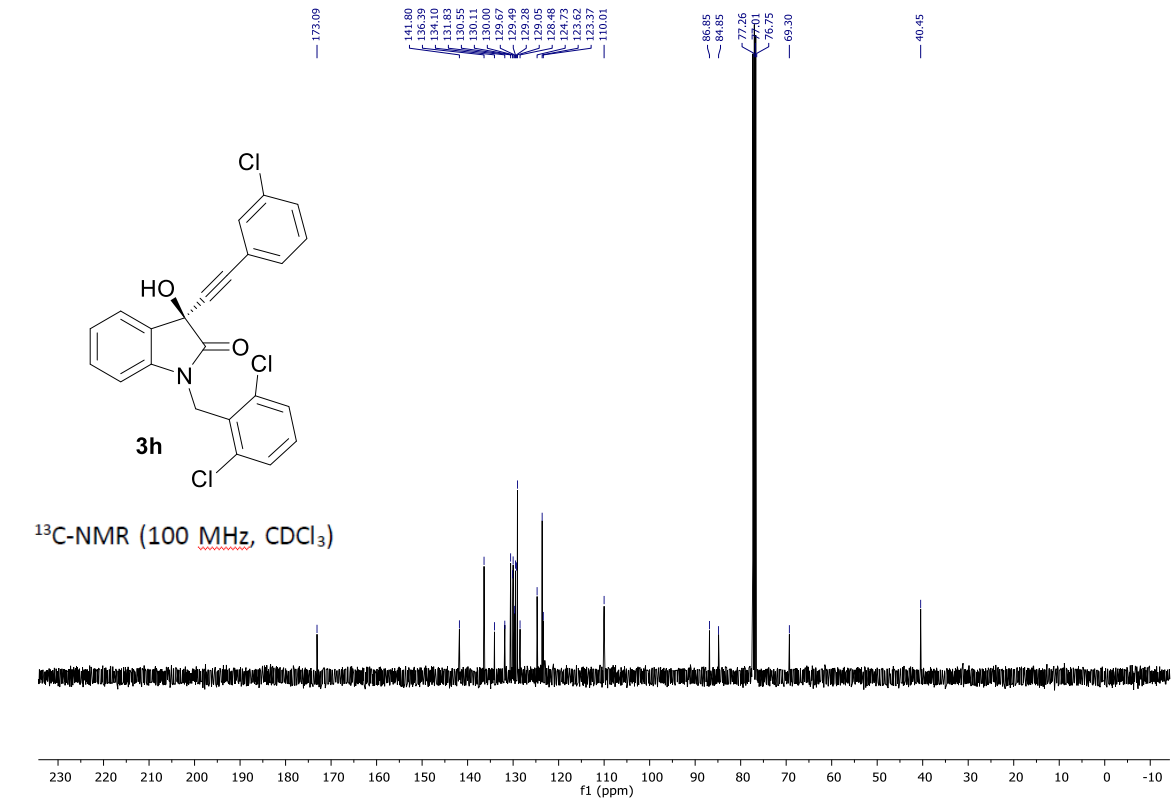

H3CO
HO
O
N
Cl
Cl
3f
1H NMR (500 MHz, CDCl3)
f1 (ppm)

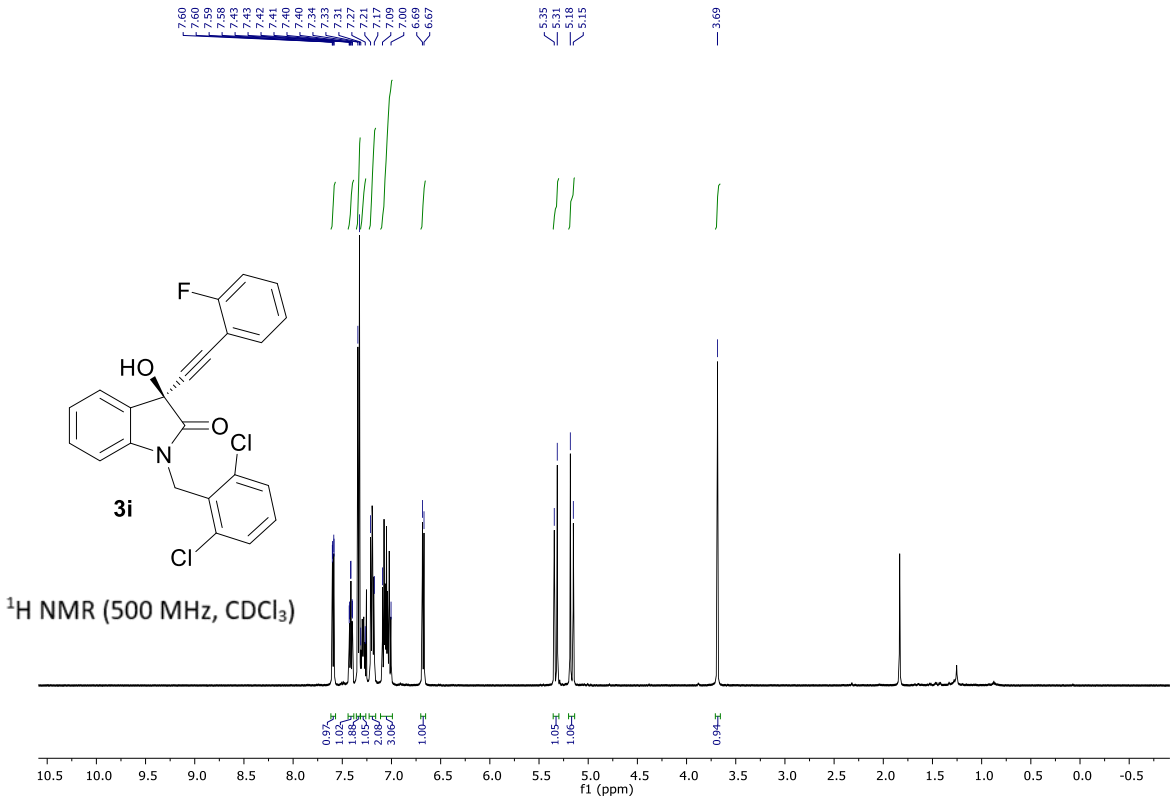

H3CO
HO
O
N
Cl
Cl
3f
13C-NMR (100 MHz, CDCl3)
f1 (ppm)


7.59
7.57
7.35
7.33
7.26
7.11
7.10
7.08
7.06
6.69
6.67
5.35
5.31
5.19
5.15
3.57
2.29
H3C
HO
O
N
Cl
Cl
3g
1H NMR (500 MHz, CDCl3)
1.00
1.94
6.03
1.06
0.99
0.98
0.99
0.79
2.70
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

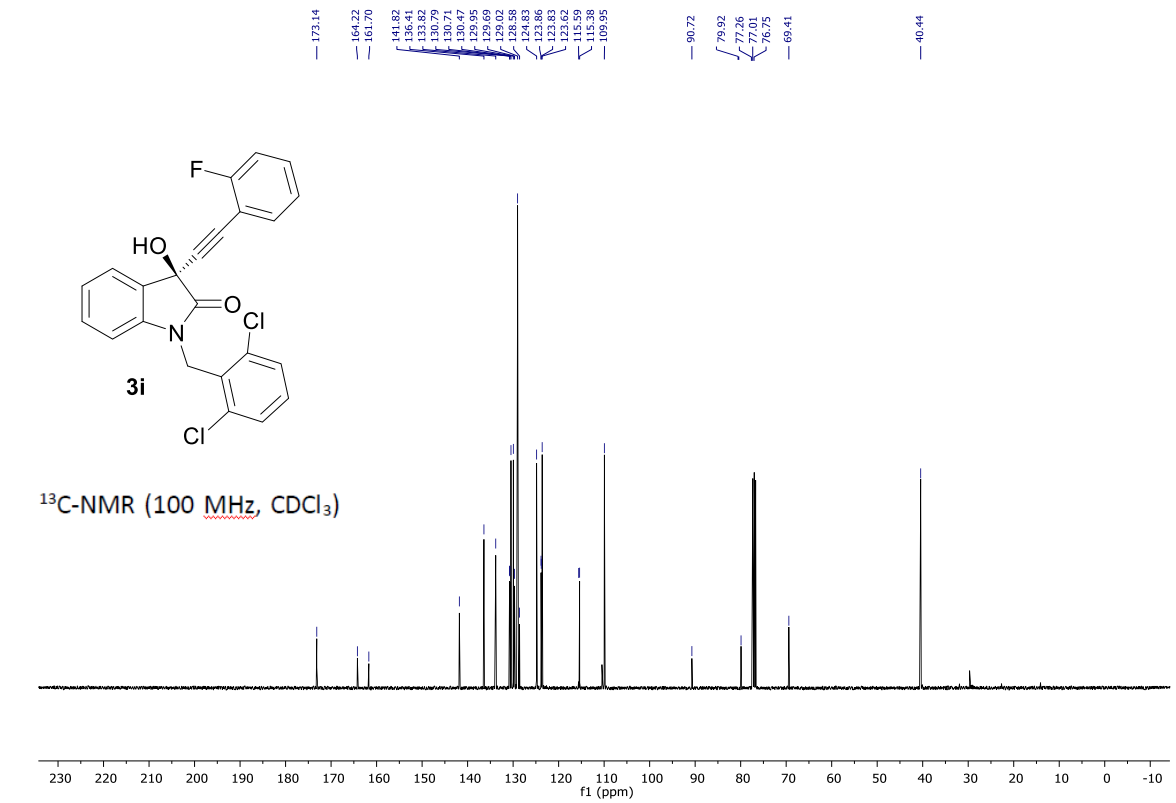

173.35
141.79
137.90
136.41
132.59
130.35
129.93
129.83
129.77
129.08
129.02
128.88
128.10
124.72
123.54
121.47
109.90
86.64
85.28
77.26
77.01
76.75
69.38
40.41
21.13
H3C
HO
O
N
Cl
Cl
3g
13C-NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
HO
O
N
Cl
Cl
3h
^{1}H-NMR (400 MHz, $CDCl_3$)
f1 (ppm)


Cl
HO
O
N
Cl
Cl
3h
^{13}C-NMR (100 MHz, $CDCl_3$)
f1 (ppm)

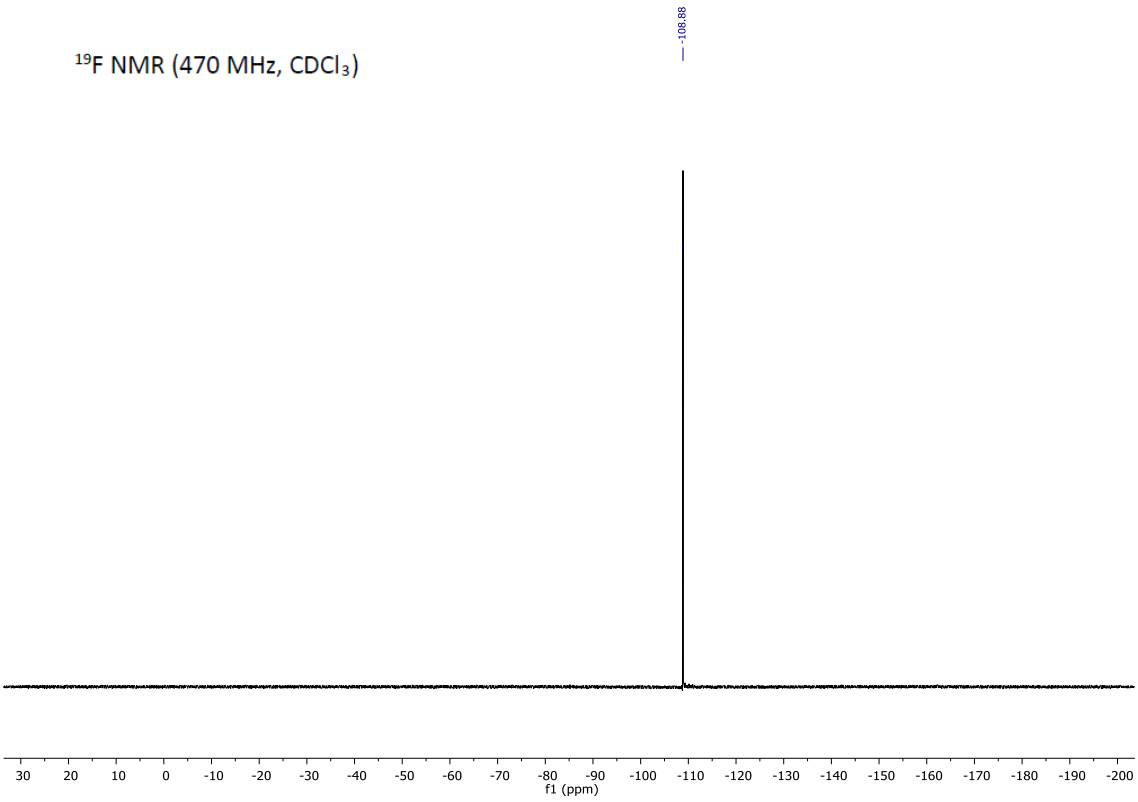


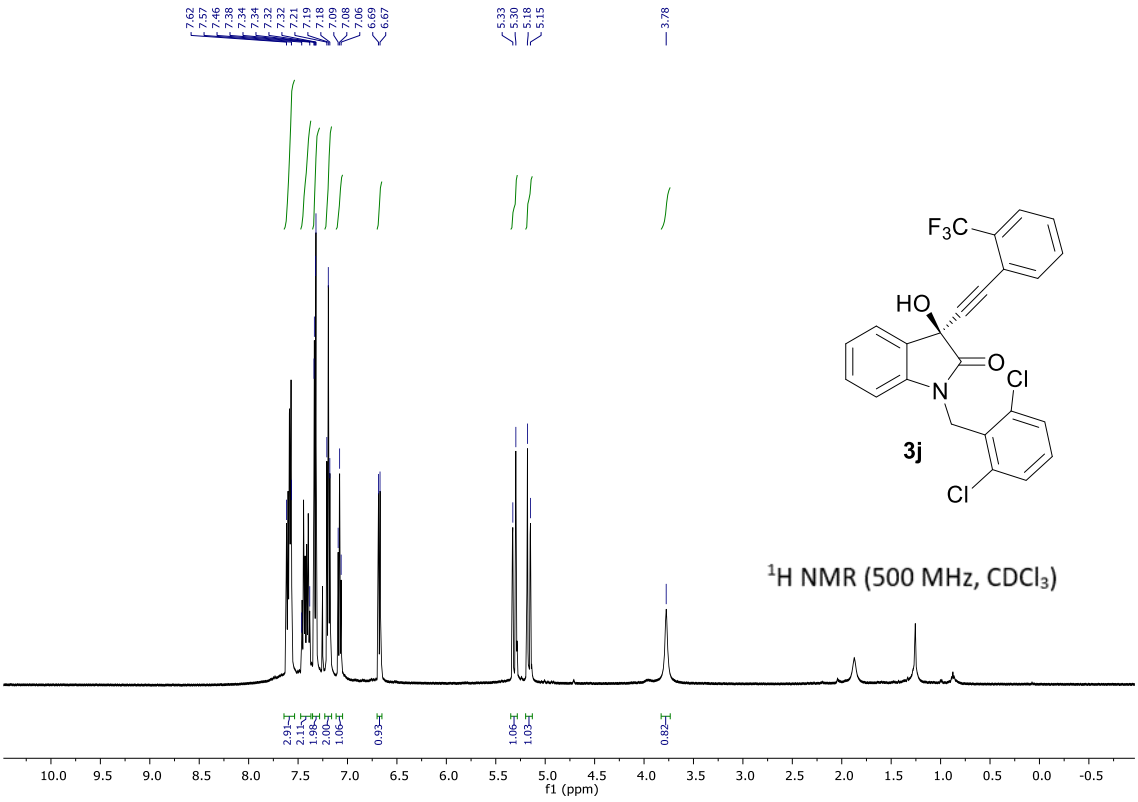
^{1}H NMR (500 MHz, $CDCl_3$)

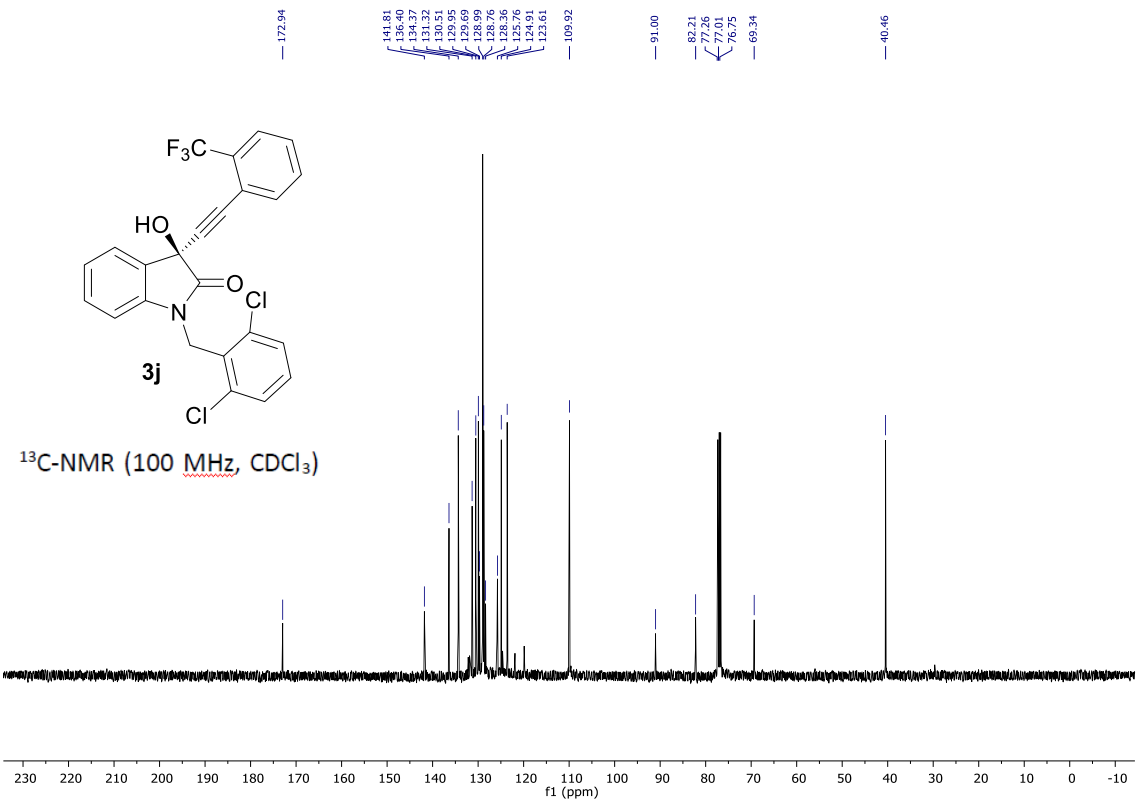


^{13}C-NMR (100 MHz, $CDCl_3$)

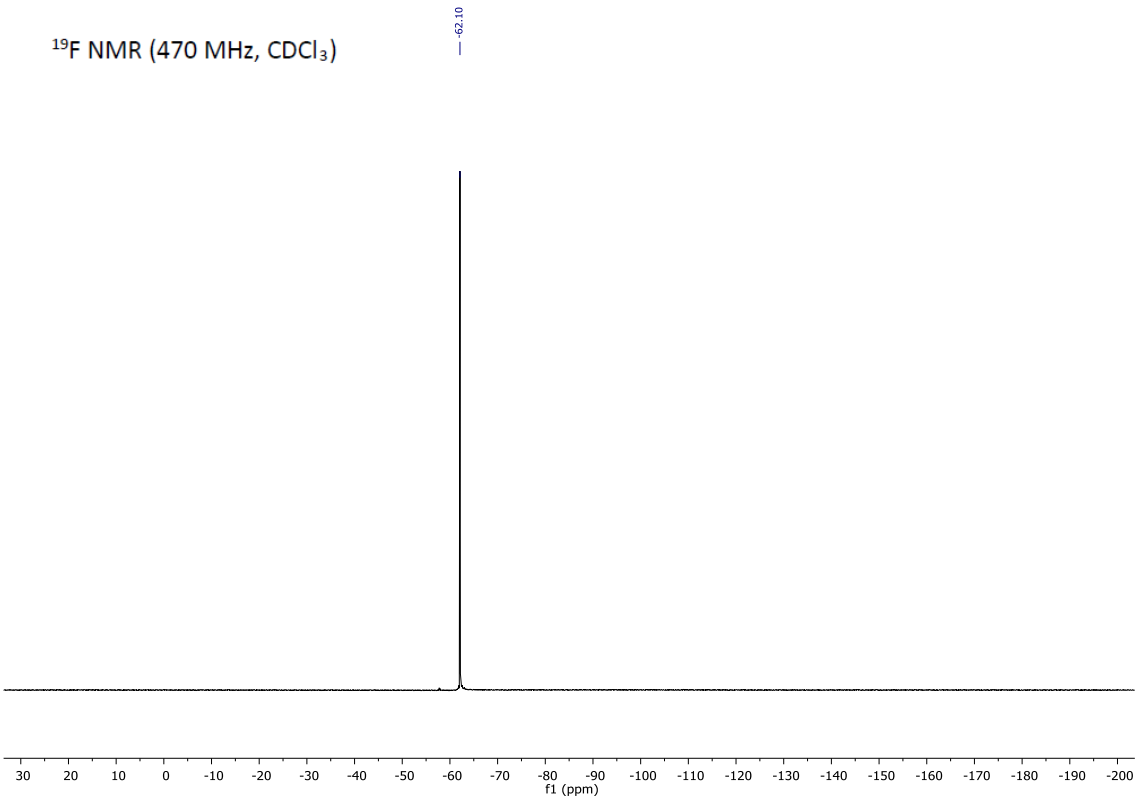
^{19}F NMR (470 MHz, $CDCl_3$)

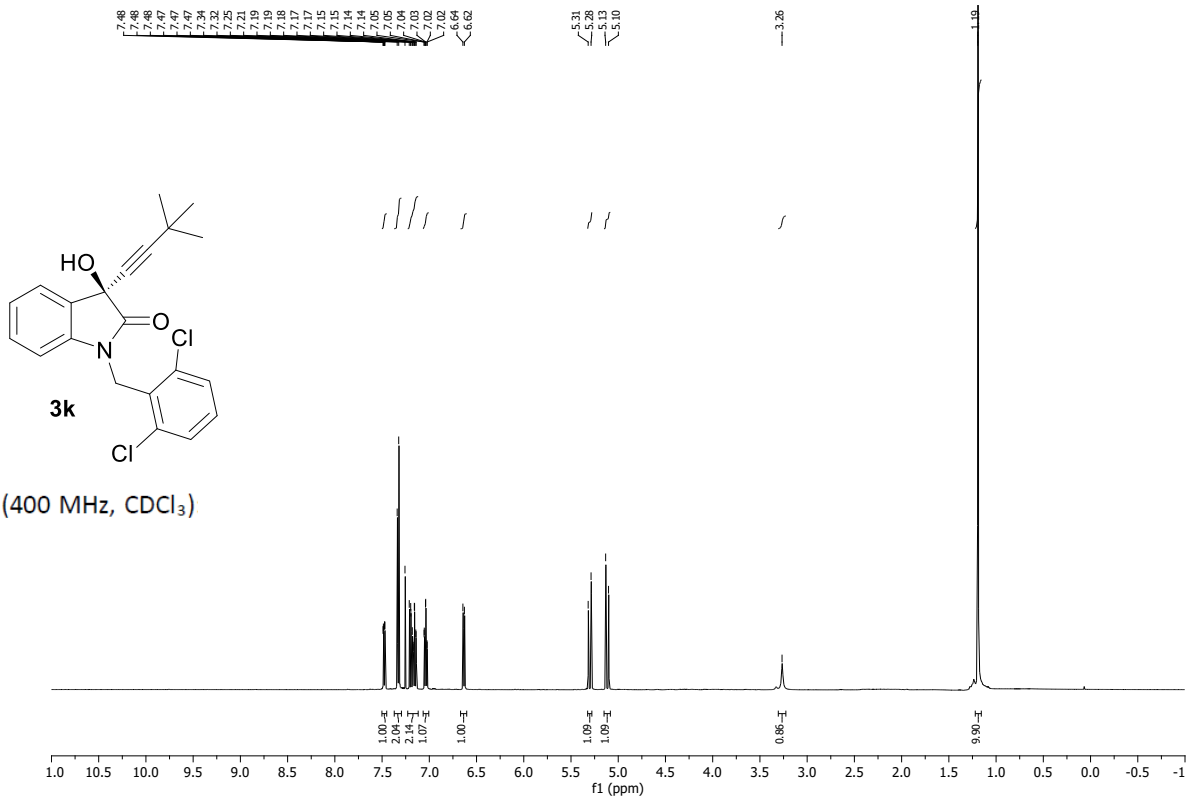



7.62
7.57
7.46
7.38
7.34
7.34
7.32
7.32
7.21
7.19
7.18
7.09
7.08
7.06
6.69
6.67
5.33
5.30
5.18
5.15
3.78
F3C
HO
O
Cl
N
Cl
3j
1H NMR (500 MHz, CDCl3)
2.91
2.11
1.98
2.00
1.06
0.93
1.06
1.03
0.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

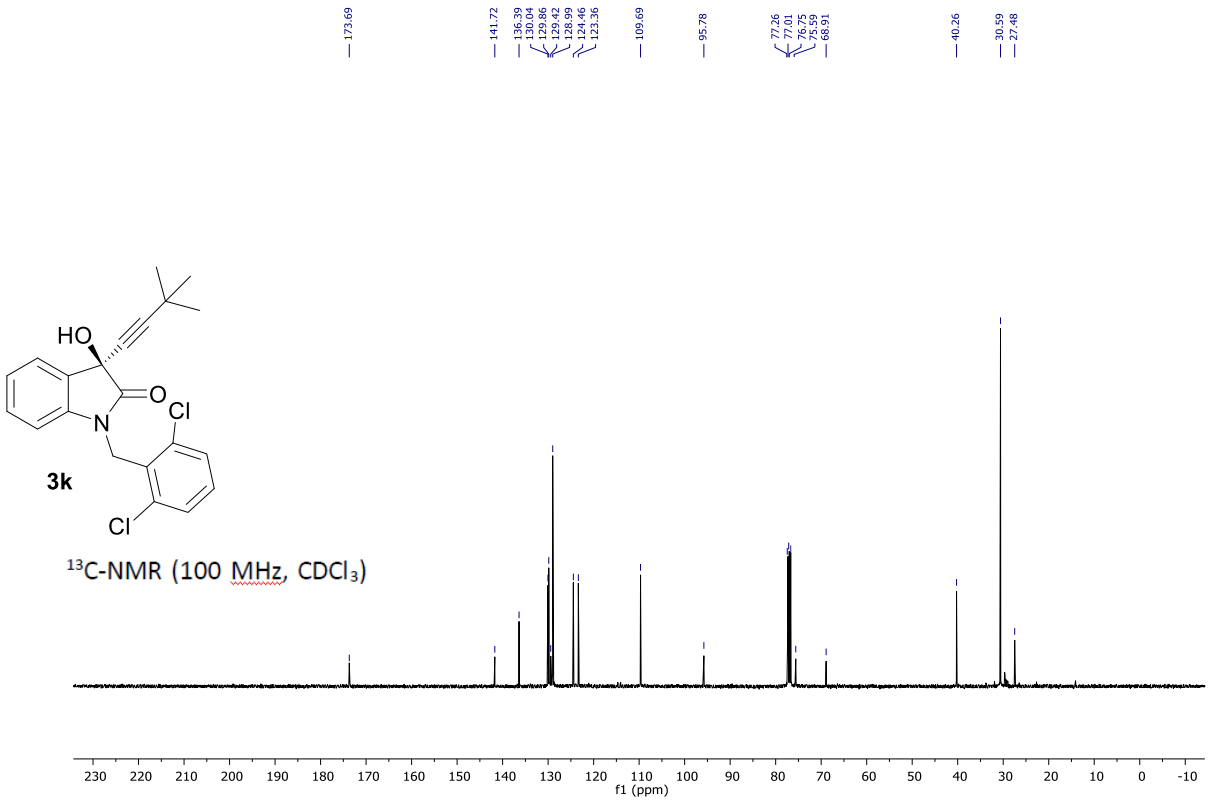

172.94
141.81
136.40
134.37
131.32
130.51
129.95
129.69
128.99
128.76
128.36
124.56
124.91
123.61
109.92
91.00
82.21
77.26
77.01
76.75
69.34
40.46
F3C
HO
O
Cl
N
Cl
3j
13C-NMR (100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{19}F NMR (470 MHz, $CDCl_3$)

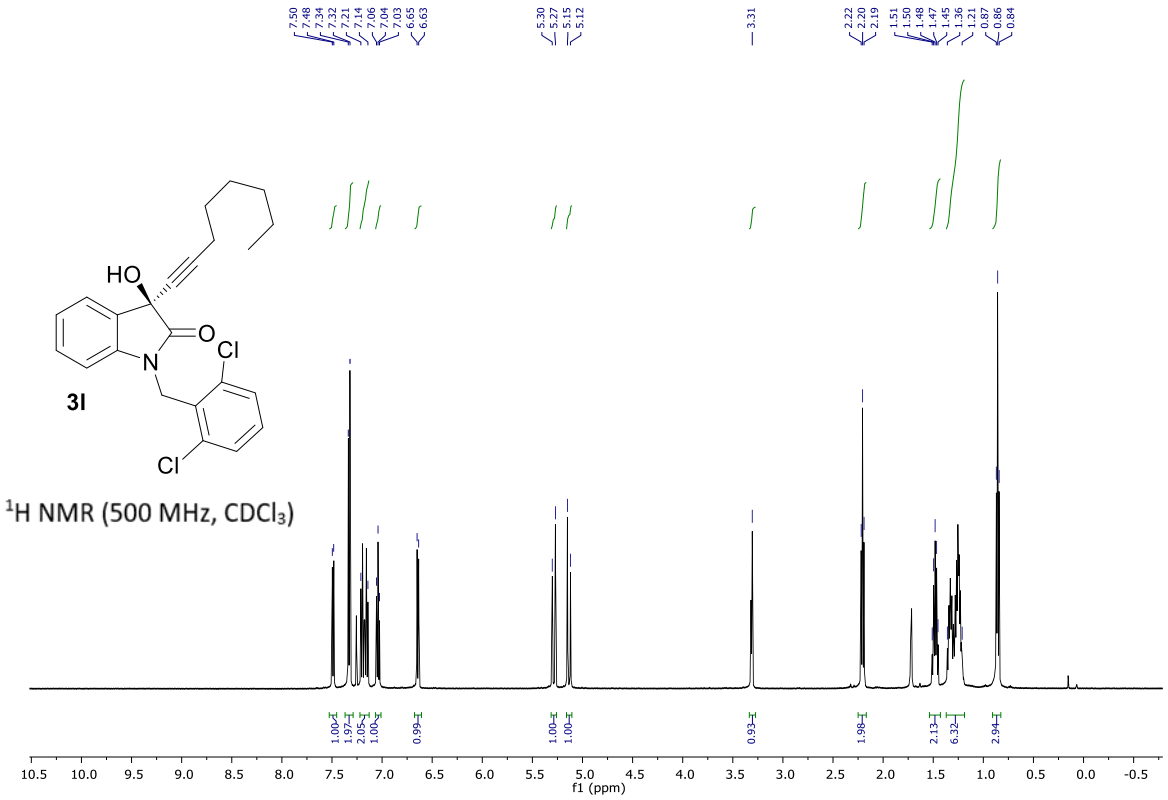


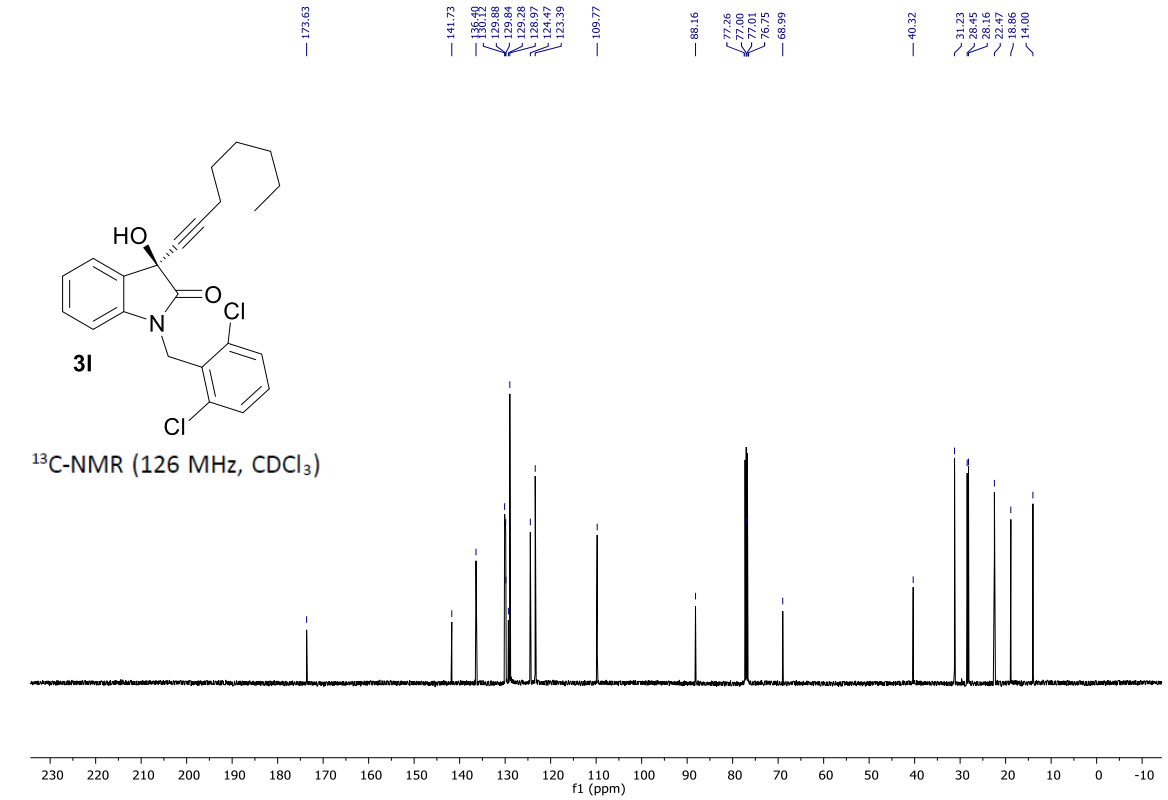


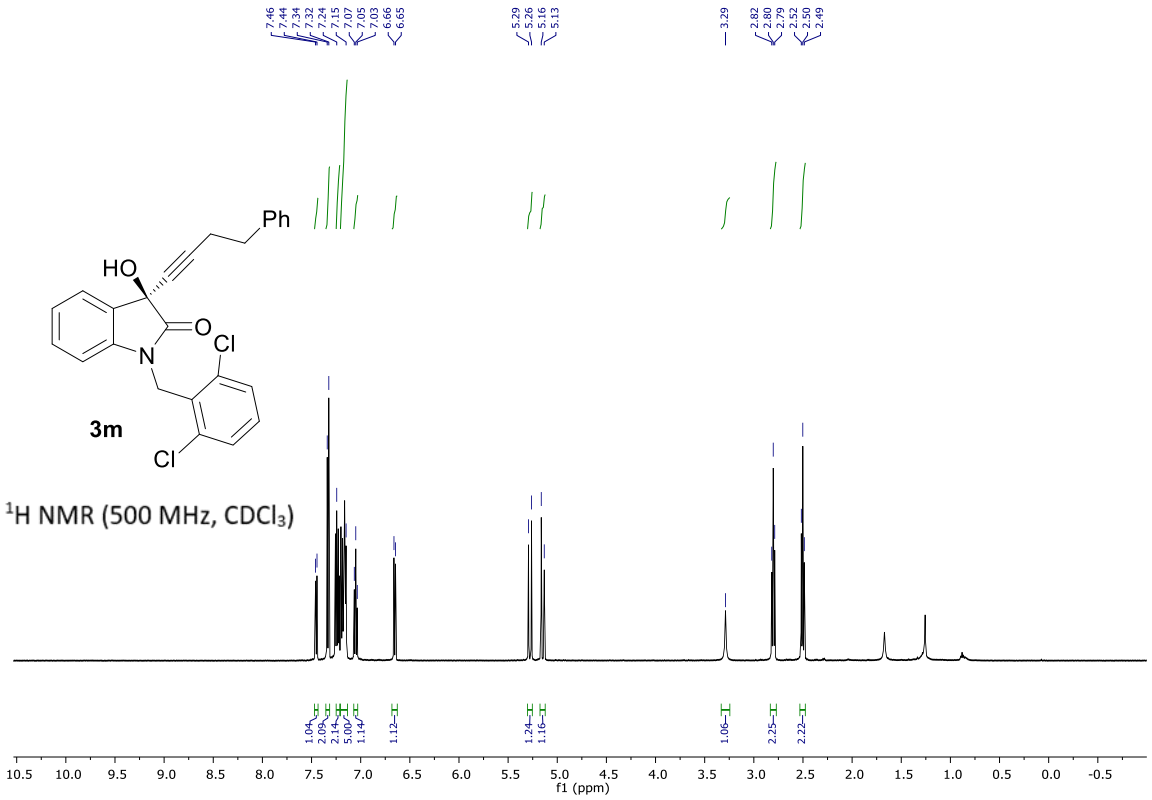
^{1}H-NMR (400 MHz, $CDCl_3$)

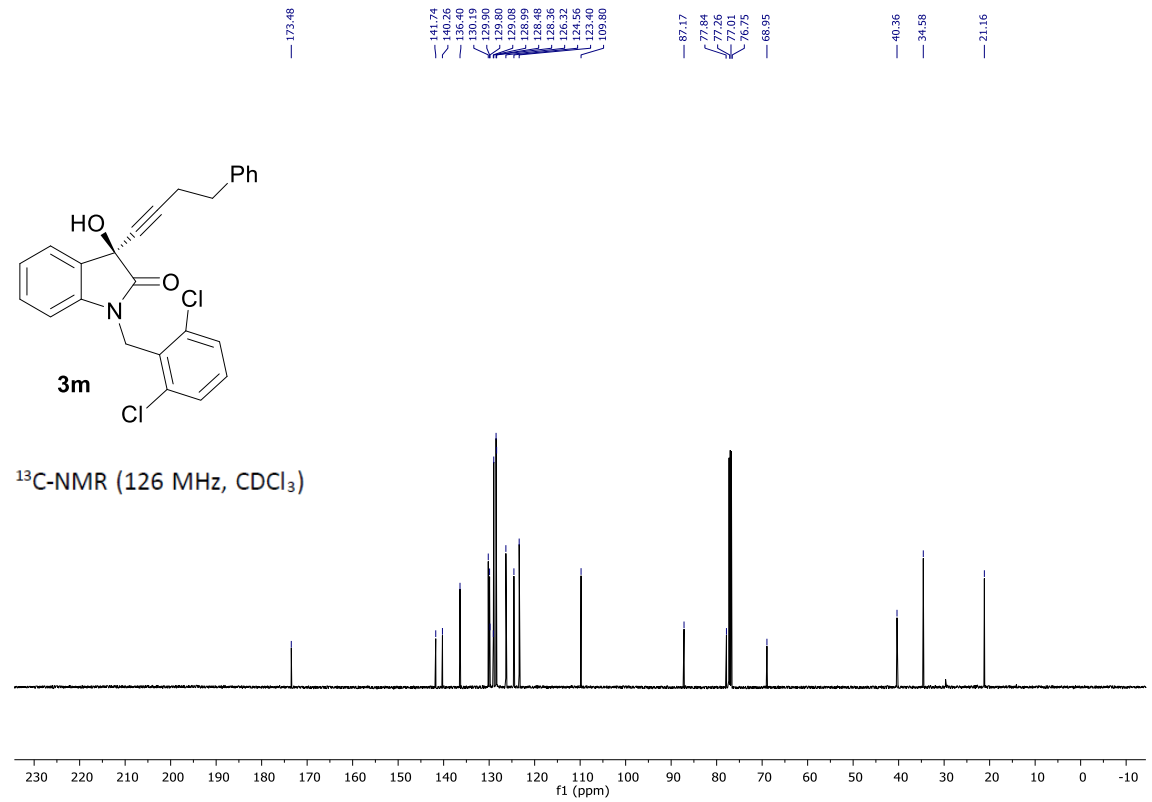


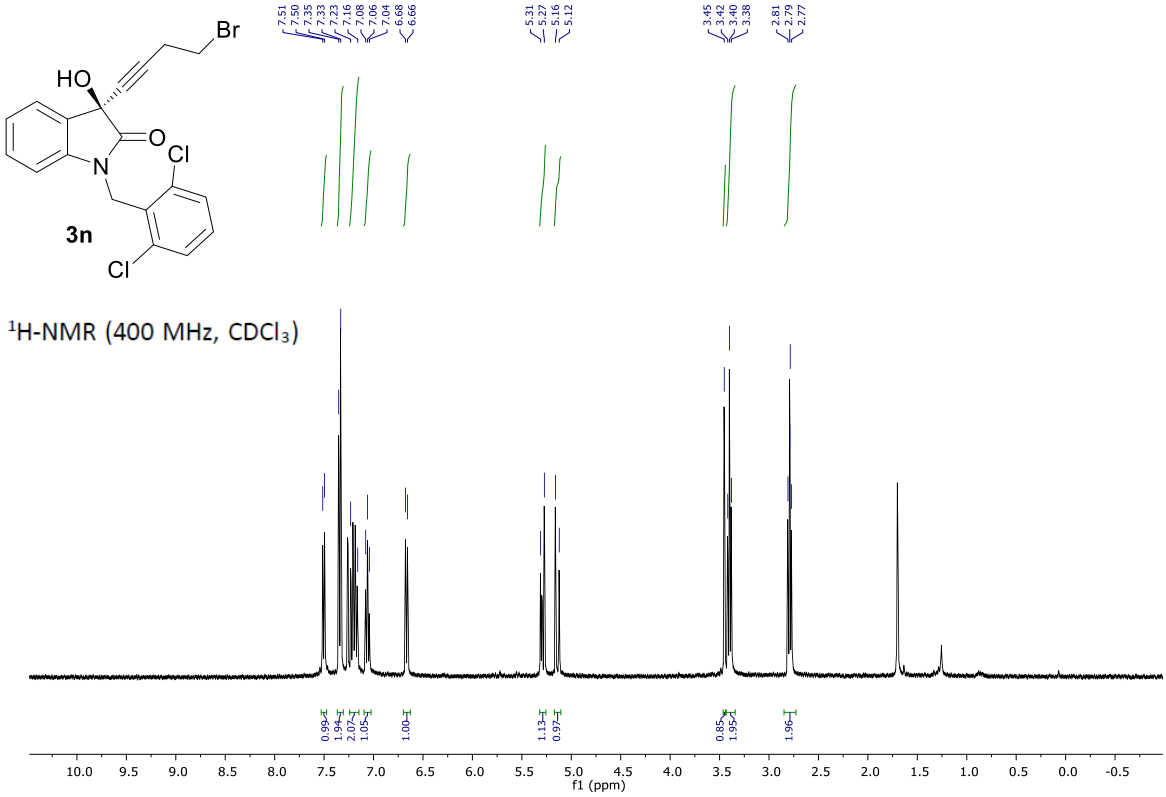
^{13}C-NMR (100 MHz, $CDCl_3$)


HO
O
N
Cl
Cl
3l
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

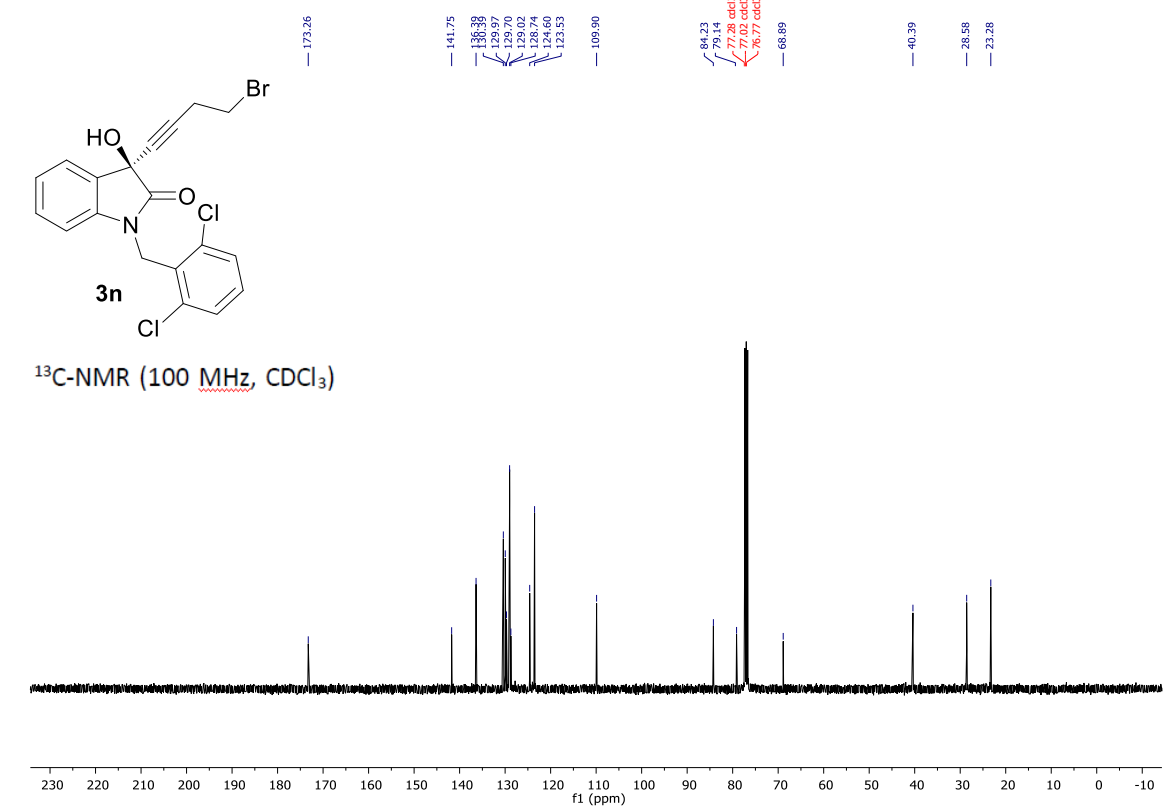

HO
O
N
Cl
Cl
3l
^{13}C-NMR (126 MHz, $CDCl_3$)
f1 (ppm)


Ph
HO
O
N
Cl
Cl
3m
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

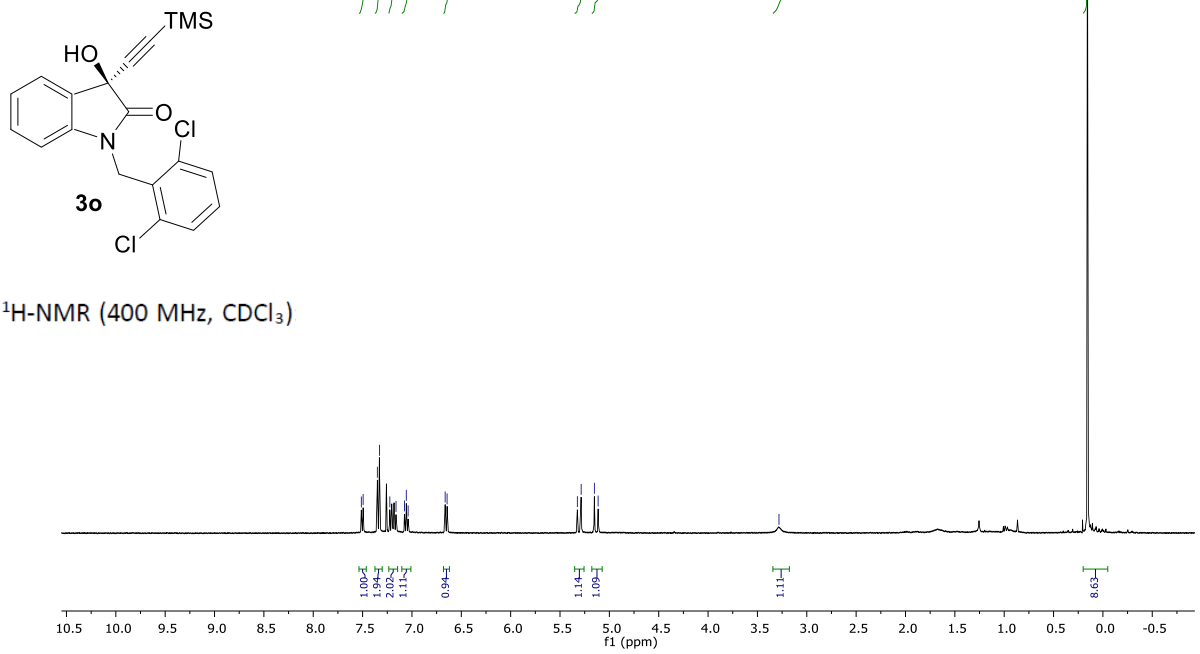

Ph
HO
O
N
Cl
Cl
3m
^{13}C-NMR (126 MHz, $CDCl_3$)
f1 (ppm)



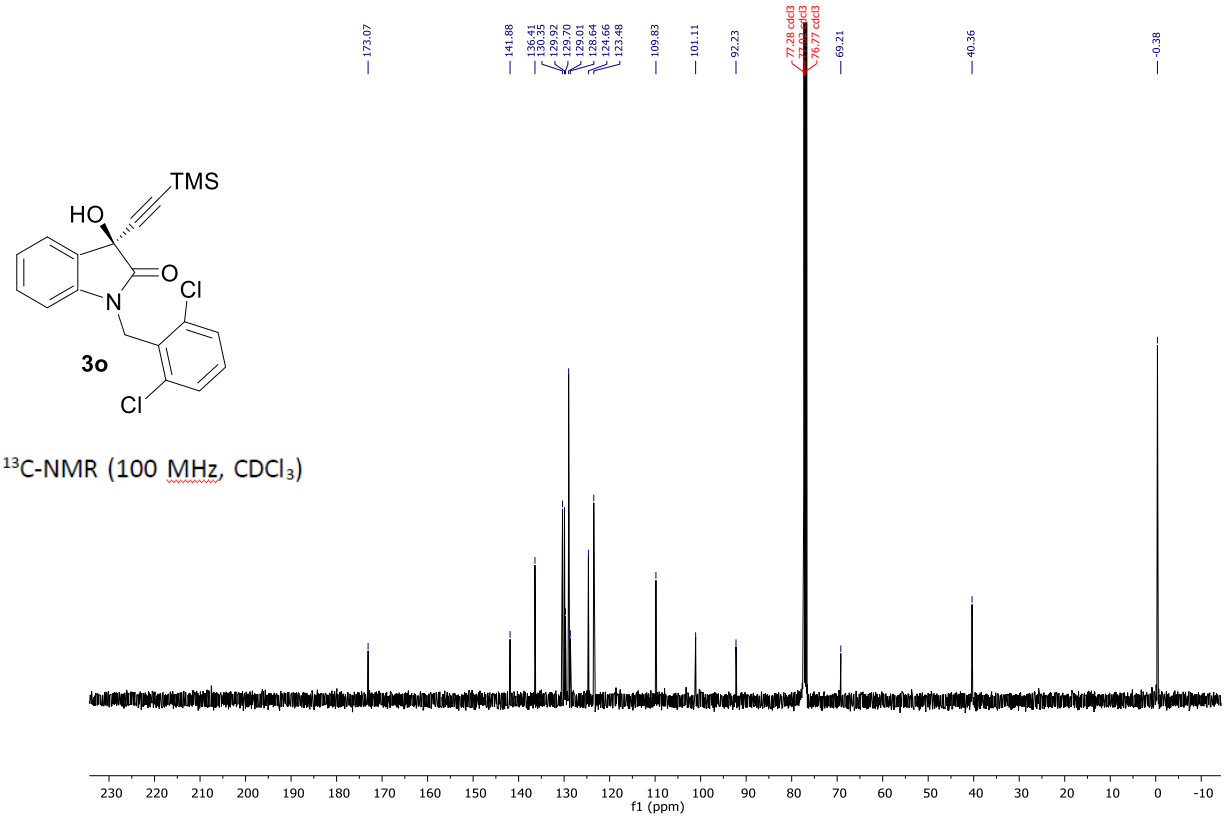
^{1}H-NMR (400 MHz, $CDCl_3$)



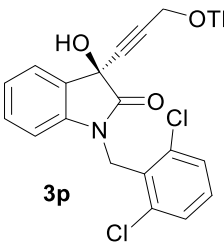
^{13}C-NMR (100 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)

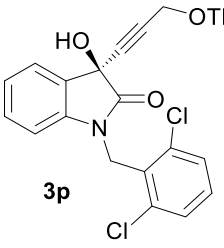


^{13}C-NMR (100 MHz, $CDCl_3$)



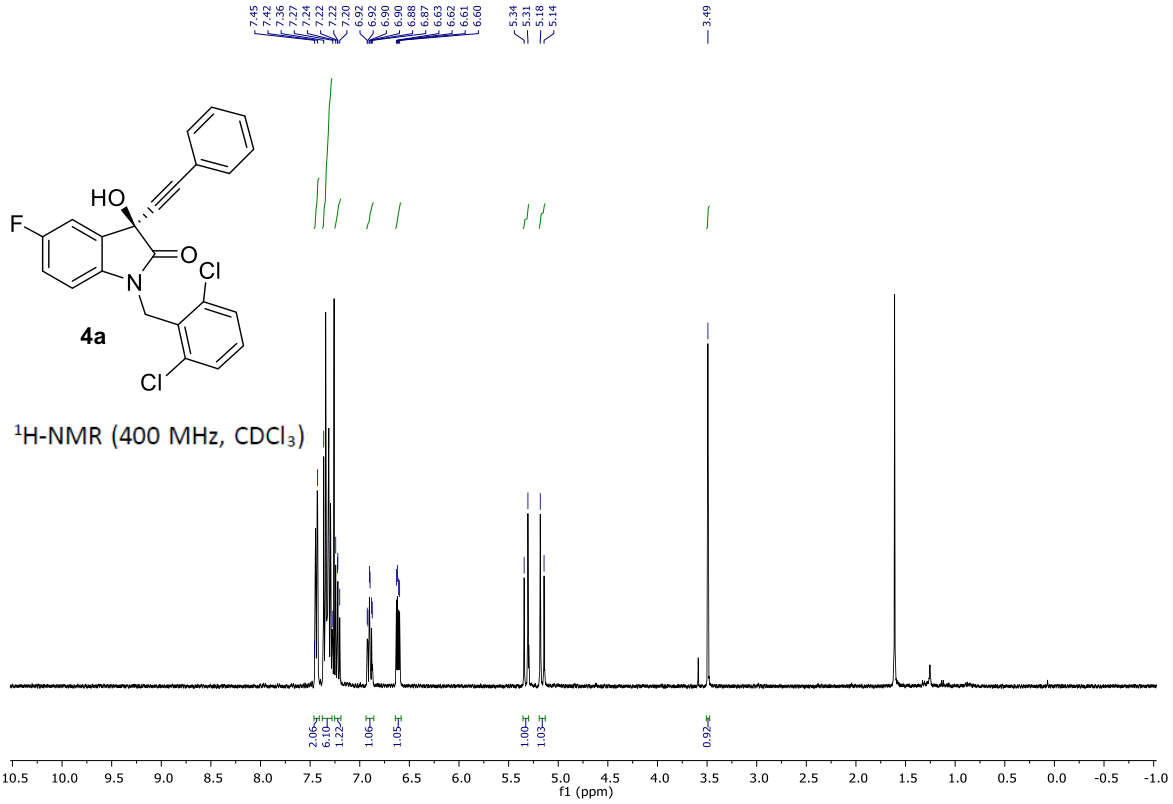
3p

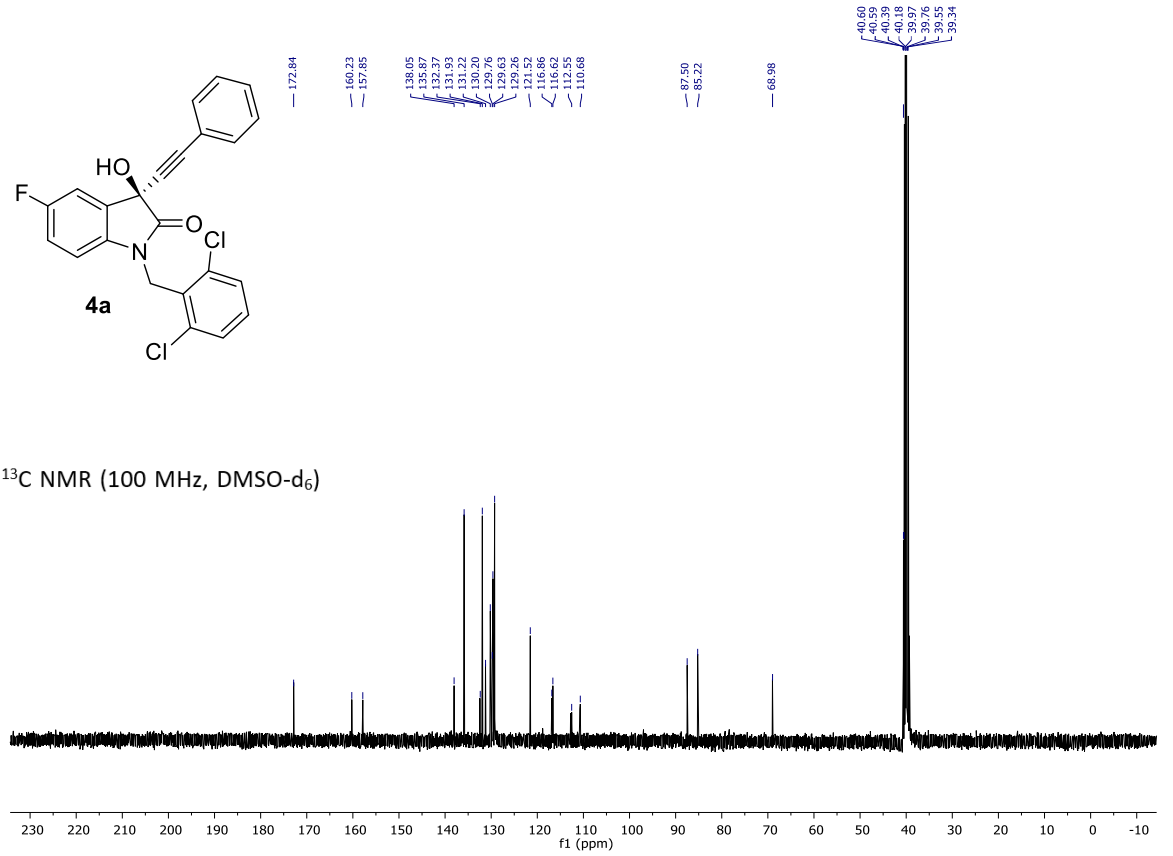
^{1}H-NMR (400 MHz, $CDCl_3$)

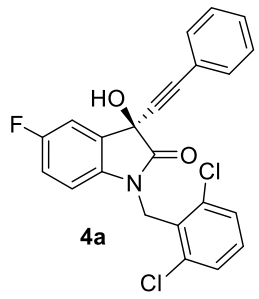


3p

^{13}C-NMR (100 MHz, $CDCl_3$)

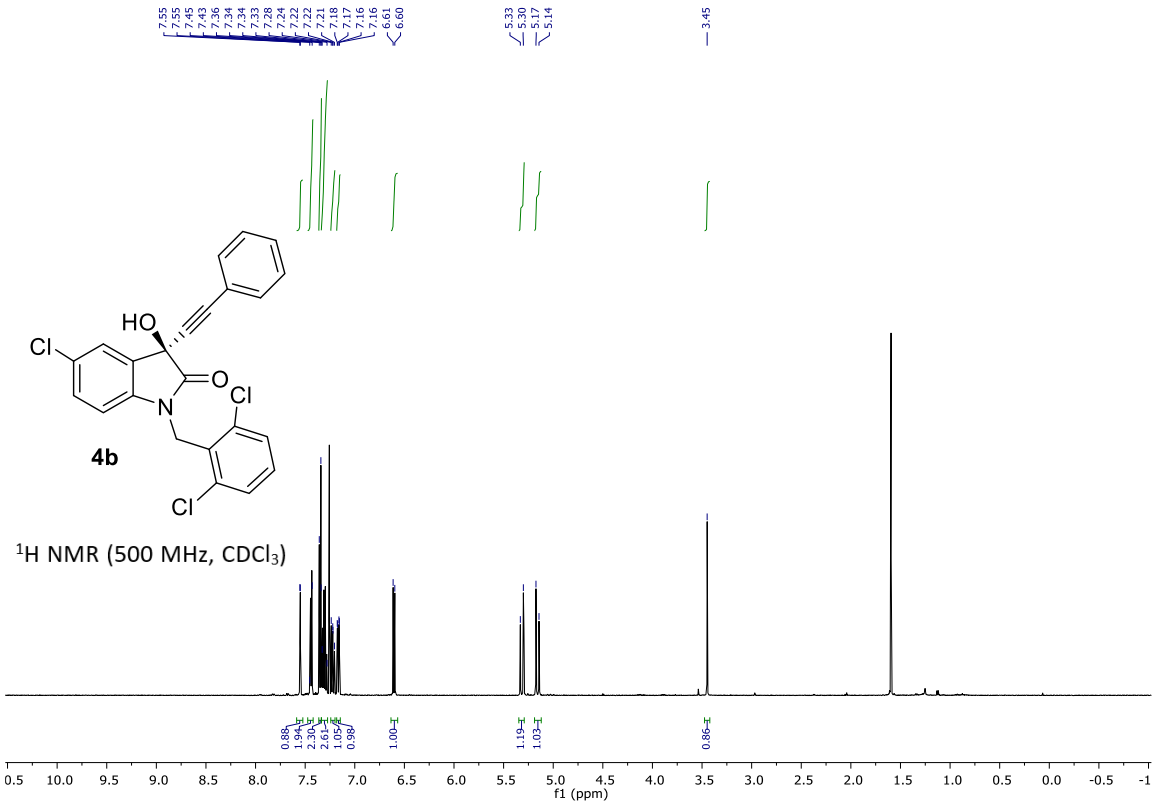

HO
F
O
N
Cl
Cl
4a
1H-NMR (400 MHz, CDCl3)
f1 (ppm)

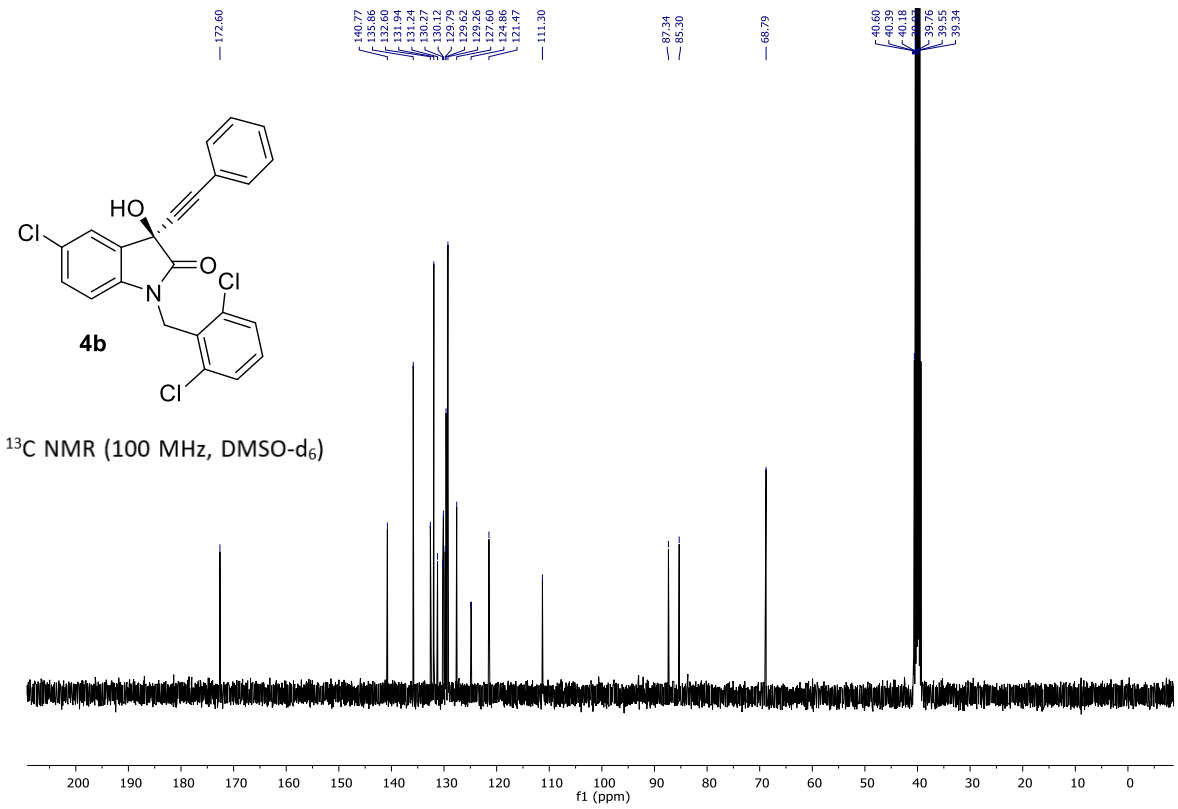

HO
F
O
N
Cl
Cl
4a
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)

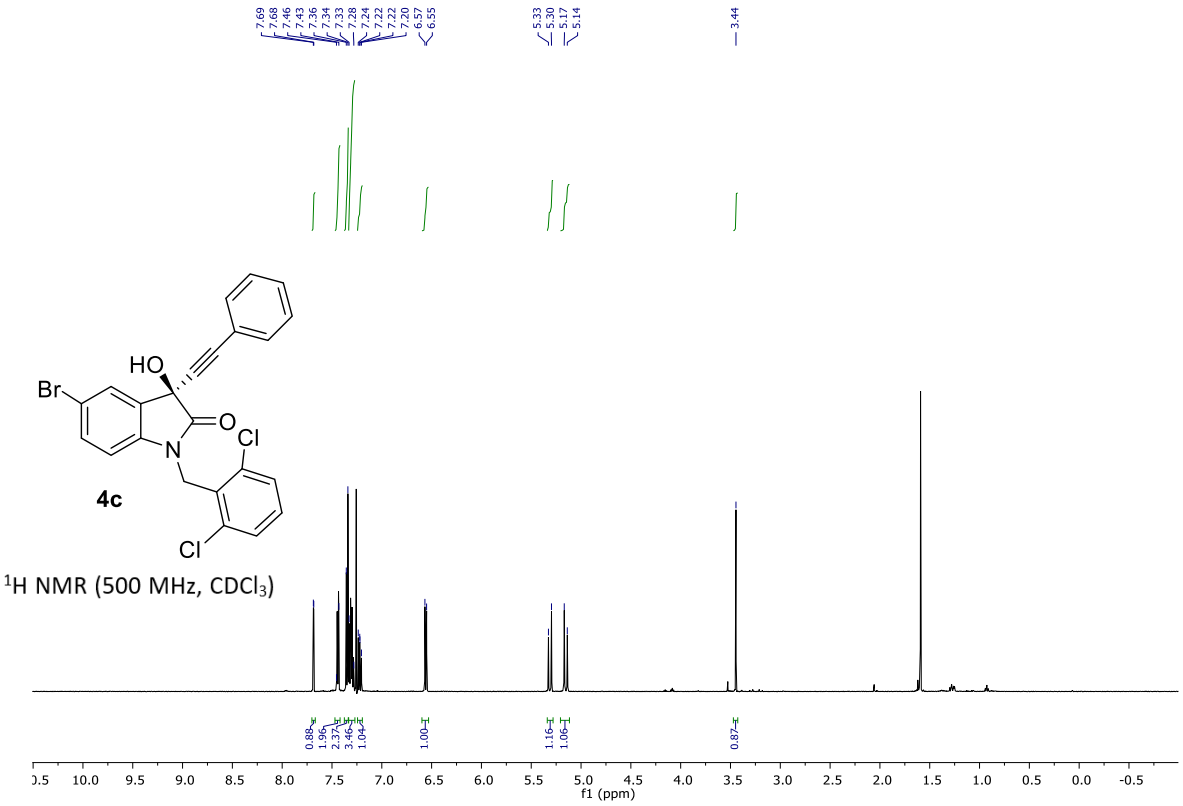


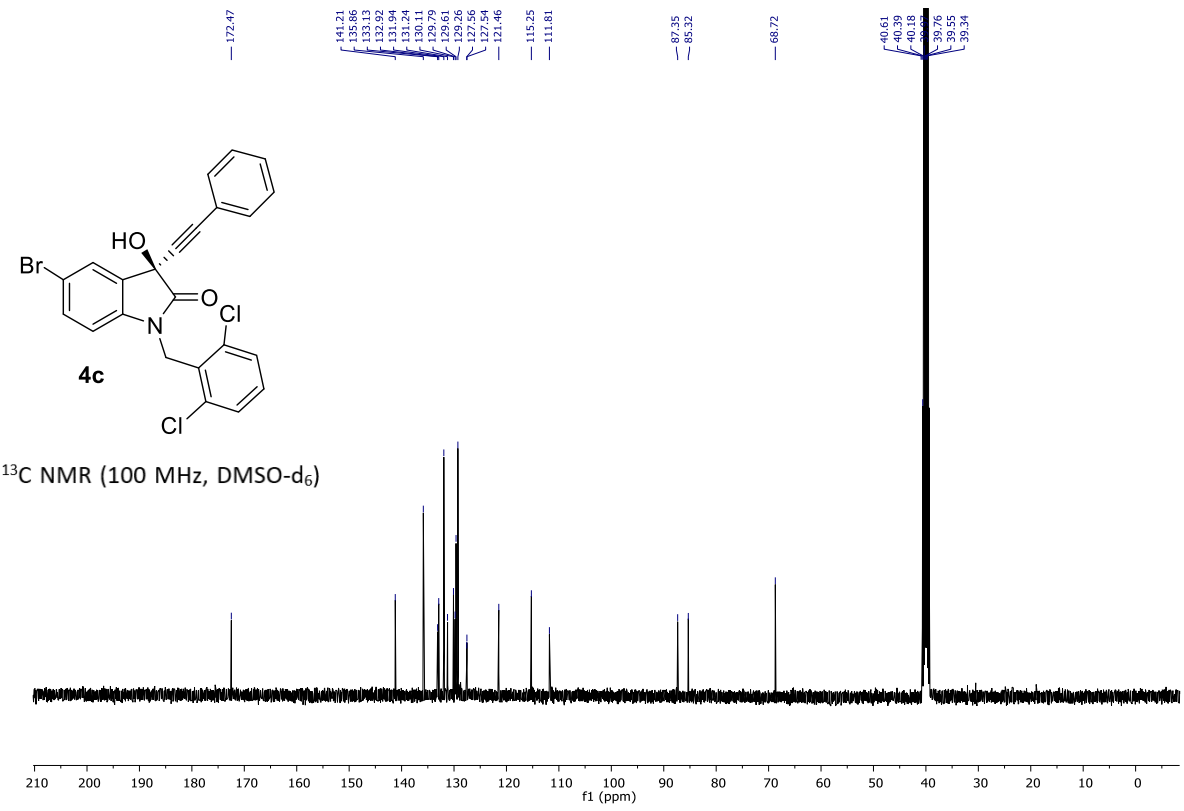
4a

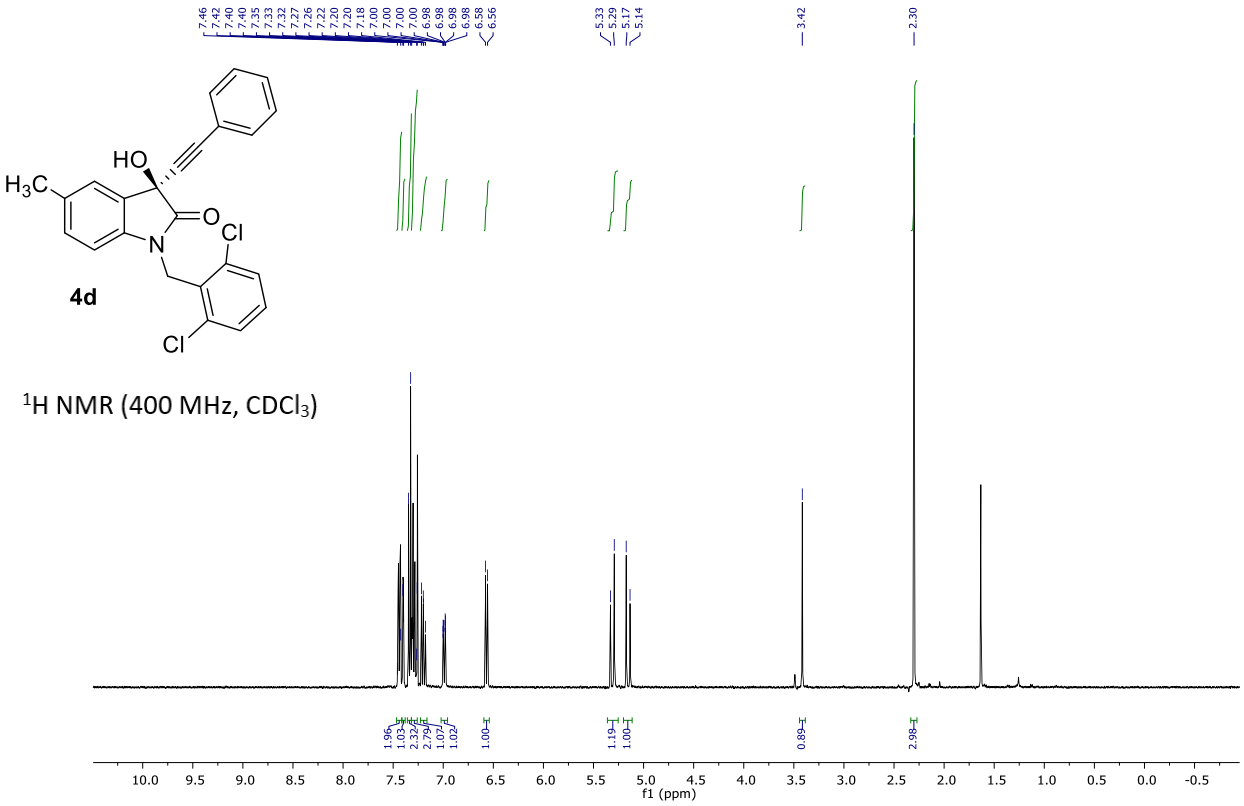
^{19}F NMR (376 MHz, $CDCl_3$)


HO
Cl
O
Cl
N
Cl
4b
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

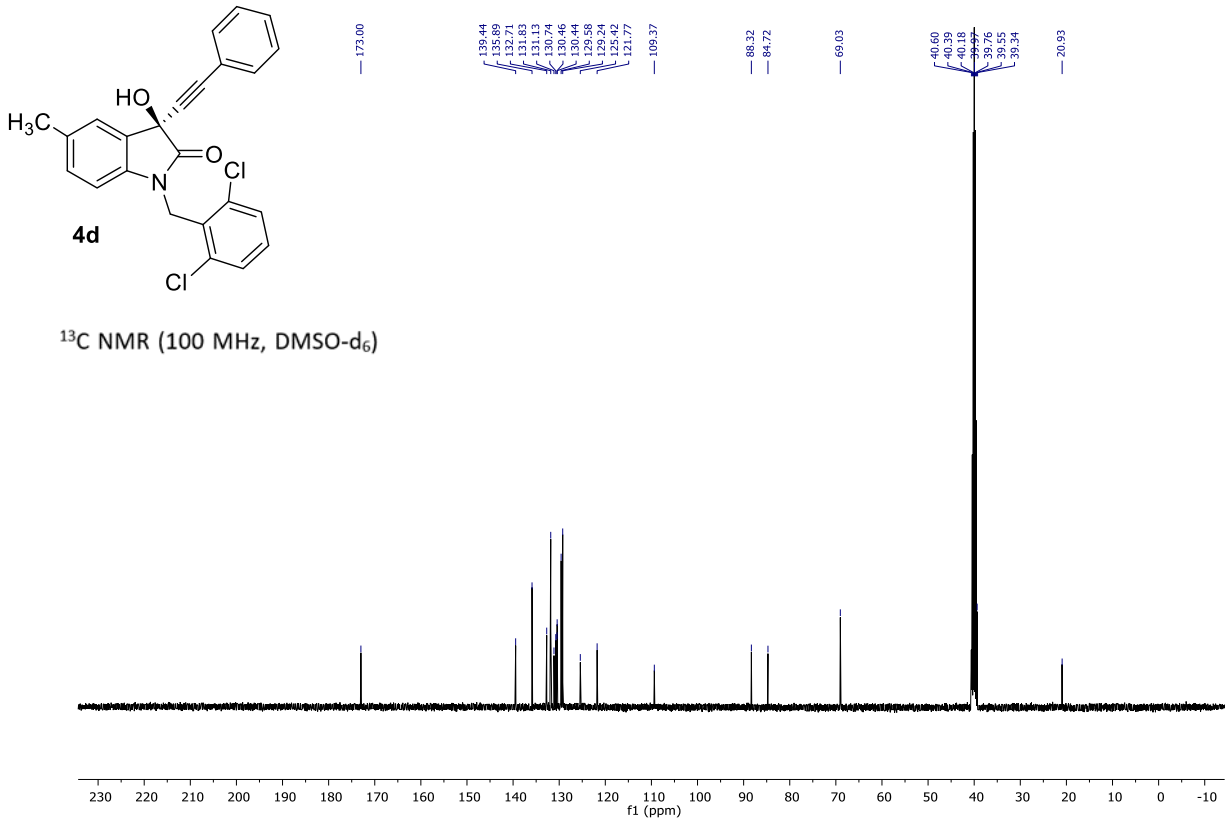

HO
Cl
O
Cl
N
Cl
4b
^{13}C NMR (100 MHz, DMSO-d_6)
f1 (ppm)


HO
Br
O
Cl
N
Cl
4c
1H NMR (500 MHz, CDCl3)
f1 (ppm)

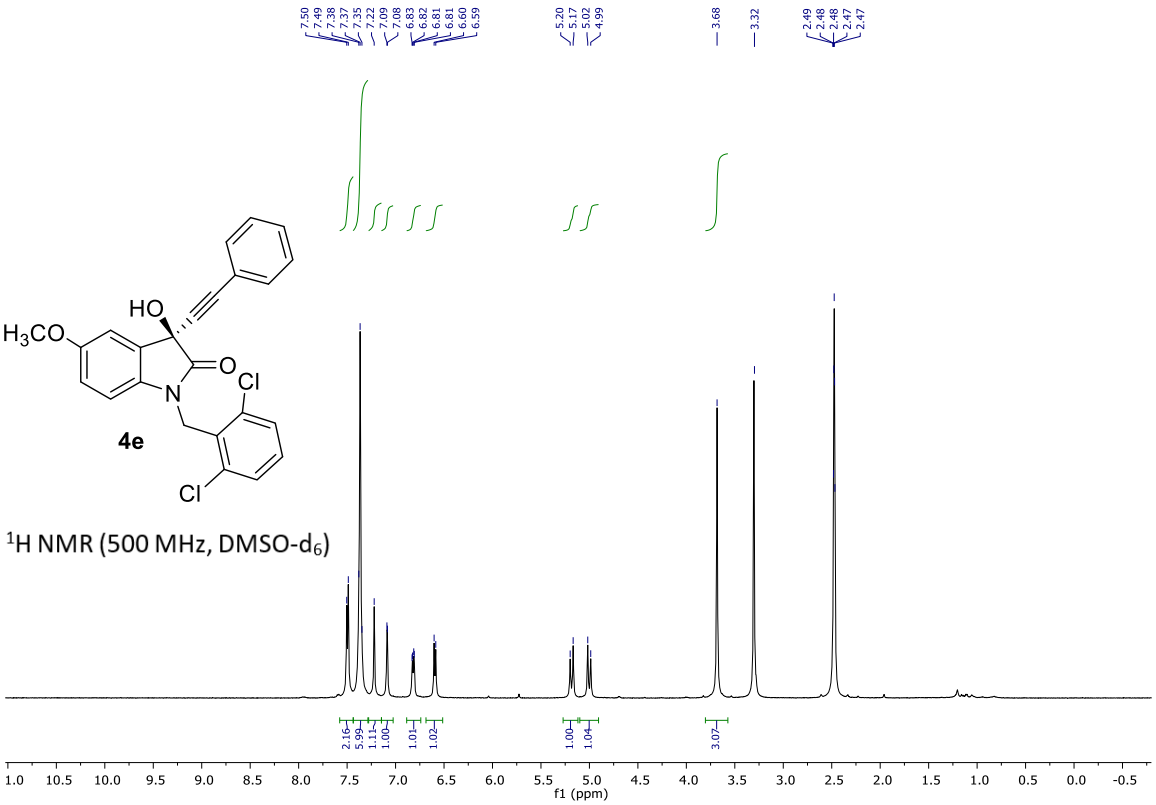

HO
Br
O
Cl
N
Cl
4c
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)

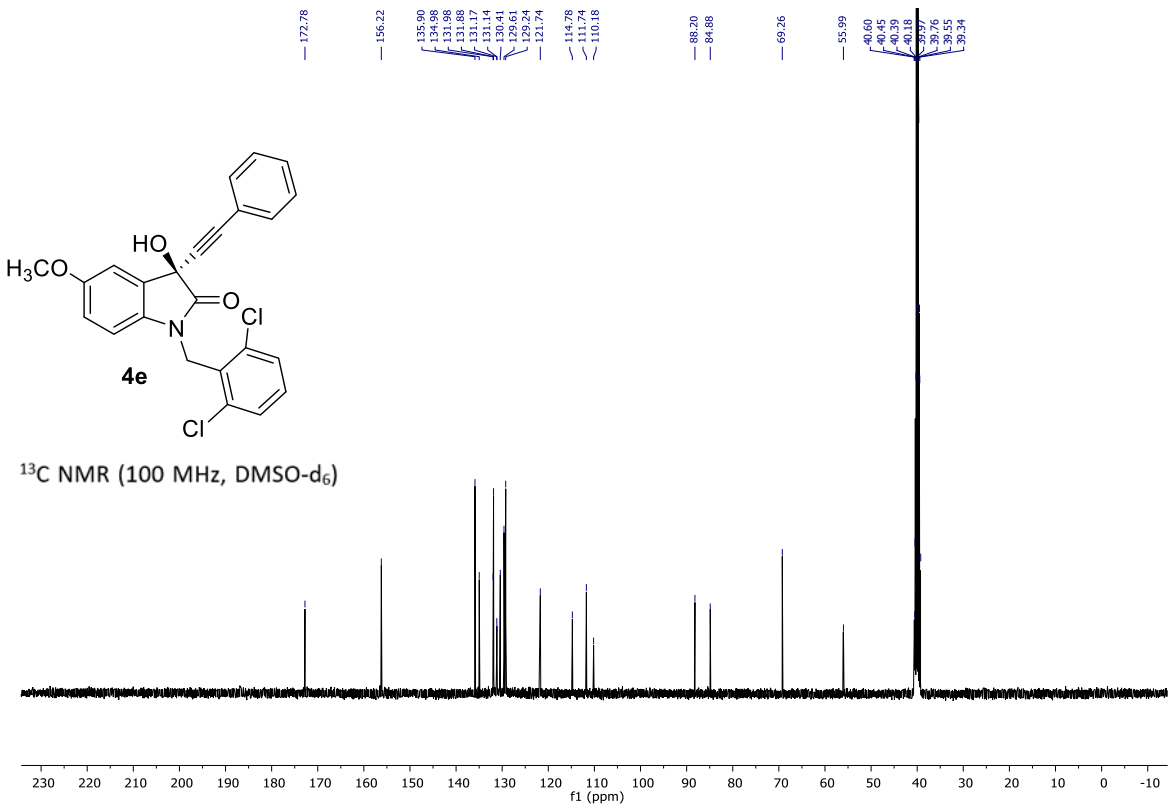


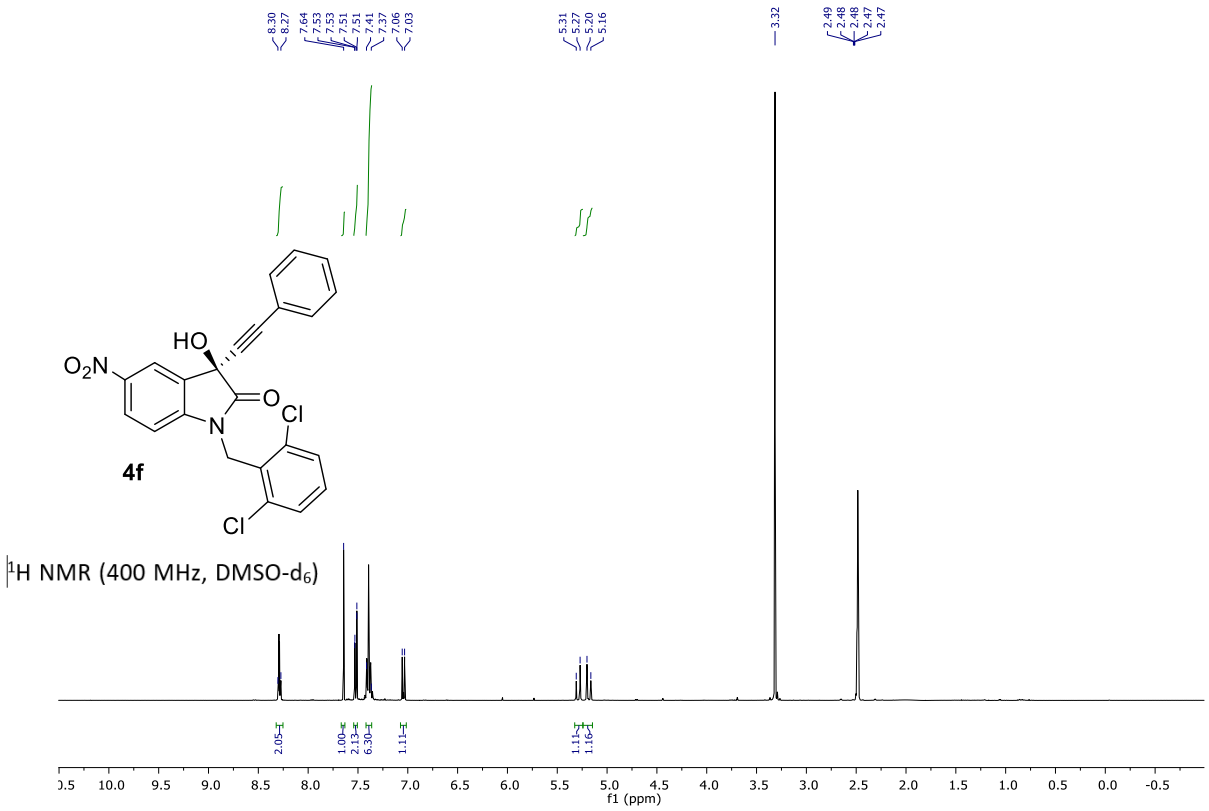
^{1}H NMR (400 MHz, $CDCl_3$)



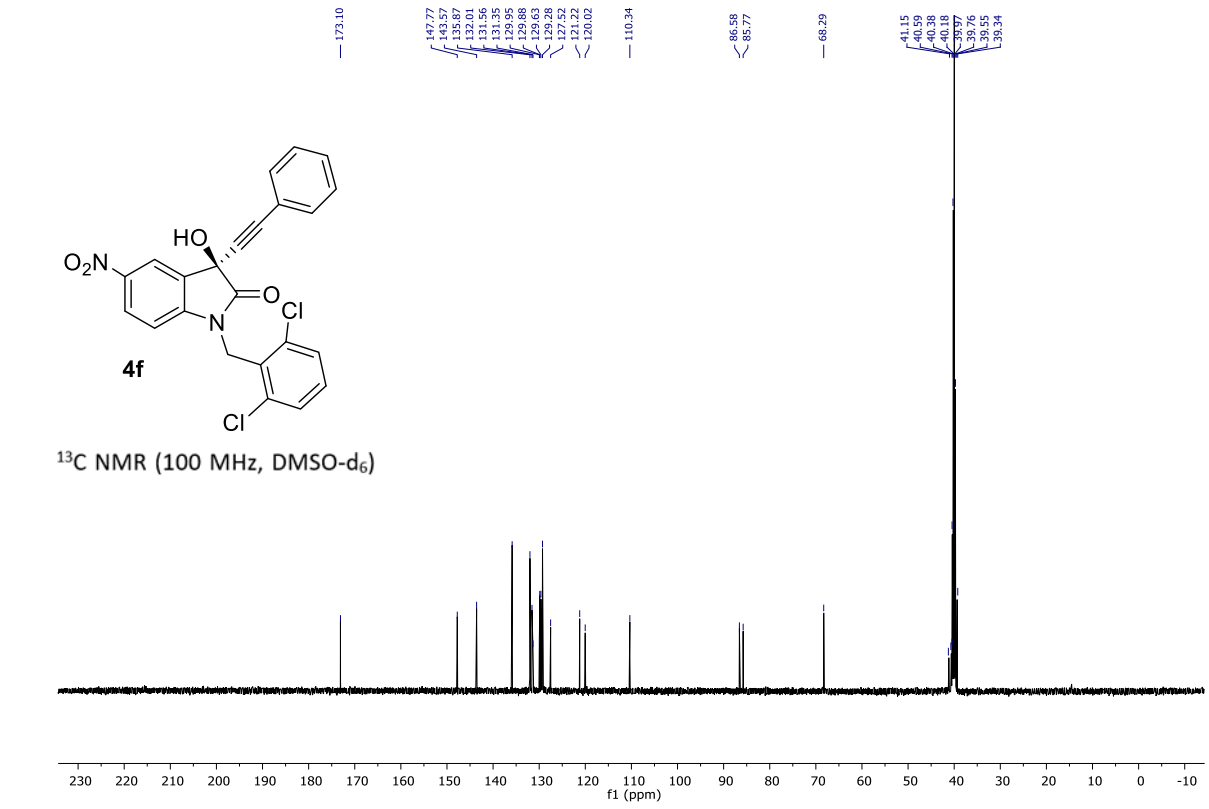
^{13}C NMR (100 MHz, DMSO-d_6)


7.50
7.49
7.38
7.37
7.35
7.22
7.09
7.08
6.83
6.82
6.81
6.81
6.60
6.59
5.20
5.17
5.02
4.99
3.68
3.32
2.49
2.48
2.48
2.47
2.47
HO
H3CO
O
N
Cl
Cl
4e
1H NMR (500 MHz, DMSO-d6)
2.16
5.99
1.11
1.00
1.01
1.02
1.00
1.04
3.07
f1 (ppm)

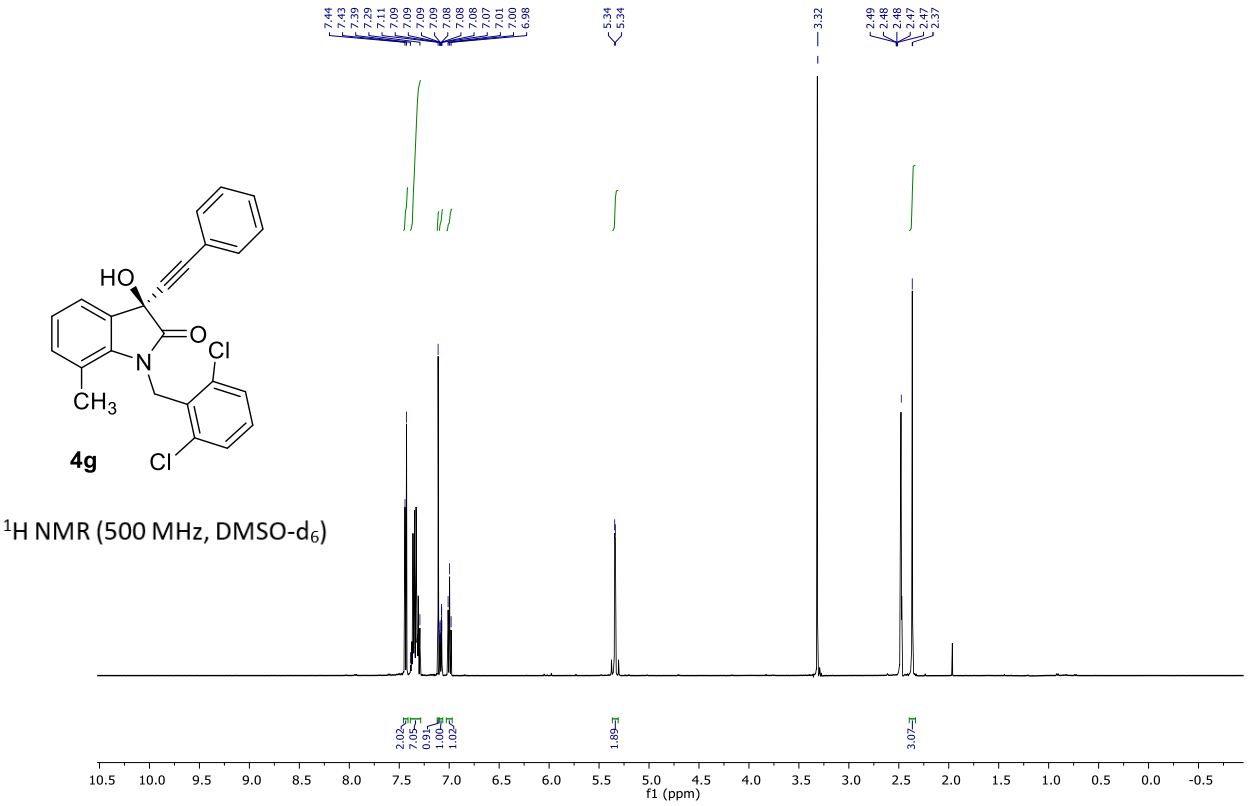

172.78
156.22
135.90
134.98
131.98
131.88
131.17
131.14
130.41
129.61
129.24
121.74
114.78
111.74
110.18
88.20
84.88
69.26
55.99
40.60
40.45
40.39
40.18
39.97
39.76
39.55
39.34
HO
H3CO
O
N
Cl
Cl
4e
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)

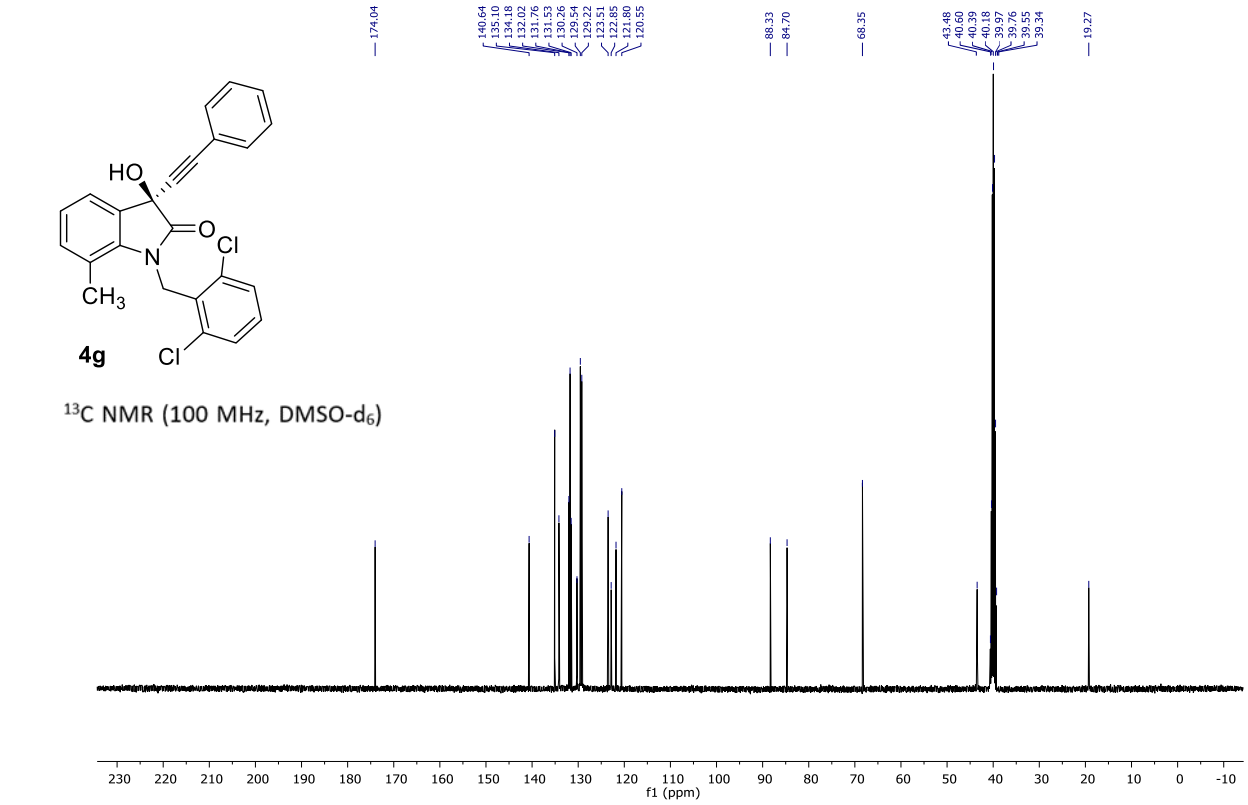


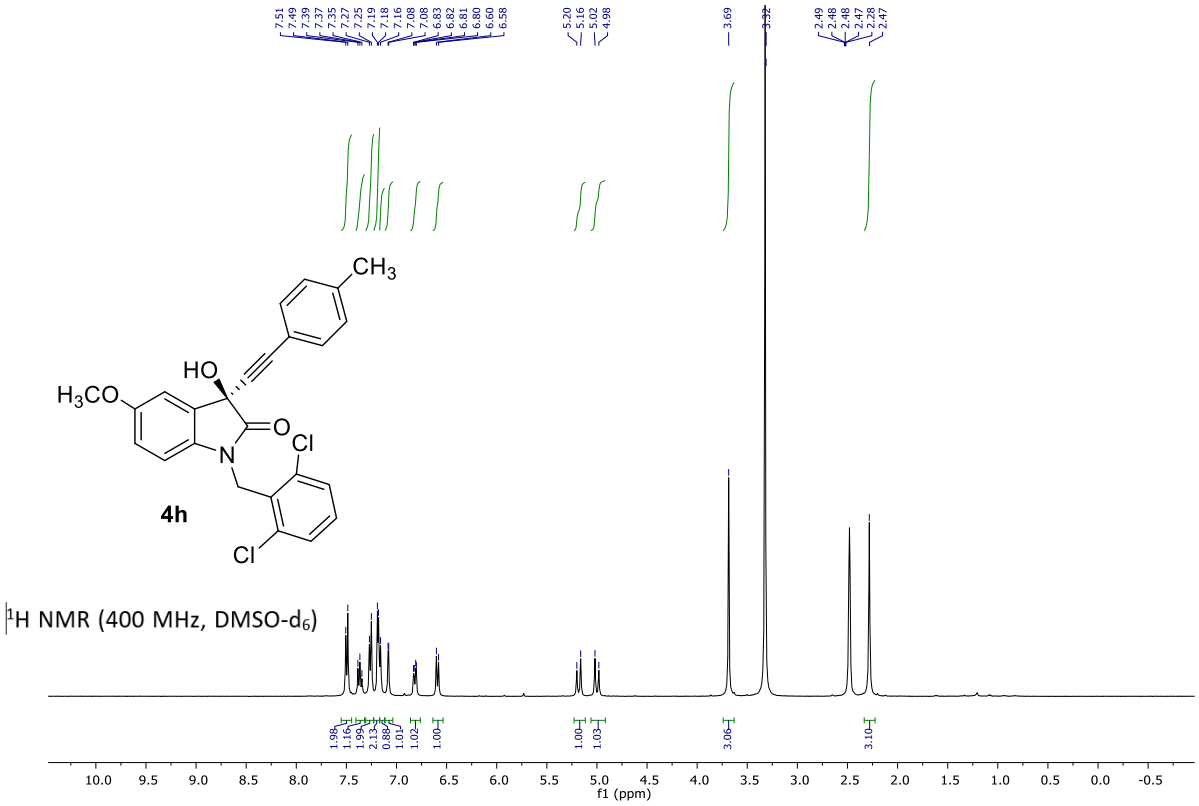
^{1}H NMR (400 MHz, DMSO-d$_6$)

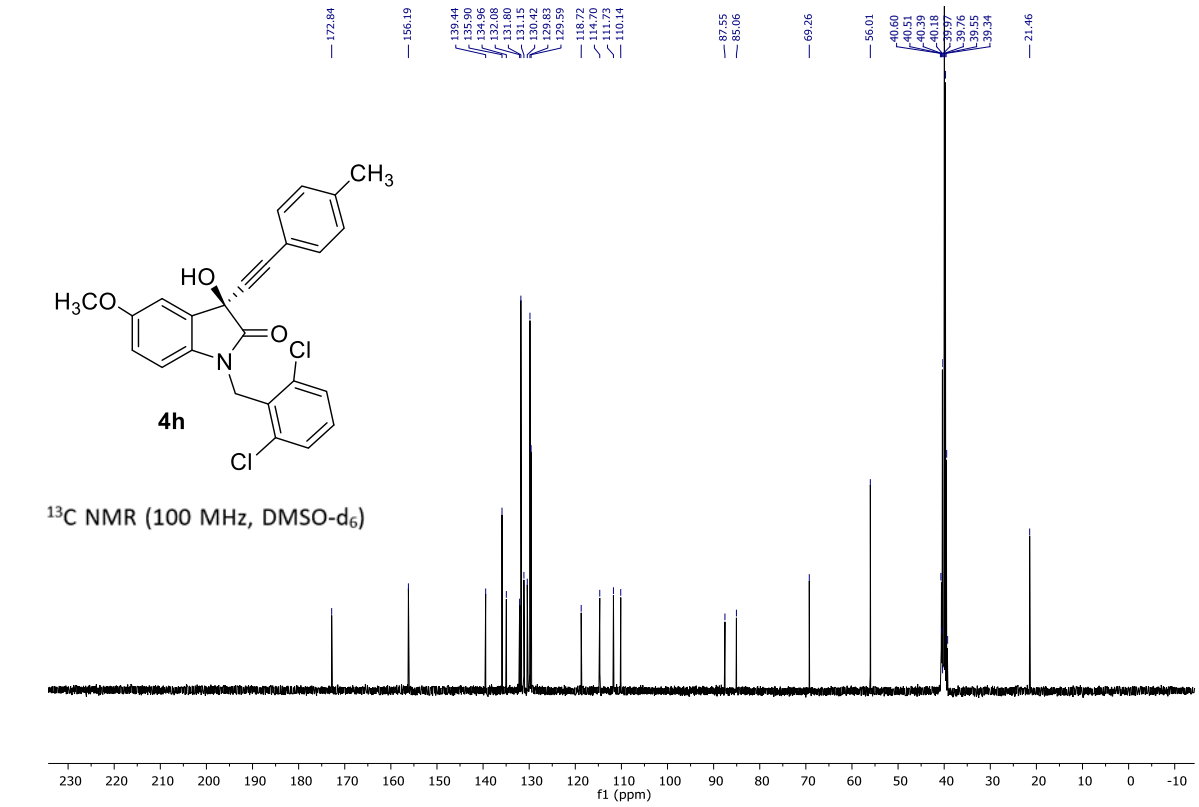


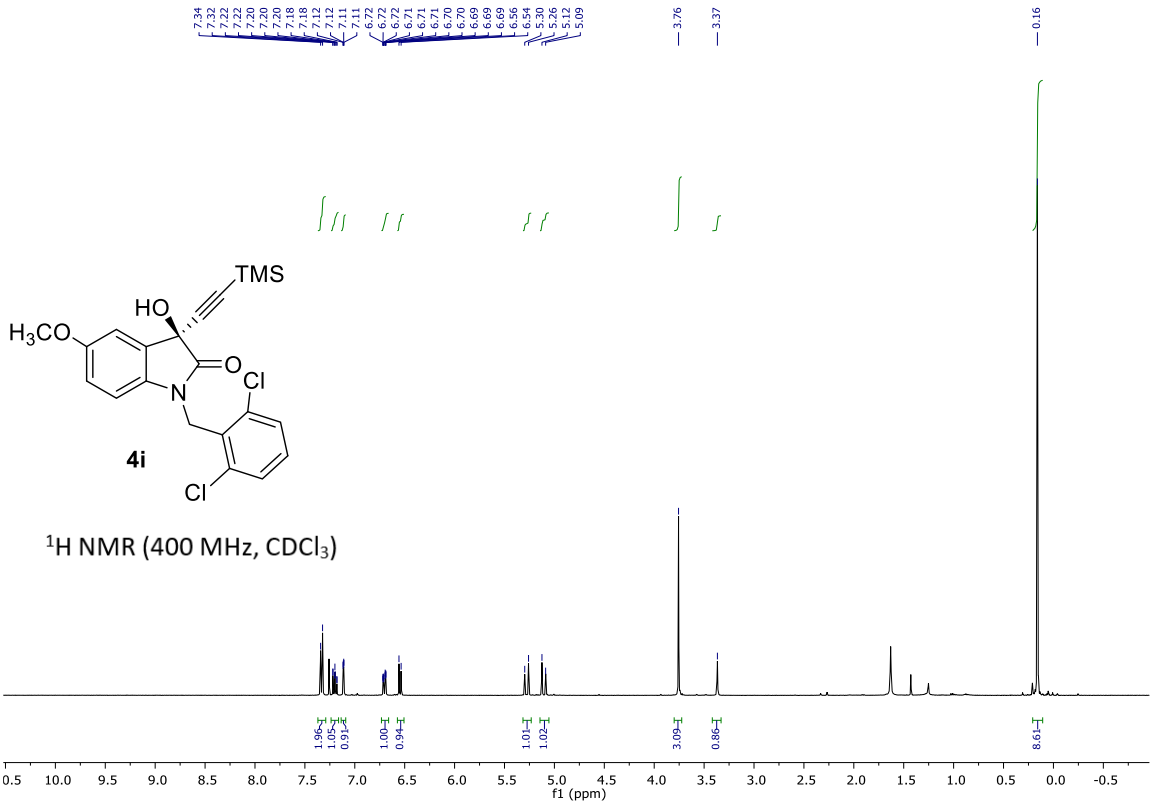
^{13}C NMR (100 MHz, DMSO-d$_6$)

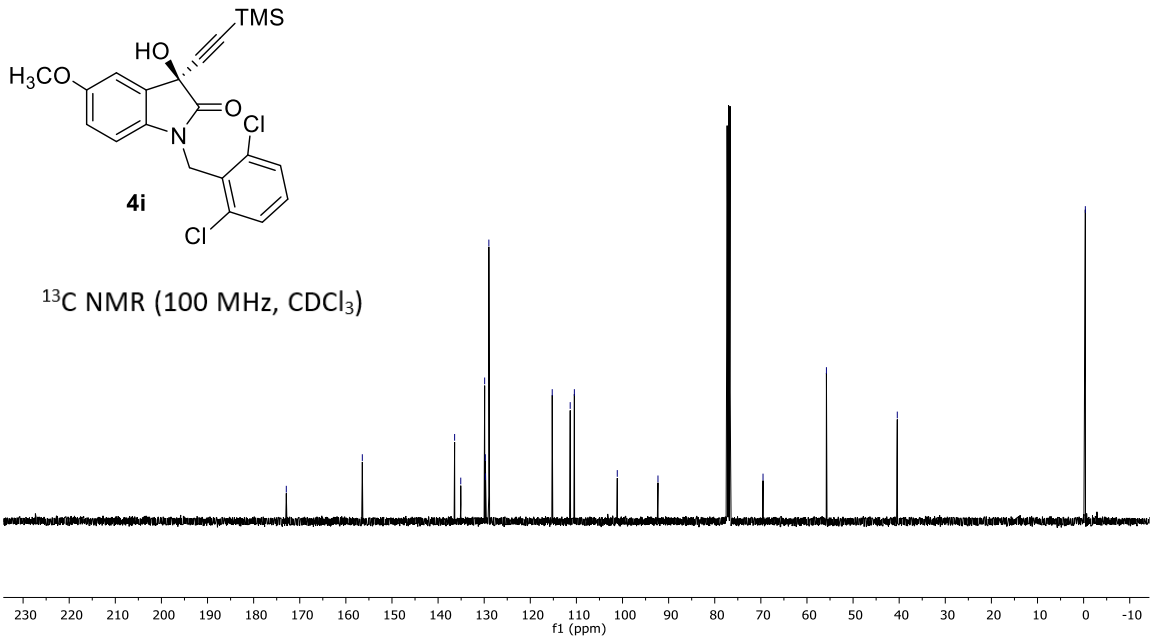

HO
O
N
Cl
CH3
Cl
4g
1H NMR (500 MHz, DMSO-d6)
f1 (ppm)

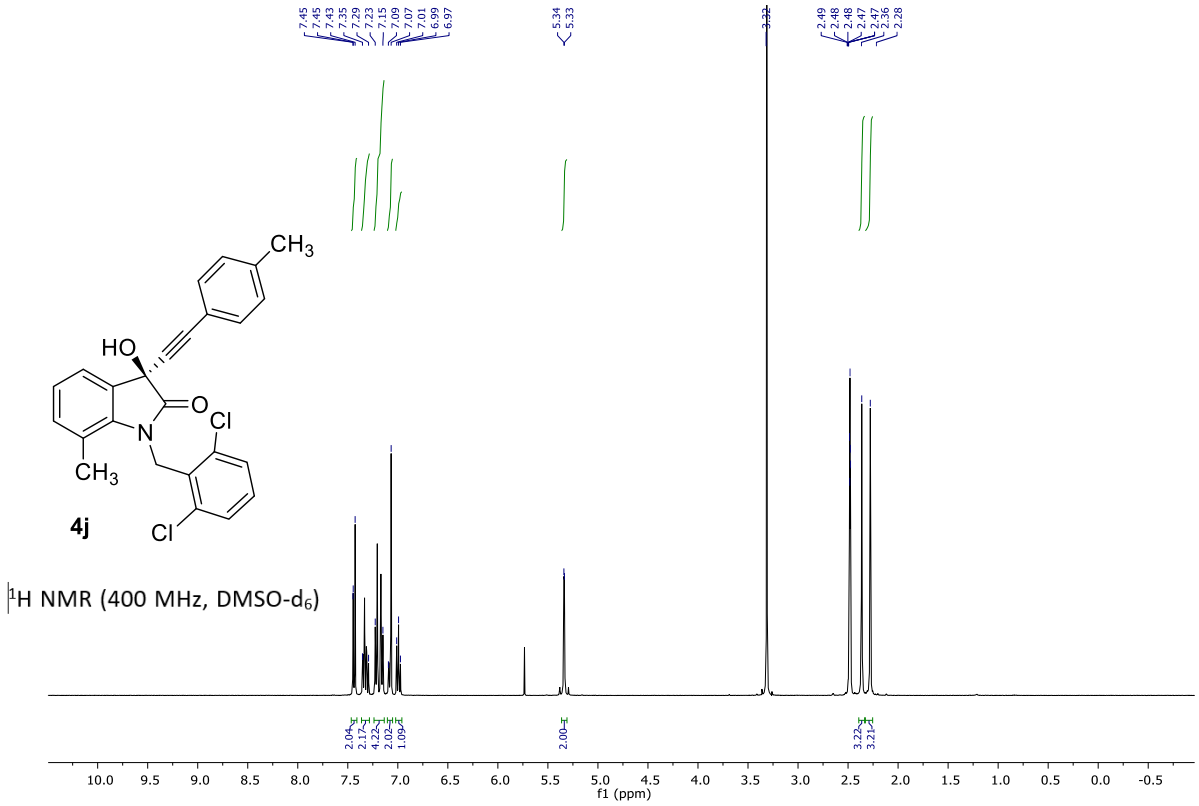

HO
O
N
Cl
CH3
Cl
4g
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)

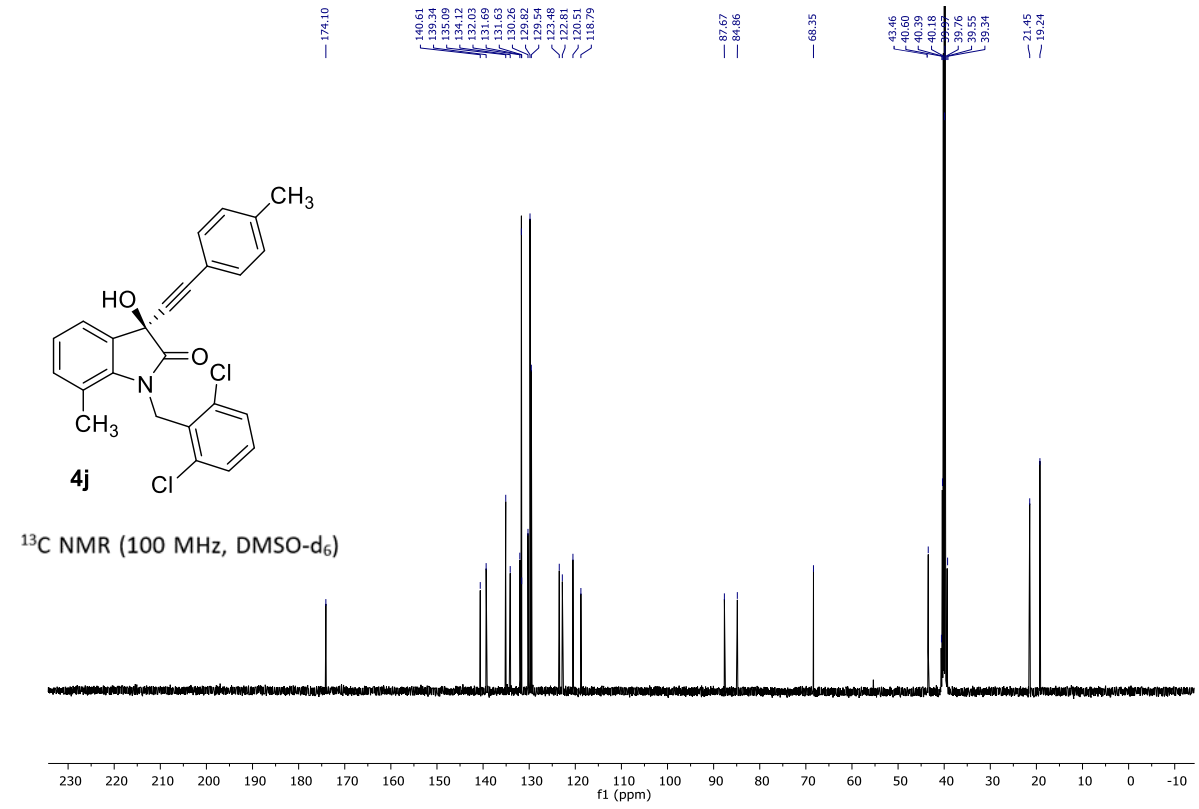

7.51
7.49
7.39
7.37
7.35
7.27
7.25
7.19
7.18
7.16
7.08
7.08
6.83
6.82
6.81
6.80
6.60
6.58
5.20
5.16
5.02
4.98
3.69
3.32
2.49
2.48
2.48
2.47
2.47
2.47
CH3
HO
H3CO
O
N
Cl
Cl
4h
1H NMR (400 MHz, DMSO-d6)
1.98
1.16
1.99
2.13
0.88
1.01
1.02
1.00
1.00
1.03
3.06
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

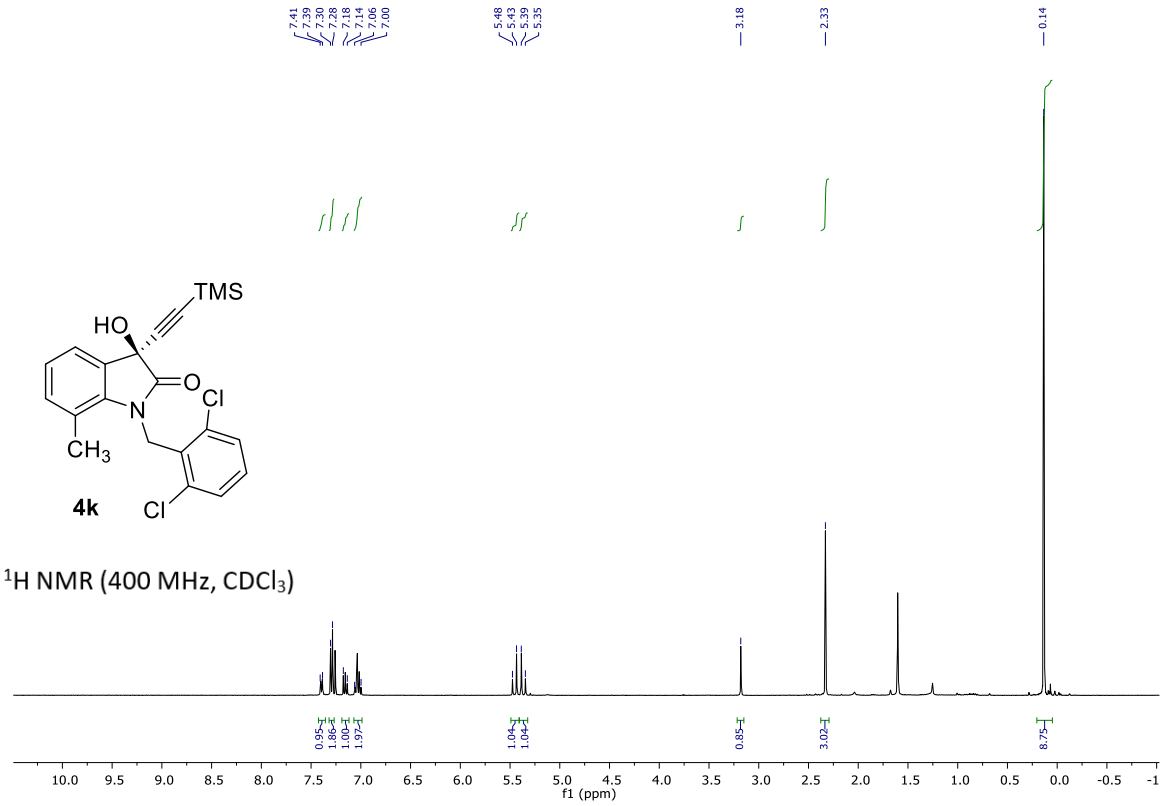

172.84
156.19
139.44
135.90
134.96
132.08
131.80
131.15
130.42
129.83
129.59
118.72
114.70
111.73
110.14
87.55
85.06
69.26
56.01
40.60
40.51
40.39
40.18
39.97
39.76
39.55
39.34
21.46
CH3
HO
H3CO
O
N
Cl
Cl
4h
13C NMR (100 MHz, DMSO-d6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

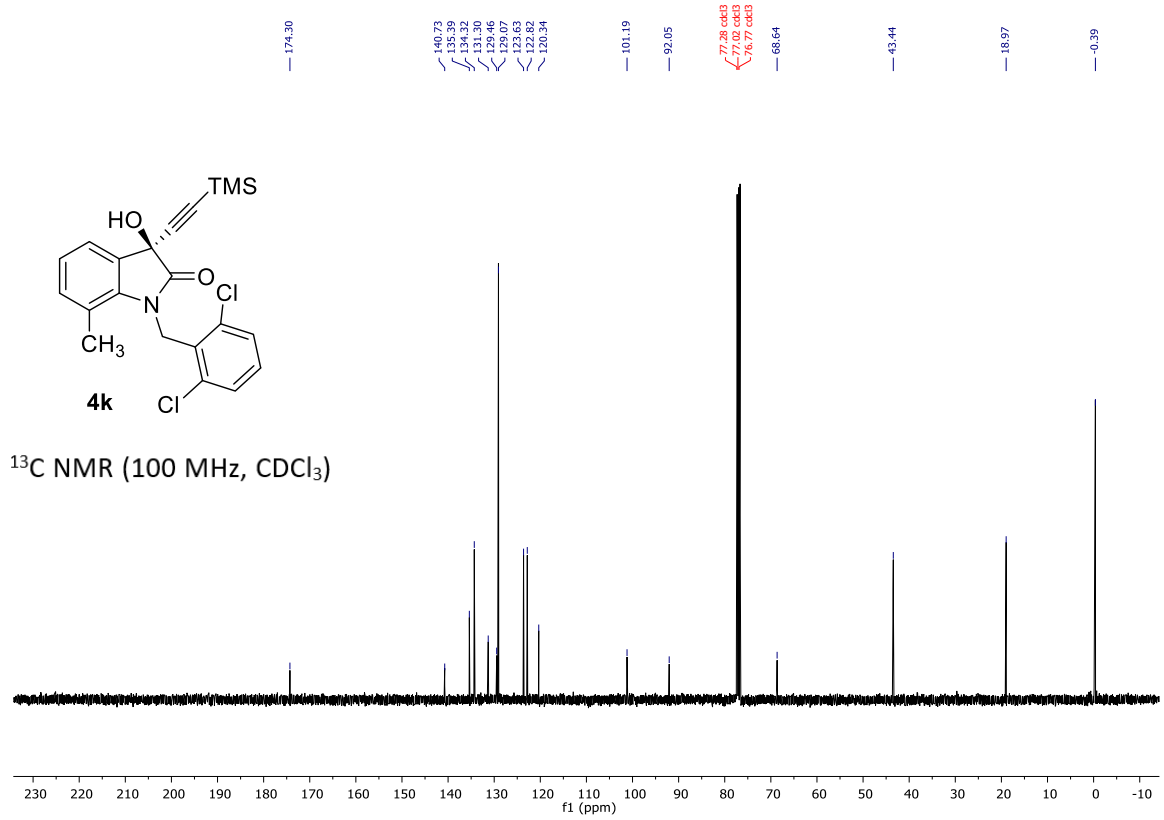

TMS
HO
H3CO
O
N
Cl
Cl
4i
1H NMR (400 MHz, CDCl3)
f1 (ppm)

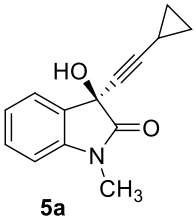

TMS
HO
H3CO
O
N
Cl
Cl
4i
13C NMR (100 MHz, CDCl3)
f1 (ppm)


4j
^{1}H NMR (400 MHz, DMSO-d$_6$)
f1 (ppm)


4j
^{13}C NMR (100 MHz, DMSO-d$_6$)
f1 (ppm)

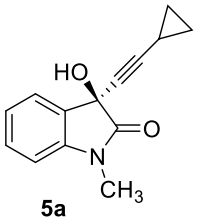

TMS
HO
O
Cl
N
CH3
Cl
4k
1H NMR (400 MHz, CDCl3)
f1 (ppm)


TMS
HO
O
Cl
N
CH3
Cl
4k
13C NMR (100 MHz, CDCl3)
f1 (ppm)



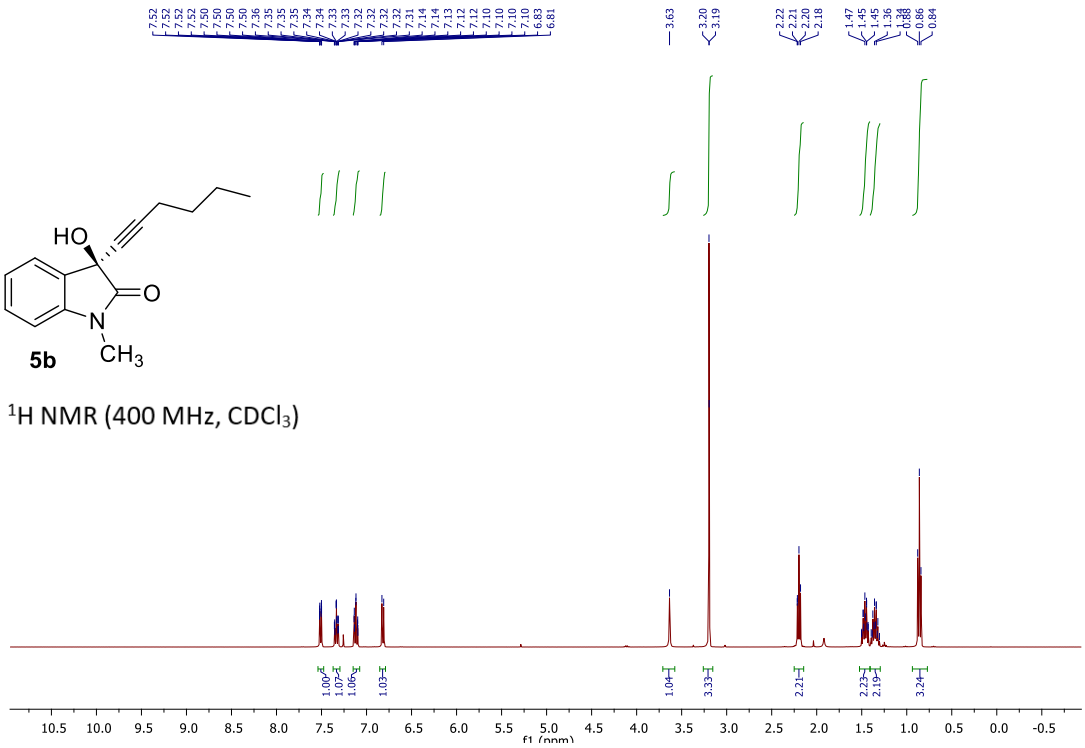
5a

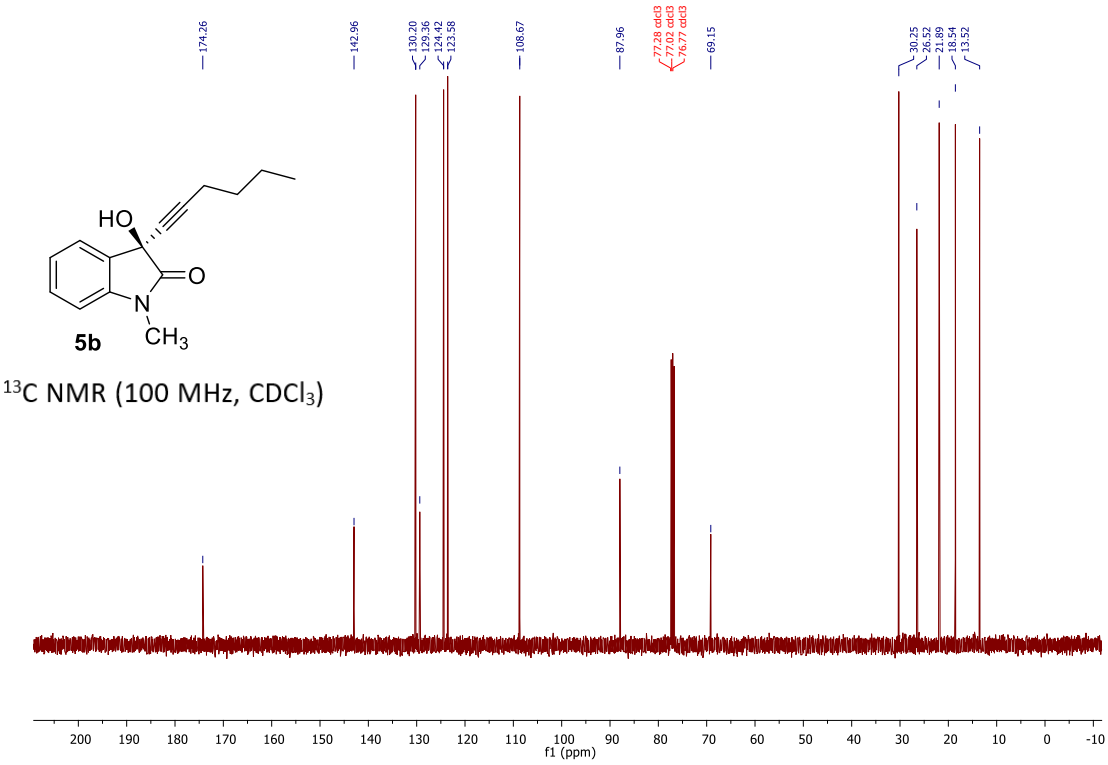
^{1}H NMR (400 MHz, $CDCl_3$)

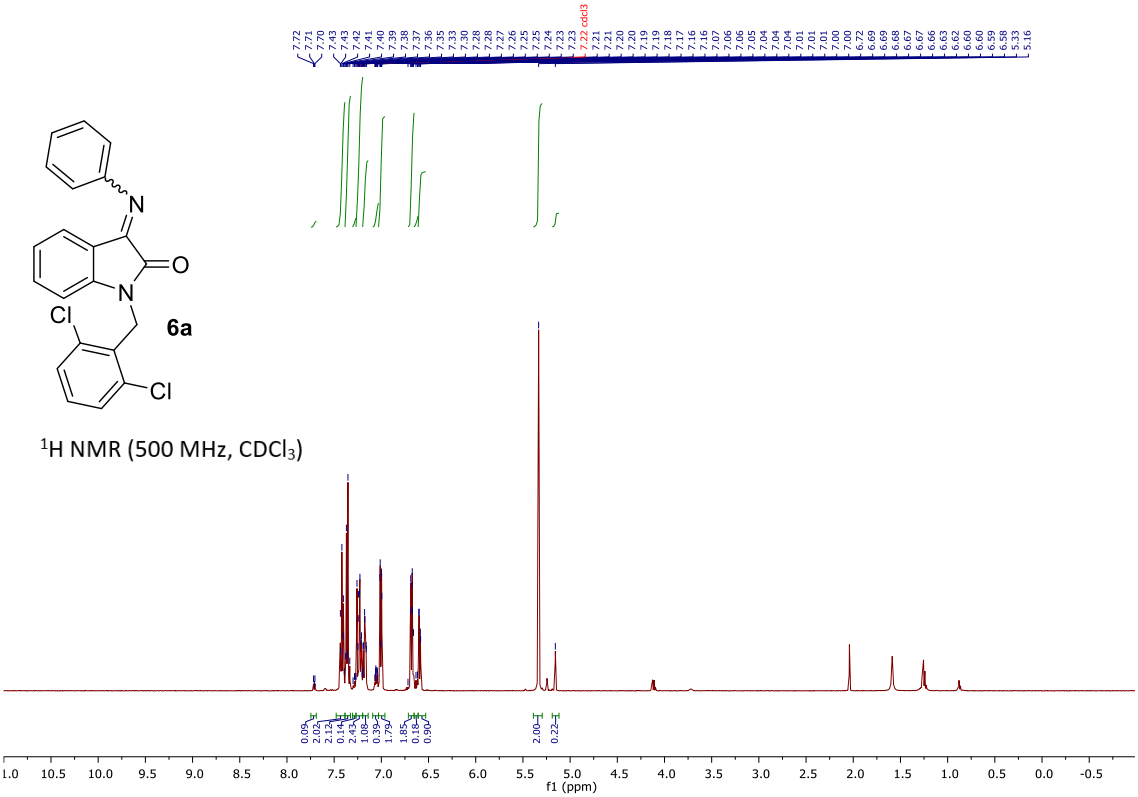


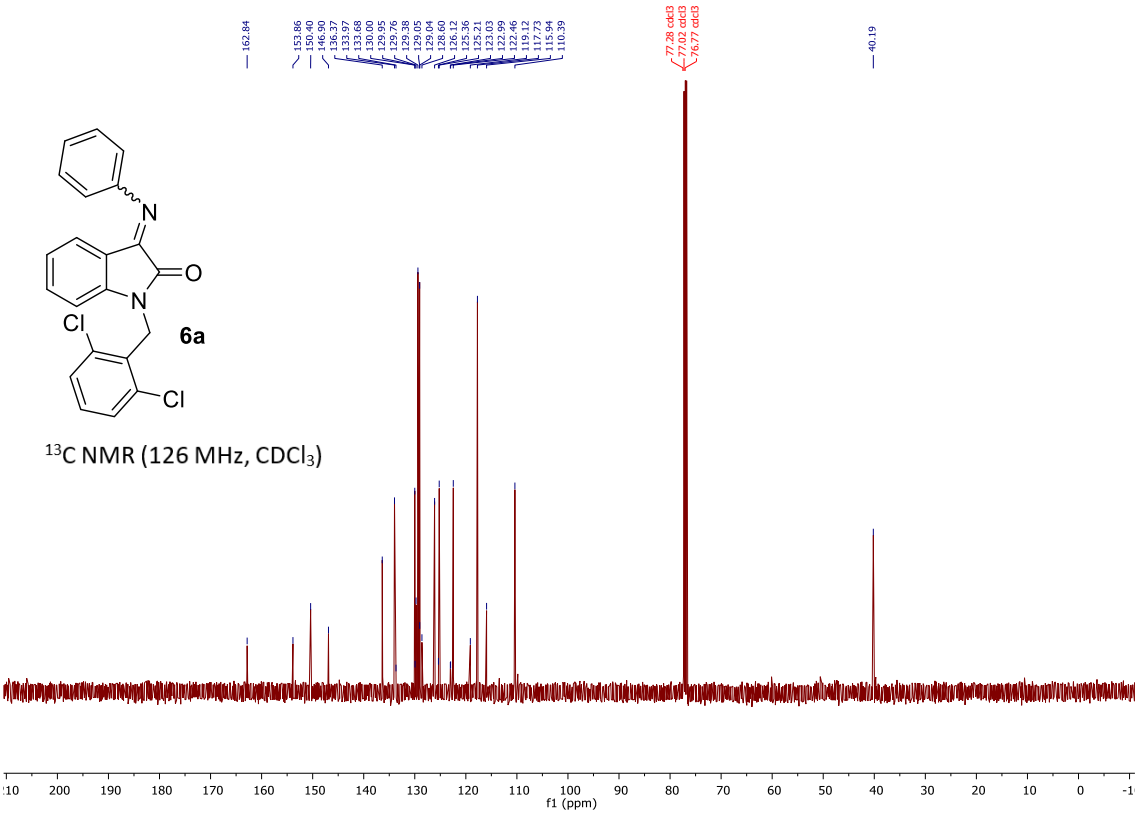
5a

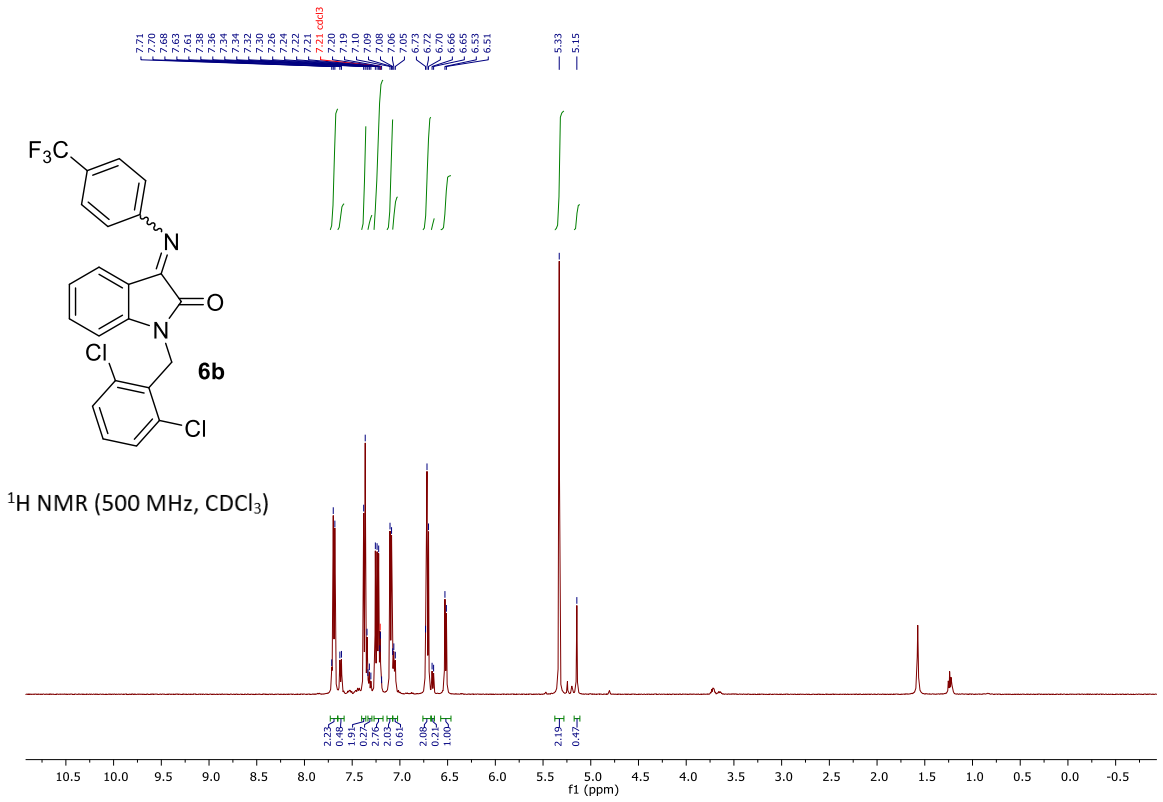
^{13}C NMR (100 MHz, $CDCl_3$)

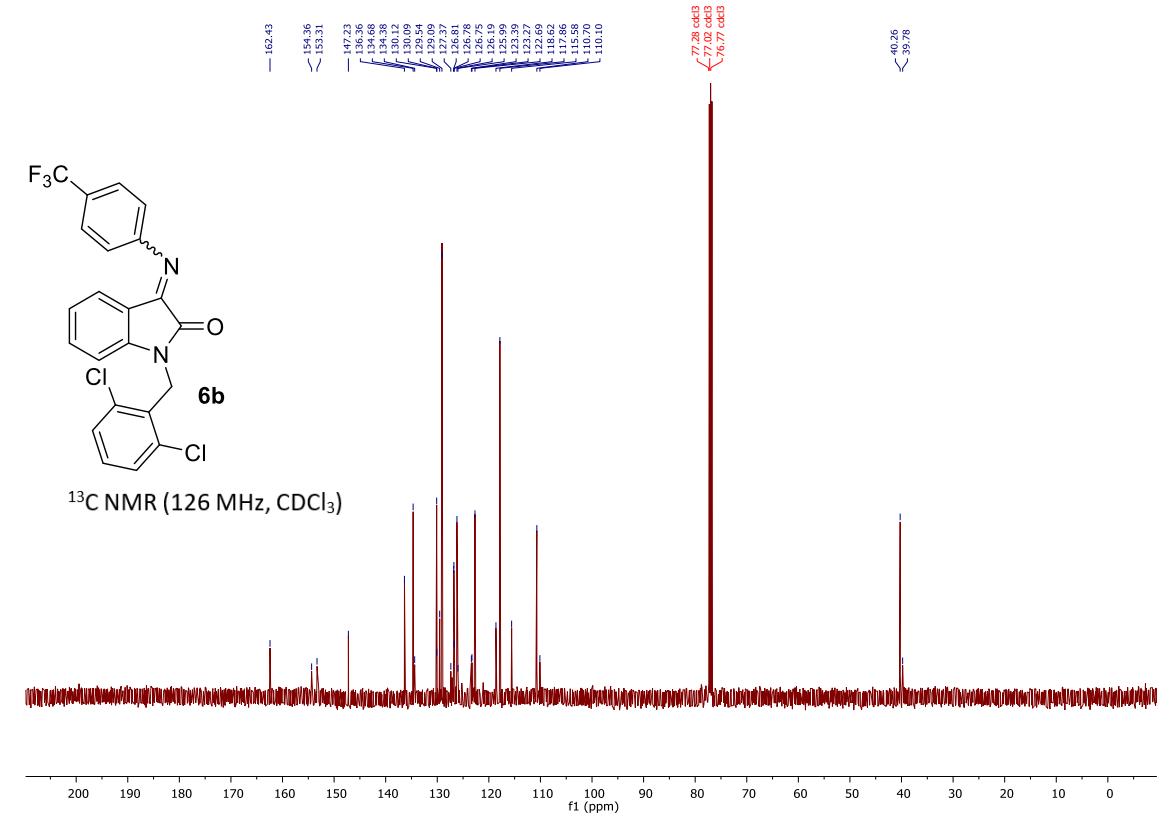

HO
O
N
CH3
5b
1H NMR (400 MHz, CDCl3)

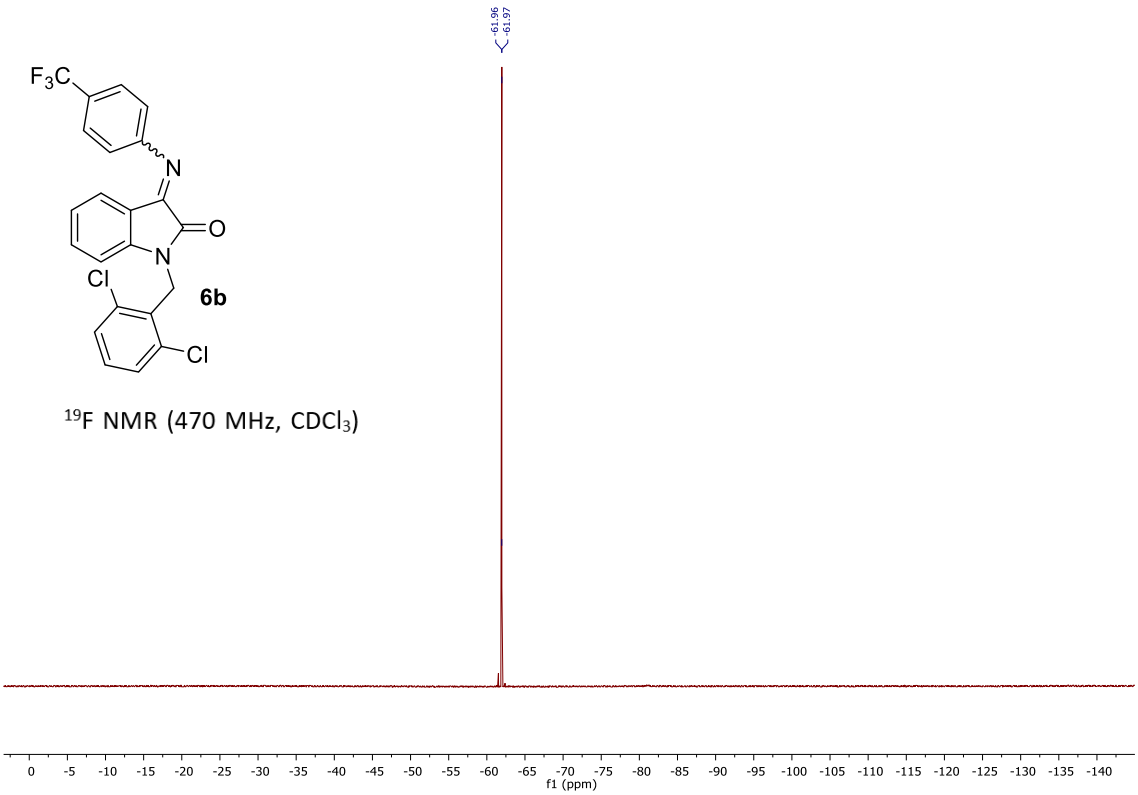

HO
O
N
CH3
5b
13C NMR (100 MHz, CDCl3)


6a
1H NMR (500 MHz, CDCl3)
f1 (ppm)

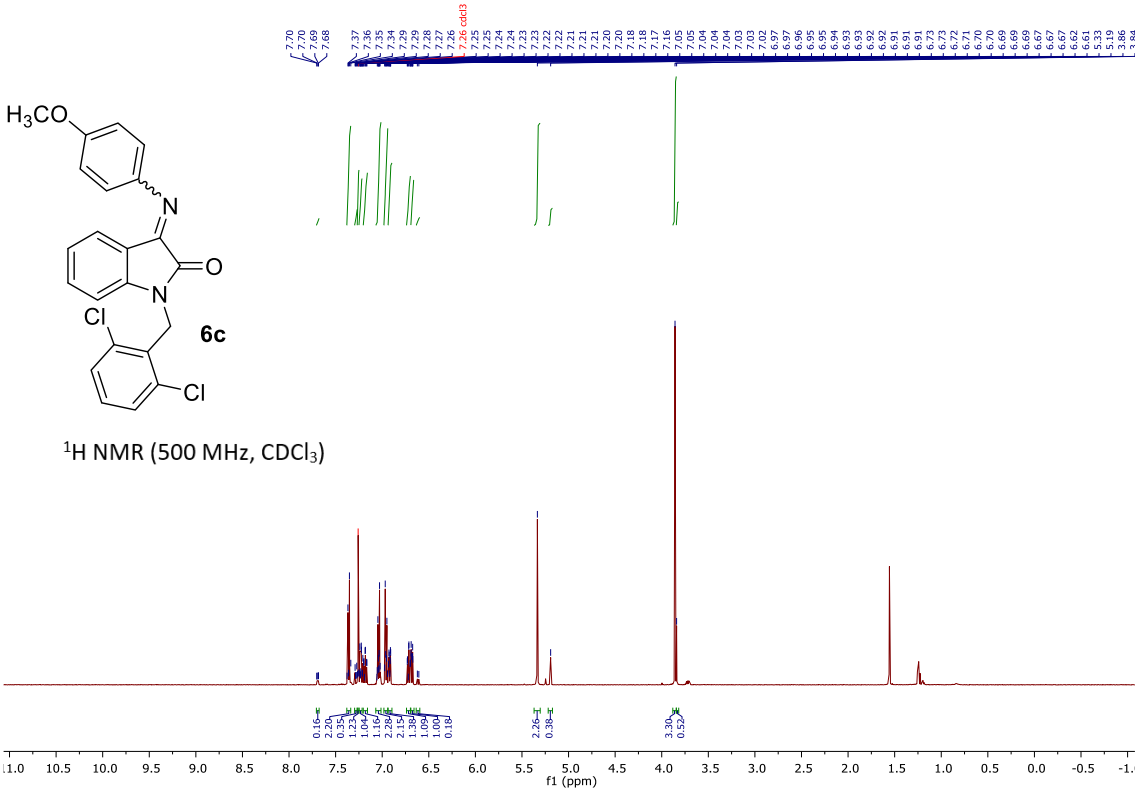

6a
13C NMR (126 MHz, CDCl3)
f1 (ppm)


F3C
N
O
N
Cl
Cl
6b
1H NMR (500 MHz, CDCl3)
f1 (ppm)

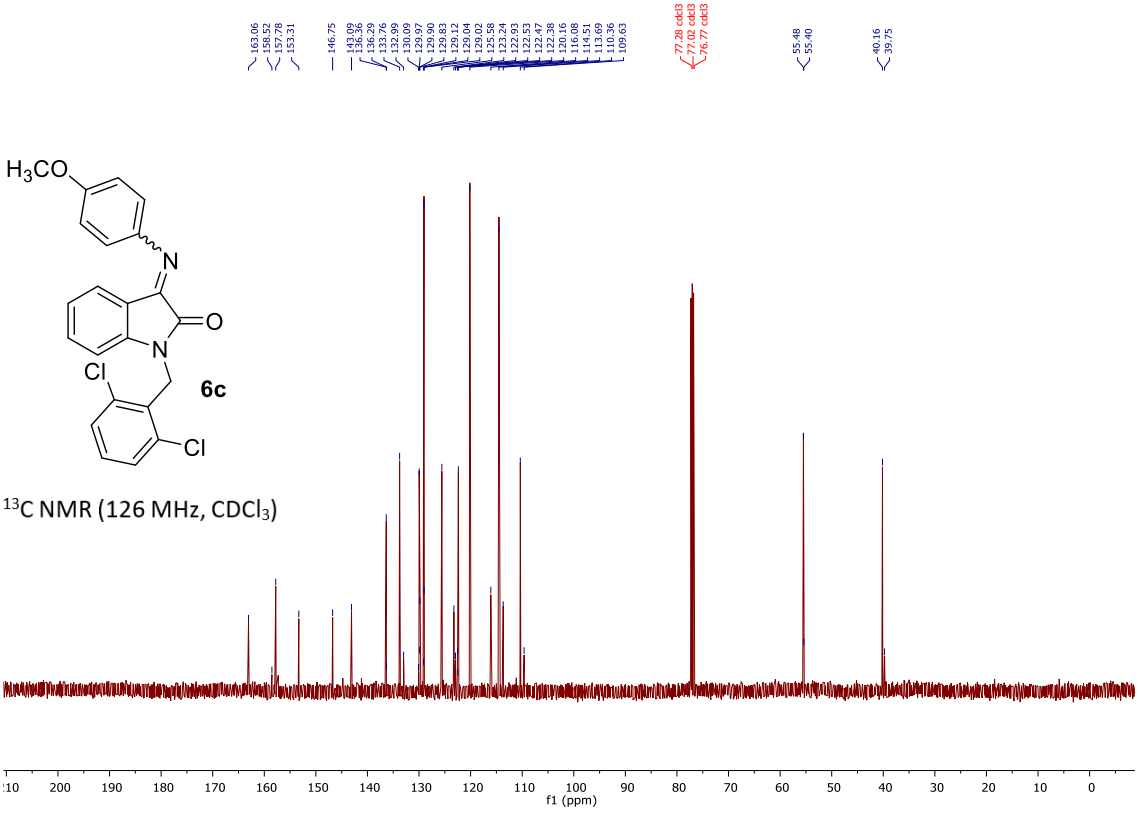

F3C
N
O
N
Cl
Cl
6b
13C NMR (126 MHz, CDCl3)
f1 (ppm)



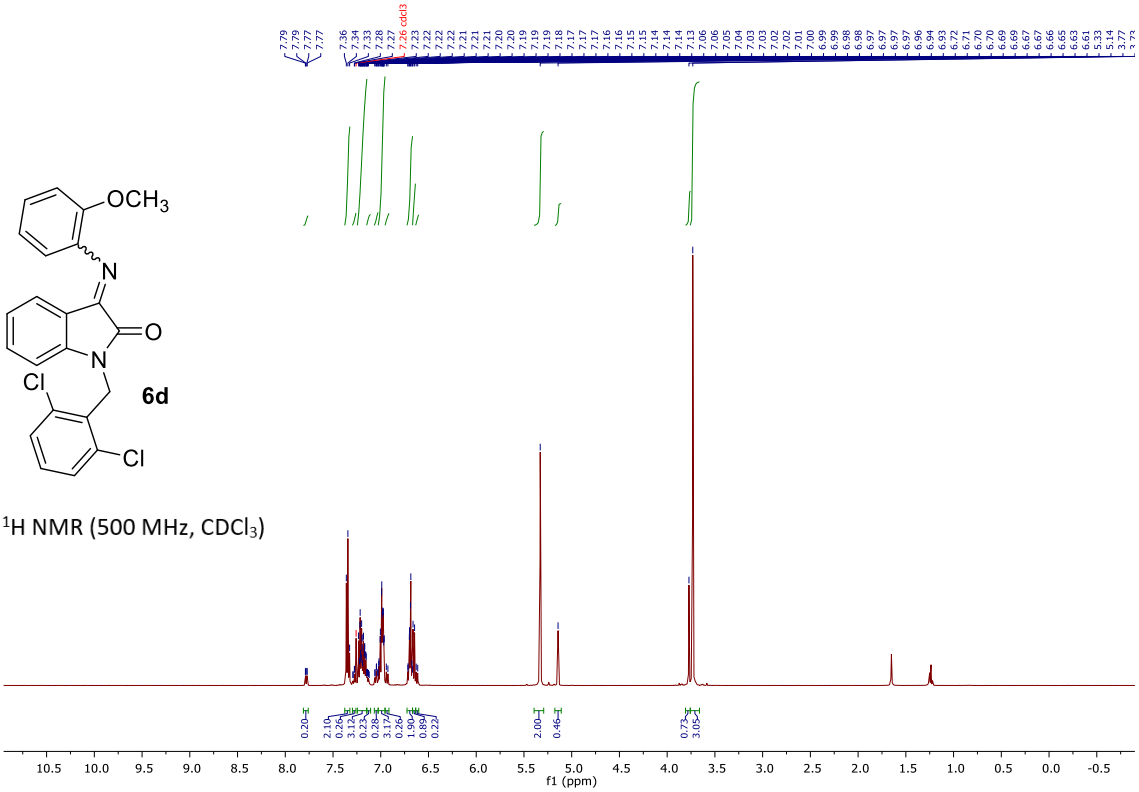
^{19}F NMR (470 MHz, $CDCl_3$)

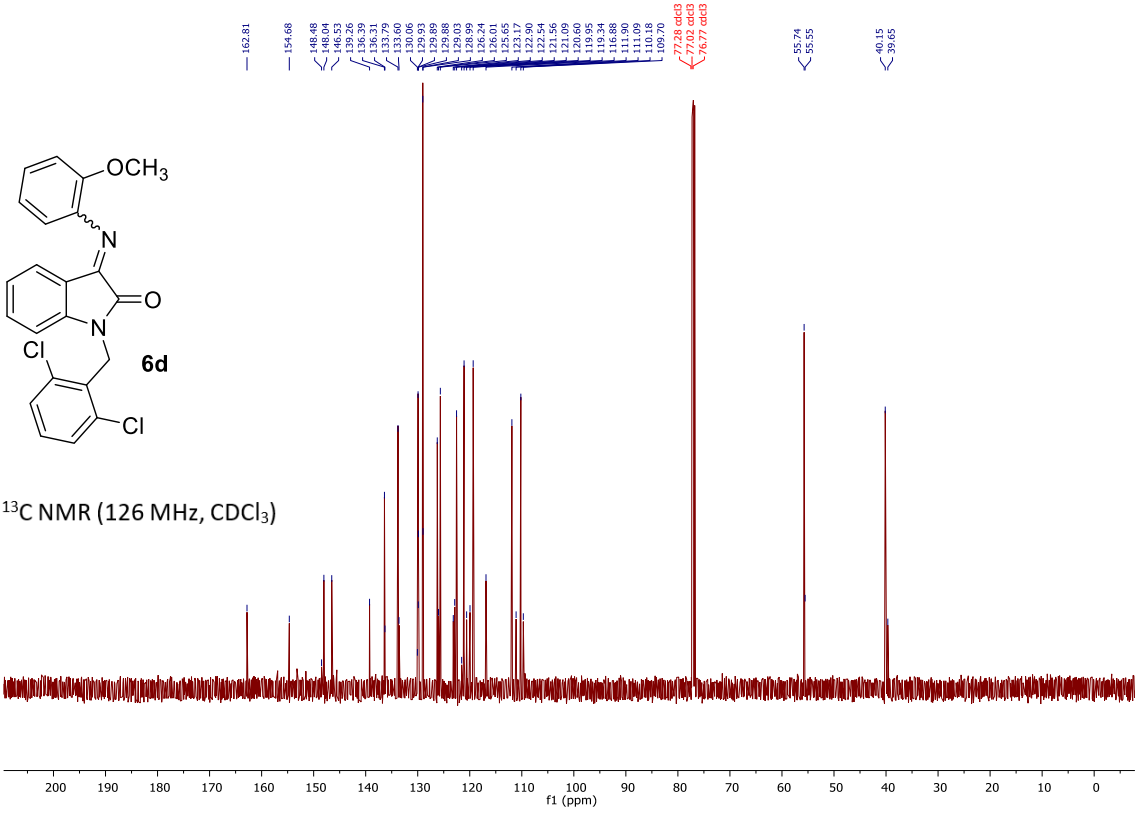


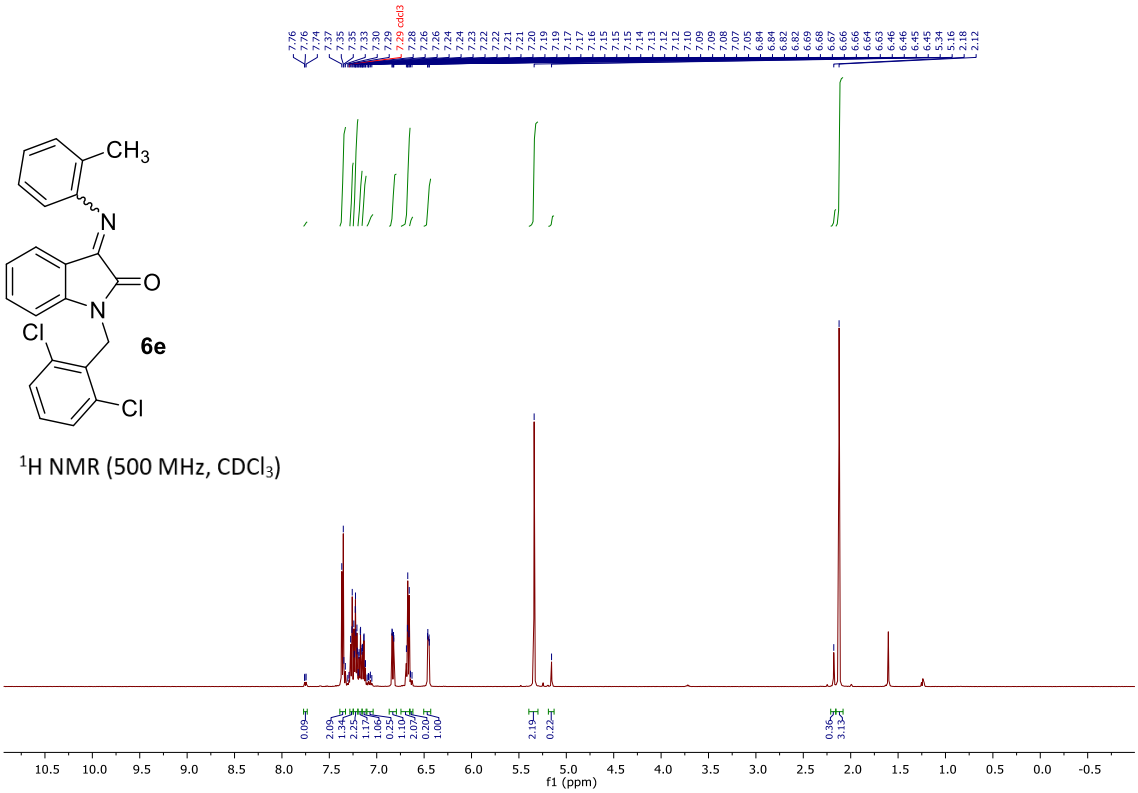
^{1}H NMR (500 MHz, $CDCl_3$)

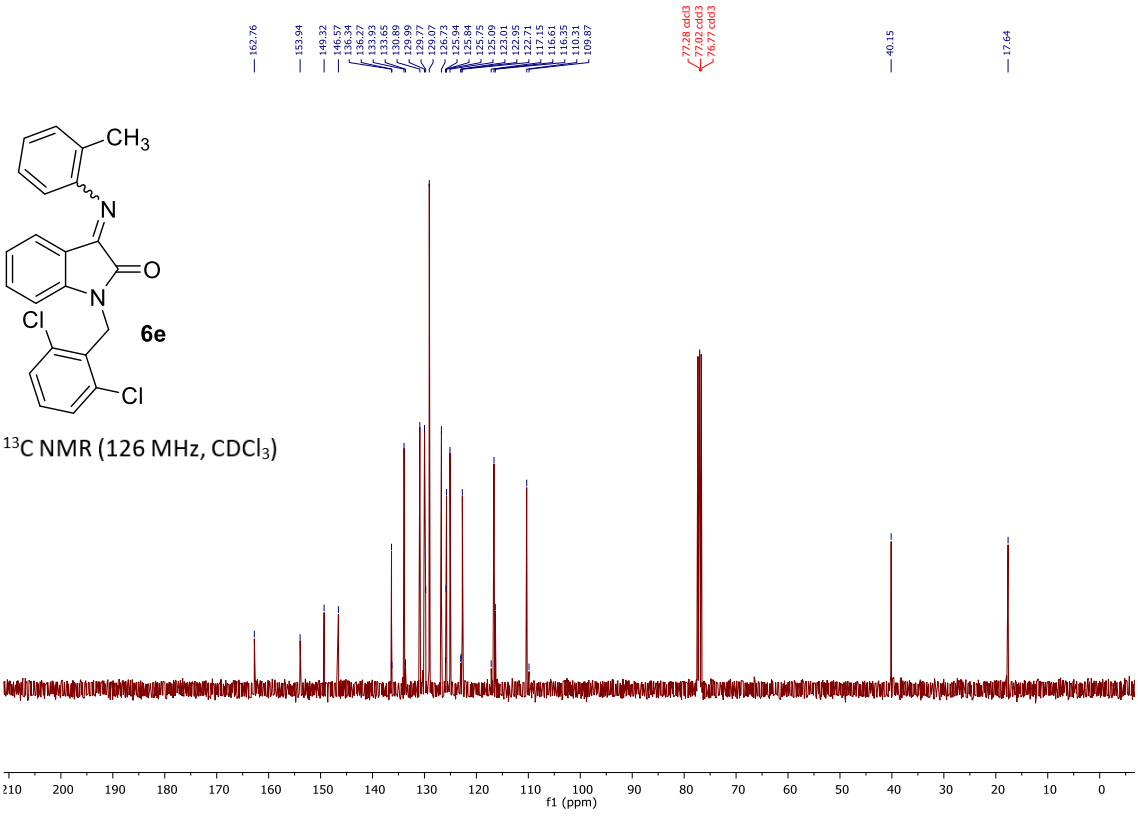


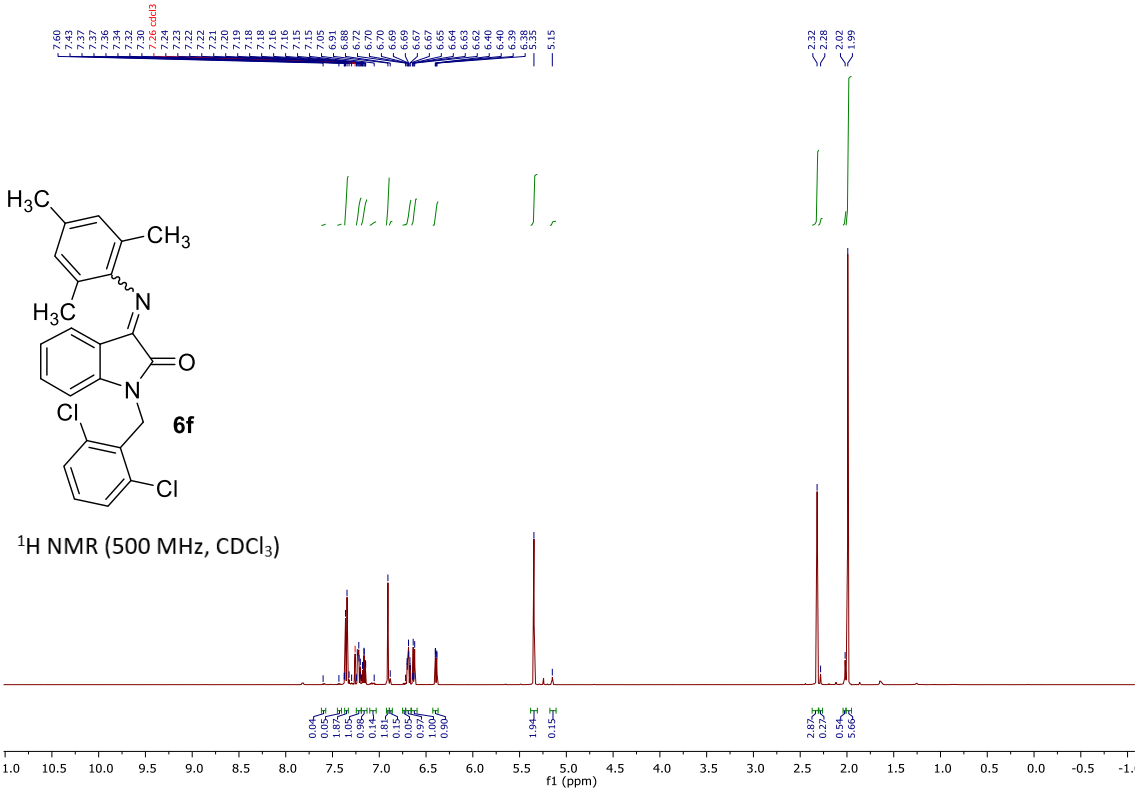
^{13}C NMR (126 MHz, $CDCl_3$)

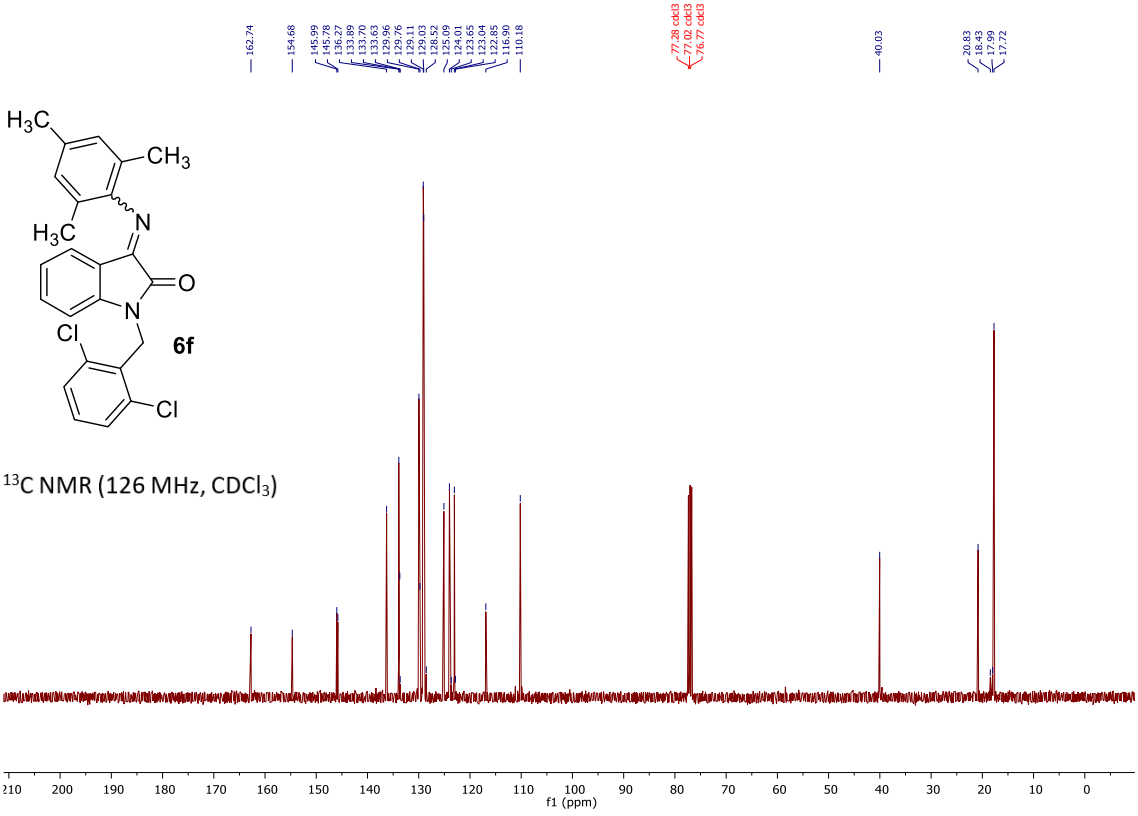

OCH3
N
O
N
Cl
Cl
6d
1H NMR (500 MHz, CDCl3)
f1 (ppm)

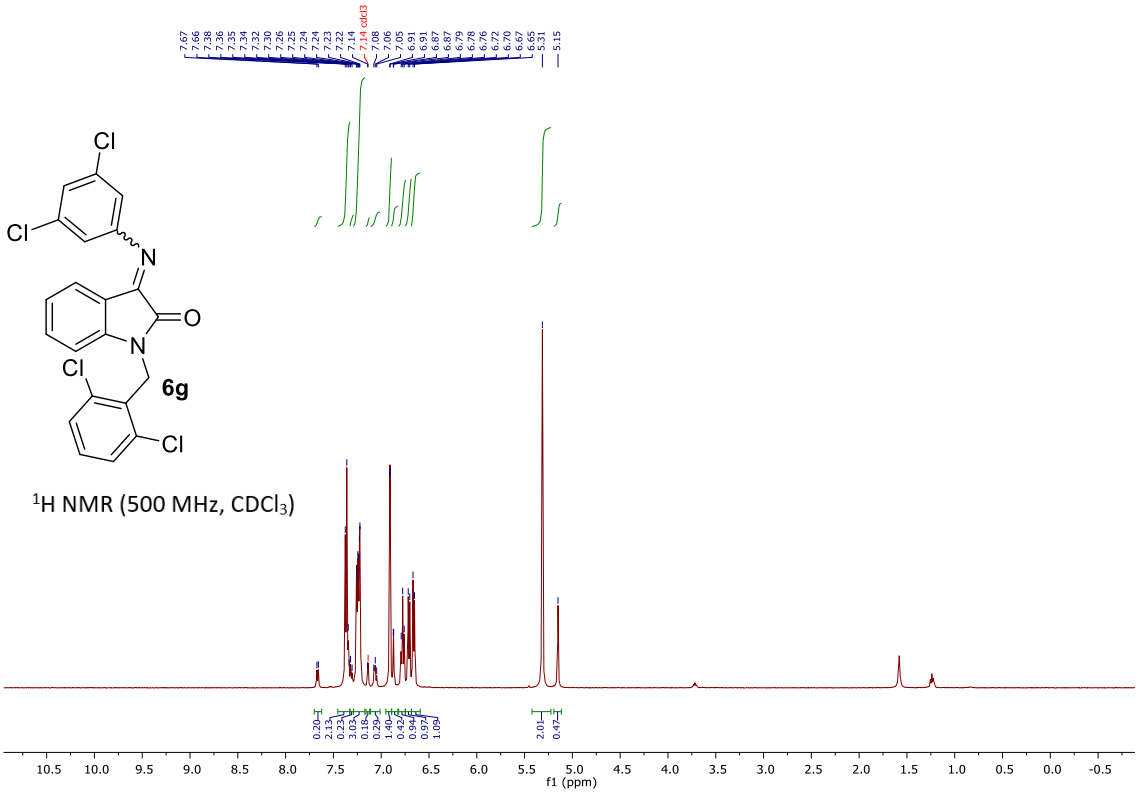

OCH3
N
O
N
Cl
Cl
6d
13C NMR (126 MHz, CDCl3)
f1 (ppm)

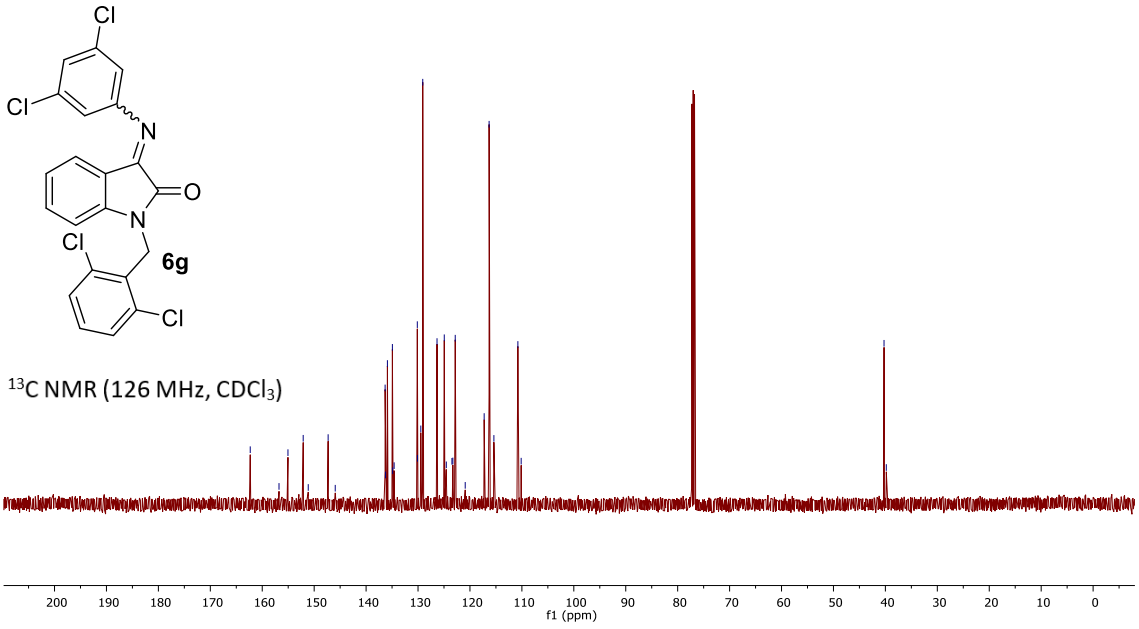

CH3
N
O
N
Cl
Cl
6e
1H NMR (500 MHz, CDCl3)
f1 (ppm)

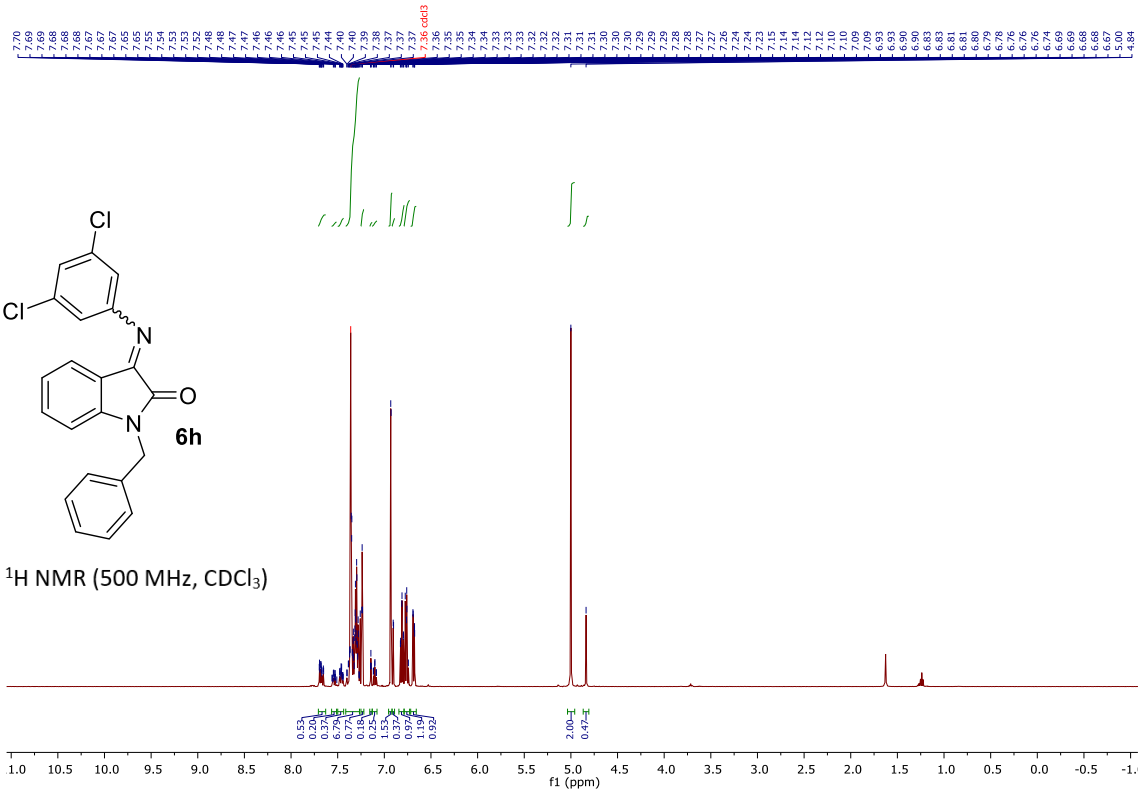

CH3
N
O
N
Cl
Cl
6e
13C NMR (126 MHz, CDCl3)
f1 (ppm)

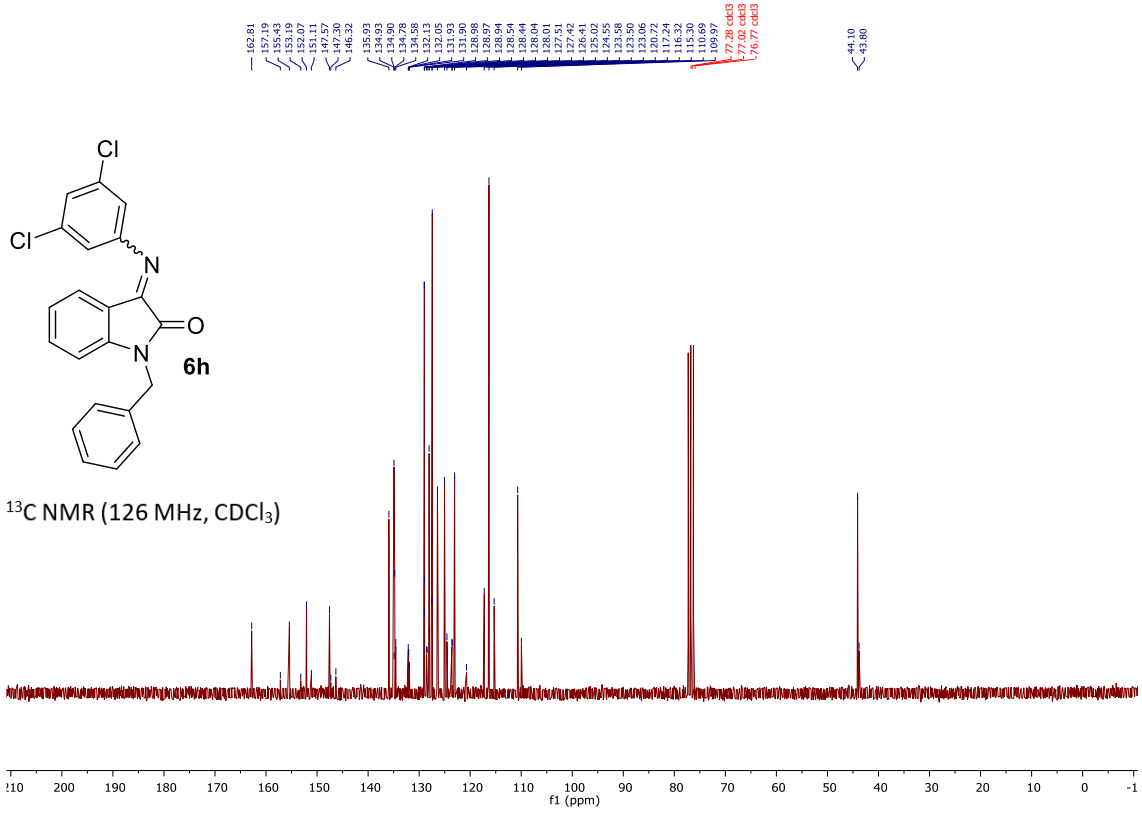

6f
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

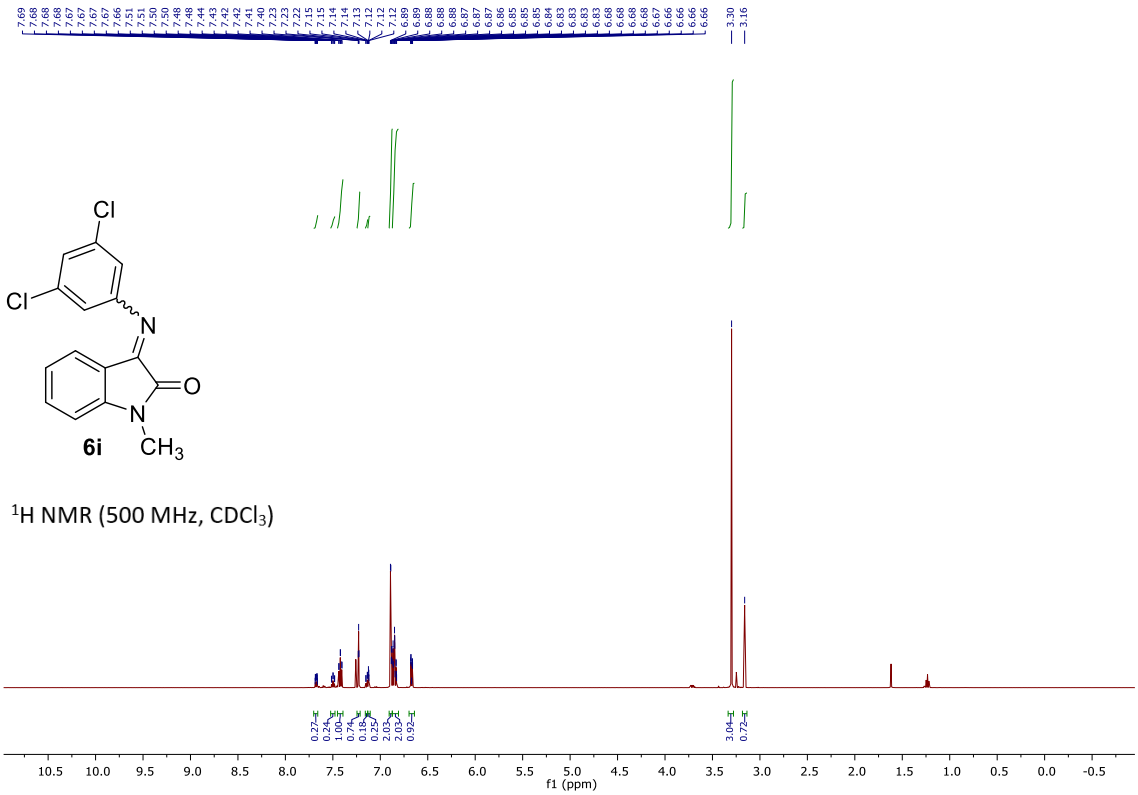

6f
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

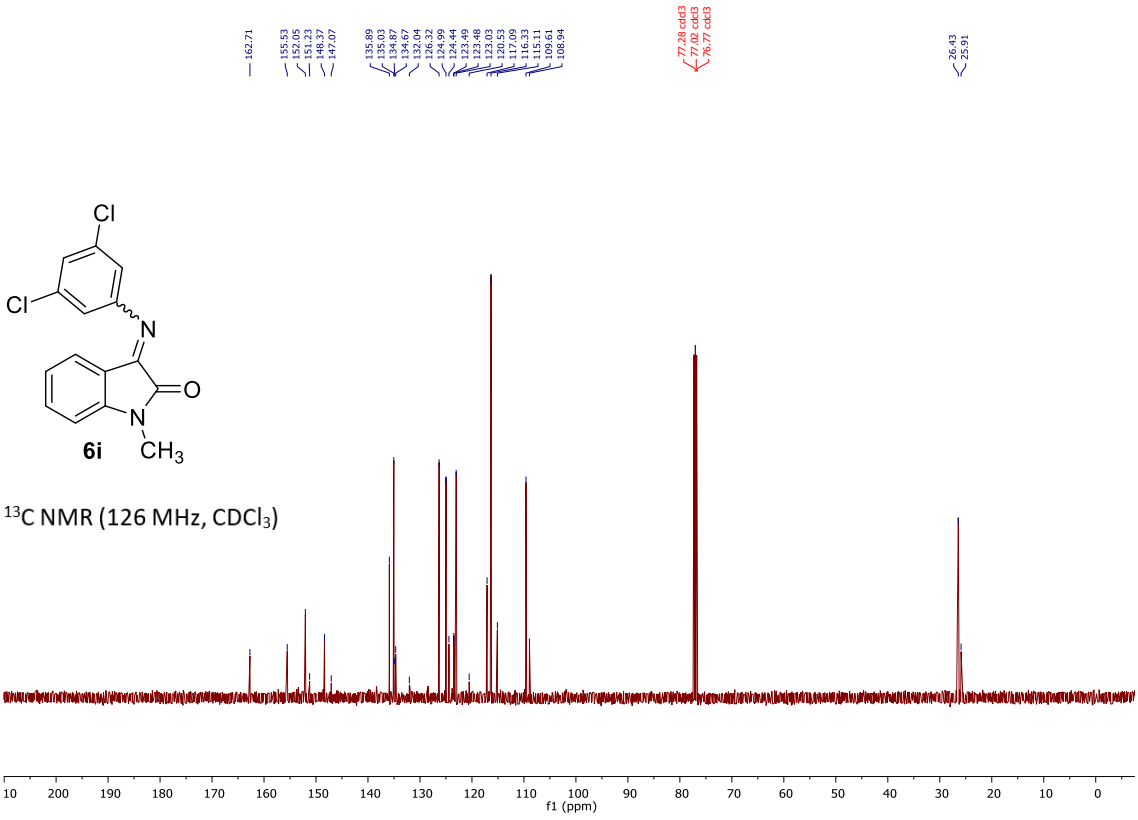

Cl
Cl
N
O
N
Cl
6g
Cl
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

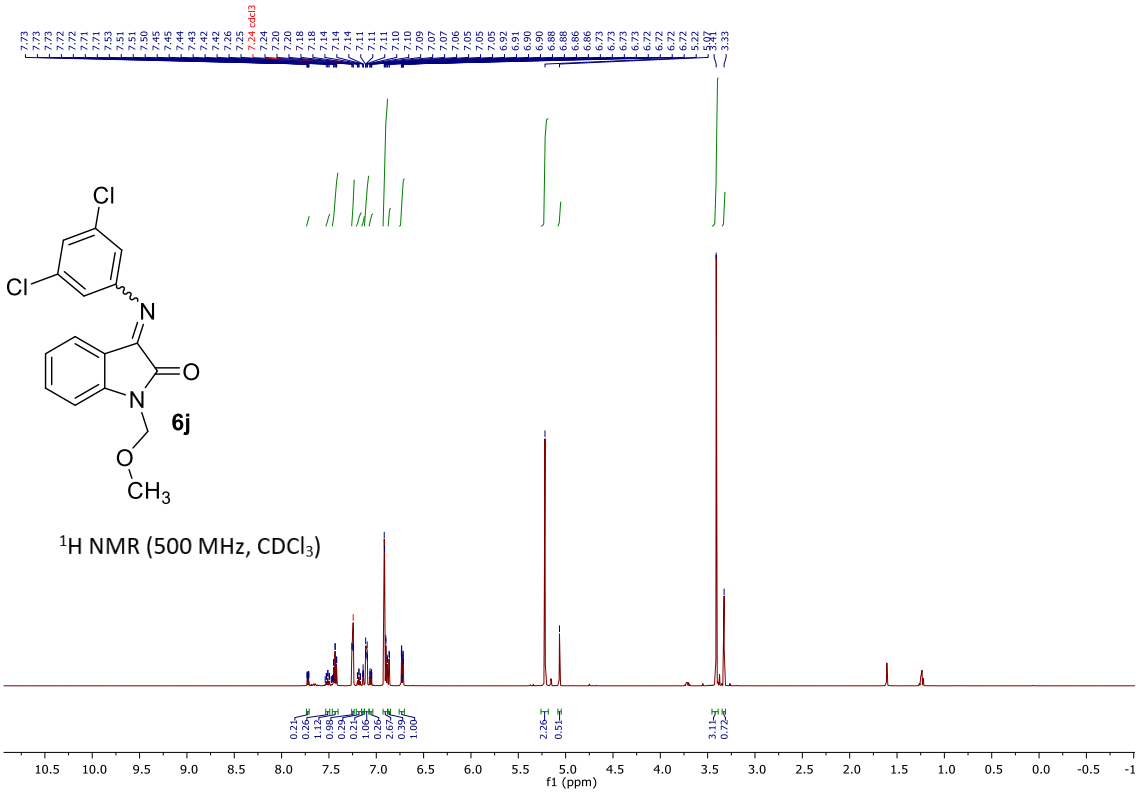

Cl
Cl
N
O
N
Cl
6g
Cl
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

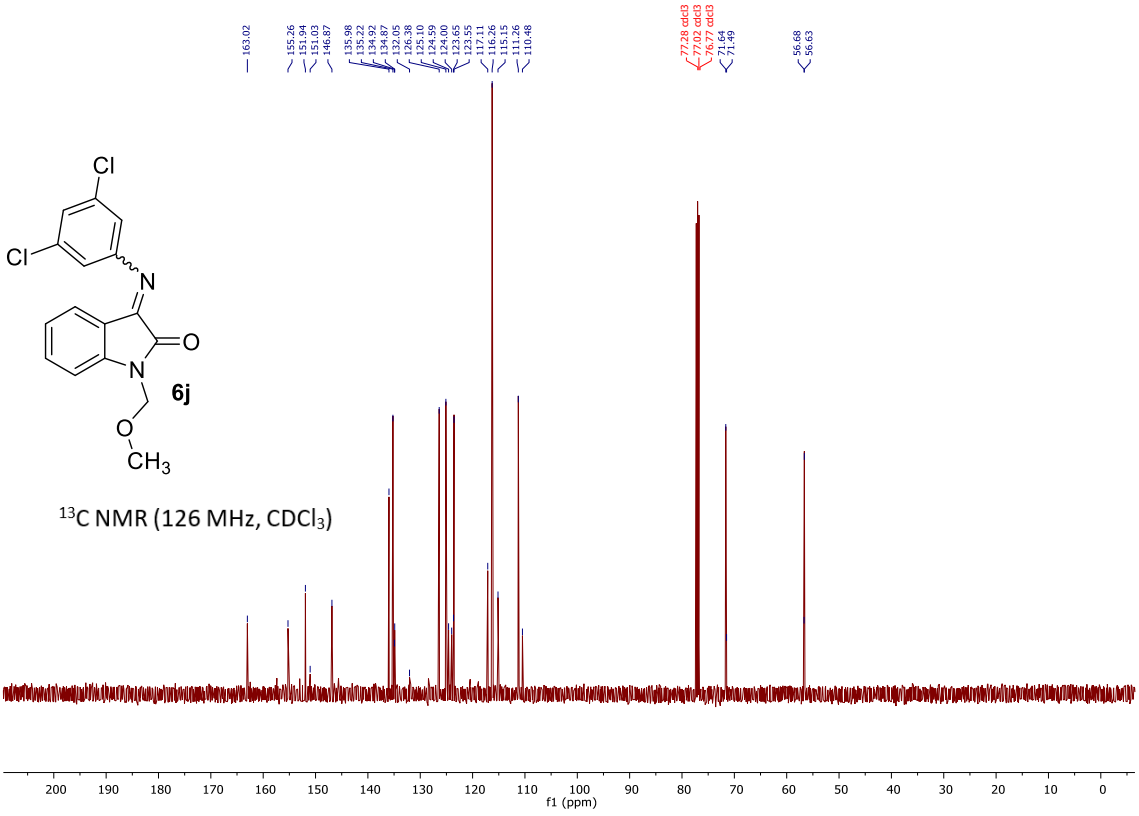

Cl
Cl
N
O
N
6h
1H NMR (500 MHz, CDCl3)
f1 (ppm)

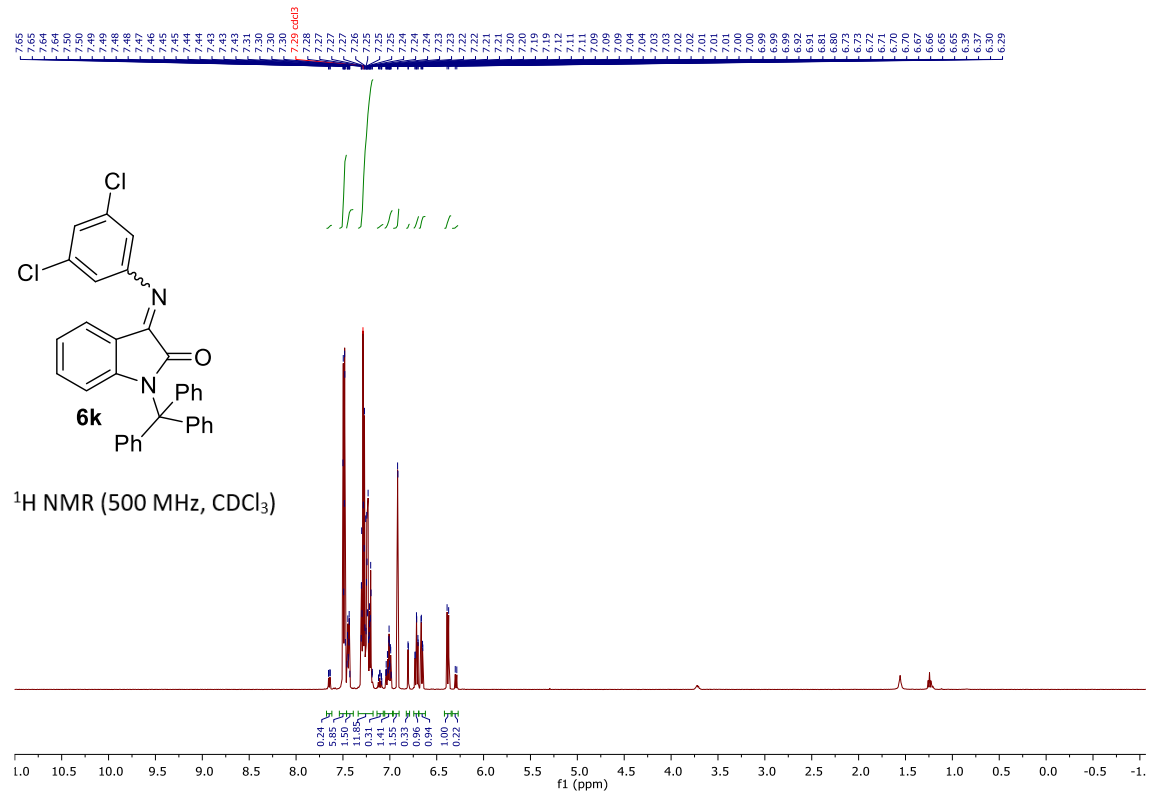

Cl
Cl
N
O
N
6h
13C NMR (126 MHz, CDCl3)
f1 (ppm)

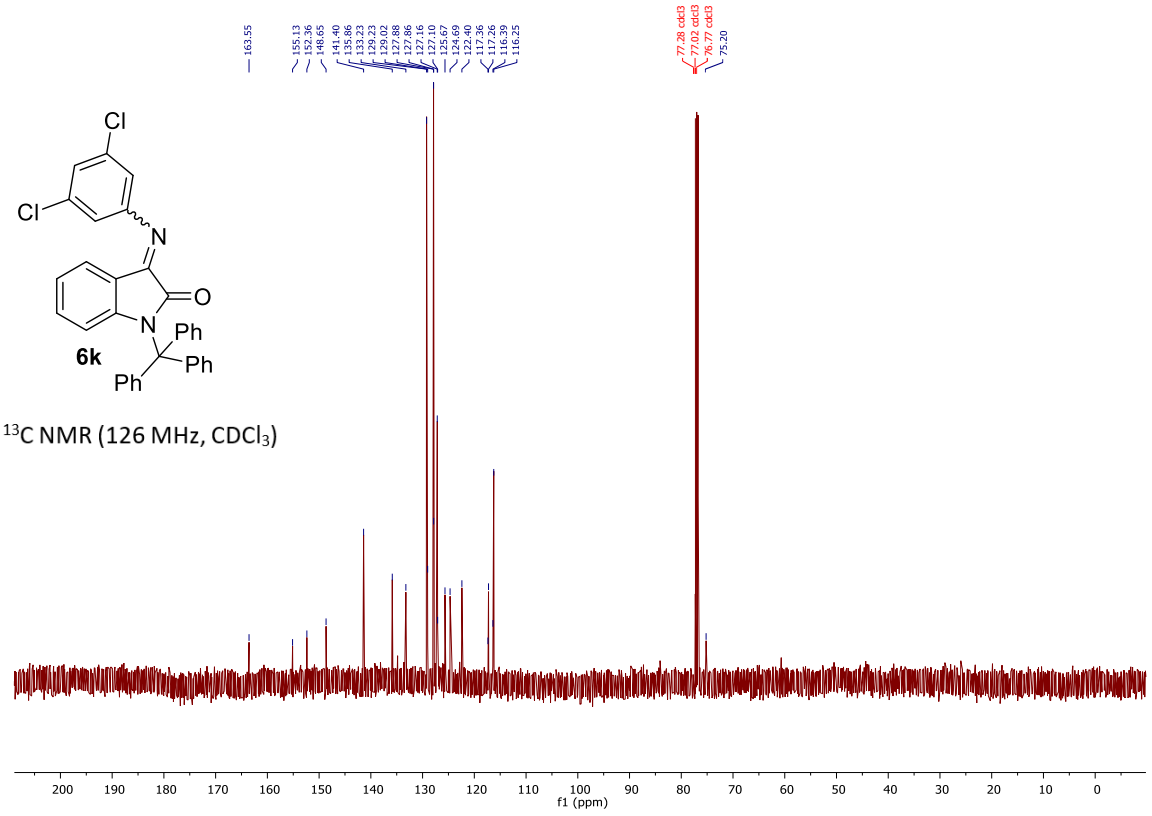

Cl
Cl
N
O
N
CH3
6i
1H NMR (500 MHz, CDCl3)
f1 (ppm)

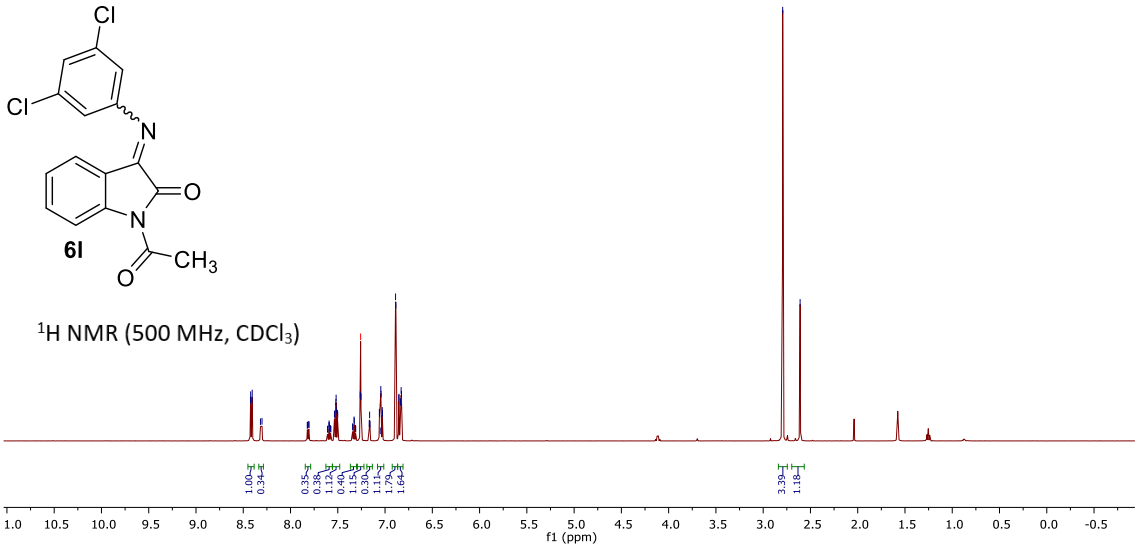

Cl
Cl
N
O
N
CH3
6i
13C NMR (126 MHz, CDCl3)
f1 (ppm)

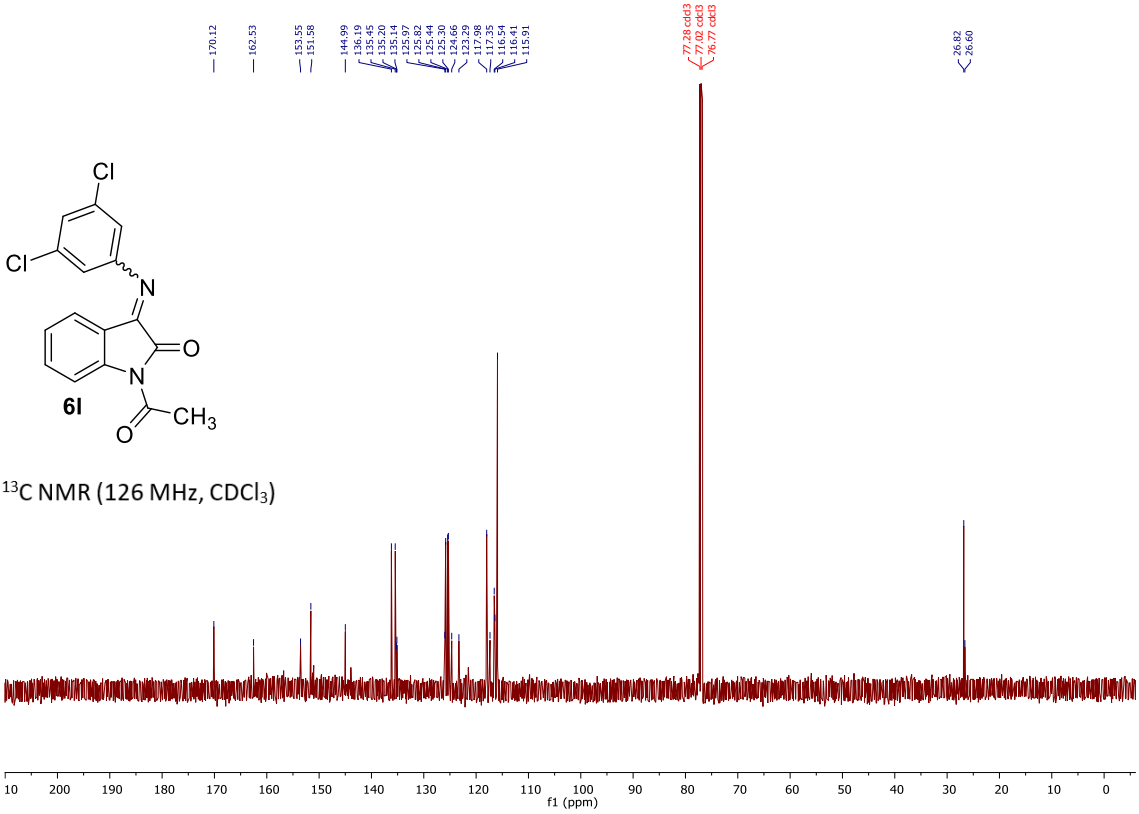

Cl
Cl
N
O
N
6j
O
CH3
1H NMR (500 MHz, CDCl3)
f1 (ppm)

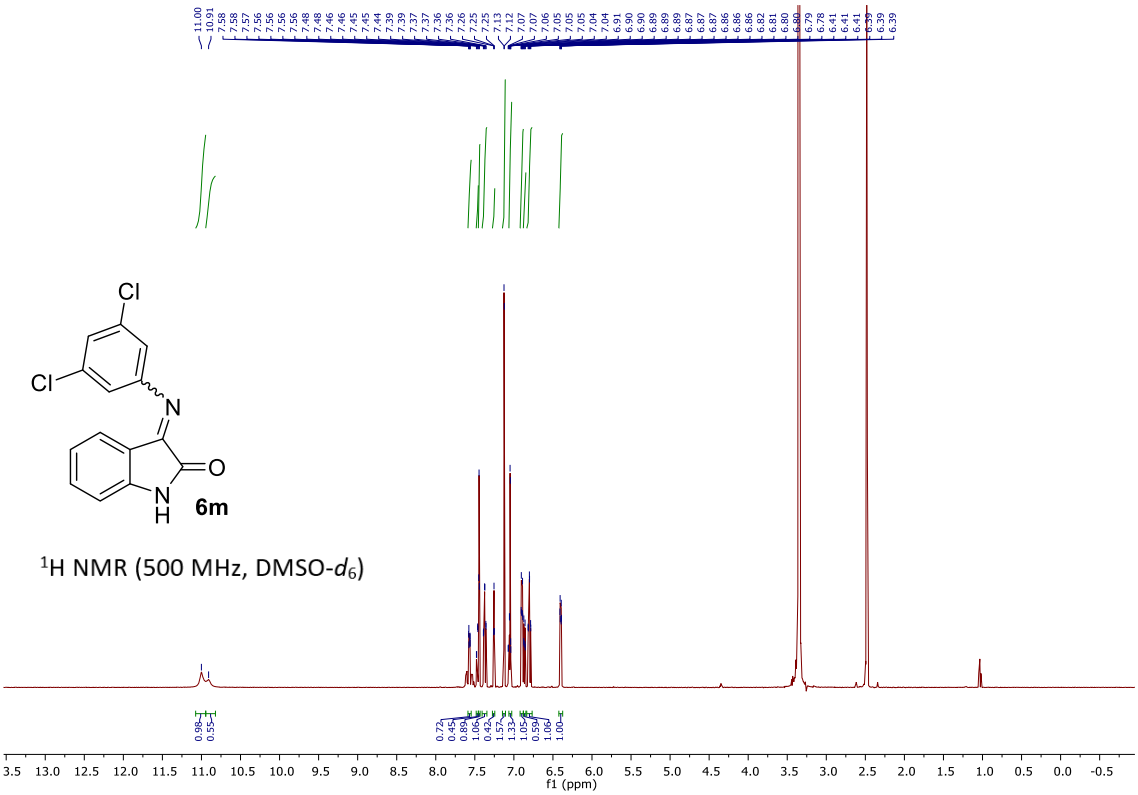

Cl
Cl
N
O
N
6j
O
CH3
13C NMR (126 MHz, CDCl3)
f1 (ppm)


Cl
Cl
N
O
N
Ph
Ph
Ph
6k
1H NMR (500 MHz, CDCl3)
f1 (ppm)

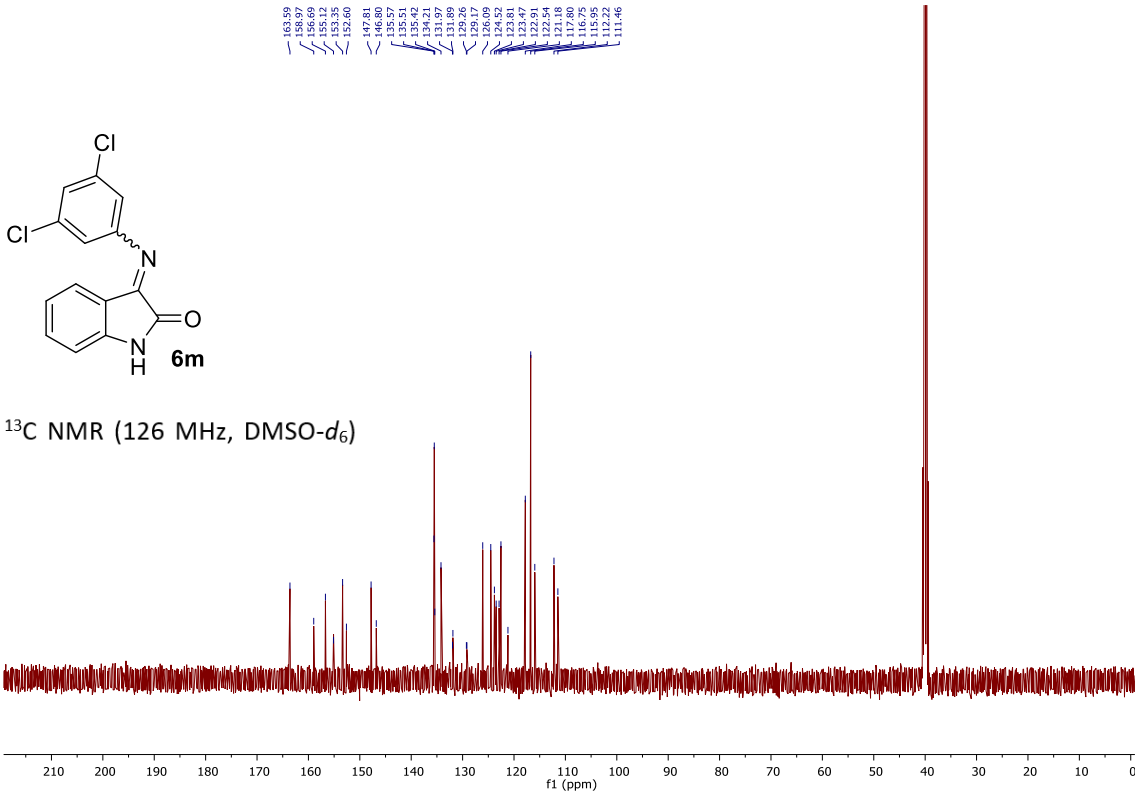

Cl
Cl
N
O
N
Ph
Ph
Ph
6k
13C NMR (126 MHz, CDCl3)
f1 (ppm)


Cl
Cl
N
O
N
O
CH3
6l
1H NMR (500 MHz, CDCl3)
f1 (ppm)

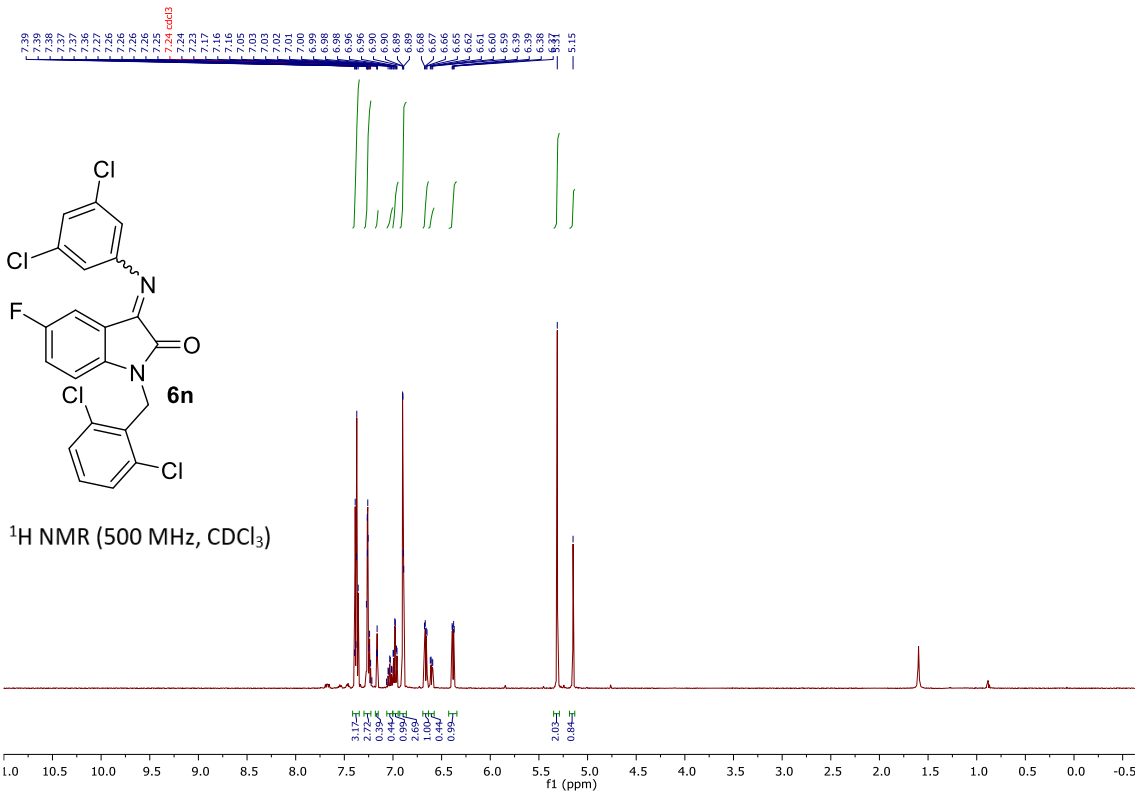

Cl
Cl
N
O
N
O
CH3
6l
13C NMR (126 MHz, CDCl3)
f1 (ppm)

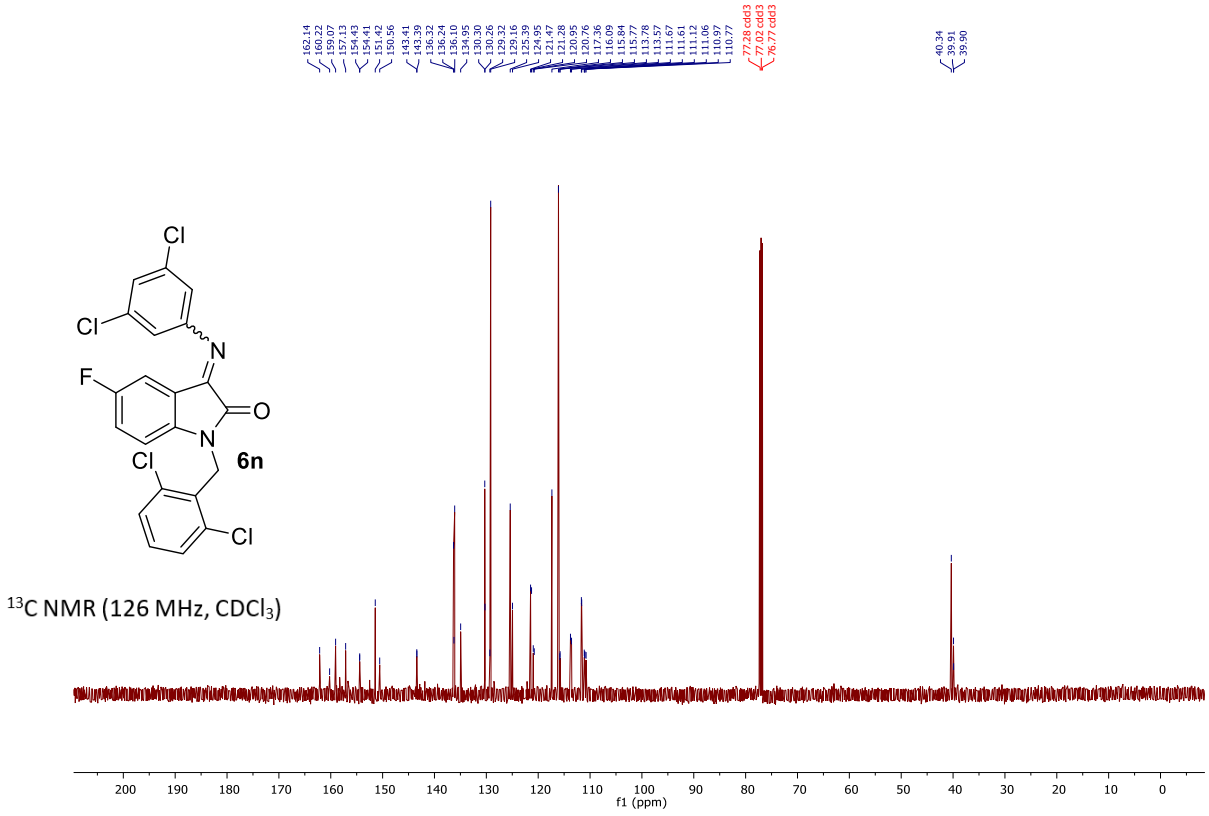


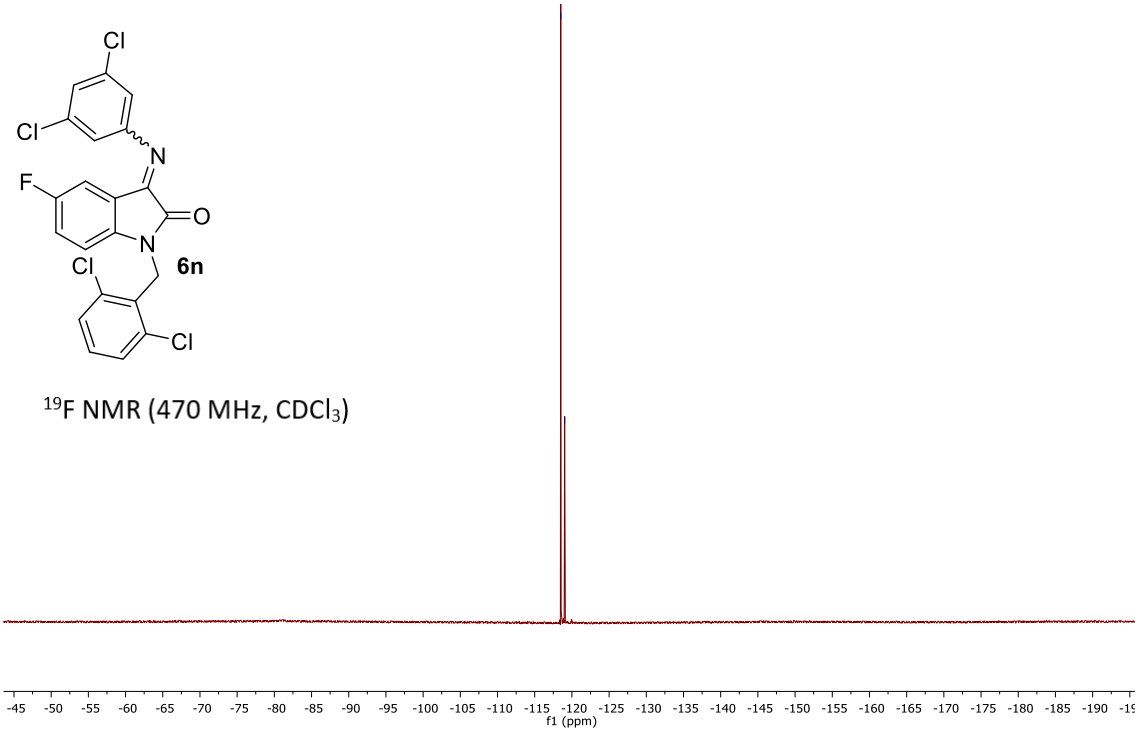
^{1}H NMR (500 MHz, DMSO-d_6)



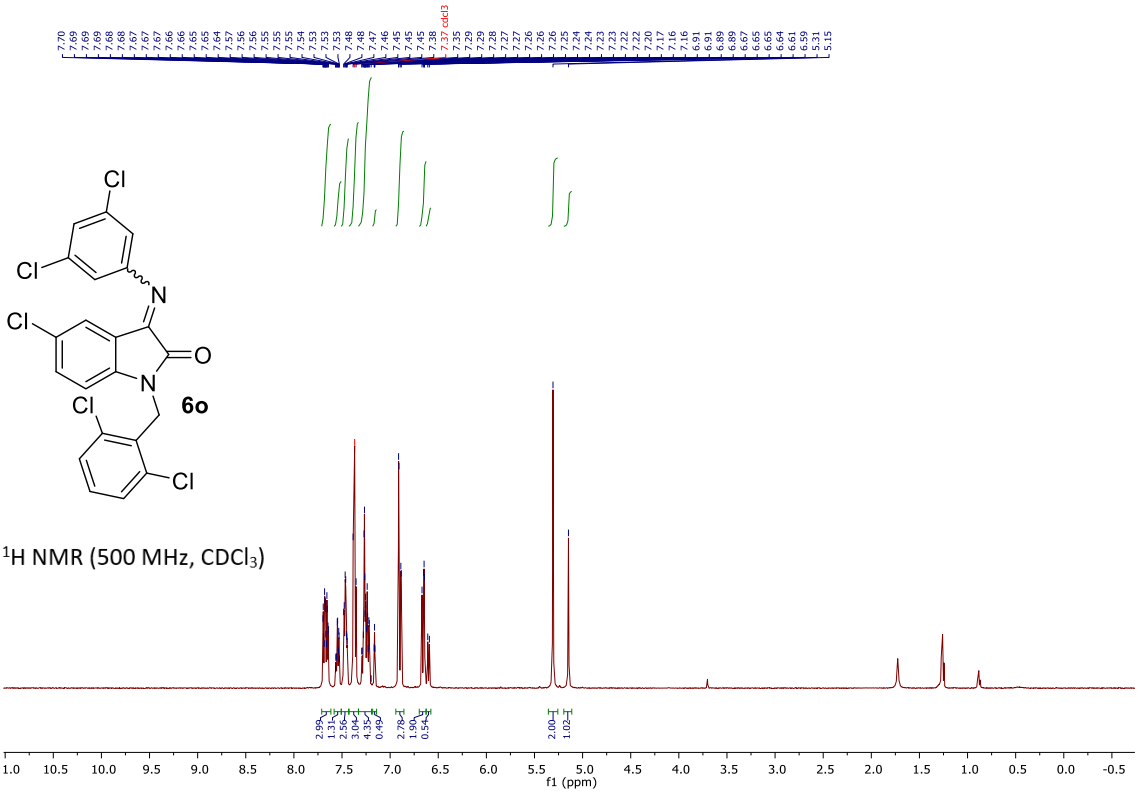
^{13}C NMR (126 MHz, DMSO-d_6)

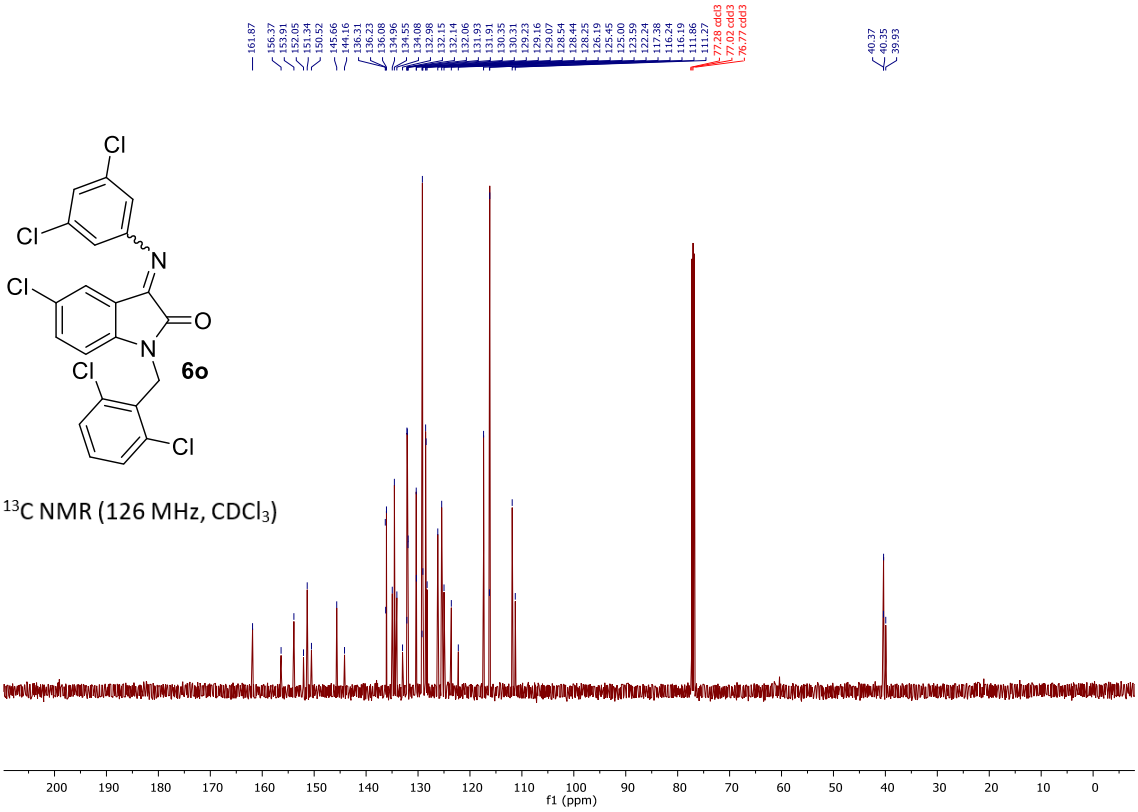

Cl
Cl
N
F
O
N
Cl
6n
Cl
1H NMR (500 MHz, CDCl3)
f1 (ppm)

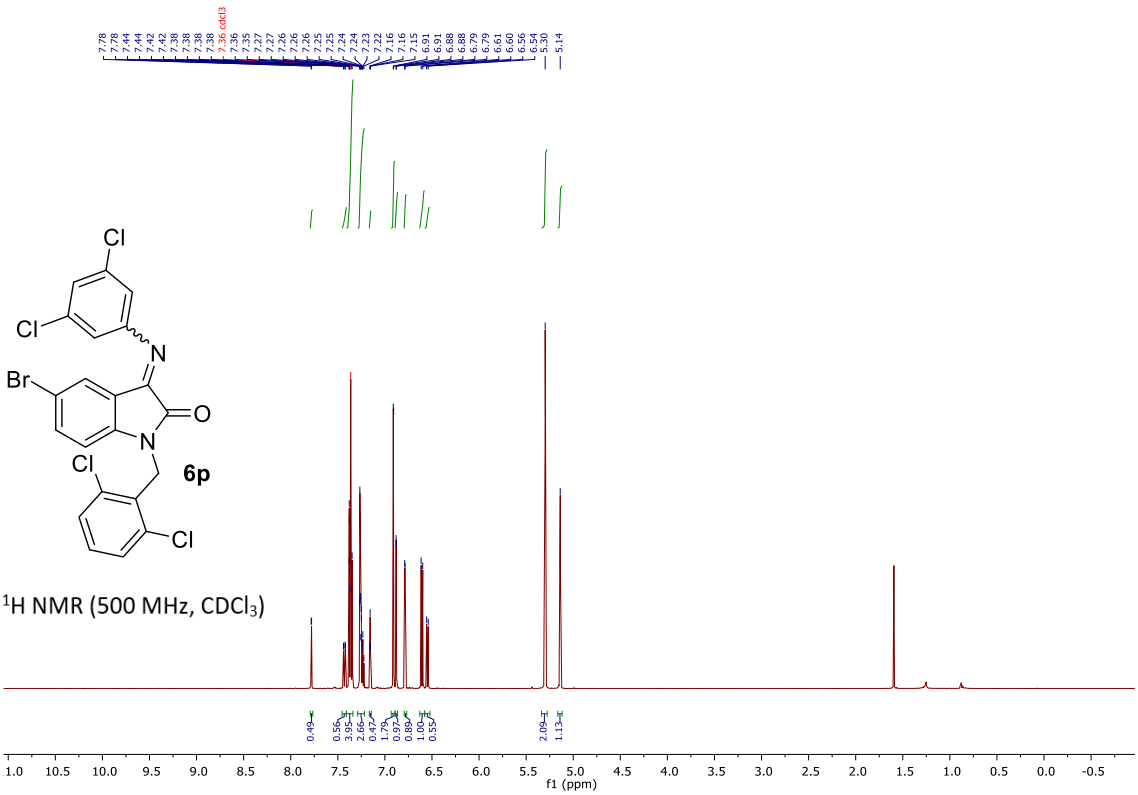

Cl
Cl
N
F
O
N
Cl
6n
Cl
13C NMR (126 MHz, CDCl3)
f1 (ppm)

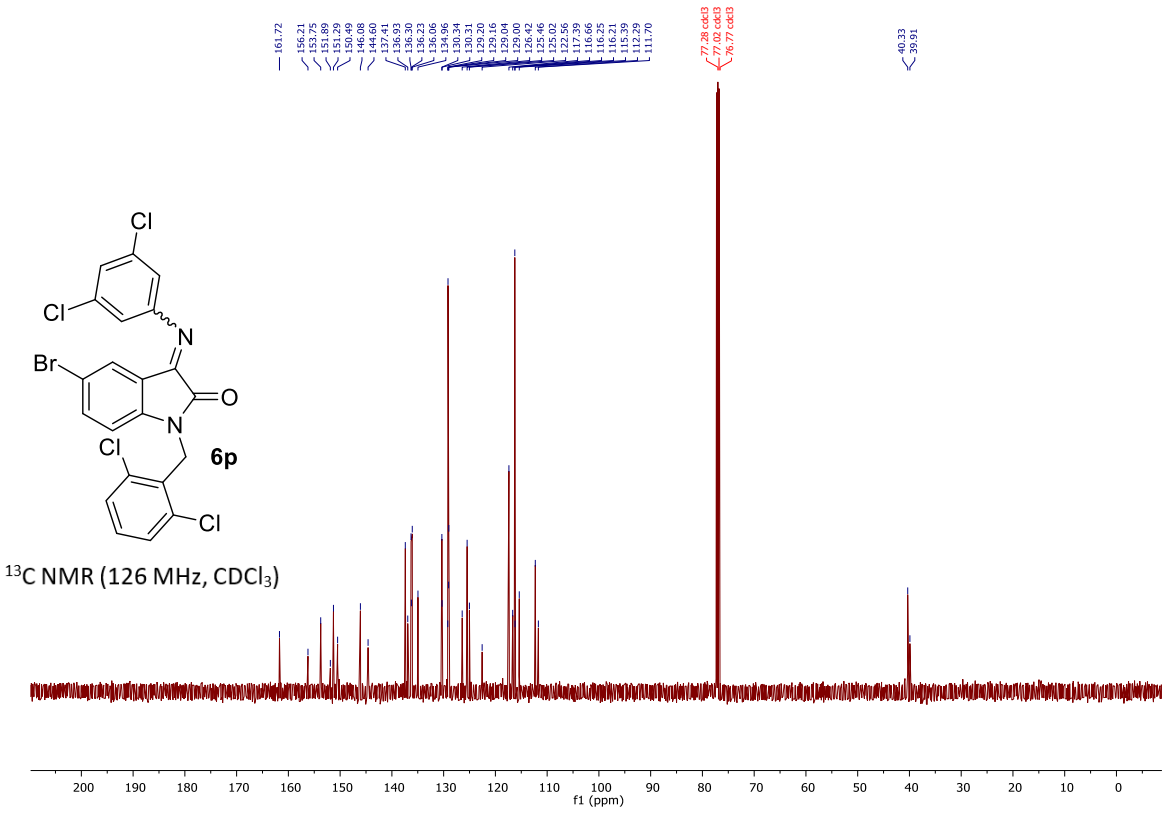


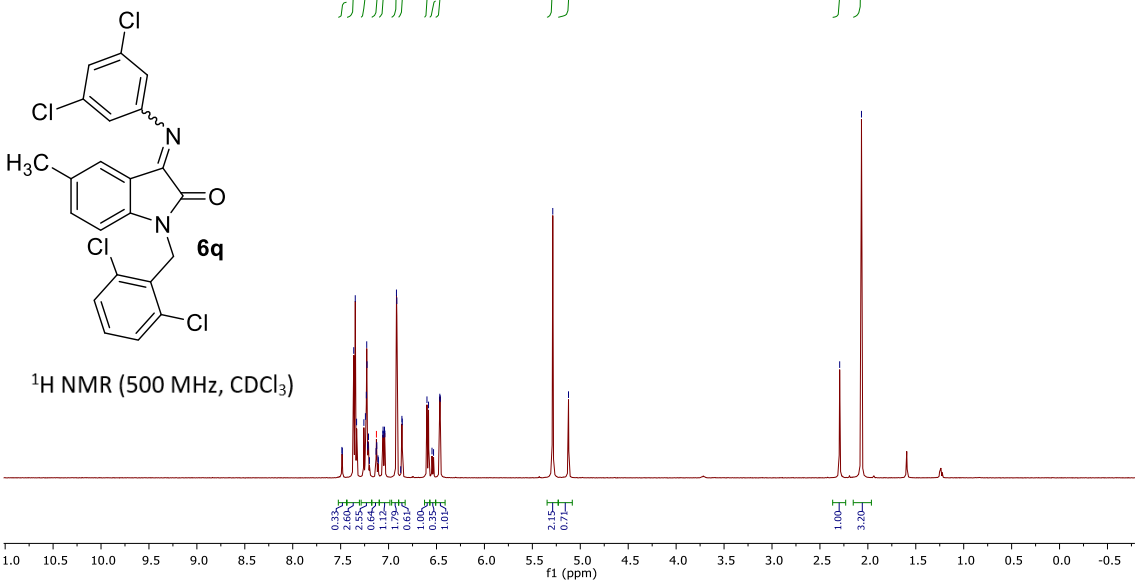
^{19}F NMR (470 MHz, $CDCl_3$)

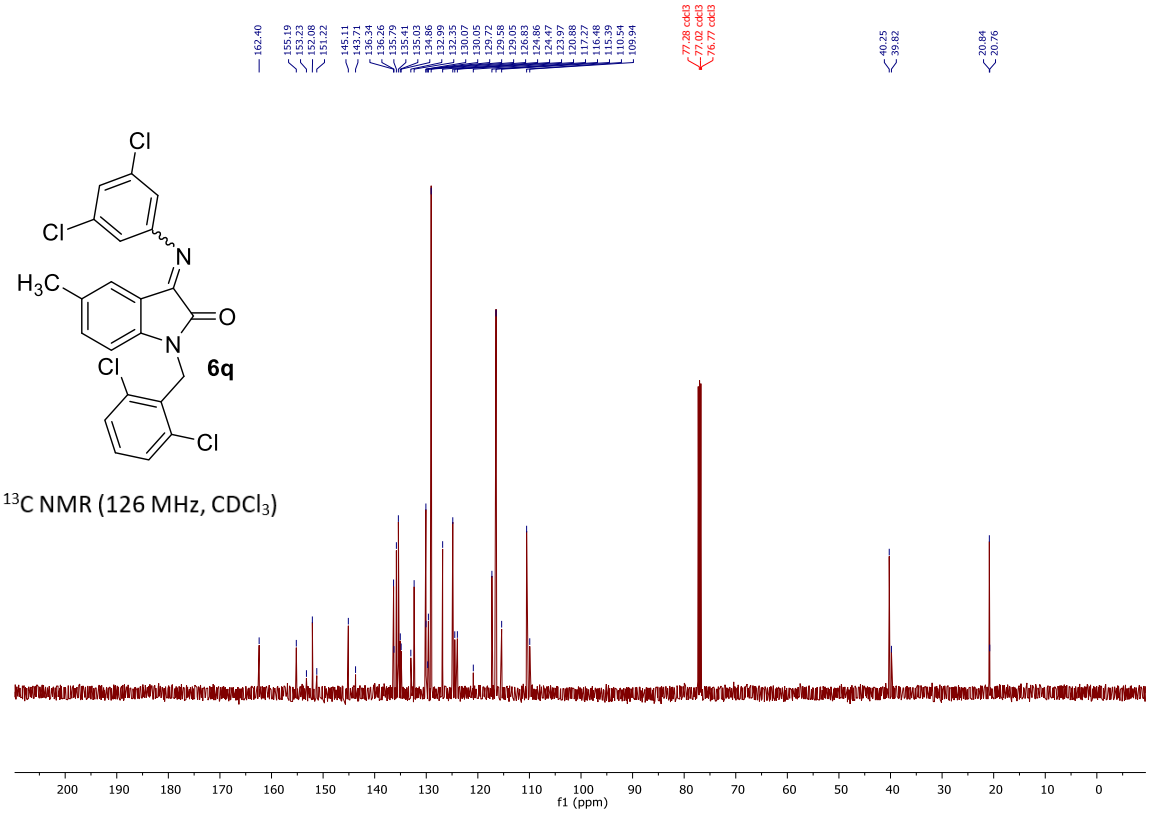

Cl
Cl
N
Cl
O
N
Cl
6o
Cl
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)


Cl
Cl
N
Cl
O
N
Cl
6o
Cl
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

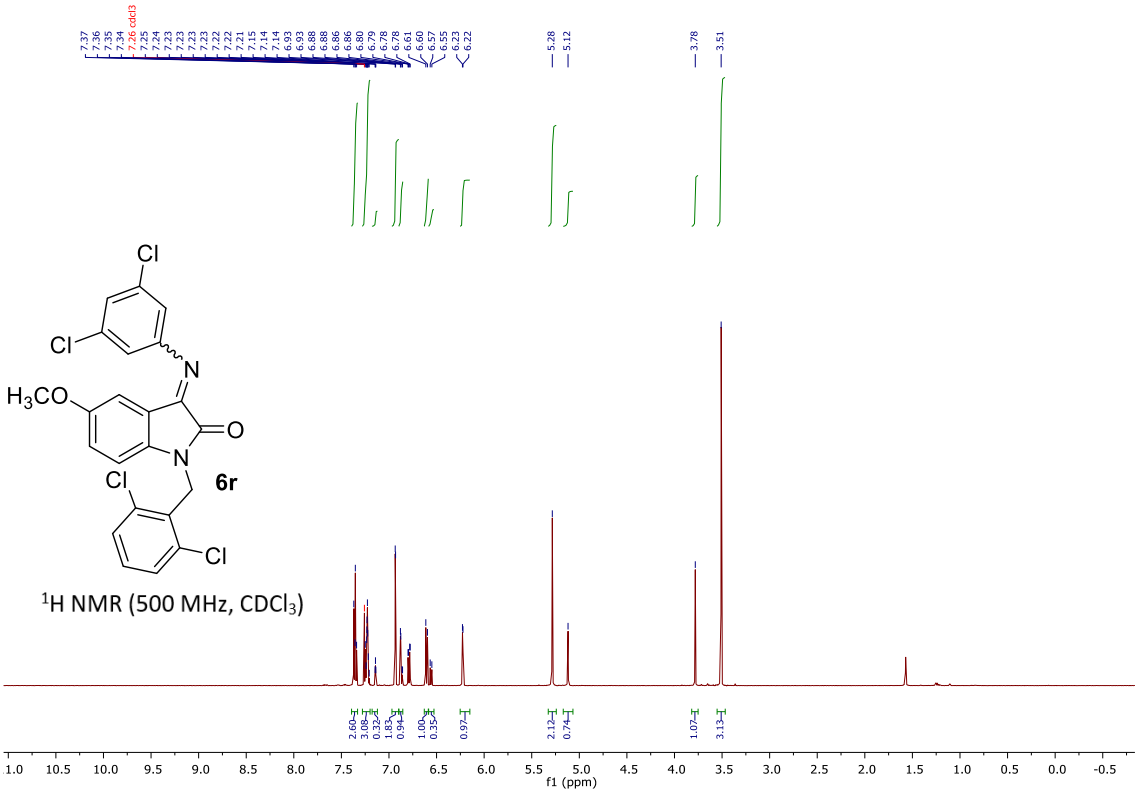

Cl
Cl
N
Br
O
N
Cl
6p
Cl
1H NMR (500 MHz, CDCl3)
f1 (ppm)

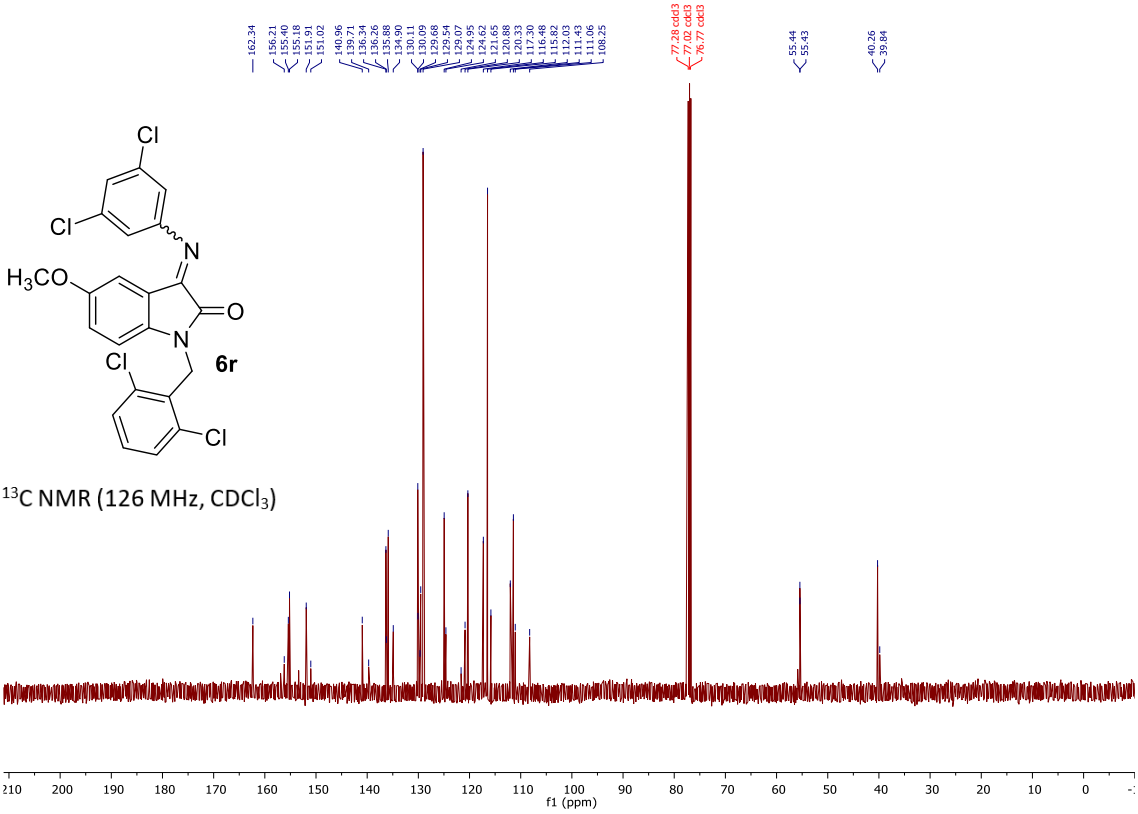

Cl
Cl
N
Br
O
N
Cl
6p
Cl
13C NMR (126 MHz, CDCl3)
f1 (ppm)

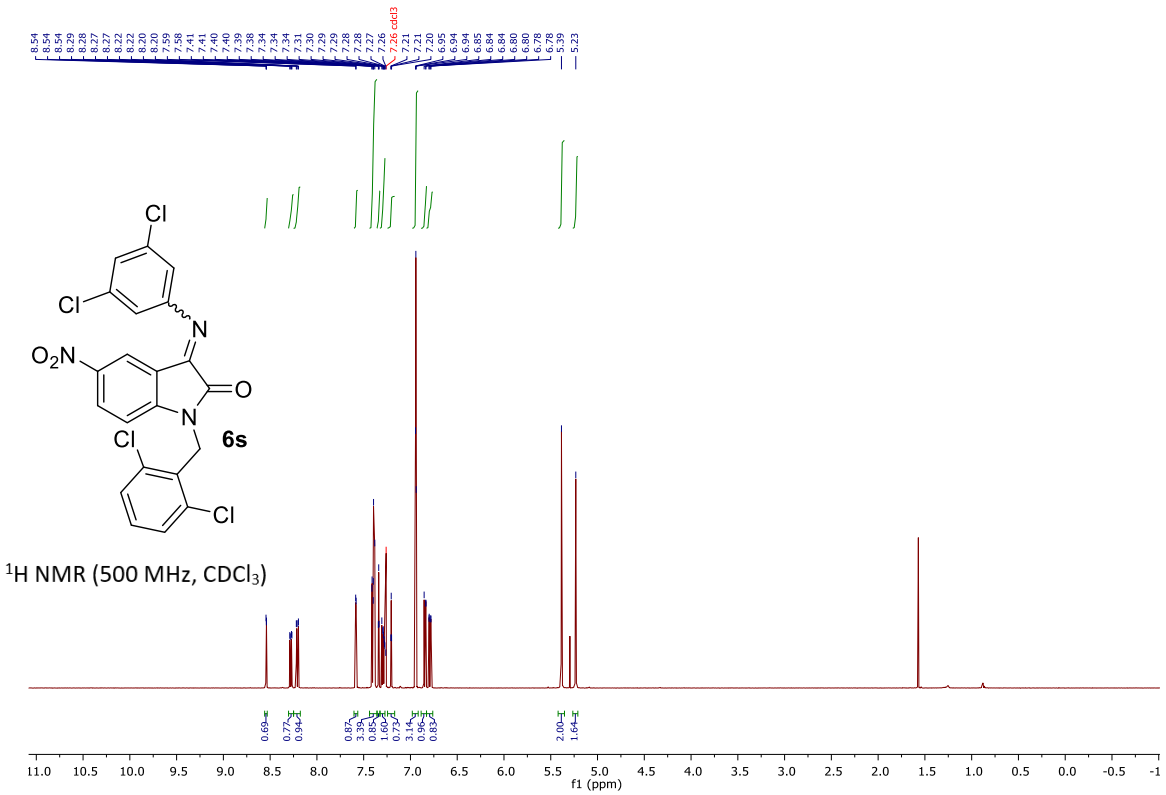

Cl
Cl
N
H3C
O
N
Cl
6q
Cl
1H NMR (500 MHz, CDCl3)
f1 (ppm)

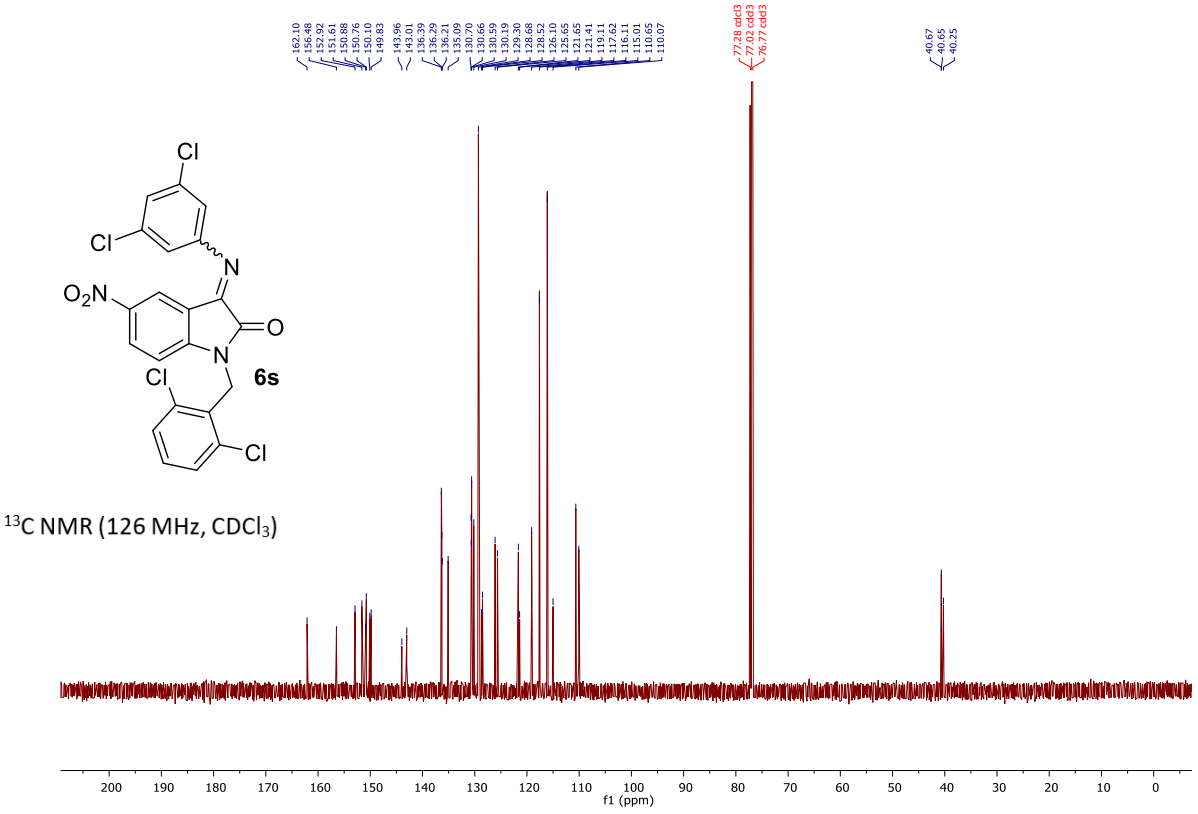

Cl
Cl
N
H3C
O
N
Cl
6q
Cl
13C NMR (126 MHz, CDCl3)
f1 (ppm)

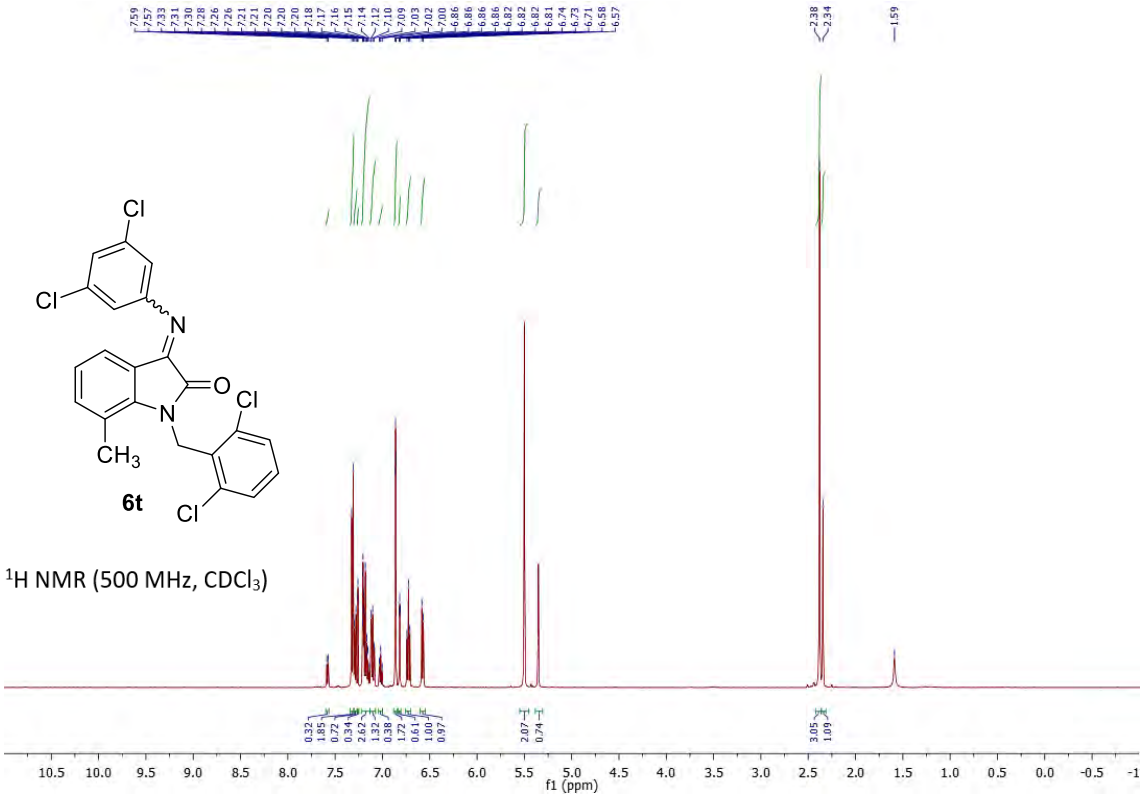
1r:

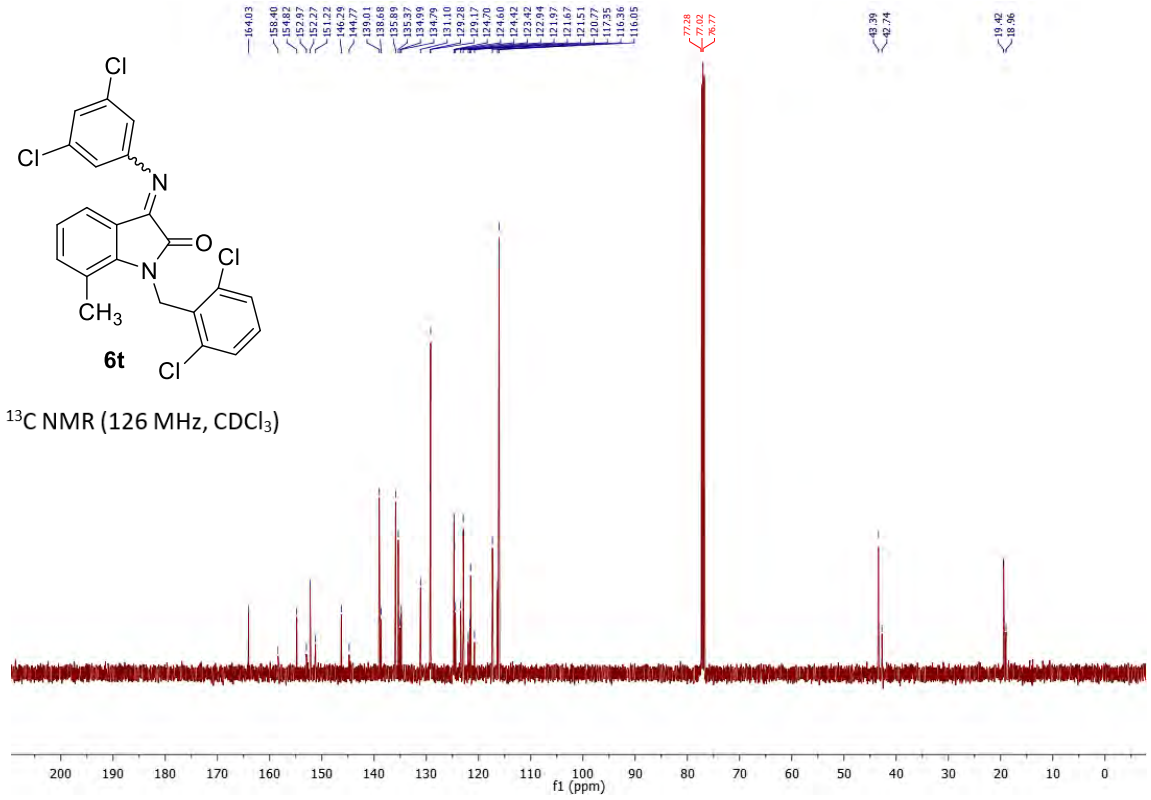

Cl
Cl
N
H3CO
O
N
Cl
6r
Cl
1H NMR (500 MHz, CDCl3)
f1 (ppm)

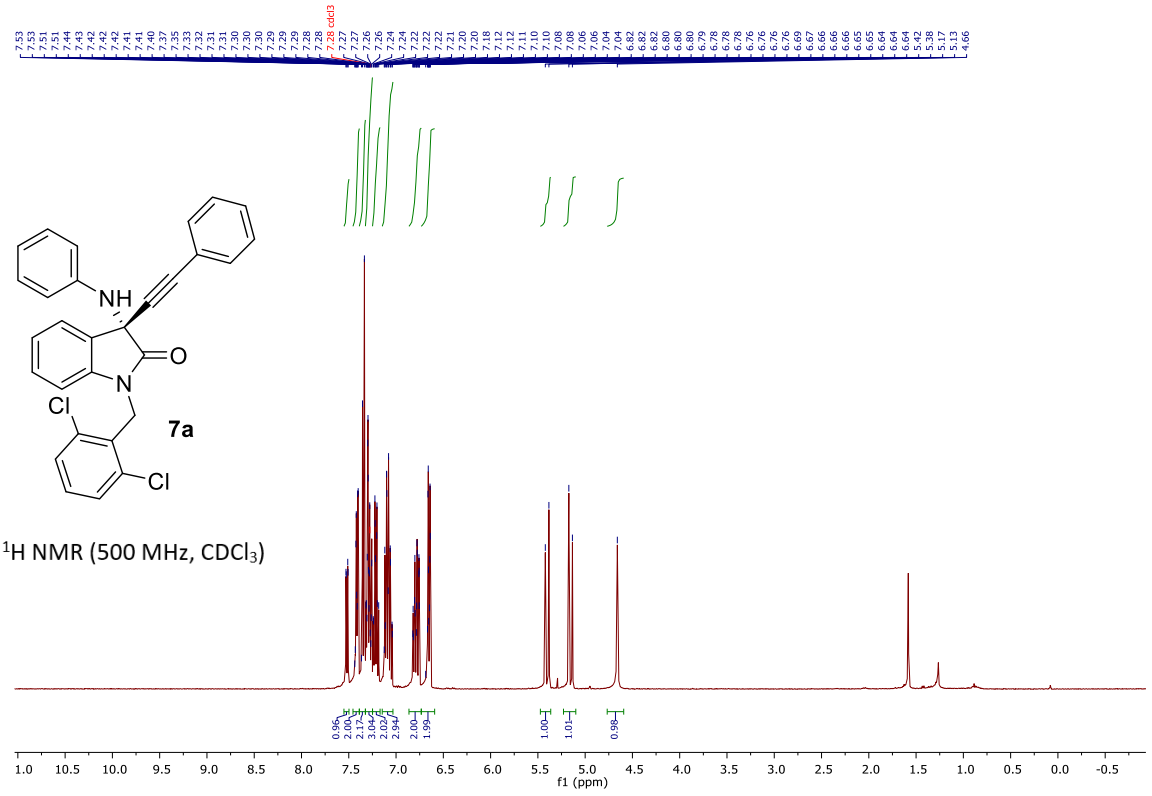

Cl
Cl
N
H3CO
O
N
Cl
6r
Cl
13C NMR (126 MHz, CDCl3)
f1 (ppm)

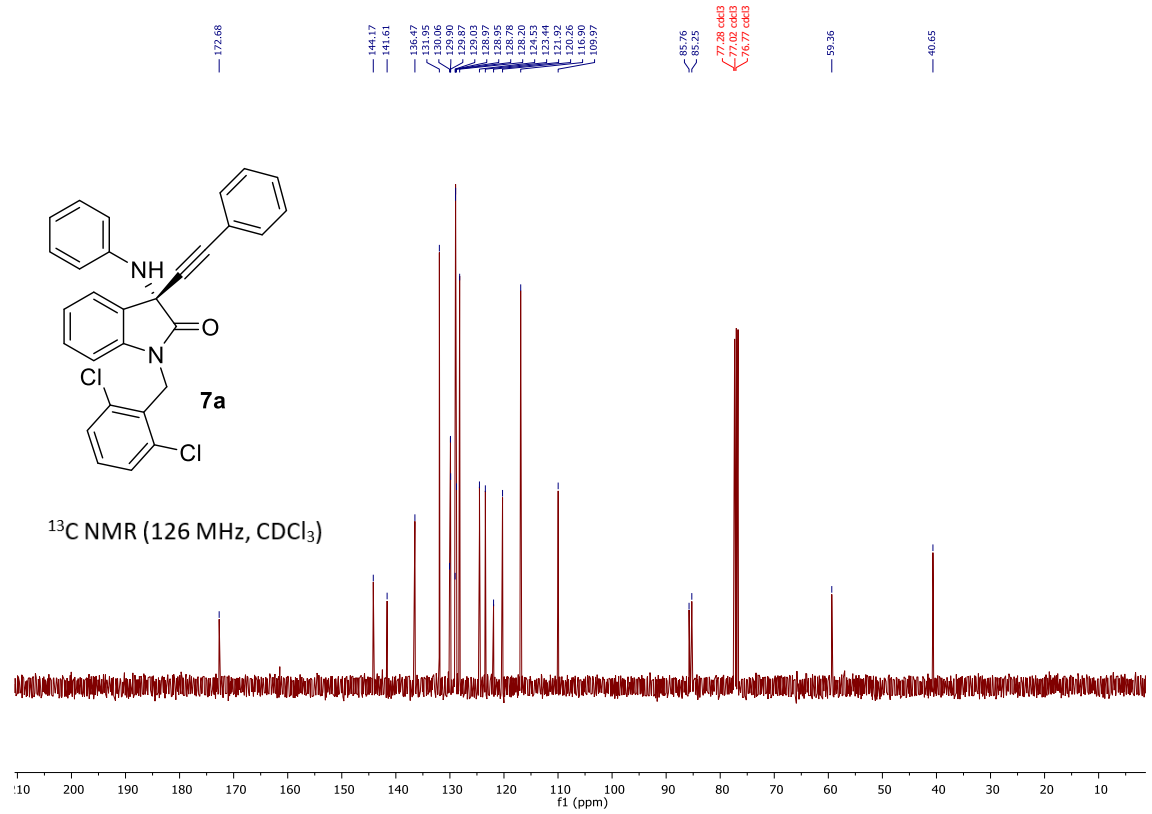

Cl
Cl
N
O2N
O
N
Cl
6s
Cl
1H NMR (500 MHz, CDCl3)
f1 (ppm)

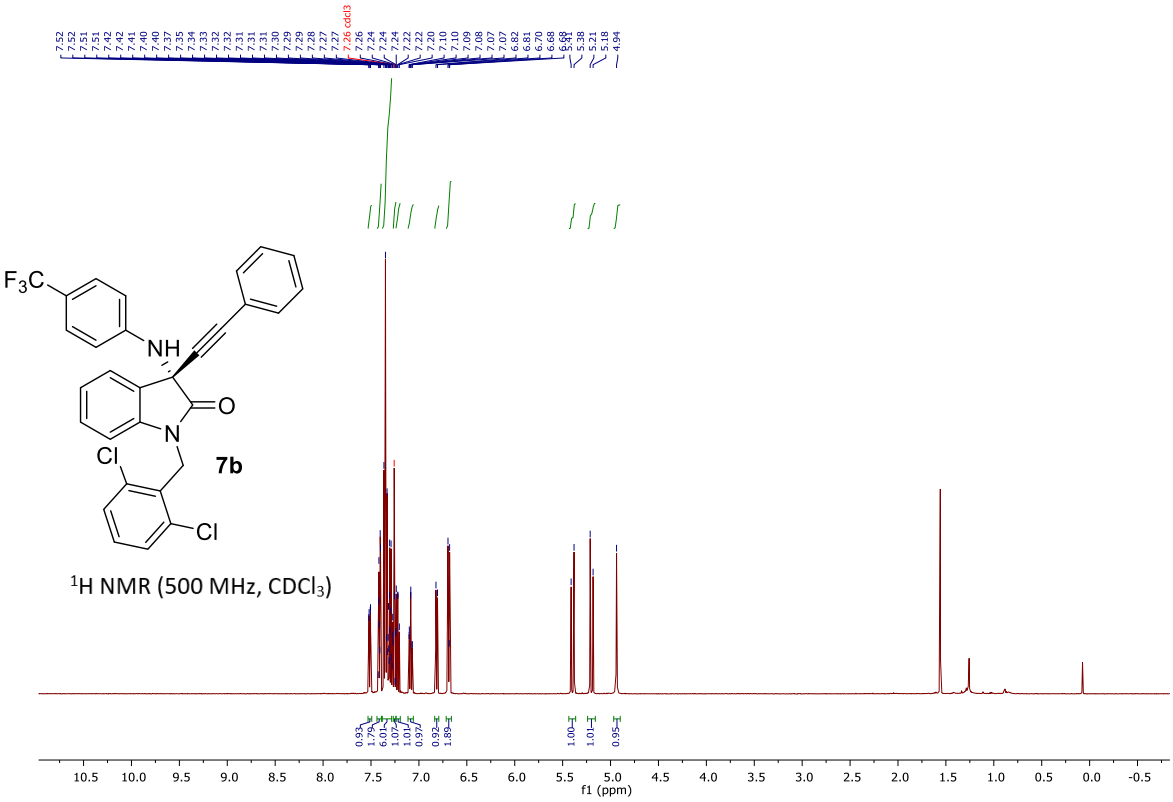

Cl
Cl
N
O2N
O
N
Cl
6s
Cl
13C NMR (126 MHz, CDCl3)
f1 (ppm)

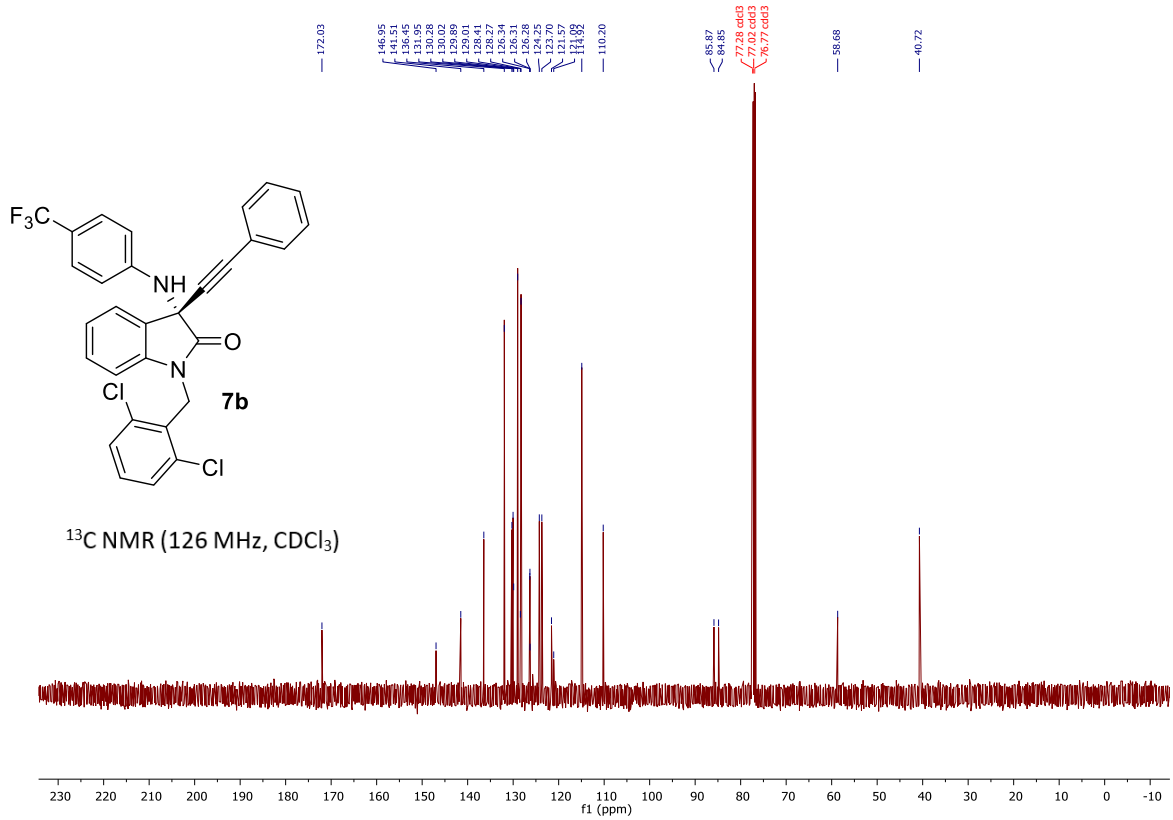

Cl
Cl
N
O
N
Cl
CH3
Cl
6t
1H NMR (500 MHz, CDCl3)
f1 (ppm)

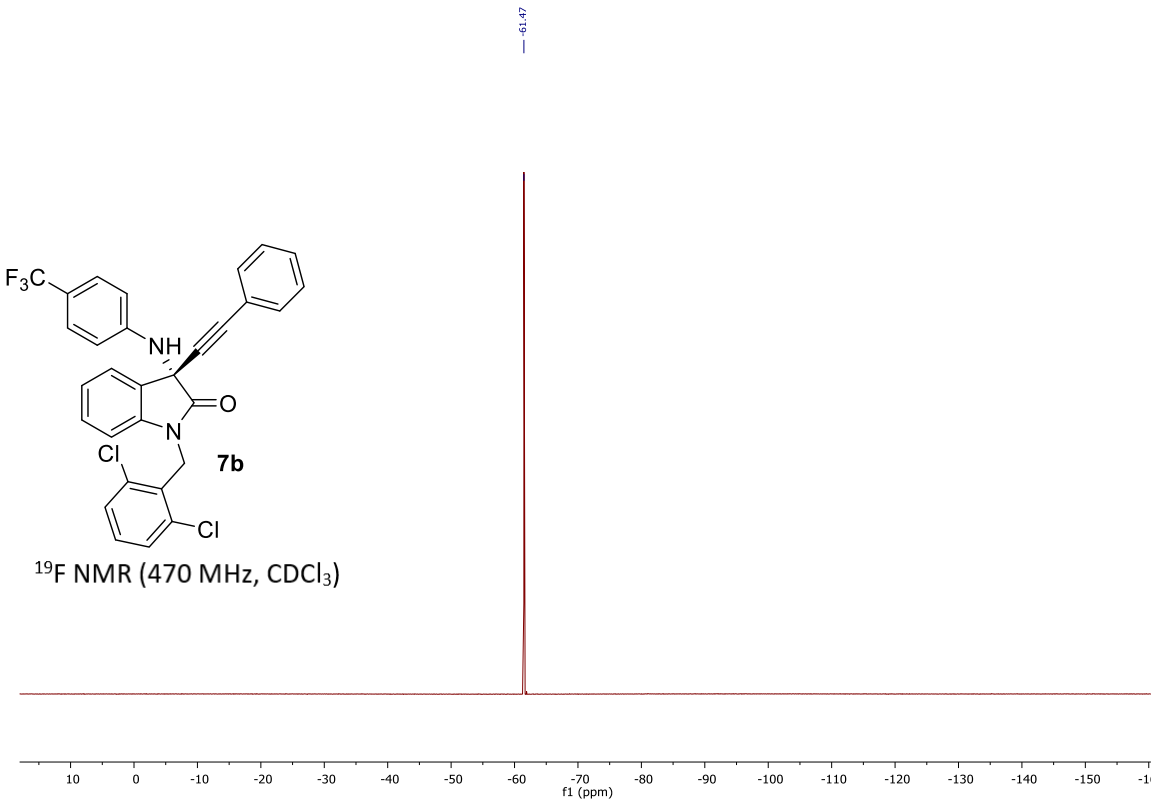

Cl
Cl
N
O
N
Cl
CH3
Cl
6t
13C NMR (126 MHz, CDCl3)
f1 (ppm)

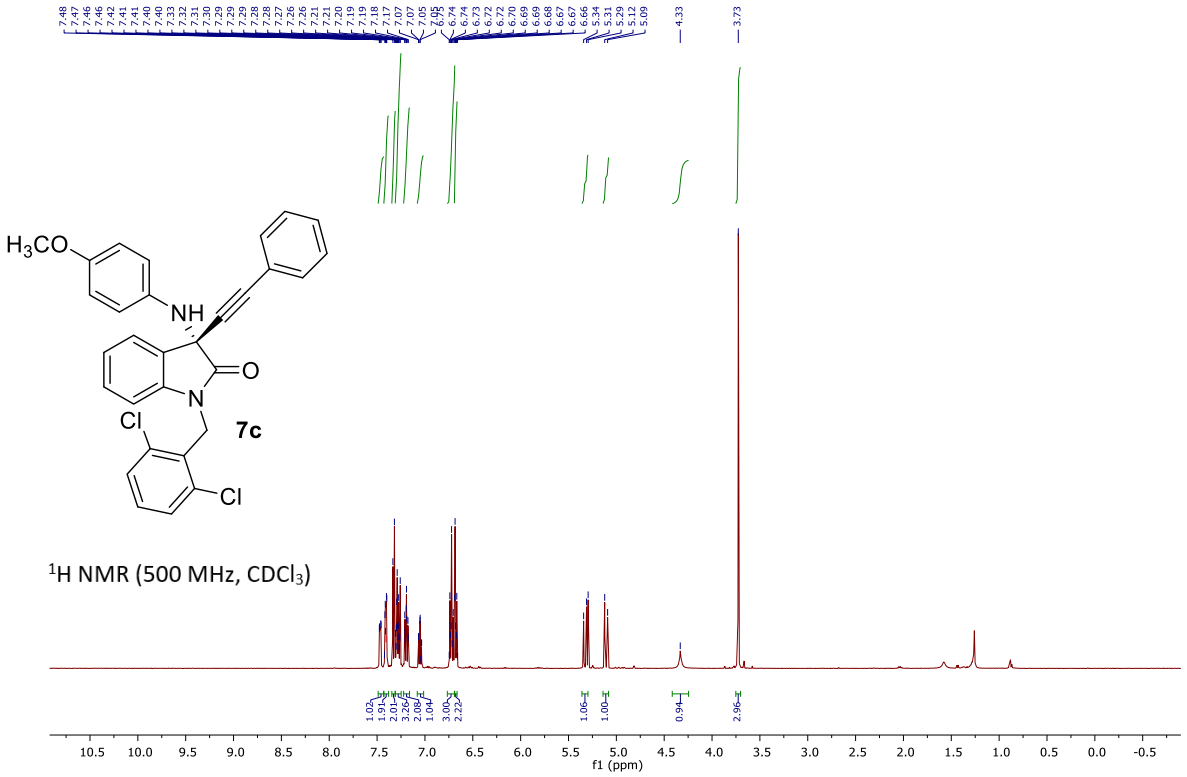

NH
O
N
Cl
Cl
7a
1H NMR (500 MHz, CDCl3)
f1 (ppm)

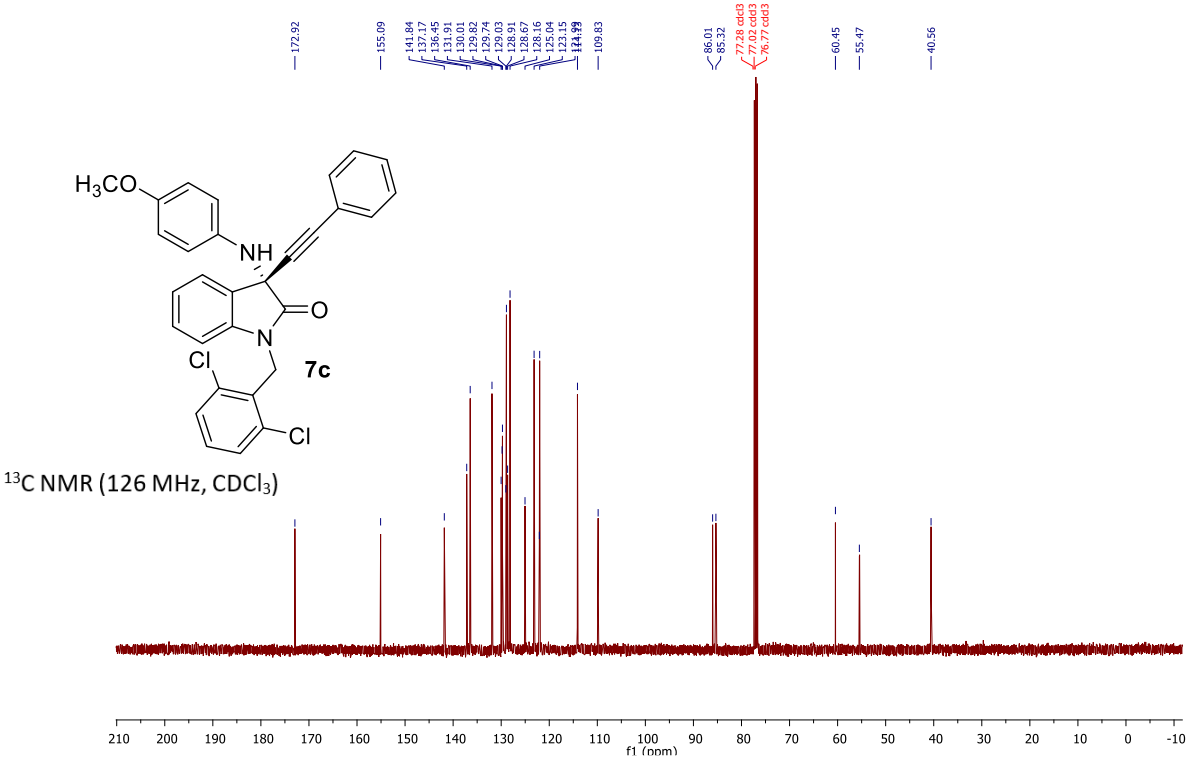

NH
O
N
Cl
Cl
7a
13C NMR (126 MHz, CDCl3)
f1 (ppm)

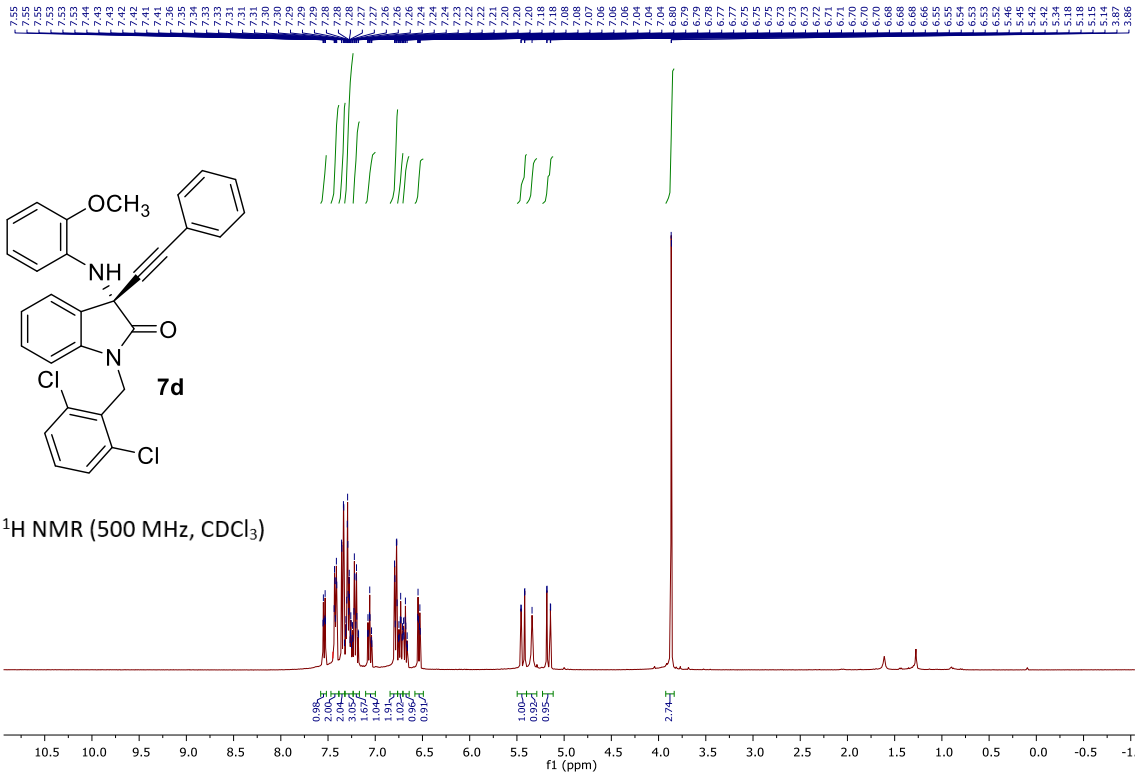

F3C
NH
O
N
Cl
Cl
7b
1H NMR (500 MHz, CDCl3)
f1 (ppm)


F3C
NH
O
N
Cl
Cl
7b
13C NMR (126 MHz, CDCl3)
f1 (ppm)

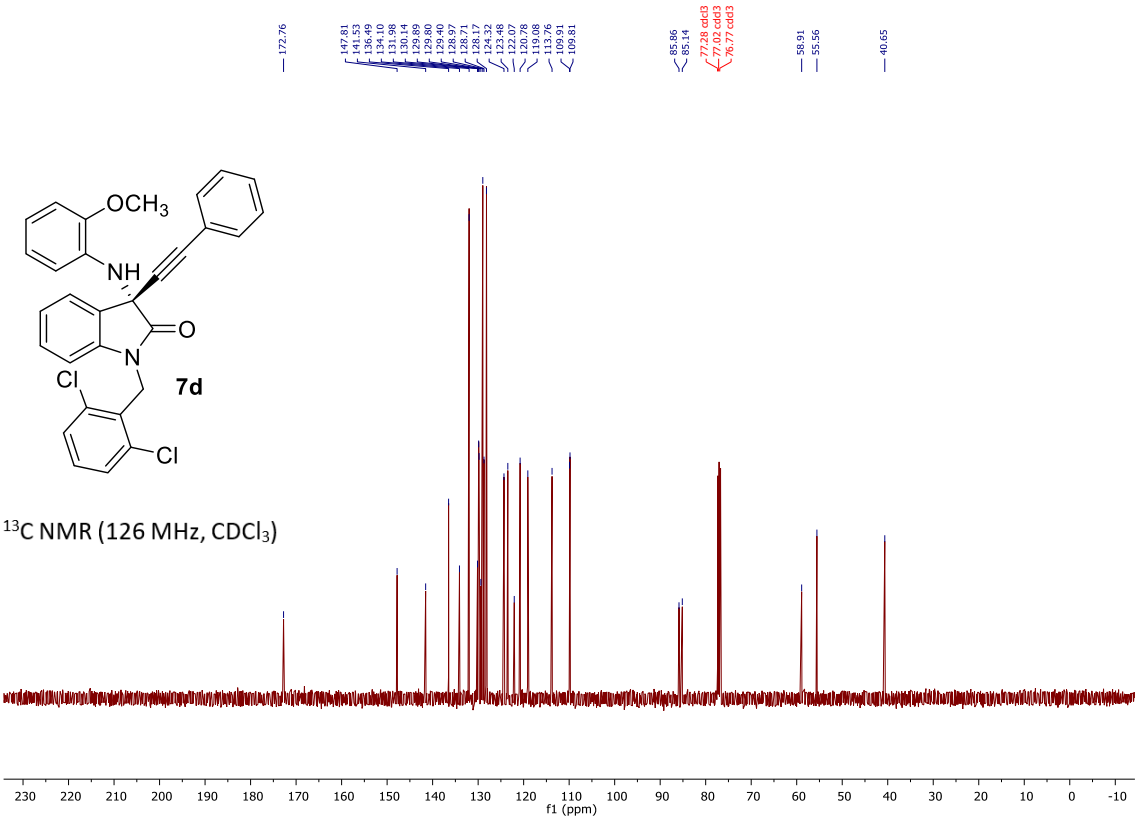

-61.47
F3C
NH
O
N
Cl
Cl
7b
19F NMR (470 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


H3CO
NH
O
N
Cl
Cl
7c
1H NMR (500 MHz, CDCl3)
f1 (ppm)

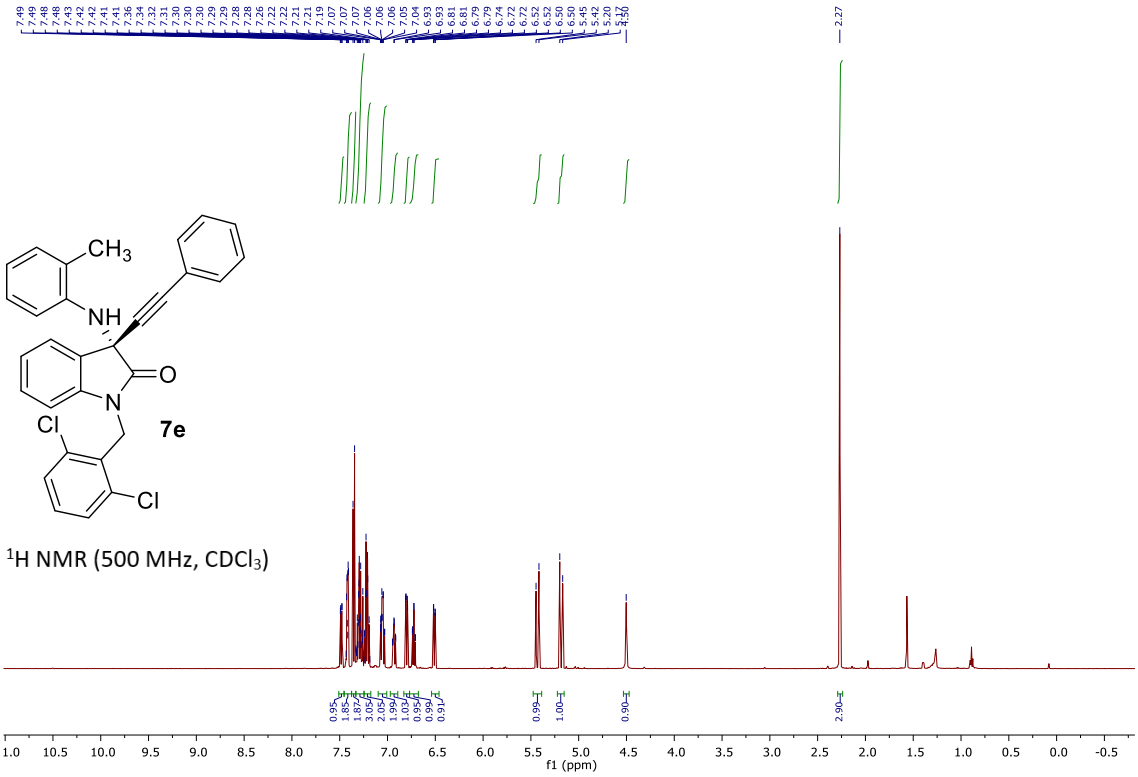

H3CO
NH
O
N
Cl
Cl
7c
13C NMR (126 MHz, CDCl3)
f1 (ppm)

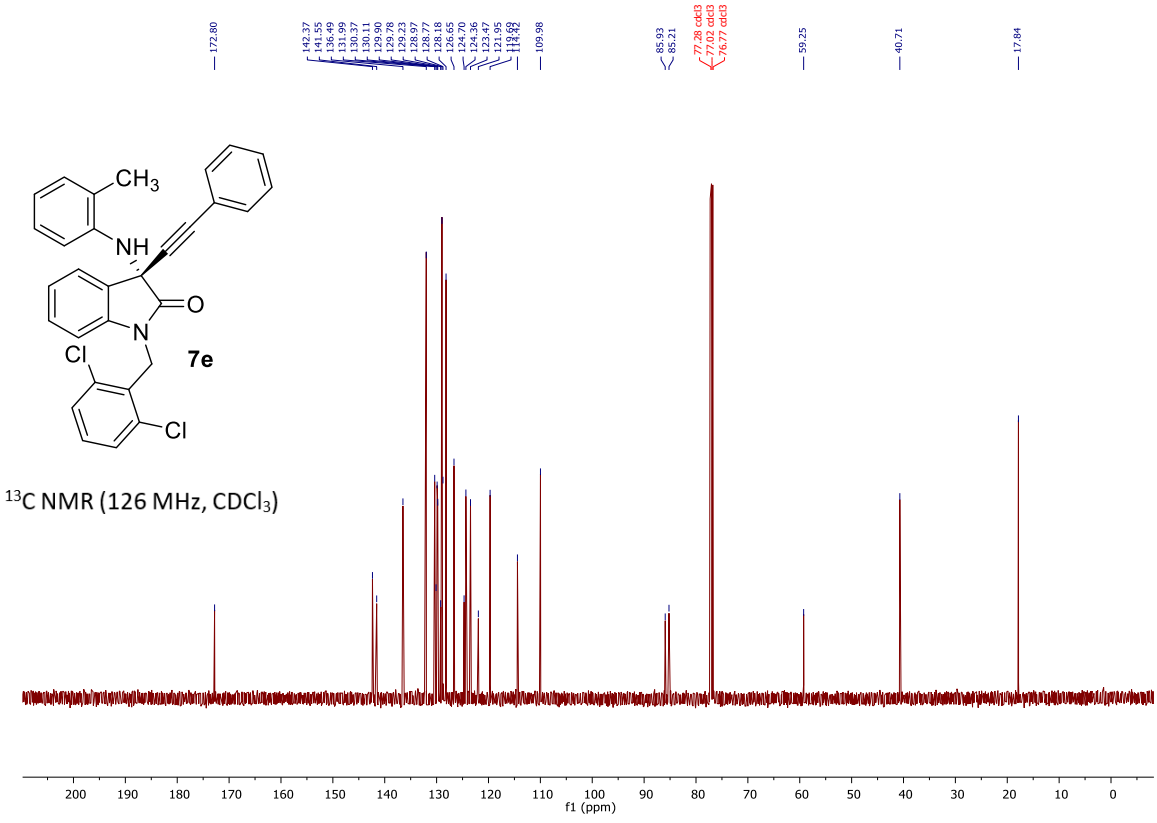


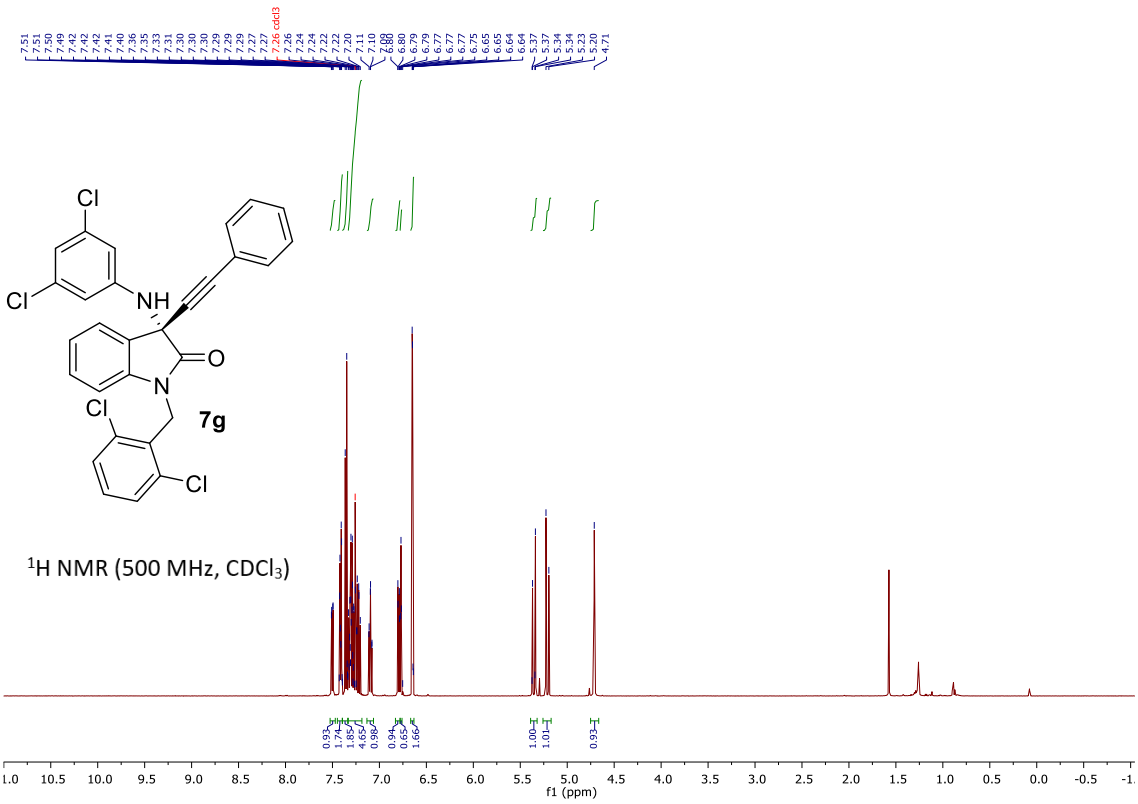
^{1}H NMR (500 MHz, $CDCl_3$)

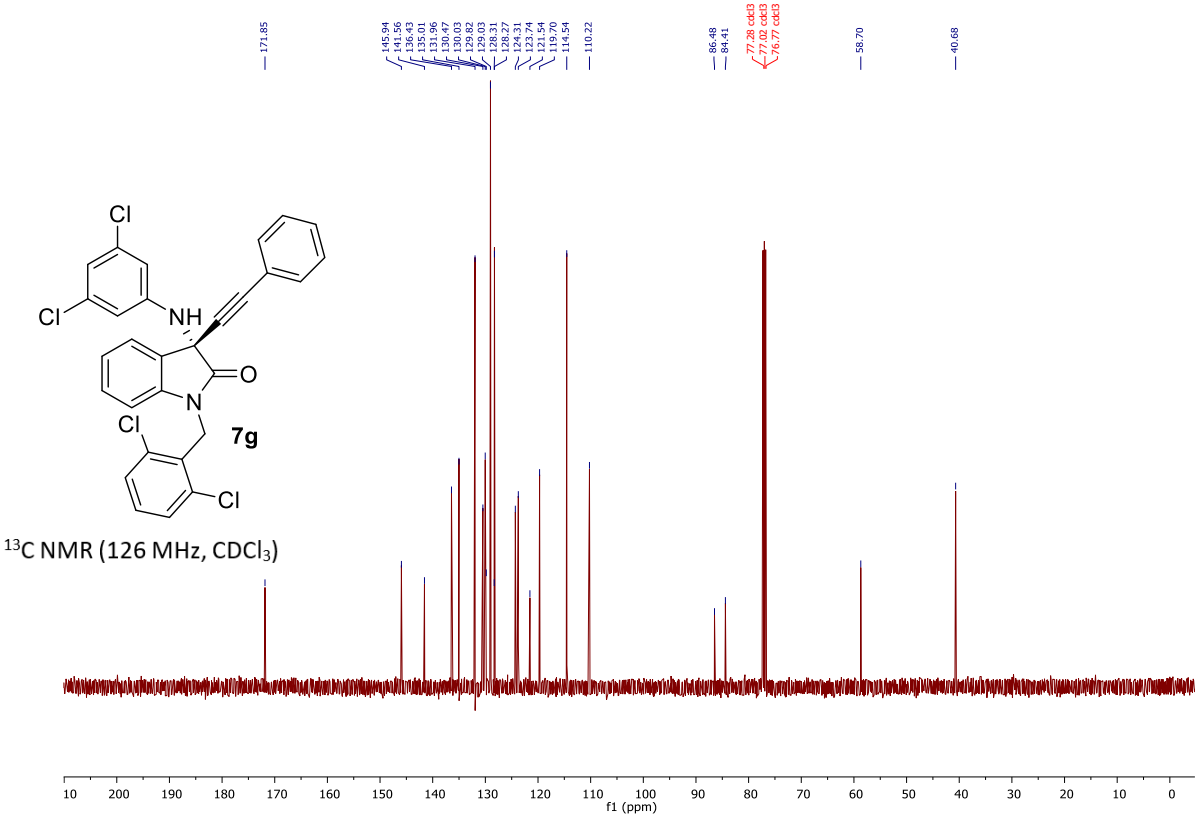


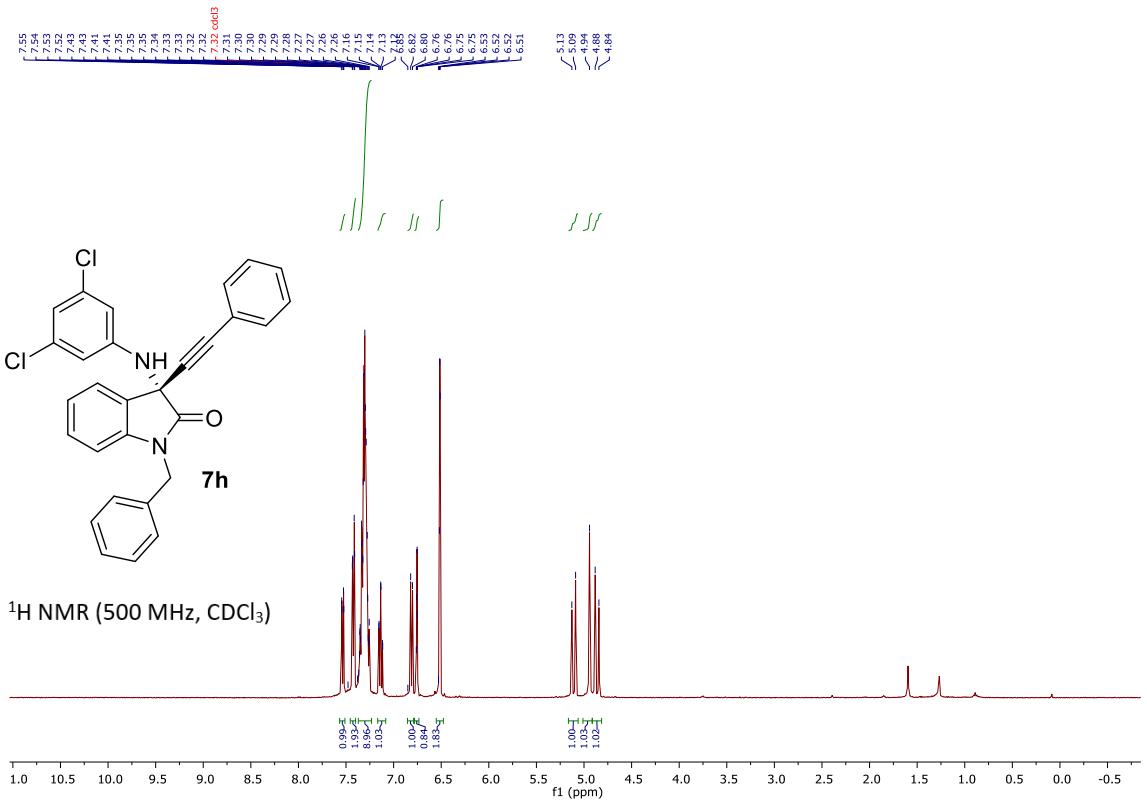
^{13}C NMR (126 MHz, $CDCl_3$)

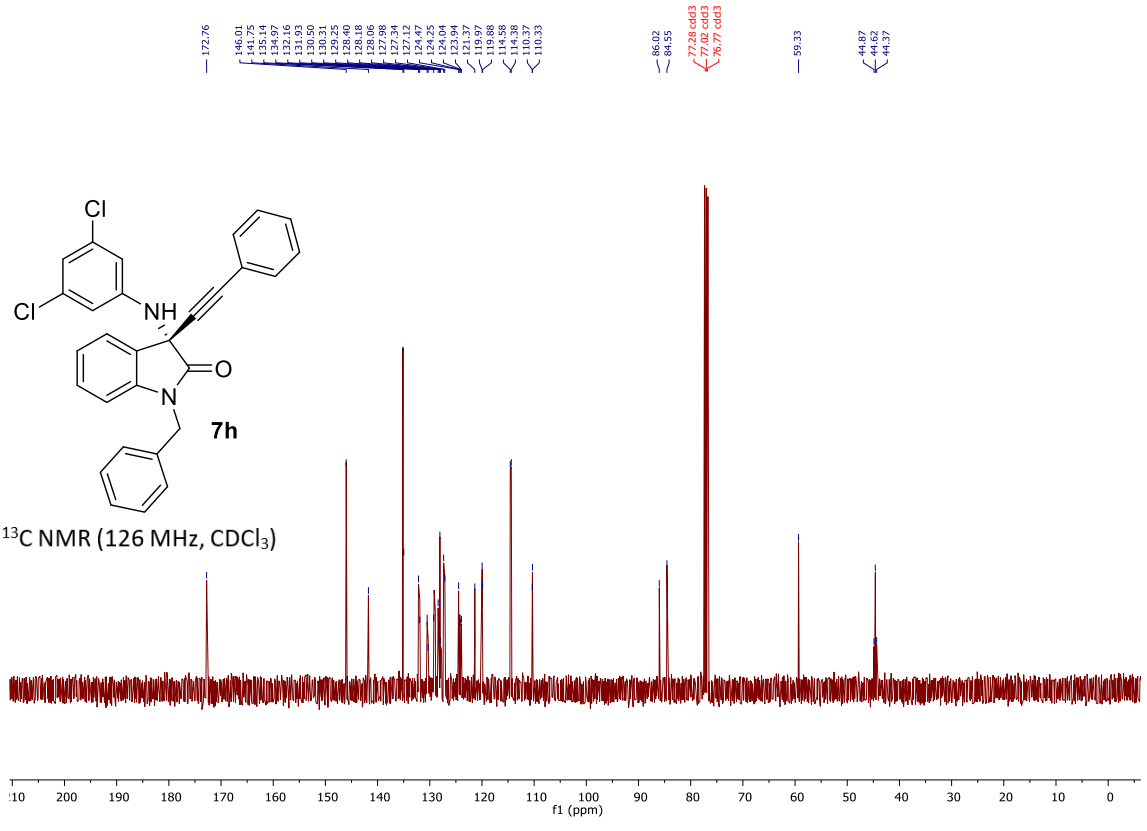

CH3
NH
O
N
Cl
Cl
7e
1H NMR (500 MHz, CDCl3)
f1 (ppm)

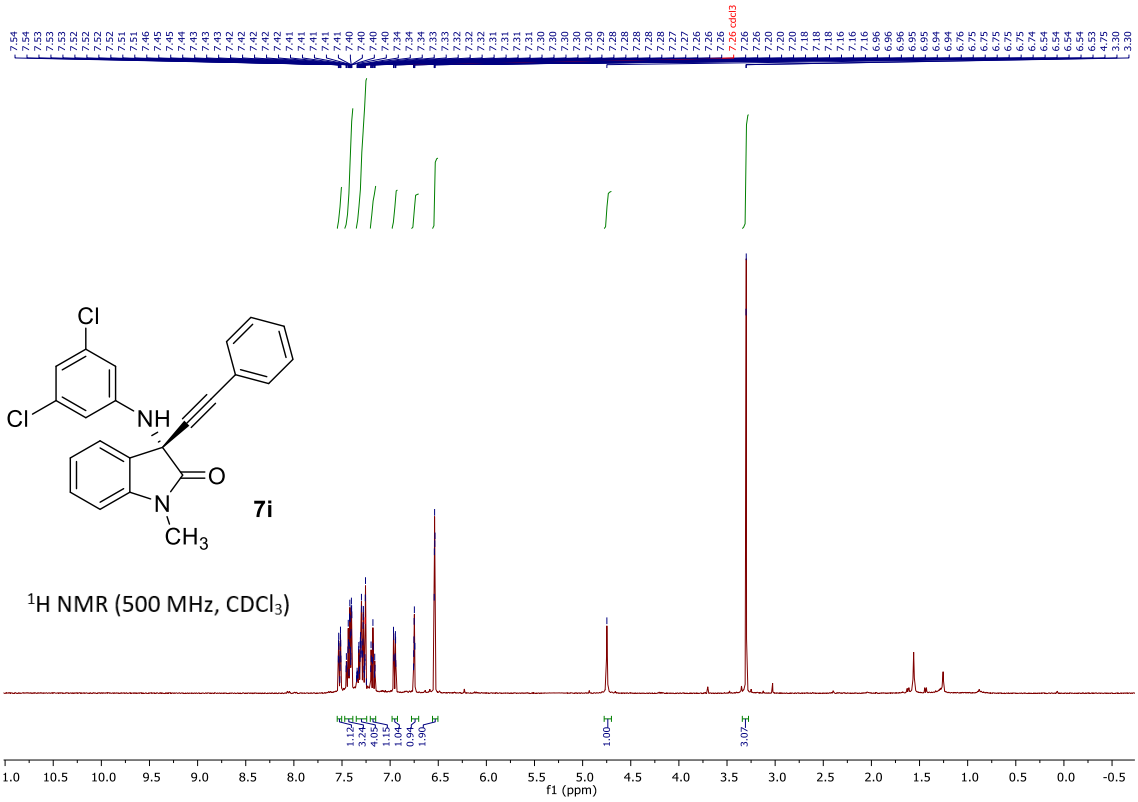

CH3
NH
O
N
Cl
Cl
7e
13C NMR (126 MHz, CDCl3)
f1 (ppm)

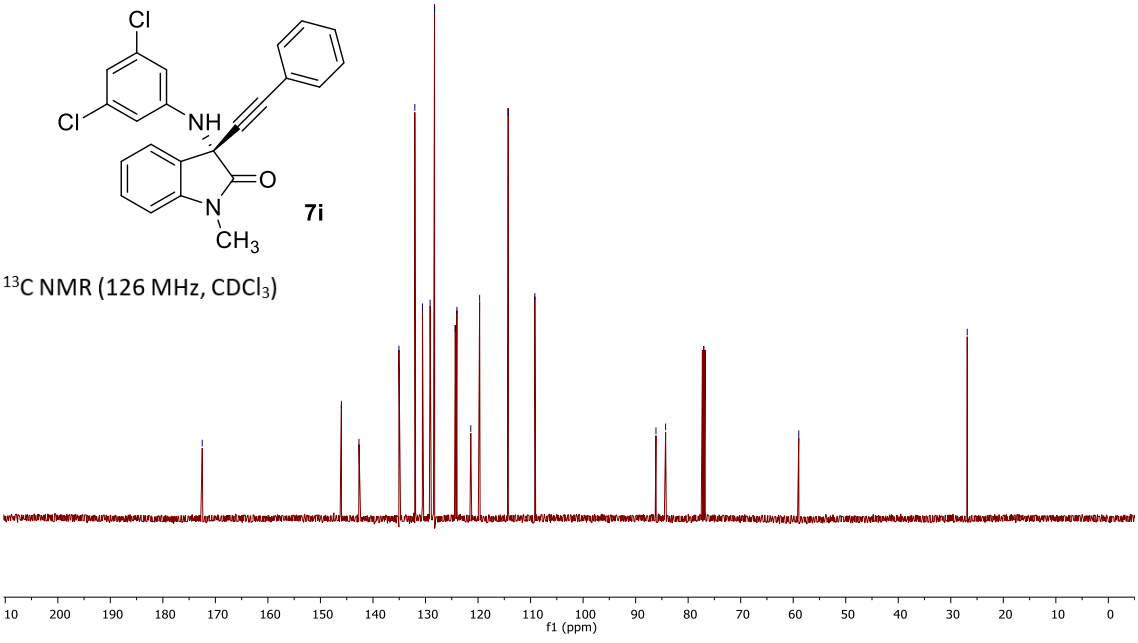

Cl
Cl
NH
O
N
Cl
Cl
7g
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

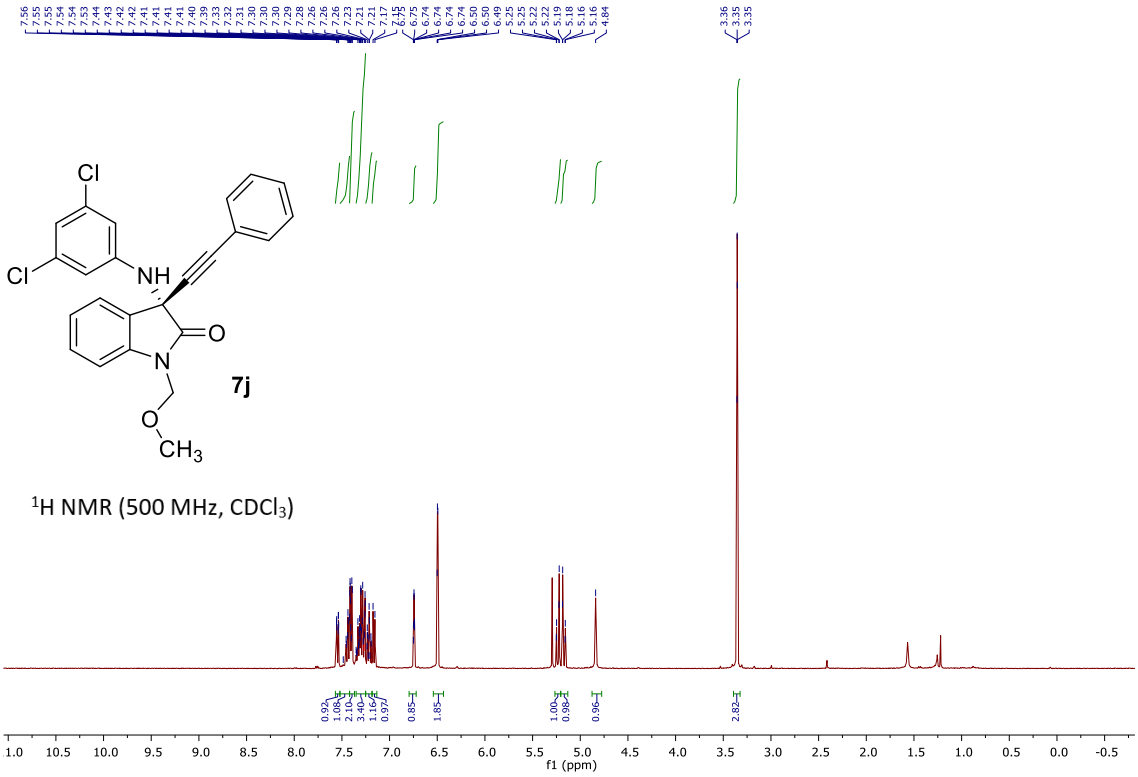

Cl
Cl
NH
O
N
Cl
Cl
7g
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

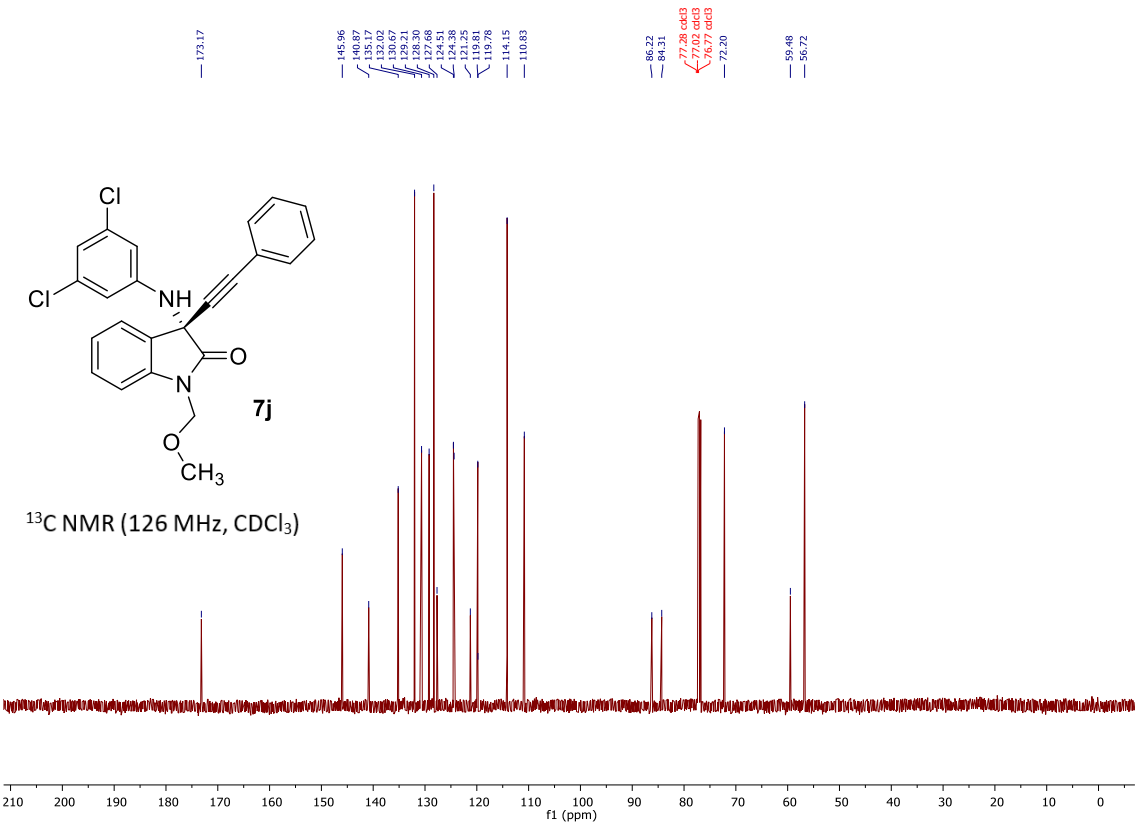

Cl
Cl
NH
O
N
7h
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)

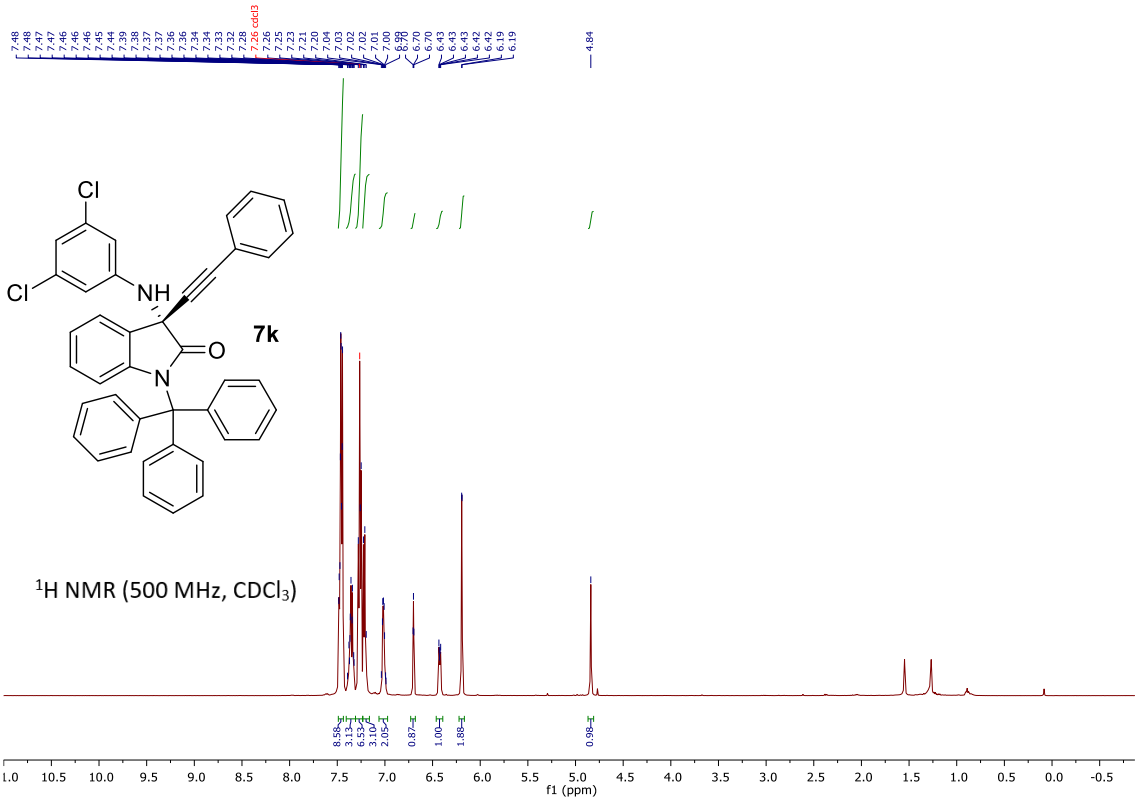

Cl
Cl
NH
O
N
7h
^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)

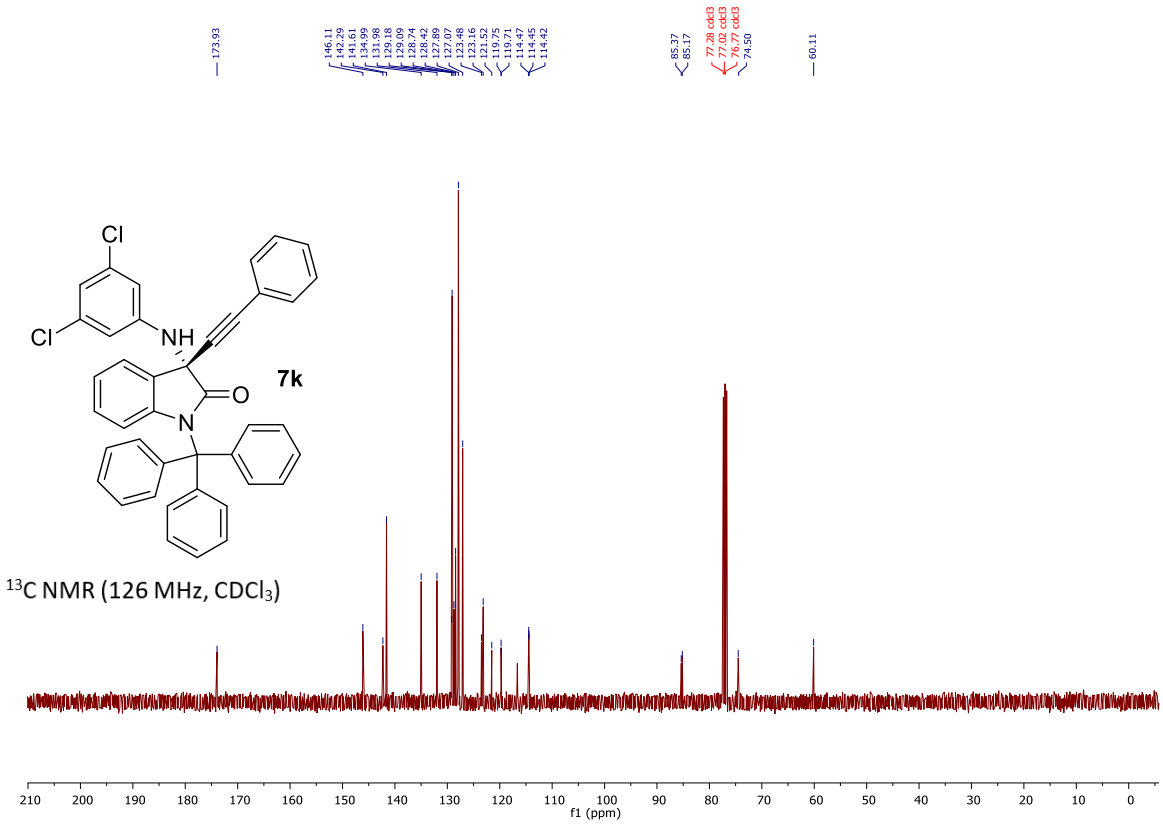

Cl
Cl
NH
O
N
CH3
7i
1H NMR (500 MHz, CDCl3)
f1 (ppm)

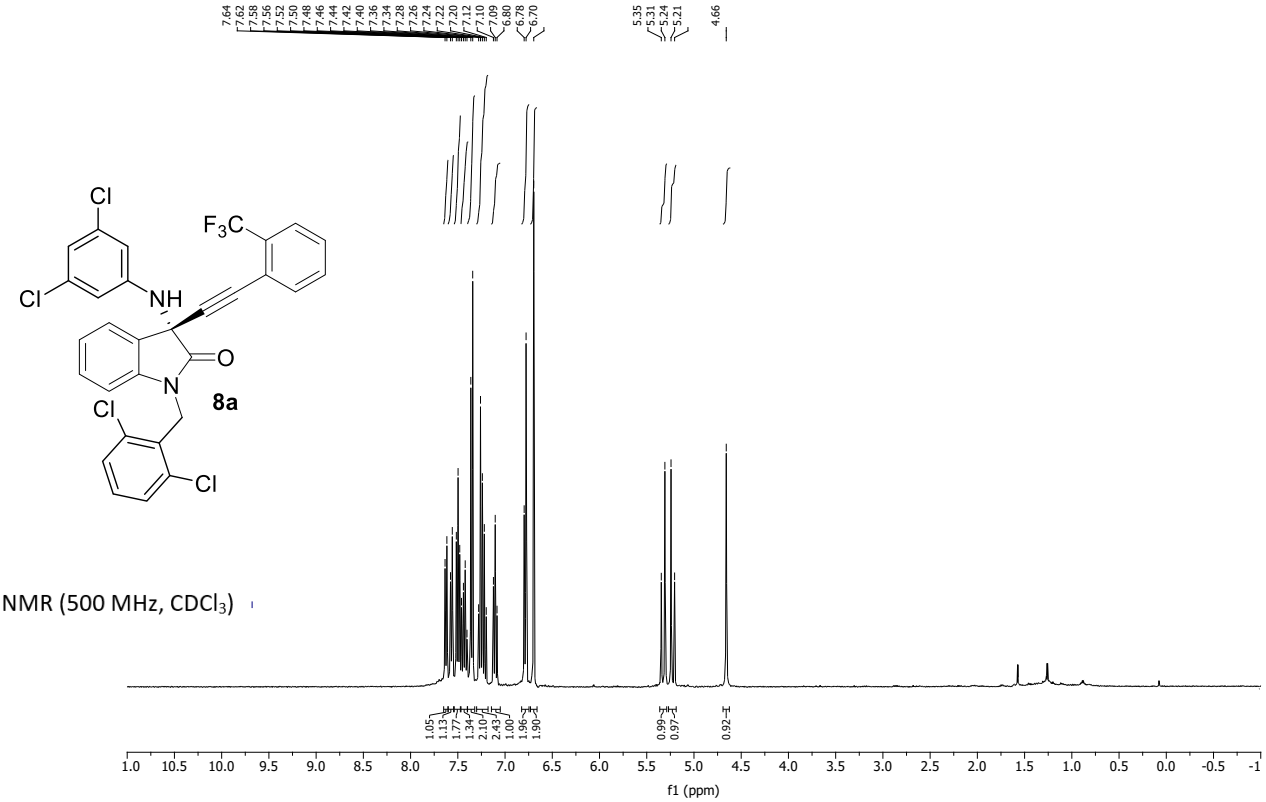

Cl
Cl
NH
O
N
CH3
7i
13C NMR (126 MHz, CDCl3)
f1 (ppm)


Cl
Cl
NH
O
N
O
CH3
7j
1H NMR (500 MHz, CDCl3)
f1 (ppm)

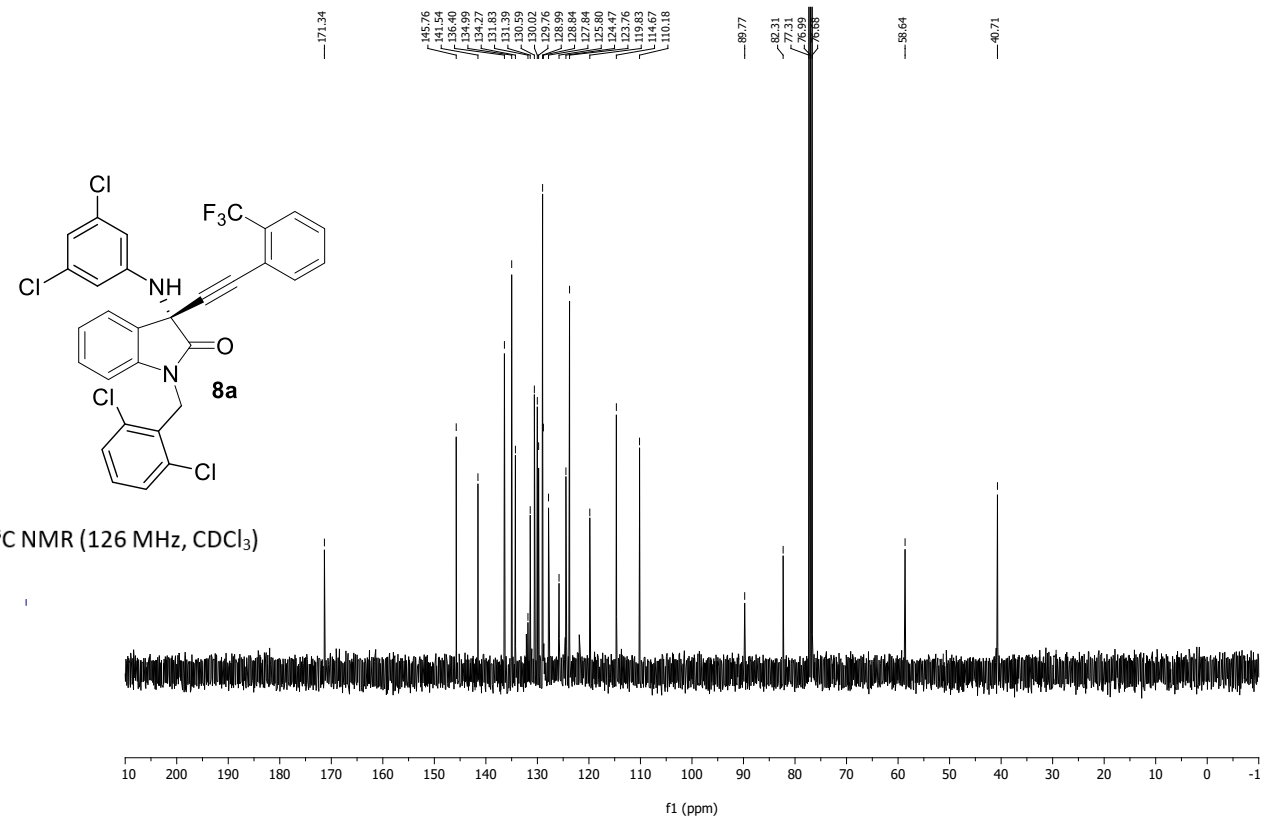

Cl
Cl
NH
O
N
O
CH3
7j
13C NMR (126 MHz, CDCl3)
f1 (ppm)


Cl
Cl
NH
O
N
7k
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

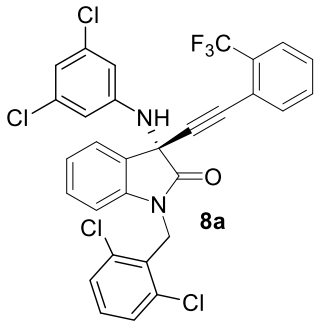

Cl
Cl
NH
O
N
7k
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)



^{1}H NMR (500 MHz, $CDCl_3$)

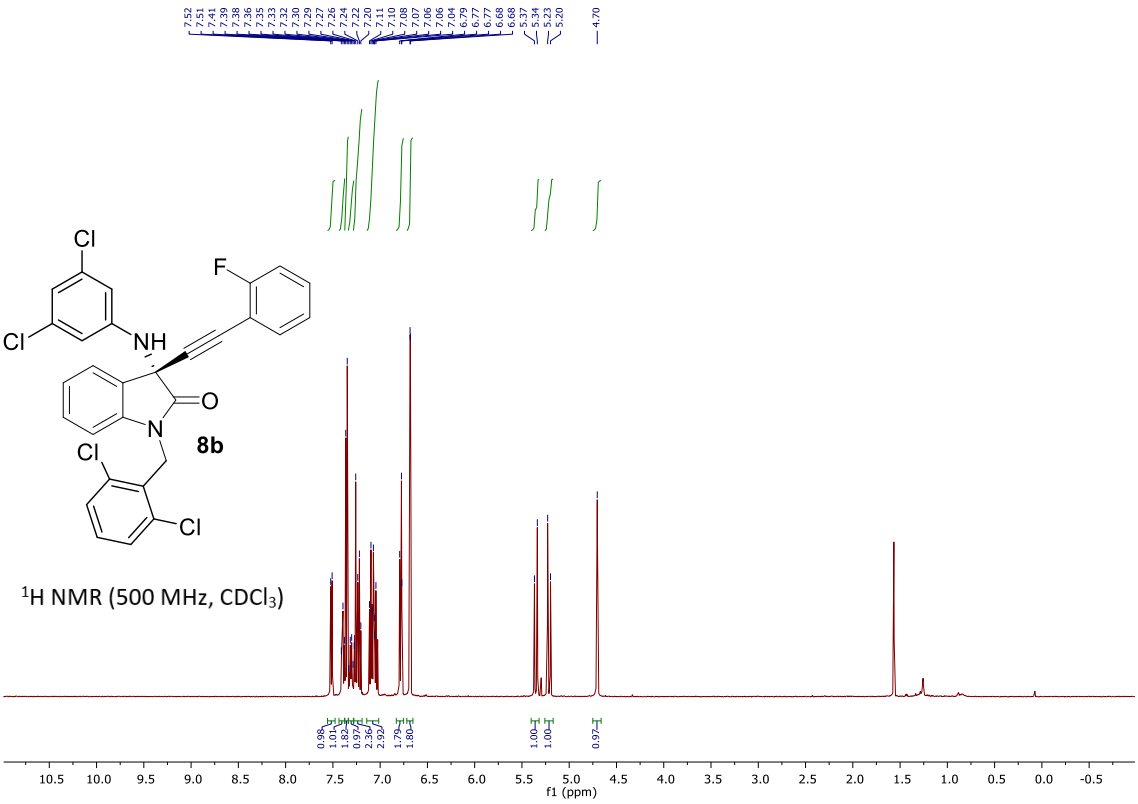


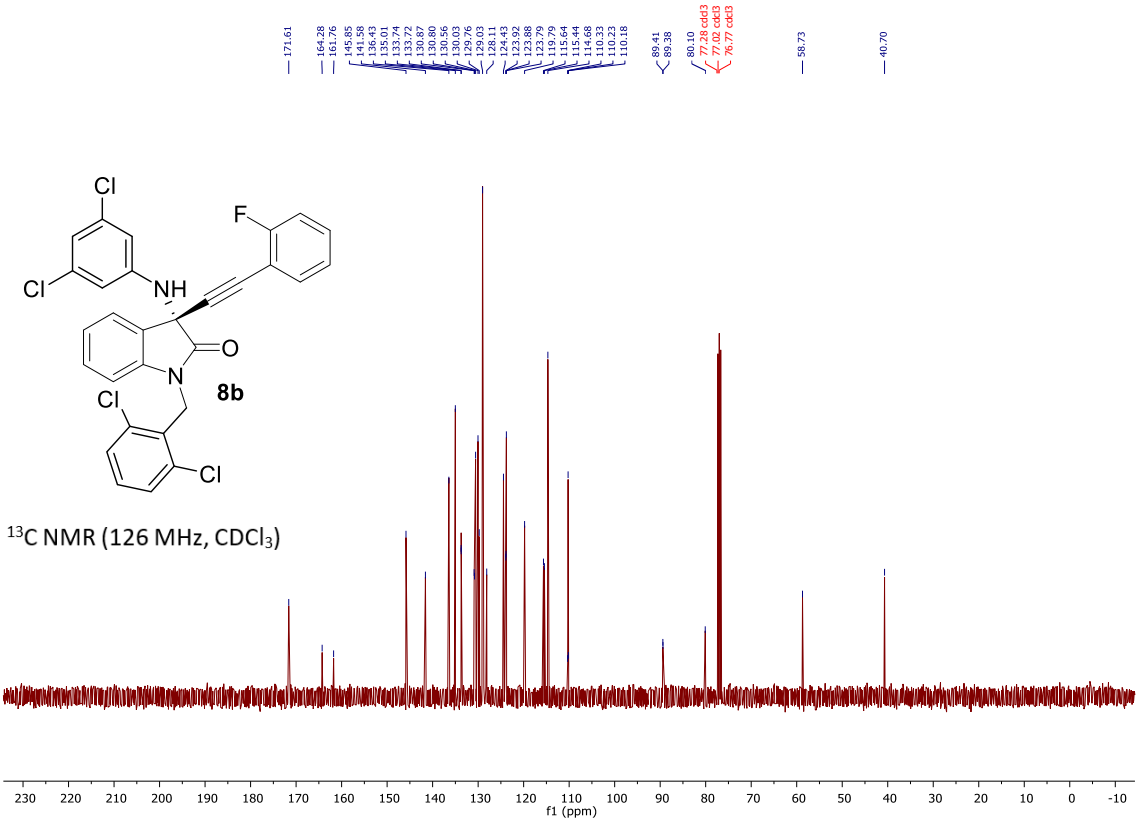
^{13}C NMR (126 MHz, $CDCl_3$)

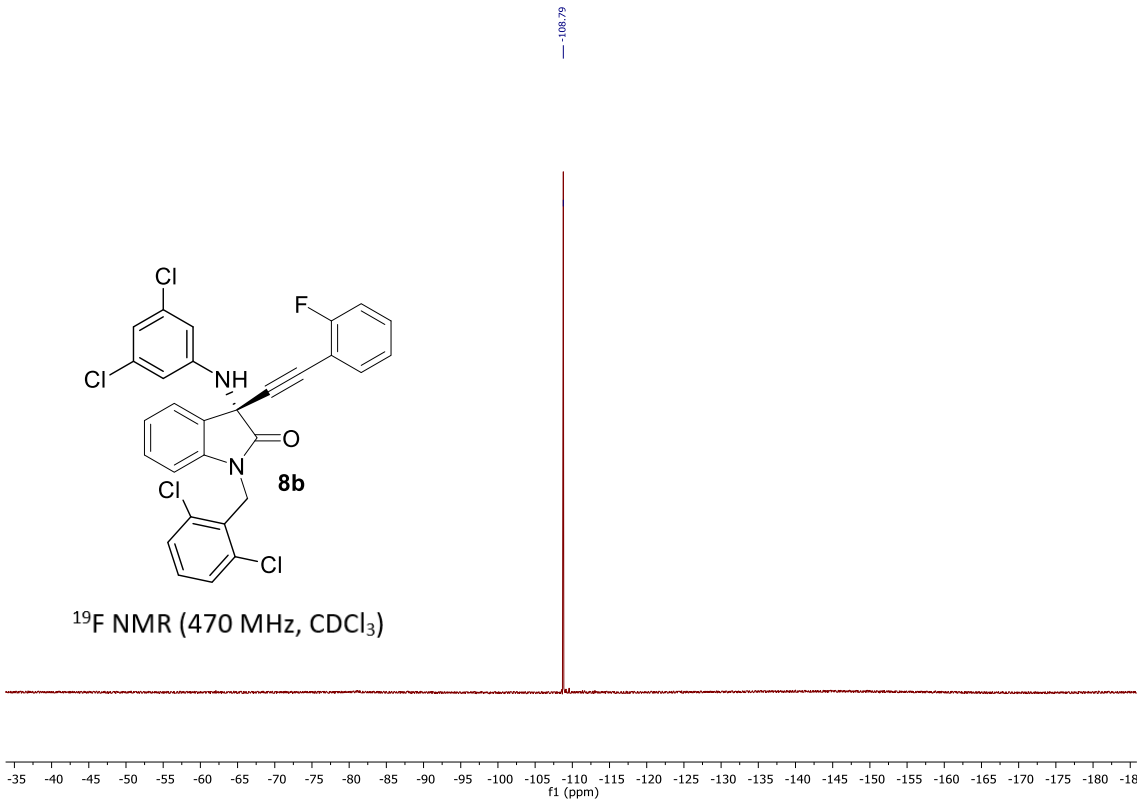


8a

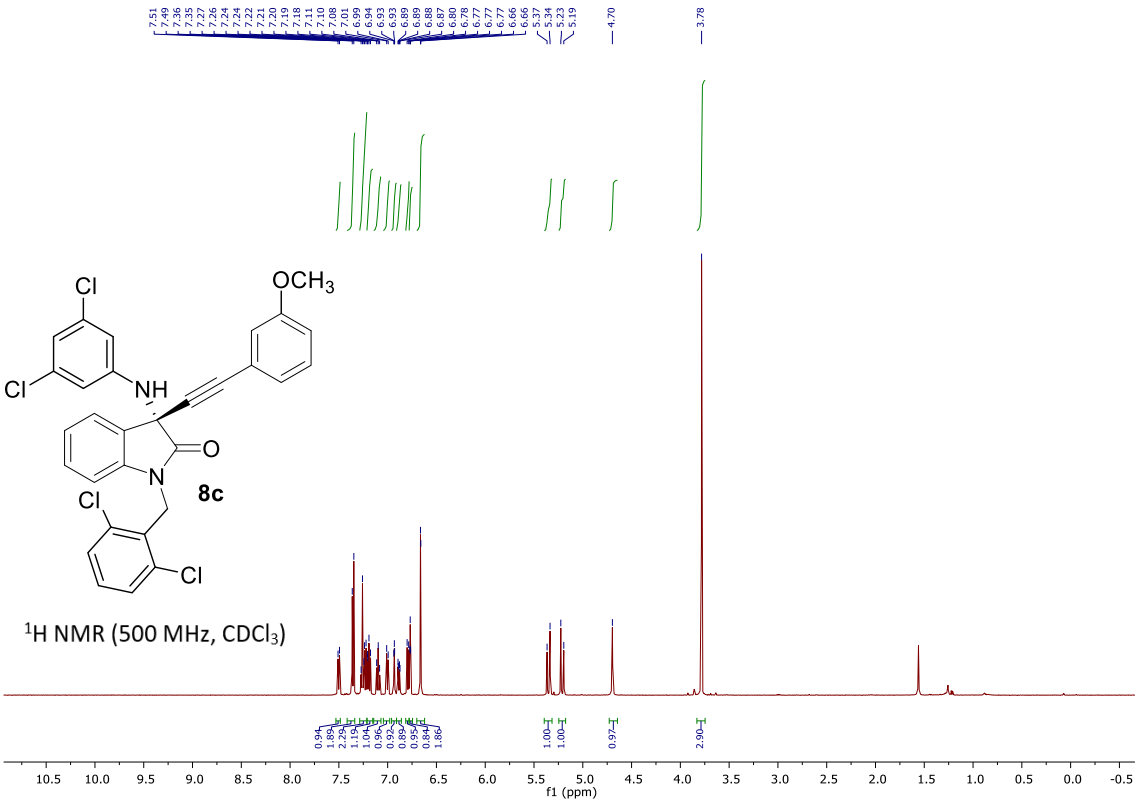
^{19}F NMR (470 MHz, $CDCl_3$)

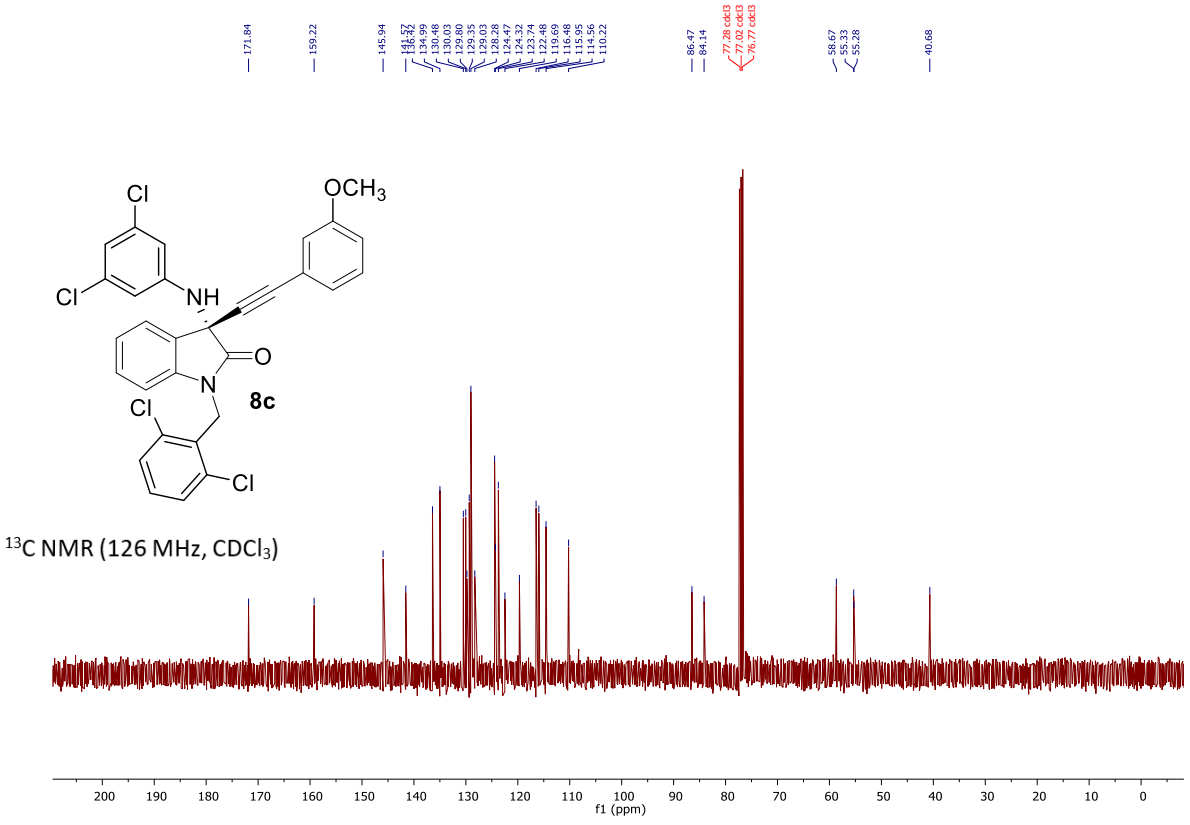

Cl
F
Cl
NH
O
N
8b
Cl
Cl
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

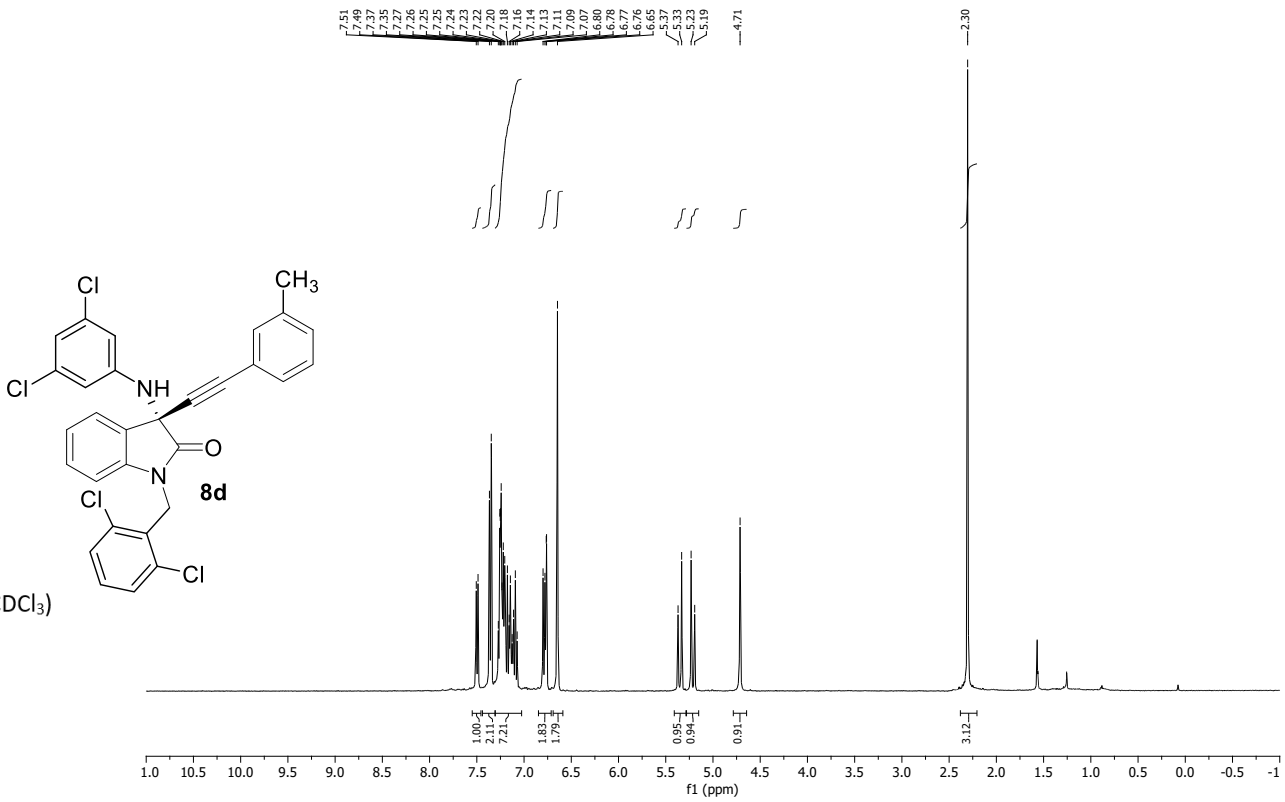

Cl
F
Cl
NH
O
N
8b
Cl
Cl
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)



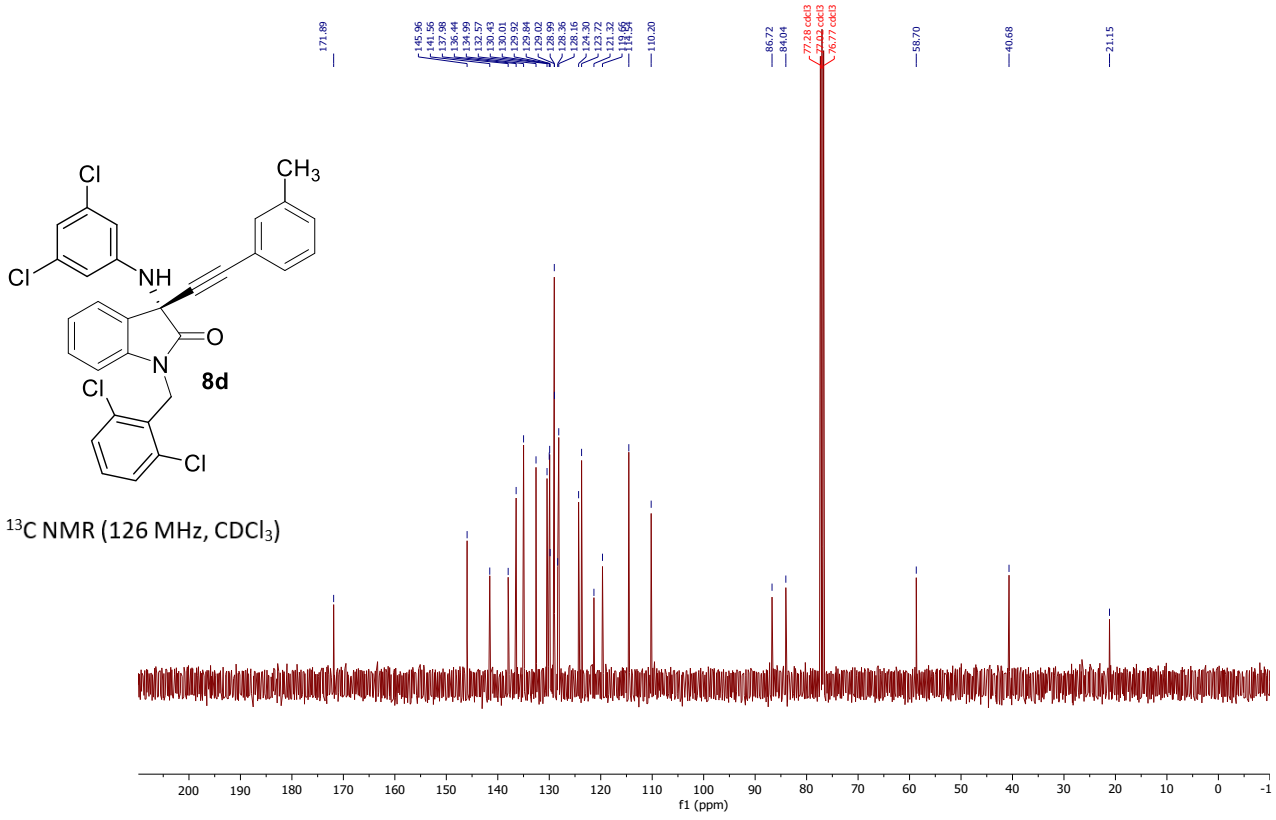
^{19}F NMR (470 MHz, $CDCl_3$)


Cl
OCH3
Cl
NH
O
N
Cl
Cl
8c
1H NMR (500 MHz, CDCl3)
f1 (ppm)

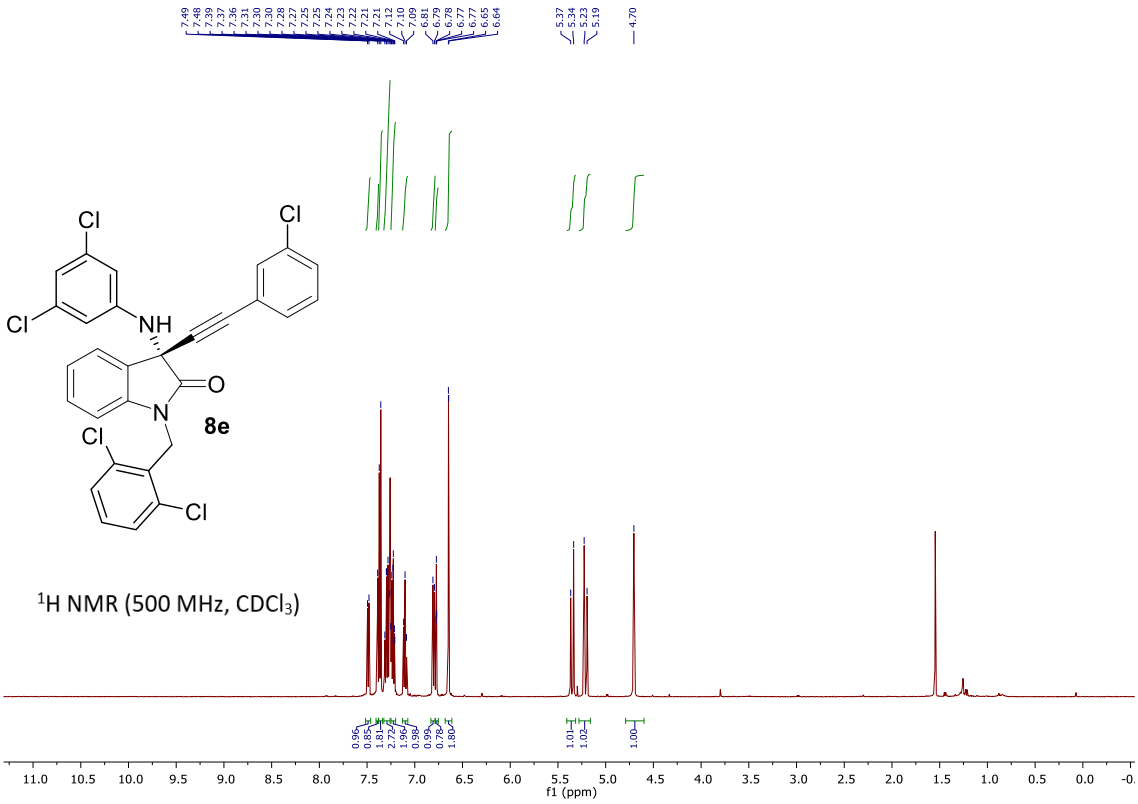

Cl
OCH3
Cl
NH
O
N
Cl
Cl
8c
13C NMR (126 MHz, CDCl3)
f1 (ppm)



) MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)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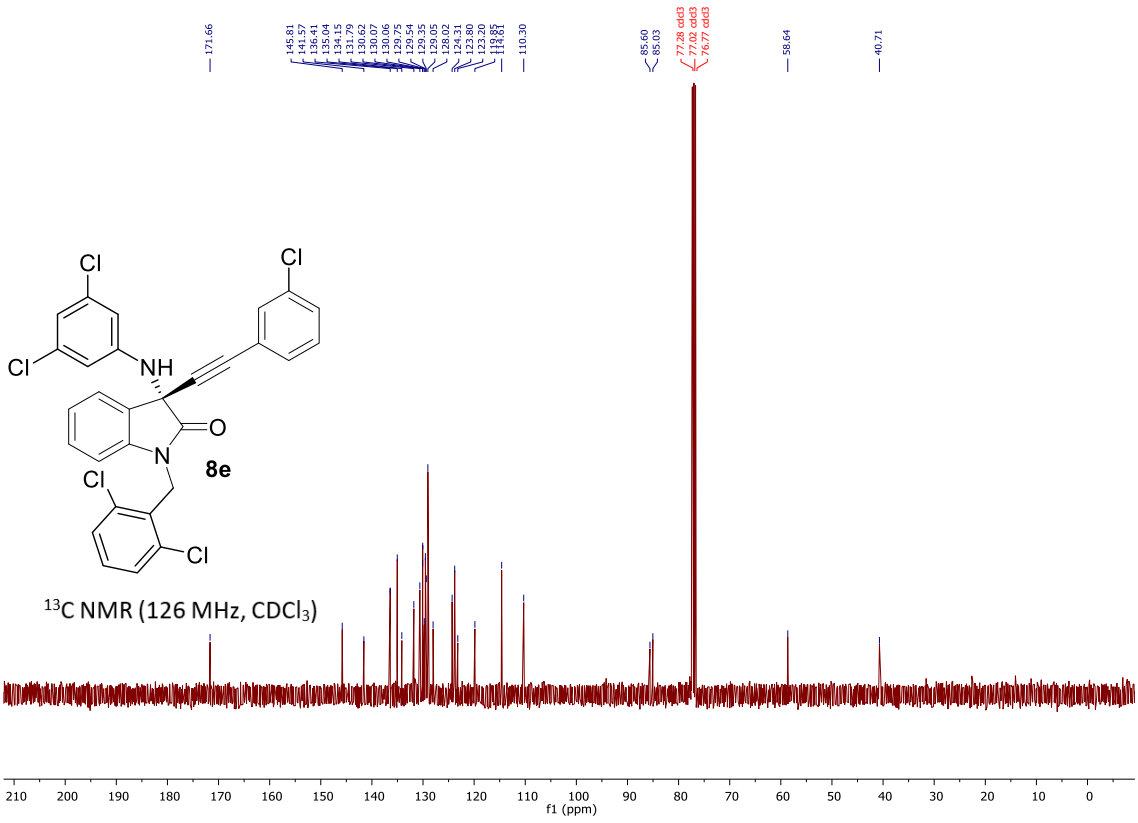
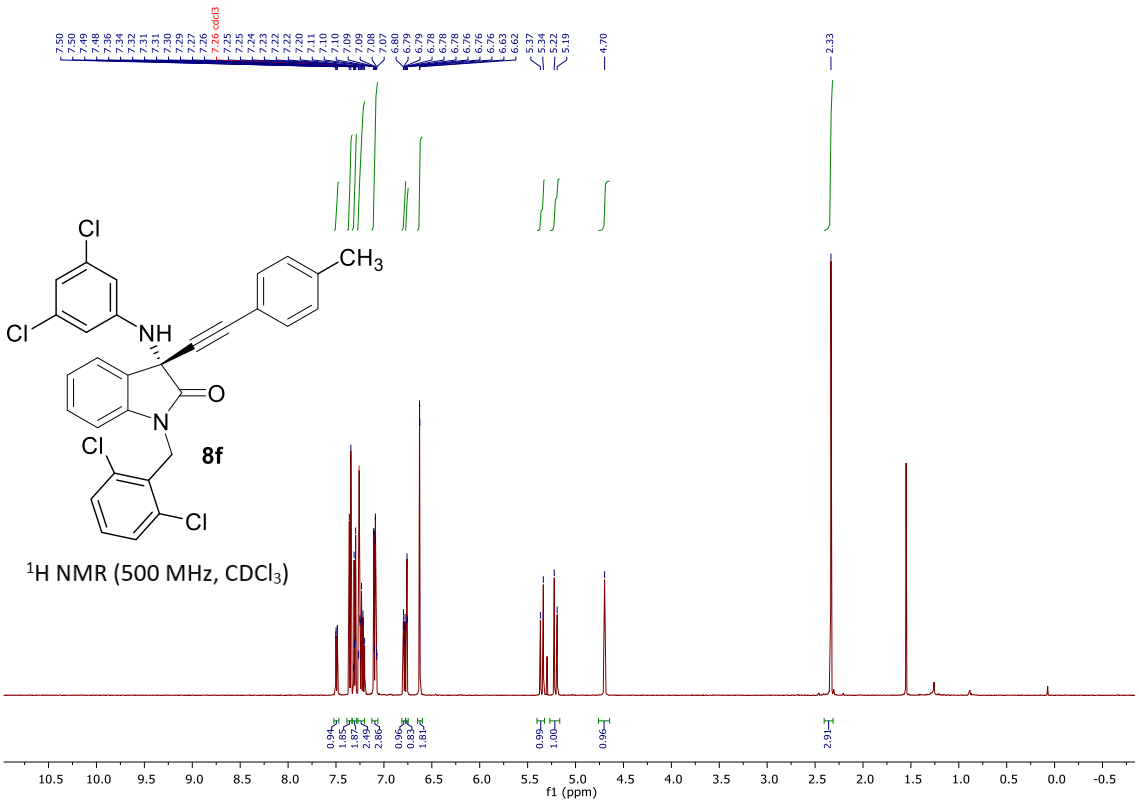
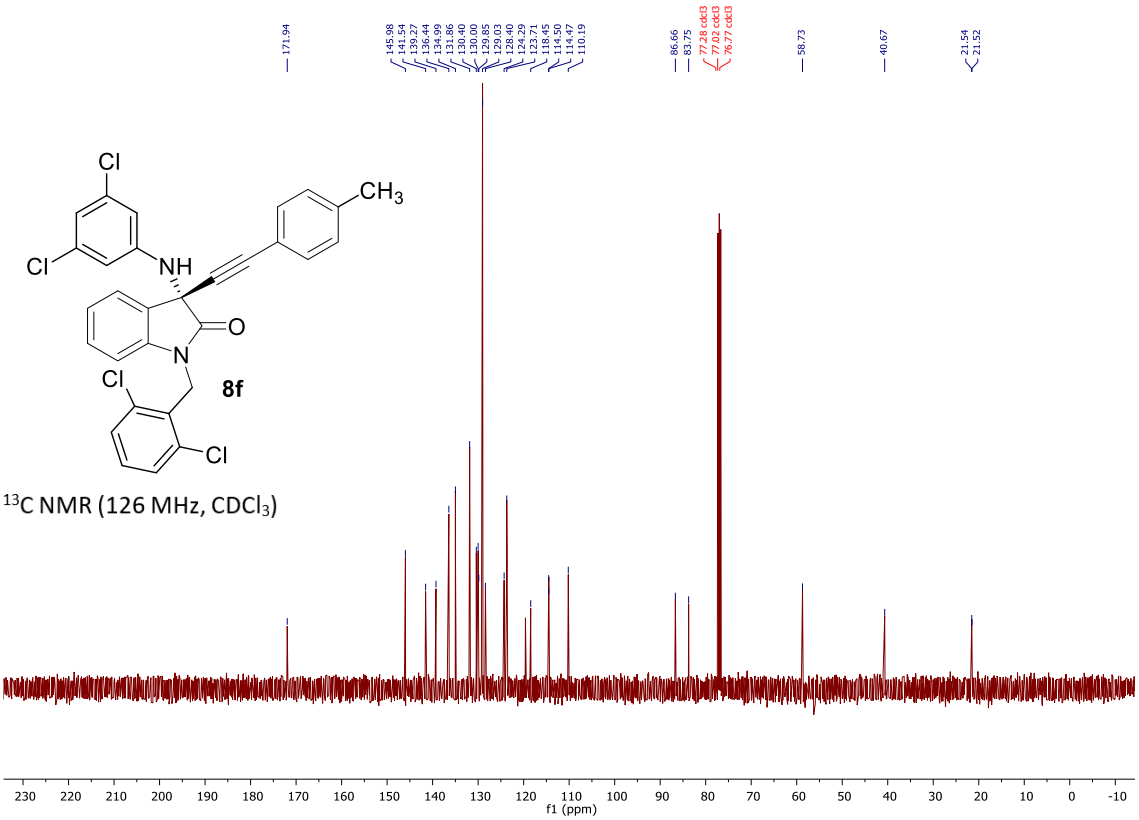
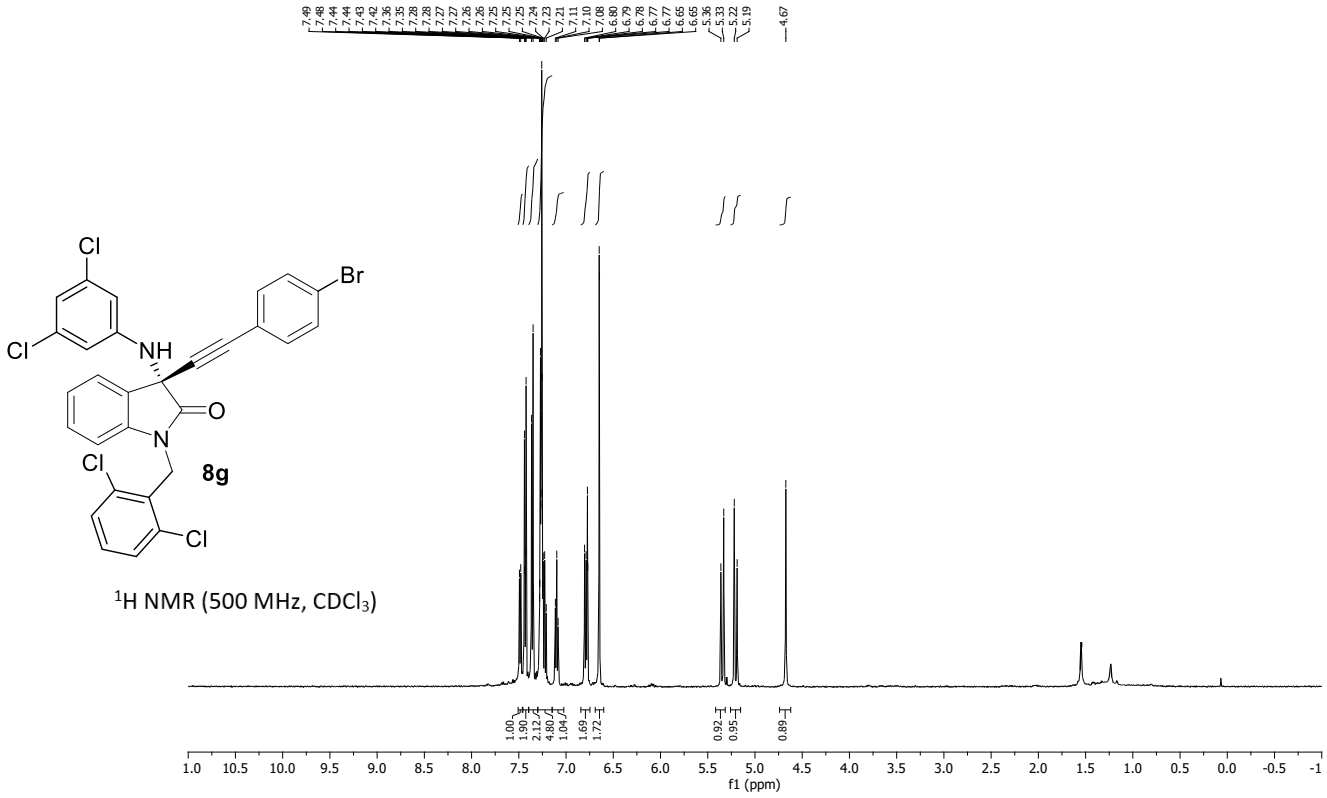
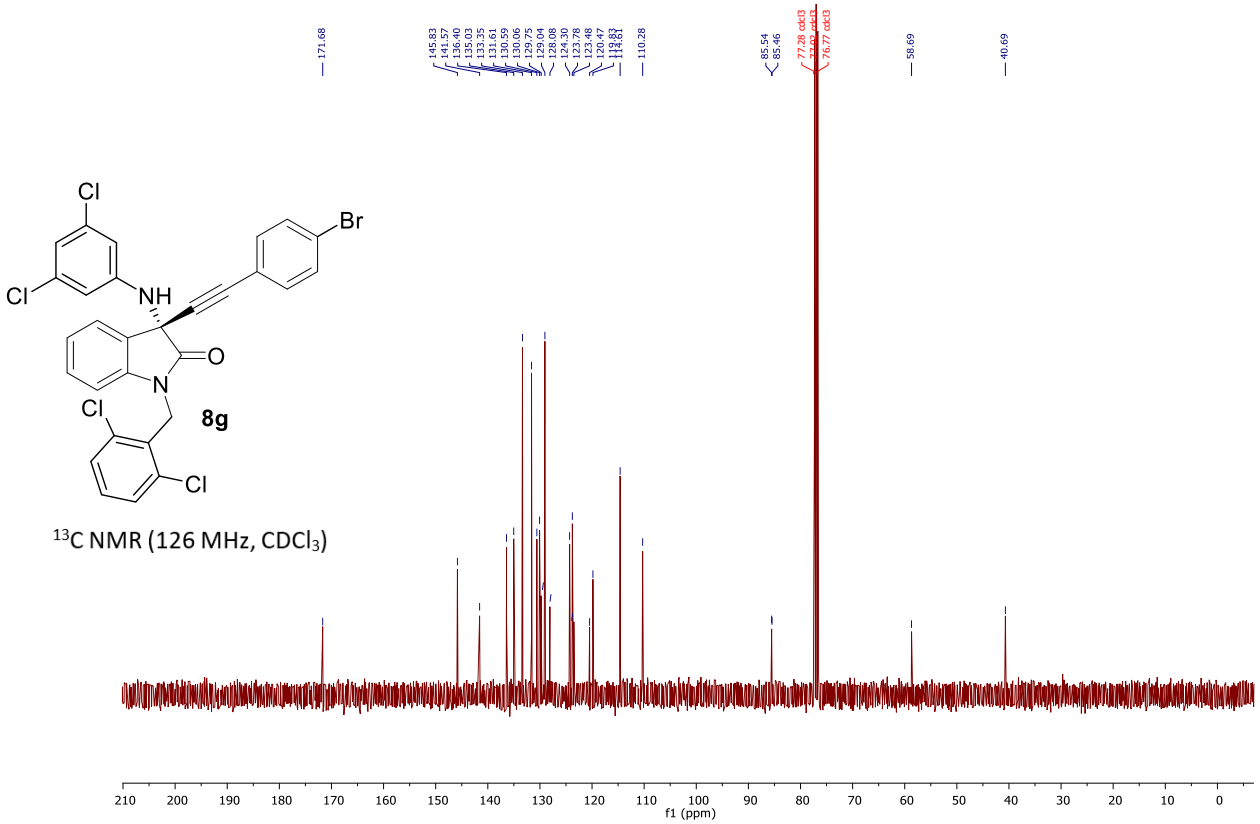
Cl
Cl
NH
O
N
Cl
Cl
8e
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

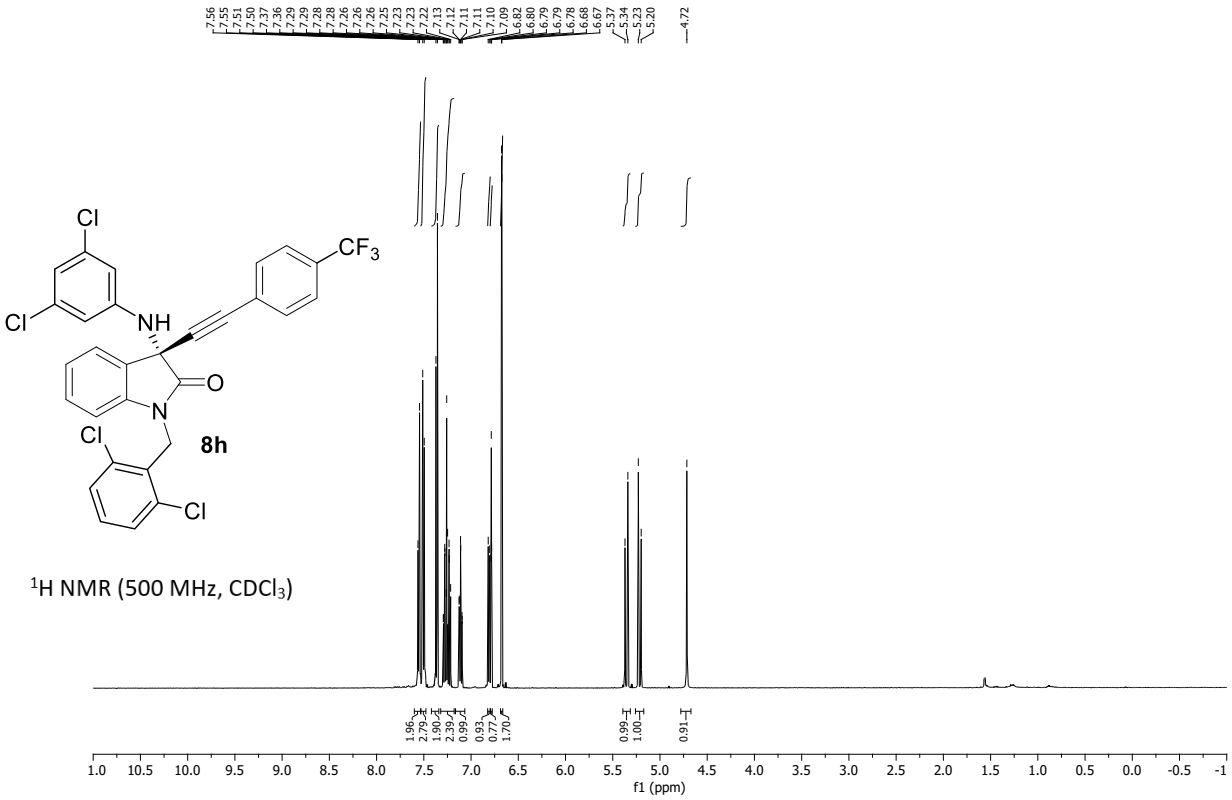

Cl
Cl
Cl
NH
O
N
Cl
Cl
8e
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

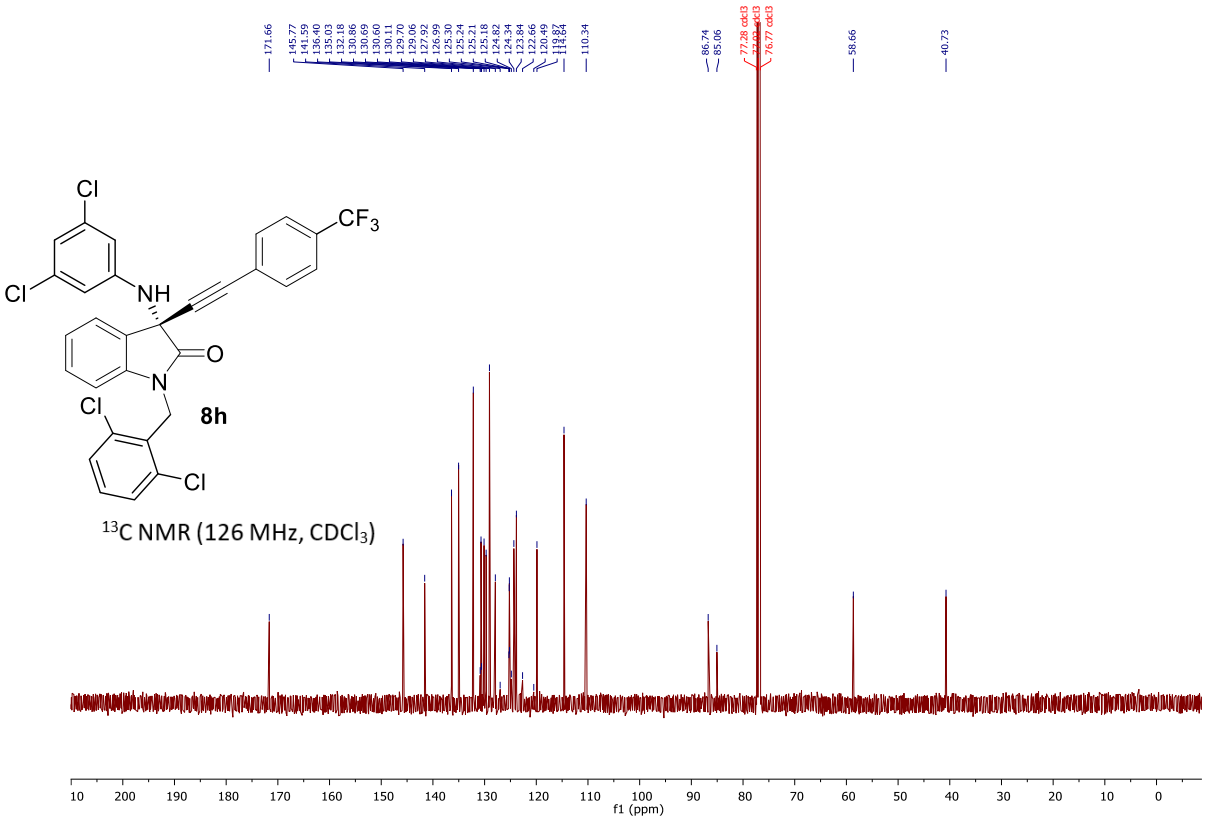

Cl
Cl
NH
CH3
O
N
Cl
Cl
8f
1H NMR (500 MHz, CDCl3)
f1 (ppm)

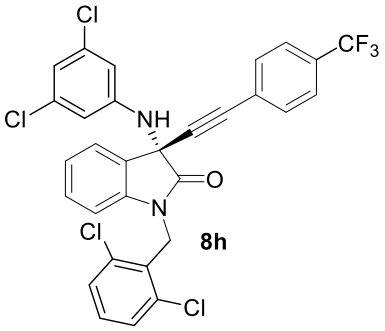

Cl
Cl
NH
CH3
O
N
Cl
Cl
8f
13C NMR (126 MHz, CDCl3)
f1 (ppm)


Cl
Br
Cl
NH
O
N
Cl
Cl
8g
1H NMR (500 MHz, CDCl3)
f1 (ppm)


Cl
Br
Cl
NH
O
N
Cl
Cl
8g
13C NMR (126 MHz, CDCl3)
f1 (ppm)

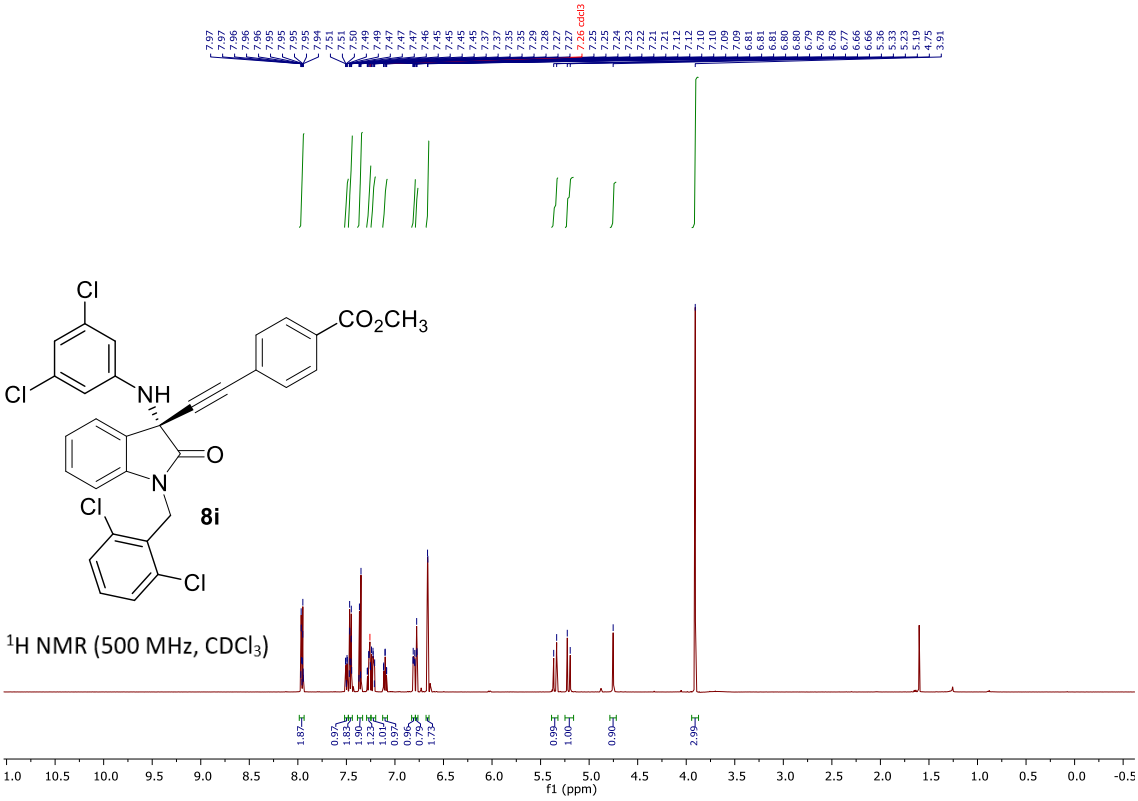

Cl
Cl
NH
CF3
O
N
Cl
Cl
8h
1H NMR (500 MHz, CDCl3)
f1 (ppm)

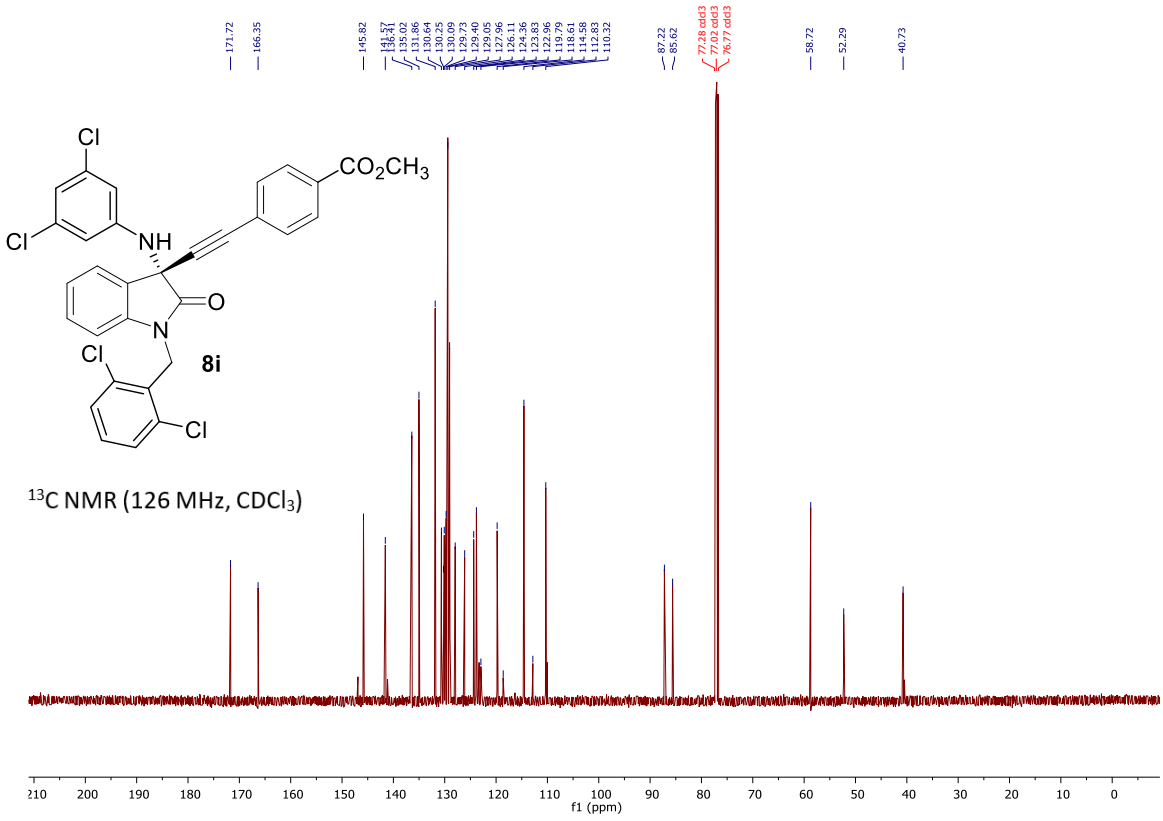

Cl
Cl
NH
CF3
O
N
Cl
Cl
8h
13C NMR (126 MHz, CDCl3)
f1 (ppm)

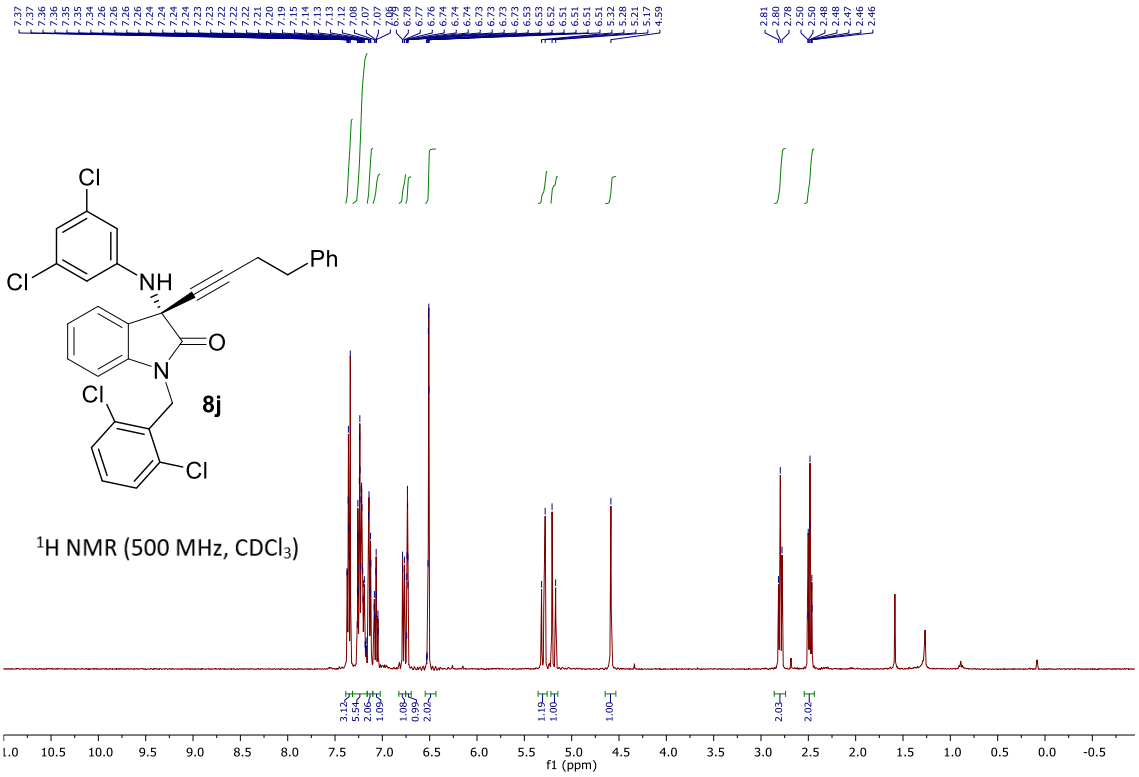


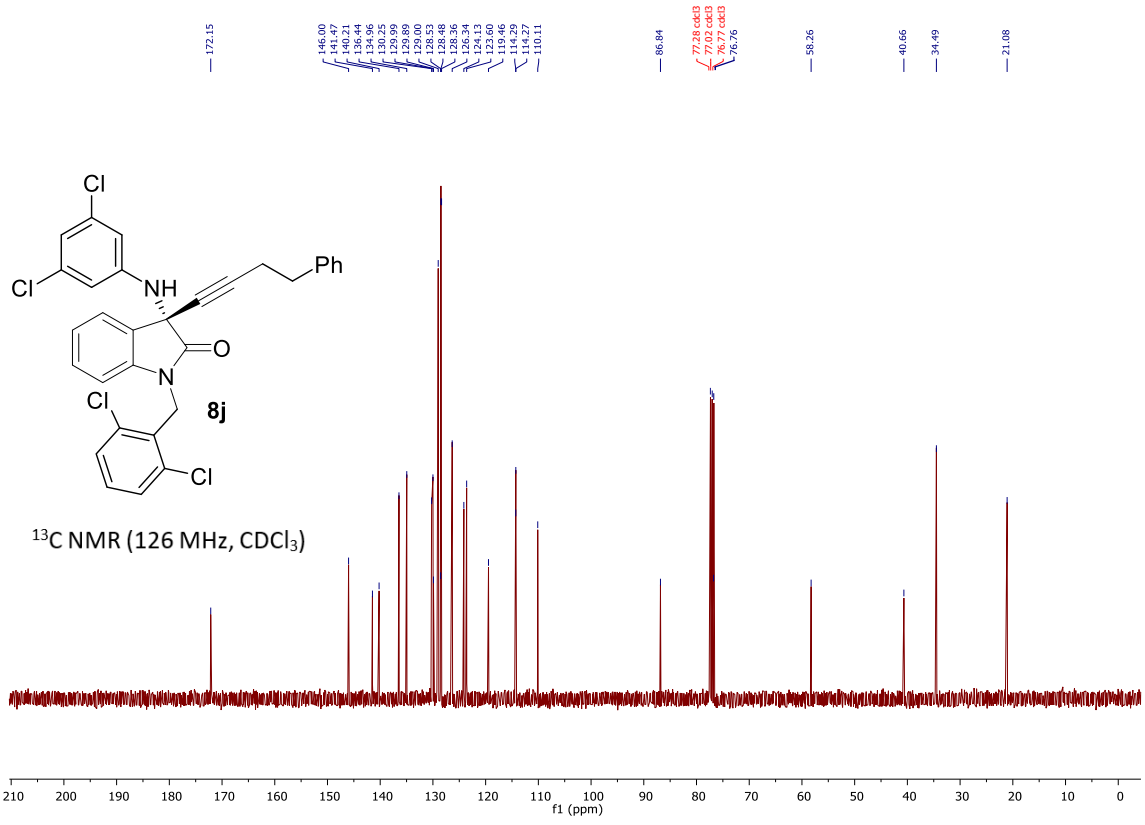
8h

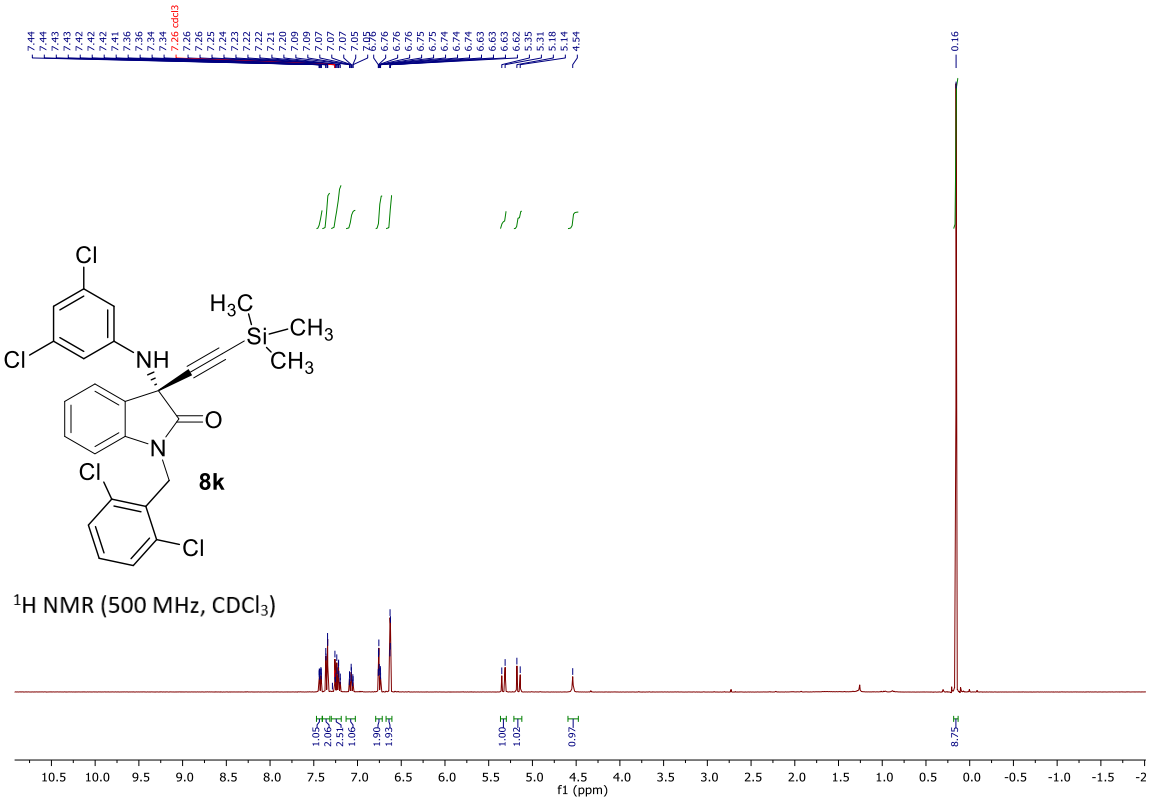
^{19}F NMR (470 MHz, $CDCl_3$)

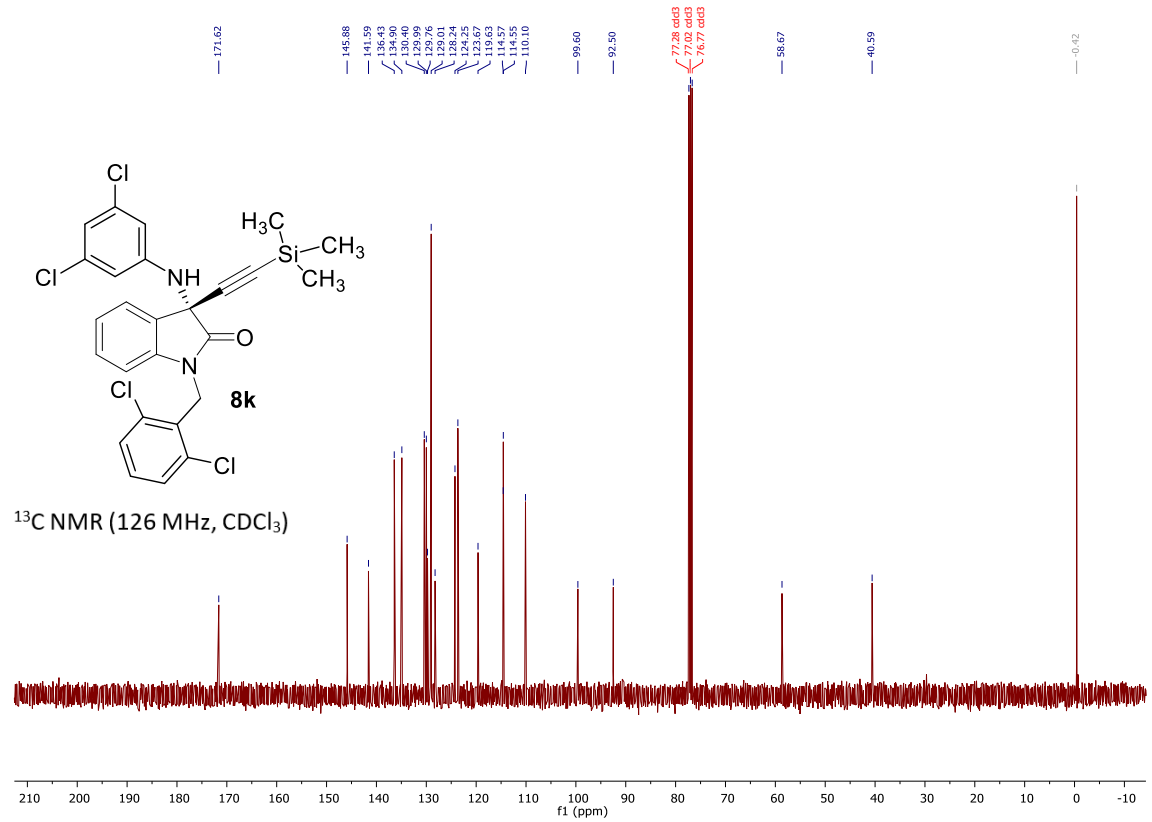

Cl
Cl
NH
CO2CH3
O
N
Cl
Cl
8i
1H NMR (500 MHz, CDCl3)
f1 (ppm)

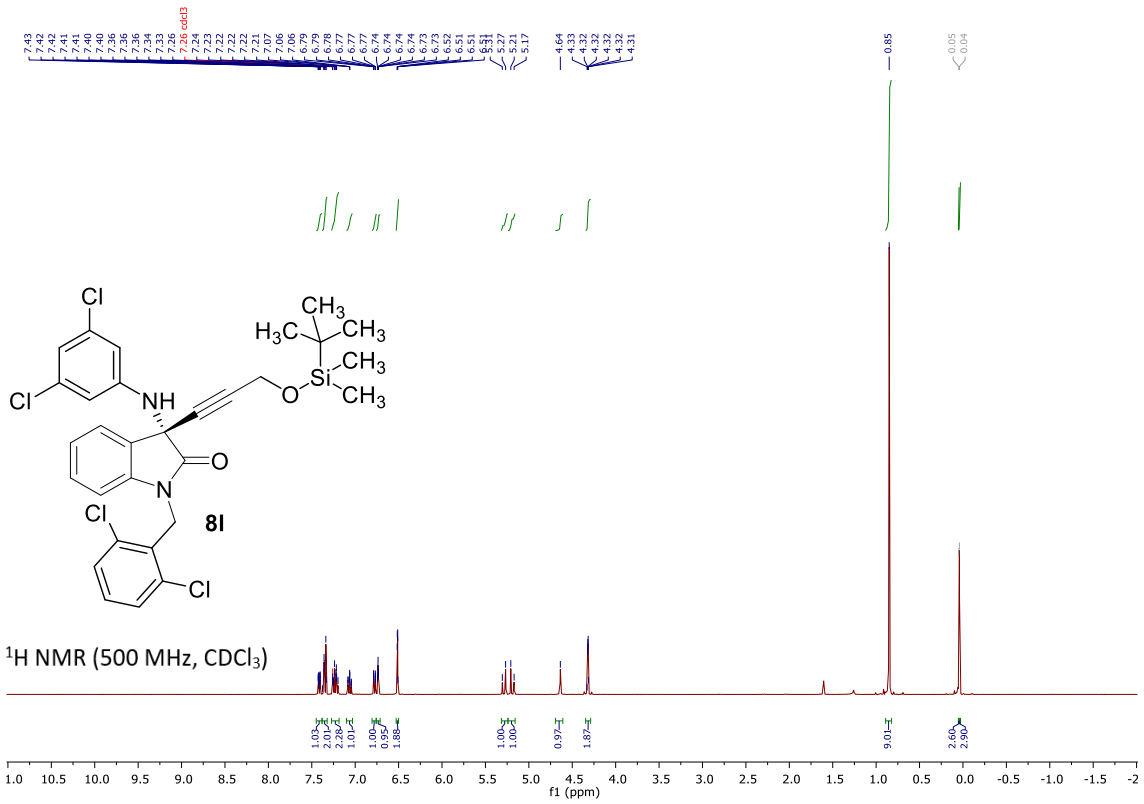

Cl
Cl
NH
CO2CH3
O
N
Cl
Cl
8i
13C NMR (126 MHz, CDCl3)
f1 (ppm)

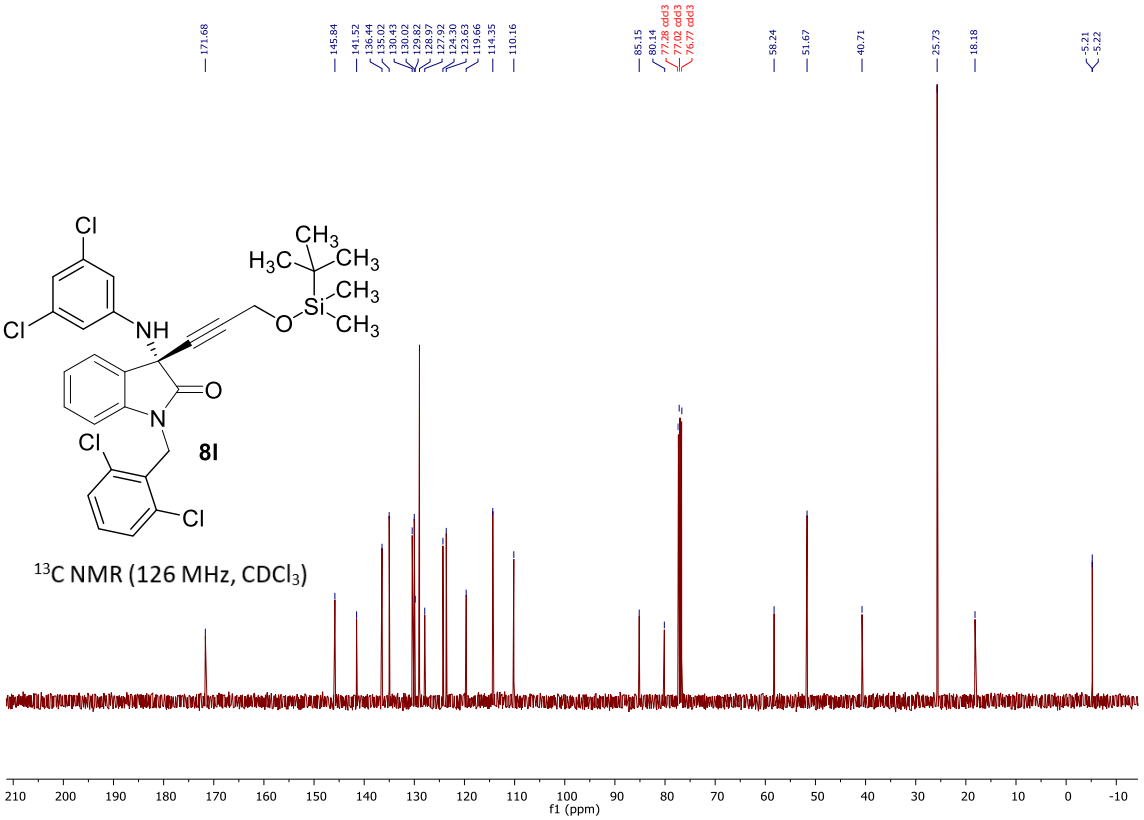

Cl
Cl
NH
Ph
O
N
Cl
Cl
8j
1H NMR (500 MHz, CDCl3)
f1 (ppm)

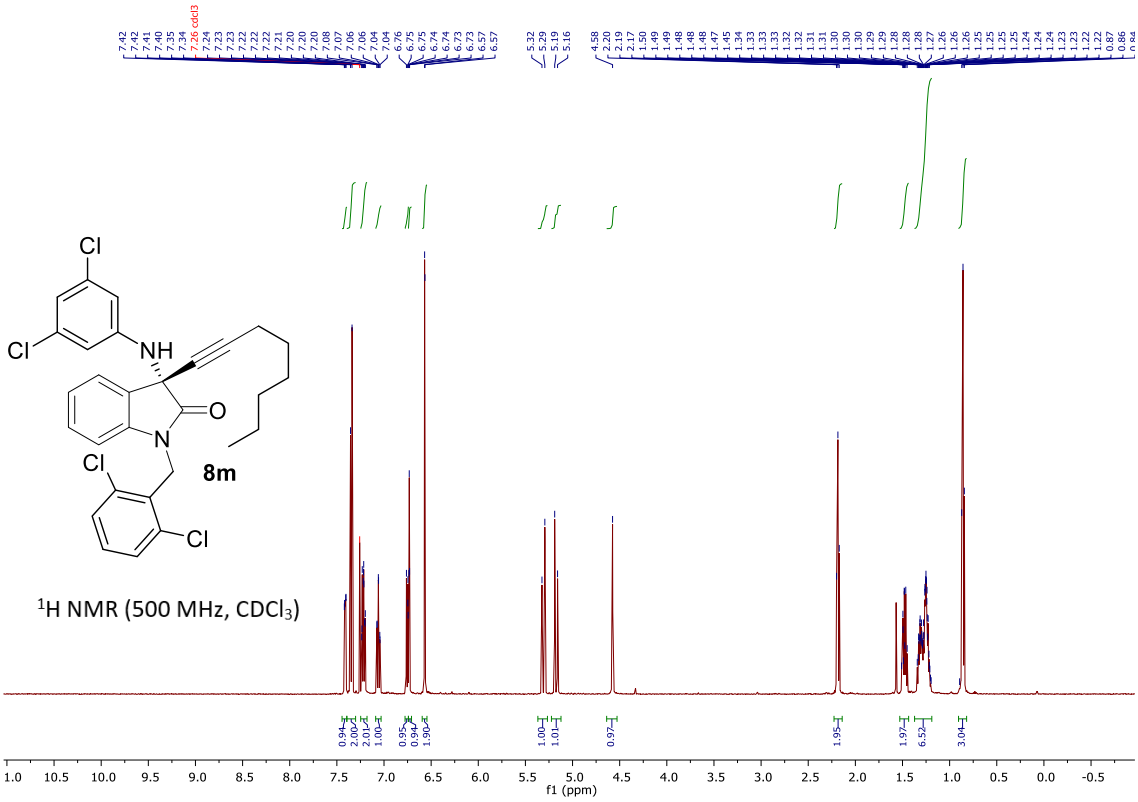

Cl
Cl
NH
Ph
O
N
Cl
Cl
8j
13C NMR (126 MHz, CDCl3)
f1 (ppm)

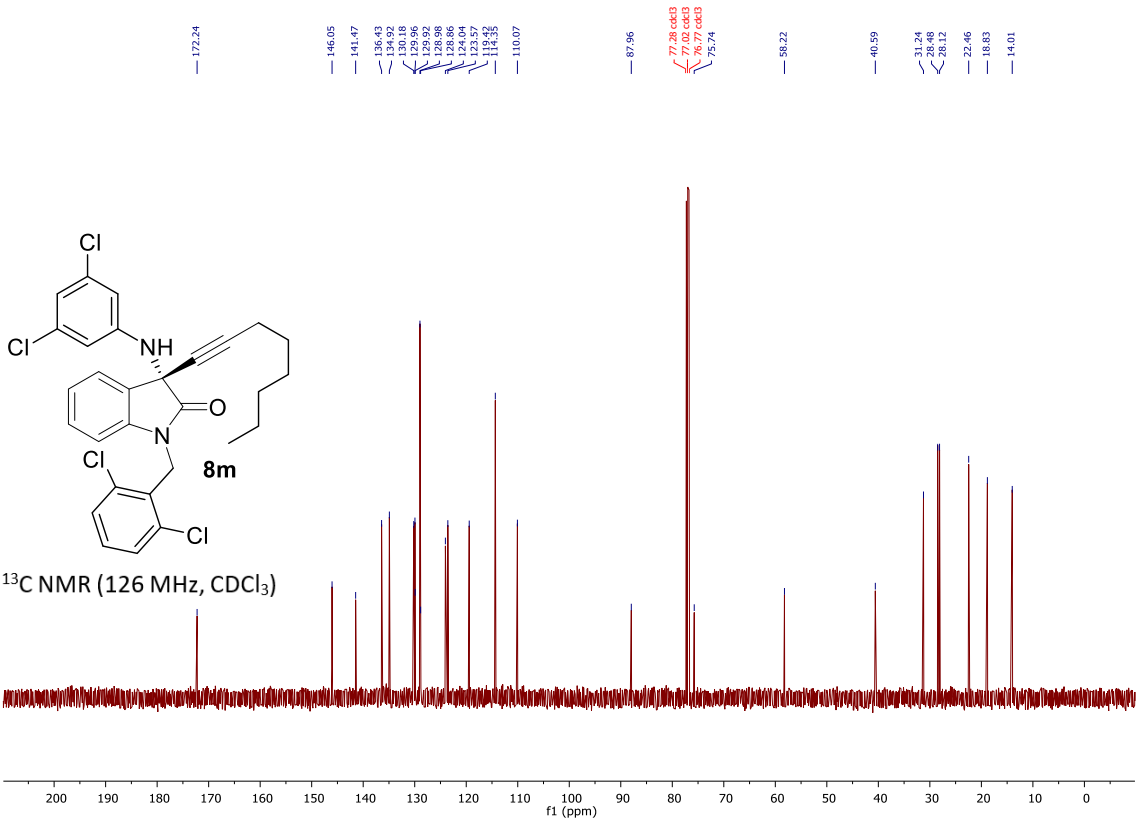

Cl
Cl
NH
H3C
Si
CH3
CH3
O
N
Cl
Cl
8k
1H NMR (500 MHz, CDCl3)
f1 (ppm)

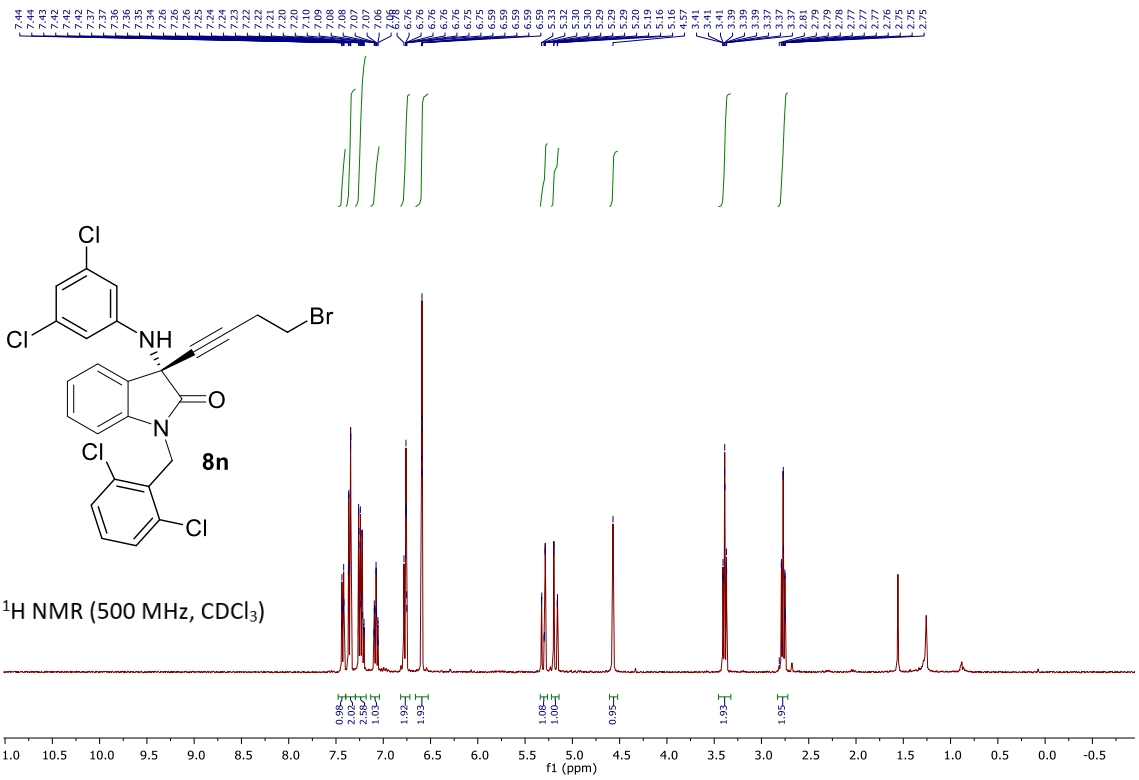

Cl
Cl
NH
H3C
Si
CH3
CH3
O
N
Cl
Cl
8k
13C NMR (126 MHz, CDCl3)
f1 (ppm)


8l
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)


8l
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)


Cl
Cl
NH
O
N
Cl
Cl
8m
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)


Cl
Cl
NH
O
N
Cl
Cl
8m
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)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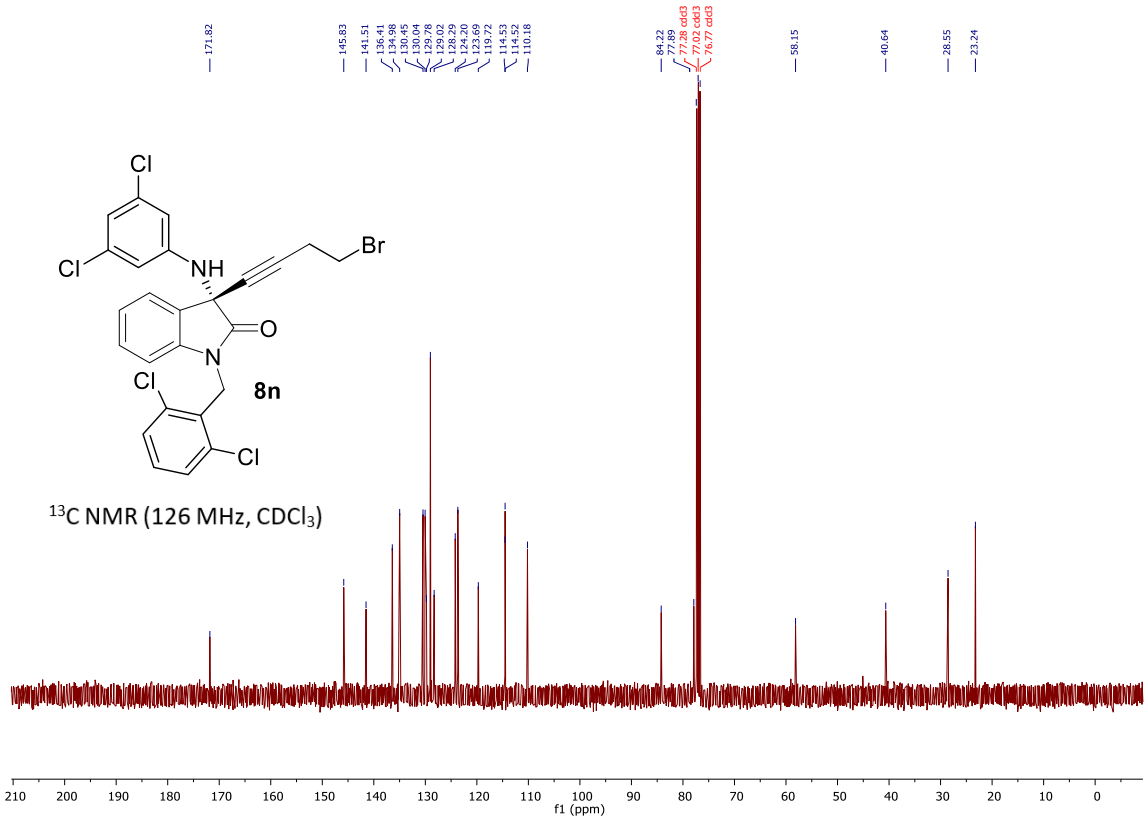
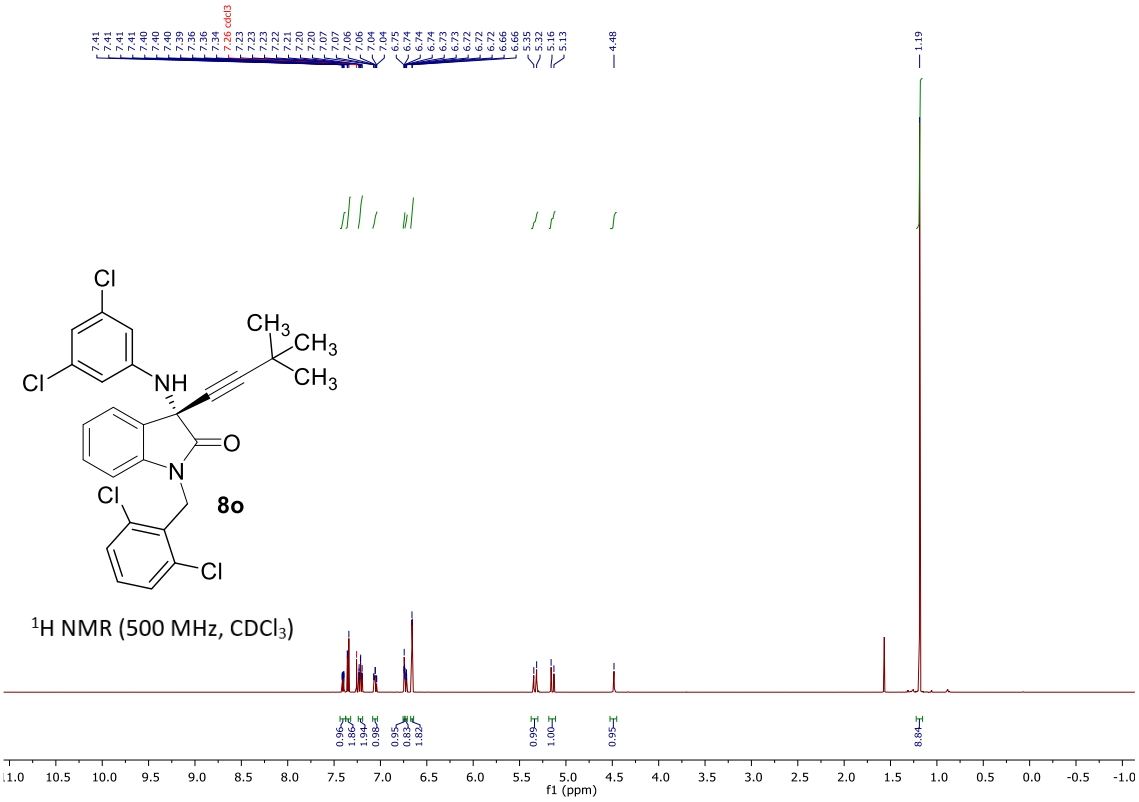
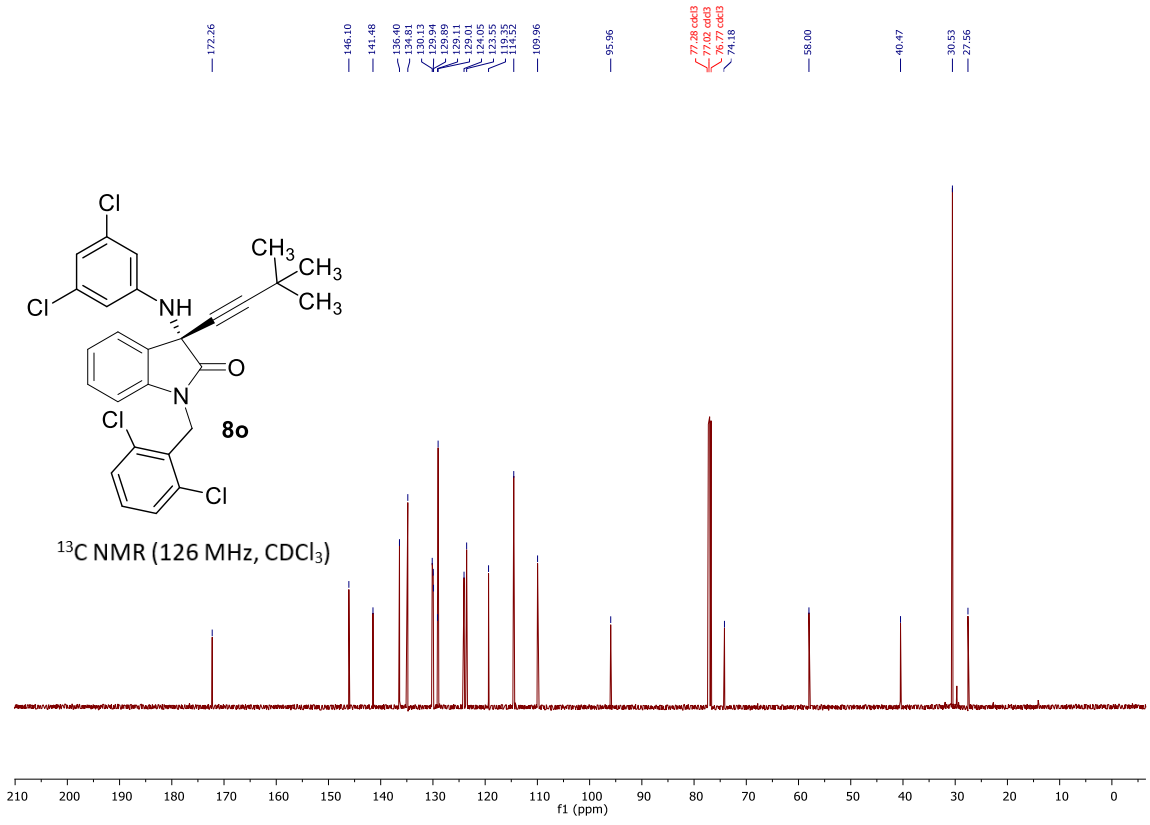
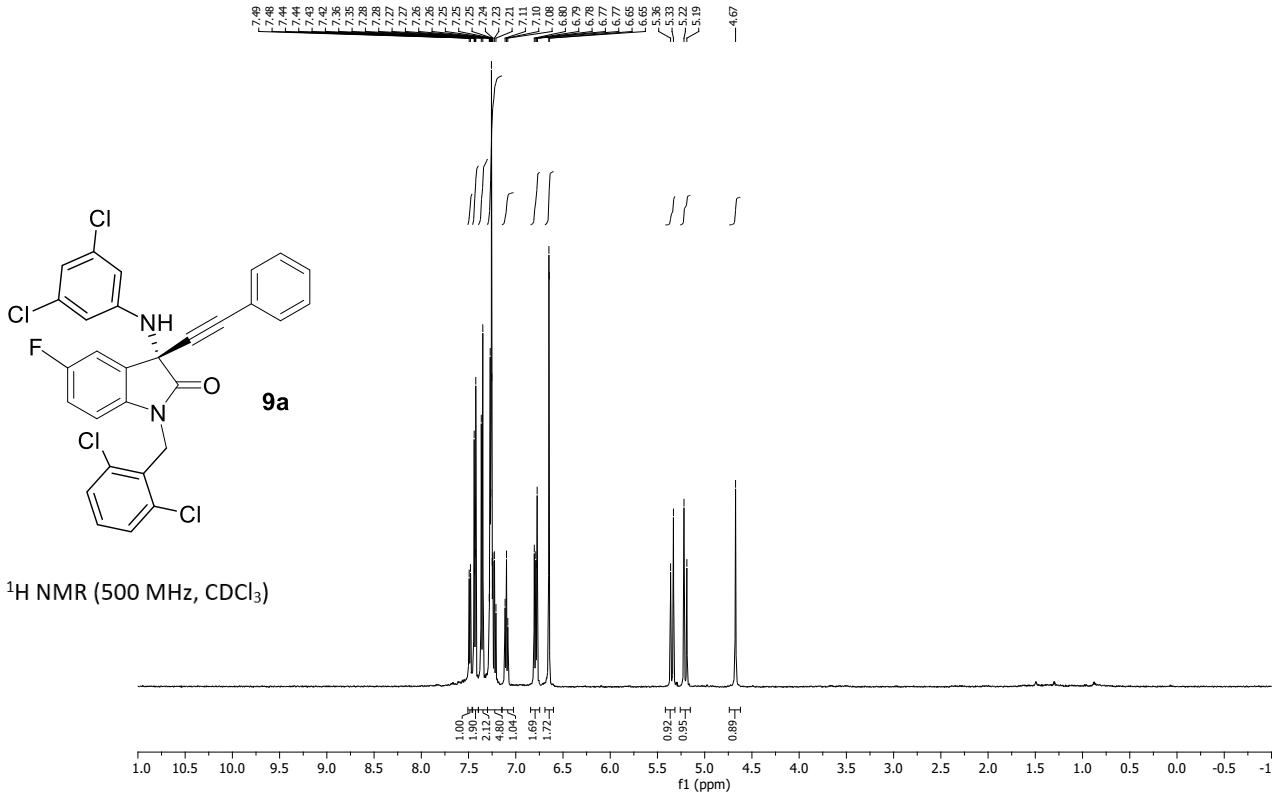
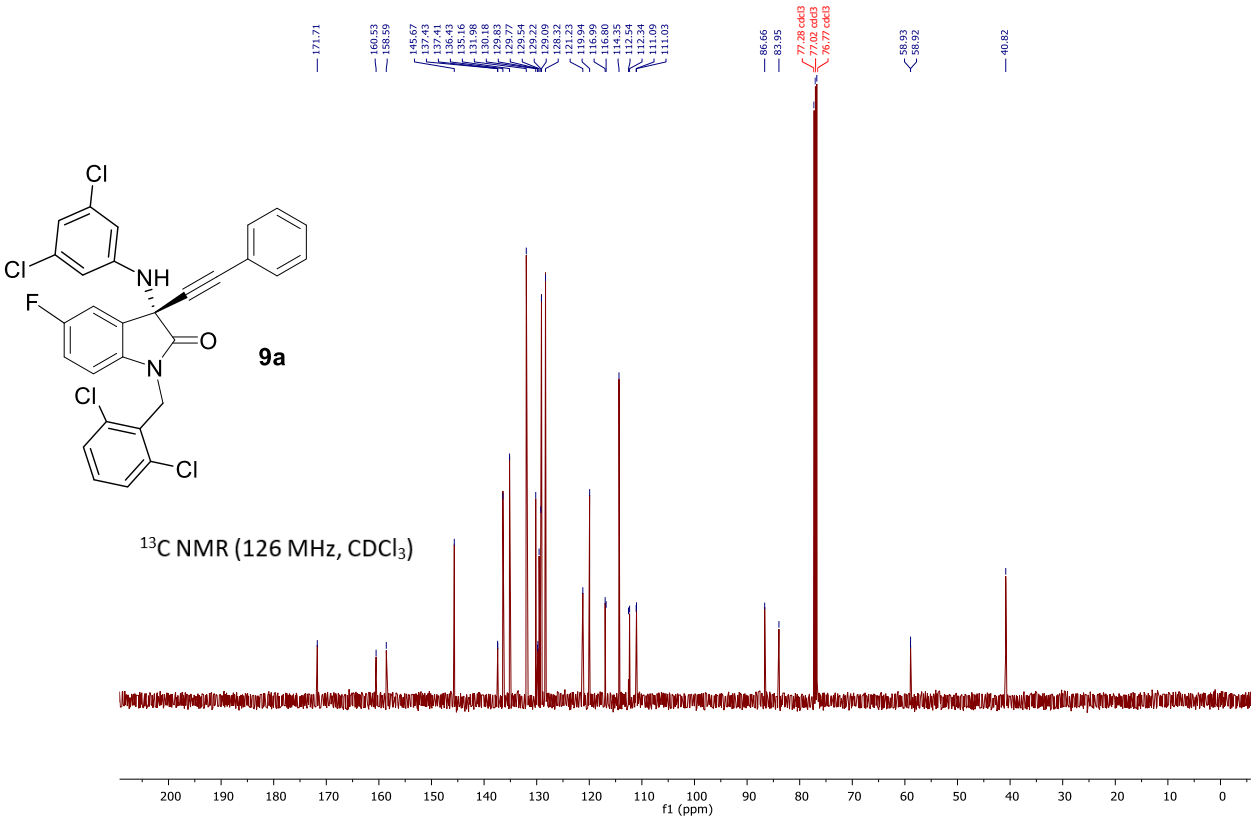
Cl
NH
Br
O
N
Cl
Cl
8n
1H NMR (500 MHz, CDCl3)
f1 (ppm)

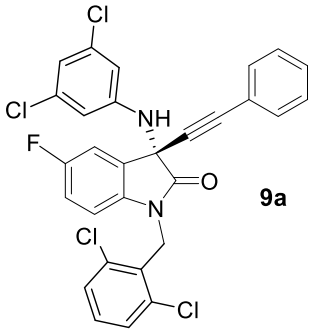

Cl
Cl
NH
Br
O
N
Cl
Cl
8n
13C NMR (126 MHz, CDCl3)
f1 (ppm)


Cl
Cl
NH
CH3
CH3
CH3
O
N
Cl
Cl
8o
1H NMR (500 MHz, CDCl3)
f1 (ppm)


Cl
Cl
NH
CH3
CH3
CH3
O
N
Cl
Cl
8o
13C NMR (126 MHz, CDCl3)
f1 (ppm)

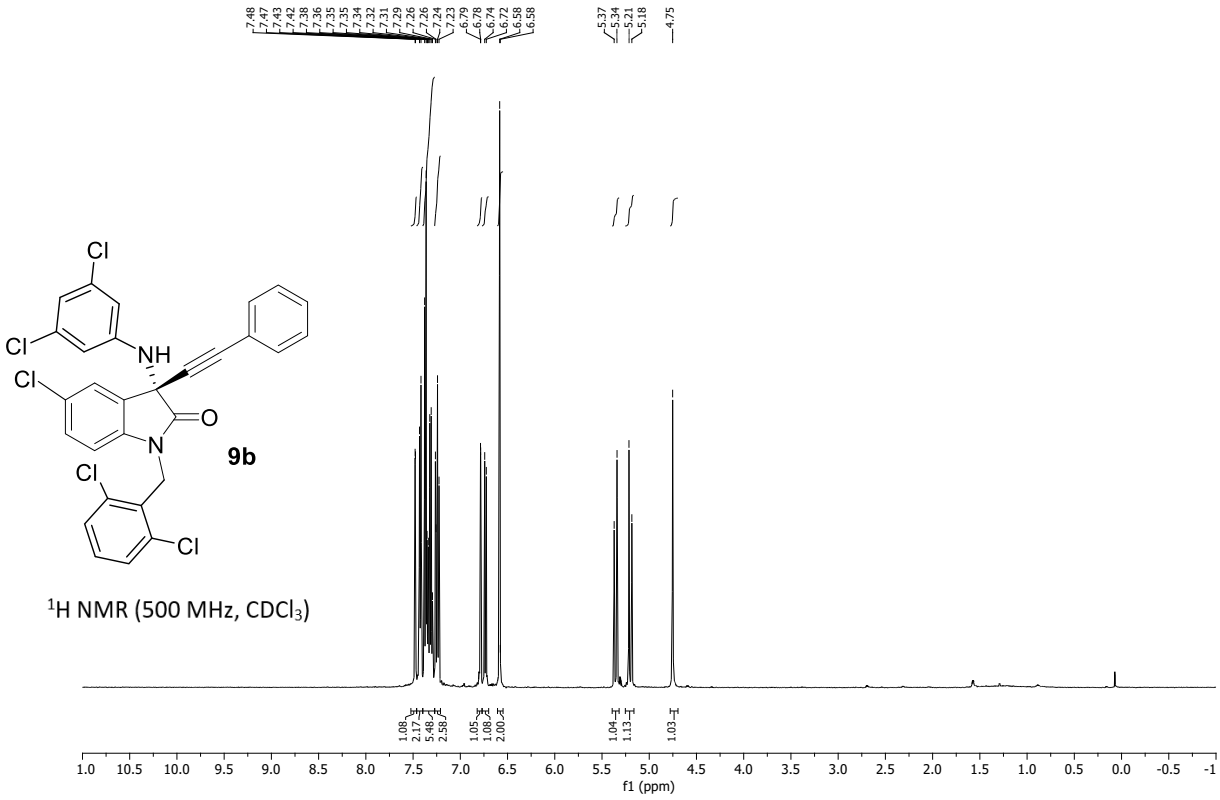

Cl
Cl
NH
F
O
N
Cl
Cl
9a
1H NMR (500 MHz, CDCl3)
f1 (ppm)

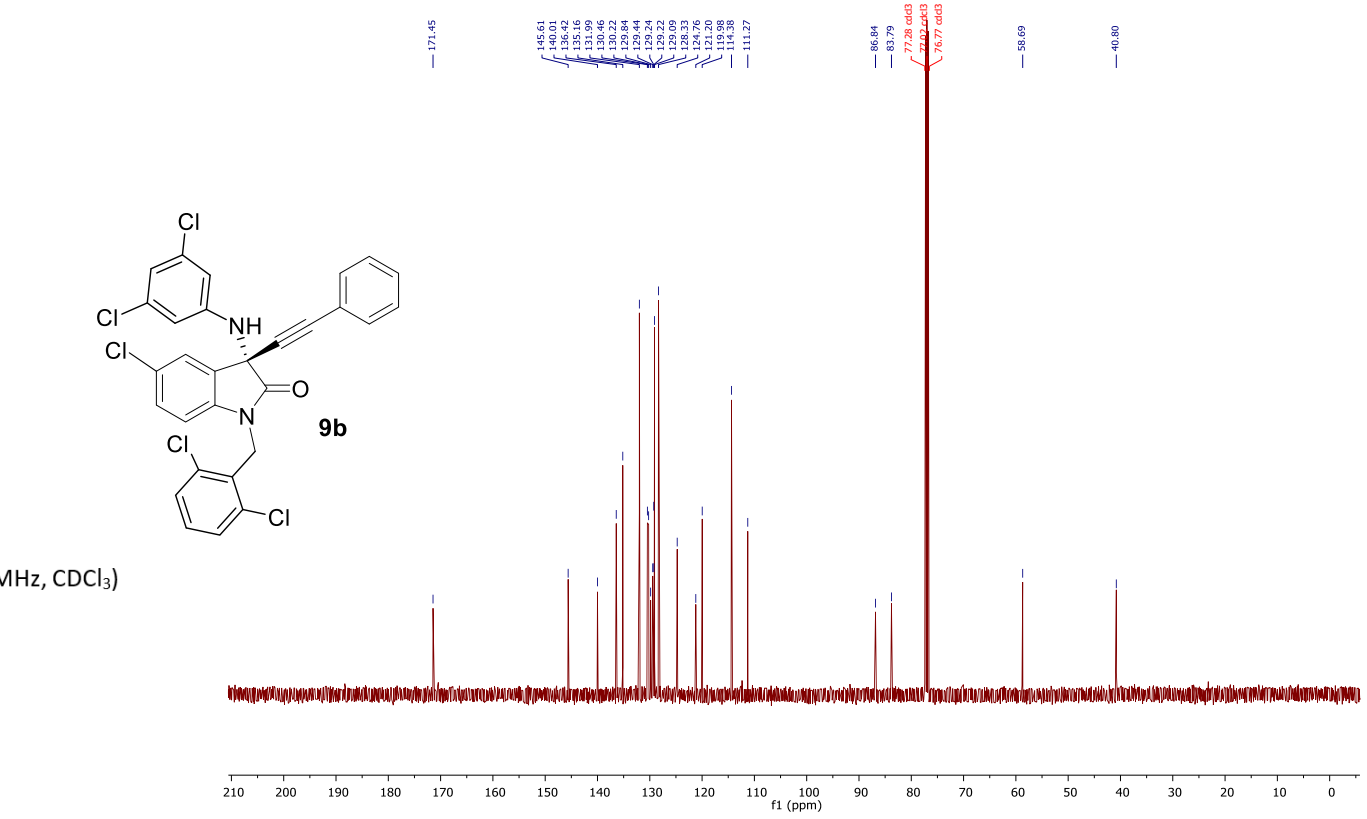

Cl
Cl
NH
F
O
N
Cl
Cl
9a
13C NMR (126 MHz, CDCl3)
f1 (ppm)

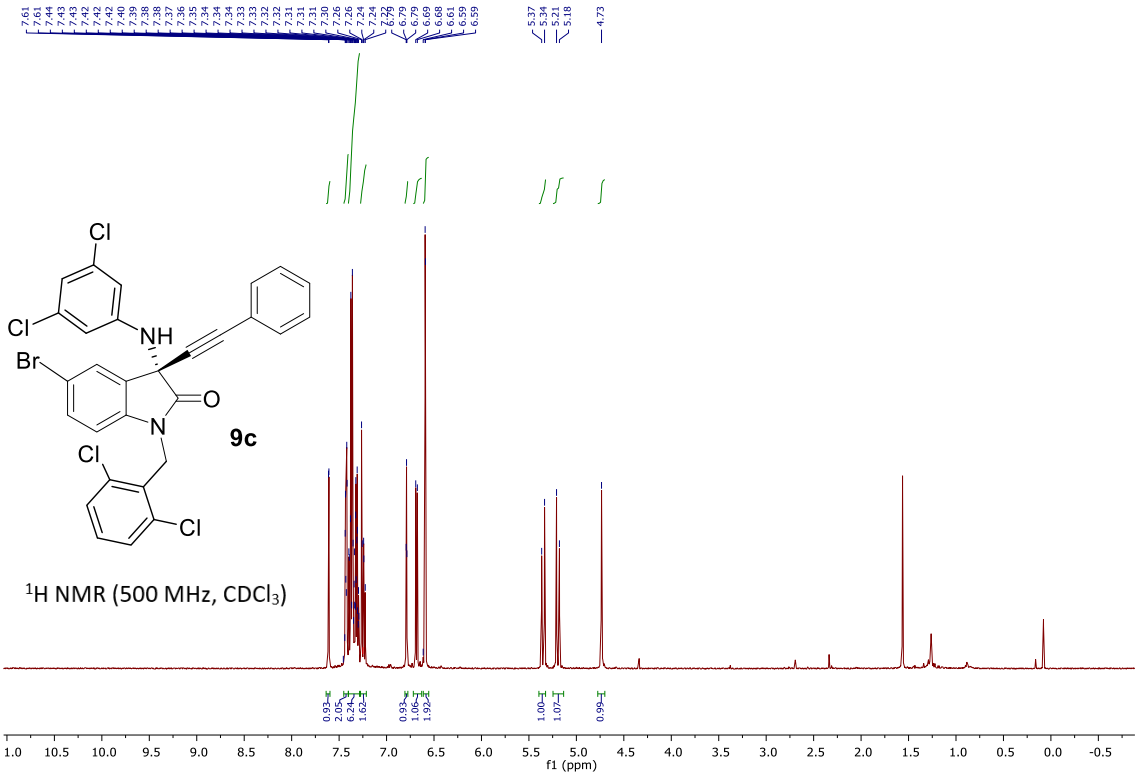


9a

^{19}F NMR (470 MHz, $CDCl_3$)


Cl
Cl
NH
Cl
O
N
Cl
Cl
9b
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)


Cl
Cl
NH
Cl
O
N
Cl
Cl
9b
MHz, $CDCl_3$)
f1 (ppm)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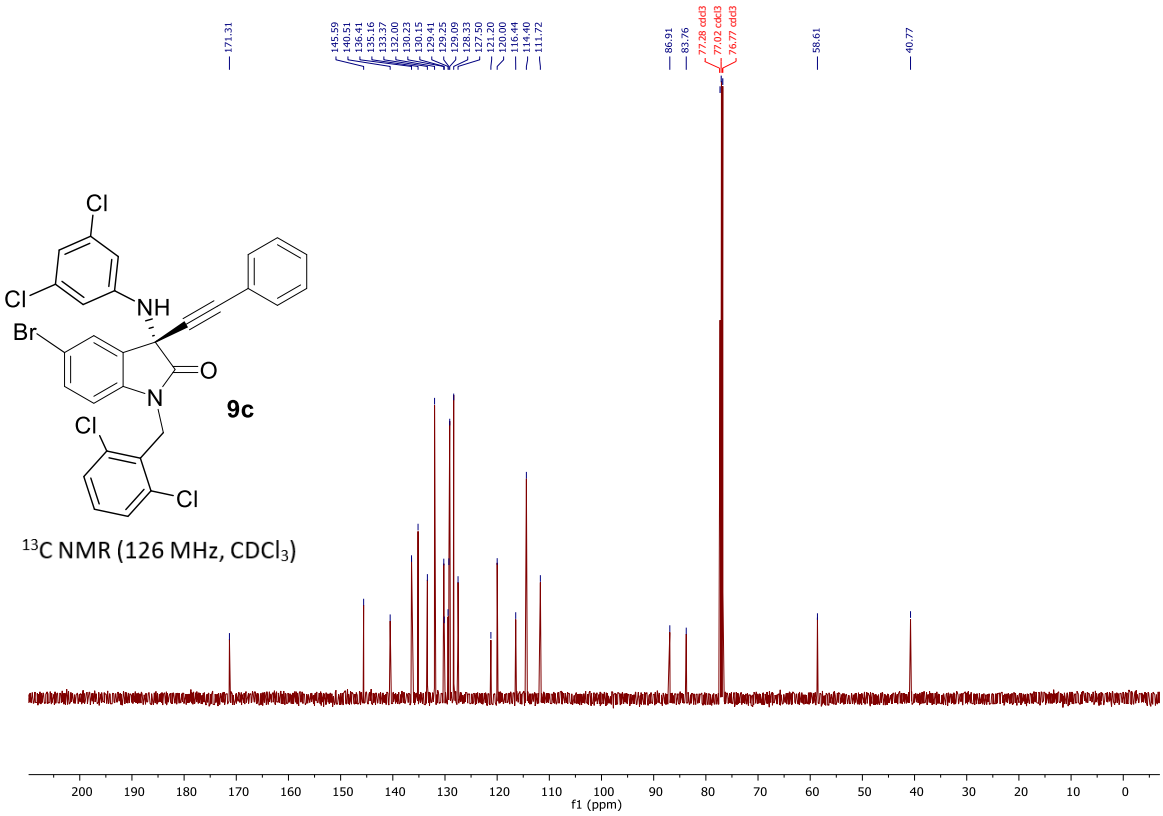
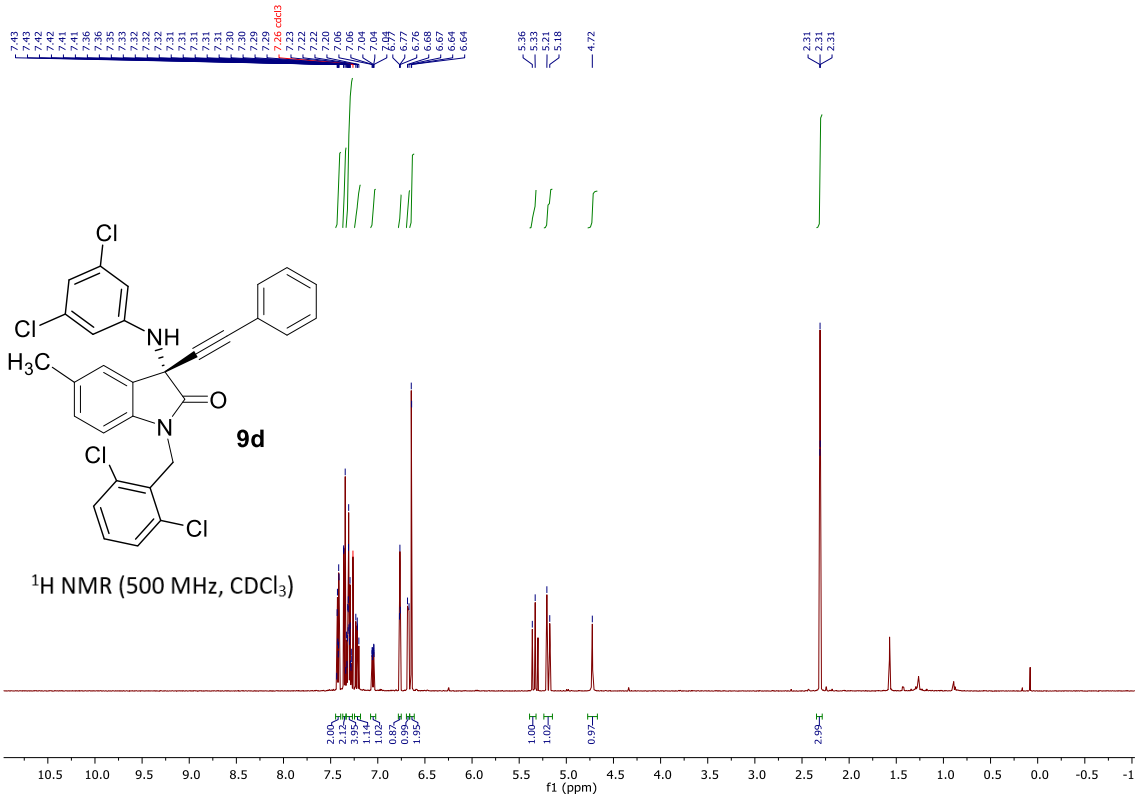
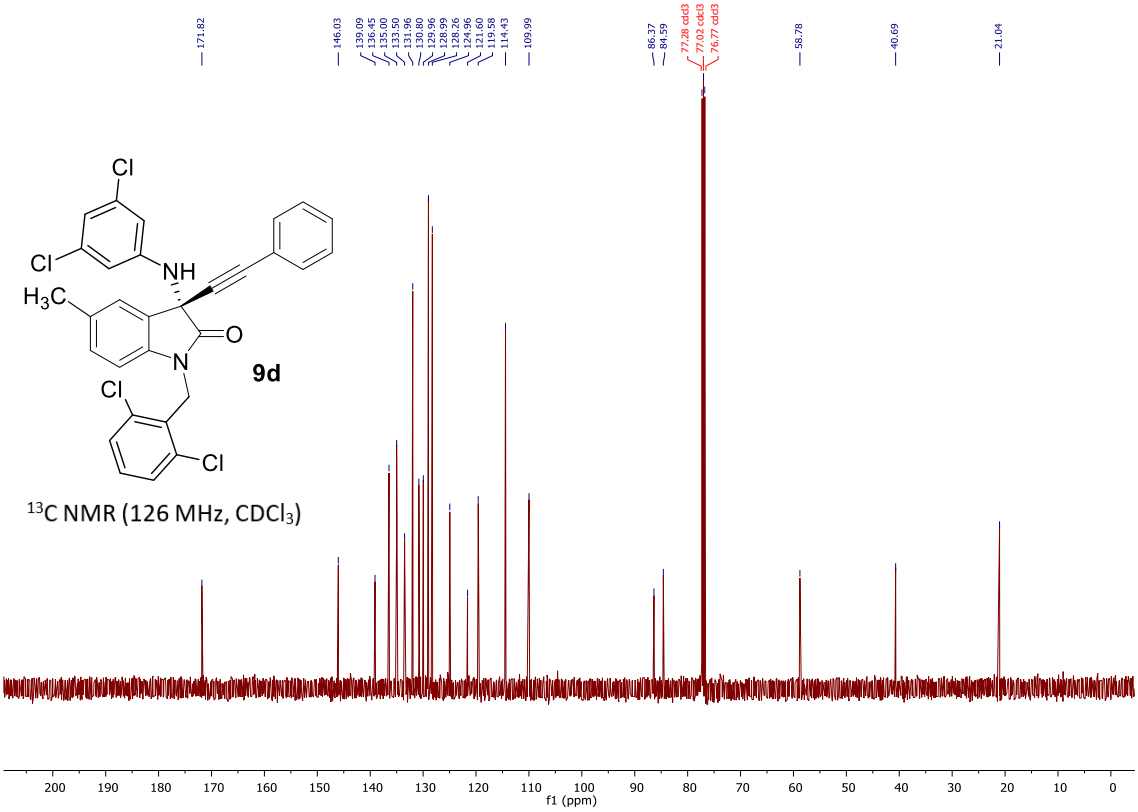
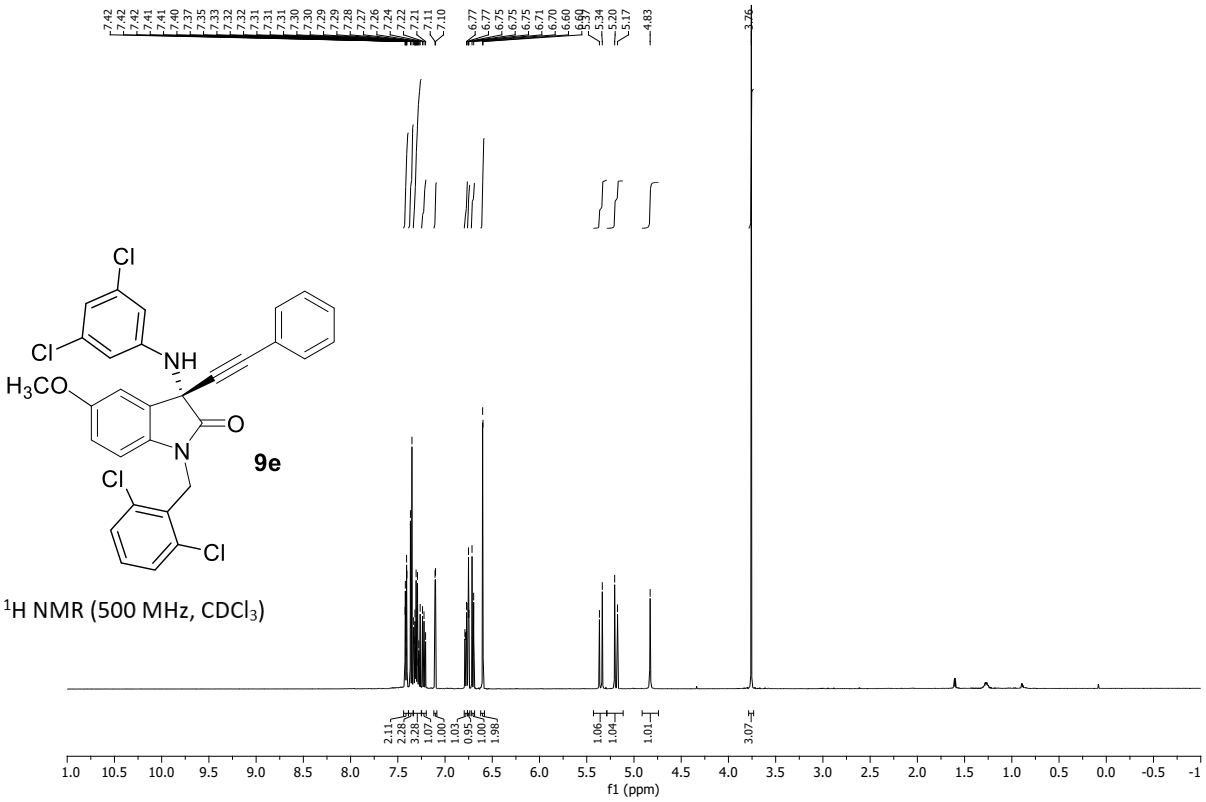
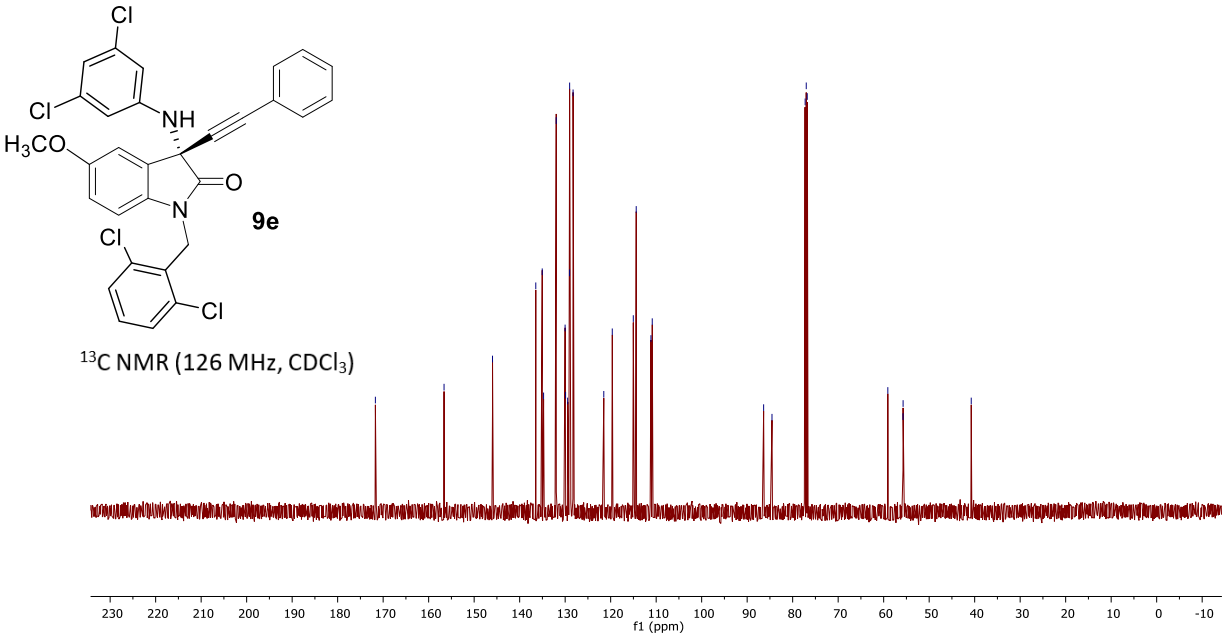
Cl
NH
Br
O
N
Cl
Cl
9c
1H NMR (500 MHz, CDCl3)
f1 (ppm)

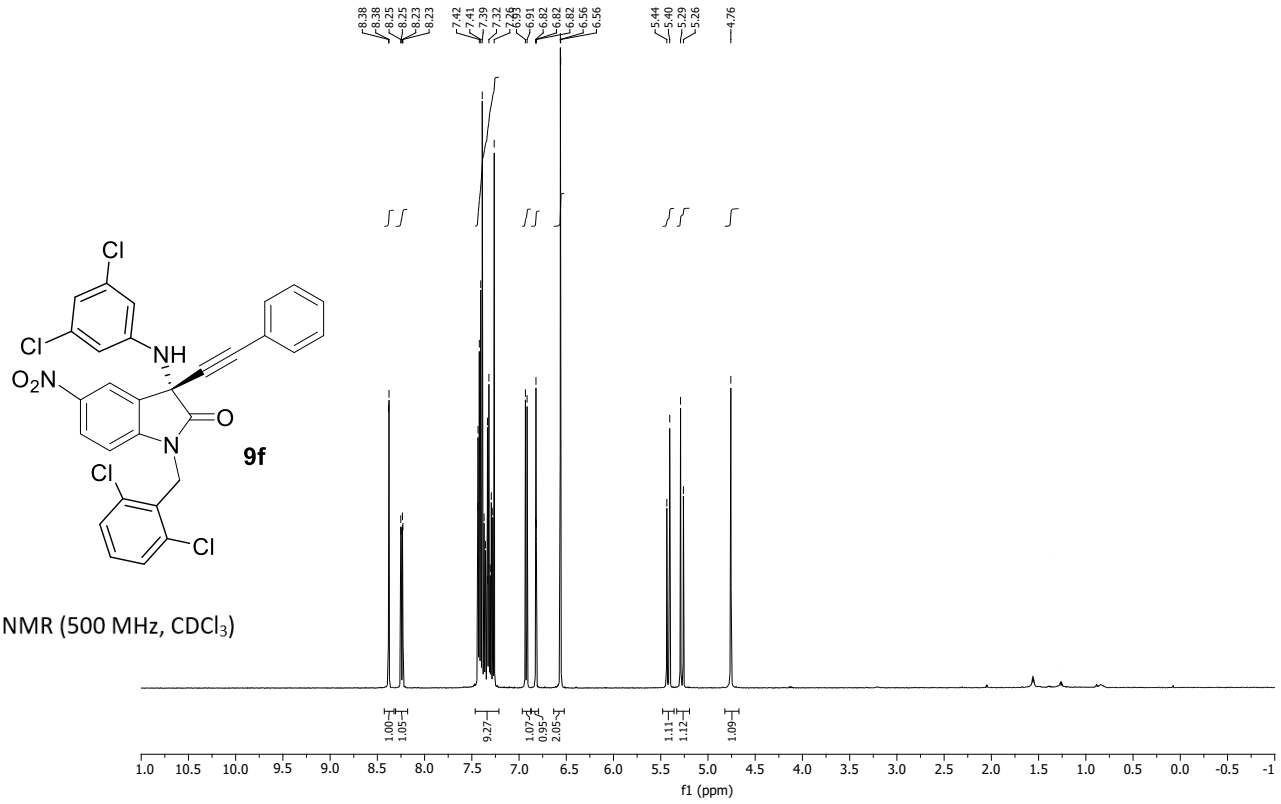

Cl
Cl
NH
Br
O
N
Cl
Cl
9c
13C NMR (126 MHz, CDCl3)
f1 (ppm)


Cl
Cl
NH
H3C
O
N
Cl
Cl
9d
1H NMR (500 MHz, CDCl3)
f1 (ppm)

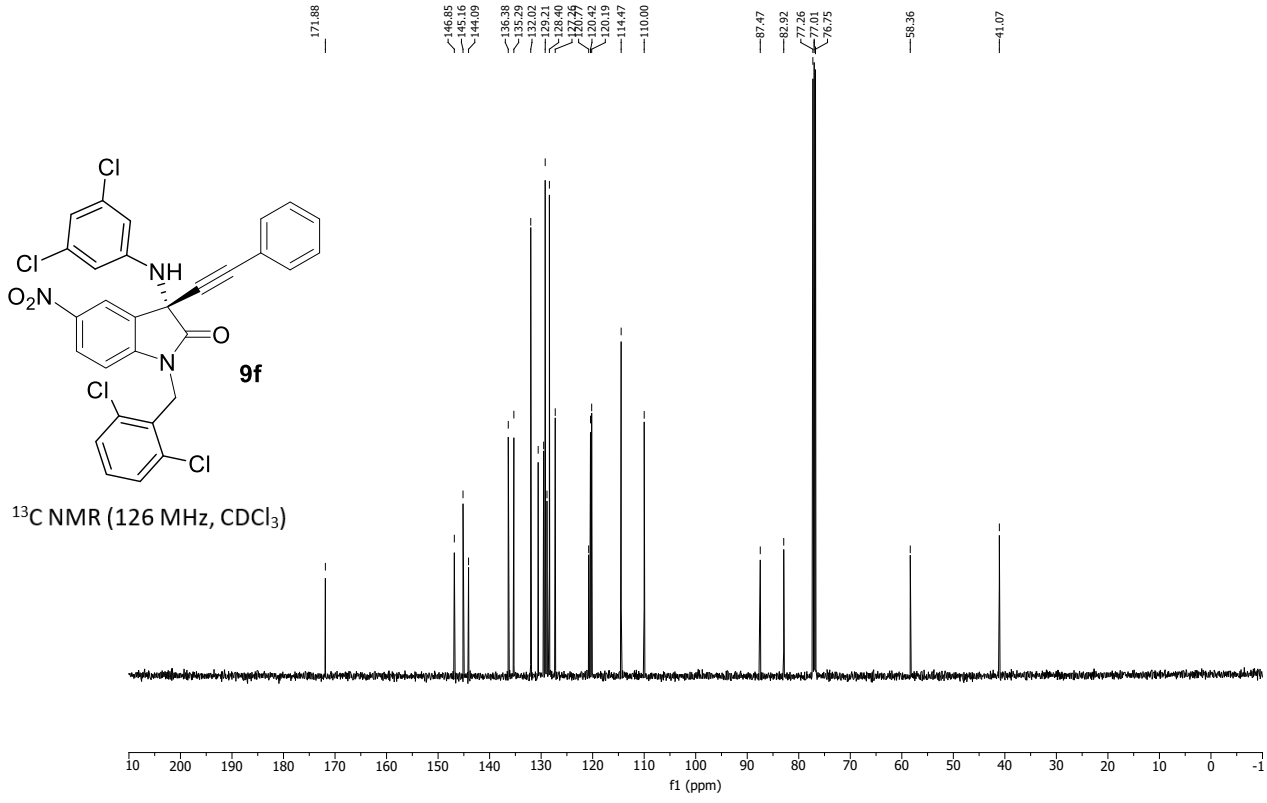

Cl
Cl
NH
H3C
O
N
Cl
Cl
9d
13C NMR (126 MHz, CDCl3)
f1 (ppm)


Cl
Cl
NH
H3CO
O
N
Cl
Cl
9e
1H NMR (500 MHz, CDCl3)
f1 (ppm)

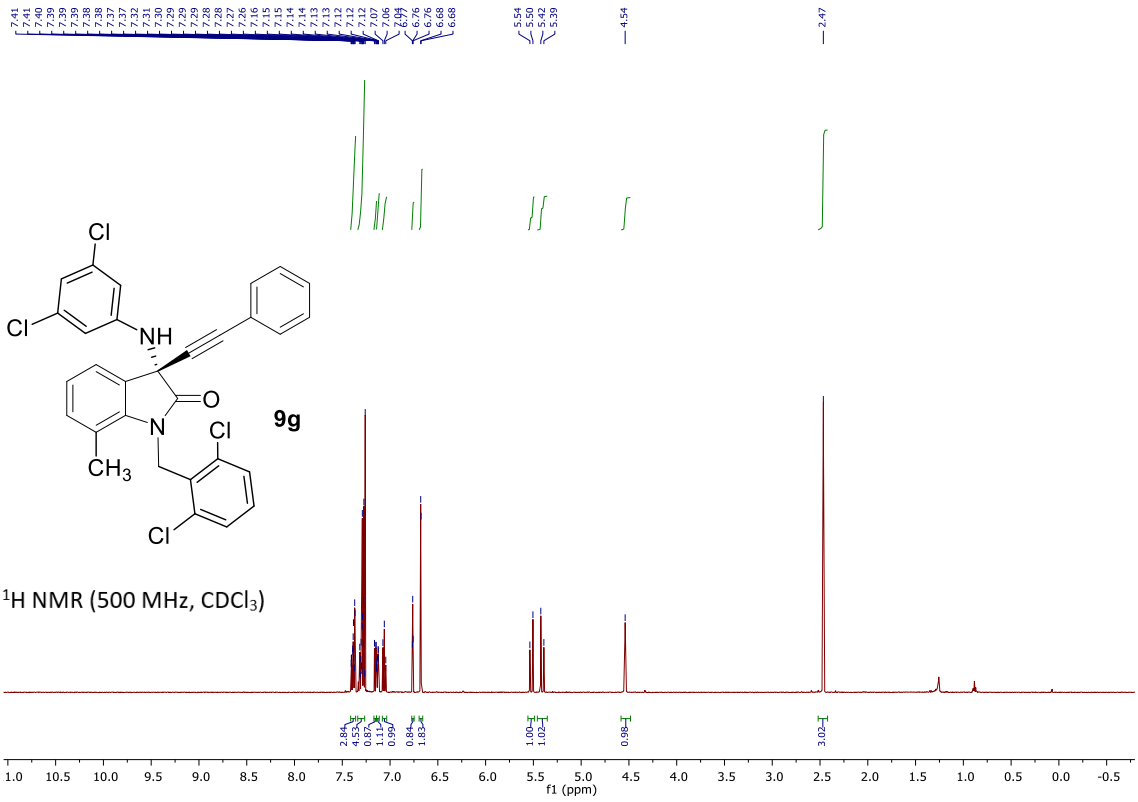

Cl
Cl
NH
H3CO
O
N
Cl
Cl
9e
13C NMR (126 MHz, CDCl3)
f1 (ppm)

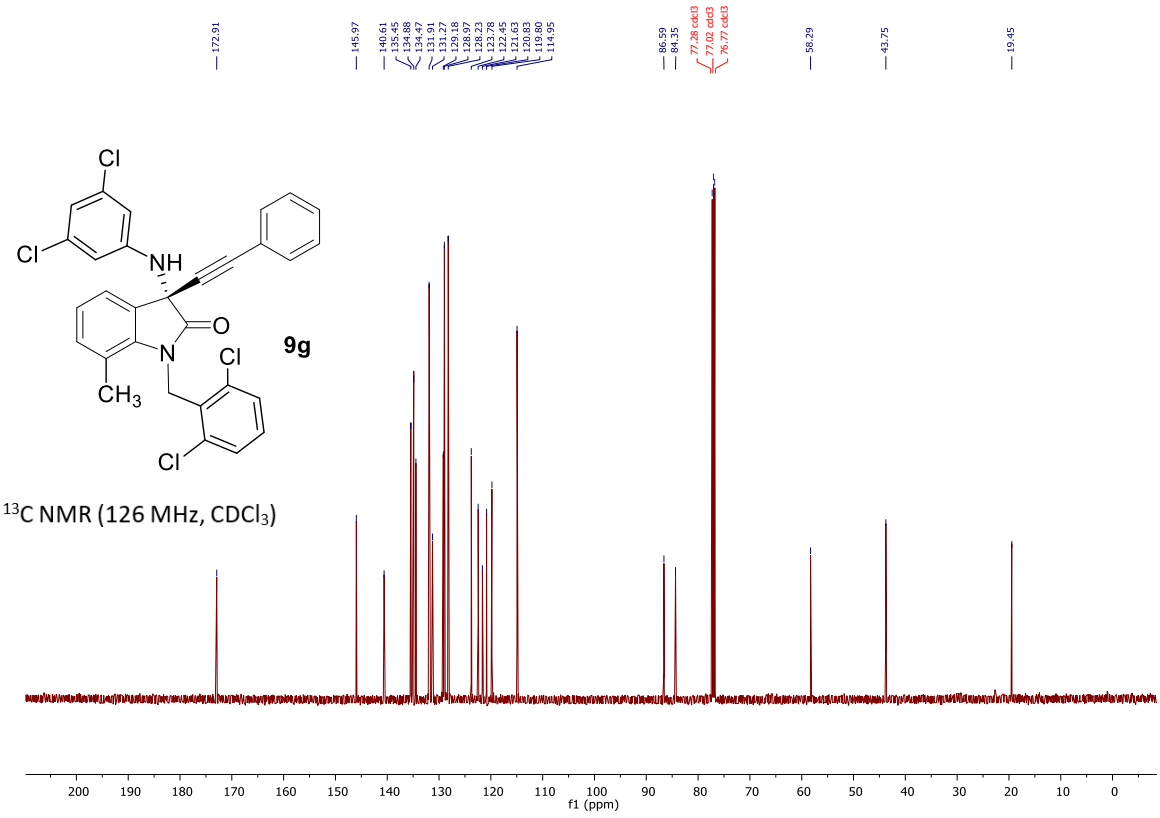


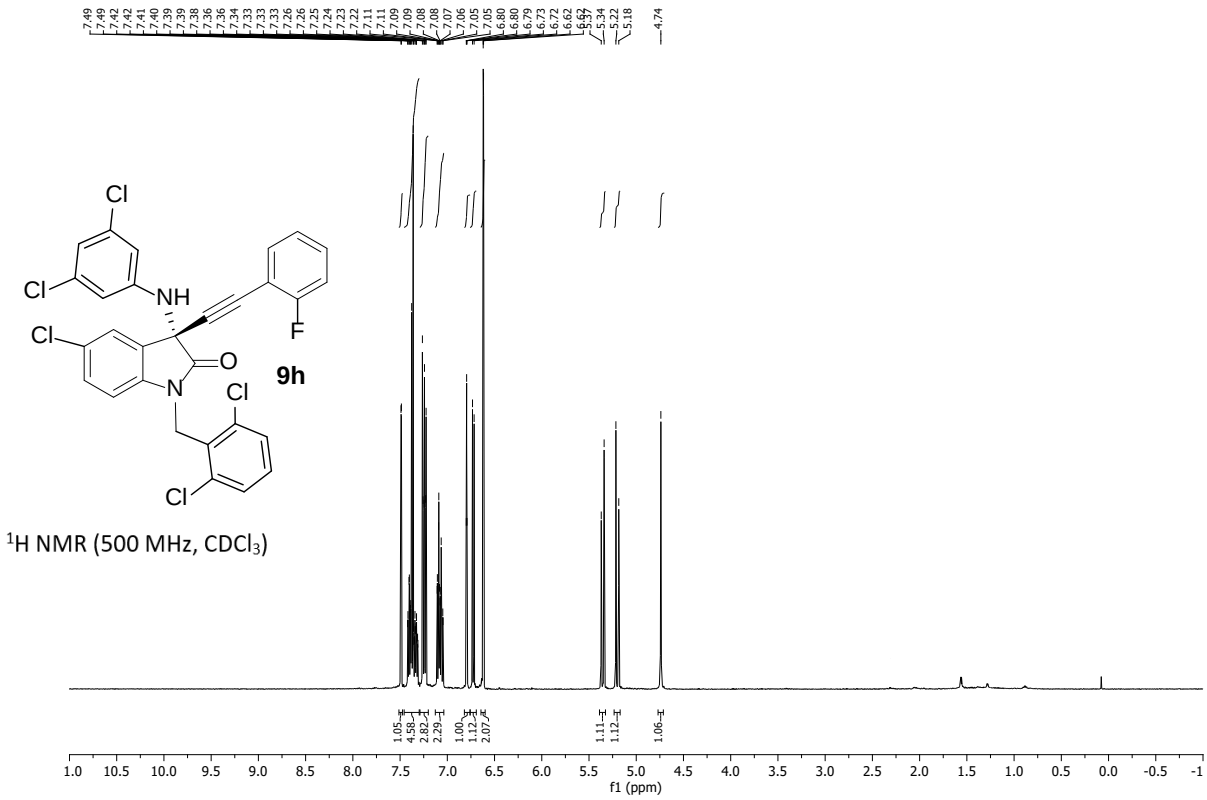
^{1}H NMR (500 MHz, $CDCl_3$)



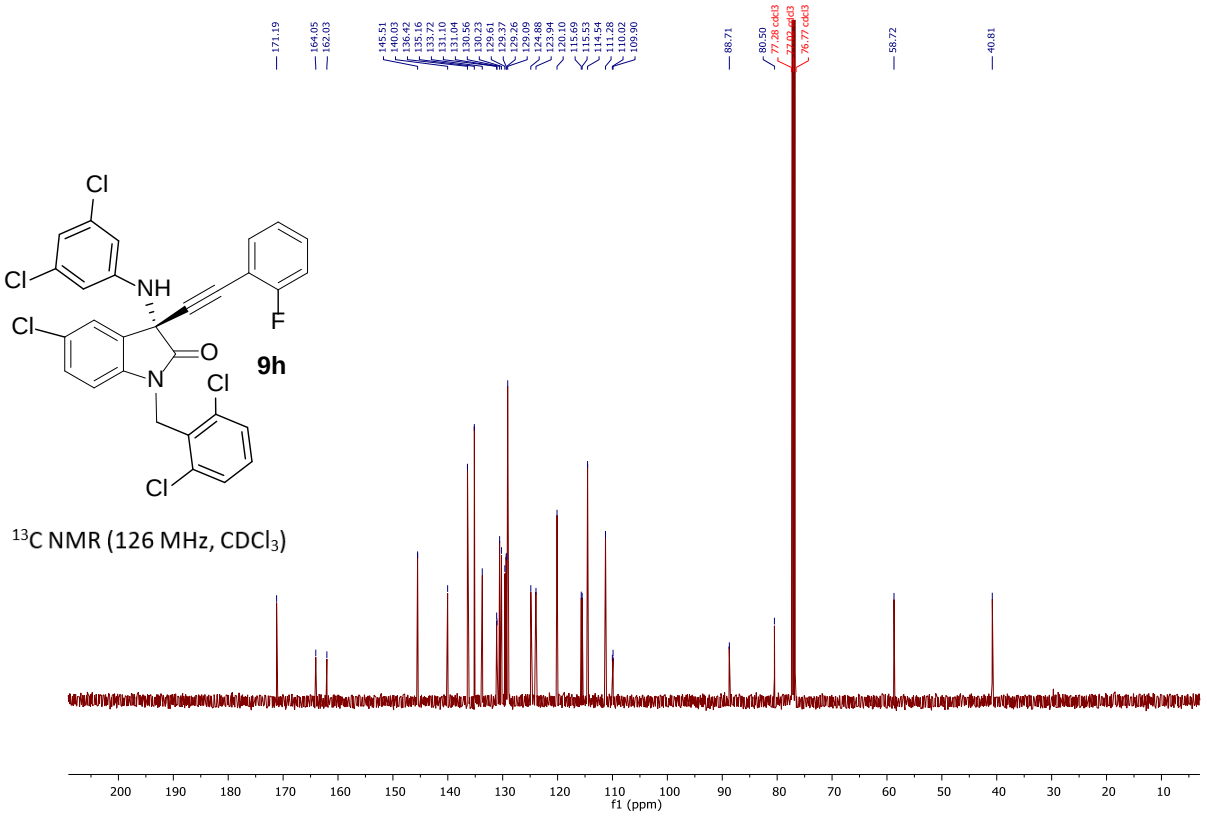
^{13}C NMR (126 MHz, $CDCl_3$)


Cl
Cl
NH
O
N
Cl
CH3
Cl
9g
1H NMR (500 MHz, CDCl3)
f1 (ppm)

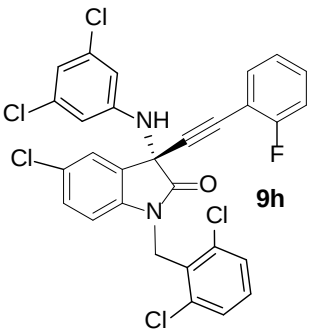

Cl
Cl
NH
O
N
Cl
CH3
Cl
9g
13C NMR (126 MHz, CDCl3)
f1 (ppm)



^{1}H NMR (500 MHz, $CDCl_3$)

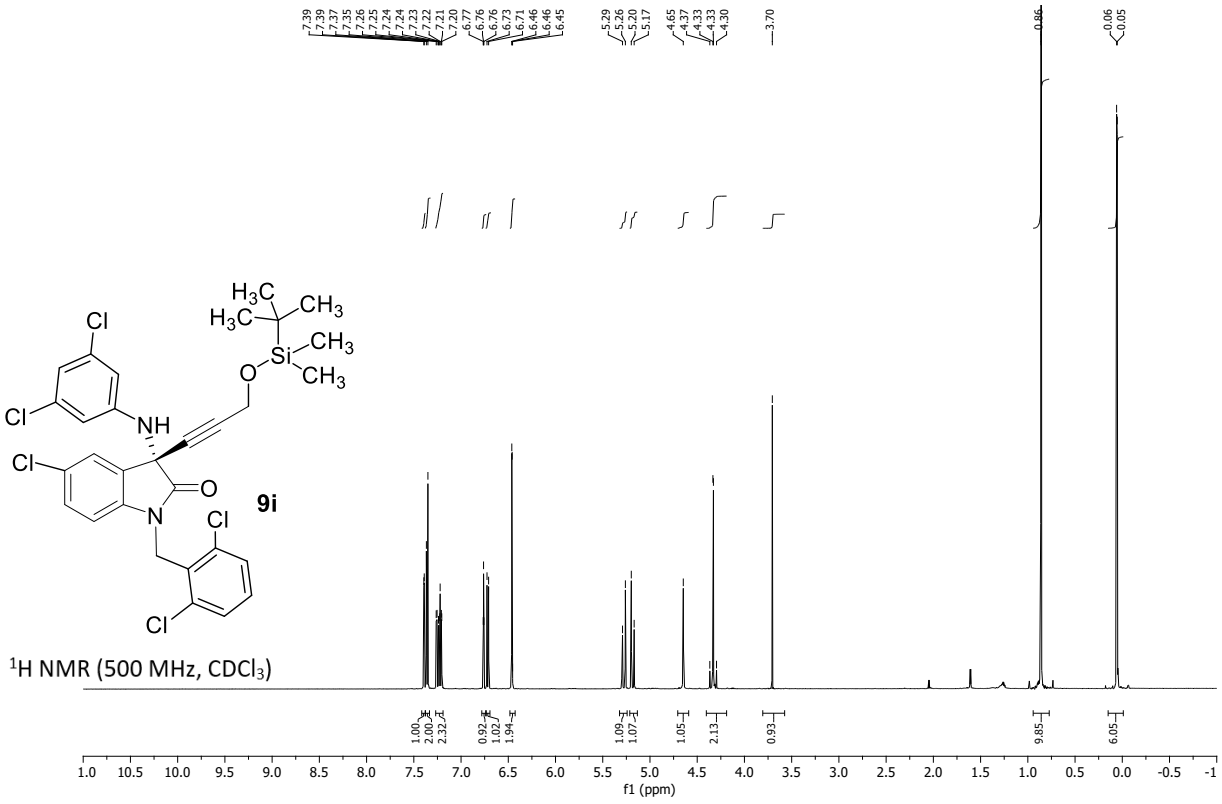


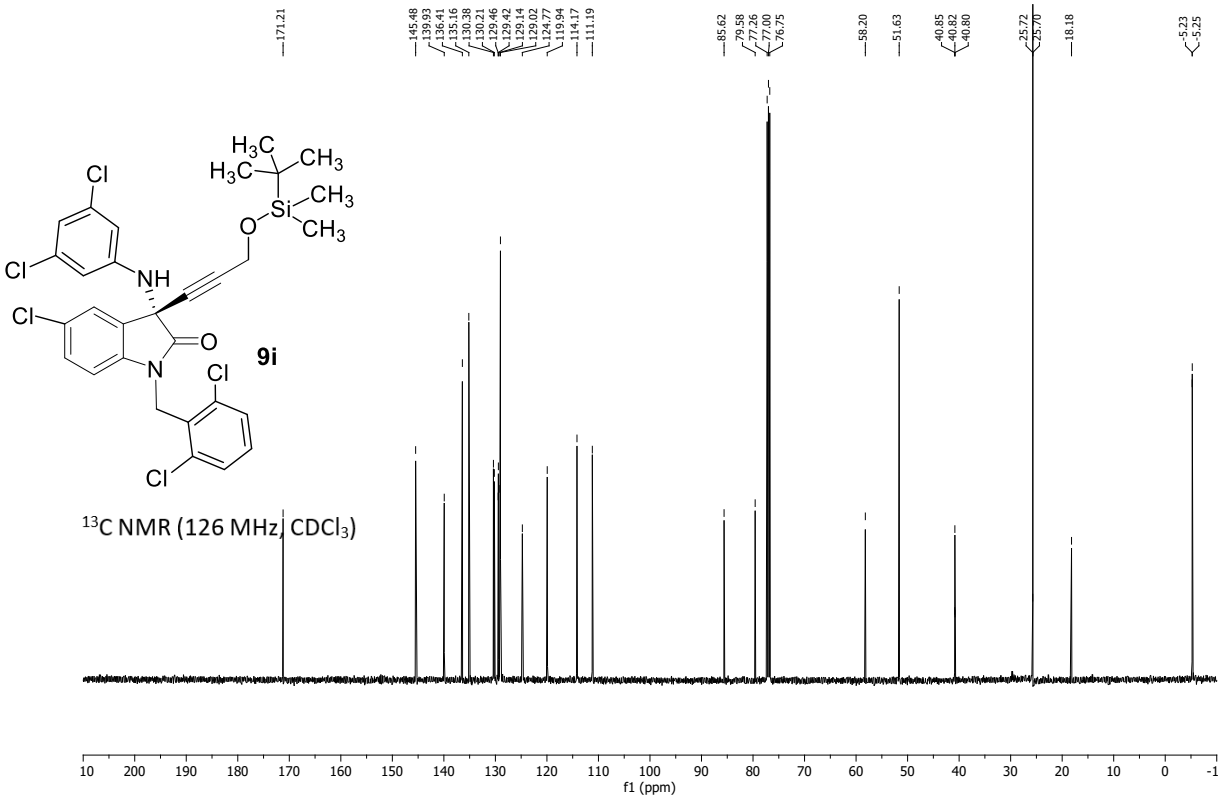
^{13}C NMR (126 MHz, $CDCl_3$)

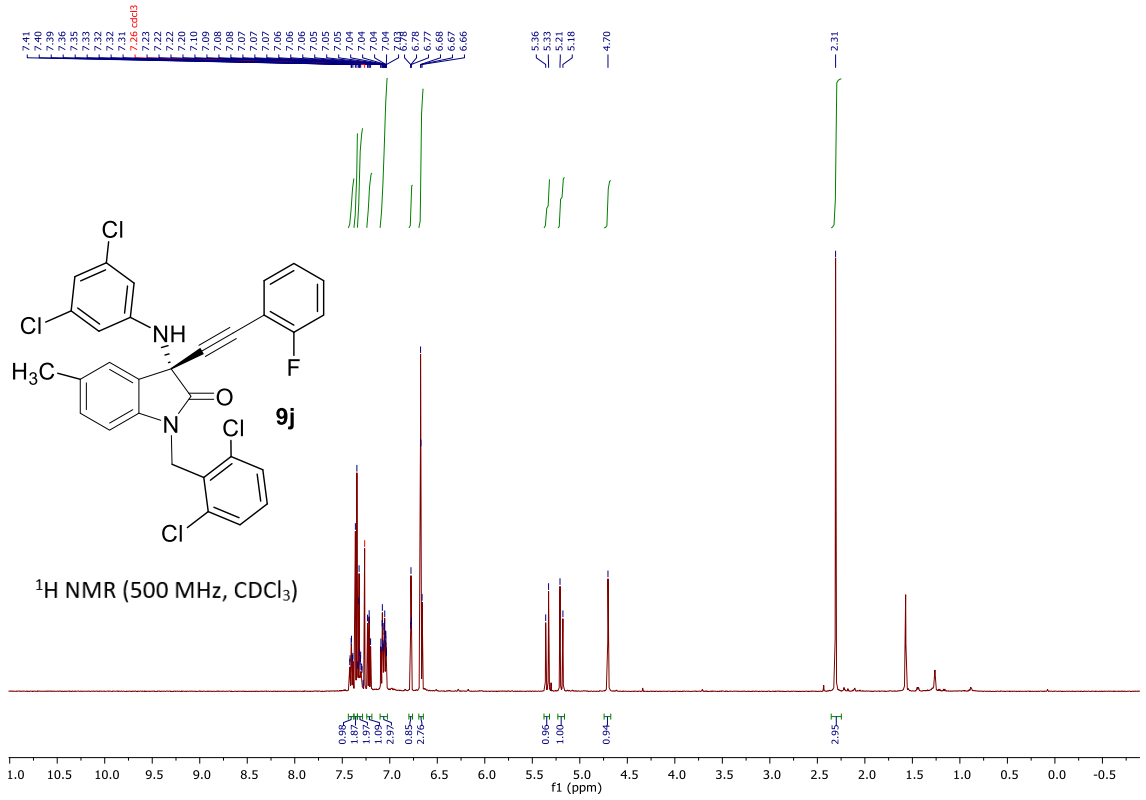


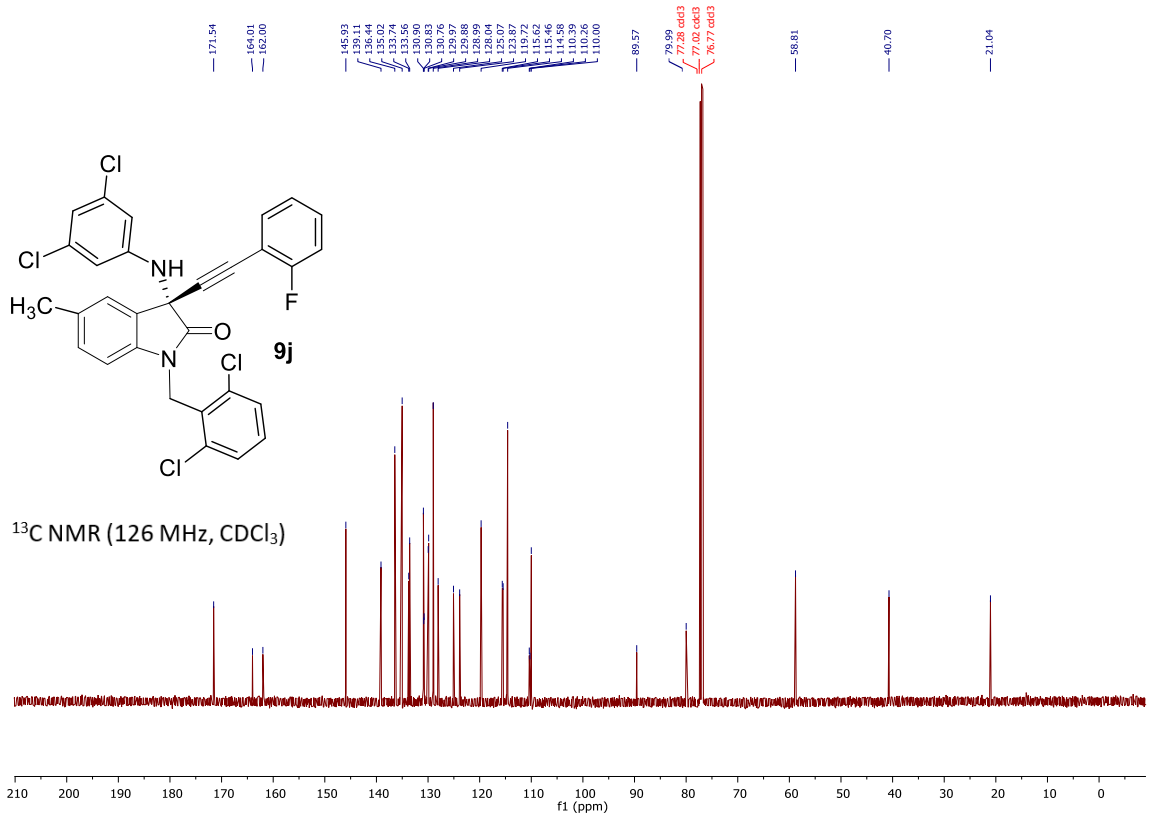
9h

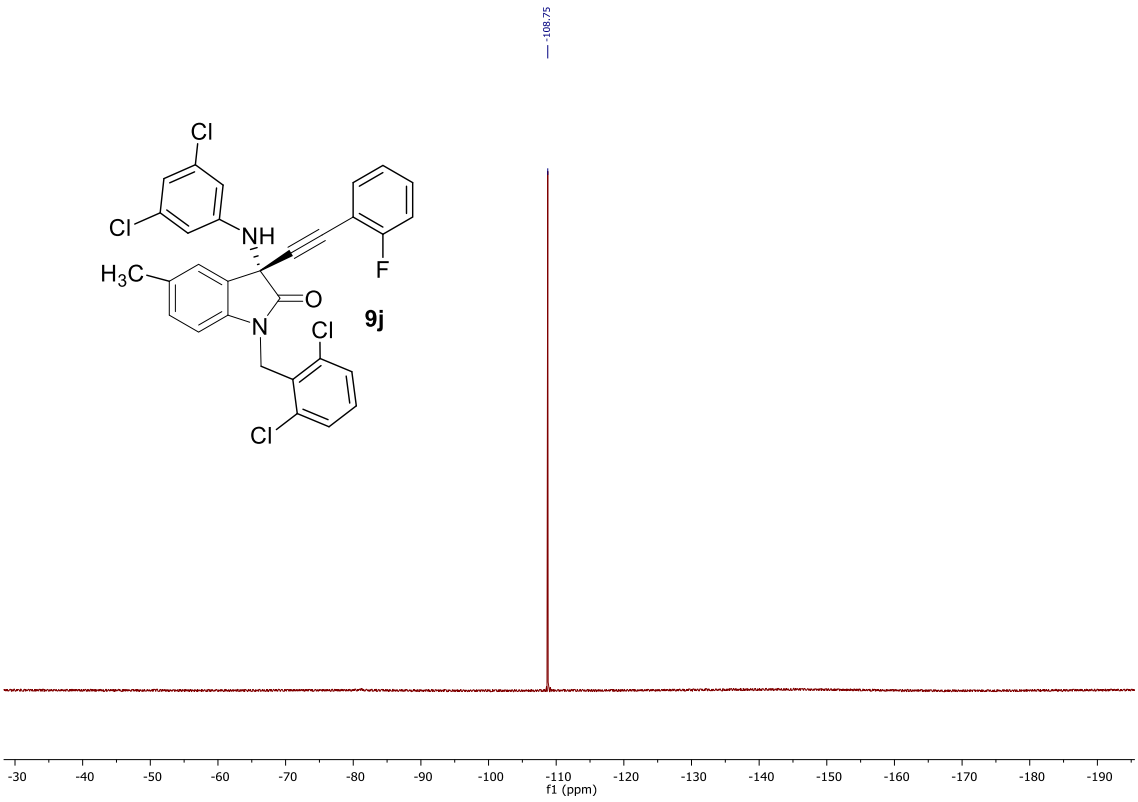
^{19}F NMR (470 MHz, $CDCl_3$)

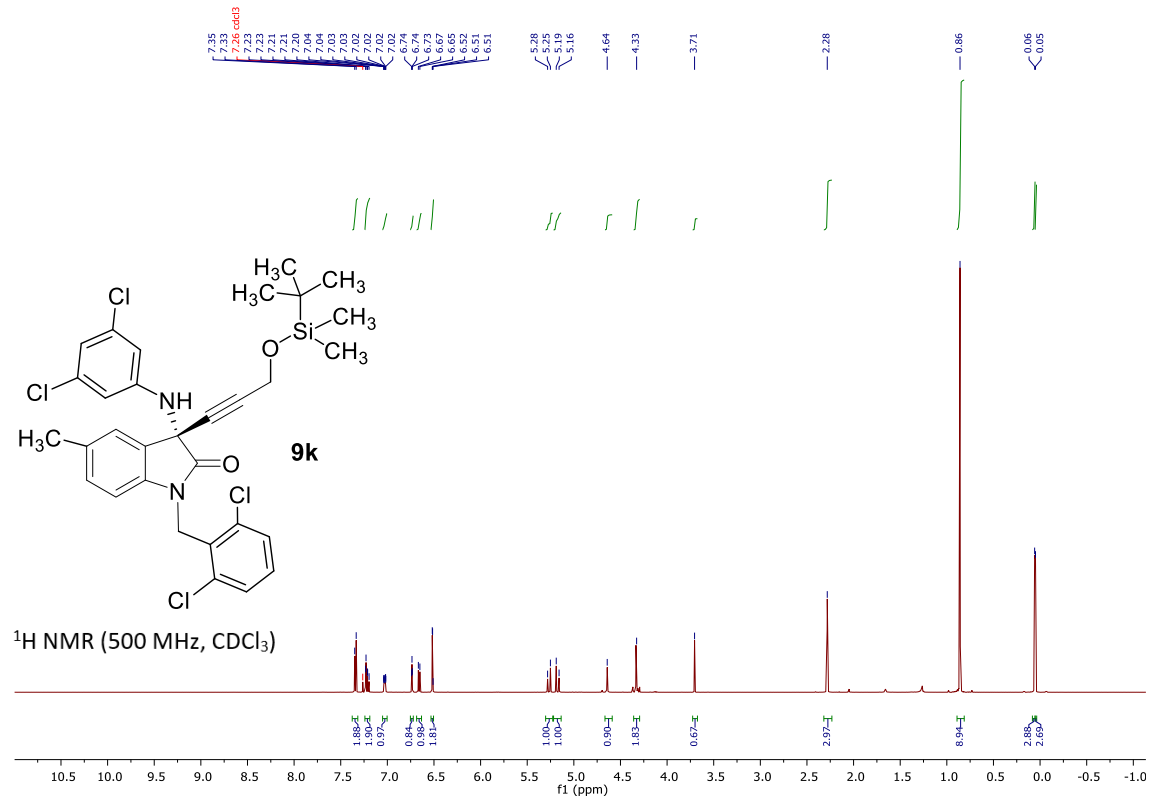

9i
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

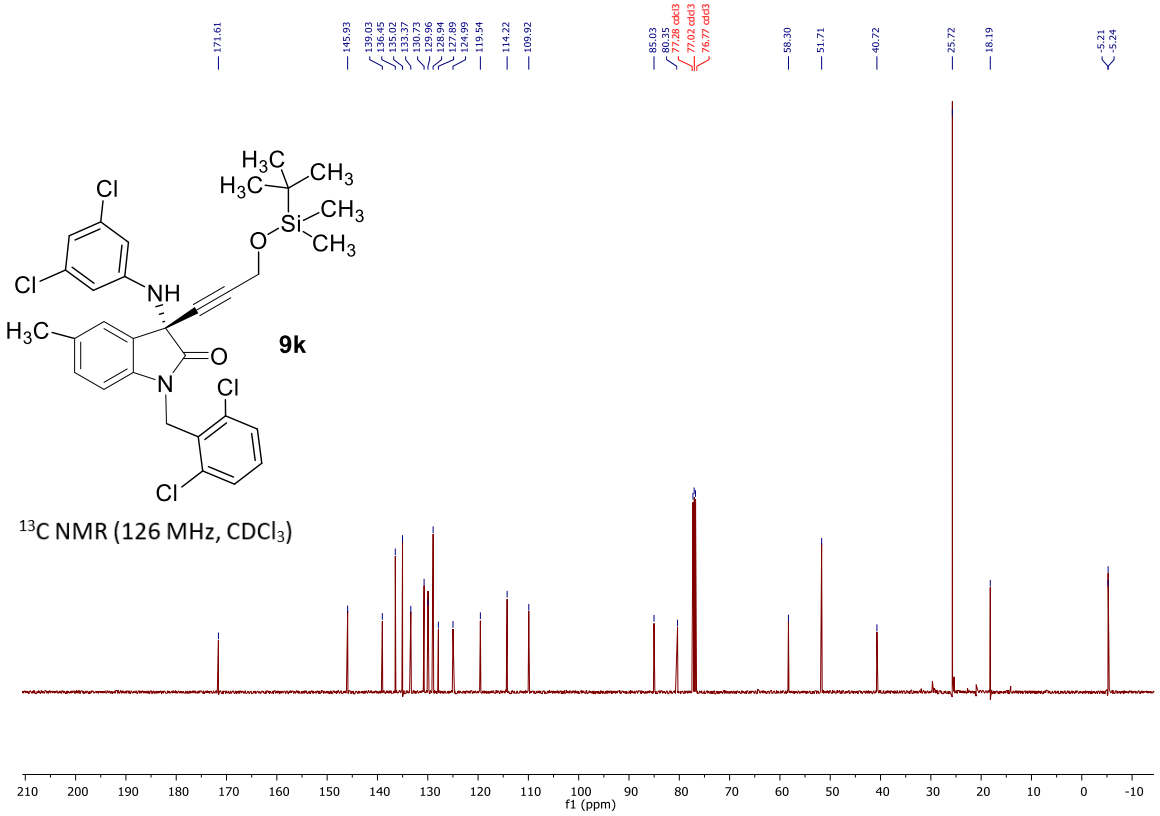

9i
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

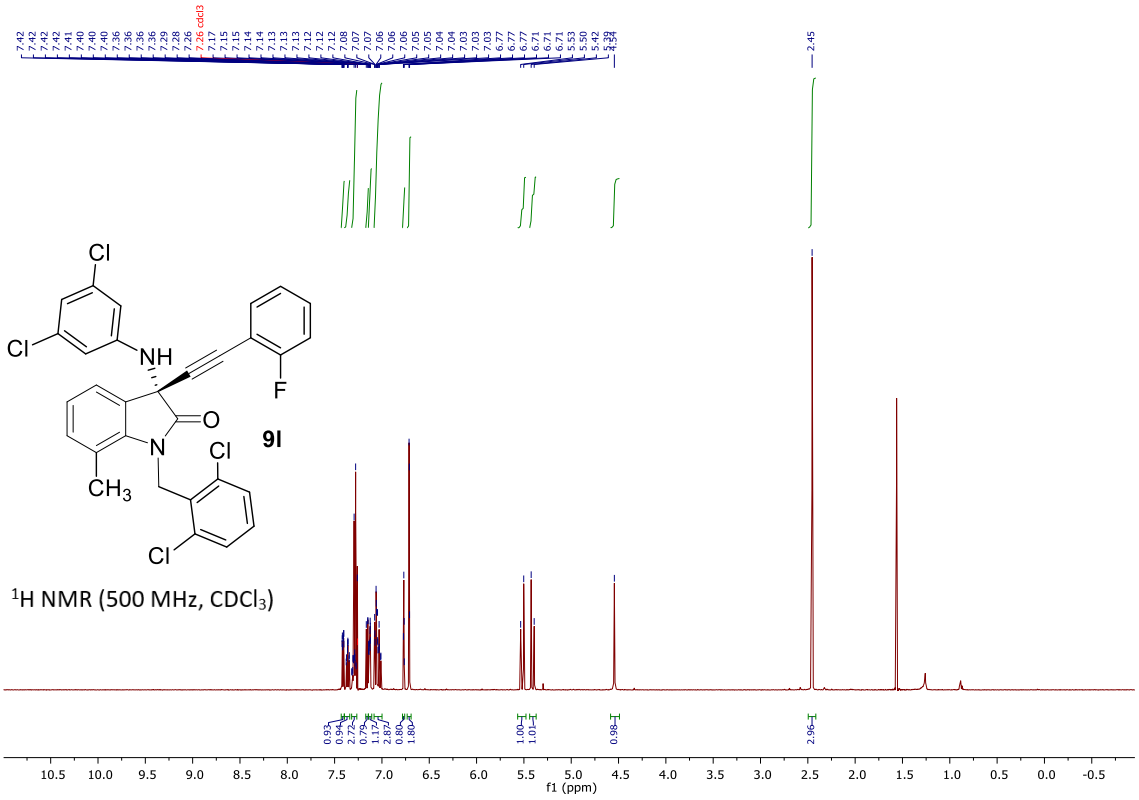

Cl
Cl
NH
F
H3C
O
N
Cl
Cl
9j
1H NMR (500 MHz, CDCl3)
f1 (ppm)

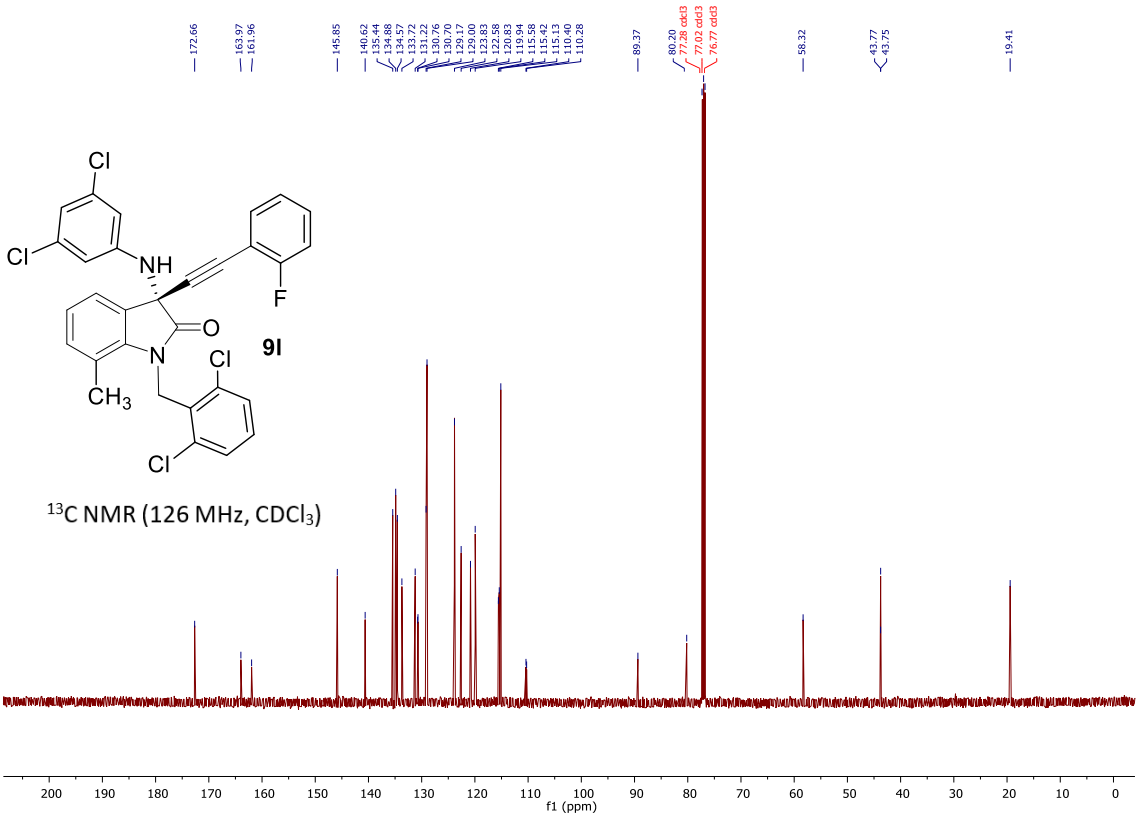

Cl
Cl
NH
F
H3C
O
N
Cl
Cl
9j
13C NMR (126 MHz, CDCl3)
f1 (ppm)

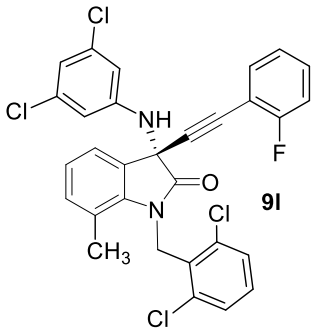

-108.75
Cl
Cl
NH
F
H3C
O
N
Cl
Cl
9j
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


9k
1H NMR (500 MHz, CDCl3)
f1 (ppm)


9k
13C NMR (126 MHz, CDCl3)
f1 (ppm)

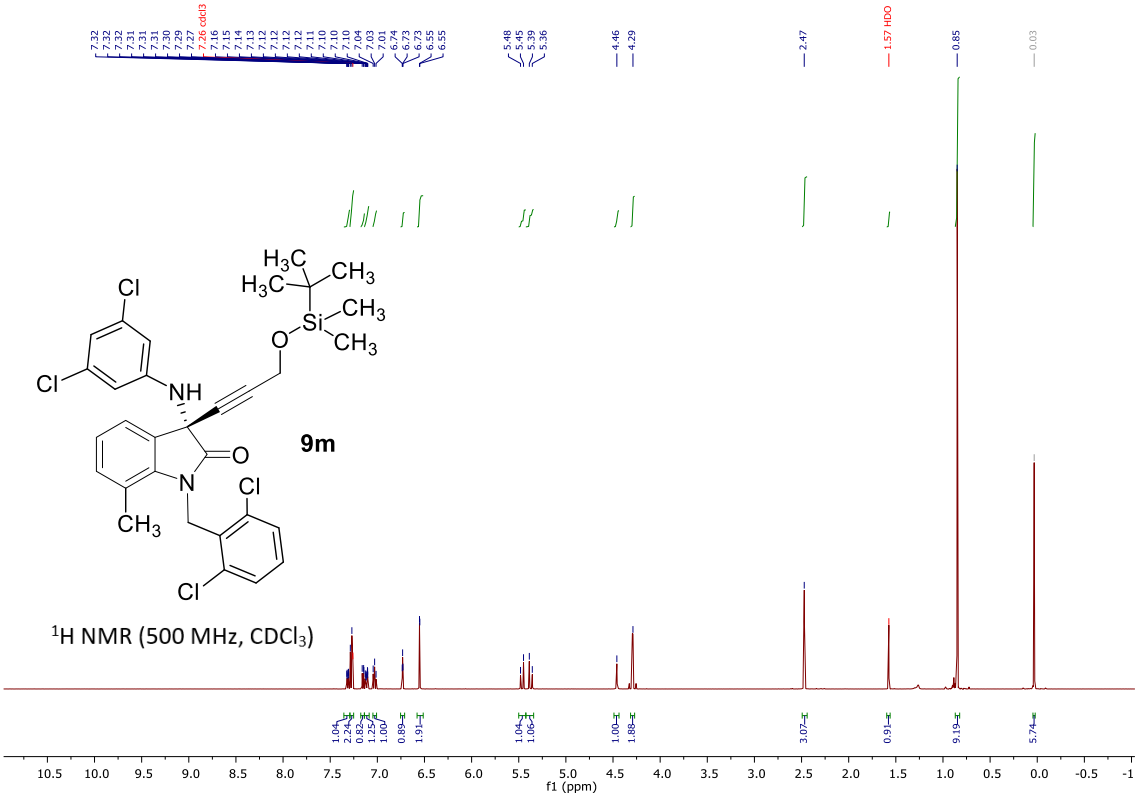

Cl
Cl
NH
F
O
N
Cl
CH3
Cl
9l
1H NMR (500 MHz, CDCl3)
f1 (ppm)

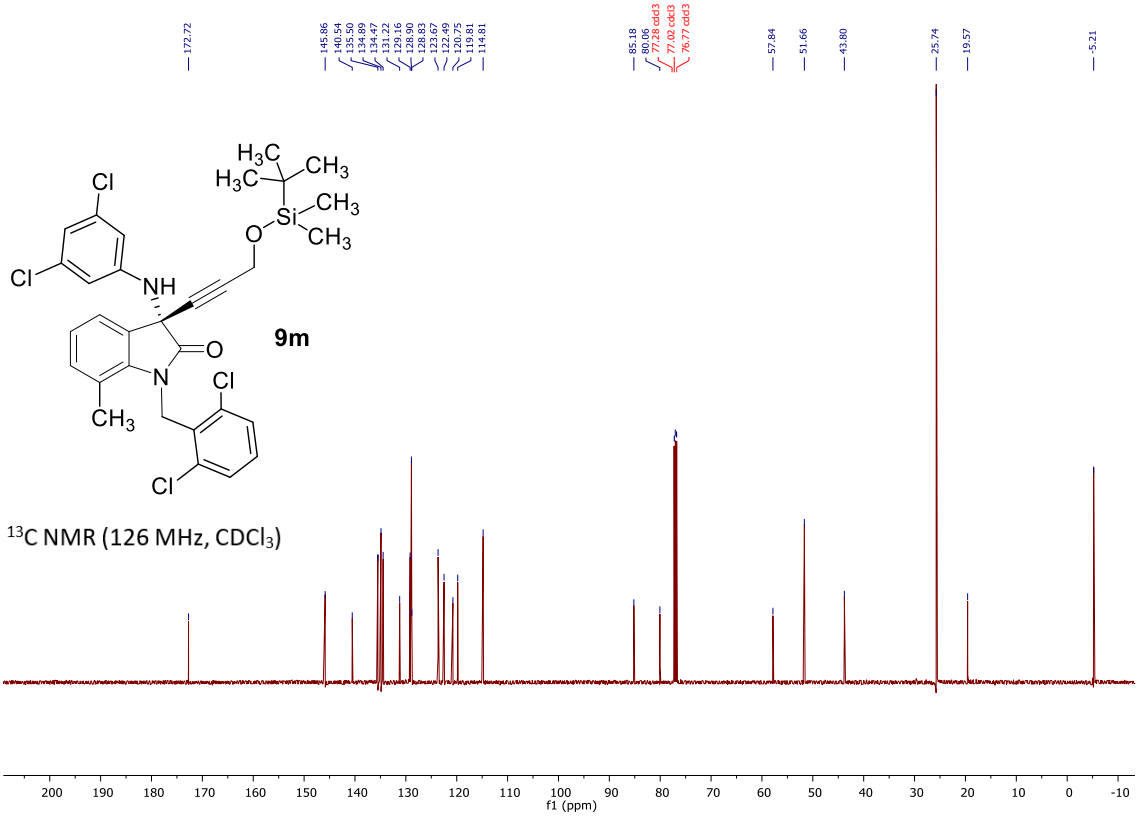

Cl
Cl
NH
F
O
N
Cl
CH3
Cl
9l
13C NMR (126 MHz, CDCl3)
f1 (ppm)



9l

^{19}F NMR (470 MHz, $CDCl_3$)


9m
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)

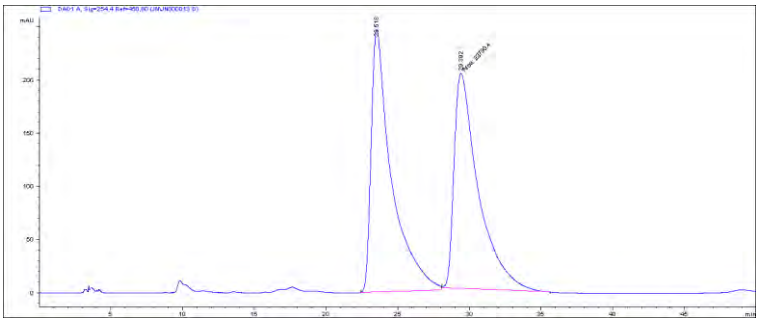

9m
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

7. HPLC Data.

(*R*)-3-hydroxy-1-methyl-3-(phenylethynyl)indolin-2-one (2a).

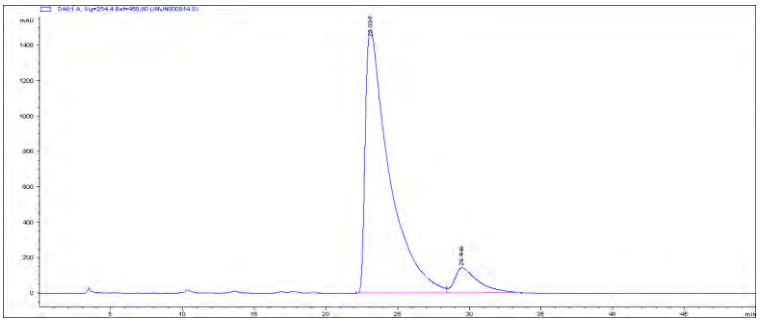
Chiralpak AS-H, hexane:isopropanol = 95:5 , 1 ml min^{-1}, λ = 254 nm: t_R (major) = 23.1 min, t_R (minor) = 29.5 min.

Racemic sample



#	Time	Area	Height	Width	Area%	Symmetry
1	23.518	24449.1	246.5	1.317	50.683	0.345
2	29.392	23790.4	202.2	1.9613	49.317	0.38

Enantioselective reaction, er = 91:9

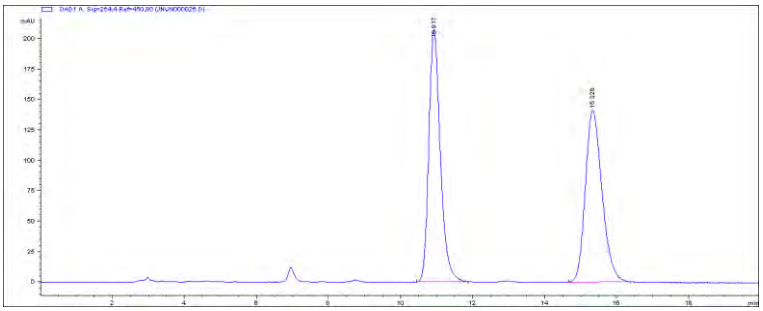


#	Time	Area	Height	Width	Area%	Symmetry
1	23.094	172895.1	1488.9	1.3708	91.450	0.272
2	29.449	16163.7	142.7	1.3727	8.550	0.42

(*R*)-1-benzyl-3-hydroxy-3-(phenylethynyl)indolin-2-one (2b).

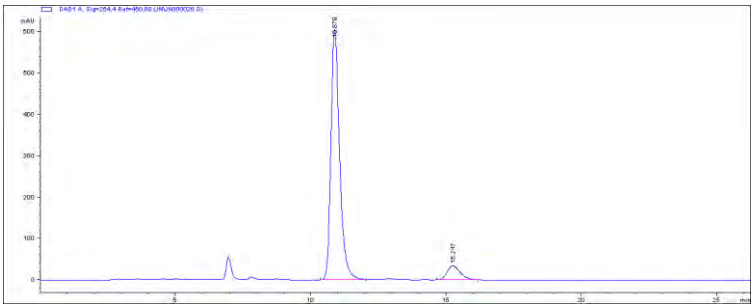
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 10.9 min, t_R (minor) = 15.2 min.

Racemic sample



#	Time	Area	Height	Width	Area%	Symmetry
1	10.917	4616.6	207.4	0.3397	50.370	0.729
2	15.326	4548.8	141.1	0.4881	49.630	0.748

Enantioselective reaction, er = 92:8

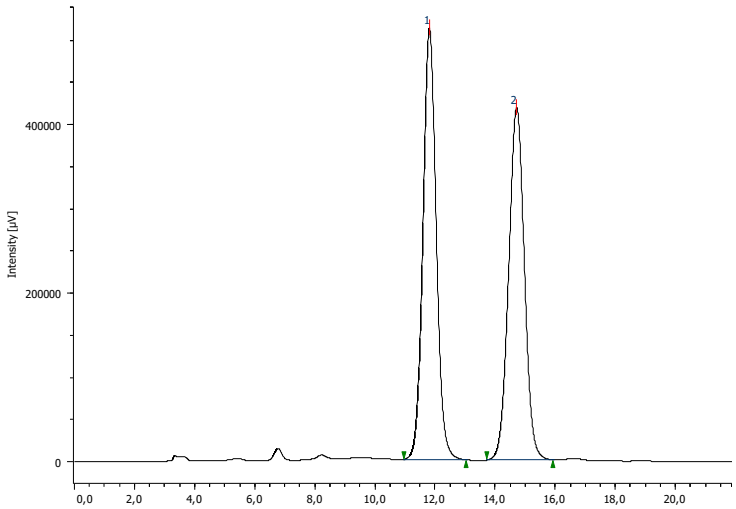


#	Time	Area	Height	Width	Area%	Symmetry
1	10.879	13522.2	605.7	0.3373	92.180	0.698
2	15.247	1147.1	34.2	0.4905	7.820	0.733

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(phenylethynyl)indolin-2-one (2c).

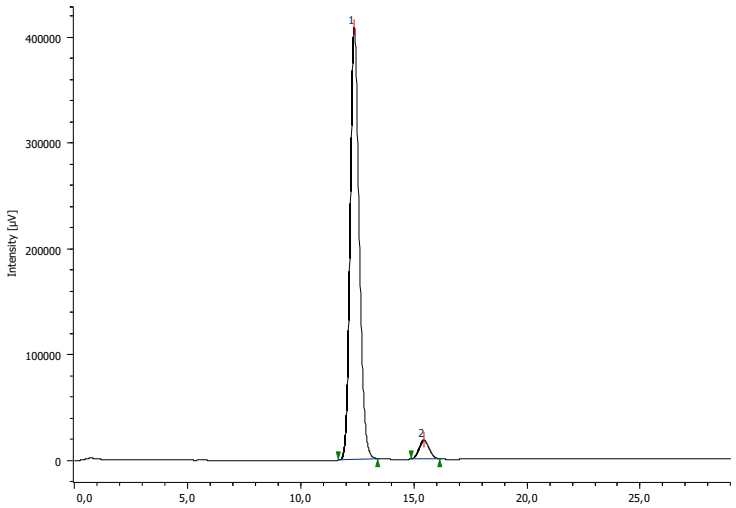
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 12.1 min, t_R (minor) = 15.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,800	15693724	511060	50,777	55,037	1,054
2	14,700	15213682	417523	49,223	44,963	0,999

Enantioselective reaction, er = 96:4

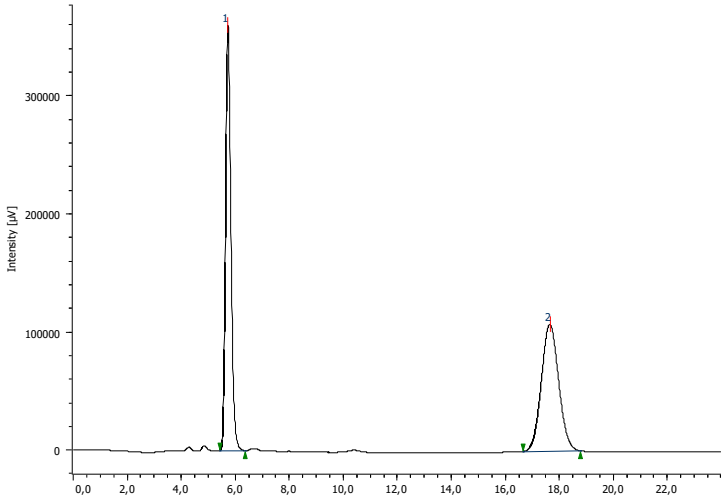


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	12,092	19263764	711684	96,346	96,780	1,190
2	15,100	730634	23678	3,654	3,220	1,108

(*R*)-3-hydroxy-3-(phenylethynyl)-1-tritylindolin-2-one (2d).

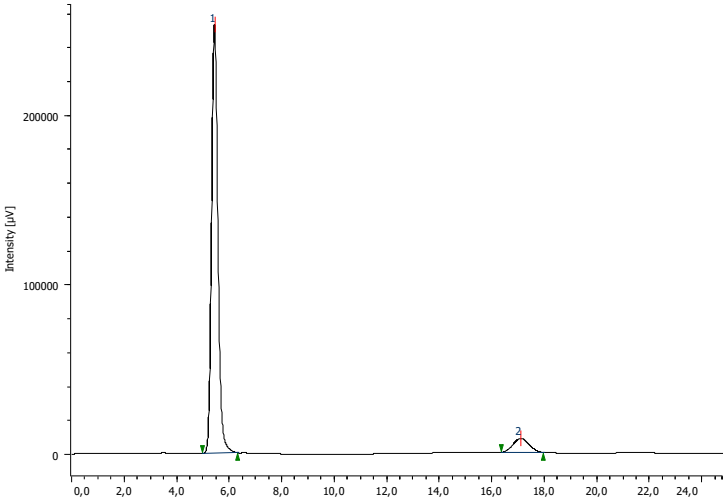
Chiralpak AD-H, hexane:isopropanol = 70:30 , 1 mL min^{-1}, λ = 254 nm: t_R (major) = 5.4 min, t_R (minor) = 17.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	5,725	4995101	359429	50,963	77,021	1,200
2	17,625	4806365	107235	49,037	22,979	1,059

Enantioselective reaction, er = 92:8

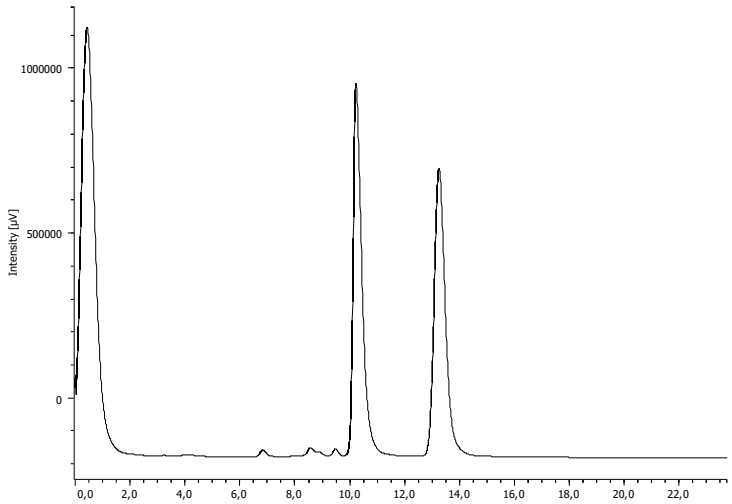


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	5,442	4169408	252007	92,334	96,892	1,156
2	17,092	346181	8083	7,666	3,108	1,062

(*R*)-1-acetyl-3-hydroxy-3-(phenylethynyl)indolin-2-one (2e).

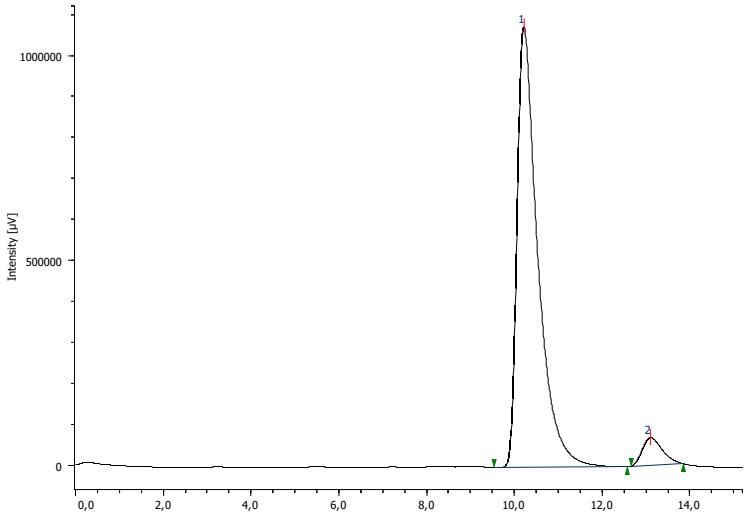
Chiralpak AS-H, hexane:isopropanol = 90:10 , 1 mL min^{-1}, λ = 254 nm: t_R (major) = 10.2 min, t_R (minor) = 13.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,217	24943107	1127694	50,316	56,462	1,782
2	13,233	24629997	869555	49,684	43,538	1,305

Enantioselective reaction, er = 93:7

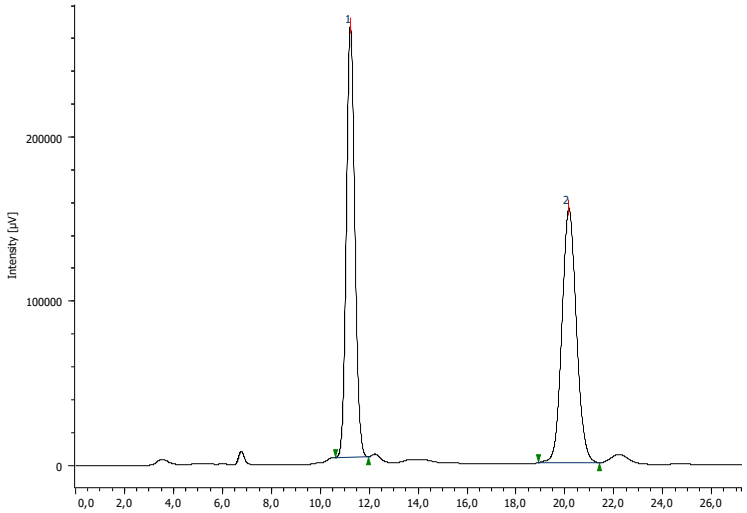


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,208	32827354	1072682	93,290	94,116	1,920
2	13,092	2361148	67062	6,710	5,884	1,344

(*R*)-3-hydroxy-3-(phenylethynyl)-1-tosylindolin-2-one (2f).

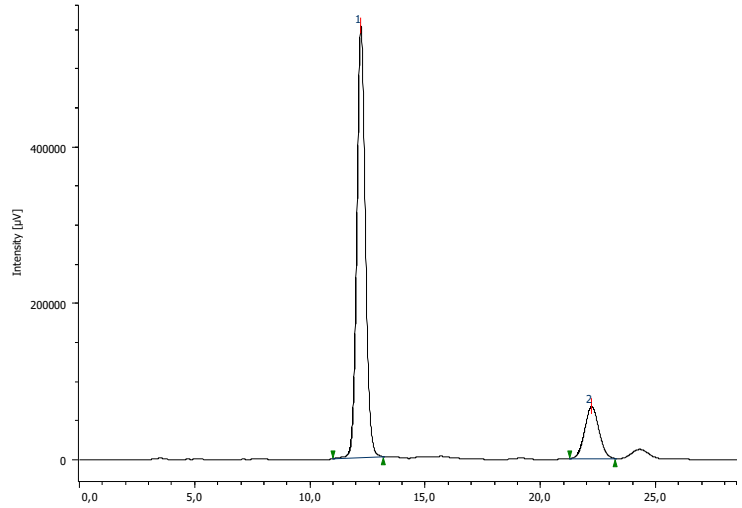
Chiralpak AD-H, hexane:isopropanol = 70:30 , 1 mL min^{-1}, λ = 254 nm: t_R (major) = 12.2 min, t_R (minor) = 22.2 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,217	6321805	262109	49,960	62,888	1,091
2	20,133	6331906	154679	50,040	37,112	1,092

Enantioselective reaction, er = 83:17

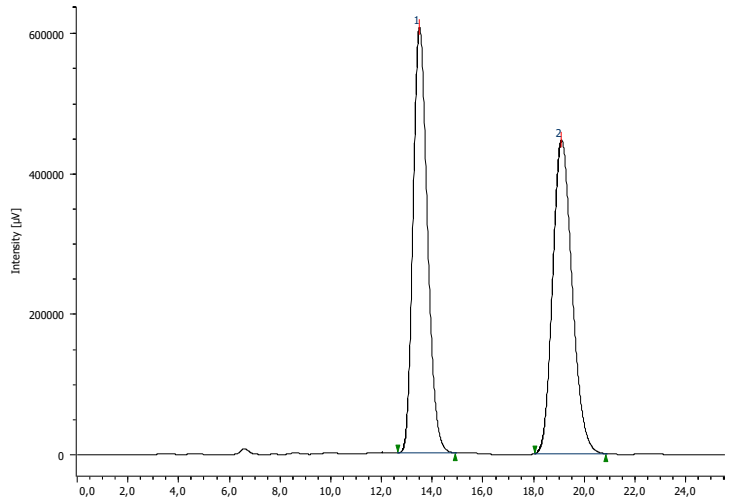


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	12,200	14179231	550338	83,158	89,251	1,068
2	22,192	2871699	66283	16,842	10,749	1,053

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-((4-methoxyphenyl)ethynyl)indolin-2-one (3a).

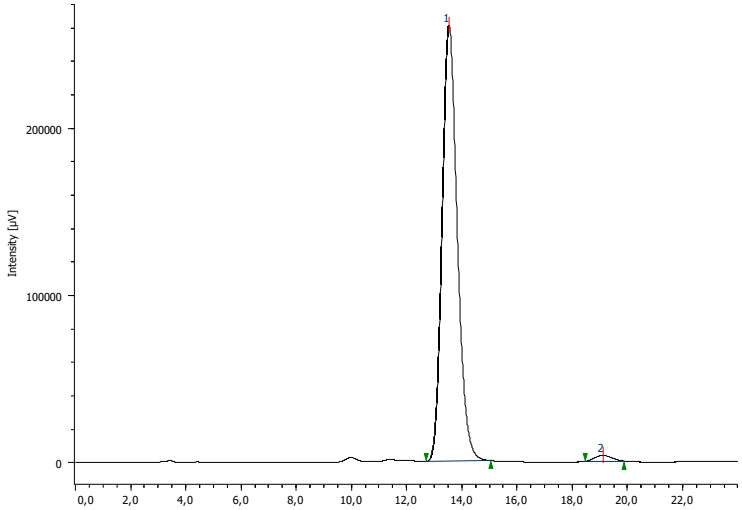
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 13.5 min, t_R (minor) = 19.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	13,483	23678390	604613	49,978	57,566	1,208
2	19,075	23699418	445680	50,022	42,434	1,189

Enantioselective reaction, er = 99:1

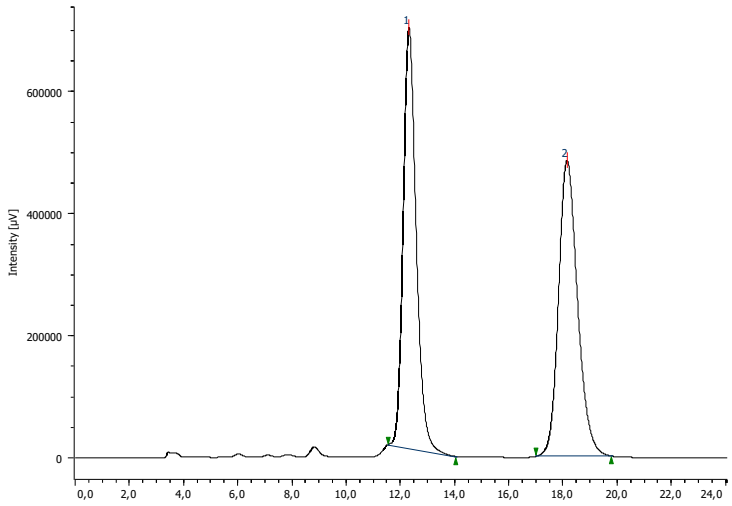


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	13,517	9862943	260309	98,530	98,708	1,206
2	19,092	147196	3407	1,470	1,292	1,078

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(p-tolylethynyl)indolin-2-one (3b).

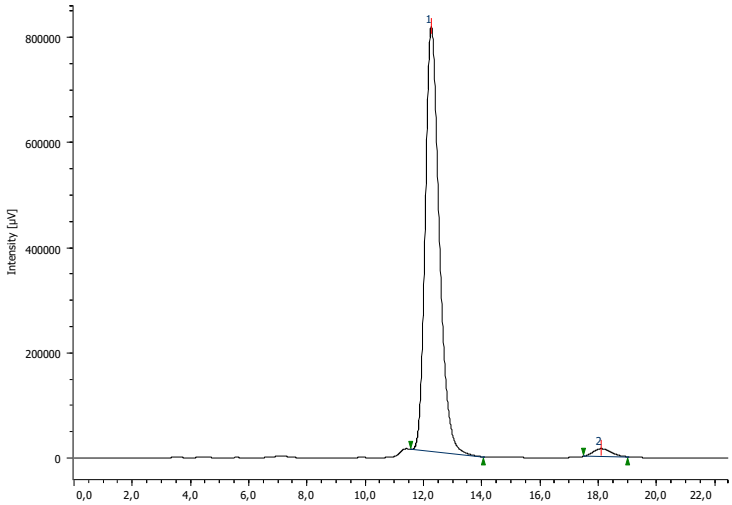
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 12.3 min, t_R (minor) = 18.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	12,300	22909432	687970	49,303	58,721	1,244
2	18,133	23556727	483621	50,697	41,279	1,195

Enantioselective reaction, er = 98:2

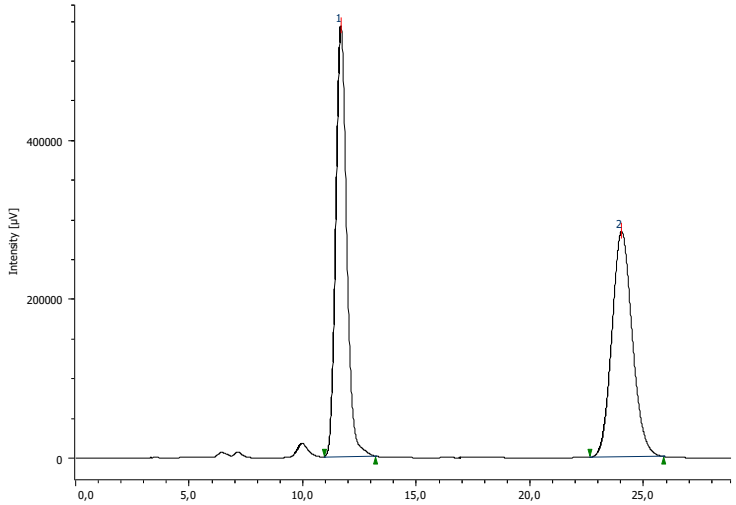


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	12,258	27000531	807052	97,660	98,172	1,266
2	18,083	646918	15031	2,340	1,828	1,193

(*R*)-3-((4-bromophenyl)ethynyl)-1-(2,6-dichlorobenzyl)-3-hydroxyindolin-2-one (3c).

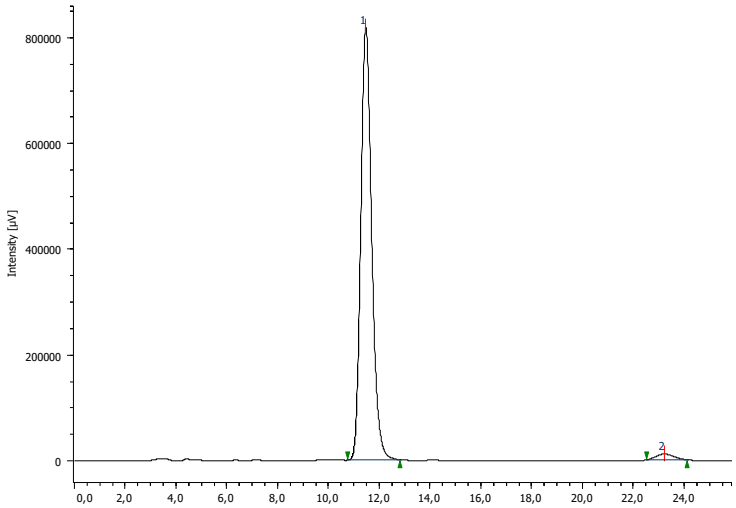
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 11.5 min, t_R (minor) = 23.2 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,667	17923699	541457	50,341	65,653	1,142
2	24,000	17681150	283264	49,659	34,347	1,121

Enantioselective reaction, er = 98:2

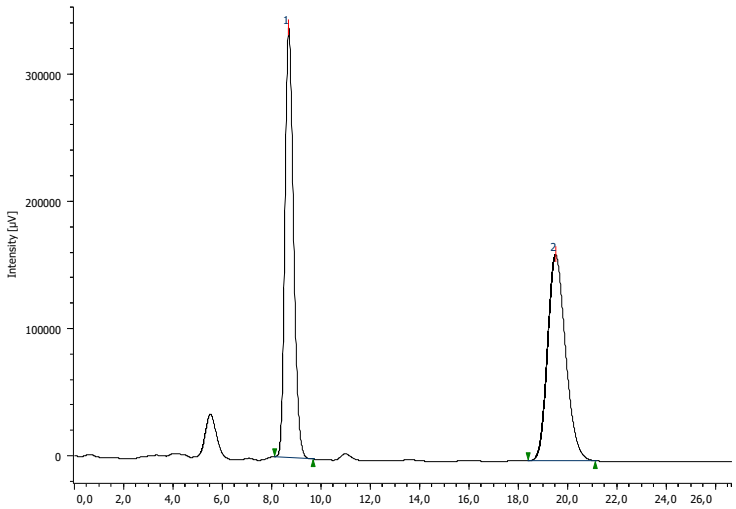


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,458	24539125	817193	97,867	98,682	1,184
2	23,192	534912	10917	2,133	1,318	1,131

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-((4-(trifluoromethyl)phenyl)ethynyl)indolin-2-one (3d).

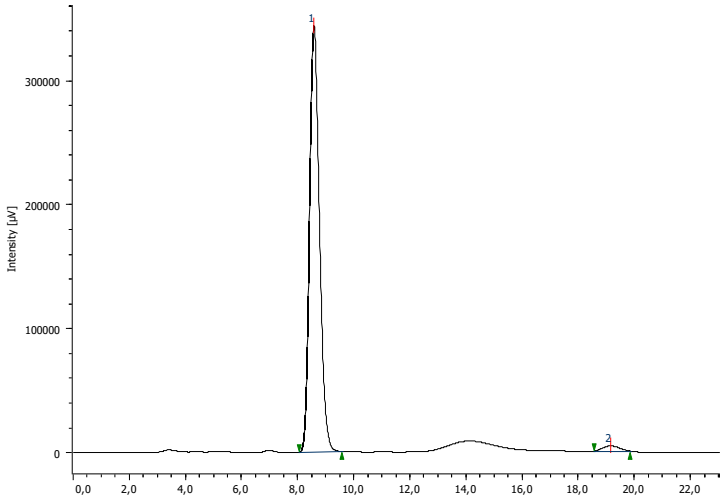
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 8.6 min, t_R (minor) = 19.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	8,683	8196550	337075	50,050	67,534	1,203
2	19,483	8180110	162042	49,950	32,466	1,226

Enantioselective reaction, er = 98:2

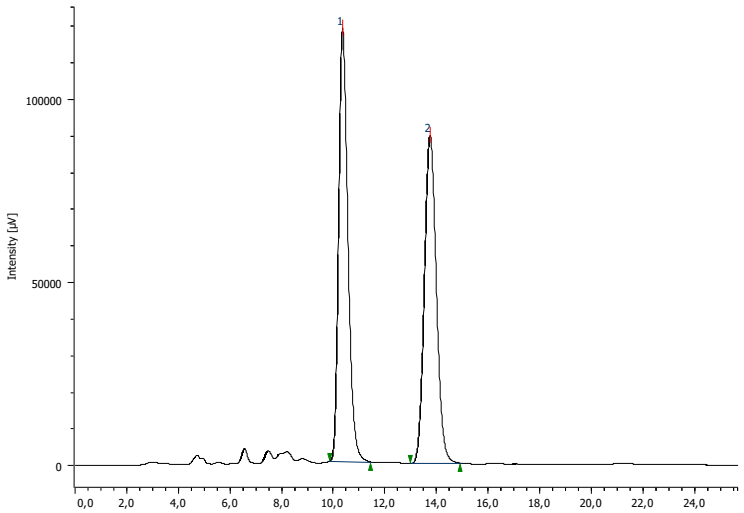


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	8,575	8398289	342965	97,969	98,772	1,210
2	19,133	174143	4263	2,031	1,228	1,083

Methyl (*R*)-4-((1-(2,6-dichlorobenzyl)-3-hydroxy-2-oxoindolin-3-yl)ethynyl)benzoate (3e).

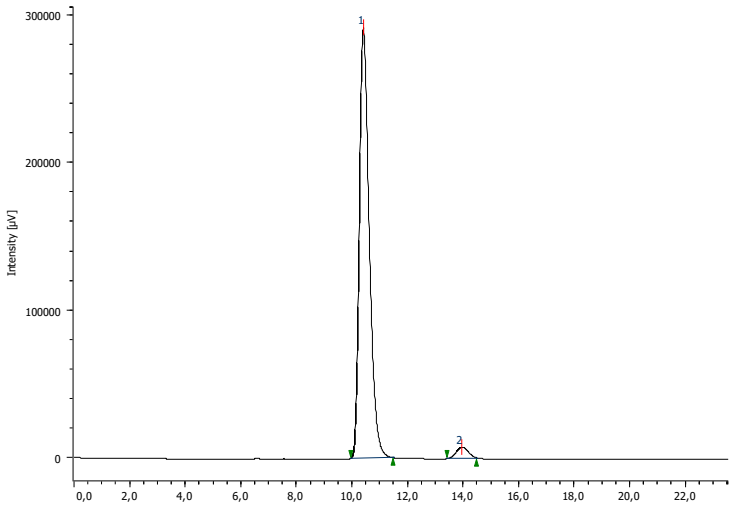
Phenomenex Lux-Cellulose-1, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 10.4 min, t_R (minor) = 13.9 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,350	2970144	118194	51,027	56,975	1,283
2	13,733	2850535	89257	48,973	43,025	1,117

Enantioselective reaction, er = 97:3

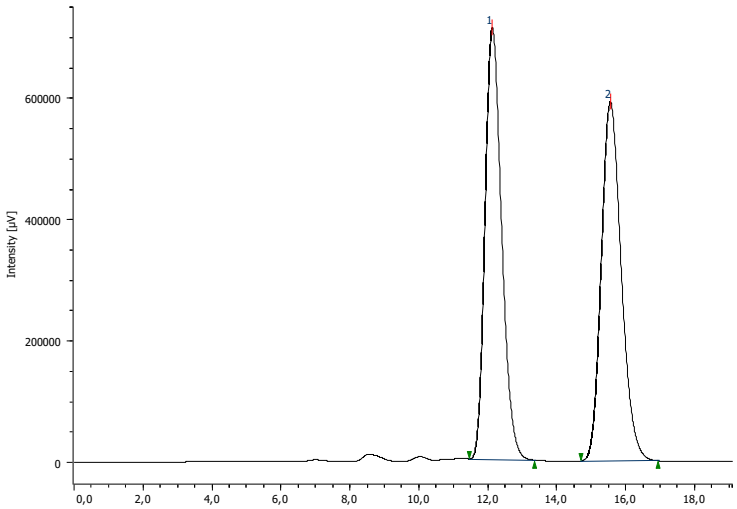


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,400	7256051	291102	97,017	97,520	1,391
2	13,950	223118	7403	2,983	2,480	1,021

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-((3-methoxyphenyl)ethynyl)indolin-2-one (3f).

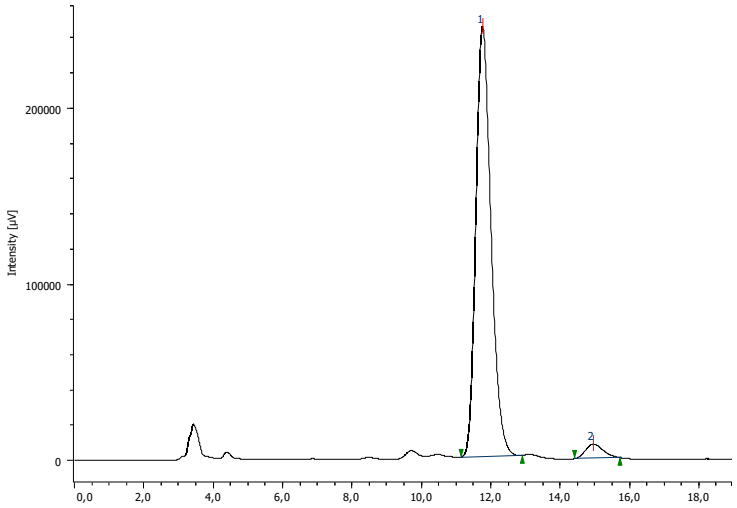
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 11.8 min, t_R (minor) = 14.9 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	12,117	23624311	709948	49,795	54,572	1,252
2	15,533	23818944	590980	50,205	45,428	1,198

Enantioselective reaction, 96:4

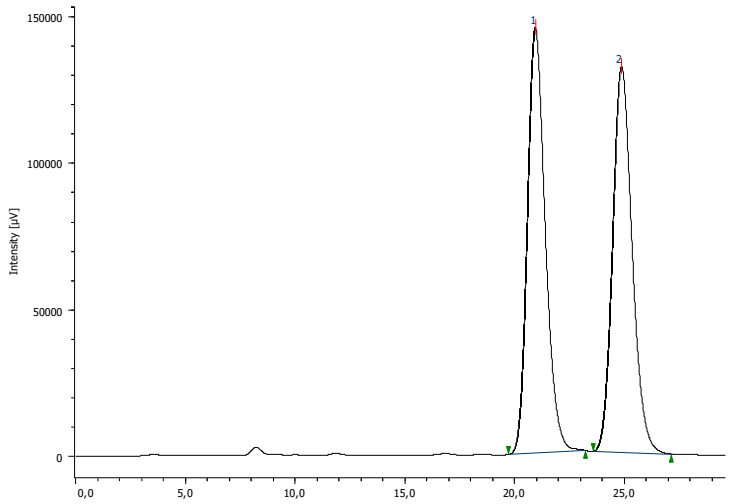


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,750	7359961	243454	96,276	96,795	1,247
2	14,942	284718	8060	3,724	3,205	1,238

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(m-tolylethynyl)indolin-2-one (3g).

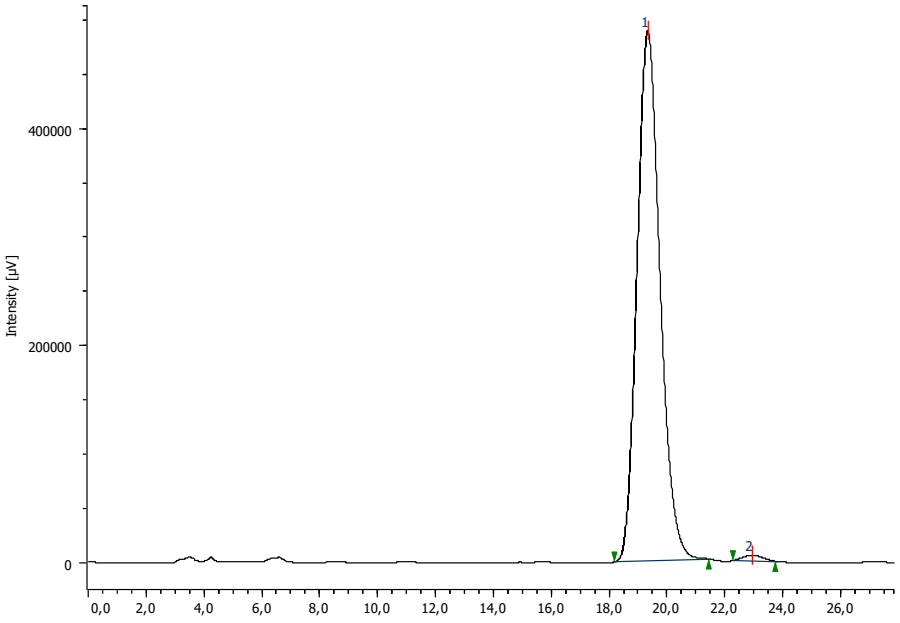
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 19.3 min, t_R (minor) = 22.9 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	20,917	8166796	144891	50,151	52,427	1,239
2	24,842	8117560	131479	49,849	47,573	1,171

Enantioselective reaction, er = 99:1

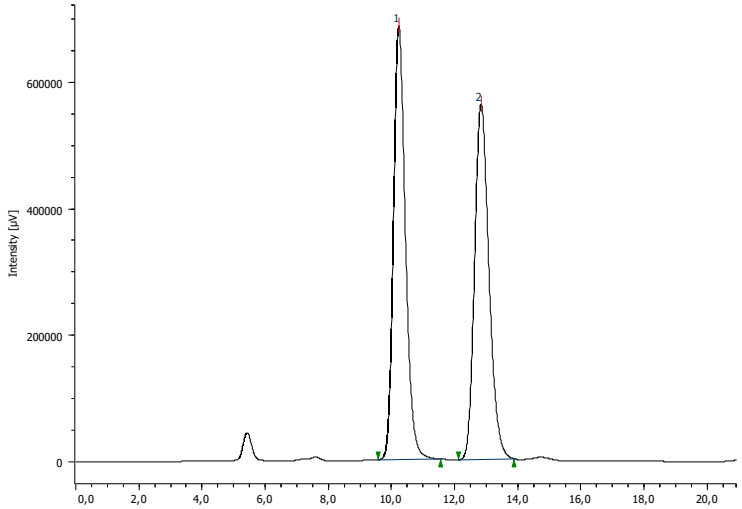


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	19,308	26899301	487777	99,081	98,935	1,179
2	22,917	249530	5253	0,919	1,065	1,090

(*R*)-3-((3-chlorophenyl)ethynyl)-1-(2,6-dichlorobenzyl)-3-hydroxyindolin-2-one (3h).

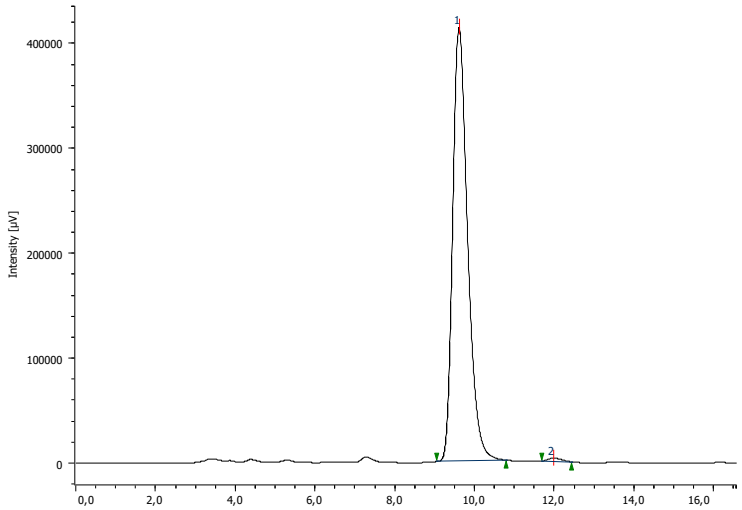
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 9.6 min, t_R (minor) = 12.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,217	17917447	684605	50,348	54,969	1,230
2	12,817	17669578	560836	49,652	45,031	1,224

Enantioselective reaction, 99:1

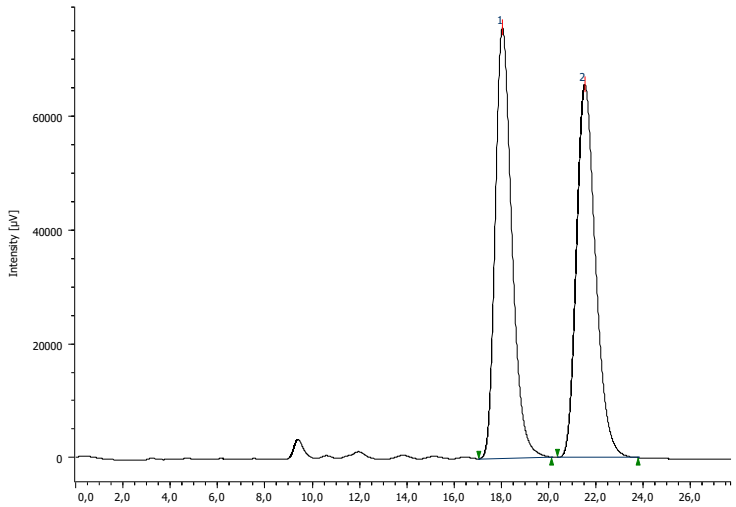


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	9,600	10605960	412798	99,292	99,227	1,347
2	11,975	75612	3214	0,708	0,773	1,218

(*R*)-1-(2,6-dichlorobenzyl)-3-((2-fluorophenyl)ethynyl)-3-hydroxyindolin-2-one (3i).

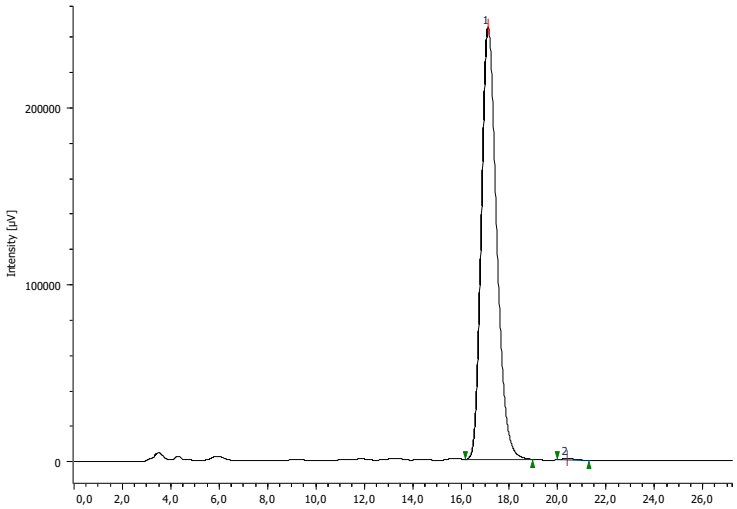
Chiralpak AD-H, hexane:isopropanol = 80:20, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 17.1 min, t_R (minor) = 20.4 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	18,017	3703129	75430	50,443	53,568	1,306
2	21,508	3638041	65382	49,557	46,432	1,256

Enantioselective reaction, er: >99:1

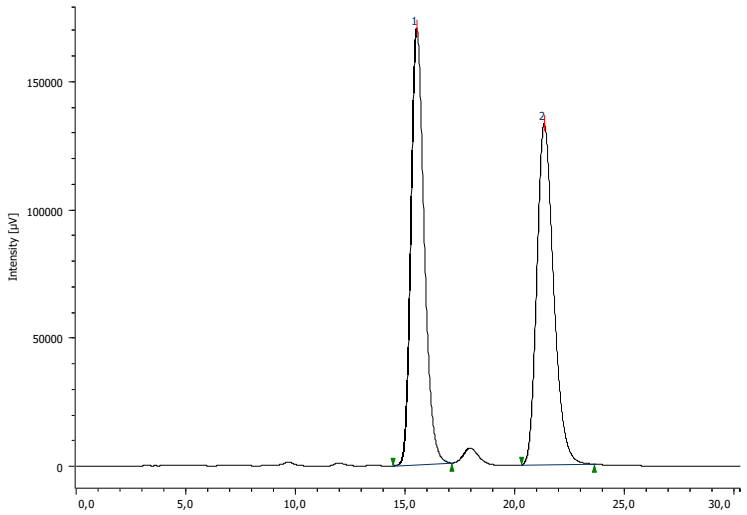


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	17,100	10675673	243944	99,723	99,708	1,254
2	20,358	29678	713	0,277	0,292	1,503

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-((2-(trifluoromethyl)phenyl)ethynyl)indolin-2-one (3j).

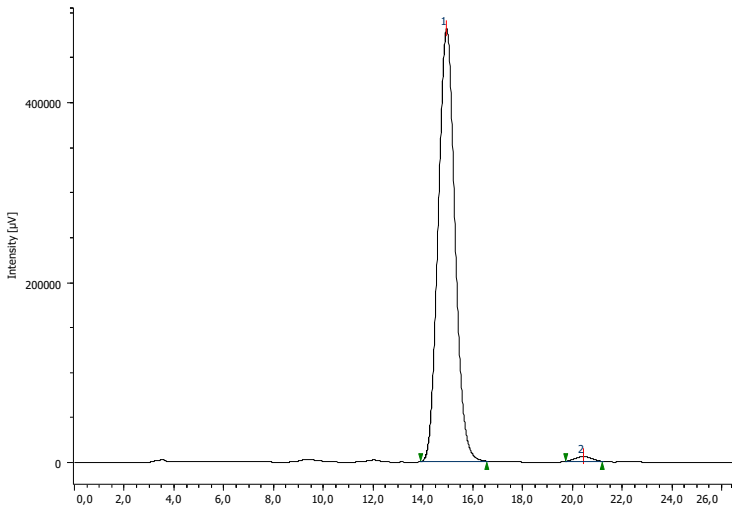
Chiralpak AD-H, hexane:isopropanol = 80:20, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 14.9 min, t_R (minor) = 20.4 min.

Racemic sample



#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	15,508	7132803	169899	50,083	56,100	1,273
2	21,308	7109075	132954	49,917	43,900	1,269

Enantioselective reaction, er = 99:1

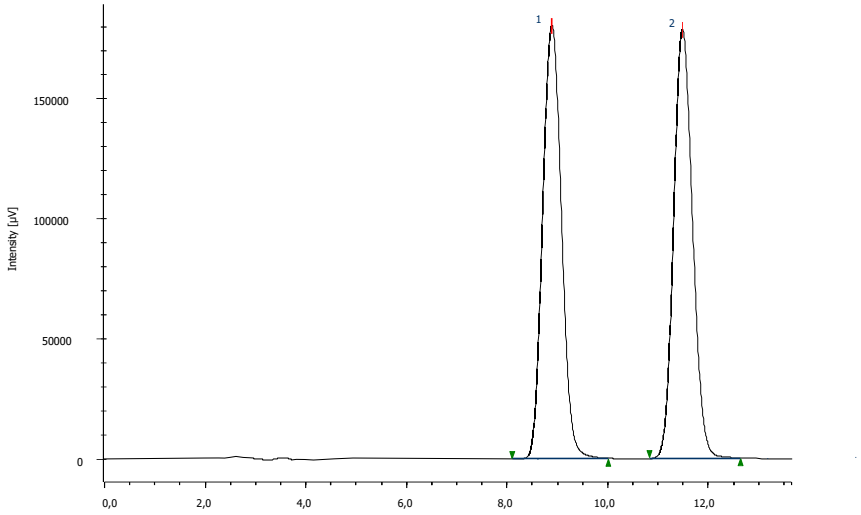


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	14,933	22449414	479903	98,897	98,914	1,068
2	20,425	250402	5271	1,103	1,086	1,012

(*R*)-1-(2,6-dichlorobenzyl)-3-(3,3-dimethylbut-1-yn-1-yl)-3-hydroxyindolin-2-one (3k).

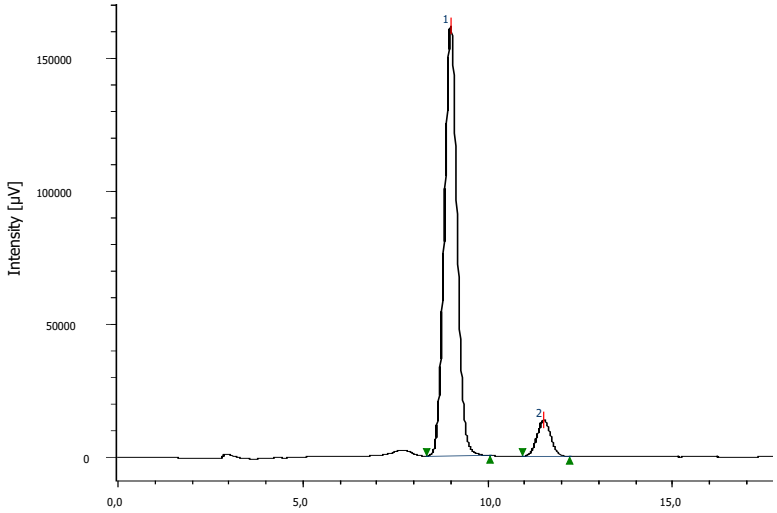
Phenomenex Lux-Cellulose-1, hexane:isopropanol = 90:10, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 9.0 min, t_R (minor)= 11.5 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	9,156	6860023	181043	50,284	50,255	1,080
2	11,545	6782597	179206	49,716	49,745	1,116

Enantioselective reaction, er = 92:8

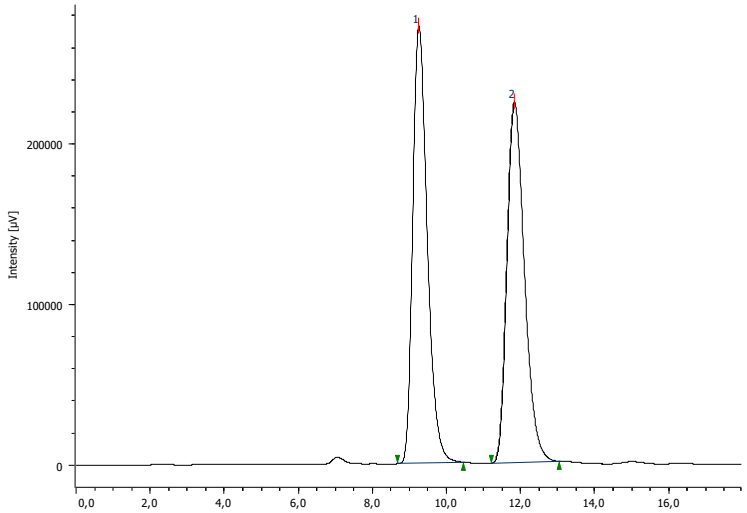


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	8,983	3876892	161128	91,665	92,205	1,043
2	11,500	352506	13621	8,335	7,795	1,021

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(oct-1-yn-1-yl)indolin-2-one (3l).

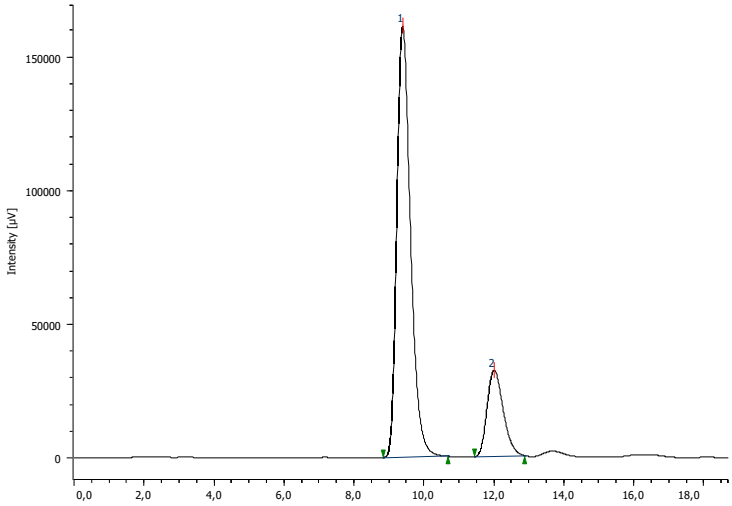
Chiralpak AD-H, hexane:isopropanol = 80:20, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 9.4, t_R (minor) = 12.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	9,242	7390368	271630	50,199	54,822	1,352
2	11,825	7331806	223847	49,801	45,178	1,297

Enantioselective reaction, er = 81:19

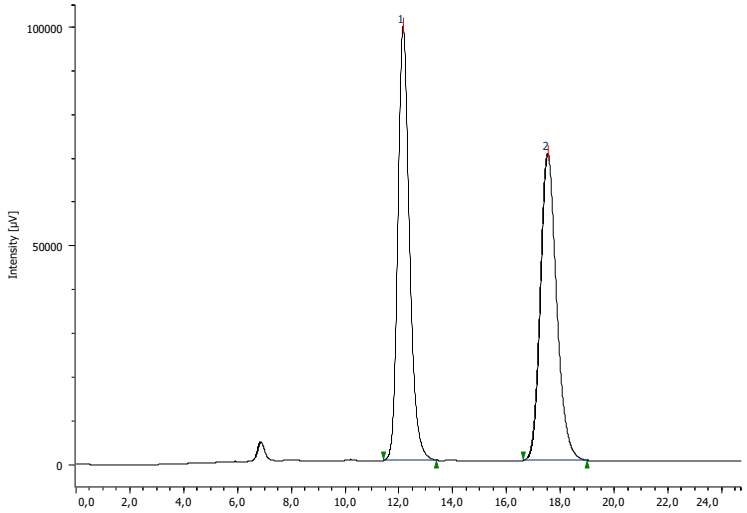


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	9,383	4355968	160910	80,913	83,324	1,343
2	11,992	1027561	32204	19,087	16,676	1,273

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(4-phenylbut-1-yn-1-yl)indolin-2-one (3m).

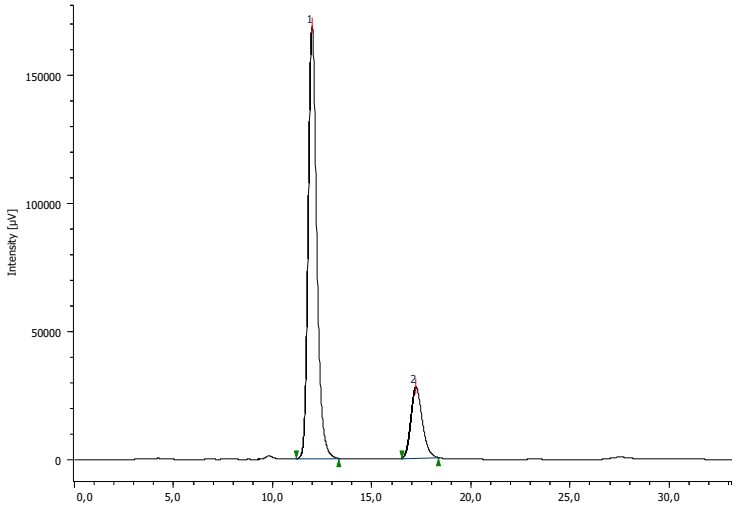
Chiralpak AD-H, hexane:isopropanol = 70:30 , 1 mL min^{-1}, λ = 254 nm: t_R (major) = 12.0 min, t_R (minor) = 17.2 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	12,142	2962496	99099	50,411	58,589	1,219
2	17,508	2914156	70043	49,589	41,411	1,214

Enantioselective reaction, er = 82:18

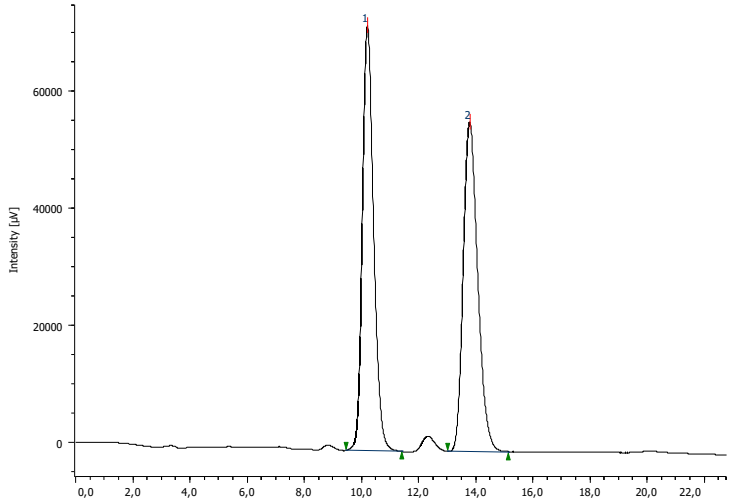


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,975	4961663	168331	81,795	85,899	1,245
2	17,200	1104302	27634	18,205	14,101	1,231

(*R*)-3-(4-bromobut-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-hydroxyindolin-2-one (3n).

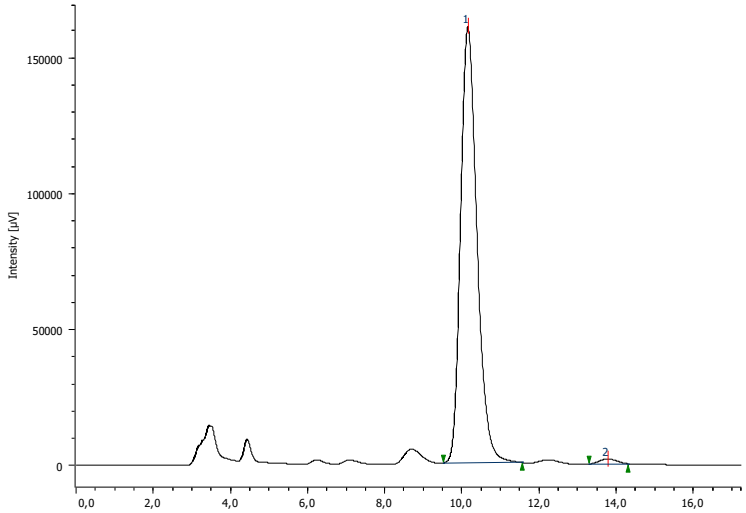
Chiralpak AD-H, hexane:isopropanol = 70:30 , 1 mL min^{-1}, λ = 254 nm: t_R (major) = 10.1 min, t_R (minor) = 13.8 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,200	1991764	72498	50,260	56,360	1,211
2	13,775	1971154	56137	49,740	43,640	1,237

Enantioselective reaction, er = 99:1

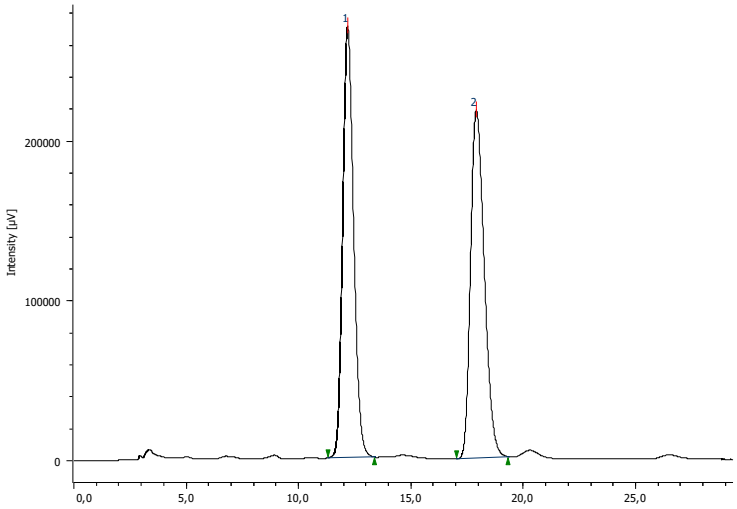


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,142	4701559	160353	98,771	98,848	1,266
2	13,758	58507	1869	1,229	1,152	1,084

(*S*)-1-(2,6-dichlorobenzyl)-3-hydroxy-3-((trimethylsilyl)ethynyl)indolin-2-one (3o).

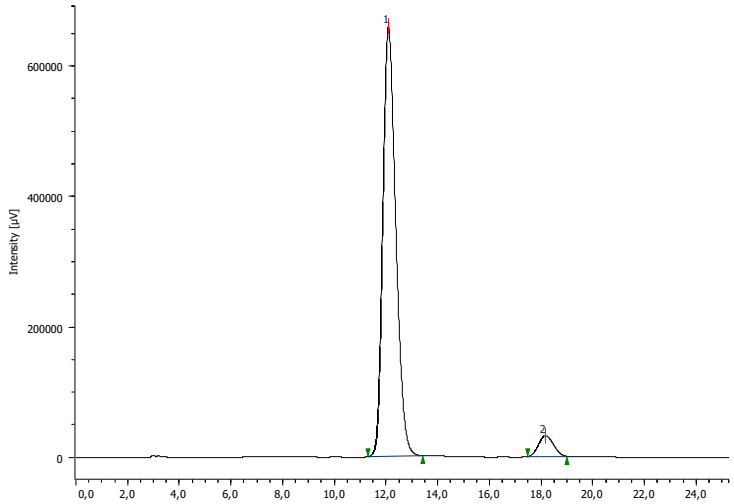
Phenomenex Lux-Cellulose-1, hexane:isopropanol = 95:5 , 1 mL min^{-1}, λ = 254 nm: t_R (major) = 12.1 min, t_R (minor) = 18.2 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	12,167	9123669	269698	49,801	55,372	1,185
2	17,892	9196432	217371	50,199	44,628	1,289

Enantioselective reaction, er = 95:5

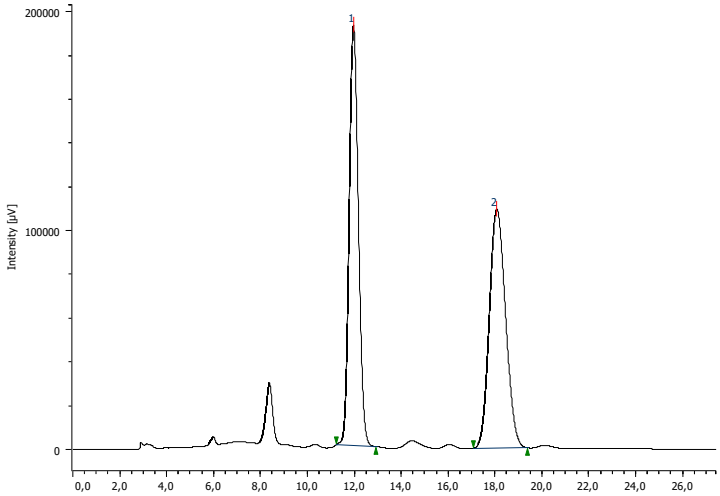


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	12,075	23012119	657697	94,734	95,370	1,264
2	18,150	1279240	31929	5,266	4,630	1,079

(*R*)-3-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-hydroxyindolin-2-one (3p).

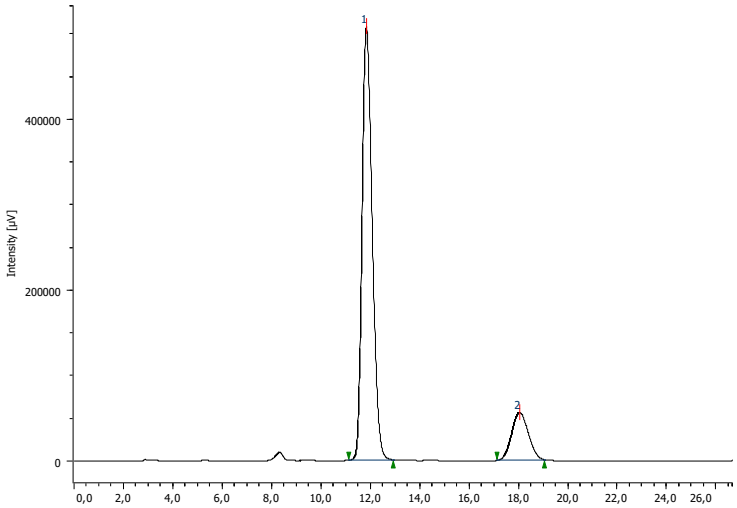
Phenomenex Lux-Cellulose-1, hexane:isopropanol = 90:10, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 11.8 min, t_R (minor) = 18.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,950	5220459	191695	49,806	63,718	1,135
2	18,058	5261167	109154	50,194	36,282	1,129

Enantioselective reaction, er = 85:15

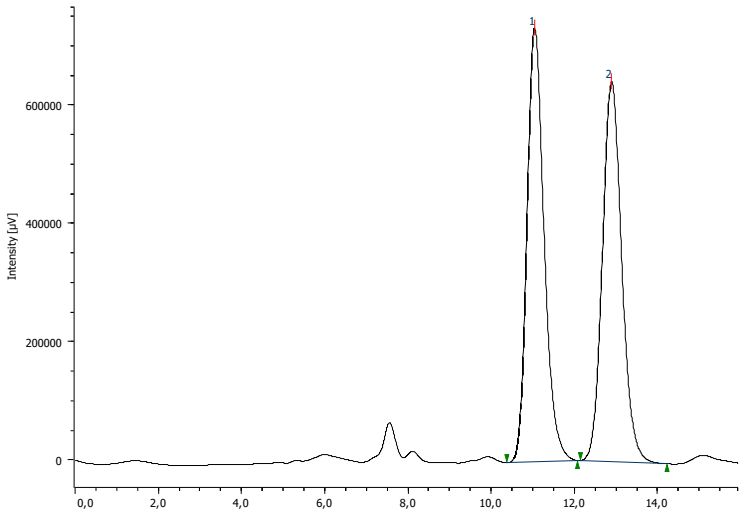


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,825	14522859	506608	84,668	90,083	1,268
2	18,025	2629861	55770	15,332	9,917	1,073

(*R*)-1-(2,6-dichlorobenzyl)-5-fluoro-3-hydroxy-3-(phenylethynyl)indolin-2-one (4a).

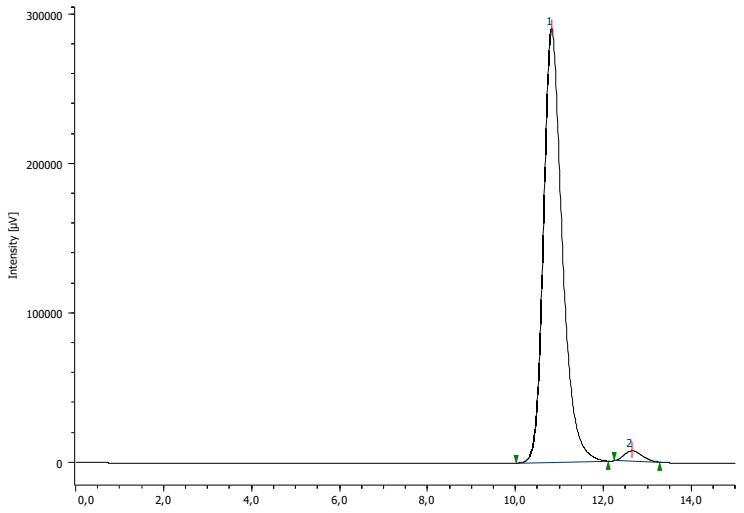
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 10.8 min, t_R (minor) = 12.6 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,025	20942047	731914	50,377	53,308	1,250
2	12,875	20628390	641071	49,623	46,692	1,128

Enantioselective reaction, er = 98:2

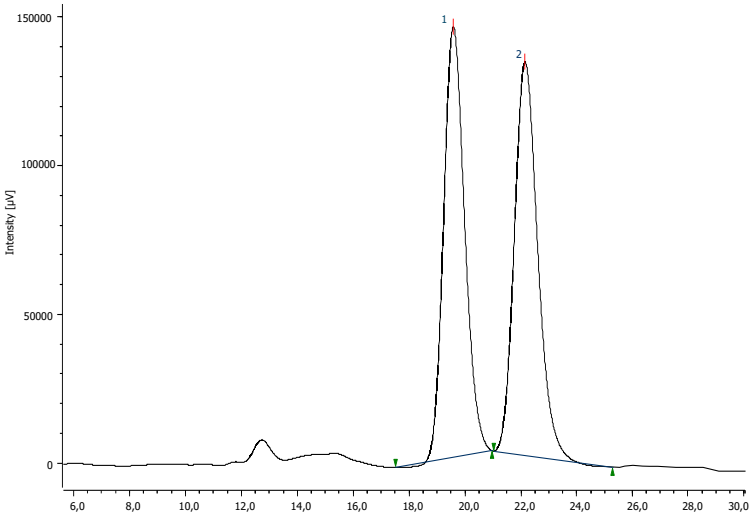


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,808	8579771	290087	97,728	97,641	1,299
2	12,633	199493	7010	2,272	2,359	1,221

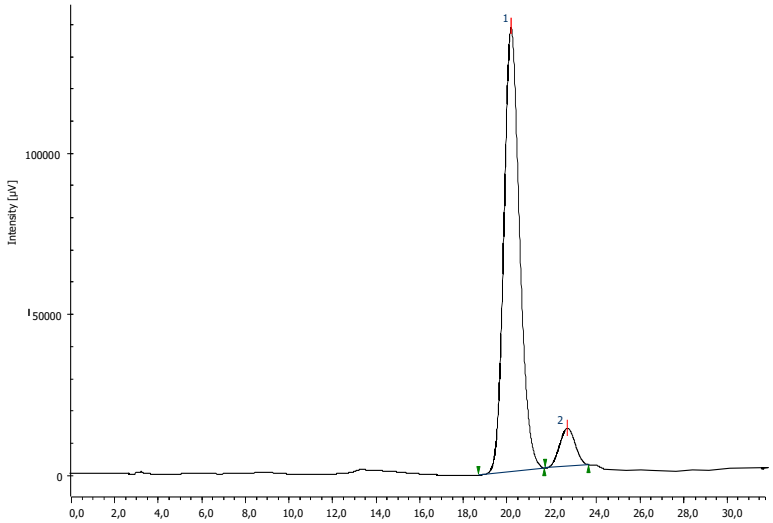
(*R*)-5-chloro-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(phenylethynyl)indolin-2-one (4b).

Chiralpak AD-H, hexane:isopropanol = 85:15, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 20.1 min, t_R (minor) = 22.7 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	19,567	7570414	144648	49,718	52,282	1,157
2	22,125	7656352	132019	50,282	47,718	1,206

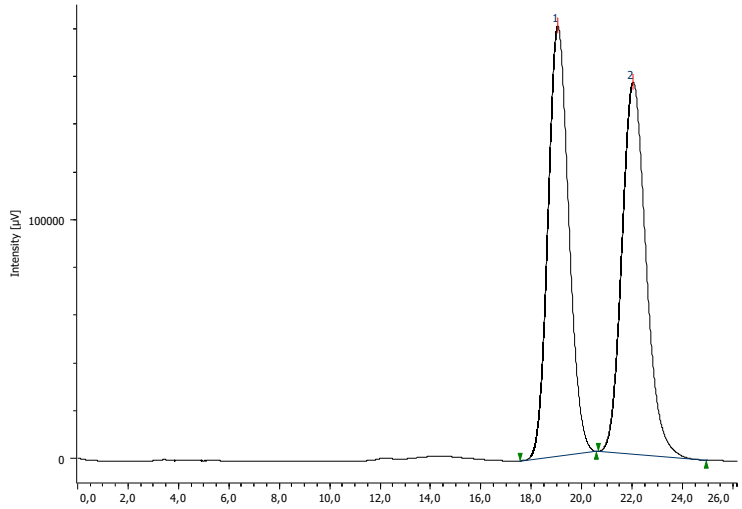


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	20,100	6859223	137435	92,058	92,032	1,171
2	22,658	591789	11900	7,942	7,968	1,009

(*R*)-5-bromo-1-(2,6-dichlorobenzyl)-3-hydroxy-3-(phenylethynyl)indolin-2-one (4c).

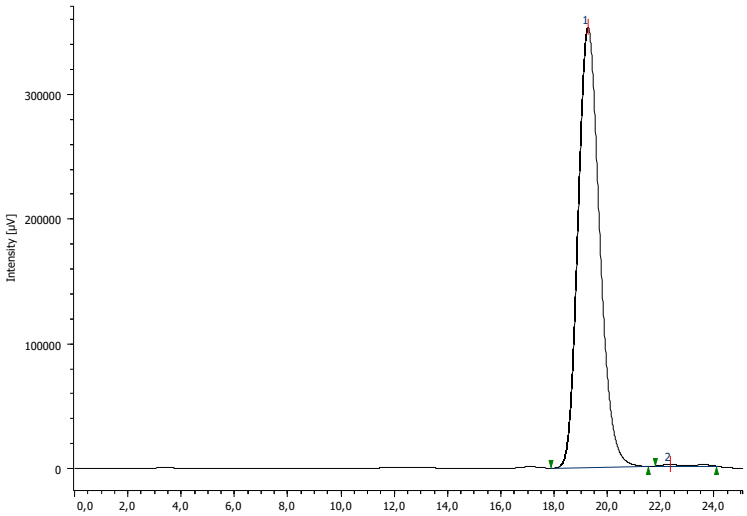
Chiralpak AD-H, hexane:isopropanol = 85:15, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 19.3 min, t_R (minor) = 22.3 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	19,025	10324358	180036	50,127	53,615	1,111
2	22,008	10272127	155756	49,873	46,385	1,178

Enantioselective reaction, er = 99:1

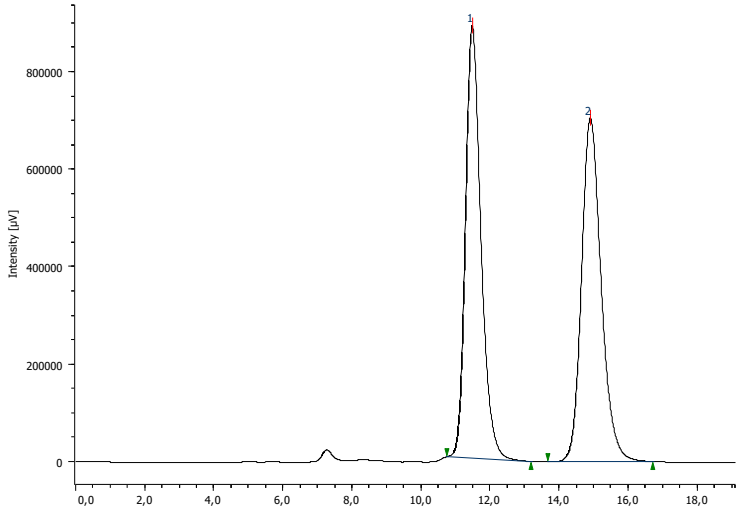


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	19,250	19767803	352281	99,458	99,627	1,183
2	22,325	107632	1321	0,542	0,373	2,071

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-5-methyl-3-(phenylethynyl)indolin-2-one (4d).

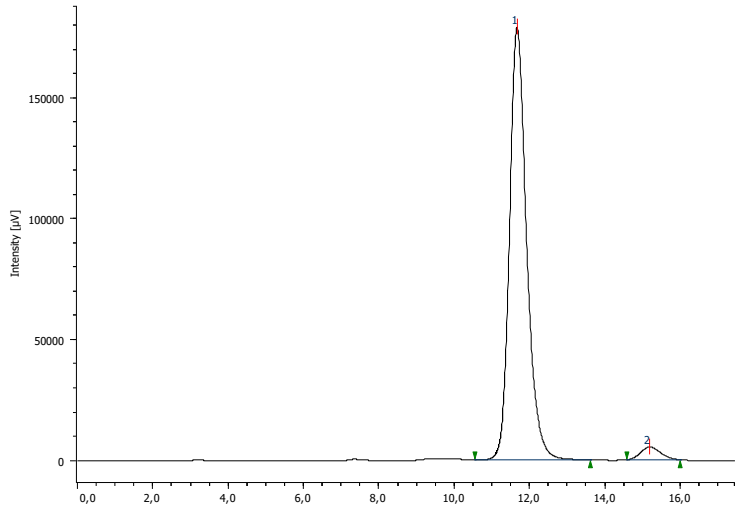
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 11.7 min, t_R (minor) = 15.2 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,475	27646300	885002	49,770	55,682	1,258
2	14,892	27901805	704373	50,230	44,318	1,201

Enantioselective reaction, er = 97:3

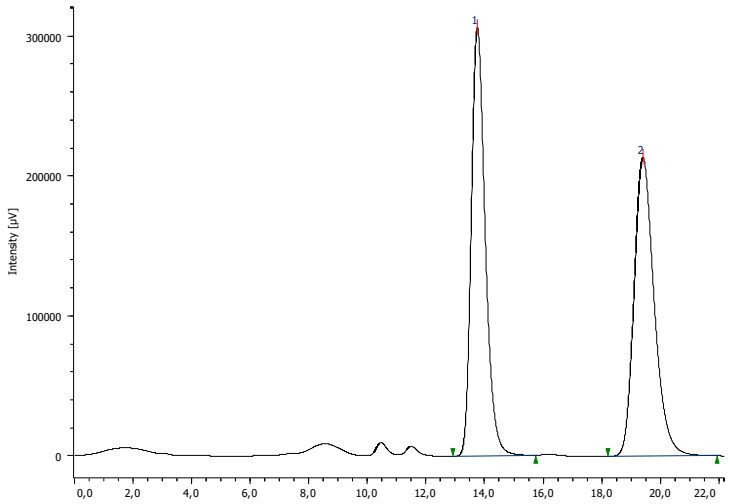


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,658	5632506	178637	96,649	97,136	1,234
2	15,175	195276	5266	3,351	2,864	1,153

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-5-methoxy-3-(phenylethynyl)indolin-2-one (4e).

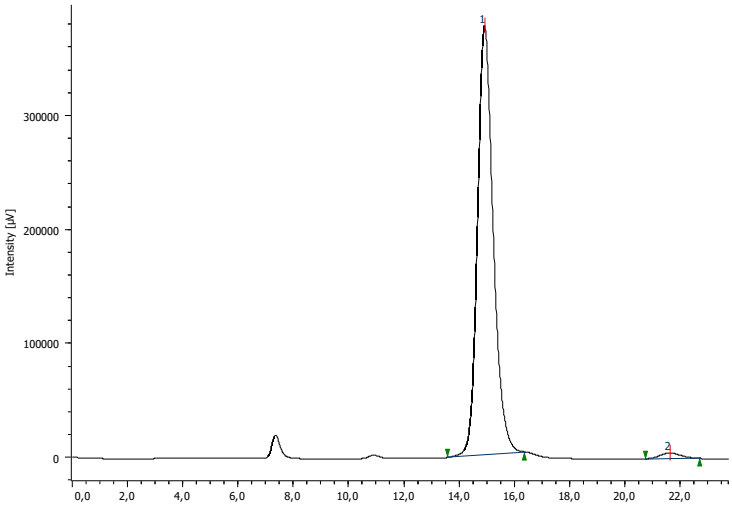
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 14.9 min, t_R (minor) = 21.6 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	14,758	22867066	467423	50,826	59,774	1,080
2	21,300	22123582	314564	49,174	40,226	1,073

Enantioselective reaction, er = 98:2

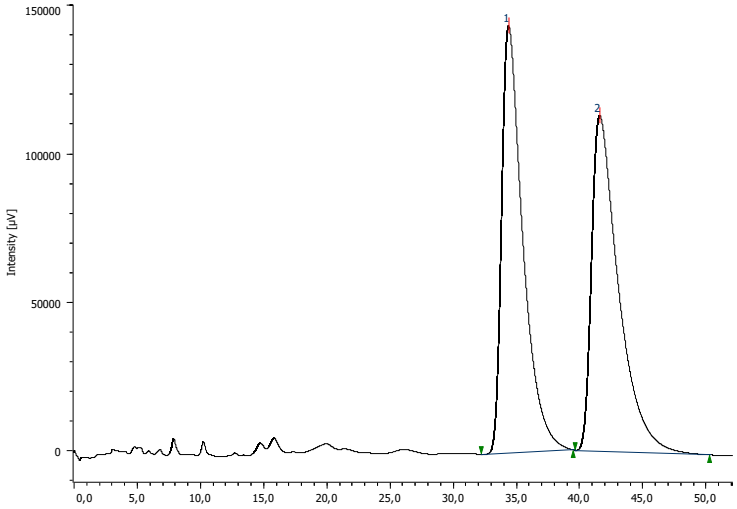


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	14,908	14796215	375419	98,250	98,692	1,211
2	21,600	263614	4976	1,750	1,308	1,137

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-5-nitro-3-(phenylethynyl)indolin-2-one (4f).

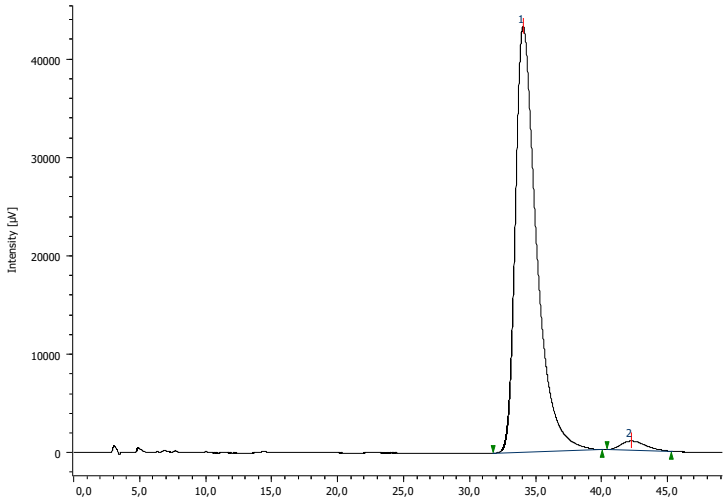
Phenomenex Lux Amylose-2, hexane:isopropanol = 80:20, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 34.0 min, t_R (minor) = 42.2 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	34,333	16750566	143759	50,098	56,002	1,902
2	41,525	16685310	112942	49,902	43,998	2,120

Enantioselective reaction,

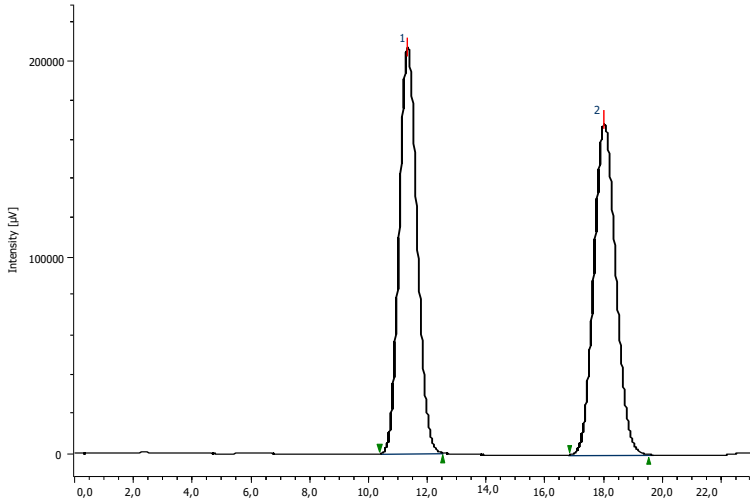


#	v	Area	Height	Area%	Height%	Symmetry Factor
1	34,017	4824282	43189	97,520	97,860	1,638
2	42,158	122678	944	2,480	2,140	1,327

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-7-methyl-3-(phenylethynyl)indolin-2-one (4g).

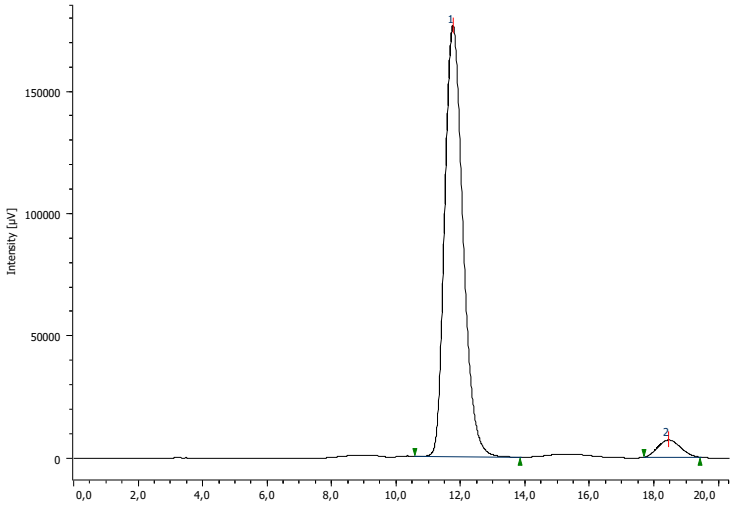
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 11.8 min, t_R (minor) = 18.4 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,358	11314847	207334	50,836	55,227	1,106
2	18,094	10942771	168088	49,164	44,773	1,102

Enantioselective reaction, er = 95:5

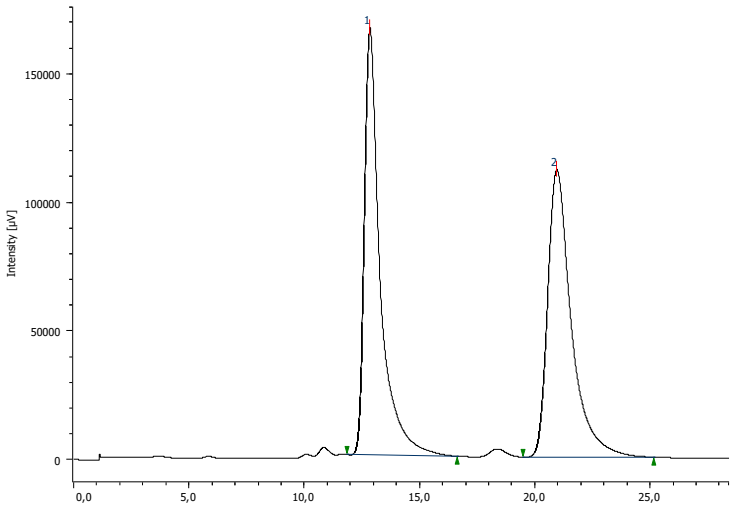


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	11,750	6906031	175901	95,268	96,174	1,258
2	18,442	343061	6997	4,732	3,826	1,107

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-5-methoxy-3-(p-tolylethynyl)indolin-2-one (4h).

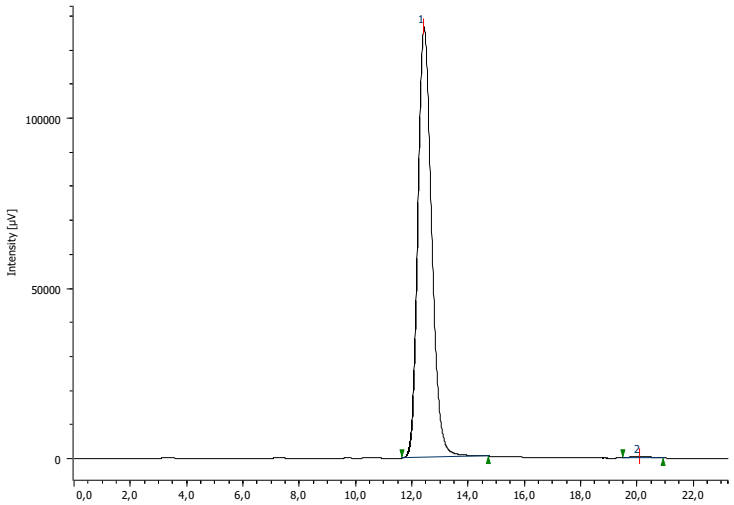
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 12.4 min, t_R (minor) = 20.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	12,833	7949084	165769	49,977	59,768	2,009
2	20,933	7956526	111585	50,023	40,232	1,644

Enantioselective reaction, er = 99:1

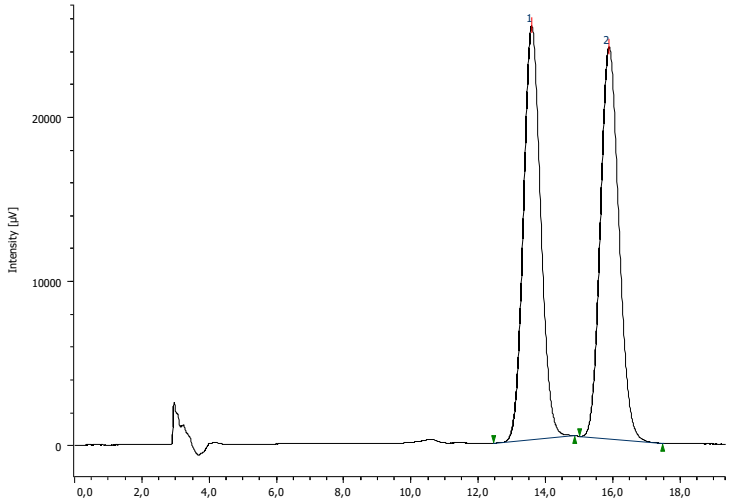


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	12,417	4324618	126200	99,485	99,596	1,222
2	20,067	22375	512	0,515	0,404	1,168

(*S*)-1-(2,6-dichlorobenzyl)-3-hydroxy-5-methoxy-3-((trimethylsilyl)ethynyl)indolin-2-one (4i).

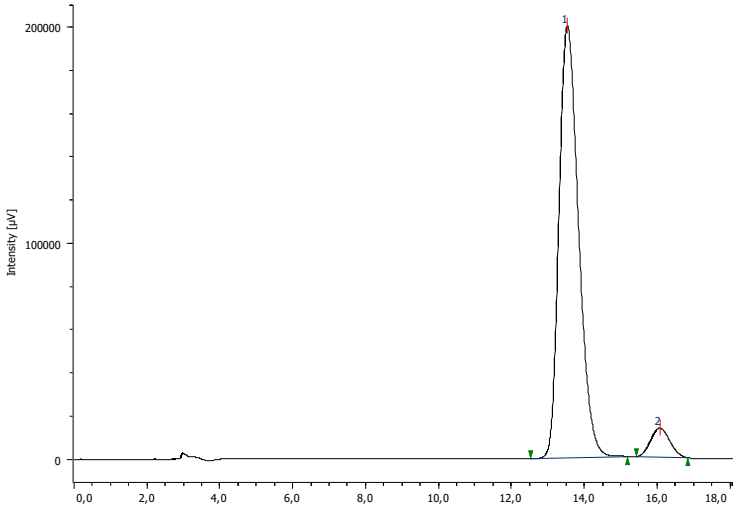
Phenomenex Lux Cellulose-1, hexane:isopropanol = 95:5, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 13.5 min, t_R (minor) = 16.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	13,567	898037	25158	49,793	51,377	1,107
2	15,867	905514	23809	50,207	48,623	1,127

Enantioselective reaction, er = 94:6

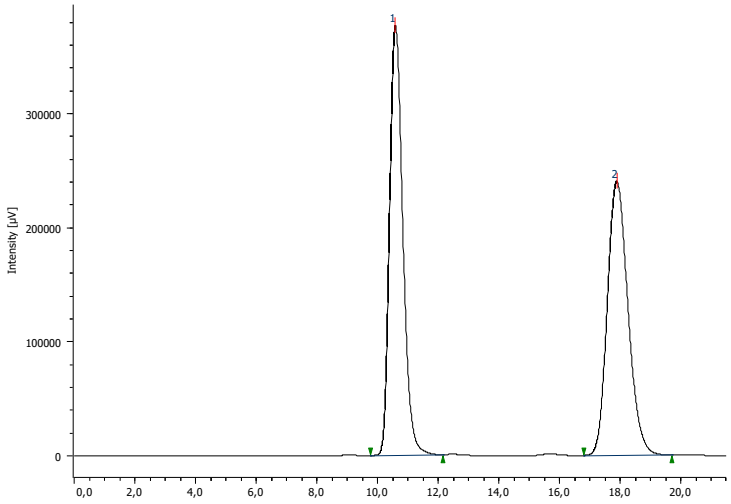


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	13,525	7386618	199452	93,782	93,707	1,282
2	16,050	489728	13393	6,218	6,293	1,103

(*R*)-1-(2,6-dichlorobenzyl)-3-hydroxy-7-methyl-3-(p-tolylethynyl)indolin-2-one (4j).

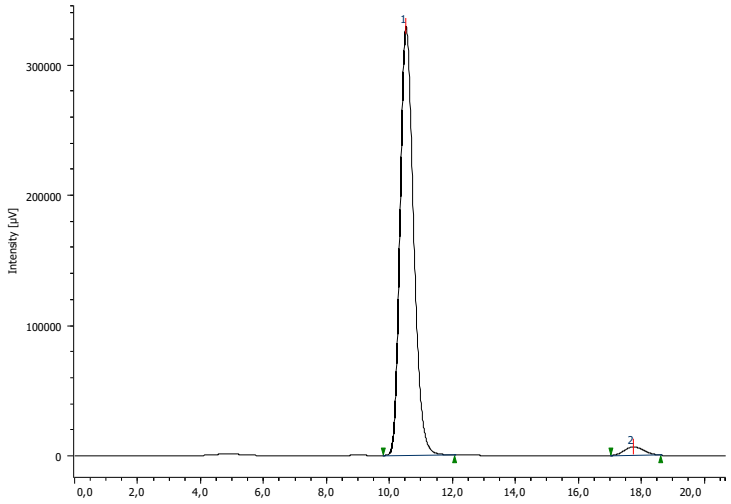
Chiralpak AD-H, hexane:isopropanol = 70:30, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 10.5 min, t_R (minor) = 17.7 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,575	11335157	375676	50,101	61,067	1,262
2	17,858	11289362	239508	49,899	38,933	1,190

Enantioselective reaction, er = 97:3

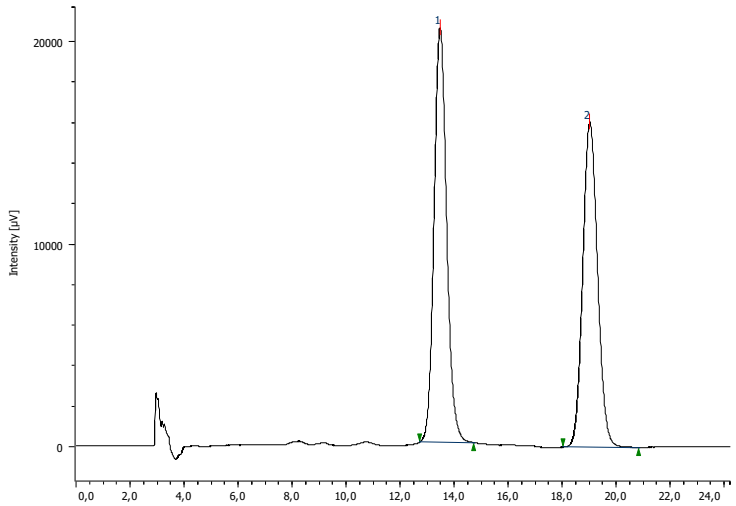


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	10,517	9823331	328626	97,191	98,058	1,240
2	17,725	283937	6508	2,809	1,942	1,124

(*S*)-1-(2,6-dichlorobenzyl)-3-hydroxy-7-methyl-3-((trimethylsilyl)ethynyl)indolin-2-one (4k).

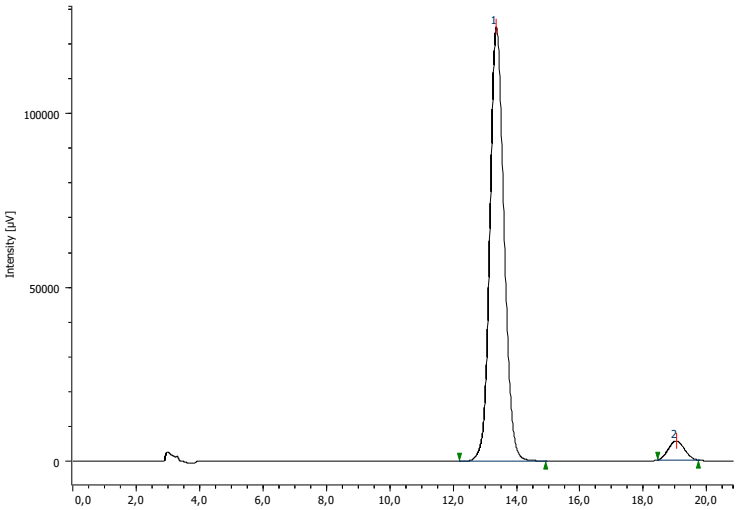
Phenomenex Lux Cellulose-1, hexane:isopropanol = 95:5, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 13.4 min, t_R (minor) = 19.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	13,467	659246	20443	51,815	56,040	1,113
2	19,000	613052	16036	48,185	43,960	1,093

Enantioselective reaction, er = 95:5

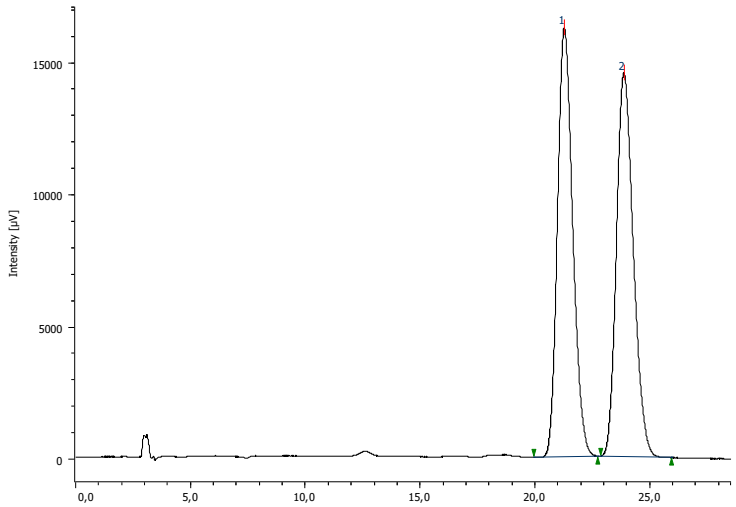


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	13,350	3848166	124543	95,262	95,792	1,110
2	19,008	191401	5471	4,738	4,208	1,079

(*R*)-3-(cyclopropylethynyl)-3-hydroxy-1-methylindolin-2-one (5a).

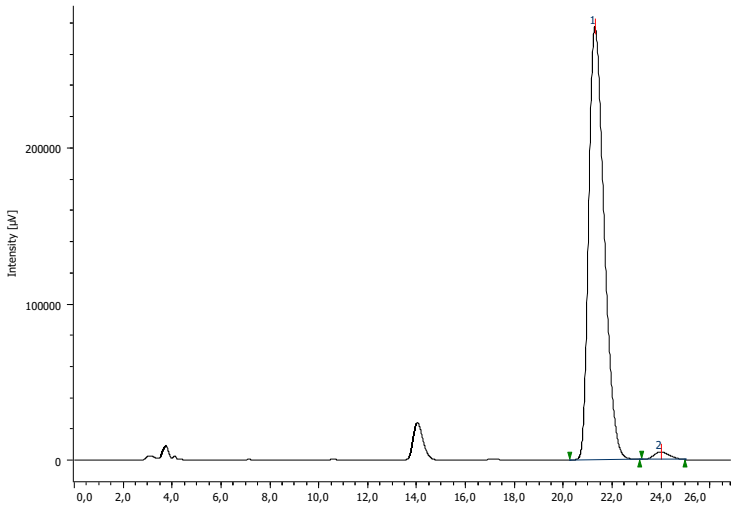
Phenomenex Lux i-Amylose-3, hexane:isopropanol = 90:10, 1 mL min^{-1}, λ = 254 nm): t_R (major) = 21.3 min, t_R (minor) = 24.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	21,258	747055	16195	50,149	52,755	1,185
2	23,850	742612	14504	49,851	47,245	1,203

Enantioselective reaction, er = 98:2

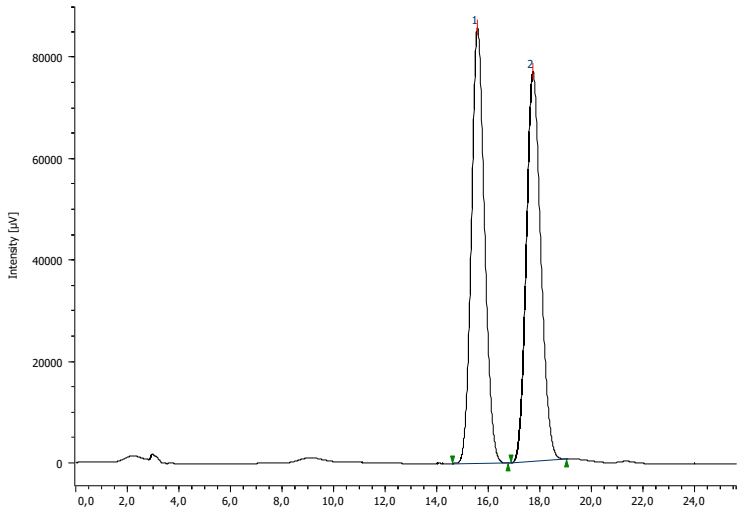


#	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	21,267	12107407	276503	98,221	98,280	1,381
2	23,958	219245	4839	1,779	1,720	1,209

(*R*)-3-(hex-1-yn-1-yl)-3-hydroxy-1-methylindolin-2-one (5b).

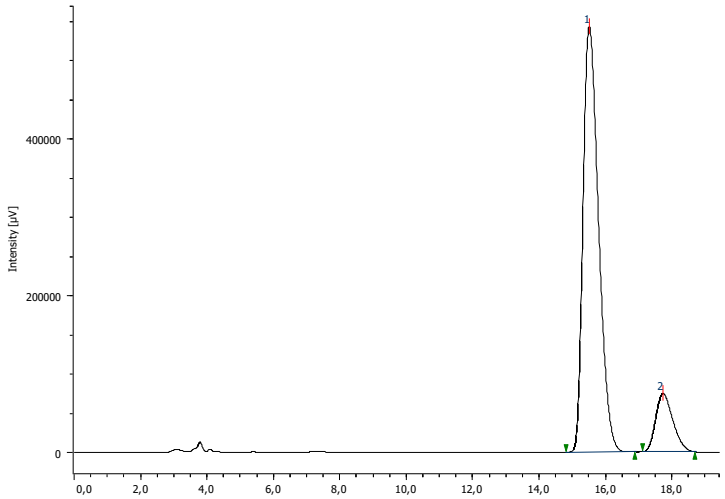
Phenomenex Lux i-Amylose-3, hexane:isopropanol = 90:10, 1 mL min^{-1}, λ = 254 nm: t_R (major) = 15.5 min, t_R (minor) = 17.7 min.

Racemic sample



#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	15,558	3026708	85667	50,317	52,763	1,105
2	17,700	2988584	76696	49,683	47,237	1,143

Enantioselective reaction, er = 87:13

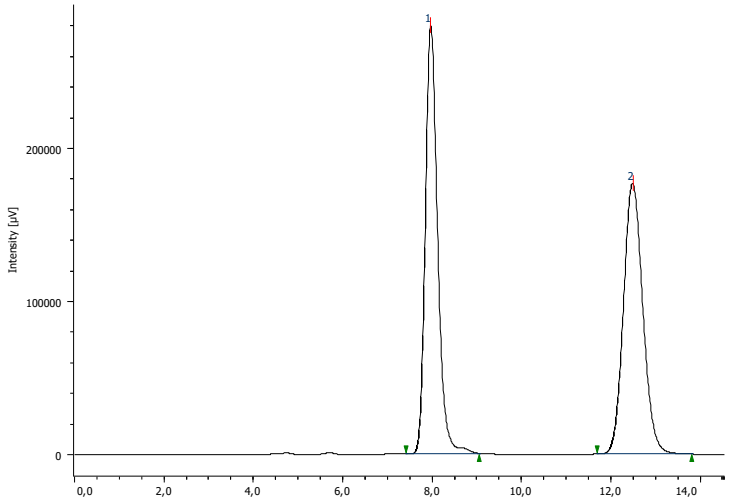


#	tR	Area	Height	Area%	Height%	Symmetry Factor
1	15,492	17584576	542024	86,882	87,956	1,392
2	17,717	2655027	74220	13,118	12,044	1,259

(*S*)-1-(2,6-Dichlorobenzyl)-3-(phenylamino)-3-(phenylethynyl)indolin-2-one (7a).

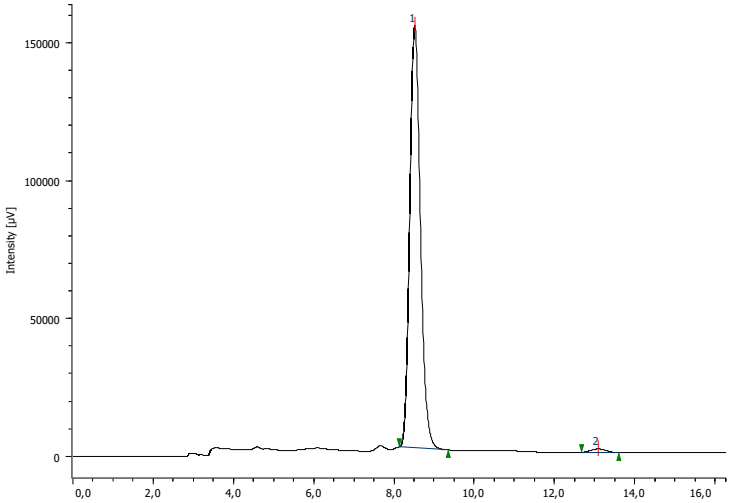
Phenomenex Lux Cellulose-1, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 8.5 min, t_R (minor) = 13.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	7,958	5348468	279106	50,120	61,268	7,090	1,251
2	12,475	5322889	176444	49,880	38,732	N/A	1,106

Enantioselective reaction, er = 99:1

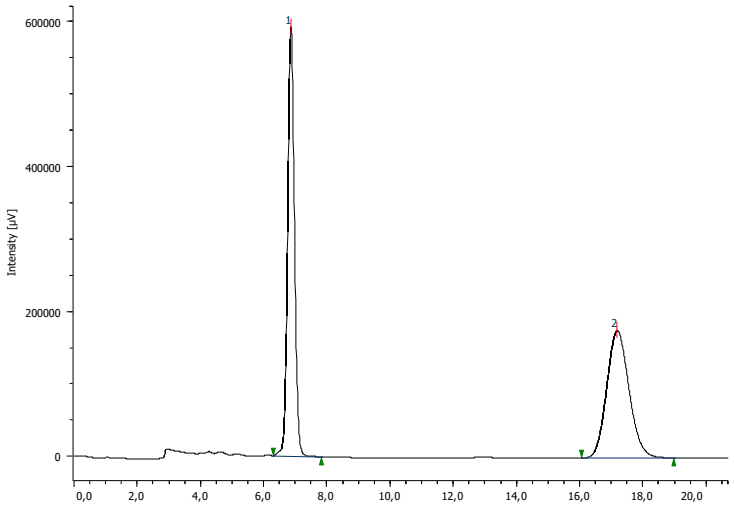


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	8,508	2805336	153080	98,849	99,187	7,688	1,165
2	13,075	32665	1255	1,151	0,813	N/A	1,081

(*S*)-1-(2,6-Dichlorobenzyl)-3-(phenylethynyl)-3-((4-(trifluoromethyl)phenyl)amino)indolin-2-one (7b).

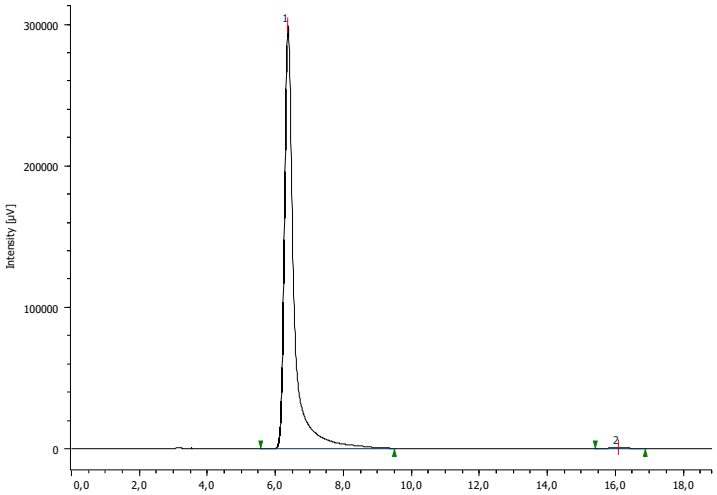
Phenomenex Lux Cellulose-1, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 6.4 min, t_R (minor) = 16.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,858	8817880	590546	50,677	77,106	12,366	1,056
2	17,167	8582147	175343	49,323	22,894	N/A	1,130

Enantioselective reaction, er >99:1

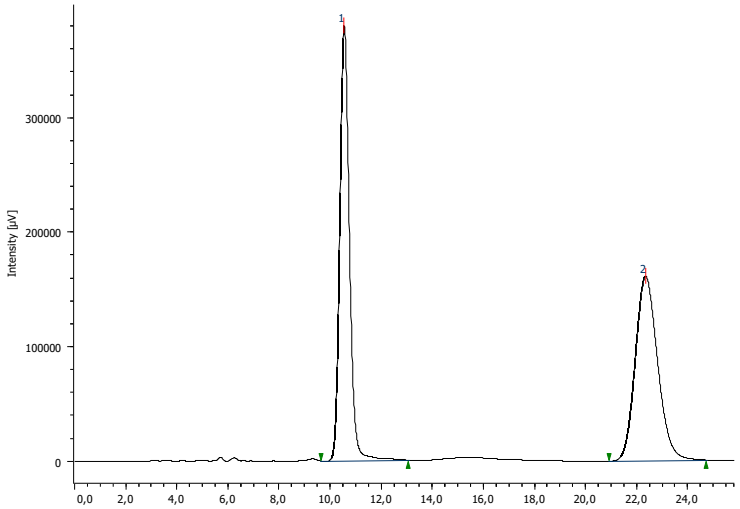


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,367	5883547	298233	99,655	99,842	12,032	1,892
2	16,067	20375	471	0,345	0,158	N/A	1,095

(*S*)-1-(2,6-Dichlorobenzyl)-3-((4-methoxyphenyl)amino)-3-(phenylethynyl)indolin-2-one (7c).

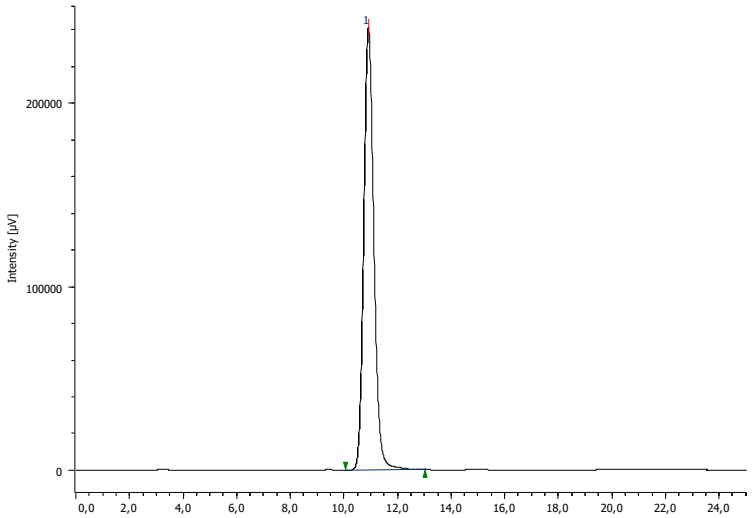
Phenomenex Lux Cellulose-1, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 10.9 min, t_R (minor) = 22.3 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	10,542	9972761	379071	50,433	70,195	10,442	1,148
2	22,317	9801631	160957	49,567	29,805	N/A	1,166

Enantioselective reaction, er >99:1

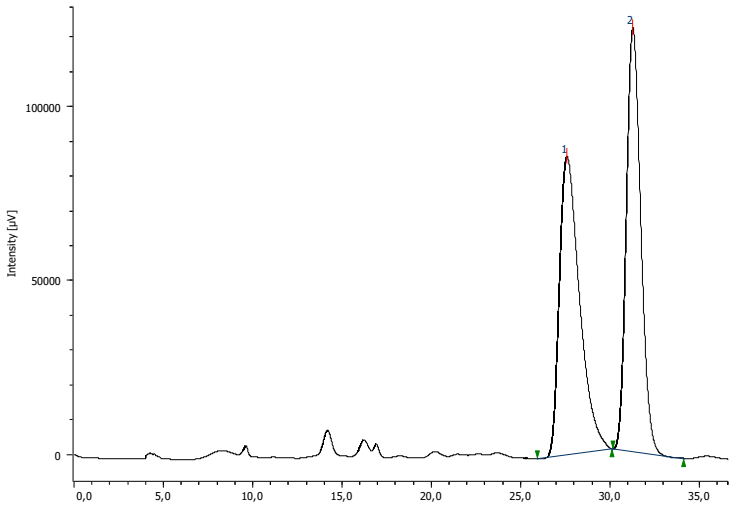


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	10,900	6359209	240596	100,000	100,000	N/A	1,159

(*S*)-1-(2,6-Dichlorobenzyl)-3-((2-methoxyphenyl)amino)-3-(phenylethynyl)indolin-2-one (7d).

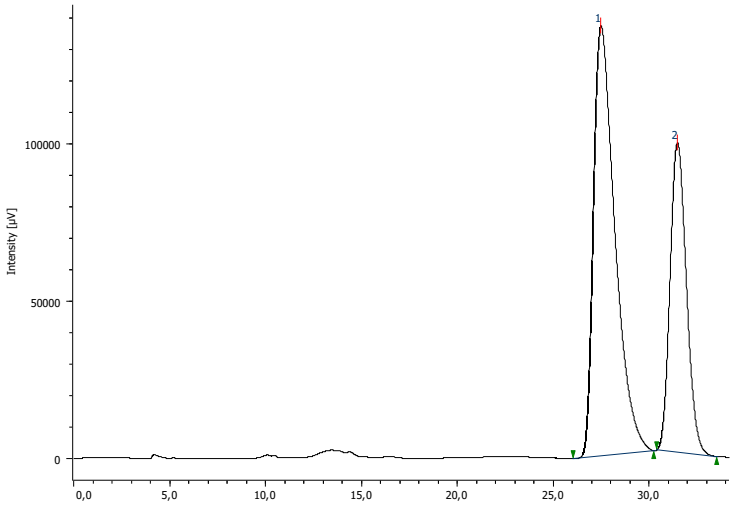
Phenomenex Lux Cellulose-1, hexane:2-propanol 93:7, 0.7 mL/min, λ = 254 nm, t_R (major) = 27.5 min, t_R (minor) = 31.4 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	27,567	6714091	85607	49,415	41,331	2,090	1,605
2	31,242	6873170	121517	50,585	58,669	N/A	1,193

Enantioselective reaction, er = 65:35

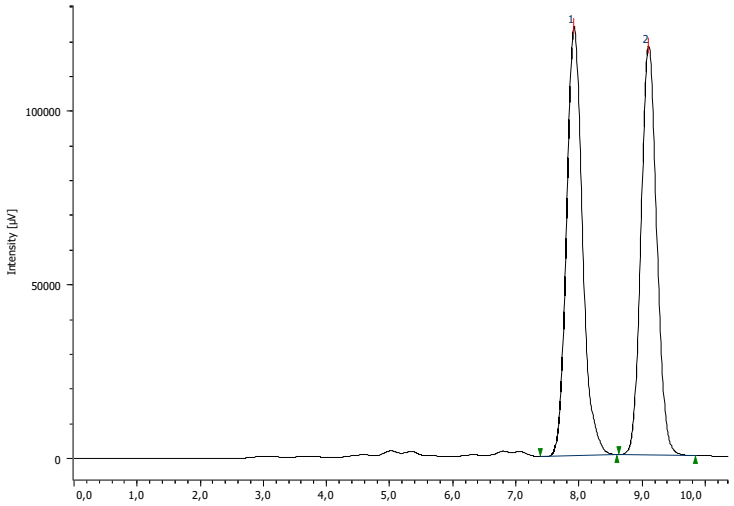


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	27,467	10618467	136260	64,629	58,160	2,225	1,719
2	31,442	5811505	98026	35,371	41,840	N/A	1,186

(*S*)-1-(2,6-Dichlorobenzyl)-3-(phenylethynyl)-3-(o-tolylamino)indolin-2-one (7e).

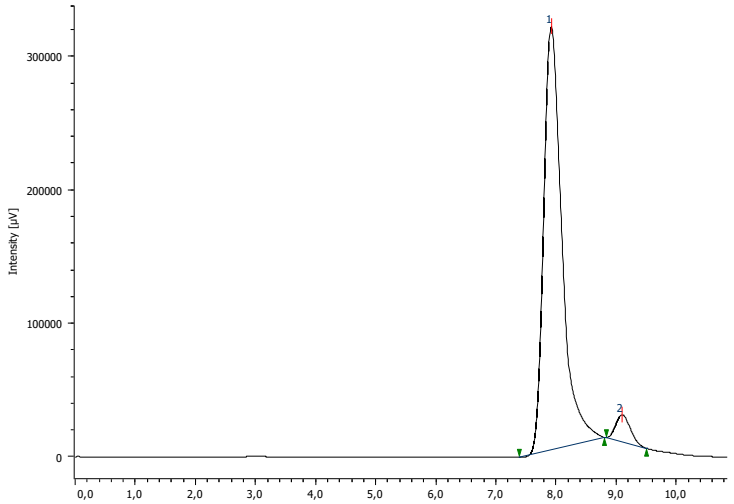
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 7.9 min, t_R (minor) = 9.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	7,908	2165439	123292	51,507	51,199	2,614	1,207
2	9,092	2038727	117515	48,493	48,801	N/A	1,079

Enantioselective reaction, er = 95:5

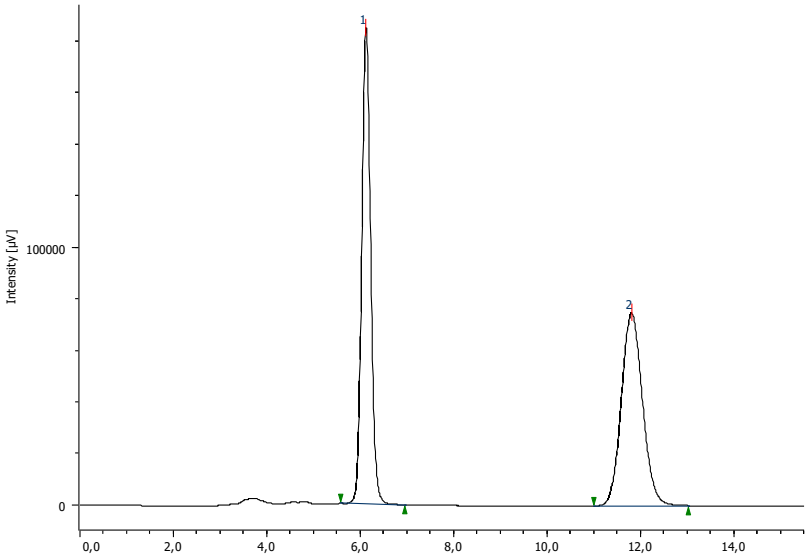


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	7,908	6683669	316446	95,146	93,959	2,416	1,534
2	9,092	340993	20347	4,854	6,041	N/A	1,173

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(phenylethynyl)indolin-2-one (7g).

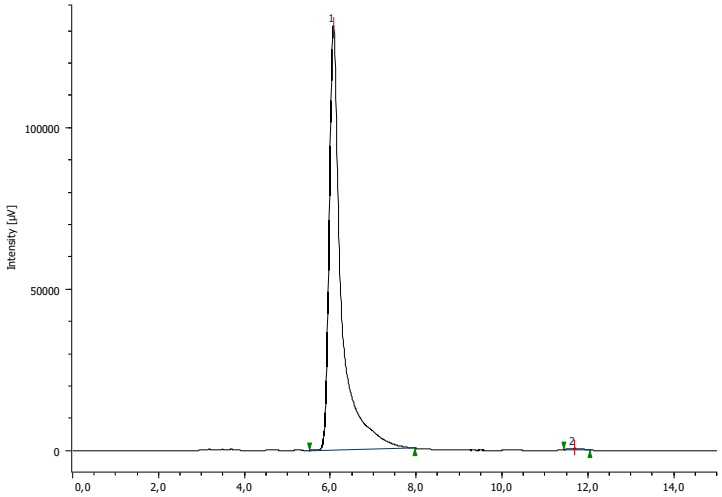
Phenomenex Lux Cellulose-1, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 6.1 min, t_R (minor) = 11.7 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,117	2437170	184292	50,859	71,156	9,748	1,102
2	11,800	2354860	74705	49,141	28,844	N/A	1,092

Enantioselective reaction, er > 99:1

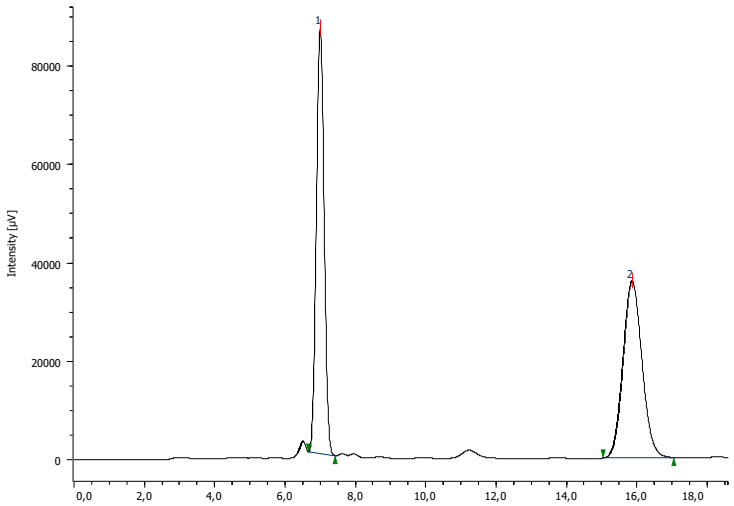


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,067	2597643	131188	99,637	99,664	11,100	2,449
2	11,667	9459	442	0,363	0,336	N/A	1,205

(*S*)-1-Benzyl-3-((3,5-dichlorophenyl)amino)-3-(phenylethynyl)indolin-2-one (7h).

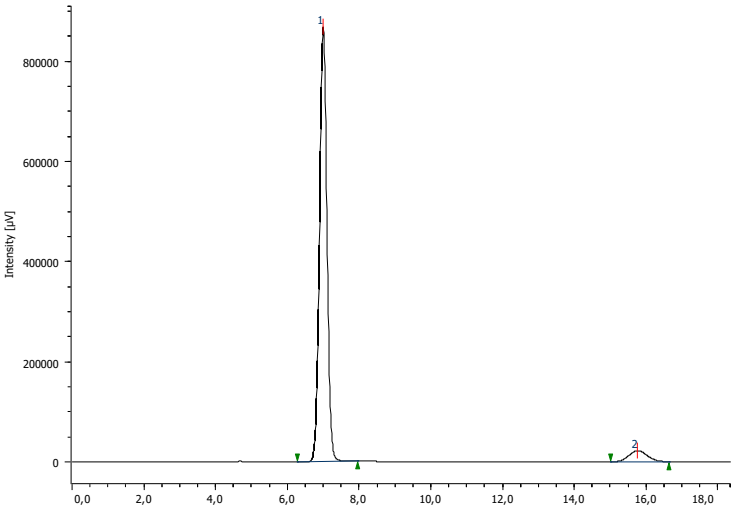
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 6.9 min, t_R (minor) = 15.7 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,992	1327930	86355	49,658	70,678	12,688	1,026
2	15,850	1346204	35826	50,342	29,322	N/A	1,088

Enantioselective reaction, er = 94:6

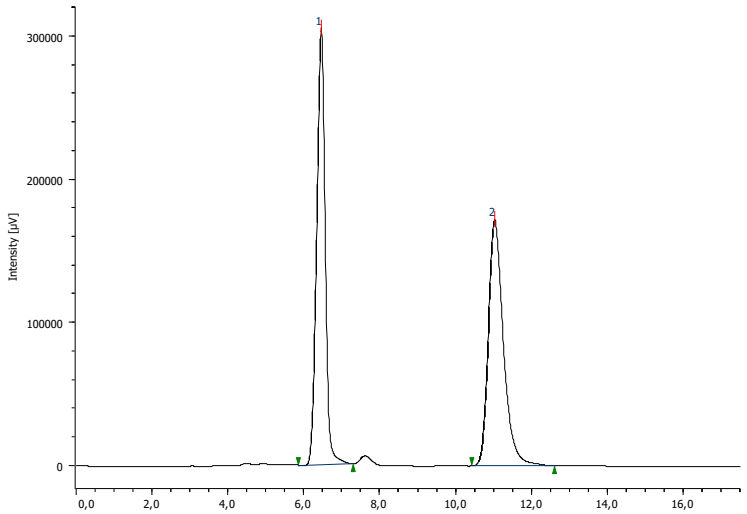


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,992	12440453	866077	94,029	97,512	13,280	1,031
2	15,750	789926	22095	5,971	2,488	N/A	1,075

(*S*)-3-((3,5-Dichlorophenyl)amino)-1-methyl-3-(phenylethynyl)indolin-2-one (7i).

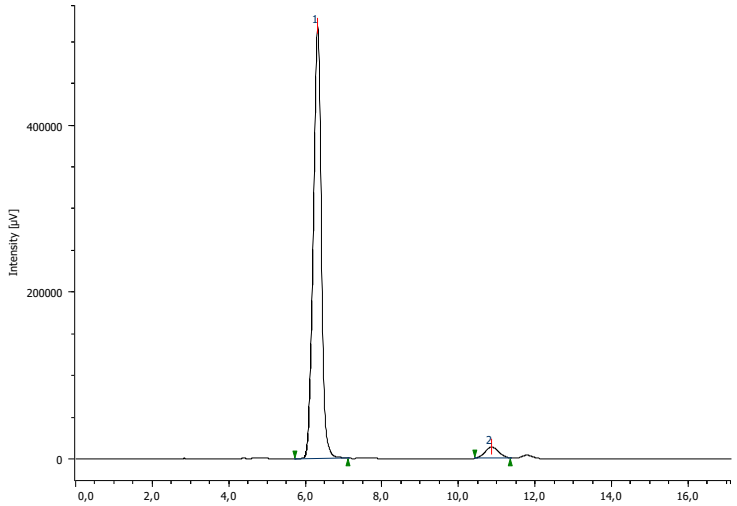
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 6.3 min, t_R (minor) = 10.8 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,458	4680723	304415	49,712	63,947	8,432	0,949
2	11,017	4734868	171625	50,288	36,053	N/A	1,351

Enantioselective reaction, er = 94:4

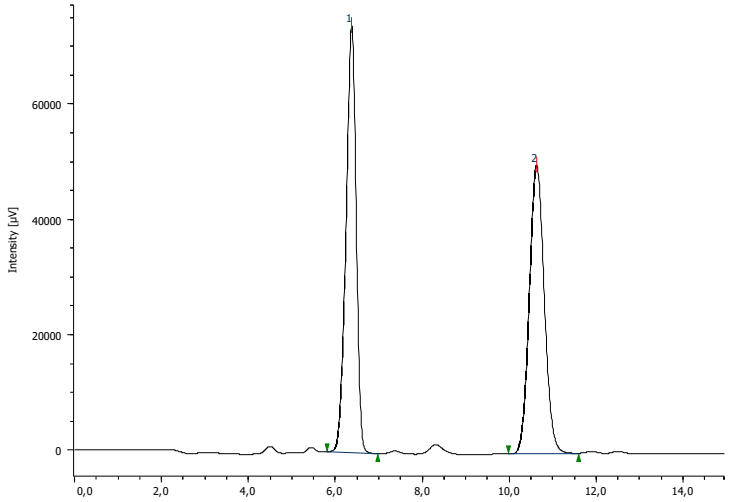


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,317	7543980	517030	95,734	97,490	8,604	0,940
2	10,850	336139	13312	4,266	2,510	N/A	1,062

(*S*)-3-((3,5-Dichlorophenyl)amino)-1-(methoxymethyl)-3-(phenylethynyl)indolin-2-one (7j).

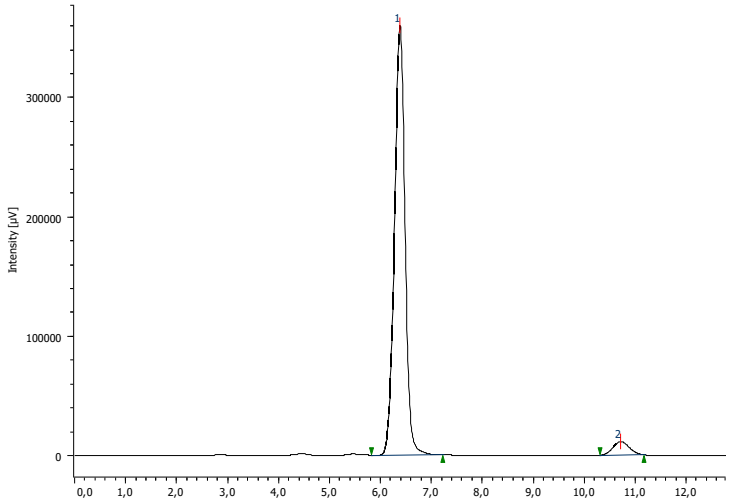
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 6.4 min, t_R (minor) = 10.7 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,367	1203885	73895	50,270	59,664	8,097	0,884
2	10,617	1190946	49957	49,730	40,336	N/A	1,073

Enantioselective reaction, er = 95:5

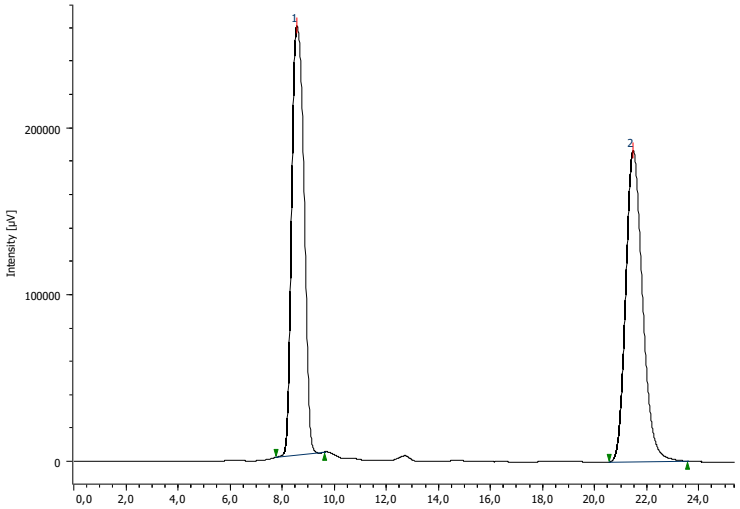


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,375	5148123	358976	95,345	96,959	8,959	0,986
2	10,708	251351	11257	4,655	3,041	N/A	1,061

(*S*)-3-((3,5-Dichlorophenyl)amino)-3-(phenylethynyl)-1-tritylindolin-2-one (7k).

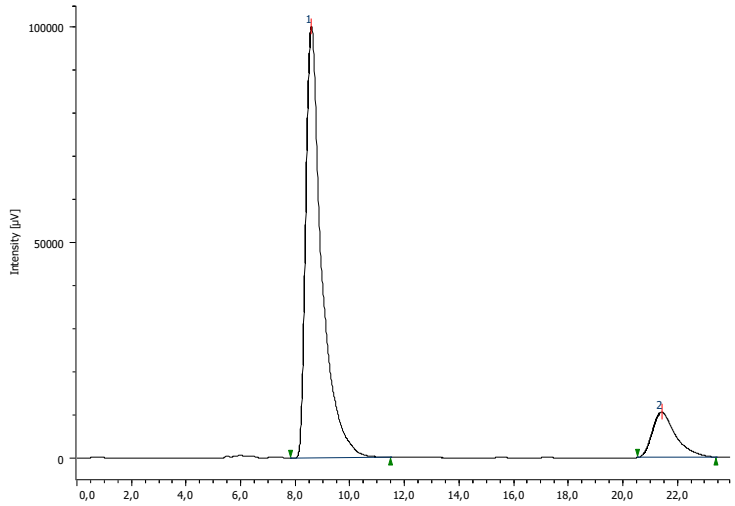
Phenomenex Lux Cellulose-1, hexane:2-propanol 83:17, 0.5 mL/min, λ = 254 nm, t_R (major) = 8.6 min, t_R (minor) = 21.4 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	8,558	8410685	256691	50,236	57,959	12,469	1,160
2	21,458	8331615	186191	49,764	42,041	N/A	1,223

Enantioselective reaction, er =87:13

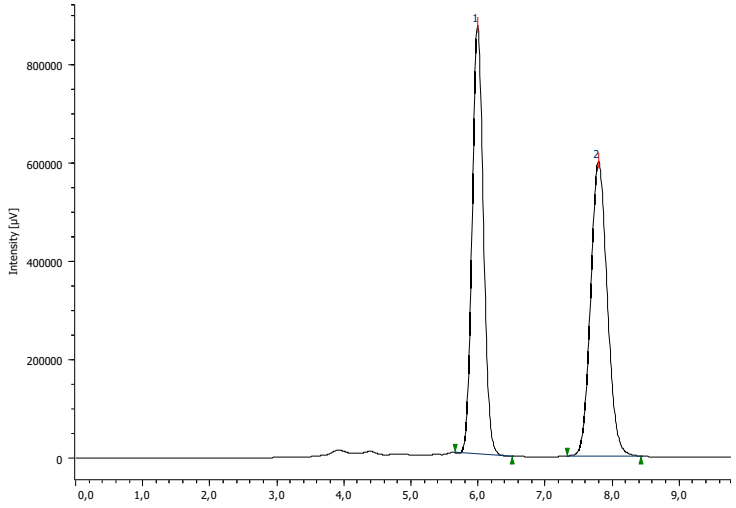


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	8,583	4044837	99705	86,713	90,540	10,755	2,016
2	21,392	619815	10418	13,287	9,460	N/A	1,554

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((2-(trifluoromethyl)phenyl)ethynyl)indolin-2-one (8a).

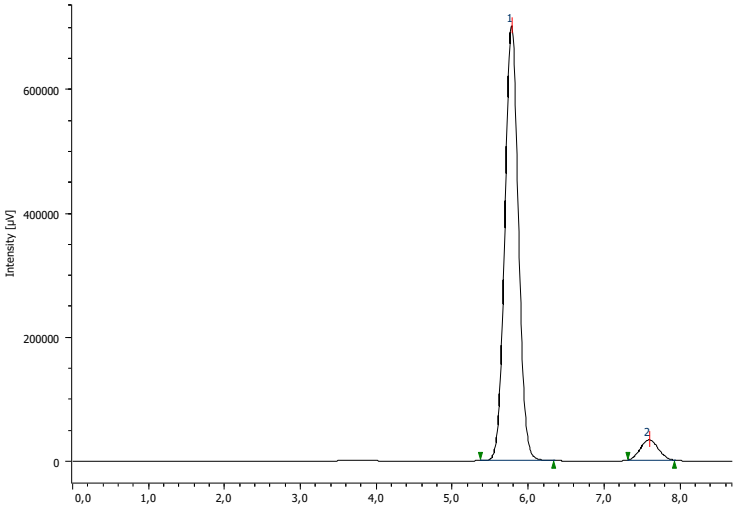
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 5.8 min, t_R (minor) = 7.6 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	5,983	10201366	870823	49,785	59,264	4,750	1,092
2	7,783	10289537	598583	50,215	40,736	N/A	1,129

Enantioselective reaction, er = 94:6

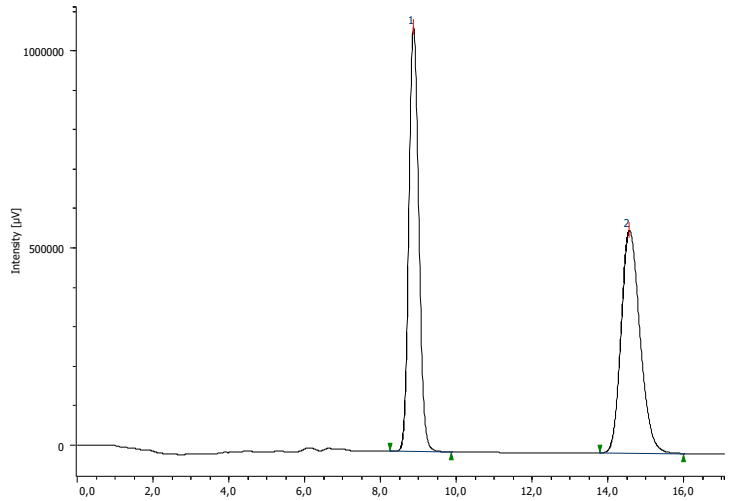


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	5,775	8713324	700493	94,159	95,549	4,681	1,027
2	7,583	540488	32628	5,841	4,451	N/A	1,063

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((2-fluorophenyl)ethynyl)indolin-2-one (8b).

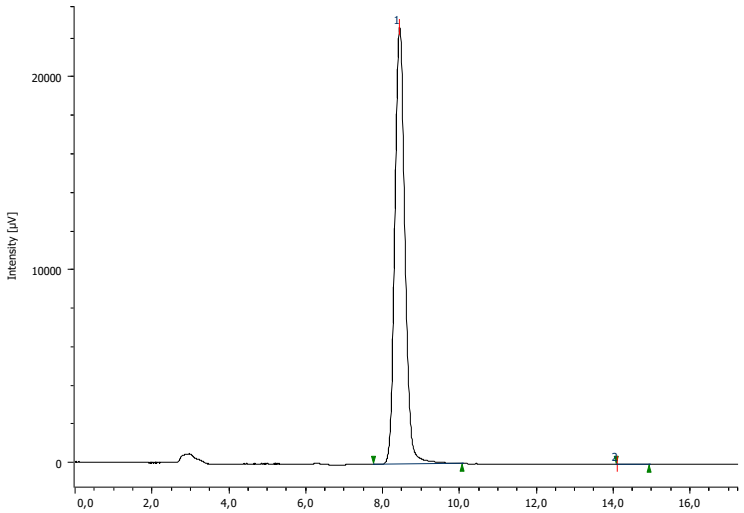
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 8.4 min, t_R (minor) = 14.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	8,867	19541723	1073631	50,194	65,617	8,246	1,091
2	14,550	19390631	562586	49,806	34,383	N/A	1,223

Enantioselective reaction, er > 99%

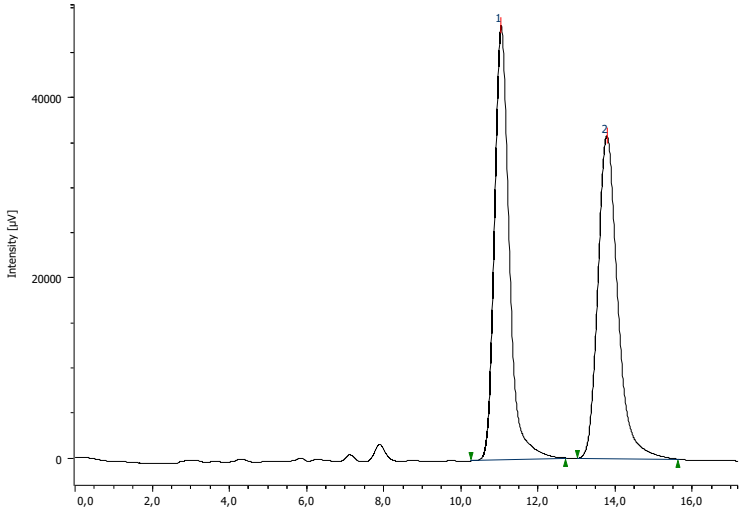


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	8,433	411476	22597	99,996	99,977	21,458	1,120
2	14,100	15	5	0,004	0,023	N/A	8,228

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((3-methoxyphenyl)ethynyl)indolin-2-one (8c).

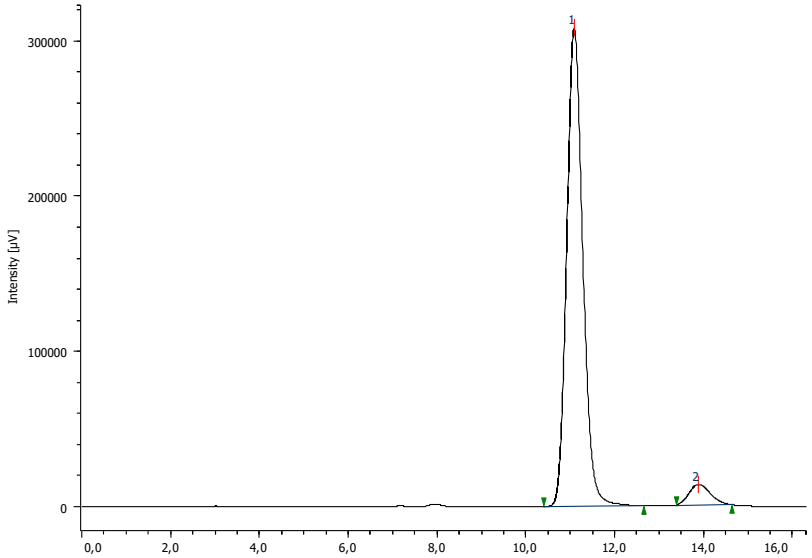
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 11.1 min, t_R (minor) = 13.8 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	11,033	1289676	48099	50,364	57,376	3,514	1,262
2	13,767	1271013	35732	49,636	42,624	N/A	1,274

Enantioselective reaction, er = 95:5

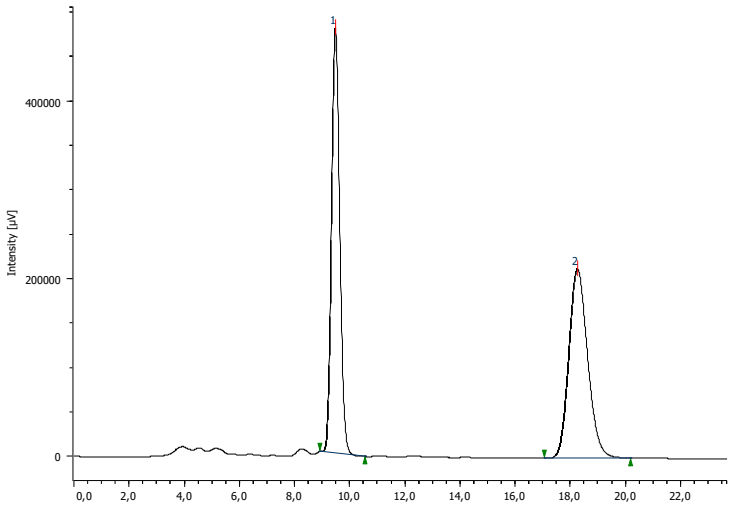


#	tR	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	11,075	7754694	307253	94,610	95,881	3,619	1,149
2	13,875	441809	13198	5,390	4,119	N/A	1,191

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(m-tolylethynyl)indolin-2-one (8d).

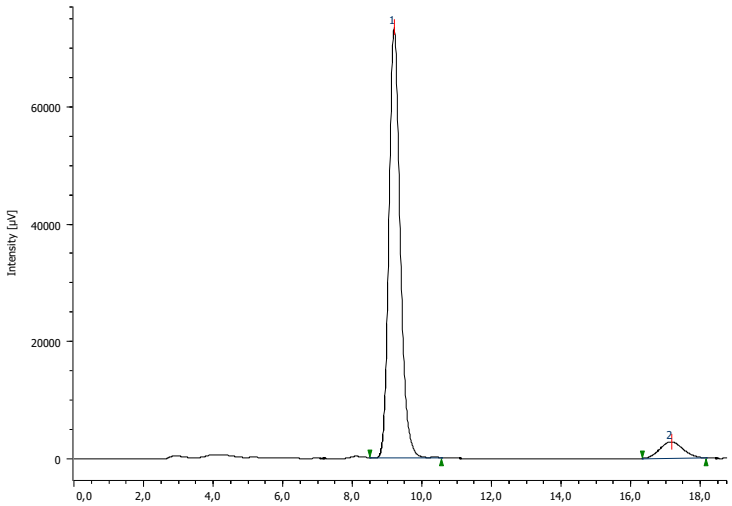
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 9.2 min, t_R (minor) = 17.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	9,467	9899936	477822	49,600	69,192	9,845	1,125
2	18,233	10059431	212750	50,400	30,808	N/A	1,178

Enantioselective reaction, er = 93:7

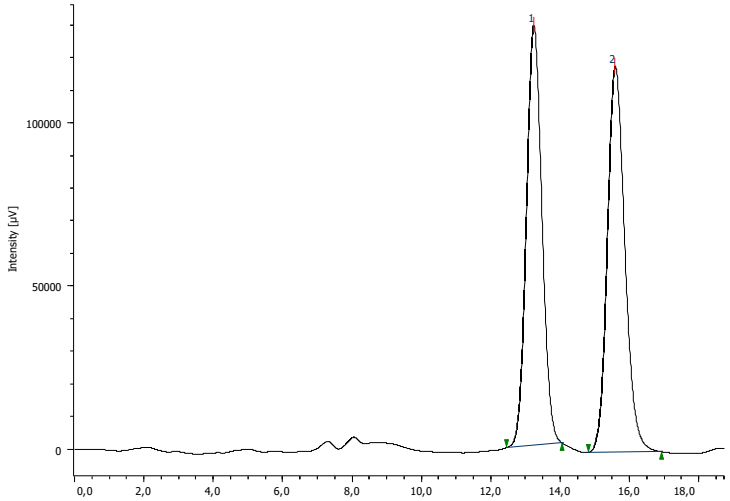


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	9,192	1634859	73101	92,729	96,322	8,869	1,186
2	17,142	128183	2791	7,271	3,678	N/A	1,090

(*S*)-3-((3-Chlorophenyl)ethynyl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)indolin-2-one (8e).

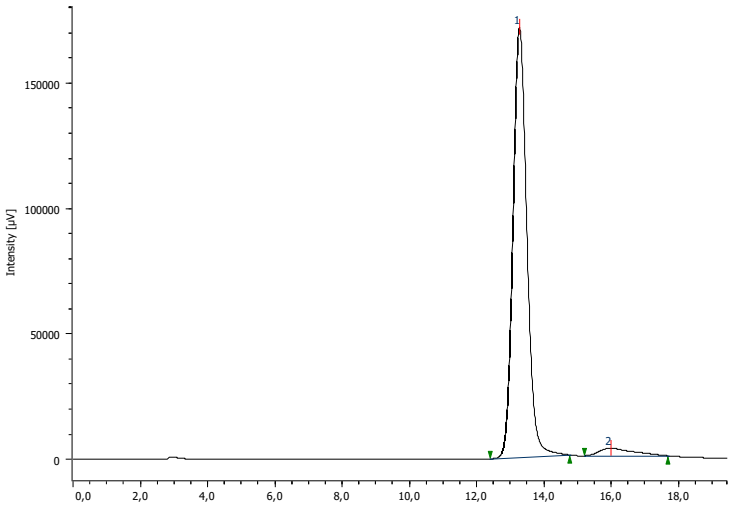
Phenomenex Lux Cellulose-1, hexane:2-propanol 90:10, 1 mL/min, λ = 254 nm, t_R (major) = 13.3 min, t_R (minor) = 16.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	13,225	3987726	128500	49,076	52,091	2,718	1,079
2	15,567	4137903	118186	50,924	47,909	N/A	1,185

Enantioselective reaction, er = 96:4

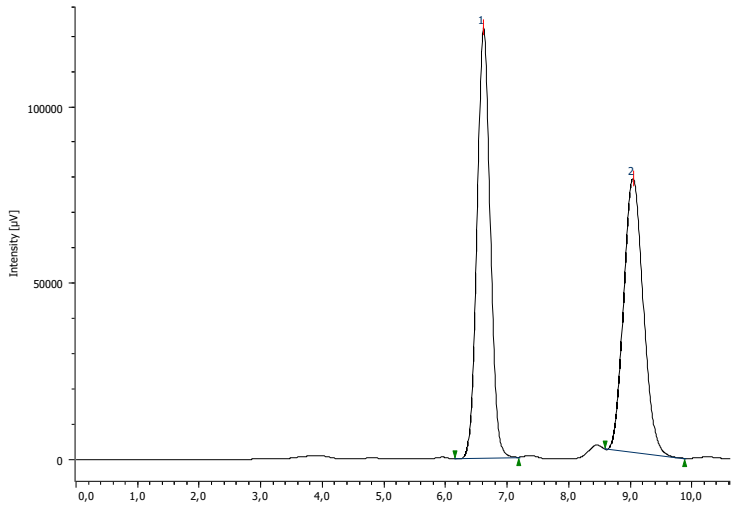


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	13,258	4929553	171233	95,820	98,254	2,049	1,128
2	15,967	215041	3043	4,180	1,746	N/A	1,682

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(p-tolylethynyl)indolin-2-one (8f).

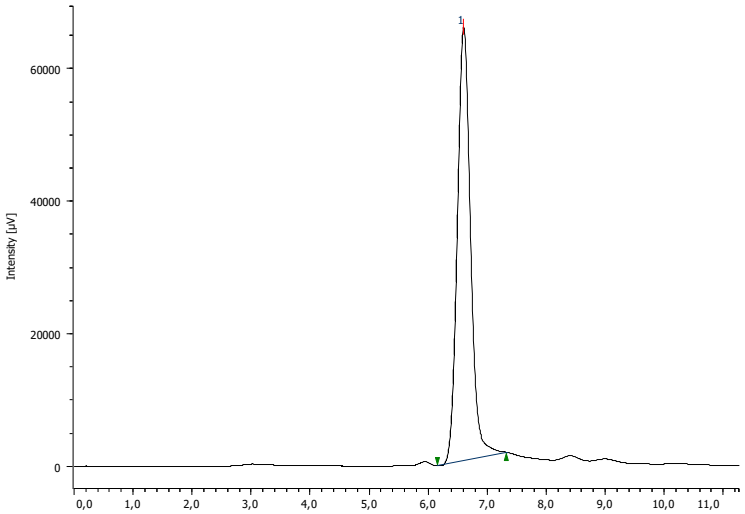
Phenomenex Lux Cellulose-1, hexane:2-propanol 70:30, 1 mL/min, λ = 1 nm, t_R (major) = 6.6 min, t_R (minor) = 9.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,608	1813813	121777	51,432	61,127	4,981	1,043
2	9,033	1712839	77442	48,568	38,873	N/A	1,118

Enantioselective reaction, er > 99%

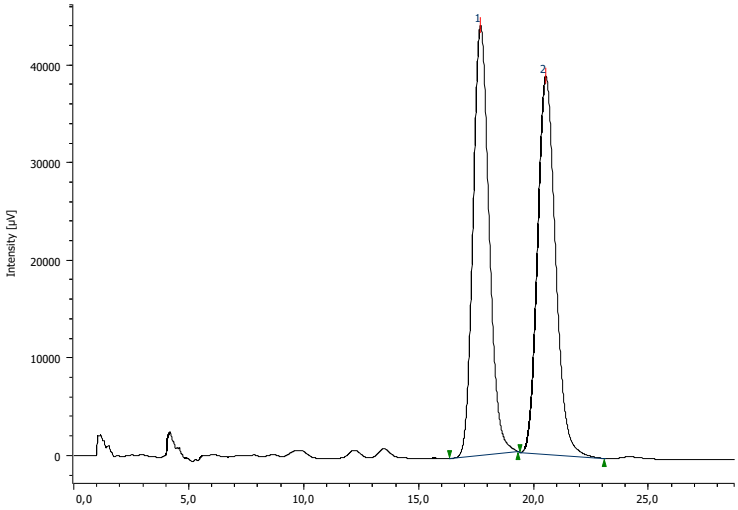


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	6,592	999769	65269	100,000	100,000	N/A	1,130

(*S*)-3-((4-Bromophenyl)ethynyl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)indolin-2-one (8g).

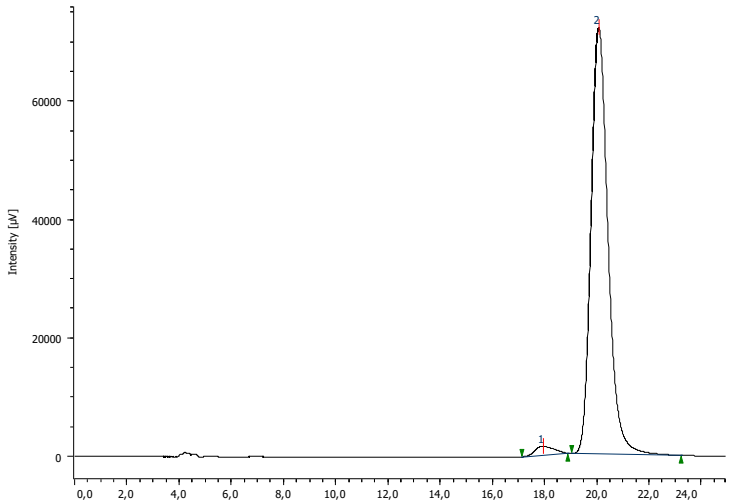
Phenomenex Lux Cellulose-1, hexane:2-propanol 90:10, 0.7 mL/min, λ = 254 nm, t_R (major) = 20.0 min, t_R (minor) = 17.9 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	17,675	2123594	43922	50,190	53,192	2,127	1,158
2	20,517	2107517	38651	49,810	46,808	N/A	1,162

Enantioselective reaction, er = 98:2

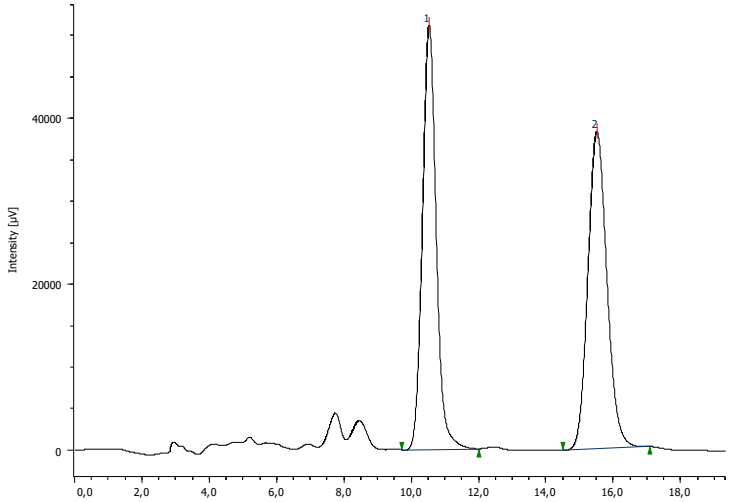


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	17,925	74360	1486	2,251	2,024	1,668	1,200
2	20,050	3229631	71922	97,749	97,976	N/A	1,221

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((4-(trifluoromethyl)phenyl)ethynyl)indolin-2-one (8h).

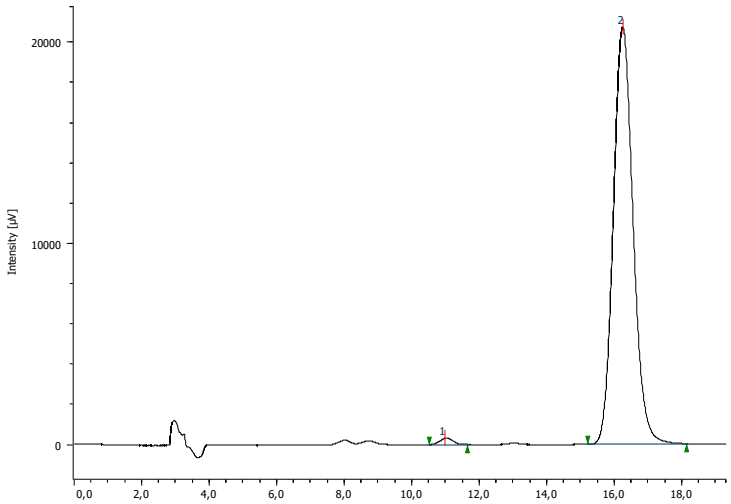
Phenomenex Lux Cellulose-1, hexane:2-propanol 90:10, 1 mL/min, λ = 254 nm, t_R (major) = 16.2 min, t_R (minor) = 11.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	10,517	1443928	51005	49,164	57,224	5,716	1,111
2	15,492	1493058	38127	50,836	42,776	N/A	1,135

Enantioselective reaction, er = 99:1

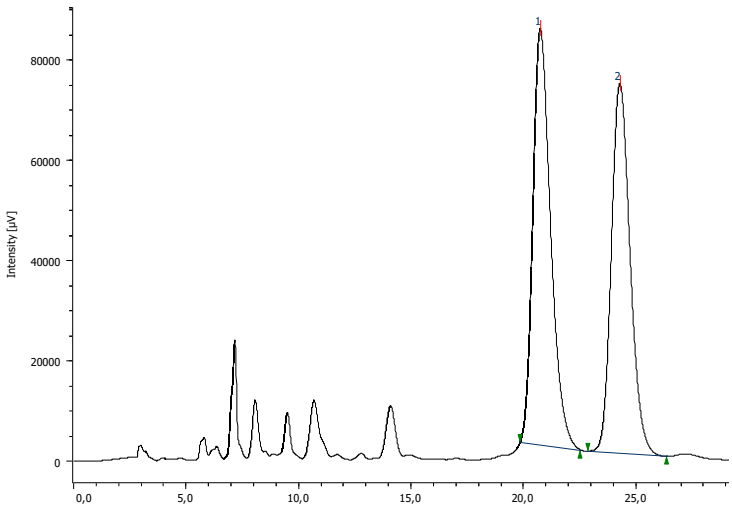


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	10,983	8807	322	1,042	1,533	5,891	1,139
2	16,233	836482	20679	98,958	98,467	N/A	1,124

Methyl (*S*)-4-((1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-2-oxoindolin-3-yl)ethynyl)benzoate (8i).

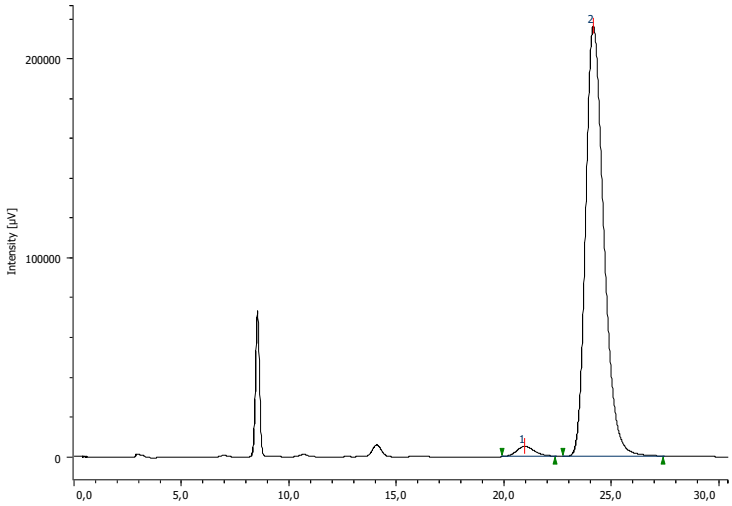
Phenomenex Lux Cellulose-1, hexane:2-propanol 90:10, 1 mL/min, λ = 254 nm, t_R (major) = 24.1 min, t_R (minor) = 20.9 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	20,717	4568504	82894	51,810	52,956	2,409	1,334
2	24,250	4249266	73641	48,190	47,044	N/A	1,194

Enantioselective reaction, er = 98:2

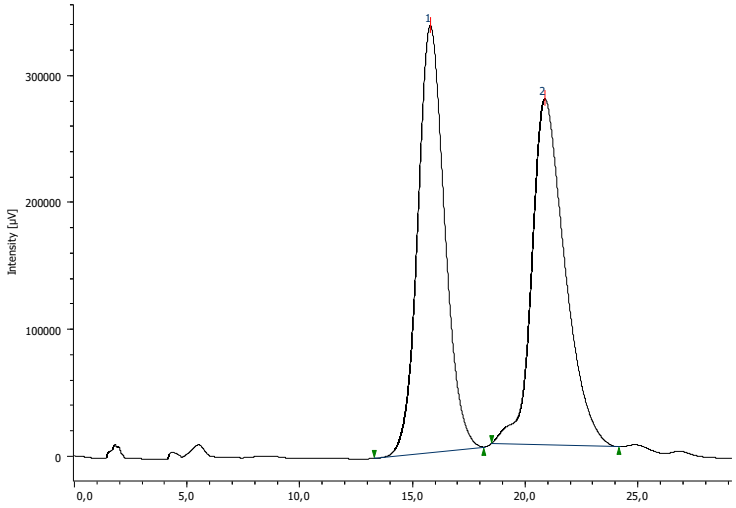


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	20,942	296135	5088	2,288	2,303	2,110	1,179
2	24,125	12647265	215823	97,712	97,697	N/A	1,300

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(4-phenylbut-1-yn-1-yl)indolin-2-one (8j).

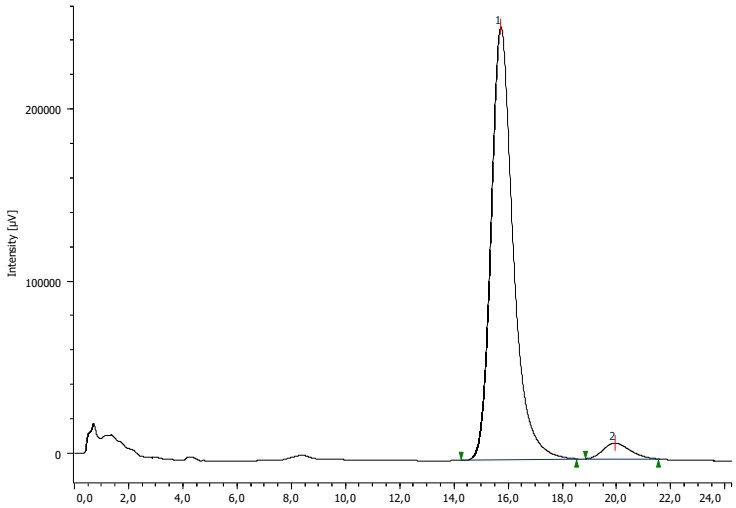
Phenomenex Lux Cellulose-2, hexane:2-propanol 95:5, 0.7 mL/min, λ = 254 nm, t_R (major) = 15.7 min, t_R (minor) = 19.9 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	15,767	28060181	336226	50,224	55,238	2,156	1,114
2	20,850	27809571	272464	49,776	44,762	N/A	1,167

Enantioselective reaction, er = 96:4

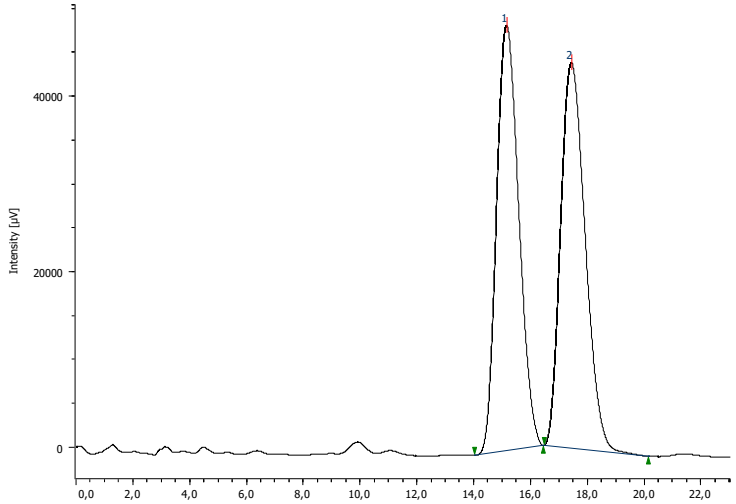


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	15,717	14219710	250674	95,720	96,487	2,578	1,298
2	19,917	635755	9128	4,280	3,513	N/A	1,240

(*R*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((trimethylsilyl)ethynyl)indolin-2-one (8k).

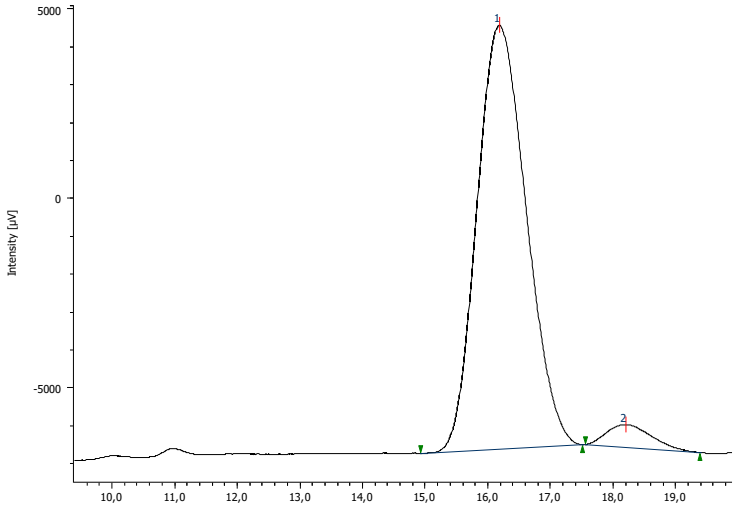
Phenomenex Lux i-Amylose-3, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 16.2 min, t_R (minor) = 18.2 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	15,142	2626705	48404	49,992	52,430	1,489	1,186
2	17,417	2627495	43917	50,008	47,570	N/A	1,256

Enantioselective reaction, er = 95:5

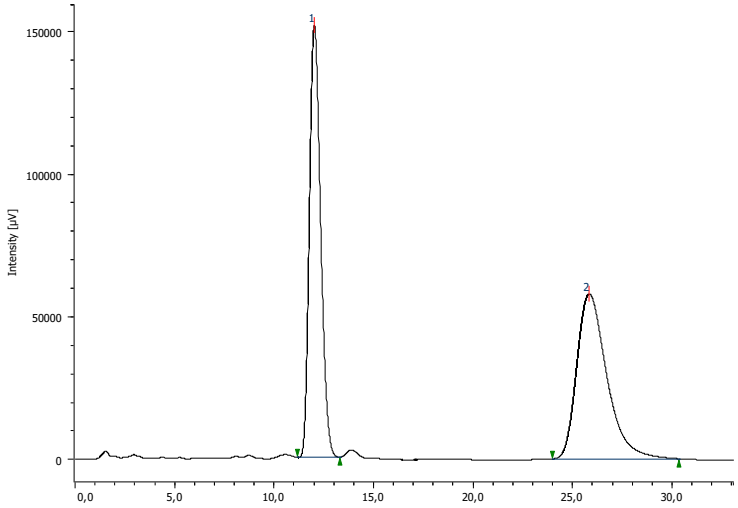


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	16,175	609809	11165	95,256	94,881	1,422	1,164
2	18,192	30372	602	4,744	5,119	N/A	1,300

(*S*)-3-(3-((*Tert*-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)indolin-2-one (8l).

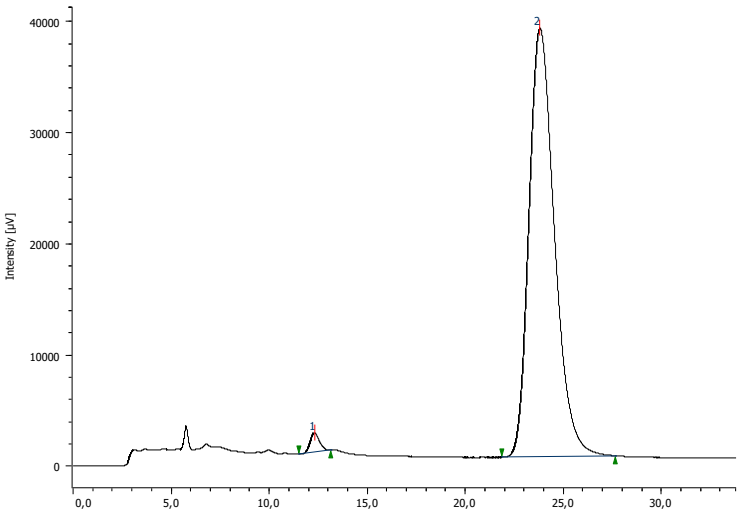
Phenomenex Lux i-Amylose-3, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 23.8 min, t_R (minor) = 12.3 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	12,017	5900761	151125	49,448	72,353	7,464	1,209
2	25,800	6032620	57746	50,552	27,647	N/A	1,440

Enantioselective reaction, er = 98:2

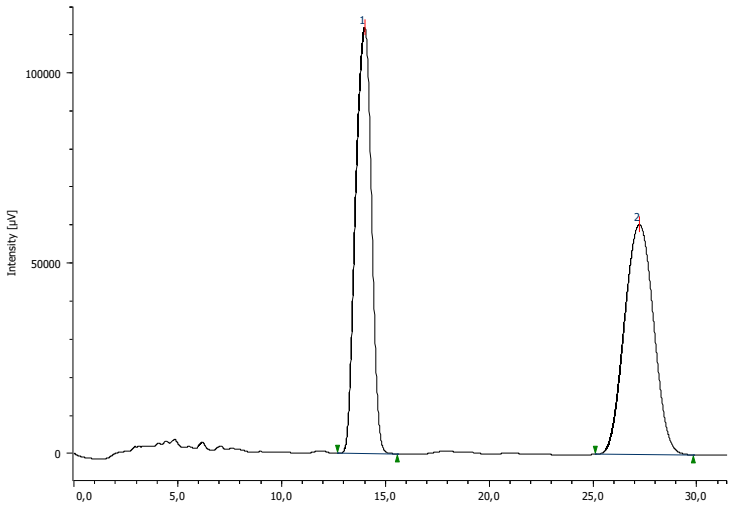


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	12,292	57886	1735	1,636	4,316	7,124	1,196
2	23,783	3479886	38475	98,364	95,684	N/A	1,290

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(oct-1-yn-1-yl)indolin-2-one (8m).

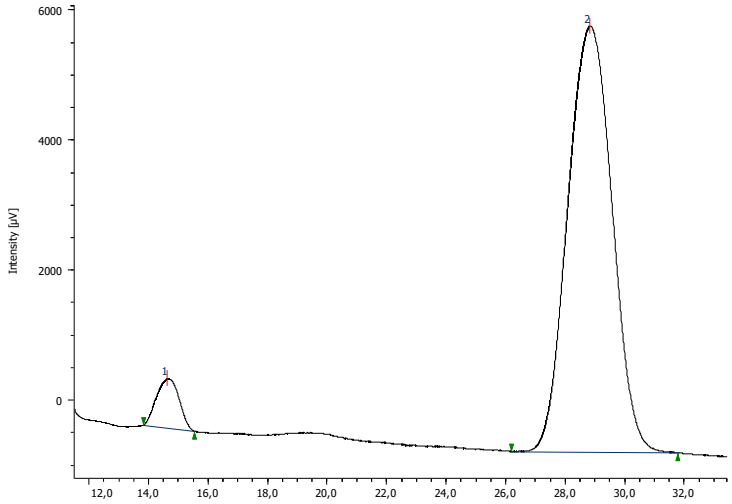
Phenomenex Lux i-Amylose-1, hexane:2-propanol 70:30, 1 mL/min, λ = 254 nm, t_R (major) = 28.8 min, t_R (minor) = 14.6 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	13,992	5907090	111577	50,083	64,910	6,398	0,936
2	27,208	5887527	60318	49,917	35,090	N/A	1,019

Enantioselective reaction, er = 94:6

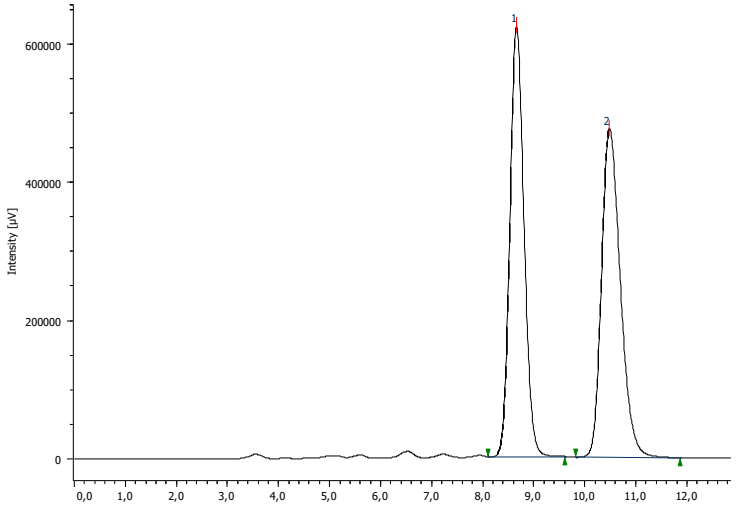


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	14,633	39832	755	5,562	10,348	6,582	1,014
2	28,808	676306	6538	94,438	89,652	N/A	1,036

(*S*)-3-(4-Bromobut-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)indolin-2-one (8n).

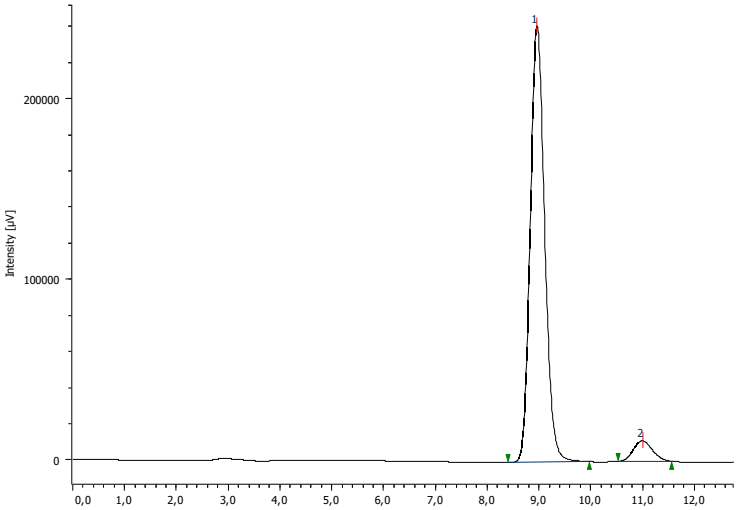
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 8.9 min, t_R (minor) = 10.9 min.

Racemic sample:



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	8,650	11979540	622659	49,655	56,741	3,115	1,112
2	10,467	12146161	474703	50,345	43,259	N/A	1,294

Enantioselective compound, er = 94:6

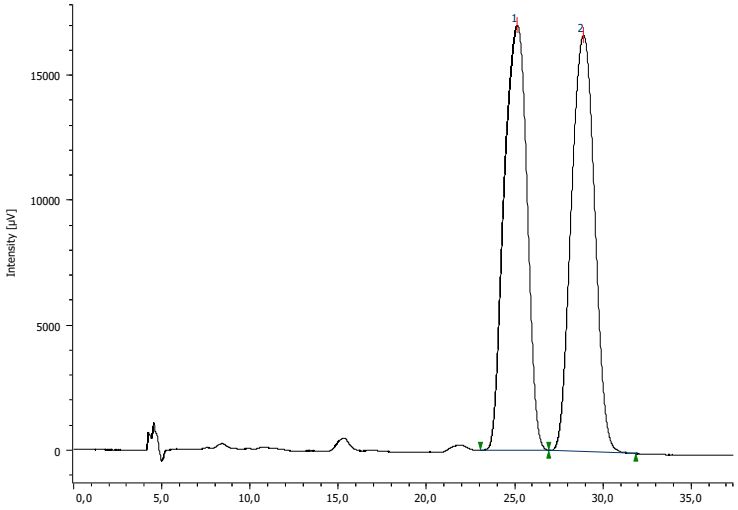


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	8,950	4664270	240932	94,134	95,508	3,429	1,142
2	10,983	290645	11333	5,866	4,492	N/A	1,113

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(3,3-dimethylbut-1-yn-1-yl)indolin-2-one (8o).

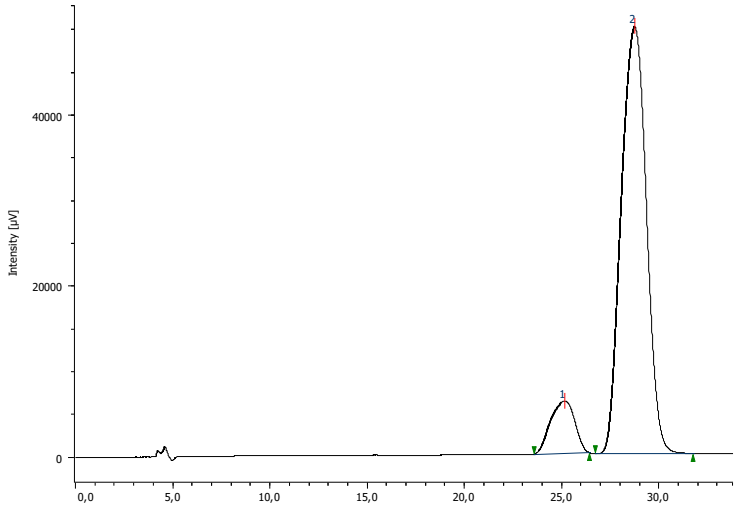
Phenomenex Lux i-Amylose-1, hexane:2-propanol 90:10, 0.7 mL/min, λ = 254 nm, t_R (major) = 28.7 min, t_R (minor) = 25.1 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	25,108	1521444	16953	49,907	50,485	1,481	0,934
2	28,858	1527128	16627	50,093	49,515	N/A	1,012

Enantioselective reaction, er = 89:11

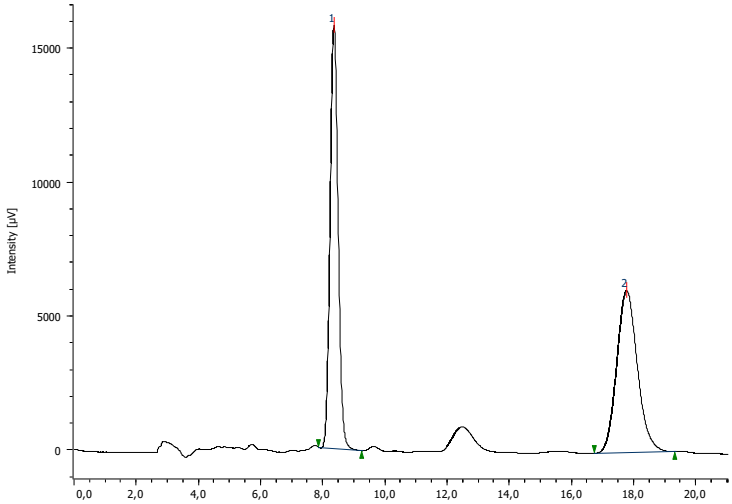


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	25,125	529296	6120	10,584	10,932	1,455	0,901
2	28,717	4471380	49864	89,416	89,068	N/A	1,010

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-5-fluoro-3-(phenylethynyl)indolin-2-one (9a).

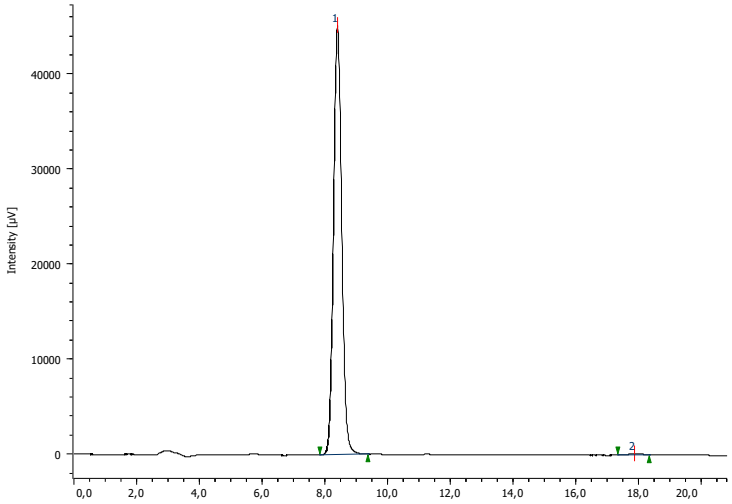
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 8.4 min, t_R (minor) = 17.9 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	8,350	282360	15761	50,330	72,303	11,262	1,094
2	17,750	278654	6038	49,670	27,697	N/A	1,145

Enantioselective reaction, er > 99:1

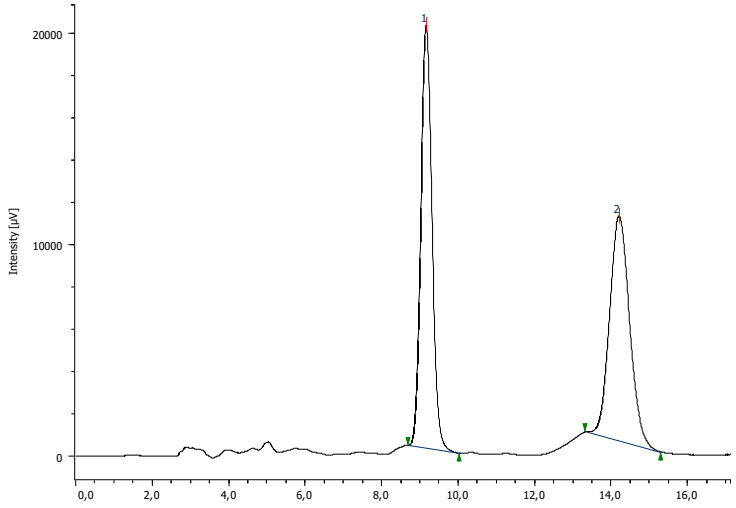


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	8,392	826169	45057	99,570	99,767	12,865	1,085
2	17,867	3571	105	0,430	0,233	N/A	0,901

(*S*)-5-Chloro-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(phenylethynyl)indolin-2-one (9b).

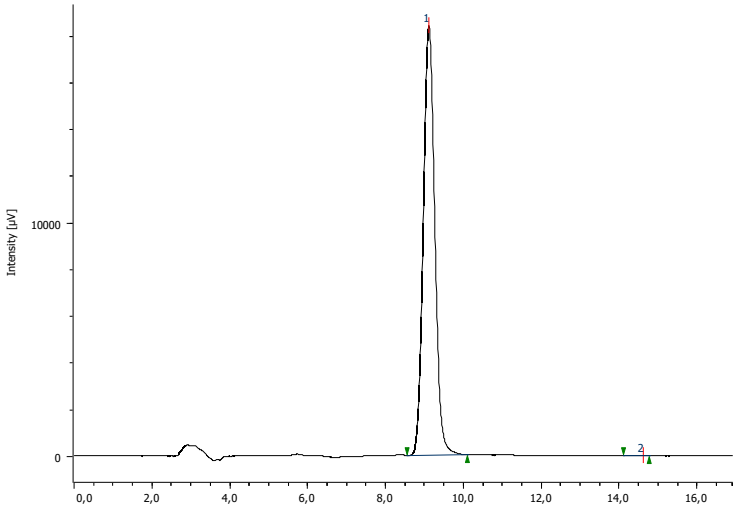
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 9.1 min, t_R (minor) = 14.6 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	9,158	403248	19940	51,076	65,274	6,784	1,081
2	14,192	386261	10608	48,924	34,726	N/A	1,102

Enantioselective reaction, er > 99:1

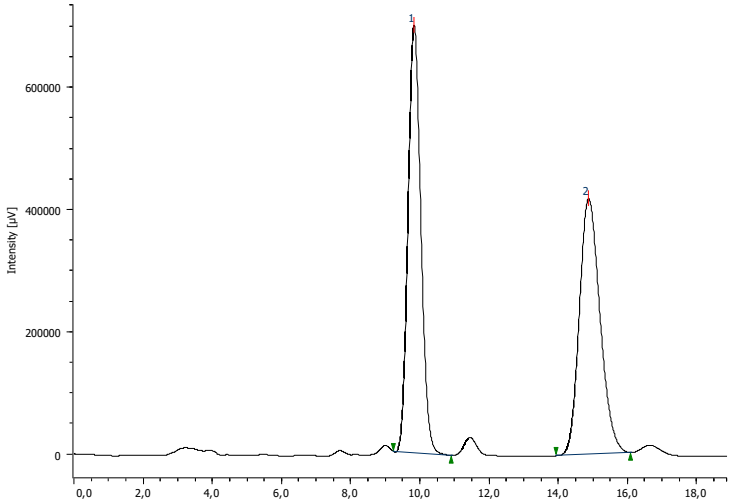


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	9,100	372318	18351	99,972	99,970	8,573	1,103
2	14,608	103	5	0,028	0,030	N/A	0,607

(*S*)-5-Bromo-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-(phenylethynyl)indolin-2-one (9c).

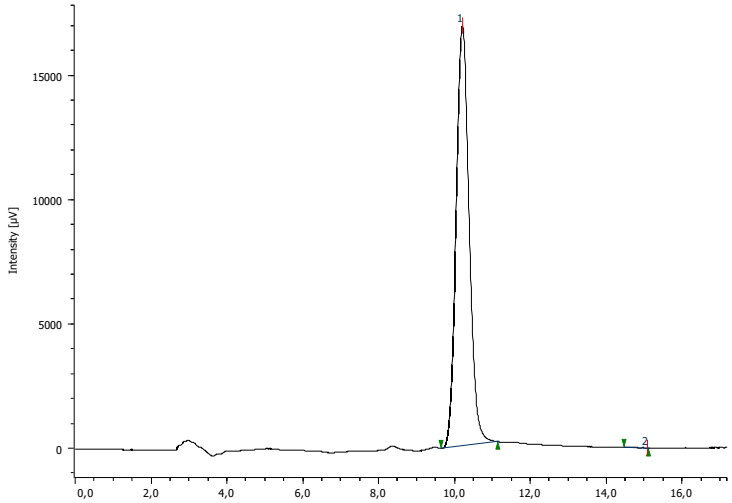
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 10.2 min, t_R (minor) = 14.9 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	9,817	17957244	698342	50,782	62,553	5,700	1,129
2	14,858	17404495	418056	49,218	37,447	N/A	1,198

Enantioselective reaction, er > 99:1

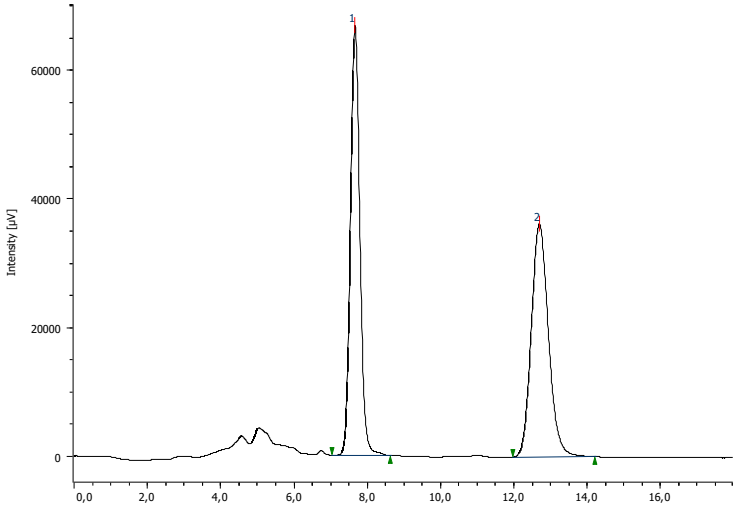


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	10,200	404058	16859	99,987	99,995	N/A	1,105
2	15,075	51	1	0,013	0,005	N/A	N/A

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-5-methyl-3-(phenylethynyl)indolin-2-one (9d).

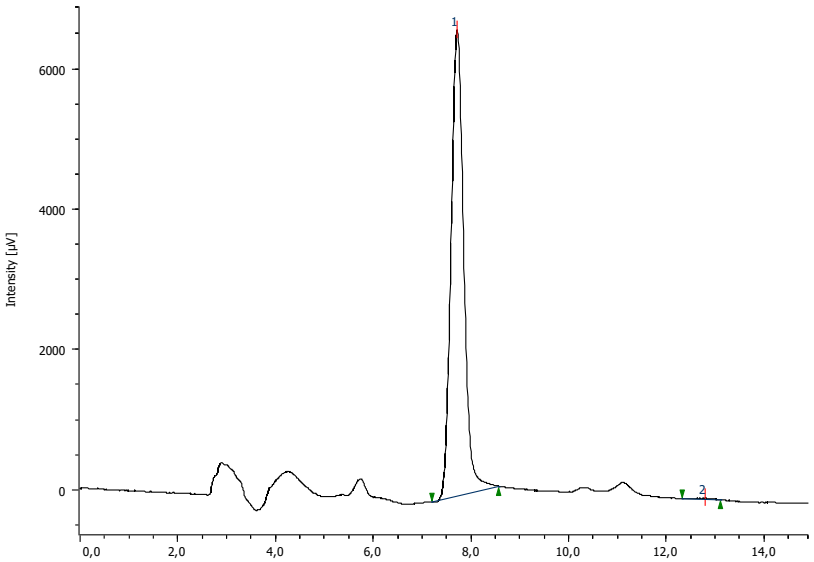
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 7.7 min, t_R (minor) = 12.7 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	7,650	1195414	66723	50,379	64,845	7,709	1,100
2	12,675	1177430	36173	49,621	35,155	N/A	1,152

Enantioselective reaction,er > 99:1

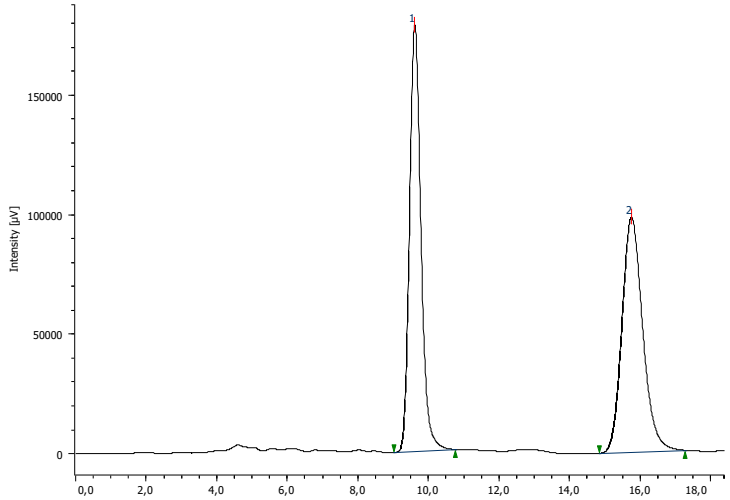


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	7,708	119781	6631	99,763	99,763	9,651	1,120
2	12,767	284	16	0,237	0,237	N/A	0,822

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-5-methoxy-3-(phenylethynyl)indolin-2-one (9e).

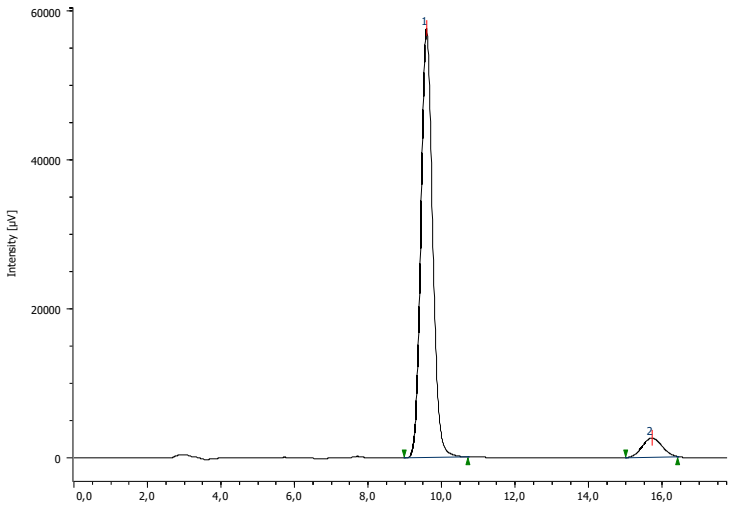
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 9.6 min, t_R (minor) = 15.7 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	9,600	4030540	177973	50,151	64,448	7,524	1,196
2	15,733	4006327	98176	49,849	35,552	N/A	1,202

Enantioselective reaction, er = 93:7

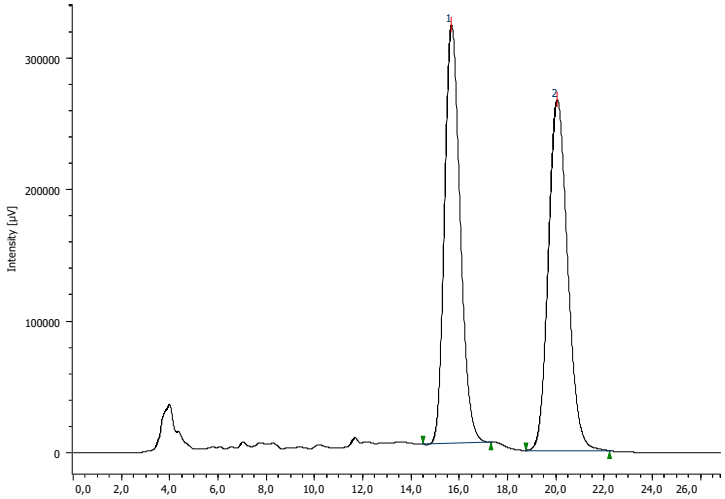


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	9,575	1263982	57407	92,914	95,728	7,731	1,109
2	15,700	96395	2562	7,086	4,272	N/A	1,021

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-5-nitro-3-(phenylethynyl)indolin-2-one (9f).

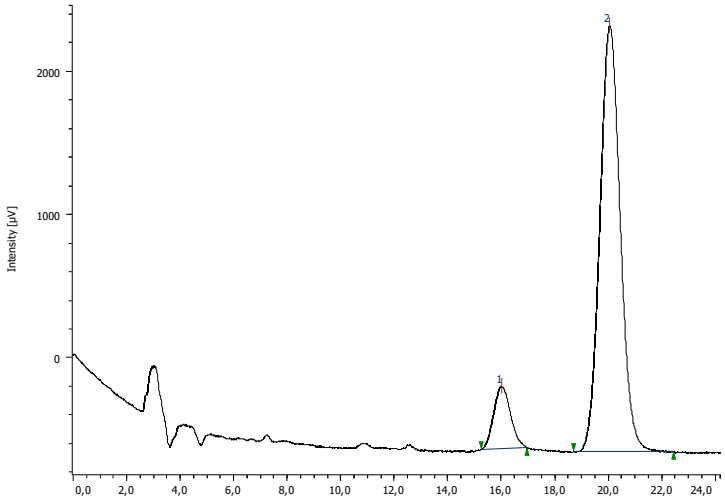
Phenomenex Lux Cellulose-1, hexane:2-propanol 70:30, 1 mL/min, λ = 254 nm, t_R (major) = 20.0 min, t_R (minor) = 16.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	15,658	14233286	317107	49,216	54,391	3,346	1,204
2	20,033	14686472	265910	50,784	45,609	N/A	1,141

Enantioselective reaction, er = 89:11

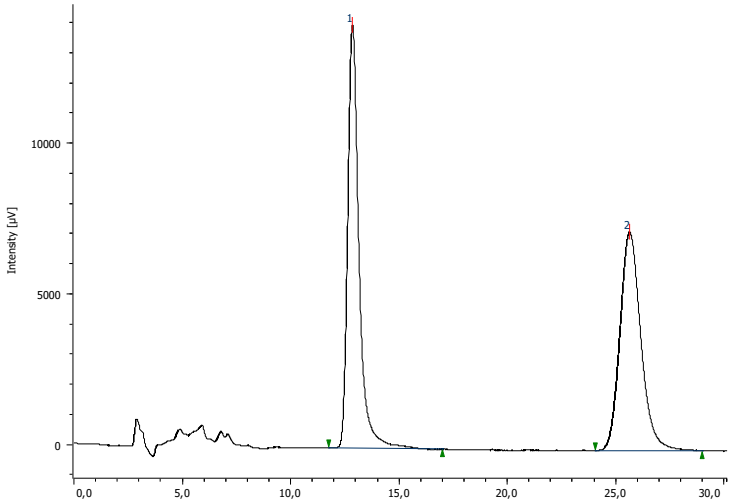


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	15,983	19004	434	10,796	12,757	3,173	1,165
2	20,025	157020	2969	89,204	87,243	N/A	1,089

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-7-methyl-3-(phenylethynyl)indolin-2-one (9g).

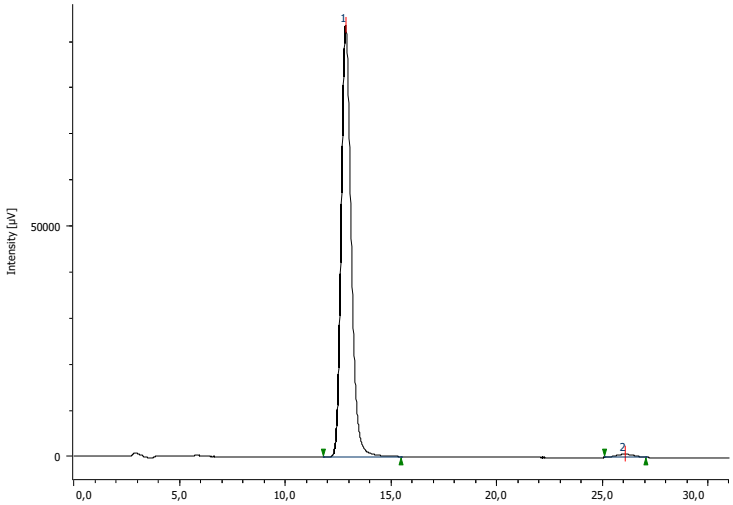
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 12.8 min, t_R (minor) = 26.0 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	12,842	501165	13992	50,765	65,927	9,909	1,421
2	25,617	486064	7232	49,235	34,073	N/A	1,183

Enantioselective reaction, er = 99:1

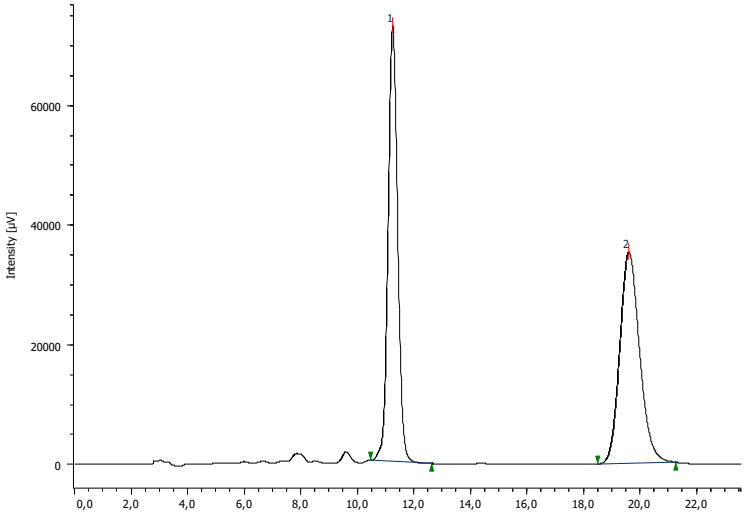


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	12,850	3026876	93399	98,736	99,287	10,864	1,229
2	26,042	38734	671	1,264	0,713	N/A	1,021

(*S*)-5-chloro-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((2-fluorophenyl)ethynyl)indolin-2-one (9h).

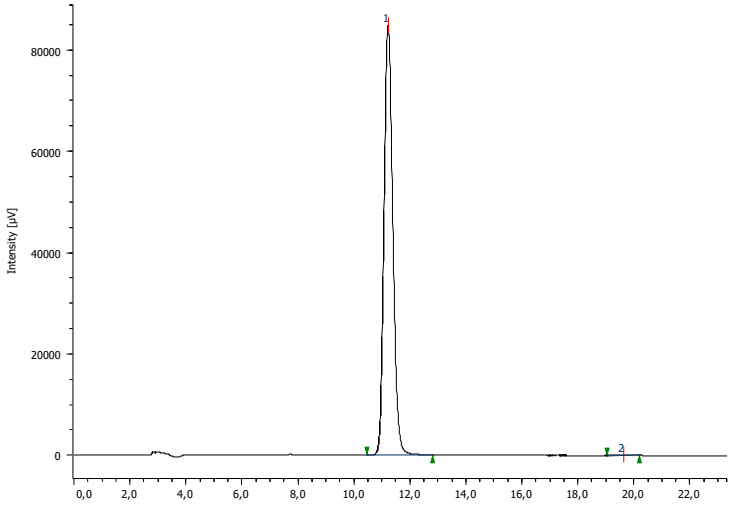
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 11.2 min, t_R (minor) = 19.6 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	11,242	1725349	72693	50,017	67,314	8,870	1,061
2	19,583	1724188	35299	49,983	32,686	N/A	1,177

Enantioselective reaction, er > 99:1

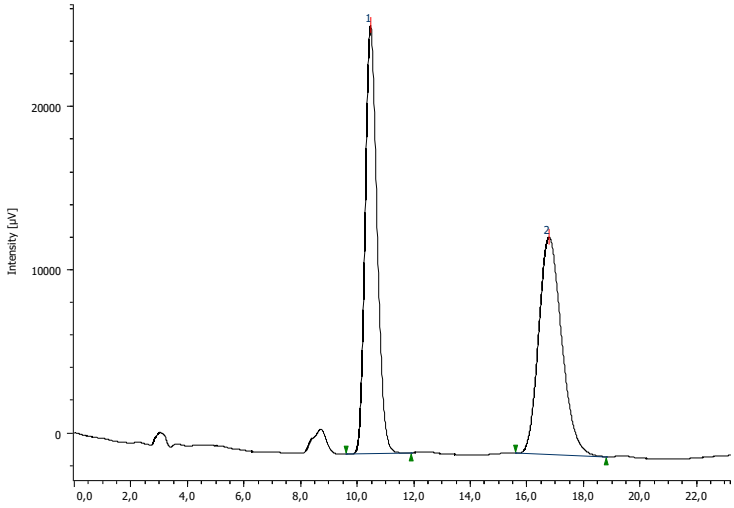


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	11,208	1875118	84601	99,815	99,893	9,895	1,151
2	19,600	3481	90	0,185	0,107	N/A	0,979

(*S*)-3-(3-((*Tert*-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-5-chloro-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)indolin-2-one (9i).

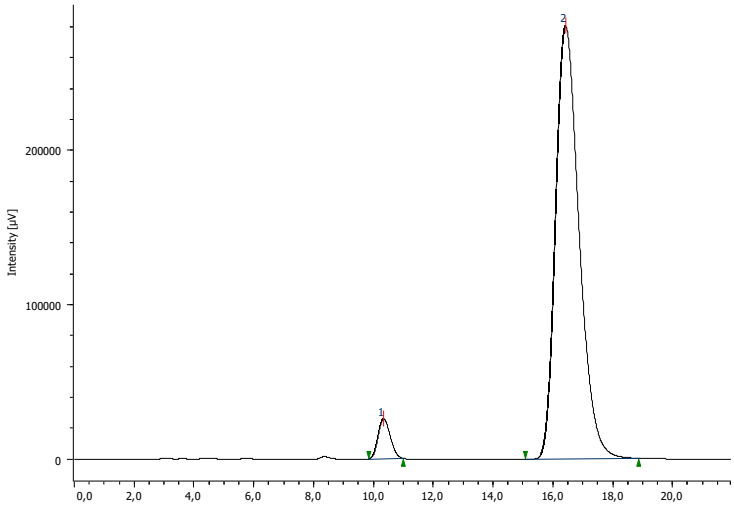
Phenomenex Lux i-Amylose-3, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 16.8 min, t_R (minor) = 10.5 min.

Racemic sample, er = 95:5



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	10,458	766110	26189	50,634	66,299	5,637	1,183
2	16,758	746930	13312	49,366	33,701	N/A	1,219

Enantioselective reaction,er = 95:5

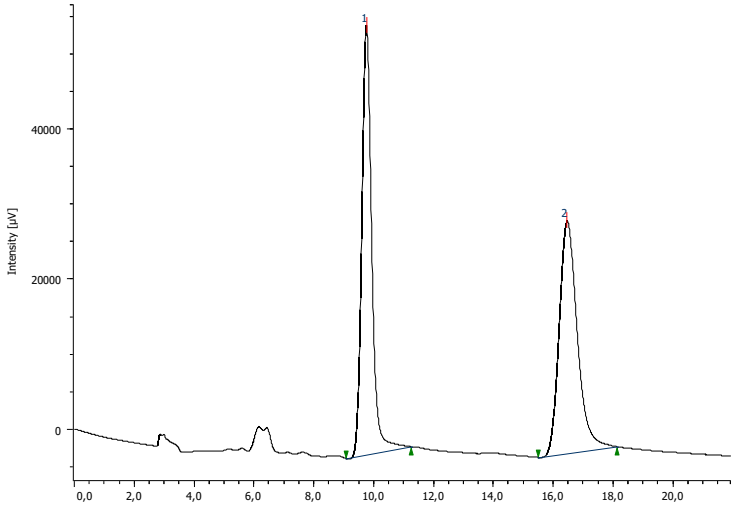


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	10,325	735682	25839	4,605	8,451	5,563	1,164
2	16,400	15240398	279918	95,395	91,549	N/A	1,325

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((2-fluorophenyl)ethynyl)-5-methylindolin-2-one (9j).

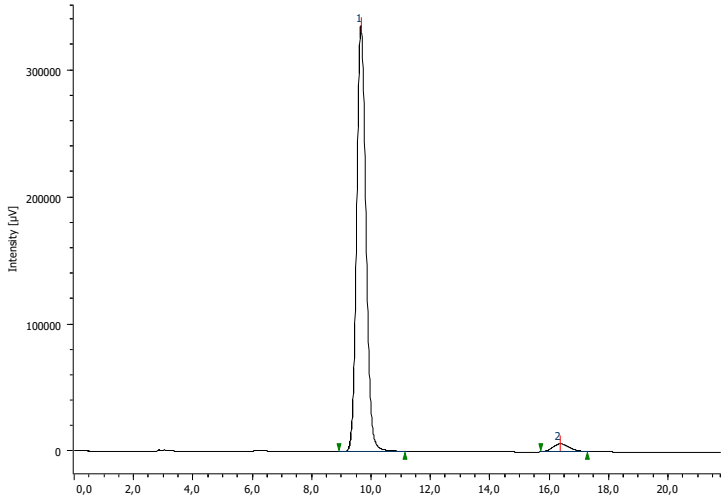
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 9.7 min, t_R (minor) = 16.4 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	9,750	1330804	57048	50,620	64,870	8,117	1,176
2	16,450	1298201	30894	49,380	35,130	N/A	1,302

Enantioselective reaction, er = 97:3

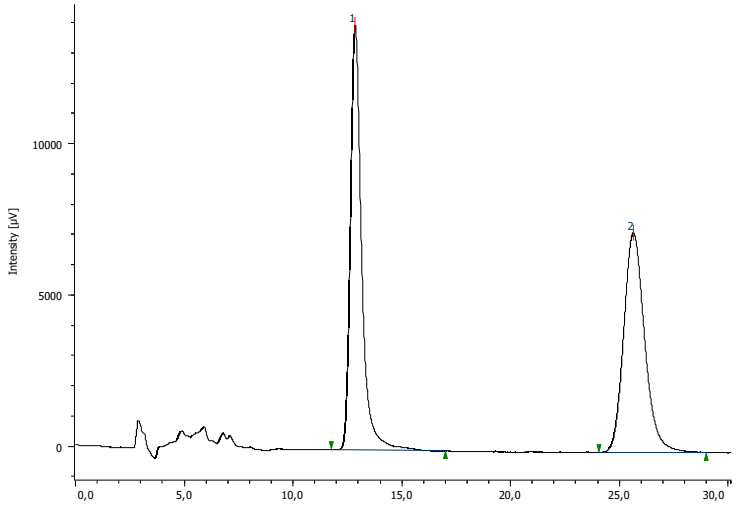


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	9,650	7289487	334646	96,791	98,201	8,304	1,112
2	16,358	241706	6129	3,209	1,799	N/A	1,145

(*S*)-3-(3-((*Tert*-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-5-methylindolin-2-one (9k).

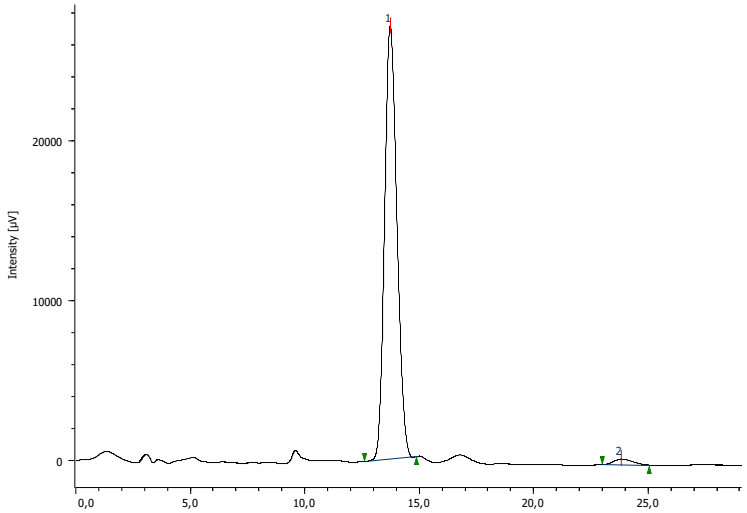
Phenomenex Lux i-Amylose-3, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 13.7 min, t_R (minor) = 23.8 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	12,842	501165	13992	50,765	65,927	9,909	1,421
2	25,617	486064	7232	49,235	34,073	N/A	1,183

Enantioselective reaction, er = 98:2

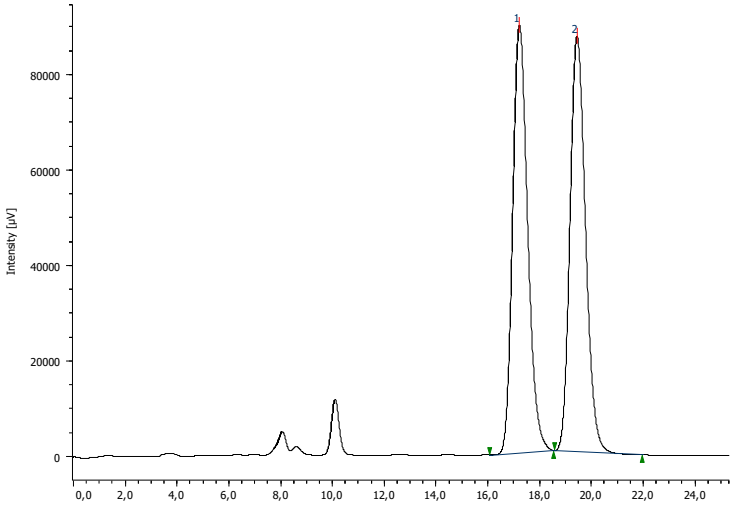


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	13,717	1013852	27033	97,981	98,661	7,899	1,150
2	23,775	20894	367	2,019	1,339	N/A	1,320

(*S*)-1-(2,6-Dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-3-((2-fluorophenyl)ethynyl)-7-methylindolin-2-one (9l).

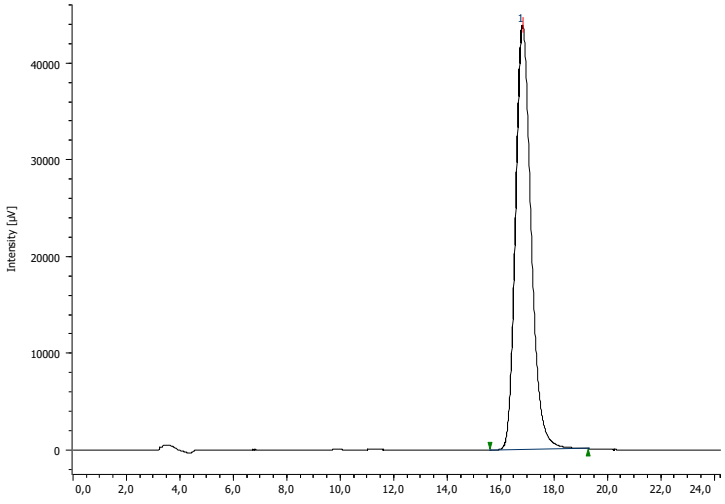
Phenomenex Lux Cellulose-1, hexane:2-propanol 80:20, 1 mL/min, λ = 254 nm, t_R (major) = 16.8 min, t_R (minor) = 19.4 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	17,200	3580996	89371	49,860	50,714	2,097	1,215
2	19,425	3601059	86854	50,140	49,286	N/A	1,177

Enantioselective reaction, er > 99:1

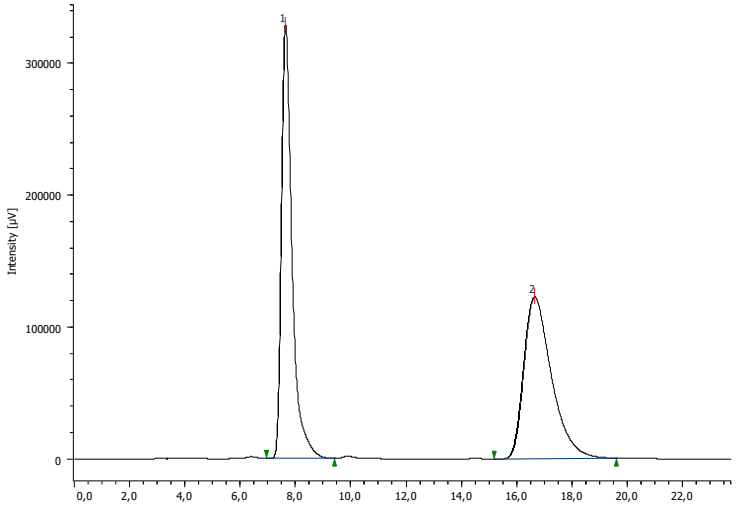


#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	16,808	1770573	43722	100,000	100,000	N/A	1,219

(*S*)-3-(3-((*Tert*-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-1-(2,6-dichlorobenzyl)-3-((3,5-dichlorophenyl)amino)-7-methylindolin-2-one (9m).

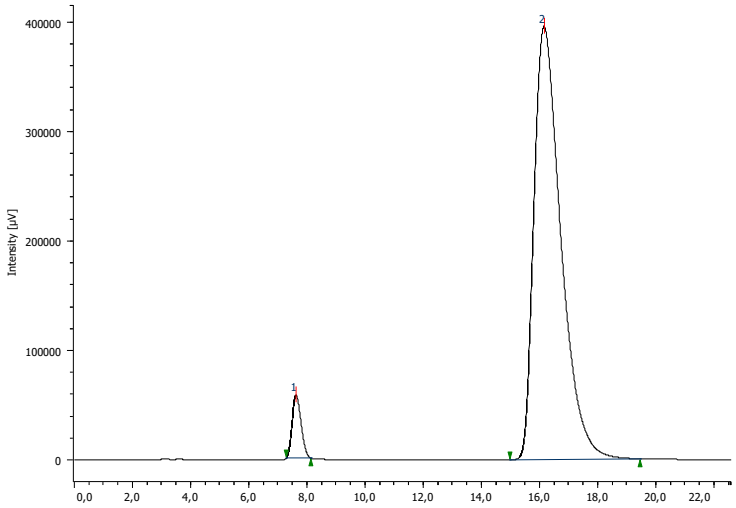
Phenomenex Lux i-Amylose-3, hexane:2-propanol 60:40, 1 mL/min, λ = 254 nm, t_R (major) = 16.1 min, t_R (minor) = 7.6 min.

Racemic sample



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	7,633	8691797	327692	50,447	72,781	7,430	1,712
2	16,633	8537779	122549	49,553	27,219	N/A	1,513

Enantioselective reaction, er = 95:5



#	t_R	Area	Height	Area%	Height%	Resolution	Symmetry Factor
1	7,625	1219472	57391	4,569	12,685	7,633	1,180
2	16,142	25471803	395038	95,431	87,315	N/A	1,600

12. X-Ray structure and crystal data of 2e and 8c

12.1. X-Ray structure and crystal data of 2e

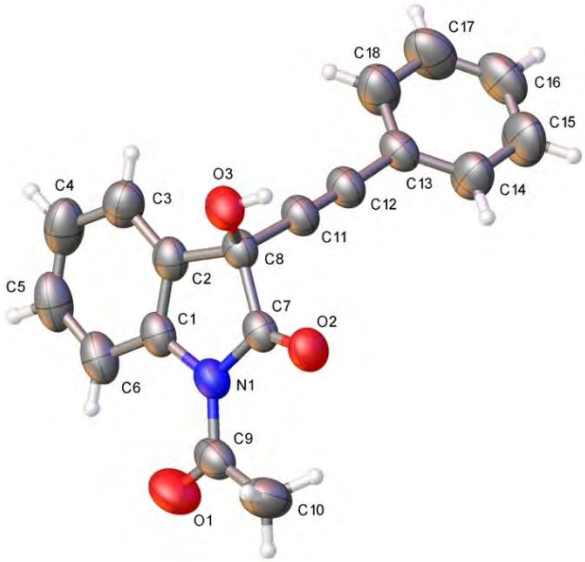


Table 1 Crystal data and structure refinement for 2e.

Empirical formula	$C_{18}H_{13}NO_3$
Formula weight	291.29
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.3533(2)
b/Å	5.06800(10)
c/Å	13.1835(2)
α/°	90
β/°	101.957(2)
γ/°	90
Volume/Å^3	742.10(2)
Z	2
ρ_{calc}g/cm^3	1.304
μ/mm^{-1}	0.731
F(000)	304.0

Crystal size/mm^3	0.275 × 0.112 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.854 to 151.194
Index ranges	-12 ≤ h ≤ 14, -6 ≤ k ≤ 5, -16 ≤ l ≤ 16
Reflections collected	13704
Independent reflections	2887 [R_{int} = 0.0272, R_{sigma} = 0.0190]
Data/restraints/parameters	2887/1/202
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0329, wR_2 = 0.0854
Final R indexes [all data]	R_1 = 0.0369, wR_2 = 0.0893
Largest diff. peak/hole / e Å^{-3}	0.11/-0.11
Flack parameter	0.01(13)

Table 4 Bond Lengths for 2e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C9	1.205(3)	C5	C6	1.385(4)
O2	C7	1.205(2)	C7	C8	1.548(3)
O3	C8	1.407(3)	C8	C11	1.473(3)
N1	C1	1.434(3)	C9	C10	1.478(4)
N1	C7	1.400(2)	C11	C12	1.190(3)
N1	C9	1.419(3)	C12	C13	1.440(3)
C1	C2	1.383(3)	C13	C14	1.372(4)
C1	C6	1.392(3)	C13	C18	1.371(4)
C2	C3	1.377(3)	C14	C15	1.385(3)
C2	C8	1.504(3)	C15	C16	1.363(4)
C3	C4	1.397(4)	C16	C17	1.359(5)
C4	C5	1.377(5)	C17	C18	1.387(4)

Table 5 Bond Angles for 2e.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C7	N1	C1	109.26(17)	O3	C8	C11	113.04(17)
C7	N1	C9	126.64(18)	C2	C8	C7	101.84(16)
C9	N1	C1	124.09(17)	C11	C8	C2	110.14(16)
C2	C1	N1	110.00(16)	C11	C8	C7	109.62(18)
C2	C1	C6	120.8(2)	O1	C9	N1	118.9(2)
C6	C1	N1	129.2(2)	O1	C9	C10	122.5(3)
C1	C2	C8	110.00(19)	N1	C9	C10	118.6(2)
C3	C2	C1	121.9(2)	C12	C11	C8	176.3(2)
C3	C2	C8	128.1(2)	C11	C12	C13	178.0(3)
C2	C3	C4	117.8(3)	C14	C13	C12	120.7(2)
C5	C4	C3	119.9(3)	C18	C13	C12	120.2(2)
C4	C5	C6	122.8(2)	C18	C13	C14	119.1(2)
C5	C6	C1	116.8(3)	C13	C14	C15	120.3(3)
O2	C7	N1	127.0(2)	C16	C15	C14	120.2(3)
O2	C7	C8	124.60(18)	C17	C16	C15	119.9(2)
N1	C7	C8	108.40(16)	C16	C17	C18	120.2(3)
O3	C8	C2	111.27(18)	C13	C18	C17	120.3(3)
O3	C8	C7	110.37(16)				

Crystal structure determination of 2e

Crystal Data for $C_{18}H_{13}NO_3$ (M =291.29 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 11.3533(2) Å, b = 5.06800(10) Å, c = 13.1835(2) Å, β = 101.957(2)°, V = 742.10(2) Å^3, Z = 2, T = 296.15 K, μ(CuKα) = 0.731 mm^{-1}, *Dcalc* = 1.304 g/cm^3, 13704 reflections measured (6.854° ≤ 2Θ ≤ 151.194°), 2887 unique (R_{int} = 0.0272, R_{sigma} = 0.0190) which were used in all calculations. The final R_1 was 0.0329 (I > 2σ(I)) and wR_2 was 0.0893 (all data).

12.2. X-Ray structure and crystal data of 8c.

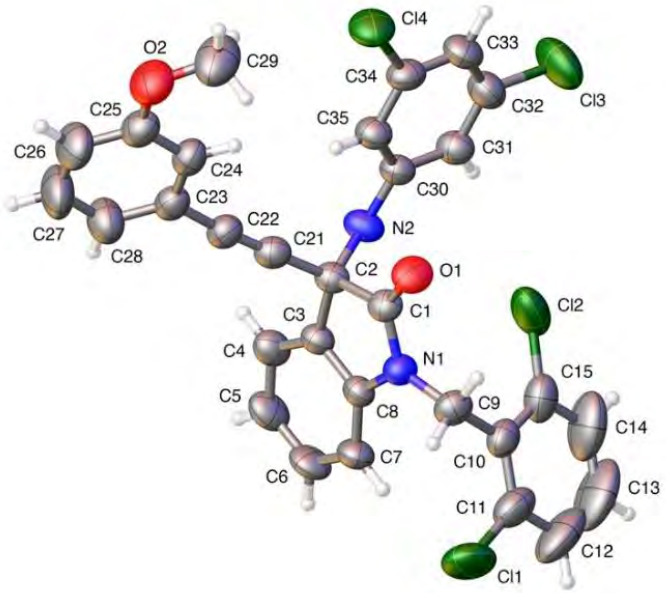


Table 1. Crystal Data and Structure Refinement for 8c.

Empirical formula	$C_{30}H_{20}Cl_4N_2O_2$
Formula weight	582.28
Temperature/K	298.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.1758(3)
b/Å	5.34020(10)
c/Å	21.8778(6)
α/°	90
β/°	101.147(3)
γ/°	90
Volume/Å^3	1395.68(6)
Z	2
ρ_{calc}g/cm^3	1.386
μ/mm^{-1}	4.102
F(000)	596.0
Crystal size/mm^3	0.411 × 0.052 × 0.045
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.4 to 150.118

Index ranges	$-15 \le h \le 15, -6 \le k \le 6, -27 \le l \le 18$
Reflections collected	9628
Independent reflections	5556 [R_{int} = 0.0237, R_{sigma} = 0.0355]
Data/restraints/parameters	5556/49/348
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.1124
Final R indexes [all data]	R_1 = 0.0528, wR_2 = 0.1189
Largest diff. peak/hole / e $Å^{-3}$	0.33/-0.51
Flack parameter	-0.004(9)

Table 2. Bond Lengths for 8c.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C11	1.738(7)	C9	C10	1.506(6)
Cl2	C15	1.741(6)	C10	C11	1.394(7)
Cl3	C32	1.738(5)	C10	C15	1.392(7)
Cl4	C34	1.740(5)	C11	C12	1.374(10)
O1	C1	1.217(5)	C12	C13	1.365(14)
O2	C25	1.356(6)	C13	C14	1.383(14)
O2	C29	1.391(7)	C14	C15	1.382(9)
N1	C1	1.361(5)	C21	C22	1.193(6)
N1	C8	1.405(5)	C22	C23	1.437(6)
N1	C9	1.456(5)	C23	C24	1.395(6)
N2	C2	1.467(5)	C23	C28	1.381(7)
N2	C30	1.396(5)	C24	C25	1.386(6)
C1	C2	1.561(5)	C25	C26	1.367(8)
C2	C3	1.514(5)	C26	C27	1.363(9)
C2	C21	1.465(5)	C27	C28	1.387(8)
C3	C4	1.370(6)	C30	C31	1.386(6)
C3	C8	1.384(5)	C30	C35	1.400(6)
C4	C5	1.392(6)	C31	C32	1.380(6)

Table 2. Bond Lengths for 8c.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C5	C6	1.372(7)	C32	C33	1.379(7)
C6	C7	1.389(7)	C33	C34	1.371(7)
C7	C8	1.384(5)	C34	C35	1.382(6)

Table 3. Bond Angles for 8c.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C25	O2	C29	118.1(4)	C13	C12	C11	119.5(8)
C1	N1	C8	111.5(3)	C12	C13	C14	120.6(7)
C1	N1	C9	121.6(3)	C15	C14	C13	119.3(8)
C8	N1	C9	126.9(3)	C10	C15	Cl2	120.2(4)
C30	N2	C2	124.2(3)	C14	C15	Cl2	118.2(6)
O1	C1	N1	125.4(4)	C14	C15	C10	121.6(7)
O1	C1	C2	126.7(3)	C22	C21	C2	179.2(5)
N1	C1	C2	107.7(3)	C21	C22	C23	174.0(5)
N2	C2	C1	109.1(3)	C24	C23	C22	118.2(4)
N2	C2	C3	109.5(3)	C28	C23	C22	122.0(4)
C3	C2	C1	101.3(3)	C28	C23	C24	119.9(4)
C21	C2	N2	112.2(3)	C25	C24	C23	120.1(4)
C21	C2	C1	111.1(3)	O2	C25	C24	124.6(5)
C21	C2	C3	113.0(3)	O2	C25	C26	115.8(5)
C4	C3	C2	129.8(4)	C26	C25	C24	119.6(5)
C4	C3	C8	121.1(4)	C27	C26	C25	120.3(5)
C8	C3	C2	109.1(3)	C26	C27	C28	121.5(5)
C3	C4	C5	117.9(4)	C23	C28	C27	118.6(5)
C6	C5	C4	121.0(4)	N2	C30	C35	122.1(4)
C5	C6	C7	121.3(4)	C31	C30	N2	119.2(4)
C8	C7	C6	117.2(4)	C31	C30	C35	118.6(4)
C3	C8	N1	110.0(3)	C32	C31	C30	119.3(4)
C3	C8	C7	121.4(4)	C31	C32	Cl3	118.7(4)
C7	C8	N1	128.6(4)	C33	C32	Cl3	118.0(4)

Table 3. Bond Angles for 8c.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	C9	C10	113.9(4)	C33	C32	C31	123.3(4)
C11	C10	C9	121.6(5)	C34	C33	C32	116.4(4)
C15	C10	C9	121.5(4)	C33	C34	Cl4	119.2(3)
C15	C10	C11	116.9(5)	C33	C34	C35	122.8(4)
C10	C11	Cl1	120.1(4)	C35	C34	Cl4	118.1(4)
C12	C11	Cl1	117.8(6)	C34	C35	C30	119.6(4)
C12	C11	C10	122.1(7)				

Crystal structure determination of 8c

Crystal Data. $C_{30}H_{20}Cl_4N_2O_2$ (*M* =582.28 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 12.1758(3) Å, *b* = 5.34020(10) Å, *c* = 21.8778(6) Å, *β* = 101.147(3)°, *V* = 1395.68(6) Å^3, *Z* = 2, *T* = 298.15 K, μ(Cu Kα) = 4.102 mm^{-1}, *Dcalc* = 1.386 g/cm^3, 9628 reflections measured (7.4° ≤ 2Θ ≤ 150.118°), 5556 unique (R_{int} = 0.0237, R_{sigma} = 0.0355) which were used in all calculations. The final R_1 was 0.0453 (I > 2σ(I)) and wR_2 was 0.1189 (all data).