Electronic Supplementary Information (ESI)

Chiral Phosphoric Acid-Catalyzed Direct Asymmetric Mannich Reaction of Cyclic *C*-Acylimines with Simple Ketones: Facile Access to C2-Quaternary Indolin-3-ones

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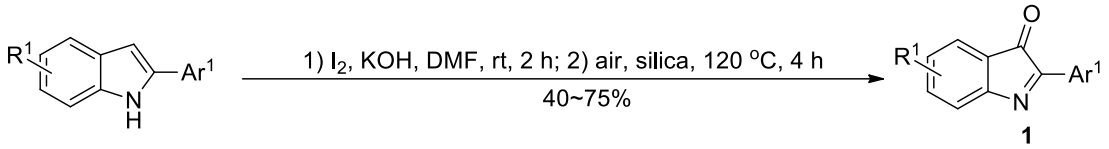
General information

^{1}H, ^{13}C and ^{19}F were recorded on Bruker AV 400 MHz instrument at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR), or Bruker AV 600 MHz instrument at 600 MHz (^{1}H NMR), 150 MHz (^{13}C NMR), as well as 565 MHz (^{19}F NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external CCl_3F, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). MS were recorded on a VG ZABHS spectrometer with the ESI resource.High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker miorOTOF-QII instrument. Optical rotations were determined using an Autopol IV-T. IR spectra were recordedon an AVATAR 360 FT-IR spectromer. HPLC analyses were carried out on a HewlettPackard Model HP 1200 instrument. X-ray structural analysis was conducted on the Bruker APEX-II CCD instrument.

Materials: Tetrahydrofuran (THF), diethyl ether, and toluene were distilled from sodium/benzophenone prior to use; CH_2Cl_2 was distilled from CaH_2; All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200–300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography. 2-aryl substituted 3*H*-indol-3-ones **1**,[1] 1'*H*,3*H*-[2,3'-biindol]-3-ones,[2] 1'-tosyl-1'*H*,3*H*-[2,3'-biindol]-3-one **5a**,[3] 2-aryl indoles,[4] and chiral phosphoric acids **4a**–**j**[5] were prepared according to the reported procedures.

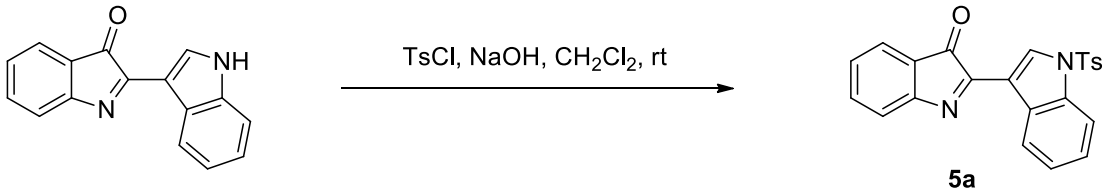
General procedure for synthesis of 2-aryl substituted 3*H*-indol-3-ones 1[1]



1

A solution of I_2 (4.38 g, 17.2 mmol) in DMF (30 mL) was dropped into a solution of 2-aryl indoles (17.1 mmol) and KOH (2.39 g, 42.7 mmol) in DMF (30 mL) at rt and stirred for 2 h. The mixture was then purged with air, silica (7.10 g) was added and the mixture heated to 120 ℃ for 4 h. Upon cooling, water (200 mL) was added and the mixture extracted with ethyl acetate (3 × 100 mL). The organic extracts were combined, dried (Na_2SO_4), filtered and concentrated in vacuo. Purification by flash chromatography on silica get eluting with petroleum ether/ethyl acetate (5:1) gave the 2-aryl substituted 3*H*-indol-3-ones **1** as red solids (40~75%).

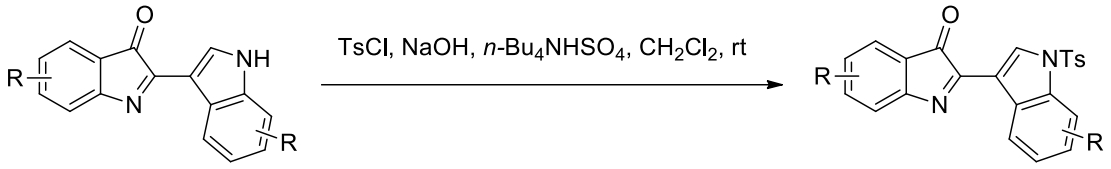
***N*-tosylation of 1'*H*,3*H*-[2,3'-biindol]-3-ones for synthesis of substrates 5**



5a

A mixture of 246.3 mg (1.0 mmol) of 1'*H*,3*H*-[2,3'-biindol]-3-one, 10 mL of CH_2C1_2 and 48.0 mg (1.2 mmol) of NaOH was stirred for 15 minutes. Then TsCl (285.9 mg, 1.5 mmol) was added in one portion and the mixture was stirred at room temperature until no 1'*H*,3*H*-[2,3'-biindol]-3-one was detected by TLC. The solution was washed exhaustively with water, dried with Na_2SO_4 and concentrated. The material was passed through a plug of silica gel (eluting with 30% petroleum ether/CH_2Cl_2 to CH_2Cl_2) and concentrated to furnish a red solid (345.1 mg, 86%). Spectral data

were in complete agreement with reported values.[3]



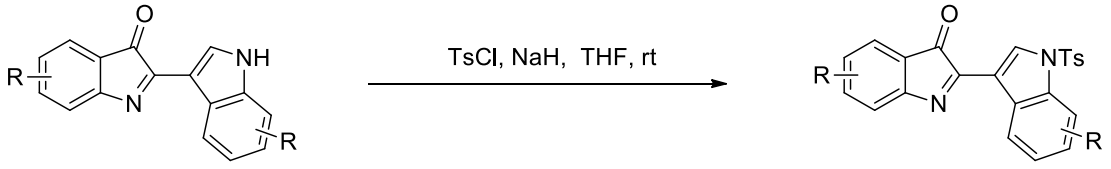
5j, R= 5-Me, 92%
5k, R= 5-F, 83%
5l, R= 5-Cl, 80%

To a solution of the corresponding 1'*H*,3*H*-[2,3'-biindol]-3-one (1.0 equiv.) in anhydrous DCM (0.1 M) was added *n*-Bu_4NHSO_4 (0.1 equiv.) followed by addition of freshly powdered NaOH (4.0 equiv.). The resultant solution was allowed to stir at room temperature for 10 minutes before addition of TsCl (2.0 equiv.) and then allowed to stir at room temperature (monitored via TLC – typically 0.5-1 hours). After this time, the reaction was quenched with H_2O (equal to reaction solvent volume), the organic phase was collected, and the aqueous phase was extracted three times with CH_2Cl_2 (equal to reaction volume). The combined organic phases dried over $MgSO_4$, filtered and solvent removed under reduced pressure. The material was passed through a plug of silica gel (eluting with 30% petroleum ether/CH_2Cl_2 to CH_2Cl_2) and concentrated to furnish a red solid which was used without further purification for its low solubility.

5,5'-dimethyl-1'-tosyl-1'*H*,3*H*-[2,3'-biindol]-3-one (5j): m.p.: 212–214 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.32 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.36 (s, 1H), 7.30 (s, 2H), 7.27 – 7.18 (m, 3H), 2.49 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H); **HRMS (ESI)** found m/z 429.1265 $[M + H]^+$, calcd for $C_{25}H_{21}N_2O_3S$ 429.1273.

5,5'-difluoro-1'-tosyl-1'*H*,3*H*-[2,3'-biindol]-3-one (5k): m.p.: 256–258 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.22 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.96 (dd, *J* = 9.1, 4.3 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.23 – 7.11 (m, 2H), 2.37 (s, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –113.11 (ddd, *J* = 8.8, 6.3, 4.2 Hz, 1F), –117.37 (td, *J* = 8.9, 4.3 Hz, 1F); **HRMS (ESI)** found m/z 437.0763 $[M + H]^+$, calcd for $C_{23}H_{15}F_2N_2O_3S$ 437.0771.

5,5'-dichloro-1'-tosyl-1'*H*,3*H*-[2,3'-biindol]-3-one (5l): m.p.: 251–252 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.46 (m, 2H), 7.42 – 7.35 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H); **HRMS (ESI)** found m/z 469.0176 $[M + H]^+$, calcd for $C_{23}H_{15}Cl_2N_2O_3S$ 469.0180.



5m, R= 5-Br, 96%
5n, R= 6-Br, 91%

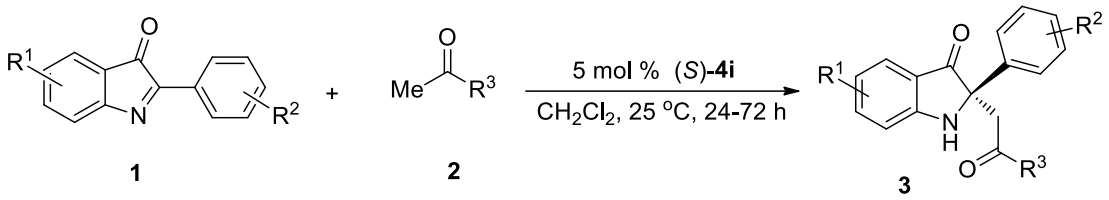
Sodium hydride (1.1 equiv.) was carefully added to a solution of 1'*H*,3*H*-[2,3'-biindol]-3-one (1.0 equiv.) in anhydrous THF (0.1 M) at 0 ℃. The mixture was stirred at this temperature for 15 minutes. Then TsCl (1.02 equiv.) was added in one portion and the mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), the crude mixture was extracted with CH_2Cl_2 and the organic layer was dried over Na_2SO_4, concentrated under reduced pressure. The material was passed through a plug of silica gel (eluting with 30% petroleum

ether/CH_2Cl_2 to CH_2Cl_2) and concentrated to furnish a red solid which was used without further purification for its low solubility.

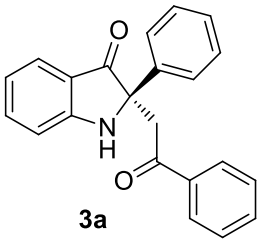
5,5'-dibromo-1'-tosyl-1'*H*,3*H*-[2,3'-biindol]-3-one (5m): m.p.: 169–171 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.69 (d, *J* = 2.0 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.67 (dt, *J* = 4.5, 2.1 Hz, 2H), 7.52 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H); **HRMS (ESI)** found m/z 556.9171 $[M + H]^+$, calcd for $C_{23}H_{15}Br_2N_2O_3S$ 556.9170.

6,6'-dibromo-1'-tosyl-1'*H*,3*H*-[2,3'-biindol]-3-one (5n): m.p.: 275–278 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 1.6 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 1.2 Hz, 1H), 7.51 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 2.38 (s, 3H); **HRMS (ESI)** found m/z 556.9175 $[M + H]^+$, calcd for $C_{23}H_{15}Br_2N_2O_3S$ 556.9170.

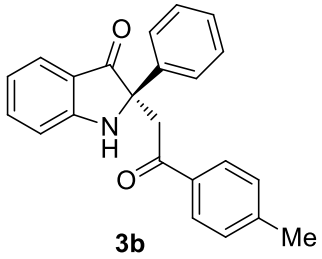
General procedure for the reaction of 2-aryl-3*H*-indol-3-ones 1 with simple ketones 2



To a 10 mL Schlenk flask equipped with a stirring bar was added 2-aryl substituted 3*H*-indol-3-ones **1** (0.1 mmol), chiral phosphoric acid (*S*)-**4i** (0.005 mmol, 5 mol %), CH_2Cl_2 (1 mL). Simple ketones **2** (1.0 mmol, 10.0 equiv) was added to the mixture. Then the resulting mixture was stirred at room temperature until the completion of the reaction (monitored by TLC), concentrated under vacuum, and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 4/1) to give the desired product **3**.

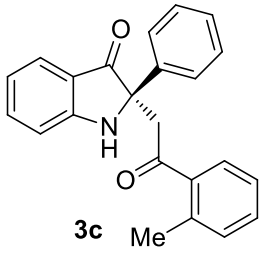


(*R*)-2-(2-oxo-2-phenylethyl)-2-phenylindolin-3-one (3a): yellow solid; 31.4 mg; 96% yield; 86% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 88% yield, 96% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 14.9 min (major) and t_R = 21.4 min (minor)]; m.p.: 149–151 °C; $[\alpha]_D^{20}$ – 41.6 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.64 – 7.52 (m, 4H), 7.52 – 7.38 (m, 3H), 7.27 (ddd, *J* = 9.3, 3.7, 2.1 Hz, 2H), 7.22 – 7.15 (m, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.84 – 6.73 (m, 1H), 6.31 (s, br, 1H), 4.43 (d, *J* = 18.0 Hz, 1H), 3.17 (d, *J* = 18.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.8, 197.9, 160.4, 138.1, 137.9, 136.7, 133.9, 128.9, 128.8, 128.2, 127.7, 125.8, 125.4, 119.0, 118.3, 111.9, 69.4, 44.8; **IR (KBr)** ν 3434, 2958, 2925, 1718, 1693, 1615, 1480, 1227, 1069, 747 cm^{-1}; **HRMS (ESI)** found m/z 328.1339 $[M + H]^+$, calcd for $C_{22}H_{18}NO_2$ 328.1338. Physical and spectral properties of this material were identical to those previously reported in literature.[6]



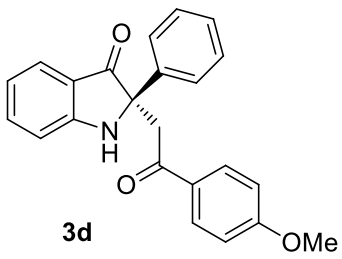
3b

(*R*)-2-(2-oxo-2-(*p*-tolyl)ethyl)-2-phenylindolin-3-one (3b): yellow solid; 33.5 mg; 98% yield; 87% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 94% yield, 90% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 11.9 min (major) and t_R = 20.5 min (minor)]; m.p.: 179–181 ^oC; $[\alpha]_D^{20}$ – 48.7 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.64 – 7.52 (m, 3H), 7.48 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.31-7.17 (m, 5H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.32 (s, br, 1H), 4.42 (d, *J* = 17.8 Hz, 1H), 3.13 (d, *J* = 17.8 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.9, 197.5, 160.4, 144.8, 138.2, 137.9, 134.3, 129.5, 128.8, 128.4, 127.6, 125.7, 125.5, 118.9, 118.3, 111.9, 69.5, 44.6, 21.8; **IR (KBr)** ν 3381, 2964, 2854, 1693, 1619, 1227, 1190, 1054, 744 cm^{-1}; **HRMS** (ESI) found m/z 342.1495 $[M + H]^+$, calcd for $C_{23}H_{20}NO_2$ 342.1494. Physical and spectral properties of this material were identical to those previously reported in literature.[6]



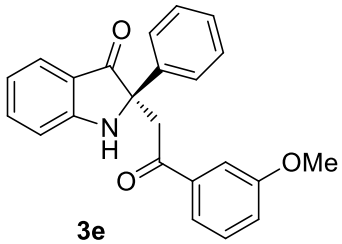
3c

(*R*)-2-(2-oxo-2-(*o*-tolyl)ethyl)-2-phenylindolin-3-one (3c): yellow solid; 25.6 mg; 75% yield; 83% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 62% yield, 96% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 11.5 min (major) and t_R = 16.5 min (minor)]; m.p.: 76–78 ^oC; $[\alpha]_D^{20}$ – 38.1 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 8.6 Hz, 3H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.16 (m, 5H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.36 (s, br, 1H), 4.30 (d, *J* = 17.3 Hz, 1H), 3.13 (d, *J* = 17.3 Hz, 1H), 2.26 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 202.1, 200.6, 128.8, 128.8, 127.7, 126.0, 125.8, 125.6, 119.1, 118.4, 112.0, 69.8, 47.7, 21.2; **IR (KBr)** ν 3385, 2961, 2920, 2851, 1689, 1622, 1093, 750 cm^{-1}; **HRMS** (ESI) found m/z 342.1487 $[M + H]^+$, calcd for $C_{23}H_{20}NO_2$ 342.1494.



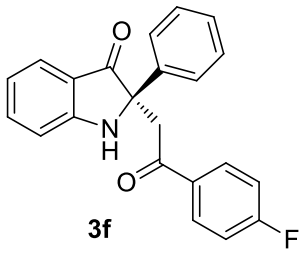
3d

(*R*)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-2-phenylindolin-3-one (3d): yellow solid; 32.9 mg; 92% yield; 94% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 87% yield, 99% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 15.3 min (major) and t_R = 32.5 min (minor)]; m.p.: 203–204 °C; $[\alpha]_D^{20}$ – 44.2 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.56 (dd, *J* = 9.9, 8.4 Hz, 3H), 7.52 – 7.46 (m, 1H), 7.30 – 7.17 (m, 4H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.36 (s, br, 1H), 4.39 (d, *J* = 17.7 Hz, 1H), 3.86 (s, 3H), 3.10 (d, *J* = 17.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0, 196.3, 164.1, 160.4, 138.3, 137.9, 130.6, 129.9, 128.8, 127.6, 125.7, 125.5, 118.9, 118.3, 114.0, 111.9, 69.5, 55.6, 44.4; **IR (KBr)** ν 3392, 2965, 2838, 1682, 1625, 1225, 740 cm^{-1}; **HRMS** (ESI) found m/z 358.1449 $[M + H]^+$, calcd for $C_{23}H_{20}NO_3$ 358.1443. Physical and spectral properties of this material were identical to those previously reported in literature.[7]



3e

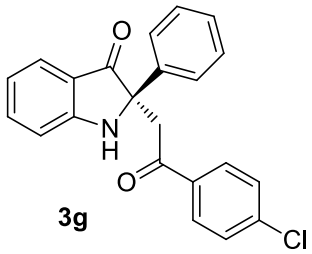
(*R*)-2-(2-(3-methoxyphenyl)-2-oxoethyl)-2-phenylindolin-3-one (3e): yellow solid; 33.2 mg; 93% yield; 78% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 91% yield, 80% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 7.3 min (major) and t_R = 8.2 min (minor)]; m.p.: 97–99 °C; $[\alpha]_D^{20}$ – 42.5 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.46 (m, 5H), 7.37 (dd, *J* = 16.4, 8.4 Hz, 2H), 7.31-7.20 (m, 3H), 7.12 (d, *J* = 6.6 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.26 (s, br, 1H), 4.42 (d, *J* = 18.0 Hz, 1H), 3.81 (s, 3H), 3.19 (d, *J* = 18.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.7, 197.8, 160.3, 160.0, 138.1, 137.9, 129.9, 128.9, 127.7, 125.8, 125.4, 121.0, 120.6, 119.0, 118.3, 112.1, 111.9, 69.4, 55.6, 45.0; **IR (KBr)** ν 3386, 2963, 2843, 1695, 1623, 1517, 1220, 742 cm^{-1}; **HRMS** (ESI) found m/z 358.1443 $[M + H]^+$, calcd for $C_{23}H_{20}NO_3$ 358.1440.



3f

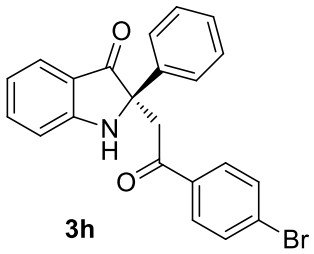
(*R*)-2-(2-(4-fluorophenyl)-2-oxoethyl)-2-phenylindolin-3-one (3f): yellow solid; 32.1 mg; 93% yield; 85% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 90% yield, 89% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 11.3 min (major) and t_R = 24.3 min (minor)]; m.p.: 138–140 °C; $[\alpha]_D^{20}$ – 45.2 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.04 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.91 (s, br, 1H), 7.54 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.50 – 7.43 (m, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.32 (dd, *J* = 11.5, 4.4 Hz, 4H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.05 – 6.94 (m, 1H), 6.72 (t, *J* = 7.3 Hz, 1H),

4.19 (d, *J* = 17.4 Hz, 1H), 3.75 (d, *J* = 18.1 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 200.8, 195.2, 165.4 (d, *J* = 252.2 Hz), 161.4, 139.5, 137.2, 133.4 (d, *J* = 2.8 Hz), 131.4 (d, *J* = 9.5 Hz), 128.6, 127.5, 125.8, 124.6, 118.5, 117.7, 115.9 (d, *J* = 21.9 Hz), 112.2, 69.0, 45.9; **IR (KBr)** ν 3380, 2955, 2920, 2851, 2336, 1683, 1327, 1208, 551 cm^{-1}; **HRMS** (ESI) found m/z 346.1242 [M + H]$^+$, calcd for $C_{22}H_{17}FNO_2$ 346.1243. Physical and spectral properties of this material were identical to those previously reported in literature.[8]



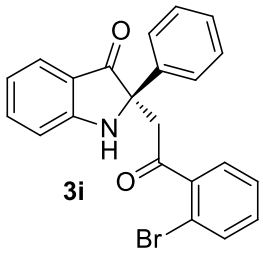
3g

(*R*)-2-(2-(4-chlorophenyl)-2-oxoethyl)-2-phenylindolin-3-one (3g): yellow solid; 34.0 mg; 94% yield; 87% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 92% yield, 90% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 12.5 min (major) and t_R = 26.3 min (minor)]; m.p.: 171–174 °C; $[\alpha]_D^{20}$ – 53.3 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.51 (m, 3H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.31-7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.23 (s, br, 1H), 4.38 (d, *J* = 17.9 Hz, 1H), 3.16 (d, *J* = 17.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6, 196.7, 160.3, 140.4, 138.0, 138.0, 135.0, 129.6, 129.2, 128.9, 127.8, 125.8, 125.4, 119.1, 118.3, 111.9, 69.3, 44.9; **IR (KBr)** ν 3443, 2965, 2923, 2850, 1697, 1675, 748, 510 cm^{-1}; **HRMS** (ESI) found m/z 362.0943 [M + H]$^+$, calcd for $C_{22}H_{17}ClNO_2$ 362.0948. Physical and spectral properties of this material were identical to those previously reported in literature.[7]



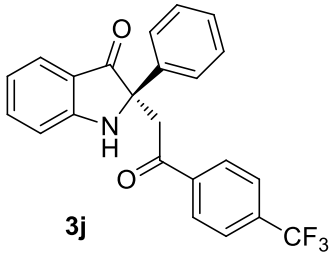
3h

(*R*)-2-(2-(4-bromophenyl)-2-oxoethyl)-2-phenylindolin-3-one (3h): yellow solid; 38.6 mg; 95% yield; 85% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 89% yield, 93% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 18.2 min (major) and t_R = 37.4 min (minor)]; m.p.: 178–180 °C; $[\alpha]_D^{20}$ – 46.6 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.58 (dd, *J* = 8.0, 3.7 Hz, 3H), 7.55 – 7.51 (m, 2H), 7.51 – 7.44 (m, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.22 (s, br, 1H), 4.37 (d, *J* = 17.9 Hz, 1H), 3.16 (d, *J* = 17.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6, 196.9, 160.3, 138.0, 138.0, 135.4, 132.2, 129.7, 129.2, 128.9, 127.8, 125.8, 125.4, 119.1, 118.3, 111.9, 69.3, 44.9; **IR (KBr)** ν 3440, 3059, 2923, 2851, 1690, 1675, 730, 628 cm^{-1}; **HRMS** (ESI) found m/z 406.0441 [M + H]$^+$, calcd for $C_{22}H_{17}BrNO_2$ 406.0443. Physical and spectral properties of this material were identical to those previously reported in literature.[8]



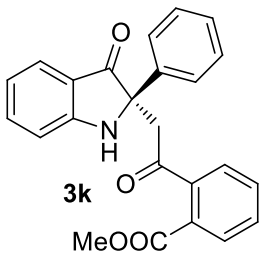
3i

(*R*)-2-(2-(2-bromophenyl)-2-oxoethyl)-2-phenylindolin-3-one (3i): yellow solid; 32.5 mg; 80% yield; 78% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 70% yield, 96% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 80/20, 254 nm UV detector, 0.8 mL/min, t_R = 29.0 min (minor) and t_R = 33.1 min (major)]; m.p.: 53–55 ^oC; $[\alpha]_D^{20}$ – 27.7 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 4H), 7.49 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.26 – 7.19 (m, 3H), 7.16 – 7.08 (m, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.84 – 6.76 (m, 1H), 6.24 (s, 1H), 4.25 (d, *J* = 17.3 Hz, 1H), 3.25 (d, *J* = 17.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.9, 200.1, 160.2, 141.0, 137.9, 137.8, 133.9, 132.2, 128.9, 128.8, 127.8, 127.5, 125.7, 119.2, 118.9, 118.4, 112.1, 69.5, 49.3; **IR (KBr)** ν 3392, 2959, 2920, 2850, 1670, 1486, 1210, 701 cm^{-1}; **HRMS** (ESI) found m/z 406.0438 $[M + H]^+$, calcd for $C_{22}H_{17}BrNO_2$ 406.0443.



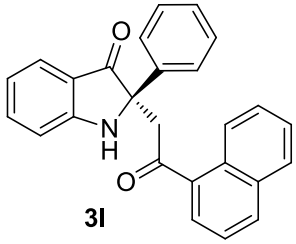
3j

(*R*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-2-phenylindolin-3-one (3j): yellow solid; 36.4 mg; 92% yield; 88% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 91% yield, 90% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 12.9 min (major) and t_R = 24.0 min (minor)]; m.p.: 56–58 ^oC; $[\alpha]_D^{20}$ – 47.4 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.23 (dd, *J* = 8.3, 6.2 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.17 (s, br, 1H), 4.42 (d, *J* = 17.9 Hz, 1H), 3.24 (d, *J* = 17.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.4, 197.0, 160.3, 139.2, 138.0, 137.9, 135.2 (d, *J* = 32.9 Hz), 128.9, 128.6, 127.9, 125.9 (dd, *J* = 7.2, 3.6 Hz), 125.8, 125.3, 119.2, 118.3, 111.9, 69.2, 45.3; **IR (KBr)** ν 3380, 2953, 2924, 2853, 1688, 1323, 1119, 510 cm^{-1}; **HRMS** (ESI) found m/z 396.1208 $[M + H]^+$, calcd for $C_{23}H_{17}F_3NO_2$ 396.1211. Physical and spectral properties of this material were identical to those previously reported in literature.[8]



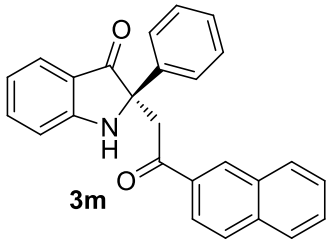
3k

(*R*)-2-(2-(2-bromophenyl)-2-oxoethyl)-2-phenylindolin-3-one (3k): yellow solid; 29.2 mg; 76% yield; 85% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 76% yield, 85% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 22.8 min (minor) and t_R = 30.0 min (major)]; m.p.: 185–187 °C; $[\alpha]_D^{20}$ – 37.2 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (m, 1H), 7.66 – 7.60 (m, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.47 – 7.43 (m, 2H), 7.32 – 7.20 (m, 3H), 7.03 (d, *J* = 8.3 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.34 (s, br, 1H), 3.97 (d, *J* = 17.2 Hz, 1H), 3.77 (s, 3H), 3.32 (d, *J* = 17.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.5, 200.8, 167.1, 160.6, 142.8, 138.3, 137.7, 132.5, 130.3, 130.0, 128.7, 128.2), 127.8, 126.4, 125.9, 125.6, 119.1, 118.9, 112.4, 69.3, 52.7, 49.5; **IR (KBr)** ν 3392, 2952, 2916, 2860, 1710, 1613, 1462, 551 cm^{-1}; **HRMS** (ESI) found m/z 386.1388 $[M + H]^+$, calcd for $C_{24}H_{20}NO_4$ 386.1392.



3l

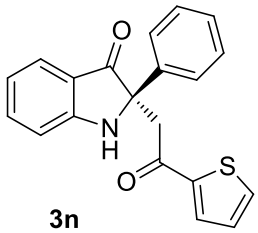
(*R*)-2-(2-(naphthalen-1-yl)-2-oxoethyl)-2-phenylindolin-3-one (3l): yellow solid; 34.7 mg; 92% yield; 79% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 76% yield, 99% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 14.1 min (major) and t_R = 19.2 min (minor)]; m.p.: 133–135 °C; $[\alpha]_D^{20}$ – 49.1 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.81 (m, 2H), 7.63 – 7.55 (m, 3H), 7.54 – 7.44 (m, 4H), 7.32 – 7.26 (m, 2H), 7.25 – 7.18 (m, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.88 – 6.73 (m, 1H), 6.41 (s, br, 1H), 4.43 (d, *J* = 17.3 Hz, 1H), 3.35 (d, *J* = 17.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.0, 200.6, 160.4, 138.2, 137.9, 135.5, 134.0, 133.5, 130.0, 128.9, 128.6, 128.3, 128.2, 127.8, 126.7, 125.8, 125.7, 125.6, 124.4, 119.1, 118.4, 112.0, 69.9, 48.2; **IR (KBr)** ν 3344, 2964, 2920, 2850, 1673, 1472, 1187, 819, 751, 530 cm^{-1}; **HRMS** (ESI) found m/z 378.1486 $[M + H]^+$, calcd for $C_{26}H_{19}NO_2$ 378.1494.



3m

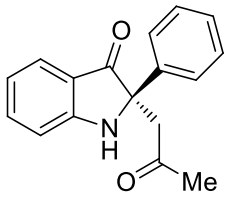
(*R*)-2-(2-(naphthalen-2-yl)-2-oxoethyl)-2-phenylindolin-3-one (3m): yellow solid; 33.9 mg; 90% yield; 77% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 82% yield, 97% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 14.8 min (major) and t_R = 24.9 min (minor)]; m.p.: 212–214 °C; $[\alpha]_D^{20}$ – 49.9 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.04 – 7.90 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.54 (m, 5H), 7.53-7.49 (m, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.18 (m, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.87 – 6.76 (m, 1H), 6.36 (s, br, 1H), 4.61 (d, *J* = 17.8 Hz, 1H), 3.30 (d, *J* = 17.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.9, 197.8, 160.4, 138.2, 137.9, 136.0, 134.1, 132.6, 130.4, 129.8, 129.0, 128.8, 128.8, 127.9, 127.7, 127.1, 125.8,

125.5, 123.6, 119.0, 118.4, 112.0, 69.6, 44.9; **IR (KBr)** ν 3336, 2956, 2922, 2852, 1673, 1490, 1165, 820, 755, 527 cm^{-1}; **HRMS** (ESI) found m/z 378.1489 $[M + H]^+$, calcd for $C_{26}H_{19}NO_2$ 378.1494. Physical and spectral properties of this material were identical to those previously reported in literature.[8]



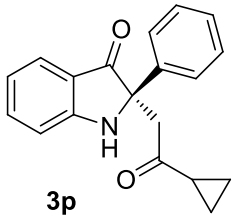
3n

(*R*)-2-(2-oxo-2-(thiophen-2-yl)ethyl)-2-phenylindolin-3-one (3n): yellow solid; 31.3 mg; 94% yield; 74% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 72% yield, 97% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 18.0 min (major) and t_R = 22.6 min (minor)]; m.p.: 115–117°C; $[\alpha]_D^{20}$ – 31.7 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.06 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.99 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.96 (s, br, 1H), 7.57 – 7.50 (m, 2H), 7.46 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.36 – 7.29 (m, 2H), 7.28 – 7.20 (m, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.81 – 6.59 (m, 1H), 4.13 (d, *J* = 17.5 Hz, 1H), 3.68 (d, *J* = 17.5 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 200.5, 189.6, 161.4, 143.8, 139.3, 137.3, 135.5, 134.3, 129.1, 128.7, 127.6, 125.8, 124.6, 118.4, 117.7, 112.1, 69.1, 46.1; **IR (KBr)** ν 3375, 2956, 2916, 2854, 1687, 1620, 1466, 749 cm^{-1}; **HRMS** (ESI) found m/z 334.0894 $[M + H]^+$, calcd for $C_{20}H_{16}NO_2S$ 334.0902.



3o

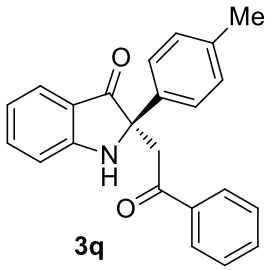
(*R*)-2-(2-oxopropyl)-2-phenylindolin-3-one (3o): yellow solid; 24.1 mg; 91% yield; 80% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 77% yield, 98% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 18.1 min (major) and t_R = 28.1 min (minor)]; m.p.: 67–69 °C; $[\alpha]_D^{20}$ – 37.0 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 3H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.20 (m, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.11 (s, br, 1H), 3.73 (d, *J* = 17.3 Hz, 1H), 2.72 (d, *J* = 17.3 Hz, 1H), 2.10 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.9, 200.4, 160.2, 138.0, 137.8, 128.8, 127.8, 125.7, 125.5, 119.1, 118.4, 112.1, 69.1, 49.6, 31.6; **IR (KBr)** ν 3403, 2965, 2917, 2857, 1697, 1625, 1220, 752 cm^{-1}; **HRMS** (ESI) found m/z 266.1175 $[M + H]^+$, calcd for $C_{17}H_{16}NO_2$ 266.1181.



3p

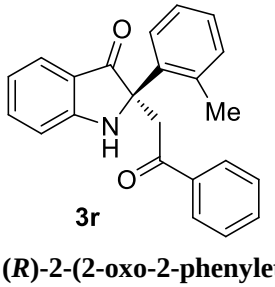
(*R*)-2-(2-cyclopropyl-2-oxoethyl)-2-phenylindolin-3-one (3p): yellow solid; 22.9 mg; 79% yield;

65% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 62% yield, 86% ee); [determined by **HPL**C analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 9.4 min (major) and t_R = 11.9 min (minor)]; m.p.: 108–110 °C; $[\alpha]_D^{20}$ – 34.1 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 3H), 7.51 – 7.43 (m, 1H), 7.31 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.26 – 7.20 (m, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.10 (s, br, 1H), 3.82 (d, *J* = 17.0 Hz, 1H), 2.89 (d, *J* = 17.0 Hz, 1H), 1.91 (tt, *J* = 7.3, 5.4 Hz, 1H), 1.03 – 0.90 (m, 1H), 0.89 – 0.74 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.9, 200.7, 160.3, 138.2, 137.8, 128.7, 127.7, 125.6, 125.6, 119.0, 118.5, 112.1, 69.3, 49.6, 22.0, 11.5, 11.4; **IR (KBr)** ν 3405, 2933, 2864, 1710, 1619, 1380, 1175 cm^{-1}; **HRMS** (ESI) found m/z 292.1337 $[M + H]^+$, calcd for $C_{19}H_{18}NO_2$ 292.1338.



3q

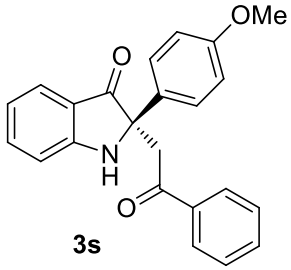
(*R*)-2-(2-oxo-2-phenylethyl)-2-(*p*-tolyl)indolin-3-one (3q): yellow solid; 31.1 mg; 91% yield; 87% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 83% yield, 96% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 8.7 min (major) and t_R = 15.1 min (minor)]; m.p.: 206–207 °C; $[\alpha]_D^{20}$ – 44.1 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 7.66 (m, 2H), 7.62 – 7.54 (m, 2H), 7.53 – 7.41 (m, 3H), 7.33 (d, *J* = 6.3 Hz, 2H), 7.21 – 7.11 (m, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.83 – 6.74 (m, 1H), 6.25 (s, br, 1H), 4.43 (d, *J* = 17.9 Hz, 1H), 3.17 (d, *J* = 17.9 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.8, 198.0, 160.3, 138.4, 138.0, 137.9, 136.7, 133.9, 128.9, 128.7, 128.6, 128.3, 126.0, 125.8, 122.5, 118.9, 118.3, 111.9, 69.4, 44.8, 21.8; **IR (KBr)** ν 3381, 2964, 2920, 2853, 1693, 1617, 1218, 1050, 743 cm^{-1}; **HRMS** (ESI) found m/z 342.1490 $[M + H]^+$, calcd for $C_{23}H_{20}NO_2$ 342.1494. Physical and spectral properties of this material were identical to those previously reported in the literature.[7]



3r

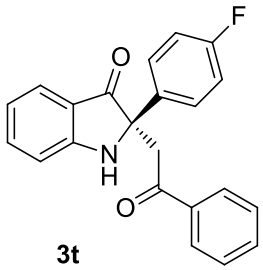
(*R*)-2-(2-oxo-2-phenylethyl)-2-(*o*-tolyl)indolin-3-one (3r): yellow solid; 30.6 mg; 90% yield; 88% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 86% yield, 92% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 9.0 min (major) and t_R = 18.6 min (minor)]; m.p.: 185–187 °C; $[\alpha]_D^{20}$ – 42.6 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.50 (dd, *J* = 11.2, 4.3 Hz, 3H), 7.19 – 7.13 (m, 1H), 7.13 – 7.03 (m, 3H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.89 – 6.81 (m, 1H), 6.52 (s, br, 1H), 4.41 (d, *J* = 18.1 Hz, 1H), 3.01 (d, *J* = 18.1 Hz, 1H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.1, 198.6, 159.5, 137.8, 137.5, 136.5, 135.6, 134.2, 132.5, 129.0, 128.3, 128.3, 128.1, 125.9, 125.1, 119.5, 119.0,

112.6, 71.6, 43.8, 20.9; **IR (KBr)** ν 3380, 2961, 2923, 2853, 1696, 1620, 1220, 1063, 744 cm^{-1}; **HRMS** (ESI) found m/z 342.1487 $[M + H]^+$, calcd for $C_{23}H_{20}NO_2$ 342.1494.



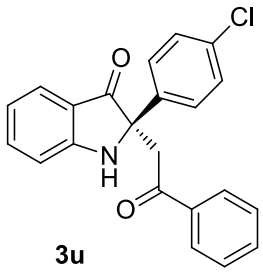
3s

(*R*)-2-(4-methoxyphenyl)-2-(2-oxo-2-phenylethyl)indolin-3-one (3s): yellow solid; 32.8 mg; 92% yield; 93% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 92% yield, 93% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 21.2 min (major) and t_R = 26.8 min (minor)]; m.p.: 120–122 °C; $[\alpha]_D^{20}$ – 48.7 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 – 7.80 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.52 – 7.40 (m, 5H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.83-6.78 (m, 3H), 6.28 (s, br, 1H), 4.40 (d, *J* = 17.9 Hz, 1H), 3.73 (s, 3H), 3.14 (d, *J* = 17.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.1, 198.1, 160.3, 159.2, 137.8, 136.7, 133.9, 130.1, 128.9, 128.2, 126.6, 125.8, 118.9, 118.3, 114.2, 111.9, 69.0, 55.3, 44.7; **IR (KBr)** ν 3393, 2965, 2850, 1692, 1620, 1323, 1222, 751 cm^{-1}; **HRMS** (ESI) found m/z 358.1448 $[M + H]^+$, calcd for $C_{23}H_{20}NO_3$ 358.1443. Physical and spectral properties of this material were identical to those previously reported in the literature.[7]



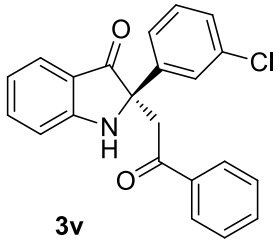
3t

(*R*)-2-(4-fluorophenyl)-2-(2-oxo-2-phenylethyl)indolin-3-one (3t): yellow solid; 33.6 mg; 85% yield; 81% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 73% yield, 96% ee); [determined by **HPLC** analysis Daicel Chirapak OD-H, *n*-hexane/*i*-PrOH = 95/5, 254 nm UV detector, 1.0 mL/min, t_R = 30.1 min (minor) and t_R = 40.2 min (major)]; m.p.: 163–165 °C; $[\alpha]_D^{20}$ – 44.8 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.72 – 7.34 (m, 7H), 7.02 – 6.87 (m, 3H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.33 (s, br, 1H), 4.39 (d, *J* = 17.9 Hz, 1H), 3.15 (d, *J* = 17.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.7, 198.0, 162.4 (d, *J* = 246.3 Hz), 160.2, 138.1, 136.6, 134.0, 133.9 (d, *J* = 3.2 Hz), 128.9, 128.2, 127.3 (d, *J* = 8.3 Hz), 125.8, 119.2, 118.1, 115.6 (d, *J* = 21.6 Hz), 112.0, 68.9, 45.0; **IR (KBr)** ν 3430, 2927, 2900, 2853, 1689, 1615, 1353, 1232, 749 cm^{-1}; **HRMS** (ESI) 346.1238 $[M + H]^+$, calcd for $C_{22}H_{17}FNO_2$ 346.1243.



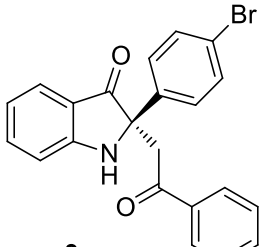
3u

(*R*)-2-(4-chlorophenyl)-2-(2-oxo-2-phenylethyl)indolin-3-one (3u): yellow solid; 29.6 mg; 82% yield; 76% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 69% yield, 93% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 14.7 min (major) and t_R = 17.0 min (minor)]; m.p.: 151–153 °C; $[\alpha]_D^{20}$ – 43.3 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.81 (m, 2H), 7.59 (dt, *J* = 7.4, 3.5 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.50 – 7.38 (m, 3H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.31 (s, br, 1H), 4.39 (d, *J* = 18.0 Hz, 1H), 3.15 (d, *J* = 18.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.3, 197.8, 160.2, 138.1, 136.8, 136.5, 134.1, 133.7, 128.9, 128.9, 128.2, 127.0, 125.8, 119.2, 118.0, 112.0, 68.9, 44.9; **IR (KBr)** ν 3387, 2957, 2920, 2853, 1686, 1603, 759 cm^{-1}; **HRMS** (ESI) found m/z 362.0943 $[M + H]^+$, calcd for $C_{22}H_{17}ClNO_2$ 362.0948. Physical and spectral properties of this material were identical to those previously reported in literature.[7]



3v

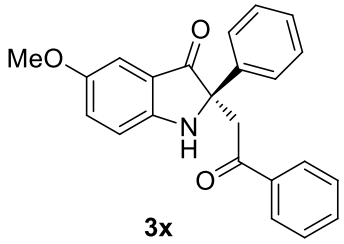
(*R*)-2-(3-chlorophenyl)-2-(2-oxo-2-phenylethyl)indolin-3-one (3v): yellow solid; 29.9 mg; 83% yield; 81% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 72% yield, 94% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 8.9 min (major) and t_R = 13.6 min (minor)]; m.p.: 118–120 °C; $[\alpha]_D^{20}$ – 46.2 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H), 7.58 (t, *J* = 5.8 Hz, 3H), 7.54 – 7.40 (m, 4H), 7.25 – 7.14 (m, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.29 (s, br, 1H), 4.38 (d, *J* = 18.0 Hz, 1H), 3.17 (d, *J* = 18.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 197.7, 160.2, 140.4, 138.2, 136.5, 134.7, 134.1, 130.0, 128.9, 128.2, 127.9, 125.9, 125.8, 123.8, 119.3, 118.0, 112.1, 68.9, 45.0; **IR (KBr)** ν 3381, 2961, 2926, 2859, 1695, 1615, 753 cm^{-1}; **HRMS** (ESI) found m/z 362.0939 $[M + H]^+$, calcd for $C_{22}H_{17}ClNO_2$ 362.0948.



3w

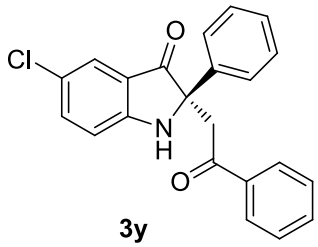
(*R*)-2-(4-bromophenyl)-2-(2-oxo-2-phenylethyl)indolin-3-one (3w): yellow solid; 32.4 mg; 80% yield; 75% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 65% yield, 93% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 80/20, 254 nm UV detector, 0.8 mL/min, t_R = 40.3 min (major) and t_R = 45.4 min (minor)]; m.p.: 157–159 °C; $[\alpha]_D^{20}$ – 39.6 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 2H), 7.57 (dd, *J* = 13.2, 7.3 Hz, 2H), 7.52 – 7.35 (m, 7H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.41 (s, br, 1H), 4.39 (d, *J* = 18.1 Hz, 1H), 3.17 (d, *J* = 18.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.3, 197.8, 160.2, 138.2, 137.4, 136.5, 134.1, 131.9, 129.0, 128.2, 127.4, 125.8, 121.9, 119.3, 118.0, 112.0, 69.0, 44.9 cm^{-1}; **IR (KBr)** ν 3390, 2965, 2910, 2852, 1701, 1610, 750 cm^{-1}; **HRMS**

(ESI) found m/z 406.0441 $[M + H]^+$, calcd for $C_{22}H_{17}BrNO_2$ 406.0443.



3x

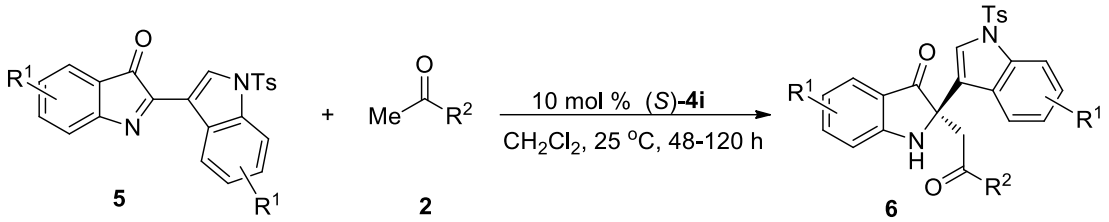
(*R*)-5-methoxy-2-(2-oxo-2-phenylethyl)-2-phenylindolin-3-one (3x): yellow solid; 33.5 mg; 94% yield; 91% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 94% yield, 91% ee); [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 13.4 min (major) and t_R = 18.7 min (minor)]; m.p.: 156–158 °C; $[\alpha]_D^{20}$ – 43.5 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 7.80 (m, 2H), 7.61 – 7.53 (m, 3H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.29 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.25 – 7.15 (m, 2H), 7.01 (d, *J* = 2.6 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.02 (s, br, 1H), 4.41 (d, *J* = 17.8 Hz, 1H), 3.76 (s, 3H), 3.21 (d, *J* = 17.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0, 197.9, 156.3, 153.5, 138.4, 136.7, 133.8, 128.9, 128.8, 128.6, 128.3, 127.7, 125.5, 118.5, 113.5, 105.4, 70.4, 55.9, 45.0; **IR (KBr)** ν 3396, 2961, 2910, 2854, 1688, 1610, 1600, 742 cm^{-1}; **HRMS** (ESI) found m/z 358.1448 $[M + H]^+$, calcd for $C_{23}H_{20}NO_3$ 358.1443.



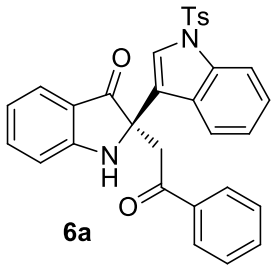
3y

(*R*)-5-chloro-2-(2-oxo-2-phenylethyl)-2-phenylindolin-3-one (3y): yellow solid; 30.6 mg; 85% yield; 82% ee, (after recrystallization from petroleum ether/ethyl acetate, mother liquid, 80% yield, 88% ee) ; [determined by **HPLC** analysis Daicel Chirapak OD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 11.9 min (minor) and t_R = 14.8 min (major)]; m.p.: 148–150 °C; $[\alpha]_D^{20}$ – 39.2 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 7.75 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 3H), 7.48 – 7.41 (m, 3H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 (dd, *J* = 8.3, 6.2 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.32 (s, br, 1H), 4.42 (d, *J* = 17.9 Hz, 1H), 3.20 (d, *J* = 17.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.7, 197.7, 158.6, 137.8, 137.6, 136.5, 134.0, 129.0, 128.9, 128.2, 127.9, 125.4, 124.9, 124.2, 119.4, 113.1, 70.2, 44.8; **IR (KBr)** ν 3380, 2961, 2912, 1702, 1688, 1610, 748 cm^{-1}; **HRMS** (ESI) found m/z 362.0947 $[M + H]^+$, calcd for $C_{22}H_{17}ClNO_2$ 362.0948. Physical and spectral properties of this material were identical to those previously reported in literature.[7]

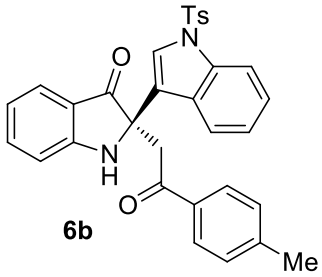
General procedure for the reaction of 1'-tosyl-1'*H*,3*H*-[2,3'-biindol]-3-ones 5 with simple ketones 2



To a 10 mL Schlenk flask equipped with a stirring bar was added 1'-tosyl-1'*H*,3*H*-[2,3'-biindol]-3-ones **5** (0.1 mmol), chiral phosphoric acid (*S*)-**4i** (0.01 mmol, 10 mol %), CH_2Cl_2 (1 mL). Simple ketones **2** (1.0 mmol, 10.0 equiv) was added to the mixture. Then the resulting mixture was stirred at room temperature until the completion of the reaction (monitored by TLC), concentrated under vacuum, and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 2/1) to give the desired product **6**.

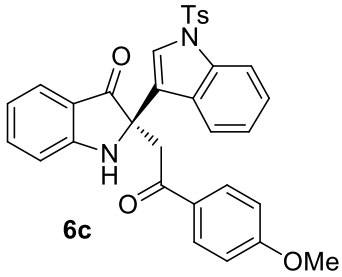


(*R*)-2-(2-oxo-2-phenylethyl)-2-(1-tosyl-1*H*-indol-3-yl)indolin-3-one (6a): yellow solid; 44.7 mg; 86% yield; 93% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 17.2 min (major) and t_R = 25.6 min (minor)]; m.p.: 209–212 °C; $[\alpha]_D^{20}$ – 22.4 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (t, *J* = 7.5 Hz, 3H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 6.5 Hz, 4H), 7.60 – 7.49 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 3H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.31 (s, br, 1H), 4.38 (d, *J* = 17.5 Hz, 1H), 3.24 (d, *J* = 17.5 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.3, 197.5, 160.1, 145.0, 138.1, 136.5, 135.7, 134.9, 134.0, 129.9, 128.9, 128.3, 128.2, 126.9, 125.6, 124.8, 124.6, 123.5, 121.6, 120.5, 119.3, 118.9, 113.8, 112.4, 66.8, 43.9, 21.7; **IR (KBr)** ν 3390, 3152, 2940, 2919, 2716, 1720, 1616, 1368, 1173, 755 cm^{-1}; **HRMS** (ESI) found m/z 521.1528 $[M + H]^+$, calcd for $C_{31}H_{25}N_2O_4S$ 521.1535.



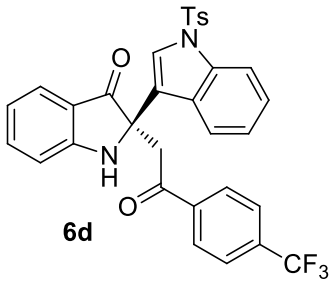
(*R*)-2-(2-oxo-2-(*p*-tolyl)ethyl)-2-(1-tosyl-1*H*-indol-3-yl)indolin-3-one (6b): yellow solid; 49.1 mg; 92% yield; 90% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 21.0 min (major) and t_R = 31.5 min (minor)]; m.p.: 252–253 °C; $[\alpha]_D^{20}$ – 25.3 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 11.3, 2.9 Hz, 4H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.23 (dd, *J* = 16.5, 8.5 Hz, 3H), 7.13 (dd, *J* = 12.1, 7.9 Hz, 3H), 6.96 (d, *J* = 8.2 Hz, 1H),

6.85 (t, *J* = 7.4 Hz, 1H), 6.35 (s, br, 1H), 4.35 (d, *J* = 17.5 Hz, 1H), 3.18 (d, *J* = 17.4 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.4, 197.2, 160.1, 145.0, 145.0, 138.1, 135.7, 135.0, 134.1, 129.9, 129.6, 128.4, 126.9, 125.6, 124.8, 124.6, 123.5, 121.6, 120.6, 119.3, 119.0, 113.8, 112.5, 66.9, 43.7, 21.8, 21.7; **IR (KBr)** ν 3388, 3142, 2956, 2923, 2726, 1722, 1611, 1362, 1170, 751 cm^{-1}; **HRMS** (ESI) found m/z 535.1687 $[M + H]^+$, calcd for $C_{32}H_{27}N_2O_4S$ 535.1692.



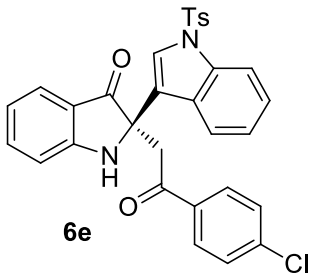
6c

(*R*)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-2-(1-tosyl-1*H*-indol-3-yl)indolin-3-one (6c): yellow solid; 49.5 mg; 90% yield; 99% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 29.7 min (major) and t_R = 49.5 min (minor)]; m.p.: 239–241 °C; $[\alpha]_D^{20}$ – 21.6 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (t, *J* = 9.4 Hz, 3H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 7.5, 5.6 Hz, 4H), 7.57 – 7.46 (m, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.18 – 7.08 (m, 3H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.39 (s, br, 1H), 4.32 (d, *J* = 17.2 Hz, 1H), 3.86 (s, 3H), 3.14 (d, *J* = 17.2 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.5, 196.0, 164.2, 160.2, 145.0, 138.1, 135.7, 135.0, 130.6, 129.9, 129.7, 128.4, 126.9, 125.6, 124.8, 124.7, 123.5, 121.7, 120.6, 119.3, 119.0, 114.1, 113.8, 112.5, 67.0, 55.7, 43.4, 21.7; **IR (KBr)** ν 3380, 3162, 2940, 2859, 1698, 1610, 1328, 747 cm^{-1}; **HRMS** (ESI) found m/z 551.1644 $[M + H]^+$, calcd for $C_{32}H_{27}N_2O_5S$ 551.1641.



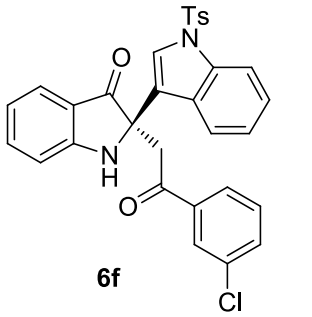
6d

(*R*)-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-2-(1-tosyl-1*H*-indol-3-yl)indolin-3-one (6d): yellow solid; 51.1 mg; 87% yield; 90% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 20.8 min (major) and t_R = 28.7 min (minor)]; m.p.: 189–191 °C; $[\alpha]_D^{20}$ – 24.0 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.69 – 7.60 (m, 6H), 7.54 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.15 (dd, *J* = 10.9, 4.4 Hz, 3H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.88 (dd, *J* = 11.0, 3.8 Hz, 1H), 6.14 (s, br, 1H), 4.36 (d, *J* = 17.5 Hz, 1H), 3.33 (d, *J* = 17.5 Hz, 1H), 2.31 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0, 196.6, 160.1, 145.2, 139.1, 138.2 (d, *J* = 3.2 Hz), 135.8, 135.2, 134.9 (d, *J* = 7.5 Hz), 130.0, 128.5, 128.0, 126.9, 125.9 (q, *J* = 3.7 Hz), 125.6, 125.0, 124.5, 123.6, 121.6, 120.2, 119.6, 119.1, 113.9, 112.5, 66.6, 44.5, 21.7; **IR (KBr)** ν 3380, 3162, 3065, 2970, 2739, 1691, 1613, 1321, 757 cm^{-1}; **HRMS** (ESI) found m/z 589.1410 $[M + H]^+$, calcd for $C_{32}H_{24}F_3N_2O_4S$ 589.1409.



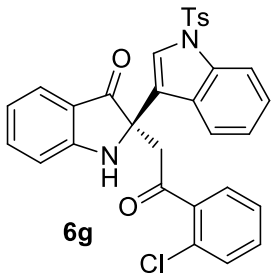
6e

(*R*)-2-(2-(4-chlorophenyl)-2-oxoethyl)-2-(1-tosyl-1*H*-indol-3-yl)indolin-3-one (6e): yellow solid; 52.0 mg; 94% yield; 93% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 24.3 min (major) and t_R = 40.6 min (minor)]; m.p.: 228–230 °C; $[\alpha]_D^{20}$ – 32.2 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.59 (m, 4H), 7.56 – 7.48 (m, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.23 (dd, *J* = 12.0, 4.6 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 3H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.22 (s, br, 1H), 4.31 (d, *J* = 17.4 Hz, 1H), 3.24 (d, *J* = 17.4 Hz, 1H), 2.31 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 196.3, 160.1, 145.1, 140.5, 138.1, 135.8, 135.0, 134.8, 130.0, 129.6, 129.2, 128.2, 126.9, 125.6, 124.9, 124.6, 123.5, 121.6, 120.3, 119.5, 119.0, 113.9, 112.5, 66.8, 44.0, 21.7; **IR (KBr)** ν 3390, 3152, 2960, 2853, 1671, 1324, 745 cm^{-1}; **HRMS** (ESI) found m/z 555.1147 $[M + H]^+$, calcd for $C_{31}H_{24}ClN_2O_4S$ 555.1145.



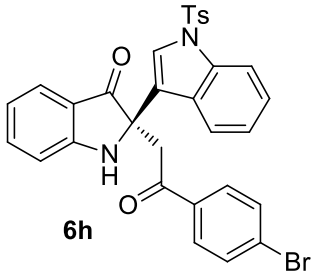
6f

(*R*)-2-(2-(3-chlorophenyl)-2-oxoethyl)-2-(1-tosyl-1*H*-indol-3-yl)indolin-3-one (6f): yellow solid; 47.6 mg; 86% yield; 92% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 14.8 min (major) and t_R = 20.0 min (minor)]; m.p.: 100–103 °C; $[\alpha]_D^{20}$ – 34.2 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 1H), 7.82 (s, 1H), 7.77 – 7.70 (m, 2H), 7.63 (dd, *J* = 10.4, 5.9 Hz, 4H), 7.57 – 7.48 (m, 2H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.30 – 7.20 (m, 1H), 7.15 (t, *J* = 8.3 Hz, 3H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.19 (s, br, 1H), 4.32 (d, *J* = 17.5 Hz, 1H), 3.25 (d, *J* = 17.5 Hz, 1H), 2.31 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0, 196.3, 160.0, 145.1, 138.2, 138.0, 135.8, 135.3, 134.9, 133.9, 130.2, 130.0, 128.2, 128.1, 126.9, 126.3, 125.6, 124.9, 124.6, 123.6, 121.6, 120.3, 119.5, 119.0, 113.9, 112.4, 66.7, 44.2, 21.7; **IR (KBr)** ν 3384, 2955, 2920, 2850, 1681, 1334, 1151, 705 cm^{-1}; **HRMS** (ESI) found m/z 555.1137 $[M + H]^+$, calcd for $C_{31}H_{24}ClN_2O_4S$ 555.1145.



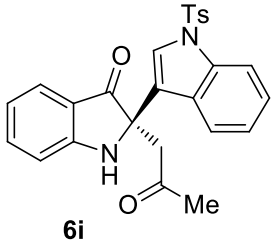
6g

(*R*)-2-(2-(2-chlorophenyl)-2-oxoethyl)-2-(1-tosyl-1*H*-indol-3-yl)indolin-3-one (6g): yellow solid; 35.9 mg; 65% yield; 97% ee; [determined by **HPLC** analysis Daicel Chirapak OD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 13.5 min (major) and t_R = 18.6 min (minor)]; m.p.: 91–93 °C; $[\alpha]_D^{20}$ – 26.4 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.70 (dd, *J* = 8.1, 4.4 Hz, 3H), 7.64 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.36 – 7.26 (m, 2H), 7.20 (dd, *J* = 12.9, 7.8 Hz, 3H), 7.13 – 7.05 (m, 2H), 7.04 – 6.97 (m, 2H), 6.87 (t, *J* = 7.3 Hz, 1H), 6.16 (s, br, 1H), 4.32 (d, *J* = 16.8 Hz, 1H), 3.28 (d, *J* = 16.8 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0, 199.7, 160.0, 145.2, 138.6, 138.1, 135.8, 135.0, 132.4, 131.1, 130.6, 130.0, 129.1, 128.0, 127.0, 125.6, 124.9, 124.7, 123.4, 121.8, 120.1, 119.6, 119.0, 113.7, 112.6, 67.2, 48.3, 21.7; **IR (KBr)** ν 3381, 2957, 2916, 2843, 1682, 1330, 1153, 735 cm^{-1}; **HRMS** (ESI) found m/z 555.1141 $[M + H]^+$, calcd for $C_{31}H_{24}ClN_2O_4S$ 555.1145.



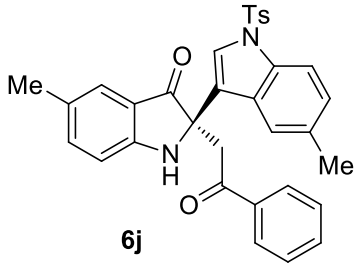
6h

(*R*)-2-(2-(4-bromophenyl)-2-oxoethyl)-2-(1-tosyl-1*H*-indol-3-yl)indolin-3-one (6h): yellow solid; 57.4 mg; 96% yield; 94% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 26.8 min (minor) and t_R = 42.1 min (major)]; m.p.: 237–238 °C; $[\alpha]_D^{20}$ – 26.2 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 3H), 7.68 – 7.59 (m, 4H), 7.58 – 7.48 (m, 3H), 7.29 – 7.21 (m, 1H), 7.14 (t, *J* = 7.8 Hz, 3H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.20 (s, br, 1H), 4.31 (d, *J* = 17.4 Hz, 1H), 3.23 (d, *J* = 17.4 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 196.5, 160.1, 145.1, 138.1, 135.7, 135.2, 134.9, 132.2, 130.0, 129.7, 129.3, 128.1, 126.9, 125.6, 124.9, 124.5, 123.5, 121.6, 120.3, 119.5, 119.0, 113.9, 112.5, 66.7, 44.0, 21.7; **IR (KBr)** ν 3389, 2964, 2926, 2833, 1672, 1343, 1129, 755 cm^{-1}; **HRMS** (ESI) found m/z 599.0636 $[M + H]^+$, calcd for $C_{31}H_{24}BrN_2O_4S$ 599.0640.



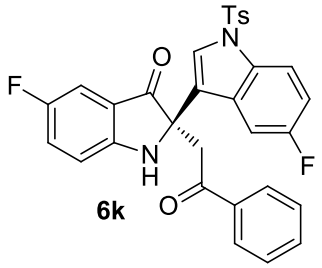
6i

(*R*)-2-(2-oxopropyl)-2-(1-tosyl-1*H*-indol-3-yl)indolin-3-one (6i): yellow solid; 39.2 mg; 86% yield; 96% ee; [determined by **HPLC** analysis Daicel Chirapak OD-H, *n*-hexane/*i*-PrOH = 80/20, 254 nm UV detector, 1.0 mL/min, t_R = 20.7 min (major) and t_R = 33.9 min (minor)]; m.p.: 116–118 °C; $[\alpha]_D^{20}$ – 18.5 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.62 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.52 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.17 (dd, *J* = 12.8, 4.7 Hz, 3H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.85 (t, *J* = 7.3 Hz, 1H), 6.11 (s, br, 1H), 3.74 (d, *J* = 17.0 Hz, 1H), 2.78 (d, *J* = 17.0 Hz, 1H), 2.31 (s, 3H), 2.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.5, 200.0, 160.0, 145.1, 138.1, 135.8, 135.0, 130.0, 128.1, 126.9, 125.5, 124.9, 124.6, 123.5, 121.8, 120.2, 119.5, 118.9, 113.9, 112.6, 66.7, 48.3, 31.5, 21.7; **IR (KBr)** ν 3385, 3141, 2918, 2862, 1700, 1616, 1368, 1178 cm^{-1}; **HRMS** (ESI) found m/z 459.1371 $[M + H]^+$, calcd for $C_{26}H_{23}N_2O_4S$ 459.1379. Physical and spectral properties of this material were identical to those previously reported in literature.[3]



6j

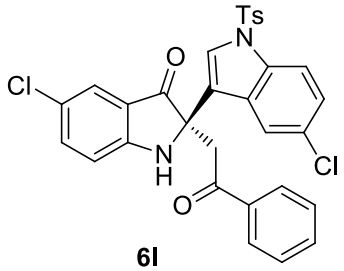
(*R*)-5-methyl-2-(5-methyl-1-tosyl-1*H*-indol-3-yl)-2-(2-oxo-2-phenylethyl)indolin-3-one (6j): yellow solid; 50.4 mg; 92% yield; 89% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 21.2 min (major) and t_R = 24.1 min (minor)]; m.p.: 128–131 °C; $[\alpha]_D^{20}$ – 19.9 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.49 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 3H), 7.36 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.06 (s, br, 1H), 4.34 (d, *J* = 17.5 Hz, 1H), 3.27 (d, *J* = 17.5 Hz, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.5, 197.4, 158.6, 144.8, 139.4, 136.6, 135.0, 134.1, 133.9, 133.0, 129.9, 128.9, 128.8, 128.6, 128.2, 126.9, 126.2, 124.8, 124.7, 121.5, 120.6, 119.4, 113.5, 112.5, 67.2, 44.1, 21.7, 20.7; **IR (KBr)** ν 3405, 3145, 2938, 2861, 1710, 1619, 1373, 1176, 926 cm^{-1}; **HRMS** (ESI) found m/z 549.1846$[M + H]^+$, calcd for $C_{33}H_{29}N_2O_4S$ 549.1848.



6k

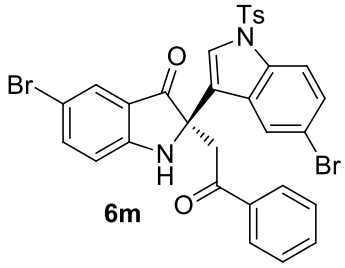
(*R*)-5-fluoro-2-(5-fluoro-1-tosyl-1*H*-indol-3-yl)-2-(2-oxo-2-phenylethyl)indolin-3-one (6k): yellow solid; 51.7 mg; 93% yield; 97% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 17.3 min (minor) and t_R = 24.0 min (major)]; m.p.: 113–115 °C; $[\alpha]_D^{20}$ – 25.6 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 2H), 7.81 (dd, *J* = 9.1, 4.5 Hz, 1H), 7.68 (s, 1H), 7.59 (dd, *J* = 14.0, 7.9 Hz, 3H), 7.48 – 7.39 (m, 3H), 7.29 (ddd, *J* = 10.9, 8.6, 3.4 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.96 (ddd, *J* =

8.4, 7.8, 3.1 Hz, 2H), 6.22 (s, br, 1H), 4.30 (d, *J* = 17.5 Hz, 1H), 3.23 (d, *J* = 17.5 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.9, 197.4, 160.7, 158.1 (d, *J* = 41.7 Hz), 156.7, 155.5, 145.3, 136.3, 134.7, 134.2, 132.1, 130.0, 129.1 (d, *J* = 10.3 Hz), 129.0, 128.2, 126.9, 126.3 (d, *J* = 25.4 Hz), 126.3, 120.2 (d, *J* = 4.1 Hz), 119.3 (d, *J* = 7.4 Hz), 114.9 (d, *J* = 9.6 Hz), 113.8 (d, *J* = 7.4 Hz), 113.2, 112.9, 110.4, 110.2, 107.7, 107.4, 67.8, 43.9, 21.7; **IR (KBr)** ν 3409, 2966, 2924, 2850, 2361, 2340, 1753, 1700, 1630, 1492, 1376, 1309, 1260, 1229, 1193, 916, 790 cm^{-1}; **HRMS** (ESI) found m/z 557.1345 $[M + H]^+$, calcd for $C_{31}H_{23}F_2N_2O_4S$ 557.1347.



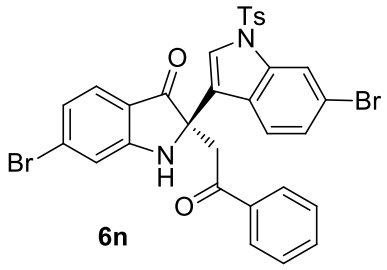
6l

(*R*)-5-chloro-2-(5-chloro-1-tosyl-1*H*-indol-3-yl)-2-(2-oxo-2-phenylethyl)indolin-3-one (6l): yellow solid; 52.9 mg; 90% yield; 95% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 15.8 min (minor) and t_R = 22.7 min (major)]; m.p.: 121–123 °C; $[\alpha]_D^{20}$ – 31.8 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.77 (dd, *J* = 11.7, 5.4 Hz, 2H), 7.64 (s, 1H), 7.63 – 7.55 (m, 4H), 7.52 – 7.42 (m, 3H), 7.22 – 7.13 (m, 3H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.32 (s, br, 1H), 4.31 (d, *J* = 17.5 Hz, 1H), 3.21 (d, *J* = 17.5 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.9, 197.3, 158.2, 145.4, 138.2, 134.6, 134.3, 134.1, 130.1, 129.5, 129.3, 129.0, 128.3, 126.9, 125.9, 125.3, 124.9, 124.8, 121.4, 119.9, 119.6, 114.9, 113.8, 67.6, 44.0, 21.7; **IR (KBr)** ν 3409, 2966, 2924, 2850, 1700, 1630, 1376, 1309, 1193, 916, 790 cm^{-1}; **HRMS** (ESI) found m/z 589.0759 $[M + H]^+$, calcd for $C_{31}H_{23}Cl_2N_2O_4S$ 589.0756.



6m

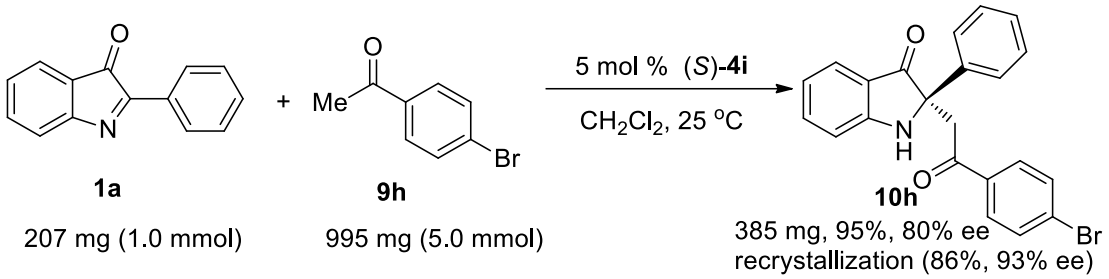
(*R*)-5-bromo-2-(5-bromo-1-tosyl-1*H*-indol-3-yl)-2-(2-oxo-2-phenylethyl)indolin-3-one (6m): yellow solid; 60.3 mg; 89% yield; 94% ee; [determined by **HPLC** analysis Daicel Chirapak OD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 18.2 min (minor) and t_R = 28.6 min (major)]; m.p.: 258–260 °C; $[\alpha]_D^{20}$ – 36.1 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 8.9 Hz, 2H), 7.64 (s, 1H), 7.59 (dd, *J* = 13.4, 7.3 Hz, 4H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.33 (dd, *J* = 8.8, 1.4 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.35 (s, br, 1H), 4.31 (d, *J* = 17.6 Hz, 1H), 3.22 (d, *J* = 17.5 Hz, 1H), 2.32 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ198.7, 197.3, 158.5, 145.4, 140.7, 136.2, 134.6, 134.4, 134.2, 130.1, 129.8, 129.0, 128.3, 128.0, 127.9, 126.9, 125.8, 124.5, 120.4, 119.5, 117.2, 115.2, 114.2, 111.6, 67.4, 44.0, 21.7; **IR (KBr)** ν 3443, 2956, 2920, 2856, 1705, 1627, 1366, 1194, 923, 750 cm^{-1}; **HRMS** (ESI) found m/z 676.9738 $[M + H]^+$, calcd for $C_{31}H_{23}Br_2N_2O_4S$ 676.9745.



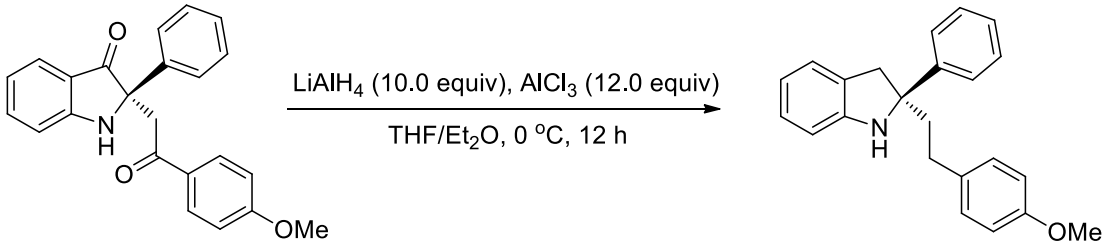
6n

(*R*)-6-bromo-2-(6-bromo-1-tosyl-1*H*-indol-3-yl)-2-(2-oxo-2-phenylethyl)indolin-3-one (6n): yellow solid; 58.7 mg; 87% yield; 95% ee; [determined by **HPLC** analysis Daicel Chirapak IA, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 17.2 min (major) and t_R = 31.2 min (minor)]; m.p.: 148–150 °C; $[\alpha]_D^{20}$ – 20.8 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.5 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.67 – 7.54 (m, 5H), 7.45 (t, *J* = 7.9 Hz, 3H), 7.27 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.18 (dd, *J* = 10.0, 4.7 Hz, 3H), 6.99 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.39 (s, br, 1H), 4.32 (d, *J* = 17.6 Hz, 1H), 3.19 (d, *J* = 17.6 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.9, 197.4, 160.2, 145.5, 136.4, 136.3, 134.7, 134.3, 133.7, 130.2, 129.0, 128.2, 126.9, 126.7, 125.0, 123.1, 122.8, 119.9, 118.8, 117.6, 116.9, 115.4, 67.1, 43.8, 21.8; **IR (KBr)** ν 3444, 2957, 2848, 1731, 1638, 1363, 1190, 926, 743 cm^{-1}; **HRMS** (ESI) found m/z 676.9752 $[M + H]^+$, calcd for $C_{31}H_{23}Br_2N_2O_4S$ 676.9745.

Scaled-up synthesis and further transformations

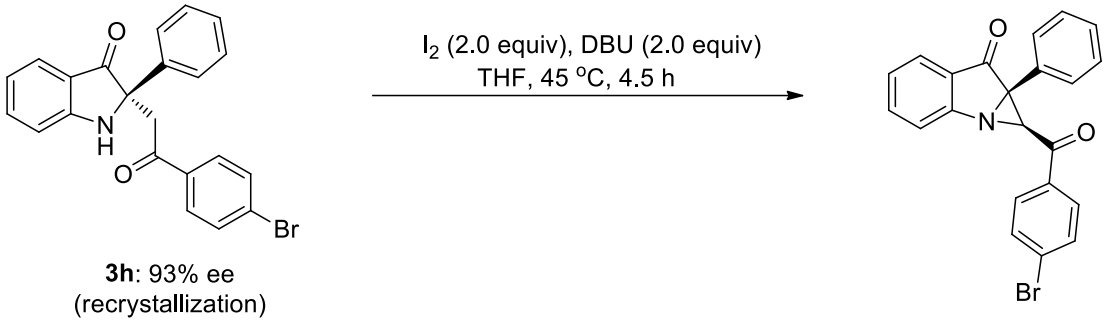


To a 50 mL Schlenk flask equipped with a stirring bar was added 2-phenyl-3*H*-indol-3-one **1a** (207 mg, 1.0 mmol), chiral phosphoric acid (*S*)-**4i** (43.2 mg, 0.05 mmol, 5 mol %), CH_2Cl_2 (10 mL). 4'-Bromoacetophene **2h** (995 mg, 5.0 mmol, 5.0 equiv) was added to the mixture. Then the resulting mixture was stirred at room temperature until the completion of the reaction (monitored by TLC), concentrated under vacuum, and the residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 4/1) to give the desired product **3h** (385 mg, 95%, 80% ee), 93% ee after one recrystallization.



3d (53.5 mg, 0.15 mmol) was dissolved to THF/Et_2O (1/1, 1.5 mL) and $LiAlH_4$ (56.9 mg, 1.5 mmol) was added to the solution at 0 °C. After being stirred for 1 h, $AlCl_3$ (finely crushed under N_2 atmosphere, 240.0 mg, 1.8 mmol) was added at 0 °C.[10] After being stirred for 12 h, the reaction was quenched by adding H_2O. The mixture was extracted with CH_2Cl_2 three times and the

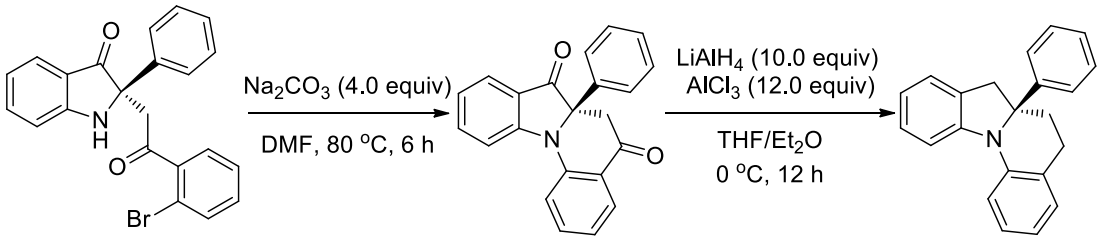
combined organic phase was dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the product **7** (39.5 mg, 80%, 84% ee).



3h: 93% ee
(recrystallization)

8, 85%, 90% ee

A mixture of **3h** (77.2 mg, 0.19 mmol), I_2 (98 mg, 0.38 mmol), and DBU (116 mg, 0.76 mmol) was stirred in 1.6 mL of THF at 40 ℃ for 4.5 h until the disappearance of **3h** as determined by TLC.[7] The reaction mixture was quenched with aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2 (15 mL × 3). The organic extracts were dried over Na_2SO_4, filtered, and concentrated to give a residue, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1) to afford the product **8** (65.2 mg, 85%, 90% ee).



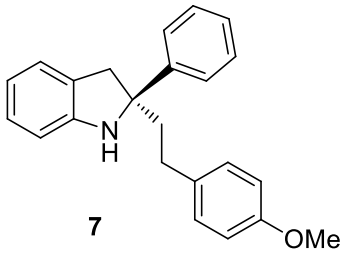
3i: 96% ee
(recrystallization)

9, 48%, 88% ee

10, 82%, 87% ee

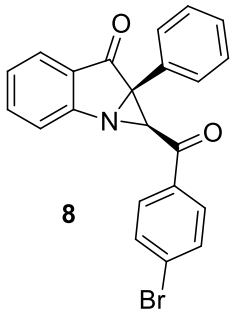
A solution of Mannich adduct **3i** (60.9 mg, 0.15 mmol) (96% ee after one recrystallization from petroleum ether/ethyl acetate), Na_2CO_3 (63.6 mg, 0.60 mmol, 4.0 equiv) was stirred in 3.0 mL of DMF at 80 ℃ for 6 h.[9] Then the reaction was quenched with water, followed by extraction using ethyl acetate (5 mL × 3), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (eluting with petroleum ether/ethyl acetate = 5/1) to afford **9** (23.4 mg, 48%, 88% ee) as yellow solid.

Then **9** (23.4 mg, 0.07 mmol) was dissolved to THF/Et_2O (1/1, 1 mL) and $LiAlH_4$ (26.7 mg, 0.7 mmol) was added to the solution at 0 °C. After being stirred for 1 h, $AlCl_3$ (finely crushed under N_2 atmosphere, 112.8 mg, 0.85 mmol) was added at 0 °C. After being stirred for 12 h, the reaction was quenched by adding H_2O. The mixture was extracted with CH_2Cl_2 three times and the combined organic phase was dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the product **10** (16.9 mg, 82%, 87% ee).



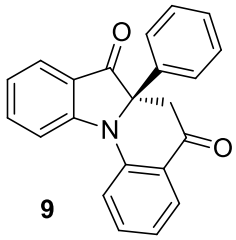
7

(*S*)-2-(4-methoxyphenethyl)-2-phenylindoline (7): white solid; 39.5 mg; 80% yield; 84% ee; [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 60/40, 254 nm UV detector, 1.0 mL/min, t_R = 8.7 min (minor) and t_R = 10.6 min (major)]; m.p.: 52–56 °C; $[\alpha]_D^{20}$ – 9.8 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.12 – 6.99 (m, 4H), 6.79 (t, *J* = 7.7 Hz, 3H), 6.71 (t, *J* = 7.3 Hz, 1H), 5.59 (brs, 1H), 4.42 (d, *J* = 10.0 Hz, 1H), 3.77 (s, 3H), 3.25 (t, *J* = 16.0 Hz, 2H), 2.50 (dd, *J* = 14.5, 10.9 Hz, 1H), 2.06 (dd, *J* = 14.5, 1.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 150.4, 146.9, 137.3, 128.6, 127.8, 127.7, 126.9, 126.5, 126.0, 124.7, 118.6, 113.9, 110.1, 72.6, 69.7, 55.4, 49.5, 46.9; **IR (KBr)** ν 3363, 3285, 2905, 2840, 1423, 1347, 1158, 919, 571, 545 cm^{-1}; **HRMS** (ESI) found m/z 330.1862 $[M + H]^+$, calcd for $C_{23}H_{24}NO$ 330.1858.



8

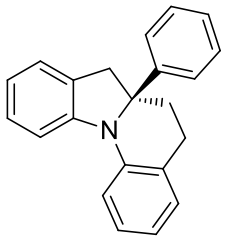
(1*S*,7a*S*)-1-(4-bromobenzoyl)-7a-phenyl-1*H*-azirino[1,2-*a*]indol-7(7a*H*)-one (8): yellow solid; 65.2 mg; 85% yield; 90% ee; [determined by **HPLC** analysis Daicel Chirapak OD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 11.1 min (major) and t_R = 13.1 min (minor)]; m.p.: 158–161 °C; $[\alpha]_D^{20}$ – 54.3 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.65 (m, 4H), 7.65 – 7.59 (m, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.32 – 7.19 (m, 3H), 3.84 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.5, 187.4, 165.7, 136.4, 134.1, 132.2, 129.9, 129.5, 128.8, 128.6, 128.4, 128.3, 127.3, 126.4, 122.0, 72.7, 59.2; **IR (KBr)** ν 3384, 3065, 2930, 2843, 1691, 1677, 1123, 919, 733, 628 cm^{-1}; **HRMS** (ESI) found m/z 404.0283 $[M + H]^+$, calcd for $C_{22}H_{15}BrNO_2$ 404.0286.



9

(*R*)-6a-phenyl-6,6a-dihydroindolo[1,2-*a*]quinoline-5,7-dione (9): yellow solid; 23.4 mg; 48% yield; 88% ee; [determined by **HPLC** analysis Daicel Chirapak AD-H, *n*-hexane/*i*-PrOH = 70/30, 254 nm UV detector, 1.0 mL/min, t_R = 9.0 min (major) and t_R = 11.9 min (minor)]; m.p.: 204–206 °C; $[\alpha]_D^{20}$ - 37.6 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.77 (dd,

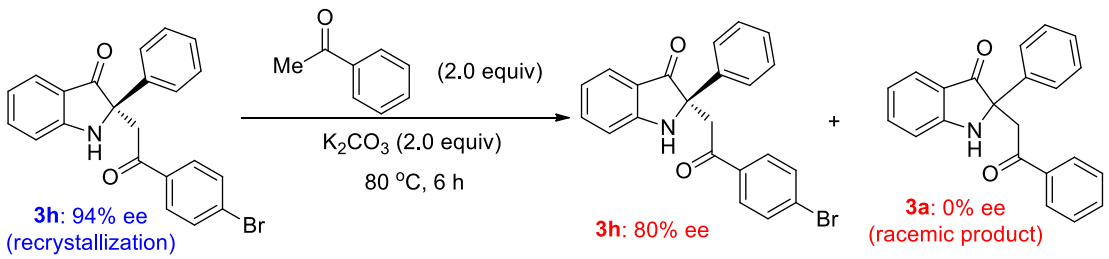
J = 18.1, 7.9 Hz, 3H), 7.72 – 7.61 (m, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.24 (dt, *J* = 23.1, 6.9 Hz, 3H), 7.08 (dd, *J* = 11.4, 7.0 Hz, 2H), 3.68 (d, *J* = 16.7 Hz, 1H), 3.01 (d, *J* = 16.7 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.1, 191.2, 154.7, 142.3, 138.1, 135.7, 134.5, 129.2, 128.6, 126.7, 126.5, 123.8, 123.1, 121.5, 121.1, 119.9, 110.3, 73.1, 44.2; **IR (KBr)** ν 3116, 3061, 2836, 1710, 1675, 1642, 1495, 1461, 1319, 1302, 923, 750 cm^{-1}; **HRMS** (ESI) found m/z 326.1176 $[M + H]^+$, calcd for $C_{22}H_{16}NO_2$ 326.1181.

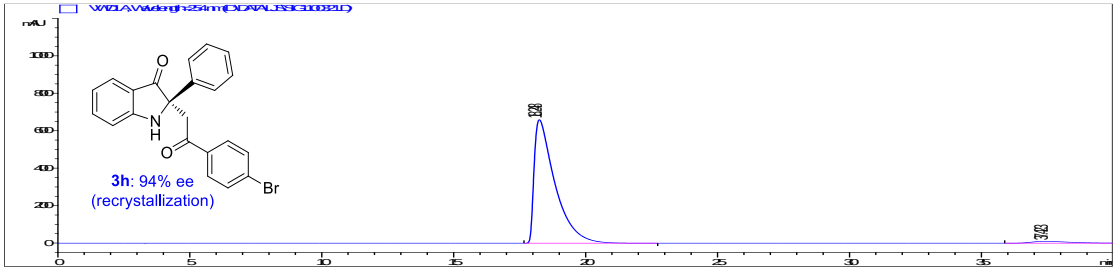


10

(*S*)-6a-phenyl-5,6,6a,7-tetrahydroindolo[1,2-*a*]quinoline (10): pale white solid; 16.9 mg; 82% yield; 87% ee; [determined by **HPLC** analysis Daicel Chirapak OD-H, *n*-hexane/*i*-PrOH = 98/2, 254 nm UV detector, 1.0 mL/min, t_R = 9.5 min (minor) and t_R = 11.3 min (major)]; m.p.: 64–66 °C; $[\alpha]_D^{20}$ - 5.2 (*c* 1.0, CH_2Cl_2); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.39 (dt, *J* = 3.2, 1.8 Hz, 2H), 7.28 – 7.20 (m, 4H), 7.19 – 7.13 (m, 1H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 7.0 Hz, 1H), 6.90 (td, *J* = 7.4, 1.1 Hz, 1H), 6.82 – 6.72 (m, 1H), 3.28 (dd, *J* = 15.7, 7.7 Hz, 2H), 2.66 (dd, *J* = 16.8, 5.1 Hz, 1H), 2.53 – 2.44 (m, 1H), 2.44 – 2.34 (m, 1H), 2.22 (td, *J* = 13.1, 5.6 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.7, 145.3, 141.1, 129.8, 128.6, 128.3, 127.6, 127.4, 126.5, 126.3, 126.0, 125.2, 122.1, 121.8, 119.6, 108.6, 69.5, 45.9, 30.8, 25.0; **IR (KBr)** ν 2956, 2921, 1645, 1626, 1485, 1349, 1162, 575 cm^{-1}; **HRMS** (ESI) found m/z 298.1565 $[M + H]^+$, calcd for $C_{20}H_{20}N$ 298.1596.

Control experiment





Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
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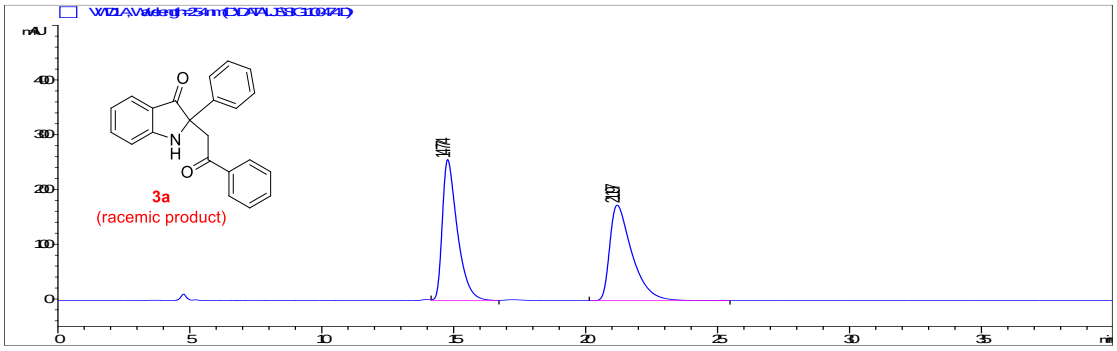
2	37.423	1021.7	10.2	1.3954	0.513	2.751



Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.774	10210.5	257.5	0.5907	0.52	49.990
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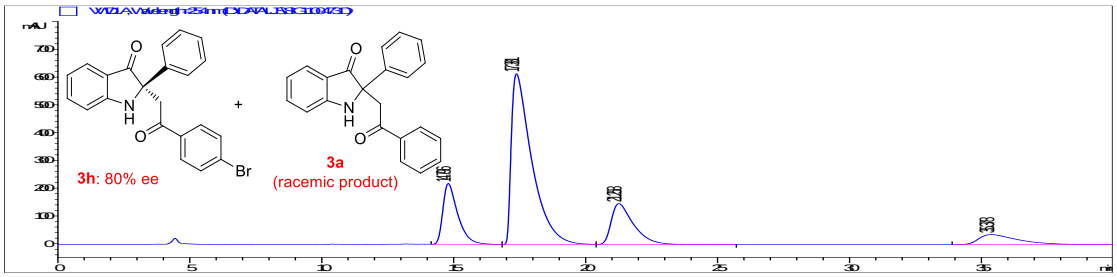

Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.796	8580	218.9	0.5826	0.529	15.904
2	17.381	33070.9	614.4	0.7969	0.307	61.301
3	21.258	8633	147.2	0.8704	0.475	16.002
4	35.378	3664.2	36	1.448	0.446	6.792

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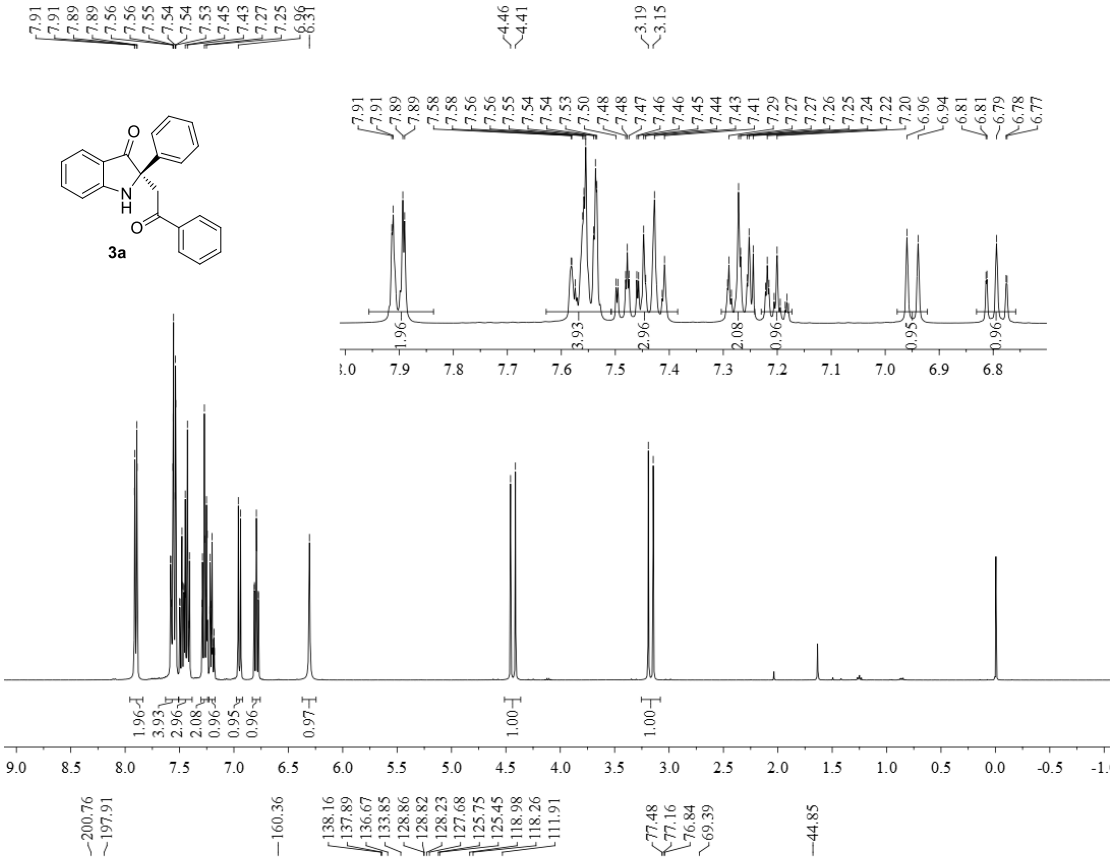
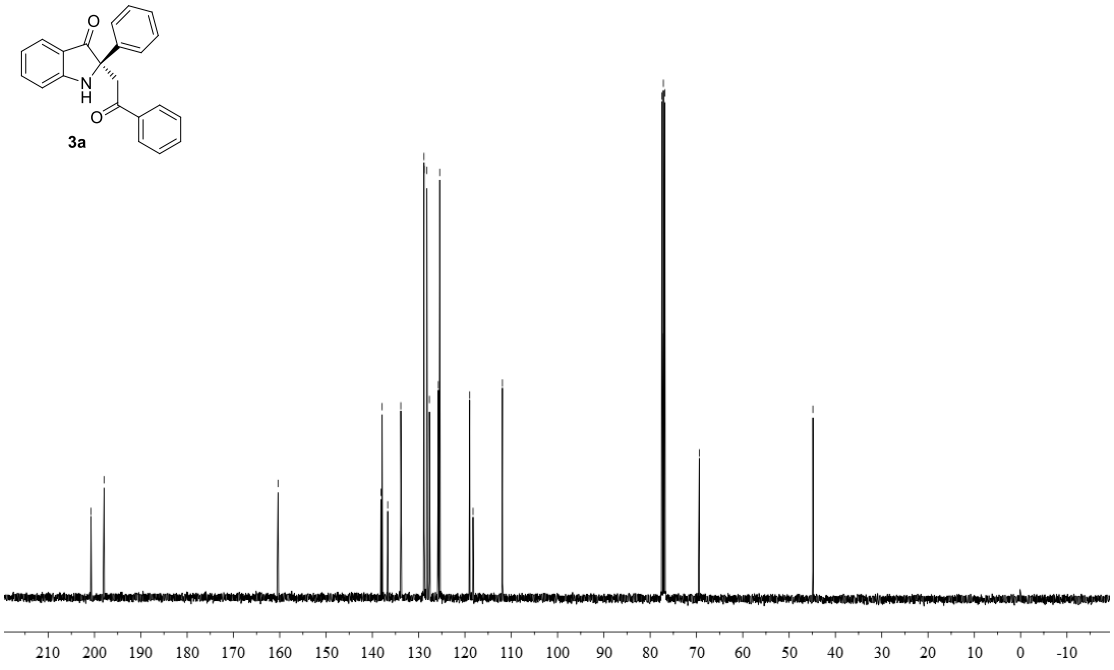
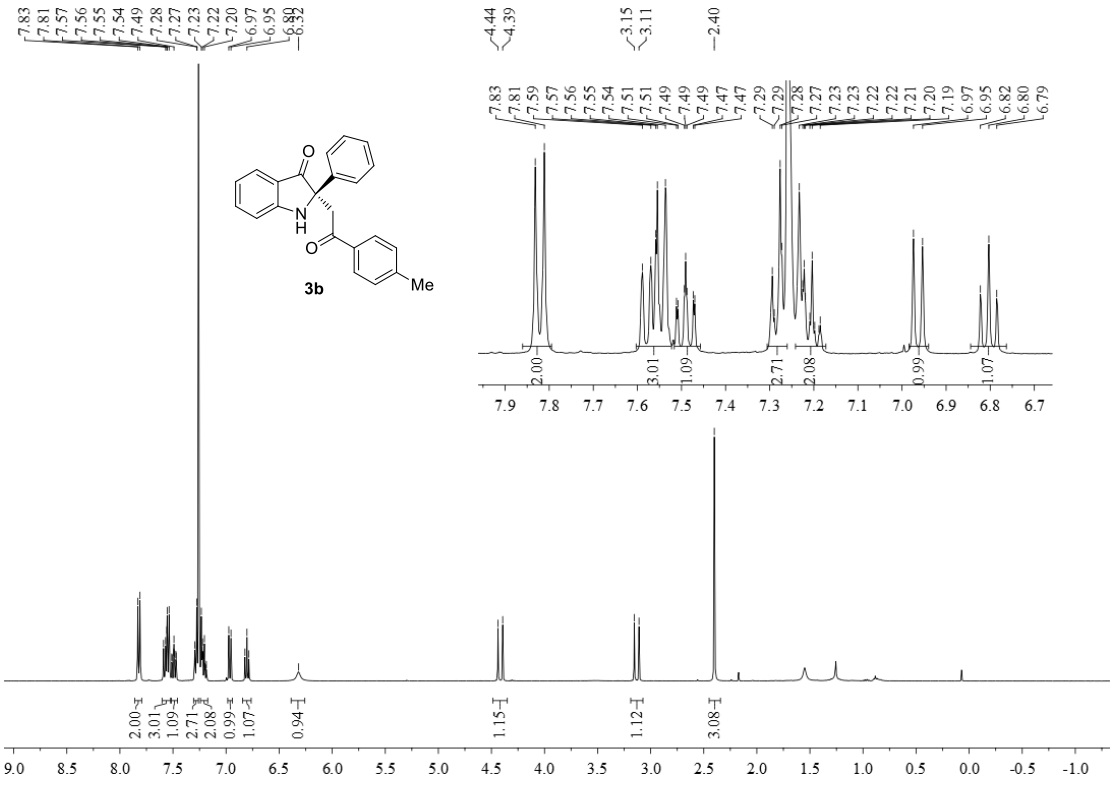
NMR spectra of the related compounds



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6.95
6.88
6.32
4.44
4.39
3.15
3.11
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H
O
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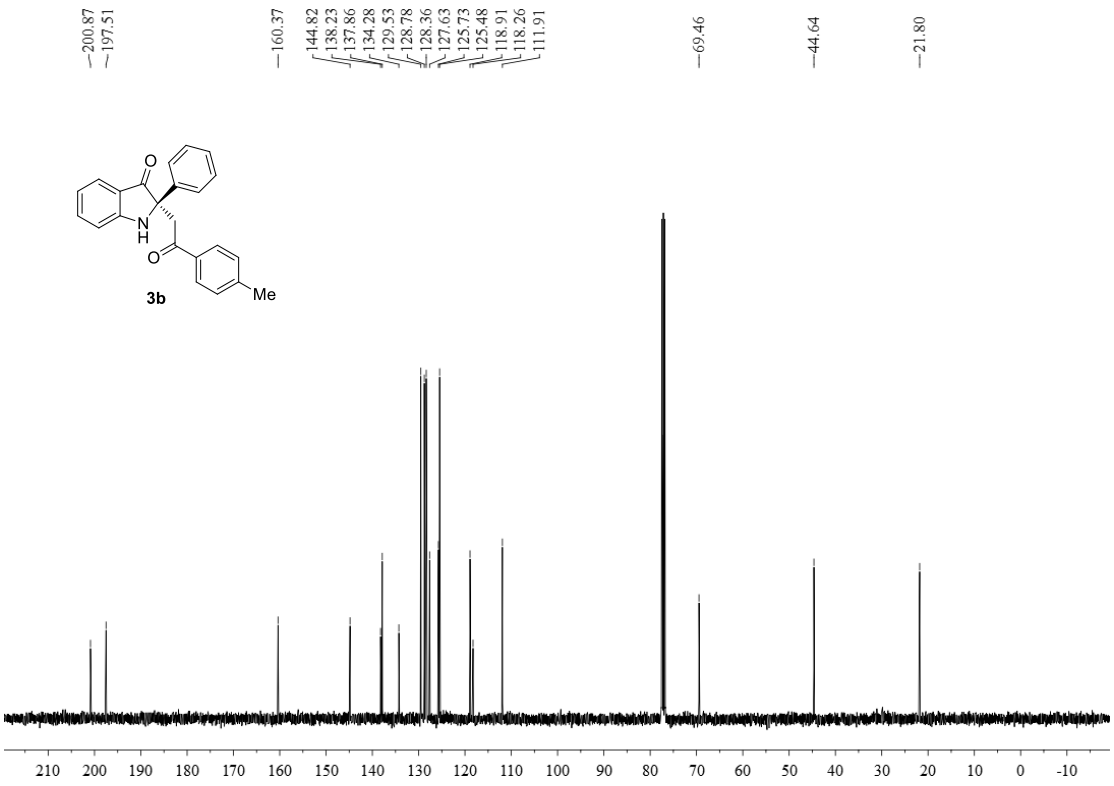
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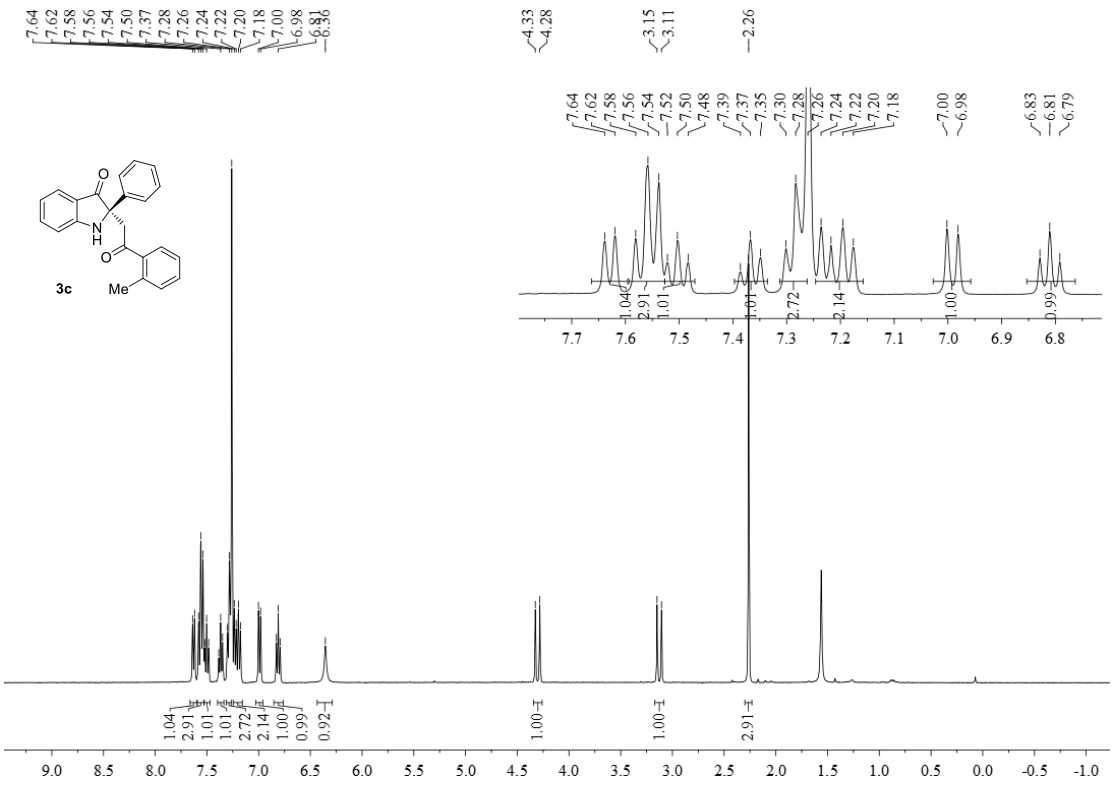
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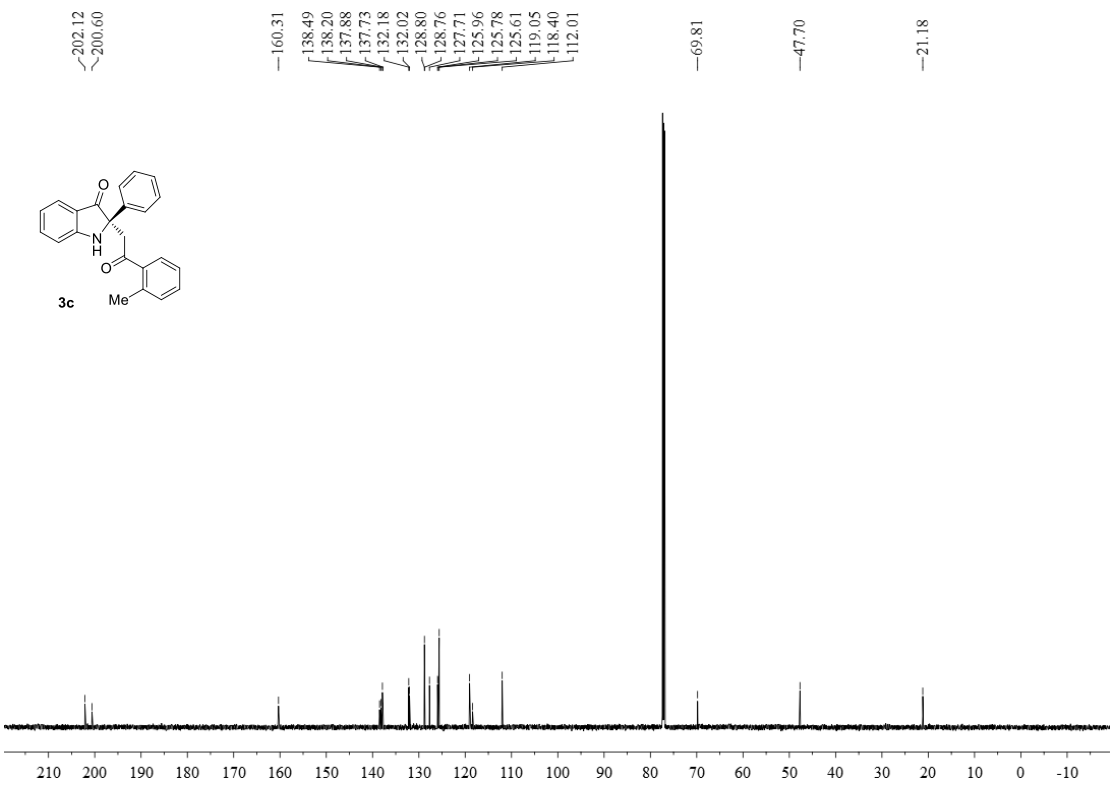
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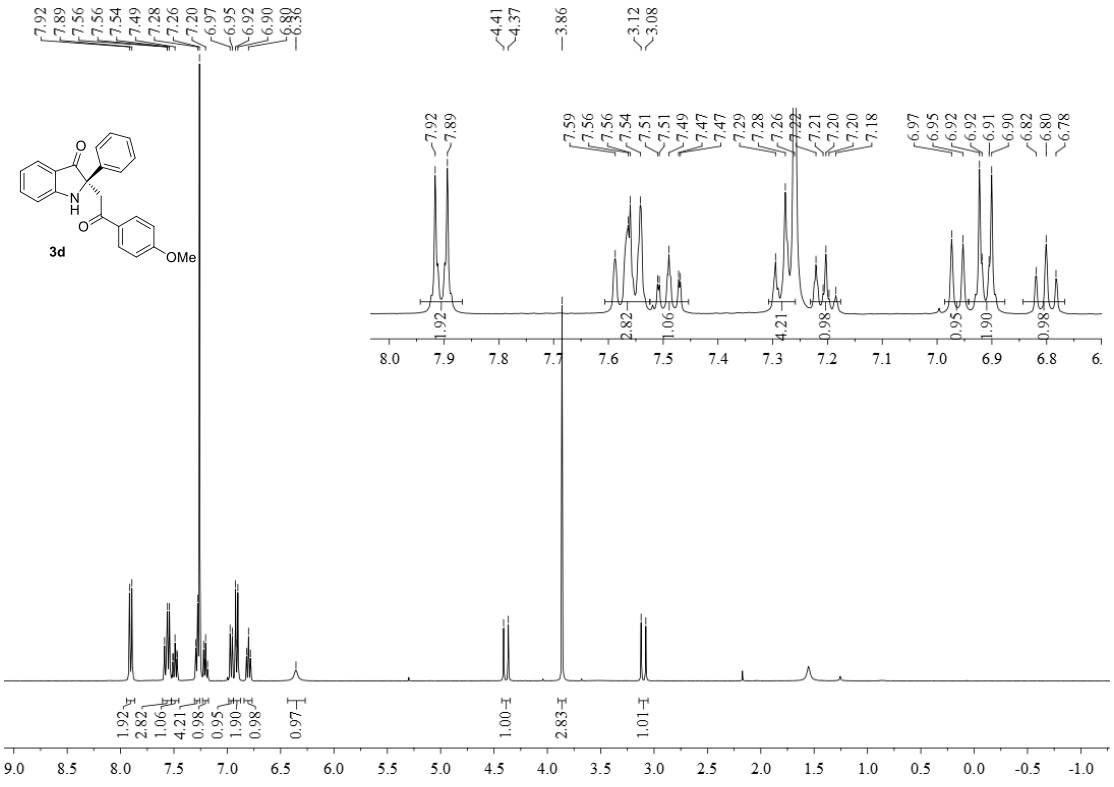
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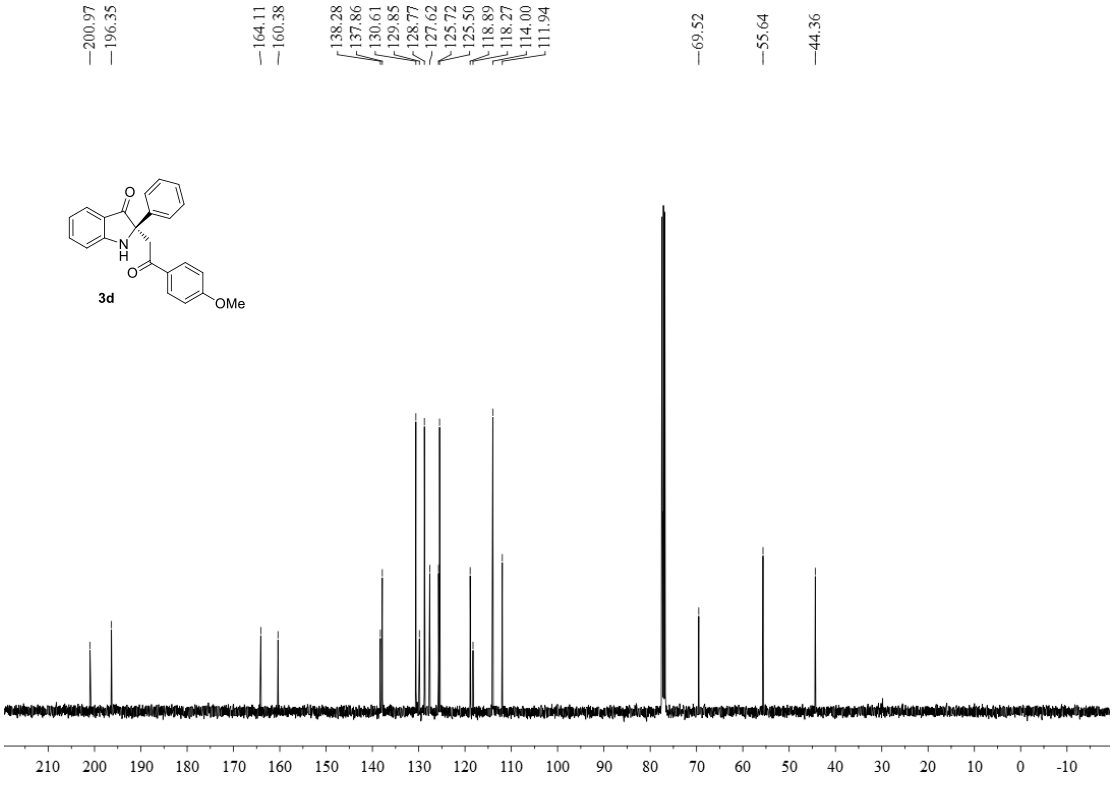
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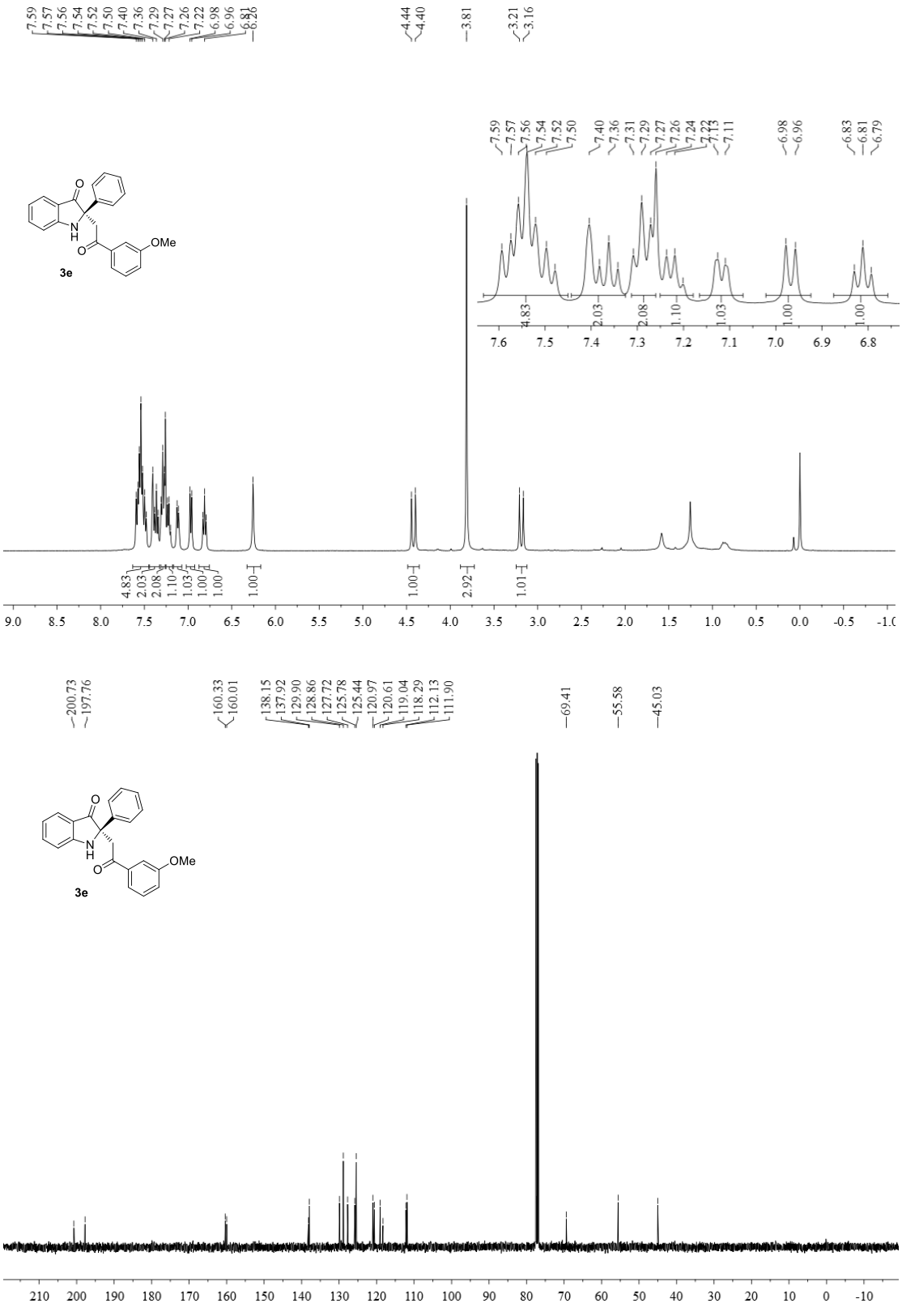
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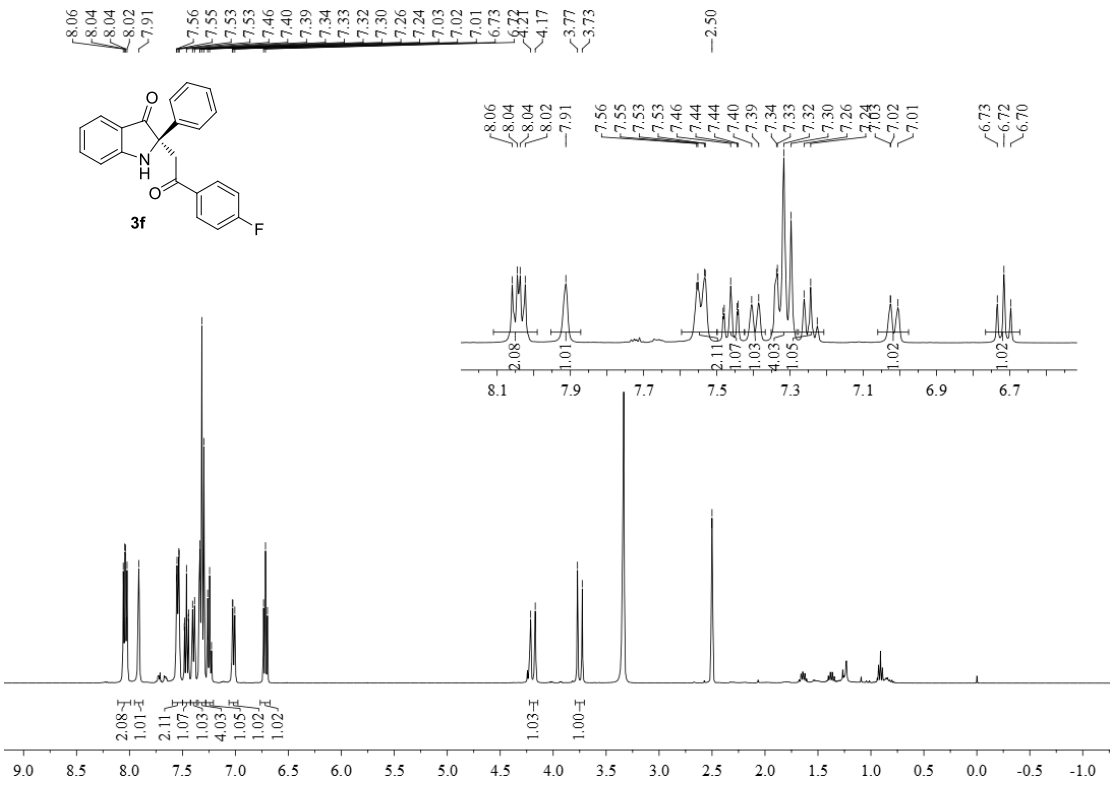
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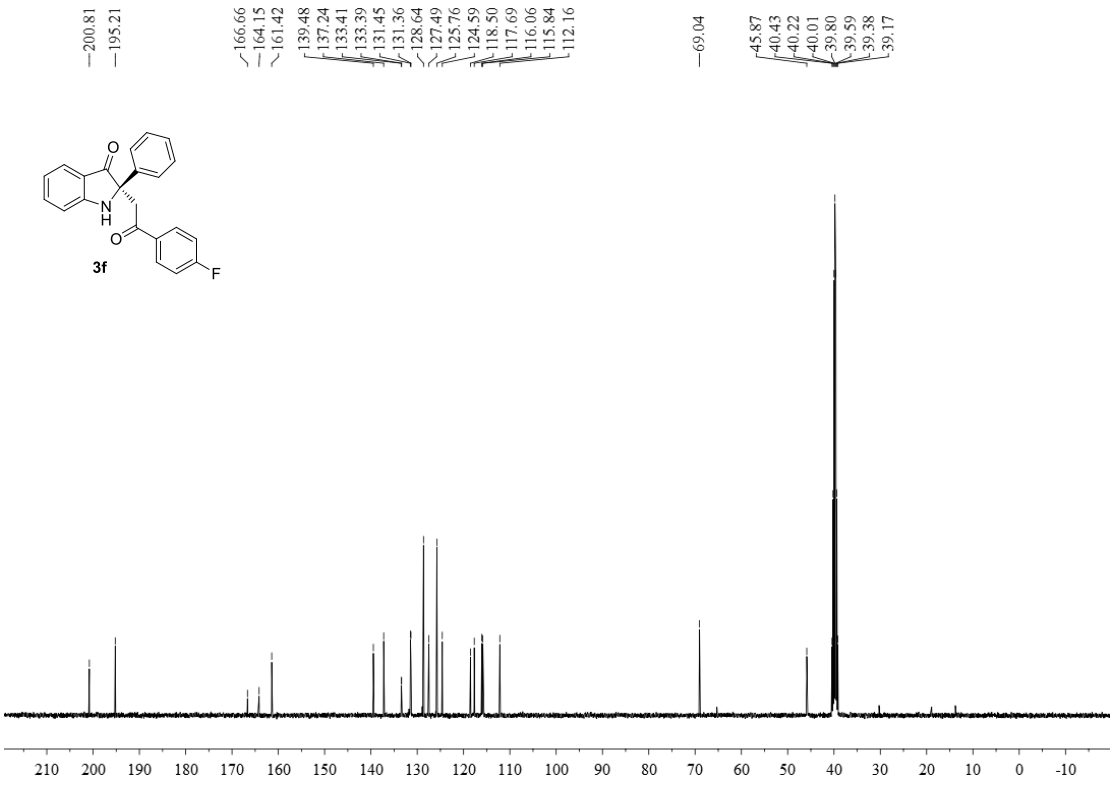
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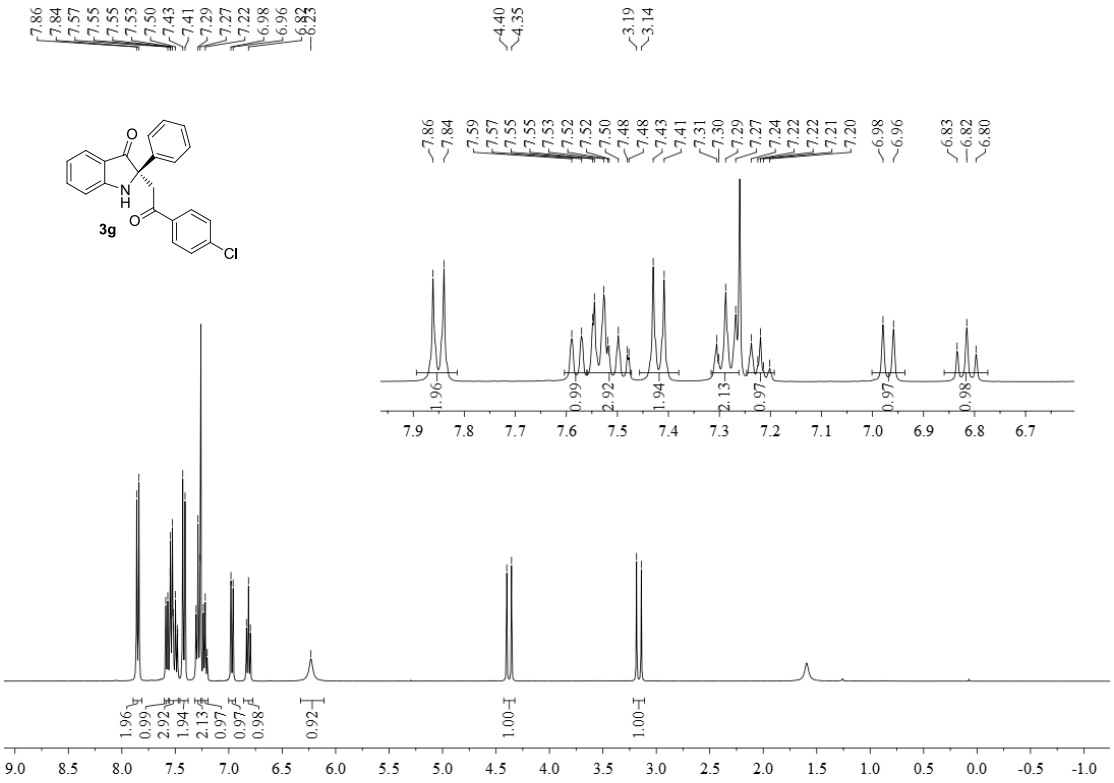
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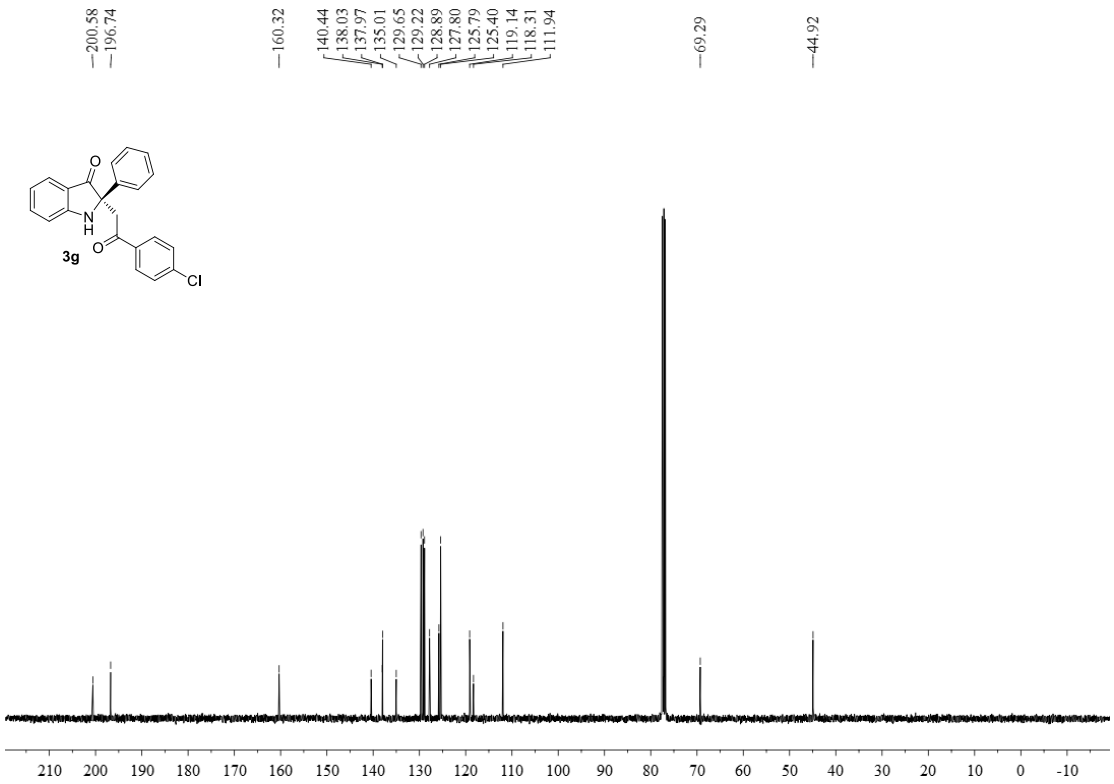
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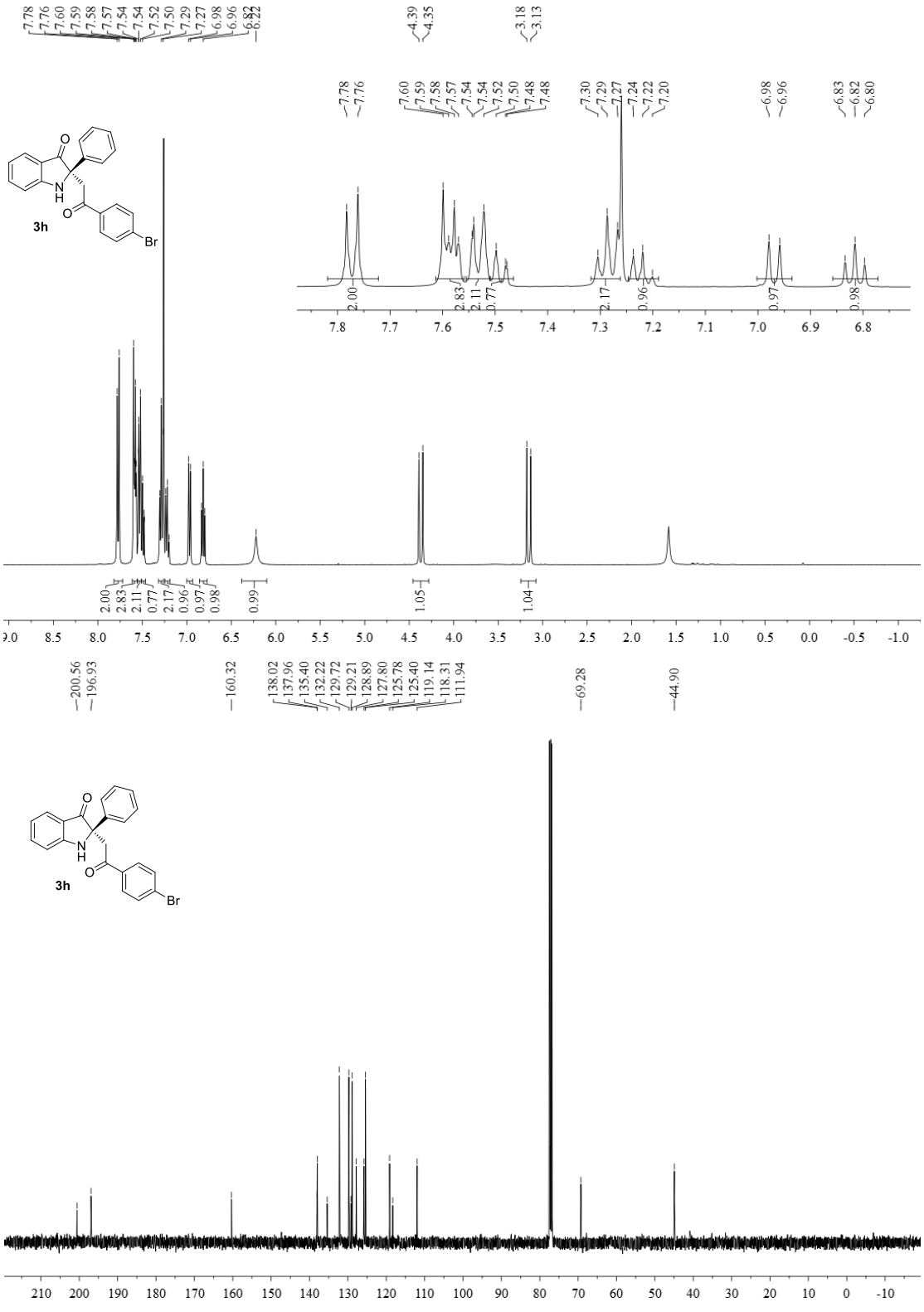
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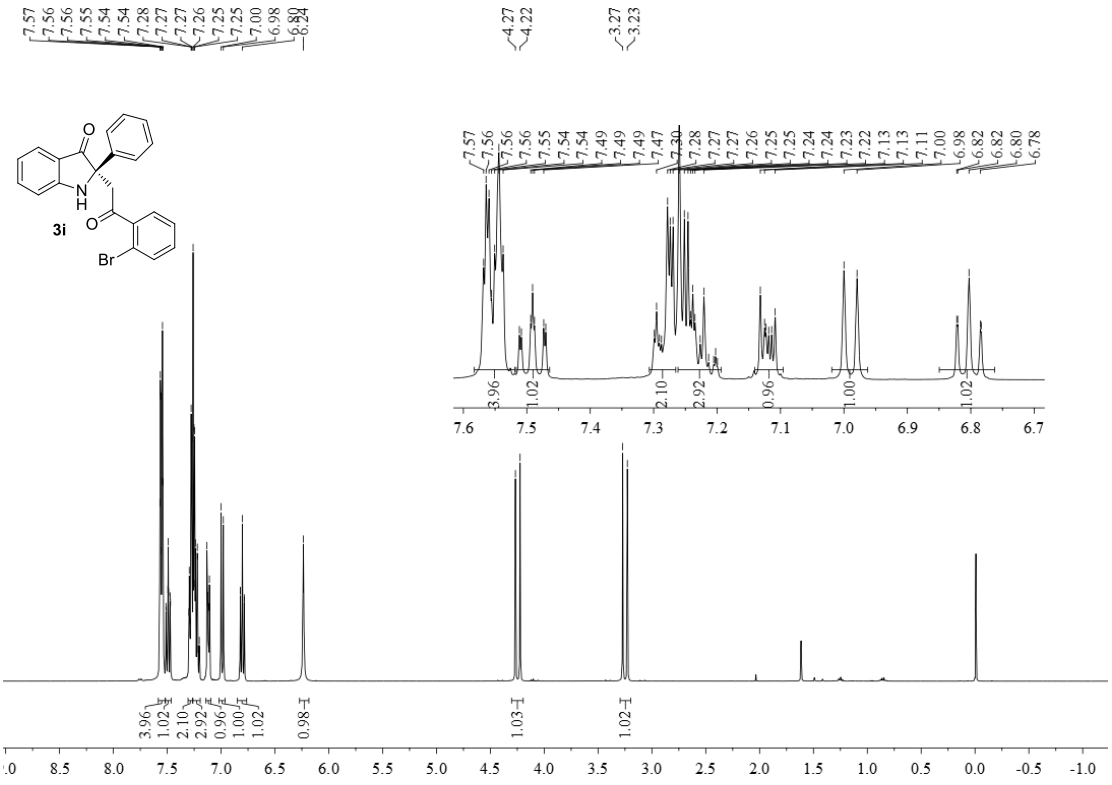
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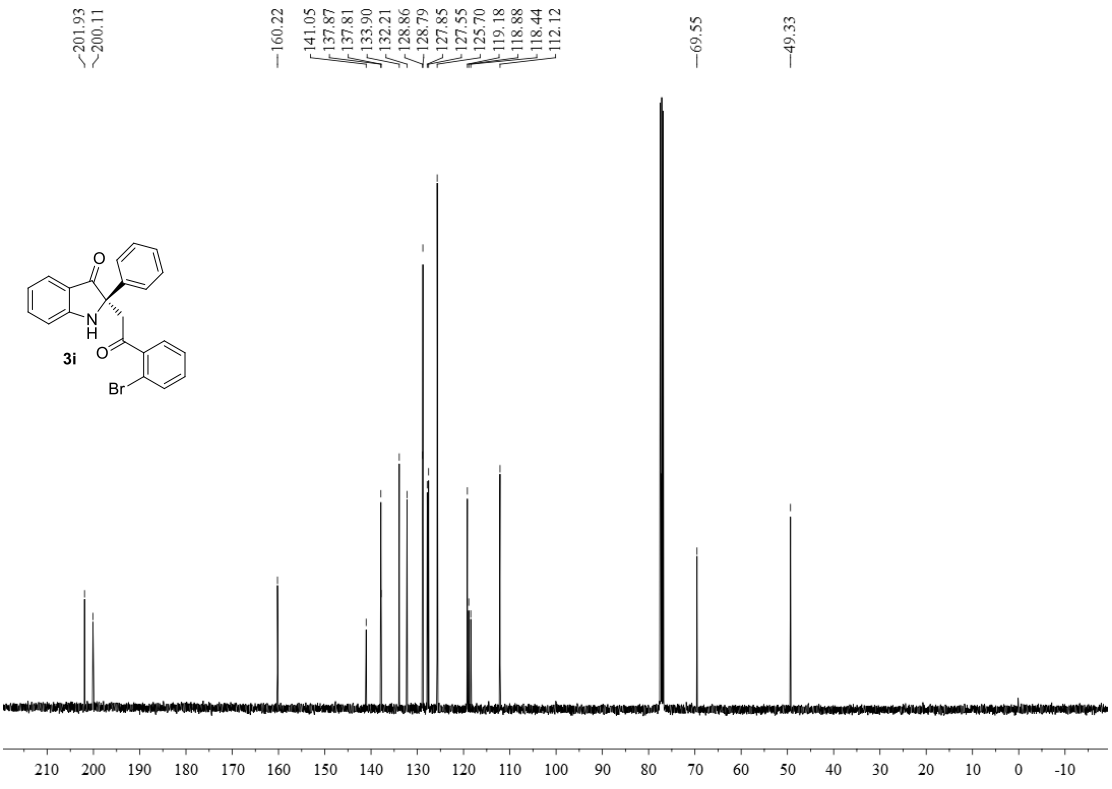
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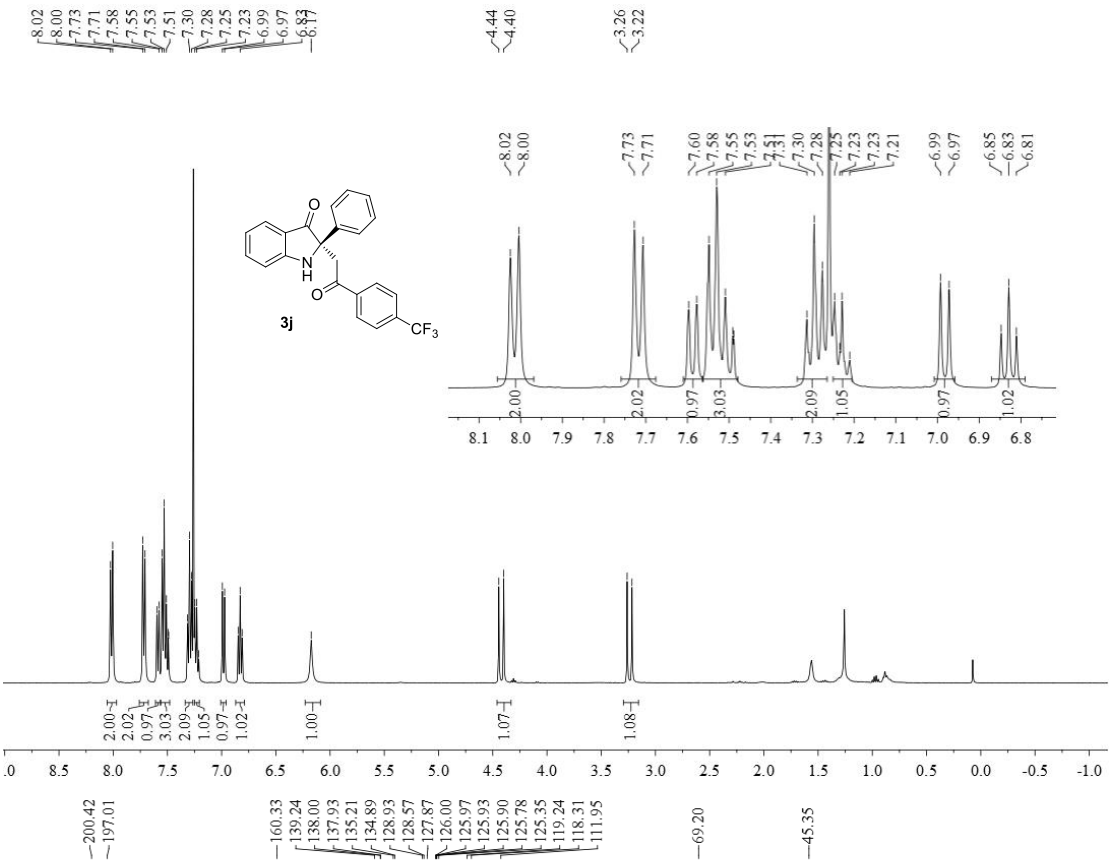
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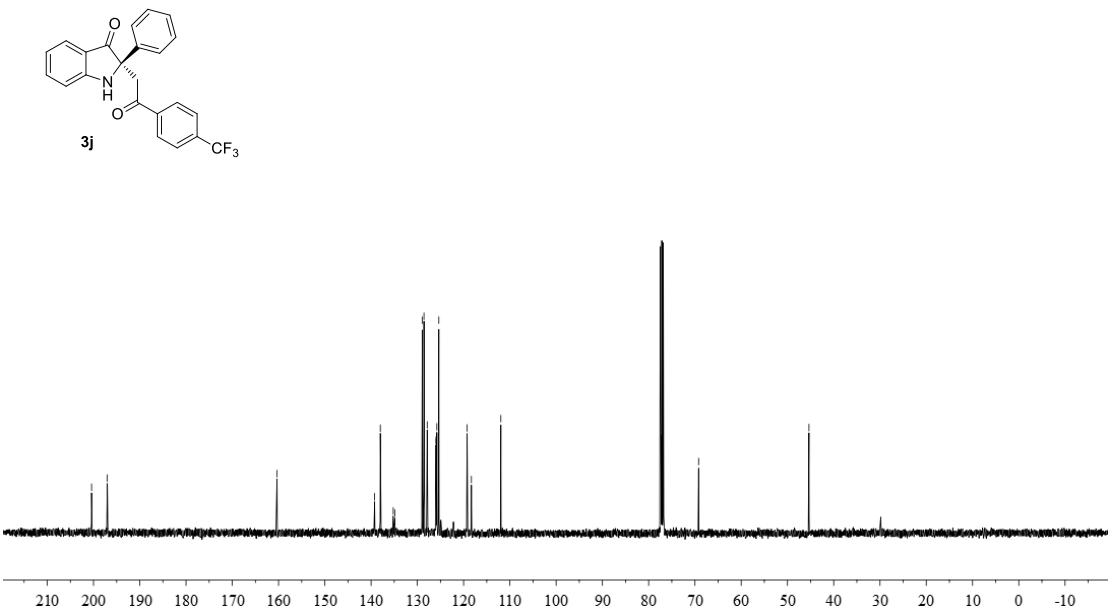
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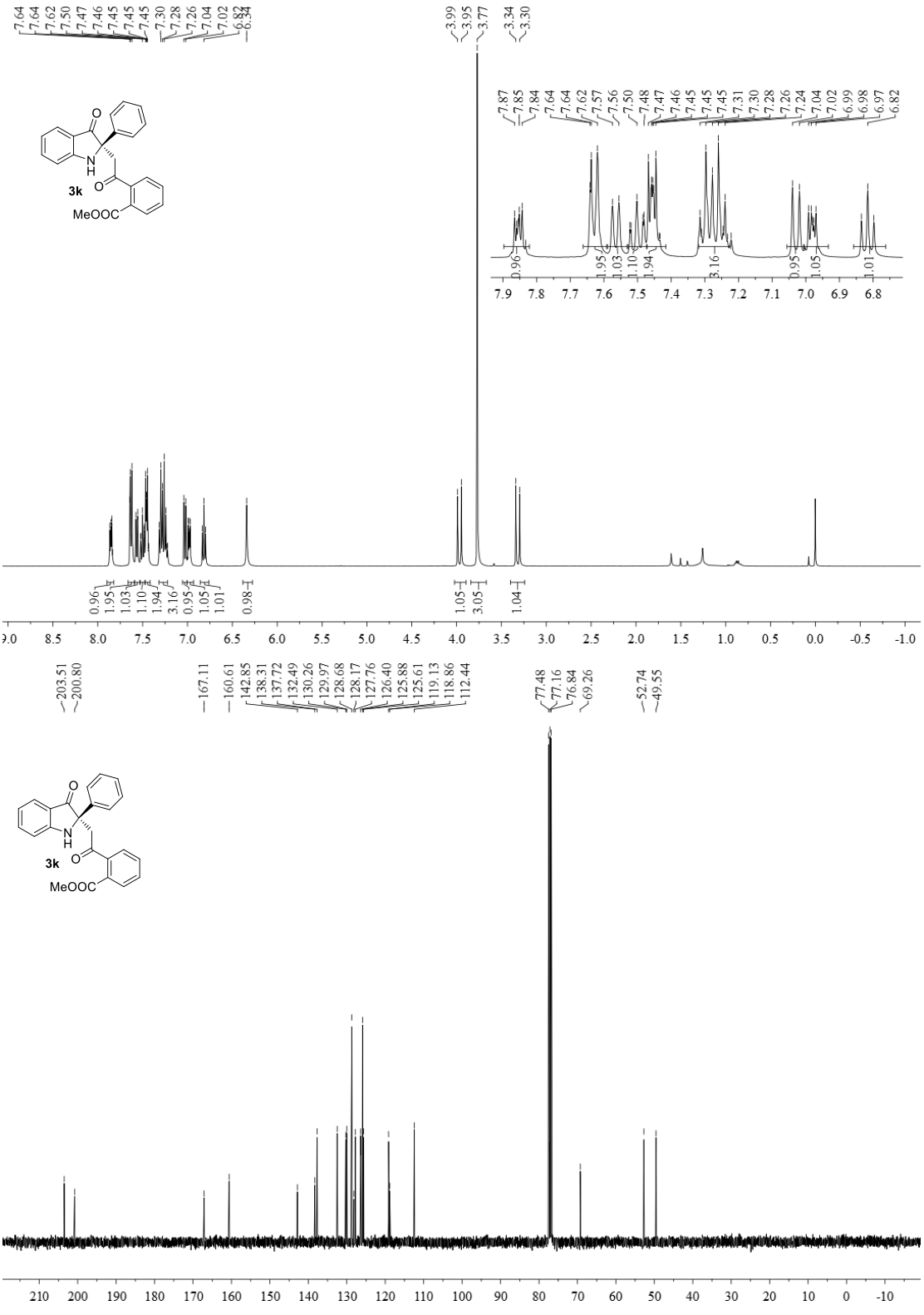
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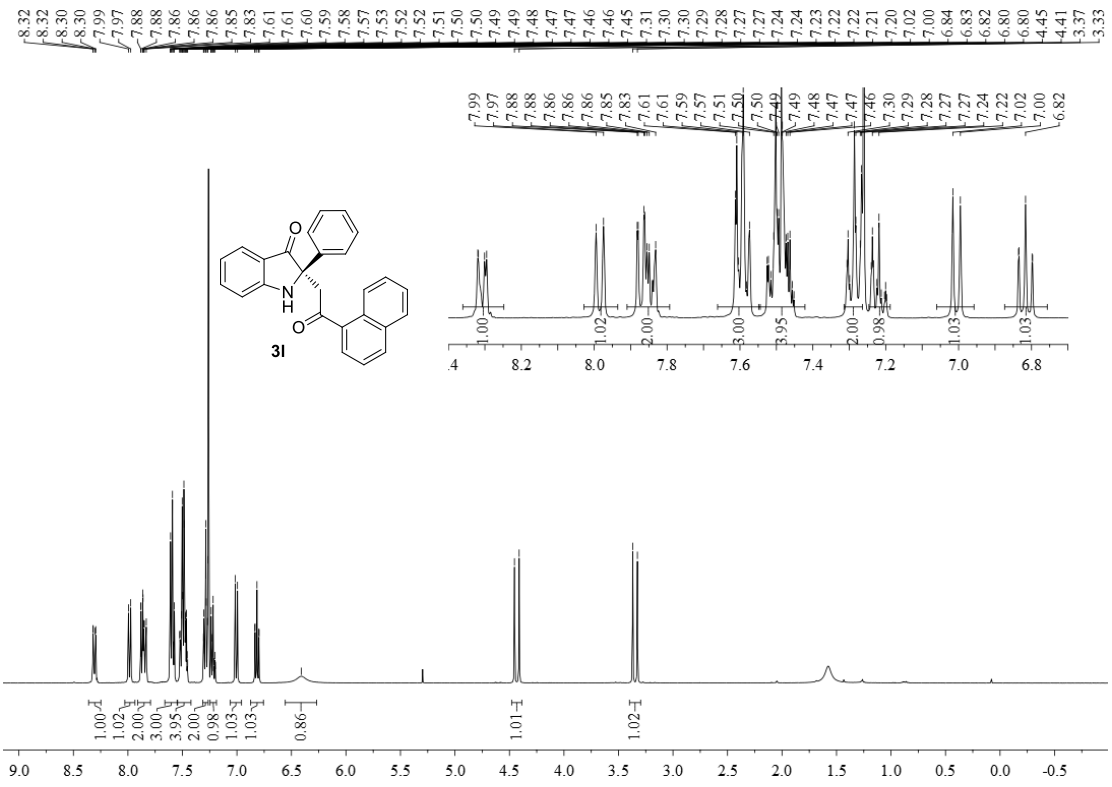
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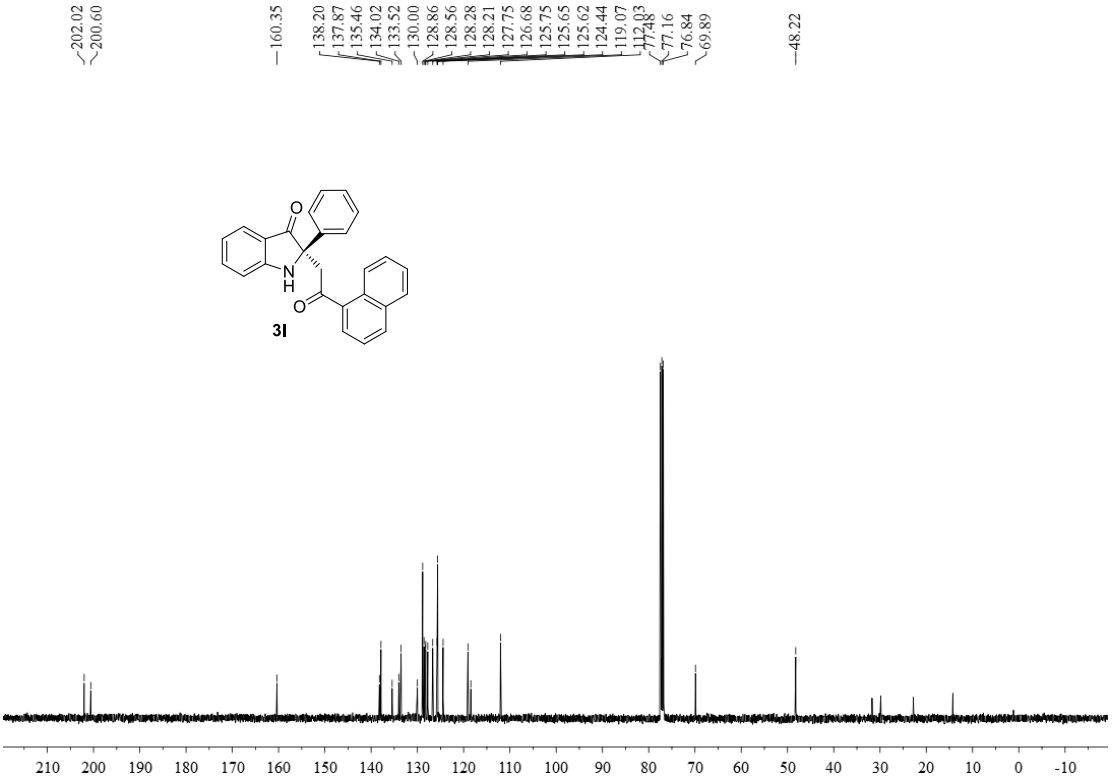
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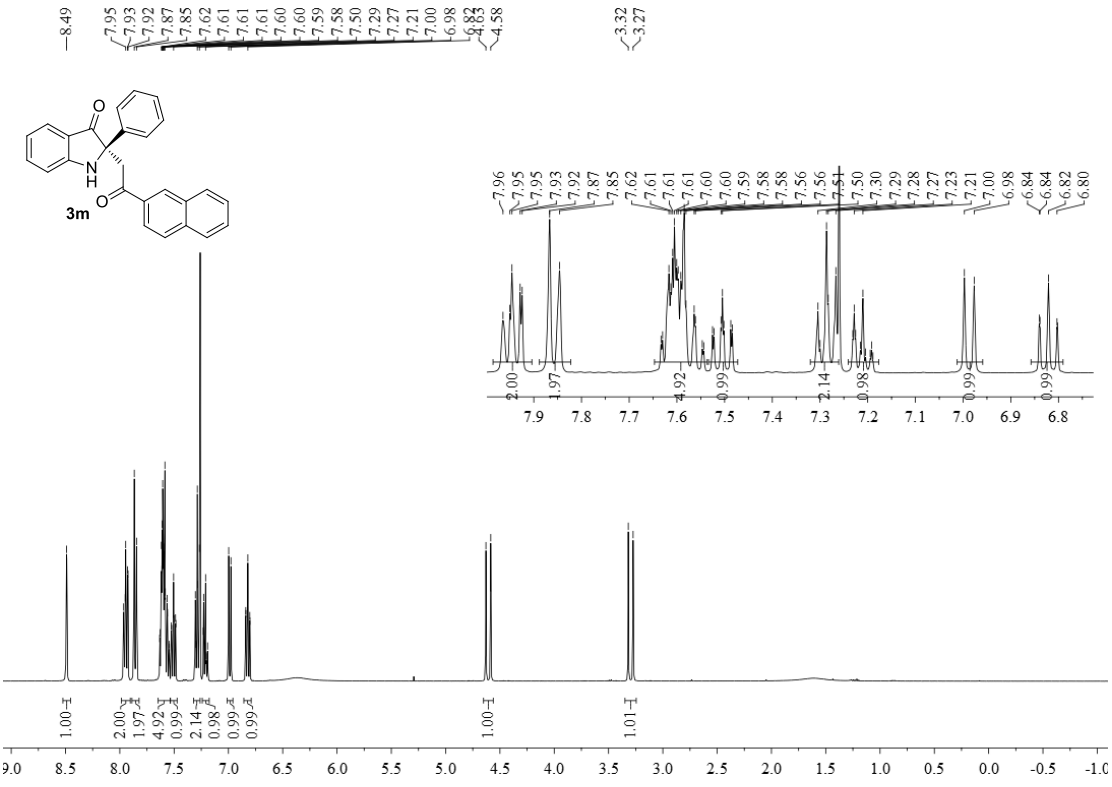
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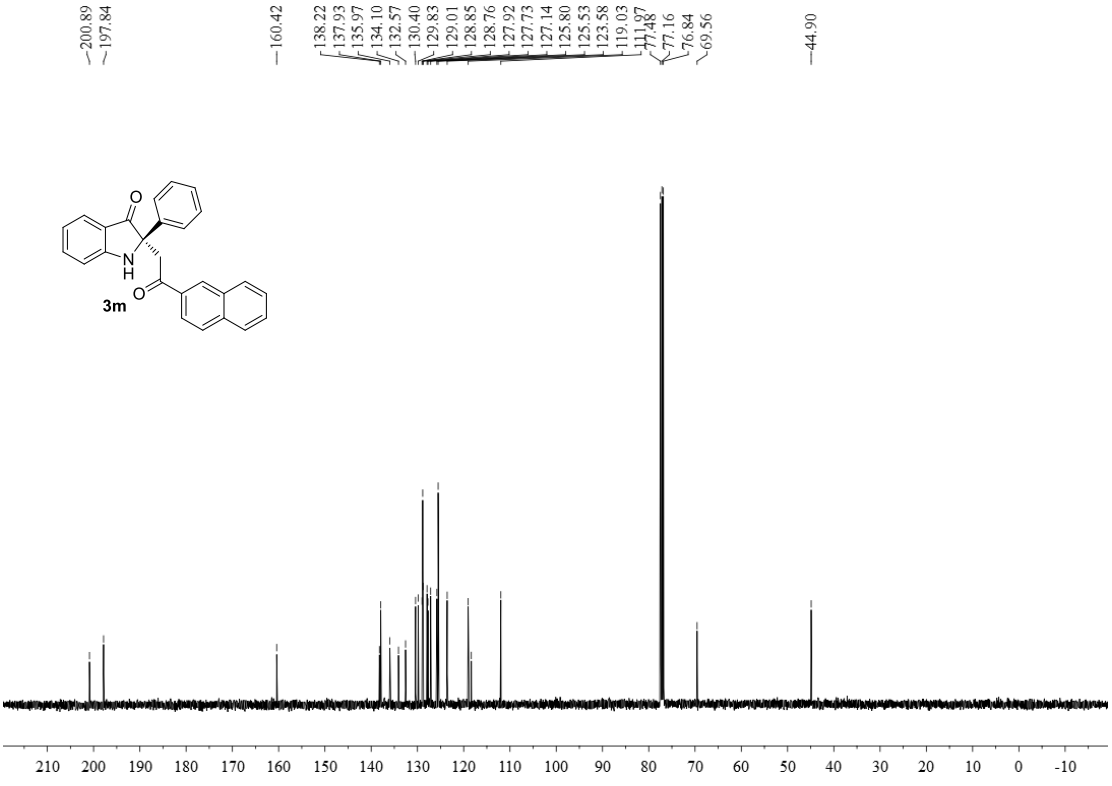
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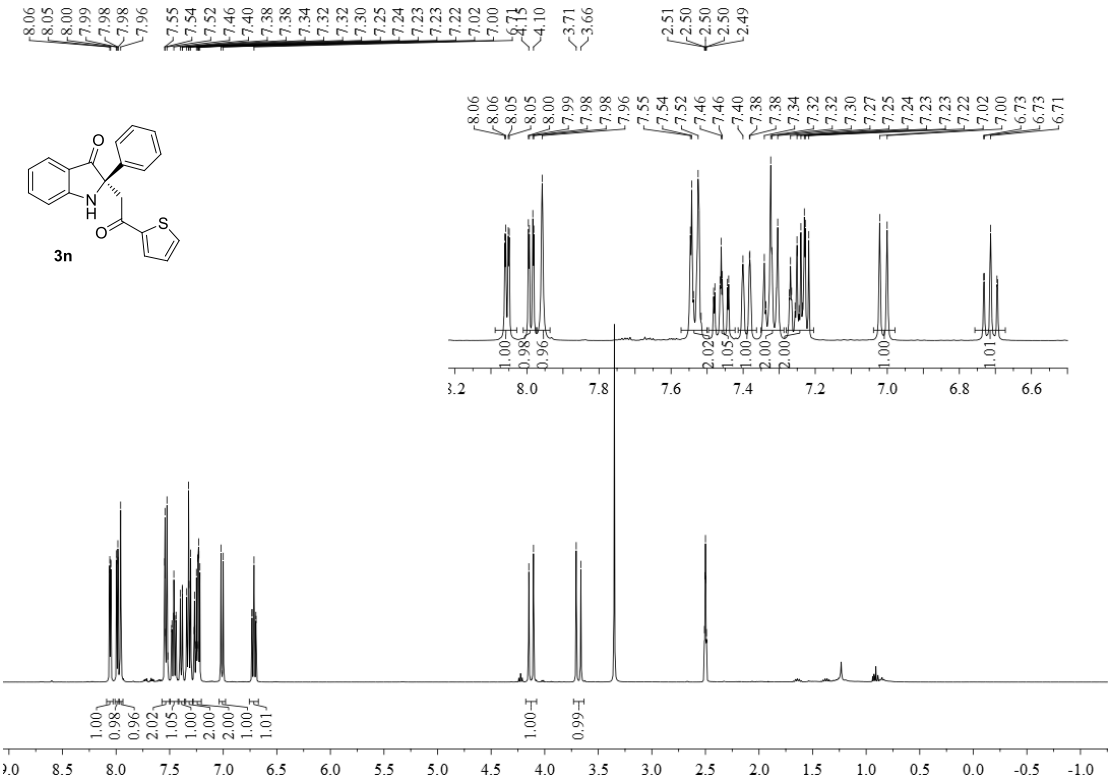
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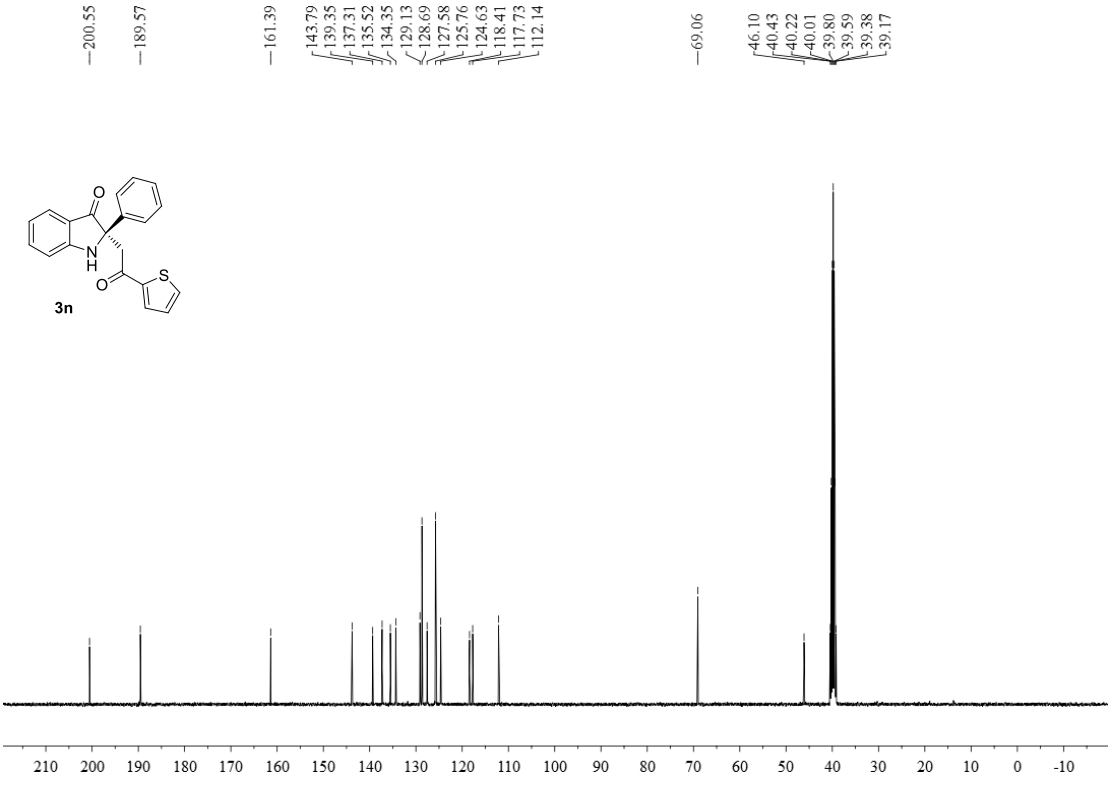
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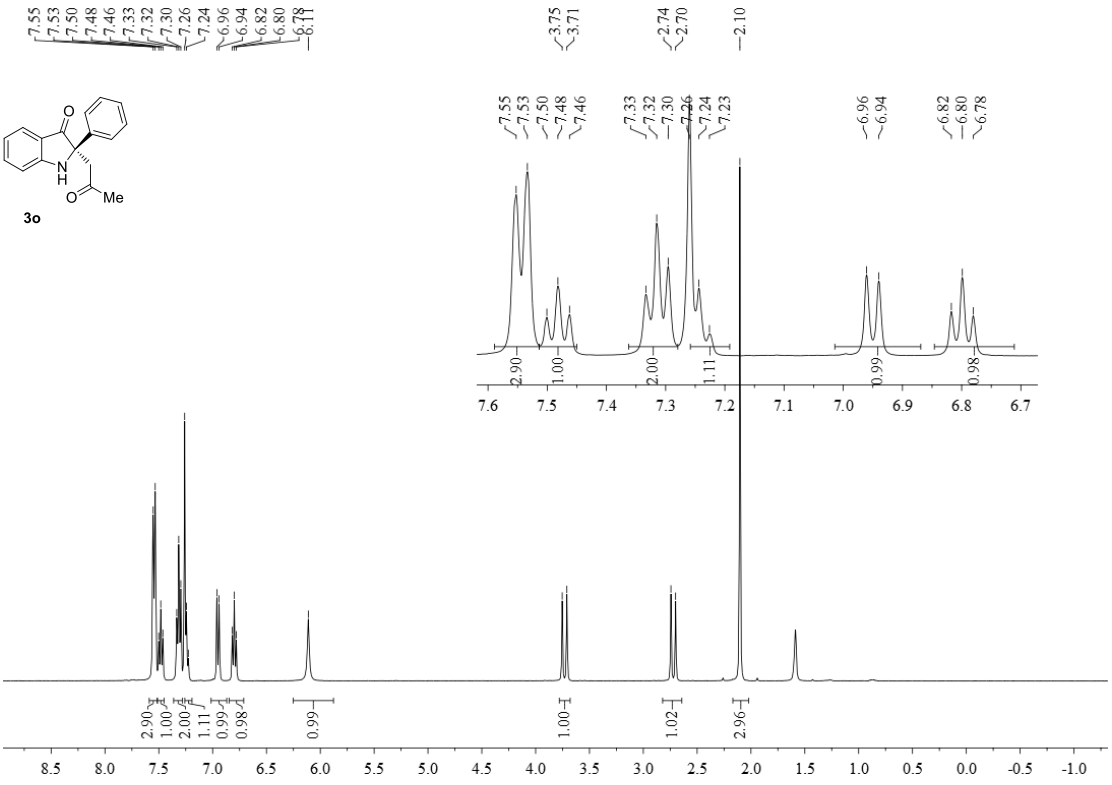
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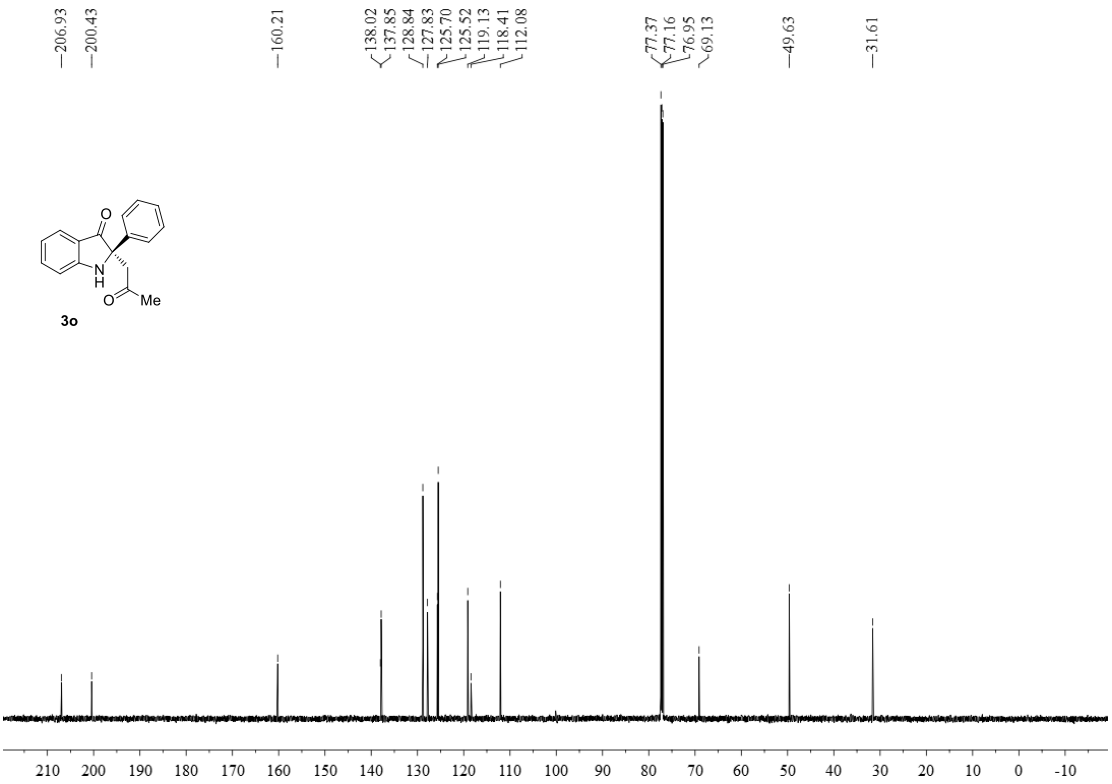
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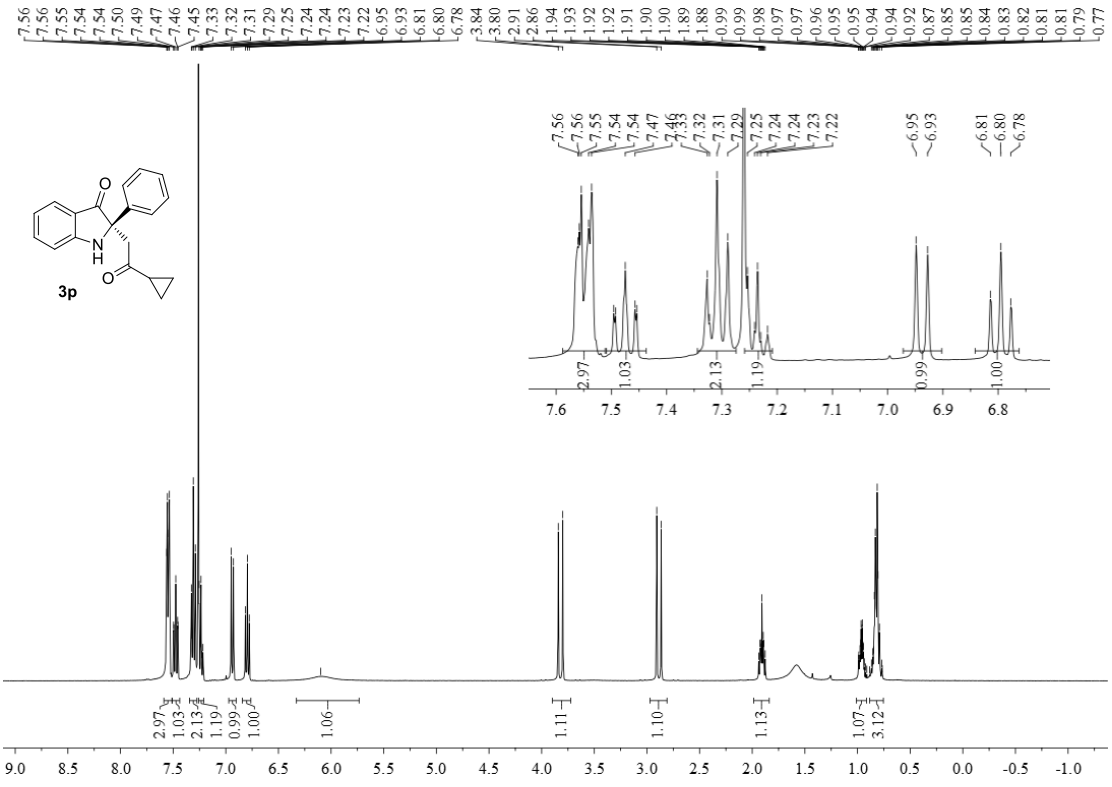
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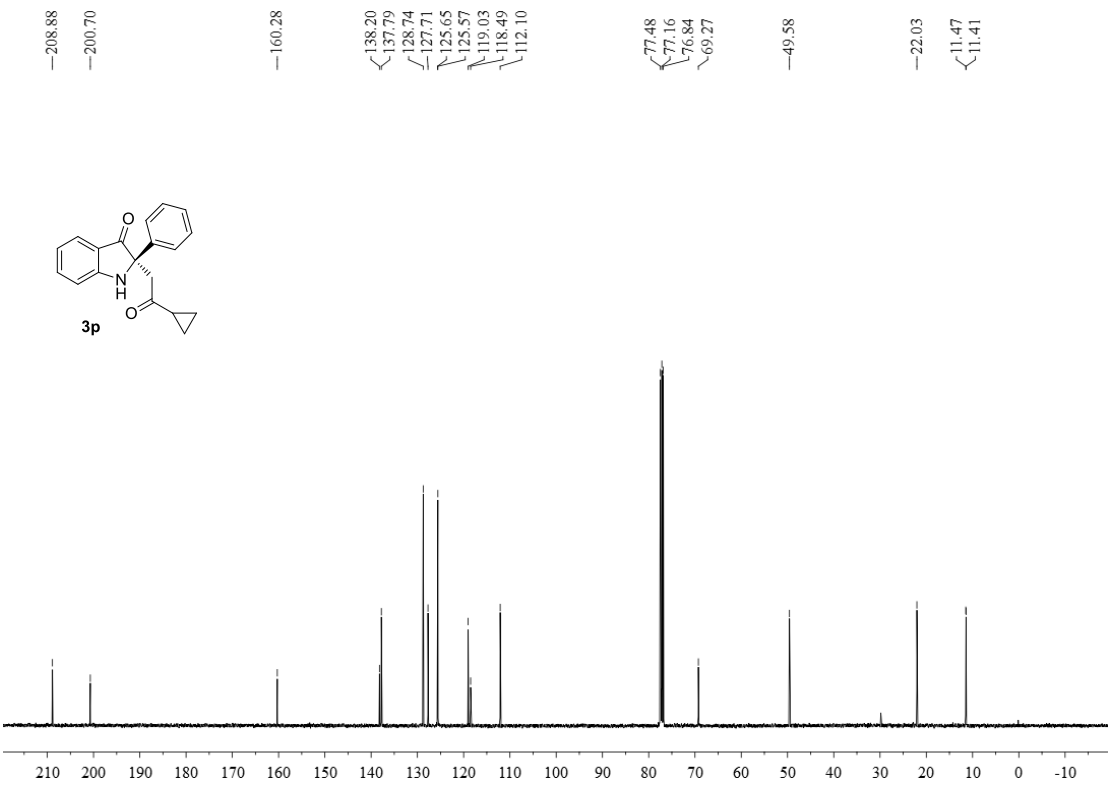
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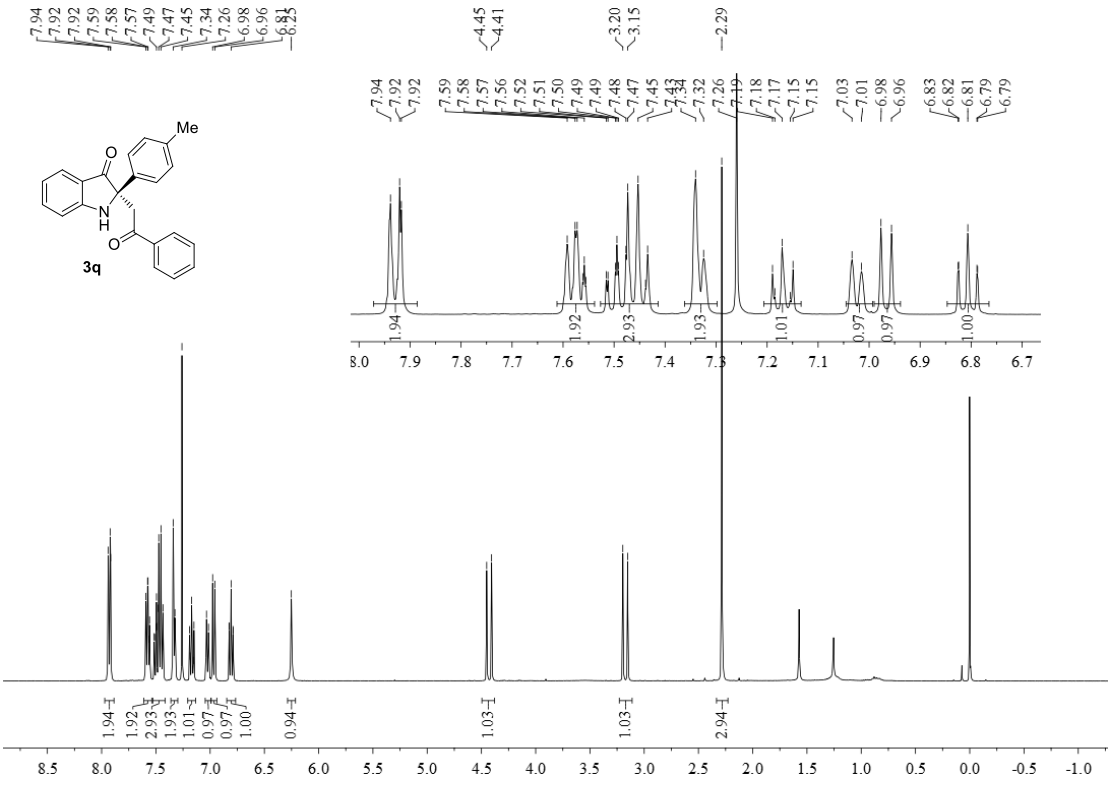
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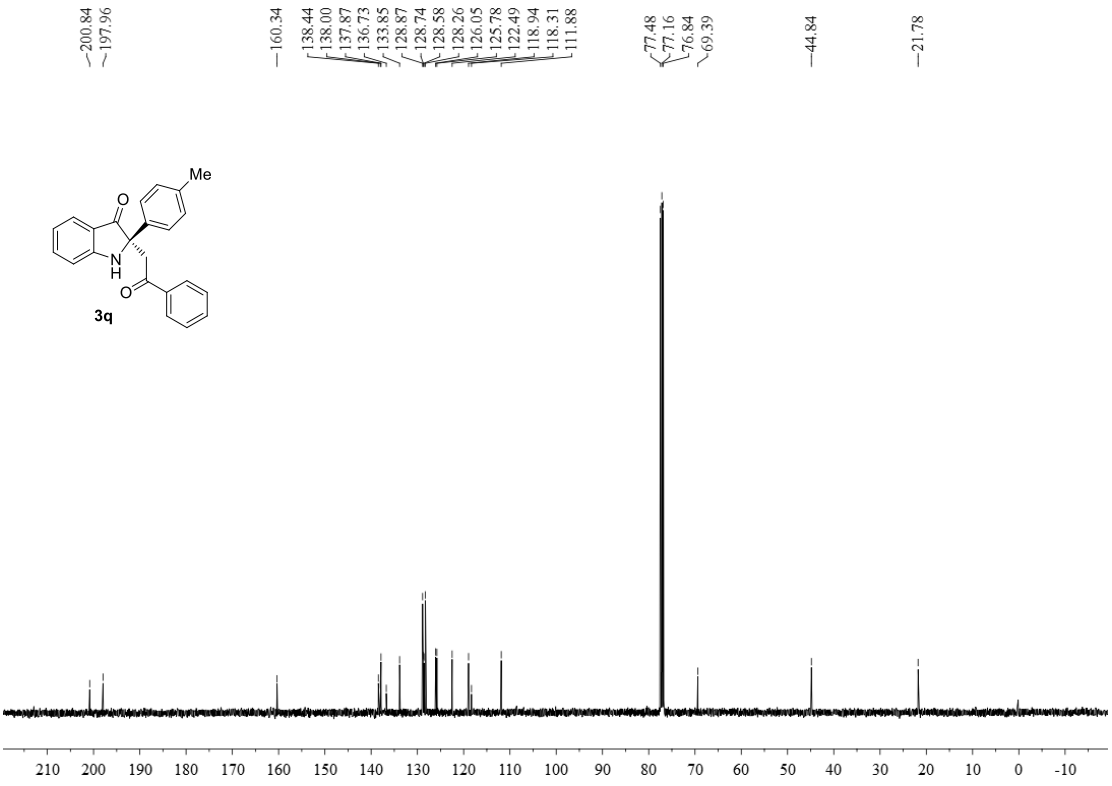
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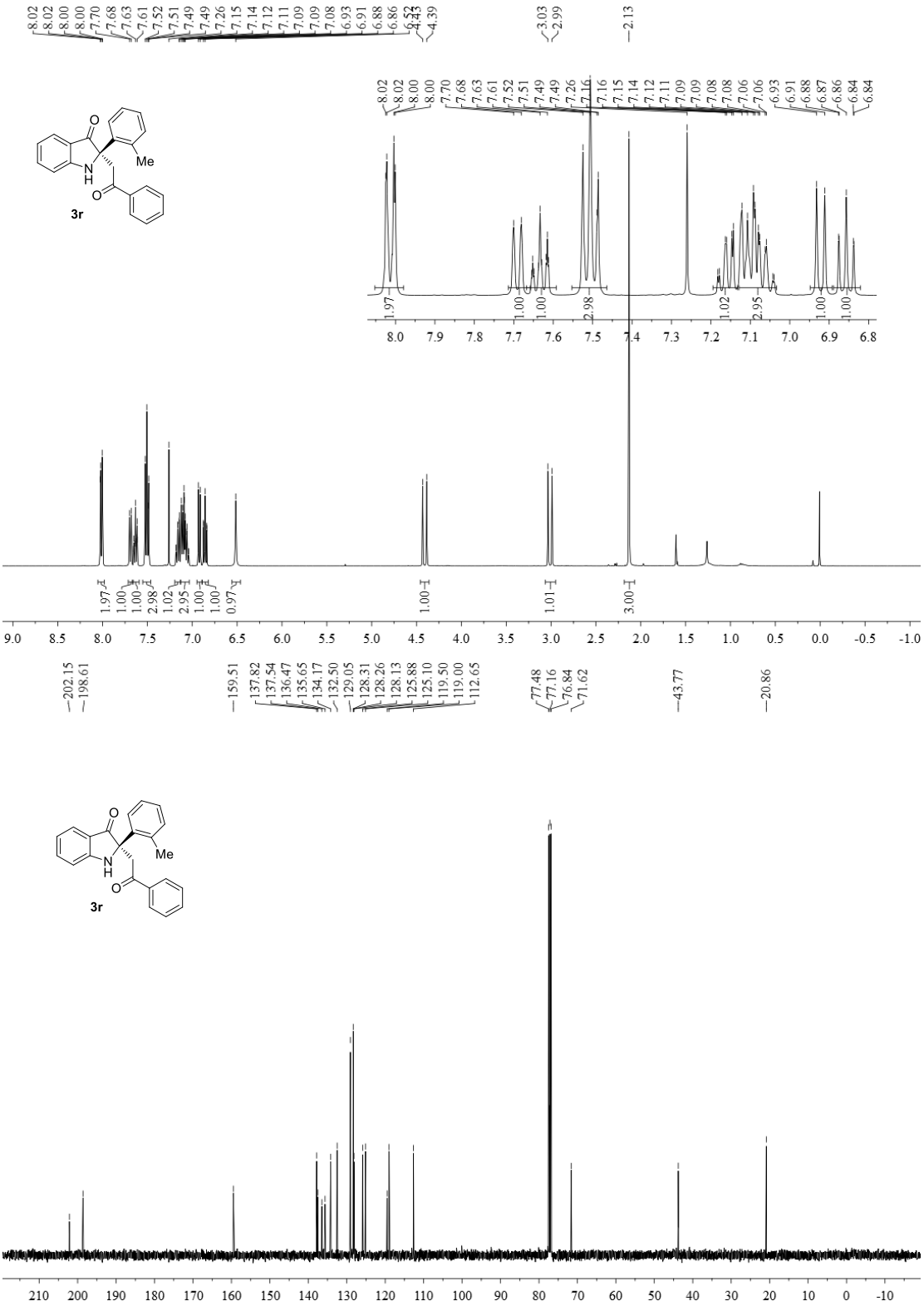
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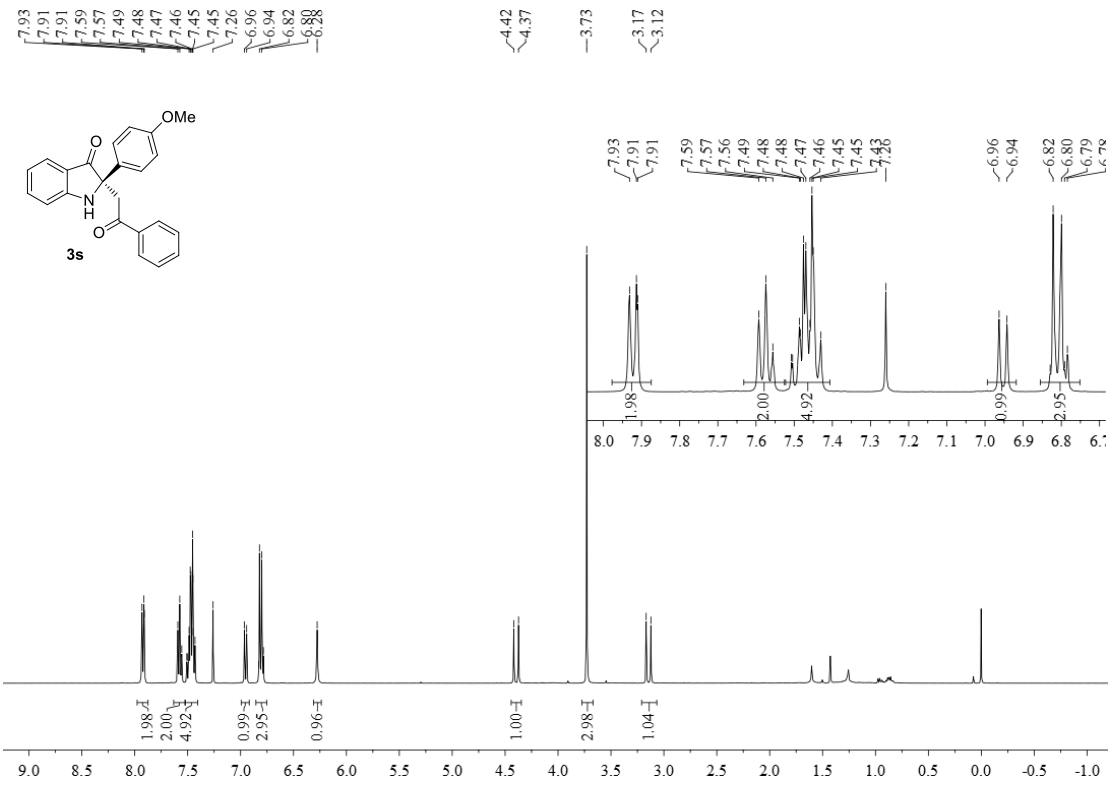
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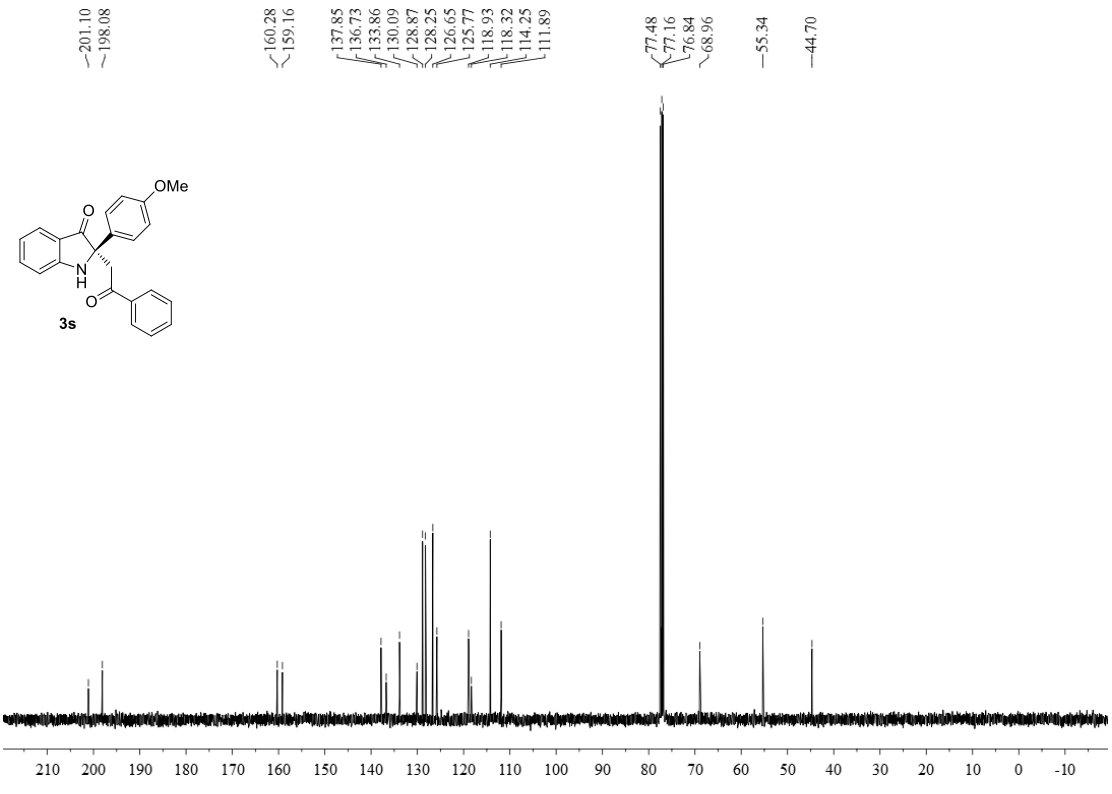
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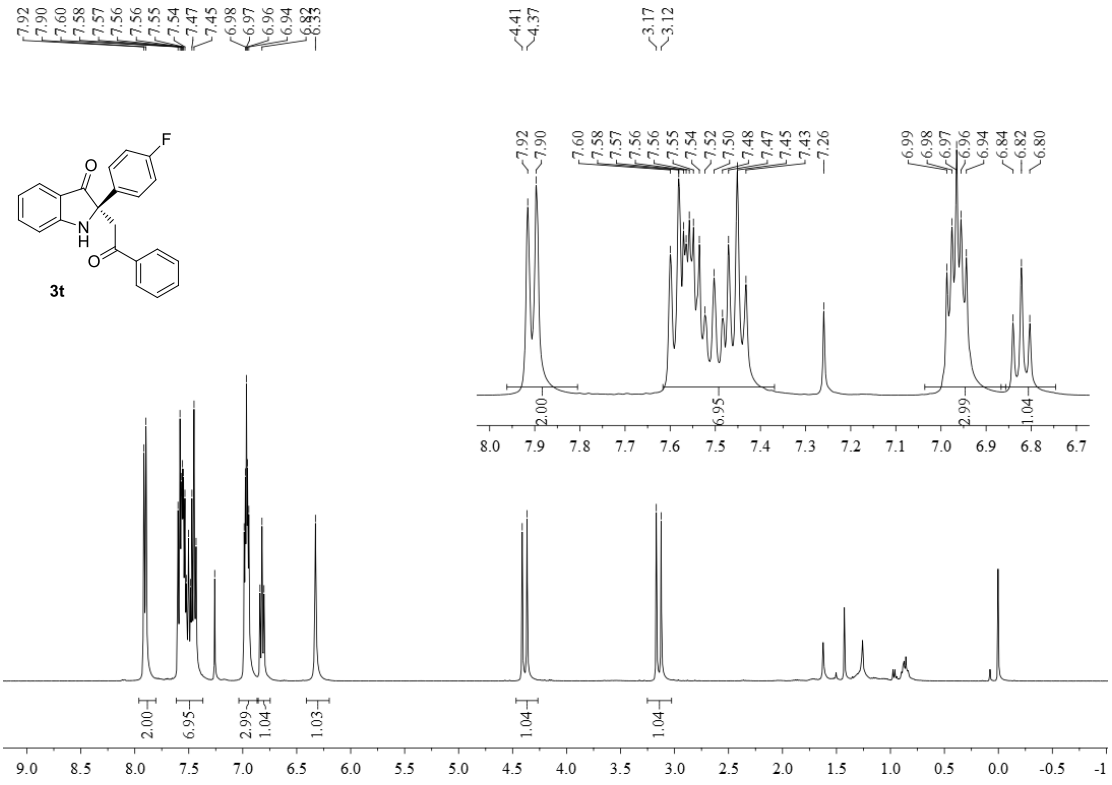
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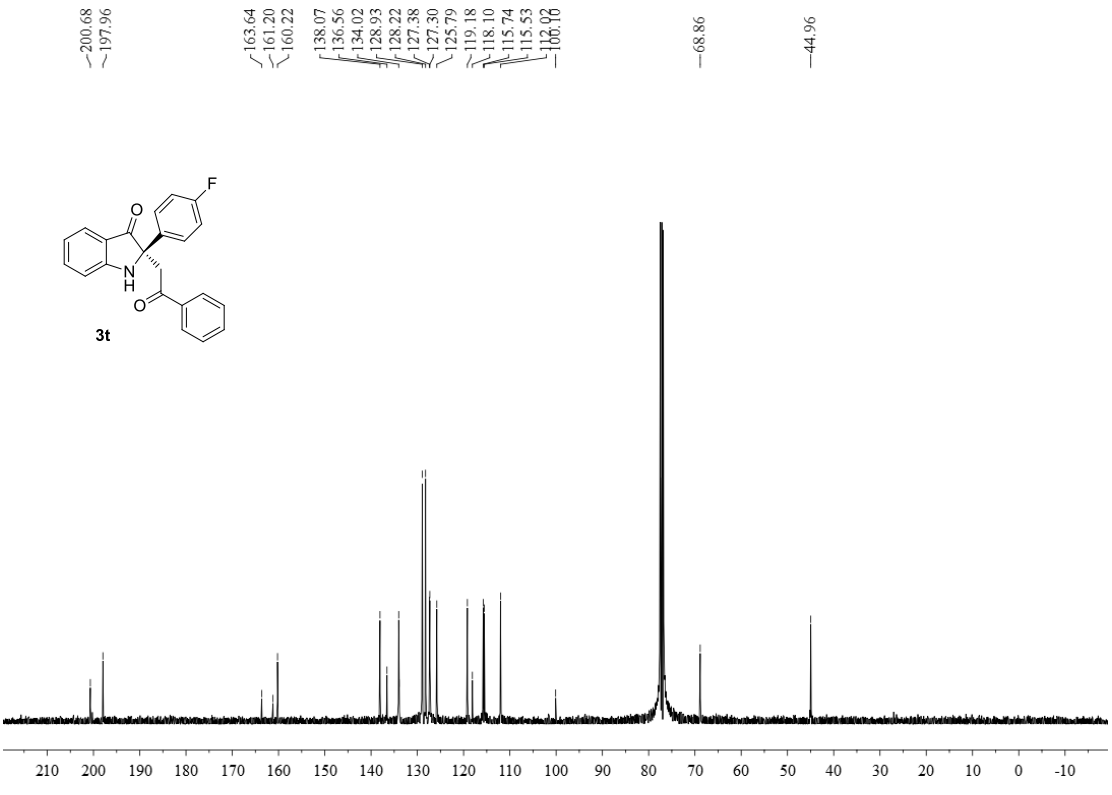
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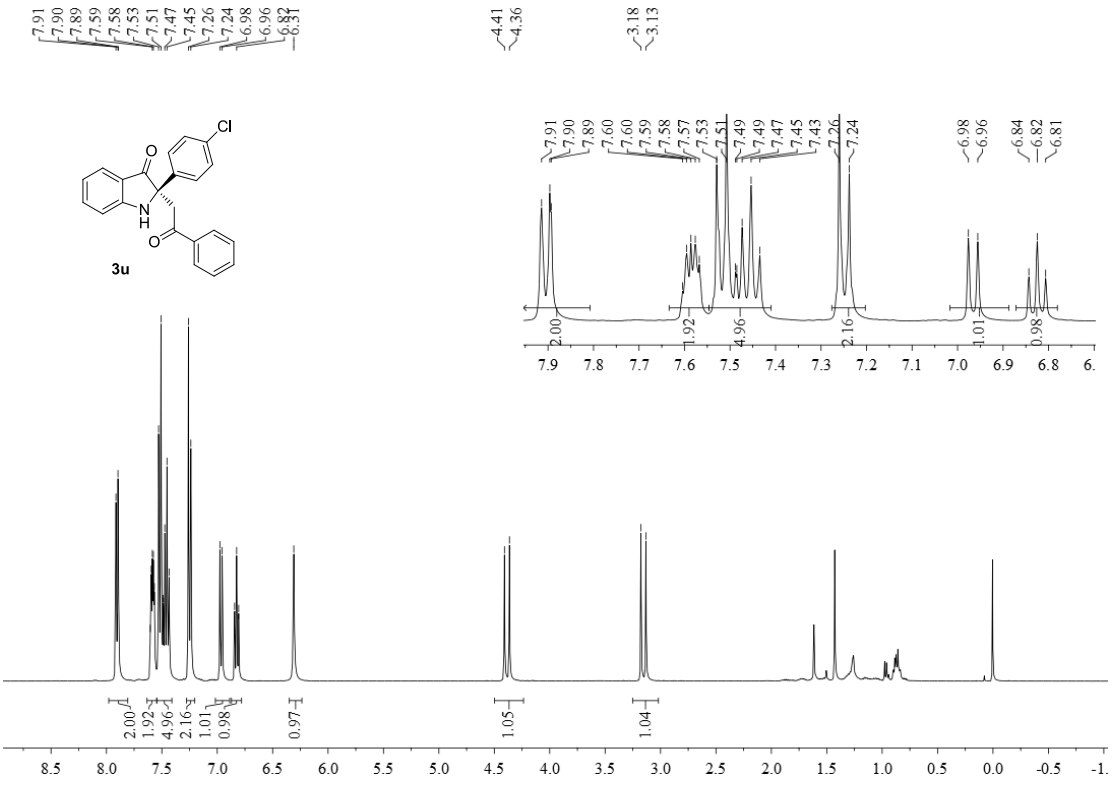
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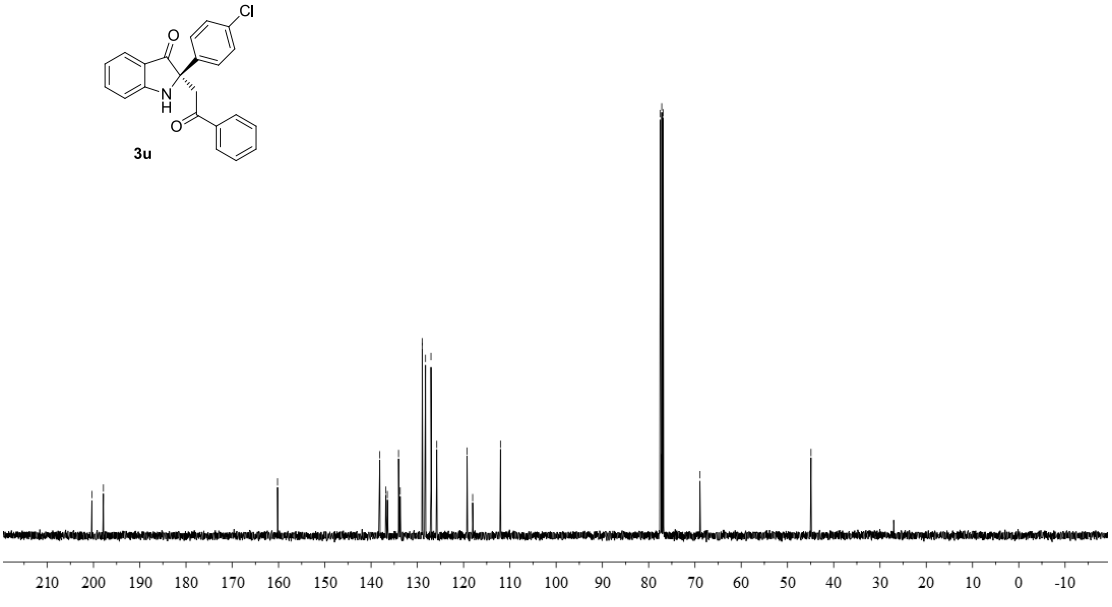
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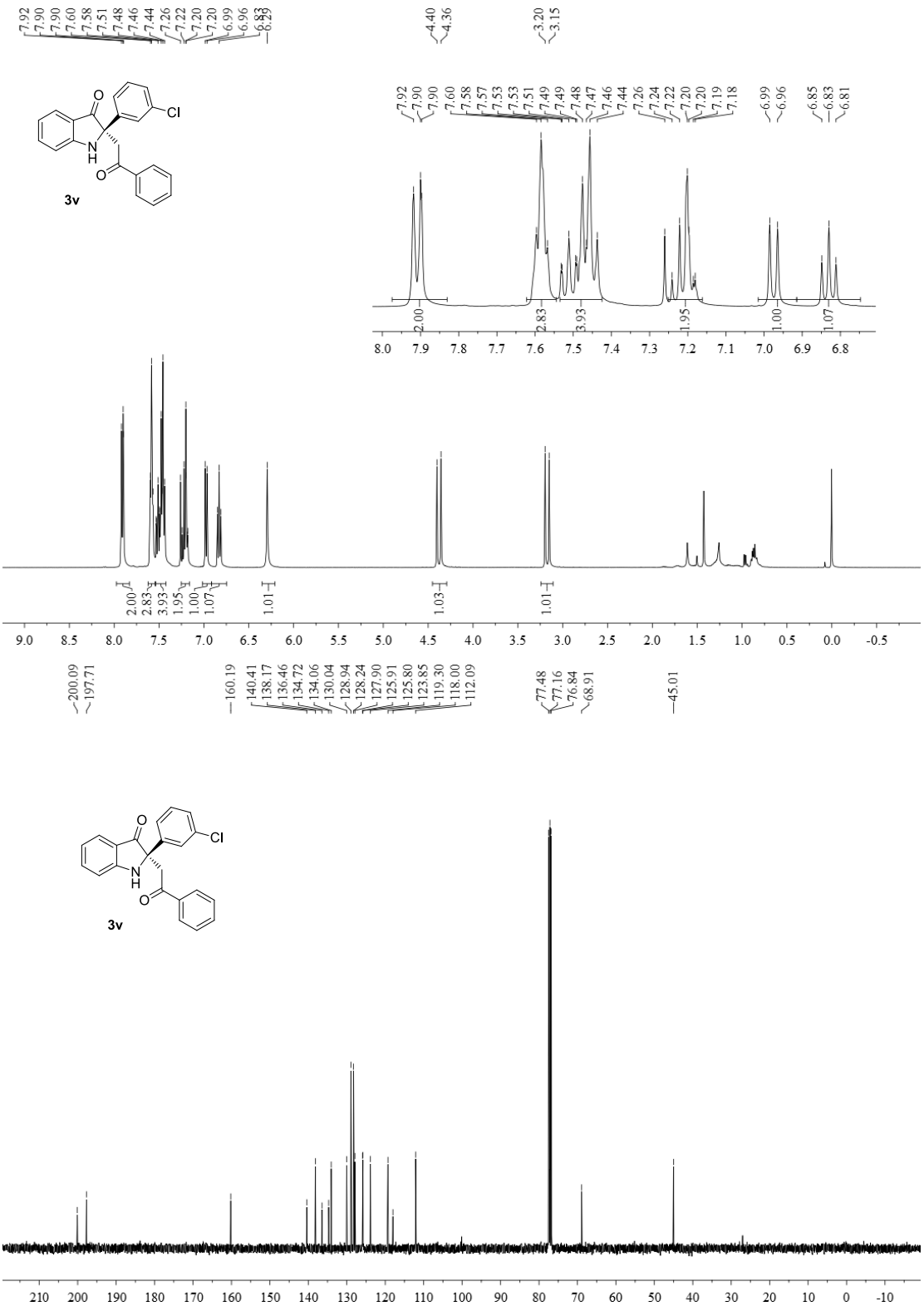
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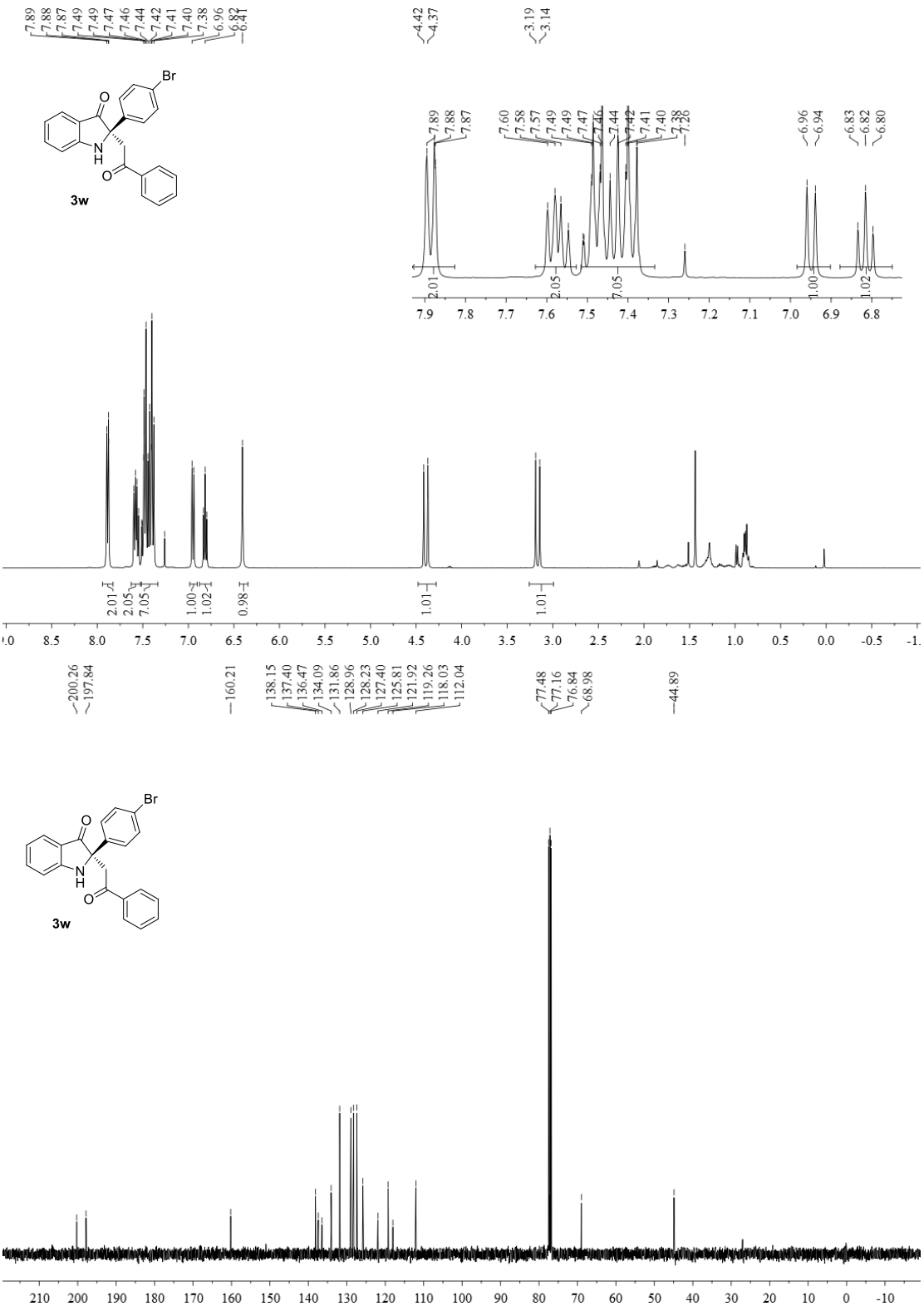
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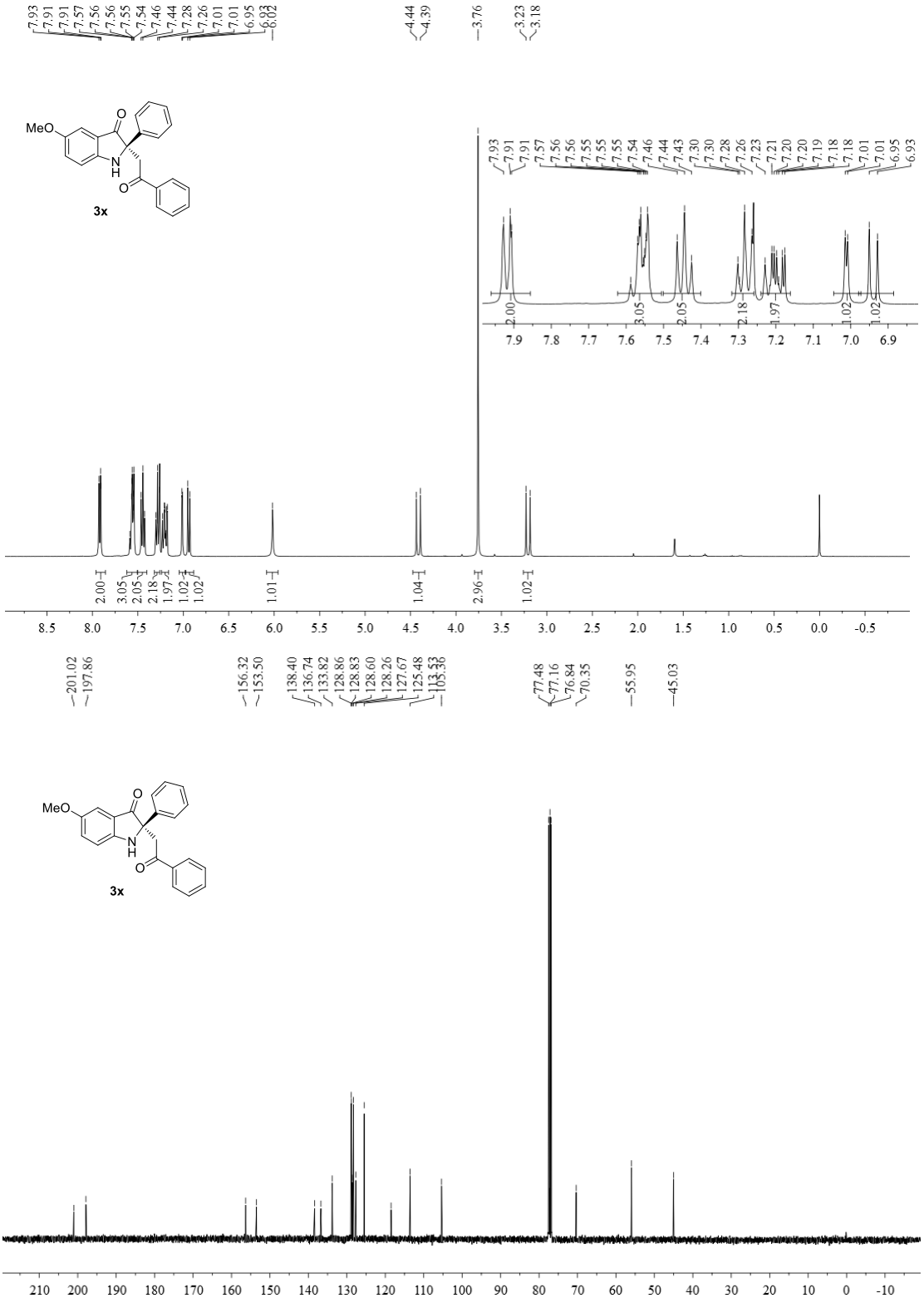
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H
O
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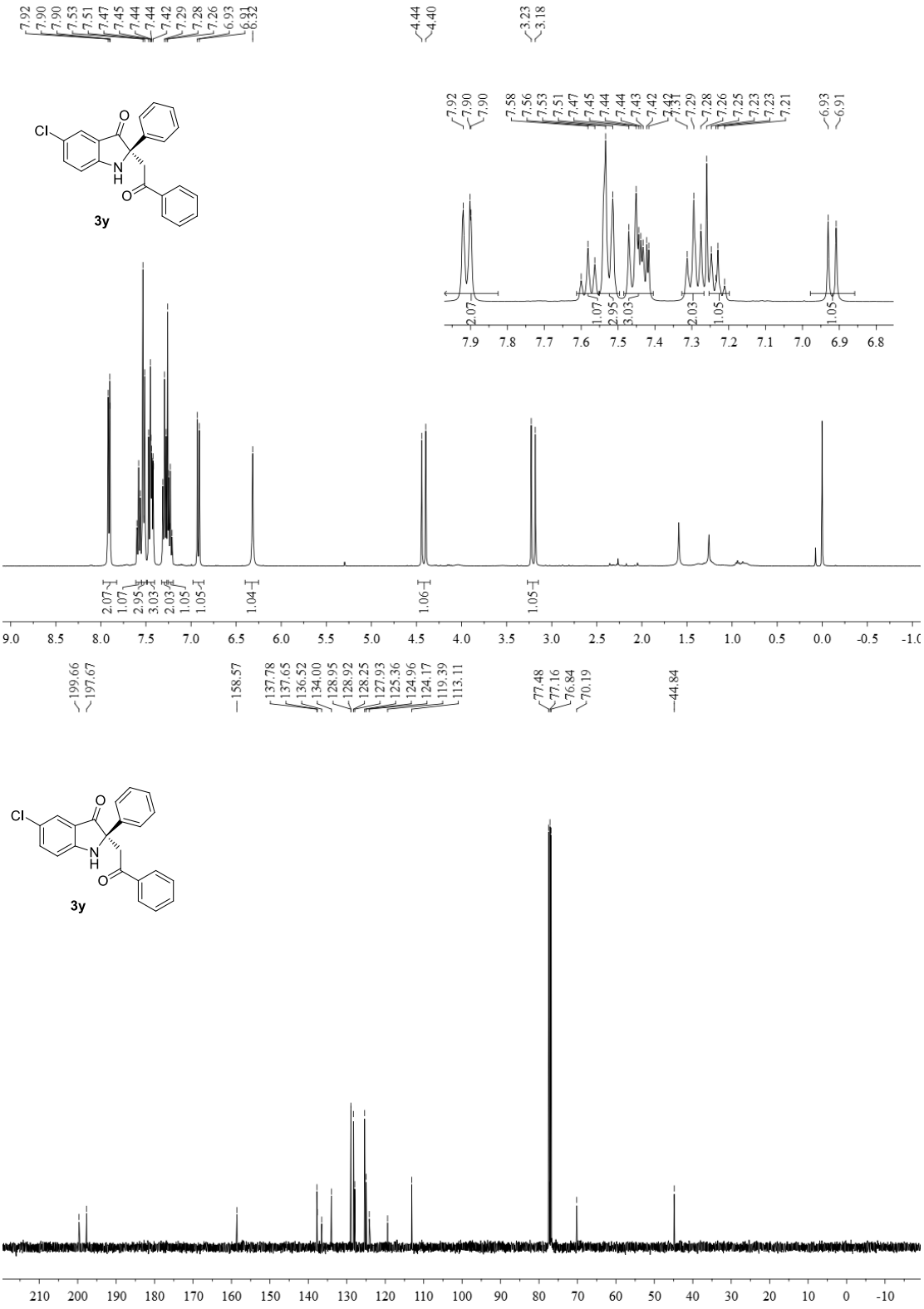
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H
O
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1.06
1.05
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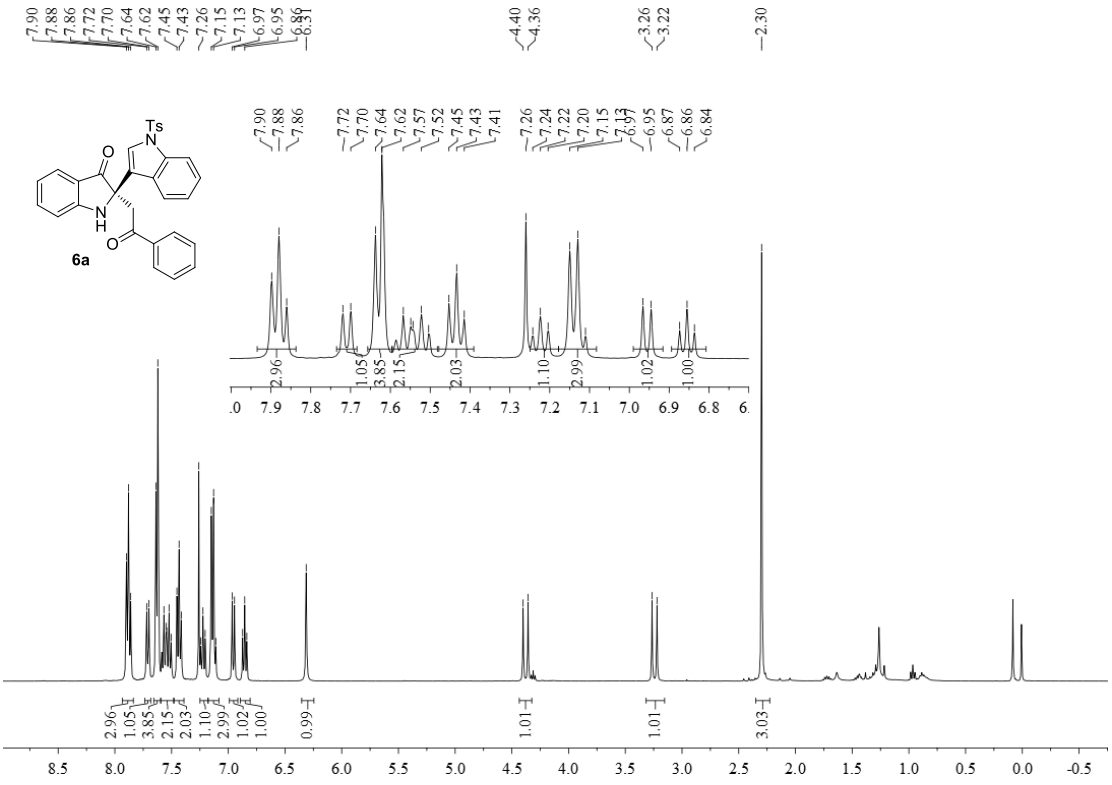
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O
N
H
O
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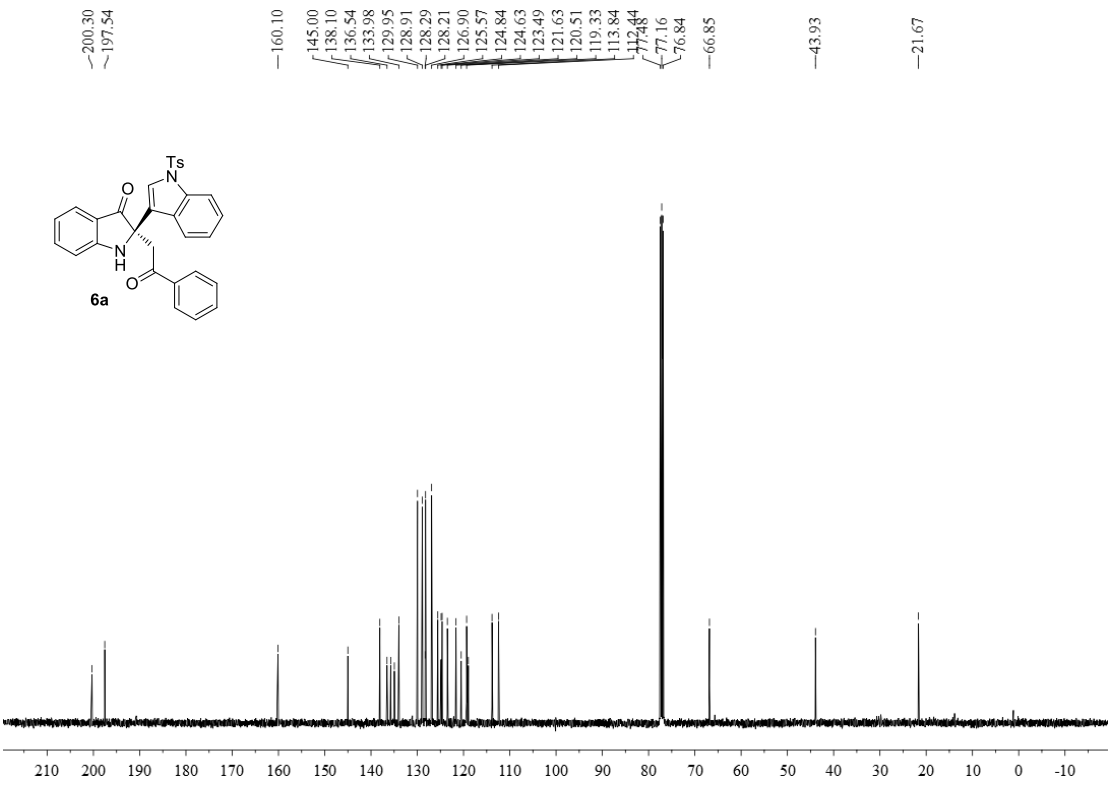
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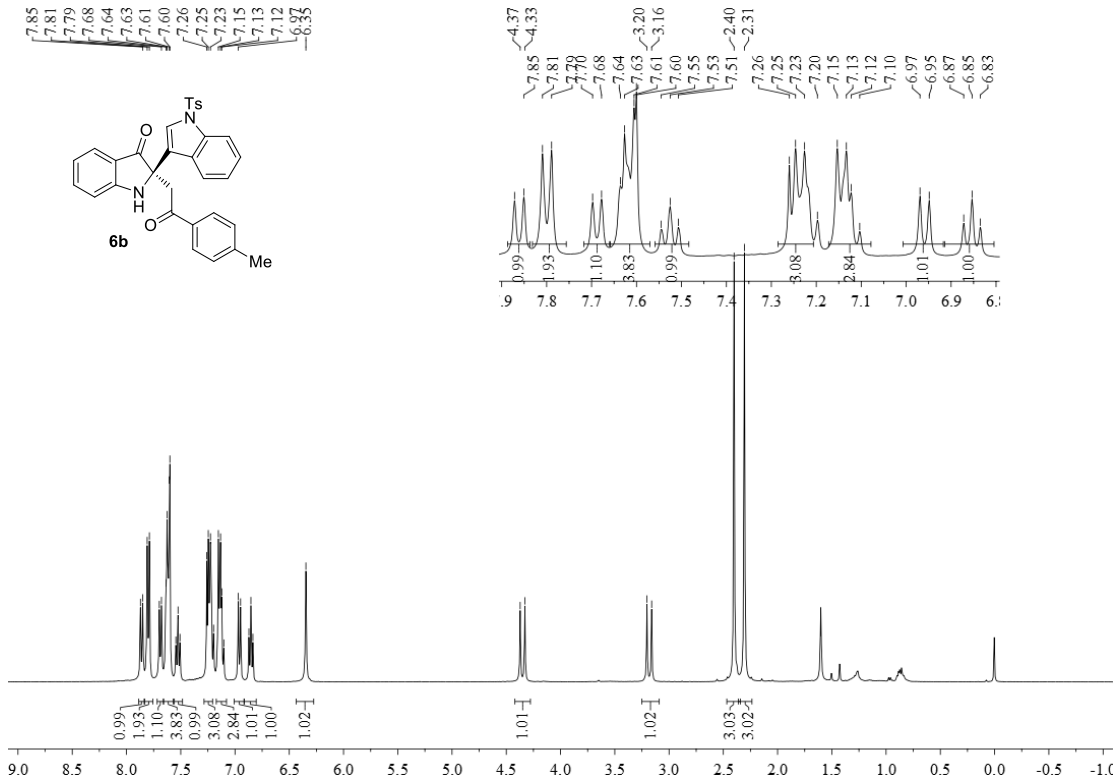
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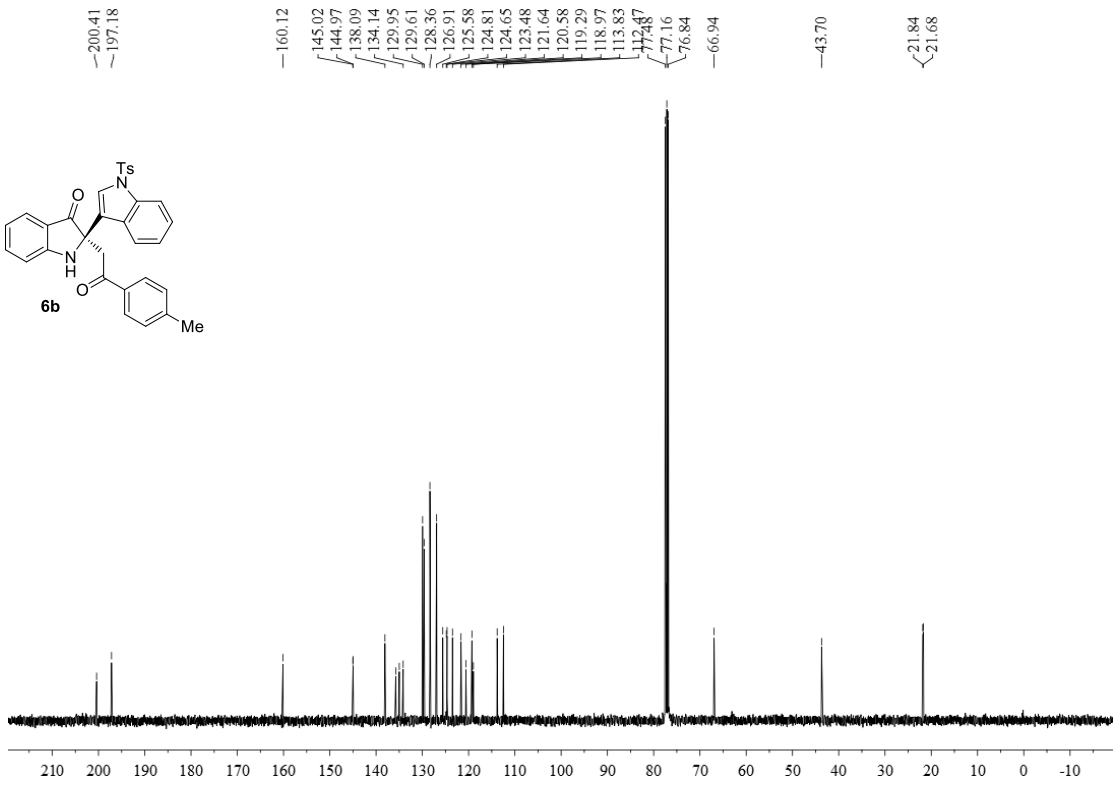
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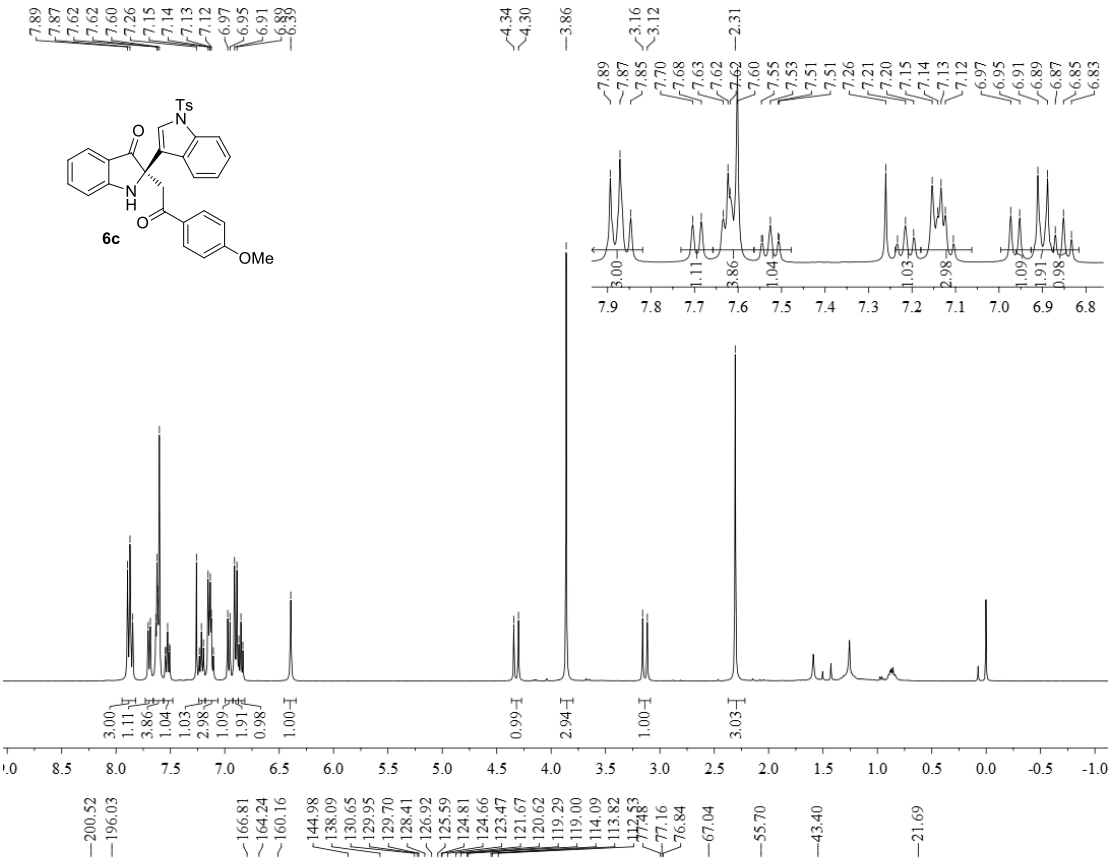
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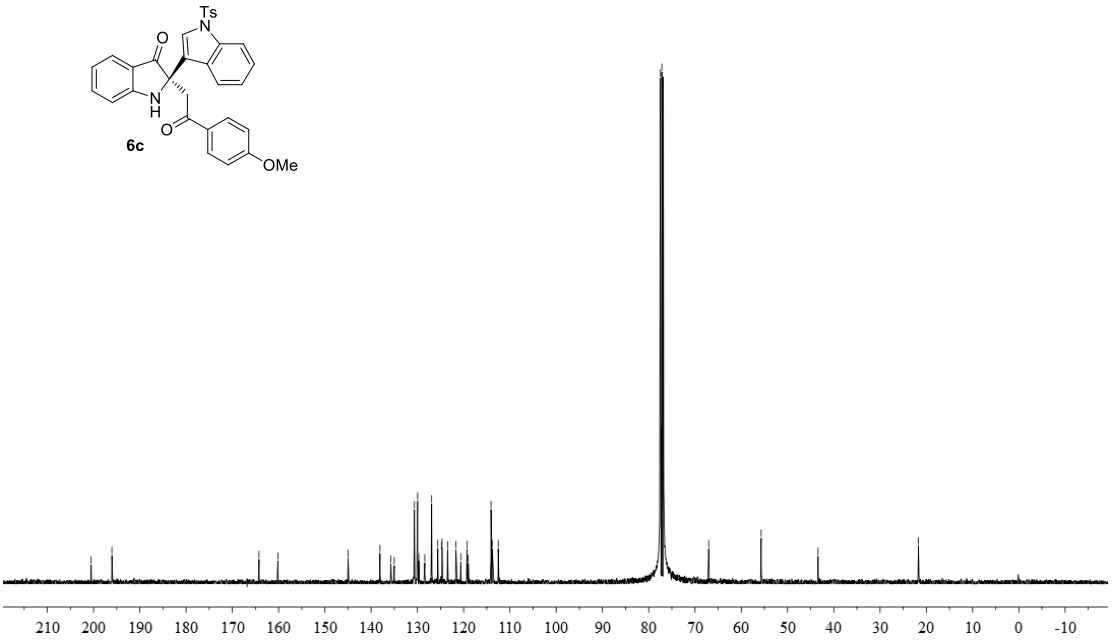
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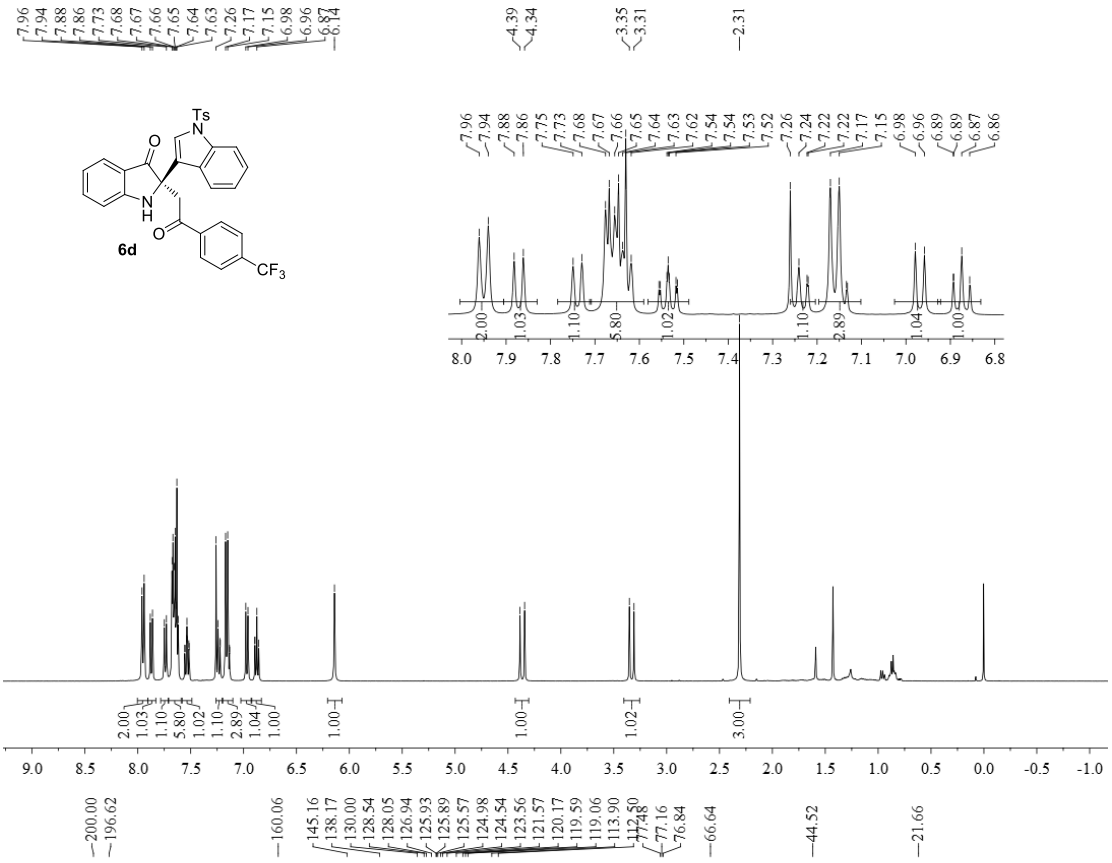
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1.04
1.00
1.00
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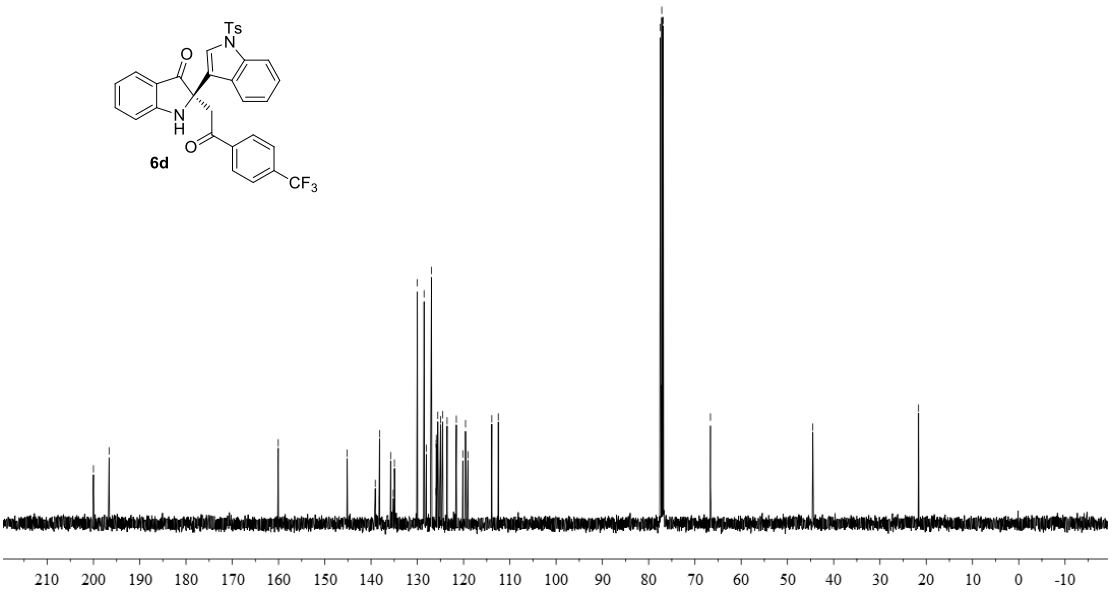
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CF3
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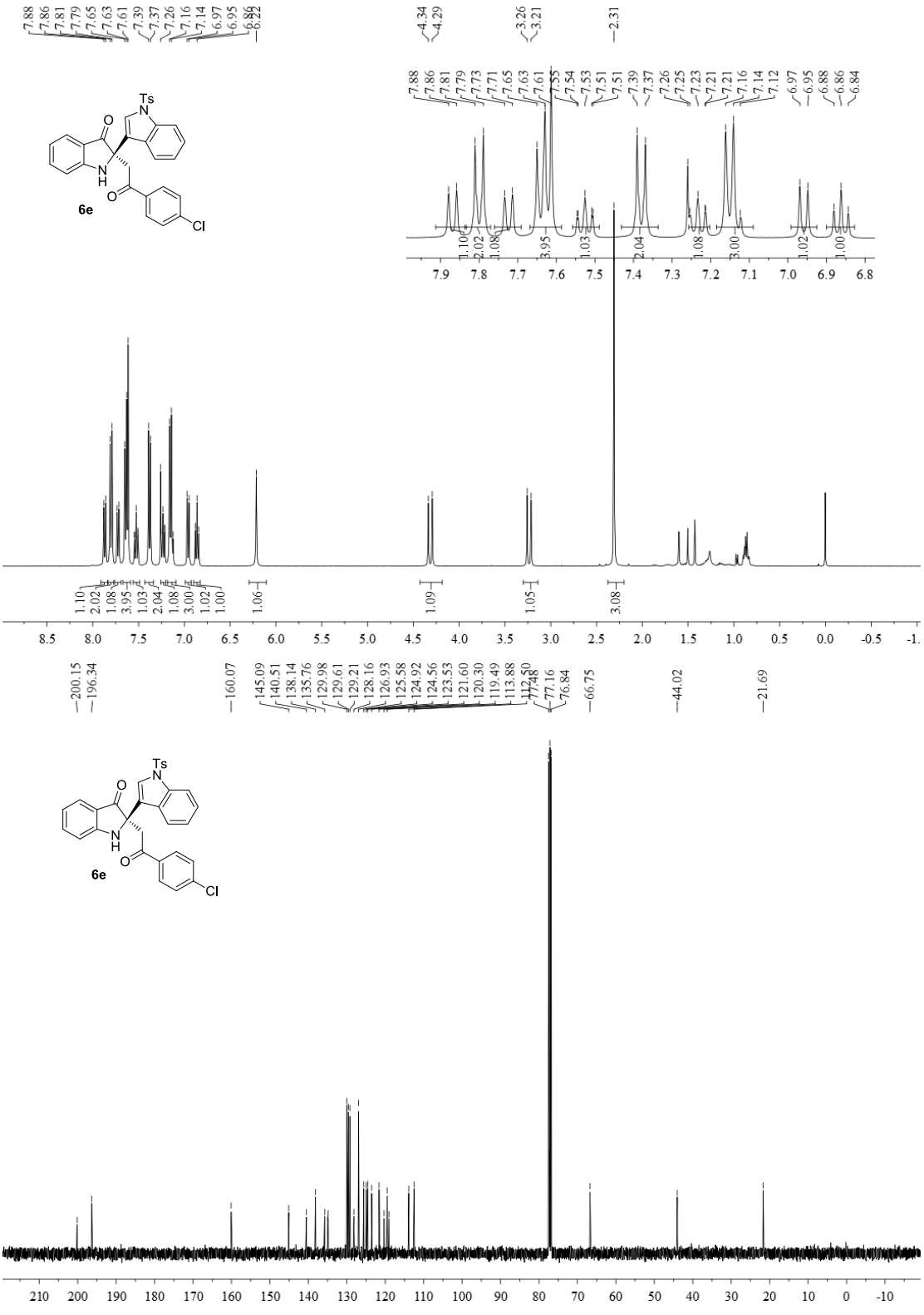
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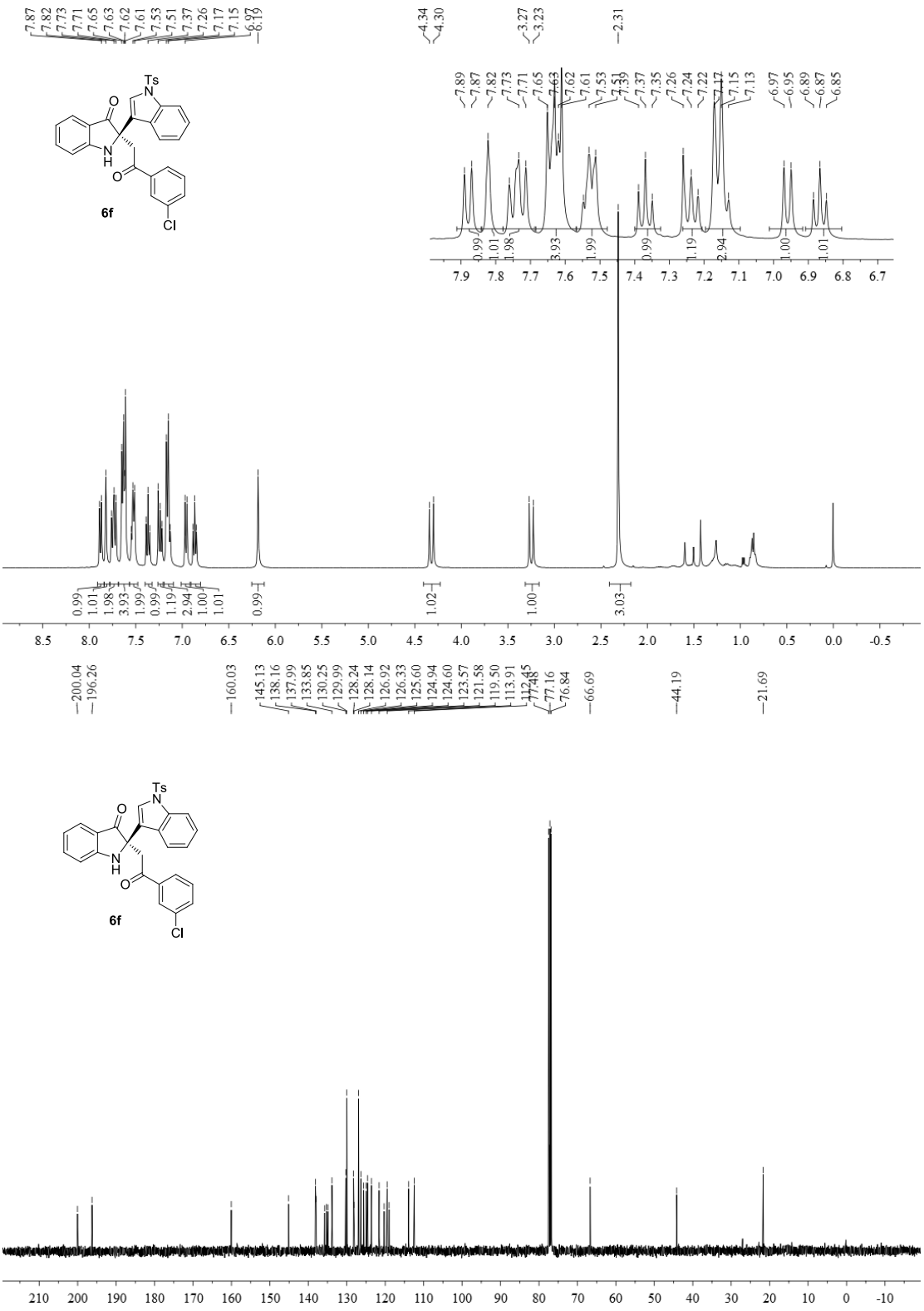
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Cl
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Ts
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Cl
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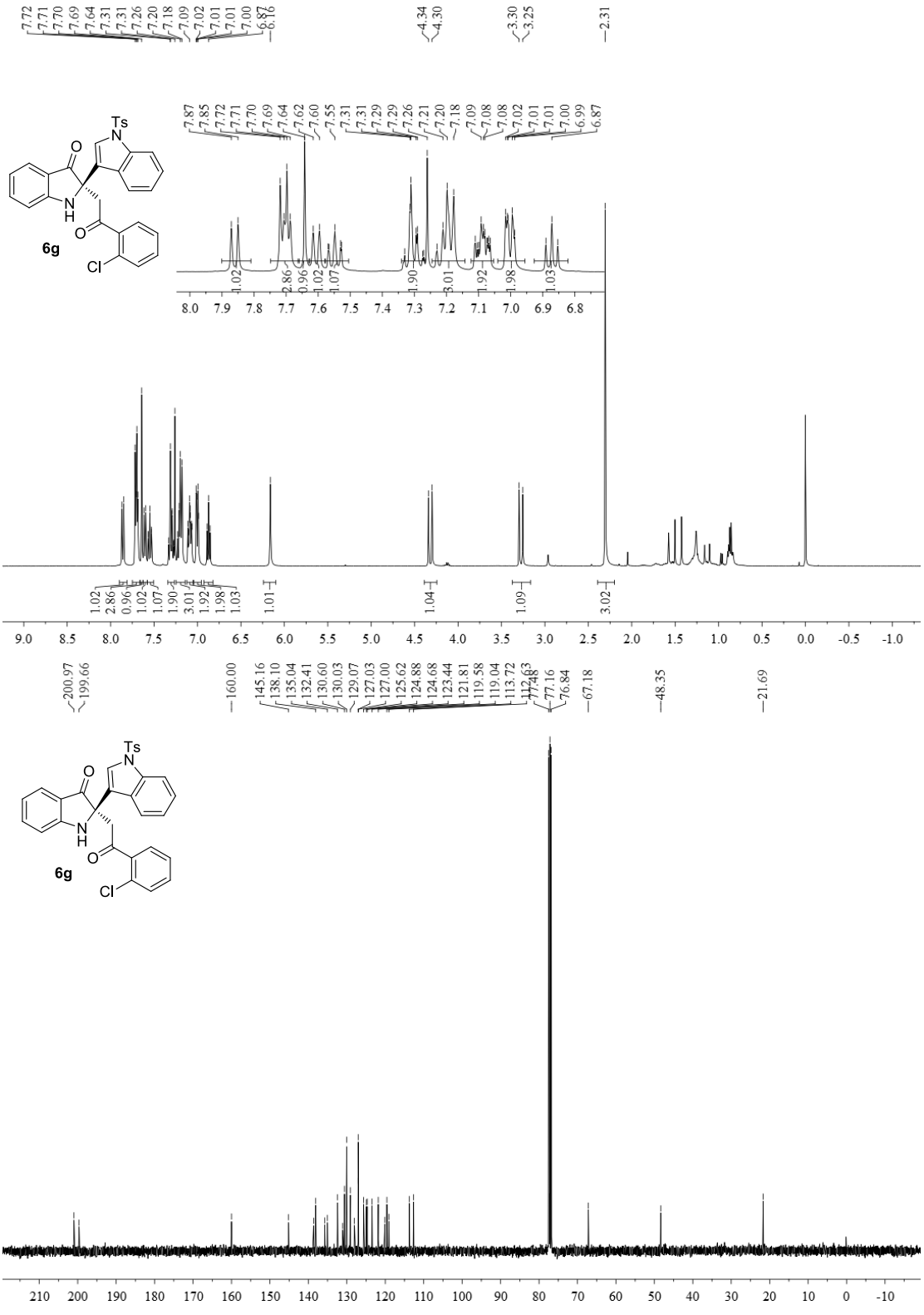
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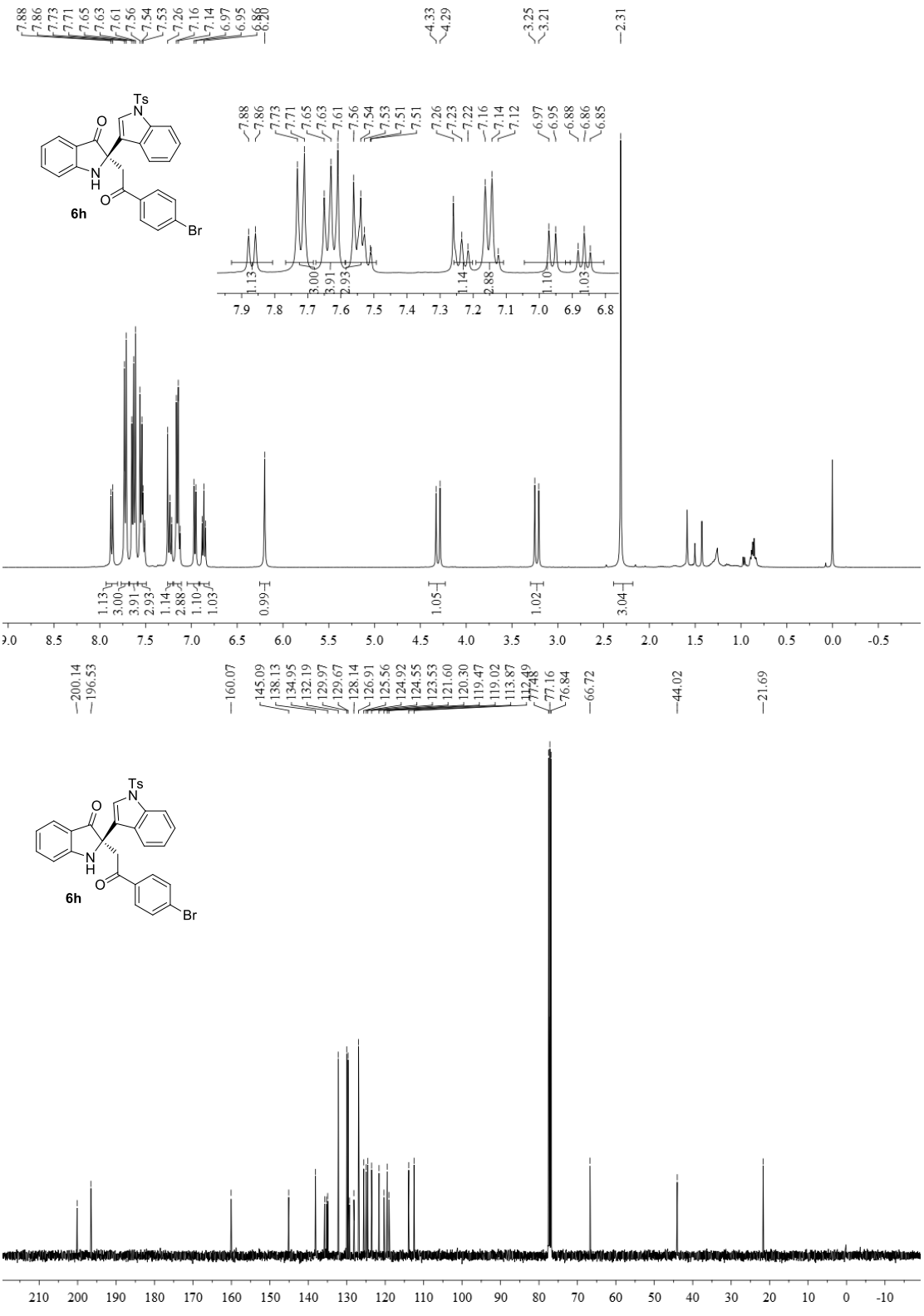
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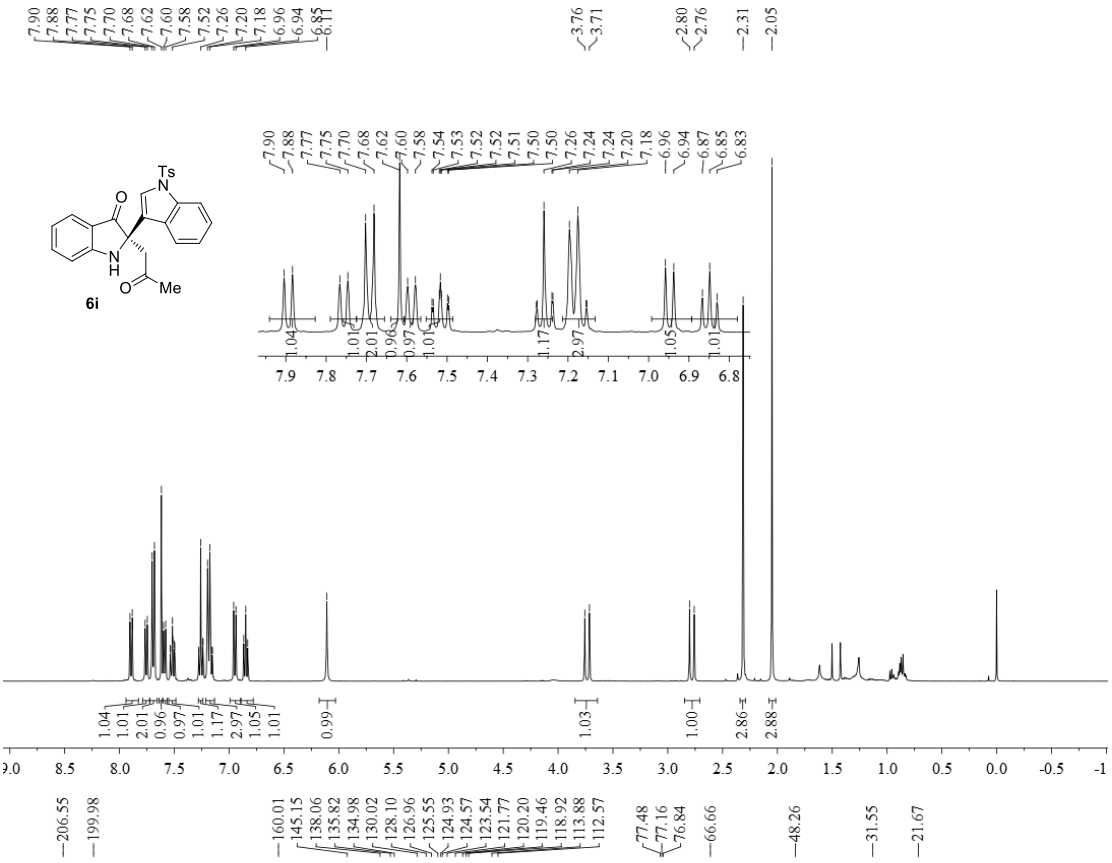
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H
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Me
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H
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Me
6i
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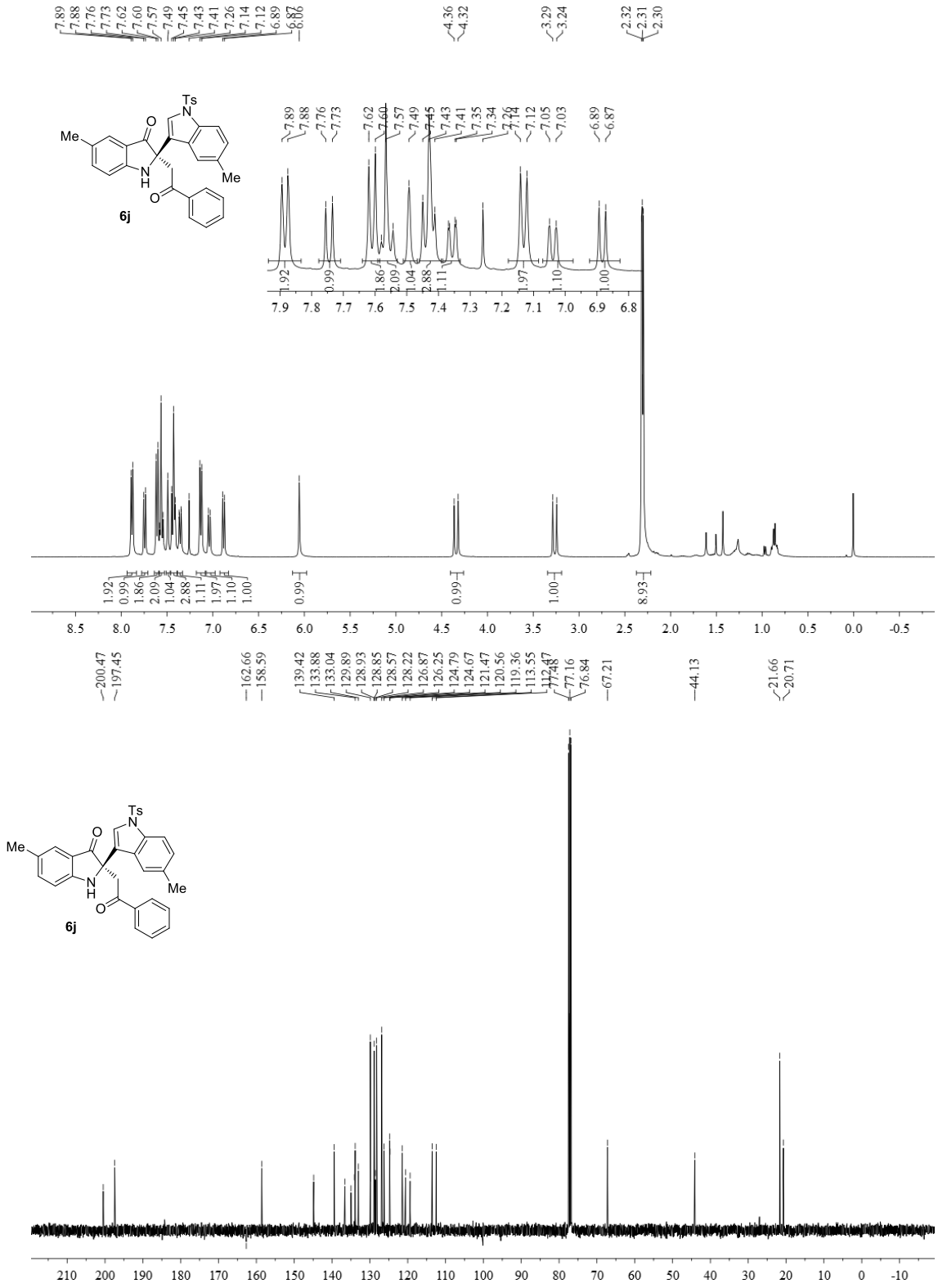
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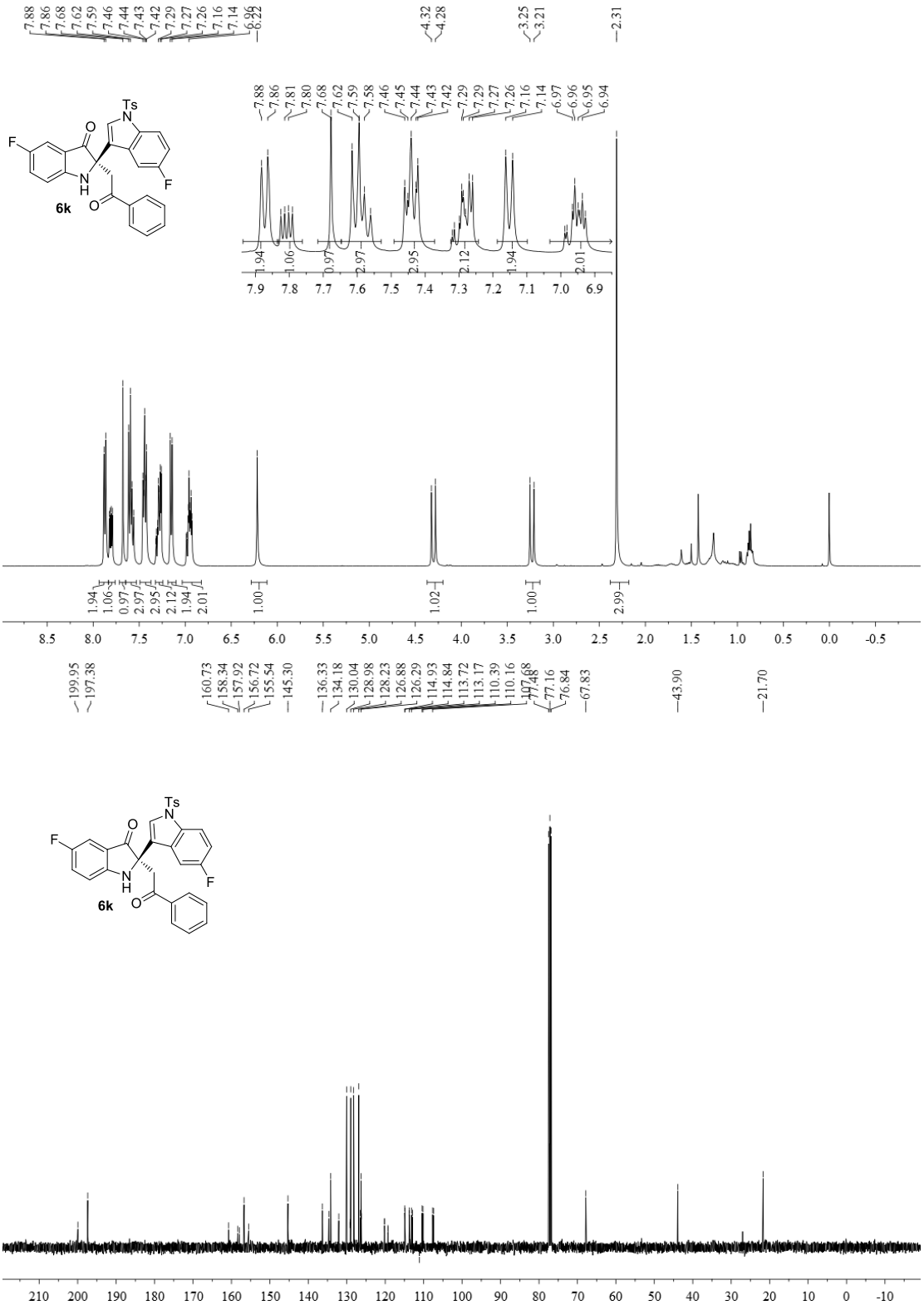
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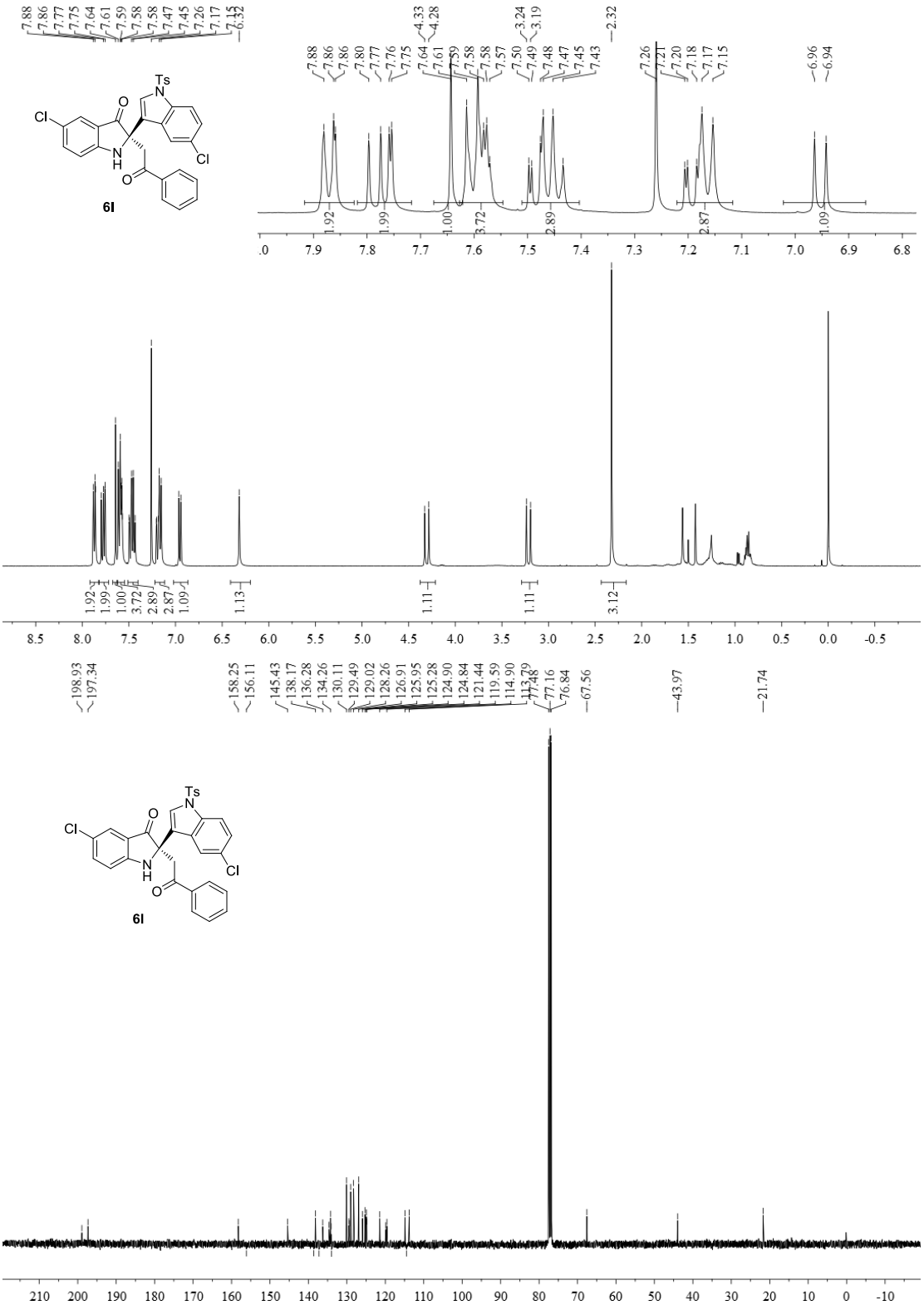
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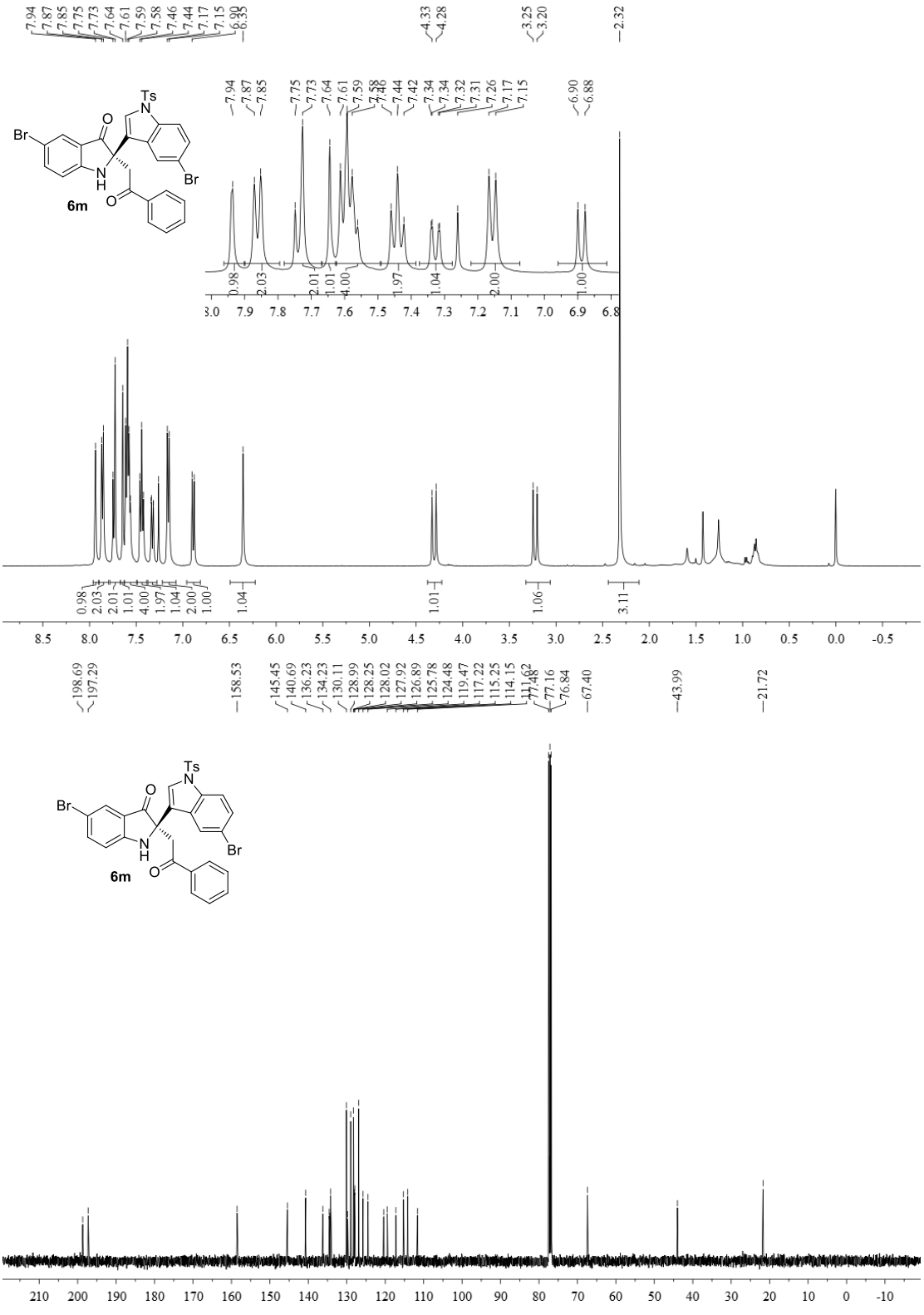
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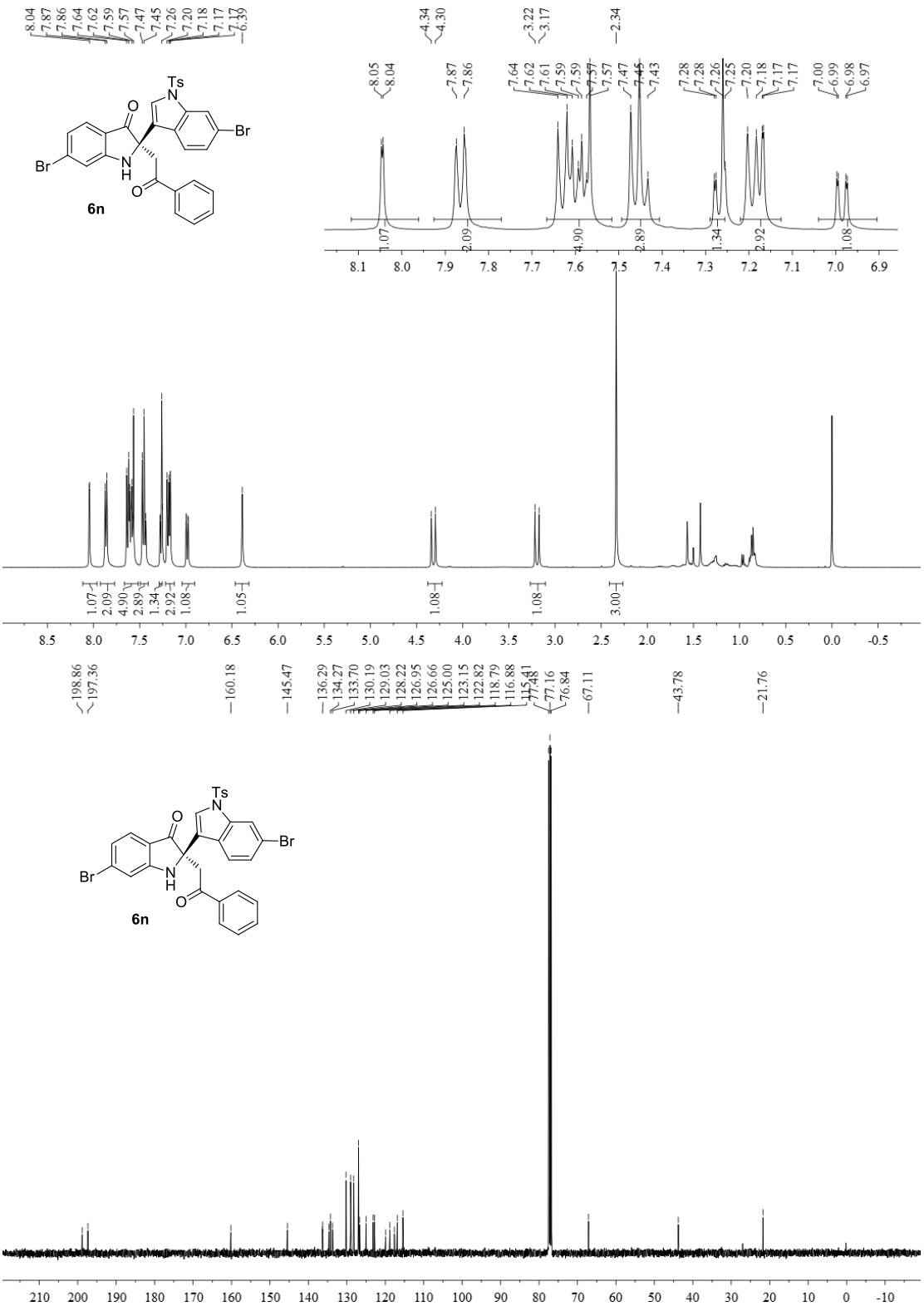
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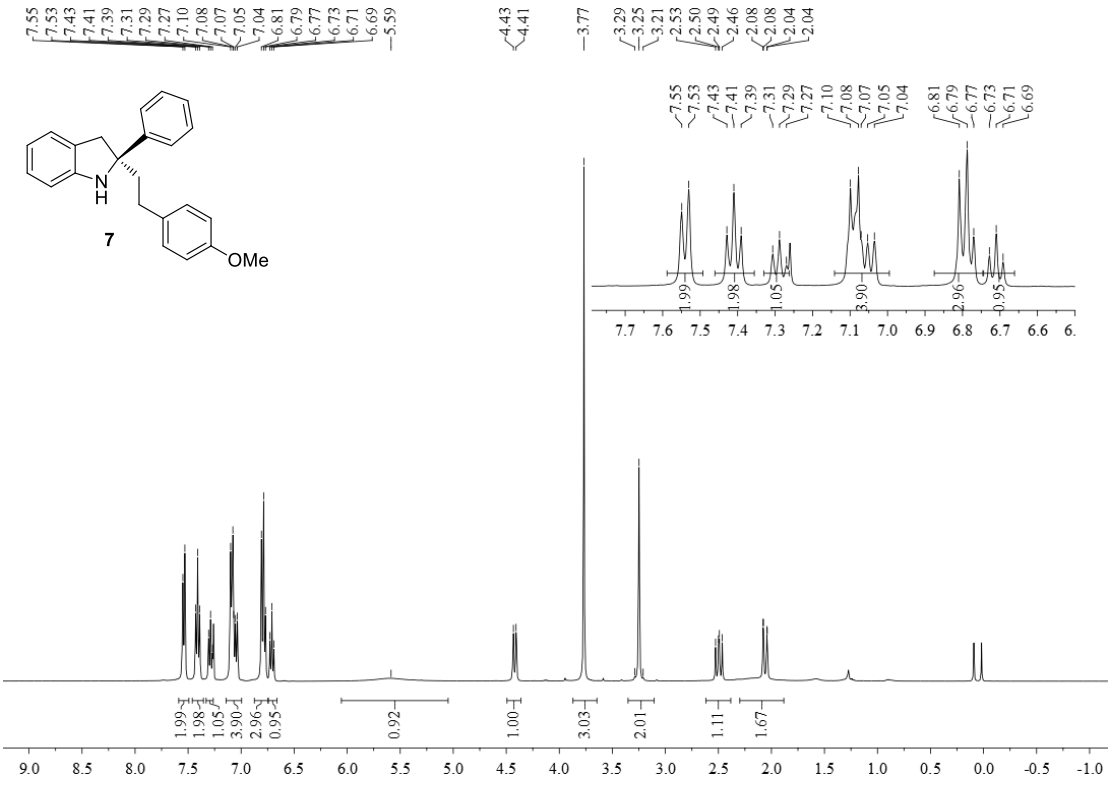
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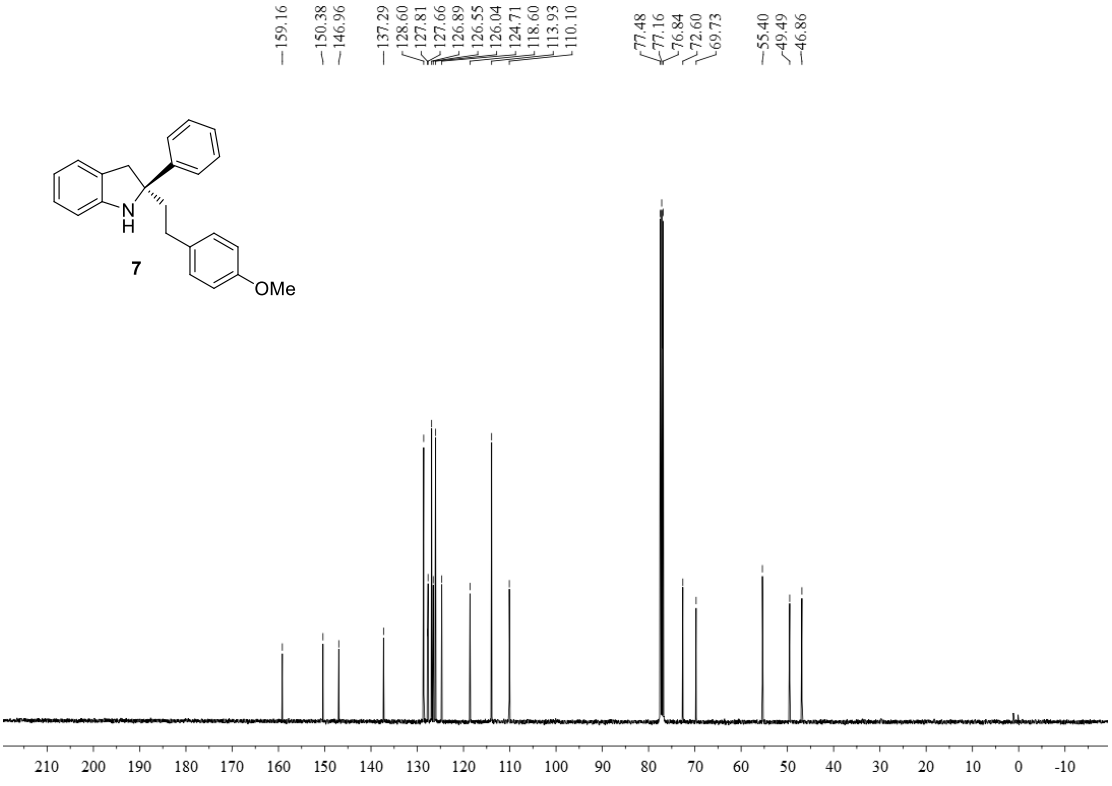
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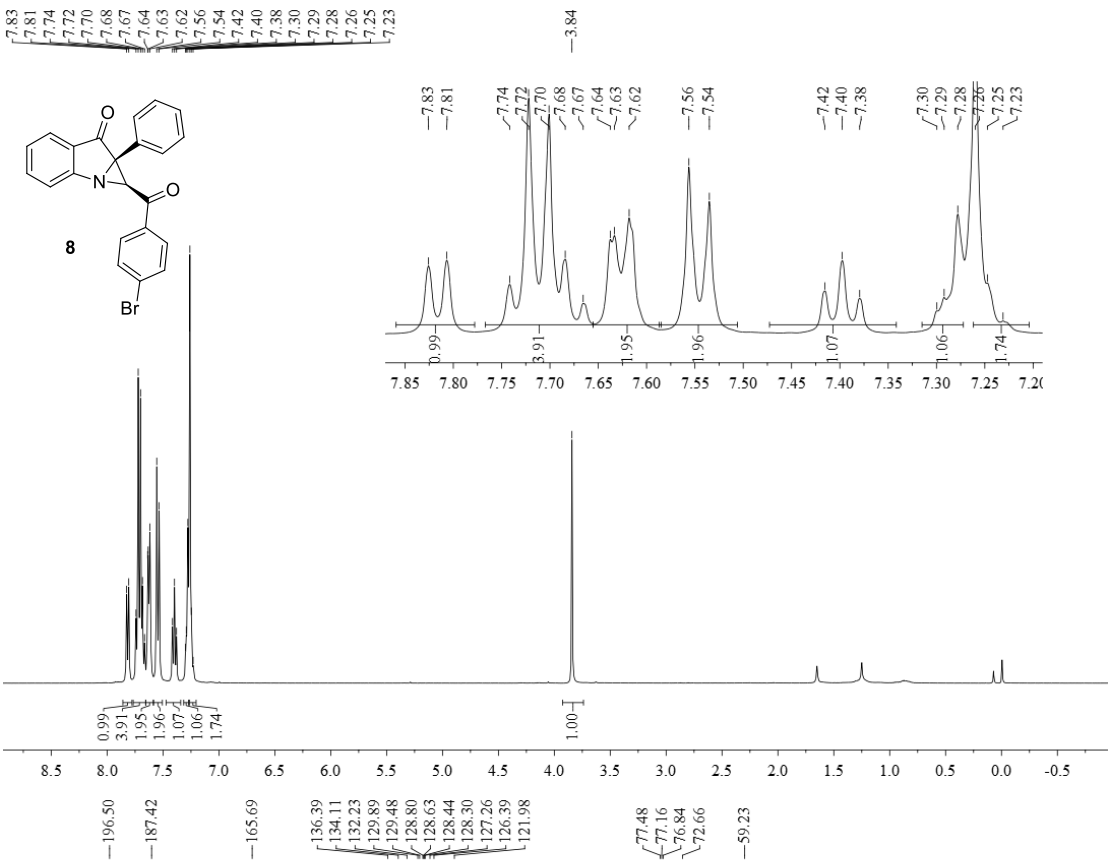
OMe
7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7.23
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O
Br
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1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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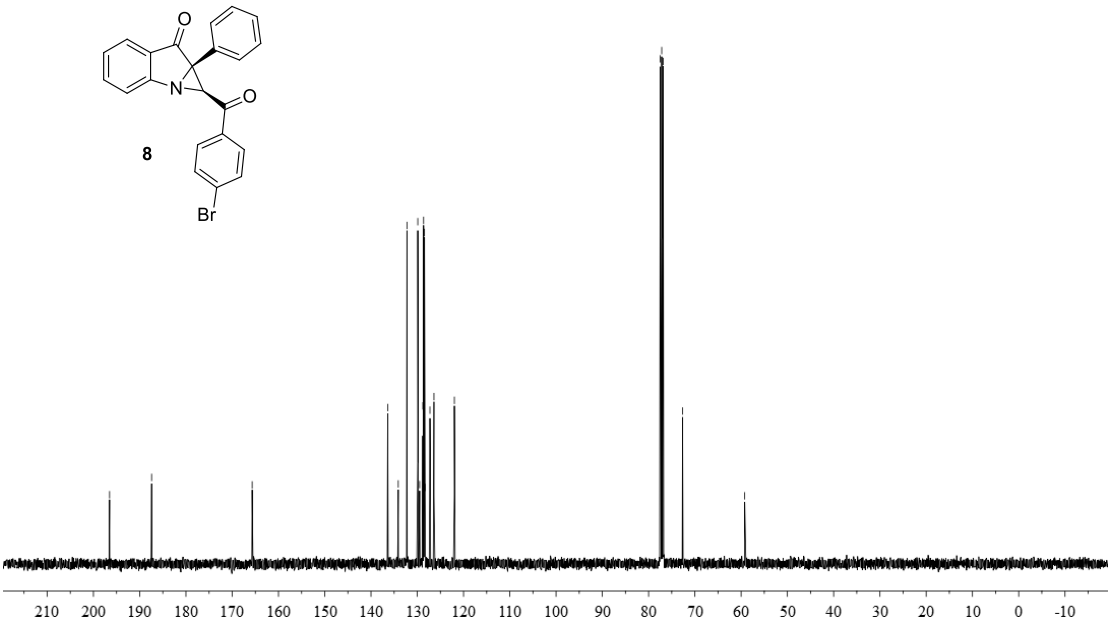
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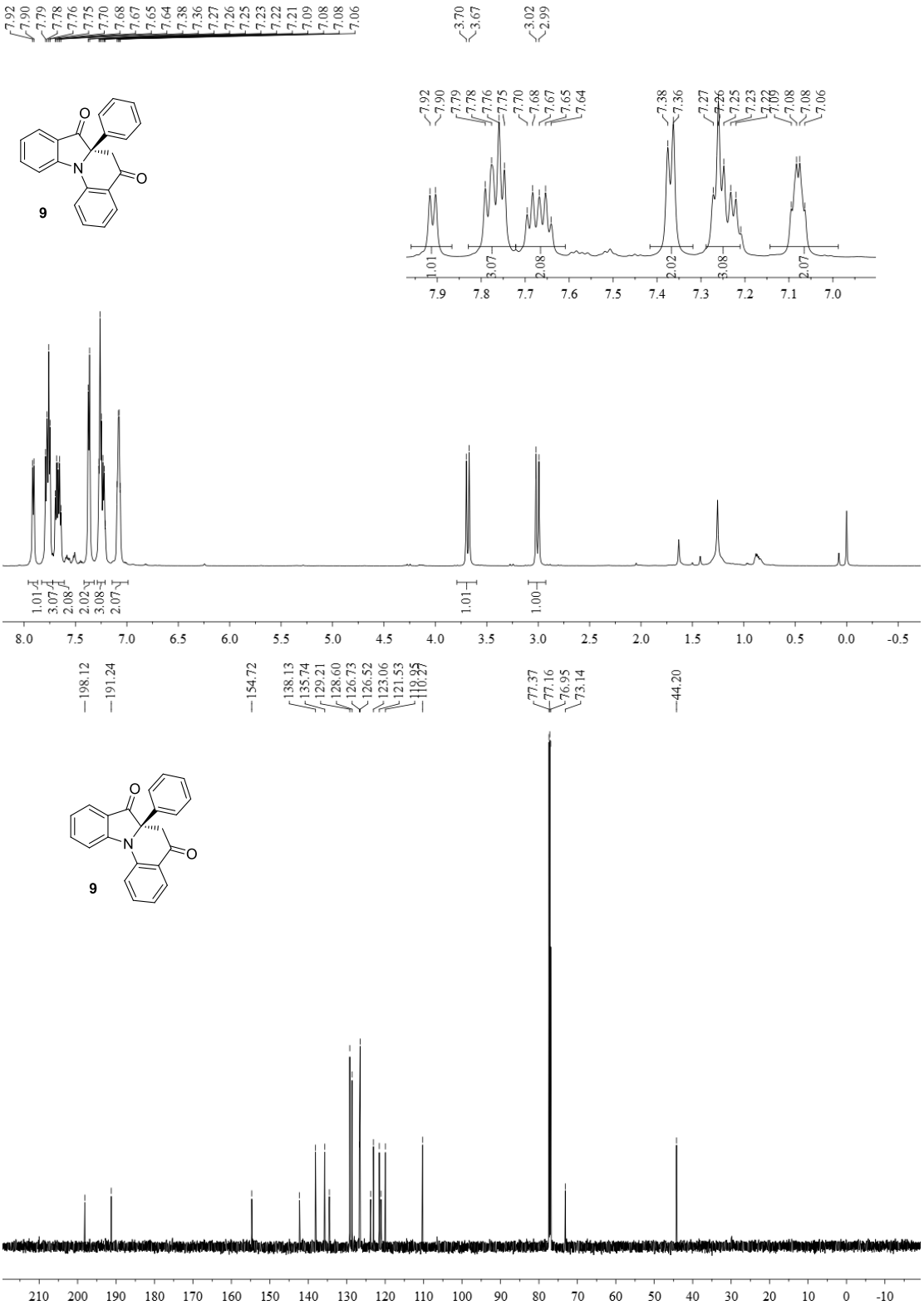
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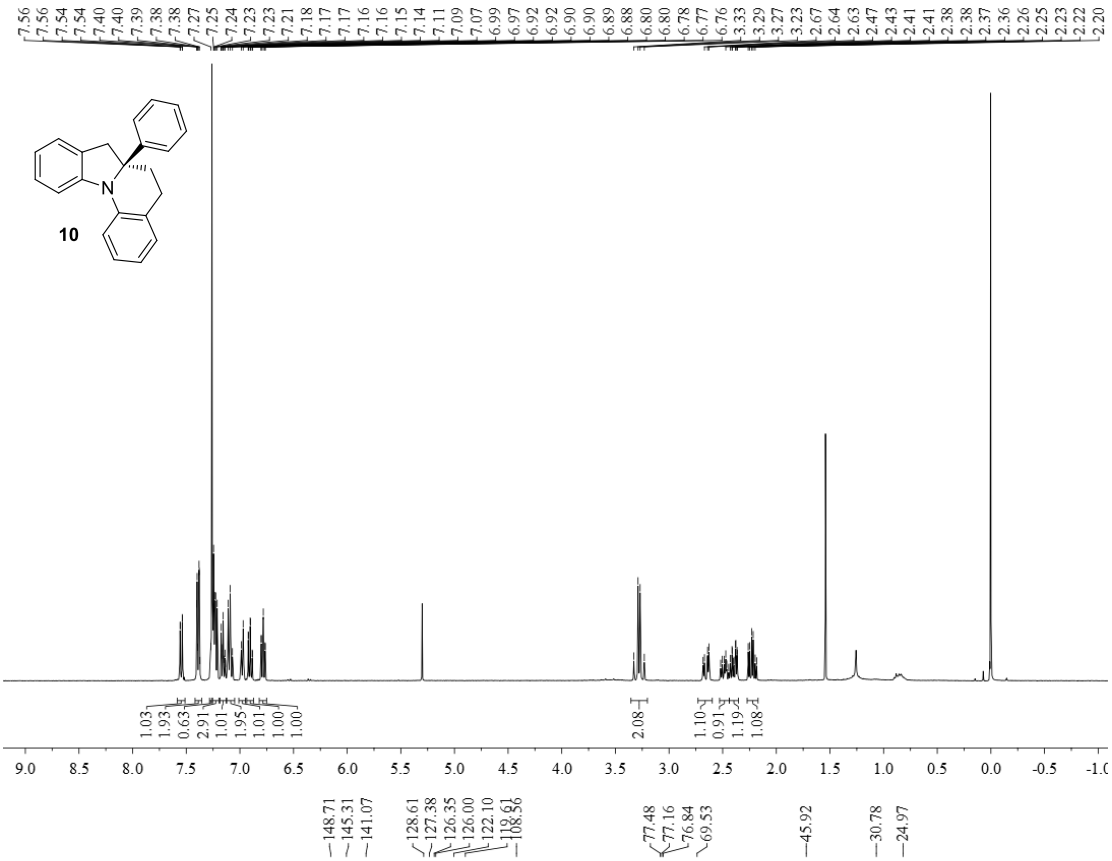
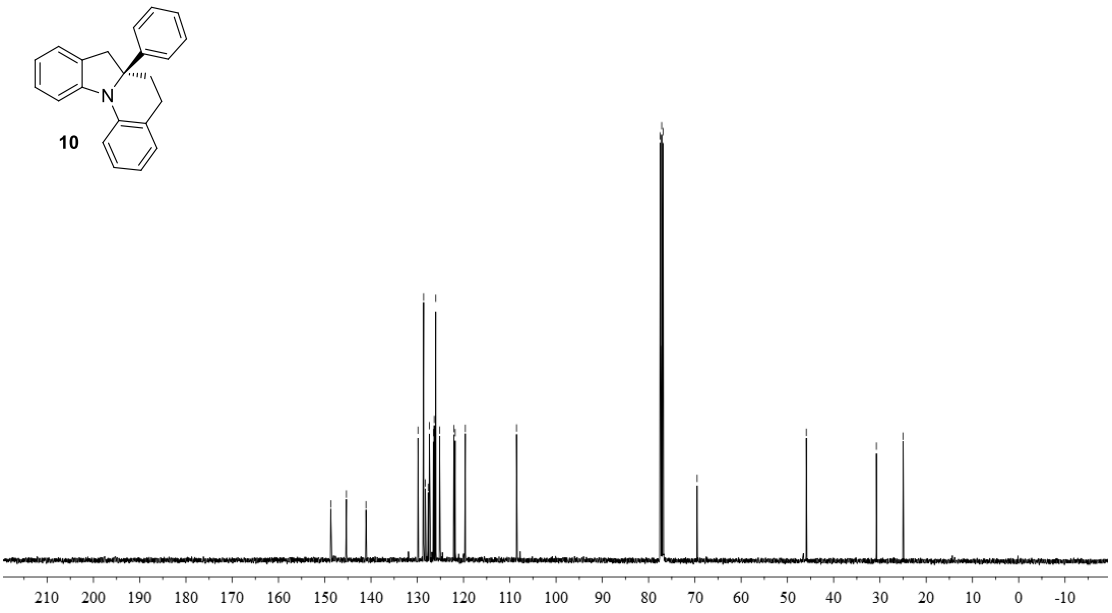
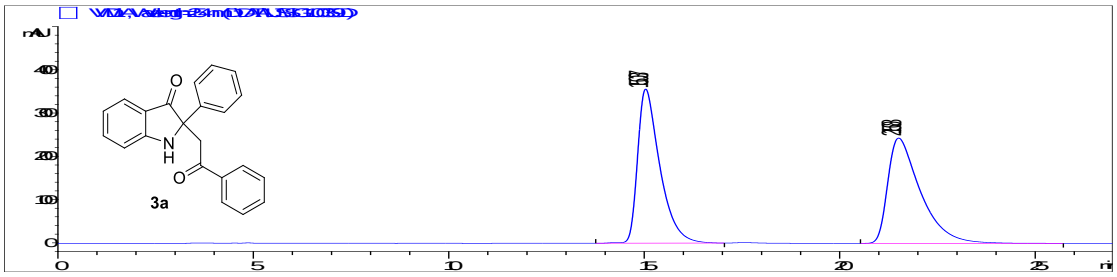
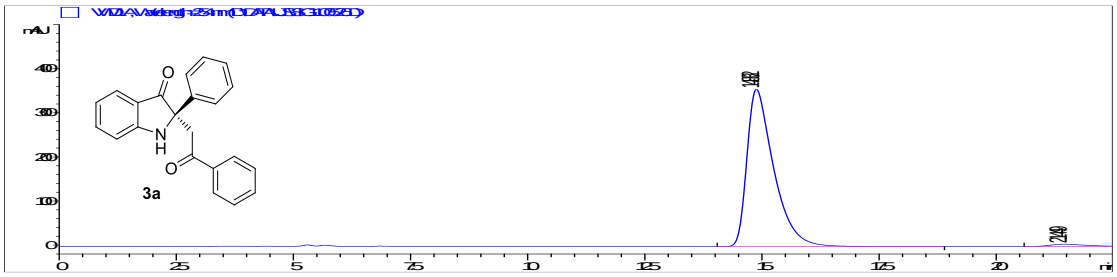




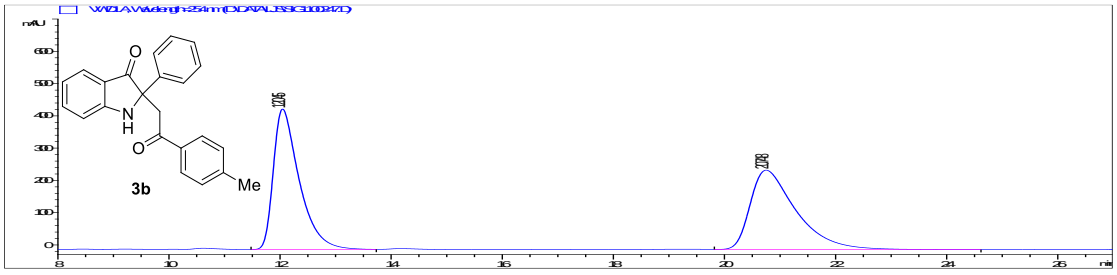
HPLC charts of the related compounds



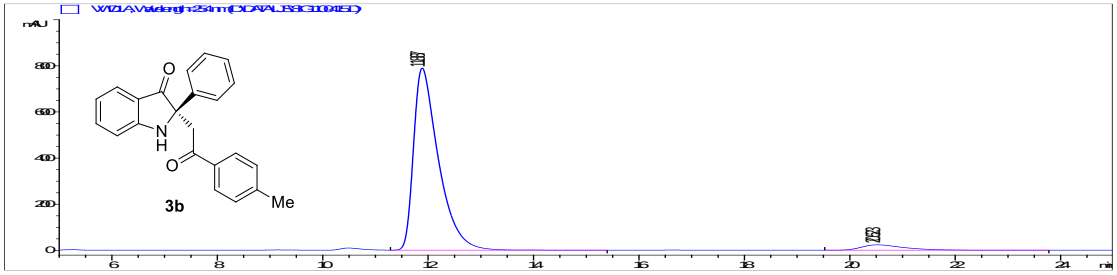
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	15.037	14092.4	356.6	0.5892	0.533	49.934
2	21.508	14129.7	243.5	0.8633	0.463	50.066



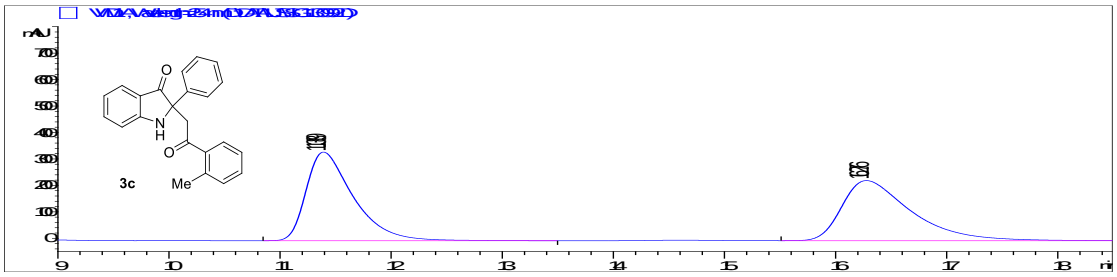
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.882	14102	356.3	0.5899	0.512	98.023
2	21.449	284.4	5	0.8001	0.544	1.977



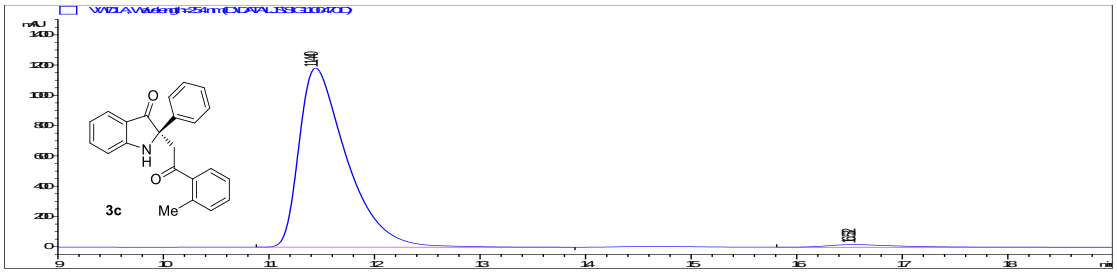
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	12.045	14099.9	435.3	0.4827	0.52	49.910
2	20.748	14150.5	246.3	0.8508	0.496	50.090



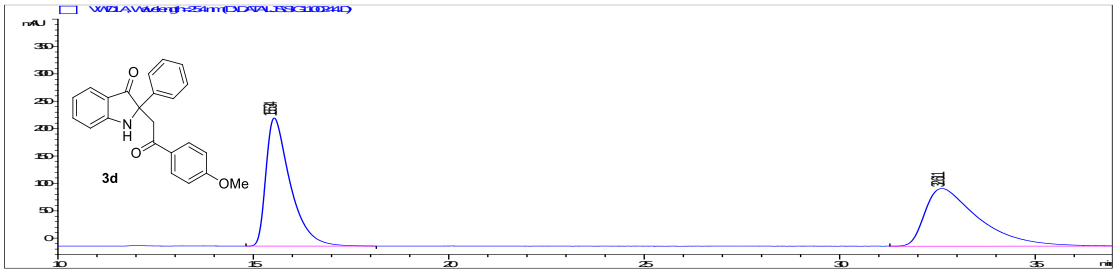
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.887	25928.2	789.3	0.491	0.493	95.161
2	20.523	1318.3	23.3	0.8367	0.551	4.839



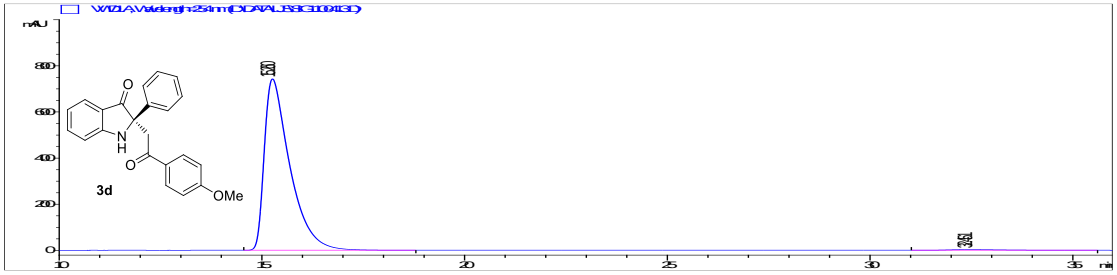
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.389	9879.2	335.1	0.4401	0.54	50.011
2	16.276	9874.7	227.3	0.6407	0.512	49.989



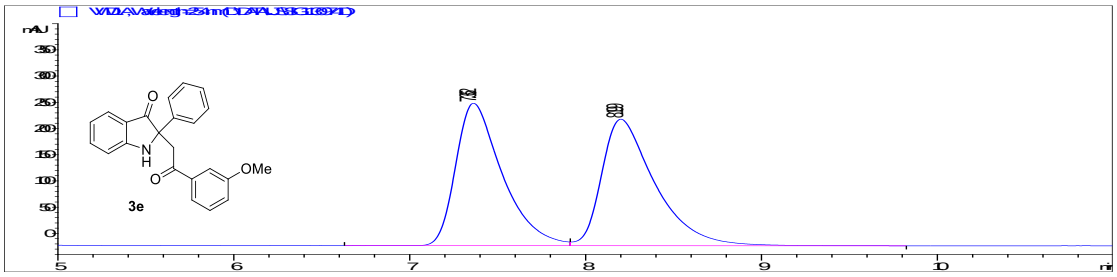
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.44	36907.9	1182.9	0.4659	0.492	97.942
2	16.532	775.4	17.1	0.6594	0.541	2.058



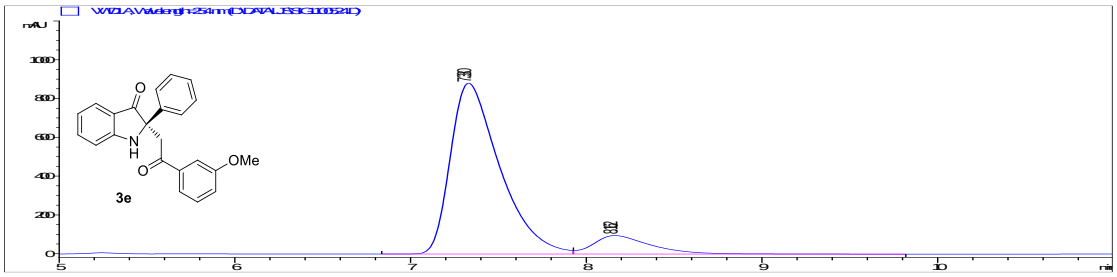
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	15.534	10081	234	0.6454	0.481	50.168
2	32.611	10013.6	105.2	1.3468	0.428	49.832



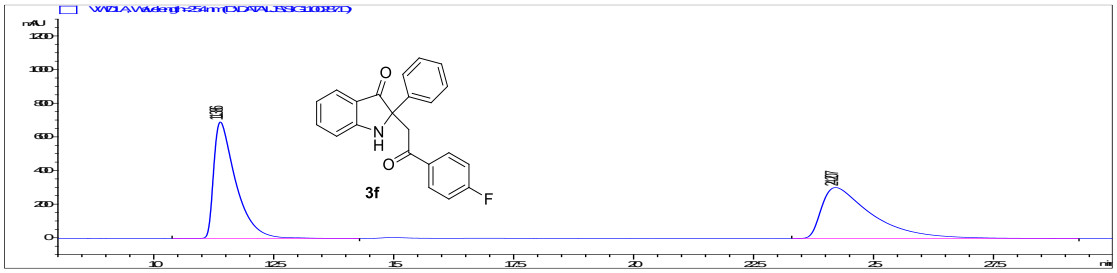
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	15.26	32434	742.5	0.6436	0.435	99.254
2	32.451	243.8	2.7	1.0637	0.595	0.746



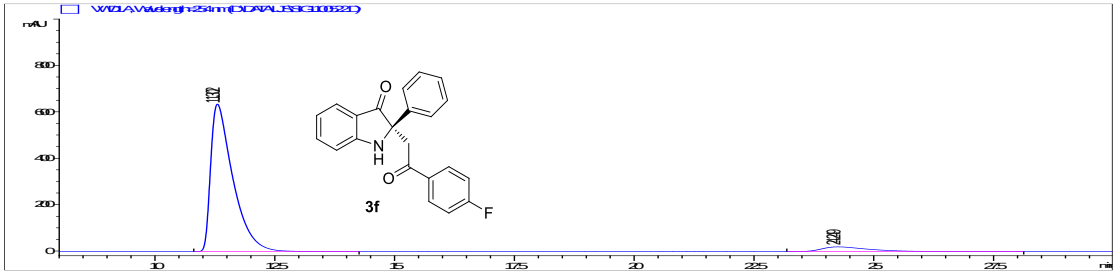
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	7.362	5008.2	271.5	0.2763	0.583	49.545
2	8.199	5100.2	241.2	0.3137	0.523	50.455



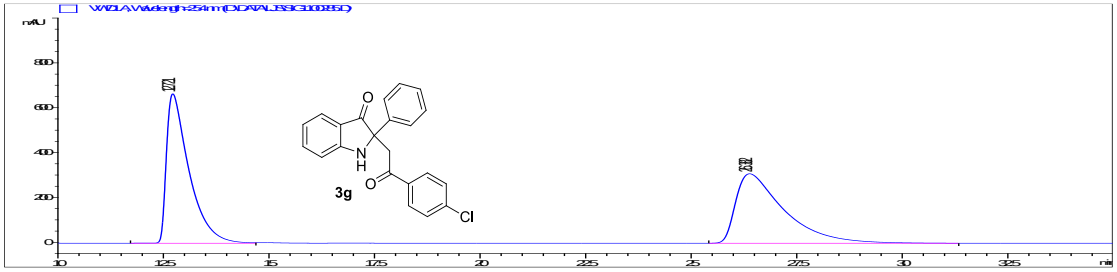
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	7.33	17168.9	880.4	0.2945	0.551	89.922
2	8.162	2138.9	95.1	0.3351	0.56	10.078



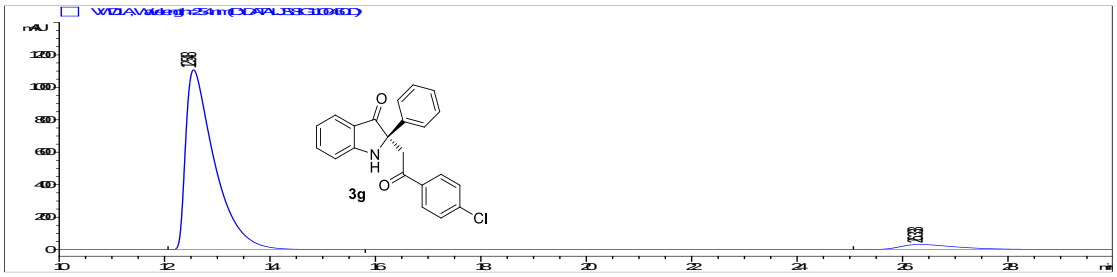
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.386	22135	692.3	0.472	0.395	50.041
2	24.207	22098.7	302.9	1.0347	0.353	49.959



Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.302	20472.7	635.8	0.4776	0.402	94.527
2	24.249	1416.9	20.5	0.988	0.482	5.473

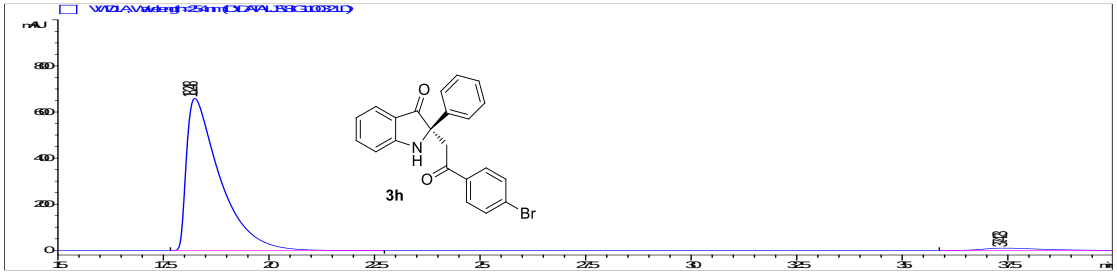


Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	12.721	24701.7	666	0.5463	0.356	50.092
2	26.382	24611.3	309.6	1.1458	0.371	49.908

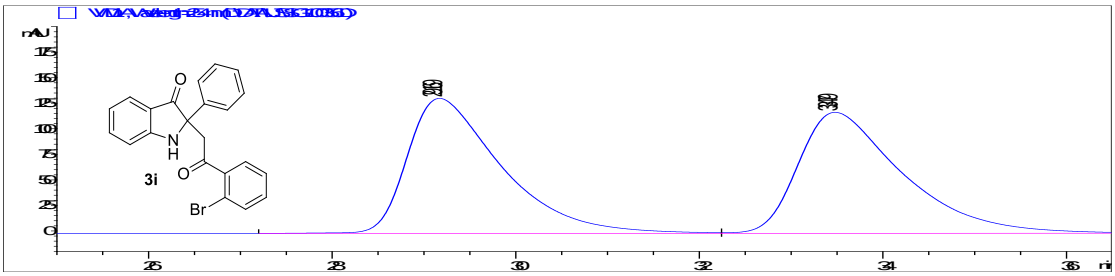


Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	12.548	41799	1107.7	0.5567	0.344	94.644
2	26.333	2365.4	31.4	1.0779	0.491	5.356

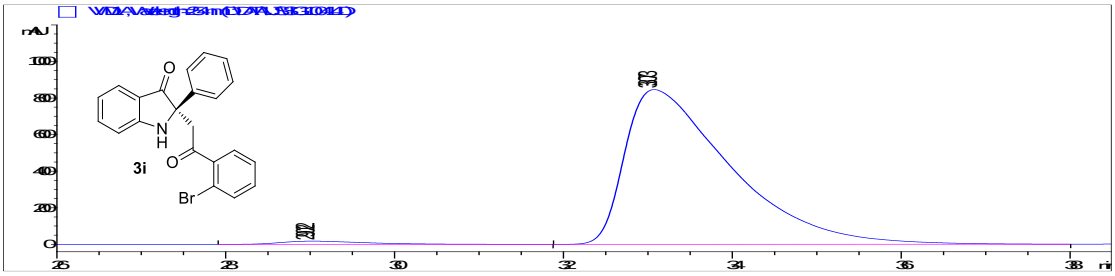
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	17.742	38870.4	725.3	0.7766	0.296	50.218
2	35.474	38533.2	365.7	1.4682	0.338	49.782



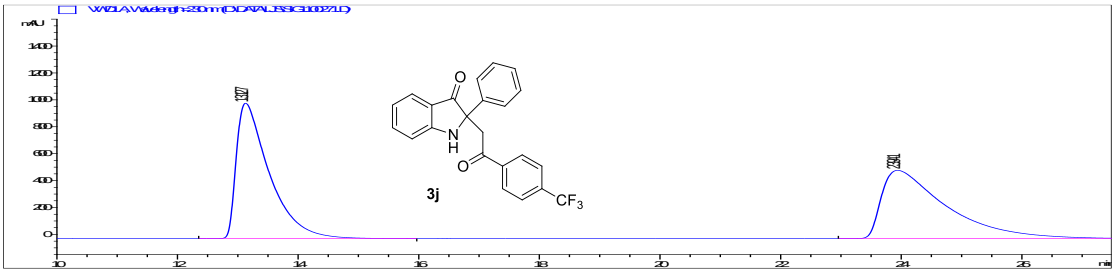
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	18.248	36122.7	659.6	0.802	0.303	97.249
2	37.423	1021.7	10.2	1.3954	0.513	2.751



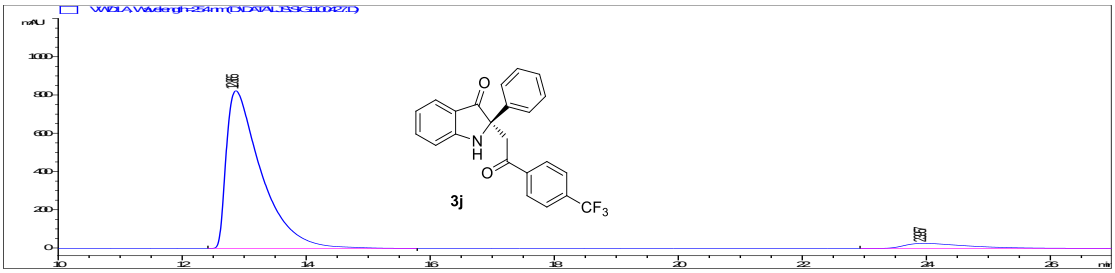
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	29.169	9414	132.1	1.0675	0.487	50.115
2	33.479	9370.8	118.4	1.1738	0.512	49.885



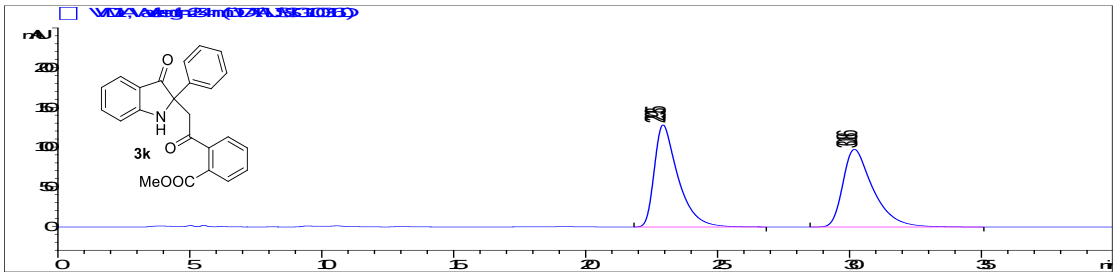
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	29.022	1237.9	17.6	1.0062	0.53	1.658
2	33.073	73416	846.1	1.251	0.358	98.342



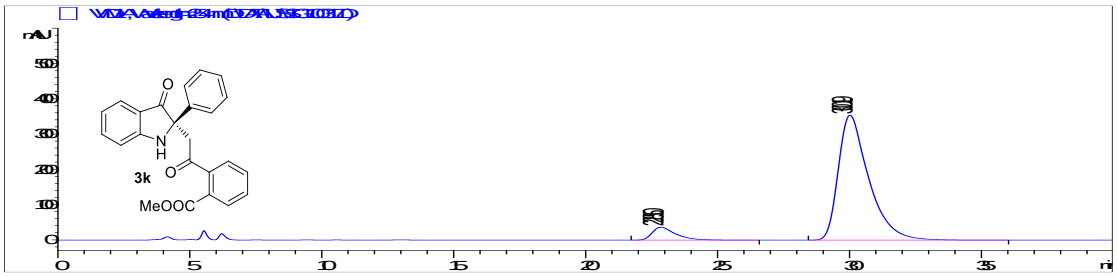
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	13.127	38292.5	1006.2	0.5547	0.359	50.238
2	23.941	37929.3	507.4	1.0526	0.308	49.762



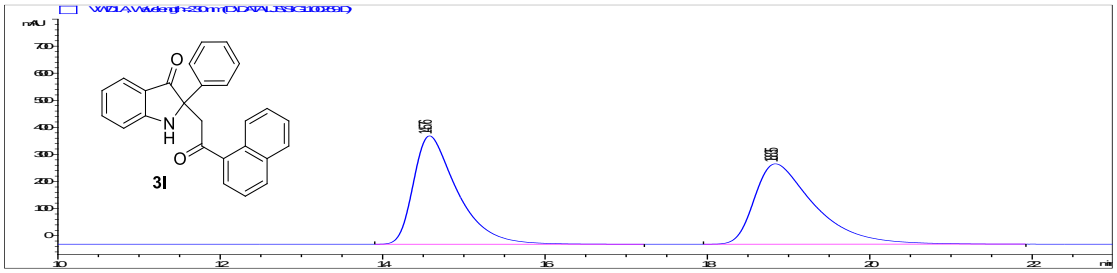
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	12.865	32208.9	824.2	0.5724	0.342	94.918
2	23.957	1868.2	26.5	1.0111	0.401	5.082



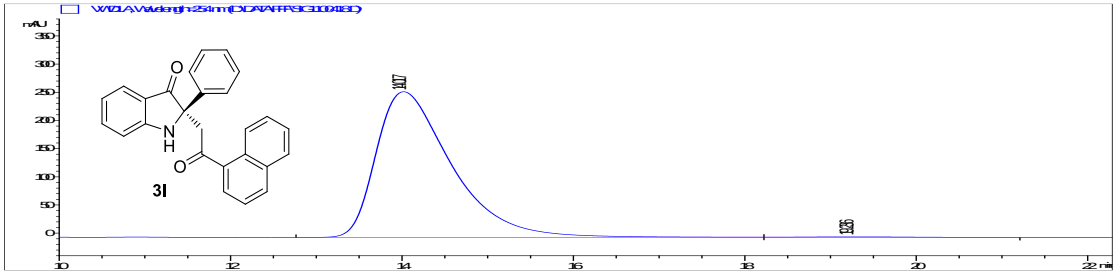
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	22.935	8037.2	128.6	0.9157	0.54	50.848
2	30.186	7769	97.7	1.1574	0.578	49.152



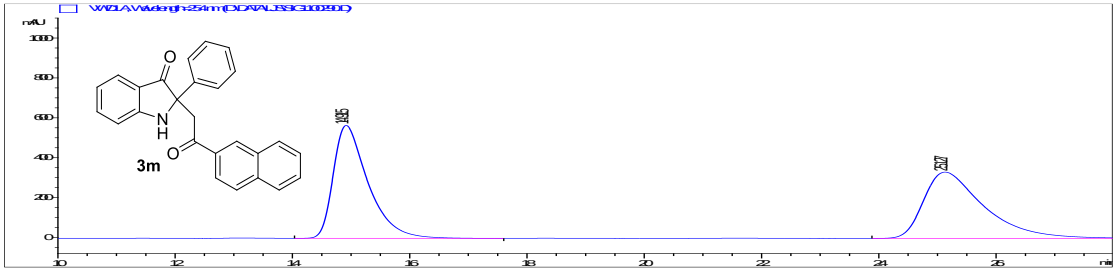
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	22.85	2271.4	36.7	0.9193	0.547	7.414
2	30.019	28364.1	354.1	1.1704	0.583	92.586



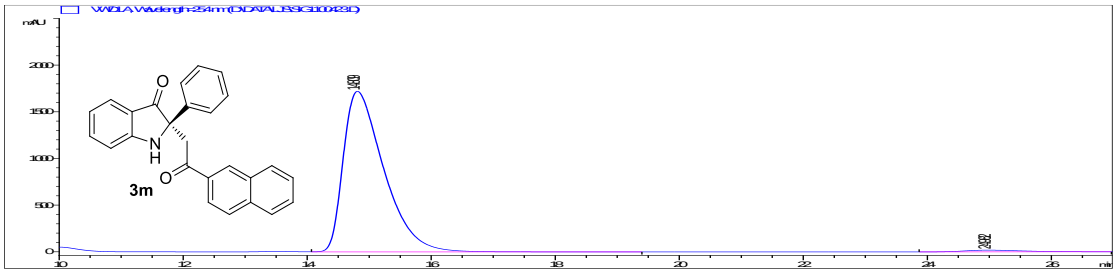
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.576	15020.2	400.1	0.5515	0.54	49.634
2	18.835	15241.8	296.9	0.762	0.494	50.366



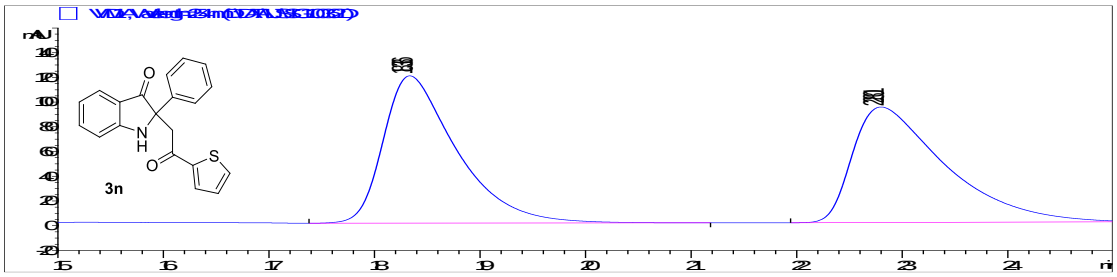
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.017	15783.5	258.4	0.9207	0.535	99.638
2	19.236	57.3	7.6E-1	0.8942	0.627	0.362



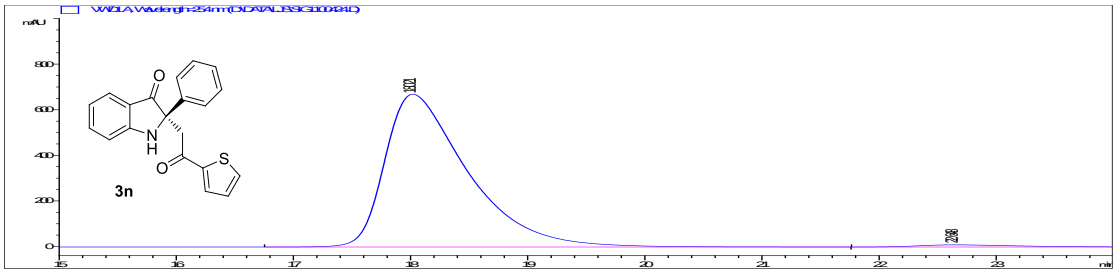
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.915	23346.5	565.9	0.6124	0.547	49.610
2	25.127	23713.7	332	1.0664	0.511	50.390



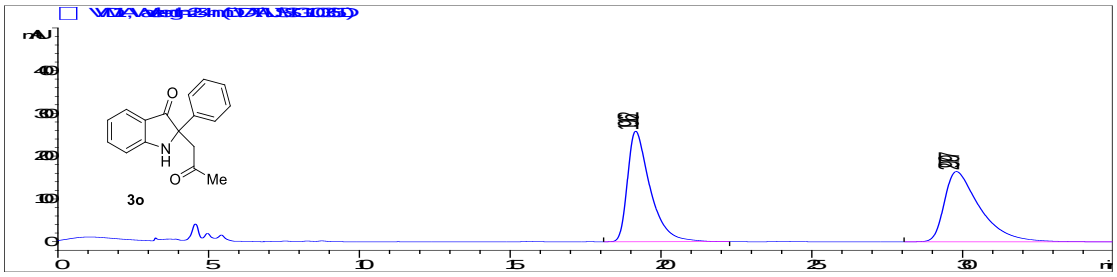
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.809	78192	1720.2	0.6876	0.502	98.479
2	24.982	1207.5	18.7	0.9543	0.639	1.521



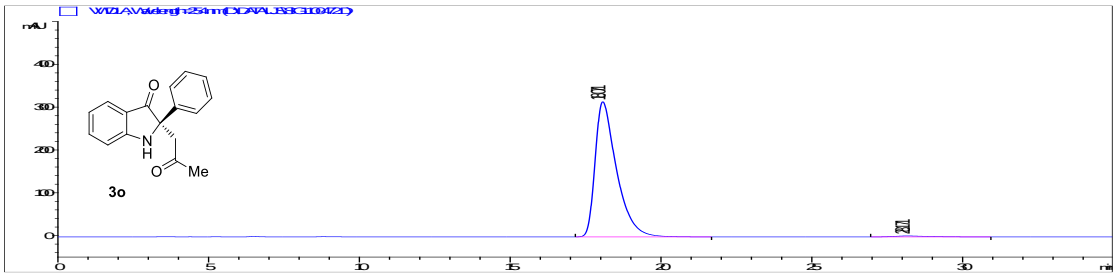
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	18.336	5767.4	119.2	0.7159	0.531	50.275
2	22.801	5704.2	93.5	0.8806	0.416	49.725



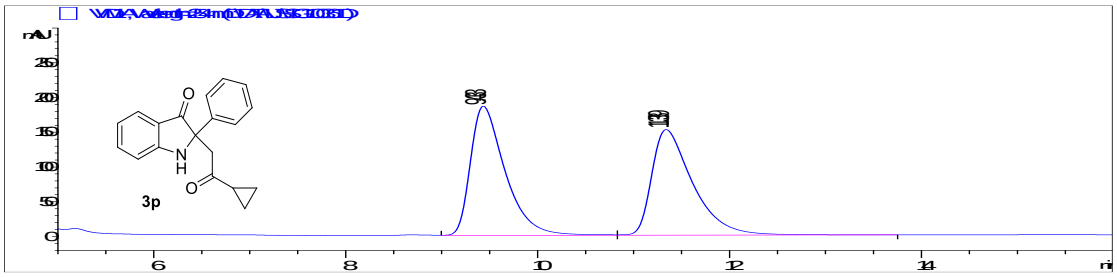
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	18.021	32867.7	669.9	0.7325	0.478	98.359
2	22.648	548.3	9.4	0.8524	0.511	1.641



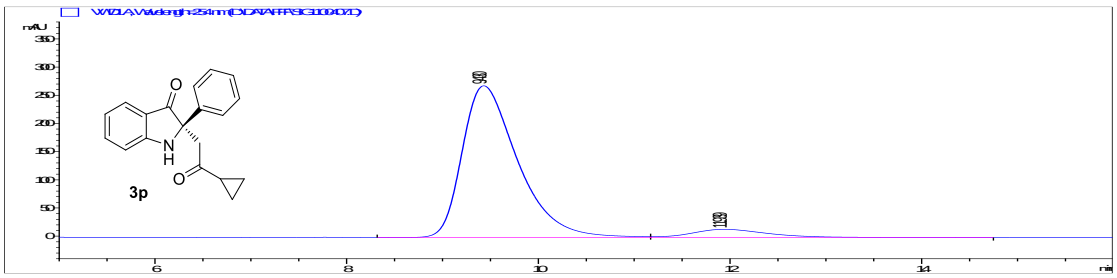
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	19.162	2102.5	90.8	0.343	0.586	50.533
2	29.797	2058.2	78.1	0.3976	0.552	49.467



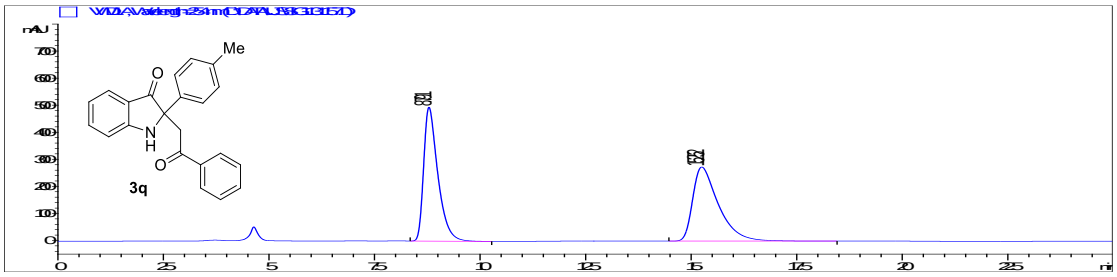
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	18.071	15598.2	315.7	0.7278	0.524	98.894
2	28.171	174.5	2.3	0.9251	0.597	1.106



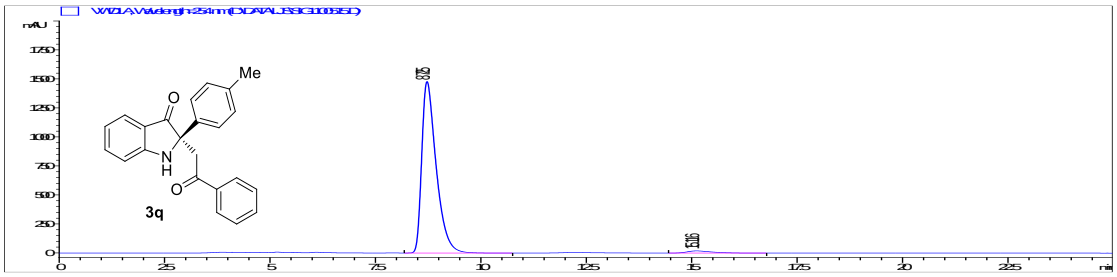
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	9.433	4666.8	185.8	0.3774	0.551	50.947
2	11.339	4493.3	151.9	0.4442	0.509	49.053



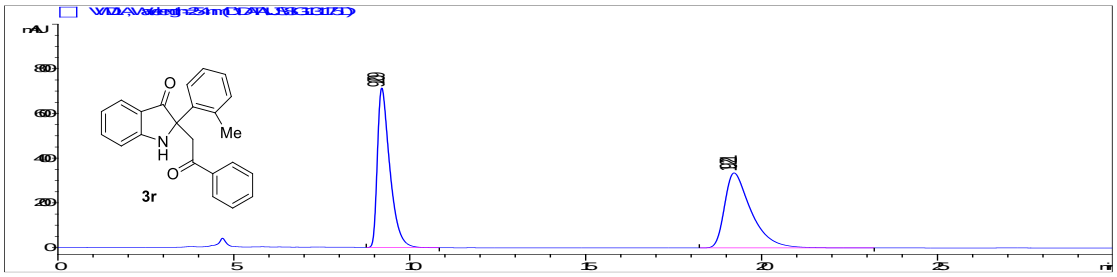
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	9.43	10872.5	269.4	0.6135	0.594	92.997
2	11.939	818.8	14.7	0.8266	0.694	7.003



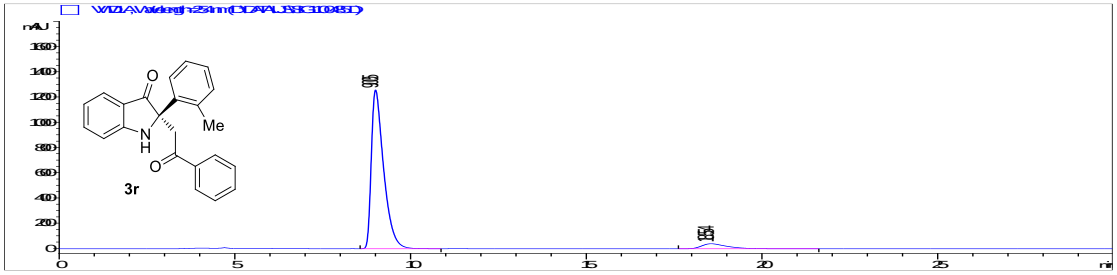
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.791	11530.9	494.9	0.3475	0.56	49.886
2	15.252	11583.5	273.8	0.6275	0.504	50.114



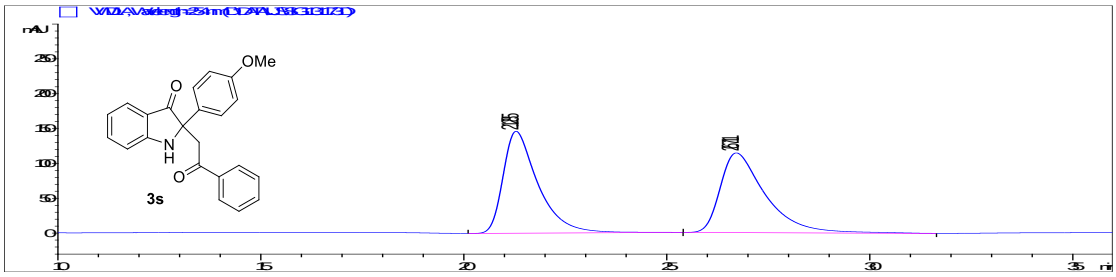
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.725	35143.6	1477.8	0.3561	0.538	97.901
2	15.116	753.3	18.7	0.6051	0.57	2.099



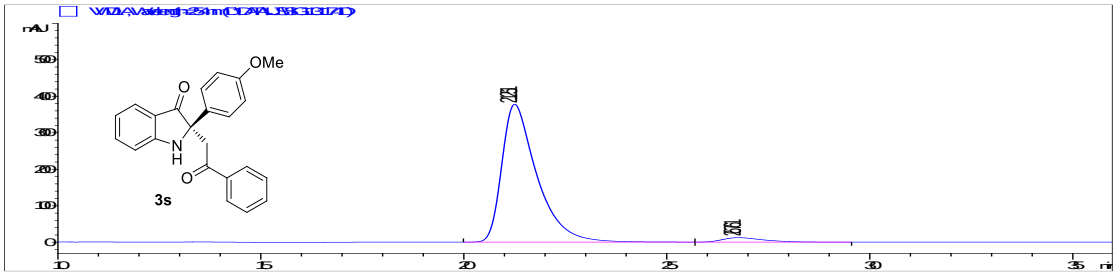
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	9.209	17488.7	713.4	0.3675	0.507	49.816
2	19.221	17617.8	335.8	0.7752	0.516	50.184



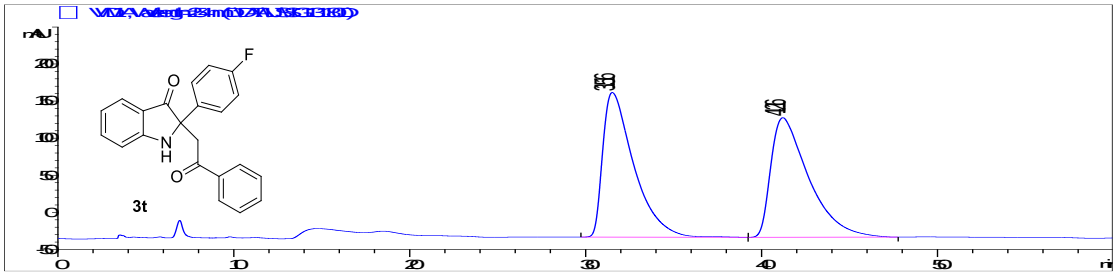
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	9.005	30708.5	1258.9	0.3632	0.485	95.837
2	18.554	2017	39.9	0.7407	0.553	4.163



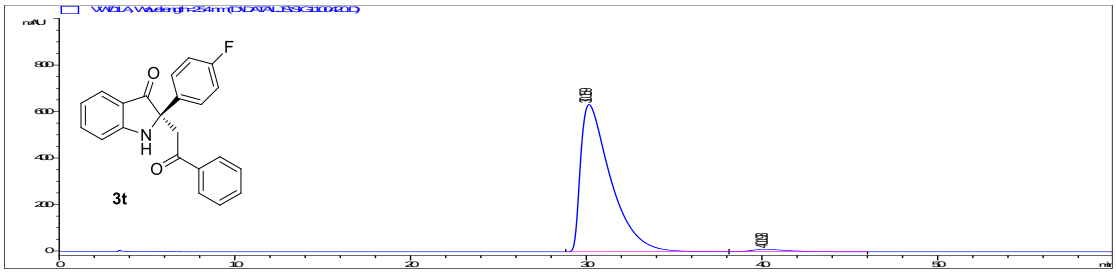
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	21.285	8756	146.2	0.885	0.546	49.798
2	26.711	8827.2	114.3	1.1397	0.51	50.202



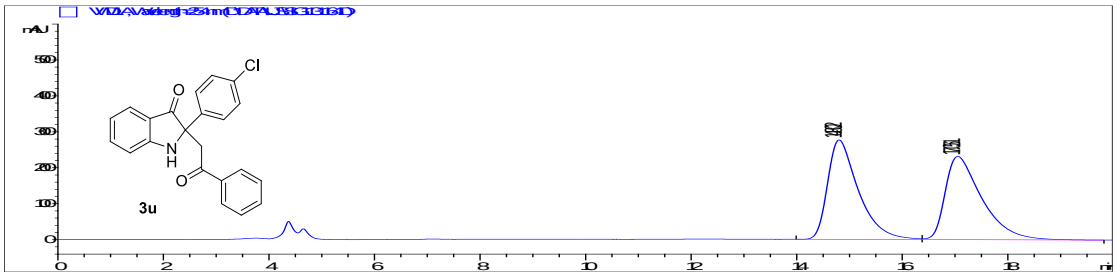
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	21.251	22633.9	377.5	0.8859	0.537	96.411
2	26.761	842.5	12.2	1.0187	0.602	3.589



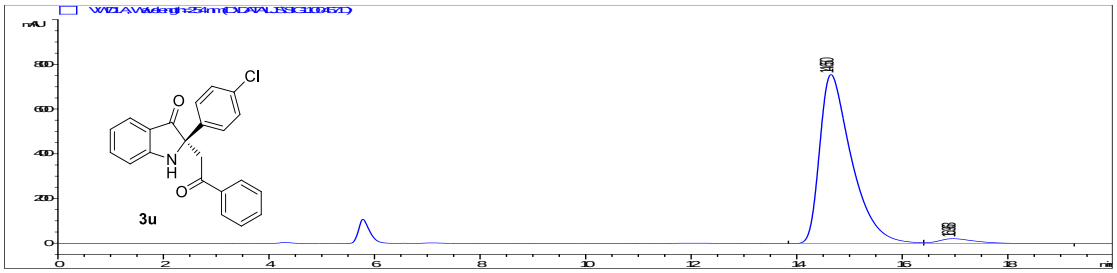
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	31.516	23947.5	194.9	1.806	0.411	49.870
2	41.216	24072.5	161.2	2.1874	0.436	50.130



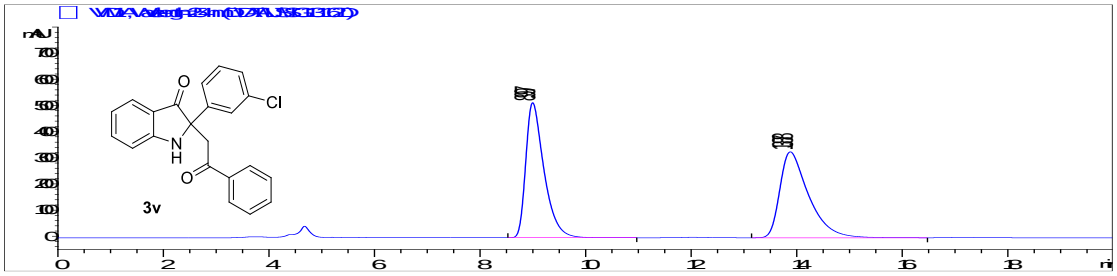
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	30.159	75283.3	633.4	1.7448	0.358	98.115
2	40.193	1446.7	10.3	1.7235	0.574	1.885



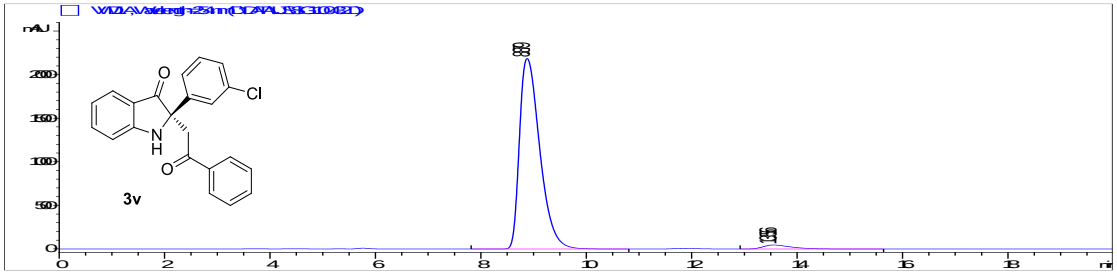
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.802	11226.7	276.6	0.6016	0.552	50.105
2	17.051	11179.9	231.7	0.7173	0.485	49.895



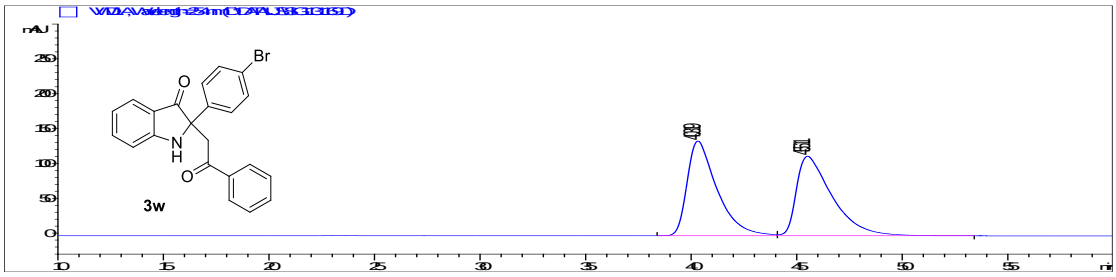
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.65	31677.8	756.4	0.6226	0.513	96.685
2	16.963	1086	22	0.7214	0.603	3.315



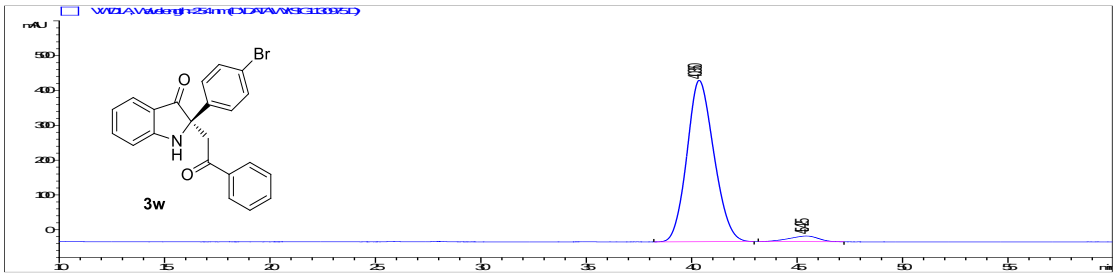
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.997	12370.6	516.1	0.3582	0.567	49.866
2	13.878	12437	328.3	0.5613	0.529	50.134



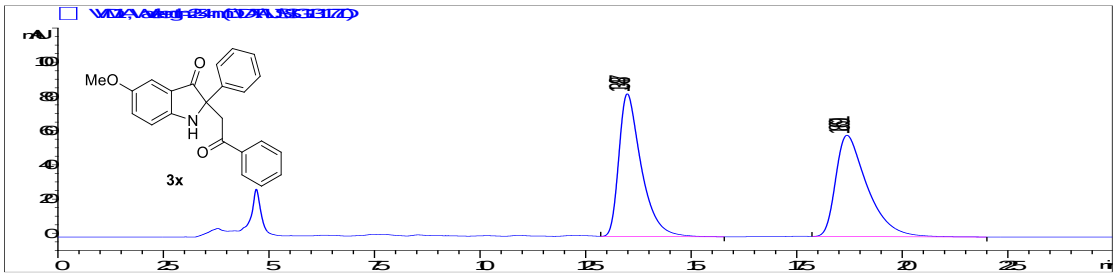
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.879	58437.9	2185.9	0.4138	0.566	97.151
2	13.556	1713.6	46.1	0.5502	0.554	2.849



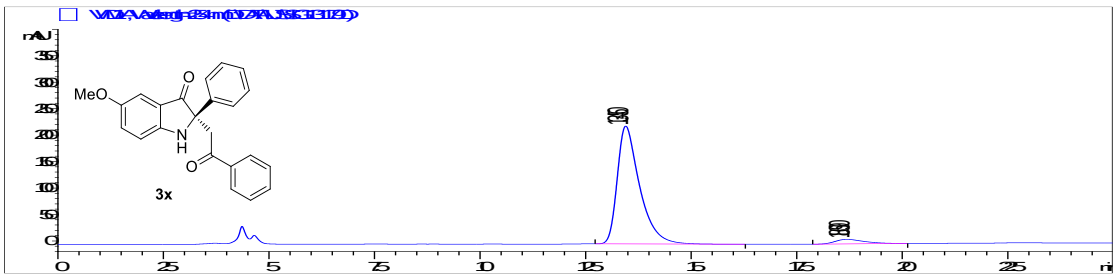
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	40.319	13364.7	135.9	1.471	0.52	49.896
2	45.511	13420.2	114.1	1.7649	0.415	50.104



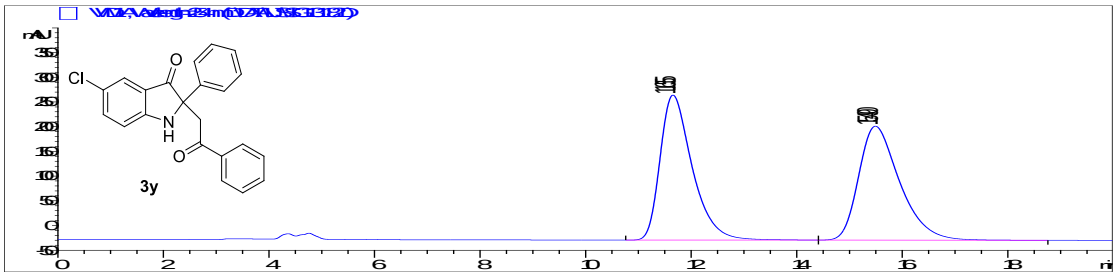
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	40.35	41275.4	463.7	1.353	0.804	96.257
2	45.425	1604.9	16.4	1.1604	1.367	3.743



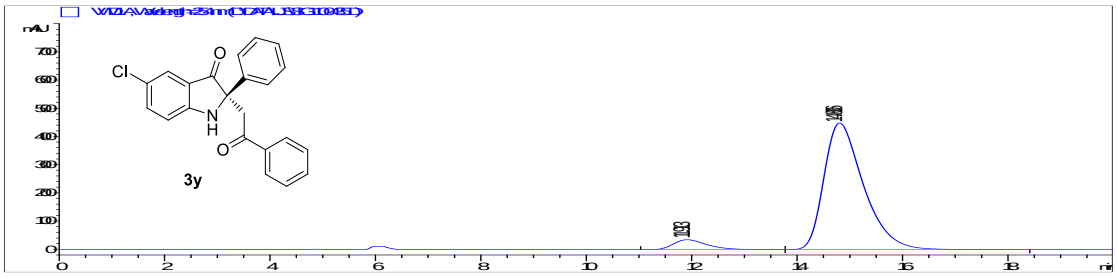
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	13.487	3077.1	83.5	0.5496	0.559	50.095
2	18.691	3065.5	59.2	0.7643	0.519	49.905



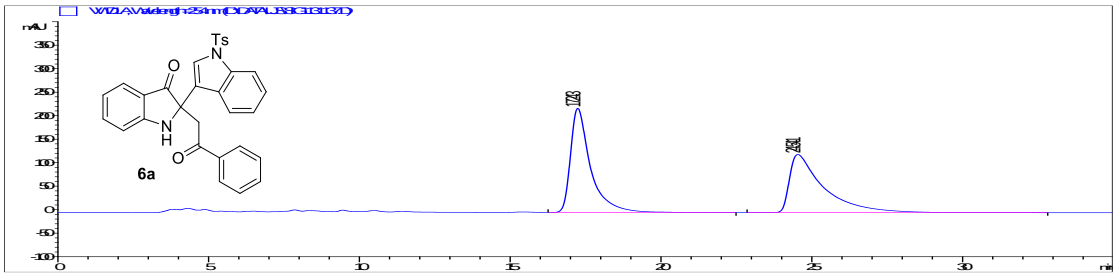
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	13.45	8197.6	222.8	0.5487	0.567	95.208
2	18.69	412.6	8.6	0.6988	0.63	4.792



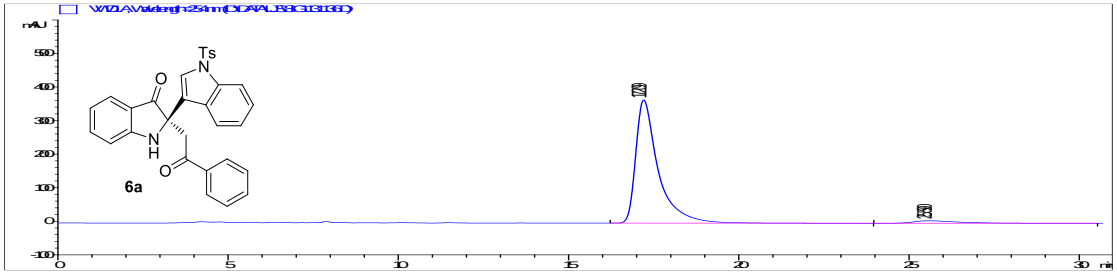
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.655	12396.7	293.5	0.6442	0.626	49.940
2	15.49	12426.5	230.6	0.8151	0.647	50.060



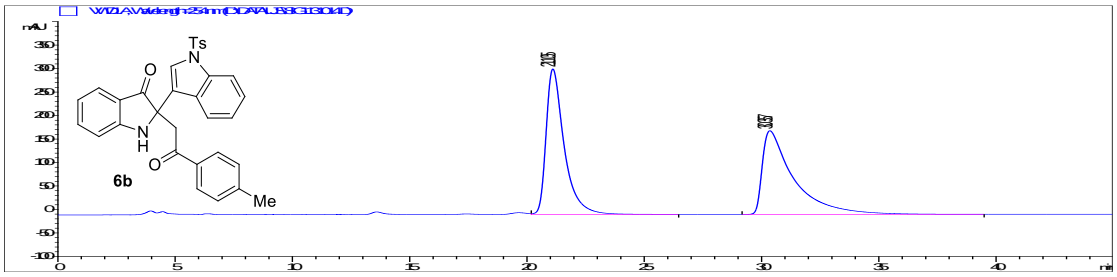
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.913	1587.5	35.3	0.6814	0.643	6.355
2	14.806	23394.9	449.2	0.794	0.618	93.645



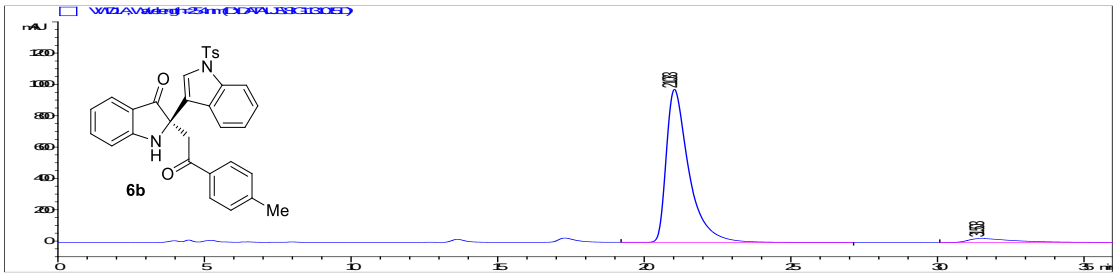
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	17.243	10242.3	221.6	0.679	0.522	51.321
2	24.541	9715	123.6	1.1033	0.294	48.679



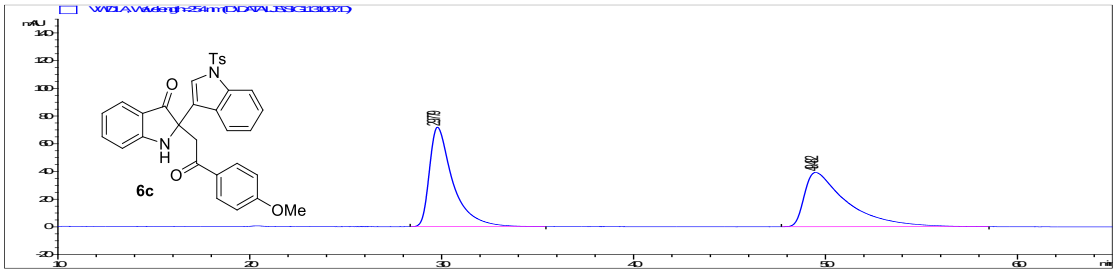
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	17.209	16848	367.4	0.6806	0.502	96.226
2	25.59	660.8	7.3	1.3203	0.478	3.774



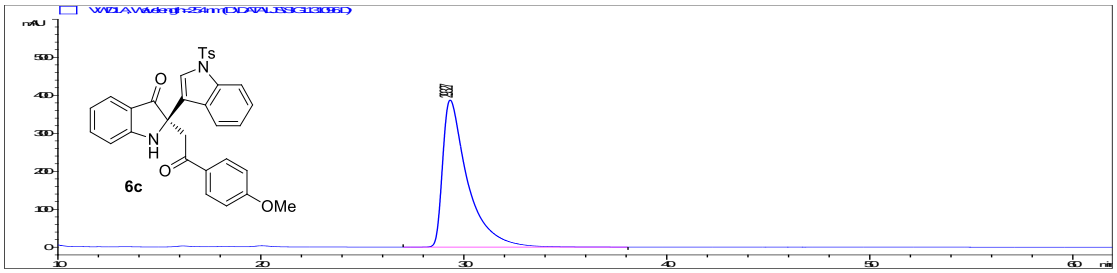
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	21.105	16612.9	309.8	0.8003	0.555	50.044
2	30.357	16583.9	178.1	1.3191	0.284	49.956



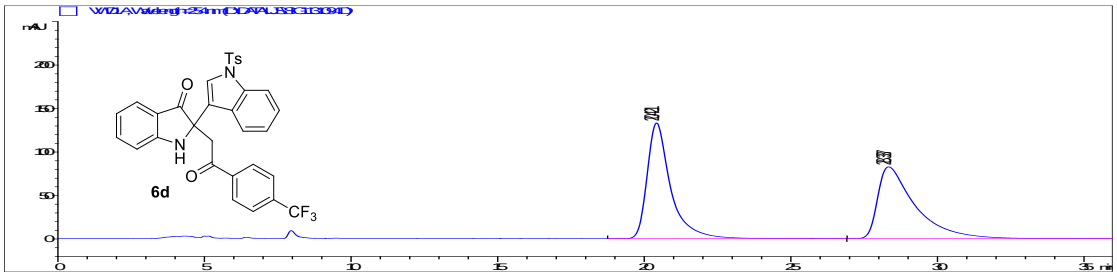
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	21.033	52507.6	977.7	0.8013	0.525	95.045
2	31.503	2737.1	25.3	1.5261	0.361	4.955



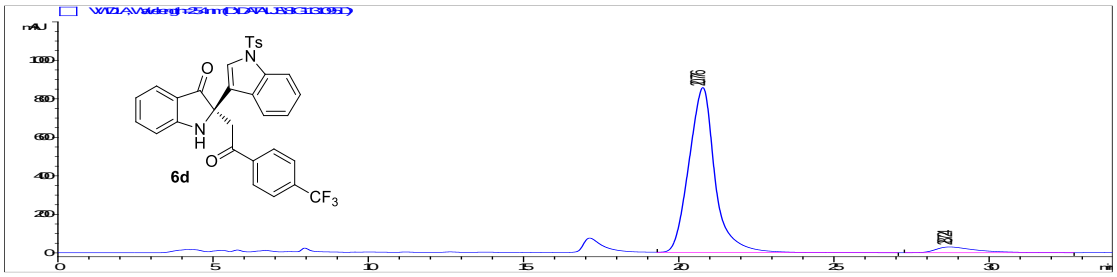
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	29.779	6055.7	71.8	1.243	0.486	50.043
2	49.482	6045.3	39.2	2.0708	0.331	49.957



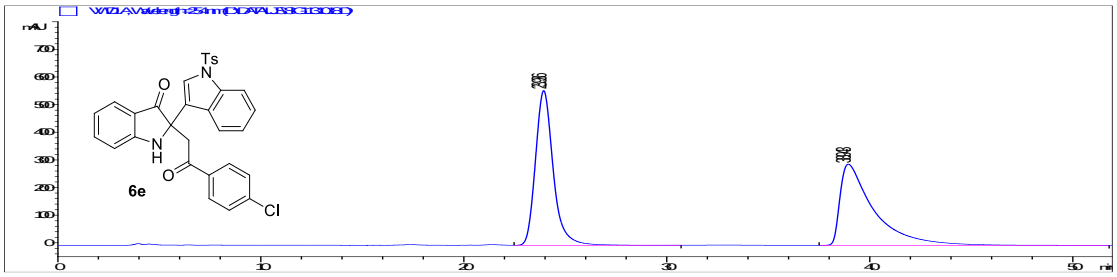
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	29.327	33004.9	387.3	1.2418	0.393	100.000



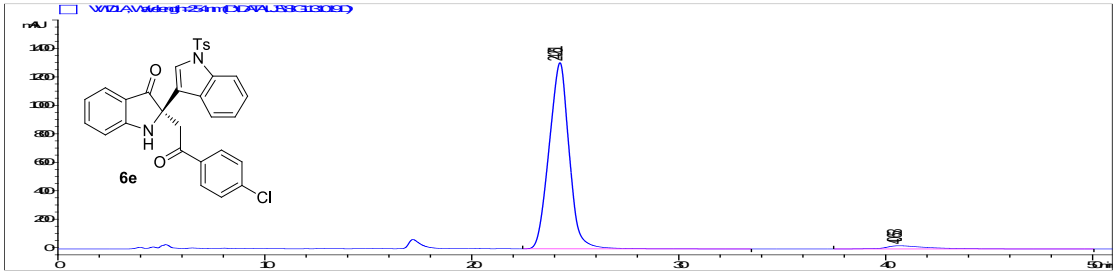
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	20.421	7410.1	133	0.8304	0.606	50.090
2	28.337	7383.5	82.5	1.2941	0.374	49.910



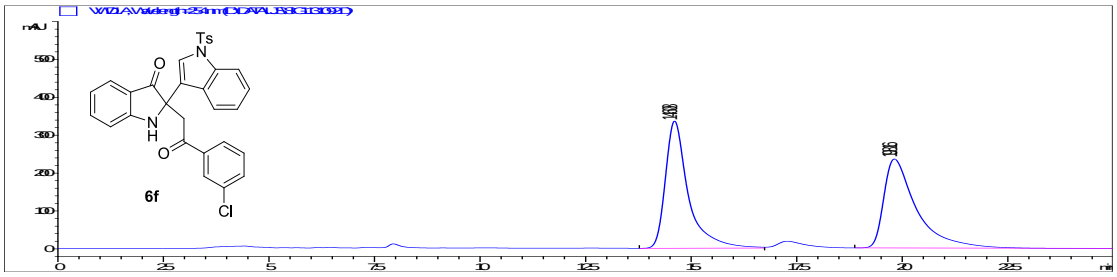
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	20.776	49914.4	857.1	0.8891	1.034	94.931
2	28.724	2665.5	29.6	1.2996	0.476	5.069



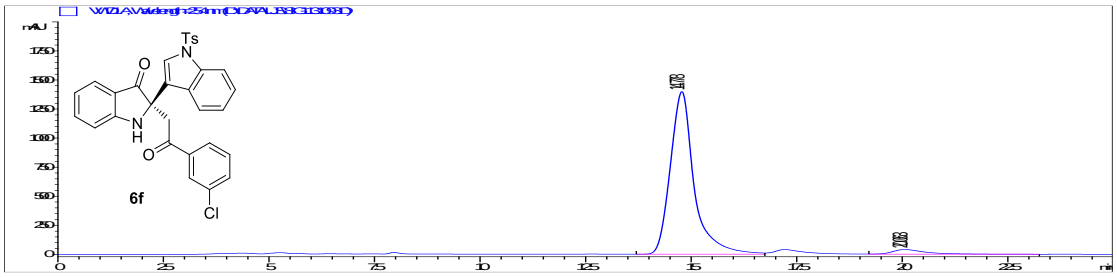
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	23.936	33974.3	559.5	0.9356	0.8	49.961
2	38.943	34027.9	293.7	1.637	0.292	50.039



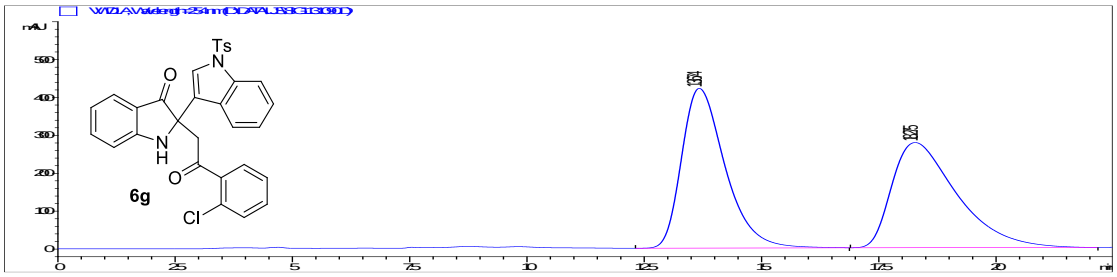
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	24.261	87756.7	1307.9	1.0216	1.101	96.507
2	40.653	3176.2	22.4	1.9943	0.446	3.493



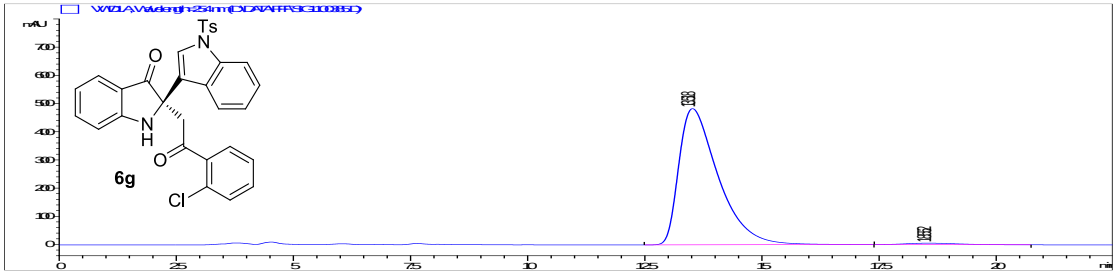
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.608	12677.5	335.6	0.5572	0.606	50.070
2	19.816	12642.2	235.1	0.7905	0.439	49.930



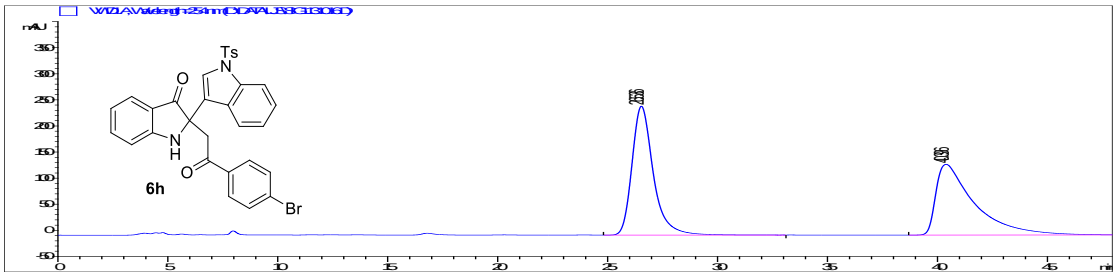
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.778	54575.1	1398.3	0.5893	0.838	96.051
2	20.063	2243.6	40.3	0.8178	0.551	3.949



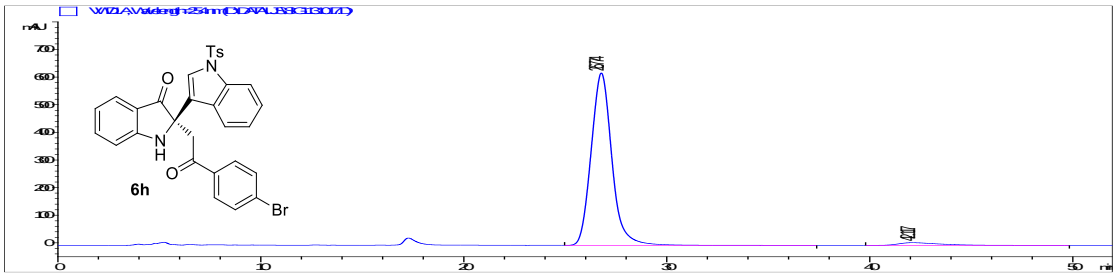
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	13.674	27105.4	421.4	0.9834	0.645	50.366
2	18.275	26711	277.5	1.4668	0.519	49.634



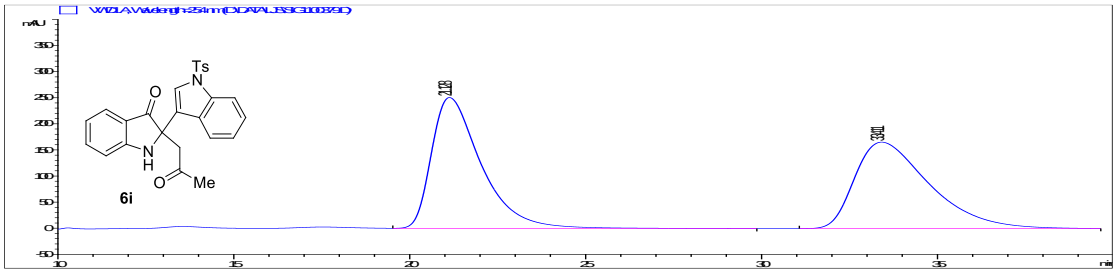
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	13.518	28234.5	483.4	0.8794	0.494	98.627
2	18.552	393.2	5.2	0.9823	0.705	1.373



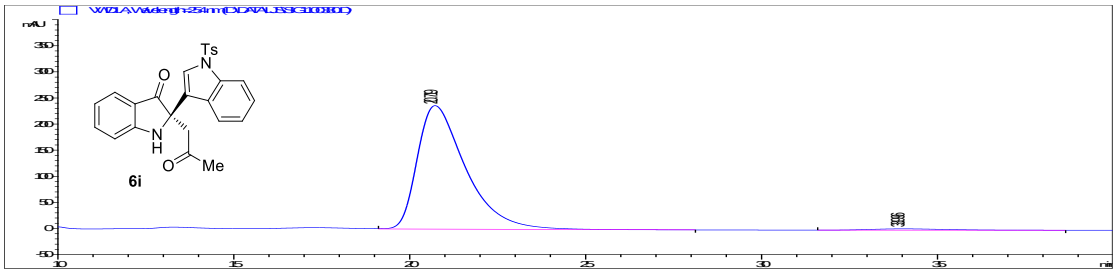
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	26.536	16626.4	247	1.024	0.727	50.052
2	40.396	16592	135.4	1.7504	0.322	49.948



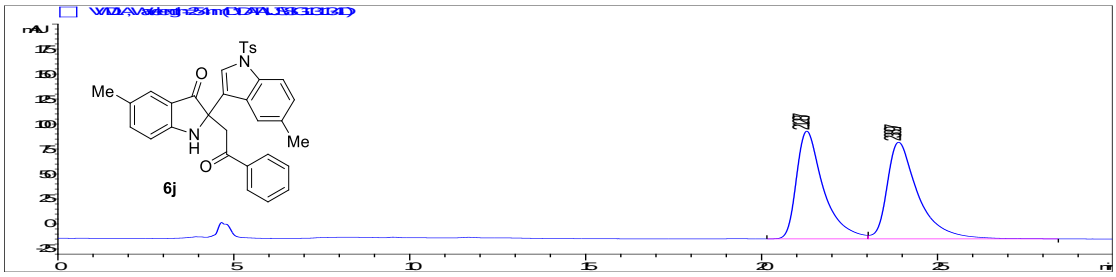
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	26.774	44178.5	623.8	1.0941	0.895	96.899
2	42.117	1414	9.7	2.1142	0.463	3.101



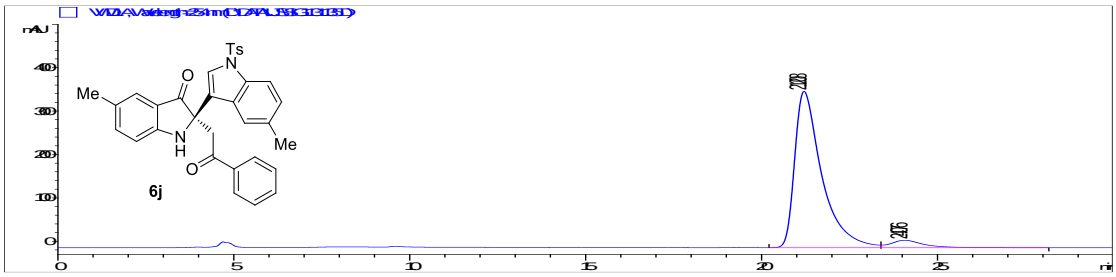
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	21.128	24636.6	250.7	1.4843	0.526	50.238
2	33.411	24403.6	165.5	2.2531	0.529	49.762



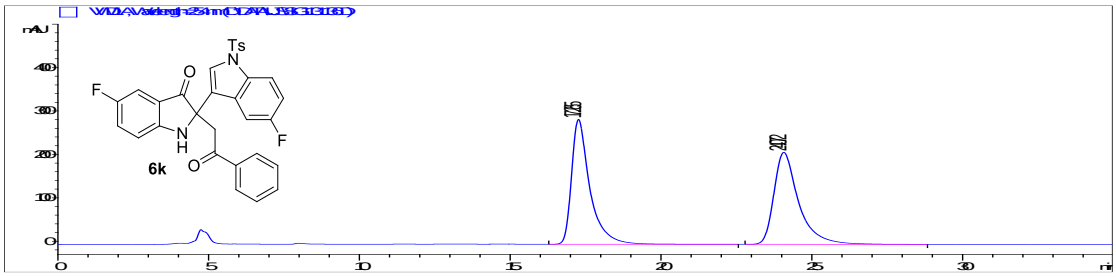
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	20.719	22598.3	236.6	1.4552	0.54	98.386
2	33.996	370.8	2.5	1.7358	0.68	1.614



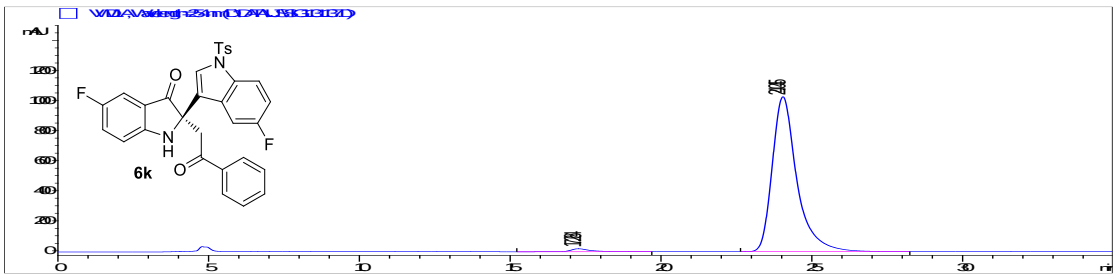
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	21.287	5734	107.7	0.7929	0.572	49.203
2	23.897	5919.8	96.6	0.8956	0.546	50.797



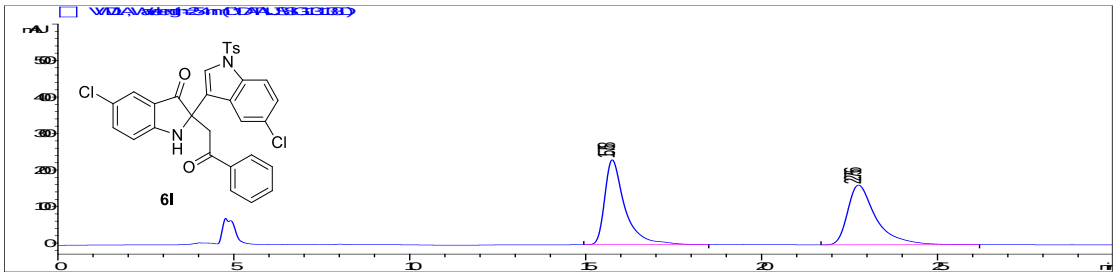
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	21.208	19246.4	360.3	0.7892	0.487	94.447
2	24.076	1131.7	17.1	0.9583	0.662	5.553



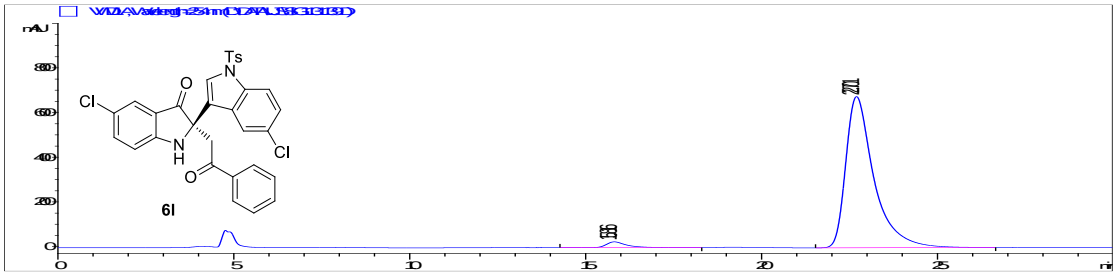
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	17.265	12103.9	287.4	0.6225	0.56	50.116
2	24.072	12047.8	211.8	0.8471	0.612	49.884



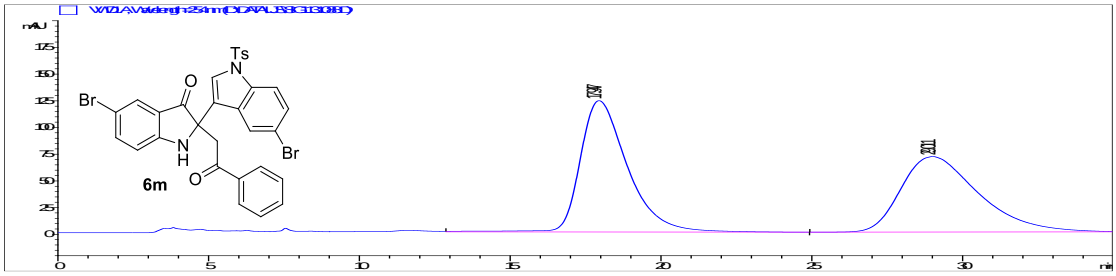
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	17.264	881	19.6	0.6583	0.605	1.486
2	24.045	58408.4	1030.1	0.8566	0.708	98.514



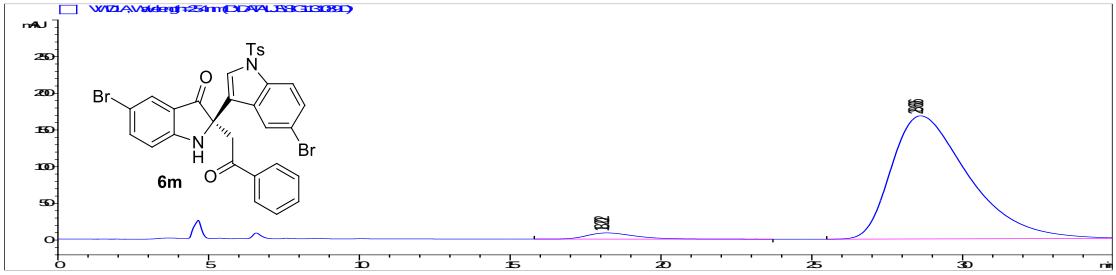
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	15.758	9247.7	232.4	0.5866	0.542	50.217
2	22.756	9167.9	163.7	0.8251	0.571	49.783



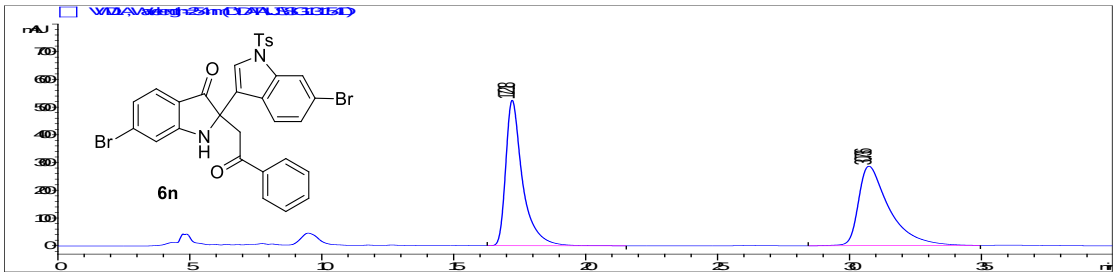
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	15.816	1066.7	26	0.6042	0.617	2.755
2	22.701	37652.2	677.1	0.8322	0.567	97.245



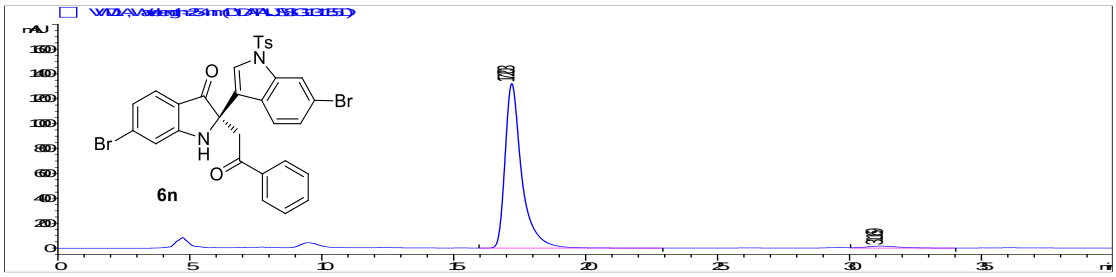
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	17.947	13430.2	123	1.6471	0.636	51.486
2	29.011	12655.2	70.8	2.6105	0.645	48.514



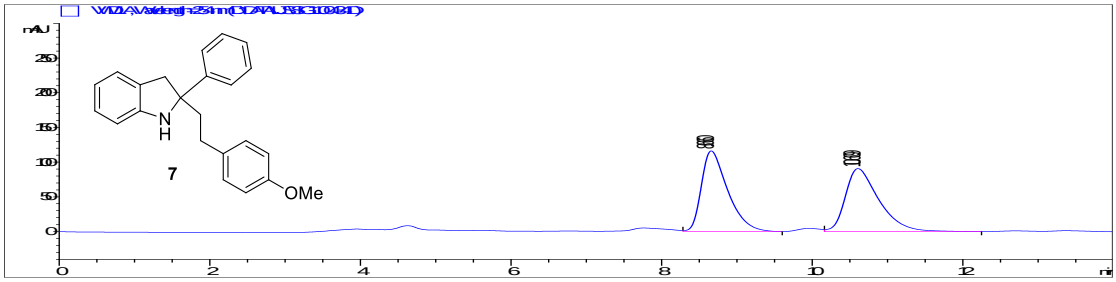
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	18.202	939.1	8.5	1.6793	0.659	3.045
2	28.606	29903.9	167.7	2.7558	0.562	96.955



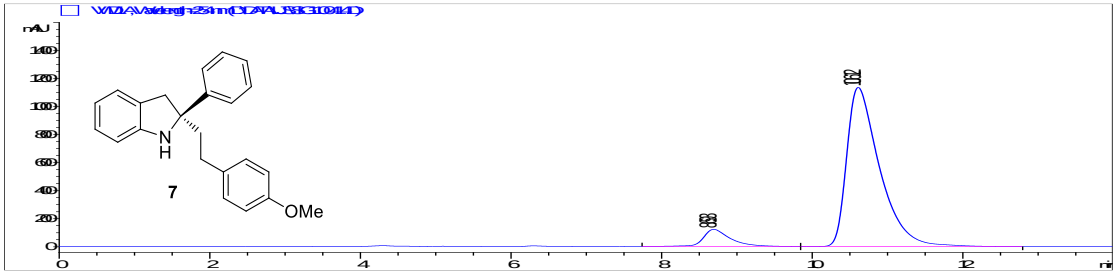
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	17.218	23196.8	525	0.6523	0.57	49.992
2	30.736	23204.6	286.7	1.18	0.479	50.008



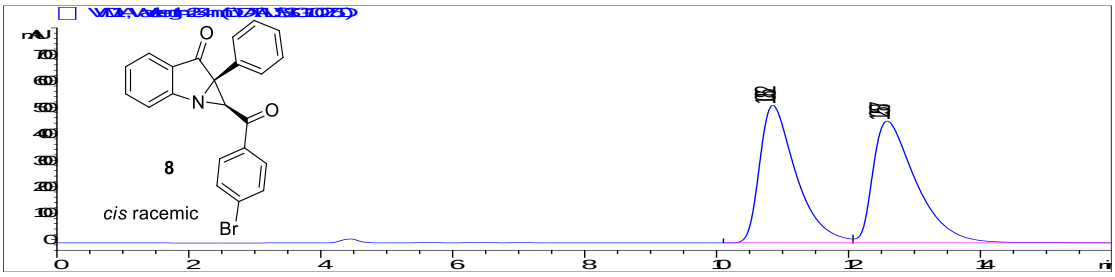
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	17.203	57824.7	1322.4	0.6499	0.616	97.624
2	31.169	1407.5	16.2	1.2896	0.746	2.376



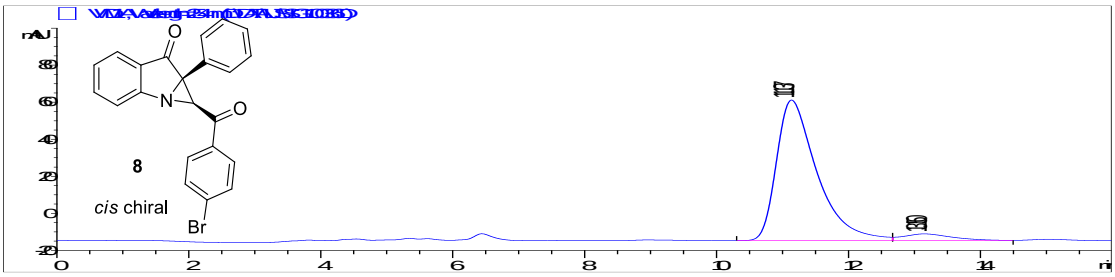
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.66	2821.5	116.2	0.3649	0.565	50.092
2	10.609	2811.1	90.7	0.4664	0.572	49.908



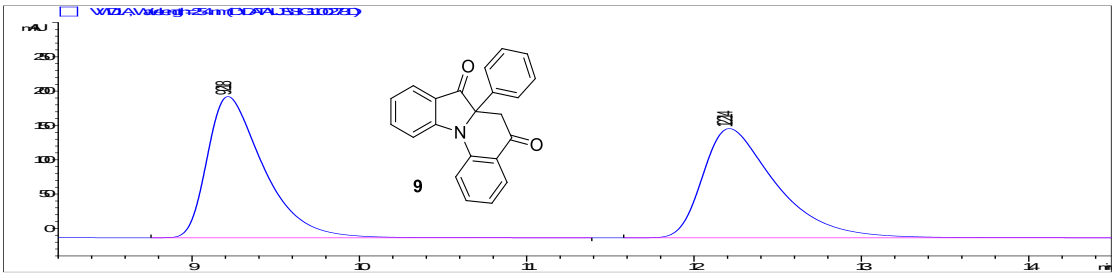
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.693	3111.4	122.4	0.3693	0.622	8.296
2	10.612	34394.5	1134.2	0.4528	0.501	91.704



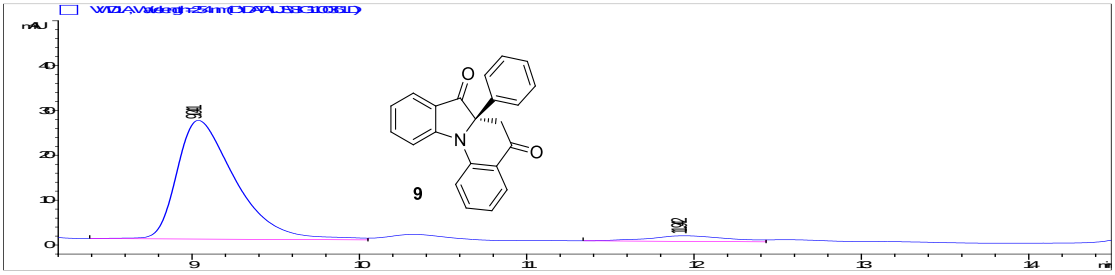
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	10.852	19992.3	519.7	0.5769	0.522	48.872
2	12.587	20915.5	460.1	0.6876	0.458	51.128



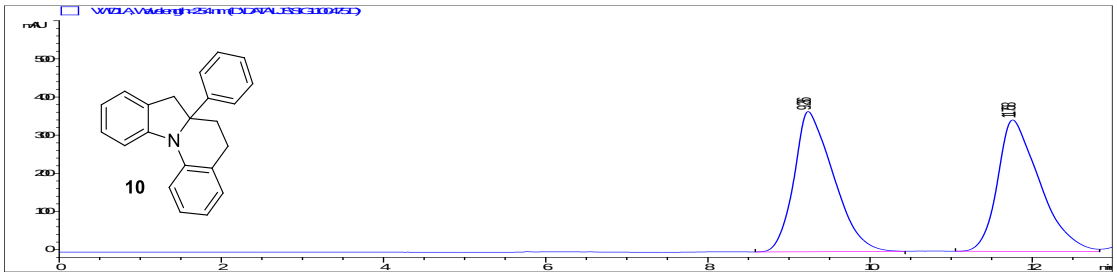
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.137	3227.6	75.8	0.6336	0.55	94.878
2	13.15	174.2	3.5	0.6884	0.734	5.122



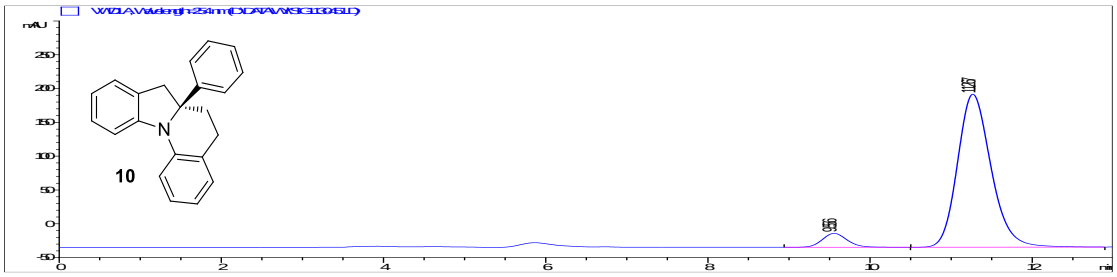
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	9.217	4817.1	205.7	0.3518	0.538	49.795
2	12.214	4856.8	159.2	0.455	0.528	50.205



Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	9.041	642.4	26.5	0.3706	0.544	93.954
2	11.942	41.3	1.3	0.475	0.793	6.046



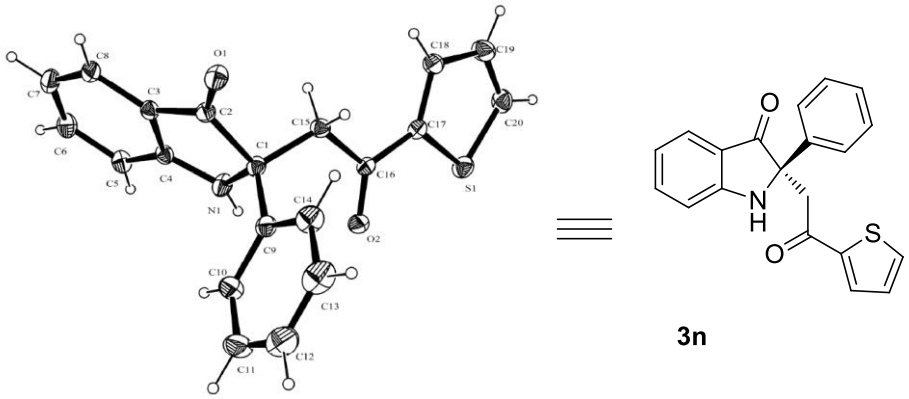
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	9.041	642.4	26.5	0.3706	0.544	93.954
2	11.942	41.3	1.3	0.475	0.793	6.046



Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	9.556	433.9	20.4	0.3293	0.863	6.272
2	11.267	6484.9	226.2	0.4451	0.796	93.728

X-Ray crystallographic data

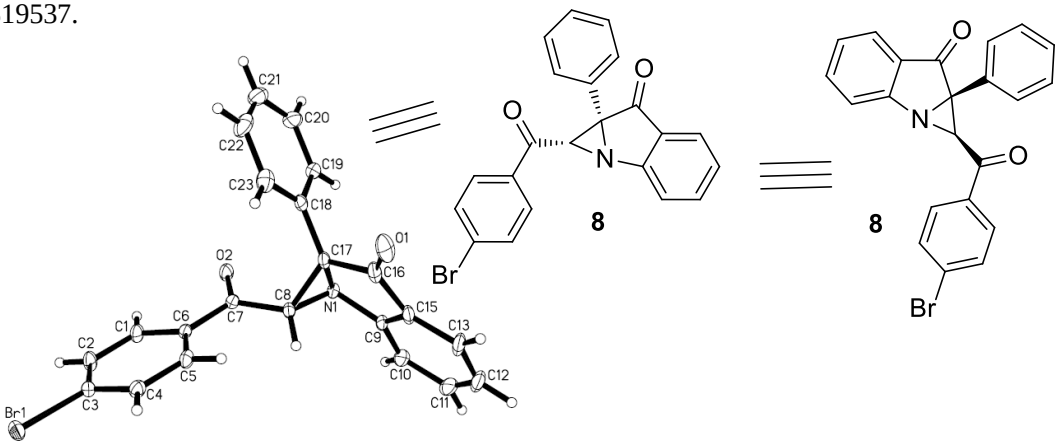
The X-ray crystallographic structures for **3n**. ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC, number 1852757.



3n

Empirical formula	$C_{20}H_{15}NO_2S.DMSO$
Identification code	chq_0629
Formula weight	411.52
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 7.94450(9) Å alpha = 90 deg. b = 10.19612(12) Å beta = 90 deg. c = 25.8377(2) Å gamma = 90 deg.
Volume	2092.94(4) $Å^3$
Z, Calculated density	4, 1.306 Mg/m^3
Absorption coefficient	2.488 mm^{-1}
F (000)	864
Crystal size	0.12 x 0.1 x 0.08 mm^3
Theta range for data collection	3.421 to 66.592 deg.
Limiting indices	-9<=h<=9, -12<=k<=12, -30<=l<=30
Reflections collected / unique	43576/ 3709 [R(int) = 0.0293]
Completeness to theta = 66.592	100.0 %
Max. and min. transmission	1.00000 and 0.86200
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3709 / 0 / 255
Goodness-of-fit on F^2	1.078
Final R indices [I>2sigma(I)]	R_1 = 0.0327, wR_2 = 0.0896
R indices (all data)	R_1 = 0.0337, wR_2 = 0.0905
Absolute structure parameter	0.002(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.211 and -0.349 e.$Å^{-3}$

The X-ray crystallographic structures for **8**. ORTEP representation with 50% probability thermal ellipsoids. Solvent is omitted for clarity. Crystal data have been deposited to CCDC, number 1819537.



Empirical formula	$C_{22}H_{14}BrNO_2.CHCl_3$
Identification code	b
Formula weight	523.61
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.9551(9) Å alpha = 102.790(2) deg. b = 10.2283(9) Å beta = 98.700(2) deg. c = 11.7216(9) Å gamma = 103.152(2) deg.
Volume	1107.55(16) $Å^3$
Z, Calculated density	2, 1.570 Mg/m^3
Absorption coefficient	2.238 mm^{-1}
F (000)	524
Crystal size	0.45 x 0.34 x 0.24 mm^3
Theta range for data collection	2.40 to 25.00 deg.
Limiting indices	-11<=h<=11, -12<=k<=12, -13<=l<=13
Reflections collected / unique	19987 / 3879 [R(int) = 0.0469]
Completeness to theta = 25.00	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3879 / 0 / 271
Goodness-of-fit on F^2	0.931
Final R indices [I>2sigma(I)]	R_1 = 0.0380, wR_2 = 0.1136
R indices (all data)	R_1 = 0.0509, wR_2 = 0.1217
Extinction coefficient	n/a
Largest diff. peak and hole	0.565 and -0.526 $e.Å^{-3}$