Supporting Information

Copper-Catalyzed Enantioselective Mukaiyama aldol Reaction of Silyl Enol Ethers with isatins

Jindong Li,[a] Yanan Li,[a] Jianan Sun,[a] Yang Gui,[a] Yekai Huang,[a] Zhenggen Zha[a] and Zhiyong Wang*[a]

[a]Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Soft Matter Chemistry & Center for Excellence in Molecular Synthesis of Chinese Academy of Sciences, Collaborative Innovation Center of Suzhou Nano Science and Technology & School of Chemistry and Materials Science in University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Fax: (+86)551-63603185
E-mail: zwang3@ustc.edu.cn

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Part I Experimental Section

1.1 General information

^{1}H NMR and ^{13}C NMR were recorded on a Bruker-400MHz Spectrometer (^{1}H NMR: 400MHz, ^{13}C NMR: 100MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz, respectively. HPLC analysis was carried out on an Agilent 1100 series HPLC with a multiple wavelength detector. Chiralpak AD-H columns were purchased from Daicel Chemical Industries, LTD. Optical rotations were measured on a PerKinElmer™ Polarimeter (Model 343). HRMS (ESI) were recorded on a Waters™ Q-TOF Premier. IR spectra were recorded on Thermo Scientific Nicolet iS10. Commercially available compounds were used without further purification. Solvents were purified according to the standard procedures unless otherwise noted. Ligands[1], various silyl enol ethers [2], N-methyl isatin[3], N-benzyl isatin[4], were prepared according to literature procedures.

1.2 General procedures of the Mukaiyama aldol reactions (3ab as an example)

A mixture of Ligand (**L_4**, 5.6 mg, 0.01 mmol), $CuBr_2$ (2.2 mg, 0.01 mmol), $AgSbF_6$ (6.86 mg, 0.02 mmol), N-Ethylmorpholine (1.27 μL, 0.01 mmol) in *i*-PrOH (1.0 mL) was stirred for 1.5h at ambient atmosphere. Then centrifugal to remove the precipitate, and isatin **1a** (14.7 mg, 0.1 mmol) and water (20 uL, 1 mmol) were added to the supernatant. And the resulting mixture was cooled to -10 °C. After 30 min, the silicon enolates **2b** (100 uL, 0.45mmol) was added slowly and carried out at -10 °C. After reactions were finished (monitored by TLC), and extracted with ethyl acetate (3 × 3 mL). The organic phase was dried with Na_2SO_4 and evaporated in vacuum. Purification by flash column chromatograph (petroleum ether / ethyl acetate = 2:1) afforded **3ab** as a white solid: 91% yield, 26.6mg, 97% ee, >20:1 dr.

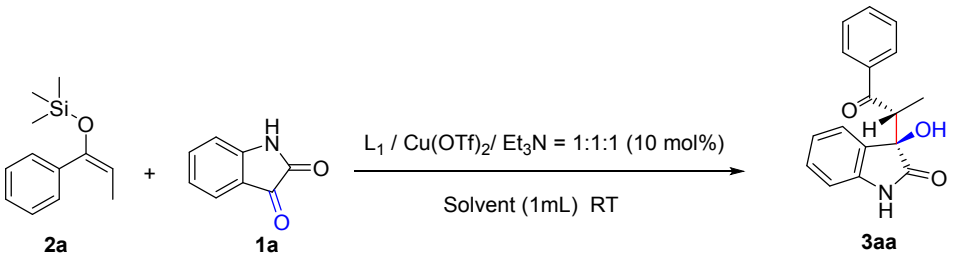
1.3 Procedure for Asymmetric Mukaiyama aldol reaction on a gram scale

A mixture of Ligand (**L_4**, 112 mg, 0.2 mmol), $CuBr_2$ (44 mg, 0.2 mmol), $AgSbF_6$ (137.2 mg, 0.4 mmol), N-Ethylmorpholine (27.8 μL, 0.2 mmol) in *i*-PrOH (20 mL) was stirred for 1.5 h at ambient atmosphere. Then centrifugal to remove the precipitate, and isatin **1c** (1.8 g, 10 mmol) and water (2 mL, 0.1 mol) were added to the supernatant. And the resulting mixture was cooled to -10 °C. After 30 min, the silicon enolates **2b** (10 mL, 45mmol) was added slowly

and carried out at -10 °C. After reactions were finished (monitored by TLC), and extracted with ethyl acetate (3 × 50 mL). The organic phase was dried with Na_2SO_4 and evaporated in vacuum. Purification by flash column chromatograph (petroleum ether / ethyl acetate = 2:1) afforded **3cb** as a white solid: 91% yield, 2.9g, 99% ee, 11:1 dr.

1.4 Optimization of the reaction conditions for the model reaction[a]

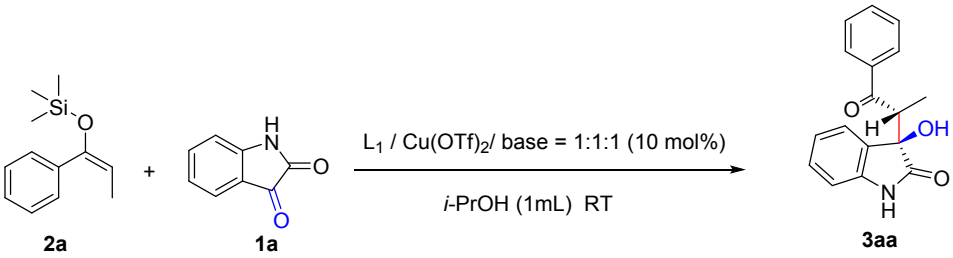
(a) Effect of solvent:[a]



entry	solvent	yield[b] (%)	ee[c] (%)	dr[d]
1	MeOH	81	69	2:1
2	EtOH	74	73	3:1
3	*i*-PrOH	80	81	3:1
4	CF_3CH_2OH	38	11	1:1
5	MTBE	45	25	2:1
6	THF	57	73	2:1

[a]Unless otherwise noted, the reaction of **1a** (0.1 mmol) and **2a** (0.45 mmol) was performed in the presence of $\mathbf{L_1}$ (10 mol %), Et_3N (10 mol %), and $Cu(OTf)_2$ (10 mol %) in solvent (1.0 mL) at RT. [b]Isolated yield. [c] Determined by chiral HPLC analysis. [d] Determined by crude ^1H NMR.

(b) Effect of bsae:[a]

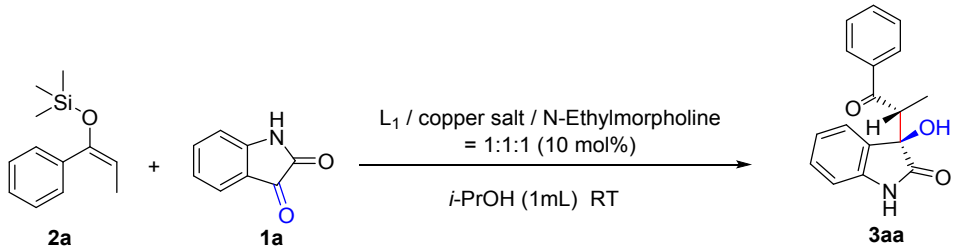


entry	base	yield[b] (%)	ee[c] (%)	dr[d]
1	Et_3N	81	81	3:1

2	DBU	61	81	3:1
3	N-Ethylmorpholine	80	83	3:1
4	Piperidine	82	77	3:1
5	DABCO	79	82	3:1
6	DIPEA	80	59	3:1
7	Li_2CO_3	63	73	3:1
8	Cs_2CO_3	78	71	3:1
9	*t*-BuOK	70	79	3:1

[a]Unless otherwise noted, the reaction of **1a** (0.1 mmol) and **2a** (0.45 mmol) was performed in the presence of $\mathbf{L_1}$ (10 mol %), base (10 mol %), and $Cu(OTf)_2$ (10 mol %) in *i*-PrOH (1.0 mL) at RT. [b]Isolated yield. [c] Determined by chiral HPLC analysis. [d] Determined by crude ^{1}H NMR.

(b) Effect of copper salts:[a]

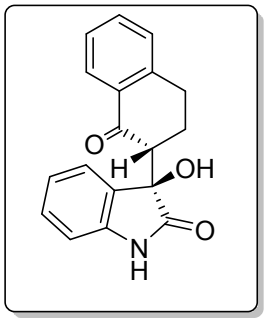


entry	copper salt	yield[b] (%)	ee[c] (%)	dr[d]
1	$Cu(OTf)_2$	80	83	3:1
2	$Cu(OAc)_2{\cdot}H_2O$	44	55	2:1
3	$CuCl_2{\cdot}2H_2O$	72	79	3:1
4	$CuBr_2$	70	67	3:1
5	$CuClO_4{\cdot}6H_2O$	61	81	3:1
6	$Cu(SbF_6)_2$	83	83	5:1

[a]The reaction of **1a** (0.1 mmol) and **2a** (0.45 mmol) was performed in the presence of $\mathbf{L_1}$ (10 mol %), N-Ethylmorpholine (10 mol %), and copper salt (10 mol %) in *i*-PrOH (1.0 mL) at RT. [b]Isolated yield. [c] Determined by chiral HPLC analysis. [d] Determined by crude ^{1}H NMR.

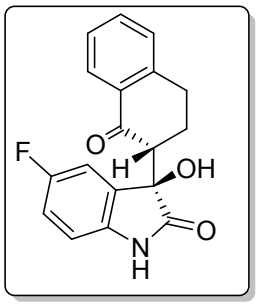
1.5 Experimental data of 3-substituted 3-hydroxy-2-oxindole

(R)-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3ab)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 91% yield, 26.6 mg; mp = 176-178 °C; $[\alpha]_D^{20}$ +101.4 (c = 0.49, $CHCl_3$, 97% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R = 7.9 min (minor), t_R = 20.4 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.91-7.89 (dd, J_1 = 9.1 Hz, J_2 = 1.2 Hz, 1H), 7.47-7.43 (td, J_1 = 7.5 Hz, J_2 = 1.4 Hz, 1H), 7.28-7.18 (m, 4H), 6.91-6.85 (m, 2H), 3.33-3.28 (m, 1H), 3.04-2.95 (m, 1H), 2.86-2.80 (dt, J_1 = 16.7 Hz, J_2 = 3.8 Hz, 1H), 2.21-2.15 (m, 1H), 1.75-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 177.3,144.4, 141.1, 134.6, 132.2, 129.85, 129.83, 128.8, 127.5, 127.0, 124.9, 123.2, 110.7, 79.3, 51.9, 28.5, 24.6; IR (film, ν/cm-1):3281, 2452, 1708, 1670, 1612, 1597, 1479, 1468, 1458, 1353, 1336, 1317, 1228, 1205, 1153, 1090, 1069, 767, 745; HRMS (ESI) m/z calcd for $C_{18}H_{15}NO_3$ $[M+H]^+$ 294.1130, found 294.1134.

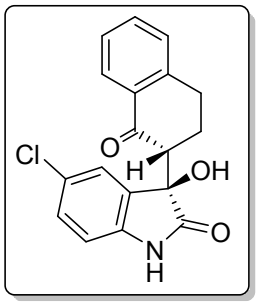
(R)-5-fluoro-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3bb)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 90% yield, 28.0 mg; mp = 205-207 °C; $[\alpha]_D^{20}$ +15.2 (c = 0.33, $CHCl_3$, 91% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 230 nm, t_R = 7.8 min (minor), t_R = 20.1 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.92-7.90 (d, J = 7.4 Hz, 1H), 7.52-7.48 (td, J_1 = 7.4 Hz, J_2 = 1.2 Hz, 1H), 7.31-7.24 (m, 2H), 7.07-7.05 (dd, J_1 = 8.2Hz, J_2 = 2.5 Hz, 1H), 6.99-6.94 (m, 1H), 6.88-6.84 (m, 1H), 3.39-3.35 (m, 1H), 3.09-3.03 (m, 1H), 2.96-2.90 (m, 1H), 2.32-2.26 (m, 1H), 1.89-1.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 177.1, 159.2 ($^1J_{CF}$=240.4 Hz), 144.3, 136.9 ($^4J_{CF}$= 1.9 Hz), 134.8, 132.0, 131.3 ($^3J_{CF}$= 7.6 Hz), 128.8, 127.7, 127.1, 116.2 ($^2J_{CF}$=23.4 Hz), 113.1 ($^2J_{CF}$=25.0 Hz), 111.4 ($^3J_{CF}$= 7.8 Hz), 79.5, 51.9, 28.5, 24.5; IR (film, ν/cm^{-1}):3236, 2921, 2850, 2361, 1716, 1627, 1597, 1478, 1456, 1304, 1262, 1104, 778, 750; HRMS (ESI) m/z calcd for $C_{18}H_{14}FNO_3$ $[M+H]^+$ 312.1036, found 312.1036. ‘

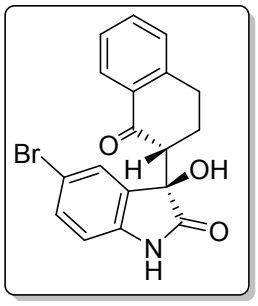
(R)-5-chloro-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3cb)

The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 95% yield, 31.1 mg; mp = 198-201 °C; $[\alpha]_D^{20}$ +101.2 (c = 0.39, $CHCl_3$, 99% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R



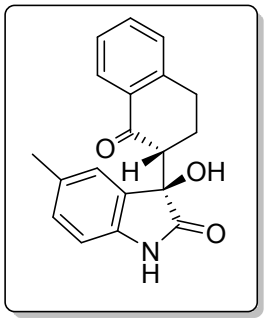
= 8.1 min (minor), t_R = 20.6 min (major); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.39 (s, 1H), 7.70-7.68 (m, 1H), 7.55-7.50 (m, 1H), 7.34-7.29 (m, 3H), 7.24-7.22 (m, 1H), 6.84-6.82 (m, 1H), 6.18 (s, 1H), 3.64-3.60 (dd, J_1 = 13.6 Hz, J_2 = 4.0 Hz, 1H), 3.12-2.99 (m, 2H), 2.62-2.58 (m, 1H), 2.32-2.20 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 197.8, 178.1, 144.9, 142.1, 136.2, 134.0, 132.7, 129.3, 126.9, 126.6, 125.6, 123.8, 111.1, 74.3, 54.7, 24.2, 21.2; IR (film, ν/cm^{-1}):3347, 2941, 2360, 1735, 1716, 1667, 1620, 1597, 1482, 1367, 1315, 1149, 884, 831, 813, 795, 750; HRMS (ESI) m/z calcd for $C_{18}H_{14}ClNO_3$ $[M+H]^+$ 328.0740, found 328.0737.

(R)-5-bromo-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3db)



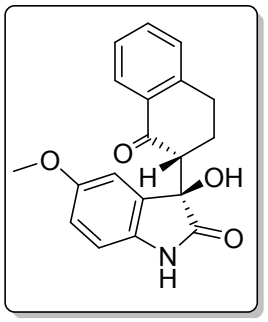
The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 89% yield, 33.1 mg; mp = 188-190 °C; $[\alpha]_D^{20}$ +22.3 (c = 0.30, $CHCl_3$, 97% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 254 nm, t_R = 18.4 min (minor), t_R = 22.4 min (major); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.39 (s, 1H), 7.69-7.67 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H), 7.55-7.51 (td, J_1 = 7.4 Hz, J_2 = 1.4 Hz, 1H), 7.42-7.41 (d, J = 2.0 Hz, 1H), 7.37-7.27 (m, 3H), 6.79-6.77 (d, J = 8.2 Hz, 1H), 6.16 (s, 1H), 3.64-3.60 (dd, J_1 = 13.6 Hz, J_2 = 4.0 Hz, 1H), 3.12-2.98 (m, 2H), 2.61-2.57 (m, 1H), 2.30-2.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 176.3, 144.2, 139.9, 134.8, 132.7, 132.0, 131/.9, 128.8, 128.3, 127.6, 127.1, 116.0, 112.0, 79.0, 51.9, 28.6, 24.5; IR (film, ν/cm^{-1}): 3339, 2918, 2849, 2476, 1716, 1667, 1615, 1598, 1365, 1314, 1228, 1171, 1147, 1113, 883, 827; HRMS (ESI) m/z calcd for $C_{18}H_{14}BrNO_3$ $[M+H]^+$ 372.0235, found 372.0234.

(R)-3-hydroxy-5-methyl-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3eb)



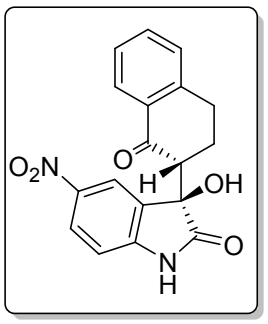
The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 91% yield, 27.9 mg; mp = 175-177 °C; $[\alpha]_D^{20}$ +168.6 (c = 0.7, $CHCl_3$, 98% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 254 nm, t_R = 7.9 min (minor), t_R = 15.1 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.96-7.93 (dd, J_1 = 7.9 Hz, J_2 = 1.1 Hz, 1H), 7.52-7.47 (td, J_1 = 7.5 Hz, J_2 = 1.4 Hz, 1H), 7.33-7.29 (t, J = 7.5 Hz, 1H), 7.25-7.23 (d, J = 7.6 Hz, 1H), 7.07-7.02 (m, 2H), 6.78-6.76 (d, J = 7.8 Hz, 1H), 3.34-3.30 (m, 1H), 3.07-2.99 (m, 1H), 2.89-2.82 (dt, J_1 = 16.8 Hz, J_2 = 3.8 Hz, 1H), 2.22-2.17 (m, 4H), 1.77-1.67 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 199.6, 178.3, 144.4, 139.6, 133.8, 132.6, 131.9, 130.9, 129.4, 128.5, 126.5, 126.3, 124.8, 109.6, 77.3, 53.0, 28.3, 24.3, 19.7; IR (film, ν/cm^{-1}): 3339, 2918, 2849, 2476, 1716, 1667, 1615, 1598, 1365, 1314, 1228, 1171, 1147, 1113, 883, 827; HRMS (ESI) m/z calcd for $C_{19}H_{18}NO_3$ $[M+H]^+$ 308.1287, found 308.1287.

(R)-3-hydroxy-5-methoxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3fb)



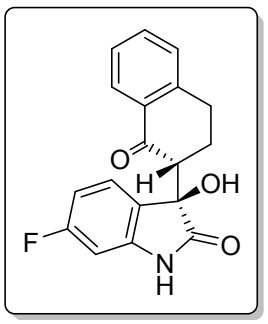
The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a yellow oil: 88% yield, 28.4 mg; $[\alpha]_D^{20}$ +17.0 (c = 0.24, $CHCl_3$, 92% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R = 10.3 min (minor), t_R = 20.2 min (major); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.09 (s, 1H), 7.72-7.70 (m, 1H), 7.54-7.50 (td, J_1 = 7.3 Hz, J_2 = 1.3 Hz, 1H), 7.32-7.28 (m, 2H), 6.87-6.86 (m, 1H), 6.75-6.70 (m, 2H), 6.0 (s, 1H), 3.63 (s, 3H), 3.50-3.45 (dd, J_1 = 13.3 Hz, J_2 = 4.1 Hz,1H), 3.09-2.92 (m, 2H), 2.54-2.51 (m, *1*H), 2.21-2.10 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 199.5, 178.2, 156.0, 144.4, 135.2, 133.8, 132.6, 131.9, 128.5, 126.5, 126.4, 113.9, 111.2, 110.3, 77.6, 54.7, 53.0, 28.2, 24.3; IR (film, ν/cm^{-1}): 3262, 2918, 2849, 2361, 1718, 1676, 1598, 1353, 1301, 1261, 1204, 1155, 871, 806; HRMS (ESI) m/z calcd for $C_{19}H_{17}NO_4$ $[M+H]^+$ 324.1236, found 324.1234.

(R)-3-hydroxy-5-nitro-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3gb)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a yellow oil: 75% yield, 25.3 mg; $[\alpha]_D^{20}$ +98.8 (c = 0.47, $CHCl_3$, 99% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R = 9.8 min (minor), t_R = 30.4 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 8.15-8.09 (m, 2H), 7.73-7.71 (d, J = 7.8 Hz, 1H), 7.42-7.38 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.21-7.15 (m, 2H), 6.97-6.95 (d, J = 8.0 Hz, 1H), 3.49-3.43 (dd, J_1 = 13.7 Hz, J_2 = 4.0 Hz, 1H), 3.09-3.01 (m, 1H), 2.96-2.90 (dt, J_1 = 16.0 Hz, J_2 = 3.8 Hz, 1H), 2.49-2.43 (m, 1H), 2.10-2.03 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 198.3, 178.9, 148.8, 144.4, 143.1, 133.6, 133.5, 132.3, 129.4, 128.5, 126.4, 126.2, 125.9, 119.1, 109.4, 74.9, 54.5, 28.9, 24.0; IR (film, ν/cm^{-1}): 3263, 2917, 2849, 2458, 1712, 1676, 1617, 1595, 1330, 1360, 1217, 1063, 975, 871, 799, 753; HRMS (ESI) m/z calcd for $C_{18}H_{14}N_2O_5$ $[M+Na]^+$ 361.0800, found 361.0793.

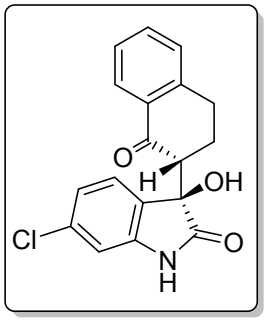
(R)-6-fluoro-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3hb)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 85% yield, 26.4 mg, mp = 229-231 °C; $[\alpha]_D^{20}$ +162.9 (c = 0.41, $CHCl_3$, 98% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R = 8.3 min (minor), t_R = 24.6 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.93-7.91 (d, J = 7.8 Hz, 1H), 7.53-7.49 (m, 1H), 7.33-7.27 (m, 3H), 6.71-6.66 (m, 2H), 3.41-3.36 (dd, J_1 = 13.4 Hz, J_2 = 4.1 Hz, 1H), 3.09-3.04 (m, 1H), 2.97-2.91 (dt, J_1 = 16.7 Hz, J_2 = 3.7 Hz, 1H), 2.33-2.27 (m, 1H), 1.91-1.80 (m, 1H), 2.15-2.03 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 199.1, 178.7, 163.6 (^1J=243.2 Hz), 144.3, 144.0 (^3J=12.1 Hz), 133.7, 132.5, 128.5, 127.0 (^4J= 3.1 Hz),

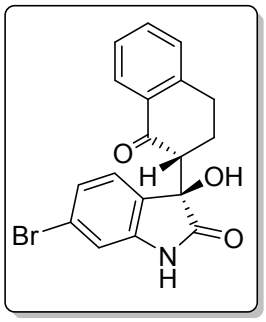
126.5, 126.3, 125.4 (^3J= 9.9 Hz), 107.9 (^2J= 22.2 Hz), 98.1 (^2J=27.3 Hz), 76.2, 53.5, 28.5, 24.3**;** IR (film, ν/cm^{-1}): 3263, 2917, 2849, 2458, 1712, 1676, 1617, 1595, 1330, 1360, 1217, 1063, 975, 871, 799, 753; HRMS (ESI) m/z calcd for $C_{18}H_{14}FNO_3$ $[M+Na]^+$ 334.0855, found 334.0854.

(R)-6-chloro-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3ib)



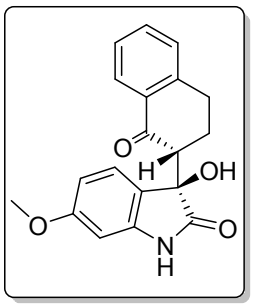
The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a yellow oil: 87% yield, 28.8mg; $[\alpha]_D^{20}$ +123.9 (c = 0.72, $CHCl_3$, 93% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R = 8.7 min (minor), t_R = 34.1 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.89-7.86 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 1H), 7.51-7.47 (td, J_1 = 7.4 Hz, J_2 = 1.4 Hz, 1H), 7.30-7.22 (m, 3H), 6.94-6.91 (m, 2H), 3.39-3.35 (dd, J_1 = 13.5 Hz, J_2 = 4.2 Hz, 1H), 3.11-3.02 (m, 1H), 2.96-2.90 (dt, J_1 = 16.6 Hz, J_2 = 3.8 Hz, 1H), 2.35-2.28 (m, 1H), 1.93-1.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 176.7, 144.3, 142.1, 135.5, 134.7, 132.1, 128.8, 128.2, 127.5, 127.0, 126.1, 123.2, 111.1, 78.7, 51.9, 28.5, 24.6**;** IR (film, ν/cm^{-1}): 3262, 2921, 2850, 2361, 1721, 1610, 1597, 1482, 1454, 1360, 1317, 1183, 1156, 892, 855; HRMS (ESI) m/z calcd for $C_{18}H_{14}ClNO_3$ $[M+H]^+$ 328.0740, found 328.0738.

(R)-6-bromo-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3jb)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 89% yield, 33.1mg, mp = 202-205 °C; $[\alpha]_D^{20}$ +98.8 (c = 0.52, $CHCl_3$, 93% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 254 nm, t_R = 9.2 min (minor), t_R = 37.2 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.88-7.86 (m, 1H), 7.50-7.46 (td, J_1 = 7.4 Hz, J_2 = 1.3 Hz, 1H), 7.29-7.24 (m, 2H), 7.18-7.16 (m, 1H), 7.09-7.05 (m, 2H), 3.39-3.35 (dd, J_1 = 13.5 Hz, J_2 = 4.2 Hz, 1H), 3.10-302 (m, 1H), 2.96-2.90 (dt, J_1 = 16.5 Hz, J_2 = 3.8 Hz, 1H), 2.35-2.29 (m, 1H), 1.94-1.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 176.7, 144.3, 142.2, 134.7, 132.1, 128.8, 128.7, 127.5, 127.0, 126.4, 126.2, 123.4, 114.0, 78.8, 51.8, 28.8, 24.8**;** IR (film, ν/cm^{-1}): 3308, 2919, 2870, 2848, 2460, 1706, 1673, 1602, 1478, 1454, 1323, 1304, 1153, 1114, 867, 805; HRMS (ESI) m/z calcd for $C_{18}H_{14}BrNO_3$ $[M+H]^+$ 372.0235, found 372.0236.

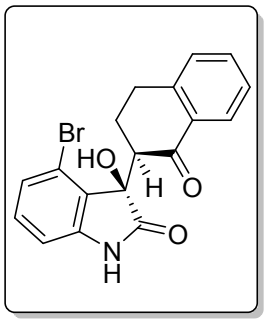
(R)-3-hydroxy-6-methoxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3kb)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 84% yield, 27.1mg, mp = 182-184 °C; $[\alpha]_D^{20}$ +110.3 (c = 0.95, $CHCl_3$, 95% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate =

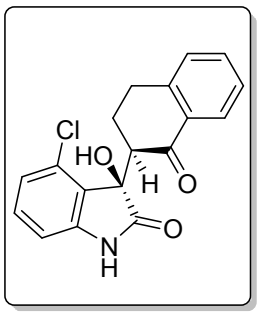
1.0 mL/min, T = 23°C, UV = 230 nm, t_R = 11.5 min (minor), t_R = 41.6 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.95-7.93 (d, *J* = 7.8 Hz, 1H), 7.50-7.46 (m, 1H), 7.31-7.27 (t, *J* = 7.4 Hz, 1H), 7.23-7.22 (d, *J* = 7.5 Hz, 1H), 7.15-7.13 (d, *J* = 8.2 Hz, 1H), 6.48-6.43 (m, 2H), 3.73 (s, 3H), 3.29-3.26 (m, 1H), 3.06-2.97 (m, 1H), 2.86-2.82 (m, 1H) 2.16-2.10 (m, 1H), 1.70-1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 177.6, 161.1, 144.4, 142.3, 134.5, 132.2, 128.8, 127.4, 126.9, 125.9, 121.6, 107.8, 97.7, 78.9, 55.4, 52.1, 28.5, 24.6**;** IR (film, ν/cm^{-1}): 3292, 2917, 2849, 2476, 1723, 1675, 1618, 1597, 1353, 1305, 1261, 1215, 1174, 1155, 1108, 890, 860, 837, 813; HRMS (ESI) m/z calcd for $C_{19}H_{17}NO_4$ $[M+Na]^+$ 346.1055, found 346.1053.

(R)-4-bromo-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3lb)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a yellow oil: 83% yield, 30.8 mg; $[\alpha]_D^{20}$ +96.4 (c = 0.42, $CHCl_3$, 98% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R = 8.3 min (minor), t_R = 60.6 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.73-7.71 (d, *J* = 7.8 Hz, 1H), 7.50-7.47 (t, *J* = 7.4 Hz, 1H), 7.32-7.31 (d, *J* = 7.6 Hz, 1H), 7.26-7.22 (t, *J* = 7.5 Hz, 1H), 7.15-7.07 (m, 2H), 6.90-6.88 (d, *J* = 7.4 Hz, 1H), 4.23-4.18 (dd, J_1 = 16.6 Hz, J_2 = 3.8 Hz, 1H), 3.14-3.04 (m, 2H), 2.82-2.78 (m, 1H), 2.61-2.50 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 198.0, 178.7, 144.8, 144.4, 133.4, 132.4, 130.8, 130.3, 128.5, 126.3, 126.1, 126.0, 117.7, 108.9, 75.8, 53.0, 29.5, 23.3; IR (film, ν/cm^{-1}): 2917, 2849, 1731, 1612, 1582, 1445, 1301, 1259, 1208, 1140, 1073, 872, 751,695; HRMS (ESI) m/z calcd for $C_{18}H_{14}BrNO_3$ $[M+Na]^+$ 394.0055, found 394.0054.

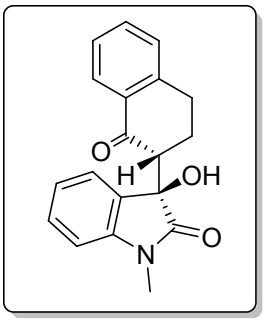
(R)-4-chloro-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3mb)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 89% yield, 29.1 mg, mp = 183-185 °C; $[\alpha]_D^{20}$ +221.1 (c = 0.86, $CHCl_3$, 91% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 254 nm, t_R = 8.5 min (minor), t_R = 57.6 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.68-7.63 (d, *J* = 7.8 Hz, 1H), 7.41-7.38 (t, *J* = 7.2 Hz, 1H), 7.23-7.21 (d, *J* = 7.6 Hz, 1H), 7.17-7.09 (m, 2H), 6.82-6.80 (d, *J* = 8.1 Hz, 1H), 6.76-6.74 (d, *J* = 7.7 Hz, 1H), 3.99-3.95 (dd, J_1 = 13.7 Hz, J_2 = 4.1 Hz, 1H), 3.02-2.99 (m, 2H), 2.71-2.64 (m, 1H), 2.48-2.36 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 198.2, 178.5, 144.5, 144.4, 133.4, 132.4, 130.1, 129.7, 129.1, 128.5, 126.3, 126.1, 122.9, 108.4, 75.5, 52.9, 29.4, 23.4; IR (film, ν/cm^{-1}): 3350, 3205, 2923, 2851, 1979, 1697, 1619, 1593, 1534, 1364, 1317, 1226, 1178, 1123, 935, 907, 889, 822; HRMS (ESI) m/z calcd for $C_{18}H_{14}ClNO_3$ $[M+H]^+$ 328.0740, found 328.0740.

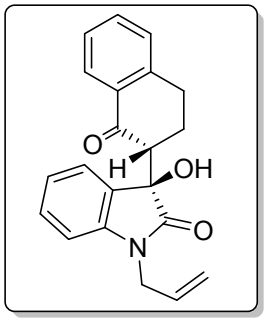
(R)-3-hydroxy-1-methyl-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3nb)

The title compound was prepared according to the general working procedure and purified by flash



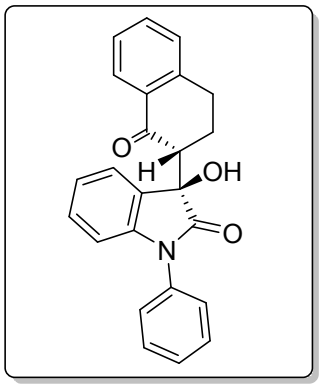
column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a yellow oil: 85% yield, 26.1 mg; $[\alpha]_D^{20}$ +108.1 (c = 0.55, $CHCl_3$, 98% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R = 6.4 min (minor), t_R = 7.8 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.96-7.94 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 1H),7.58-7.54 (m, 1H), 7.40-7.34 (m, 1H), 7.40-7.34 (m, 4H), 7.08-7.06 (m, 2H), 3.51-3.46 (m, 1H), 3.29 (s, 3H), 3.19-3.12 (m, 1H), 3.02-2.96 (m, 1H), 2.37-2.31 (m, 1H), 1.97-1.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 176.6, 144.3, 143.8, 134.5, 132.2, 129.7, 129.4, 128.7, 127.4, 126.9, 124.6, 123.3, 108.4, 78.7, 51.9, 28.5, 26.2, 24.6; IR (film, ν/cm^{-1}): 3403, 3056, 2920, 2849, 2519, 2360, 2068, 1708, 1681, 1610, 1597, 1428, 1376, 1353, 1320, 1221, 1156, 1118, 893, 792; HRMS (ESI) m/z calcd for $C_{18}H_{17}NO_3$ $[M+H]^+$ 308.1287, found 308.128.

(R)-1-allyl-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (3ob)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a yellow oil: 88% yield, 29.3 mg; $[\alpha]_D^{20}$ +95.8 (c = 0.38, $CHCl_3$, 97% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R = 7.9 min (minor), t_R = 9.3 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.87-7.85 (dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H),7.49-7.45 (td, J_1 = 7.4 Hz, J_2 = 1.4 Hz, 1H), 7.31-7.23 (m, 4H), 7.0-6.93 (m, 3H), 5.90-5.83 (m, 1H), 5.38-5.33 (m, 1H), 5.23-5.20 (m, 1H), 4.42-4.28 (m, 2H), 3.44-3.40 (dd, J_1 = 13.4 Hz, J_2 = 4.2 Hz, 1H), 3.09-3.0 (m, 1H), 2.93-2.87 (dt, J_1 = 16.6 Hz, J_2 = 3.8 Hz, 1H), 2.34-2.28 (m, 1H), 1.94-1.83 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 198.9, 176.4, 144.3, 143.1, 133.7, 132.5, 131.2, 131.0, 129.1, 128.5, 126.5, 126.3, 123.4, 122.6, 116.5, 109.3, 76.0, 53.8, 41.7, 28.6, 24.3; IR (film, ν/cm^{-1}): 3387, 3057, 2920, 2520, 1713, 1681, 1610, 1597, 1487, 1357, 1303, 1181, 1102, 988, 929, 809, 792; HRMS (ESI) m/z calcd for $C_{21}H_{19}NO_3$ $[M+H]^+$ 334.1443, found 334.1438.

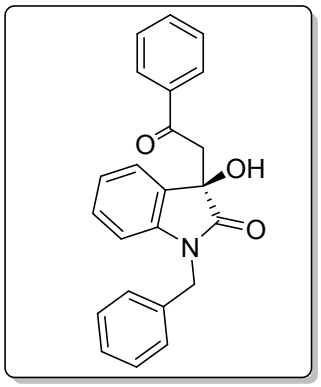
(R)-3-hydroxy-3-((R)-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-1-phenylindolin-2-one (3pb)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a yellow oil: 91% yield, 33.6 mg; $[\alpha]_D^{20}$ +141.3 (c = 0.98, $CHCl_3$, 99% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R = 9.2 min (minor), t_R = 15.2 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.86-7.83 (m, 1H),7.58-7.54 (m, 2H), 7.49-7.44 (m, 4H), 7.39-7.37 (dd, J_1 = 7.4 Hz, J_2 = 0.8 Hz, 1H), 7.28-7.21 (m, 3H), 7.06-7.02 (td, J_1 = 7.5 Hz, J_2 = 0.9 Hz, 1H), 6.74-6.72 (d, J = 7.8 Hz, 1H), 3.56-3.52 (m, 1H), 3.14-3.07 (m, 1H), 3.03-2.97 (dt, J_1 = 16.2 Hz, J_2 = 3.9 Hz, 1H), 2.60-2.53 (m, 1H), 2.20-2.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 174.0, 144.3, 143.8, 134.6, 133.9, 132.2, 129.7, 129.6,

129.3, 128.8, 128.3, 127.5, 127.0, 126.4, 124.9, 123.8, 109.8, 78.8, 52.4, 28.6, 24.7; IR (film, ν/cm^{-1}): 3404, 3062, 2923, 2851, 2516, 1721, 1679, 1610, 1595, 1498, 1480, 1465, 1454, 1359, 1321, 1298, 1176, 1156, 1103, 1050, 893, 839; HRMS (ESI) m/z calcd for $C_{24}H_{19}NO_3$ $[M+H]^+$ 370.1443, found 370.1445.

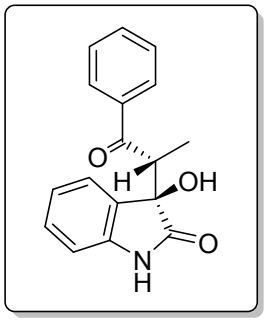
(R)-1-benzyl-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (3qc)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 91% yield, 32.5 mg, mp = 161-164 °C; $[\alpha]_D^{20}$ +66.5 (c = 0.73, $CHCl_3$, 95% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 240 nm, t_R = 9.8 min (minor), t_R = 17.3 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.81-7.79 (d, *J* = 7.4 Hz, 1H), 7.49-7.46 (m, 1H), 7.40-7.33 (m, 3H), 7.25-7.22 (t, *J* = 7.6 Hz, 1H), 7.18-7.14 (t, *J* = 7.2 Hz, 1H), 7.08-7.04 (t, *J* = 7.6 Hz, 1H), 6.88-6.84 (t, *J* = 7.4 Hz, 1H), 6.66-6.64 (d, *J* = 7.8 Hz, 1H), 4.87 (s, 2H), 4.07-4.03 (d, *J* = 17.4 Hz, 1H), 3.74-3.69 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 196.7, 178.1, 143.4, 136.3, 135.9, 133.2, 130.5, 129.1, 128.36, 128.30, 127.7, 127.1, 127.0, 122.9, 122.5, 109.4, 73.4, 45.5, 43.3; IR (film, ν/cm^{-1}): 3028, 2455, 1694, 1673, 1609, 1578, 1487, 1464, 1447, 1388, 1372, 1345, 1297, 1261, 1212, 1179, 1132, 1115, 1091, 1054, 1003, 946, 817, 733; HRMS (ESI) m/z calcd for $C_{23}H_{19}NO_3$ $[M+H]^+$ 358.1443, found 358.1440.

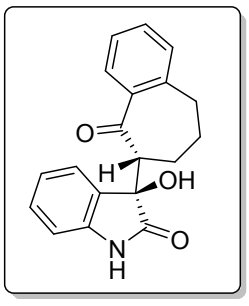
(3R)-3-hydroxy-3-(1-oxo-1-phenylpropan-2-yl)indolin-2-one (3aa)

The title compound was prepared according to the general working procedure and purified by flash



column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a white solid: 91% yield, 28.0 mg, mp = 147-150 °C; $[\alpha]_D^{20}$ +34.0 (c = 0.60, $CHCl_3$, 91% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 230 nm, t_R = 30.0 min (minor), t_R = 41.4 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 8.02-8.00 (m, 2H), 7.59-7.54 (m, 1H), 7.48-7.44 (m, 2H), 7.42-7.39 (m, 1H), 7.21-7.17 (td, J_1 = 7.7 Hz, J_2 = 1.2 Hz, 1H), 6.95-6.91 (td, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H), 6.85-6.83 (m, 1H), 4.37-4.32 (m, 1H), 1.14-1.13(d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 202.0, 179.8, 142.0, 137.5, 132.8, 129.7, 129.2, 128.3, 128.2, 125.3, 121.8, 109.5, 76.9, 46.4, 11.3; IR (film, ν/cm^{-1}): 2917, 2848, 1727, 1667, 1618, 1598, 1518, 1455, 1518, 1455, 1331, 1217, 1148, 1154, 1122, 1091, 1069, 999, 911, 843, 788, 746; HRMS (ESI) m/z calcd for $C_{17}H_{15}NO_3$ $[M+Na]^+$ 304.0950, found 304.0947.

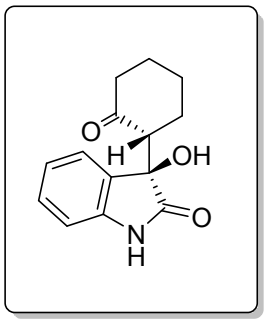
(R)-3-hydroxy-3-((R)-5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulen-6-yl)indolin-2-one (3ad)



The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a yellow oil: 85% yield, 26.1

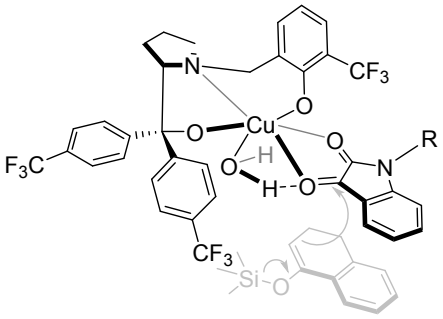
mg, mp = 147-150 °C; $[\alpha]_D^{20}$ +51.6 (c = 0.67, $CHCl_3$, 95% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 254 nm, t_R = 15.1 min (minor), t_R = 17.1 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.49-7.47 (d, *J* = 7.4 Hz, 1H), 7.41-7.37 (t, *J* = 7.5 Hz, 2H), 7.28-7.26 (d, *J* = 7.4 Hz, 1H), 7.24-7.20 (t, *J* = 7.6 Hz, 2H), 6.97-6.93 (t, *J* = 7.5 Hz, 1H), 6.90-6.86 (m, 1H), 3.78-3.73 (dd, J_1 = 11.6 Hz, J_2 = 5.6 Hz, 1H), 3.14-3.07 (m, 1H), 3.02-2.95 (m, 1H), 2.16-2.09 (m, 1H), 2.07-1.99 (m, 1H), 1.96-1.88 (m, 1H), 1.61-1.53 (m, 1H); ^{13}C NMR (100 MHz, CD_3OH): δ 204.3, 179.3, 142.5, 139.5, 131.4, 129.8, 129.1, 127.4, 125.9, 124.7, 121.9, 109.6, 76.1, 56.5, 32.9, 25.2, 23.9; IR (film, ν/cm^{-1}): 3357, 2917, 2849, 1720, 1618, 1459, 1259, 1208, 1016, 872, 799, 753, 695; HRMS (ESI) m/z calcd for $C_{19}H_{17}NO_3$ $[M+H]^+$ 308.1287, found 308.1284.

(R)-3-hydroxy-3-((R)-2-oxocyclohexyl)indolin-2-one (3ae)

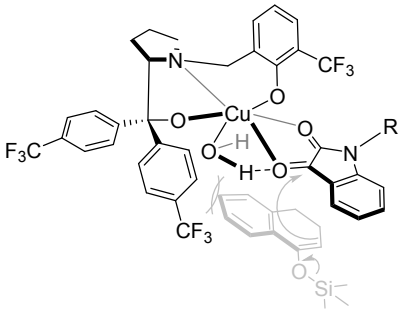


The title compound was prepared according to the general working procedure and purified by flash column chromatography (petroleum ether / ethyl acetate = 2:1) to give the product as a yellow oil: 83% yield, 20.3 mg; $[\alpha]_D^{20}$ +17.2 (c = 0.22, $CHCl_3$, 97% *ee*); HPLC: Daicel Chiralpak AD-H, hexane: 2-propanol = 70:30, flow rate = 1.0 mL/min, T = 23°C, UV = 254 nm, t_R = 7.8 min (minor), t_R = 8.6 min (major); ^{1}H NMR (400 MHz, CD_3OD): δ 7.42-7.40 (m, 1H), 7.22-7.18 (td, J_1 = 7.7 Hz, J_2 = 1.2 Hz, 1H), 6.99-6.95 (td, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H), 6.86-6.84 (m, 1H), 3.27-3.22 (m, 1H), 2.46-2.37 (m, 1H), 2.26-2.16 (m, 2H), 2.09-2.04 (m, 1H), 1.87-1.83 (m, 1H), 1.73-1.66 (m, 1H), 1.58-1.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.1, 177.2, 141.0, 129.8, 129.7, 125.8, 123.2, 110.4, 78.2, 55.5, 42.7, 28.1, 26.7, 24.2; IR (film, ν/cm^{-1}): 3197, 2919, 2850, 2359, 1706, 1616, 1467, 1338, 1260, 1197, 1158, 1113, 1041, 1019, 942, 872, 796, 749, 667; HRMS (ESI) m/z calcd for $C_{14}H_{15}NO_3$ $[M+H]^+$ 246.1130, found 246.1129.

1.6 A Plausible Structure of the Transition State

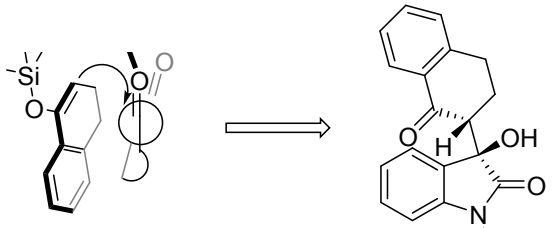


Si face attack
π–π stacking interaction



Si face attack
No π–π stacking interaction
Large steric hindrance

||



Cram's rule

References:

(1) (a) Guo, F.; Lai, G.; Xiong, S.; Wang, S.; Wang, Z. *Chem. -Eur. J.* **2010**, *16*, 6438; (b) Zhang, S.; Xu, K.; Guo, F.; Hu, Y.; Zha, Z.; Wang, Z. *Chem. -Eur. J.* **2014**, *20*, 979.

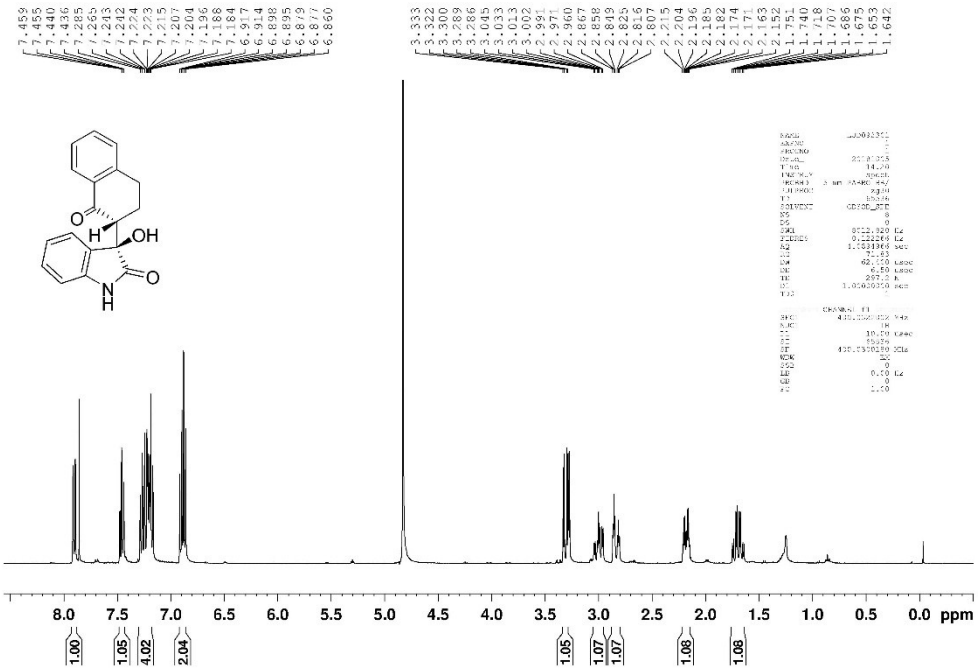
(2) (a) Mori, K.; Bernotas, R. *Tetddron: Asymmetry.* **1990**, 1, 87; (b) Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron*, **1987**, *43*, 2075; (c) Fang, J.; Ren, J.; Wang, Z. -W. *Tetrahedron Letters,* **2008**, 49, 6659; (d) Khan, I.; Reed-Berendt, B.; Melen, R. L.; Morrill, L. C. *Angew. Chem. Int. Ed.* **2018**, *57*, 12356.

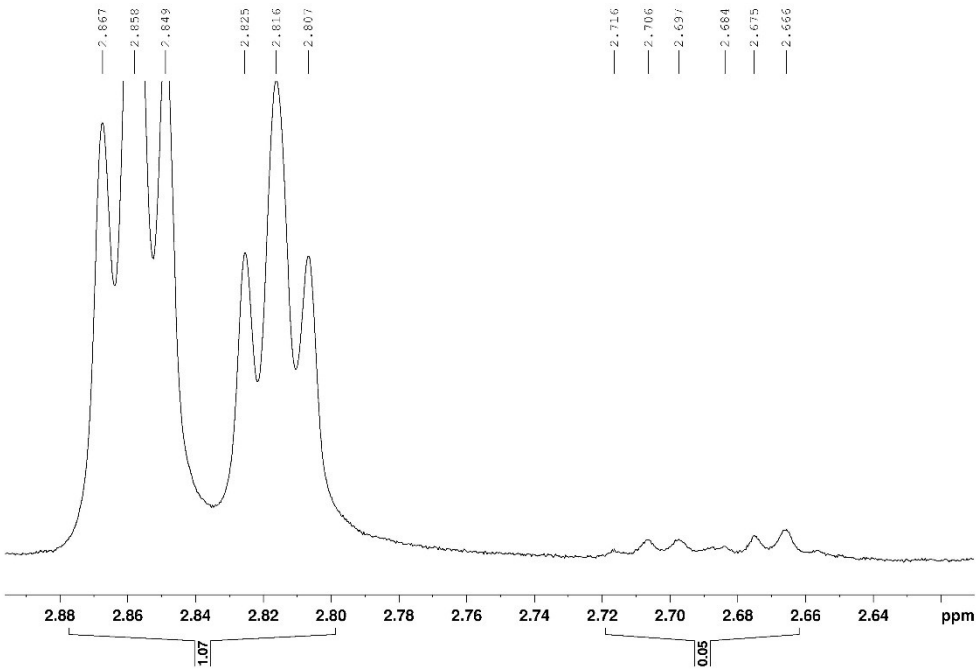
(3) Li, C.; Guo, F.; Xu, K.; Zhang, S.; Hu, Y.; Zha, Z.;Wang, Z. *Org. Lett.* **2014**, *16*, 3192.

(4) Liu, Z.; Gu, P.; Shi, M.; McDowell, P.; Li, G. *Org. Lett*. **2011**, *13*, 2314.

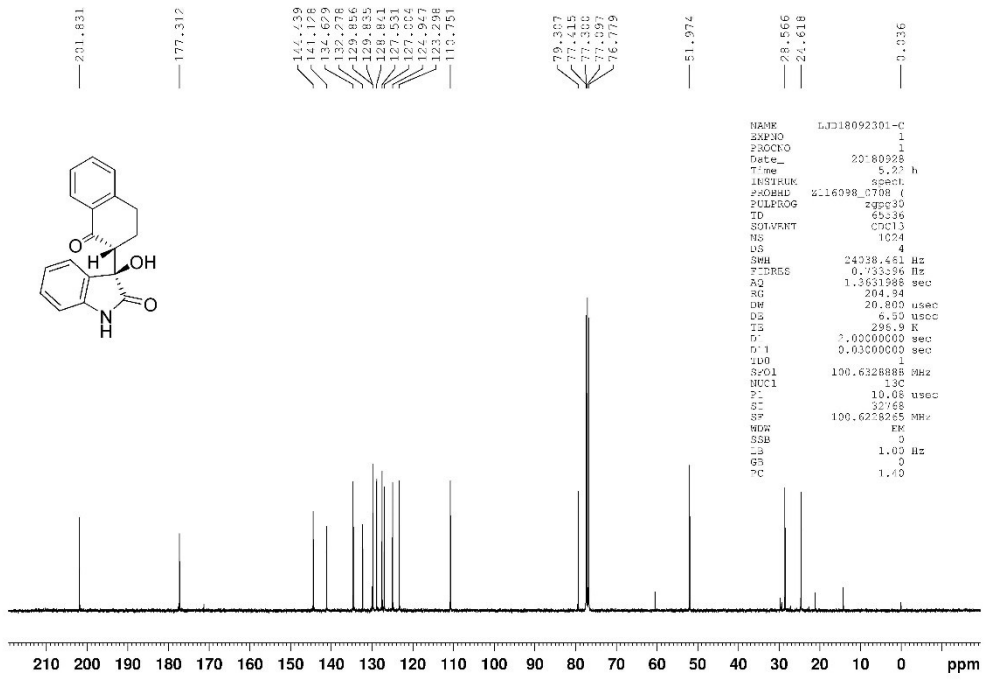
Part II ^{1}H NMR & ^{13}C NMR

^{1}H NMR of **3ab**

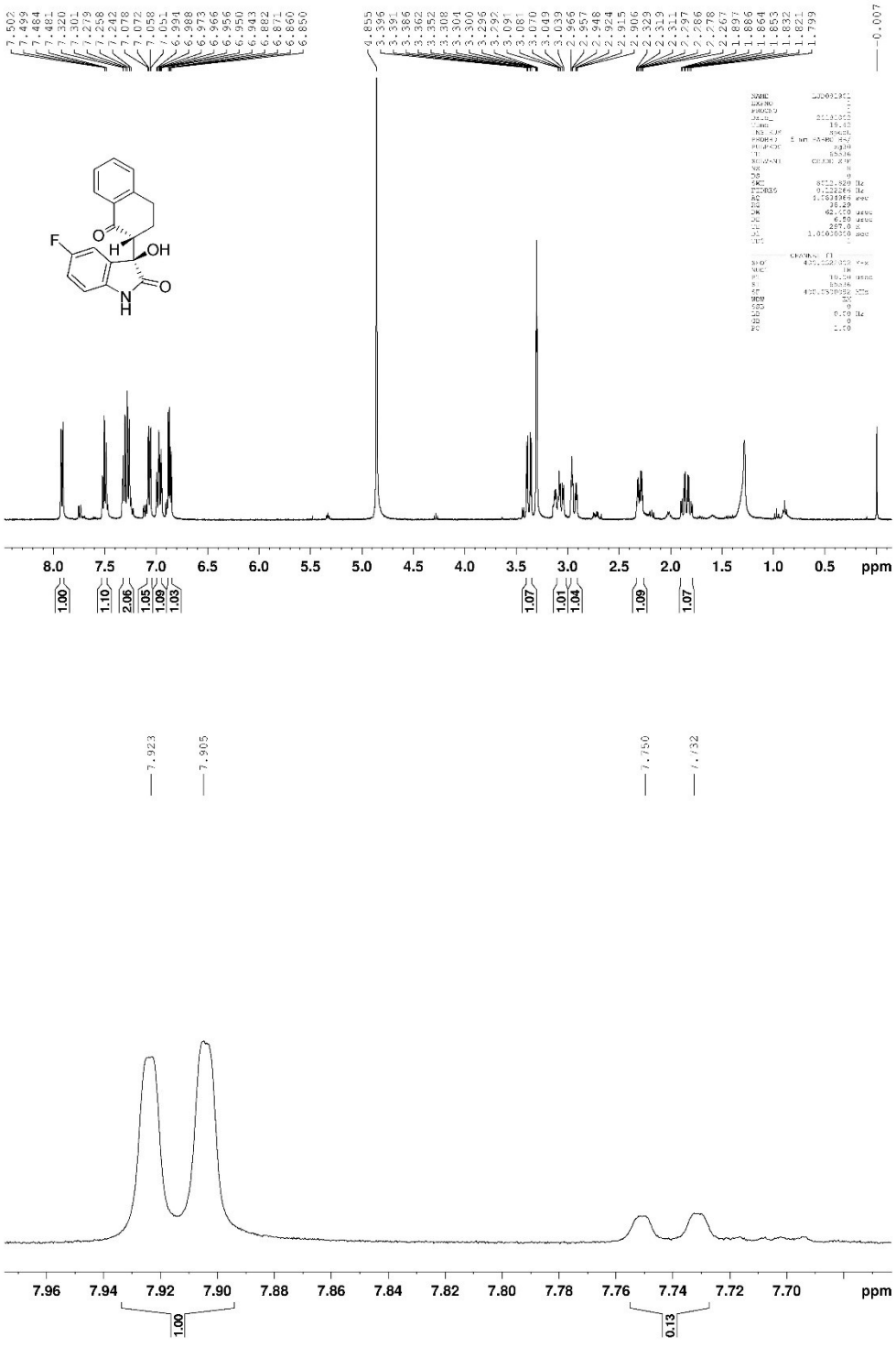




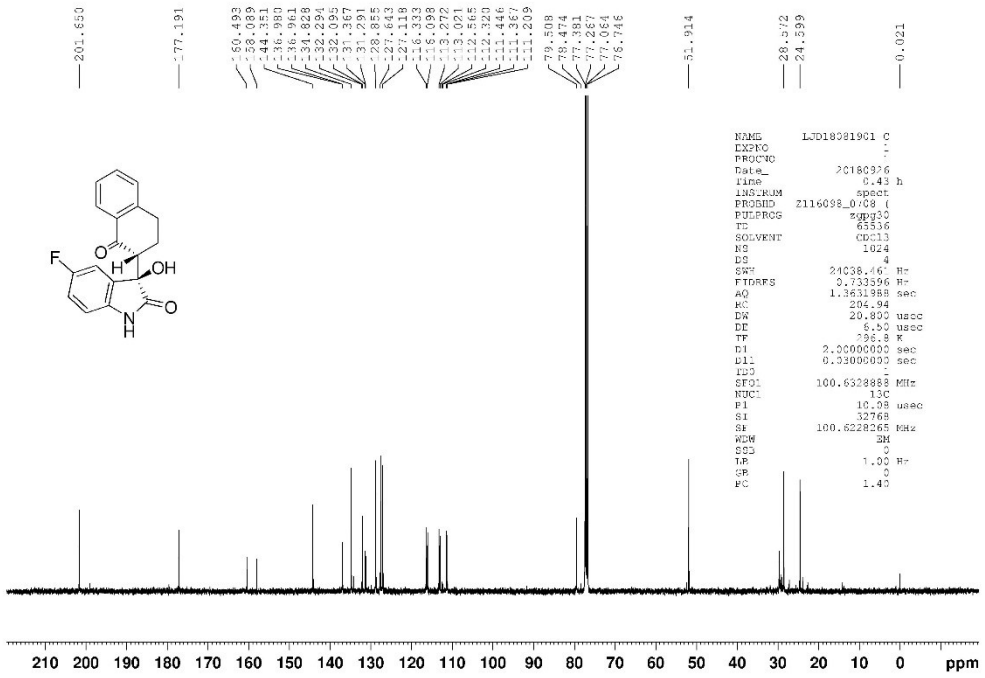
^{13}C NMR of **3ab**



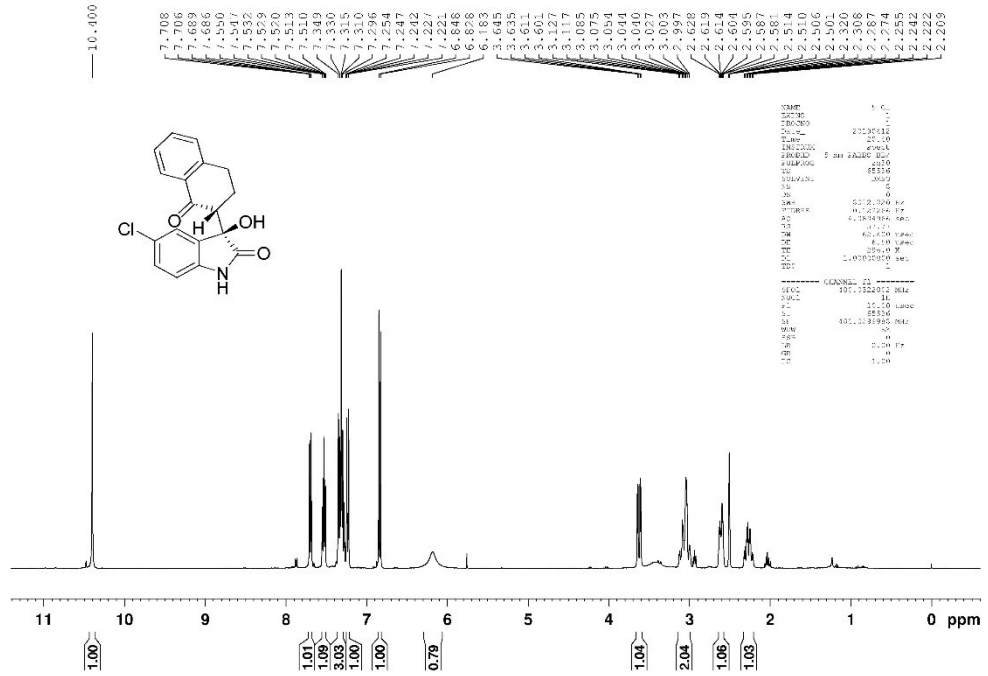
^{1}H NMR of **3bb**

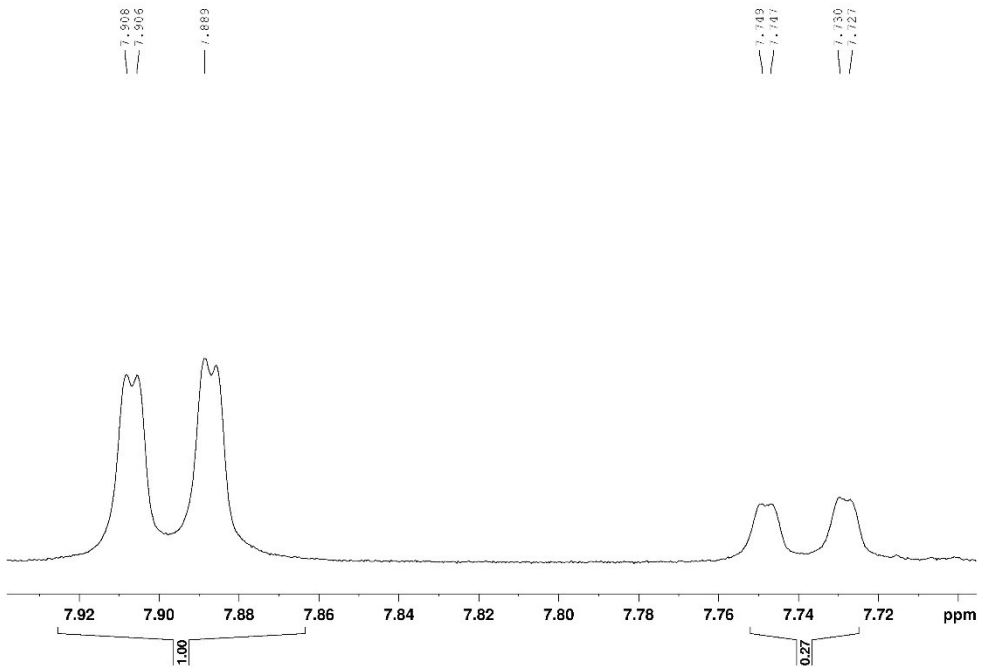


^{13}C NMR of **3bb**

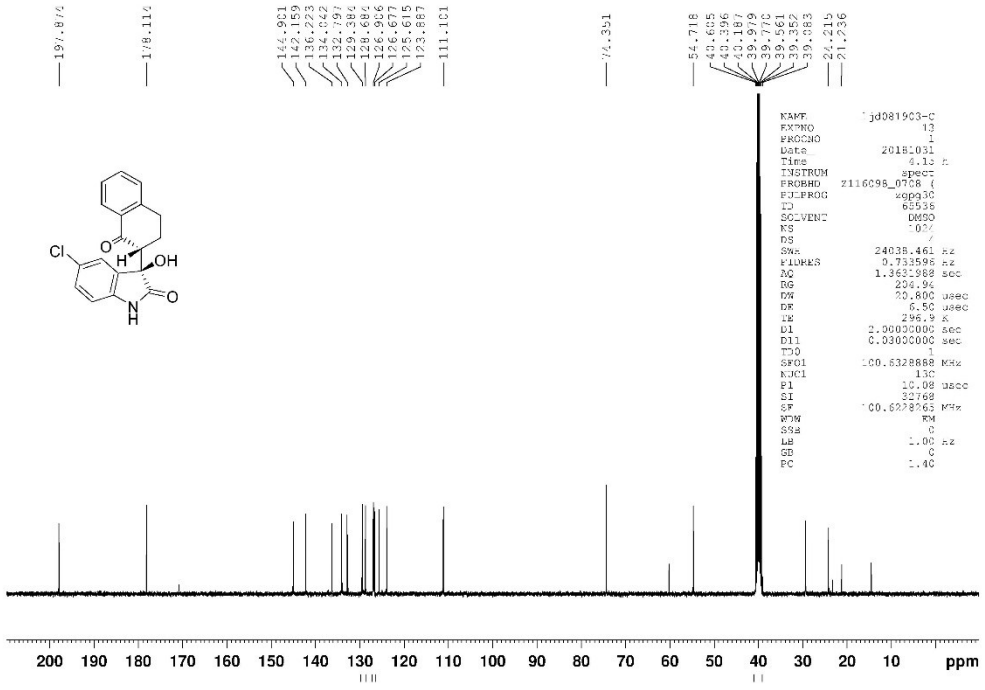


^{1}H NMR of **3cb**

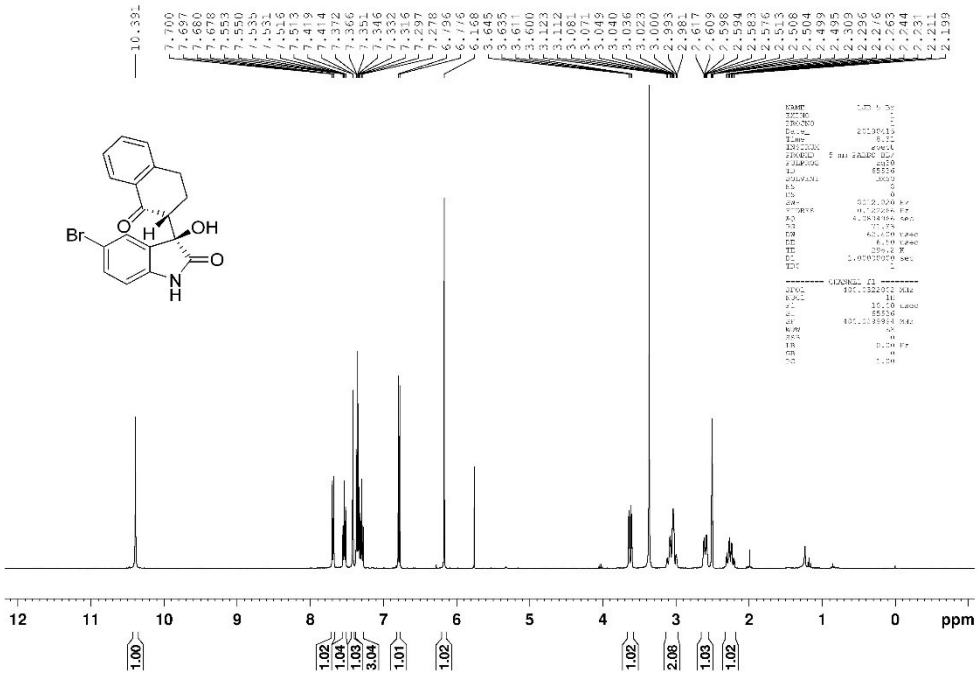




^{13}C NMR of **3cb**



^{1}H NMR of **3db**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7.680
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7.550
7.531
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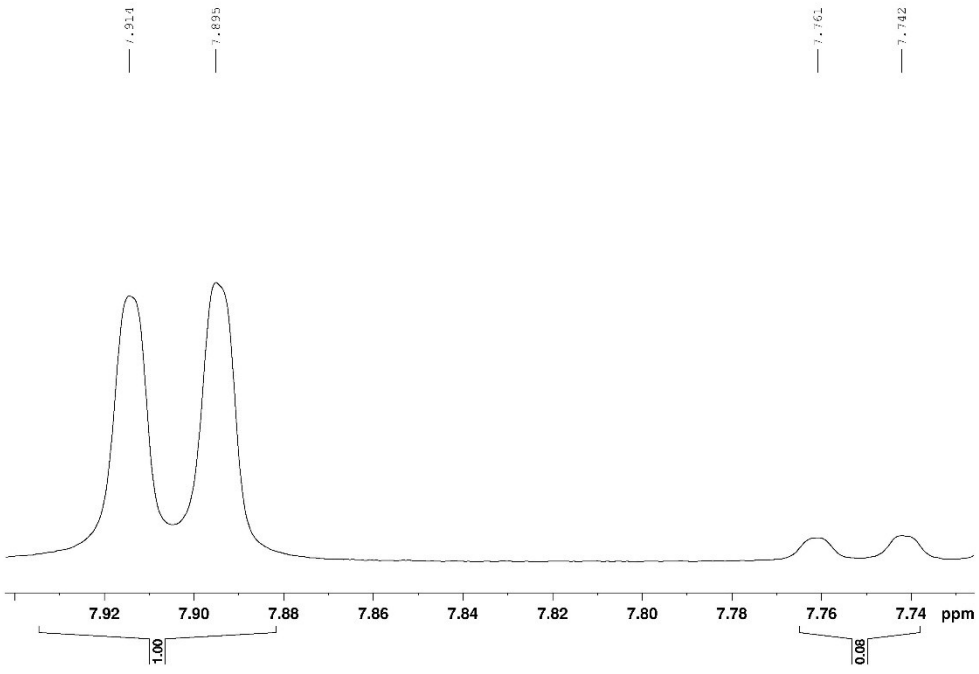
7.513
7.419
7.414
7.372
7.366
7.351
7.346
7.332
7.316
7.297
7.278
6.796
6.776
6.168
3.645
3.635
3.611
3.600
3.123
3.112
3.081
3.071
3.049
3.040
3.036
3.023
3.000
2.993
2.981
2.617
2.609
2.598
2.594
2.583
2.576
2.513
2.508
2.504
2.499
2.495
2.309
2.296
2.276
2.263
2.244
2.231
2.211
2.193
Br
O
H
OH
O
N
H
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
1.04
1.03
3.04
1.01
1.02
1.02
2.08
1.03
1.02


7.914
7.895
7.761
7.742
7.92
7.90
7.88
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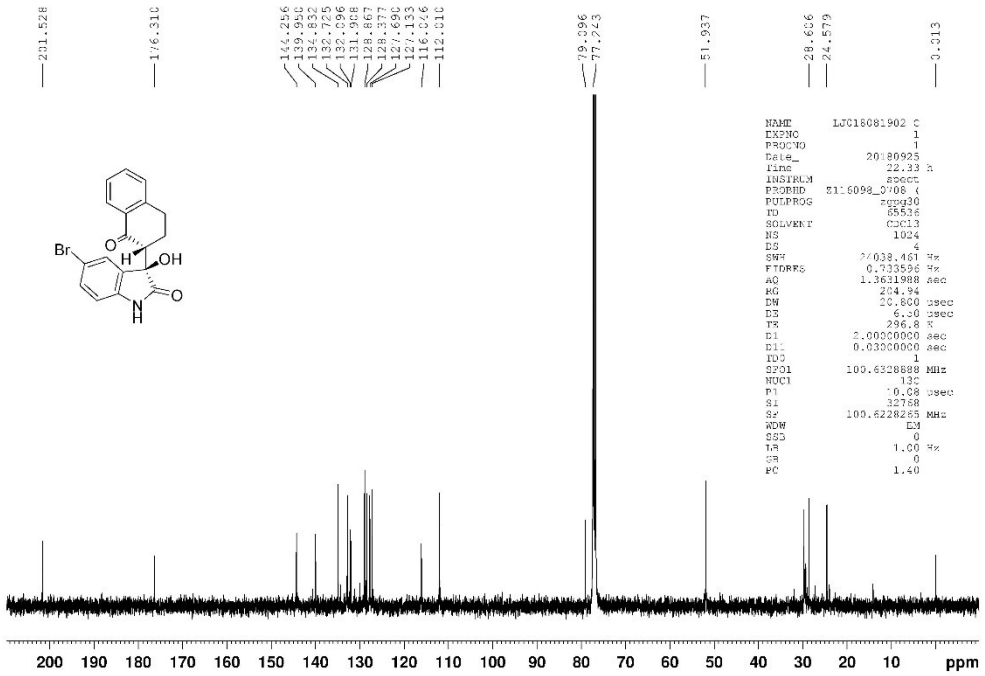
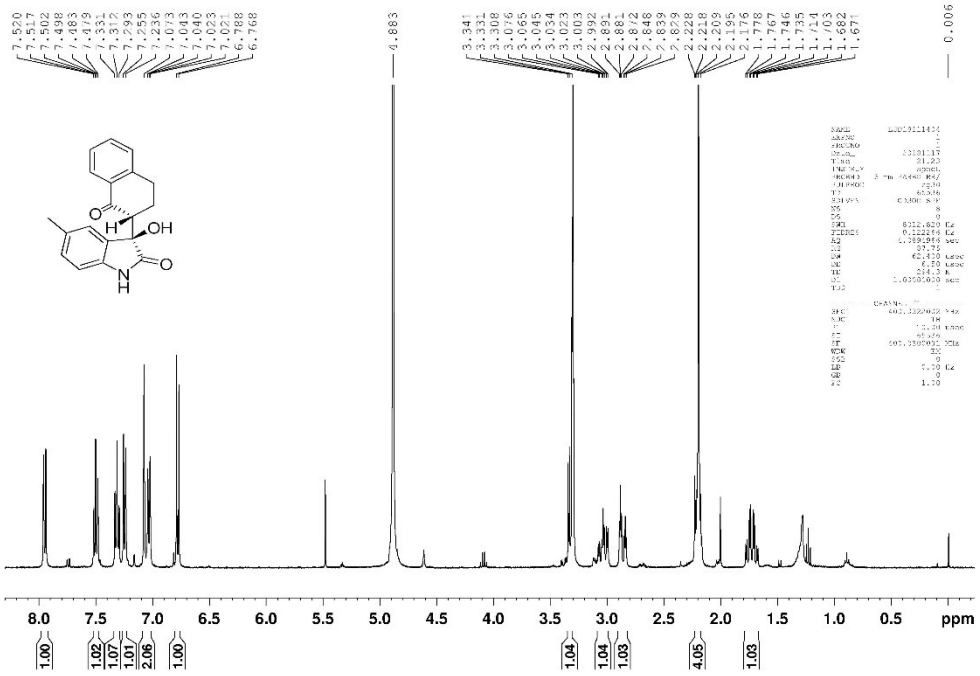
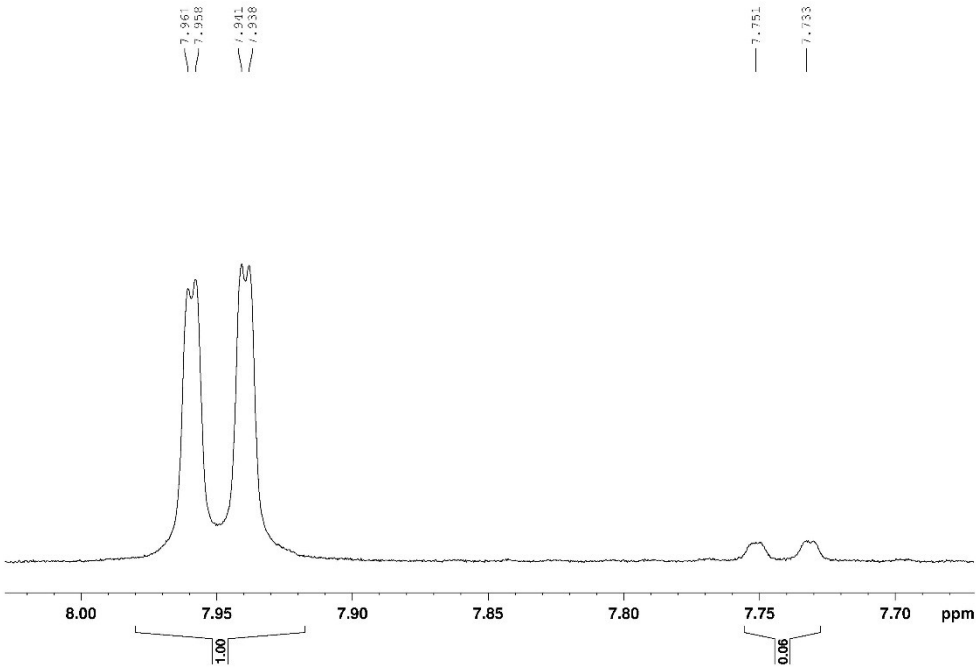
7.82
7.80
7.78
7.76
7.74
ppm
1.00
0.08

^{13}C NMR of **3db**

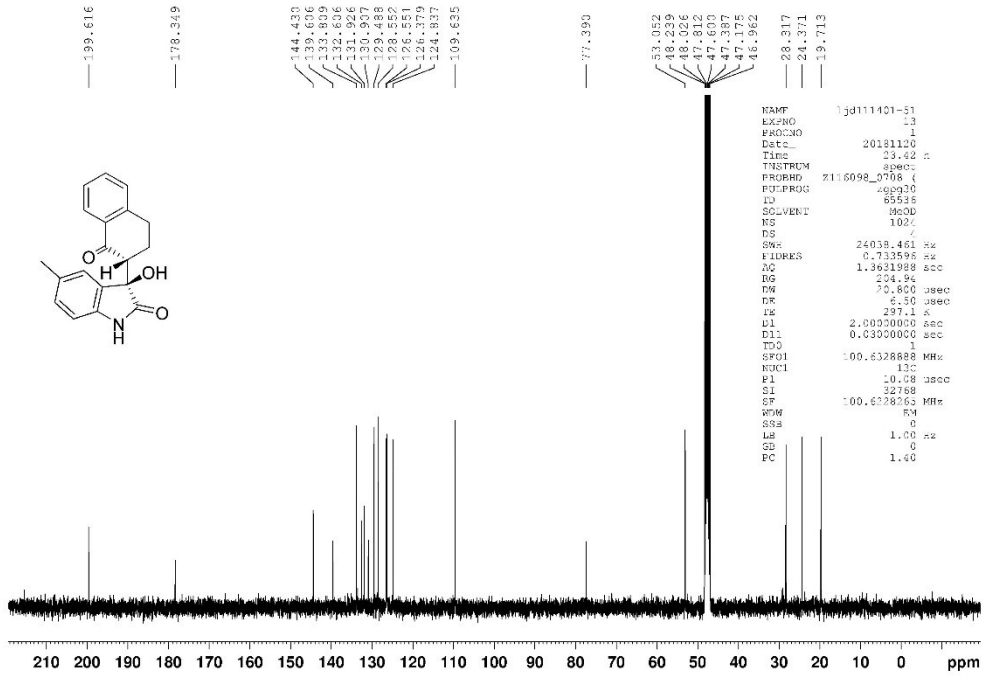


^{1}H NMR of **3eb**

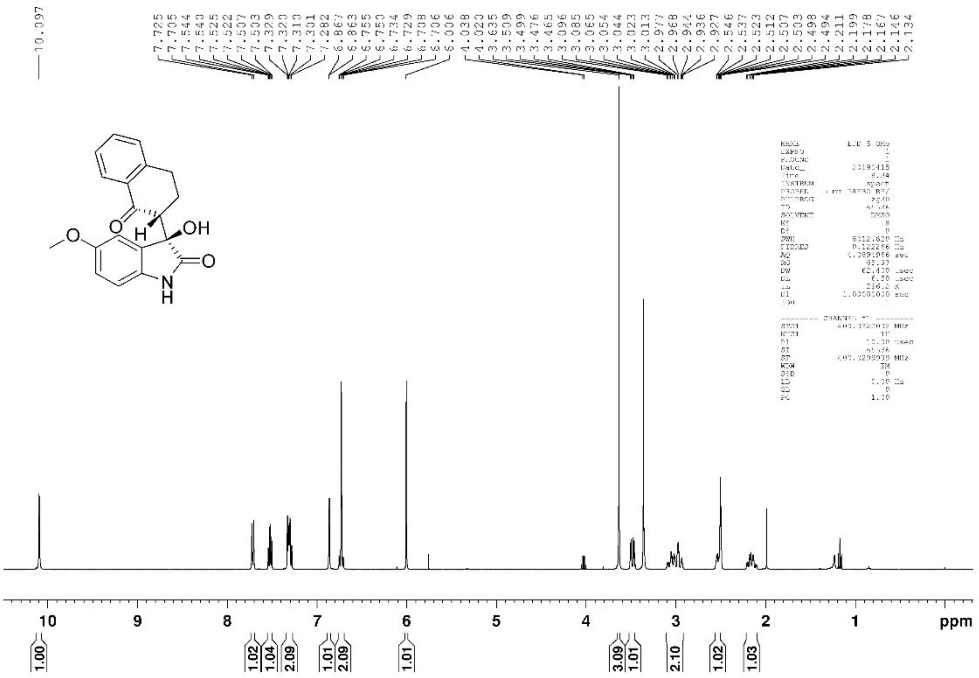


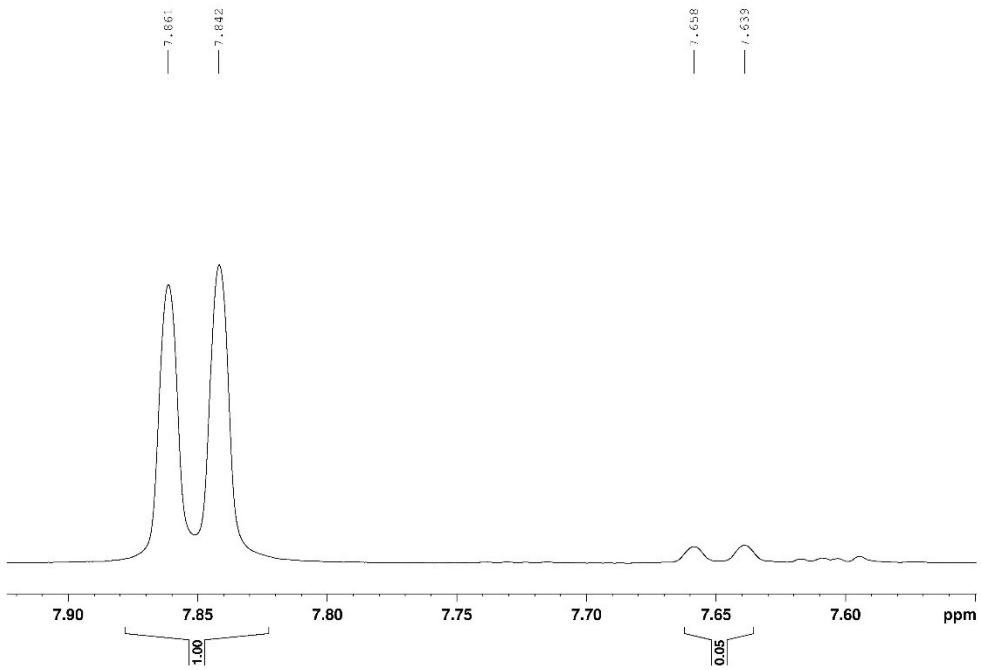


^{13}C NMR of **3eb**

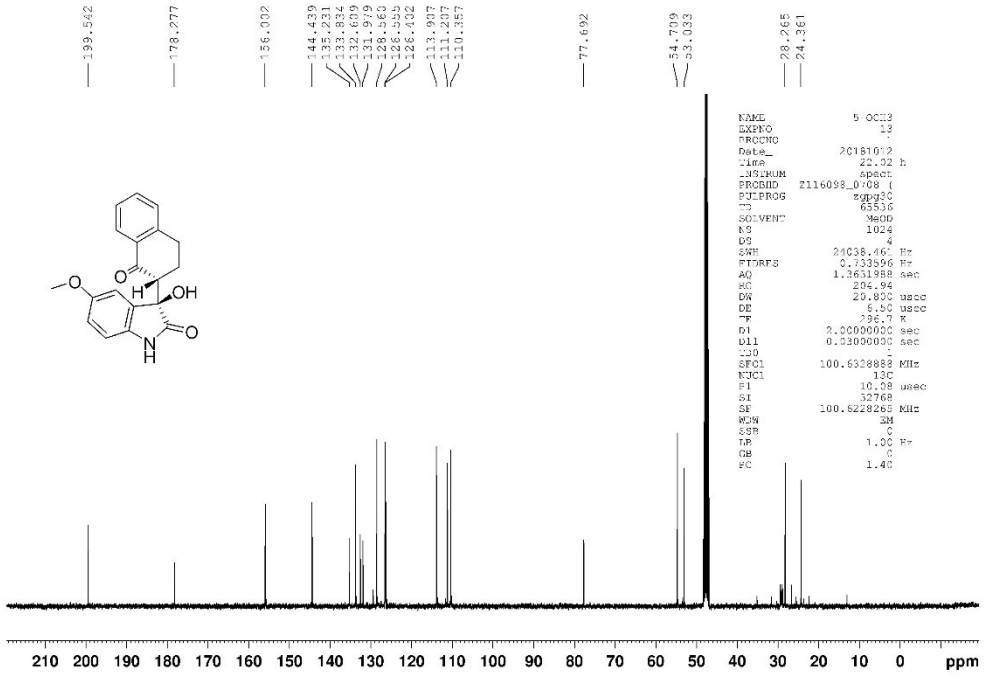


^{1}H NMR of **3fb**

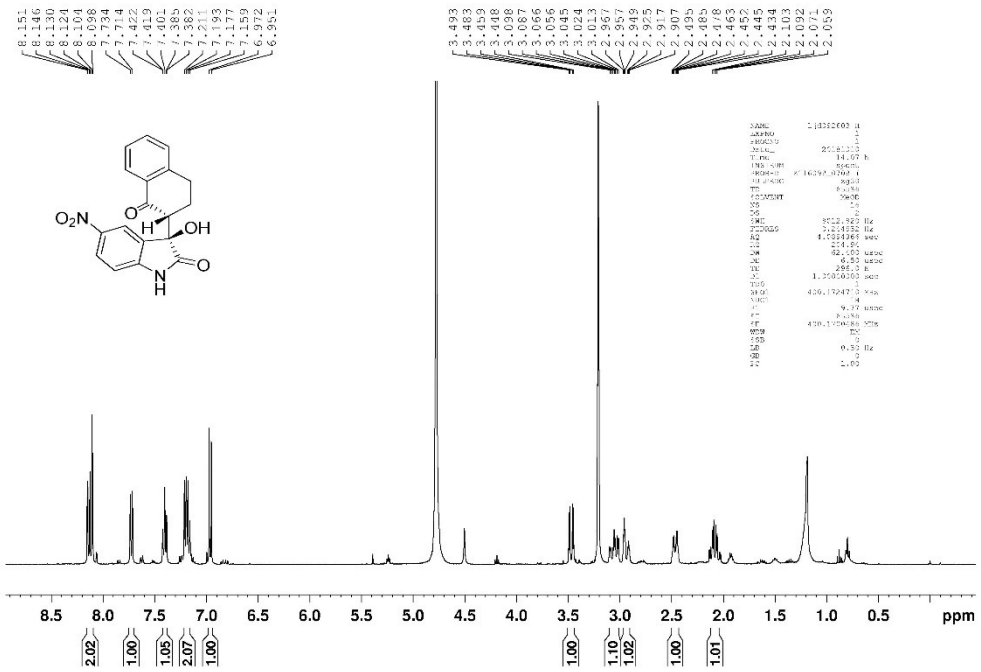




^{13}C NMR of **3fb**



^{1}H NMR of **3gb**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8.146
8.130
8.124
8.104
8.098
7.734
7.714
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7.382
7.211
7.193
7.177
7.159
6.972
6.951
3.493
3.483
3.459
3.448
3.098
3.087
3.066
3.056
3.045
3.024
3.013
2.967
2.949
2.945
2.917
2.907
2.495
2.485
2.468
2.463
2.452
2.445
2.434
2.103
2.092
2.071
2.059
O2N
OH
O
H
N
H
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
ppm
2.02
1.00
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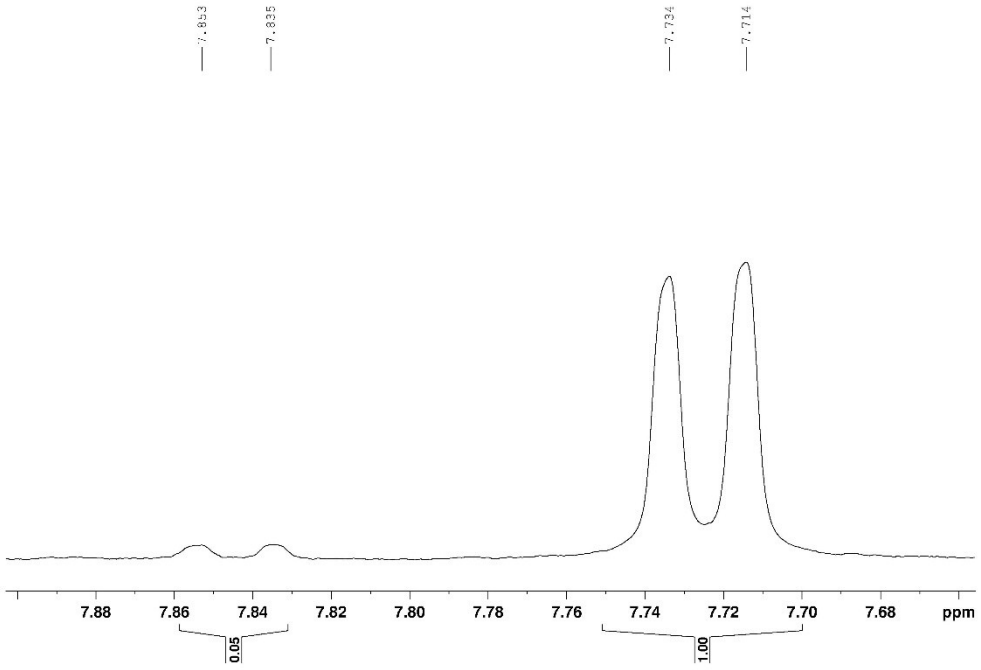
1.00
1.10
1.02
1.00
1.01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7.84
7.82
7.80
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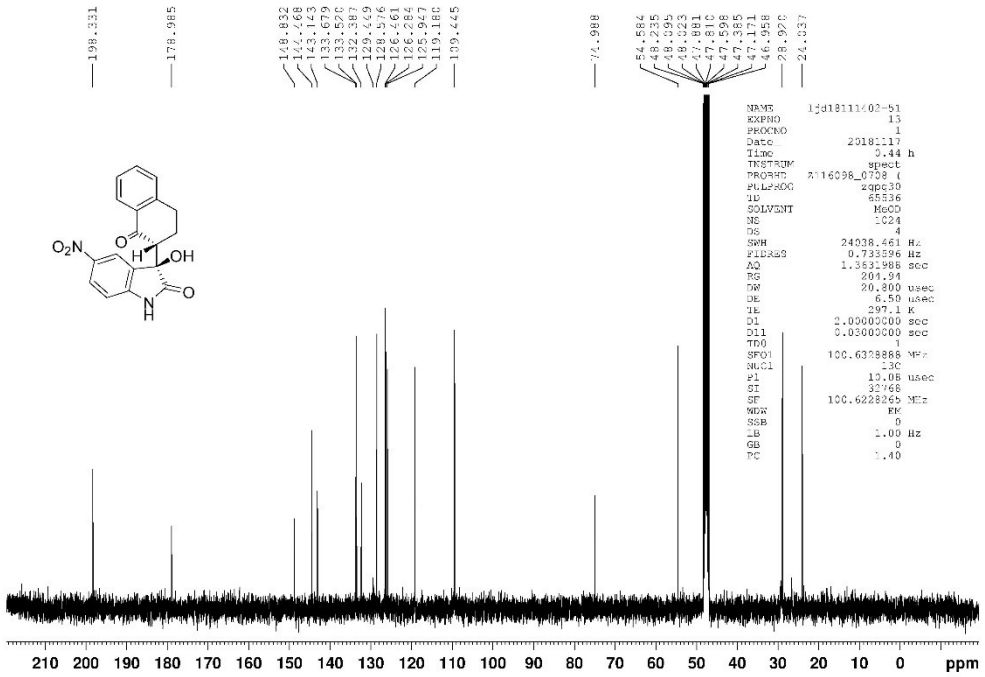
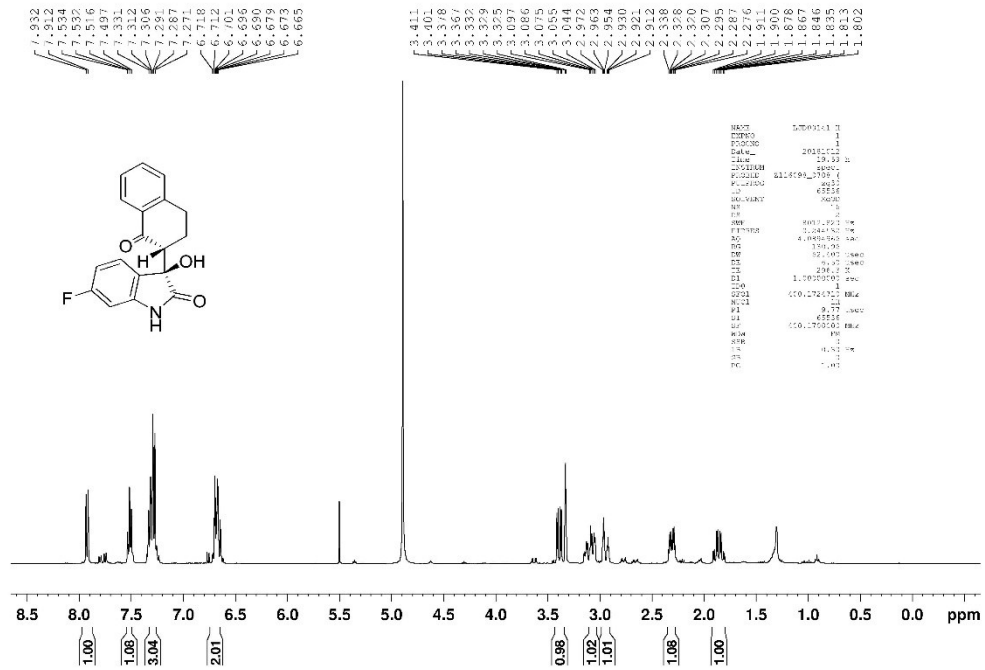
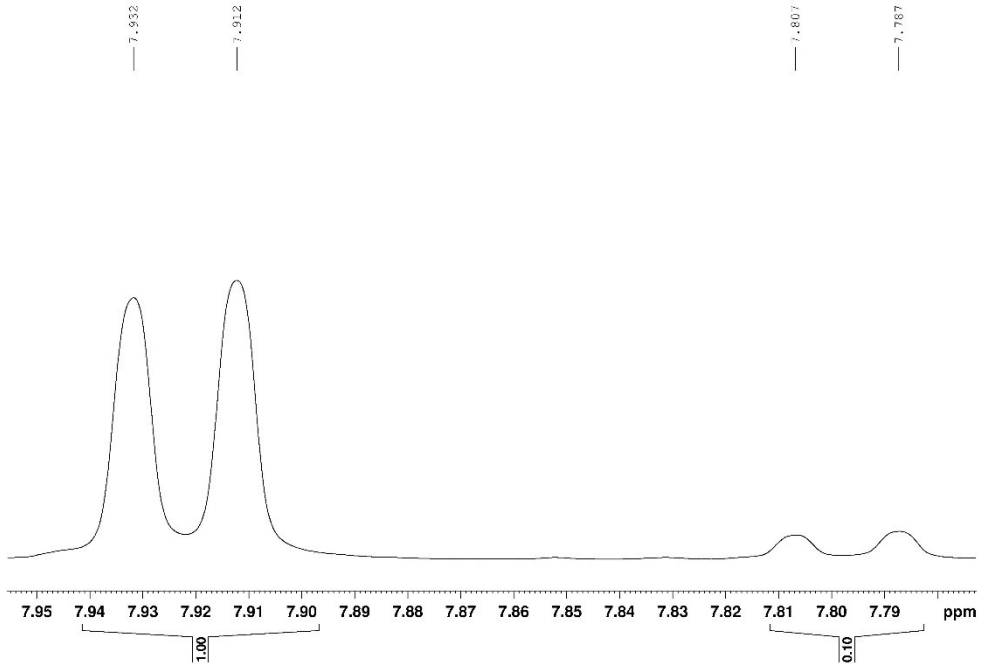
7.76
7.74
7.72
7.70
7.68
ppm
0.05
1.00

^{13}C NMR of **3gb**

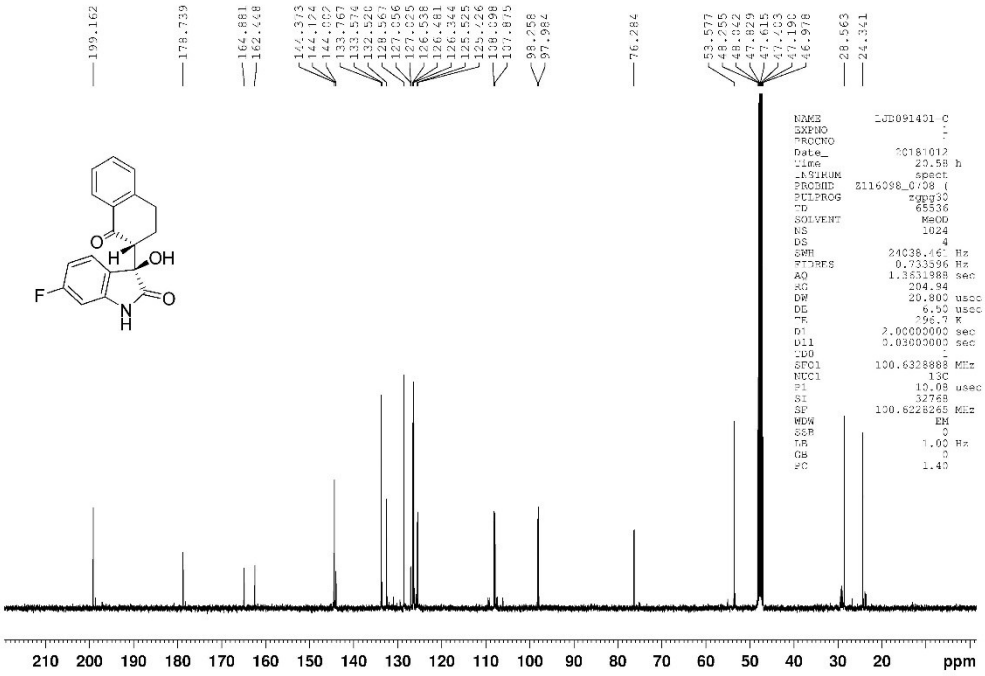


^{1}H NMR of **3hb**

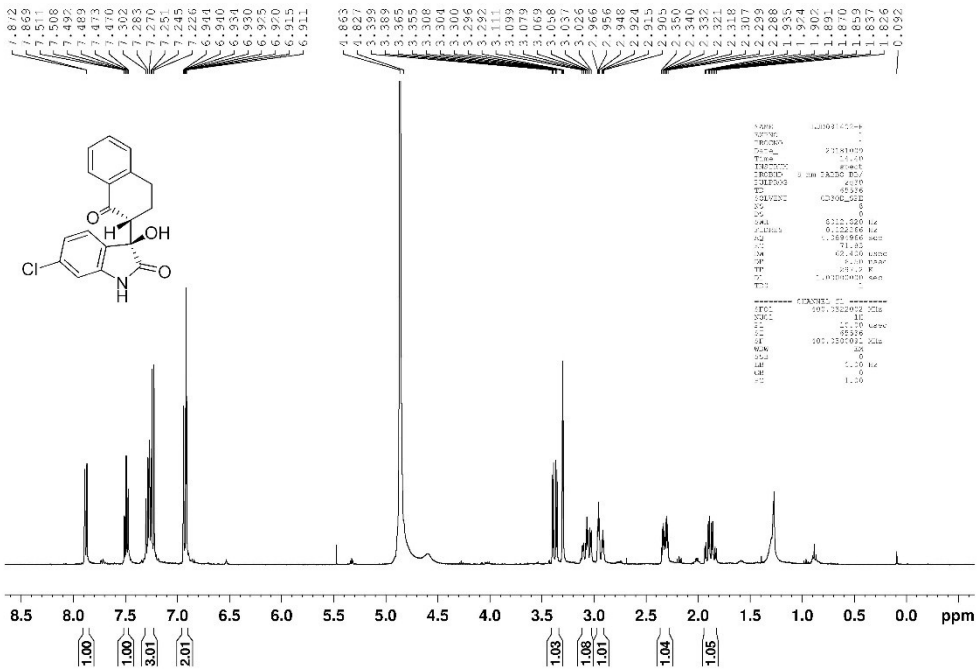




^{13}C NMR of **3hb**



^{1}H NMR of **3ib**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7.489
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7.470
7.302
7.283
7.270
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6.944
6.940
6.934
6.930
6.925
6.920
6.915
6.911
4.863
4.827
3.389
3.365
3.355
3.308
3.304
3.300
3.296
3.292
3.111
3.099
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2.318
2.307
2.299
2.288
1.935
1.904
1.902
1.891
1.870
1.859
1.837
1.826
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H
OH
Cl
N
H
O
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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
ppm
1.00
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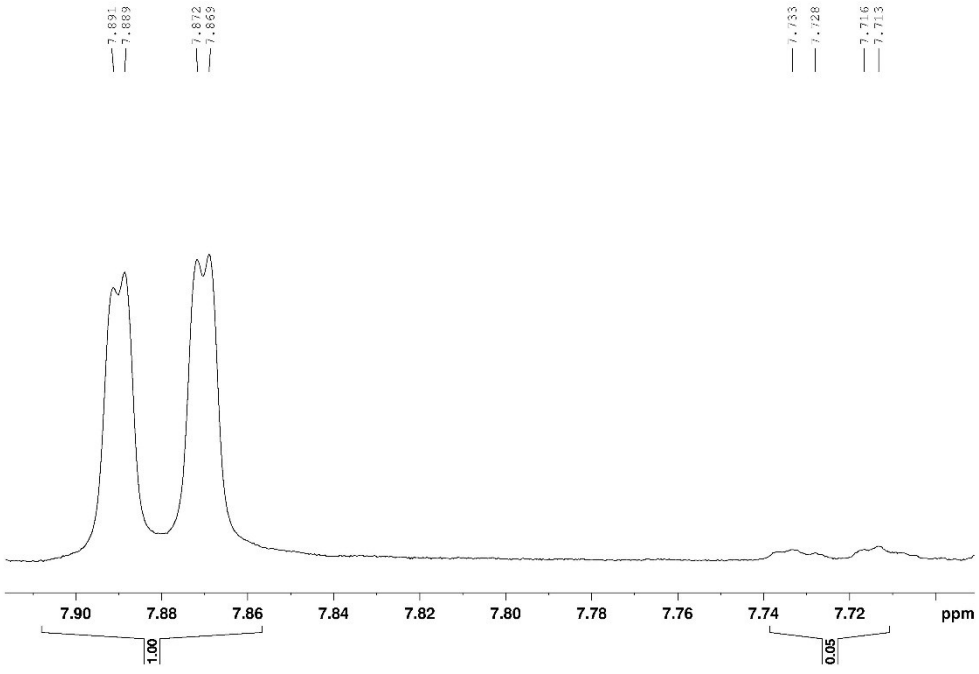
2.01
1.03
1.08
1.01
1.04
1.05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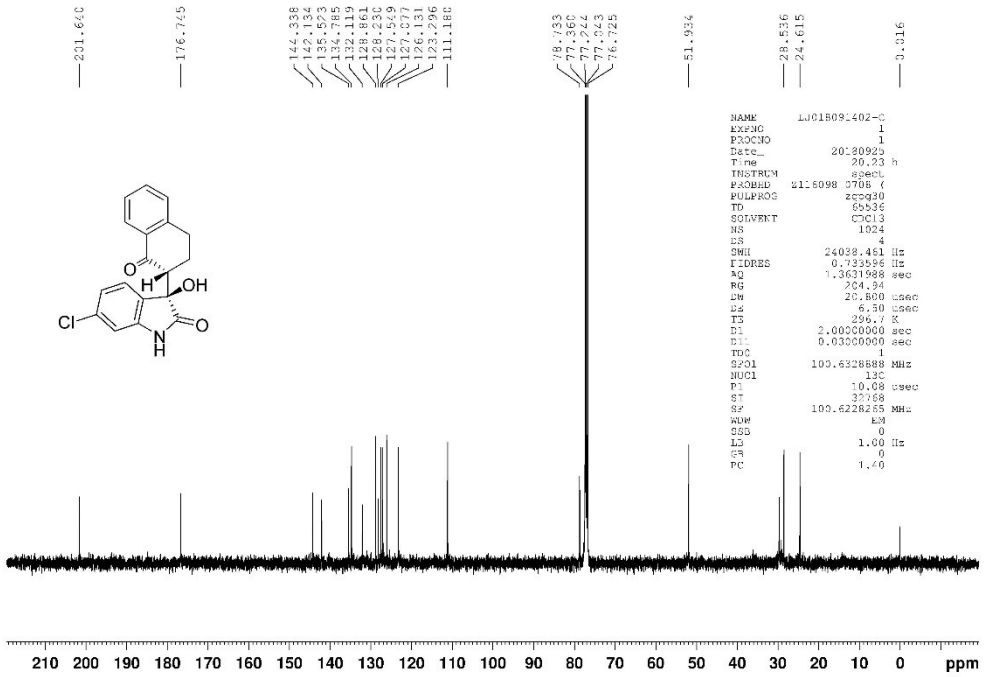
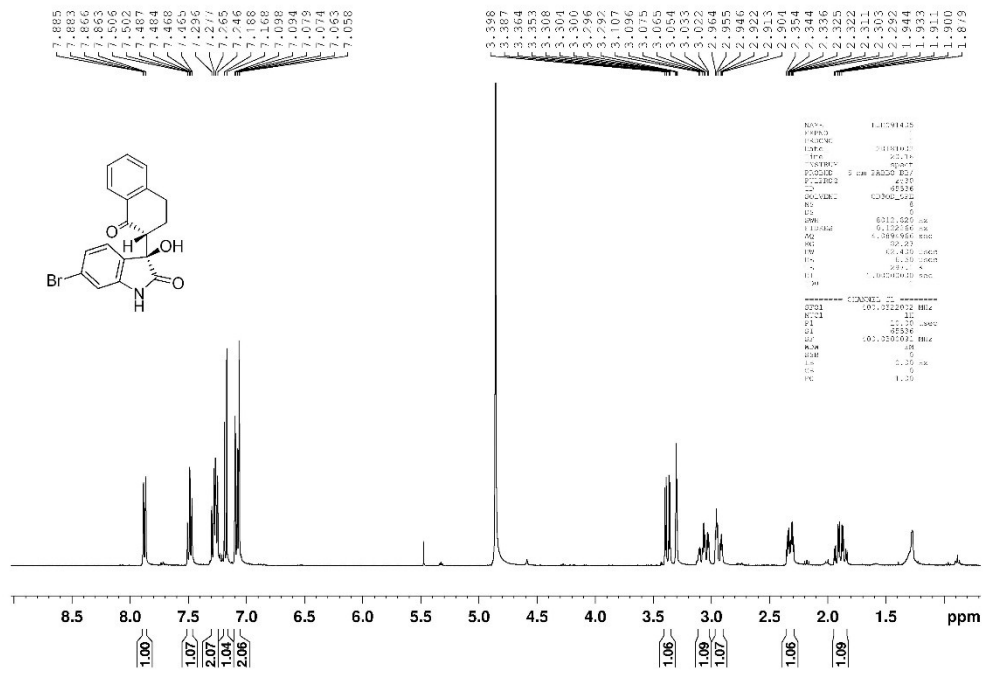
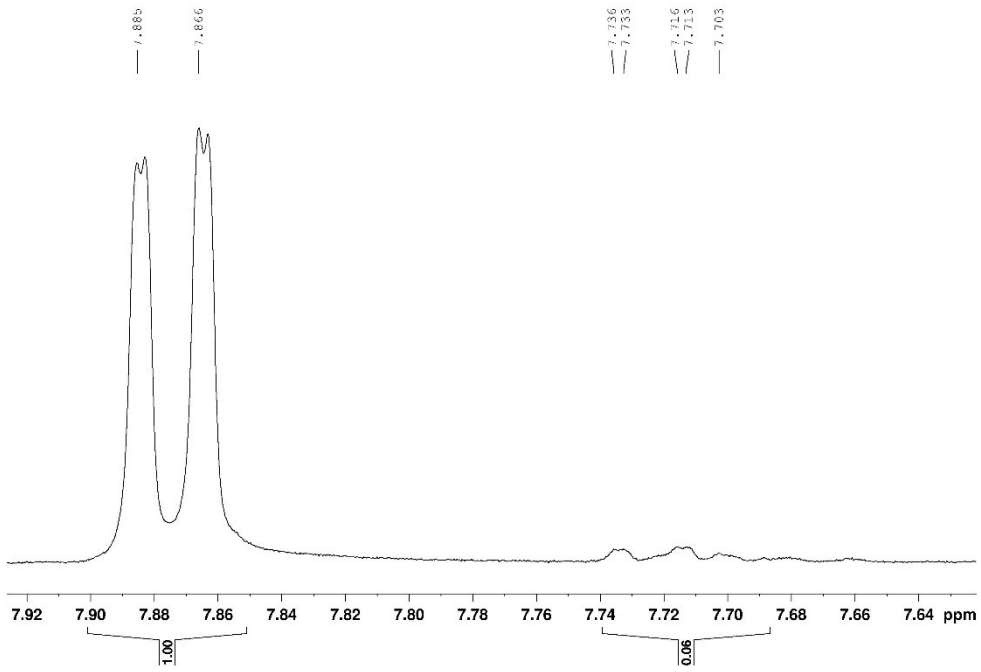
7.869
7.733
7.728
7.716
7.713
7.90
7.88
7.86
7.84
7.82
7.80
7.78
7.76
7.74
7.72
ppm
1.00
0.05

^{13}C NMR of **3ib**

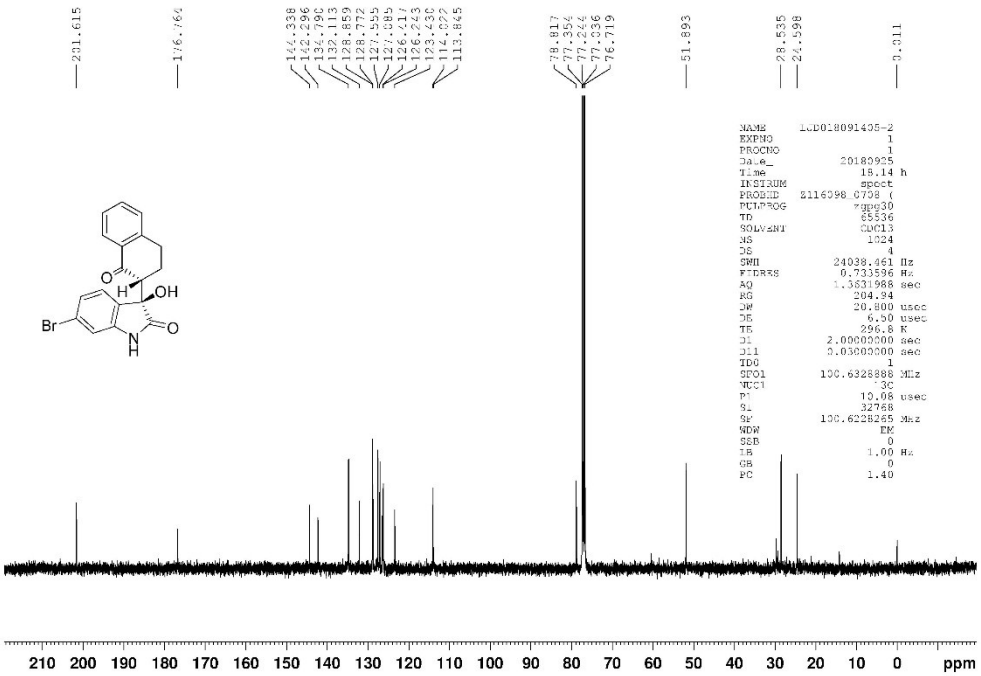


^{1}H NMR of **3jb**

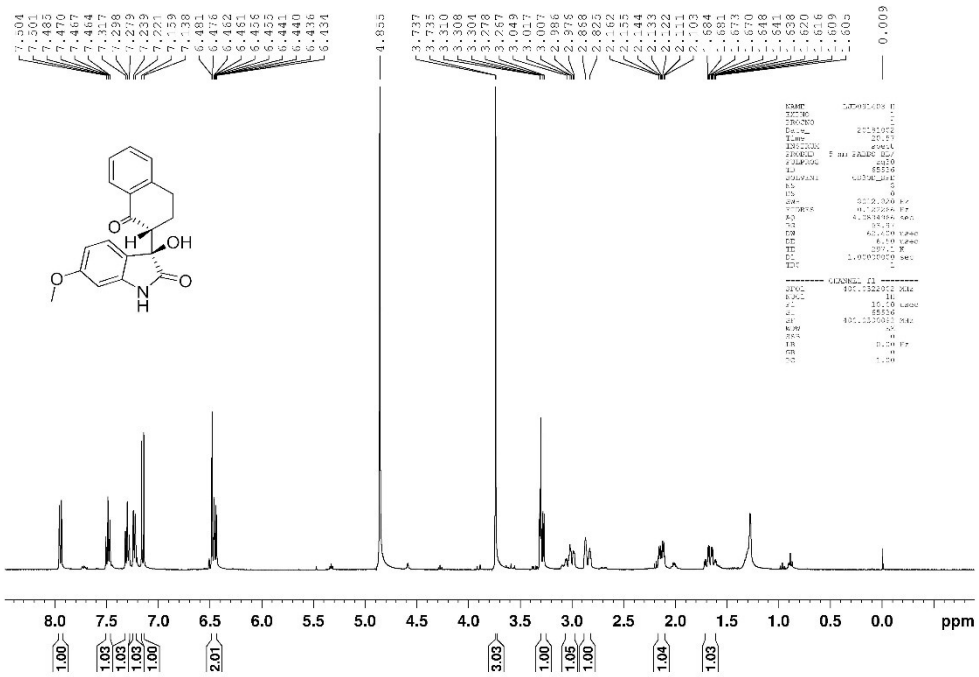


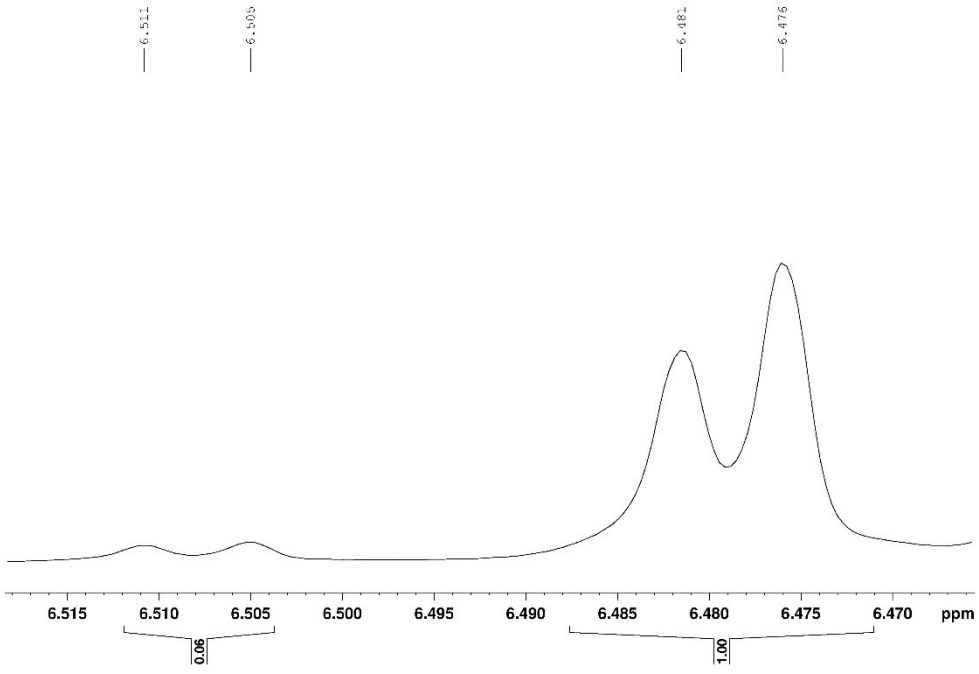


^{13}C NMR of **3jb**

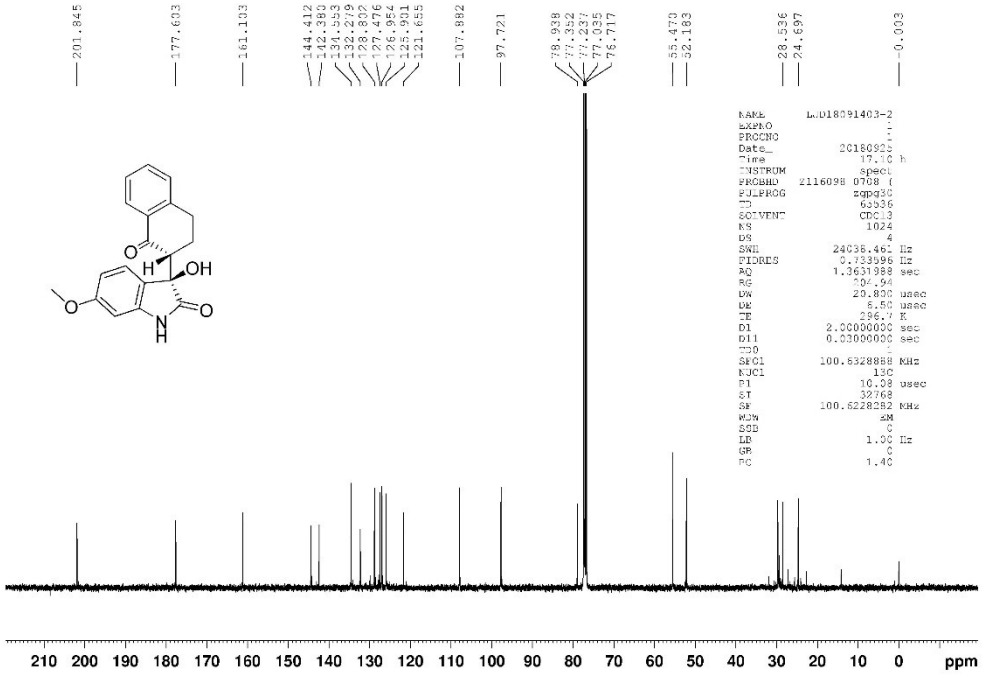


^{1}H NMR of **3kb**

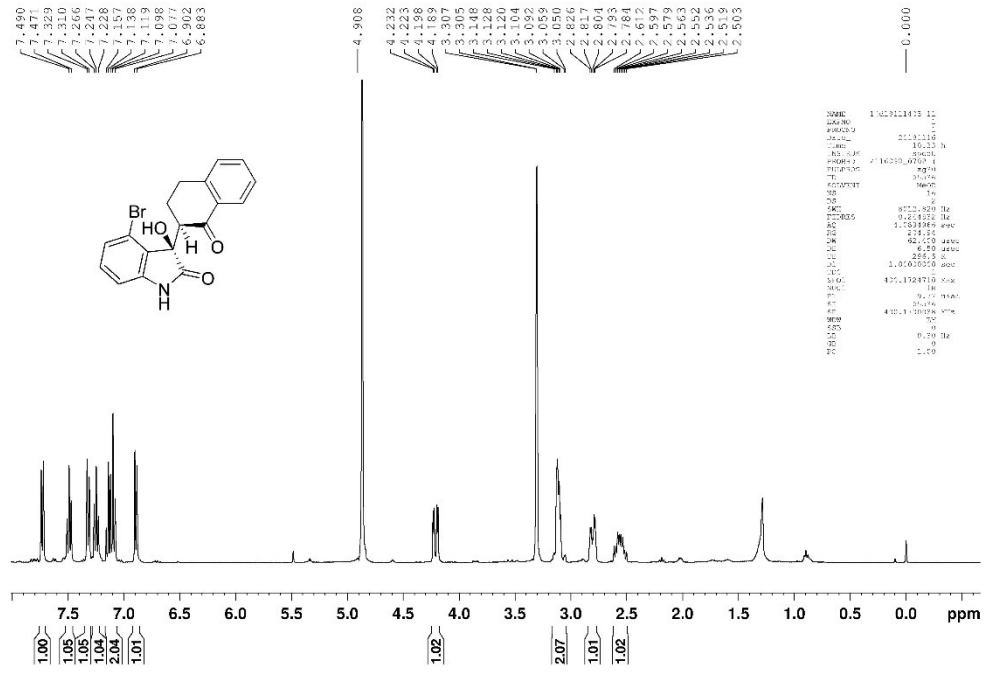

7.504
7.501
7.485
7.470
7.467
7.464
7.317
7.298
7.279
7.239
7.221
7.159
7.138
6.481
6.476
6.462
6.461
6.456
6.455
6.441
6.440
6.436
6.434
4.855
3.737
3.735
3.310
3.308
3.304
3.278
3.267
3.049
3.017
3.007
2.986
2.975
2.868
2.825
2.562
2.555
2.544
2.533
2.522
2.511
2.503
1.684
1.681
1.673
1.670
1.648
1.641
1.638
1.620
1.616
1.609
1.605
0.009
O
H
OH
O
N
H
O
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
ppm
1.00
1.03
1.03
1.03
1.00
2.01
3.03
1.00
1.05
1.00
1.04
1.03

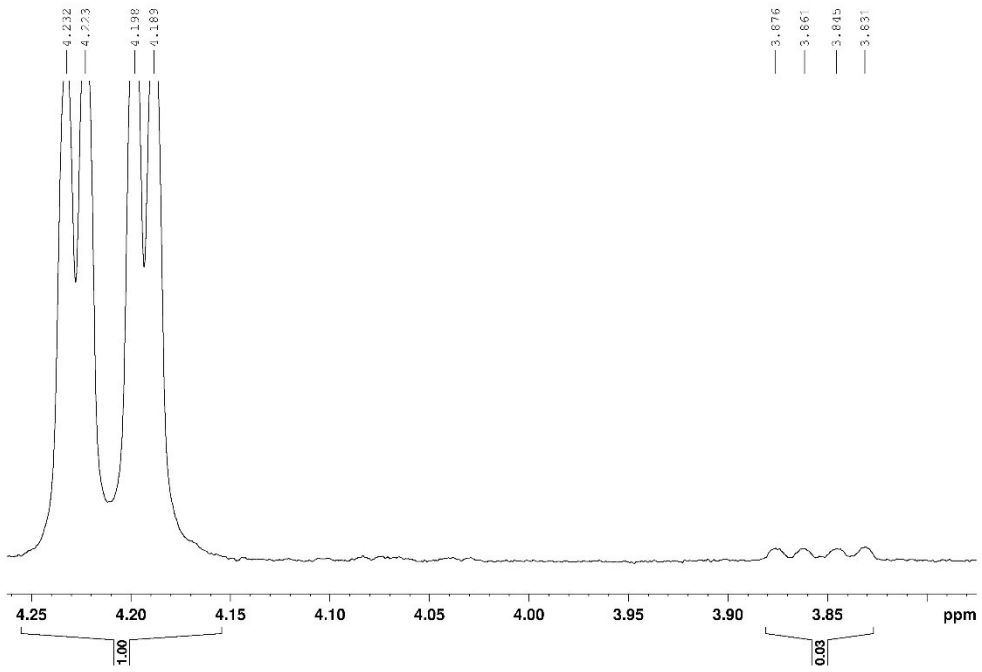

6.511
6.505
6.481
6.476
6.515
6.510
6.505
6.500
6.495
6.490
6.485
6.480
6.475
6.470
ppm
0.06
1.00

^{13}C NMR of **3kb**

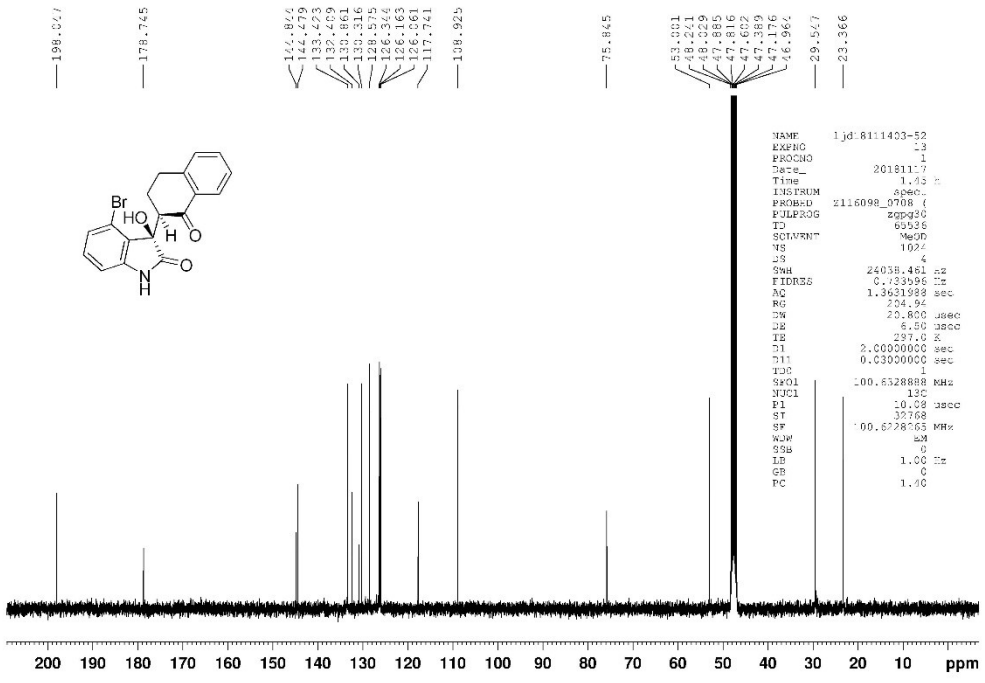


^{1}H NMR of **3lb**

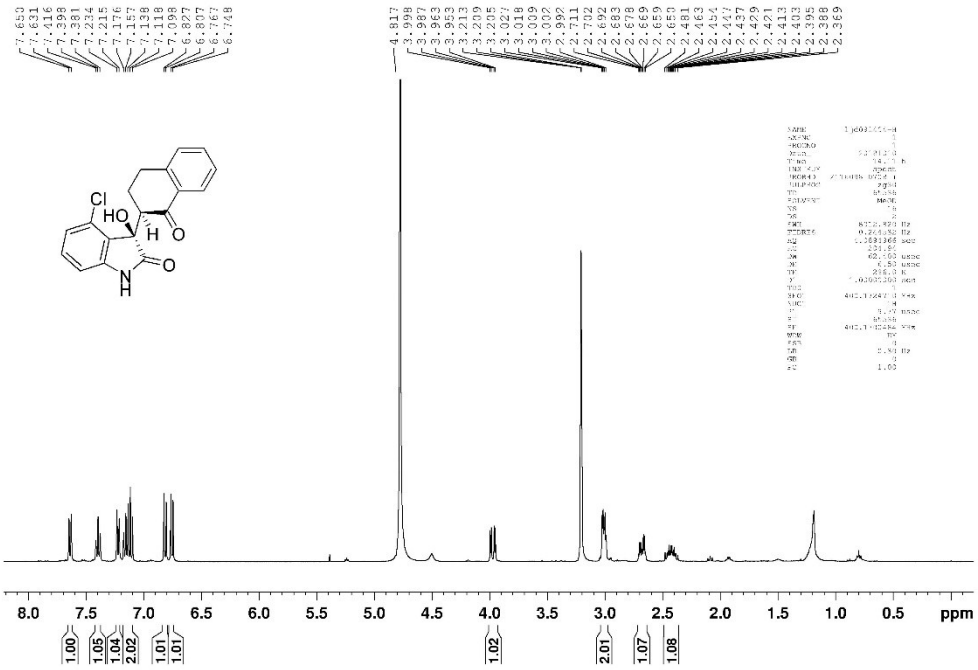


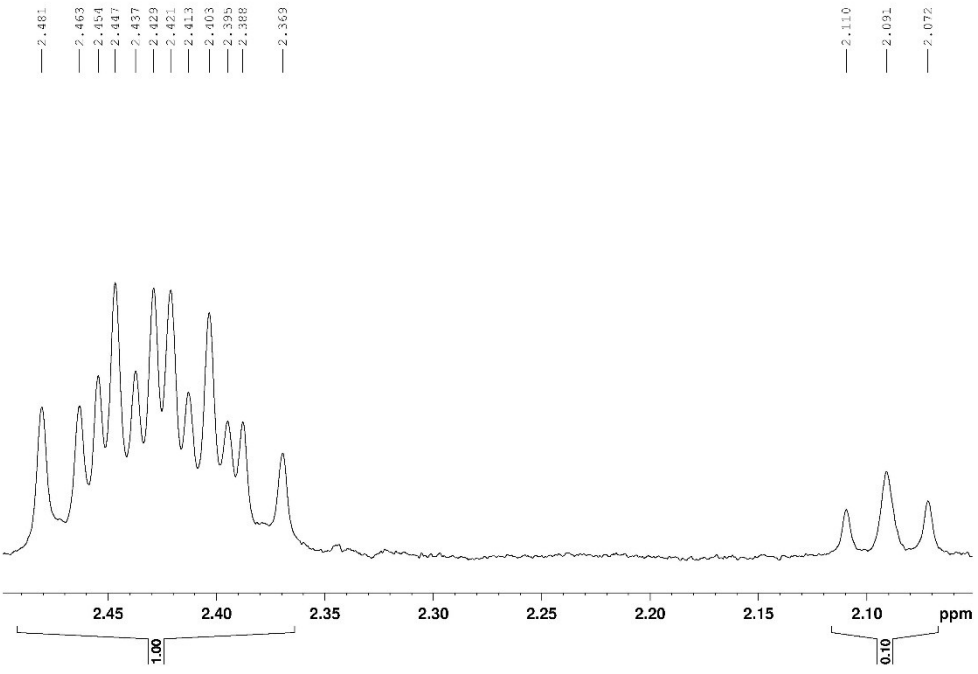


^{13}C NMR of **3lb**

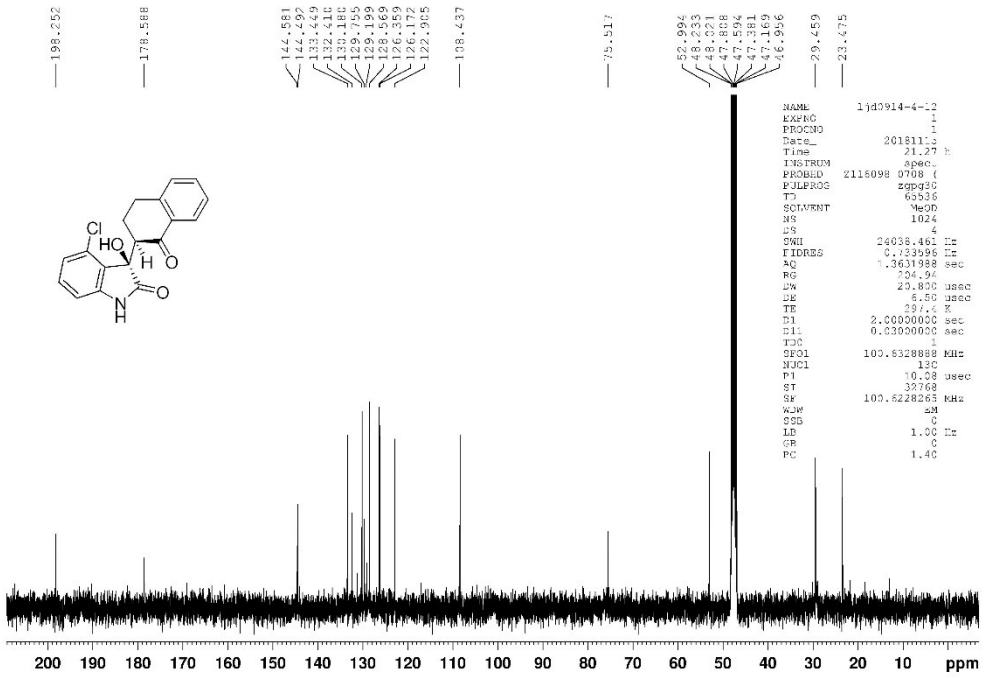


^{1}H NMR of **3mb**

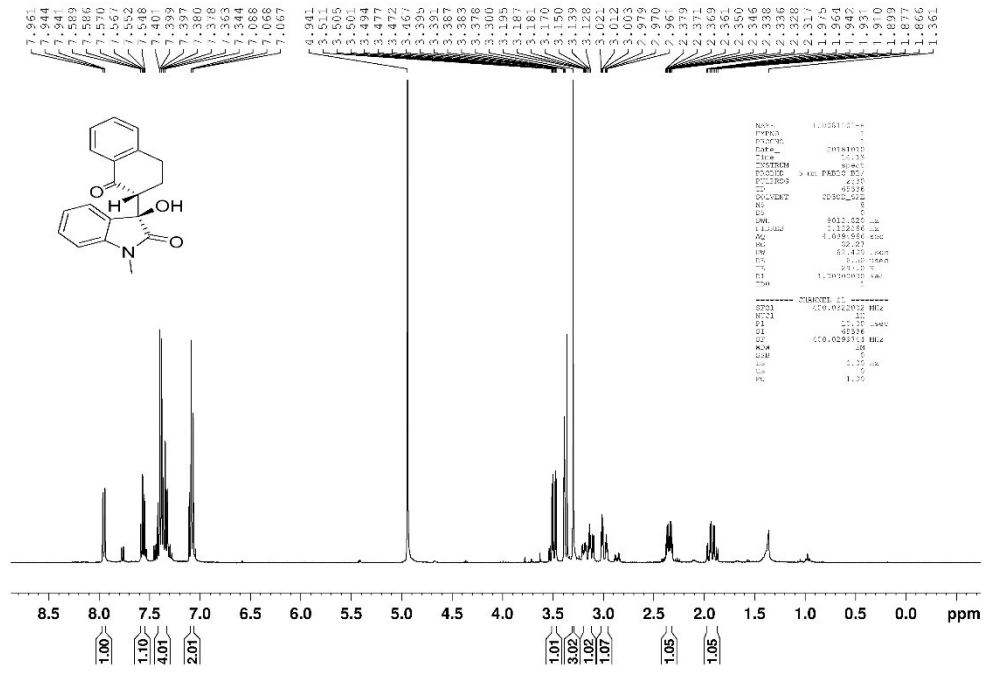

7.653
7.631
7.416
7.398
7.381
7.234
7.215
7.176
7.157
7.138
7.098
6.827
6.807
6.767
6.748
4.817
3.998
3.987
3.963
3.953
3.213
3.209
3.205
3.027
3.018
3.009
3.002
2.992
2.711
2.702
2.692
2.683
2.678
2.669
2.659
2.650
2.481
2.463
2.454
2.447
2.437
2.429
2.421
2.413
2.403
2.395
2.388
2.369
Cl
HO
H
O
O
N
H
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
ppm
1.00
1.05
1.04
2.02
1.01
1.01
1.02
2.01
1.07
1.08

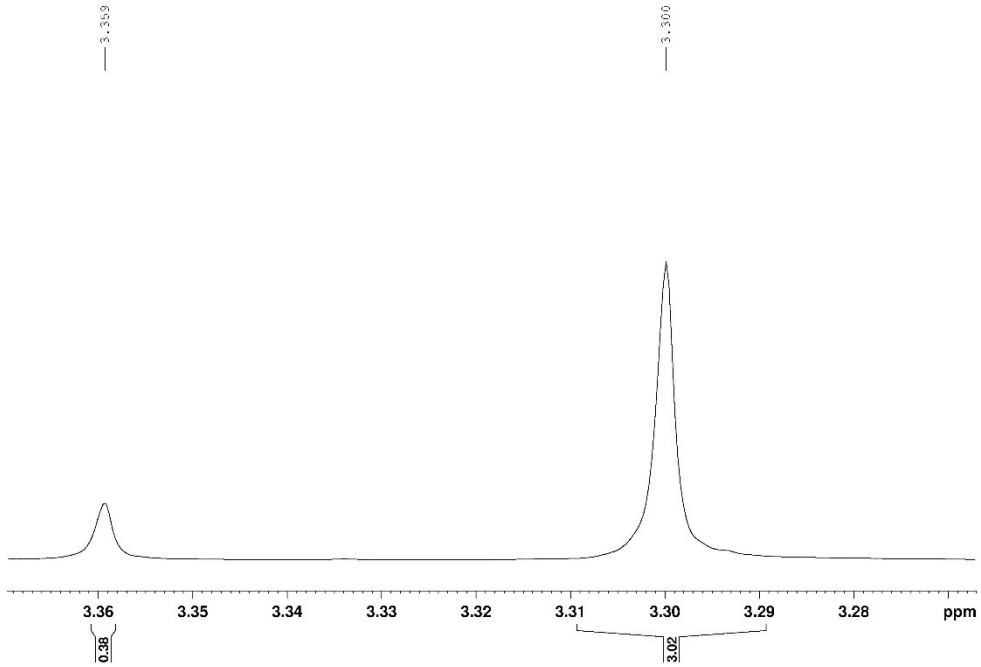

2.481
2.463
2.454
2.447
2.437
2.429
2.421
2.413
2.403
2.395
2.388
2.369
2.110
2.091
2.072
2.45
2.40
2.35
2.30
2.25
2.20
2.15
2.10
ppm
1.00
0.10

^{13}C NMR of **3mb**

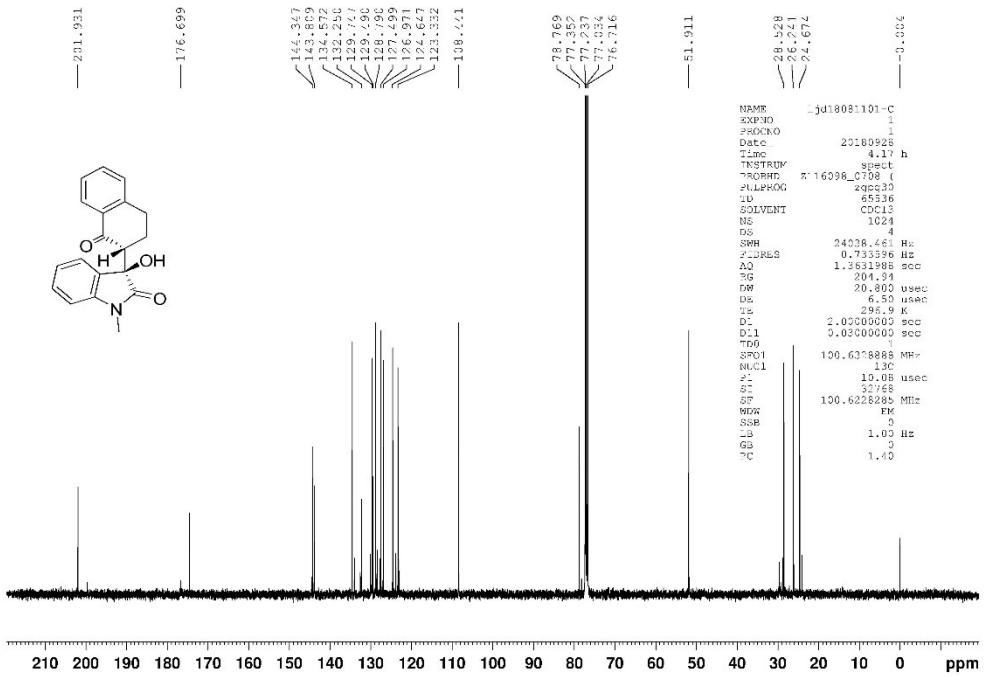


^{1}H NMR of **3nb**

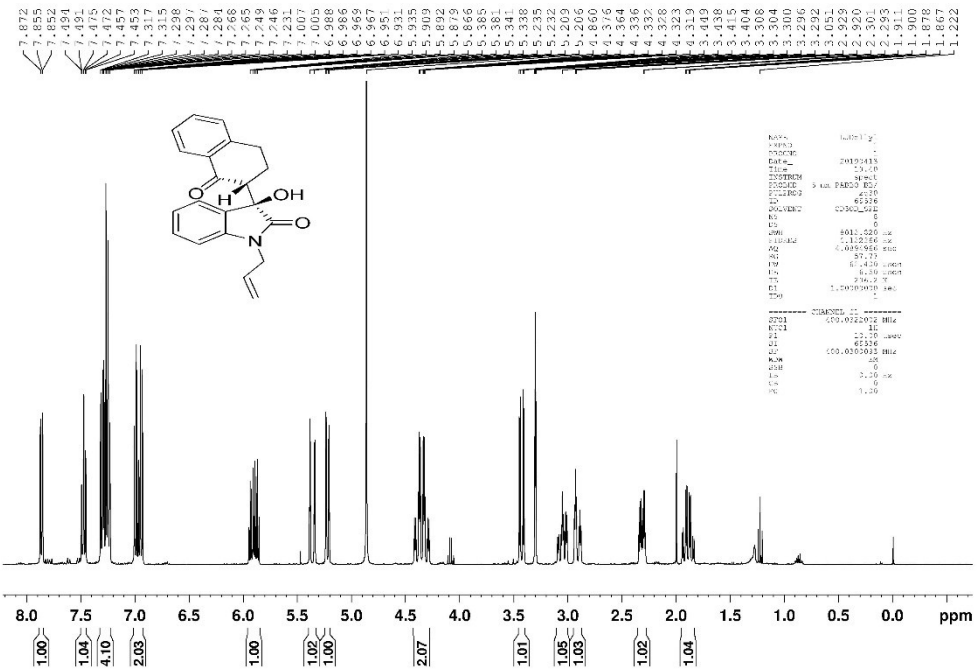


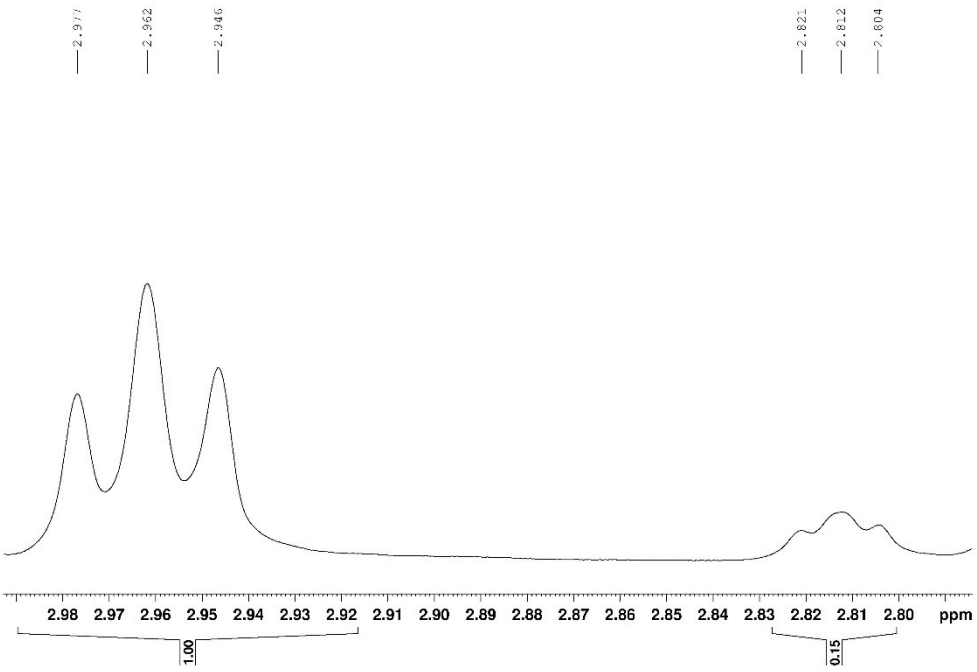


^{13}C NMR of **3nb**

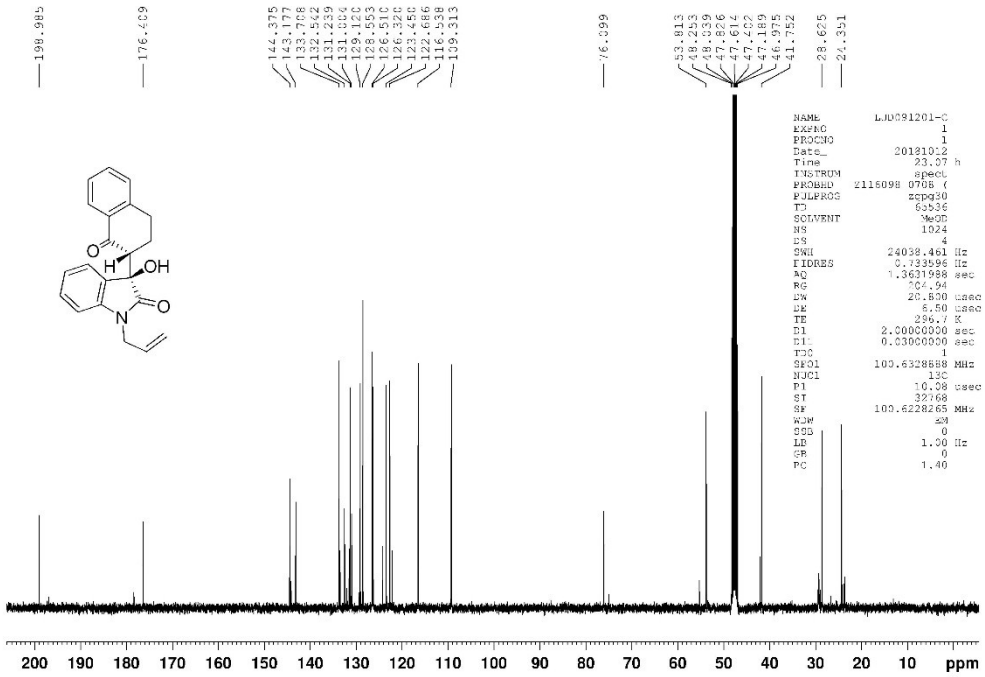


^{1}H NMR of **3ob**

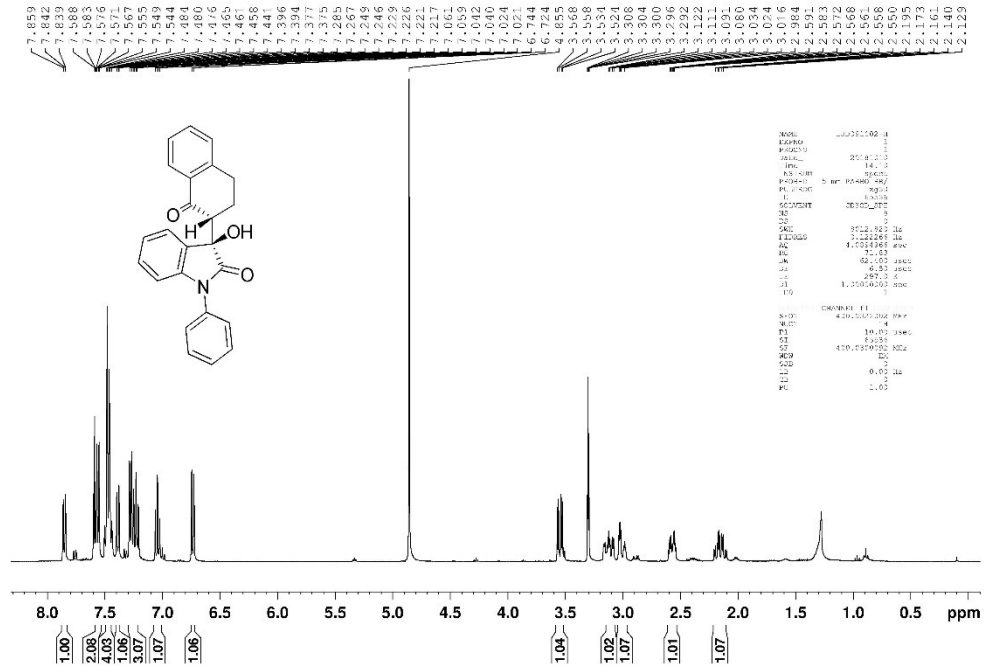


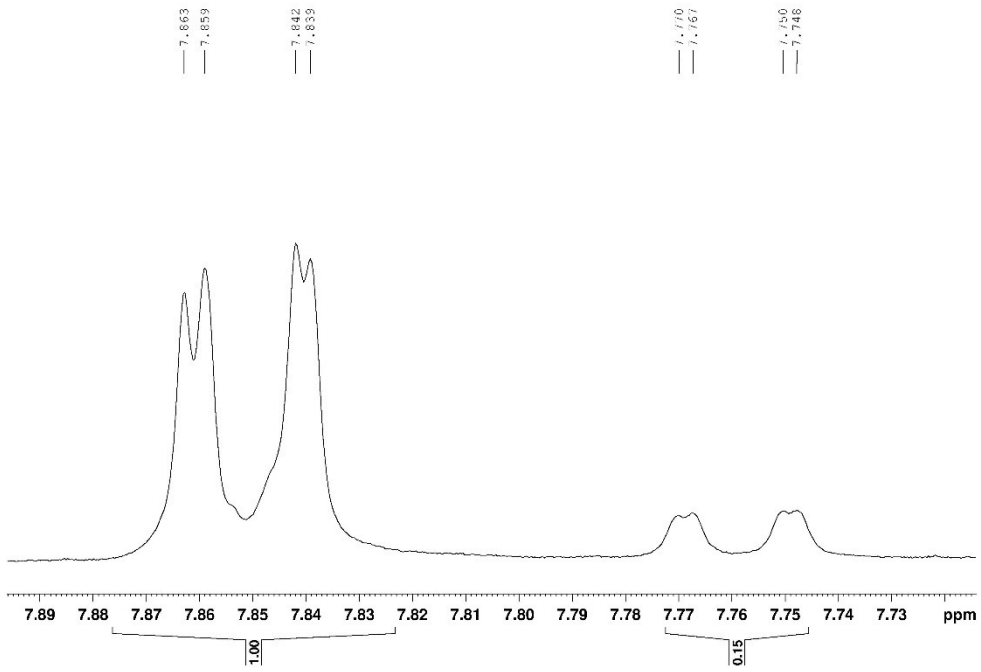


^{13}C NMR of **3ob**

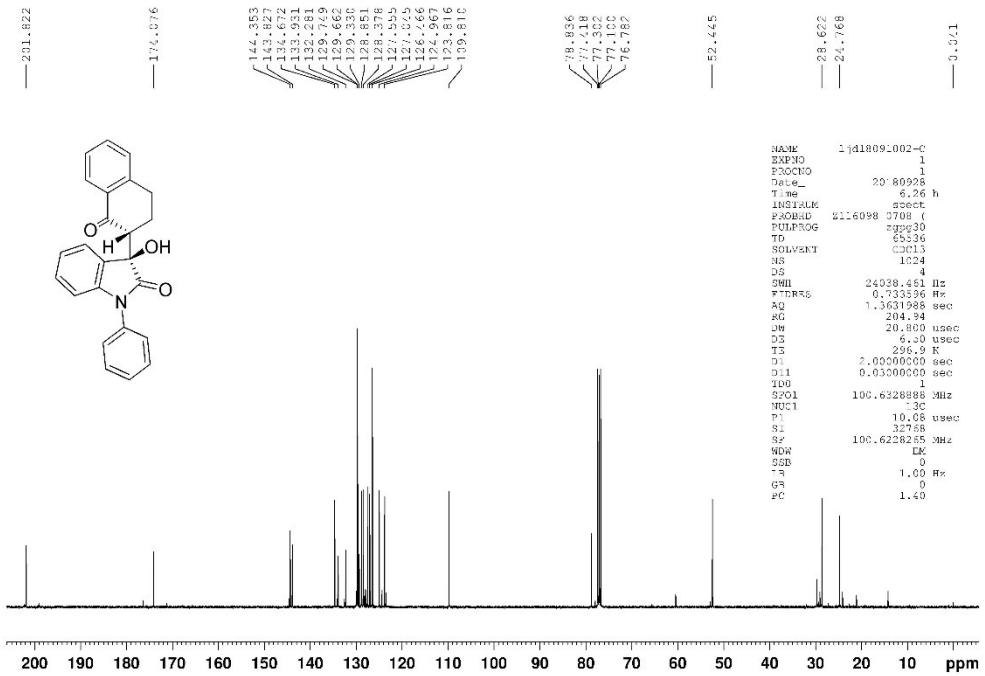


^{1}H NMR of **3pb**

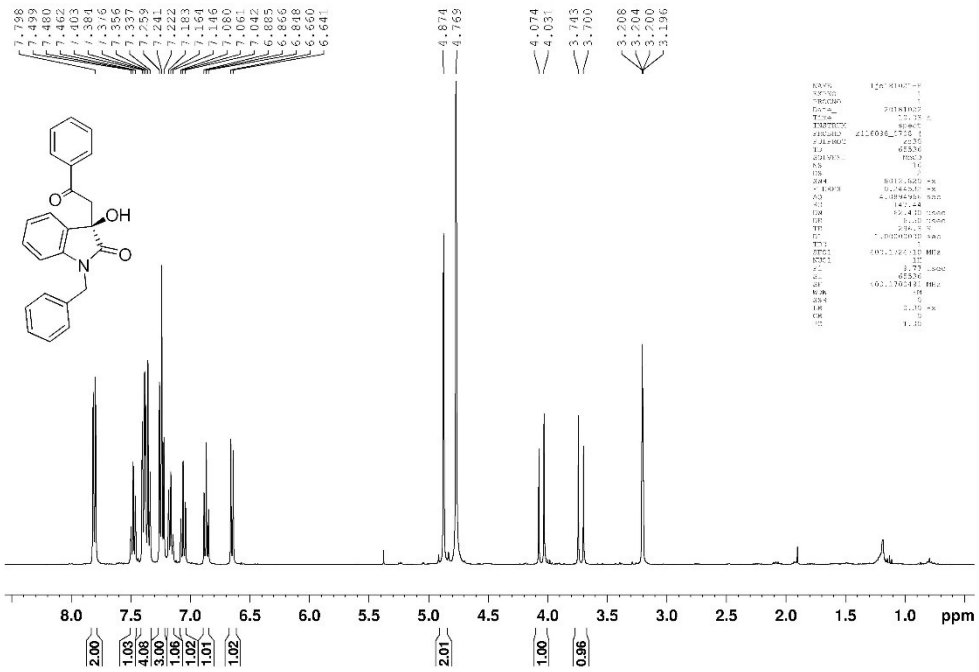




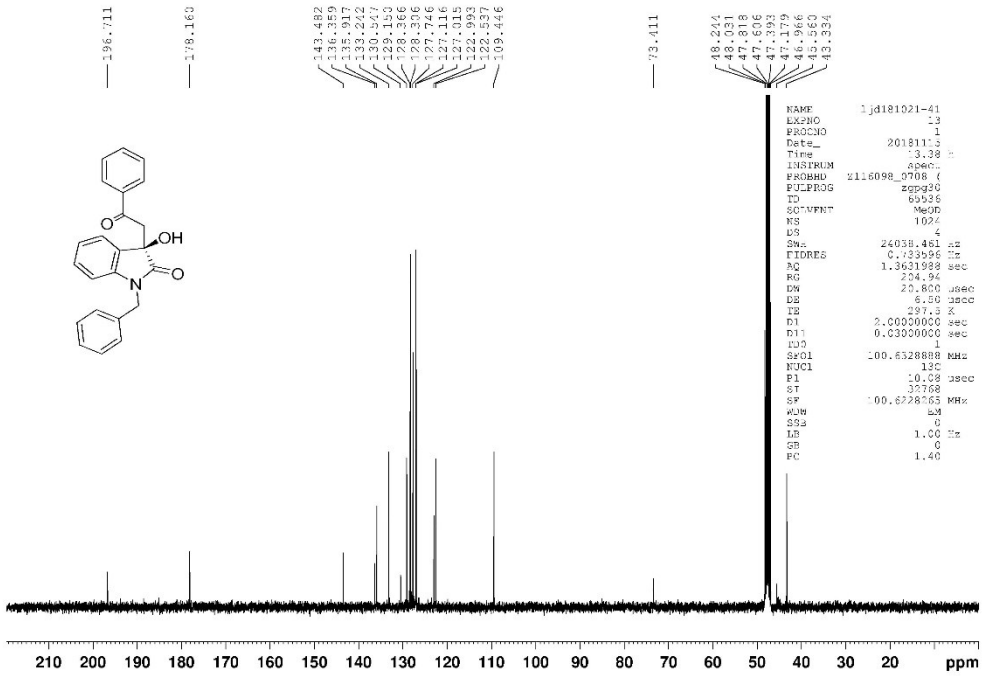
^{13}C NMR of **3pb**



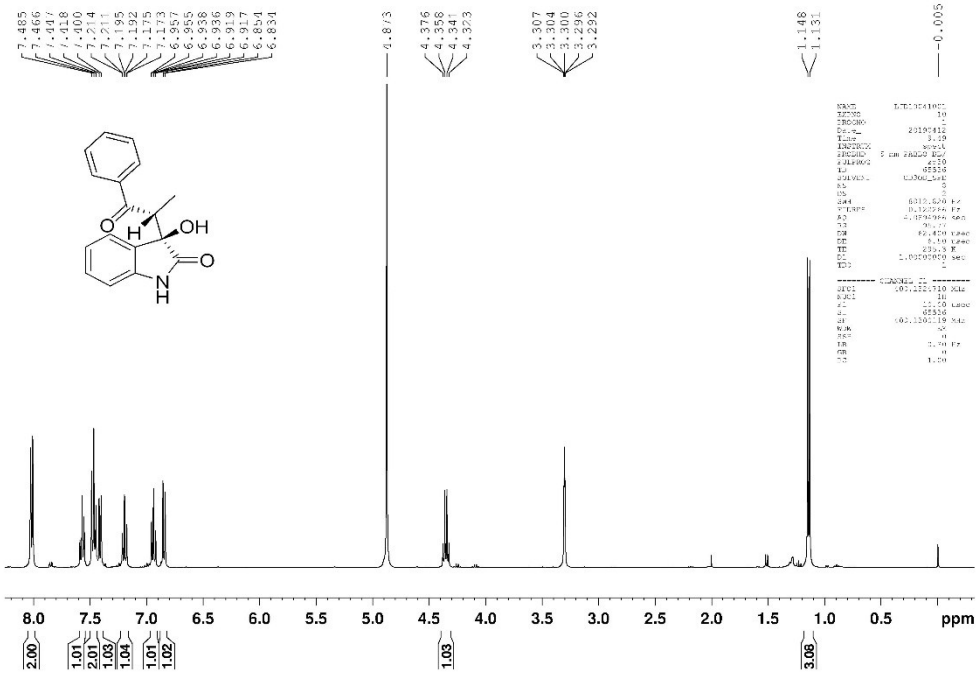
^{1}H NMR of **3qc**

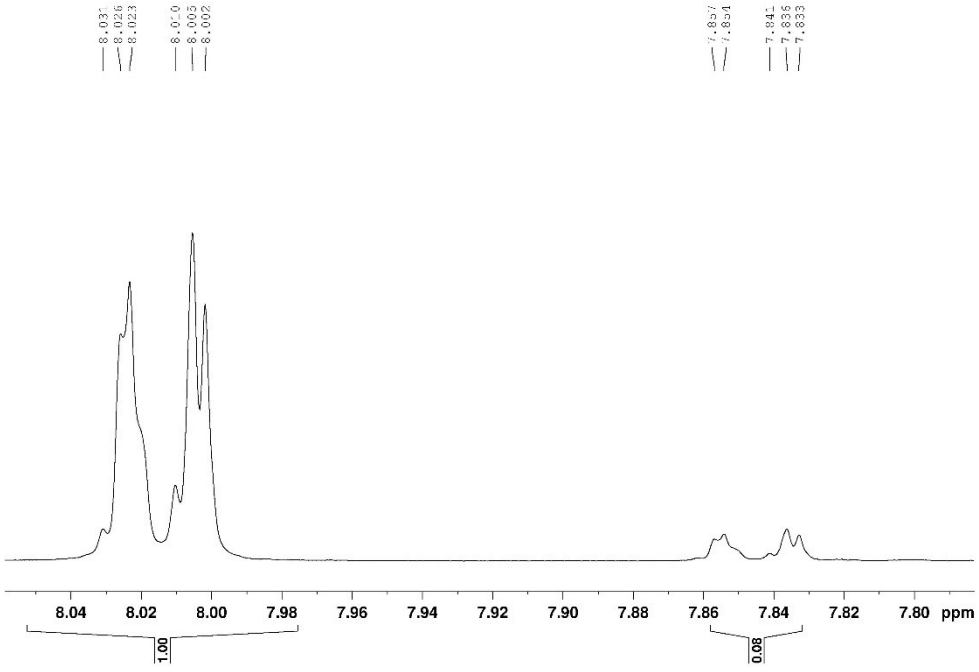


^{13}C NMR of **3qc**

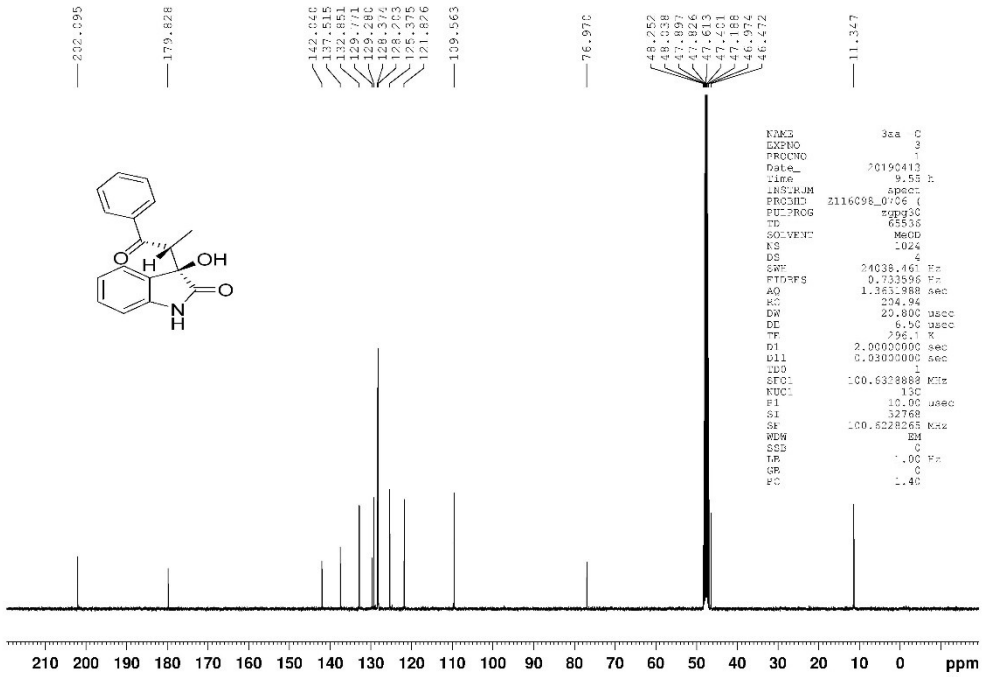


^{1}H NMR of **3aa**

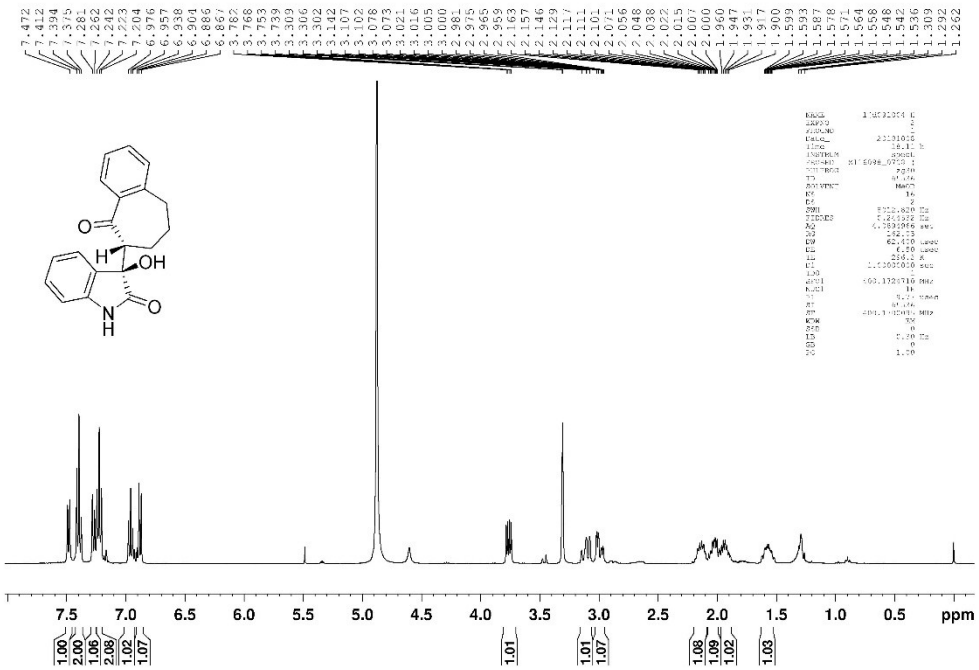

7.485
7.466
7.418
7.400
7.214
7.211
7.195
7.192
7.175
7.173
6.957
6.955
6.938
6.936
6.919
6.917
6.854
6.834
4.873
4.376
4.358
4.341
4.323
3.307
3.304
3.300
3.296
3.292
1.148
1.131
0.005
O
H
OH
O
N
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.01
2.01
1.03
1.04
1.01
1.02
1.03
3.06

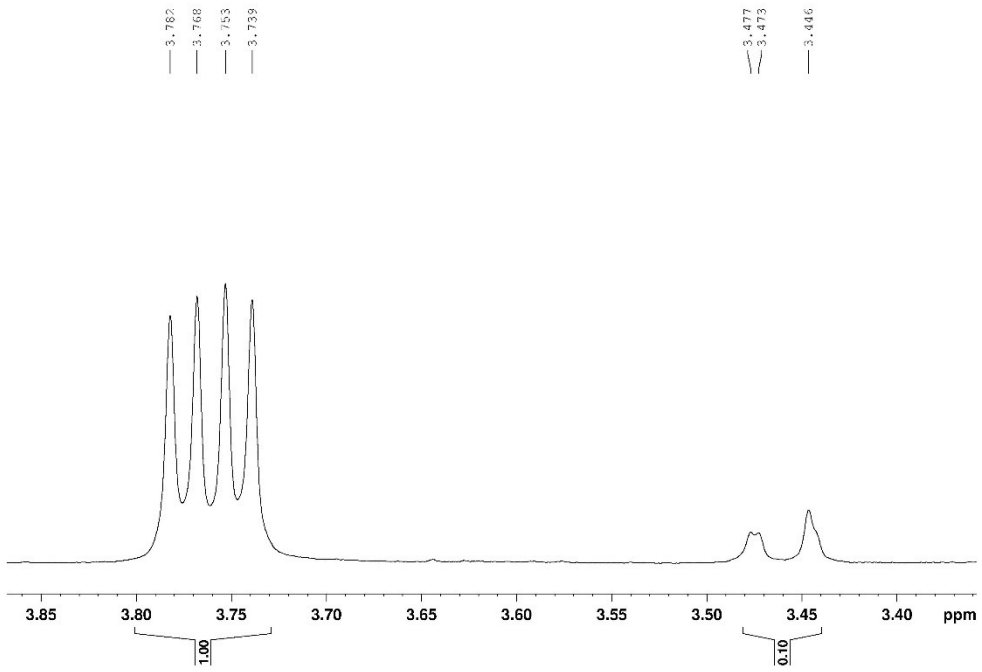

8.031
8.026
8.023
8.000
8.005
8.002
7.837
7.834
7.841
7.835
7.833
8.04
8.02
8.00
7.98
7.96
7.94
7.92
7.90
7.88
7.86
7.84
7.82
7.80
ppm
1.00
0.06

^{13}C NMR of **3aa**

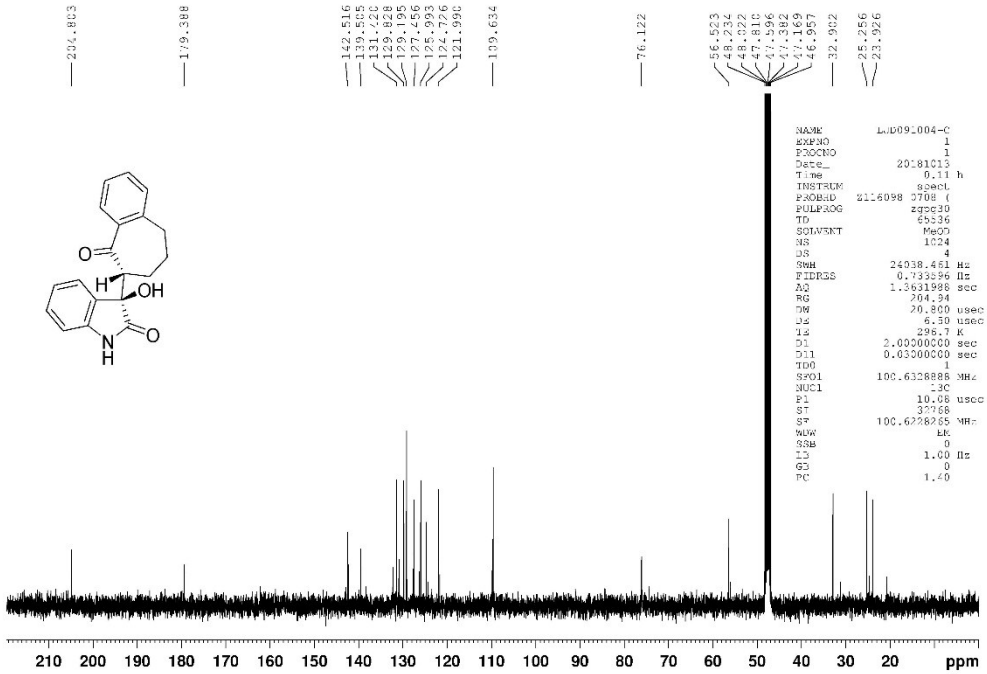


^{1}H NMR of **3ad**

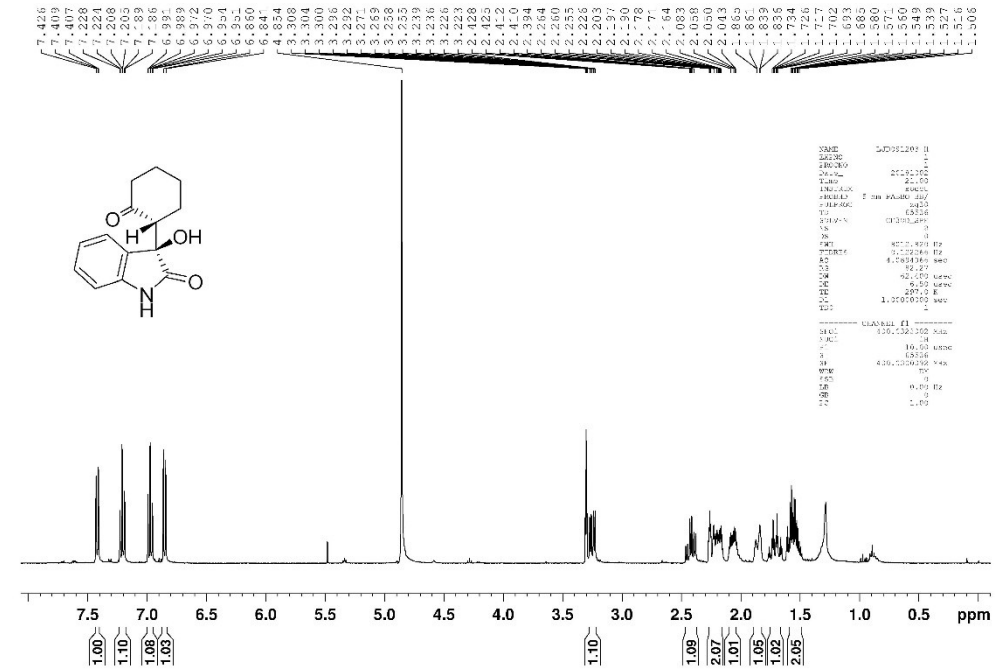


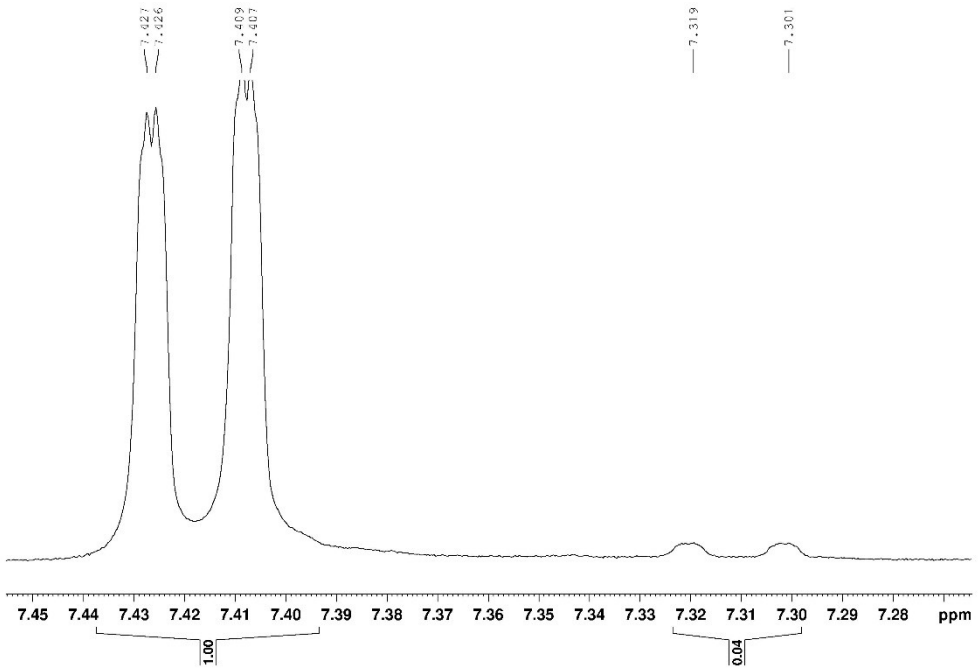


^{13}C NMR of **3ad**

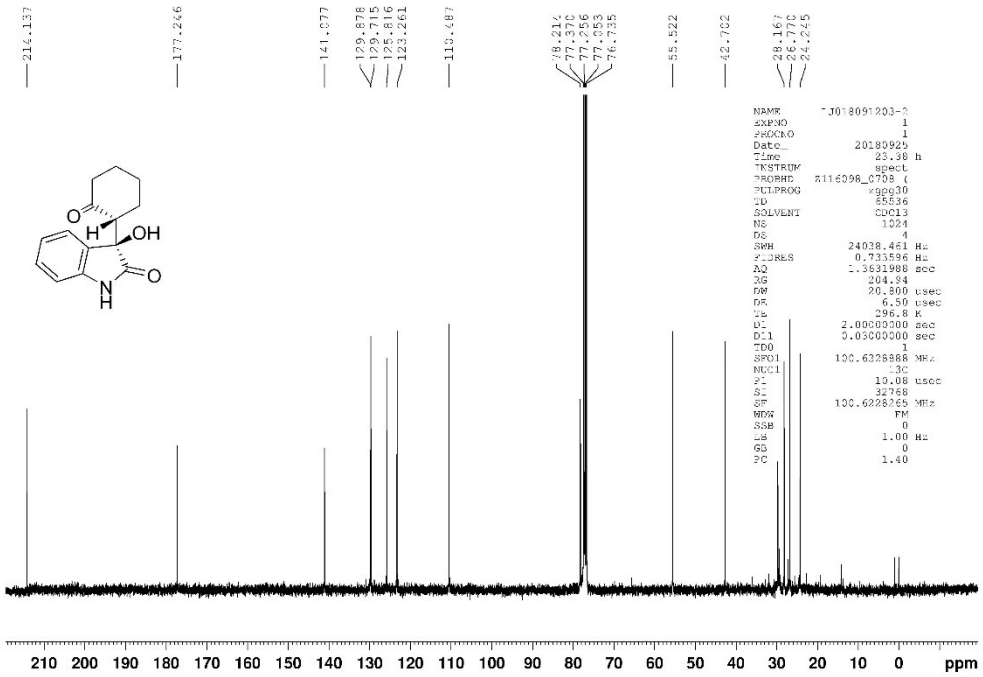


^{1}H NMR of **3ae**


O
H
OH
O
N
H
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
ppm
1.00
1.10
1.08
1.03
1.10
1.09
2.07
1.01
1.05
1.02
2.05


7.427
7.426
7.409
7.407
7.319
7.301
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
ppm
1.00
0.04

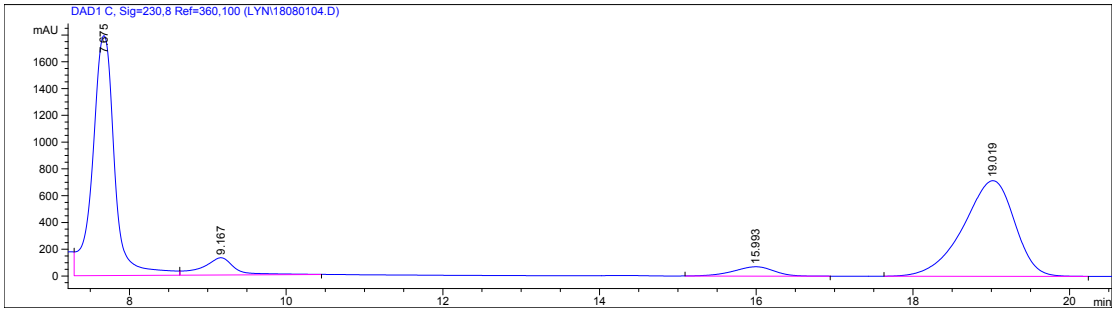
^{13}C NMR of **3ae**



Part III HPLC data

3ab

Racemic sample

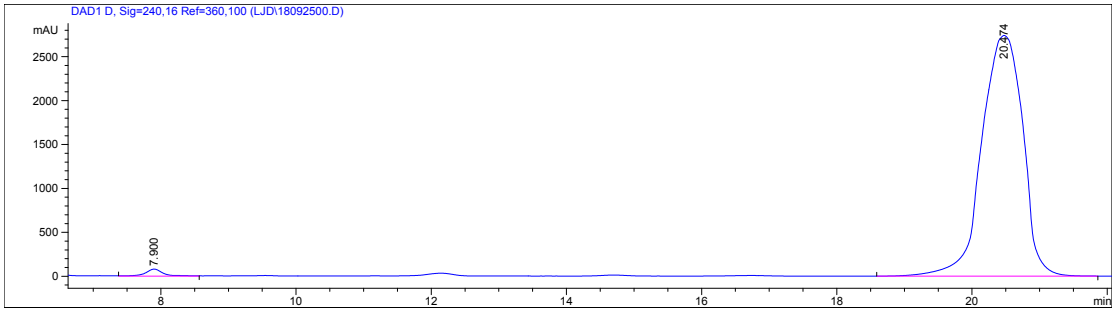


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.675	VV	0.2928	3.48359e4	1791.70056	47.2941
2	9.167	VB	0.4060	3715.16602	129.01198	5.0438
3	15.993	BB	0.5463	2506.29175	69.57664	3.4026
4	19.019	BB	0.6926	3.26007e4	714.18481	44.2595
Totals :				7.36581e4	2704.47400	

Results obtained with enhanced integrator!

Asymmetric version:



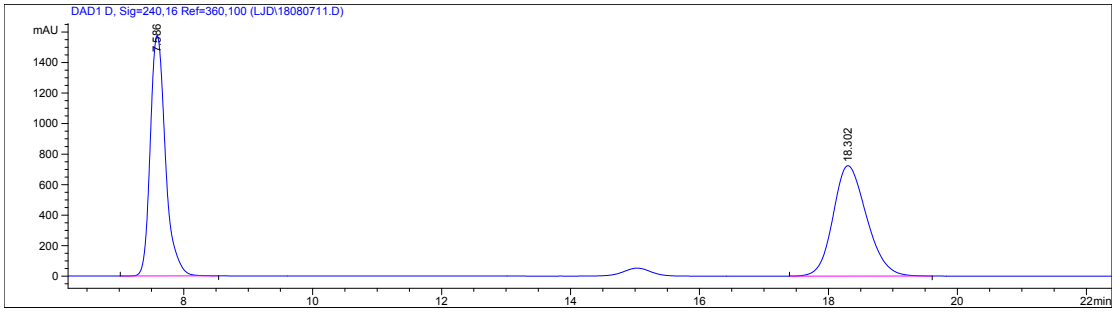
Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.900	VB	0.2687	1489.54260	80.18667	1.2784
2	20.474	VB	0.5699	1.15028e5	2739.52368	98.7216
Totals :				1.16517e5	2819.71035	

Results obtained with enhanced integrator!

3bb

Racemic sample

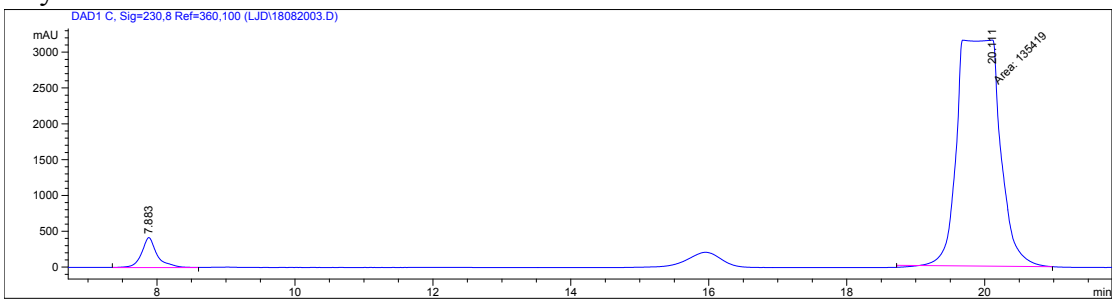


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.586	PB	0.2521	2.56735e4	1575.40234	49.5863
2	18.302	BB	0.5530	2.61019e4	723.28241	50.4137
Totals :				5.17754e4	2298.68475	

Results obtained with enhanced integrator!

Asymmetric version:



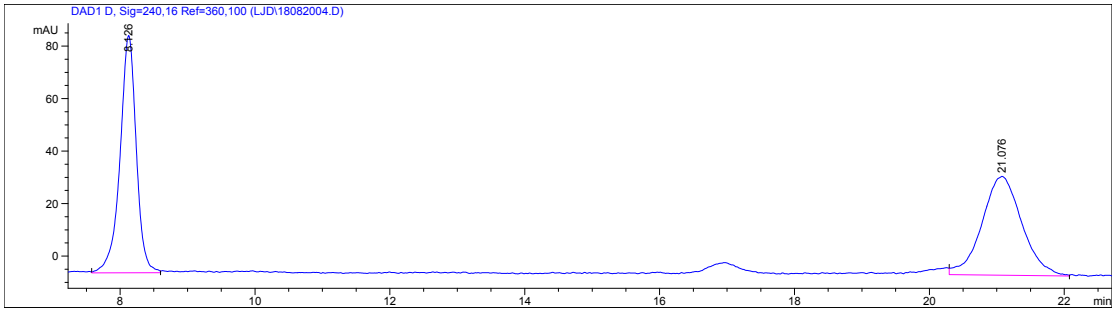
Signal 2: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.883	VB	0.2243	6617.15674	418.96082	4.6588
2	20.111	MM	0.7155	1.35419e5	3154.58423	95.3412
Totals :				1.42036e5	3573.54504	

Results obtained with enhanced integrator!

3cb

Racemic sample

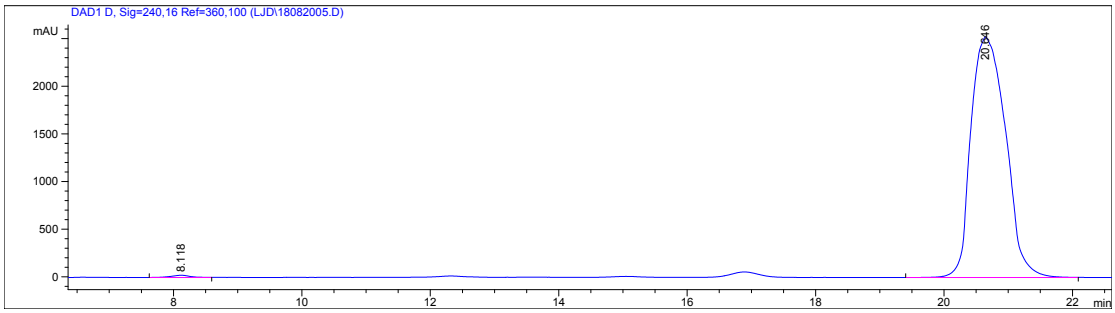


Signal 3: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.126	VV	0.2536	1515.42920	90.37933	49.5591
2	21.076	VV	0.5023	1542.39075	37.62316	50.4409
Totals :				3057.81995	128.00249	

Results obtained with enhanced integrator!

Asymmetric version:



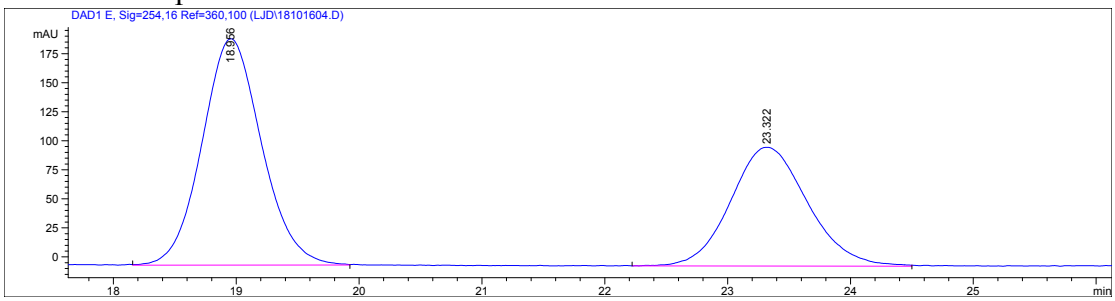
Signal 3: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.118	BV	0.2883	478.63980	23.23573	0.5042
2	20.646	BB	0.4605	9.44470e4	2524.61646	99.4958
Totals :				9.49257e4	2547.85219	

Results obtained with enhanced integrator!

3db

Racemic sample

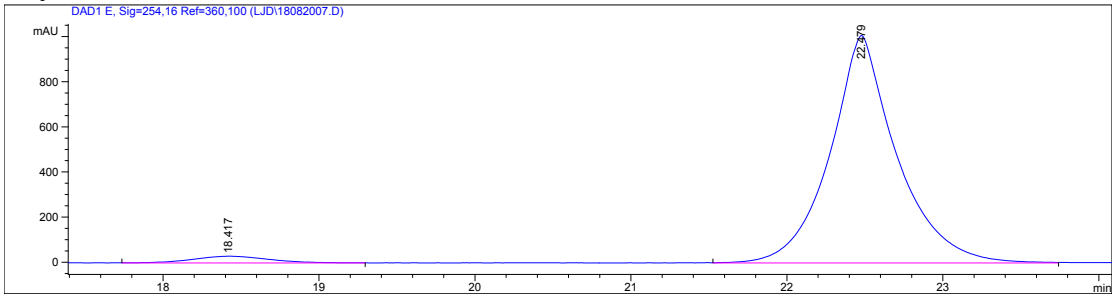


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.956	VV	0.5009	6562.18604	194.84789	59.5425
2	23.322	VB	0.5969	4458.82715	102.22092	40.4575
Totals :				1.10210e4	297.06880	

Results obtained with enhanced integrator!

Asymmetric version:



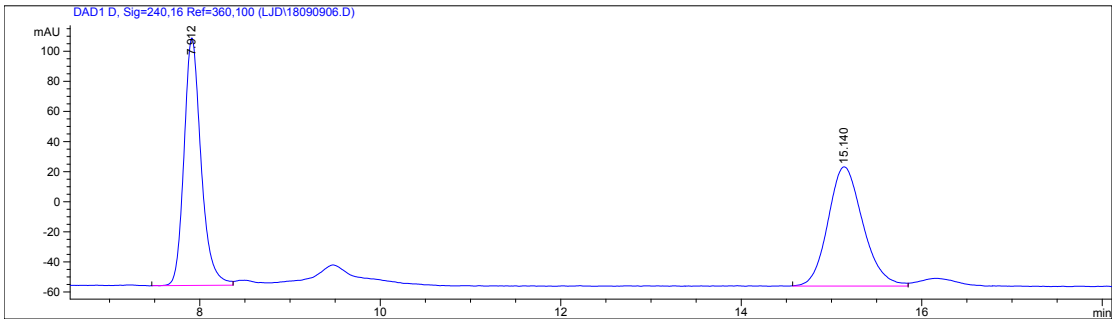
Signal 4: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.417	VB	0.4139	1015.76978	29.78581	3.2822
2	22.479	VV	0.3985	2.99325e4	1007.86664	96.7178
Totals :				3.09483e4	1037.65245	

Results obtained with enhanced integrator!

3eb

Racemic sample

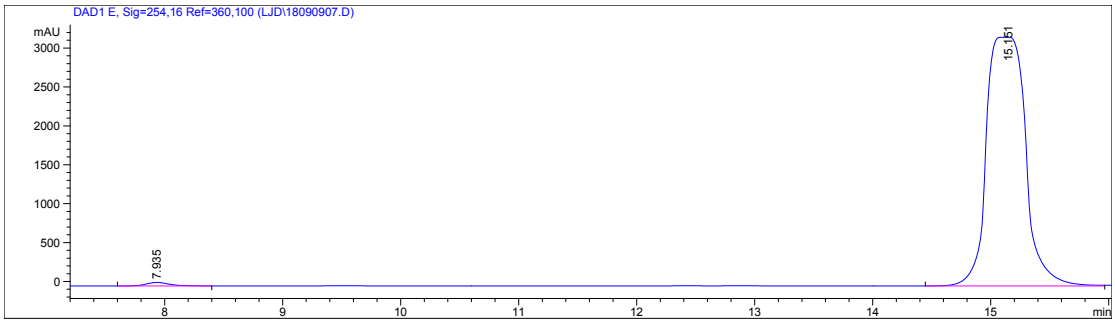


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.912	PB	0.1992	2160.67969	164.51219	50.4221
2	15.140	BB	0.4007	2124.50171	79.25435	49.5779
Totals :				4285.18140	243.76654	

Results obtained with enhanced integrator!

Asymmetric version:



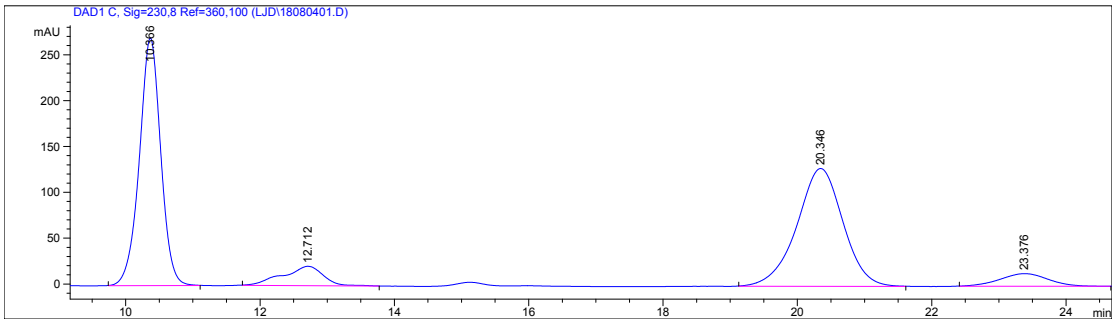
Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.935	VB	0.2021	598.00000	44.70562	0.8109
2	15.151	BB	0.3151	7.31475e4	3195.17407	99.1891
Totals :				7.37455e4	3239.87969	

Results obtained with enhanced integrator!

3fb

Racemic sample

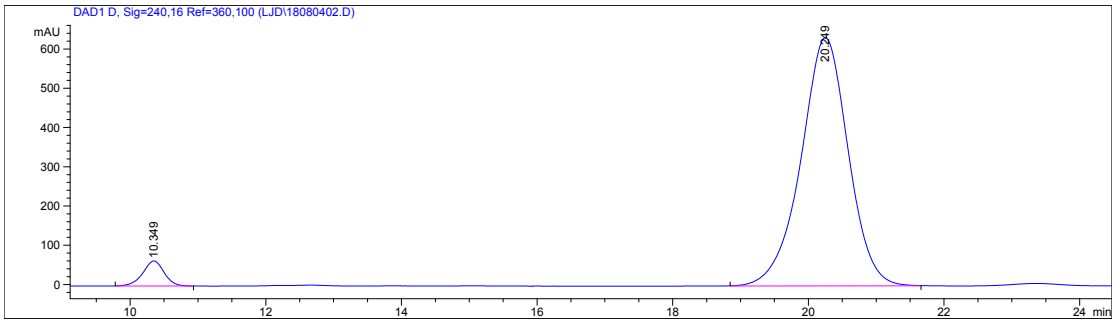


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.366	BB	0.3362	5978.97217	270.17441	43.6015
2	12.712	BB	0.5854	894.14624	21.22902	6.5205
3	20.346	BB	0.7245	6152.46631	128.52344	44.8667
4	23.376	BB	0.6858	687.19269	13.73321	5.0113
Totals :				1.37128e4	433.66008	

Results obtained with enhanced integrator!

Asymmetric version:



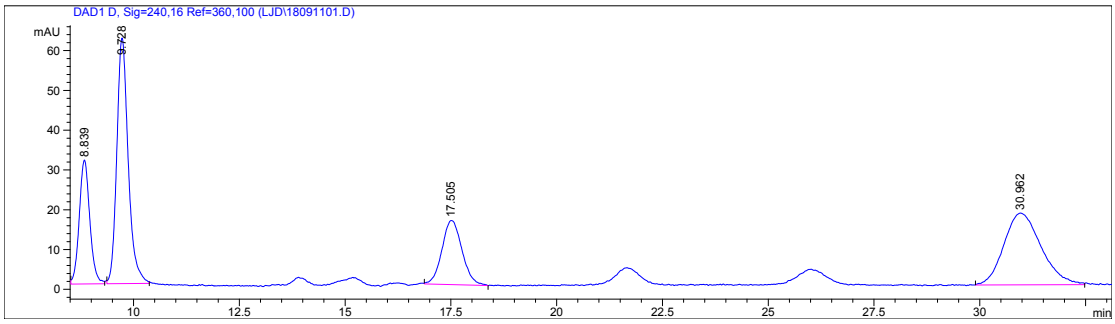
Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.349	BB	0.3322	1403.83240	63.91968	4.3877
2	20.249	BB	0.7323	3.05909e4	632.50098	95.6123
Totals :				3.19948e4	696.42066	

Results obtained with enhanced integrator!

3gb

Racemic sample

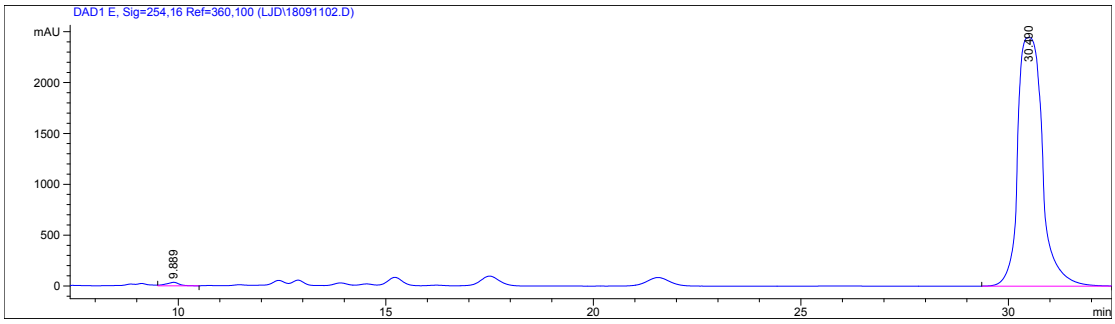


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.839	VB	0.2562	539.87201	31.14570	16.2286
2	9.728	BB	0.2824	1155.24670	61.72187	34.7268
3	17.505	BP	0.4090	531.50330	16.10513	15.9770
4	30.962	BV	0.7442	1100.04565	18.01979	33.0675
Totals :				3326.66766	126.99250	

Results obtained with enhanced integrator!

Asymmetric version:



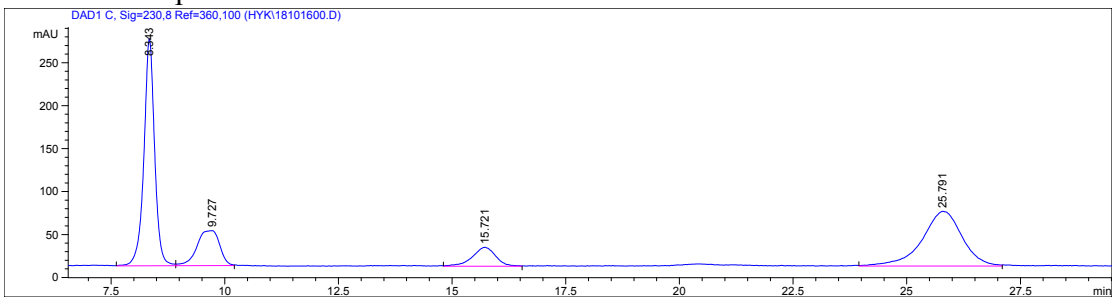
Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.889	VV	0.3089	759.41522	34.48971	0.7518
2	30.490	BBA	0.5465	1.00258e5	2444.53052	99.2482
Totals :				1.01018e5	2479.02023	

Results obtained with enhanced integrator!

3hb

Racemic sample

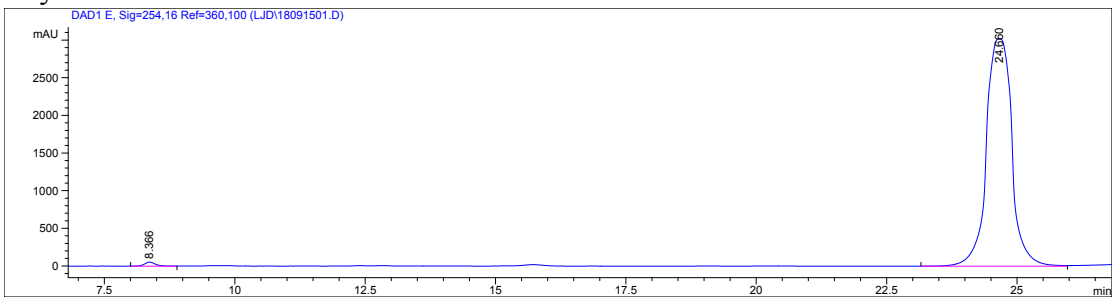


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.343	BB	0.2416	4337.87939	264.19507	41.5157
2	9.727	BV	0.4481	1405.78979	40.58850	13.4541
3	15.721	VV	0.4271	783.01459	22.00497	7.4938
4	25.791	VV	0.7294	3922.08276	63.78209	37.5363
Totals :				1.04488e4	390.57063	

Results obtained with enhanced integrator!

Asymmetric version:



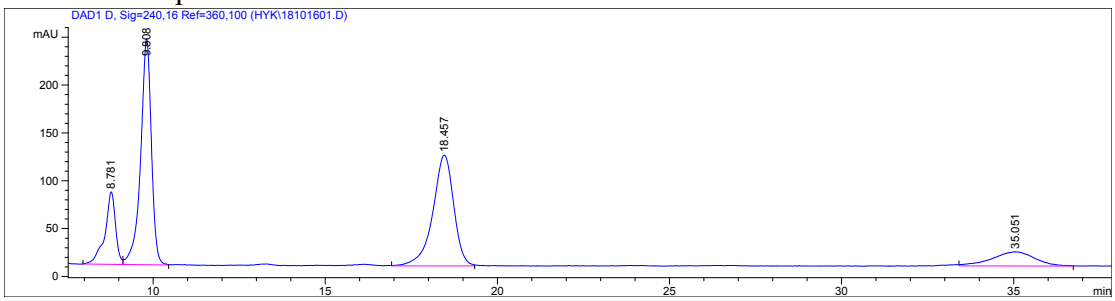
Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.366	VB	0.2193	783.59772	53.36525	0.7631
2	24.660	VV	0.5196	1.01902e5	3020.62793	99.2369
Totals :				1.02685e5	3073.99318	

Results obtained with enhanced integrator!

3ib

Racemic sample

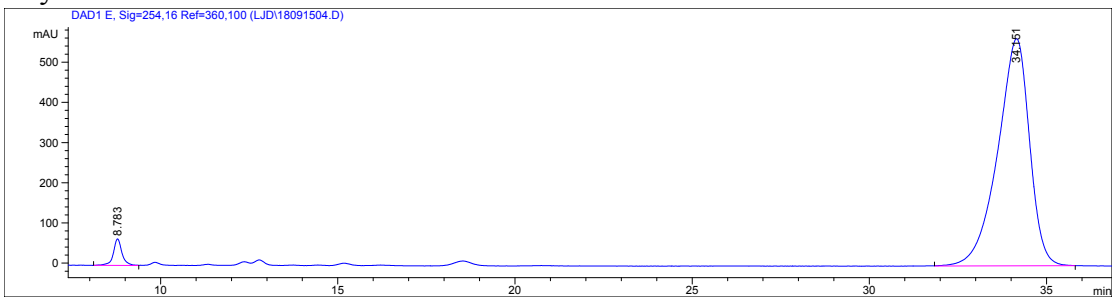


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.781	BV	0.3115	1634.90100	75.82829	12.6273
2	9.808	VV	0.3244	5149.72754	236.15472	39.7744
3	18.457	BV	0.6091	4891.39355	115.73641	37.7791
4	35.051	BV	1.0178	1271.31848	14.71653	9.8191
Totals :				1.29473e4	442.43596	

Results obtained with enhanced integrator!

Asymmetric version:



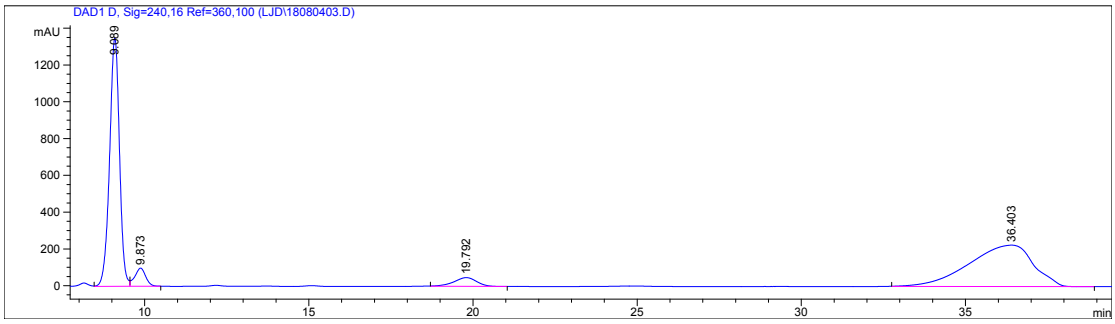
Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.783	PB	0.2510	1114.87671	66.02354	3.0642
2	34.151	BB	0.9143	3.52687e4	564.98499	96.9358
Totals :				3.63836e4	631.00852	

Results obtained with enhanced integrator!

3jb

Racemic sample

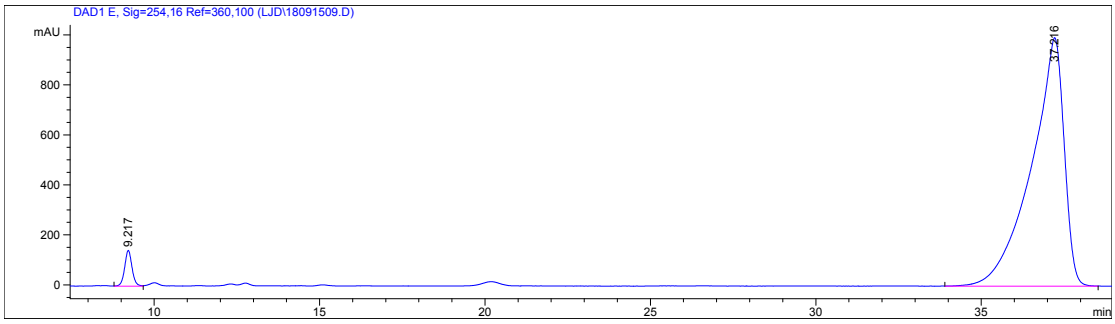


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.089	VV	0.3203	2.82749e4	1350.28369	44.7169
2	9.873	VB	0.3444	2275.38135	98.91264	3.5985
3	19.792	BP	0.7252	2260.37939	47.33094	3.5748
4	36.403	BPA	1.7748	3.04204e4	225.08093	48.1098
Totals :				6.32311e4	1721.60820	

Results obtained with enhanced integrator!

Asymmetric version:



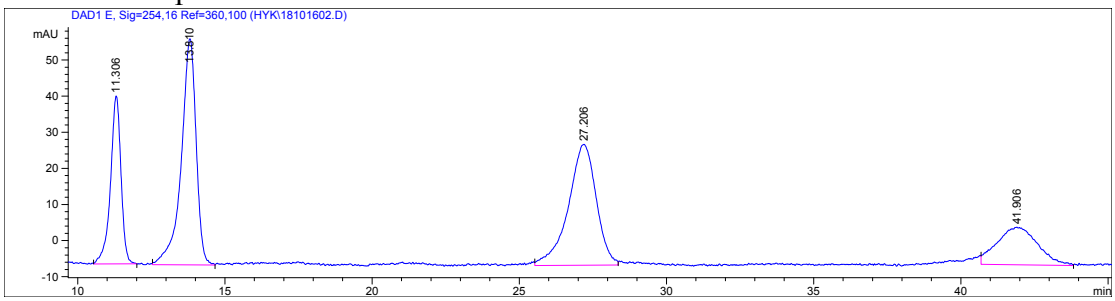
Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.217	VV	0.2357	2228.91016	143.10284	3.1581
2	37.216	VV	0.8260	6.83491e4	994.30804	96.8419
Totals :				7.05780e4	1137.41089	

Results obtained with enhanced integrator!

3kb

Racemic sample

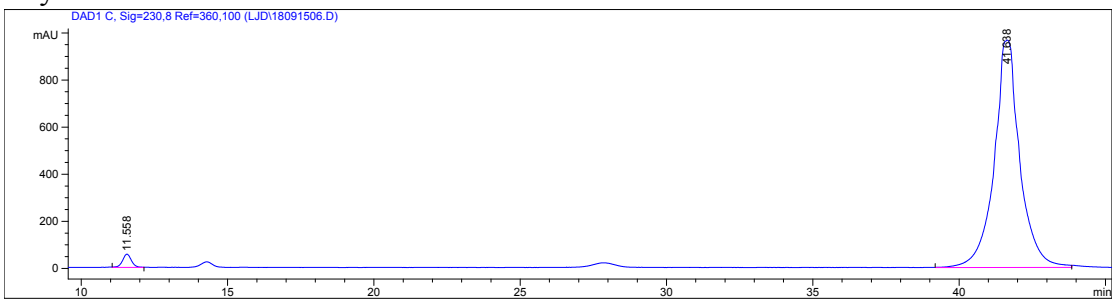


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.306	VB	0.3494	1152.89844	46.47765	17.5740
2	13.810	BV	0.4936	2198.26538	62.61521	33.5088
3	27.206	VV	0.7797	2207.90894	33.46795	33.6558
4	41.906	VV	1.1312	1001.18280	10.41811	15.2613
Totals :				6560.25555	152.97892	

Results obtained with enhanced integrator!

Asymmetric version:



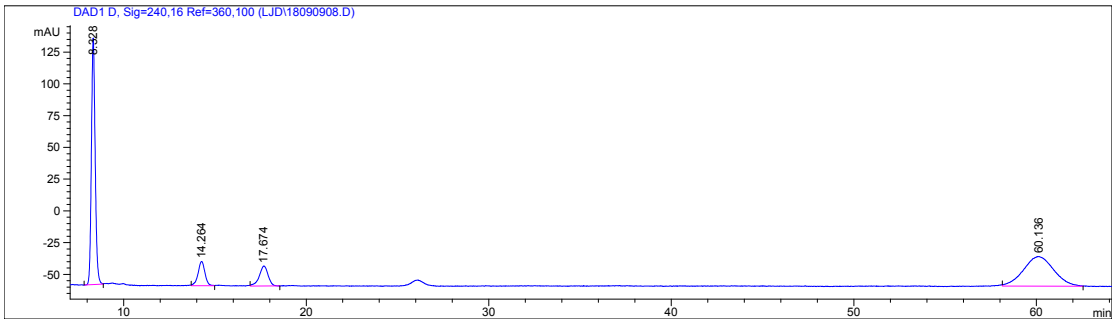
Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.558	VV	0.3173	1197.17786	56.48870	2.0047
2	41.638	VB	0.7453	5.85206e4	965.28320	97.9953
Totals :				5.97178e4	1021.77190	

Results obtained with enhanced integrator!

3lb

Racemic sample

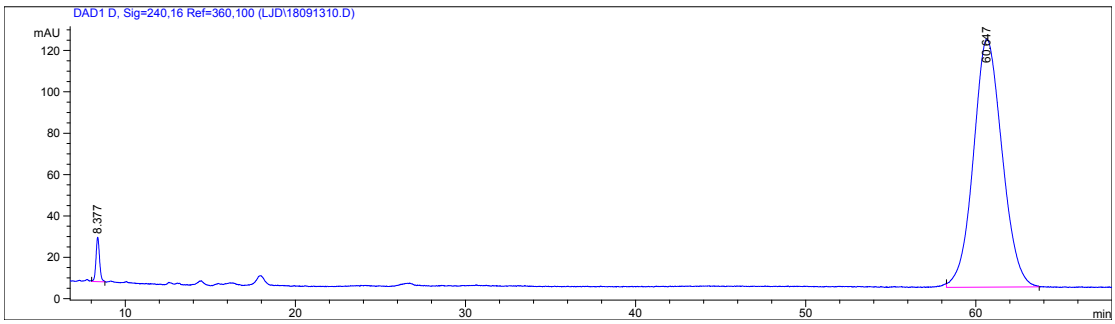


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.328	PB	0.2195	2786.68066	194.05388	42.9380
2	14.264	BP	0.3662	496.84735	19.05232	7.6556
3	17.674	BB	0.4286	526.24005	15.71640	8.1085
4	60.136	BV	1.3439	2680.24023	23.37192	41.2979
Totals :				6490.00830	252.19452	

Results obtained with enhanced integrator!

Asymmetric version:



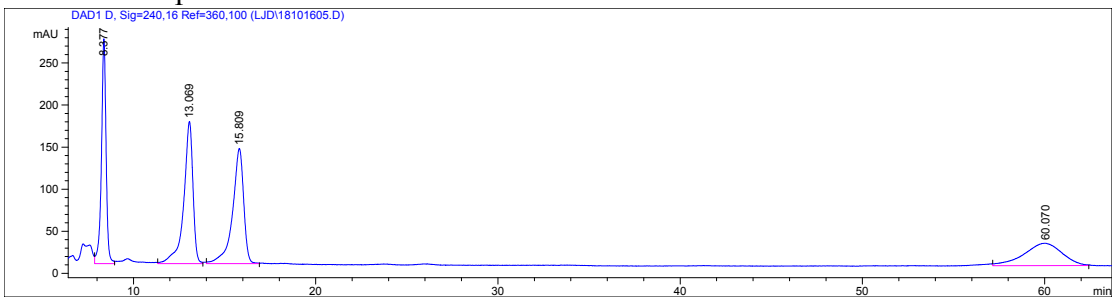
Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.377	VB	0.2183	313.68506	21.48586	2.1856
2	60.647	BB	1.3807	1.40384e4	120.01304	97.8144
Totals :				1.43521e4	141.49889	

Results obtained with enhanced integrator!

3mb

Racemic sample

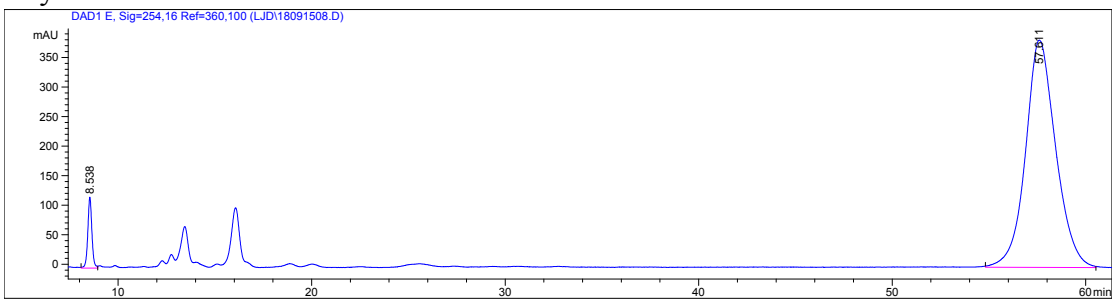


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.377	VB	0.2629	4740.11084	267.34802	23.3246
2	13.069	VV	0.5083	5941.88184	168.96892	29.2381
3	15.809	BB	0.6001	5792.06738	136.76631	28.5009
4	60.070	BV	1.7082	3848.33862	26.46956	18.9364
Totals :				2.03224e4	599.55281	

Results obtained with enhanced integrator!

Asymmetric version:



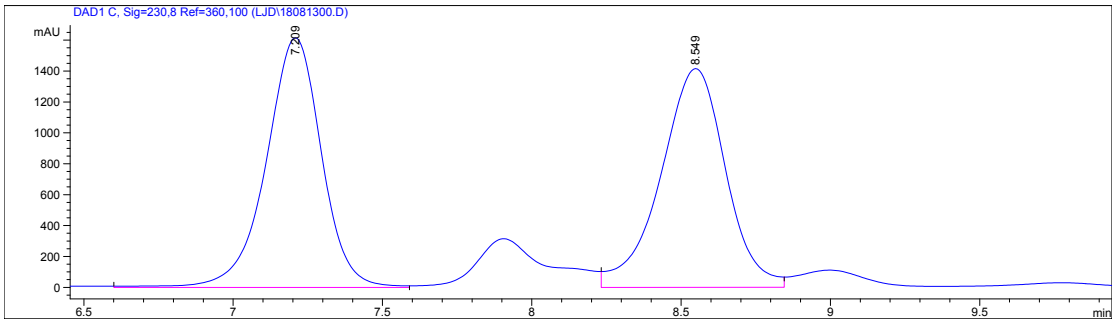
Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.538	BB	0.2262	1771.12000	119.96414	4.0841
2	57.611	VV	1.2779	4.15956e4	384.57690	95.9159
Totals :				4.33667e4	504.54105	

Results obtained with enhanced integrator!

3nb

Racemic sample

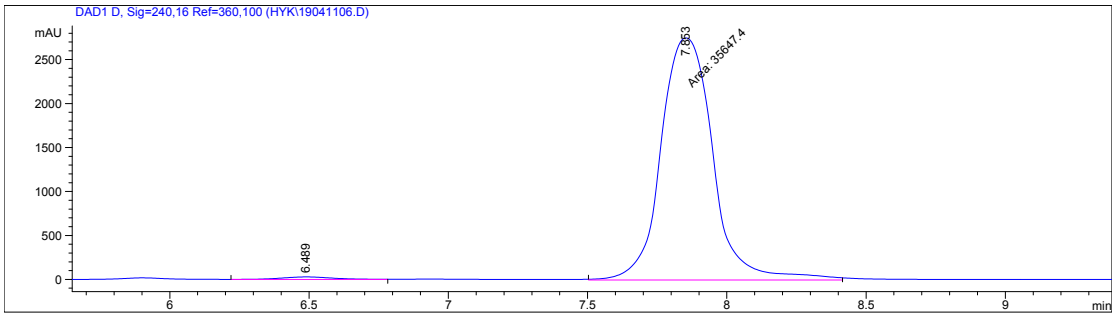


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.209	VV	0.1964	2.08335e4	1615.74463	49.3770
2	8.549	VV	0.2300	2.13592e4	1415.79272	50.6230
Totals :				4.21927e4	3031.53735	

Results obtained with enhanced integrator!

Asymmetric version:



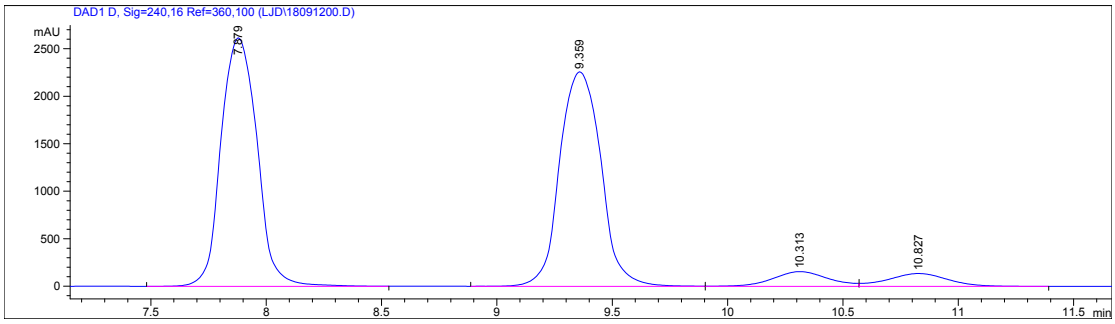
Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.489	VV	0.2047	394.82864	29.39762	1.0955
2	7.853	MM	0.2157	3.56474e4	2754.58887	98.9045
Totals :				3.60423e4	2783.98649	

Results obtained with enhanced integrator!

3ob

Racemic sample

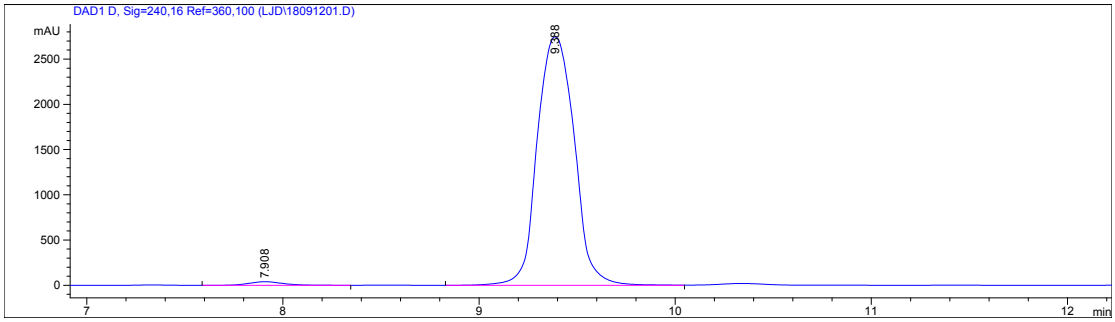


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.879	VB	0.1823	2.83293e4	2615.99854	46.2040
2	9.359	VV	0.2087	2.79982e4	2257.77661	45.6641
3	10.313	VV	0.2533	2568.42871	155.00015	4.1890
4	10.827	VB	0.2706	2417.55420	135.20712	3.9429
Totals :				6.13135e4	5163.98242	

Results obtained with enhanced integrator!

Asymmetric version:



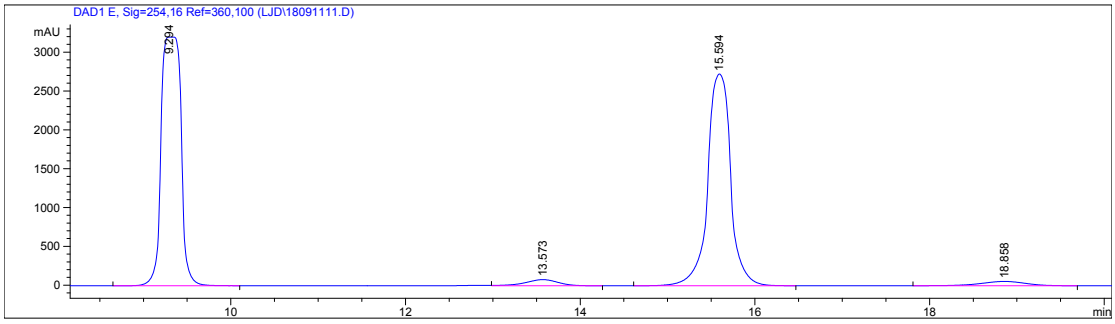
Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.908	VB	0.1960	528.12909	40.53514	1.4452
2	9.388	VV	0.2228	3.60154e4	2749.39160	98.5548
Totals :				3.65435e4	2789.92674	

Results obtained with enhanced integrator!

3pb

Racemic sample

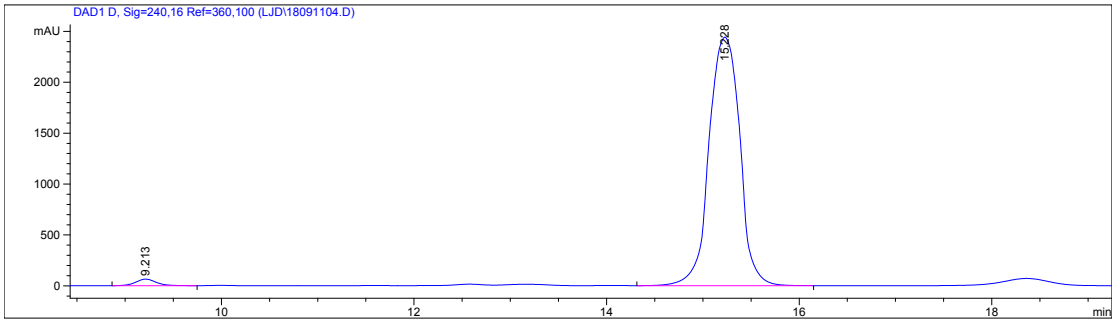


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.294	VB	0.2131	5.02235e4	3200.12305	48.3111
2	13.573	VB	0.3894	2050.19409	78.83678	1.9721
3	15.594	VB	0.2886	4.96773e4	2726.61816	47.7857
4	18.858	BV	0.4781	2007.45410	56.01735	1.9310
Totals :				1.03959e5	6061.59535	

Results obtained with enhanced integrator!

Asymmetric version:



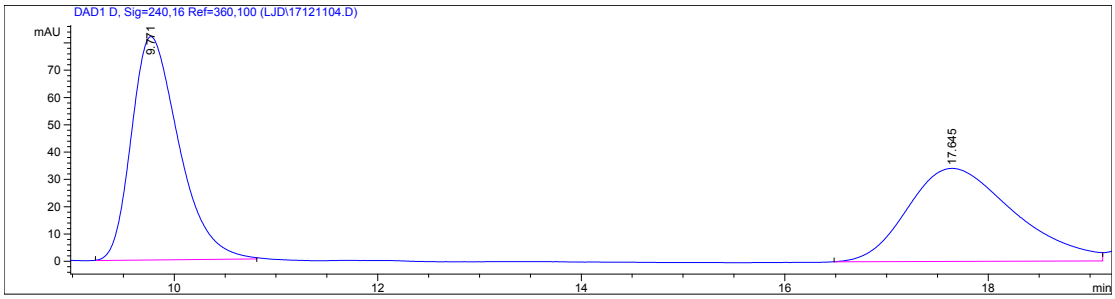
Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.213	BV	0.2287	981.03802	64.76698	1.7811
2	15.228	VB	0.3765	5.40997e4	2442.09985	98.2189
Totals :				5.50807e4	2506.86684	

Results obtained with enhanced integrator!

3qc

Racemic sample

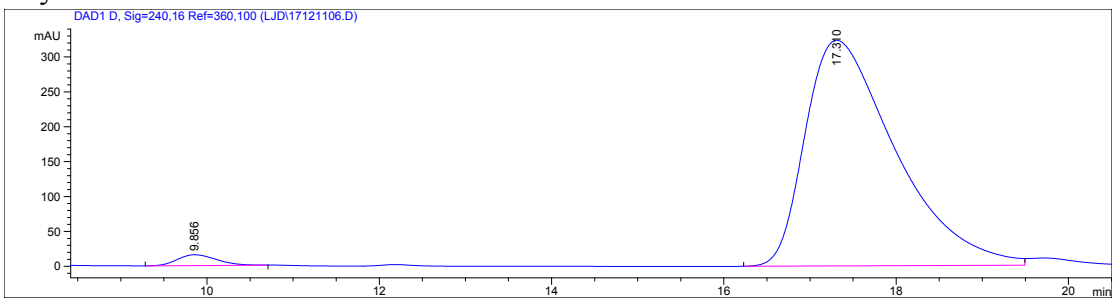


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.771	BB	0.4991	2645.16162	81.82700	51.7251
2	17.645	BV	1.0271	2468.72534	34.08263	48.2749
Totals :				5113.88696	115.90963	

Results obtained with enhanced integrator!

Asymmetric version:



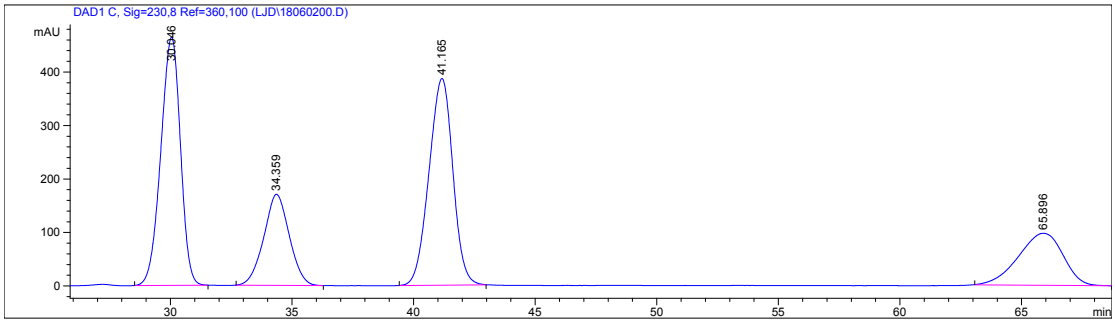
Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.856	PB	0.4943	489.47516	15.50457	2.0330
2	17.310	BB	1.0951	2.35867e4	323.32935	97.9670
Totals :				2.40761e4	338.83391	

Results obtained with enhanced integrator!

3aa

Racemic sample

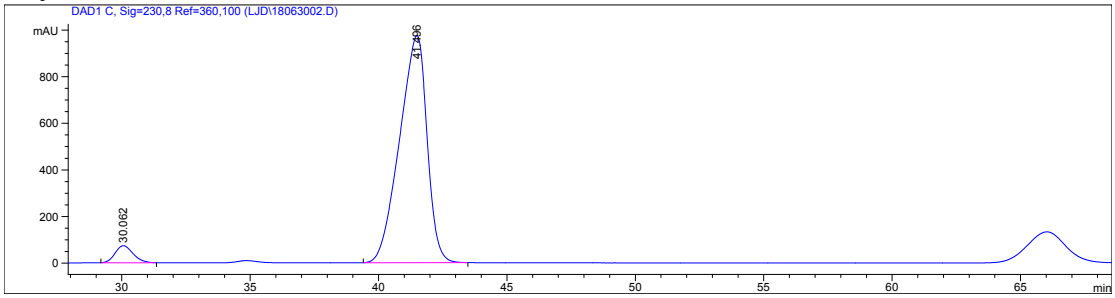


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.046	BB	0.8785	2.60466e4	464.27426	33.6885
2	34.359	BB	1.0769	1.24248e4	170.36404	16.0702
3	41.165	BB	1.0527	2.64113e4	386.73834	34.1602
4	65.896	BBA	1.5633	1.24333e4	97.26680	16.0812
Totals :				7.73161e4	1118.64345	

Results obtained with enhanced integrator!

Asymmetric version:



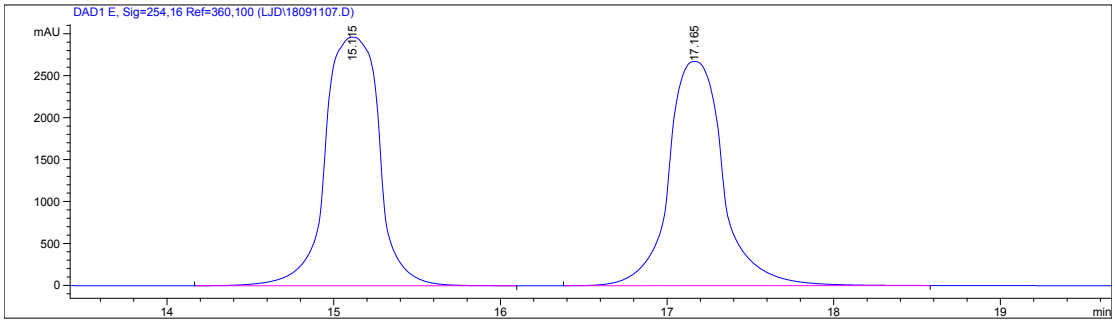
Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.062	BB	0.7428	3583.64795	73.50460	4.7110
2	41.496	BB	1.0971	7.24859e4	975.28894	95.2890
Totals :				7.60695e4	1048.79354	

Results obtained with enhanced integrator!

3ad

Racemic sample

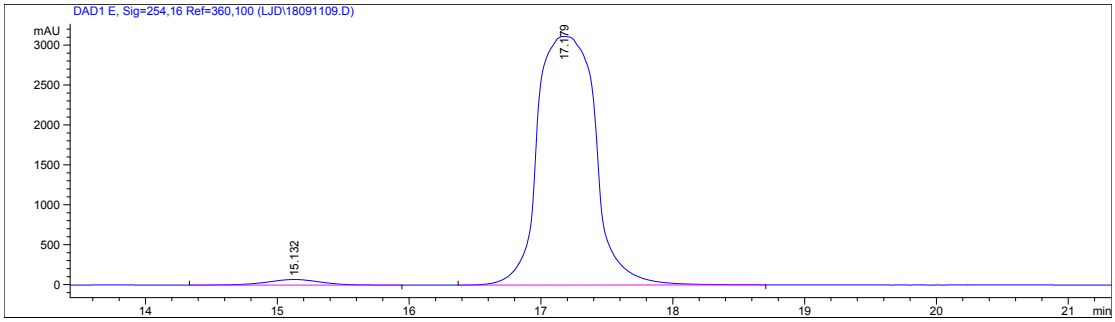


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.115	PB	0.3279	6.60251e4	2963.95947	52.2491
2	17.165	BB	0.3573	6.03410e4	2673.52197	47.7509
Totals :				1.26366e5	5637.48145	

Results obtained with enhanced integrator!

Asymmetric version:



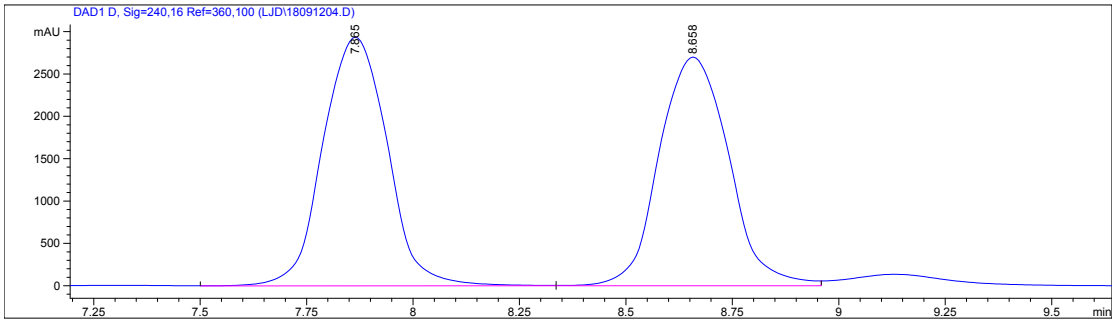
Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.132	BB	0.4150	2007.77673	70.34444	2.0851
2	17.179	BB	0.4013	9.42826e4	3113.42725	97.9149
Totals :				9.62903e4	3183.77168	

Results obtained with enhanced integrator!

3ae

Racemic sample

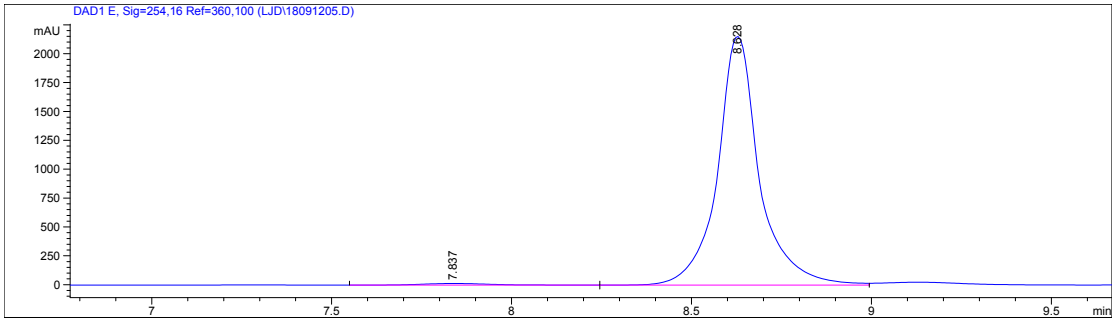


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.865	VV	0.1764	3.08036e4	2936.23096	50.1223
2	8.658	VV	0.1904	3.06533e4	2700.55957	49.8777
Totals :				6.14569e4	5636.79053	

Results obtained with enhanced integrator!

Asymmetric version:



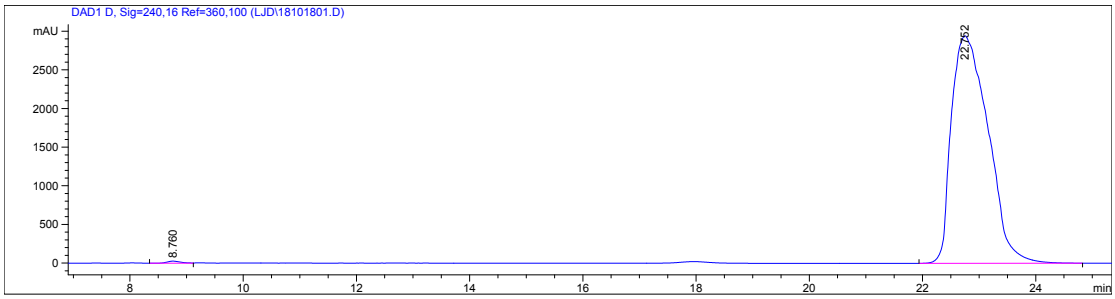
Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.837	VV	0.1909	181.96271	14.25587	1.0325
2	8.628	VV	0.1185	1.74421e4	2153.25488	98.9675
Totals :				1.76241e4	2167.51076	

Results obtained with enhanced integrator!

3cb (Gram scale)

Asymmetric version:



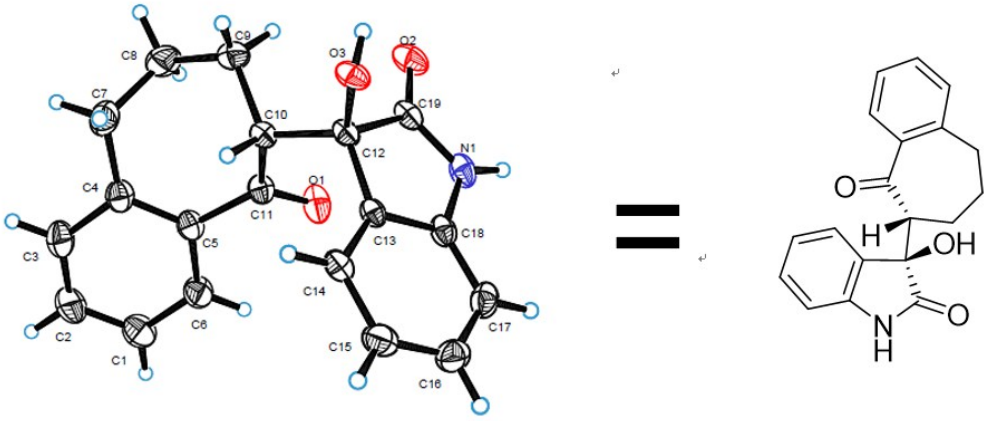
Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.760	VV	0.2546	451.85510	26.54964	0.3400
2	22.752	BB	0.5572	1.32430e5	2941.99805	99.6600
Totals :				1.32881e5	2968.54769	

Results obtained with enhanced integrator!

Part IV Crystal data

A single crystal for X-ray analysis of **3ad** was obtained by recrystallation from MeOH/petroleum ether



CCDC-1886489

Table 1 Crystal data and structure refinement for 3ad.

Empirical formula	$C_{19}H_{17}NO_3$

Formula weight	307.33
Temperature/K	291(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.72310(10)
b/Å	5.89620(10)
c/Å	13.7204(2)
α/°	90
β/°	99.6750(10)
γ/°	90
Volume/Å^3	775.394(19)
Z	2
ρ_{calc}g/cm^3	1.316
μ/mm^{-1}	0.723
F(000)	324.0
Crystal size/mm^3	0.290 × 0.250 × 0.200
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.226 to 147.88
Index ranges	-12 ≤ h ≤ 12, -6 ≤ k ≤ 7, -14 ≤ l ≤ 17
Reflections collected	14052
Independent reflections	2942 [R_{int} = 0.0294, R_{sigma} = 0.0168]
Data/restraints/parameters	2942/1/209
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0328, wR_2 = 0.0862
Final R indexes [all data]	R_1 = 0.0336, wR_2 = 0.0875
Largest diff. peak/hole / e Å^{-3}	0.10/-0.18
Flack parameter	0.05(12)