Supporting Information

Enantioselective synthesis of α-(3-pyrrolyl)methanamines with aza-tetrasubstituted center under metal-free conditions

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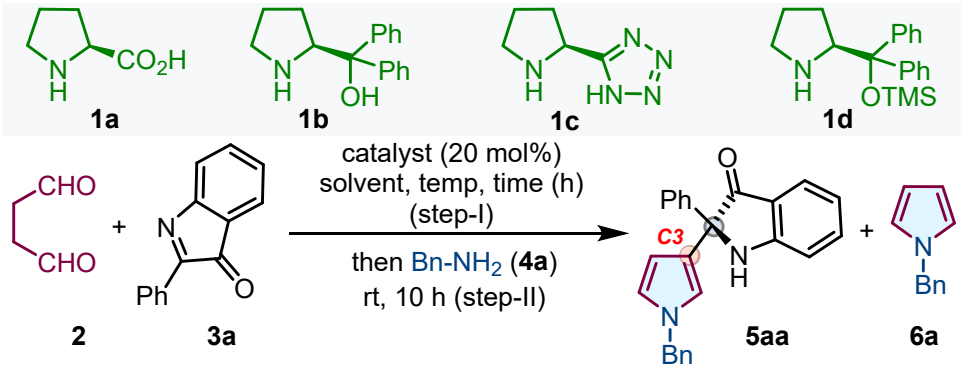
1.0 General Methods:

Unless otherwise stated, all commercially available compounds were used as received without further purification. All solvents employed in the reactions were distilled from appropriate drying agents. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on Merck silica gel 60 F254 precoated plates (0.25 mm). Column chromatographic purification was performed using silica gel (100−200 mesh) and petroleum ether/EtOAc mixture. Chemical yields refer to pure, isolated substances. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$/DMSO-d_6 on a BRUKER-AV400 and spectral data were reported in ppm. ^{13}C NMR spectra were recorded on a BRUKER-AV400 (100 MHz) spectrometer with complete proton decoupling. ^{19}F NMR spectra were recorded on a BRUKER-AV400 (376 MHz). High-resolution mass spectra were recorded using the quadrupole electrospray ionization (ESI) technique. Melting points were determined by an EZ-Melt, Automated Melting Point Apparatus, and specific rotation was measured through a RUDOLPH Polarimeter. Enantiomeric ratio (er) was determined on a Water-2998 instrument with CHIRALPAK columns using hexane/*iso*-propanol.

2.0 Typical procedure for the enantioselective synthesis of 5:

An oven-dried 20 mL Schlenk tube was charged with L-Proline **1a** (7.0 mg, 0.06 mmol), succinaldehyde **2** (3.0 M aq. sol., 200 µL, 0.6 mmol) and 2-aryl-3*H*-indol-3-one **3** (0.3 mmol, 1.0 equiv.) in DMF (2.0 mL) at 10 °C and stirred at the same temperature for 7 h. Next, primary aliphatic/aromatic amine **4** (0.6 mmol, 2.0 equiv.) was added to the same vessel and stirred for 8 h at room temperature. The reaction mixture was quenched with ice-cold water (3.0 mL) and extracted with ethyl acetate (3 × 5.0 mL). The combined organic layer was washed with brine (3.0 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum, giving a crude product, which was purified by silica gel column chromatography (hexanes/ethyl acetate) to yield pyrroles **5**.

Table S1: Optimization of reaction conditions with 2-phenyl-3*H*-indol-3-one **3a**[a]



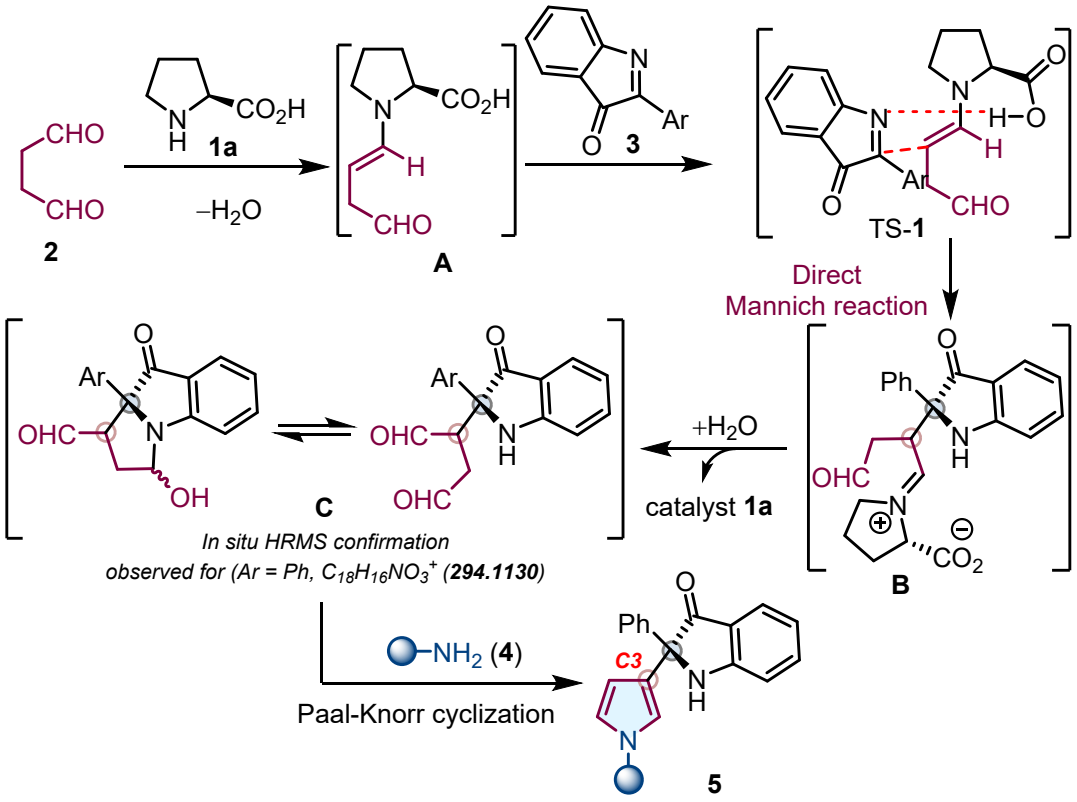
Entry	Catalyst	Conditions (step-I / step-II)	Yield **5aa** (%)[b]	Yield **6a** (%)[c]	**5aa** (er)[d]
1	**1a**	DMSO, rt, 8 h / Bn-NH_2, rt, 10 h	54	25	85:15
2	**1a**	DMF, rt, 6 h / -	67	20	92:8
3	**1a**	CH_3CN, rt, 6 h / -	35	30	80:20
4	**1a**	1,4-dioxane, rt, 9 h / -	48	25	82:18
5	**1a**	THF, rt, 9 h / -	53	25	85:15
6	**1b**	DMF, rt, 14 h / -	<10	50	N.D.
7	**1c**	DMF, rt, 10 h / -	42	30	88:12
8[e]	**1d**	DMF, $PhCO_2H$ (20 mol%), rt, 10 h / -	55	25	85:15
9	**1a**	DMF, 20 °C, 6 h / -	67	15	95:5

10	**1a**	**DMF, 10 °C, 7 h / -**	**73**	**<10**	**99:1**
11	**1a**	THF, 0 °C, 10 h / -	54	15	99:1

[a]The reaction was carried out using **2** (3.0 M sol, 0.6 mmol), **3a** (0.3 mmol, 1.0 equiv.), **1** (0.06 mmol, 20 mol%), solvent (2.0 mL), temp, time (h) (step-I); **4** (0.6 mmol), rt, 10 h (step-II). [b]Isolated yield of **5aa** refers to **3a**. [c]Isolated yield of **6a** refers to **4a**. [d]Determined using stationary chiral columns. [e]$PhCO_2H$ (20 mol%) was used as an additive. N. D. = Not Determined.

3.0 Reaction Mechanism and in situ HRMS:

Reaction Mechanism for 5: Based on the earlier reports on direct Mannich reaction, a reaction mechanism for **5** has been proposed for the present outcome (Scheme S1). An amine-catalyzed direct Mannich reaction between enamine-A and cyclic imine **3** proceeded through TS-1, leading to intermediate-**B**. A resulting suitably functionalized 1,4-dialdehyde **C**, generated through the regeneration of catalyst **1a** from **B**, underwent a Paal-Knorr reaction with a primary amine **4** furnished chiral C3-substituted pyrrole **5**.

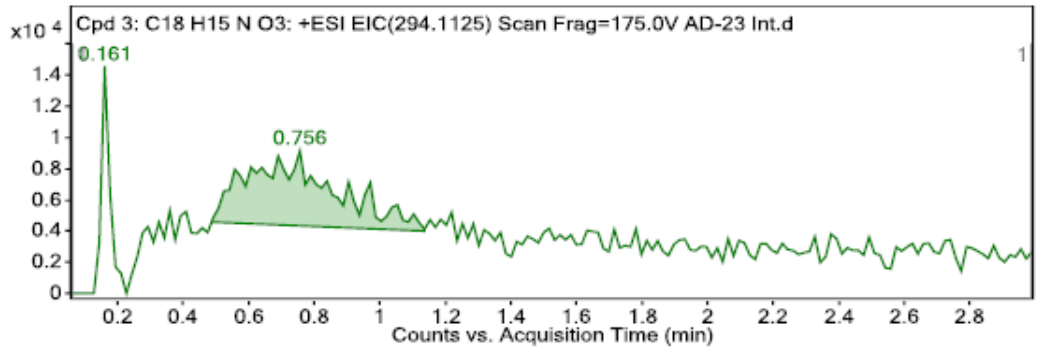


Scheme S1. Plausible reaction mechanism for the developed protocol.

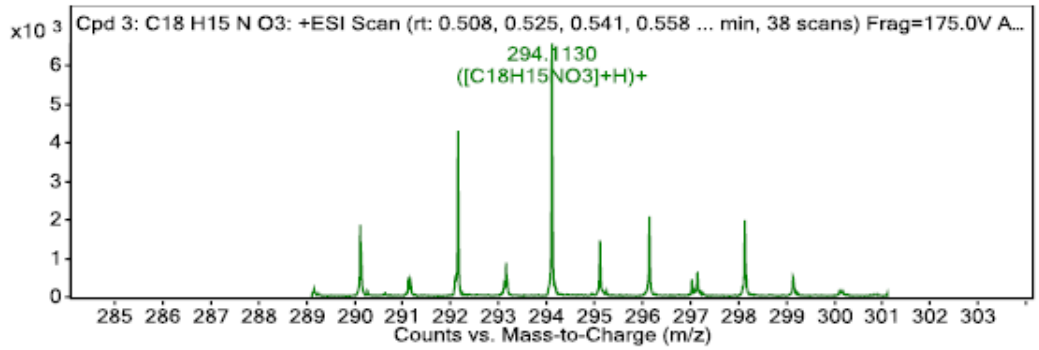
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 3: C18 H15 N O3	0.756	293.1053	6598	C18 H15 N O3	293.1052	0.23

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C18 H15 N O3	294.113	0.756	Find By Formula	293.1053

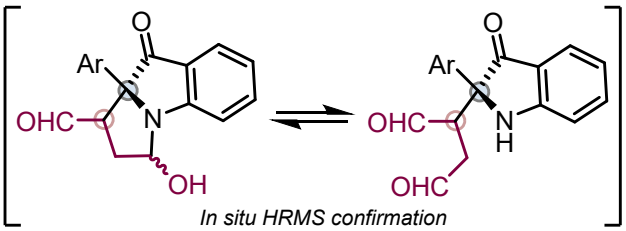


MS Zoomed Spectrum



MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
294.113	294.1125	-1.84	1	6598.43	C18H15NO3	(M+H)+
295.1148	295.1157	3.34	1	1487.37	C18H15NO3	(M+H)+
296.1061	296.1185	41.58	1	127.45	C18H15NO3	(M+H)+



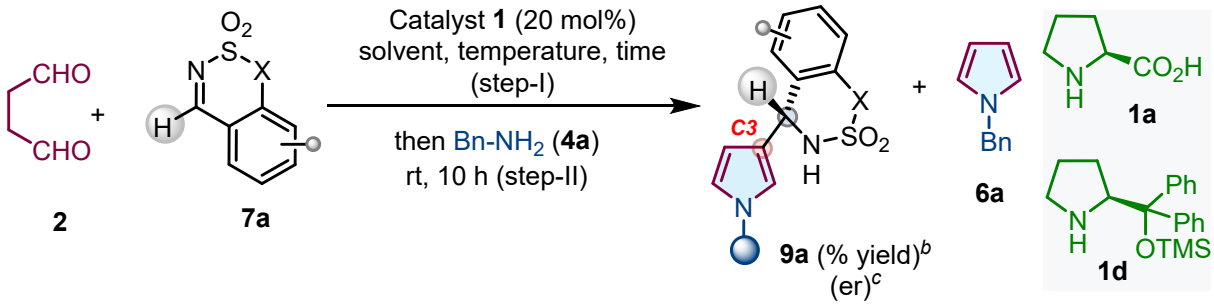
In situ HRMS confirmation
*observed for (Ar = Ph, $C_{18}H_{16}NO_3^+$ (**294.1130**)*

Figure S1: The in-situ HRMS analysis of the reaction

4.0 The typical procedure for the enantioselective synthesis of 9/10:

An oven-dried Schlenck tube was charged with cyclic *N*-sulfonyl aldimine/ketimine **7/8** (0.3 mmol, 1.0 equiv.), succinaldehyde **2** (3.0 M aq. sol, 200 µL, 0.6 mmol), (*S*)-2-(diphenyl-((trimethylsilyl)oxy)methyl)pyrrolidine **1d** (19.5 mg, 0.06 mmol), and benzoic acid (7.3 mg, 0.06 mmol) in THF (2.0 mL) at –30 °C. The reaction mixture was stirred at the same temperature for 48 h. Later, primary aliphatic/aromatic amine **4** (0.6 mmol, 2.0 equiv.) was added to the same vessel and stirred for 8 h at room temperature. The reaction mixture was quenched with ice-cold water (3.0 mL) and extracted with ethyl acetate (3 × 5.0 mL). The combined organic layer was washed with brine (3.0 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The column chromatographic purification on silica gel using hexanes/ethyl acetate to furnish pyrroles **9/10**.

Table S2: Optimization of reaction conditions for *N*-sulfonyl aldimines **9/10**[a]

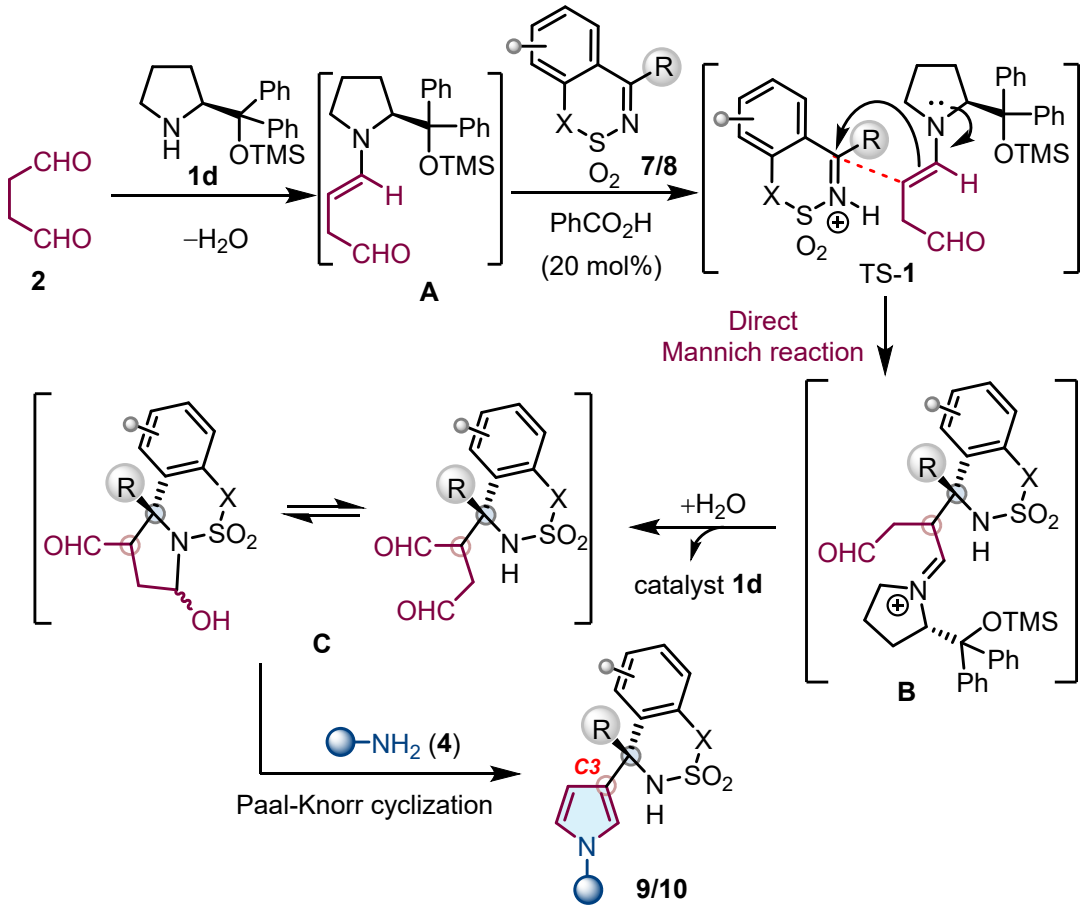


Entry	Catalyst	Conditions (step-I / step-II)	Additive (20 mol%)	Yield **5aa** (%)[b]	Yield **6a** (%)[c]	**5aa** (er)[d]
1	**1a**	DMF, 10 °C, 7 h / Bn-NH_2, rt, 10 h	-	52	25	60:40
2	**1a**	DMF, 0 °C, 10 h / -	-	45	30	60:40
3	**1d**	DMF, 10 °C, 12 h / -	$PhCO_2H$	48	20	62:38
4	**1d**	CH_2Cl_2, 10 °C, 12 h / -	$PhCO_2H$	58	20	63:37
5	**1d**	THF, 10 °C, 12 h / -	$PhCO_2H$	68	20	66:34
6	**1d**	THF, 0 °C, 16 h / -	$PhCO_2H$	70	20	69:31
7	**1d**	THF, –10 °C, 18 h / -	$PhCO_2H$	72	20	70:30
8	**1d**	THF, –20 °C, 30 h / -	$PhCO_2H$	70	15	76:24
9	**1d**	**THF, –30 °C, 48 h / -**	**$PhCO_2H$**	**75**	**<10**	**80:20**
10	**1d**	THF, –40 °C, 60 h / -	$PhCO_2H$	68	15	80:20

11	**1d**	THF, –30 °C, 72 h / -	-	<10	40	N.D.
12	**1d**	THF, 0 °C, 72 h / -	-	32	40	75:25

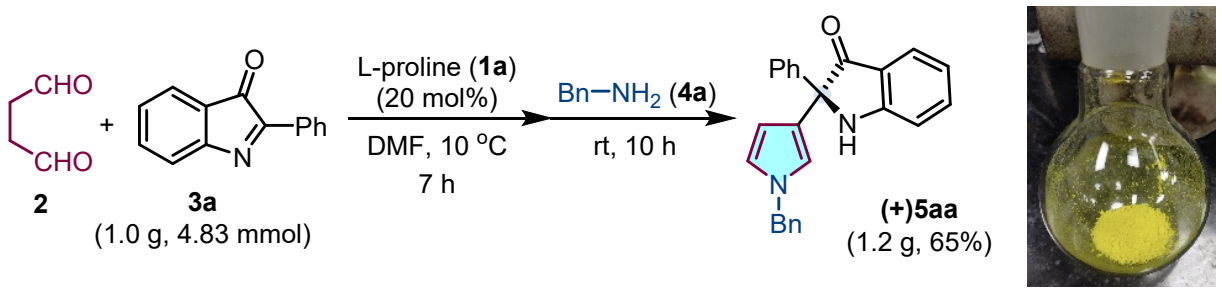
[a]The reaction was carried out using **2** (3.0 M sol, 0.6 mmol), *N*-sulfonyl imine **7/8** (0.3 mmol), cat **1** (0.06 mmol), additive (0.06 mmol), solvent (2.0 mL), temp, time (h) (step-I); **4** (0.6 mmol), rt, 10 h (step-II). [b]Isolated yield of **9a** refers to **7a.** [c]Isolated yield of **6a** refers to **4a**. [d]Determined using stationary chiral columns. N. D. = Not Determined.

5.0 Reaction Mechanism for 9/10: Based on the earlier reports on direct Mannich reaction, a reaction mechanism for **9**/**10** has been proposed for the present outcome (Scheme S2). An amine-catalyzed direct Mannich reaction between enamine-**A** and cyclic *N*-sulfimines **7**/**8** proceeded through TS-1, leading to intermediate-**B**. A resulting suitably functionalized 1,4-dialdehyde **C**, generated through the regeneration of catalyst **1d** from **B**, underwent a Paal-Knorr reaction with a primary amine **4** furnished chiral C3-substituted pyrrole **9/10**.



Scheme S2. Plausible reaction mechanism for the developed protocol.

6.0 Gram Scale Synthesis of 5aa:



An oven-dried Schlenck tube was charged with L-Proline **1a** (111 mg, 0.96 mmol), succinaldehyde **2** (3.0 M aq. sol., 3.3 mL, 9.66 mmol) and 2-phenyl-3*H*-indol-3-one **3a** (1.0 g, 4.83 mmol, 1.0 equiv.) in DMF (30 mL) at 10 °C and stirred at the same temperature for 7 h. Next, benzylamine **4a** (1.0 g, 9.66 mmol) was added to the same vessel and stirred at room temperature for an additional 10 h. The reaction mixture was quenched with ice-cold water (10.0 mL) and extracted with EtOAc (3 × 10.0 mL). The combined organic layer was washed with brine (10.0 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, giving a crude mixture, which was purified using silica gel column chromatography (hexanes/ethyl acetate) to yield pyrrole **5aa** (1.2 g, 65% yield).

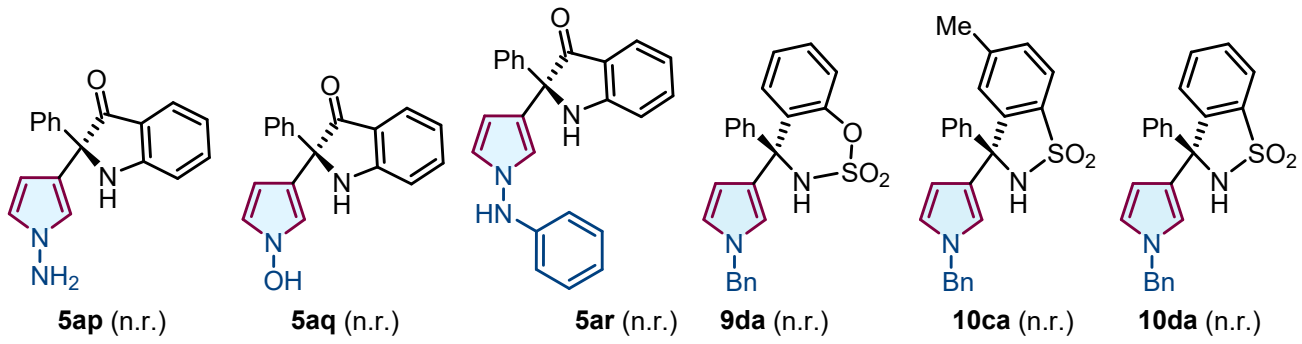
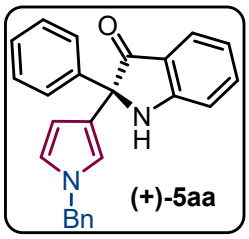


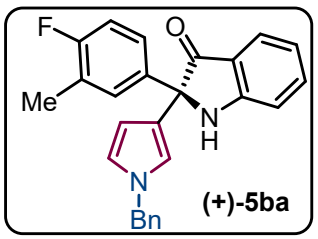
Figure S2: List of examples that failed to produce under optimized conditions.

7.0 Spectral Data for the Synthesized Compounds

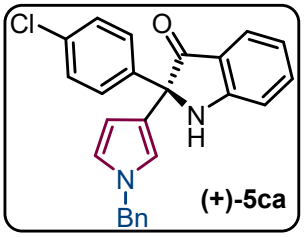
(*R*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5aa): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (79 mg, 73% yield, mp = 133-135 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99.5:0.5), t_R= 26.6 min (major), 35.0 min (minor). $[\alpha]_D^{25}$= +39.7 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.47 (m, 1H), 7.34 – 7.26 (m, 6H), 7.13 (d, *J* = 1.4 Hz, 1H), 7.11 (s, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.87 – 6.82 (m, 1H), 6.71 (t, *J* = 2.0 Hz, 1H), 6.63 (t, *J* = 2.5 Hz, 1H), 6.06 (dd, *J* = 2.7, 1.9 Hz, 1H), 5.14 (s, 1H), 4.98 (s, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.1, 160.3, 140.9, 137.6, 137.2, 128.7 (2C), 128.2 (2C), 127.7, 127.5, 127.2 (2C), 126.8 (2C), 123.9, 121.9, 120.2, 119.7, 119.3, 112.5, 107.6, 71.2, 53.6. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O^+$ 365.1648; Found: 365.1651.



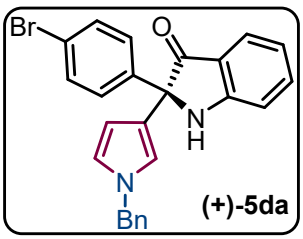
(*R*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-2-(4-fluoro-3-methylphenyl)indolin-3-one (5ba): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (96 mg, 71% yield, mp = 118-120 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99:1), t_R= 21.8 min (major), 28.8 min (minor). $[\alpha]_D^{25}$= +41.2 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 7.1 Hz, 1H), 7.54 – 7.46 (m, 1H), 7.31 (d, *J* = 17.3 Hz, 5H), 7.14 (d, *J* = 5.9 Hz, 2H), 6.99 – 6.91 (m, 2H), 6.88 (s, 1H), 6.69 (d, *J* = 23.8 Hz, 2H), 6.06 (s, 1H), 5.16 (s, 1H), 5.01 (s, 2H), 2.24 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.1, 160.3, 137.5, 137.3, 136.3 (d, *J* = 3.3 Hz),130.0 (d, *J* = 5.2 Hz), 129.9, 128.7, 127.8, 127.2, 126.0, 125.9, 125.6, 124.4 (d, *J* = 17.4 Hz), 124.0, 122.0, 120.1, 119.4, 114.7, 114.5, 112.6, 107.5, 70.7, 53.5, 14.7 (d, *J* = 3.5 Hz). **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{26}H_{22}FN_2O^+$ 397.1711; Found: 397.1715.



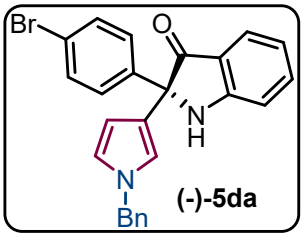
(*R*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-2-(4-chlorophenyl)indolin-3-one (5ca): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (86 mg, 72% yield, mp = 152-154 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10 flow rate 1.0 mL/min, *I* = 230 nm) was used to measure the enantiomeric ratio (*er* = 99.5:0.5), t_R= 29.0 min (major), 37.8 min (minor). $[\alpha]_D^{25}$= +42.5 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.61 (m, 1H), 7.52 – 7.46 (m, 3H), 7.35 – 7.26 (m, 4H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 1.7 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.88 – 6.83 (m, 1H), 6.68 (t, *J* = 2.0 Hz, 1H), 6.63 (t, *J* = 2.5 Hz, 1H), 6.02 (dd, *J* = 2.8, 1.9 Hz, 1H), 5.16 (s, 1H), 4.97 (s, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 200.7, 160.3, 139.5, 137.4, 137.4, 133.4, 128.8 (2C), 128.4 (2C), 128.3 (2C), 127.8, 127.2 (2C), 125.6, 123.8, 122.1, 120.1, 119.6, 119.5, 112.8, 107.5, 70.7, 53.5. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{25}H_{20}ClN_2O^+$ 399.1259; Found: 399.1265.



(*R*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-2-(4-bromophenyl)indolin-3-one (5da): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (94 mg, 71% yield, mp = 161-163 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99.5:0.5), t_R= 19.5 min (major), 25.4 min (minor). $[\alpha]_D^{25}$= +35.8 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 7.3 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.46 – 7.40 (m, 4H), 7.35 – 7.28 (m, 3H), 7.13 – 7.09 (m, 2H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.89 – 6.84 (m, 1H), 6.65 (dt, *J* = 21.5, 2.2 Hz, 2H), 6.01 (dd, *J* = 2.8, 1.8 Hz, 1H), 5.16 (s, 1H), 4.97 (s, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 200.6, 160.3, 140.1, 137.4, 137.5, 131.2 (2C), 128.8 (4C), 127.9, 127.2 (2C), 125.6, 123.7, 122.1, 121.7, 120.1, 119.6, 119.5, 112.8, 107.5, 70.7, 53.6. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{25}H_{20}BrN_2O^+$ 443.0754; Found: 443.0759.

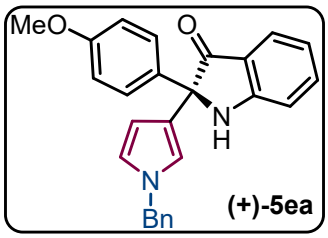


(*S*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-2-(4-bromophenyl)indolin-3-one (*ent*-5da): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (91 mg, 69% yield); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0

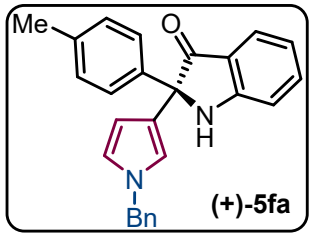


mL/min, I = 254 nm) was used to measure the enantiomeric ratio (*er* = 2:98), t_R= 19.5 min (minor), 25.5 min (major). $[\alpha]_D^{25}$= –27.6 (*c* 0.1, CH_2Cl_2).

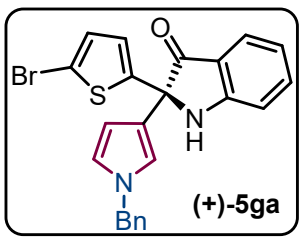
(*R*)-2-(1-benzyl-1*H*-pyrrol-3-yl)-2-(4-methoxyphenyl)indolin-3-one (5ea): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (80 mg, 68% yield, mp = 156-158 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, I = 254 nm) was used to measure the enantiomeric ratio (*er* = 99.5:0.5), t_R= 20.1 min (major), 28.1 min (minor). $[\alpha]_D^{25}$= +48.8 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 8.5 Hz, 2H), 7.31 (dt, J = 11.2, 6.8 Hz, 3H), 7.12 (d, J = 7.0 Hz, 2H), 6.90 (d, J = 8.2 Hz, 1H), 6.84 (t, J = 3.1 Hz, 2H), 6.82 (s, 1H), 6.70 (s, 1H), 6.63 (s, 1H), 6.06 (s, 1H), 5.15 (s, 1H), 4.98 (s, 2H), 3.77 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.5, 160.3, 159.1, 137.7, 137.2, 133.1, 128.8, 128.1, 127.8, 127.2, 125.6, 124.1, 121.9, 120.2, 119.7, 119.2, 113.7, 112.6, 107.7, 70.8, 55.3, 53.5. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O_2^+$ 395.1754; Found: 394.1762.



(*R*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-2-(p-tolyl)indolin-3-one (5fa): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (71 mg, 63% yield, mp = 127-129 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, I = 254 nm) was used to measure the enantiomeric ratio (*er* = 98:2), t_R= 33.2 min (major), 40.7 min (minor). $[\alpha]_D^{25}$= +41.3 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.61 (m, 1H), 7.46 (m, 1H), 7.42 – 7.38 (m, 2H), 7.31 (m, 3H), 7.13 – 7.09 (m, 4H), 6.90 (d, J = 8.2 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.71 (t, J = 2.0 Hz, 1H), 6.62 (t, J = 2.5 Hz, 1H), 6.06 (dd, J = 2.8, 1.8 Hz, 1H), 5.15 (s, 1H), 4.98 (s, 2H), 2.31 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.3, 160.3, 138.0, 137.6, 137.3, 137.2, 129.0 (2C), 128.7 (2C), 127.7, 127.2 (2C), 126.7 (2C), 125.6, 124.0, 121.9, 120.2, 119.7, 119.2, 112.5, 107.7, 71.1, 53.5, 21.0. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O^+$ 379.1805; Found: 379.1807.

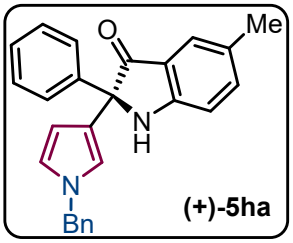


(*R*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-2-(5-bromothiophen-2-yl)indolin-3-one (5ga): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (87 mg, 65%

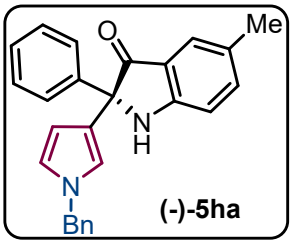


yield, mp = 149-151 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 95/5, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = >99:1), t_R= 37.1 min (major), 47.4 min (minor). $[\alpha]_D^{25}$= +48.6 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.48 (m, 1H), 7.35 – 7.24 (m, 2H), 7.18 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.14 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.12 – 7.08 (m, 2H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.89 – 6.85 (m, 1H), 6.77 (t, *J* = 2.0 Hz, 1H), 6.61 (t, *J* = 2.5 Hz, 1H), 6.15 (dd, *J* = 2.8, 1.8 Hz, 1H), 5.29 (s, 1H), 4.97 (s, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 199.7, 160.0, 145.5, 137.6, 137.4, 128.8 (2C), 127.8, 127.2 (2C), 127.2, 125.9, 125.3, 124.8, 123.8, 121.9, 120.0, 119.8, 119.2, 112.7, 107.3, 69.0, 53.6. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{23}H_{18}BrN_2OS^+$ 449.0318; Found: 449.0319.

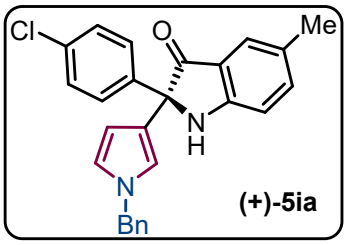
(*R*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-5-methyl-2-phenylindolin-3-one (5ha): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (76 mg, 67% yield, mp = 122-124 °C); **HPLC** (IC column, *n*-hexane/*iso*-propanol = 92.5/7.5, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99:1), t_R= 31.6 min (minor), 38.6 min (major). $[\alpha]_D^{25}$= +38.2 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.44 (s, 1H), 7.30 (m, 8H), 7.13 (d, *J* = 7.0 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.74 – 6.71 (m, 1H), 6.63 (t, *J* = 2.2 Hz, 1H), 6.09 – 6.06 (m, 1H), 5.05 (s, 1H), 4.98 (s, 2H), 2.30 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.3, 158.9, 141.2, 138.7, 137.7, 128.9, 128.7 (2C), 128.2 (2C), 127.7, 127.4, 127.2 (2C), 126.9 (2C), 124.9, 124.2, 121.9, 120.2, 119.9, 112.6, 107.7, 71.6, 53.5, 20.5. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O^+$ 379.1805; Found: 379.1809.



(*S*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-5-methyl-2-phenylindolin-3-one (*ent*-5ha): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (65 mg, 57% yield); **HPLC** (IC column, *n*-hexane/*iso*-propanol = 92.5/7.5, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 1:99), t_R= 31.8 min (major), 38.6 min (minor). $[\alpha]_D^{25}$= –36.4 (*c* 0.1, CH_2Cl_2).

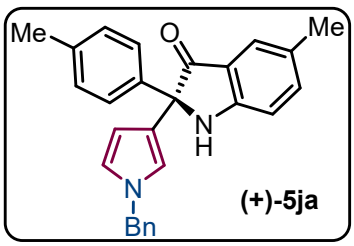


(*R*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-2-(4-chlorophenyl)-5-methylindolin-3-one (5ia): Purification



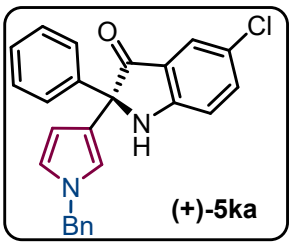
was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (84 mg, 68% yield, mp = 138-141 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = >99:1), t_R= 21.6 min (major), 28.3 min (minor). $[\alpha]_D^{25}$= +46.3 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.42 (s, 1H), 7.27 (s, 5H), 7.24 (s, 1H), 7.13 – 7.09 (m, 2H), 6.87 (s, 1H), 6.62 (s, 2H), 5.99 (d, *J* = 4.4 Hz, 1H), 4.97 (s, 2H), 4.94 (s, 1H), 2.29 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 200.8, 158.8, 139.7, 138.8, 137.4, 133.3, 129.2, 128.7 (2C), 128.4 (2C), 128.2 (2C), 127.8, 127.2 (2C), 124.9, 124.1, 122.0, 120.1, 119.8, 112.8, 107.4, 71.0, 53.5, 20.5. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{26}H_{22}ClN_2O^+$ 413.1415; Found: 413.1419.

(*R*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-5-methyl-2-(p-tolyl)indolin-3-one (5ja): Purification was done



using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (72 mg, 61% yield, mp = 125-127 °C); **HPLC** (IC column, *n*-hexane/*iso*-propanol = 85:15, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99.5:0.5), t_R= 16.2 min (minor), 25.7 min (major). $[\alpha]_D^{25}$= +43.2 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (s, 1H), 7.42 – 7.39 (m, 2H), 7.34 – 7.26 (m, 5H), 7.14 – 7.09 (m, 4H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.71 (t, *J* = 2.0 Hz, 1H), 6.62 (t, *J* = 2.5 Hz, 1H), 6.06 (dd, *J* = 2.8, 1.8 Hz, 1H), 5.00 (s, 1H), 4.98 (s, 2H), 2.31 (s, 3H), 2.29 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.4, 158.8, 138.6, 138.3, 137.7, 137.1, 128.9 (2C), 128.8, 128.7 (2C), 127.7, 127.2 (2C), 126.8 (2C), 124.9, 124.2, 121.8, 120.2, 119.9, 112.6, 107.7, 71.5, 53.5, 21.0, 20.5. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{27}H_{25}N_2O^+$ 393.1961; Found: 393.1967.

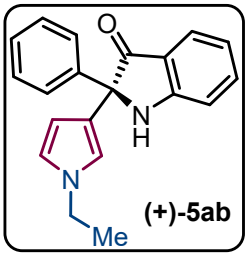
(*R*)-2-(1-Benzyl-1*H*-pyrrol-3-yl)-5-chloro-2-phenylindolin-3-one (5ka): Purification was done



using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (85 mg, 71% yield, mp = 143-145 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er*

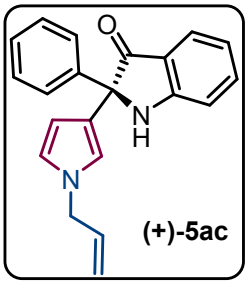
= 99:1), t_R= 19.1 min (major), 24.7 min (minor). $[\alpha]_D^{25}$= +35.9 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 – 7.71 (m, 1H), 7.52 (dd, *J* = 9.5, 2.2 Hz, 2H), 7.49 (d, *J* = 6.9 Hz, 2H), 7.33 – 7.28 (m, 5H), 7.12 (d, *J* = 6.9 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 1H), 6.70 – 6.61 (m, 2H), 6.03 (s, 1H), 5.25 (s, 1H), 4.98 (s, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 199.7, 158.8, 140.4, 139.7, 137.5, 128.8 (2C), 128.4 (2C), 127.9, 127.8, 127.7, 127.1 (2C), 126.83 (2C), 123.4, 122.1, 121.1, 120.2, 114.1, 111.2, 107.6, 71.9, 53.5. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{25}H_{20}ClN_2O^+$ 399.1259; Found: 399.1255.

(*R*)-2-(1-Ethyl-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5ab): Purification was done using



hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (55 mg, 61% yield, mp = 89-91 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99:1), t_R= 14.4 min (major), 17.7 min (minor). $[\alpha]_D^{25}$= +44.3 (*c* 0.1, CH_2Cl_2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.50 – 7.44 (m, 1H), 7.32 – 7.27 (m, 2H), 7.26 (s, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.87 – 6.81 (m, 1H), 6.64 (m, 2H), 5.99 (q, *J* = 2.2 Hz, 1H), 5.14 (s, 1H), 3.85 (qd, *J* = 7.4, 1.9 Hz, 2H), 1.38 (td, *J* = 7.4, 1.8 Hz, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.2, 160.3, 141.0, 137.2, 128.2 (2C), 127.5, 126.9 (2C), 125.5, 123.4, 120.8, 119.7, 119.3, 119.1, 112.6, 106.9, 71.2, 44.3, 16.4. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O^+$ 303.1492; Found: 303.1498.

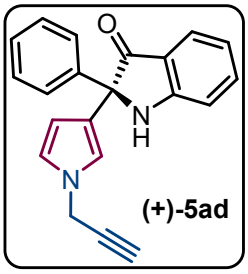
(*R*)-2-(1-Allyl-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5ac): Purification was done using



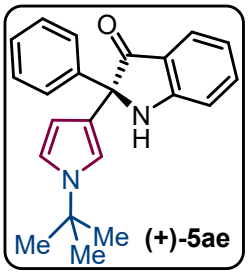
hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (69 mg, 73% yield, mp = 94-96 °C); **HPLC** (IC column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = >99:1), t_R= 27.3 min (minor), 44.0 min (major). $[\alpha]_D^{25}$= +46.2 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.53 (m, 2H), 7.47 (m, 1H), 7.33 – 7.24 (m, 3H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.65 (t, *J* = 2.0 Hz, 1H), 6.62 (t, *J* = 2.5 Hz, 1H), 6.04 (dd, *J* = 2.7, 1.9 Hz, 1H), 5.99 – 5.88 (m, 1H), 5.22 – 5.19 (m, 1H), 5.19 – 5.11 (m, 2H), 4.40 (m, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.2, 160.3, 140.9, 137.2, 133.9, 128.2, 127.5, 126.9, 125.5,

123.7, 121.5, 119.7, 119.3, 118.0, 112.6, 110.4, 107.4, 71.2, 52.3. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{21}H_{19}N_2O^+$ 315.1492; Found: 315.1495.

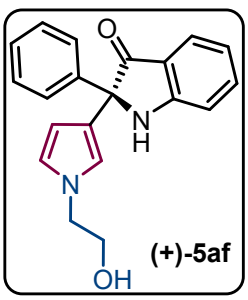
(*R*)-2-Phenyl-2-(1-(prop-2-yn-1-yl)-1*H*-pyrrol-3-yl)indolin-3-one (5ad): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (64 mg, 68% yield, mp = 106-108 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99.5:0.5), t_R= 17.7 min (major), 21.6 min (minor). $[\alpha]_D^{25}$= +42.8 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.7 – 7.6 (m, 1H), 7.5 – 7.5 (m, 2H), 7.5 (m, 1H), 7.3 – 7.3 (m, 3H), 6.9 (s, 1H), 6.9 – 6.8 (m, 1H), 6.7 (d, *J* = 2.3 Hz, 2H), 6.1 (d, *J* = 2.3 Hz, 1H), 5.2 (s, 1H), 4.6 (d, *J* = 2.6 Hz, 2H), 2.4 (t, *J* = 2.6 Hz, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.0, 160.3, 140.7, 137.3, 128.3 (2C), 127.6, 126.9 (2C), 125.6, 124.4, 121.3, 119.6, 119.5, 119.4, 112.6, 108.1, 77.7, 74.0, 71.1, 38.8. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{21}H_{17}N_2O^+$ 313.1335; Found: 313.1338.



(*R*)-2-(1-(Tert-butyl)-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5ae): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (62 mg, 63% yield, mp = 93-95 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 230 nm) was used to measure the enantiomeric ratio (*er* = 99.5:0.5), t_R= 17.7 min (major), 20.9 min (minor). $[\alpha]_D^{25}$= +49.7 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (m, 1H), 7.55 – 7.51 (m, 2H), 7.48 (m, 1H), 7.34 – 7.23 (m, 3H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.88 – 6.83 (m, 1H), 6.83 – 6.80 (m, 2H), 6.02 (dd, *J* = 2.8, 2.0 Hz, 1H), 5.19 (s, 1H), 1.50 (s, 9H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.2, 160.4, 141.2, 137.1, 128.2 (2C), 127.4, 126.9 (2C), 125.5, 122.7, 119.7, 119.2, 118.4, 116.7, 112.6, 106.5, 71.4, 55.0, 30.7 (3C). **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O^+$ 331.1805; Found: 331.1811.

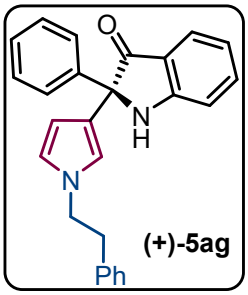


(*R*)-2-(1-(2-Hydroxyethyl)-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5af): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (64 mg, 67% yield, mp = 123-125 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 97:3), t_R=



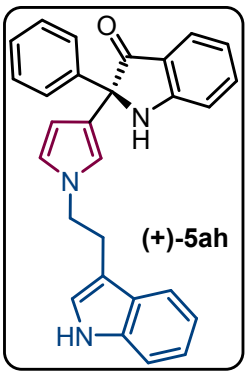
39.9 min (major), 51.0 min (minor). $[\alpha]_D^{25}$= +49.5 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.21 (m, 3H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.64 – 6.59 (m, 2H), 6.00 (s, 1H), 5.32 (s, 1H), 3.85 (t, *J* = 5.0 Hz, 2H), 3.72 (t, *J* = 4.9 Hz, 2H), 2.36 (s, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.6, 160.5, 140.7, 137.5, 128.3 (2C), 127.6, 126.9 (2C), 125.6, 123.9, 122.0, 119.9, 119.4, 119.3, 112.6, 107.5, 71.2, 62.5, 52.1. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O_2^+$ 319.1441; Found: 319.1436.

(*R*)-2-(1-Phenethyl-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5ag): Purification was done using



hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (78 mg, 69% yield, mp = 113-115 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99:1), t_R= 15.4 min (major), 19.2 min (minor). $[\alpha]_D^{25}$= +57.1 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.6 (d, *J* = 7.7 Hz, 1H), 7.5 – 7.5 (m, 3H), 7.3 – 7.2 (m, 7H), 7.1 (s, 2H), 6.9 (d, *J* = 8.2 Hz, 1H), 6.9 (t, *J* = 7.4 Hz, 1H), 6.6 (d, *J* = 2.2 Hz, 2H), 6.0 (t, *J* = 2.2 Hz, 1H), 5.1 (s, 1H), 4.0 (t, *J* = 7.4 Hz, 2H), 3.0 (t, *J* = 7.4 Hz, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.1, 160.4, 141.0, 138.2, 137.2, 128.7 (2C), 128.5 (2C), 128.2 (2C), 127.5, 126.9 (2C), 126.6, 125.6, 123.4, 121.3, 119.7, 119.7, 119.3, 112.6, 107.2, 71.2, 51.4, 38.2. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O^+$ 379.1805; Found: 379.1809.

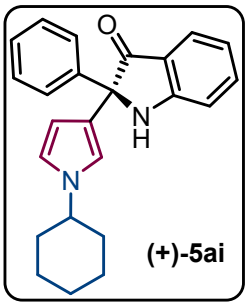
(*R*)-2-(1-(2-(1*H*-indol-3-yl)ethyl)-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5ah): Purification was



done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (85 mg, 68% yield, mp = 115-117 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99:1), t_R= 30.8 min (major), 40.1 min (minor). $[\alpha]_D^{25}$= +53.7 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.1 (s, 1H), 7.7 (d, *J* = 7.1 Hz, 1H), 7.5 (dd, *J* = 20.8, 6.9 Hz, 4H), 7.4 – 7.2 (m, 4H), 7.2 (m, 2H), 6.9 (d, *J* = 7.9 Hz, 1H), 6.9 – 6.8 (m, 1H), 6.7 (s, 1H), 6.6 (d, *J* = 16.2 Hz, 2H), 6.0 (s, 1H), 5.2 (s, 1H), 4.1 (t, *J* = 6.2 Hz, 2H), 3.2

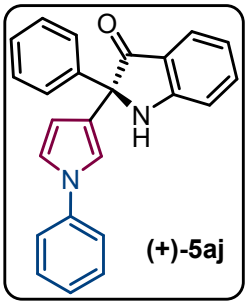
– 3.1 (m, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.5, 160.5, 140.9, 137.3, 136.2, 128.2 (2C), 127.6, 127.1, 127.0 (2C), 125.6, 123.3, 122.4, 122.0, 121.4, 119.8, 119.6, 119.3, 119.3, 118.4, 112.6, 112.2, 111.3, 107.1, 71.4, 50.6, 27.7. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{28}H_{24}N_3O^+$ 418.1914; Found: 418.1911.

(*R*)-2-(1-Cyclohexyl-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5ai): Purification was done using



hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (74 mg, 69% yield, mp = 117-119 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99.5:0.5), t_R= 24.1 min (major), 31.8 min (minor). $[\alpha]_D^{25}$= +45.5 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.61 (m, 1H), 7.54 – 7.49 (m, 2H), 7.47 (m, 1H), 7.32 – 7.26 (m, 4H), 7.25 – 7.22 (m, 1H), 6.92 (dt, *J* = 8.2, 0.8 Hz, 1H), 6.84 (m, 1H), 6.71 – 6.67 (m, 2H), 5.14 (s, 1H), 3.71 (tt, *J* = 11.8, 3.8 Hz, 1H), 2.09 – 2.02 (m, 2H), 1.84 (dt, *J* = 13.0, 3.5 Hz, 2H), 1.69 (m, 1H), 1.63 – 1.58 (m, 1H), 1.56 – 1.50 (m, 1H), 1.36 (m, 2H), 1.28 – 1.14 (m, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.3, 160.4, 141.1, 137.2, 128.1 (2C), 127.4, 126.9 (2C), 125.5, 122.7, 119.7, 119.2 (2C), 117.7, 112.6, 106.4, 71.3, 58.8, 34.5 (2C), 25.6 (2C), 25.4. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{24}H_{26}N_2O^+$ 357.1961; Found: 357.1967.

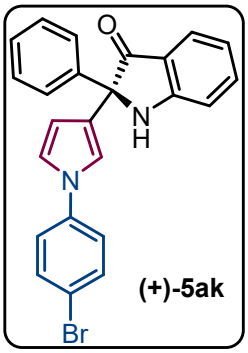
(*R*)-2-Phenyl-2-(1-phenyl-1*H*-pyrrol-3-yl)indolin-3-one (5aj): Purification was done using



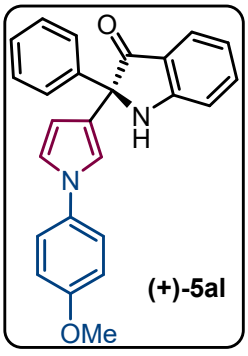
hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (68 mg, 65% yield, mp = 98-100 °C); **HPLC** (IC column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 94:6), t_R= 26.6 min (minor), 45.1 min (major). $[\alpha]_D^{25}$= +35.9 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.52 – 7.47 (m, 1H), 7.41 – 7.27 (m, 7H), 7.25 – 7.20 (m, 1H), 7.08 (m, 2H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.23 (dd, *J* = 2.9, 1.8 Hz, 1H), 5.21 (s, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 210.1, 160.3, 140.6, 140.3, 137.4, 129.5 (2C), 128.3 (2C), 127.7, 126.9 (2C), 125.9, 125.8, 125.6, 120.4,

120.1 (2C), 119.6, 119.5, 118.2, 112.6, 109.5, 71.1. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{24}H_{19}N_2O^+$ 351.1492; Found: 351.1489.

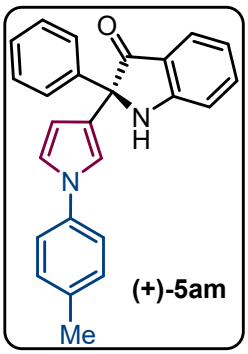
(*R*)-2-(1-(4-bromophenyl)-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5ak): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (91 mg, 71% yield, mp = 105-107 °C); **HPLC** (IC column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 94:6), t_R= 14.5 min (minor), 28.1 min (major). $[\alpha]_D^{25}$= +38.1 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.7 (d, *J* = 7.7 Hz, 1H), 7.6 – 7.5 (m, 2H), 7.5 (m, 3H), 7.3 (m, 3H), 7.2 – 7.2 (m, 2H), 7.1 – 7.0 (m, 2H), 6.9 (d, *J* = 8.2 Hz, 1H), 6.9 – 6.8 (m, 1H), 6.3 (d, *J* = 2.9 Hz, 1H), 5.3 (s, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 200.9, 160.4, 140.5, 139.4, 137.5, 132.6, 128.4, 127.8, 126.9, 126.4, 125.7, 121.8, 120.1, 119.6, 119.6, 118.9, 118.1, 112.6, 110.1, 71.1. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{24}H_{18}BrN_2O^+$ 429.0597; Found: 429.0595.



(*R*)-2-(1-(4-Methoxyphenyl)-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5al): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (82 mg, 72% yield, mp = 95-97 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99:1), t_R= 35.0 min (major), 44.6 min (minor). $[\alpha]_D^{25}$= +42.6 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (m, 1H), 7.59 – 7.55 (m, 2H), 7.49 (m, 1H), 7.35 – 7.28 (m, 3H), 7.27 (d, *J* = 2.8 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.00 (t, *J* = 2.1 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.94 – 6.83 (m, 4H), 5.21 (s, 1H), 3.81 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 200.9, 160.3, 157.7, 140.7, 137.3, 134.0, 128.3 (2C), 127.6, 126.9 (2C), 125.6, 125.4, 122.0 (2C), 120.5, 119.7, 119.4, 118.6, 114.6 (2C), 112.6, 109.0, 71.2, 55.5. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O_2^+$ 381.1598; Found: 381.1597.

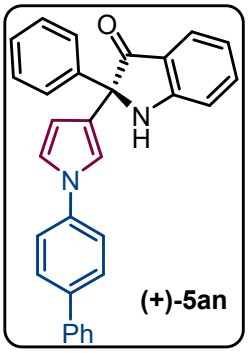


(*R*)-2-Phenyl-2-(1-(p-tolyl)-1*H*-pyrrol-3-yl)indolin-3-one (5am): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (73 mg, 67% yield, mp = 101-103 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0

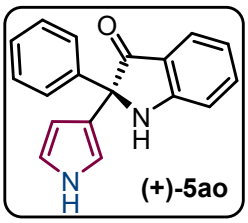


mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99:1), t_R= 23.1 min (major), 28.5 min (minor). $[\alpha]_D^{25}$= +48.3 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.31 (m, 3H), 7.25 – 7.15 (m, 4H), 7.03 (d, *J* = 2.5 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.21 (s, 1H), 5.24 (s, 1H), 2.35 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 210.0, 160.3, 140.6, 138.0, 137.4, 135.5, 130.0 (2C), 128.4 (2C), 127.7, 126.9 (2C), 125.6, 125.5, 120.4 (2C), 120.2, 119.6, 119.4, 118.3, 112.6, 109.2, 71.1, 20.8. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O^+$ 365.1648; Found: 365.1656.

(*R*)-2-(1-([1,1'Biphenyl]-4-yl)-1*H*-pyrrol-3-yl)-2-phenylindolin-3-one (5an): Purification was done using hexanes/ethyl acetate (9/1) as eluent; Yellow solid; (87 mg, 68% yield, mp = 123-125 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99.5:0.5), t_R= 17.8 min (major), 22.1 min (minor). $[\alpha]_D^{25}$= +47.3 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.57 (m, 6H), 7.53 – 7.48 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.39 – 7.29 (m, 4H), 7.15 (t, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.86 (s, 1H), 6.27 (dd, *J* = 2.9, 1.8 Hz, 1H), 5.27 (s, 1H).**^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 200.9, 160.4, 140.6, 140.1, 139.5, 138.7, 137.5, 128.9 (2C), 128.4 (2C), 128.1 (2C), 127.8, 127.4, 126.9 (4C), 126.0, 125.7, 120.5 (2C), 120.1, 119.7, 119.5, 118.2, 112.6, 109.7, 71.1. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{30}H_{23}N_2O_2^+$ 427.1805; Found: 427.1808.

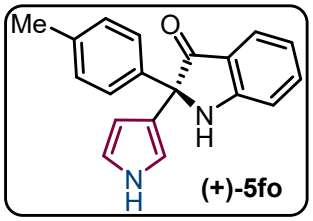


(*R*)-2-Phenyl-2-(1*H*-pyrrol-3-yl)indolin-3-one (5ao): Purification was done using hexanes/ethyl acetate (8/2) as eluent; Yellow solid; (51 mg, 62% yield, mp = 139-141 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 95/5, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 96:4), t_R= 65.4 min (major), 74.3 min (minor). $[\alpha]_D^{25}$= +46.2 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.50 – 7.45 (m, 1H), 7.33 – 7.27 (m, 3H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 2.6 Hz, 2H), 6.12 (q, *J* = 2.5 Hz, 1H). **^{13}C{1H} NMR (100**

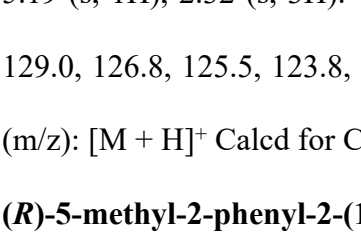


MHz, $CDCl_3$) δ 201.1, 160.3, 140.9, 137.3, 128.2 (2C), 127.5, 126.9 (2C), 125.5, 123.9, 119.7, 119.3, 118.8, 116.9, 112.5, 107.4, 71.1. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{18}H_{15}N_2O^+$ 275.1179; Found: 275.1177.

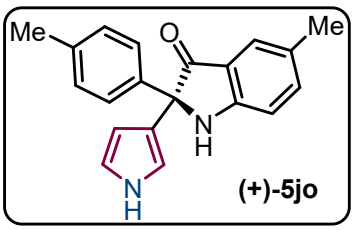
(*R*)-2-(1*H*-pyrrol-3-yl)-2-(p-tolyl)indolin-3-one (5fo): Purification was done using hexanes/ethyl acetate (8/2) as eluent; Yellow solid; (53 mg, 61% yield, mp = 135-137 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 98.5:1.5), t_R= 33.1 min (major), 39.3 min (minor). $[\alpha]_D^{25}$= +42.8 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.74 (s, 2H), 6.12 (d, *J* = 4.2 Hz, 1H), 5.19 (s, 1H), 2.32 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.4, 160.3, 137.9, 137.3, 137.3, 129.0, 126.8, 125.5, 123.8, 119.6, 119.2, 118.8, 116.8, 112.5, 107.4, 71.0, 21.0. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O^+$ 289.1335; Found: 289.1337.



(*R*)-5-methyl-2-phenyl-2-(1*H*-pyrrol-3-yl)indolin-3-one (5ho): Purification was done using hexanes/ethyl acetate (8/2) as eluent; Yellow solid; (55 mg, 64% yield, mp = 145-147 °C); **HPLC** (IC column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99.5:0.5), t_R= 11.5 min (minor), 14.6 min (major). $[\alpha]_D^{25}$= +52.4 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.3 (s, 1H), 7.5 (d, *J* = 7.0 Hz, 2H), 7.5 (s, 1H), 7.3 (m, *J* = 13.7, 7.2 Hz, 4H), 6.9 (d, *J* = 8.3 Hz, 1H), 6.8 (s, 2H), 6.2 – 6.1 (m, 1H), 5.1 (s, 1H), 2.3 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 201.4, 158.9, 141.2, 138.8, 129.0, 128.2, 127.5, 127.0, 124.9, 124.1, 119.9, 118.8, 116.9, 112.7, 107.4, 71.6, 20.6. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{19}H_{17}N_2O^+$ 289.1335; Found: 289.1339.

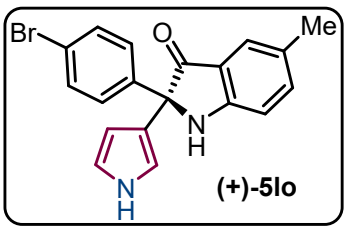


(*R*)-5-Methyl-2-(1*H*-pyrrol-3-yl)-2-(p-tolyl)indolin-3-one (5jo): Purification was done using hexanes/ethyl acetate (8/2) as eluent; Yellow solid; (55 mg, 61% yield, mp = 151-153 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric



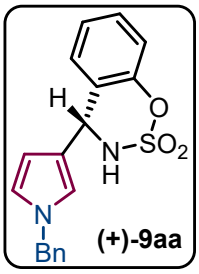
ratio (*er* = 99:1), t_R= 21.4 min (major), 28.3 min (minor). $[\alpha]_D^{25}$= +46.3 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 10.69 (s, 1H), 7.85 (s, 1H), 7.28 (dd, *J* = 11.5, 8.6 Hz, 3H), 7.19 (s, 1H), 6.83 (d, *J* = 8.9 Hz, 3H), 6.69 (s, 1H), 6.66 – 6.59 (m, 1H), 6.01 – 5.96 (m, 1H), 3.70 (s, 3H), 2.20 (s, 3H). **^{13}C{1H} NMR (100 MHz, DMSO-*d*$_6$)** δ 201.3, 159.8, 158.8, 139.1, 134.2, 128.1, 126.4, 124.1, 123.3, 118.4, 117.9, 116.3, 113.7, 112.0, 107.3, 70.8, 55.5, 20.5. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O^+$ 303.1492; Found: 303.1497.

(*R*)-2-(4-Bromophenyl)-5-methyl-2-(1*H*-pyrrol-3-yl)indolin-3-one (5lo): Purification was done using hexanes/ethyl acetate (8/2) as eluent; Yellow solid; (69 mg, 63% yield, mp = 161-163 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99:1), t_R= 21.3 min (major), 27.8 min (minor). $[\alpha]_D^{25}$= +44.1 (*c* 0.1, CH_2Cl_2).



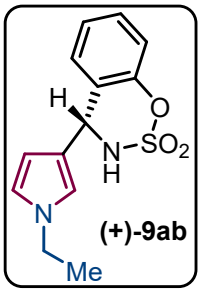
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.76 (s, 1H), 7.95 (s, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 3H), 7.21 (s, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.71 (q, *J* = 3.4, 2.8 Hz, 1H), 6.66 (q, *J* = 3.0 Hz, 1H), 6.02 – 5.98 (m, 1H), 2.20 (s, 3H). **^{13}C{1H} NMR (100 MHz, DMSO-*d*$_6$)** δ 205.2, 164.6, 146.5, 144.1, 136.0, 134.0, 131.6, 129.0, 127.4, 125.5, 123.4, 122.4, 121.2, 117.0, 111.9, 75.5, 25.2. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{19}H_{16}BrN_2O^+$ 367.0441; Found: 367.0447.

(*R*)-4-(1-Benzyl-1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (9aa): Purification was done using hexanes/ethyl acetate (9/1) as eluent; off white solid; (77 mg, 75% yield, mp = 148-150 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 20:80), t_R= 11.5 min (minor), 13.7 min (major). $[\alpha]_D^{25}$= +39.5 (*c* 0.1, CH_2Cl_2).



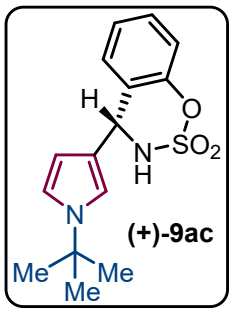
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 5H), 7.15 (d, *J* = 6.9 Hz, 2H), 7.10 (s, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.77 (s, 1H), 6.70 (t, *J* = 2.4 Hz, 1H), 6.06 – 6.04 (m, 1H), 5.88 (s, 1H), 5.05 (s, 2H), 4.70 (s, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 151.2, 137.3, 129.4, 128.9 (2C), 128.6, 128.0, 127.2 (2C), 124.9, 122.8, 122.6, 121.2, 120.8, 118.5, 107.8, 55.7, 53.6. **HRMS (ESI-TOF)** (m/z): $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O_3S^+$ 341.0954; Found: 341.0949.

(*R*)-4-(1-Ethyl-1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (9ab):



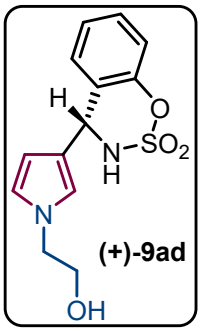
Purification was done using hexanes/ethyl acetate (9/1) as eluent; light brown solid; (58 mg, 70% yield, mp = 128-130 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 20:80), t_R= 22.7 min (minor), 26.7 min (major). $[\alpha]_D^{25}$= +35.7 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.29 (m, 1H), 7.14 – 7.12 (m, 1H), 7.11 (s, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.78 (t, *J* = 1.8 Hz, 1H), 6.70 (t, *J* = 2.4 Hz, 1H), 6.03 – 6.00 (m, 1H), 5.90 (d, *J* = 8.5 Hz, 1H), 4.66 (d, *J* = 8.0 Hz, 1H), 3.95 (q, *J* = 7.3 Hz, 2H), 1.46 (t, *J* = 7.3 Hz, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 151.2, 129.3, 128.7, 124.9, 122.9, 121.4, 120.2, 120.1, 118.5, 107.2, 55.8, 44.4, 16.5. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{15}N_2O_3S^+$ 279.0798, found: 279.0793.

(*R*)-4-(1-(Tert-butyl)-1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (9ac):



Purification was done using hexanes/ethyl acetate (9/1) as eluent; light brown soild; (65 mg, 71% yield, mp = 139-141 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 15:85), t_R= 12.7 min (minor), 14.9 min (major). $[\alpha]_D^{25}$= +56.3 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (m, 1H), 7.11 – 7.08 (m, 2H), 7.05 – 7.01 (m, 1H), 6.91 (t, *J* = 2.1 Hz, 1H), 6.84 – 6.81 (m, 1H), 5.98 (dd, *J* = 2.9, 1.9 Hz, 1H), 5.89 (s, 1H), 4.59 (s, 1H), 1.54 (s, 9H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 151.1, 129.2, 128.6, 124.8, 122.9, 119.6, 119.1, 118.4, 117.8, 106.6, 55.9, 55.2, 30.6 (3C). **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{19}N_2O_3S^+$ 307.1111, found: 307.1115.

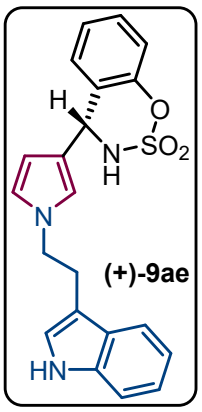
(*R*)-4-(1-(2-Hydroxyethyl)-1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide



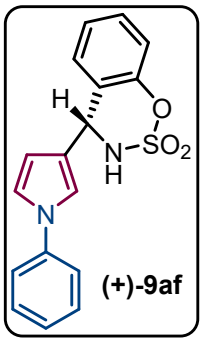
(9ad): Purification was done using hexanes/ethyl acetate (7/3) as eluent; light brown solid; (64 mg, 73% yield, mp = 163-165 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 16:84), t_R= 16.5 min (minor), 20.1 min (major). $[\alpha]_D^{25}$= +39.4 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 – 7.27 (m, 1H), 7.12 –

7.09 (m, 2H), 7.01 (dd, J = 8.2, 3.6 Hz, 1H), 6.73 – 6.70 (m, 1H), 6.66 (t, J = 2.3 Hz, 1H), 6.04 – 6.01 (m, 1H), 5.84 (s, 1H), 3.94 (m, 2H), 3.80 (t, J = 5.0 Hz, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 151.2, 129.4, 128.6, 124.9, 122.8, 122.2, 121.1, 120.8, 118.5, 107.9, 62.6, 55.6, 52.1. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{15}N_2O_4S^+$ 295.0747, found: 295.0746.

(*R*)-4-(1-(2-(1*H*-indol-3-yl)ethyl)-1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (9ae): Purification was done using hexanes/ethyl acetate (8/2) as eluent; light brown solid; (86 mg, 73% yield, mp = 155-157 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, I = 254 nm) was used to measure the enantiomeric ratio (*er* = 15:85), t_R= 20.0 min (minor), 24.2 min (major). $[\alpha]_D^{25}$= +43.6 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (s, 1H), 7.42 (dd, J = 18.7, 8.0 Hz, 2H), 7.28 (m, 2H), 7.12 (dt, J = 18.3, 7.4 Hz, 2H), 7.01 (t, J = 8.3 Hz, 2H), 6.88 – 6.85 (m, 1H), 6.65 (d, J = 2.7 Hz, 1H), 6.50 (s, 1H), 6.01 (d, J = 4.8 Hz, 1H), 5.82 (d, J = 8.6 Hz, 1H), 4.54 (d, J = 8.6 Hz, 1H), 4.22 – 4.10 (m, 2H), 3.22 (t, J = 6.8 Hz, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 151.1, 136.1, 129.3, 128.7, 127.2, 124.9, 122.8, 122.3, 122.2, 121.8, 121.0, 120.1, 119.4, 118.5, 118.2, 112.3, 111.4, 107.5, 55.7, 50.8, 27.8. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{20}N_3O_3S^+$ 394.1220, found: 394.1226.

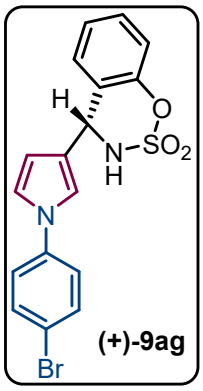


(*R*)-4-(1-Phenyl-1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (9af): Purification was done using hexanes/ethyl acetate (8/2) as eluent; off white solid; (70 mg, 72% yield, mp = 171-173 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, I = 254 nm) was used to measure the enantiomeric ratio (*er* = 13:87), t_R= 11.1 min (minor), 13.1 min (major). $[\alpha]_D^{25}$= +58.3 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 – 7.45 (m, 2H), 7.43 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 7.19 (t, J = 2.0 Hz, 1H), 7.16 (dd, J = 6.4, 1.2 Hz, 2H), 7.13 – 7.11 (m, 1H), 7.08 – 7.04 (m, 1H), 6.25 (dd, J = 2.9, 1.8 Hz, 1H), 5.99 (d, J = 8.0 Hz, 1H), 4.81 (d, J = 8.0 Hz, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 151.2, 140.0, 129.7, 129.5, 128.6, 126.4, 125.0, 122.6, 122.5, 120.9, 120.6,



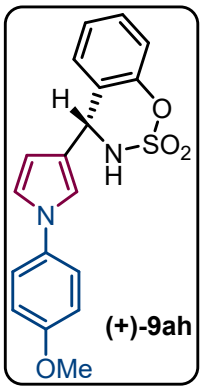
119.4, 118.6, 109.5, 55.6. **HRMS (ESI-TOF)** *m/z*: [M + H] $^+$ Calcd for $C_{17}H_{15}N_2O_3S^+$ 327.0798, found: 327.0791.

(*R*)-4-(1-(4-Bromophenyl)-1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide

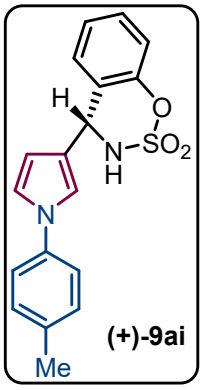


(9ag): Purification was done using hexanes/ethyl acetate (8/2) as eluent; light brown solid; (71 mg, 70% yield, mp = 177-179 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 16:84), t_R= 22.3 min (minor), 26.5 min (major). $[\alpha]_D^{25}$= +59.1 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 – 7.57 (m, 2H), 7.38 – 7.33 (m, 1H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.28 (d, *J* = 1.9 Hz, 1H), 7.16 (d, *J* = 4.0 Hz, 3H), 7.08 (dd, *J* = 5.1, 2.1 Hz, 2H), 6.28 – 6.24 (m, 1H), 5.98 (d, *J* = 7.4 Hz, 1H), 4.70 (d, *J* = 7.1 Hz, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 151.2, 139.0, 132.7 (2C), 129.6, 128.4, 125.0, 123.0, 122.2, 122.0 (2C), 120.8, 119.6, 119.2, 118.7, 109.9, 55.5. **HRMS (ESI-TOF)** *m/z*: [M + H] $^+$ Calcd for $C_{17}H_{14}BrN_2O_3S^+$ 404.9903, found: 404.9908.

(*R*)-4-(1-(4-Methoxyphenyl)-1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide



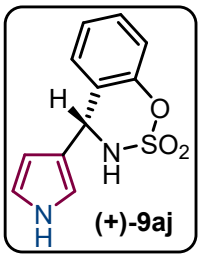
(9ah): Purification was done using hexanes/ethyl acetate (8/2) as eluent; off white solid; (77 mg, 72% yield, mp = 153-155 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 11:89), t_R= 19.1 min (minor), 23.2 min (major). $[\alpha]_D^{25}$= +45.2 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.27 (m, 3H), 7.20 – 7.12 (m, 2H), 7.10 – 7.07 (m, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 7.03 – 7.00 (m, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.21 (s, 1H), 5.98 (s, 1H), 4.78 (s, 1H), 3.86 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 158.1, 151.2, 133.6, 129.5, 128.6, 125.0, 122.6, 122.3, 122.1, 121.2, 119.8, 118.6, 114.8, 109.0, 55.7, 55.6. **HRMS (ESI-TOF)** *m/z*: [M + H] $^+$ Calcd for $C_{18}H_{17}N_2O_4S^+$ 357.0904, found: 357.0908.



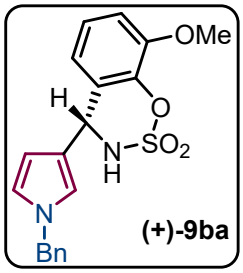
(*R*)-4-(1-(*p*-Tolyl)-1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (9ai): Purification was done using hexanes/ethyl acetate (8/2) as eluent; off

white solid; (94 mg, 71% yield, mp = 142-144 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 265 nm) was used to measure the enantiomeric ratio (*er* = 21:79), t_R= 16.6 min (minor), 19.6 min (major). $[\alpha]_D^{25}$= +51.2 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.23 (m, 6H), 7.16 – 7.12 (m, 3H), 7.07 – 7.05 (m, 1H), 7.05 – 7.02 (m, 1H), 6.21 (dd, *J* = 2.8, 1.8 Hz, 1H), 5.97 (s, 1H), 4.78 (s, 1H), 2.40 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 151.2, 137.7, 136.2, 130.2 (2C), 129.4, 128.6, 125.0 (2C), 122.5, 122.2 (2C), 120.9, 120.5, 119.4, 118.6, 109.2, 55.6, 20.8. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O_3S^+$ 341.0954, found: 341.0955.

(*R*)-4-(1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (9aj): Purification was done using hexanes/ethyl acetate (7/3) as eluent; light brown solid; (49 mg, 65% yield, mp = 165-167 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 275 nm) was used to measure the enantiomeric ratio (*er*= 15:85), t_R= 10.5 min (minor), 12.2 min (major). $[\alpha]_D^{25}$= +38.2 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (s, 1H), 7.32 (m, 1H), 7.12 (td, *J* = 7.6, 1.0 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.05 – 7.01 (m, 1H), 6.89 (d, *J* = 2.0 Hz, 1H), 6.82 (q, *J* = 2.5 Hz, 1H), 6.11 (q, *J* = 2.5 Hz, 1H), 5.94 (s, 1H), 4.86 – 4.68 (m, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 151.1, 129.4, 128.70, 125.0, 122.8, 120.4, 119.5, 118.5, 118.1, 107.5, 55.6. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{11}N_2O_3S^+$ 251.0485, found: 251.0483.

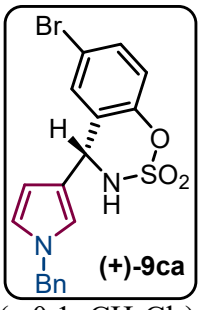


(*R*)-4-(1-Benzyl-1*H*-pyrrol-3-yl)-8-methoxy-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (9ba): Purification was done using hexanes/ethyl acetate (8/2) as eluent; light brown solid; (84 mg, 76% yield, mp = 129-131 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 230 nm) was used to measure the enantiomeric ratio (*er* = 10:90), t_R= 19.4 min (minor), 23.9 min (major). $[\alpha]_D^{25}$= +52.8 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.31 (m, 3H), 7.18 – 7.14 (m, 2H), 7.04 (t, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 1.9 Hz, 1H), 6.71 (t, *J* = 2.5 Hz, 1H), 6.67 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.07 (dd, *J* = 2.6, 1.8 Hz, 1H), 5.90 (s, 1H), 5.07 (s, 2H), 4.66 (s, 1H), 3.88 (s, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 148.6, 140.9, 137.2, 128.9 (2C), 128.0,



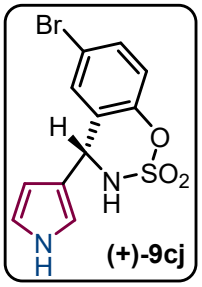
127.2 (2C), 124.3, 123.8, 122.6, 121.1, 120.9, 119.7, 111.6, 107.8, 56.2, 55.8, 53.6. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{19}N_2O_4S^+$ 371.1060, found: 371.1058.

(*R*)-4-(1-benzyl-1*H*-pyrrol-3-yl)-6-bromo-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide



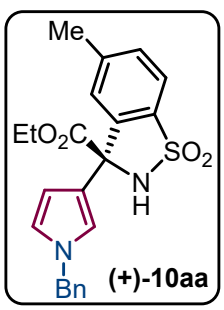
(9ca): Purification was done using hexanes/ethyl acetate (8/2) as eluent; light brown solid; (95 mg, 76% yield, mp = 145-147 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 230 nm) was used to measure the enantiomeric ratio (*er* = 9:91), t_R= 12.6 min (minor), 15.9 min (major). $[\alpha]_D^{25}$= +55.2 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.33 (m, 4H), 7.23 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.17 (d, *J* = 6.8 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.79 (t, *J* = 1.9 Hz, 1H), 6.74 (t, *J* = 2.5 Hz, 1H), 6.09 – 6.05 (m, 1H), 5.85 (d, *J* = 8.6 Hz, 1H), 5.09 (s, 2H), 4.72 (d, *J* = 8.7 Hz, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 150.2, 137.1, 132.5, 131.4, 128.9 (2C), 128.1, 127.2 (2C), 124.9, 123.0, 121.1, 120.3, 120.0, 117.6, 107.7, 55.4, 53.7. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{16}BrN_2O_3S^+$ 419.0060, found: 419.0065.

(*R*)-6-Bromo-4-(1*H*-pyrrol-3-yl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazine 2,2-dioxide (9cj):



Purification was done using hexanes/ethyl acetate (7/3) as eluent; light brown solid; (62 mg, 63% yield, mp = 162-164 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 15:85), t_R= 26.7 min (minor), 33.2 min (major). $[\alpha]_D^{25}$= + 41.3(*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.18 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 6.10 (s, 1H), 5.88 (d, *J* = 6.7 Hz, 1H), 4.87 – 4.76 (m, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 150.2, 132.5, 131.3, 124.9, 120.3, 119.8, 119.7, 118.1, 117.6, 107.4, 55.3. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{10}BrN_2O_3S^+$ 328.9590, found: 328.9591.

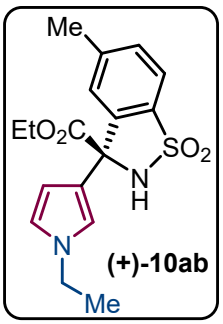
Ethyl (*R*)-3-(1-benzyl-1*H*-pyrrol-3-yl)-5-methyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate



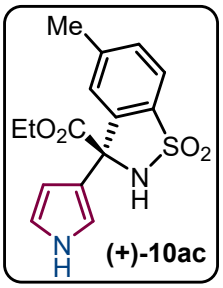
1,1-dioxide (10aa): Purification was done using hexanes/ethyl acetate (8/2) as eluent; light brown solid; (89 mg, 72% yield, mp = 139-141 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was

used to measure the enantiomeric ratio (*er* = 15:85), t_R= 12.7 min (minor), 14.9 min (major). $[\alpha]_D^{25}$= +44.3 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.59 (s, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.30 (s, 1H), 7.10 (d, *J* = 6.6 Hz, 2H), 6.80 (t, *J* = 1.9 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 6.27 – 6.23 (m, 1H), 5.86 (s, 1H), 4.98 (s, 2H), 4.32 (m, 2H), 2.45 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 169.6, 144.2, 139.1, 137.2, 132.0, 131.1, 128.8 (2C), 127.9, 127.2 (2C), 126.8, 123.0, 122.0, 120.7, 119.9, 107.4, 67.1, 63.4, 53.6, 21.9, 14.0. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_4S^+$ 411.1373, found: 411.1375.

Ethyl (*R*)-3-(1-ethyl-1*H*-pyrrol-3-yl)-5-methyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (10ab): Purification was done using hexanes/ethyl acetate (8/2) as eluent; light brown solid; (71 mg, 68% yield, mp = 133-135 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 20:80), t_R= 22.7 min (minor), 26.7 min (major). $[\alpha]_D^{25}$= +42.8 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 1H), 6.74 (t, *J* = 2.0 Hz, 1H), 6.60 (t, *J* = 2.5 Hz, 1H), 6.22 – 6.20 (m, 1H), 5.85 (s, 1H), 4.33 (qd, *J* = 7.1, 1.9 Hz, 2H), 3.85 (q, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 1.36 (dt, *J* = 14.7, 7.2 Hz, 6H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 169.7, 144.2, 139.2, 131.9, 131.0, 126.9, 122.5, 120.9, 120.7, 118.8, 106.7, 67.2, 63.4, 44.5, 22.0, 16.3, 14.1. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2O_4S^+$ 349.1217, found: 349.1214.

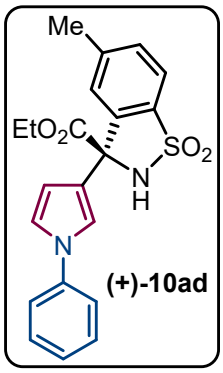


Ethyl (*R*)-5-methyl-3-(1*H*-pyrrol-3-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (10ac): Purification was done using hexanes/ethyl acetate (7/3) as eluent; light brown solid; (56 mg, 58% yield, mp = 152-154 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 265 nm) was used to measure the enantiomeric ratio (*er* = 15:85), t_R= 27.6 min (minor), 31.4 min (major). $[\alpha]_D^{25}$= +46.5 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 6.80 (q, *J* = 2.0 Hz, 1H), 6.71 (q, *J* = 2.6 Hz, 1H), 6.28 (q, *J* = 2.7 Hz, 1H), 5.91 (s, 1H), 4.33 (m, 2H), 2.45 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C{1H} NMR (100 MHz,**

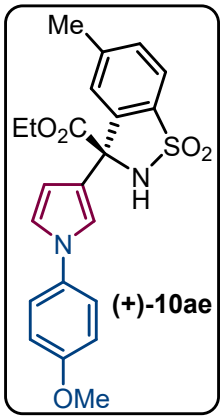


$CDCl_3$) δ 169.6, 144.2, 139.1, 131.9, 131.1, 126.8, 122.9, 120.7, 119.0, 116.7, 107.0, 67.1, 63.4, 21.9, 14.0. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}N_2O_4S^+$ 321.0904, found: 321.0909.

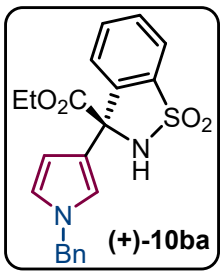
Ethyl (*R*)-5-methyl-3-(1-phenyl-1*H*-pyrrol-3-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (10ad): Purification was done using hexanes/ethyl acetate (8/2) as eluent; light brown solid; (77 mg, 65% yield, mp = 138-140 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 13:87), t_R= 11.1 min (minor), 13.1 min (major). $[\alpha]_D^{25}$= +48.3 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.41 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.33 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.18 (t, *J* = 2.1 Hz, 1H), 7.03 – 7.01 (m, 1H), 6.45 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.00 (s, 1H), 4.37 (qd, *J* = 7.1, 2.2 Hz, 2H), 2.48 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 169.4, 144.3, 140.1, 138.8, 131.9, 131.2, 129.6, 126.7, 126.2, 124.9, 120.8, 120.6, 120.4, 118.0, 109.1, 67.0, 63.6, 22.0, 14.1. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_4S^+$ 397.1217, found: 397.1219.



Ethyl (*R*)-3-(1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)-5-methyl-2,3-dihydrobenzo [d]isothiazole-3-carboxylate 1,1-dioxide (10ae): Purification was done using hexanes/ethyl acetate (8/2) as eluent; light brown solid; (90 mg, 71% yield, mp = 158-160 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 90/10, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 23:77), t_R= 44.4 min (minor), 52.3 min (major). $[\alpha]_D^{25}$= +53.9 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (s, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 3.4 Hz, 2H), 7.41 (t, *J* = 2.0 Hz, 1H), 7.28 – 7.23 (m, 3H), 6.76 – 6.73 (m, 1H), 6.32 (s, 1H), 4.70 (m, 2H), 4.15 (s, 3H), 2.81 (s, 3H), 1.70 (t, *J* = 7.1 Hz, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 169.5, 158.0, 144.3, 138.9, 133.7, 131.9, 131.2, 126.7, 124.4, 122.3 (2C), 120.8, 120.7, 118.3, 114.6 (2C), 108.5, 67.0, 63.5, 55.5, 21.9, 14.0. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_5S^+$ 427.1322, found: 427.1327.

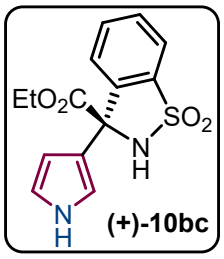


Ethyl (*R*)-3-(1-benzyl-1*H*-pyrrol-3-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide



(10ba): Purification was done using hexanes/ethyl acetate (8/2) as eluent; light brown solid; (82 mg, 69% yield, mp = 125-127 °C); **HPLC** (IA column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 265 nm) was used to measure the enantiomeric ratio (*er* = 12:88), t_R= 22.1 min (minor), 25.0 min (major). $[\alpha]_D^{25}$= +43.7 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.8 (d, *J* = 7.8 Hz, 1H), 7.7 (d, *J* = 7.6 Hz, 1H), 7.6 (t, *J* = 7.5 Hz, 1H), 7.5 (t, *J* = 7.5 Hz, 1H), 7.3 (q, *J* = 9.2, 7.8 Hz, 3H), 7.1 (d, *J* = 6.7 Hz, 2H), 6.8 (s, 1H), 6.6 – 6.6 (m, 1H), 6.3 (s, 1H), 5.9 (s, 1H), 5.0 (s, 2H), 4.3 (qt, *J* = 10.7, 5.3 Hz, 2H), 1.3 (t, *J* = 7.1 Hz, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 169.6, 138.8, 137.2, 134.7, 133.2, 130.1, 128.8 (2C), 127.9, 127.2 (2C), 126.8, 122.9, 122.1, 121.0, 119.9, 107.4, 67.3, 63.5, 53.6, 14.0. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}N_2O_4S^+$ 397.1217, found: 397.1222.

Ethyl (*R*)-3-(1*H*-pyrrol-3-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (10bc):



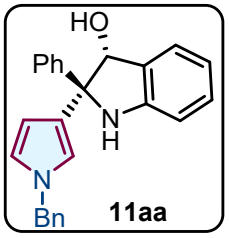
Purification was done using hexanes/ethyl acetate (7/3) as eluent; light brown solid; (51 mg, 56% yield, mp = 142-144 °C); **HPLC** (IB column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 230 nm) was used to measure the enantiomeric ratio (*er* = 12:88), t_R= 15.5 min (minor), 20.1 min (major). $[\alpha]_D^{25}$= +41.2 (*c* 0.1, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 (s, 1H), 7.88 (s, 1H), 7.80 – 7.75 (m, 1H), 7.66 (td, *J* = 7.7, 1.2 Hz, 1H), 7.59 (td, *J* = 7.6, 1.0 Hz, 1H), 6.89 (q, *J* = 2.0 Hz, 1H), 6.76 (q, *J* = 2.6 Hz, 1H), 6.34 (q, *J* = 2.7 Hz, 1H), 5.97 (s, 1H), 4.36 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 169.5, 138.7, 134.7, 133.1, 130.1, 126.6, 123.0, 120.8, 118.8, 117.0, 107.1, 67.2, 63.5, 14.0. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}N_2O_4S^+$ 307.0747, found: 307.0742.

Diastereoselective reduction of 5aa to 11aa:

To a stirred solution of **5aa** (36.4 mg, 0.1 mmol) in 1,4-dioxane (4.0 mL) was added LiBr (34.7 mg, 0.4 mmol, 4 equiv.), $NaBH_4$ (80 mg, 2.1 mmol, 21 equiv.) portion-wise in an oven-dried Schlenck tube at room temperature and combined mixture was stirred for 16 h. Upon completion, the reaction was quenched with aq. NH_4Cl solution (2.0 mL) and extracted with ethyl acetate (2 × 4.0 mL). The

combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The silica-gel column chromatographic purification of the crude material furnished pyrrole **11aa** (24 mg, 66% yield).

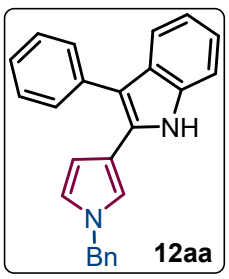
(2*R*,3*S*)-2-(1-benzyl-1*H*-pyrrol-3-yl)-2-phenylindolin-3-ol (11aa): (mp = 142 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.7 (d, *J* = 7.3 Hz, 2H), 7.4 (t, *J* = 7.5 Hz, 2H), 7.4 – 7.3 (m, 5H), 7.2 (t, *J* = 7.6 Hz, 1H), 7.1 (d, *J* = 1.3 Hz, 1H), 7.0 (s, 1H), 6.8 (d, *J* = 7.3 Hz, 1H), 6.7 (d, *J* = 7.8 Hz, 1H), 6.5 (t, *J* = 2.5 Hz, 1H), 6.3 (t, *J* = 1.9 Hz, 1H), 5.9 (d, *J* = 4.5 Hz, 1H), 5.5 (d, *J* = 10.9 Hz, 1H), 4.9 (s, 2H), 4.5 (s, 1H), 2.3 (d, *J* = 10.9 Hz, 1H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 149.3, 146.0, 137.6, 130.2, 129.2, 128.8 (2C), 128.1 (2C), 127.8, 127.0 (2C), 126.9, 126.2 (2C), 125.5, 125.1, 121.5, 122.0, 119.3, 109.7, 107.7, 80.9, 73.8, 53.4. **HRMS (ESI-TOF)** *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O^+$ 367.1805, found: 367.1807.



Procedure for the rearrangement reaction to 12aa:

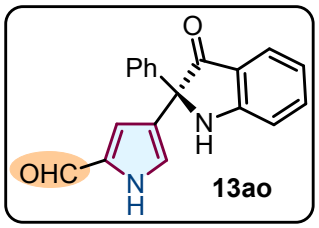
To a stirred solution of **11aa** (36.6 mg, 0.1 mmol) in 1,4-dioxane (4.0 mL) was added conc. HCl (350 µL) and the combined reaction mixture was stirred at 50 °C for 30 minutes. The reaction mixture was cooled and quenched with aq. $NaHCO_3$ solution (3.0 mL) and cold water (3.0 mL) and extracted with ethyl acetate (2 × 4.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The silica-gel column chromatographic purification of the crude material furnished rearranged product **12aa** (27 mg, 76% yield).

2-(1-benzyl-1*H*-pyrrol-3-yl)-3-phenyl-1*H*-indole (12aa): (mp = 124 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.1 (s, 1H), 7.9 – 7.8 (m, 1H), 7.6 (s, 2H), 7.4 (s, 7H), 7.2 (s, 3H), 6.8 (d, *J* = 17.5 Hz, 2H), 6.3 (s, 1H), 5.1 (s, 2H). **^{13}C{1H} NMR (100 MHz, $CDCl_3$)** δ 138.5, 136.0, 133.6, 133.2, 129.3, 128.7 (2C), 128.5 (2C), 128.2 (2C), 127.6, 127.4, 126.9 (2C), 122.4, 121.3, 120.2, 120.1, 120.0, 117.1, 110.8, 110.0, 109.7, 53.4. **HRMS (ESI-TOF)** *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2^+$ 349.1699, found: 349.1674.



Procedure for Vilsmeier–Haack reaction to 13ao:

To a mixture of **5ao** (50 mg, 0.18 mmol) and DMF (14 µL, 0.18 mmol, 1 equiv.) was added $POCl_3$ (42 µL, 0.45 mmol, 2.5 equiv.) at 0 °C and stirred at rt for 3 h. The reaction mixture was neutralized with 1N NaOH solution (1.0 mL) and extracted with ethyl acetate (2× 3.0 mL). The combined organic layer was washed with brine (5.0 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude mixture was purified by column chromatography (hexanes/EtOAc) to yield formylated pyrrole **13ao** (sticky semi-solid, 40 mg, 72% yield).



(*R*)-3-(3-oxo-2-phenylindolin-2-yl)-1*H*-pyrrole-2-carbaldehyde (13ao): HPLC (IA column, *n*-hexane/*iso*-propanol = 80/20, flow rate 1.0 mL/min, *I* = 254 nm) was used to measure the enantiomeric ratio (*er* = 99:1), t_R= 12.7 min (major), 16.1 min (minor). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.0 (s, 1H), 9.5 (s, 1H), 8.6 (d, *J* = 9.8 Hz, 1H), 7.8 (d, *J* = 8.1 Hz, 1H), 7.8 (s, 1H), 7.4 (m, 7H), 7.1 (t, *J* = 1.6 Hz, 1H), 7.0 (t, *J* = 2 Hz, 1H). **^{13}C {1H} NMR (100 MHz, $CDCl_3$)** δ 196.8, 179.5, 161.0, 151.1, 138.0, 137.5, 133.3, 129.2 (2C), 127.2 (2C), 125.7, 125.6, 125.3, 123.7, 121.7, 119.8, 118.0, 72.7. **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}N_2O_2^+$ 303.1055, found: 303.1057.

8.0 Single crystal X-ray Diffraction Experiment and Analysis

Crystal structure of compound 5ab (Exp 898_AD-28)

The single crystals data collection and data reductions were carried out employing CrysAlis PRO on a single crystal Rigaku-Oxford XtaLAB Pro Kappa dual home/near diffractometer. The crystals were kept at 93(2) K during data collection using CuKα(λ=1.54184 Å) radiation source. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.

Single Crystal structure, Cell parameters and structure data of compound (5ab) [exp_898-AD-28] (CCDC 2165854): The single crystals of compound $C_{20}H_{18}N_2O$ (exp_898-AD-28) were obtained

as slight yellow blocks through the slow evaporation of $CHCl_3$. The Crystal Data for $C_{20}H_{18}N_2O$ (M =302.36 g/mol): trigonal, space group $P3_2$ (no. 145), a = 15.2367(5) Å, c = 18.0166(5) Å, V = 3622.3(3) Å^3, Z = 9, T = 93(2) K, μ(Cu Kα) = 0.611 mm^{-1}, *Dcalc* = 1.247 g/cm^3, 14266 reflections measured (8.306° ≤ 2Θ ≤ 160.316°), 6302 unique (R_{int} = 0.0527, R_{sigma} = 0.0678) which were used in all calculations. The final R_1 was 0.0670 (I > 2σ(I)) and wR_2 was 0.1859 (all data). The crystallographic details of the compound (exp_898-AD-28) are deposited to the Cambridge Crystallographic (CCDC 2165854). The ORTEP diagram as the crystal structure of **5ab (CCDC 2165854)** is illustrated in Figure S1. The molecule has one chiral centre with (*R*)-stereochemistry at the existing chiral center. The crystal data and structure refinement for compound **5ab** are shown in Table S3.

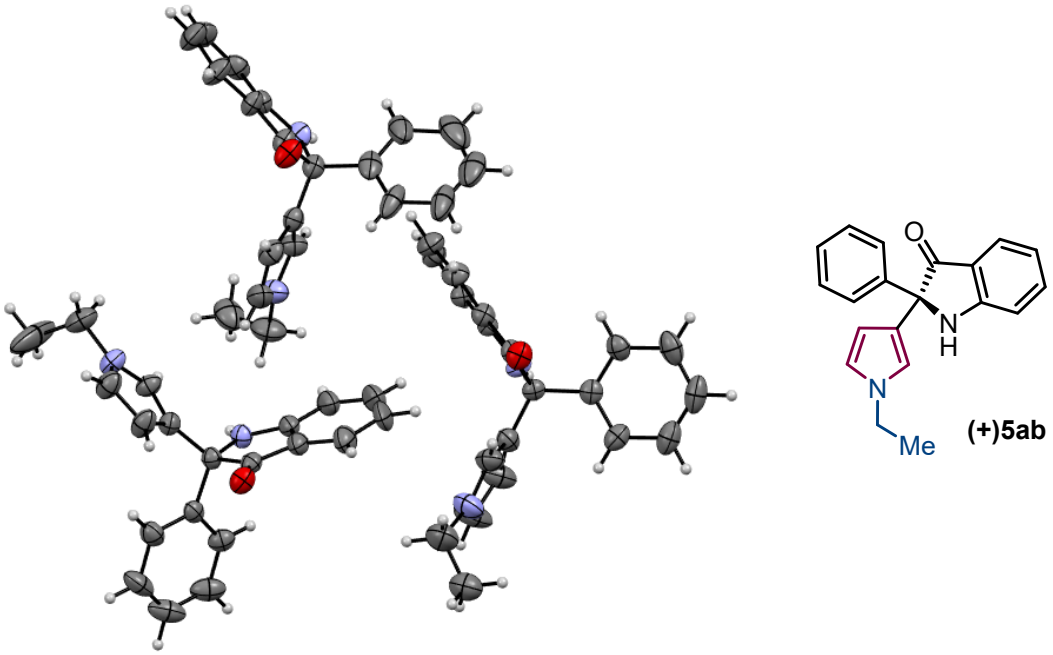


Figure S3. ORTEP diagram of compound (Exp 898_AD-28). Thermal ellipsoids are drawn at 50% probability level. **(CCDC 2165854)**

Table S3 Crystal data and structure refinement for exp_898-AD-28.

Identification code	exp_898-AD-28
Empirical formula	$C_{20}H_{18}N_2O$
Formula weight	302.36
Temperature/K	93(2)

Crystal system	trigonal
Space group	$P3_2$
a/Å	15.2367(5)
b/Å	15.2367(5)
c/Å	18.0166(5)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	3622.3(3)
Z	9
ρ_{calc}g/cm^3	1.247
μ/mm^{-1}	0.611
F(000)	1440.0
Crystal size/mm^3	0.15 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.306 to 160.316
Index ranges	-17 ≤ h ≤ 19, -18 ≤ k ≤ 17, -10 ≤ l ≤ 22
Reflections collected	14266
Independent reflections	6302 [R_{int} = 0.0527, R_{sigma} = 0.0678]
Data/restraints/parameters	6302/1/625
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0670, wR_2 = 0.1747
Final R indexes [all data]	R_1 = 0.0776, wR_2 = 0.1859
Largest diff. peak/hole / e Å^{-3}	0.50/-0.24
Flack parameter	0.1(4)
CCDC	2165854

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
```

```
2.a Secondary CH2 refined with riding coordinates:
 C119(H11A,H11B), C19(H19A,H19B), C219(H21A,H21B)
2.b Aromatic/amide H refined with riding coordinates:
 N101(H101), N1(H1), N201(H201), C115(H115), C202(H202), C203(H203), C2(H2),
 C114(H114), C15(H15), C113(H113), C18(H18), C210(H210), C21(H21), C204(H204),
 C112(H112), C214(H214), C217(H217), C17(H17), C118(H118), C211(H211),
 C117(H117), C4(H4), C110(H110), C212(H212), C111(H111), C215(H215), C105(H105),
  C102(H102), C213(H213), C218(H218), C3(H3), C14(H14), C5(H5), C13(H13),
 C12(H12), C10(H10), C104(H104), C103(H103), C11(H11)
2.c Idealised Me refined as rotating group:
 C220(H22A,H22B,H22C), C20(H20A,H20B,H20C), C120(H12A,H12B,H12C)
```

This report has been created with Olex2, compiled on 2020.11.12 svn.r5f609507 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Crystal structure of compound 9ab (exp_1355_AD-686_20230202)

The single crystals data collection and data reductions were carried out employing CrysAlis PRO on a single crystal Rigaku-Oxford XtaLAB Pro Kappa dual home/near diffractometer. The crystals were kept at 93(2) K during data collection using CuKα(λ=1.54184 Å) radiation source. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.

Single Crystal structure, Cell parameters and structure data of compound (9ab) [exp_1355_AD-686_20230202] (CCDC 2361190):

The single crystals of compound $C_{13}H_{14}N_2O_3S$ (exp_1355_AD-686_20230202) were obtained as light brown blocks through the slow evaporation of CH_2Cl_2. The Crystal Data for $C_{13}H_{14}N_2O_3S$ (M =278.32 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 9.0312(2) Å, b = 16.1924(3) Å, c = 9.2203(2) Å, β = 97.644(2)°, V = 1336.37(5) Å^3, Z = 4, T = 133(2) K, μ(Cu Kα) = 2.217 mm^{-1}, *Dcalc* = 1.383 g/cm^3, 7241 reflections measured (9.882° ≤ 2Θ ≤ 159.136°), 2808 unique (R_{int} = 0.0296, R_{sigma} = 0.0363) which were used in all calculations. The final R_1 was 0.0404 (I > 2σ(I)) and wR_2 was 0.1129 (all data). The crystallographic details of the compound (exp_1355_AD-686_20230202) are deposited to the Cambridge Crystallographic (CCDC 2361190). The ORTEP diagram as the crystal structure of **9ab** is illustrated in Figure S4. The molecule has one chiral centre

with (*R*)-stereochemistry at the existing chiral centre. The crystal data and structure refinement for compound **9ab** are shown in Table S4.

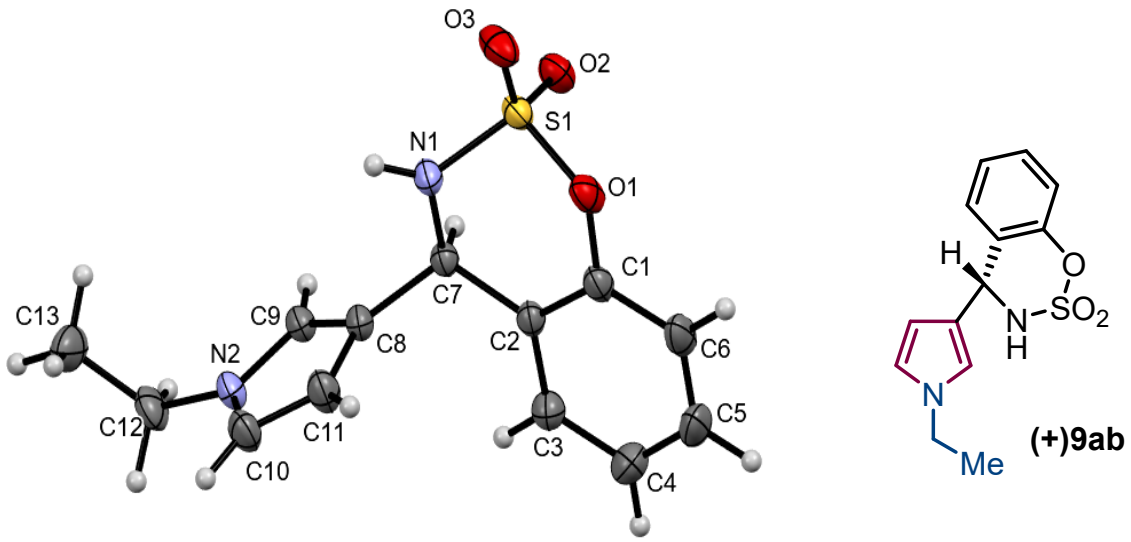


Figure S4. The ORTEP diagram of compound (exp_1355_AD-686_20230202) with atomic numbering. The thermal ellipsoids are drawn at 50 % probability level. CCDC 2361190.

Table S4 Crystal data and structure refinement for exp_1355_AD-686_20230202.

Identification code	exp_1355_AD-686_20230202
Empirical formula	$C_{13}H_{14}N_2O_3S$
Formula weight	278.32
Temperature/K	133(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.0312(2)
b/Å	16.1924(3)
c/Å	9.2203(2)
α/°	90
β/°	97.644(2)

γ/°	90
Volume/Å^3	1336.37(5)
Z	4
ρ_{calc}g/cm^3	1.383
μ/mm^{-1}	2.217
F(000)	584.0
Crystal size/mm^3	0.11 × 0.07 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.882 to 159.136
Index ranges	-11 ≤ h ≤ 10, -19 ≤ k ≤ 11, -11 ≤ l ≤ 11
Reflections collected	7241
Independent reflections	2808 [R_{int} = 0.0296, R_{sigma} = 0.0363]
Data/restraints/parameters	2808/0/173
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.1101
Final R indexes [all data]	R_1 = 0.0440, wR_2 = 0.1129
Largest diff. peak/hole / e Å^{-3}	0.56/-0.70
CCDC	2361190

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C7(H7)
2.b Secondary CH2 refined with riding coordinates:
 C12(H12A,H12B)
2.c Aromatic/amide H refined with riding coordinates:
 N1(H1), C3(H3), C4(H4), C5(H5), C6(H6), C9(H9), C10(H10), C11(H11)
2.d Idealised Me refined as rotating group:
 C13(H13A,H13B,H13C)
```

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Crystal structure of compound 11aa (AD959_20240828)

The Single crystals data collection and data reductions were carried out employing CrysAlis PRO on a single crystal Rigaku-Oxford XtaLAB Pro II AFC12 (RINC): Kappa single diffractometer. The crystals were kept at 100 K during data collection using microfocus Mo Kα (λ = 0.71073) radiation source. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.

Single Crystal structure, Cell parameters and structure data of compound (11aa) [AD959_20240828] (CCDC 2380259):

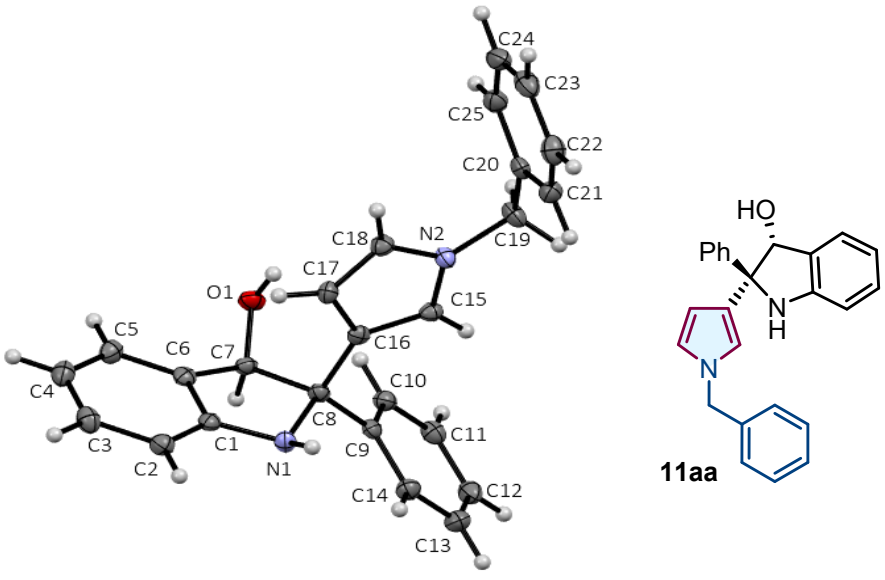


Figure S5. The ORTEP diagram of compound (AD959_20240828). The thermal ellipsoids are drawn at the 50 % probability level. (CCDC 2380259).

The single crystals of compound $C_{25}H_{22}N_2O$ **[AD959_20240828]** (AD959) are grown as yellow blocks from a chloroform solution. The compound **Data** for $C_{25}H_{22}N_2O$ (M =366.44 g/mol): orthorhombic, space group $P2_12_12$ (no. 18), a = 19.9908(8) Å, b = 15.7652(5) Å, c = 5.8187(2) Å, V = 1833.82(11) Å^3, Z = 4, T = 100 K, μ(Mo Kα) = 0.081 mm^{-1}, *Dcalc* = 1.327 g/cm^3, 14236 reflections measured (3.29° ≤ 2Θ ≤ 56.098°), 4140 unique (R_{int} = 0.0315, R_{sigma} = 0.0435) which were used in all calculations. The final R_1 was 0.0382 (I > 2σ(I)) and wR_2 was 0.0860 (all data). A single neutral molecule, $C_{25}H_{22}N_2O$, resolved per asymmetric unit and four molecules are occupied in a crystallographic unit cell. The crystallographic details of the compound (AD959_20240828) are deposited to the Cambridge Crystallographic (CCDC 2380259). The ORTEP diagram with atom numbering is displayed in Figure S5. The compound AD959 possesses two chiral centres named C7 and C8. Both of the C7 and C8 centres are disposed of in (*R, R*) chiral configurations. The crystal data and structure refinement for compound **11aa** are shown in Table S5.

Table S5 Crystal data and structure refinement for 11aa (AD959_20240828).

Identification code	AD959_20240828
Empirical formula	$C_{25}H_{22}N_2O$
Formula weight	366.44
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	19.9908(8)
b/Å	15.7652(5)
c/Å	5.8187(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1833.82(11)
Z	4
ρ_{calc}g/cm^3	1.327
μ/mm^{-1}	0.081
F(000)	776.0
Crystal size/mm^3	0.4 × 0.2 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.29 to 56.098
Index ranges	-25 ≤ h ≤ 25, -20 ≤ k ≤ 20, -7 ≤ l ≤ 7
Reflections collected	14236
Independent reflections	4140 [R_{int} = 0.0315, R_{sigma} = 0.0435]
Data/restraints/parameters	4140/0/254

Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0382, wR_2 = 0.0828
Final R indexes [all data]	R_1 = 0.0452, wR_2 = 0.0860
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.22
Flack parameter	-0.9(7)
CCDC	2380259

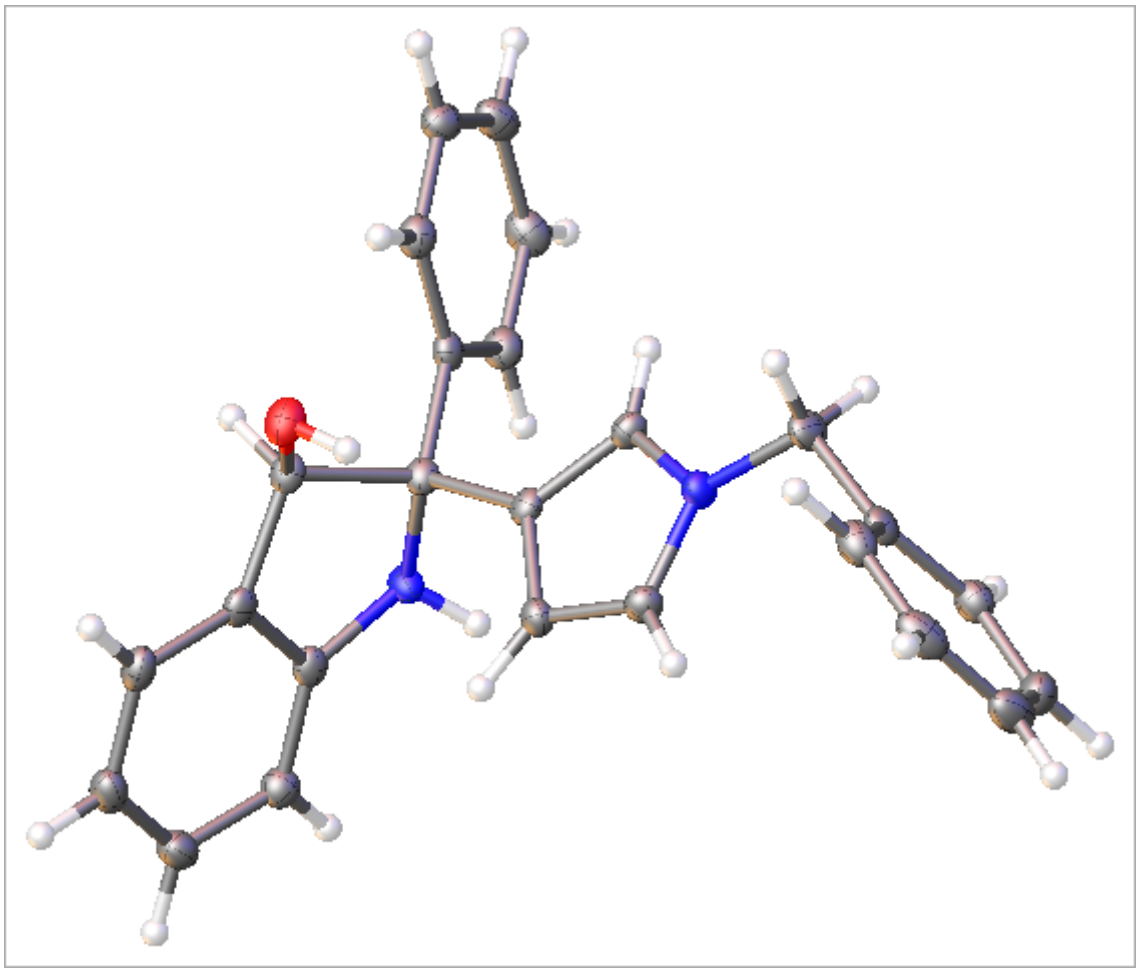
Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H) groups
 At 1.5 times of:
  All O(H) groups
2.a Riding coordinates:
 N1(H1A)
2.b Ternary CH refined with riding coordinates:
 C7(H7)
2.c Secondary CH2 refined with riding coordinates:
 C19(H19A,H19B)
2.d Aromatic/amide H refined with riding coordinates:
 C2(H2), C3(H3), C4(H4), C5(H5), C10(H10), C11(H11), C12(H12), C13(H13),
 C14(H14), C15(H15), C17(H17), C18(H18), C21(H21), C22(H22), C23(H23), C24(H24),
  C25(H25)
2.e Idealised tetrahedral OH refined as rotating group:
 O1(H1)
```

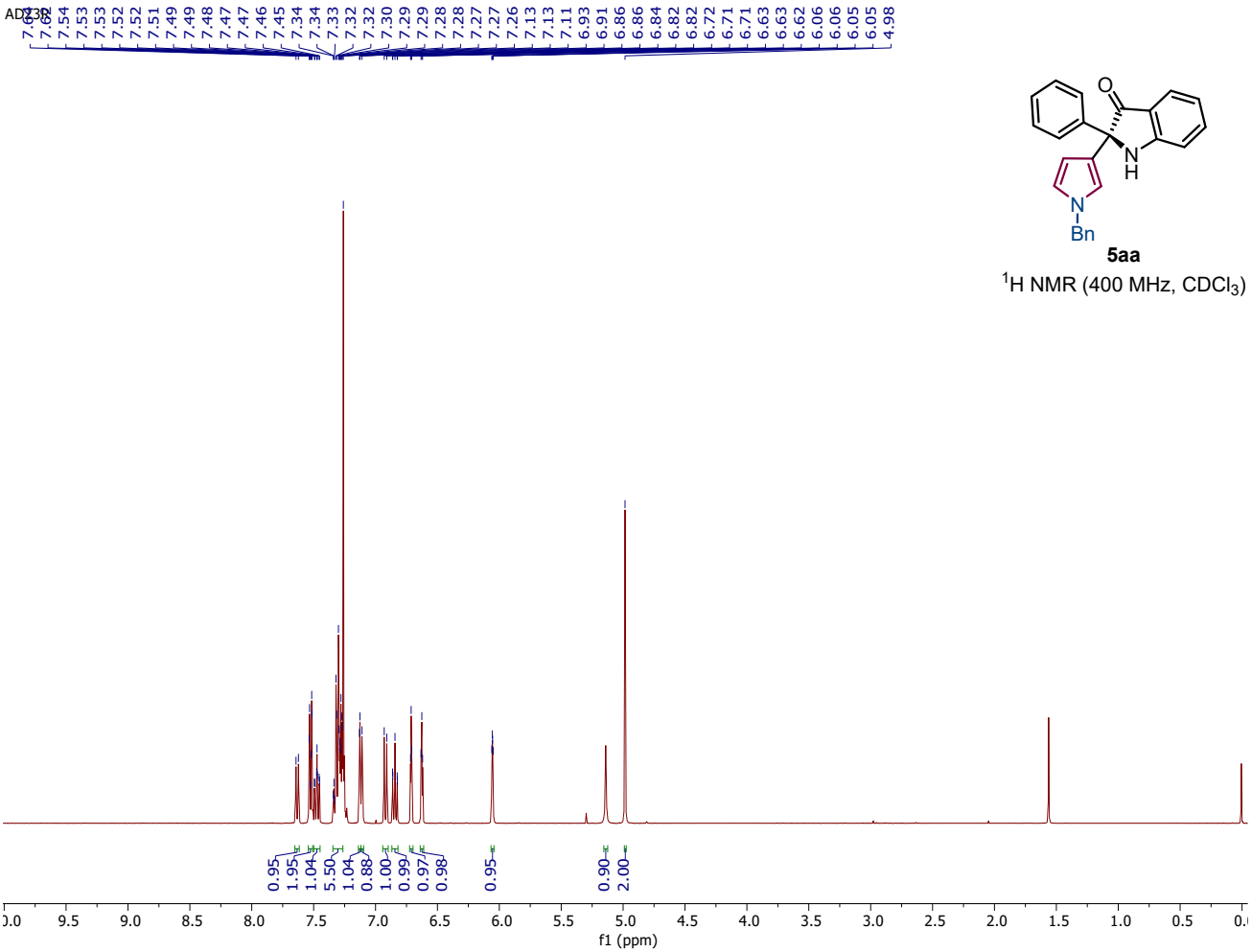
This report has been created with Olex2, compiled on 2024.02.16 svn.r378c4104 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.



References:

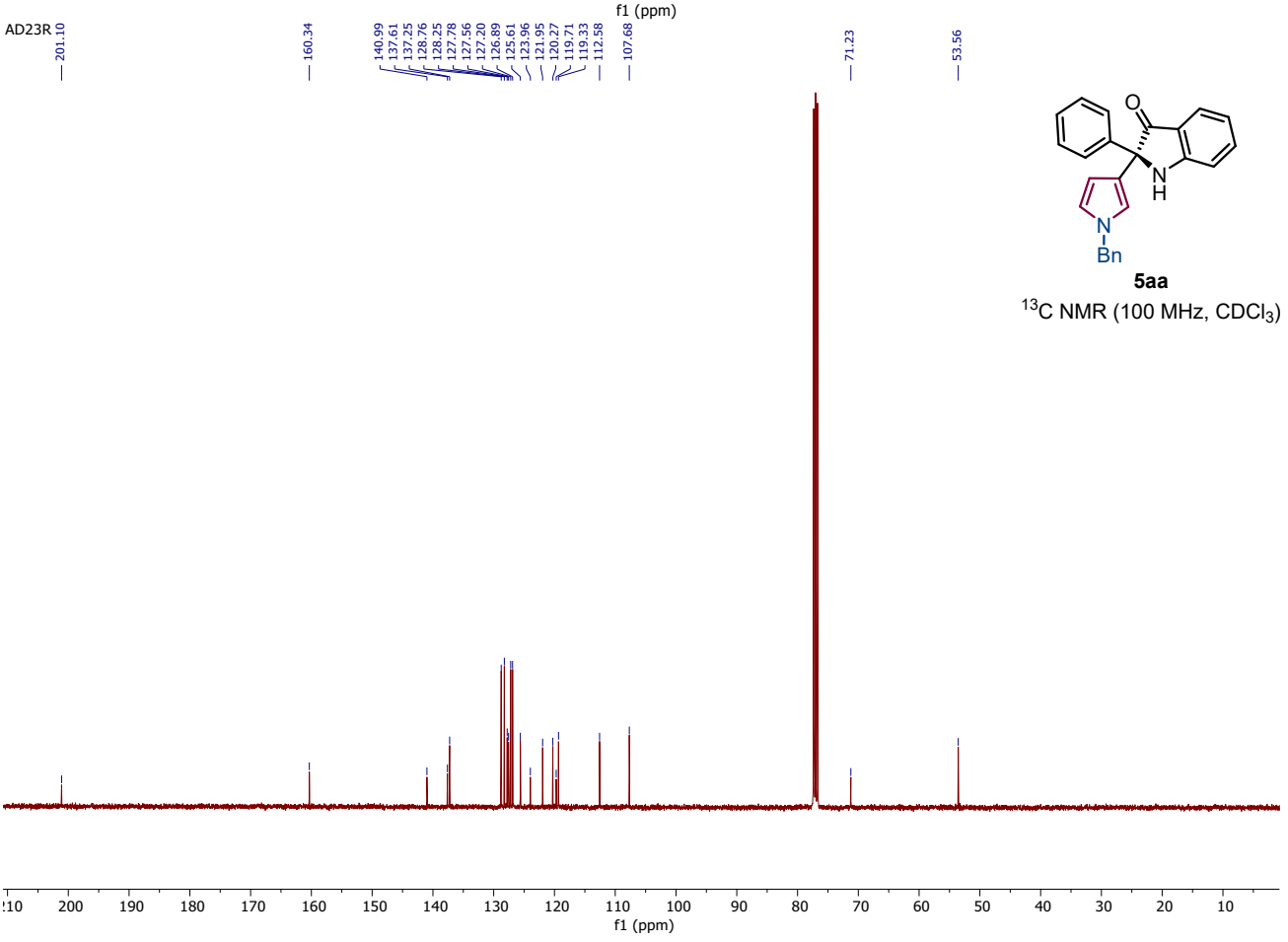
1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

9.0 Single crystal X-ray Diffraction Experiment and Analysis



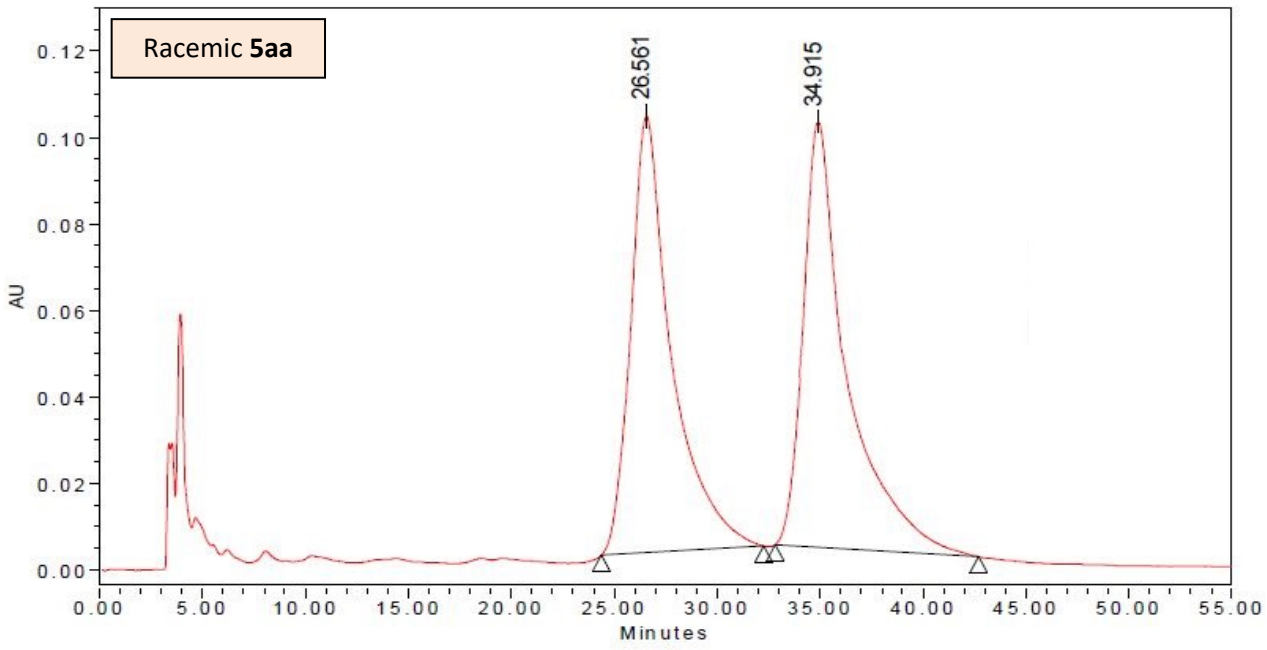
5aa

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



5aa

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



Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

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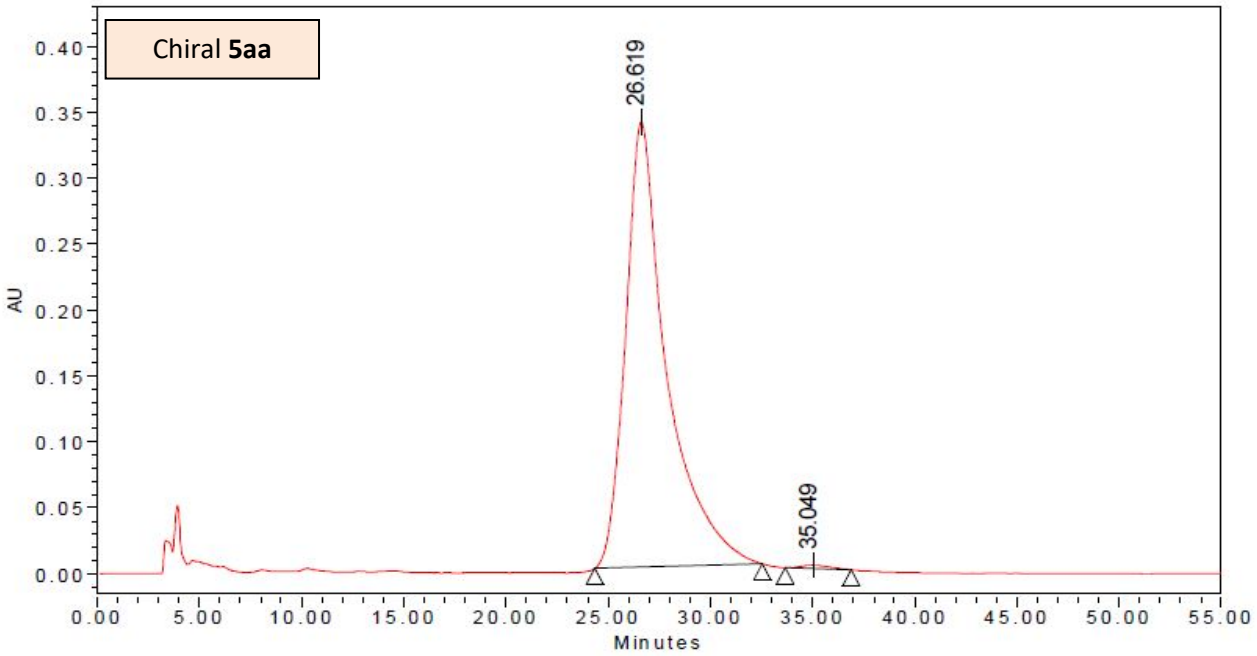
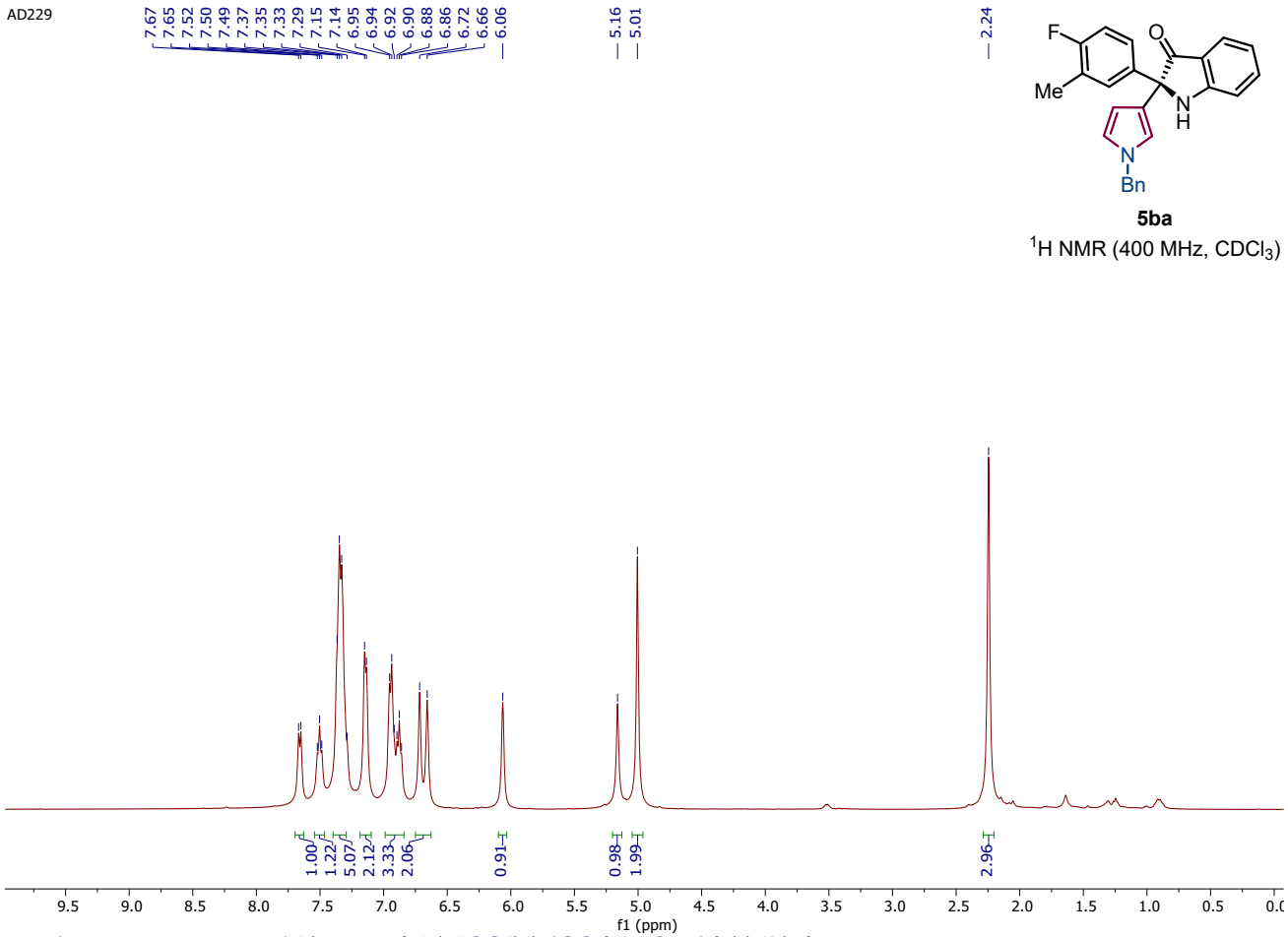


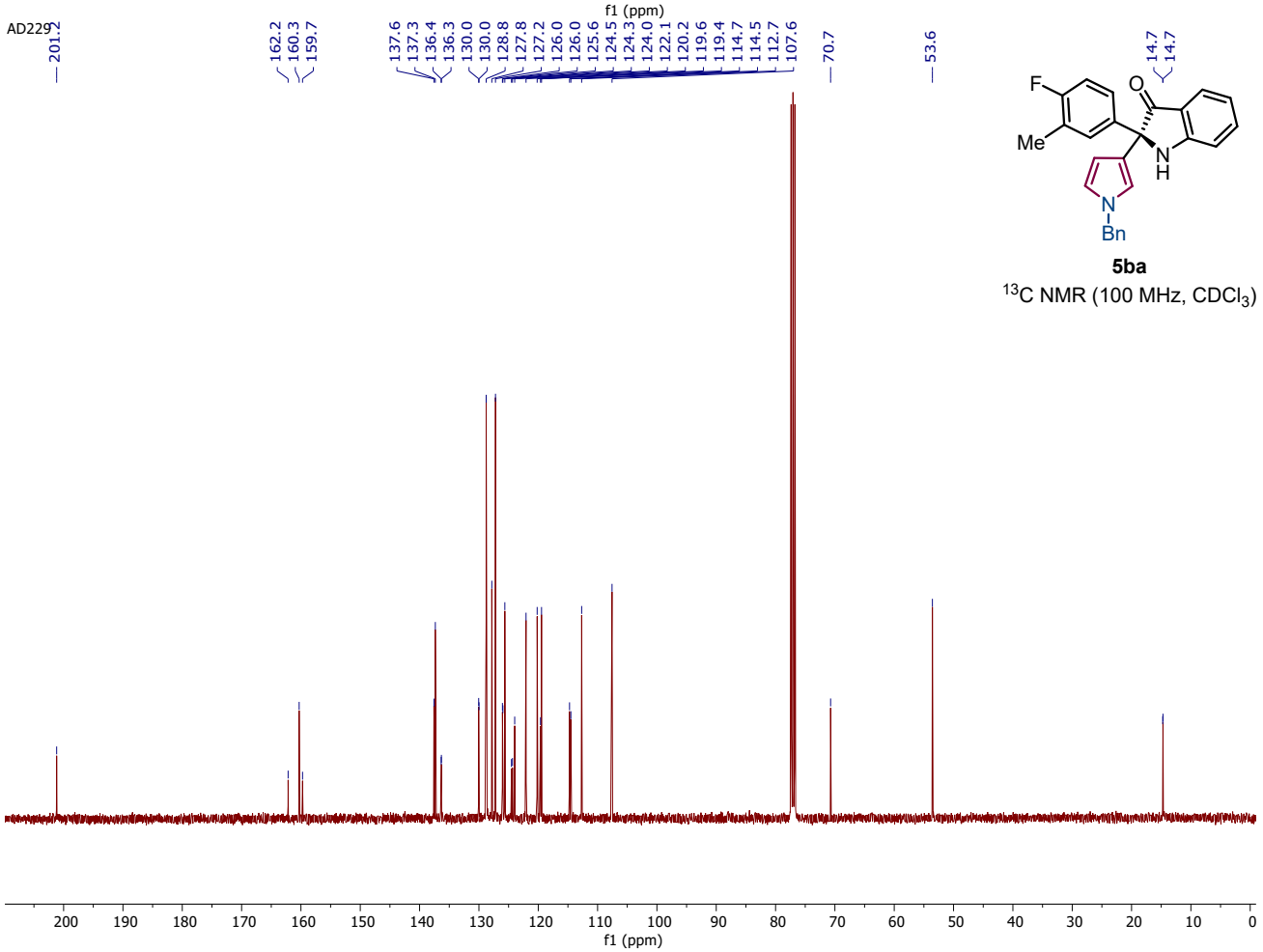
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	26.619	47333720	99.45	337573
2	2998 PDA 254.0 nm (2998 (200-400)nm)	35.049	261933	0.55	2680



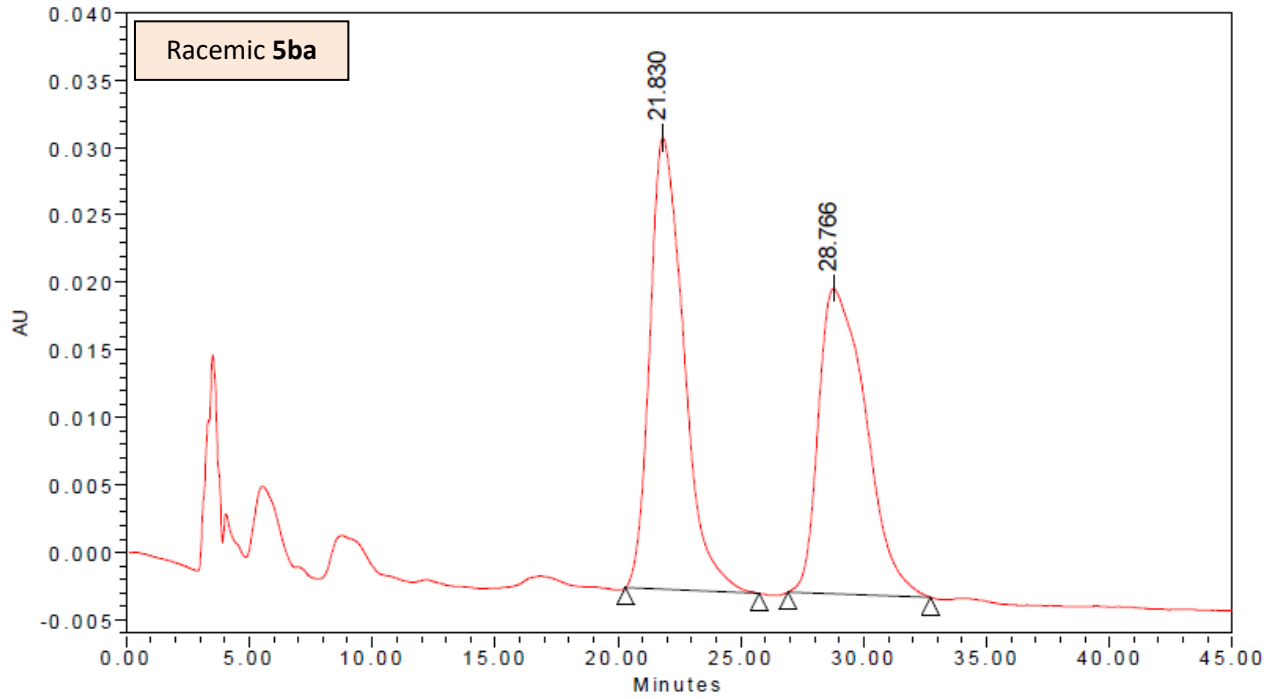
5ba

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



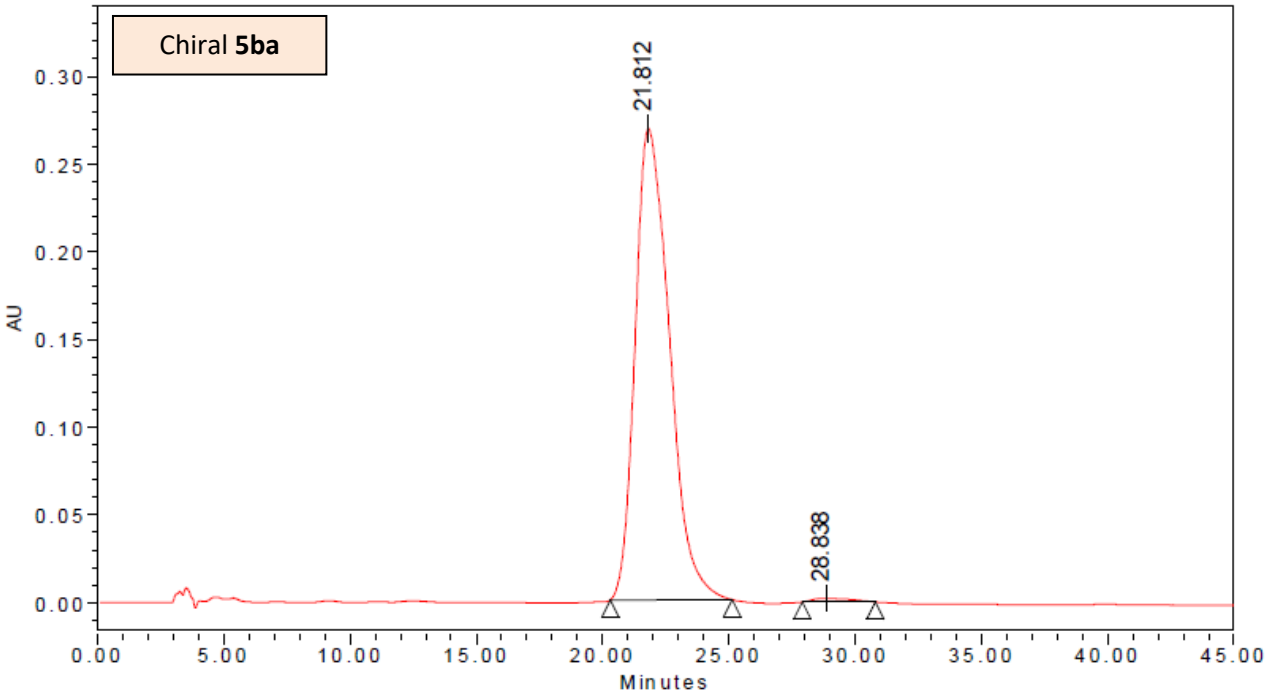
5ba

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



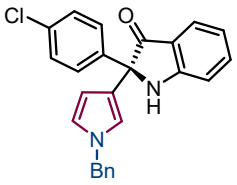
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	21.830	3213728	51.60	33422
2	2998 PDA 254.0 nm (2998 (200-400)nm)	28.766	3014109	48.40	22617



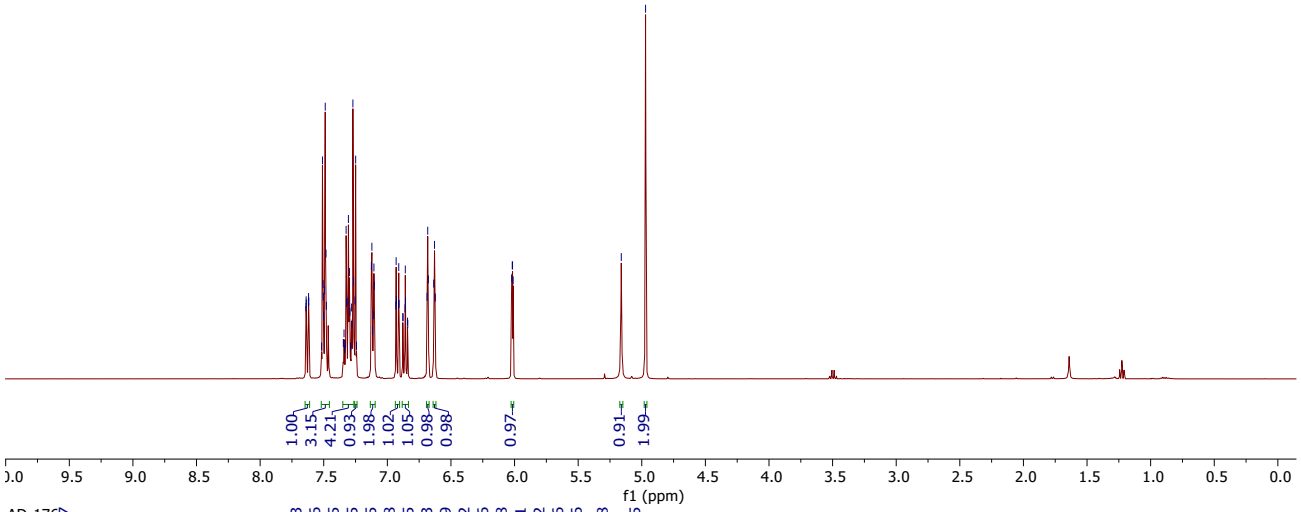
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

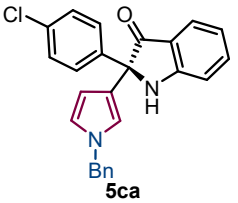
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	21.812	25372557	99.12	268528
2	2998 PDA 254.0 nm (2998 (200-400)nm)	28.838	224482	0.88	2147



5ca

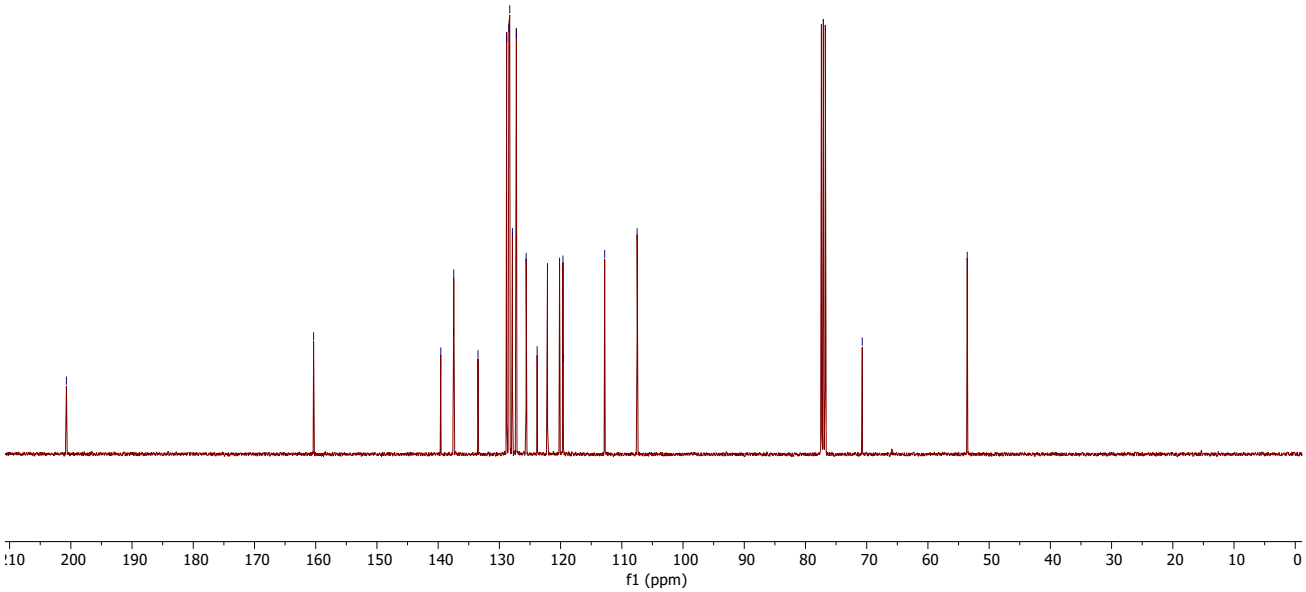
^{1}H NMR (400 MHz, $CDCl_3$)

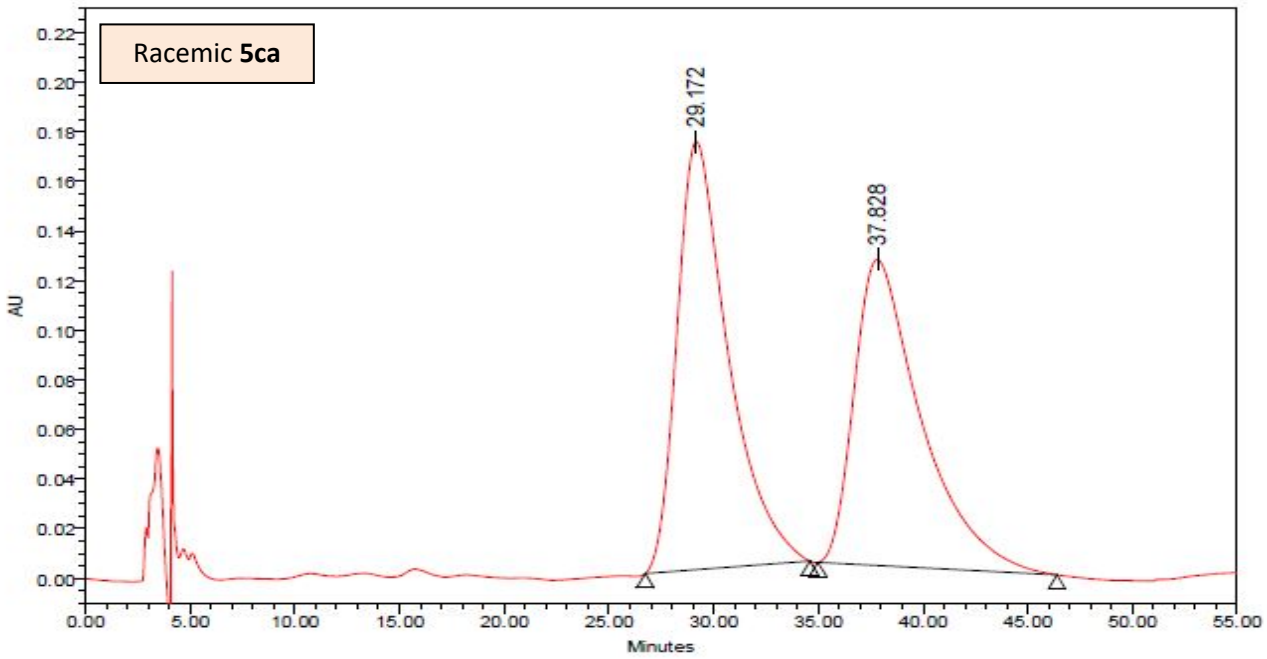




5ca

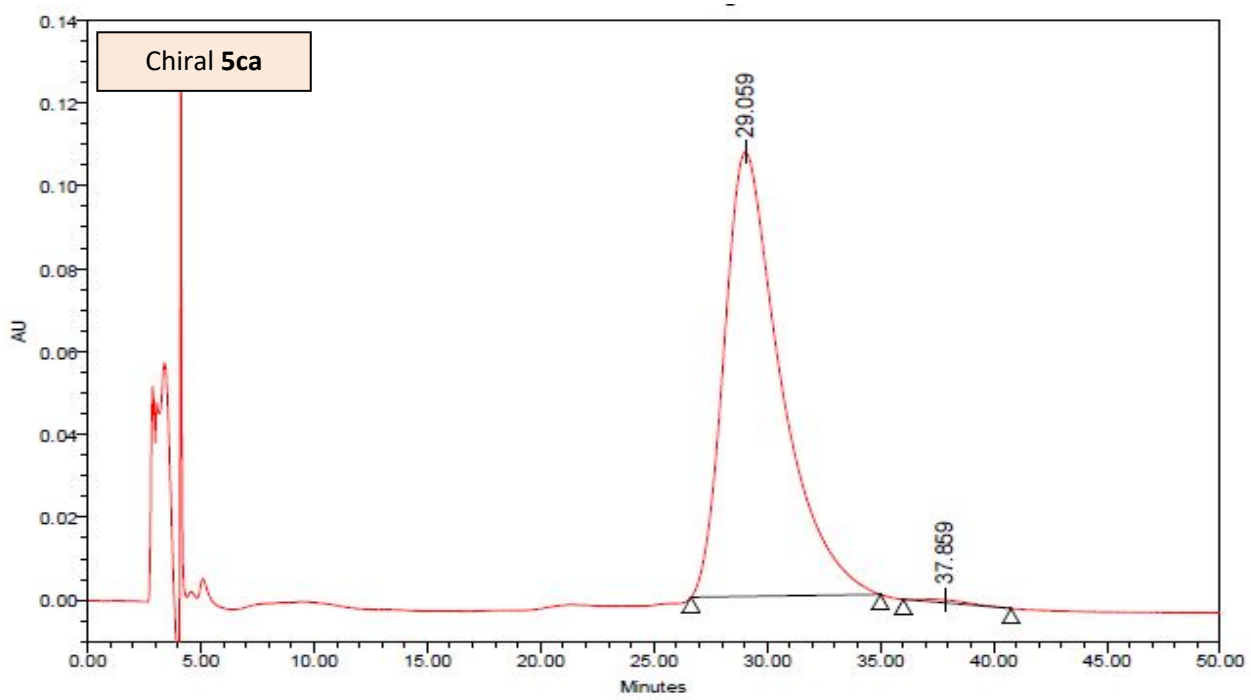
^{13}C NMR (100 MHz, $CDCl_3$)





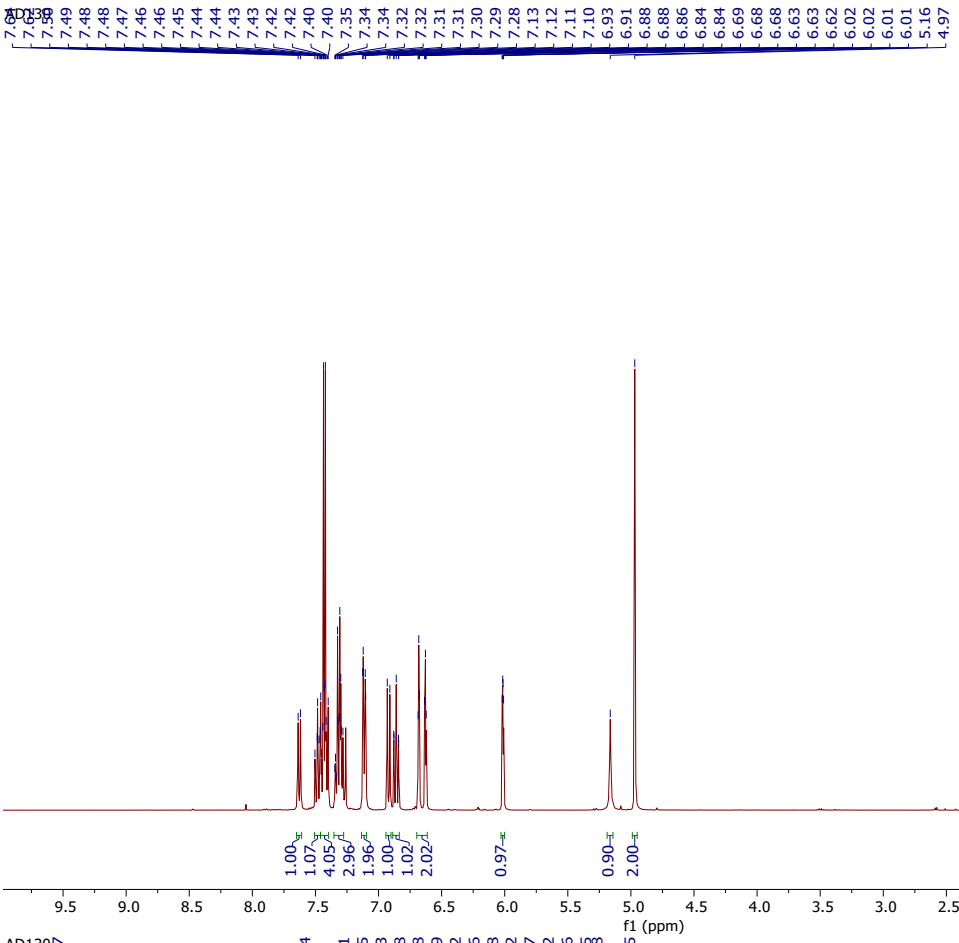
Processed Channel: PDA 230.0 nm

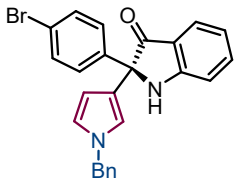
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 230.0 nm	29.172	29486971	51.88	172553
2	PDA 230.0 nm	37.828	27347863	48.12	123293



Processed Channel: PDA 230.0 nm

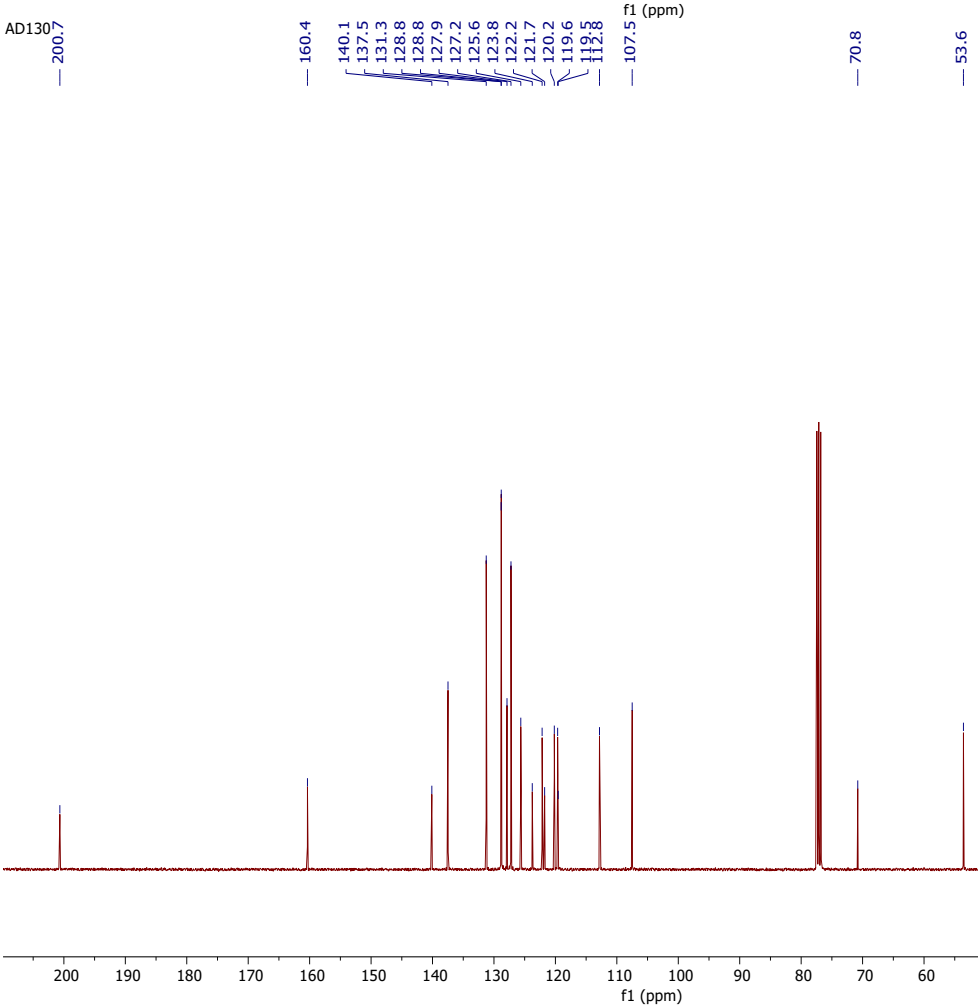
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 230.0 nm	29.059	18635436	99.47	107232
2	PDA 230.0 nm	37.859	99858	0.53	849

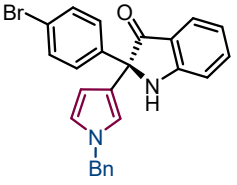




5da

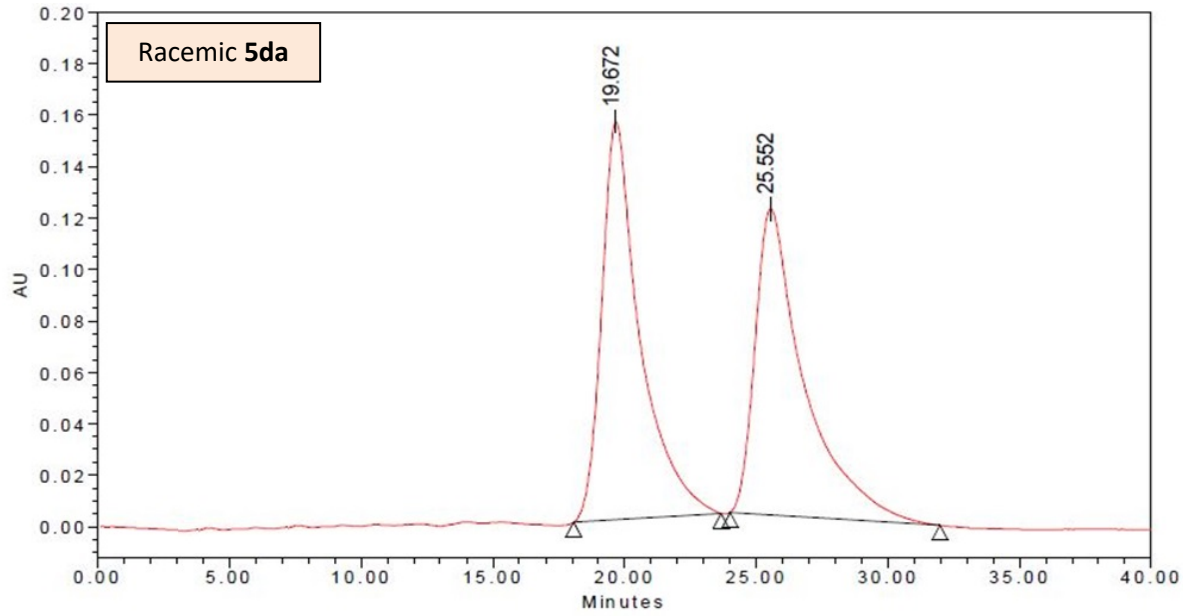
^{1}H NMR (400 MHz, $CDCl_3$)





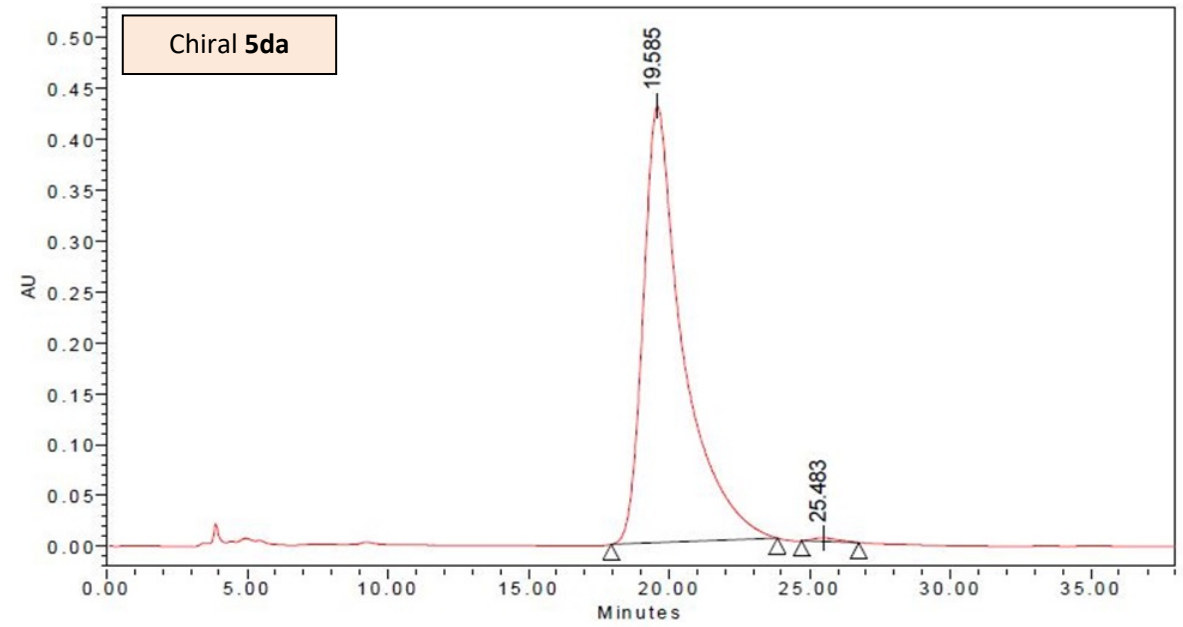
5da

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



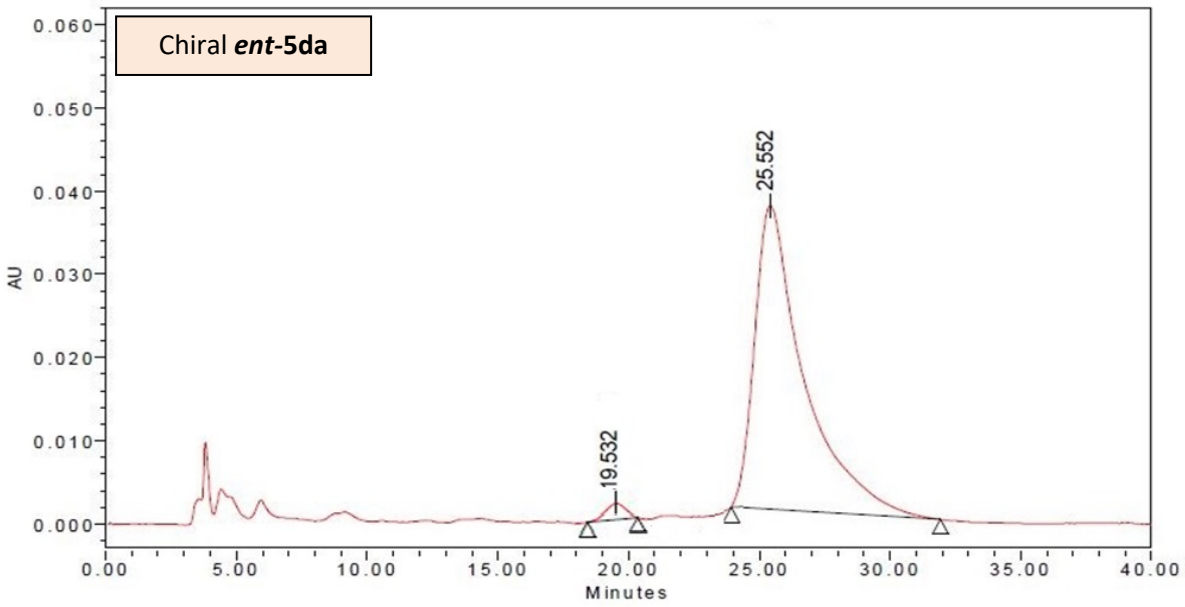
Processed Channel: 2998 PDA 280.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 280.0 nm (2998 (200-400)nm)	19.672	16379831	51.18	154999
2	2998 PDA 280.0 nm (2998 (200-400)nm)	25.552	15419144	48.82	119052



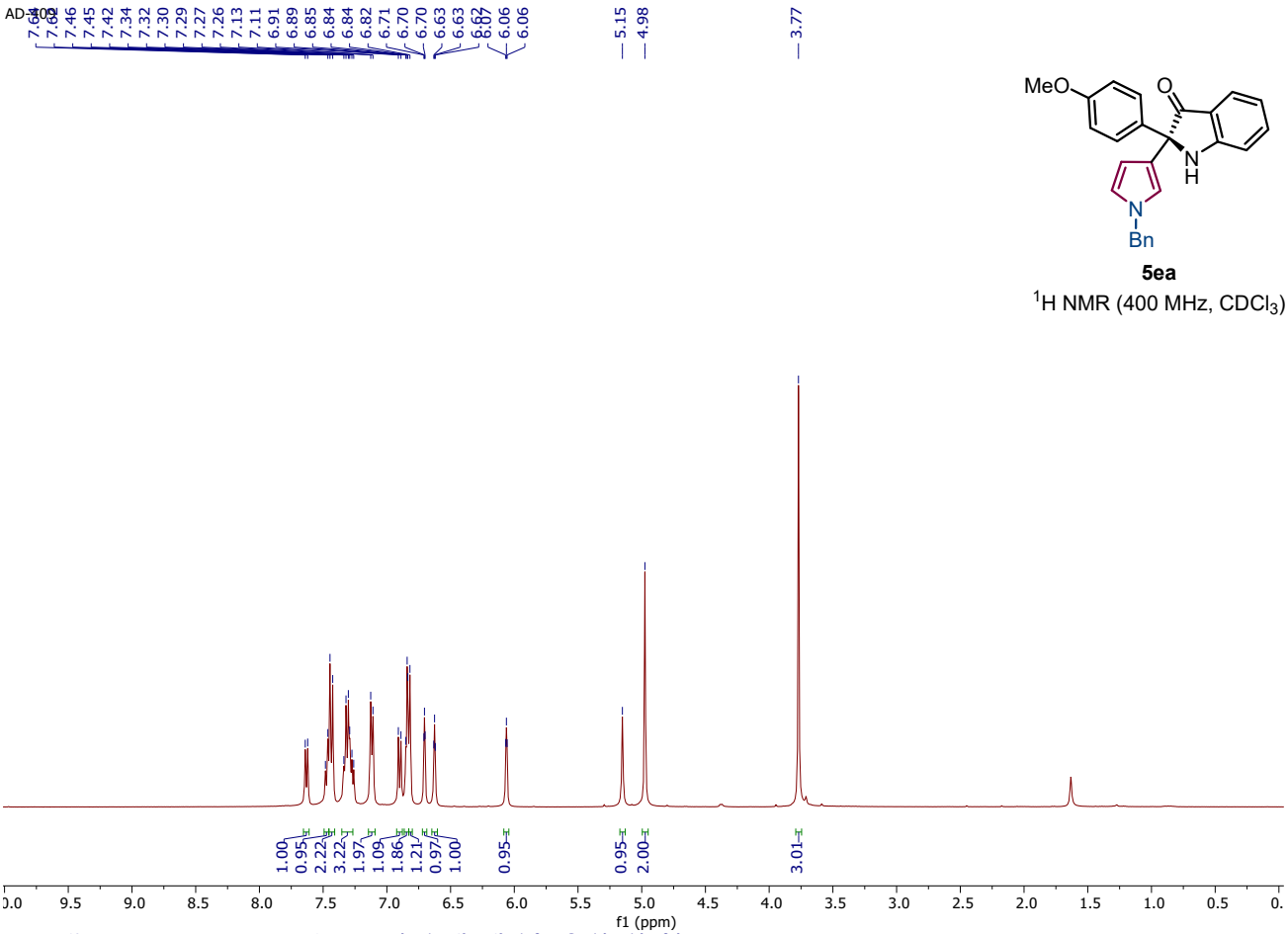
Processed Channel: 2998 PDA 280.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 280.0 nm (2998 (200-400)nm)	19.585	42296145	99.67	429280
2	2998 PDA 280.0 nm (2998 (200-400)nm)	25.483	223399	0.33	3393



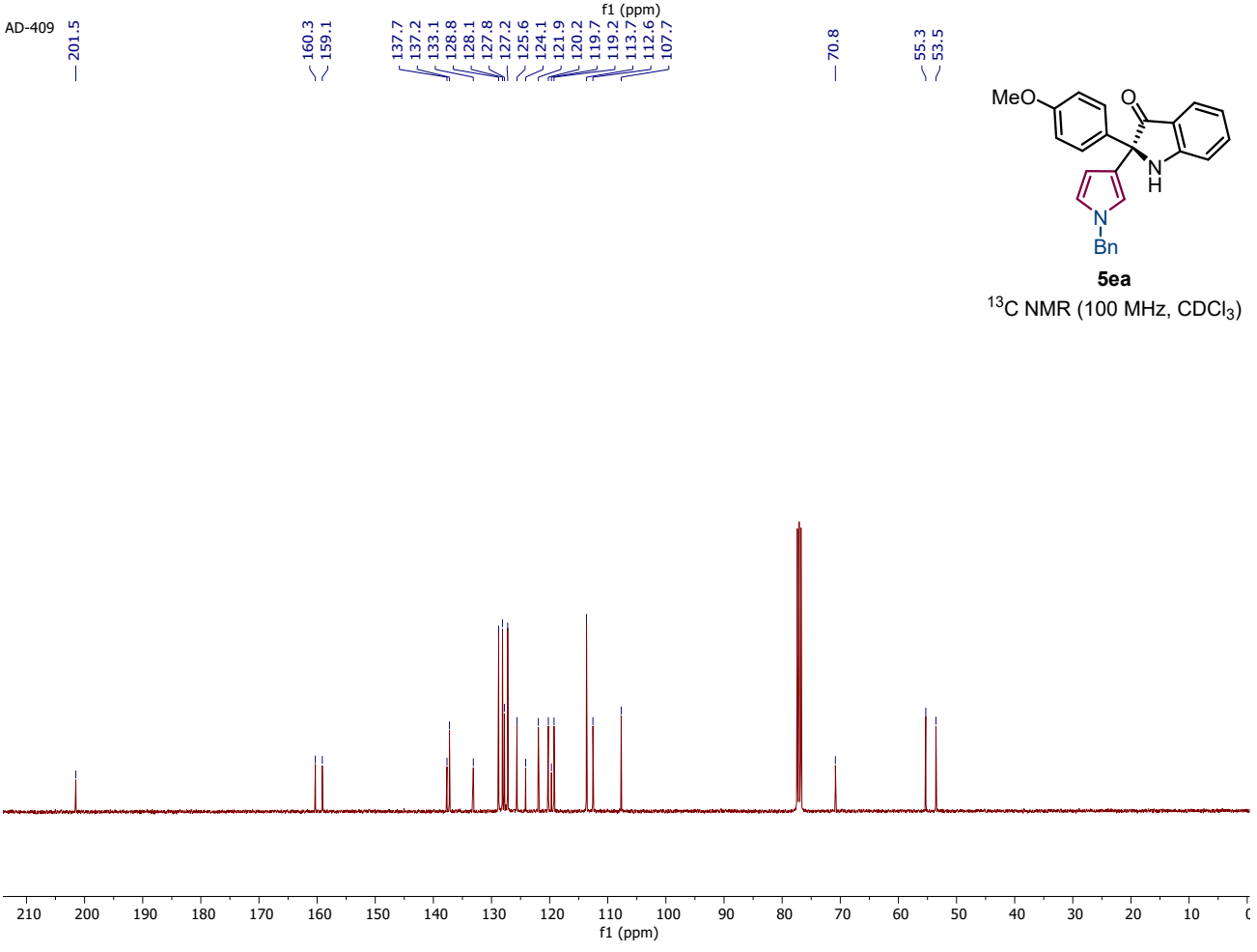
Processed Channel: 2998 PDA 280.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 280.0 nm (2998 (200-400)nm)	19.532	197110	2.25	1085
2	2998 PDA 280.0 nm (2998 (200-400)nm)	25.552	8543128	97.75	45458



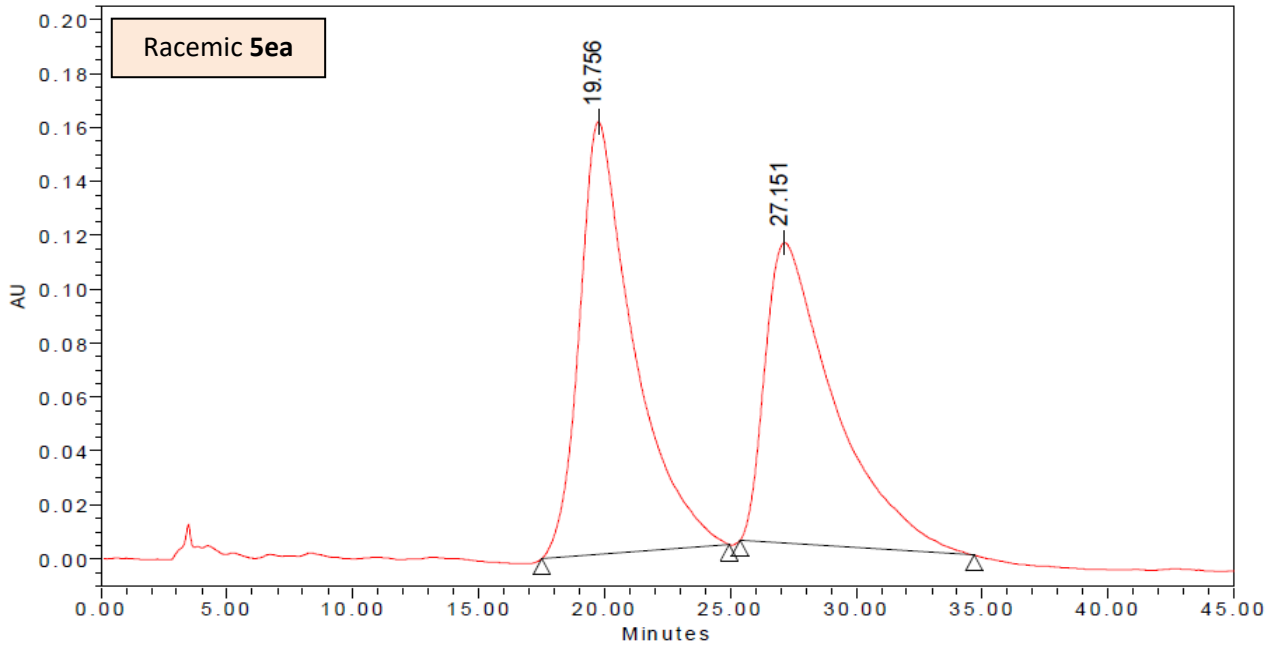
5ea

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



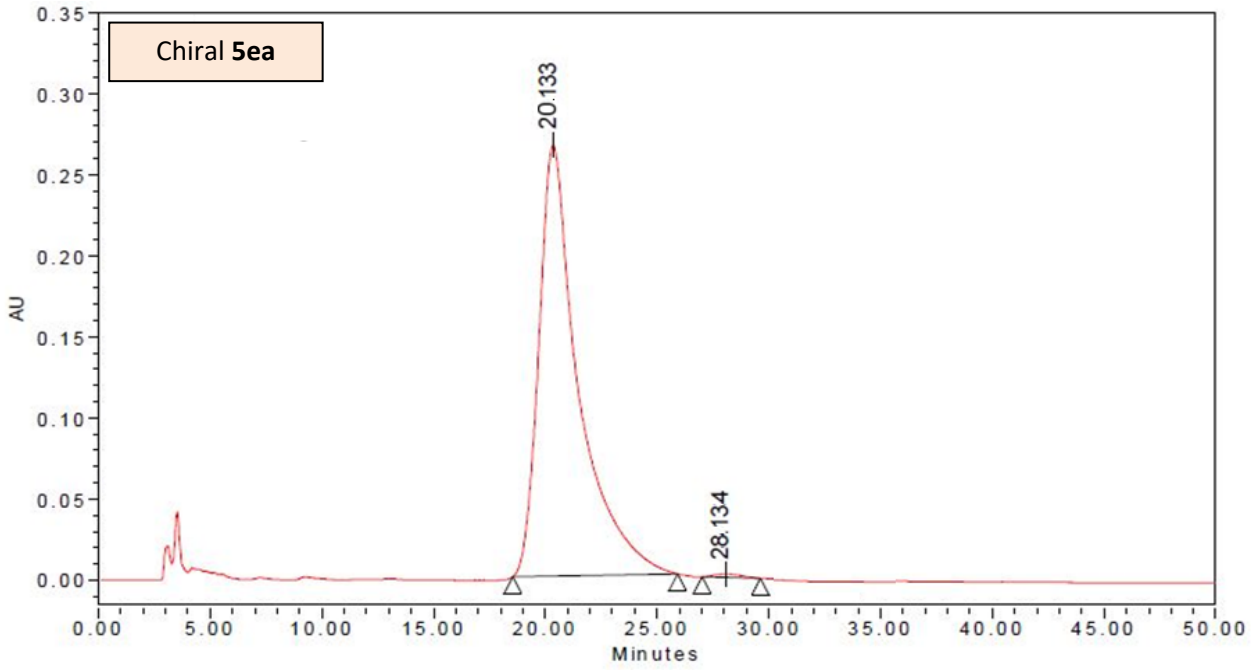
5ea

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



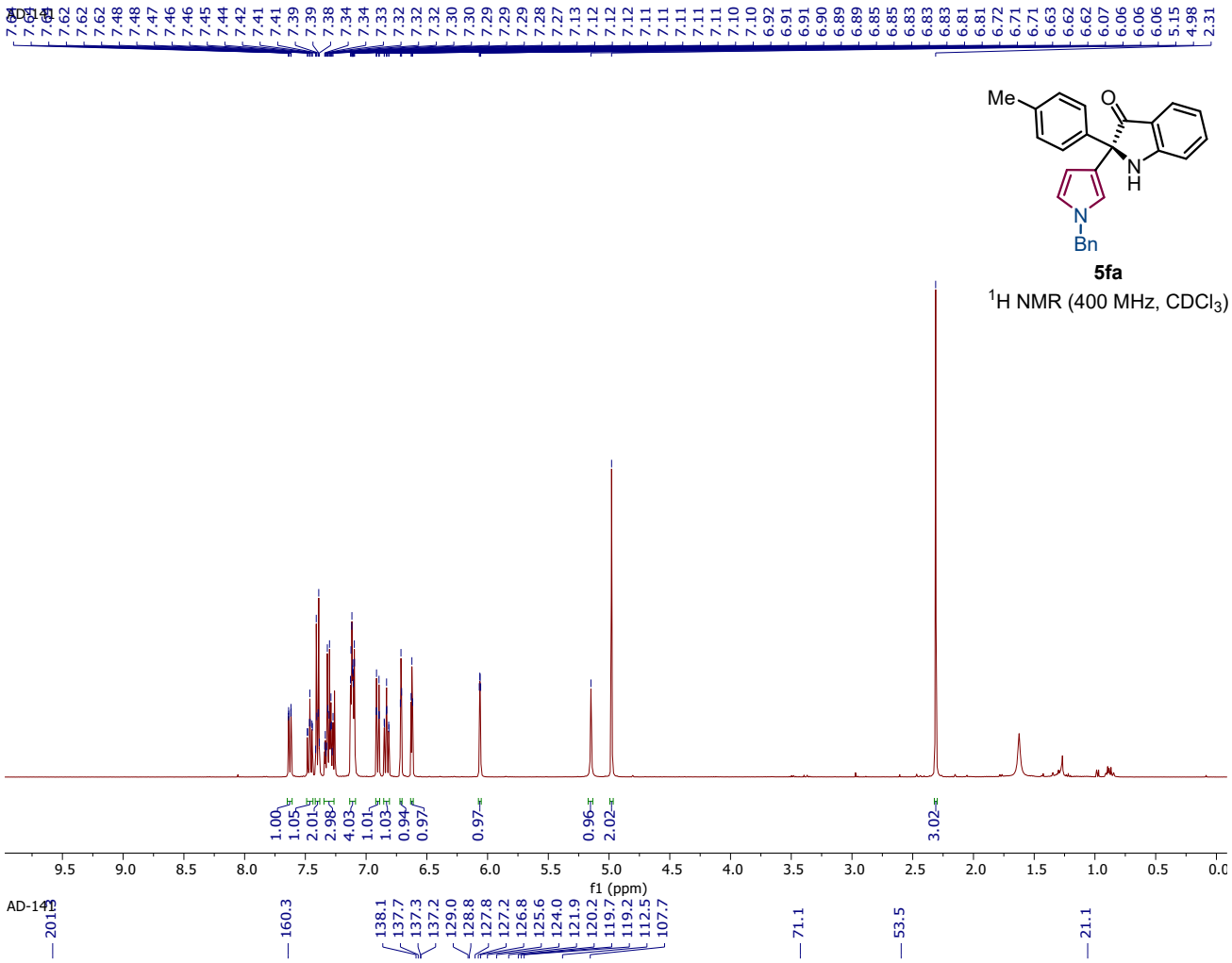
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	19.756	24003309	52.95	160371
2	2998 PDA 254.0 nm (2998 (200-400)nm)	27.151	21330070	47.05	111431



Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	20.133	32745997	99.47	265847
2	2998 PDA 254.0 nm (2998 (200-400)nm)	28.134	173406	0.53	2078

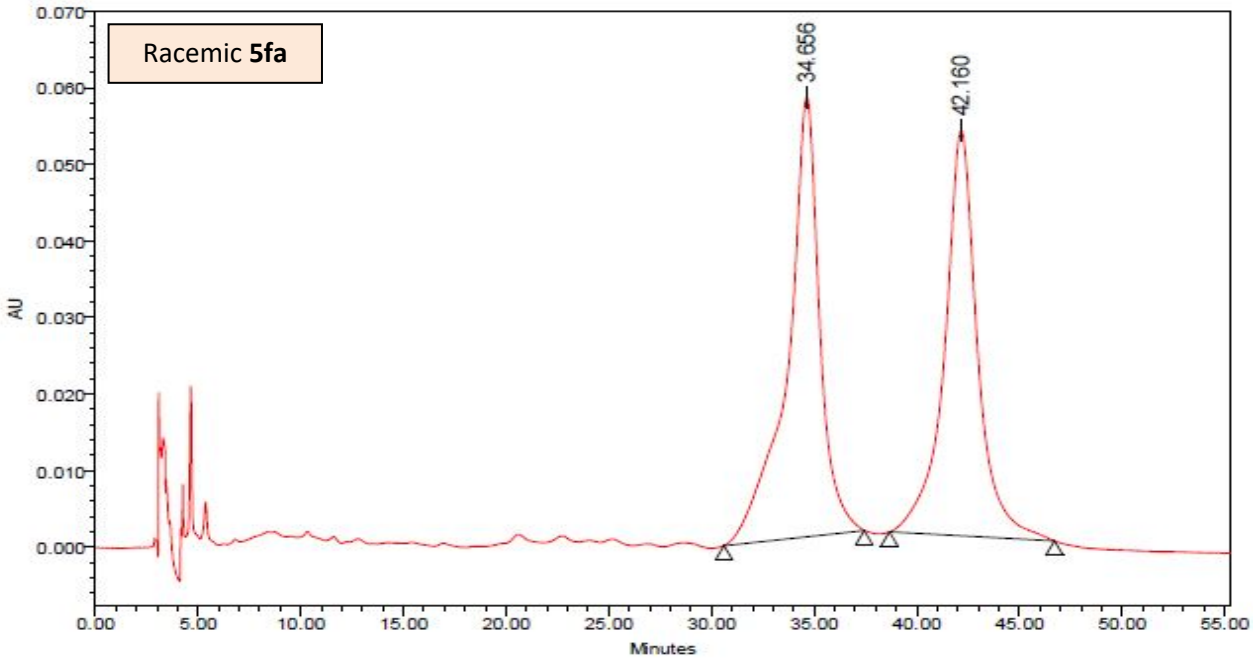


5fa

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

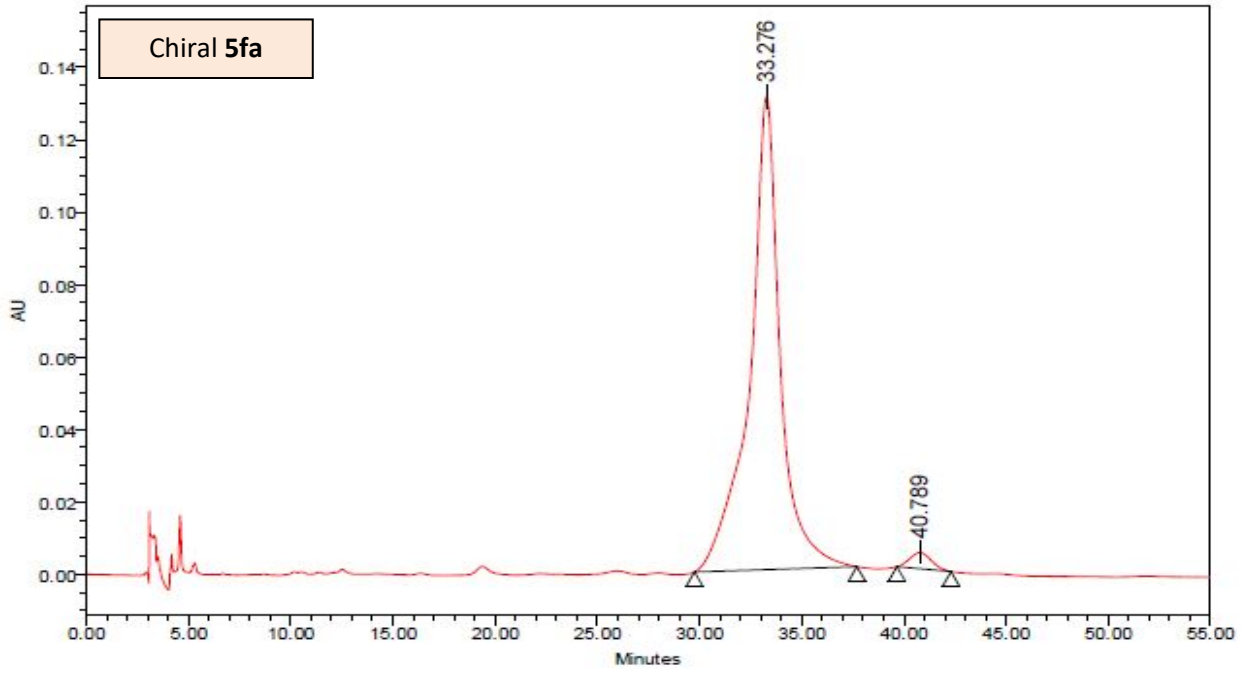
5fa

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



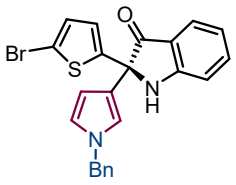
Processed Channel: PDA 254.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	34.656	6211552	51.04	57395
2	PDA 254.0 nm	42.160	5959403	48.96	52894



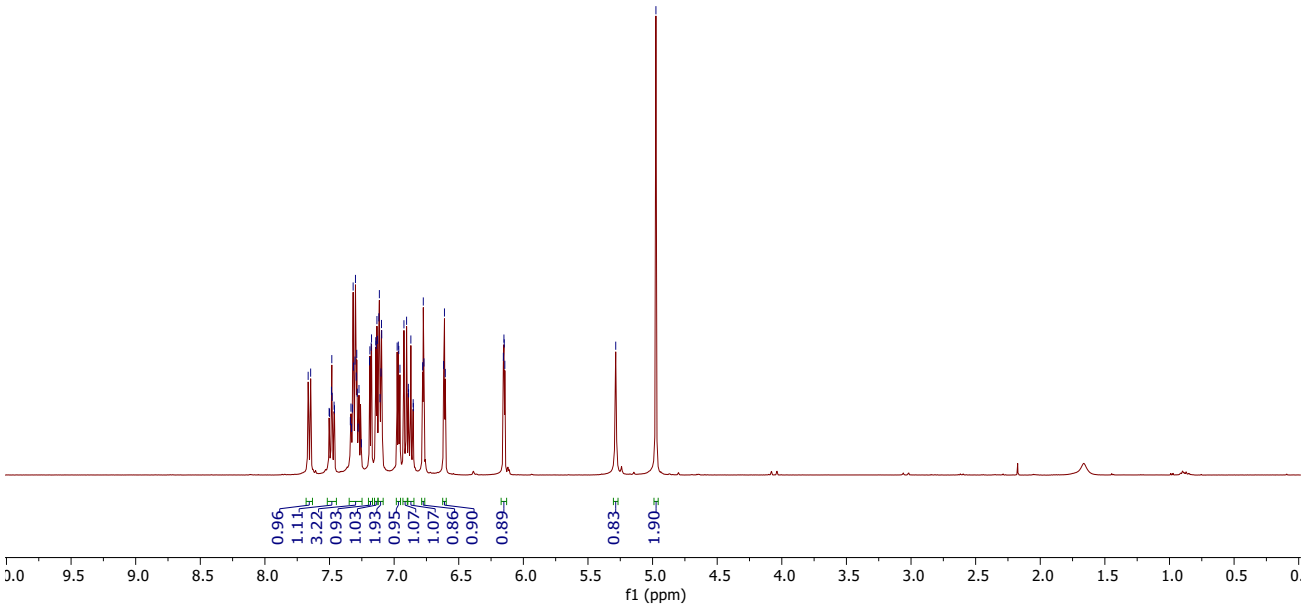
Processed Channel: PDA 254.0 nm

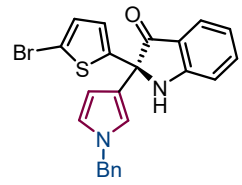
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	33.276	13586723	97.64	130578
2	PDA 254.0 nm	40.789	327905	2.36	4506



5ga

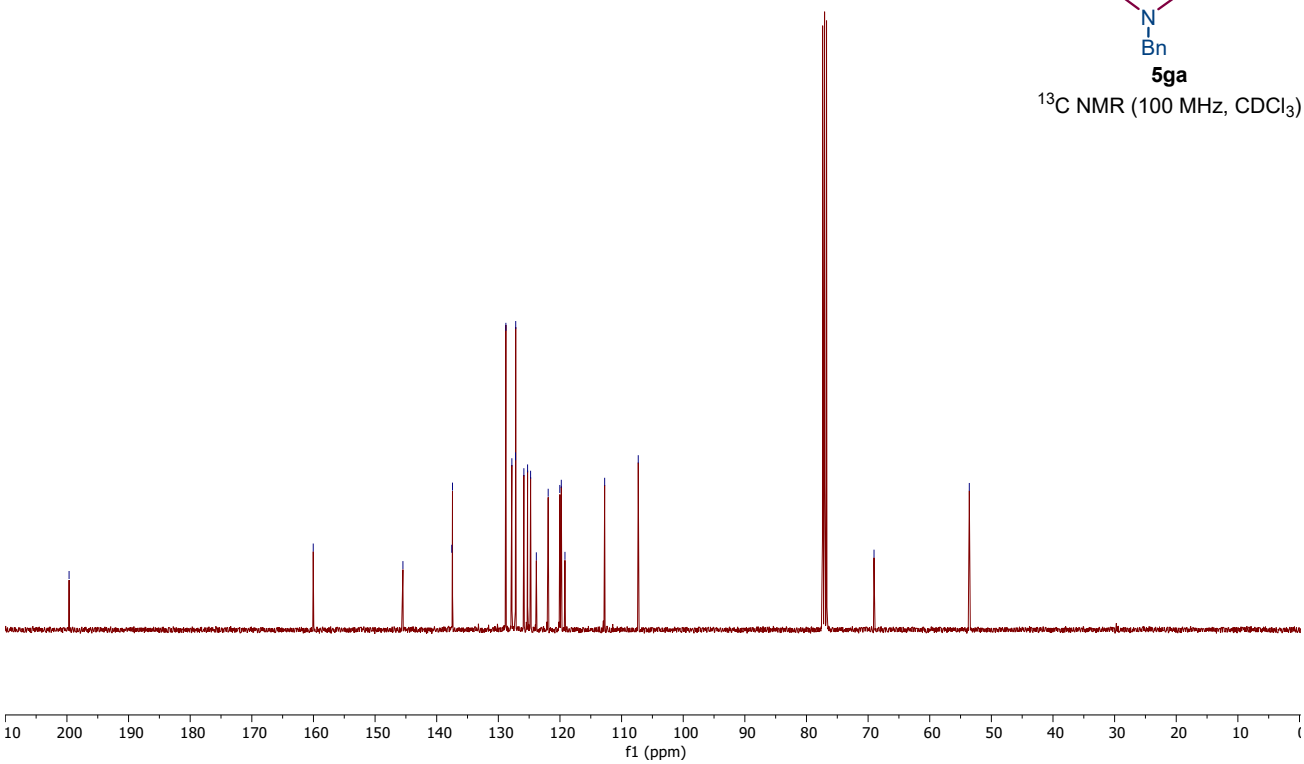
^{1}H NMR (400 MHz, $CDCl_3$)

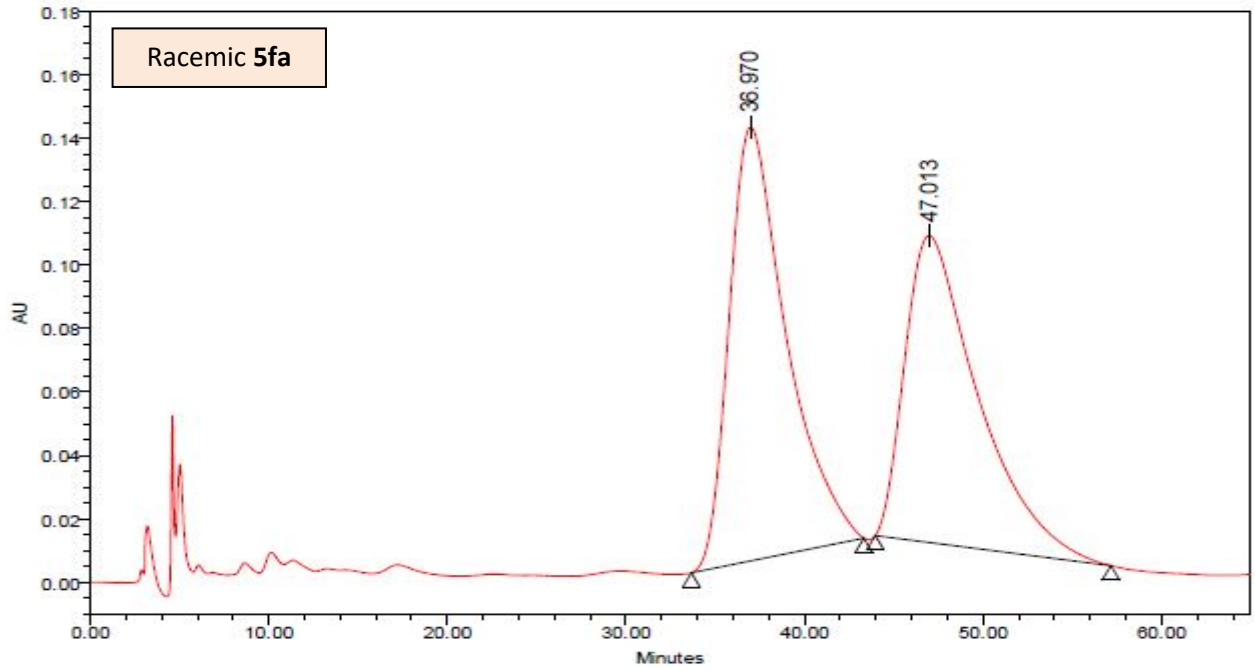




5ga

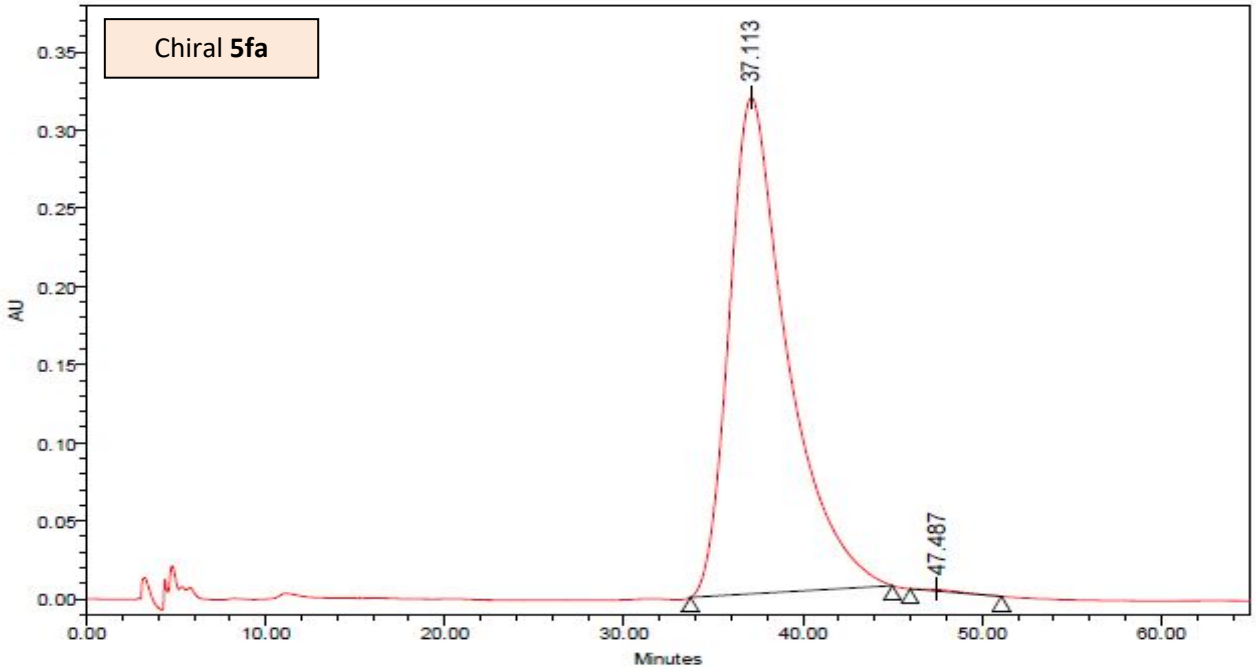
^{13}C NMR (100 MHz, $CDCl_3$)





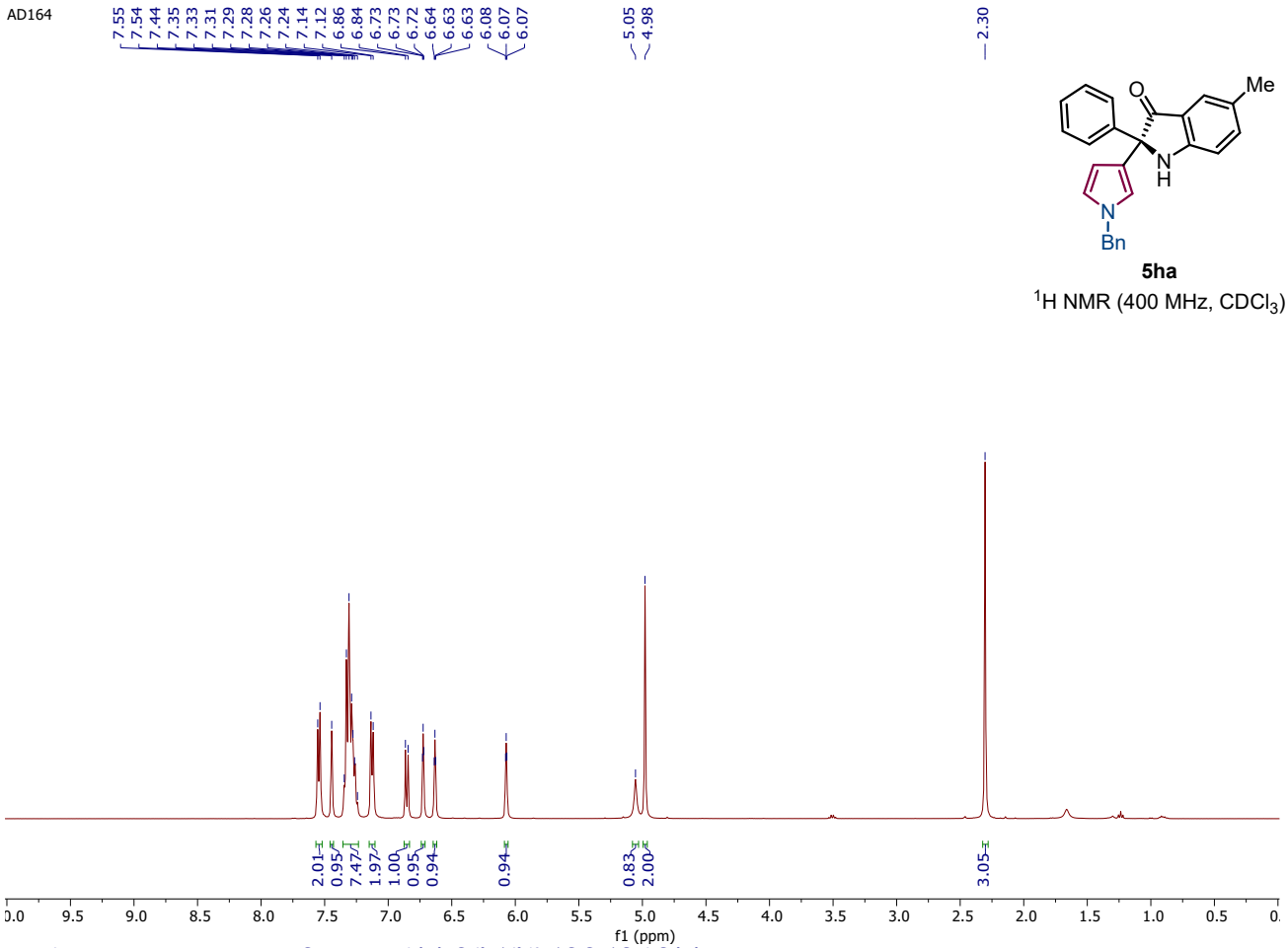
Processed Channel: PDA 254.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	36.970	30451164	52.55	136739
2	PDA 254.0 nm	47.013	27500487	47.45	96704



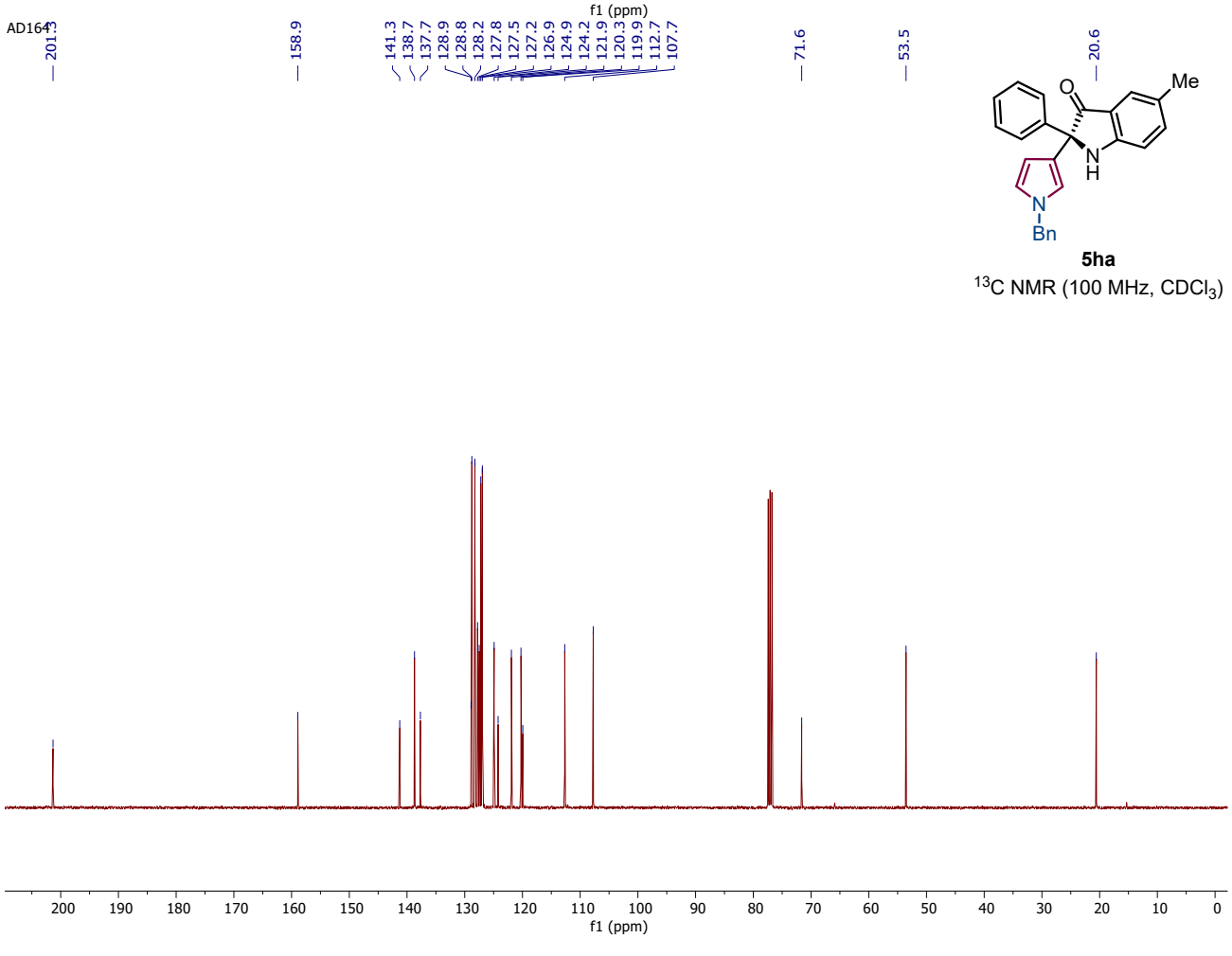
Processed Channel: PDA 254.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	37.113	71771575	99.80	317588
2	PDA 254.0 nm	47.487	141813	0.20	1061



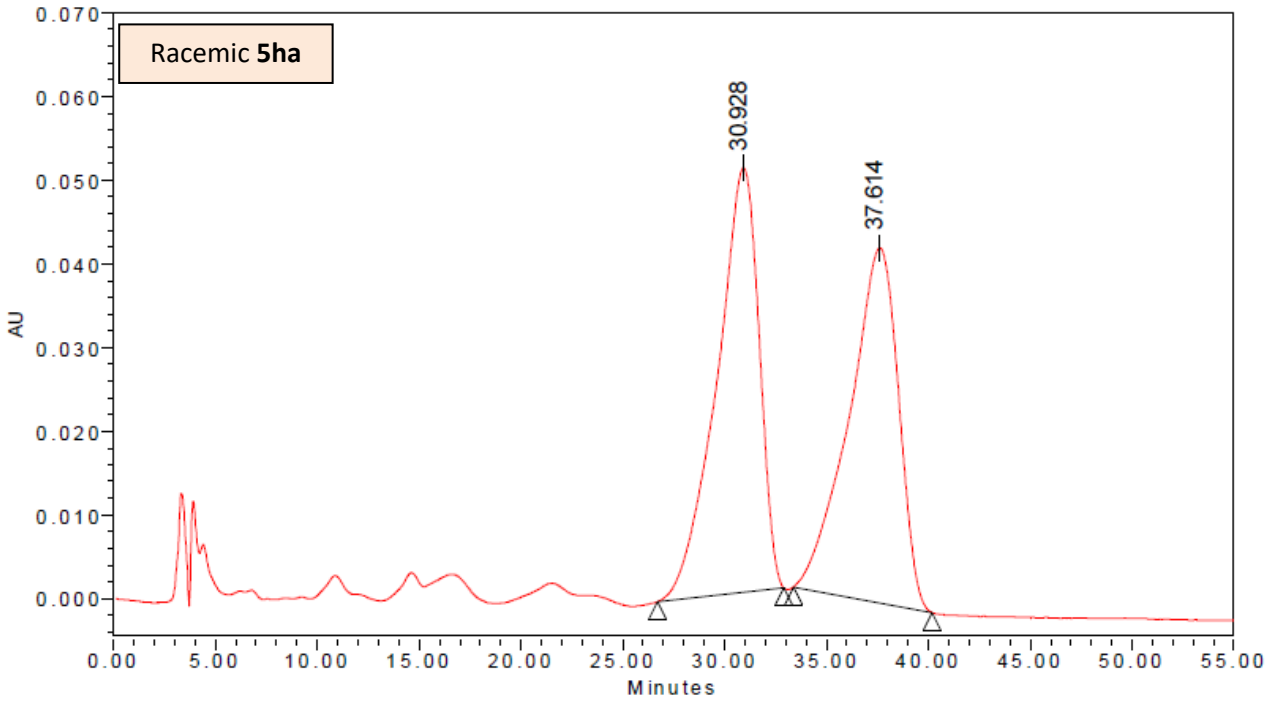
5ha

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



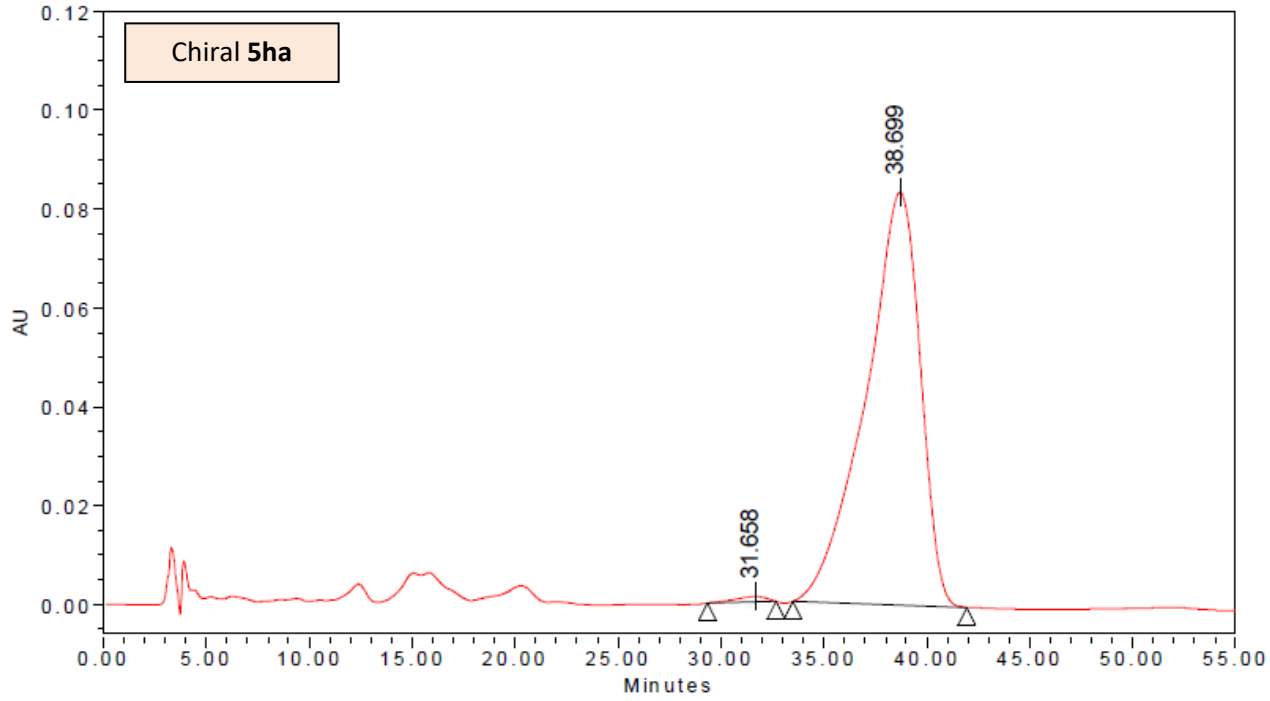
5ha

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



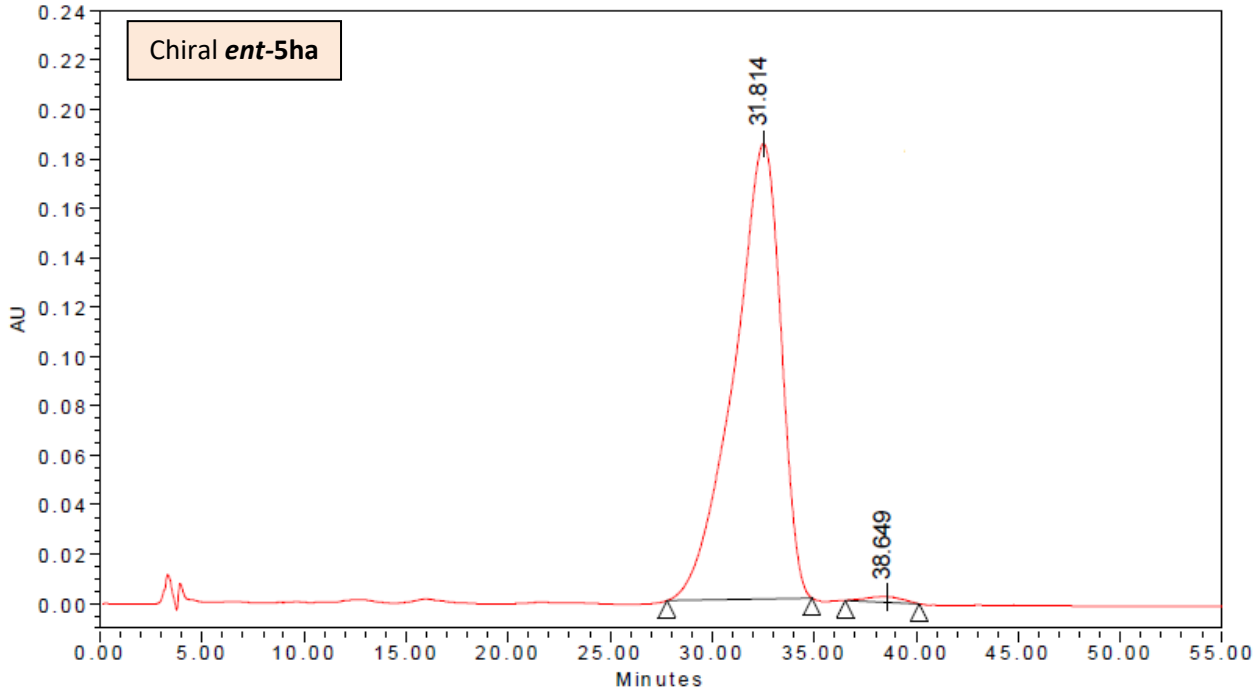
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	30.928	7310330	50.58	50702
2	2998 PDA 254.0 nm (2998 (200-400)nm)	37.614	7143012	49.42	42424



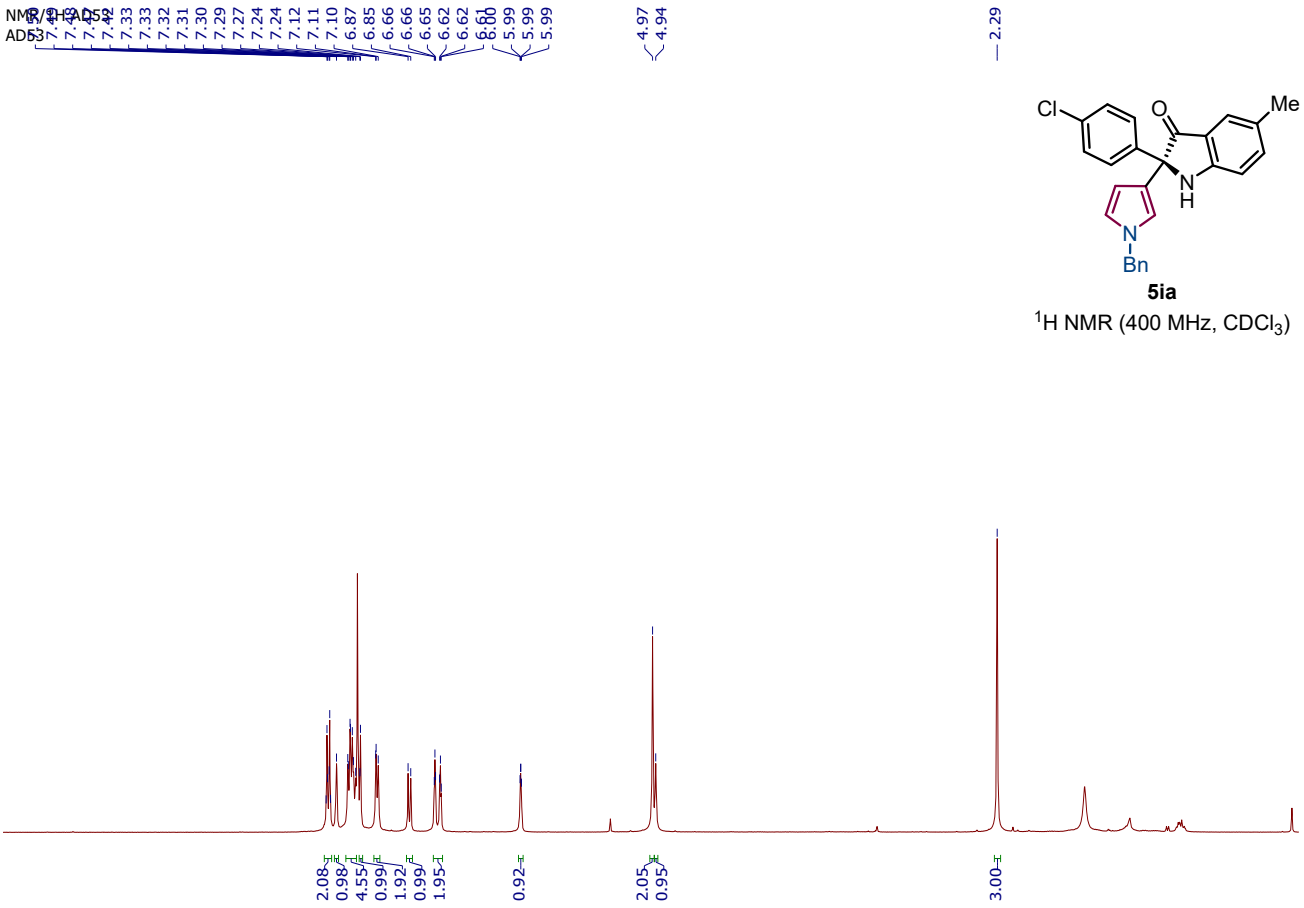
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	31.658	118675	0.77	1129
2	2998 PDA 254.0 nm (2998 (200-400)nm)	38.699	15390803	99.23	83570



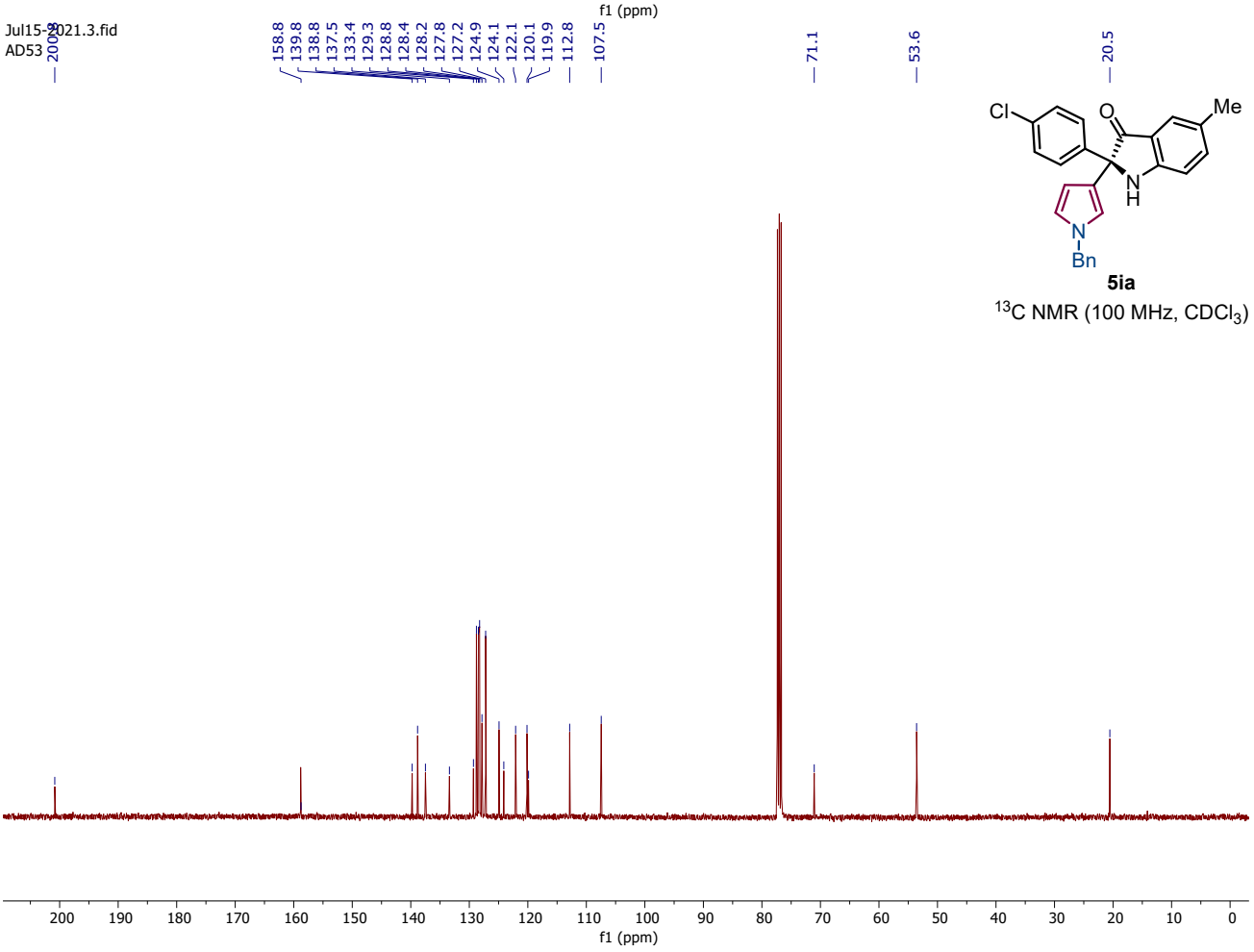
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	31.814	29465995	99.06	184276
2	2998 PDA 254.0 nm (2998 (200-400)nm)	38.649	281045	0.94	2305



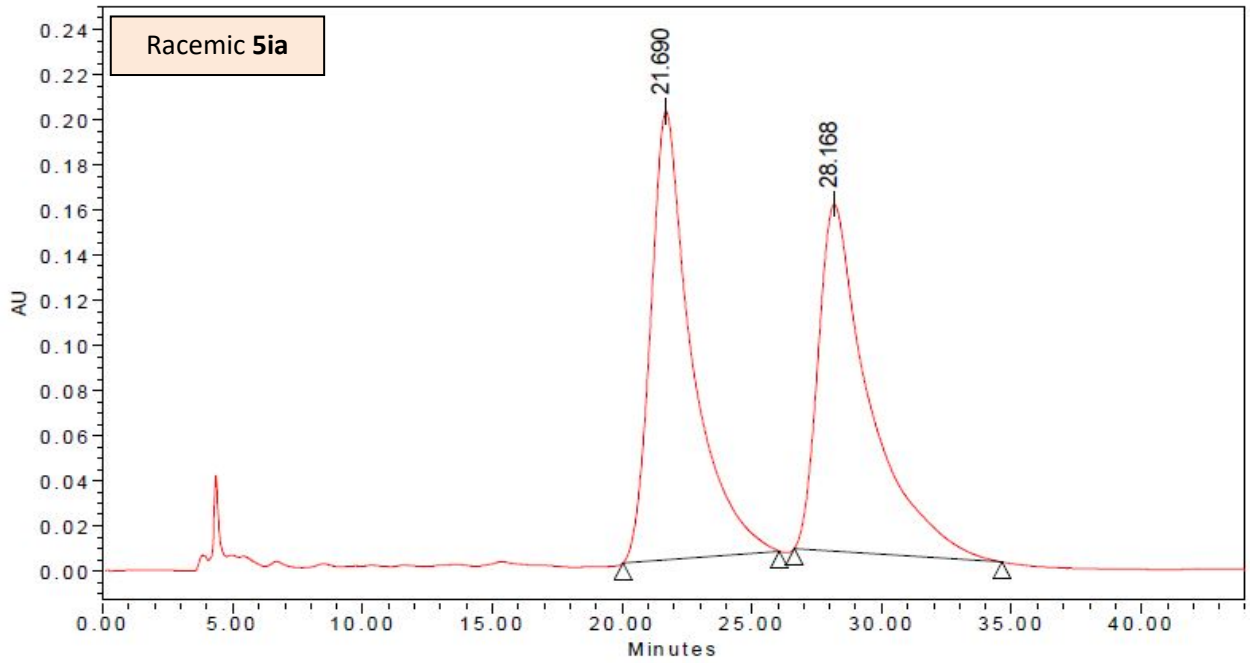
5ia

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



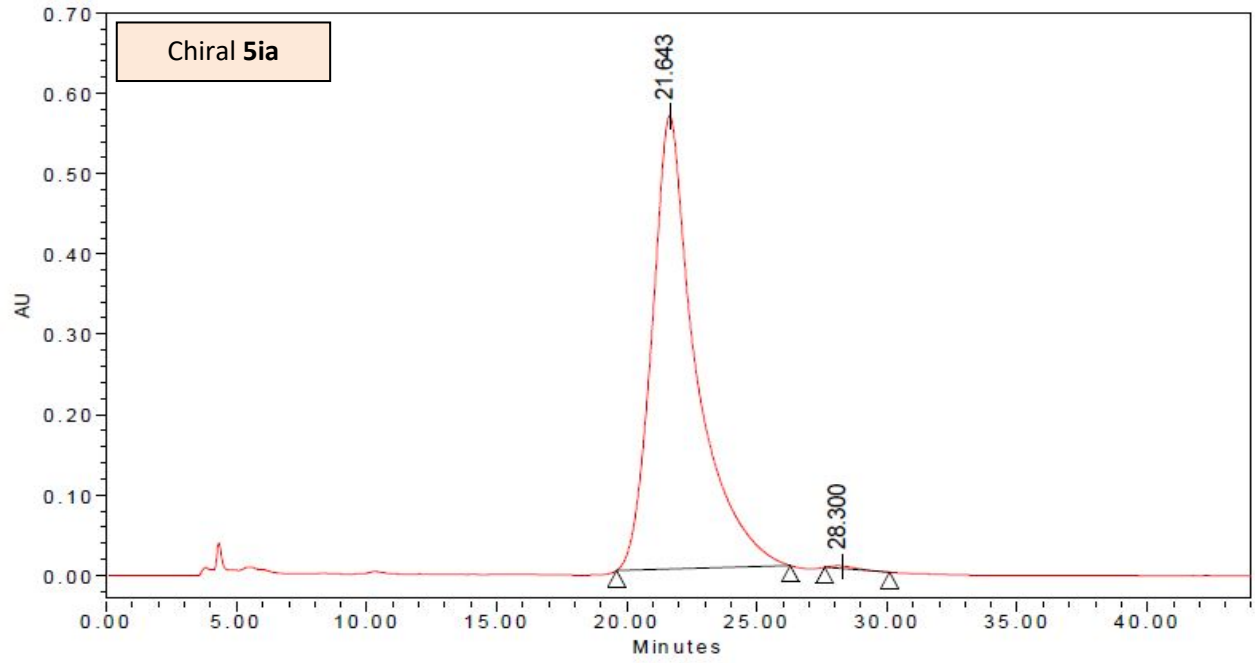
5ia

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



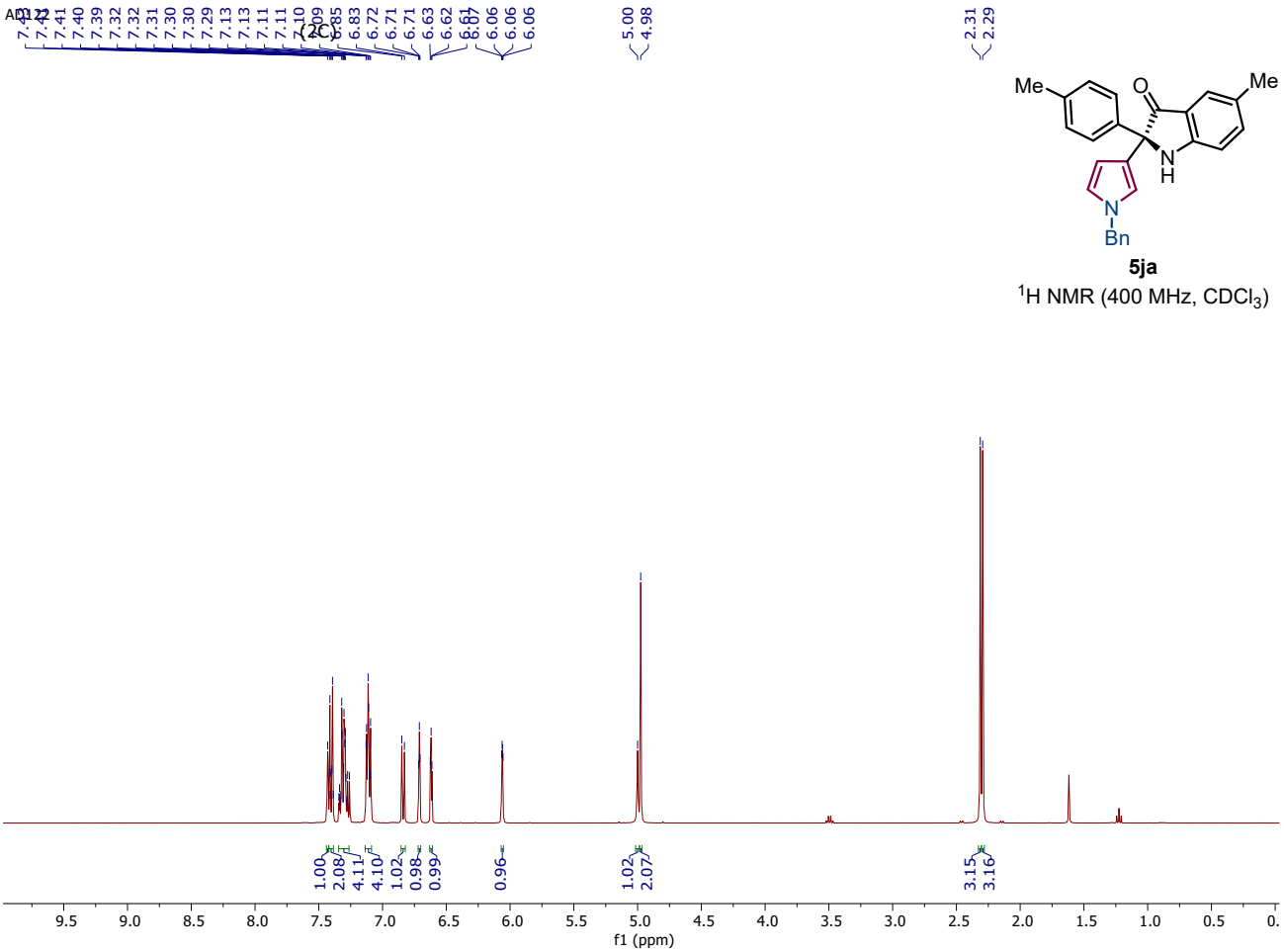
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	21.690	21926315	51.03	198639
2	2998 PDA 254.0 nm (2998 (200-400)nm)	28.168	21039218	48.97	153562



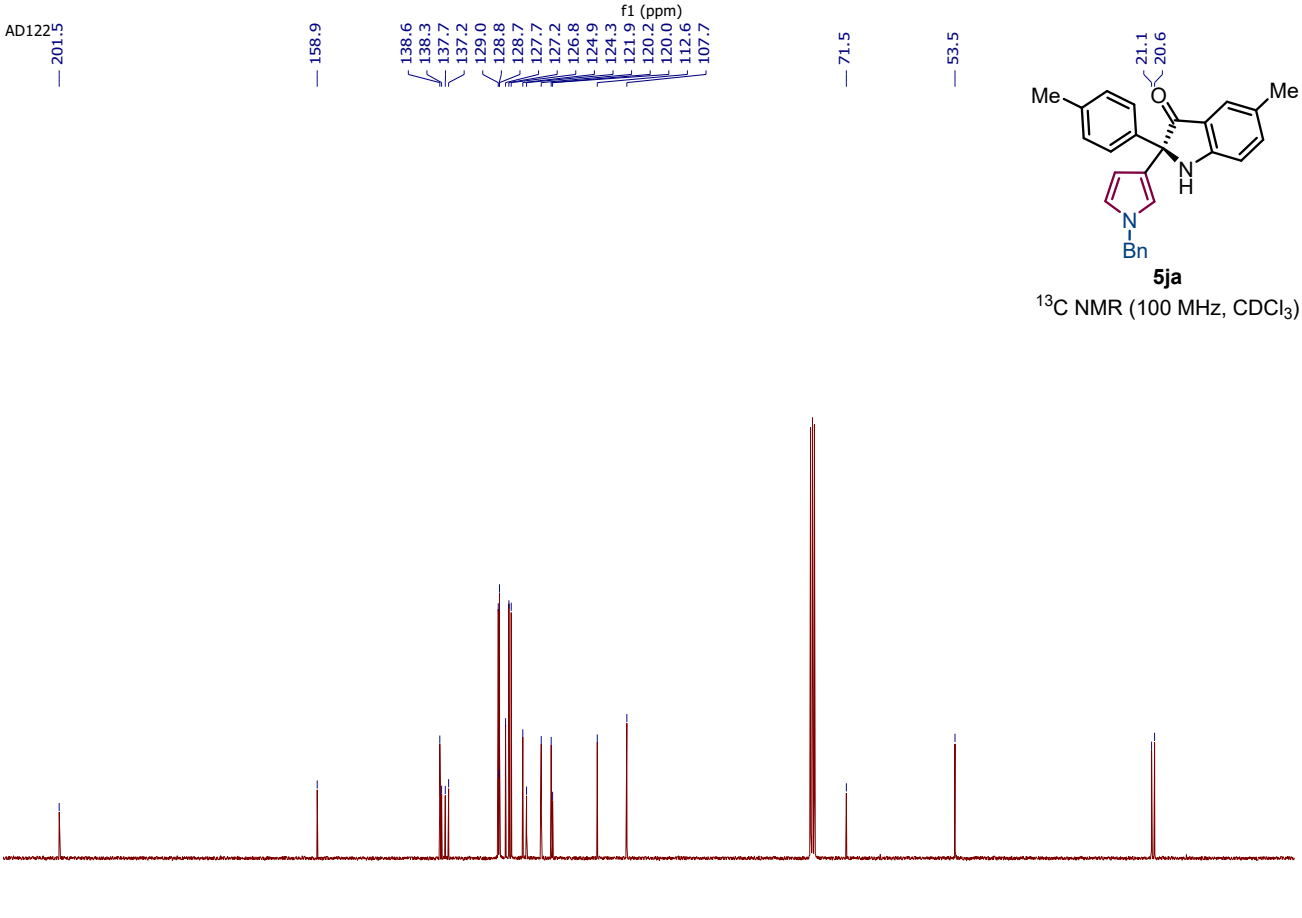
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	21.643	66285818	99.67	564240
2	2998 PDA 254.0 nm (2998 (200-400)nm)	28.300	221154	0.33	3260



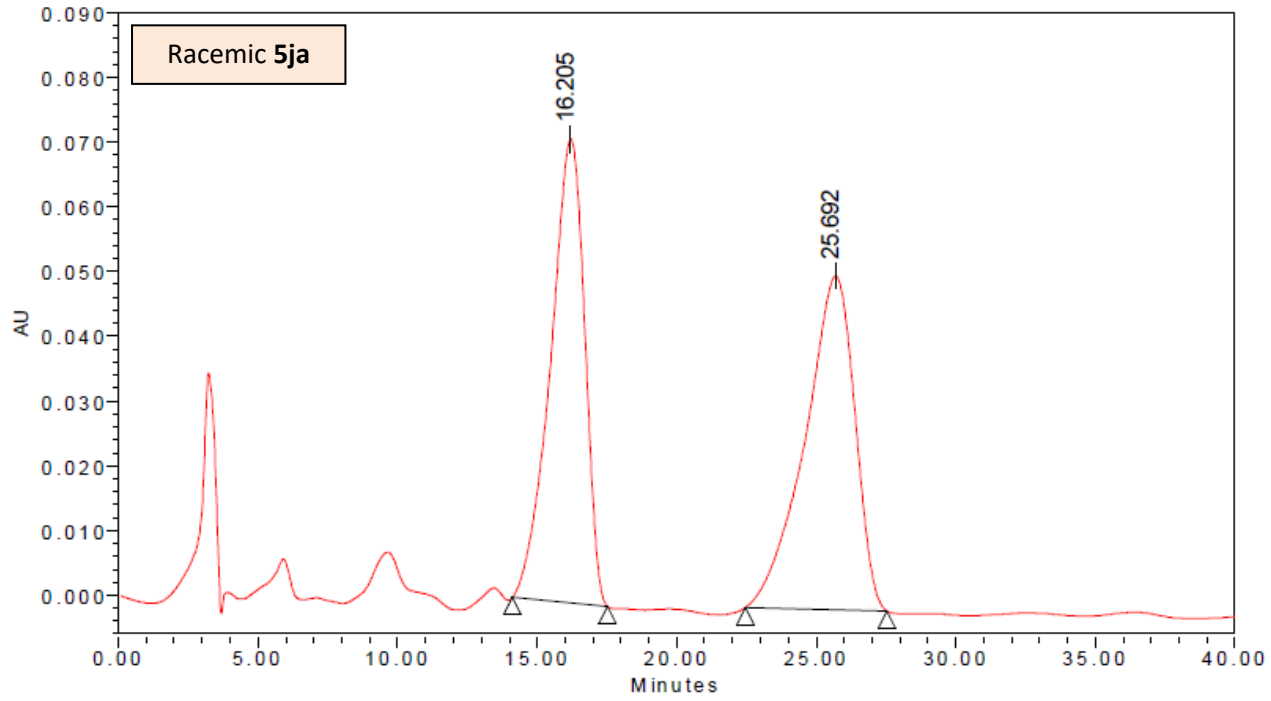
5ja

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



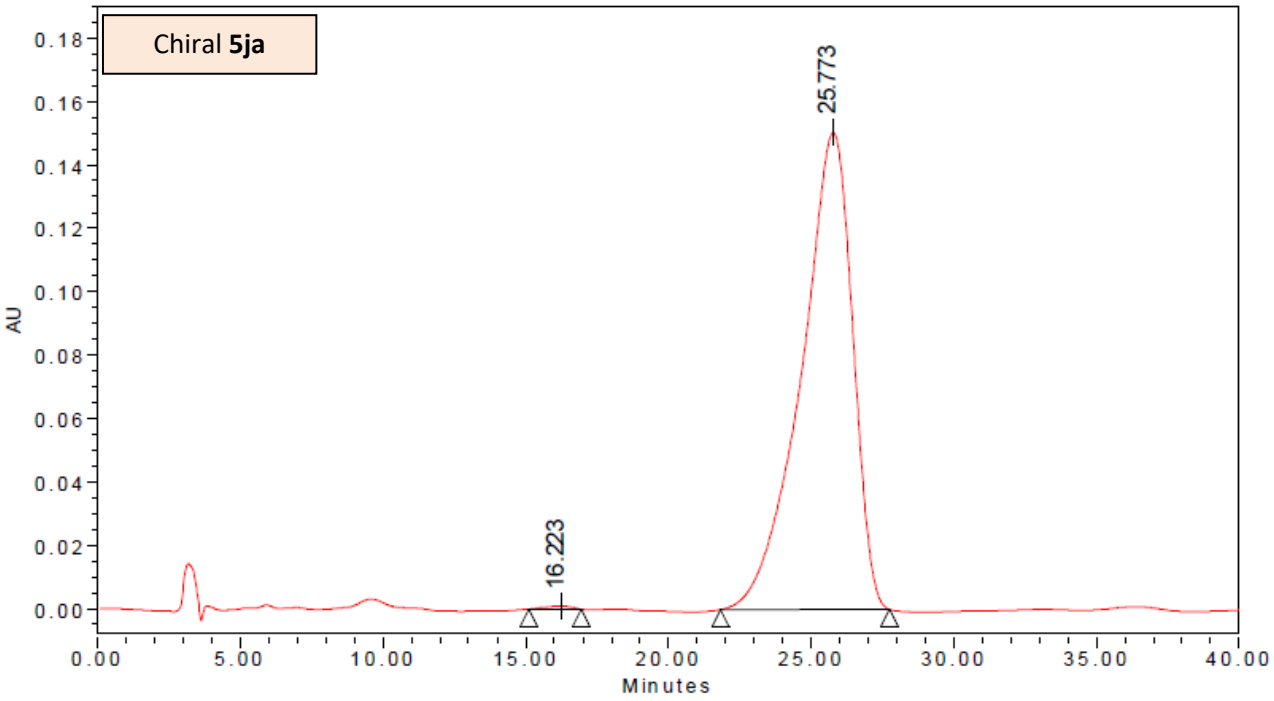
5ja

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



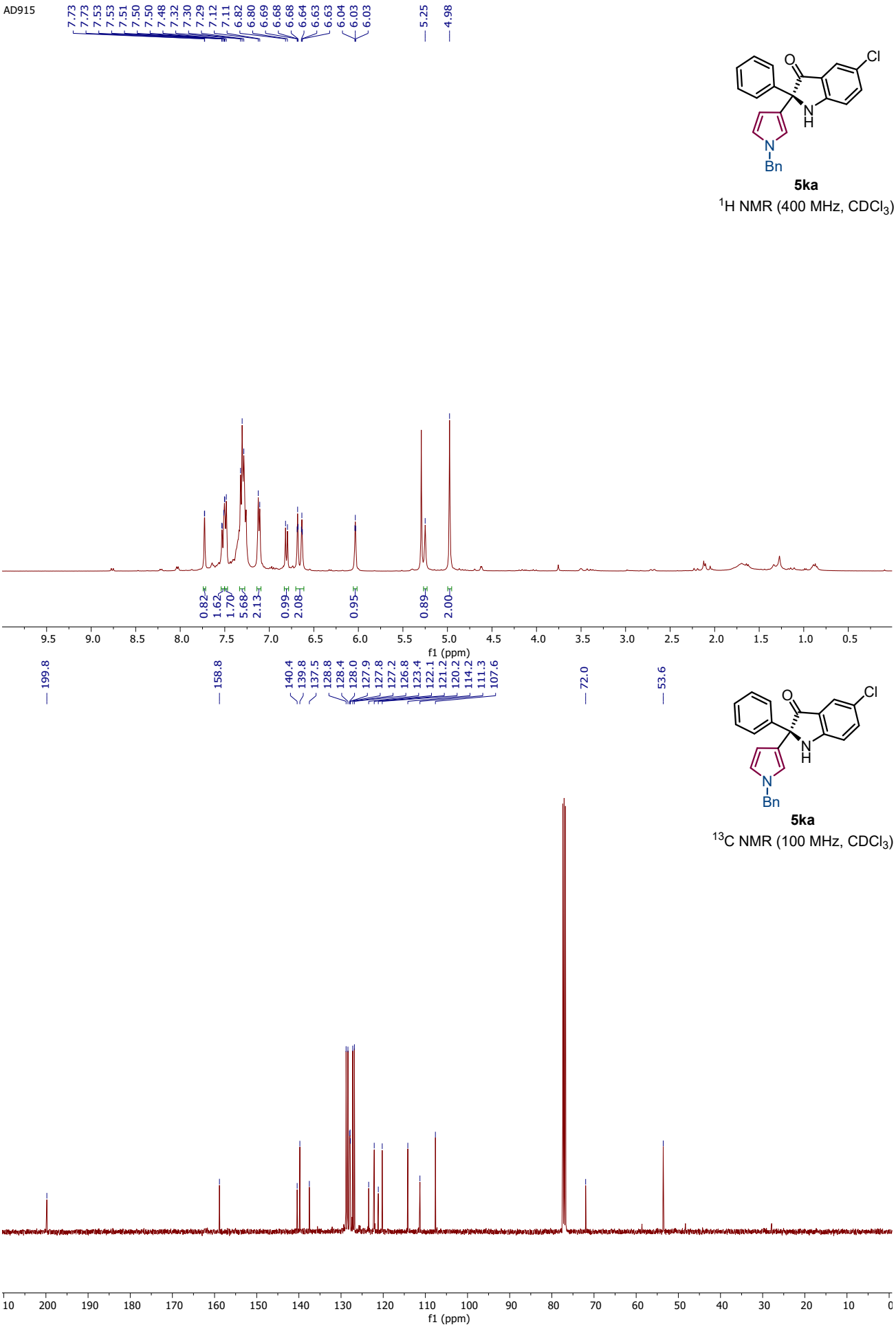
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

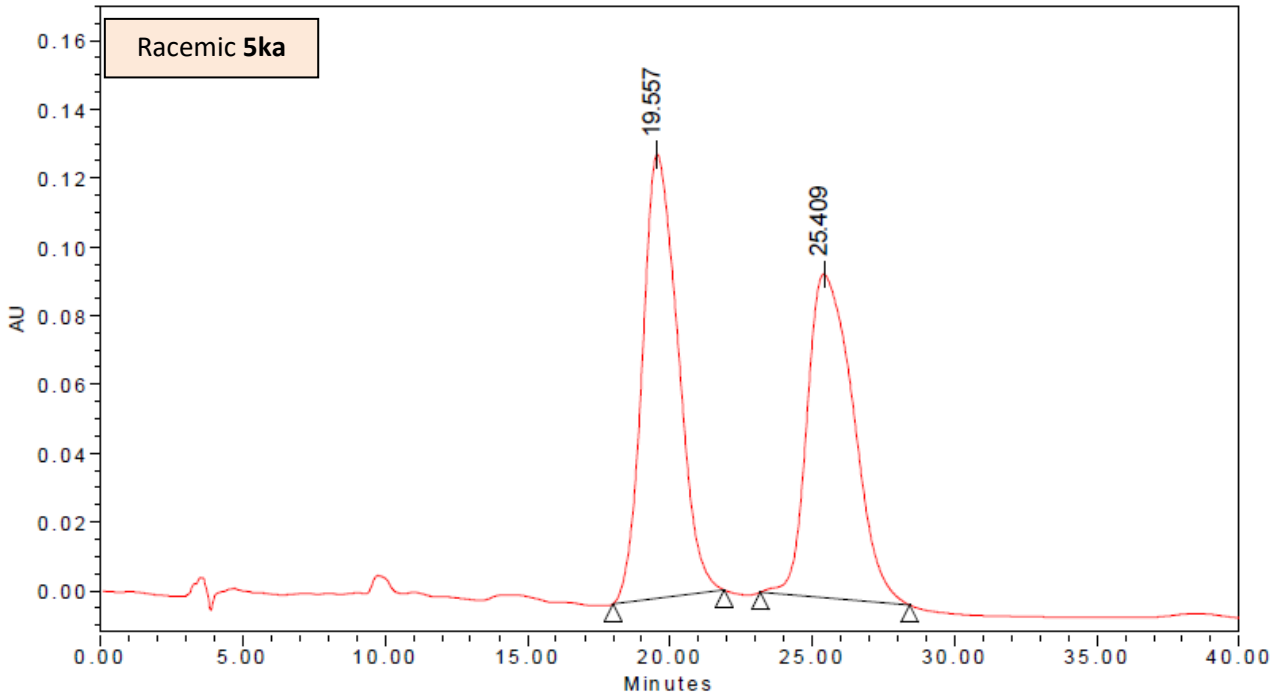
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	16.205	6085464	48.73	71690
2	2998 PDA 254.0 nm (2998 (200-400)nm)	25.692	6402182	51.27	51534



Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

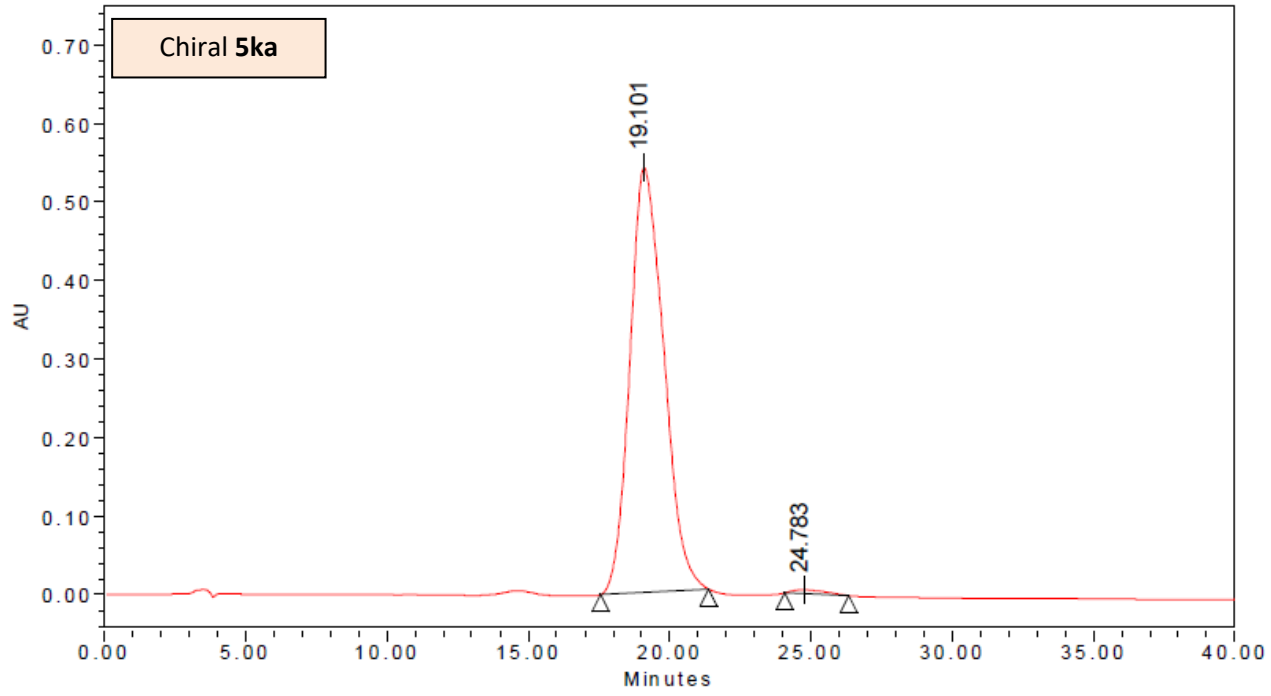
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	16.223	60430	0.32	958
2	2998 PDA 254.0 nm (2998 (200-400)nm)	25.773	18819868	99.68	150532


AD915
7.73
7.73
7.53
7.53
7.51
7.50
7.50
7.48
7.32
7.30
7.29
7.12
7.11
6.82
6.80
6.69
6.68
6.68
6.64
6.63
6.63
6.04
6.03
6.03
5.25
4.98
Cl
O
N
H
N
Bn
5ka
1H NMR (400 MHz, CDCl3)
0.82
1.62
1.70
5.68
2.13
0.99
2.08
0.95
0.89
2.00
f1 (ppm)
199.8
158.8
140.4
139.8
137.5
128.8
128.4
128.0
127.9
127.8
127.2
126.8
123.4
122.1
121.2
120.2
114.2
111.3
107.6
72.0
53.6
5ka
13C NMR (100 MHz, CDCl3)
f1 (ppm)



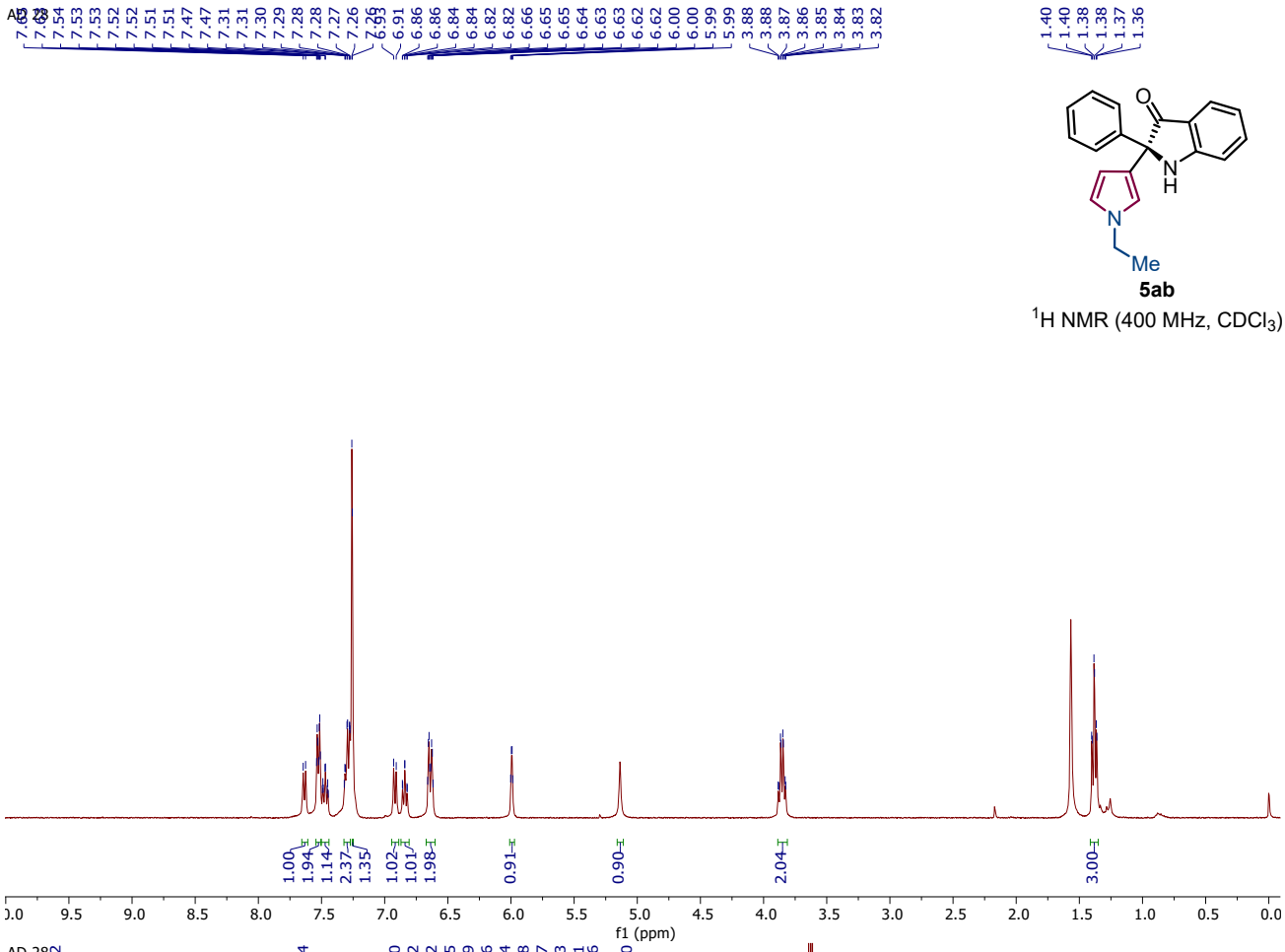
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	19.557	11183328	51.39	129175
2	2998 PDA 254.0 nm (2998 (200-400)nm)	25.409	10577084	48.61	94066



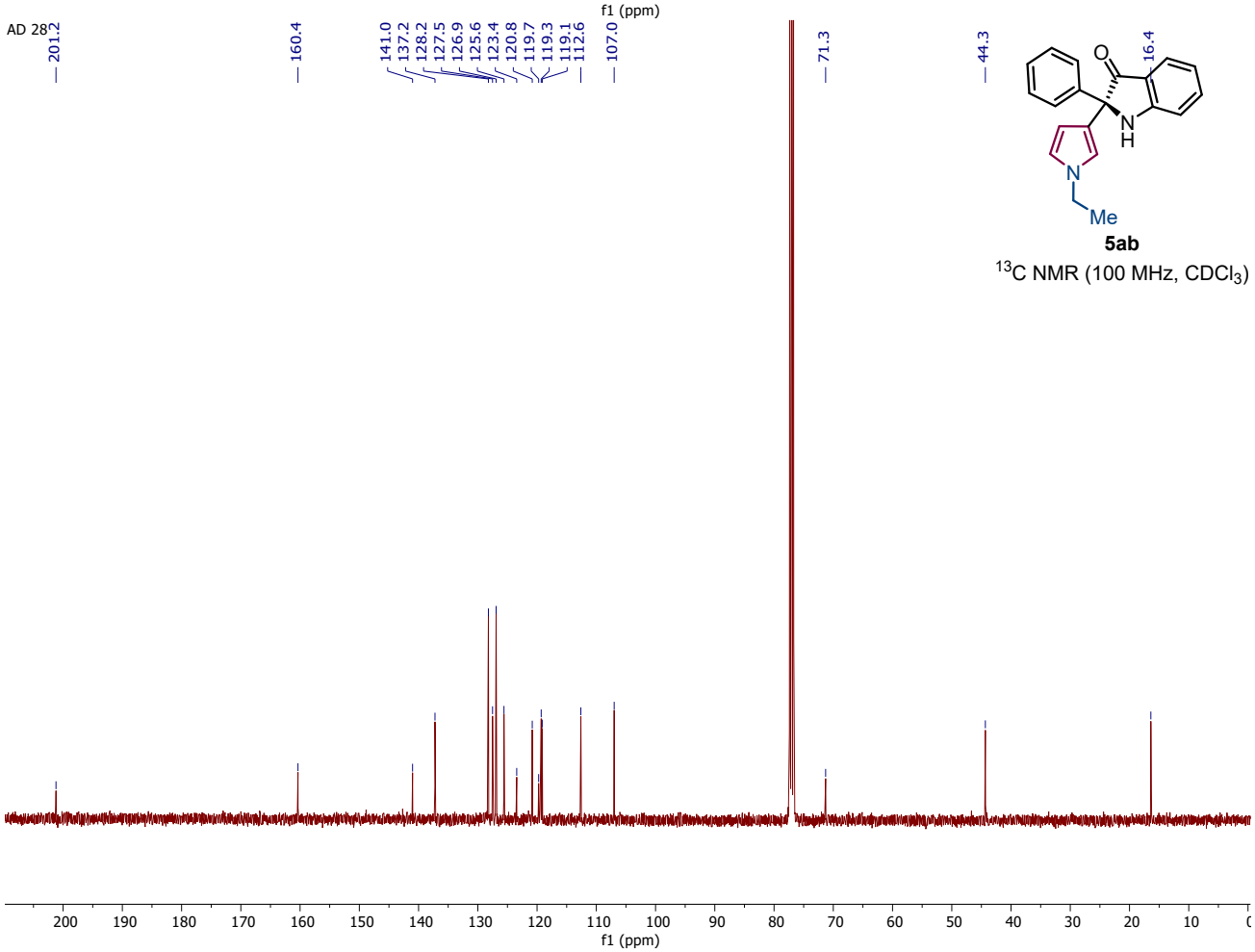
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	19.101	45075522	99.10	540769
2	2998 PDA 254.0 nm (2998 (200-400)nm)	24.783	409187	0.90	4996



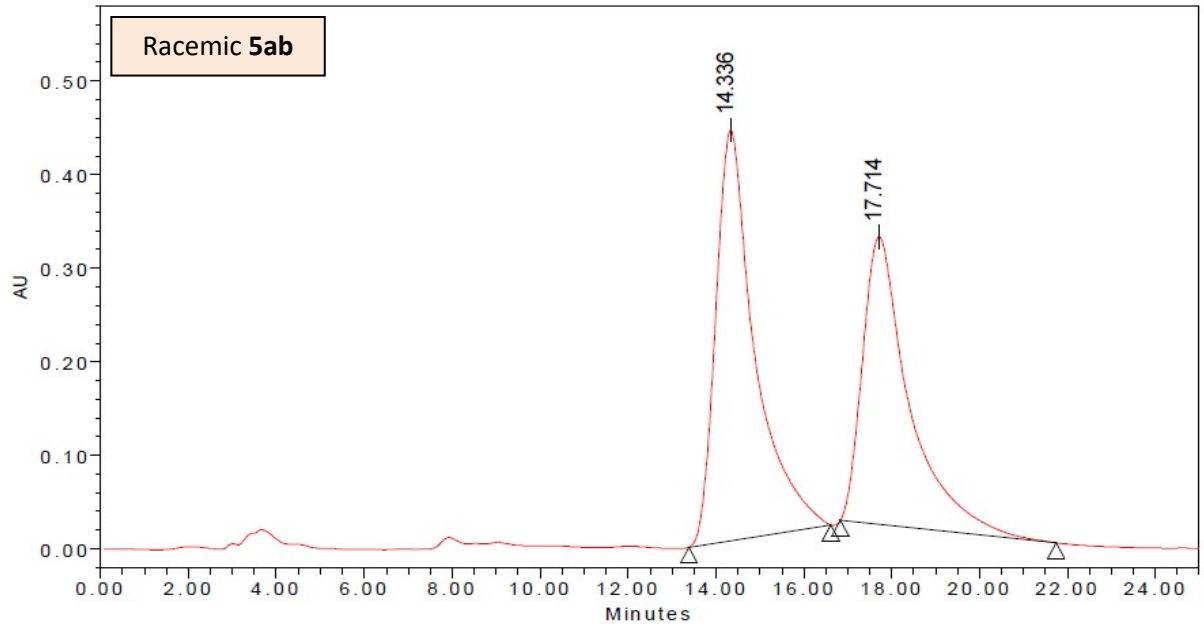
5ab

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



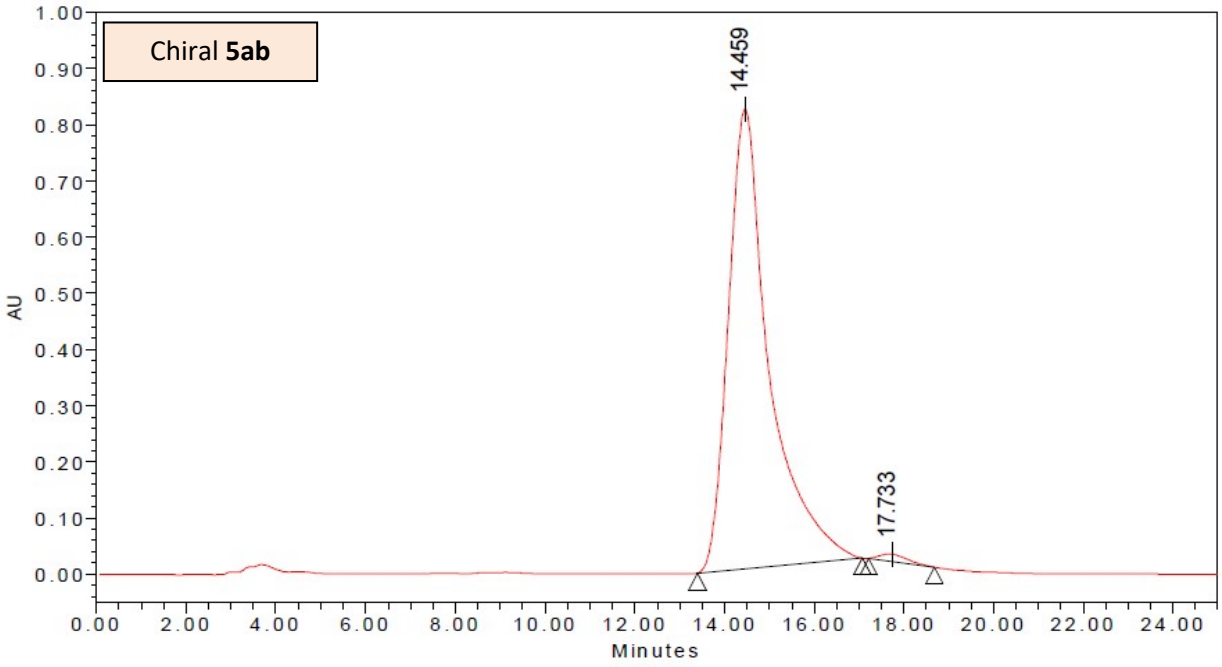
5ab

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



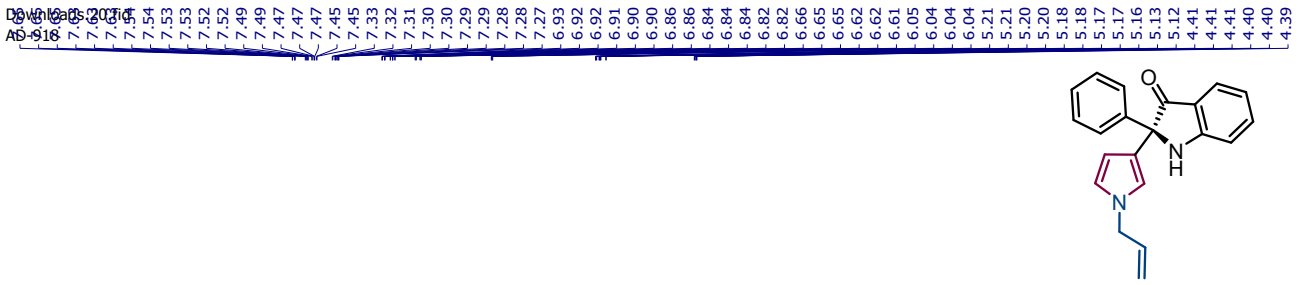
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	14.336	27181547	54.53	438566
2	2998 PDA 254.0 nm (2998 (200-400)nm)	17.714	22668829	45.47	307485



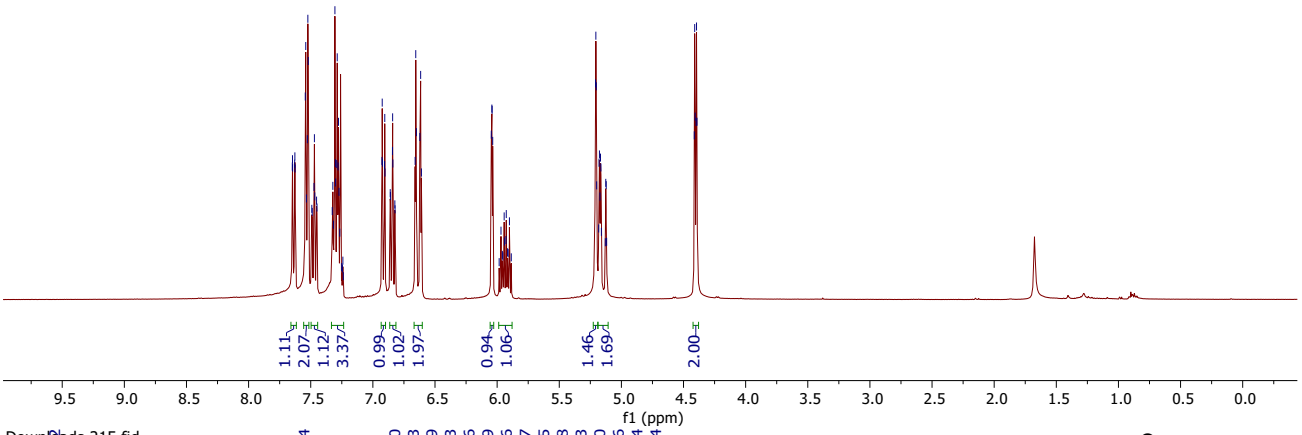
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

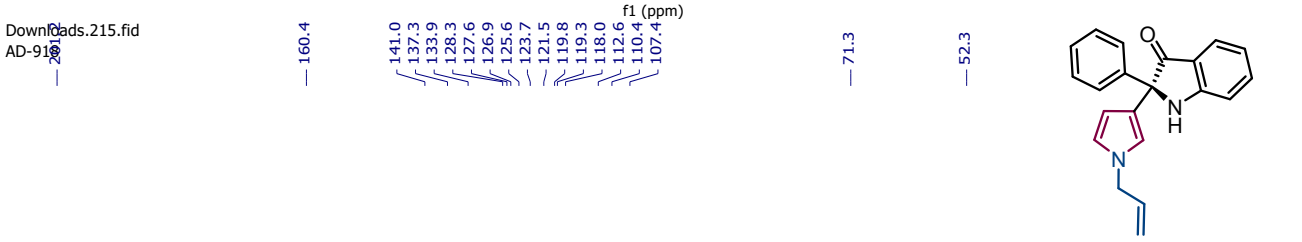
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	14.459	52114285	98.95	818094
2	2998 PDA 254.0 nm (2998 (200-400)nm)	17.733	553661	1.05	12942



5ac

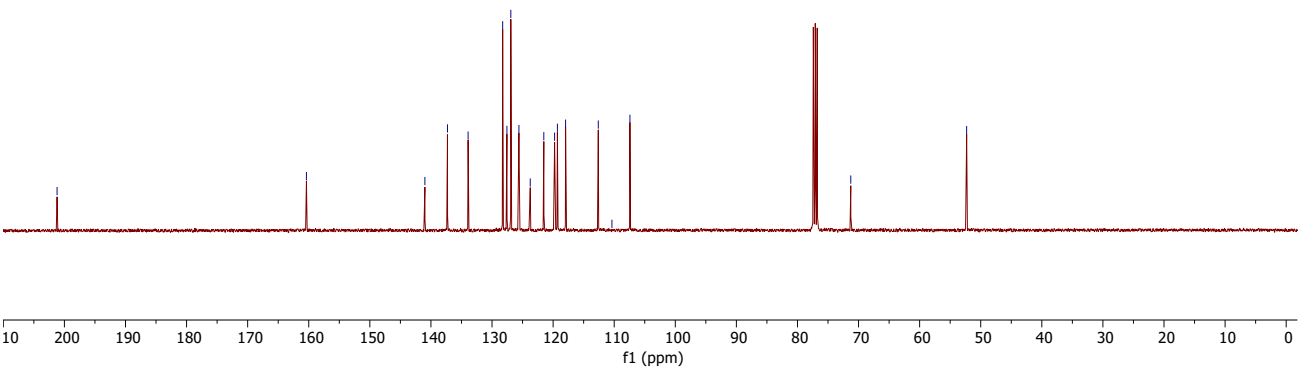
^{1}H NMR (400 MHz, $CDCl_3$)

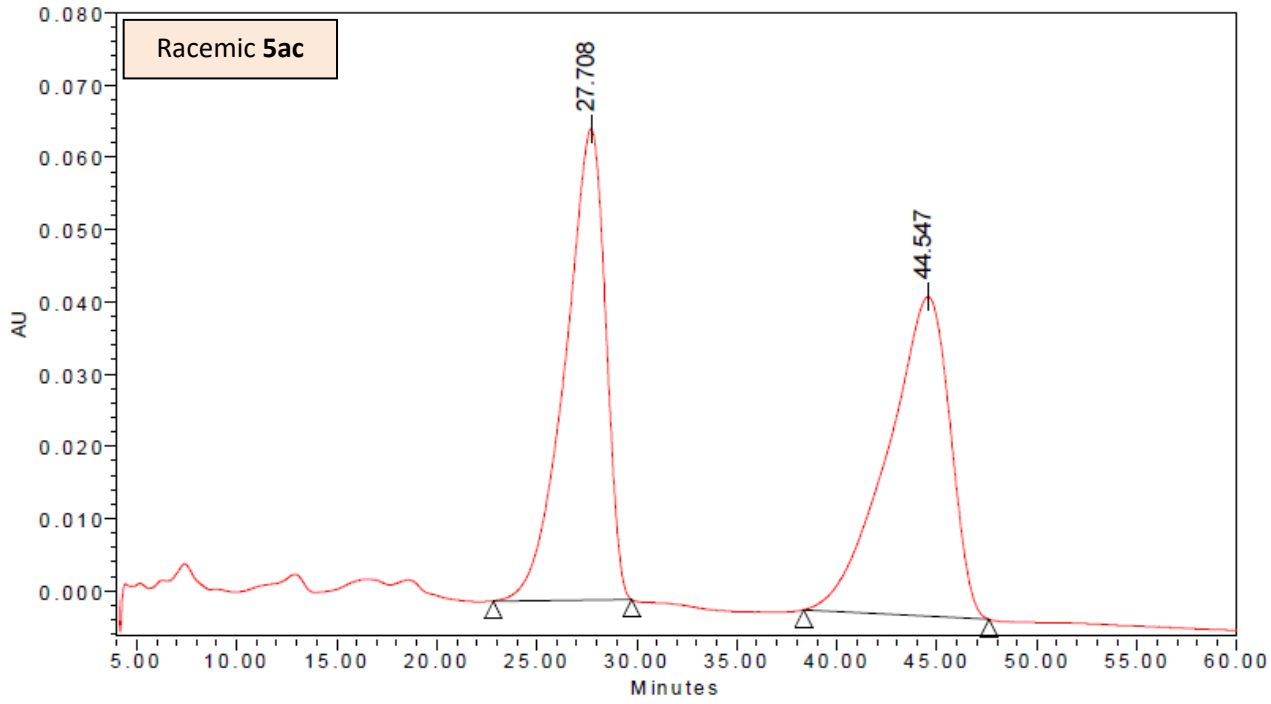




5ac

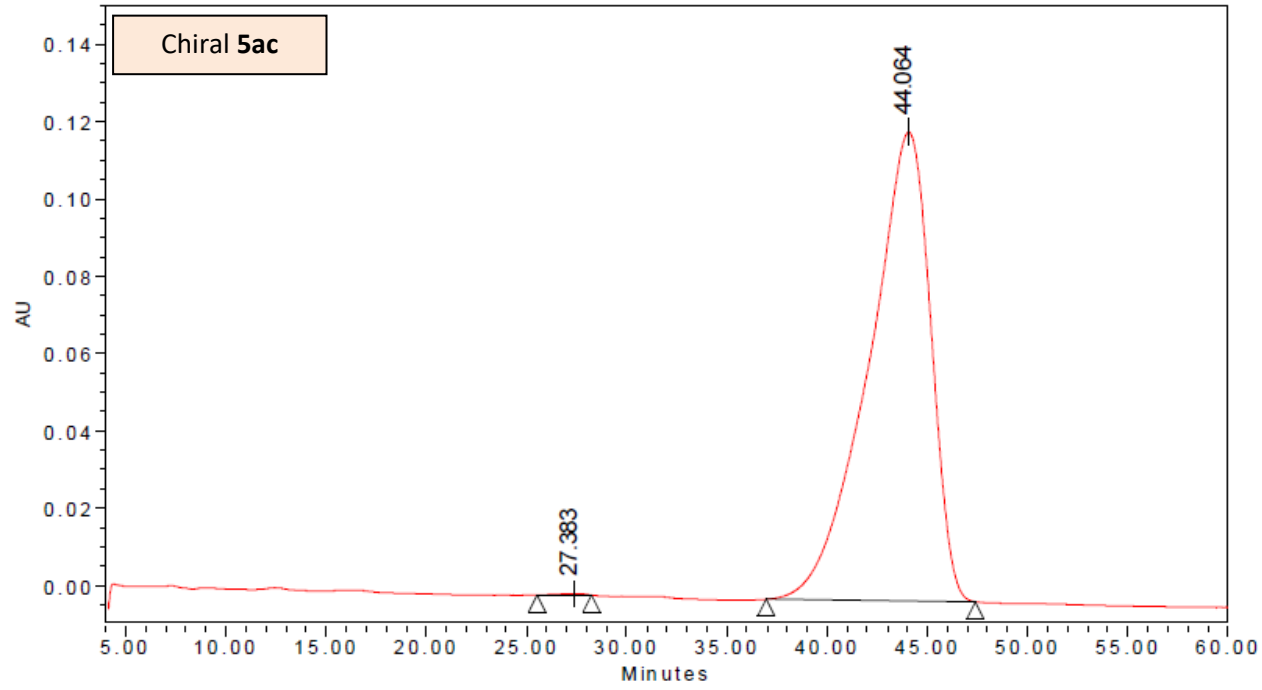
^{13}C NMR (100 MHz, $CDCl_3$)





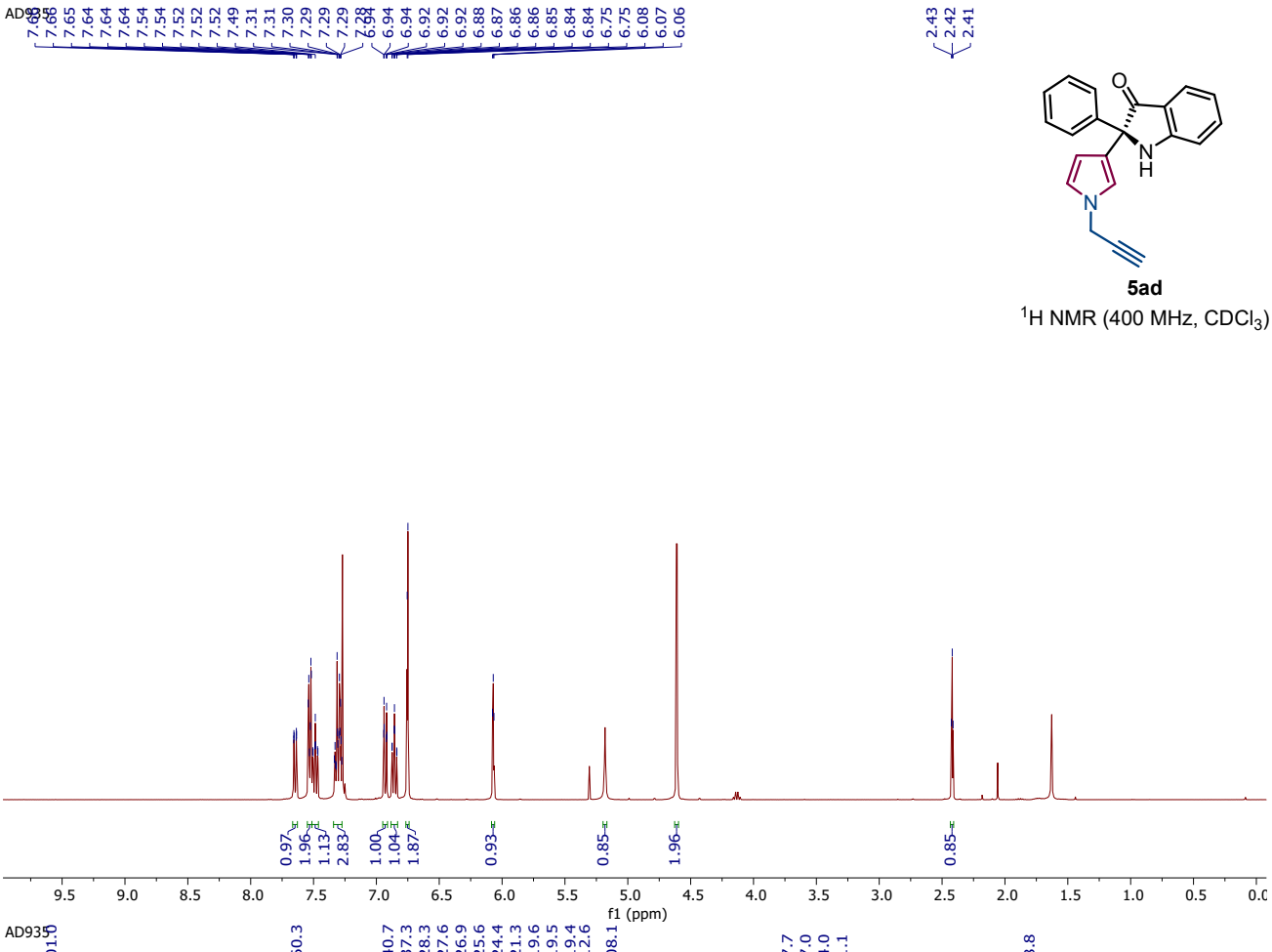
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	27.708	9147838	48.84	65204
2	2998 PDA 254.0 nm (2998 (200-400)nm)	44.547	9584071	51.16	44224



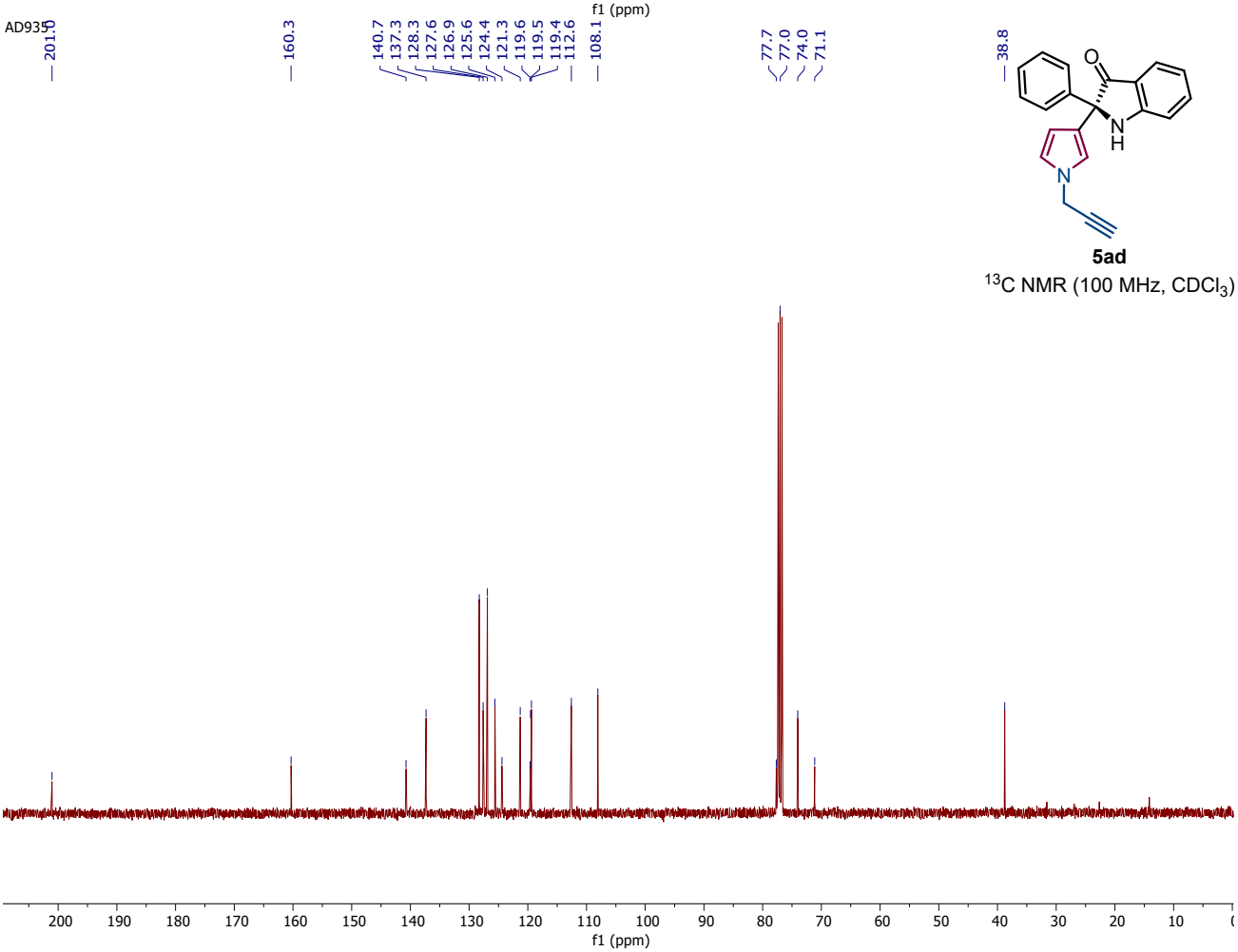
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	27.383	34608	0.13	390
2	2998 PDA 254.0 nm (2998 (200-400)nm)	44.064	25933586	99.87	121240



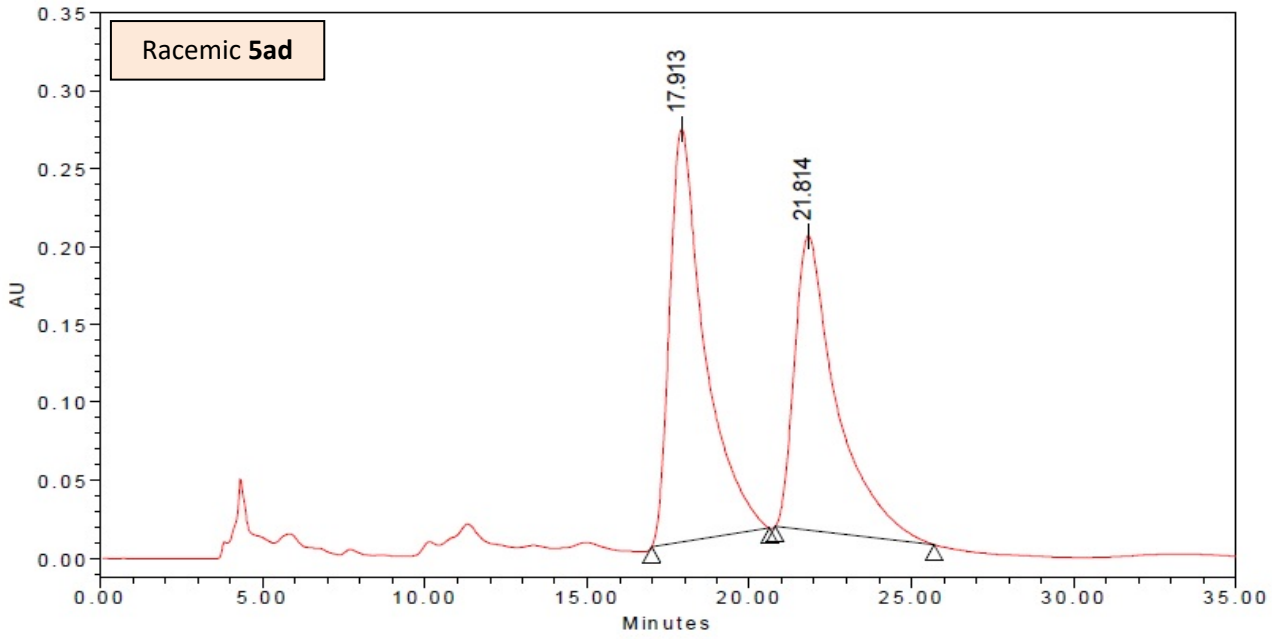
5ad

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



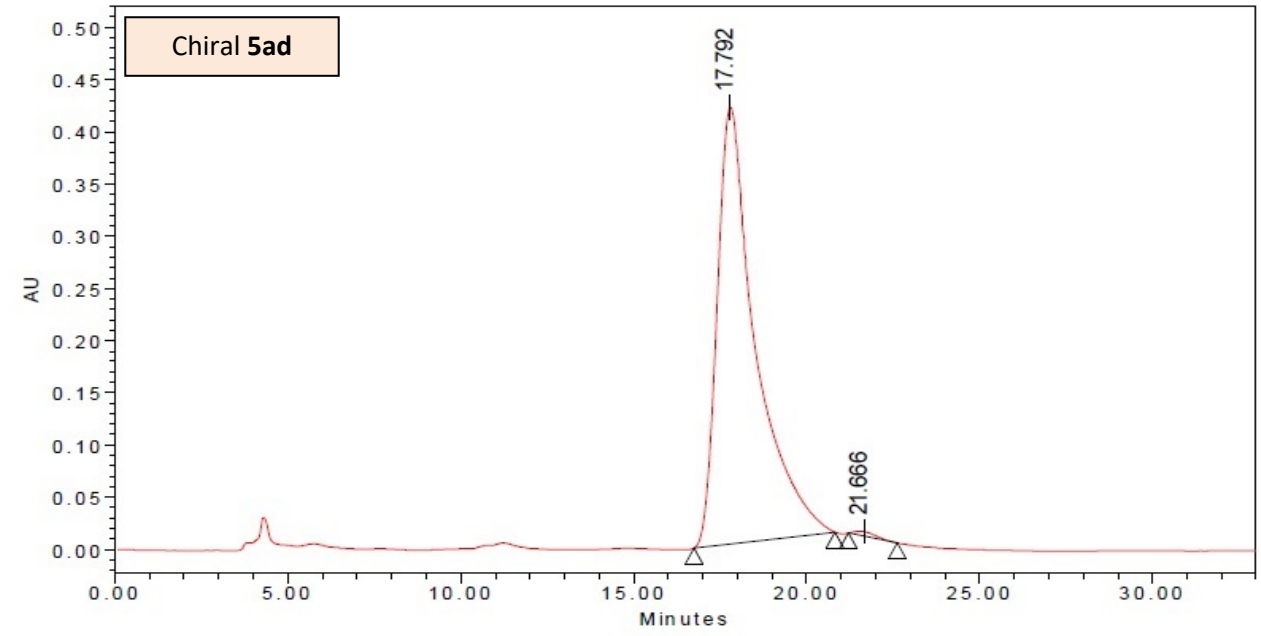
5ad

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



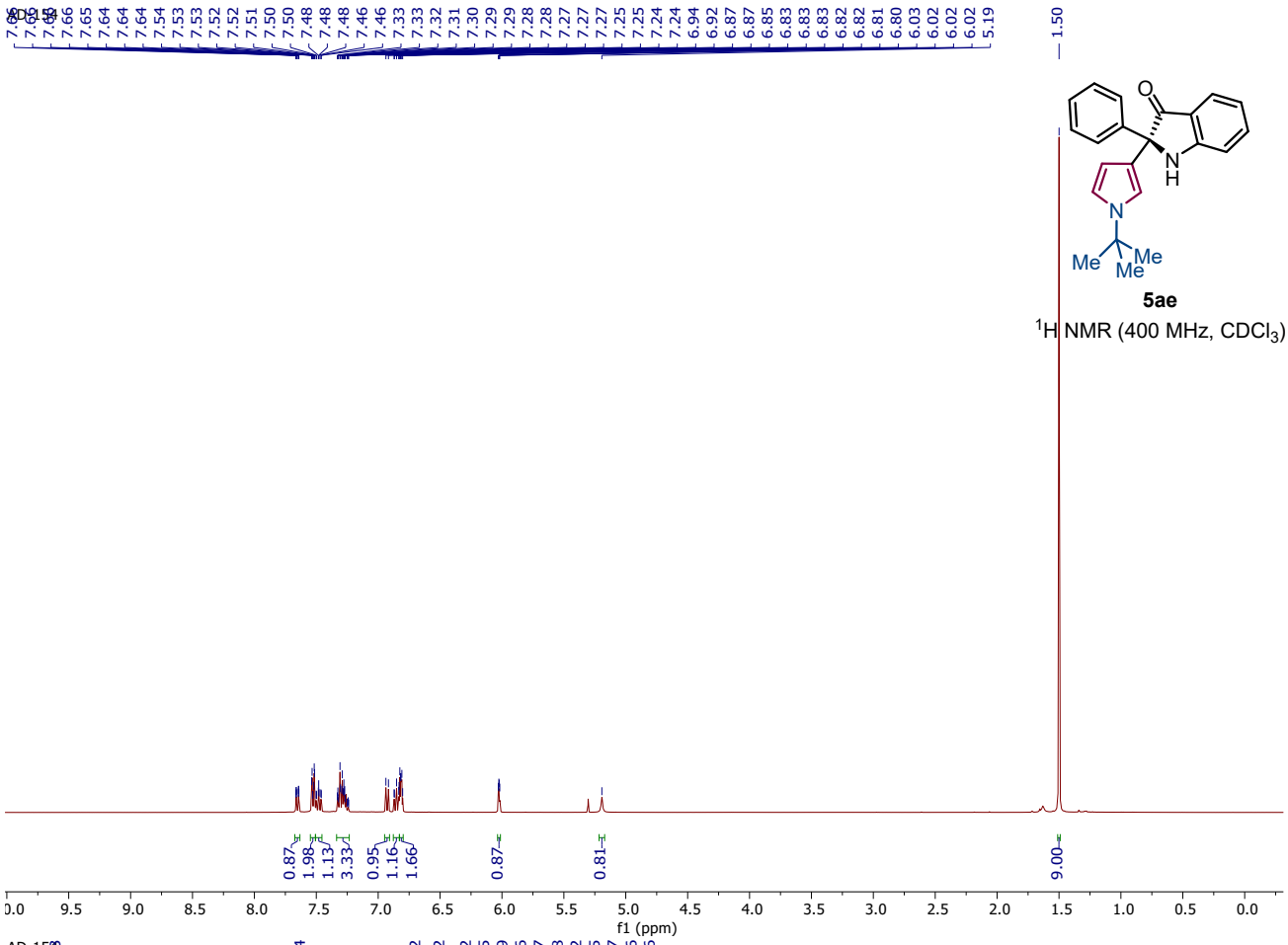
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	17.913	19854027	53.84	264667
2	2998 PDA 254.0 nm (2998 (200-400)nm)	21.814	17022756	46.16	188817



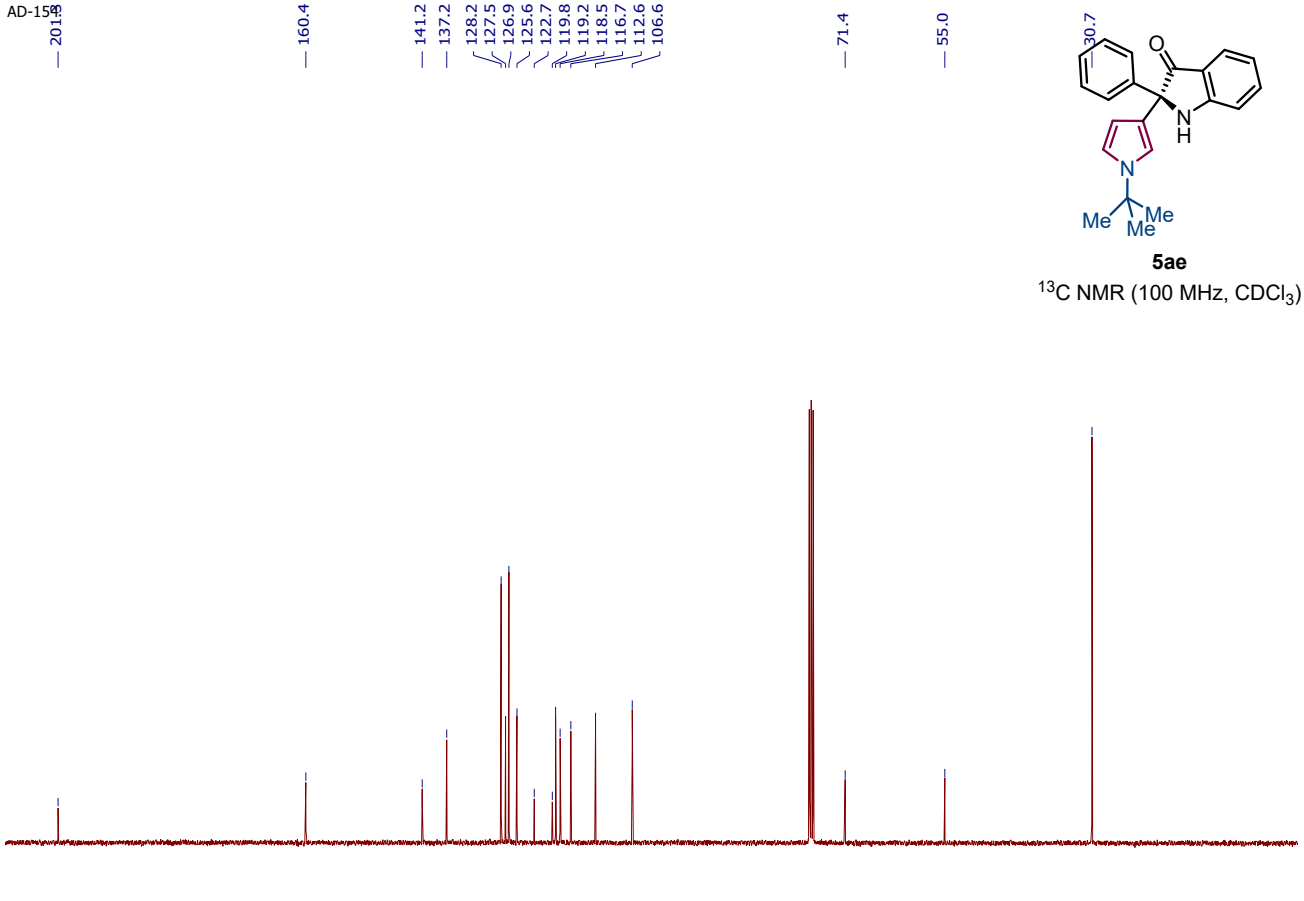
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	17.792	32233406	99.41	418231
2	2998 PDA 254.0 nm (2998 (200-400)nm)	21.666	191117	0.59	4590



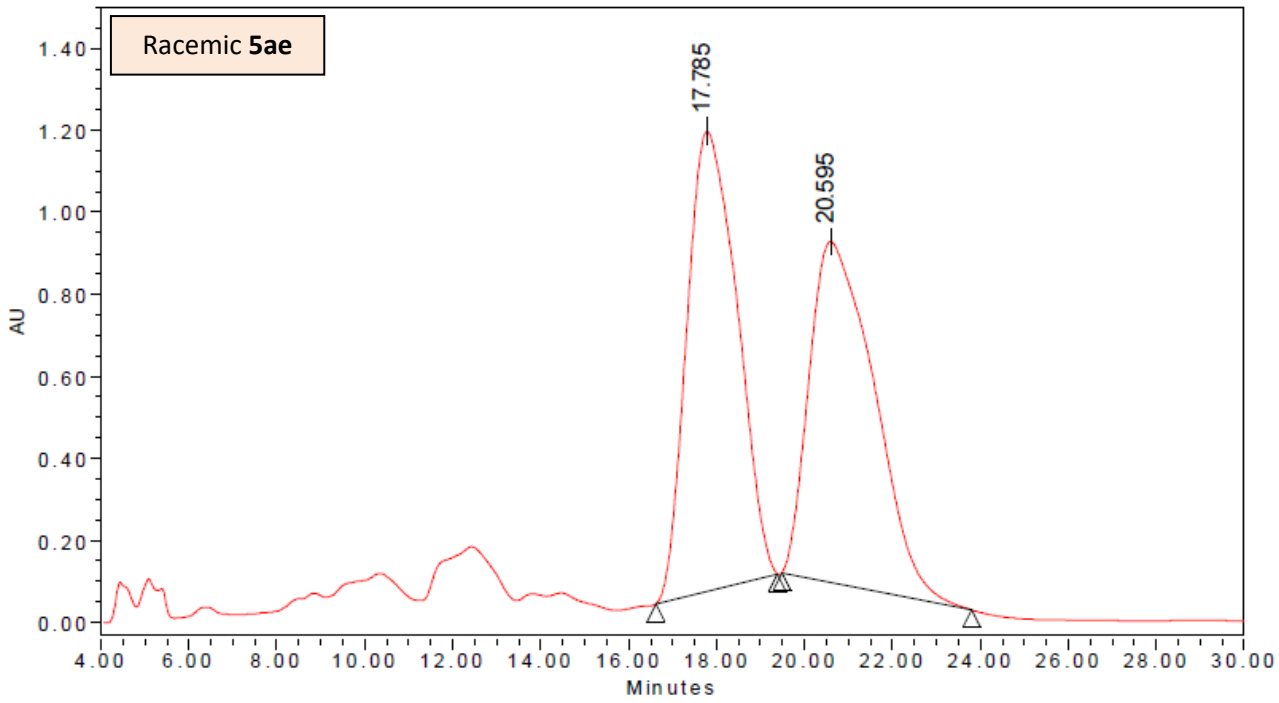
5ae

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



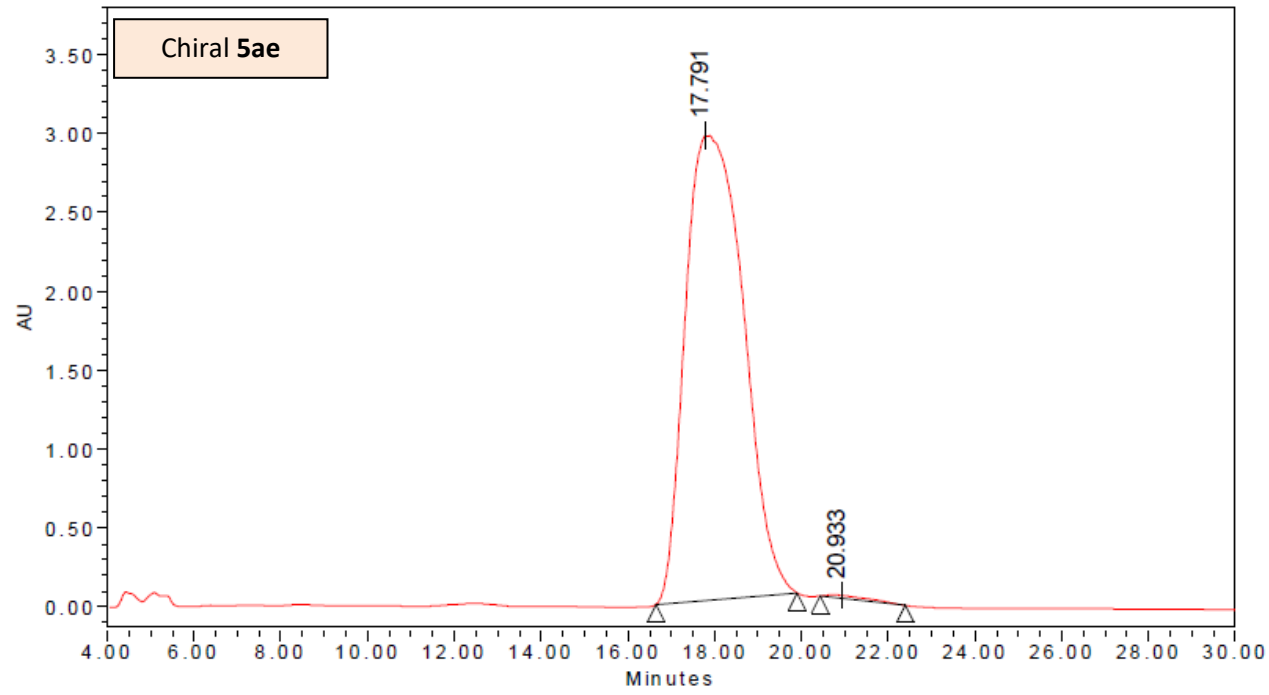
5ae

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



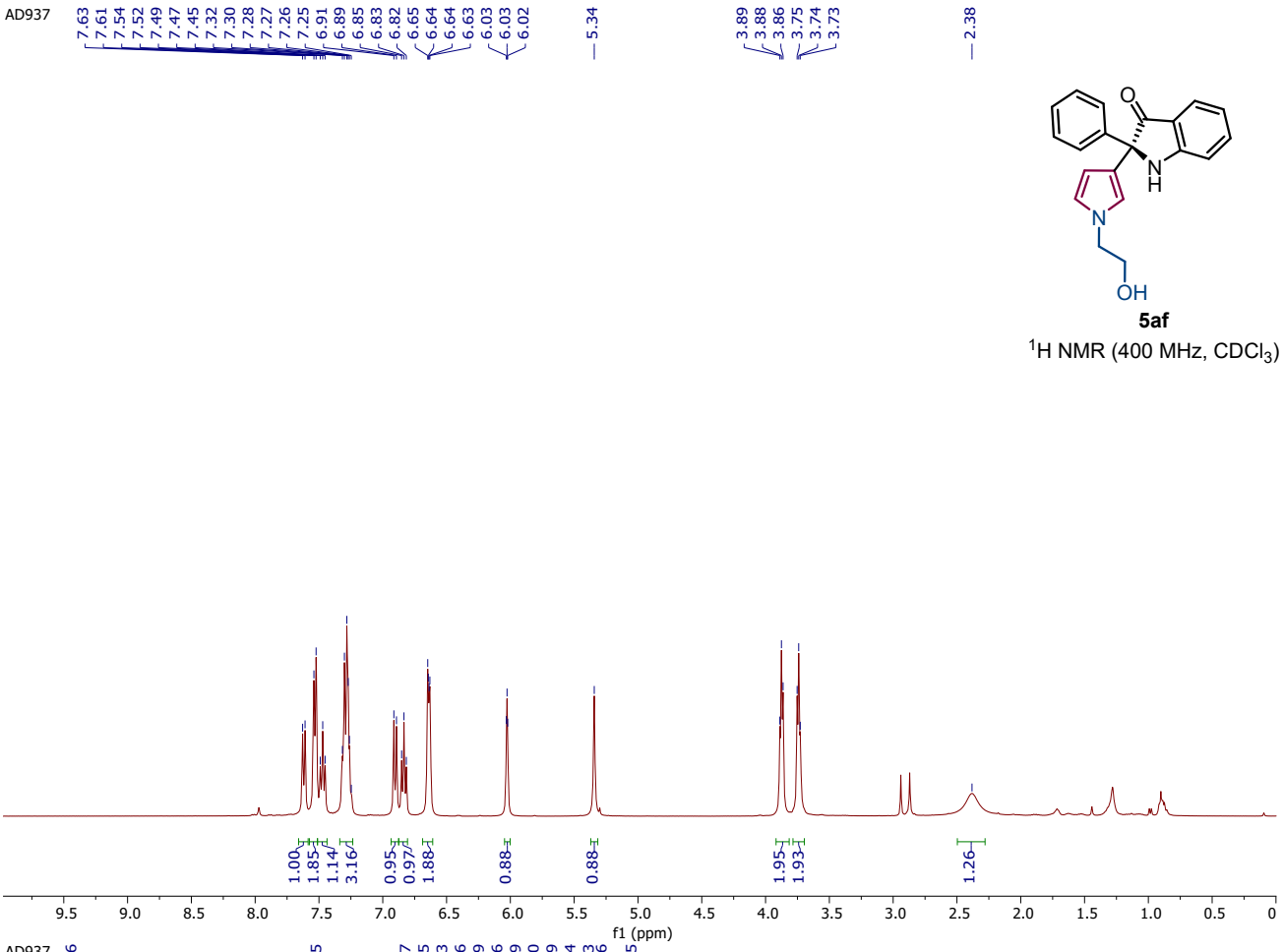
Processed Channel: 2998 PDA 230.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 230.0 nm (2998 (200-400)nm)	17.785	88687272	50.85	1121637
2	2998 PDA 230.0 nm (2998 (200-400)nm)	20.595	85722517	49.15	832076



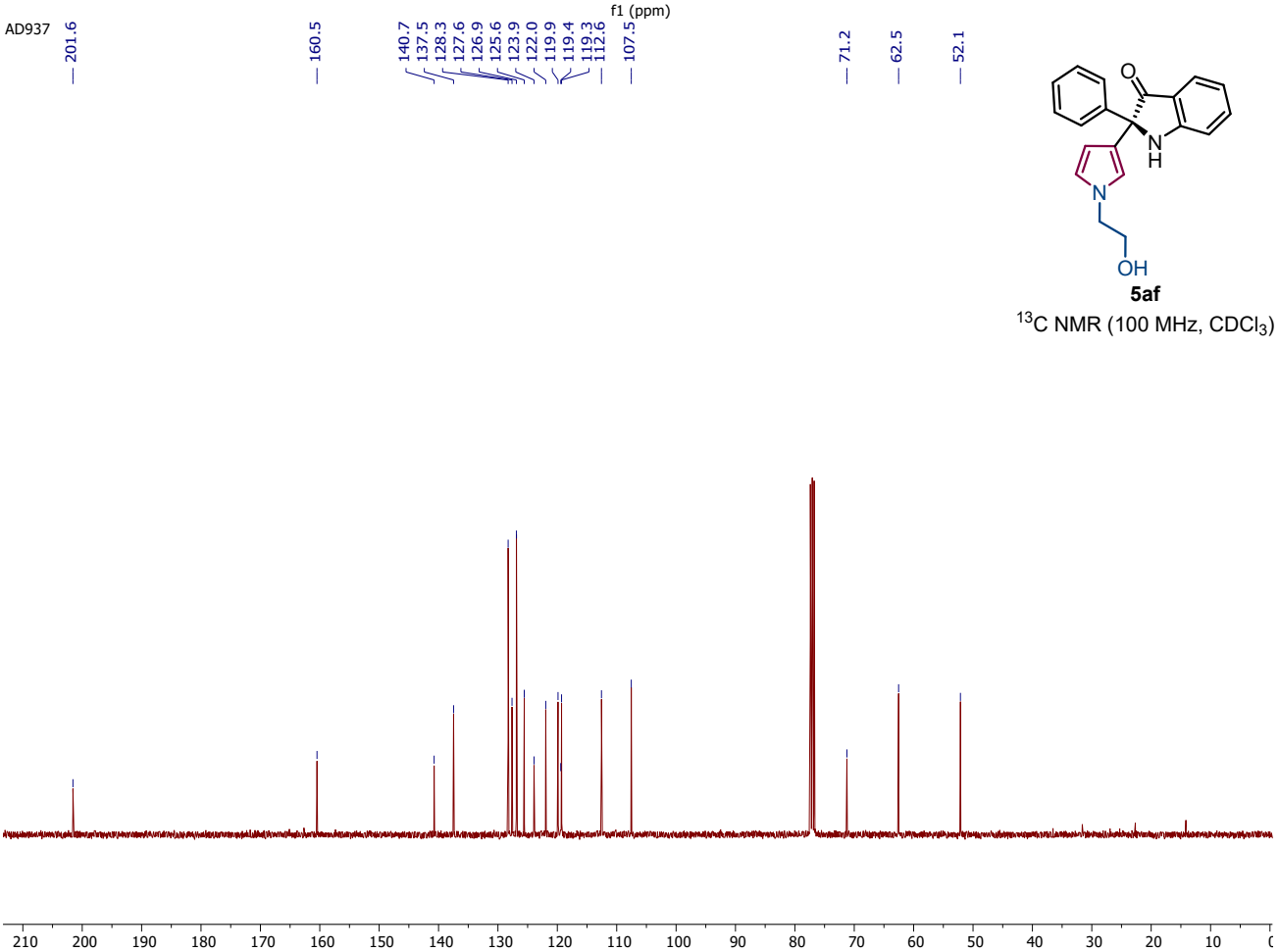
Processed Channel: 2998 PDA 230.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 230.0 nm (2998 (200-400)nm)	17.791	274106843	99.49	2944425
2	2998 PDA 230.0 nm (2998 (200-400)nm)	20.933	1402412	0.51	18566



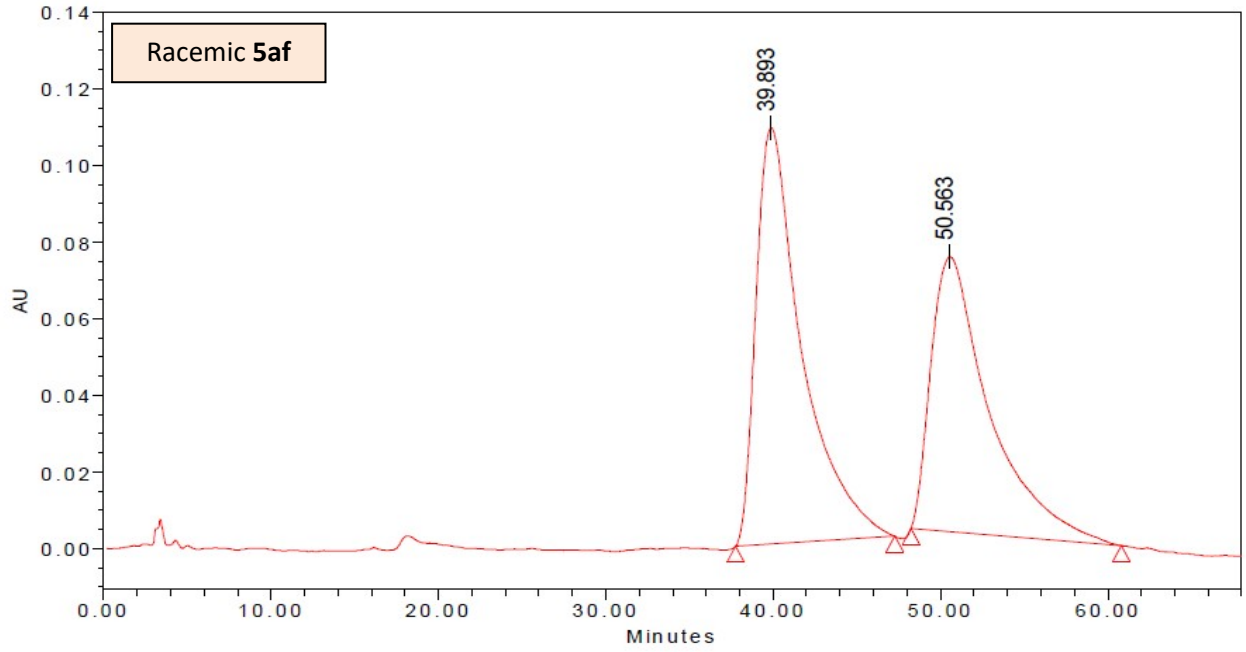
5af

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



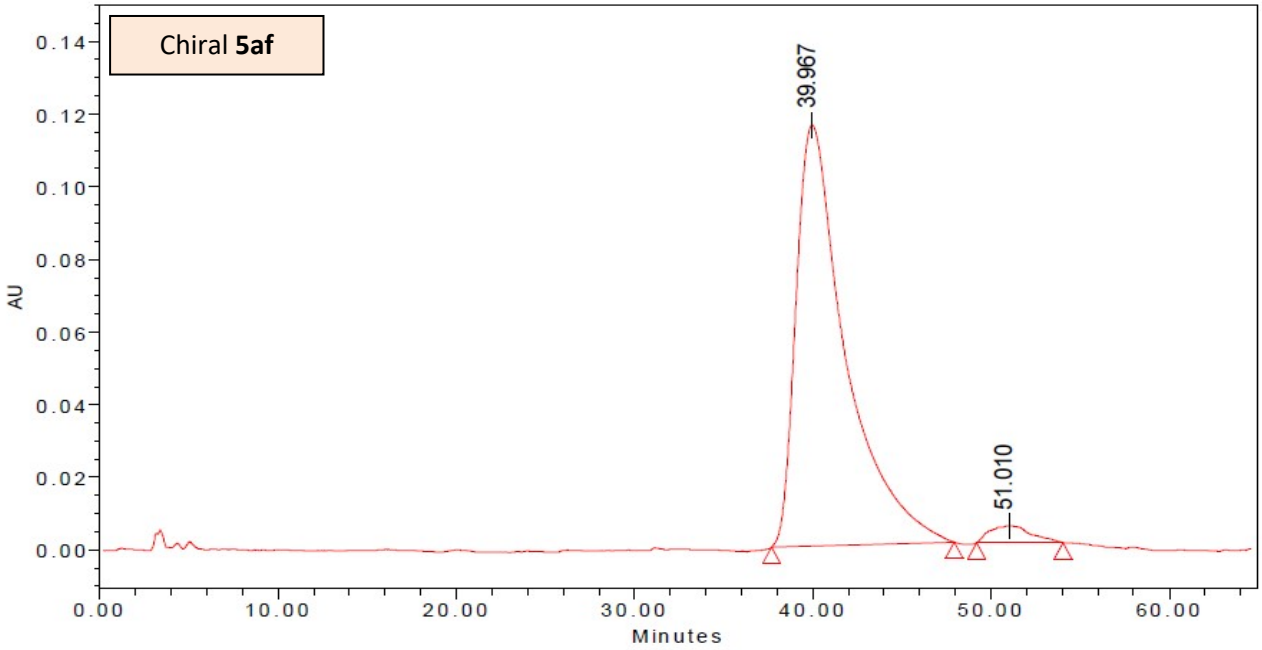
5af

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



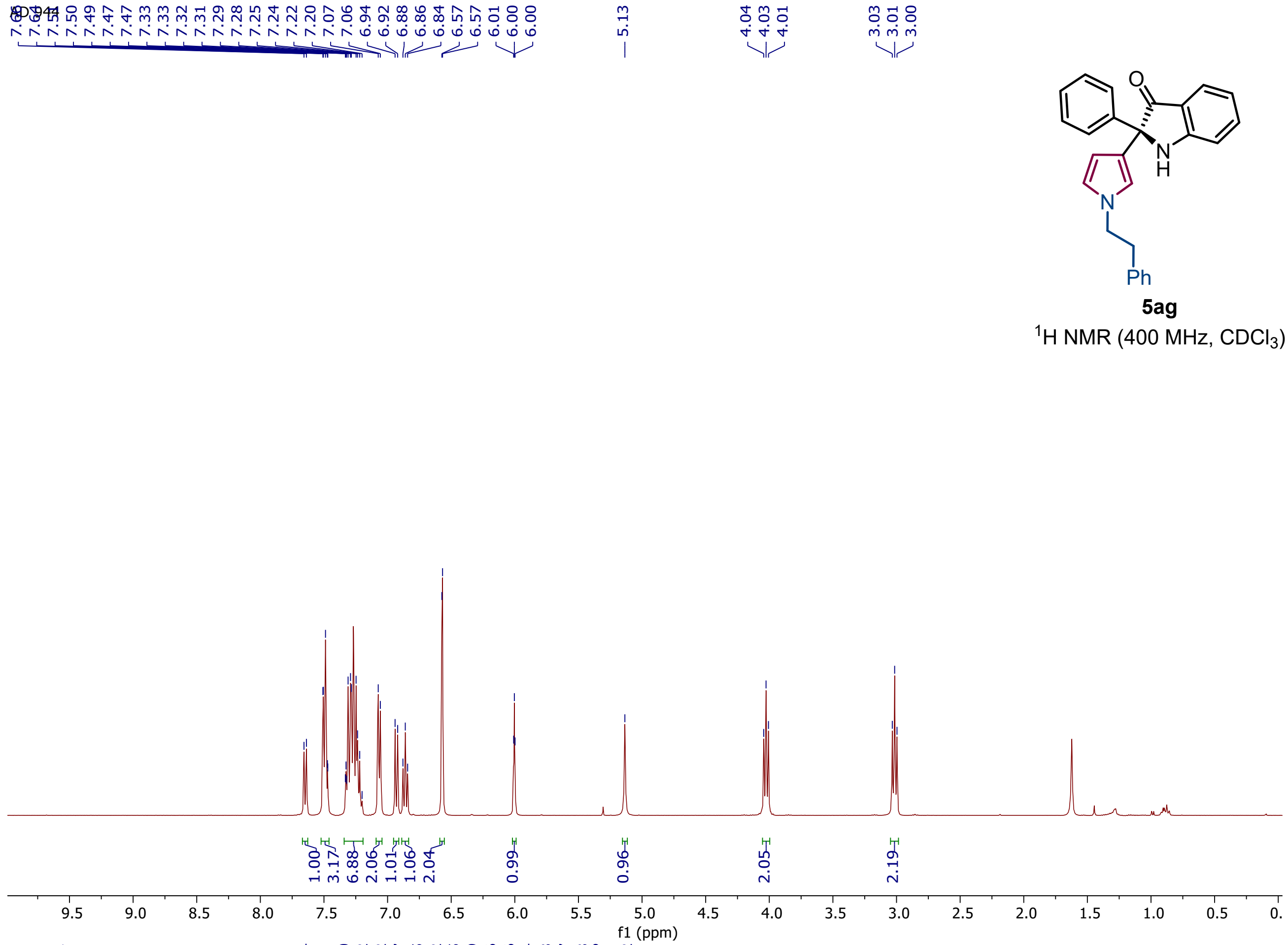
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	39.893	20719365	54.42	108558
2	2998 PDA 254.0 nm (2998 (200-400)nm)	50.563	17356802	45.58	71710



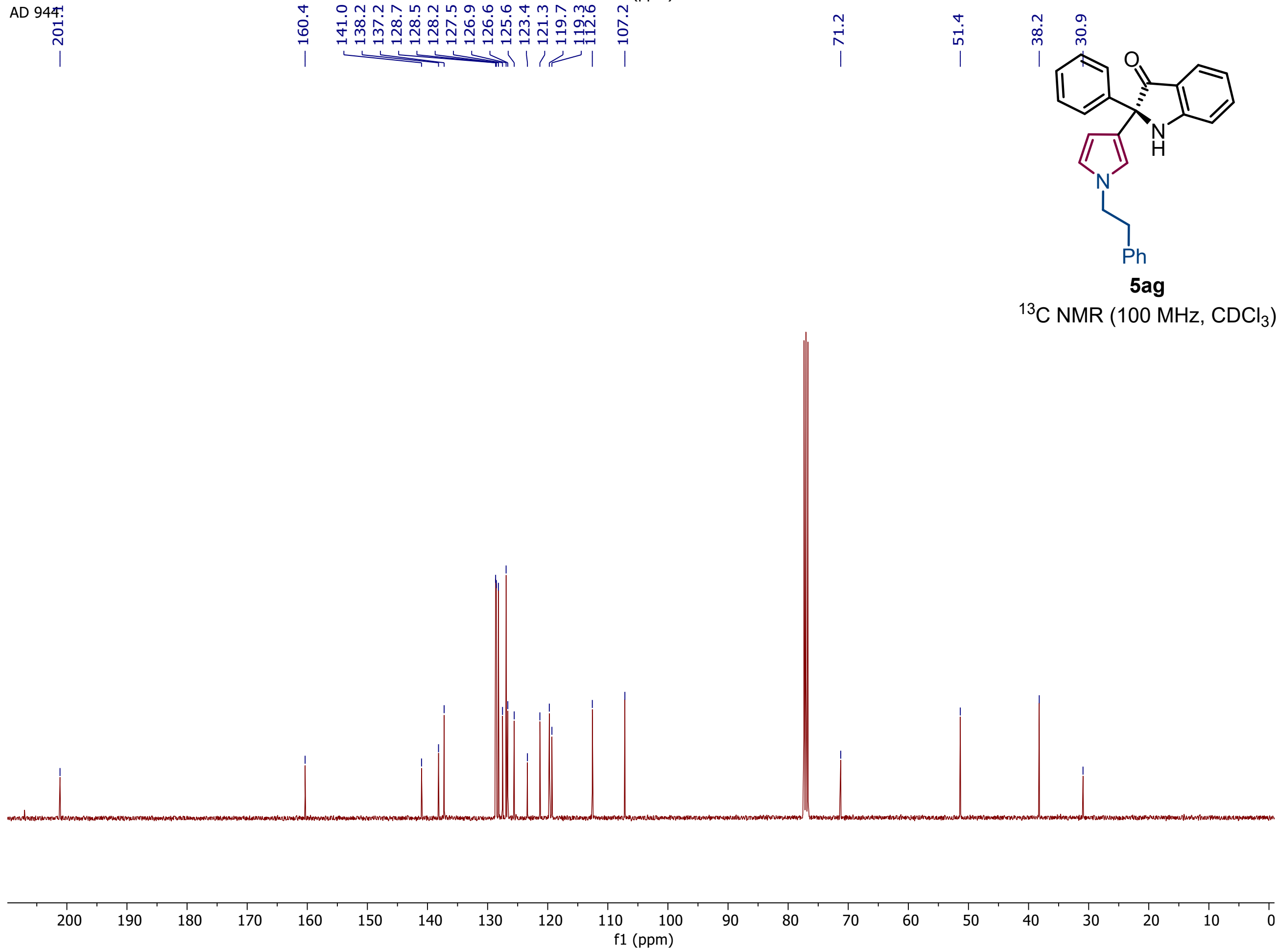
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	39.967	22446230	96.75	115926
2	2998 PDA 254.0 nm (2998 (200-400)nm)	51.010	753646	3.25	4666



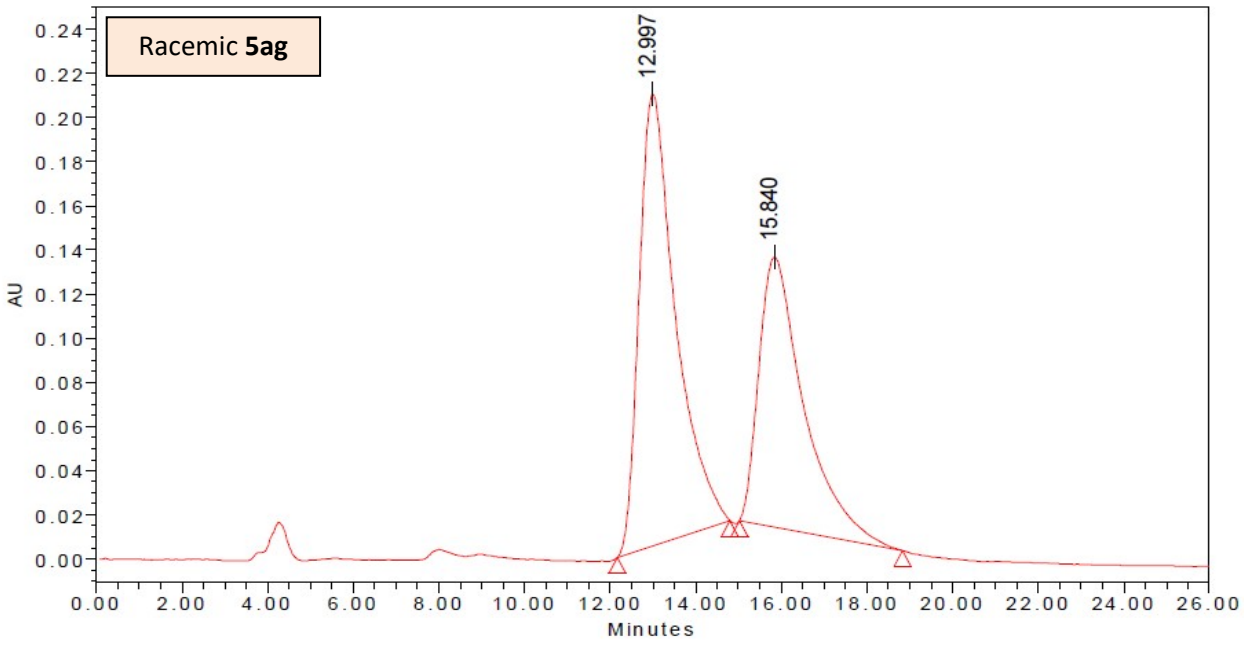
5ag

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



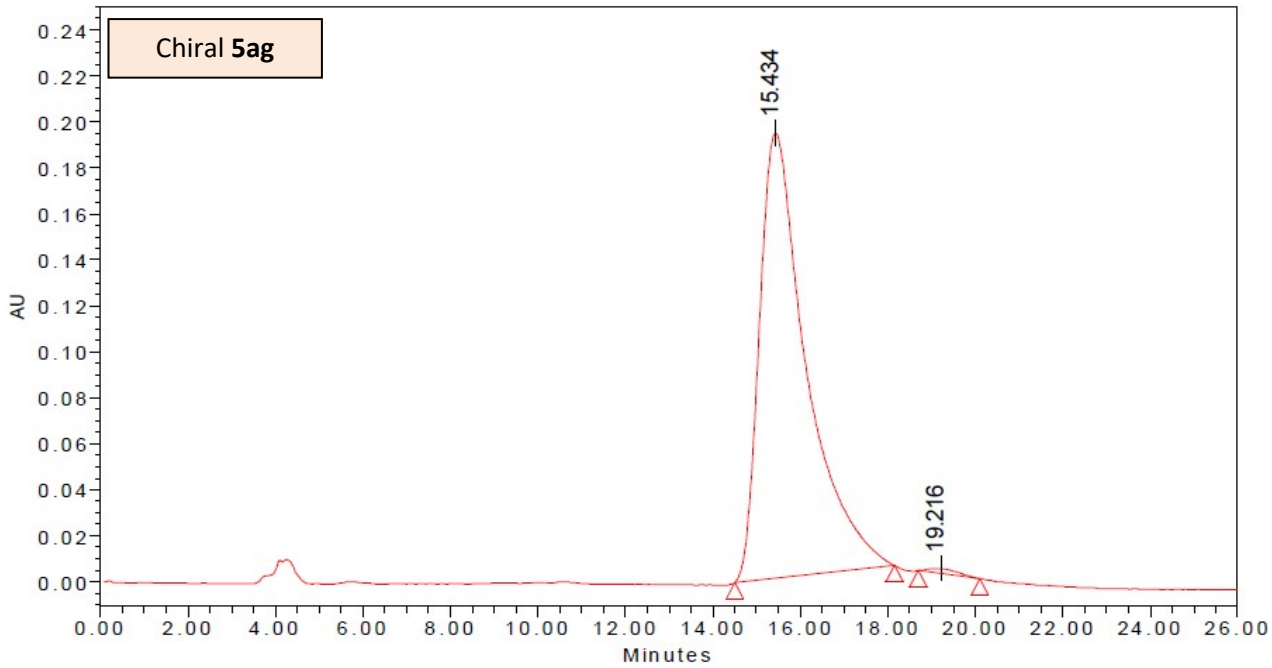
5ag

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



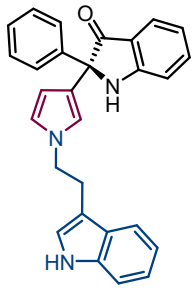
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	12.997	12157492	57.67	204772
2	2998 PDA 254.0 nm (2998 (200-400)nm)	15.840	8924581	42.33	122463



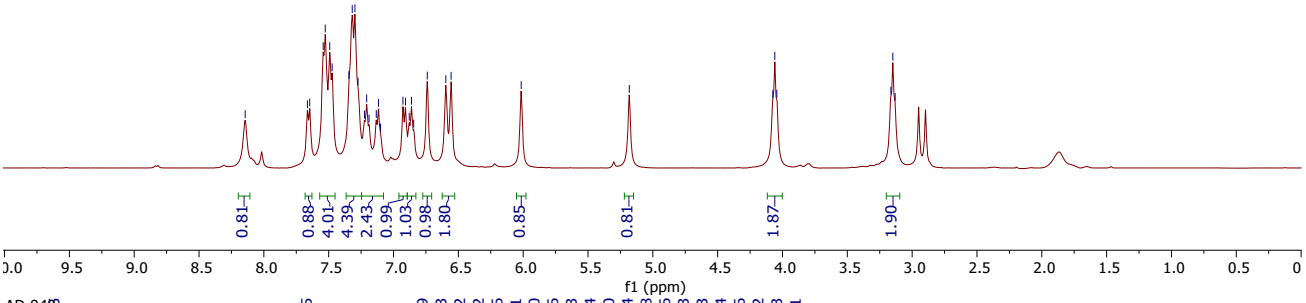
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

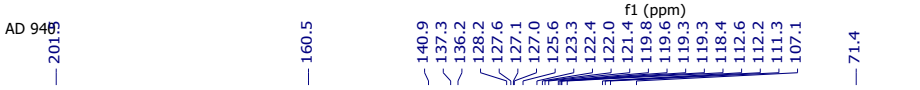
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	15.434	14401137	99.31	193641
2	2998 PDA 254.0 nm (2998 (200-400)nm)	19.216	100739	0.69	2195

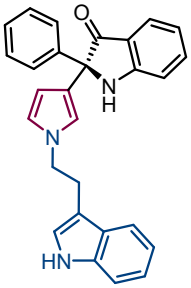


5ah

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

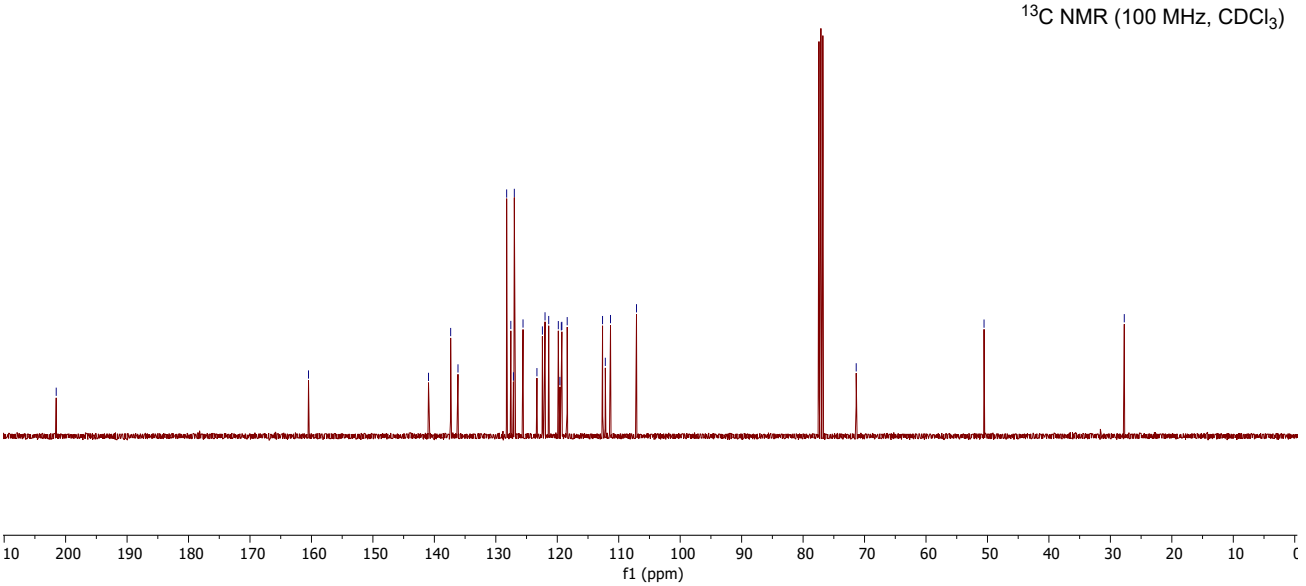


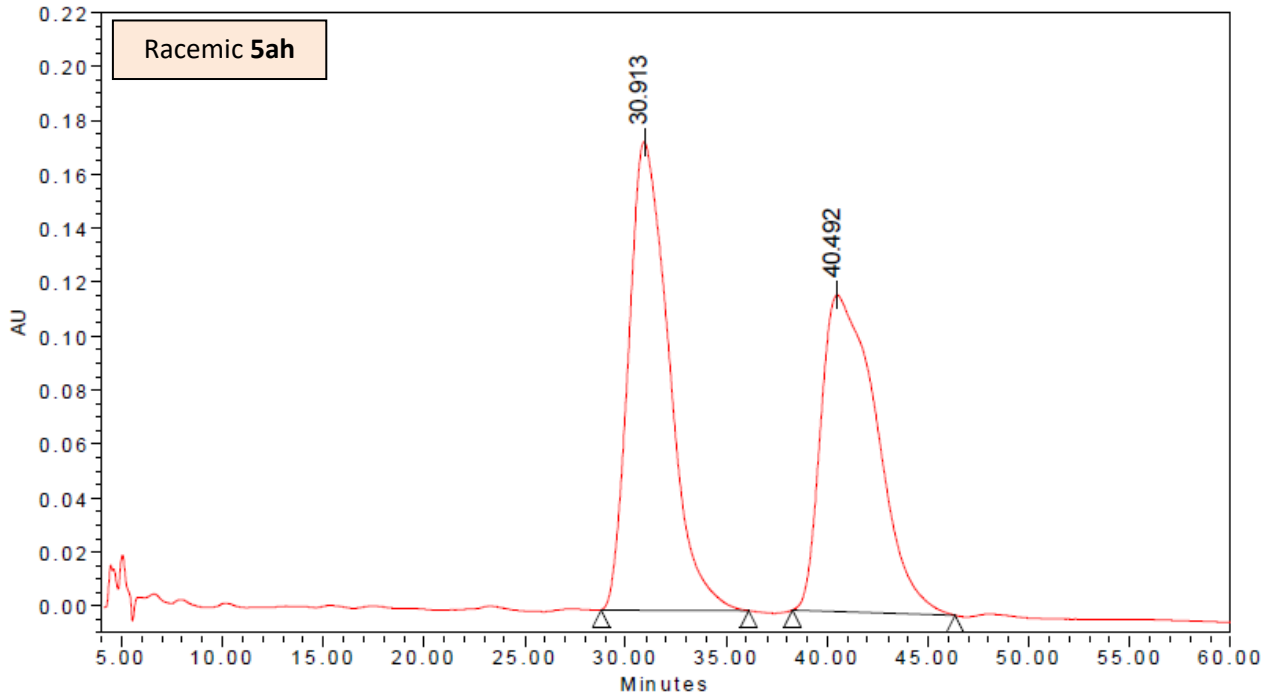




5ah

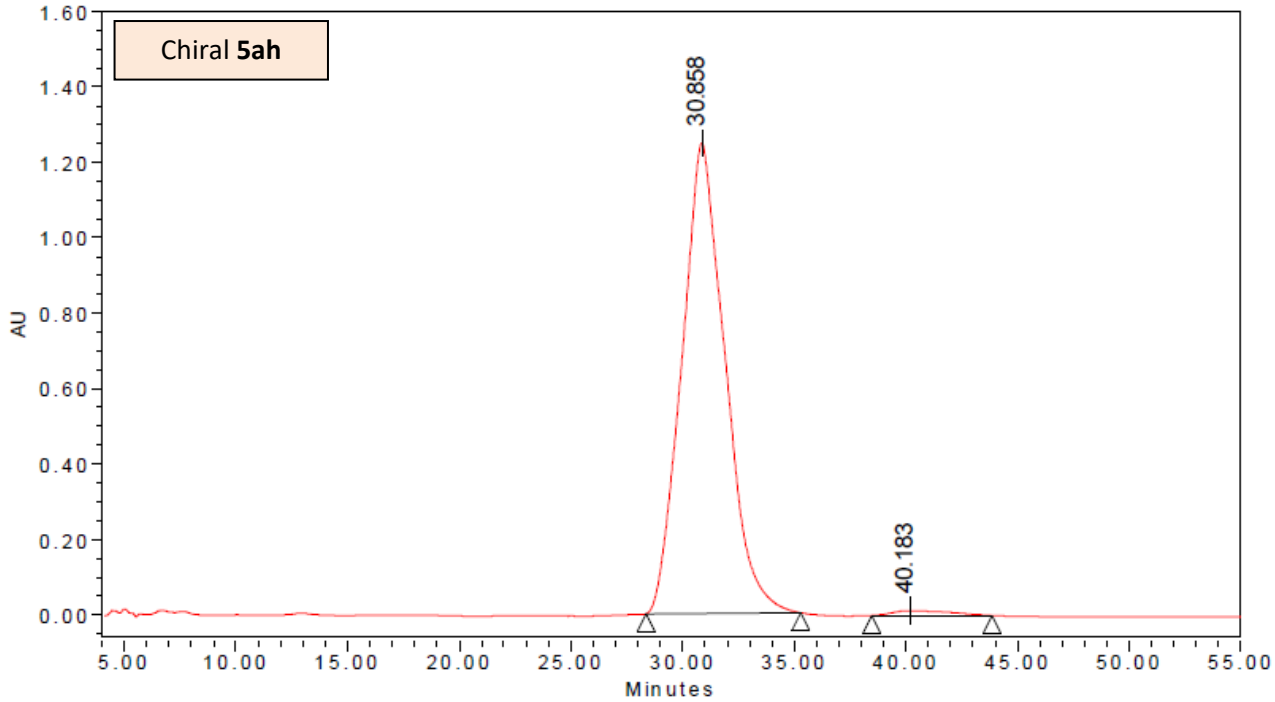
^{13}C NMR (100 MHz, $CDCl_3$)





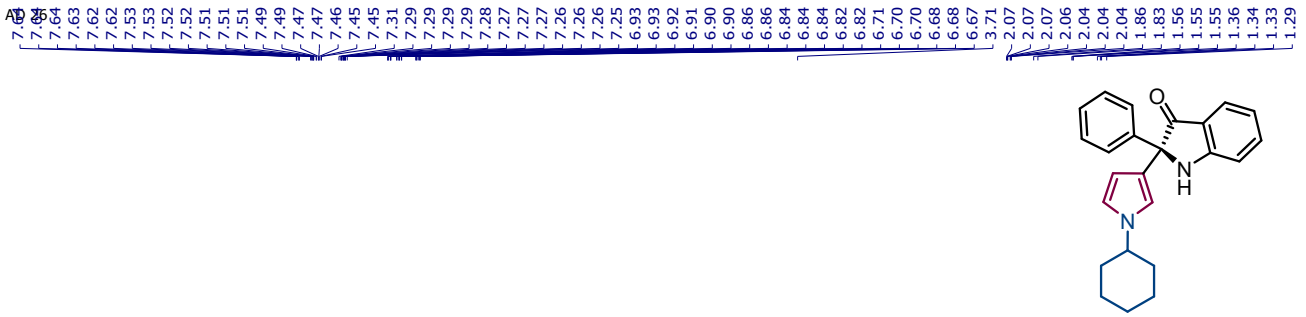
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	30.913	24078620	51.69	173486
2	2998 PDA 254.0 nm (2998 (200-400)nm)	40.492	22502693	48.31	117246



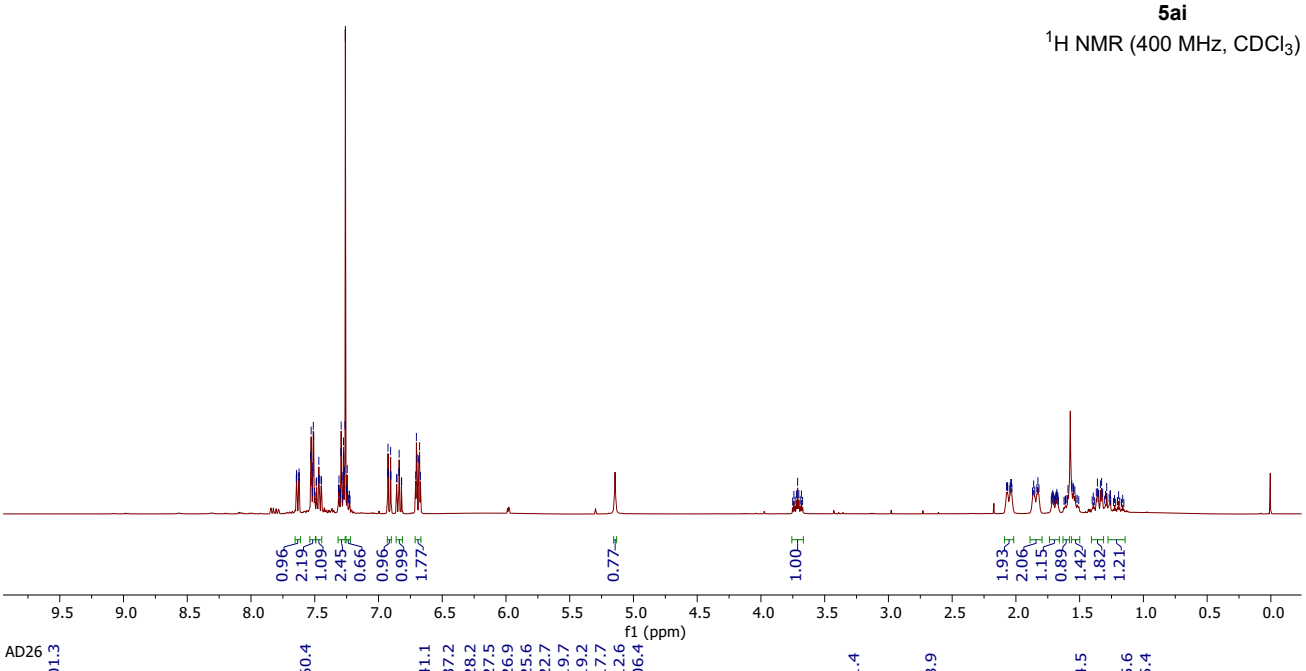
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

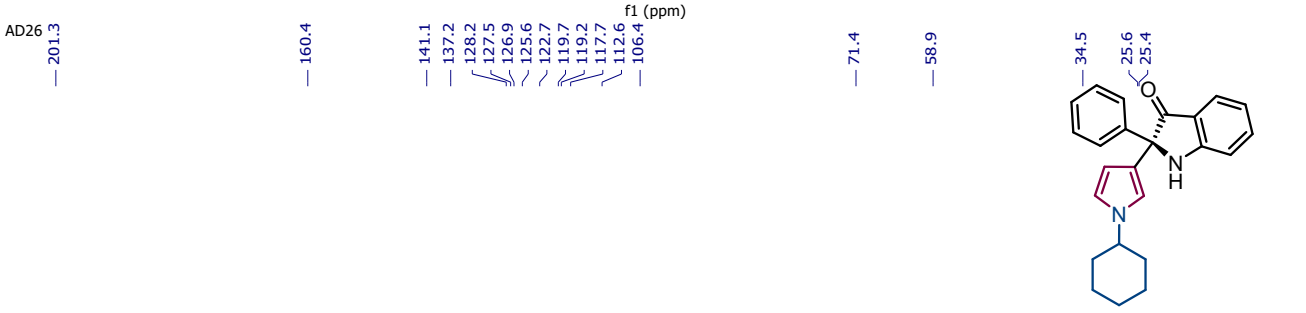
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	30.858	167599298	98.70	1247262
2	2998 PDA 254.0 nm (2998 (200-400)nm)	40.183	2206670	1.30	12435



5ai

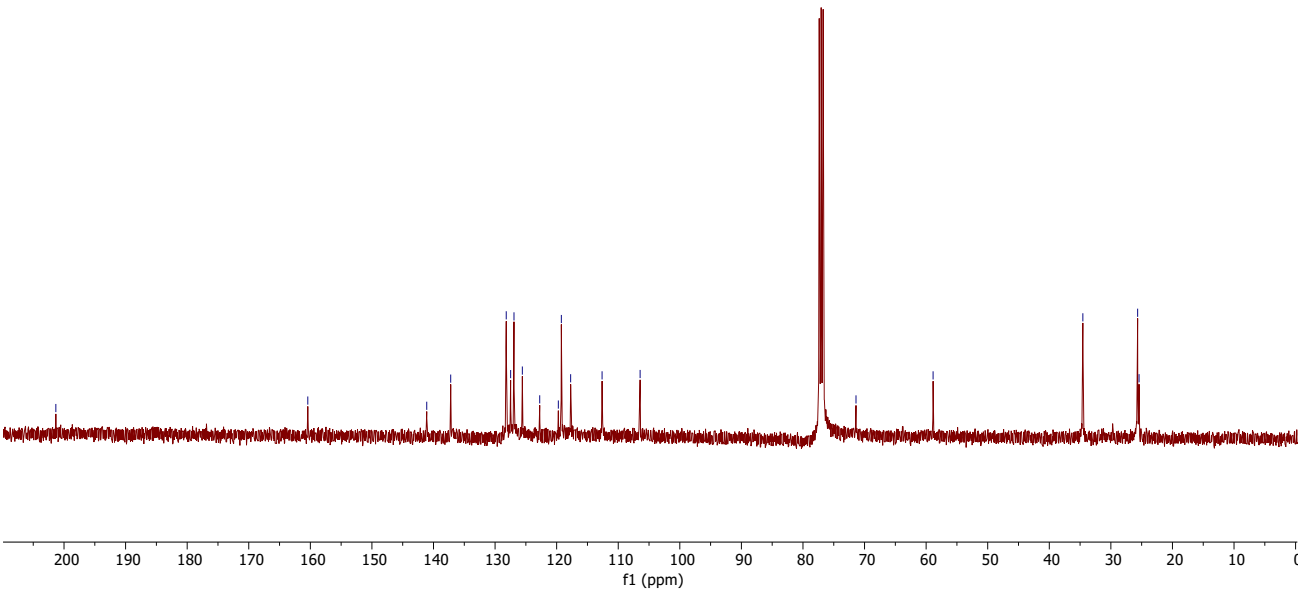
^{1}H NMR (400 MHz, $CDCl_3$)

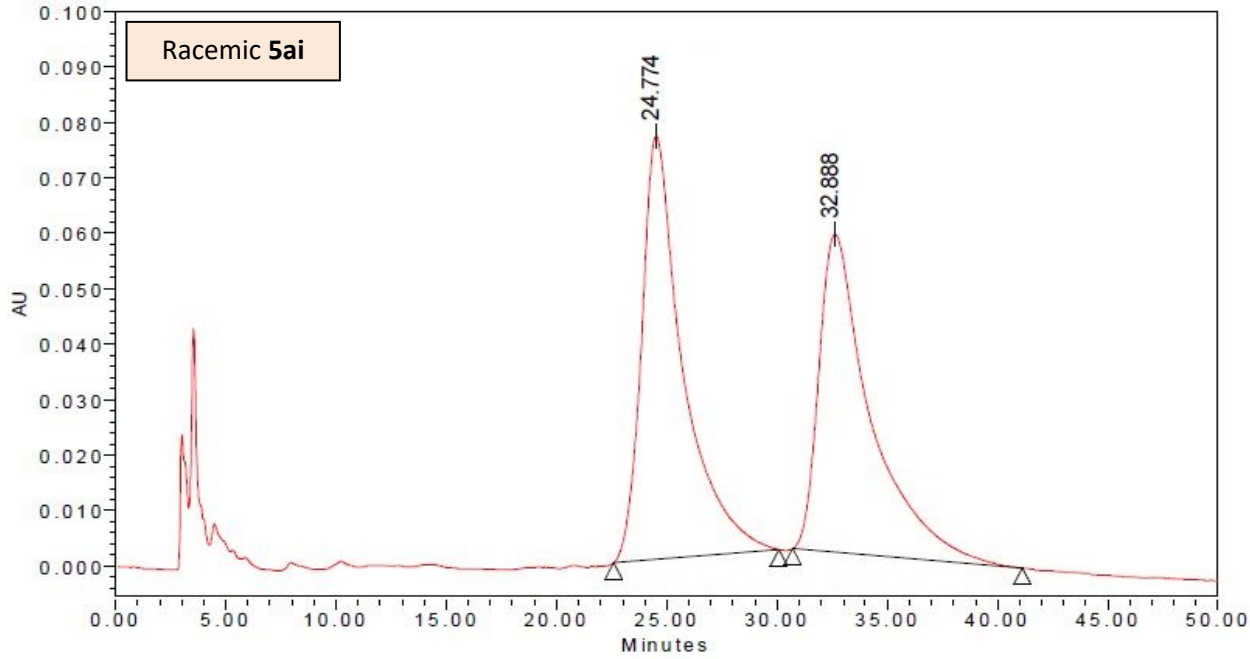




5ai

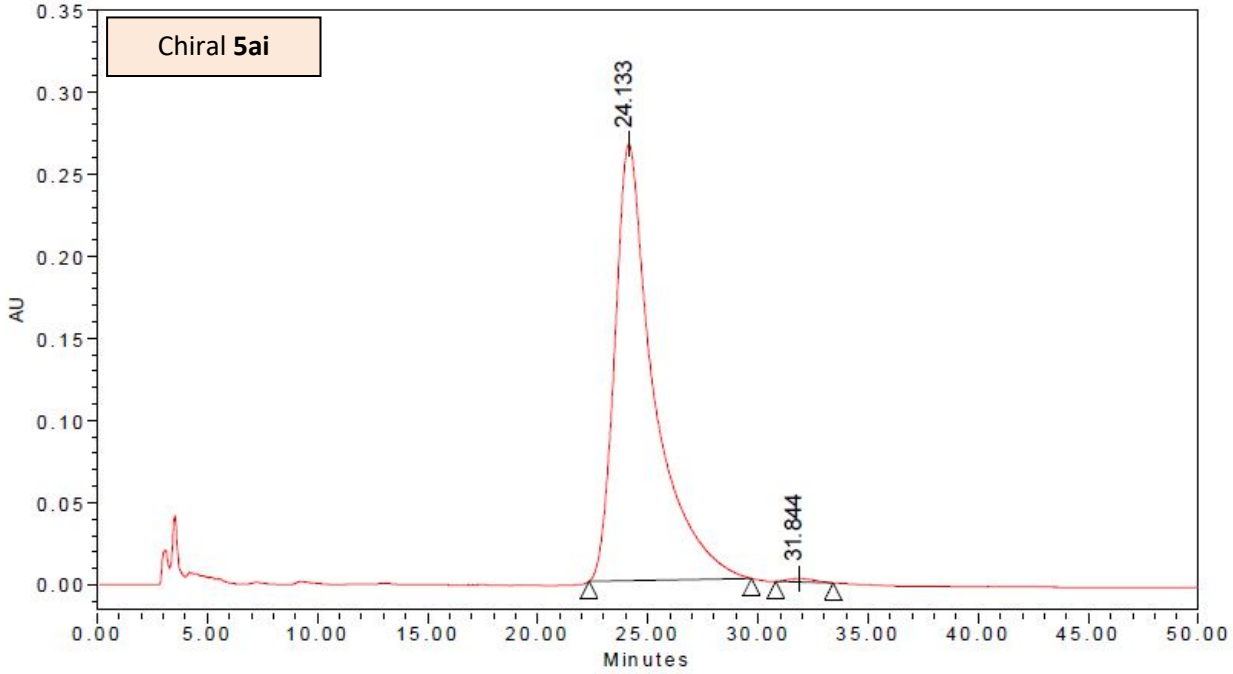
^{13}C NMR (100 MHz, $CDCl_3$)





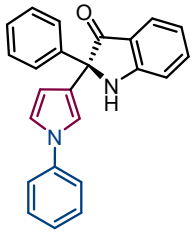
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	24.774	9954689	51.58	76326
2	2998 PDA 254.0 nm (2998 (200-400)nm)	32.888	9345920	48.42	57278



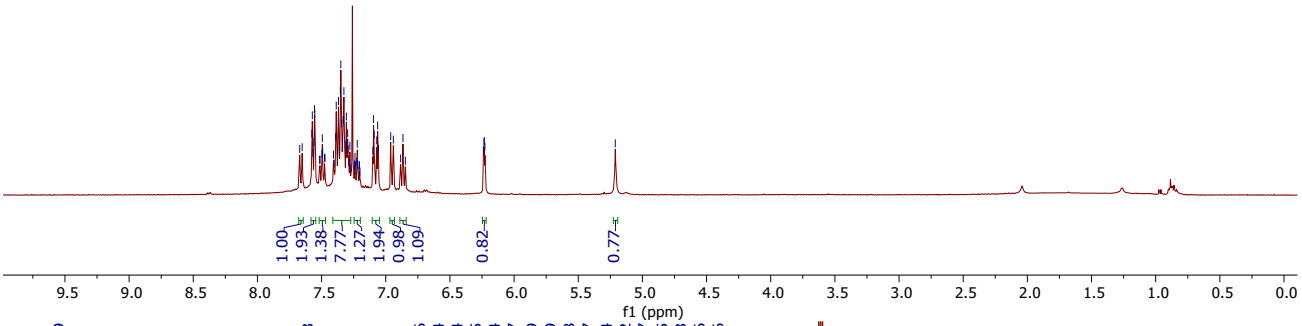
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

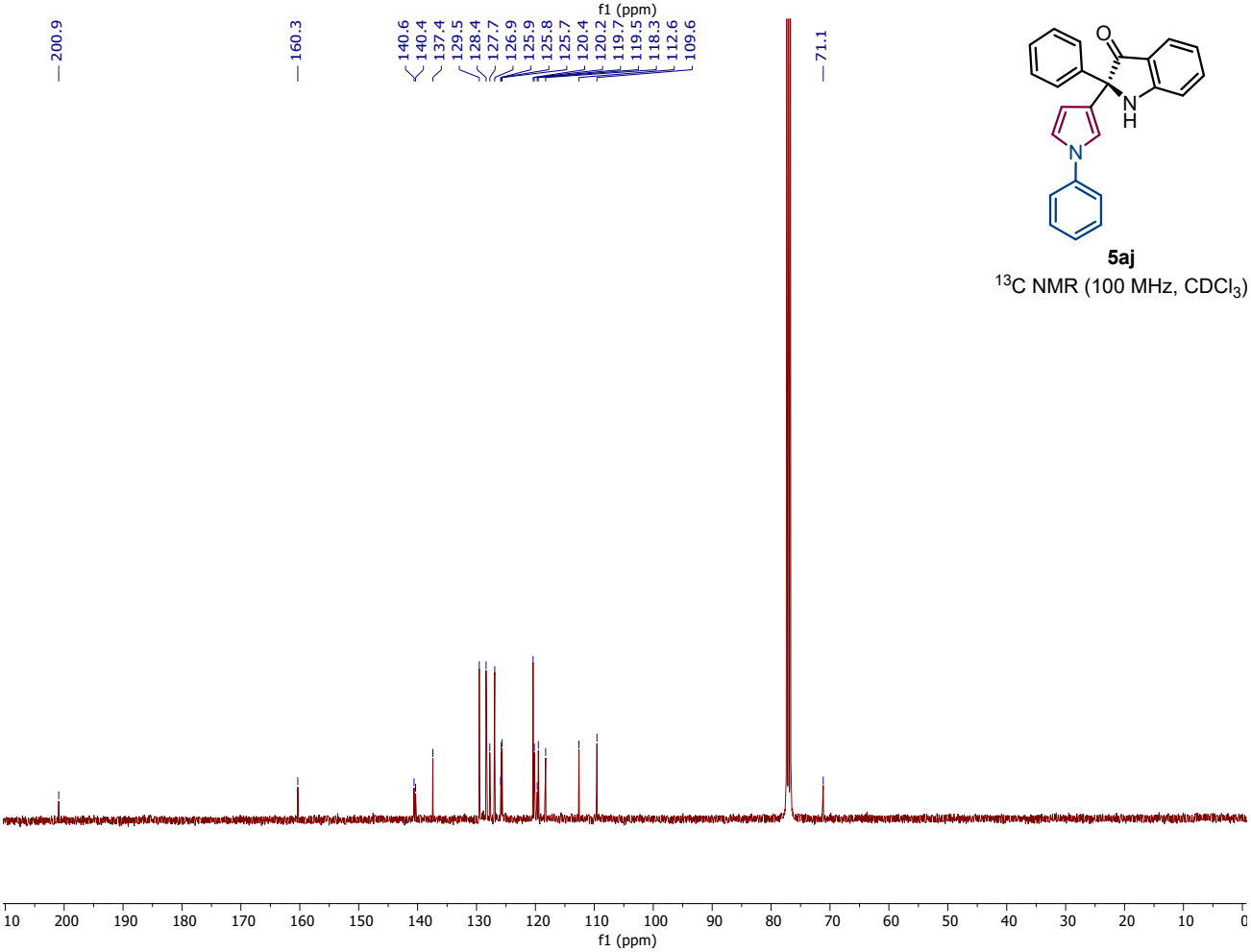
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	24.133	32745997	99.47	265847
2	2998 PDA 254.0 nm (2998 (200-400)nm)	31.844	173406	0.53	2078



5aj

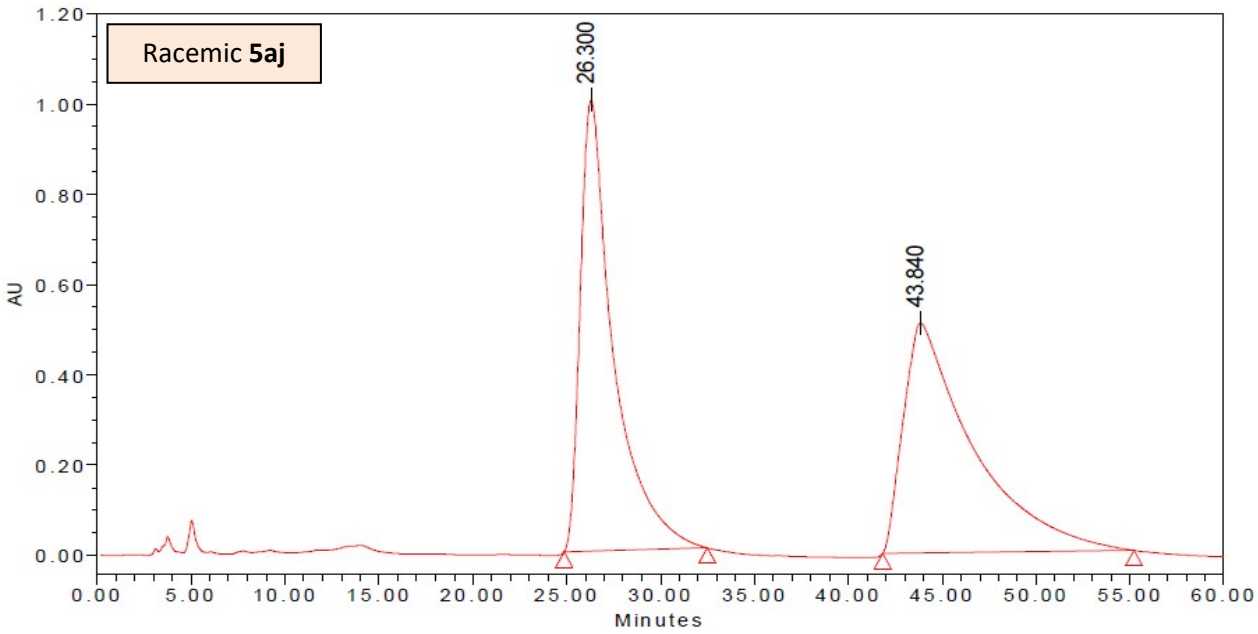
^{1}H NMR (400 MHz, $CDCl_3$)





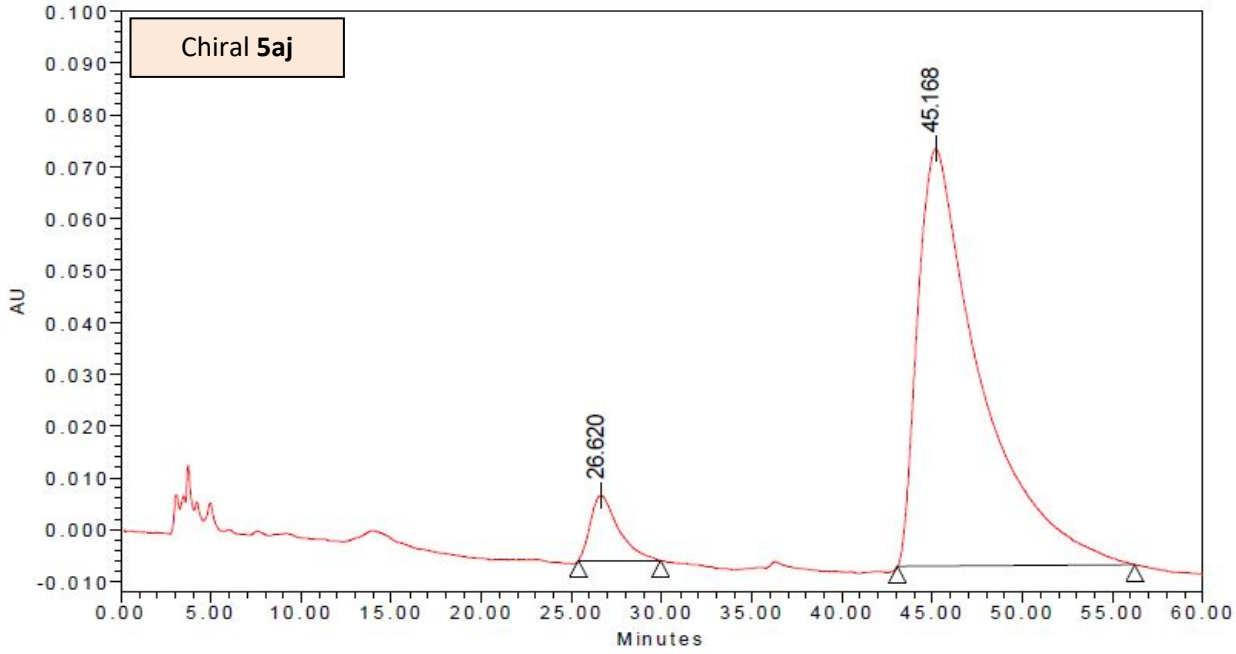
5aj

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



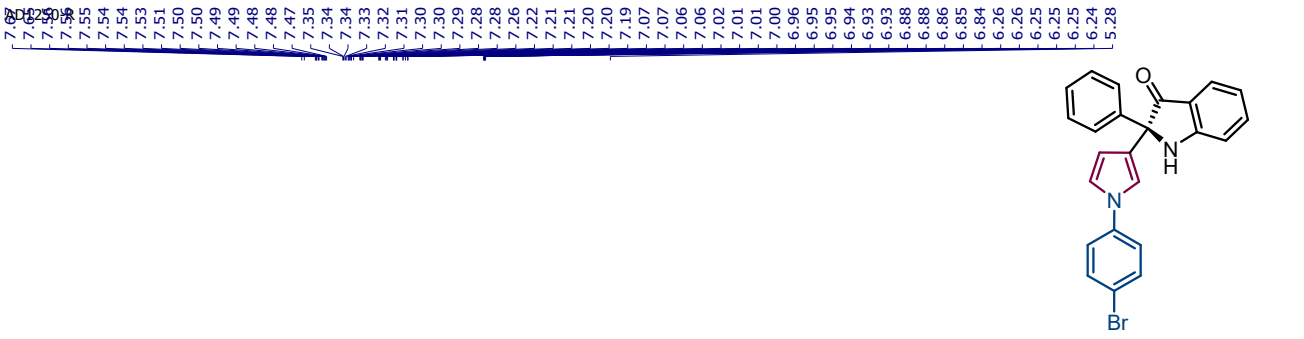
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	26.300	123372346	48.59	999983
2	2998 PDA 254.0 nm (2998 (200-400)nm)	43.840	130532728	51.41	509082



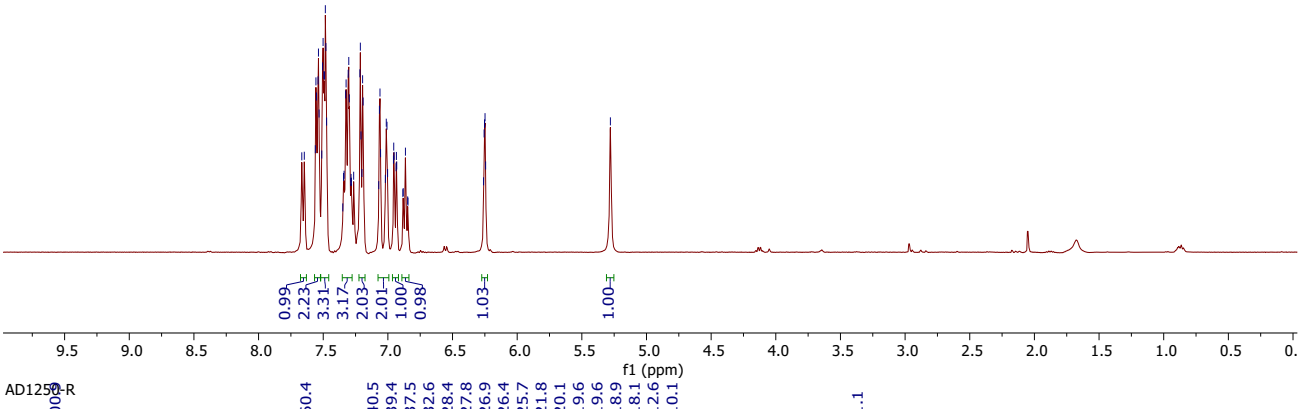
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

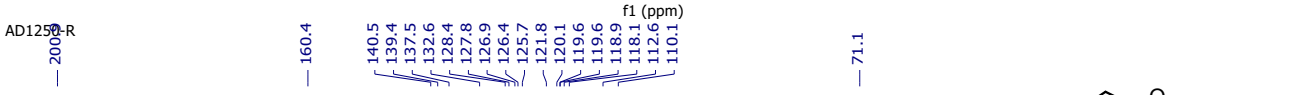
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	26.620	1360519	6.55	12618
2	2998 PDA 254.0 nm (2998 (200-400)nm)	45.168	19402108	93.45	80450

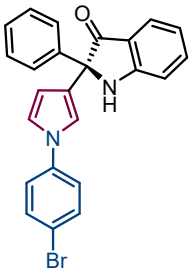


5ak

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

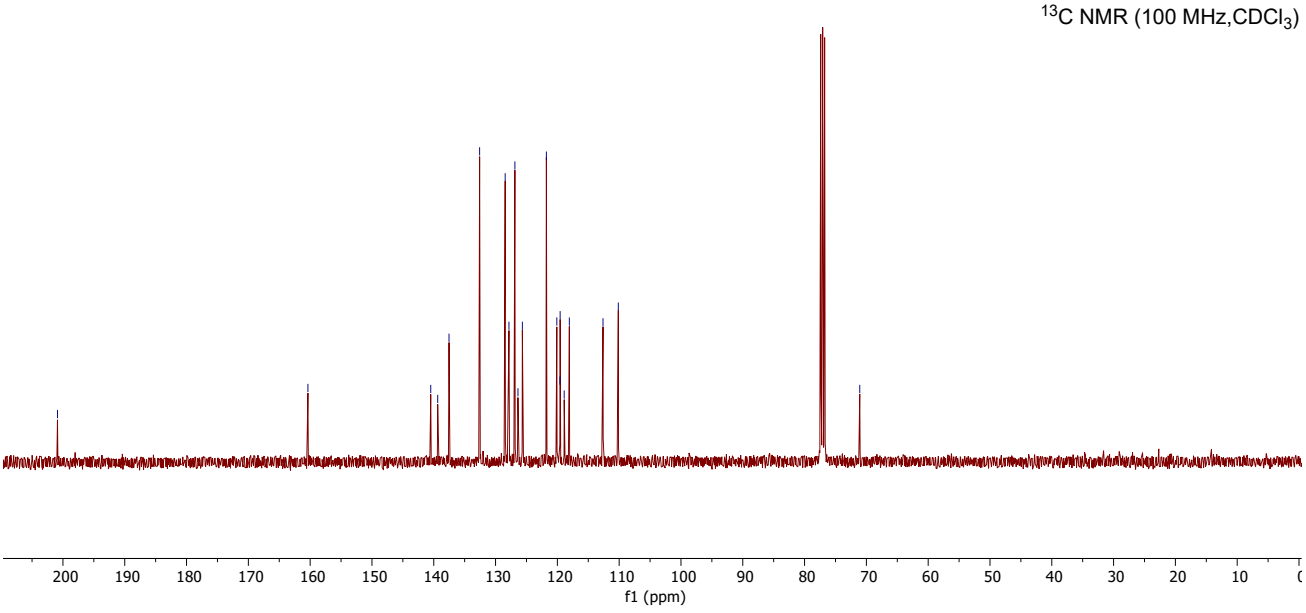


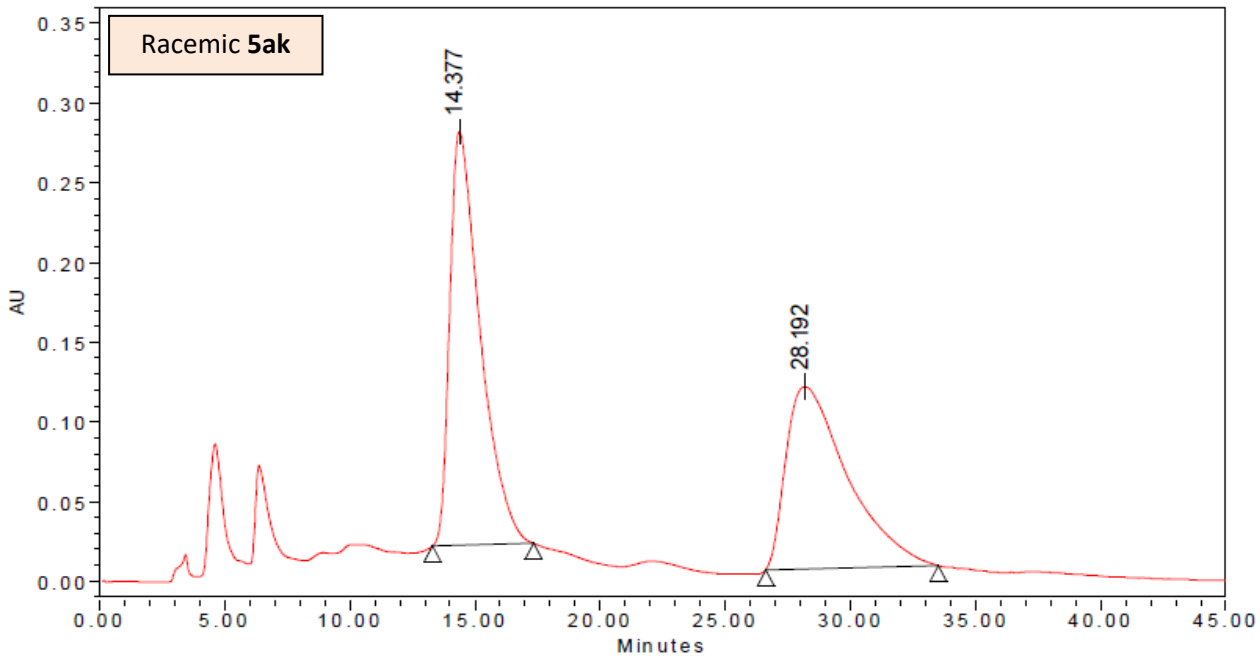




5ak

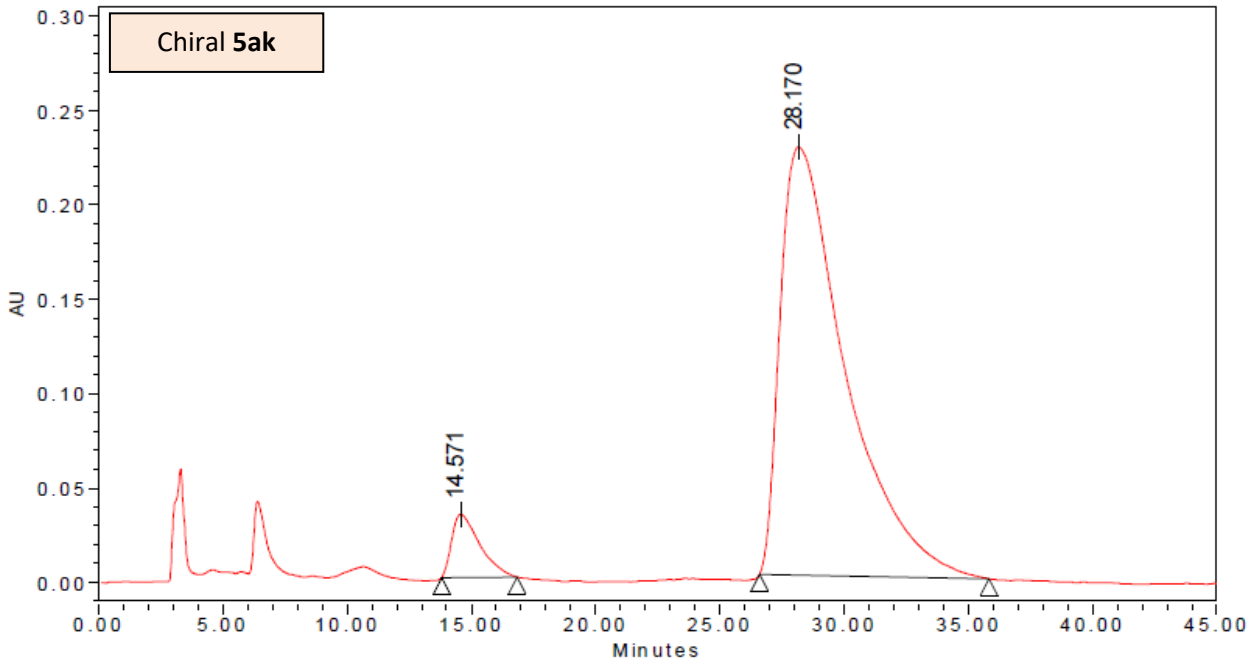
^{13}C NMR (100 MHz,$CDCl_3$)





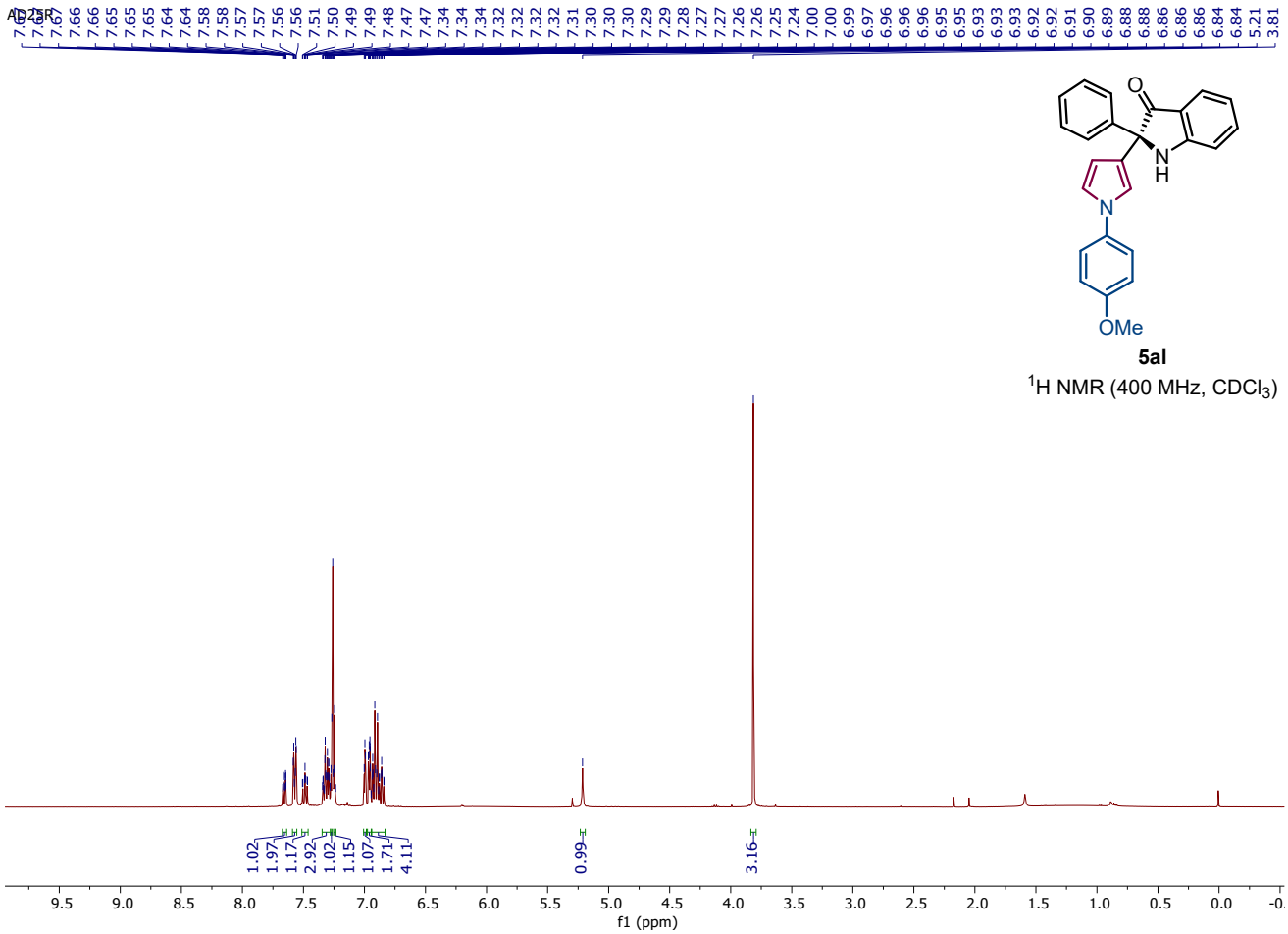
Processed Channel: 2998 PDA 280.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 280.0 nm (2998 (200-400)nm)	14.377	22011078	53.02	259822
2	2998 PDA 280.0 nm (2998 (200-400)nm)	28.192	19504889	46.98	114222



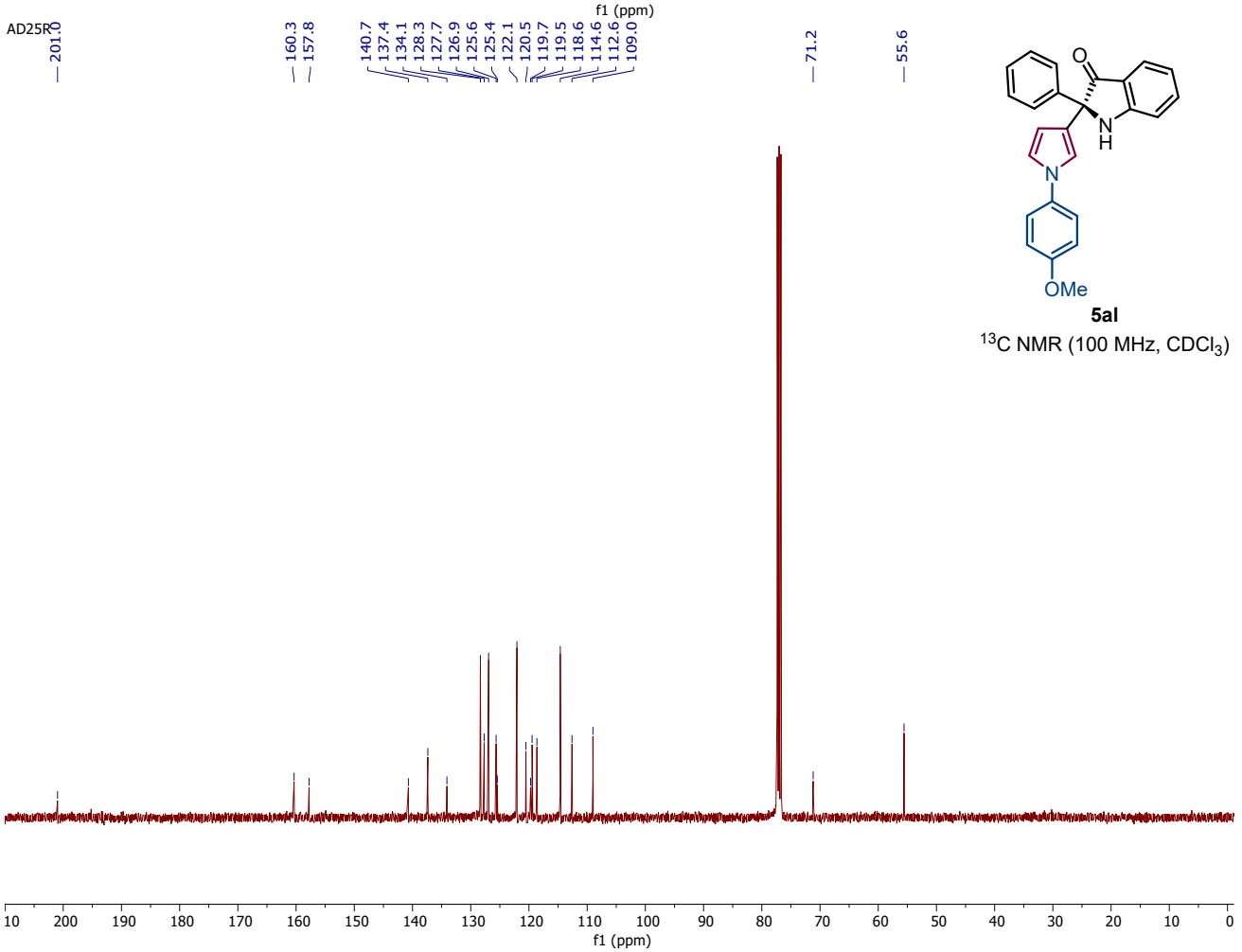
Processed Channel: 2998 PDA 280.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 280.0 nm (2998 (200-400)nm)	14.571	2619993	5.96	33356
2	2998 PDA 280.0 nm (2998 (200-400)nm)	28.170	41336693	94.04	226714



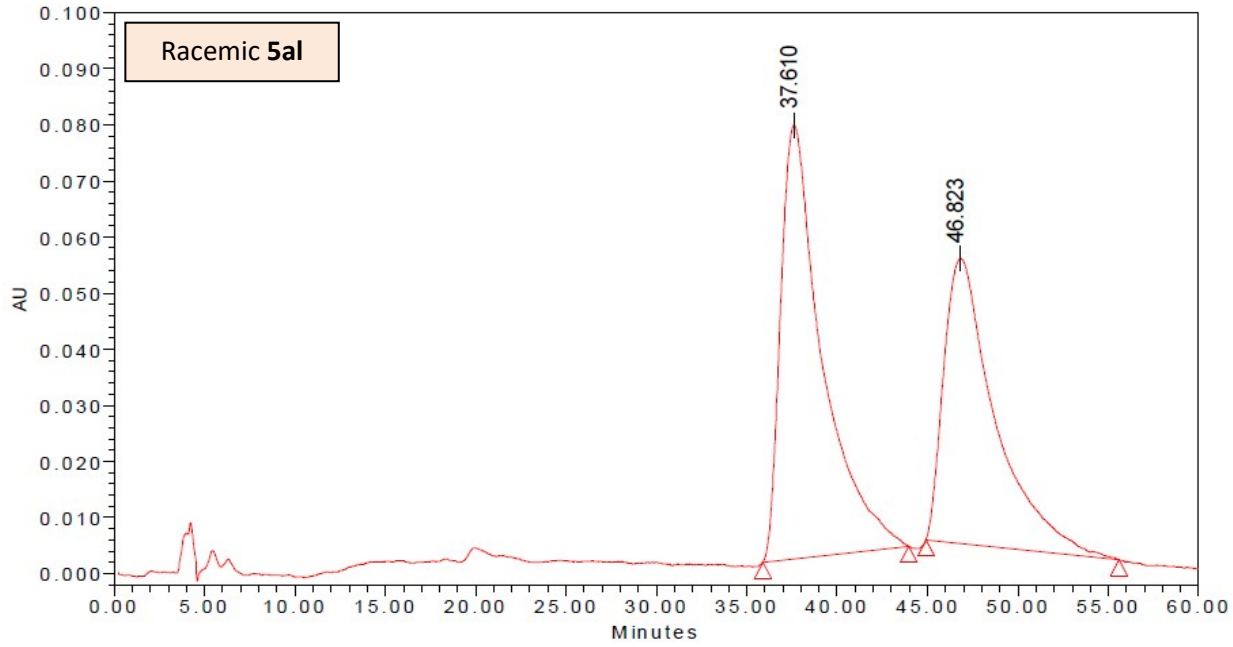
5al

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



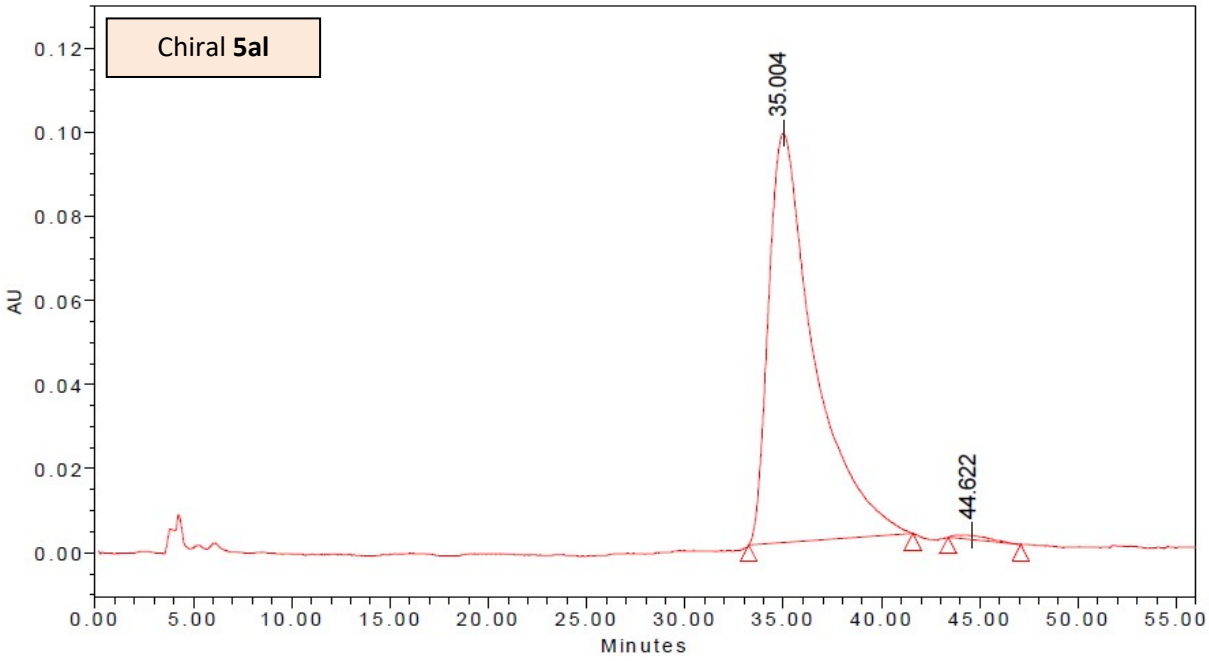
5al

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



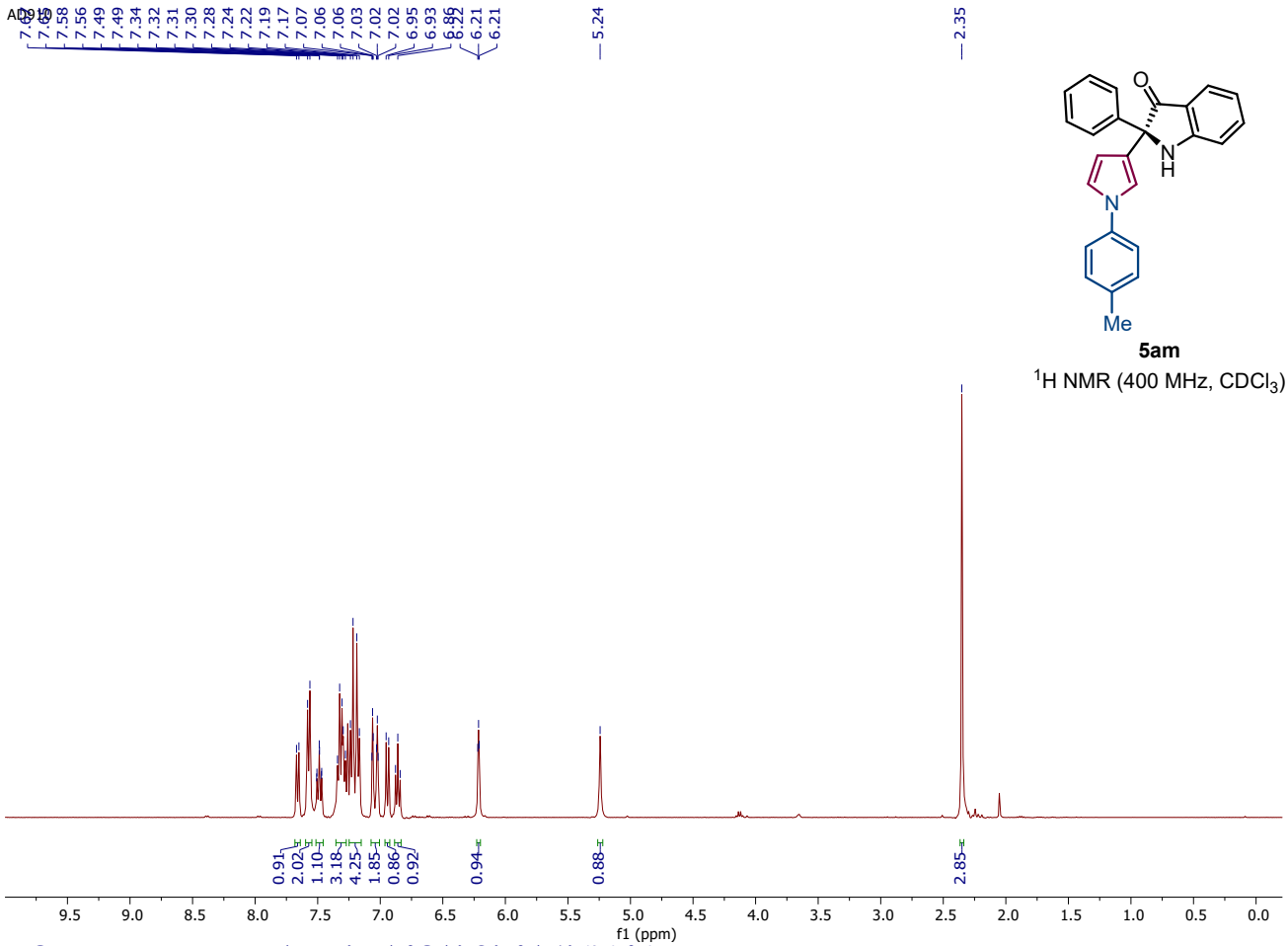
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	37.610	12366630	55.24	77344
2	2998 PDA 254.0 nm (2998 (200-400)nm)	46.823	10020162	44.76	50846



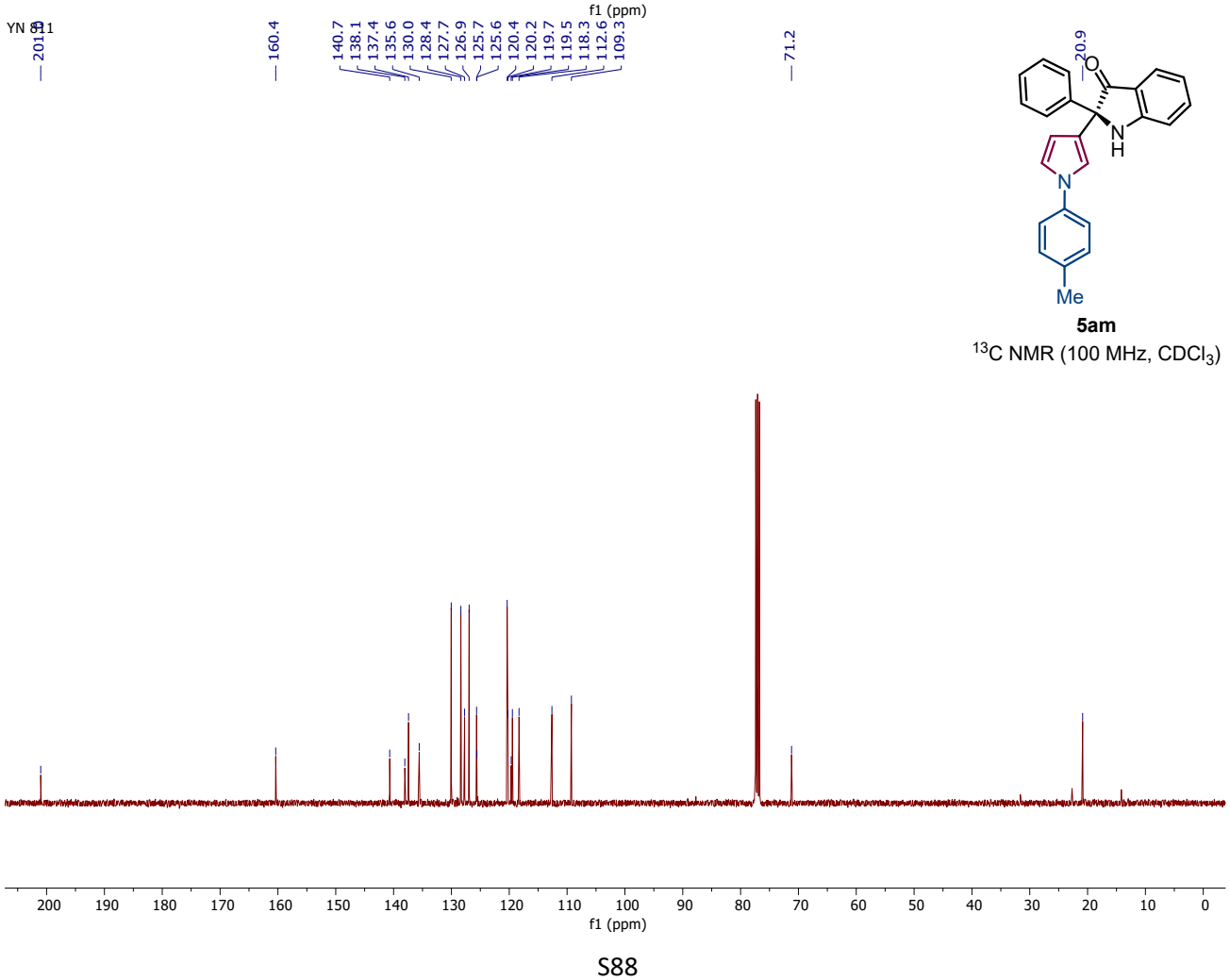
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	35.004	15738426	99.20	97287
2	2998 PDA 254.0 nm (2998 (200-400)nm)	44.622	127385	0.80	1044



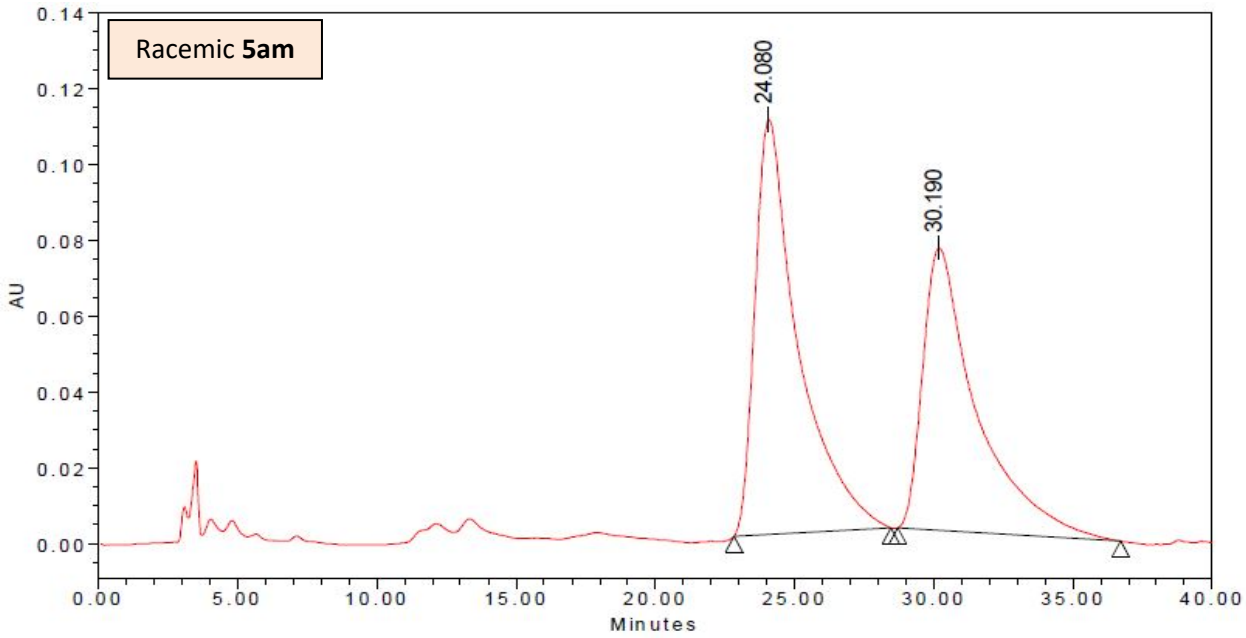
5am

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



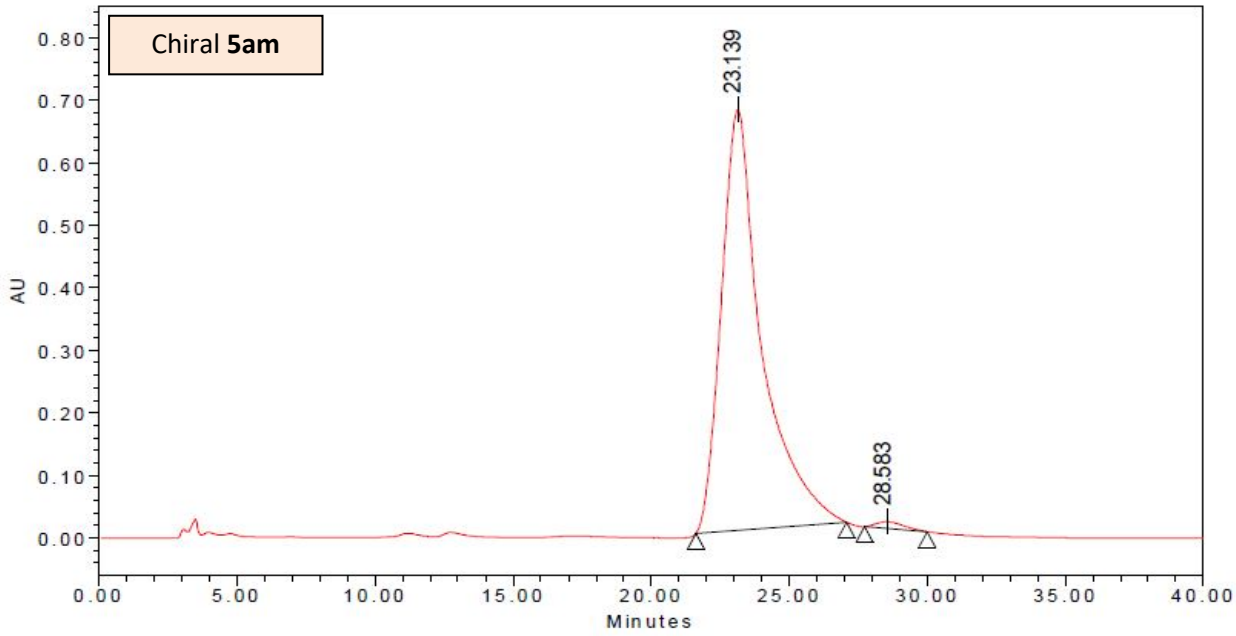
5am

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



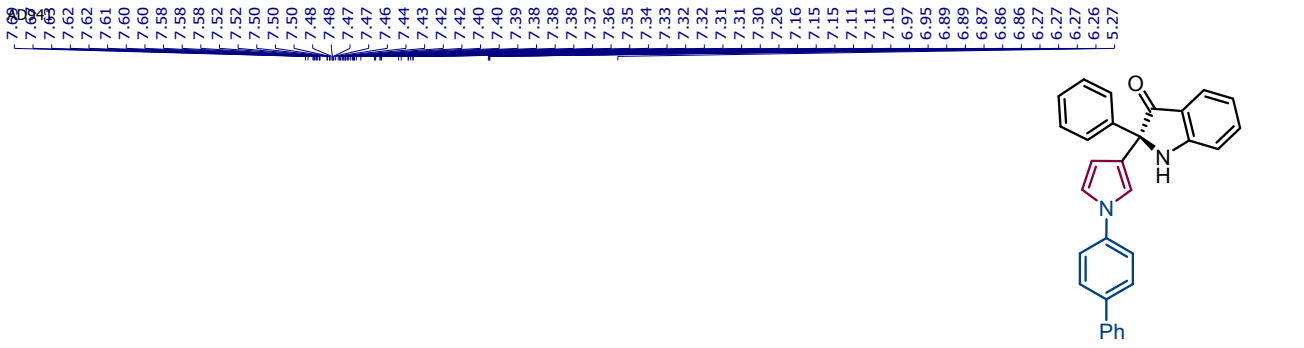
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	24.080	11833258	54.26	109321
2	2998 PDA 254.0 nm (2998 (200-400)nm)	30.190	9975049	45.74	74464



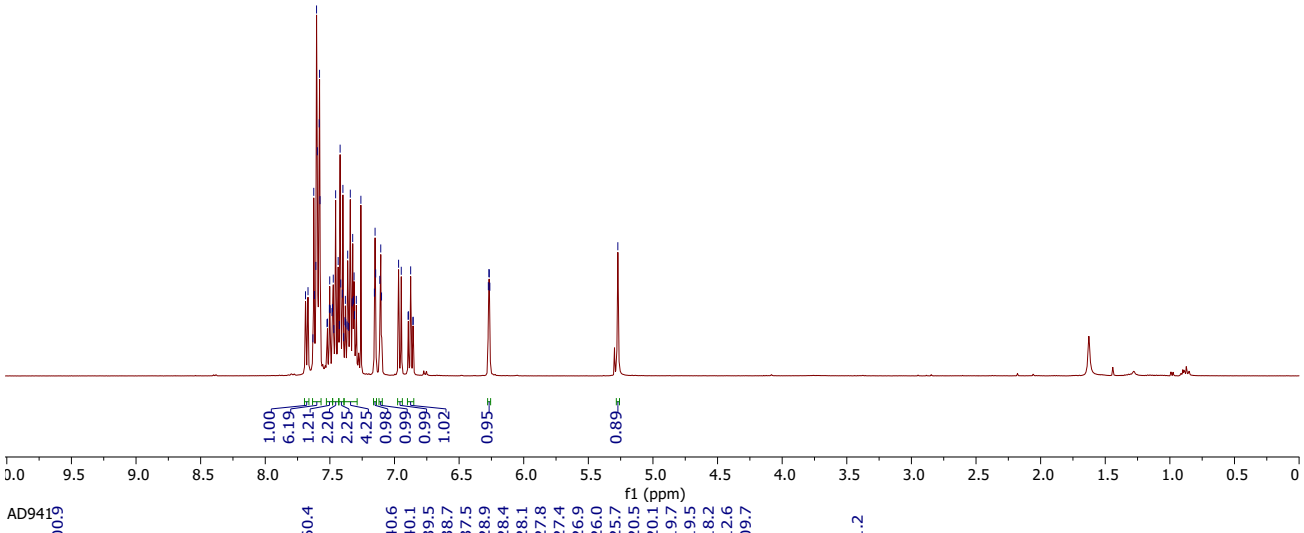
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

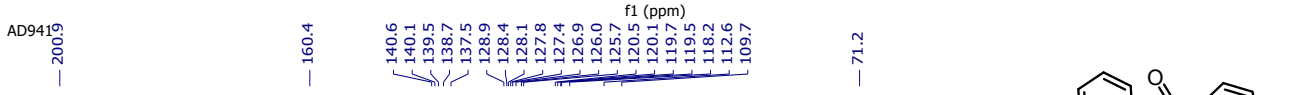
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	23.139	68682260	98.93	672815
2	2998 PDA 254.0 nm (2998 (200-400)nm)	28.583	745655	1.07	10760

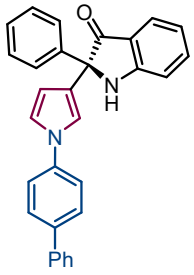


5an

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

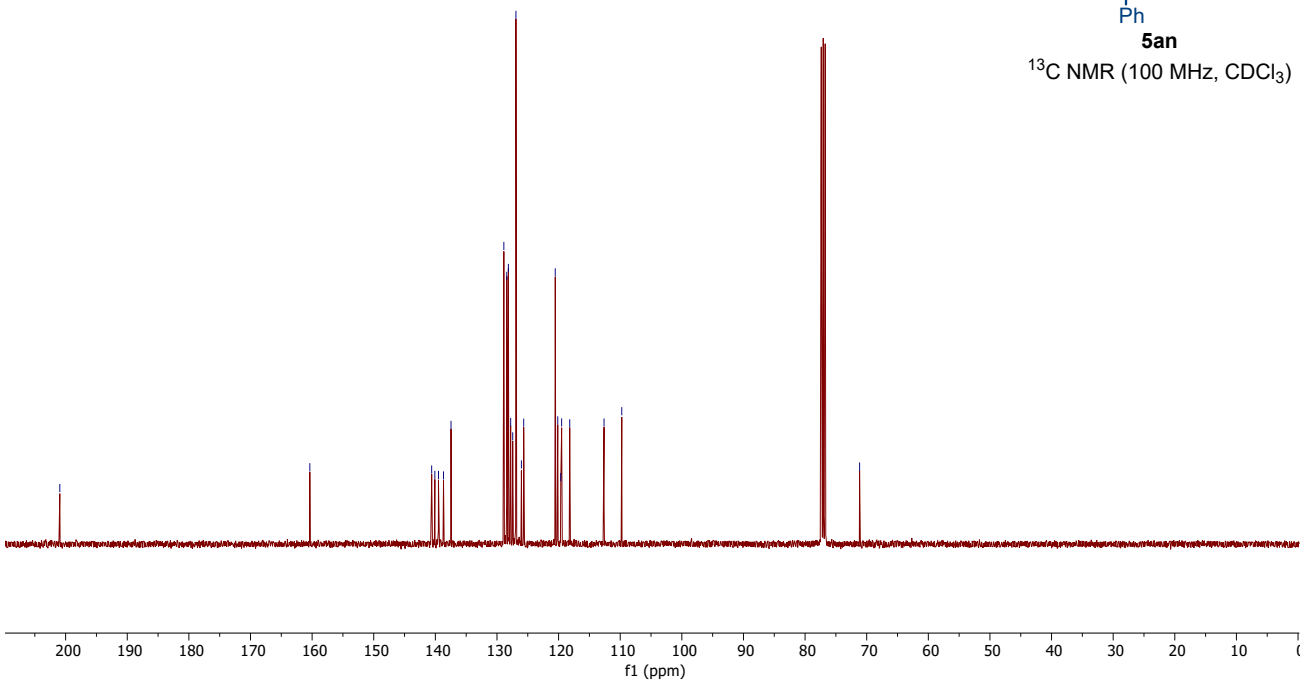


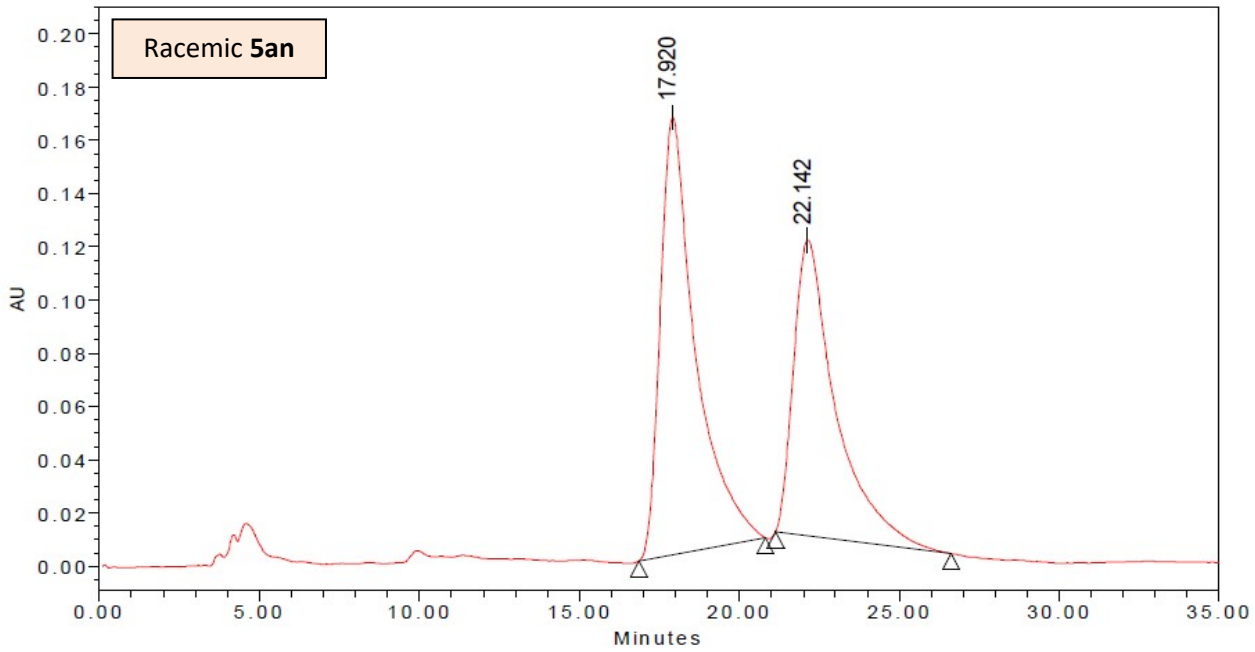




5an

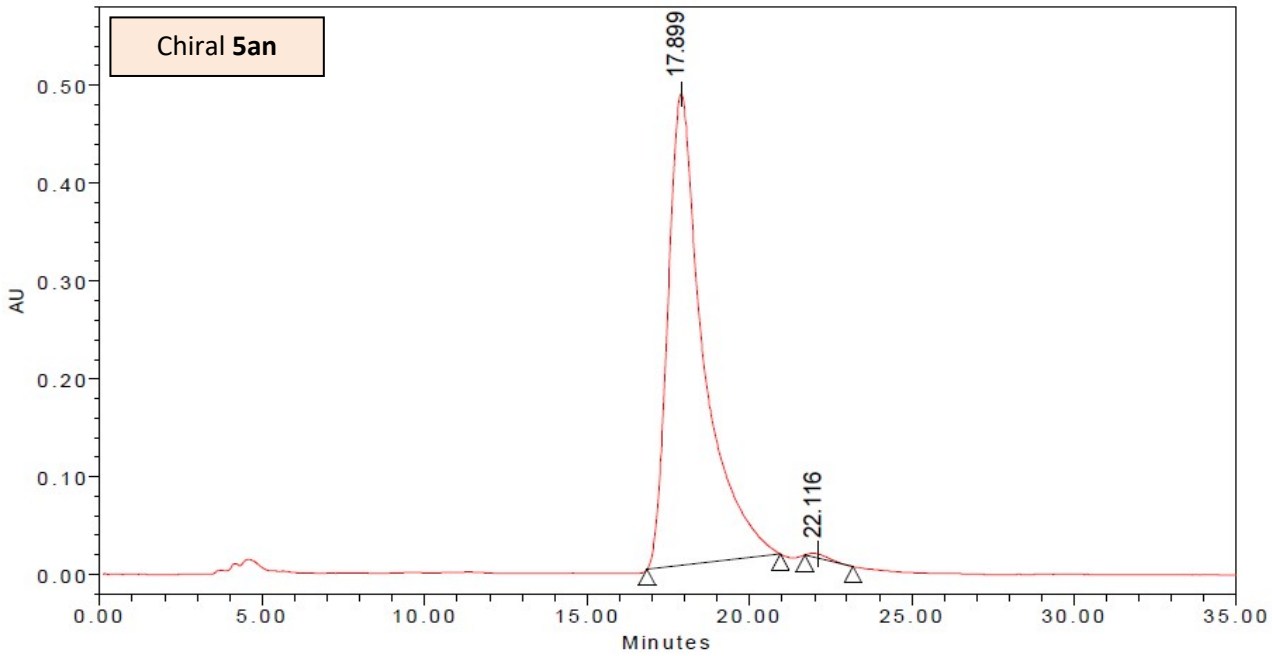
^{13}C NMR (100 MHz, $CDCl_3$)





Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

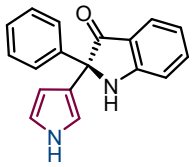
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	17.920	12620115	55.45	164189
2	2998 PDA 254.0 nm (2998 (200-400)nm)	22.142	10140931	44.55	111055



Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

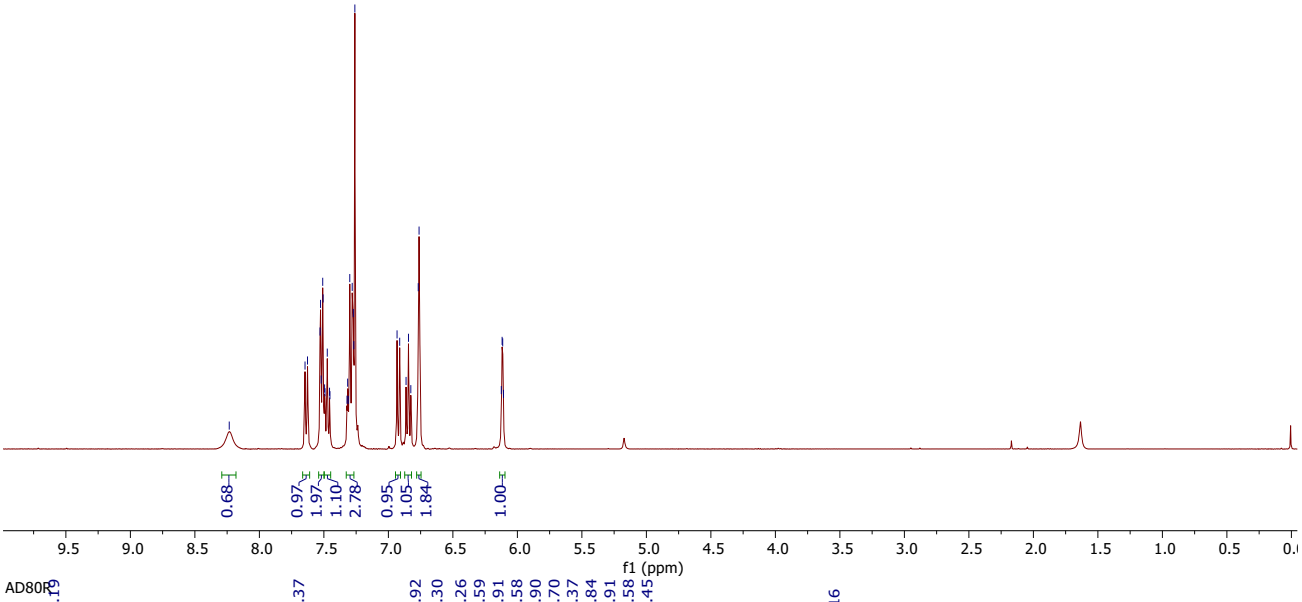
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	17.899	36726643	99.53	481751
2	2998 PDA 254.0 nm (2998 (200-400)nm)	22.116	174044	0.47	4370

AD80R

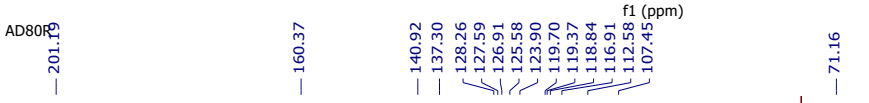


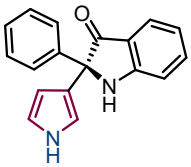
5ao

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



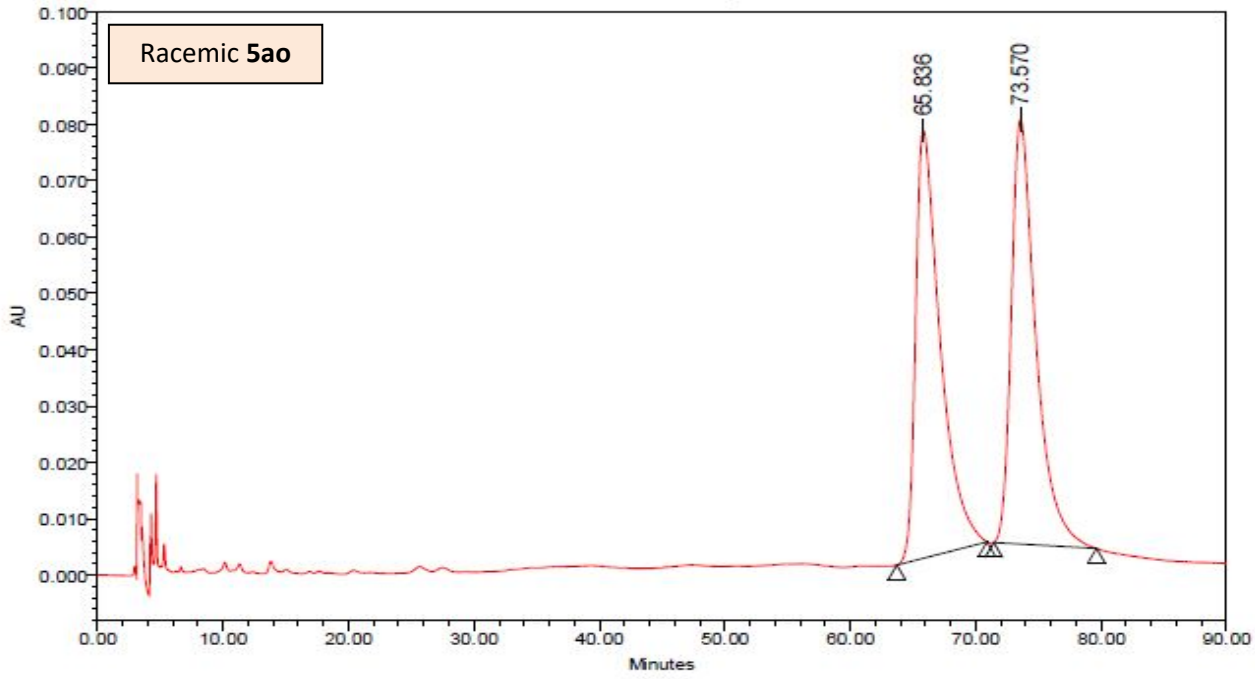
AD80R





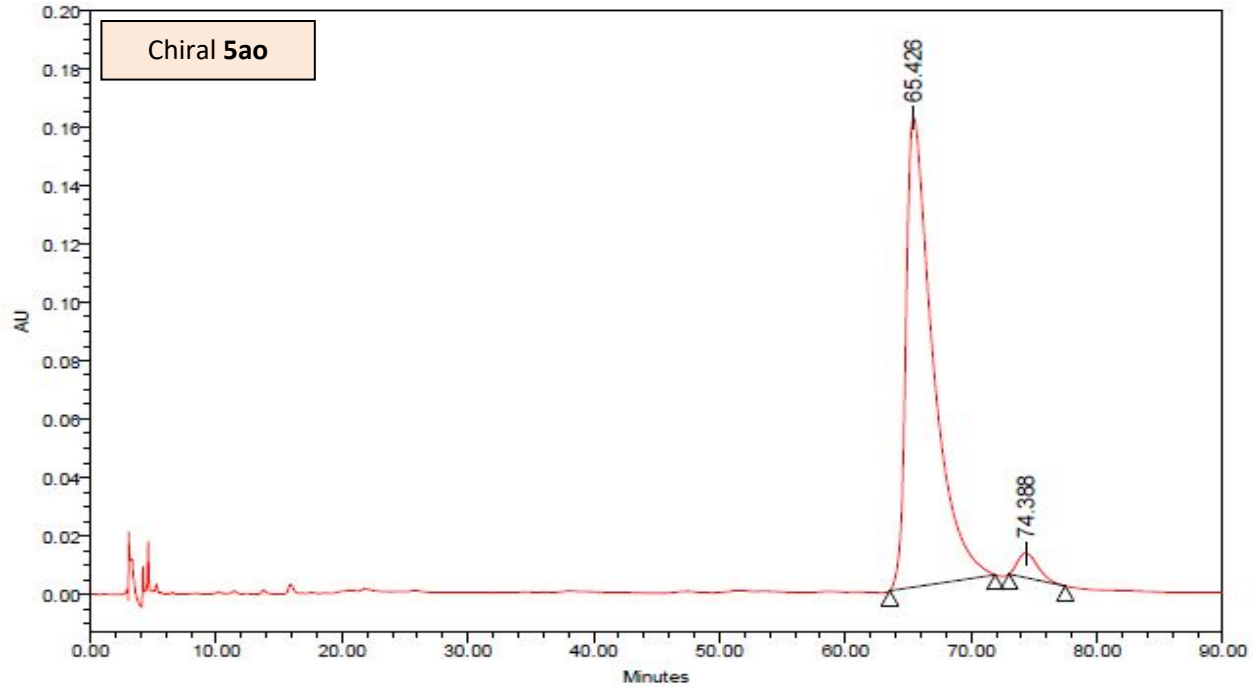
5ao

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



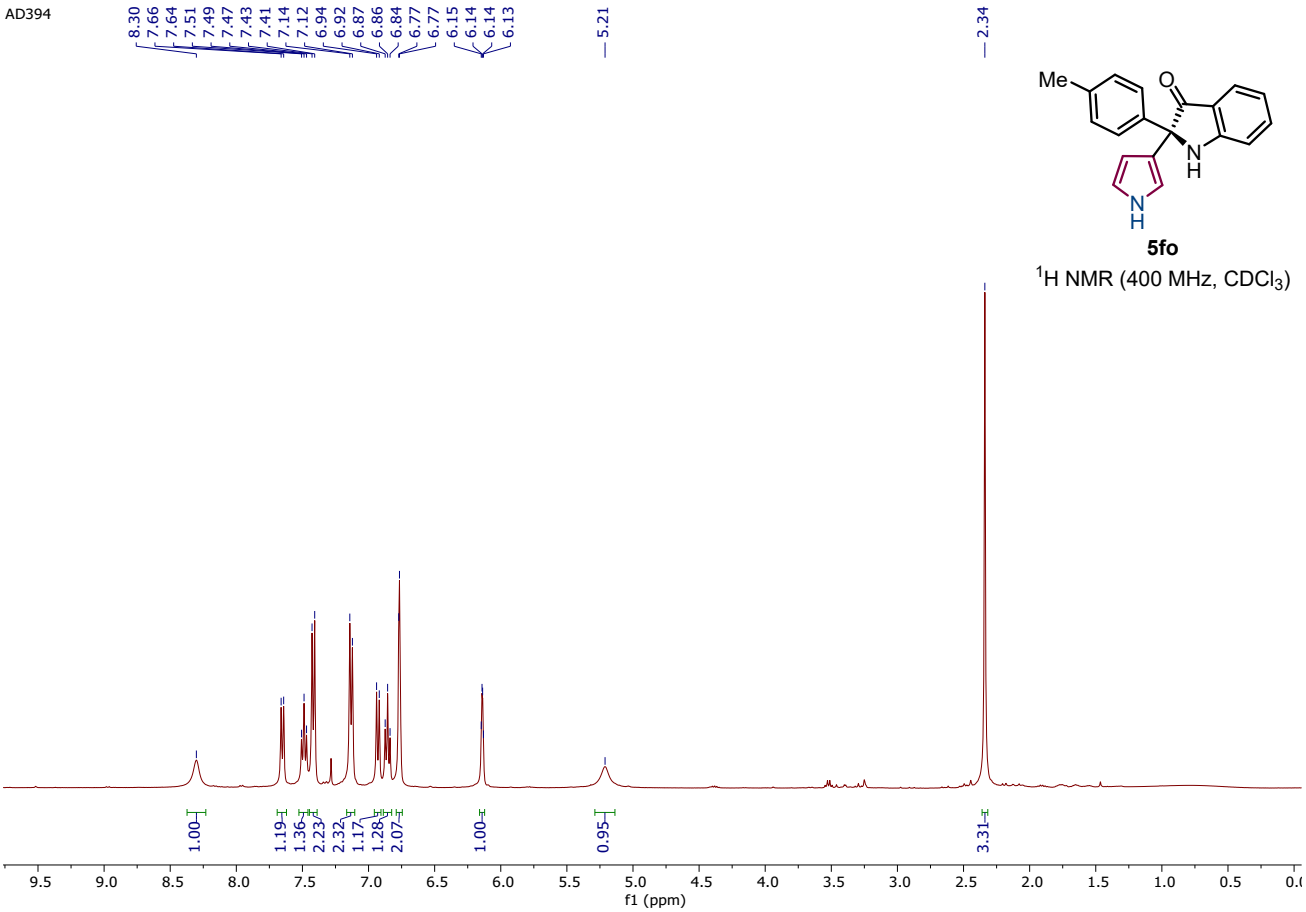
Processed Channel: PDA 254.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	65.836	10408084	50.32	75962
2	PDA 254.0 nm	73.570	10276031	49.68	75349



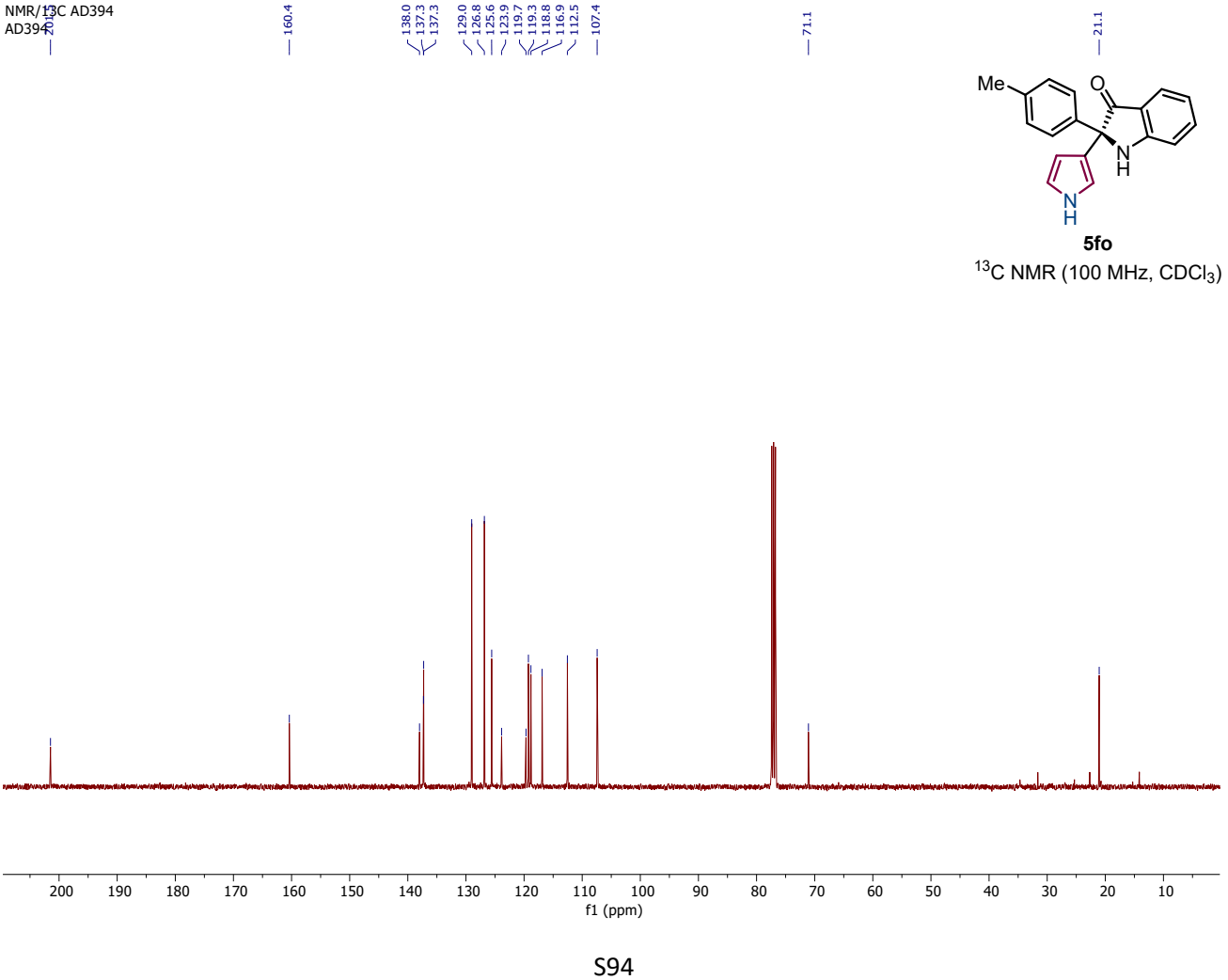
Processed Channel: PDA 254.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	65.426	24042286	96.22	160963
2	PDA 254.0 nm	74.388	943954	3.78	8475



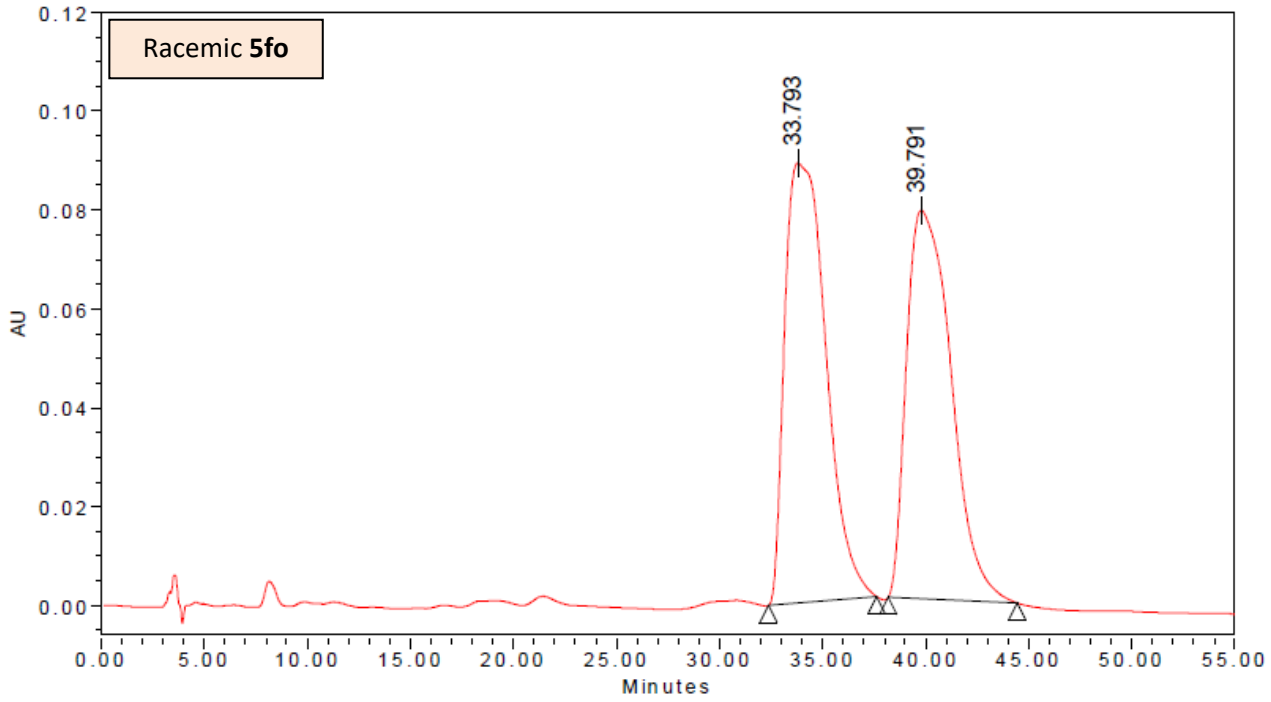
5fo

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



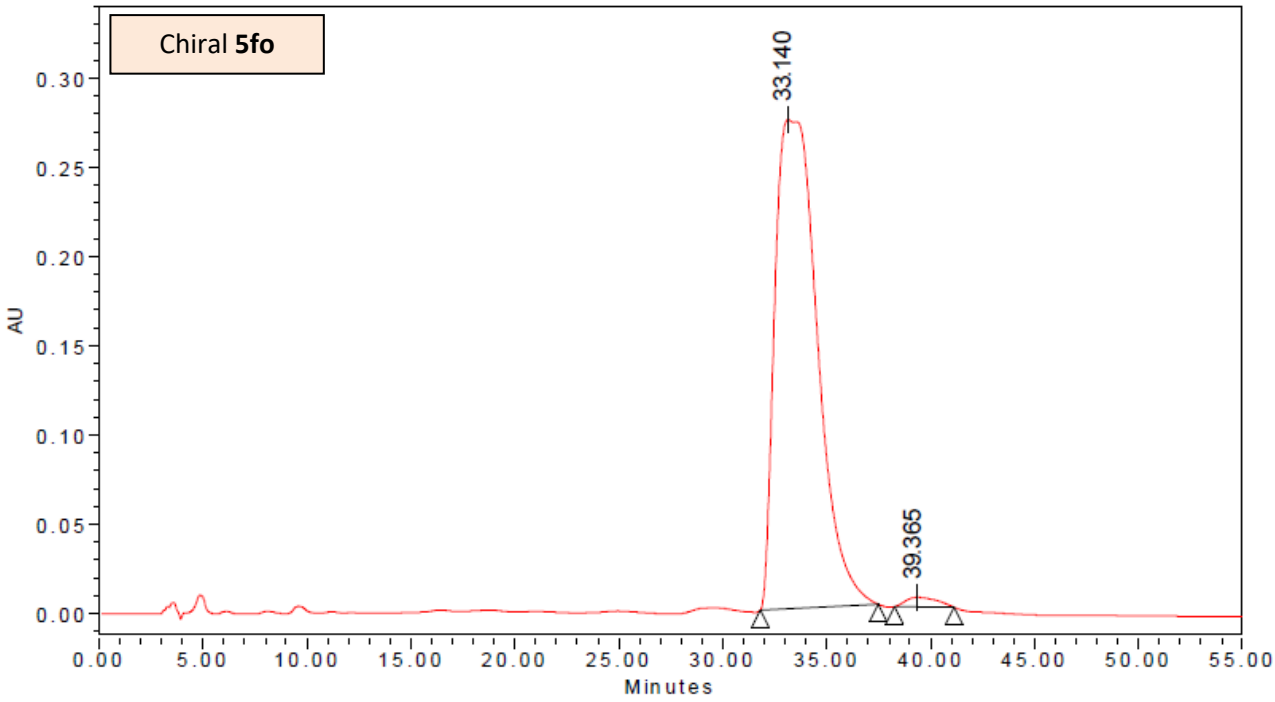
5fo

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



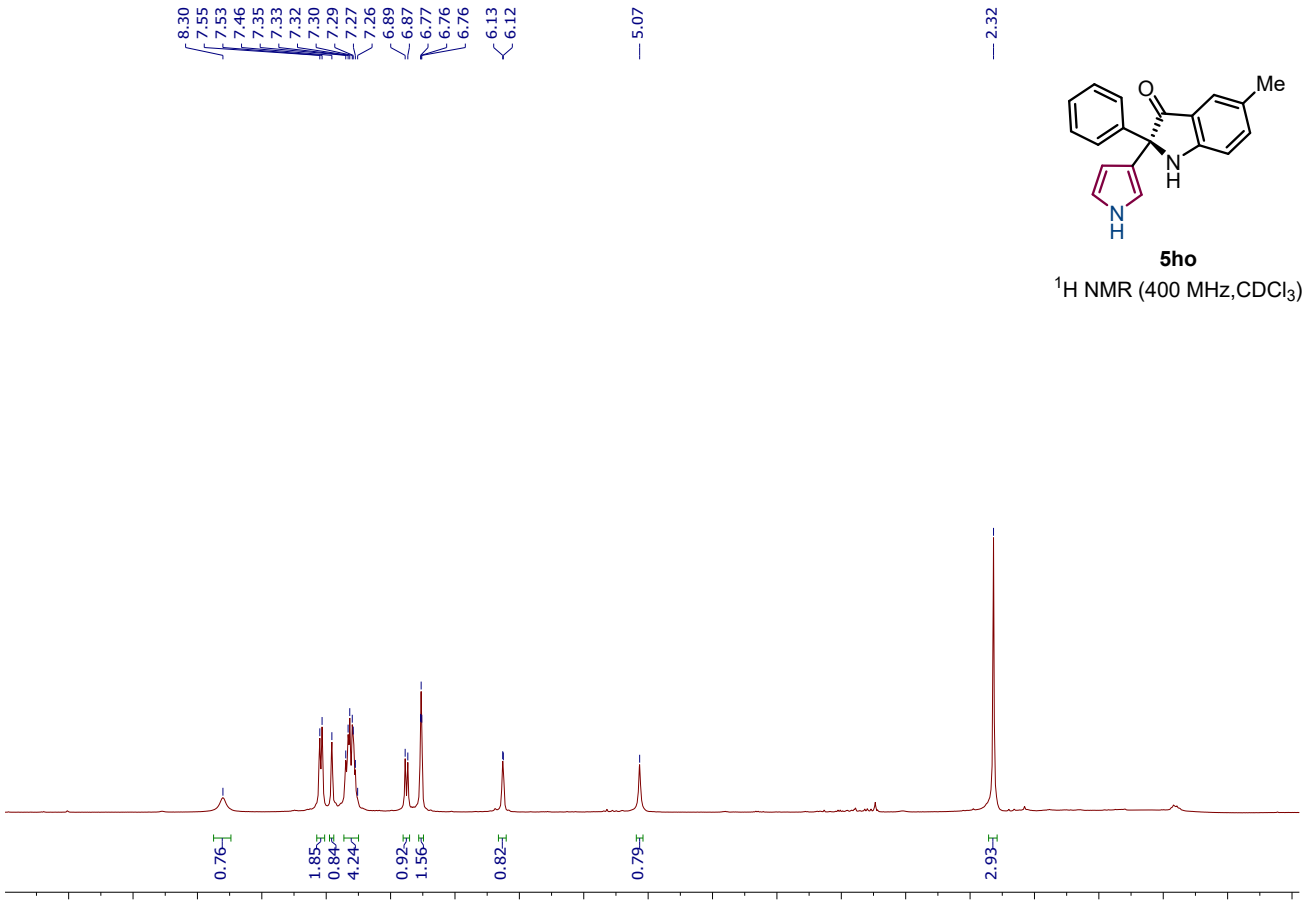
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	33.793	12388207	51.09	89046
2	2998 PDA 254.0 nm (2998 (200-400)nm)	39.791	11858369	48.91	78594



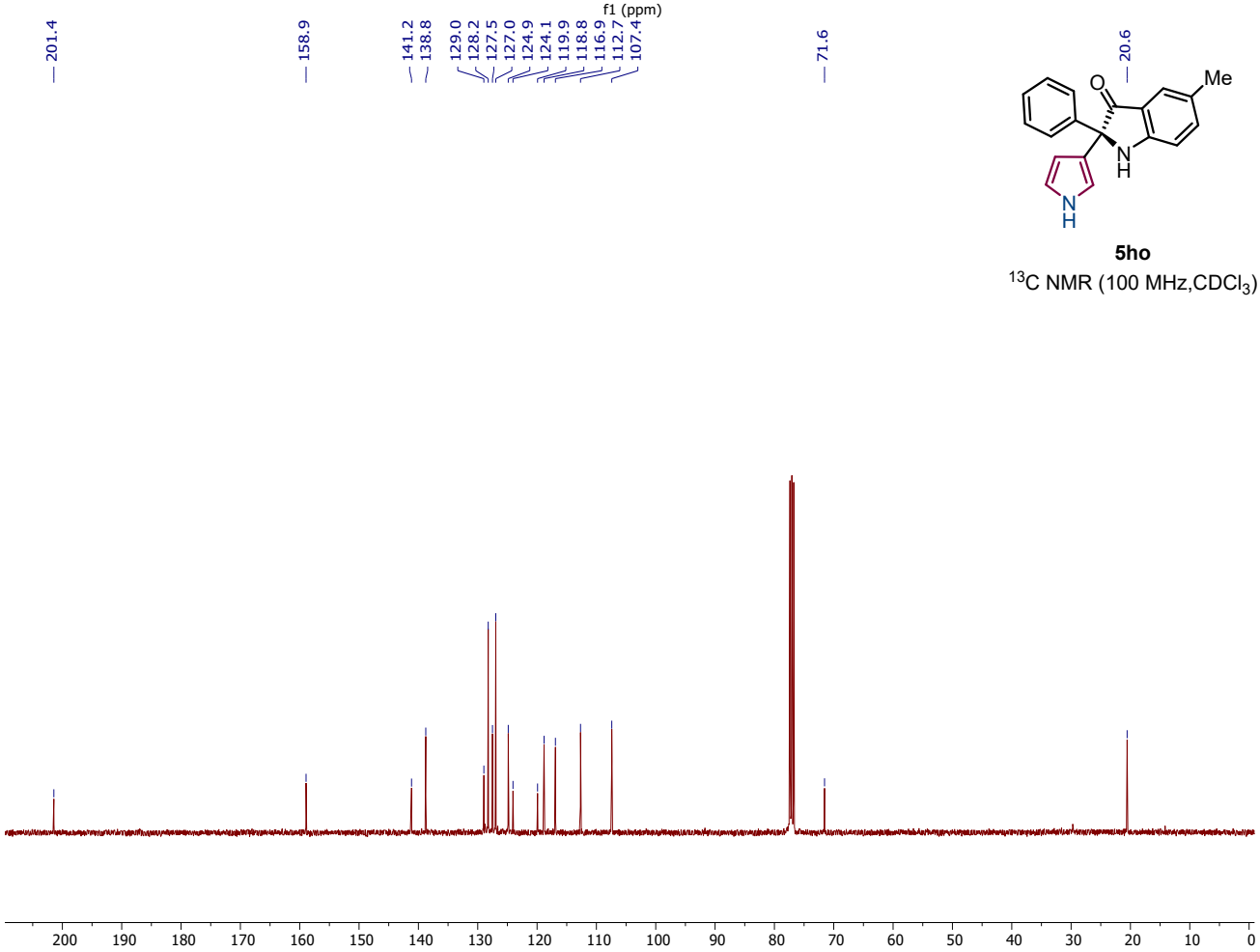
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	33.140	38857860	98.55	273936
2	2998 PDA 254.0 nm (2998 (200-400)nm)	39.365	570539	1.45	5380



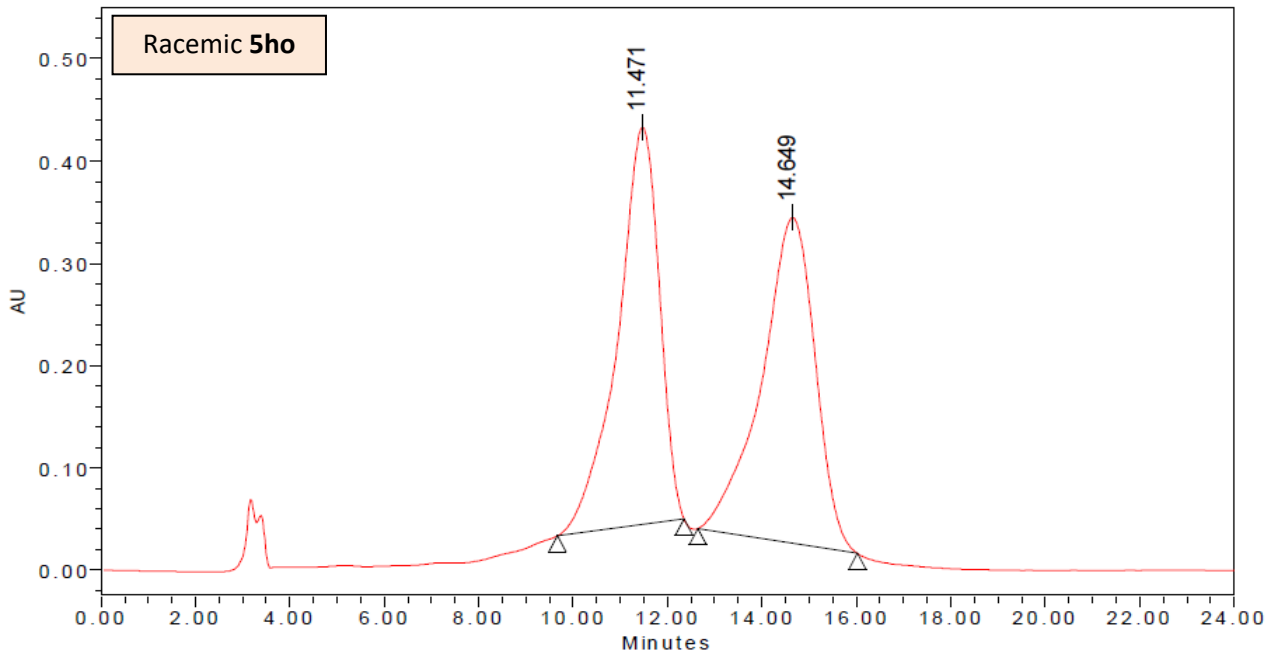
5ho

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



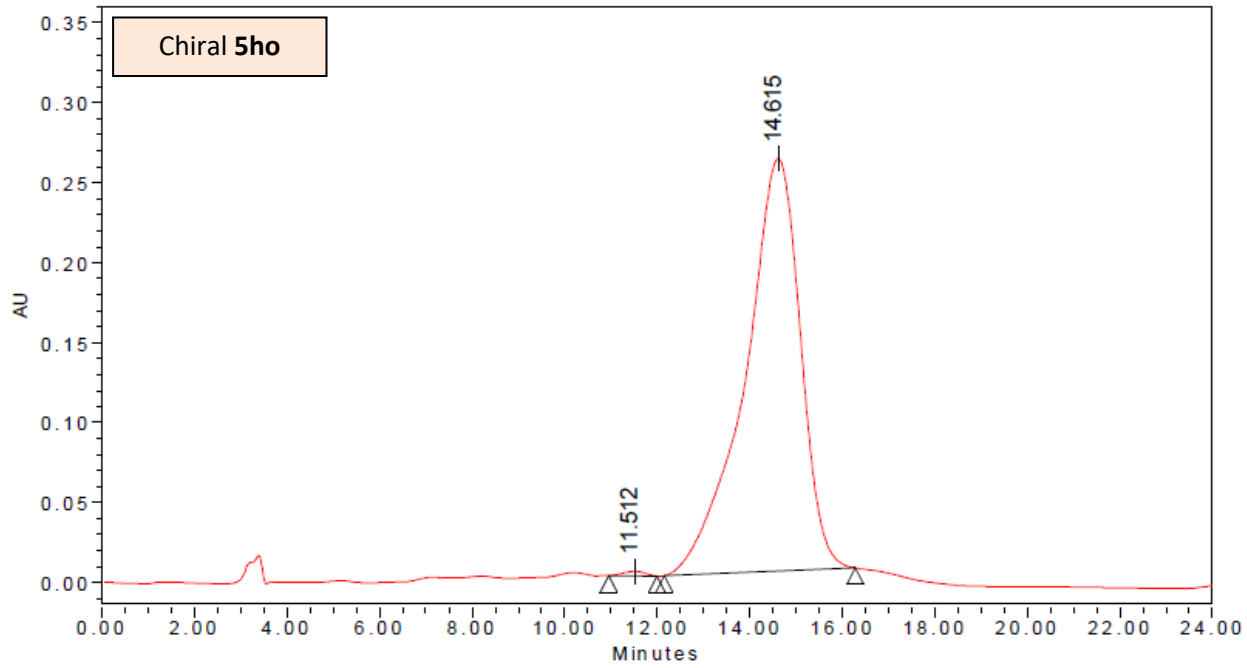
5ho

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



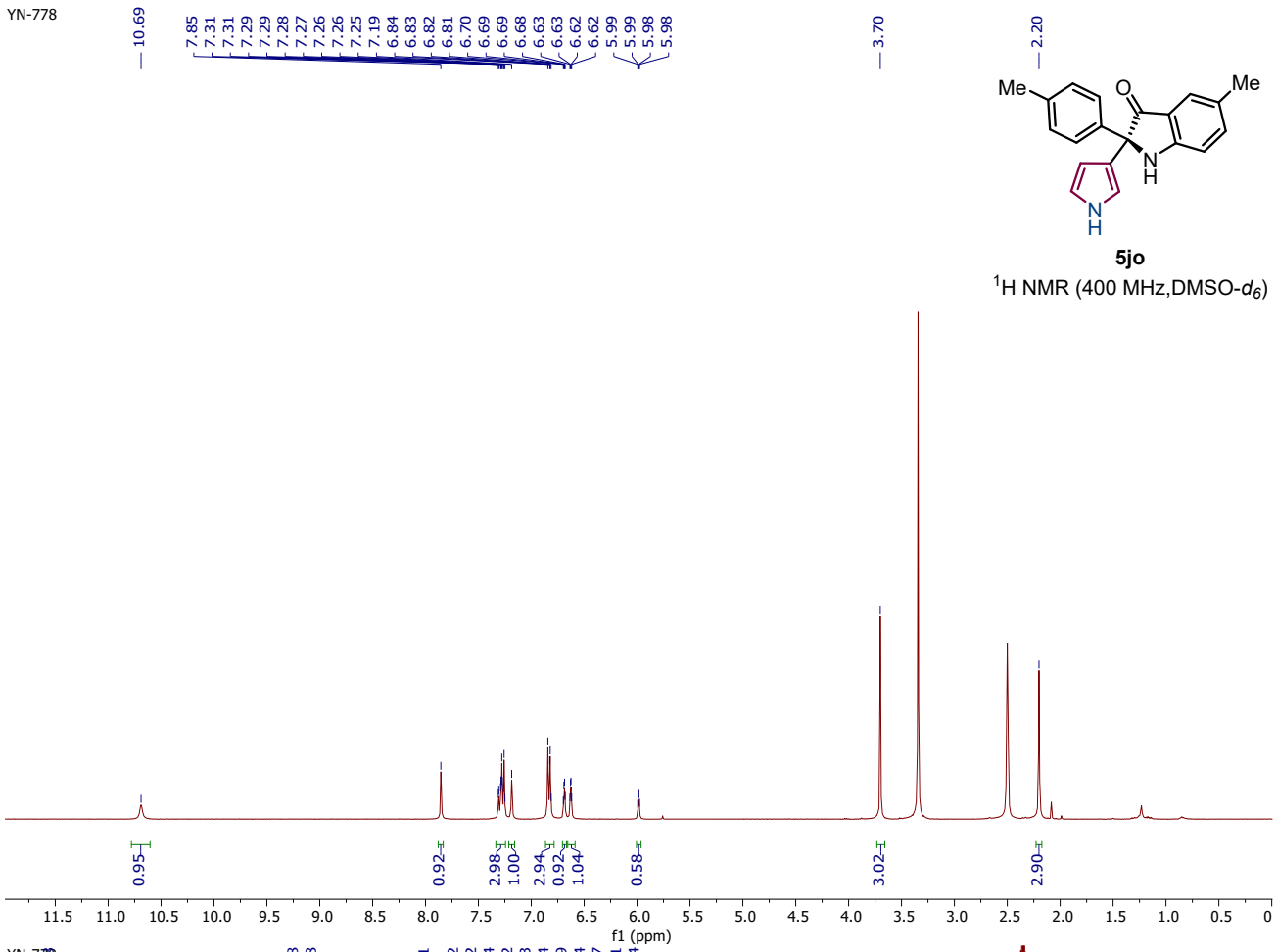
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	11.471	23865974	48.74	388295
2	2998 PDA 254.0 nm (2998 (200-400)nm)	14.649	25100286	51.26	318242



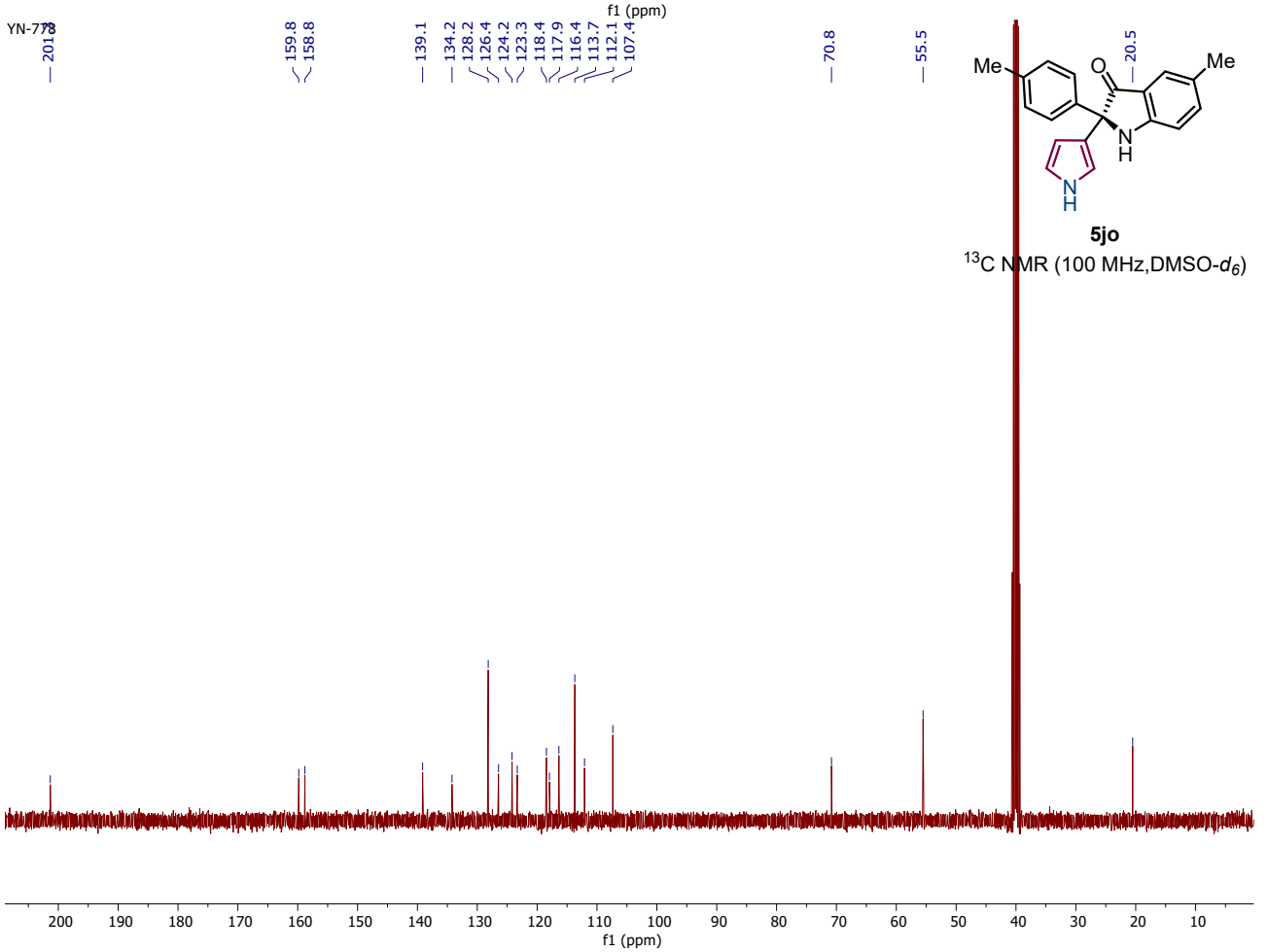
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	11.512	96625	0.45	2879
2	2998 PDA 254.0 nm (2998 (200-400)nm)	14.615	21510997	99.55	258022



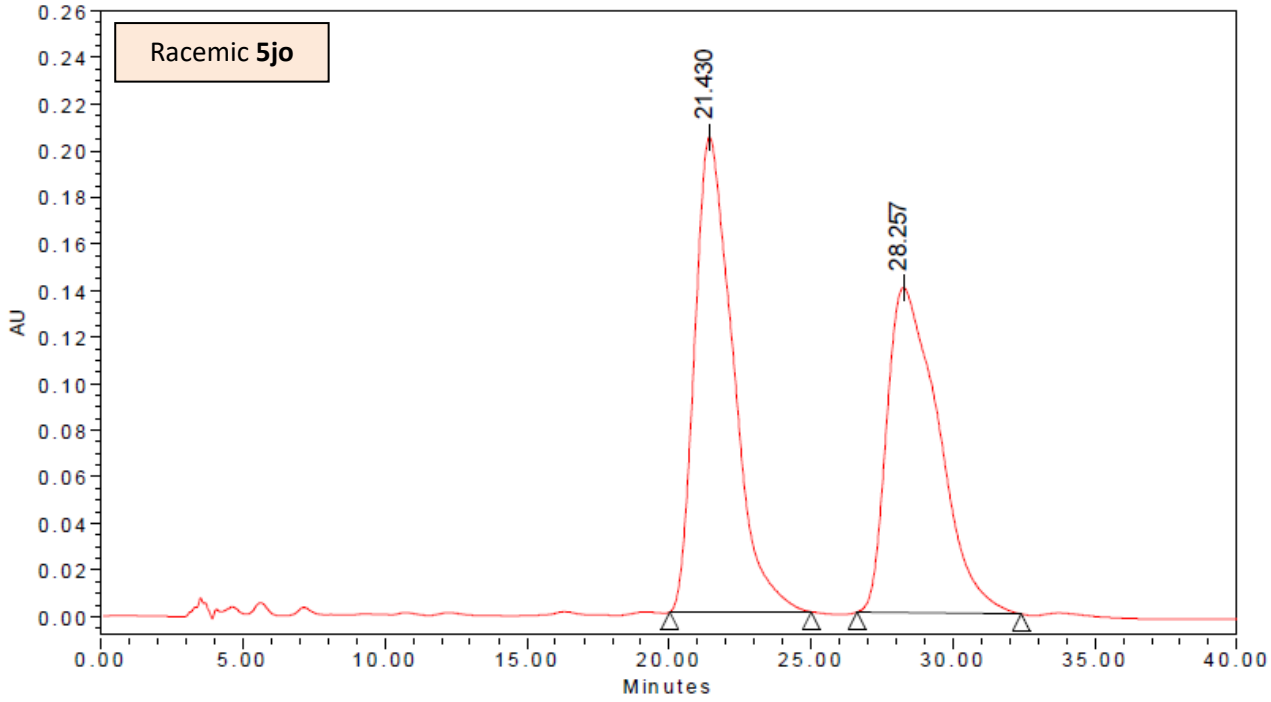
5jo

^{1}H NMR (400 MHz,DMSO-d_6)



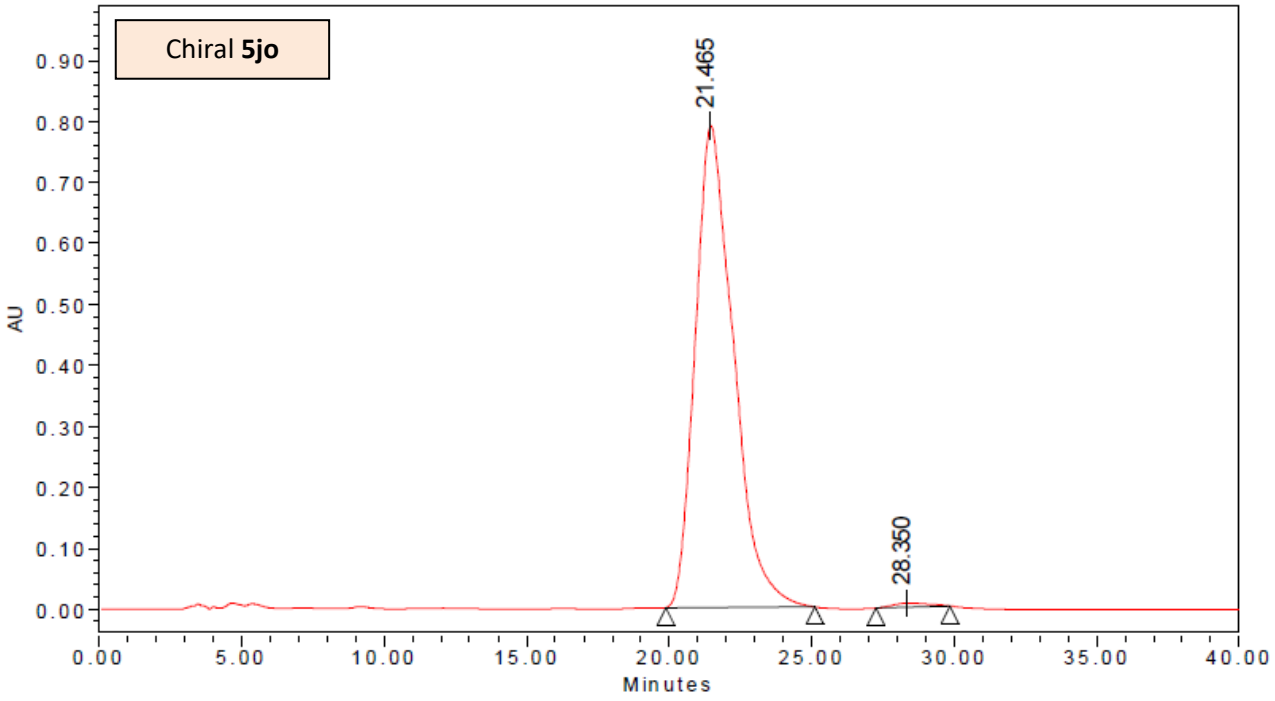
5jo

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



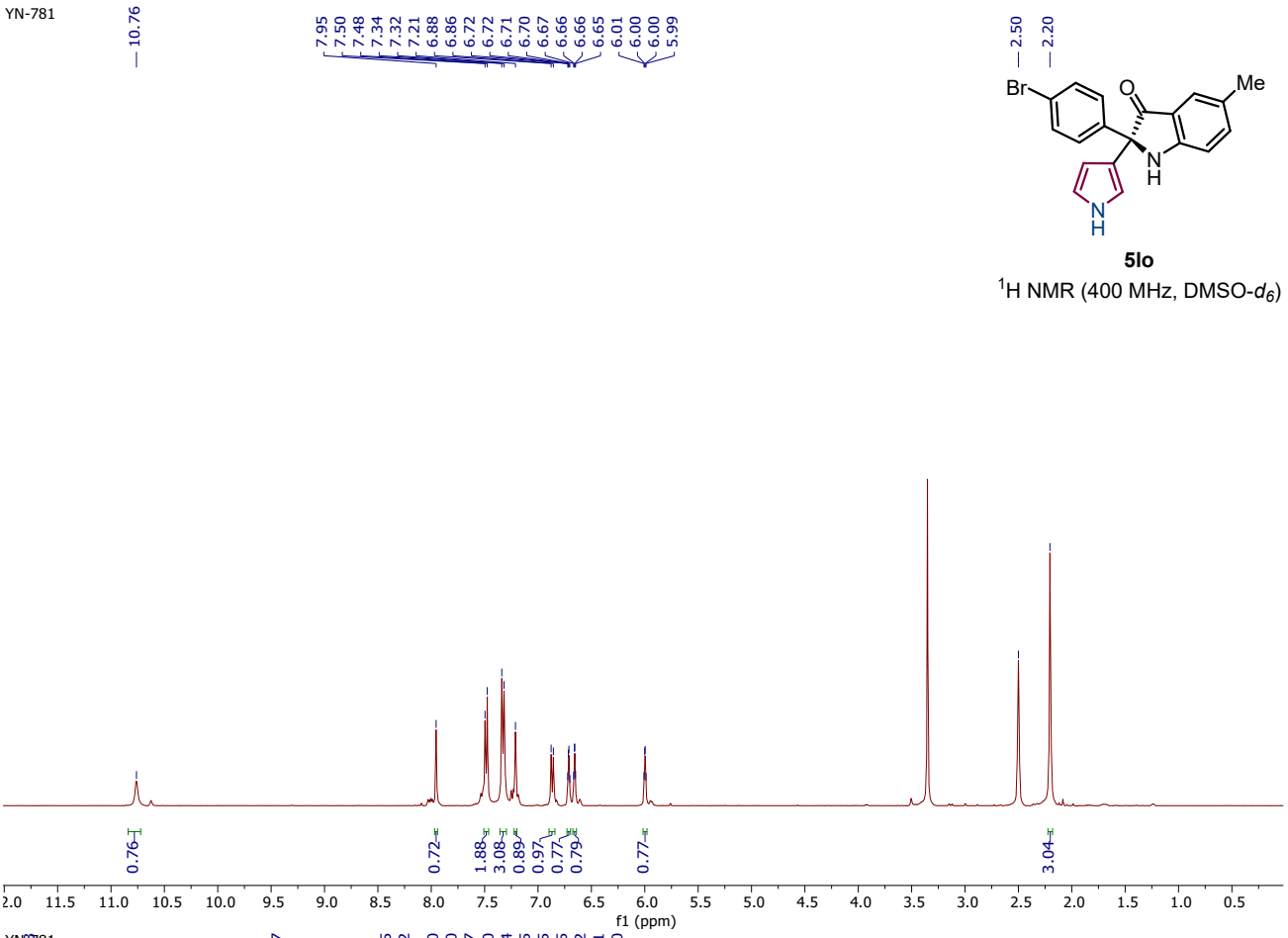
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	21.430	19128287	52.05	203893
2	2998 PDA 254.0 nm (2998 (200-400)nm)	28.257	17624910	47.95	139517



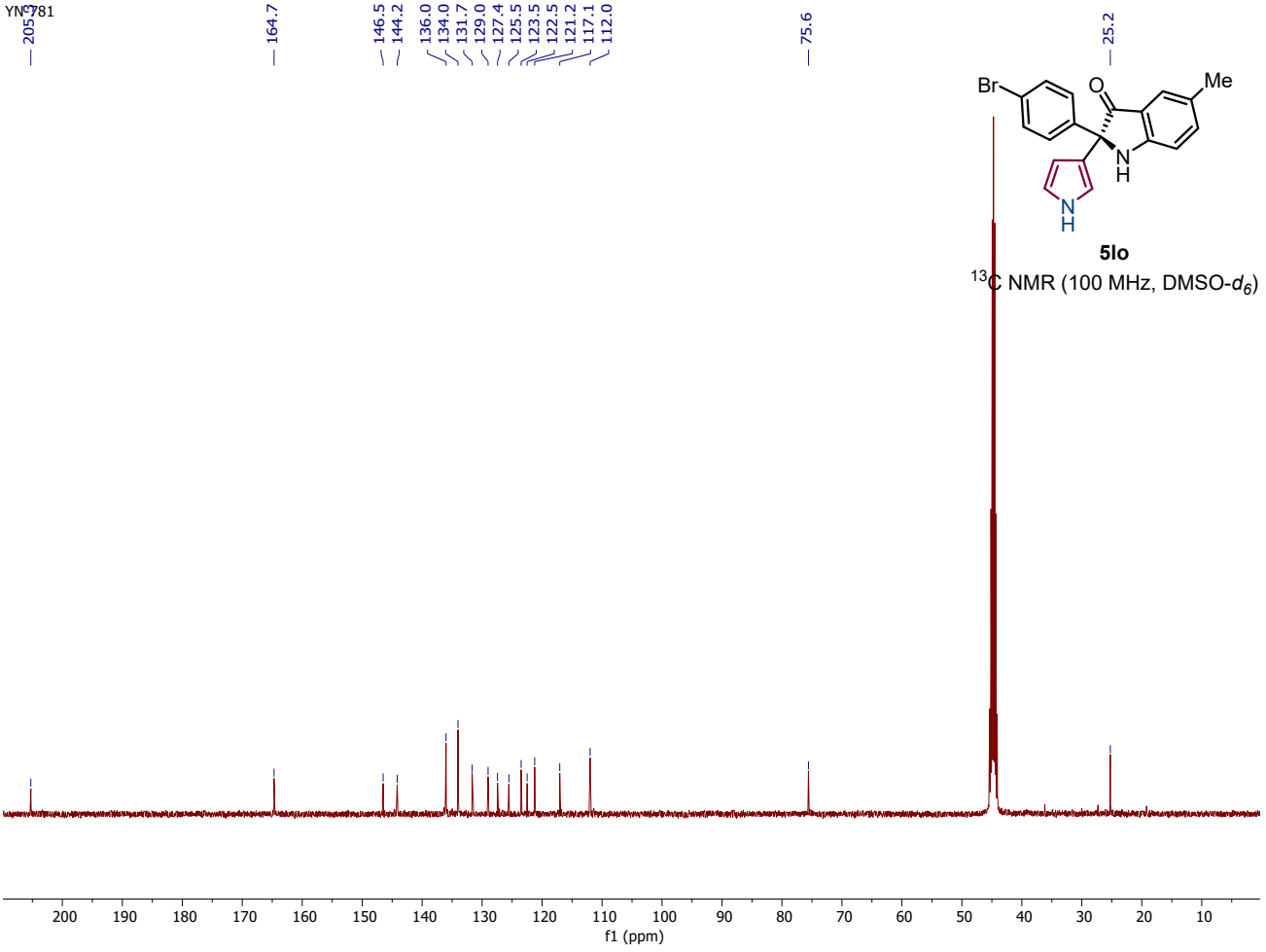
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	21.465	73701857	99.21	790452
2	2998 PDA 254.0 nm (2998 (200-400)nm)	28.350	585818	0.79	6756



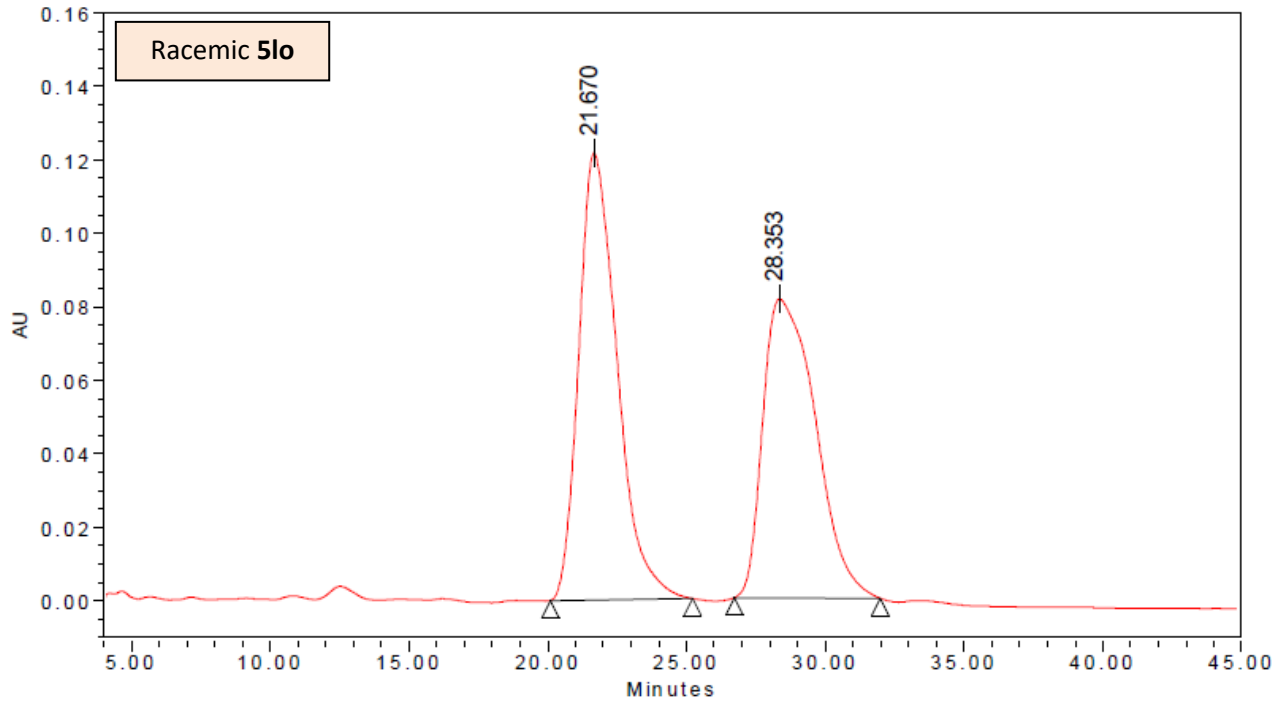
5lo

^{1}H NMR (400 MHz, DMSO-d_6)



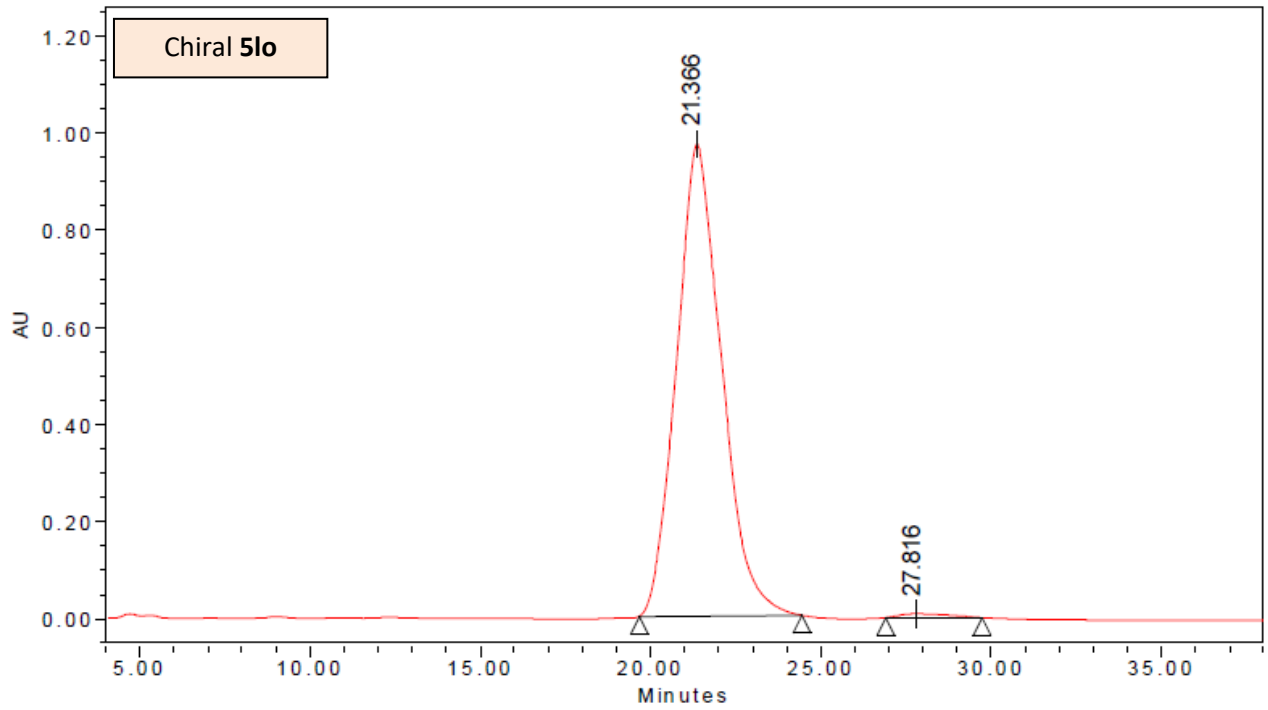
5lo

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



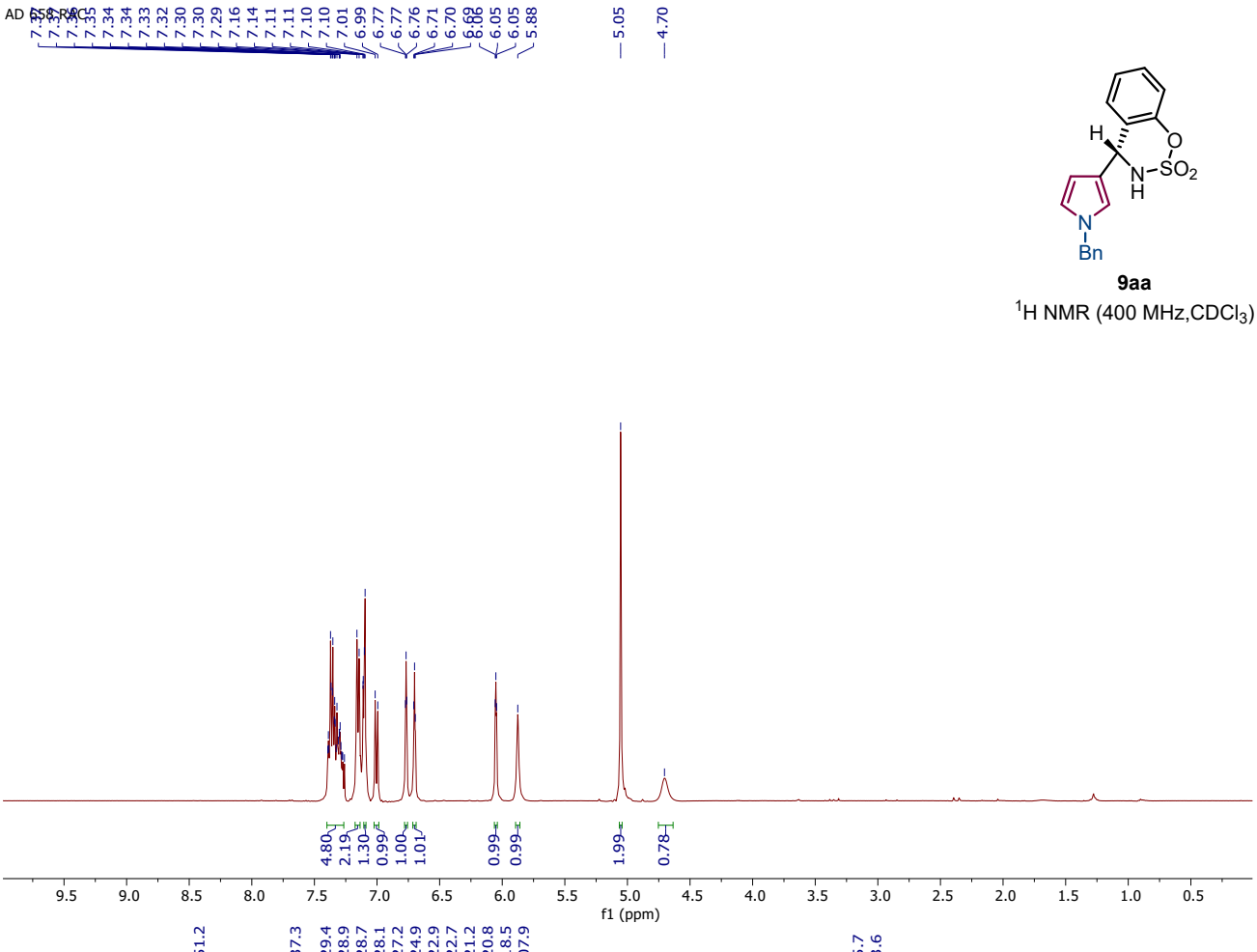
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	21.670	11669474	52.12	121590
2	2998 PDA 254.0 nm (2998 (200-400)nm)	28.353	10721507	47.88	81341



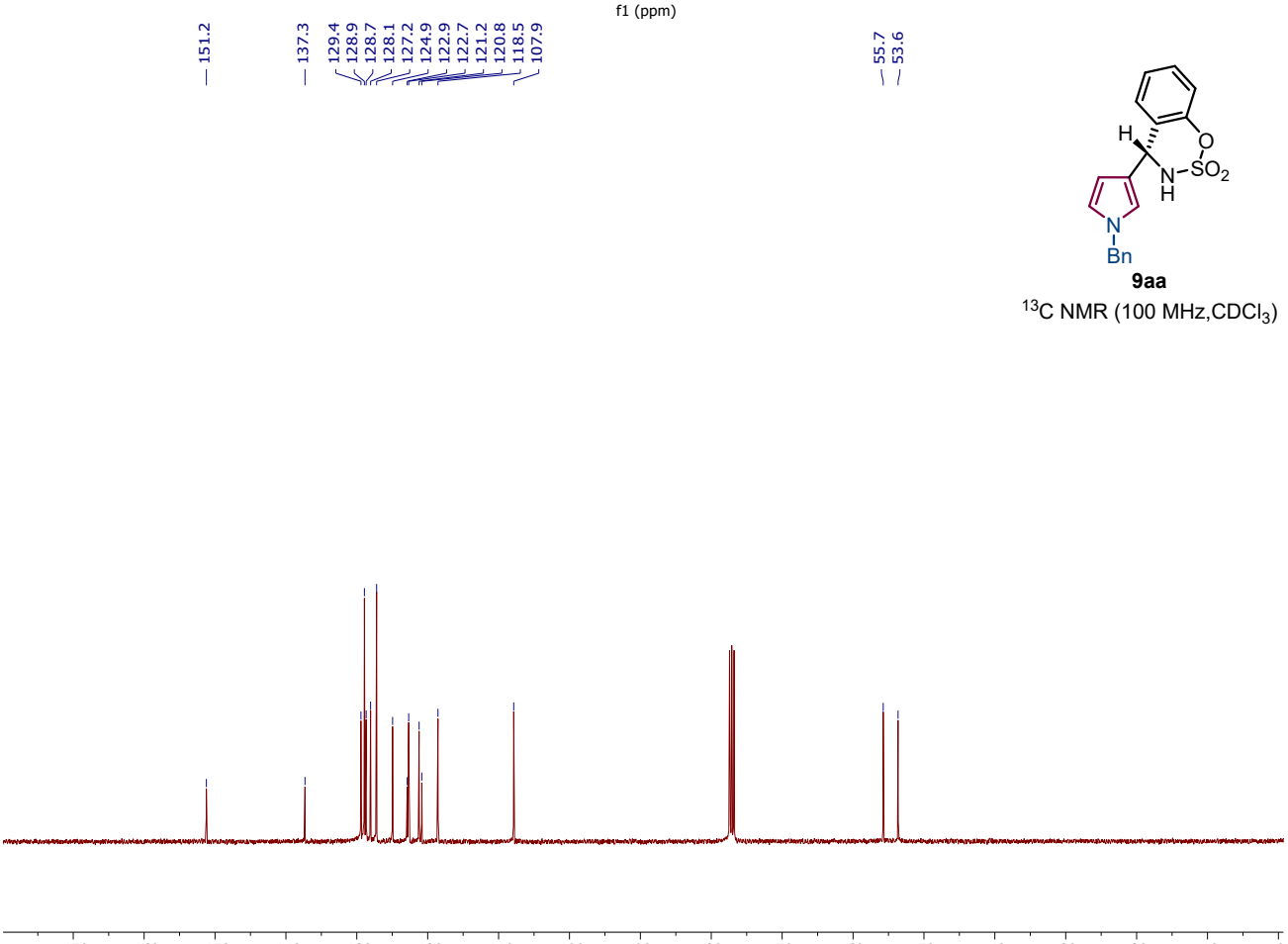
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	21.366	89210381	99.14	972452
2	2998 PDA 254.0 nm (2998 (200-400)nm)	27.816	776543	0.86	7823



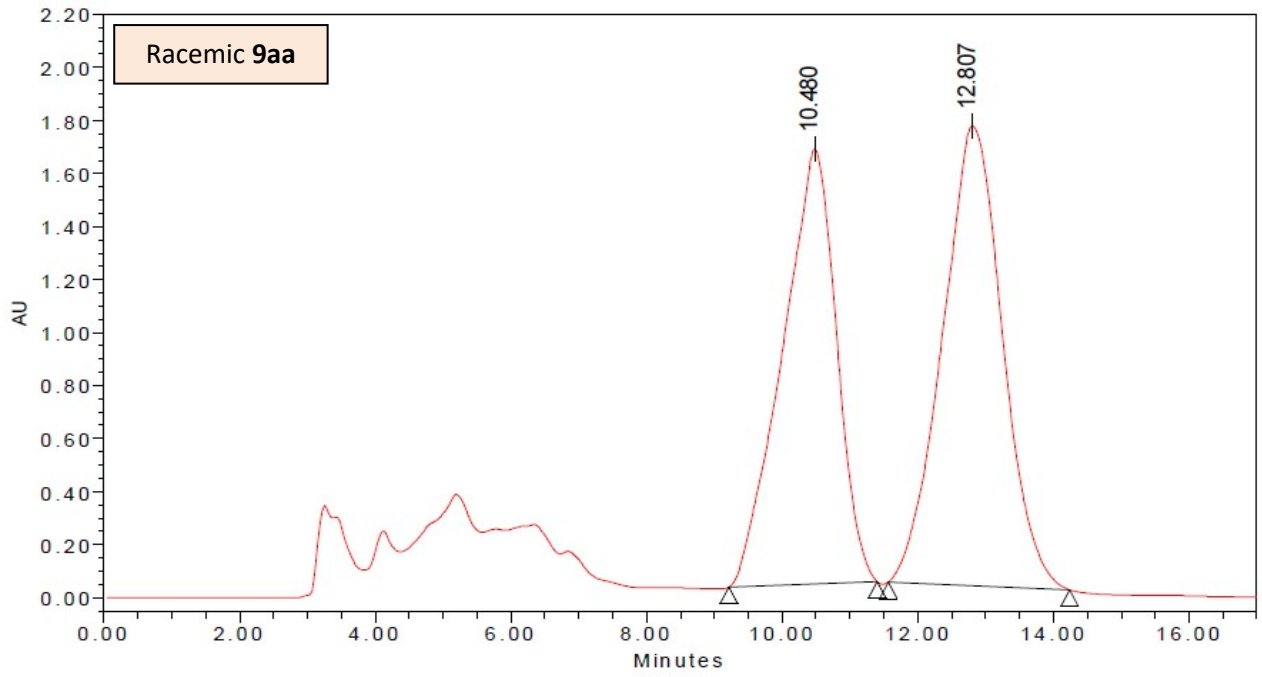
9aa

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



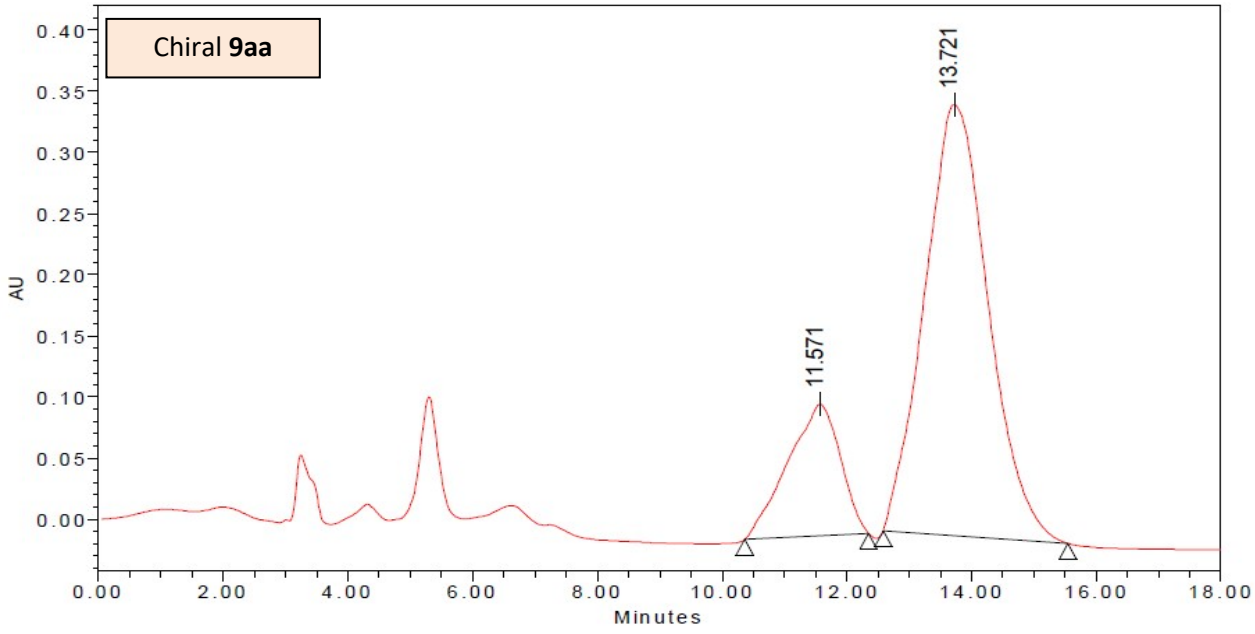
9aa

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



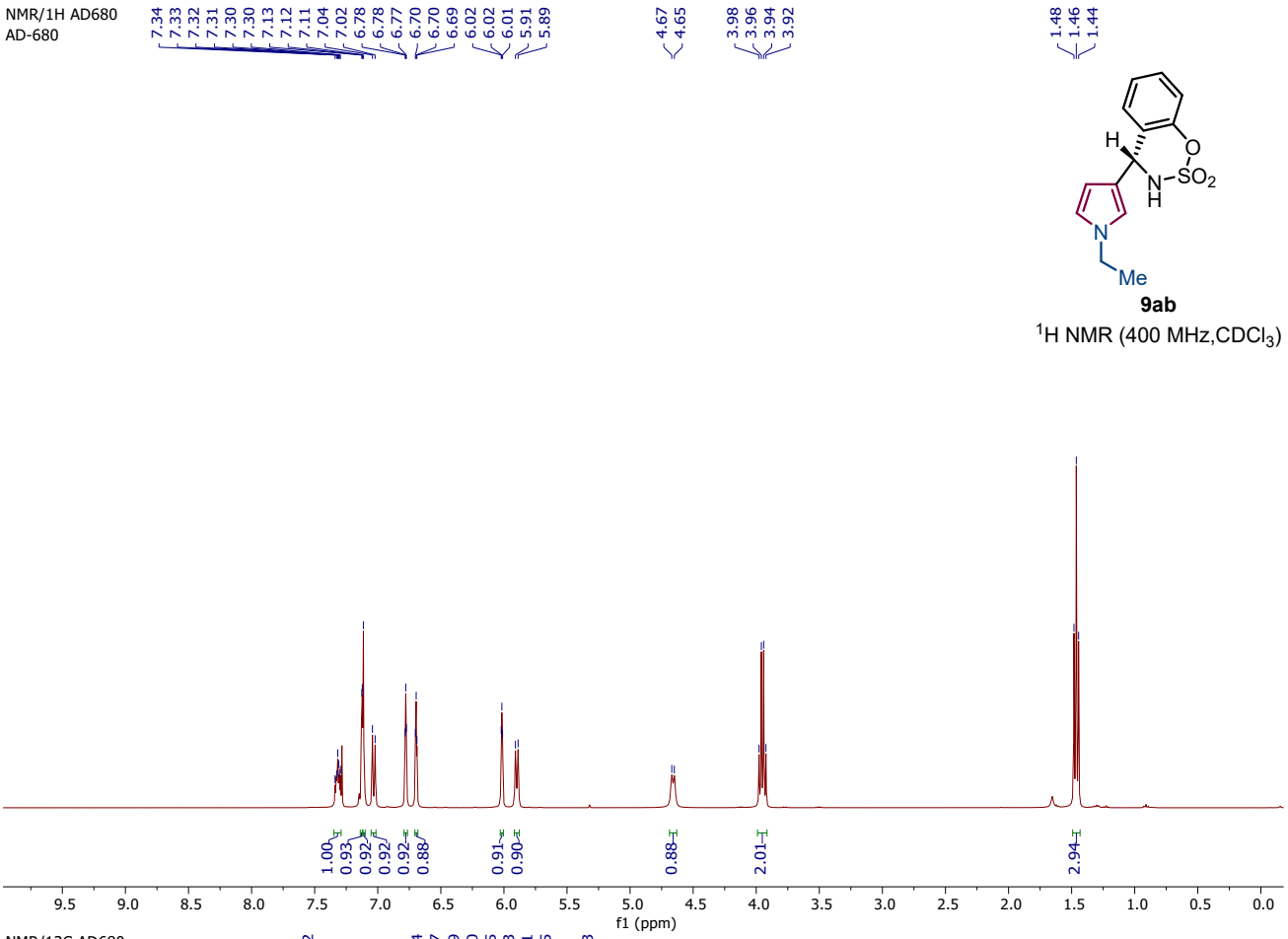
Processed Channel: 2998 PDA 230.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 230.0 nm (2998 (200-400)nm)	10.480	90886507	46.00	1641341
2	2998 PDA 230.0 nm (2998 (200-400)nm)	12.807	106712158	54.00	1734538



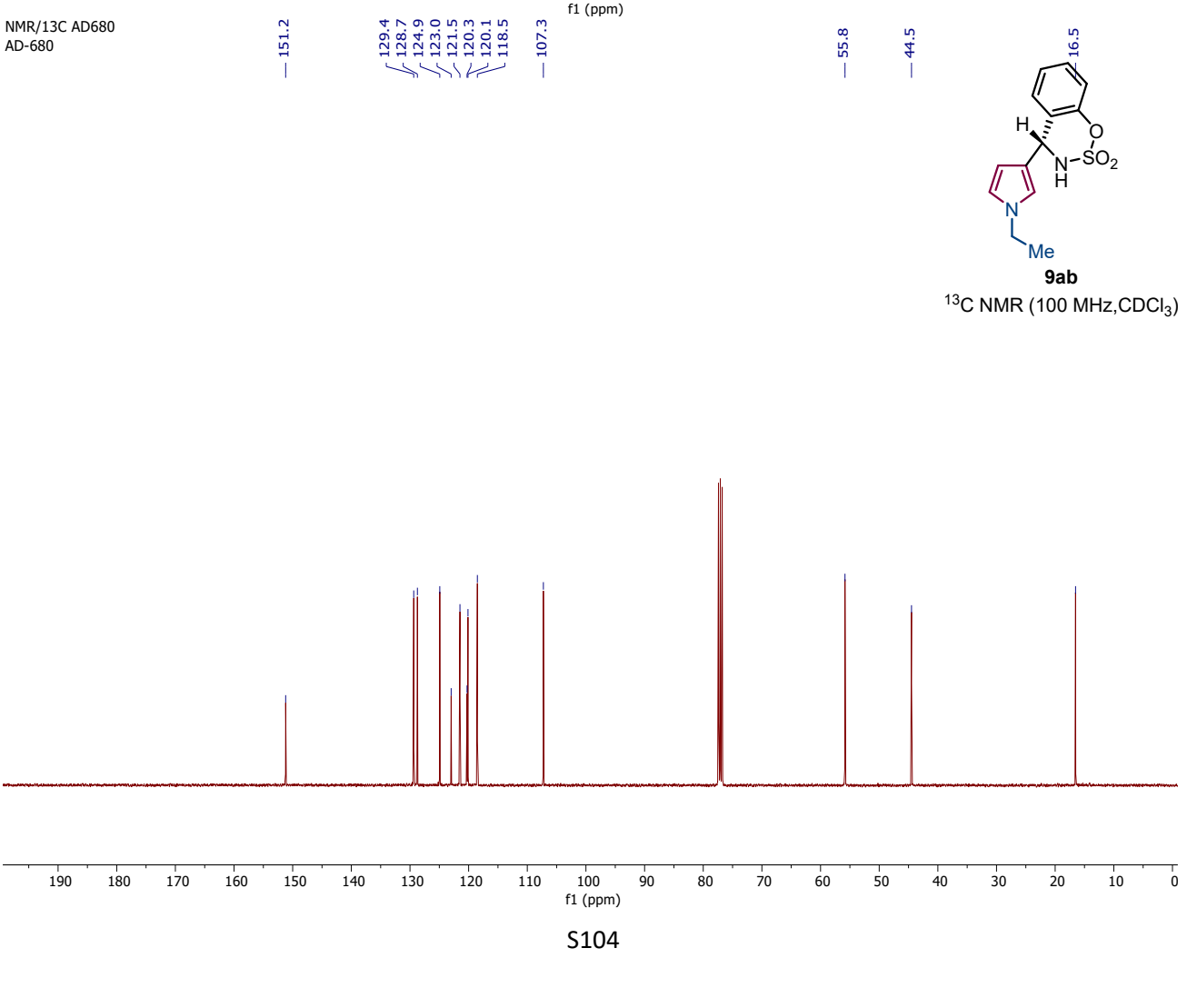
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	11.571	6288995	20.04	107564
2	2998 PDA 254.0 nm (2998 (200-400)nm)	13.721	25098599	79.96	352357



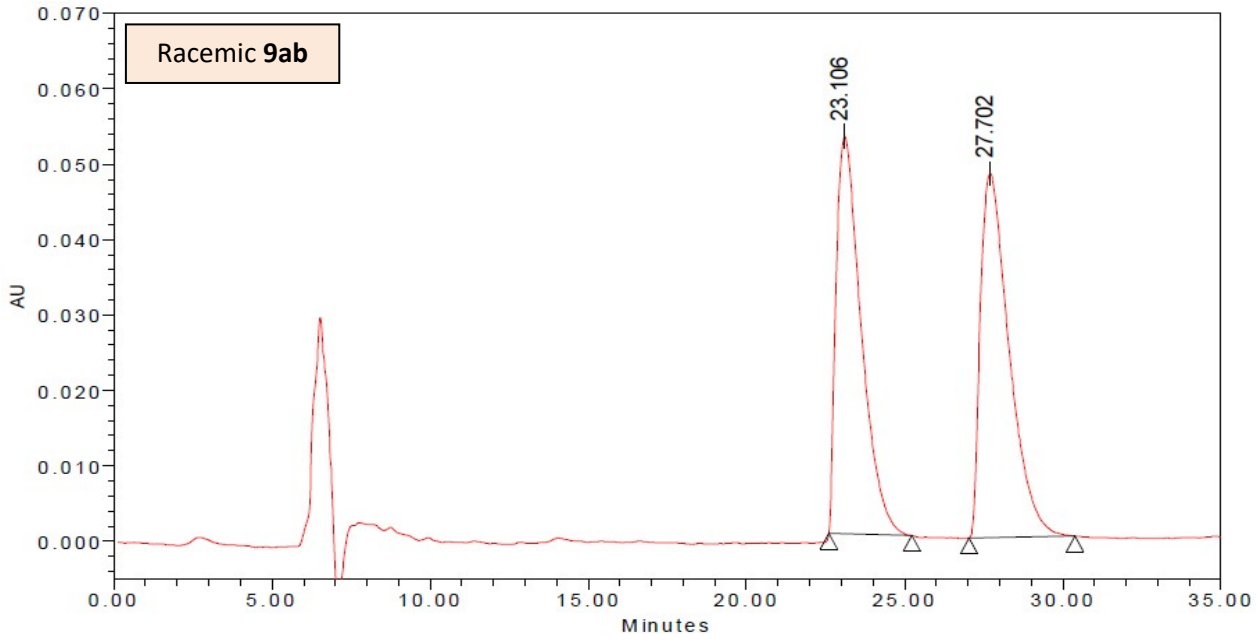
9ab

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



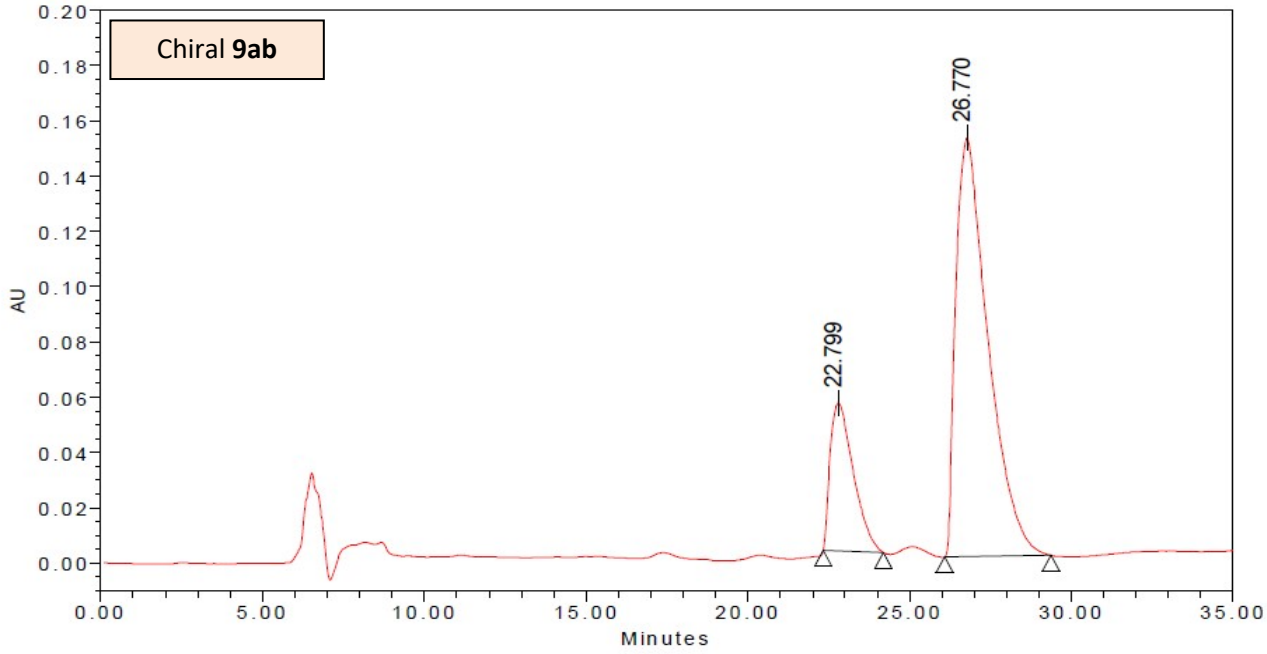
9ab

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



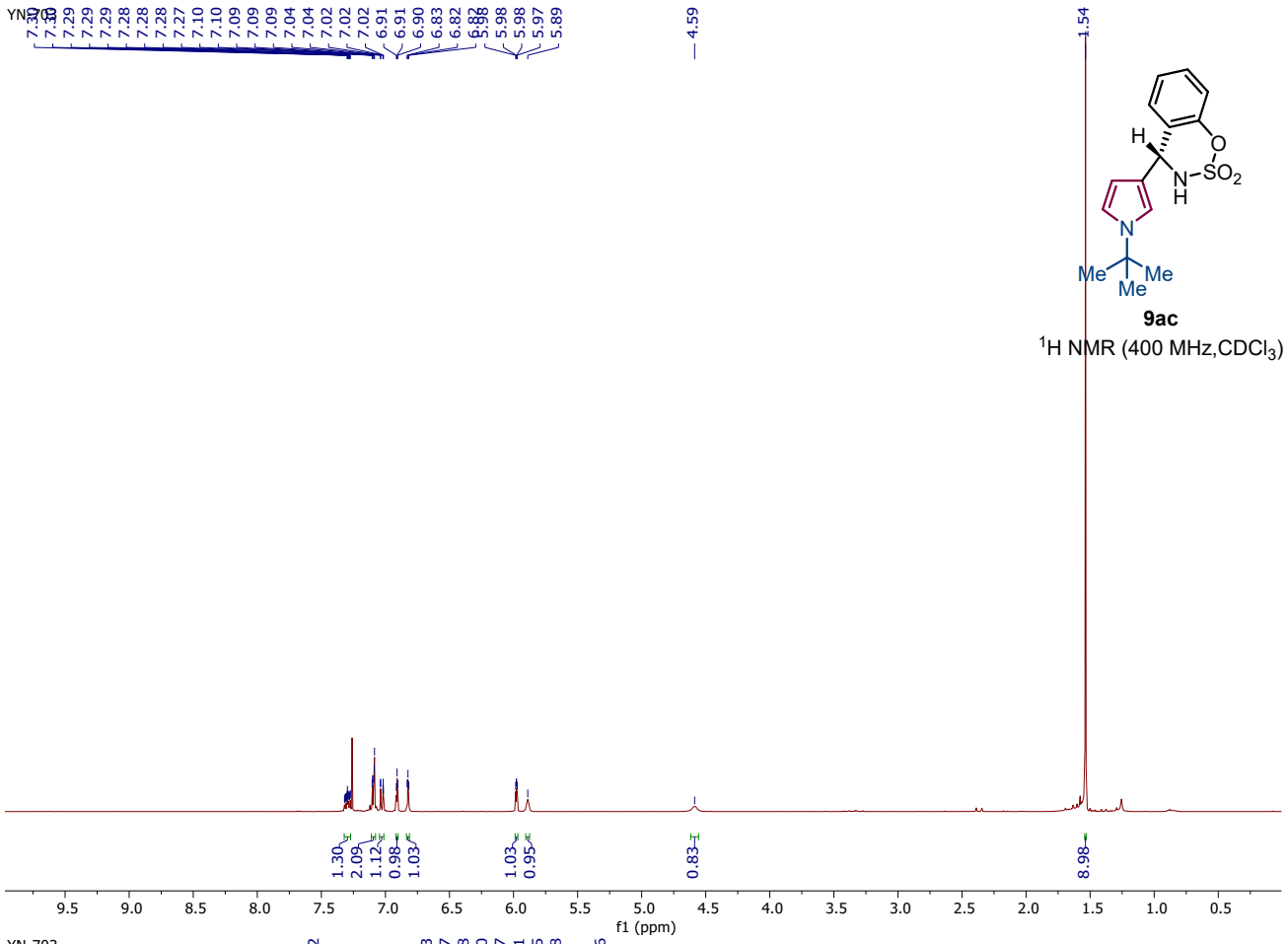
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	23.106	2899891	48.81	52736
2	2998 PDA 254.0 nm (2998 (200-400)nm)	27.702	3041604	51.19	48231



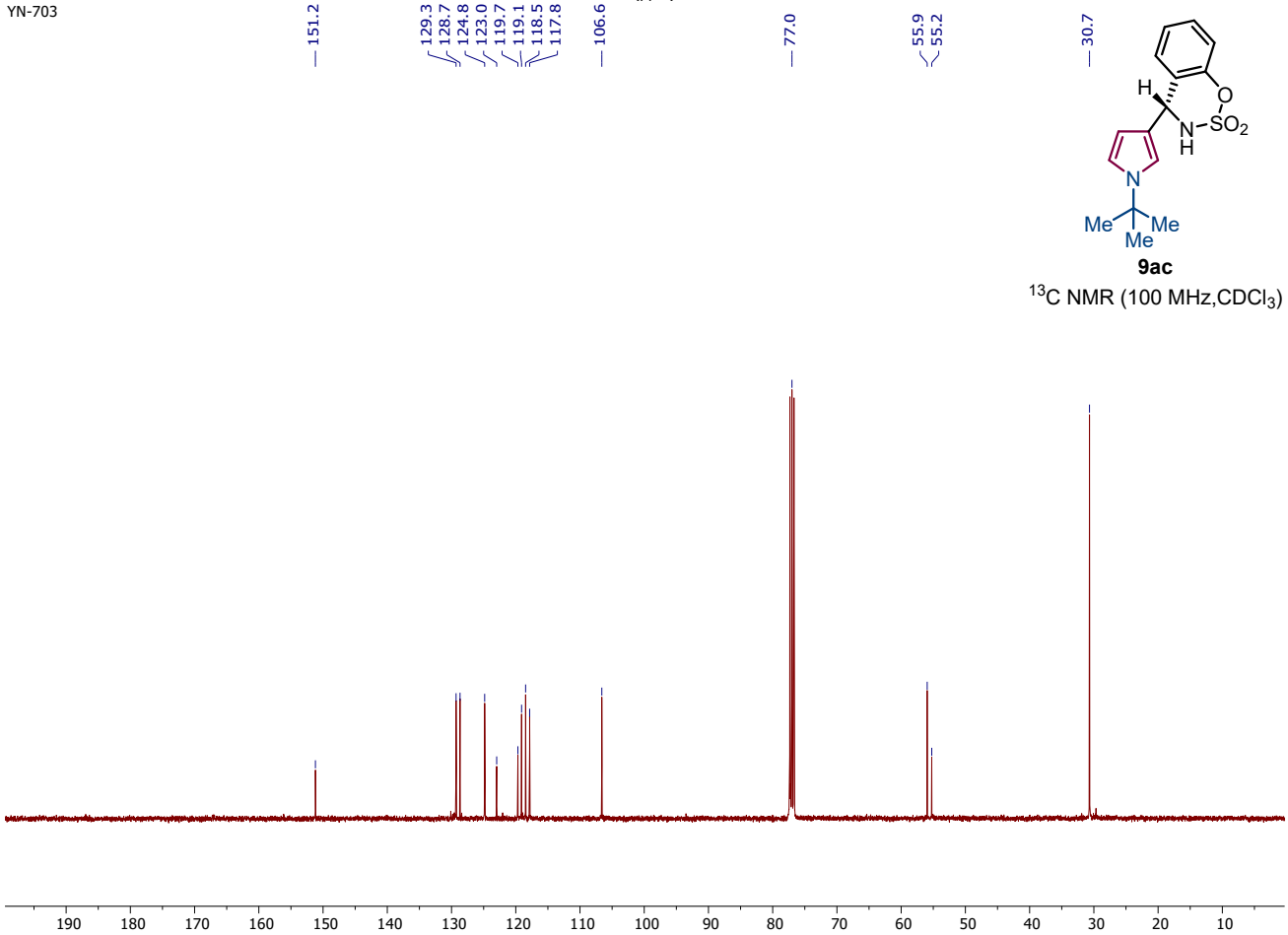
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	22.799	2665395	20.22	53402
2	2998 PDA 254.0 nm (2998 (200-400)nm)	26.770	10514044	79.78	151403



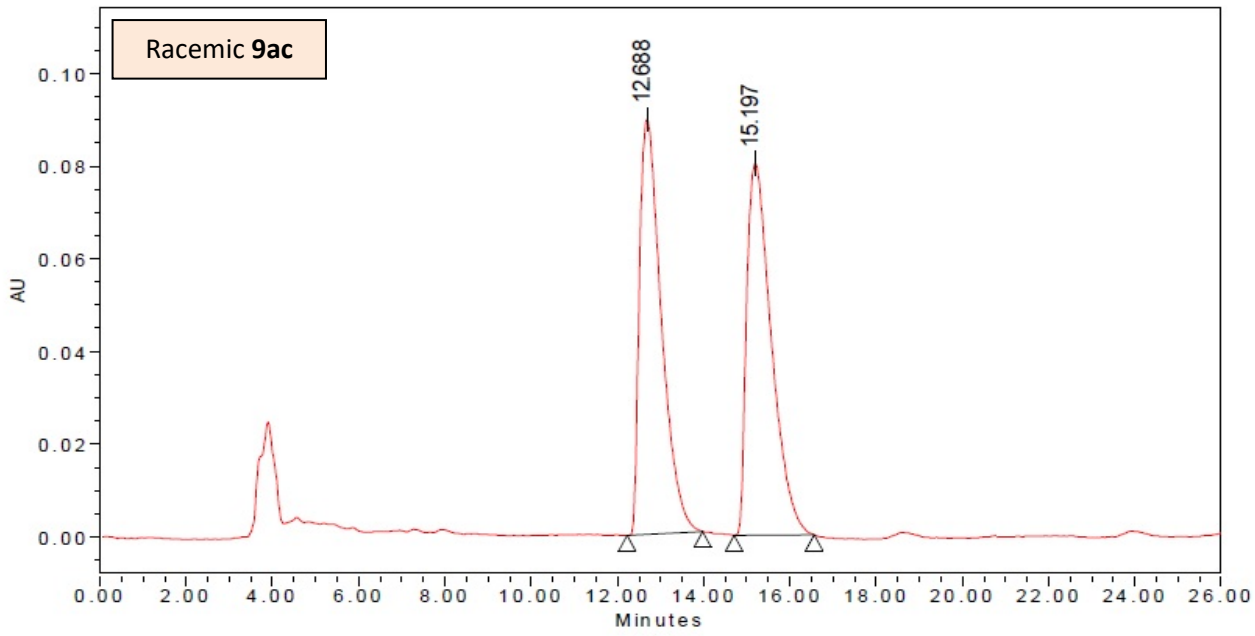
9ac

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



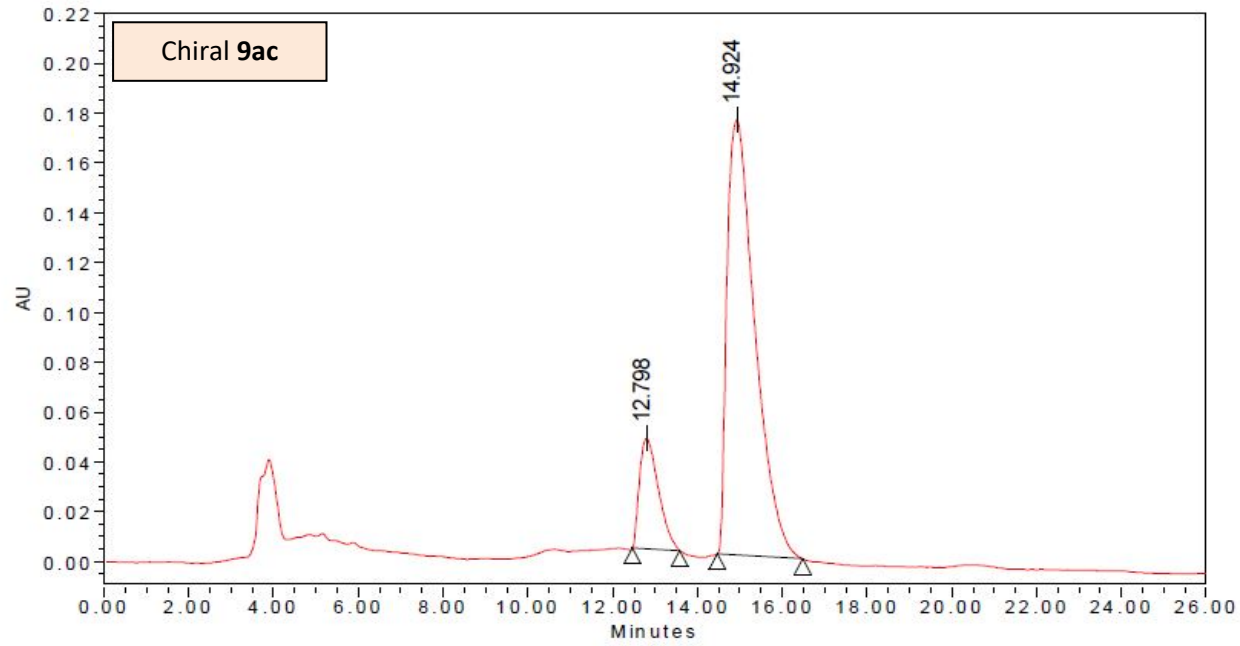
9ac

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



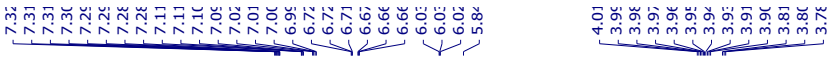
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

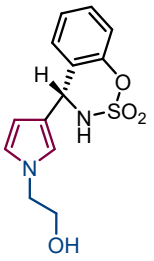
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	12.688	3156642	49.75	89543
2	2998 PDA 254.0 nm (2998 (200-400)nm)	15.197	3188144	50.25	80215



Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

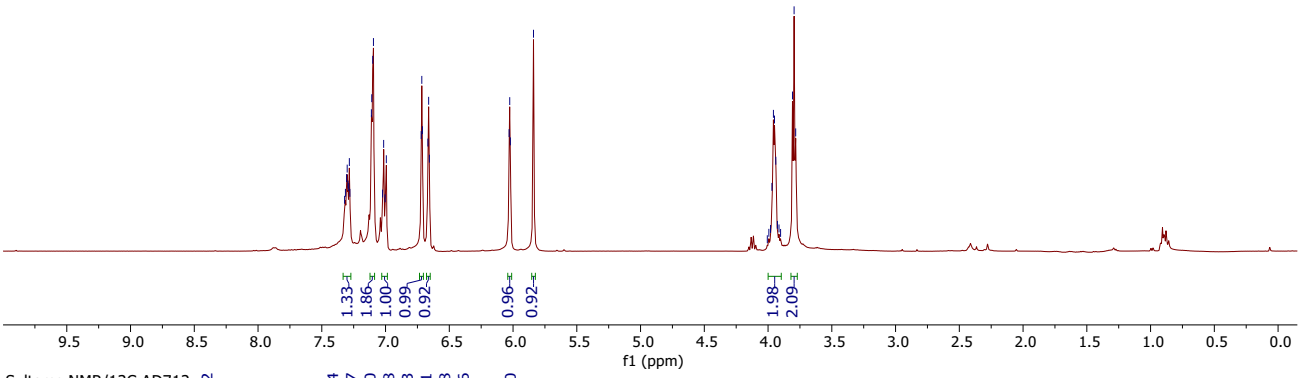
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	12.798	1374734	14.69	44285
2	2998 PDA 254.0 nm (2998 (200-400)nm)	14.924	7983697	85.31	174676



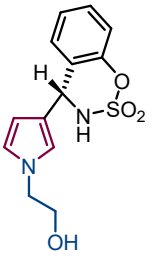


9ad

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

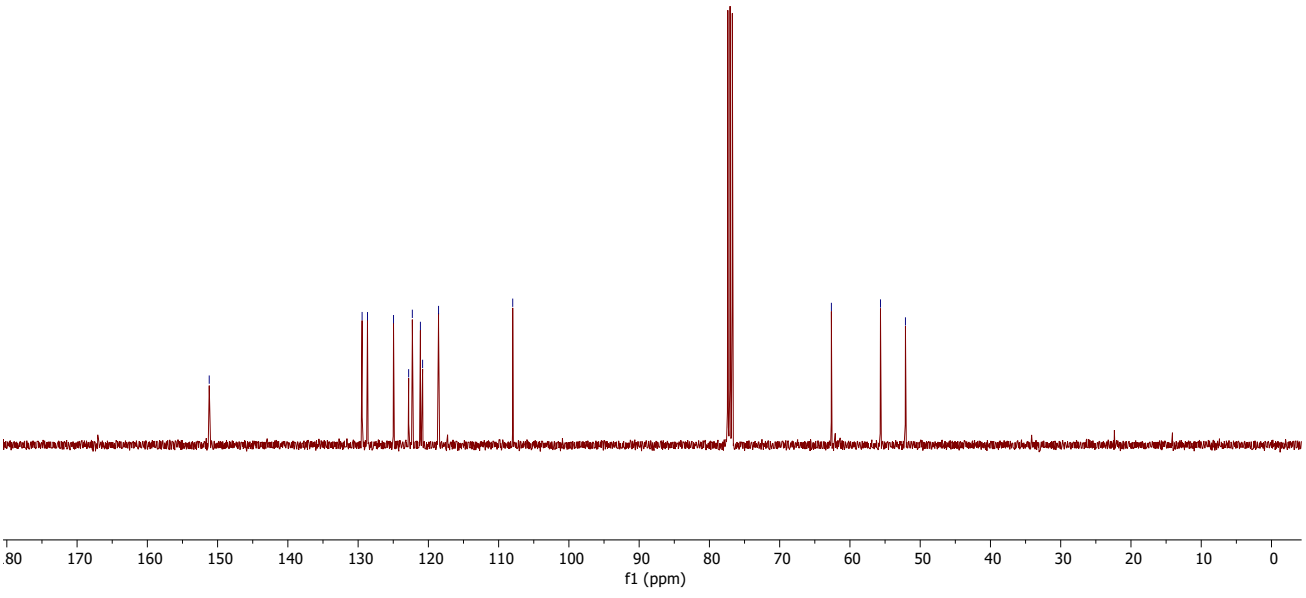


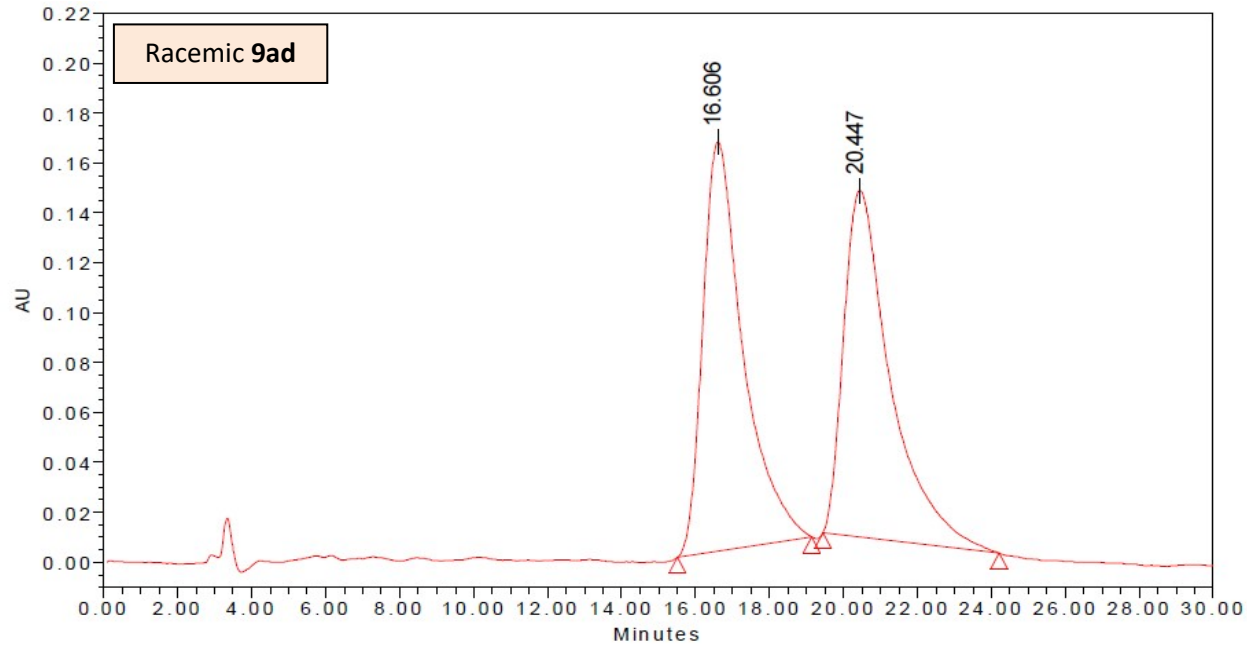
Sultams NMR/13C AD712
AD-712



9ad

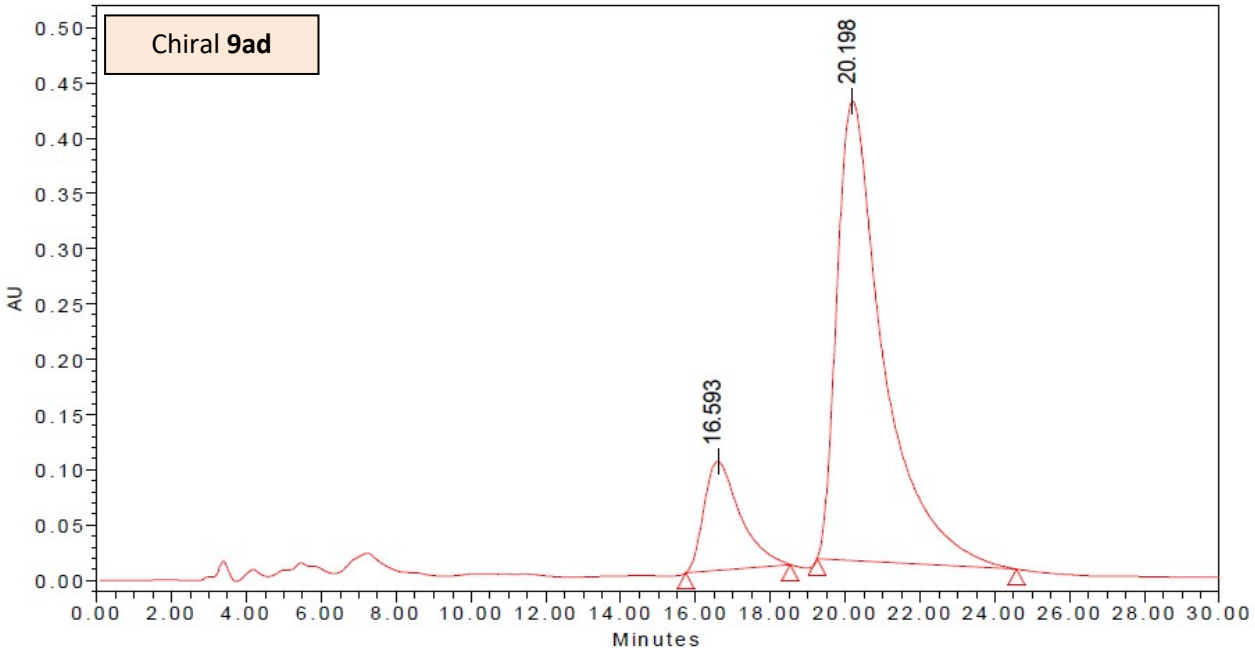
^{13}C NMR (100 MHz,$CDCl_3$)





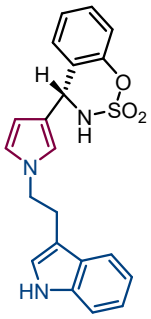
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	16.606	12451599	50.48	164146
2	2998 PDA 254.0 nm (2998 (200-400)nm)	20.447	12215265	49.52	138851



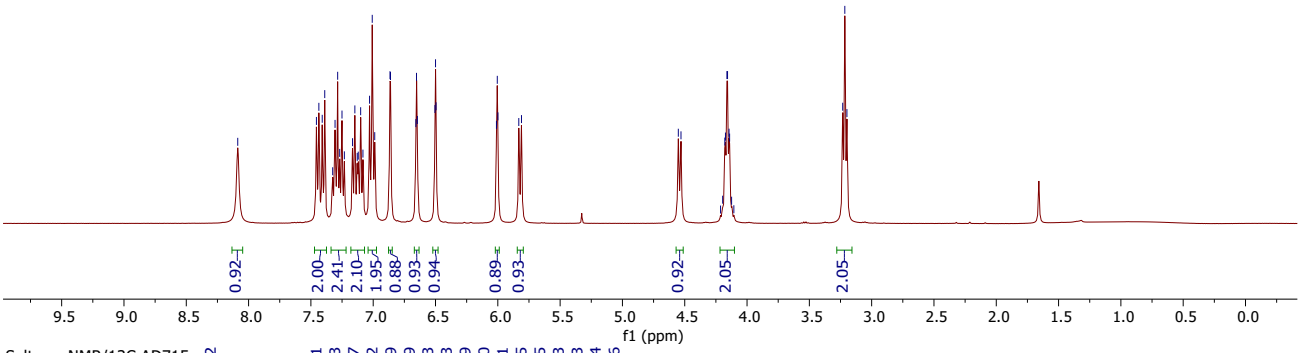
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	16.593	6623828	15.55	98627
2	2998 PDA 254.0 nm (2998 (200-400)nm)	20.198	35978987	84.45	415925

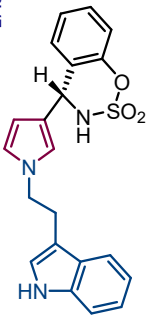


9ae

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

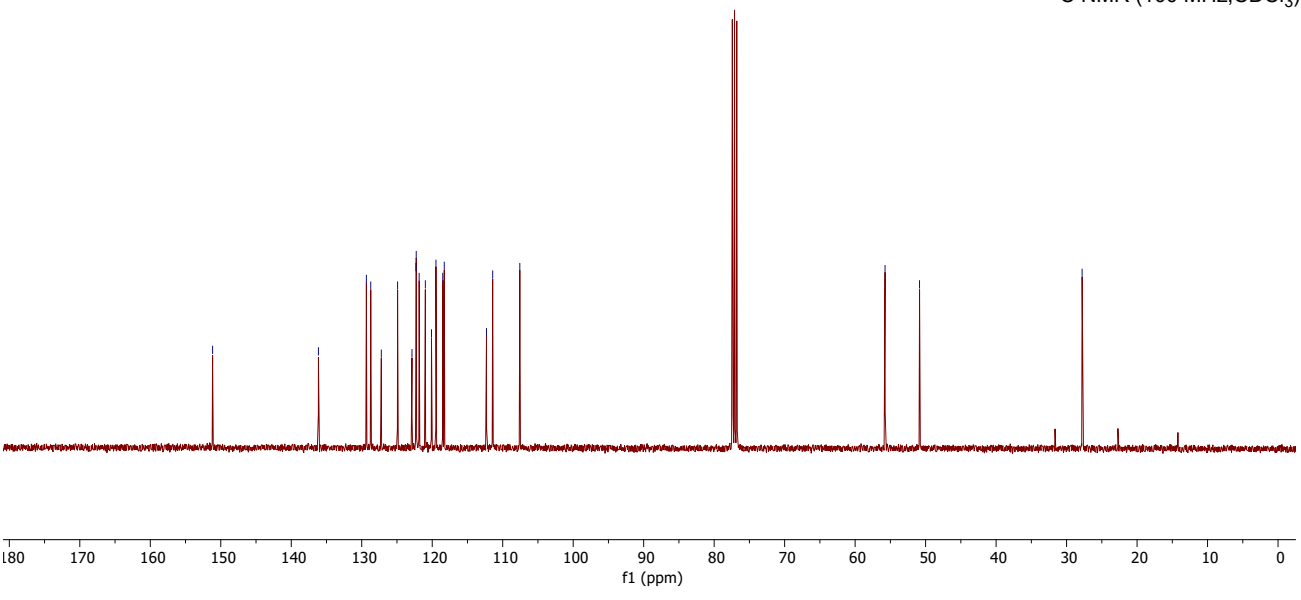


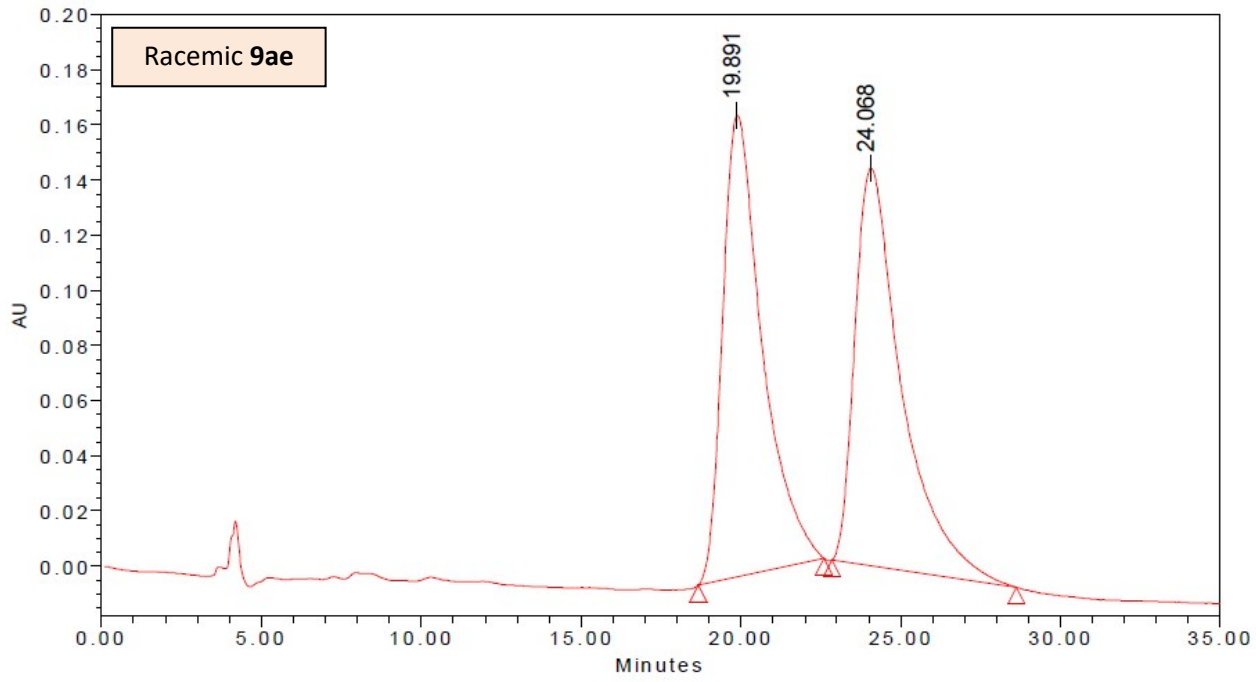
Sultams NMR/13C AD715
AD-715 RAC



9ae

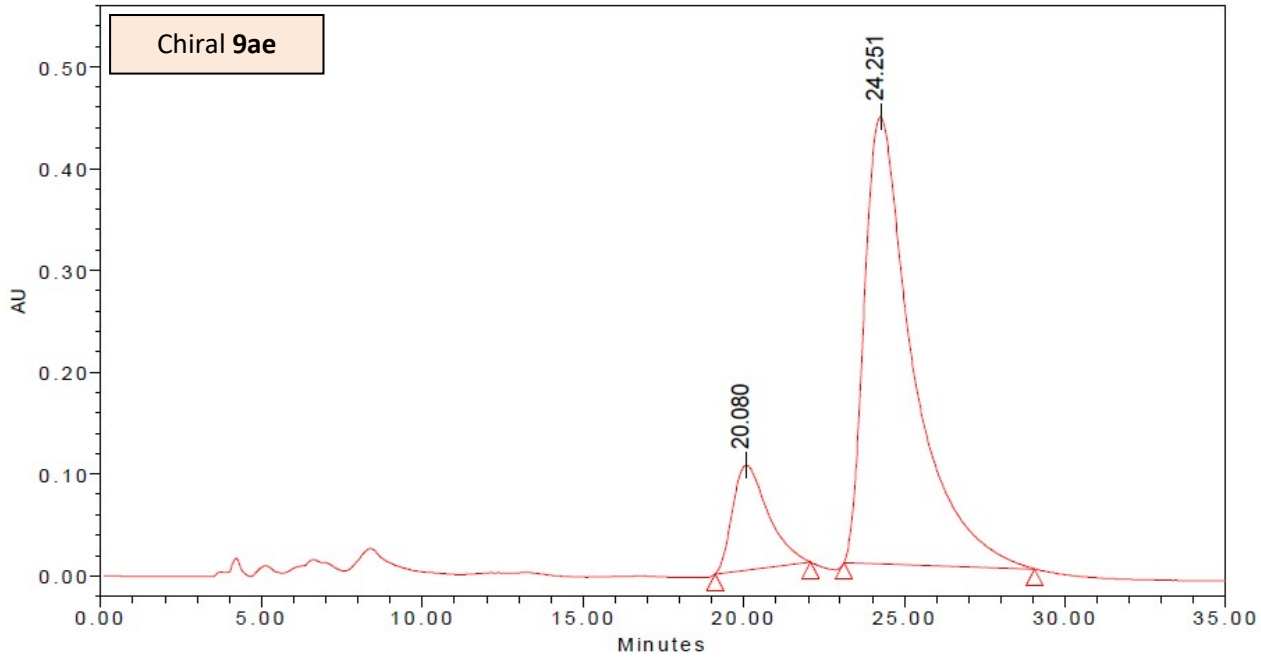
^{13}C NMR (100 MHz,$CDCl_3$)





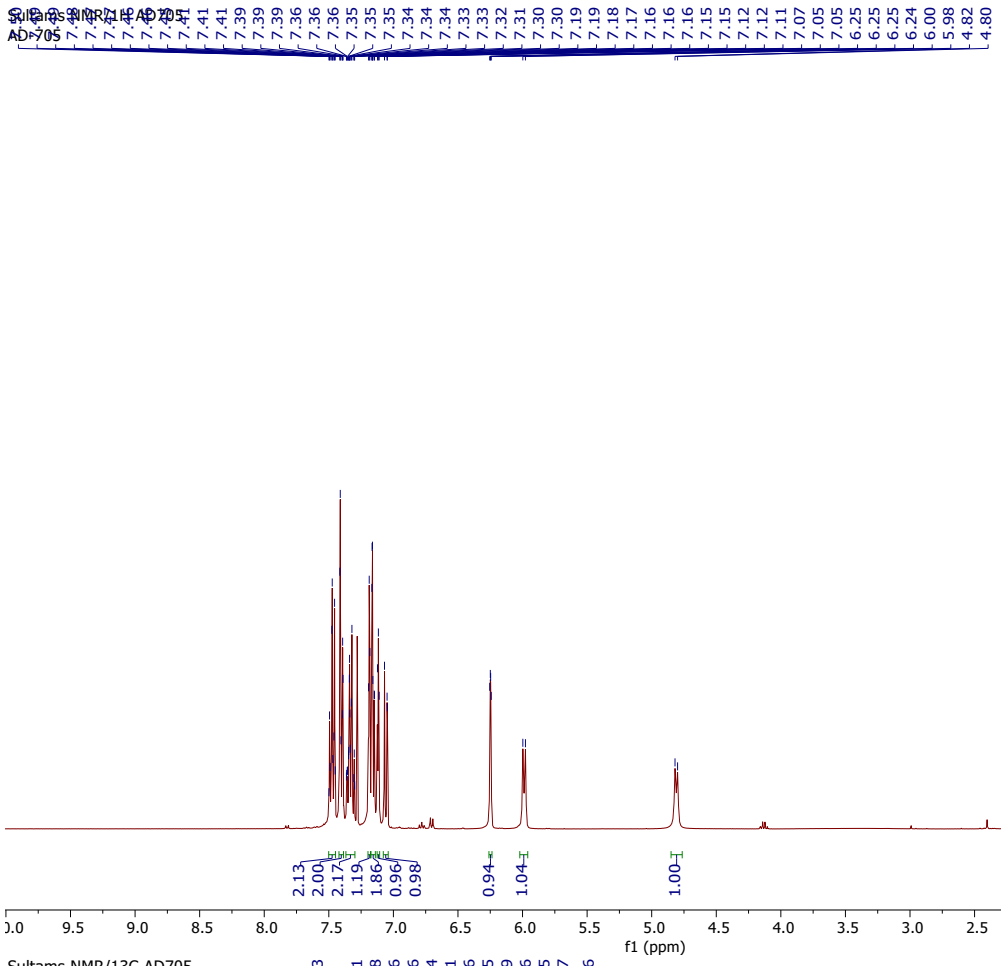
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

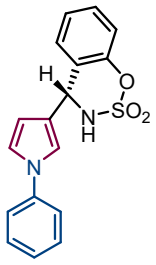
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	19.891	14460236	49.65	167402
2	2998 PDA 254.0 nm (2998 (200-400)nm)	24.068	14661975	50.35	144097



Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

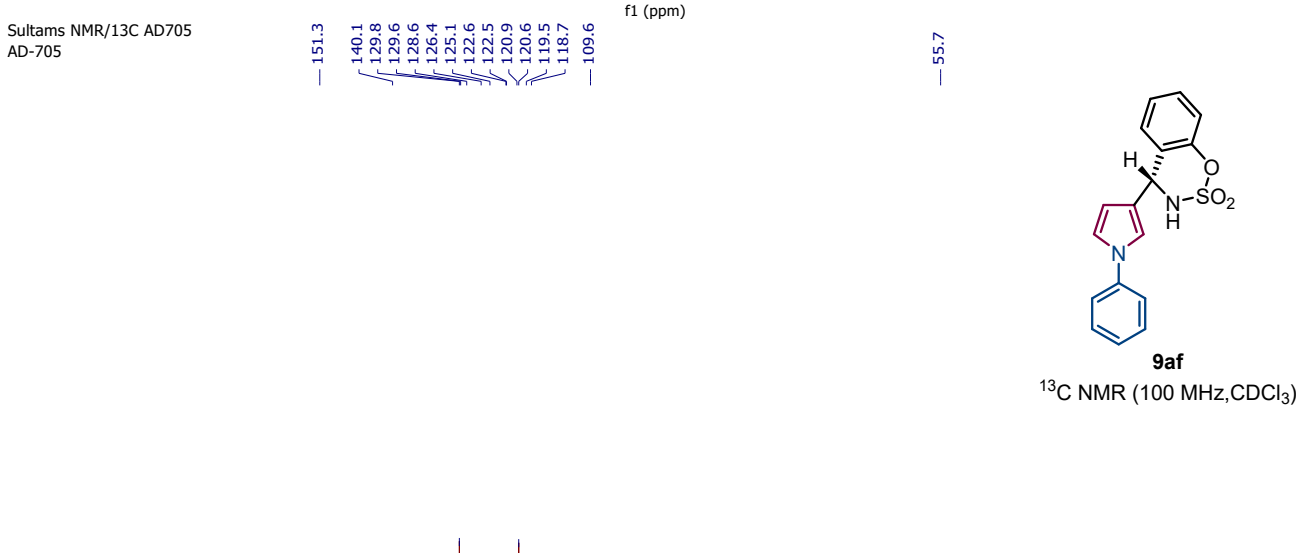
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	20.080	7942937	14.70	102820
2	2998 PDA 254.0 nm (2998 (200-400)nm)	24.251	46108245	85.30	439249





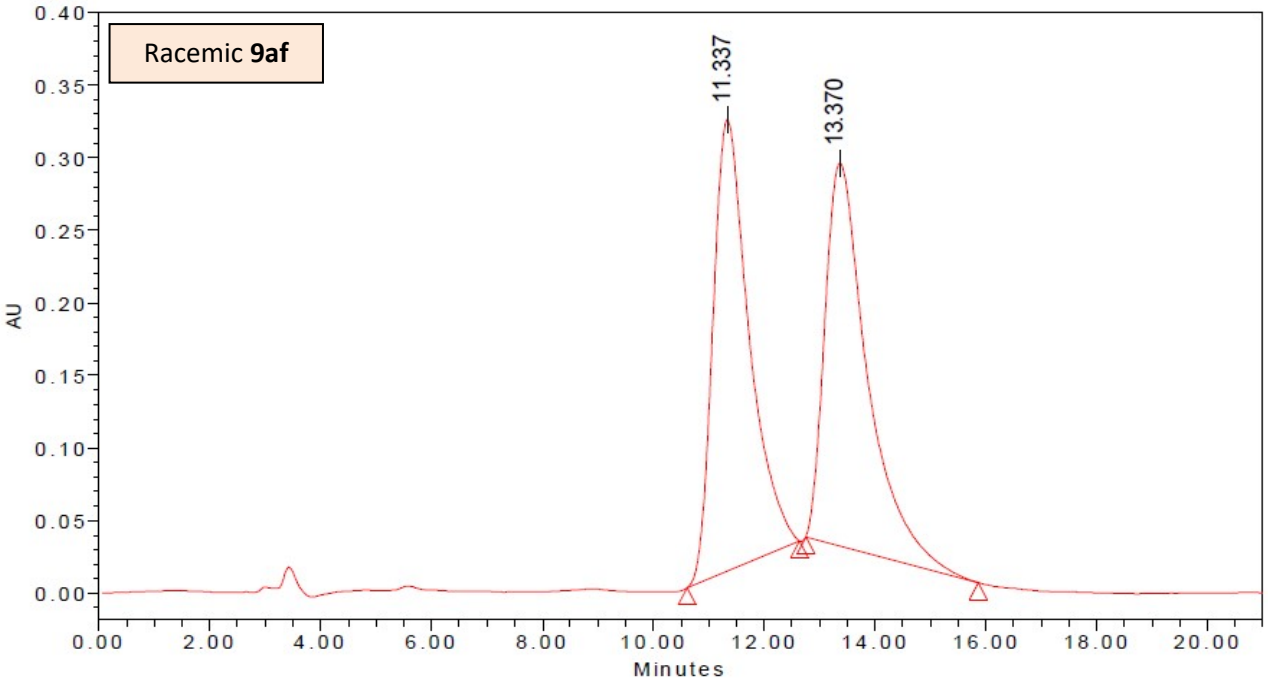
9af

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



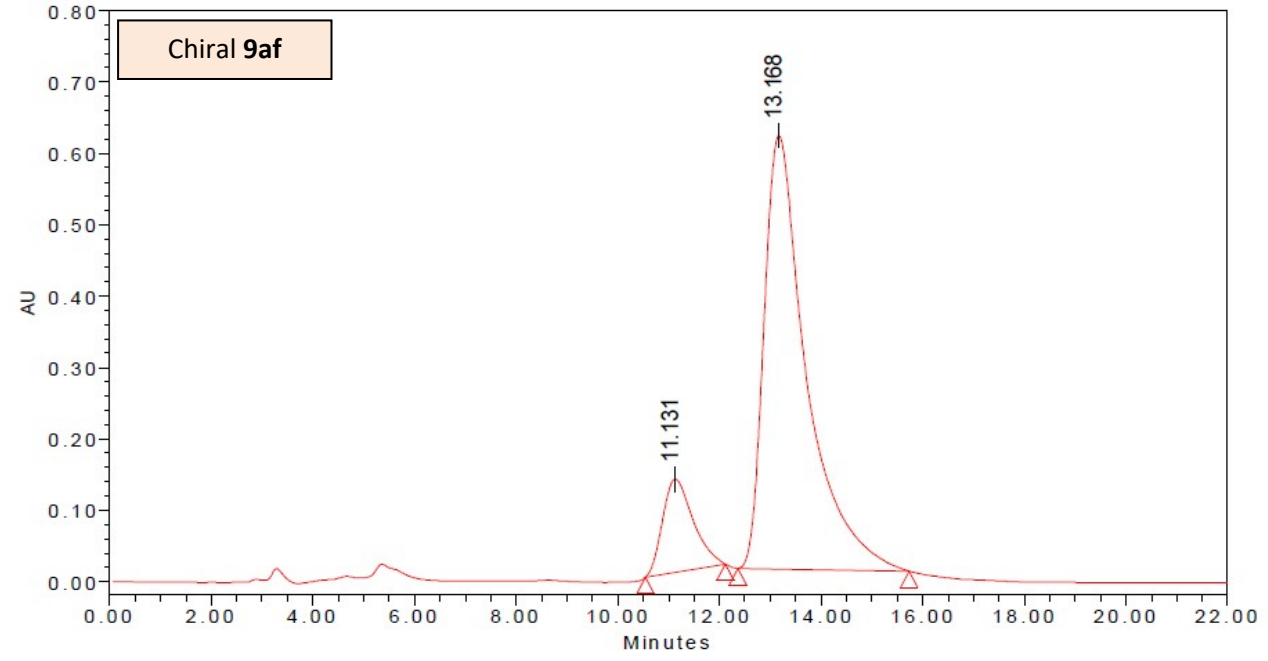
9af

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



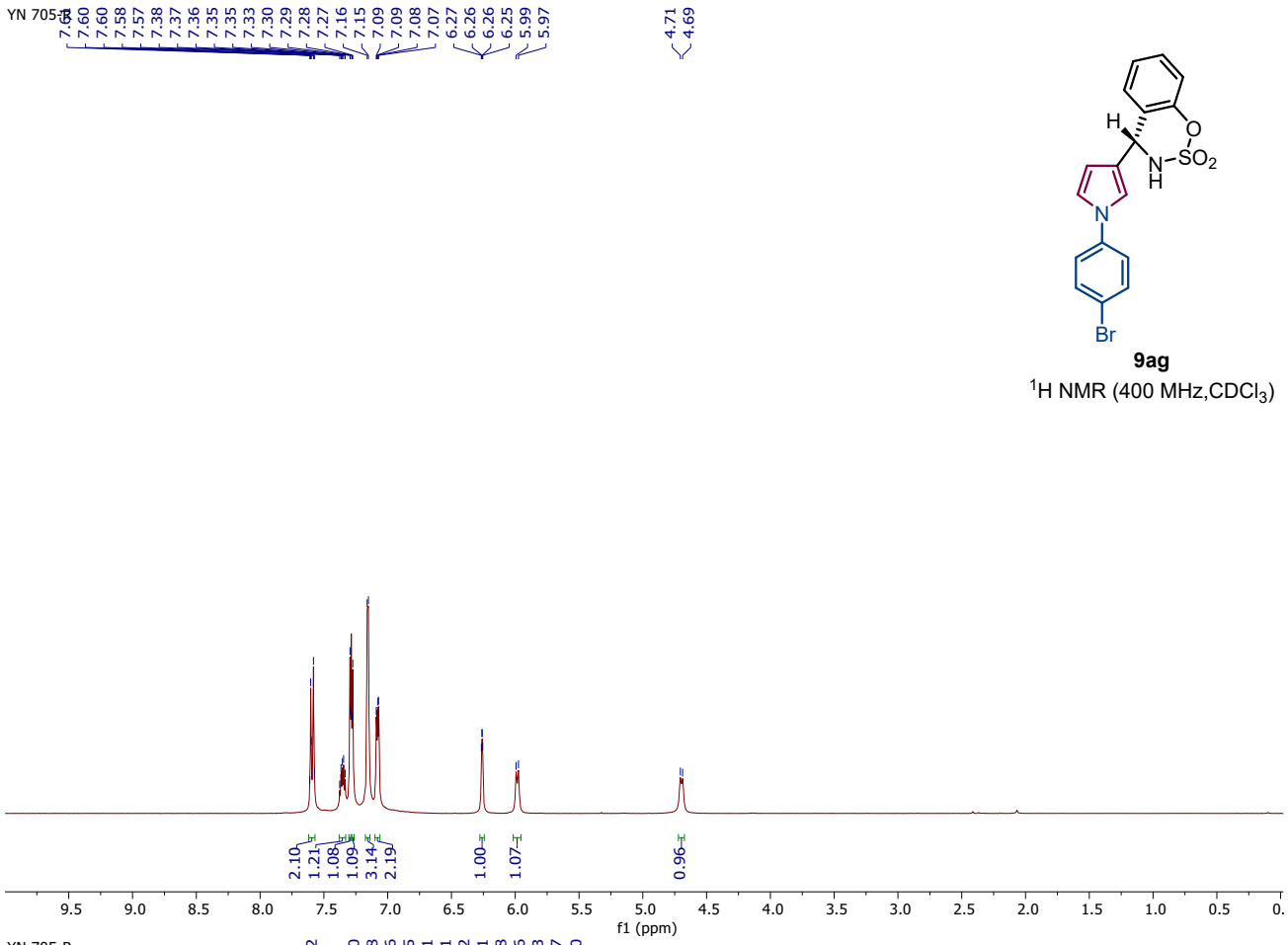
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	11.337	14137968	50.13	310849
2	2998 PDA 254.0 nm (2998 (200-400)nm)	13.370	14064732	49.87	263666



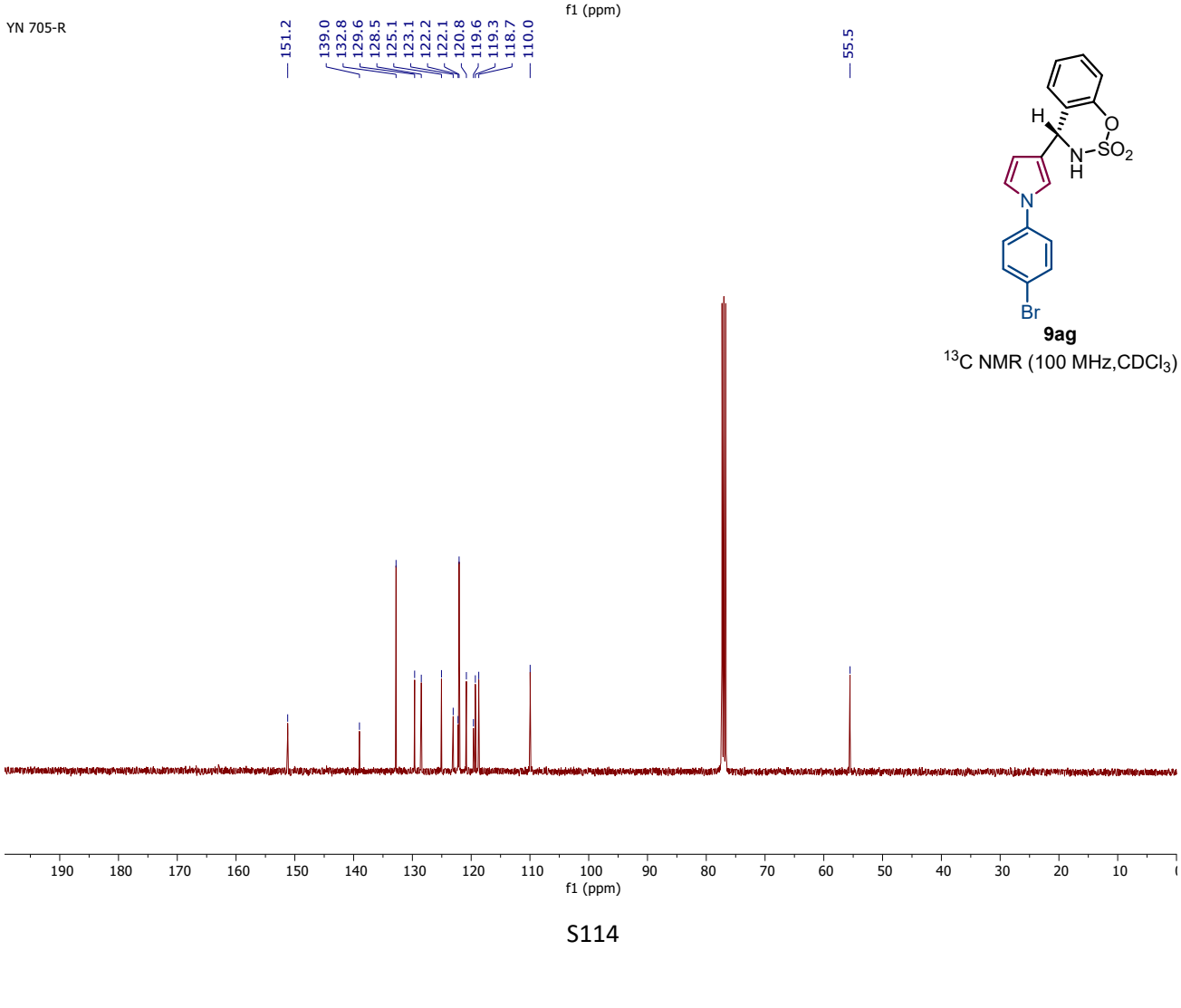
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	11.131	5457309	13.45	130670
2	2998 PDA 254.0 nm (2998 (200-400)nm)	13.168	35108722	86.55	607411



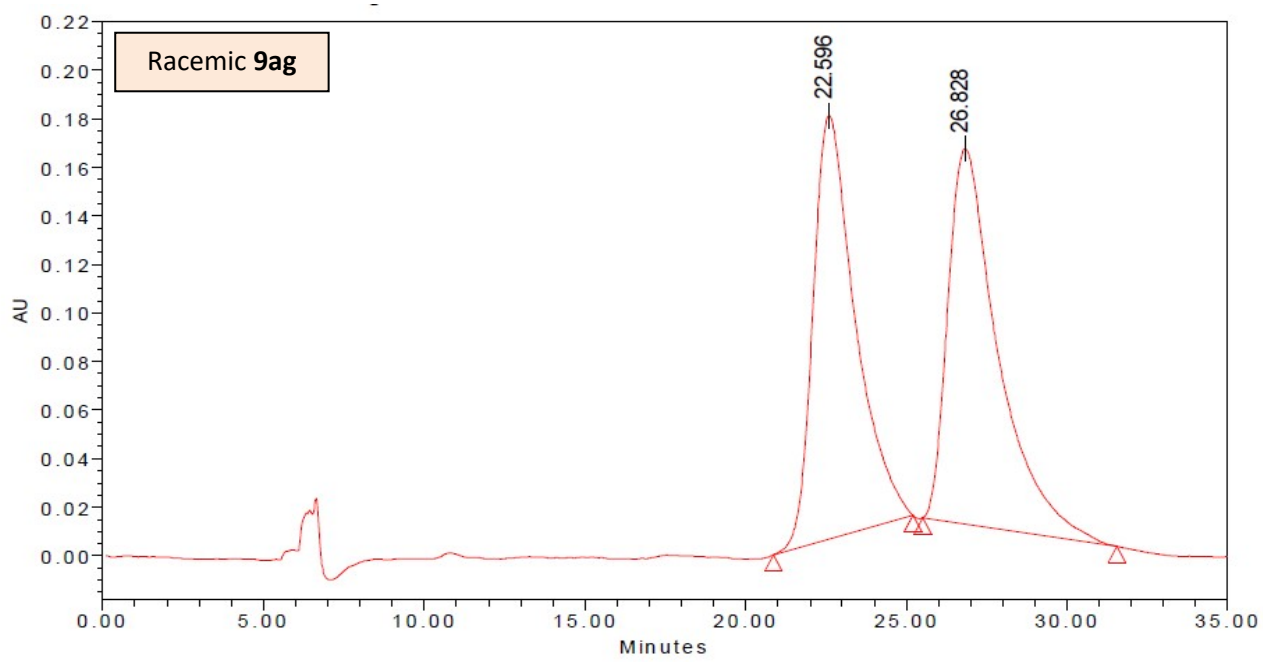
9ag

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



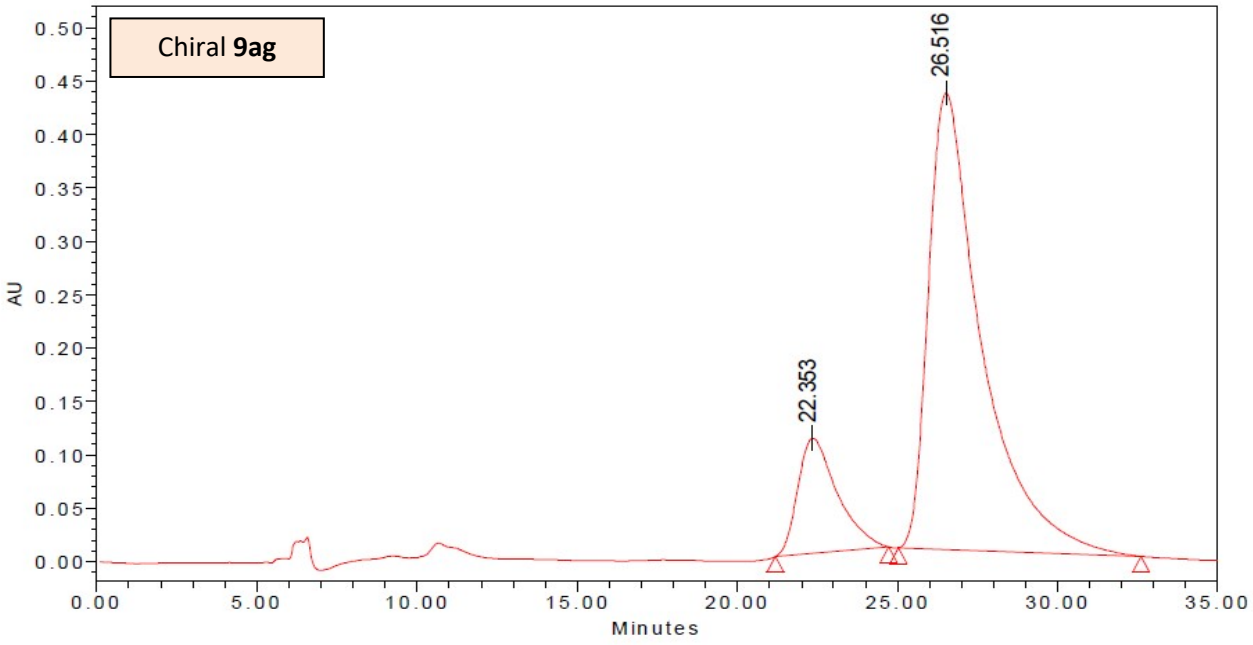
9ag

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



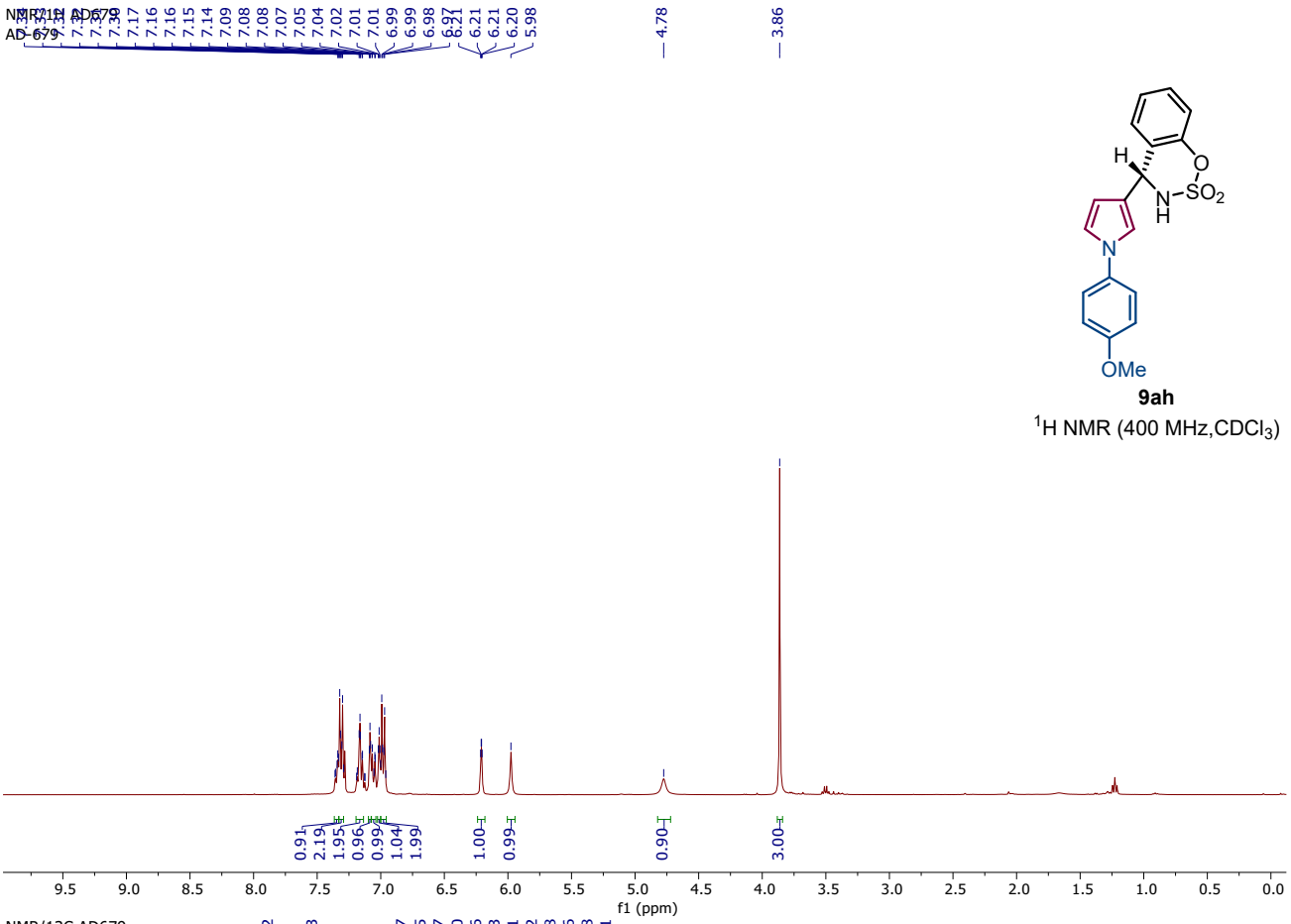
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	22.596	15944507	48.74	174327
2	2998 PDA 254.0 nm (2998 (200-400)nm)	26.828	16770515	51.26	154565



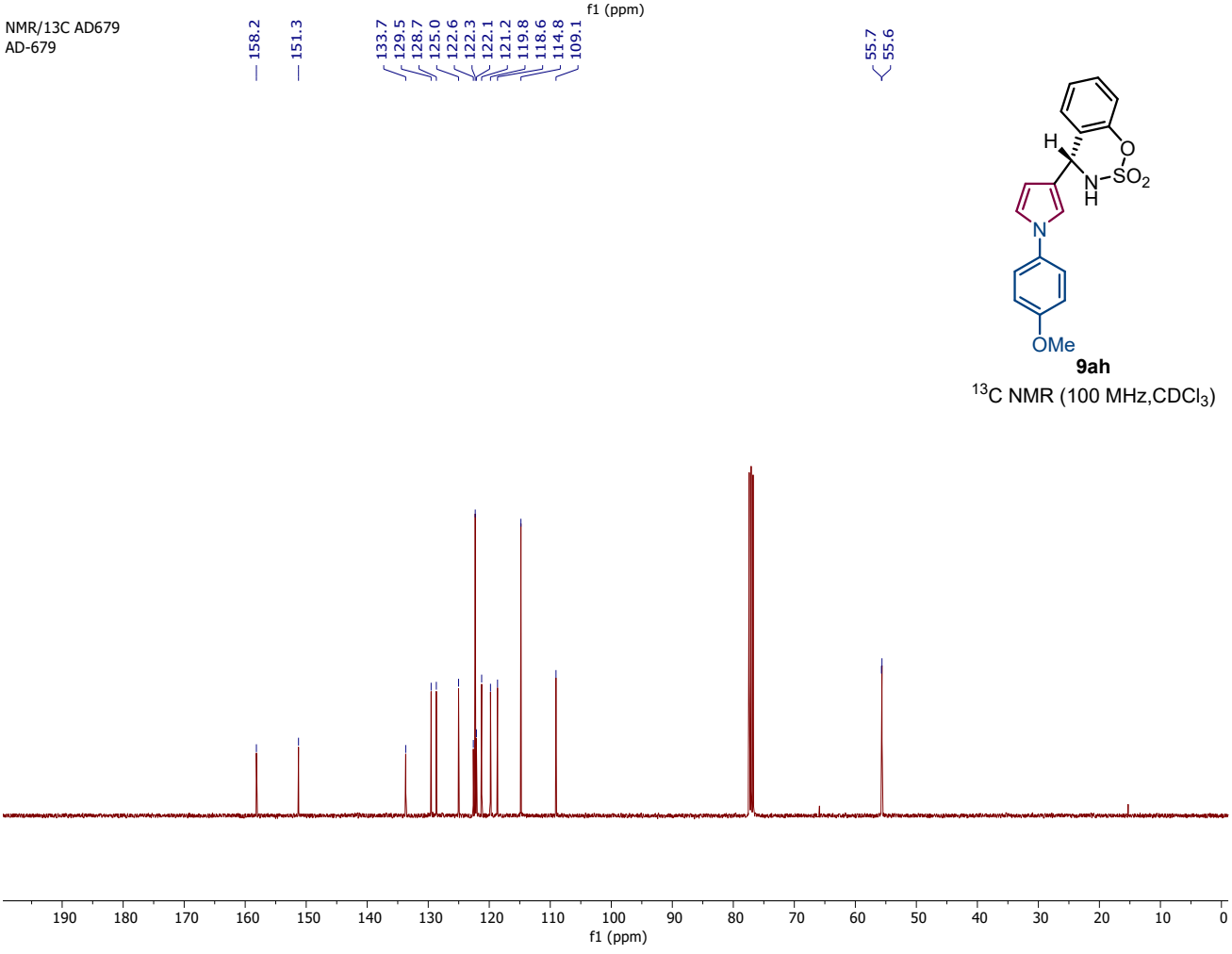
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	22.353	9233777	15.72	107743
2	2998 PDA 254.0 nm (2998 (200-400)nm)	26.516	49523289	84.28	427334



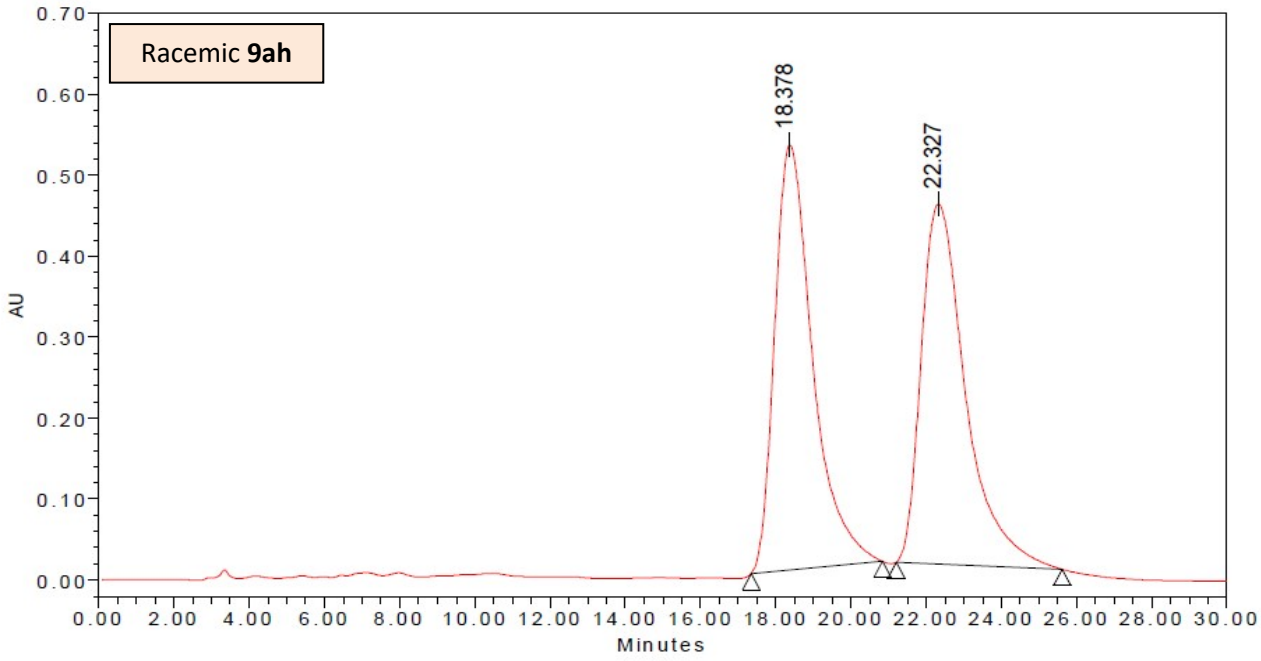
9ah

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



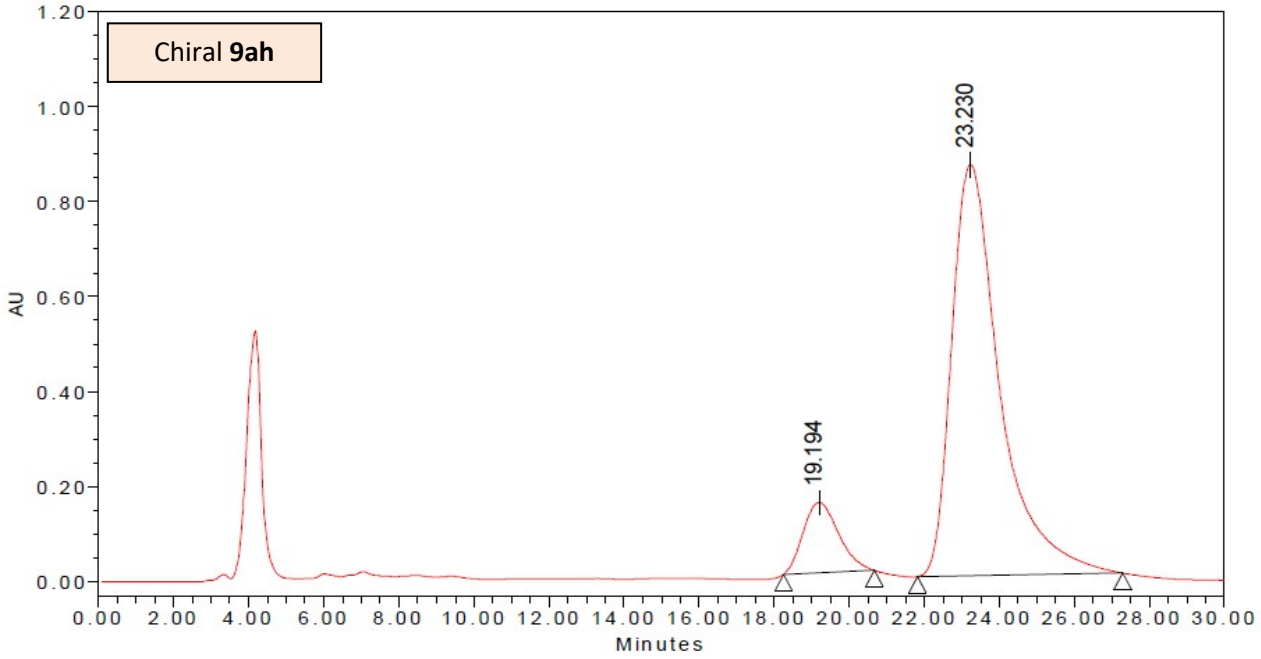
9ah

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



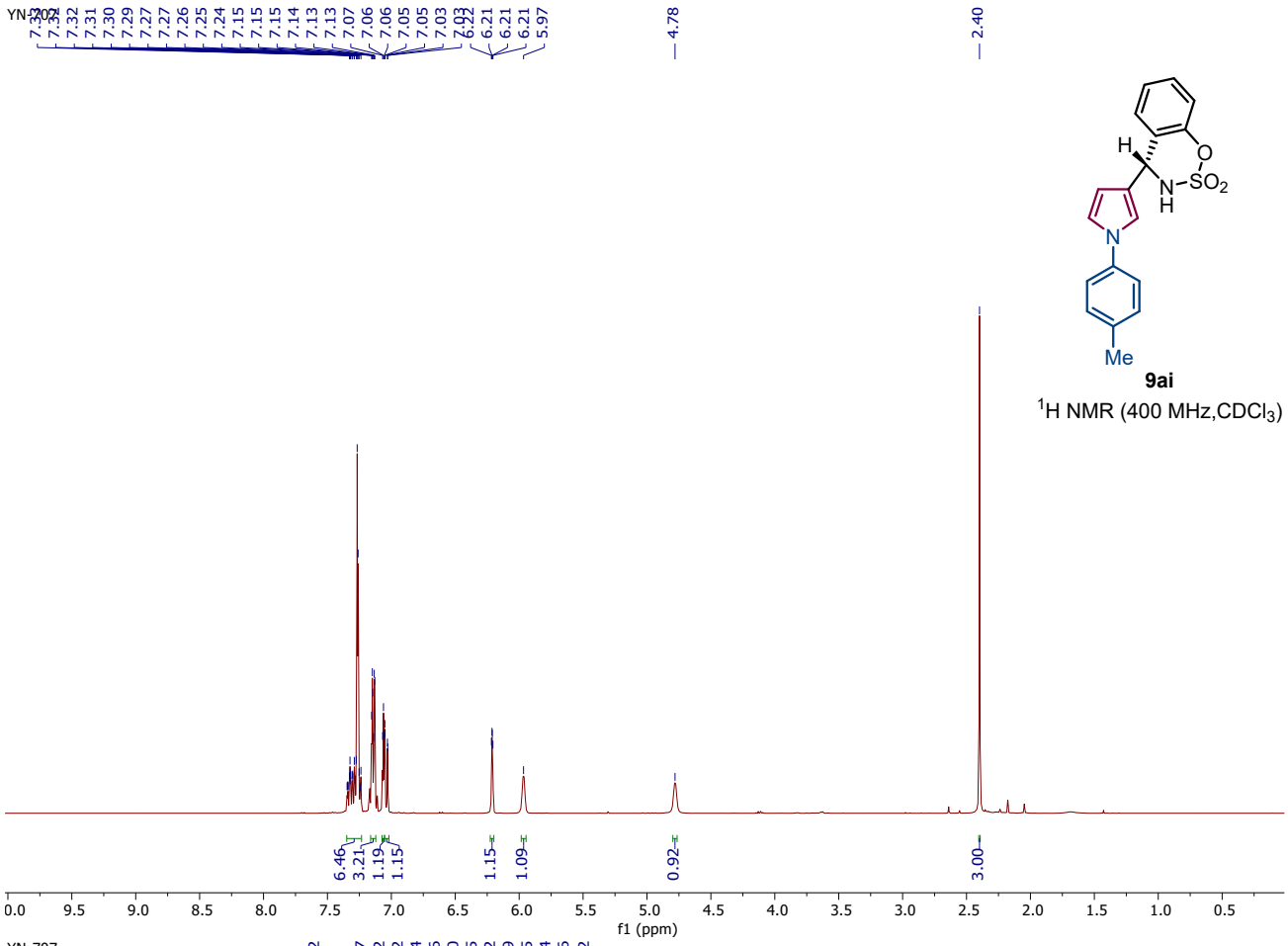
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	18.378	36827563	50.27	524814
2	2998 PDA 254.0 nm (2998 (200-400)nm)	22.327	36430564	49.73	444371



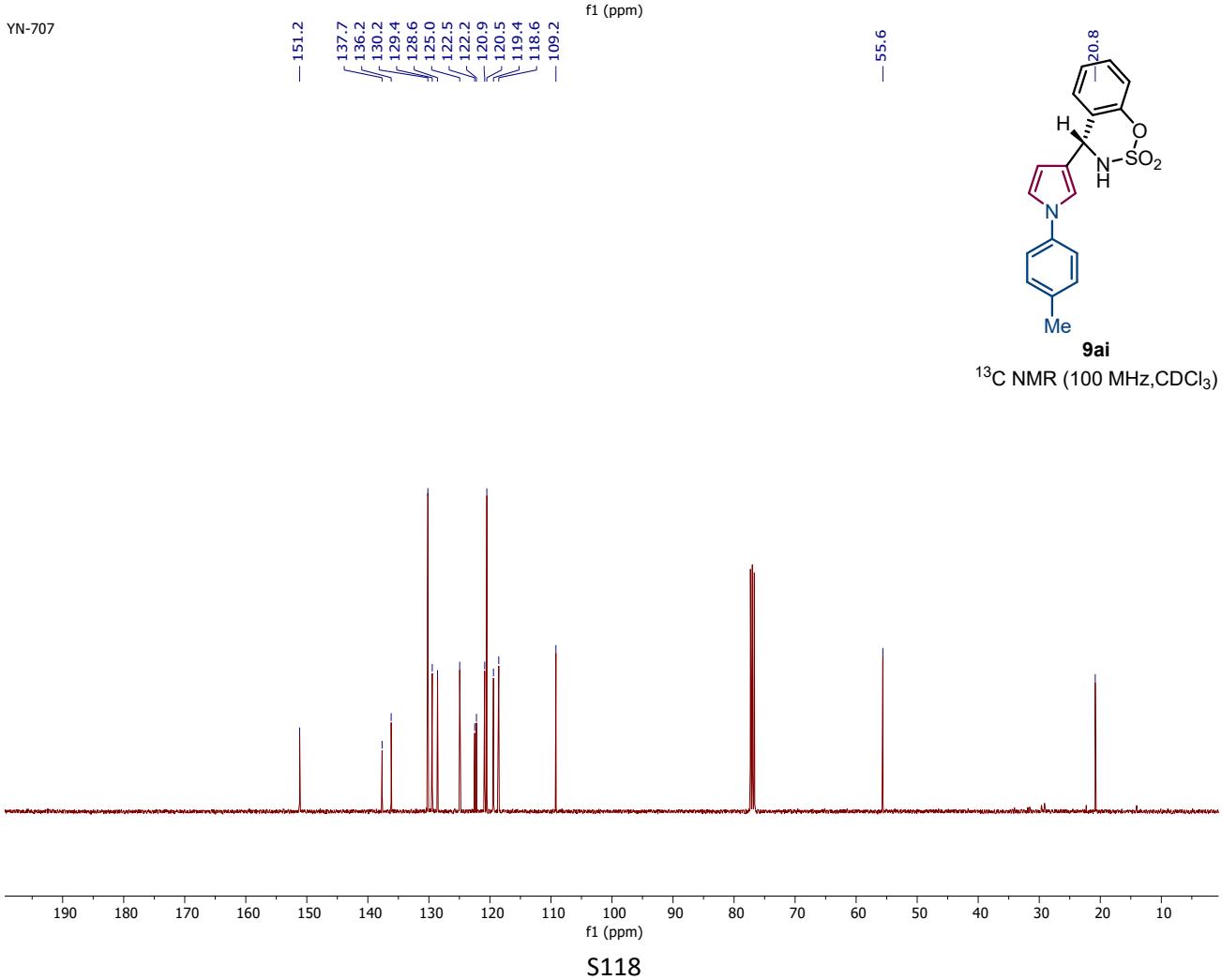
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	19.194	9714733	11.16	148057
2	2998 PDA 254.0 nm (2998 (200-400)nm)	23.230	77345141	88.84	865839



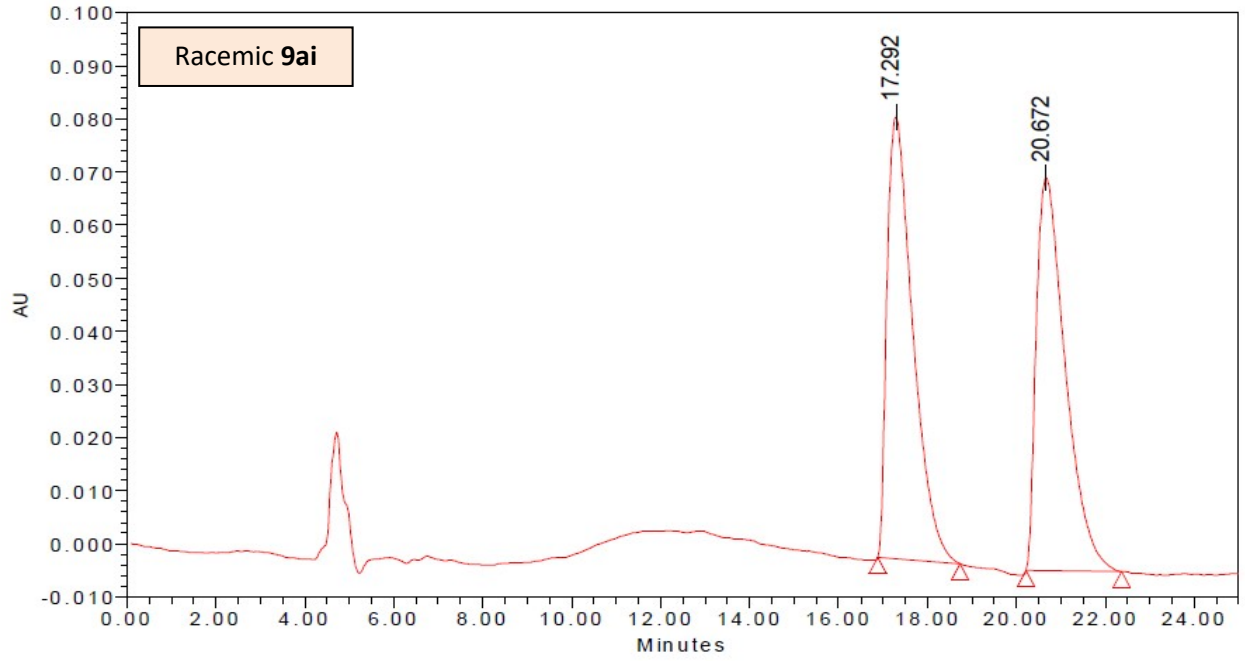
9ai

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



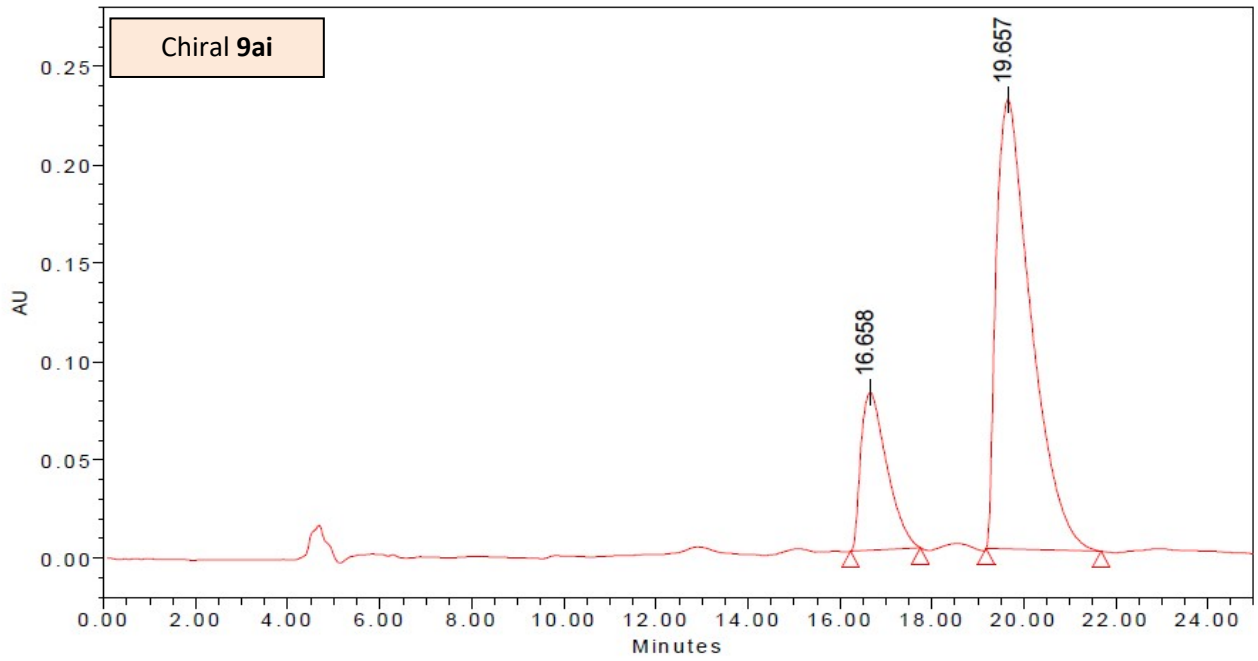
9ai

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



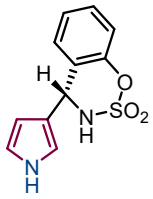
Processed Channel: 2998 PDA 265.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 265.0 nm (2998 (200-400)nm)	17.292	3352805	49.94	83190
2	2998 PDA 265.0 nm (2998 (200-400)nm)	20.672	3360627	50.06	73891



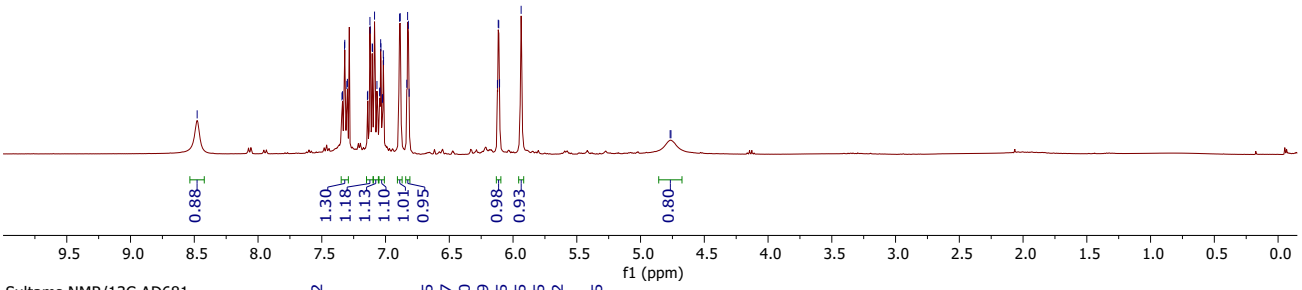
Processed Channel: 2998 PDA 265.0 nm (2998 (200-400)nm)

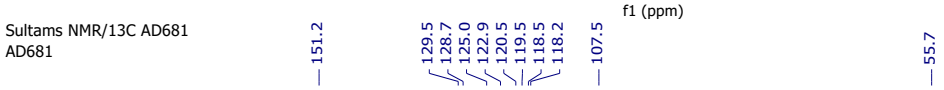
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 265.0 nm (2998 (200-400)nm)	16.658	3145225	20.76	80245
2	2998 PDA 265.0 nm (2998 (200-400)nm)	19.657	12007187	79.24	228496

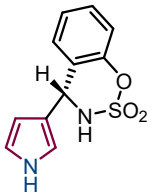


9aj

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

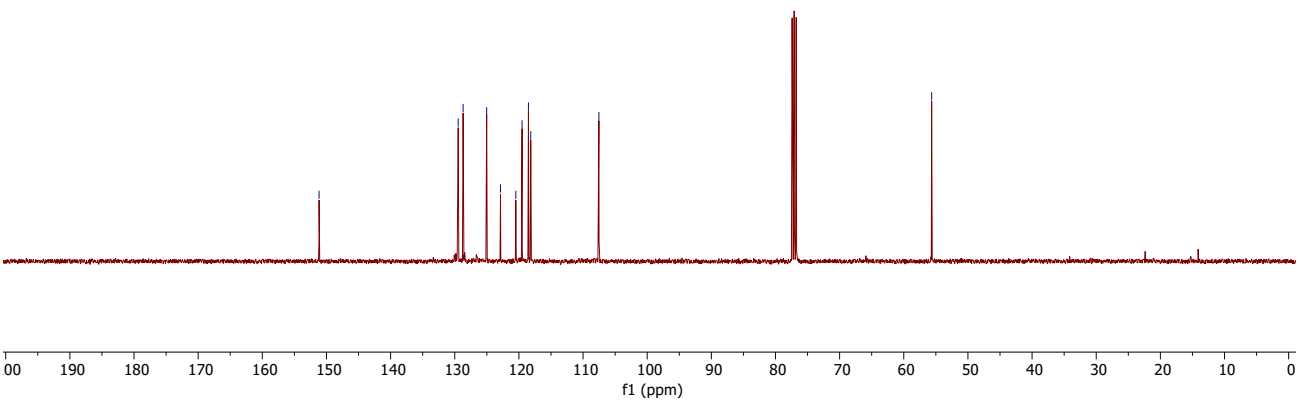


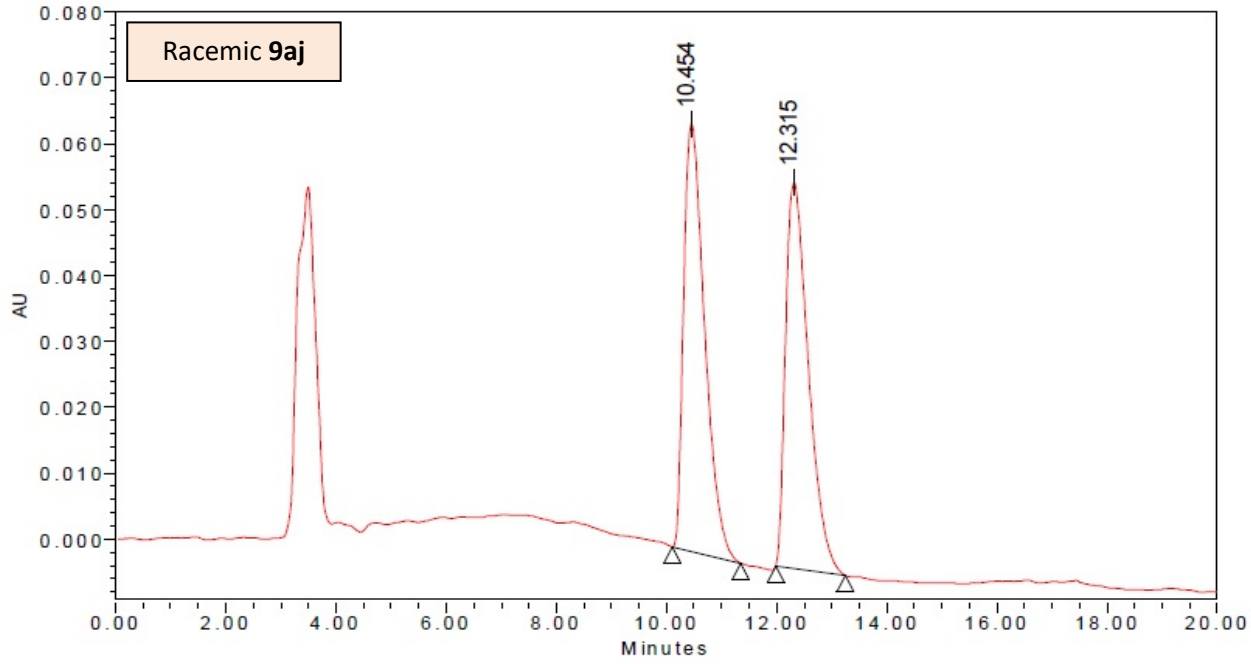




9aj

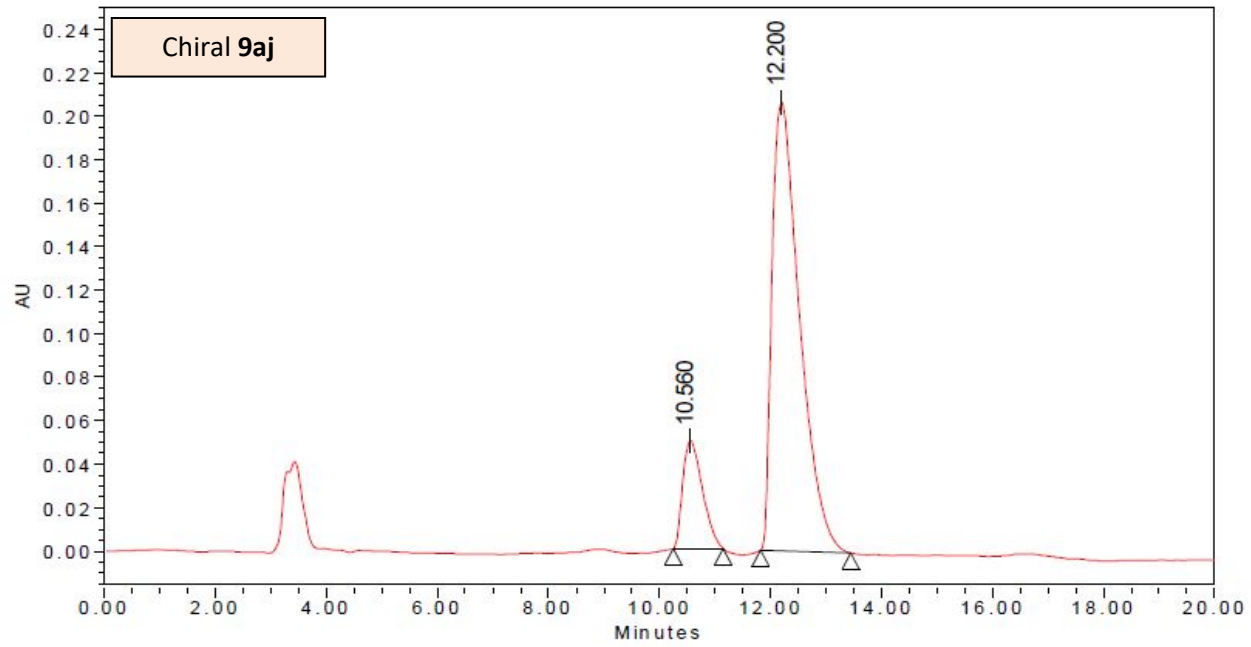
^{13}C NMR (100 MHz,$CDCl_3$)





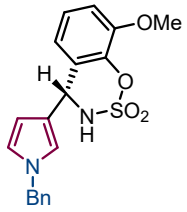
Processed Channel: 2998 PDA 275.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 275.0 nm (2998 (200-400)nm)	10.454	1711833	50.37	64853
2	2998 PDA 275.0 nm (2998 (200-400)nm)	12.315	1686800	49.63	58610



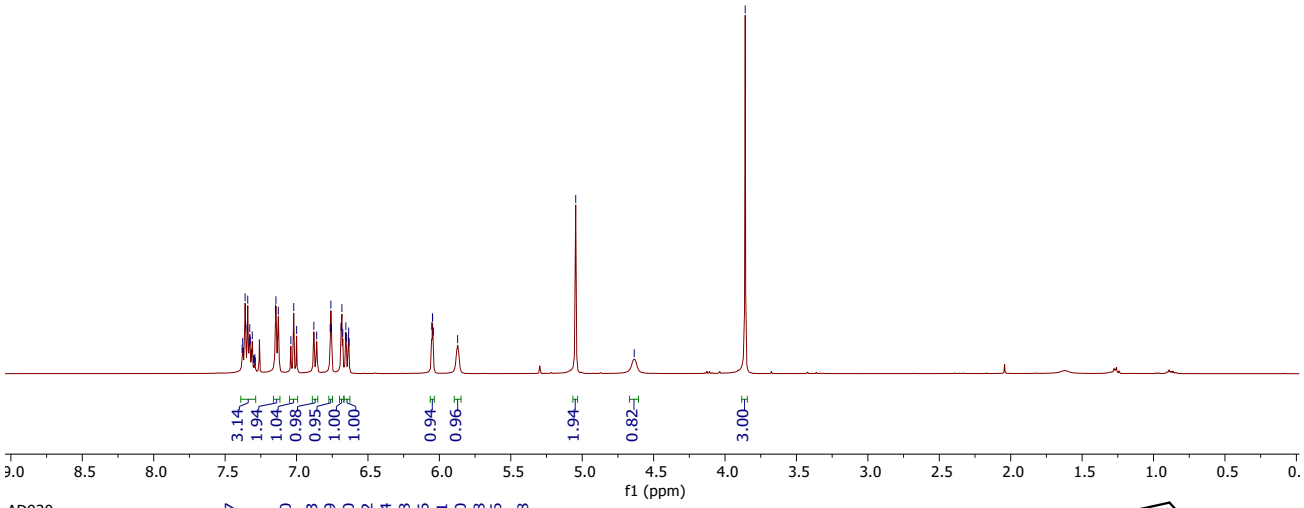
Processed Channel: 2998 PDA 275.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 275.0 nm (2998 (200-400)nm)	10.560	1218693	14.57	49460
2	2998 PDA 275.0 nm (2998 (200-400)nm)	12.200	7146145	85.43	206402

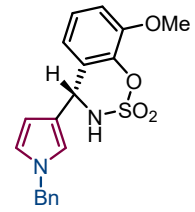


9ba

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

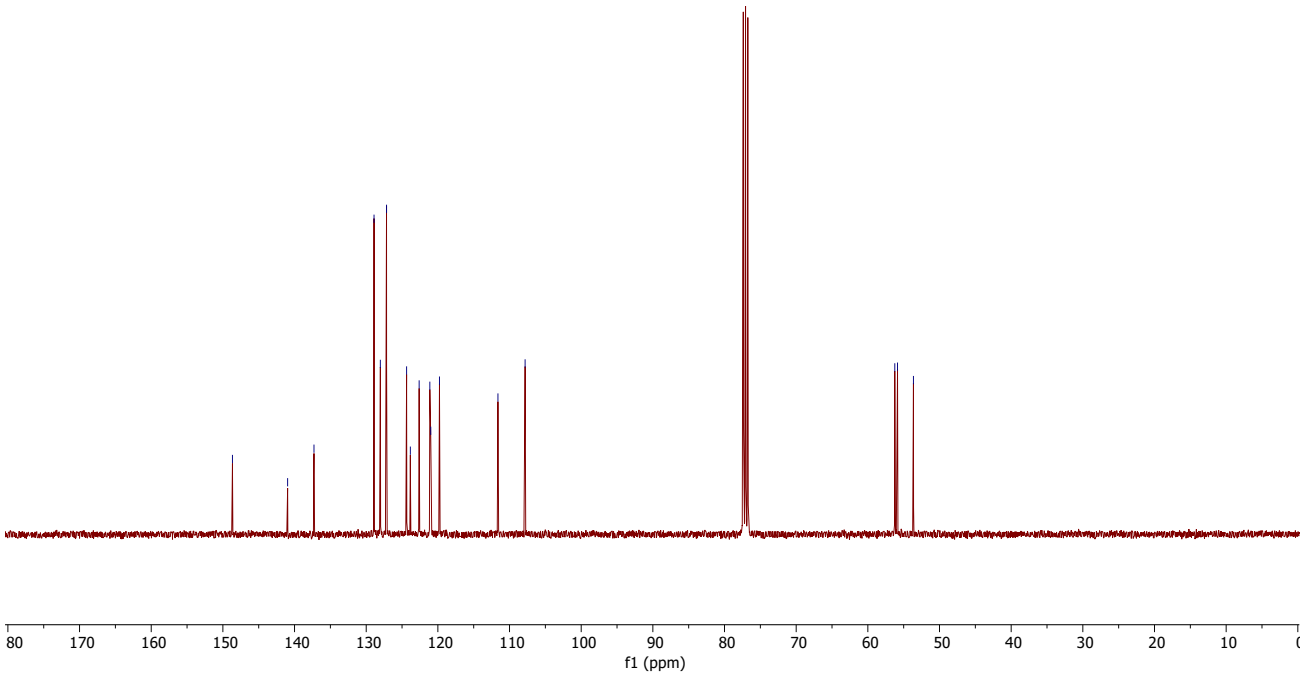


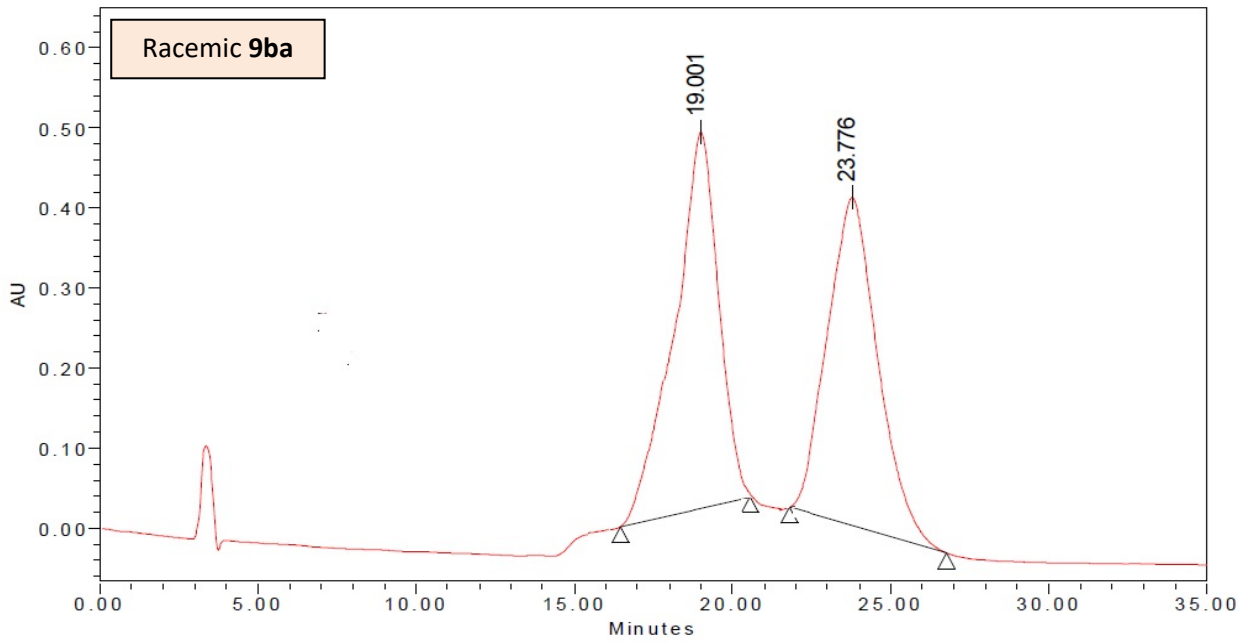
AD920



9ba

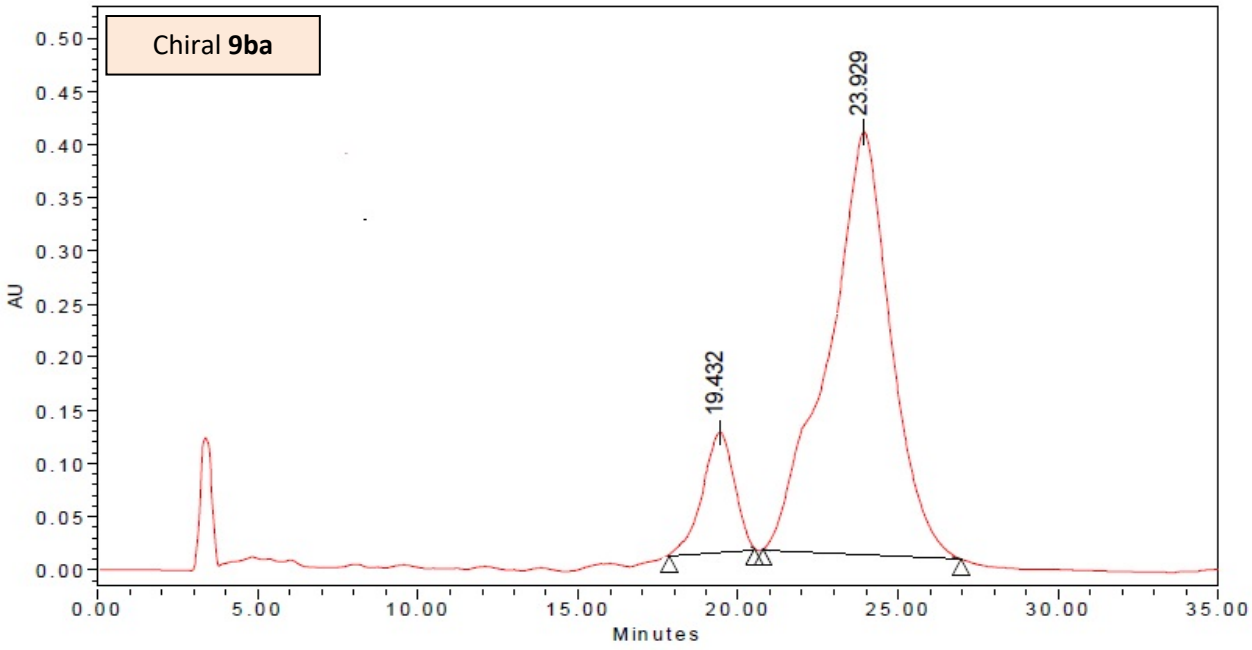
^{13}C NMR (100 MHz,$CDCl_3$)





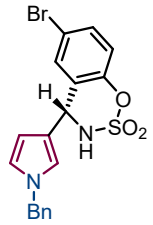
Processed Channel: 2998 PDA 230.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 230.0 nm (2998 (200-400)nm)	19.001	54603261	50.02	469503
2	2998 PDA 230.0 nm (2998 (200-400)nm)	23.776	54553323	49.98	409445



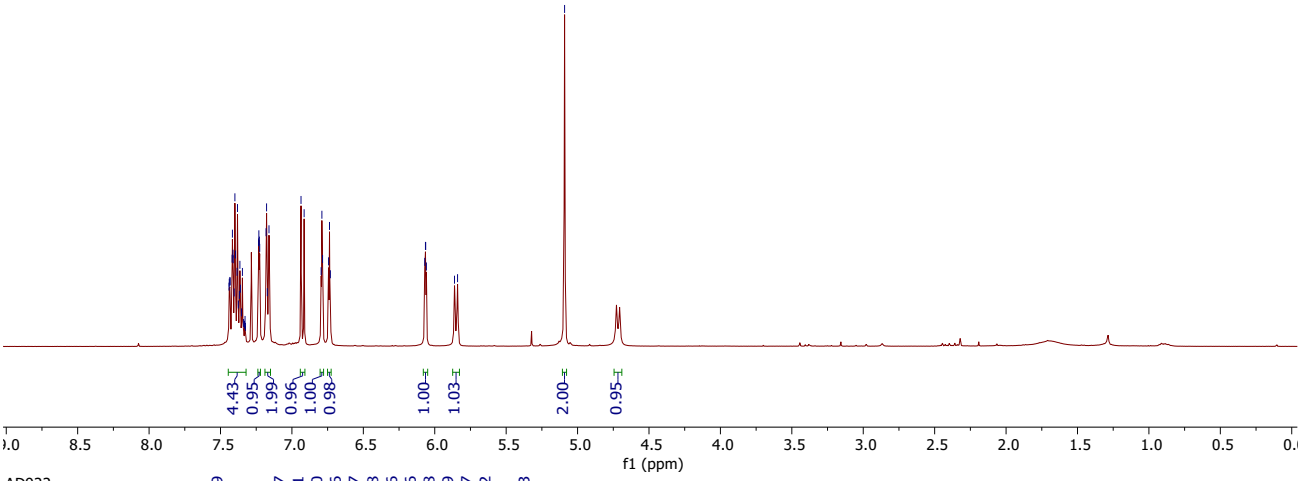
Processed Channel: 2998 PDA 230.0 nm (2998 (200-400)nm)

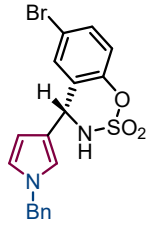
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 230.0 nm (2998 (200-400)nm)	19.432	5458220	9.59	93496
2	2998 PDA 230.0 nm (2998 (200-400)nm)	23.929	51450149	90.41	380883



9ca

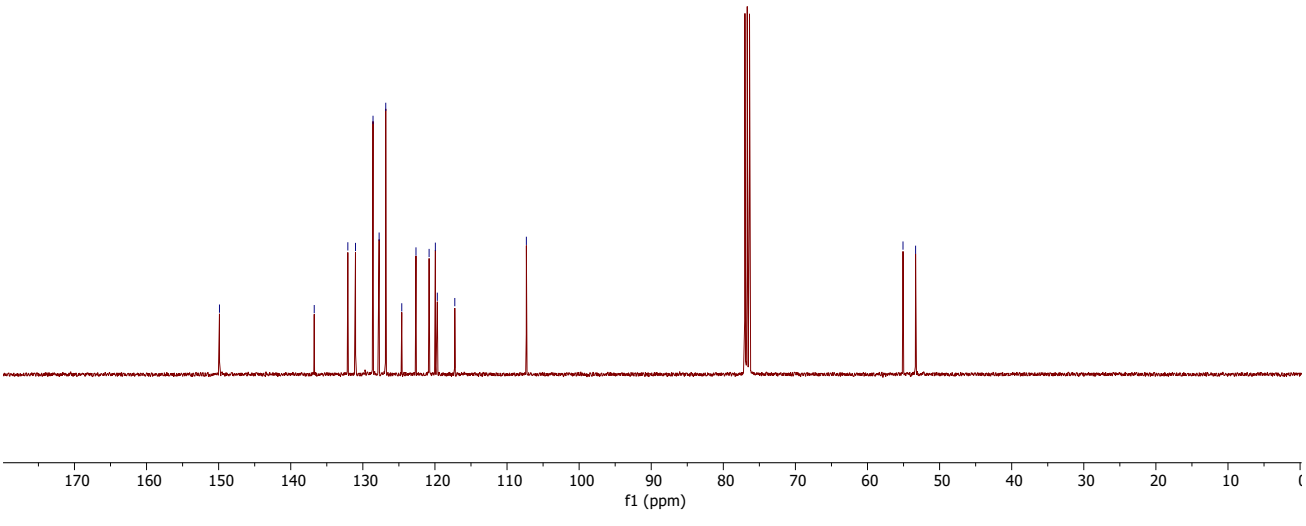
^{1}H NMR (400 MHz,$CDCl_3$)

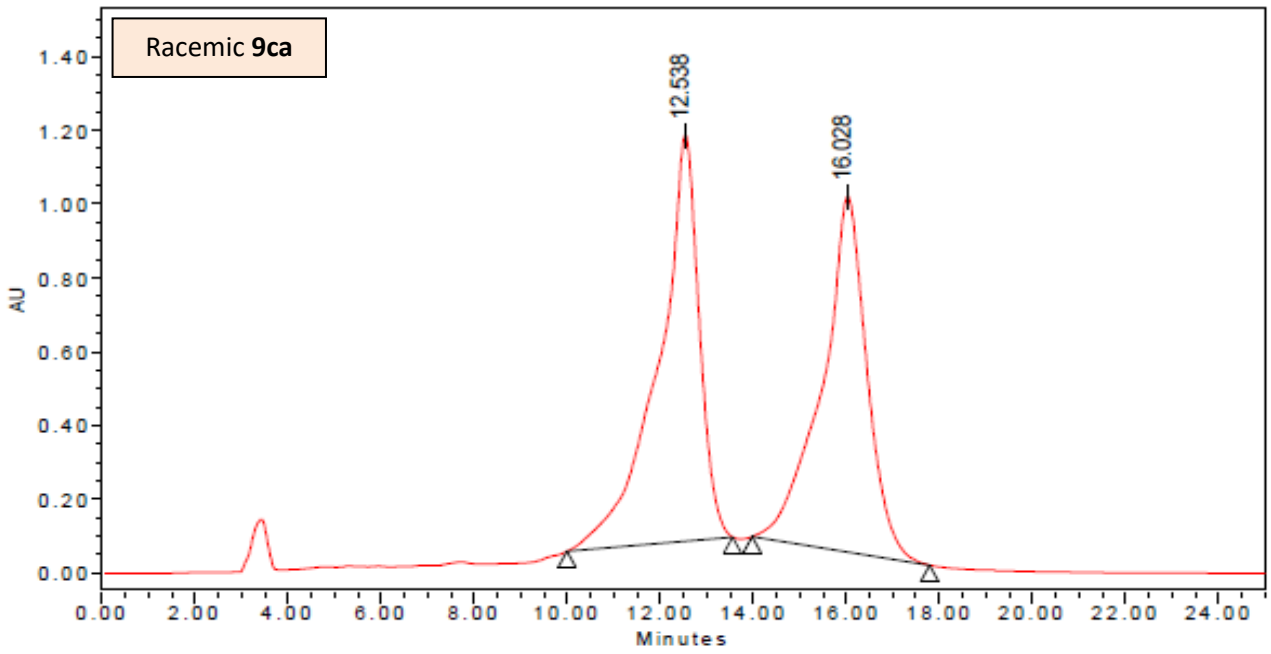




9ca

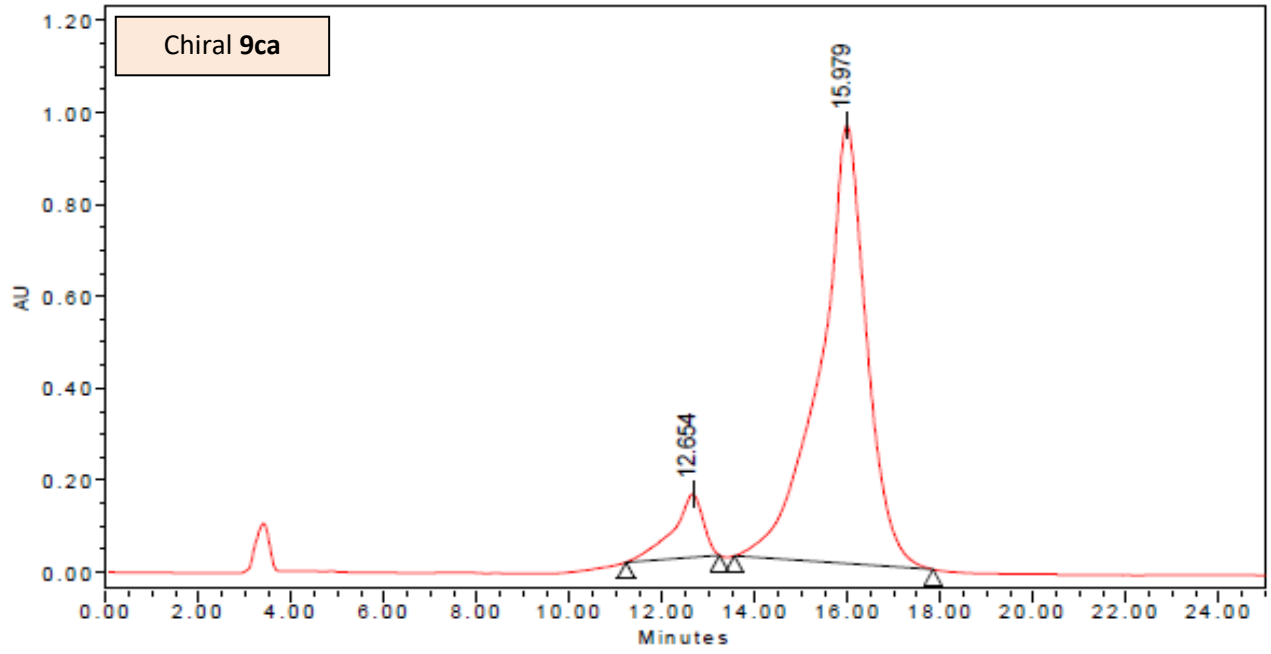
^{13}C NMR (100 MHz, $CDCl_3$)





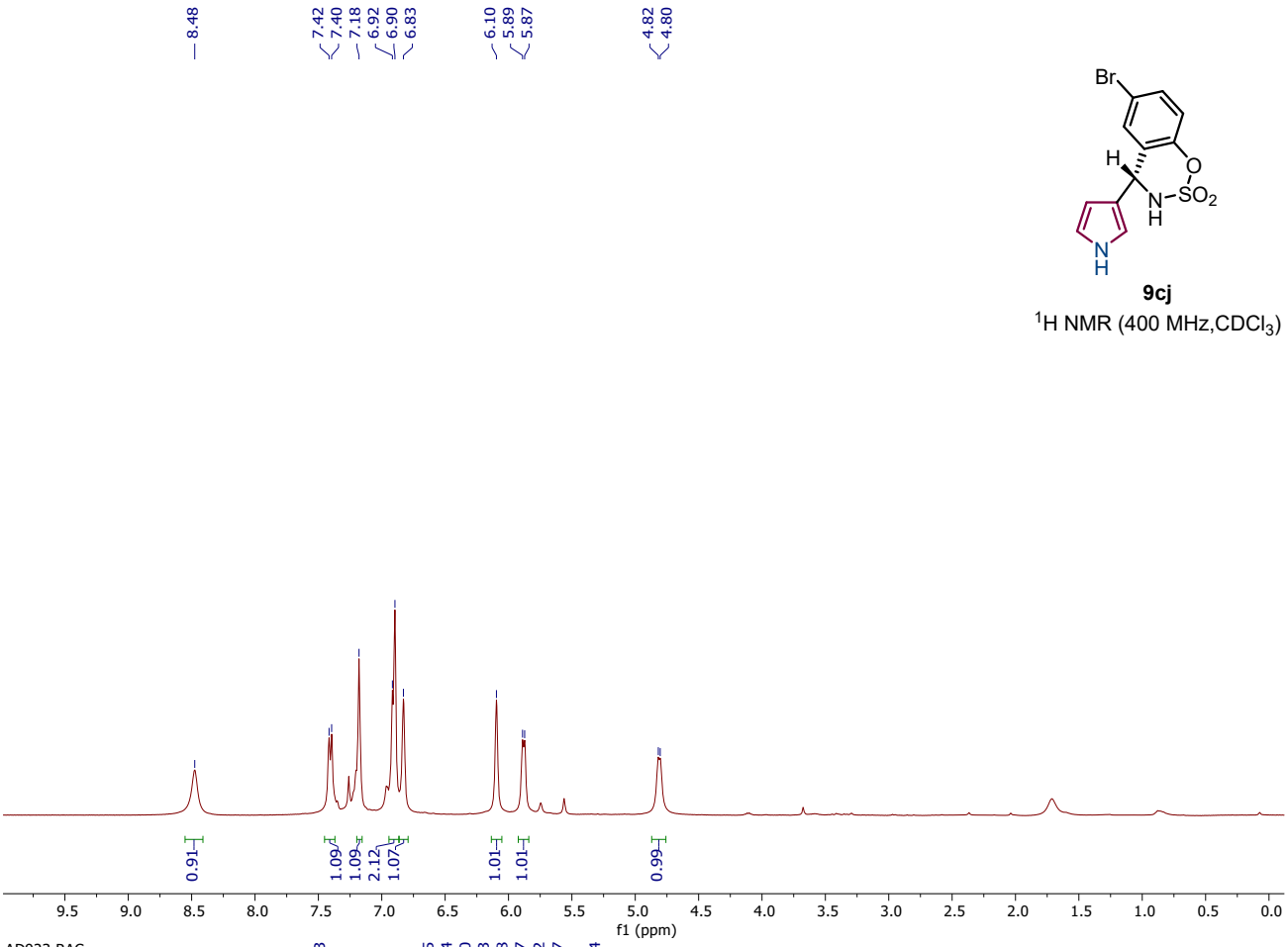
Processed Channel: 2998 PDA 230.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 230.0 nm (2998 (200-400)nm)	12.538	67203611	50.87	1100121
2	2998 PDA 230.0 nm (2998 (200-400)nm)	16.028	64899799	49.13	963778



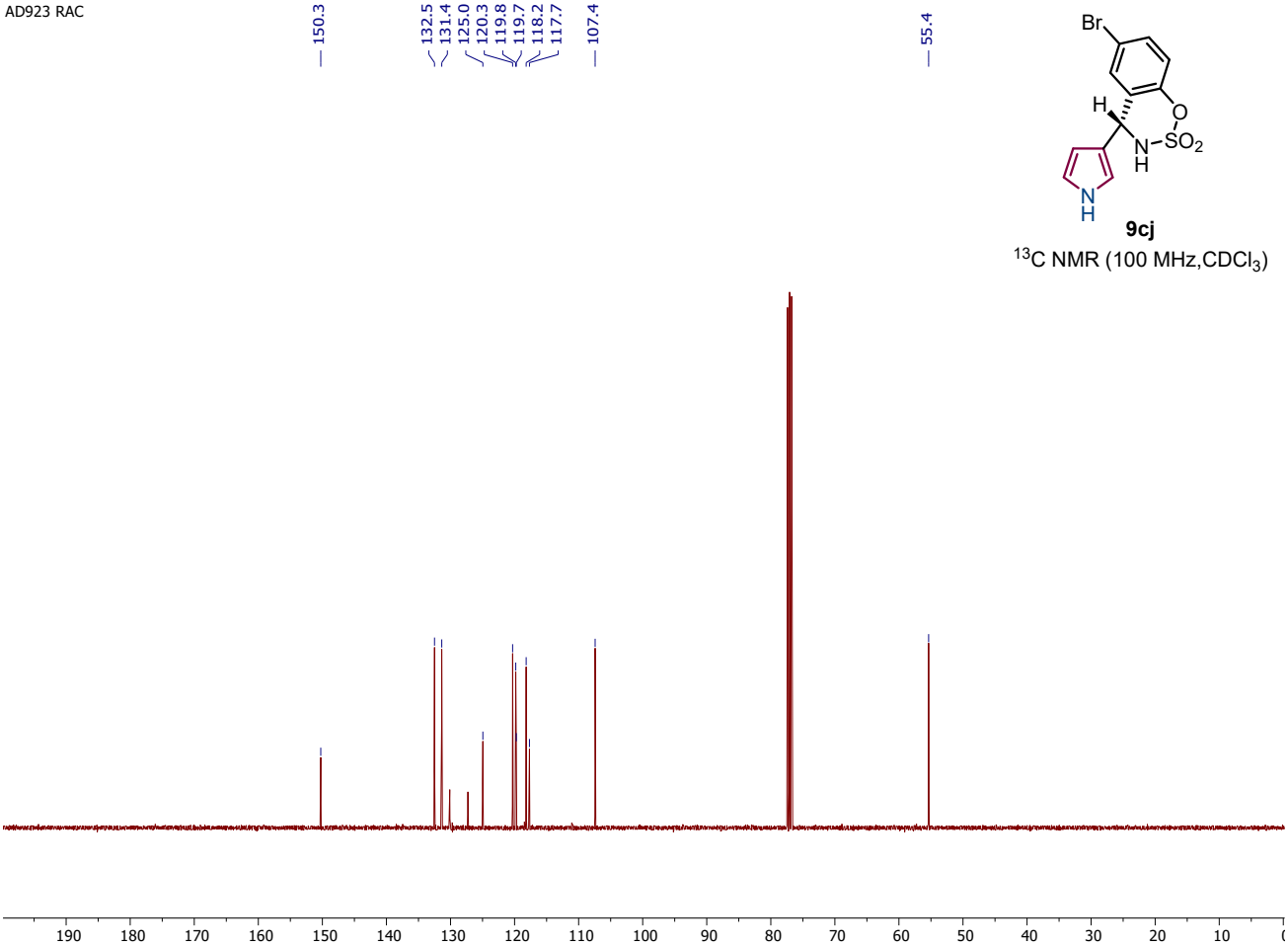
Processed Channel: 2998 PDA 230.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 230.0 nm (2998 (200-400)nm)	12.654	6265817	8.58	137510
2	2998 PDA 230.0 nm (2998 (200-400)nm)	15.979	66731553	91.42	952738



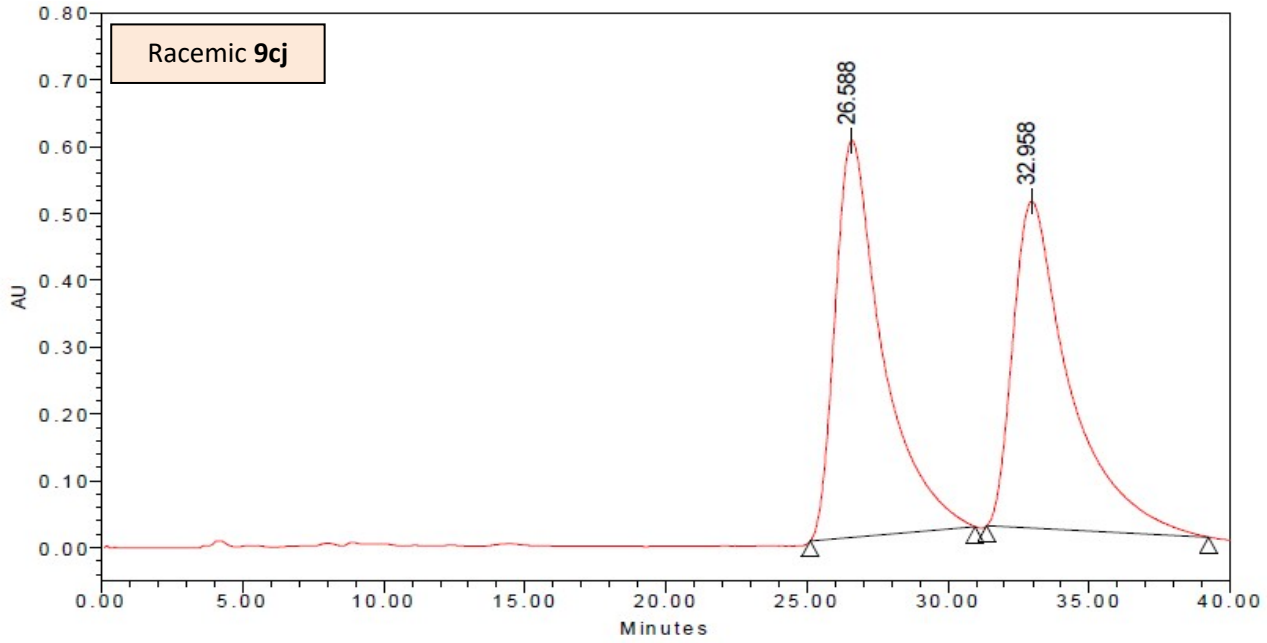
9cj

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



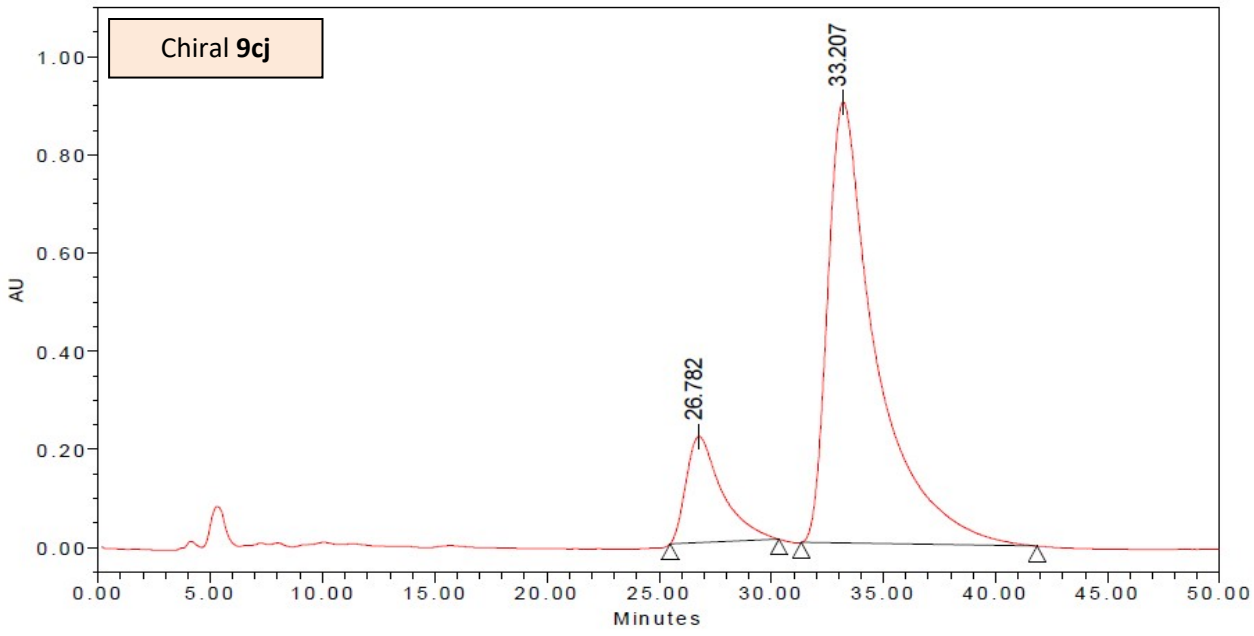
9cj

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



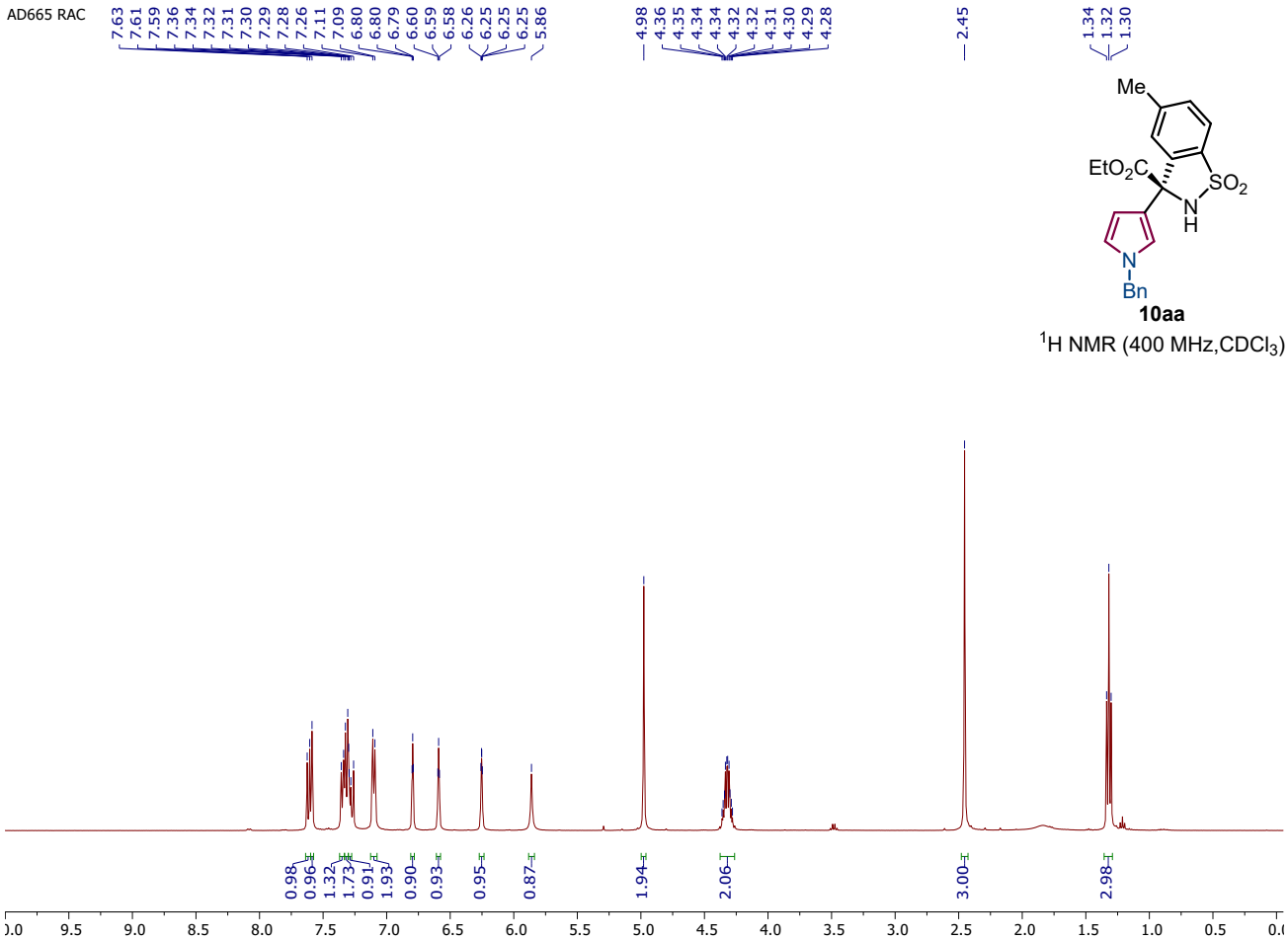
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

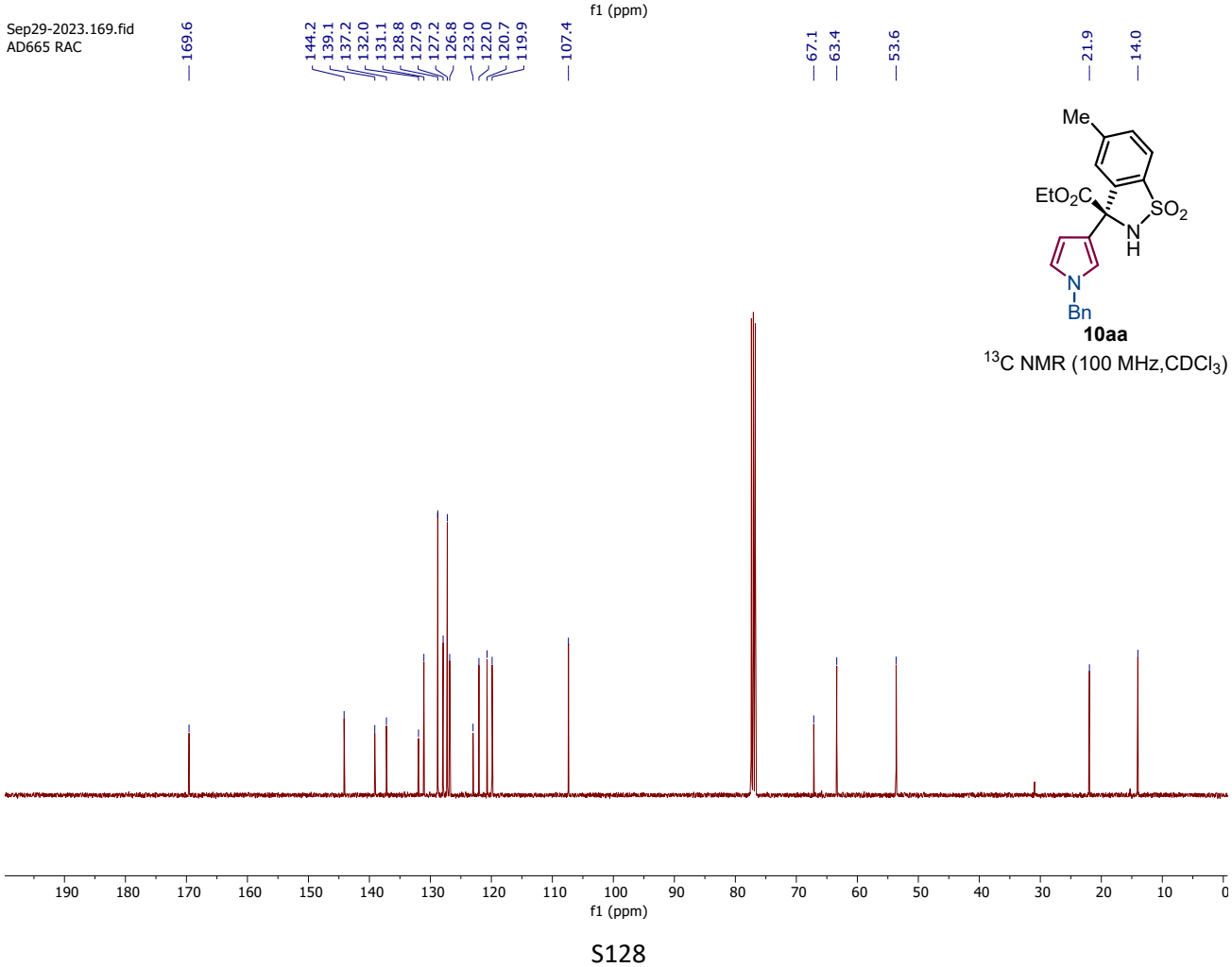
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	26.588	69646650	50.59	593830
2	2998 PDA 254.0 nm (2998 (200-400)nm)	32.958	68029354	49.41	488682

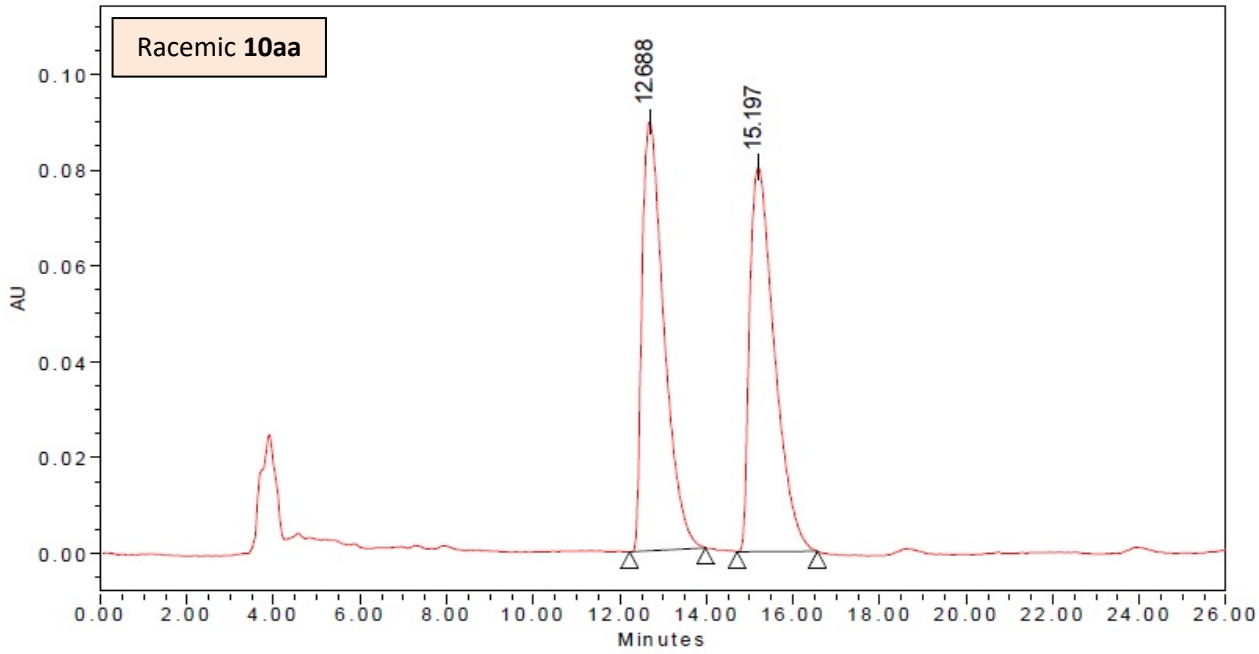


Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	26.782	23952258	15.05	216102
2	2998 PDA 254.0 nm (2998 (200-400)nm)	33.207	135157155	84.95	898563

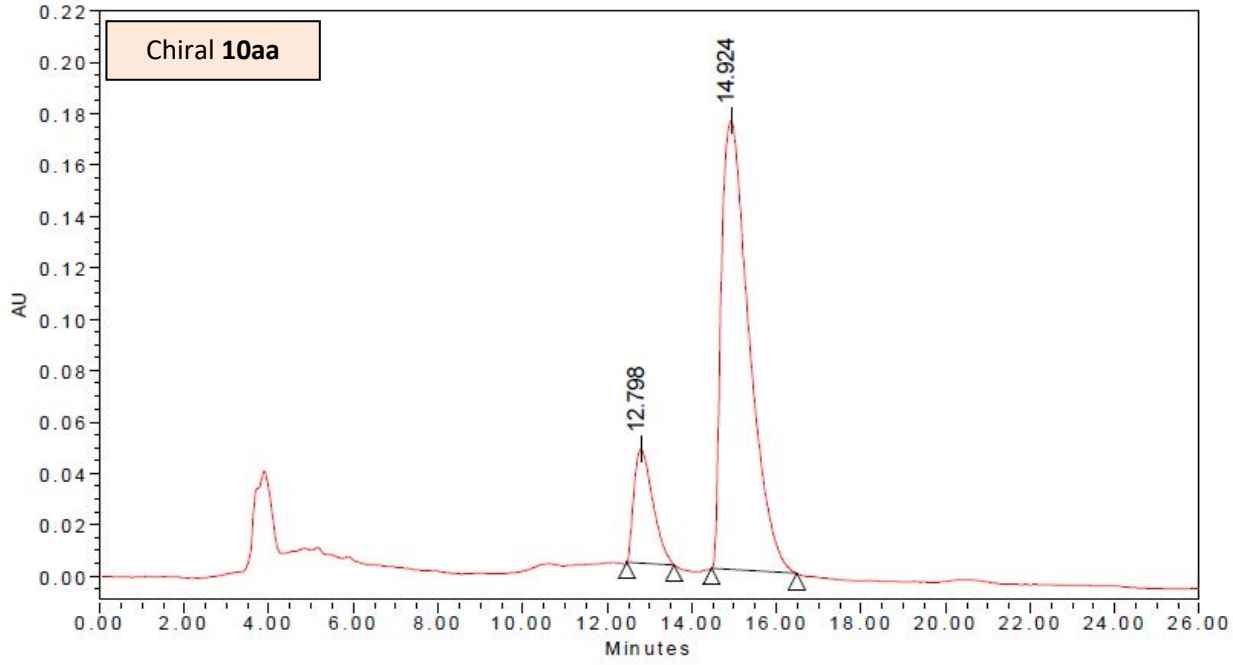

AD665 RAC
7.63 7.61 7.59 7.36 7.34 7.32 7.31 7.30 7.29 7.28 7.26 7.11 7.09 6.80 6.80 6.79 6.60 6.59 6.58 6.26 6.25 6.25 6.25 5.86
4.98 4.36 4.35 4.34 4.34 4.32 4.32 4.31 4.30 4.29 4.28
2.45
1.34 1.32 1.30
Me
EtO2C
SO2
N
H
N
Bn
10aa
1H NMR (400 MHz,CDCl3)
0.98 0.96 1.32 1.73 0.91 1.93 0.90 0.93 0.95 0.87 1.94 2.06 3.00 2.98
f1 (ppm)


Sep29-2023.169.fid
AD665 RAC
169.6
144.2 139.1 137.2 132.0 131.1 128.8 127.9 127.2 126.8 123.0 122.0 120.7 119.9
107.4
67.1 63.4
53.6
21.9
14.0
Me
EtO2C
SO2
N
H
N
Bn
10aa
13C NMR (100 MHz,CDCl3)
f1 (ppm)



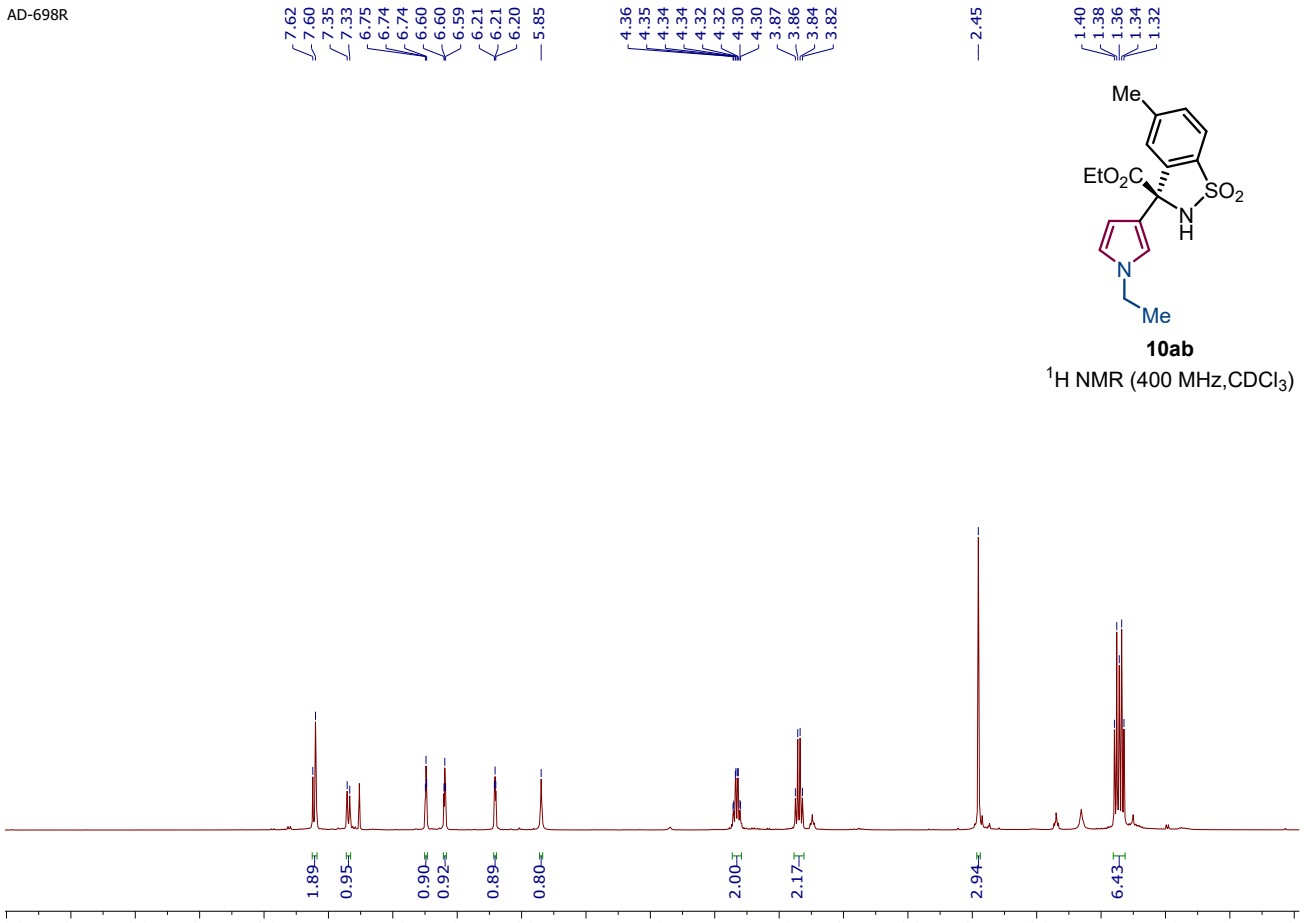
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	12.688	3156642	49.75	89543
2	2998 PDA 254.0 nm (2998 (200-400)nm)	15.197	3188144	50.25	80215



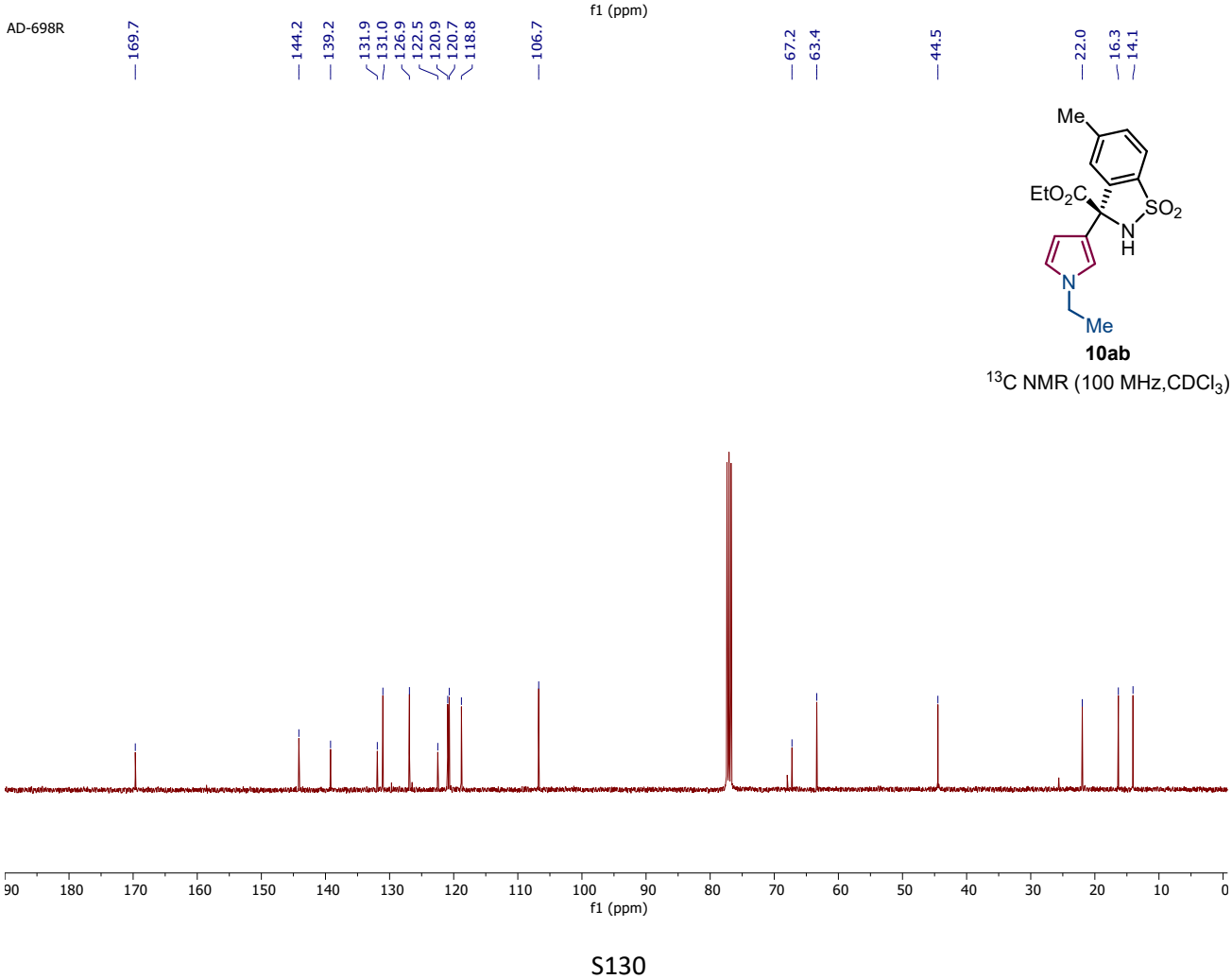
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	12.798	1374734	14.69	44285
2	2998 PDA 254.0 nm (2998 (200-400)nm)	14.924	7983697	85.31	174676



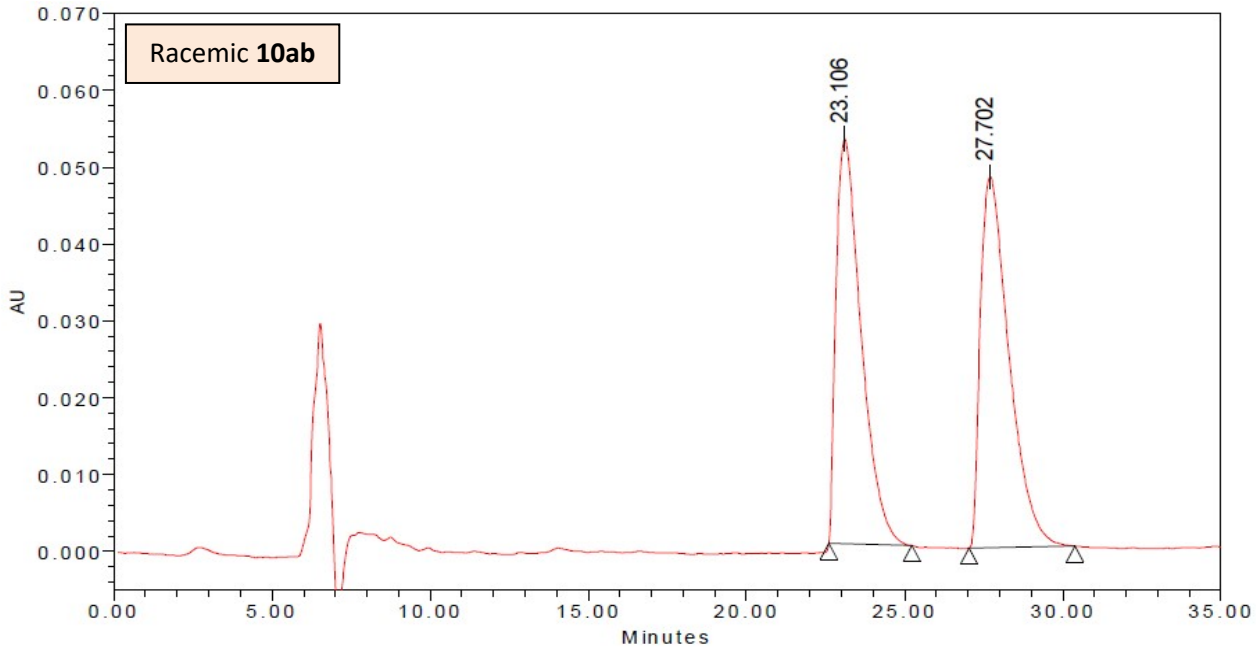
10ab

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



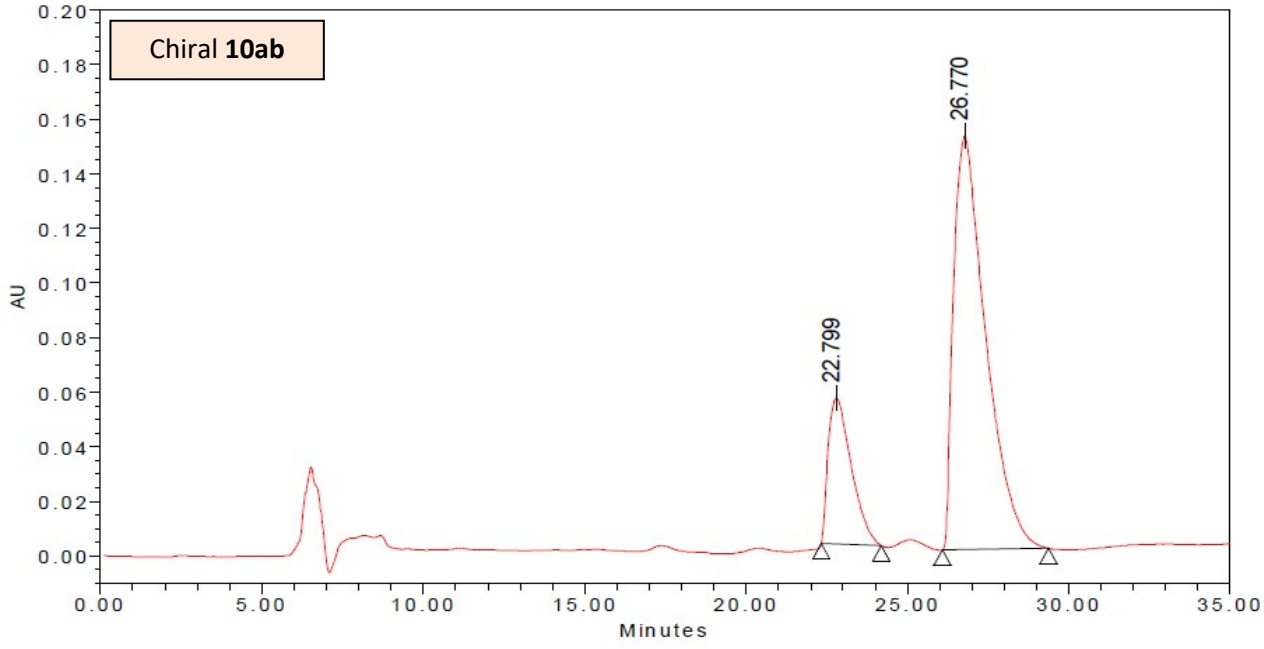
10ab

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



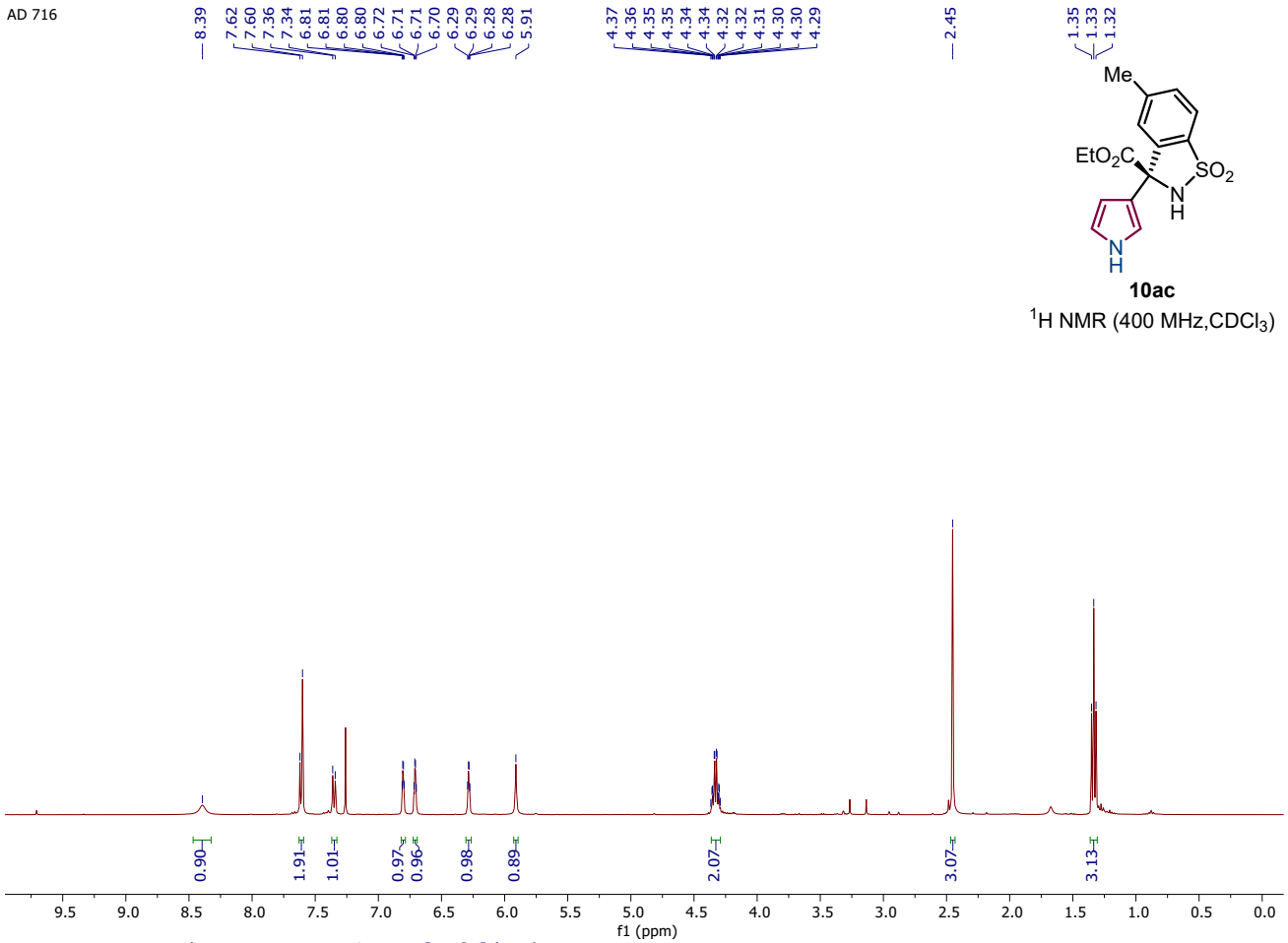
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	23.106	2899891	48.81	52736
2	2998 PDA 254.0 nm (2998 (200-400)nm)	27.702	3041604	51.19	48231



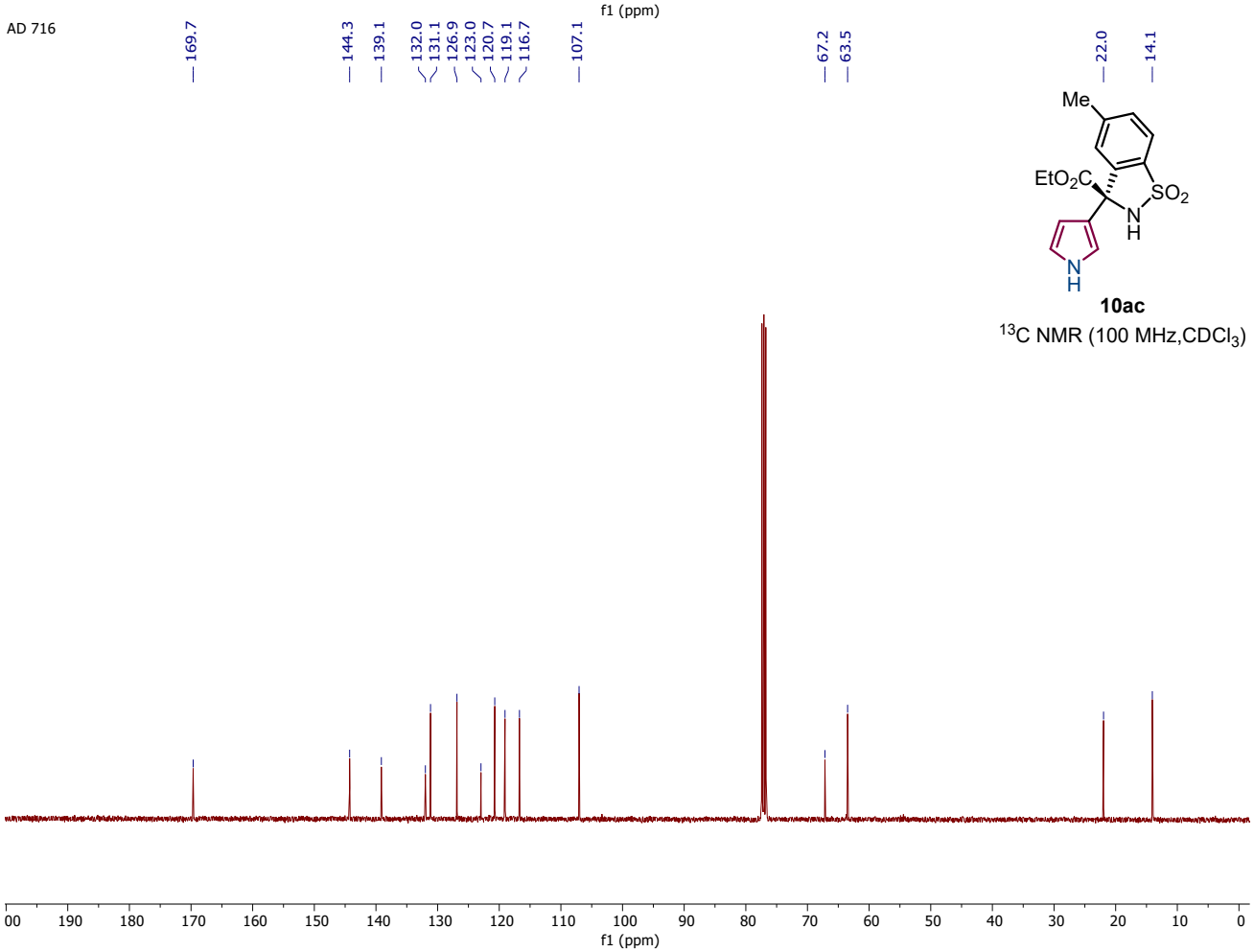
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	22.799	2665395	20.22	53402
2	2998 PDA 254.0 nm (2998 (200-400)nm)	26.770	10514044	79.78	151403



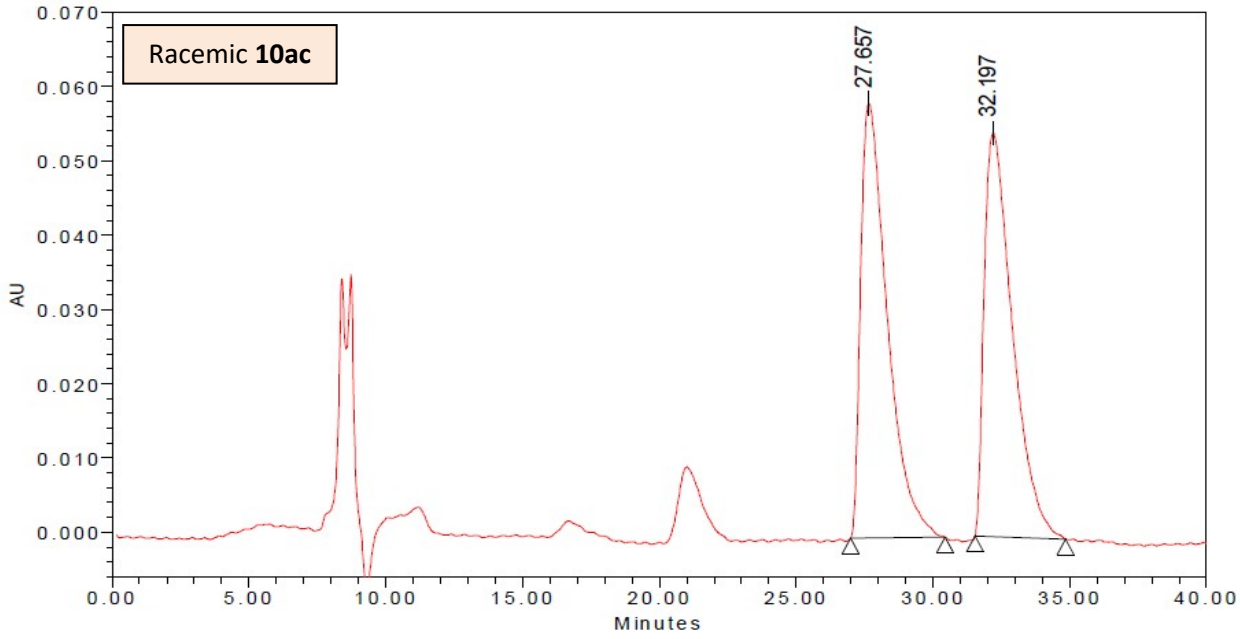
10ac

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



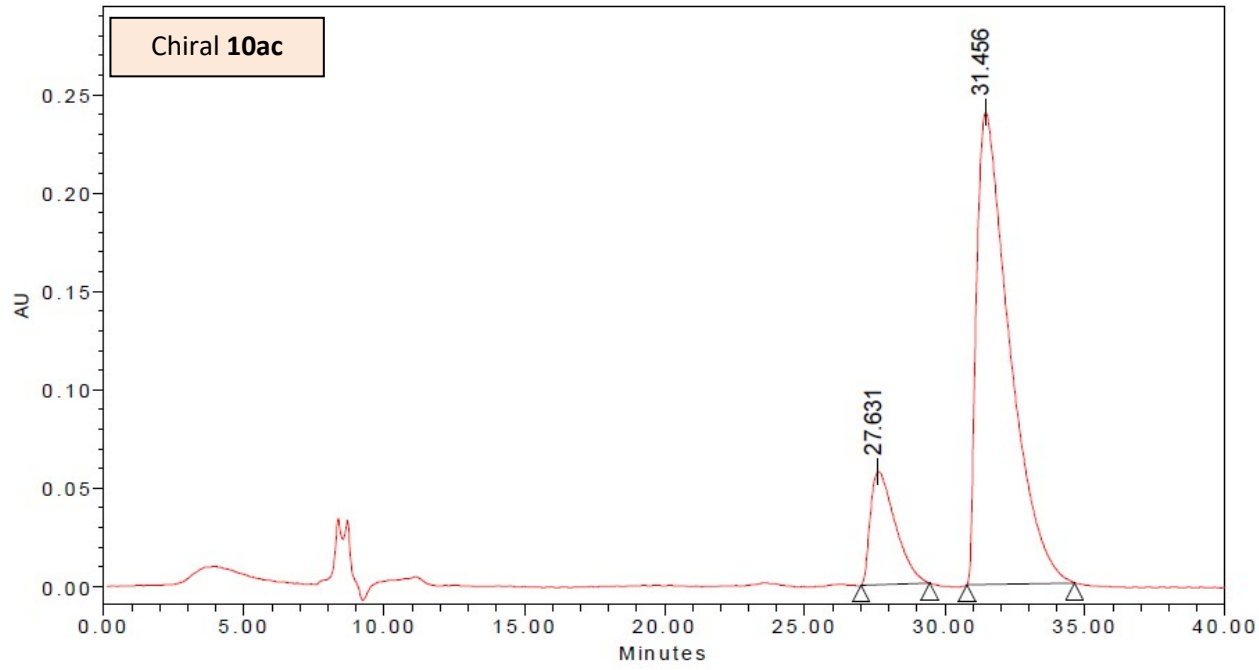
10ac

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



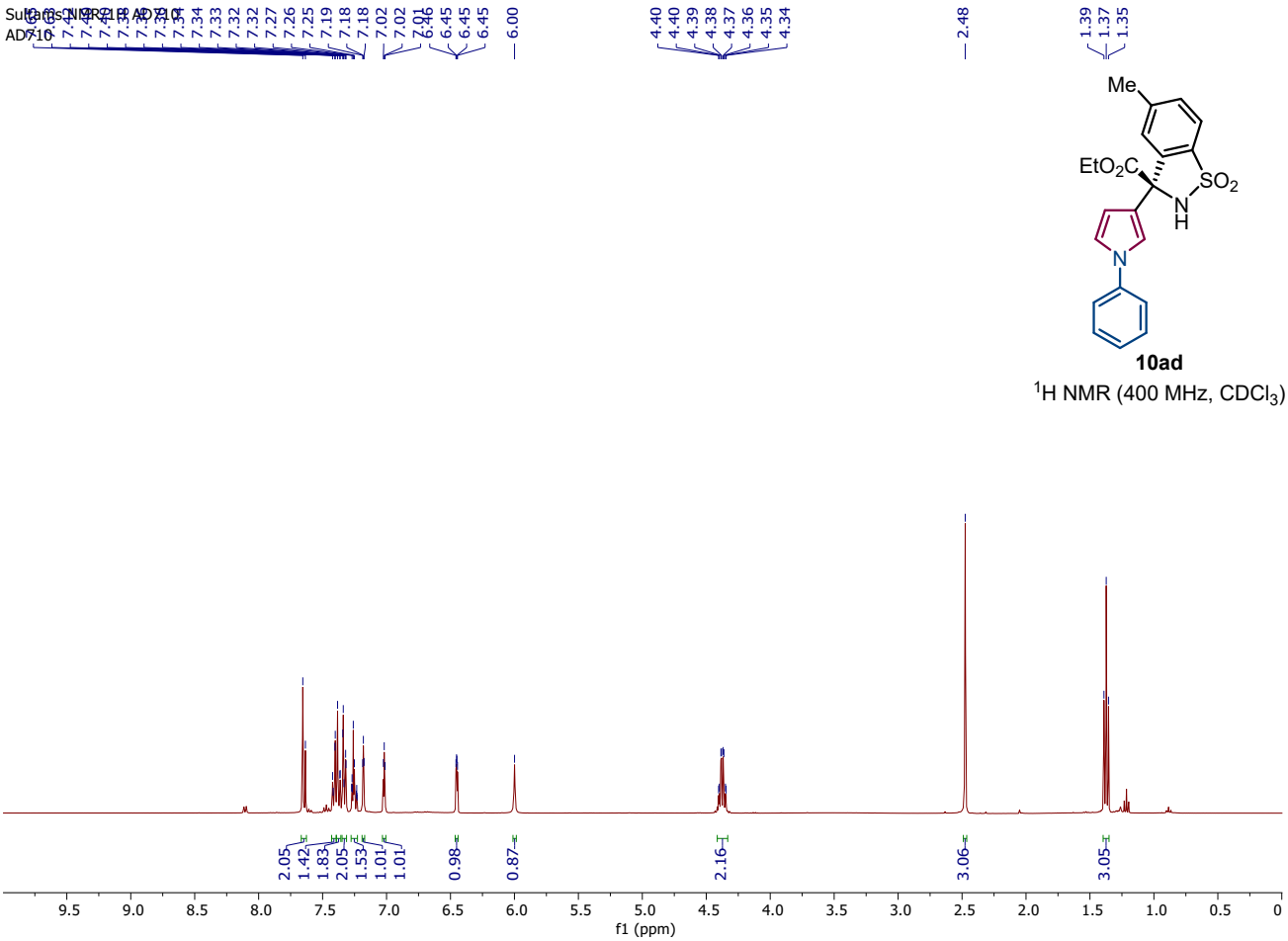
Processed Channel: 2998 PDA 265.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 265.0 nm (2998 (200-400)nm)	27.657	3962339	50.36	58497
2	2998 PDA 265.0 nm (2998 (200-400)nm)	32.197	3905150	49.64	54353



Processed Channel: 2998 PDA 265.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 265.0 nm (2998 (200-400)nm)	27.631	3565454	15.37	57604
2	2998 PDA 265.0 nm (2998 (200-400)nm)	31.456	19639476	84.63	240150

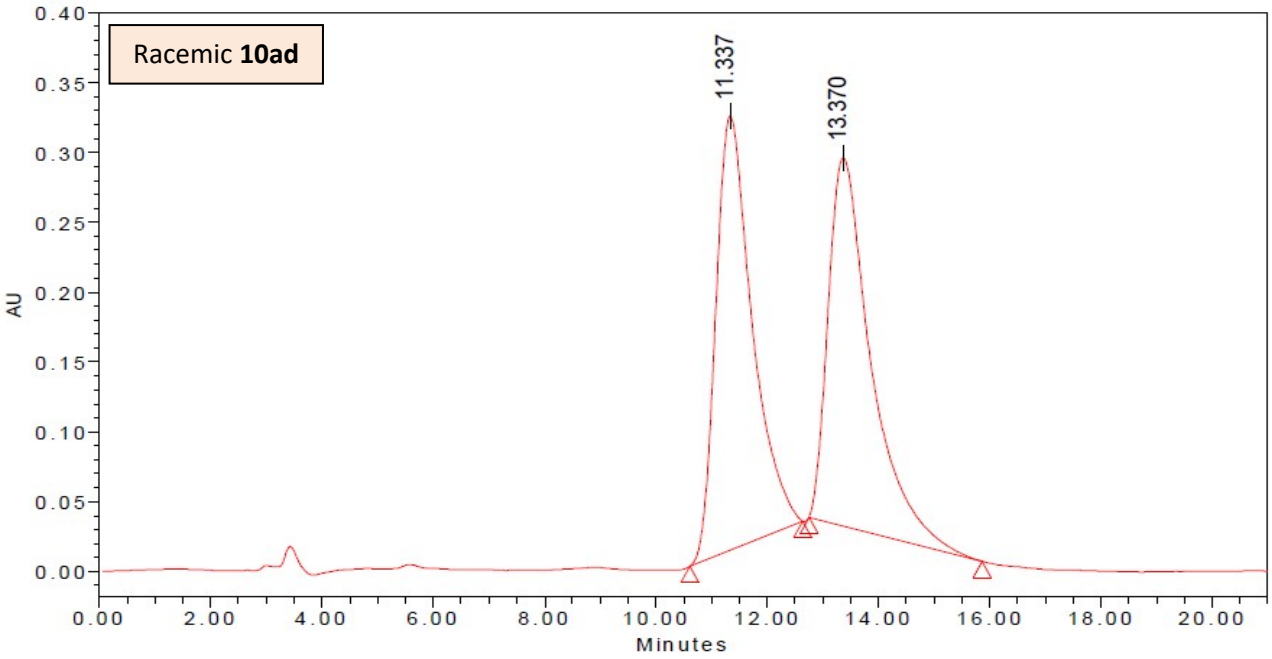


10ad

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

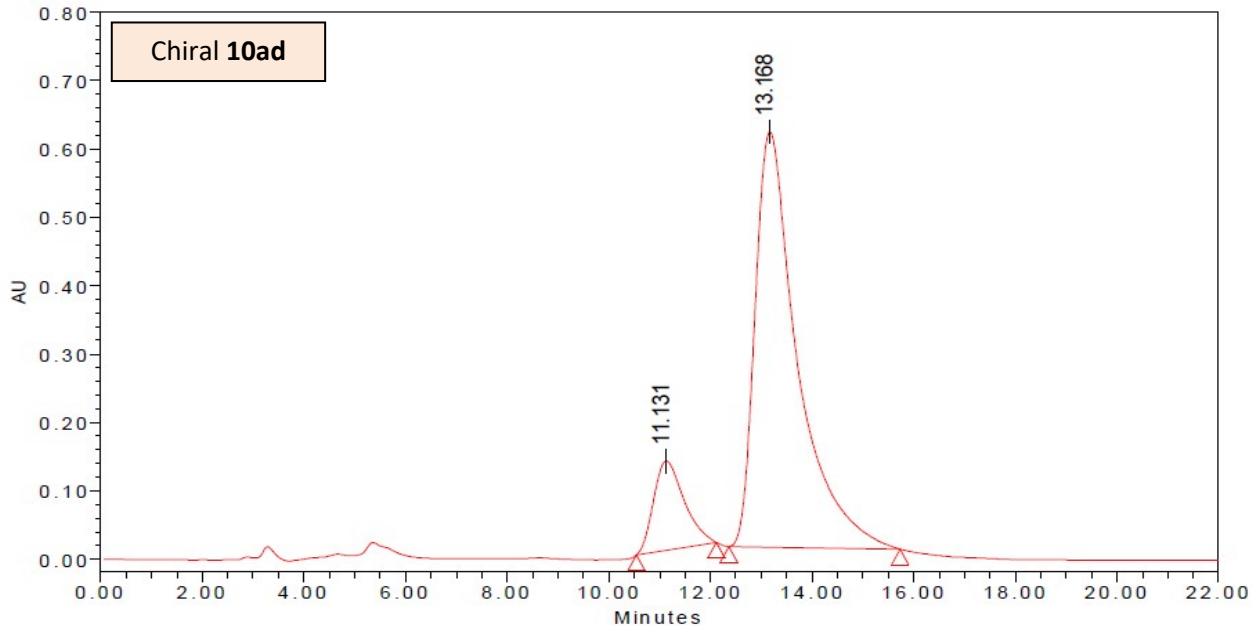
10ad

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



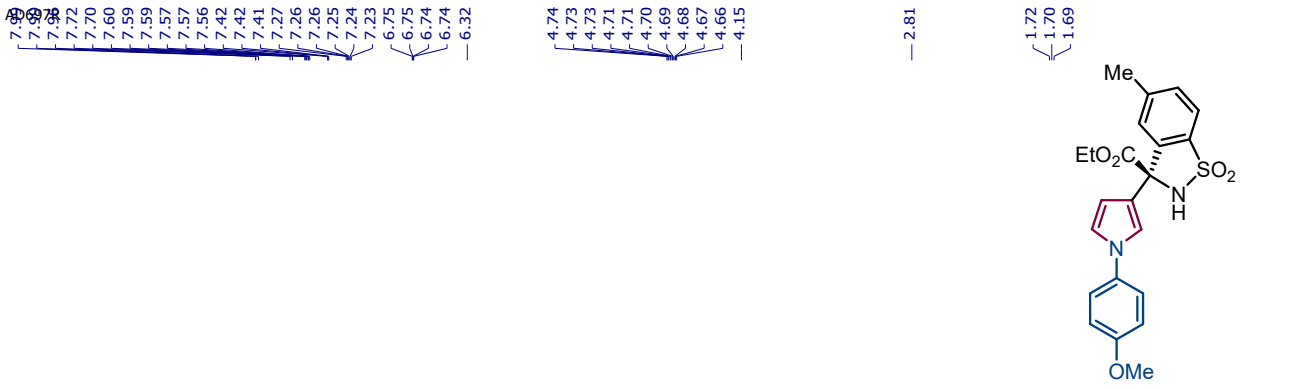
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	11.337	14137968	50.13	310849
2	2998 PDA 254.0 nm (2998 (200-400)nm)	13.370	14064732	49.87	263666



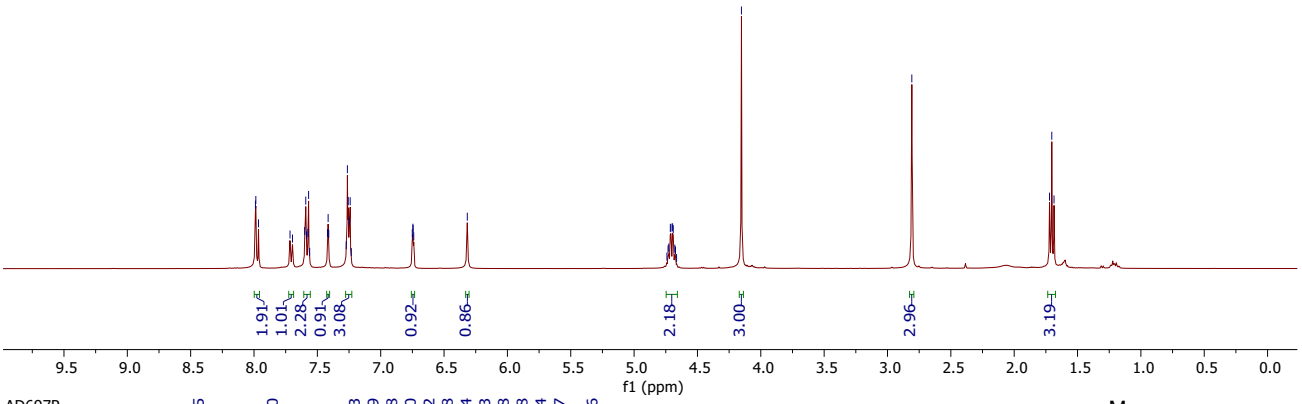
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

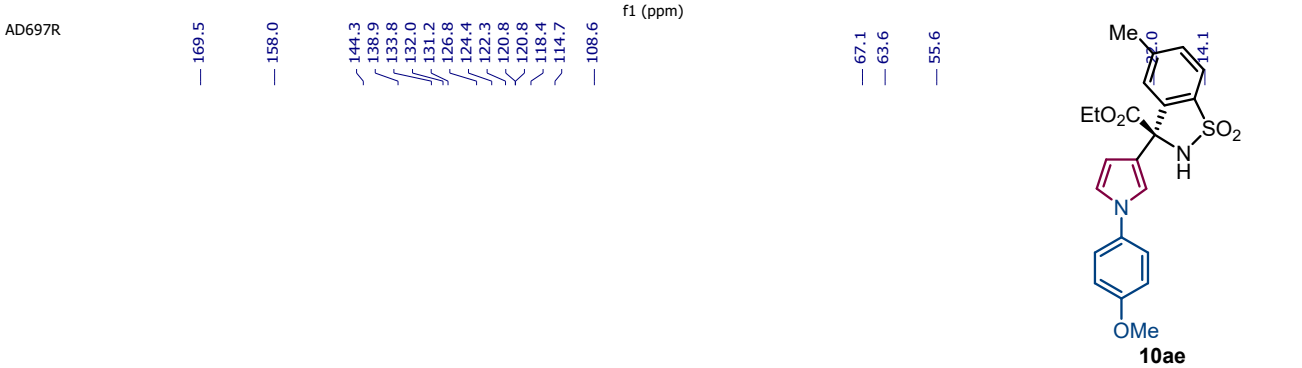
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	11.131	5457309	13.45	130670
2	2998 PDA 254.0 nm (2998 (200-400)nm)	13.168	35108722	86.55	607411



10ae

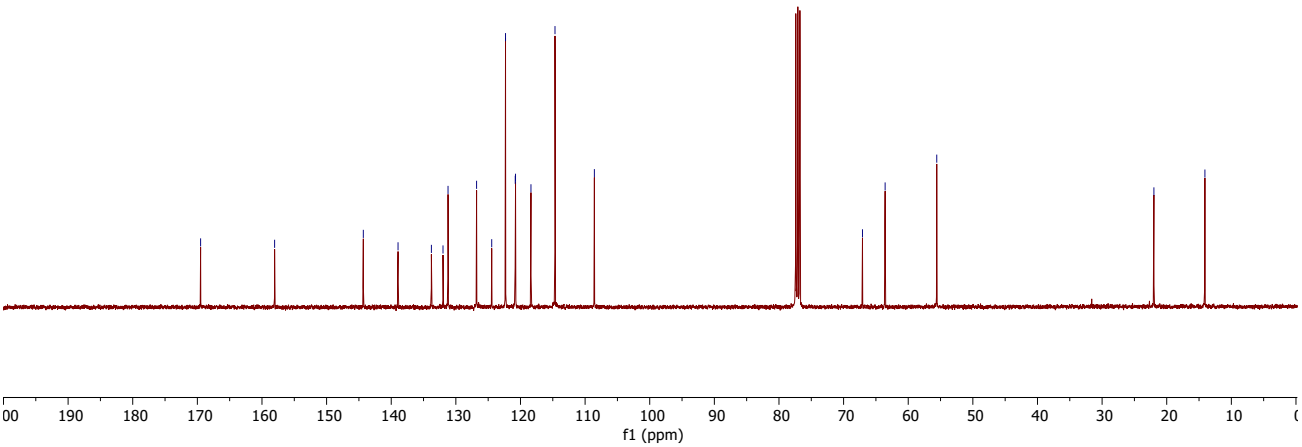
^{1}H NMR (400 MHz,$CDCl_3$)

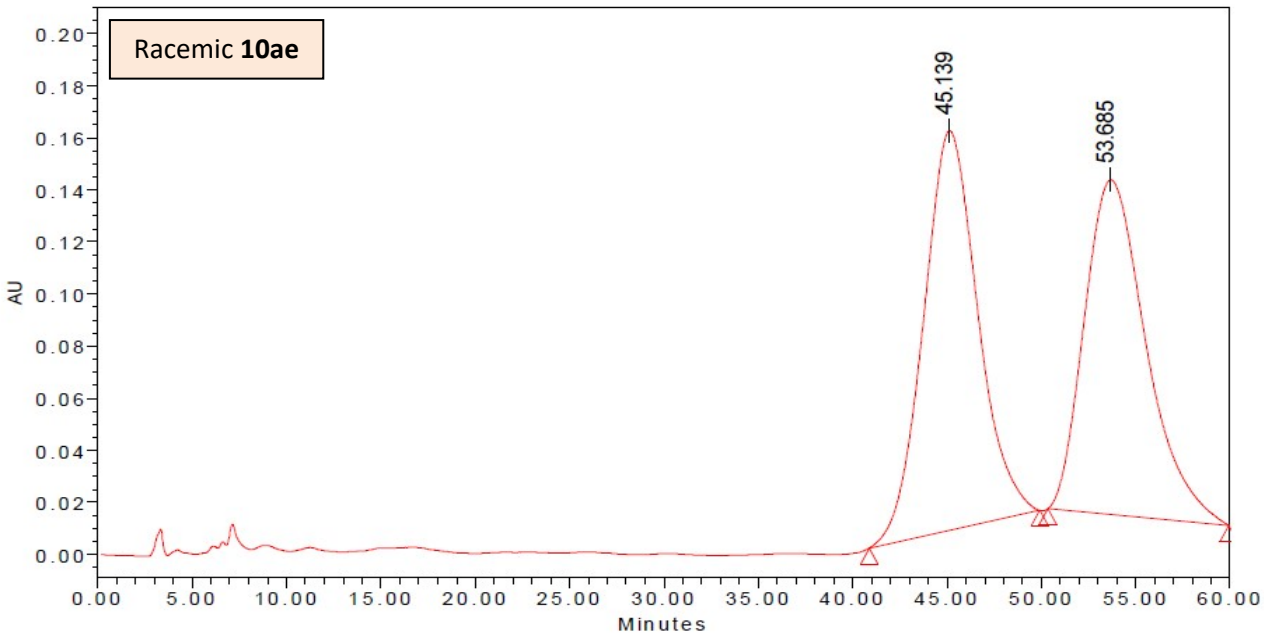




10ae

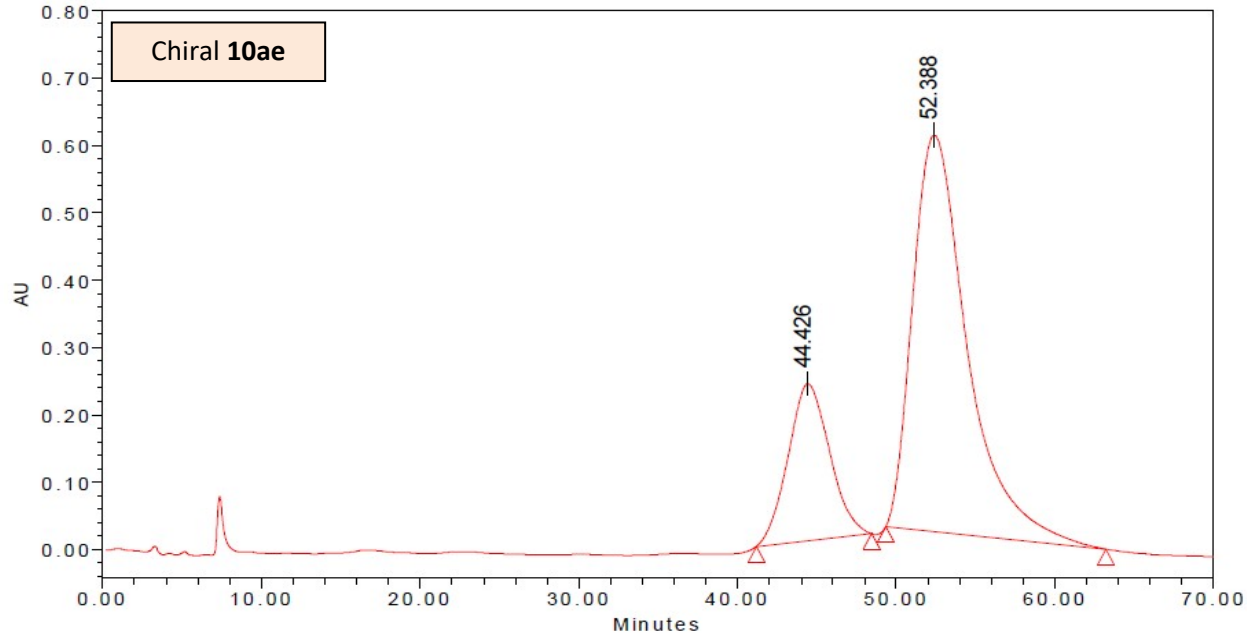
^{13}C NMR (100 MHz,$CDCl_3$)





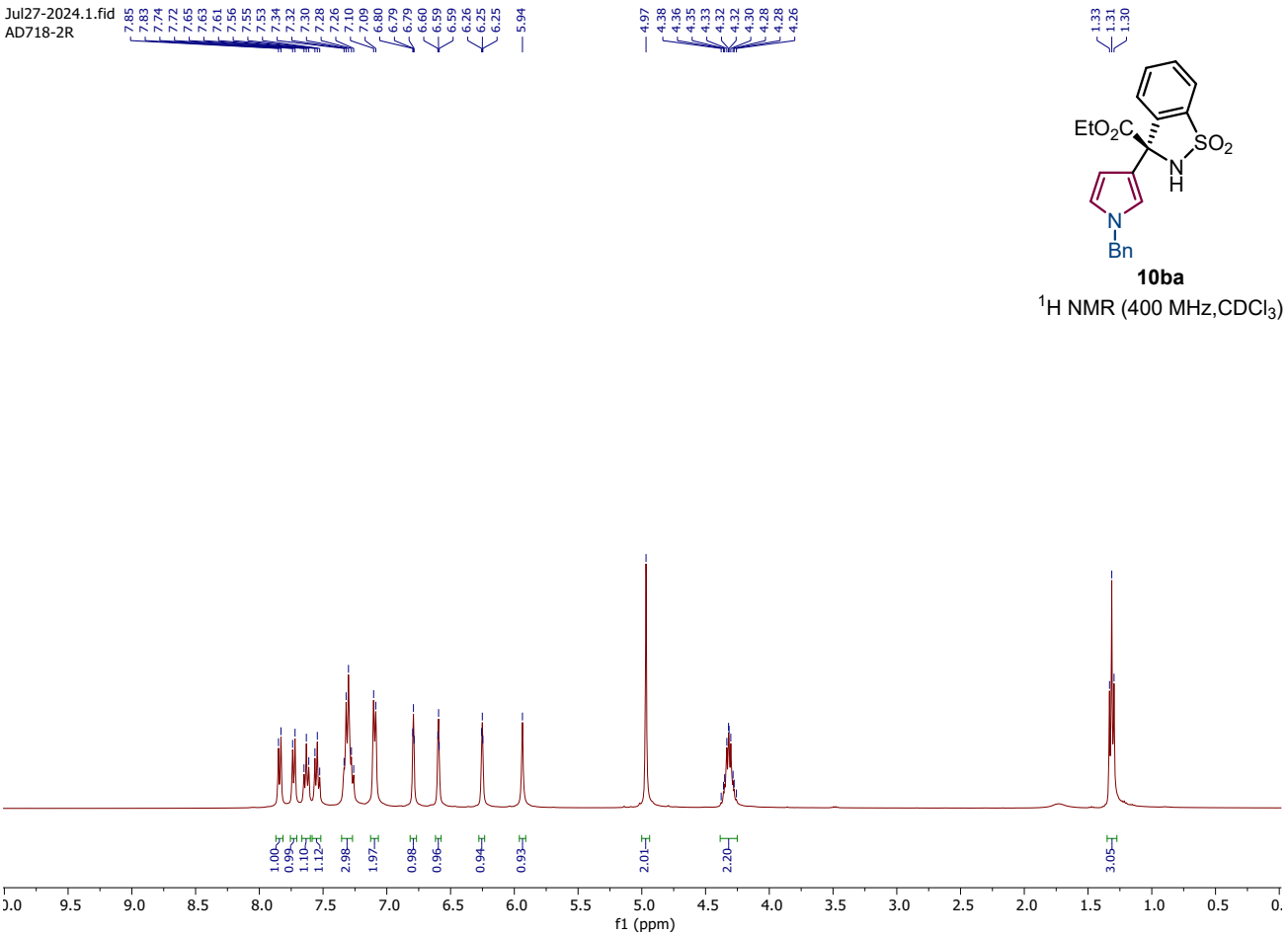
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	45.139	30678234	51.27	153465
2	2998 PDA 254.0 nm (2998 (200-400)nm)	53.685	29159618	48.73	128512



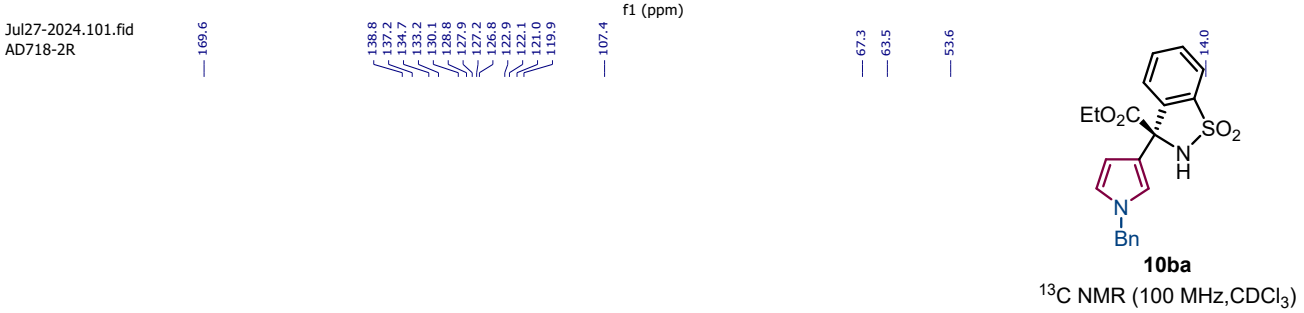
Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	44.426	42417545	23.15	233291
2	2998 PDA 254.0 nm (2998 (200-400)nm)	52.388	140814515	76.85	588442



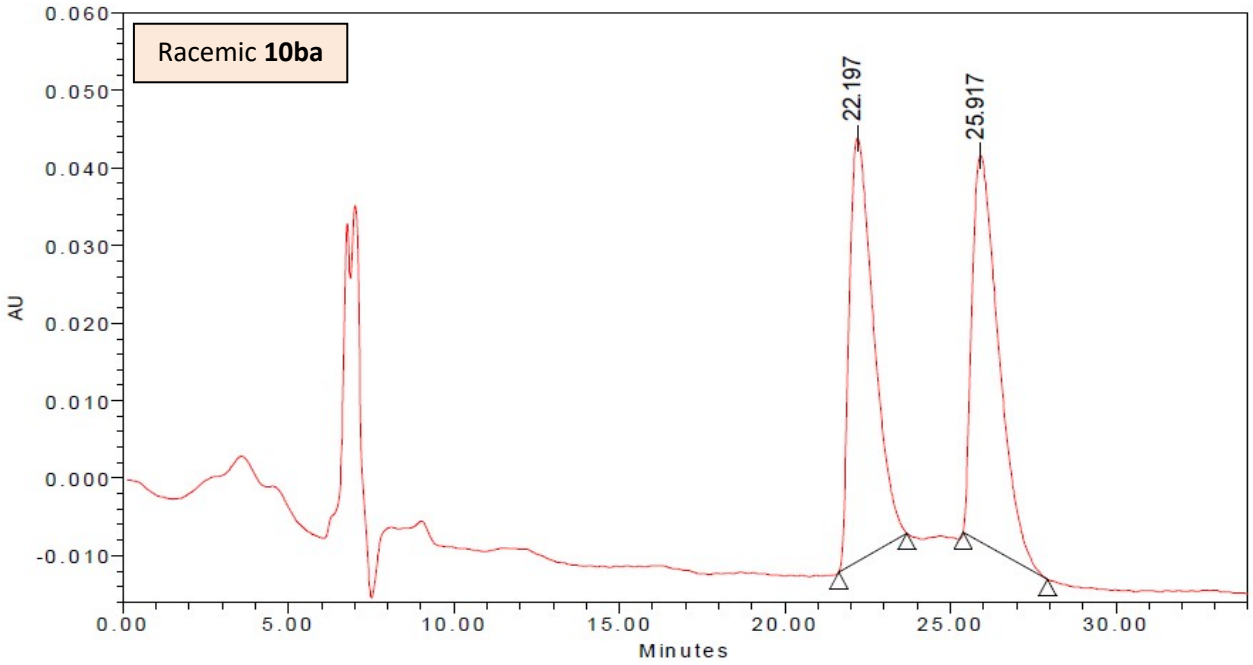
10ba

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



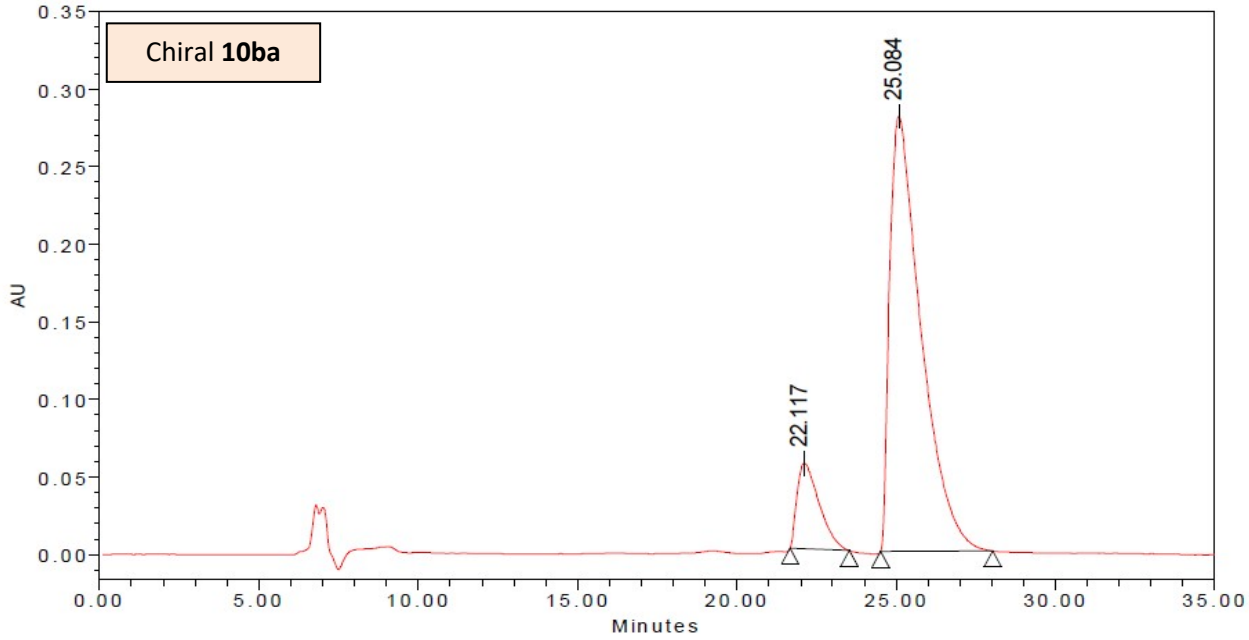
10ba

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



Processed Channel: 2998 PDA 265.0 nm (2998 (200-400)nm)

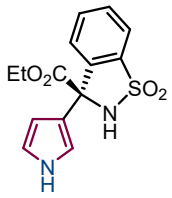
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 265.0 nm (2998 (200-400)nm)	22.197	2803798	50.09	54610
2	2998 PDA 265.0 nm (2998 (200-400)nm)	25.917	2793561	49.91	49863



Processed Channel: 2998 PDA 265.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 265.0 nm (2998 (200-400)nm)	22.117	2677157	12.21	55136
2	2998 PDA 265.0 nm (2998 (200-400)nm)	25.084	19250903	87.79	280434

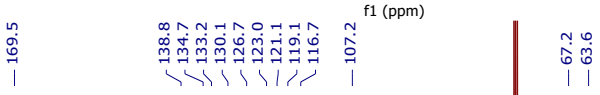
Sultams NMR/1H AD719
AD-719

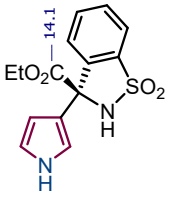


10bc

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

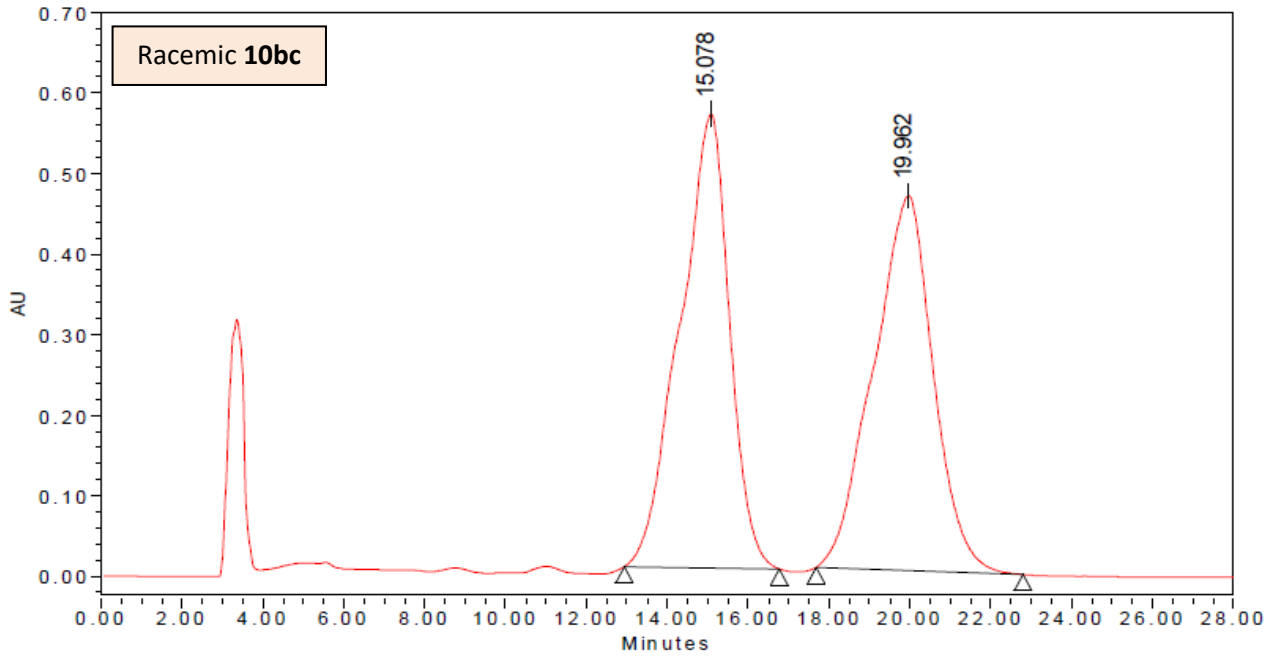
Sultams NMR/13C AD719
AD-719





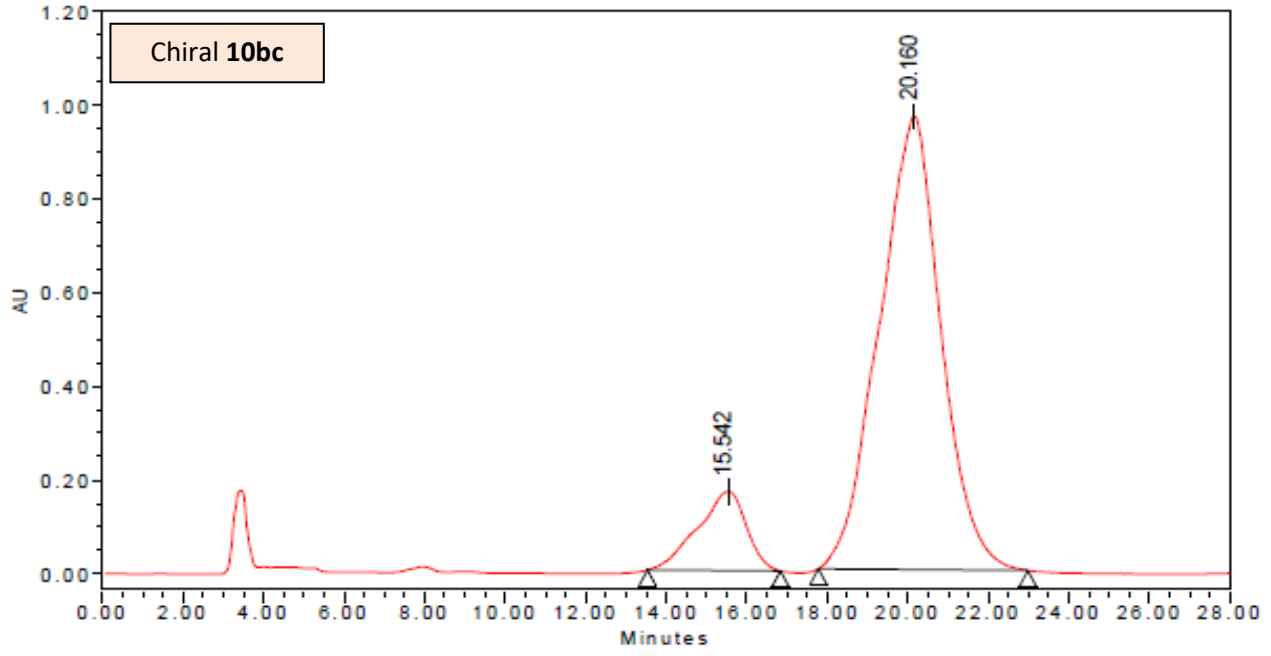
10bc

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



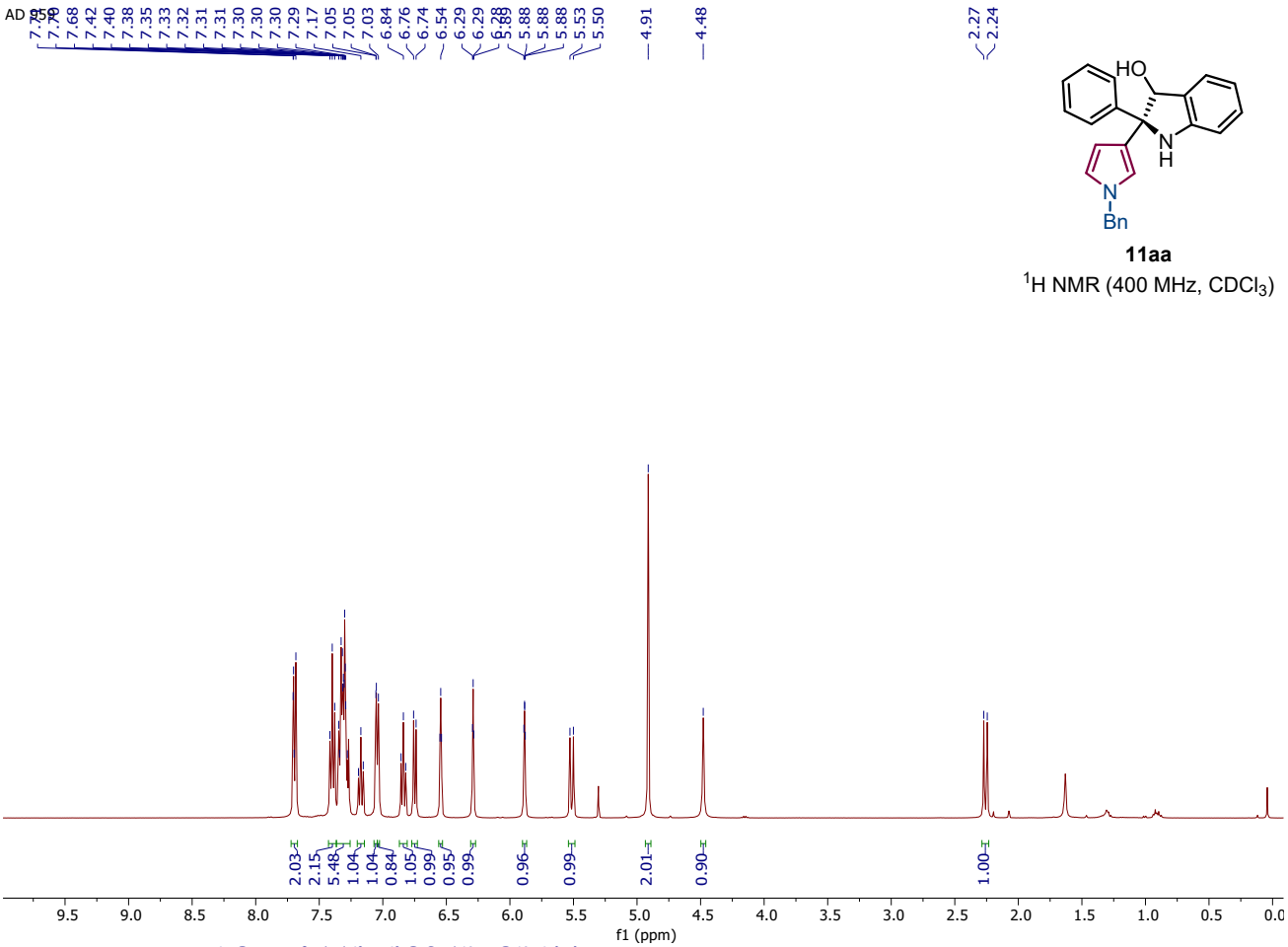
Processed Channel: 2998 PDA 230.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 230.0 nm (2998 (200-400)nm)	15.078	47884507	50.02	563614
2	2998 PDA 230.0 nm (2998 (200-400)nm)	19.962	47845863	49.98	465420



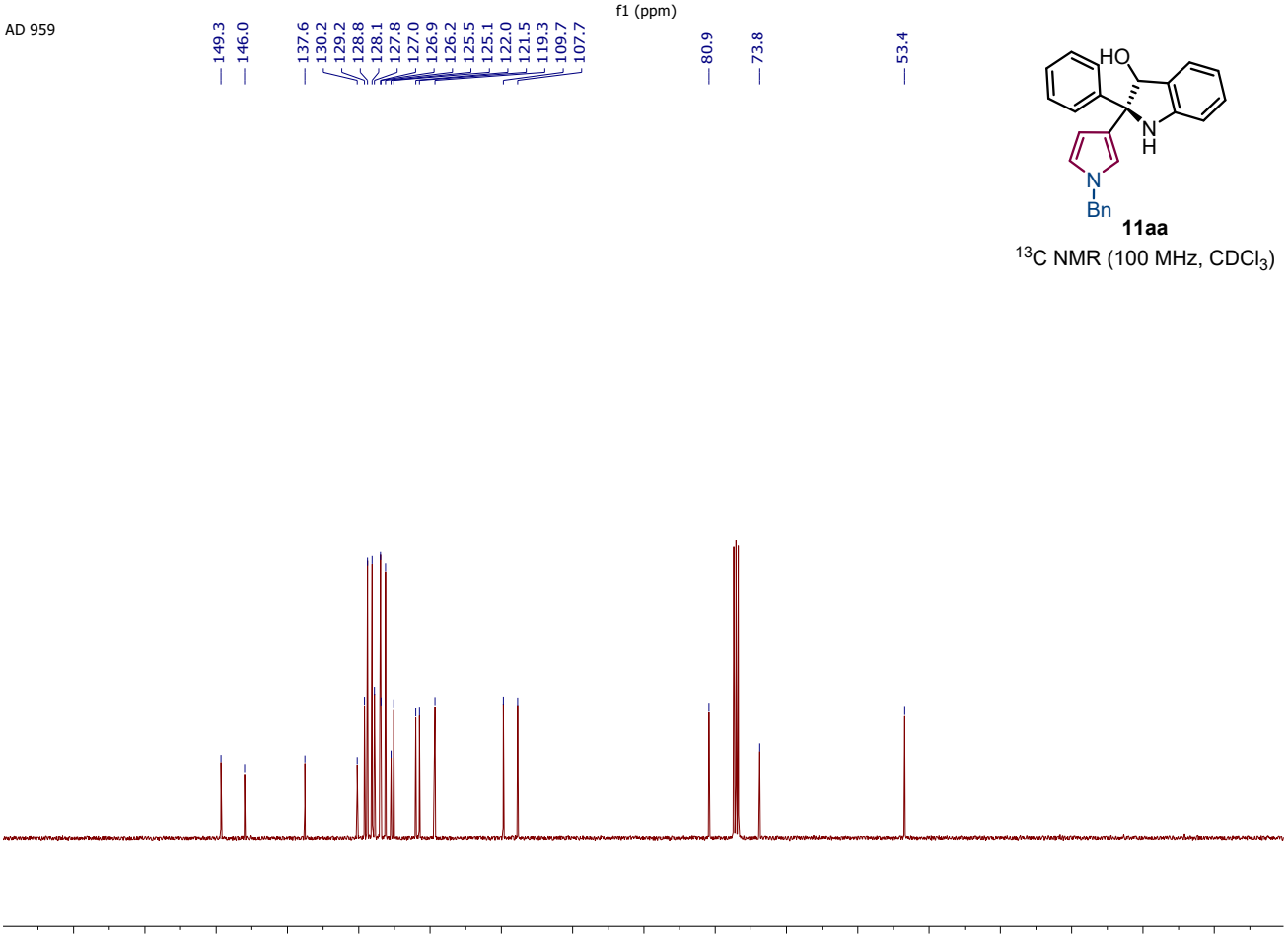
Processed Channel: 2998 PDA 230.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 230.0 nm (2998 (200-400)nm)	15.542	14209734	12.13	168540
2	2998 PDA 230.0 nm (2998 (200-400)nm)	20.160	102961823	87.87	967558



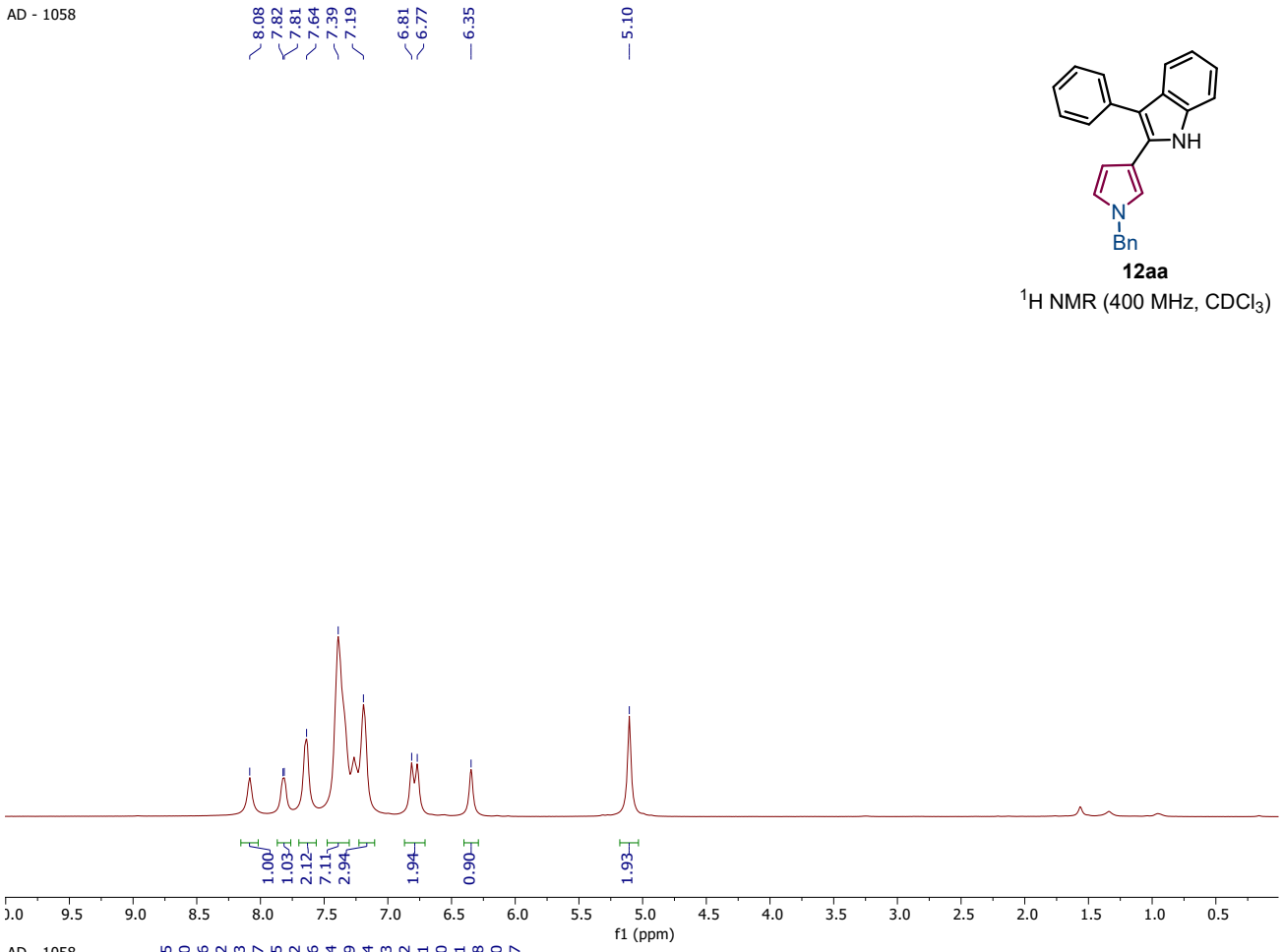
11aa

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



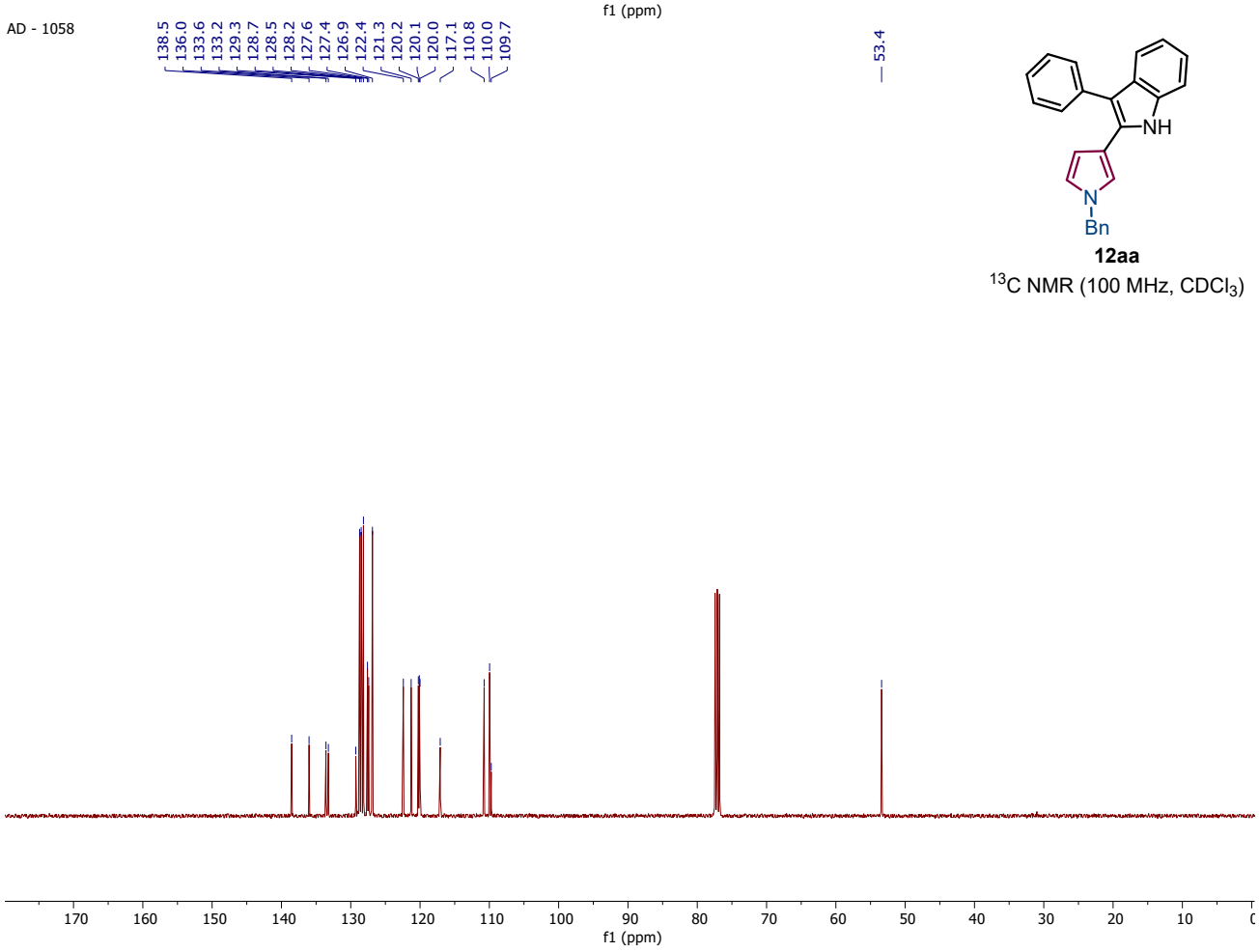
11aa

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



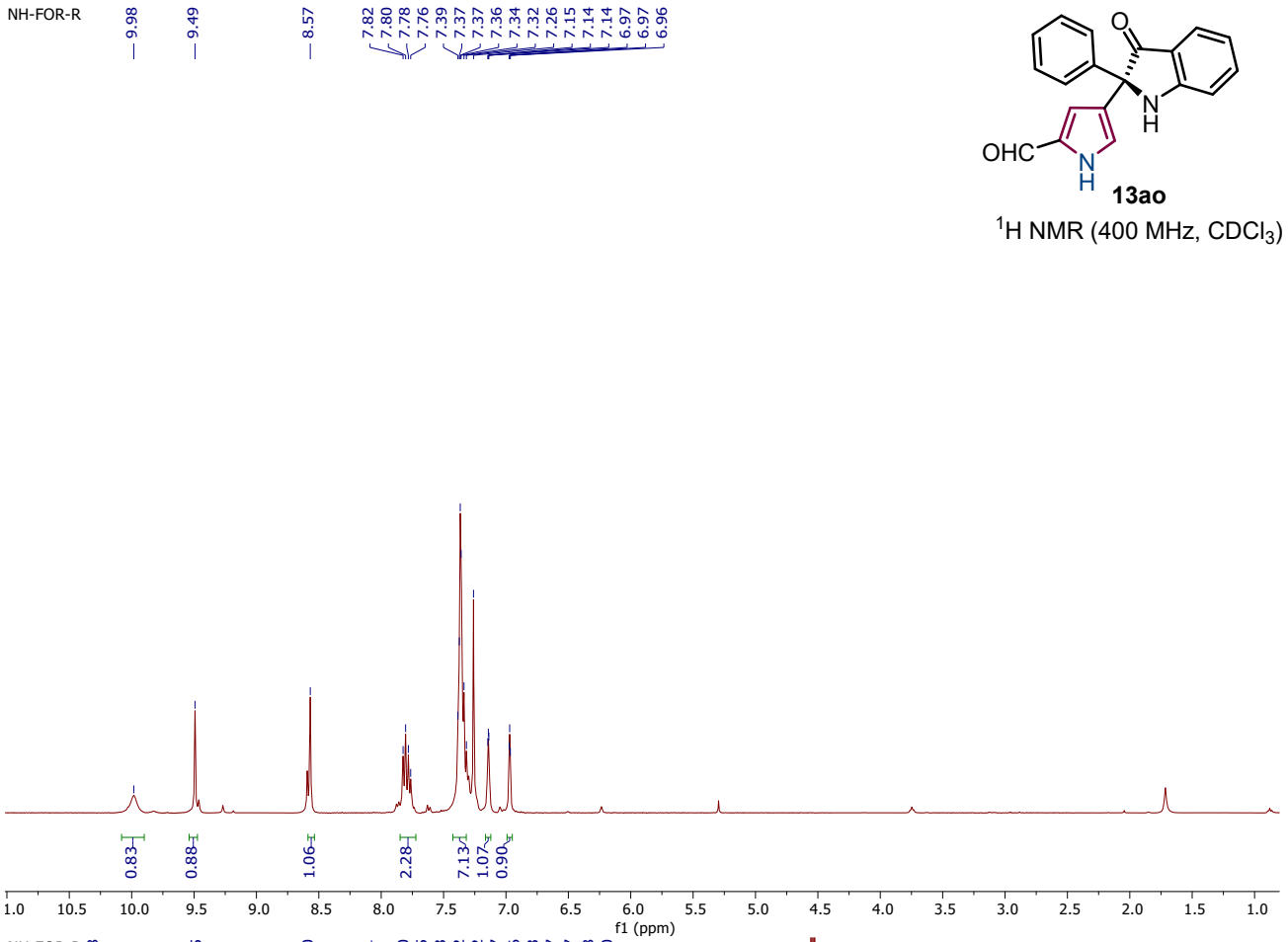
12aa

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



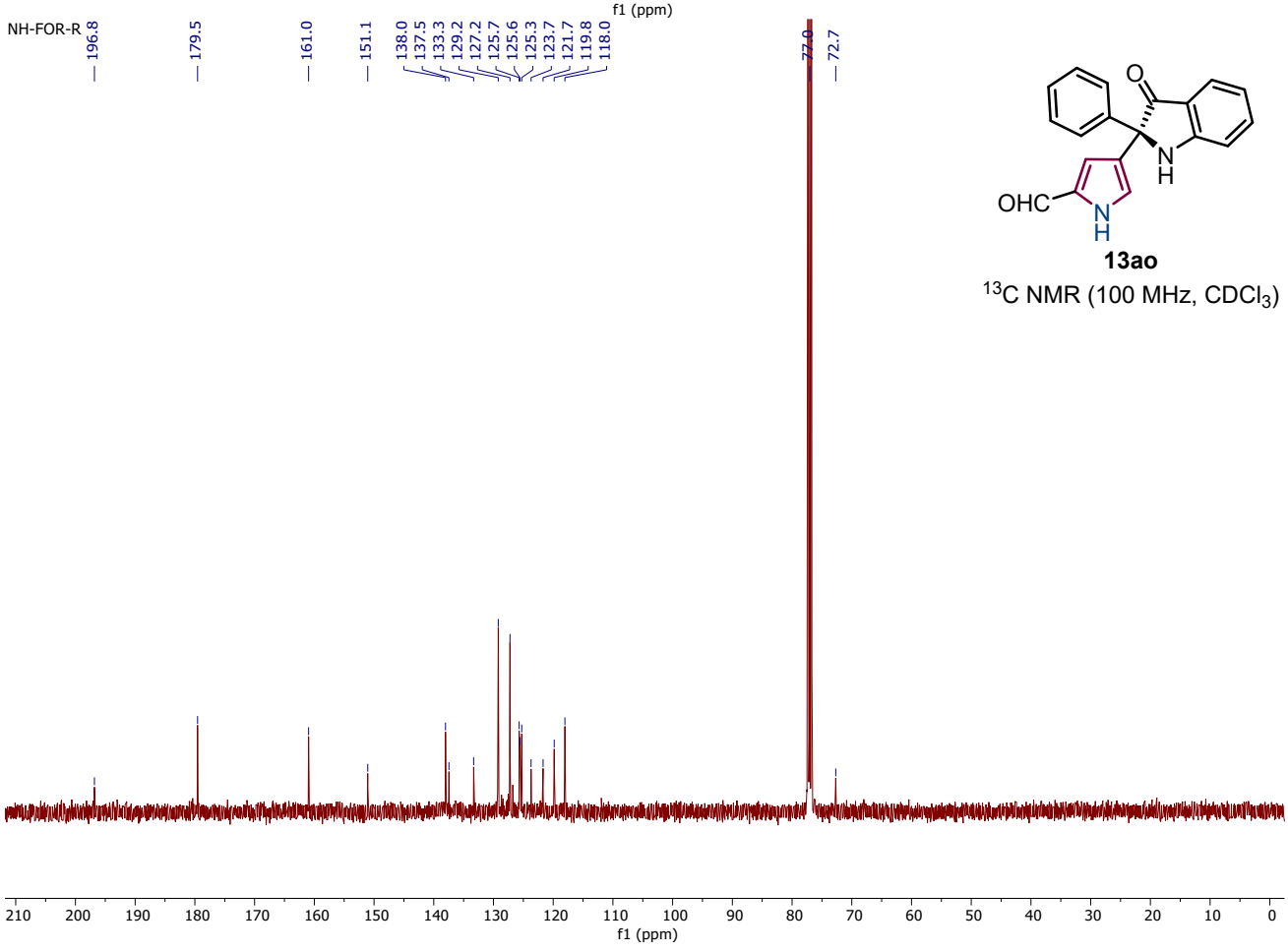
12aa

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



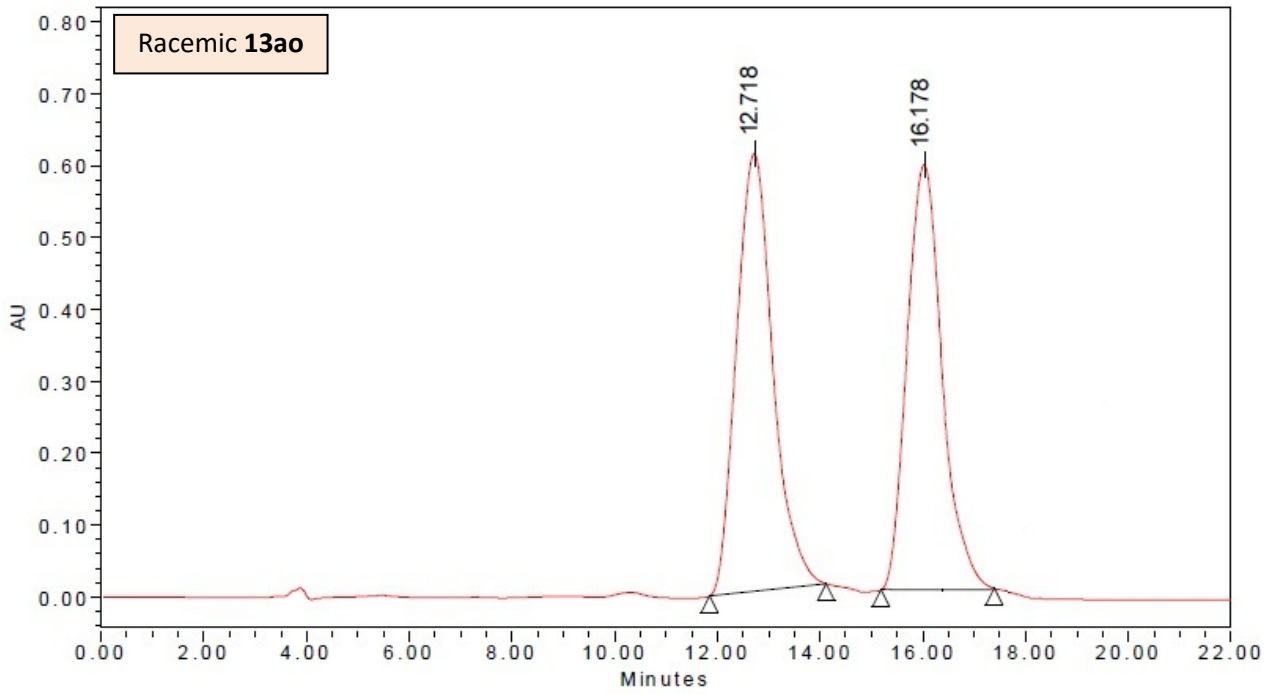
13ao

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



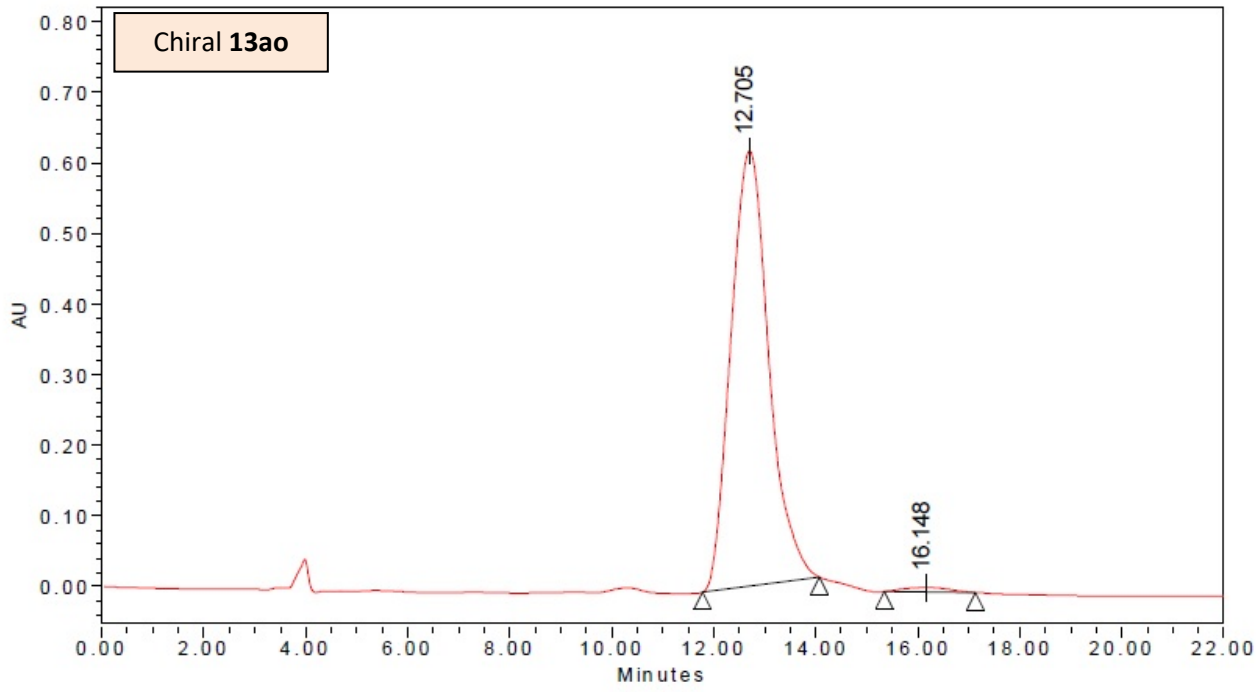
13ao

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



Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	12.718	29930164	51.79	608478
2	2998 PDA 254.0 nm (2998 (200-400)nm)	16.178	28439100	49.21	608307



Processed Channel: 2998 PDA 254.0 nm (2998 (200-400)nm)

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 PDA 254.0 nm (2998 (200-400)nm)	12.705	31782593	98.77	615696
2	2998 PDA 254.0 nm (2998 (200-400)nm)	16.148	394166	1.23	6220