Supporting Information

Neighboring Group-Directed [2+2+2] Cycloaddition to Access C-N Axially Chiral Indoles

Xuan Zhang,[a] Qi Teng,*[a] Yanru Ren,[a] Baitong Wei,[a] Chen-Ho Tung,[a] and Zhenghu Xu*[a,b,c]

a.Key Lab for Colloid and Interface Chemistry of Education Ministry, School of chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China. E-mail: xuzh@sdu.edu.cn

b.State Key Laboratory of Organometallic Chemistry Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences Shanghai 200032, PR China.

c.Key Laboratory of Precise Synthesis of Functional Molecules of Zhejiang Province, School of Science, Westlake University, No. 18 Shilongshan Road, Hangzhou 310024, China.

Correspondence and requests for materials should be addressed to Z. X. (xuzh@sdu.edu.cn).

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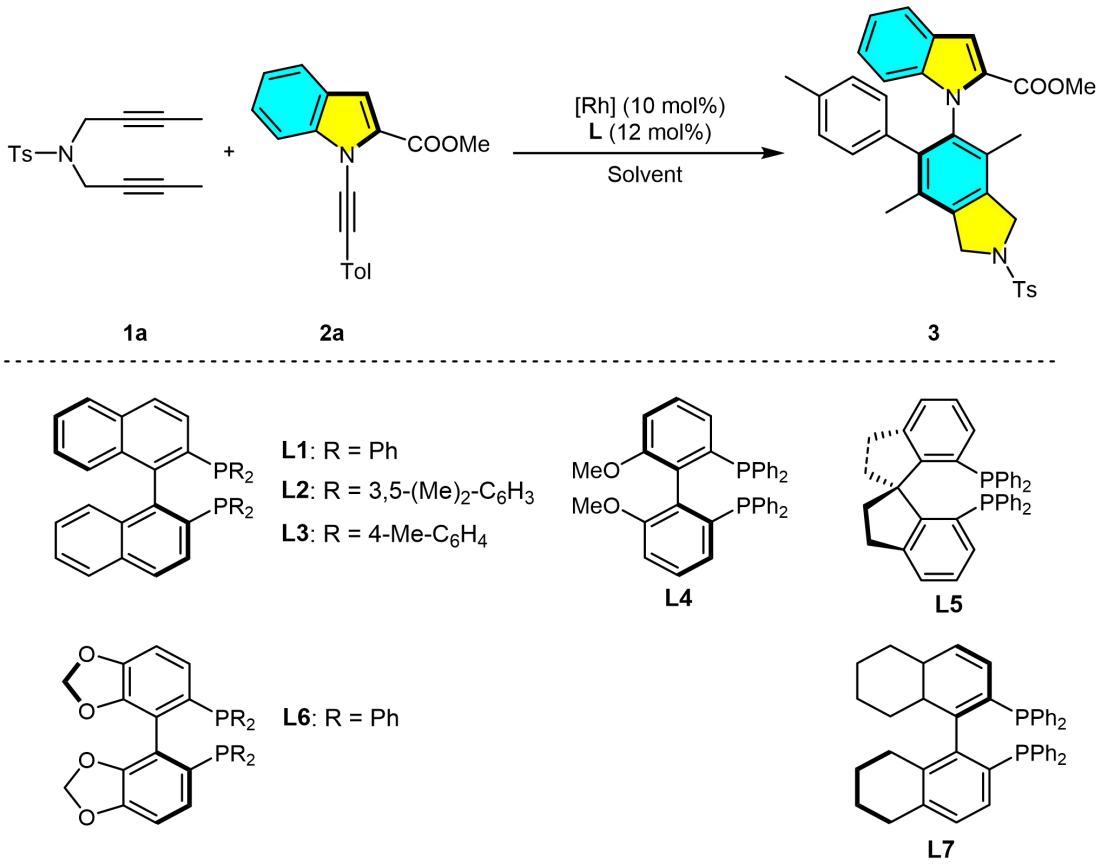
1. General information

The solvents used in the reaction were dried by CaH_2 or purchased from J&K or local companies unless additional notes, and all the reagents were obtained commercially and used without further purification. All the reactions were performed in the overdried glassware with magnetic stirring under nitrogen atmosphere. Column chromatography was performed with silica gel (100-200 mesh) as the stationary phase. Solvent compositions are given in (v/v). Reactions were monitored by TLC. All NMR spectra were recorded on Bruker-500 MHz spectrometer in $CDCl_3$, and the chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz respectively. High resolution mass spectra (HRMS) were measured on the Bruker-Impact II instruments obtained by the Analytical Center for Structural Constituent and Physical Property in Shandong University. All substitutes were prepared according to the reported methods.[1-5]

2. Optimization of the reaction conditions

Table S1. Investigation of the conditions for the construction of **C-N** axially chiral biaryls.[a]

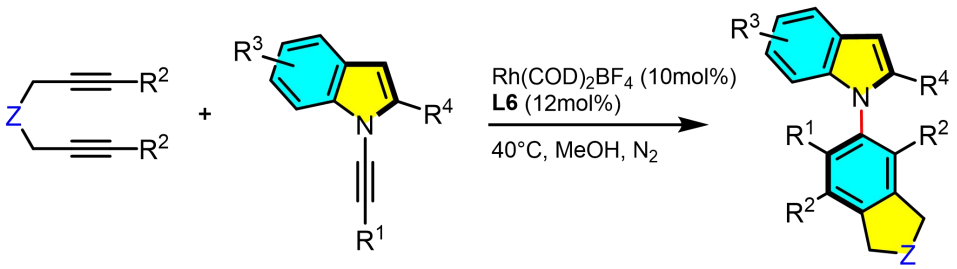


entry	metal	ligand	solvent	additive	temperature	yield/%[b]	e.e./%[c]
1	$Rh(COD)_2BF_4$	**L1**	DCE	-	0	n.r.	-
2[d]	$Rh(COD)_2BF_4$	**L1**	DCE	-	23	42	98
3	$Rh(COD)_2BF_4$	**L1**	DCE	-	40	32	97
4	$Rh(COD)_2BF_4$	**L1**	DCE	-	60	48	97
5	$Rh(COD)_2BF_4$	**L1**	DCE	$Sc(OTf)_3$	40	n.r.	-
6	$Rh(COD)_2BF_4$	**L1**	DCE	$Y(OTf)_3$	40	n.r.	-
7	$Rh(COD)_2BF_4$	**L1**	DCE	$Ni(OTf)_2$	40	64	98
8	$Rh(COD)_2BF_4$	**L1**	DCE:CH_3OH=3:1	-	40	66	97
9	$Rh(COD)_2BF_4$	**L1**	CH_3OH	-	40	69	97
10	$Rh(COD)_2BF_4$	**L1**	DCM	-	40	25	-
11	$Rh(COD)_2BF_4$	**L1**	Acetone	-	40	32	-
12	$Rh(COD)_2BF_4$	**L1**	PhMe	-	40	12	-
13	$Rh(COD)_2BF_4$	**L1**	CH_3CN	-	40	trace	-
14	$Rh(COD)_2BF_4$	**L1**	Cyclohexane	-	40	trace	-
15	$Rh(COD)_2BF_4$	**L1**	CH_3OH	LiOTf	40	72	97
16	$Rh(COD)_2BF_4$	**L1**	CH_3OH	$Ni(OTf)_2$	40	74	97
17	$Rh(COD)_2BF_4$	**L1**	CH_3OH	$Cu(OTf)_2$	40	76	96
18	$[Rh(COD)Cl]_2$	**L1**	CH_3OH	-	40	38	93
19[e]	$Rh(COD)_2BF_4$	**L1**	CH_3OH	-	40	59	-
20	$Rh(COD)_2BF_4$	**L2**	CH_3OH	-	40	47	90
21	$Rh(COD)_2BF_4$	**L3**	CH_3OH	-	40	81	95
22	$Rh(COD)_2BF_4$	**L4**	CH_3OH	-	40	89	97
23	$Rh(COD)_2BF_4$	**L5**	CH_3OH	-	40	72	-63
24	**$Rh(COD)_2BF_4$**	**L6**	**CH_3OH**	**-**	**40**	**93**	**98**
25	$Rh(COD)_2BF_4$	**L7**	CH_3OH	-	40	65	-90
26[f]	$Rh(COD)_2BF_4$	**L6**	CH_3OH	-	40	44	98
27[f]	$Rh(COD)_2BF_4$	**L6**	CH_3OH	$Zn(OTf)_2$	40	73	98

[a] Reaction conditions: A mixture of 1 (0.1 mmol), 2 (0.15 mmol), metal (10 mol%), ligand (12 mol%), solvent (2 mL) under N_2 for 12 hours. [b] Isolated yields. [c] Determined by HPLC analysis using a chiral stationary phase. [d] Extend the reaction time to 48 hours. [e] Slowly add a CH_3OH (1 mL) solution of 1 (0.1 mmol) to a CH_3OH (1 mL) solution of 2 (0.15 mmol) at a constant rate in 3 hours; [f] Chang the amount of $Rh(COD)_2BF_4$ to 2.5mol%.

3. Procedure for the [2+2+2] Cycloaddition reaction.

General procedure for the asymmetric synthesis of **3**



1 **2** **3**

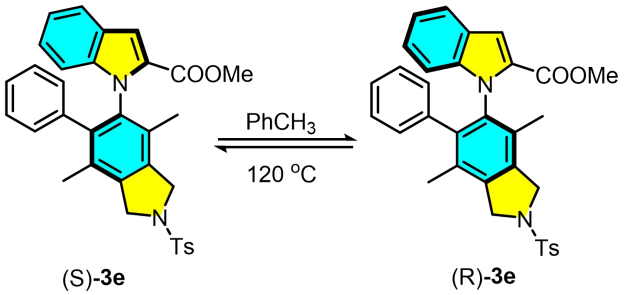
N-alkynyl indole **2** (0.15 mmol, 1.5 equiv.), diyne **1** (0.1 mmol, 1.0 equiv.), $Rh(COD)_2BF_4$ (4.1 mg, 0.010 mmol, 10 mol%), and **L6** (7.3 mg, 0.012 mmol, 12

mol%) were dissolved in dried solvent of CH_3OH (2.0 mL). The mixture were heated to 40 °C and stirred for 12 h in a water bath. The reaction was monitored by TLC. The mixture was allowed to cool down to the room temperature and concentrated in vacuo. The residue was purified by silica gel (100-200 mesh) column chromatography to get the corresponding product **3**.

4. Thermal racemization experiments

We studied the configurational stability of **3e** at 120 °C. 20 mg of **3e** (99% ee) was dissolved $PhCH_3$ and heated in a sealed tube for the corresponding time. The configuration remains very stable and no recemization occurred in 72 hrs.

Table S2. Thermal racemization experiments



(S)-**3e** (R)-**3e**

time/h	**3e** ee (%)
0	99
1	99
2	99
4	99
6	99
12	99
24	99
36	99
48	99
60	99
72	99

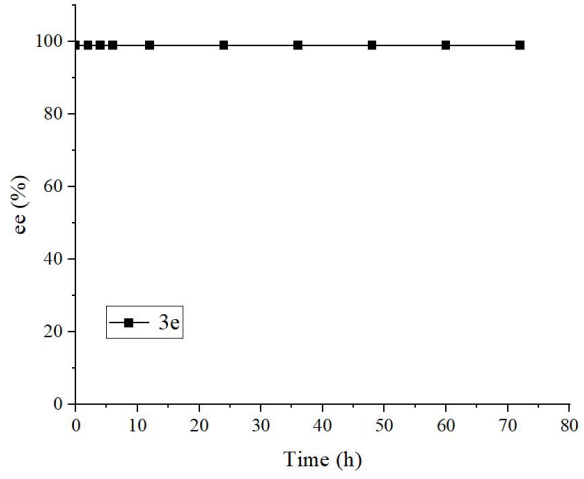
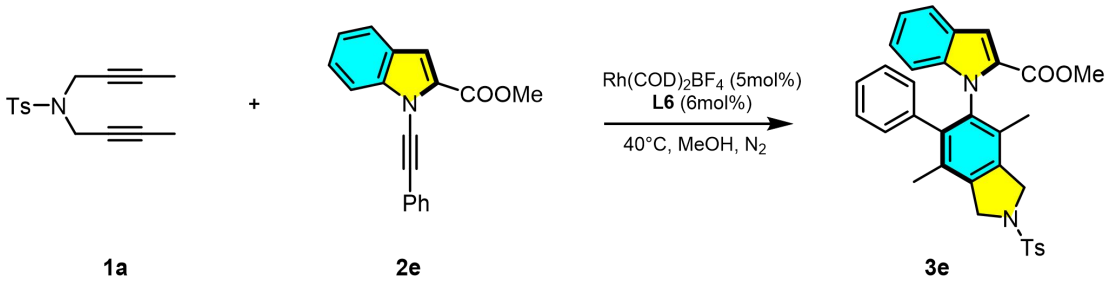


Figure S1. Thermal racemization experiments

5. Gram-scale experiment and synthetic applications

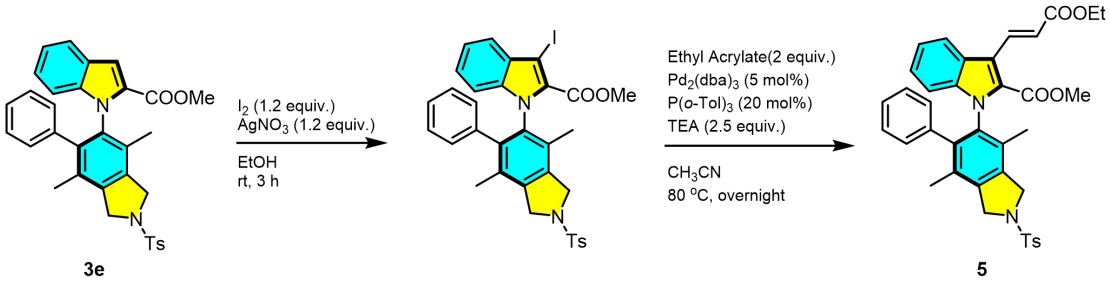
5.1 Gram-scale experiment



1a **2e** **3e**

N-alkynyl indole **2e** (434 mg, 1.5 mmol, 1.5 equiv.), diyne **1a** (275.4 mg, 1 mmol, 1.0 equiv.), $Rh(COD)_2BF_4$ (20.3 mg, 0.05 mmol, 5 mol%), and **L6** (36.63 mg, 0.06 mmol, 6 mol%) were dissolved in dried solvent of CH_3OH (20.0 mL). The mixture were heated to 40 °C and stirred for 12 h in a water bath. The reaction was monitored by TLC. The mixture was allowed to cool down to the room temperature and concentrated in vacuo. The residue was purified by silica gel (100-200 mesh) column chromatography with petroleum ether/ethyl acetate (10:1) as eluent to get the corresponding **3e** (0.385 g, 70% yield, 99% ee).

5.2 Synthesis of **5** via an iodination and a Heck coupling reaction

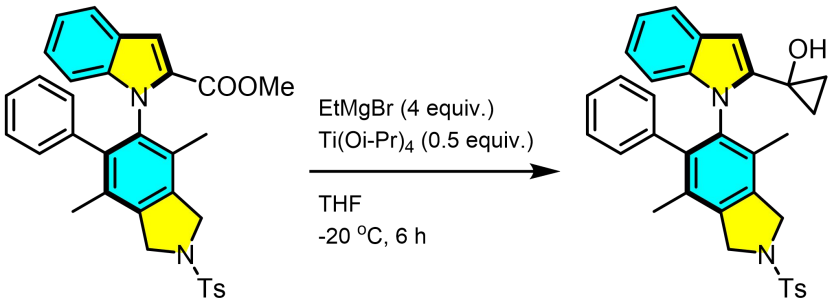


3e **5**

To a solution of **3e** (110.0 mg, 0.2 mmol, 1.0 equiv.) and $AgNO_3$ (40.8 mg, 0.24 mmol, 1.2 equiv.) in ethanol (0.25 mL) were added iodine (60.9 mg, 0.24 mmol, 1.2 equiv.) in ethanol (0.35 mL) under air at the room temperature. The mixture was kept in the dark and stirred at the ambient environment for 10 h. The reaction was monitored by NMR. The mixture was poured into saturated $Na_2S_2O_3$ solution and extracted by ethyl acetate (3 x 10 mL), and the organic phase was dried by Na_2SO_4 and concentrated in vacuo to obtain the raw product.

To a solution of raw product in CH_3CN (1.0 mL) were added ethyl acrylate (22.0 μL, 0.20 mmol, 2.0 equiv.), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 5 mol%), P(*o*-Tol)$_3$ (6.1 mg, 0.020 mmol, 20 mol%) and triethylamine (35.0 μL, 0.25 mmol, 2.5 equiv.) under nitrogen atmosphere. The mixture was heated to 80 °C and stirred overnight. The reaction was monitored by TLC. After the reacts were consumed completely, the mixture was poured into water and extracted by dichloromethane (3 x 5 mL). The organic phase was dried by Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel (100-200 mesh) column chromatography with petroleum ether/ethyl acetate (8:1) as the eluent to obtain **5** (51.7 mg, white solid, 40% yield, 97% ee).

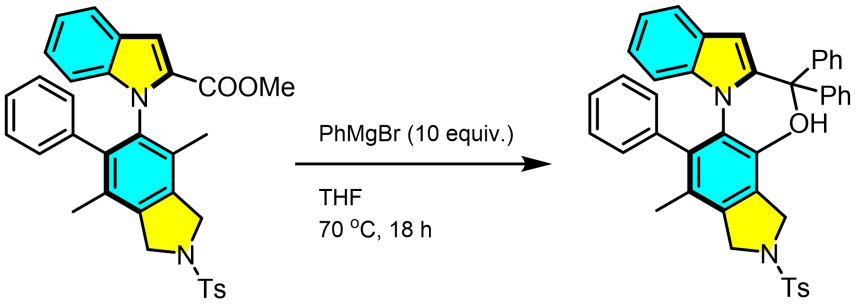
5.3 Synthesis of **6** via a Kulinkovich cyclopropanation



3e **6**

To a solution of **3e** (55.0 mg, 0.10 mmol, 1.0 equiv.) in dried THF (1 mL) was added Ti(Oi-Pr)$_4$ (14.8μL, 0.05 mmol, 0.5 equiv.) and EtMgBr (0.13 mL, 3M in diethyl ether, 0.40 mmol, 4 equiv.) dropwise by syringe under nitrogen atmosphere at 0 °C. The mixture was cooled down to -20 °C and stirred for 6 h. The reaction was monitored by TLC. After the reacts were consumed completely, the reaction was allowed to warm to the room temperature and quenched by saturated NH_4Cl solution. The mixture was extracted by ethyl acetate (3 x 10 mL) and the organic phase was washed with brine. The organic phase was dried by Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel (100-200 mesh) column chromatography with petroleum ether/ethyl acetate (8:1) as the eluent to obtain **6** (32.8 mg, white solid, 60% yield, 99% ee).

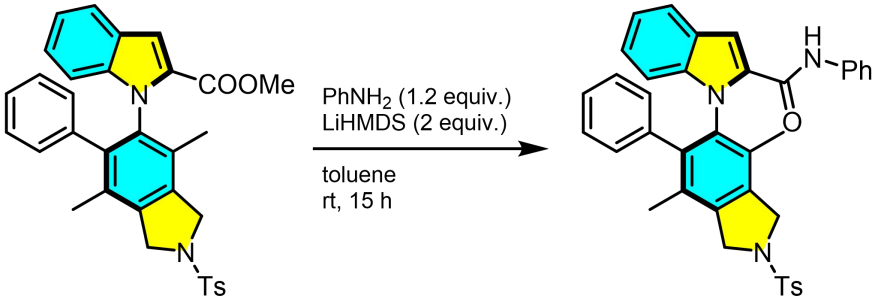
5.4 Synthesis of **7** via a Grignard reaction



3e **7**

To a solution of **3e** (55.0 mg, 0.1 mmol, 1.0 equiv.) in dried THF (1 mL) was added PhMgBr (1.0 mL, 1M in THF, 1.0 mmol, 10 equiv.) dropwise by syringe under nitrogen atmosphere at 0 ºC. The mixture was heated to 70 ºC and stirred for 18 h. The reaction was monitored by TLC. After the reacts were consumed completely, the reaction was allowed to cool down to the room temperature and quenched by saturated NH_4Cl solution. The mixture was extracted by ethyl acetate (3 x 10 mL) and the organic phase was washed with brine. The organic phase was dried by Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel (100-200 mesh) column chromatography with petroleum ether/ethyl acetate (8:1) as the eluent to obtain **7** (51.2 mg, white solid, 76% yield, 97% ee).

5.5 Synthesis of **8** via an amination

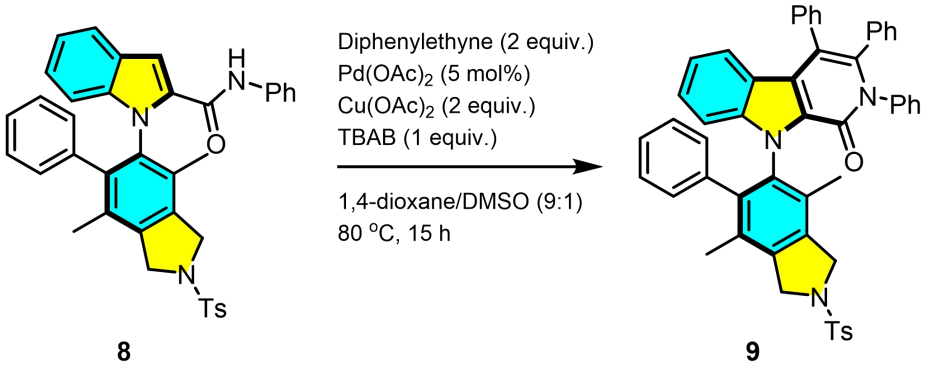


3e **8**

To a solution of **3e** (55.0 mg, 0.10 mmol, 1.0 equiv.) in dried toluene (1 mL) were added aniline (11.0 μL, 0.12 mmol, 1.2 equiv.) and LiHMDS (0.20 mL, 1 M in THF, 0.20 mmol, 2.0 equiv.) dropwise by syringe under nitrogen atmosphere at the

room temperature. The mixture was stirred for 15 h at the ambient temperature. The reaction was monitored by TLC. After the reacts were consumed completely, the reaction was allowed to warm to the room temperature and quenched by saturated NH_4Cl solution. The mixture was extracted by ethyl acetate (3 x 5 mL) and the organic phase was washed with water and brine. The organic phase was dried by Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel (100-200 mesh) column chromatography with petroleum ether/ethyl acetate (8:1) as the eluent to obtain **8** (53.1 mg, white solid, 87% yield, 99% ee).

5.6 Synthesis of **9** via an oxidative cyclization



8 **9**

To a solution of **8** (61.1 mg, 0.10 mmol, 1.0 equiv.) and diphenylethyne (35.6 mg, 0.20 mmol, 2.0 equiv.) in a mixed solvent of 1,4-dioxane/DMSO (9:1, 2 mL) were added $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 5 mol%), $Cu(OAc)_2$ (36.3 mg, 0.20 mmol, 2.0 equiv.) and TBAB (32.2 mg, 0.10 mmol, 1.0 equiv.). The mixture was heated to 80 °C and stirred for 15 h. The reaction was monitored by TLC. After the reacts were consumed completely, the mixture were filtered on a pad of celite and concentrated in vacuo. The residue was purified by silica gel (100-200 mesh) column chromatography with petroleum ether/ethyl acetate (8:1) as the eluent to obtain **9** (51.1 mg, white solid, 65% yield, 99% ee).

6. X-ray crystallographic data for 3n

A suitable crystal was selected and analyzed on a Rigaku XtaLAB Synergy diffractometer. The crystal structures have been deposited at The Cambridge Crystallographic Data Centre (CCDC: 2312158). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.com.ac.uk/data_request/cif.

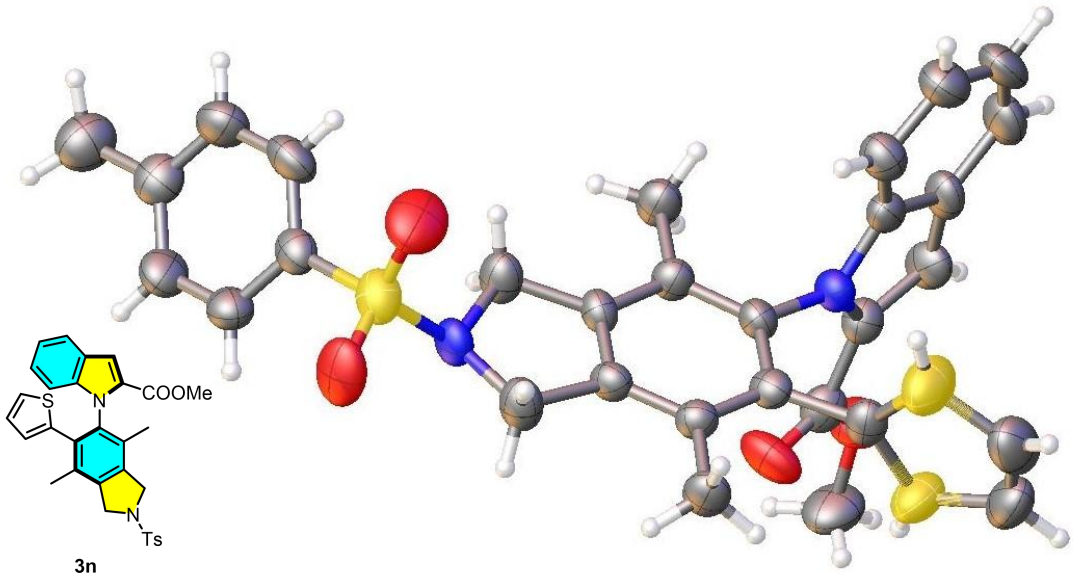
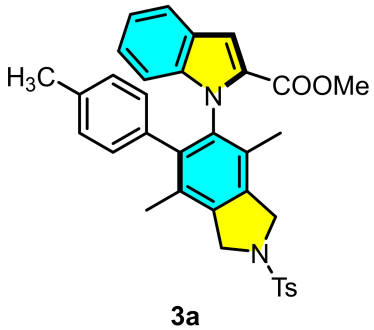
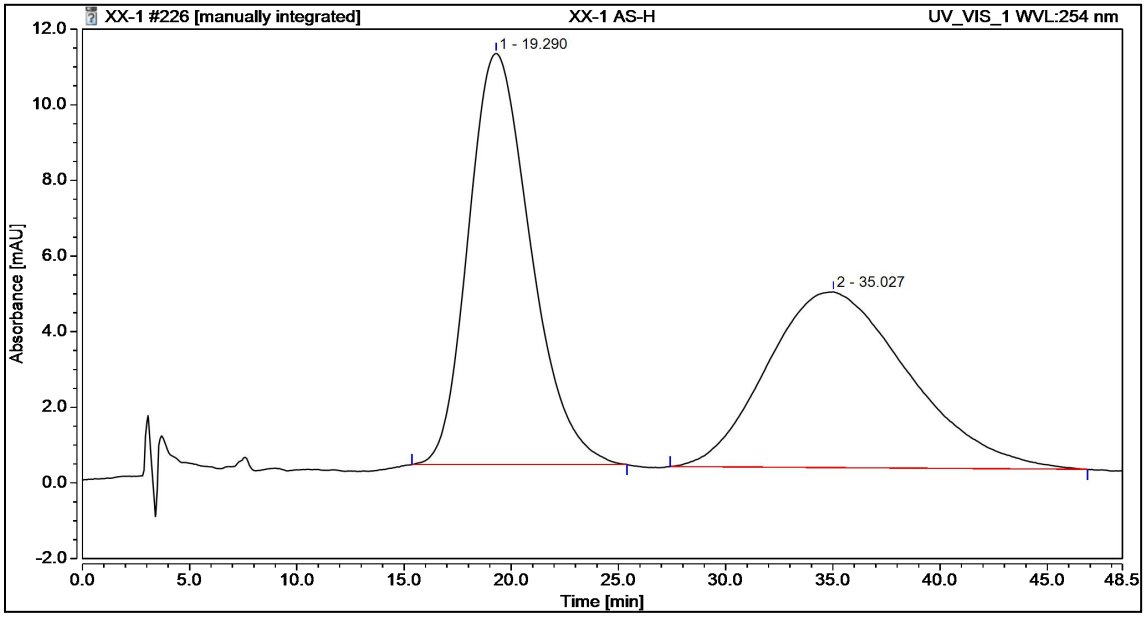


Figure S2 X-ray crystal structure of **3n** (CCDC: 2312158. Thermal ellipsoids are drawn at 50% probability.)

7. Characterization of Products 3a-3c, 3e-3x, 5-9

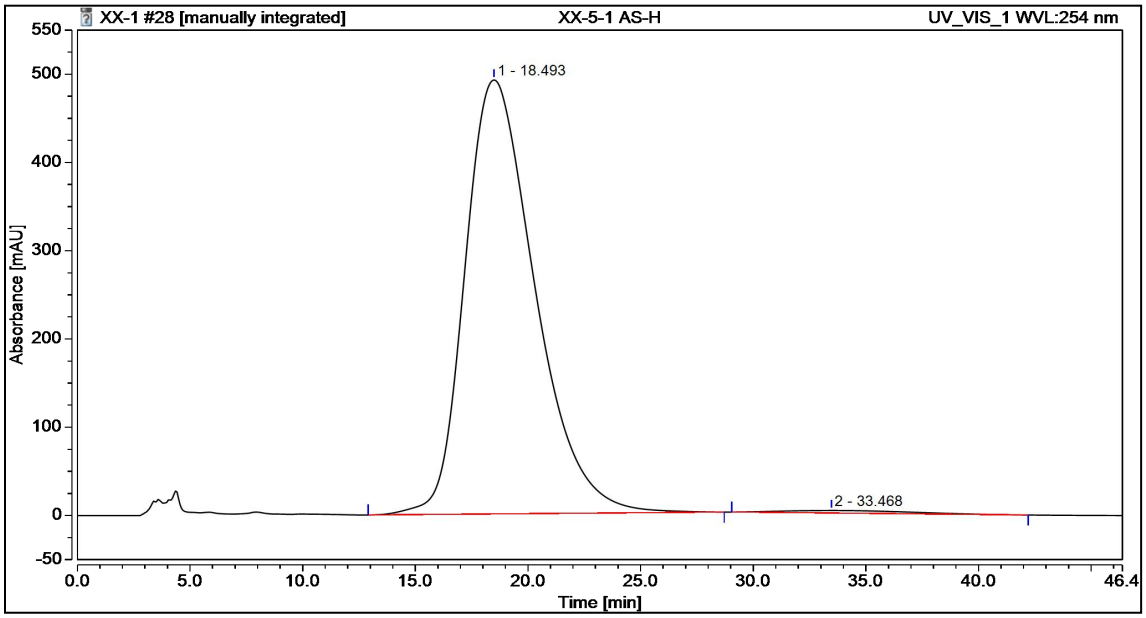


White solid, 53.7 mg, 93% yield, 98% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 85/15, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 18.49 min, t (minor) = 33.47 min]. $[\alpha]_D^{20}$ = - 30.4°(c = 1.0, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 10.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.06 (s, 1H), 6.92 – 6.77 (m, 3H), 6.61 (d, *J* = 8.2 Hz, 1H), 6.41 (d, *J* = 9.6 Hz, 1H), 4.80 – 4.54 (m, 4H), 3.73 (s, 3H), 2.47 (s, 3H), 2.13 (s, 3H), 1.90 (s, 3H), 1.71 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.75, 142.74, 140.12, 138.77, 135.37, 134.83, 134.48, 133.64, 132.93, 132.81, 128.93, 128.40, 127.67, 127.47, 127.27, 127.11, 127.06, 126.63, 126.60, 124.76, 124.26, 121.32, 119.81, 110.44, 109.29, 52.96, 52.70, 50.48, 20.54, 20.05, 15.97, 13.09. **HRMS (ESI, m/z)** Calcd for $C_{34}H_{32}N_2O_4S$ $(M+H)^+$: 565.2156; Found: 565.2142.



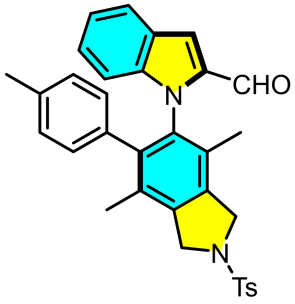
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.290	36.626	10.871	50.75	70.05	n.a.
2		35.027	35.550	4.648	49.25	29.95	n.a.
Total:			**72.177**	**15.519**	**100.00**	**100.00**	



Integration Results

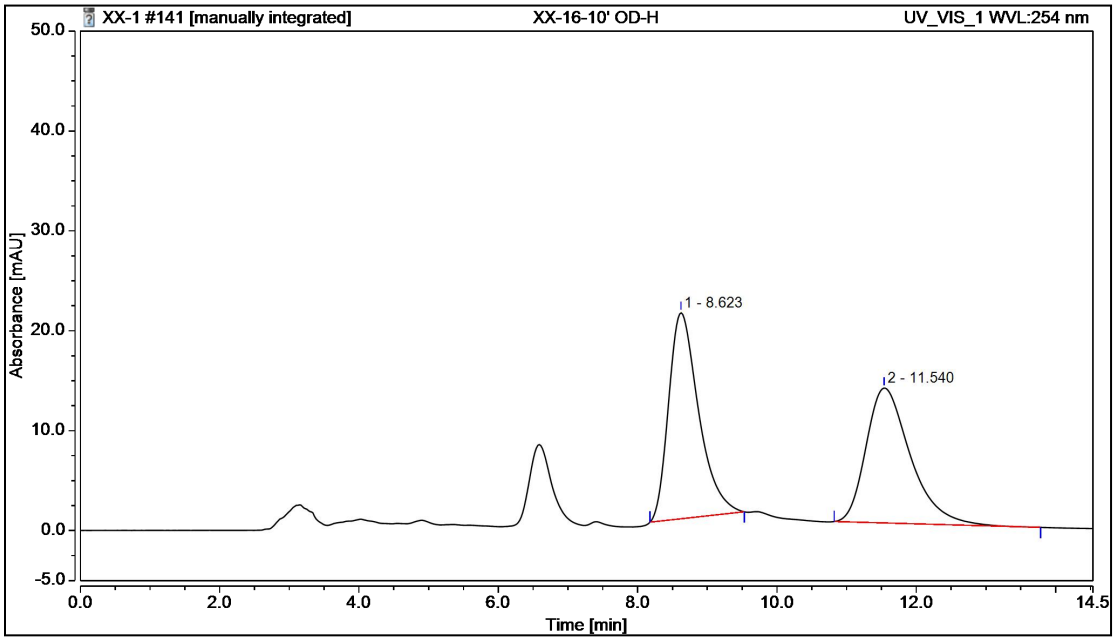
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.493	1771.926	491.788	98.90	99.42	n.a.
2		33.468	19.652	2.891	1.10	0.58	n.a.
Total:			**1791.578**	**494.679**	**100.00**	**100.00**	



3b

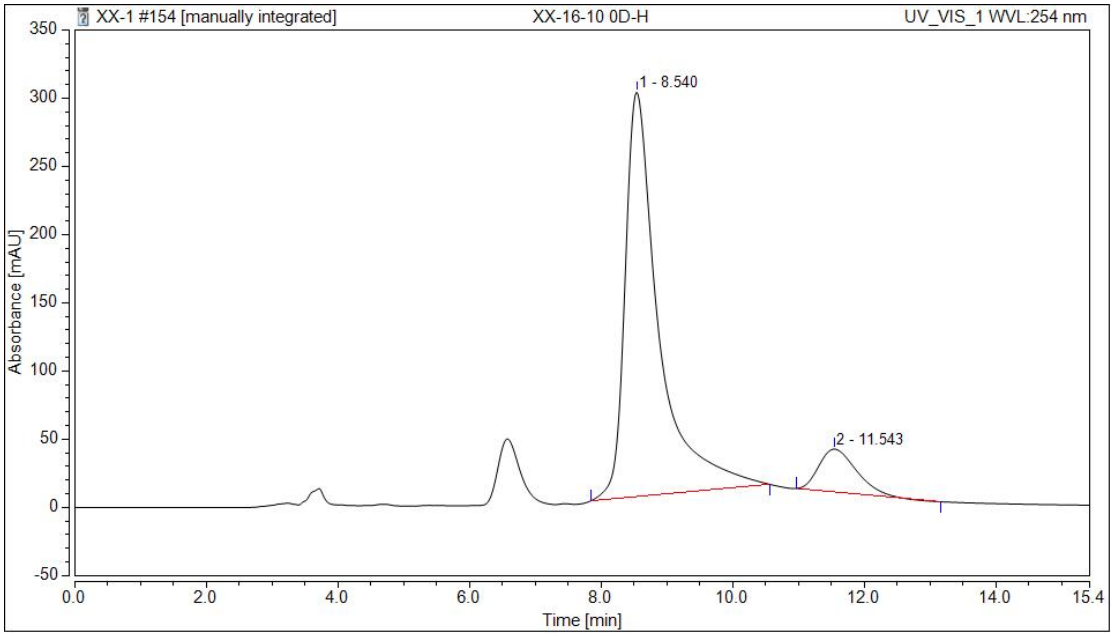
White solid, 27.8 mg, 52% yield, 79% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 80/20, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 8.62 min, t (minor) = 11.59 min]. $[\alpha]_D^{20}$ = -46.8°(c = 0.8, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.59 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 1H), 7.11 (d, *J* = 9.1 Hz, 1H), 7.08 (s, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 9.7 Hz, 1H), 6.62 (d, *J* = 6.5 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 4.75 (d, *J* = 10.2 Hz, 2H), 4.64 (d, *J* = 11.4 Hz, 2H), 2.47 (s, 3H), 2.13 (s, 3H), 1.91 (s, 3H), 1.67 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 181.67, 143.83, 141.22, 140.70, 136.52, 136.13, 135.93, 134.94, 134.92, 133.91, 133.75, 130.00, 129.69, 128.86, 128.43, 128.31, 128.10, 127.66, 127.63,

127.08, 125.99, 123.14, 121.26, 116.39, 111.58, 54.00, 53.73, 21.59, 21.06, 17.01, 14.04. **HRMS (ESI, m/z)** Calcd for $C_{33}H_{30}N_2O_3S$ $(M+H)^+$: 535.2049; Found: 535.2059.



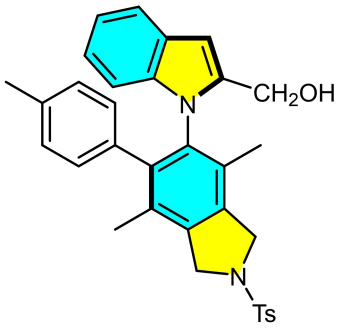
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.623	10.292	20.623	50.80	60.43	n.a.
2		11.540	9.970	13.505	49.20	39.57	n.a.
Total:			**20.262**	**34.128**	**100.00**	**100.00**	



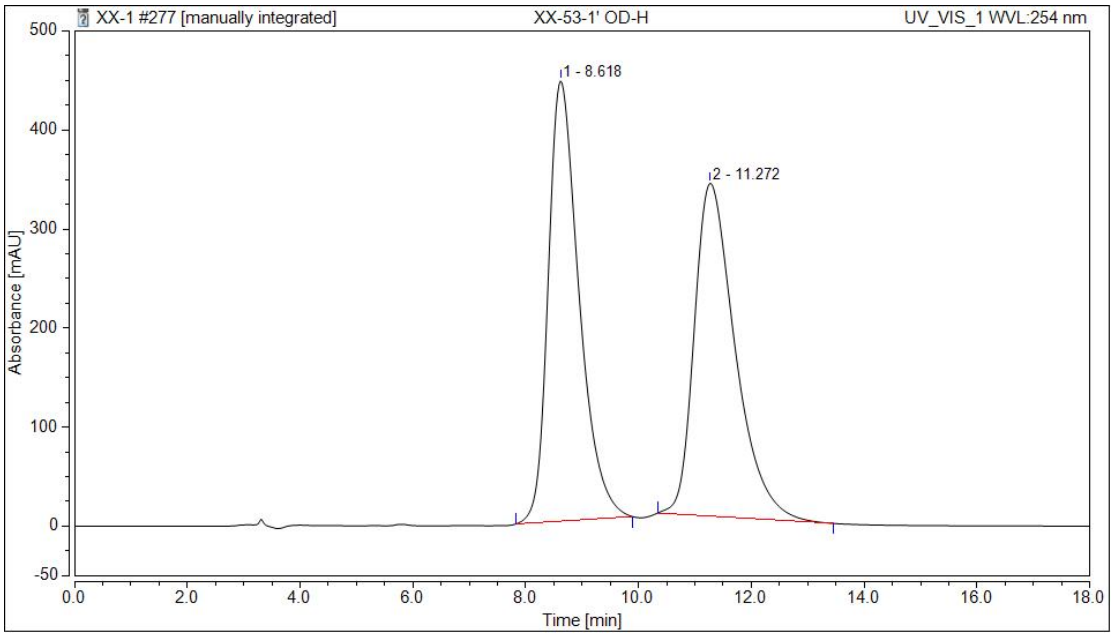
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.540	176.046	296.647	89.44	90.42	n.a.
2		11.543	20.777	31.428	10.56	9.58	n.a.
Total:			**196.823**	**328.075**	**100.00**	**100.00**	

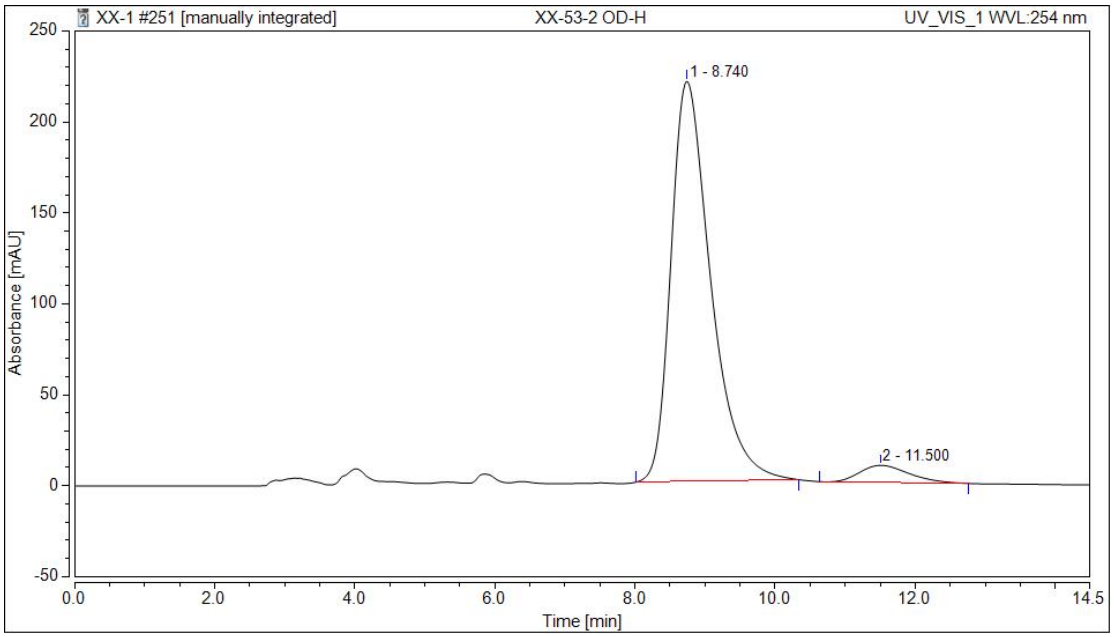


3c

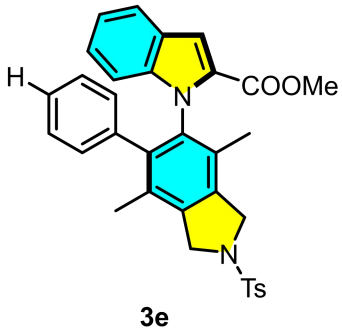
White solid, 14.5 mg, 27% yield, 90% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 80/20, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 8.74 min, t (minor) = 11.50 min]. $[\alpha]_D^{20}$ = -110.3°(c = 1.8, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.14 – 7.10 (m, 1H), 7.08 – 7.04 (m, 1H), 7.01 – 6.93 (m, 2H), 6.84 (d, J = 8.2 Hz, 1H), 6.62 (d, J = 6.0 Hz, 1H), 6.46 (d, J = 5.9 Hz, 1H), 6.33 (s, 1H), 4.72 – 4.63 (m, 4H), 4.26 (s, 2H), 2.45 (s, 3H), 2.14 (s, 3H), 1.96 (s, 3H), 1.65 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.84, 141.77, 139.13, 138.81, 136.86, 136.26, 135.21, 134.43, 133.65, 130.12, 130.01, 129.73, 128.77, 128.69, 128.26, 127.98, 127.69, 127.36, 122.21, 120.66, 119.84, 110.47, 101.68, 57.38, 54.01, 53.72, 21.61, 21.10, 17.27, 14.14. **HRMS (ESI, m/z)** Calcd for $C_{33}H_{32}N_2O_3S$ $(M+H)^+$: 536.2134; Found: 536.2134.



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.618	281.516	444.645	49.97	56.95	n.a.
2		11.272	281.908	336.180	50.03	43.05	n.a.
Total:			**563.424**	**780.825**	**100.00**	**100.00**	



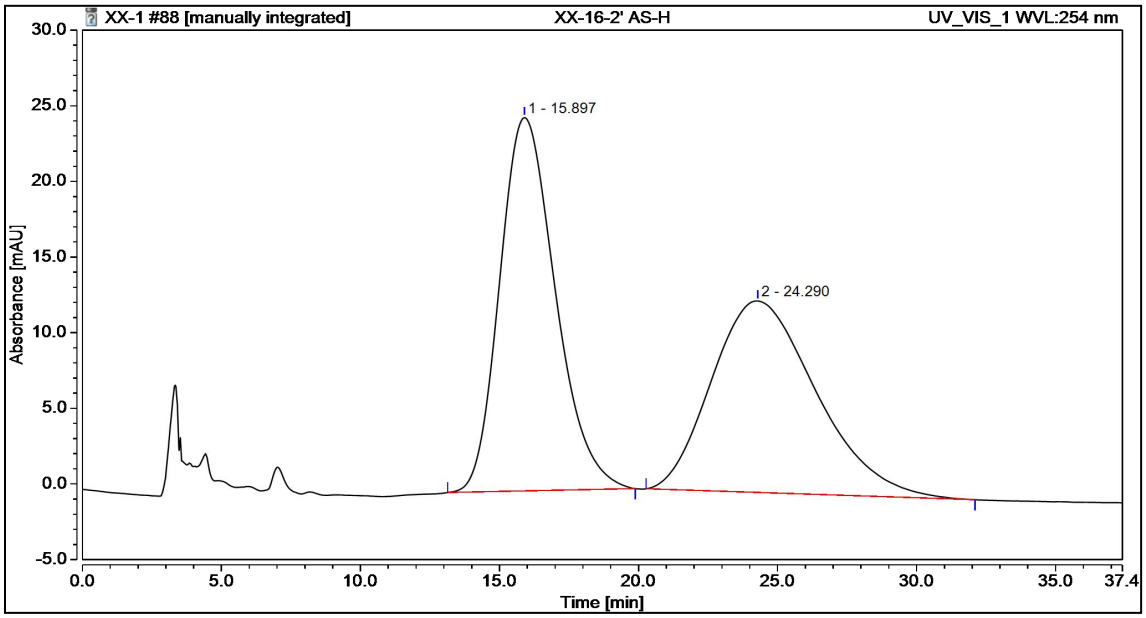
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.740	144.048	219.966	94.94	95.91	n.a.
2		11.500	7.681	9.388	5.06	4.09	n.a.
Total:			**151.729**	**229.354**	**100.00**	**100.00**	



3e

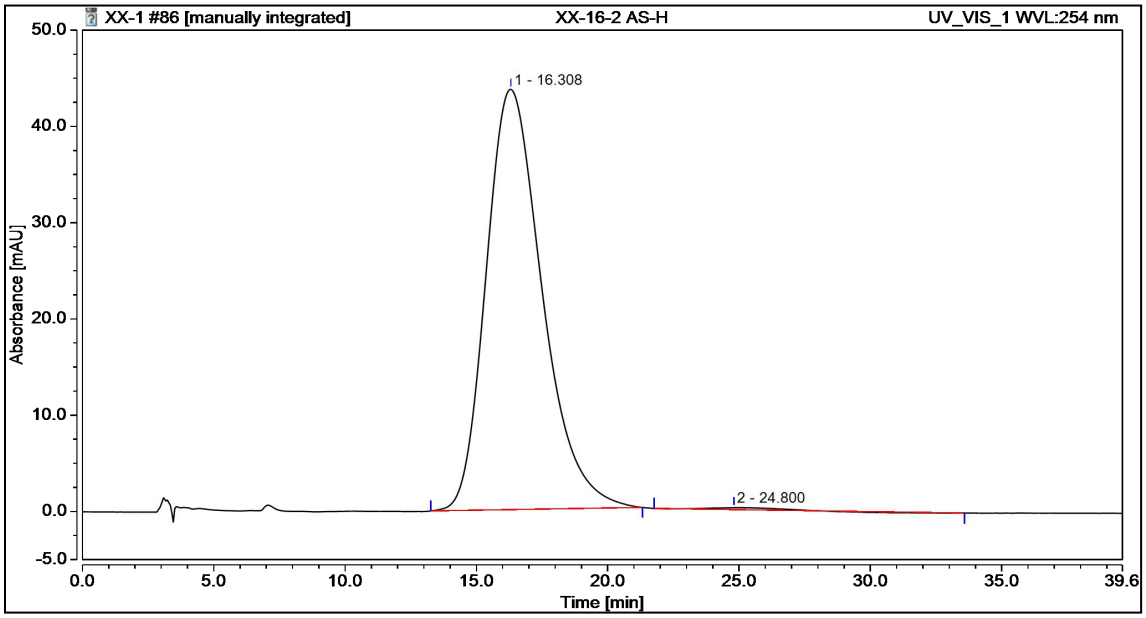
White solid, 53.3 mg, 97% yield, 99% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 80/20, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 16.30 min, t (minor) = 24.80 min]. $[\alpha]_D^{20}$ = - 25.2°(c = 1.8, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.09 (q, *J* = 8.0 Hz, 2H), 7.04 (s, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.3 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 4.79 – 4.63 (m, 4H), 3.72

(s, 3H), 2.46 (s, 3H), 1.91 (s, 3H), 1.75 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.79, 143.79, 141.08, 139.82, 136.88, 135.83, 135.61, 134.90, 134.04, 129.97, 129.25, 128.91, 128.60, 128.35, 127.81, 127.67, 127.36, 127.22, 126.96, 125.81, 125.35, 122.39, 120.91, 111.45, 110.36, 53.99, 53.74, 51.51, 21.56, 16.96, 14.15. **HRMS (ESI, m/z)** Calcd for $C_{33}H_{30}N_2O_4S$ $(M+H)^+$: 551.1999; Found: 551.2007.

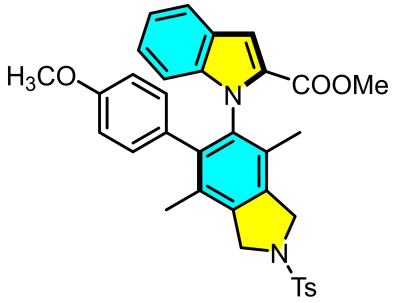


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.897	57.206	24.683	50.94	66.09	n.a.
2		24.290	55.104	12.664	49.06	33.91	n.a.
Total:			**112.310**	**37.347**	**100.00**	**100.00**	

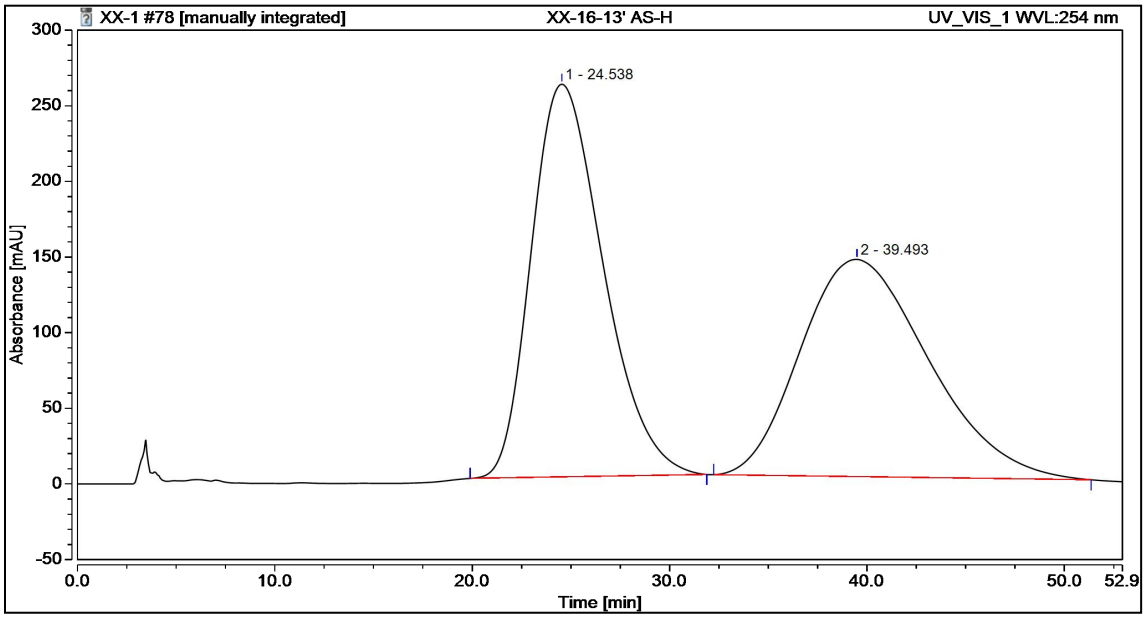


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.308	107.830	43.670	99.66	99.53	n.a.
2		24.800	0.371	0.207	0.34	0.47	n.a.
Total:			**108.201**	**43.877**	**100.00**	**100.00**	



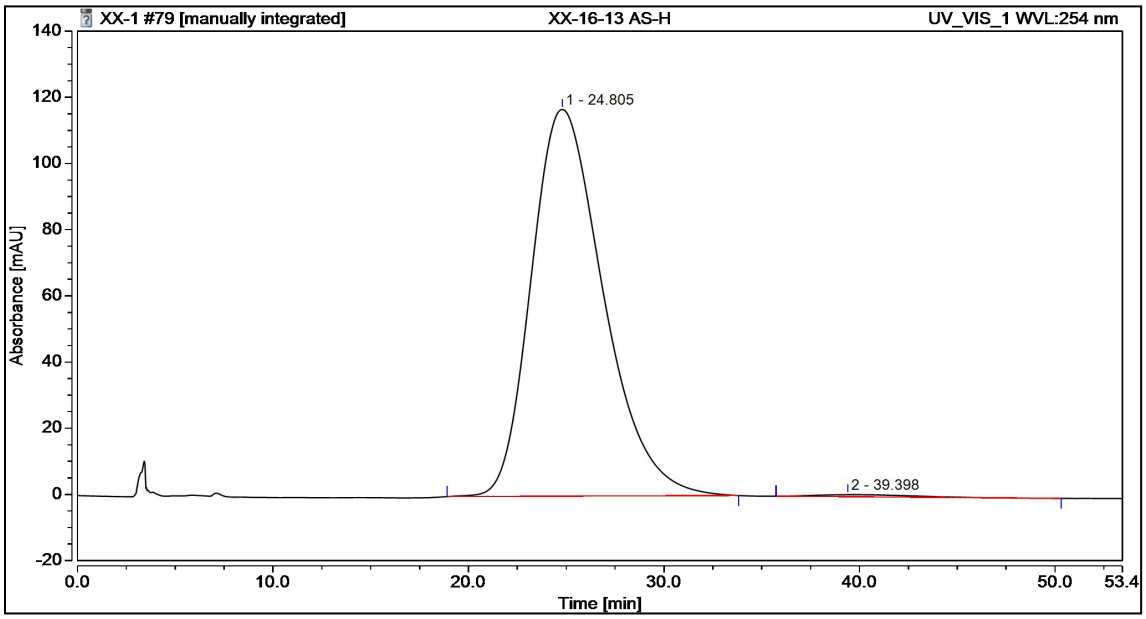
3f

White solid, 48.1 mg, 83% yield, 98% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 80/20, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 24.80 min, t (minor) = 39.40 min]. $[\alpha]_D^{20}$ = - 54.6°(c = 0.7, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.84 (t, *J* = 8.7 Hz, 2H), 6.64 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.43 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.33 (dd, *J* = 8.5, 2.7 Hz, 1H), 4.79 – 4.61 (m, 4H), 3.72 (s, 3H), 3.63 (s, 3H), 2.47 (s, 3H), 1.91 (s, 3H), 1.72 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.79, 143.81, 140.06, 139.74, 135.97, 135.70, 135.18, 134.01, 130.61, 130.55, 129.97, 129.49, 129.43, 129.38, 128.72, 128.19, 127.66, 125.83, 125.50, 122.52, 121.04, 114.57, 114.44, 114.40, 114.27, 111.27, 110.64, 53.94, 53.71, 51.54, 21.55, 16.93, 14.11. **HRMS (ESI, m/z)** Calcd for $C_{34}H_{32}N_2O_5S$ $(M+H)^+$: 581.2104; Found: 581.2106.



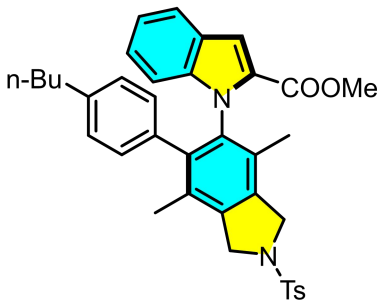
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.538	1096.132	259.572	50.41	64.39	n.a.
2		39.493	1078.125	143.583	49.59	35.61	n.a.
Total:			**2174.258**	**403.155**	**100.00**	**100.00**	



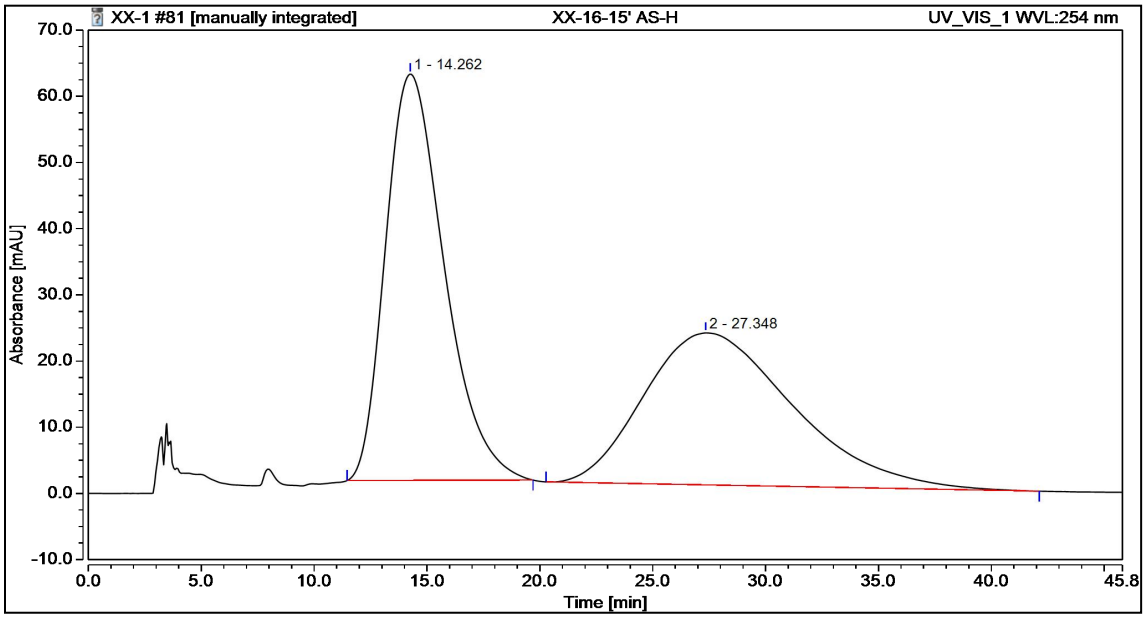
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.805	498.457	116.844	99.26	99.47	n.a.
2		39.398	3.704	0.623	0.74	0.53	n.a.
Total:			**502.161**	**117.468**	**100.00**	**100.00**	



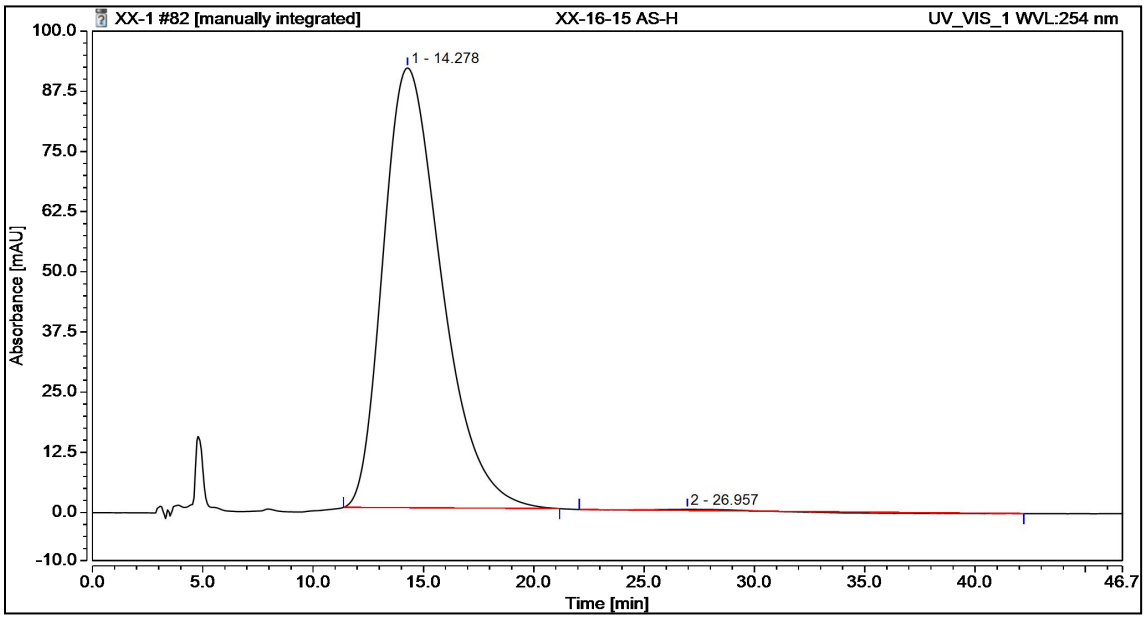
3g

White solid, 51.5 mg, 85% yield, 99% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 85/15, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 14.28 min, t (minor) = 26.96 min]. $[\alpha]_D^{20}$ = - 48.0°(c = 1.5, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.89 (d, *J* = 9.8 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 9.7 Hz, 1H), 6.37 (d, *J* = 9.7 Hz, 1H), 4.80 – 4.61 (m, 4H), 3.72 (s, 3H), 2.46 (s, 3H), 2.39 (t, *J* = 7.6 Hz, 2H), 1.92 (s, 3H), 1.75 (s, 3H), 1.41 (dd, *J* = 8.1, 5.7 Hz, 2H), 1.16 (q, *J* = 7.5 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.80, 143.79, 141.35, 141.16, 139.83, 135.98, 135.48, 134.64, 133.94, 129.98, 129.36, 128.70, 128.49, 128.42, 127.67, 127.59, 127.38, 127.36, 125.84, 125.24, 122.30, 120.81, 111.52, 110.31, 54.01, 53.76, 51.49, 35.07, 33.19, 21.97, 21.59, 17.05, 14.21, 13.93. **HRMS (ESI, m/z)** Calcd for $C_{37}H_{38}N_2O_4S$ $(M+H)^+$: 607.2625; Found: 607.2633.



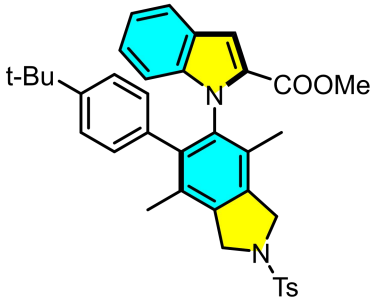
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.262	185.193	61.402	51.30	72.77	n.a.
2		27.348	175.827	22.971	48.70	27.23	n.a.
Total:			**361.020**	**84.374**	**100.00**	**100.00**	



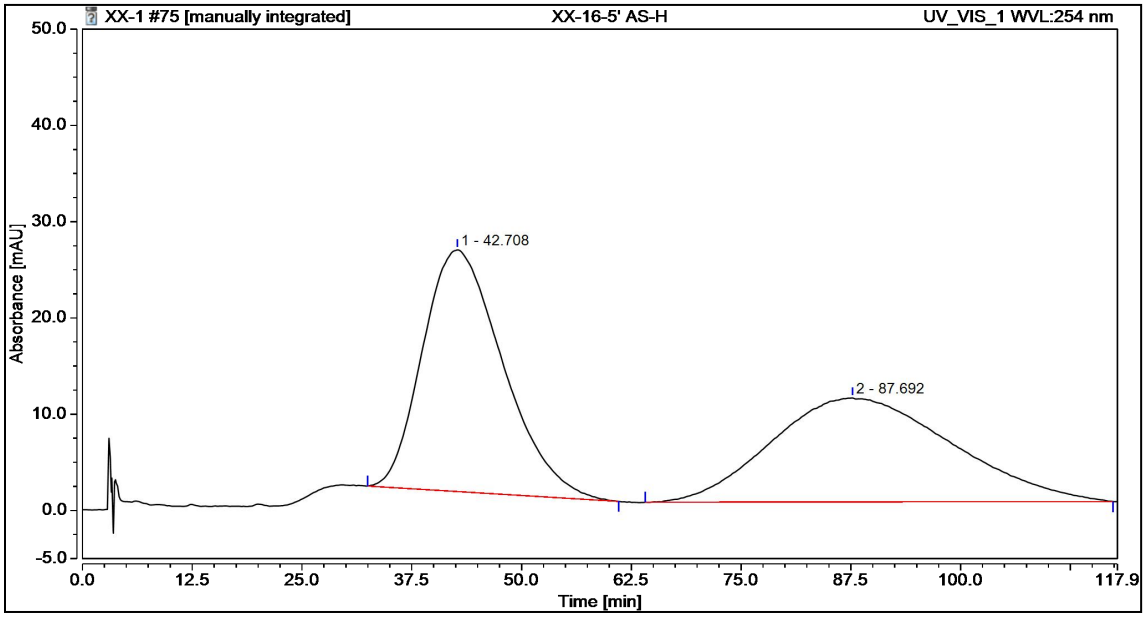
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.278	279.949	91.380	99.85	99.73	n.a.
2		26.957	0.418	0.247	0.15	0.27	n.a.
Total:			**280.366**	**91.627**	**100.00**	**100.00**	



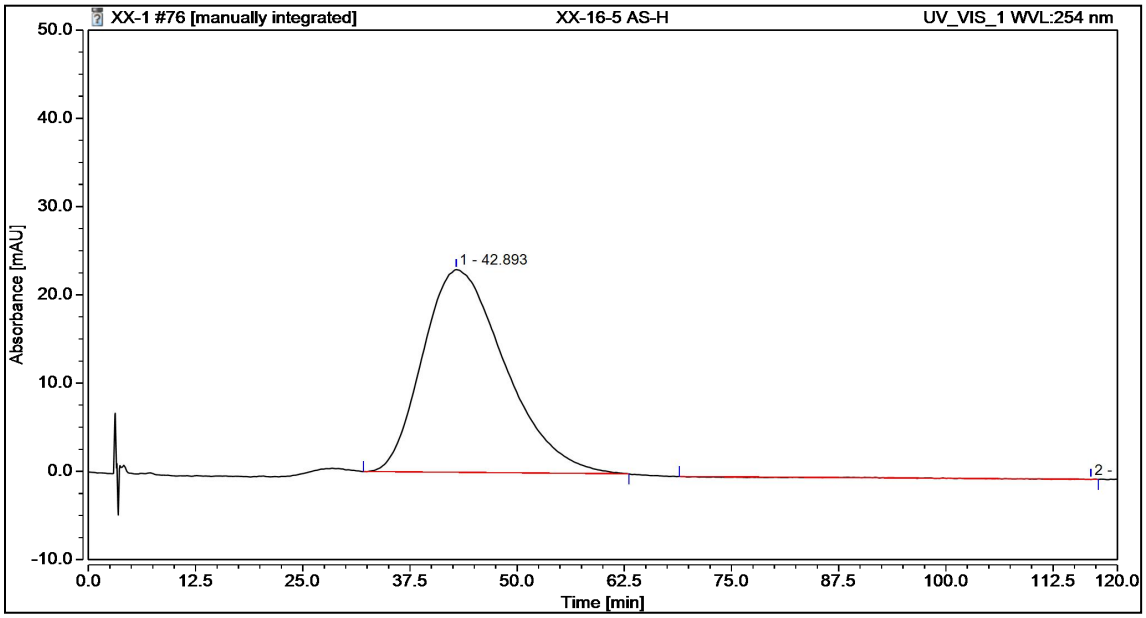
3h

White solid, 52.1 mg, 86% yield, 99% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 95/5, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 42.90 min, t (minor) = 87.69 min]. $[\alpha]_D^{20}$ = - 50.5°(c = 1.9, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (s, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.12 – 6.97 (m, 3H), 6.89 – 6.74 (m, 3H), 6.39 (s, 1H), 4.70 (dd, *J* = 57.3, 11.9 Hz, 4H), 3.71 (s, 3H), 2.46 (s, 3H), 1.93 (s, 3H), 1.74 (s, 3H), 1.13 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.79, 149.62, 143.77, 141.13, 139.90, 136.07, 135.49, 133.72, 129.99, 128.61, 127.68, 125.91, 125.23, 124.11, 122.29, 120.81, 111.56, 110.34, 54.04, 53.78, 51.46, 34.28, 31.17, 21.58, 17.11, 14.21. **HRMS (ESI, m/z)** Calcd for $C_{37}H_{38}N_2O_4S$ $(M+H)^+$: 607.2625; Found: 607.2619.

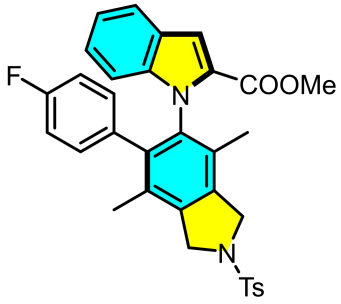


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		42.708	266.887	25.114	50.96	69.92	n.a.
2		87.692	256.849	10.806	49.04	30.08	n.a.
Total:			**523.736**	**35.920**	**100.00**	**100.00**	



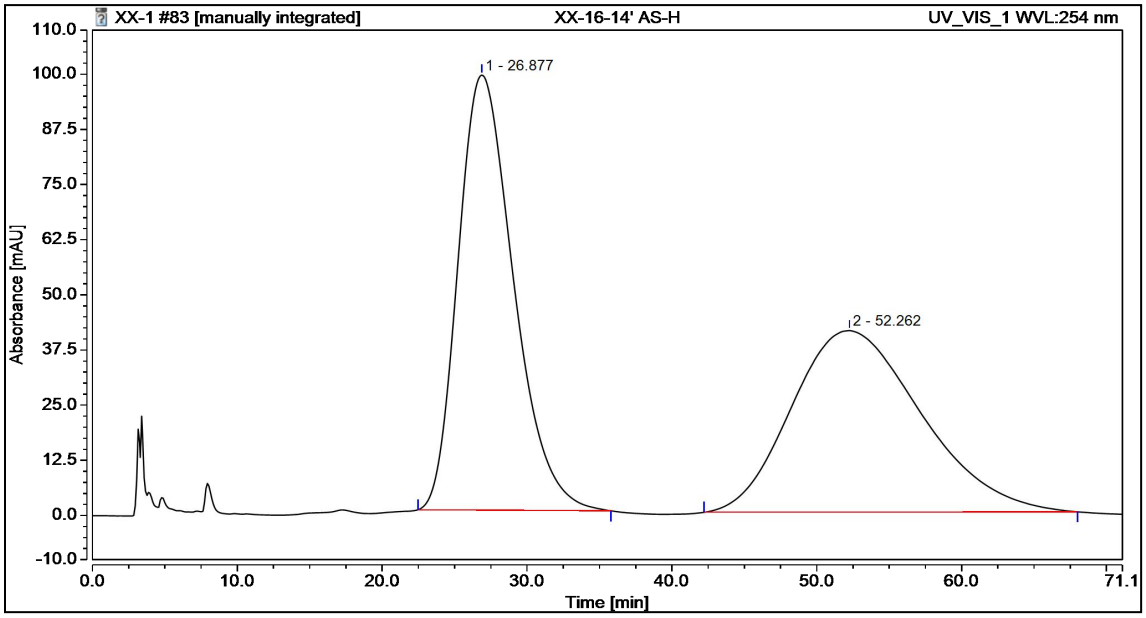
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		42.893	255.935	22.988	99.91	99.92	n.a.
2		116.897	0.225	0.019	0.09	0.08	n.a.
Total:			**256.160**	**23.008**	**100.00**	**100.00**	



3i

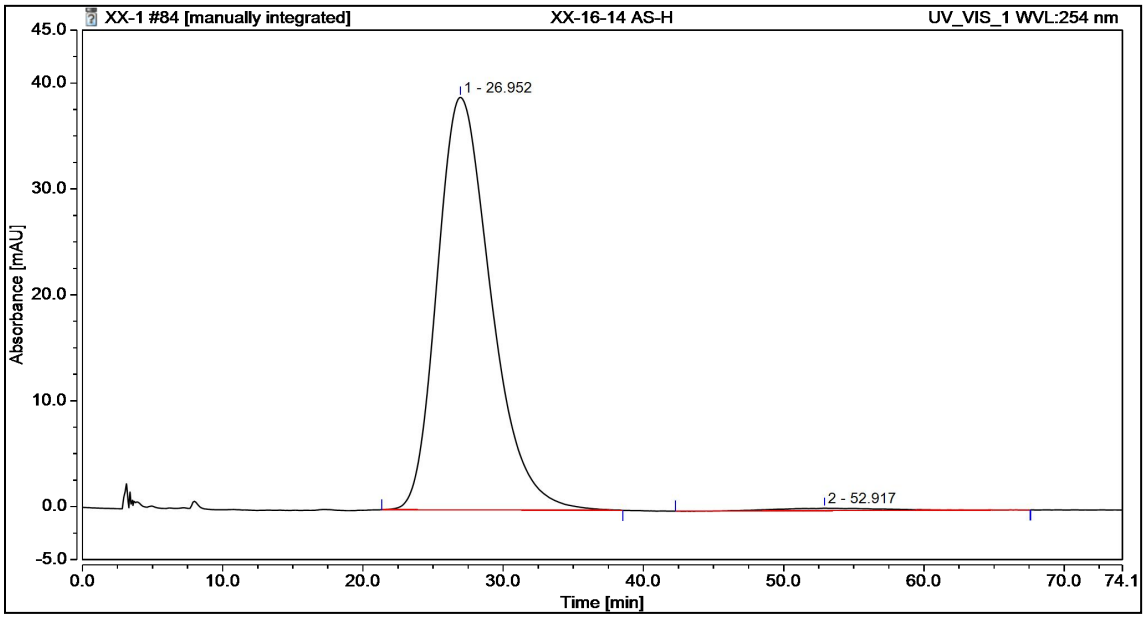
White solid, 47.1 mg, 83% yield, 98% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 85/15, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 26.95 min, t (minor) = 52.92 min]. $[\alpha]_D^{20}$ = - 17.4°(c = 1.9, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.3 Hz, 1H), 7.14 – 7.04 (m, 2H), 6.94 – 6.75 (m, 3H), 6.49 (d, *J* = 6.9 Hz, 2H), 4.70 (dd, *J* = 56.0, 13.2 Hz, 4H), 3.73 (s, 3H), 2.47 (s, 3H), 1.90 (s, 3H), 1.73 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.79, 143.81, 140.06, 139.74, 135.70, 135.18, 134.01, 130.61, 129.97, 129.49, 129.43, 129.38, 128.72, 128.19, 127.66, 125.83, 125.50, 122.52, 121.04, 114.57, 114.44, 114.40, 114.27, 111.27, 110.64, 53.94, 53.71, 51.54, 21.55, 16.93, 14.11.

HRMS (ESI, m/z) Calcd for $C_{33}H_{29}FN_2O_4S$ $(M+H)^+$: 569.1904; Found: 569.1909.



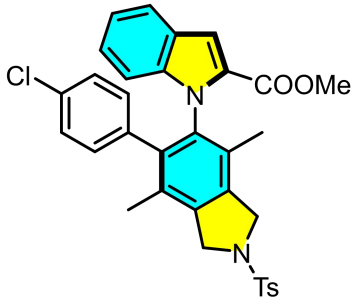
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.877	437.120	98.595	50.60	70.55	n.a.
2		52.262	426.674	41.153	49.40	29.45	n.a.
Total:			**863.794**	**139.748**	**100.00**	**100.00**	



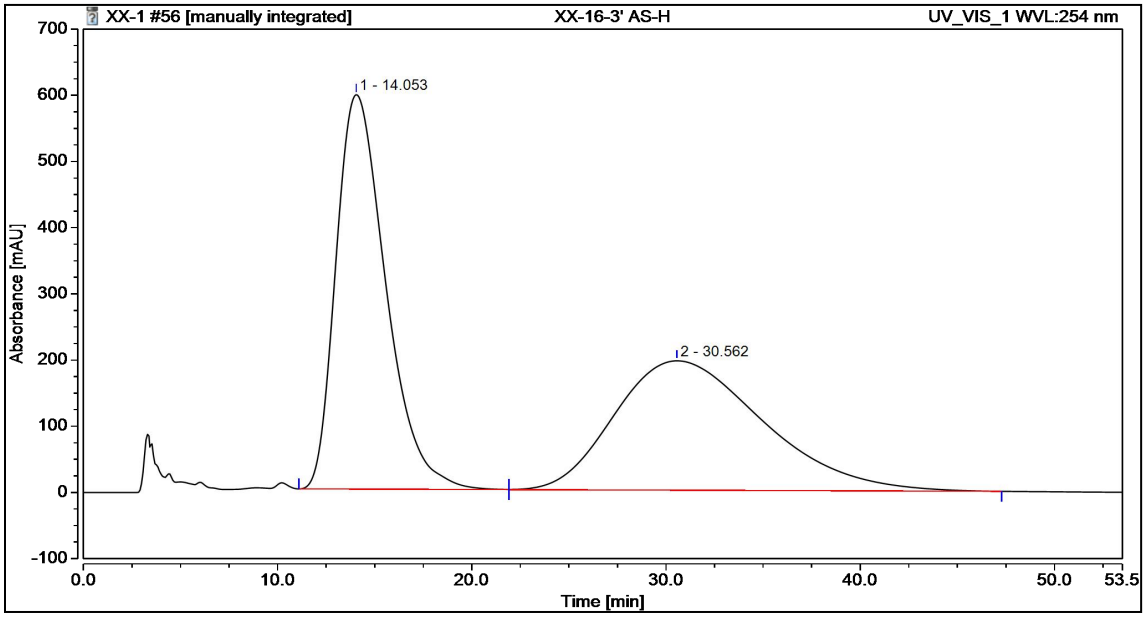
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.952	173.190	38.974	98.81	99.39	n.a.
2		52.917	2.088	0.240	1.19	0.61	n.a.
Total:			**175.279**	**39.214**	**100.00**	**100.00**	



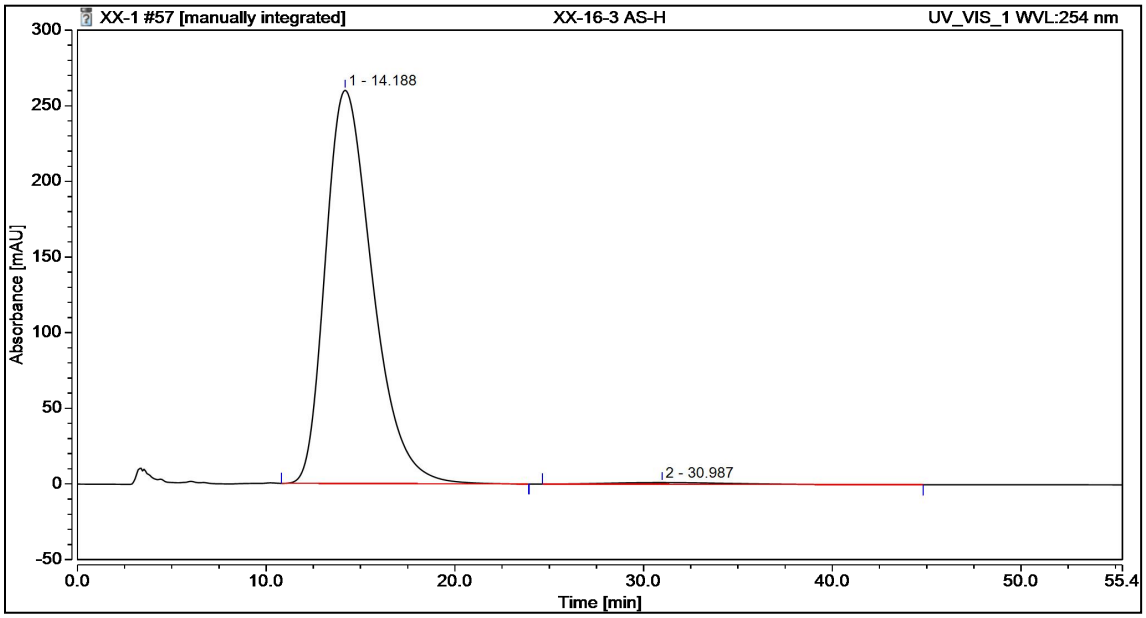
3j

White solid, 38.0 mg, 65% yield, 98% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 70/30, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 14.19 min, t (minor) = 31.00 min]. $[\alpha]_D^{20}$ = - 49.5°(c = 1.3, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 6.3 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.14 – 7.06 (m, 3H), 6.91 – 6.76 (m, 3H), 6.48 (d, *J* = 10.4 Hz, 1H), 4.81 – 4.58 (m, 4H), 3.73 (s, 3H), 2.43 (s, 3H), 1.89 (s, 3H), 1.71 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.79, 143.82, 139.89, 139.73, 135.76, 135.41, 135.32, 132.97, 130.35, 129.97, 129.22, 129.20, 128.79, 127.74, 127.66, 125.83, 125.55, 122.59, 121.08, 111.23, 110.78, 53.93, 53.70, 51.57, 21.56, 16.93, 14.06. **HRMS (ESI, m/z)** Calcd for $C_{33}H_{29}ClN_2O_4S$ $(M+H)^+$: 585.1609; Found: 585.1636.



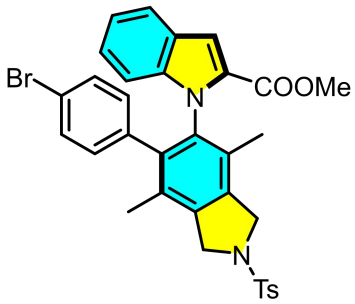
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.053	1771.309	596.083	50.55	75.30	n.a.
2		30.562	1732.938	195.539	49.45	24.70	n.a.
Total:			**3504.247**	**791.622**	**100.00**	**100.00**	



Integration Results

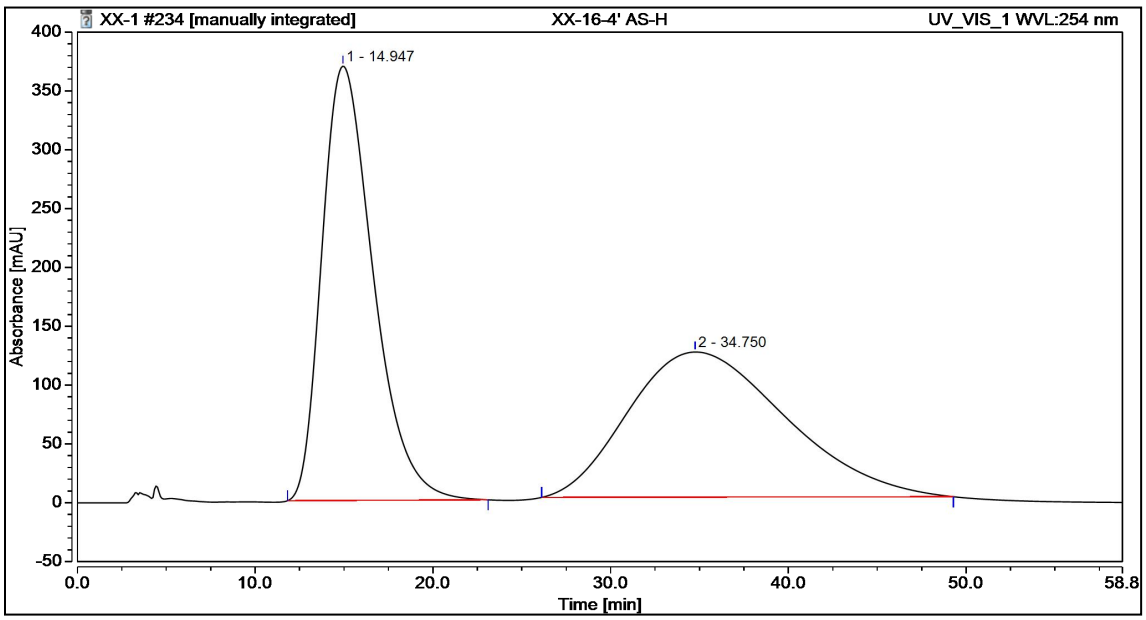
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.188	749.897	259.956	98.90	99.58	n.a.
2		30.987	8.342	1.107	1.10	0.42	n.a.
Total:			**758.239**	**261.063**	**100.00**	**100.00**	



3k

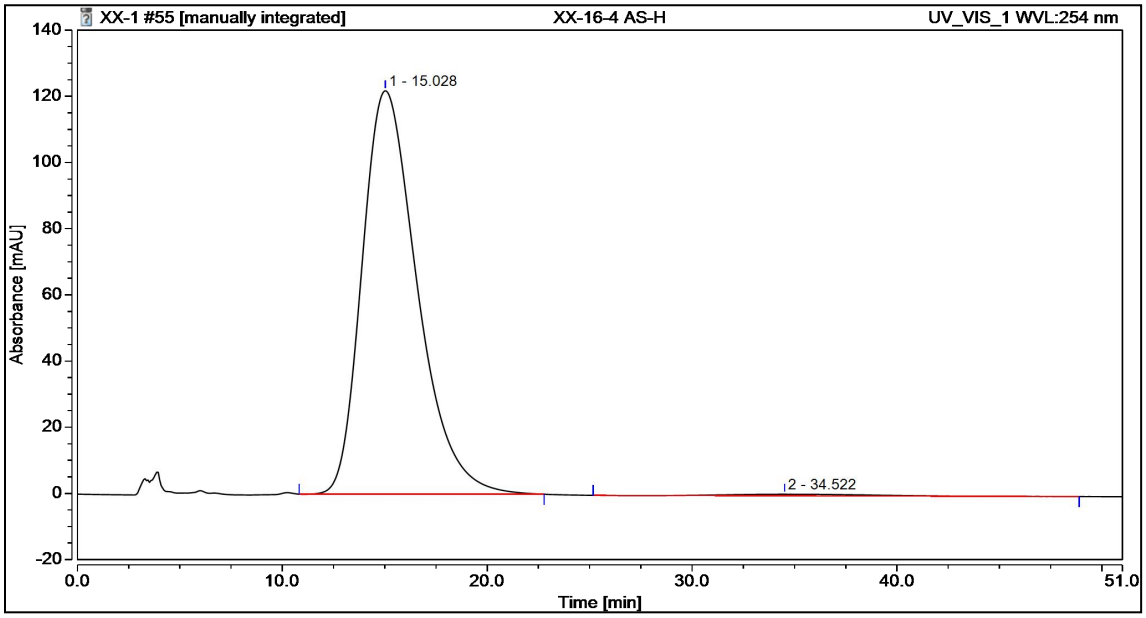
White solid, 35.8 mg, 57% yield, 98% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 70/30, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 15.03 min, t (minor) = 34.52 min]. $[\alpha]_D^{20}$ = - 64.2°(c = 0.9, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 2H), 7.13 – 7.08 (m, 2H), 6.94 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.43 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.75 (d, *J* = 12.5 Hz, 2H), 4.62 (d, *J* = 12.6 Hz, 2H), 3.73 (s, 3H), 2.47 (s, 3H), 1.89 (s, 3H), 1.70 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.78, 143.82, 139.89, 139.74, 135.91, 135.78, 135.69, 135.35, 130.69, 130.59, 129.97, 129.53, 129.16, 128.81, 128.10, 127.66, 125.84, 125.56, 122.61, 121.22, 121.09, 111.21, 110.82,

53.92, 53.70, 51.57, 21.56, 16.93, 14.04. **HRMS (ESI, m/z)** Calcd for $C_{33}H_{29}BrN_2O_4S$ $(M+H)^+$: 629.1104; Found: 629.1106.



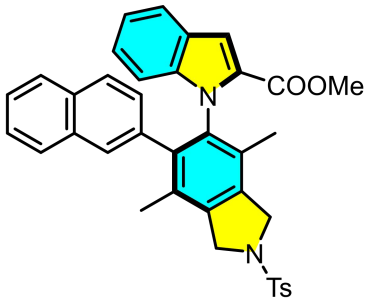
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.947	1235.135	369.191	49.37	74.95	n.a.
2		34.750	1266.617	123.360	50.63	25.05	n.a.
Total:			**2501.752**	**492.551**	**100.00**	**100.00**	



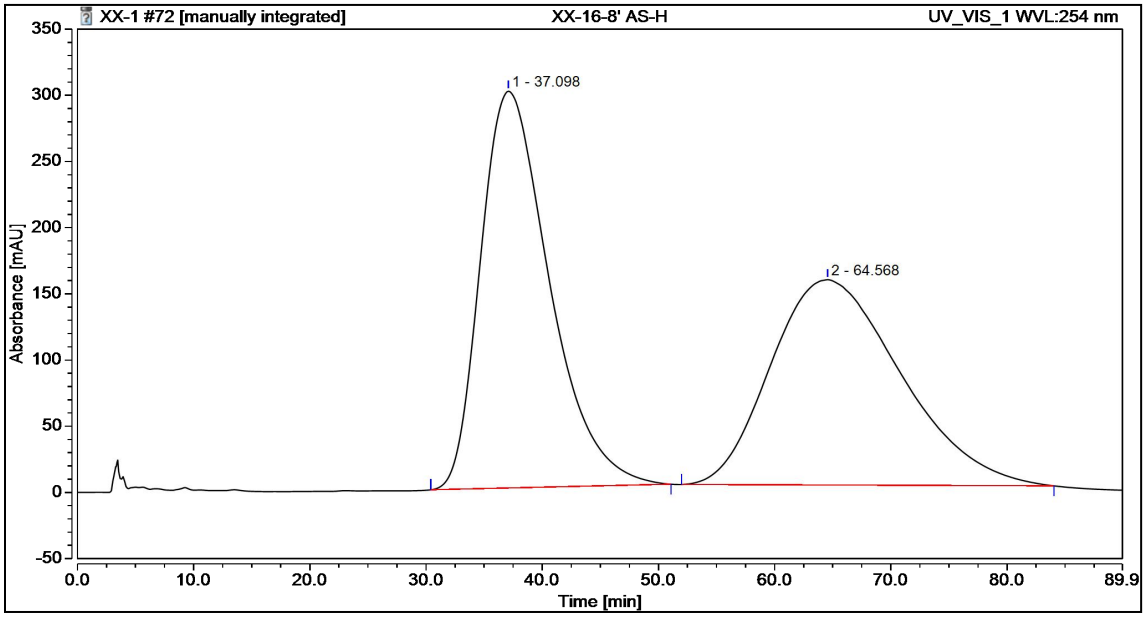
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.028	380.009	121.924	98.99	99.60	n.a.
2		34.522	3.869	0.491	1.01	0.40	n.a.
Total:			**383.878**	**122.414**	**100.00**	**100.00**	



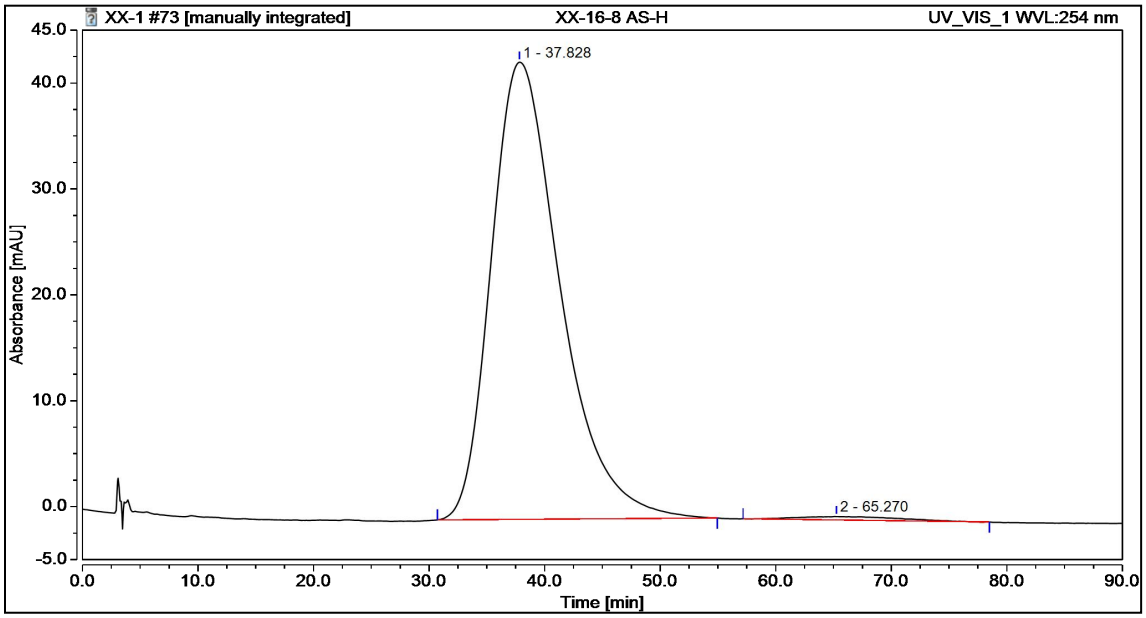
3l

White solid, 43.2 mg, 72% yield, 98% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak AS-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 90/10, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 37.83 min, t (minor) = 65.27 min]. $[\alpha]_D^{20}$ = - 80.8°(c = 1.6, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 7.9 Hz, 2H), 7.68 – 7.56 (m, 2H), 7.51 – 7.15 (m, 8H), 7.10 – 6.87 (m, 4H), 4.84 – 4.62 (m, 4H), 3.71 (d, *J* = 6.7 Hz, 3H), 2.45 (s, 3H), 1.91 (s, 3H), 1.77 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.90, 161.77, 143.83, 135.66, 133.91, 130.00, 128.14, 127.69, 127.66, 127.61, 127.38, 127.16, 126.99, 126.94, 126.76, 126.05, 125.87, 125.74, 125.71, 125.69, 125.45, 125.42, 122.46, 120.97, 120.92, 111.50, 111.34, 110.63, 110.47, 53.80, 51.44, 26.94, 21.60, 17.06, 14.19. **HRMS (ESI, m/z)** Calcd for $C_{37}H_{32}N_2O_4S$ $(M+H)^+$: 601.2156; Found: 601.2170.



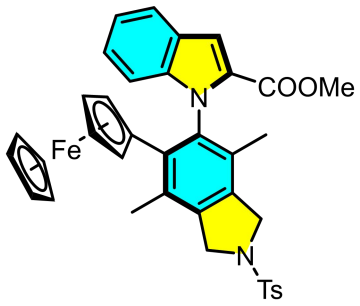
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		37.098	2058.129	299.779	50.61	65.90	n.a.
2		64.568	2008.827	155.127	49.39	34.10	n.a.
Total:			**4066.956**	**454.906**	**100.00**	**100.00**	



Integration Results

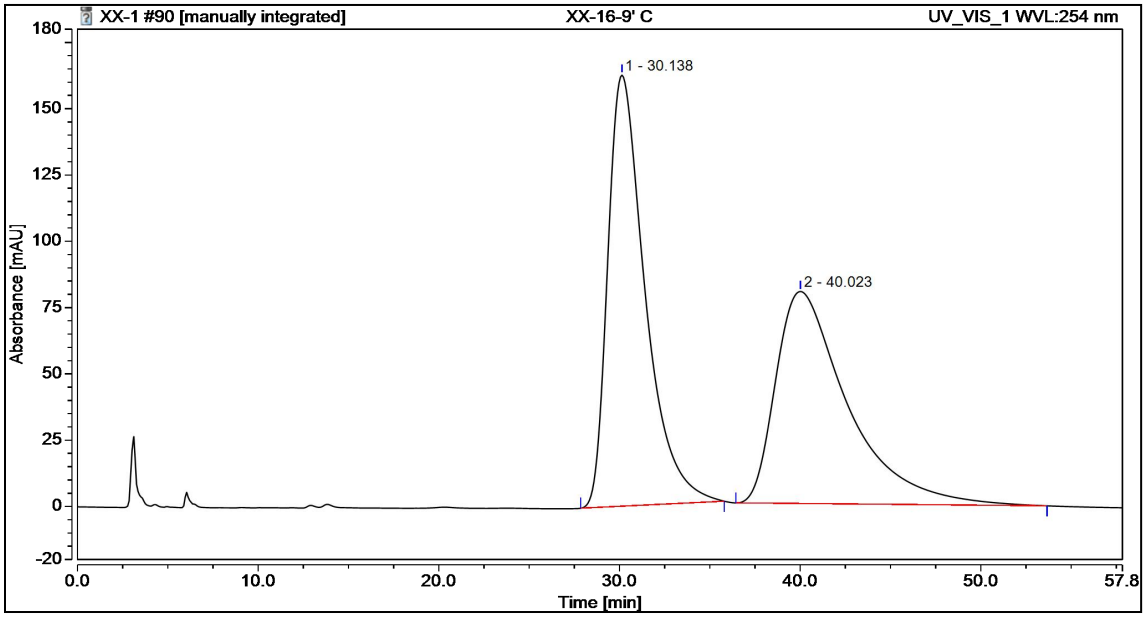
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		37.828	298.598	43.182	98.87	99.24	n.a.
2		65.270	3.398	0.332	1.13	0.76	n.a.
Total:			**301.996**	**43.515**	**100.00**	**100.00**	



3m

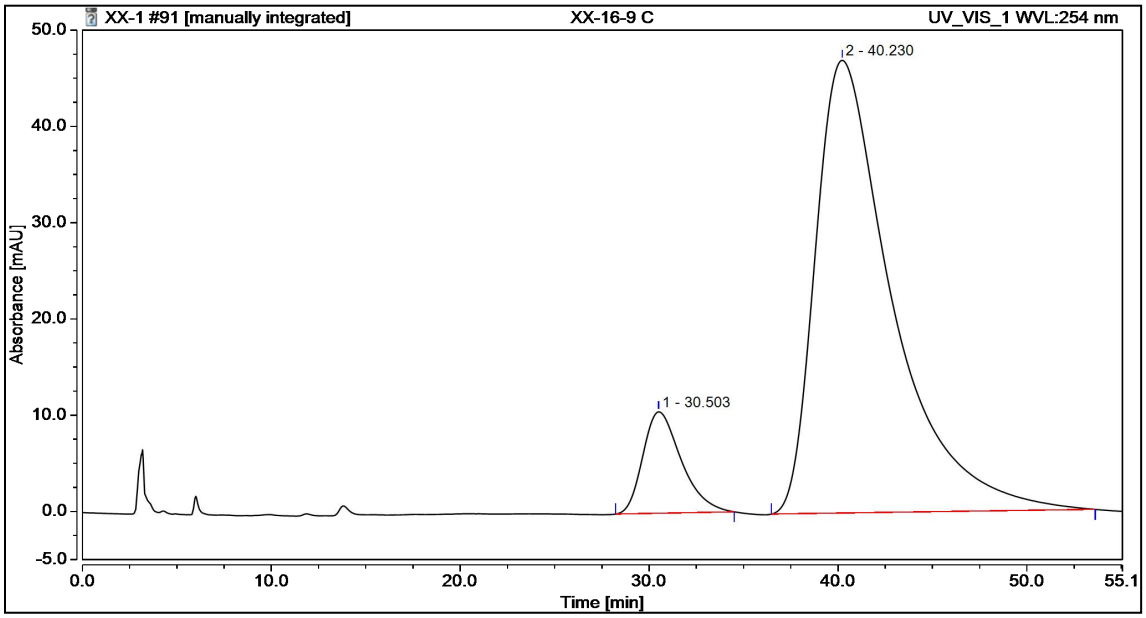
Brown solid, 30.9 mg, 47% yield, 80% ee. [Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; *n*-hexane/2-propanol = 70/30, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 40.23 min, t (minor) = 30.50 min]. $[\alpha]_D^{20}$ = 54.3°(c = 0.8, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 9.4 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 9.3 Hz, 1H), 4.77 (d, *J* = 12.3 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 2H), 4.56 (d, *J* = 15.1 Hz, 1H), 4.00 (s, 6H), 3.84 (d, *J* = 8.7 Hz, 2H), 3.62 (s, 3H), 3.29 (s, 1H), 2.82 (s, 3H), 2.46 (s, 3H), 1.57 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.78, 143.82, 139.89, 139.74, 135.91, 135.78, 135.69, 135.35, 130.69, 130.59, 129.97, 129.53, 129.16, 128.81, 128.10, 127.66, 125.84, 125.56,

122.61, 121.22, 121.09, 111.21, 110.82, 53.92, 53.70, 51.57, 21.56, 16.93, 14.04. **HRMS (ESI, m/z)** Calcd for $C_{37}H_{34}FeN_2O_4S$ $(M+H)^+$: 659.1661; Found: 659.1661.



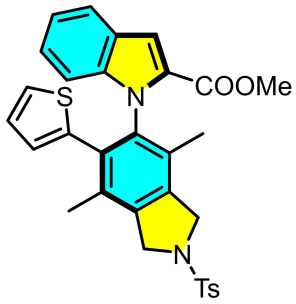
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.138	388.759	162.575	51.39	67.03	n.a.
2		40.023	367.720	79.961	48.61	32.97	n.a.
Total:			**756.480**	**242.535**	**100.00**	**100.00**	



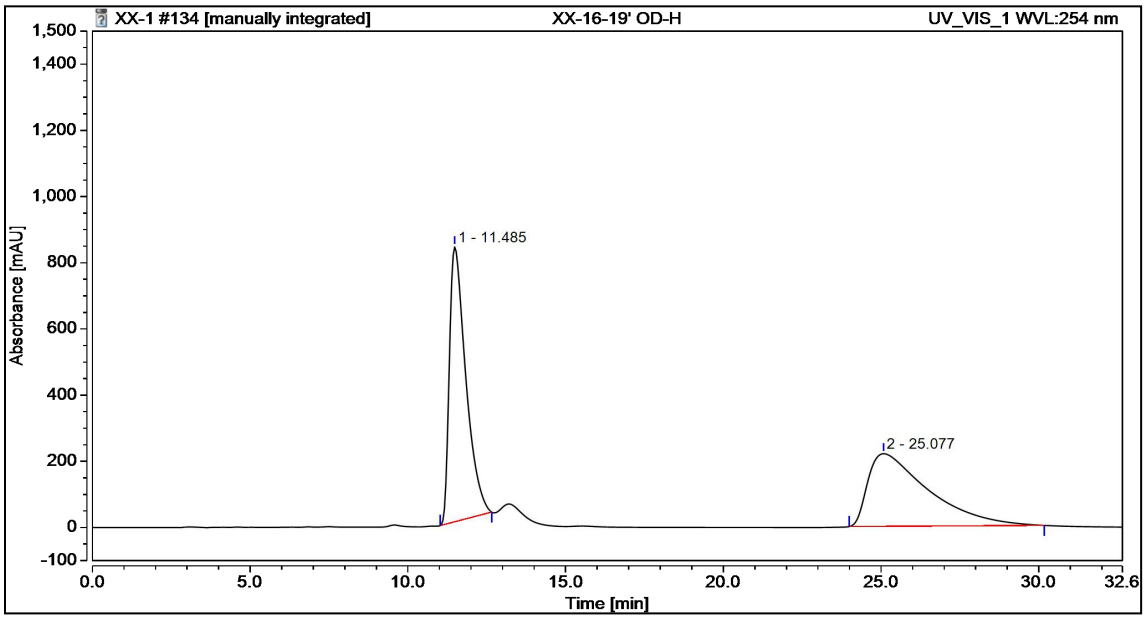
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.503	24.859	10.548	10.08	18.32	n.a.
2		40.230	221.674	47.034	89.92	81.68	n.a.
Total:			**246.533**	**57.582**	**100.00**	**100.00**	

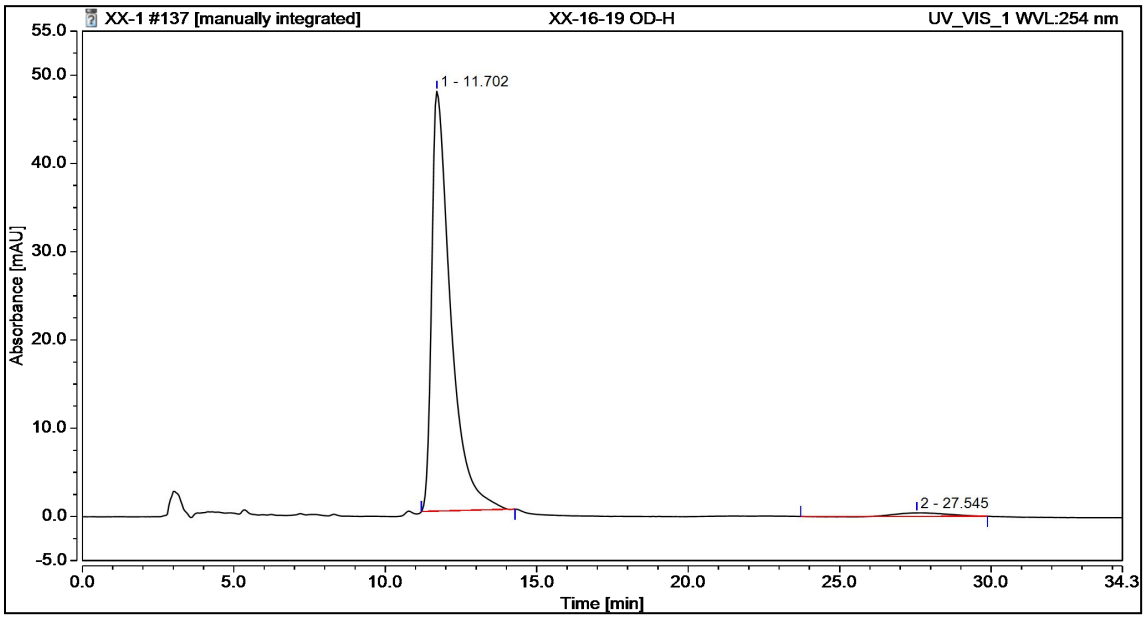


3n

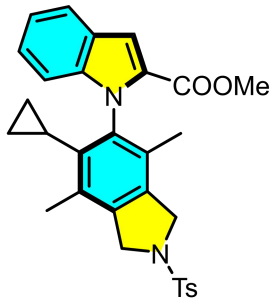
White solid, 47.2 mg, 85% yield, 96% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 90/10, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 11.70 min, t (minor) = 27.55 min]. $[\alpha]_D^{20}$ = - 19.4°(c = 0.35, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.14 (s, 1H), 7.11 (dd, *J* = 8.5, 6.5 Hz, 1H), 6.99 (d, *J* = 5.1 Hz, 1H), 6.83 (d, *J* = 7.4 Hz, 1H), 6.65 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.37 (dd, *J* = 3.5, 1.2 Hz, 1H), 4.78 – 4.61 (m, 4H), 3.74 (s, 3H), 2.46 (s, 3H), 2.01 (s, 3H), 1.74 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.74, 143.84, 139.98, 137.19, 136.62, 136.01, 135.65, 133.92, 133.78, 131.28, 129.99, 128.92, 128.62, 127.64, 126.92, 126.08, 125.92, 125.63, 125.41, 122.46, 121.04, 111.38, 110.45, 53.95, 53.75, 51.58, 21.56, 17.08, 14.19. **HRMS (ESI, m/z)** Calcd for $C_{31}H_{28}N_2O_4S_2$ $(M+H)^+$: 557.1563; Found: 557.1565.



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.485	502.779	830.884	50.80	79.09	n.a.
2		25.077	487.036	219.620	49.20	20.91	n.a.
Total:			**989.815**	**1050.504**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.702	34.469	47.588	97.94	99.17	n.a.
2		27.545	0.726	0.399	2.06	0.83	n.a.
Total:			**35.195**	**47.987**	**100.00**	**100.00**	

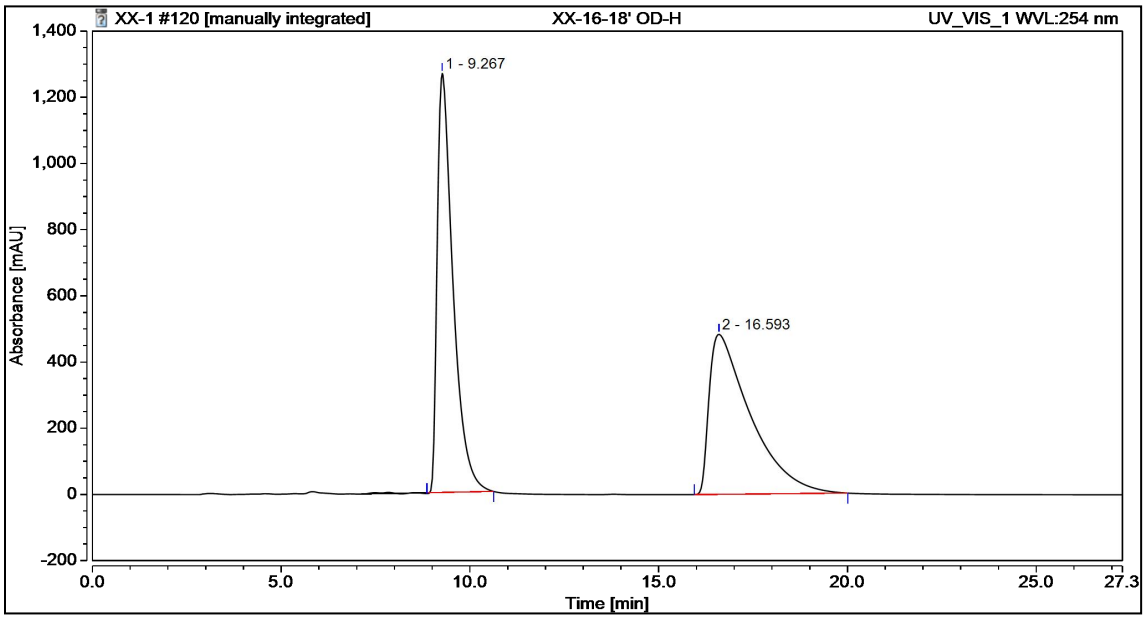


3o

White solid, 44.2 mg, 86% yield, 80% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 90/10, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 9.27 min, t (minor) = 17.65 min]. $[\alpha]_D^{20}$ = 34.0°(c = 1.9, $CHCl_3$).**^{1}H NMR (500 MHz, $CDCl_3$)** ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.43 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 4.75 – 4.51 (m, 4H), 3.76 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H), 1.62 (s, 3H).

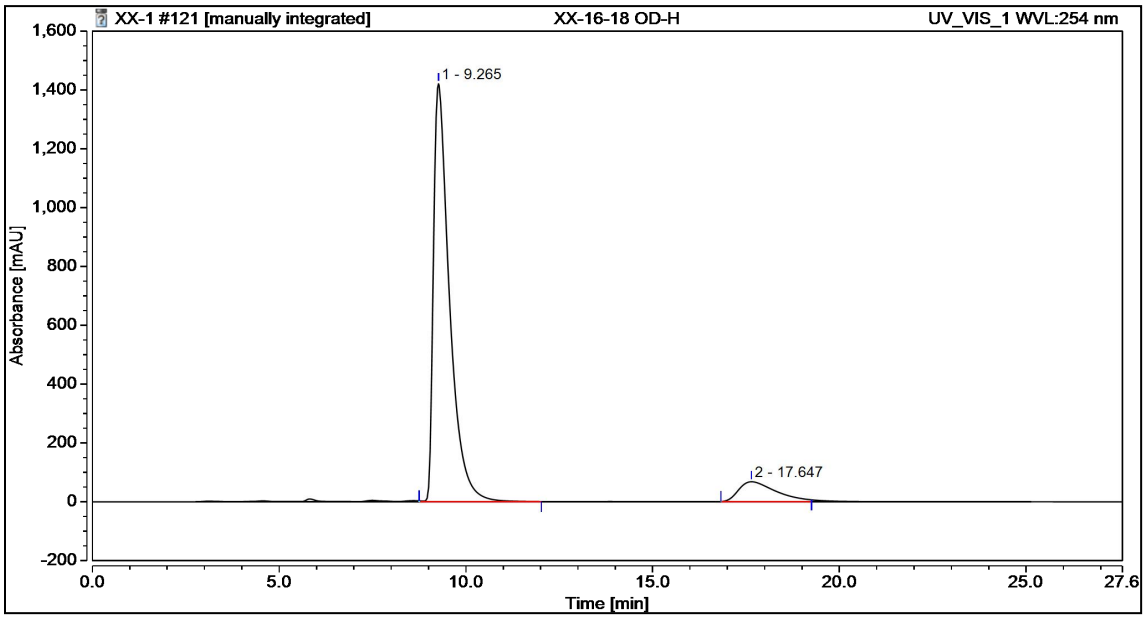
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.78, 143.70, 139.59, 138.20, 137.69, 135.43, 134.03, 133.85, 131.85, 129.91, 128.51, 128.47, 127.62, 126.02, 125.58, 122.60, 121.04, 111.37, 110.63, 53.97, 53.70, 51.63, 21.53, 16.56, 13.92, 10.98, 5.92, 5.47.

HRMS (ESI, m/z) Calcd for $C_{30}H_{30}N_2O_4S$ $(M+H)^+$: 515.1999; Found: 515.2001.



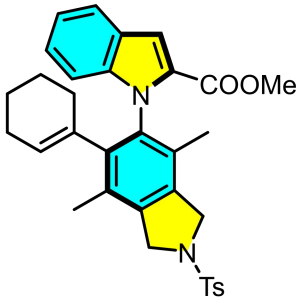
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.267	613.566	1266.254	50.05	72.35	n.a.
2		16.593	612.219	483.866	49.95	27.65	n.a.
Total:			**1225.785**	**1750.120**	**100.00**	**100.00**	



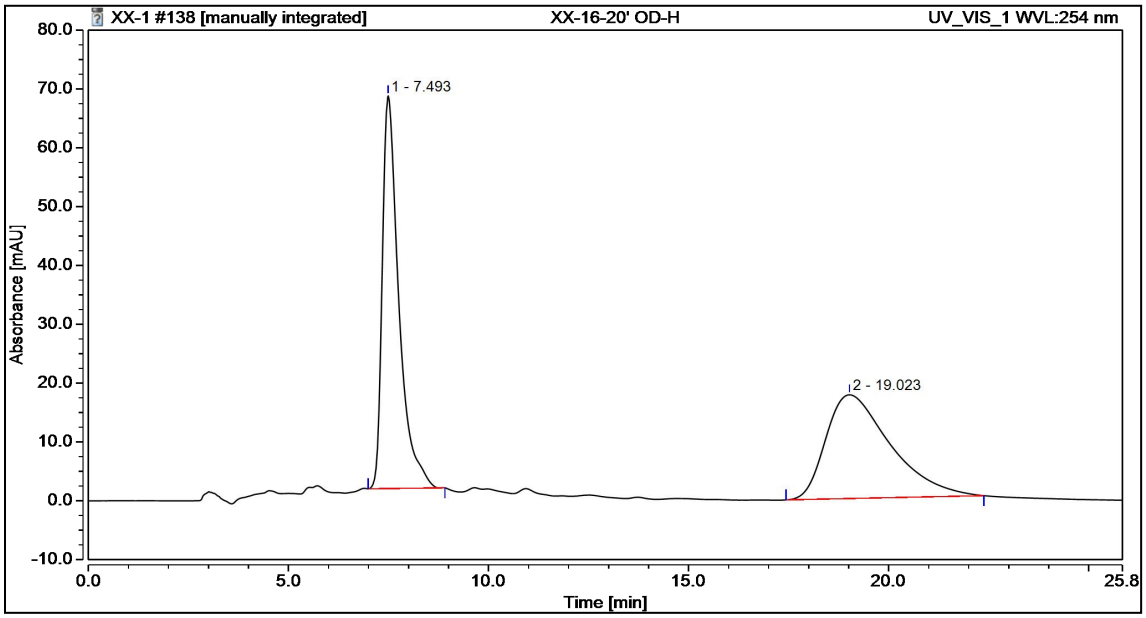
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.265	707.902	1421.252	89.87	95.42	n.a.
2		17.647	79.778	68.279	10.13	4.58	n.a.
Total:			**787.680**	**1489.531**	**100.00**	**100.00**	

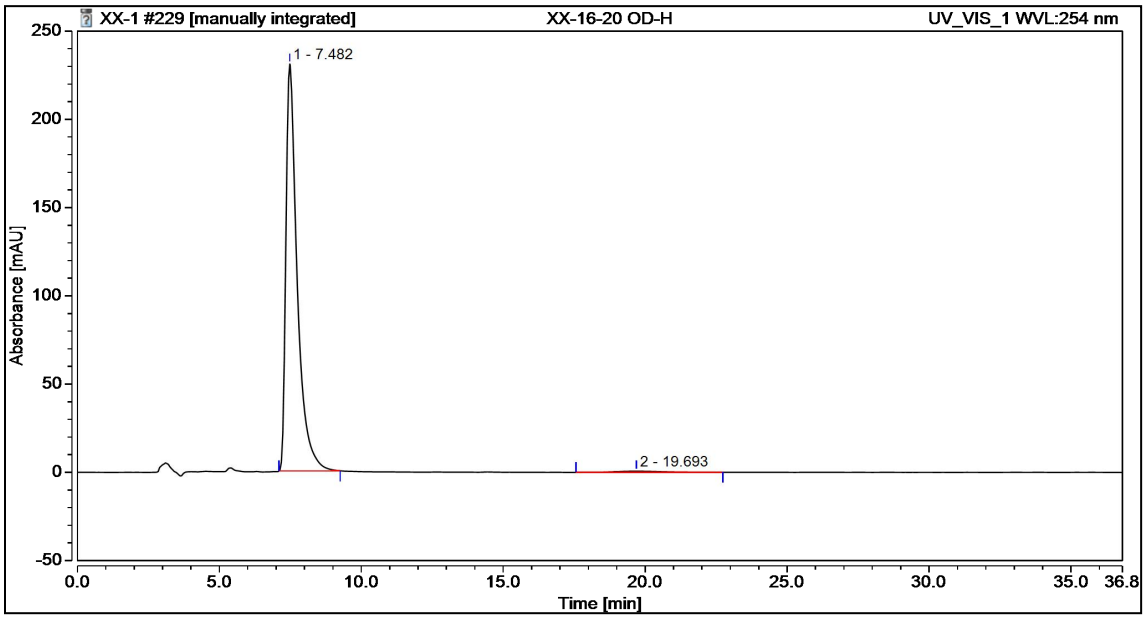


3p

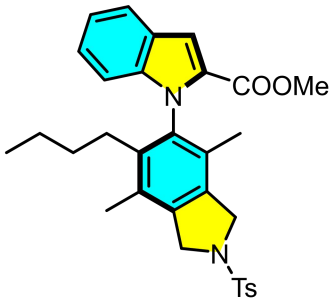
White solid, 18.8 mg, 34% yield, 98% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 90/10, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 7.48 min, t (minor) = 19.69 min]. $[\alpha]_D^{20}$ = 25.4°(c = 0.8, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.83 (dd, *J* = 8.3, 2.2 Hz, 2H), 7.68 (t, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.26 (s, 1H), 7.23 – 7.18 (m, 1H), 7.16 – 7.11 (m, 1H), 6.76 (d, *J* = 7.2 Hz, 1H), 5.06 (d, *J* = 132.0 Hz, 1H), 4.75 – 4.55 (m, 4H), 3.74 (d, *J* = 7.3 Hz, 3H), 2.46 (s, 3H), 2.06 (d, *J* = 7.9 Hz, 3H), 1.77 (s, 3H), 1.71 (s, 2H), 1.54 (s, 2H), 1.26 (s, 2H), 1.00 – 0.80 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$** δ 161.96, 143.74, 142.97, 140.64, 139.75, 135.41, 134.42, 133.82, 129.98, 129.95, 128.54, 127.66, 127.14, 126.58, 125.93, 125.22, 122.41, 120.94, 112.11, 111.43, 110.64, 109.81, 53.99, 53.69, 51.57, 28.96, 25.15, 22.29, 21.57, 16.24, 14.24. **HRMS (ESI, m/z)** Calcd for $C_{33}H_{34}N_2O_4S$ $(M+H)^+$: 555.2312; Found: 555.2326.



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.493	32.011	66.749	49.32	79.10	n.a.
2		19.023	32.896	17.636	50.68	20.90	n.a.
Total:			**64.907**	**84.386**	**100.00**	**100.00**	



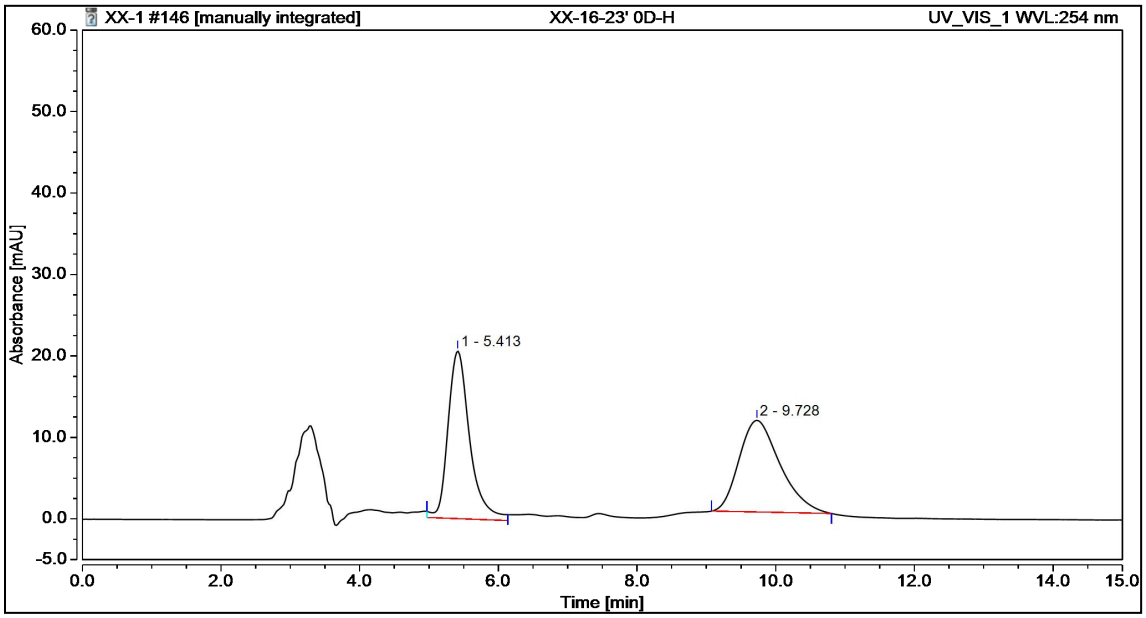
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.482	106.315	230.588	98.79	99.72	n.a.
2		19.693	1.305	0.652	1.21	0.28	n.a.
Total:			**107.620**	**231.240**	**100.00**	**100.00**	



3q

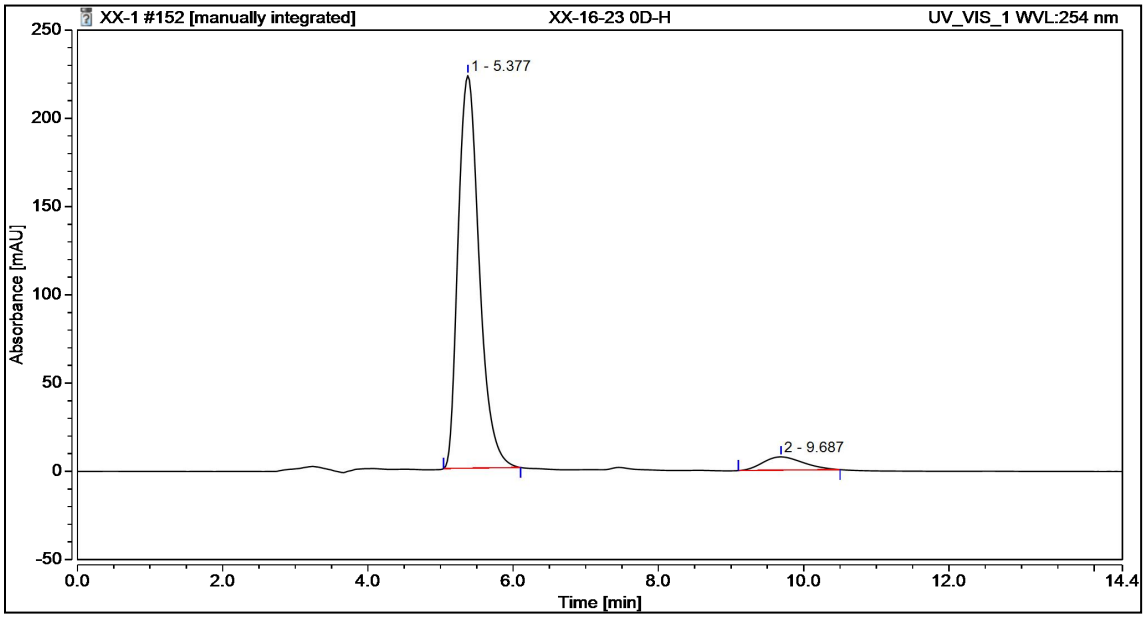
White solid, 14.3 mg, 27% yield, 88% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 80/20, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 5.38 min, t (minor) = 9.69 min]. $[\alpha]_D^{20}$ = 20.8°(c = 1.8, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.43 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.14 (m, 2H), 6.73 (d, *J* = 7.2 Hz, 1H), 4.74 – 4.64 (m, 2H), 4.58 (dd, *J* = 22.6, 14.0 Hz, 2H), 3.75 (s, 3H), 2.42 (s, 3H), 2.17 (s, 3H), 2.09 – 2.03 (m, 1H), 1.97 – 1.90 (m, 1H), 1.59 (s, 3H), 1.12

– 1.03 (m, 2H), 0.97 (dt, J = 14.6, 6.9 Hz, 2H), 0.54 (d, J = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.61, 143.71, 139.84, 139.81, 135.96, 135.78, 133.98, 133.11, 129.93, 129.02, 128.98, 128.30, 127.64, 126.05, 125.58, 122.54, 121.24, 111.44, 110.81, 54.06, 53.63, 51.64, 31.72, 26.93, 22.80, 21.56, 15.82, 13.99, 13.40. **HRMS (ESI, m/z)** Calcd for $C_{31}H_{34}N_2O_4S$ $(M+H)^+$: 531.2312; Found: 531.2319.

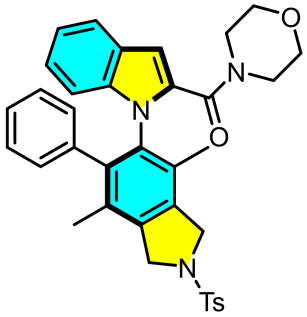


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.413	7.485	20.579	49.25	64.65	n.a.
2		9.728	7.713	11.251	50.75	35.35	n.a.
Total:			**15.198**	**31.830**	**100.00**	**100.00**	

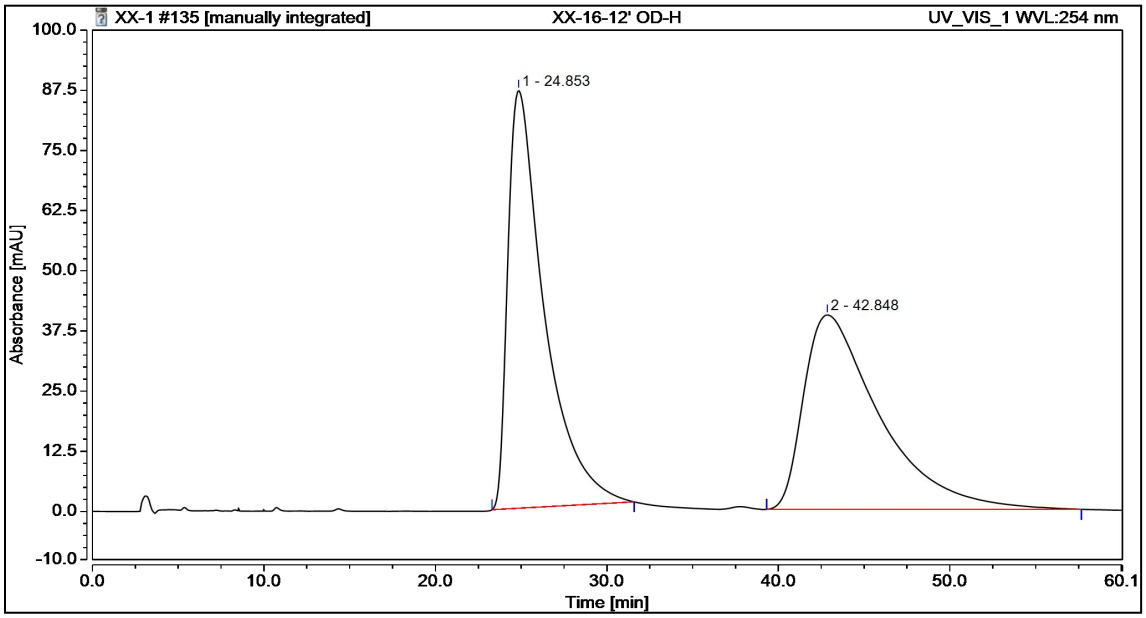


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.377	74.917	222.535	93.92	96.73	n.a.
2		9.687	4.849	7.525	6.08	3.27	n.a.
Total:			**79.766**	**230.059**	**100.00**	**100.00**	



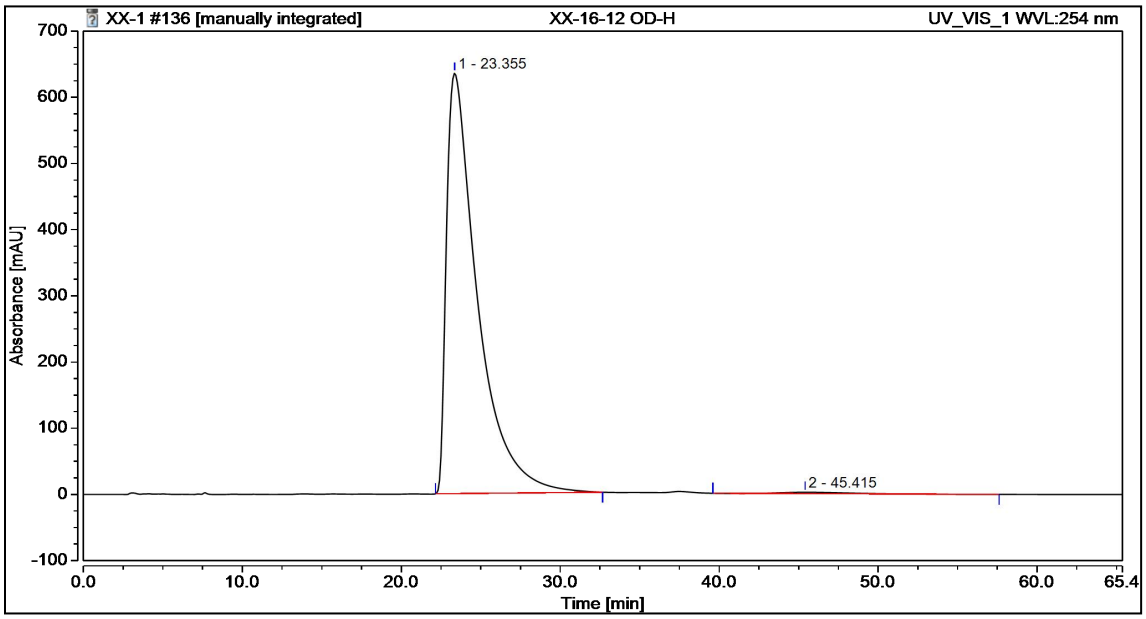
3r

White solid, 48.4 mg, 80% yield, 99% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 90/10, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 23.36 min, t (minor) = 45.42 min]. $[\alpha]_D^{20}$ = - 124.1°(c = 0.9, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.15 – 7.10 (m, 1H), 7.07 – 7.01 (m, 2H), 6.90 (d, *J* = 9.2 Hz, 1H), 6.82 (t, *J* = 8.3 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.43 (s, 1H), 4.77 (td, *J* = 12.7, 2.8 Hz, 2H), 4.61 (dd, *J* = 21.7, 14.6 Hz, 2H), 3.79 – 3.24 (m, 8H), 2.47 (s, 3H), 1.89 (s, 3H), 1.80 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.07, 143.81, 140.19, 138.88, 137.28, 135.70, 135.34, 135.00, 133.90, 130.34, 129.98, 129.92, 129.15, 129.03, 127.93, 127.84, 127.65, 127.49, 126.94, 125.52, 124.45, 121.65, 120.78, 111.11, 105.83, 66.81, 54.01, 53.76, 21.58, 17.11, 14.66. **HRMS (ESI, m/z)** Calcd for $C_{36}H_{35}N_3O_4S$ $(M+H)^+$: 606.2421; Found: 606.2428.



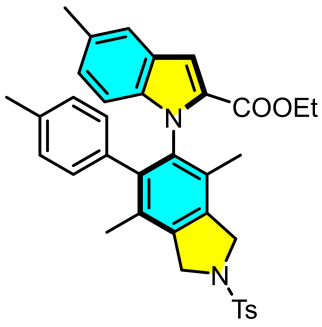
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.853	214.024	86.803	50.81	68.25	n.a.
2		42.848	207.207	40.388	49.19	31.75	n.a.
Total:			**421.231**	**127.191**	**100.00**	**100.00**	



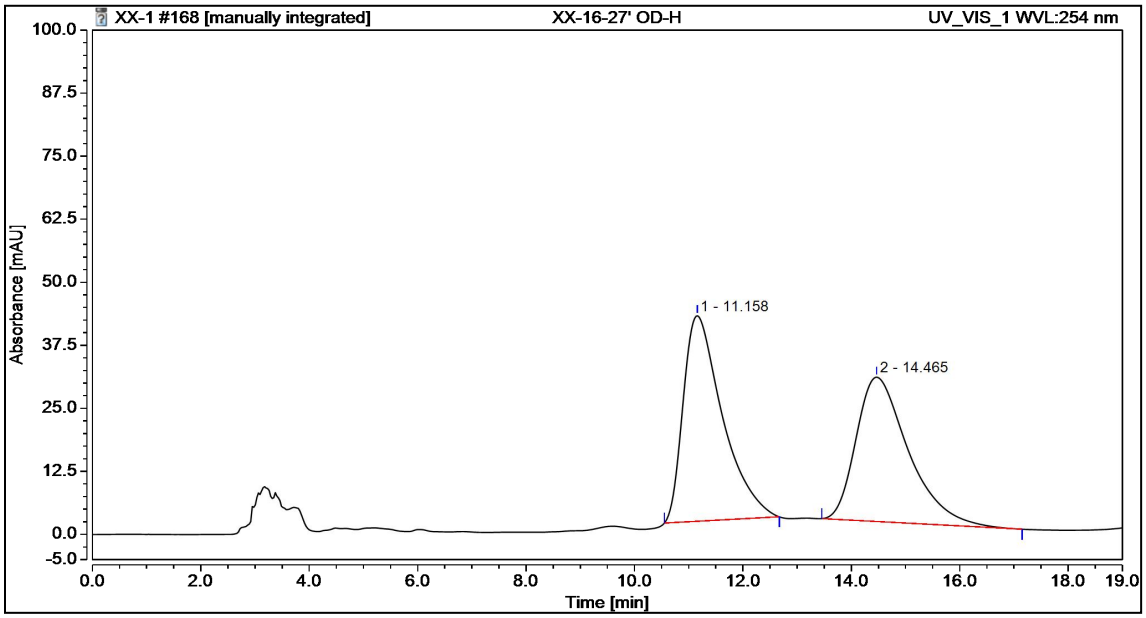
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.355	1432.948	635.384	99.38	99.68	n.a.
2		45.415	8.908	2.023	0.62	0.32	n.a.
Total:			**1441.856**	**637.406**	**100.00**	**100.00**	

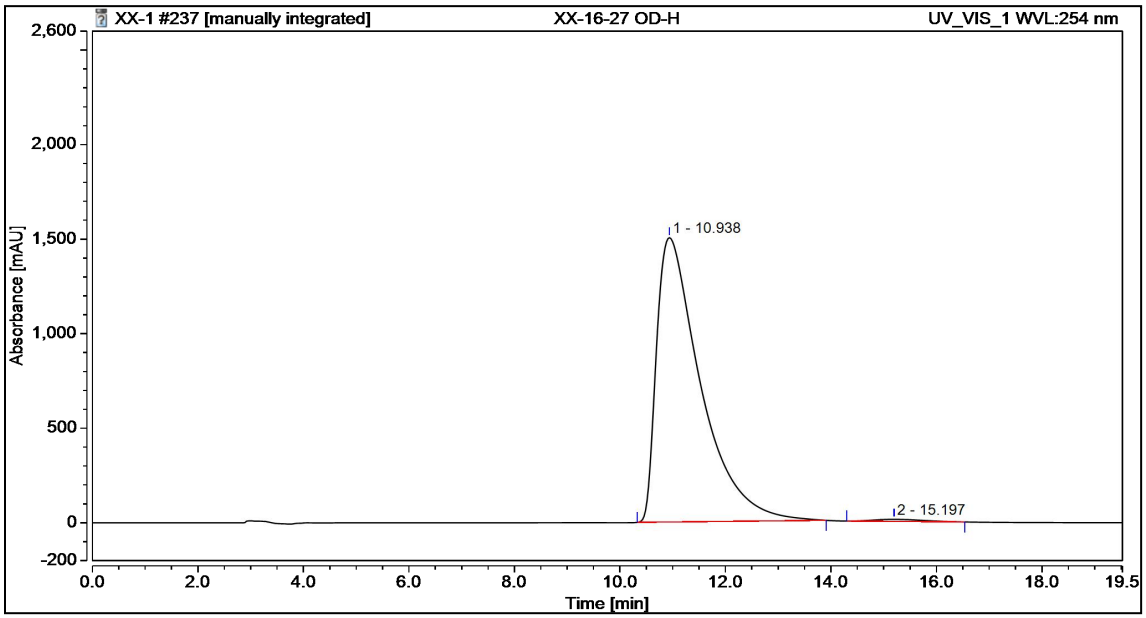


3s

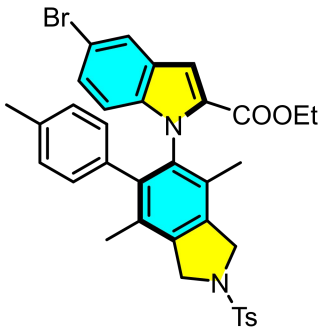
White solid, 34.3 mg, 58% yield, 98% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 95/5, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 10.94 min, t (minor) = 15.20 min]. $[\alpha]_D^{20}$ = - 42.7°(c = 0.4, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.31 (s, 1H), 7.26 (s, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.90 (d, *J* = 9.7 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.42 (d, *J* = 9.8 Hz, 1H), 4.77 – 4.59 (m, 4H), 4.24 – 4.08 (m, 2H), 2.47 (s, 3H), 2.40 (s, 3H), 2.15 (s, 3H), 1.89 (s, 3H), 1.70 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.39, 143.76, 141.12, 138.30, 136.33, 136.13, 135.33, 134.58, 133.92, 130.05, 129.95, 129.33, 128.79, 128.60, 128.50, 128.14, 127.66, 127.59, 127.18, 126.02, 121.63, 111.09, 109.65, 60.24, 54.00, 53.74, 21.58, 21.39, 21.11, 17.00, 14.26, 14.11. **HRMS (ESI, m/z)** Calcd for $C_{36}H_{36}N_2O_4S$ $(M+H)^+$:593.2468; Found: 593.2482.



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.158	34.158	40.771	51.68	58.74	n.a.
2		14.465	31.941	28.635	48.32	41.26	n.a.
Total:			**66.099**	**69.406**	**100.00**	**100.00**	



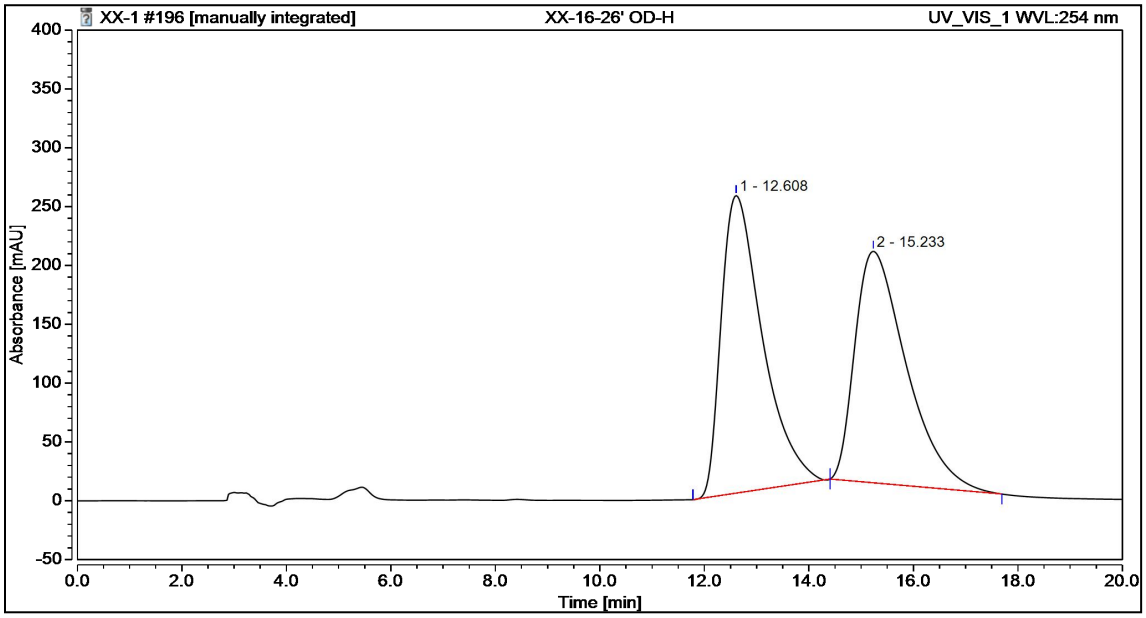
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.938	1452.155	1503.897	99.18	99.27	n.a.
2		15.197	12.060	11.001	0.82	0.73	n.a.
Total:			**1464.215**	**1514.898**	**100.00**	**100.00**	



3t

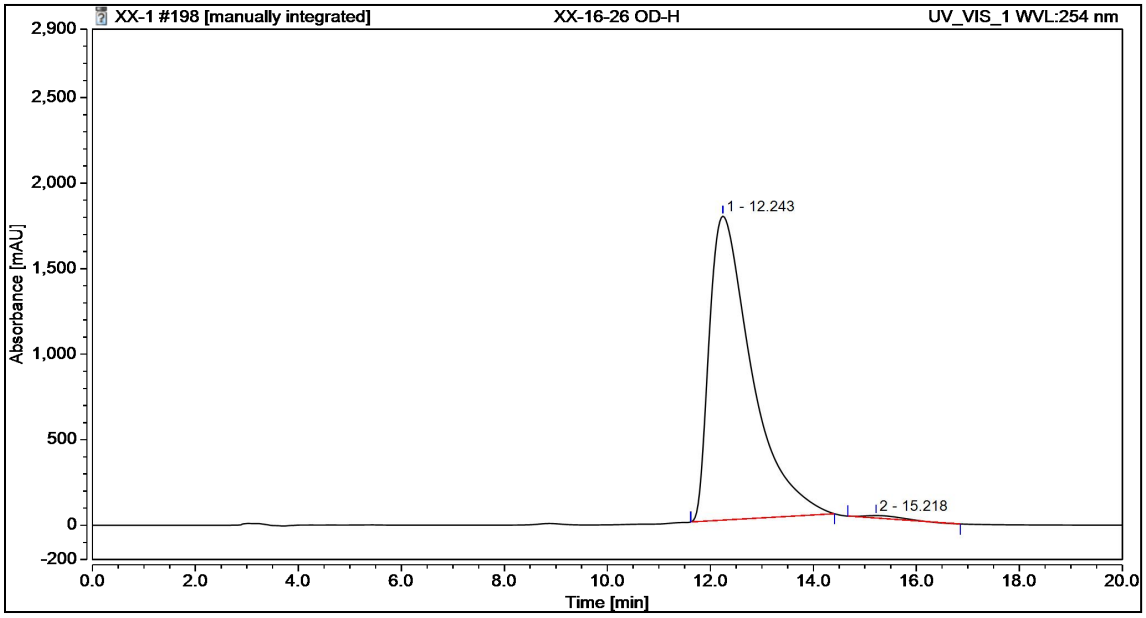
White solid, 45.9 mg, 70% yield, 99% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 95/5, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 12.24 min, t (minor) = 15.22 min]. $[\alpha]_D^{20}$ = - 67.0°(c = 1.2, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.28 (dd, *J* = 8.8, 1.9 Hz, 1H), 6.99 (s, 1H), 6.90 (d, *J* = 9.8 Hz, 1H), 6.76 (dd, *J* = 17.7, 8.3 Hz, 2H), 6.65 (d, *J* = 9.6 Hz, 1H), 6.39 (d, *J* = 9.7 Hz, 1H), 4.68 (dd, *J* = 49.2, 12.1 Hz, 4H), 4.18 (ddd, *J* = 39.5, 10.8,

7.1 Hz, 2H), 2.46 (s, 3H), 2.15 (s, 3H), 1.89 (s, 3H), 1.70 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.99, 143.81, 141.01, 138.21, 136.60, 135.78, 135.50, 134.77, 133.89, 133.63, 129.97, 129.75, 129.59, 128.60, 128.35, 128.29, 128.13, 127.66, 127.51, 127.25, 124.67, 114.00, 112.96, 109.27, 53.97, 53.69, 26.93, 16.99, 14.23, 14.14, 14.09. **HRMS (ESI, m/z)** Calcd for $C_{35}H_{33}BrN_2O_4S$ $(M+H)^+$: 657.1417; Found: 657.1411.

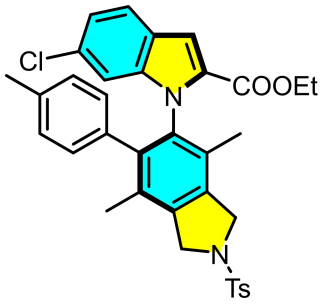


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.608	231.054	252.939	50.68	56.25	n.a.
2		15.233	224.865	196.762	49.32	43.75	n.a.
Total:			**455.918**	**449.701**	**100.00**	**100.00**	

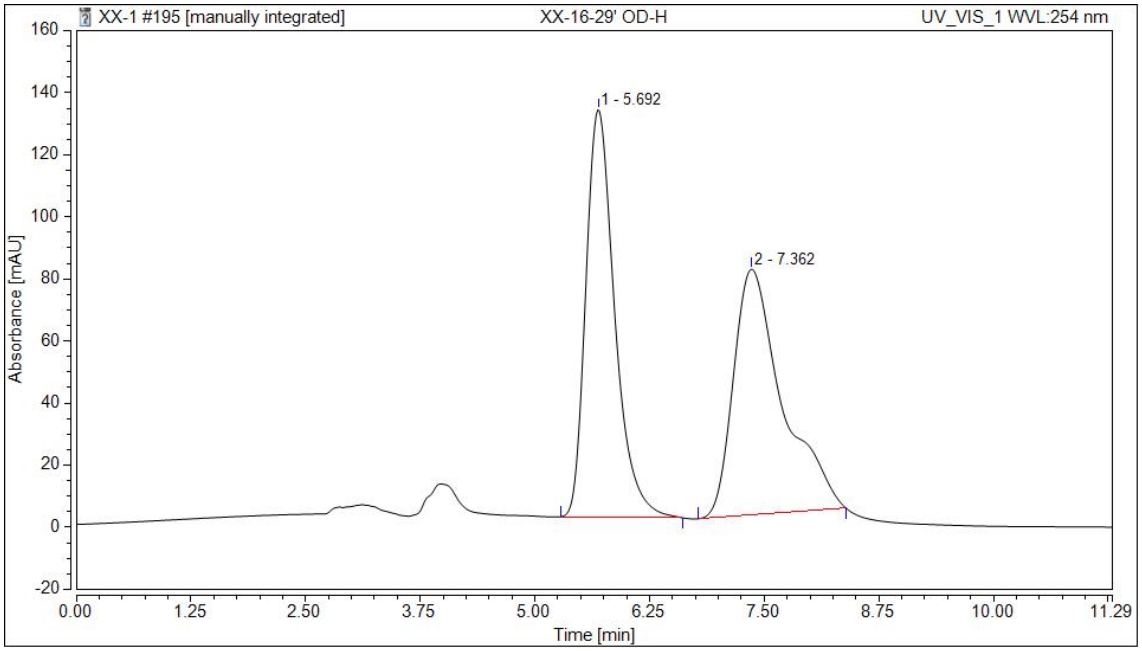


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.243	1697.168	1776.961	99.26	99.18	n.a.
2		15.218	12.680	14.760	0.74	0.82	n.a.
Total:			**1709.848**	**1791.721**	**100.00**	**100.00**	



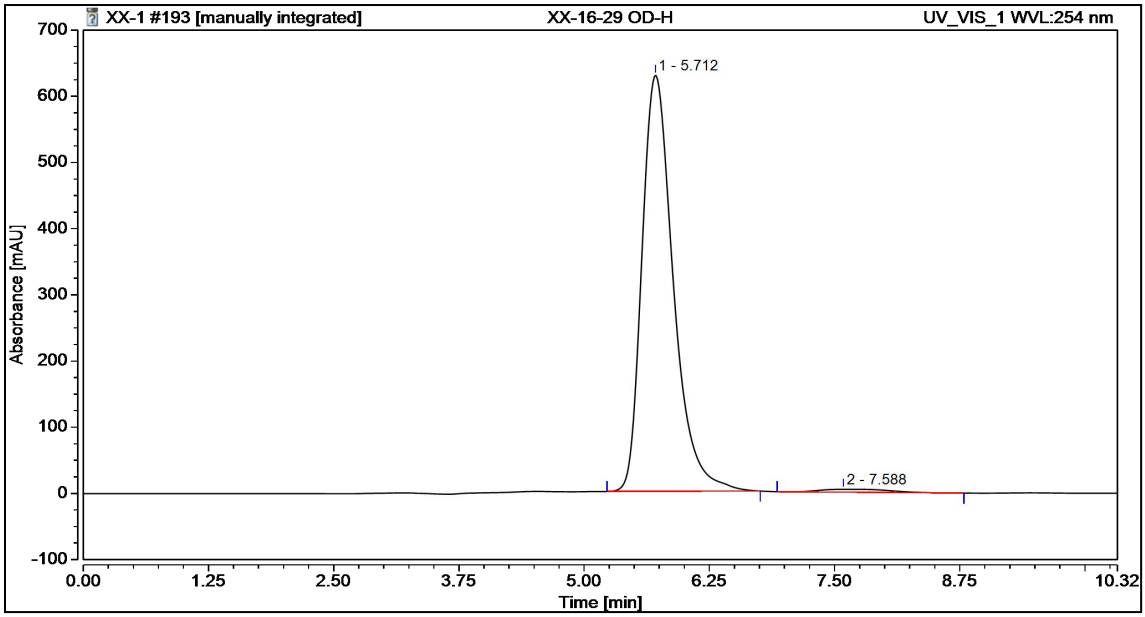
3u

White solid, 45.3 mg, 74% yield, 97% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 80/20, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 5.71 min, t (minor) = 7.59 min]. $[\alpha]_D^{20}$ = -85.0°(c = 2.0, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 6.9 Hz, 2H), 6.90 (d, *J* = 9.8 Hz, 1H), 6.84 (s, 1H), 6.78 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.43 (d, *J* = 9.7 Hz, 1H), 4.78 – 4.63 (m, 4H), 4.18 (ddq, *J* = 40.8, 10.8, 7.1 Hz, 2H), 2.46 (s, 3H), 2.15 (s, 3H), 1.90 (s, 3H), 1.73 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.03, 143.81, 140.98, 139.98, 136.56, 135.82, 135.45, 134.82, 133.90, 133.67, 131.26, 129.99, 129.61, 129.59, 128.64, 128.36, 128.27, 128.23, 127.65, 127.57, 124.27, 123.32, 121.87, 111.10, 110.14, 60.51, 53.99, 53.73, 21.59, 21.09, 16.98, 14.23. **HRMS (ESI, m/z)** Calcd for $C_{35}H_{33}ClN_2O_4S$ $(M+H)^+$: 613.1922; Found: 613.1917.



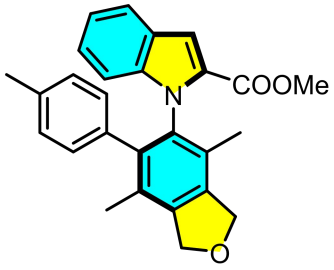
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.692	47.820	131.332	49.51	62.39	n.a.
2		7.362	48.769	79.186	50.49	37.61	n.a.
Total:			**96.589**	**210.519**	**100.00**	**100.00**	



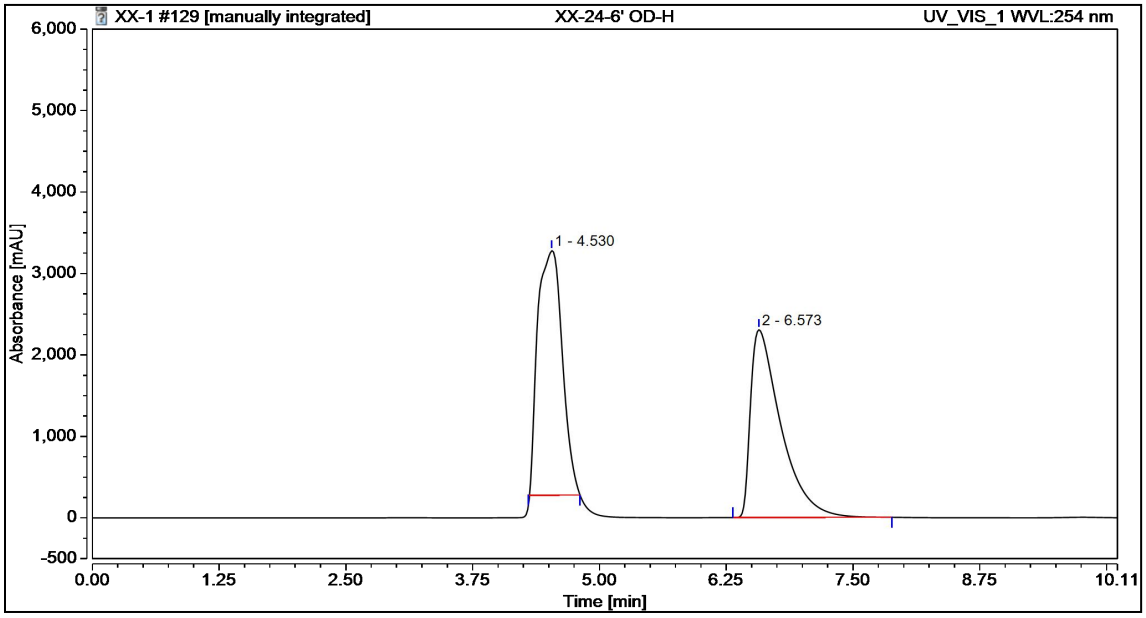
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.712	228.421	628.851	98.43	99.30	n.a.
2		7.588	3.644	4.402	1.57	0.70	n.a.
Total:			**232.065**	**633.253**	**100.00**	**100.00**	



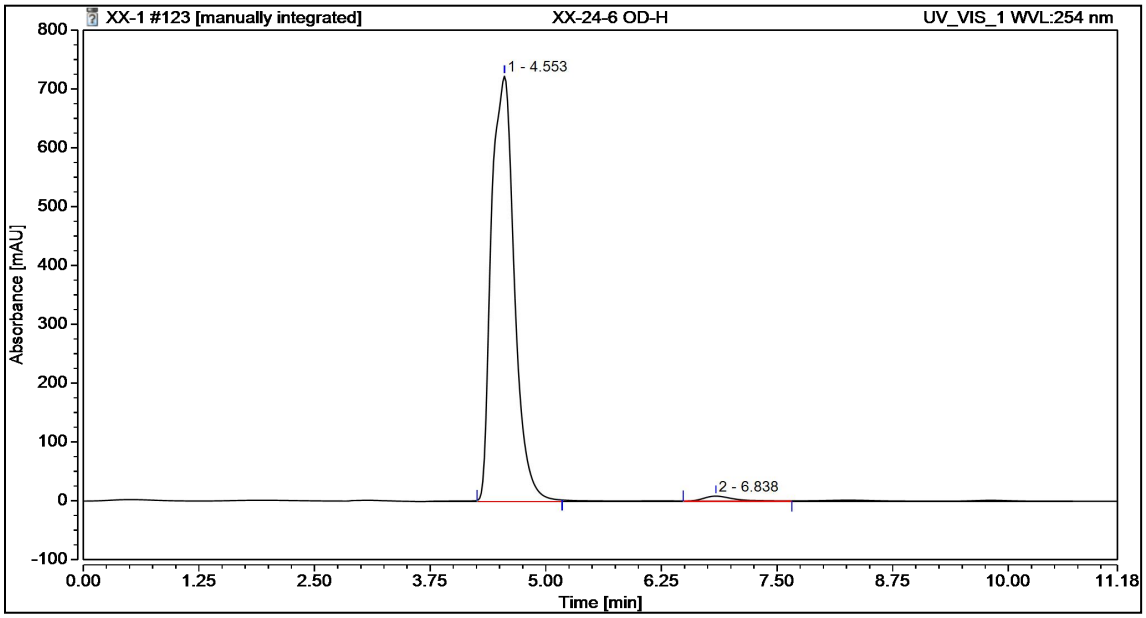
3v

White solid, 24.2 mg, 59% yield, 96% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 90/10, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 4.55 min, t (minor) = 6.84 min]. $[\alpha]_D^{20}$ = -70.5°(c = 1.0, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 9.5 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.96 – 6.91 (m, 2H), 6.88 (s, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.48 (d, *J* = 9.7 Hz, 1H), 5.23 (d, *J* = 2.5 Hz, 4H), 3.76 (s, 3H), 2.15 (s, 3H), 1.93 (s, 3H), 1.75 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.78, 140.65, 139.94, 138.32, 137.54, 136.22, 135.50, 134.20, 128.90, 128.53, 128.12, 128.05, 127.95, 127.80, 127.10, 125.81, 125.16, 122.29, 120.74, 111.65, 110.21, 74.30, 74.02, 51.49, 21.09, 17.11, 14.26. **HRMS (ESI, m/z)** Calcd for $C_{27}H_{25}NO_3$ $(M+H)^+$: 412.1907; Found:412.1919.

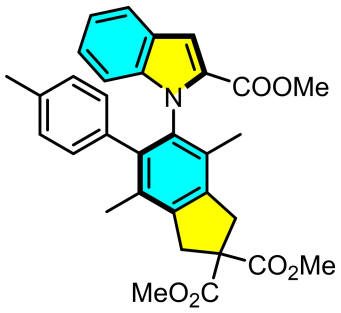


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.530	838.889	3003.432	51.28	56.57	n.a.
2		6.573	797.111	2305.770	48.72	43.43	n.a.
Total:			**1635.999**	**5309.202**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.553	207.343	723.147	98.16	98.76	n.a.
2		6.838	3.887	9.063	1.84	1.24	n.a.
Total:			**211.230**	**732.210**	**100.00**	**100.00**	

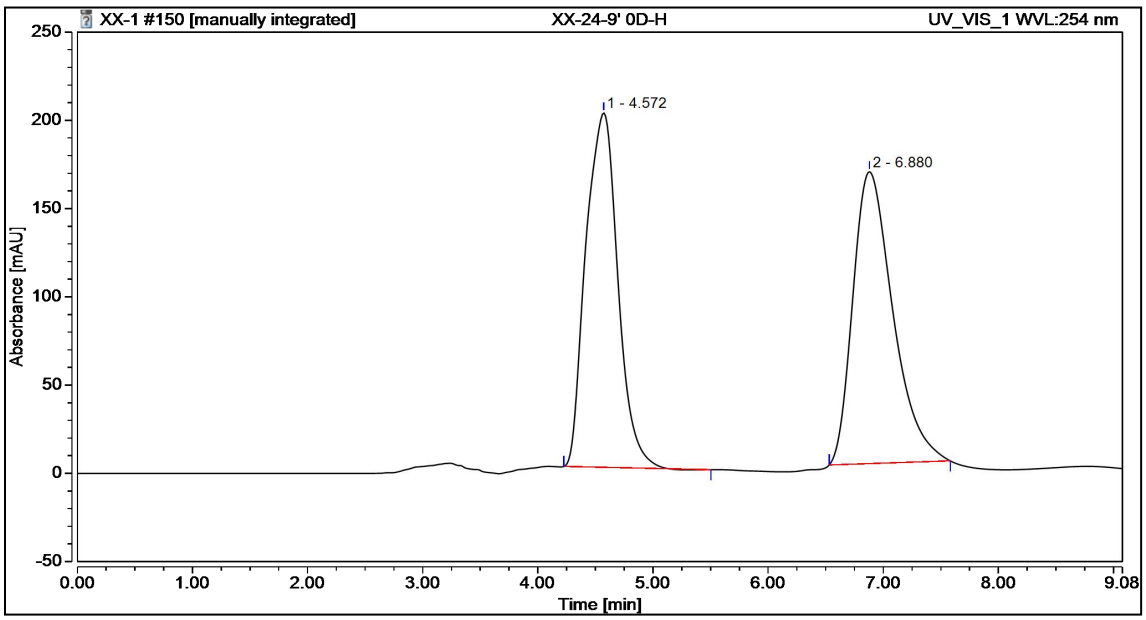


3w

White solid, 33.6 mg, 64% yield, 96% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 80/20, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 4.56 min, t (minor) = 6.90 min]. $[\alpha]_D^{20}$ = -38.5°(c = 1.0, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 9.0 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.09 (d, *J* = 7.0 Hz, 1H), 7.07 (s, 1H), 6.93 – 6.89 (m, 2H), 6.85 (d, *J* = 9.7 Hz, 1H), 6.60 (d, *J* = 10.1 Hz, 1H), 6.43 (d, *J* = 7.7 Hz, 1H), 3.82 (s, 6H), 3.74 (s, 4H), 3.70 (s, 3H), 2.14 (s, 3H), 1.96 (s, 3H), 1.76 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.66, 172.18, 161.75, 140.07, 139.94, 138.99, 138.19, 135.98, 134.73, 130.16, 129.32, 128.96, 128.55, 128.00, 127.95, 127.78, 125.70, 125.03, 122.16,

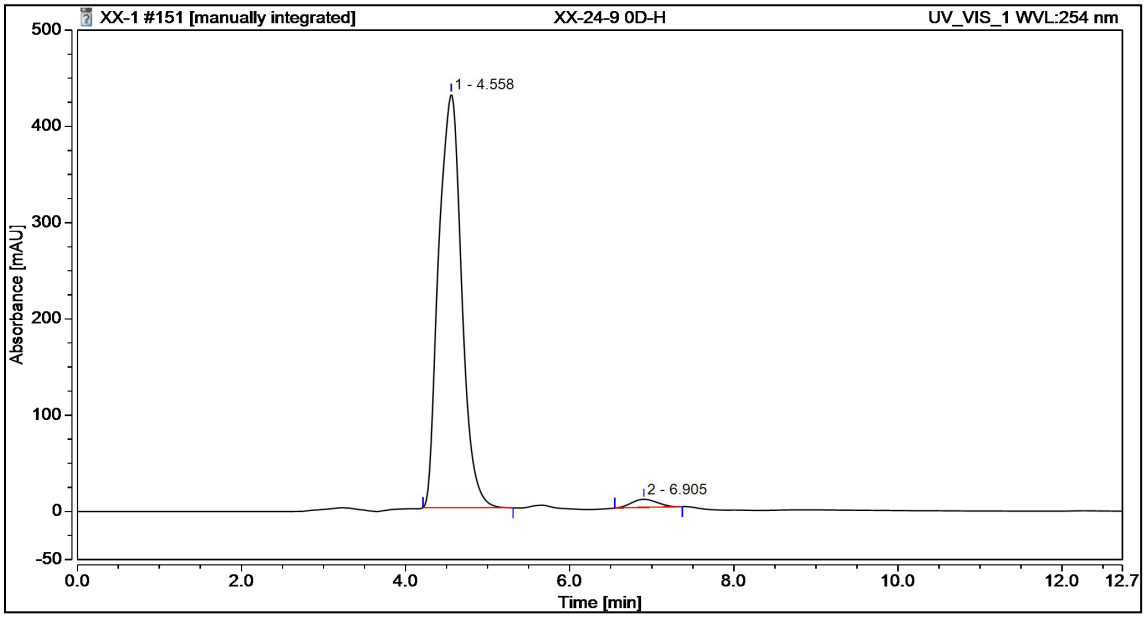
120.62, 111.87, 110.05, 59.22, 53.15, 53.11, 51.46, 40.59, 26.93, 21.10, 17.27, 14.32.

HRMS (ESI, m/z) Calcd for $C_{32}H_{31}NO_6$ $(M+H)^+$: 526.2224; Found: 526.2237.



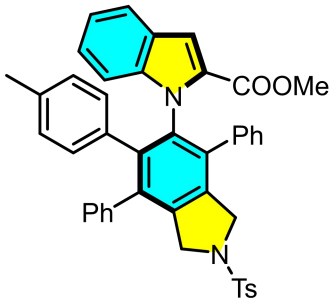
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.572	64.677	200.846	49.33	54.84	n.a.
2		6.880	66.444	165.412	50.67	45.16	n.a.
Total:			**131.121**	**366.259**	**100.00**	**100.00**	



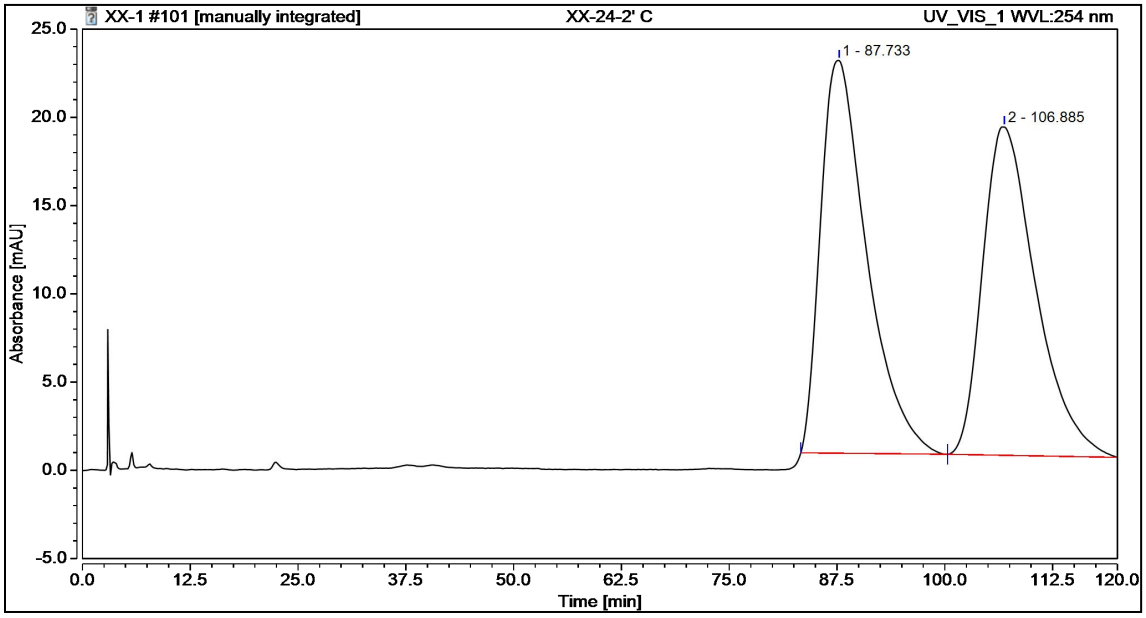
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.558	139.099	429.708	97.85	98.06	n.a.
2		6.905	3.058	8.481	2.15	1.94	n.a.
Total:			**142.157**	**438.188**	**100.00**	**100.00**	



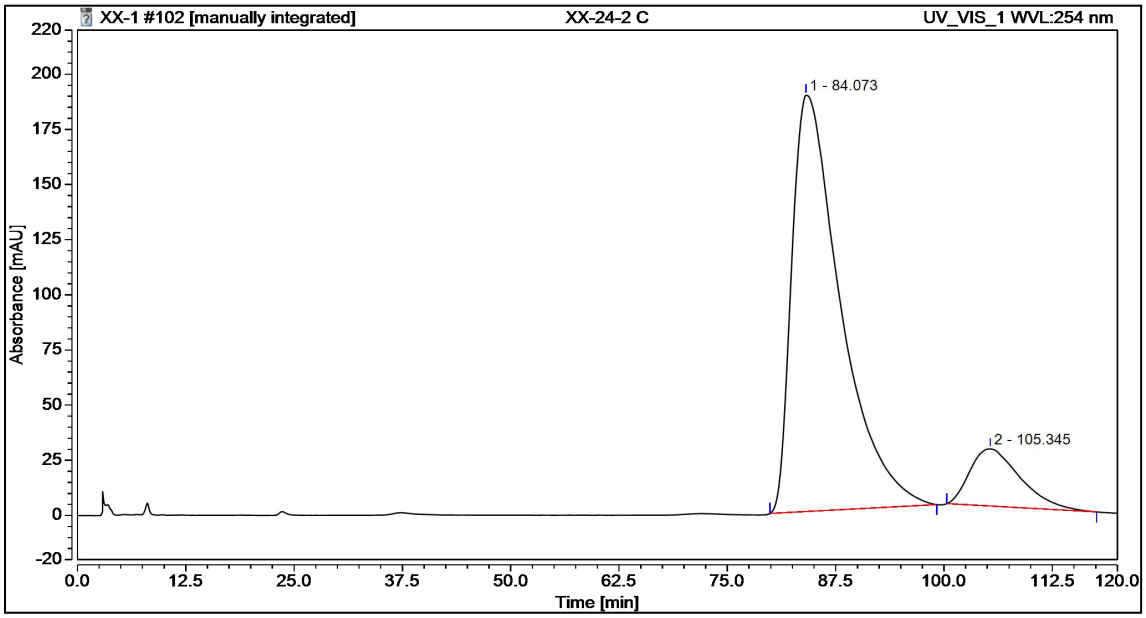
3x

White solid, 23.4 mg, 34% yield, 75% ee. [Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; *n*-hexane/2-propanol = 98/2, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 84.07 min, t (minor) = 105.35 min]. $[\alpha]_D^{20}$ = - 19.3°(c = 0.2, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.35 (dd, *J* = 11.3, 7.9 Hz, 3H), 7.20 – 7.13 (m, 4H), 7.10 – 6.88 (m, 9H), 6.81 (s, 1H), 6.74 – 6.31 (m, 4H), 4.63 – 4.44 (m, 4H), 3.71 (s, 3H), 2.46 (s, 3H), 1.98 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.06, 143.74, 140.68, 140.06, 138.13, 137.08, 135.90, 135.78, 135.77, 135.55, 135.41, 135.19, 133.70, 133.15, 129.91, 129.29, 129.07, 128.02, 127.91, 127.81, 127.64, 127.62, 127.52, 127.01, 125.46, 124.91, 122.08, 120.63, 111.86, 110.37, 54.26, 53.92, 51.45, 21.57, 20.99. **HRMS (ESI, m/z)** Calcd for $C_{44}H_{36}N_2O_4S$ $(M+H)^+$: 689.2469; Found: 689.2451.

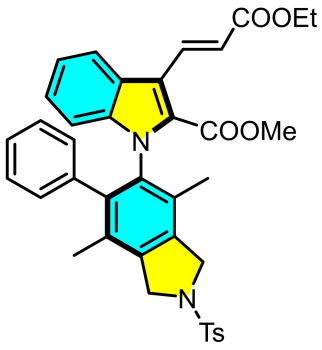


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		87.733	138.217	22.259	50.98	54.46	n.a.
2		106.885	132.907	18.615	49.02	45.54	n.a.
Total:			**271.124**	**40.874**	**100.00**	**100.00**	



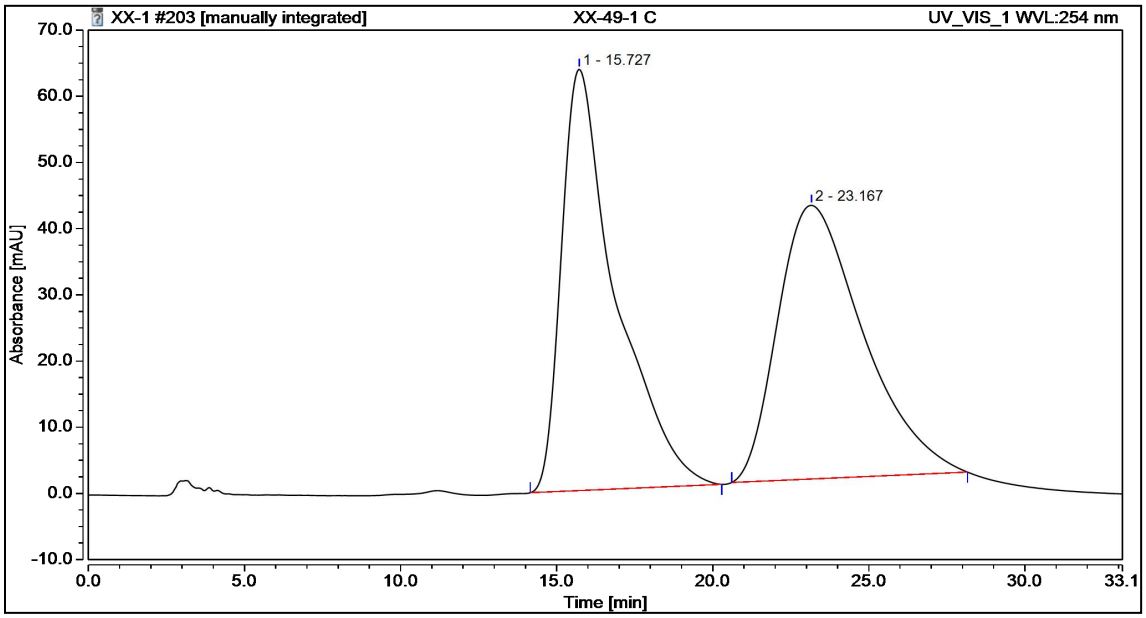
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		84.073	1228.178	188.774	87.55	87.93	n.a.
2		105.345	174.701	25.920	12.45	12.07	n.a.
Total:			**1402.879**	**214.694**	**100.00**	**100.00**	



5

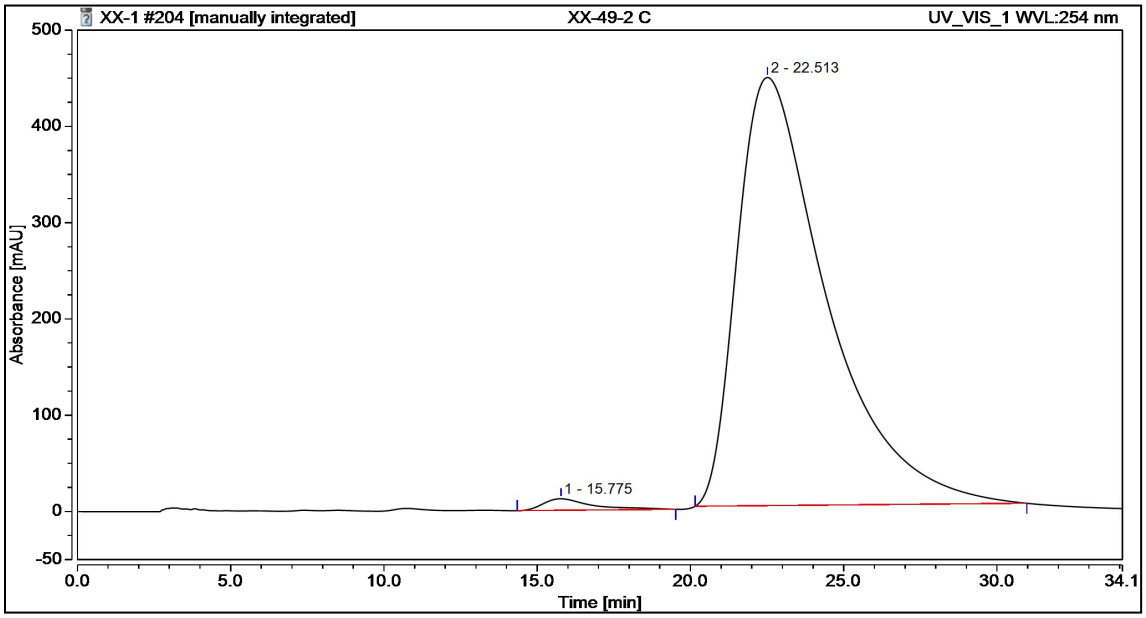
White solid, 51.7 mg, 40% yield, 97% ee. [Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; *n*-hexane/2-propanol = 50/50, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 22.51 min, t (minor) = 15.78 min]. $[\alpha]_D^{20}$ = 29.8°(c = 2.1, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 16.3 Hz, 1H), 7.87 (dd, *J* = 15.5, 8.3 Hz, 3H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 6.8 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 2H), 6.77 (t, *J* = 8.3 Hz, 1H), 6.51 (d, *J* = 16.2 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 4.80 – 4.60 (m, 4H), 4.26 (qd, *J* = 7.2, 2.0 Hz, 2H), 3.81 (s, 3H), 2.47 (s, 3H), 1.92 (s, 3H), 1.78 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ

167.61, 161.69, 143.86, 140.47, 139.41, 137.70, 136.35, 135.92, 135.66, 135.05, 133.92, 130.00, 129.50, 128.76, 128.73, 128.32, 127.68, 127.60, 127.58, 127.51, 127.48, 127.31, 126.05, 124.26, 122.46, 122.00, 119.09, 117.62, 112.00, 60.35, 53.94, 53.69, 52.13, 21.59, 17.00, 14.39, 14.33. **HRMS (ESI, m/z)** Calcd for $C_{38}H_{36}N_2O_6S$ $(M+NH_4)^+$: 666.2632; Found: 666.2634.

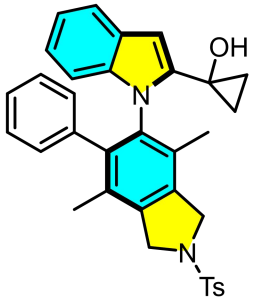


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.727	127.878	63.665	49.36	60.62	n.a.
2		23.167	131.175	41.357	50.64	39.38	n.a.
Total:			**259.053**	**105.023**	**100.00**	**100.00**	

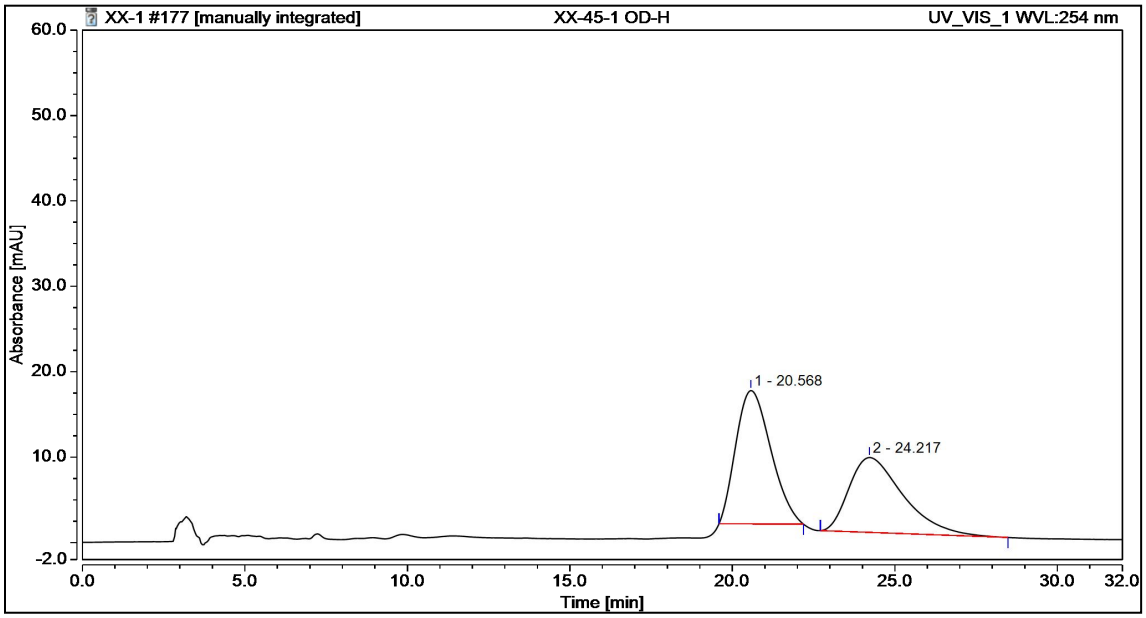


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.775	22.186	12.017	1.45	2.63	n.a.
2		22.513	1504.512	444.814	98.55	97.37	n.a.
Total:			**1526.698**	**456.830**	**100.00**	**100.00**	



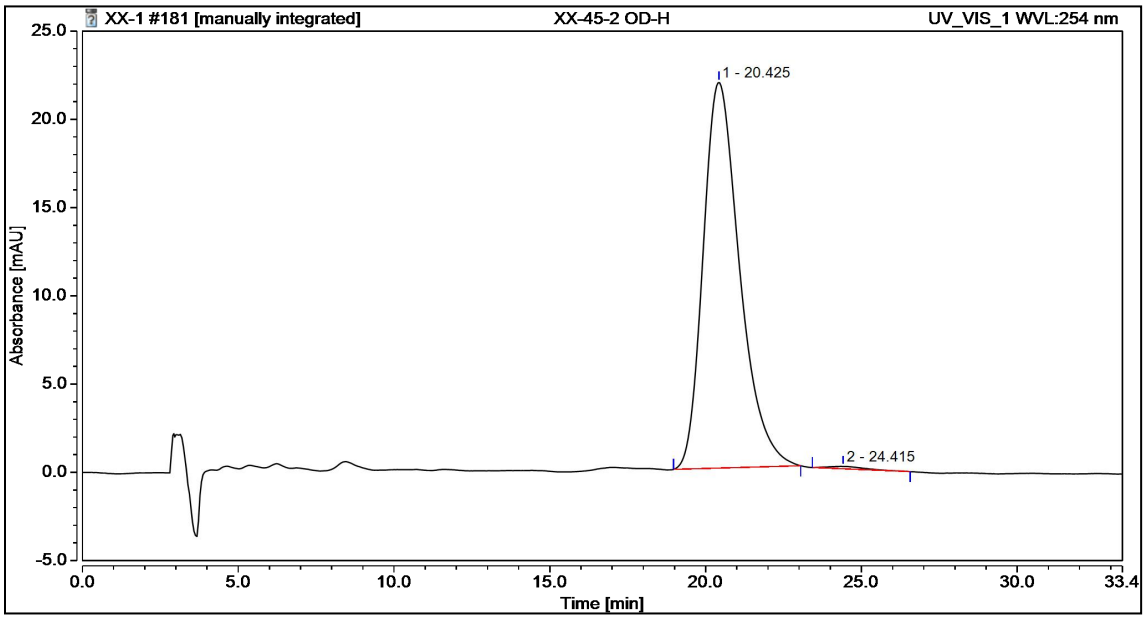
6

White solid, 32.8 mg, 60% yield, 99% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 90/10, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 20.43 min, t (minor) = 24.42 min]. $[\alpha]_D^{20}$ = - 79.4°(c = 0.4, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 8.5 Hz, 2H), 7.15 – 7.02 (m, 3H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.20 (s, 1H), 4.69 (dd, *J* = 28.2, 2.5 Hz, 4H), 2.46 (s, 3H), 2.02 (s, 3H), 1.60 (s, 3H), 0.92 – 0.83 (m, 2H), 0.83 – 0.74 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 143.83, 141.53, 141.33, 139.71, 136.86, 136.36, 135.76, 135.29, 133.97, 130.18, 129.99, 129.62, 128.60, 128.02, 127.67, 127.34, 127.22, 126.80, 122.15, 120.56, 119.96, 110.37, 100.54, 54.04, 53.68, 51.58, 21.60, 17.57, 16.41, 14.83, 14.31. **HRMS (ESI, m/z)** Calcd for $C_{34}H_{32}N_2O_3S$ $(M+H)^+$: 549.2206; Found: 549.2218.



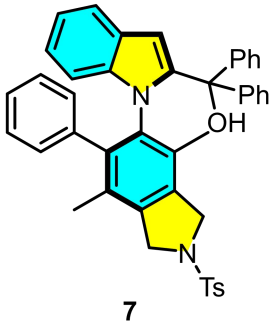
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.568	19.500	15.622	53.53	64.04	n.a.
2		24.217	16.928	8.771	46.47	35.96	n.a.
Total:			**36.428**	**24.393**	**100.00**	**100.00**	



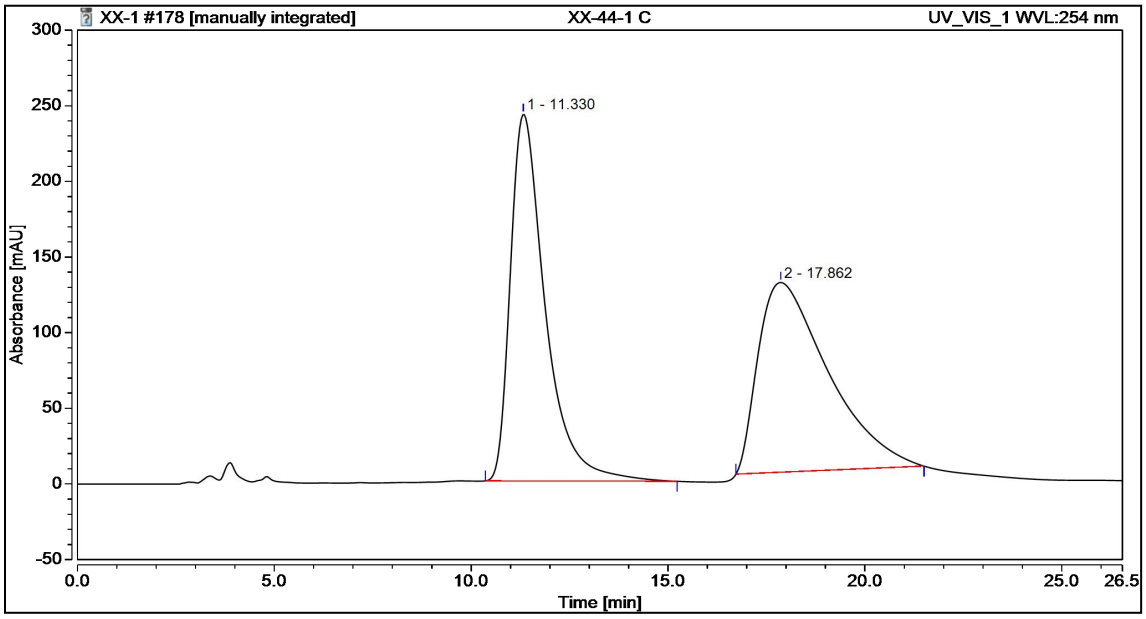
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.425	29.670	21.870	99.37	99.35	n.a.
2		24.415	0.189	0.144	0.63	0.65	n.a.
Total:			**29.859**	**22.014**	**100.00**	**100.00**	

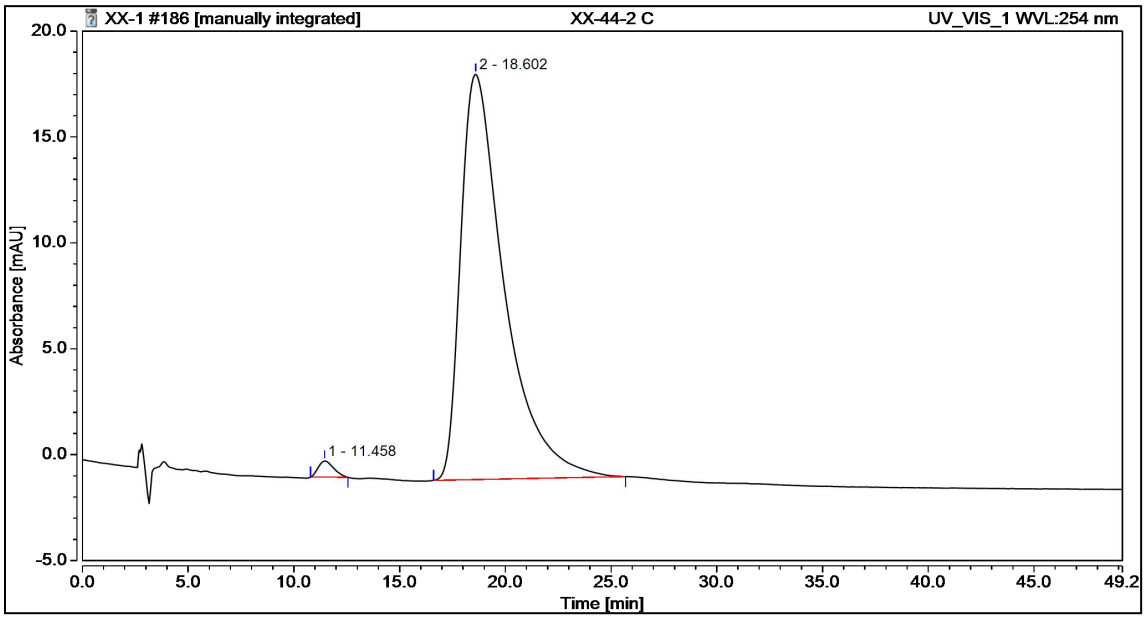


7

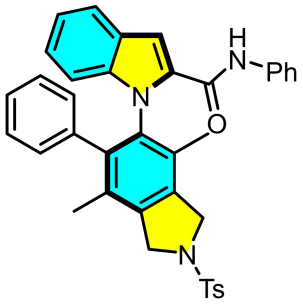
White solid, 51.2 mg, 76% yield, 97% ee. [Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; *n*-hexane/2-propanol = 80/20, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 18.60 min, t (minor) = 11.46 min]. $[\alpha]_D^{20}$ = - 80.6°(c = 1.5, $CHCl_3$).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.40 (t, *J* = 8.6 Hz, 3H), 7.30 – 7.12 (m, 12H), 7.11 – 7.03 (m, 2H), 6.83 – 6.79 (m, 1H), 6.79 – 6.75 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.79 (s, 1H), 4.77 – 4.60 (m, 2H), 4.48 (s, 2H), 2.46 (s, 3H), 1.94 (s, 3H), 0.96 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.51, 143.92, 143.82, 143.57, 141.96, 140.44, 137.26, 136.26, 135.88, 135.02, 134.01, 130.38, 130.06, 129.97, 129.35, 128.09, 127.83, 127.74, 127.69, 127.67, 127.62, 127.46, 127.33, 127.25, 127.12, 126.21, 122.24, 120.59, 119.97, 110.72, 106.35, 80.02, 54.04, 53.64, 21.60, 17.46, 13.54. **HRMS (ESI, m/z)** Calcd for $C_{44}H_{38}N_2O_3S$ $(M+H)^+$: 675.2676; Found: 675.6766.



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.330	248.926	242.461	49.06	65.90	n.a.
2		17.862	258.515	125.455	50.94	34.10	n.a.
Total:			**507.441**	**367.916**	**100.00**	**100.00**	



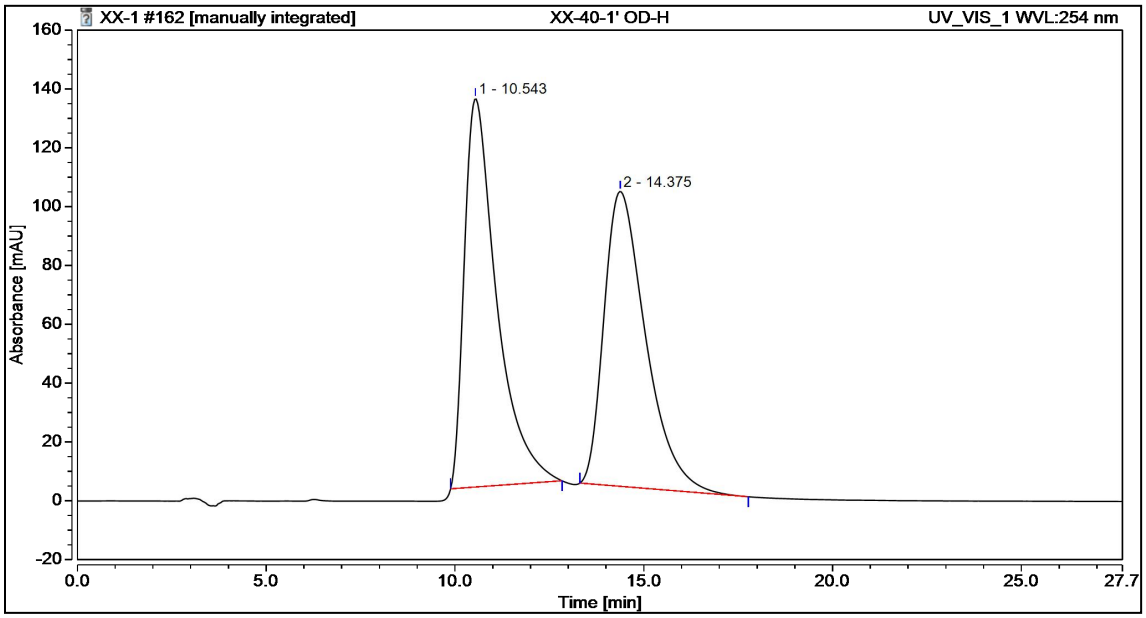
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.458	0.648	0.767	1.40	3.85	n.a.
2		18.602	45.649	19.148	98.60	96.15	n.a.
Total:			**46.298**	**19.915**	**100.00**	**100.00**	



8

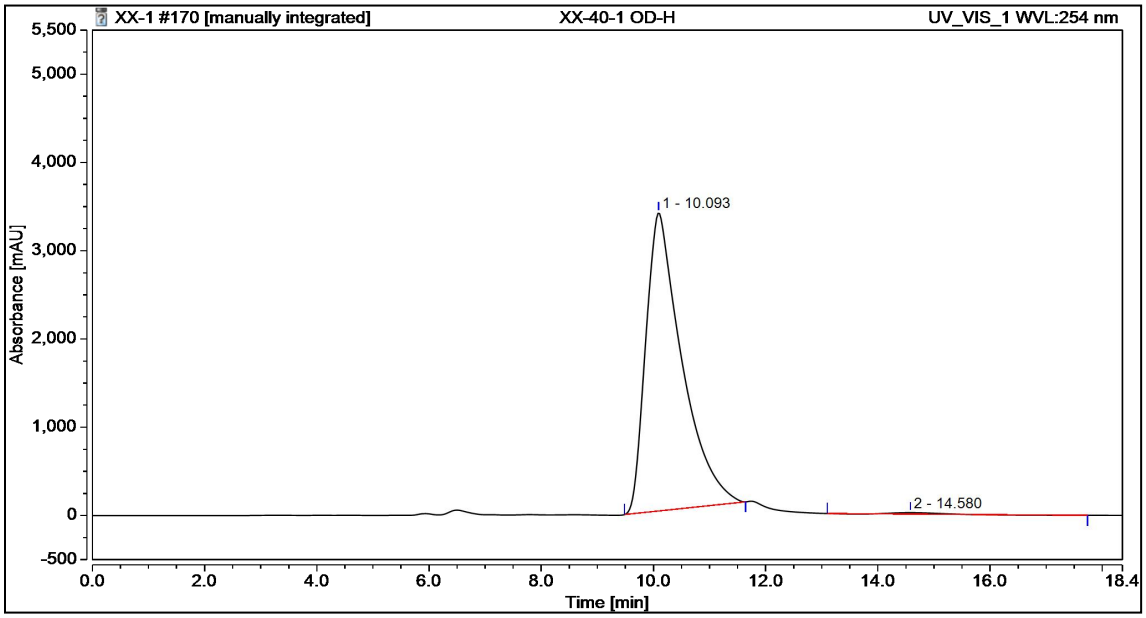
White solid, 53.1 mg, 87% yield, 99% ee. [Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250X4.6 mm 5u column; *n*-hexane/2-propanol = 80/20, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 10.09 min, t (minor) = 14.58 min]. $[\alpha]_D^{20}$ = - 18.8°(c = 1.2, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.35 (m, 4H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 5.8 Hz, 2H), 7.16 – 7.02 (m, 4H), 6.99 (d, *J* = 7.1 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.81 – 6.76 (m, 1H), 6.75 (s, 1H), 6.38 (d, *J* = 7.3 Hz, 1H), 4.82 – 4.56 (m, 4H), 2.47 (s, 3H),

1.89 (s, 3H), 1.86 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 159.50, 143.85, 140.43, 139.52, 137.56, 136.99, 135.70, 135.57, 135.01, 133.80, 133.04, 130.02, 129.74, 129.20, 129.06, 128.74, 127.66, 127.59, 127.46, 127.26, 126.92, 125.92, 124.93, 124.36, 121.88, 121.08, 119.88, 111.39, 104.69, 54.02, 53.83, 21.59, 16.97, 14.55. **HRMS (ESI, m/z)** Calcd for $C_{38}H_{33}N_3O_3S$ $(M+H)^+$: 612.2315; Found: 612.2303.

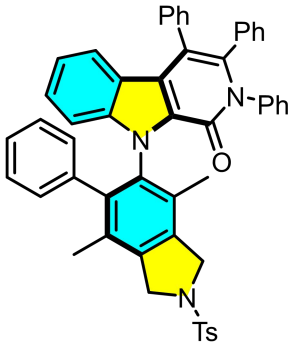


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.543	130.877	132.080	50.49	56.84	n.a.
2		14.375	128.356	100.276	49.51	43.16	n.a.
Total:			**259.233**	**232.356**	**100.00**	**100.00**	

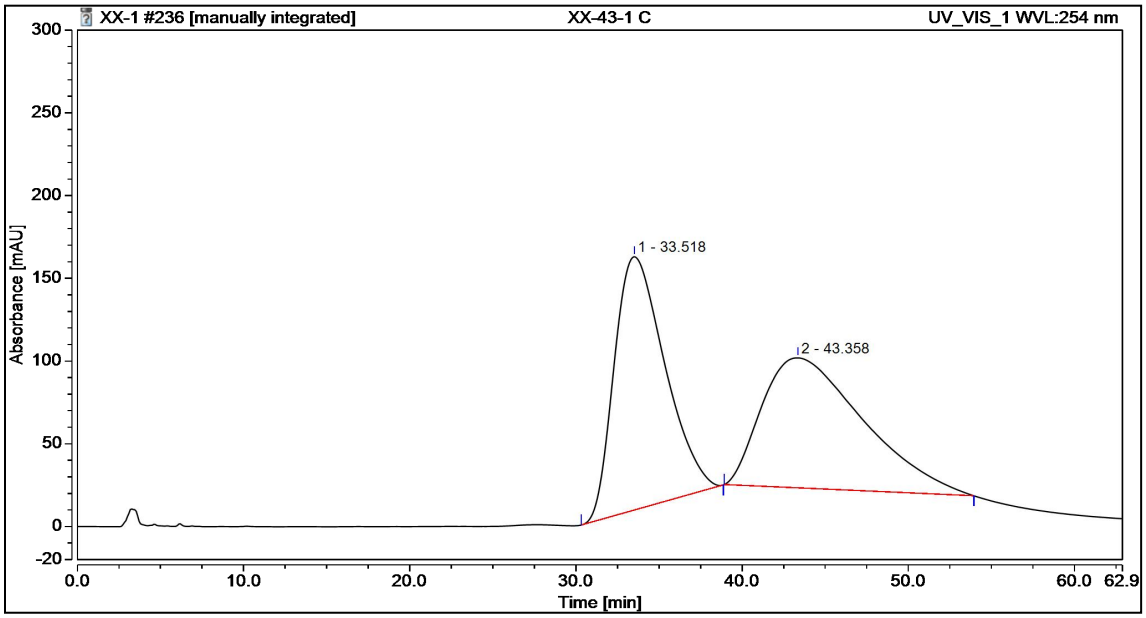


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.093	2512.703	3380.588	99.62	99.52	n.a.
2		14.580	9.499	16.271	0.38	0.48	n.a.
Total:			**2522.202**	**3396.859**	**100.00**	**100.00**	



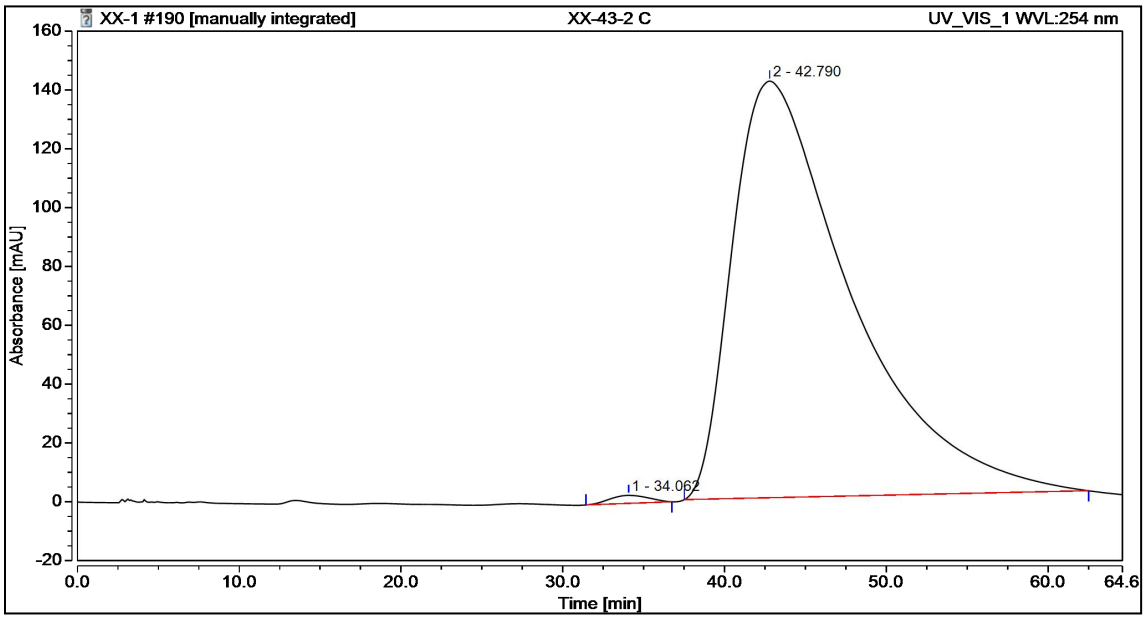
9

White solid, 51.1 mg, 65% yield, 99% ee. [Chiral HPLC analysis of the product: Phenomenex 00G-4457-E0 250X4.6 mm 5u column; *n*-hexane/2-propanol = 80/20, flow rate =1.0 mL/min, λ = 254 nm, t (major) = 42.79 min, t (minor) = 34.06 min]. $[\alpha]_D^{20}$ = 112.6°(c = 1.6, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.3 Hz, 1H), 7.23 – 6.96 (m, 14H), 6.87 (dd, *J* = 7.3, 2.8 Hz, 5H), 6.77 (t, *J* = 7.5 Hz, 2H), 6.58 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 4.87 – 4.44 (m, 4H), 2.42 (s, 3H), 1.99 (s, 3H), 1.88 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.57, 143.83, 142.05, 141.25, 139.45, 137.63, 137.13, 136.96, 135.80, 135.32, 134.63, 134.56, 133.54, 131.56, 131.44, 131.00, 130.92, 130.04, 129.95, 129.78, 129.39, 128.80, 128.51, 128.49, 128.47, 127.98, 127.96, 127.88, 127.59, 127.38, 127.24, 127.08, 127.07, 127.03, 126.97, 126.84, 126.65, 126.59, 124.76, 122.77, 122.02, 120.21, 116.66, 111.41, 54.13, 53.94, 21.55, 16.90, 14.77. **HRMS (ESI, m/z)** Calcd for $C_{52}H_{41}N_3O_3S$ $(M+H)^+$: 788.2941; Found: 788.2939.



Integration Results

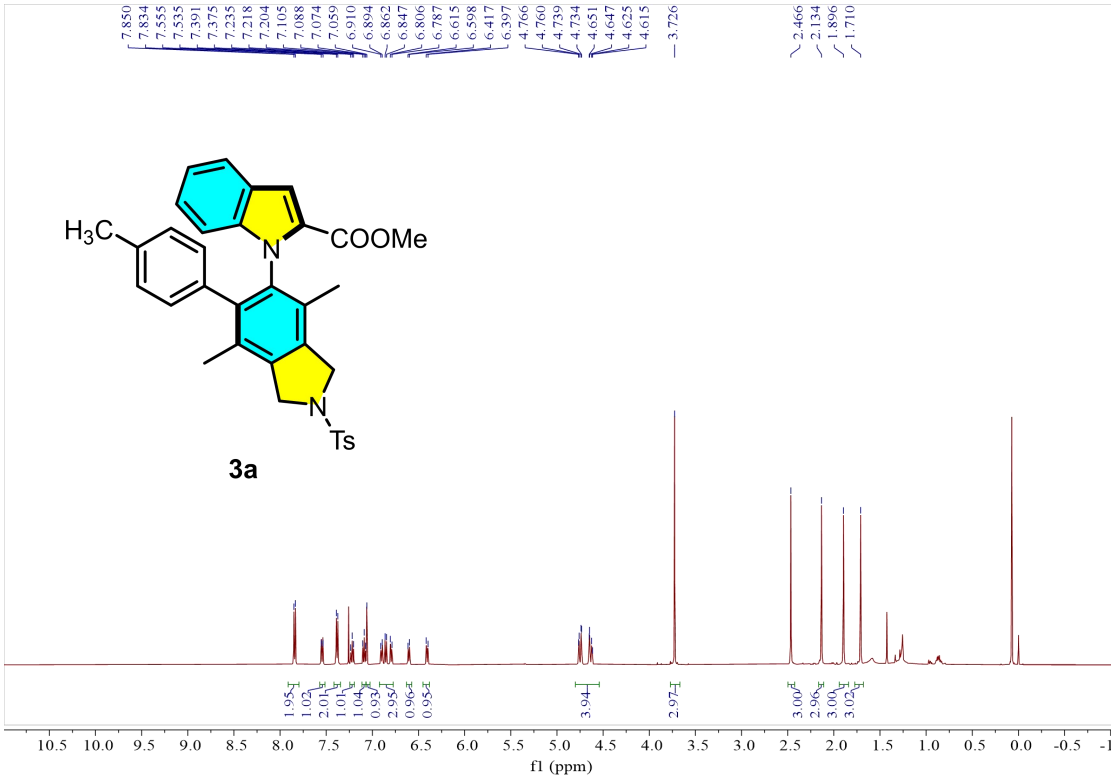
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33.518	538.896	153.120	49.22	66.10	n.a.
2		43.358	555.953	78.542	50.78	33.90	n.a.
Total:			**1094.849**	**231.662**	**100.00**	**100.00**	

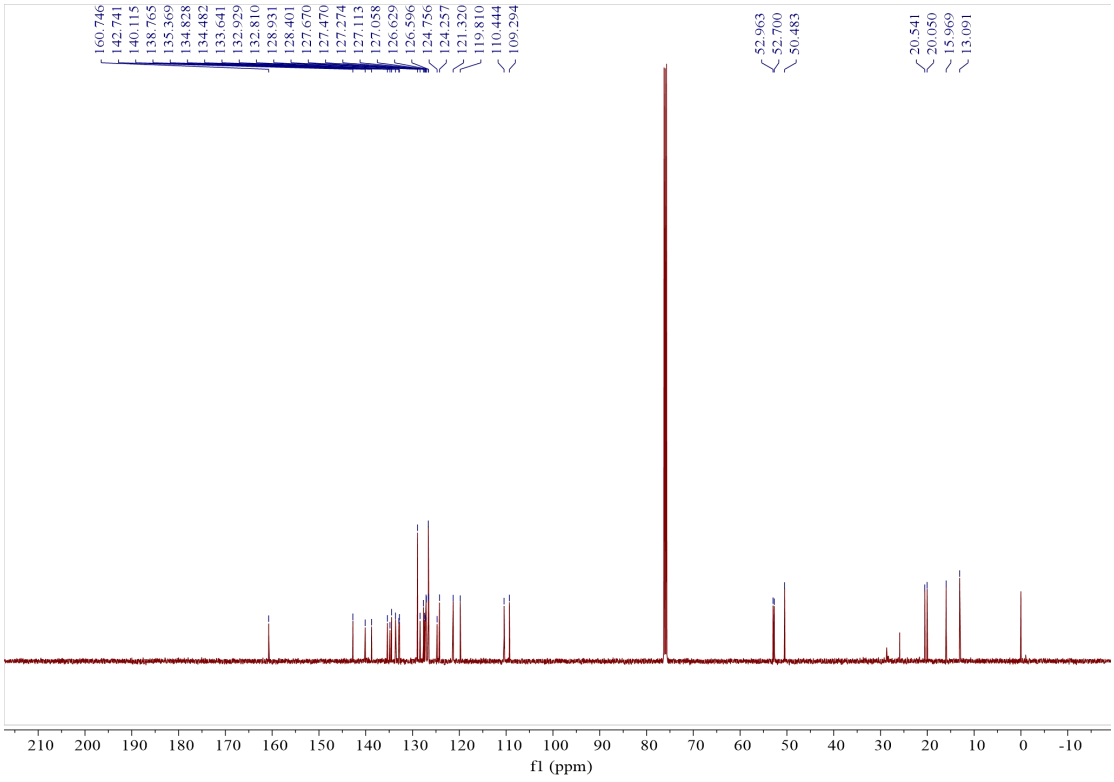


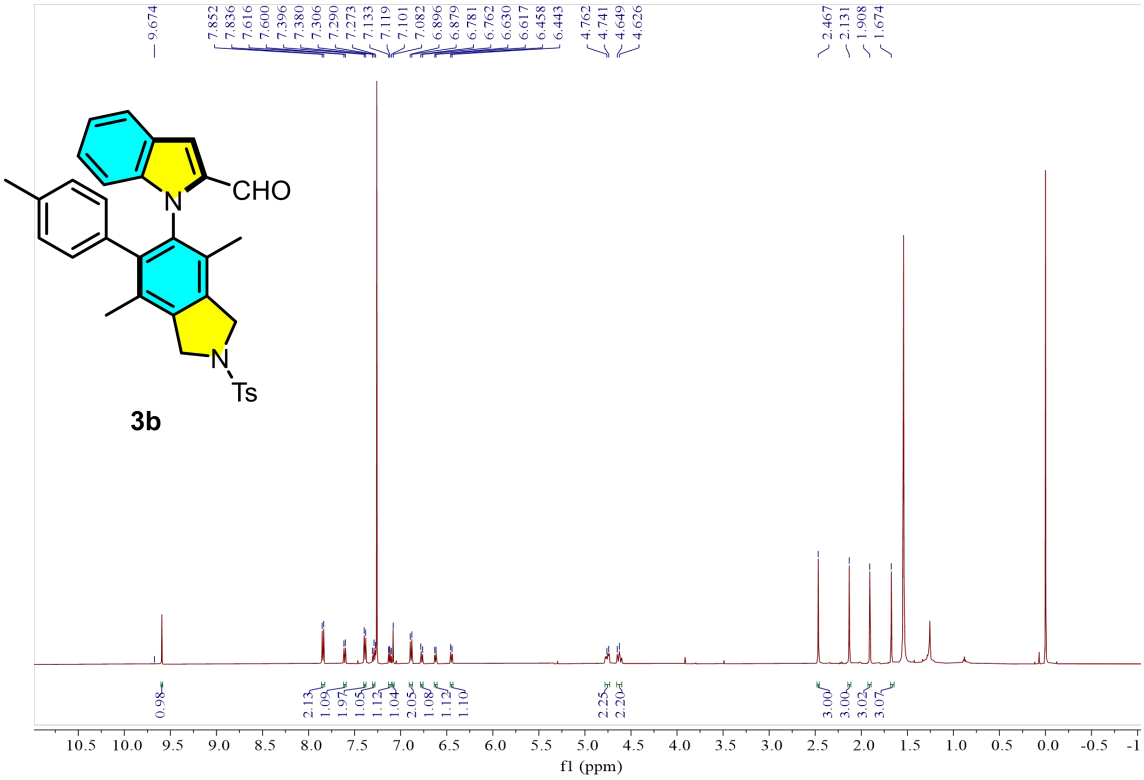
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		34.062	7.632	2.744	0.63	1.90	n.a.
2		42.790	1202.327	141.659	99.37	98.10	n.a.
Total:			**1209.959**	**144.403**	**100.00**	**100.00**	

8. NMR spectra



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6.879
6.781
6.762
6.630
6.617
6.458
6.443
4.762
4.741
4.649
4.626
2.467
2.131
1.908
1.674
CHO
N
N
Ts
3b
0.98
2.13
1.09
1.97
1.05
1.12
1.04
2.05
1.08
1.12
1.10
2.25
2.20
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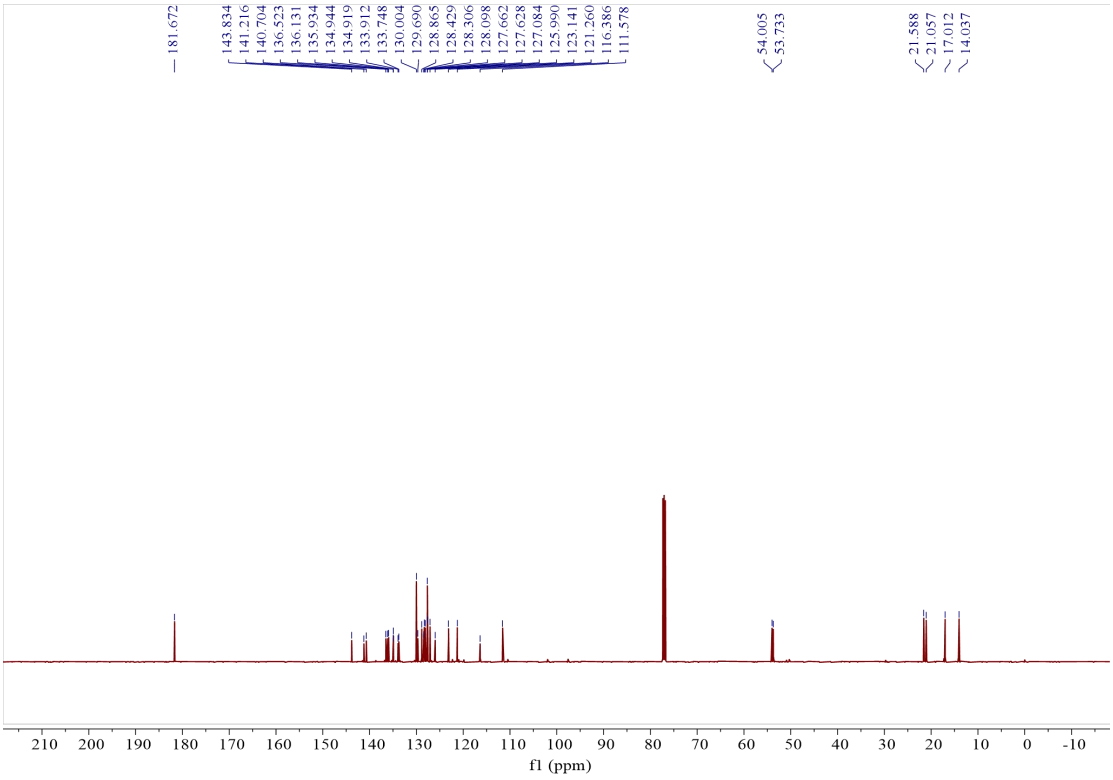
3.00
3.02
3.07
f1 (ppm)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129.690
128.865
128.429
128.306
128.098
127.662
127.628
127.084
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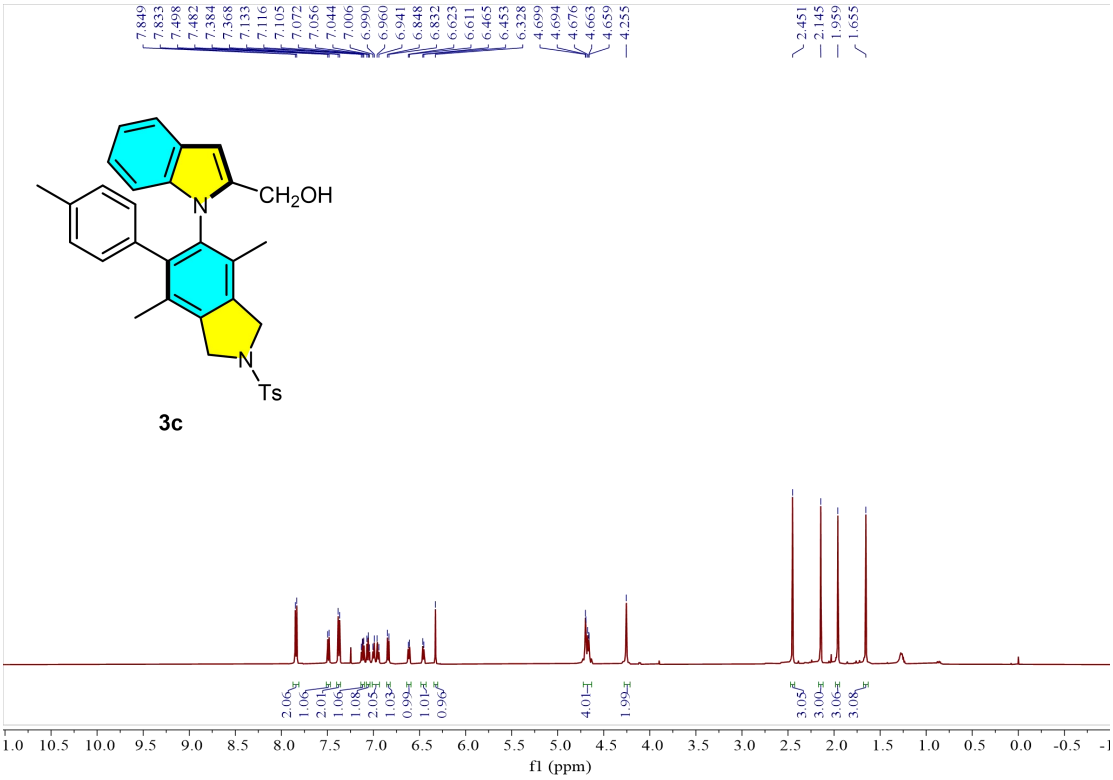
116.386
111.578
54.005
53.733
21.588
21.057
17.012
14.037
f1 (ppm)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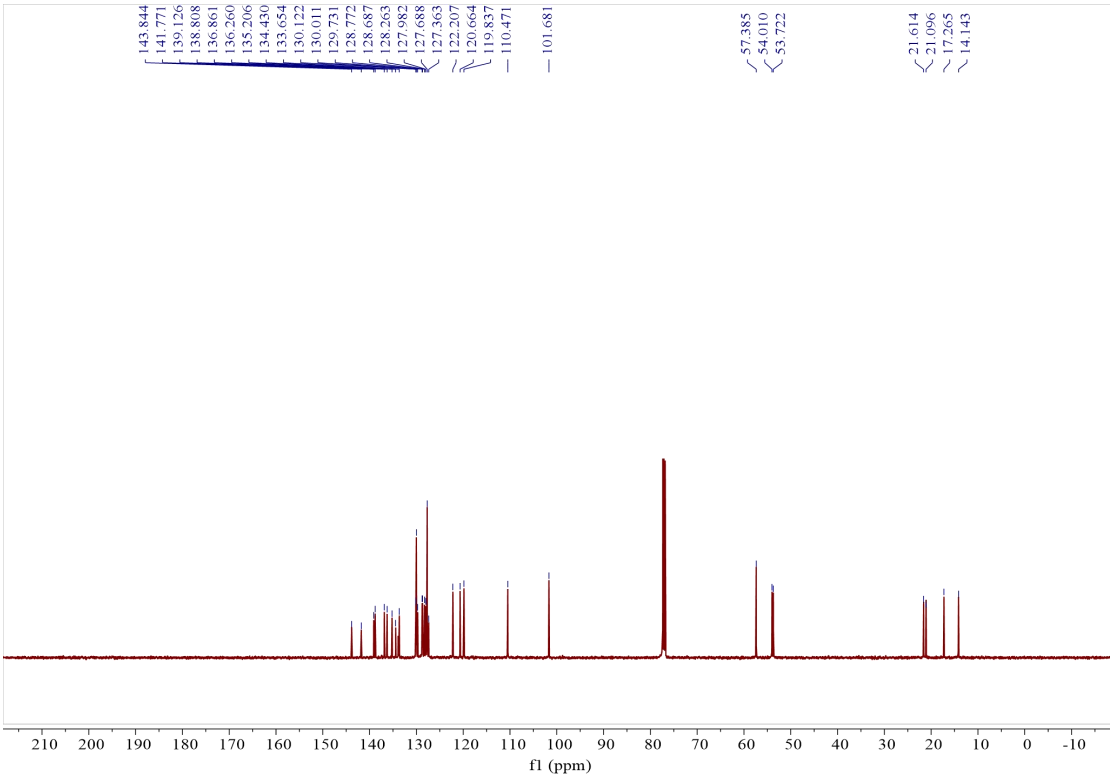
7.116
7.105
7.072
7.056
7.044
7.006
6.990
6.960
6.941
6.848
6.832
6.623
6.611
6.465
6.453
6.328
4.699
4.694
4.676
4.663
4.659
4.255
2.451
2.145
1.959
1.655
CH2OH
N
N
Ts
2.06
1.06
2.01
1.06
1.08
2.05
1.03
0.99
1.01
0.96
4.01
1.99
3.05
3.00
3.06
3.08
f1 (ppm)

3c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128.772
128.687
128.263
127.982
127.688
127.363
122.207
120.664
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54.010
53.722
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21.096
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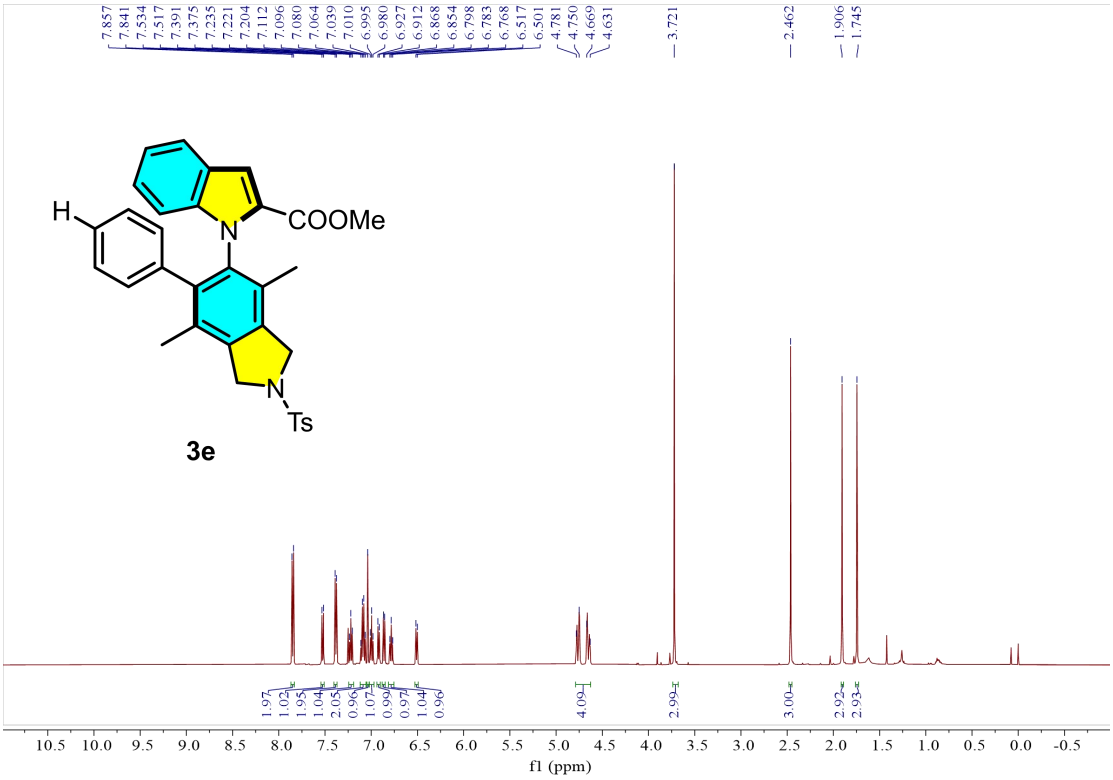
14.143
f1 (ppm)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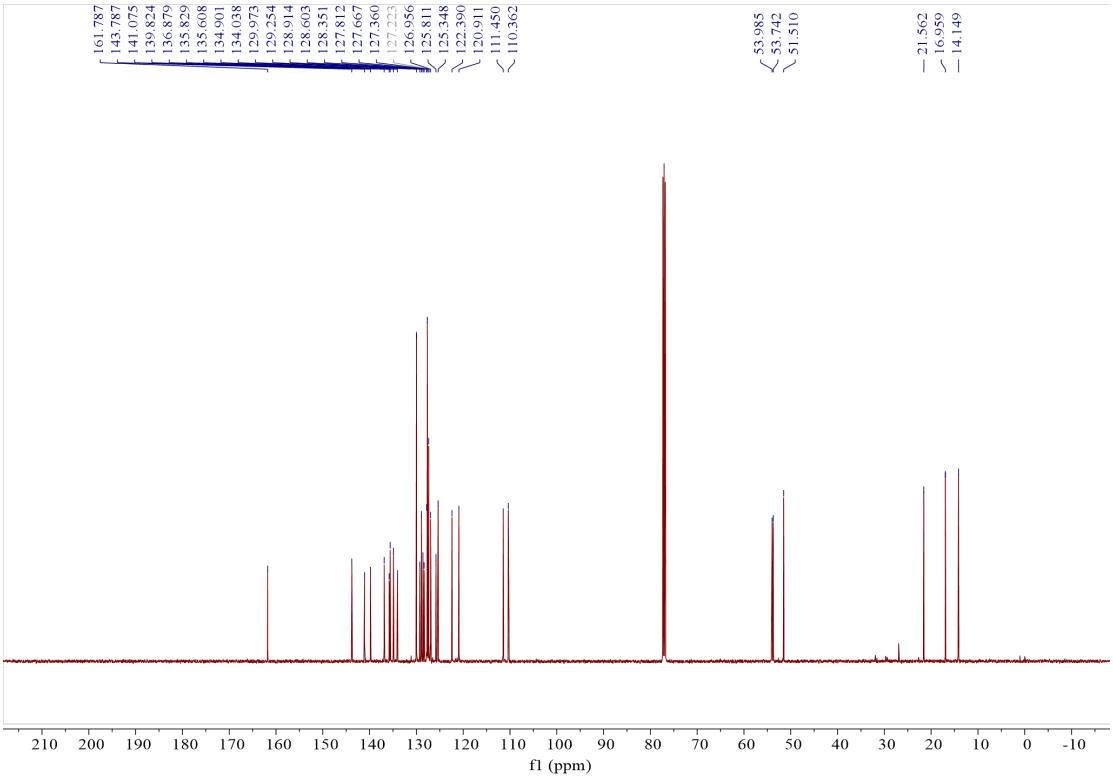
7.221
7.204
7.112
7.096
7.080
7.064
7.039
7.010
6.995
6.980
6.927
6.912
6.868
6.854
6.798
6.783
6.768
6.517
6.501
4.781
4.750
4.669
4.631
3.721
2.462
1.906
1.745
H
COOMe
N
N
Ts
3e
1.97
1.02
1.95
1.04
2.05
0.96
1.07
0.99
0.97
1.04
0.96
4.09
2.99
3.00
2.92
2.93
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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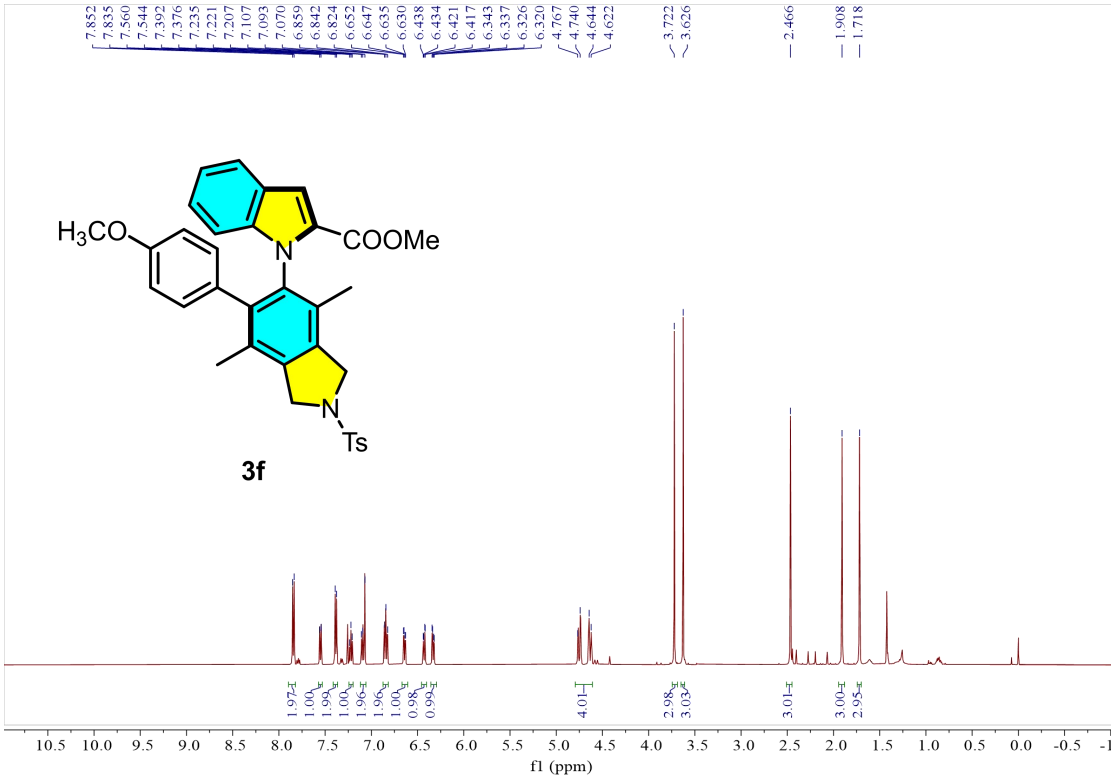
128.603
128.351
127.812
127.667
127.360
127.223
126.956
125.811
125.348
122.390
120.911
111.450
110.362
53.985
53.742
51.510
21.562
16.959
14.149
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.544
7.392
7.376
7.235
7.221
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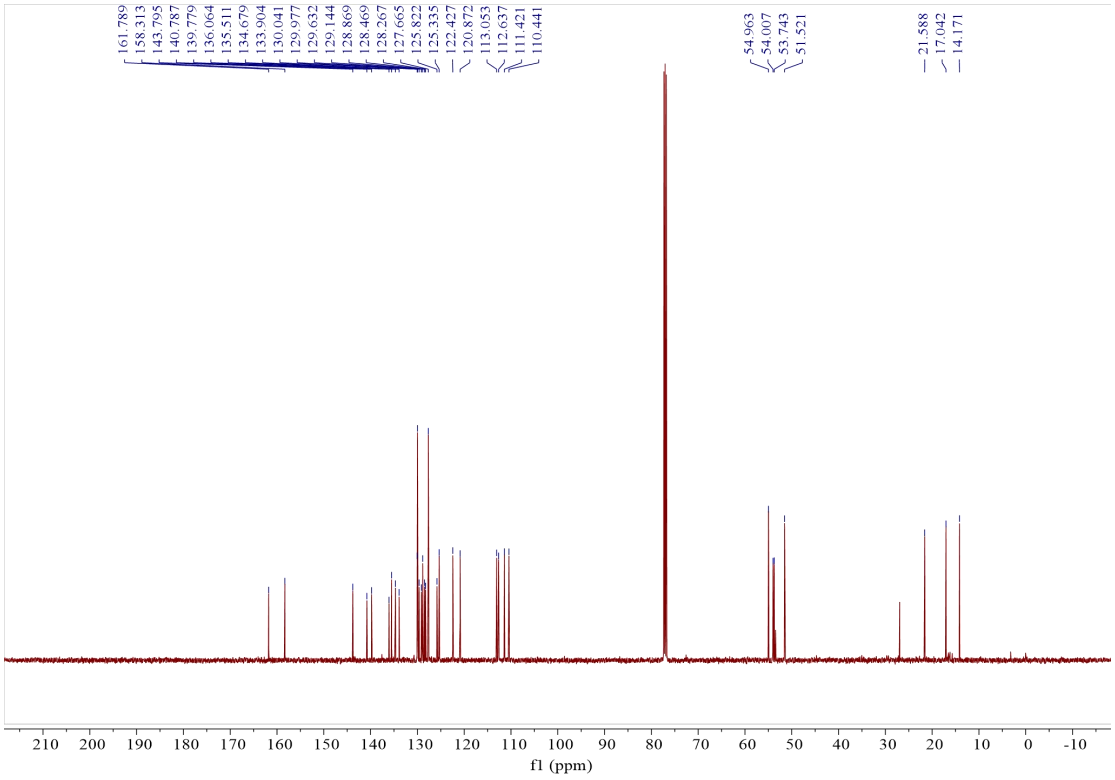
7.107
7.093
7.070
6.859
6.842
6.824
6.652
6.647
6.635
6.630
6.438
6.434
6.421
6.417
6.343
6.337
6.326
6.320
4.767
4.740
4.644
4.622
3.722
3.626
2.466
1.908
1.718
H3CO
COOMe
N
N
Ts
1.97
1.00
1.99
1.00
1.96
1.00
0.98
0.99
4.01
2.98
3.03
3.01
3.00
2.95
f1 (ppm)

3f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130.041
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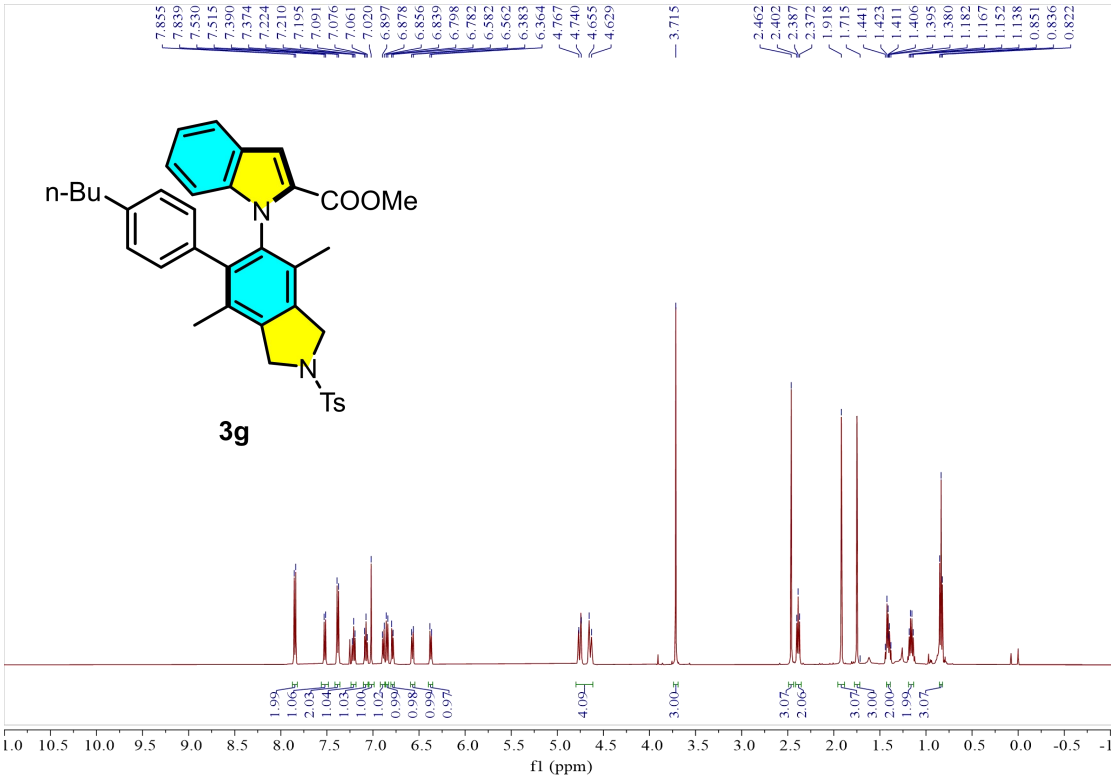
129.632
129.144
128.869
128.469
128.267
127.665
125.822
125.335
122.427
120.872
113.053
112.637
111.421
110.441
54.963
54.007
53.743
51.521
21.588
17.042
14.171
f1 (ppm)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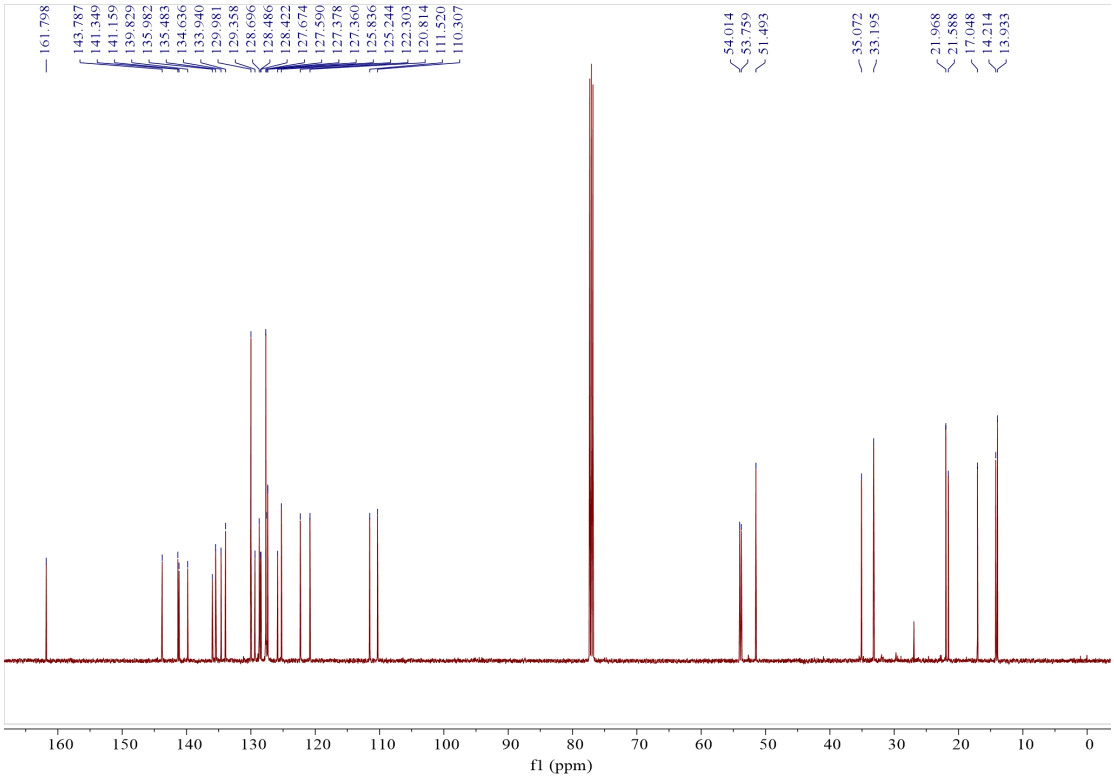
7.210
7.195
7.091
7.076
7.061
7.020
6.897
6.878
6.856
6.839
6.798
6.782
6.582
6.562
6.383
6.364
4.767
4.740
4.655
4.629
3.715
2.462
2.402
2.387
2.372
1.918
1.715
1.441
1.423
1.411
1.406
1.395
1.380
1.182
1.167
1.152
1.138
0.851
0.836
0.822
n-Bu
COOMe
N
N
Ts
3g
1.99
1.06
2.03
1.04
1.03
1.00
1.03
0.99
0.98
0.99
0.97
4.09
3.00
3.07
2.06
3.07
3.00
2.00
1.99
3.07
f1 (ppm)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128.486
128.422
127.674
127.590
127.378
127.360
125.836
125.244
122.303
120.814
111.520
110.307
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51.493
35.072
33.195
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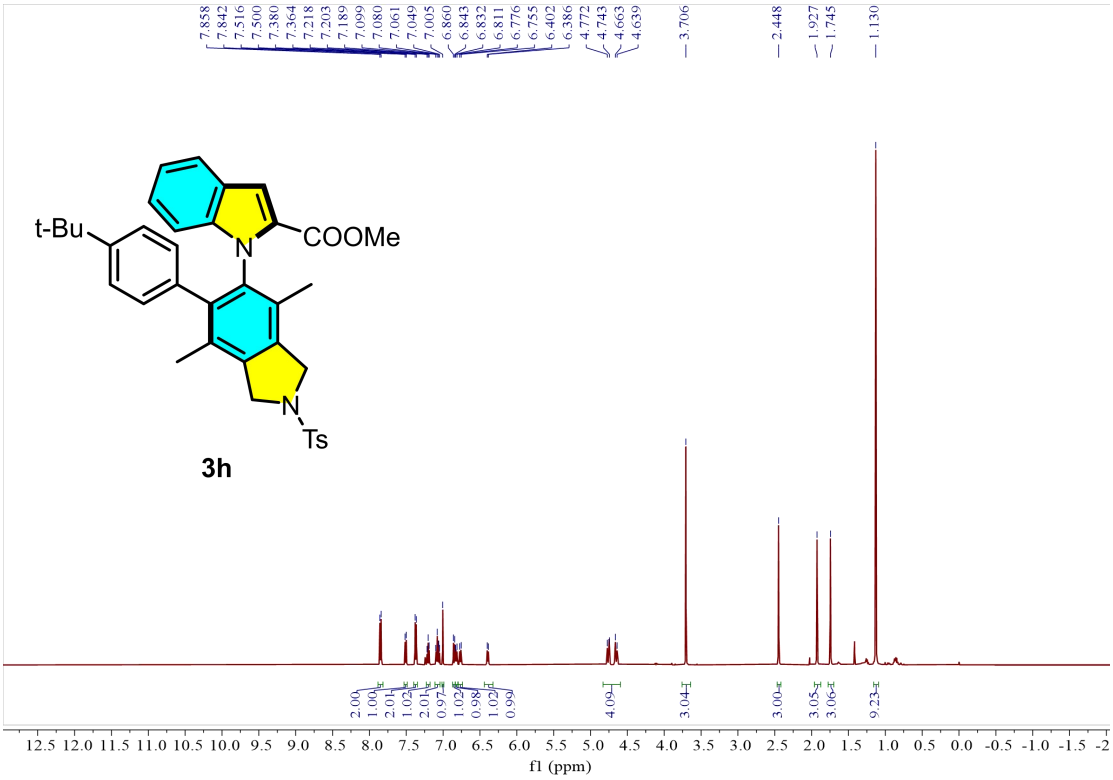
17.048
14.214
13.933
f1 (ppm)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7.380
7.364
7.218
7.203
7.189
7.099
7.080
7.061
7.049
7.005
6.860
6.843
6.832
6.811
6.776
6.755
6.402
6.386
4.772
4.743
4.663
4.639
3.706
2.448
1.927
1.745
1.130
t-Bu
COOMe
N
N
Ts
3h
2.00
1.00
2.01
1.02
2.01
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0.98
1.02
0.99
4.09
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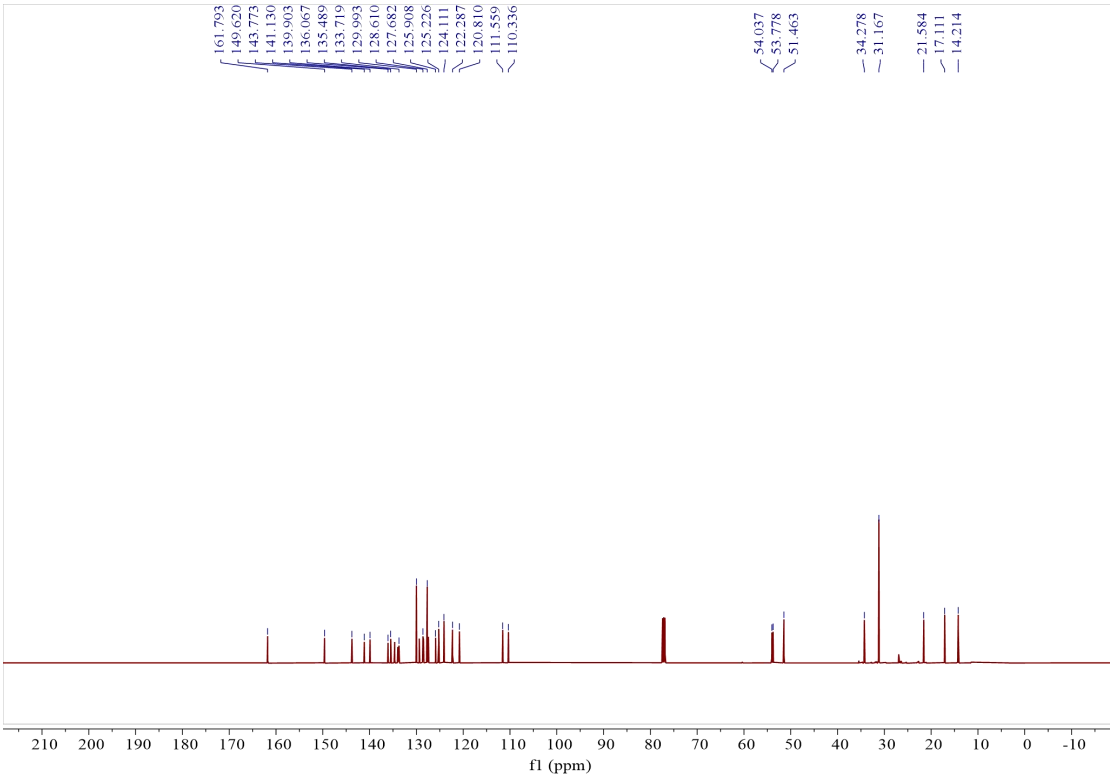
3.00
3.05
3.06
9.23
f1 (ppm)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133.719
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127.682
125.908
125.226
124.111
122.287
120.810
111.559
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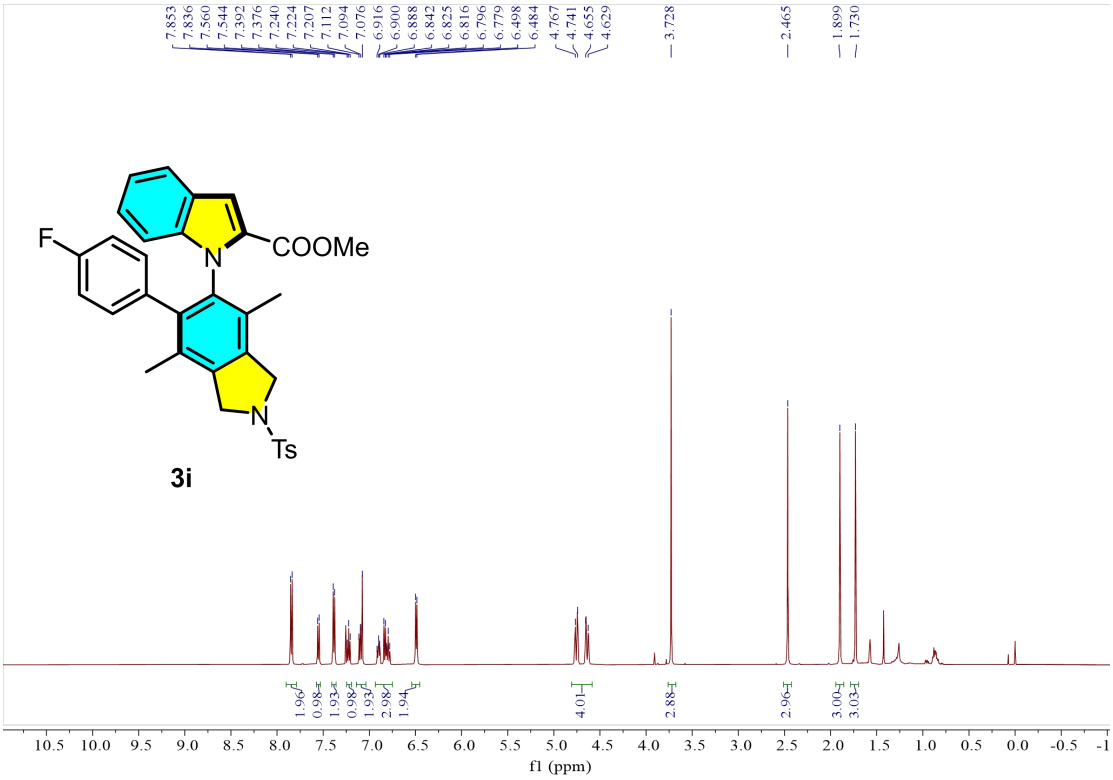
54.037
53.778
51.463
34.278
31.167
21.584
17.111
14.214
f1 (ppm)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7.560
7.544
7.392
7.376
7.240
7.224
7.207
7.112
7.094
7.076
6.916
6.900
6.888
6.842
6.825
6.816
6.796
6.779
6.498
6.484
4.767
4.741
4.655
4.629
3.728
2.465
1.899
1.730
F
COOMe
N
N
Ts
1.96
0.98
1.93
0.98
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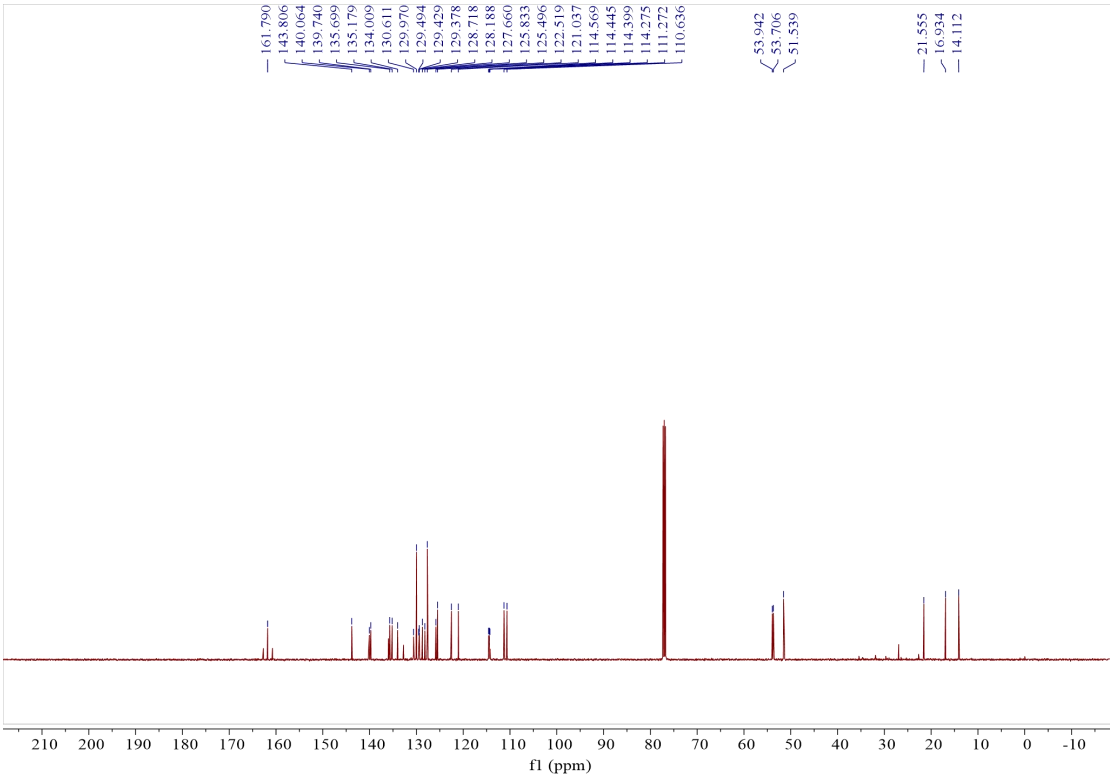
2.98
1.94
4.01
2.88
2.96
3.00
3.03
f1 (ppm)

3i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130.611
129.970
129.494
129.429
129.378
128.718
128.188
127.660
125.833
125.496
122.519
121.037
114.569
114.445
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111.272
110.636
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21.555
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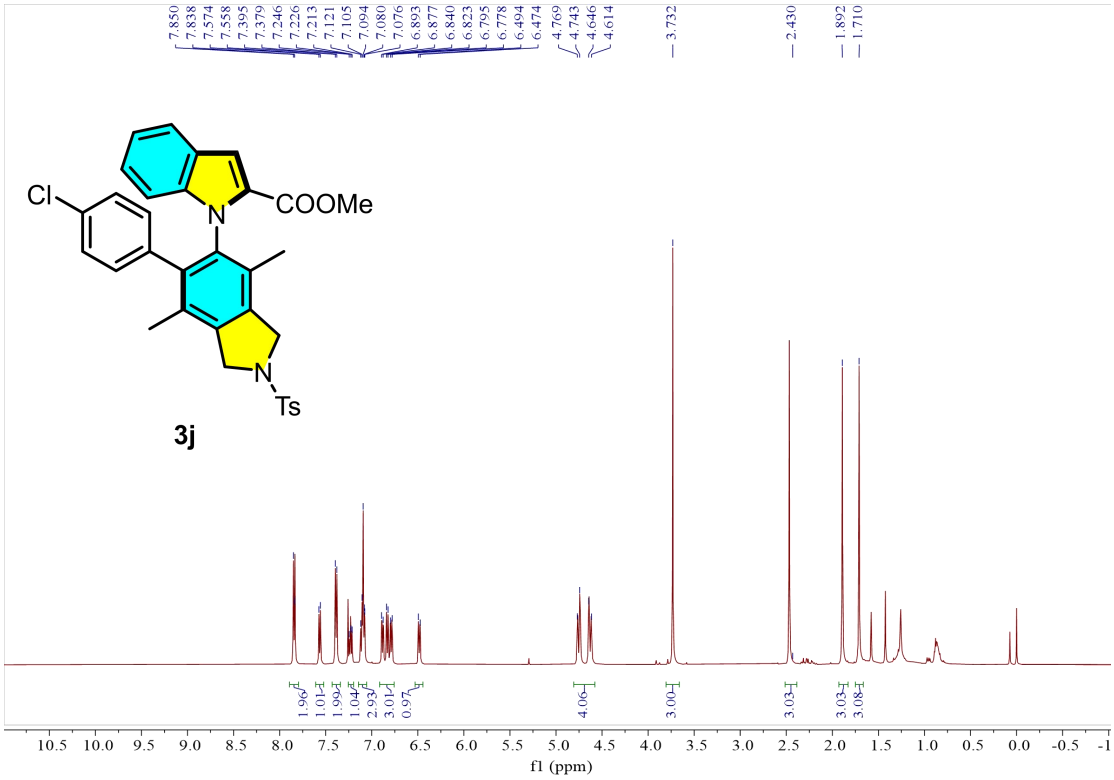
14.112
f1 (ppm)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7.105
7.094
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7.076
6.893
6.877
6.840
6.823
6.795
6.778
6.494
6.474
4.769
4.743
4.646
4.614
3.732
2.430
1.892
1.710
Cl
COOMe
N
N
Ts
1.96
1.01
1.99
1.04
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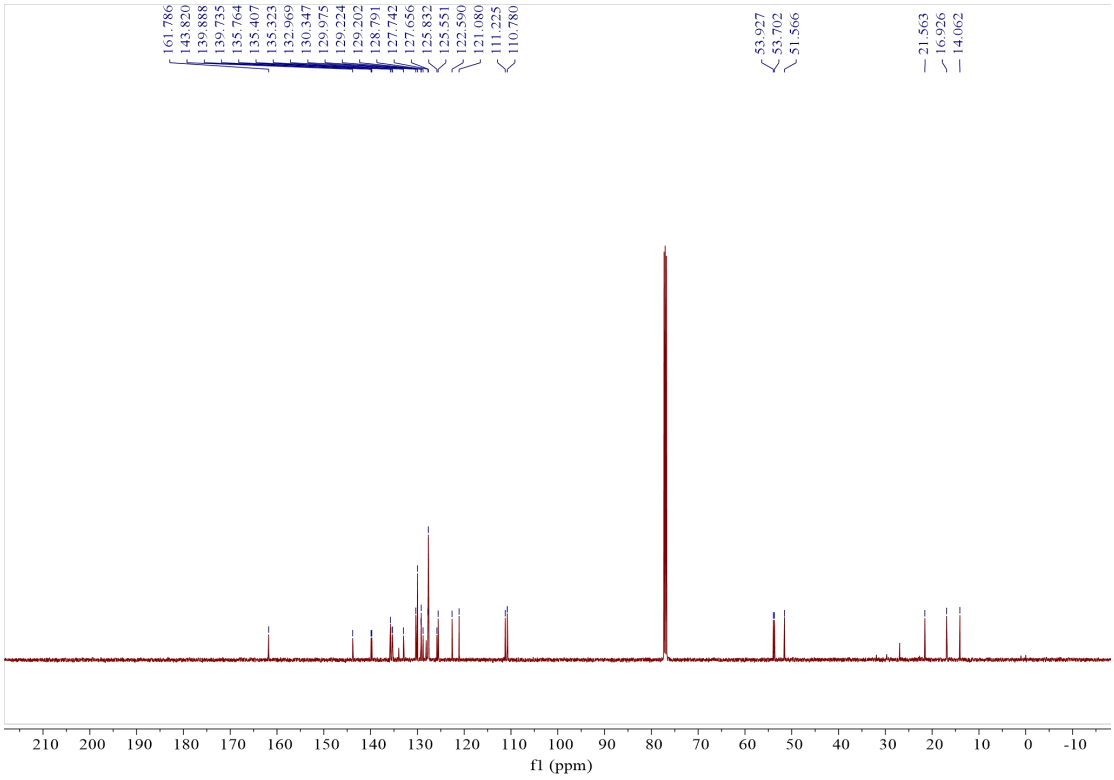
3.01
0.97
4.06
3.00
3.03
3.03
3.08
f1 (ppm)

3j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128.791
127.742
127.656
125.832
125.551
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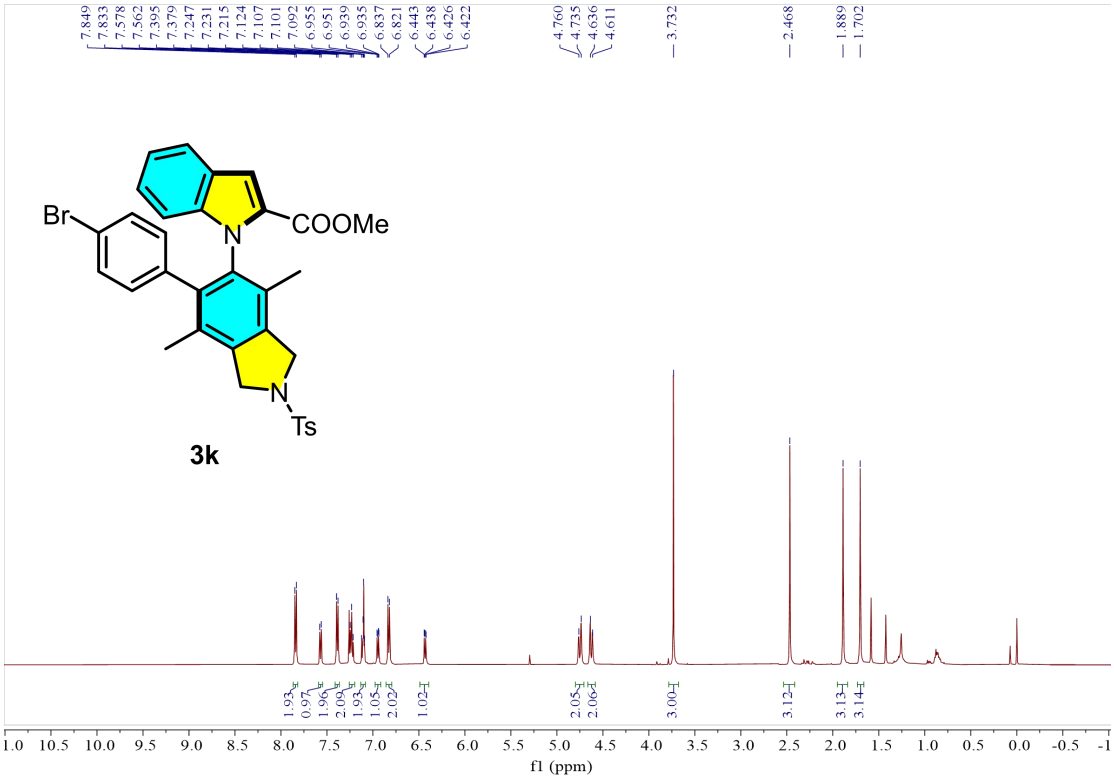
14.062
f1 (ppm)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7.379
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7.231
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7.101
7.092
6.955
6.951
6.939
6.935
6.837
6.821
6.443
6.438
6.426
6.422
4.760
4.735
4.636
4.611
3.732
2.468
1.889
1.702
Br
N
COOMe
N
Ts
3k
1.93
0.97
1.96
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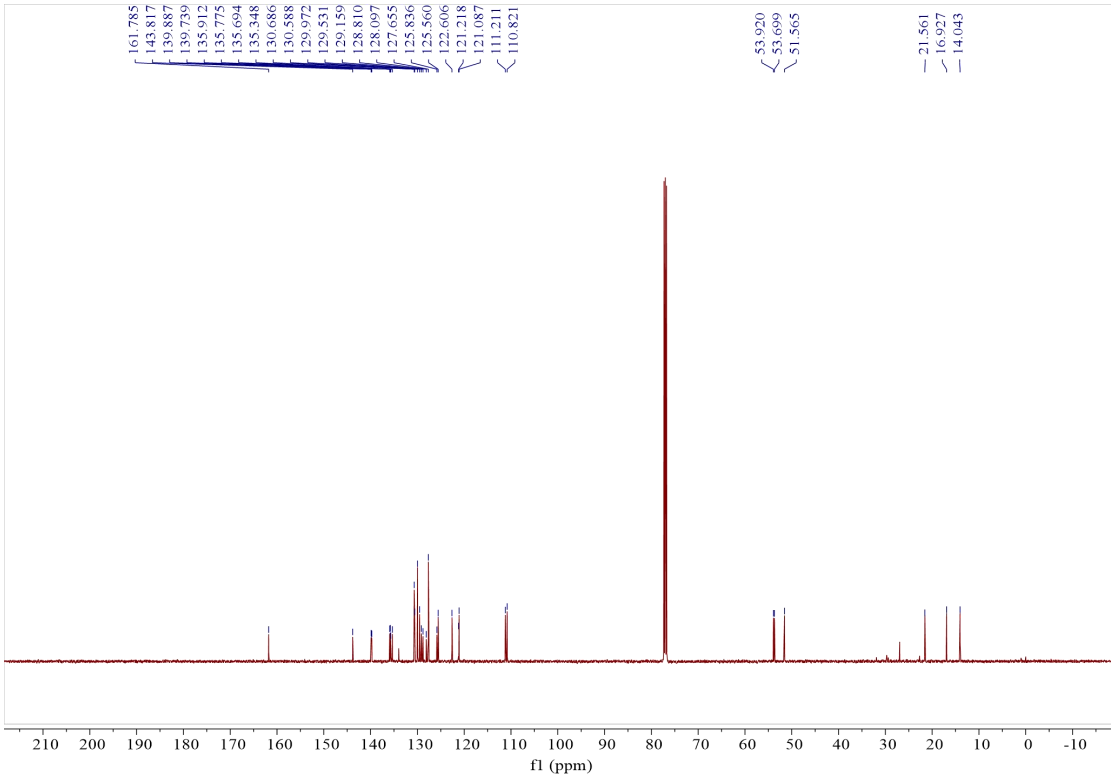
2.02
1.02
2.05
2.06
3.00
3.12
3.13
3.14
f1 (ppm)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129.159
128.810
128.097
127.655
125.836
125.560
122.606
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21.561
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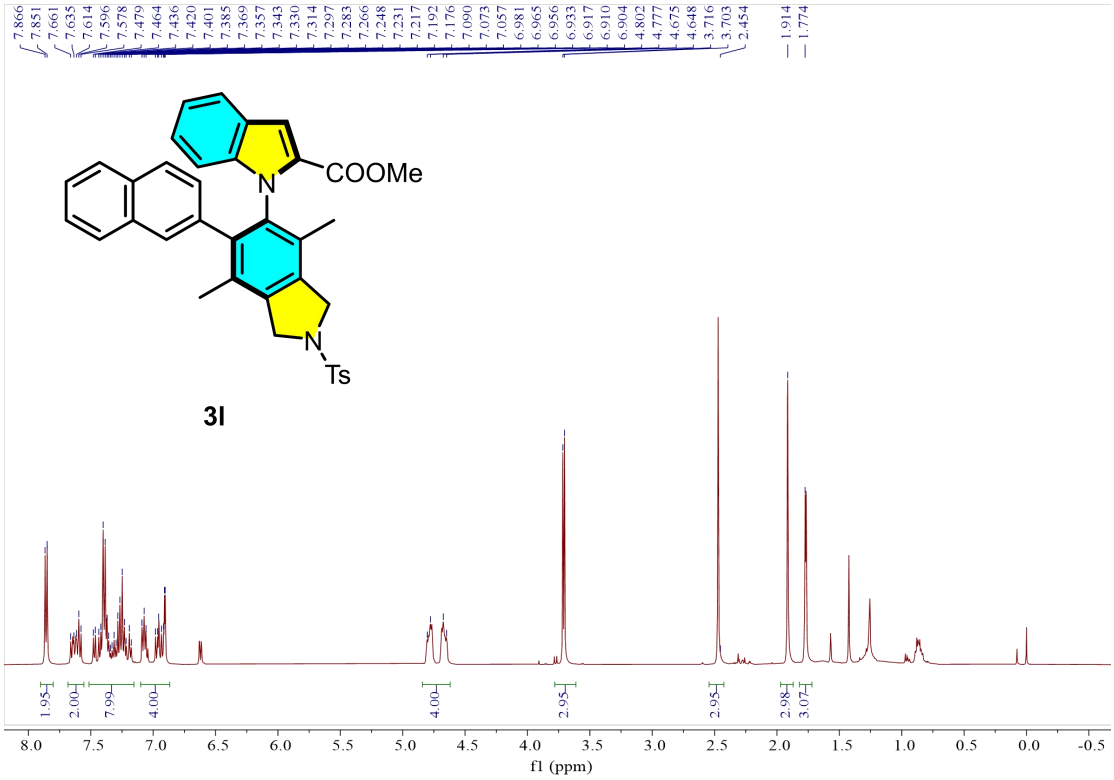
14.043
f1 (ppm)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7.401
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7.369
7.357
7.343
7.330
7.314
7.297
7.283
7.266
7.248
7.231
7.217
7.192
7.176
7.090
7.073
7.057
6.981
6.965
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6.933
6.917
6.910
6.904
4.802
4.777
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4.648
3.716
3.703
2.454
1.914
1.774
COOMe
N
N
Ts
3l
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2.00
7.99
4.00
4.00
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3.07
8.0
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7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
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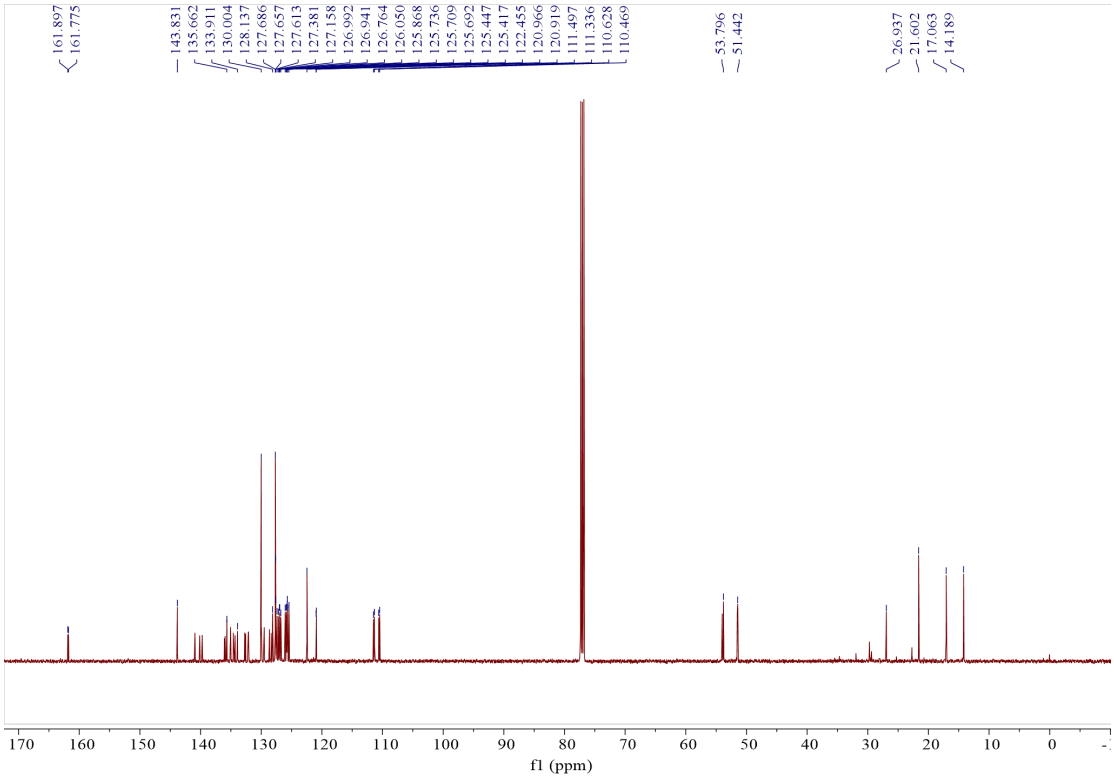
0.5
0.0
-0.5
f1 (ppm)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126.992
126.941
126.764
126.050
125.868
125.736
125.709
125.692
125.447
125.417
122.455
120.966
120.919
111.497
111.336
110.628
110.469
53.796
51.442
26.937
21.602
17.063
14.189
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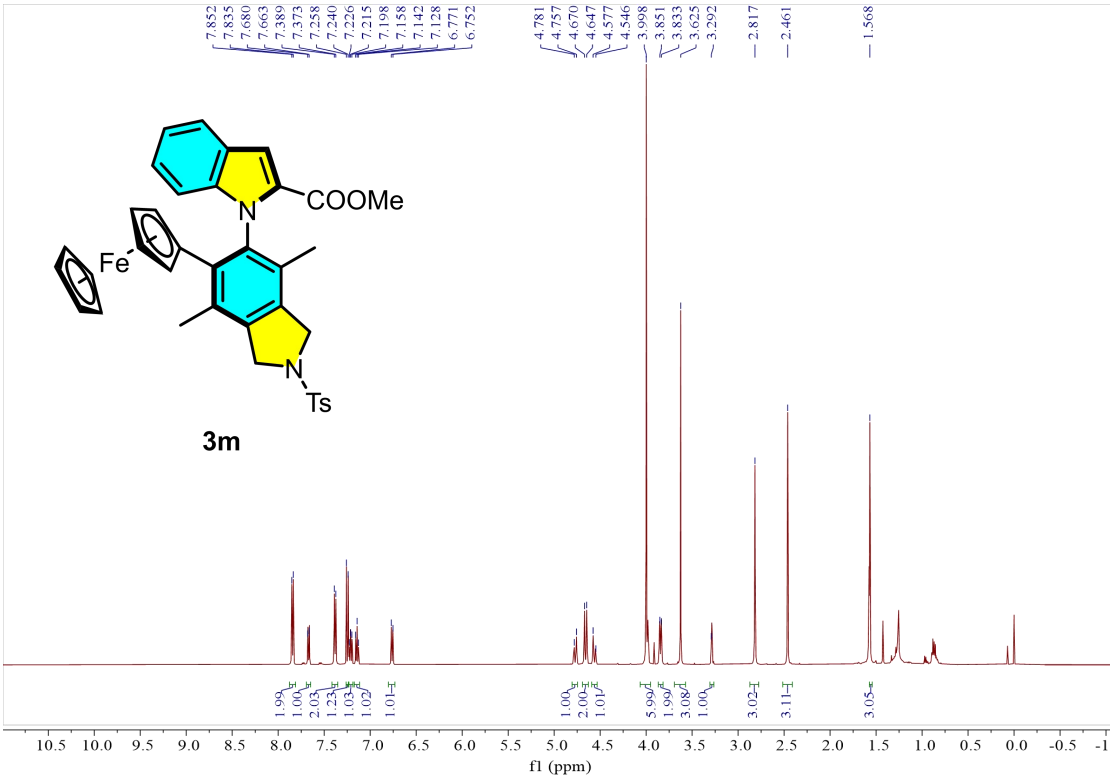
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.757
4.670
4.647
4.577
4.546
3.998
3.851
3.833
3.625
3.292
2.817
2.461
1.568
COOMe
N
Fe
N
Ts
3m
1.99
1.00
2.03
1.23
1.03
1.02
1.01
1.00
2.00
1.01
5.99
1.99
3.08
1.00
3.02
3.11
3.05
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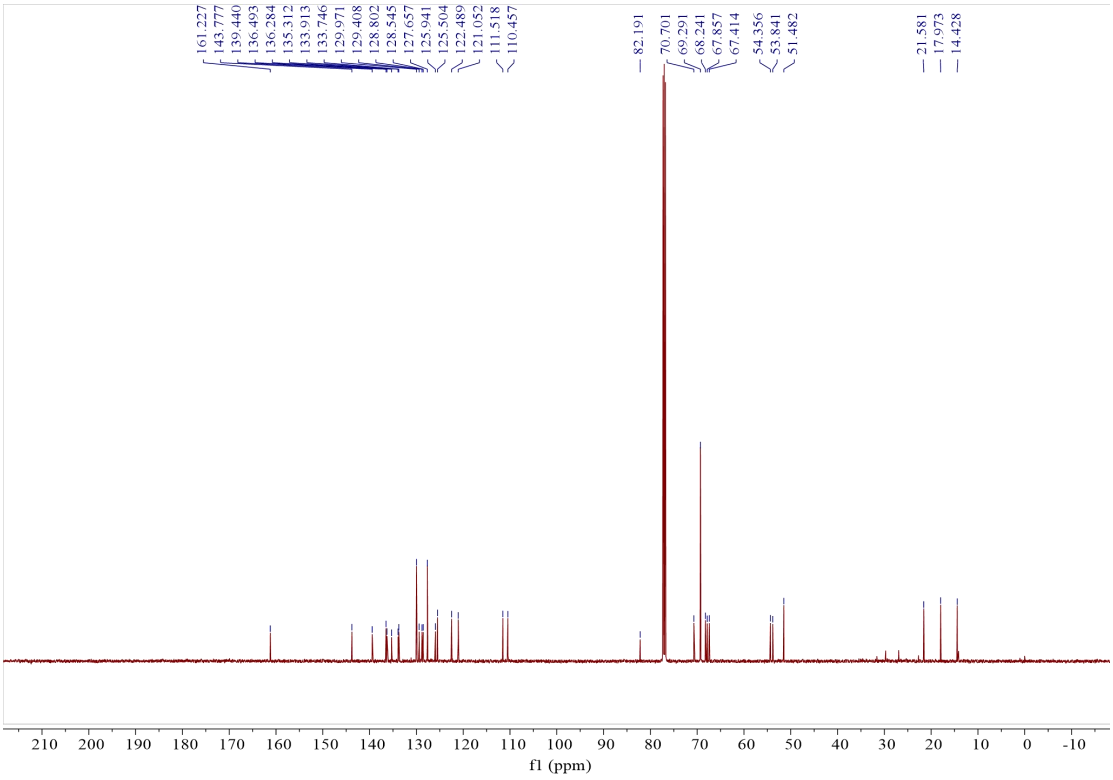
f1 (ppm)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128.545
127.657
125.941
125.504
122.489
121.052
111.518
110.457
82.191
70.701
69.291
68.241
67.857
67.414
54.356
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21.581
17.973
14.428
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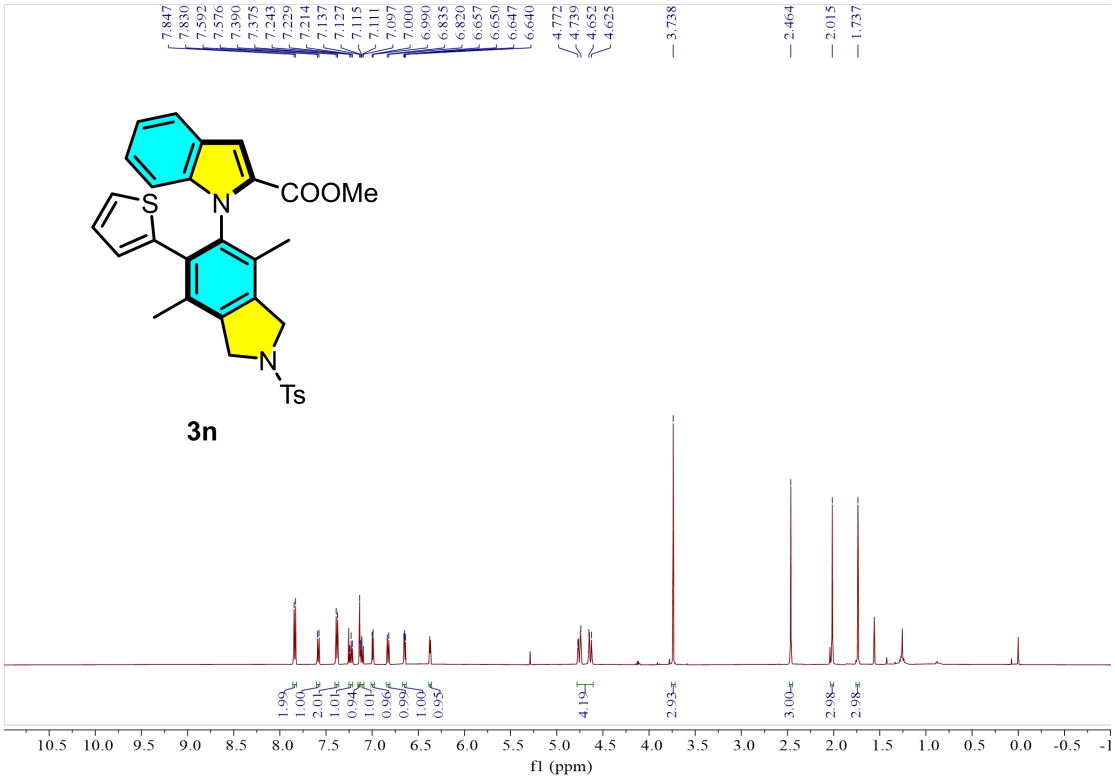
f1 (ppm)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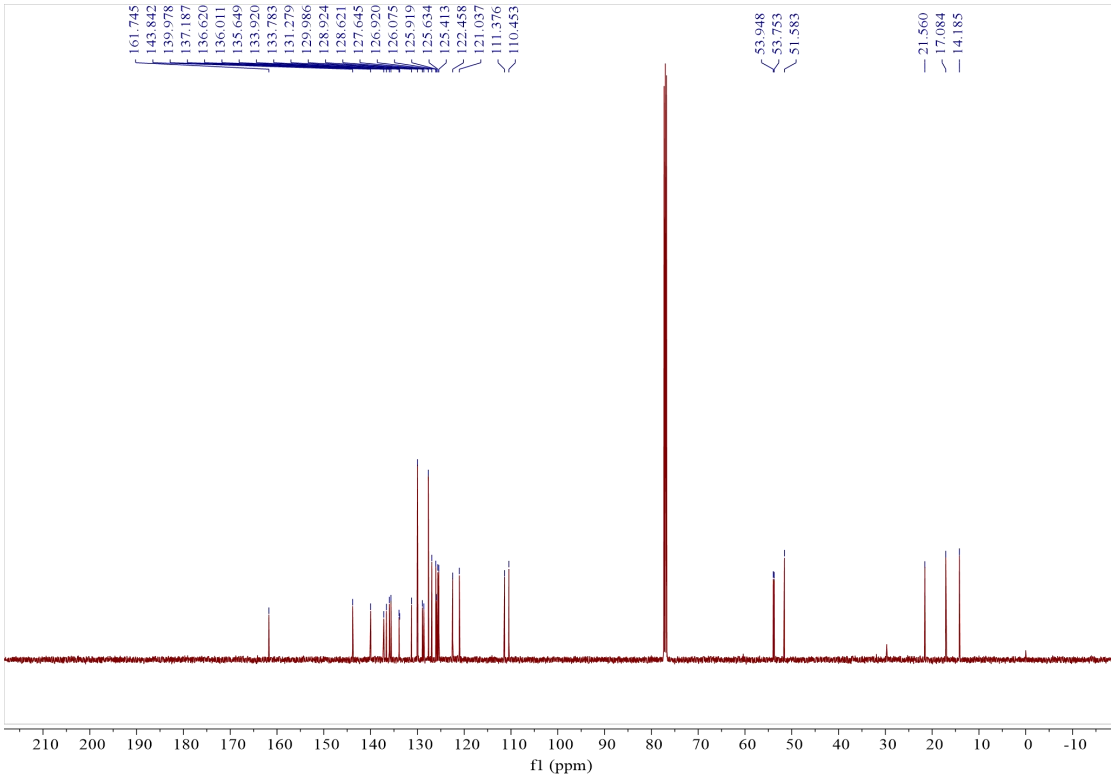
7.097
7.000
6.990
6.835
6.820
6.657
6.650
6.647
6.640
4.772
4.739
4.652
4.625
3.738
2.464
2.015
1.737
COOMe
S
N
N
Ts
1.99
1.00
2.01
1.01
0.94
1.01
0.96
0.99
1.00
0.95
4.19
2.93
3.00
2.98
2.98
f1 (ppm)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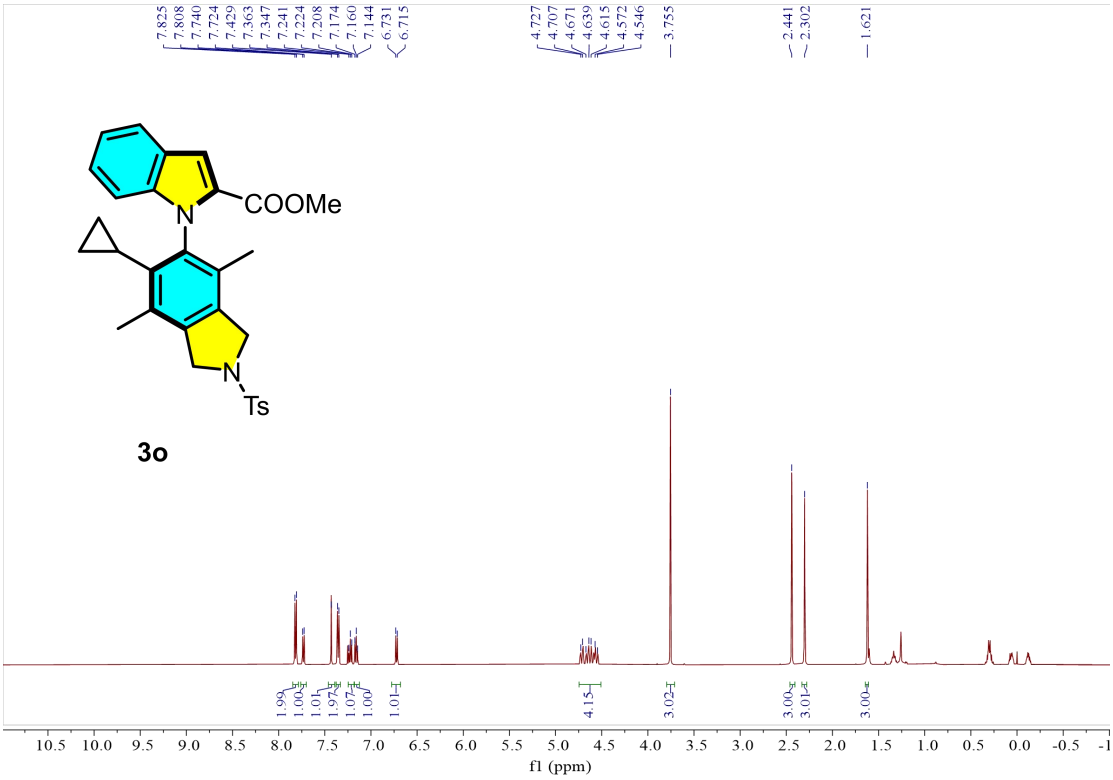
127.645
126.920
126.075
125.919
125.634
125.413
122.458
121.037
111.376
110.453
53.948
53.753
51.583
21.560
17.084
14.185
f1 (ppm)

3n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7.241
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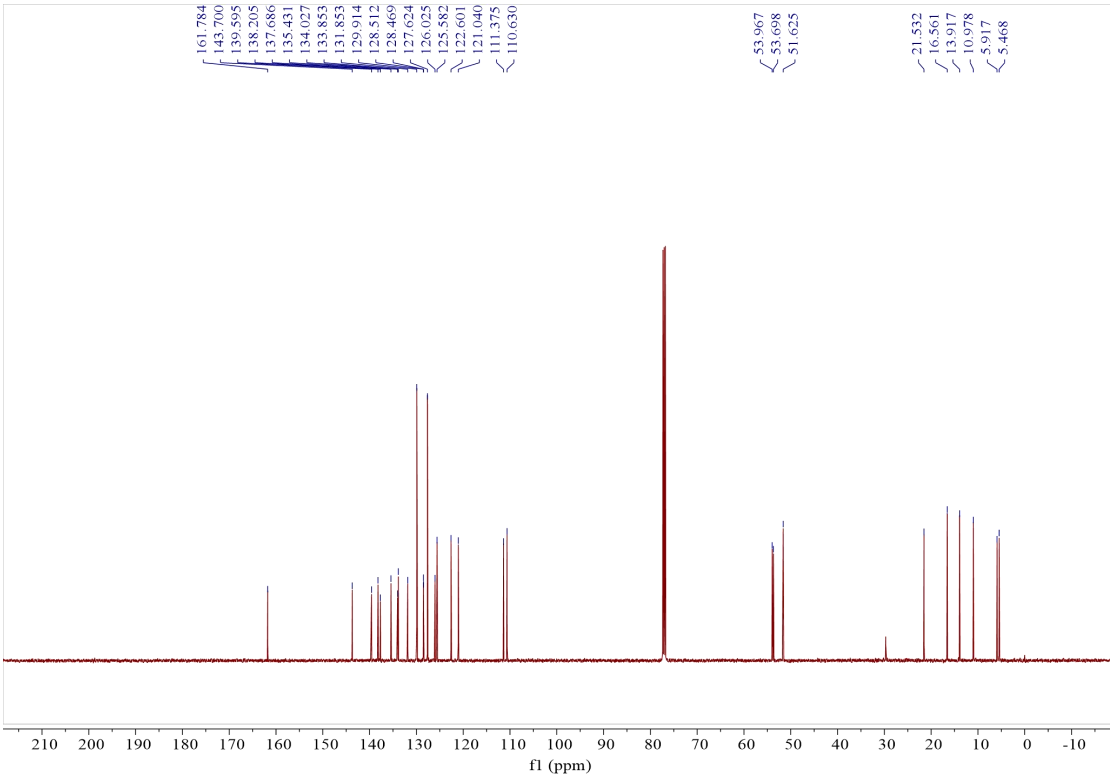
7.144
6.731
6.715
4.727
4.707
4.671
4.639
4.615
4.572
4.546
3.755
2.441
2.302
1.621
COOMe
N
N
Ts
3o
1.99
1.00
1.01
1.97
1.07
1.00
1.01
4.15
3.02
3.00
3.01
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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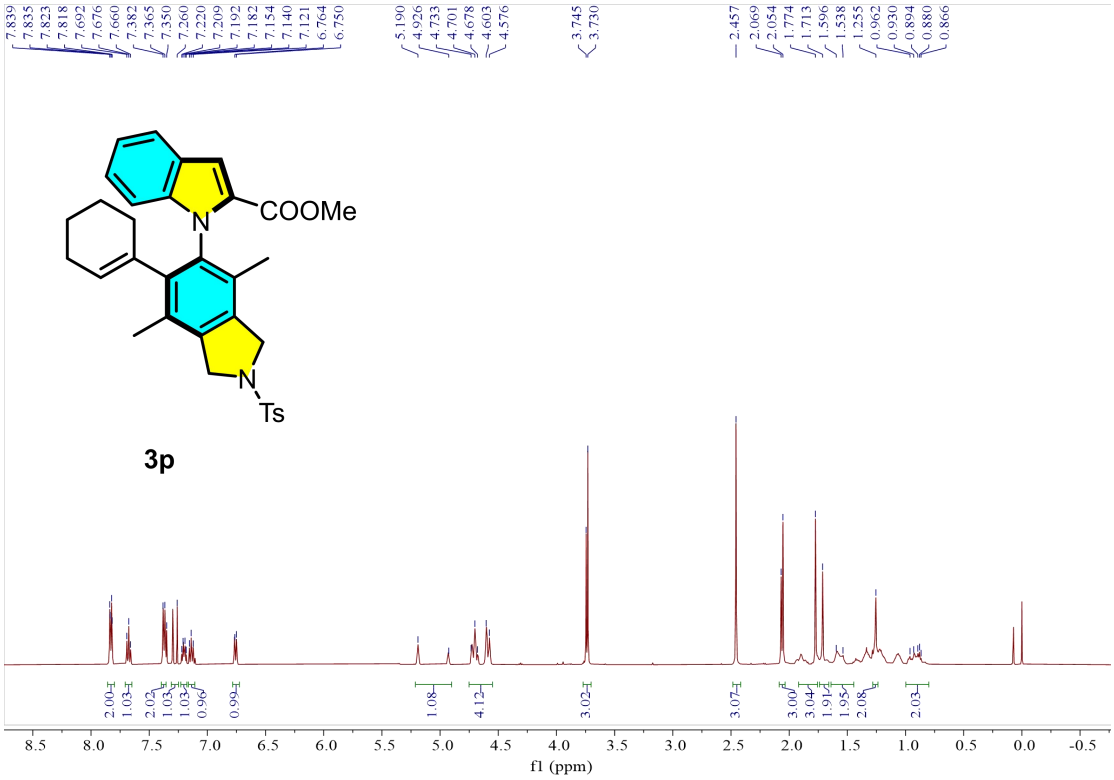
127.624
126.025
125.582
122.601
121.040
111.375
110.630
53.967
53.698
51.625
21.532
16.561
13.917
10.978
5.917
5.468
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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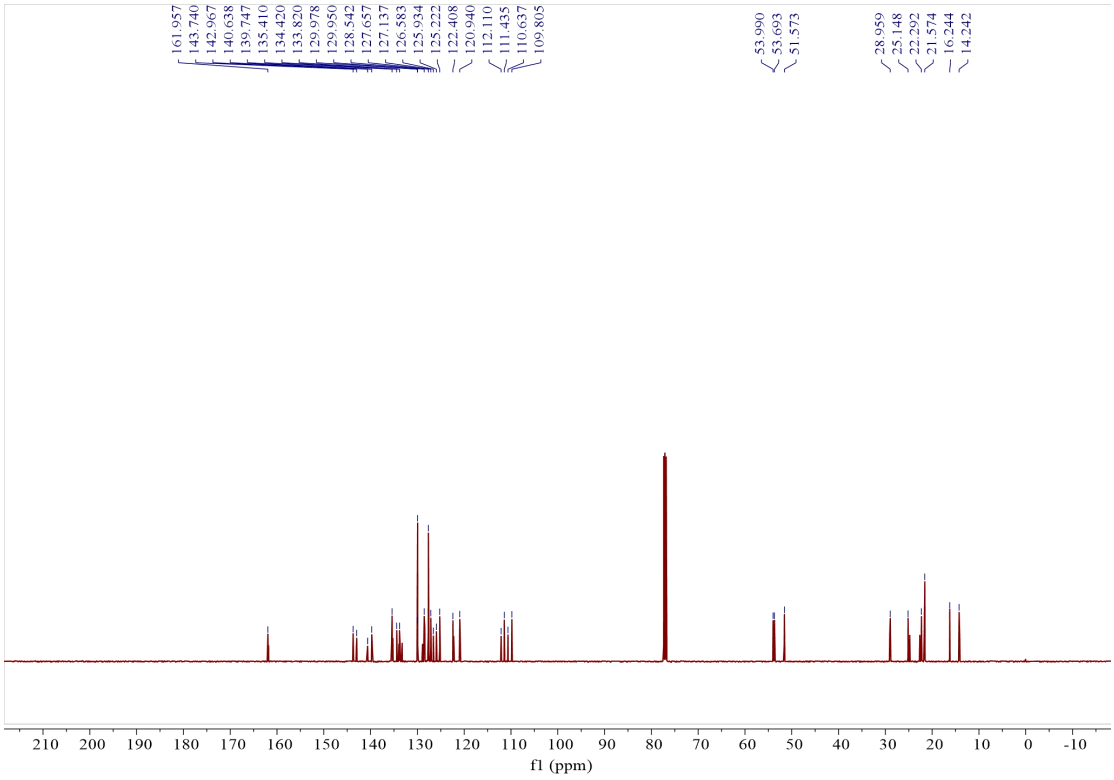
7.220
7.209
7.192
7.182
7.154
7.140
7.121
6.764
6.750
5.190
4.926
4.733
4.701
4.678
4.603
4.576
3.745
3.730
2.457
2.069
2.054
1.774
1.713
1.596
1.538
1.255
0.962
0.930
0.894
0.880
0.866
COOMe
N
N
Ts
3p
2.00
1.03
2.02
1.03
1.03
0.96
0.99
1.08
4.12
3.02
3.07
3.00
3.04
1.91
1.95
2.08
2.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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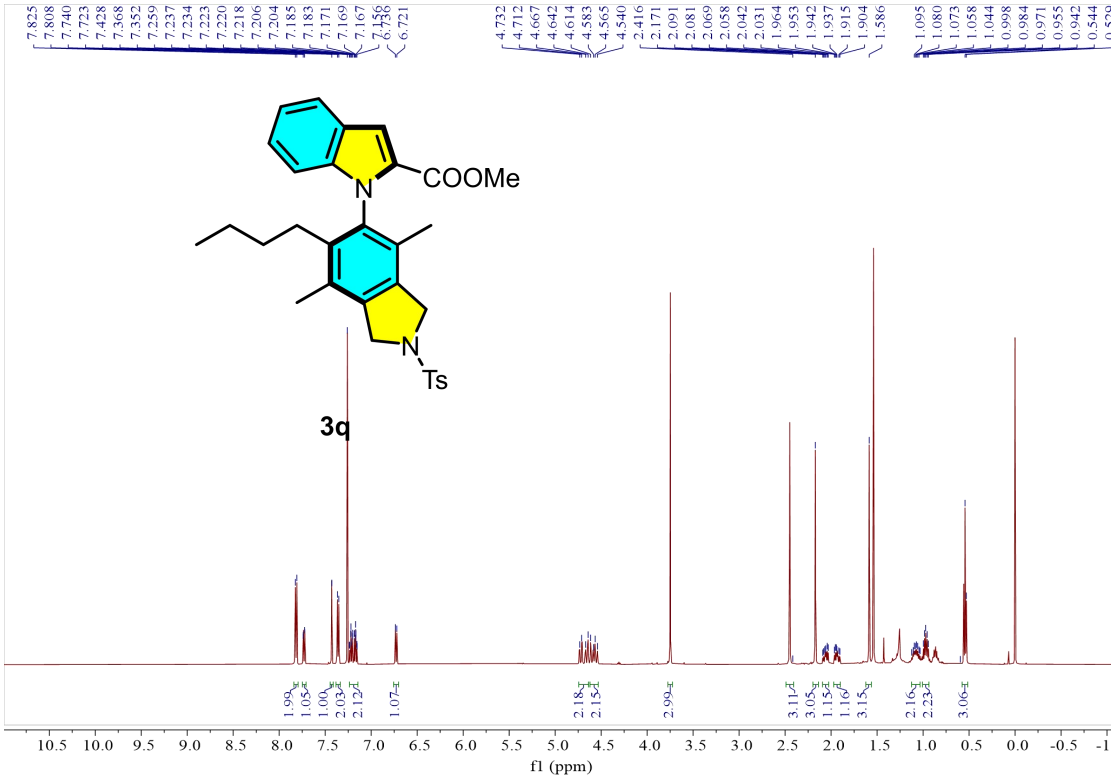
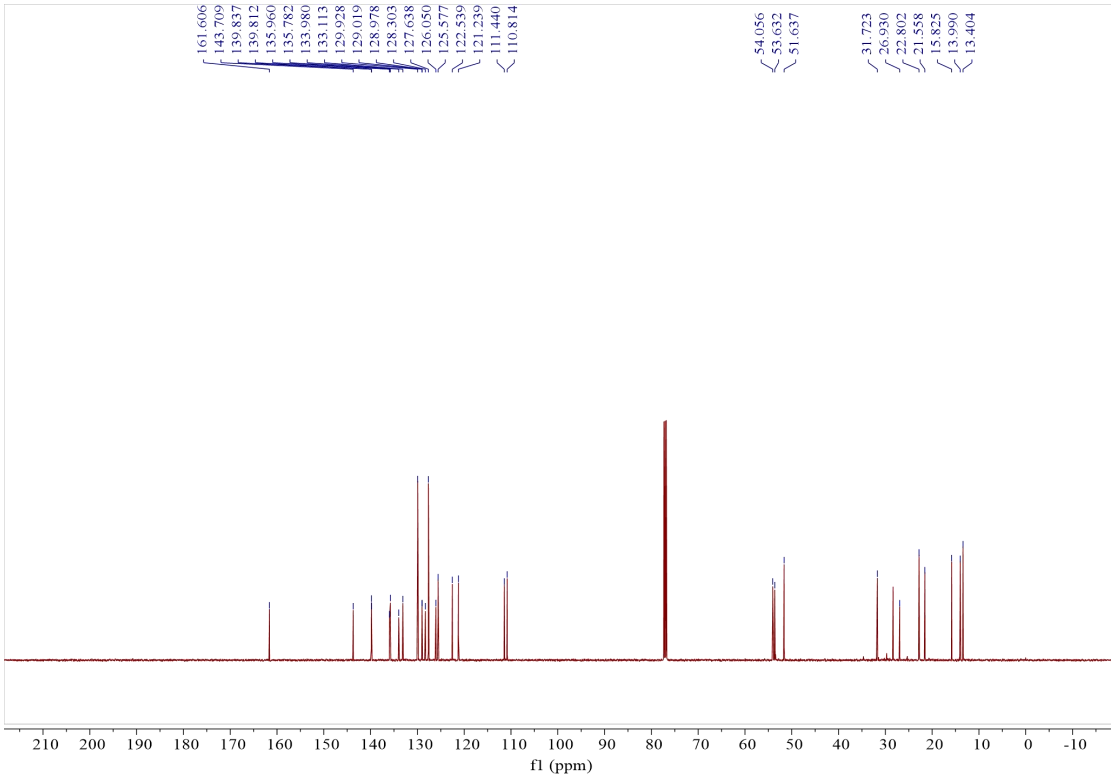
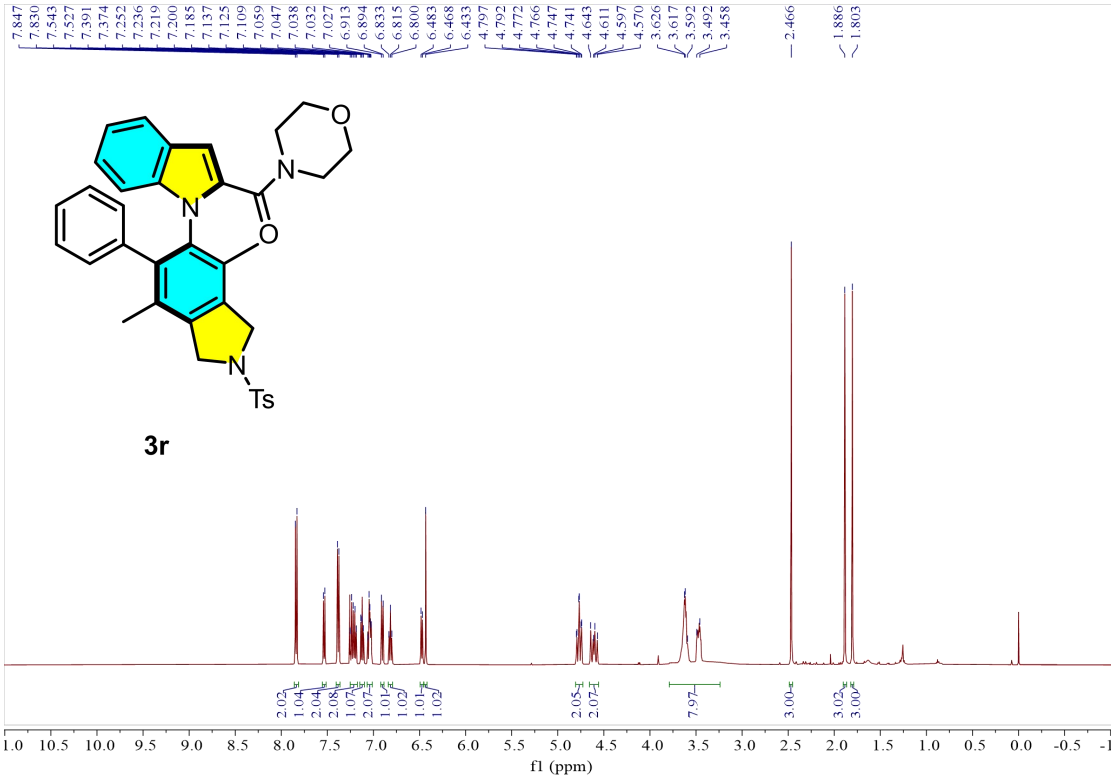
127.137
126.583
125.934
125.222
122.408
120.940
112.110
111.435
110.637
109.805
53.990
53.693
51.573
28.959
25.148
22.292
21.574
16.244
14.242
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


COOMe
N
N
Ts
3q
f1 (ppm)


f1 (ppm)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7.527
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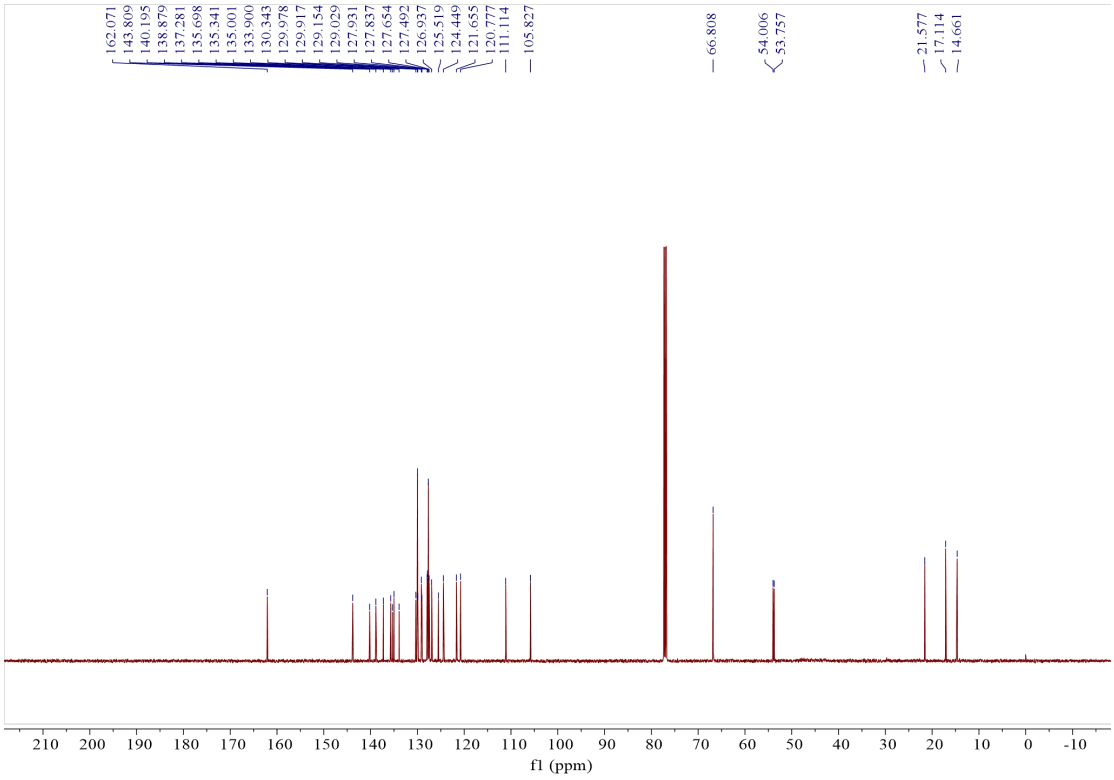
7.374
7.252
7.236
7.219
7.200
7.185
7.137
7.125
7.109
7.059
7.047
7.038
7.032
7.027
6.913
6.894
6.833
6.815
6.800
6.483
6.468
6.433
4.797
4.792
4.772
4.766
4.747
4.741
4.643
4.611
4.597
4.570
3.626
3.617
3.592
3.492
3.458
2.466
1.886
1.803
O
N
N
O
N
Ts
2.02
1.04
2.04
2.08
1.07
2.07
1.01
1.02
1.01
1.02
2.05
2.07
7.97
3.00
3.02
3.00
f1 (ppm)

3r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129.029
127.931
127.837
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127.492
126.937
125.519
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111.114
105.827
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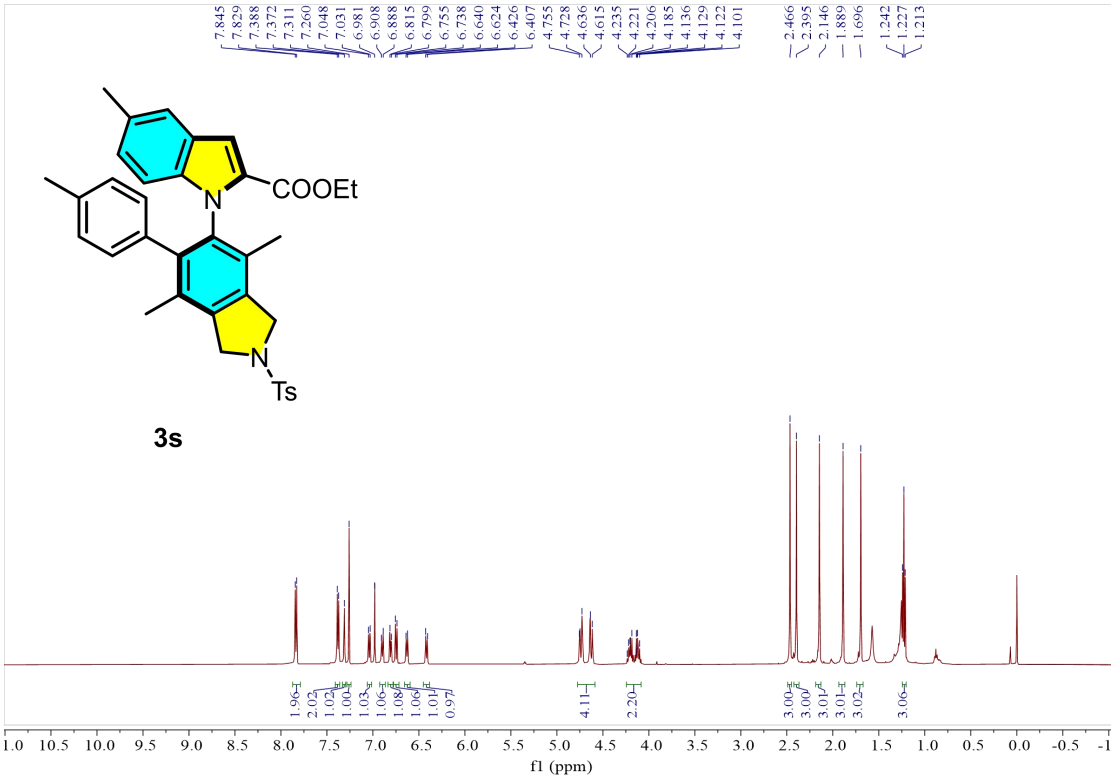
54.006
53.757
21.577
17.114
14.661
f1 (ppm)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6.755
6.738
6.640
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6.426
6.407
4.755
4.728
4.636
4.615
4.235
4.221
4.206
4.185
4.136
4.129
4.122
4.101
2.466
2.395
2.146
1.889
1.696
1.242
1.227
1.213
COOEt
N
N
Ts
3s
1.96
2.02
1.02
1.00
1.03
1.06
1.08
1.06
1.01
0.97
4.11
2.20
3.00
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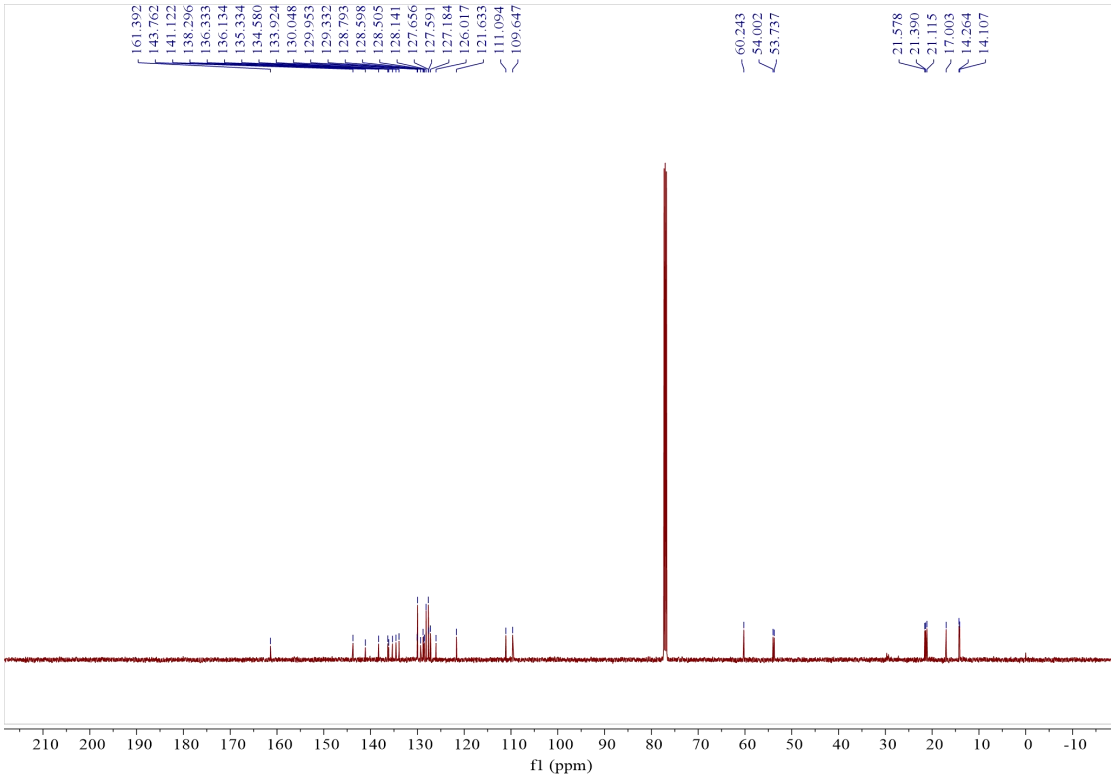
3.01
3.01
3.02
3.06
f1 (ppm)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129.332
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128.505
128.141
127.656
127.591
127.184
126.017
121.633
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21.578
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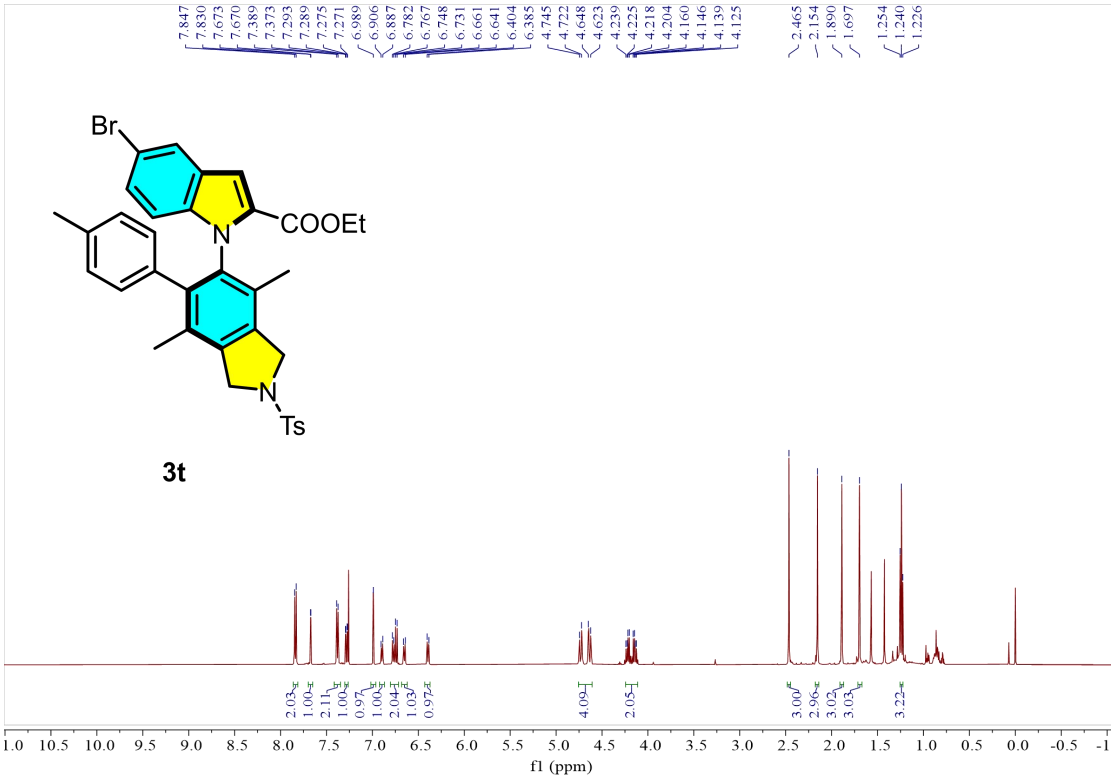
14.107
f1 (ppm)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6.906
6.887
6.782
6.767
6.748
6.731
6.661
6.641
6.404
6.385
4.745
4.722
4.648
4.623
4.239
4.225
4.218
4.204
4.160
4.146
4.139
4.125
2.465
2.154
1.890
1.697
1.254
1.240
1.226
Br
COOEt
N
N
Ts
2.03
1.00
2.11
1.00
0.97
1.00
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4.09
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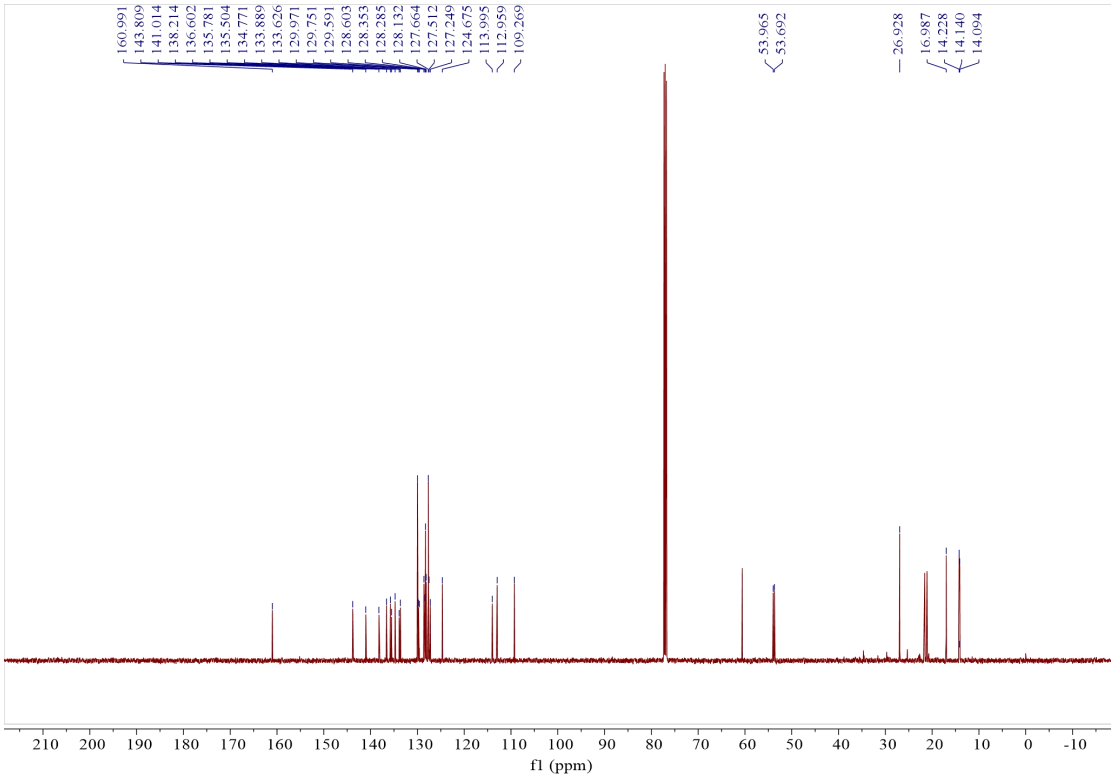
3.00
2.96
3.02
3.03
3.22
f1 (ppm)

3t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134.771
133.889
133.626
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129.591
128.603
128.353
128.285
128.132
127.664
127.512
127.249
124.675
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109.269
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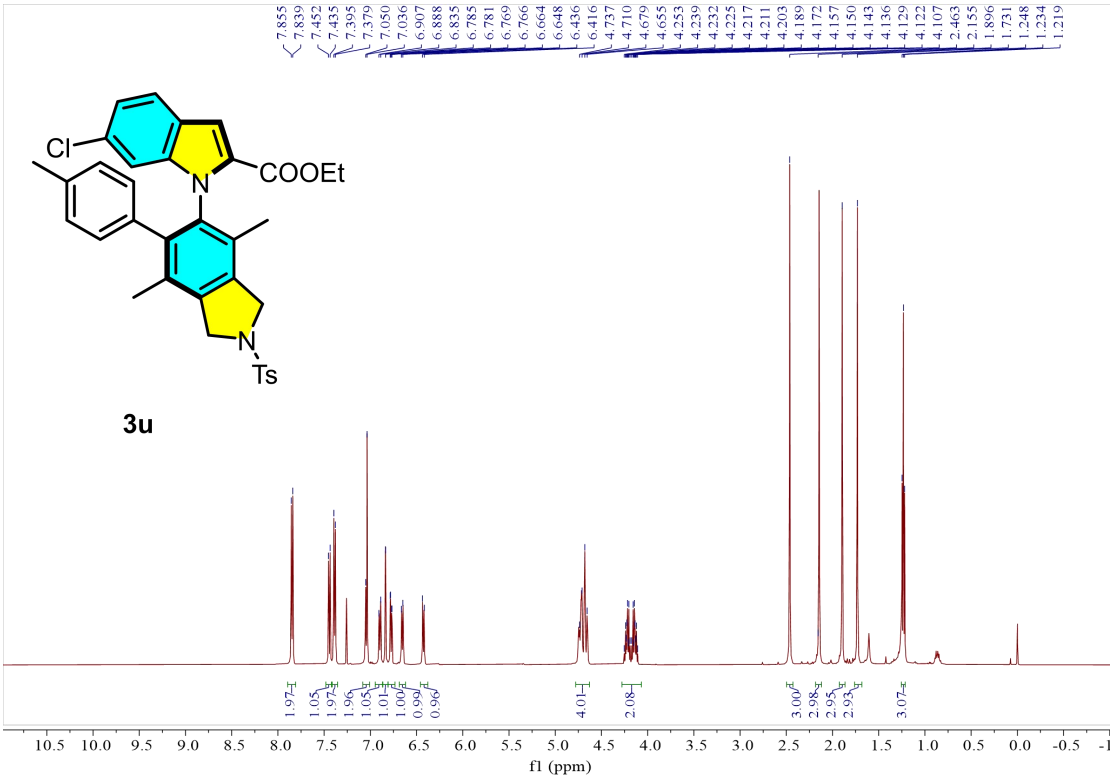
14.094
f1 (ppm)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6.781
6.769
6.766
6.664
6.648
6.436
6.416
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4.710
4.679
4.655
4.253
4.239
4.232
4.225
4.217
4.211
4.203
4.189
4.172
4.157
4.150
4.143
4.136
4.129
4.122
4.107
2.463
2.155
1.896
1.731
1.248
1.234
1.219
Cl
N
COOEt
N
Ts
3u
1.97
1.05
1.97
1.96
1.03
1.01
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2.08
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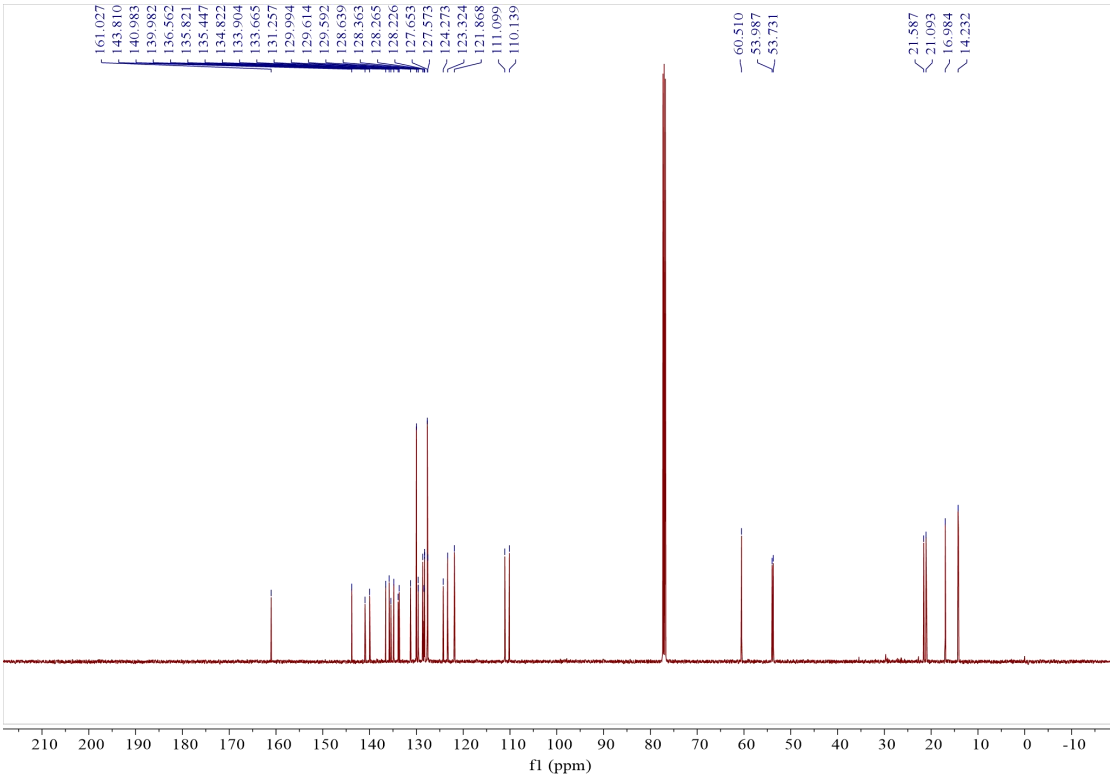
2.98
2.95
2.93
3.07
f1 (ppm)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128.639
128.363
128.265
128.226
127.655
127.573
124.273
123.324
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60.510
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21.093
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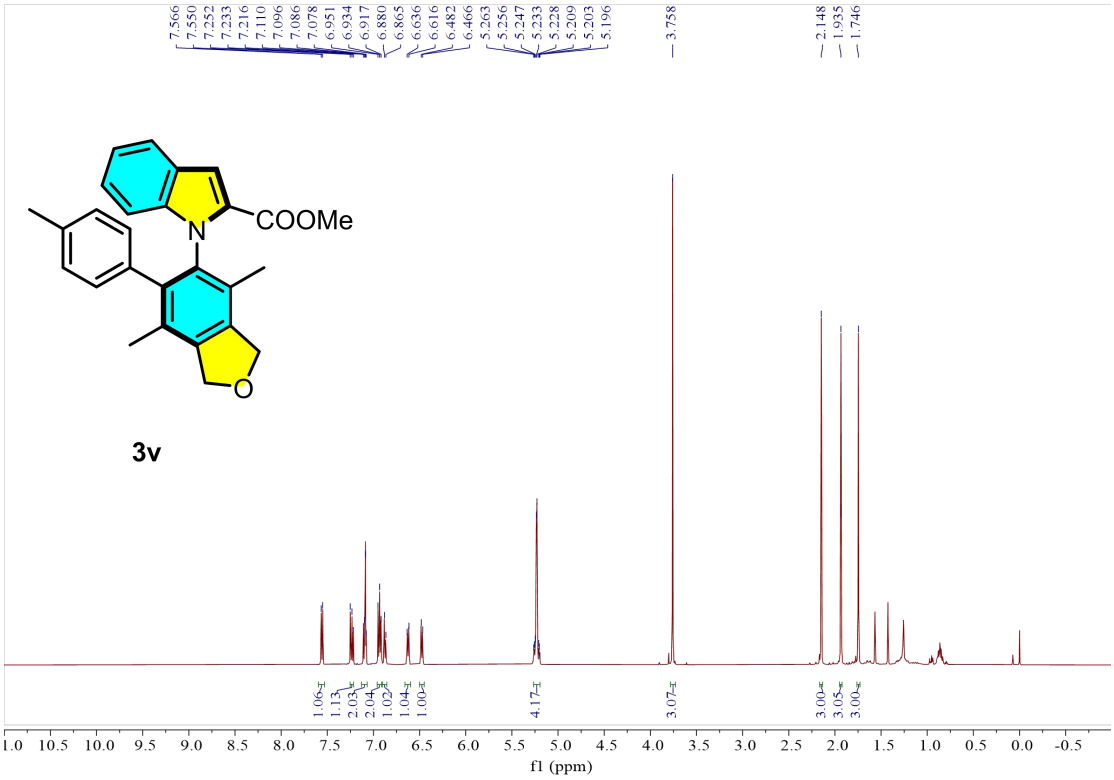
14.232
f1 (ppm)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7.086
7.078
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6.934
6.917
6.880
6.865
6.636
6.616
6.482
6.466
5.263
5.256
5.247
5.233
5.228
5.209
5.203
5.196
3.758
2.148
1.935
1.746
COOMe
N
O
1.06
1.13
2.03
2.04
1.02
1.04
1.00
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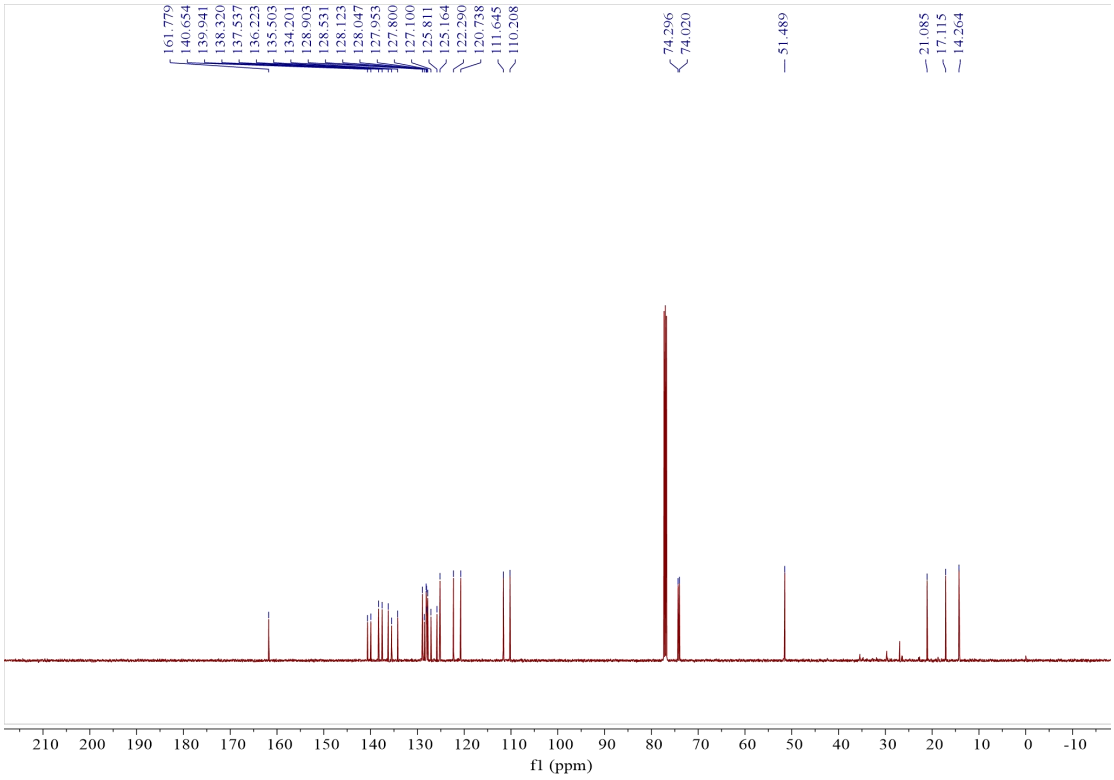
3.07
3.00
3.05
3.00
f1 (ppm)

3v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128.123
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127.953
127.800
127.100
125.811
125.164
122.290
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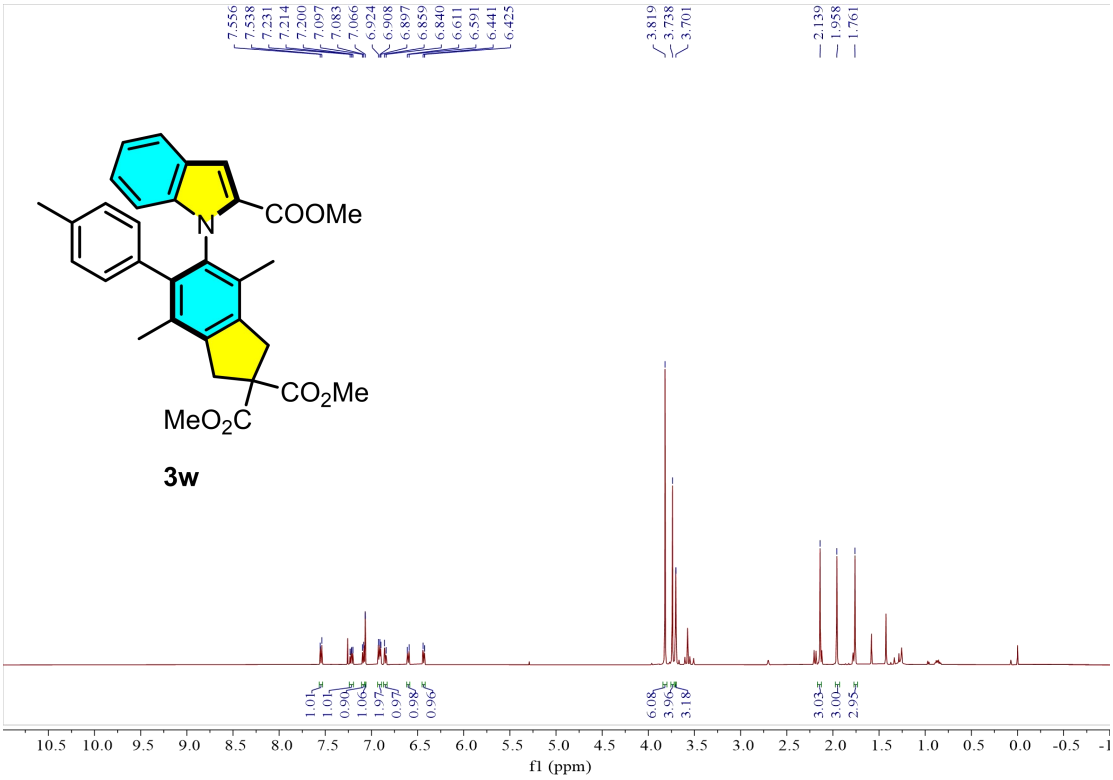
74.296
74.020
51.489
21.085
17.115
14.264
f1 (ppm)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7.083
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6.908
6.897
6.859
6.840
6.611
6.591
6.441
6.425
3.819
3.738
3.701
2.139
1.958
1.761
COOMe
N
CO2Me
MeO2C
3w
1.01
1.01
0.90
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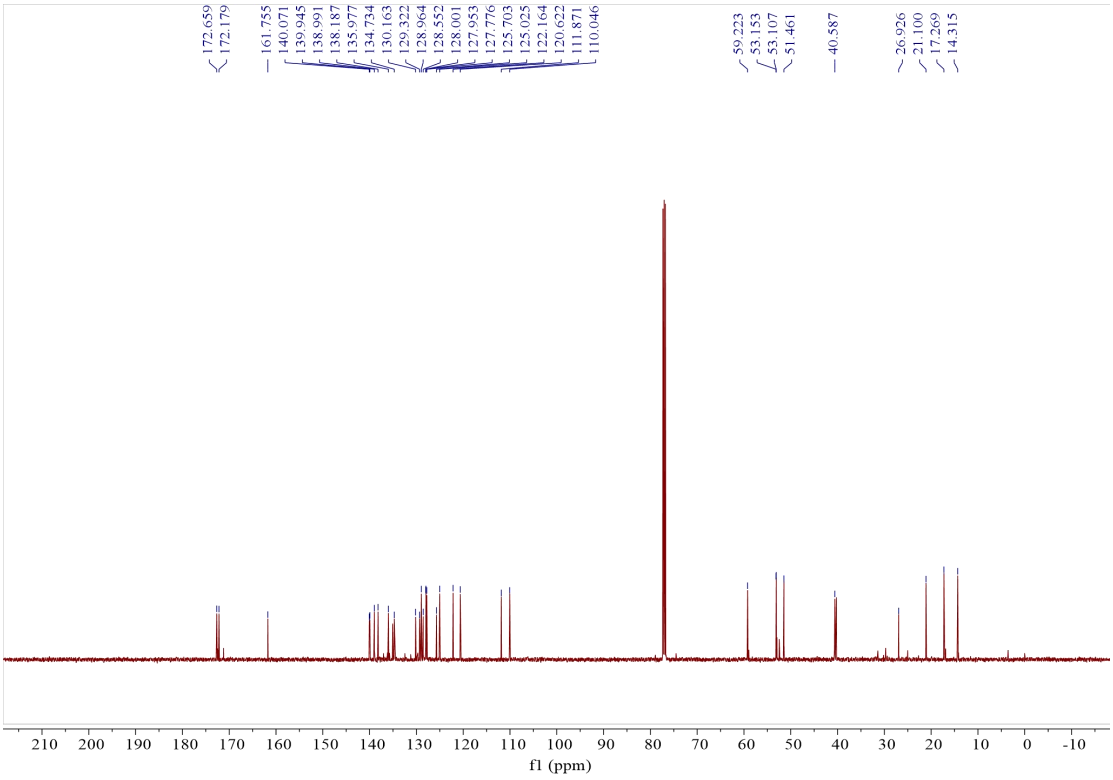
0.98
0.96
6.08
3.96
3.18
3.03
3.00
2.95
f1 (ppm)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129.322
128.964
128.552
128.001
127.953
127.776
125.703
125.025
122.164
120.622
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53.153
53.107
51.461
40.587
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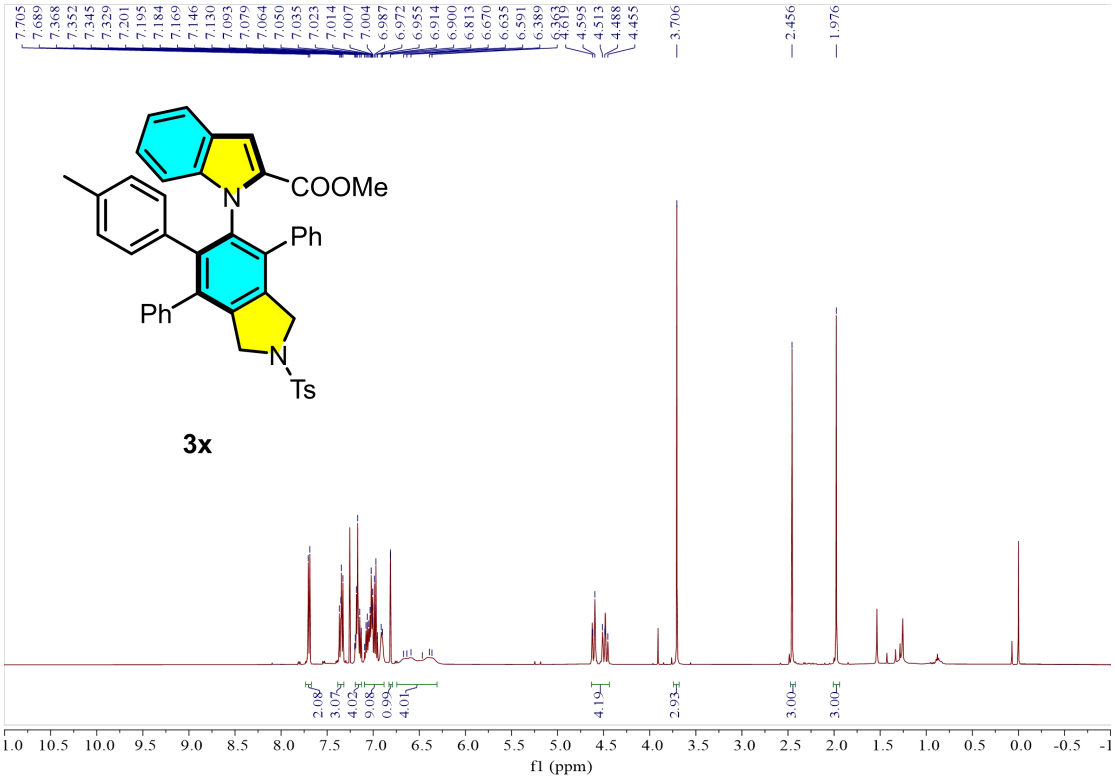
21.100
17.269
14.315
f1 (ppm)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7.079
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7.035
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7.007
7.004
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6.972
6.955
6.914
6.900
6.813
6.670
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6.389
6.363
4.619
4.595
4.513
4.488
4.455
3.706
2.456
1.976
COOMe
N
Ph
Ph
N
Ts
3x
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3.07
4.02
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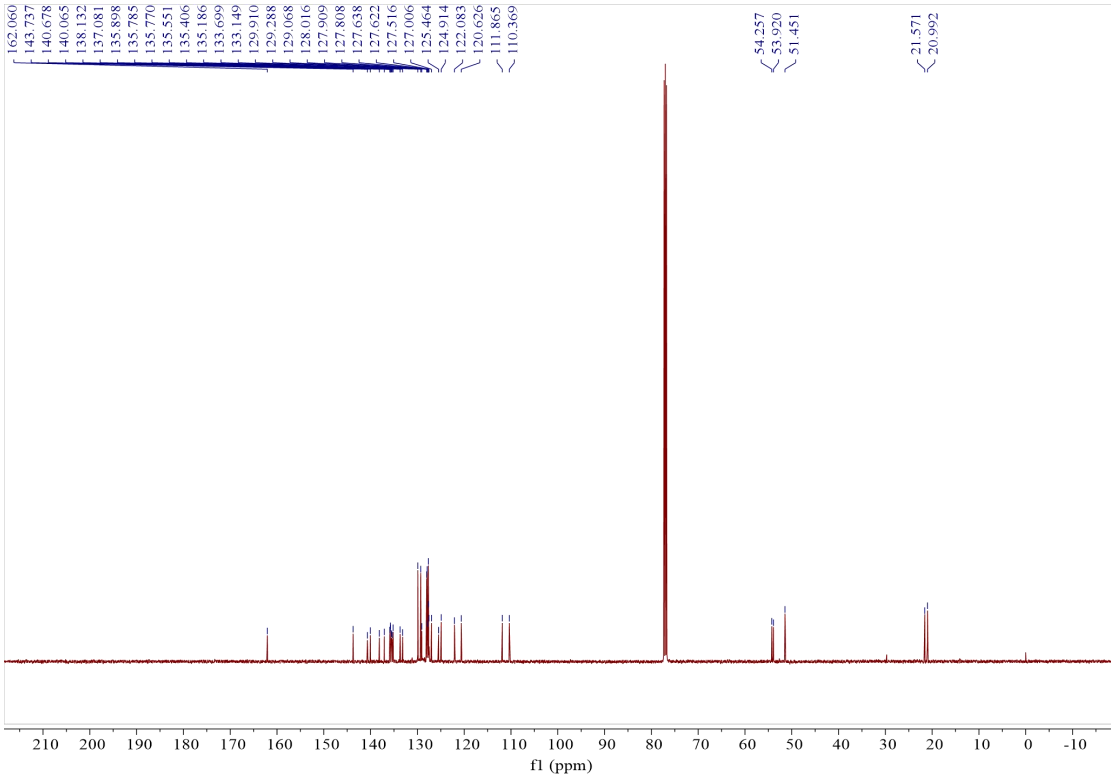
4.19
2.93
3.00
3.00
f1 (ppm)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133.699
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129.910
129.288
129.068
128.016
127.909
127.808
127.638
127.622
127.516
127.006
125.464
124.914
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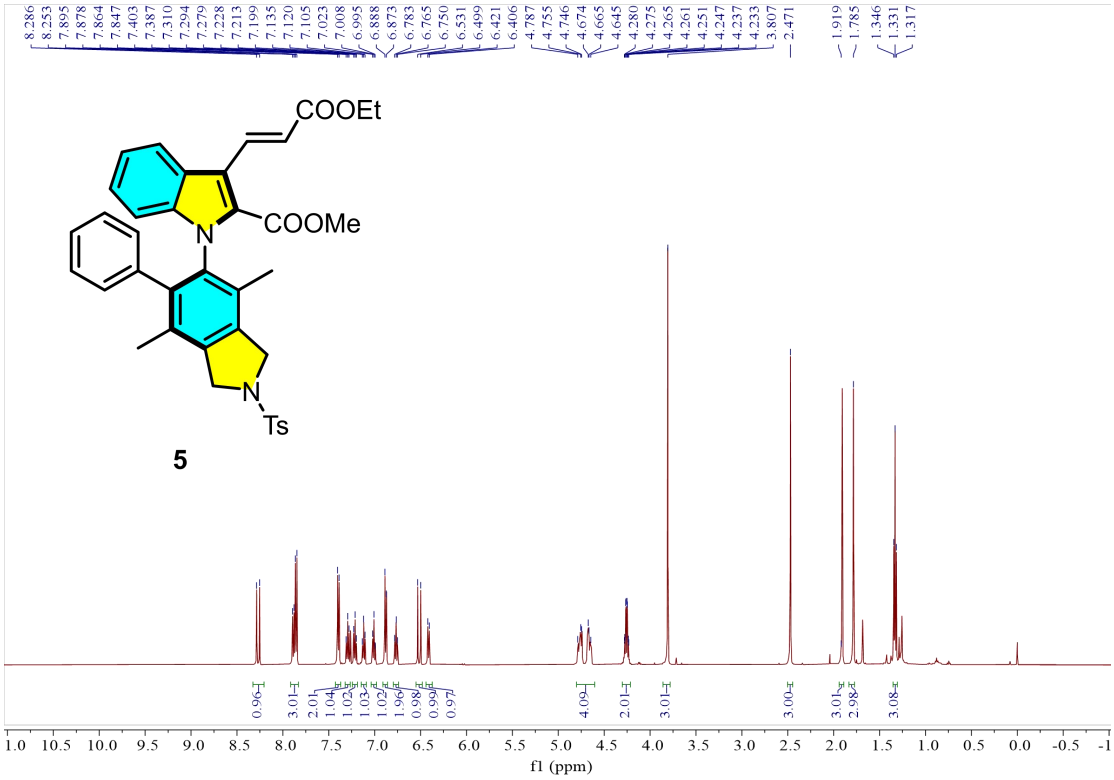
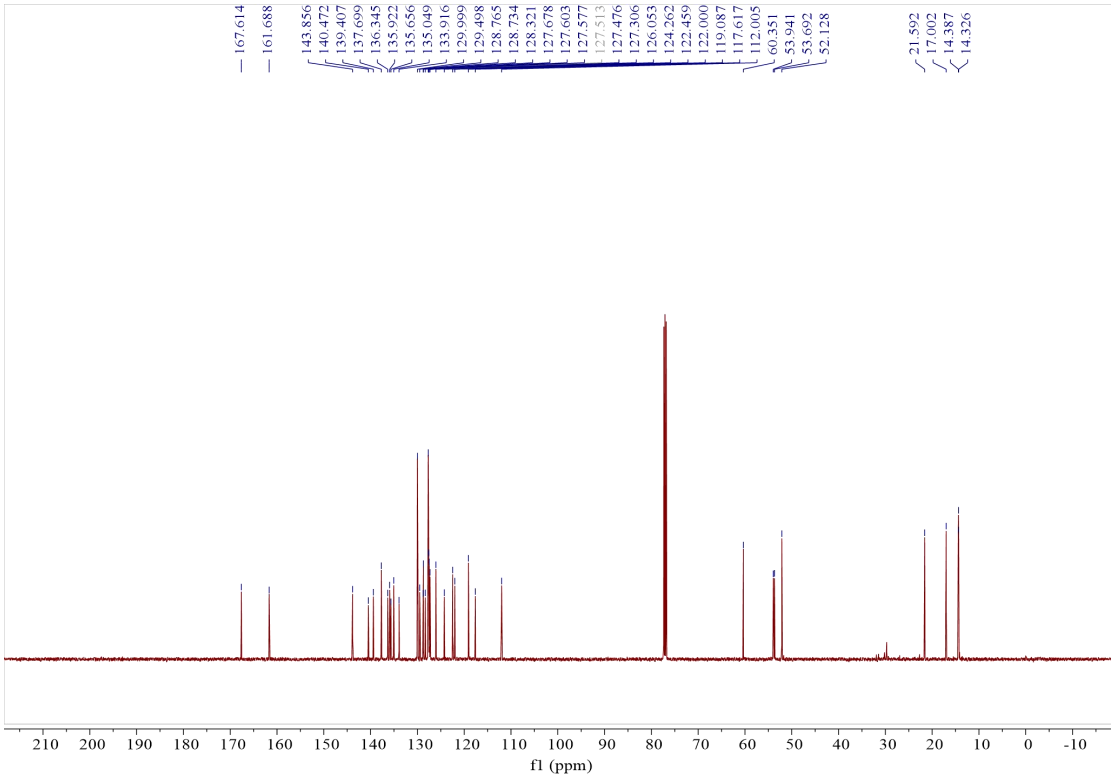
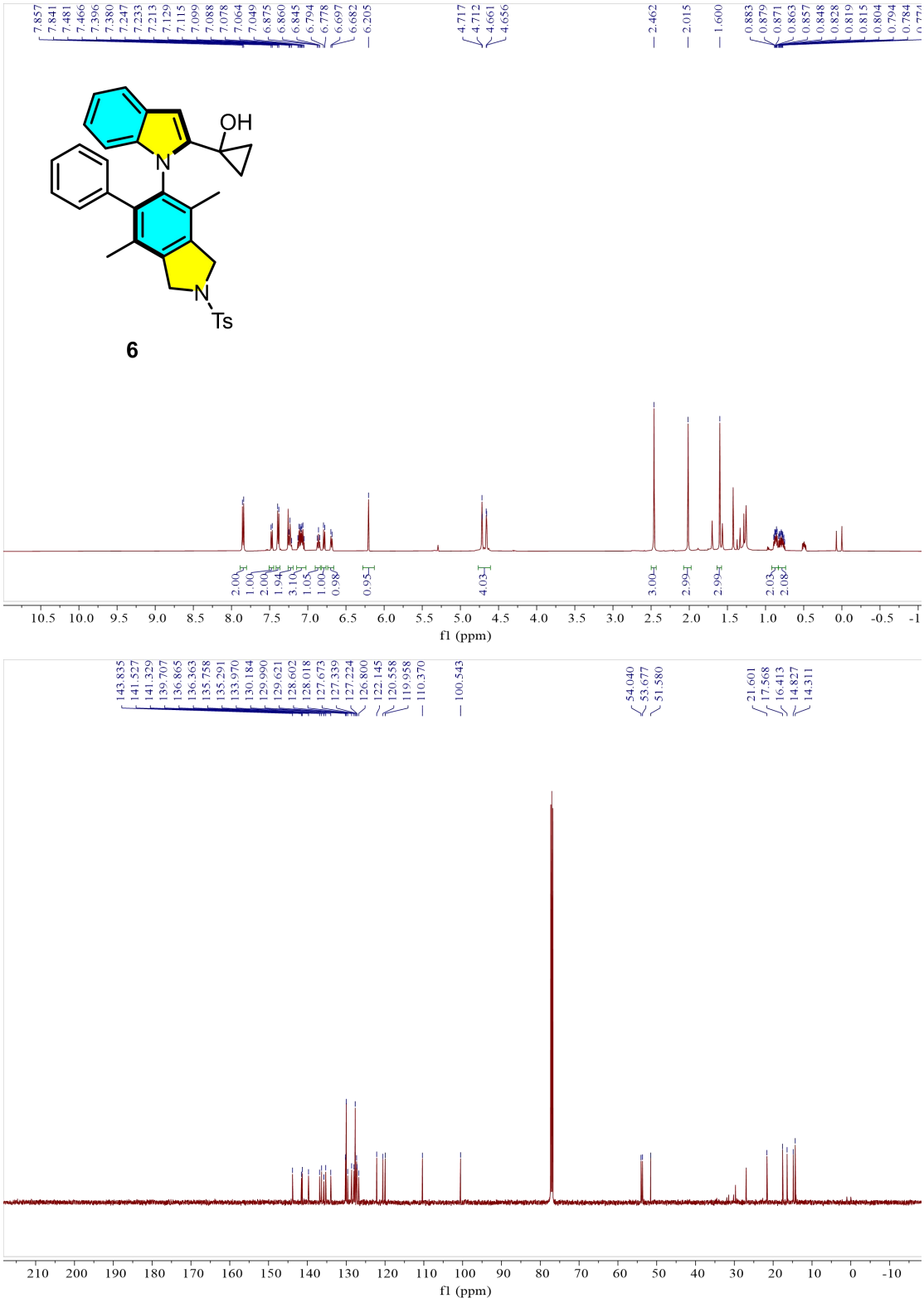
120.626
111.865
110.369
54.257
53.920
51.451
21.571
20.992
f1 (ppm)


COOEt
COOMe
N
N
Ts
5
f1 (ppm)


f1 (ppm)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7.064
7.049
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6.697
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4.717
4.712
4.661
4.656
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2.015
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0.828
0.819
0.815
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0.794
0.784
OH
N
N
Ts
6
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1.00
2.00
1.94
3.10
1.05
1.00
0.98
0.95
4.03
3.00
2.99
2.99
2.03
2.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)
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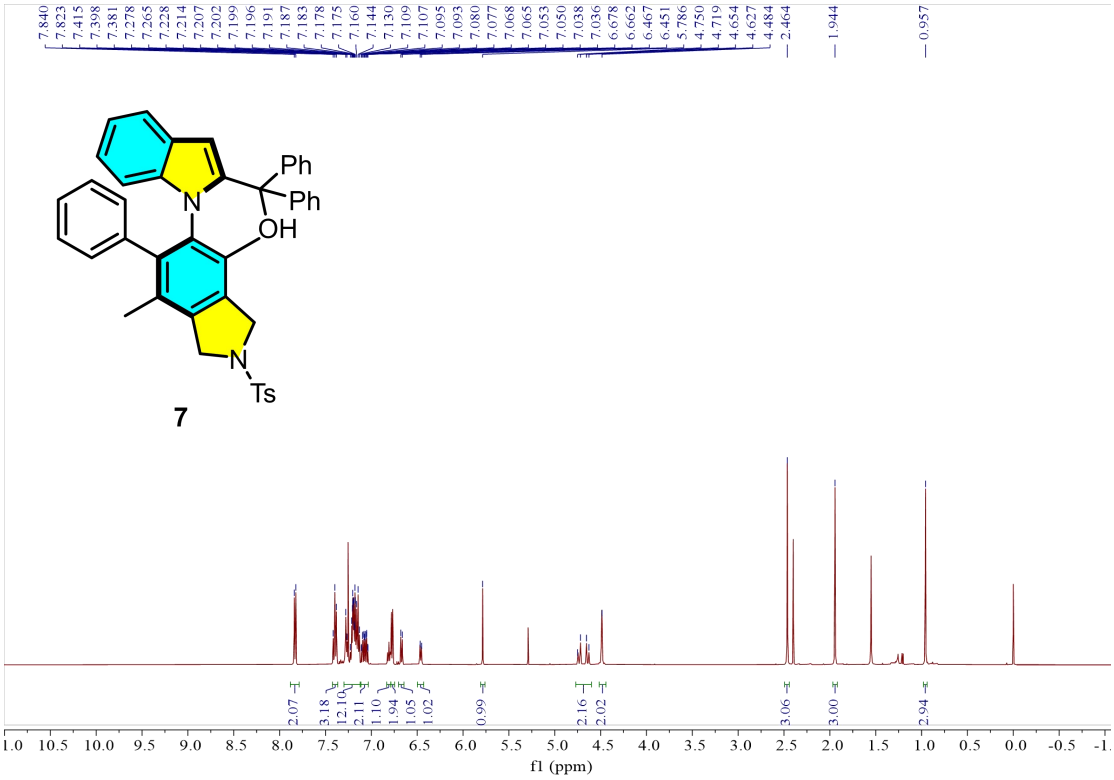
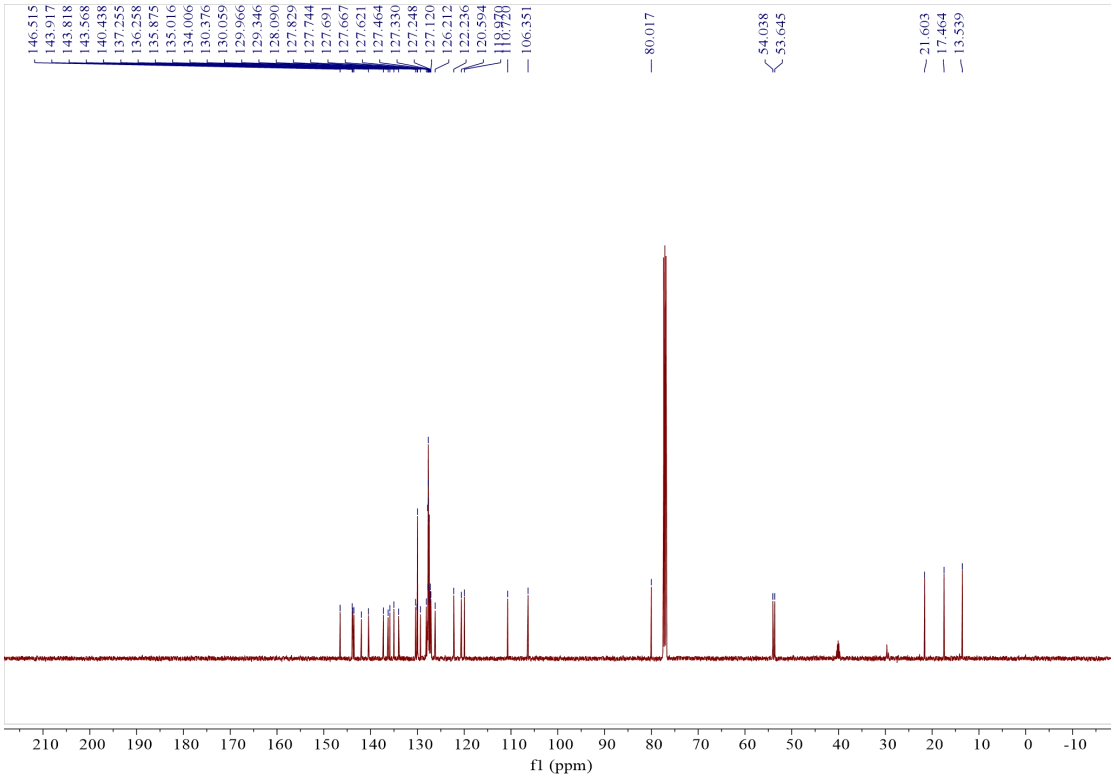
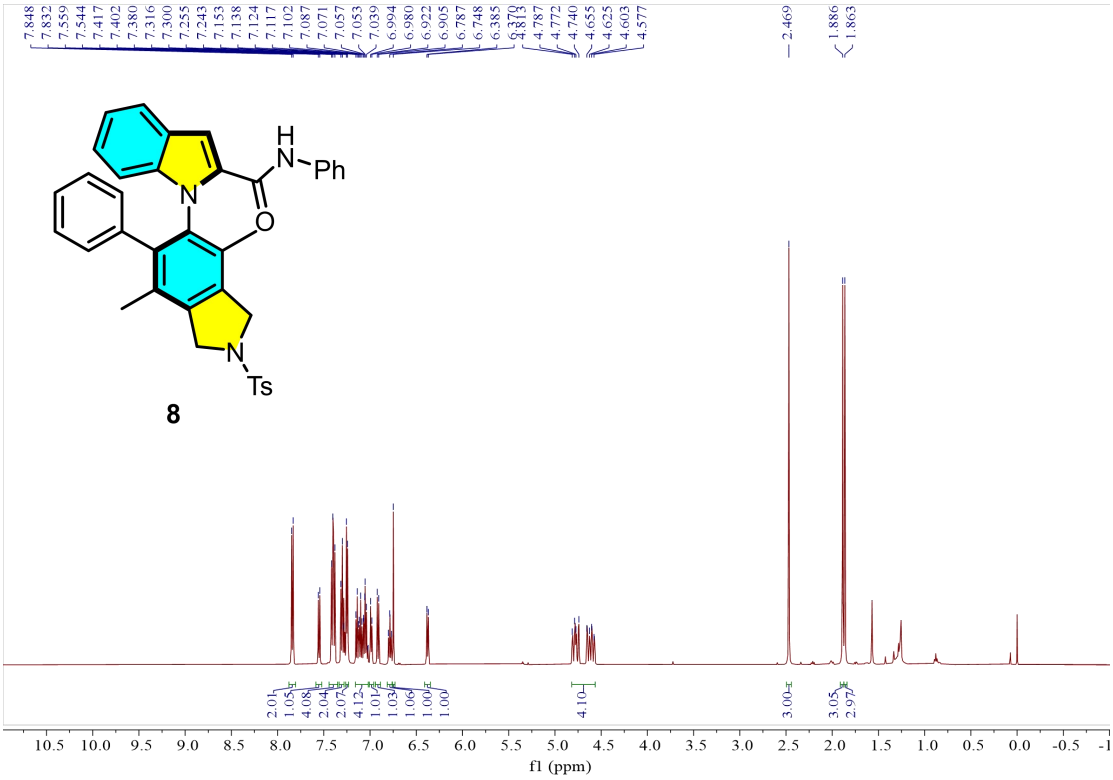
141.527
141.329
139.707
136.865
136.363
135.758
135.291
133.970
130.184
129.990
129.621
128.602
128.018
127.673
127.339
127.224
126.800
122.145
120.558
119.958
110.370
100.543
54.040
53.677
51.580
21.601
17.568
16.413
14.827
14.311
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
Ph
OH
N
N
Ts
7
f1 (ppm)


f1 (ppm)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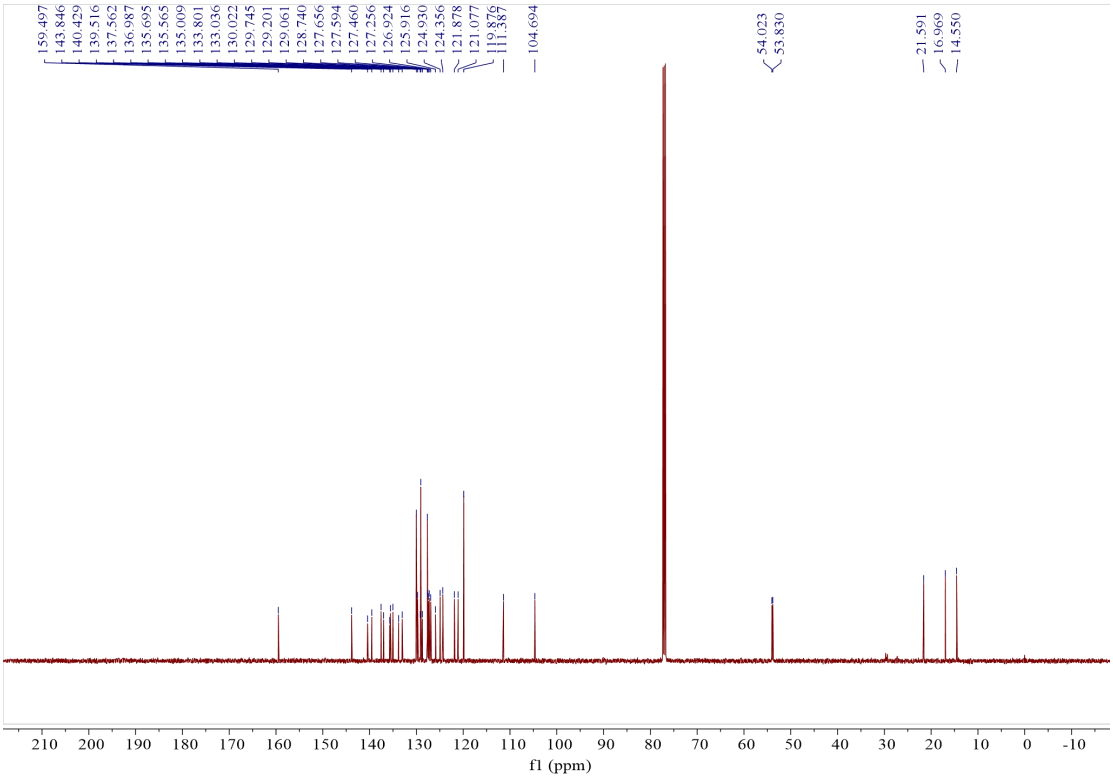
7.832
7.559
7.544
7.417
7.402
7.380
7.316
7.300
7.255
7.243
7.153
7.138
7.124
7.117
7.102
7.087
7.071
7.057
7.053
7.039
6.994
6.980
6.922
6.905
6.787
6.748
6.385
6.370
4.813
4.787
4.772
4.740
4.655
4.625
4.603
4.577
2.469
1.886
1.863
H
N
Ph
N
O
N
Ts
8
2.01
1.05
4.08
2.04
2.07
4.12
1.01
1.03
1.06
1.00
1.00
4.10
3.00
3.05
2.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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143.846
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139.516
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133.801
133.036
130.022
129.745
129.201
129.061
128.740
127.656
127.594
127.460
127.256
126.924
125.916
124.930
124.356
121.878
121.077
119.876
111.387
104.694
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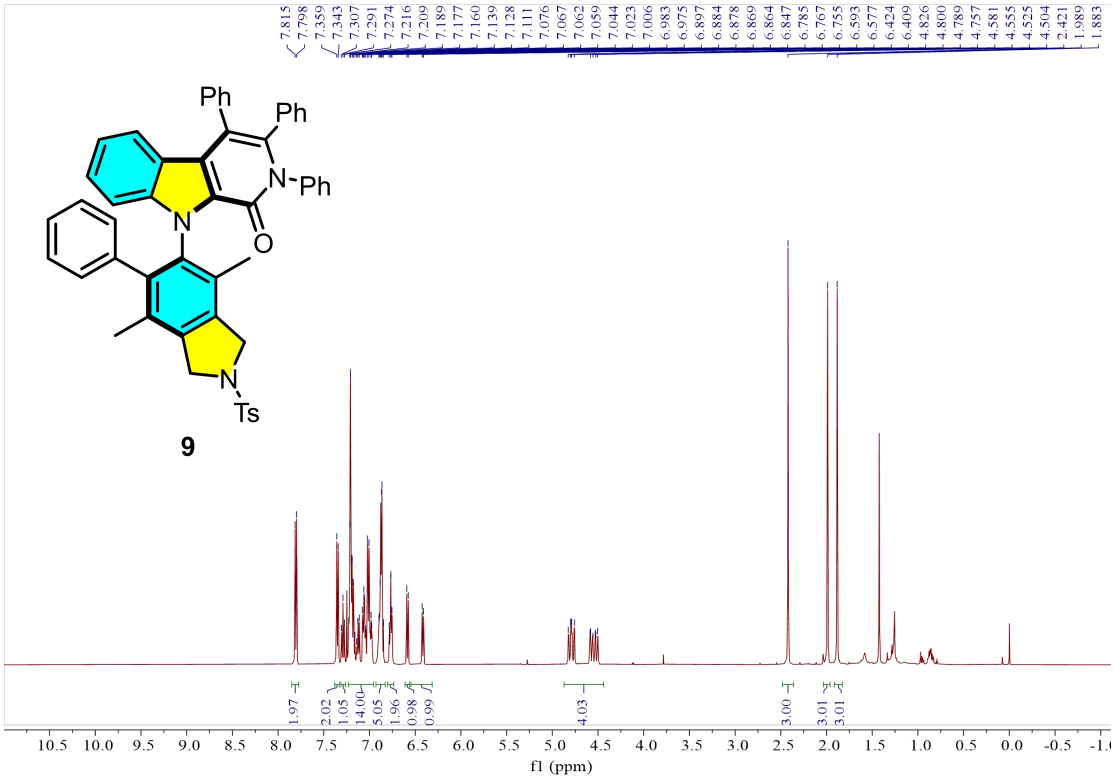
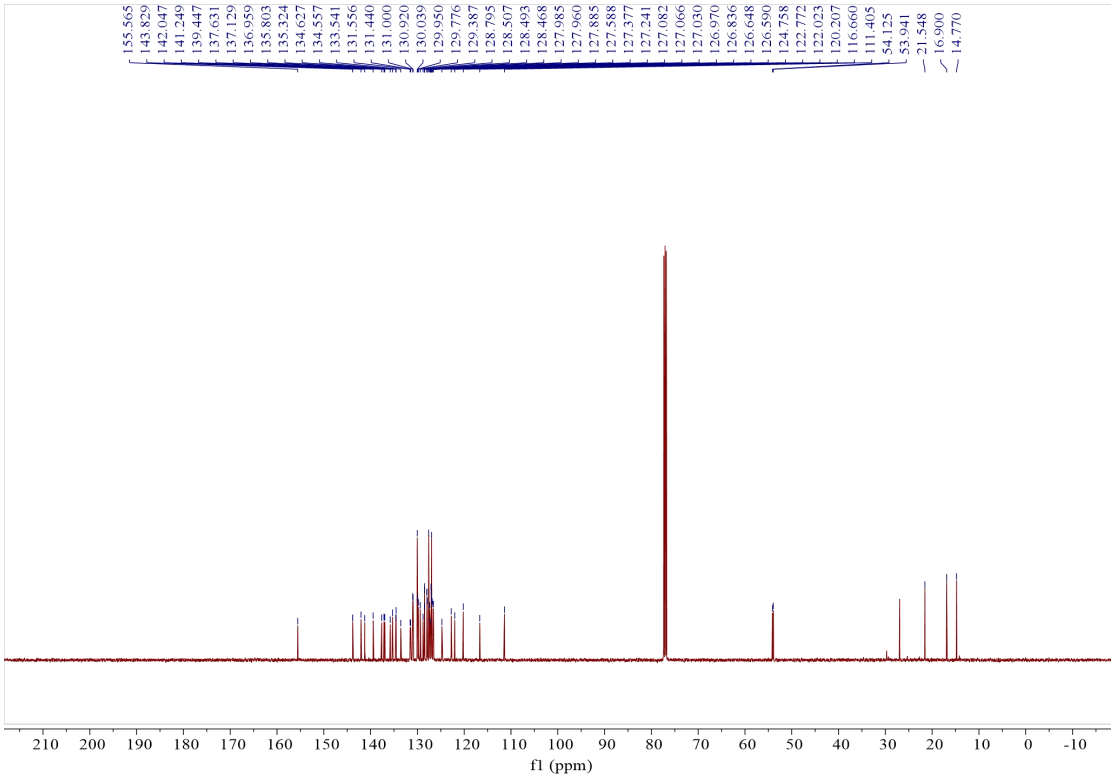
21.591
16.969
14.550
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
Ph
N-Ph
N
O
N
Ts
9
f1 (ppm)


f1 (ppm)

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