

**Pd-catalyzed enantio- and diastereoselective synthesis of N-N
atropisomeric indoles *via* N-alkylation reaction**

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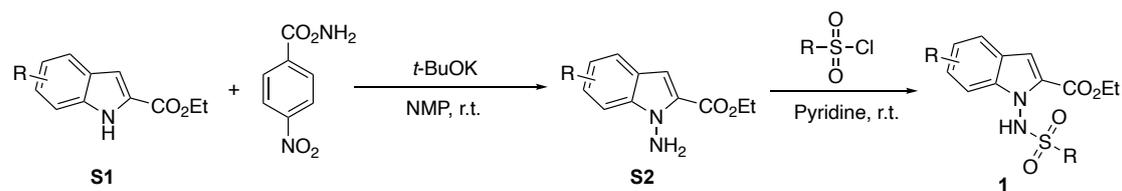
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1. General Information

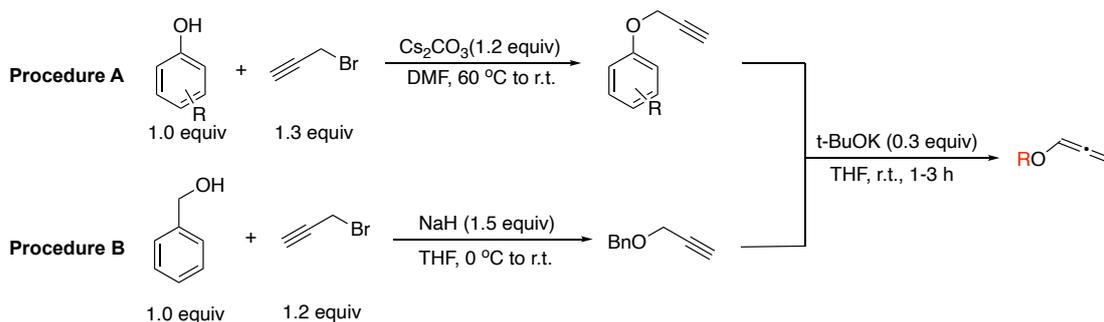
Unless otherwise noted, materials were purchased from commercial suppliers and used directly. All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Reactions were monitored using thin-layer chromatography (TLC) on silica gel plates. Visualization of the developed plates was performed under UV light (254 nm). Column chromatography was performed on silica gel (200~300 mesh). ^1H , ^{13}C , and ^{19}F NMR were measured either on a Bruker AVANCE III 500 (500 MHz) or on a Varian DLG 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad. All first-order splitting patterns were assigned on the base of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). High resolution mass spectrometer analysis (HRMS) was performed on Synapt G2-Si HDMS. Enantiomeric excesses (ee) were determined by Agilent 1100 at 25 °C with UV detector at 254 nm. Chiralcel brand chiral columns from Daicel Chemical Industries were used with models AD, IA, IC in 4.6 x 250 mm size. The racemic products used to determine the ee values were synthesized using racemic catalyst. Optical rotations were measured on a AUTOPOL IV Polarimeter and the concentration (c) is given in g/100 mL. Melting Point (MP): Melting points were measured on a Cossim X-4 micro melting point apparatus.

2. General Procedure for the Synthesis of Substrates 1^[1]



To a solution of **S1** (1 eq.) in NMP (20 mL) were added t-BuOK (1.2 eq.), and the mixture was stirred for 30 minutes. Then solution of O-(4-nitrobenzoyl)hydroxylamine (1.2 eq.) in NMP (10 mL) was added and the reaction mixture at room temperature and stirred for 2-10 h. Then the reaction mixture was extracted with ethyl acetate (25 mL × 3). The combined organic extracts were washed with water, dried over sodium sulfate and concentrated. The residue was purified by silica gel column chromatography to provide compound **S2**. To a 10 mL flask charged with compound **S2** (1 eq.) and Sulfonyl chloride (1.2 eq.) was added pyridine (5 mL). Then the reaction was carried out by stirring at room temperature for 12 h. The reaction mixture was quenched with water (50 mL), and extracted with ethyl acetate (50 mL × 3). The organic phase was washed with water, dried over sodium sulfate and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate =10:1-5:1, v/v) to afford compound **1**.

3. General Procedure for the Synthesis of Substrates 2



Procedure A^[2]: Mixture of the corresponding phenol (1.0 eq.) and anhydrous Cs_2CO_3 (1.2 eq.) in DMF (40 mL) was heated to 60 °C for half an hour under inert atmosphere. The reaction mixture was then cooled to room temperature and propargyl bromide (98%, with 0.3% MgO stabilizer, 1.3 equiv.) was added slowly. After completion of the reaction (TLC), the mixture was diluted with ether and washed at least 3 times with brine. Obtained crude product after solvent evaporation was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate =200:1- 100:1, v/v) to afford propargyl ether.

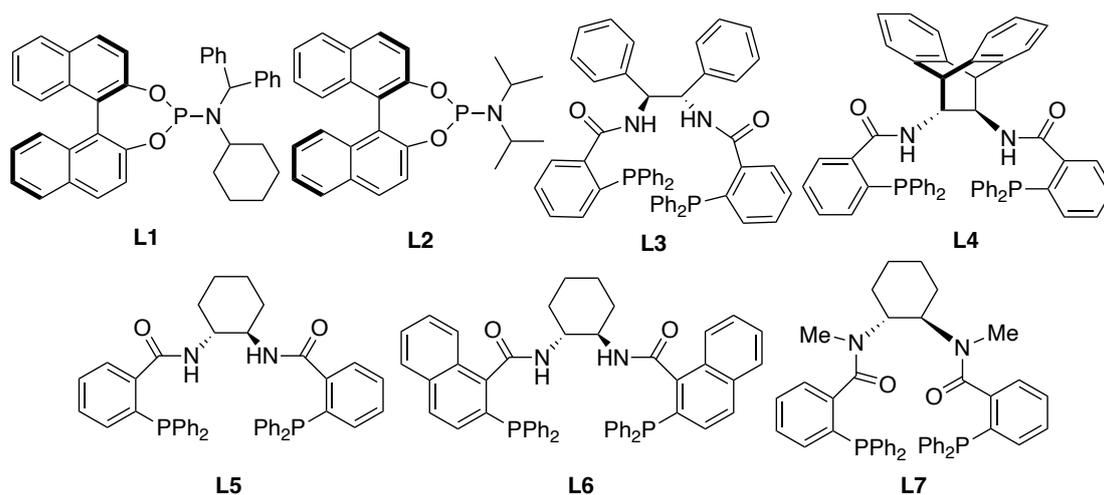
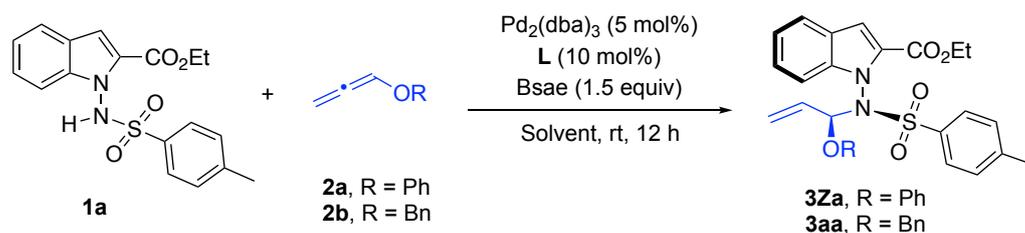
Procedure B^[3]: To a solution of benzyl alcohols (1.0 eq.) in THF (40 mL) was added NaH (1.5 eq.) and propargyl bromide (1.2 eq.) at 0 °C. The reaction was stirred at rt. After the reaction was complete (the reaction time is usually within 1-2 h), the reaction was quenched with sat aq NH_4Cl . The quenched mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were washed with equal volume of sat aq NaCl and dried over anhyd Na_2SO_4 . After filtration and concentration, the crude product was purified using silica gel flash column chromatography (petroleum ether/ ethyl acetate =200:1- 100:1, v/v) to give benzyl propargyl ether.

Potassium tert-butoxide (3.0 mmol, 0.3 equiv.) was added at room temperature to a solution of propargyl ether (10 mmol, 1 equiv.) in THF (25 mL). The suspension was stirred at room temperature for the appropriate time, then filtered through a diatomaceous-earth pad and washed with n-heptane. The solvent mixture was removed

in vacuo and the crude residue was purified by column chromatography (petroleum ether/ ethyl acetate = 100:1, v/v) to give allenyl ether **2**.

Caution: The product **2** is easily spoiled in air and should be made on the spot!

4. Optimization of the Reaction Conditions

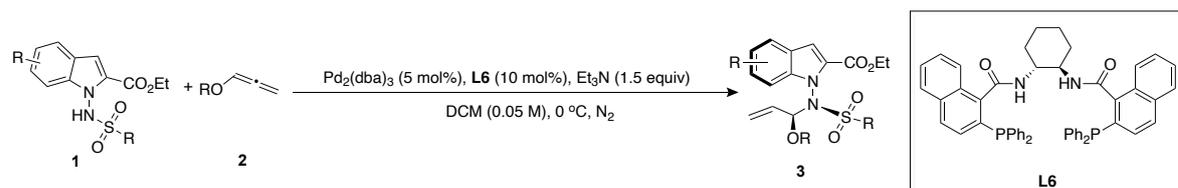


entry ^a	2	ligand	solvent	base	[Pd]	yield [%] ^b	ee ^c	dr ^d
1	2a	L1	DCM	Et ₃ N	Pd ₂ (dba) ₃	56	0	3:1
2	2a	L2	DCM	Et ₃ N	Pd ₂ (dba) ₃	68	0	3:1
3	2a	L3	DCM	Et ₃ N	Pd ₂ (dba) ₃	76	72	5:1
4	2a	L4	DCM	Et ₃ N	Pd ₂ (dba) ₃	66	20	3:1
5	2a	L5	DCM	Et ₃ N	Pd ₂ (dba) ₃	69	68	2:1
6	2a	L6	DCM	Et ₃ N	Pd ₂ (dba) ₃	88	90	5:1
7	2a	L7	DCM	Et ₃ N	Pd ₂ (dba) ₃	51	26	3:1
8	2a	L6	DCE	Et ₃ N	Pd ₂ (dba) ₃	83	76	3:1
9	2a	L6	toluene	Et ₃ N	Pd ₂ (dba) ₃	60	0	2:1
10	2a	L6	MeCN	Et ₃ N	Pd ₂ (dba) ₃	78	72	2:1
11	2a	L6	1,4-dioxane	Et ₃ N	Pd ₂ (dba) ₃	53	30	2:1
12	2a	L6	THF	Et ₃ N	Pd ₂ (dba) ₃	39	30	2:1
13	2a	L6	DCM	Cs₂CO₃	Pd ₂ (dba) ₃	62	70	2:1
14	2a	L6	DCM	DIPEA	Pd ₂ (dba) ₃	82	88	3:1
15	2a	L6	DCM	pyridine	Pd ₂ (dba) ₃	45	78	2:1
16	2a	L6	DCM	^tBuOK	Pd ₂ (dba) ₃	trace	-	-
17	2a	L6	DCM	DBU	Pd ₂ (dba) ₃	75	86	3:1
18	2a	L6	DCM	Et ₃ N	Pd₂(allyl)₂Cl₂	92	80	5:1
19	2a	L6	DCM	Et ₃ N	Pd(dppf)Cl₂	97	4	5:1
20	2a	L6	DCM	Et ₃ N	Pd(PPh₃)₂Cl₂	trace	-	-
21	2a	L6	DCM	Et ₃ N	Pd(OAc)₂	trace	-	-
22	2a	L6	DCM	Et ₃ N	Pd(aMphos)Cl₂	89	88	3:1

23 ^e	2a	L6	DCM	Et ₃ N	Pd ₂ (dba) ₃	90	94	5:1
24 ^e	2b	L6	DCM	Et ₃ N	Pd ₂ (dba) ₃	92	92	10:1
25 ^{e,f}	2b	L6	DCM	Et ₃ N	Pd ₂ (dba) ₃	92	96	10:1

^a All reactions were carried out with **1a** (0.1 mmol), **2** (0.12 mmol), [Pd] (5.0 mol%), ligand (10 mol%), Base (0.15 mmol), and solvent at room temperature for 12 h under a nitrogen atmosphere unless otherwise stated. ^b Isolated yield based on **1**. ^c The ee was determined by via HPLC on the chiral stationary phase. ^d The two diastereomers were not separable by column chromatography, and the dr value was determined by ¹H NMR spectroscopy of the crude mixture. ^e In 2 ml solvent. ^f 0 °C.

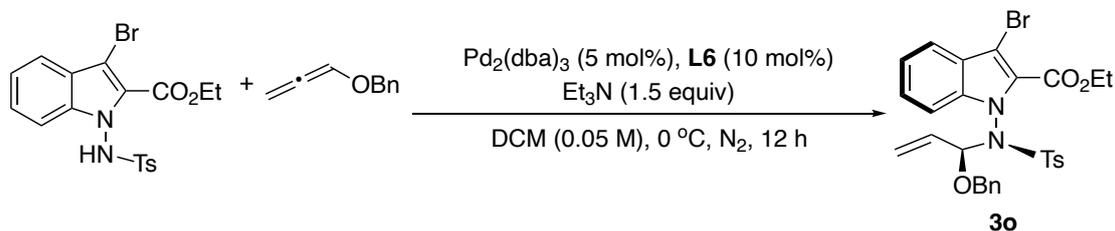
5. General Procedure for the Synthesis of Product 3



A mixture of compound **1** (0.1 mmol), allenyl ether **2** (0.12 mmol), Pd₂(dba)₃ (5 mol%), ligand **6** (10 mol%) and Et₃N (1.5 equiv) in DCM (2.0 mL) was stirred at 0 °C for 12 h, and then the solvent was removed under reduced pressure. The residue was purified through flash column chromatography (petroleum ether/ ethyl acetate = 10:1-5:1, v/v) on silica gel to afford product **3** as a colorless oil.

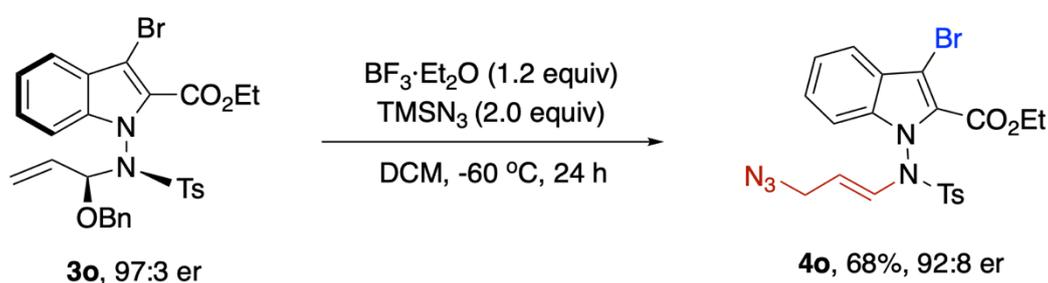
6. The Large-scale Reaction and Synthetic Transformations

a) The large-scale reaction of **3o**



A mixture of compound **1** (2.18 g, 5.0 mmol), allenyl ether **2** (0.88 g, 6.0 mmol), $\text{Pd}_2(\text{dba})_3$ (0.23 g, 0.25 mol), ligand **6** (0.39 g, 0.5 mol) and Et_3N (1.05 ml, 0.76 g, 7.5 equiv) in DCM (100 mL) was stirred at $0\text{ }^\circ\text{C}$ for 12 h, and then the solvent was removed under reduced pressure. The residue was purified through flash column chromatography (petroleum ether/ ethyl acetate = 10:1-5:1, v/v) on silica gel to afford product **3o** as a colorless oil in 92% yield, 10:1 dr and 97:3 er.

b) Further transformation of **3o**^[4]



The reaction mixture of **3o** (0.2 mmol) and TMSN_3 (2.0 equiv.) in DCM (2.0 mL) solvent was stirred at $-60\text{ }^\circ\text{C}$, then $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.2 equiv.) was added slowly and the mixture was stirred at this temperature. Upon reaction completion, the reaction mixture was poured into water (5 mL) and extracted with DCM three times. The combined organic layers were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude mass was purified by flash column chromatography (petroleum ether/ ethyl acetate = 10:1-5:1, v/v) to provide **4o**.

7. Stability Examination^{[4][5]}

Approximately 1 mg of an enantioenriched sample **3g** was dissolved in the toluene solvent and heated at 100 °C. The change in enantiomeric excess and diastereomeric excess over time was monitored *via* chiral HPLC.

This data was plotted as $(\ln[de_0/de_t])$ versus time (seconds). The gradient of this graph corresponds to the racemization constant, $K_{\text{racemization}}(k_{\text{rac}})$, at the specified temperature. The rate constant for enantiomerization, $K_{\text{enantiomerization}}(k_{\text{ent}})$, is related to the racemization rate constant according to the following equation:

$$k_{\text{ent}} = 1/2 k_{\text{rac}} = 1/2 \text{ slope}$$

The barrier to rotation, $\Delta G_{\text{enantiomerization}}^\ddagger$, was subsequently calculated using the following form of the Eyring equation:

$$\Delta G_{\text{ent}}^\ddagger = \ln\left(\frac{k_B T_1}{h \times k_{\text{ent}}}\right) RT$$

Where: R = Gas constant = $8.31454 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, h = Planck constant = $6.62608 \times 10^{-34} \text{ J}\cdot\text{s}$, k_B = Boltzmann constant = $1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$, and $T_1 = 373.15 \text{ K}$, temperature racemization studies were conducted at, in Kelvin.

Employing the hypothesis that $\Delta G_{\text{enantiomerization}}^\ddagger$ is independent of temperature, it is possible to extrapolate the racemization constant to other temperatures, in this case 25 °C, according to the following relationship:

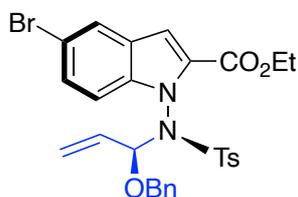
$$k_{\text{rac at } 25^\circ\text{C}} = 2 \cdot k_{\text{ent at } 25^\circ\text{C}} = 2 \cdot \frac{k_B T_2}{h} \cdot e\left(\frac{-\Delta G_{\text{ent}}^\ddagger}{RT_2}\right)$$

Where $T_2 = 298.15 \text{ K}$ (25 °C)

The half-life at 25 °C is calculated as follows:

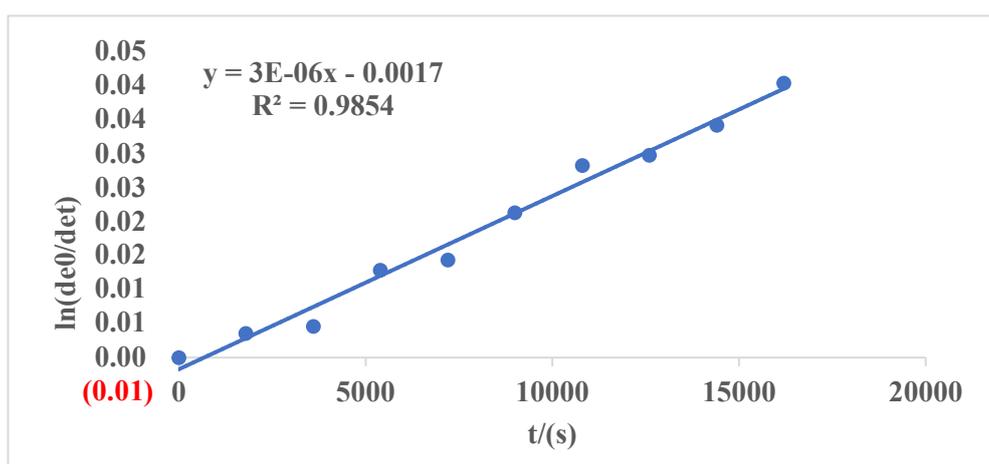
$$t_{1/2} = \ln 2 / k_{\text{rac at } 25^\circ\text{C}}$$

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-5-bromo-1*H*-indole-2-carboxylate(3g**)**



3g, 92%, 10:1 d.r., 95:5 er

t/s	ee (%)	de (%)	ln(de ₀ /de _t)
0	90.10	83.52	0.00000
1800	89.52	83.22	0.00360
3600	88.96	83.14	0.00456
5400	88.62	82.45	0.01289
7200	87.94	82.33	0.01435
9000	87.62	81.76	0.02130
10800	87.22	81.19	0.02829
12600	86.64	81.46	0.02977
14400	86.11	80.71	0.03422
16200	85.78	80.21	0.04044



$$k_{ent} = 1/2 k_{rac} = 1/2 \text{ slope} = 1.5 \times 10^{-6} \text{ s}^{-1}$$

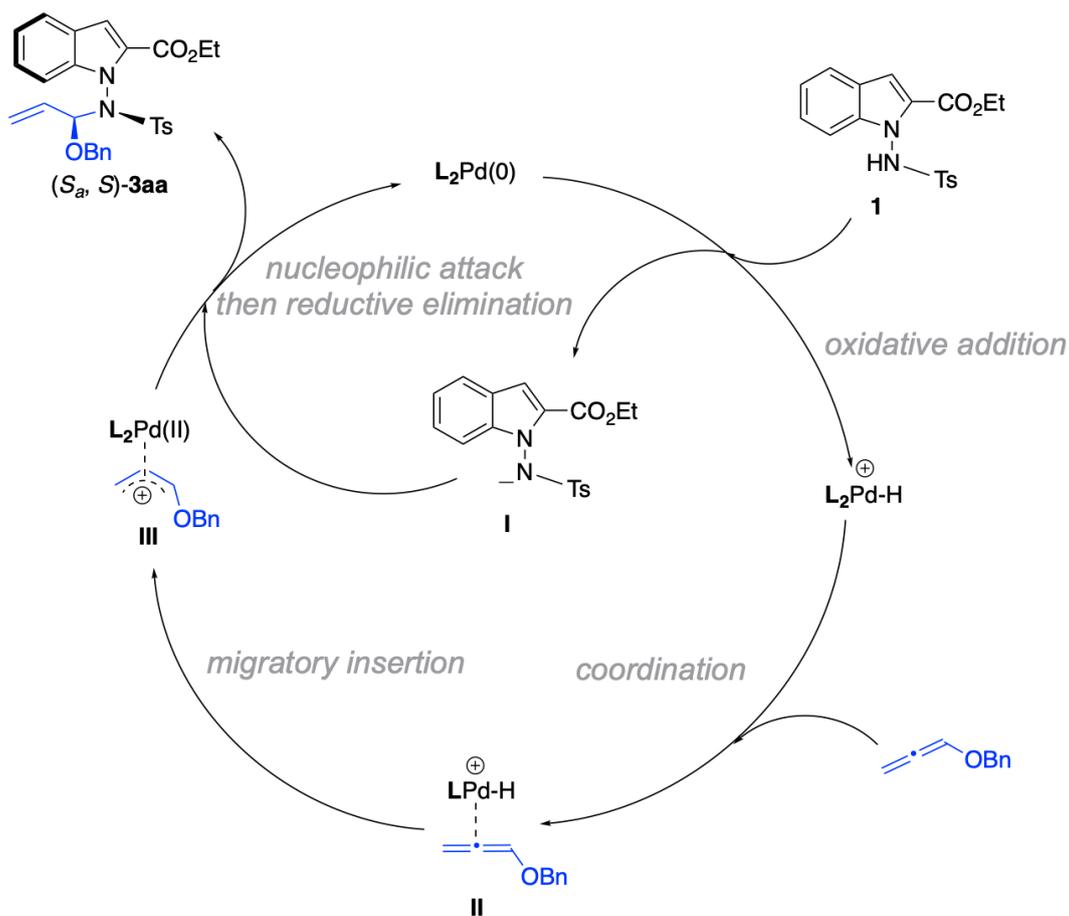
$$t_{1/2} = \ln 2 / k_{rac} \approx 64.18 \text{ h}$$

$$\Delta G_{ent}^{\ddagger} = \ln \left(\frac{k_B T_1}{h \times k_{ent}} \right) RT = 133.70 \text{ kJ} \cdot \text{mol}^{-1} = 31.95 \text{ kcal} \cdot \text{mol}^{-1}$$

$$k_{rac \text{ at } 25 \text{ } ^\circ\text{C}} = 2 \cdot k_{ent \text{ at } 25 \text{ } ^\circ\text{C}} = 2 \cdot \frac{k_B T_2}{h} \cdot e\left(\frac{-\Delta G_{ent}^\ddagger}{RT_2}\right) = 4.70 \times 10^{-11} \text{ s}^{-1}$$

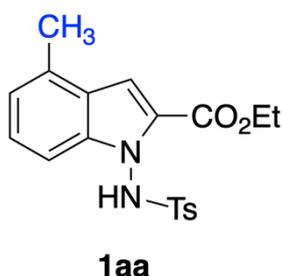
$$t_{1/2} = \ln 2 / k_{rac \text{ at } 25 \text{ } ^\circ\text{C}} \approx 467.77 \text{ years}$$

8. Plausible Mechanism



9. Characterization Data

Ethyl 4-methyl-1-((4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate (**1aa**)



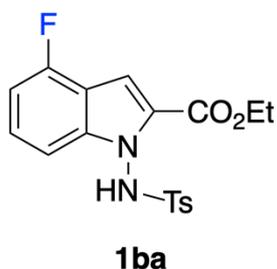
White solid, 78% yield; m.p.163.2-163.6 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.98 (s, 1H), 7.60 (dd, *J* = 11.0, 8.4 Hz, 3H), 7.45 – 7.40 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.26 (s, 1H), 7.14 (m, *J* = 7.1, 1.0 Hz, 1H), 4.18 (s, 2H), 2.68 (s, 3H), 2.57 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.78, 145.00, 138.36, 133.06, 131.96, 129.58, 129.25, 126.74, 124.48, 123.61, 122.20, 109.72, 108.68, 77.48, 77.16, 76.84, 60.96, 21.73, 18.29, 14.24.

HRMS (ESI, *m/z*): exact mass calculated for [M-H]⁻ (C₁₉H₁₉N₂O₄S⁻) requires *m/z* 371.1060, found, 371.1073.

Ethyl 4-fluoro-1-((4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(**1ba**)



White solid, 88% yield; m.p.148.6-149.4 °C.

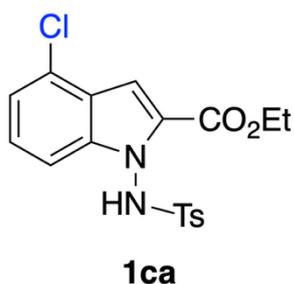
¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 1H), 7.54 (dd, *J* = 8.4, 1.6 Hz, 3H), 7.44 – 7.38 (m, 1H), 7.37 – 7.30 (m, 2H), 7.26 (s, 1H), 6.97 (ddd, *J* = 9.9, 7.8, 0.7 Hz, 1H), 4.15 (s, 2H), 2.54 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.39, 145.28, 132.69, 129.69, 129.24, 127.16, 127.08, 125.29, 113.58, 108.33, 106.62, 106.43, 105.92, 77.48, 77.16, 76.84, 61.24, 21.74, 14.17.

¹⁹F NMR (377 MHz, CDCl₃) δ -121.34.

HRMS (ESI, *m/z*): exact mass calculated for [M-H]⁻ (C₁₈H₁₆FN₂O₄S⁻) requires *m/z* 375.0809, found, 375.0819.

Ethyl 4-chloro-1-((4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(**1ca**)



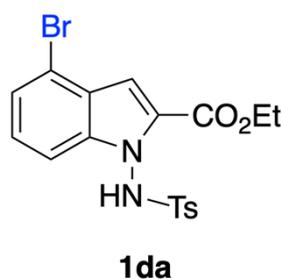
Light yellow solid, 87% yield; m.p.177.3-178.2 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.86 (s, 1H), 7.56 (m, *J* = 8.4, 1.0 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.28 (dd, *J* = 8.4, 7.5 Hz, 1H), 7.22 – 7.17 (m, 3H), 7.16 (d, *J* = 0.9 Hz, 1H), 4.02 (s, 2H), 2.41 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.41, 145.29, 138.96, 132.62, 129.71, 129.26, 127.69, 126.98, 125.55, 122.53, 121.84, 110.98, 108.19, 77.48, 77.16, 76.85, 61.28, 21.74, 14.18.

HRMS (ESI, *m/z*): exact mass calculated for [M-H]⁻ (C₁₈H₁₆ClN₂O₄S⁻) requires *m/z* 391.0514, found, 391.0525.

Ethyl 4-bromo-1-((4-methylphenyl)sulfonamido)-1H-indole-2-carboxylate(1da)



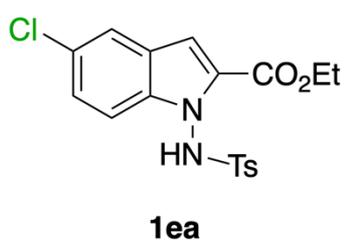
White solid, 86% yield; m.p.172.6-174.4 °C .

¹H NMR (400 MHz, CDCl₃) δ 8.85 (s, 1H), 7.61 (m, *J* = 8.4, 0.9 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.37 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.10 (d, *J* = 1.0 Hz, 1H), 4.02 (s, 2H), 2.41 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.40, 145.29, 138.67, 132.61, 129.72, 129.25, 127.25, 125.56, 125.09, 124.33, 116.32, 111.54, 109.84, 77.48, 77.16, 76.84, 61.29, 21.74, 14.18.

HRMS (ESI, *m/z*): exact mass calculated for [M-H]⁻ (C₁₈H₁₆BrN₂O₄S⁻) requires *m/z* 435.0008, found, 435.0020.

Ethyl 5-chloro-1-((4-methylphenyl)sulfonamido)-1H-indole-2-carboxylate(1ea)



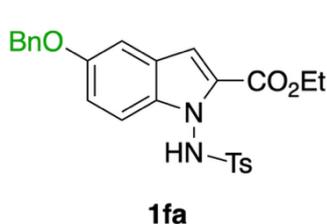
White solid, 75% yield; m.p.170.6-171.6 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.83 (s, 1H), 7.59 – 7.53 (m, 2H), 7.42 – 7.38 (m, 2H), 7.31 (dd, *J* = 9.0, 1.9 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 0.9 Hz, 1H), 4.02 (s, 2H), 2.41 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.42, 145.30, 136.63, 132.65, 129.69, 129.20, 127.83, 127.04, 126.16, 124.28, 121.53, 113.47, 109.16, 77.48, 77.16, 76.84, 61.25, 21.74, 14.18.

HRMS (ESI, m/z): exact mass calculated for $[\text{M-H}]^-$ ($\text{C}_{18}\text{H}_{16}\text{ClN}_2\text{O}_4\text{S}^-$) requires m/z 391.0514, found, 391.0525.

Ethyl 5-(benzyloxy)-1-((4-methylphenyl)sulfonamido)-1H-indole-2-carboxylate(1fa)



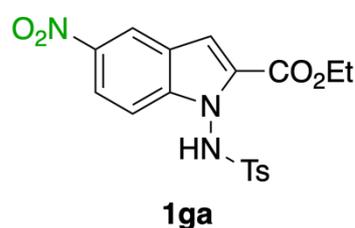
Light yellow solid, 87% yield; m.p.123.7-125.6 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.82 (s, 1H), 7.55 (d, $J = 9.1$ Hz, 1H), 7.49 – 7.45 (m, 2H), 7.43 – 7.38 (m, 4H), 7.36 – 7.32 (m, 1H), 7.18 (d, $J = 8.1$ Hz, 2H), 7.13 (dd, $J = 9.1, 2.4$ Hz, 1H), 7.05 (d, $J = 2.4$ Hz, 1H), 6.96 (d, $J = 0.9$ Hz, 1H), 5.09 (s, 2H), 4.01 (s, 2H), 2.40 (s, 3H), 1.22 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.65, 154.82, 145.05, 137.26, 133.84, 132.89, 129.58, 129.21, 128.71, 128.08, 127.65, 125.26, 123.84, 118.54, 113.20, 109.52, 103.98, 77.48, 77.16, 76.84, 70.75, 60.93, 21.72, 14.22.

HRMS (ESI, m/z): exact mass calculated for $[\text{M-H}]^-$ ($\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_5\text{S}^-$) requires m/z 463.1322, found, 463.1329.

Ethyl 1-((4-methylphenyl)sulfonamido)-5-nitro-1H-indole-2-carboxylate(1ga)



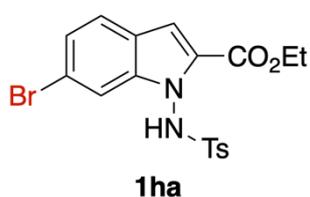
White solid, 84% yield; m.p.200.1-202.4 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.90 (s, 1H), 8.59 (d, $J = 2.1$ Hz, 1H), 8.22 (dd, $J = 9.3, 2.2$ Hz, 1H), 7.69 (d, $J = 9.2$ Hz, 1H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.24 – 7.19 (m, 3H), 4.06 (s, 2H), 2.42 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 160.97, 145.71, 143.61, 140.63, 132.38, 129.88, 129.18, 128.21, 122.58, 121.31, 119.69, 112.81, 111.33, 61.73, 21.78, 14.15.

HRMS (ESI, m/z): exact mass calculated for $[\text{M-H}]^-$ ($\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}_6\text{S}^-$) requires m/z 402.0754, found, 402.0771.

Ethyl 6-bromo-1-((4-methylphenyl)sulfonamido)-1H-indole-2-carboxylate(1ha)



White solid, 88% yield; m.p.159.8-159.9 °C.

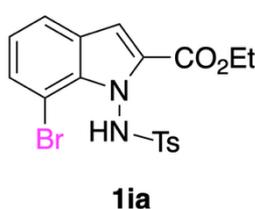
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.72 (s, 1H), 7.55 (m, $J = 1.6$, 0.7 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.25 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.04 (d, $J = 1.0$ Hz, 1H), 4.08 (s,

2H), 2.42 (s, 3H), 1.25 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.47, 145.49, 138.79, 132.92, 129.75, 129.20, 126.08, 125.80, 123.57, 122.27, 120.50, 114.92, 109.99, 77.48, 77.16, 76.84, 61.29, 21.78, 14.22.

HRMS (ESI, m/z): exact mass calculated for $[\text{M-H}]^-$ ($\text{C}_{18}\text{H}_{16}\text{BrN}_2\text{O}_4\text{S}^-$) requires m/z 435.0008, found, 435.0021.

Ethyl 7-bromo-1-((4-methylphenyl)sulfonamido)-1H-indole-2-carboxylate(1ia)



Yellow solid, 77% yield; m.p.157.4-158.8 °C.

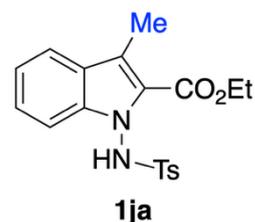
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.60 (s, 1H), 7.56 (ddd, $J = 10.5$, 7.7, 1.0 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.20 – 7.17 (m, 2H), 7.12 (s, 1H), 7.05 (m, $J = 7.8$ Hz, 1H), 4.08 (dq, $J = 10.8$, 7.1 Hz, 1H),

3.92 (dq, $J = 10.8$, 7.2 Hz, 1H), 2.41 (s, 3H), 1.25 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.96, 144.93, 135.49, 133.54, 132.26, 129.62, 129.27, 128.49, 126.74, 123.28, 121.96, 111.32, 105.42, 77.48, 77.16, 76.84, 61.25, 21.73, 14.15.

HRMS (ESI, m/z): exact mass calculated for $[\text{M-H}]^-$ ($\text{C}_{18}\text{H}_{16}\text{BrN}_2\text{O}_4\text{S}^-$) requires m/z 435.0008, found, 435.0019.

Ethyl 3-methyl-1-((4-methylphenyl)sulfonamido)-1H-indole-2-carboxylate(1ja)



White solid, 83% yield; m.p.173.4-175.8 °C .

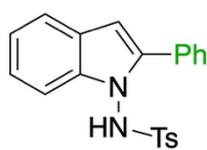
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.83 (s, 1H), 7.60 (m, $J = 8.1$, 1.0 Hz, 1H), 7.53 (dd, $J = 8.4$, 1.0 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.34

(ddd, $J = 8.3, 7.0, 1.1$ Hz, 1H), 7.20 – 7.15 (m, 3H), 4.04 (d, $J = 45.6$ Hz, 2H), 2.44 (s, 3H), 2.41 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.57, 144.89, 137.76, 133.31, 129.46, 129.14, 126.69, 124.80, 122.13, 121.40, 121.29, 120.37, 111.82, 77.48, 77.16, 76.84, 60.86, 21.69, 14.24, 10.42.

HRMS (ESI, m/z): exact mass calculated for $[\text{M-H}]^-$ ($\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_4\text{S}^-$) requires m/z 371.1060, found, 371.1073.

4-methyl-*N*-(2-phenyl-1*H*-indol-1-yl)benzenesulfonamide(1ka)



1ka

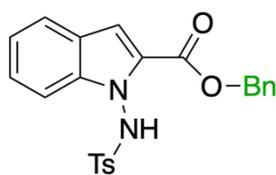
Light yellow solid, 72% yield; m.p.174.0-176.5 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.74 (s, 1H), 7.55 (m, $J = 7.7, 1.1$ Hz, 1H), 7.47 (m, $J = 8.1, 0.9$ Hz, 1H), 7.27 – 7.19 (m, 7H), 7.17 – 7.15 (m, 2H), 6.92 – 6.88 (m, 2H), 6.47 (d, $J = 0.9$ Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 144.56, 139.71, 137.84, 133.92, 130.80, 129.48, 128.45, 128.24, 128.18, 127.68, 126.02, 123.22, 121.68, 120.69, 110.86, 102.83, 77.48, 77.16, 76.84, 21.69.

HRMS (ESI, m/z): exact mass calculated for $[\text{M-H}]^-$ ($\text{C}_{21}\text{H}_{17}\text{N}_2\text{O}_2\text{S}^-$) requires m/z 361.1005, found, 361.1015.

Benzyl 1-((4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(1la)



1la

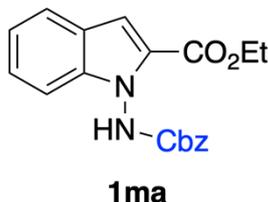
White solid, 87% yield; m.p.141.1-143.2 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.84 (s, 1H), 7.64 (dd, $J = 8.4, 1.1$ Hz, 1H), 7.58 (dd, $J = 8.1, 1.0$ Hz, 1H), 7.42 – 7.35 (m, 6H), 7.34 – 7.30 (m, 2H), 7.18 (ddd, $J = 8.0, 7.0, 1.0$ Hz, 1H), 7.14 – 7.08 (m, 3H), 4.98 (d, $J = 23.9$ Hz, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.56, 145.19, 138.46, 135.17, 132.78, 129.57, 129.26, 128.81, 128.65, 128.16, 126.71, 124.73, 123.46, 122.42, 122.27, 112.18, 110.52, 77.48, 77.16, 76.84, 66.55, 21.71.

HRMS (ESI, m/z): exact mass calculated for $[M-H]^-$ ($C_{23}H_{19}N_2O_4S^-$) requires m/z 419.1060, found, 419.1075.

Ethyl 1-(((benzyloxy)carbonyl)amino)-1*H*-indole-2-carboxylate(1ma)



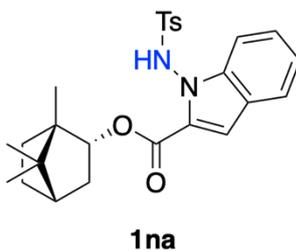
White solid, 89% yield; m.p.107.5-108.3 °C.

1H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, $J = 8.0, 1.1$ Hz, 1H), 7.45 – 7.30 (m, 7H), 7.20 (ddd, $J = 8.1, 6.8, 1.3$ Hz, 1H), 5.22 (s, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.33 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.02, 156.41, 139.58, 135.58, 128.61, 128.45, 128.25, 126.84, 126.42, 123.69, 122.72, 121.91, 110.60, 110.09, 77.48, 77.16, 76.84, 68.16, 60.94, 14.31.

HRMS (ESI, m/z): exact mass calculated for $[M-H]^-$ ($C_{19}H_{17}N_2O_4^-$) requires m/z 337.1183, found, 337.1196.

(1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 1-((4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(1na)



White solid, 87% yield; m.p.135.8-136.6 °C; $[\alpha]_D^{25} = -47.66$ (c 0.37, CH_2Cl_2).

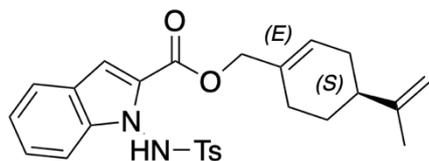
1H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.68 (d, $J = 8.6$ Hz, 1H), 7.61 (m, $J = 8.1, 1.1$ Hz, 1H), 7.44 – 7.36 (m, 3H), 7.22 – 7.15 (m, 3H), 7.09 (d, $J = 1.0$ Hz, 1H), 4.71 (d, $J = 64.6$

Hz, 1H), 2.38 (s, 3H), 2.22 (s, 1H), 1.95 (ddd, $J = 13.4, 9.4, 4.4$ Hz, 1H), 1.78 (ddt, $J = 12.2, 8.0, 3.8$ Hz, 1H), 1.70 (t, $J = 4.5$ Hz, 1H), 1.40 – 1.18 (m, 3H), 0.90 (d, $J = 6.9$ Hz, 6H), 0.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.22, 145.00, 138.32, 133.03, 129.63, 129.18, 126.53, 124.80, 123.46, 122.30, 122.21, 112.30, 109.94, 77.48, 77.16, 76.84, 47.98, 44.94, 36.79, 28.06, 27.30, 21.83, 19.78, 18.95, 13.65.

HRMS (ESI, m/z): exact mass calculated for $[M-H]^-$ ($C_{26}H_{29}N_2O_4S^-$) requires m/z 465.1842, found, 465.1850.

(S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 1-((4-methylphenyl)sulfonamido)-1H-indole-2-carboxylate(10a)



10a

White solid, 84% yield; m.p.119.6-121.4 °C; $[\alpha]_D^{25} = -27.95$ (c 0.13, CH₂Cl₂).

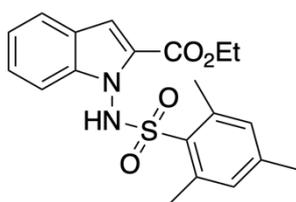
¹H NMR (400 MHz, CDCl₃) δ 8.83 (s, 1H), 7.67 – 7.56 (m, 2H), 7.45 – 7.34 (m, 3H), 7.18 (ddd, $J = 8.1, 6.9,$

0.9 Hz, 3H), 7.07 (d, $J = 0.9$ Hz, 1H), 5.84 – 5.63 (m, 1H), 4.89 – 4.65 (m, 2H), 4.32 (d, $J = 92.2$ Hz, 2H), 2.40 (s, 3H), 2.17 (tdd, $J = 12.3, 7.0, 2.8$ Hz, 2H), 2.11 – 1.93 (m, 3H), 1.91 – 1.83 (m, 1H), 1.75 (t, $J = 1.1$ Hz, 3H), 1.50 (dddd, $J = 18.6, 9.6, 7.0, 4.4$ Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 161.65, 149.47, 145.07, 138.40, 132.88, 131.97, 129.57, 129.27, 126.58, 126.55, 124.92, 123.48, 122.36, 122.22, 112.15, 110.18, 109.07, 77.48, 77.16, 76.84, 68.86, 40.85, 30.57, 27.36, 26.47, 21.80, 20.88.

HRMS (ESI, m/z): exact mass calculated for $[M-H]^-$ (C₂₆H₂₇N₂O₄S⁻) requires m/z 463.1686, found, 463.1695.

Ethyl 1-((2,4,6-trimethylphenyl)sulfonamido)-1H-indole-2-carboxylate(1pa)



1pa

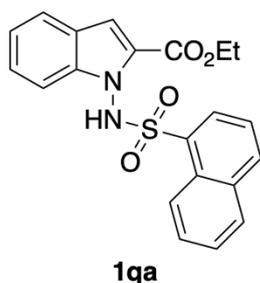
Light yellow solid, 89% yield; m.p.189.9-190.2 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.84 (s, 1H), 7.71 (m, $J = 7.9, 1.1$ Hz, 1H), 7.36 (ddd, $J = 15.2, 9.4, 8.2$ Hz, 2H), 7.26 (dd, $J = 14.7, 1.3$ Hz, 2H), 6.99 (s, 2H), 4.28 (s, 2H), 2.42 (s, 3H), 2.35 (s, 6H), 1.42 (t, $J = 7.1$ Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.89, 143.71, 141.59, 138.50, 132.05, 130.74, 126.43, 126.18, 123.51, 122.29, 121.97, 111.47, 109.95, 77.48, 77.16, 76.84, 61.17, 23.13, 21.12, 14.26.

HRMS (ESI, m/z): exact mass calculated for $[M-H]^-$ (C₂₀H₂₁N₂O₄S⁻) requires m/z 385.1216, found, 385.1231.

Ethyl 1-(naphthalene-1-sulfonamido)-1*H*-indole-2-carboxylate(1qa)



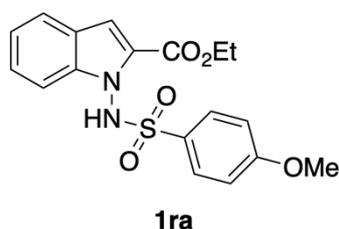
White solid, 68% yield; m.p.141.1-142.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.88 (s, 1H), 8.47 (d, *J* = 9.0 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.90 (ddd, *J* = 11.8, 8.0, 1.4 Hz, 2H), 7.63 – 7.52 (m, 3H), 7.37 – 7.32 (m, 1H), 7.13 – 7.05 (m, 3H), 6.96 (d, *J* = 0.8 Hz, 1H), 3.85 (s, 2H), 1.16 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.49, 138.36, 135.65, 134.06, 132.01, 131.89, 129.26, 128.74, 127.25, 126.28, 126.20, 124.87, 124.33, 123.50, 122.34, 121.98, 111.33, 109.95, 77.48, 77.16, 76.84, 61.01, 14.09.

HRMS (ESI, *m/z*): exact mass calculated for [M-H]⁻ (C₂₁H₁₇N₂O₄S⁻) requires *m/z* 393.0903, found, 393.0917.

Ethyl 1-((4-methoxyphenyl)sulfonamido)-1*H*-indole-2-carboxylate(1ra)



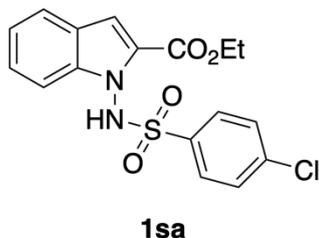
White solid, 85% yield; m.p.143.7-145.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.84 (s, 1H), 7.62 (dd, *J* = 20.1, 8.2 Hz, 2H), 7.39 (dd, *J* = 26.7, 8.2 Hz, 3H), 7.18 (m, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.05 (s, 2H), 3.83 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 164.16, 161.79, 138.38, 131.43, 127.06, 126.52, 125.15, 123.47, 122.36, 122.16, 114.17, 112.18, 110.04, 77.48, 77.16, 76.84, 61.03, 55.79, 14.19.

HRMS (ESI, *m/z*): exact mass calculated for [M-H]⁻ (C₁₈H₁₇N₂O₅S⁻) requires *m/z* 373.0852, found, 373.0860.

Ethyl 1-((4-chlorophenyl)sulfonamido)-1*H*-indole-2-carboxylate(1sa)



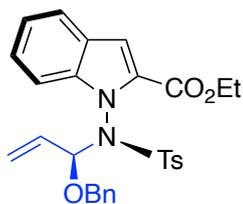
White solid, 82% yield; m.p.144.7-145.7 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.86 (s, 1H), 7.67 – 7.60 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 – 7.35 (m, 3H), 7.21 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.09 (s, 1H), 4.04 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.81, 140.86, 138.38, 134.41, 130.70, 129.27, 126.80, 124.78, 123.51, 122.50, 122.43, 112.09, 110.49, 77.48, 77.16, 76.84, 61.26, 14.21.

HRMS (ESI, *m/z*): exact mass calculated for [M-H]⁻ (C₁₇H₁₄ClN₂O₄S⁻) requires *m/z* 377.0357, found, 377.0374.

Ethyl (S)-1-((N-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-1H-indole-2-carboxylate(3aa)



3aa, 92%, 10:1 d.r., 98:2 er

Colorless oil, 92% yield, 46.4 mg, 10:1 d.r., 96% ee.

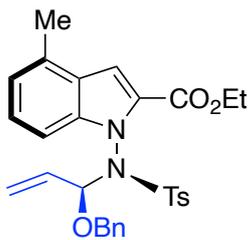
¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.37 (m, 7H), 7.10 (ddd, *J* = 7.9, 6.2, 1.8 Hz, 1H), 7.07 – 6.98 (m, 4H), 6.31 (d, *J* = 5.5 Hz, 1H), 5.55 (ddd, *J* = 17.1, 10.2, 5.5 Hz, 1H), 5.45 – 5.38 (m, 1H), 5.09 (dt, *J* = 10.2, 1.3 Hz, 1H), 4.86 (d, *J* = 11.1 Hz, 1H), 4.70 (d, *J* = 11.1 Hz, 1H), 4.34 (qt, *J* = 7.1, 3.6 Hz, 2H), 2.37 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 160.06, 144.13, 139.35, 137.56, 136.76, 130.36, 129.33, 129.16, 128.64, 128.45, 128.04, 127.83, 125.53, 123.83, 122.00, 121.89, 120.97, 112.49, 110.78, 90.96, 77.48, 77.16, 76.84, 70.86, 60.75, 21.58, 14.34.

HRMS (ESI, *m/z*): exact mass calculated for [M+Na]⁺ (C₂₈H₂₈N₂NaO₅S⁺) requires *m/z* 527.1611, found, 527.1614.

HPLC analysis: 98 : 2 er (CHIRALCEL AD column, 25 °C, *n*-hexane / *i*-PrOH = 80/20, flow rate = 0.8 mL/min, λ = 286 nm), Rt (major) = 10.3 min, Rt (minor) = 13.8 min.

Ethyl (S_a,S)-1-((N-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-4-methyl-1H-indole-2-carboxylate(3a)



3a, 97%, 5:1 d.r., 97:3 er

Colorless oil, 97% yield, 50.2 mg, 5:1 d.r., 94% ee.

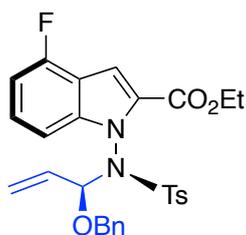
¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.39 (m, 6H), 7.28 (dd, *J* = 2.4, 1.2 Hz, 2H), 7.00 – 6.96 (m, 2H), 6.92 – 6.82 (m, 3H), 6.30 – 6.25 (m, 1H), 5.49 (ddd, *J* = 17.2, 10.0, 5.6 Hz, 1H), 5.42 – 5.35 (m, 1H), 5.09 – 5.03 (m, 1H), 4.82 (d, *J* = 11.2 Hz, 1H), 4.65 (d, *J* = 11.2 Hz, 1H), 4.33 (qd, *J* = 7.1, 3.0 Hz, 2H), 2.51 (s, 3H), 2.34 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.05, 142.94, 138.21, 136.49, 135.89, 130.45, 129.30, 128.03, 127.56, 127.32, 126.92, 126.69, 124.58, 122.70, 120.88, 119.92, 108.92, 108.23, 90.03, 76.32, 76.00, 75.69, 69.66, 59.64, 20.50, 17.03, 13.27.

HRMS (ESI, *m/z*): exact mass calculated for [M+Na]⁺ (C₂₉H₃₀N₂NaO₅S⁺) requires *m/z* 541.1768, found, 541.1763.

HPLC analysis: 97 : 3 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 80/20, flow rate = 0.8 mL/min, λ = 286 nm), Rt (major) = 8.6 min, Rt (minor) = 9.3 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-4-fluoro-1*H*-indole-2-carboxylate(3b**)**



3b, 95%, 5:1 d.r., 97:3 er

Colorless oil, 97% yield, 49.6 mg, 5:1 d.r., 94% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.34 (m, 6H), 7.26 – 7.18 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.87 (td, *J* = 8.0, 5.0 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.68 (dd, *J* = 9.8, 7.7 Hz, 1H), 6.25 (d, *J* = 5.4 Hz, 1H), 5.49 (ddd, *J* = 17.2, 10.2, 5.4 Hz, 1H), 5.34 (d, *J* = 17.1 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 4.79 (d, *J* = 11.1 Hz, 1H), 4.63 (d, *J* = 11.1 Hz, 1H), 4.26 (qq, *J* = 7.2, 3.7 Hz, 2H), 2.29 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

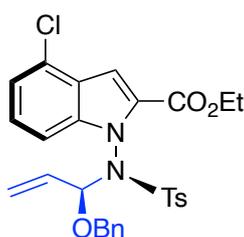
¹³C NMR (101 MHz, CDCl₃) δ 159.58, 144.28, 141.34, 137.41, 136.49, 130.21, 129.54, 129.18, 128.60, 128.42, 128.22, 128.03, 127.85, 127.74, 125.98, 125.90, 121.07, 108.60, 106.32, 90.78, 77.42, 77.10, 76.78, 70.96, 60.88, 21.52, 14.24, 14.18.

¹⁹F NMR (377 MHz, CDCl₃) δ -121.96.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{27}FN_2NaO_5S^+$) requires m/z 545.1517, found, 545.1516.

HPLC analysis: 97 : 3 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 11.9 min, R_t (minor) = 14.7 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-4-chloro-1*H*-indole-2-carboxylate(3c)



Colorless oil, 82% yield, 44.1 mg, 10:1 d.r., 92% ee.

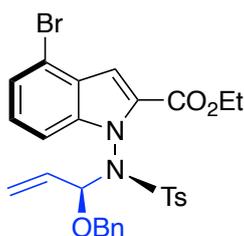
¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.39 (m, 6H), 7.34 (s, 1H), 7.33 – 7.18 (m, 1H), 7.09 (d, J = 7.3 Hz, 1H), 7.05 – 6.96 (m, 3H), 6.95 – 6.90 (m, 1H), 6.31 (d, J = 5.3 Hz, 1H), 5.55 (ddd, J = 17.4, 10.2, 5.4 Hz, 1H), 5.44 – 5.37 (m, 1H), 5.09 (dt, J = 10.2, 1.3 Hz, 1H), 4.85 (d, J = 11.1 Hz, 1H), 4.69 (d, J = 11.1 Hz, 1H), 4.32 (qq, J = 7.4, 3.7 Hz, 2H), 2.35 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.58, 144.33, 139.99, 137.37, 136.34, 130.13, 129.83, 129.22, 128.61, 128.44, 128.03, 127.88, 127.26, 125.90, 122.76, 121.56, 121.15, 111.28, 108.66, 90.69, 77.43, 77.12, 76.80, 70.97, 60.94, 21.56, 14.28.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{27}ClN_2NaO_5S^+$) requires m/z 561.1221, found, 561.1223.

HPLC analysis: 96 : 4 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 80/20, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 7.6 min, R_t (minor) = 9.3 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-4-bromo-1*H*-indole-2-carboxylate(3d)



Colorless oil, 92% yield, 53.5 mg, 10:1 d.r., 88% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.37 (m, 6H), 7.27 – 7.20 (m, 3H), 6.99 (dd, J = 11.9, 8.3 Hz, 3H), 6.84 (m, J = 8.0 Hz, 1H), 6.28 (d, J = 5.3 Hz, 1H), 5.51 (ddd, J = 17.2, 10.2, 5.4 Hz, 1H), 5.37 (dt, J = 17.1, 1.4 Hz, 1H), 5.06 (dt,

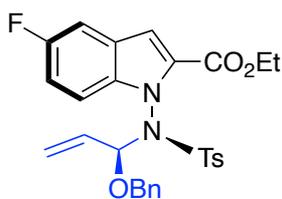
$J = 10.3, 1.4$ Hz, 1H), 4.82 (d, $J = 11.1$ Hz, 1H), 4.66 (d, $J = 11.1$ Hz, 1H), 4.29 (qq, $J = 7.2, 3.7$ Hz, 2H), 2.32 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.58, 144.35, 139.71, 137.36, 136.34, 130.13, 129.87, 129.24, 128.62, 128.45, 128.04, 127.90, 126.21, 124.80, 124.58, 121.18, 115.97, 111.85, 110.32, 90.70, 77.46, 77.14, 76.83, 70.98, 60.96, 21.66, 21.57, 14.29, 14.23.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{28}\text{H}_{27}\text{BrN}_2\text{NaO}_5\text{S}^+$) requires m/z 605.0716, found, 605.0718.

HPLC analysis: 94 : 6 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 80/20, flow rate = 0.8 mL/min, $\lambda = 286$ nm), R_t (major) = 7.8 min, R_t (minor) = 9.5 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-5-fluoro-1*H*-indole-2-carboxylate(3e)



3e, 97%, 12:1 d.r., 99:1 er

Colorless oil, 97% yield, 50.7 mg, 12:1 d.r., 98% ee.

^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.42 (m, 7H), 7.40 – 7.26 (m, 2H), 7.14 – 7.04 (m, 3H), 6.84 (td, $J = 9.1, 2.5$ Hz, 1H), 6.39 (d, $J = 5.4$ Hz, 1H), 5.64 (ddd, $J = 17.3, 10.3, 5.3$ Hz, 1H), 5.48 (d, $J = 17.3$ Hz, 1H), 5.17 (d, $J = 10.3$ Hz, 1H),

4.92 (d, $J = 11.1$ Hz, 1H), 4.77 (d, $J = 11.1$ Hz, 1H), 4.39 (qq, $J = 7.2, 3.7$ Hz, 2H), 2.42 (s, 3H), 1.47 (t, $J = 7.1$ Hz, 3H).

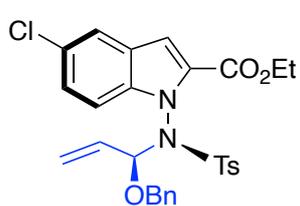
^{13}C NMR (101 MHz, CDCl_3) δ 159.68, 144.34, 137.37, 136.38, 135.73, 130.74, 130.21, 129.21, 128.59, 128.47, 128.06, 127.92, 124.18, 124.08, 120.94, 114.38, 114.12, 113.92, 113.83, 110.28, 110.23, 106.53, 106.29, 90.60, 77.47, 77.15, 76.83, 71.00, 60.85, 21.54, 14.26.

^{19}F NMR (377 MHz, CDCl_3) δ -121.67.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{28}\text{H}_{27}\text{FN}_2\text{NaO}_5\text{S}^+$) requires m/z 545.1517, found, 545.1523.

HPLC analysis: 99 : 1 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, $\lambda = 286$ nm), R_t (major) = 10 min, R_t (minor) = 10.8 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-5-chloro-1*H*-indole-2-carboxylate(3f**)**



3f, 96%, 10:1 d.r., 96:4 er

Colorless oil, 96% yield, 51.7 mg, 10:1 d.r., 96% ee.

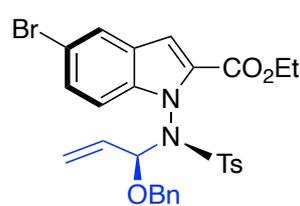
¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.46 (m, 7H), 7.38 (m, *J* = 9.6, 4.8 Hz, 1H), 7.15 – 7.04 (m, 4H), 6.41 (d, *J* = 5.3 Hz, 1H), 5.65 (ddd, *J* = 17.2, 10.2, 5.3 Hz, 1H), 5.49 (d, *J* = 17.3 Hz, 1H), 5.19 (d, *J* = 10.3 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.78 (d, *J* = 11.1 Hz, 1H), 4.41 (qq, *J* = 7.2, 3.6 Hz, 2H), 2.46 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.62, 144.41, 137.62, 137.32, 136.34, 130.49, 130.13, 129.25, 128.57, 128.47, 128.04, 127.93, 127.48, 125.86, 124.73, 121.16, 121.03, 113.93, 109.82, 90.55, 77.46, 77.14, 76.82, 71.01, 60.92, 21.57, 14.27.

HRMS (ESI, *m/z*): exact mass calculated for [M+Na]⁺ (C₂₈H₂₇ClN₂NaO₅S⁺) requires *m/z* 561.1221, found, 561.1223.

HPLC analysis: 96 :4 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 80/20, flow rate = 0.8 mL/min, λ = 286 nm), *R_t* (major) = 8.7 min, *R_t* (minor) = 9.5 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-5-bromo-1*H*-indole-2-carboxylate(3g**)**



3g, 92%, 10:1 d.r., 95:5 er

Colorless oil, 92% yield, 53.6 mg, 10:1 d.r., 92% ee.

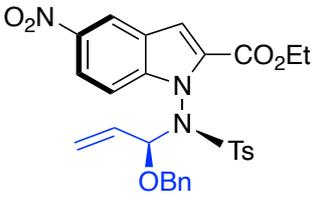
¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 1.8 Hz, 1H), 7.44 – 7.34 (m, 7H), 7.13 (s, 1H), 7.07 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 1H), 6.27 (d, *J* = 5.3 Hz, 1H), 5.51 (ddd, *J* = 17.2, 10.3, 5.3 Hz, 1H), 5.36 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.06 (dt, *J* = 10.3, 1.4 Hz, 1H), 4.81 (d, *J* = 11.1 Hz, 1H), 4.65 (d, *J* = 11.0 Hz, 1H), 4.29 (qq, *J* = 7.1, 3.7 Hz, 2H), 2.35 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.58, 144.39, 137.89, 137.29, 136.31, 130.30, 130.08, 129.23, 128.55, 128.45, 128.36, 128.01, 127.90, 125.34, 124.27, 121.04, 115.03, 114.25, 109.66, 90.53, 77.37, 77.05, 76.73, 70.99, 60.93, 21.57, 14.24.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{27}BrN_2NaO_5S^+$) requires m/z 605.0716, found, 605.0717.

HPLC analysis: 96 : 4 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 10.9 min, R_t (minor) = 12.3 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-5-nitro-1*H*-indole-2-carboxylate(3h)

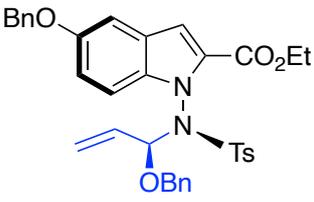

Yellow oil, 97% yield, 53.3 mg, 10:1 d.r., 84% ee.
¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, J = 2.1 Hz, 1H), 7.85 (dd, J = 9.2, 2.2 Hz, 1H), 7.47 – 7.38 (m, 7H), 7.35 (d, J = 0.9 Hz, 1H), 7.12 (d, J = 9.2 Hz, 1H), 7.01 (d, J = 8.1 Hz, 2H), 6.32 (dt, J = 5.2, 1.1 Hz, 1H), 5.56 (ddd, J = 17.2, 10.3, 5.1 Hz, 1H), 5.37 (dt, J = 17.1, 1.4 Hz, 1H), 5.08 (dt, J = 10.3, 1.3 Hz, 1H), 4.83 (d, J = 10.9 Hz, 1H), 4.68 (d, J = 10.9 Hz, 1H), 4.35 – 4.30 (m, 2H), 2.35 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.13, 144.85, 143.34, 141.89, 137.04, 135.88, 132.43, 130.94, 129.84, 129.40, 128.56, 128.52, 128.09, 123.03, 121.34, 120.25, 119.05, 113.12, 111.67, 90.26, 77.39, 77.07, 76.76, 71.26, 61.32, 21.59, 14.21.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{27}N_3NaO_7S^+$) requires m/z 572.1462, found, 572.1456.

HPLC analysis: 92 : 8 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 12.8 min, R_t (minor) = 15.8 min.

Ethyl (*S_a*,*S*)-5-(benzyloxy)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(3i)


Colorless oil, 98% yield, 59.8 mg, 10:1 d.r., 94% ee.
¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.39 (m, 10H), 7.38 – 7.34 (m, 2H), 7.15 (d, J = 0.9 Hz, 1H), 7.03 (d, J = 2.4 Hz, 1H), 6.99 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 9.1 Hz, 1H), 6.76 (dd, J = 9.1, 2.4 Hz, 1H), 6.28 (d, J = 5.5 Hz, 1H), 5.54 (ddd,

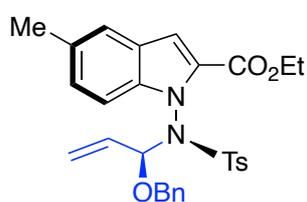
$J = 17.2, 10.2, 5.5$ Hz, 1H), 5.39 (dt, $J = 17.2, 1.4$ Hz, 1H), 5.10 – 5.07 (m, 1H), 5.05 (d, $J = 1.4$ Hz, 2H), 4.83 (d, $J = 11.3$ Hz, 1H), 4.67 (d, $J = 11.1$ Hz, 1H), 4.30 (qd, $J = 7.1, 3.5$ Hz, 2H), 2.34 (s, 3H), 1.39 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.92, 154.56, 144.11, 137.48, 137.21, 136.65, 134.60, 130.37, 129.66, 129.14, 128.60, 128.59, 128.41, 128.01, 127.97, 127.82, 127.57, 124.26, 120.84, 117.10, 113.68, 110.33, 103.80, 90.76, 77.42, 77.10, 76.79, 70.84, 70.57, 60.65, 21.56, 14.30.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{35}\text{H}_{34}\text{N}_2\text{NaO}_6\text{S}^+$) requires m/z 633.2030, found, 633.2026.

HPLC analysis: 97 : 3 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, $\lambda = 286$ nm), R_t (major) = 18.5 min, R_t (minor) = 20.1 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-5-methyl-1*H*-indole-2-carboxylate(3j)



3j, 92%, 10:1 d.r., 98:2 er

Colorless oil, 92% yield, 47.7 mg, 10:1 d.r., 94% ee.

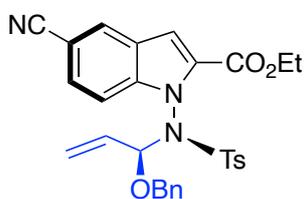
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 – 7.56 (m, 2H), 7.55 – 7.45 (m, 5H), 7.44 – 7.41 (m, 1H), 7.26 (s, 1H), 7.12 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 8.6$ Hz, 1H), 6.97 (dd, $J = 8.6, 1.6$ Hz, 1H), 6.38 (d, $J = 5.6$ Hz, 1H), 5.63 (ddd, $J = 17.2, 10.2, 5.5$ Hz, 1H), 5.49 (dt, $J = 17.2, 1.4$ Hz, 1H), 5.17 (dt, $J = 10.3, 1.3$ Hz, 1H), 4.95 (d, $J = 11.2$ Hz, 1H), 4.78 (d, $J = 11.2$ Hz, 1H), 4.40 (qt, $J = 7.1, 3.6$ Hz, 2H), 2.48 (s, 3H), 2.46 (s, 3H), 1.50 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.03, 144.01, 137.77, 137.54, 136.75, 131.21, 130.37, 129.14, 129.09, 128.60, 128.37, 127.96, 127.75, 127.40, 124.03, 121.34, 120.81, 112.28, 110.35, 90.88, 77.38, 77.07, 76.75, 70.77, 60.60, 21.55, 21.27, 14.28.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{29}\text{H}_{30}\text{N}_2\text{NaO}_5\text{S}^+$) requires m/z 541.1768, found, 541.1765.

HPLC analysis: 98 : 2 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, $\lambda = 286$ nm), R_t (major) = 11.9 min, R_t (minor) = 13.6 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-5-cyano-1*H*-indole-2-carboxylate(3k**)**



3k, 91%, 10:1 d.r., 95:5 er

Colorless oil, 91% yield, 48.2 mg, 10:1 d.r., 90% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.79 (m, 1H), 7.35 – 7.26 (m, 7H), 7.17 (m, *J* = 1.5 Hz, 1H), 7.10 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.21 (dd, *J* = 3.8, 2.6 Hz, 1H), 5.45 (ddd, *J* = 17.2, 10.3, 5.2

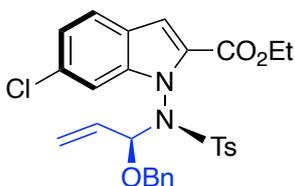
Hz, 1H), 5.28 (dt, *J* = 17.2, 1.4 Hz, 1H), 4.99 (dt, *J* = 10.4, 1.3 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.58 (d, *J* = 11.0 Hz, 1H), 4.23 (qq, *J* = 7.2, 3.6 Hz, 2H), 2.27 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.25, 144.73, 140.71, 137.09, 135.95, 131.58, 129.90, 129.35, 128.52, 128.10, 128.06, 127.63, 127.61, 123.49, 121.29, 119.58, 113.76, 110.45, 105.46, 90.31, 77.42, 77.10, 76.78, 71.19, 61.23, 21.59, 14.21.

HRMS (ESI, *m/z*): exact mass calculated for [M+Na]⁺ (C₂₉H₂₇N₃NaO₅S⁺) requires *m/z* 552.1564, found, 552.1563.

HPLC analysis: 95 : 5 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), Rt (major) = 15.8 min, Rt (minor) = 16.8 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-6-chloro-1*H*-indole-2-carboxylate(3l**)**



3l, 65%, 20:1 d.r., 96:4 er

Colorless oil, 65% yield, 35.0 mg, 20:1 d.r., 92% ee.

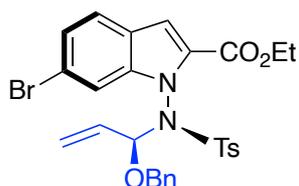
¹H NMR (400 MHz, CDCl₃) δ 7.32 (m, *J* = 3.8 Hz, 5H), 7.29 – 7.24 (m, 3H), 7.09 (d, *J* = 1.0 Hz, 1H), 6.89 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.78 – 6.72 (m, 1H), 6.24 – 6.18 (m, 1H), 5.48 (ddd, *J* = 17.2, 10.4, 5.3 Hz, 1H), 5.29 (dt, *J* = 17.3, 1.4 Hz, 1H), 5.01 (dt, *J* = 10.4, 1.3 Hz, 1H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.58 (d, *J* = 11.1 Hz, 1H), 4.25 (qt, *J* = 7.1, 3.5 Hz, 2H), 2.23 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.65, 143.76, 138.26, 136.21, 134.94, 130.51, 129.29, 129.03, 128.15, 127.65, 127.45, 126.76, 126.73, 121.74, 121.69, 121.27, 119.90, 111.77, 109.44, 89.12, 76.33, 76.01, 75.70, 69.85, 59.85, 20.47, 13.23.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{27}ClN_2NaO_5S^+$) requires m/z 561.1221, found, 561.1224.

HPLC analysis: 96 : 4 er (CHIRALCEL IC column, 25 °C, *n*-hexane / *i*-PrOH = 7/3, flow rate = 1.0 mL/min, λ = 286 nm), Rt (major) = 7.6 min, Rt (minor) = 10.4 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-6-bromo-1*H*-indole-2-carboxylate(3m)



Colorless oil, 60% yield, 34.9 mg, 18:1 d.r., 88% ee.

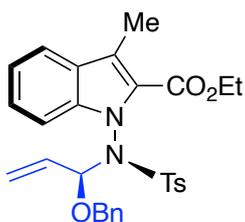
¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 3.6 Hz, 4H), 7.39 (d, J = 4.1 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.33 (d, J = 1.6 Hz, 1H), 7.19 (d, J = 1.0 Hz, 1H), 7.12 (dd, J = 8.4, 1.7 Hz, 1H), 7.03 – 6.96 (m, 1H), 6.90 (d, J = 8.1 Hz, 2H), 6.31 (dt, J = 5.3, 1.1 Hz, 1H), 5.59 (ddd, J = 17.1, 10.3, 5.3 Hz, 1H), 5.39 (dt, J = 17.4, 1.3 Hz, 1H), 5.12 (dt, J = 10.4, 1.2 Hz, 1H), 4.78 (d, J = 11.1 Hz, 1H), 4.68 (d, J = 11.1 Hz, 1H), 4.36 (qt, J = 7.1, 3.5 Hz, 2H), 2.35 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.69, 144.87, 139.47, 137.24, 135.90, 130.24, 130.01, 129.25, 128.68, 128.53, 127.77, 127.69, 125.26, 123.05, 122.64, 120.96, 119.36, 115.83, 110.48, 90.09, 77.37, 77.05, 76.74, 70.86, 60.94, 21.62, 14.28.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{27}BrN_2NaO_5S^+$) requires m/z 605.0716, found, 605.0714.

HPLC analysis: 96 : 4 er (CHIRALCEL IC column, 25 °C, *n*-hexane / *i*-PrOH = 7/3, flow rate = 1.0 mL/min, λ = 286 nm), Rt (major) = 8.0 min, Rt (minor) = 10.8 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-3-methyl-1*H*-indole-2-carboxylate(3n)



Colorless oil, 96% yield, 49.7 mg, 6:1 d.r., 96% ee.

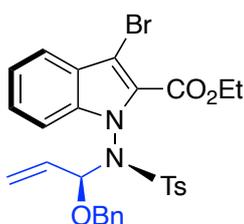
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 (m, $J = 8.0, 1.0$ Hz, 1H), 7.47 – 7.35 (m, 7H), 7.06 (ddd, $J = 8.0, 6.8, 1.2$ Hz, 1H), 6.99 – 6.90 (m, 4H), 6.28 (dd, $J = 5.6, 1.1$ Hz, 1H), 5.55 (ddd, $J = 17.2, 10.2, 5.6$ Hz, 1H), 5.41 (dt, $J = 17.0, 1.5$ Hz, 1H), 5.08 (dt, $J = 10.4, 1.2$ Hz, 1H), 4.82 (d, $J = 11.1$ Hz, 1H), 4.67 (d, $J = 11.1$ Hz, 1H), 4.49 – 4.33 (m, 2H), 2.59 (s, 3H), 2.33 (s, 3H), 1.47 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 161.13, 143.95, 138.17, 137.58, 137.08, 130.36, 129.45, 129.03, 128.56, 128.40, 128.01, 127.78, 125.87, 125.58, 125.32, 121.11, 120.75, 119.90, 111.98, 91.29, 77.41, 77.15, 76.90, 70.78, 60.60, 21.53, 14.37, 10.63.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{29}\text{H}_{30}\text{N}_2\text{NaO}_5\text{S}^+$) requires m/z 541.1768, found, 541.1764.

HPLC analysis: 98 : 2 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, $\lambda = 286$ nm), R_t (major) = 9.1 min, R_t (minor) = 9.9 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-3-bromo-1*H*-indole-2-carboxylate(3o)



Colorless oil, 97% yield, 56.5 mg, 11:1 d.r., 94% ee.

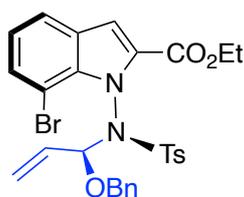
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 (m, $J = 8.0, 0.9$ Hz, 1H), 7.46 – 7.35 (m, 7H), 7.13 (ddd, $J = 8.1, 6.9, 1.1$ Hz, 1H), 7.00 (ddd, $J = 8.2, 6.9, 1.2$ Hz, 1H), 6.97 – 6.91 (m, 3H), 6.28 (dd, $J = 5.5, 1.0$ Hz, 1H), 5.57 (ddd, $J = 17.1, 10.2, 5.5$ Hz, 1H), 5.41 (dt, $J = 17.2, 1.3$ Hz, 1H), 5.10 (dt, $J = 10.4, 1.2$ Hz, 1H), 4.81 (d, $J = 11.0$ Hz, 1H), 4.66 (d, $J = 11.0$ Hz, 1H), 4.50 – 4.34 (m, 2H), 2.32 (s, 3H), 1.48 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.46, 144.33, 137.84, 137.36, 136.41, 129.94, 129.17, 128.57, 128.45, 128.06, 127.90, 126.96, 126.47, 124.77, 122.41, 121.26, 120.77, 112.22, 100.27, 90.94, 77.43, 77.12, 76.80, 71.00, 61.37, 21.55, 14.23.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{28}\text{H}_{27}\text{BrN}_2\text{NaO}_5\text{S}^+$) requires m/z 605.0716, found, 605.0717.

HPLC analysis: 97 : 3 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), Rt (major) = 9.3 min, Rt (minor) = 10.0 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-7-bromo-1*H*-indole-2-carboxylate(3p)



3p, 81%, 20:1 d.r., 80:20 er (r.t.)

Colorless oil, 81% yield, 47.0 mg, 20:1 d.r., 60% ee.

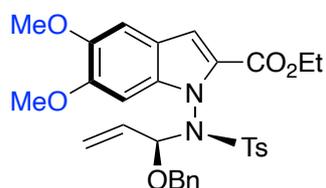
¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.50 (m, 4H), 7.25 – 7.16 (m, 6H), 7.07 – 7.00 (m, 3H), 6.41 (d, J = 12.4 Hz, 1H), 5.01 (ddd, J = 12.5, 9.4, 6.9 Hz, 1H), 4.77 (dd, J = 11.5, 6.9 Hz, 1H), 4.64 (dd, J = 11.5, 9.5 Hz, 1H), 4.50 (d, J = 12.1 Hz, 1H), 4.41 (d, J = 12.1 Hz, 1H), 3.93 – 3.76 (m, 2H), 2.41 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.46, 151.25, 142.68, 135.58, 135.31, 134.85, 131.28, 128.76, 128.48, 127.31, 127.07, 126.79, 126.11, 125.27, 121.92, 120.80, 111.28, 103.68, 95.63, 76.31, 75.99, 75.68, 70.03, 59.49, 20.51, 12.99.

HRMS (ESI, *m/z*): exact mass calculated for [M+Na]⁺ (C₂₈H₂₇BrN₂NaO₅S⁺) requires *m/z* 605.0716, found, 605.0719.

HPLC analysis: 80: 20 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), Rt (major) = 15.4 min, Rt (minor) = 16.2 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-5,6-dimethoxy-1*H*-indole-2-carboxylate(3q)



3q, 94%, 10:1 d.r., 99:1 er

Colorless oil, 94% yield, 53.1 mg, 10:1 d.r., 98% ee.

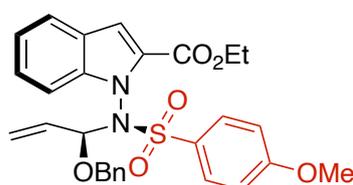
¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.45 (m, 2H), 7.41 (dd, J = 7.4, 2.3 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.12 (s, 1H), 6.98 (d, J = 8.1 Hz, 2H), 6.87 (s, 1H), 6.39 (s, 1H), 6.32 (d, J = 5.4 Hz, 1H), 5.56 (ddd, J = 17.2, 10.2, 5.4 Hz, 1H), 5.42 (dt, J = 17.3, 1.4 Hz, 1H), 5.13 (dt, J = 10.2, 1.3 Hz, 1H), 4.76 (d, J = 10.2 Hz, 1H), 4.58 (d, J = 10.2 Hz, 1H), 4.29 (qq, J = 6.9, 3.7 Hz, 2H), 3.84 (s, 3H), 3.08 (s, 3H), 2.30 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.87, 149.47, 146.40, 144.07, 137.31, 137.03, 134.19, 130.11, 129.14, 128.82, 128.50, 128.38, 128.07, 127.82, 120.83, 116.56, 110.68, 101.87, 94.90, 90.31, 77.42, 77.11, 76.79, 70.83, 60.38, 56.03, 54.88, 21.44, 14.33.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{30}\text{H}_{32}\text{N}_2\text{NaO}_7\text{S}^+$) requires m/z 587.1822, found, 587.1821.

HPLC analysis: 99: 1 er (CHIRALCEL AD column, 25 °C, *n*-hexane / *i*-PrOH = 7/3, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 10.3 min, R_t (minor) = 11.6 min.

Ethyl (S_a,S)-1-((*N*-(1-(benzyloxy)allyl)-4-methoxyphenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Xa)



Colorless oil, 96% yield, 49.9 mg, 10:1 d.r., 96% ee.

^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, J = 7.5 Hz, 1H), 7.47 – 7.33 (m, 7H), 7.22 (s, 1H), 7.08 – 6.99 (m, 3H), 6.63 – 6.57 (m, 2H), 6.28 (d, J = 5.5 Hz, 1H), 5.52 (ddd, J = 17.3, 10.2, 5.5 Hz, 1H), 5.38 (dt, J = 17.2, 1.4 Hz,

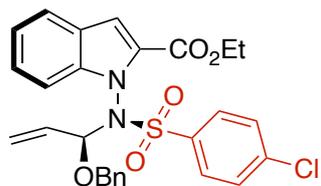
1H), 5.05 (dt, J = 10.2, 1.3 Hz, 1H), 4.81 (d, J = 11.1 Hz, 1H), 4.66 (d, J = 11.1 Hz, 1H), 4.31 (qt, J = 6.8, 3.4 Hz, 2H), 3.75 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.42, 160.03, 139.28, 137.56, 131.12, 130.79, 130.31, 129.38, 128.42, 127.98, 127.79, 125.51, 123.80, 121.96, 121.81, 120.89, 113.64, 112.46, 110.68, 90.85, 77.40, 77.08, 76.77, 70.78, 60.71, 55.58, 14.29.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{28}\text{H}_{28}\text{N}_2\text{NaO}_6\text{S}^+$) requires m/z 543.1560, found, 543.1564.

HPLC analysis: 99: 1 er (CHIRALCEL AD column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 20.1 min, R_t (minor) = 25.4 min.

Ethyl (S_a,S)-1-((*N*-(1-(benzyloxy)allyl)-4-chlorophenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Xb)



3Xb, 96%, 20:1 d.r., 97:3 er

Colorless oil, 96% yield, 50.3 mg, 20:1 d.r., 94% ee.

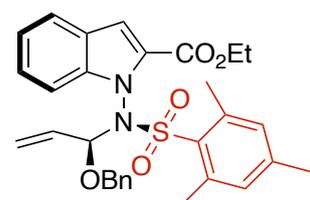
¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.55 (m, 1H), 7.49 – 7.37 (m, 7H), 7.26 (d, *J* = 1.0 Hz, 1H), 7.14 – 7.04 (m, 4H), 6.99 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.29 (d, *J* = 5.3 Hz, 1H), 5.51 (ddd, *J* = 17.2, 9.8, 5.4 Hz, 1H), 5.45 – 5.39 (m, 1H), 5.12 – 5.07 (m, 1H), 4.79 (d, *J* = 11.0 Hz, 1H), 4.68 (d, *J* = 11.0 Hz, 1H), 4.34 (qd, *J* = 7.1, 3.0 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 160.00, 139.75, 139.11, 138.24, 137.27, 130.08, 130.01, 129.16, 128.73, 128.53, 128.09, 128.01, 125.74, 123.85, 122.18, 122.07, 121.40, 112.02, 110.89, 91.22, 77.42, 77.10, 76.78, 70.85, 60.83, 14.31.

HRMS (ESI, *m/z*): exact mass calculated for [M+Na]⁺ (C₂₇H₂₅ClN₂NaO₅S⁺) requires *m/z* 547.1065, found, 547.1066.

HPLC analysis: 97: 3 er (CHIRALCEL AD column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), Rt (major) = 11.6 min, Rt (minor) = 15.1 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-2,4,6-trimethylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Xc)



3Xc, 97%, 10:1 d.r., 95:5 er

Colorless oil, 97% yield, 51.6 mg, 10:1 d.r., 90% ee.

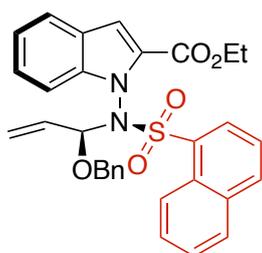
¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.5 Hz, 1H), 7.45 (m, *J* = 7.5, 3.3 Hz, 3H), 7.33 (m, *J* = 7.4 Hz, 2H), 7.26 (m, *J* = 7.2 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.07 (m, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.73 (s, 2H), 6.27 (d, *J* = 4.2 Hz, 1H), 5.79 (ddd, *J* = 17.1, 10.4, 4.4 Hz, 1H), 5.32 (dt, *J* = 17.1, 1.6 Hz, 1H), 5.07 (d, *J* = 11.4 Hz, 1H), 4.97 (dt, *J* = 10.5, 1.5 Hz, 1H), 4.74 (d, *J* = 11.4 Hz, 1H), 3.83 (ddq, *J* = 65.0, 10.8, 7.1 Hz, 2H), 2.17 (s, 9H), 1.10 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.00, 141.85, 140.75, 138.95, 136.76, 130.64, 130.22, 129.87, 127.35, 127.32, 126.76, 126.56, 124.79, 122.77, 121.00, 120.30, 118.93, 113.84, 109.76, 89.17, 76.32, 76.00, 75.69, 70.28, 59.09, 19.88, 13.05.

HRMS (ESI, *m/z*): exact mass calculated for [M+Na]⁺ (C₃₀H₃₂N₂NaO₅S⁺) requires *m/z* 555.1924, found, 555.1926.

HPLC analysis: 95: 5 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), Rt (major) = 6.7 min, Rt (minor) = 7.7 min.

Ethyl (*S_a*,*S*)-1-(*N*-(1-(benzyloxy)allyl)naphthalene-1-sulfonamido)-1*H*-indole-2-carboxylate(3Xd)



3Xd, 98%, 10:1 d.r., 97:3 er

Colorless oil, 98% yield, 52.9 mg, 10:1 d.r., 94% ee.

¹H NMR (400 MHz, CDCl₃) δ 8.57 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 7.7 Hz, 2H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.58 (m, 3H), 7.46 (m, *J* = 7.8 Hz, 1H), 7.36 (dd, *J* = 5.6, 2.3 Hz, 4H), 7.19 – 7.09 (m, 4H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.33 (d, *J* = 12.1 Hz, 1H), 5.14 – 5.00 (m, 2H), 4.61 – 4.57

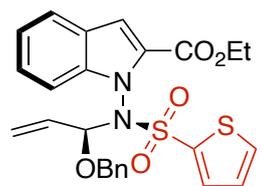
(m, 1H), 4.55 (s, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 3.98 – 3.88 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 158.91, 150.32, 139.40, 135.29, 133.65, 133.61, 133.19, 129.73, 127.95, 127.77, 127.65, 127.41, 127.21, 126.91, 126.28, 125.76, 124.72, 123.95, 123.23, 122.33, 120.98, 120.77, 110.67, 110.42, 96.97, 76.25, 76.00, 75.74, 70.08, 59.43, 13.00.

HRMS (ESI, *m/z*): exact mass calculated for [M+Na]⁺ (C₃₁H₂₈N₂NaO₅S⁺) requires *m/z* 563.1611, found, 563.1609.

HPLC analysis: 97: 3 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 10/1, flow rate = 0.5 mL/min, λ = 286 nm), Rt (major) = 16.5 min, Rt (minor) = 18.2 min.

Ethyl (*S_a*,*S*)-1-(*N*-(1-(benzyloxy)allyl)thiophene-2-sulfonamido)-1*H*-indole-2-carboxylate(3Xe)



3Xe, 99%, 10:1 d.r., 95:5 er

Yellow oil, 99% yield, 49.1 mg, 10:1 d.r., 90% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.40 (m, 1H), 7.31 (m, *J* = 6.5, 1.7 Hz, 3H), 7.29 – 7.19 (m, 3H), 7.15 – 7.11 (m, 2H), 6.97 – 6.88 (m, 3H), 6.68 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.16 (dd, *J* = 5.5, 1.2 Hz, 1H), 5.38 (ddd, *J* = 17.2, 10.1,

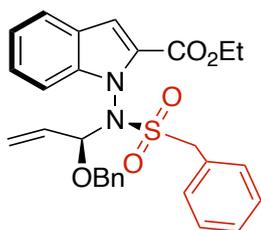
5.5 Hz, 1H), 5.25 (dt, $J = 17.0, 1.4$ Hz, 1H), 4.93 (dt, $J = 10.3, 1.3$ Hz, 1H), 4.72 (d, $J = 11.2$ Hz, 1H), 4.54 (d, $J = 11.1$ Hz, 1H), 4.21 (qd, $J = 7.1, 1.6$ Hz, 2H), 1.26 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.00, 139.29, 138.25, 136.33, 133.40, 132.35, 129.05, 128.23, 127.35, 127.07, 126.81, 126.07, 124.64, 122.72, 121.05, 120.87, 120.17, 110.69, 109.86, 90.32, 76.34, 76.02, 75.70, 70.02, 59.74, 13.26.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{25}\text{H}_{24}\text{N}_2\text{NaO}_5\text{S}_2^+$) requires m/z 519.1019, found, 519.1020.

HPLC analysis: 95: 5 er (CHIRALCEL AD column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, $\lambda = 286$ nm), R_t (major) = 13.4 min, R_t (minor) = 15.7 min.

Ethyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-1-phenylmethyl)sulfonamido)-1*H*-indole-2-carboxylate(3Xf)



Colorless oil, 97% yield, 48.9 mg, 20:1 d.r., 78% ee.

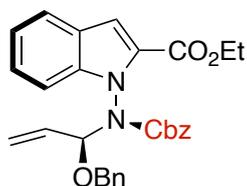
^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.4$ Hz, 1H), 7.69 (d, $J = 7.9$ Hz, 1H), 7.54 (d, $J = 7.1$ Hz, 2H), 7.49 – 7.44 (m, 2H), 7.42 – 7.37 (m, 2H), 7.35 (s, 1H), 7.33 – 7.22 (m, 6H), 6.15 (d, $J = 5.7$ Hz, 1H), 5.57 (ddd, $J = 17.3, 9.9, 5.7$ Hz, 1H), 5.47 (dd, $J = 17.2, 1.9$ Hz, 1H), 5.16 (dd, $J = 9.9, 1.9$ Hz, 1H), 4.79 (d, $J = 11.0$ Hz, 1H), 4.71 (d, $J = 10.9$ Hz, 1H), 4.65 (d, $J = 13.1$ Hz, 1H), 4.43 – 4.38 (m, 2H), 4.36 (d, $J = 9.6$ Hz, 1H), 1.42 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 160.35, 139.80, 137.44, 131.05, 130.24, 129.57, 128.83, 128.68, 128.65, 128.36, 128.15, 127.68, 126.44, 124.23, 122.75, 122.29, 121.54, 111.54, 110.98, 91.83, 77.43, 77.11, 76.80, 71.04, 62.80, 60.99, 14.30.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{28}\text{H}_{28}\text{N}_2\text{NaO}_5\text{S}^+$) requires m/z 527.1611, found, 527.1614.

HPLC analysis: 89: 11 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, $\lambda = 286$ nm), R_t (major) = 14.0 min, R_t (minor) = 21.2 min.

Ethyl (*S_a*,*S*)-1-((1-(benzyloxy)allyl)((benzyloxy)carbonyl)amino)-1*H*-indole-2-carboxylate(3Xg)



Colorless oil, 94% yield, 45.5 mg, 5:1 d.r., 94% ee; $[\alpha]_D^{25} = -73.88$ (c 0.13, CH₂Cl₂).

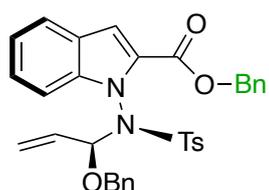
¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.37 (m, *J* = 8.5 Hz, 5H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 10.0 Hz, 5H), 7.14 (s, 2H), 6.27 (d, *J* = 5.4 Hz, 1H), 5.46 – 5.31 (m, 3H), 5.18 (d, *J* = 12.6 Hz, 1H), 5.01 – 4.89 (m, 2H), 4.83 (d, *J* = 12.2 Hz, 1H), 4.07 (dt, *J* = 52.6, 10.0 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 160.55, 156.29, 139.25, 138.13, 132.30, 129.30, 128.28, 128.18, 127.87, 127.40, 125.45, 123.72, 122.36, 121.53, 119.13, 111.17, 109.56, 87.43, 77.37, 77.05, 76.73, 71.72, 68.06, 60.64, 14.11.

HRMS (ESI, *m/z*): exact mass calculated for [M+Na]⁺ (C₂₉H₂₈N₂NaO₅S⁺) requires *m/z* 507.1890, found, 507.1893.

HPLC analysis: 97: 3 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 75/1, flow rate = 0.8 mL/min, λ = 286 nm), *R_t* (major) = 17.3 min, *R_t* (minor) = 18.2 min.

Benzyl (*S_a*,*S*)-1-((*N*-(1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Ya)



Colorless oil, 98% yield, 55.5 mg, 10:1 d.r., 98% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.38 (m, *J* = 7.9, 1.1 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.29 – 7.25 (m, 6H), 7.24 – 7.19 (m, 3H), 7.12 (d, *J* = 0.8 Hz, 1H), 6.94 – 6.84 (m, 3H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.06 (dd, *J* = 5.8, 1.1 Hz, 1H), 5.29 (ddd, *J* = 17.2, 10.3, 5.8 Hz, 1H), 5.15 (d, *J* = 8.2 Hz, 2H), 5.07 (dt, *J* = 17.2, 1.3 Hz, 1H), 4.82 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.64 (d, *J* = 11.2 Hz, 1H), 4.48 (d, *J* = 11.1 Hz, 1H), 2.15 (s, 3H).

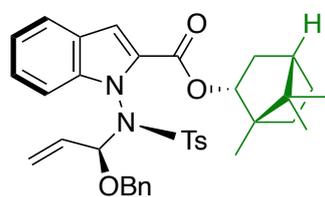
¹³C NMR (101 MHz, CDCl₃) δ 158.68, 143.07, 138.33, 136.41, 135.55, 134.78, 129.08, 128.04, 127.83, 127.56, 127.51, 127.41, 127.32, 127.25, 126.94, 126.72, 124.56,

122.68, 120.94, 120.83, 119.98, 111.37, 110.07, 89.82, 76.36, 76.04, 75.72, 69.68, 65.31, 20.47.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{33}H_{30}N_2NaO_5S^+$) requires m/z 589.1768, found, 589.1773.

HPLC analysis: 99: 1 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 14.3 min, R_t (minor) = 19.1 min.

(1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 1-((*N*-((*S*_a, *S*)-1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Yc)



Colorless oil, 96% yield, 58.8 mg, 14:1 d.r., 98% ee.

3Yc, 96%, 14:1 dr
From (-)-borneol

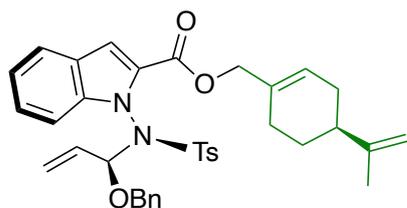
¹H NMR (400 MHz, CDCl₃) δ 7.59 (m, J = 7.8, 1.1 Hz, 1H), 7.51 – 7.38 (m, 7H), 7.26 (s, 1H), 7.13 – 7.07 (m, 2H), 7.06 – 7.03 (m, 1H), 7.01 (d, J = 8.1 Hz, 2H), 6.35 (d, J = 5.5 Hz, 1H), 5.55 (ddd, J = 17.2, 10.2, 5.4 Hz, 1H), 5.42 (dt, J = 17.2, 1.4 Hz, 1H), 5.14 (ddd, J = 10.0, 3.6, 2.0 Hz, 1H),

5.08 (dt, J = 10.2, 1.3 Hz, 1H), 4.88 (d, J = 11.2 Hz, 1H), 4.70 (d, J = 11.1 Hz, 1H), 2.47 – 2.41 (m, 1H), 2.36 (s, 3H), 2.16 (ddd, J = 12.5, 9.0, 4.4 Hz, 1H), 1.85 (tt, J = 12.2, 4.0 Hz, 1H), 1.48 – 1.27 (m, 3H), 1.14 (dd, J = 13.8, 3.5 Hz, 1H), 1.00 (s, 3H), 0.96 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 160.21, 144.01, 139.34, 137.55, 136.77, 130.30, 129.09, 128.64, 128.38, 127.99, 127.75, 125.39, 123.75, 121.86, 121.82, 120.89, 112.53, 110.34, 90.90, 80.19, 77.38, 77.06, 76.74, 70.88, 49.19, 47.99, 44.99, 36.64, 28.07, 27.45, 21.56, 19.79, 18.93, 13.67.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{36}H_{40}N_2NaO_5S^+$) requires m/z 635.2550, found, 635.2545.

((*S*)-4-isopropylcyclohex-1-en-1-yl)methyl 1-((*N*-((*S*_a, *S*)-1-(benzyloxy)allyl)-4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Yd)



3Yd, 99%, 10:1 dr
From perillyl alcohol

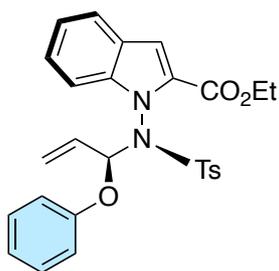
Colorless oil, 99% yield, 60.4 mg, 10:1 d.r., 96% ee.

¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.47 – 7.36 (m, 7H), 7.29 – 7.22 (m, 2H), 7.06 (m, *J* = 8.8, 2.0 Hz, 1H), 7.02 (dd, *J* = 3.8, 1.4 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.30 (dd, *J* = 5.4, 1.2 Hz, 1H), 5.87 (q, *J* = 3.6 Hz, 1H), 5.58 – 5.48 (m,

1H), 5.38 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.05 (dt, *J* = 10.3, 1.3 Hz, 1H), 4.85 (d, *J* = 11.1 Hz, 1H), 4.76 (dt, *J* = 3.0, 1.7 Hz, 2H), 4.70 (d, *J* = 4.3 Hz, 1H), 4.67 (d, *J* = 3.3 Hz, 1H), 4.59 (d, *J* = 12.2 Hz, 1H), 2.34 (s, 3H), 2.25 – 2.16 (m, 4H), 2.03 (tdd, *J* = 14.9, 8.1, 2.8 Hz, 1H), 1.91 (ddt, *J* = 12.8, 4.4, 2.1 Hz, 1H), 1.77 (s, 3H), 1.58 – 1.49 (m, 1H).
¹³C NMR (101 MHz, CDCl₃) δ 159.85, 149.65, 144.07, 139.38, 137.52, 136.70, 132.63, 130.33, 129.10, 129.00, 128.64, 128.39, 128.01, 127.79, 125.98, 125.51, 123.76, 121.95, 121.85, 120.91, 112.47, 110.77, 108.84, 90.85, 77.40, 77.08, 76.77, 70.86, 68.49, 40.88, 30.57, 27.42, 26.51, 21.57, 20.84.

HRMS (ESI, *m/z*): exact mass calculated for [M+Na]⁺ (C₃₆H₃₈N₂NaO₅S⁺) requires *m/z* 633.2394, found, 633.2387.

Ethyl (*S_a*, *S*)-1-((4-methyl-*N*-(1-phenoxymethyl)phenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Za)



3Za, 92%, 5:1 dr, 97:3 er

Colorless oil, 92% yield, 45.1 mg, 5:1 d.r., 94% ee; [α]_D = -20.95 (c 0.29, CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.9 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.29 (d, *J* = 0.9 Hz, 1H), 7.13 – 7.03 (m, 8H), 7.00 (d, *J* = 4.4, 1.3 Hz, 1H), 5.83 (ddd, *J* = 17.2, 10.6, 4.5 Hz, 1H), 5.30 (dt, *J* = 17.2, 1.3 Hz,

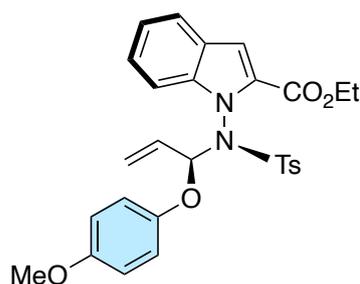
1H), 5.06 (dt, *J* = 10.6, 1.2 Hz, 1H), 4.44 – 4.34 (m, 2H), 2.40 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.14, 155.51, 143.41, 138.05, 135.68, 128.62, 128.51, 128.45, 128.24, 127.62, 124.44, 122.94, 121.20, 121.04, 120.87, 120.53, 115.52, 111.34, 109.79, 87.62, 76.33, 76.01, 75.69, 59.81, 20.56, 13.26.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{27}H_{26}N_2NaO_5S^+$) requires m/z 513.1455, found, 513.1459.

HPLC analysis: 97: 3 er (CHIRALCEL AD column, 25 °C, *n*-hexane / *i*-PrOH = 7/3, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 15.2 min, R_t (minor) = 16.7 min.

Ethyl (*S_a*, *S*)-1-((*N*-(1-(4-methoxyphenoxy)allyl)-4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Zb)



Colorless oil, 92% yield, 47.9 mg, 10:1 d.r., 88% ee; $[\alpha]_D^{25}$ = -38.84 (c 0.18, CH_2Cl_2).

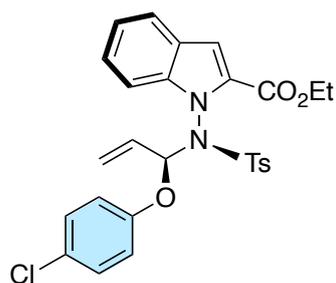
1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.7 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.26 (s, 1H), 7.12 – 7.06 (m, 4H), 7.05 – 7.01 (m, 3H), 6.90 – 6.86 (m, 2H), 6.82 (d, J = 4.9 Hz, 1H), 5.72 (ddd, J = 17.2, 10.5, 4.9 Hz, 1H), 5.28 (d, J = 17.3 Hz, 1H), 5.04 (d, J = 10.5 Hz, 1H), 4.36 (qd, J = 7.2, 1.5 Hz, 2H), 3.81 (s, 3H), 2.39 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.09, 154.00, 149.44, 143.35, 138.07, 135.75, 128.78, 128.44, 128.24, 127.61, 124.45, 122.92, 121.02, 120.86, 120.54, 117.33, 113.70, 111.35, 109.74, 89.17, 76.25, 76.00, 75.74, 59.78, 54.68, 20.57, 13.27.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{28}N_2NaO_6S^+$) requires m/z 543.1560, found, 543.1553.

HPLC analysis: 94: 6 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 16.2 min, R_t (minor) = 23.2 min.

Ethyl (*S_a*, *S*)-1-((*N*-(1-(4-chlorophenoxy)allyl)-4-methylphenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Zc)



3Zc, 87%, 10:1 dr, 90:10 er

Colorless oil, 87% yield, 45.6 mg, 10:1 d.r., 80% ee; $[\alpha]_D^{25} = -59.43$ (c 0.23, CH_2Cl_2).

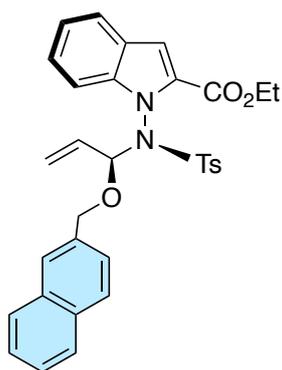
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 – 7.45 (m, 3H), 7.27 (dd, $J = 8.4, 1.0$ Hz, 1H), 7.15 (s, 1H), 7.14 – 7.12 (m, 2H), 7.11 (s, 1H), 7.07 – 7.02 (m, 3H), 6.74 – 6.68 (m, 2H), 6.21 (dt, $J = 5.6, 1.4$ Hz, 1H), 6.01 (ddd, $J = 17.2, 10.4, 5.5$ Hz, 1H), 5.41 (dt, $J = 17.2, 1.2$ Hz, 1H), 5.22 (dt, $J = 10.5, 1.2$ Hz, 1H), 3.94 (qq, $J = 10.8, 7.1$ Hz, 2H), 2.32 (s, 3H), 1.14 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 158.82, 154.38, 143.37, 139.13, 135.66, 130.54, 128.37, 128.32, 127.78, 127.44, 126.23, 125.04, 122.81, 121.21, 121.16, 119.63, 117.12, 111.70, 110.71, 92.06, 76.31, 75.99, 75.68, 59.62, 20.59, 13.18.

HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{27}\text{H}_{25}\text{ClN}_2\text{NaO}_5\text{S}^+$) requires m/z 547.1065, found, 547.1068.

HPLC analysis: 90: 10 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 15/2, flow rate = 0.8 mL/min, $\lambda = 286$ nm), R_t (major) = 12.9 min, R_t (minor) = 16.5 min.

Ethyl (*S_a*, *S*)-1-((4-methyl-*N*-(1-(naphthalen-2-ylmethoxy)allyl)phenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Zd)



3Zd, 89%, 7:1 dr, 97:3 er

Colorless oil, 89% yield, 48.4 mg, 7:1 d.r., 94% ee.

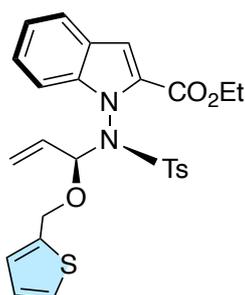
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 – 7.84 (m, 4H), 7.58 – 7.51 (m, 4H), 7.49 – 7.45 (m, 2H), 7.26 (s, 1H), 7.12 – 7.06 (m, 2H), 7.02 (ddd, $J = 7.6, 5.5, 2.4$ Hz, 1H), 6.92 (dd, $J = 8.7, 2.6$ Hz, 2H), 6.37 (d, $J = 5.6$ Hz, 1H), 5.55 (ddt, $J = 13.5, 8.9, 4.0$ Hz, 1H), 5.43 (dt, $J = 16.8, 2.4$ Hz, 1H), 5.11 – 5.07 (m, 1H), 5.00 (dd, $J = 11.4, 3.3$ Hz, 1H), 4.83 (d, $J = 11.4$ Hz, 1H), 4.33 (qt, $J = 7.1, 3.5$ Hz, 2H), 2.28 (s, 3H), 1.41 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 158.97, 143.02, 138.24, 135.67, 133.94, 132.26, 131.96, 129.23, 128.26, 128.07, 127.52, 127.01, 126.88, 126.72, 125.56, 125.16, 124.93, 124.41, 122.76, 120.92, 120.80, 119.95, 111.45, 109.70, 89.87, 76.33, 76.02, 75.70, 69.76, 59.66, 20.41, 13.23.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{32}H_{30}N_2NaO_5S^+$) requires m/z 577.1768, found, 577.1768.

HPLC analysis: 97: 3 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 75/5, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 17.4 min, R_t (minor) = 23.4 min.

Ethyl (*S_a*, *S*)-1-((4-methyl-*N*-(1-(thiophen-2-ylmethoxy)allyl)phenyl)sulfonamido)-1*H*-indole-2-carboxylate(3Ze)



Yellow oil, 95% yield, 48.5 mg, 5:1 d.r., 98% ee.

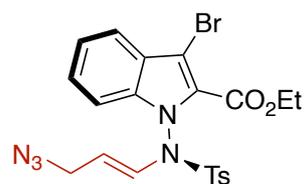
¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.55 (m, 1H), 7.54 – 7.45 (m, 2H), 7.39 (dd, J = 5.1, 1.2 Hz, 1H), 7.29 (td, J = 3.4, 2.0 Hz, 1H), 7.14 (dd, J = 3.4, 1.1 Hz, 1H), 7.11 – 7.06 (m, 3H), 7.05 (s, 1H), 7.04 – 6.99 (m, 2H), 6.32 (dd, J = 5.5, 1.1 Hz, 1H), 5.55 (ddd, J = 17.3, 10.2, 5.4 Hz, 1H), 5.41 (dt, J = 17.2, 1.4 Hz, 1H), 5.09 (dt, J = 10.2, 1.3 Hz, 1H), 5.03 (d, J = 11.9 Hz, 1H), 4.91 – 4.82 (m, 1H), 4.37 – 4.32 (m, 2H), 2.38 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 160.04, 144.14, 139.90, 139.24, 136.58, 130.09, 129.27, 129.17, 128.59, 126.68, 126.66, 125.98, 125.50, 123.76, 121.88, 121.81, 121.01, 112.48, 110.74, 90.31, 77.39, 77.07, 76.75, 65.31, 60.72, 21.56, 14.28.

HRMS (ESI, m/z): exact mass calculated for $[M+Na]^+$ ($C_{26}H_{26}N_2NaO_5S_2^+$) requires m/z 533.1175, found, 533.1176.

HPLC analysis: 97: 3 er (CHIRALCEL IA column, 25 °C, *n*-hexane / *i*-PrOH = 30/1, flow rate = 0.8 mL/min, λ = 286 nm), R_t (major) = 23.8 min, R_t (minor) = 42.9 min.

ethyl (*S_a*, *E*)-1-((*N*-(3-azidoprop-1-en-1-yl)-4-methylphenyl)sulfonamido)-3-bromo-1*H*-indole-2-carboxylate(4o)



4o, 68%, 92:8 er

White solid, 68% yield, 35.2 mg, 84% ee; m.p. 152.1-153.6 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.66 (m, J = 8.0, 1.0 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.37 – 7.33 (m, 1H), 7.24 – 7.20 (m, 3H), 7.15 – 7.11 (m, 1H), 6.54 (dt, J = 8.5, 0.9 Hz, 1H), 4.45 (ddd,

$J = 13.5, 7.7, 6.9$ Hz, 1H), 4.24 (dddd, $J = 17.9, 10.8, 7.1, 3.6$ Hz, 2H), 3.74 (qdd, $J = 13.6, 7.3, 1.1$ Hz, 2H), 2.42 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.66, 145.44, 135.88, 134.60, 130.06, 129.98, 128.03, 127.24, 125.29, 123.00, 121.61, 110.72, 102.27, 101.77, 77.37, 77.05, 76.73, 61.44, 50.18, 21.65, 14.05.

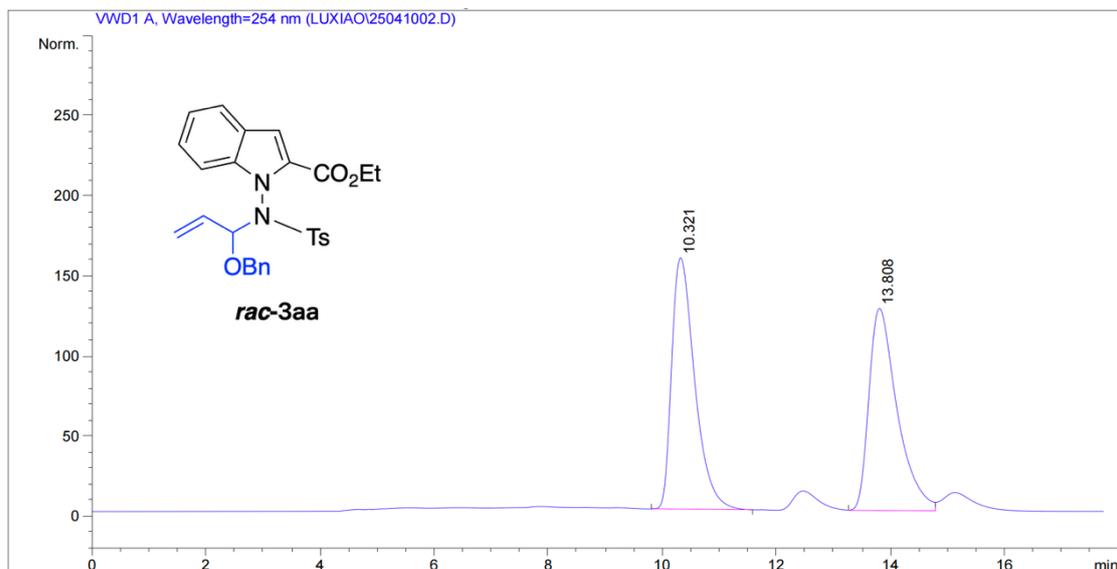
HRMS (ESI, m/z): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{21}\text{H}_{20}\text{BrN}_5\text{NaO}_4\text{S}^+$) requires m/z 540.0312, found, 540.0312.

HPLC analysis: 92: 8 er (CHIRALCEL AD column, 25 °C, *n*-hexane / *i*-PrOH = 7/3, flow rate = 0.8 mL/min, $\lambda = 286$ nm), R_t (major) = 7.8 min, R_t (minor) = 9.1 min.

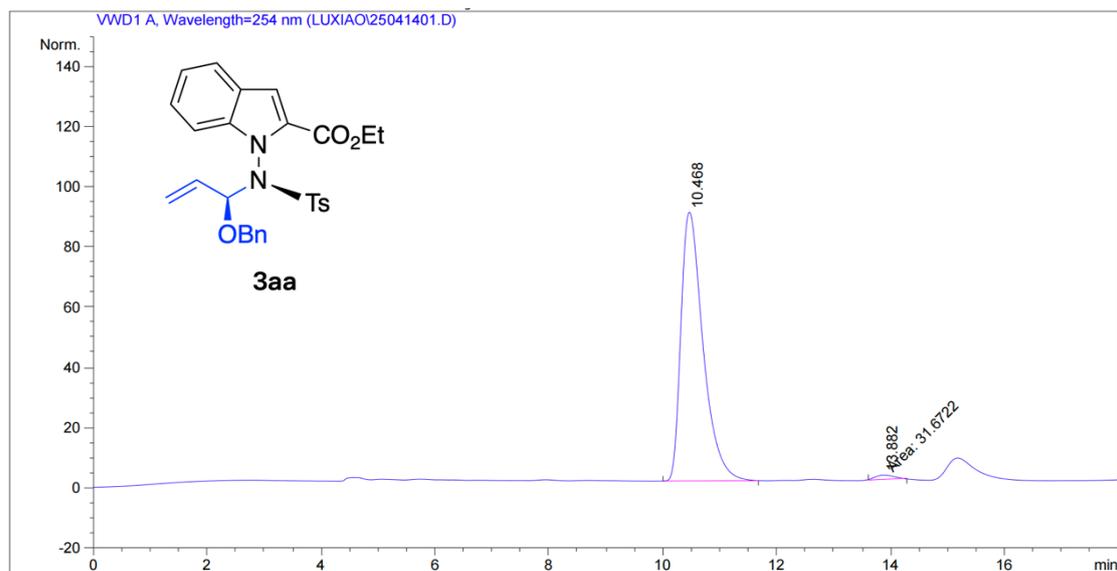
10. References

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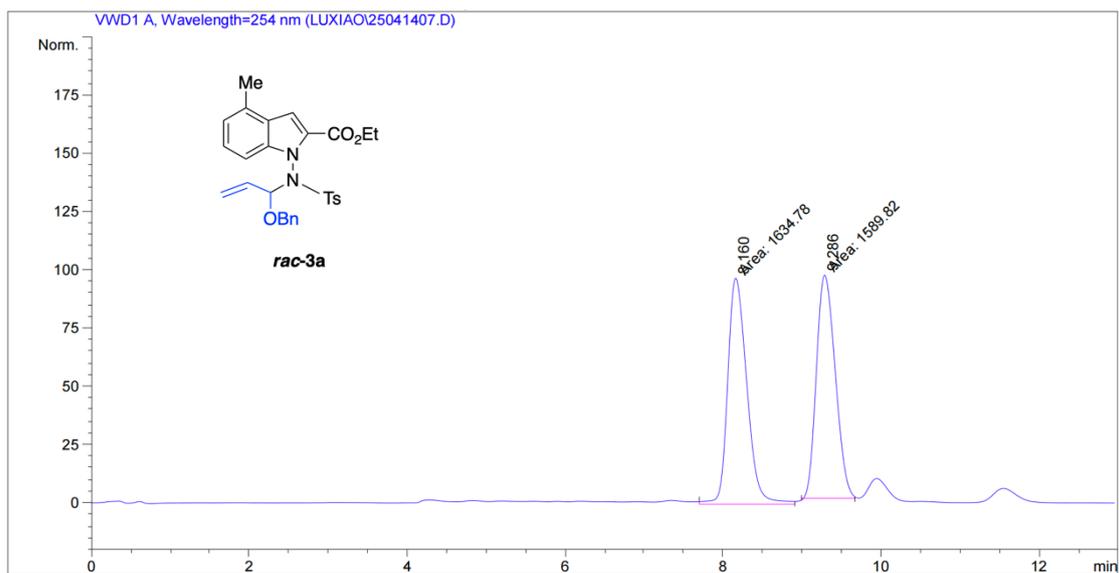
11. HPLC Traces for Products



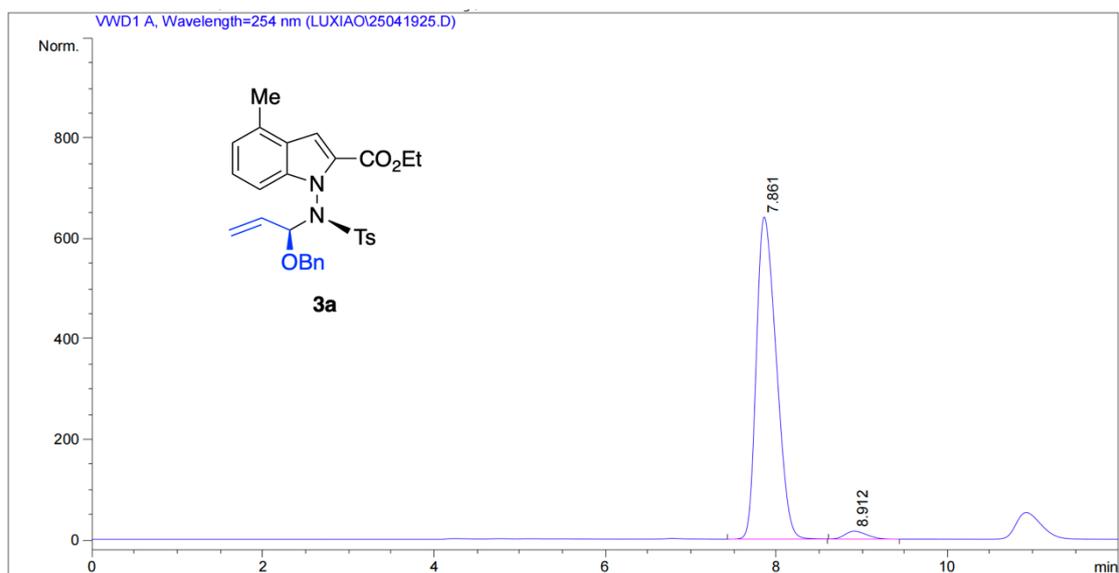
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	10.321	BP	0.4308	4404.62158		156.92546	50.3344
2	13.808	VV	0.5183	4346.08838		126.19796	49.6656



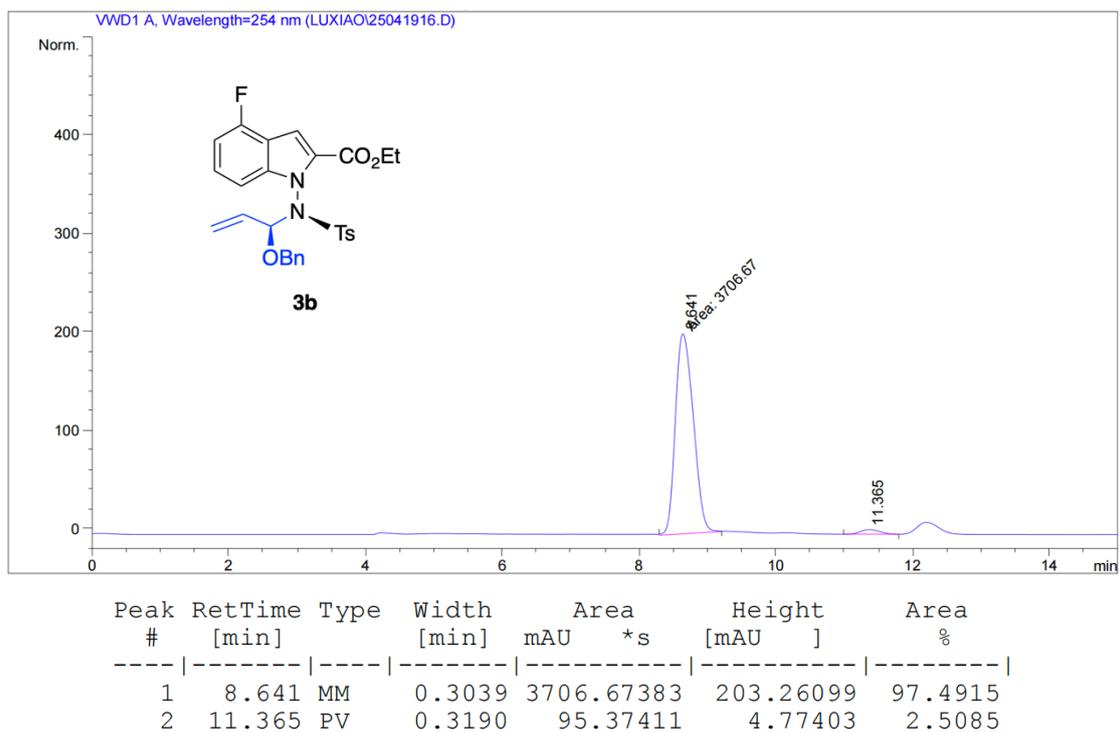
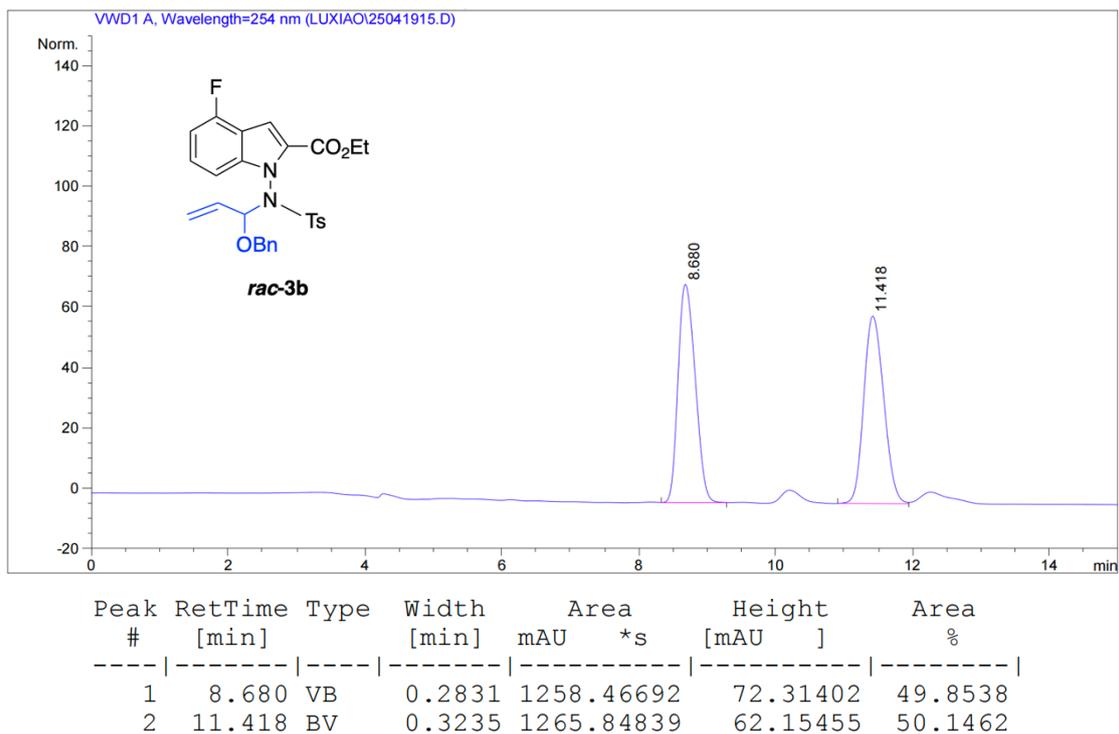
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	10.468	BB	0.4108	2409.06250		89.30689	98.7023
2	13.882	MM	0.3715	31.67224		1.42102	1.2977

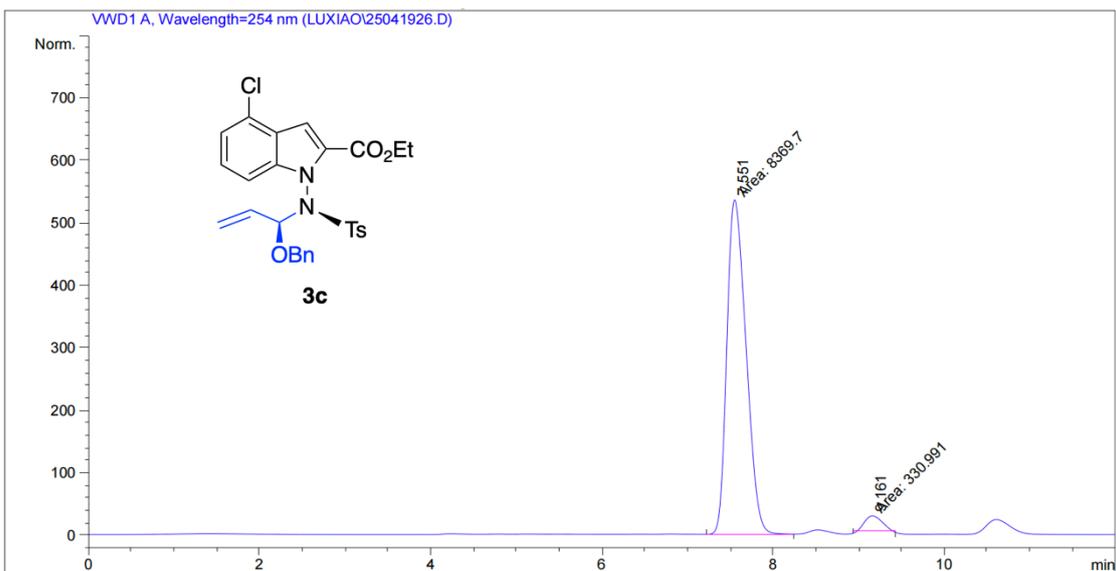
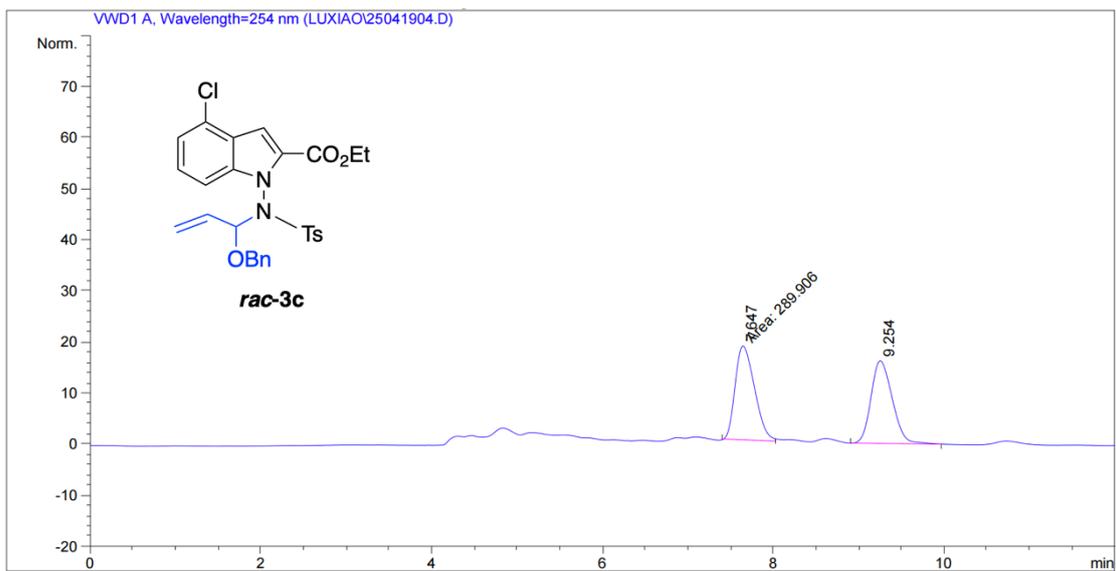


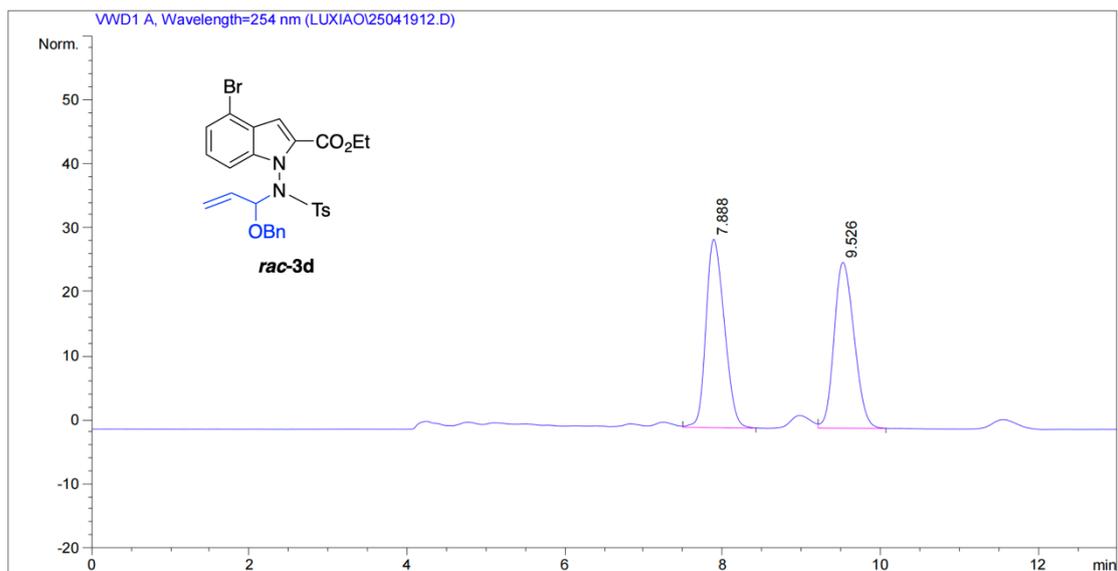
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.160	MM	0.2812	1634.77820	96.89325	50.6971
2	9.286	MM	0.2767	1589.81812	95.76729	49.3029



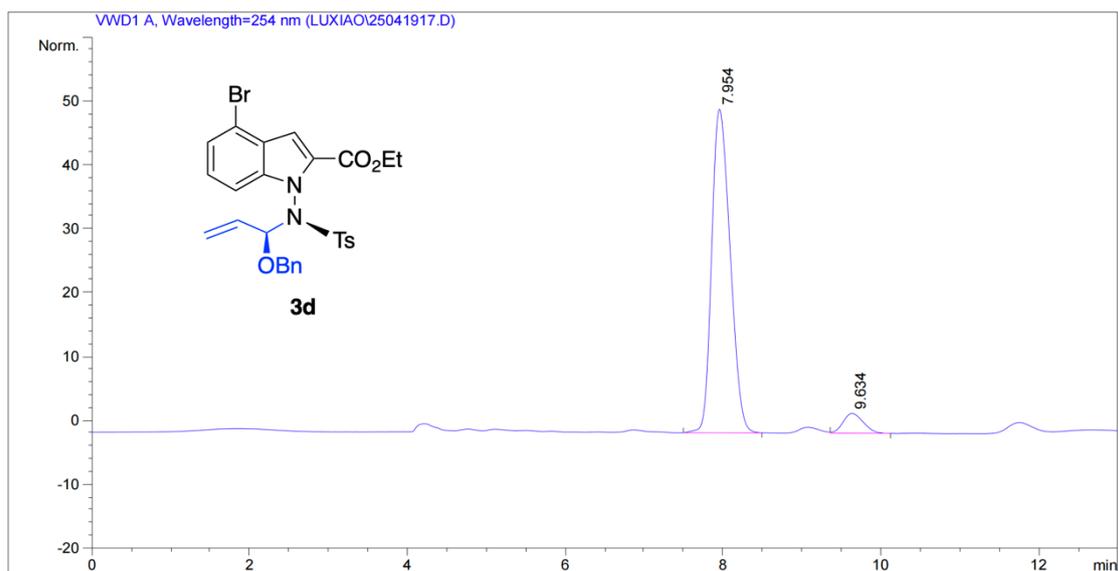
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.861	BB	0.2598	1.03683e4	641.75342	97.3178
2	8.912	BB	0.2847	285.76065	15.84361	2.6822



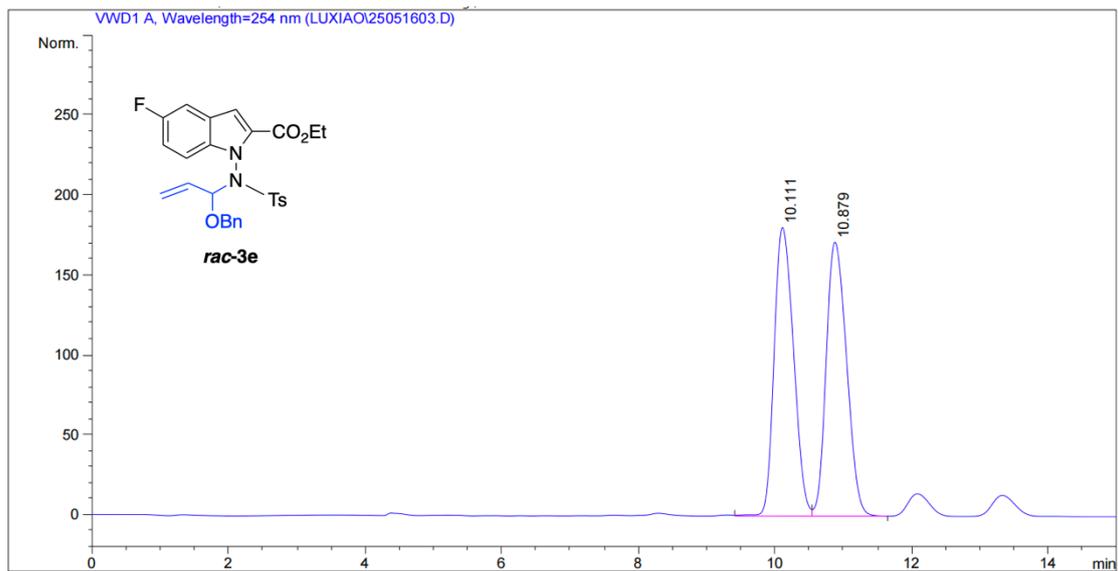




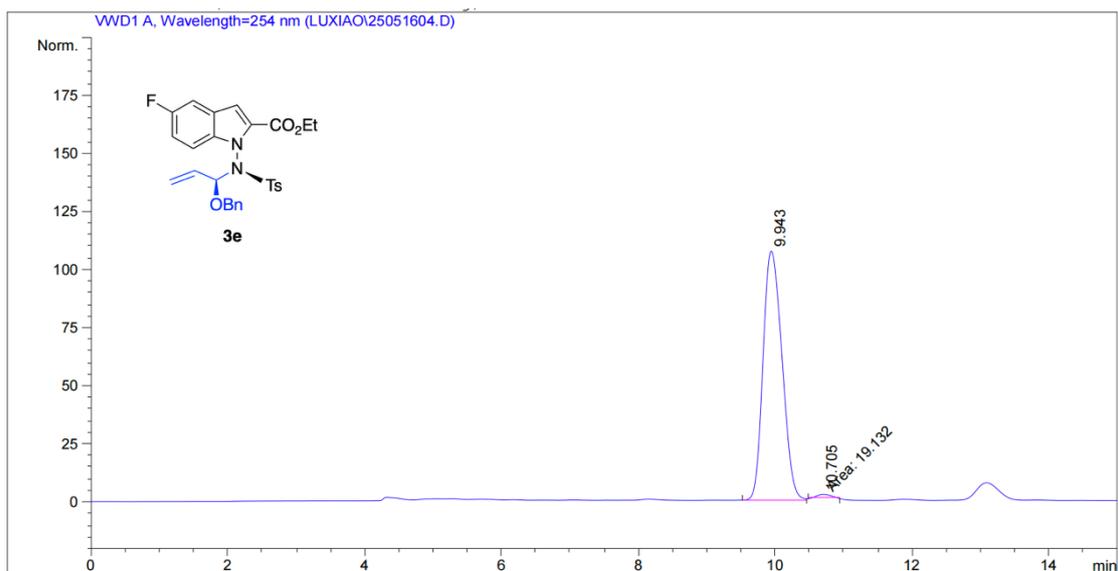
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.888	VB	0.2541	475.49603	29.41538	50.8863
2	9.526	VB	0.2778	458.93216	25.93767	49.1137



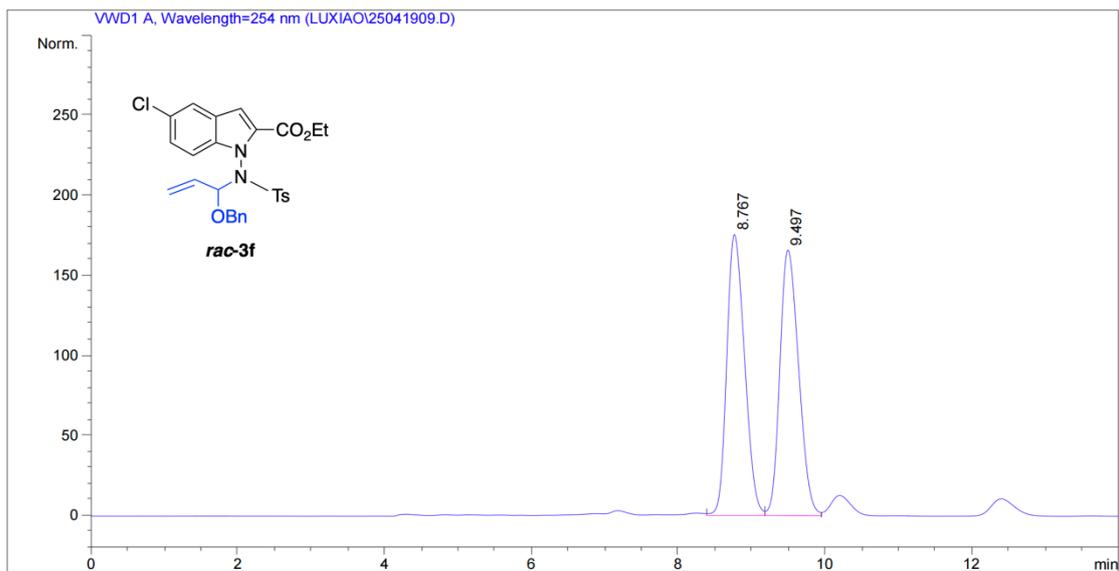
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.954	BB	0.2581	823.62756	50.66286	93.6245
2	9.634	VB	0.2797	56.08599	3.11861	6.3755



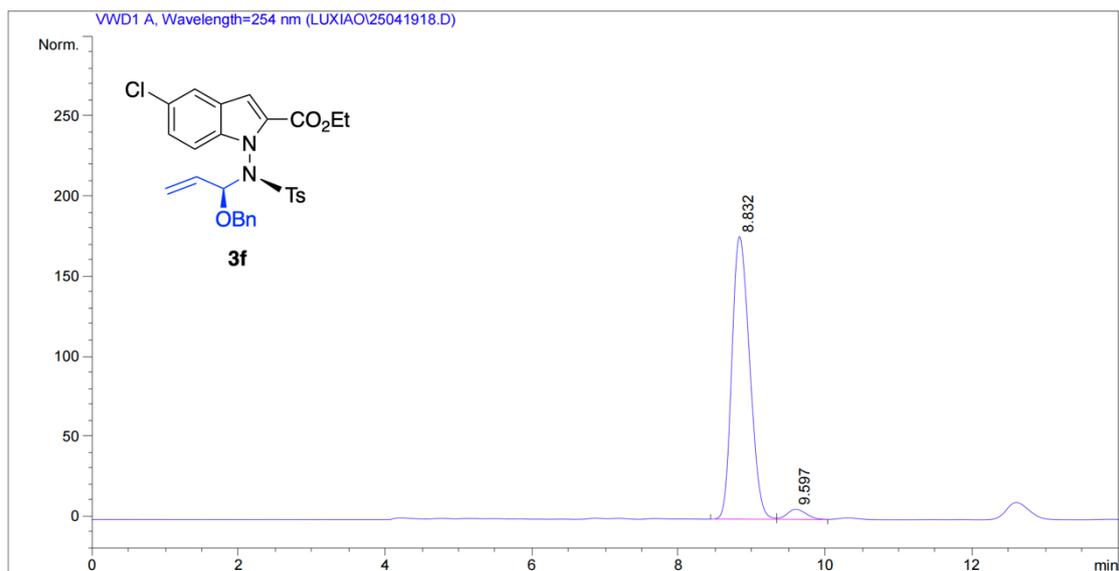
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	10.111	VV	0.3190	3562.57031		180.53566	50.0078
2	10.879	VB	0.3341	3561.46582		171.39973	49.9922



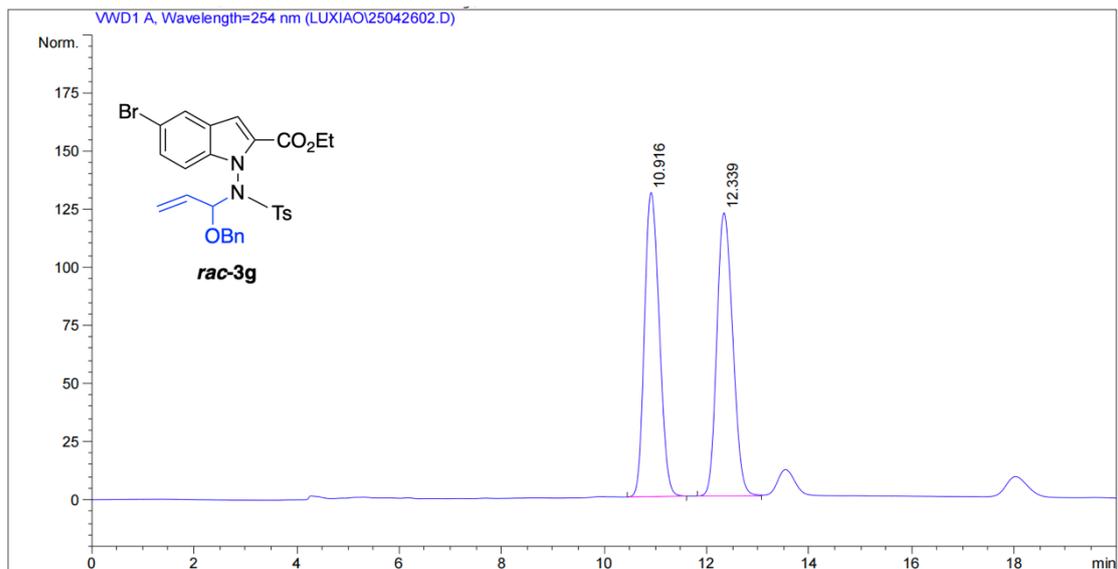
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	9.943	BV	0.3107	2065.65894		107.20204	99.0823
2	10.705	MM	0.2242	19.13199		1.42208	0.9177



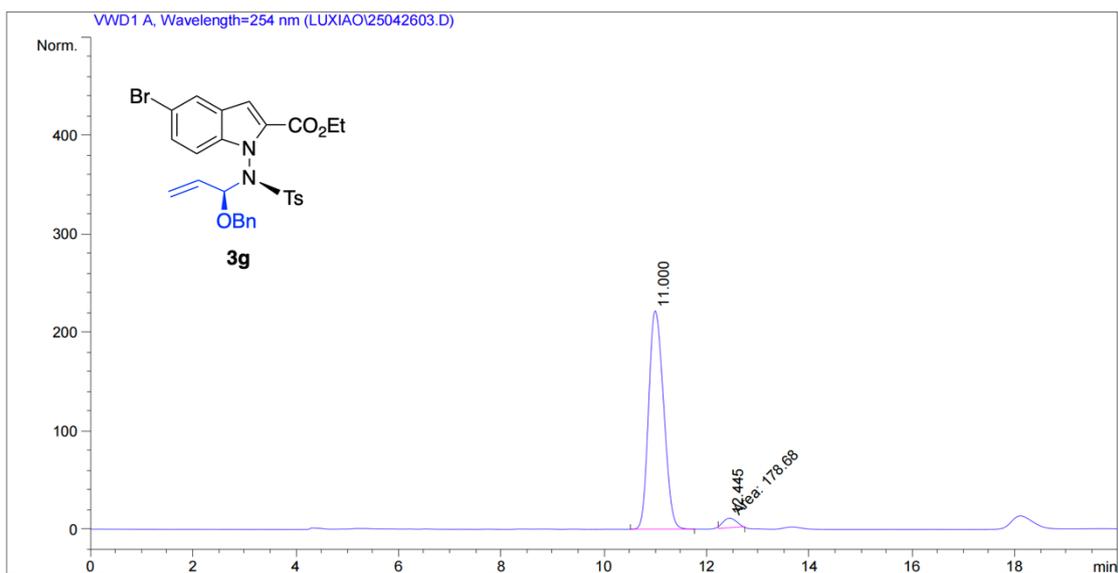
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.767	VV	0.2654	2965.23926	175.66354	50.0998
2	9.497	VV	0.2789	2953.42651	165.98575	49.9002



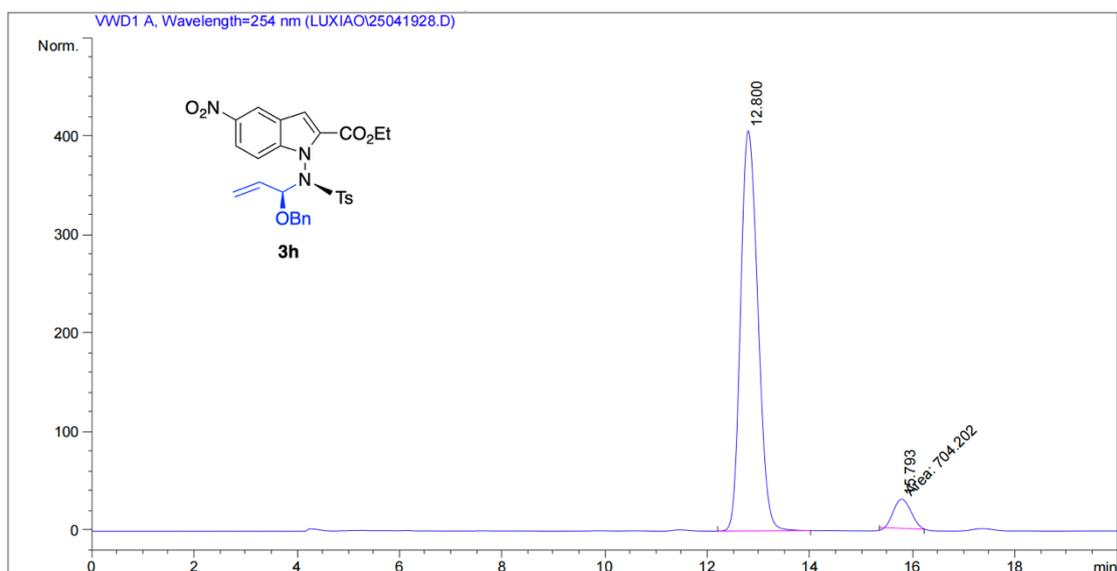
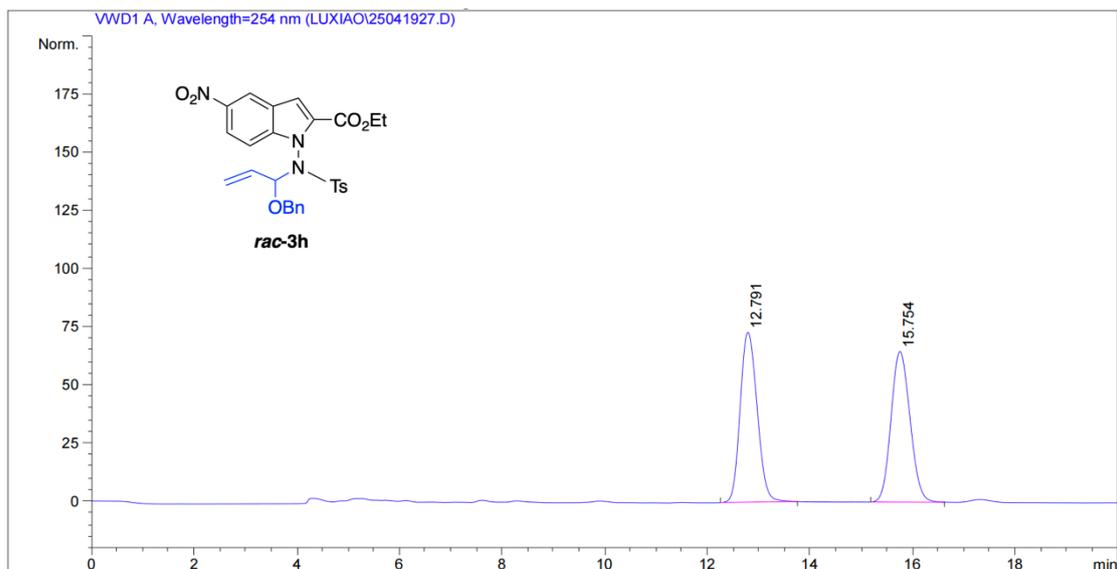
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.832	BV	0.2661	2971.83447	176.66324	96.2503
2	9.597	VV	0.2803	115.77455	6.37414	3.7497

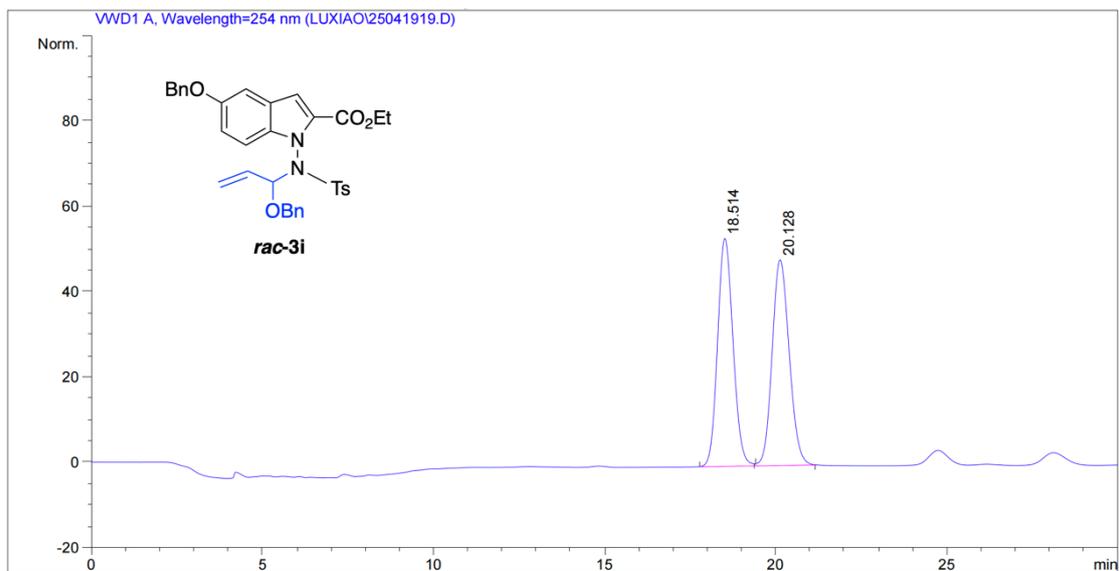


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.916	BB	0.3215	2624.65283	130.76936	49.8940
2	12.339	BB	0.3458	2635.80151	121.70657	50.1060

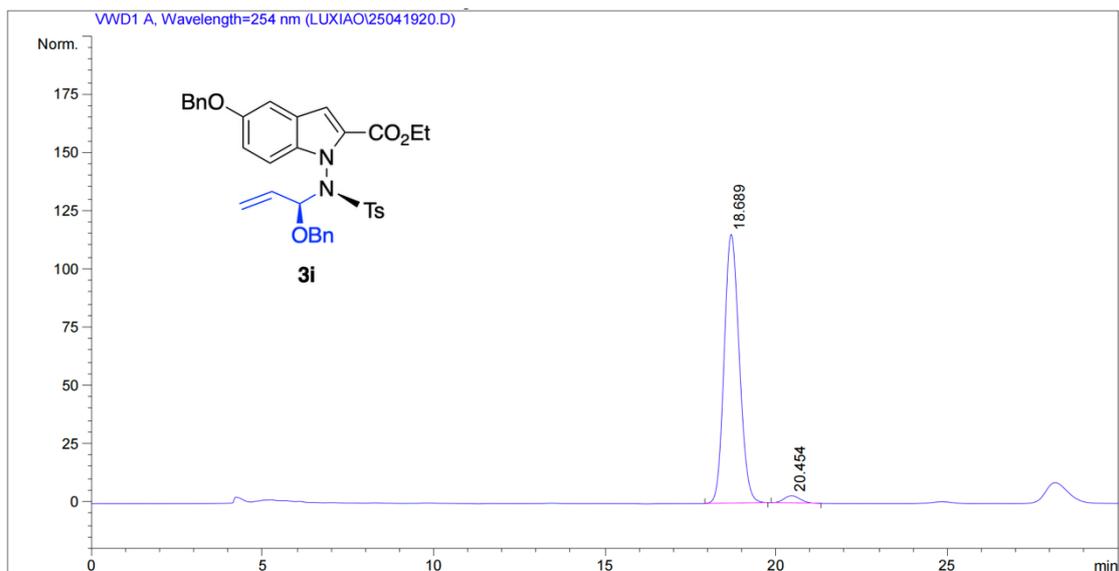


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.000	PB	0.3262	4508.55762	221.59831	96.1879
2	12.445	MM	0.3013	178.67987	9.88329	3.8121

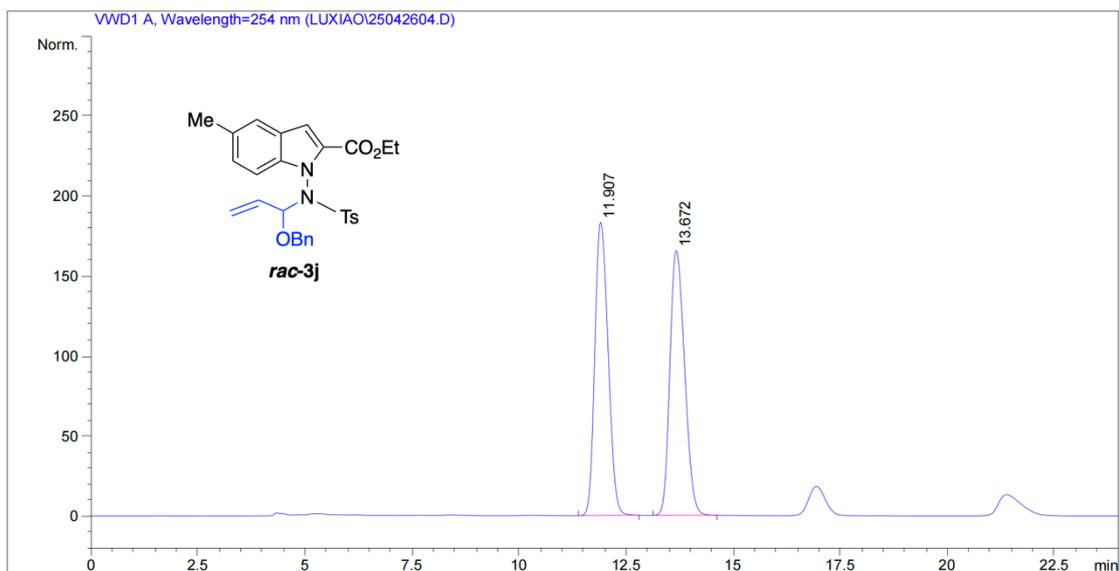




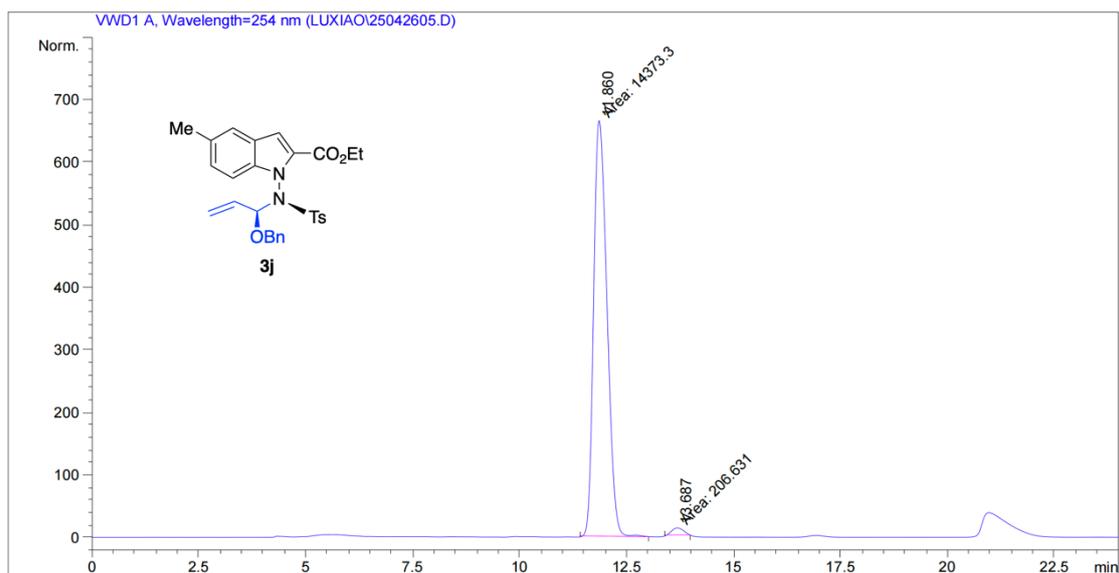
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.514	BB	0.4855	1675.57092	53.39049	50.0109
2	20.128	BB	0.5408	1674.83740	48.20216	49.9891



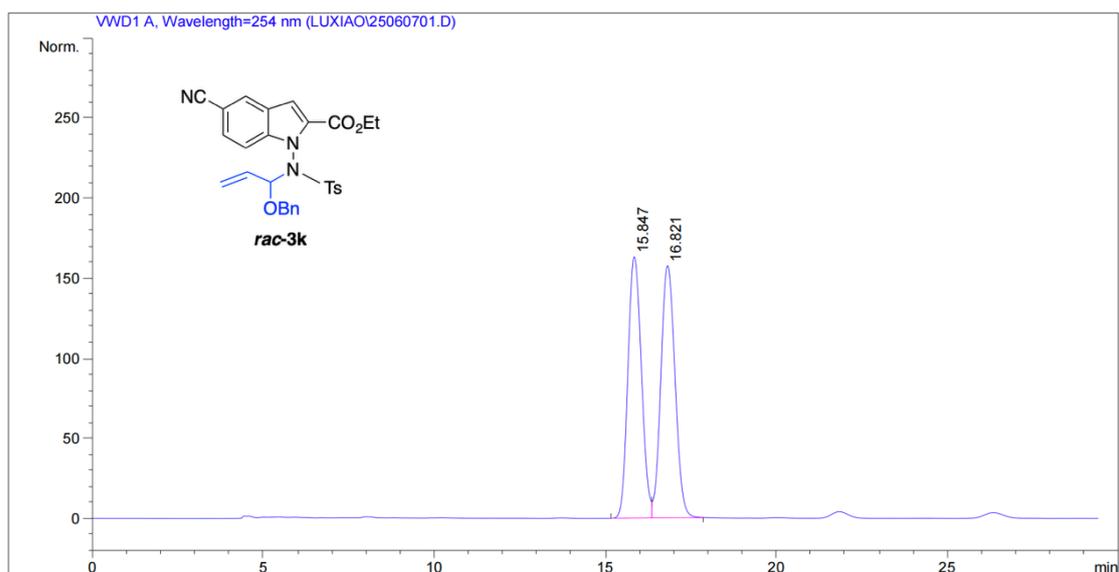
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.689	BB	0.4772	3538.50684	115.38987	97.2301
2	20.454	PP	0.4893	100.80637	3.10574	2.7699



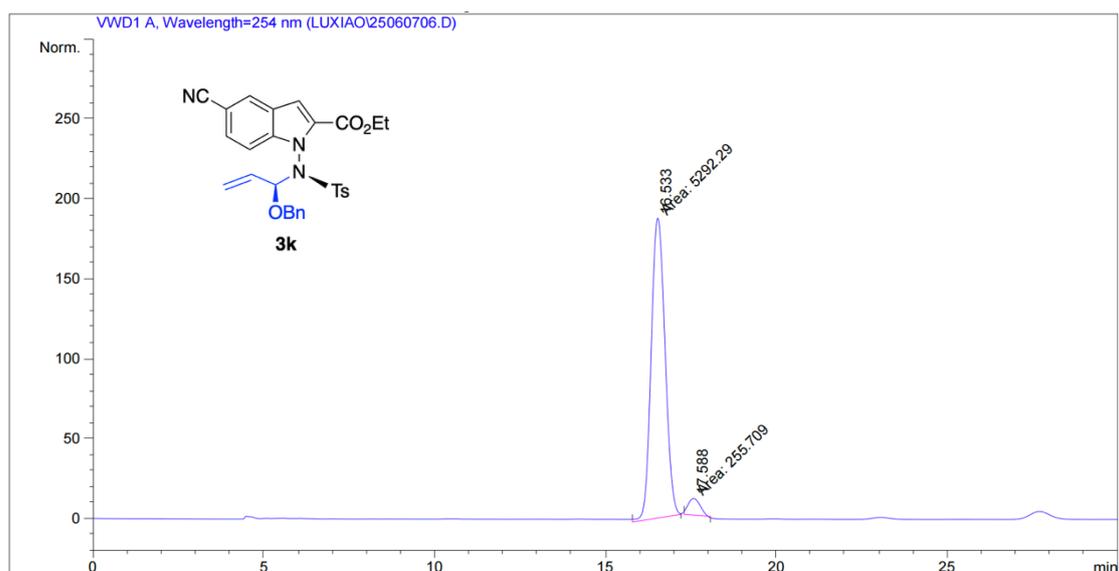
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.907	BB	0.3447	3948.19678	183.14310	49.9450
2	13.672	PB	0.3781	3956.89233	165.39867	50.0550



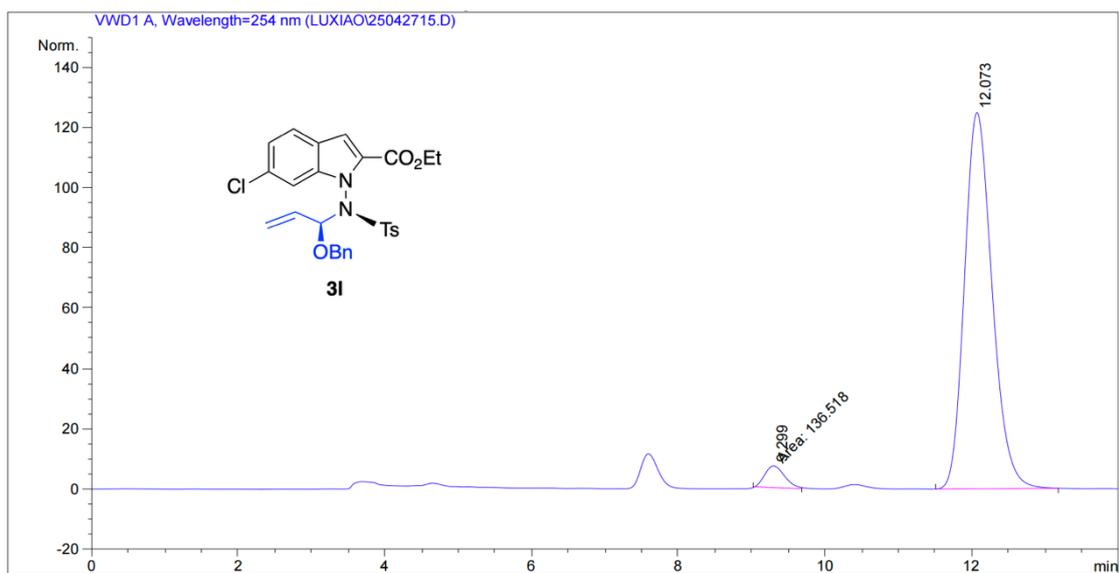
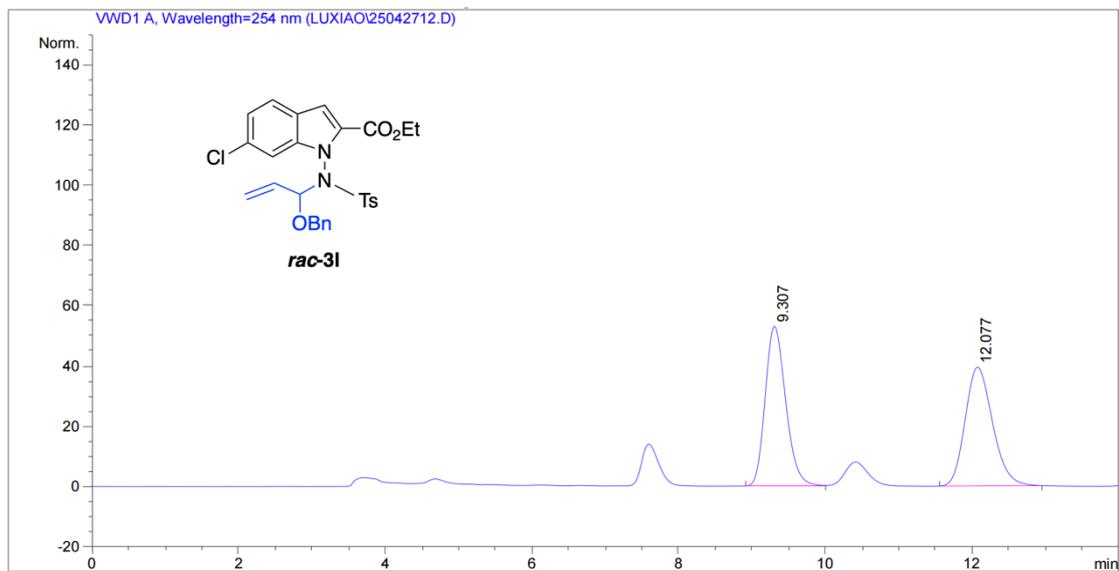
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.860	MM	0.3606	1.43733e4	664.32684	98.5828
2	13.687	MM	0.3079	206.63123	11.18365	1.4172

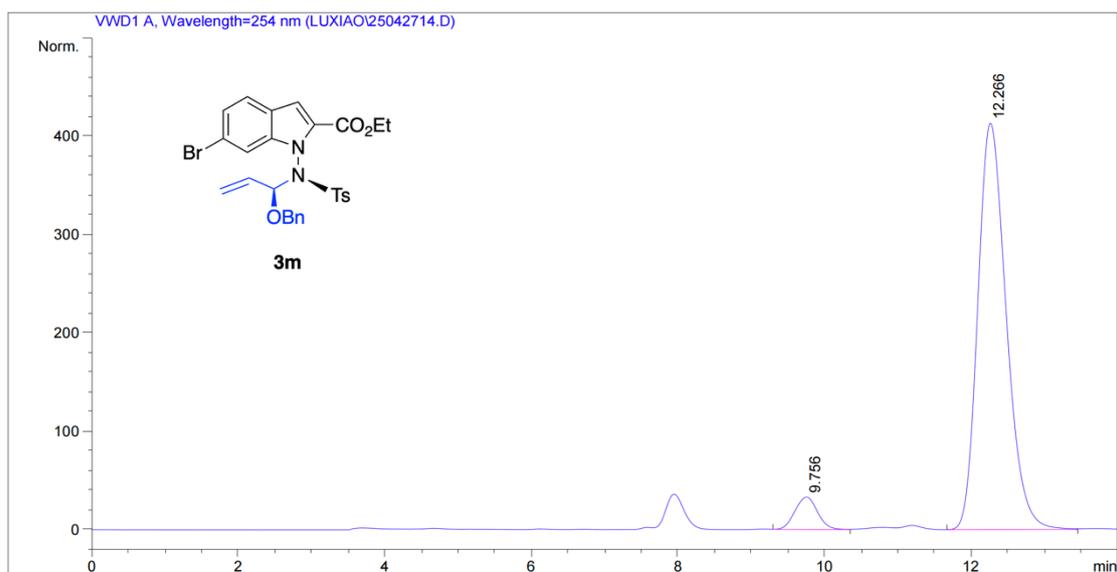
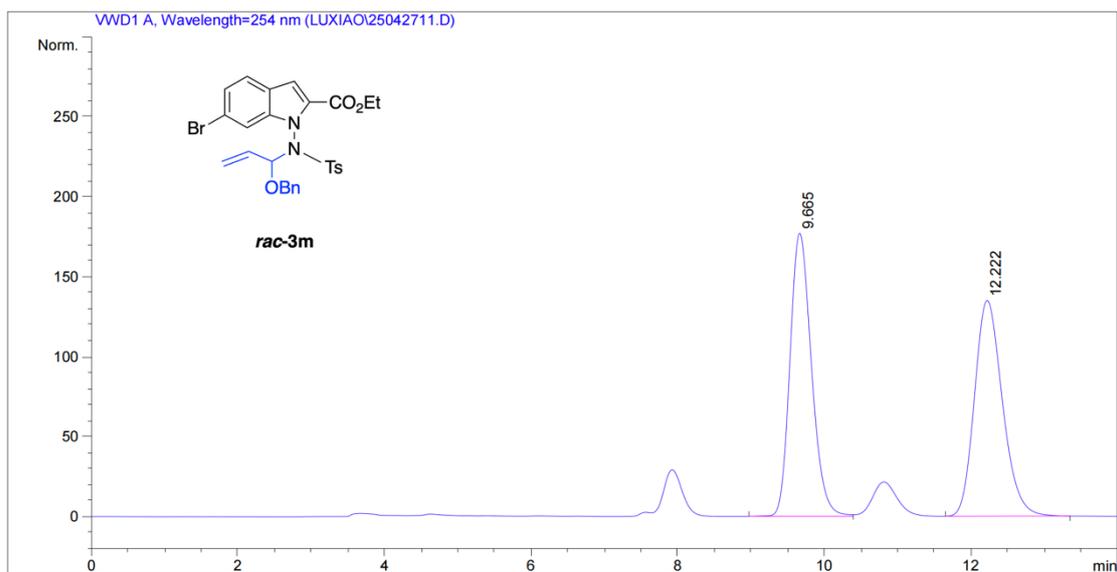


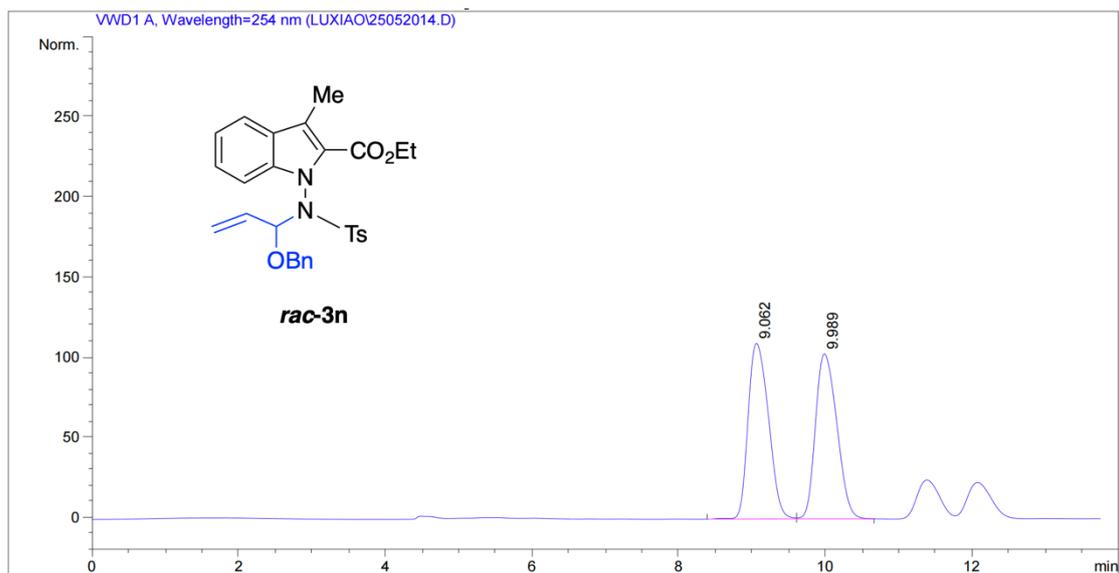
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	15.847	BV	0.4373	4487.12695	163.17982	49.6722	
2	16.821	VB	0.4547	4546.35156	157.52032	50.3278	



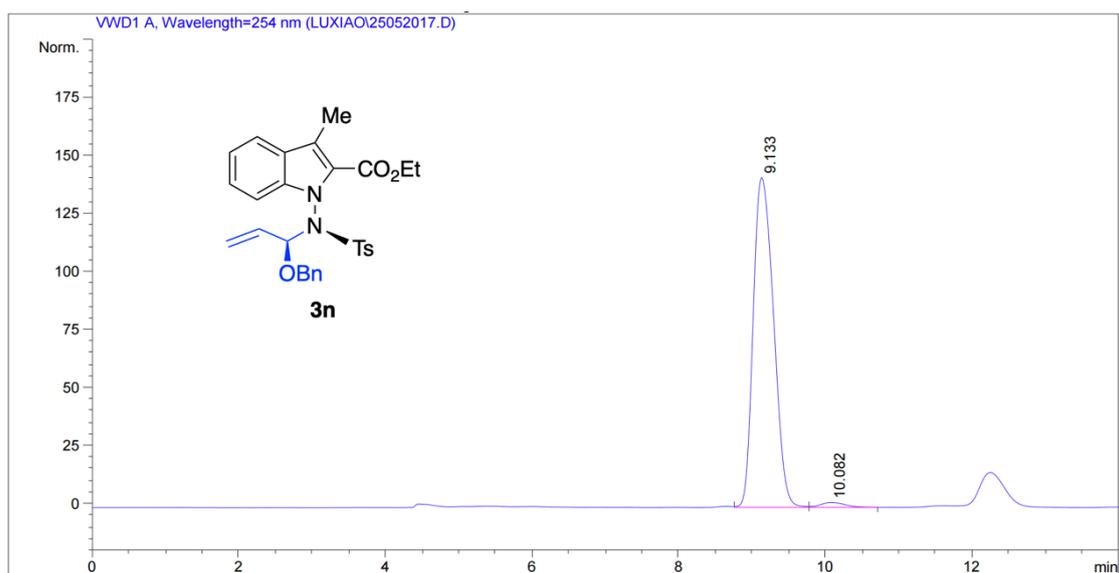
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	16.533	MM	0.4699	5292.29346	187.71732	95.3910	
2	17.588	MM	0.4063	255.70885	10.48926	4.6090	



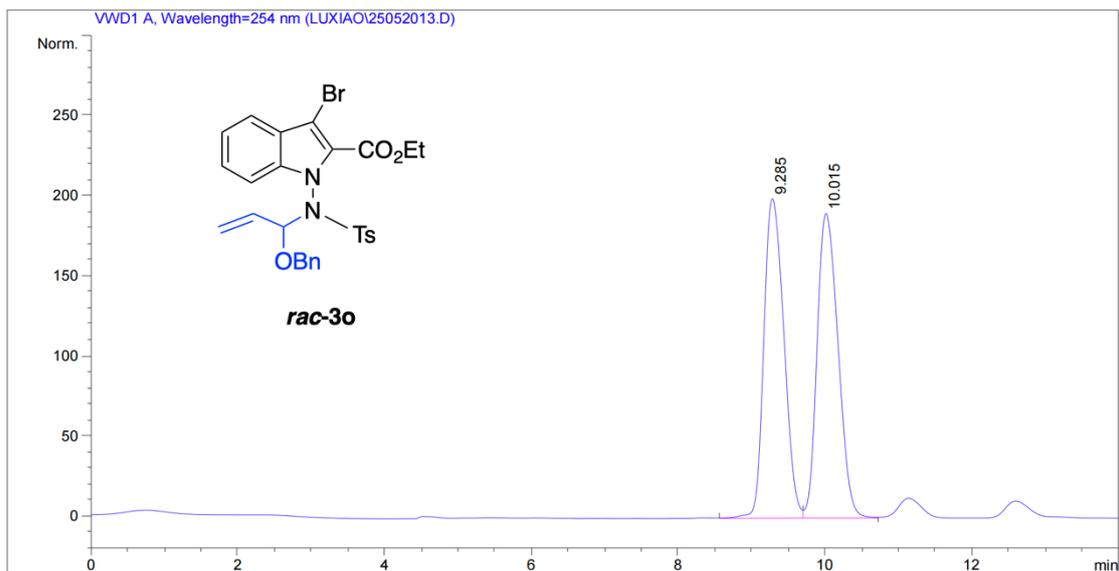




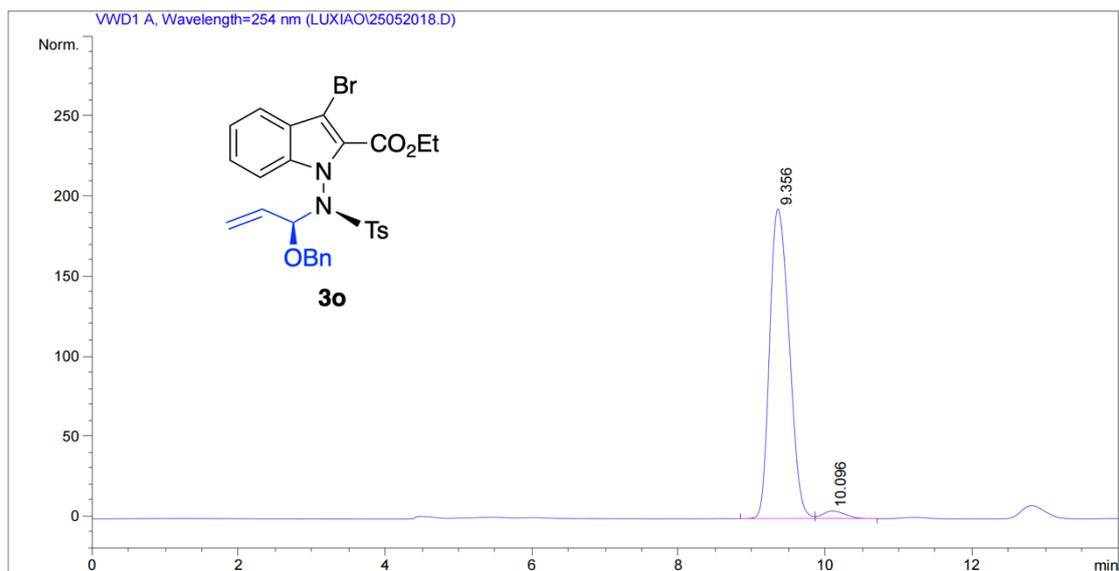
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.062	BV	0.3177	2124.05249	109.64350	50.3749
2	9.989	VB	0.3302	2092.43848	103.00372	49.6251



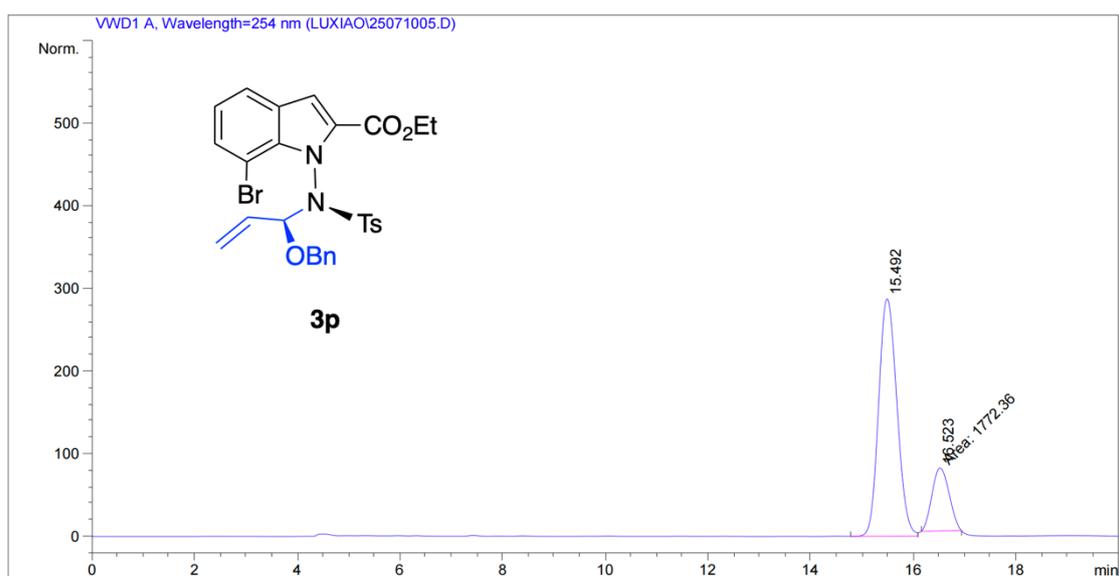
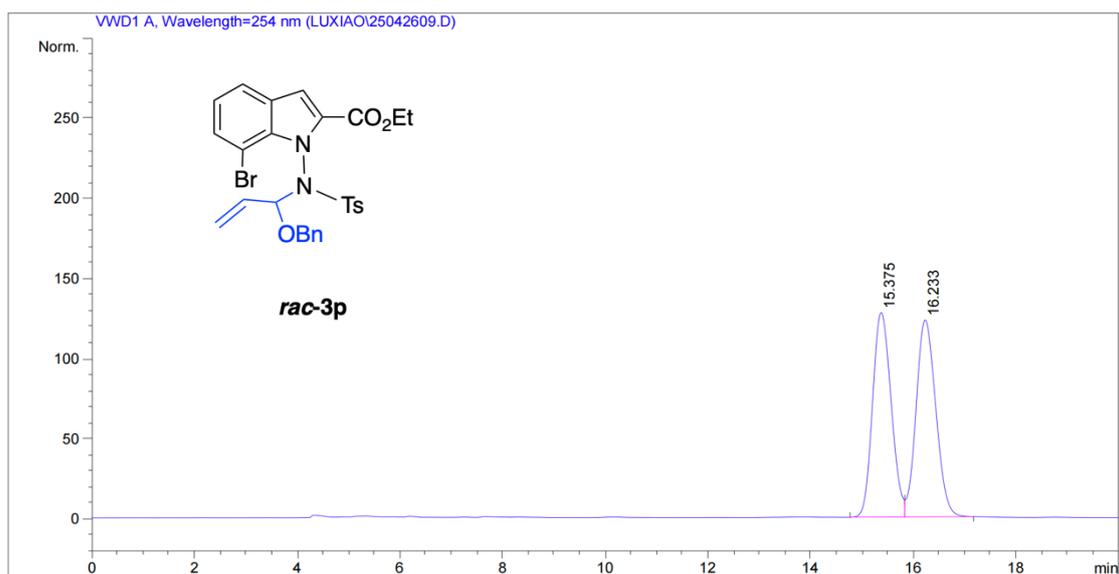
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.133	VB	0.3150	2733.33179	141.92854	98.2259
2	10.082	BB	0.3655	49.36708	2.12666	1.7741

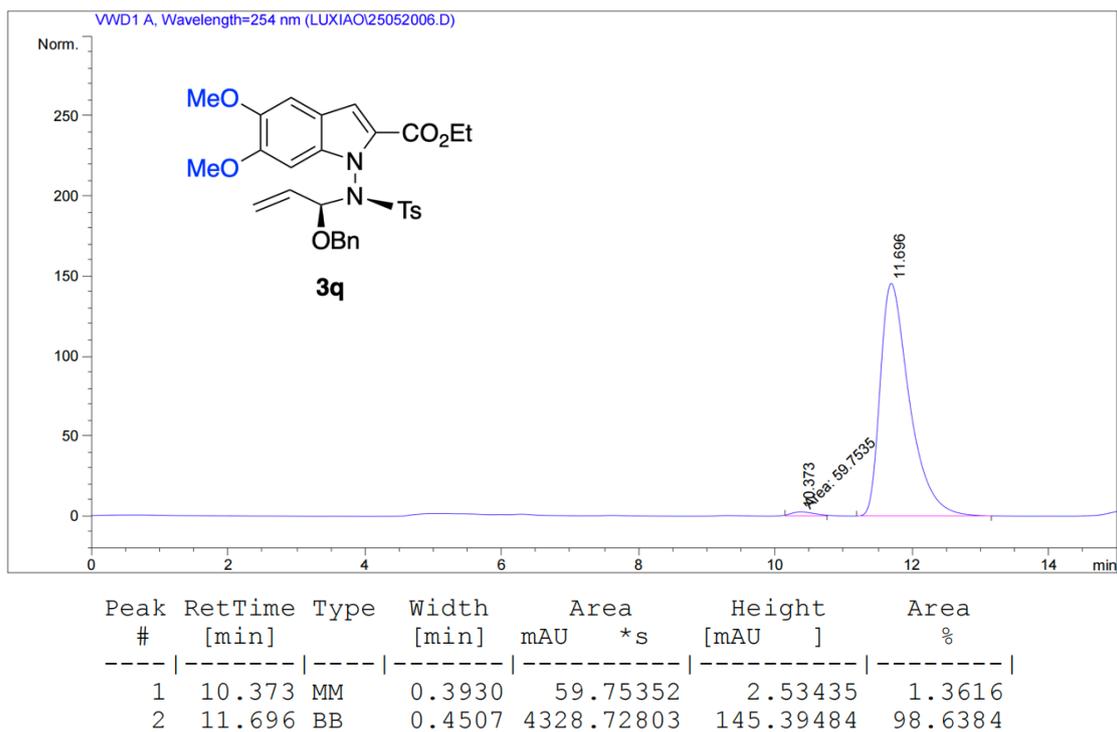
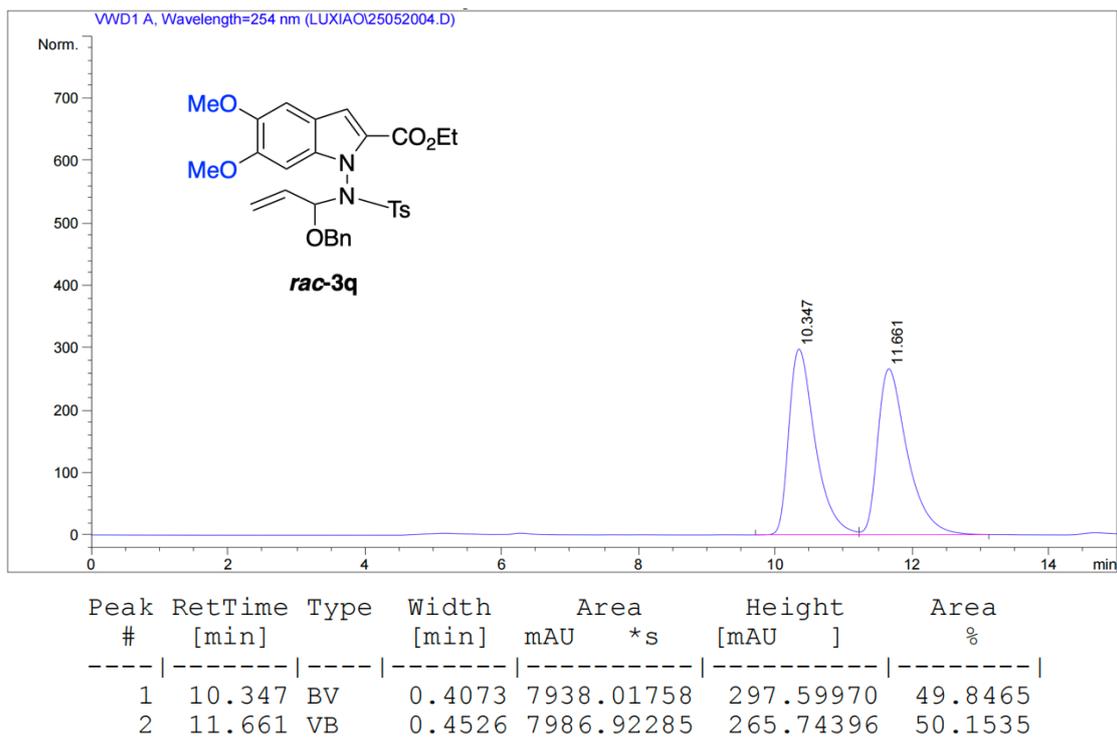


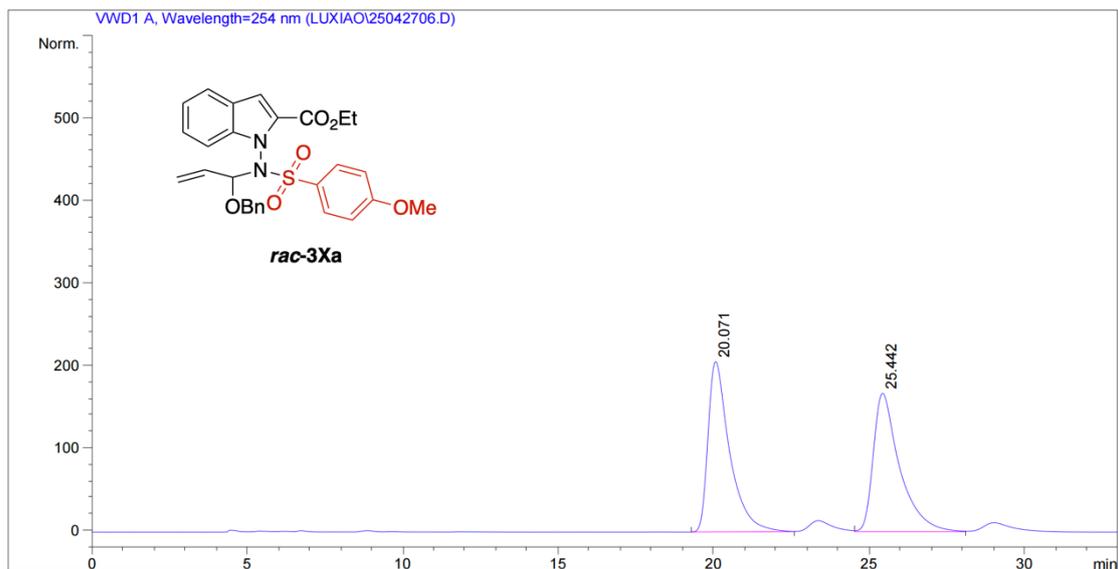
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.285	VV	0.3072	3783.18848	199.41379	50.0525
2	10.015	VB	0.3190	3775.25317	190.14014	49.9475



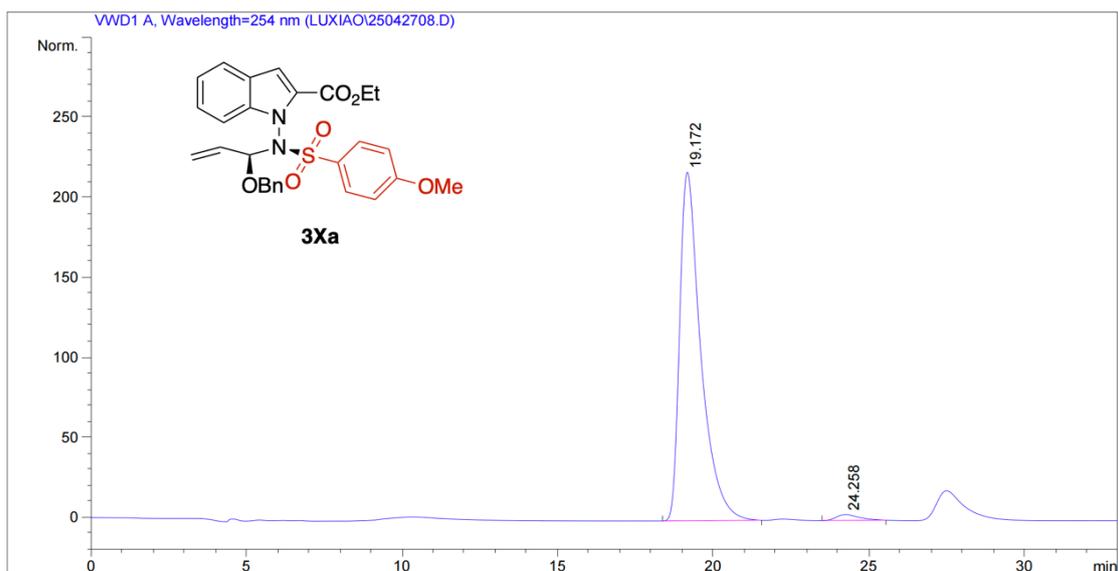
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.356	BV	0.3021	3585.99048	193.50067	97.2598
2	10.096	VB	0.3380	101.03128	4.70346	2.7402



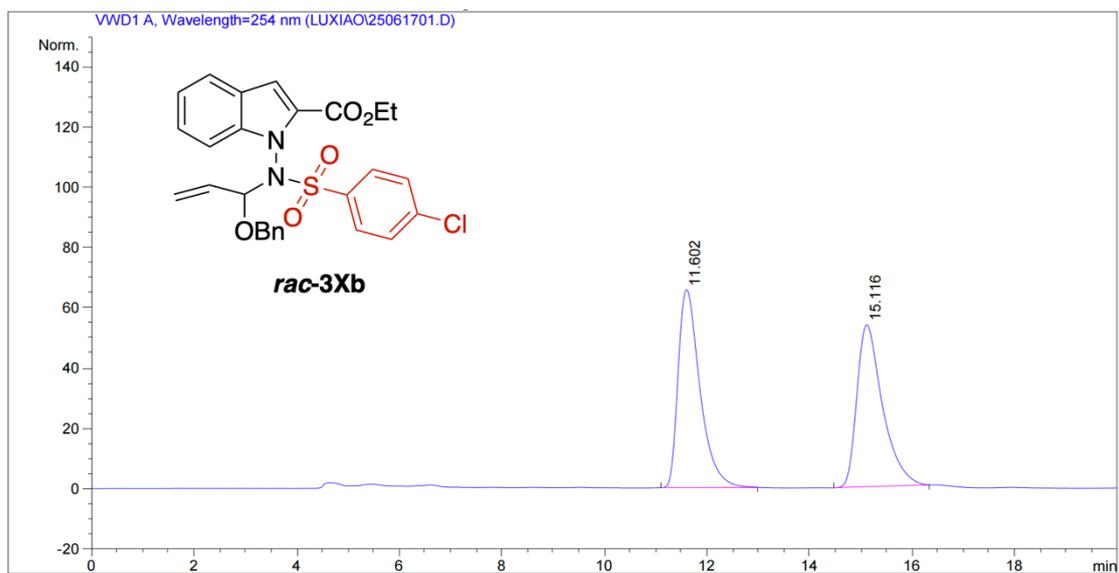




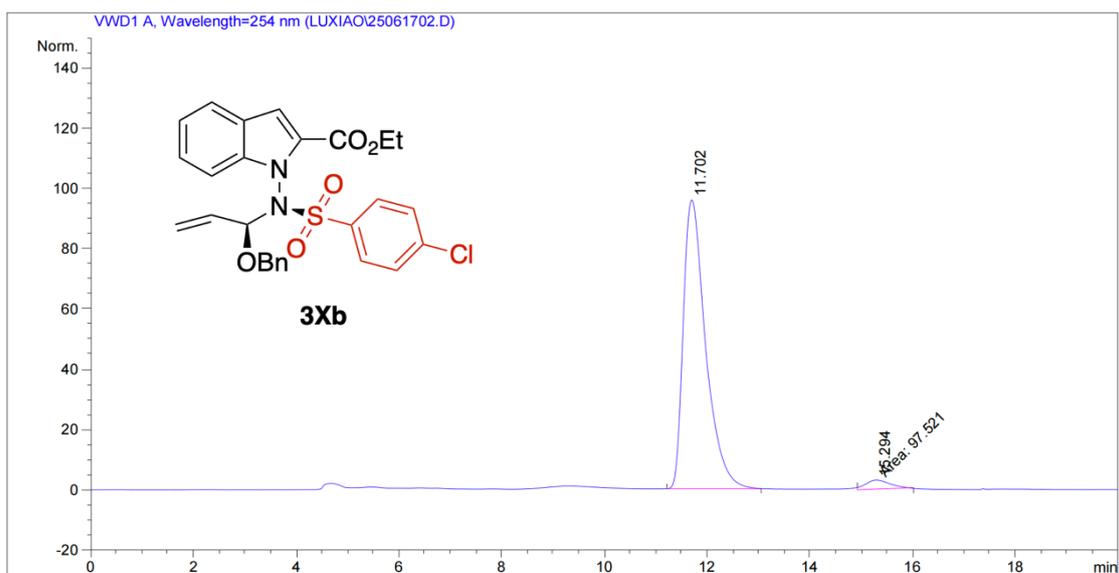
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	20.071	BB	0.7148	1.00074e4	206.18736	50.2946
2	25.442	VB	0.8612	9890.15820	167.71603	49.7054



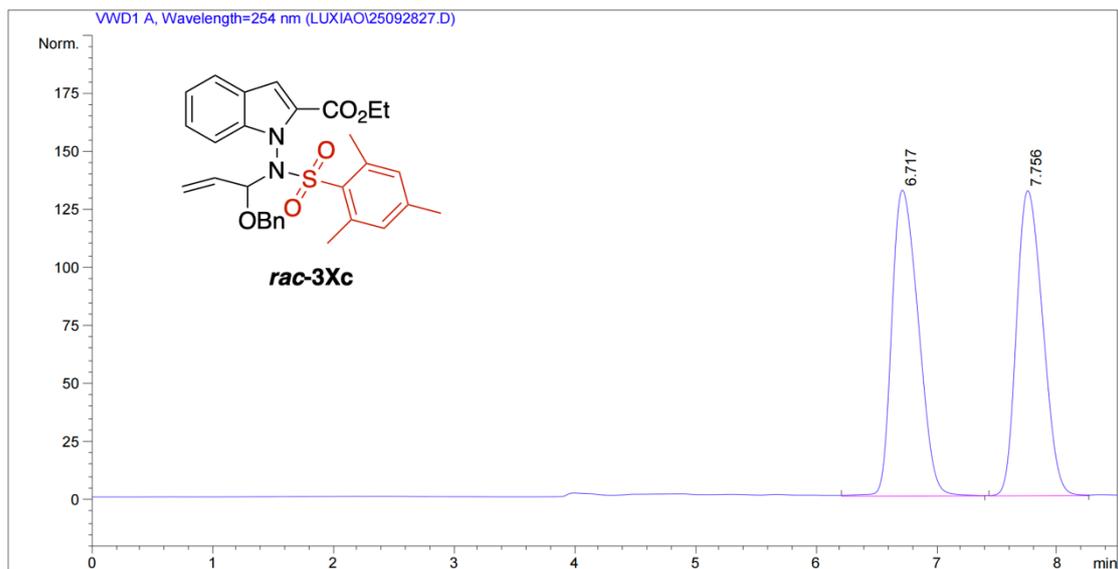
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	19.172	BB	0.7018	1.02992e4	217.75363	98.1859
2	24.258	PB	0.6827	190.29410	3.71084	1.8141



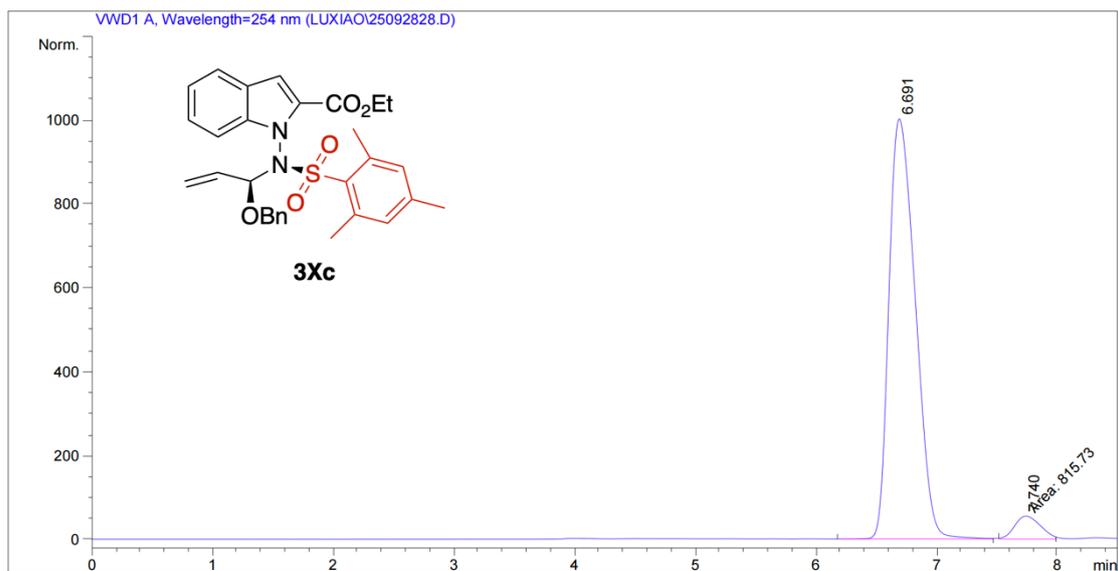
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.602	BB	0.4531	1944.80115	65.69645	50.9778
2	15.116	PB	0.5249	1870.19568	53.80899	49.0222



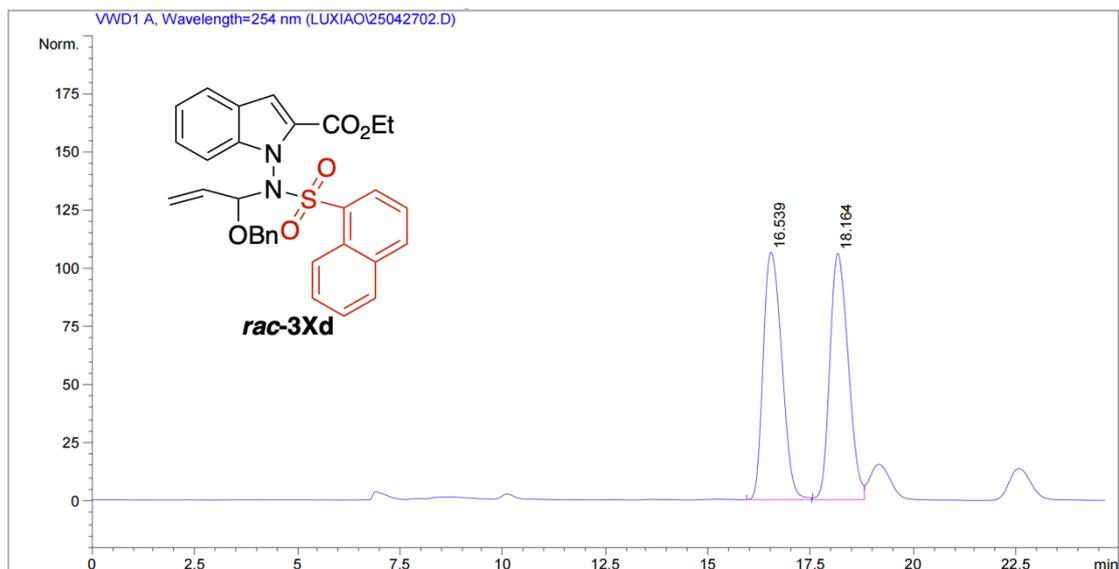
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.702	BB	0.4629	2894.11328	95.86120	96.7402
2	15.294	MM	0.5461	97.52098	2.97629	3.2598



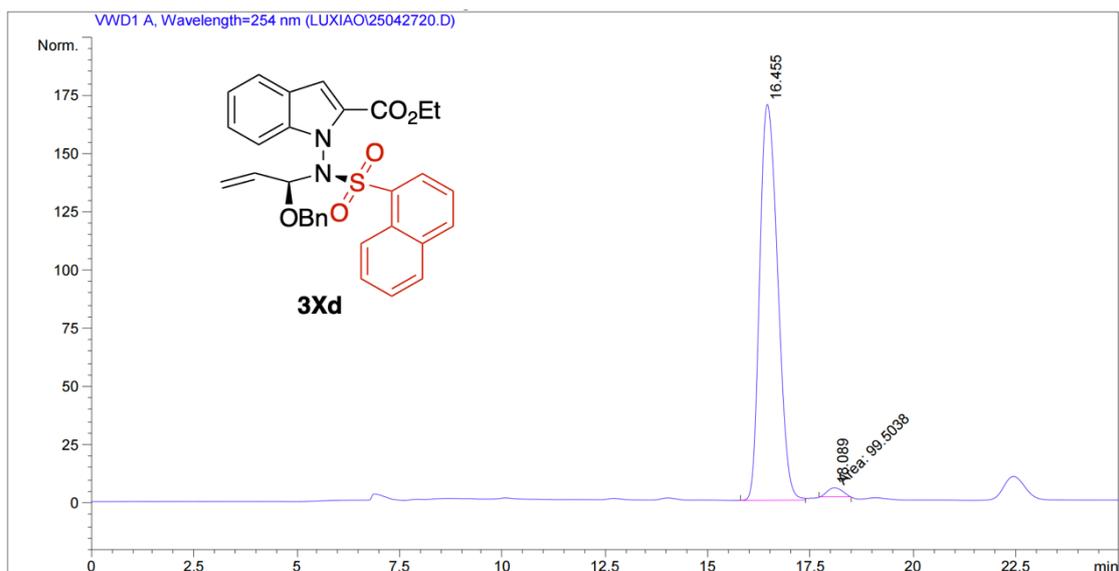
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.717	BB	0.2481	2010.99670	131.65886	50.3821
2	7.756	BV	0.2429	1980.49353	131.33159	49.6179



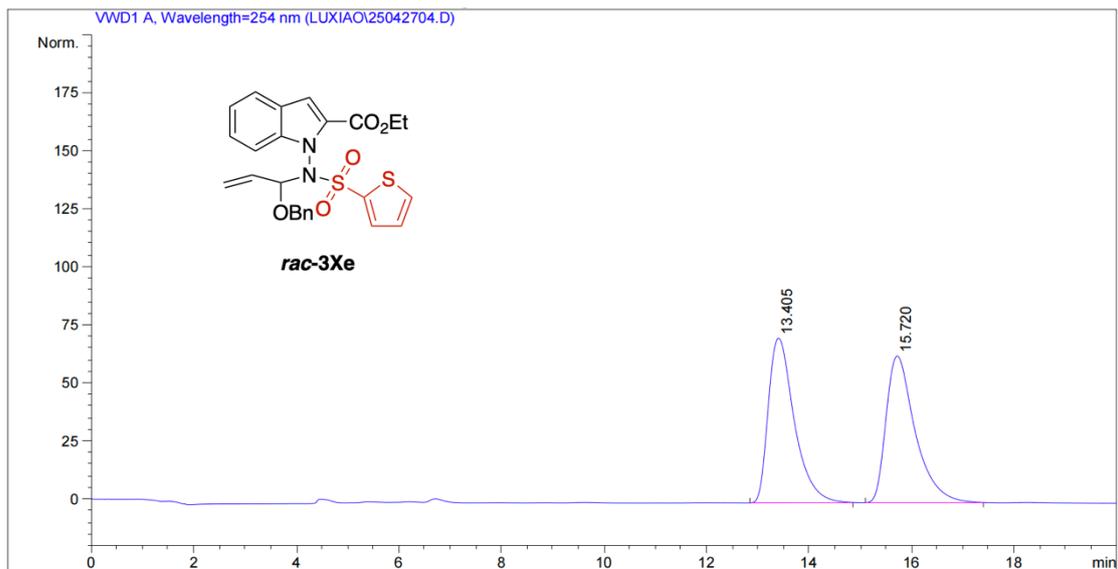
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.691	VV	0.2481	1.51695e4	1001.14038	94.8970
2	7.740	MM	0.2479	815.73035	54.83280	5.1030



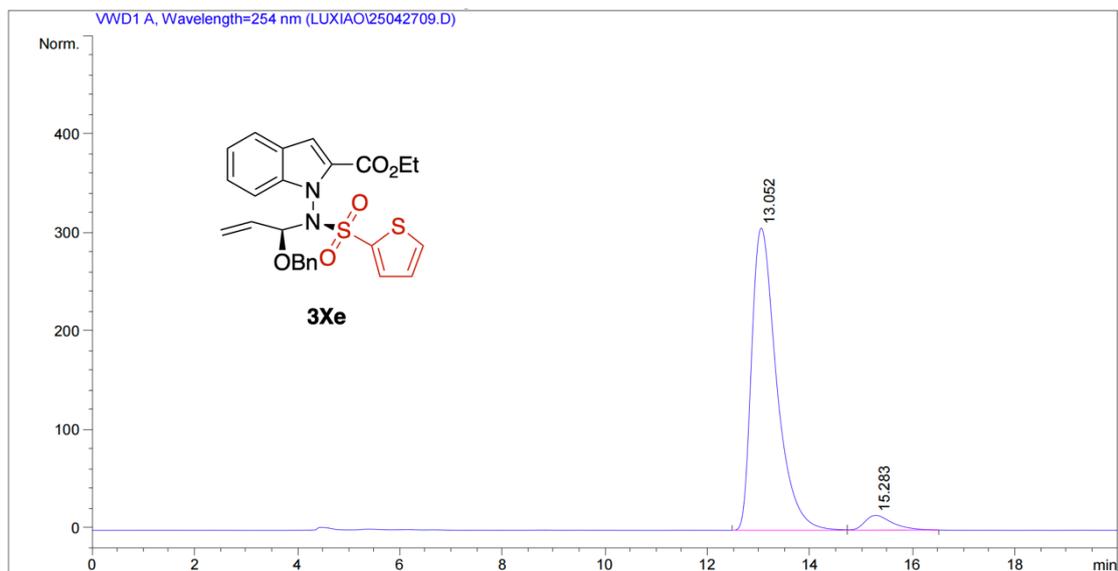
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	16.539	BB	0.5098	3343.70703	106.26682	50.3053
2	18.164	BV	0.5011	3303.12061	105.80059	49.6947



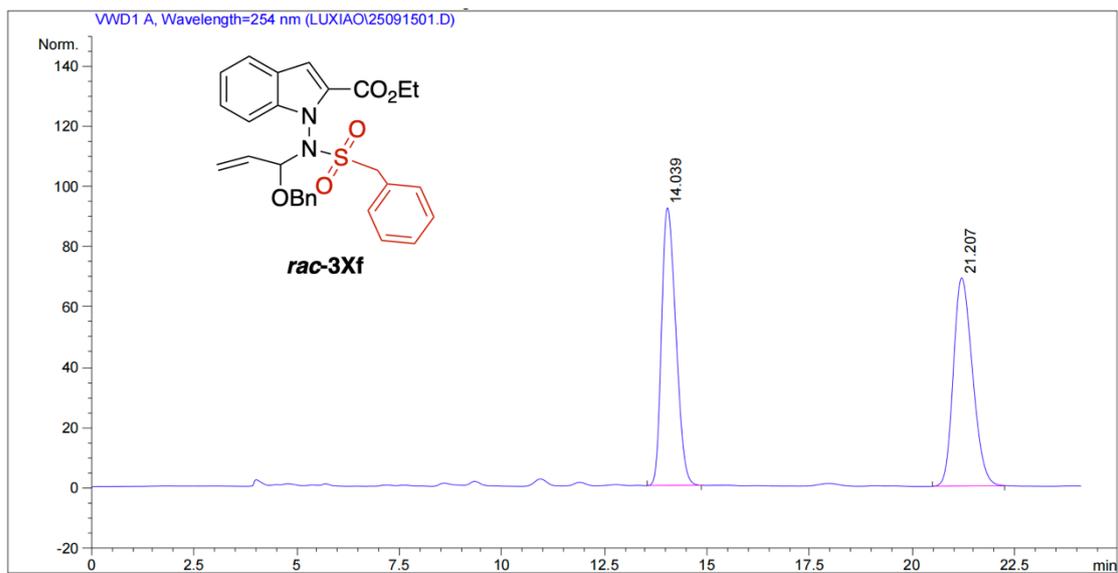
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1	16.455	BB	0.4889	5167.94824	169.84863	98.1110
2	18.089	MM	0.4283	99.50381	3.87178	1.8890



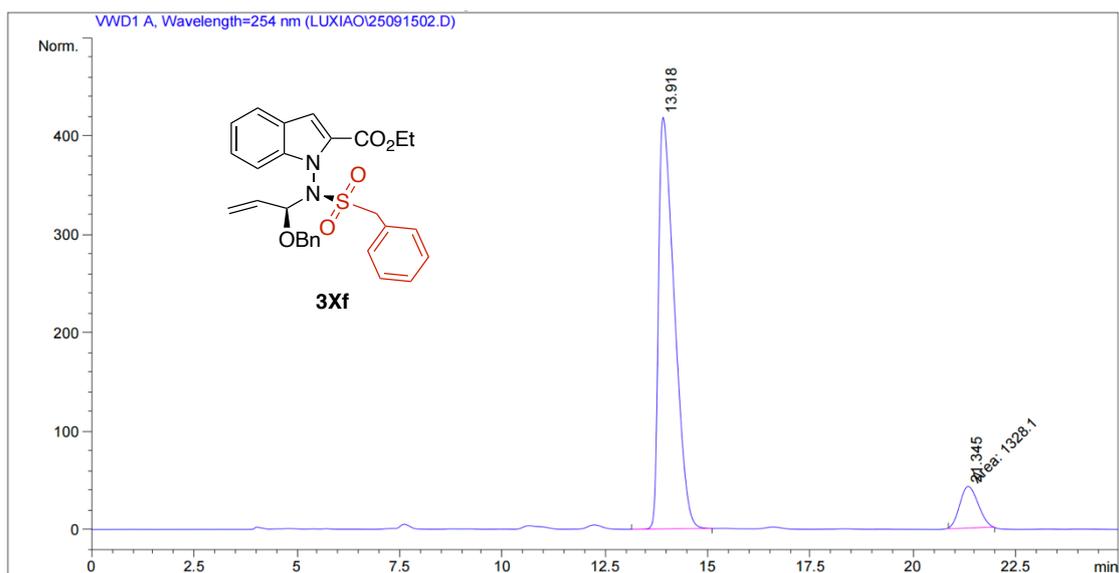
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.405	BB	0.5408	2497.47632	70.85645	50.0896
2	15.720	BB	0.5955	2488.54248	63.09873	49.9104



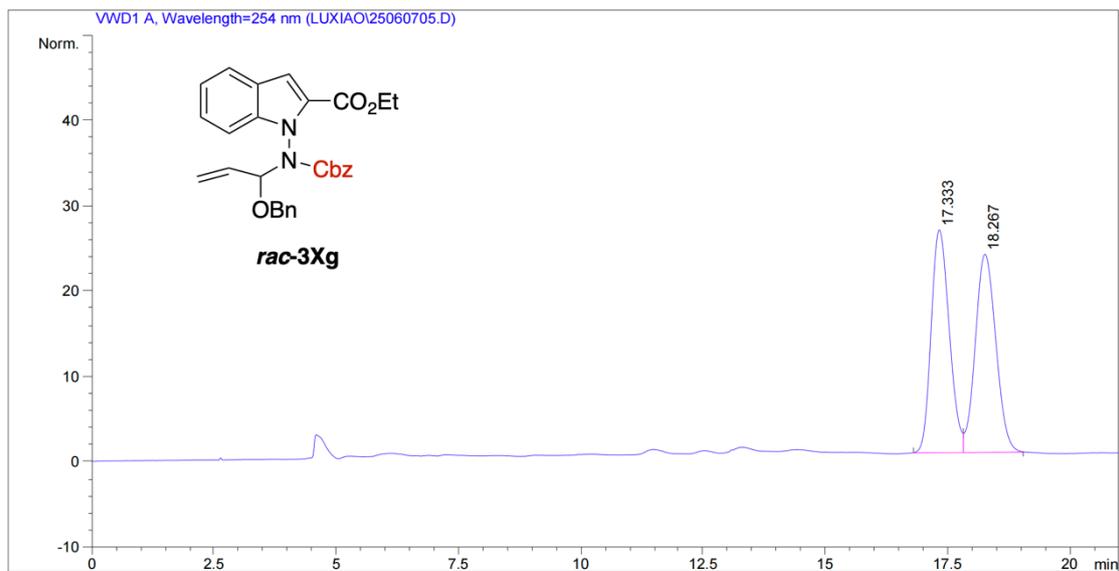
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.052	BB	0.5161	1.03520e4	306.67862	94.8508
2	15.283	BB	0.5580	561.97681	14.99701	5.1492



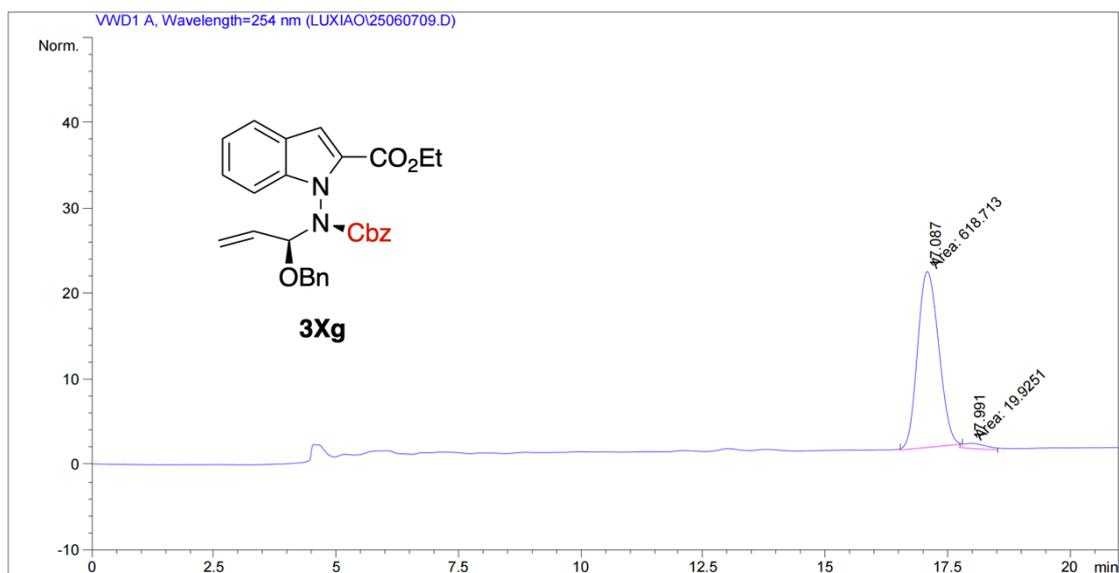
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	14.039	PB	0.3819	2234.80176		92.15344	49.8114
2	21.207	BB	0.5081	2251.72876		69.12962	50.1886



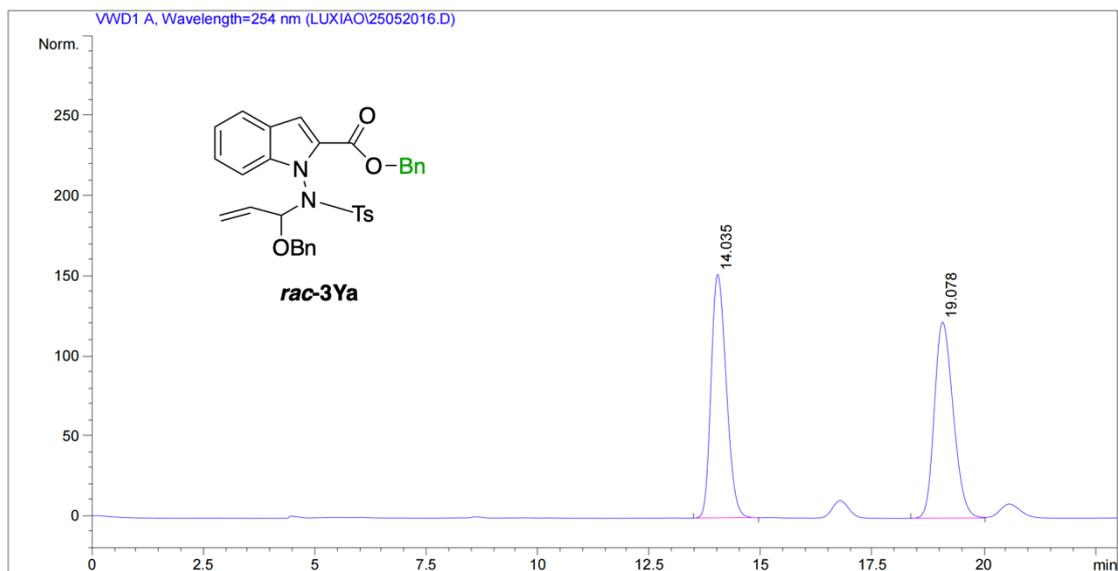
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	13.918	PB	0.4053	1.12329e4		417.92288	89.4268
2	21.345	MM	0.5214	1328.09778		42.45250	10.5732



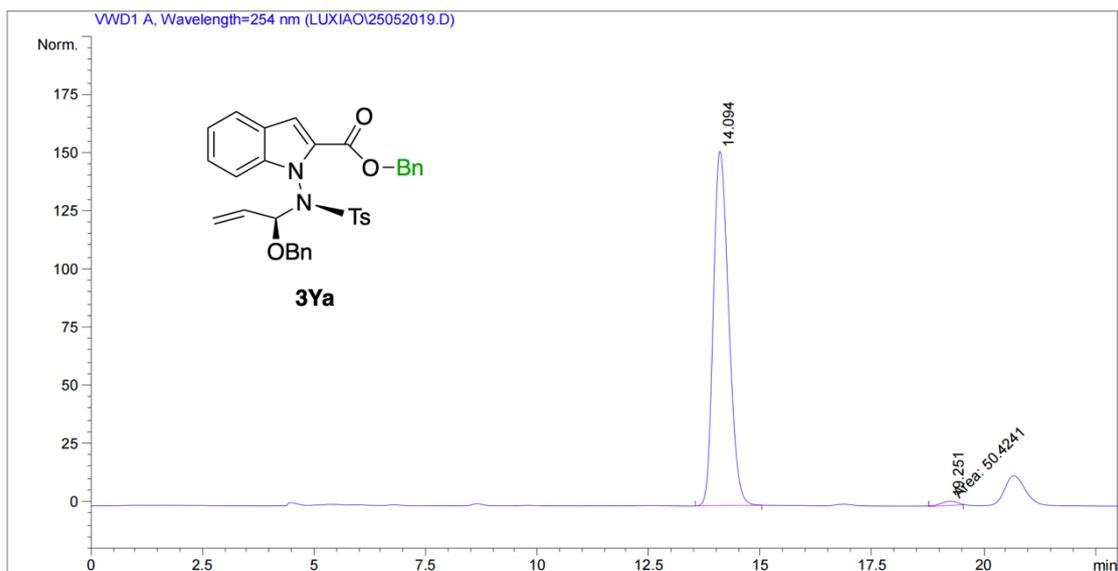
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.333	BV	0.4059	674.41681	26.13274	49.7643
2	18.267	VB	0.4555	680.80499	23.23092	50.2357



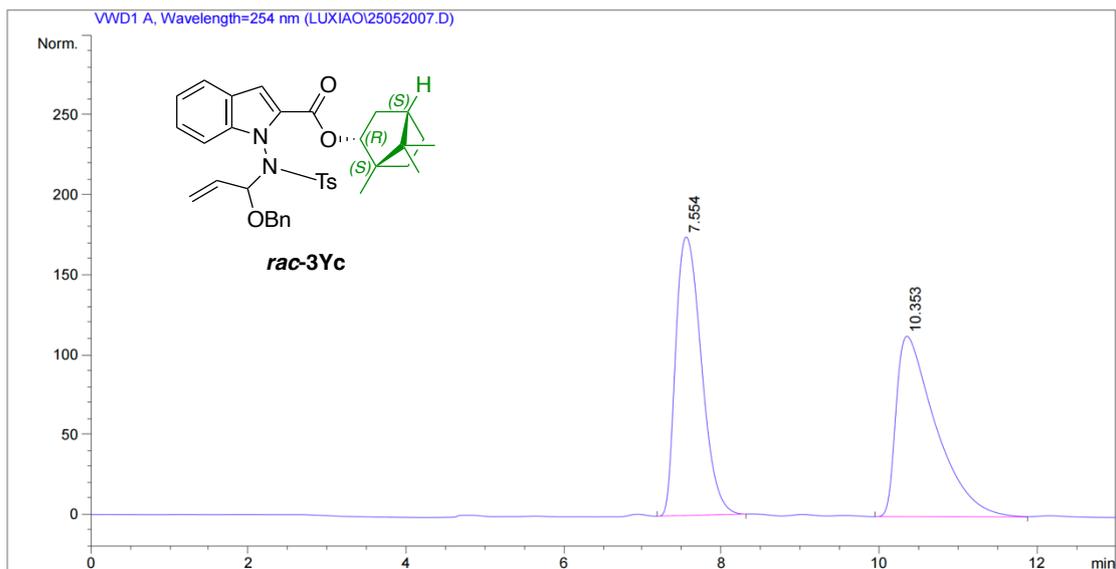
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.087	MM	0.5010	618.71326	20.58442	96.8801
2	17.991	MM	0.5361	19.92507	6.19398e-1	3.1199



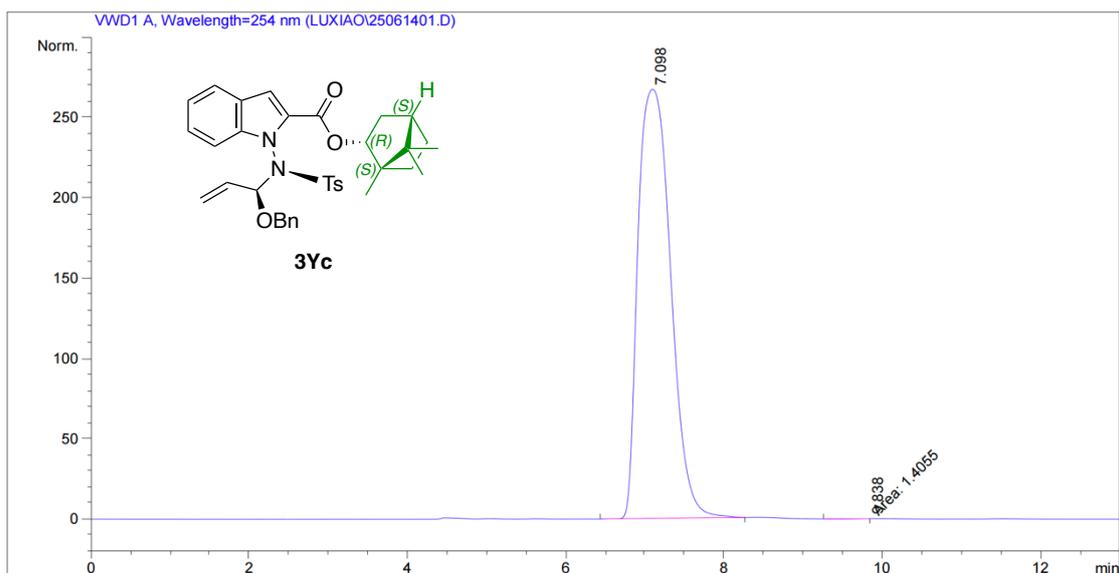
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.035	BB	0.3726	3609.68970	152.31662	49.9209
2	19.078	BB	0.4626	3621.13013	122.56503	50.0791



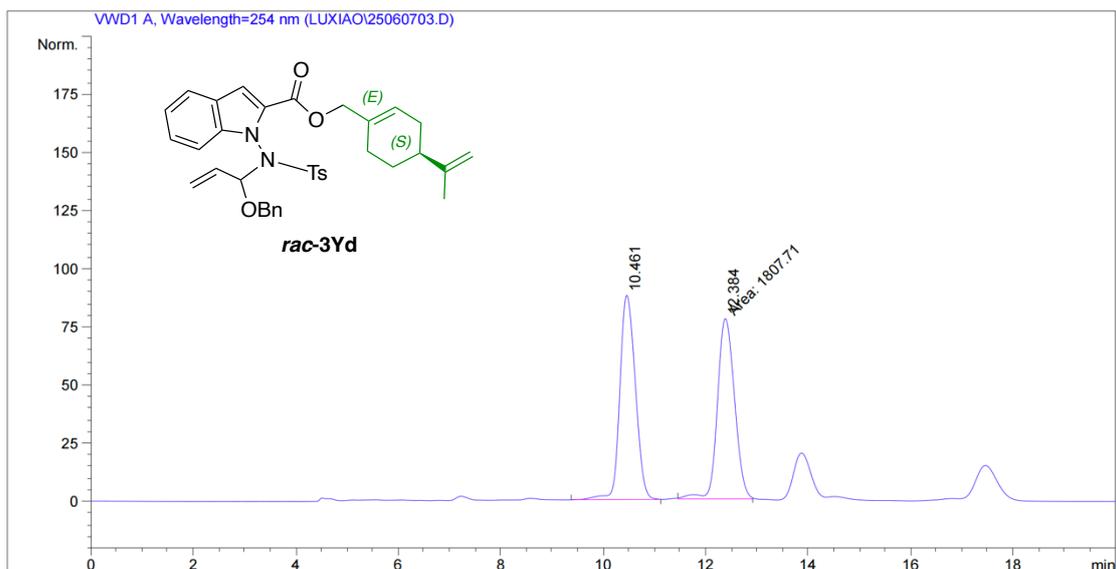
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.094	BB	0.3750	3639.64917	152.24170	98.6335
2	19.251	MM	0.4414	50.42414	1.90408	1.3665



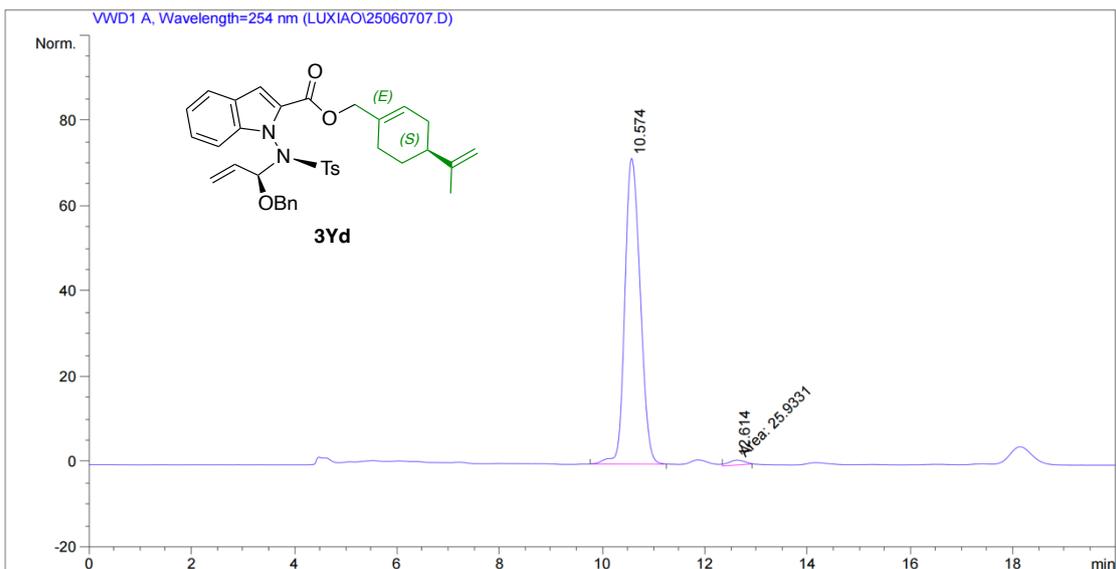
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	7.554	VB	0.3619	3951.37280		174.39471	49.8982
2	10.353	VB	0.5186	3967.49585		113.05510	50.1018



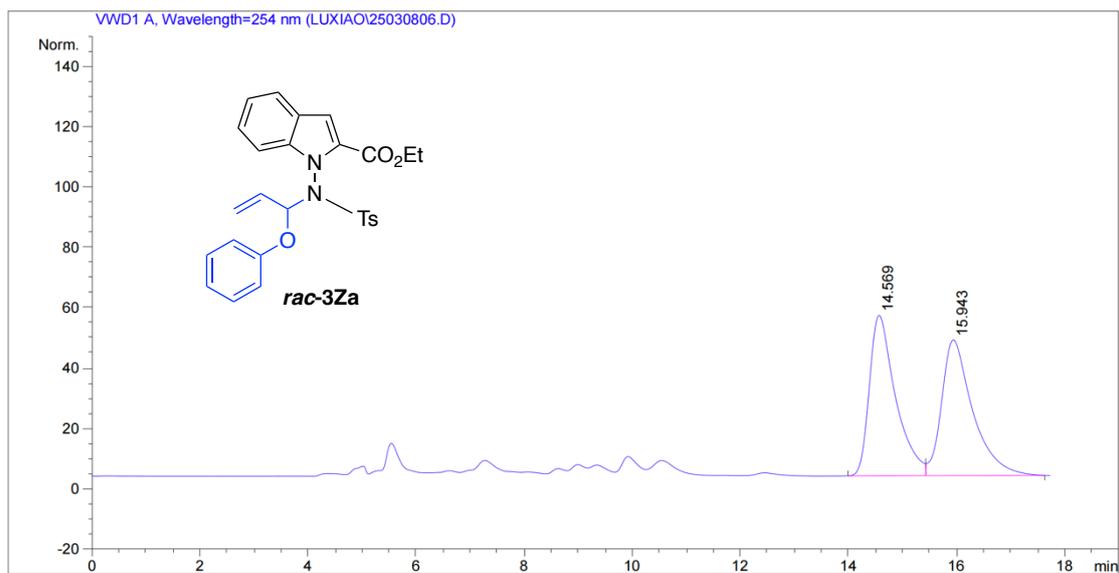
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	7.098	PB	0.4655	7661.52881		267.24121	99.9817
2	9.838	MM	0.1421	1.40550		1.64866e-1	0.0183



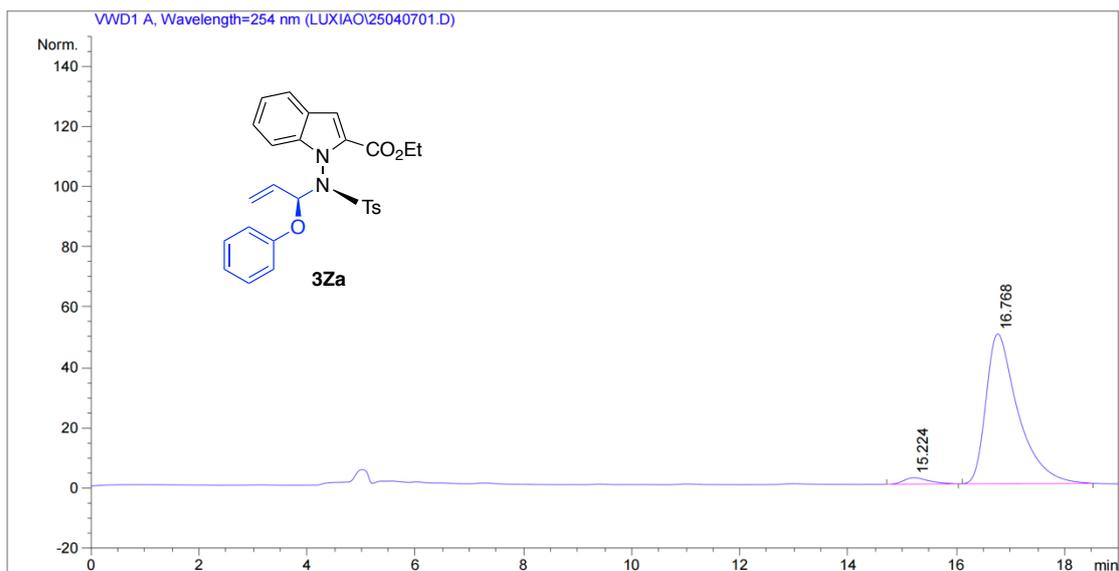
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.461	BB	0.3371	1857.56726	87.79173	50.6801
2	12.384	MM	0.3886	1807.71228	77.52942	49.3199



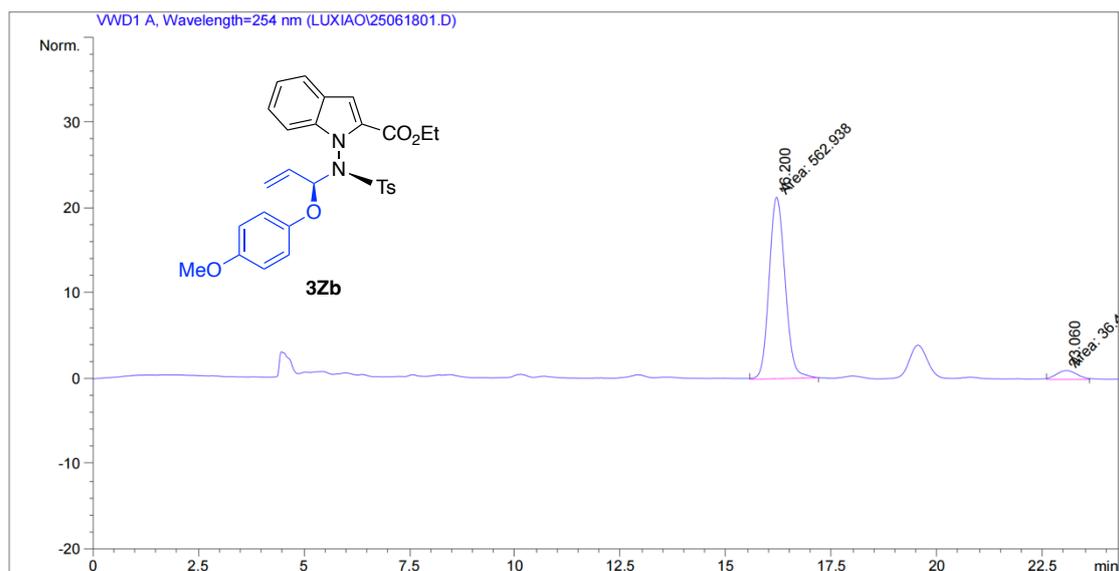
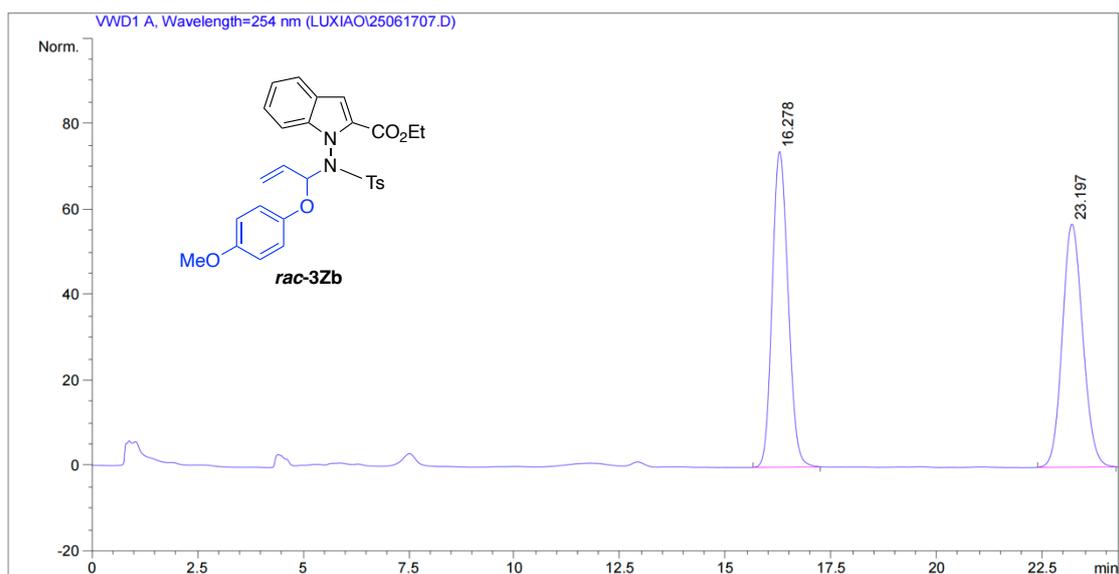
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.574	BB	0.3339	1496.40820	71.65813	98.2965
2	12.614	MM	0.3704	25.93306	1.16689	1.7035

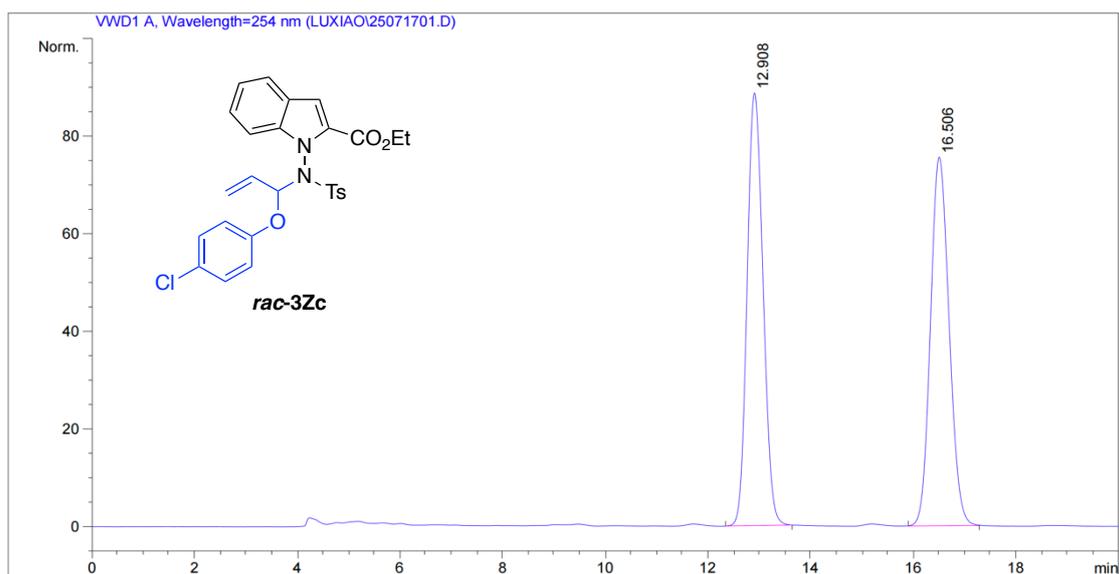


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.569	BV	0.4938	1785.98462	53.16443	49.7613
2	15.943	VB	0.5873	1803.11584	44.96156	50.2387

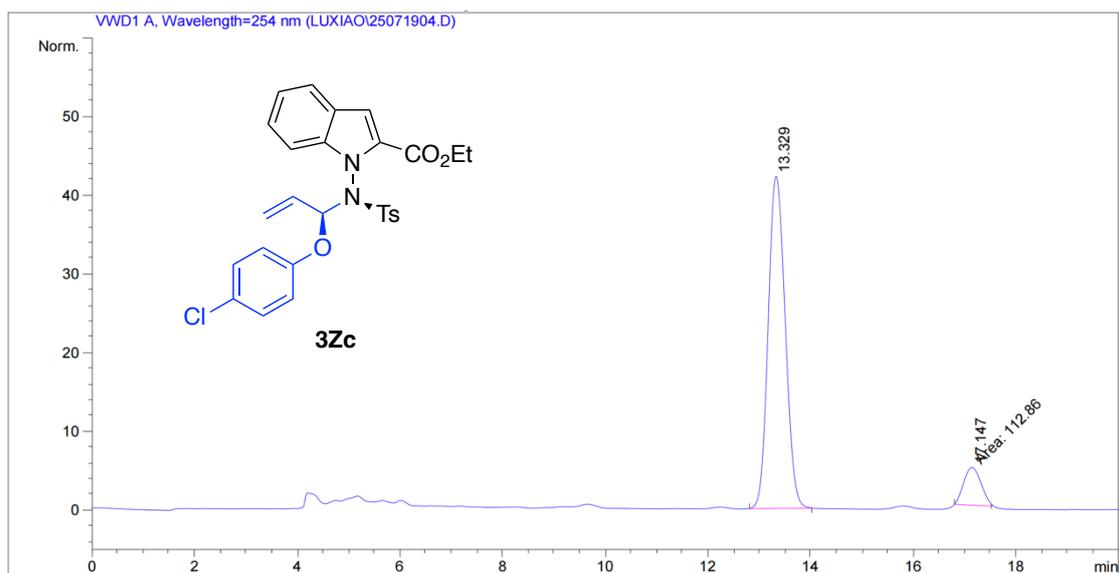


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.224	BB	0.4514	70.89474	2.15143	3.3438
2	16.768	BB	0.6055	2049.29224	49.78313	96.6562

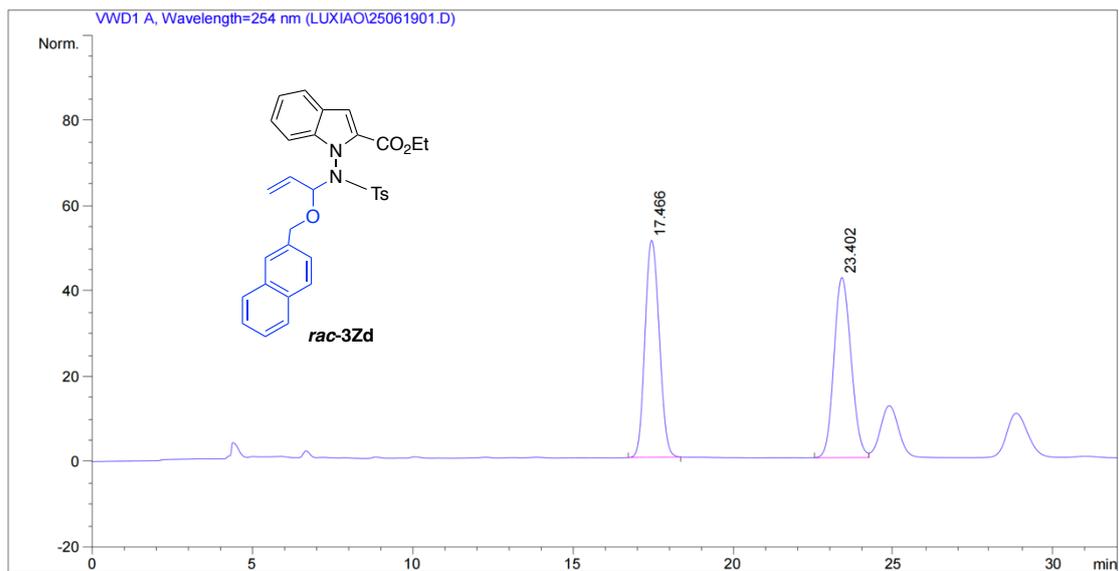




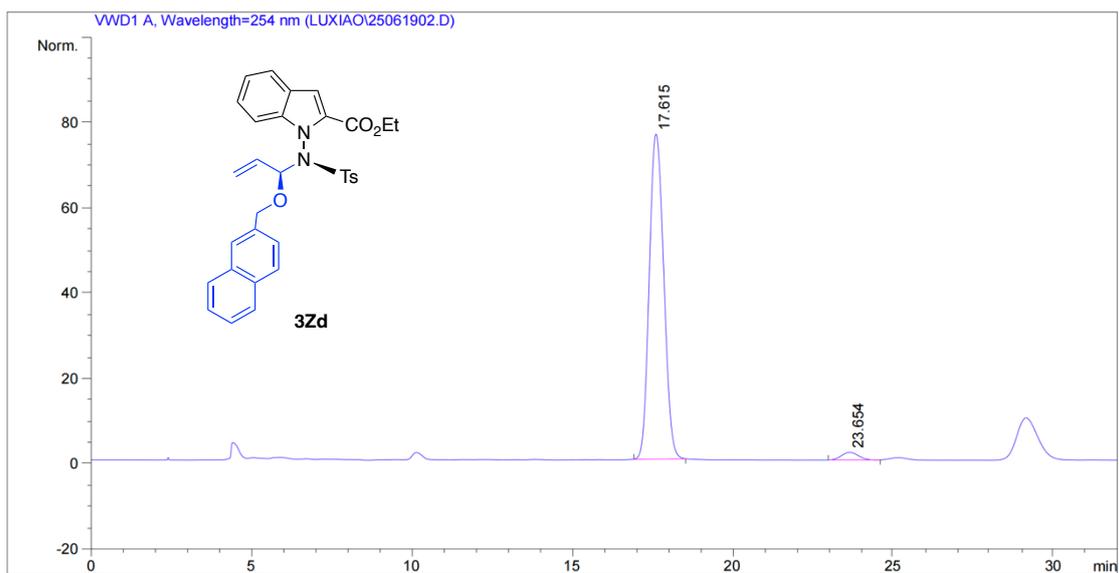
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.908	BB	0.3416	1908.65918	88.60422	50.0585
2	16.506	BB	0.3963	1904.20105	75.47649	49.9415



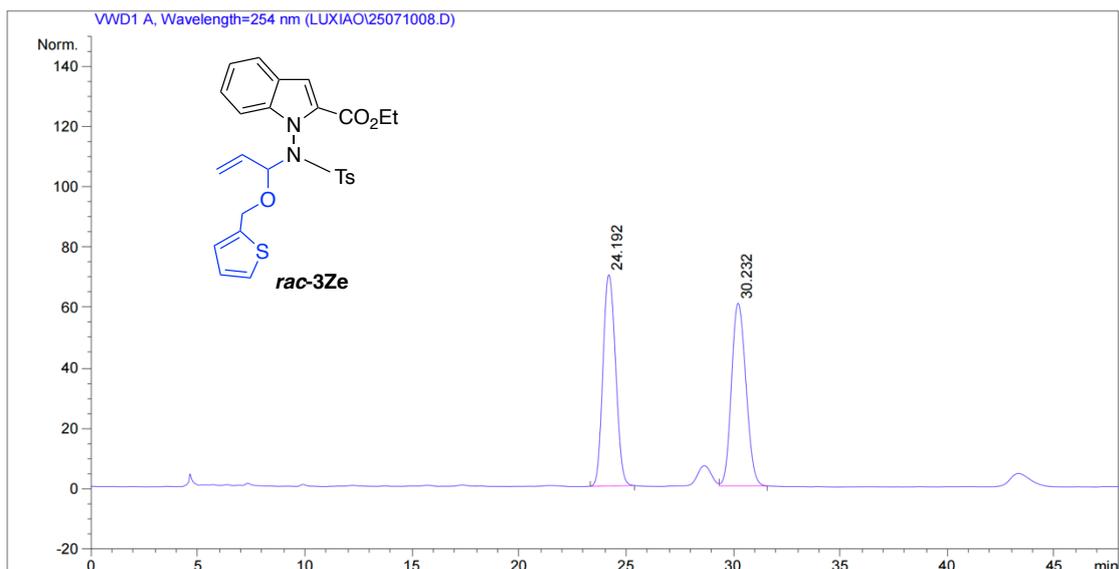
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.329	BB	0.3665	972.18182	42.17601	89.5986
2	17.147	MM	0.3916	112.85978	4.80383	10.4014



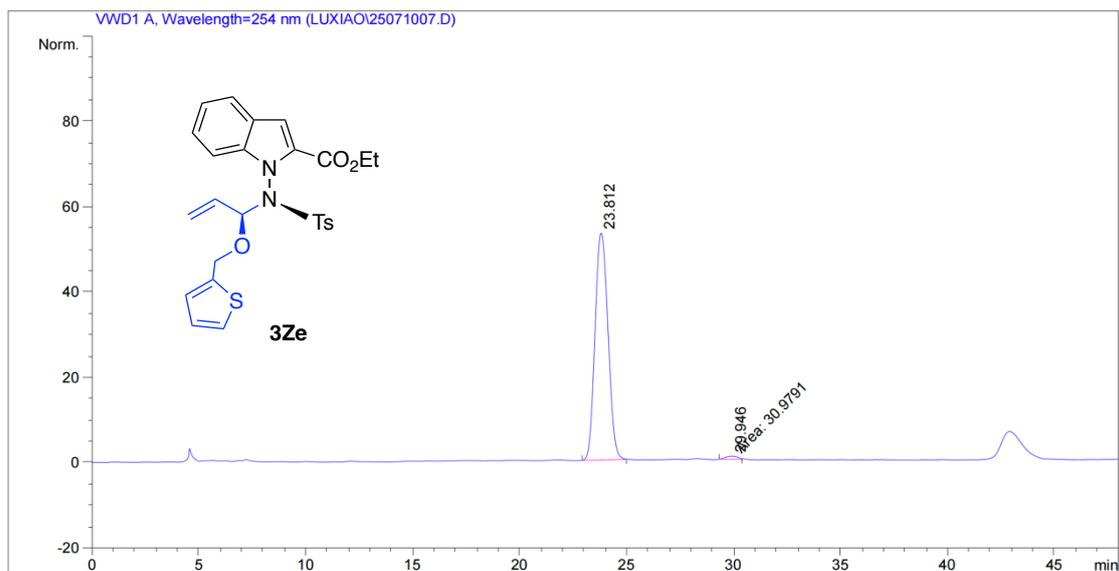
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.466	BB	0.4976	1579.52478	50.87360	50.1317
2	23.402	BV	0.5814	1571.22754	42.20721	49.8683



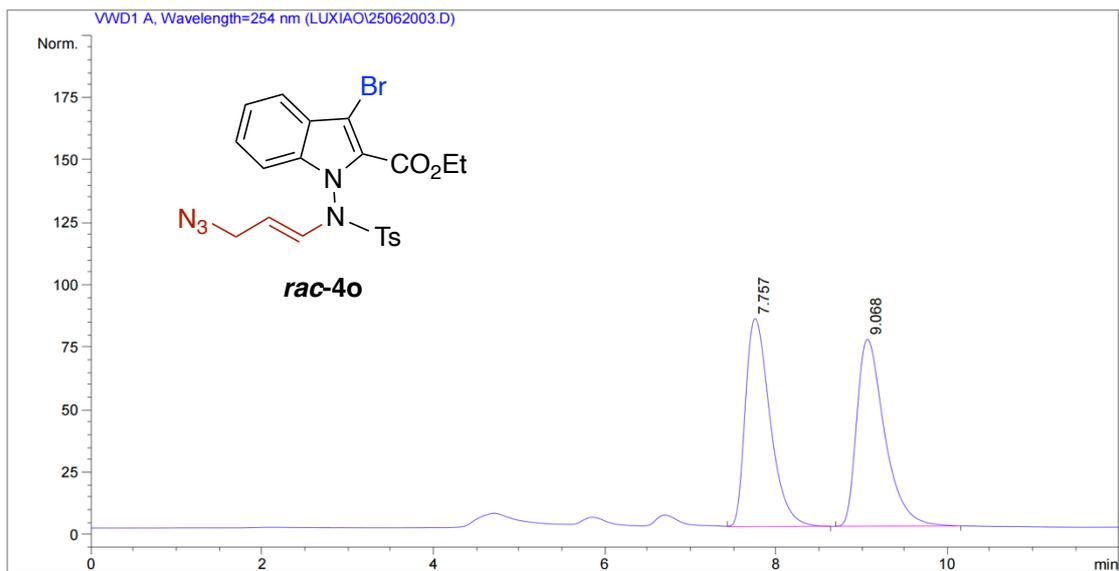
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.615	BB	0.4977	2394.63135	76.19564	97.2789
2	23.654	BB	0.4628	66.98257	1.79570	2.7211



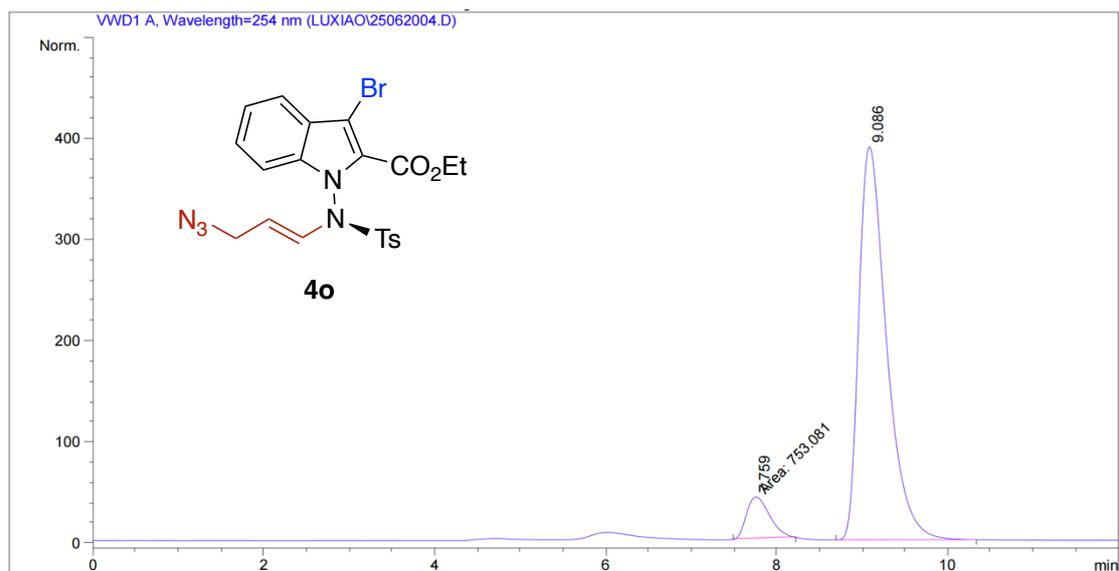
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.192	BB	0.6466	2886.05762	70.05086	50.2946
2	30.232	VB	0.7358	2852.25024	60.56515	49.7054



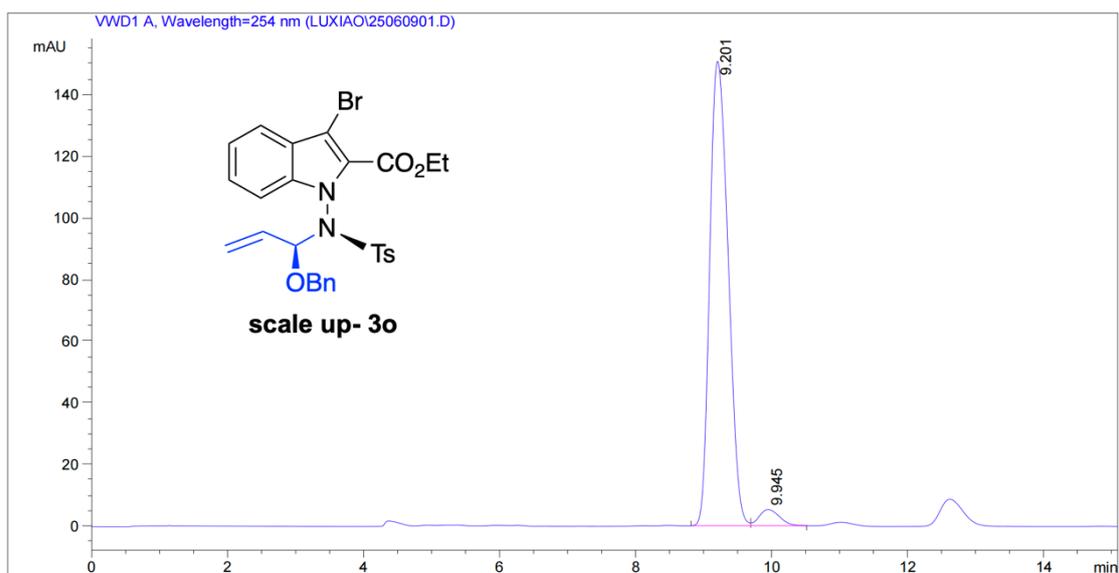
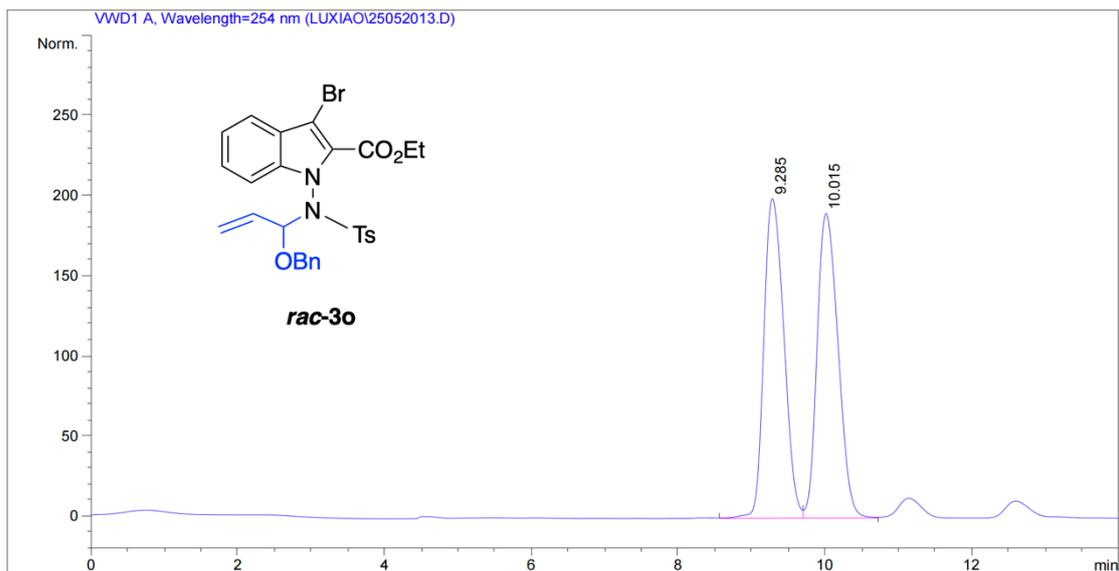
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.812	BB	0.6623	2242.39917	53.17676	98.6373
2	29.946	MM	0.6793	30.97906	7.60054e-1	1.3627



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.757	BB	0.3132	1674.57666	83.26773	49.6696
2	9.068	BB	0.3445	1696.85364	74.87743	50.3304



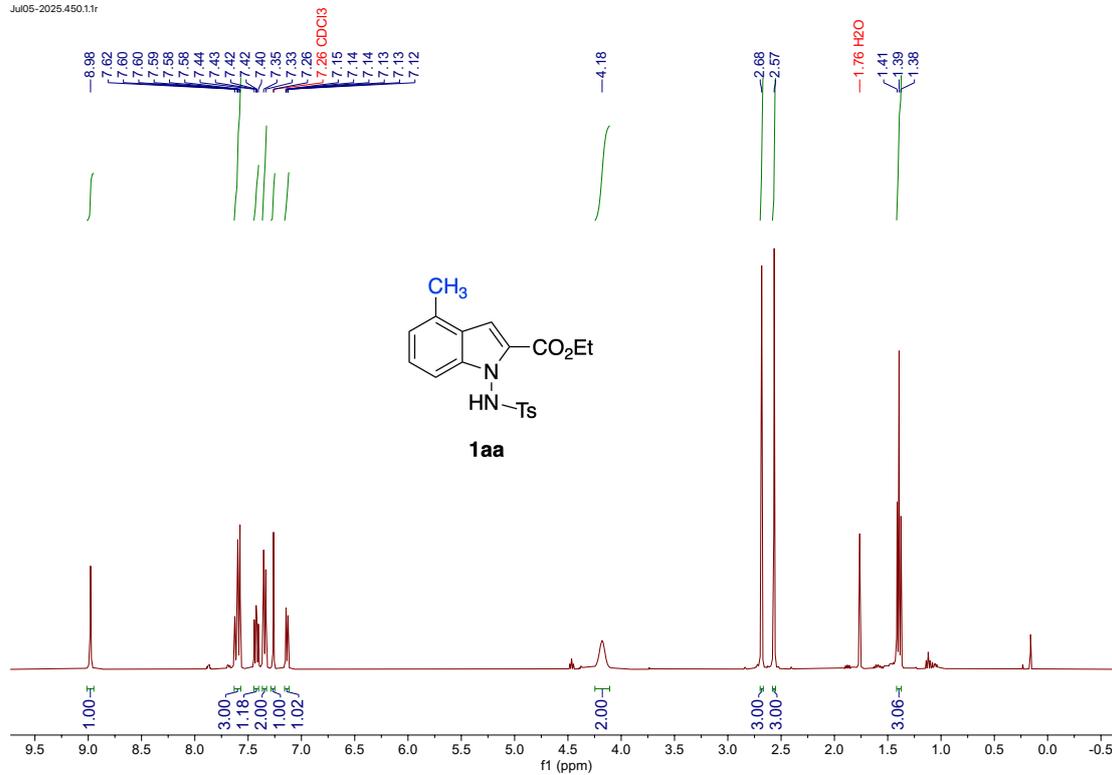
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.759	MM	0.3087	753.08130	40.66520	7.9417
2	9.086	BB	0.3424	8729.54980	388.28561	92.0583



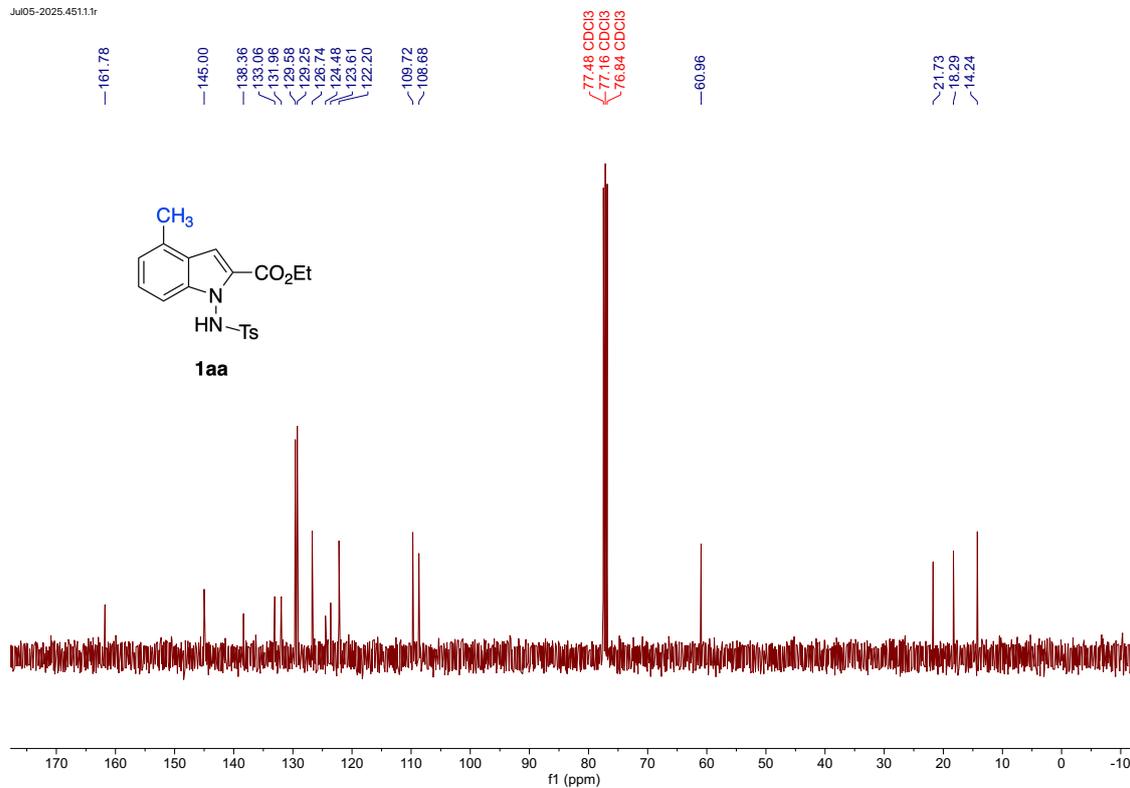
12. ¹H and ¹³C NMR Spectra for Substrates 1 and Products 3

a) Substrates 1

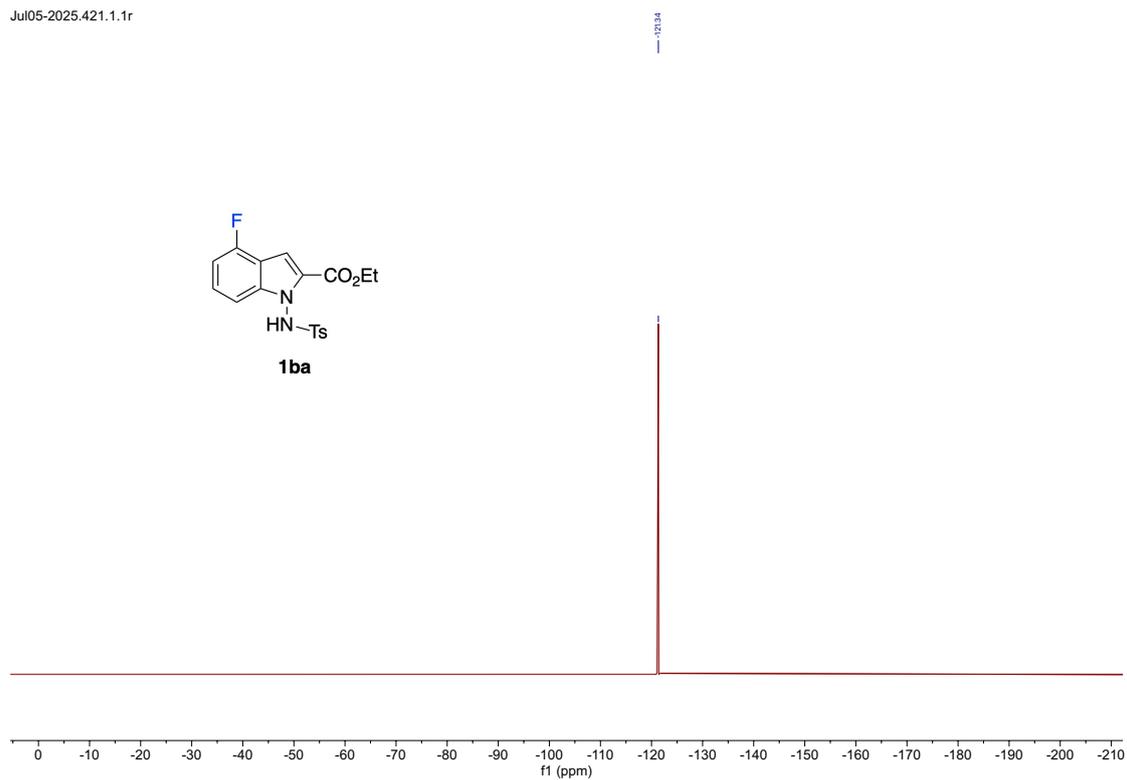
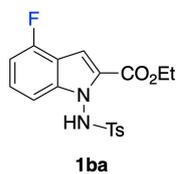
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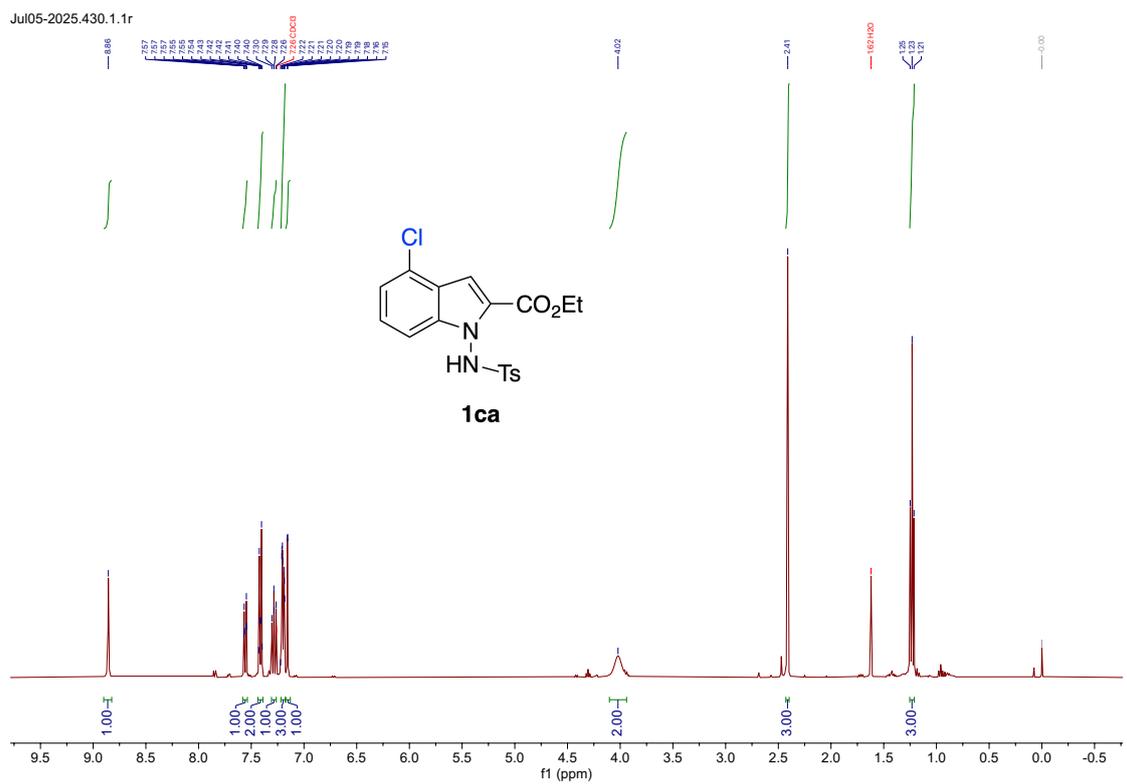
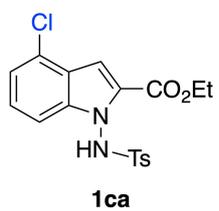
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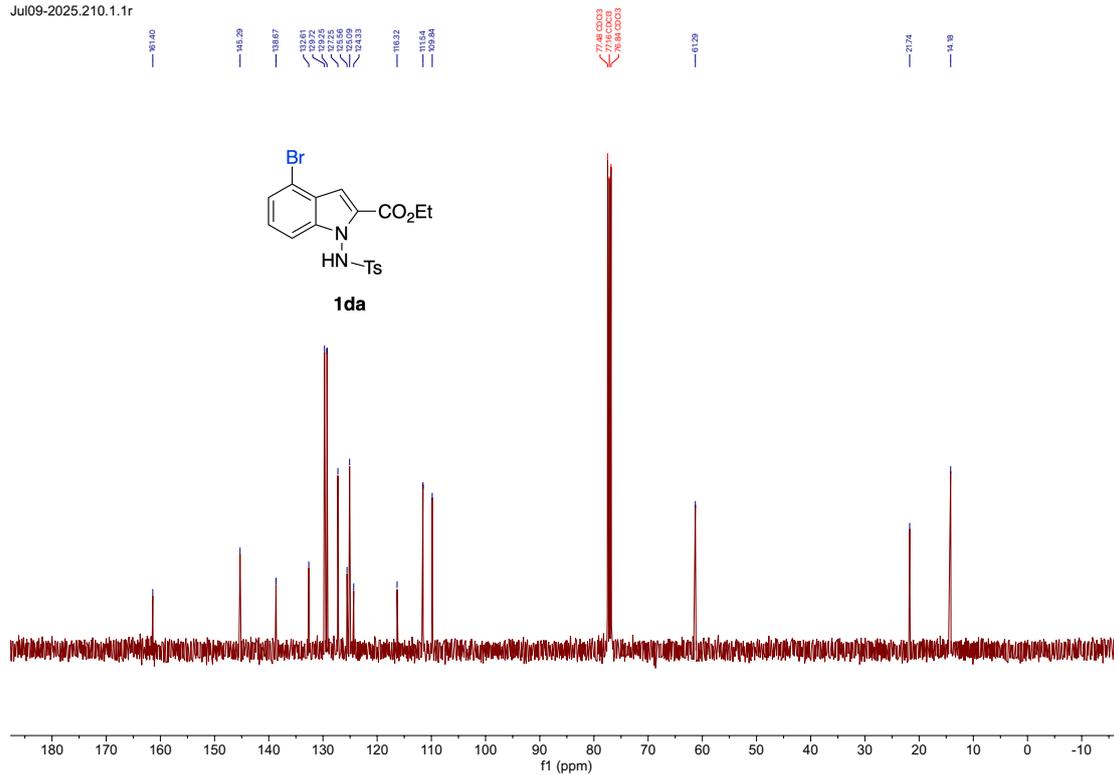
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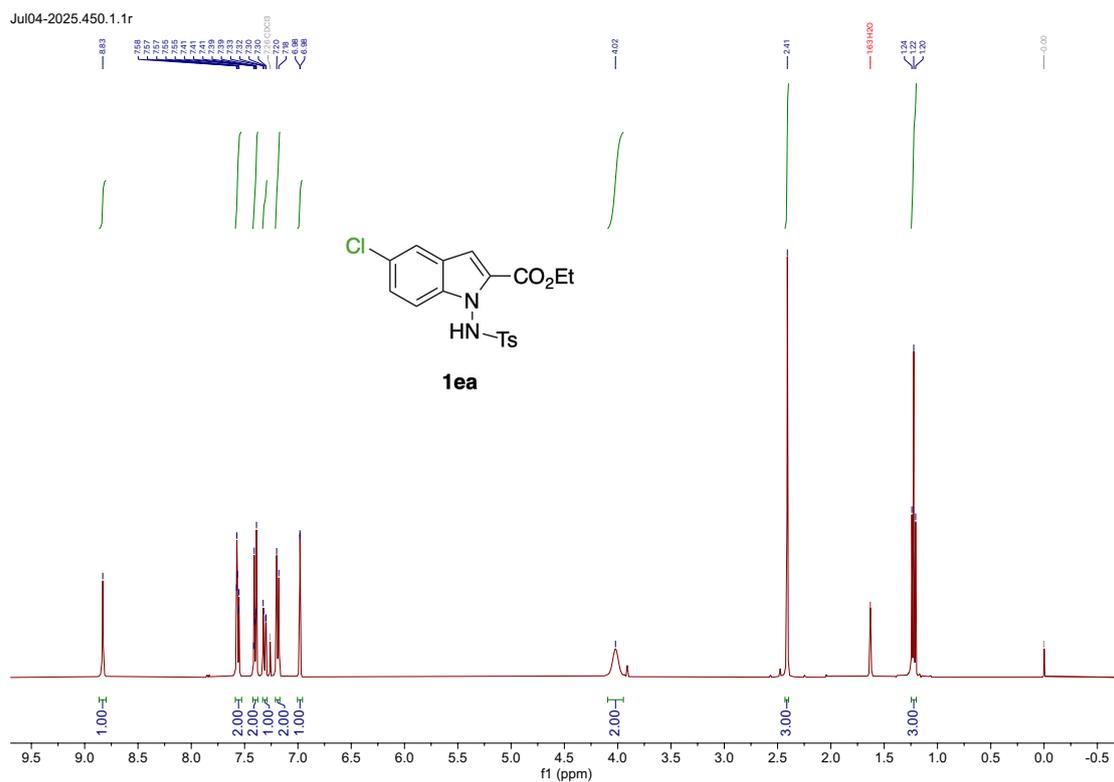
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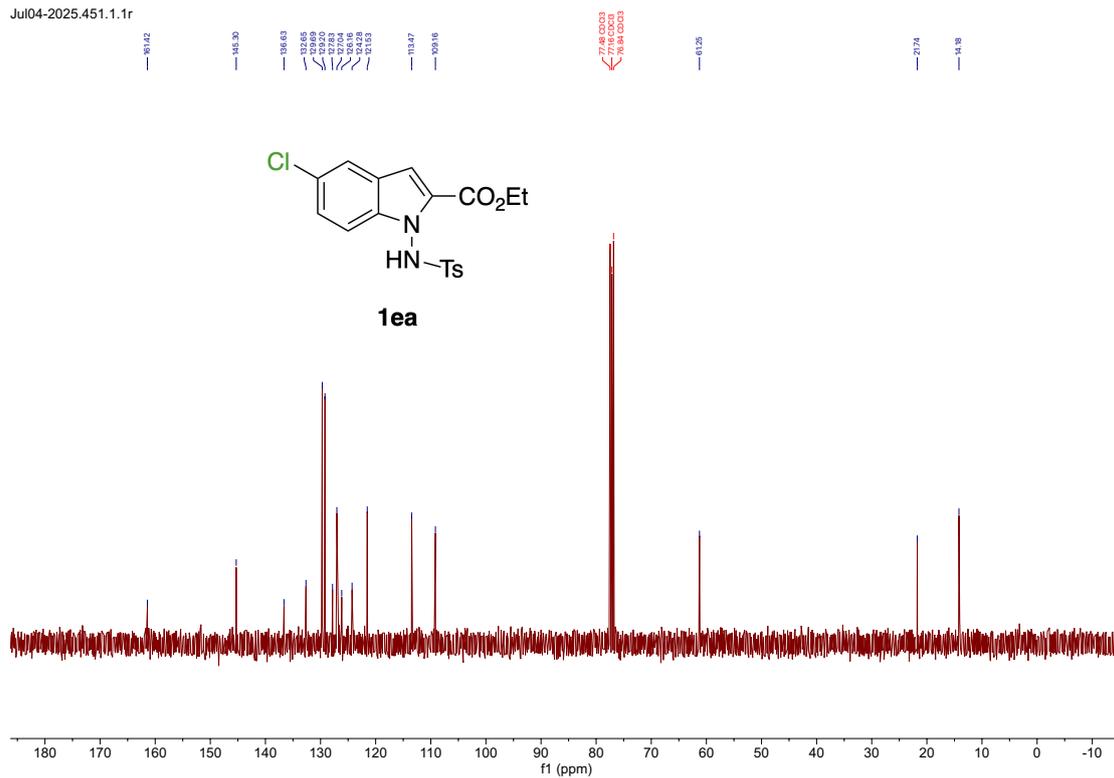
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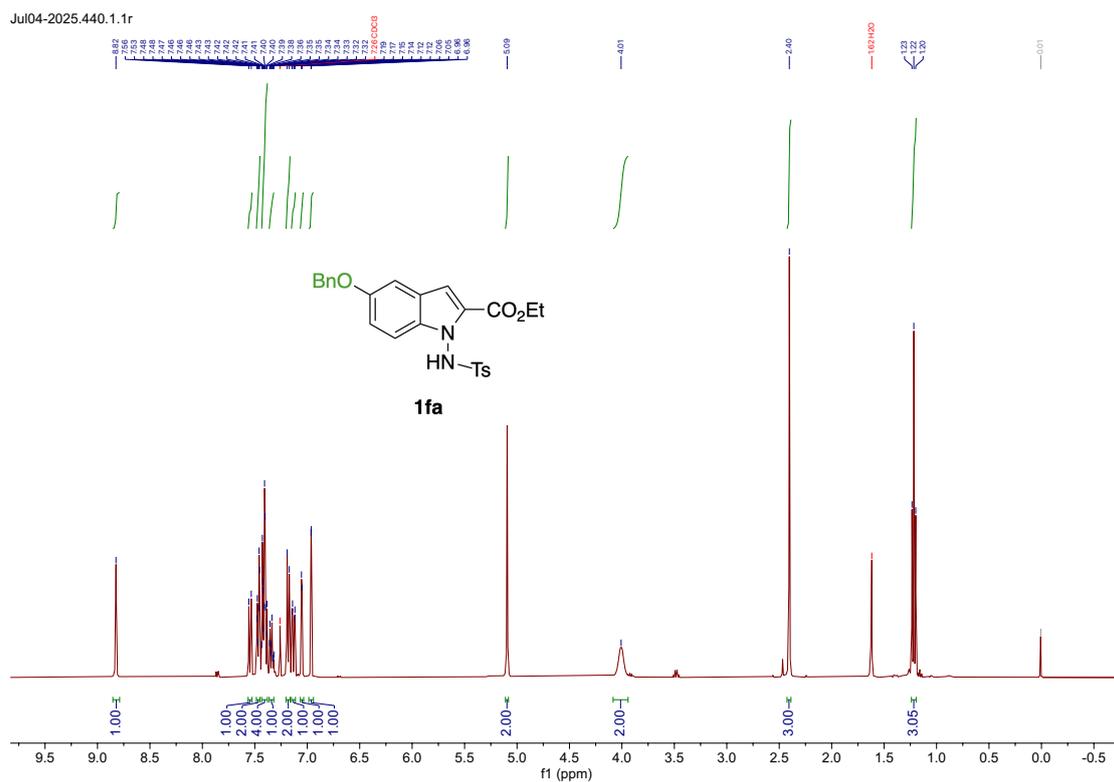
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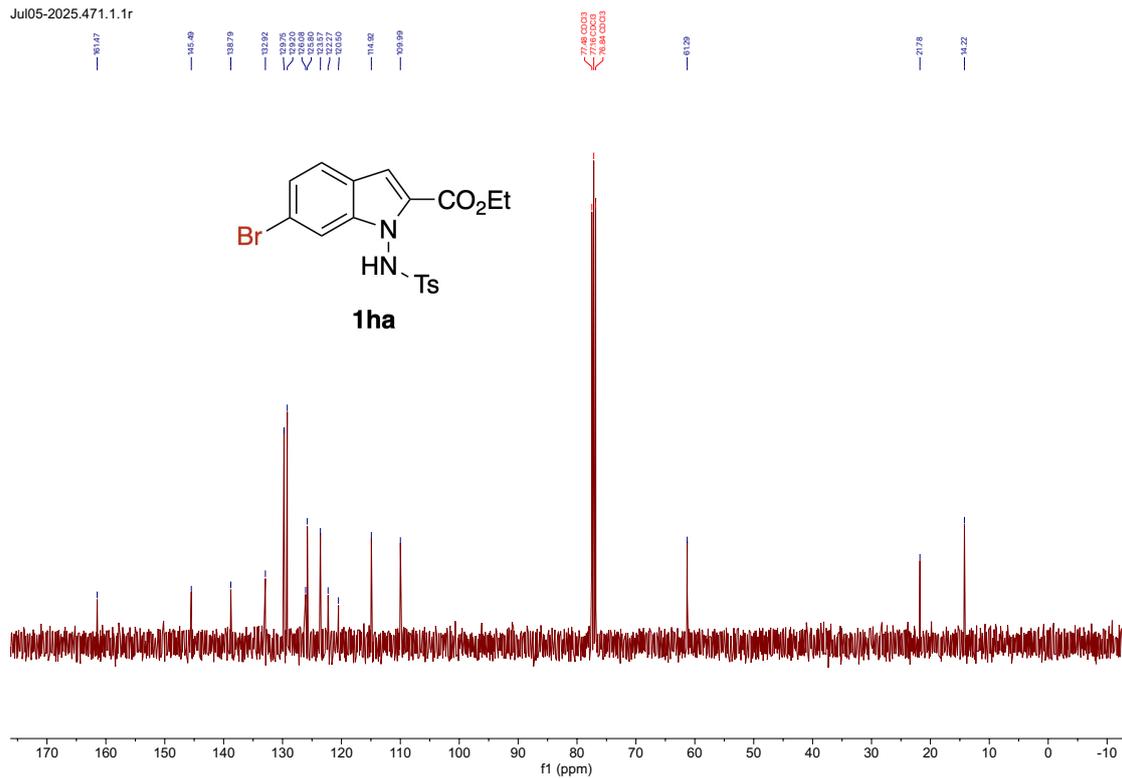
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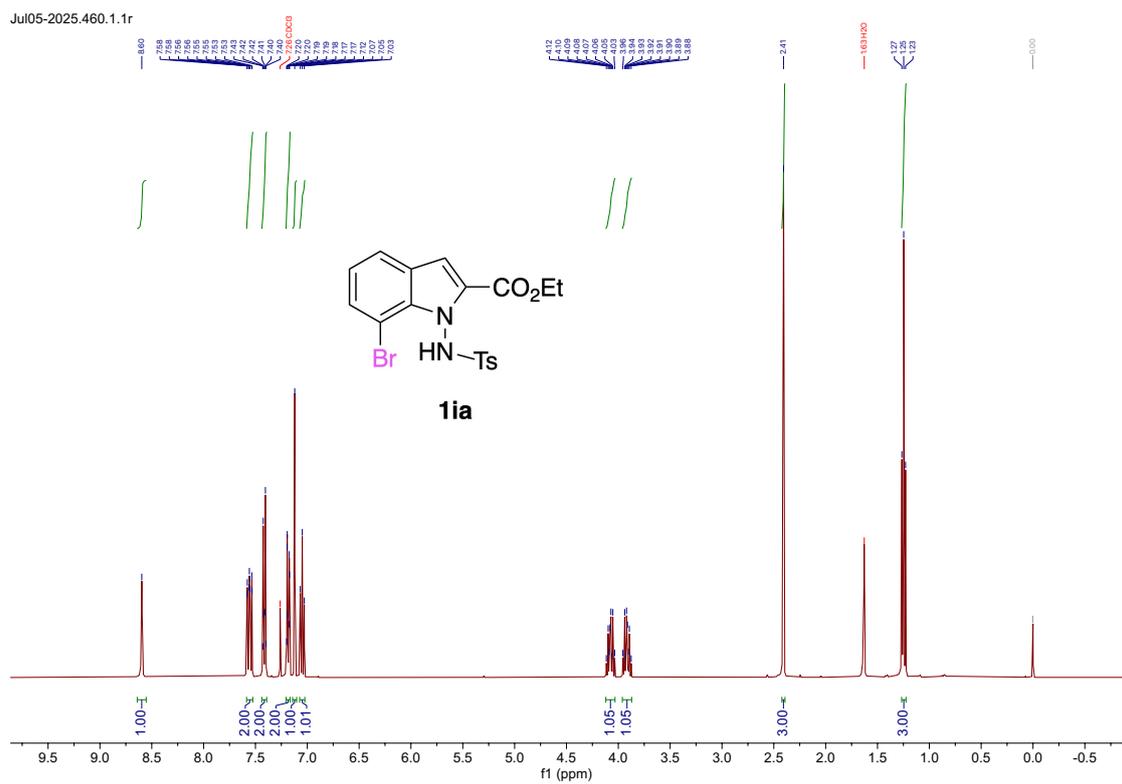
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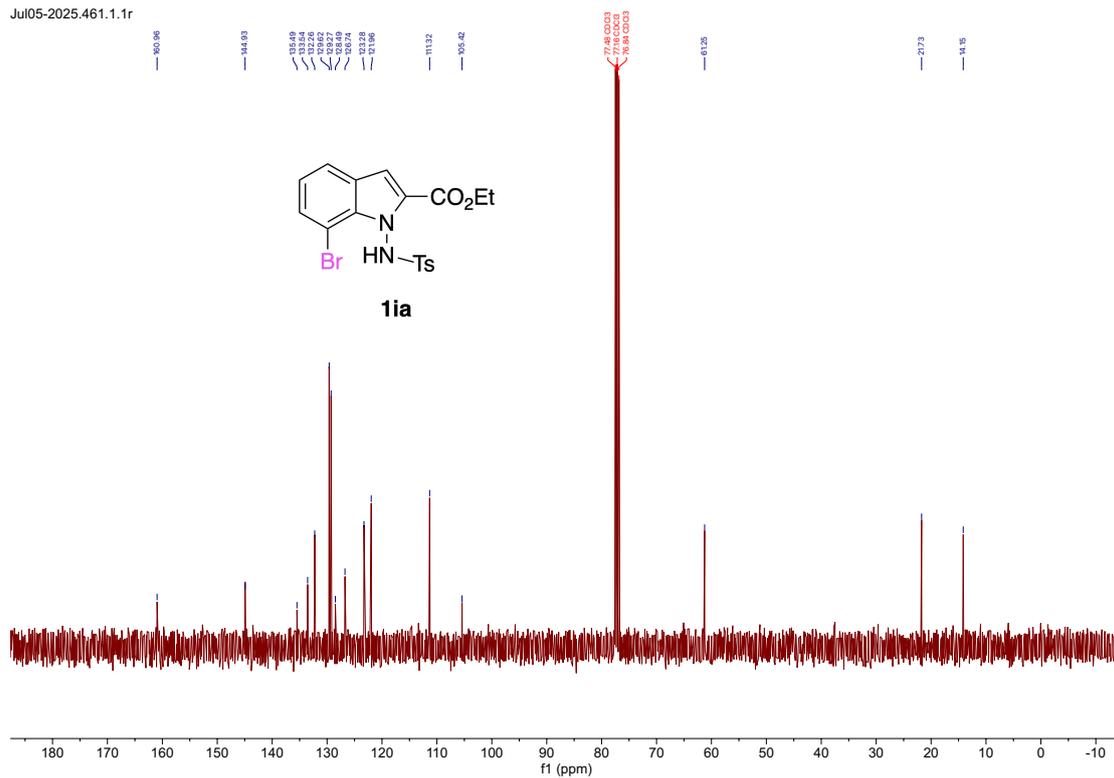
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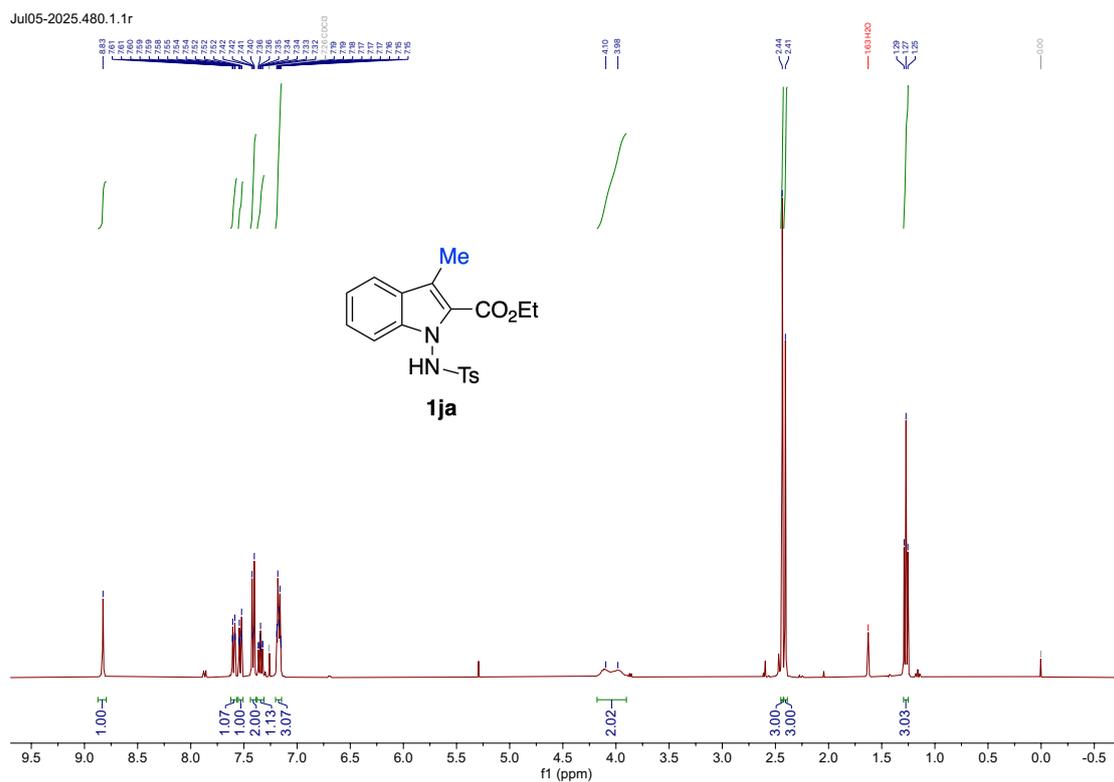
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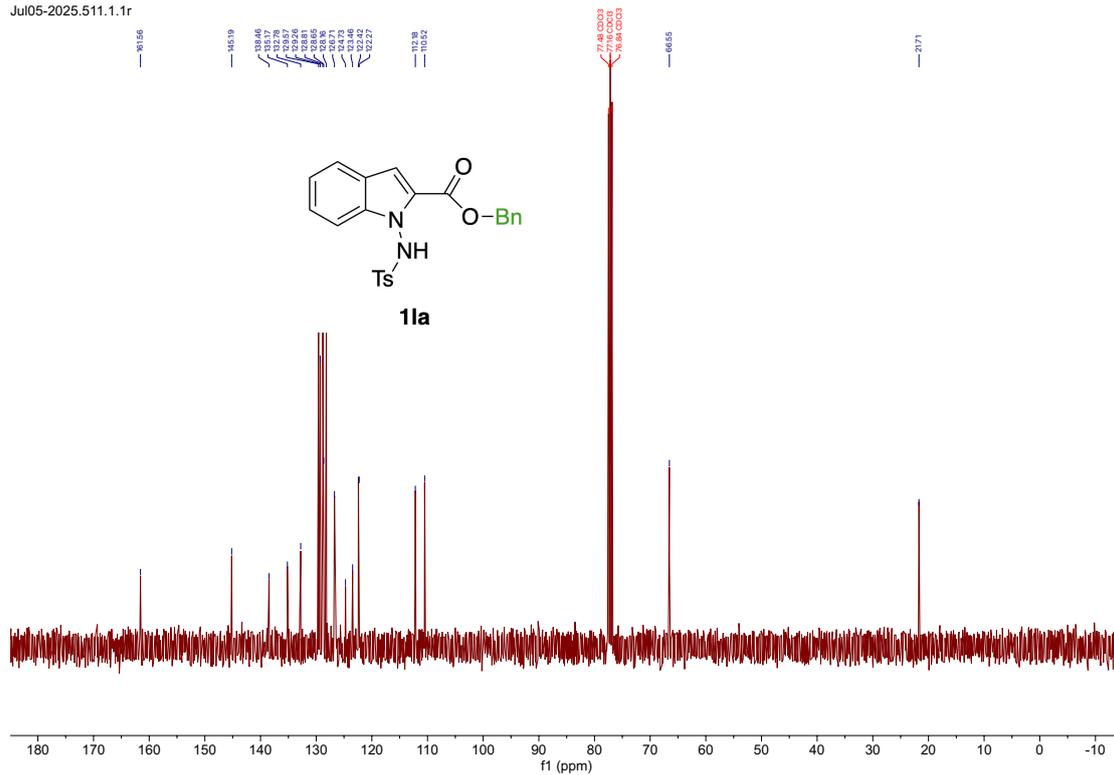
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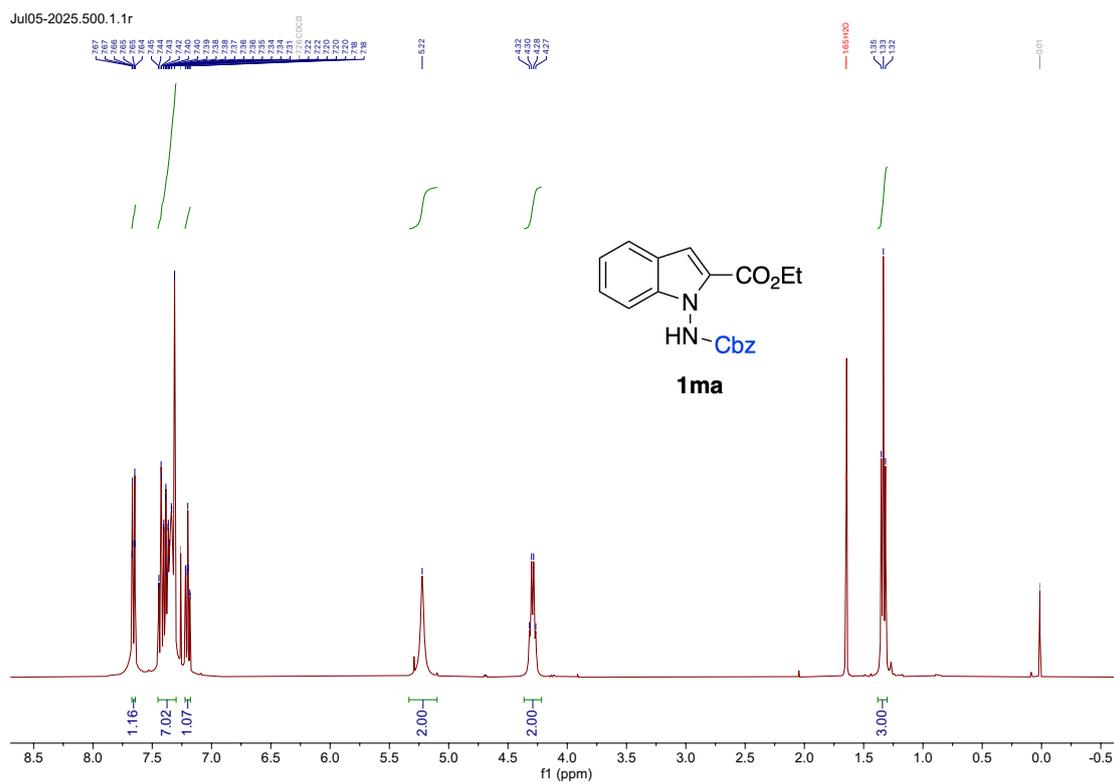
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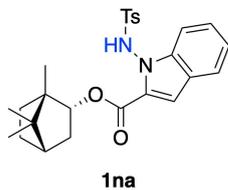
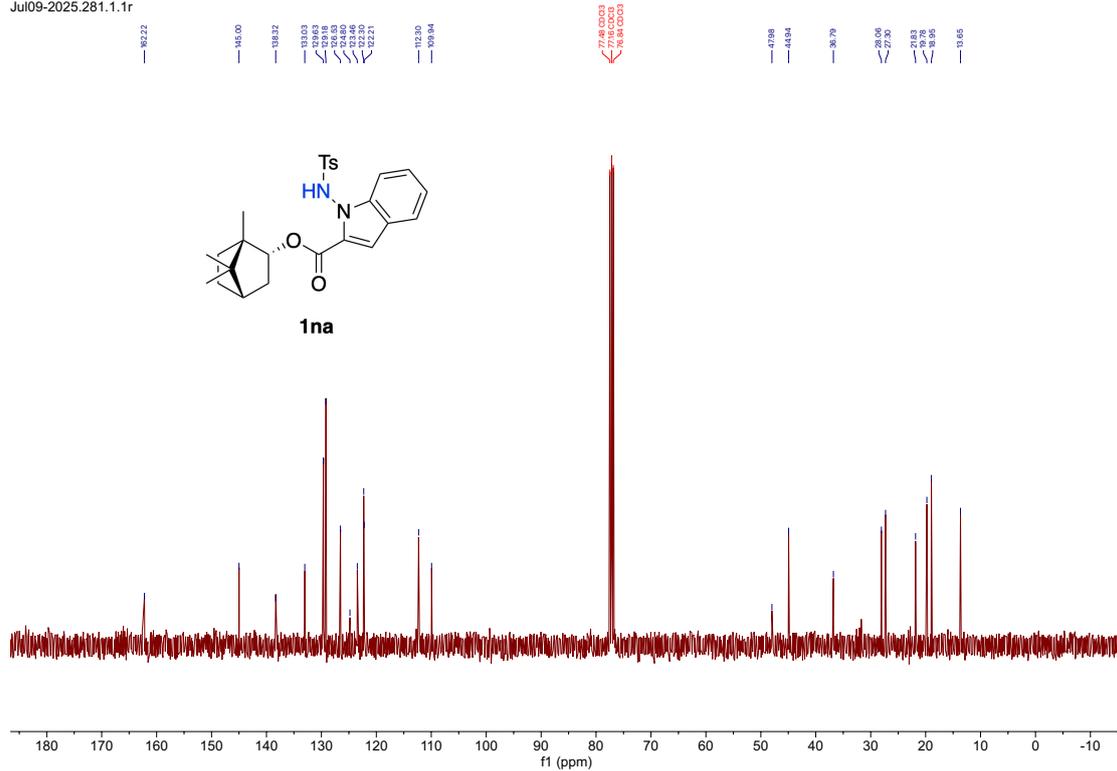
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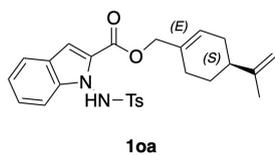
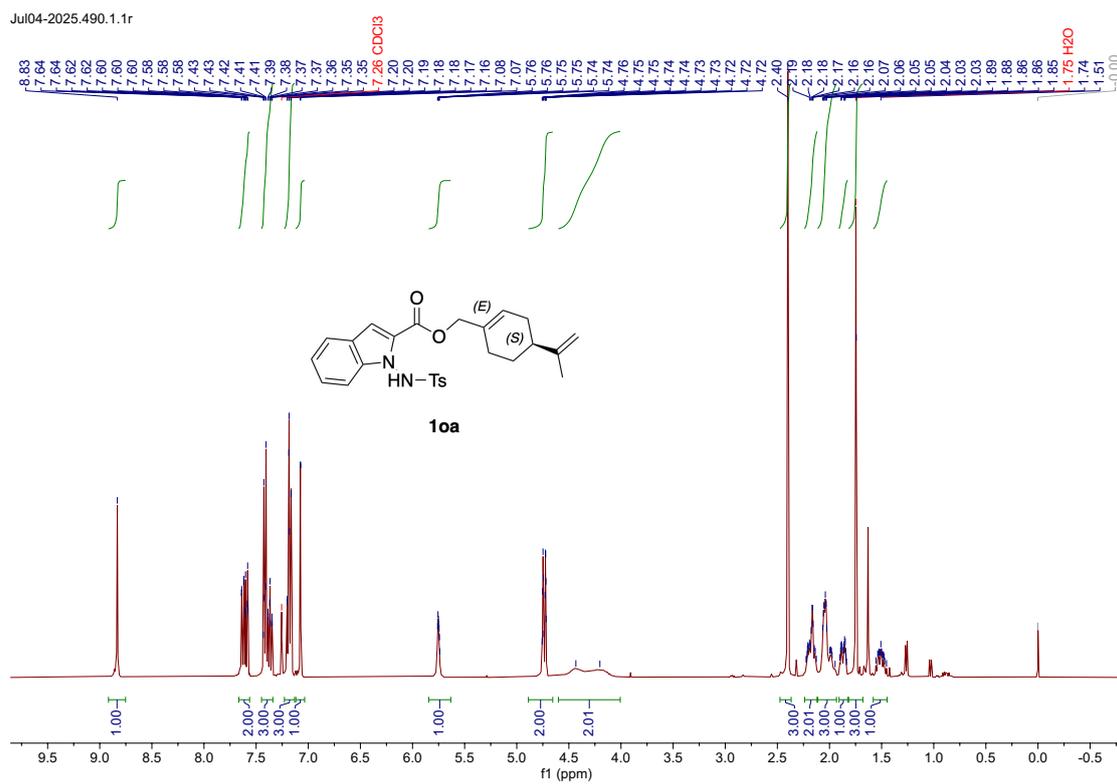
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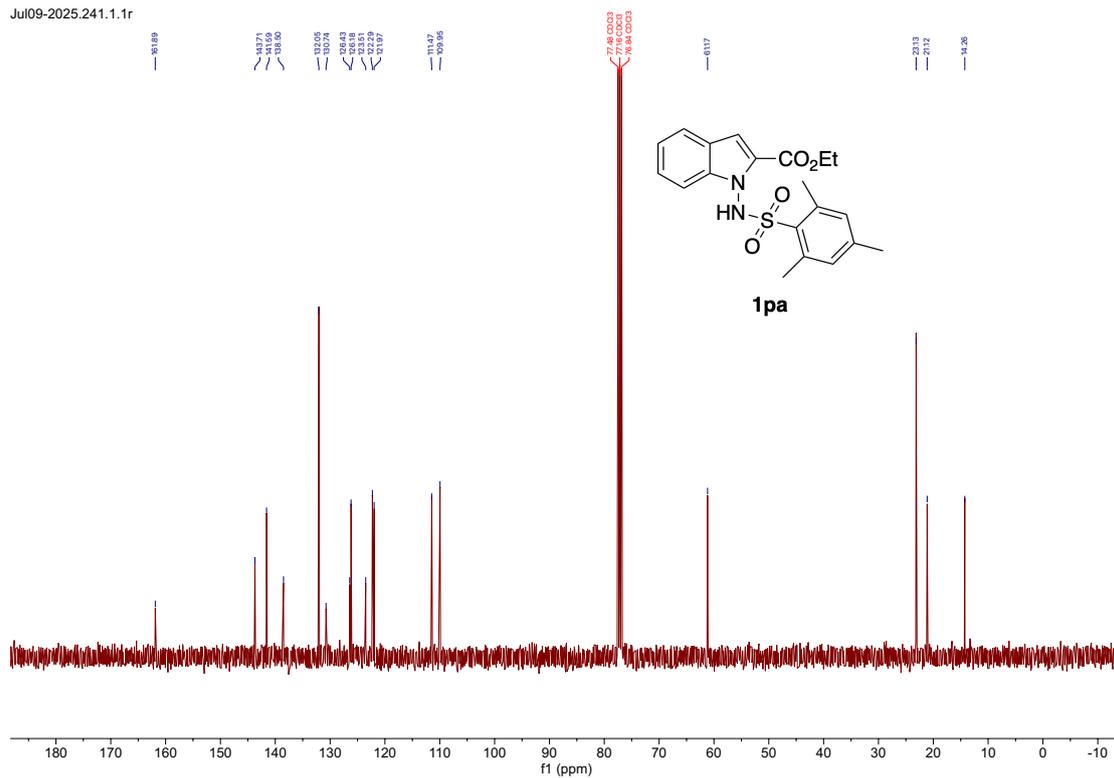
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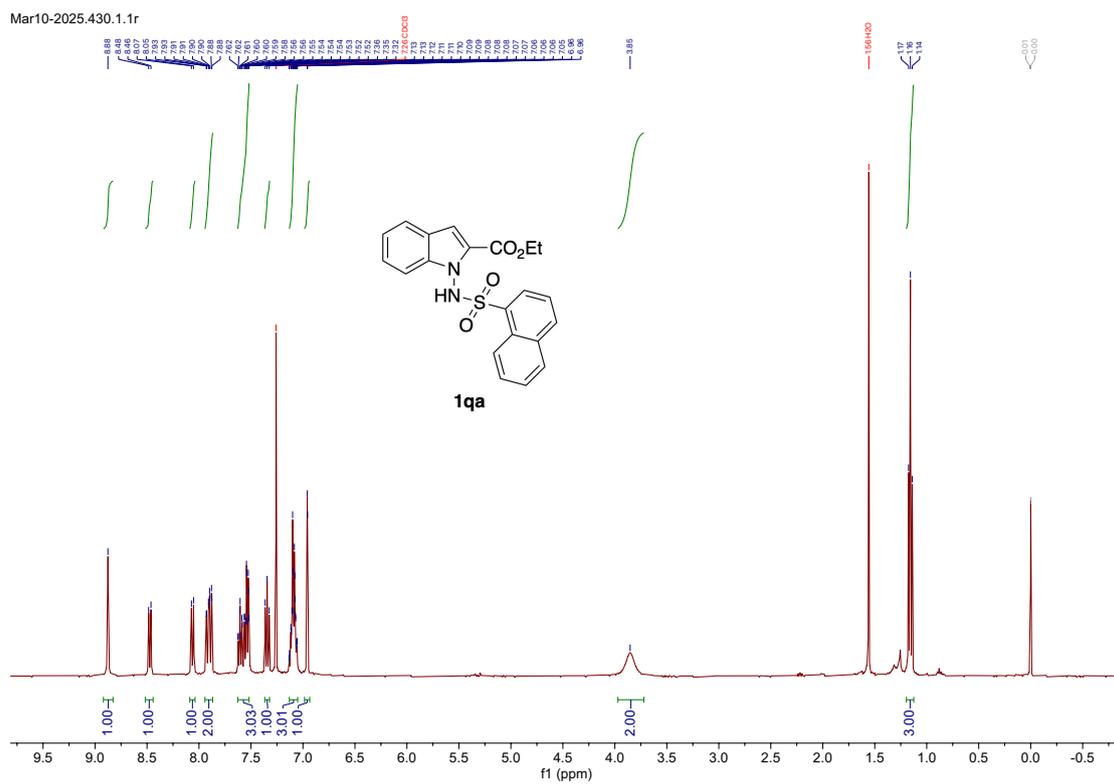
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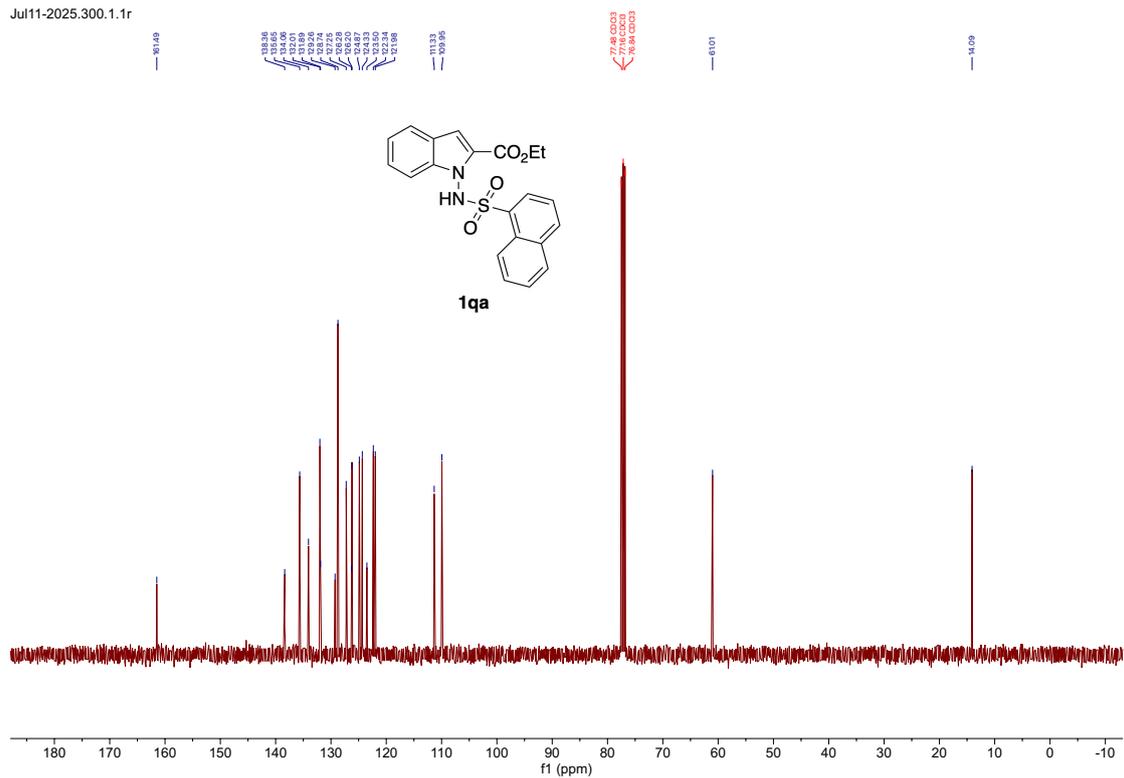
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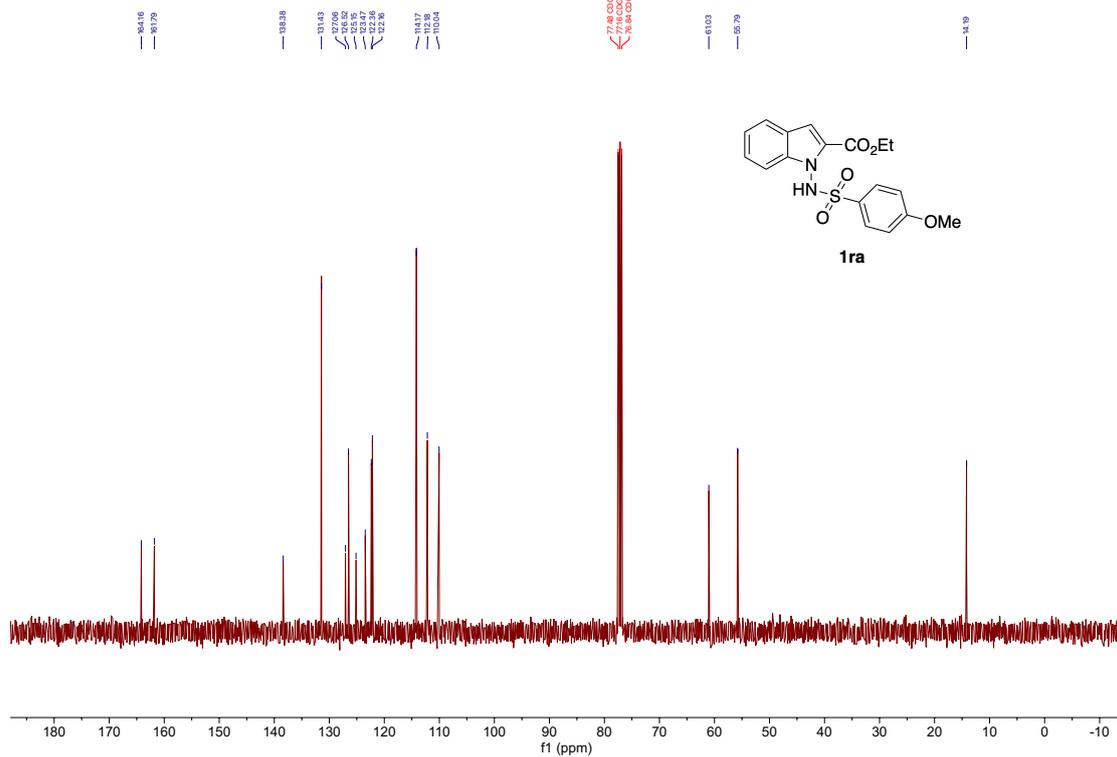
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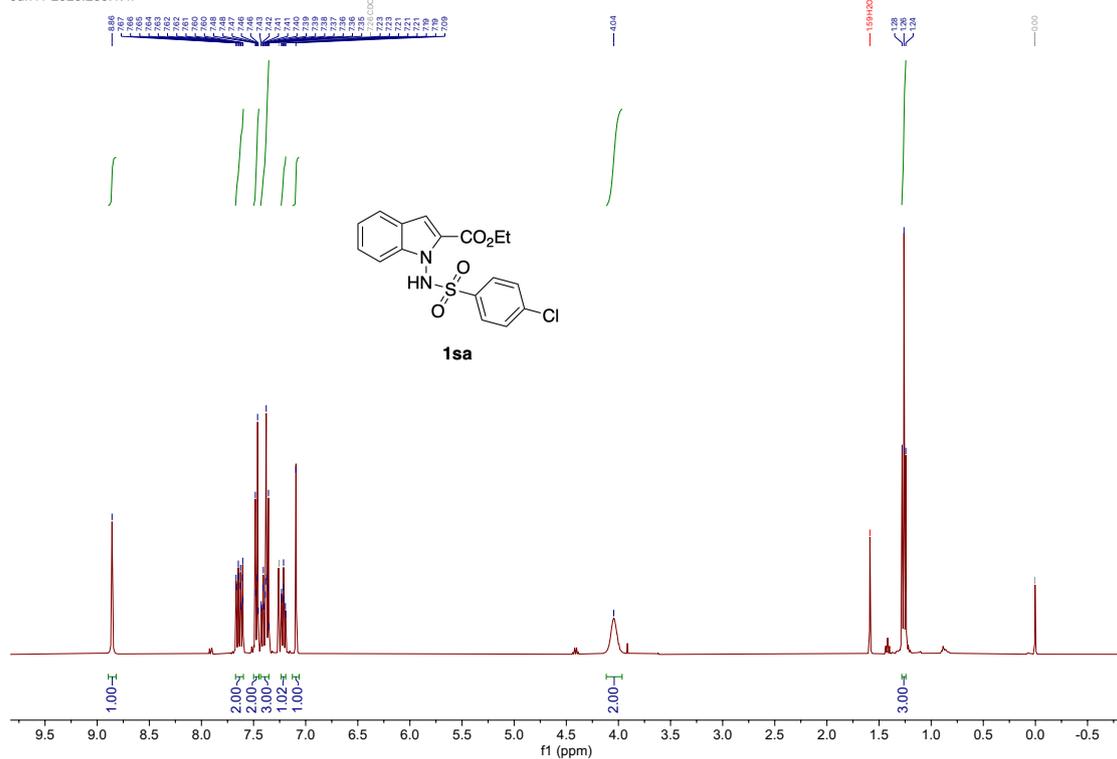
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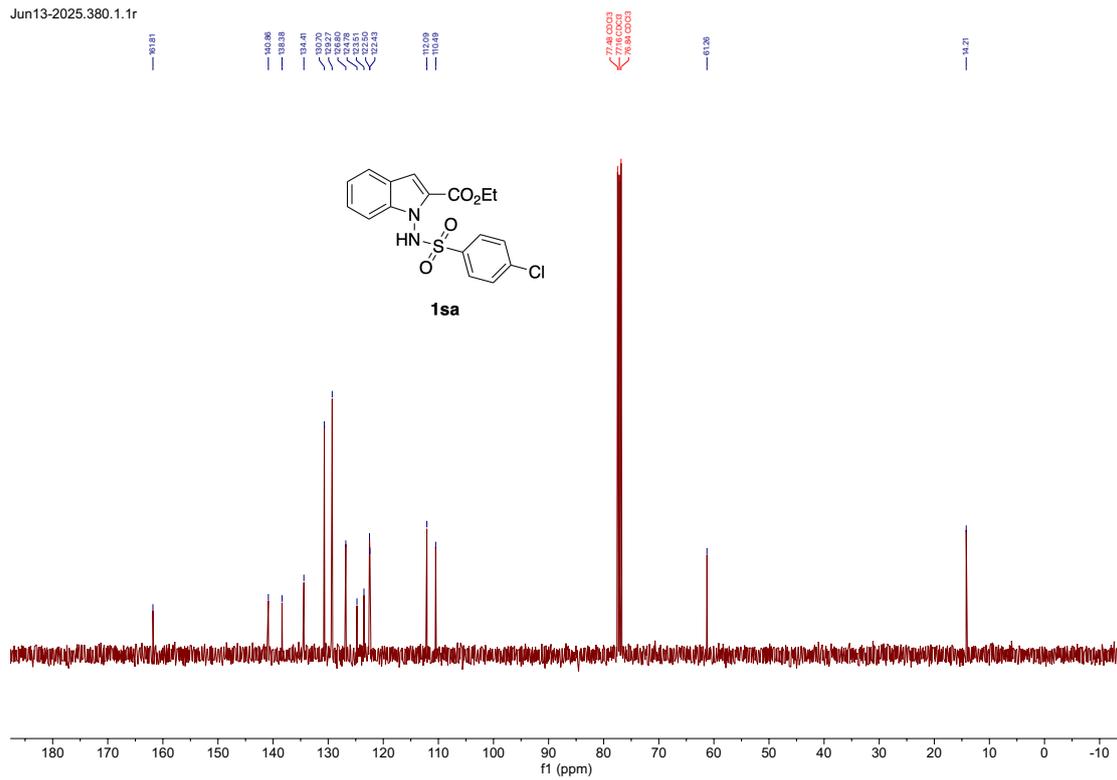
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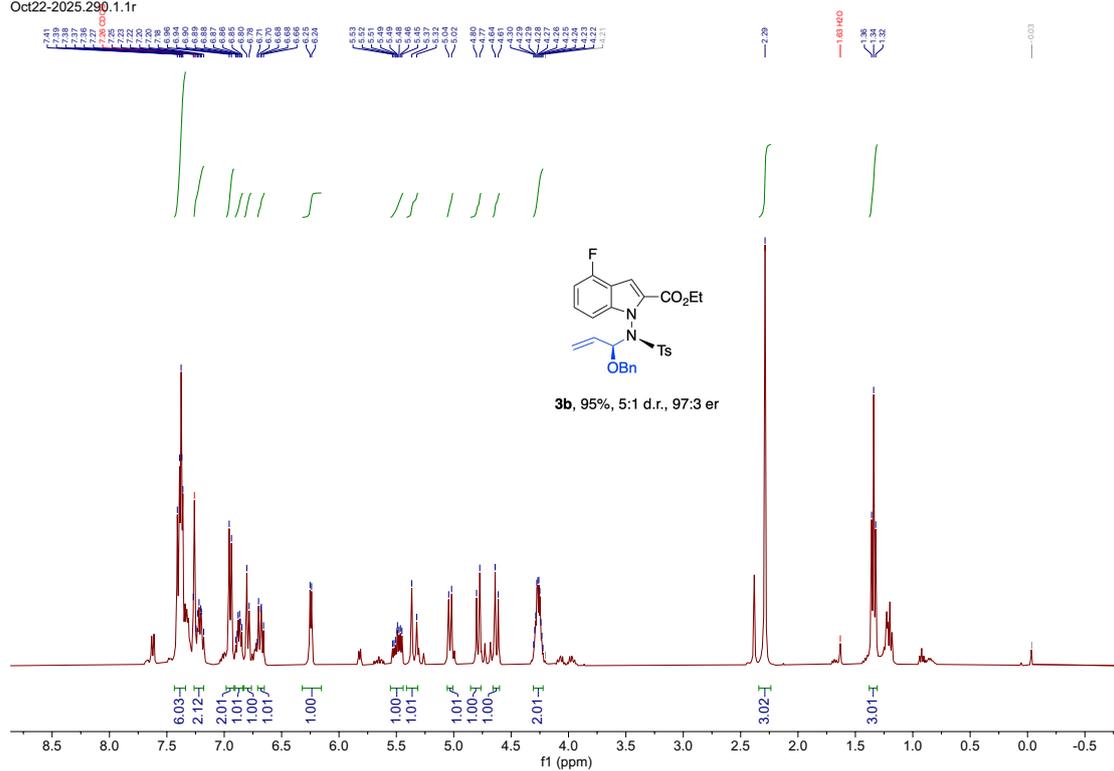
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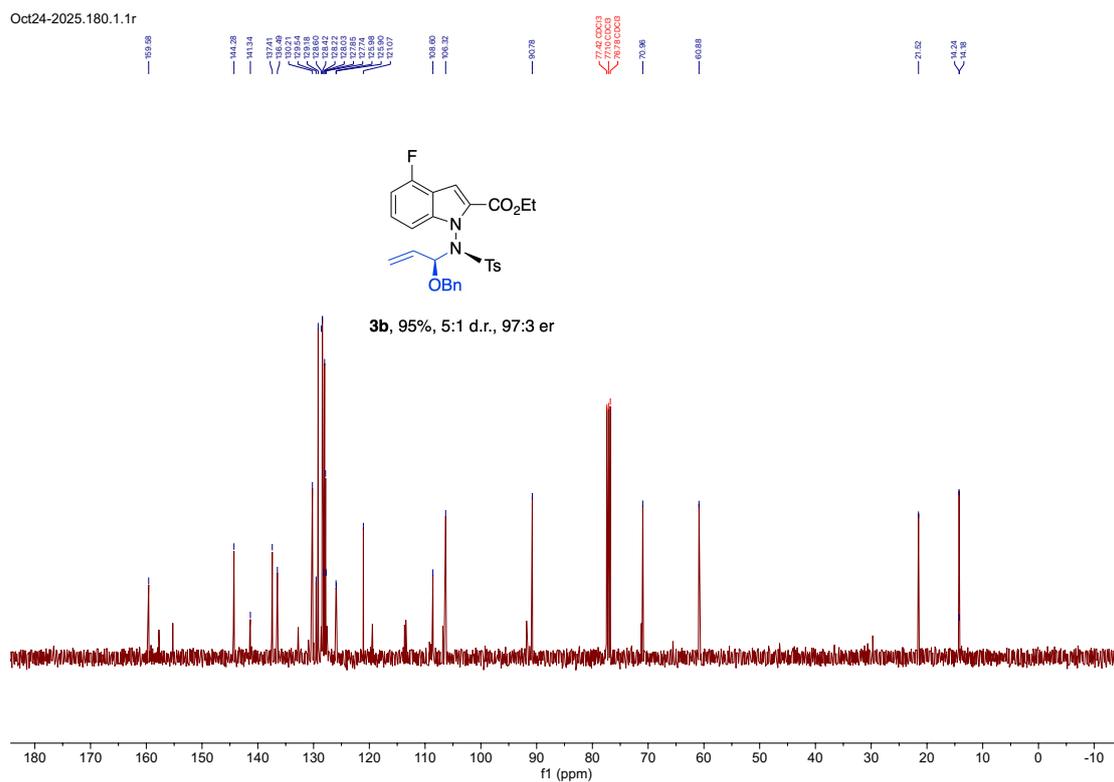
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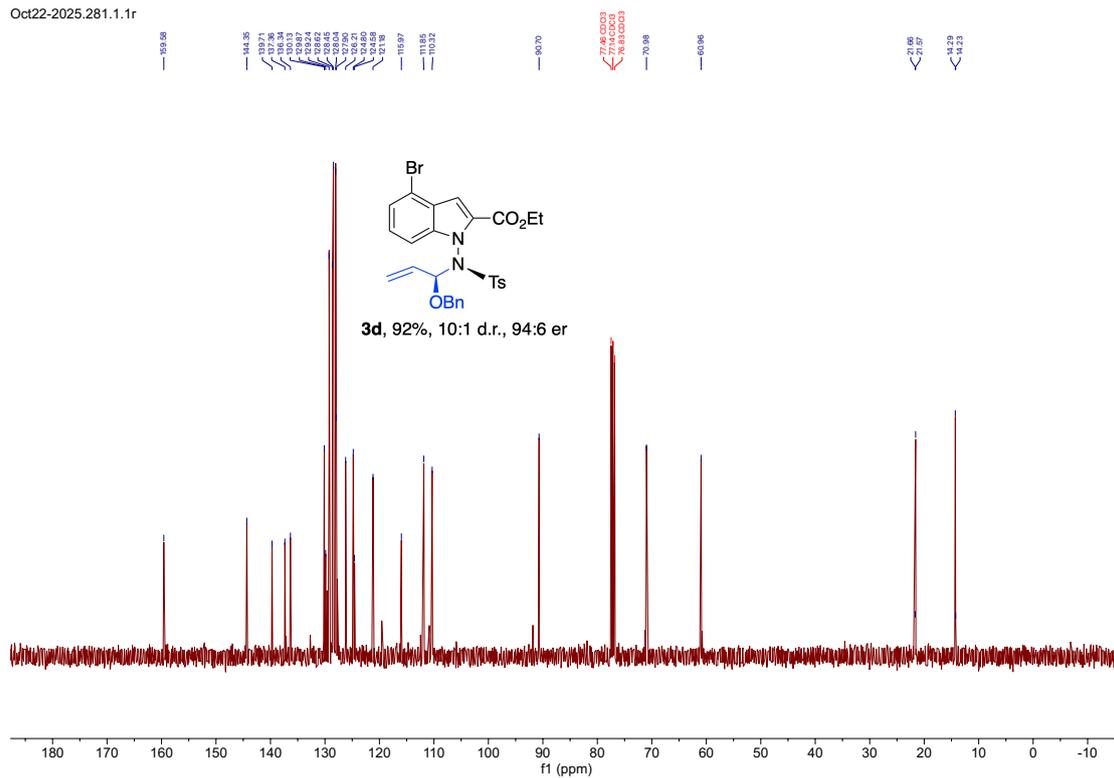
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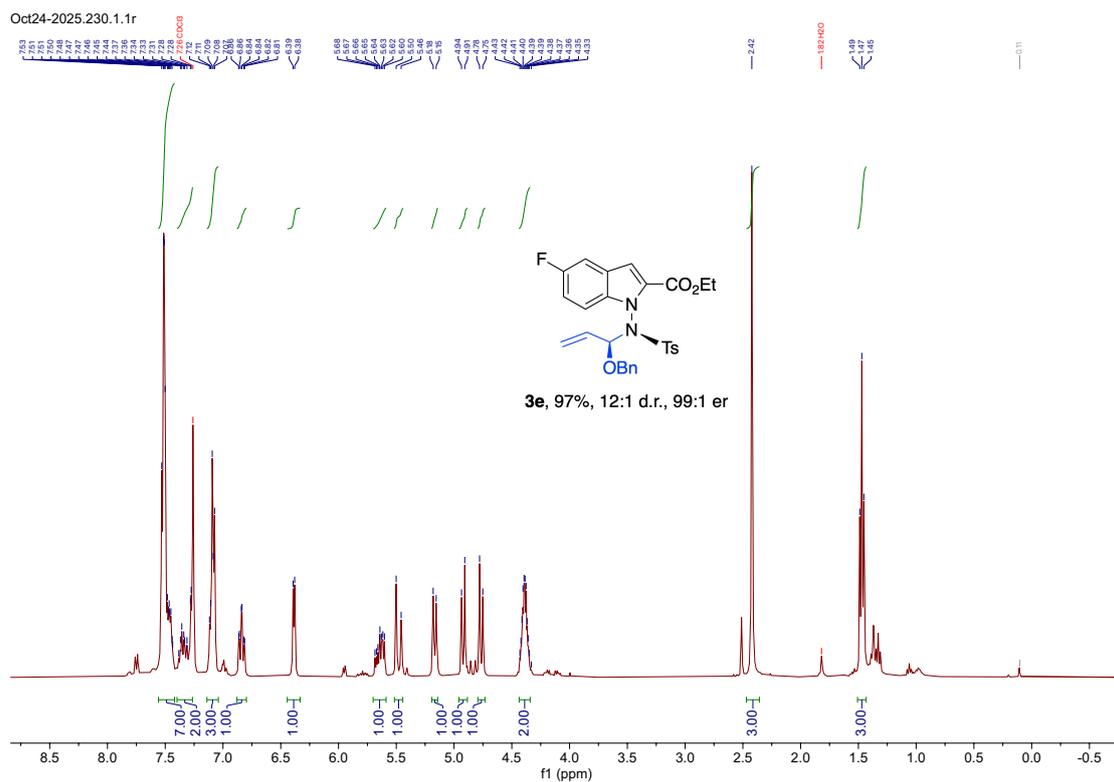
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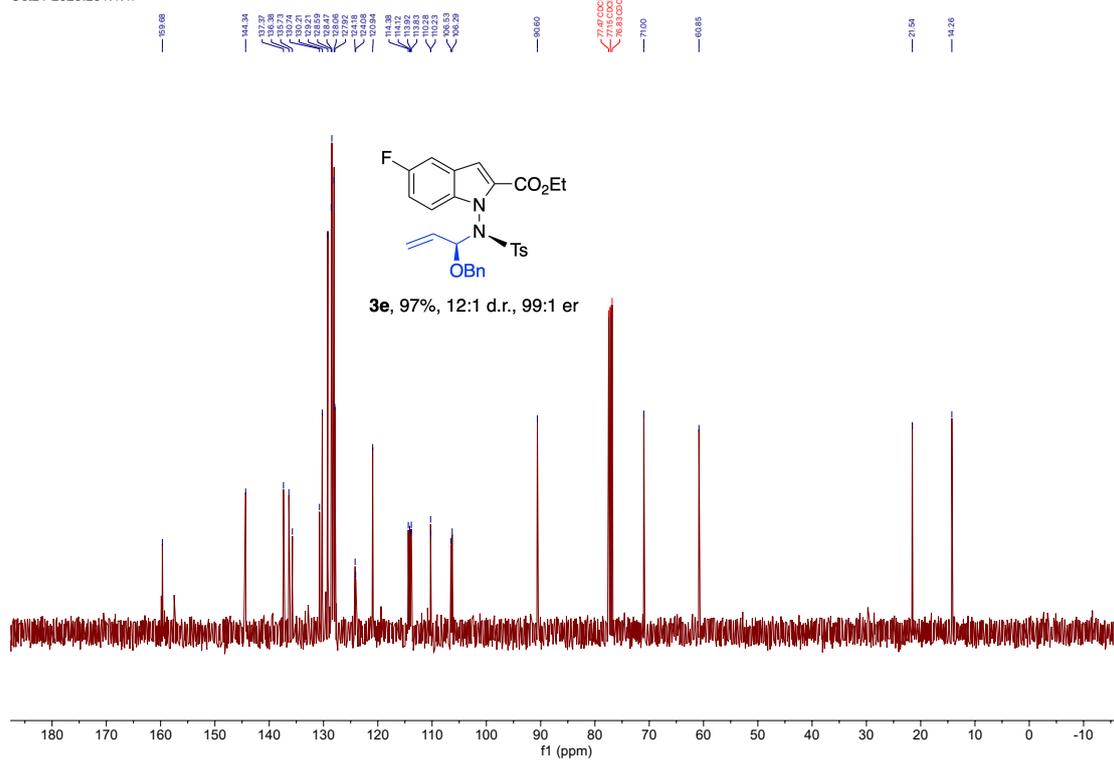
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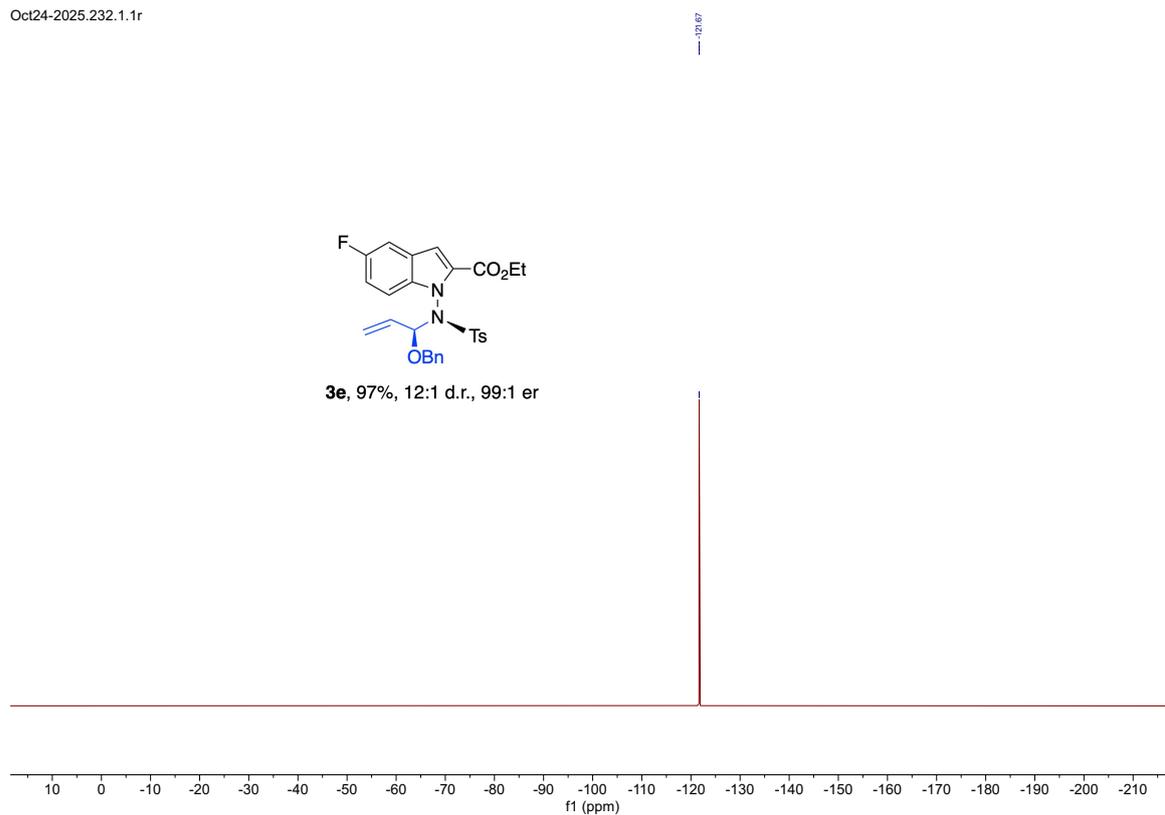
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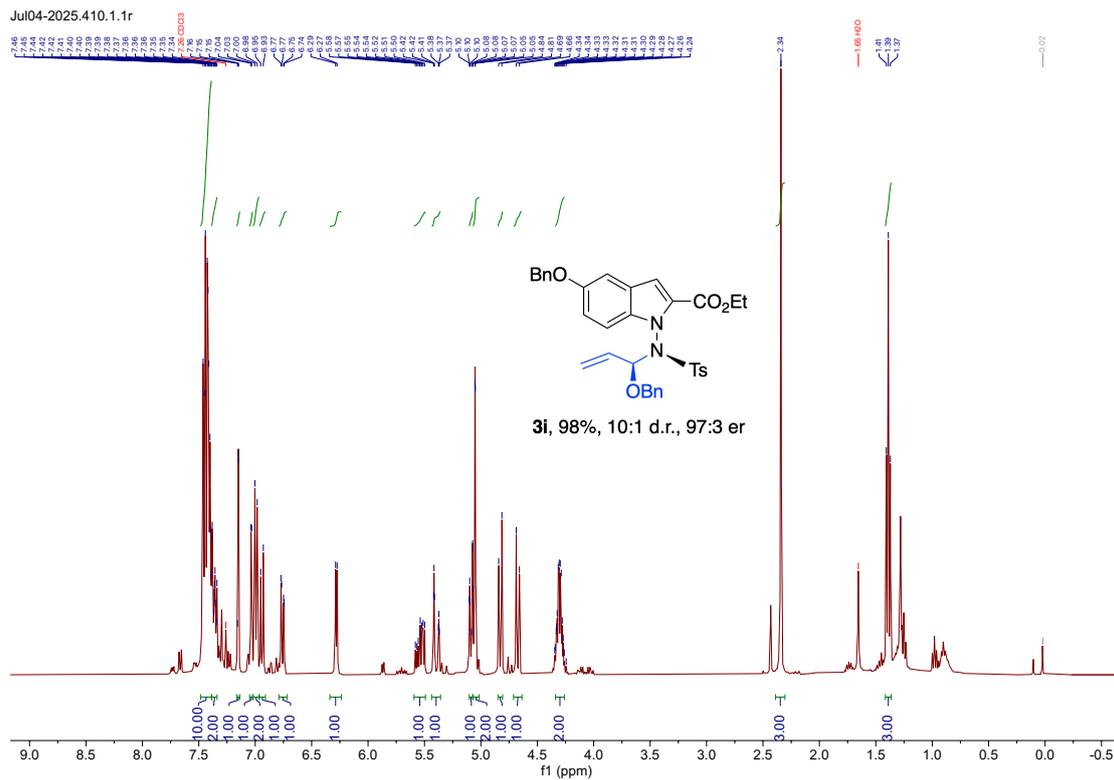
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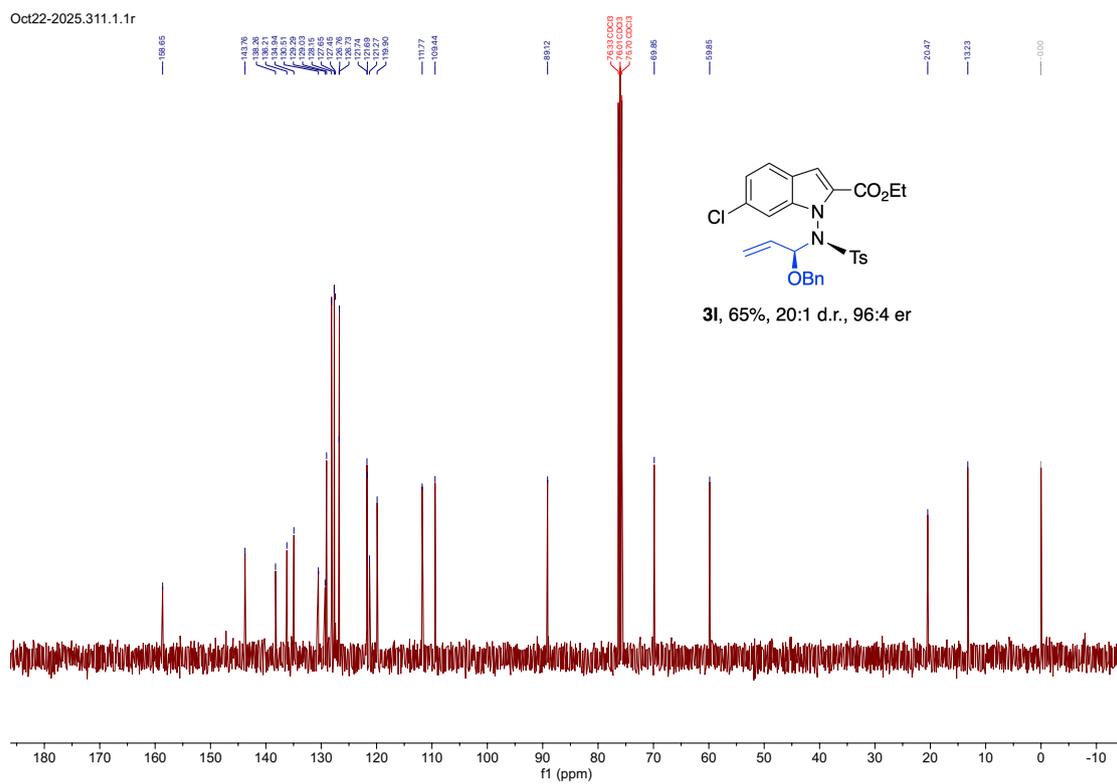
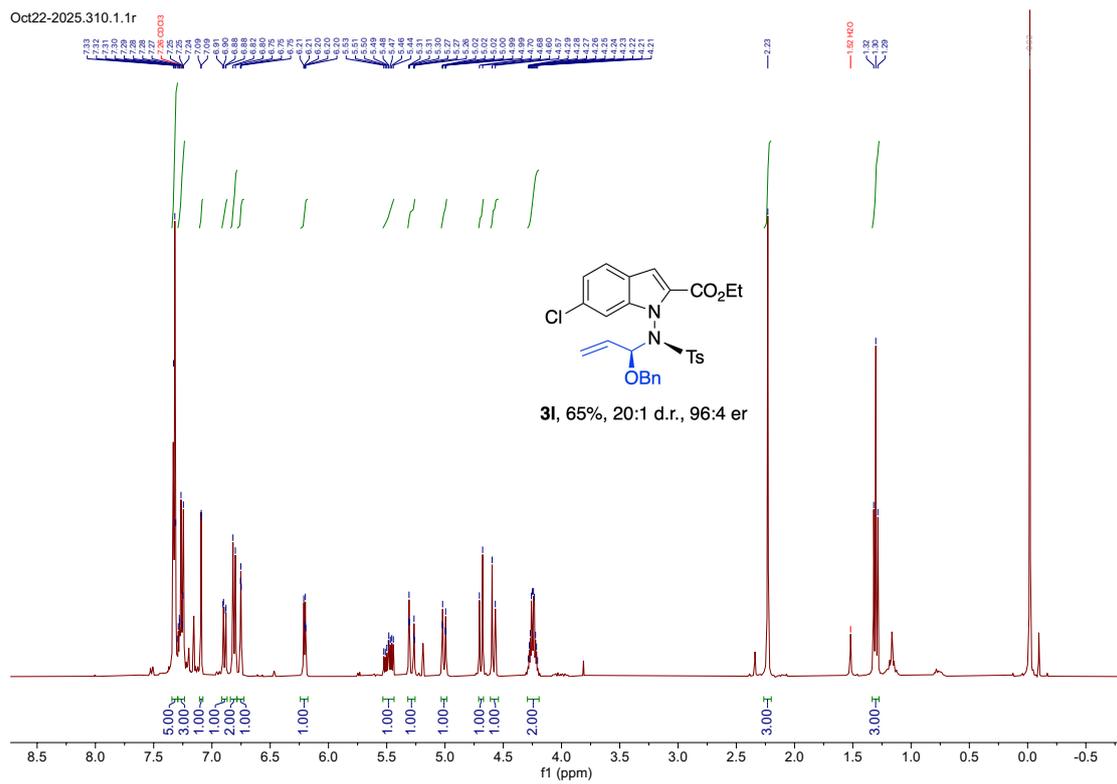


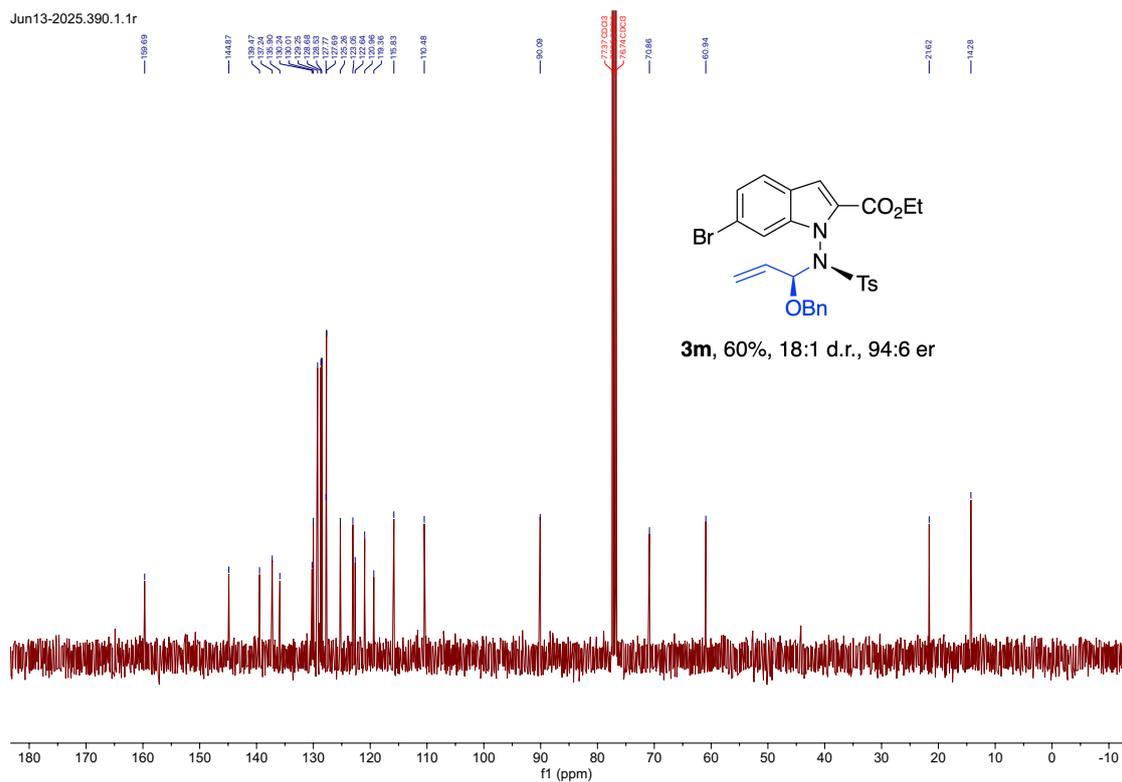
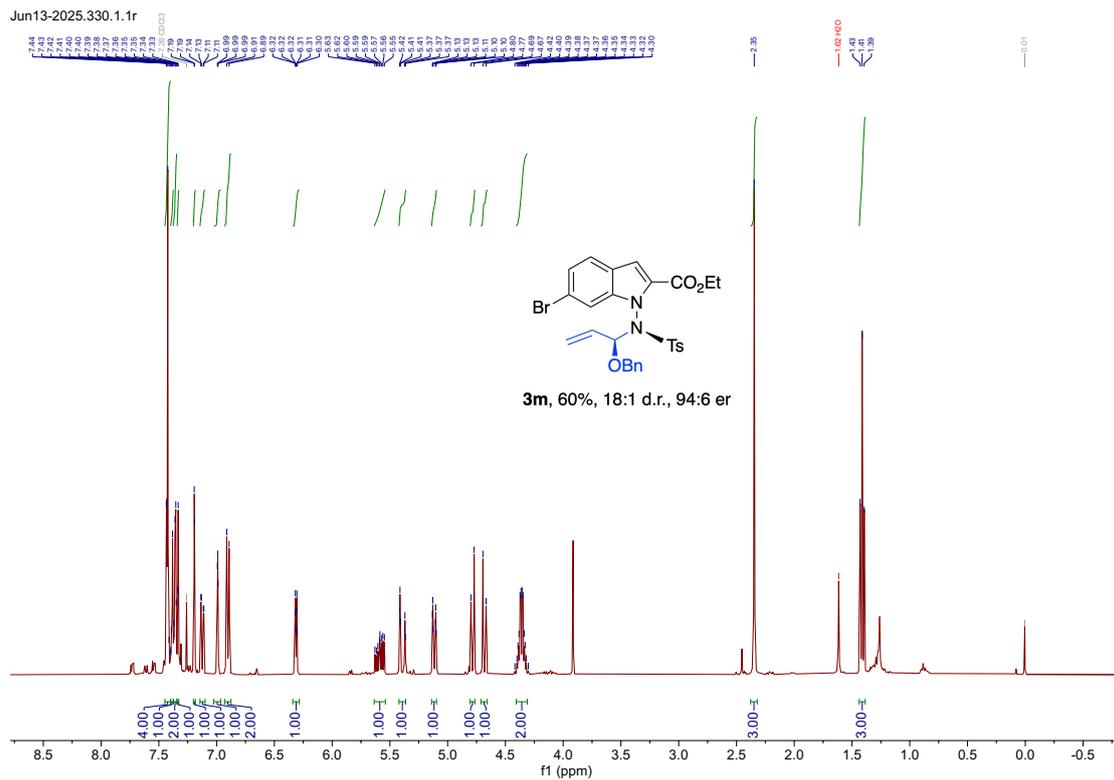
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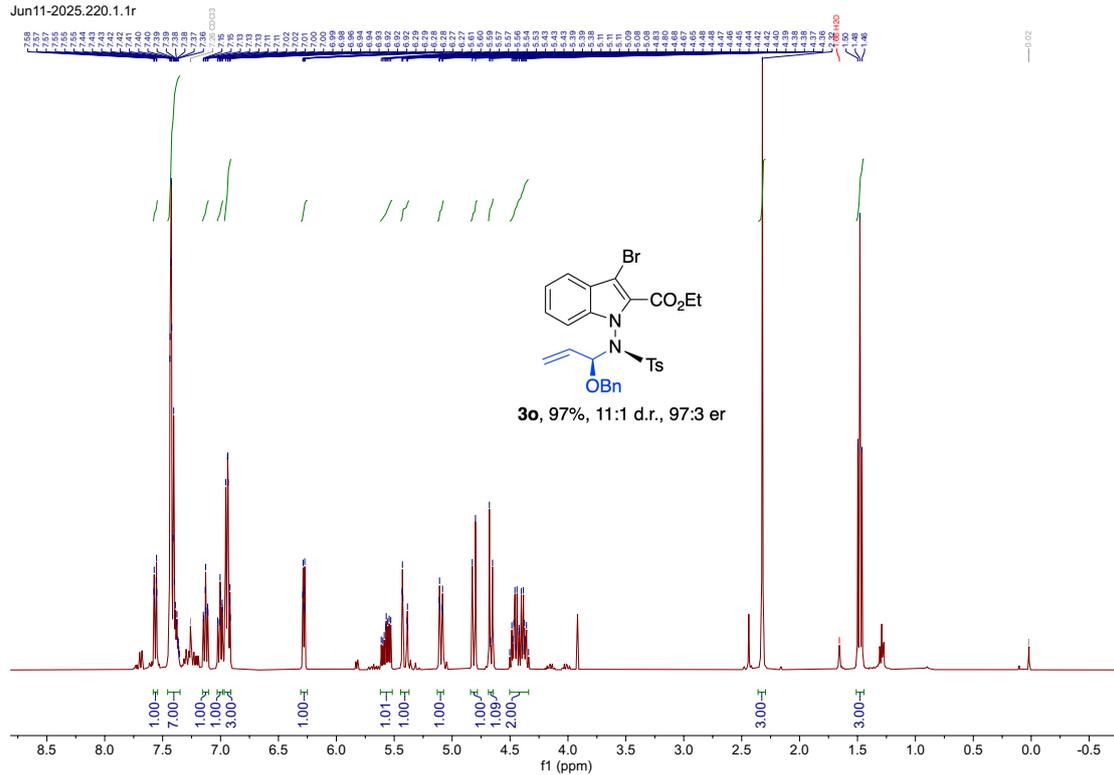
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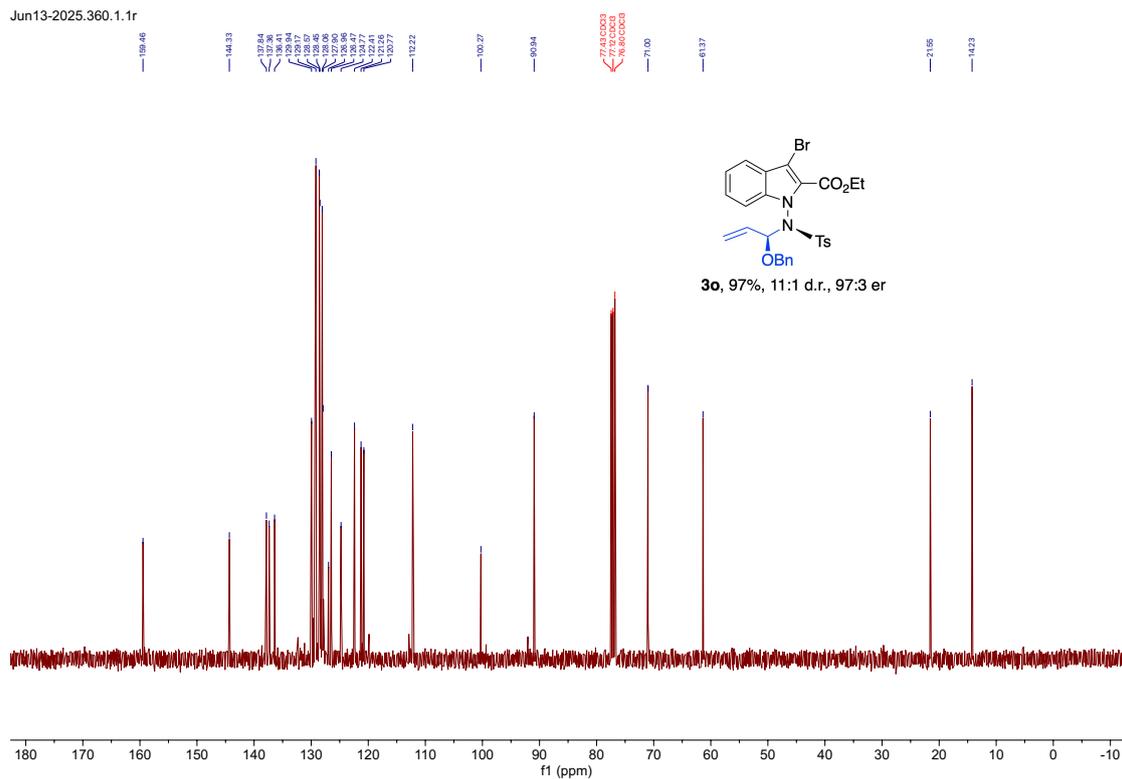


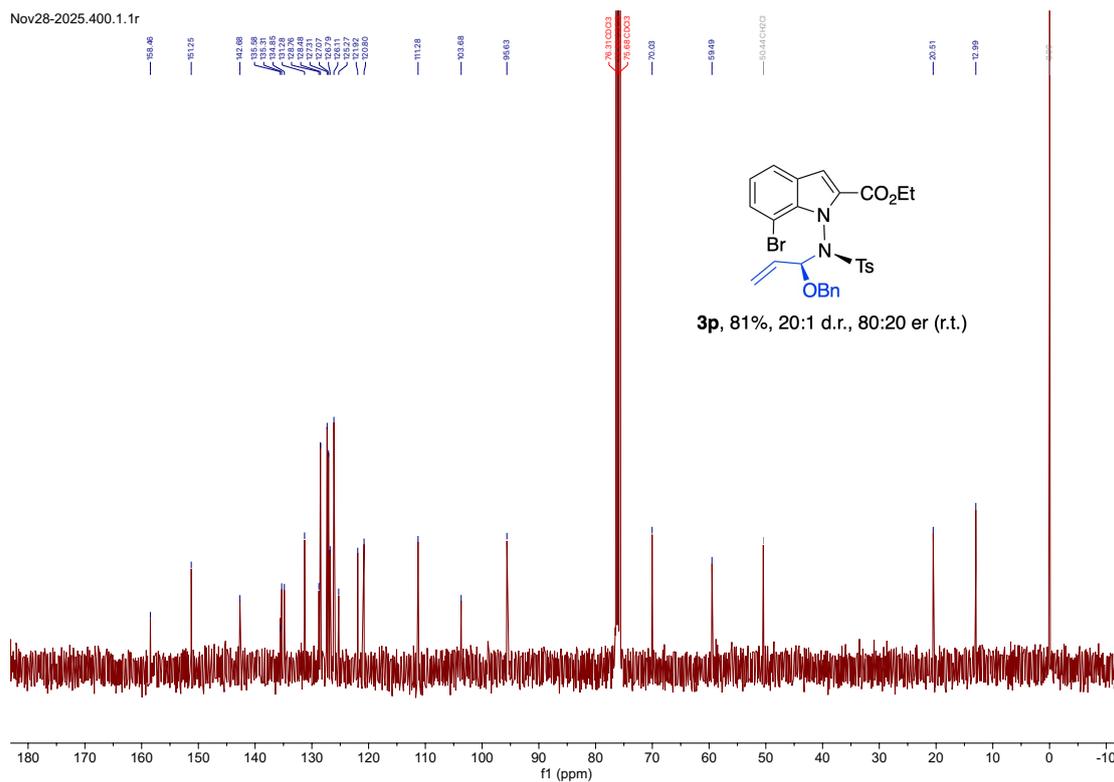
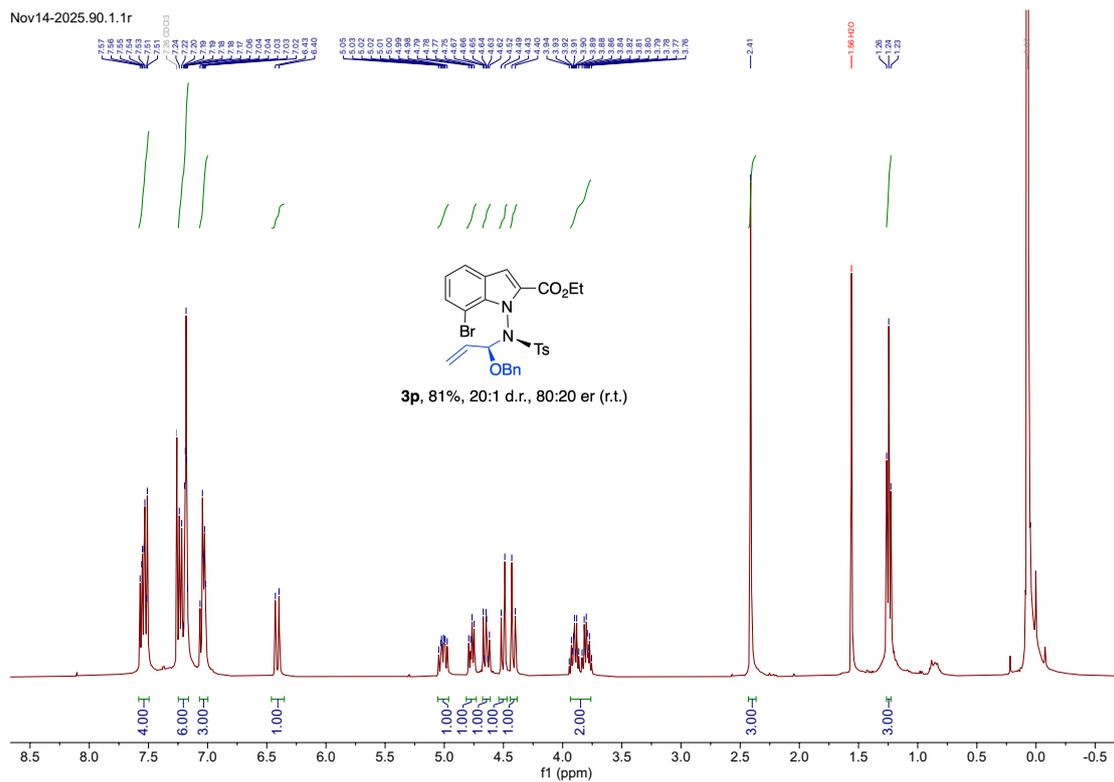


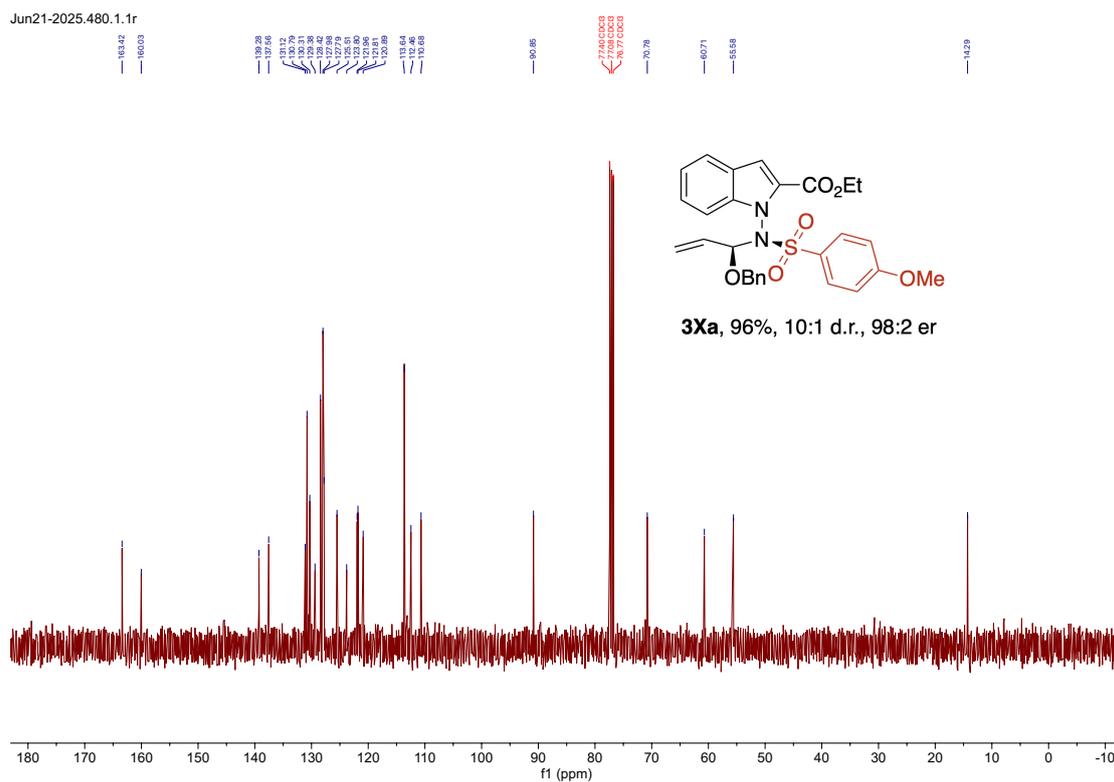
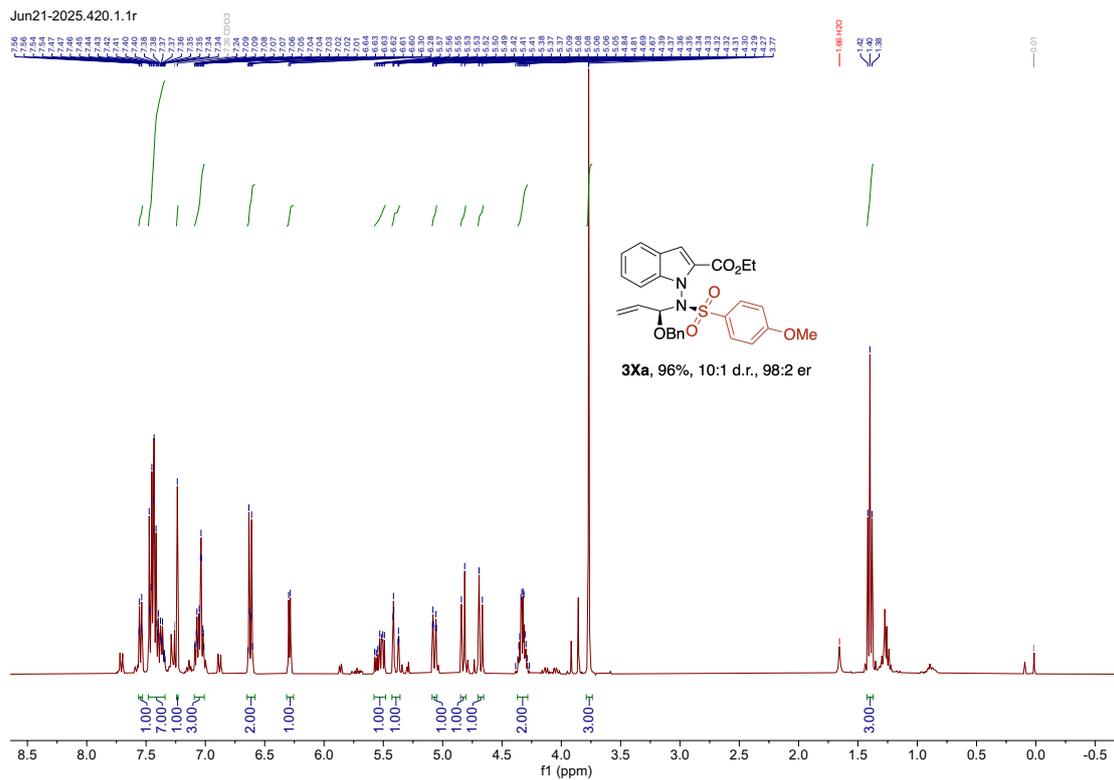
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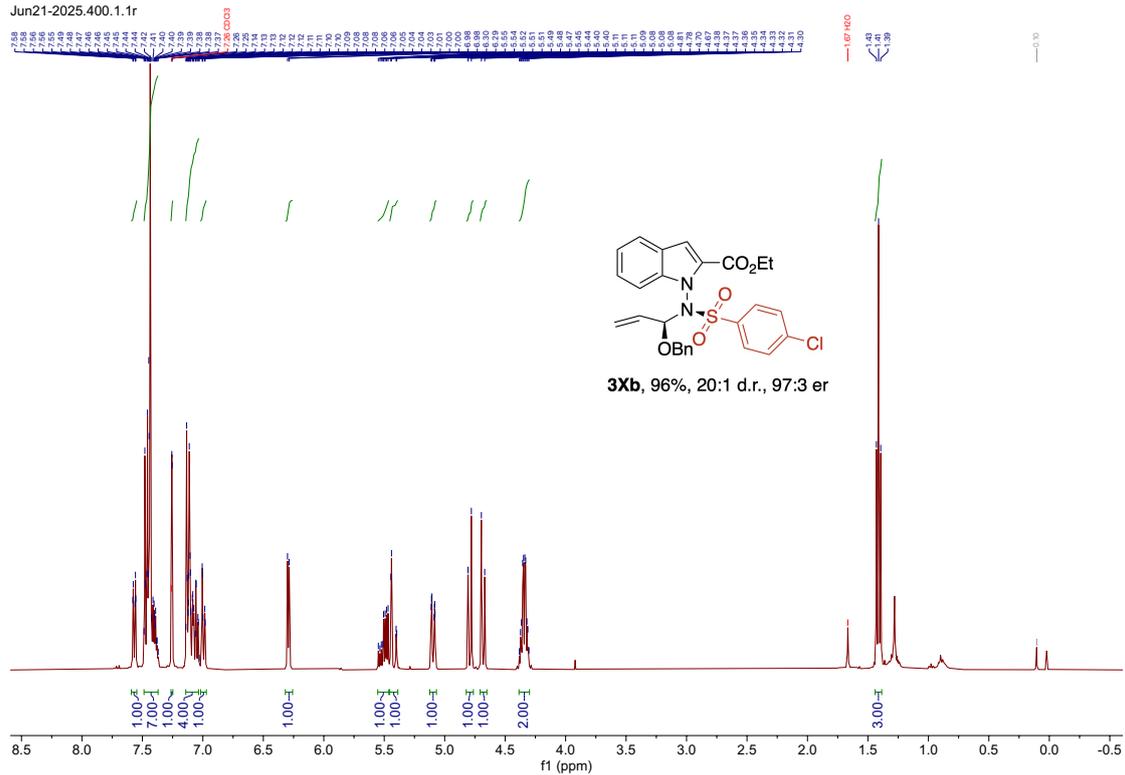
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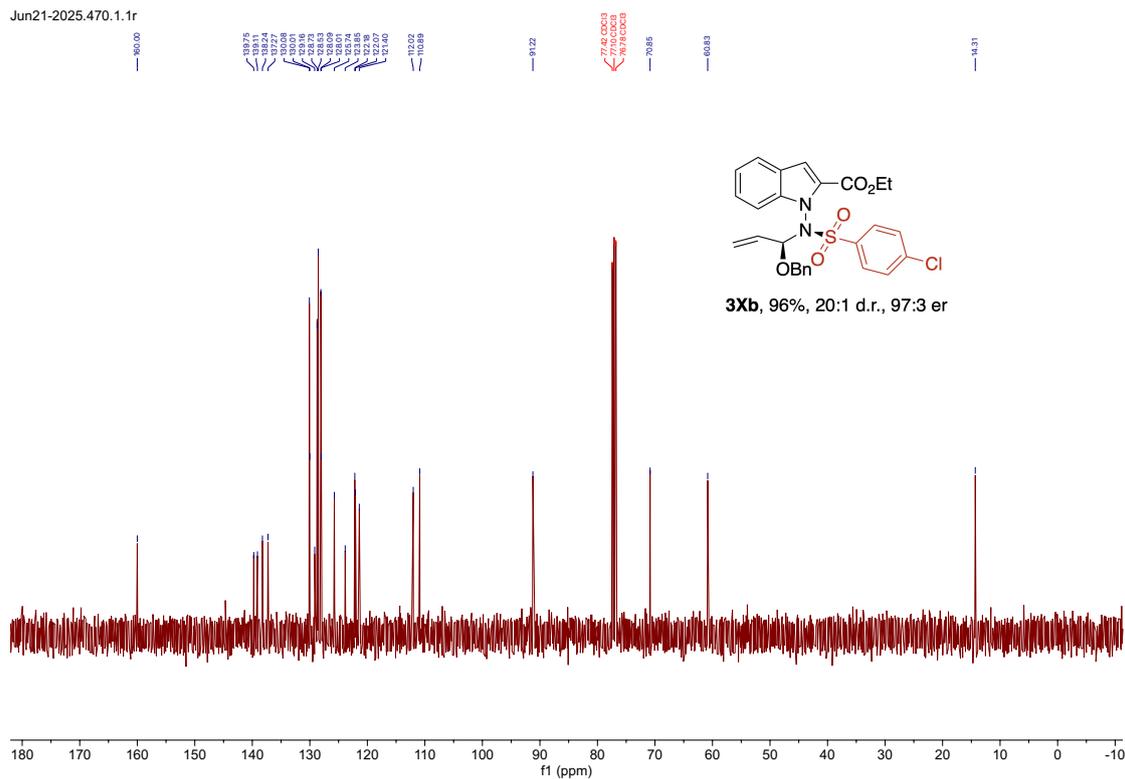




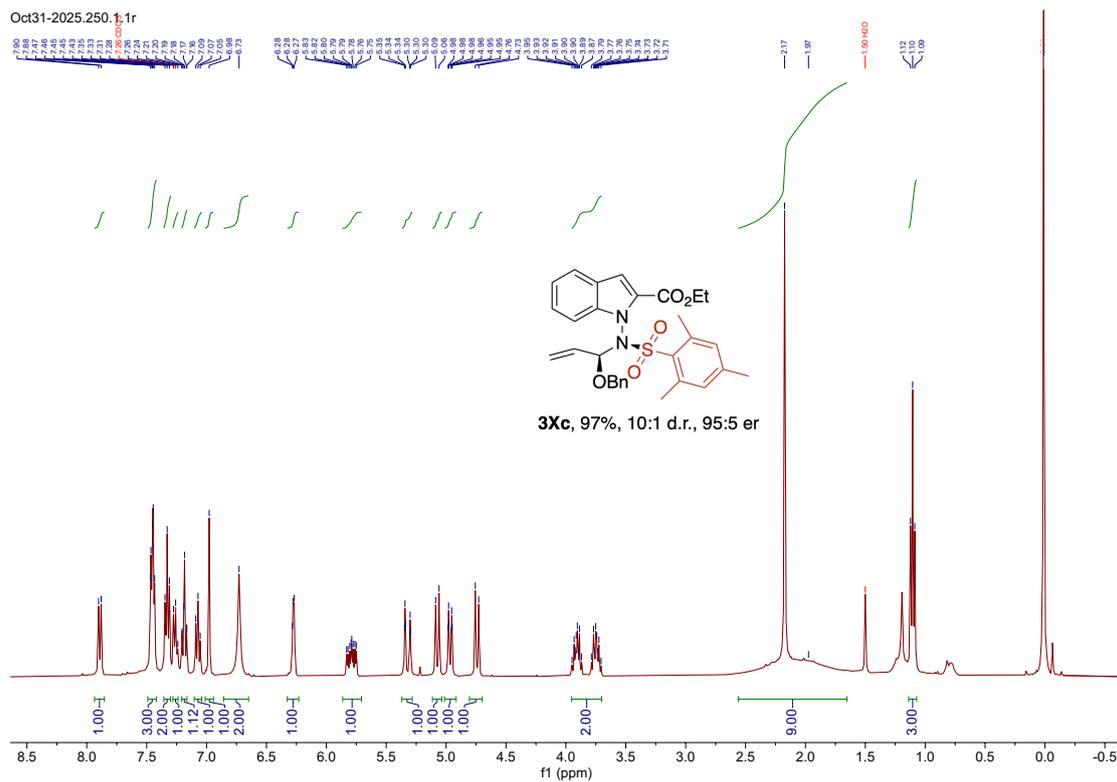
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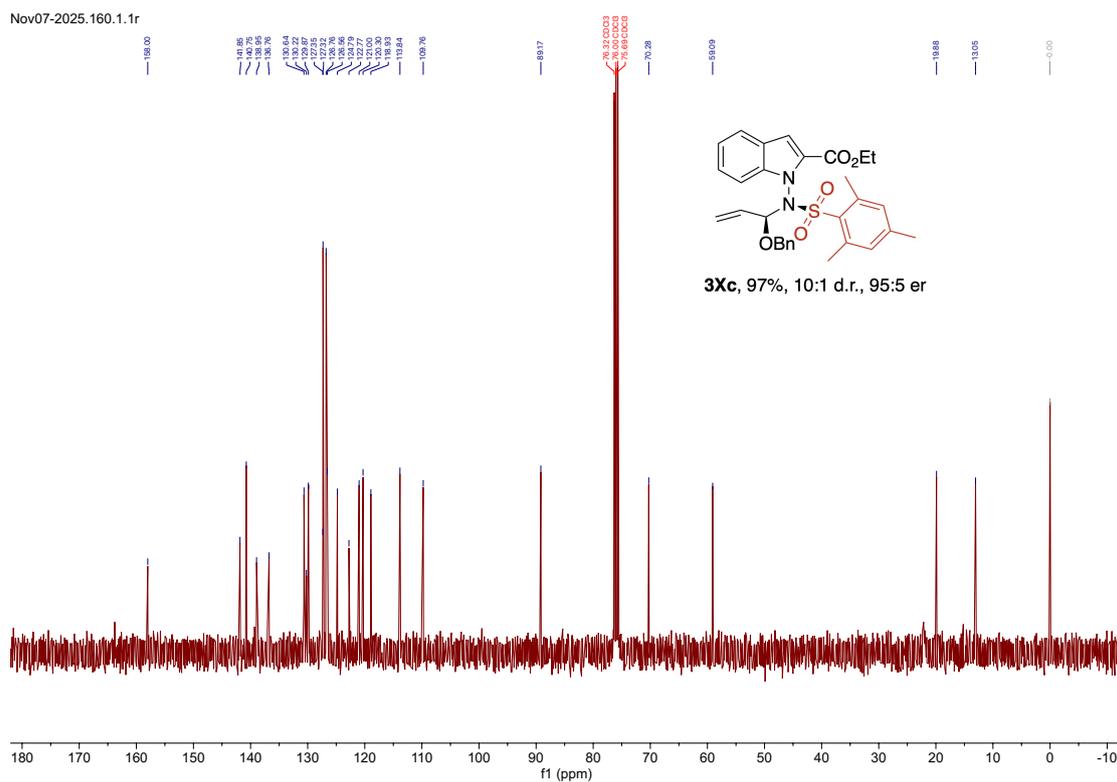
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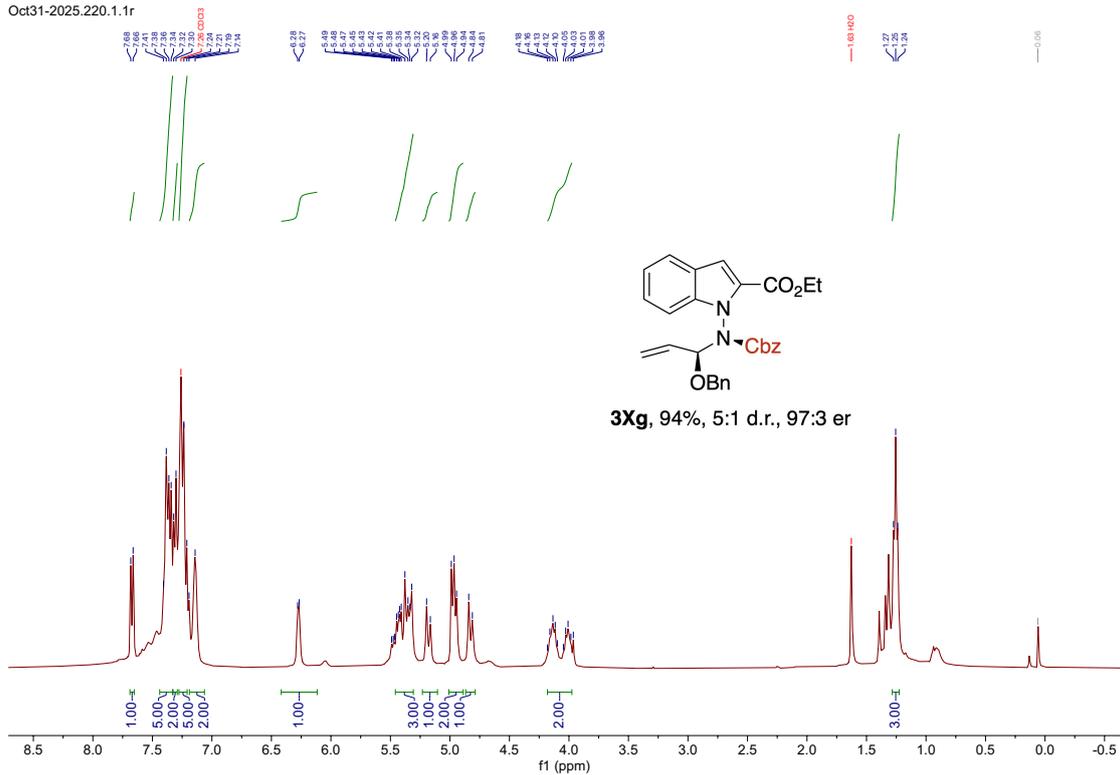
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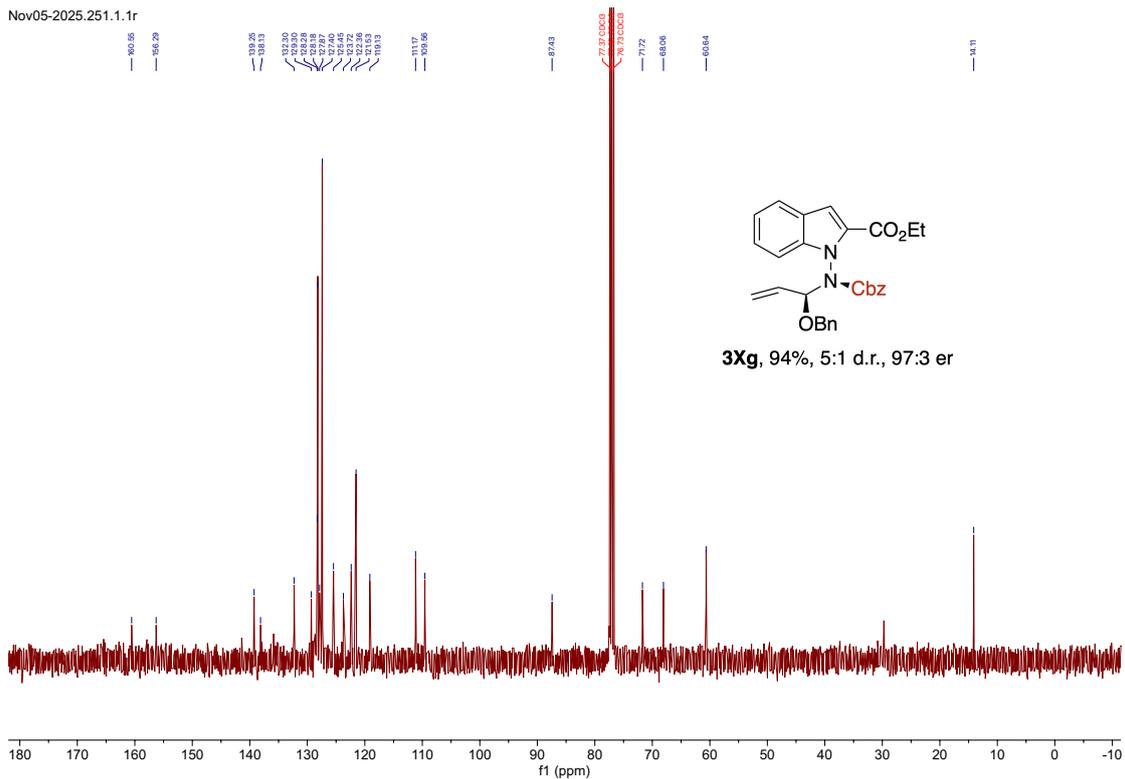
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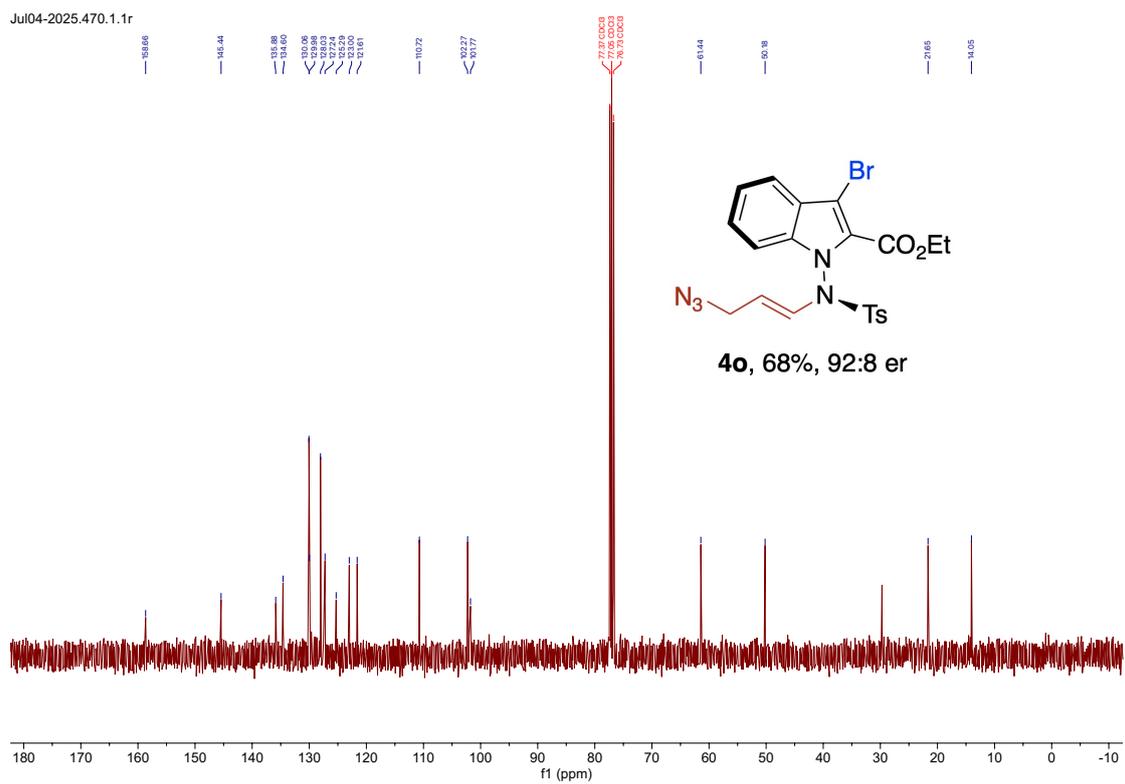
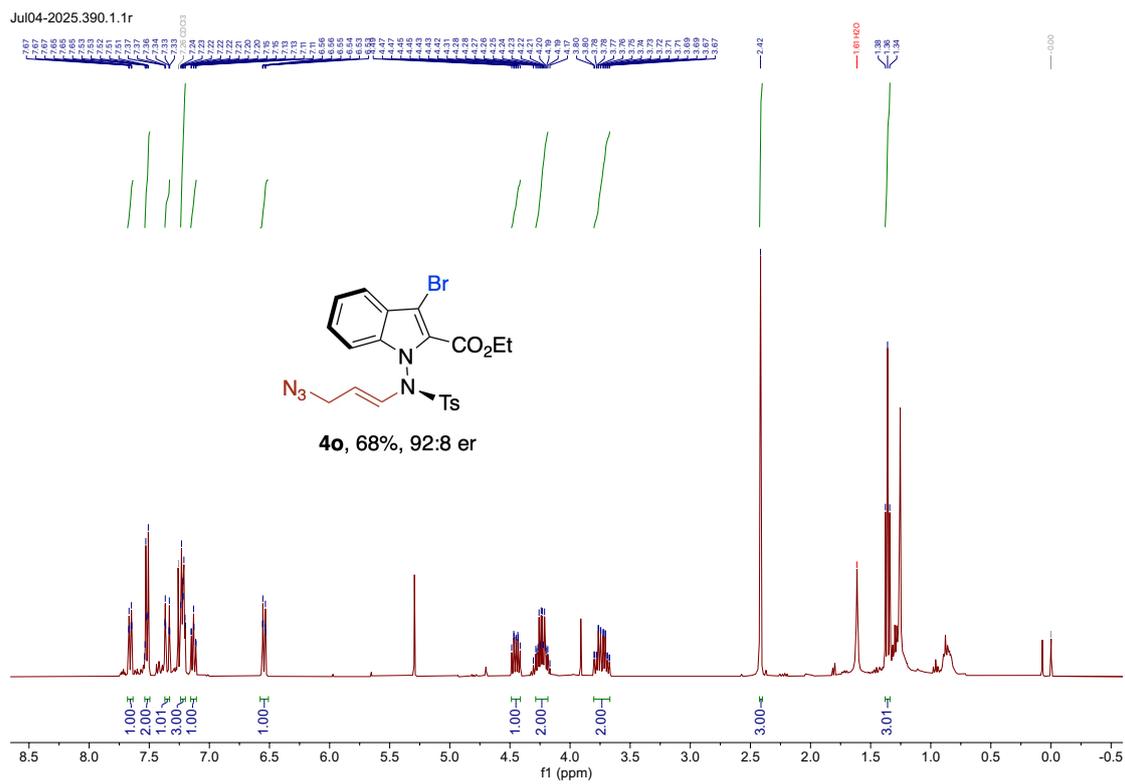


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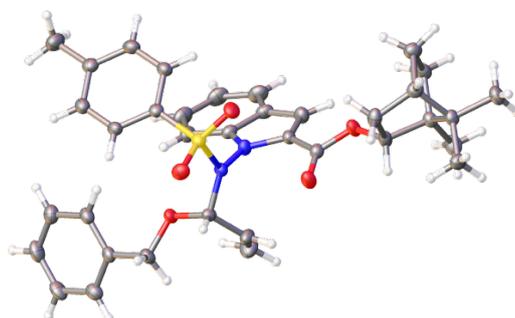


Nov05-2025.251.1.1r





13.X-ray Crystallography of 3Yc



CCDC 2512096

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/>.

Crystal data and structure refinement for CCDC 2512096 (3Yc).

Identification code	1
Empirical formula	C ₃₆ H ₄₀ N ₂ O ₅ S
Formula weight	612.76
Temperature/K	120.00
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	10.589(3)
b/Å	14.436(4)
c/Å	21.145(7)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3232.5(17)
Z	4
ρ _{calc} /cm ³	1.259
μ/mm ⁻¹	0.145
F(000)	1304.0
Crystal size/mm ³	0.5 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.302 to 53.324
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -26 ≤ l ≤ 26
Reflections collected	64551
Independent reflections	6788 [R _{int} = 0.1054, R _{sigma} = 0.0515]
Data/restraints/parameters	6788/0/409
Goodness-of-fit on F ²	1.042
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0415, wR ₂ = 0.0946
Final R indexes [all data]	R ₁ = 0.0524, wR ₂ = 0.1015
Largest diff. peak/hole / e Å ⁻³	0.19/-0.35
Flack parameter	0.09(4)