

Electronic Supplementary Information

Catalytic Asymmetric 1,4-Type Friedel-Crafts (Hetero)Arylation of 1-Azadienes: Highly Enantioselective Synthesis of Chiral Hetero-Triarylmethanes

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1 General Information

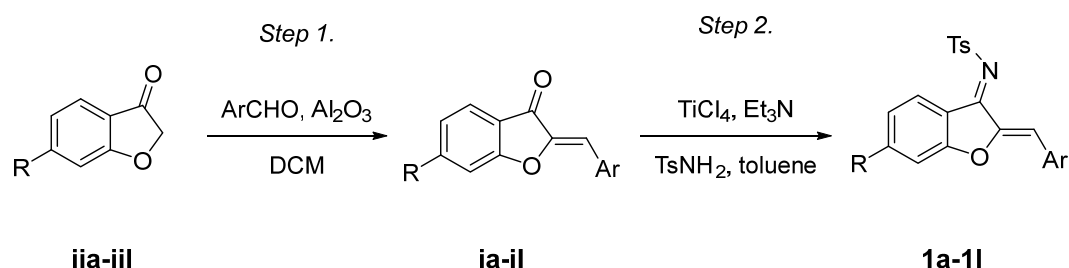
Unless otherwise specified, all reactions were carried out under argon atmosphere in anhydrous conditions. All the solvents were purified according to the standard procedures. All chemicals which are commercially available were used without further purification unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365nm).

^1H -NMR and ^{13}C -NMR spectra were recorded at 400 MHz or 600 MHz spectrophotometer. Chemical shifts (δ) are expressed in ppm, and J values are given in Hz. NMR multiplicities are abbreviated as follows: s = singlet, br = broad signal, d = doublet, t = triplet, q = quartet, m = multiple, dd = doublet of doublet. Values of enantiomeric excess was determined by chiral HPLC (Agilent 1260 Infinity) with *n*-hexane and *i*-propanol as eluents. High resolution mass spectrometry (HRMS) was recorded on an ESI-ion trap Mass spectrometer (Agilent 1100 series LC/MSD, SL model). Optical rotations were measured on a Jasco P-2000 polarimeter. All chemicals and solvents were used as received without further purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh).

2 General Procedure for the Preparation of Substrates

2.1 General Procedure for the Synthesis of Azadienes

According to the known procedures,^[1] benzofuran-fused 1-azadienes **1a-1l** were synthesized. According to the known procedures,^[1b,2] benzofuran-fused enones **ia-il** were synthesized.

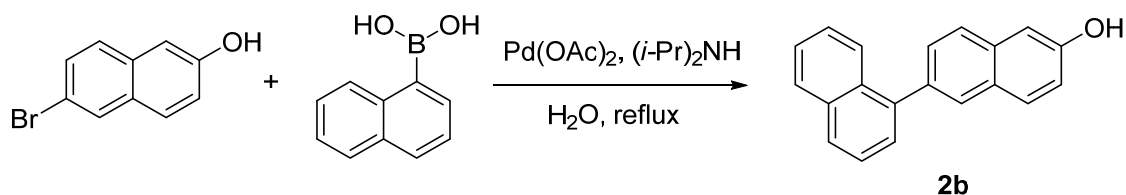


Step 1: Aluminium oxide (13.0g, activated, basic) was added to a solution of ketones **ii** (4 mmol) and aldehydes (8 mmol) in dichloromethane (30 mL). The mixture was violently stirred at room temperature under argon atmosphere. The progress of the reaction was monitored by TLC analysis. The suspension was filtered off, and the residue was washed with dichloromethane. Combined and concentrated the filtrates. The residue was purified by flash chromatography on silica gel to give enones **i**.

Step 2: 4-Methylbenzenesulfonamide (513 mg, 3.00 mmol) and heterocyclic enones **I** (3.00 mmol) were added in a round bottom flask in toluene (40 mL) and cooled to 0 °C. Then, Et₃N (0.84 mL, 6.0 mmol) and TiCl₄ (1.0 M in Toluene, 3.0 mL, 3.0 mmol) were successively added. The reaction mixture was heated to reflux for overnight. The solution was then cooled to room temperature, quenched with water (100 mL) and extracted with DCM (3 × 30 mL). The combined organic phase was dried over Na₂SO₄ and concentrated. The residue was purified by flash chromatography on silica gel to afford benzofuran-fused 1-azadienes **1**.

2.2 General Procedure for the Synthesis of β -Naphthol Derivatives

According to the known literature procedures,^[3] (6-naphthyl)- β -naphthols **2b** was synthesized. All the others β -naphthols were obtained from the commercially available.

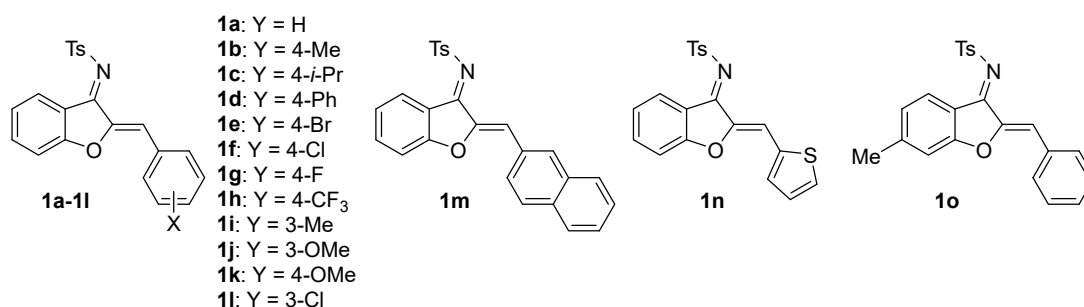


To a mixture of 6-bromonaphthalen-2-ol (1.1 g, 5 mmol, 1 eq.), 1-naphthylboronic acid (7.5 mmol, 1.5 eq.) and Pd(OAc)₂ (45 mg, 0.2 mmol, 0.04 eq.) in water (10 mL) was added diisopropylamine (1 mL). After heat to reflux for 10

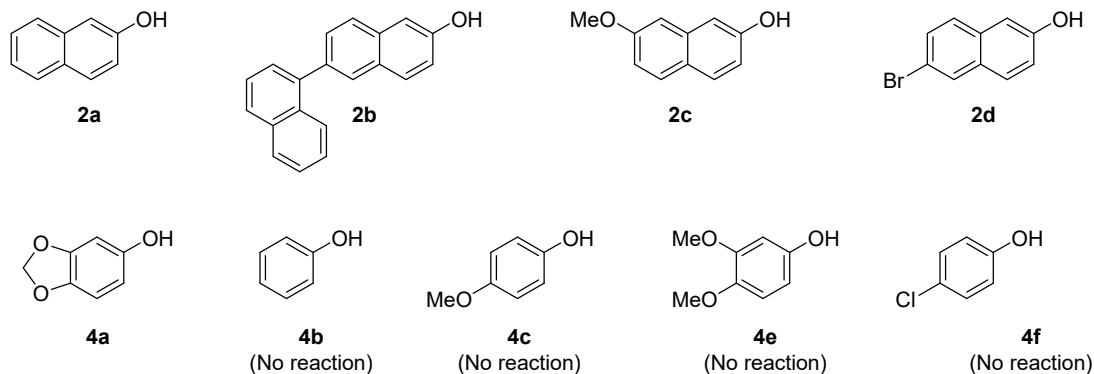
hours, the mixture was then filtered and washed with ethyl acetate (3×10 mL), The aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 , filtered and then concentrated. The residue was purified by silica gel column chromatograph (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product **2b**.

2.3 All Substrates for the Asymmetric Friedel-Crafts Reactions

(a) Substrates of Benzofuran fused 1-Azadienes



(b) Substrates of 2-Naphthols and phenols



(c) Substrates of Indoles

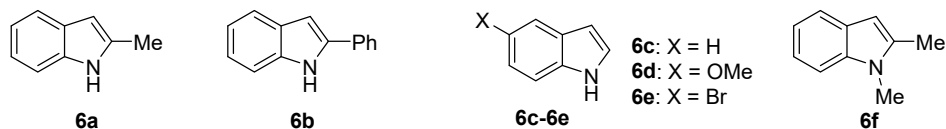


Figure S1. All the substrates employed in the asymmetric F-C reactions

3 Optimization of Asymmetric Catalytic Reactions

3.1 Asymmetric Friedel-Crafts Arylation of Azadienes and β -Naphthol

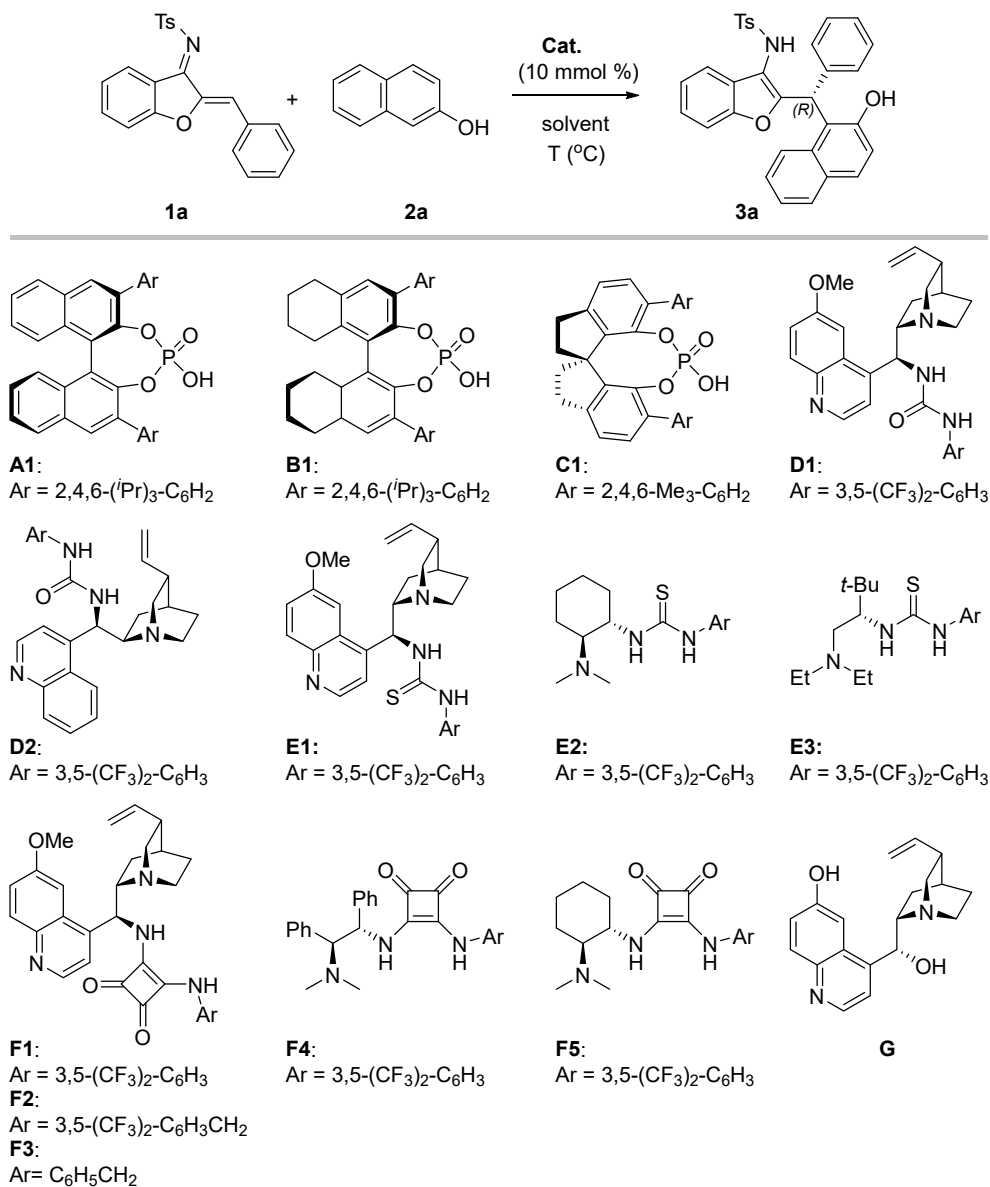


Table S1. Optimization of Friedel-Crafts Arylation of Azadienes **1a** and β -Naphthol **2a** ^a

Entry	Cat	Solvent	T (°C)	<i>t</i> (h)	Yield (%) ^b	Ee (%) ^c
1	A1	toluene	20	6	61	3 (<i>R</i>)
2	B1	toluene	20	48	48	3 (<i>S</i>)
3	C1	toluene	20	24	45	52 (<i>S</i>)

4	D1	toluene	20	18	93	85 (<i>R</i>)
5	D2	toluene	20	18	88	85 (<i>S</i>)
6	E1	toluene	20	18	88	85 (<i>R</i>)
7	E2	toluene	20	24	76	70 (<i>R</i>)
8	E3	toluene	20	24	71	38 (<i>R</i>)
9	F1	toluene	20	4	88	80 (<i>R</i>)
10	F2	toluene	20	48	87	75 (<i>R</i>)
11	F3	toluene	20	24	77	41 (<i>S</i>)
12	F4	toluene	20	48	trace	/
13	F5	toluene	20	18	89	72 (<i>R</i>)
14	G	toluene	20	6	67	21 (<i>R</i>)
15	D1	MeOH	20	72	60	0
16	D1	THF	20	48	36	17 (<i>R</i>)
17	D1	MeCN	20	48	16	65 (<i>R</i>)
18	D1	Et ₂ O	20	48	48	71 (<i>R</i>)
19	D1	CH ₂ Cl ₂	20	12	97	87 (<i>R</i>)
20	D1	(CH ₂ Cl) ₂	20	12	79	86 (<i>R</i>)
21	D1	CHCl ₃	20	18	84	87 (<i>R</i>)
22	D1	PhCF ₃	20	18	85	87 (<i>R</i>)
23	D1	toluene	-40	30	95	93 (<i>R</i>)
24	D1	toluene	-30	21	89	92 (<i>R</i>)
25	D1	toluene	-20	20	90	90 (<i>R</i>)
26	D1	CH ₂ Cl ₂	-40	48	68	42 (<i>R</i>)
27	D1	CH ₂ Cl ₂	-30	21	80	79 (<i>R</i>)
28	D1	CH ₂ Cl ₂	-20	20	80	82 (<i>R</i>)
30	D1	CH ₂ Cl ₂	40	12	86	86 (<i>R</i>)

^aUnless otherwise specified, the reaction was conducted with **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (10 mmol %) in the indicated solvent (2 mL). ^bYield of isolated product. ^cDetermined by HPLC.

3.2 Asymmetric Friedel-Crafts Heteroarylation of Azadienes and 2-Me Substituted Indoles

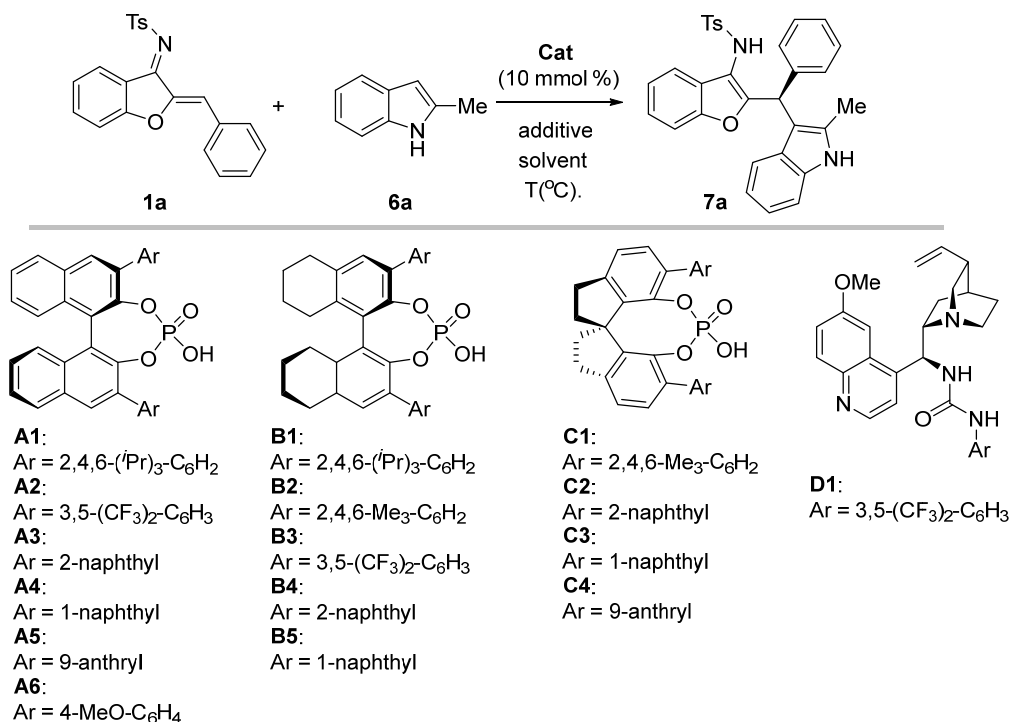


Table S2. Optimization of Friedel-Crafts Heteroarylation of Azadienes **1a** and 2-Me substituted indole **6a** ^a

Entry	Cat	additive	Solvent	T (°C)	<i>t</i>	Yield (%) ^b	ee (%) ^c
1	D1	/	toluene	20	24 h	45	40 (<i>S</i>)
2	A1	/	toluene	20	2 h	94	53 (<i>S</i>)
3	A2	/	toluene	20	10 min	96	32 (<i>S</i>)
4	A3	/	toluene	20	2 h	96	3 (<i>R</i>)
5	A4	/	toluene	20	10 min	97	13 (<i>R</i>)
6	A5	/	toluene	20	10 min	98	3 (<i>S</i>)
7	A6	/	toluene	20	10 min	93	20 (<i>R</i>)
8	B1	/	toluene	20	1 h	98	73 (<i>S</i>)
9	B2	/	toluene	20	10 min	96	53 (<i>S</i>)
10	B3	/	toluene	20	10 min	96	43 (<i>S</i>)
11	B4	/	toluene	20	10 min	97	40 (<i>R</i>)
12	B5	/	toluene	20	10 min	94	5 (<i>R</i>)
13	C1	/	toluene	20	2 h	98	31 (<i>R</i>)
14	C2	/	toluene	20	1 h	97	55 (<i>S</i>)
15	C3	/	toluene	20	30 min	94	13 (<i>S</i>)

16	C4	/	toluene	20	30 min	98	17 (<i>S</i>)
19	B1	/	toluene	20	10 min	93	7 (<i>S</i>)
20	B1	/	toluene	20	1 h	98	73 (<i>S</i>)
21	B1	/	CH ₂ Cl ₂	20	1 h	97	77 (<i>S</i>)
22	B1	/	THF	20	24 h	trace	/
23	B1	/	MeCN	20	2 h	85	73 (<i>S</i>)
24	B1	/	CH ₂ Cl ₂	20	1 h	98	84 (<i>S</i>)
25	B1	4Å MS	CH ₂ Cl ₂	20	1 h	98	87 (<i>S</i>)
26	B1	3Å MS	CH ₂ Cl ₂	20	1 h	98	88 (<i>S</i>)
27	B1	3Å MS	CH ₂ Cl ₂	0	2 h	98	90 (<i>S</i>)
28	B1	3Å MS	CH ₂ Cl ₂	-10	10 h	98	92 (<i>S</i>)

^aUnless otherwise specified, the reaction of **1a** (0.1 mmol) and **6a** (0.12 mmol) was conducted in the presence of catalyst (10 mmol %) and indicated additive (50 mg) in the indicated solvent (1 mL). ^bYield of isolated product. ^cDetermined by HPLC.

3.3 Effect of Catalyst Loading

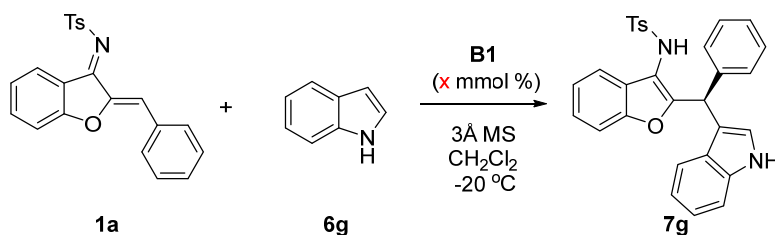
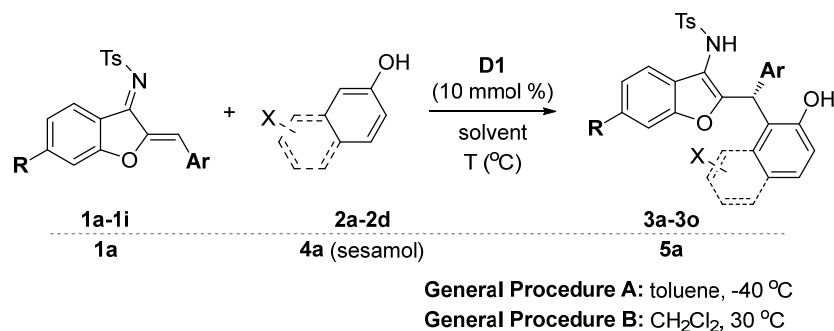


Table S3. Investigation of Catalyst loading for the Friedel-Crafts Reaction of **1a** with indole **6g**^a

Entry	B1 (x mmol %)	<i>t</i> (h)	Yield (%) ^b	ee (%) ^c
1	10	10	98	96 (<i>S</i>)
2	5	20	95	95 (<i>S</i>)
3	2.5	24	90	95 (<i>S</i>)
4	1.0	46	87	94 (<i>S</i>)

^aUnless otherwise specified, the reaction was conducted with **1a** (0.1 mmol), **6a** (0.12 mmol), **B1** (x mmol %) and 3Å MS (50 mg) in CH₂Cl₂ (1 mL). ^bYield of isolated product. ^cDetermined by HPLC. Time space yield refer to the amount of product /catalyst loading/reaction time

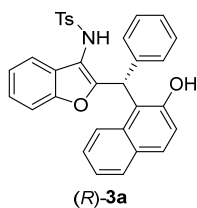
4 General Procedure for the Asymmetric Friedel-Crafts Arylation



General Procedure A: Under argon atmosphere, 1-azadienes **1** (0.1 mmol), β -naphthols **2** (0.12 mmol), the chiral urea catalyst **D1** (10 mmol %) was dissolved in toluene (2 mL). The reaction mixture was allowed to stir at -40 °C for 16 ~ 48 h. Then the reacting mixture was directly purified by silica gel chromatography with the elution of ethyl acetate/petroleum ether = 1/5 to 1/3, affording the desired products **3**.

General Procedure B: Under argon atmosphere, 1-azadienes **1** (0.1 mmol), β -naphthols **2** or sesamol **4a** (0.12 mmol) and the chiral urea catalyst **D1** (10 mmol %) was dissolved in CH₂Cl₂ (2 mL). The reaction mixture was allowed to stir at 30 °C for 12 ~ 48 h. Then the reacting mixture was directly purified by silica gel chromatography with the elution of ethyl acetate/petroleum ether = 1/5 to 1/3, affording the desired products **3** or **5a**.

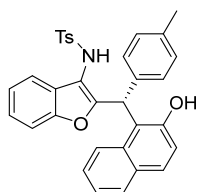
(R)-N-(2-((2-hydroxynaphthalen-1-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure A*, **(R)-3a** was obtained as white solid (30 h, 47.6 mg, 95% yield, 94% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/4); [α]_D²⁰ = -8.4 (*c* 1.0, CHCl₃); m.p. 216-217 °C; **HRMS (ESI-TOF)** calcd for C₃₂H₂₄NO₄S [*M* - *H*]⁻ : 518.1432, found: 518.1434; **¹H NMR**

(400 MHz, acetone- d^6 , ppm): δ 9.40 (s, 1H), 8.06 (s, 1H), 7.76 (dd, 1H, J = 3.5, 6.3 Hz), 7.65-7.58 (m, 2H), 7.49 (d, 2H, J = 8.4 Hz), 7.45-7.38 (m, 1H), 7.24-7.17 (m, 2H), 7.11-7.03 (m, 7H), 6.95 (d, 2H, J = 8.1 Hz), 6.66-6.64 (m, 2H), 6.31 (s, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, acetone- d^6 , ppm): δ 154.0, 153.4, 152.6, 143.8, 139.8, 136.4, 132.7, 129.9, 129.6, 128.4, 127.9, 127.6, 127.1, 126.1, 125.94, 125.86, 125.4, 124.4, 122.9, 122.8, 120.1, 118.1, 117.7, 115.8, 111.1, 37.7, 20.6; **HPLC analysis**: Daicel CHIRALCEL OD-H, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 230 nm, retention time: t_R = 5.4 min (major), t_R = 6.3 min (minor).

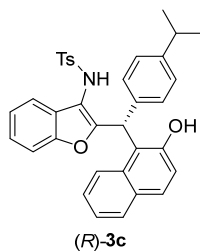
(*R*)-*N*-(2-((2-hydroxynaphthalen-1-yl)(*p*-tolyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



(*R*)-**3b**

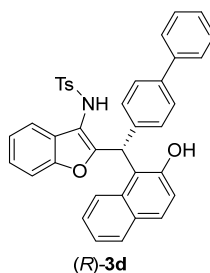
Following the *General Procedure B*, (*R*)-**3b** was obtained as white solid (24 h, 50.5 mg, 90% yield, 96% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/5); $[\alpha]_D^{20}$ = -12.2 (*c* 1.0, CHCl_3); m.p. 206-207 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{33}\text{H}_{26}\text{NO}_4\text{S}$ $[\text{M} - \text{H}]^-$: 532.1588, found: 532.1589; ^1H NMR (400 MHz, acetone- d^6 , ppm): δ 7.97-7.88 (m, 1H), 7.76-7.70 (m, 2H), 7.66-7.58 (m, 3H), 7.40-7.29 (m, 2H), 7.26-7.17 (m, 4H), 7.09 (d, 2H, J = 7.6 Hz), 6.98 (d, 2H, J = 8.0 Hz), 6.66 (d, 2H, J = 7.9 Hz), 6.39 (s, 1H), 2.29 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, acetone- d^6 , ppm): δ 154.2, 153.4, 152.6, 143.7, 136.7, 136.2, 135.2, 132.7, 129.9, 129.6, 129.5, 128.6, 128.4, 127.2, 126.1, 125.9, 125.4, 124.3, 122.8, 122.7, 120.1, 118.3, 117.7, 115.7, 111.1, 37.3, 20.5, 20.1; **HPLC analysis**: Daicel CHIRALPAK IA, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 9.7 min (minor), t_R = 13.5 min (major).

(R)-N-(2-((2-hydroxynaphthalen-1-yl)(4-isopropylphenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure A*, (R)-**3c** was obtained as white solid (16 h, 39.4 mg, 72% yield, 99% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/5); $[\alpha]_D^{20} = -8.5$ (c 1.0, CHCl_3); m.p. 203-204 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{35}\text{H}_{30}\text{NO}_4\text{S}$ $[\text{M} - \text{H}]^-$: 560.1901, found: 560.1904; **^1H NMR** (400 MHz, acetone- d_6 , ppm): δ 9.50 (br, 1H), 8.20 (br, 1H), 7.98-7.89 (m, 1H), 7.74 (d, 2H, $J = 8.66$ Hz), 7.64 (d, 2H, $J = 8.2$ Hz), 7.58 (d, 1H, $J = 7.2$ Hz), 7.37 (d, 1H, $J = 8.1$ Hz), 7.32 (d, 1H, $J = 8.9$ Hz), 7.27-7.16 (m, 4H), 7.13 (d, 2H, $J = 8.2$ Hz), 7.07 (d, 2H, $J = 8.18$ Hz), 6.71 (d, 2H, $J = 7.9$ Hz), 6.39 (s, 1H), δ 2.19 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d_6 , ppm): δ 154.3, 153.3, 152.5, 146.3, 143.7, 136.9, 136.4, 132.7, 129.9, 129.6, 129.5, 128.4, 127.7, 127.2, 126.1, 125.9, 125.4, 124.3, 122.9, 120.1, 118.3, 117.8, 115.8, 111.1, 37.4, 33.5, 23.5, 23.4, 20.6; **HPLC analysis**: Daicel CHIRALPAK AD-H, n -hexane/ i -PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 5.6$ min (minor), $t_R = 6.5$ min (major).

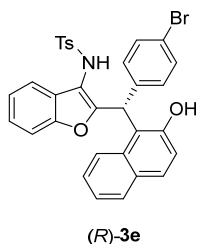
(R)-N-(2-([1,1'-biphenyl]-4-yl(2-hydroxynaphthalen-1-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure A*, (R)-**3d** was obtained as white solid (16 h, 59.6 mg, 94% yield, 98% ee) after flash chromatography (elution gradient: ethyl

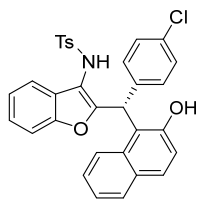
acetate/petroleum ether = 1/5); $[\alpha]_D^{20} = -6.0$ (c 1.0, CHCl_3); m.p. 181-183 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{38}\text{H}_{28}\text{NO}_4\text{S}$ $[\text{M} - \text{H}]^-$: 594.1745, found: 594.1748; **^1H NMR** (400 MHz, acetone- d_6 , ppm): δ 9.54 (br, 1H), 8.20 (br, 1H), 7.93-7.88 (m, 1H), 7.77-7.72 (m, 2H), 7.63 (d, 4H, $J = 8.1$ Hz), 7.58 (dd, 1H, $J = 1.1, 7.7$ Hz), 7.36 (d, 1H, $J = 7.92$ Hz), 7.33 (d, 1H, $J = 8.9$ Hz), 7.25-7.16 (m, 7H), 7.10 (d, 2H, $J = 8.1$ Hz), 6.83-6.77 (m, 2H), 6.45 (s, 1H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d_6 , ppm): δ 154.0, 153.4, 152.6, 143.8, 139.8, 136.3, 132.7, 129.9, 129.6, 128.4, 127.9, 127.6, 127.2, 126.1, 125.94, 125.86, 125.4, 124.4, 122.9, 122.8, 120.1, 118.1, 117.7, 115.8, 111.1, 37.7, 20.6; **HPLC analysis**: Daicel CHIRALPAK IC, n -hexane/ i -PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 7.3$ min (minor), $t_R = 8.4$ min (major).

(*R*)-*N*-(2-((4-bromophenyl)(2-hydroxynaphthalen-1-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure B*, (*R*)-**3e** was obtained as white solid (12 h, 47.6 mg, 80% yield, 91% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/5); $[\alpha]_D^{20} = -6.2$ (c 1.0, CHCl_3); m.p. 207-209 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{32}\text{H}_{23}\text{BrNO}_4\text{S}$ $[\text{M} - \text{H}]^-$: 596.0537, found: 596.0535; **^1H NMR** (600 MHz, acetone- d_6 , ppm): δ 9.58 (br, 1H), 8.21 (br, 1H), 7.87 (d, 1H, $J = 8.7$ Hz), 7.77-7.73 (m, 2H), 7.64 (d, 2H, $J = 8.4$ Hz), 7.57 (d, 1H, $J = 7.6$ Hz), 7.36-7.35 (m, 3H), 7.32 (d, 1H, $J = 9.1$ Hz), 7.25-7.18 (m, 4H), 7.11 (d, 2H, $J = 8.4$ Hz), 6.73 (d, 2H, $J = 8.0$ Hz), 6.41 (s, 1H), 2.19 (s, 3H); **^{13}C NMR** (150 MHz, acetone- d_6 , ppm): δ 153.4, 152.7, 143.8, 139.5, 136.4, 132.5, 131.0, 129.9, 129.8, 129.7, 129.6, 128.5, 127.2, 126.0, 125.7, 125.6, 124.5, 123.0, 120.2, 119.4, 117.7, 117.6, 116.0, 111.2, 37.4, 20.6; **HPLC analysis**: Daicel CHIRALPAK IC, n -hexane/ i -PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 5.9$ min (minor), $t_R = 6.6$ min (major).

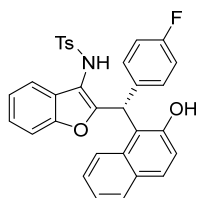
(*R*)-*N*-(2-((4-chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



(*R*)-3f

Following the *General Procedure B*, (*R*)-**3f** was obtained as white solid (12 h, 46.9 mg, 88% yield, 90% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/5); $[\alpha]_D^{20} = -11.5$ (*c* 1.0, CHCl₃); m.p. 204-206 °C; **HRMS (ESI-TOF)** calcd for C₃₂H₂₃ClNO₄S [M - H]⁻: 552.1042, found: 552.1041; **¹H NMR** (400 MHz, acetone-*d*⁶, ppm): δ 9.62 (br, 1H), 8.22 (br, 1H), 7.91-7.83 (m, 1H), 7.80-7.72 (m, 2H), 7.64 (d, 2H, *J* = 8.4 Hz), 7.60-7.51 (m, 1H), 7.37 (d, 1H, *J* = 7.9 Hz), 7.33 (d, 1H, *J* = 8.6 Hz), 7.28-7.17 (m, 6H), 7.12 (d, 2H, *J* = 8.1 Hz), 6.80 (d, 2H, *J* = 8.1 Hz), 6.43 (s, 1H), 2.19 (s, 3H); **¹³C NMR** (100 MHz, acetone-*d*⁶, ppm): δ 153.6, 153.4, 152.7, 143.8, 140.0, 136.4, 132.5, 129.9, 129.8, 129.6, 129.3, 128.5, 128.0, 127.2, 126.0, 125.7, 125.6, 125.5, 123.0, 120.1, 117.7, 117.6, 116.0, 37.3, 20.5; **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: *t*_R = 5.7 min (minor), *t*_R = 6.5 min (major).

(*R*)-*N*-(2-((4-fluorophenyl)(2-hydroxynaphthalen-1-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.

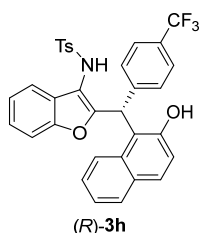


(*R*)-3g

Following the *General Procedure B*, (*R*)-**3g** was obtained as white solid (24 h, 50.4 mg, 94% yield, 89% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/5); $[\alpha]_D^{20} = -10.6$ (*c* 1.0, CHCl₃); m.p. 166-168 °C; **HRMS (ESI-TOF)** calcd for C₃₂H₂₃FNO₄S [M - H]⁻: 536.1330, found: 536.1339; **¹H NMR** (400 MHz, acetone-*d*⁶, ppm): δ 9.42 (br, 1H), 8.06 (br, 1H), 7.78-7.71 (m, 1H),

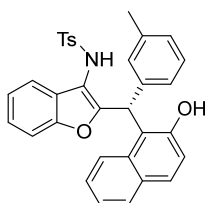
7.63-7.56 (m, 2H), 7.49 (d, 2H, $J = 8.3$ Hz), 7.44-7.40 (m, 1H), 7.21 (d, 1H, $J = 8.3$ Hz), 7.18 (d, 2H, $J = 8.8$ Hz), 7.11-7.01 (m, 4H), 6.96 (d, 2H, $J = 8.0$ Hz), 6.81 (t, 2H, $J = 8.8$ Hz), 6.71-6.64 (m, 2H), 6.29 (s, 1H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, acetone- d^6 , ppm): δ 162.4, 160.0, 153.9, 153.4, 152.6, 143.7, 136.5, 135.9 (d, $^4J_{\text{CF}} = 3.3$ Hz), 131.2 (d, $^1J_{\text{CF}} = 272.8$ Hz), 129.7, 129.6, 129.4 (d, $^3J_{\text{CF}} = 8.4$ Hz), 128.5, 126.1, 127.2, 125.6, 124.5, 123.0, 122.8, 120.1, 117.9, 117.8, 115.8, 114.6 (d, $^2J_{\text{CF}} = 21.4$ Hz), 111.2, 37.2, 20.5; ^{19}F NMR (376 MHz, acetone- d^6 , ppm): δ -118.6 (s); **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_{\text{R}} = 6.0$ min (minor), $t_{\text{R}} = 6.8$ min (major).

(*R*)-*N*-(2-((2-hydroxynaphthalen-1-yl)(4-(trifluoromethyl)phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure A*, (*R*)-**3h** was obtained as white solid (24 h, 57.0 mg, 96% yield 93% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/5); $[\alpha]_{\text{D}}^{20} = -8.3$ (c 1.0, CHCl_3); m.p. 157-159 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{33}\text{H}_{23}\text{F}_3\text{NO}_4\text{S}$ $[\text{M} - \text{H}]^-$: 586.1305, found: 586.1305; ^1H NMR (600 MHz, acetone- d^6 , ppm): δ 9.52 (br, 1H), 8.16 (br, 1H), 7.70 (d, 1H, $J = 8.3$ Hz), 7.65-7.60 (m, 2H), 7.52 (d, 2H, $J = 8.2$ Hz), 7.43-7.39 (m, 3H), 7.24 (d, 1H, $J = 8.2$ Hz), 7.21 (d, 1H, $J = 8.9$ Hz), 7.12-7.04 (m, 4H), 6.97 (d, 2H, $J = 8.2$ Hz), 6.89 (d, 2H, $J = 8.2$ Hz), 6.40 (s, 1H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, acetone- d^6 , ppm): δ 153.4, 153.3, 152.8, 144.9, 143.7, 136.5, 132.44, 130.0, 129.8, 129.6, 128.6, 128.3, 127.2, 126.0, 125.8, 125.4, 124.9, 124.86, 124.82 (q, $J_{\text{CF}} = 4.1$ Hz), 124.6, 123.0, 122.9, 120.1, 117.8, 117.3, 116.2, 111.2, 37.8, 20.4; ^{19}F NMR (376 MHz, acetone- d^6 , ppm): δ -62.7 (s); **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_{\text{R}} = 4.9$ min (minor), $t_{\text{R}} = 5.4$ min (major).

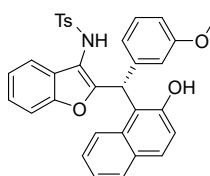
(*R*)-*N*-(2-((2-hydroxynaphthalen-1-yl)(*m*-tolyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



(*R*)-**3i**

Following the *General Procedure B*, (*R*)-**3i** was obtained as white solid (24 h, 48.2 mg, 90% yield, 87% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/4); $[\alpha]_D^{20} = -7.3$ (c 1.0, CHCl_3); m.p. 203-205 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{33}\text{H}_{26}\text{NO}_4\text{S}$ $[\text{M} - \text{H}]^-$: 532.1588, found: 532.1587; **^1H NMR** (600 MHz, acetone- d_6 , ppm): δ 9.30 (br, 1H), 8.01 (br, 1H), 7.83-7.75 (m, 1H), 7.61-7.56 (m, 2H), 7.50 (d, 2H, $J = 8.0$ Hz), 7.46 (d, 1H, $J = 7.6$ Hz), 7.20 (d, 1H, $J = 8.0$ Hz), 7.18 (d, 2H, $J = 8.8$ Hz), 7.11-7.03 (m, 4H), 6.95 (d, 2H, $J = 8.0$ Hz), 6.90 (t, 1H, $J = 7.6$ Hz), 6.85 (d, 1H, $J = 7.6$ Hz), 6.58-6.40 (m, 2H), 6.26 (s, 1H), 2.06 (s, H), 2.01 (s, 3H); **^{13}C NMR** (150 MHz, acetone- d_6 , ppm): δ 154.1, 153.4, 152.5, 143.6, 139.8, 137.2, 136.5, 132.8, 129.9, 129.5, 129.5, 128.3, 128.2, 127.8, 127.2, 126.7, 126.2, 125.9, 125.4, 124.8, 124.3, 122.9, 122.8, 120.2, 118.3, 117.7, 115.8, 111.1, 37.7, 20.7, 20.5; **HPLC analysis**: Daicel CHIRALPAK IC, n -hexane/ i -PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 8.1$ min (minor), $t_R = 10.0$ min (major).

(*R*)-*N*-(2-((2-hydroxynaphthalen-1-yl)(3-methoxyphenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.

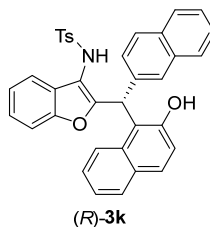


(*R*)-**3j**

Following the *General Procedure B*, (*R*)-**3j** was obtained as white solid (12 h, 53.8 mg, 98% yield, 88% ee) after flash chromatography (elution gradient: ethyl

acetate/petroleum ether = 1/5); $[\alpha]_D^{20} = -8.2$ (c 1.0, CHCl_3); m.p. 120-122 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{33}\text{H}_{26}\text{NO}_5\text{S}$ $[\text{M} - \text{H}]^-$: 548.1537, found: 548.1539; **^1H NMR** (600 MHz, acetone- d^6 , ppm): δ 9.30 (br, 1H), 8.02 (br 1H), 7.85-7.79 (m, 1H), 7.61-7.57 (m, 2H), 7.49 (d, 2H, $J = 8.4$ Hz), 7.46-7.42 (m, 1H), 7.22 (d, 1H, $J = 8.4$ Hz), 7.18 (d, 2H, $J = 8.8$ Hz), 7.11-7.04 (m, 4H), 6.95 (t, 3H, $J = 8.0$ Hz), 6.62 (dd, 1H, $J = 2.4, 8.0$ Hz), 6.29 (s, 1H), 6.25 (dd, 1H, $J = 2.4, 7.6$ Hz), 6.22 (s, 1H), 3.52 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d^6 , ppm): δ 159.6, 153.9, 152.5, 143.7, 141.4, 136.4, 132.8, 129.9, 129.5, 128.9, 128.3, 127.2, 126.1, 25.8, 125.5, 124.4, 122.9, 122.8, 120.14, 120.07, 118.2, 117.7, 115.8, 114.3, 111.1, 110.6, 54.4, 37.7, 20.5; **HPLC analysis**: Daicel CHIRALPAK IC, n -hexane/ i -PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 7.2$ min (minor), $t_R = 8.2$ min (major).

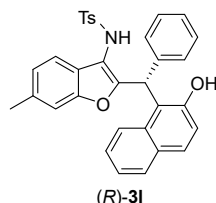
(*R*)-*N*-(2-((2-hydroxynaphthalen-1-yl)(naphthalen-2-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure A*, (*R*)-**3k** was obtained as white solid (36 h, 52.8 mg, 87% yield, 94% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/5); $[\alpha]_D^{20} = -4.5$ (c 1.0, CHCl_3); m.p. 198-200 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{36}\text{H}_{26}\text{NO}_4\text{S}$ $[\text{M} - \text{H}]^-$: 568.1588, found: 568.1587; **^1H NMR** (400 MHz, acetone- d^6 , ppm): δ 9.70 (br, 1H), 8.24 (br, 1H), 7.94 (d, 1H, $J = 8.6$ Hz), 7.88-7.83 (m, 1H), 7.78 (d, 1H, $J = 9.0$ Hz), 7.75 (d, 2H, $J = 8.6$ Hz), 7.72-7.60 (m, 4H), 7.51-7.44 (m, 2H), 7.43-7.34 (m, 2H), 7.31-7.22 (m, 3H), 7.21-7.10 (m, 2H), 6.93 (d, 2H, $J = 7.9$ Hz), 6.88 (dd, 1H, $J = 1.4, 8.6$ Hz), 6.55 (s, 1H), 1.62 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d^6 , ppm): δ 153.8, 153.6, 152.6, 143.7, 137.6, 136.0, 133.3, 132.8, 132.16, 129.9, 129.7, 129.4, 128.4, 127.8, 127.4, 127.7, 126.04, 126.02, 125.8, 125.5, 124.4, 123.0, 122.8, 120.3, 118.0, 117.6, 115.9, 111.3, 37.8, 19.9; **HPLC**

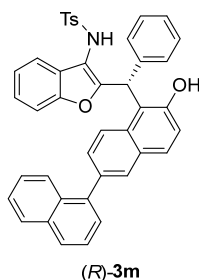
analysis: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 8.2 min (minor), t_R = 9.1 min (major).

(*R*)-*N*-(2-((2-hydroxynaphthalen-1-yl)(phenyl)methyl)-6-methylbenzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure A*, (*R*)-**3l** was obtained as white solid (36h, 43.6 mg, 82% yield, 91% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/10; $[\alpha]_D^{20}$ = -6.5 (*c* 1.0, CHCl₃); m.p. 202-203 °C; **HRMS (ESI-TOF)** calcd for C₃₃H₂₆NO₄S [M - H]⁻ : 532.1588, found: 532.1587; **¹H NMR** (400 MHz, acetone-*d*⁶, ppm): δ 9.42 (br, 1H), 8.03 (br, 1H), 7.81-7.72 (m, 1H), 7.66-7.56 (m, 2H), 7.49 (d, 2H, *J* = 8.4 Hz), 7.2 (d, 1H, *J* = 8.1 Hz), 7.20 (d, 1H, *J* = 8.9 Hz), 7.11-7.00 (m, 6H), 6.96 (d, 2H, *J* = 8.1 Hz), 6.90 (d, 1H, *J* = 8.1 Hz), 6.70-6.56 (m, 2H), 6.28 (s, 1H), 2.24 (s, 1H), 2.02 (s, 1H); **¹³C NMR** (100 MHz, acetone-*d*⁶, ppm): δ 153.8, 152.5, 143.7, 139.9, 136.3, 134.6, 132.7, 129.9, 129.6, 129.5, 128.3, 127.9, 127.6, 127.1, 126.0, 125.9, 125.3, 124.2, 123.5, 122.7, 119.7, 118.3, 117.7, 115.8, 111.3, 37.5, 20.59, 20.56; **HPLC analysis**: Daicel CHIRALPAK OD-H, *n*-hexane/*i*-PrOH = 96/4, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 11.4 min (minor), t_R = 13.2 min (major).

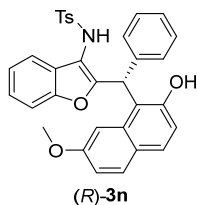
(*R*)-*N*-(2-((6'-hydroxy-[1,2'-binaphthalen]-5'-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure A*, (*R*)-**3m** was obtained as white solid (20 h, 63.2

mg, 92% yield, 95% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/4); $[\alpha]_D^{20} = -11.3$ (c 1.0, CHCl_3); m.p. 219-220 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{42}\text{H}_{30}\text{NO}_4\text{S}$ $[\text{M} - \text{H}]^-$: 644.1901 , found: 644.1898. **^1H NMR** (400 MHz, acetone- d_6 , ppm): δ 9.60 (s, 1H), 8.26 (s, 1H), 8.07 (d, 1H, $J = 8.9$ Hz), 7.94 (dd, 2H, $J = 8.1, 19.9$ Hz), 7.89-7.80 (m, 3H), 7.67 (d, 2H, $J = 8.4$ Hz), 7.62-7.48 (m, 3H), 7.47-7.35 (m, 5H), 7.87-7.16 (m, 5H), 7.13 (d, 2H, $J = 8.1$ Hz), 6.95-6.85 (m, 3H), 6.53 (s, 1H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d_6 , ppm): δ 154.1, 153.4, 152.9, 143.8, 139.8, 136.5, 135.0, 134.0, 131.9, 131.6, 129.9, 129.6, 129.2, 128.3, 128.0, 127.7, 127.6, 127.2, 127.1, 126.1, 126.15, 126.09, 125.8, 125.7, 125.6, 125.5, 124.4, 122.9, 120.1, 118.3, 118.2, 115.8, 111.2, 37.9, 20.6; **HPLC analysis**: Daicel CHIRALPAK IC, n -hexane/ i -PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 7.0$ min (minor), $t_R = 7.9$ min (major).

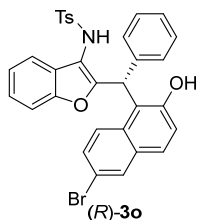
(*R*)-*N*-(2-((2-hydroxy-7-methoxynaphthalen-1-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure A*, (*R*)-**3n** was obtained as white solid (40 h, 53.6 mg, 90% yield, 91% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/5); $[\alpha]_D^{20} = -18.6$ (c 1.0, CHCl_3); m.p. 201-203 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{33}\text{H}_{27}\text{NO}_5\text{S}$ $[\text{M} - \text{H}]^-$: 548.1537, found: 548.1538; **^1H NMR** (400 MHz, acetone- d_6 , ppm): δ 9.43 (br, 1H), 8.03 (br, 1H), 7.52-7.44 (m, 5H), 7.26 (d, 1H, $J = 7.9$ Hz), 7.14 (s, 1H), 7.11-7.01 (m, 6H), 6.93 (d, 2H, $J = 8.1$ Hz), 6.72-6.64 (m, 3H), 6.27 (s, 1H), 3.38 (s, 3H), 1.97 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d_6 , ppm): δ 157.3, 154.1, 153.4, 153.1, 143.8, 139.8, 136.1, 134.0, 129.6, 129.2, 127.9, 127.6, 127.1, 126.0, 125.8, 125.1, 124.4, 123.0, 120.1, 117.6, 115.9, 115.4, 114.9, 111.2, 105.3, 54.3, 37.5, 20.5; **HPLC analysis**: Daicel CHIRALPAK AD-H, n -hexane/ i -PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time:

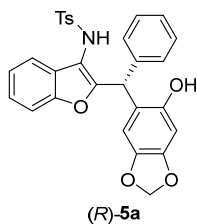
$t_R = 9.8$ min (minor), $t_R = 11.3$ min (major).

(*R*)-*N*-(2-((6-bromo-2-hydroxynaphthalen-1-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure A*, (*R*)-**3o** was obtained as white solid (41 h, 57.2 mg, 91% yield, 91% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/5); $[\alpha]_D^{20} = -1.6$ (c 1.0, CHCl_3); m.p. 206-208 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{32}\text{H}_{23}\text{BrNO}_4\text{S}$ $[\text{M} - \text{H}]^-$: 596.1537, found: 596.157; **^1H NMR** (400 MHz, acetone- d_6 , ppm): δ 9.73 (br, 1H), 8.22 (br, 1H), 7.97 (d, 1H, $J = 2.2$ Hz), 7.85 (d, 1H, $J = 9.3$ Hz), 7.76 (d, 1H, $J = 8.9$ Hz), 7.65 (d, 2H, $J = 8.3$ Hz), 7.55 (dd, 1H, $J = 0.6, 7.5$ Hz), 7.40 (d, 2H, $J = 8.9$ Hz), 7.32 (dd, 1H, $J = 2.2, 9.3$ Hz), 7.28-7.24 (m, 1H), 7.22-7.18 (m, 4H), 7.12 (d, 2H, $J = 8.1$ Hz), 6.81-6.79 (m, 2H), 6.50 (s, 1H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d_6 , ppm): δ 153.8, 153.4, 153.2, 143.7, 140.0, 136.5, 131.3, 131.1, 130.2, 130.0, 128.8, 128.3, 128.1, 127.6, 127.2, 126.08, 126.05, 124.5, 122.9, 120.1, 119.0, 118.6, 116.0, 116.0, 111.2, 37.6, 20.6; **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 6.0$ min (minor), $t_R = 6.7$ min (major).

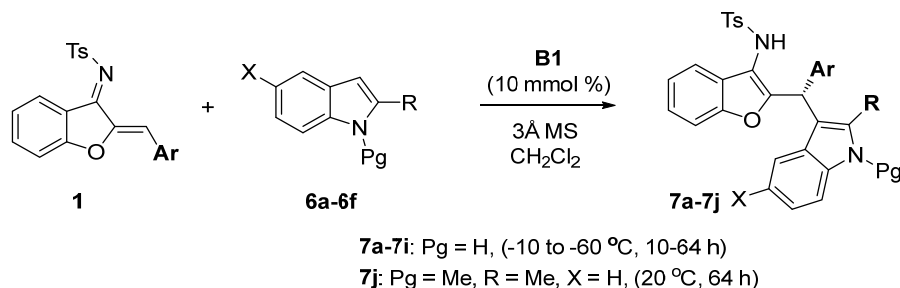
(*R*)-*N*-(2-((5-hydroxybenzo[*d*][1,3]dioxol-4-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure B*, (*R*)-**5a** was obtained as white solid (24 h, 42.6 mg, 82% yield, 84% ee) after flash chromatography (elution gradient: ethyl

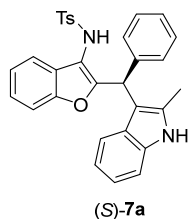
acetate/petroleum ether = 1/4); $[\alpha]_D^{20} = -13.9$ (c 1.0, CHCl_3); m.p. 198-200 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{29}\text{H}_{22}\text{NO}_6\text{S}$ $[\text{M} - \text{H}]^-$: 512.1173 , found: 512.1174; **^1H NMR** (600 MHz, acetone- d_6 , ppm): δ 8.29 (br, 1H), 8.23 (br, 1H), 7.44 (d, 2H, $J = 8.3$ Hz), 7.32-7.28 (m, 2H), 7.13-7.07 (m, 2H), 7.05-7.01 (m, 2H), 6.97 (d, 2H, $J = 8.0$ Hz), 6.93 (d, 2H, $J = 7.4$ Hz), 6.42 (s, 1H), 6.33 (s, 1H), 5.80 (s, 1H), 5.74-5.73 (m, 2H), 2.13 (s, 3H); **^{13}C NMR** (150 MHz, acetone- d_6 , ppm): δ 154.7, 153.5, 149.0, 146.7, 143.4, 140.8, 137.0, 129.4, 128.5, 127.9, 127.2, 126.3, 126.2, 124.3, 122.8, 120.1, 119.3, 114.4, 111.1, 108.7, 101.0, 97.6, 39.8, 20.6; **HPLC analysis**: Daicel CHIRALPAK IC, n -hexane/ i -PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 11.6$ min (minor), $t_R = 14.5$ min (major).

5 General Procedure for the Asymmetric Friedel-Crafts Heteroarylation



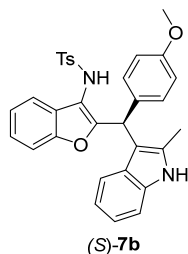
General Procedure C: Under argon atmosphere, 1-azadienes **1** (0.1 mmol), indole derivatives **6** (0.12 mmol), the chiral phosphoric acid **B1** (10 mmol %) and 3Å MS (50 mg) were added in the solution of CH_2Cl_2 (1 mL). The reaction mixture was allowed to stir at the indicated temperature for 10 ~ 64 h. Then, the reacting mixture was directly purified by silica gel chromatography with the elution of ethyl acetate/petroleum ether = 1/4 to 1/3, affording the desired products **7**.

(S)-4-methyl-N-(2-((2-methyl-1H-indol-3-yl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide.



Following the *General Procedure C*, (S)-7a was obtained as yellow solid (-10 °C, 10 h, 49.6 mg, 98% yield, 92% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/3); $[\alpha]_D^{20} = -5.7$ (*c* 1.0, CHCl₃); m.p. 108-110 °C; **HRMS (ESI-TOF)** calcd for C₃₁H₂₆NaN₂O₃S [M + Na]⁺ : 529.1556 , found: 529.1556; **¹H NMR** (400 MHz, acetone-*d*⁶, ppm): δ 9.85 (br, 1H), 8.51 (br, 1H), 7.54 (d, 2H, *J* = 8.1 Hz), 7.22 (d, 2H, *J* = 8.3 Hz), 7.17 (d, 2H, *J* = 8.1 Hz), 7.13-7.06 (m, 4H), 7.04-6.96 (m, 6H), 6.94-6.90 (m, 1H), 6.85-6.81 (m, 1H), 6.72-6.68 (m, 1H), 5.94 (s, 1H), 2.17 (s, 3H), 2.16 (s, 3H); **¹³C NMR** (100 MHz, acetone-*d*⁶, ppm): δ 156.6, 152.9, 143.5, 141.2, 137.9, 135.7, 133.1, 129.4, 128.3, 128.1, 127.9, 127.3, 126.3, 126.1, 124.1, 122.7, 120.3, 119.4, 119.3, 118.6, 113.9, 111.1, 110.3, 109.8, 38.3, 20.5, 11.4; **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 6.3 min (majorr), t_R = 7.9 min (minor).

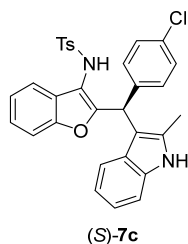
(S)-N-(2-((4-methoxyphenyl)(2-methyl-1H-indol-3-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure C*, (S)-7b was obtained as yellow solid (-10 °C, 10 h, 52.5 mg, 98% yield, 93% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/3); $[\alpha]_D^{20} = -9.2$ (*c* 1.0, CHCl₃); m.p. 141-143 °C; **HRMS (ESI-TOF)** calcd for C₃₂H₂₈NaN₂O₄S [M + Na]⁺ : 559.1662 , found: 559.1662; **¹H**

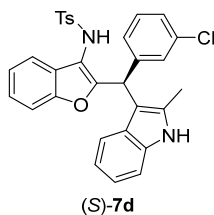
NMR (400 MHz, acetone- d^6 , ppm): δ 9.85 (br, 1H), 8.52 (s, 1H), 7.53 (d, 2H, J = 8.3 Hz), 7.23-7.20 (m, 2H), 7.12 (d, 1H, J = 8.0 Hz), 7.03-6.98 (m, 5H), 6.92-6.89 (m, 1H), 6.85-6.81 (m, 1H), 6.73-6.69 (m, 1H), 6.63-6.56 (m, 3H), 5.92 (s, 1H), 3.53 (s, 3H), 2.16 (s, 6H); **^{13}C NMR** (100 MHz, acetone- d^6 , ppm): δ 159.7, 156.6, 152.9, 143.5, 142.8, 137.9, 135.7, 133.1, 129.4, 128.8, 128.1, 127.2, 126.3, 124.1, 122.7, 120.7, 120.3, 119.4, 119.3, 118.6, 114.9, 113.9, 111.1, 110.9, 110.3, 109.7, 54.4, 38.3, 20.5, 11.4; **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 7.3 min (major), t_R = 8.7 min (minor).

(*S*)-*N*-(2-((4-chlorophenyl)(2-methyl-1H-indol-3-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



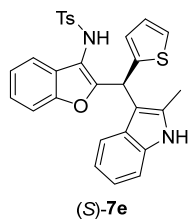
Following the *General Procedure C*, (*S*)-**7c** was obtained as yellow solid (-10 °C, 10 h, 52.8 mg, 98% yield, 90% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/3); $[\alpha]_D^{20}$ = -4.6 (c 1.0, CHCl_3); m.p. 120-122 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{31}\text{H}_{25}\text{ClNaN}_2\text{O}_3\text{S}$ $[\text{M} + \text{Na}]^+$: 563.1167, found: 563.1164; **^1H NMR** (400 MHz, acetone- d^6 , ppm): δ 9.88 (br, 1H), 8.57 (s, 1H), 7.53 (d, 2H, J = 8.4 Hz), 7.21 (d, 1H, J = 8.2 Hz), 7.16-7.11 (m, 4H), 7.05-6.99 (m, 4H), 6.96 (d, 2H, J = 8.4 Hz), 6.93-6.89 (m, 1H), 6.85-6.81 (m, 1H), 6.73-6.69 (m, 1H), 5.93 (s, 1H), 2.16 (s, 3H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d^6 , ppm): δ 156.0, 153.0, 143.6, 140.2, 137.8, 135.7, 133.2, 131.5, 130.0, 129.5, 128.0, 127.9, 127.3, 126.2, 124.3, 122.8, 120.5, 119.4, 119.1, 118.8, 114.1, 111.2, 110.4, 109.4, 37.8, 20.6, 11.4; **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 5.4 min (major), t_R = 6.4 min (minor).

(S)-N-(2-((3-chlorophenyl)(2-methyl-1H-indol-3-yl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure C*, (S)-7d was obtained as yellow solid (-10 °C, 10 h, 53.4 mg, 98% yield, 95% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/3); $[\alpha]_D^{20} = -15.1$ (*c* 1.0, CHCl₃); m.p. 145-147 °C; **HRMS (ESI-TOF)** calcd for C₃₁H₂₅ClNaN₂O₃S [M + Na]⁺: 563.1167, found: 563.1166; **¹H NMR** (400 MHz, acetone-*d*⁶, ppm): δ 9.92 (br, 1H), 8.61 (s, 1H), 7.55 (d, 2H, *J* = 8.1 Hz), 7.24 (d, 1H, *J* = 8.1 Hz), 7.18-7.07 (m, 4H), 7.05-7.01 (m, 4H), 6.96-6.91 (m, 3H), 6.86-6.83 (m, 1H), 6.74-6.71 (m, 1H), 5.94 (s, 1H), 2.18 (s, 3H), 2.15 (s, 3H); **¹³C NMR** (100 MHz, acetone-*d*⁶, ppm): δ 155.7, 153.0, 143.8, 143.6, 137.8, 135.7, 133.4, 133.3, 129.6, 129.5, 128.2, 127.8, 126.9, 126.3, 126.2, 124.3, 122.8, 120.5, 119.5, 119.1, 118.8, 114.3, 111.2, 110.5, 109.1, 38.1, 20.6, 11.4; **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: *t*_R = 5.4 min (major), *t*_R = 6.6 min (minor).

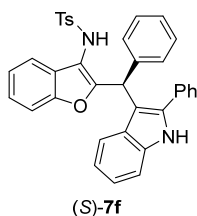
(S)-4-methyl-N-(2-((2-methyl-1H-indol-3-yl)(thiophen-2-yl)methyl)benzofuran-3-yl)benzenesulfonamide.



Following the *General Procedure C*, (S)-7e was obtained as yellow solid (-60 °C, 20 h, 45.3 mg, 88% yield, 92% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/3); $[\alpha]_D^{20} = +6.0$ (*c* 1.0, CHCl₃); m.p. 128-130 °C; **HRMS (ESI-TOF)** calcd for C₂₉H₂₄NaN₂O₃S₂ [M + Na]⁺: 535.1121, found: 535.1118; **¹H NMR** (400 MHz, acetone-*d*⁶, ppm): δ 9.89 (br, 1H), 8.52 (s, 1H), 7.53 (d, 2H, *J* = 8.3

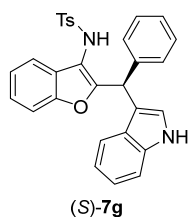
Hz), 7.39 (d, 1H, $J = 8.0$ Hz), 7.26 (d, 1H, $J = 8.1$ Hz), 7.13-7.11 (m, 2H), 7.07-7.03 (m, 3H), 6.95-6.94 (m, 1H), 6.92-6.88 (m, 1H), 6.86-6.83 (m, 1H), 6.77-6.74 (m, 2H), 6.59-6.56 (m, 1H), 6.14 (s, 1H), 2.26 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, acetone- d_6 , ppm): δ 156.0, 152.9, 145.3, 143.6, 137.8, 135.6, 133.0, 129.5, 127.7, 127.2, 126.2, 126.1, 125.4, 124.3, 124.2, 122.7, 120.4, 119.33, 119.30, 118.7, 113.4, 111.2, 110.3, 110.2; **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 6.7$ min (major), $t_R = 8.3$ min (minor).

(S)-4-methyl-N-(2-(phenyl(2-phenyl-1H-indol-3-yl)methyl)benzofuran-3-yl)-benzenesulfonamide.



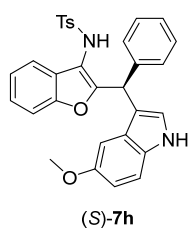
Following the *General Procedure C*, (*R*)-**7f** was obtained as yellow solid (-40 °C, 64 h, 51.1 mg, 90% yield, 89% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/4); $[\alpha]_D^{20} = +13.5$ (c 1.0, CHCl_3); m.p. 126-128 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{29}\text{H}_{24}\text{NaN}_2\text{O}_3\text{S}_2$ $[\text{M} + \text{Na}]^+$: 591.1713 , found: 591.1709; ^1H NMR (400 MHz, acetone- d_6 , ppm): δ 10.31 (br, 1H) δ 8.11 (s, 1H), 7.53-7.51 (m, 2H), 7.41-7.37 (m, 3H), 7.35-7.32 (m, 3H), 7.27-7.21 (m, 2H), 7.06-7.03 (m, 5H), 7.00-6.98 (m, 2H), 6.94-6.91 (m, 2H), 6.86-6.95 (m, 2H), 6.76-6.93 (m, 1H), 5.84 (s, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, acetone- d_6 , ppm): δ 156.5, 152.9, 143.5, 141.2, 137.6, 136.8, 136.7, 132.8, 129.5, 128.7, 128.3, 128.1, 127.9, 127.8, 127.3, 126.3, 126.2, 124.2, 122.7, 121.6, 121.1, 119.4, 119.2, 114.1, 111.2, 111.1, 110.8, 38.8, 20.6; **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 6.7$ min (major), $t_R = 8.0$ min (minor).

(S)-N-(2-(((1H-indol-3-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide.



Following the *General Procedure C*, (S)-**7g**^[4] was obtained as pink solid (-20 °C, 12 h, 48.7 mg, 99% yield, 96% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/4); $[\alpha]_{\text{D}}^{20} = -11.1$ (*c* 1.0, CHCl₃); $[\alpha]_{\text{D}}^{20} = +13.5$ (*c* 1.0, ethyl acetate); m.p. 109-111 °C; **HRMS (ESI-TOF)** calcd for C₃₀H₂₄KN₂O₃S [M + K]⁺: 531.1139, found: 512.1133; **¹H NMR** (400 MHz, acetone-*d*⁶, ppm): δ 9.98 (br, 1H), 8.68 (s, 1H), 7.47 (d, 2H, *J* = 8.2 Hz), 7.30- 7.24 (m, 3H), 7.08-7.00 (m, 8H), 6.94 (t, 1H, *J* = 7.5 Hz), 6.89(d, 2H, *J* = 8.0 Hz), 6.82 (d, 1H, *J* = 1.9 Hz), 6.77 (t, 1H, *J* = 7.5 Hz), 5.73 (s, 1H), 2.03 (s, 3H); **¹³C NMR** (100 MHz, acetone-*d*⁶, ppm): δ 155.4, 153.3, 143.5, 141.1, 137.4, 136.8, 129.4, 128.5, 128.0, 127.2, 126.8, 126.4, 124.2, 123.7, 122.7, 121.4, 120.1, 119.2, 118.7, 114.9, 113.5, 111.4, 111.1, 39.2, 20.5; **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: *t*_R = 15.6 min (major), *t*_R = 17.9 min (minor).

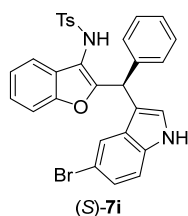
(S)-N-(2-(((5-methoxy-1H-indol-3-yl)(phenyl)methyl)benzofuran-3-yl)-4-methyl-benzenesulfonamide.



Following the *General Procedure C*, (S)-**7h** was obtained as white solid (-20 °C, 12 h, 51.4 mg, 98% yield, 93% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/4); $[\alpha]_{\text{D}}^{20} = -7.9$ (*c* 1.0, CHCl₃); m.p. 127-129 °C; **HRMS (ESI-TOF)** calcd for C₃₁H₂₆N₂NaO₄S [M + Na]⁺: 545.1505, found: 545.1506; **¹H**

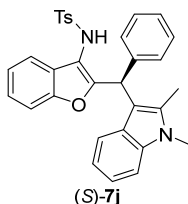
NMR (400 MHz, acetone- d^6 , ppm): δ 9.81 (br, 1H), 8.62 (s, 1H), 7.47 (d, 2H, J = 8.3 Hz), 7.24-7.21 (m, 2H), 7.16-7.03 (m, 7H), 6.99-6.95 (m, 1H), 6.89 (d, 2H, J = 8.1 Hz), 6.78 (d, 1H, J = 2.4 Hz), 6.62-6.59 (m, 2H), 5.71 (s, 1H), 3.50 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d^6 , ppm): δ 155.7, 153.8, 153.3, 143.5, 141.1, 137.5, 131.9, 129.4, 128.6, 128.0, 127.2, 126.4, 124.4, 124.2, 122.7, 119.9, 114.6, 113.6, 112.0, 111.4, 111.1, 101.3, 54.9, 39.2, 20.5; **HPLC analysis**: Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 14.6 min (major), t_R = 16.6 min (minor).

(*S*)-*N*-(2-((5-bromo-1H-indol-3-yl)(phenyl)methyl)benzofuran-3-yl)-4-methyl-benzenesulfonamide.



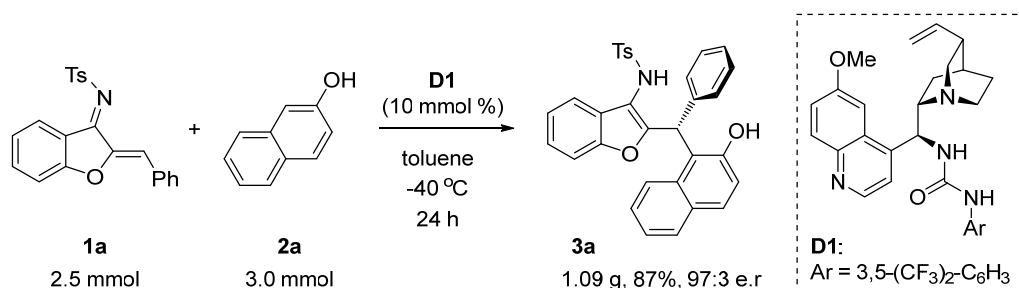
Following the *General Procedure C*, (*S*)-**7i** was obtained as yellow solid (12 h, 54.7 mg, 96% yield, 94% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/4); $[\alpha]_D^{20}$ = -13.3 (*c* 1.0, CHCl_3); m.p. 137-139 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{30}\text{H}_{23}\text{BrN}_2\text{NaO}_3\text{S}$ $[\text{M} + \text{Na}]^+$: 593.0503, found: 593.0508; **^1H NMR** (400 MHz, acetone- d^6 , ppm): δ 10.18 (br, 1H), 8.68 (s, 1H), 7.46 (d, 2H, J = 7.9 Hz), 7.29-7.22 (m, 4H), 7.08-7.04 (m, 7H), 7.01-6.97 (m, 1H), 6.01-6.85 (m, 3H), 5.71 (s, 1H), 2.00 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d^6 , ppm): δ 155.0, 153.3, 143.5, 140.8, 137.4, 135.4, 129.3, 128.6, 128.4, 128.2, 127.2, 126.7, 126.4, 125.5, 124.3, 124.1, 122.8, 121.6, 120.1, 114.7, 113.7, 113.3, 111.8, 111.1, 39.0, 20.5; **HPLC analysis**: Daicel CHIRALPAK IA, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 8.1 min (major), t_R = 9.8 min (minor).

(S)-N-(2-((1,2-dimethyl-1H-indol-3-yl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide



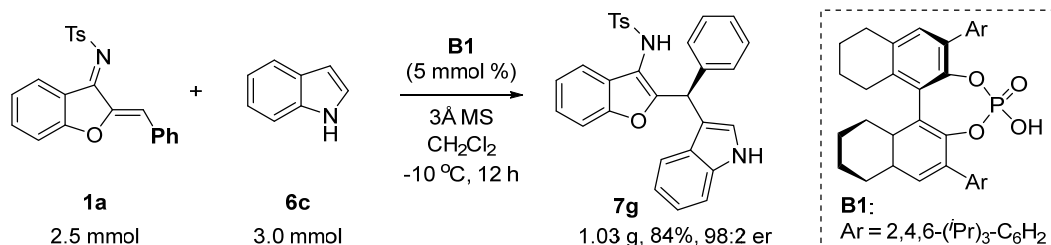
Following the *General Procedure C*, (S)-7j was obtained as white solid (64 h, 44.2 mg, 85% yield, 29% ee) after flash chromatography (elution gradient: ethyl acetate/petroleum ether = 1/3); $[\alpha]_D^{20} = -8.3$ (c 1.0, CHCl_3); m.p. 126-128 °C; **HRMS (ESI-TOF)** calcd for $\text{C}_{32}\text{H}_{26}\text{NaN}_2\text{O}_3\text{S}$ $[\text{M} + \text{Na}]^+$: 543.1748 , found: 543.1750; **^1H NMR** (400 MHz, acetone- d_6 , ppm): δ 8.45 (s, 1H), 7.53 (d, 2H, $J = 8.13$ Hz), 7.20 (t, 2H, $J = 7.2$ Hz), 7.12 (d, 1H, $J = 8.3$ Hz), 7.07-7.00 (m, 6H), 6.95 (d, 3H, $J = 8.0$ Hz), 6.88 (t, 2H, $J = 7.2$ Hz), 6.71 (t, 2H, $J = 7.4$ Hz), 6.00 (s, 1H), 3.50 (s, 3H), 2.20 (s, 3H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, acetone- d_6 , ppm): δ 156.8, 152.9, 143.5, 141.2, 138.0, 136.9, 134.6, 129.5, 128.2, 127.9, 127.3, 127.2, 126.3, 126.1, 124.1, 122.7, 120.3, 119.5, 119.3, 118.6, 114.0, 111.1, 109.7, 108.7, 38.5, 28.9, 20.6, 10.0; **HPLC analysis**: Daicel CHIRALPAK IC, n -hexane/ i -PrOH = 85/15, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: $t_R = 10.9$ min (minor), $t_R = 12.3$ min (major).

6 General Procedure for the Gram-Scale Syntheses



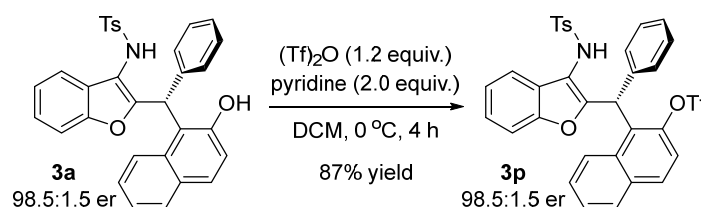
General Procedure for the Gram-Scale Synthesis of 3a: Under argon atmosphere, 1-azadienes **1a** (0.938 g, 2.5 mmol), β -naphthol **2a** (0.433 g, 3.0 mmol) and the chiral urea catalyst **D1** (144.5 mg, 10 mmol %) was dissolved in toluene (50 mL) at -40°C . The reaction mixture was allowed to stir at -40°C for 24 h. Then, the reacting mixture was concentrated, and the residues were purified by silica gel chromatography (ethyl

acetate/petroleum ether =1/5) to yield the desired product **3a** (1.09 g) in 87% yield and 97:3 er. **HPLC analysis:** Daicel CHIRALCEL OD-H, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 230 nm, retention time: t_R = 5.3 min (major), t_R = 6.3 min (minor).



General Procedure for the Gram-Scale Synthesis of 7g: Under argon atmosphere, the solution of α,β -unsaturated imine **1a** (0.938 g, 2.5 mmol) and indole derivatives **6c** (0.351 g, 3.0 mmol) in CH₂Cl₂ (50 mL) was added 3Å MS (1.25 g) and chiral phosphoric acid **B1** (95.5 mg, 5 mmol %). The reaction mixture was allowed to stir at -10 °C for 12 h. Then, the reacting mixture was concentrated, and the residues were purified by silica gel chromatography (ethyl acetate/petroleum ether =1/3) to yield the desired product **7g** (1.03 g) in 84% yield and 98:2 er. **HPLC analysis:** Daicel CHIRALPAK IC, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 15.5 min (major), t_R = 17.7 min (minor).

7 General Procedure of the Protection for 3a



Under argon atmosphere, Trifluoromethanesulfonic anhydride (0.12 mmol) was added to solution of **3a** (0.1 mmol, 98.5:1.5 er, after once recrystallization from the gram-scale synthesis) and pyridine (0.2 mmol) in DCE (2 mL) at ice bath. When the reaction finish, the resolution was then quenched with 10% HCl and extracted with

DCE. The combined organic phases were dried over Na₂SO₄ and concentrated. The residue was purified by flash chromatography on silica gel with the elution of DCM:petroleum ether = 1:1 to afford **3p** as white solid (4 h, 74.8 mg, 87% yield, 97% ee).

(R)-1-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methylnaphthalen-2-yl trifluoromethanesulfonate (3p): $[\alpha]_D^{20} = -12.6$ (c 1.0, CHCl₃); m.p. 232-234 °C; **HRMS (ESI-TOF)** calcd for C₃₂H₂₃F₃NO₆S₂ [M - H]⁻ : 650.0997, found: 650.0836; **¹H NMR** (400 MHz, CDCl₃, ppm): δ 8.12 (d, 1H, J = 8.8 Hz), 7.86 (d, 1H, J = 9.2 Hz) 7.82 (d, 1H, J = 8.2 Hz), 7.65 (d, 2H, J = 8.2 Hz), 7.50-7.36 (m, 4H), 7.29-7.13 (m, 6H), 6.98 (d, 2H, J = 7.9 Hz), 6.78 (d, 2H, J = 7.2 Hz), 6.45 (s, 1H), 6.31 (s, 1H), 2.21 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃, ppm): δ 153.4, 152.2, 146.4, 143.8, 139.0, 136.1, 133.3, 131.0, 129.5, 128.6, 128.3, 128.1, 127.6, 127.5, 127.4, 126.9, 126.7, 126.6, 125.8, 124.9, 123.4, 120.1, 118.1, 116.9, 115.7, 111.7, 39.5, 21.5, **¹⁹F NMR** (376 MHz, CDCl₃, ppm): -73.4, **HPLC analysis:** Daicel CHIRALCEL AD-H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R = 30.8 min (major), t_R = 27.6 min (minor).

8 Assignment of Absolute Configuration for Products

Experimental: Single crystals of C₃₂H₂₅NO₄S (**3a**) were obtained from *n*-Hexanes and DCM. A suitable crystal was selected and measured on a diffractometer. The crystal was kept at 298(2) K during data collection.

Crystal Data for C₃₂H₂₅NO₄S (**3a**) (M = 519.59 g/mol): orthorhombic, space group P2₁2₁2₁ (no. 19), a = 9.778(7) Å, b = 15.230(11) Å, c = 17.325(12) Å, V = 2580(3) Å³, Z = 4, T = 298(2) K, μ (MoK α) = 0.165 mm⁻¹, D_{calc} = 1.338 g/cm³, 14848 reflections measured ($3.56^\circ \leq 2\theta \leq 50.298^\circ$), 4625 unique (R_{int} = 0.0511, R_{sigma} = 0.0546) which were used in all calculations. The final R_1 was 0.0432 ($I > 2\sigma(I)$) and wR_2 was 0.1137 (all data).

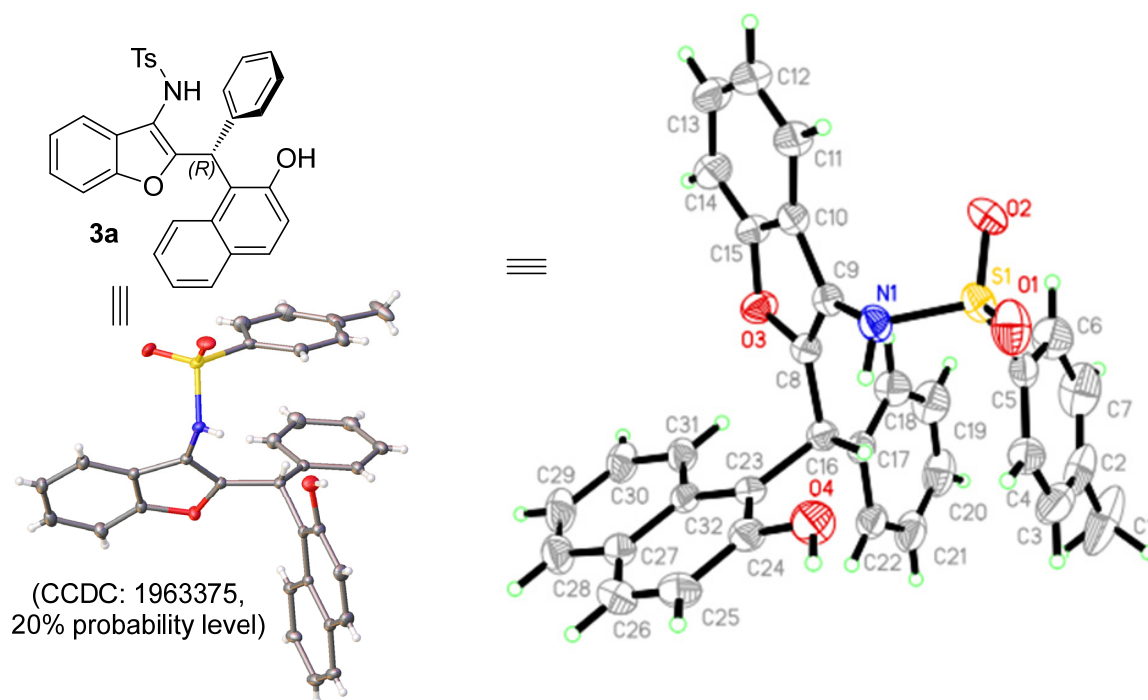


Figure S2. View of **3a**.

Table S4. Crystal data and structure refinement for **3a**.

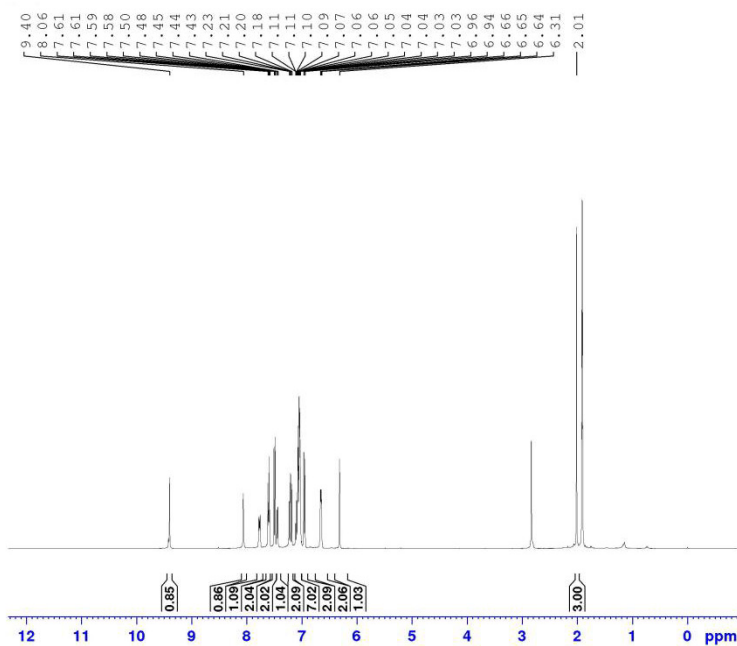
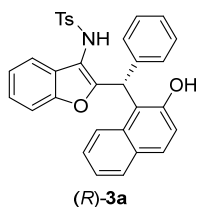
Identification code	3a
Empirical formula	C ₃₂ H ₂₅ NO ₄ S
Formula weight	519.59
Temperature/K	298(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.778(7)
b/Å	15.230(11)
c/Å	17.325(12)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2580(3)
Z	4

ρ calcg/cm ³	1.338
μ /mm ⁻¹	0.165
F(000)	1088.0
Crystal size/mm ³	0.350 × 0.310 × 0.250
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.56 to 50.298
Index ranges	-10 ≤ h ≤ 11, -18 ≤ k ≤ 18, -20 ≤ l ≤ 17
Reflections collected	14848
Independent reflections	4625 [R _{int} = 0.0511, R _{sigma} = 0.0546]
Data/restraints/parameters	4625/0/346
Goodness-of-fit on F ²	0.976
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0432, wR ₂ = 0.0956
Final R indexes [all data]	R ₁ = 0.0735, wR ₂ = 0.1137
Largest diff. peak/hole / e Å ⁻³	0.14/-0.22
Flack parameter	0.02(12)

9 References

- [1] (a) Z. Shi, Q. Tong, W. W. Y. Leong, and G. Zhong, *Chem.-Eur. J.* 2012, **18**, 9802-9806; (b) Y.-G. Zhou, Z. Gu, J.-J. Xie, and G.-F. Jiang, *Asian J. Org. Chem.* 2018, **7**, 1561-1564.
- [2] M. Wang, Z.-Q. Rong, and Y. Zhao, *Chem. Comm.* 2014, **50**, 15309-15312.
- [3] Q. Yin, S. G. Wang, X. W. Liang, D. W. Gao, J. Zheng and S-L. You, *Chem. Sci.*, 2015, **6**, 4179-4183.
- [4] H.-P. Xie, B. Wu, X.-W. Wang and Y.-G. Zhou, *Chin. J. Catal.* **2019**, **40**, 1566-1575.

10 Copies of NMR and HPLC Spectrums

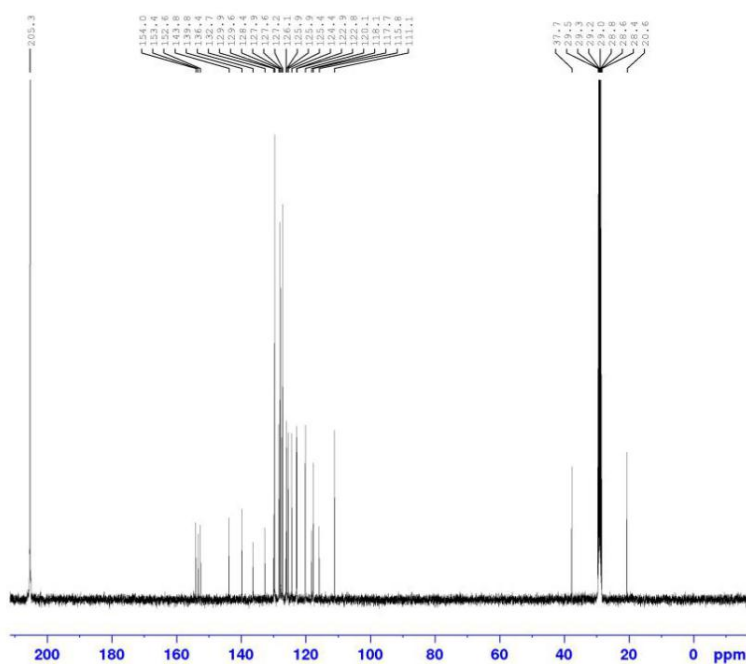


```
Current Data Parameters
NAME      R-17
EXPNO     223
PROCNO    1

F2 - Acquisition Parameters
Date_     20190419
Time      8.07
INSTRUM   spect
PROBHD     5 mm PABBO BB/
PULPROG    zg30
TD         65536
SOLVENT    Acetone
NS          8
DS          0
SWH        8012.820 Hz
FIDRES     0.122266 Hz
AQ         4.0894465 sec
RG         52.37
SW         62.400 usec
DE         6.50 usec
TE         295.1 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
SF01      400.1522058 MHz
NUC1       1H
P1         10.75 usec
PLM1       17.50000000 W

F2 - Processing parameters
SI         65536
SF         400.1500640 MHz
WDW        EM
SSB         0
LB          0.30 Hz
GB          0
PC          1.00
```



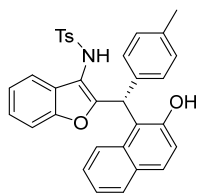
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Current Data Parameters
NAME      R-17
EXPNO     224
PROCNO    1

F2 - Acquisition Parameters
Date_     20190419
Time      8.30
INSTRUM   spect
PROBHD     5 mm PABBO BB/
PULPROG    zgpg30
TD         65536
SOLVENT    Acetone
NS          447
DS          0
SWH        25252.525 Hz
FIDRES     0.385323 Hz
AQ         1.2976128 sec
RG         195.85
DW         19.800 usec
DE         6.50 usec
TE         295.3 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

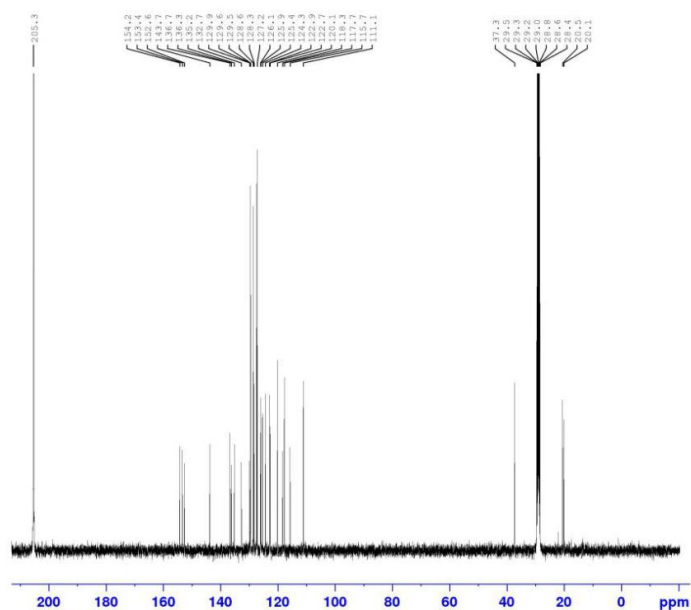
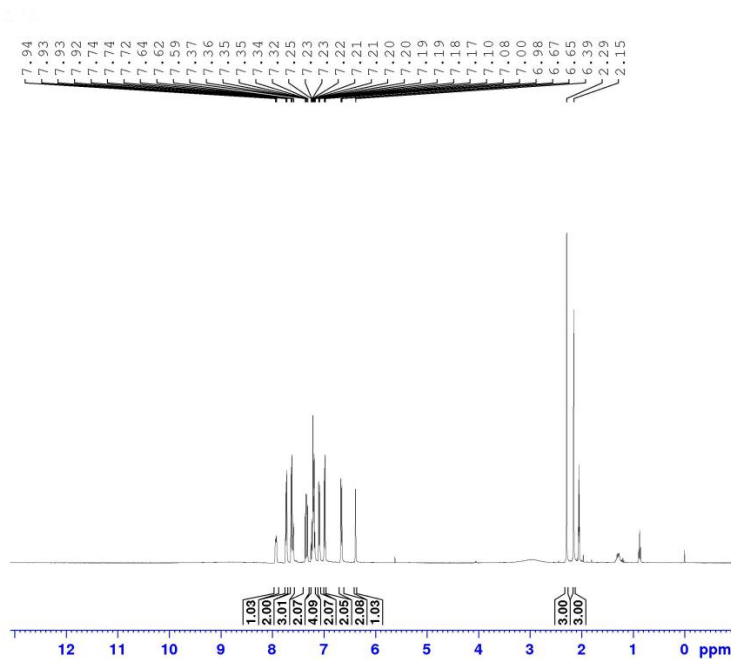
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SF01      100.6283629 MHz
NUC1       13C
P1         10.50 usec
PLM1       74.00000000 W

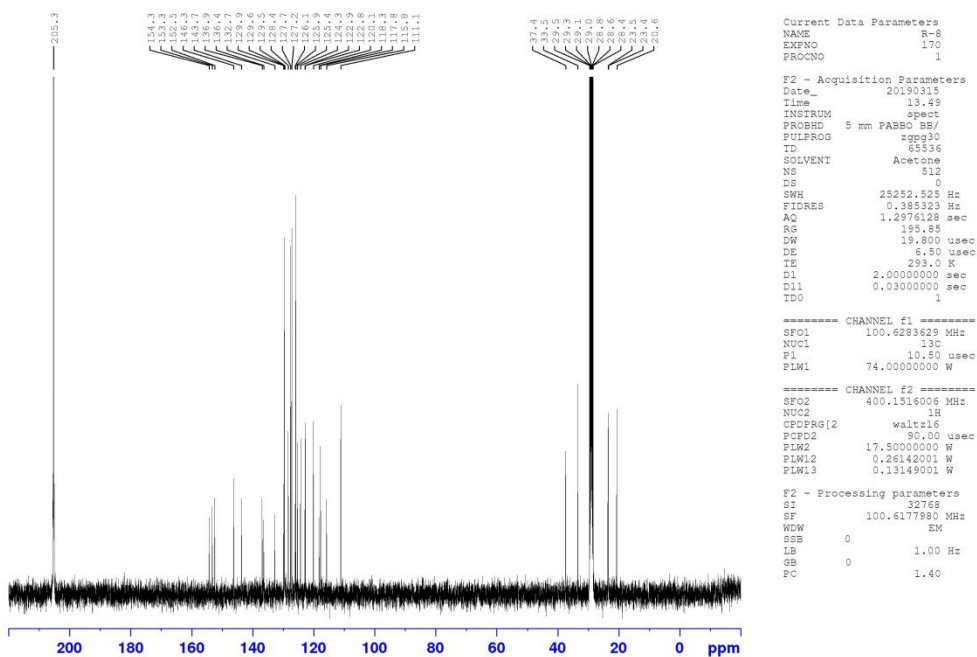
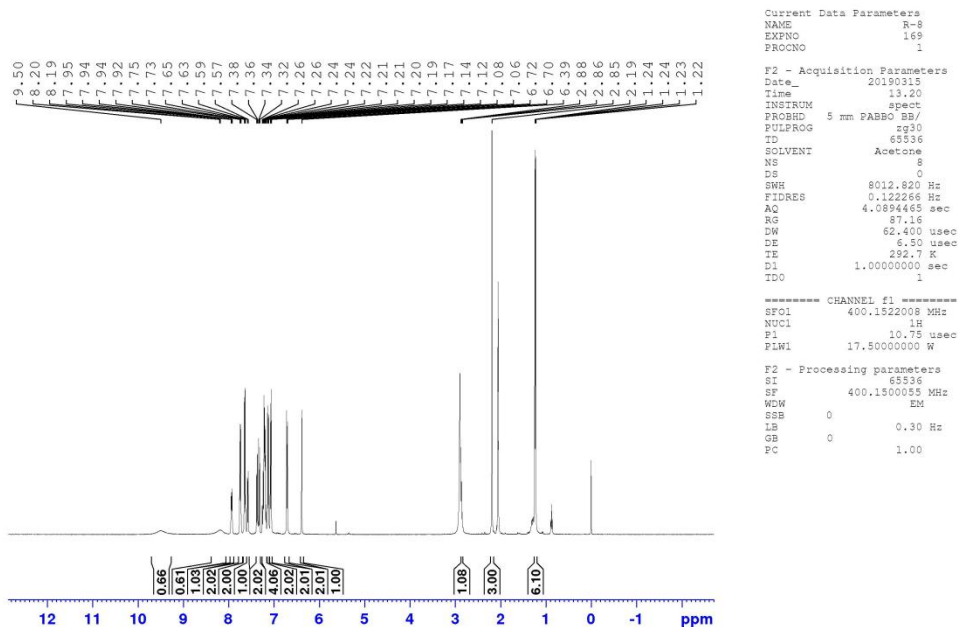
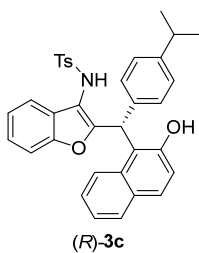
===== CHANNEL f2 =====
SF02      400.1516006 MHz
NUC2       1H
CPDPRG[2] waltz16
PCPD2     90.00 usec
PLM2      17.50000000 W
PLM12     0.26142001 W
PLM13     0.13149001 W

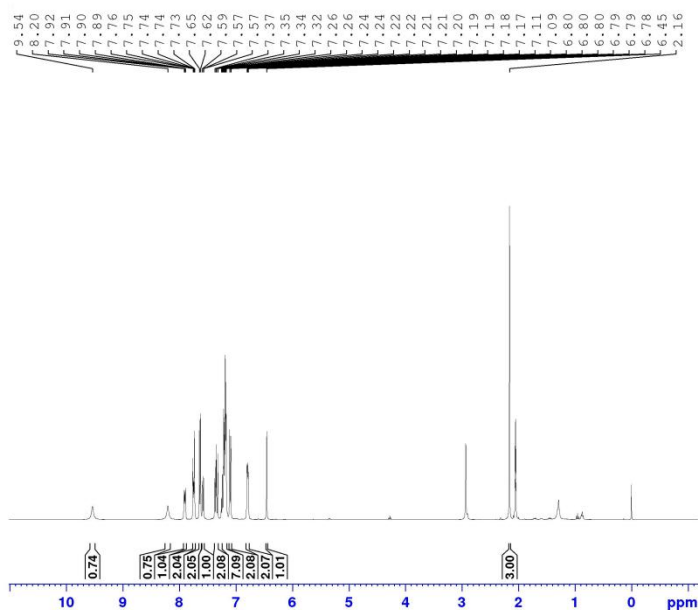
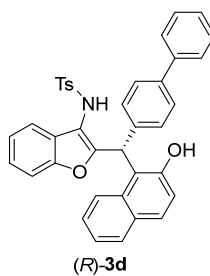
F2 - Processing parameters
SI         32768
SF         100.6177980 MHz
WDW        EM
SSB         0
LB          1.00 Hz
GB          0
PC          1.40
```



(R)-3b







```

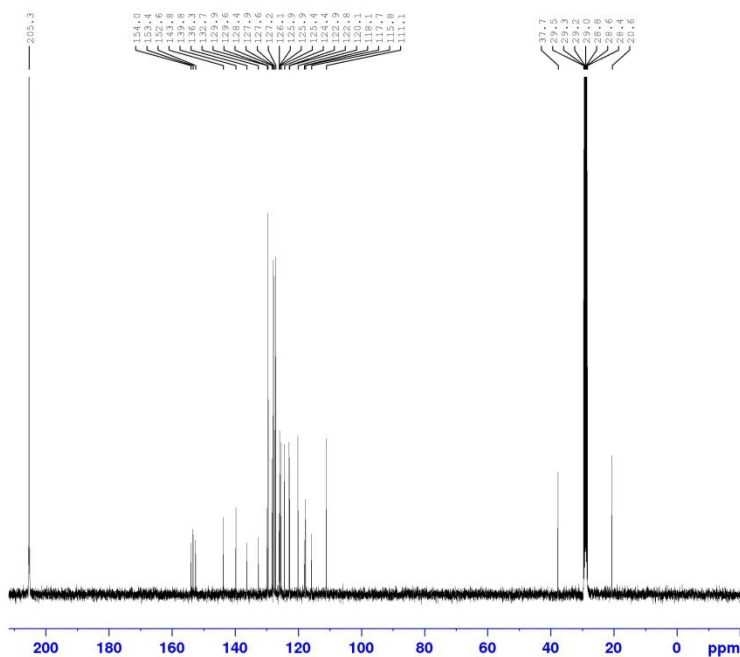
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NAME      R-7
EXPNO    175
PROCNO    1

F2 - Acquisition Parameters
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Time      1.33
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         65536
SOLVENT   Acetone
NS         8
DS         0
SWH        8012.820 Hz
FIDRES     0.122256 Hz
AQ         4.0894465 sec
RG         71.53
DM         62.400 usec
DE         6.50 usec
TE         292.6 K
D1         1.0000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      400.1522008 MHz
NUC1       1H
P1         10.75 usec
PLM1       17.5000000 W

F2 - Processing parameters
SI         65536
SF         400.1500063 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```



```

Current Data Parameters
NAME      R-7
EXPNO    176
PROCNO    1

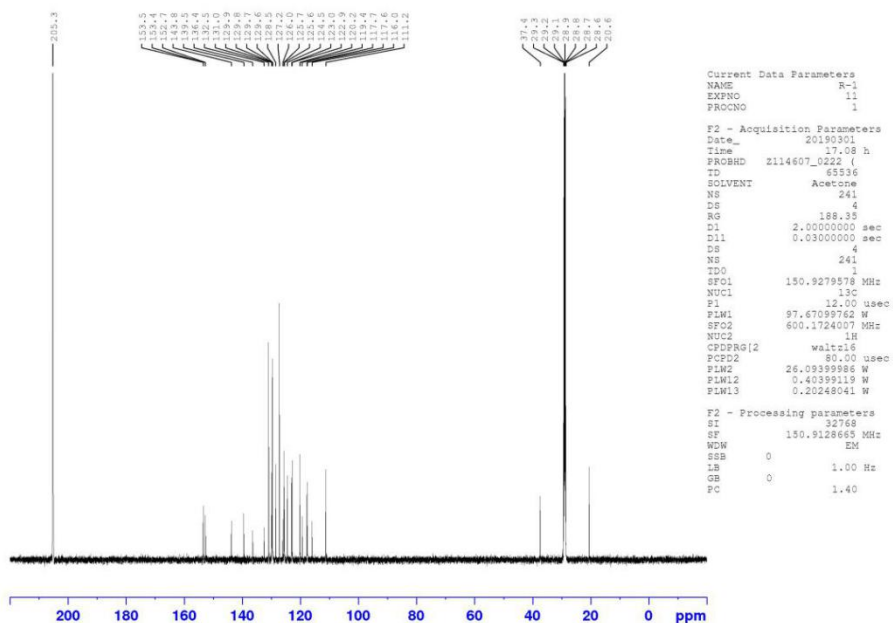
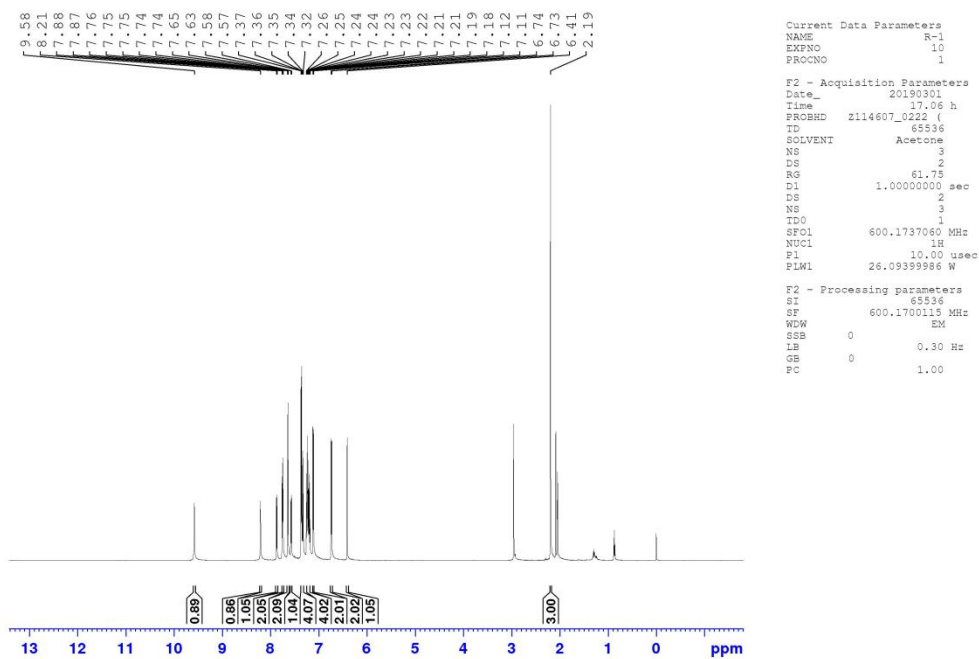
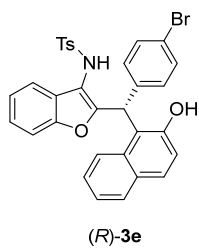
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Time      2.03
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   Acetone
NS         512
DS         0
SWH        25252.525 Hz
FIDRES     0.385323 Hz
AQ         1.2976128 sec
RG         195.85
DM         19.800 usec
DE         6.50 usec
TE         293.1 K
D1         2.0000000 sec
D11        0.0300000 sec
TD0        1

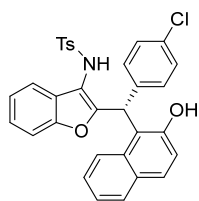
===== CHANNEL f1 =====
SFO1      100.6283629 MHz
NUC1       13C
P1         10.50 usec
PLM1       74.0000000 W

===== CHANNEL f2 =====
SFO2      400.1516006 MHz
NUC2       1H
PCPDPRG[2] waltz16
PCPD2      90.00 usec
PLM2       17.5000000 W
PLM12      0.26142001 W
PLM13      0.13149001 W

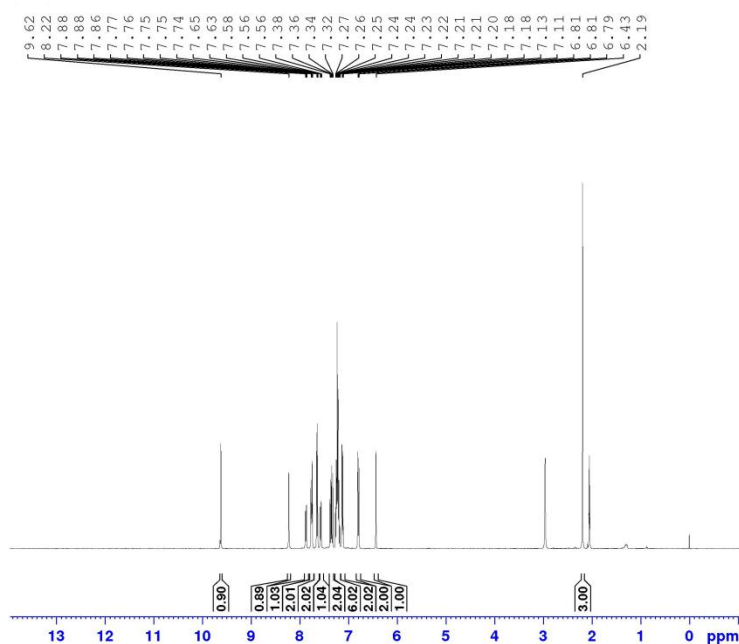
F2 - Processing parameters
SI         32768
SF         100.6177980 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

```





(R)-3f



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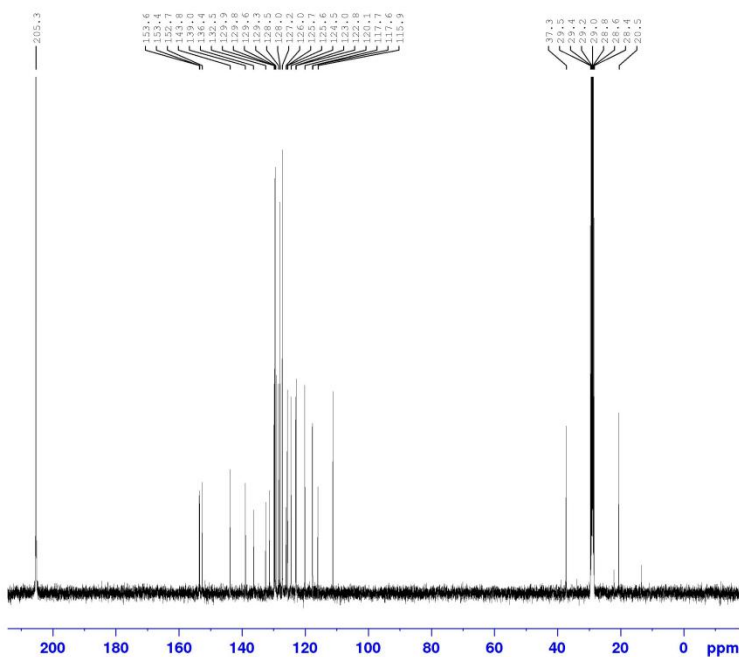
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EXPNO     187
PROCNO    1

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PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   Acetone
NS         8
DS         0
SWH        8012.820 Hz
FIDRES     0.122266 Hz
AQ         4.0894465 sec
RG         63.8
DW         62.400 usec
DE         6.50 usec
TE         294.3 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      400.1522008 MHz
NUC1       1H
P1         10.78 usec
PLW1      17.50000000 W

F2 - Processing Parameters
SI         65536
SF         400.1500065 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```



```

Current Data Parameters
NAME      R-12
EXPNO     184
PROCNO    1

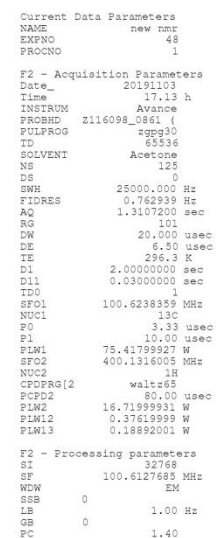
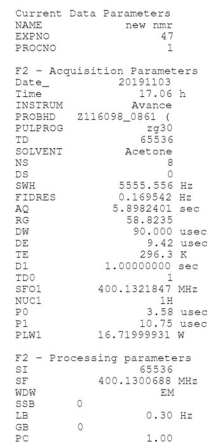
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Date_     20190325
Time      23.06
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   Acetone
NS         425
DS         0
SWH        25252.525 Hz
FIDRES     0.385323 Hz
AQ         1.2976128 sec
RG         135.85
DW         19.800 usec
DE         6.50 usec
TE         294.1 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      100.6283629 MHz
NUC1      13C
P1         10.50 usec
PLW1      74.00000000 W

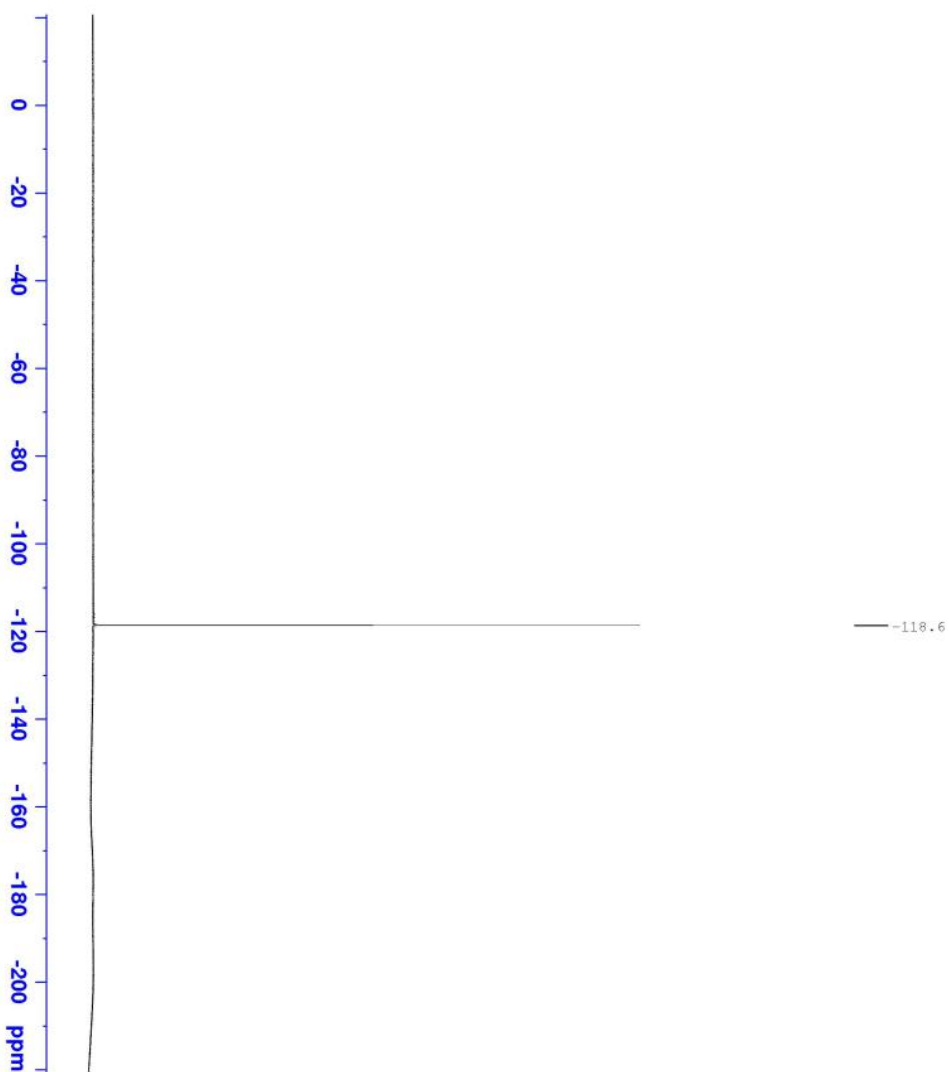
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SFO2      400.1516006 MHz
NUC2       1H
CPDPRG2   waltz16
PCPD2     90.00 usec
PLW2      17.50000000 W
PLM12     0.28142001 W
PLM13     0.13149001 W

F2 - Processing Parameters
SI         32768
SF         100.6177980 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

```



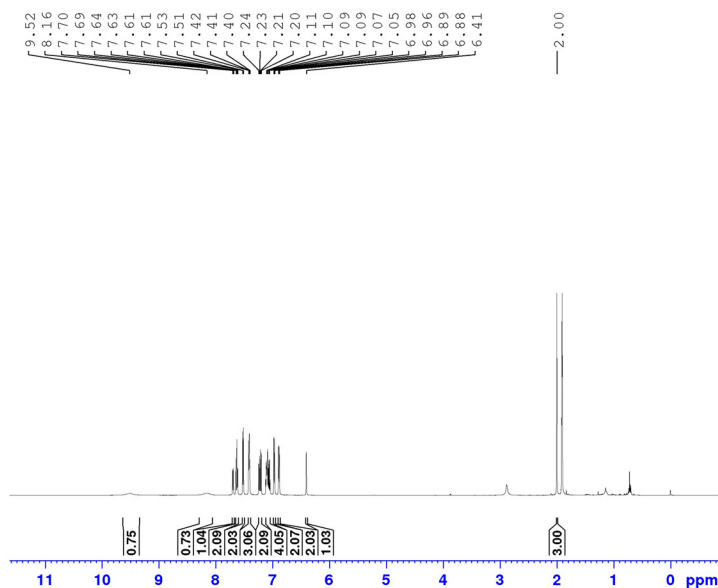
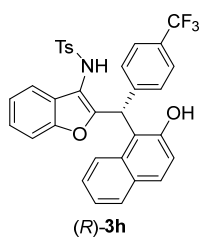
2-F



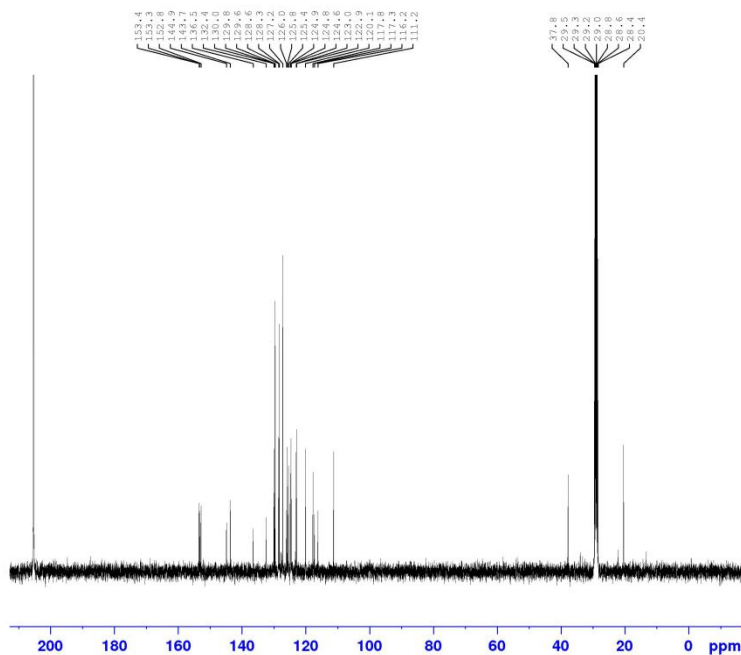
Current Data Parameters
NAME new mr
EXPNO 50
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121103
Time_ 17.19 h
INSTRUM Avance
PROBHD Z16096-0861 (29
PULPROG zgpg30
ID 131072
SOLVENT Acetone
NS 16
DS 4
SWH 90909.094 Hz
FIDRES 1.387163 Hz
AQ 0.720860 sec
RG 101
DW 5.500 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
SFO1 376.4607164 MHz
NUC1 19F
P1 18.00 usec
PLM1 16.38400078 W

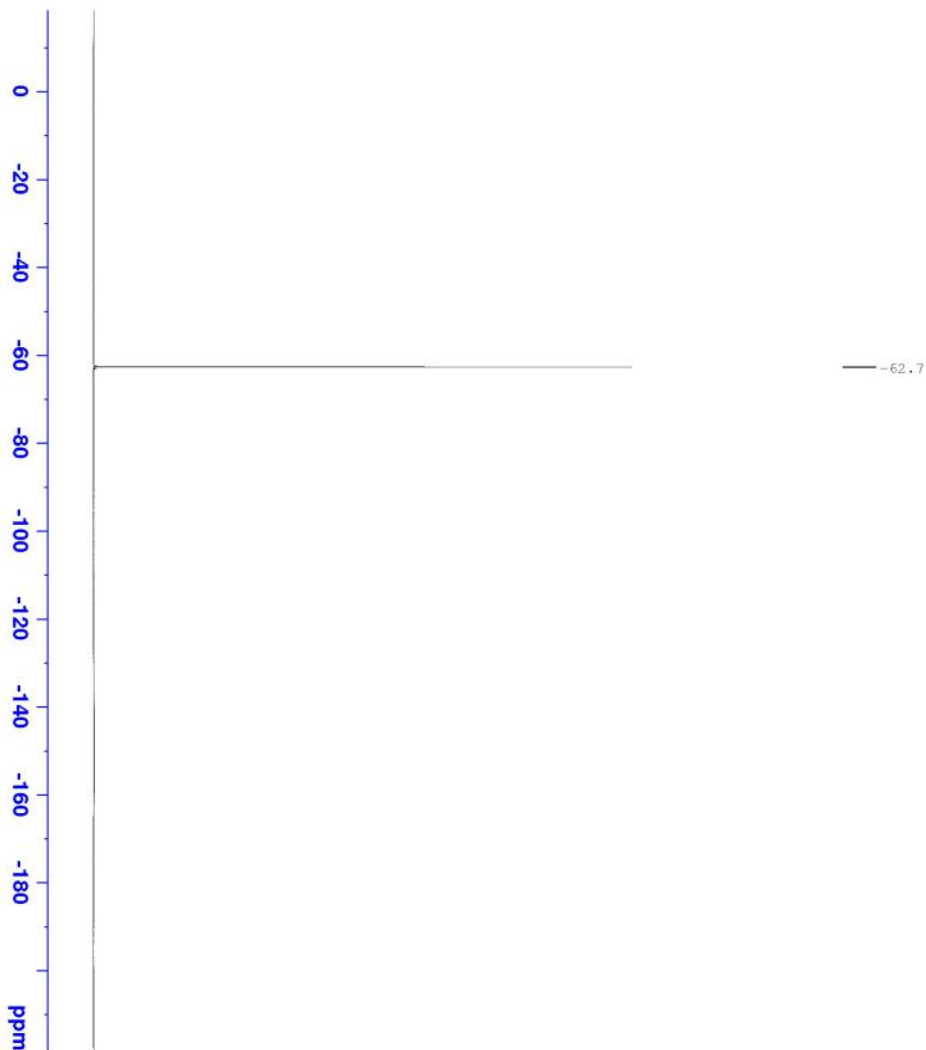
F2 - Processing parameters
SI 32768
SF 376.4607164 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME Dec11-2019-wangchengjie
EXPNO 100
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191211
Time 12.17 h
PROBHD Z114607_D222 (1
TD 65536
SOLVENT Acetone
NS 16
DS 2
RG 30.88
D1 1.00000000 sec
DS 2
NS 16
TD0
SFO1 600.1737060 MHz
NUC1 1H
P1 15.00 usec
PLW1 26.09399986 W
F2 - Processing parameters
SI 65536
SF 600.1700974 MHz
WVW 1M
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME old nmr
EXPNO 158
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190310
Time 10.23
INSTRUM spect
PROBHD 5 mm PABBO BB//
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 194
DS 0
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2876128 sec
RG 195.85
DM 19.800 usec
DE 6.50 usec
TE 292.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 100.6283629 MHz
NUC1 13C
P1 10.50 usec
PLW1 74.00000000 W
===== CHANNEL f2 =====
SFO2 400.1516006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 17.50000000 W
PLW12 0.26142001 W
PLW13 0.13149001 W
F2 - Processing parameters
SI 32768
SF 100.6177980 MHz
WVW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



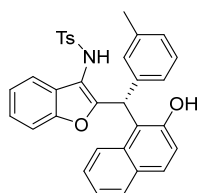
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Current Data Parameters
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EXPNO     159
PROCNO    1

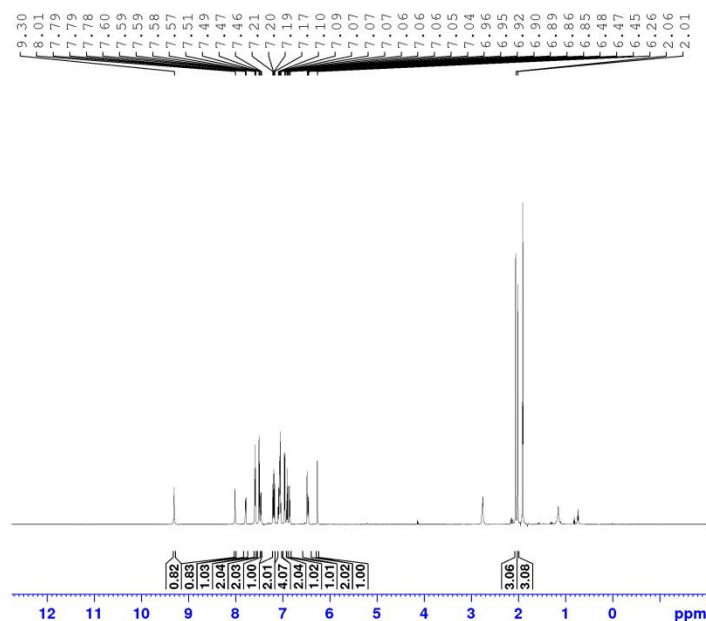
F2 - Acquisition Parameters
Date_     20190310
Time      10.34
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
ID         131072
SOLVENT   Acetone
NS         16
DS         4
SWH        89285.711 Hz
FIDRES     0.681196 Hz
AQ         0.7340032 sec
RG         195.85
DW         5.600 usec
DE         6.50 usec
TE         292.6 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1       376.4795333 MHz
NUC1       19F
P1         14.00 usec
PL1        24.85000038 W

F2 - Processing parameters
SI         65536
SF         376.5171850 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```



(R)-3i

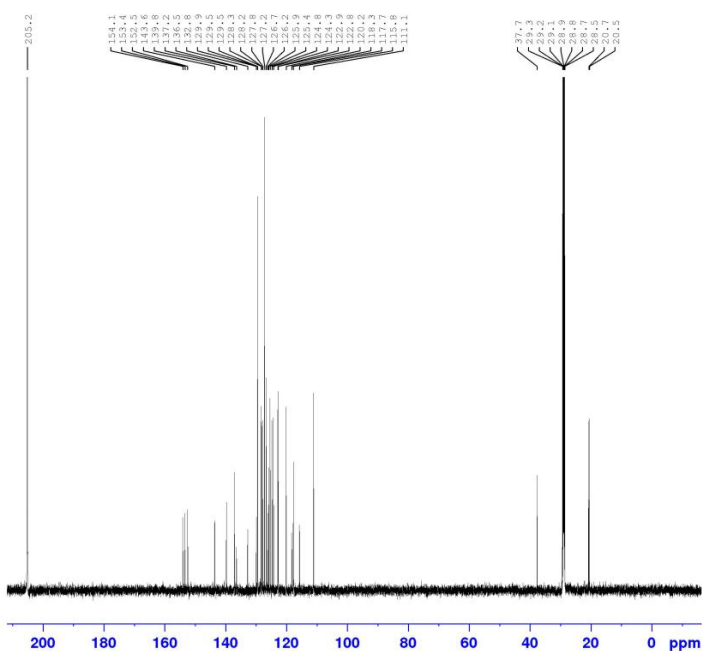


```

Current Data Parameters
NAME      R-19
EXPNO     60
PROCNO    1

F2 - Acquisition Parameters
Date_     20190411
Time      21.53 h
PROBHD    Z114607_0222 (
TD         65536
SOLVENT   Acetone
NS         2
DS         2
RG         53.41
D1         1.00000000 sec
DS         2
NS         2
TD0        1
SFO1       600.1737060 MHz
NUC1       1H
P1         10.00 usec
PLW1       26.09399986 W

F2 - Processing parameters
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SF         600.1700980 MHz
WDW        EM
SSB        0
LB         0.30 Hz
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PC         1.00
  
```

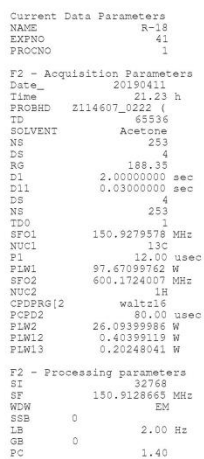
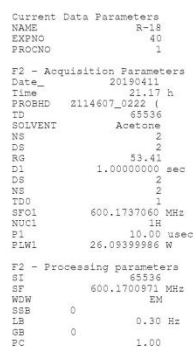


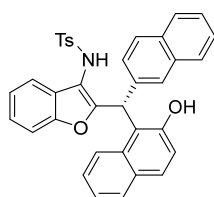
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Current Data Parameters
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EXPNO     61
PROCNO    1

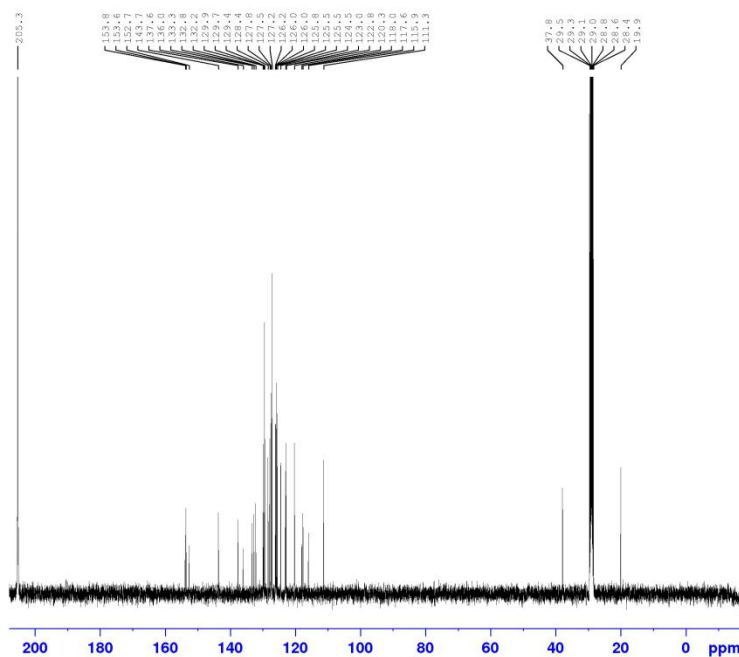
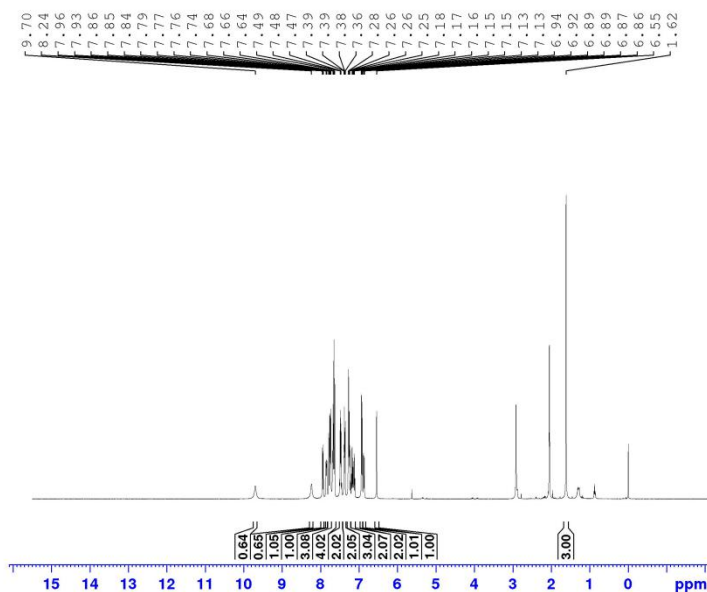
F2 - Acquisition Parameters
Date_     20190411
Time      22.08 h
PROBHD    Z114607_0222 (
TD         65536
SOLVENT   Acetone
NS         280
DS         4
RG         188.35
D1         2.00000000 sec
D11        0.03000000 sec
DS         4
NS         280
TD0        1
SFO1       150.9279578 MHz
NUC1       13C
P1         12.00 usec
PLW1       97.67099762 W
SFO2       600.1724007 MHz
NUC2       1H
CPDPRG2   waltz16
PCPD2      80.00 usec
PLM2       26.09399986 W
PLM12      0.40399119 W
PLM13      0.20248041 W

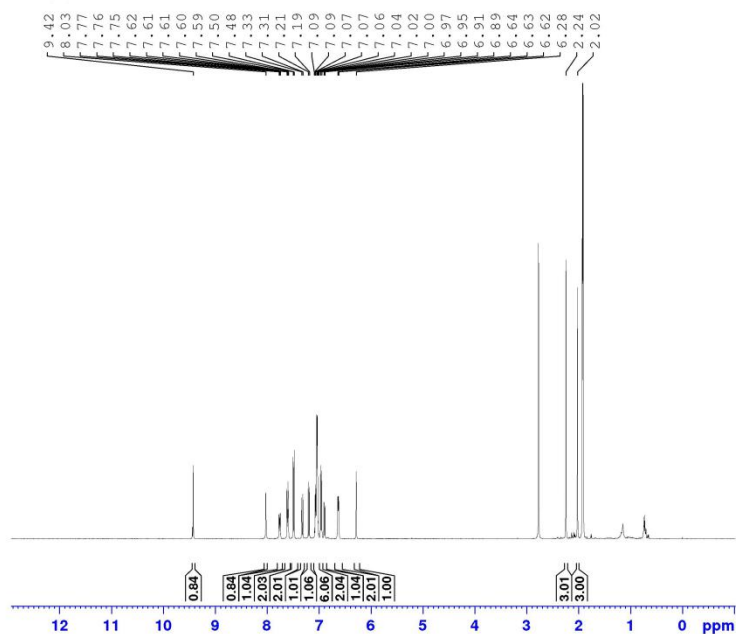
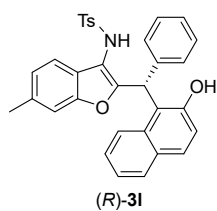
F2 - Processing parameters
SI         32768
SF         150.9128663 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```





(R)-3k





```

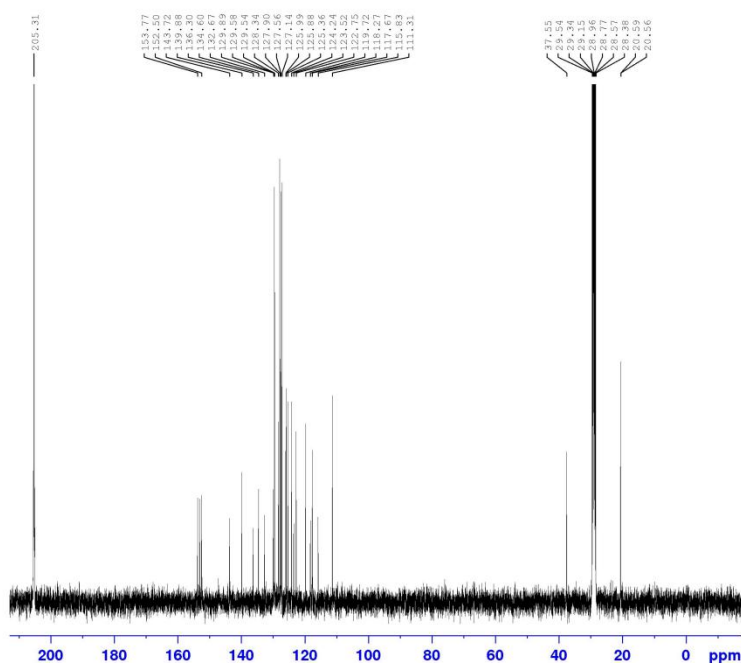
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EXPNO     194
PROCNO    1

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Time      8.34
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PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         65536
SOLVENT   Acetone
NS         8
DS         0
SWH        8012.820 Hz
FIDRES     0.122266 Hz
AQ         4.0894465 sec
RG         71.53
DW         62.400 usec
DE         6.50 usec
TE         293.1 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      400.1522008 MHz
NUC1       1H
P1         10.75 usec
PLW1       17.50000000 W

F2 - Processing parameters
SI         65536
SF         400.1500603 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```



```

Current Data Parameters
NAME      R-24
EXPNO     195
PROCNO    1

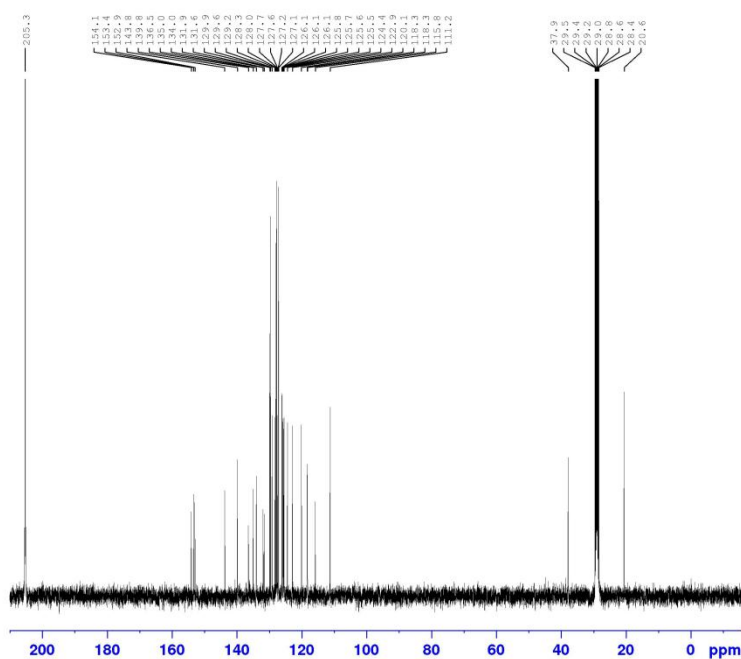
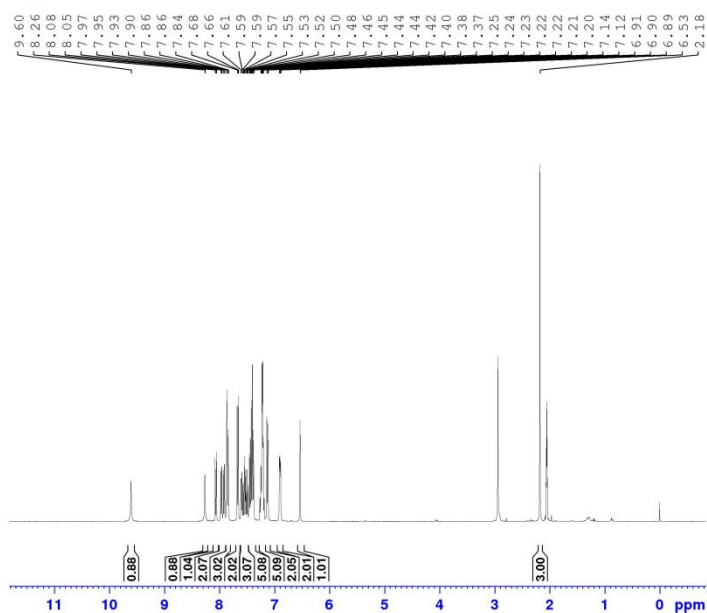
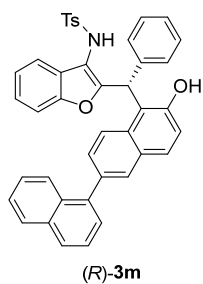
F2 - Acquisition Parameters
Date_     20190402
Time      8.41
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   Acetone
NS         512
DS         0
SWH        25252.525 Hz
FIDRES     0.385323 Hz
AQ         1.2976128 sec
RG         195.85
DW         19.800 usec
DE         6.50 usec
TE         293.4 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

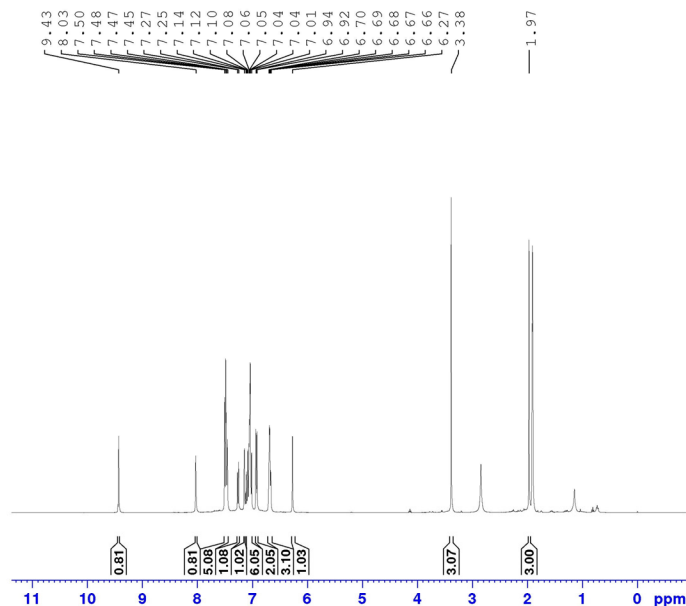
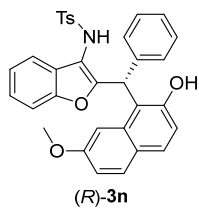
===== CHANNEL f1 =====
SFO1      100.6283629 MHz
NUC1       13C
P1         10.50 usec
PLW1       74.00000000 W

===== CHANNEL f2 =====
SFO2      400.1516006 MHz
NUC2       1H
CPDPRG2   waltz16
PCPD2     90.00 usec
PLM2      17.50000000 W
PLW2      0.26142001 W
PLM3      0.13149001 W

F2 - Processing parameters
SI         32768
SF         100.6177980 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

```





```

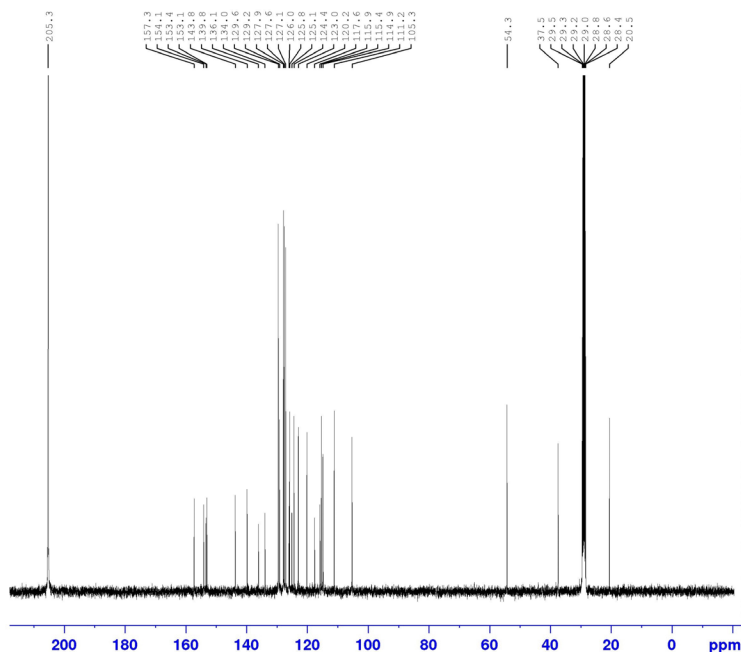
Current Data Parameters
NAME      R-4
EXPNO     250
PROCNO    1

F2 - Acquisition Parameters
Date_     20190510
Time      19.08
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         65536
SOLVENT   Acetone
NS         8
DS         0
SWH        8012.820 Hz
FIDRES     0.122266 Hz
AQ         4.0894465 sec
RG         31.56
DW         62.400 usec
DE         6.50 usec
TE         296.5 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      400.1522008 MHz
NUC1      1H
P1        10.75 usec
PLW1      17.50000000 W

F2 - Processing parameters
SI         65536
SF         400.1500643 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

```



```

Current Data Parameters
NAME      R-4
EXPNO     251
PROCNO    1

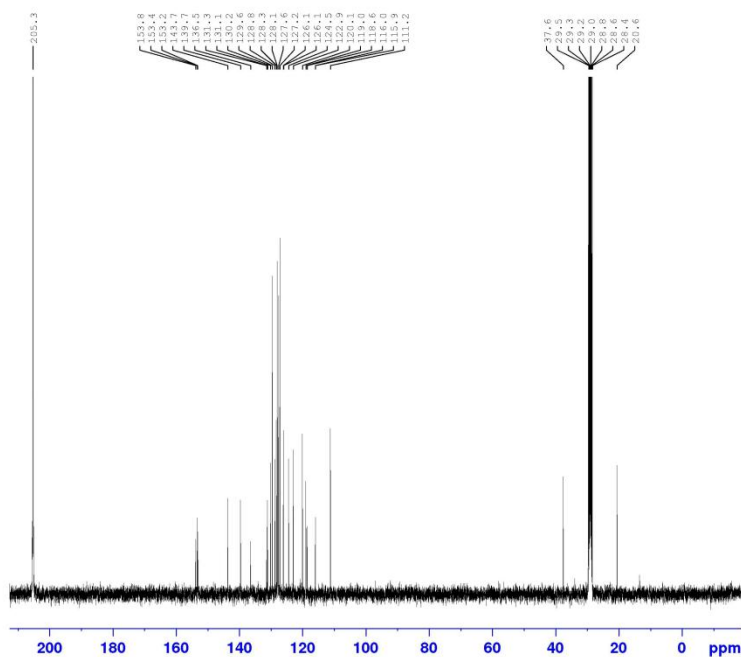
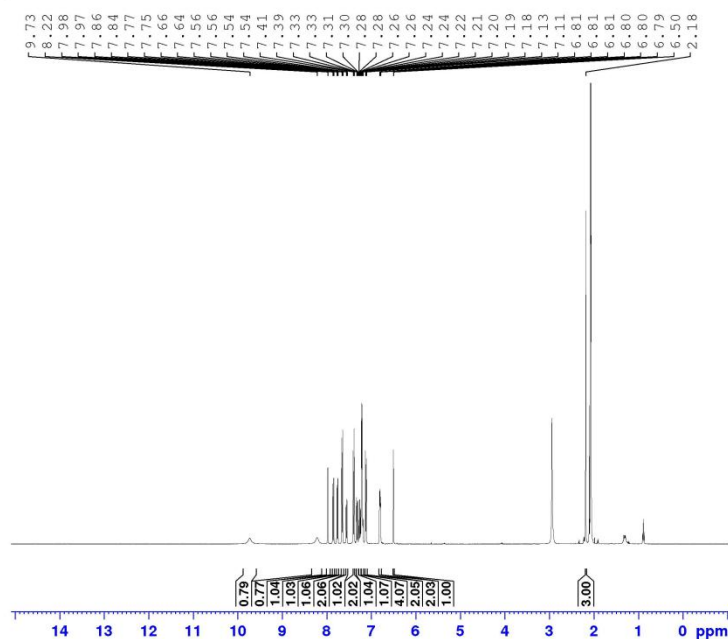
F2 - Acquisition Parameters
Date_     20190510
Time      19.22
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   Acetone
NS         512
DS         0
SWH        25252.525 Hz
FIDRES     0.385323 Hz
AQ         1.2976128 sec
RG         195.85
DW         19.800 usec
DE         6.50 usec
TE         297.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

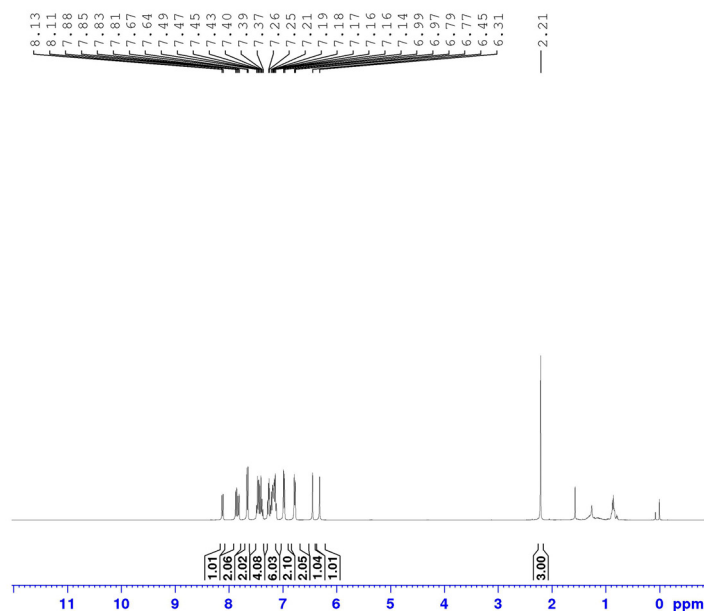
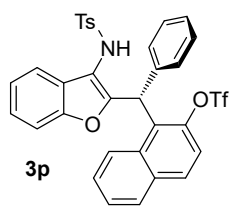
===== CHANNEL f1 =====
SFO1      100.6283629 MHz
NUC1      13C
P1        10.50 usec
PLW1      74.00000000 W

===== CHANNEL f2 =====
SFO2      400.1516006 MHz
NUC2      1H
CPDPRG2   waltz16
PCPD2     90.00 usec
PLW2      17.50000000 W
PLW12     0.26142001 W
PLW13     0.13149001 W

F2 - Processing parameters
SI         32768
SF         100.6177990 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

```



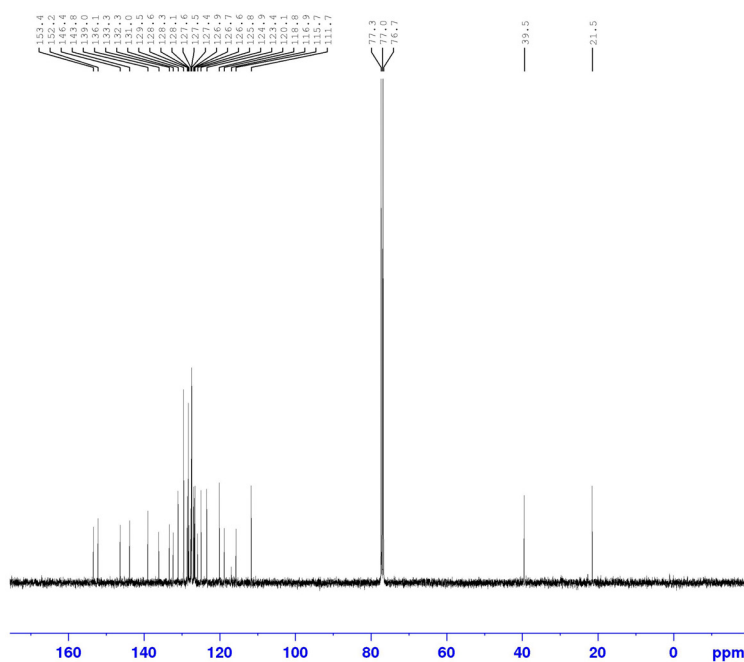


```
Current Data Parameters
NAME      old nmr
EXPNO     260
PROCNO    1

F2 - Acquisition Parameters
Date_     20190517
Time      5.23
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         0
SWH        8012.820 Hz
FIDRES     0.122266 Hz
AQ         4.089465 sec
RG         78.11
DW         62.400 usec
DE         6.50 usec
TE         297.3 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      400.1522008 MHz
NUC1       1H
P1         10.75 usec
PLW1      17.50000000 W

F2 - Processing parameters
SI         65536
SF         400.1500128 MHz
WDW        EM
SSB        0
GB         0
PC         1.00
```



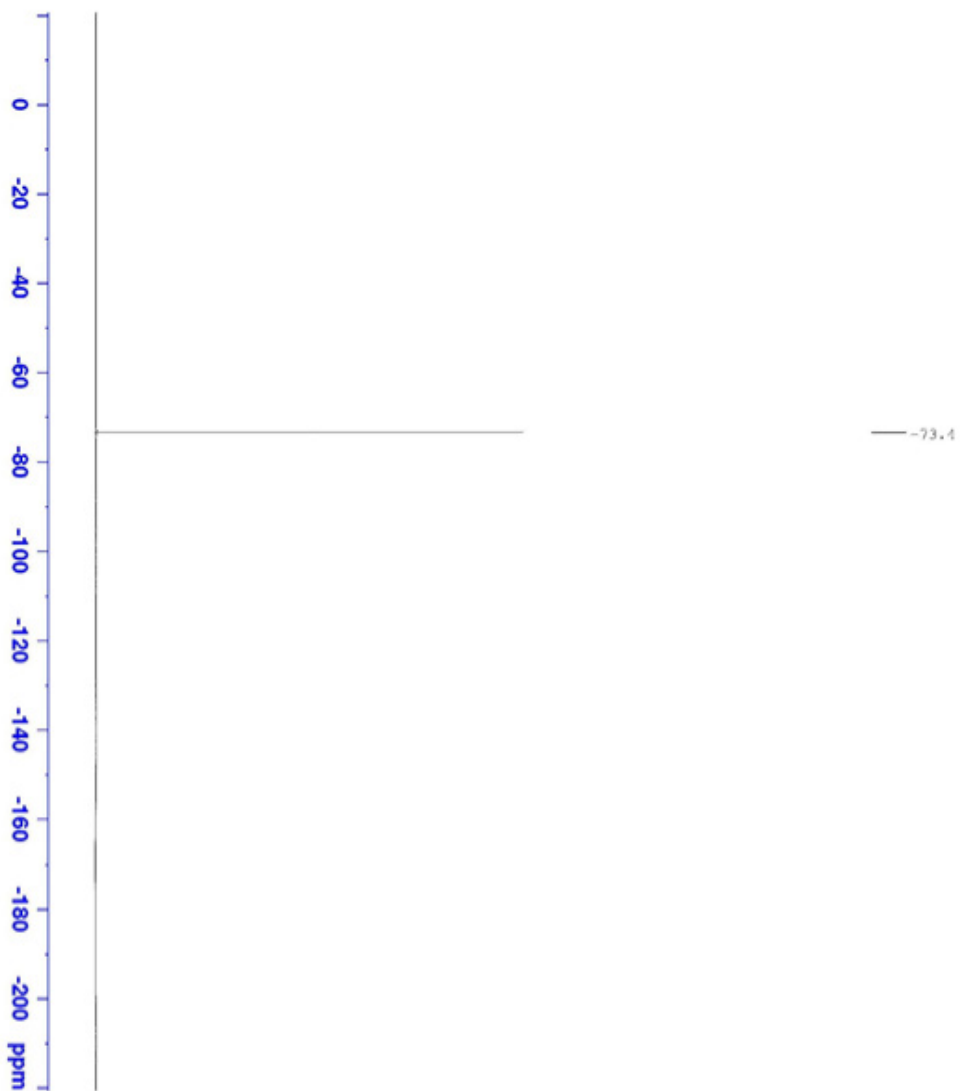
```
Current Data Parameters
NAME      old nmr
EXPNO     261
PROCNO    1

F2 - Acquisition Parameters
Date_     20190517
Time      5.53
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         512
DS         0
SWH        25252.525 Hz
FIDRES     0.385323 Hz
AQ         1.2976128 sec
RG         195.85
DW         19.800 usec
DE         6.50 usec
TE         297.8 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      100.6283629 MHz
NUC1       13C
P1         10.50 usec
PLW1      74.00000000 W

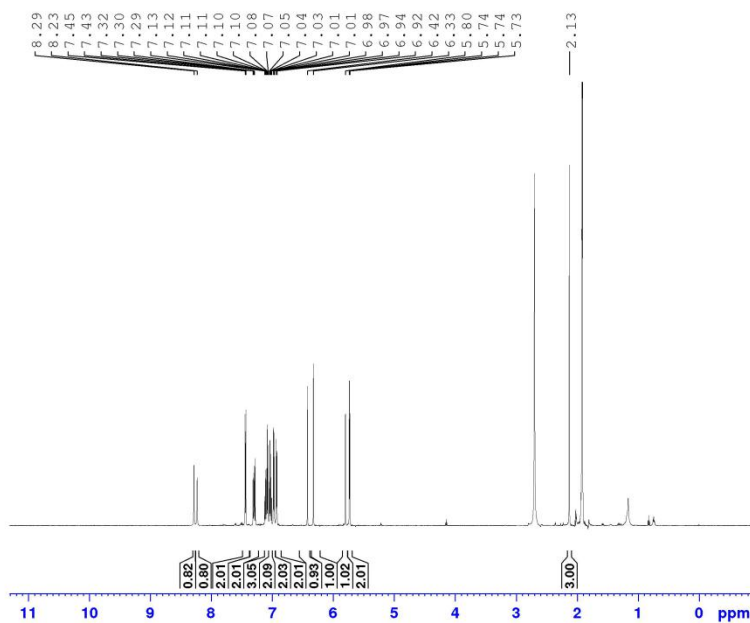
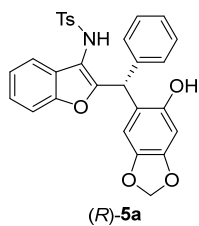
===== CHANNEL f2 =====
SFO2      400.1516006 MHz
NUC2       1H
CPDPRG2   waltz16
PCPD2     90.00 usec
PLM2      17.50000000 W
PLM12     0.26142001 W
PLM13     0.13149001 W

F2 - Processing parameters
SI         32768
SF         100.6177980 MHz
WDW        EM
SSB        0
GB         0
PC         1.40
```



```

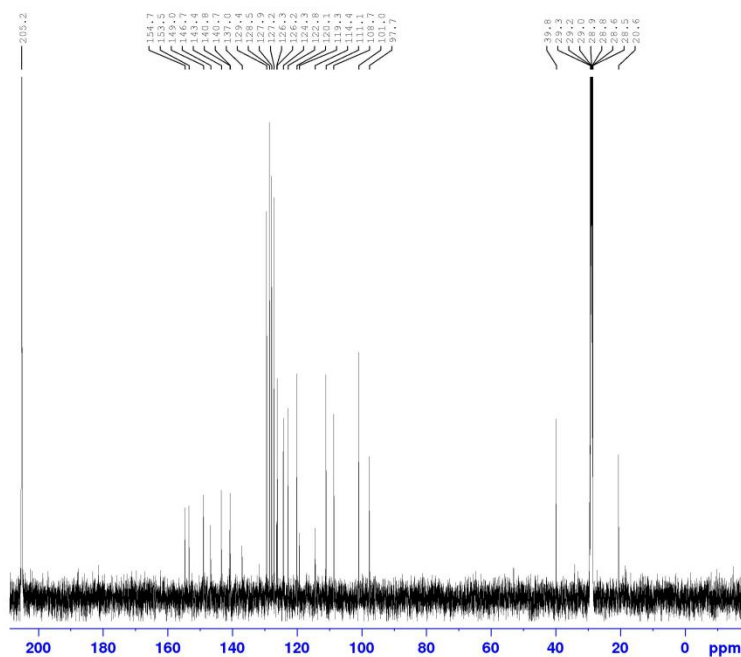
Current Data Parameters
NAME          Ref 1
EXPNO        32
PROCNO       1
F2 - Acquisition Parameters
Date_        201214
Time         1.14 h
INSTRUM      Avance
PROBHD       516098_0861 (
PULPROG      zgpg
TD           65536
FIDRES       15.072
SOLVENT      CDCl3
NS           16
DS           4
SFR          52903.004 Hz
F2REFS       1.58163 Hz
AQ           0.120550 sec
RG           512
DM           5.500 usec
DE           6.50 usec
IE           24.3 K
D-           1.0000000 sec
TD3          376.460764 MHz
SFO1         125
NUC1         13C
P-           18.00 usec
FID1         16.3840078 M
F2 - Processing parameters
SI           65536
SF           376.458662 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
  
```



Current Data Parameters
NAME R-22
EXPNO 50
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190411
Time 21.35 h
PROBHD Z114607_0222 ()
TD 65536
SOLVENT Acetone
NS 3
DS 2
RG 84.67
D1 1.00000000 sec
DS 2
NS 3
TD0 1
SFO1 600.1737060 MHz
NUC1 1H
P1 10.00 usec
PLW1 26.09399986 W

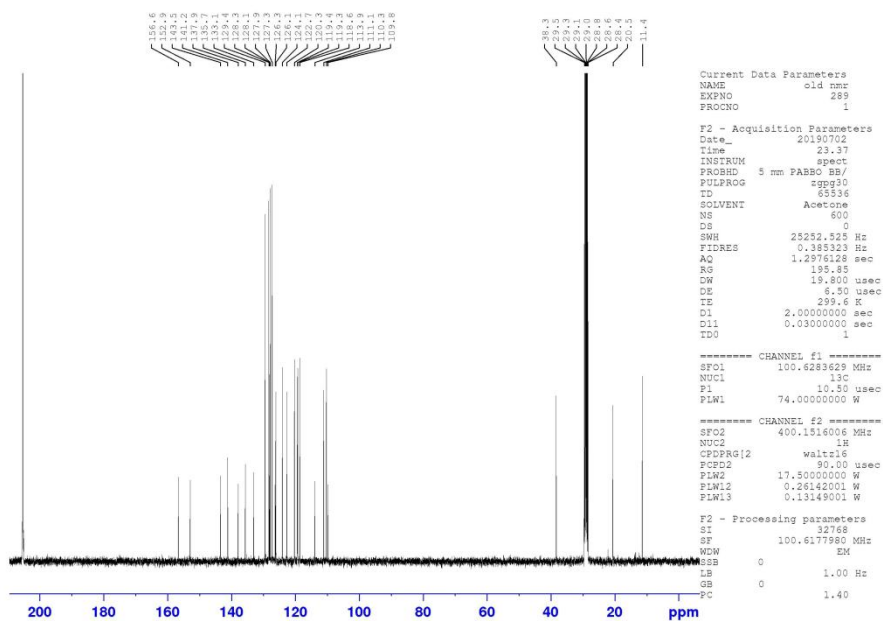
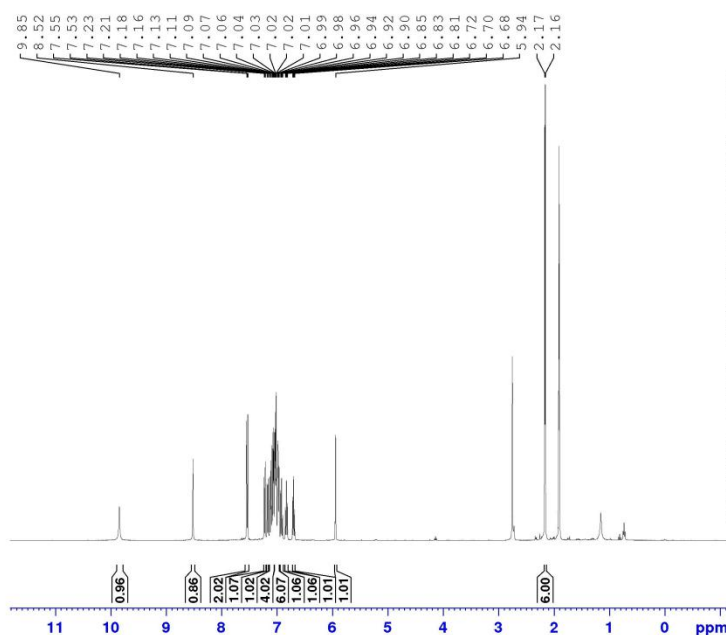
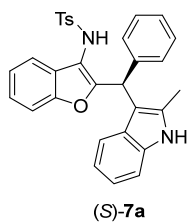
F2 - Processing parameters
SI 65536
SF 600.1700912 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



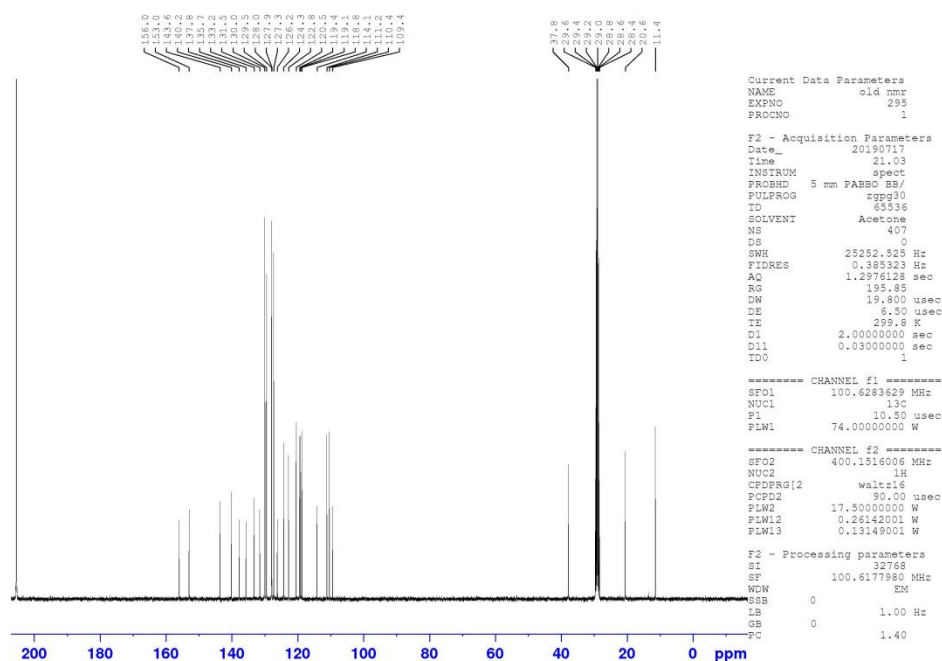
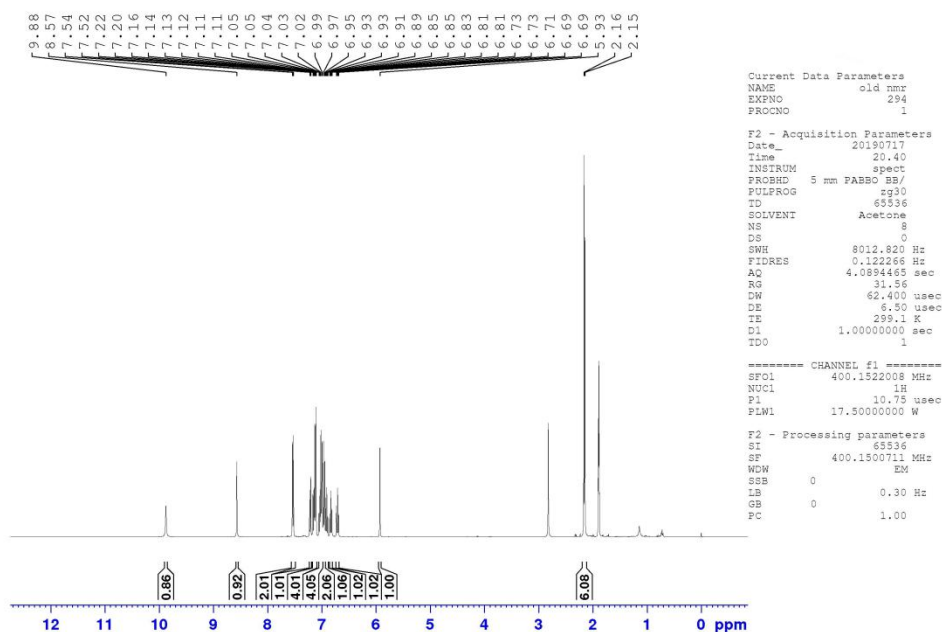
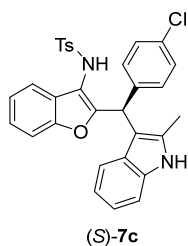
Current Data Parameters
NAME R-22
EXPNO 51
PROCNO 1

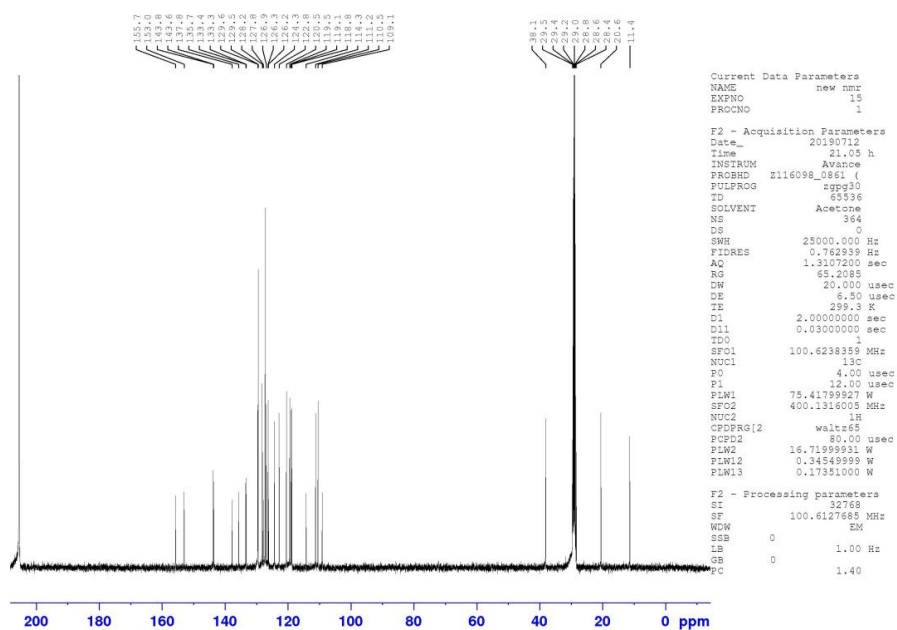
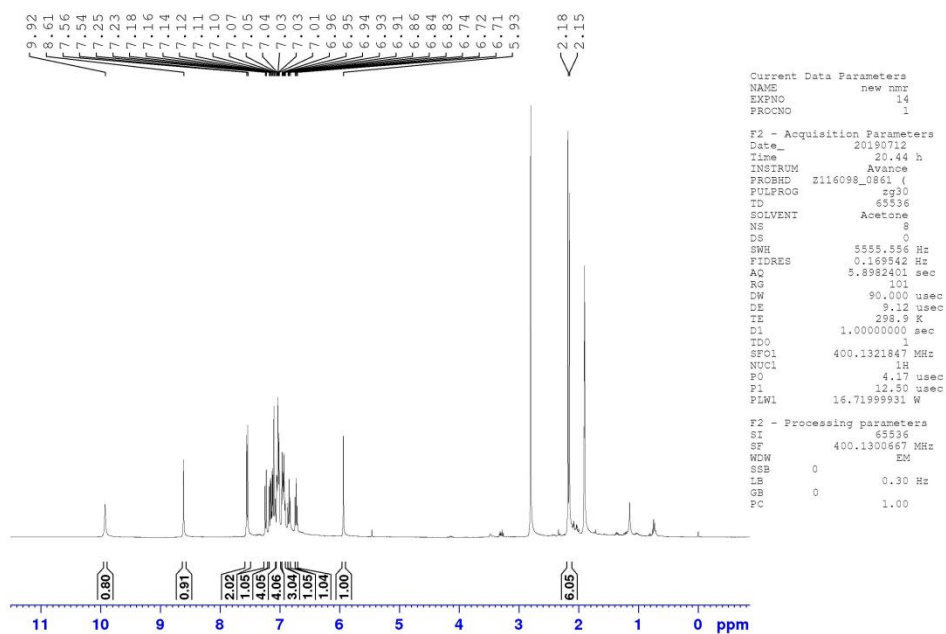
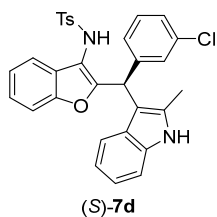
F2 - Acquisition Parameters
Date_ 20190411
Time 21.49 h
PROBHD Z114607_0222 ()
TD 65536
SOLVENT Acetone
NS 256
DS 4
RG 158.33
D1 2.00000000 sec
D11 0.03000000 sec
DS 4
NS 256
TD0 1
SFO1 150.9279578 MHz
NUC1 13C
P1 12.00 usec
PLW1 97.67099762 W
SFO2 600.1724007 MHz
NUC2 1H
CPCPRG[2] waltz16
PCPD2 80.00 usec
PLW2 26.09399986 W
PLW12 0.40399119 W
PLW13 0.20248041 W

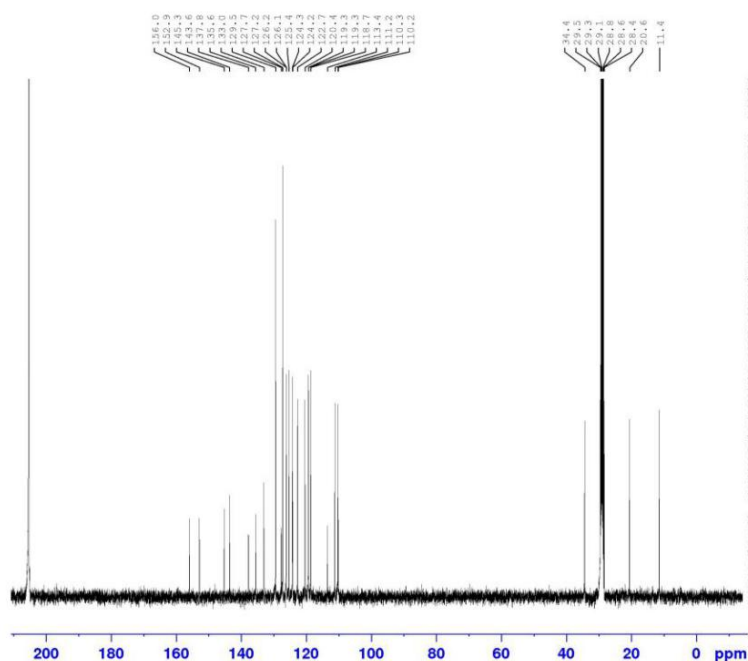
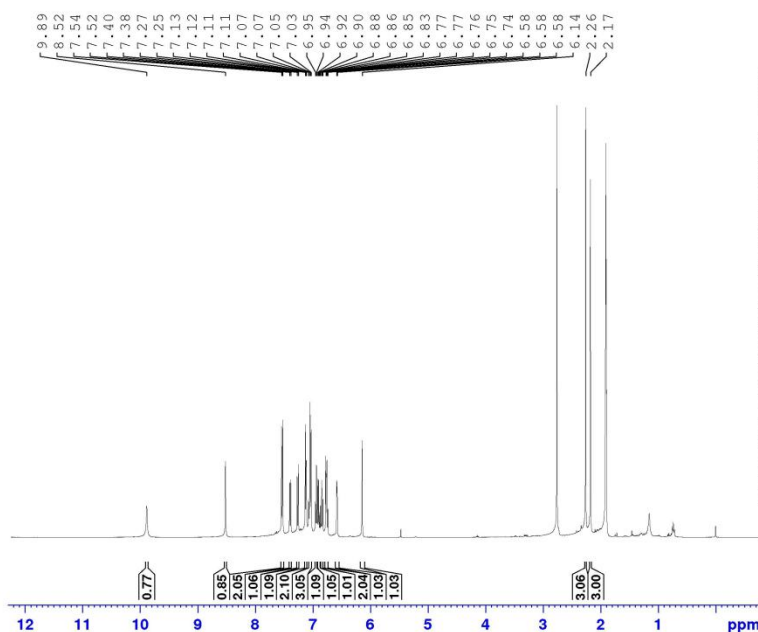
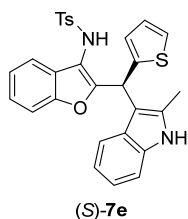
F2 - Processing parameters
SI 32768
SF 150.9128665 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

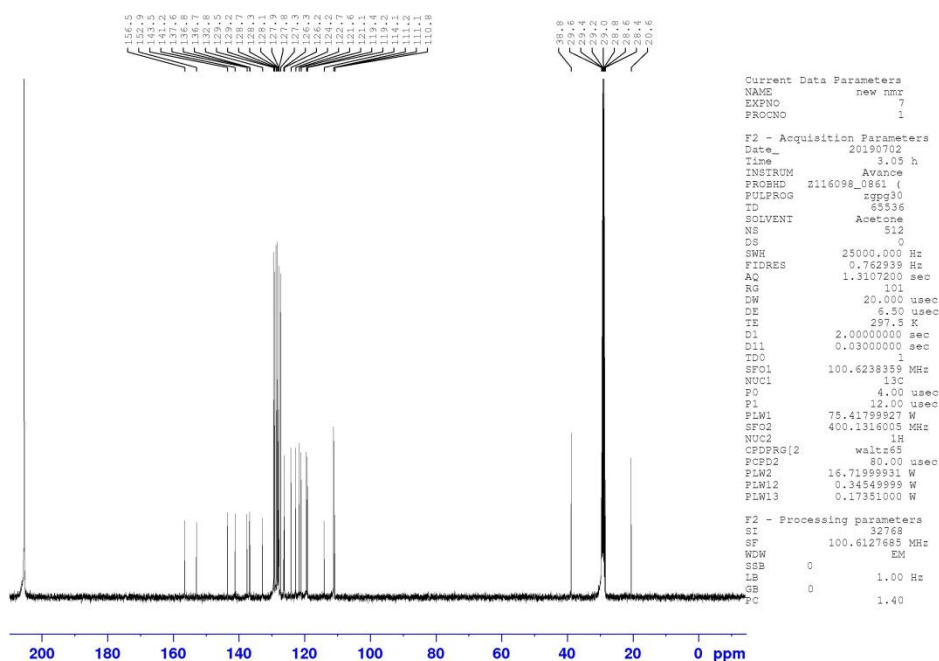
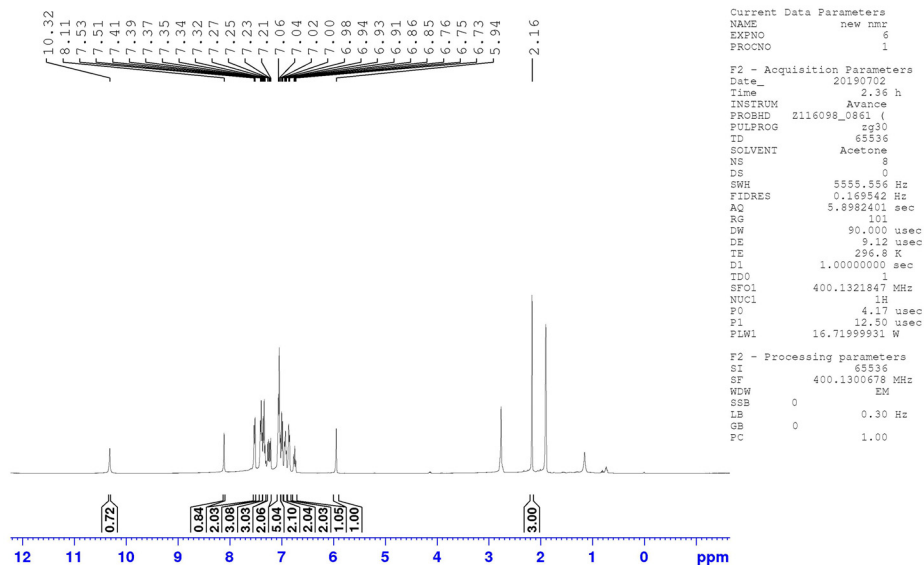
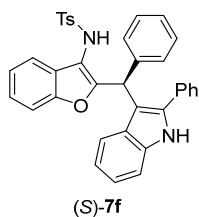


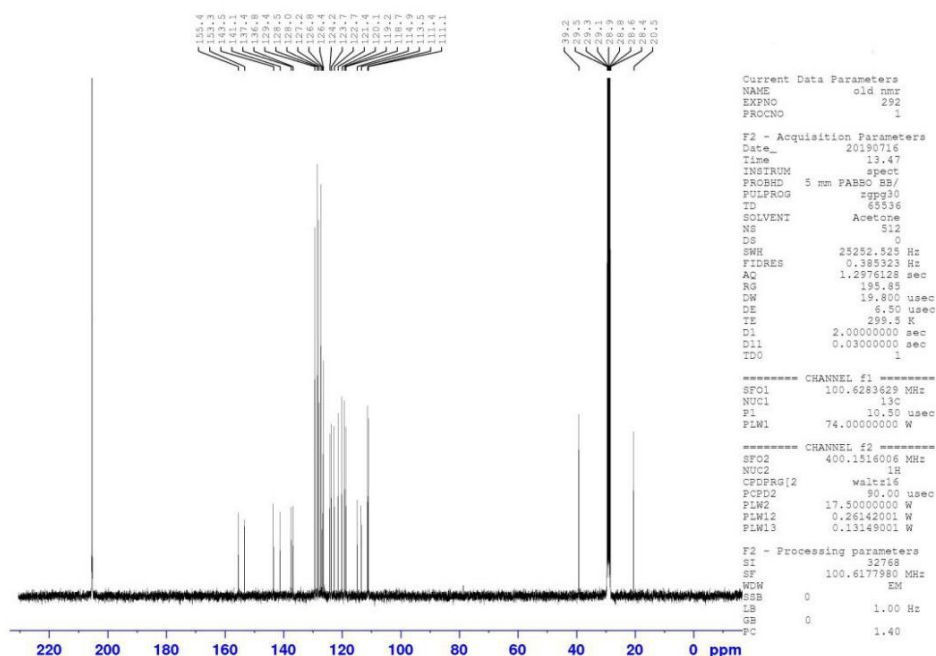
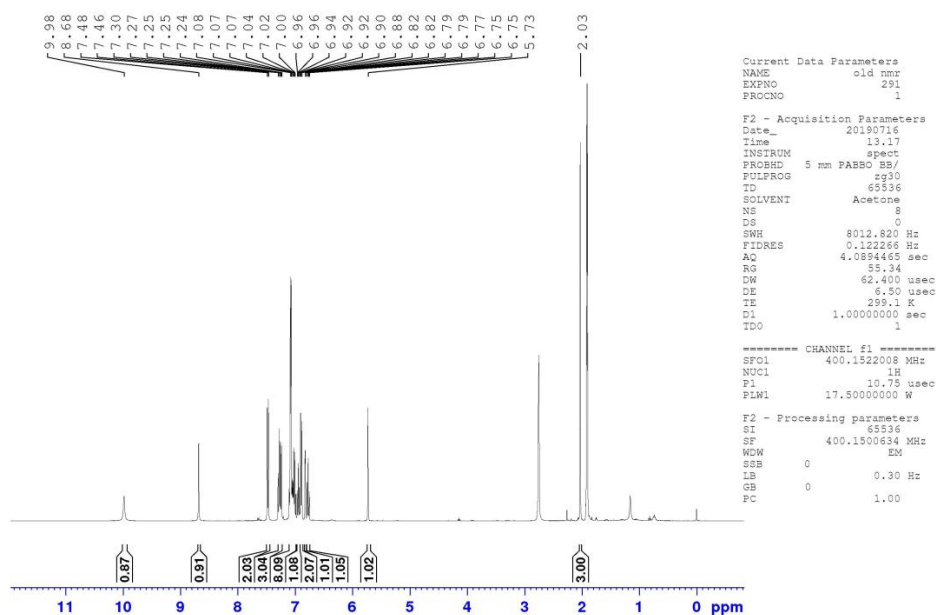
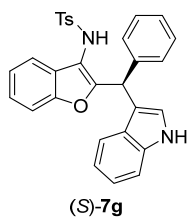


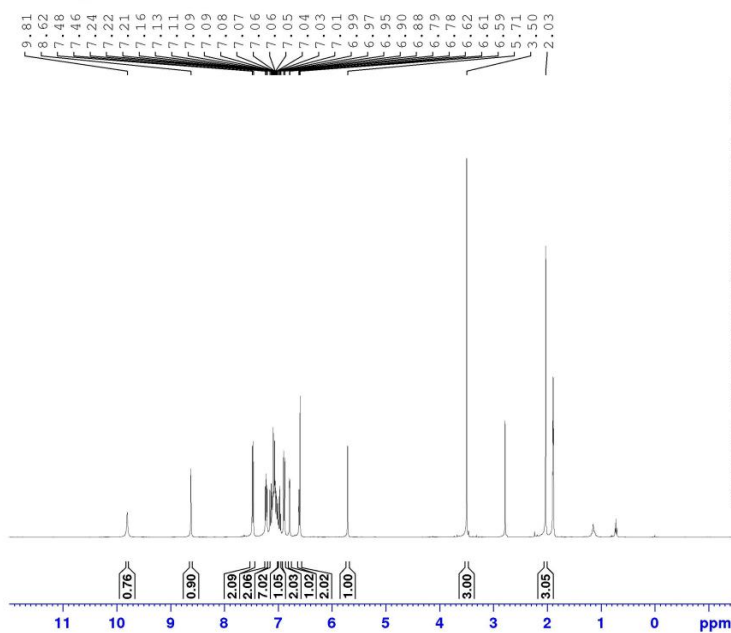
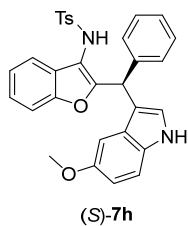








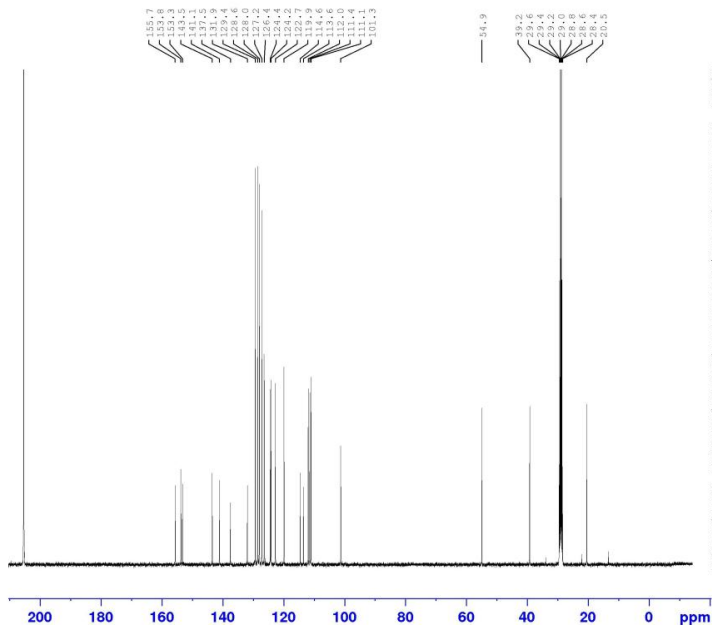




Current Data Parameters
NAME new nmr
EXPNO 28
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190717
Time 0.22 h
INSTRUM Avance
PROBHD z116098_0861 (4mm)30
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 8
DS 0
SWH 5555.556 Hz
FIDRES 0.169542 Hz
AQ 5.8982401 sec
RG 60.1347
DW 90.000 usec
DE 9.12 usec
TE 298.8 K
D1 1.00000000 sec
TDO 1
SFO1 400.1321847 MHz
NUC1 1H
PC 4.17 usec
PI 12.50 usec
PLW1 16.71999931 W

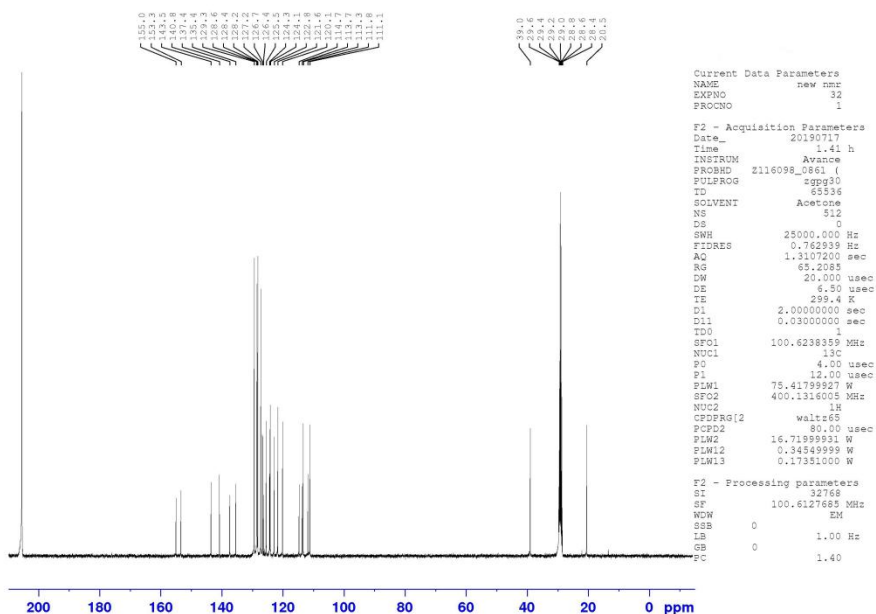
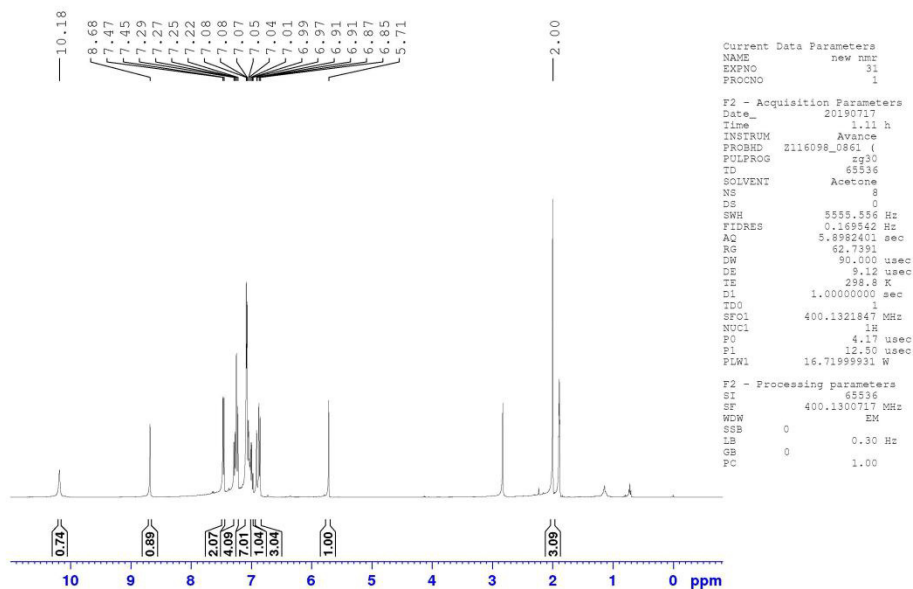
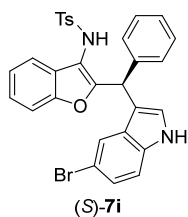
F2 - Processing parameters
SI 65536
SF 400.1300711 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

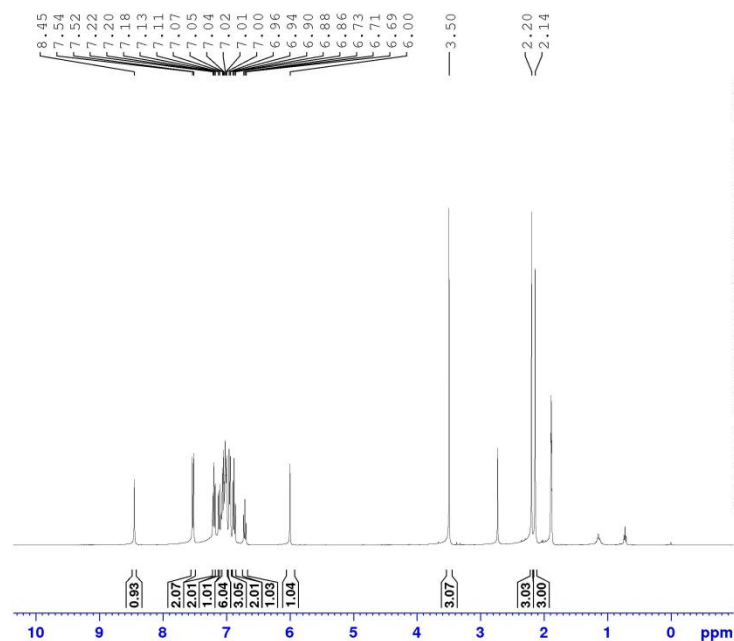
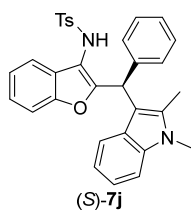


Current Data Parameters
NAME new nmr
EXPNO 29
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190717
Time 0.52 h
INSTRUM Avance
PROBHD z116098_0861 (4mm)30
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 512
DS 0
SWH 25000.000 Hz
FIDRES 0.762939 Hz
AQ 1.3107200 sec
RG 67.8168
DW 20.000 usec
DE 8.50 usec
TE 299.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TDO 1
SFO1 100.6238359 MHz
NUC1 13C
PC 4.00 usec
PI 12.00 usec
PLW1 75.41799927 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG2 waltz65
PCPD2 80.00 usec
PLW2 16.71999931 W
PLW12 0.34549999 W
PLW13 0.17351000 W

F2 - Processing parameters
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

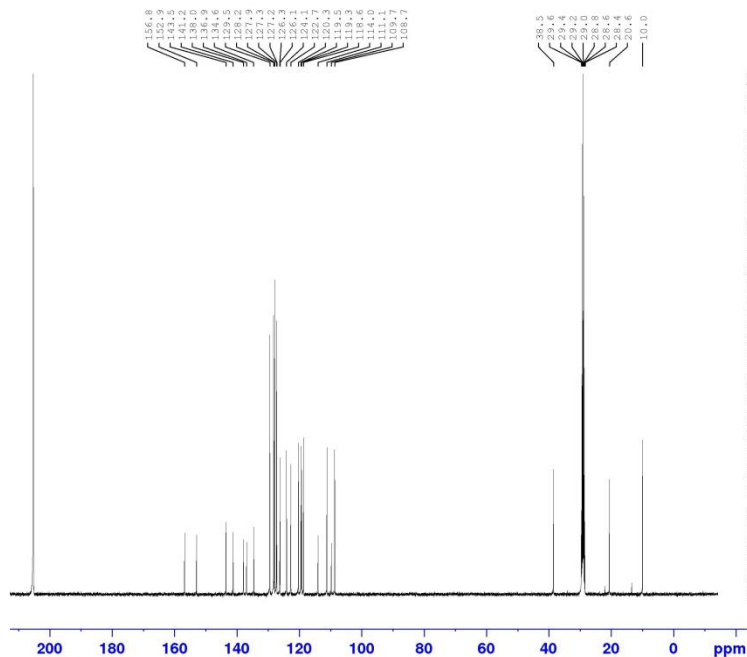




Current Data Parameters
NAME new nmr
EXPNO 25
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190716
Time 23.33 h
INSTRUM Avance
PROBHD Z116098_0861 (
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 0
SWH 5555.556 Hz
FIDRES 0.169542 Hz
AQ 5.8982401 sec
RG 58.8853
DW 90.000 usec
DE 9.12 usec
TE 298.7 K
D1 1.00000000 sec
TD0 1
SFO1 400.1321847 MHz
NUC1 1H
PC 4.17 usec
P1 12.50 usec
PLW1 16.71999931 W

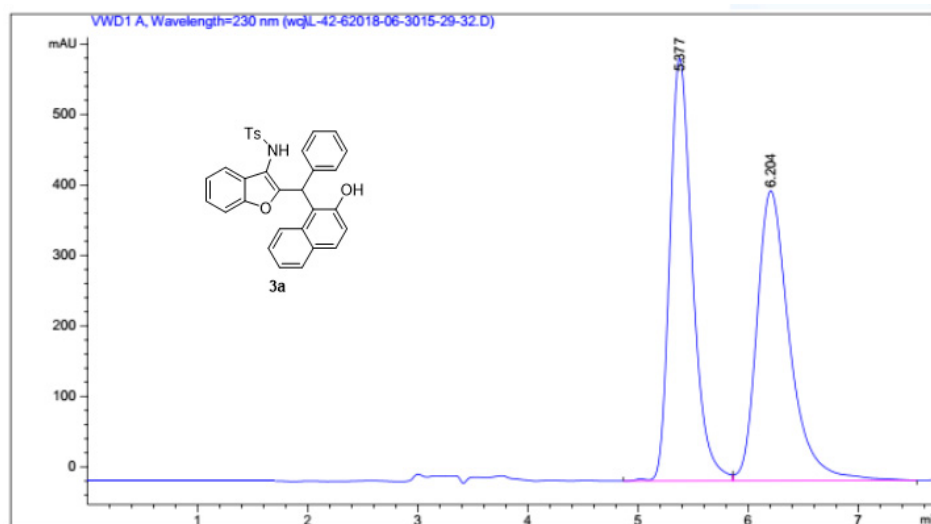
F2 - Processing parameters
SI 65536
SF 400.1300728 MHz
WDW EM
SSB 0
GB 0 0.30 Hz
LB 1.00
PC 1.00



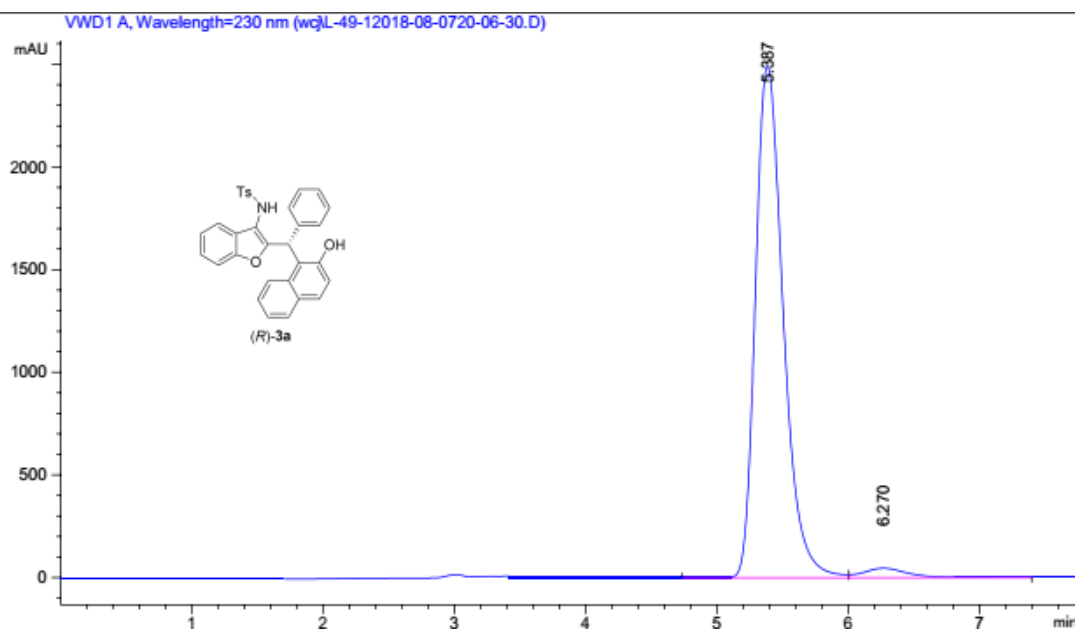
Current Data Parameters
NAME new nmr
EXPNO 26
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190717
Time 0.03 h
INSTRUM Avance
PROBHD Z116098_0861 (
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 512
DS 0
SWH 25000.000 Hz
FIDRES 0.762939 Hz
AQ 1.3107200 sec
RG 61.7765
DW 20.000 usec
DE 6.50 usec
TE 299.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6238359 MHz
NUC1 13C
PC 4.00 usec
P1 12.00 usec
PLW1 75.41799927 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG2 waltz165
PCPD2 80.00 usec
PLW2 16.71999931 W
PLW12 0.34549999 W
PLW13 0.17351000 W

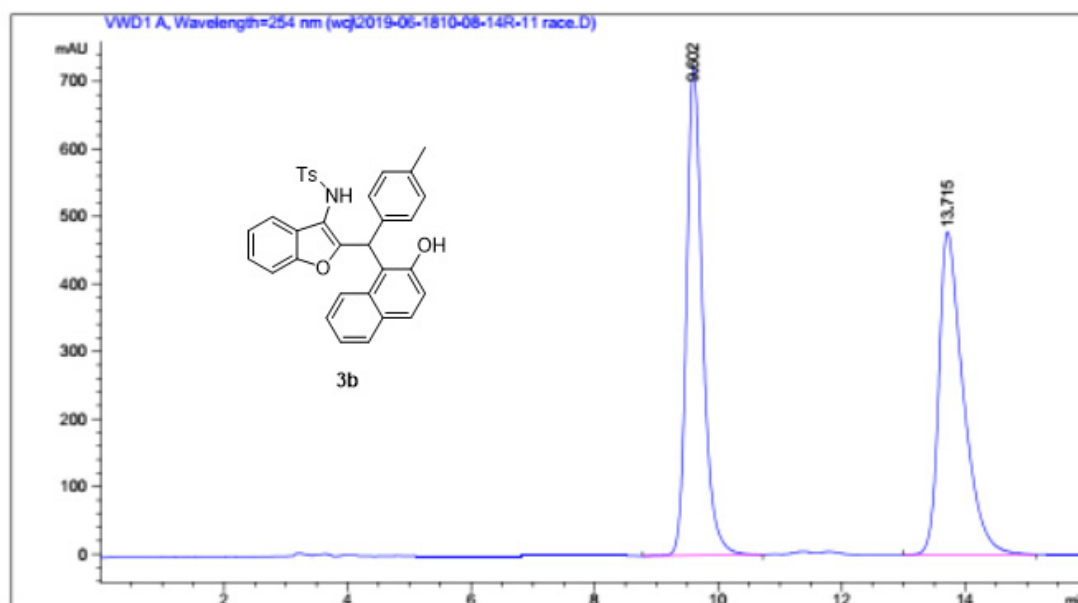
F2 - Processing parameters
SI 32768
SF 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
LB 1.40
PC 1.40



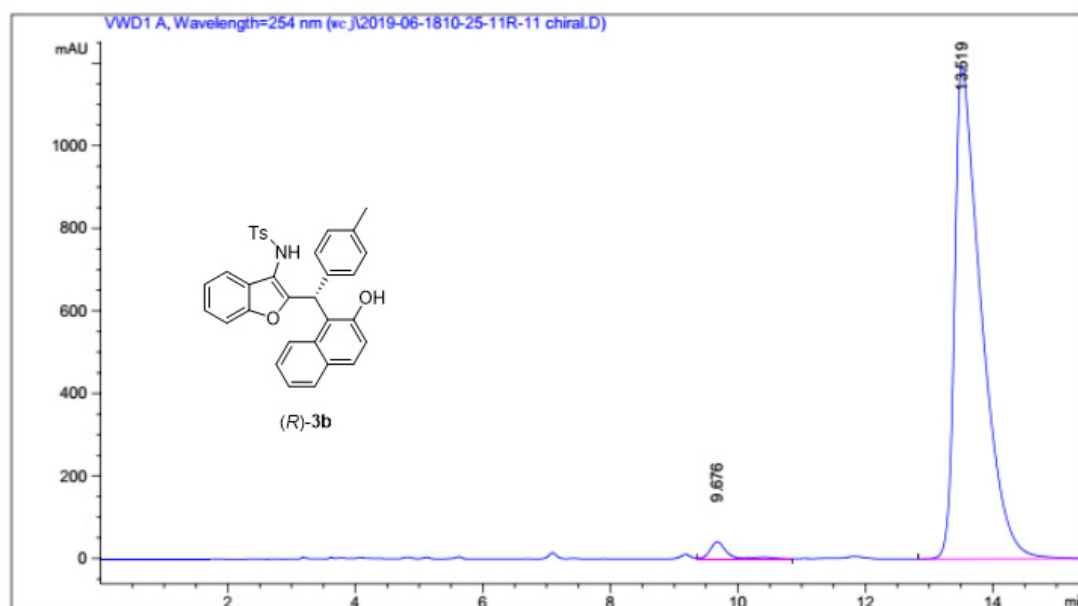
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.377	VV R	0.2171	8548.87402	599.38977	50.1947
2	6.204	VB	0.3126	8482.56738	411.24854	49.8053



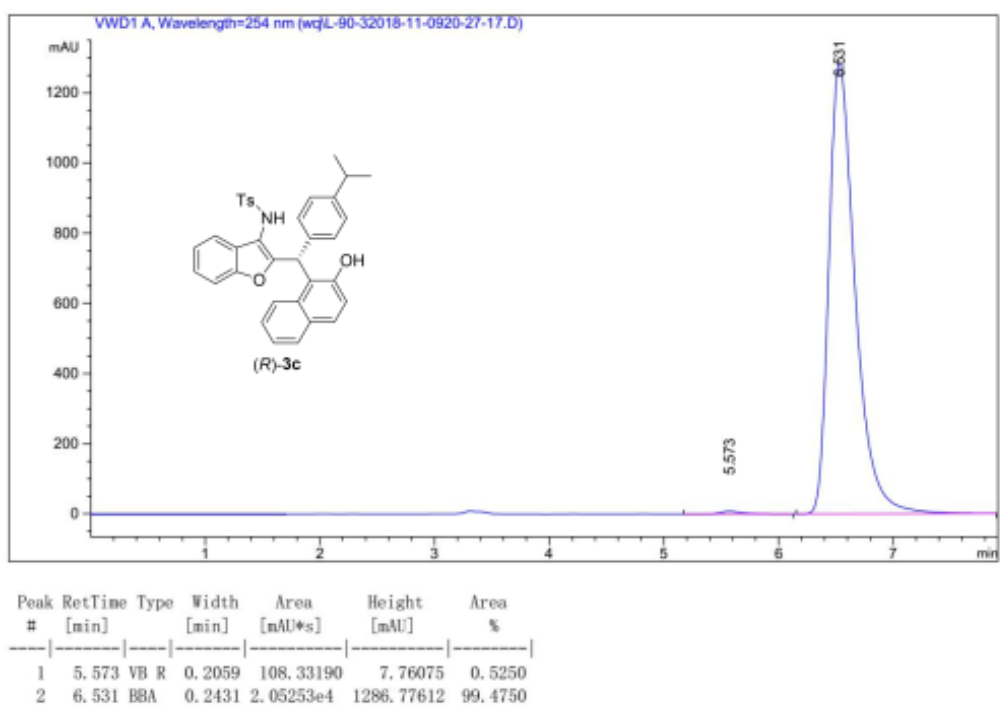
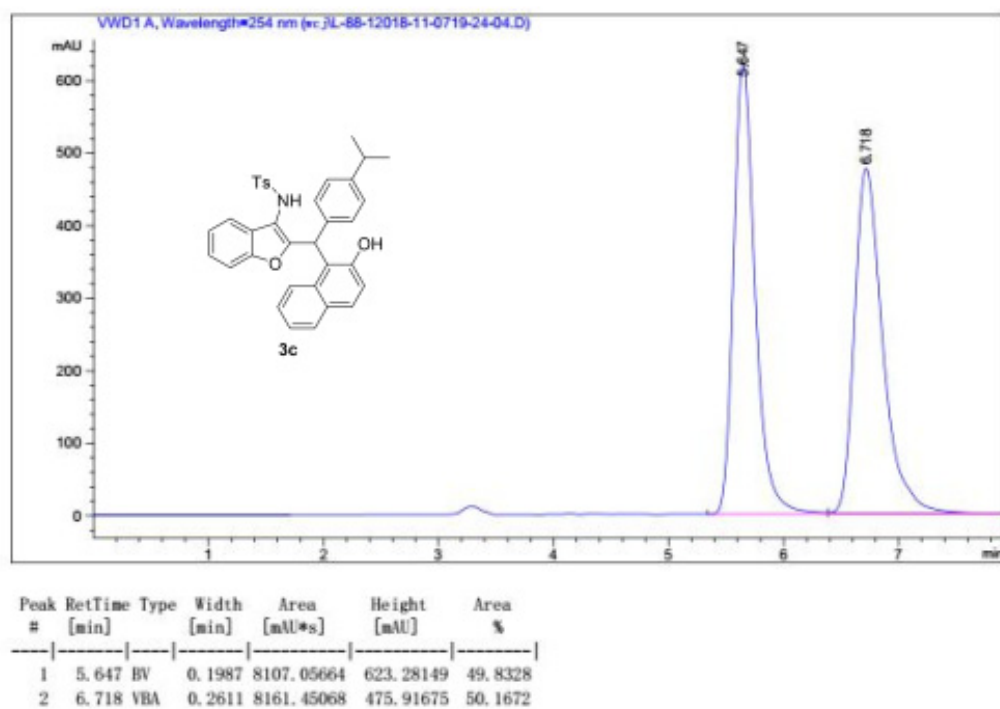
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.387	MF	0.2450	3.66390e4	2492.21802	96.9803
2	6.270	FM	0.4125	1140.85291	46.09628	3.0197

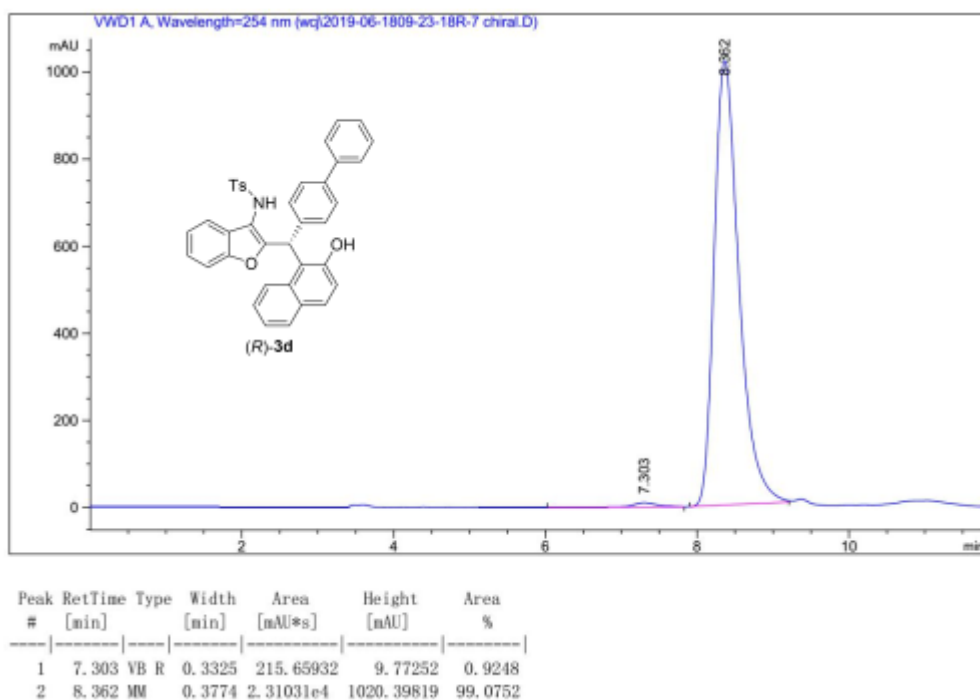
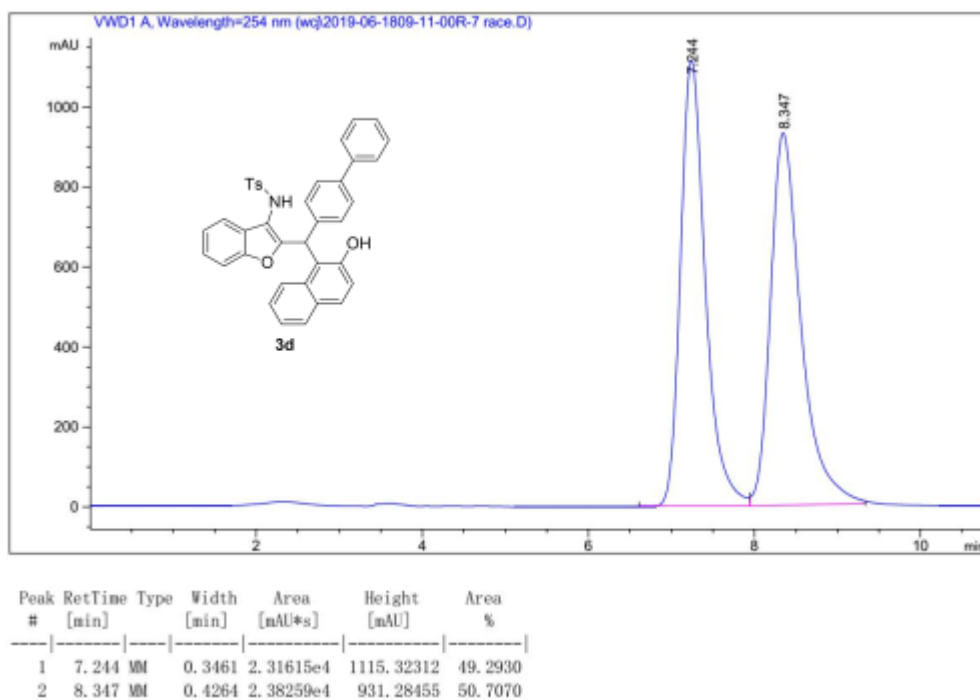


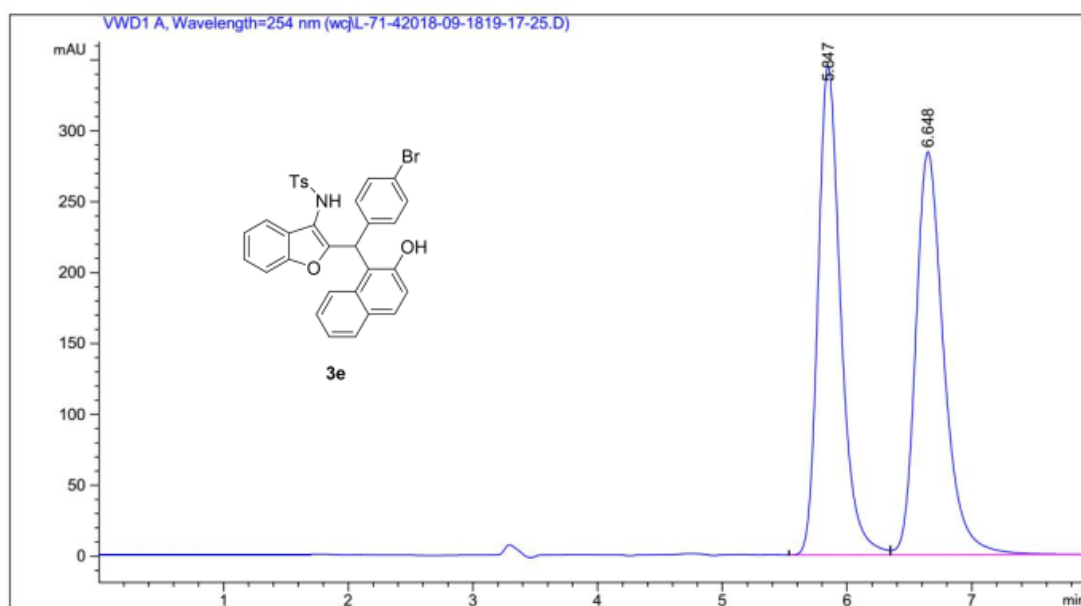
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.602	BB	0.2728	1.30948e4	724.80713	49.9604
2	13.715	BB	0.4010	1.31156e4	478.12552	50.0396



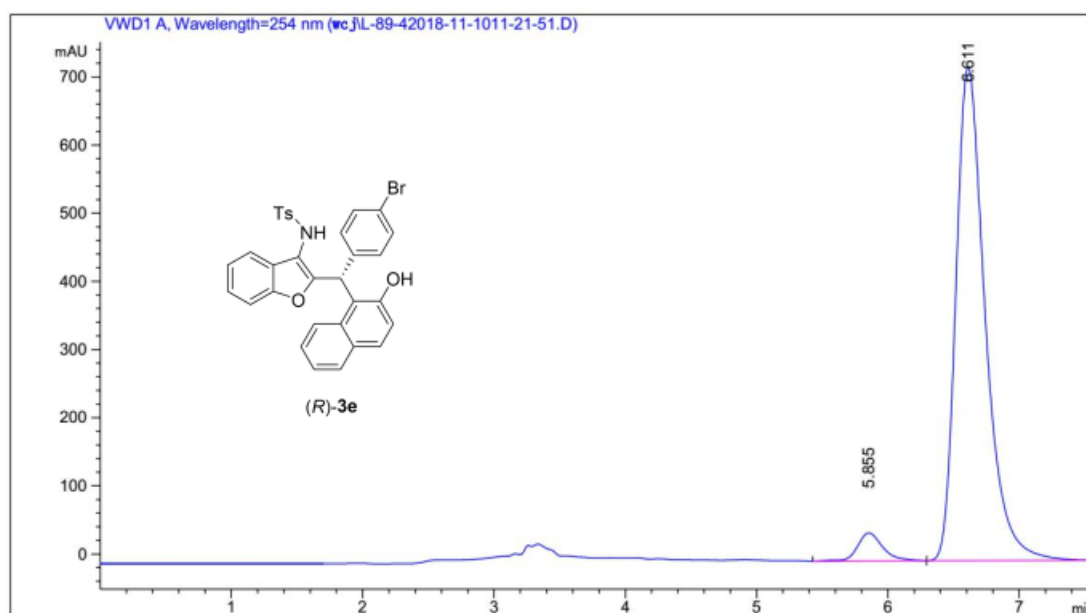
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.676	VV R	0.2506	775.81409	41.31821	2.2004
2	13.519	BBA	0.4081	3.44813e4	1193.33203	97.7996



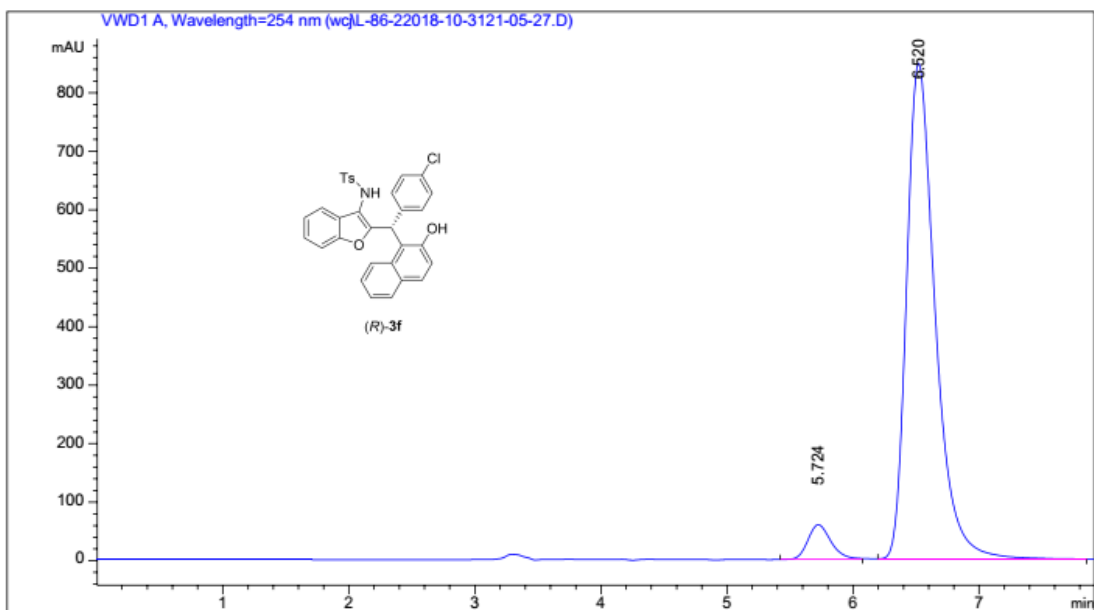
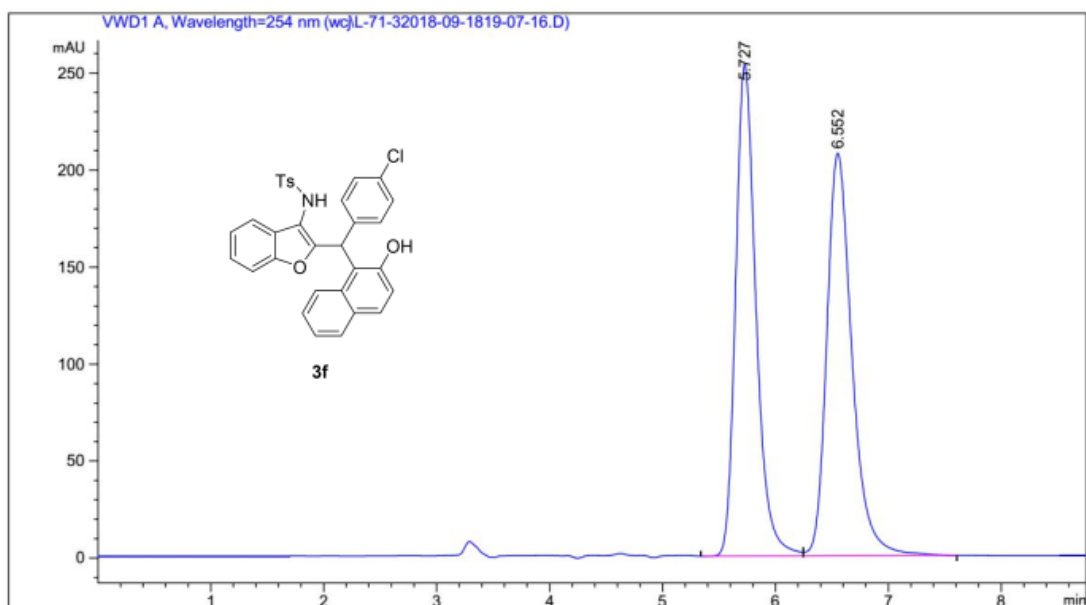


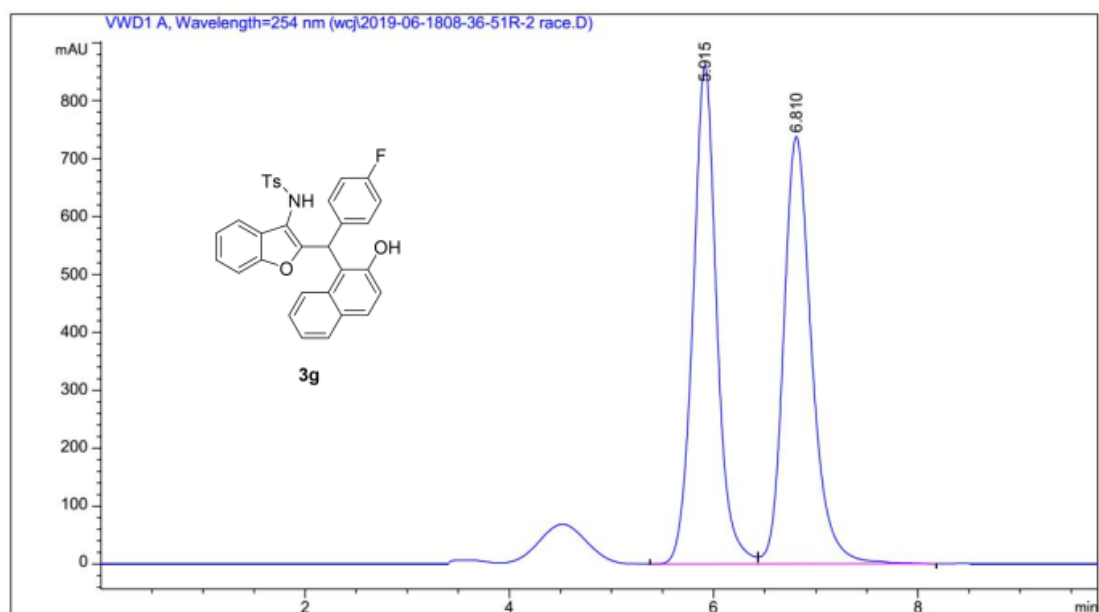


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.847	BV	0.1923	4352.83203	344.86273	49.5617
2	6.648	VBA	0.2369	4429.82275	284.14957	50.4383

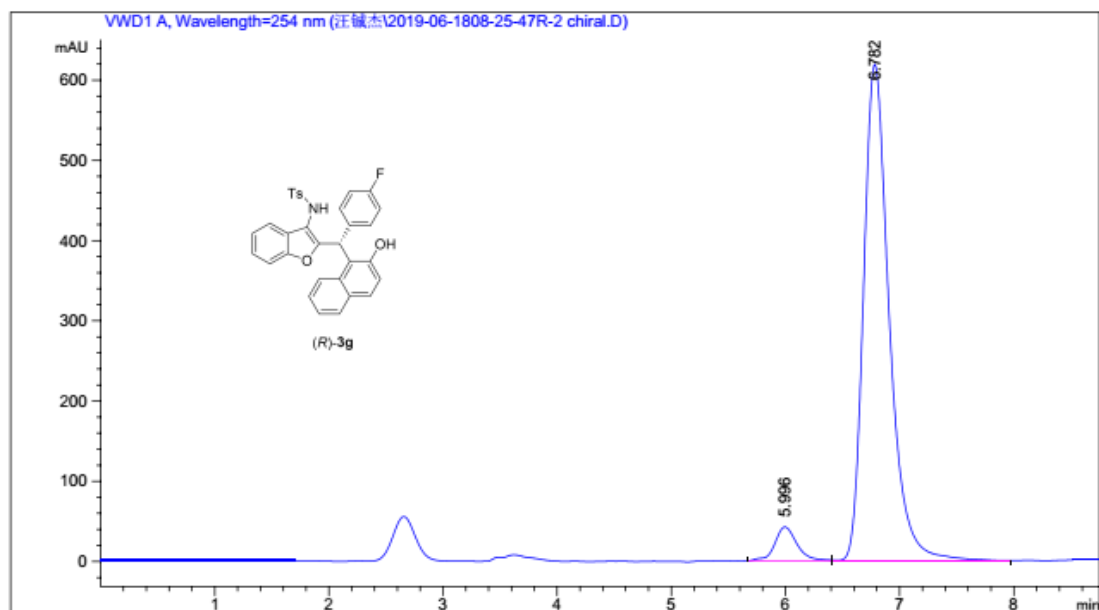


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.855	BV	0.2035	550.72144	41.06212	4.6848
2	6.611	VBA	0.2344	1.12047e4	724.74121	95.3152

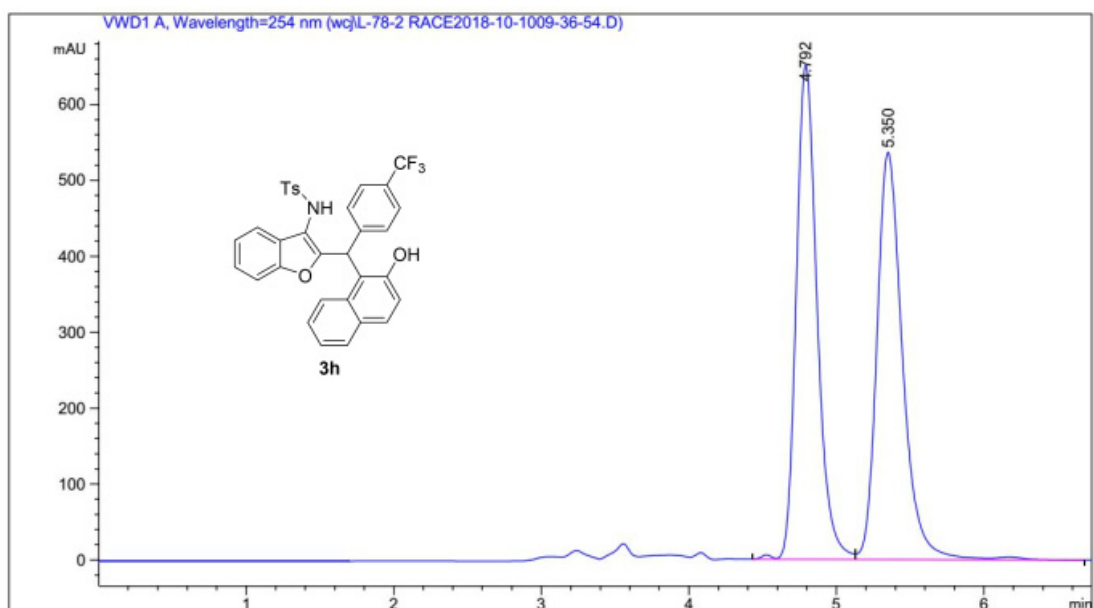




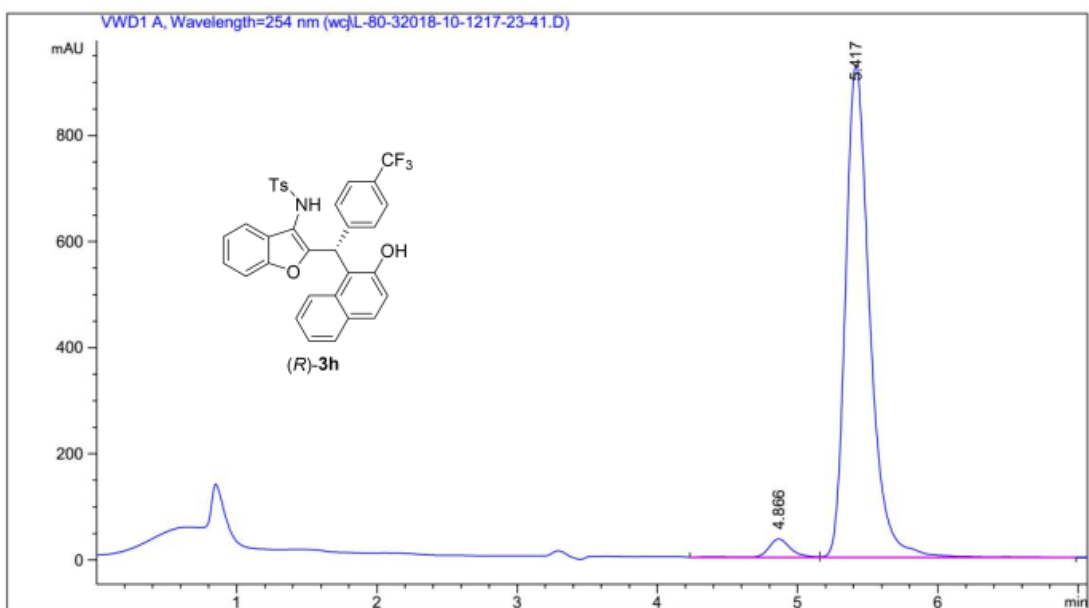
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.915	BV	0.2433	1.38740e4	859.62250	49.6817
2	6.810	VB	0.2902	1.40518e4	737.63416	50.3183



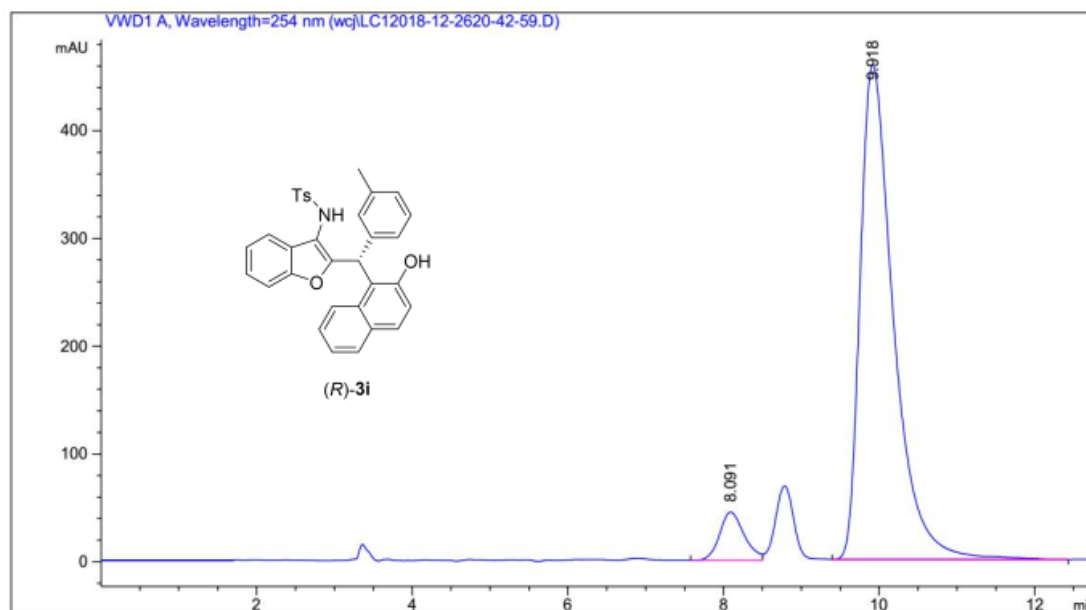
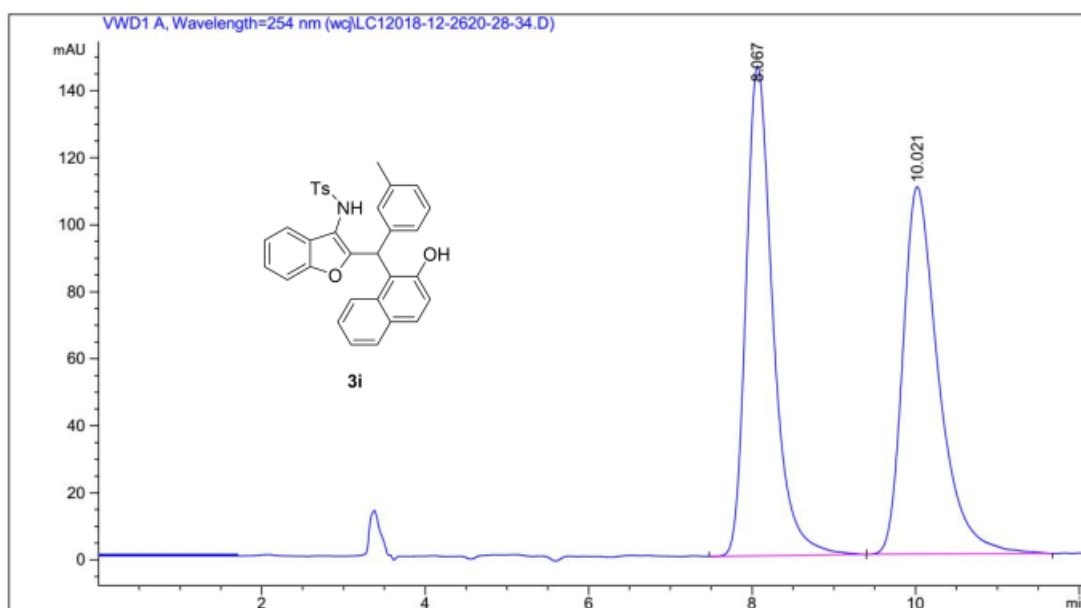
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.996	MF	0.2281	580.09808	42.38439	5.6575
2	6.782	FM	0.2604	9673.48340	619.15106	94.3425

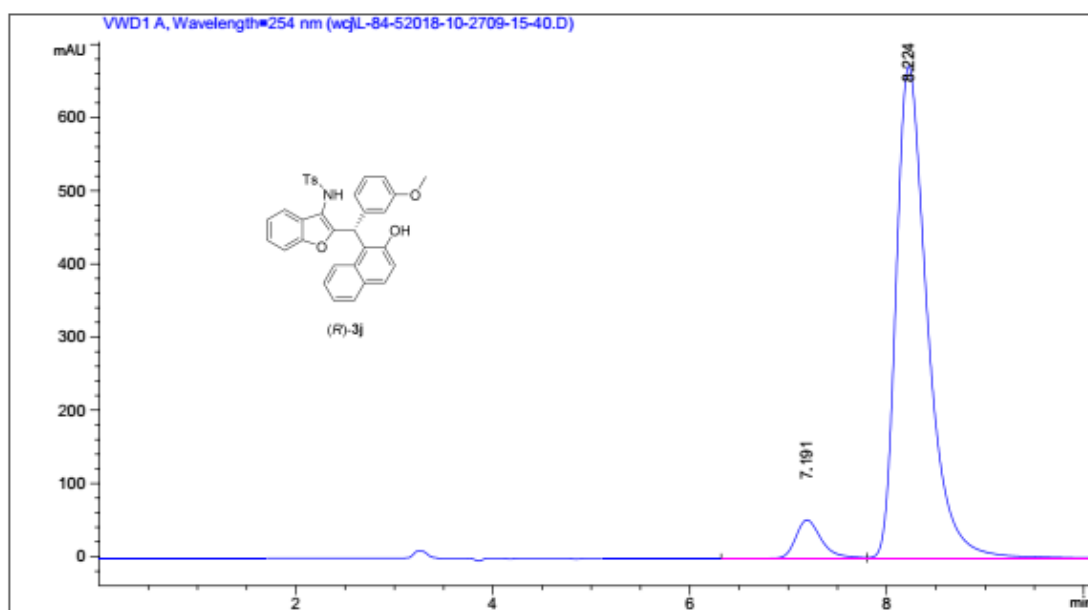
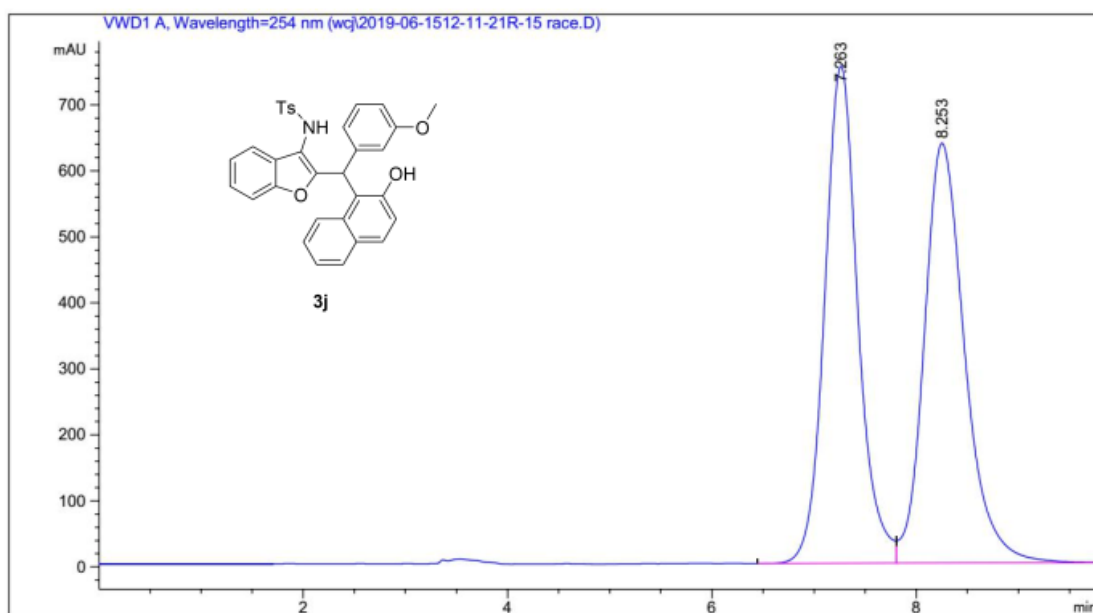


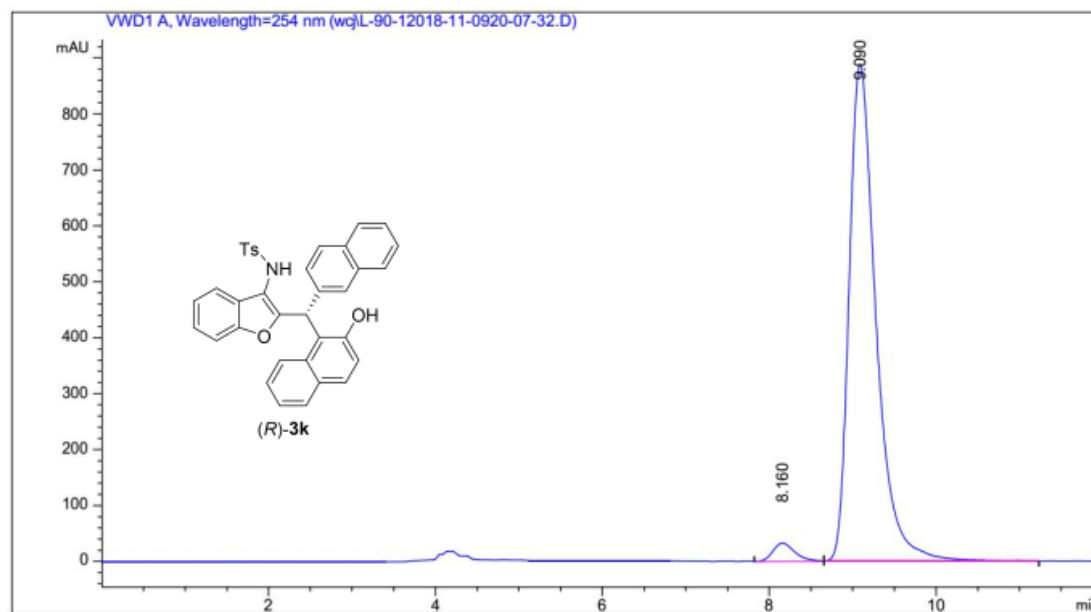
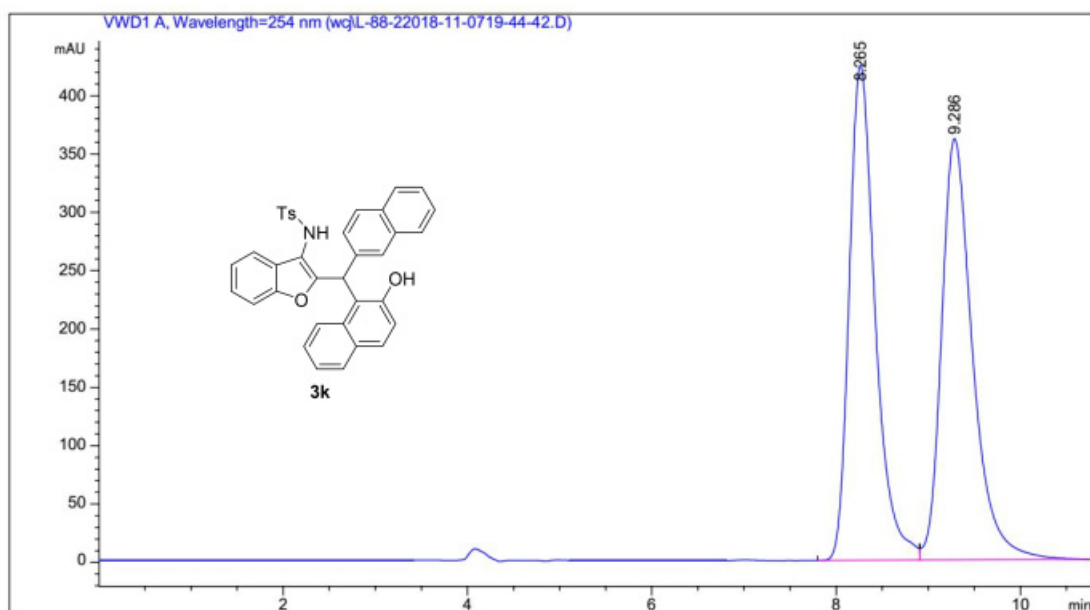
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.792	VV R	0.1499	6374.74219	650.36310	49.5533
2	5.350	VV R	0.1835	6489.68115	536.32739	50.4467

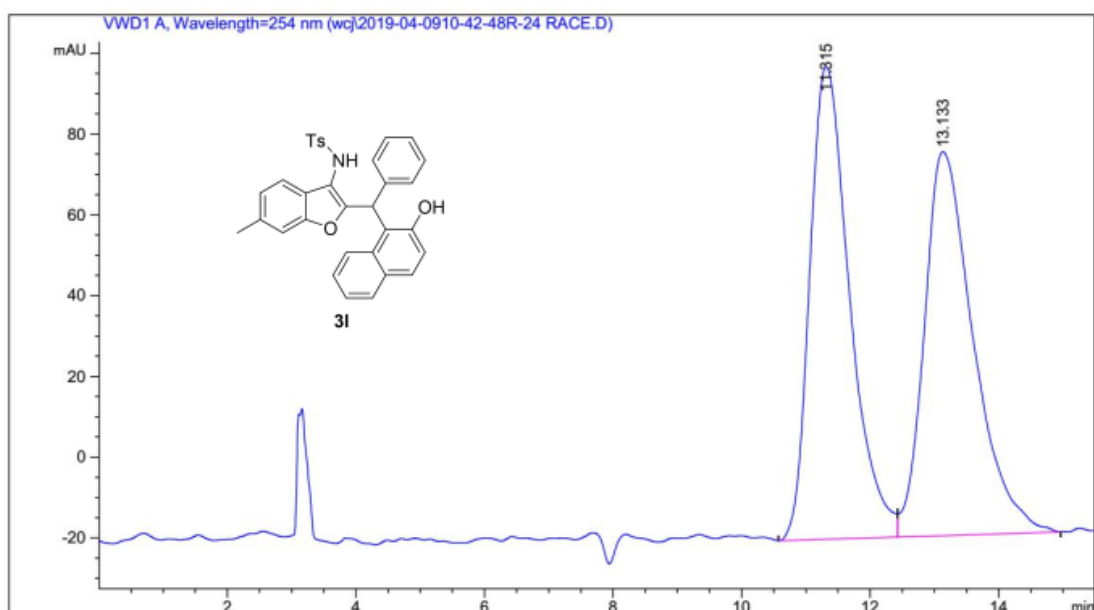


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.866	VV R	0.1709	392.83792	34.48727	3.4066
2	5.417	VV R	0.1831	1.11387e4	927.73663	96.5934

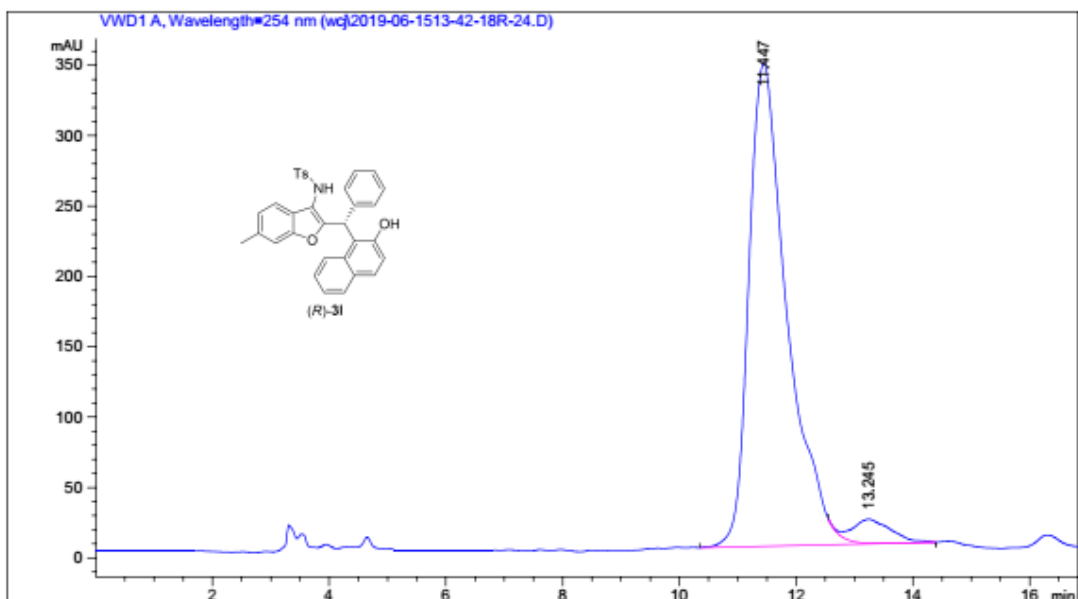




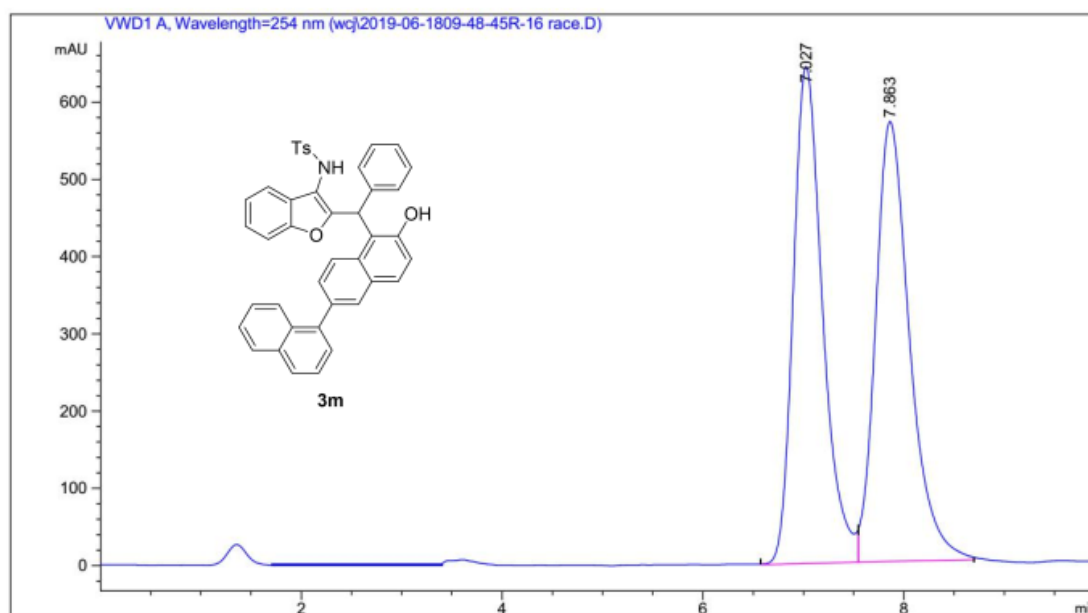




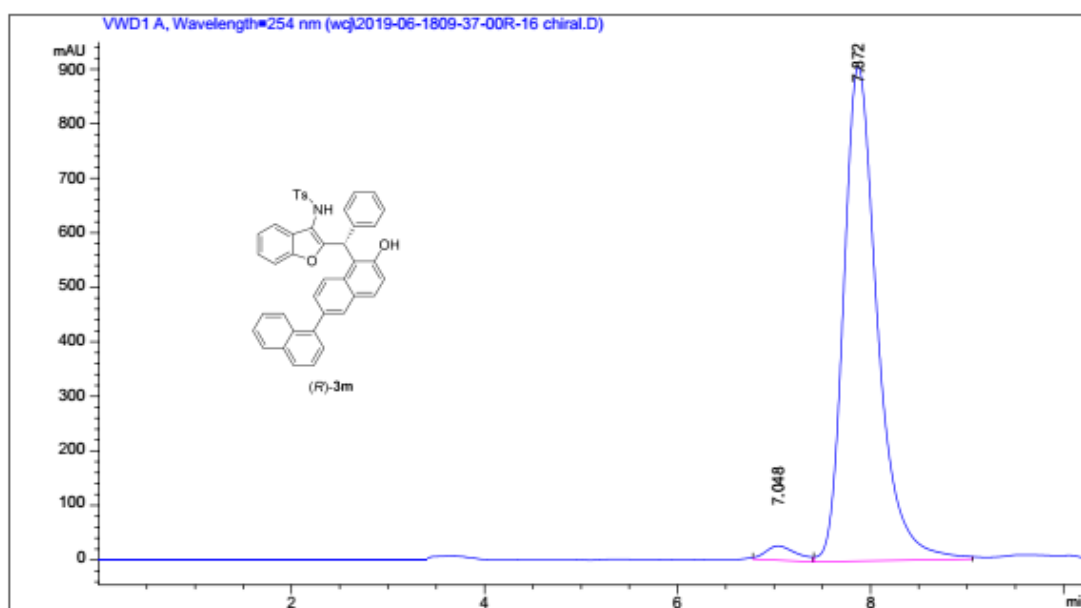
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.315	BV	0.6557	5034.02979	117.06155	50.0282
2	13.133	VB	0.7640	5028.34473	95.07822	49.9718



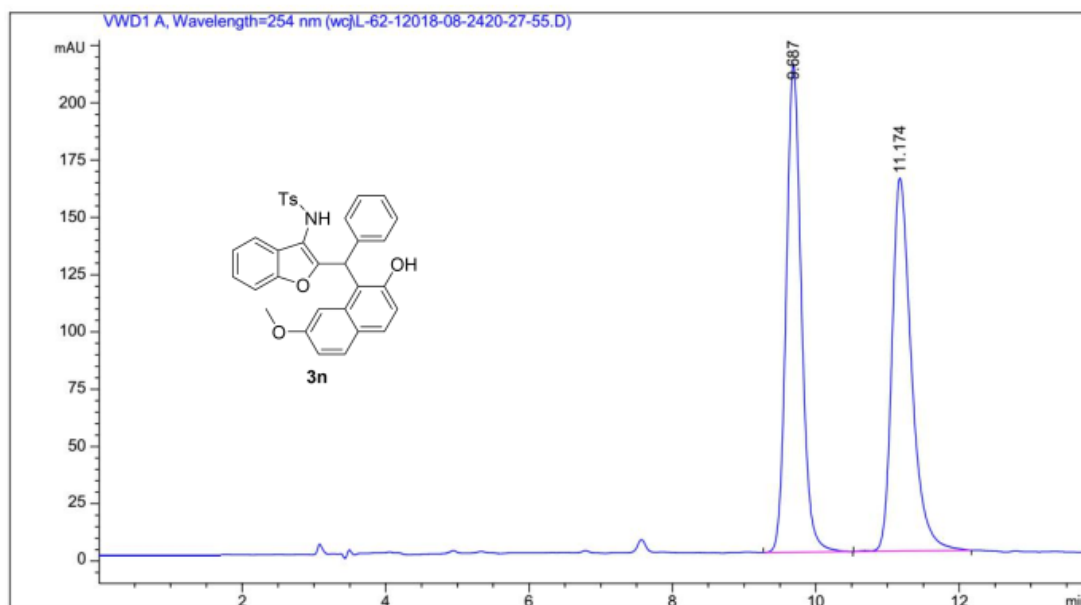
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.447	BV R	0.6918	1.56277e4	343.49097	95.2950
2	13.245	VB E	0.6290	771.58673	16.92014	4.7050



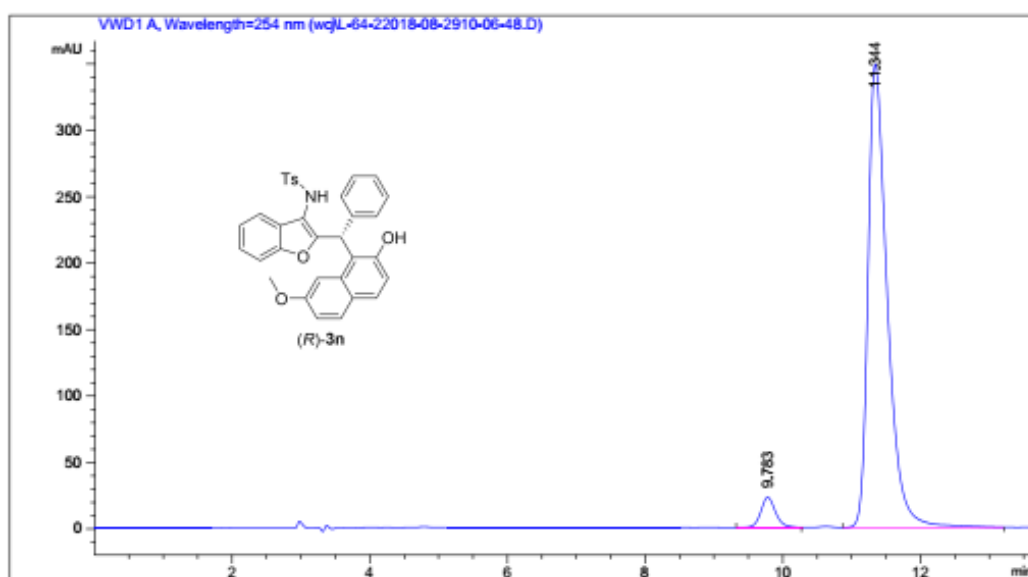
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.027	MM	0.3383	1.30573e4	643.25696	49.3267
2	7.863	MM	0.3926	1.34138e4	569.36920	50.6733



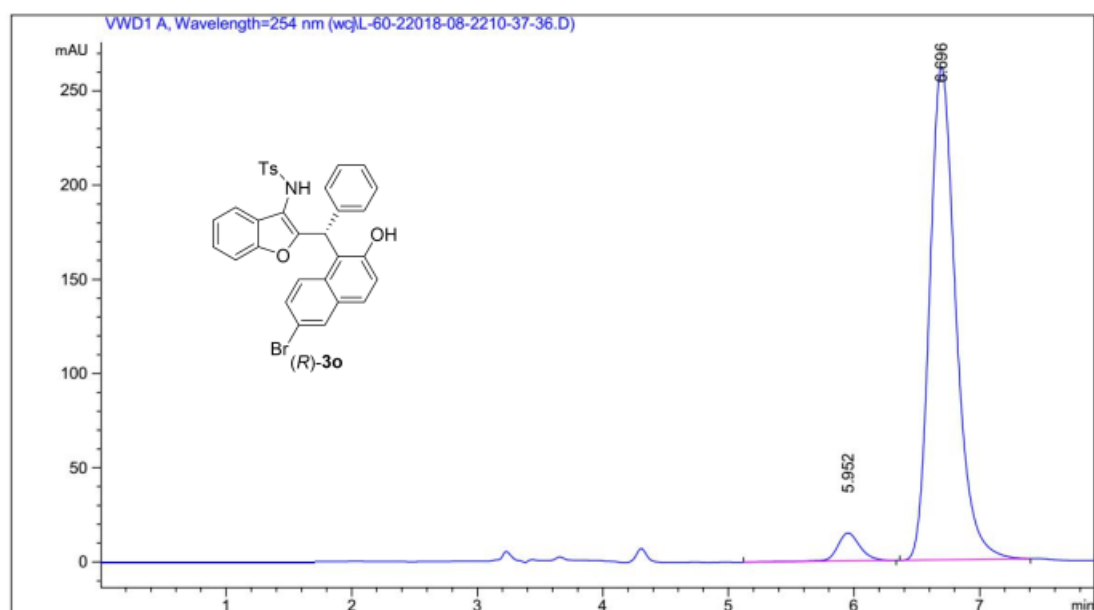
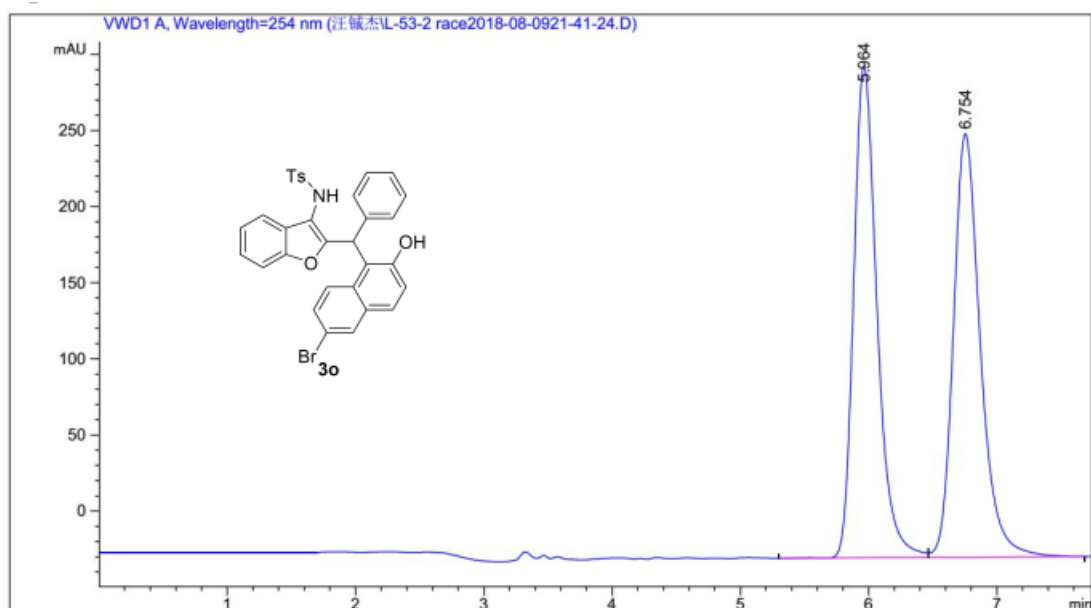
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.048	MM	0.3690	575.36865	25.98837	2.5573
2	7.872	MM	0.4031	2.19234e4	906.44177	97.4427

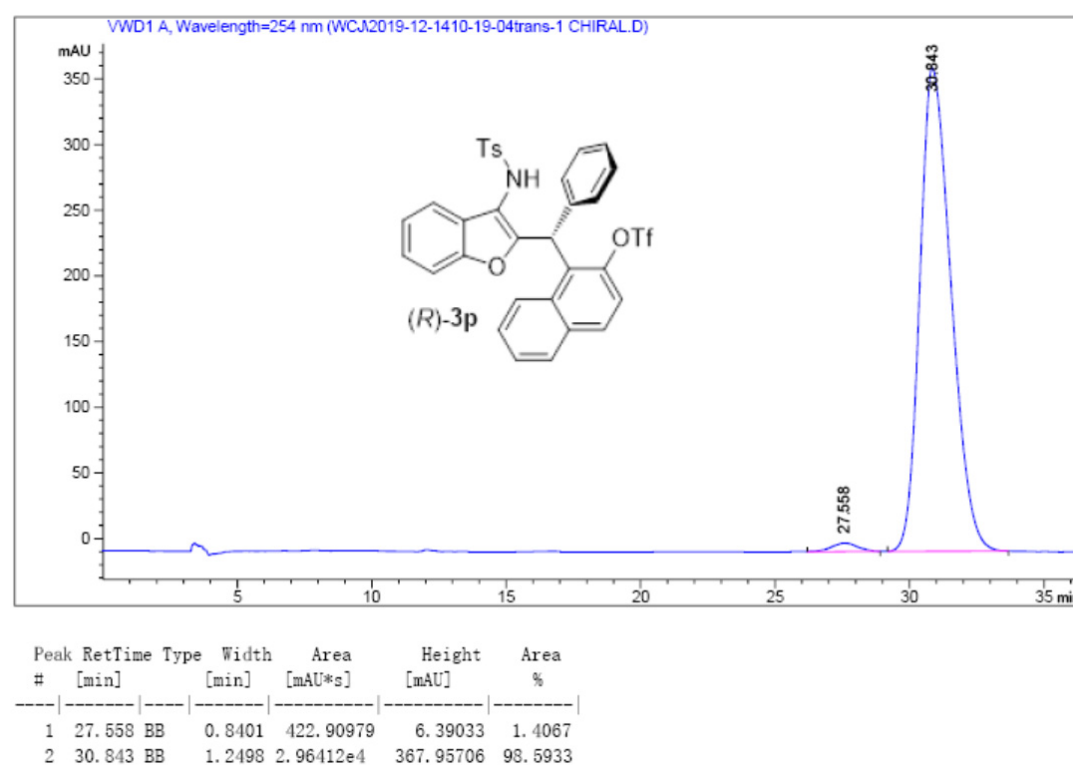
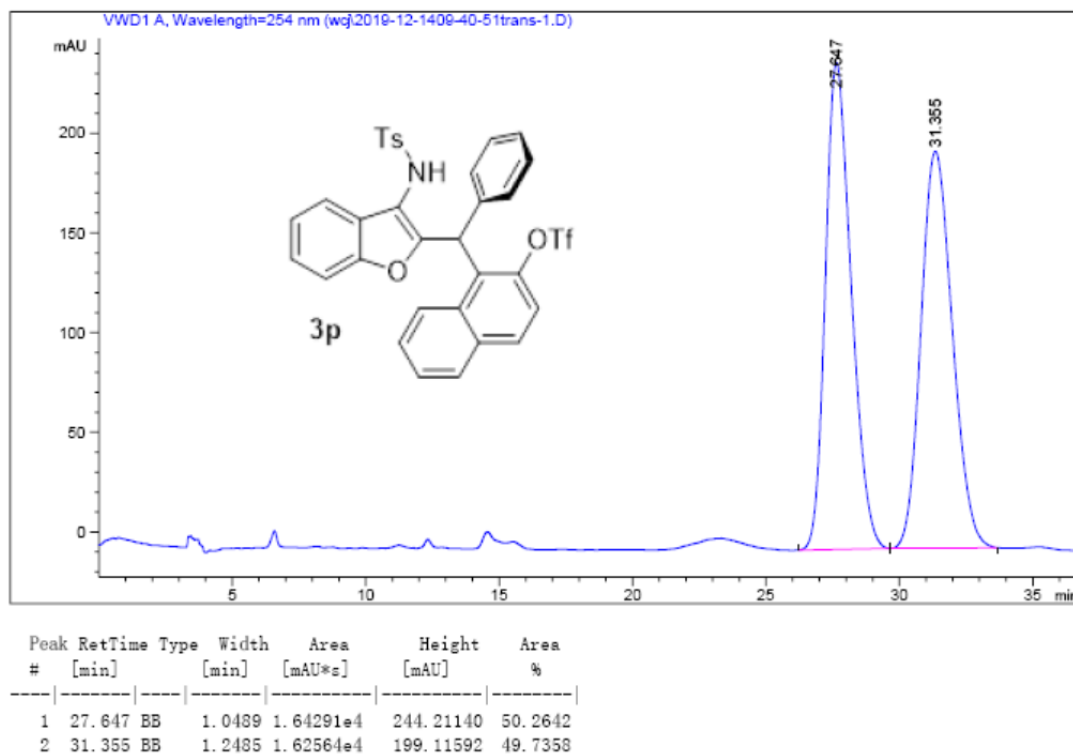


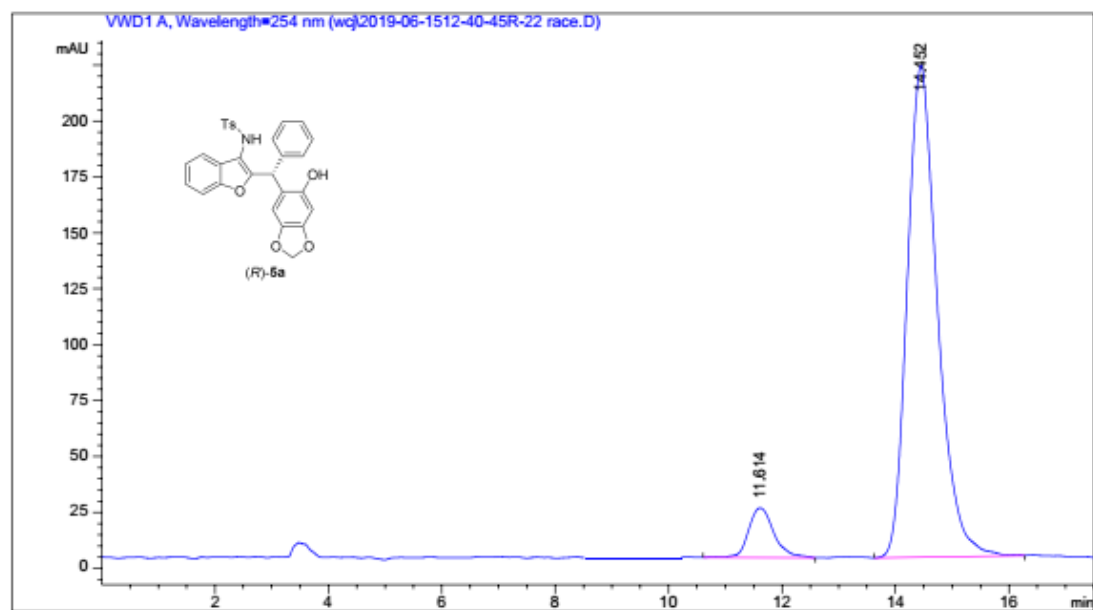
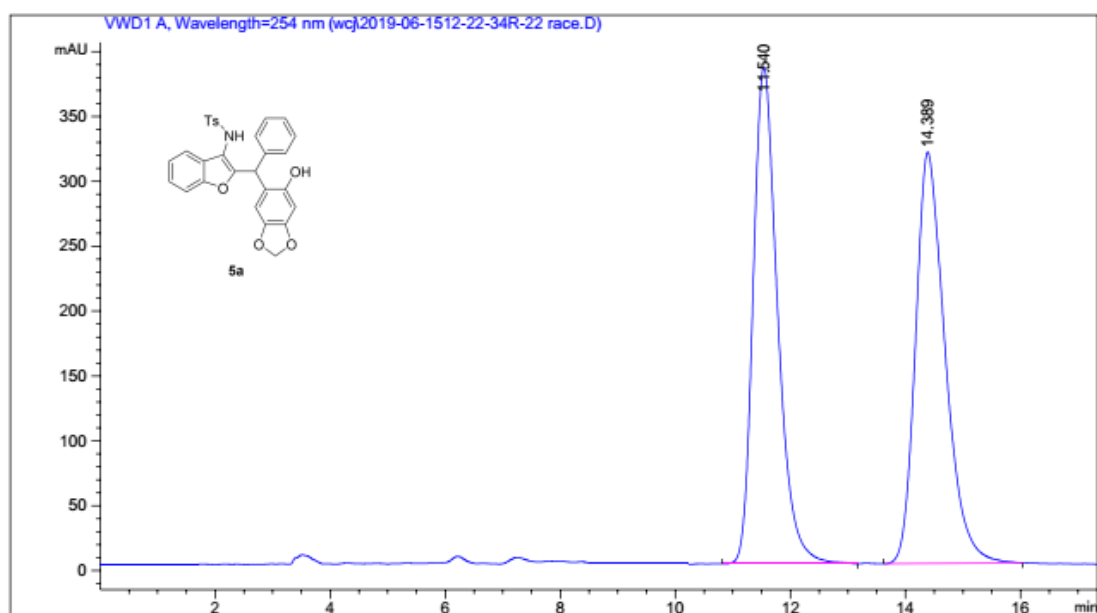
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.687	BB	0.2262	3124.36182	212.90576	50.4254
2	11.174	VB R	0.2852	3071.64966	162.75993	49.5746

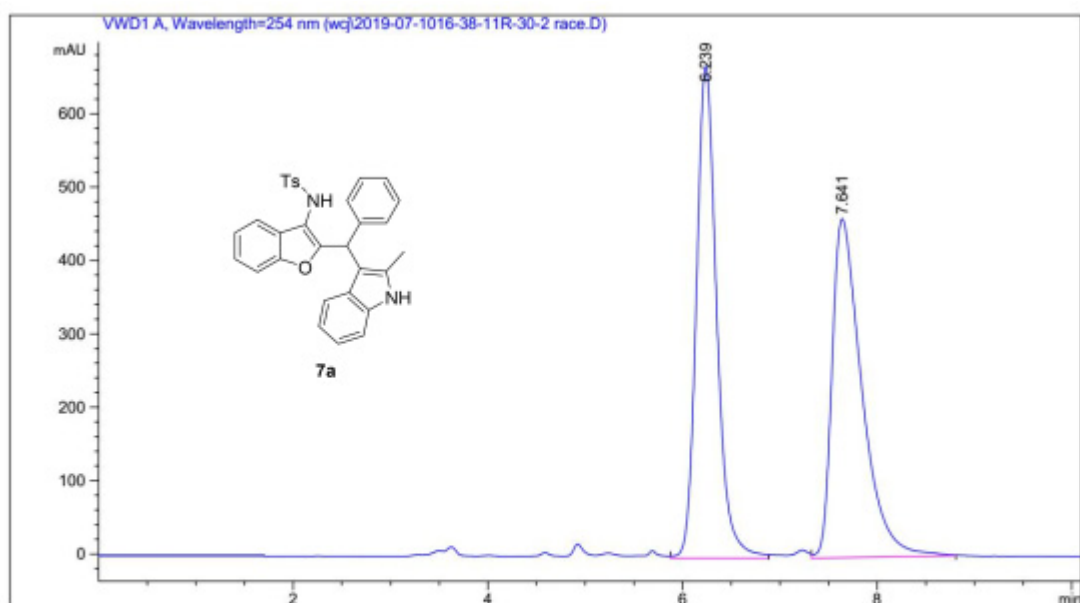


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.783	BB	0.2272	336.87836	22.69812	4.7451
2	11.344	BB	0.2891	6762.60303	348.89798	95.2549

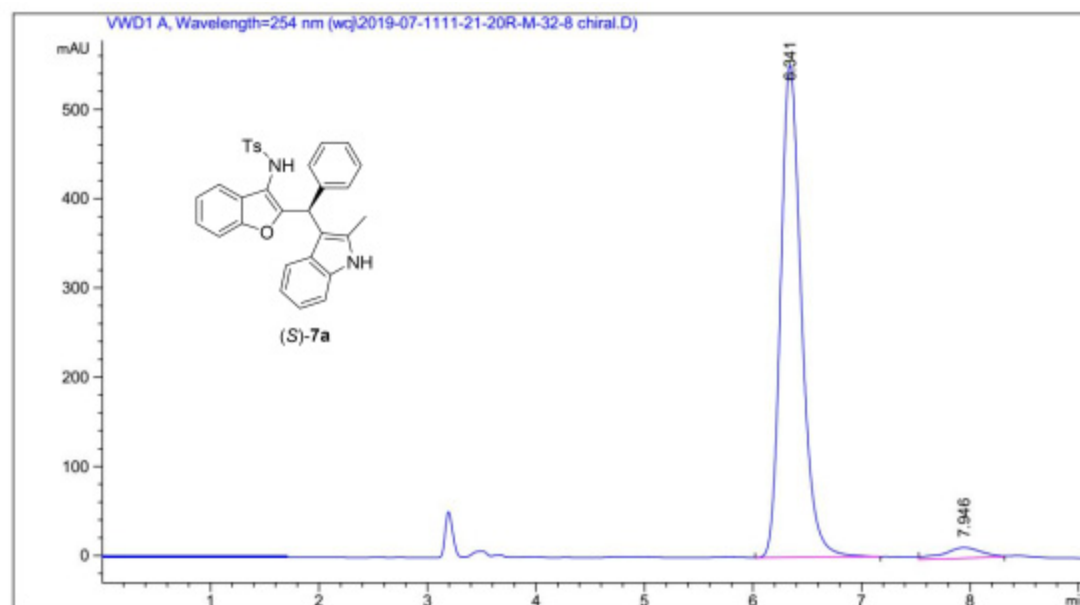




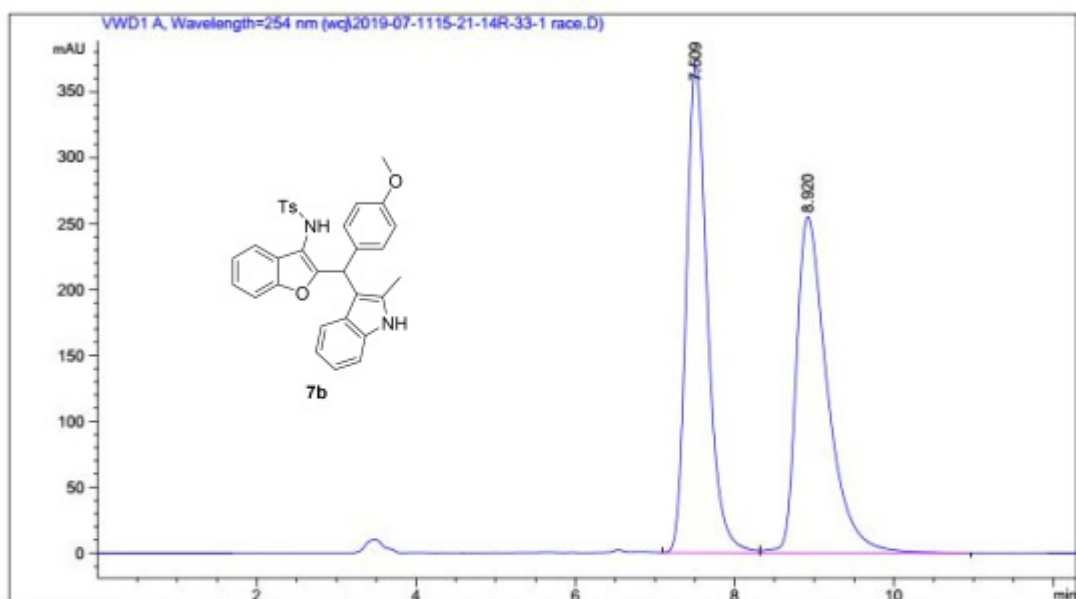




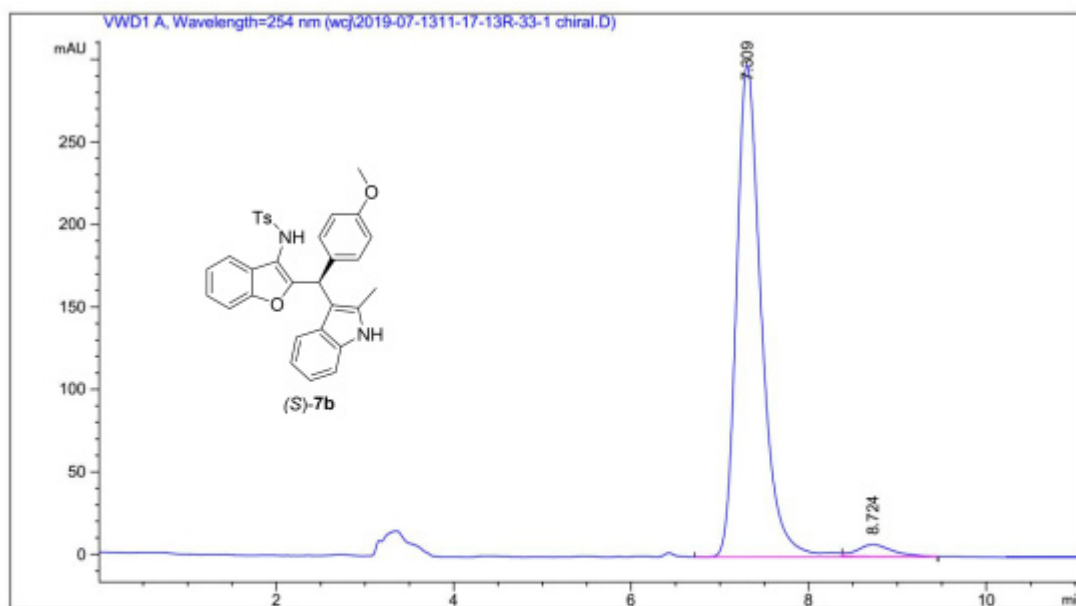
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.239	MM	0.2413	9704.95996	670.35870	49.7312
2	7.641	MM	0.3542	9809.86719	461.59543	50.2688



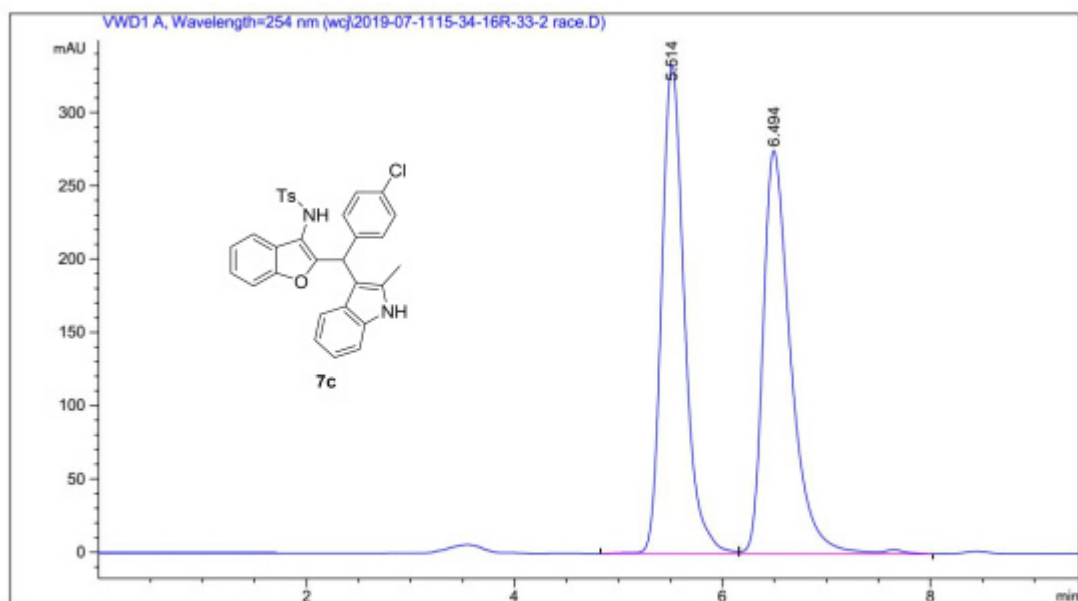
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.341	BB	0.2028	7320.74268	551.60553	96.1450
2	7.946	MM	0.4093	293.52786	11.95253	3.8550



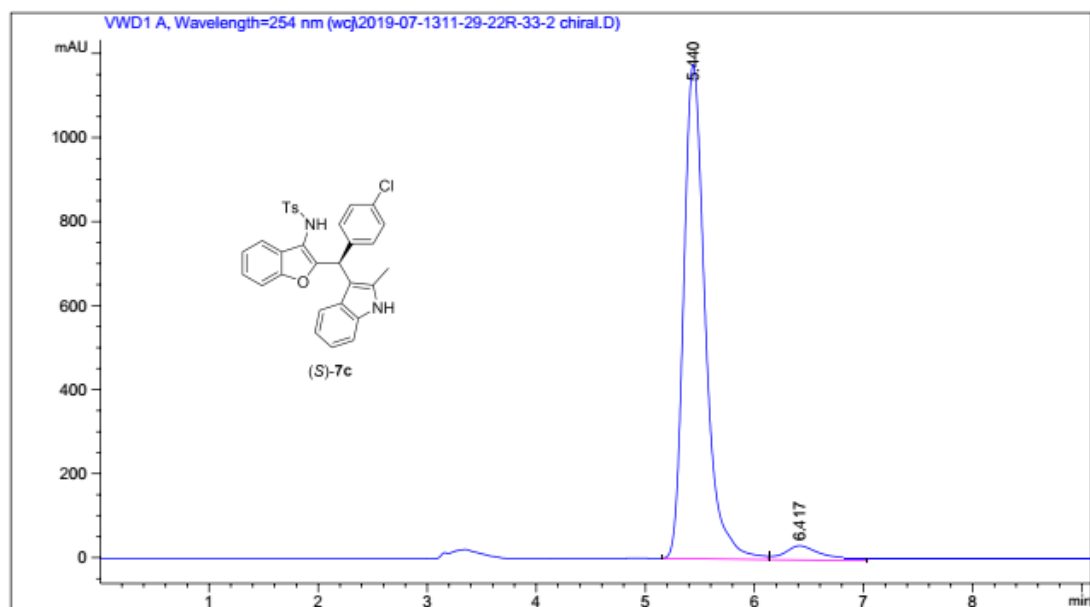
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.509	BV	0.2821	6821.78271	370.02179	49.7532
2	8.920	VB	0.4071	6889.47168	255.10687	50.2468



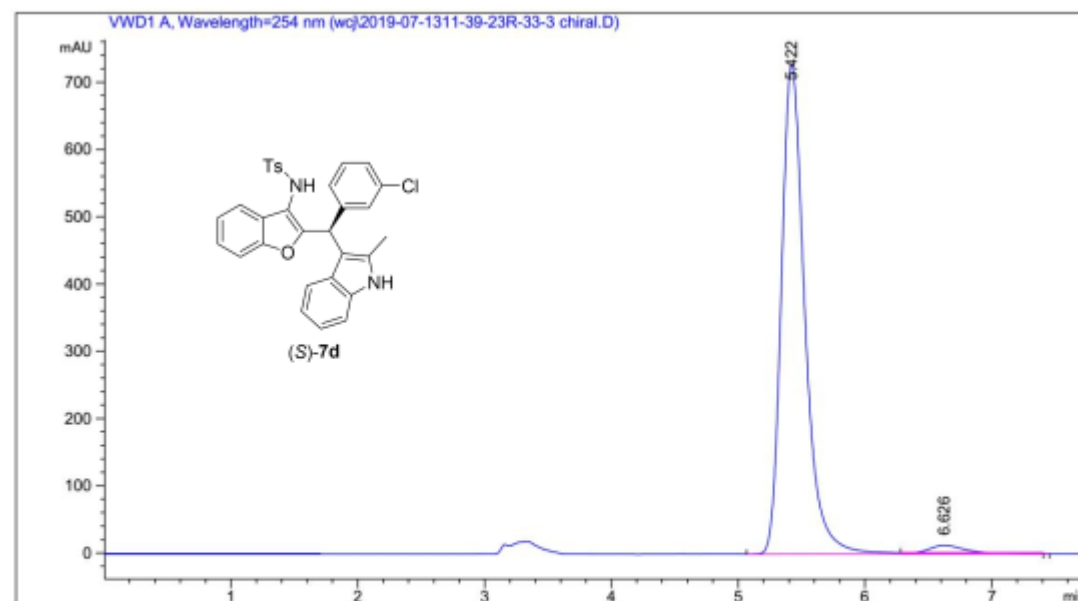
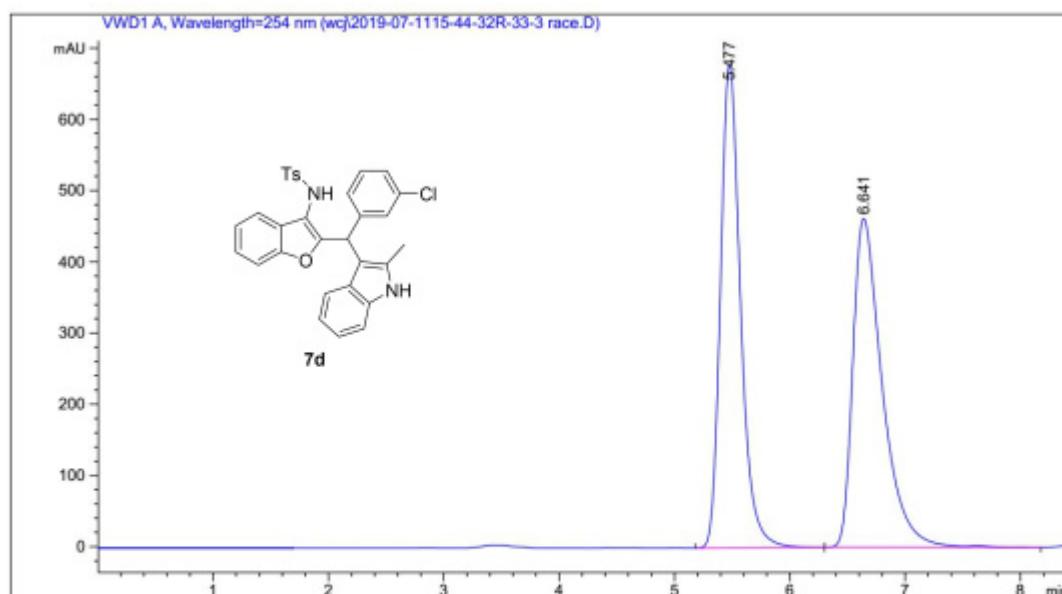
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.309	BV R	0.2932	5806.58008	298.16077	96.6673
2	8.724	VB E	0.3944	200.18649	7.29040	3.3327

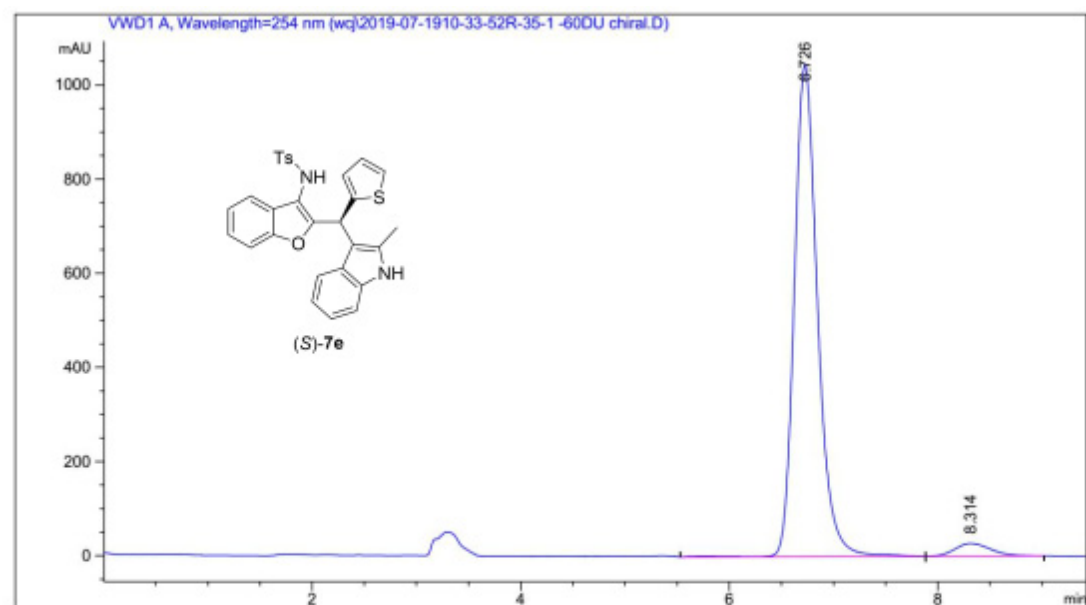
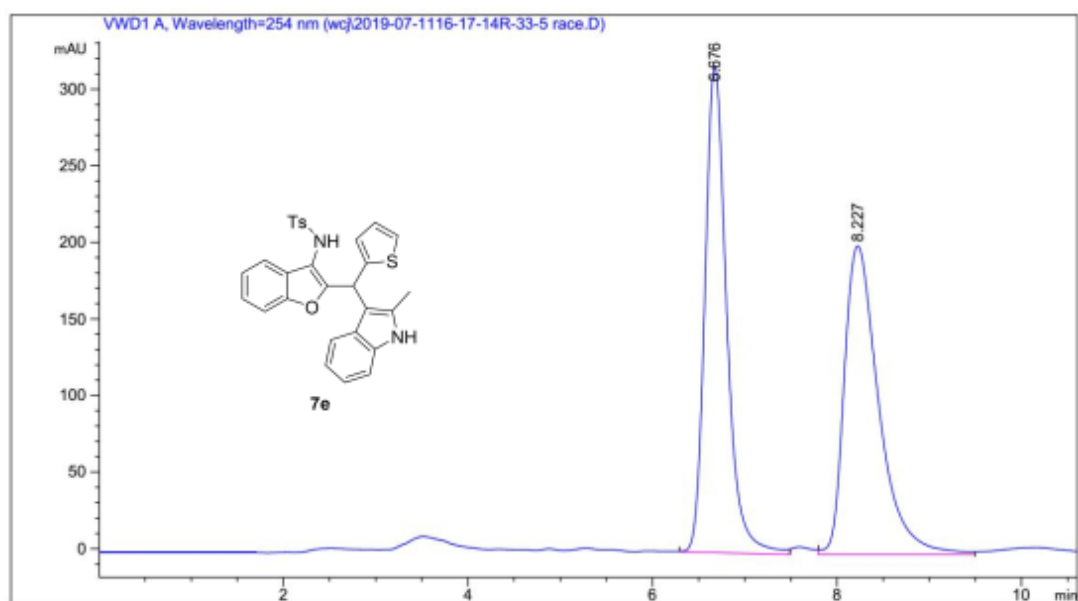


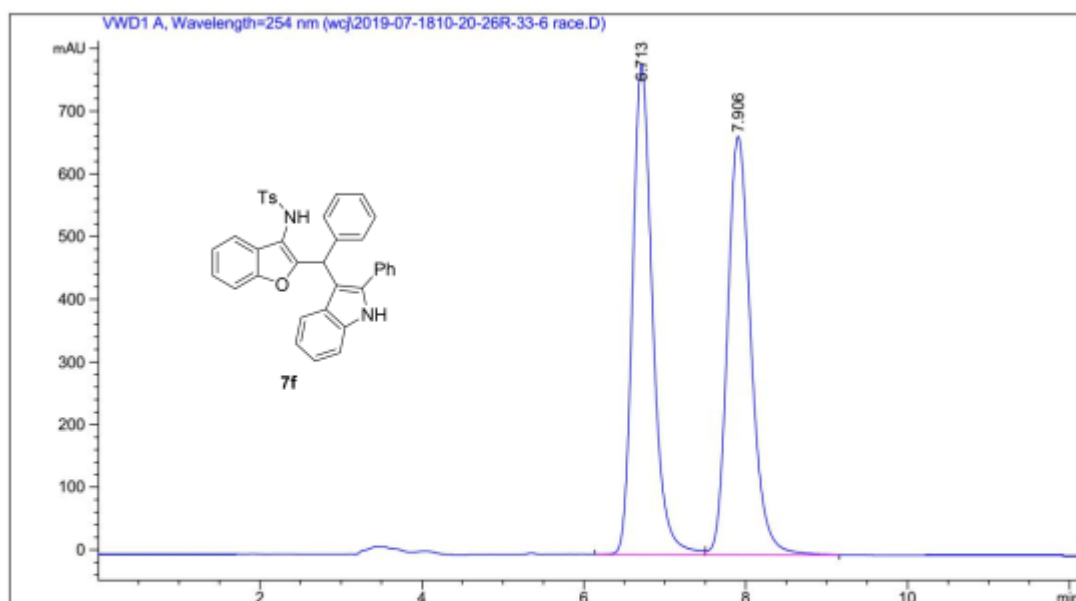
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.514	BV	0.2332	5065.26904	333.57312	49.8911
2	6.494	VV R	0.2776	5087.39014	275.04663	50.1089



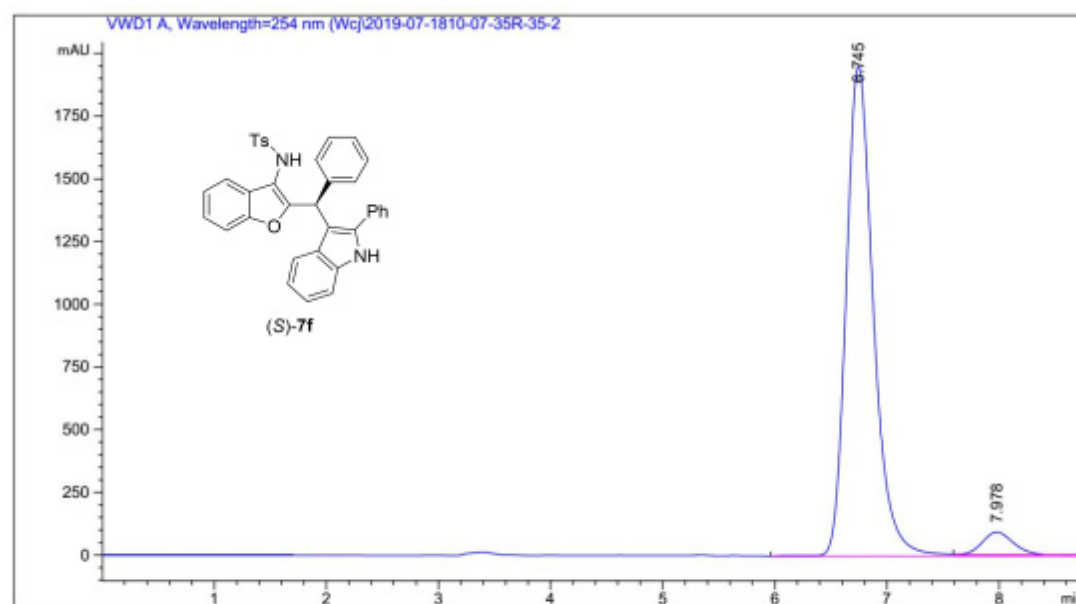
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.440	MF	0.2280	1.60986e4	1176.58972	95.0344
2	6.417	FM	0.4145	841.15784	33.81992	4.9656



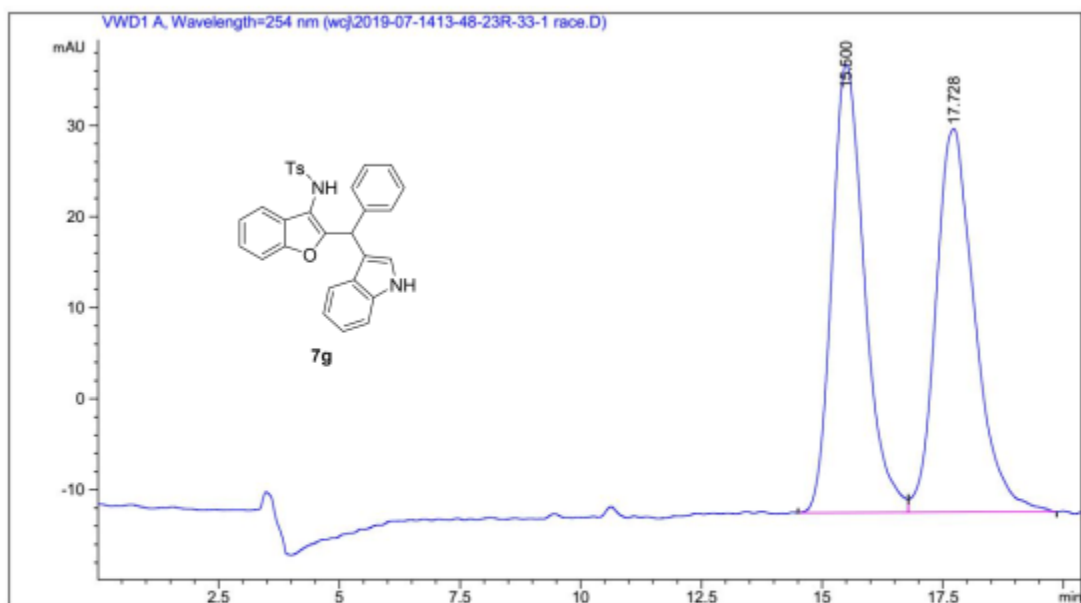




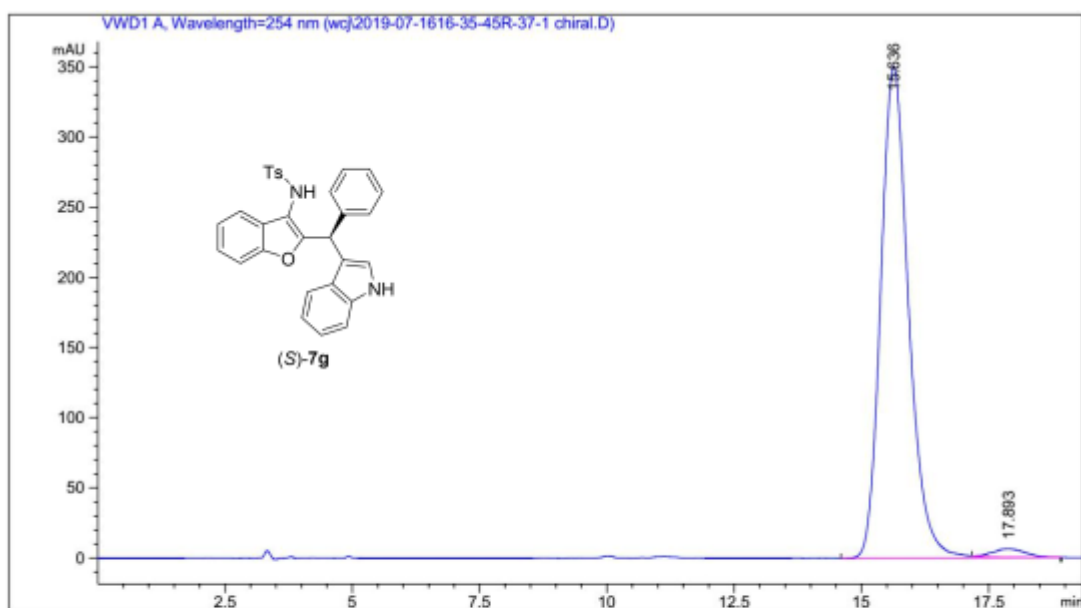
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.713	BV	0.2621	1.33808e4	780.28302	50.0201
2	7.906	VB	0.3088	1.33700e4	667.14227	49.9799



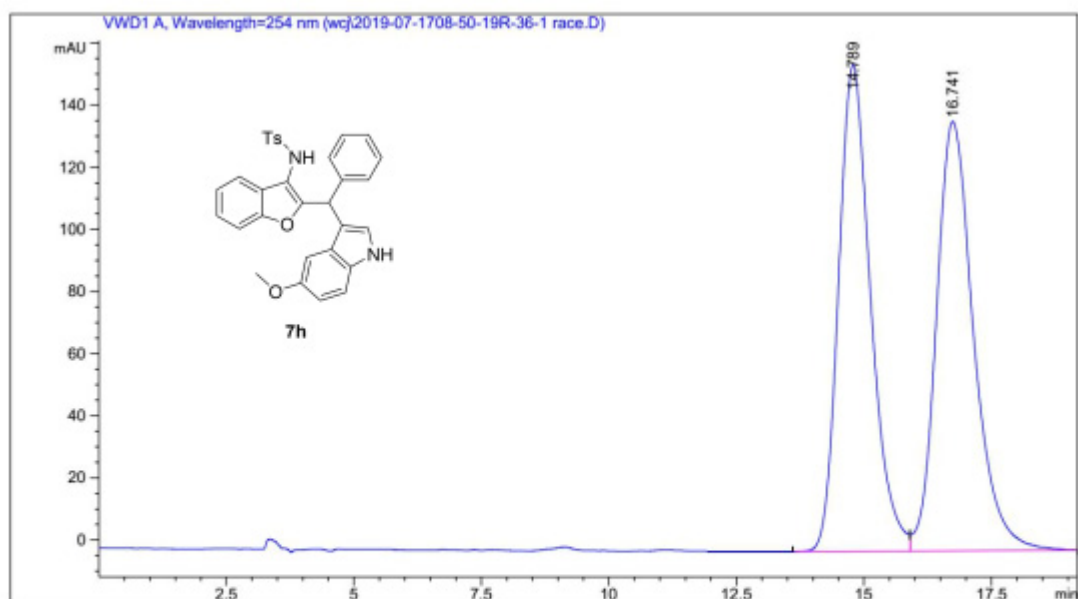
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.745	VV R	0.2576	3.29490e4	1951.76318	94.6657
2	7.978	VBAE	0.3065	1856.65039	92.36141	5.3343



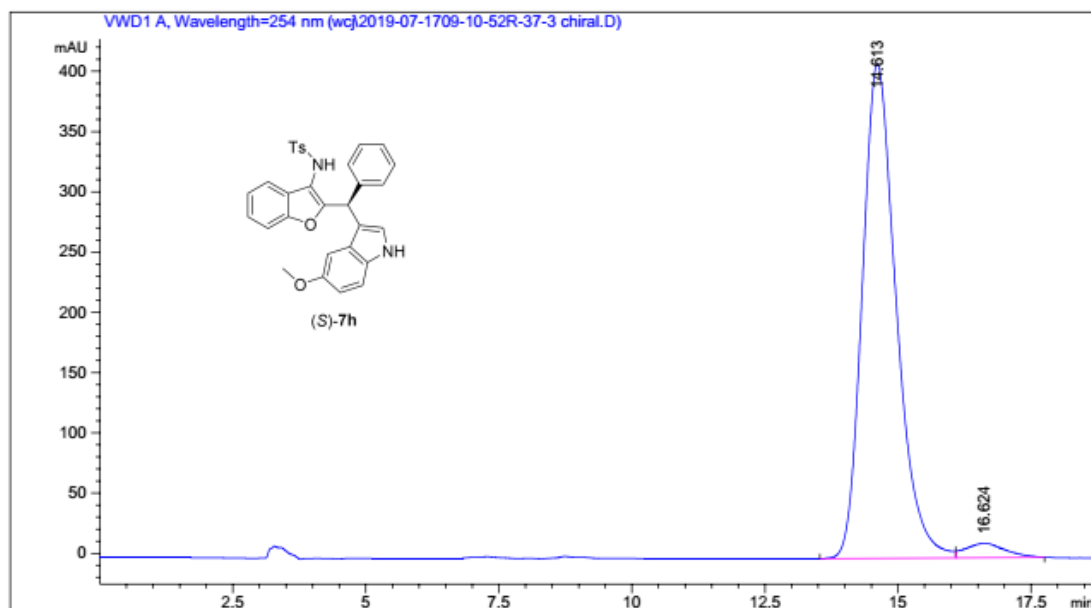
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.500	BV	0.7311	2313.56738	49.24519	49.5130
2	17.728	VB	0.8147	2359.07886	42.10588	50.4870



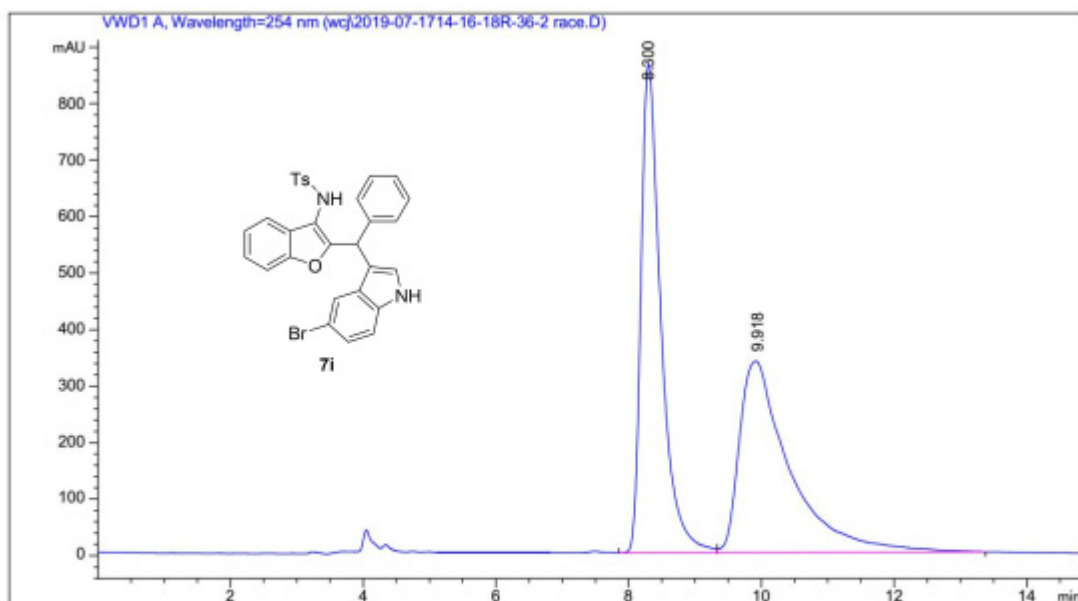
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.636	BV R	0.5882	1.32912e4	350.68134	97.9944
2	17.893	VB E	0.6373	272.02359	6.05303	2.0056



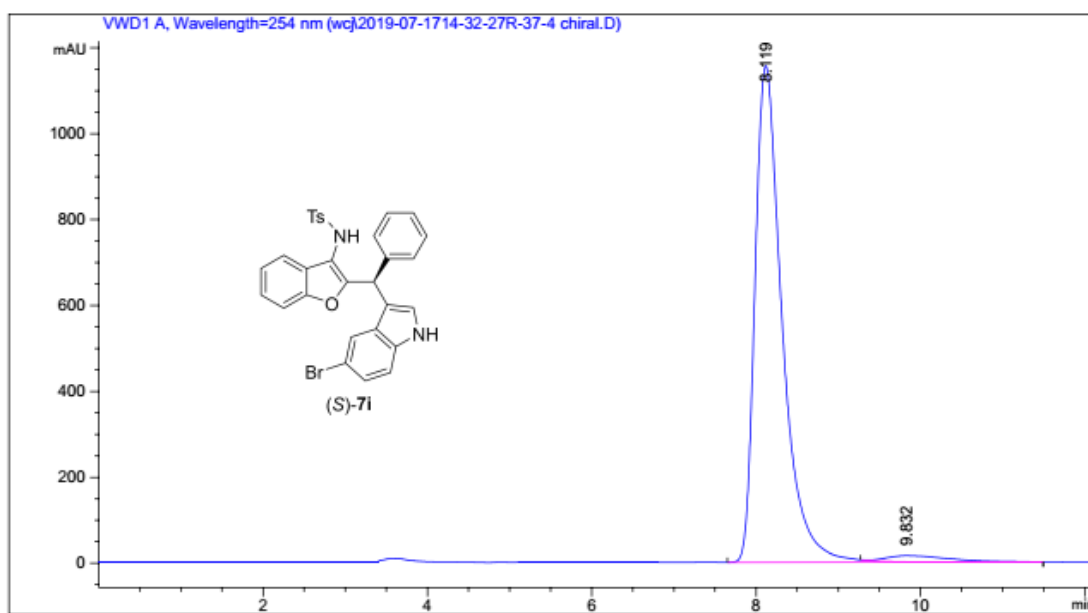
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.789	BV	0.6722	6832.19434	156.53864	49.3785
2	16.741	VBA	0.7705	7004.17188	138.15886	50.6215



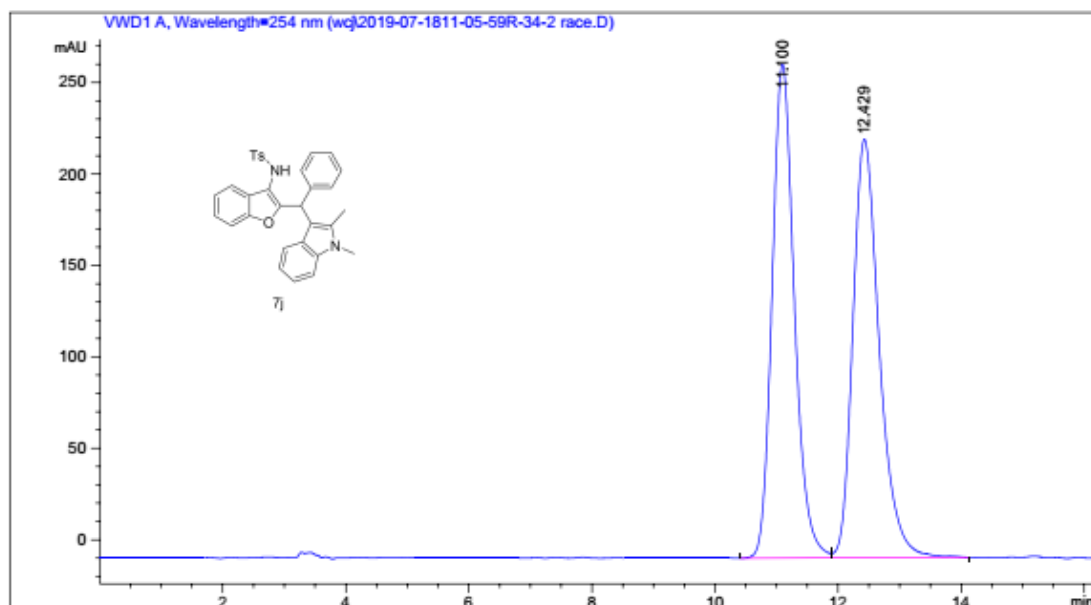
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.613	MF	0.7348	1.80885e4	410.30331	96.7242
2	16.624	FM	0.8748	612.60992	11.67148	3.2758



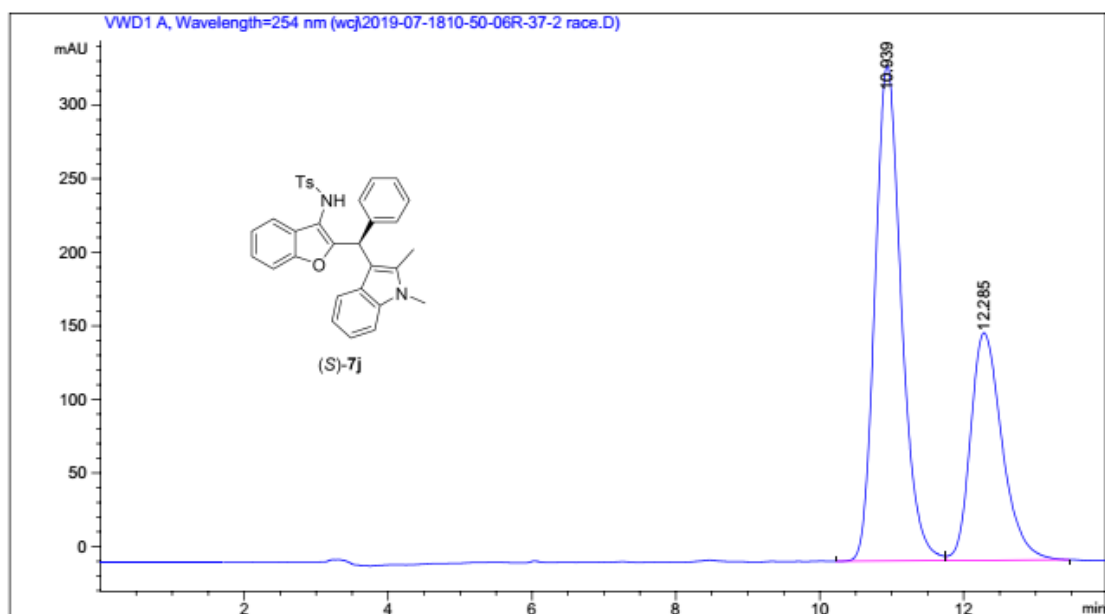
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.300	BV	0.3089	1.79915e4	864.28168	50.2686
2	9.918	VB	0.7464	1.77993e4	338.53836	49.7314



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.119	BV R	0.3437	2.65153e4	1155.68701	97.1591
2	9.832	VB E	0.7333	775.31024	14.39605	2.8409



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.100	BV	0.3854	6770.62402	270.15363	49.7913
2	12.429	VV R	0.4580	6827.37305	228.90221	50.2087



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.939	BV	0.3916	8563.68750	336.84872	64.5030
2	12.285	VB	0.4694	4712.72266	154.72401	35.4970