Supporting Information

Enantioselective Preparation of Atropisomeric Biaryl Trifluoromethylsulfanes via Ring-Opening of Cyclic Diaryliodoniums

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General Information and Materials

General Information

All reactions were carried out under a nitrogen atmosphere in oven or flame-dried glassware, unless the reaction procedure states otherwise. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer using solvent residue as an internal reference (7.26 and 77.16 ppm for $CDCl_3$, 2.50 and 39.00 ppm for DMSO-d_6, respectively). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectra (HRMS (ESI)) was recorded on a high-resolution mass spectrometer (Waters XEVO-G2 Q-TOF). Gas chromatography time of flight high resolution mass spectra (GCTOF-HRMS (EI)) was recorded on a high-resolution mass spectrometer (Waters GCT premier).

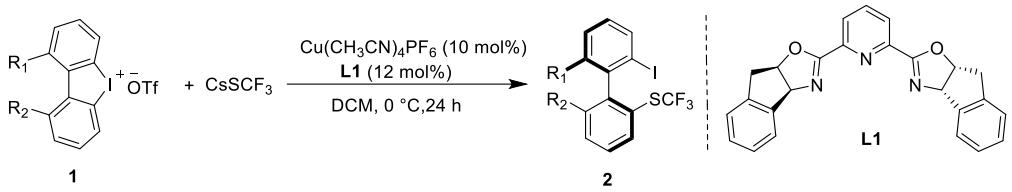
Materials

All reagents as used as super anhydrous pyridine, superdry dichloromethane (DCM), superdry tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were used as received from commercial sources and used without further purification. Diethyl ether (Et_2O) was distilled over sodium in the presence of benzophenone under an atmosphere of nitrogen. Carbon disulfide (CS_2) was distilled over anhydrous calcium chloride under an atmosphere of nitrogen. Flash column chromatography was performed using 200-300 mesh silica gel as the stationary phase. The diaryliodonium,[1,2] and sodium phenylthiosulfonate[3,4] were synthesized according to the reported literatures. $CsSCF_3$ was synthesized according to the reported literature with a little modification.[5]

Typical Procedure for Preparation of $CsSCF_3$ (Procedure A)

To an oven-dried Schlenk flask, 0.32 g (10.0 mmol) elemental sulfur was dissolved in 80 mL anhydrous tetrahydrofuran (THF) at room temperature under N_2 atmosphere. An amount of $TMSCF_3$ (12 mmol, 1.2 equiv) was added and the reaction mixture was cooled to -60℃. After sttiring for 10 minutes, a white paticipate was formed. An amount of anhydrous CsF (10.0 mmol, 1.0 equiv) was added in one portion. The mixture was kept at -60℃ for 30 min and then allowed to warm to room temperature slowly and sttired overnight to give a pale yellow mixture. The solvent was removed under reduced pressure and 30 mL fresh distilled CS_2 was added under N_2 protection. The resulting mixture was dispersed by ultrasound, filtered and washed with CS_2 for two times. The resulting colorless powder was dried in vacuum and stored in glovebox. Characterization was according to the literature report [5].

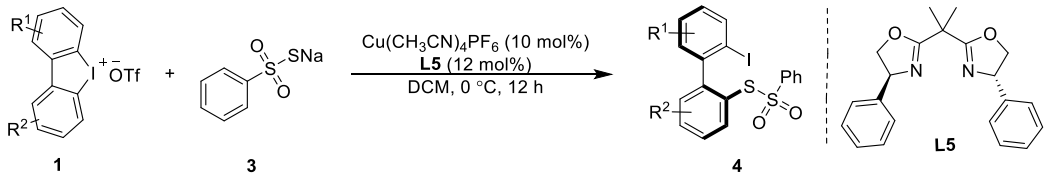
General Procedure for Copper-Catalyzed Asymmetric Ring-opening of Cyclic Diaryliodoniums with $CsSCF_3$ (Procedure B)



1 2

In a glovebox, an oven-dried Schlenk tube was sequentially charged with diaryliodoniums salts **1** (1.0 equiv), $CsSCF_3$ (1.5 equiv), $Cu(CH_3CN)_4PF_6$ (10.0 mol%) and **L1** (12.0 mol%) in dichloromethane (0.05 M for diaryliodoniums). The Schleck tube was capped, then taken out of the glovebox and stirred at 0 ℃ for 24 h. After the reaction was completed, the mixture was filtered through a pat of silica gel with ethyl acetate. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel with petroleum ether to afford the corresponding products.

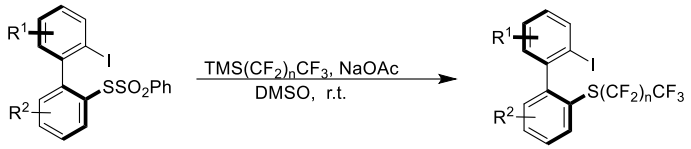
General Procedure for Peraparation of Corresponding Thiosulfonates (Procedure C)



1 3 4

Under nitrogen atmosphere, an oven-dried Schlenk tube was sequentially charged with $Cu(CH_3CN)_4PF_6$ (5.0 mol%), **L5** (6.0 mol%) and dichloromethane (0.05 M for diaryliodoniums). After stirring at room temperature for 1 h, the reaction was cooled to 0℃, and then diaryliodoniums salts **1** (1.0 equiv) and $PhSO_2SNa$ (1.5 equiv) were added. The mixture was stirred at 0 ℃ for 12 h. After the reaction was completed, the mixture was filtered through a plug of celite with ethyl acetate. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate /hexanes = 1:20) to afford the corresponding thiosulfonates **4**.

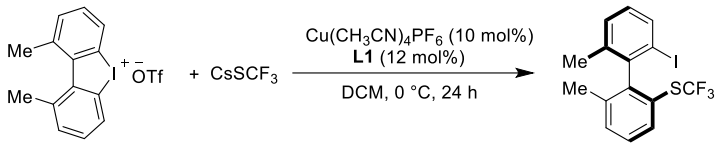
General Procedure for Preparation of Corresponding Perfluoroalkyl Sulfides (Procedure D)



4 **5 or 6** (n= 0, 1 or 2)

An oven-dried Schlenk tube was sequentially charged with the corresponding thiosulfonates **4** (1.0 equiv) and NaOAc (3.0 equiv). Anhydrous DMSO (1 M for thiosulfonates) was then added followed by dropwise addition of $TMS(CF_2)_nCF_3$ (n = 0, 1 or 2) (3.0 equiv) with stirring. Then the reaction was stirred at room temperature overnight. After the reaction was completed, it was diluted with DCM. The organic layer was washed with water (three times) and brine, then dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding perfluoroalkyl sulfides **5**.

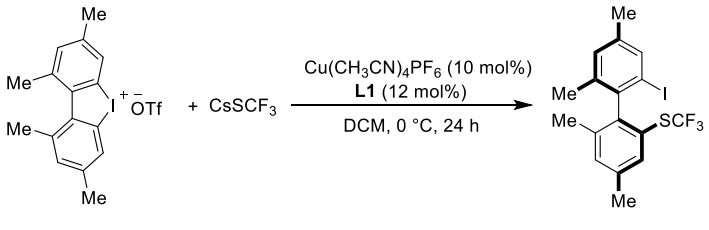
(*S*)-[2'-iodo-6,6'-dimethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (**2a**)



1a **2a**

The compound **2a** was synthesized according to **procedure B**. The reaction of diaryliodoniums salts **1a** (45.6 mg, 0.1 mmol, 1.0 equiv), $CsSCF_3$ (35.0 mg, 0.15 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 0.01 mmol, 10.0 mol%) and **L1** (4.7 mg, 0.012 mmol, 12.0 mol%) in dichloromethane (2.0 mL) afforded the corresponding product **2a** (39.5 mg, 97%, 96% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 286 nm, t_r = 5.588 min (minor), 5.791 min (major). $[\alpha]_D^{20}$ = 43.9 (c 0.51, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.75 - 7.58 (m, 1H), 7.39-7.35 (m, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 2.01 (s, 3H), 1.99 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.14. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 143.0, 138.0, 137.9, 136.8, 132.5, 132.0, 130.2, 129.7 (q, J_{C-F} = 247.5 Hz), 128.9, 128.5, 125.5, 101.3, 21.2, 20.4. HRMS (EI): calcd. for $C_{15}H_{12}F_3IS$ $[M]^+$: 407.9656; Found: 407.9658.

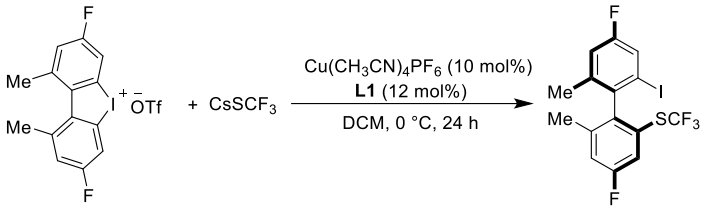
(*S*)-[2'-iodo-4,4',6,6'-tetramethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (**2b**)



1b **2b**

The compound **2b** was synthesized according to **procedure B**. The reaction of diaryliodoniums salts **1b** (48.4 mg, 0.1 mmol, 1.0 equiv), $CsSCF_3$ (35.0 mg, 0.15 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 0.01 mmol, 10.0 mol%) and **L1** (4.7 mg, 0.012 mmol, 12.0 mol%) in dichloromethane (2.0 mL) afforded the product **2b** (42.7 mg, 98%, 92% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = 4.638 min (minor), 4.950 min (major). $[\alpha]_D^{20}$ = 30.3 (c 2.28, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.46 (s, 1H), 7.18 (s, 1H), 7.08 (s, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.13. ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 140.1, 139.6, 138.6, 137.7, 137.1, 132.91, 132.89, 132.87, 131.1, 129.8 (q, J_{C-F} = 310.1 Hz), 125.2, 101.6, 21.3, 21.2, 20.8, 20.4. HRMS (EI): calcd. for $C_{17}H_{16}F_3IS$ $[M]^+$: 435.9969; Found: 435.9970.

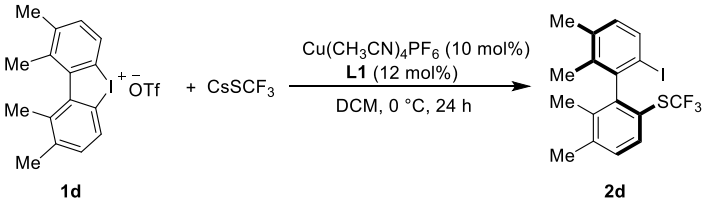
(*S*)-[4,4'-difluoro-2'-iodo-6,6'-dimethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (2c)



1c **2c**

The compound **2c** was synthesized according to **procedure B**. The reaction of diaryliodoniums salts **1c** (49.2 mg, 0.1 mmol, 1.0 equiv), $CsSCF_3$ (35.0 mg, 0.15 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 0.01 mmol, 10.0 mol%) and **L1** (4.7 mg, 0.012 mmol, 12.0 mol%) in dichloromethane (2.0 mL) afforded the product **2c** (42.6 mg, 96%, 96% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 273 nm, t_r = 5.369 min (minor), 5.650 min (major). $[\alpha]_D^{20}$ = 30.3 (c 0.43, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 9.6 Hz, 1H), 2.00 (s, 3H), 1.97 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.07, -112.00, -112.72. ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (d, J_{C-F} = 251.5 Hz), 161.8 (d, J_{C-F} = 252.5 Hz), 141.6, 140.4, 140.3, 139.84, 139.76, 138.13, 138.10, 129.4 (q, J_{C-F} = 310.1 Hz), 127.7 (d, J_{C-F} = 8.0 Hz), 124.1, 123.9, 119.0, 118.8, 118.5, 118.3, 117.5, 117.3, 101.0, 100.9, 21.5, 20.6 (d, J_{C-F} = 1.8 Hz). HRMS (EI): calcd. for $C_{15}H_{10}F_5IS$ $[M]^+$: 443.9468; Found: 443.9469.

(*S*)-[6'-iodo-2',3',5,6-tetramethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (2d)

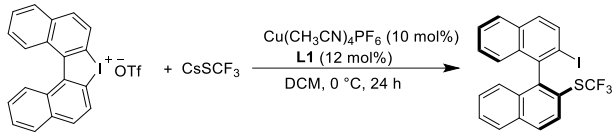


1d **2d**

The compound **2d** was synthesized according to **procedure B**. The reaction of diaryliodoniums salts **1d** (48.5 mg, 0.1 mmol, 1.0 equiv), $CsSCF_3$ (35.0 mg, 0.15 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 0.01 mmol, 10.0 mol%) and **L1** (4.7 mg, 0.012 mmol, 12.0 mol%) in dichloromethane (2.0 mL) afforded the product **2d** (43.2 mg, 99%, 91% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = 5.484 min (minor), 5.787 min (major). $[\alpha]_D^{20}$ = 38.7 (c 0.56, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H),

1.91 (s, 3H), 1.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.57. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 143.4, 139.8, 137.3, 136.9, 136.5, 136.0, 132.9, 131.1, 130.3, 129.8 (q, J_{C-F} = 310.1 Hz), 122.40, 122.38, 98.2, 20.9, 20.4, 18.1, 16.8. HRMS (EI): calcd. for $C_{17}H_{16}F_3IS$ $[M]^+$: 435.9969; Found: 435.9970.

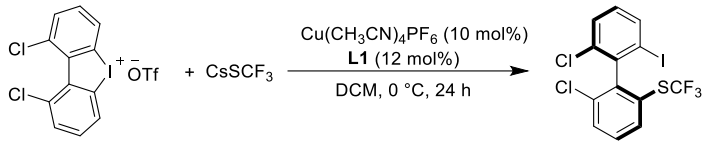
(*S*)-[2'-iodo-(1,1'-binaphthalen)-2-yl](trifluoromethyl)sulfane (2e)



1e **2e**

The compound **2e** was synthesized according to **procedure B**. The reaction of diaryliodoniums salts **1e** (52.8 mg, 0.1 mmol, 1.0 equiv), $CsSCF_3$ (35.0 mg, 0.15 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 0.01 mmol, 10.0 mol%) and **L1** (4.7 mg, 0.012 mmol, 12.0 mol%) in dichloromethane (2.0 mL) afforded the product **2e** (40.8 mg, 85%, 98% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = 15.427 min (major), 22.769 min (minor). $[\alpha]_D^{20}$ = 28.5 (c 0.52, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.02 (m, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.59-7.54 (m, 1H), 7.53-7.48 (m, 1H), 7.36-7.31 (m, 1H), 7.29-7.23 (m, 1H), 7.08 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.45. ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 140.4, 135.5, 133.9, 133.6, 132.8, 132.6, 130.8, 130.1, 129.67 (q, J_{C-F} = 310.1 Hz), 129.65, 128.34, 128.25, 127.8, 127.6, 127.3, 126.8, 126.74, 126.72, 124.0 (d, *J* = 2.0 Hz), 100.4. HRMS (EI): calcd. for $C_{21}H_{12}F_3IS$ $[M]^+$: 479.9656; Found: 479.9655.

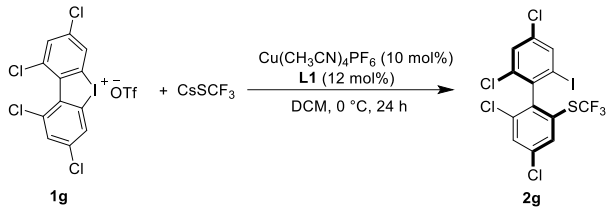
(*R*)-[2',6-dichloro-6'-iodo-(1,1'-biphenyl)-2-yl] (trifluoromethyl)sulfane (2f)



1f **2f**

The compound **2f** was synthesized according to **procedure B**. The reaction of diaryliodoniums salts **1f** (49.7 mg, 0.1 mmol, 1.0 equiv), $CsSCF_3$ (35.0 mg, 0.15 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 0.01 mmol, 10.0 mol%) and **L1** (4.7 mg, 0.012 mmol, 12.0 mol%) in dichloromethane (2.0 mL) afforded the product **2f** (44.5 mg, 99%, >99% ee). HPLC conditions: Chiralpak OD-OD, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = XX min (minor), XX min (major). $[\alpha]_D^{20}$ = 19.1 (c 1.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.62 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.51 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.98. ^{13}C NMR (101 MHz, CDCl3) δ 144.9, 140.8, 137.6, 135.3, 134.1, 134.06, 134.05, 131.7, 131.2, 130.4, 129.6, 129.2 (q, *J* = 311.1 Hz), 127.5 (d, *J* = 2.0 Hz), 100.7. HRMS (EI): calcd. for $C_{13}H_6Cl_2F_3IS$ $[M]^+$: 447.8564; Found: 447.8562.

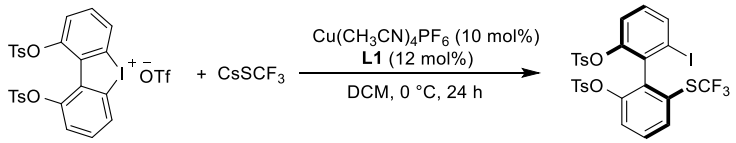
(*R*)-[2',4,4',6-tetrachloro-6'-iodo-(1,1'-biphenyl)]-2-yl(trifluoromethyl)sulfane (2g)



1g 2g

The compound **2g** was synthesized according to **procedure B**. The reaction of diaryliodoniums salts **1g** (56.6 mg, 0.1 mmol, 1.0 equiv), $CsSCF_3$ (35.0 mg, 0.15 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 0.01 mmol, 10.0 mol%) and **L1** (4.7 mg, 0.012 mmol, 12.0 mol%) in dichloromethane (2.0 mL) afforded the product **2g** (50.6 mg, 98%, 99% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = 5.145 min (minor), 5.355 min (major). $[\alpha]_D^{20}$ = 16.1 (c 0.76, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.0 Hz, 1H), 7.75 (s, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.73. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 138.5, 137.4, 136.1, 136.0, 135.9, 134.4, 133.7 (d, *J* = 1.7 Hz), 131.7, 129.7, 128.83 (d, *J* = 2.2 Hz), 128.80 (q, *J* = 310.1 Hz), 100.4. HRMS (EI): calcd. for $C_{13}H_4Cl_4F_3IS$ $[M+H]^+$: 515.7785; Found: 515.7786.

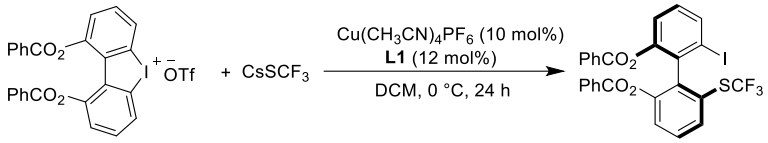
(*S*)-6-iodo-6'-[(trifluoromethyl)thio]-[1,1'-biphenyl]-2,2'-diyl bis(4-methylbenzenesulfonate) (2h)



1h 2h

The compound **2h** was synthesized according to **procedure B**. The reaction of diaryliodoniums salts **1h** (76.9 mg, 0.1 mmol, 1.0 equiv), $CsSCF_3$ (35.0 mg, 0.15 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 0.01 mmol, 10.0 mol%) and **L1** (4.7 mg, 0.012 mmol, 12.0 mol%) in dichloromethane (2.0 mL) was stirred at 40 ℃ for 48 h. After completed, the reaction mixture was filtered through a plug of celite with ethyl acetate. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (ethyl acetate/ hexanes = 1:10) to afford the product **2h** (28.8 mg, 40%, 98% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 5:95, flow: 1.0 mL/min, λ = 230 nm, t_r = 17.163 min (major), 20.585 min (minor). $[\alpha]_D^{20}$ = 17.4 (c 0.98, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.45 (m, 7H), 7.45-7.38 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 8.2 Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CHCl_3$) δ -40.39. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.9, 145.4, 145.3, 136.5, 135.9, 133.5, 133.4, 133.0, 131.7, 130.7, 130.6 (q, J_{C-F} = 286.8 Hz), 129.82, 129.80, 128.3, 128.0, 127.9, 123.5, 120.1, 101.8, 21.9, 21.8. HRMS (ESI): calcd. for $C_{27}H_{20}F_3IO_6S_3$ $[M+Na]^+$: 742.9316; Found: 742.9330.

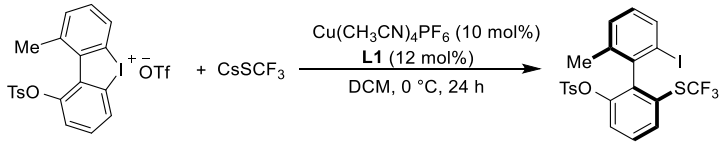
(*S*)-6-iodo-6'-[(trifluoromethyl)thio]-[1,1'-biphenyl]-2,2'-diyl dibenzoate (2i)



1i **2i**

The compound **2i** was synthesized according to **procedure B**. The reaction of diaryliodoniums salts **1i** (334 mg, 0.5 mmol, 1.0 equiv), $CsSCF_3$ (175.5 mg, 0.75 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (18.6 mg, 0.01 mmol, 10.0 mol%) and **L1** (23.6 mg, 0.012 mmol, 12.0 mol%) in dichloromethane (10.0 mL) was stirred at 40 ℃ for 24 h. After the reaction was completed, the reaction mixture was filtered through a plug of celite with ethyl acetate. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (ethyl acetate/ hexanes = 1:10) to afford the product **2i** (242 mg, 78%, 94% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, λ = 254 nm, t_r = 5.616 min (major), 7.138 min (minor). $[\alpha]_D^{20}$ = 41.0 (c 0.23, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.81 (m, 3H), 7.81-7.71 (m, 3H), 7.57-7.50 (m, 4H), 7.47-7.45 (m, 1H), 7.40-7.34 (m, 4H), 7.17 (t, *J* = 8.1 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.52. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 163.9, 149.3, 148.8, 136.1, 133.7, 133.4, 133.2, 132.3 (q, J_{C-F} = 385.8 Hz), 130.2, 130.04, 130.01, 129.0, 128.9, 128.6, 125.4, 122.7, 100.7. HRMS (ESI): calcd. for $C_{21}H_{13}F_3IO_4S$ $[M+Na]^+$: 620.9844; Found: 620.9851.

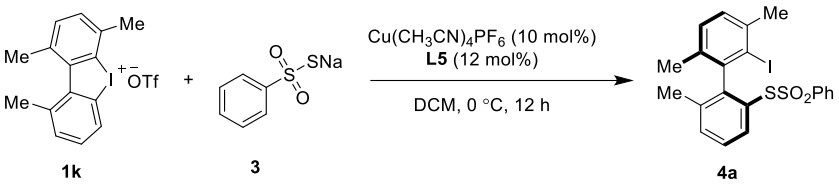
(*S*)-2'-iodo-6'-methyl-6-[(trifluoromethyl)thio]-[1,1'-biphenyl]-2-yl 4-methylbenzenesulfonate (2j)



1j **2j**

The compound **2j** was synthesized according to **procedure B**. The reaction of diaryliodoniums salts **1j** (61.3 mg, 0.1 mmol, 1.0 equiv), $CsSCF_3$ (35.0 mg, 0.15 mmol, 1.5 equiv), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 0.01 mmol, 10.0 mol%) and **L1** (4.7 mg, 0.012 mmol, 12.0 mol%) in dichloromethane (2.0 mL) was stirred at 0 ℃ for 24 h. After completed, the reaction mixture was filtered through a plug of celite with ethyl acetate. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (ethyl acetate/ hexanes = 1:10) to afford the product **2j** (25.4 mg, 45%, 99% ee). HPLC conditions: Chiralpak IC, isopropanol/hexane = 2:98, flow: 1.0 mL/min, λ = 254 nm, t_r = 9.775 min (minor), 10.450 min (major). $[\alpha]_D^{20}$ = 20.7 (c 0.64, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.70 -7.59 (m, 2H), 7.50 (t, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.19-7.15 (m, 3H), 6.97 (t, *J* = 7.8 Hz, 1H), 2.41 (s, 3H), 2.02 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.48. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 145.3, 141.0, 139.4, 138.6, 136.5, 133.8, 133.4, 130.0, 129.9, 129.8, 129.4 (q, J_{C-F} = 310.1 Hz), 128.0, 127.9, 124.4, 102.1, 21.8, 21.3. HRMS (ESI): calcd. for $C_{21}H_{16}F_3IO_3S_2Na$ $[M+Na]^+$:586.9435; Found: 586.9443.

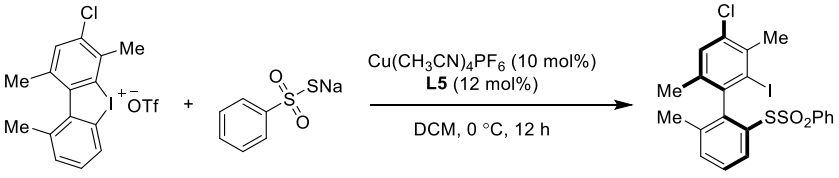
O-phenyl (*R*,1'*S*)-2'-iodo-3',6,6'-trimethyl-[1,1'-biphenyl]-2-sulfonothioate (4a)



1k 3 4a

The compound **4a** was synthesized according to **procedure C**. The reaction of $Cu(CH_3CN)_4PF_6$ (18.6 mg, 0.05 mmol, 10.0 mol%), **L5** (20.0 mg, 0.06 mmol, 12.0 mol%), diaryliodoniums salts **1k** (235.1 mg, 0.50 mmol, 1.0 equiv) and $PhSO_2SNa$ (147.0 mg, 0.75 mmol, 1.5 equiv) in dichloromethane (10.0 mL) afforded the corresponding product **4a** (232.0 mg, 94%, 94% ee). HPLC conditions: Chiralpak OX-H, isopropanol/hexane = 3:97, flow: 1.0 mL/min, λ = 254 nm, t_r = 19.273 min (minor), 32.994 min (major). $[\alpha]_D^{20}$ = 120.1 (c 0.85, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.62 -7.55 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.36-7.28 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 2.44 (s, 3H), 1.90 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 145.0, 143.1, 139.8, 137.9, 135.1, 133.8, 132.6, 132.5, 129.9, 129.24, 129.20, 128.5, 128.3, 127.8, 108.3, 29.5, 20.7, 20.2. HRMS (ESI): calcd. for $C_{21}H_{20}IO_2S_2$ $[M+H]^+$: 494.9949; Found: 494.9948.

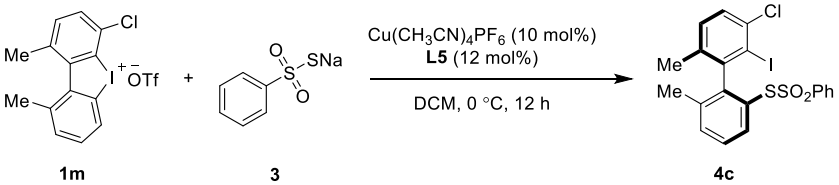
O-phenyl (*R*,1'*S*)-4'-chloro-2'-iodo-3',6,6'-trimethyl-[1,1'-biphenyl]-2-sulfonothioate (4b)



1l 3 4b

The compound **4b** was synthesized according to **procedure C**. The reaction of $Cu(CH_3CN)_4PF_6$ (18.6 mg, 0.05 mmol, 10.0 mol%), **L5** (20.0 mg, 0.06 mmol, 12.0 mol%), diaryliodoniums salts **1l** (252.4 mg, 0.50 mmol, 1.0 equiv) and $PhSO_2SNa$ (147.0 mg, 0.375 mmol, 1.5 equiv) in dichloromethane (10.0 mL) afforded the corresponding product **4b** (238.0 mg, 90%, 91% ee). HPLC conditions: Chiralpak OX-H, isopropanol/hexane = 6:94, flow: 1.0 mL/min, λ = 254 nm, t_r = 11.382 min (minor), 14.567 min (major). $[\alpha]_D^{20}$ = 118.6 (c 1.25, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.38-7.28 (m, 2H), 7.20 (s, 1H), 2.61 (s, 3H), 1.90 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 144.8, 142.4, 137.9, 137.1, 136.4, 133.9, 132.9, 132.8, 130.8, 129.3, 128.8, 128.2, 127.8, 109.3, 27.4, 20.7, 20.2. HRMS (ESI): calcd. for $C_{21}H_{18}ClIO_2S_2Na$ $[M+Na]^+$: 550.9379; Found: 550.9382.

O-phenyl (*R*,1'*S*)-3'-chloro-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-sulfonothioate (4c)

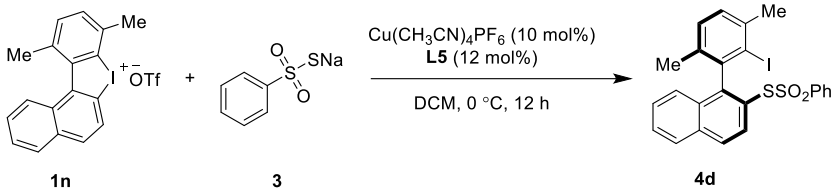


1m 3 4c

The compound **4c** was synthesized according to **procedure C**. The reaction of $Cu(CH_3CN)_4PF_6$ (18.6 mg, 0.05 mmol, 10.0 mol%), **L5** (20.0 mg, 0.06 mmol, 12.0 mol%), diaryliodoniums salts **1m**

(245.4 mg, 0.50 mmol, 1.0 equiv) and $PhSO_2SNa$ (147.0 mg, 0.75 mmol, 1.5 equiv) in dichloromethane (10.0 mL) afforded the corresponding product **4c** (252.2 mg, 98%, 98% ee). HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 2:98, flow: 1.0 mL/min, λ = 254 nm, t_r = 16.627 min (minor), 17.296 min (major). $[\alpha]_D^{20}$ = 164.8 (c 0.74, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.63-7.59 (m, 1H), 7.54-7.46 (m, 3H), 7.39-7.34 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 1.92 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 145.3, 144.7, 137.7, 136.6, 136.2, 133.9, 132.94, 132.91, 131.2, 129.3, 128.9, 128.7, 127.8, 105.5, 20.8, 20.2. HRMS (ESI): calcd. for $C_{20}H_{16}ClIO_2S_2Na$ $[M+Na]^+$: 536.9223; Found: 536.9225.

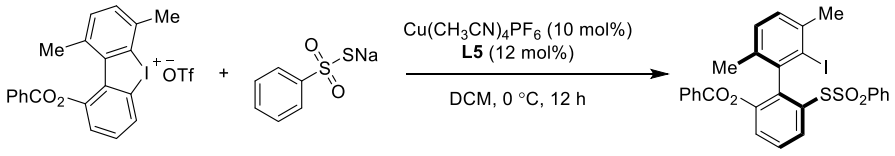
O-phenyl (*R*)-1-((*S*)-2-iodo-3,6-dimethylphenyl)naphthalene-2-sulfonothioate (4d)



1n **3** **4d**

The compound **4d** was synthesized according to **procedure C**. The reaction of $Cu(CH_3CN)_4PF_6$ (18.6 mg, 0.05 mmol, 10.0 mol%), **L5** (20.0 mg, 0.06 mmol, 12.0 mol%), diaryliodoniums salts **1n** (253.2 mg, 0.50 mmol, 1.0 equiv) and $PhSO_2SNa$ (147.0 mg, 0.75 mmol, 1.5 equiv) in dichloromethane (10.0 mL) afforded the corresponding product **4d** (233.4 mg, 88%, 97% ee). HPLC conditions: Chiralpak OX-H, isopropanol/hexane = 6:94, flow: 1.0 mL/min, λ = 254 nm, t_r = 18.188 min (minor), 28.850 min (major). $[\alpha]_D^{20}$ = 181.8 (c 0.49, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.93-7.87 (m, 2H), 7.84-7.73 (m, 3H), 7.61-7.52 (m, 2H), 7.48-7.42 (m, 2H), 7.40-7.37 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 2.48 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 145.2, 142.0, 139.8, 136.1, 134.2, 133.9, 131.9, 130.2, 129.8, 129.6, 129.3, 128.9, 128.4, 127.9, 127.8, 127.5, 126.3, 125.7, 109.1, 29.6, 20.8. HRMS (ESI): calcd. for $C_{24}H_{19}IO_2S_2[M+Na]^+$: 552.9769; Found: 552.9767.

(*S*)-2'-iodo-3',6'-dimethyl-6-[(R)-phenoxysulfonothioyl]-[1,1'-biphenyl]-2-yl benzoate (4e)

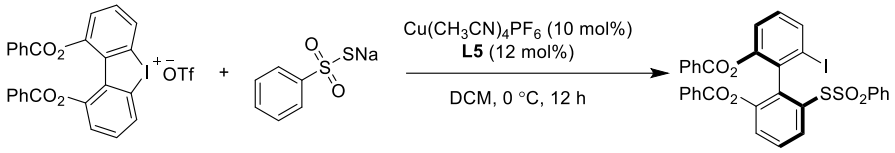


1o **3** **4e**

The compound **4e** was synthesized according to **procedure C**. The reacton of $Cu(CH_3CN)_4PF_6$ (18.6 mg, 0.05 mmol, 10.0 mol%), **L5** (20.0 mg, 0.06 mmol, 12.0 mol%), diaryliodoniums salts **1o** (288.2 mg, 0.50 mmol, 1.0 equiv) and $PhSO_2SNa$ (147.0 mg, 0.75 mmol, 1.5 equiv) in dichloromethane (10.0 mL). The residue was purified by column chromatography on silica gel (ethyl acetate /hexanes = 1:10) to afford the corresponding product **4e** (285.0 mg, 95%, 97% ee). HPLC conditions: Chiralpak OX-H, isopropanol/hexane = 10:90, flow: 1.0 mL/min, λ = 254 nm, t_r = 18.966 min (minor), 25.459 min (major). $[\alpha]_D^{20}$ = 96.0 (c 1.36, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.70-7.64 (m, 3H), 7.63-7.59 (m, 1H), 7.57-7.45 (m, 5H), 7.36-7.30 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 2.40 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 148.8, 144.6, 141.4, 139.6, 139.4, 136.0, 134.0, 133.7, 132.5, 130.0,

129.8, 129.6, 129.5, 129.33, 129.30, 129.0, 128.5, 127.9, 125.4, 108.4, 29.6, 20.8. HRMS (ESI): calcd. for $C_{27}H_{21}IO_4S_2Na$ $[M+Na]^+$: 622.9824; Found: 622.9824.

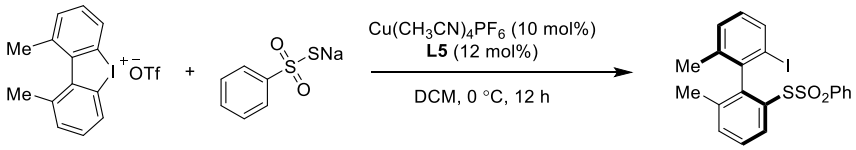
(*S*)-6-iodo-6'-[(*R*)-phenoxysulfonothioyl]-[1,1'-biphenyl]-2,2'-diyl dibenzoate (4f)



1p **3** **4f**

The compound **4f** was synthesized according to **procedure C**. The reaction of $Cu(CH_3CN)_4PF_6$ (18.6 mg, 0.05 mmol, 10.0 mol%), **L5** (20.0 mg, 0.06 mmol, 12.0 mol%), diaryliodoniums salts **1p** (334.2 mg, 0.50 mmol, 1.0 equiv) and $PhSO_2SNa$ (147.0 mg, 0. 75 mmol, 1.5 equiv) in dichloromethane (10.0 mL). The residue was purified by column chromatography on silica gel (ethyl acetate /hexanes = 1:10) and recrystallized by ethyl acetate / hexanes to afford the corresponding product **4f** (311.6 mg, 90%, >99% ee). HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm, t_r = 49.108 min (major), 60.837 min (minor). $[\alpha]_D^{20}$ = 85.2 (c 0.74, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.69 (m, 5H), 7.69-7.62 (m, 2H), 7.60-7.41 (m, 7H), 7.40-7.30 (m, 6H), 7.10 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 163.7, 149.3, 148.9, 144.1, 137.2, 135.8, 133.9, 133.8, 133.74, 133.68, 132.4, 130.6, 130.23, 130.22, 129.8, 129.7, 129.2, 128.8, 128.5, 127.8, 125.8, 122.3, 100.9. HRMS (ESI): calcd. for $C_{32}H_{22}IO_6S_2$ $[M+H]^+$: 692.9902; Found: 692.9904.

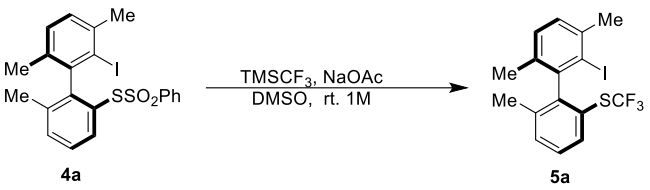
O-phenyl (*R*,1'*S*)-2'-iodo-6,6'-dimethyl-[1,1'-biphenyl]-2-sulfonothioate (4g)



1a **3** **4g**

The compound **4g** was synthesized according to **procedure C**. The reaction of $Cu(CH_3CN)_4PF_6$ (18.6 mg, 0.05 mmol, 10.0 mol%), **L5** (20.0 mg, 0.06 mmol, 12.0 mol%), diaryliodoniums salts **1a** (228.0 mg, 0.5 mmol, 1.0 equiv) and $PhSO_2SNa$ (147.0 mg, 0. 75 mmol, 1.5 equiv) in dichloromethane (10.0 mL) afforded the corresponding product **4g** (237.8 mg, 99%, 99% ee). HPLC conditions: Chiralpak OX-H, isopropanol/hexane = 3:97, flow: 1.0 mL/min, λ = 254 nm, t_r = 22.461 min (minor), 29.261 min (major). $[\alpha]_D^{20}$ = 106.5 (c 1.98, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.74 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.62-7.57 (m, 1H), 7.54 (d, *z* = 7.8 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 1.93 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 143.7, 141.5, 137.3, 136.9, 135.5, 132.8, 131.69, 131.65, 129.1, 128.7, 128.2, 127.7, 127.0, 126.8, 100.5, 20.0, 19.2. HRMS (ESI): calcd. for $C_{20}H_{17}IO_2S_2Na$ $[M+Na]^+$: 502.9612; Found: 502.9619.

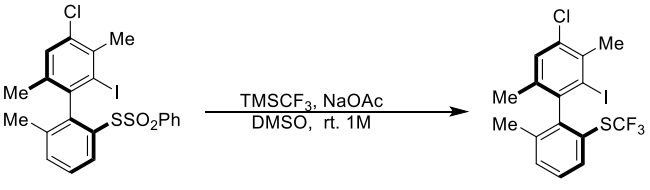
(*S*)-[2'-iodo-3',6,6'-trimethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (5a)



4a 5a

The compound **5a** was synthesized according to **procedure D**. The reaction of thiosulfonates **4a** (98.9 mg, 0.20 mmol, 1.0 equiv), NaOAc (49.2 mg, 0.60 mmol, 3.0 equiv), $TMSCF_3$ (88.7 μL, 0.60 mmol, 3.0 equiv) in DMSO (0.2 mL) afforded the corresponding product **5a** (82.8 mg, 98%, 94% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = 4.957 min (minor), 5.605 min (major). $[\alpha]_D^{20}$ = 55.1 (c 1.06, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.56 (m, 1H), 7.37-7.35 (m, 2H), 7.18 (d, *J* = 4.0 Hz, 1 H) 7.16 (d, *J* = 20.0 Hz, 1 H), 2.49 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.02. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.85, 143.55, 140.00, 137.83, 134.76, 132.14, 132.12, 131.85, 129.94, 129.7 (q, $J_{C\text{-}F}$ =310.1 Hz), 129.22, 128.67, 125.60, 125.58, 108.04, 29.58, 20.88, 20.35. HRMS (EI): calcd. for $C_{16}H_{14}F_3IS$ $[M]^+$: 421.9813; Found: 421.9810.

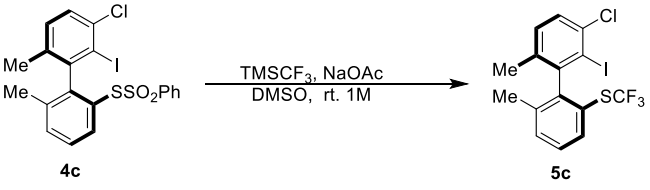
(*S*)-[2'-iodo-3',6,6'-trimethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (5b)



4b 5b

The compound **5b** was synthesized according to **procedure D**. The reaction of thiosulfonates **4b** (105.8 mg, 0.20 mmol, 1.0 equiv), NaOAc (49.2 mg, 0.60 mmol, 3.0 equiv), $TMSCF_3$ (88.7 μL, 0.60 mmol, 3.0 equiv) in DMSO (0.2 mL) afforded the corresponding product **5b** (90.4 mg, 99%, 91% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = 4.954 min (minor), 5.670 min (major). $[\alpha]_D^{20}$ = 45.7 (c 1.95, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.58 (m, 1H), 7.37 (d, *J* = 5.4 Hz, 2H), 7.32 (s, 1H), 2.65 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.01. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 142.8, 137.8, 137.3, 136.1, 132.8, 132.47, 132.45, 131.1, 130.9, 129.6 (q, $J_{C\text{-}F}$ =310.1 Hz), 128.9, 125.5, 109.1, 27.4, 20.8, 20.4. HRMS (EI): calcd. for $C_{16}H_{13}ClF_3IS$ $[M]^+$: 455.9423; Found: 455.9426.

(*S*)-[2'-iodo-3',6,6'-trimethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (5c)

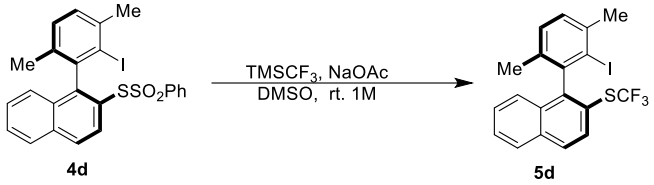


4c 5c

The compound **5c** was synthesized according to **procedure D**. The reaction of thiosulfonates **4c** (103.0 mg, 0.20 mmol, 1.0 equiv), NaOAc (49.2 mg, 0.60 mmol, 3.0 equiv), $TMSCF_3$ (88.7 μL, 0.60 mmol, 3.0 equiv) in DMSO (0.2 mL) afforded the corresponding product **5c** (87.6 mg, 99%, 98% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 273 nm, t_r = 6.010 min (minor), 7.053 min (major). $[\alpha]_D^{20}$ = 64.0 (c 0.60, $CHCl_3$). ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.70-7.64 (m, 1H), 7.43-7.34 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 1H), 1.98 (s, 3H), 1.97 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.04. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.8, 137.6, 136.9, 135.8, 132.8, 132.2, 131.3, 129.6 (q, J_{C-F} =310.1 Hz), 129.1, 128.7, 125.1 (d, *J* = 15.5 Hz), 105.4, 20.8, 20.3. HRMS (EI): calcd. for $C_{15}H_{11}ClF_3IS$ $[M]^+$: 441.9267; Found: 441.9269.

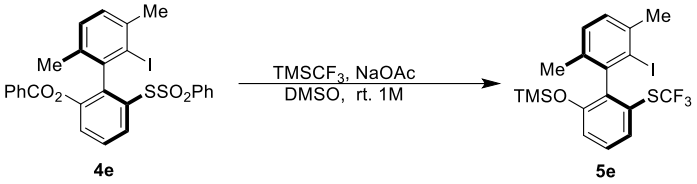
(*S*)-[2'-iodo-3',6,6'-trimethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (5d)



4d **5d**

The compound **5d** was synthesized according to **procedure D**. The reaction of thiosulfonates **4d** (106.1 mg, 0.20 mmol, 1.0 equiv), NaOAc (49.2 mg, 0.60 mmol, 3.0 equiv), $TMSCF_3$ (88.7 μL, 0.60 mmol, 3.0 equiv) in DMSO (0.2 mL) afforded the corresponding product **5d** (90.8 mg, >99%, 97% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = 7.175 min (minor), 12.659 min (major). $[\alpha]_D^{20}$ = 46.5 (c 1.05, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.99-7.87 (m, 2H), 7.84-7.82 (m, 1H), 7.56-7.53 (m, 1H), 7.42-7.39 (m, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.23-7.21 (m, 2H), 2.51 (s, 3H), 1.87 (s, 3H). ^{19}F NMR (471 MHz, $CHCl_3$) δ -39.18. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 142.5, 140.0, 135.8, 133.9, 131.9, 130.26, 130.25, 130.24, 130.22, 129.91, 129.87 (q, J_{C-F} = 310.1 Hz), 129.6, 129.1, 128.4, 127.6, 127.5, 126.1, 123.11, 123.09, 108.7, 29.6, 21.0. HRMS (EI): calcd. for $C_{19}H_{14}F_3IS$ $[M]^+$: 457.9813; Found: 457.9815.

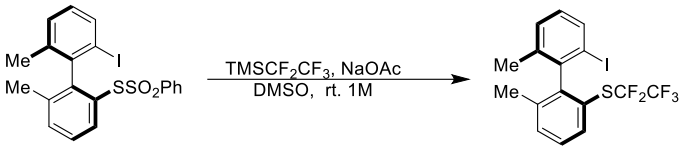
(*S*)-[2'-iodo-3',6,6'-trimethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (5e)



4e **5e**

The compound **5e** was synthesized according to **procedure D** with thiosulfonates **4e** (120.1 mg, 0.20 mmol, 1.0 equiv), NaOAc (49.2 mg, 0.60 mmol, 3.0 equiv) and $TMSCF_3$ (88.7 μL, 0.60 mmol, 3.0 equiv) in DMSO (0.2 mL). The residue was purified by column chromatography on silica gel (ethyl acetate/ hexanes = 1:10) to afford **5e** (69.5 mg, 70%, 97% ee). HPLC conditions: Chiralpak IC-IC, isopropanol/hexane = 0:100, flow: 0.3 mL/min, λ = 254 nm, t_r = 25.115 min (major), 26.266 min (minor). $[\alpha]_D^{20}$ = 48.5 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.137 (d, *J* = 5.2 Hz, 1H), 7.136 (d, *J* = 20.8 Hz, 1H), 2.48 (s, 3H), 2.04 (s, 3H), 0.06 (s, 9H). ^{19}F NMR (376 MHz, $CHCl_3$) δ -40.44. ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 140.5, 139.8, 138.2, 135.0, 128.7 (q, J_{C-F} = 312.1 Hz), 128.4, 128.3, 128.0, 126.9, 125.79, 125.76, 120.3, 108.3, 28.7, 19.9. HRMS (ESI): calcd. for $C_{18}H_{21}F_3IOSSi$ $[M+H]^+$: 497.0079; Found: 497.0087.

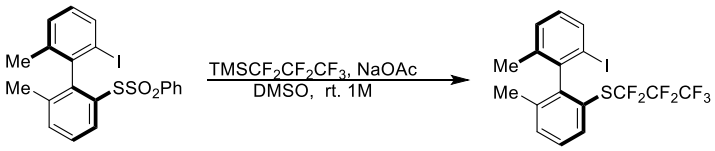
(*S*)-[2'-iodo-3',6,6'-trimethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (6a)



4g 6a

The compound **6a** was synthesized according to **procedure D**. The reaction of thiosulfonates **4g** (96.1 mg, 0.20 mmol, 1.0 equiv), NaOAc (49.2 mg, 0.60 mmol, 3.0 equiv) and $TMSCF_2CF_3$ (105.0 μL, 0.60 mmol, 3.0 equiv) in DMSO (0.2 mL) afforded the corresponding product **6a** (88.9 mg, 97%, 99% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = 5.093 min (minor), 5.500 min (major). $[\alpha]_D^{20}$ = 110.6 (c 0.68, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.74 (m, 1H), 7.71-7.64 (m, 1H), 7.44-7.34 (m, 2H), 7.30-7.24 (m, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 2.02 (s, 3H), 2.00 (s, 3H). ^{19}F NMR (376 MHz, $CHCl_3$) δ -82.90 (t, *J* = 4.1 Hz, 3F), -87.89 (dq, *J* = 225.2, 4.1 Hz, 1F), -89.26 (dq, *J* = 225.1, 4.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 143.0, 138.2, 138.0, 136.7, 134.2, 132.5, 130.1, 129.7, 129.5 (d, *J* = 59.8 Hz), 128.8, 127.5 (d, *J* = 35.0 Hz), 123.7, 120.8 (tq, *J* = 290.9 Hz, 40.4 Hz), 118.6 (qt, *J* = 290.9 Hz, 36.4 Hz), 101.3, 21.1 (d, *J* = 3.1 Hz), 20.5. HRMS (EI): calcd. for $C_{16}H_{12}F_5IS$ $[M]^+$: 457.96252; Found: 457.9624.

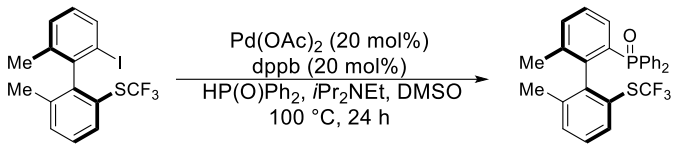
(*S*)-[2'-iodo-3',6,6'-trimethyl-(1,1'-biphenyl)-2-yl](trifluoromethyl)sulfane (6b)



4g 6b

The compound **6b** was synthesized according to **procedure D**. The reaction of thiosulfonates **4g** (96.1 mg, 0.20 mmol, 1.0 equiv), NaOAc (49.2 mg, 0.60 mmol, 3.0 equiv) and $TMSCF_2CF_2CF_3$ (122.0 μL, 0.60 mmol, 3.0 equiv) in DMSO (0.2 mL) afforded the corresponding product **6b** (14.3 mg, 14%, >99% ee). HPLC conditions: Chiralpak IB, isopropanol/hexane = 0:100, flow: 0.5 mL/min, λ = 254 nm, t_r = 8.418 min (minor), 8.804 min (major). $[\alpha]_D^{20}$ = -137.7 (c 0.18, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.30 – 7.23 (m, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 2.00 (s, 6H). ^{19}F NMR (471 MHz, $CHCl_3$) δ -80.02 (t, *J* = 9.3 Hz, 3F), -83.47 – -84.20 (m, 1F), -85.18 – -85.85 (m, 1F), -124.03 (t, *J* = 4.4 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 143.0, 138.2, 138.0, 136.7, 134.6, 132.6, 130.1, 129.6, 128.7, 123.4, 123.0 (t, *J* = 32.8 Hz), 101.3, 21.1 (d, *J* = 3.5 Hz), 20.5. HRMS (EI): calcd. for $C_{17}H_{12}F_7IS$ $[M]^+$: 507.9593; Found: 507.9592.

(*S*)-(2',6-dimethyl-6'-((trifluoromethyl)thio)-[1,1'-biphenyl]-2-yl)diphenylphosphine oxide (7a)

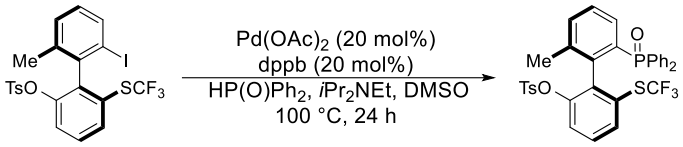


2a 7a

Under nitrogen atmosphere, an oven-dried seal tube was sequentially charged with **2a** (297.8 mg, 0.62 mmol, 1.0 equiv), diphenyl phosphine oxide (138.3 mg, 0.68 mmol, 1.1 equiv), $Pd(OAc)_2$ (27.8

mg, 20 mol%), dppb (52.9 mg, 20 mol%) in anhydrous DMSO (6.2 mL). Then *i*Pr$_2$NEt (440.3 μL, 2.48 mmol, 4.0 equiv) was added to the reaction under stirring. The reaction was stirred at 100 ℃ for 24 h. After completed, the reaction was cooled to room temperature and diluted with ethyl acetate, washed with water and brine, then dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/dichloromethane/hexanes = 1:1:2) to afford the phosphine oxide **7a**. (233.1 mg, 78%, 99% ee). HPLC conditions: Chiralpak AD-H, isopropanol/hexane = 5:95, flow: 1.0 mL/min, λ = 214 nm, t_r = 18.111 min (major), 23.475 min (minor). $[\alpha]_D^{20}$ = 34.6 (c 0.57, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.37 (m, 7H), 7.34 – 7.24 (m, 3H), 7.20 – 7.13 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 1.95 (s, 3H), 1.49 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.37. ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.92. ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.34, 143.26, 142.1, 138.5, 138.4, 138.2, 134.0 (d, J = 2.6 Hz), 133.3, 133.2, 132.8, 132.4, 132.24, 132.23, 132.2, 131.8, 131.71, 131.68, 131.6, 131.5, 131.39, 131.36, 131.21, 131.15, 131.1, 130.2 (q, *J* = 310.1 Hz), 128.5, 128.4, 128.2, 128.1, 127.3, 127.2, 20.3, 19.4. HRMS (ESI): calcd. for $C_{27}H_{22}F_3OPSNa$ $[M+Na]^+$: 505.0979; Found: 550.0980.

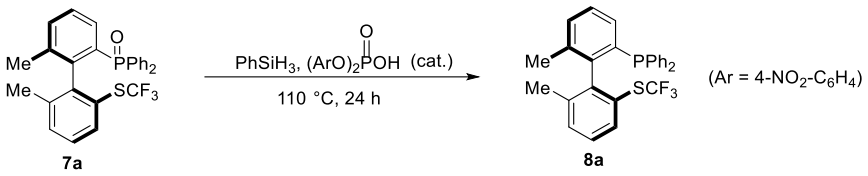
(*S*)-2'-(diphenylphosphoryl)-6'-methyl-6-((trifluoromethyl)thio)-[1,1'-biphenyl]-2-yl-4-methylbenzenesulfonate (7b)



2j **7b**, 98%, >99% ee

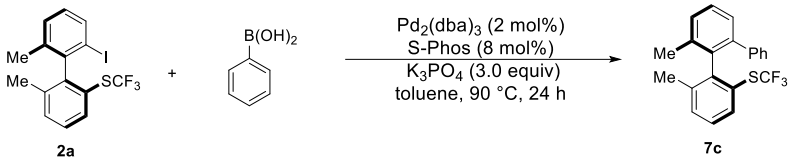
Under nitrogen atmosphere, an oven-dried seal tube was sequentially charged with **2j** (84.7 mg, 0.15 mmol, 1.0 equiv), diphenyl phosphine oxide (33.3 mg, 0.165 mmol, 1.1 equiv), $Pd(OAc)_2$ (6.7 mg, 20 mol%), dppb (12.8 mg, 20 mol%) in anhydrous DMSO (1.5 mL). Then *i*Pr$_2$NEt (106.5 μL, 0.60 mmol, 4.0 equiv) was added to the reaction under stirring. The reaction was stirred at 100 ℃ for 24 h. After completed, the reaction was cooled to room temperature and diluted with ethyl acetate, washed with water (three times) and brine, then dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/dichloromethane/hexanes = 1:1:2) to afford the phosphine oxide **7b** (93.9 mg, 98%, >99% ee). HPLC conditions: Chiralpak OX-H, isopropanol/hexane = 20:80, flow: 1.0 mL/min, λ = 254 nm, t_r = 12.389 min (major), 15.281 min (minor). $[\alpha]_D^{20}$ = -24.4 (c 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.9 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.52 – 7.33 (m, 7H), 7.32 – 7.19 (m, 6H), 7.19 – 7.09 (m, 3H), 7.05 (dd, *J* = 13.7, 7.7 Hz, 1H), 2.43 (s, 3H), 2.01 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.57. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.35. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 145.3, 139.3 (d, *J* = 9.5 Hz), 138.5 (d, *J* = 6.8 Hz), 135.1, 134.0, 133.93, 133.90, 133.4, 132.8, 132.4, 132.3, 132.2, 132.1, 131.79, 131.77, 131.6, 131.48, 131.45 (d, *J* = 2.7 Hz), 131.3, 131.2, 131.0, 130.6, 129.9 (q, *J* = 310.1 Hz), 129.7, 129.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 120.8, 21.8, 19.9. HRMS (EI): calcd. for $C_{33}H_{26}F_3O_4PS_2Na$ $[M+Na]^+$: 661.0860; Found: 661.0867.

(*S*)-(2',6-dimethyl-6'-((trifluoromethyl)thio)-[1,1'-biphenyl]-2-yl)diphenylphosphane (8a) [6]



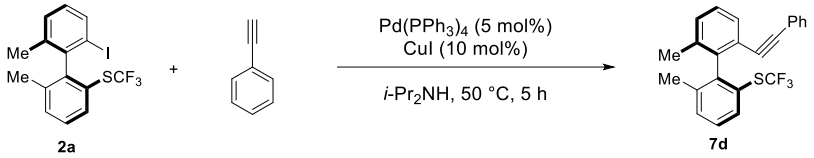
An oven-dried seal tube was sequentially charged with **7a** (96.5 mg, 0.2 mmol, 1.0 equiv) and phosphoric acid (34.0 mg, 0.1 mmol, 0.5 equiv) under nitrogen atmosphere. Then $PhSiH_3$ (0.5 mL) was added and the mixture was stirred at 110 ℃ for 24 h. After consumption of starting material, the reaction was cooled to room temperature and quenched with NaOH (1 M), extracted with ethyl acetate. The organic layer was wased with H_2O and brine, then dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/hexanes = 20:1) to afford the phosphine **8a** (87.7 mg, 94%, >99% ee). HPLC conditions: Chiralpak OD-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 273 nm, t_r = 9.234 min (minor), 10.458 min (major). $[\alpha]_D^{20}$ = 41.8 (c 0.75, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.17 (m, 11H), 7.17 – 7.11 (m, 3H), 7.06 – 7.01 (m, 1H), 1.96 (s, 3H), 1.53 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.41 (d, *J* = 3.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -14.23 (d, *J* = 3.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 144.0, 143.53, 143.45, 139.0 (d, *J* = 1.9 Hz), 138.1, 138.0, 137.0, 136.9, 136.63, 136.58, 136.0, 135.8, 134.8, 134.6, 133.7, 133.5, 132.3, 131.6, 131.4, 131.0, 130.1 (q, *J* = 310.1 Hz), 129.0, 128.54, 128.52, 128.5, 128.43, 128.35, 128.1, 126.0, 20.1, 19.7. HRMS (ESI): calcd. for $C_{27}H_{23}F_3PS$ $[M+H]^+$: 467.1210; Found: 467.1203.

Cross-coupling with arylboronic acids



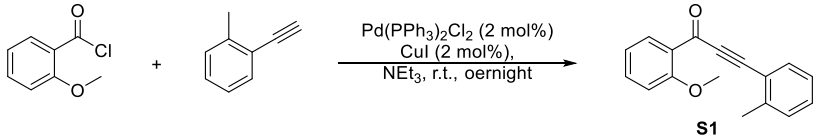
Under nitrogen atmosphere, an oven-dried seal tube was sequentially charged with **2a** (204 mg, 0.5 mmol, 1.0 equiv), Phenylboronic acid (92 mg, 0.75 mmol, 1.5 equiv), $Pd_2(dba)_3$ (9.2 mg, 2 mol%), S-Phos (16.4 mg, 8 mol%) and K_3PO_4 (318 mg, 1.5 mmol, 3.0 equiv) in toluene (2.5 mL). The reaction was stirred at 90 ℃ for 24 h. After the reaction was completed, it was cooled to room temperature and diluted with ethyl acetate, washed with water (three times) and brine, then dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/hexanes = 1:50) to afford the phosphine oxide **7c** (164.9 mg, 92%, 99% ee). HPLC conditions: Chiralpak OX-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = 5.290 min (major), 5.716 min (minor). $[\alpha]_D^{20}$ = -14.0 (c 1.28, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 6.6 Hz, 1H), 7.28 – 7.15 (m, 3H), 7.15 – 7.09 (m, 3H), 7.07 – 6.98 (m, 2H), 2.08 (s, 3H), 2.03 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.62. ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.8, 141.3, 138.6, 136.8, 136.5, 131.4, 131.2, 129.9 (q, *J* = 309.5 Hz), 129.4, 129.1, 128.2, 128.1, 127.8, 127.7, 126.7, 125.9 (d, *J* = 1.8 Hz), 20.7, 19.9. HRMS (EI): calcd. for $C_{21}H_{17}F_3SNa$ $[M]^+$: 358.1003; Found: 358.1003.

Cross-coupling with terminal alkynes



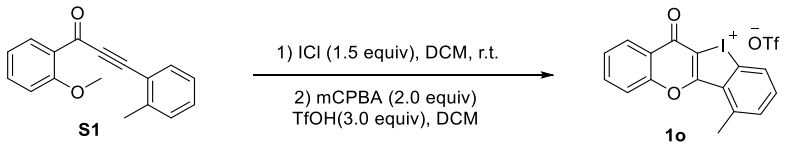
Under nitrogen atmosphere, an oven-dried Schlenk tube was sequentially charged with **2a** (163 mg, 0.4 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (23 mg, 5 mol%), CuI (7.6 mg, 10 mol%) in i-Pr_2NH (2.0 mL). Then Phenylacetylene (66 μL, 0.60 mmol, 1.5 equiv) was added. The reaction was stirred at 50 ℃ for 5 h. After the reaction was completed, it was cooled to room temperature and diluted with ethyl acetate, washed with water (three times) and brine, then dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes to dichloromethane/hexanes = 1:10) to afford the phosphine oxide **7d** (145.3 mg, 95%, 99% ee). HPLC conditions: Chiralpak OX-H, isopropanol/hexane = 0:100, flow: 1.0 mL/min, λ = 254 nm, t_r = 6.615 min (minor), 7.300 min (major). $[\alpha]_D^{20}$ = 88.6 (c 1.54, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.9 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.44 – 7.18 (m, 7H), 7.07 – 7.00 (m, 2H), 2.06 (s, 3H), 2.04 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.79. ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 141.5, 138.6, 136.4, 133.0, 132.0, 131.5, 130.3, 129.3, 128.5 (d, *J* = 6.0 Hz), 128.4, 128.33, 128.26, 128.1, 127.9, 127.8 (q, *J* = 323.2 Hz), 125.6 (d, *J* = 2.0 Hz), 123.5, 123.3, 92.8, 88.3, 20.5, 19.9. HRMS (ESI): calcd. for $C_{23}H_{18}F_3S$ $[M+H]^+$: 383.1081; Found: 383.1075.

1-(2-methoxyphenyl)-3-(o-tolyl)prop-2-yn-1-one (S1)



Under nitrogen atmosphere, an oven-dried flask was sequentially charged with $Pd(PPh_3)_2Cl_2$ (211 mg, 2 mol%), CuI (57 mg, 2 mol%) in NEt_3 (32 mL). 2-methoxybenzoyl chloride (2.56 g, 15 mmol, 1.0 equiv) and 1-ethynyl-2-methylbenzene (2.3 mL, 18 mmol, 1.2 equiv) were added by syringes respectivily. The reaction was stirred at room temperature overnight under nitrogen atmosphere before NEt_3 was removed by rotary evaporation. The remained mixture was extracted with ethyl acetate, washed with water and brine, then dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/hexanes = 20:1 to 10:1) to afford **S1** (3.89 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 6.6 Hz, 1H), 7.28 – 7.15 (m, 3H), 7.15 – 7.09 (m, 3H), 7.07 – 6.98 (m, 2H), 2.08 (s, 3H), 2.03 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.62. ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.8, 141.3, 138.6, 136.8, 136.5, 131.4, 131.2, 129.9 (q, J_{C-F} = 309.5 Hz), 129.4, 129.1, 128.2, 128.1, 127.8, 127.7, 126.7, 125.9 (d, *J* = 1.8 Hz), 20.7, 19.9. HRMS (ESI): calcd. for $C_{21}H_{18}F_3SNa$ $[M+H]^+$: 251.1072; Found: 251.1066.

6-methyl-11-oxo-11H-benzo[b]chromeno[2,3-d]iodol-10-ium triflate (1o) [7]



To a stirred solution of **S1** (2.0 g, 8.0 mmol) in CH_2Cl_2 (15 mL) was added a solution of ICl (0.6 mL, 1.5 equiv) in CH_2Cl_2 (10 mL) dropwise. The reaction proceeded at room temperature for 1h before CH_2Cl_2 was removed by rotary evaporation. The remained mixture was extracted with ethyl acetate, and the combined organic layers were washed with saturated $NaHSO_3$, H_2O and brine respectively, dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure. The crude product was filtered through a pad of silica gel with hexanes and used in the next step without further purification.

To a stirred solution of above crude product in dichloromethane (1.09 g, 3.0 mmol) was added *m*CPBA (85%, 914 mg, 1.5 equiv) in one portion. After *m*-CPBA being completely dissolved, trifluoromethanesulfonic acid (0.80 mL, 9.0 mmol, 3.0 equiv) was added dropwise at 0 °C, and was stirred at room temperature for 2 h. Dichloromethane was removed by rotary evaporation before the addition of Et_2O. The mixture was stirred for 40 min, and the solid was collected by filtration. The crude solid was washed with Et_2O three times, dried under vacuum to afford the cyclic diaryliodonium **1o** (2.20 g, 94% with two steps). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 6.6 Hz, 1H), 7.28 – 7.15 (m, 3H), 7.15 – 7.09 (m, 3H), 7.07 – 6.98 (m, 2H), 2.08 (s, 3H), 2.03 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -40.62. ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.6, 165.3, 154.7, 142.5, 135.5, 135.2, 133.8, 133.5, 133.0, 132.7, 132.3, 128.8, 128.6, 126.8, 126.6, 124.6, 124.3, 121.2, 120.2 (q, J_{C-F} = 323.2 Hz), 119.9, 118.7, 118.4, 107.1, 20.0 (d, J = 8.8 Hz). HRMS (ESI): calcd. for $C_{17}H_{10}F_3IO_5S$ $[M+TfO^-]^+$: 360.9720; Found: 360.9720.

Crystal data

Table S1 Crystal data and structure refinement for 8-149_2 (4a).

Identification code	8-149_2
Empirical formula	$C_{21}H_{19}IO_2S_2$
Formula weight	494.38
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.1814(3)
b/Å	11.4924(4)
c/Å	21.1523(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1988.82(13)
Z	4
ρ_{calc}g/cm^3	1.651
μ/mm^{-1}	1.833
F(000)	984.0

Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.852 to 59.282
Index ranges	-10 ≤ h ≤ 11, -15 ≤ k ≤ 14, -28 ≤ l ≤ 29
Reflections collected	21959
Independent reflections	5022 [R_{int} = 0.0474, R_{sigma} = 0.0437]
Data/restraints/parameters	5022/0/238
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0288, wR_2 = 0.0539
Final R indexes [all data]	R_1 = 0.0333, wR_2 = 0.0562
Largest diff. peak/hole / e Å^{-3}	0.73/-0.59
Flack/Hooft parameter	-0.016(10)/-0.011(10)

Table S2 Crystal data and structure refinement for 6-42 (7a).

Identification code	6-42
Empirical formula	$C_{27}H_{22}F_3OPS$
Formula weight	482.47
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P1
a/Å	8.3423(8)
b/Å	9.5634(7)
c/Å	15.2295(15)
α/°	89.937(7)
β/°	79.651(8)
γ/°	77.950(7)
Volume/Å^3	1168.08(19)
Z	2
ρ_{calc}g/cm^3	1.372
μ/mm^{-1}	0.249
F(000)	500.0
Crystal size/mm^3	0.12 × 0.11 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.358 to 58.896
Index ranges	-11 ≤ h ≤ 10, -11 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	15423
Independent reflections	9720 [R_{int} = 0.0497, R_{sigma} = 0.0905]
Data/restraints/parameters	9720/3/599

Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0659, wR_2 = 0.1539
Final R indexes [all data]	R_1 = 0.0791, wR_2 = 0.1677
Largest diff. peak/hole / e $Å^{-3}$	0.79/-0.43
Flack/Hooft parameter	0.05(7)/0.06(6)

Table S3 Crystal data and structure refinement for dlh-9-55-2 (7b).

Identification code	9-55-2
Empirical formula	$C_{33}H_{26}F_3O_4PS_2$
Formula weight	638.63
Temperature/K	149.99(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.1979(2)
b/Å	13.5767(2)
c/Å	24.3814(4)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	3044.68(9)
Z	4
$\rho_{calc}g/cm^3$	1.393
μ/mm^{-1}	2.564
F(000)	1320.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.252 to 147.284
Index ranges	$-7 \le h \le 11$, $-16 \le k \le 15$, $-29 \le l \le 27$
Reflections collected	10913
Independent reflections	5938 [R_{int} = 0.0438, R_{sigma} = 0.0572]
Data/restraints/parameters	5938/0/390

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^{1}H NMR, ^{19}F NMR, ^{31}P NMR, ^{13}C NMR Copies

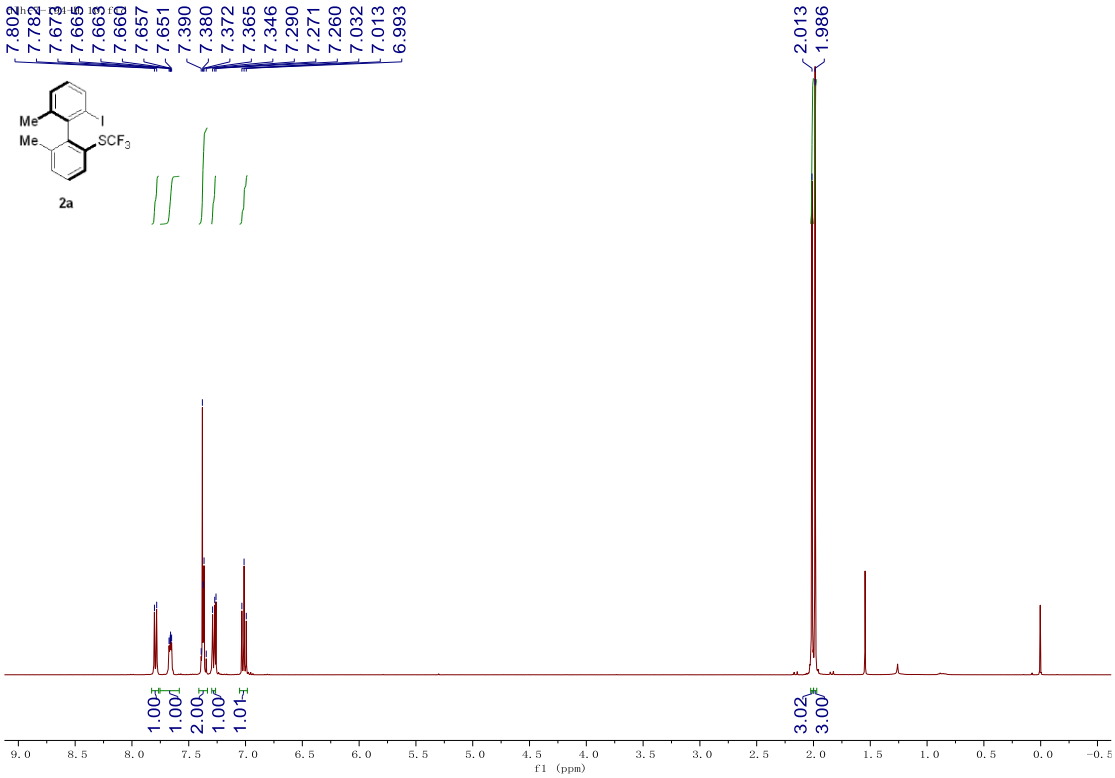


Figure S1. ^{1}H NMR spectra (400 MHz) of **2a**

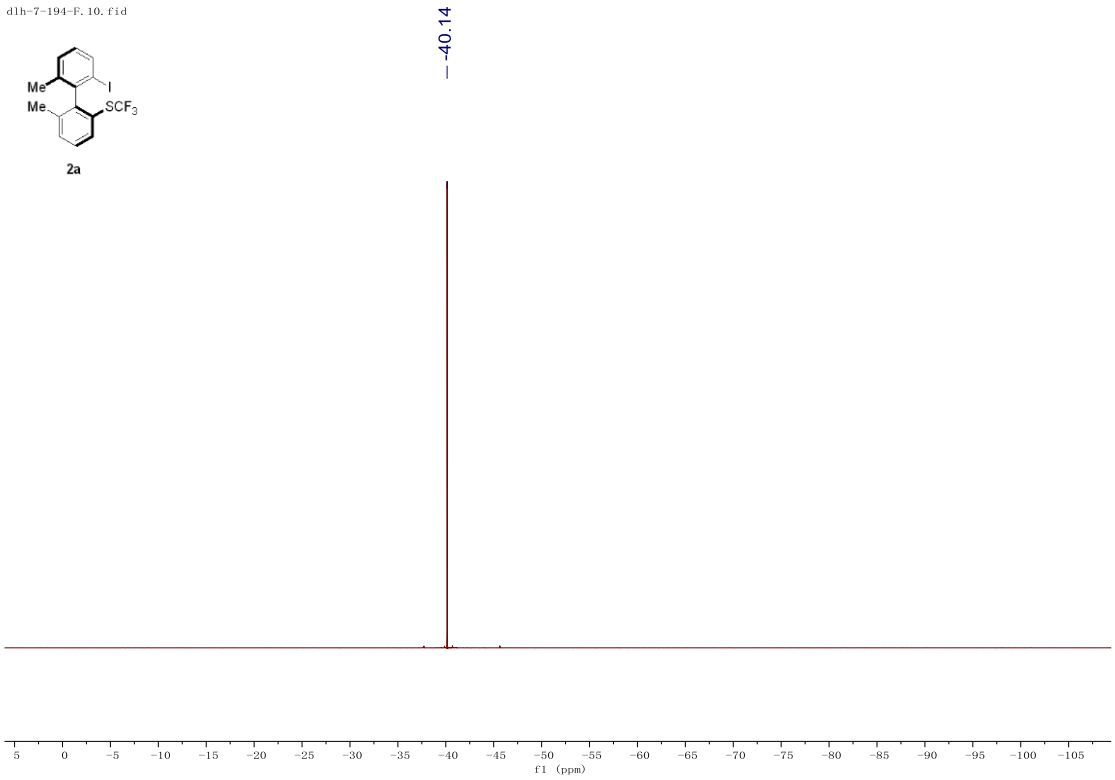


Figure S2. ^{19}FNMR spectra (471 MHz) of **2a**

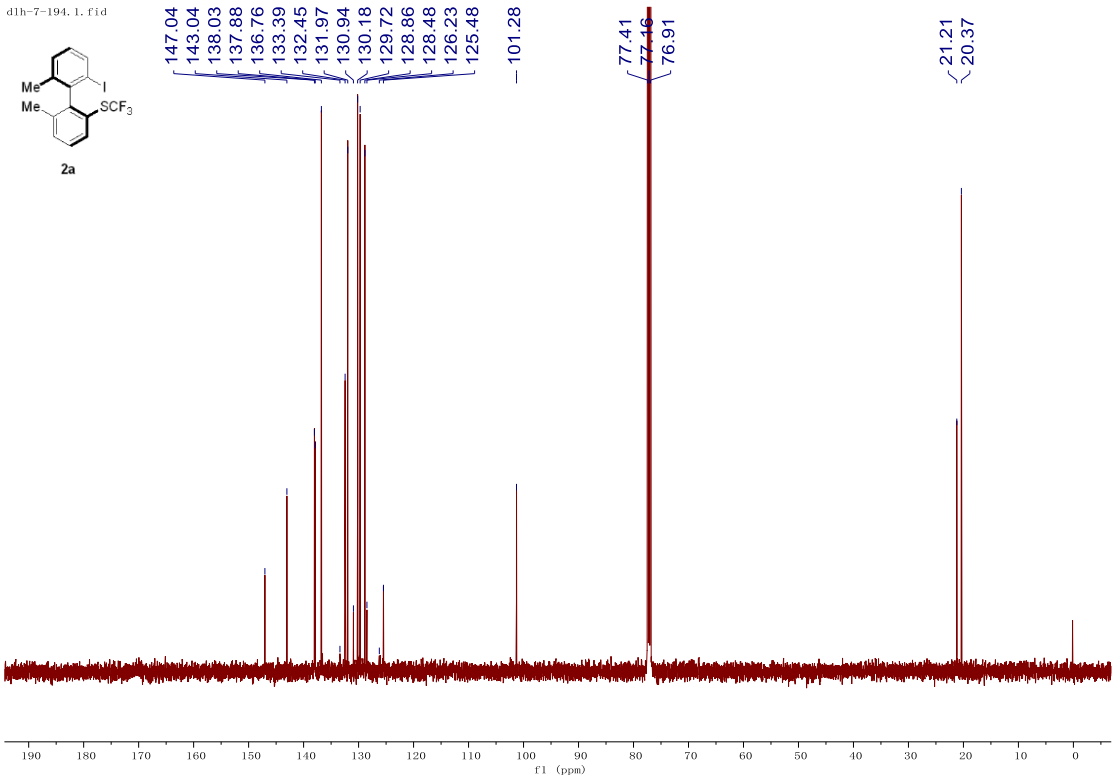


Figure S3. ^{13}C NMR spectra (101 MHz) of **2a**

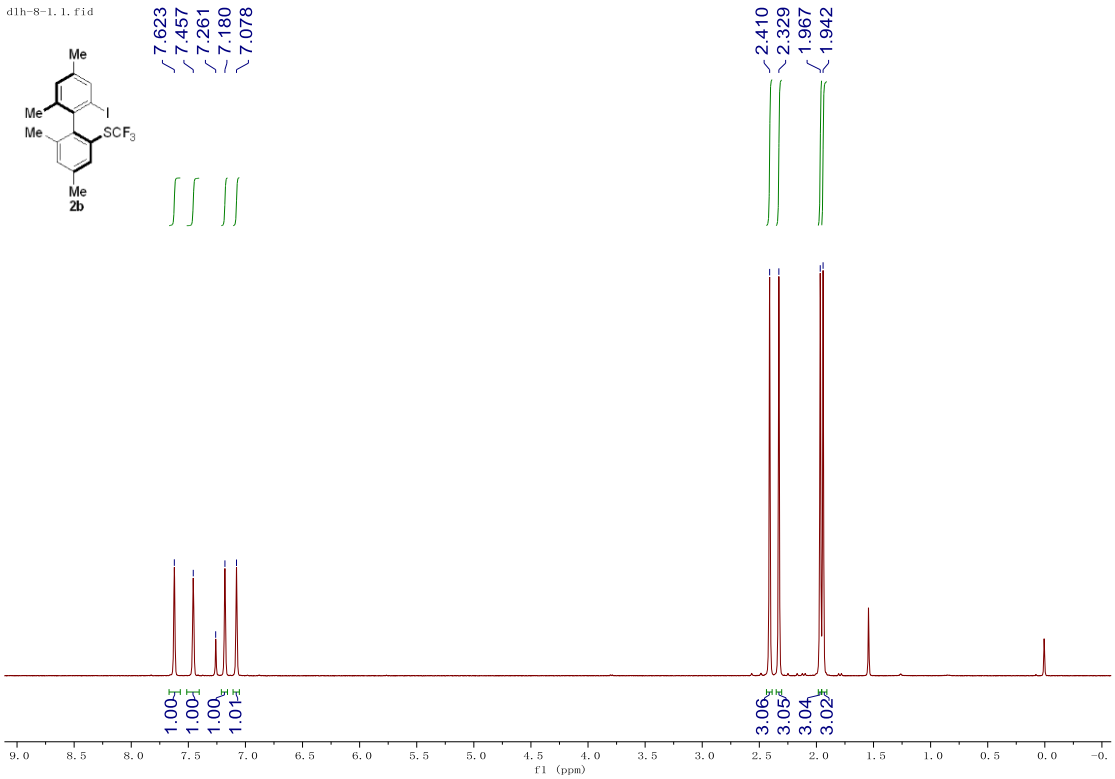


Figure S4. ^{1}H NMR spectra (400 MHz) of **2b**

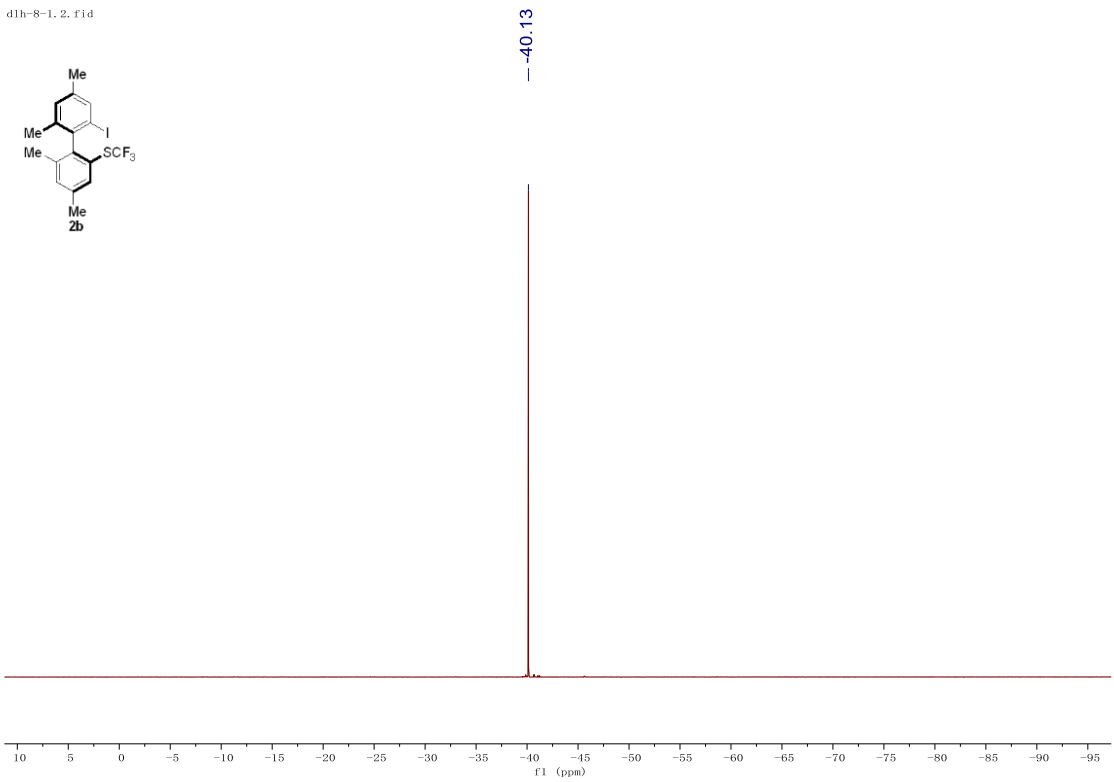


Figure S5. ^{19}FNMR spectra (471 MHz) of **2b**

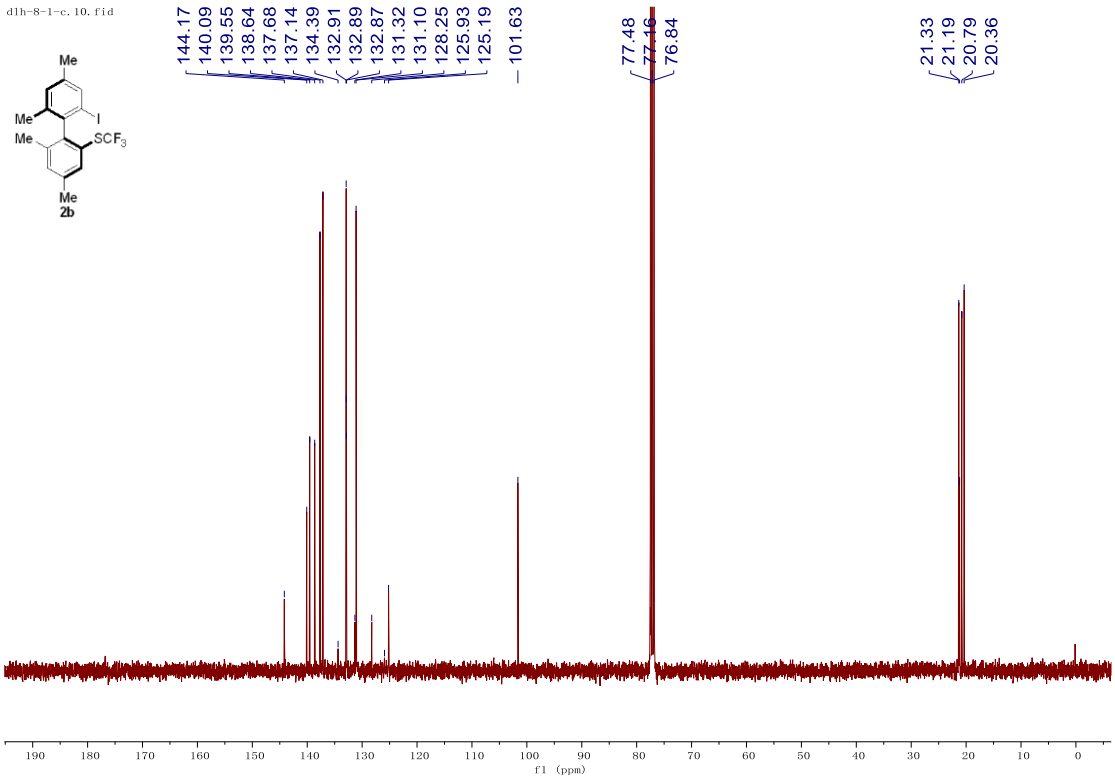


Figure S6. ^{13}C NMR spectra (101 MHz) of **2b**

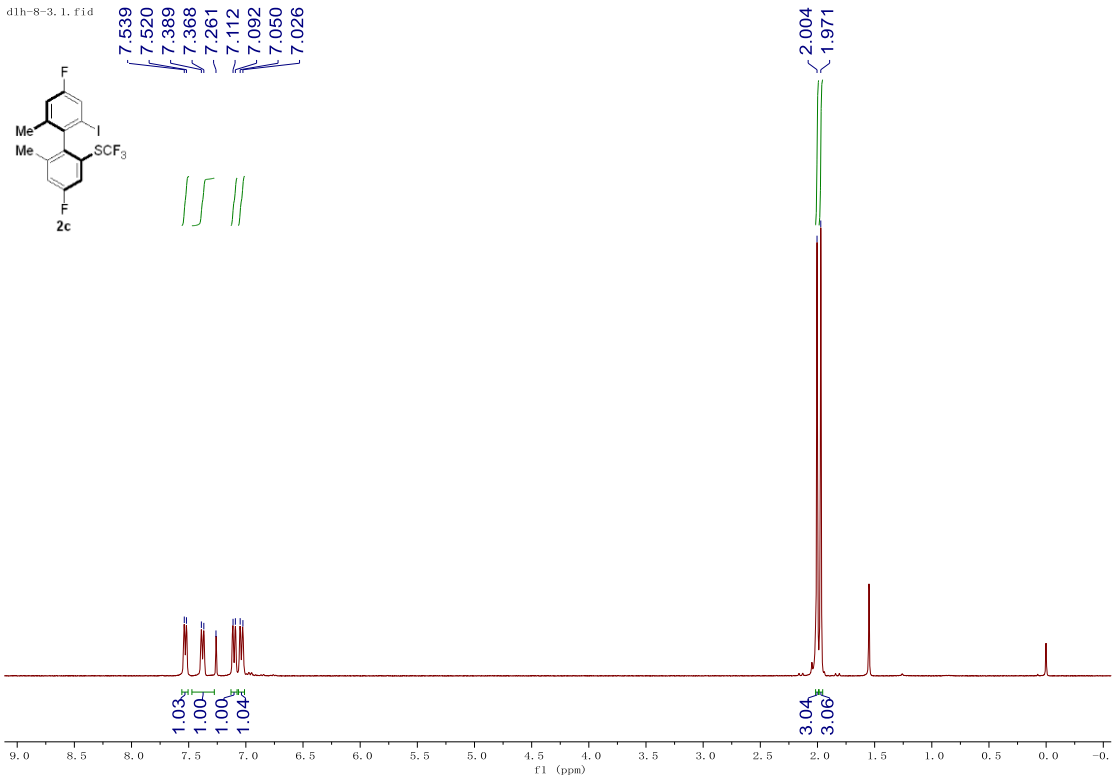


Figure S7. ^{1}H NMR spectra (400 MHz) of **2c**

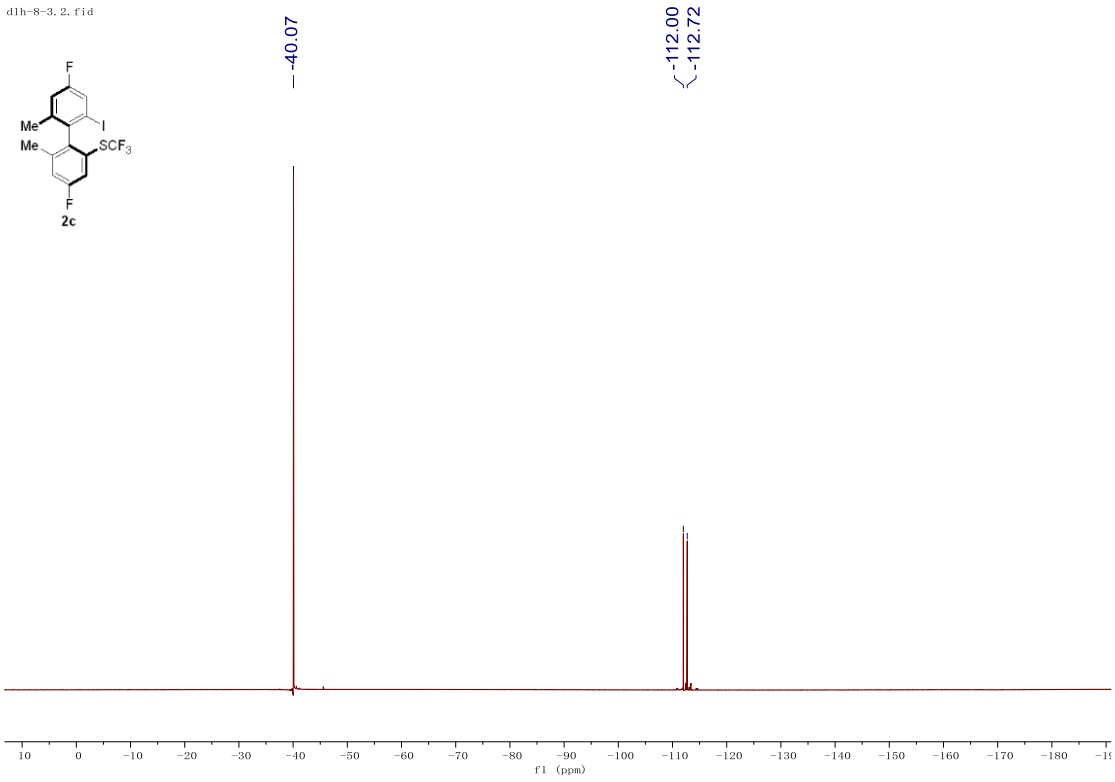


Figure S8. ^{19}FNMR spectra (471 MHz) of **2c**

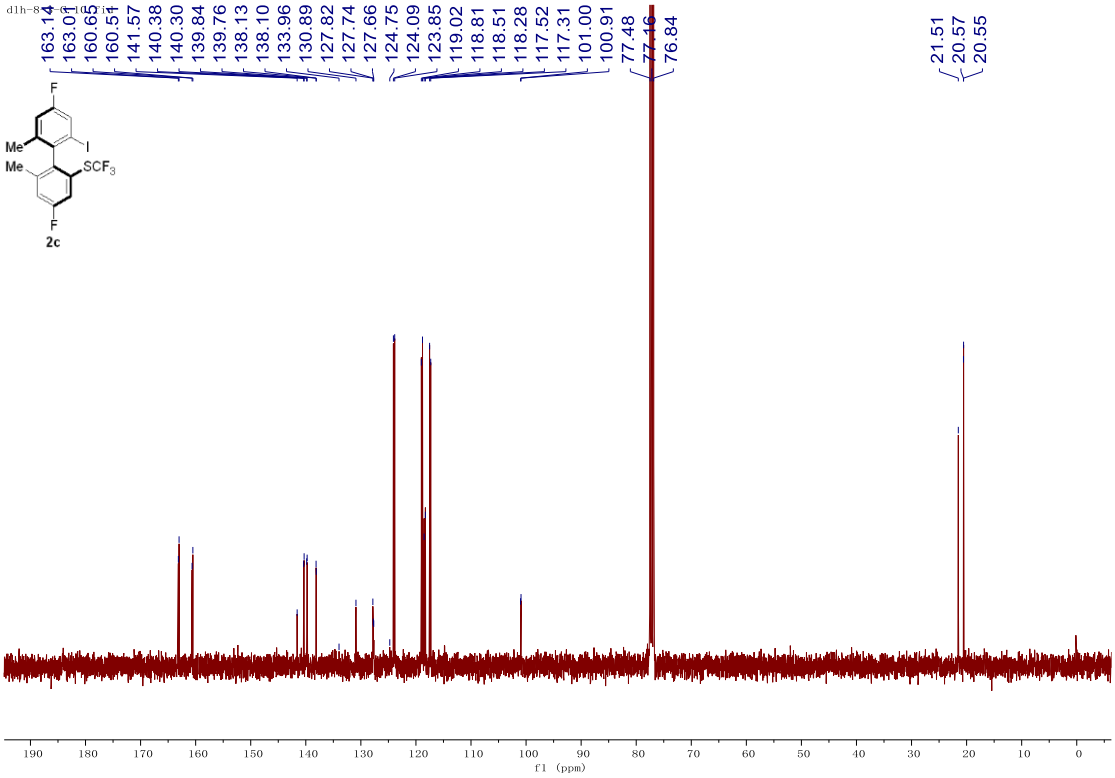


Figure S9. ^{13}C NMR spectra (101 MHz) of **2c**

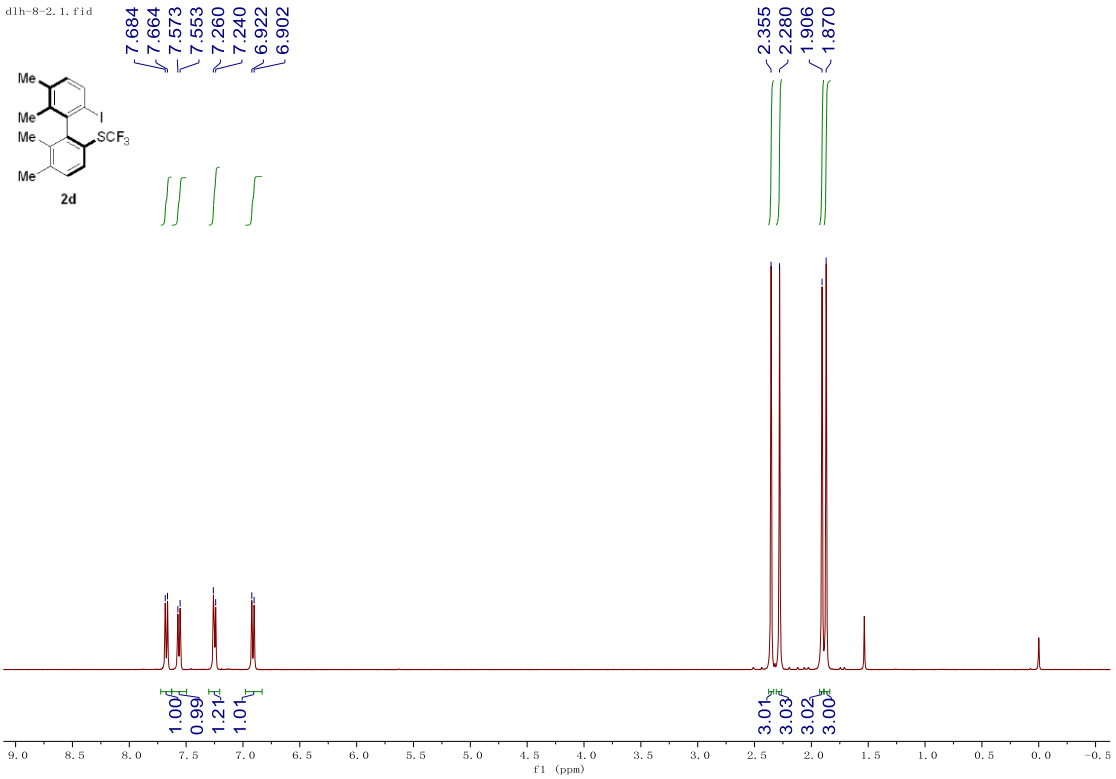


Figure S10. ^{1}H NMR spectra (400 MHz) of **2d**

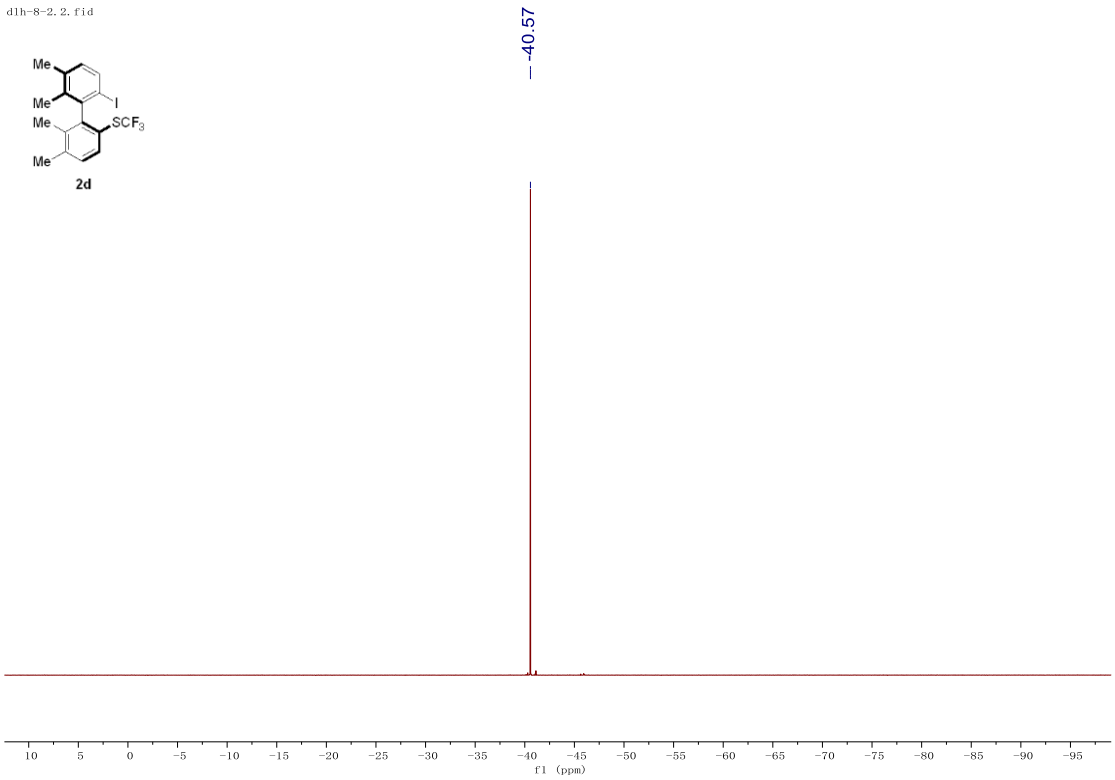


Figure S11. ^{19}FNMR spectra (471 MHz) of **2d**

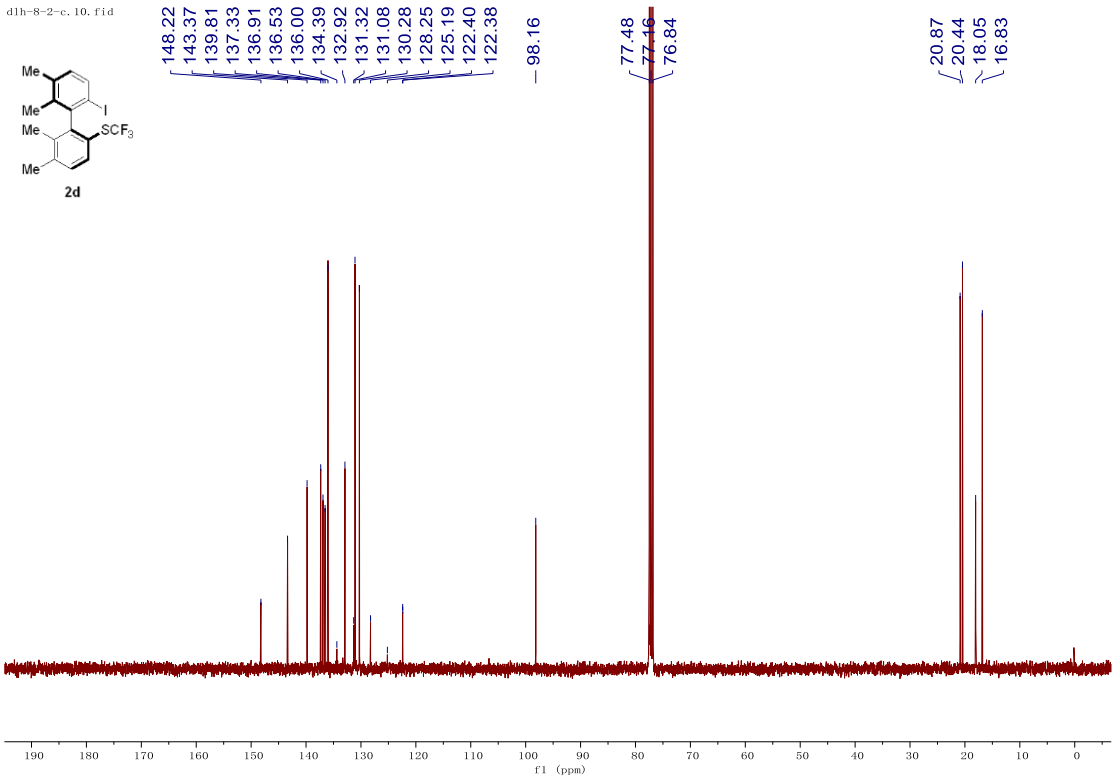


Figure S12. ^{13}C NMR spectra (101 MHz) of **2d**

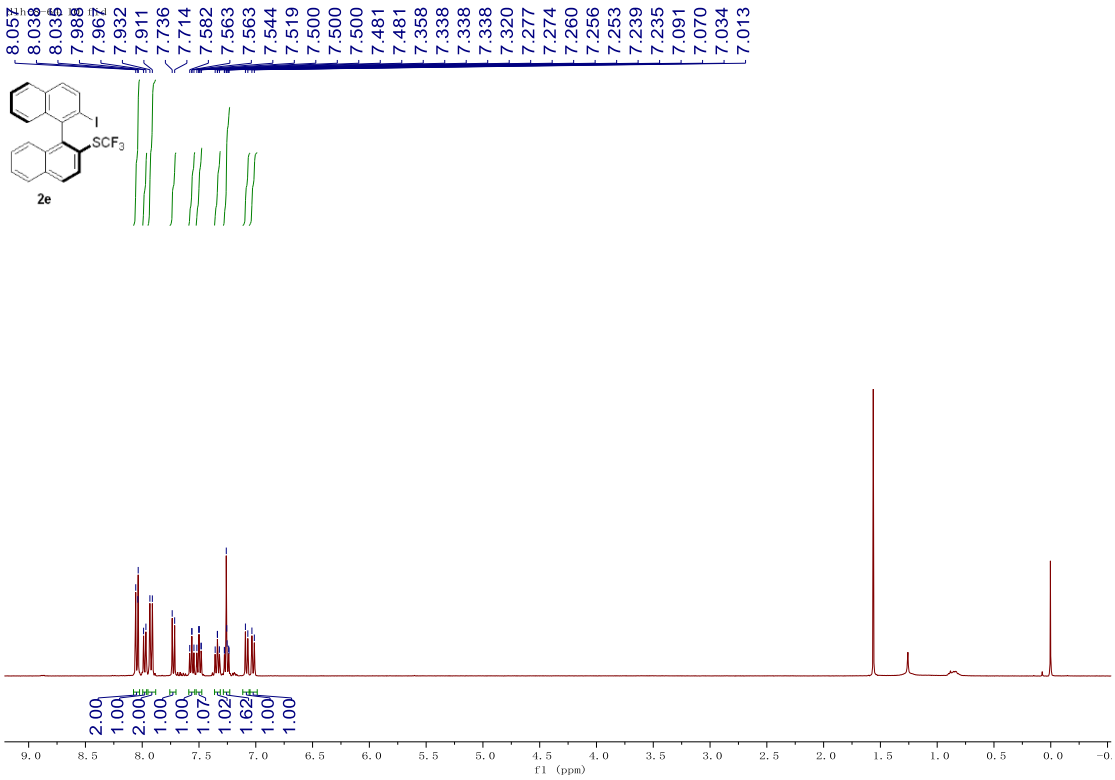


Figure S13. ^{1}H NMR spectra (400 MHz) of **2e**

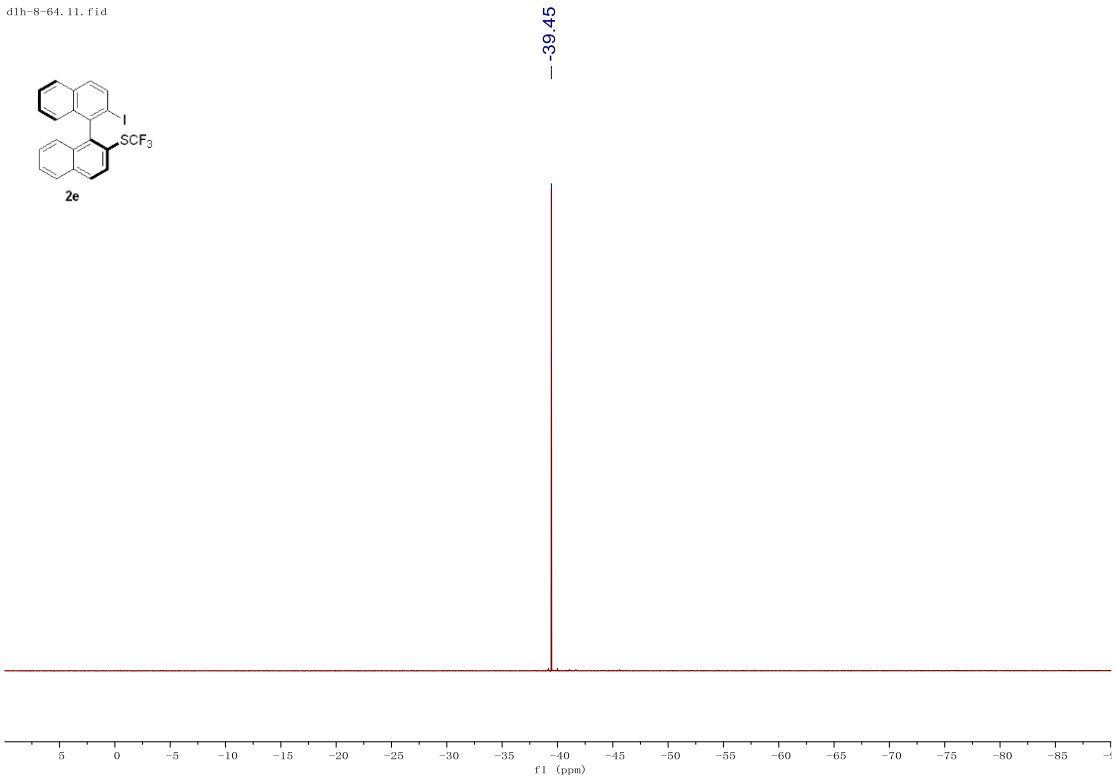


Figure S14. ^{19}FNMR spectra (471 MHz) of **2e**

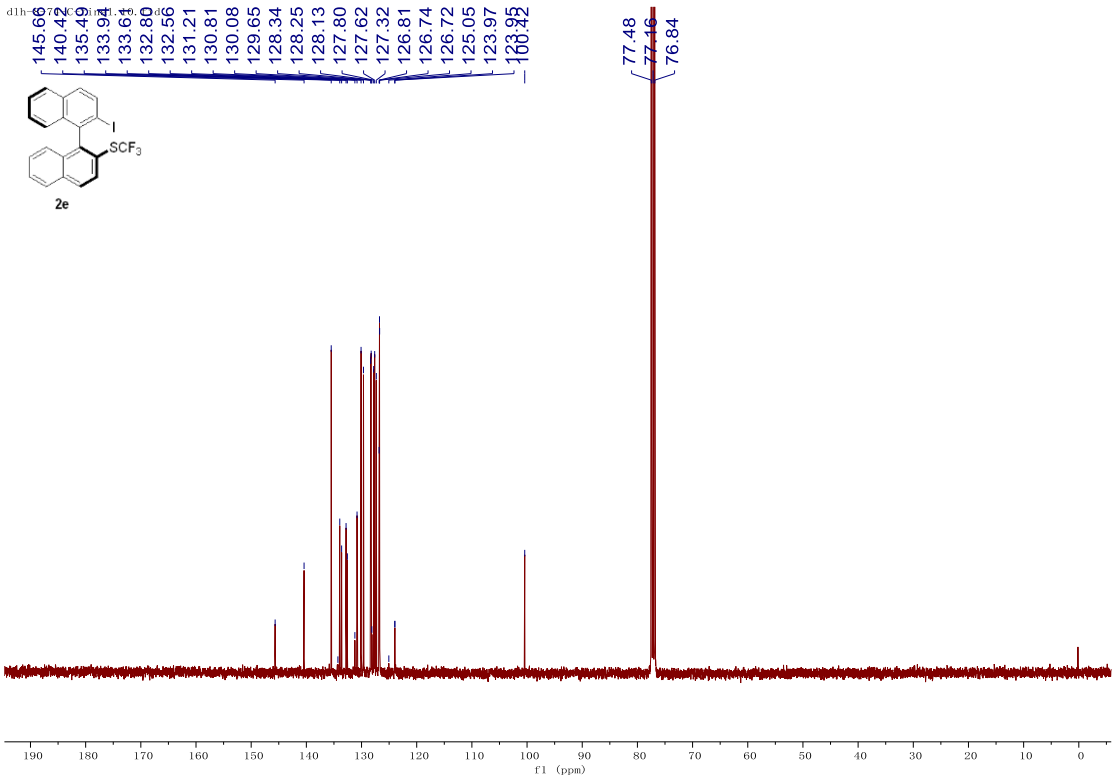


Figure S15. ^{13}C NMR spectra (101 MHz) of **2e**

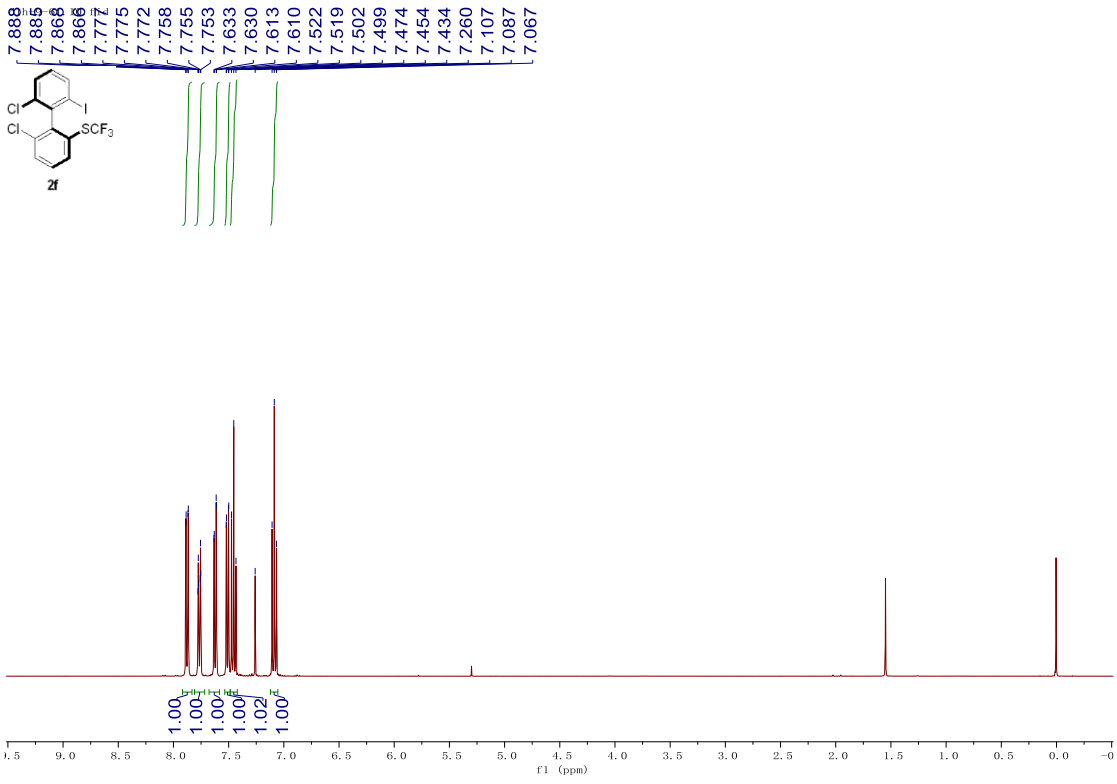


Figure S16. ^{1}H NMR spectra (400 MHz) of **2f**

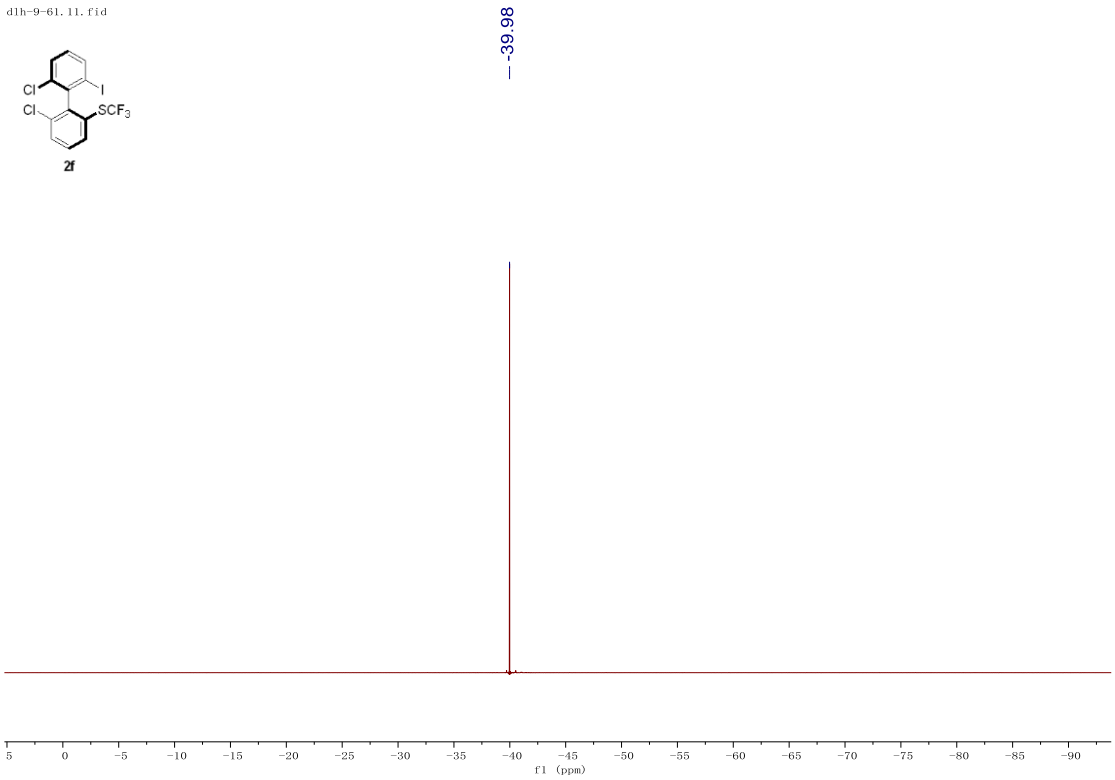


Figure S17. ^{19}FNMR spectra (471 MHz) of **2f**

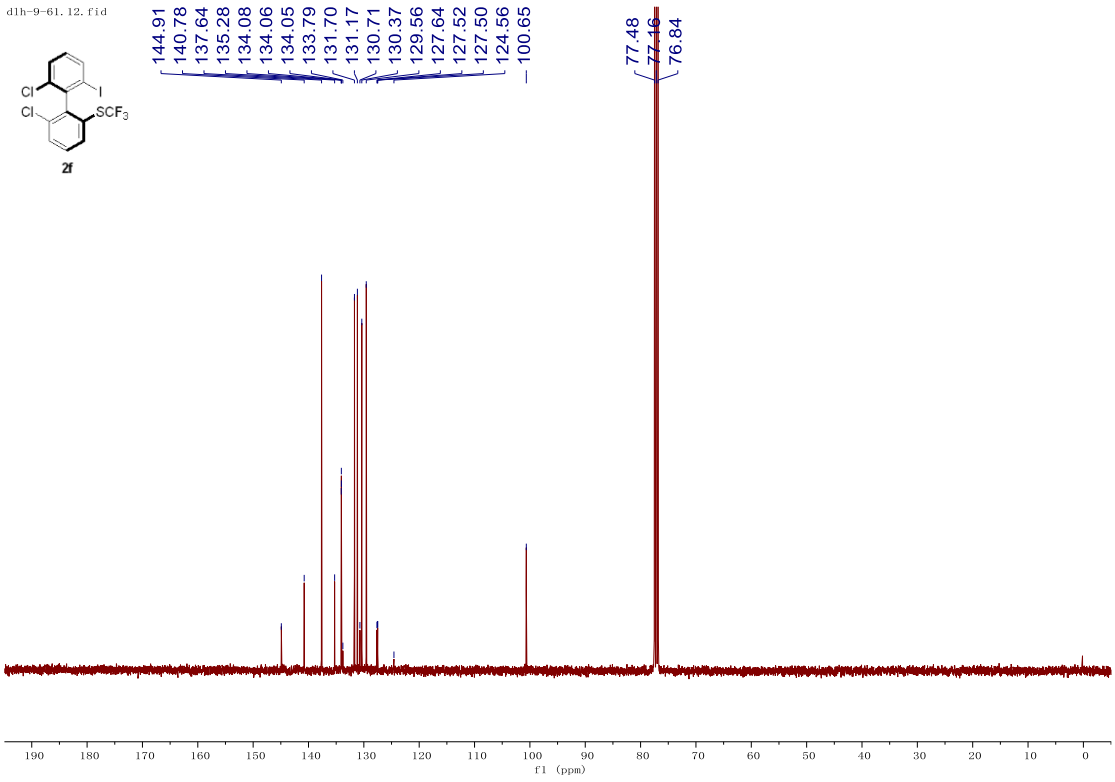


Figure S18. ^{13}C NMR spectra (101 MHz) of **2f**

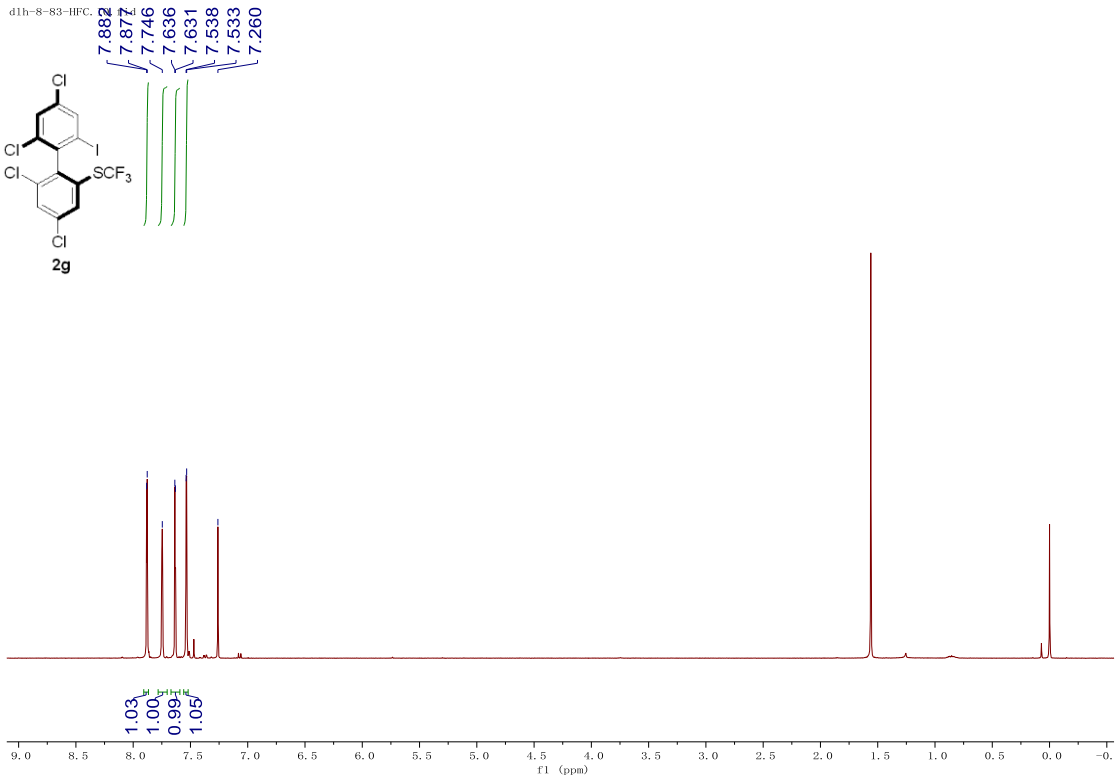


Figure S19. ^{1}H NMR spectra (400 MHz) of **2g**

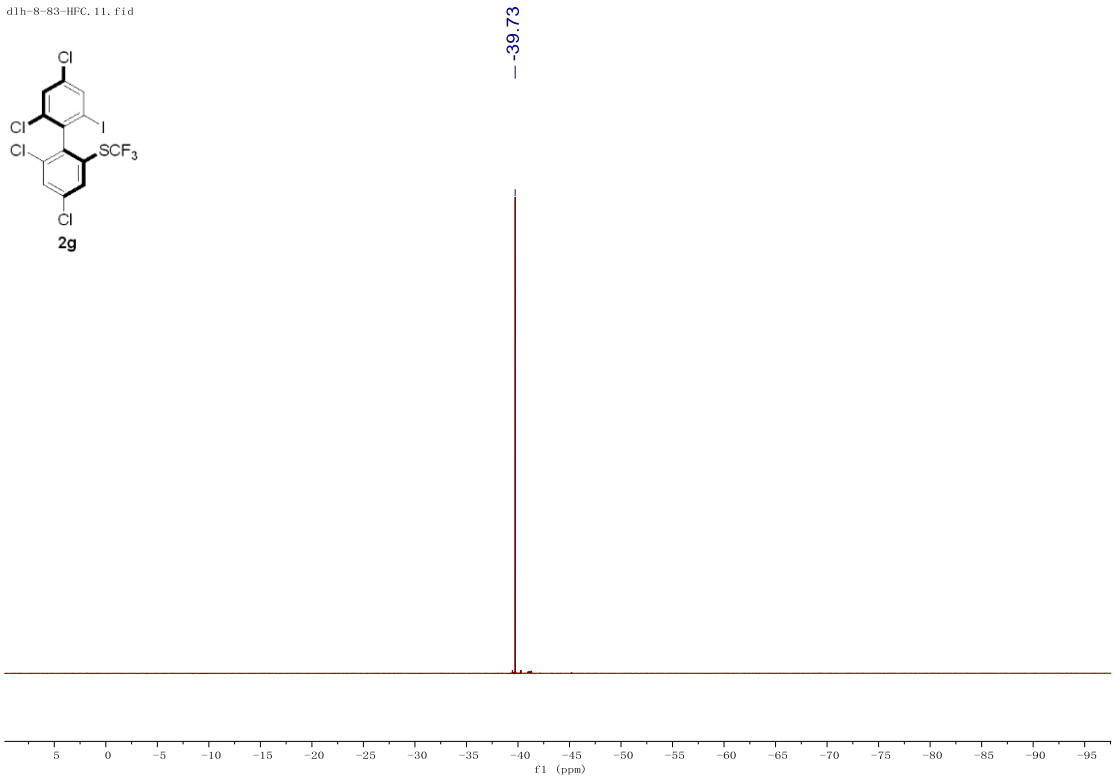


Figure S20. ^{19}FNMR spectra (471 MHz) of **2g**

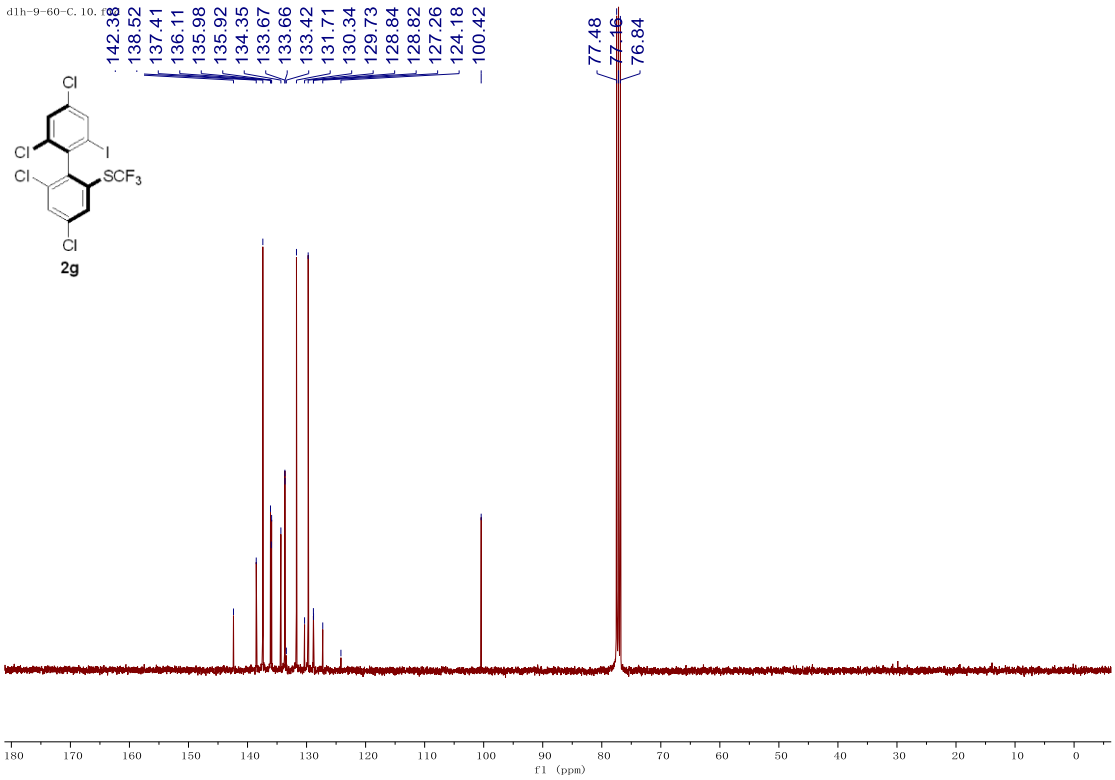


Figure S21. ^{13}C NMR spectra (101 MHz) of **2g**

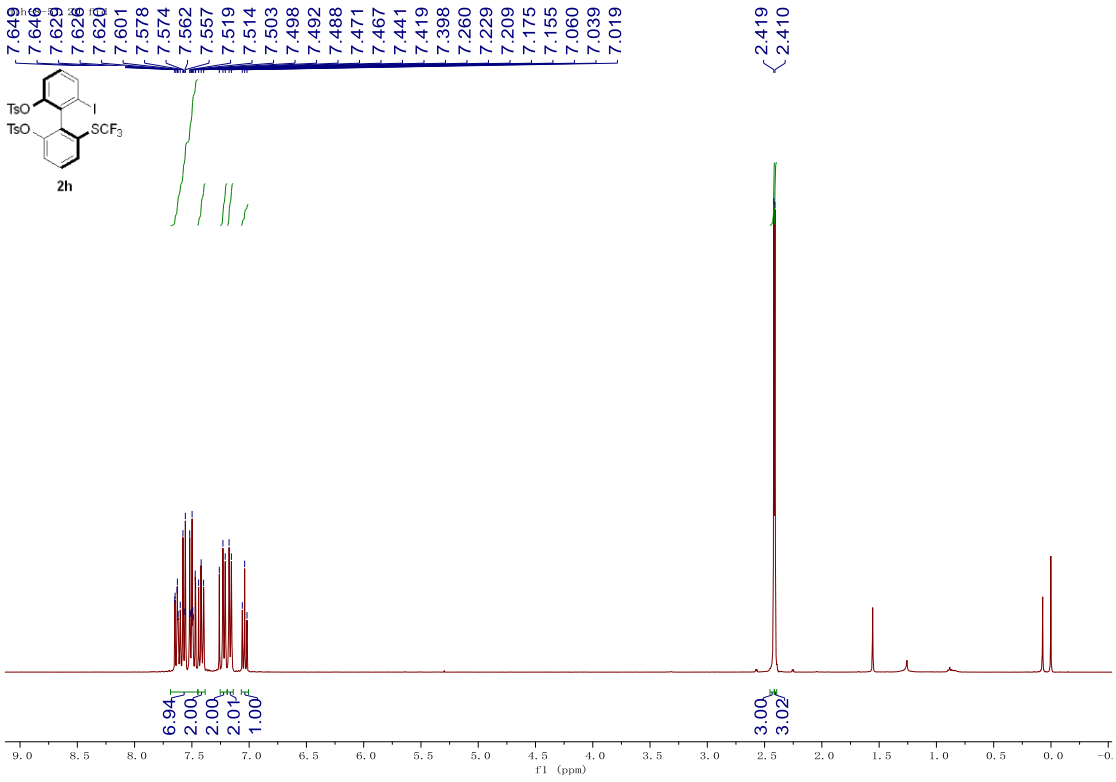


Figure S22. ^{1}H NMR spectra (400 MHz) of **2h**

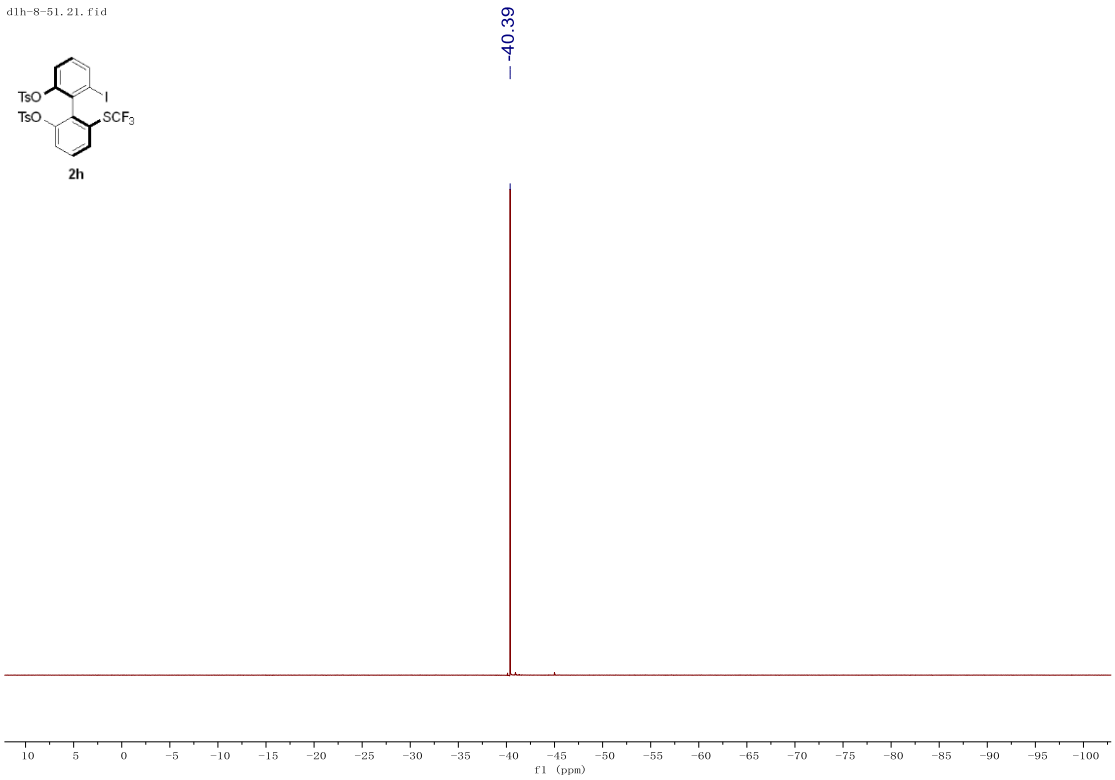


Figure S23. ^{19}FNMR spectra (471 MHz) of **2h**

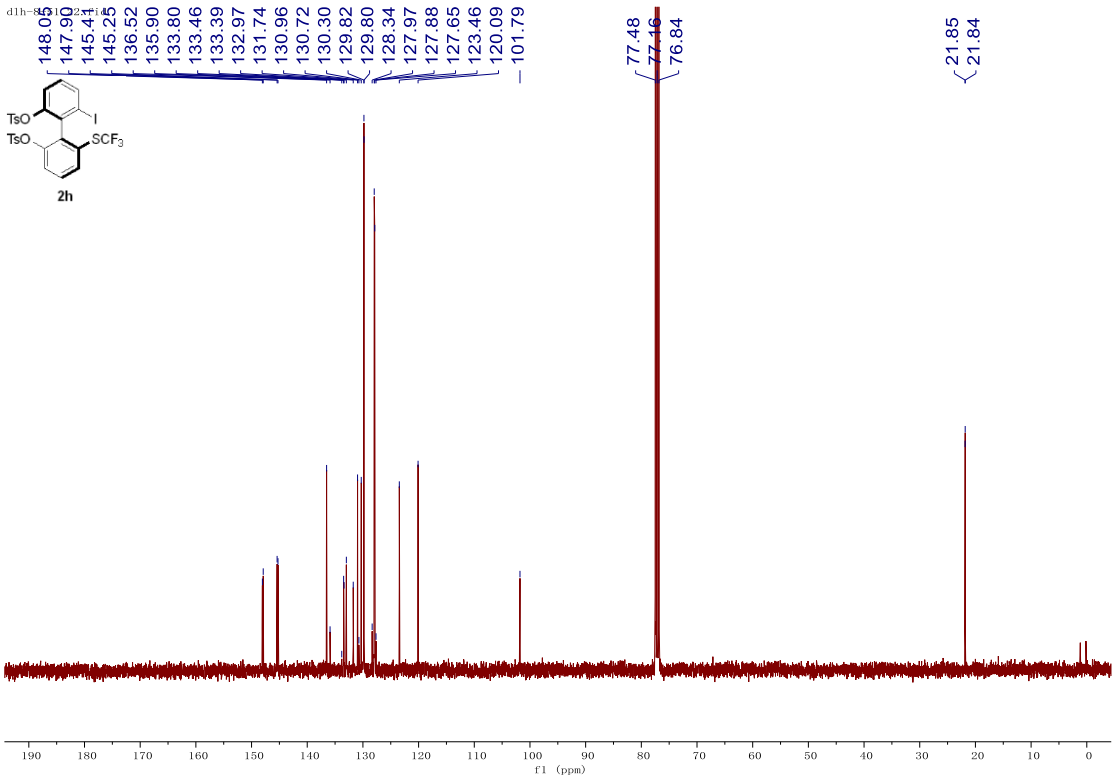


Figure S24. ^{13}C NMR spectra (101 MHz) of **2h**

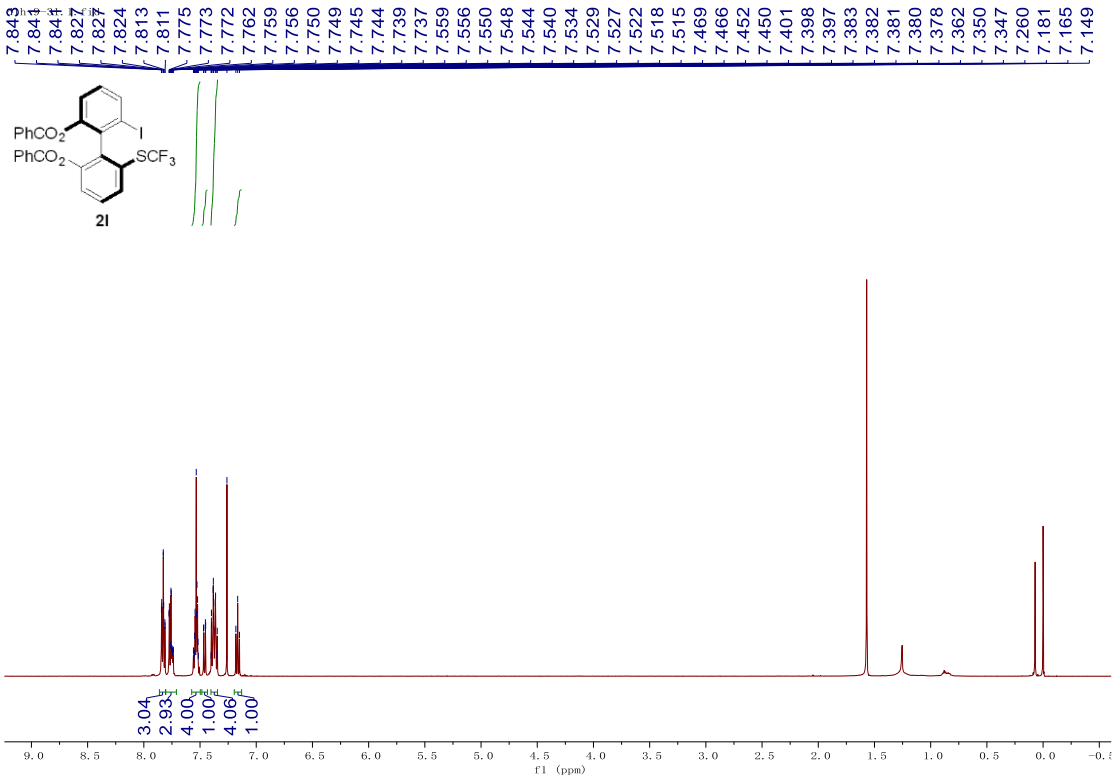


Figure S25. ^{1}H NMR spectra (400 MHz) of **2l**

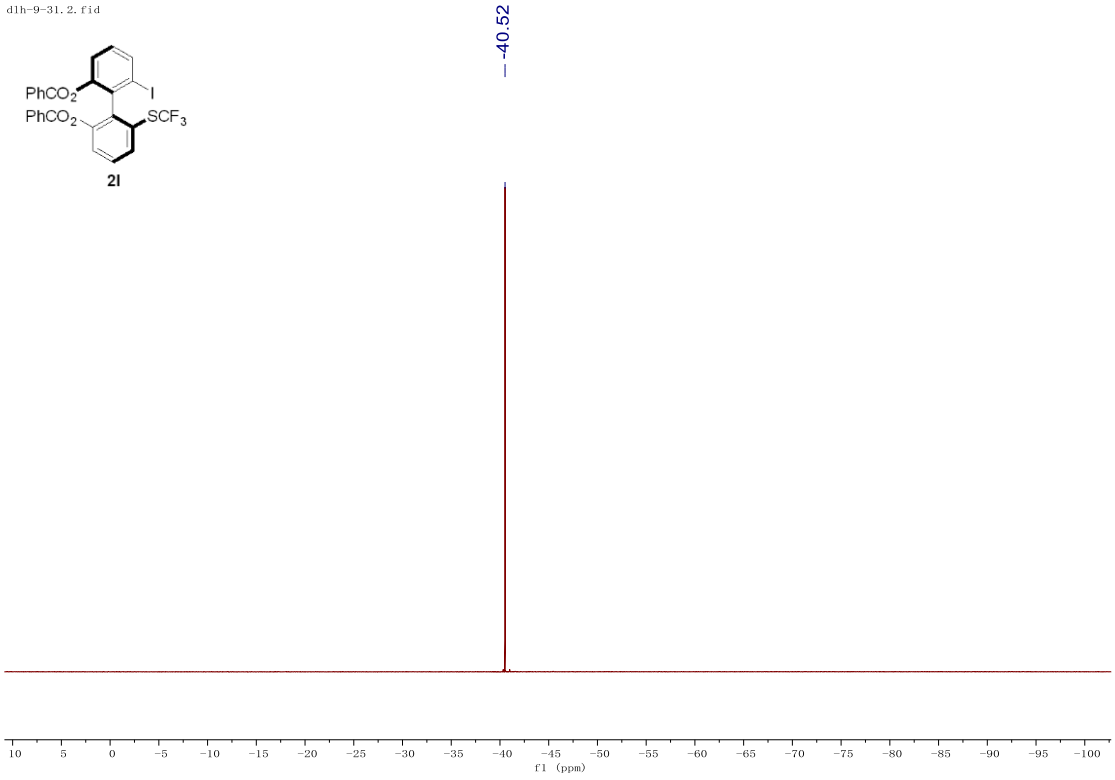


Figure S26. ^{19}FNMR spectra (471 MHz) of **2l**

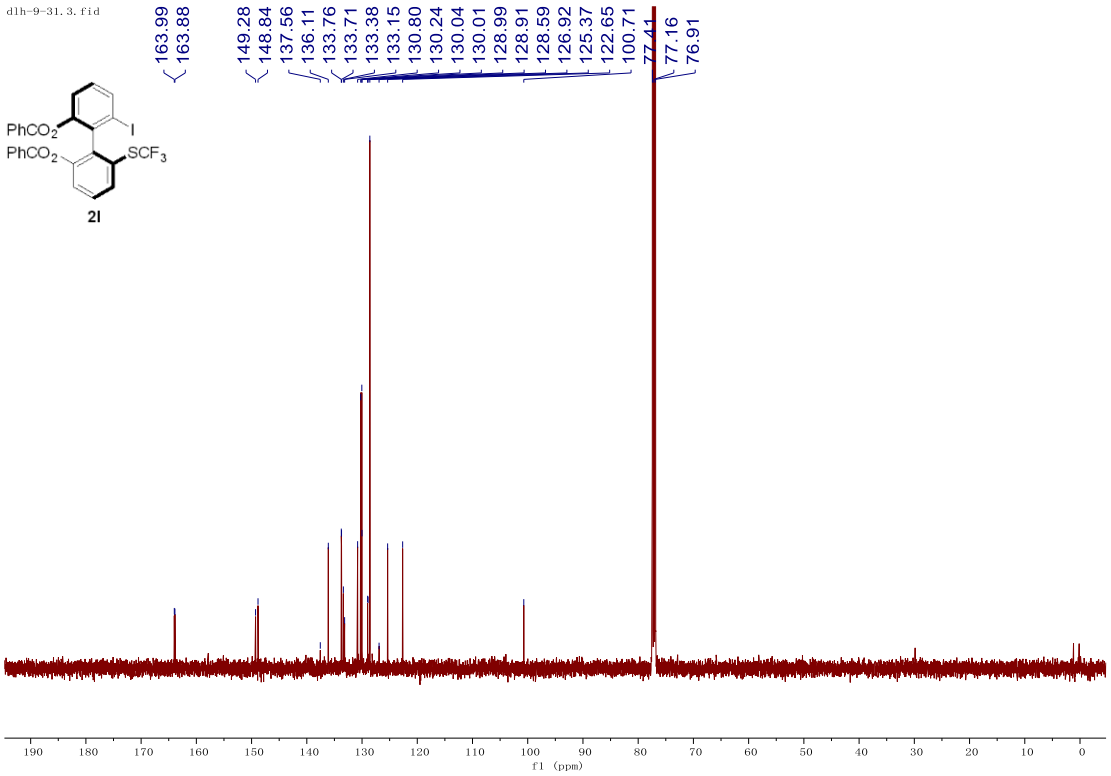


Figure S27. ^{13}C NMR spectra (101 MHz) of **2l**

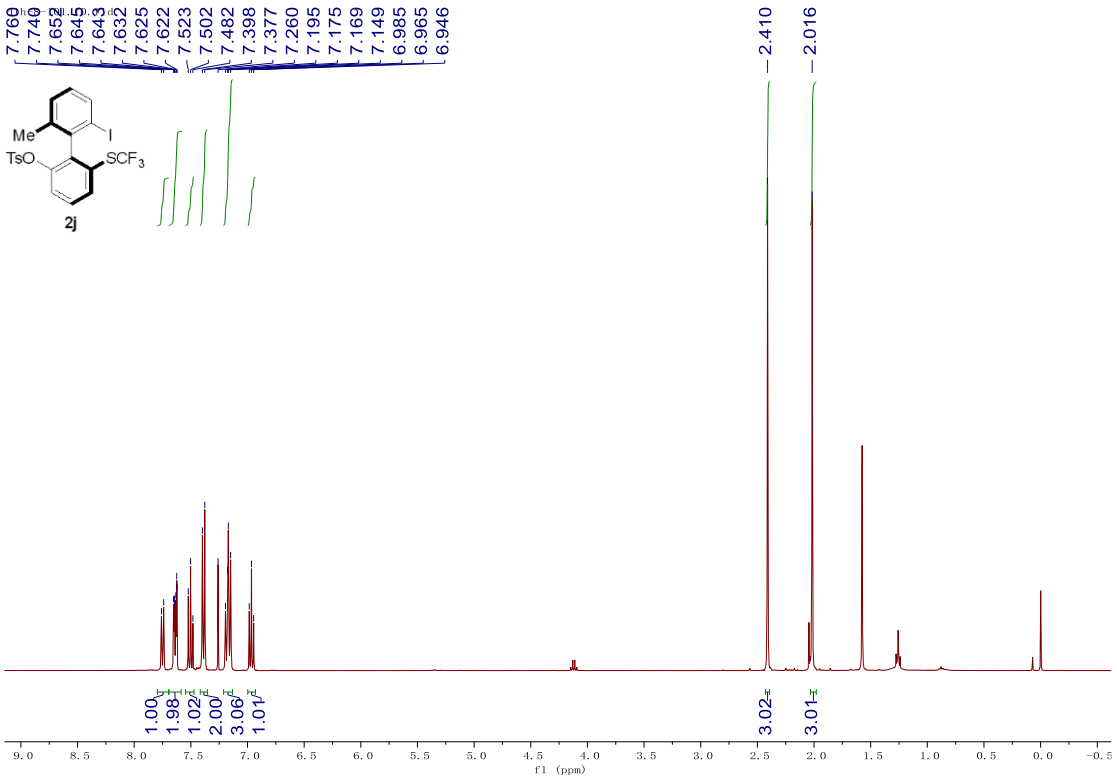


Figure S28. ^{1}H NMR spectra (400 MHz) of **2j**

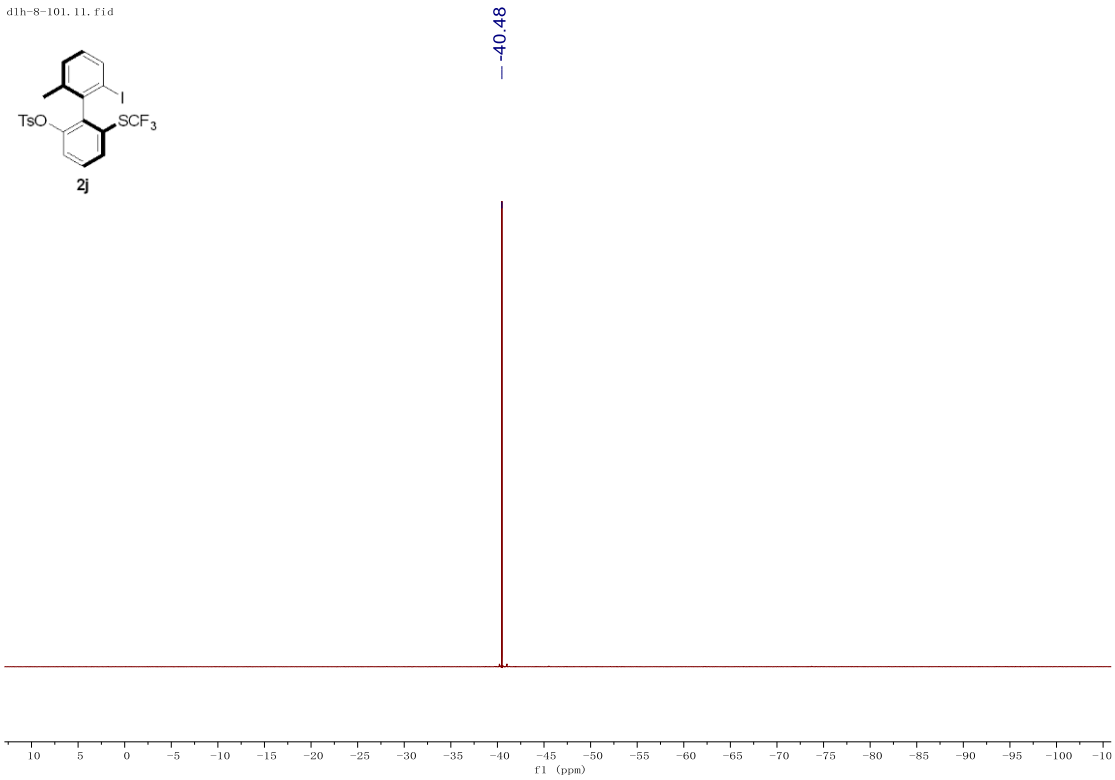


Figure S29. ^{19}FNMR spectra (471 MHz) of **2j**

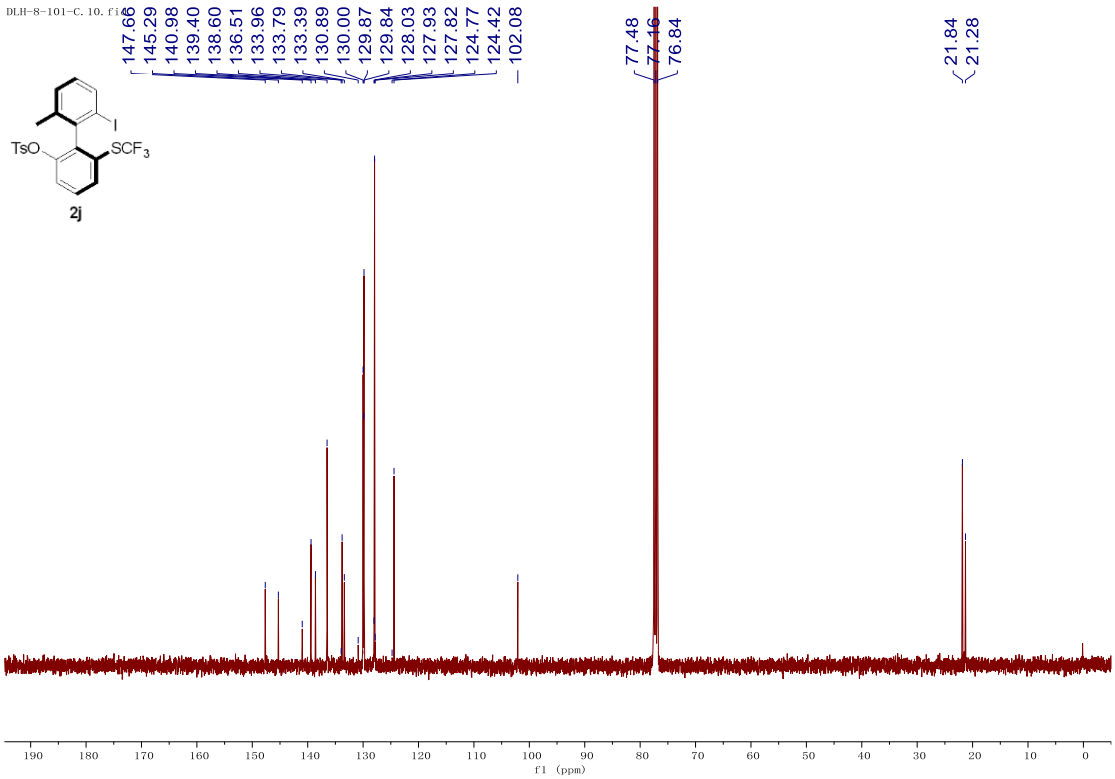


Figure S30. ^{13}C NMR spectra (101 MHz) of **2j**

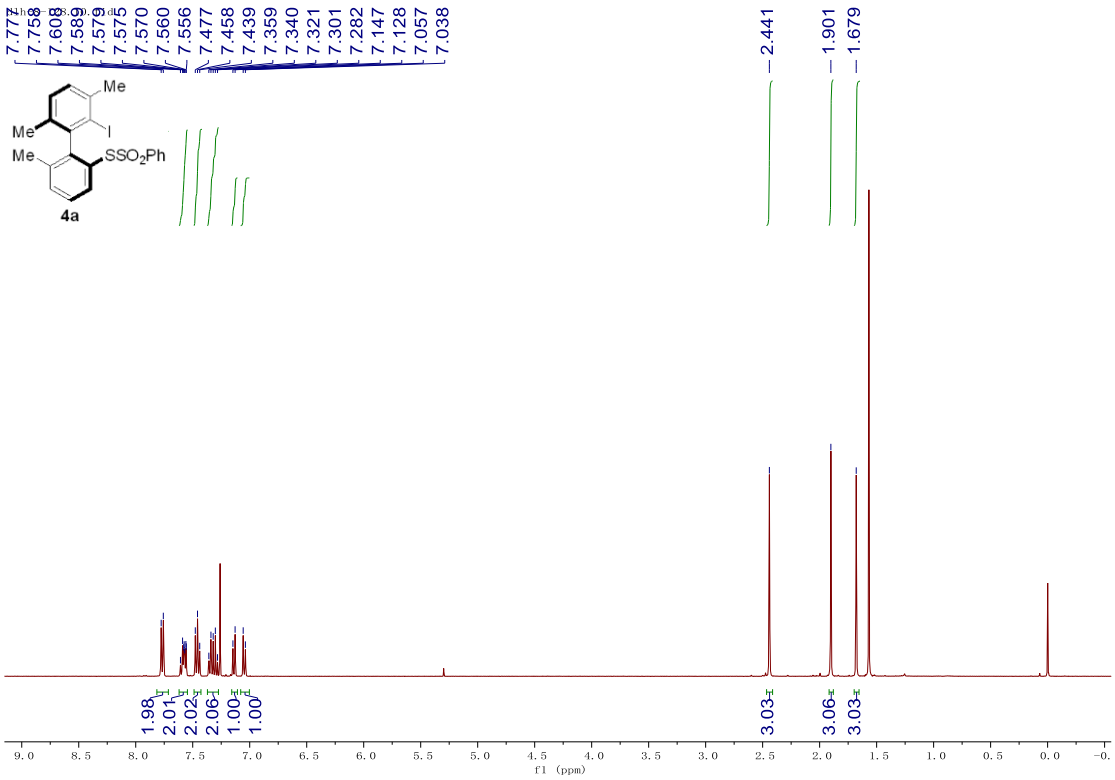


Figure S31. ^{1}H NMR spectra (400 MHz) of **4a**

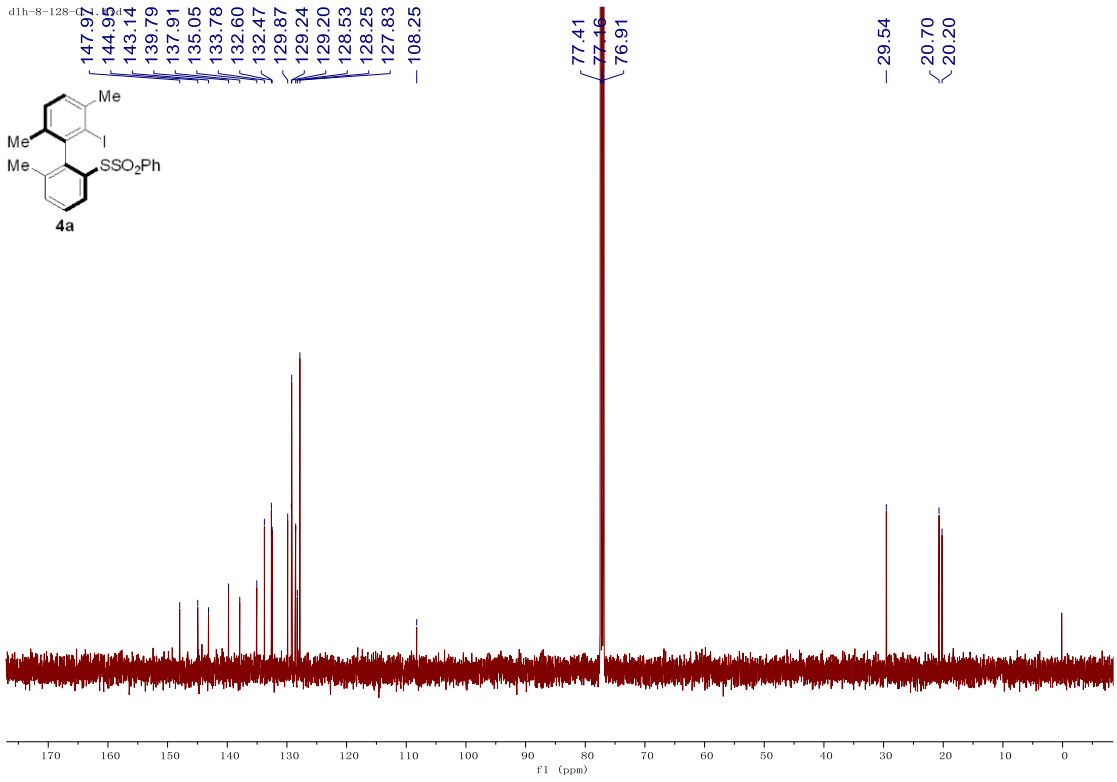


Figure S32. ^{13}C NMR spectra (101 MHz) of **4a**

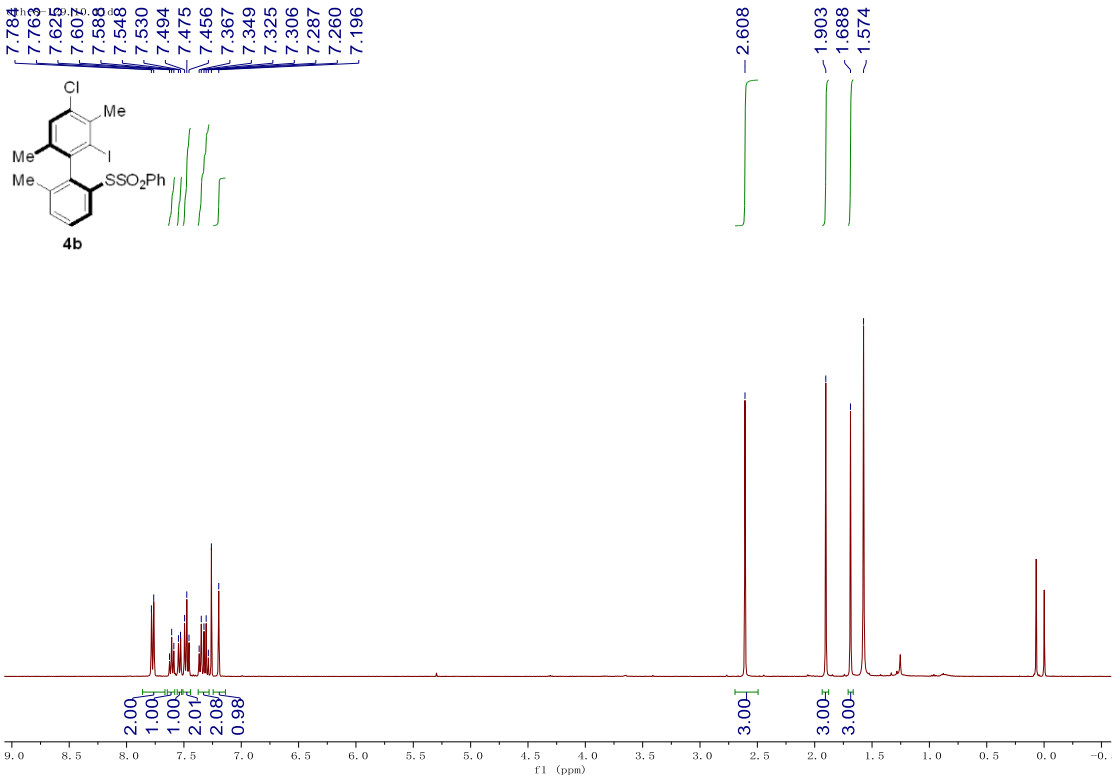


Figure S33. ^{1}H NMR spectra (400 MHz) of **4b**

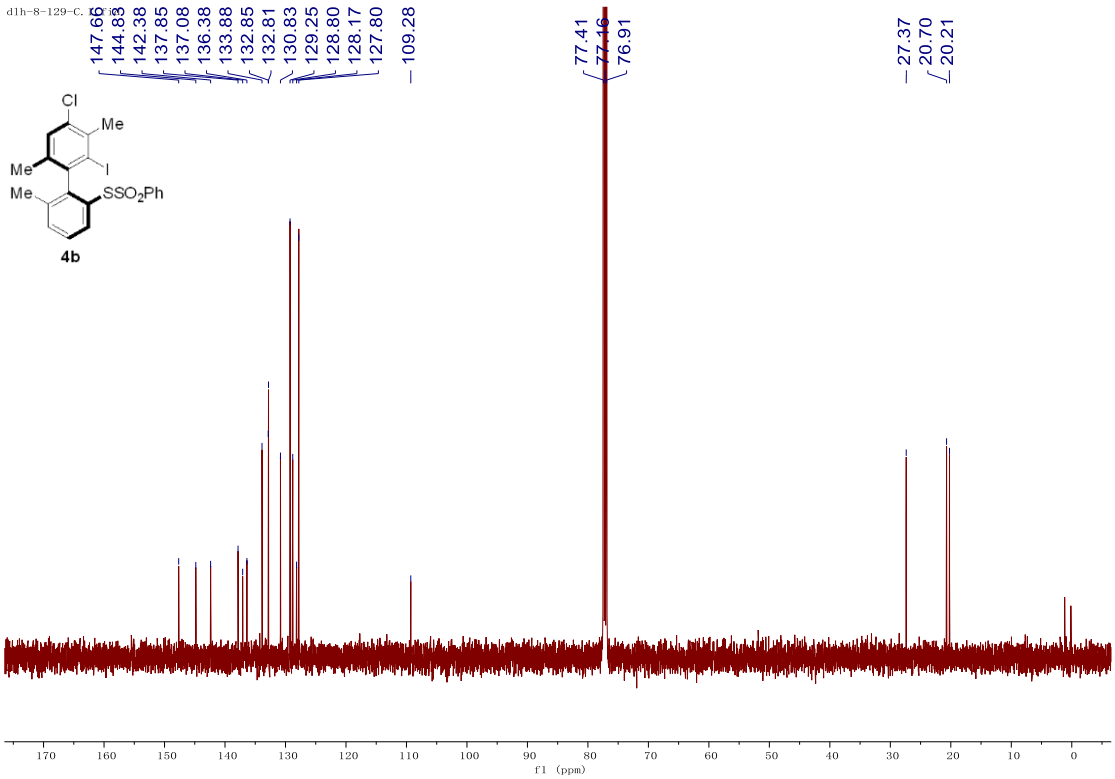


Figure S34. ^{13}C NMR spectra (101 MHz) of **4b**

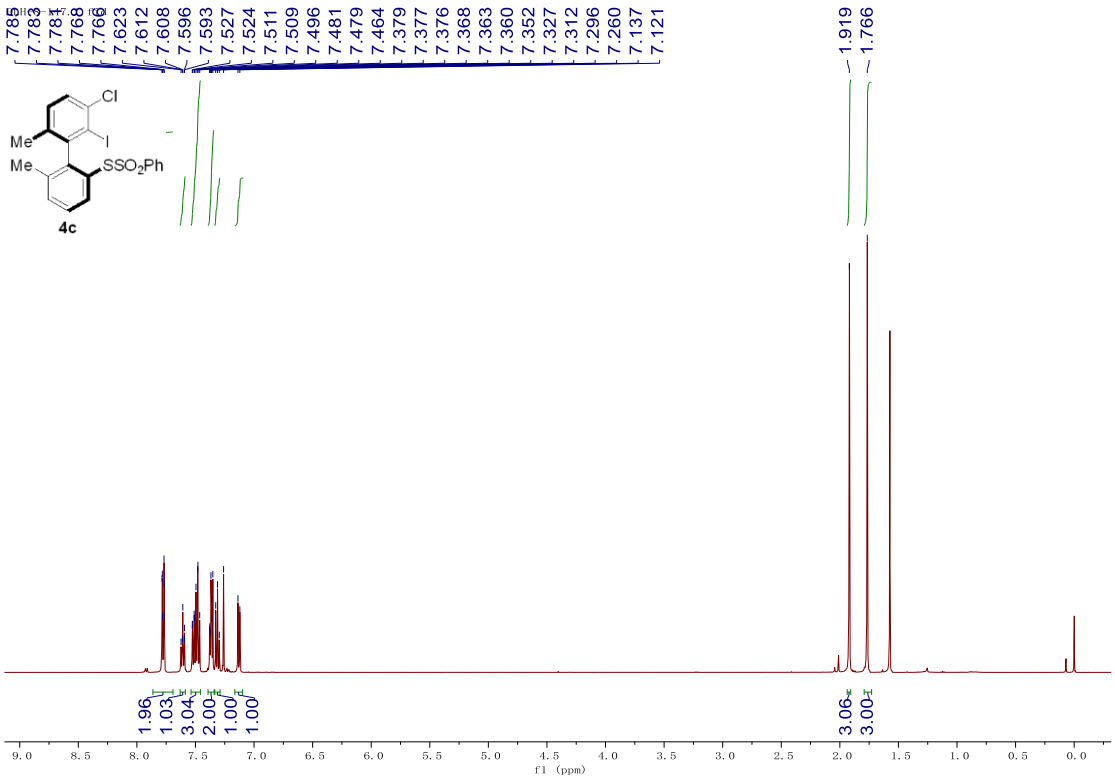


Figure S35. ^{1}H NMR spectra (400 MHz) of **4c**

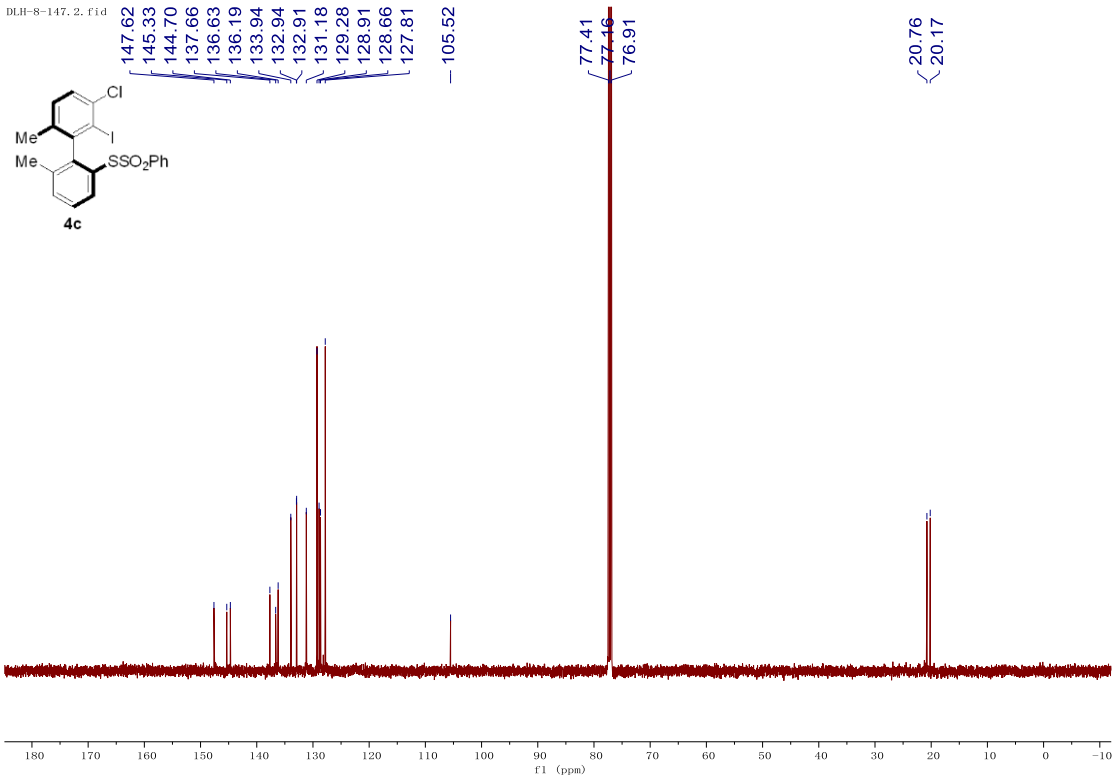


Figure S36. ^{13}C NMR spectra (101 MHz) of **4c**

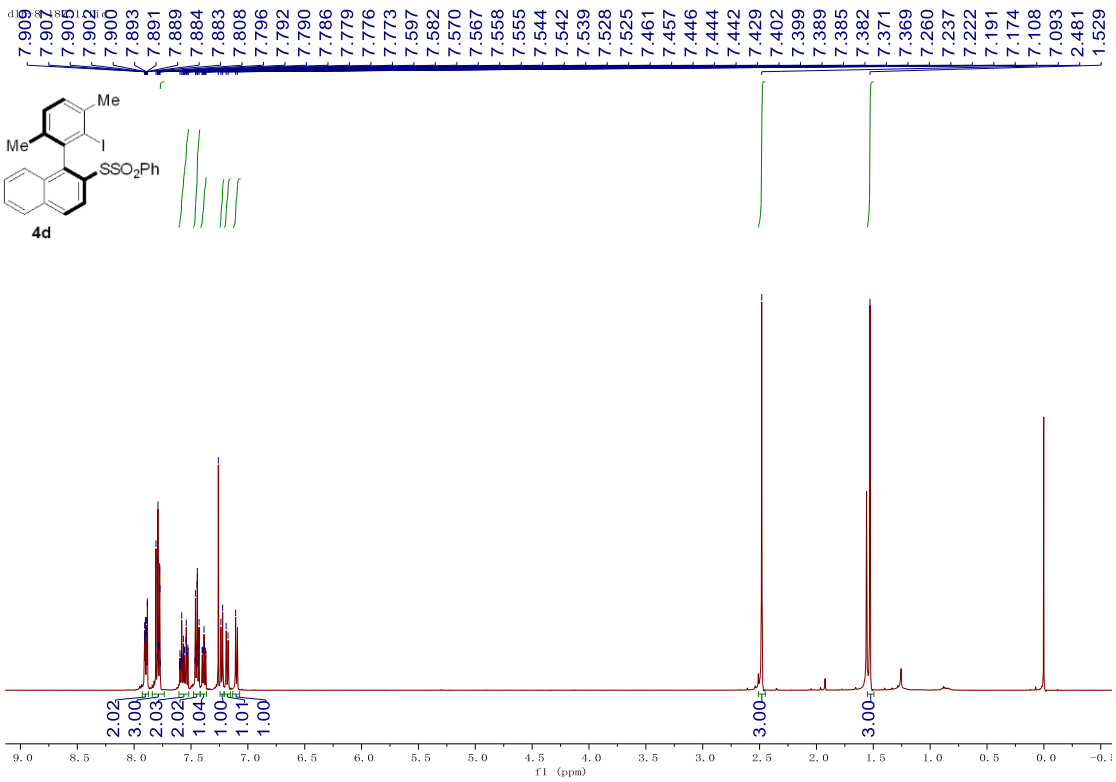


Figure S37. ^{1}H NMR spectra (400 MHz) of **4d**

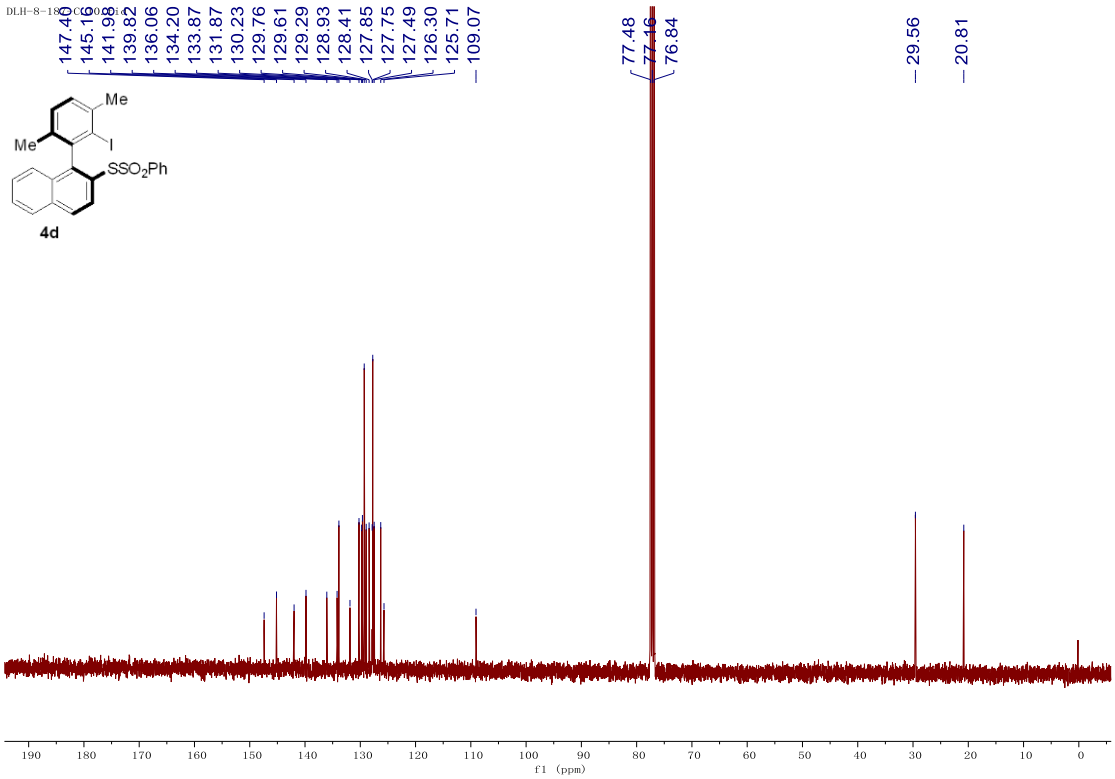


Figure S38. ^{13}C NMR spectra (101 MHz) of **4d**

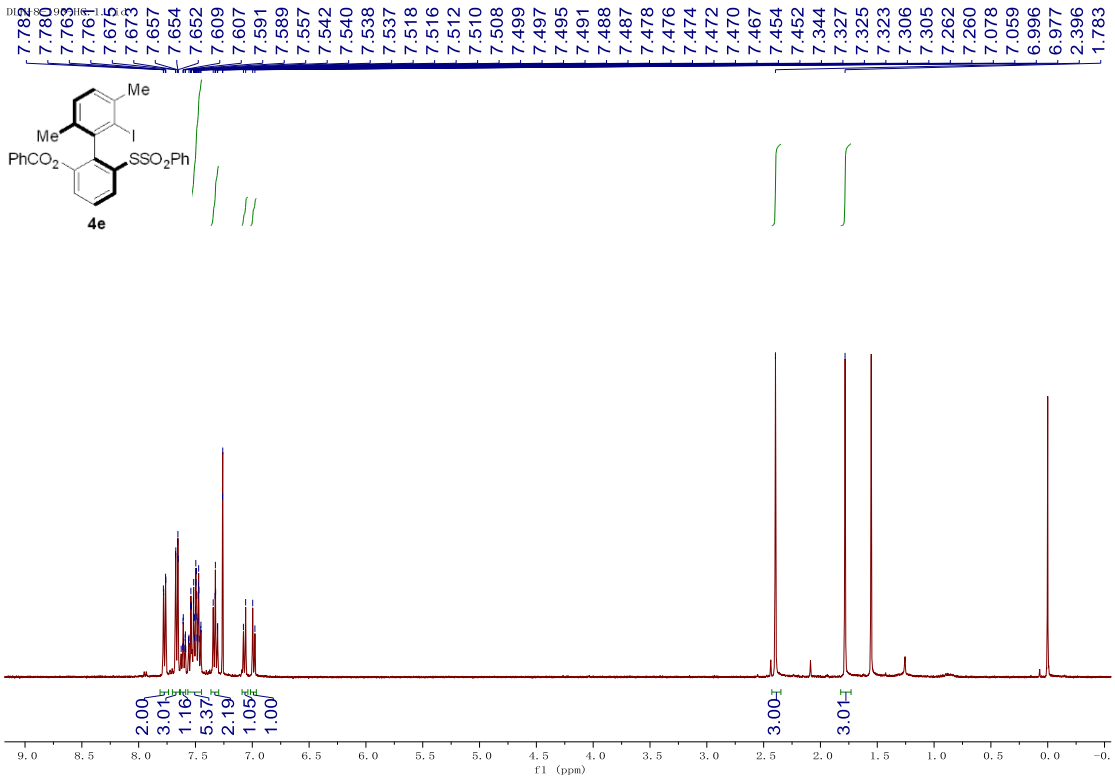


Figure S39. ^{1}H NMR spectra (400 MHz) of **4e**

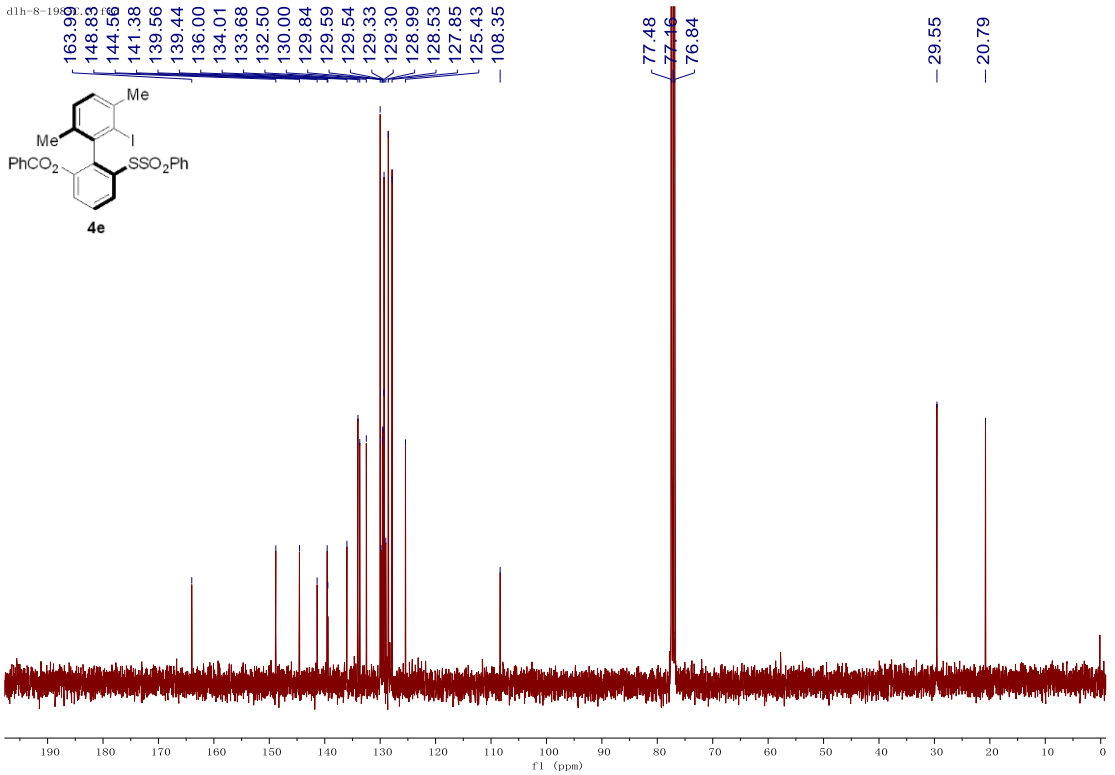


Figure S40. ^{13}C NMR spectra (101 MHz) of **4e**

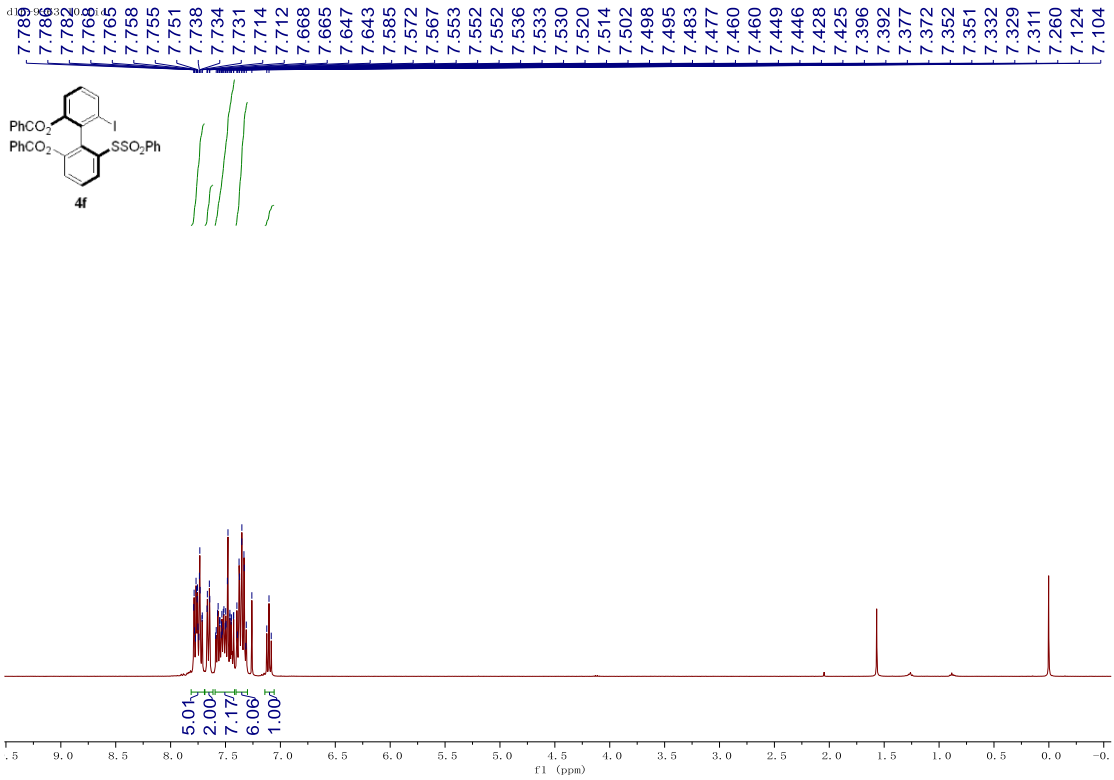


Figure S41. ^{1}H NMR spectra (400 MHz) of **4f**

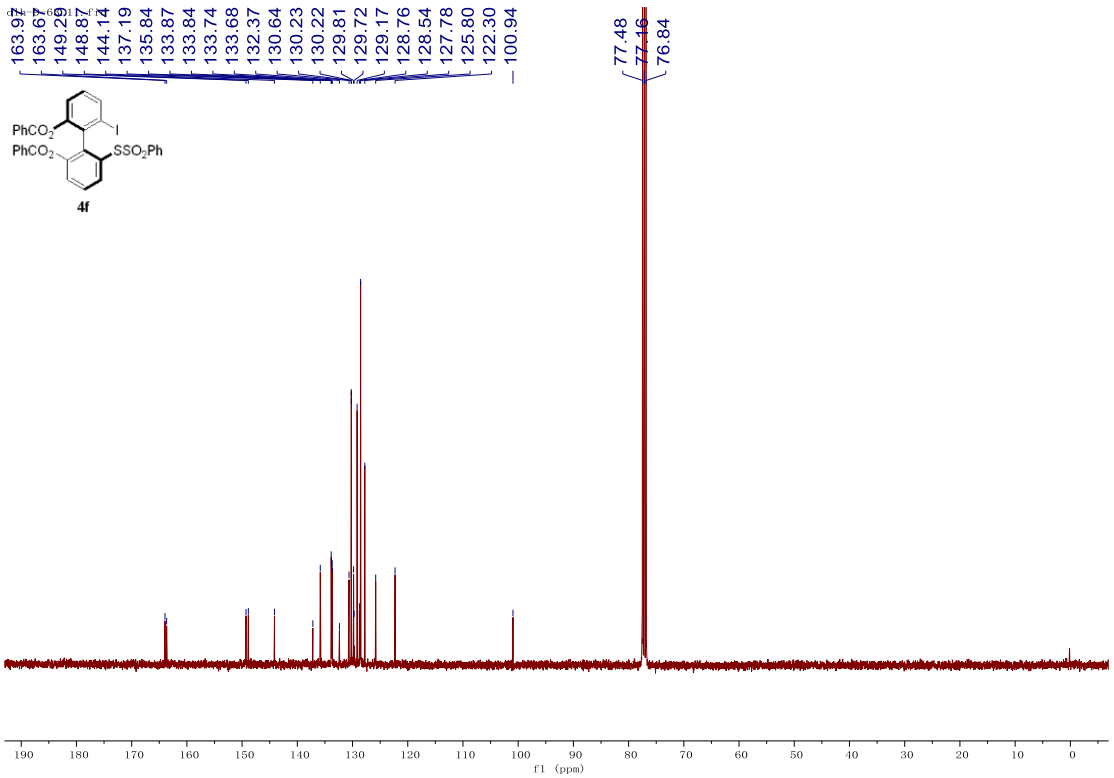


Figure S42. ^{13}C NMR spectra (101 MHz) of **4f**

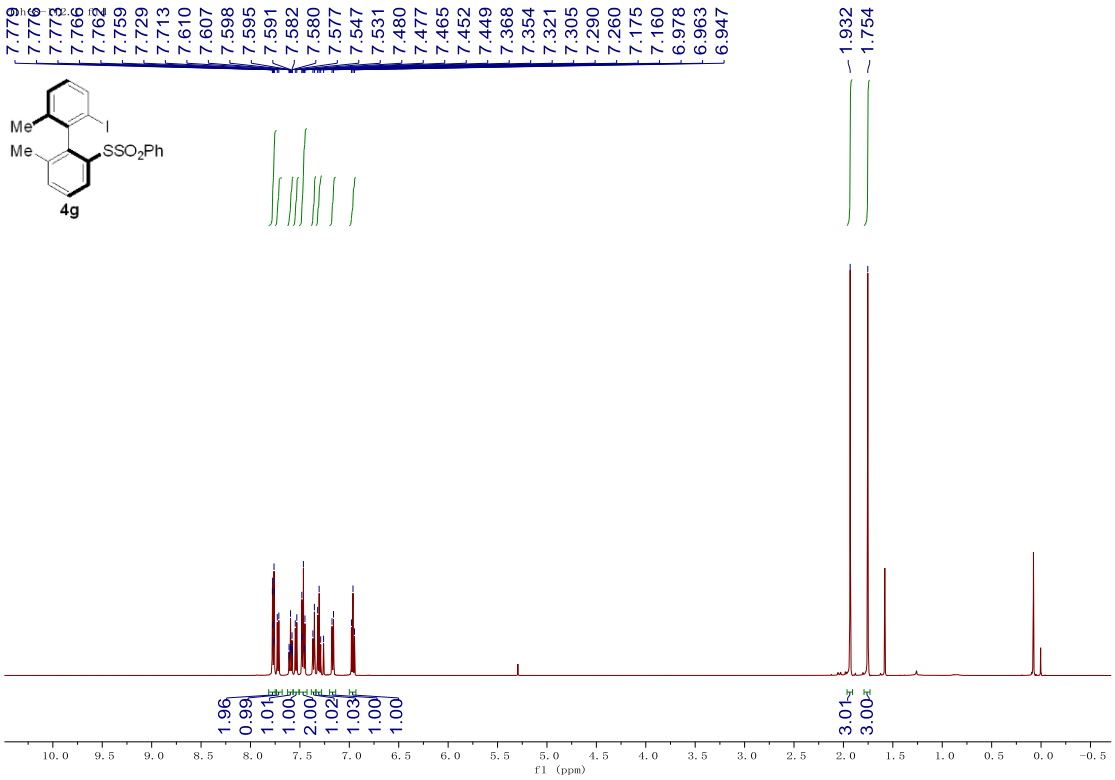


Figure S43. ^{1}H NMR spectra (400 MHz) of **4g**

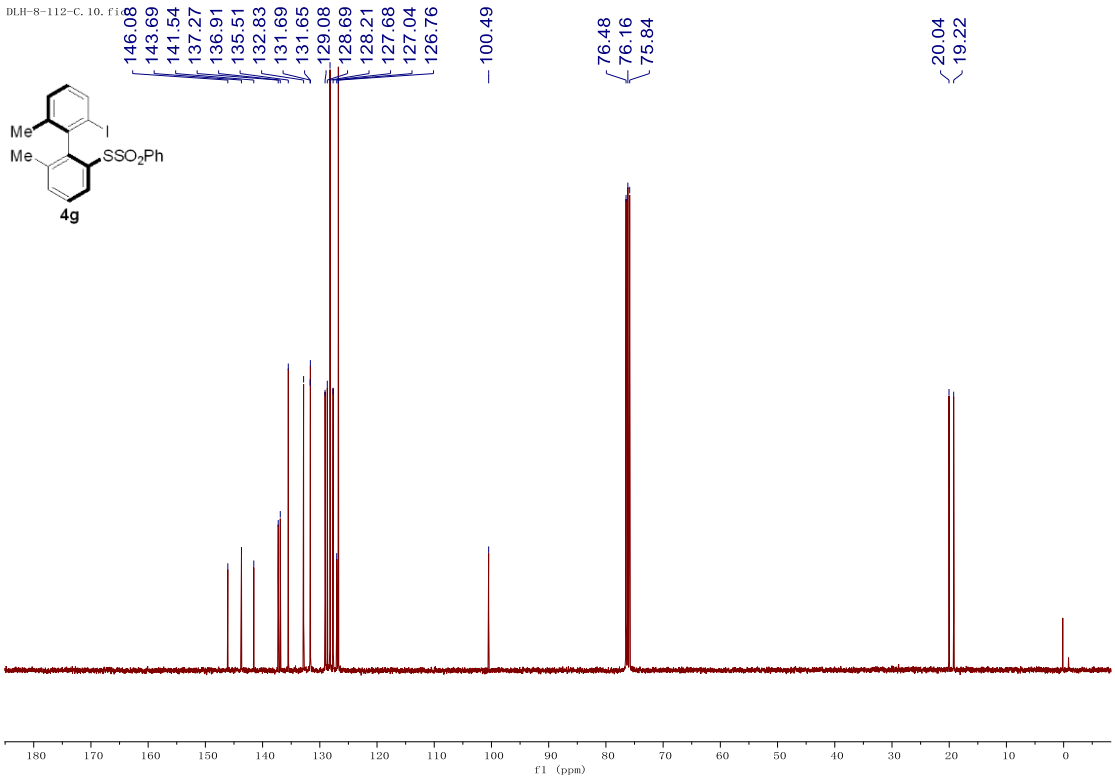


Figure S44. ^{13}C NMR spectra (101 MHz) of **4g**

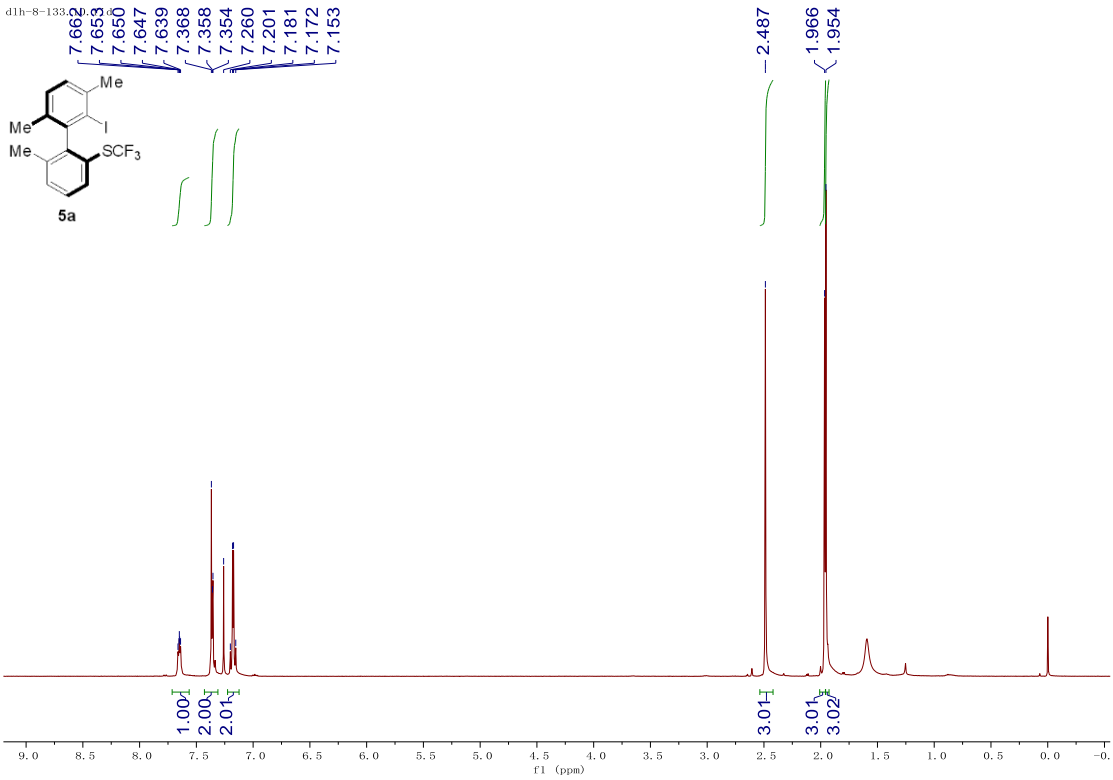


Figure S45. ^{1}H NMR spectra (400 MHz) of **5a**

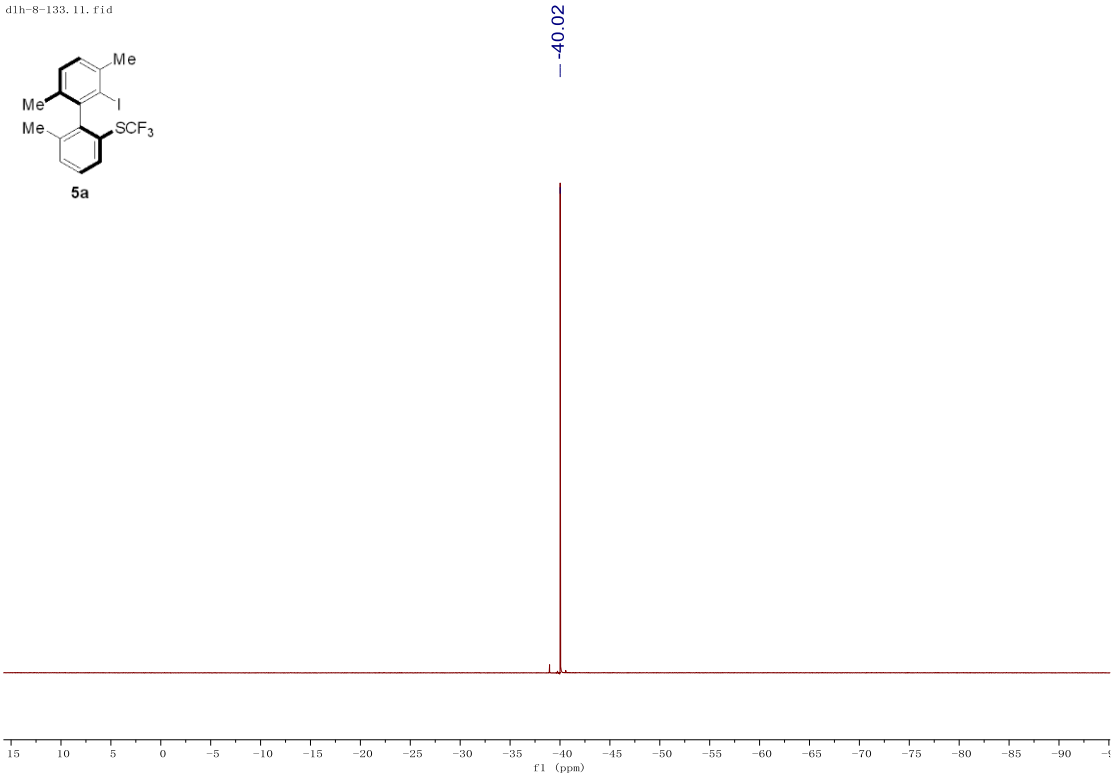


Figure S46. ^{19}FNMR spectra (471 MHz) of **5a**

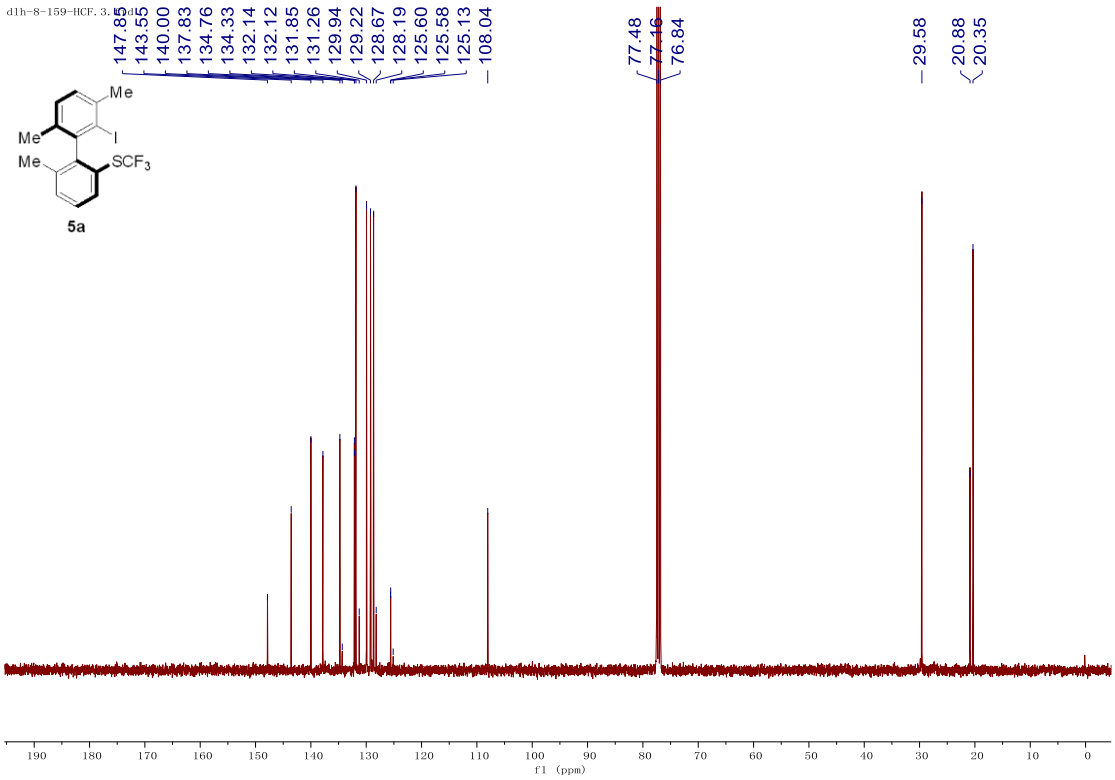


Figure S47. ^{13}C NMR spectra (101 MHz) of **5a**

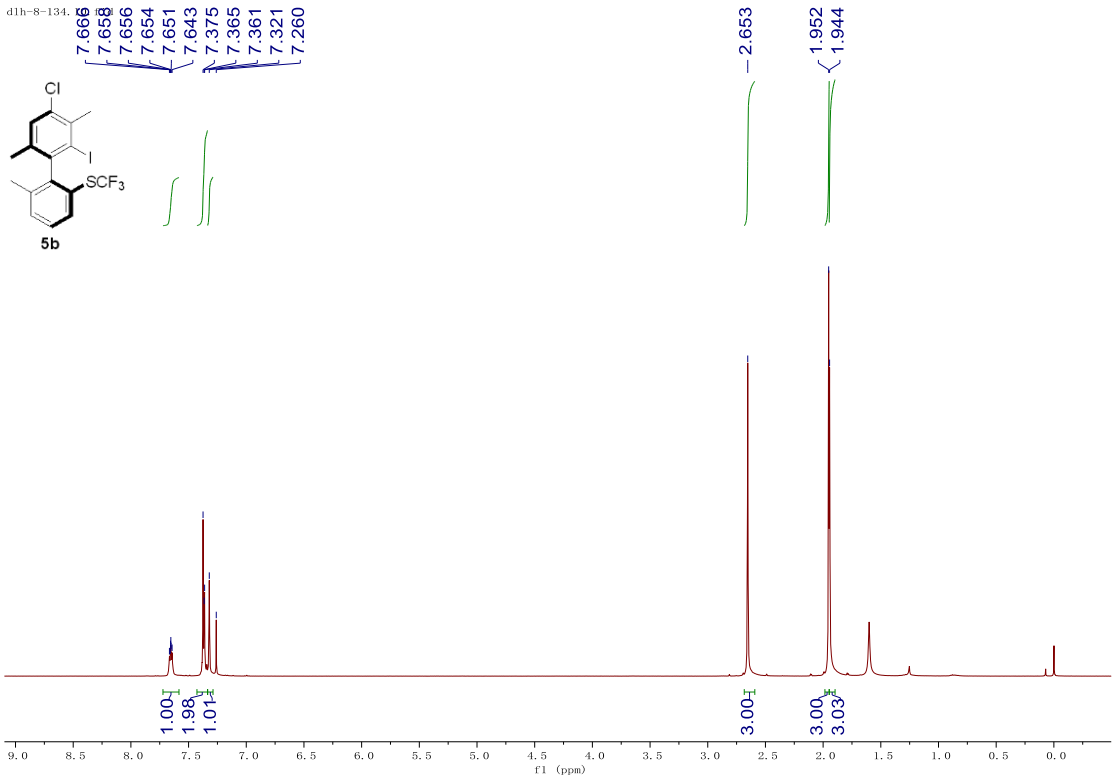


Figure S48. ^{1}H NMR spectra (400 MHz) of **5b**

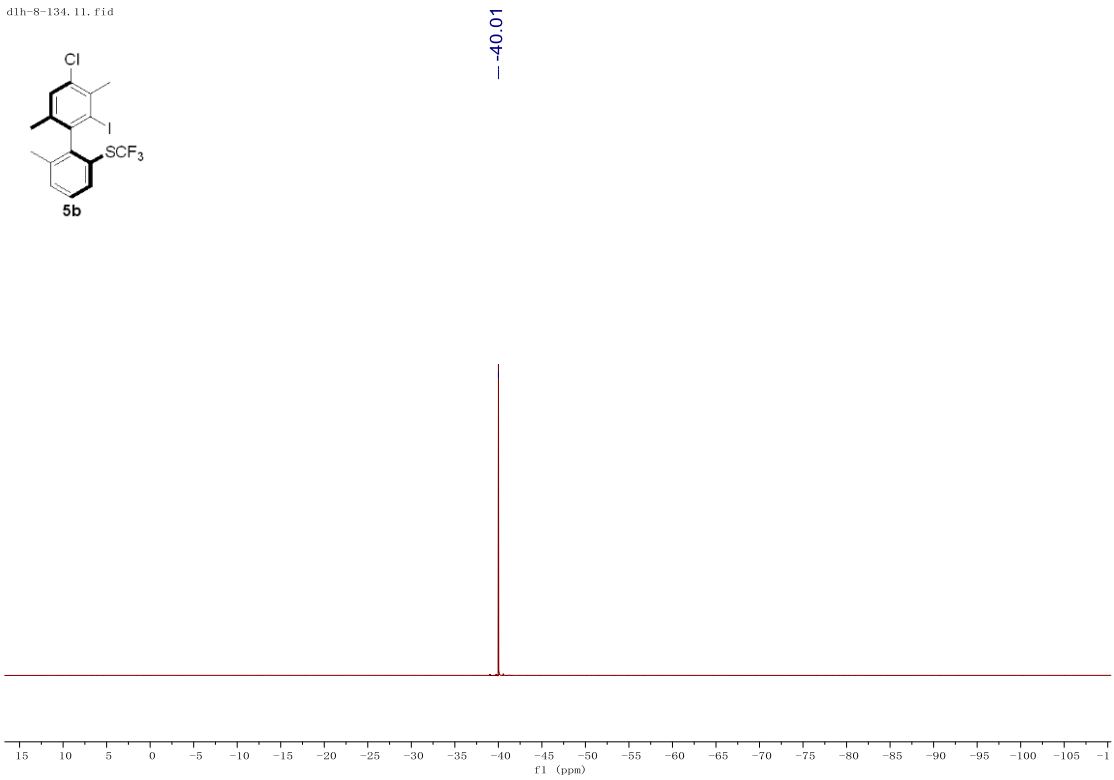


Figure S49. ^{19}FNMR spectra (471 MHz) of **5b**

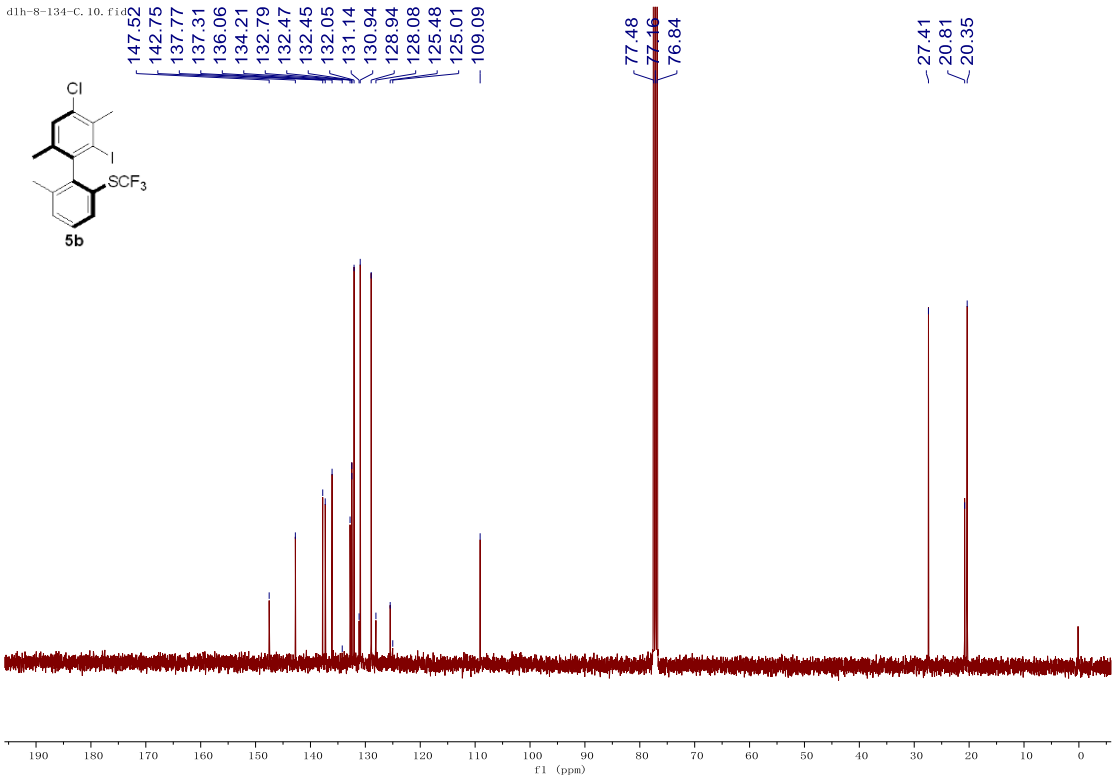


Figure S50. ^{13}C NMR spectra (101 MHz) of **5b**

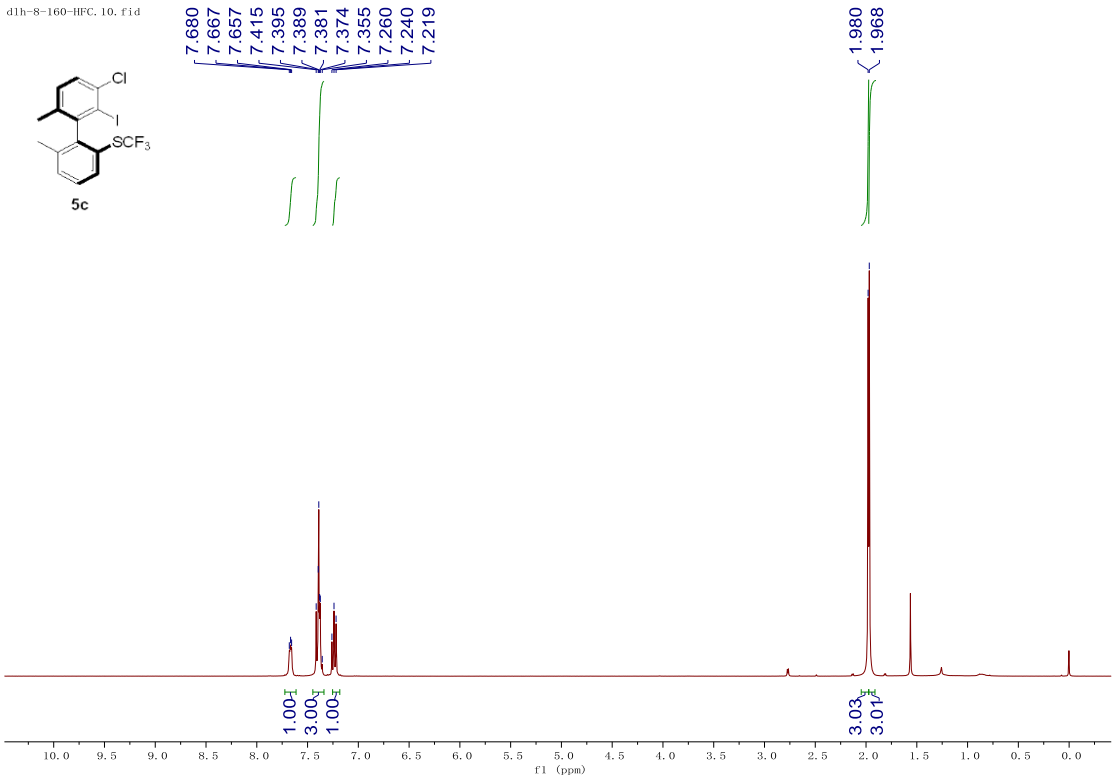


Figure S51. ^{1}H NMR spectra (400 MHz) of **5c**

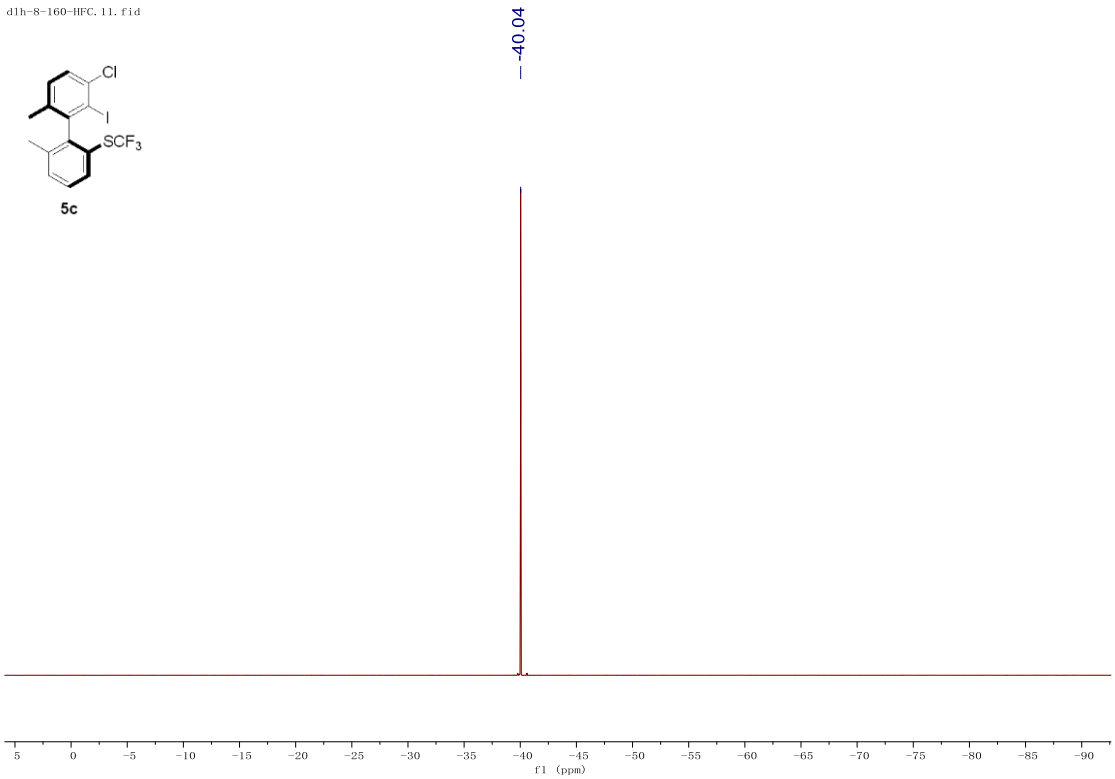


Figure S52. ^{19}FNMR spectra (471 MHz) of **5c**

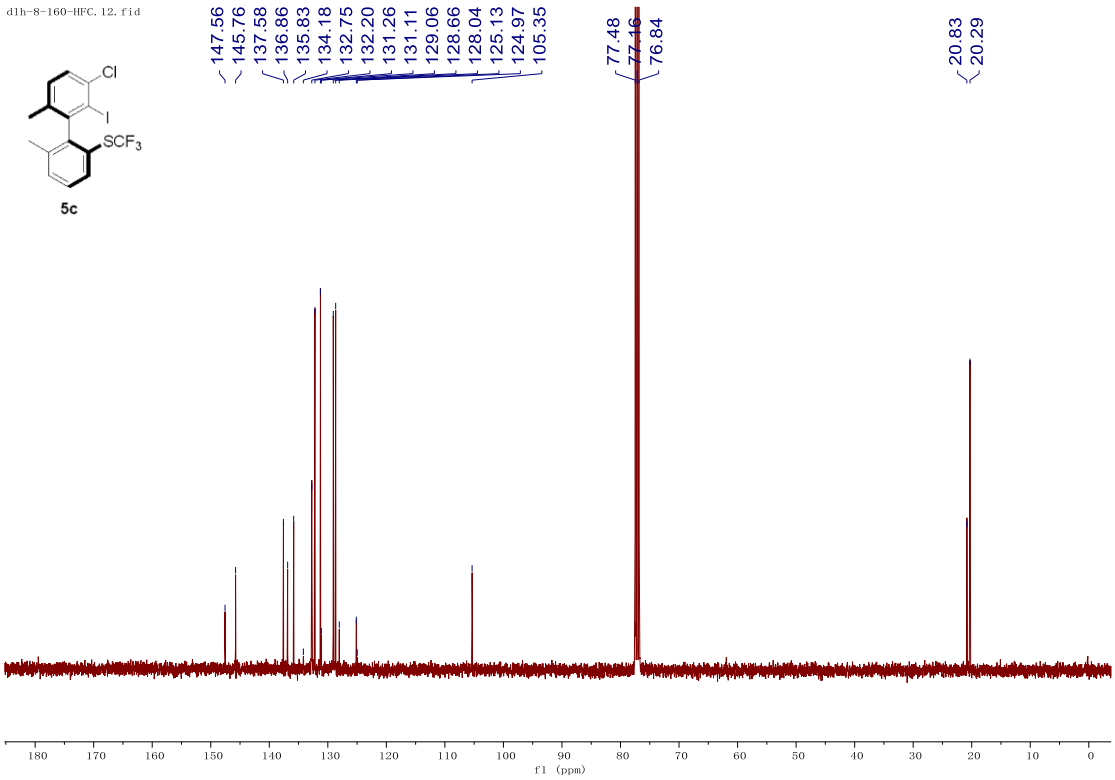


Figure S53. ^{13}C NMR spectra (101 MHz) of **5c**

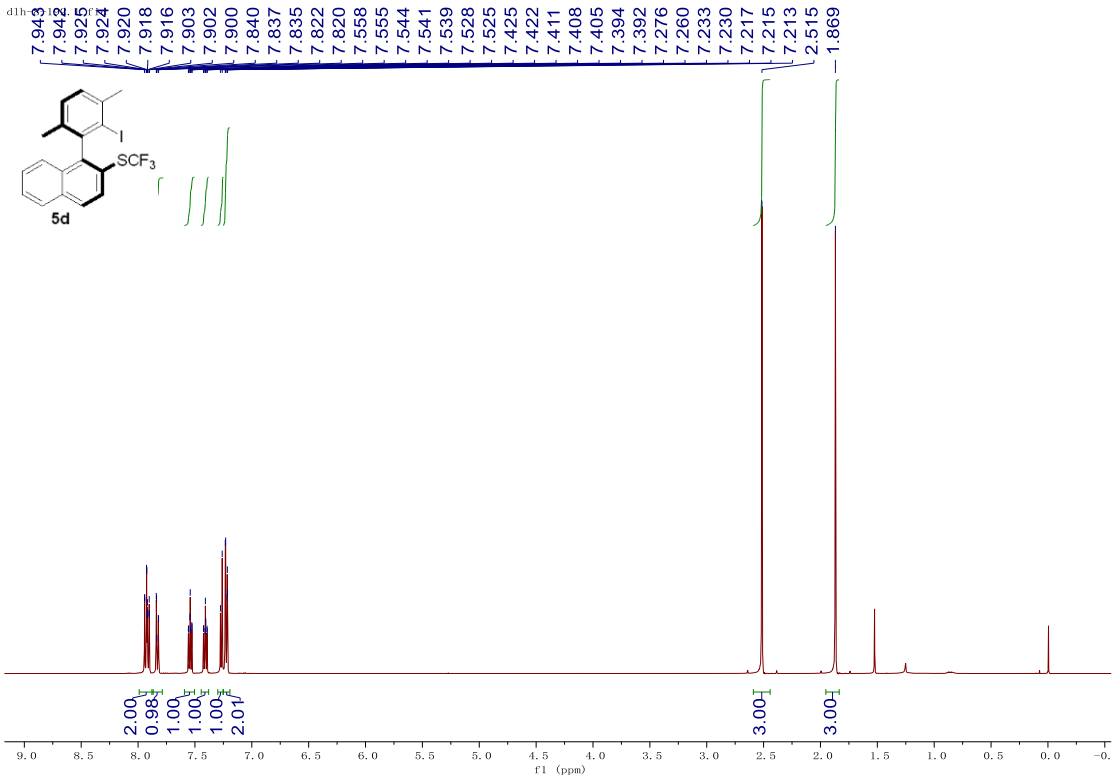


Figure S54. ^{1}H NMR spectra (400 MHz) of **5d**

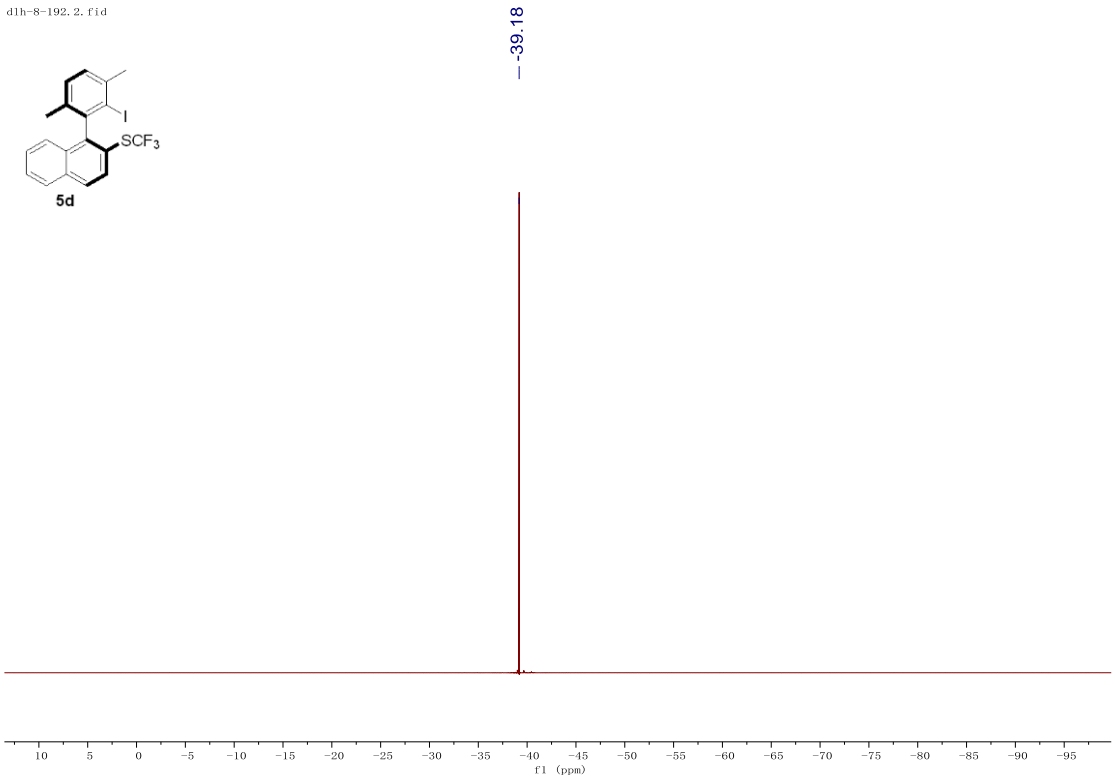


Figure S55. ^{19}FNMR spectra (471 MHz) of **5d**

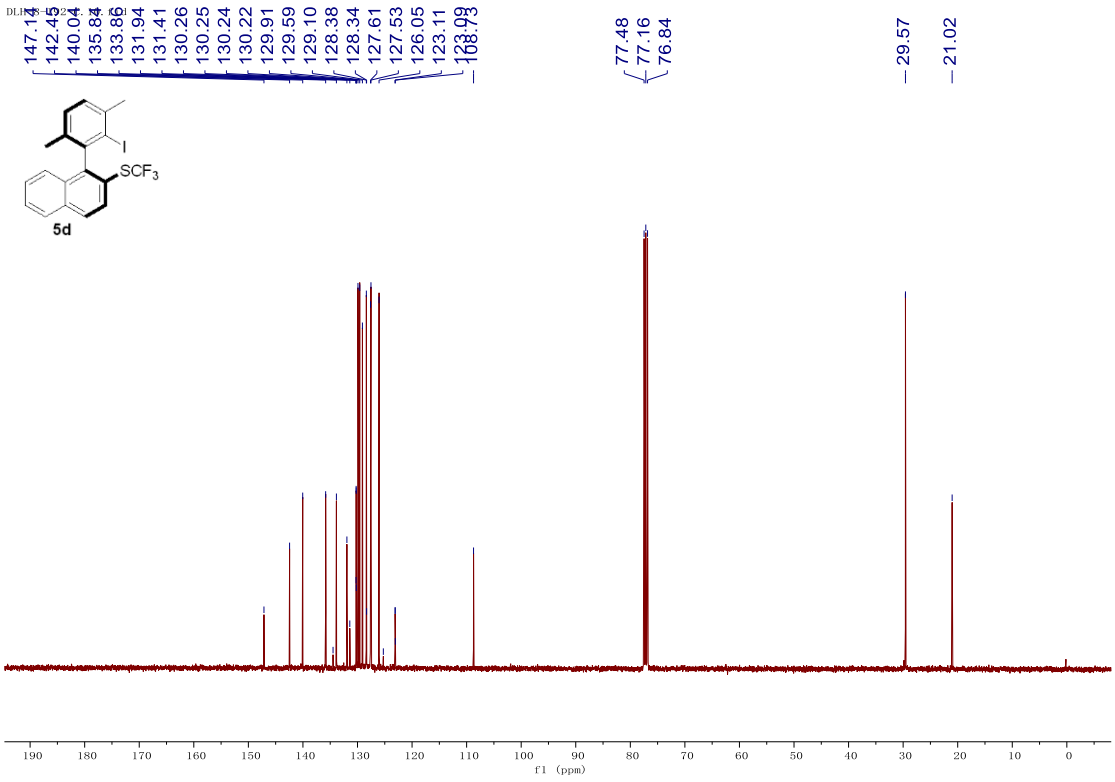


Figure S56. ^{13}C NMR spectra (101 MHz) of **5d**

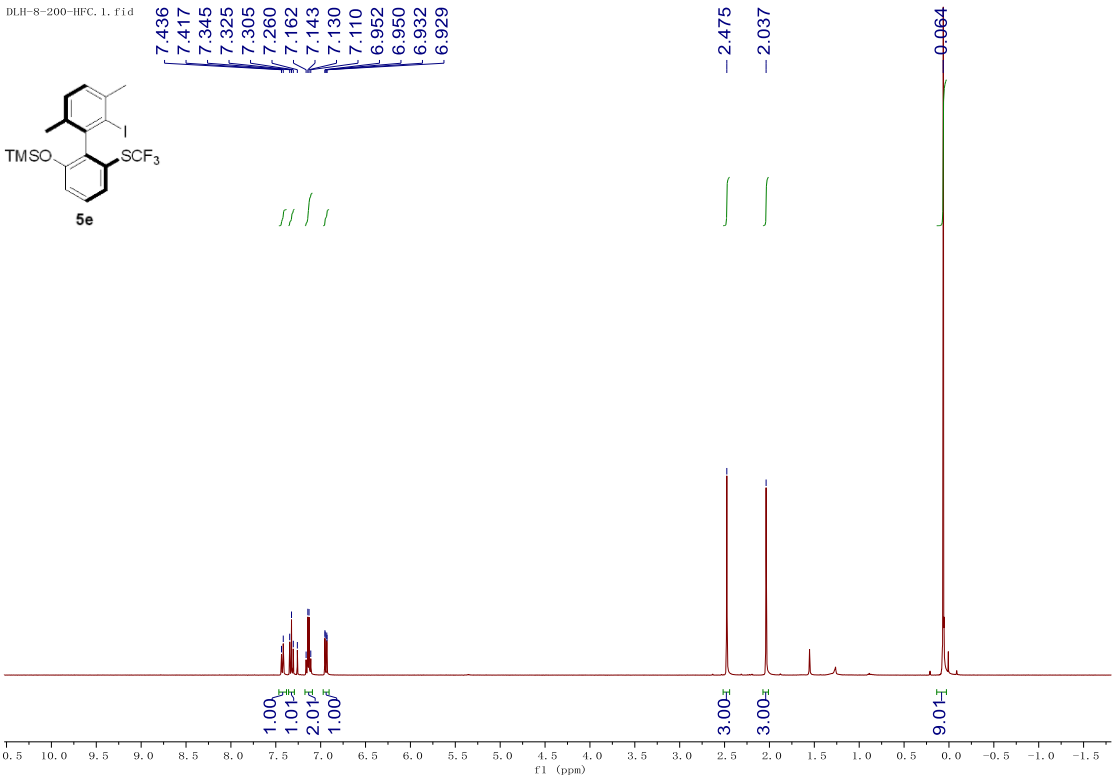


Figure S57. [1]H NMR spectra (400 MHz) of **5e**

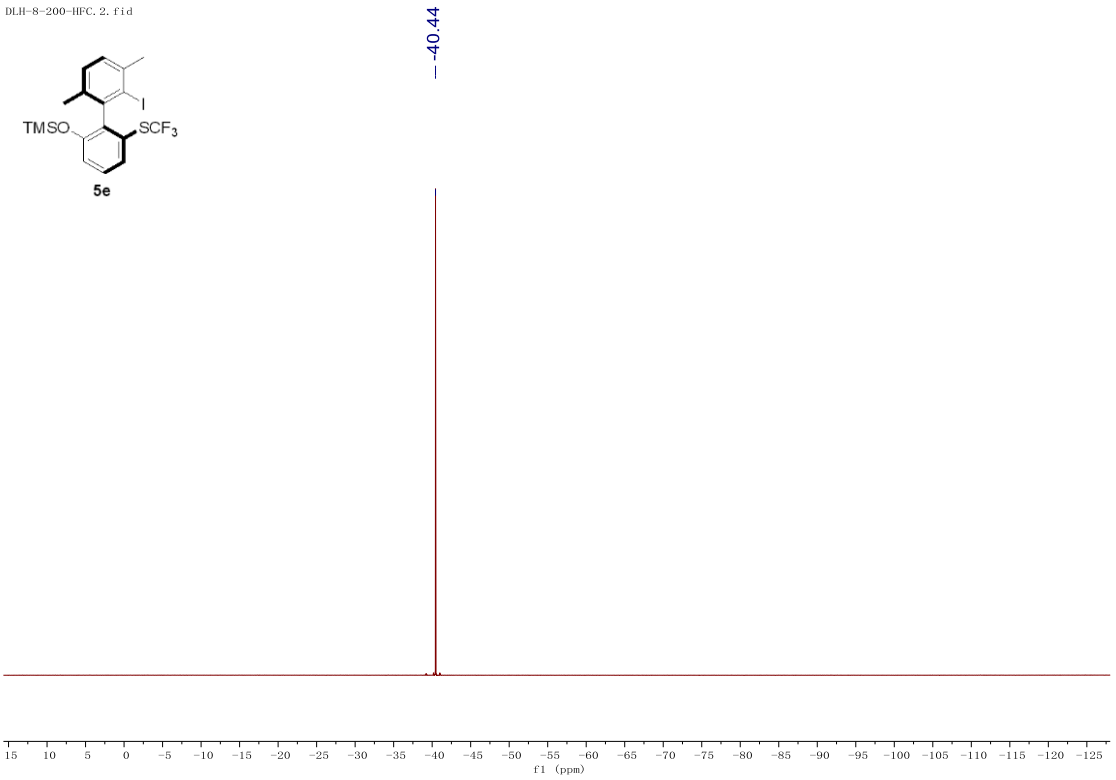


Figure S58. [19]FNMR spectra (471 MHz) of **5e**

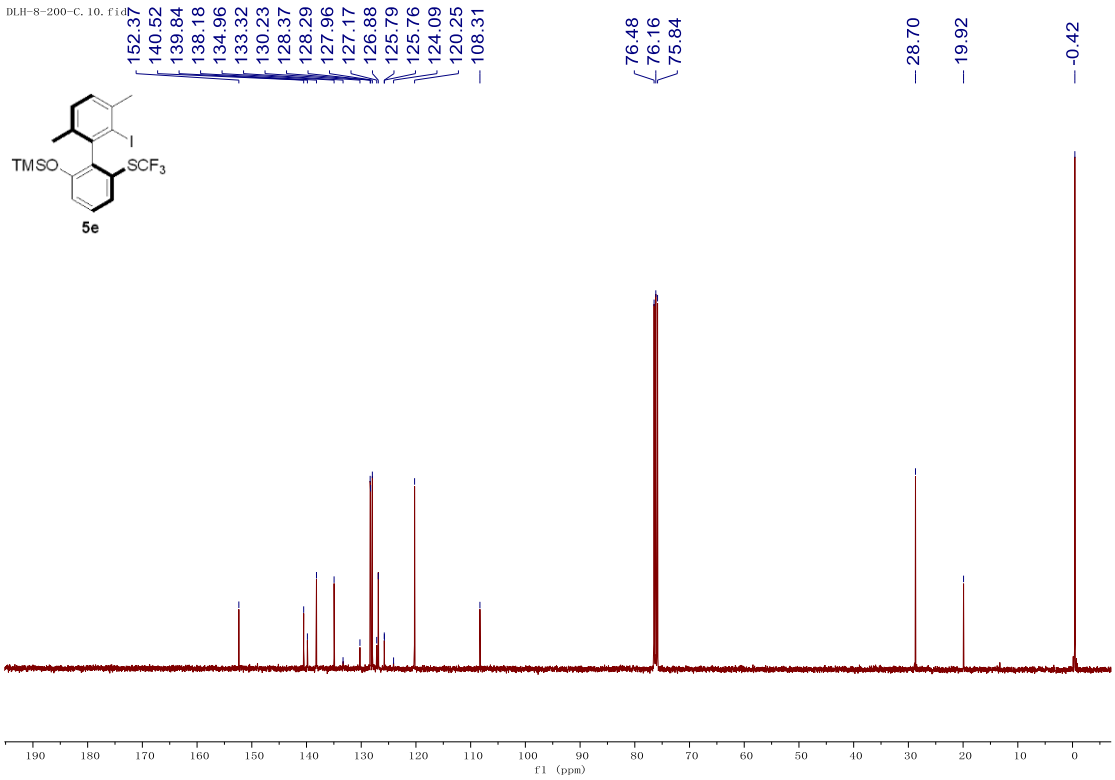


Figure S59. ^{13}C NMR spectra (101 MHz) of **5e**

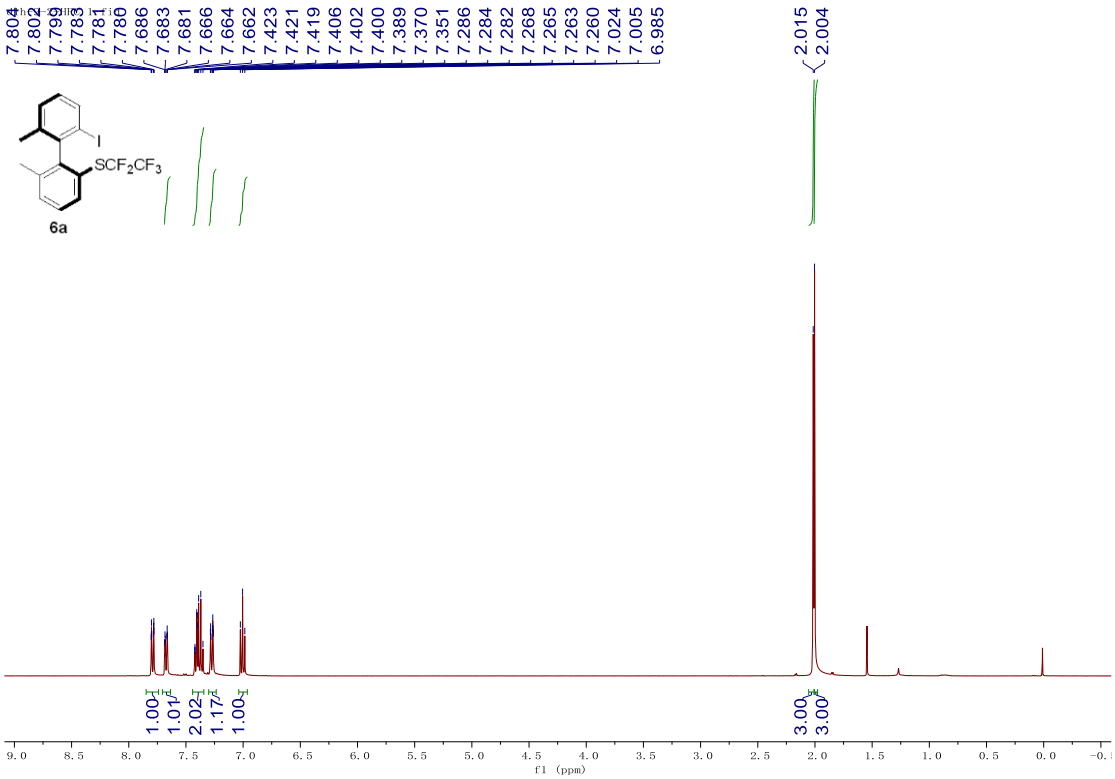


Figure S60. ^{1}H NMR spectra (400 MHz) of **6a**

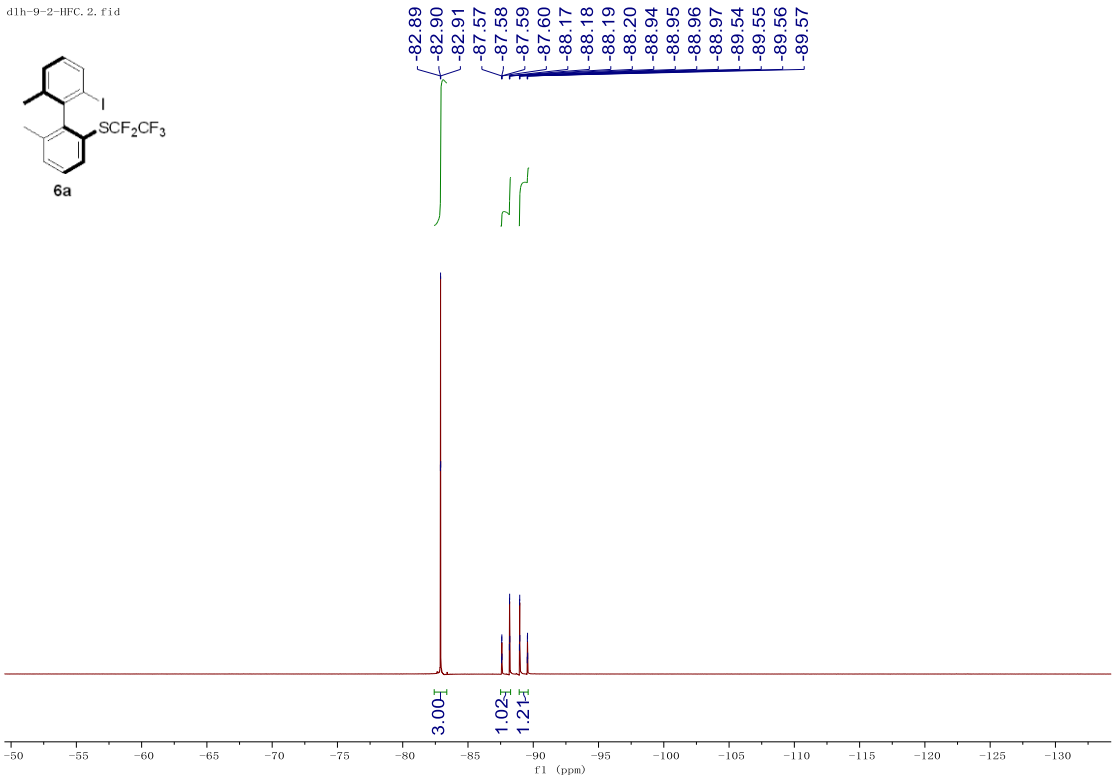


Figure S61. ^{19}FNMR spectra (471 MHz) of **6a**

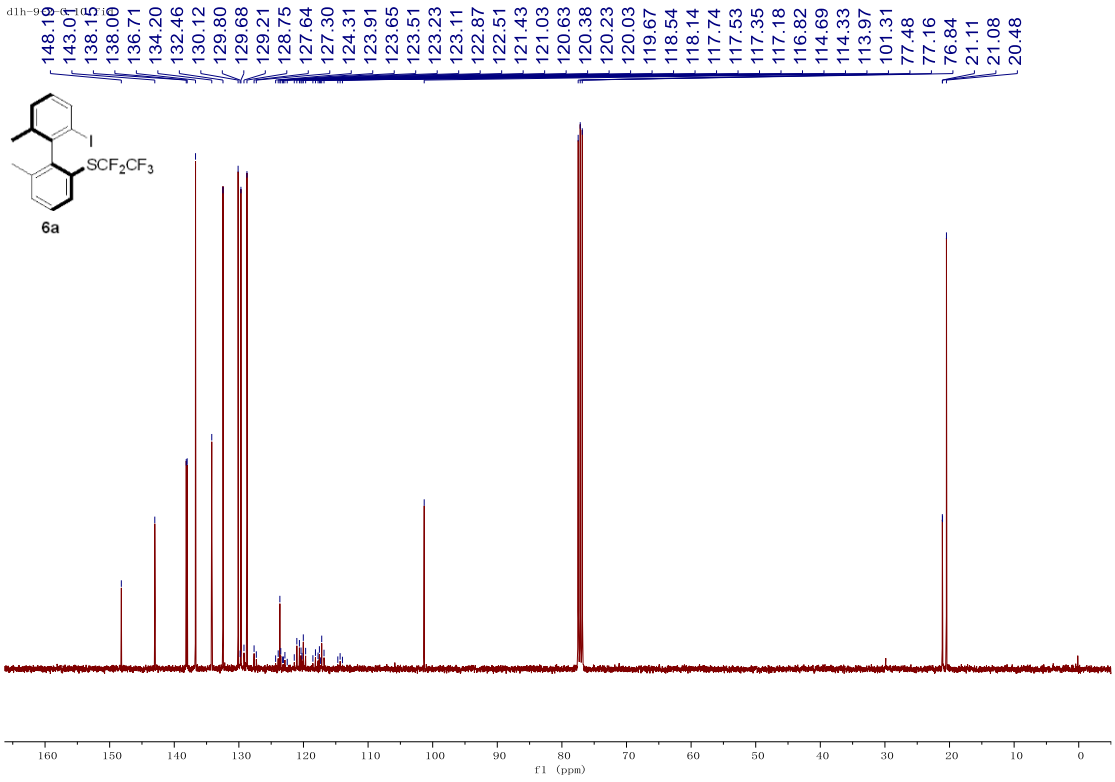


Figure S62. ^{13}C NMR spectra (101 MHz) of **6a**

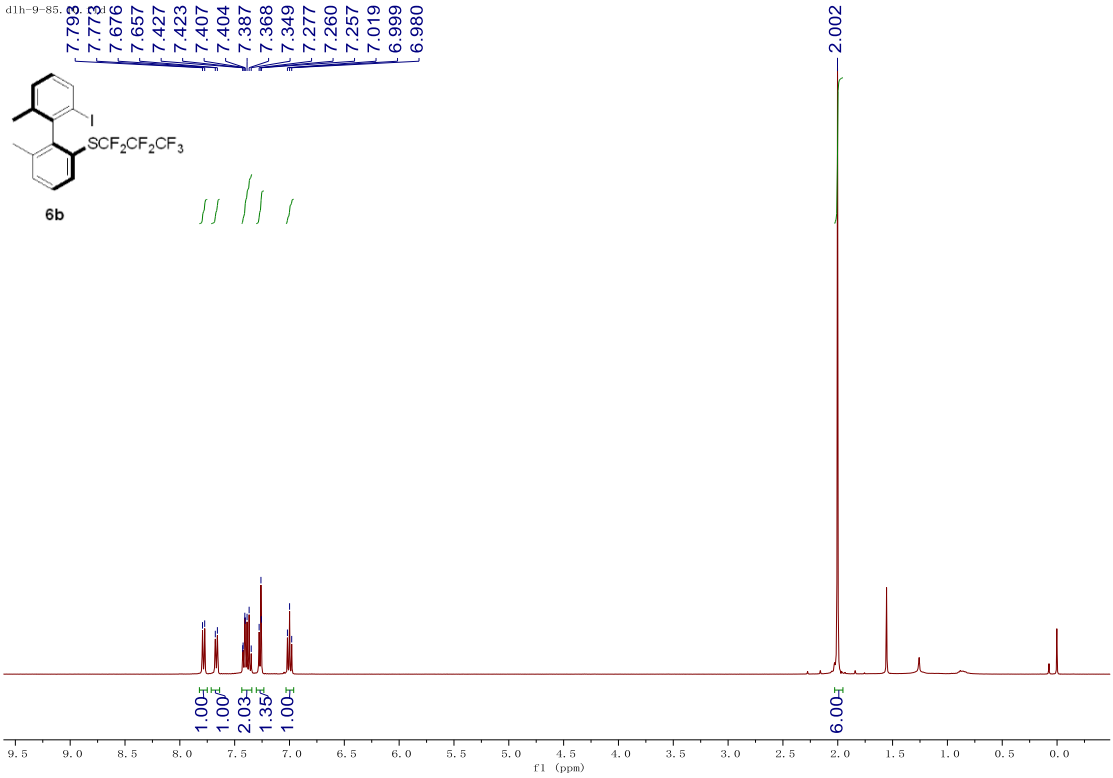


Figure S63. ^{1}H NMR spectra (400 MHz) of **6b**

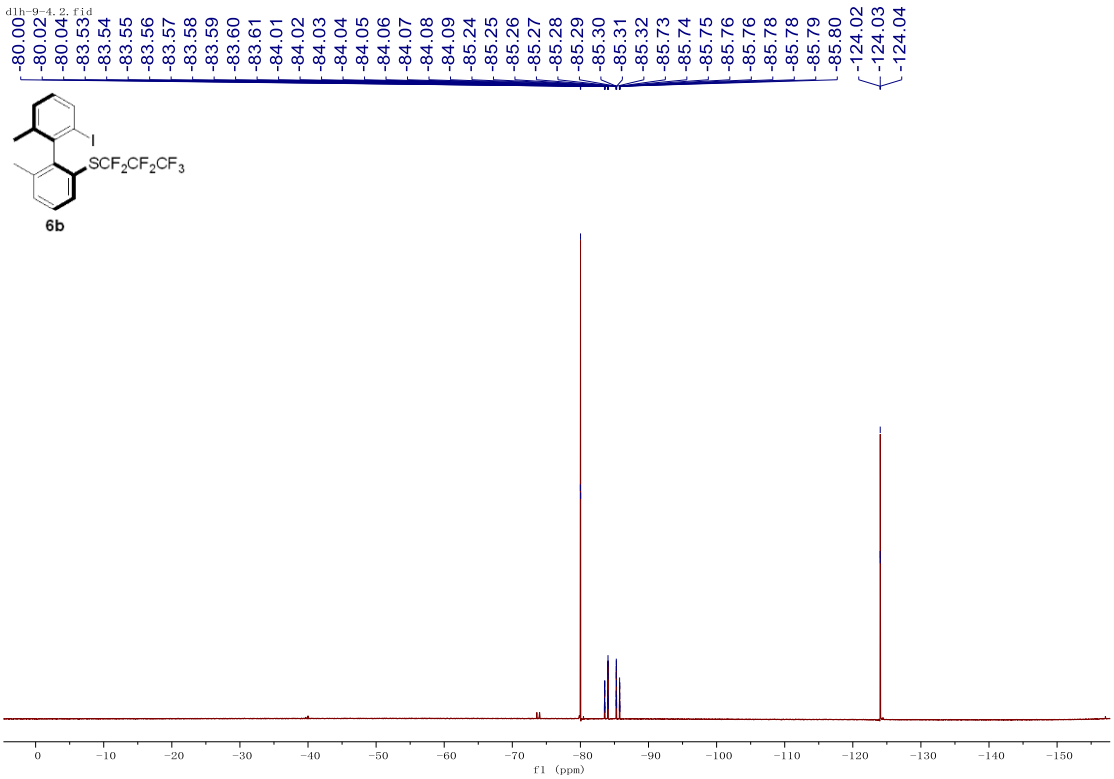


Figure S64. ^{19}F NMR spectra (471 MHz) of **6b**

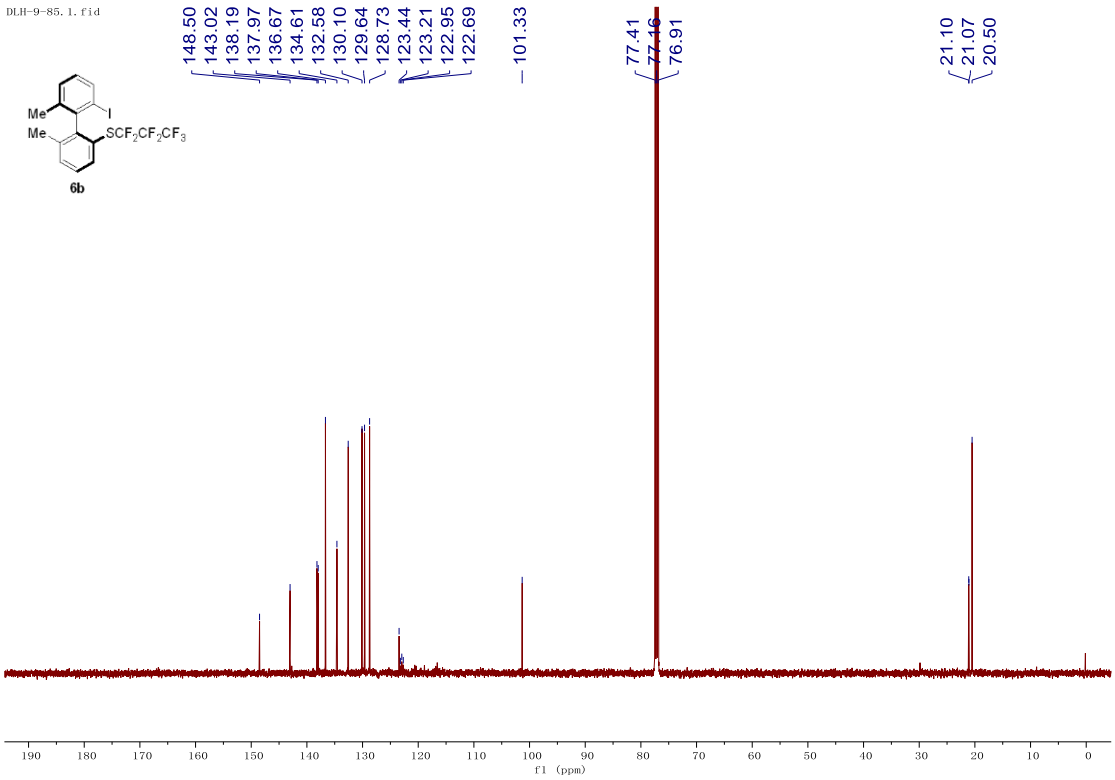


Figure S65. ^{13}C NMR spectra (101 MHz) of **6b**

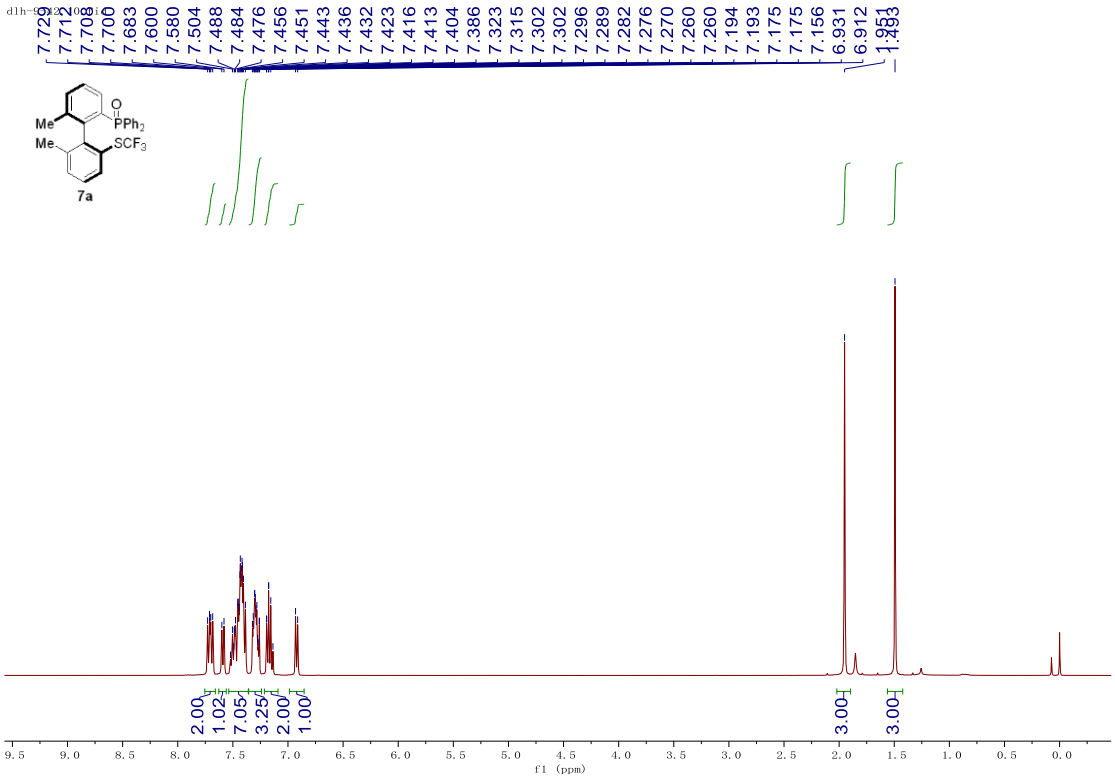


Figure S66. ^{1}H NMR spectra (400 MHz) of **7a**

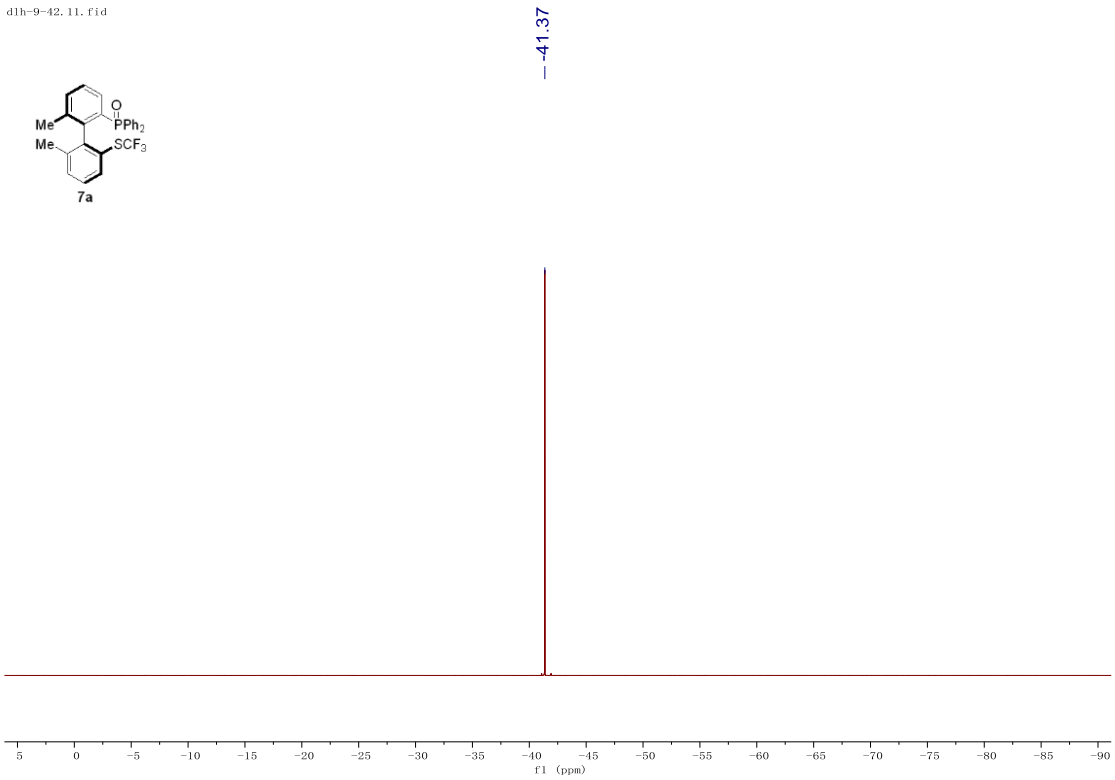


Figure S67. ^{19}F NMR spectra (376 MHz) of **7a**

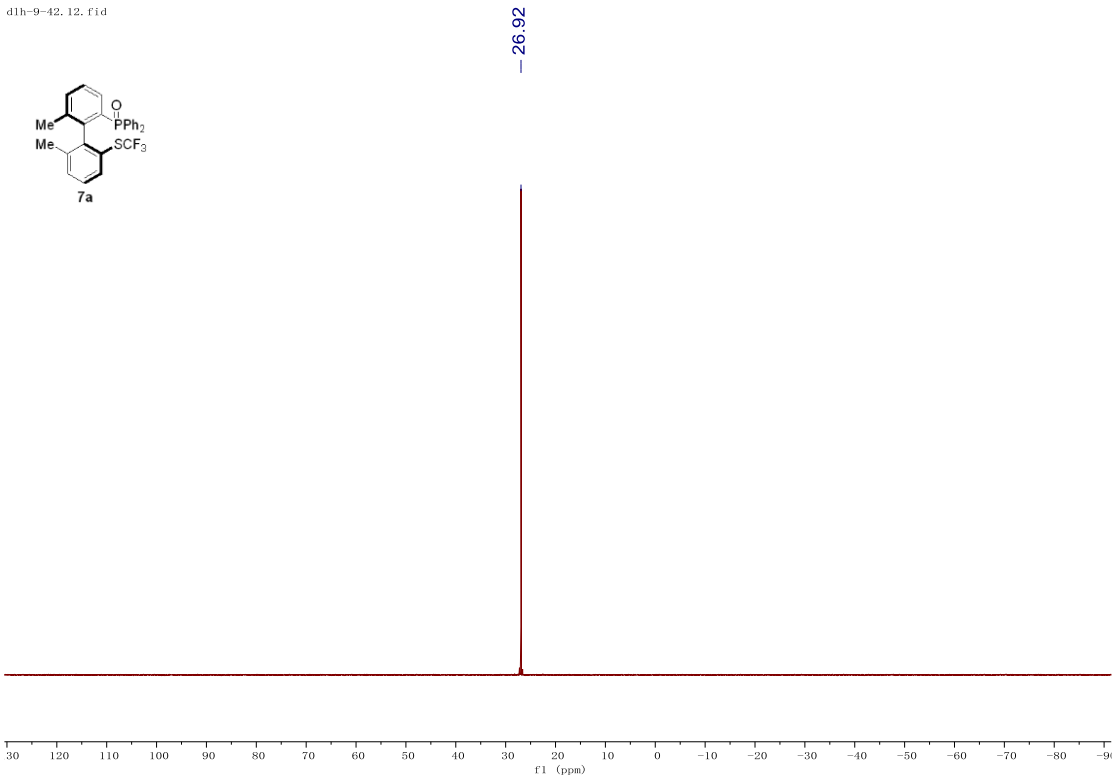


Figure S68. ^{31}P NMR spectra (162 MHz) of **7a**

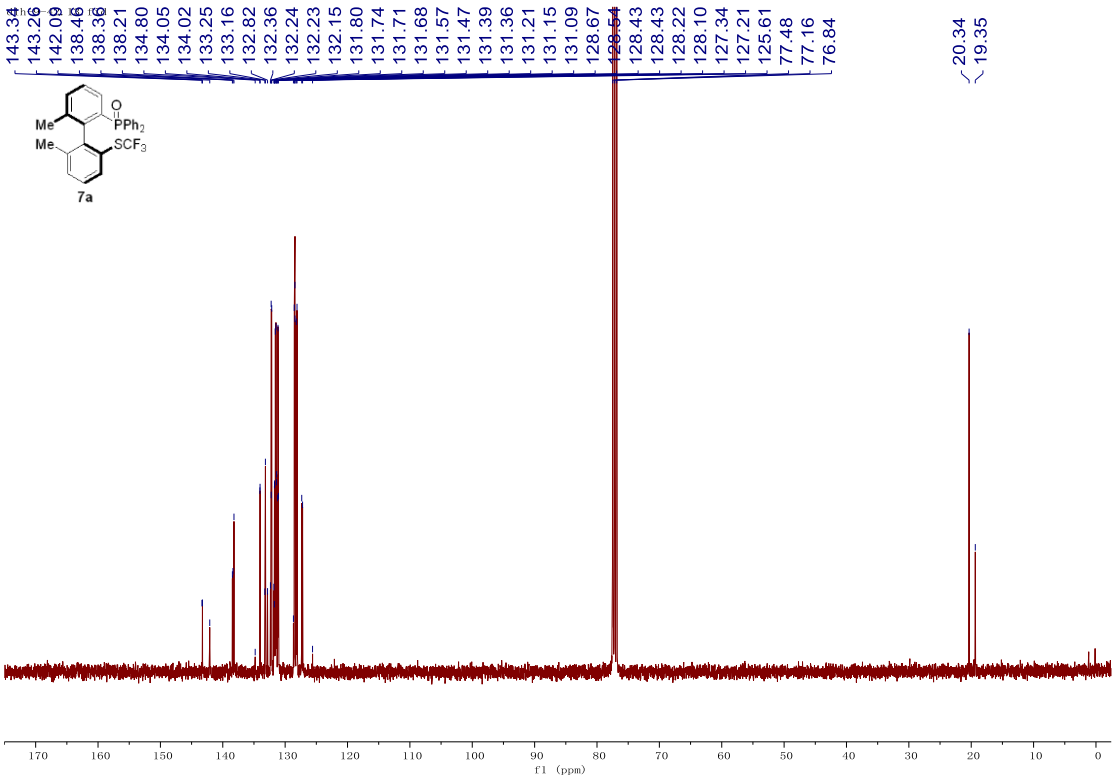


Figure S69. ^{13}C NMR spectra (126 MHz) of **7a**

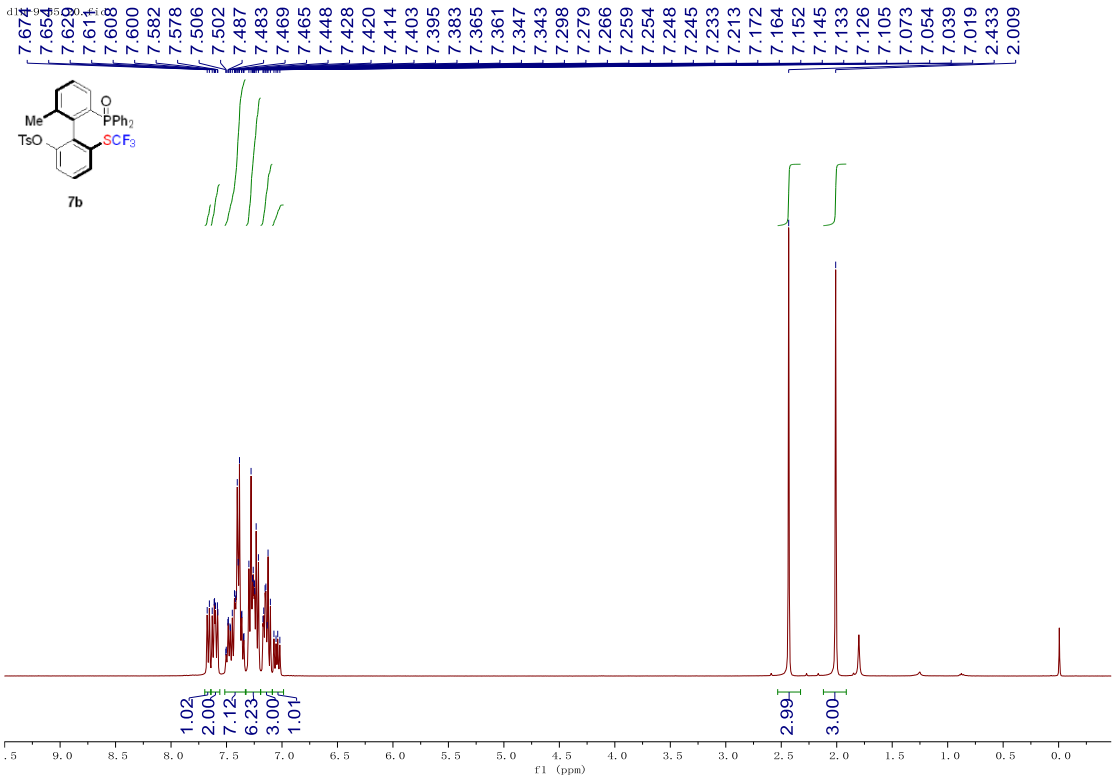


Figure S70. ^{1}H NMR spectra (400 MHz) of **7b**

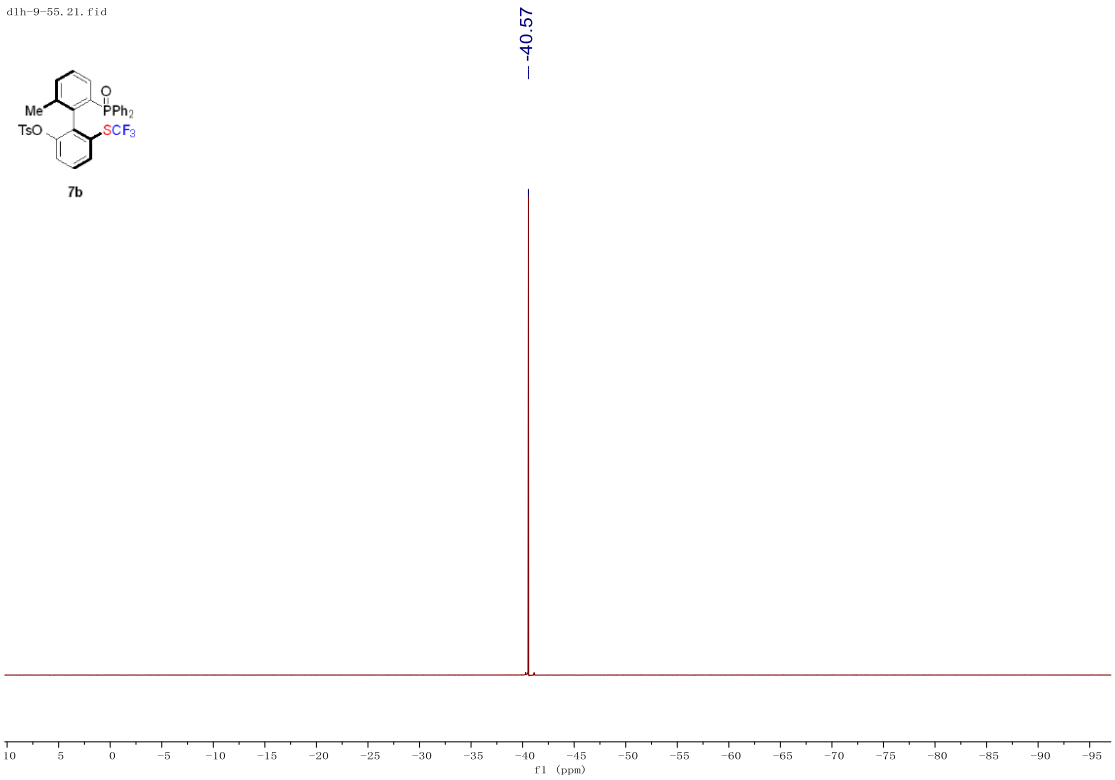


Figure S71. ^{19}F NMR spectra (376 MHz) of **7b**

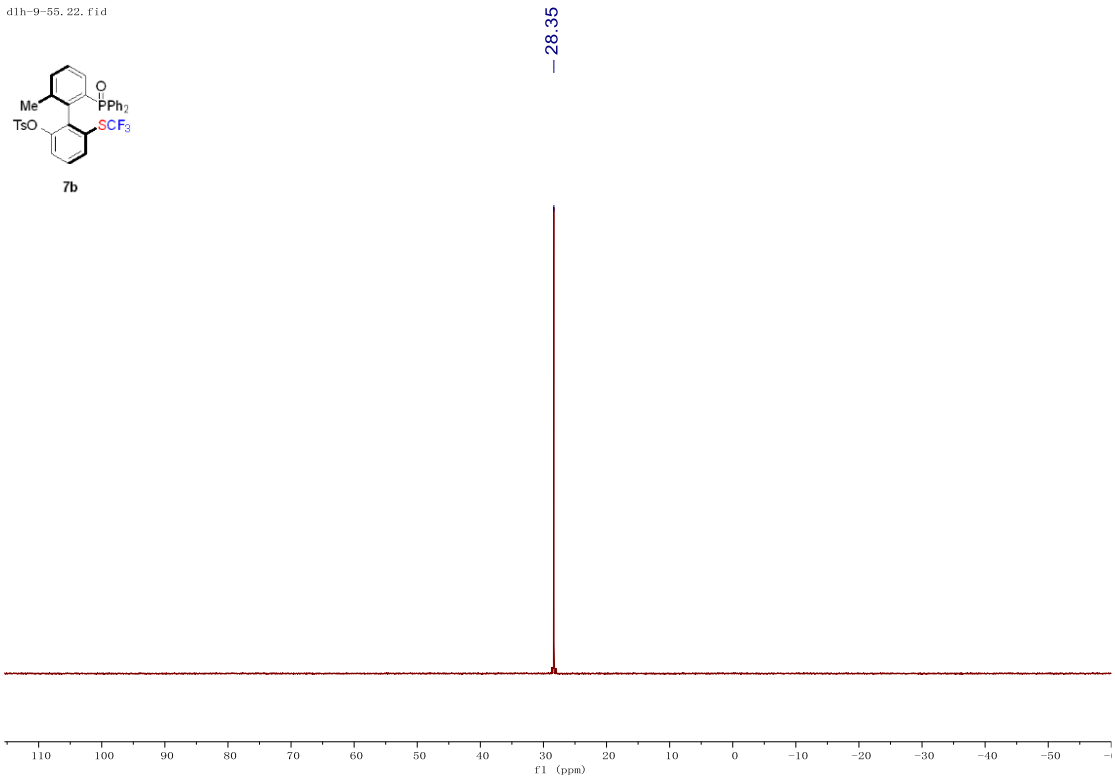


Figure S72. ^{31}P NMR spectra (162 MHz) of **7b**

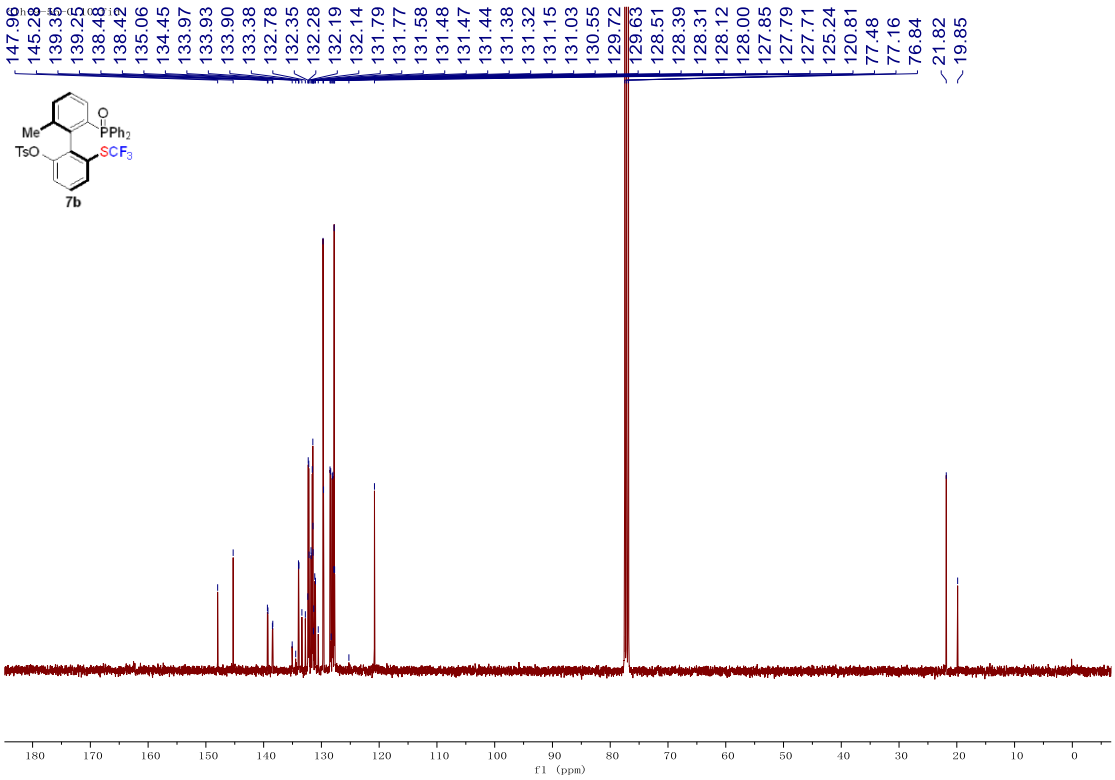


Figure S73. ^{13}C NMR spectra (126 MHz) of **7b**

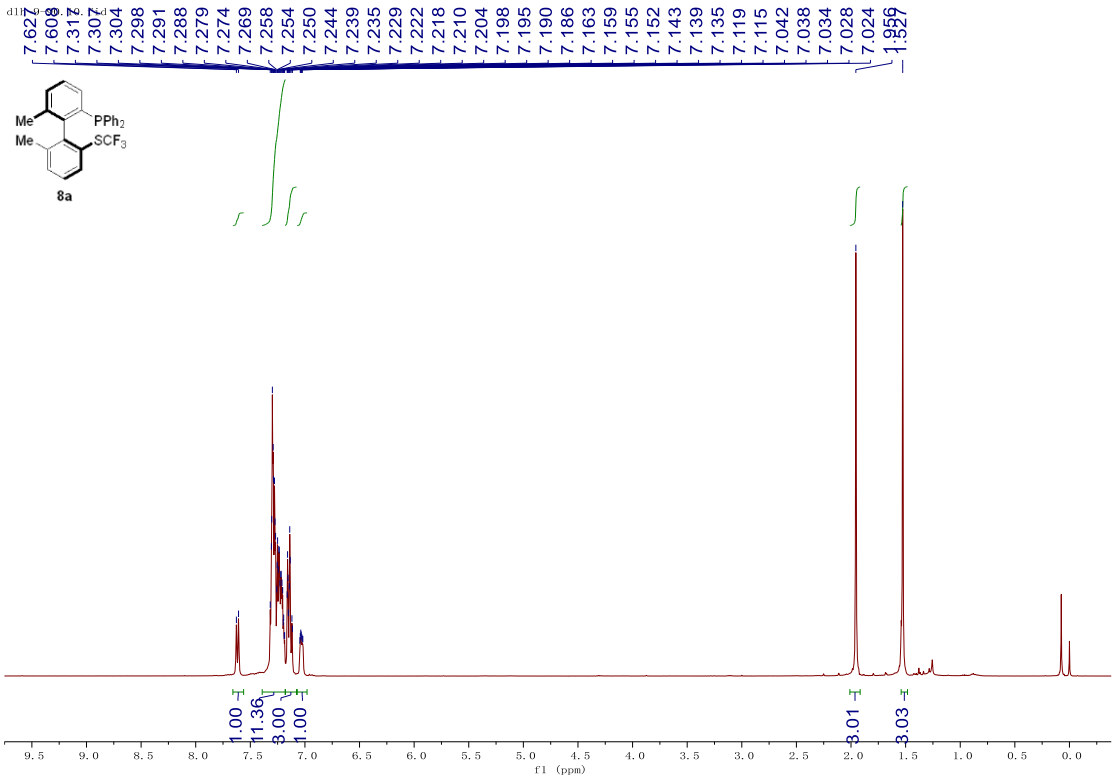


Figure S74. ^{1}H NMR spectra (400 MHz) of **8a**

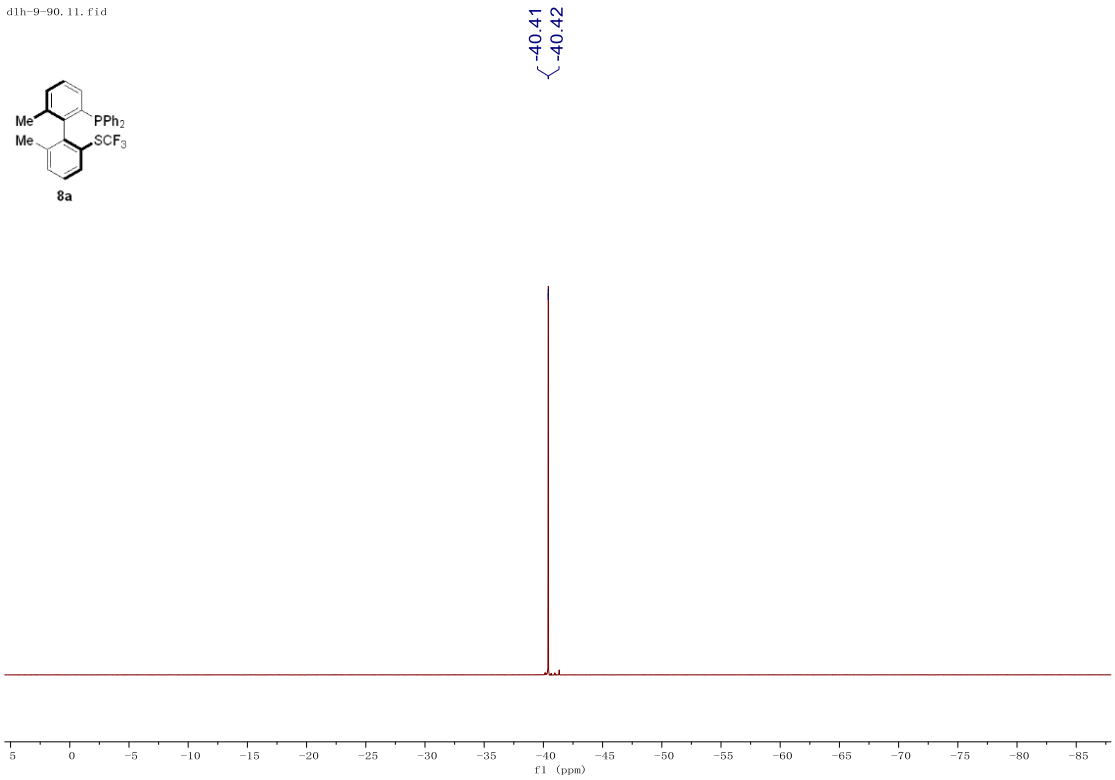


Figure S75. ^{19}F NMR spectra (376 MHz) of **8a**

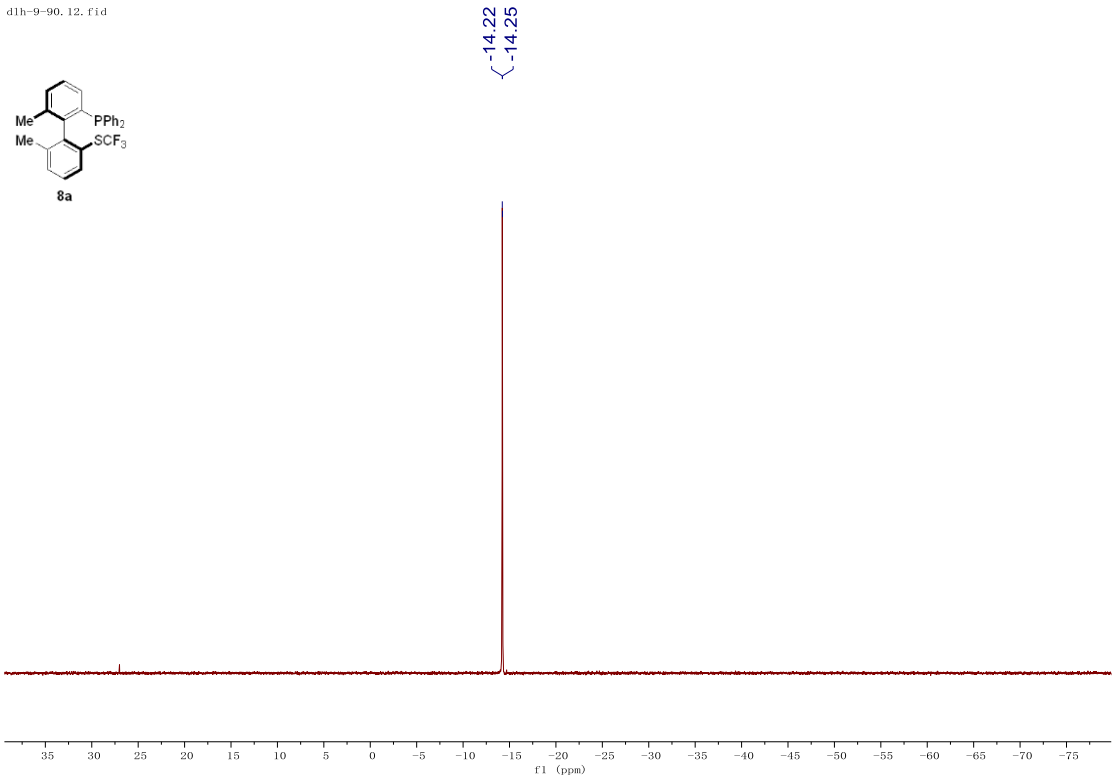


Figure S76. ^{31}P NMR spectra (142 MHz) of **8a**

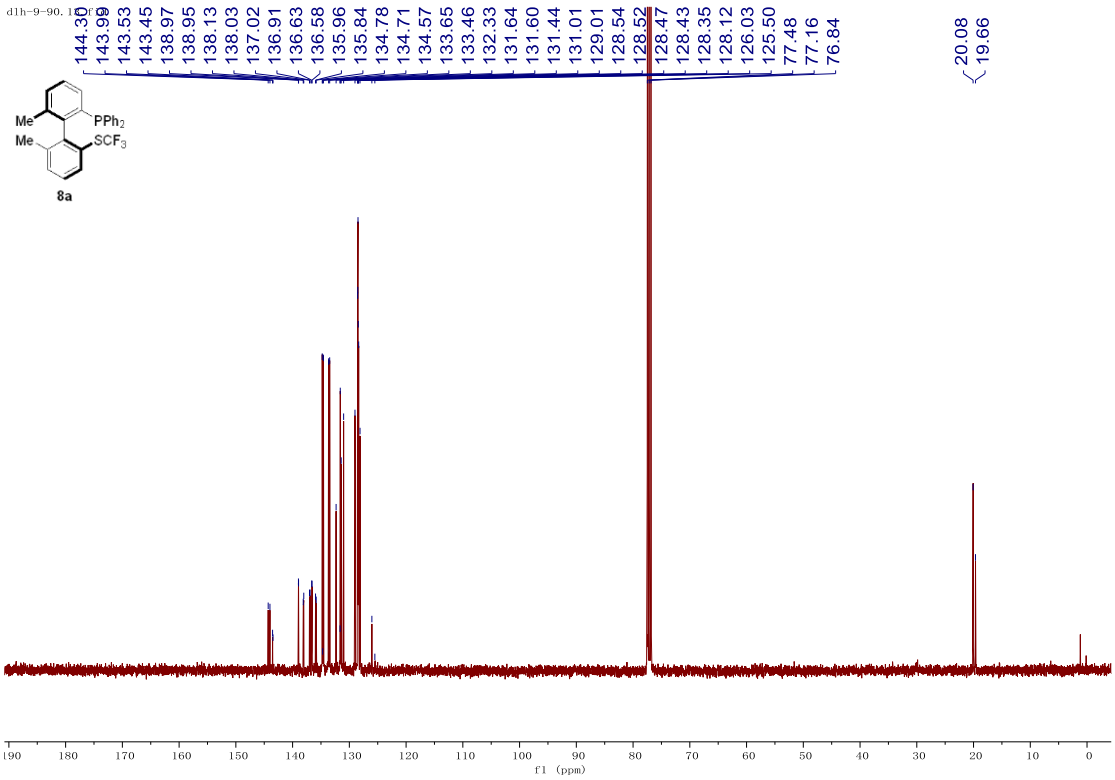


Figure S77. ^{13}C NMR spectra (101 MHz) of **8a**

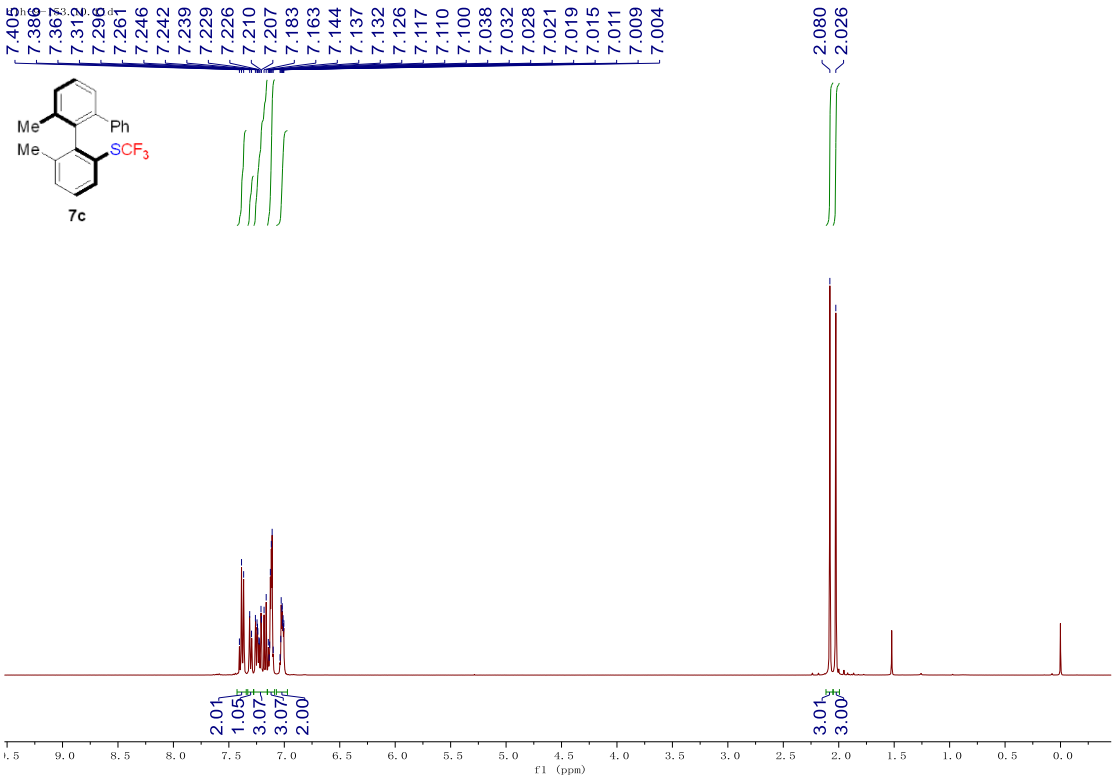


Figure S78. ^{1}H NMR spectra (400 MHz) of **7c**

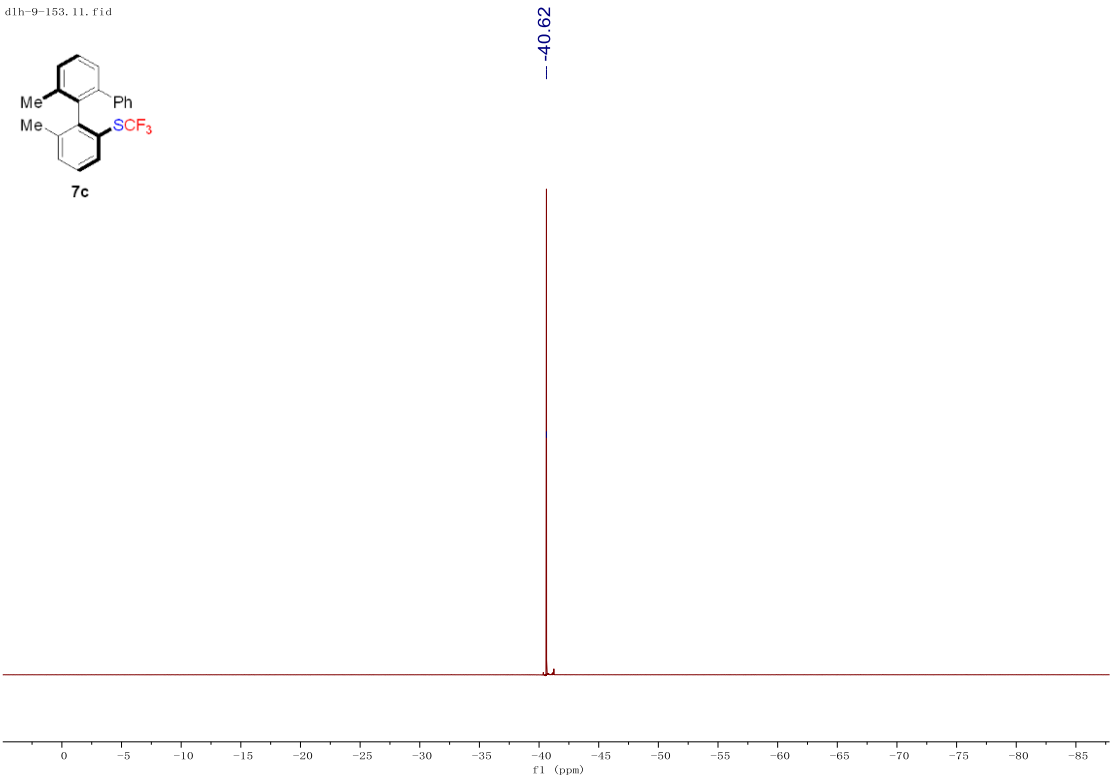


Figure S79. ^{19}FNMR spectra (471 MHz) of **7c**

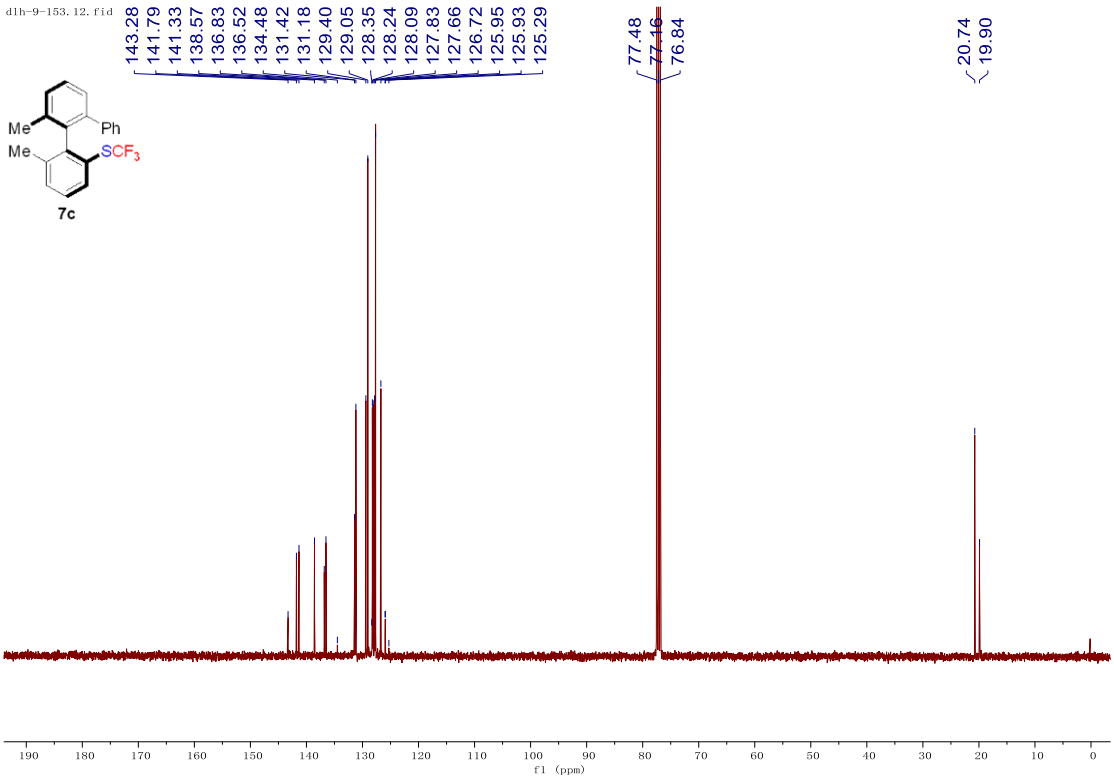


Figure S80. ^{13}C NMR spectra (101 MHz) of **7c**

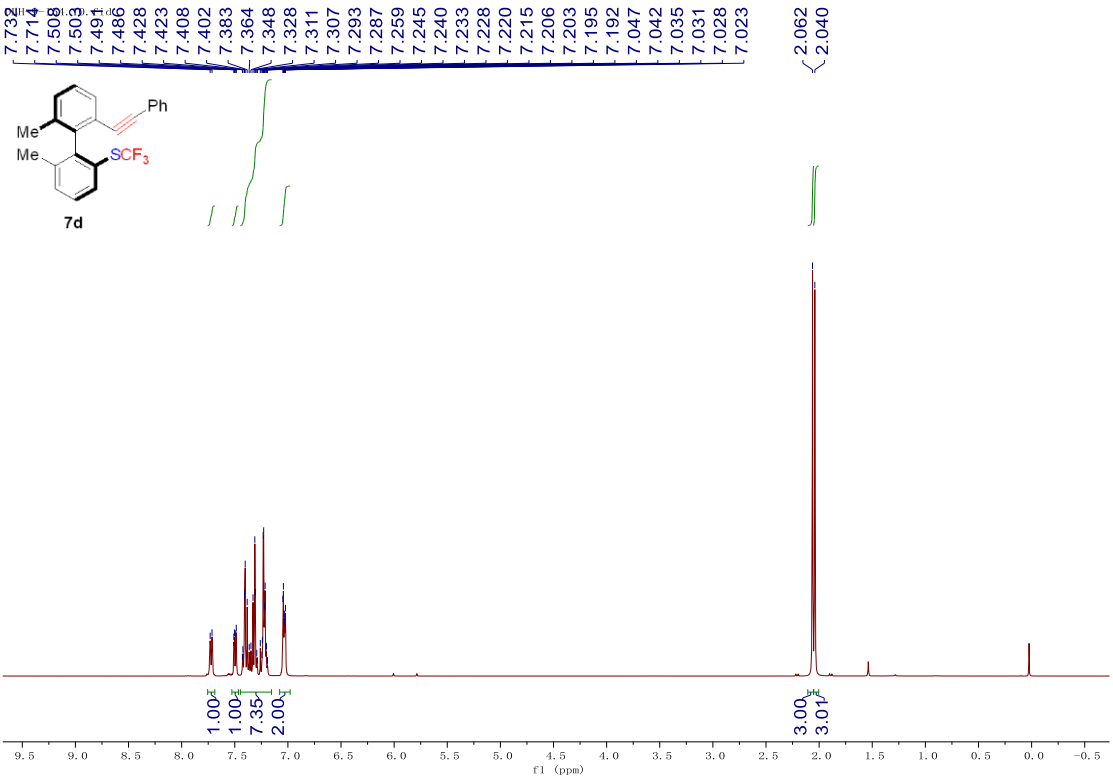


Figure S81. ^{1}H NMR spectra (400 MHz) of **7d**

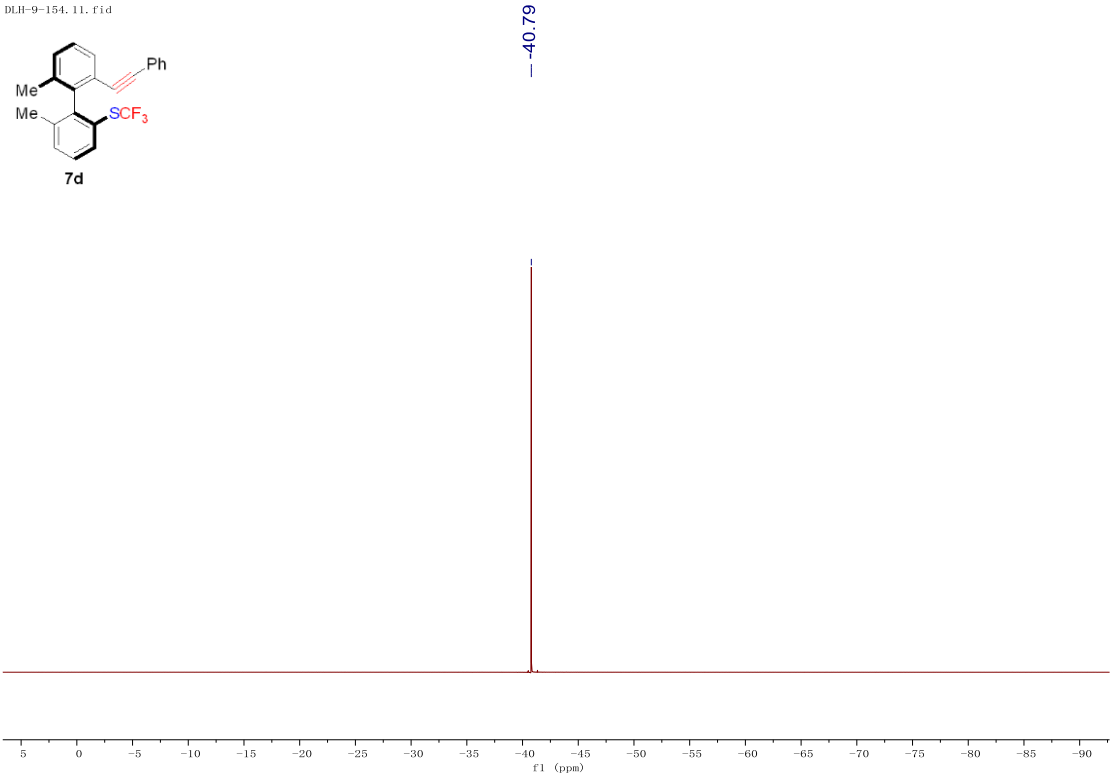


Figure S82. ^{19}FNMR spectra (471 MHz) of **7d**

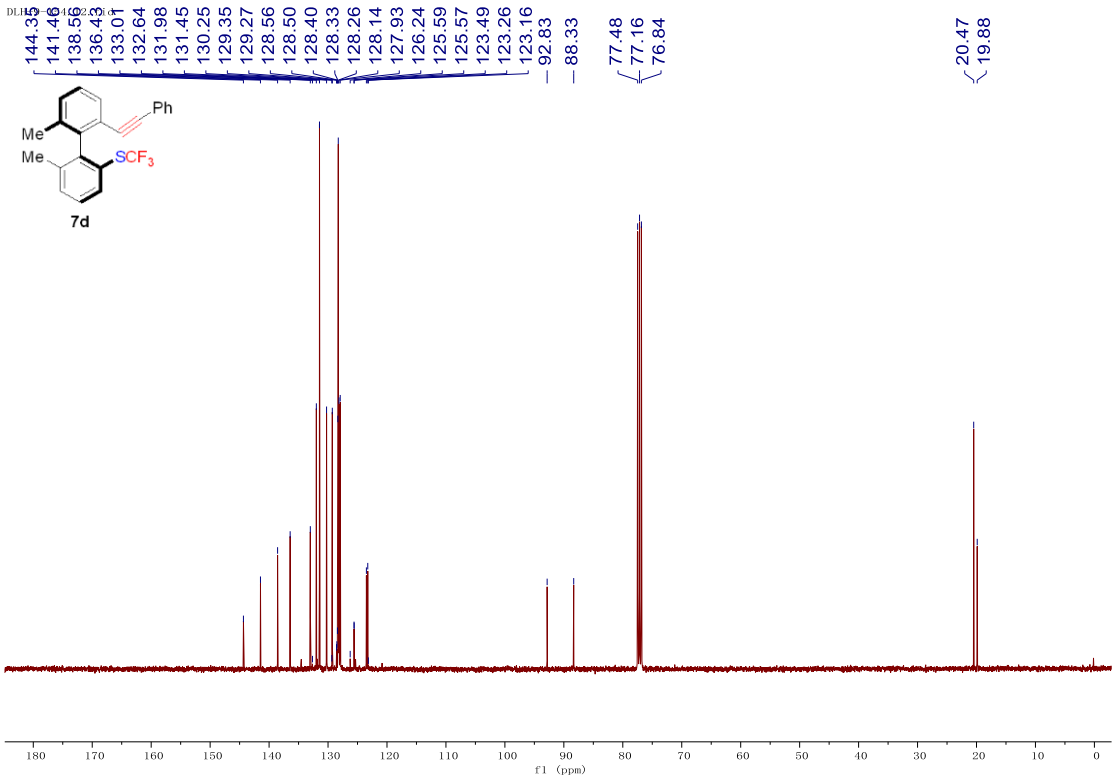


Figure S83. ^{13}C NMR spectra (101 MHz) of **7d**

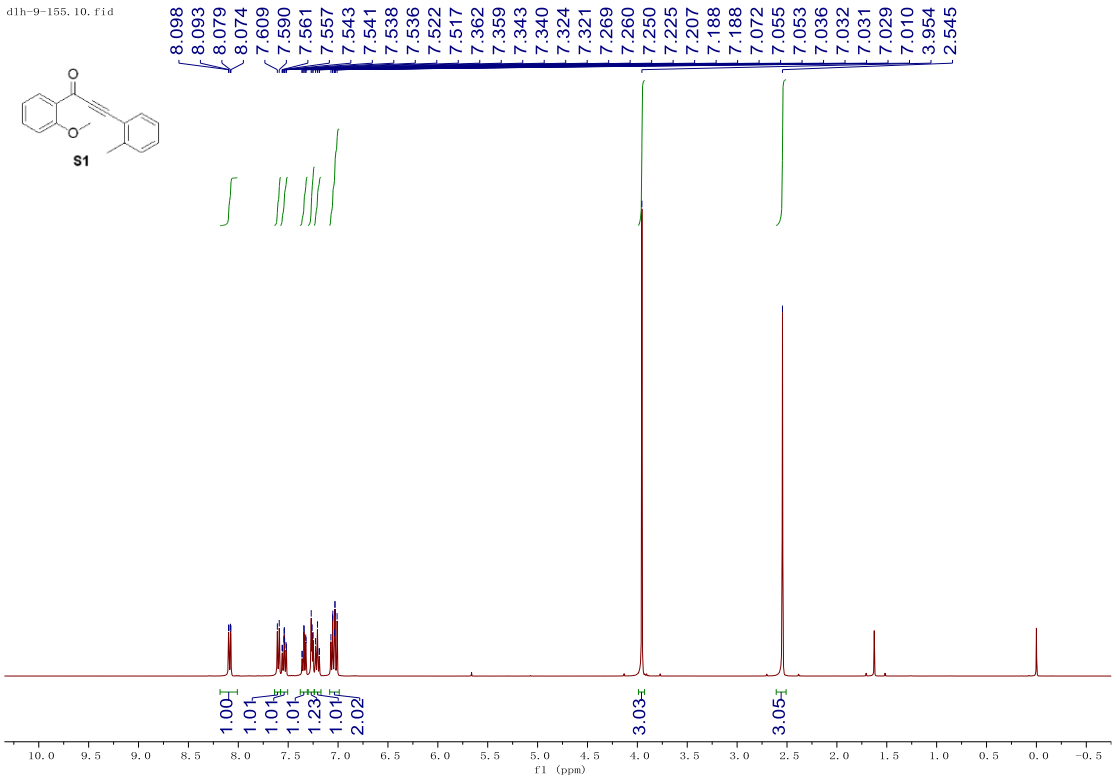


Figure S84. ^{1}H NMR spectra (400 MHz) of **S1**

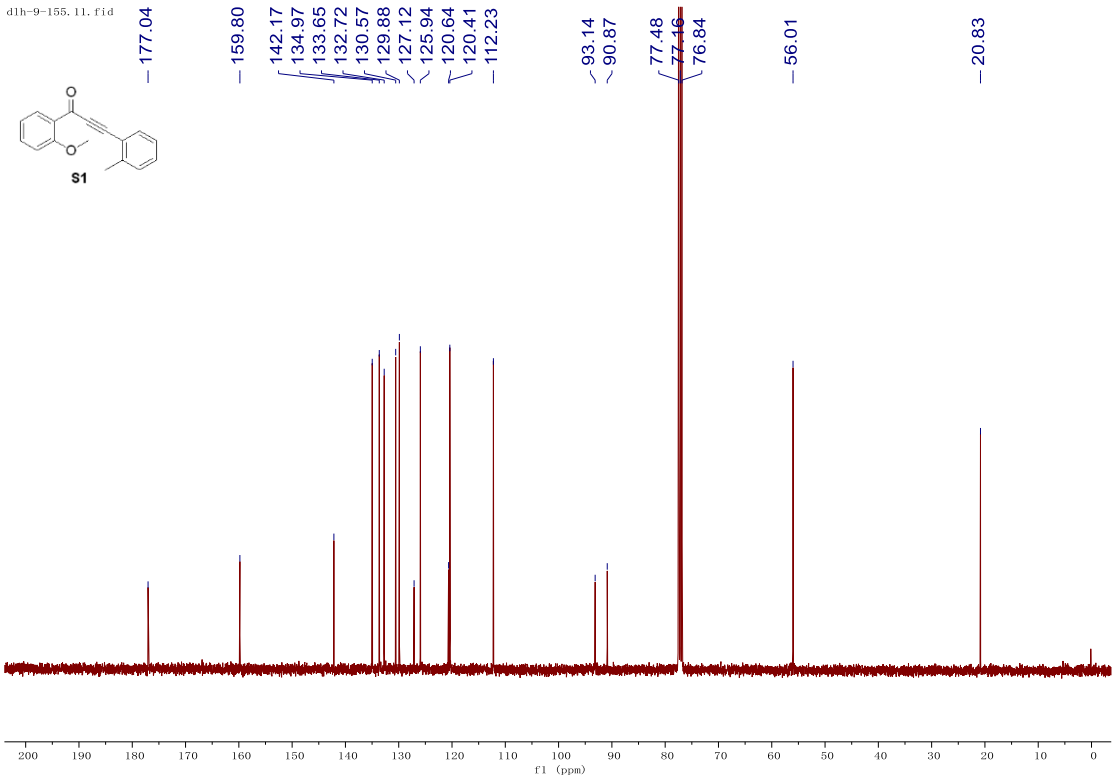


Figure S85. ^{13}C NMR spectra (101 MHz) of **S1**

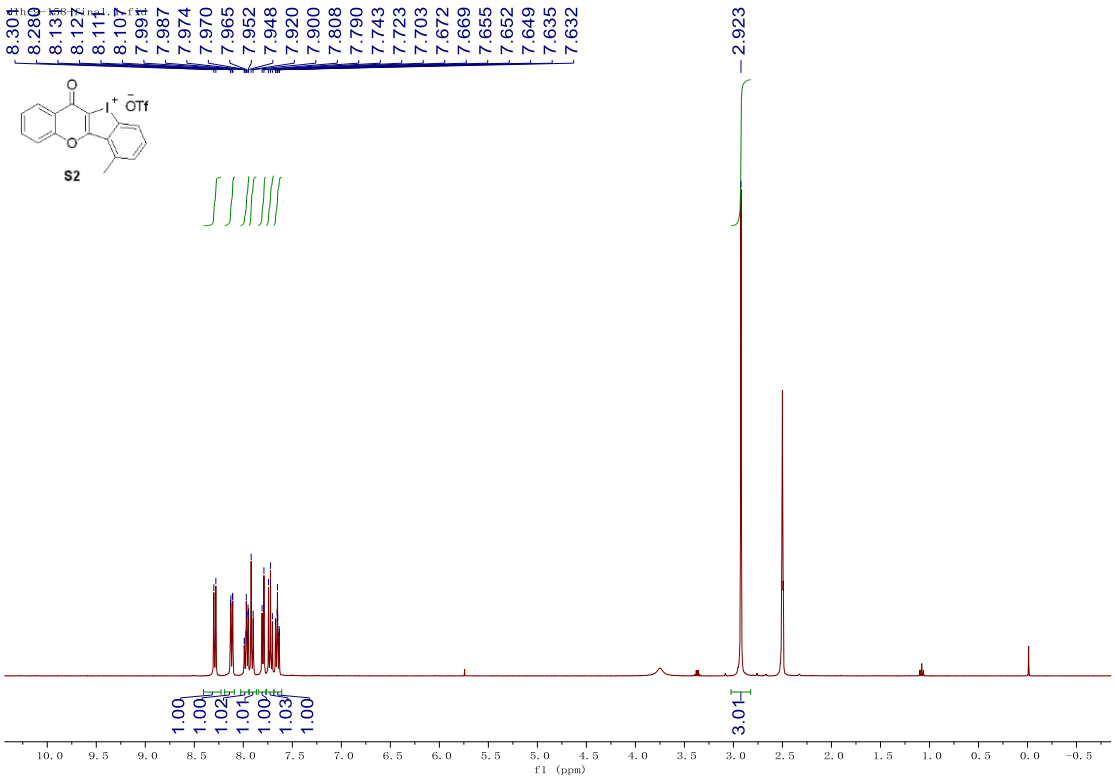


Figure S86. ^{1}H NMR spectra (400 MHz) of **S2.**

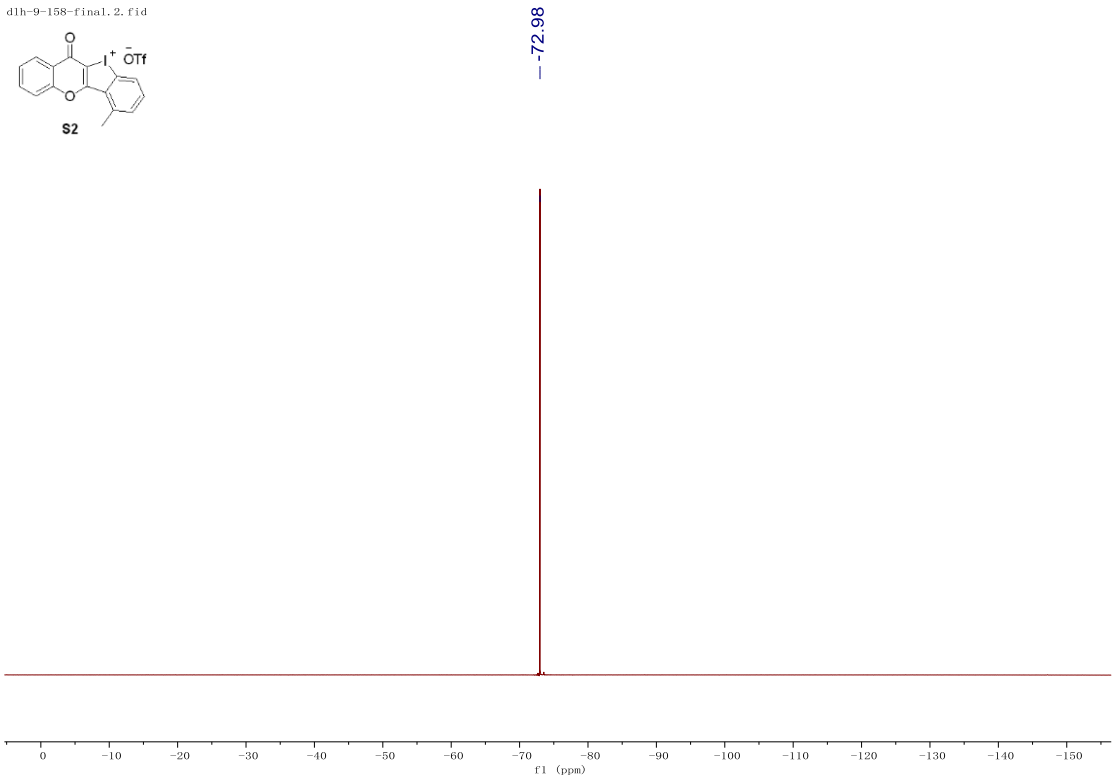


Figure S87. ^{19}FNMR spectra (471 MHz) of **S2**

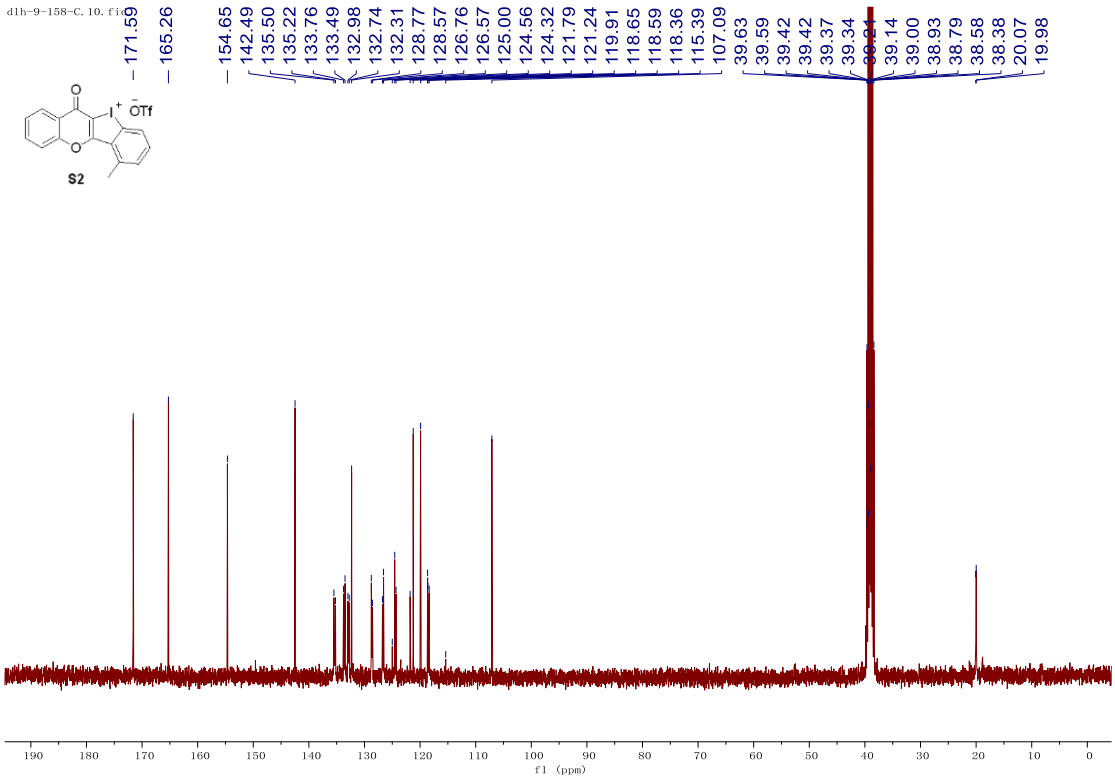
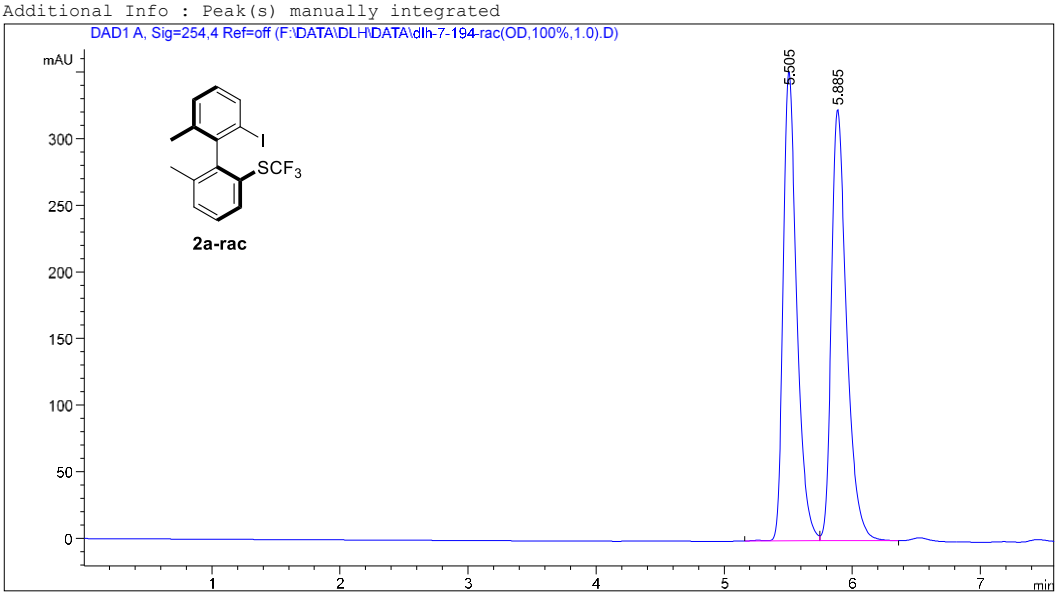


Figure S88. ^{1}H NMR spectra (400 MHz) of **S2**

HPLC Traces

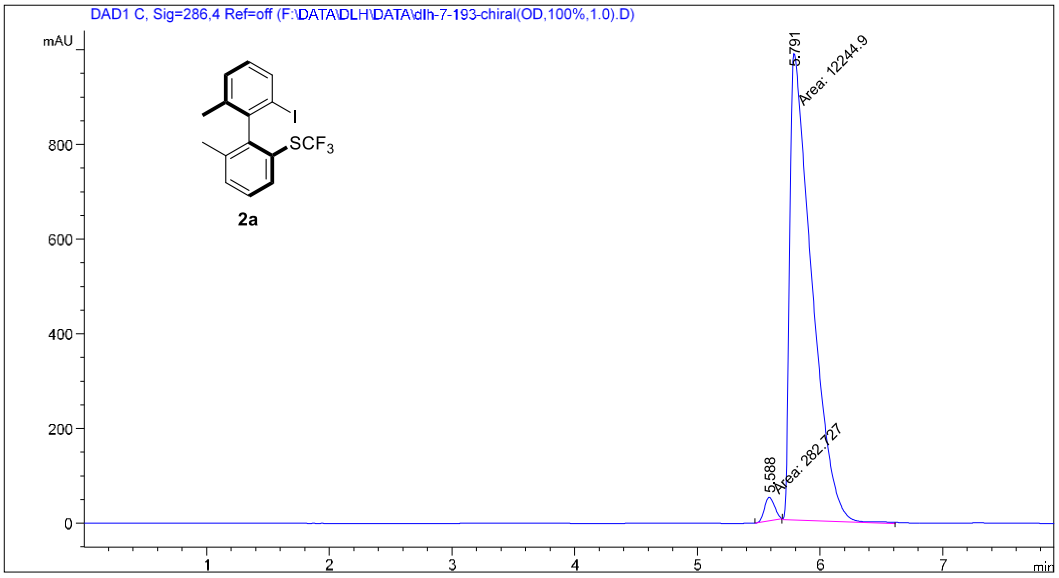
```
Data File F:\DATA\DLH\DATA\dlh-7-194-rac(OD,100%,1.0).D
Sample Name: dlh-7-194-rac(OD,100%,1.0)

    ======================================================================
    Acq. Operator   :
                                              Location :  1
    Injection Date  : 13/05/2020 12:57:42
    Acq. Method     : ZK.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    5.505 VV R  0.1118 2591.84131  352.54892  49.2210
    2    5.885 VB    0.1243 2673.88403  323.90491  50.7790

    Totals :               5265.72534  676.45383


    ======================================================================
    *** End of Report ***


LC1260 30/06/2020 09:03:51
                                                          Page 1 of 1
```

Figure S89. HPLC spectra of **2a-rac**.

```
Data File F:\DATA\DLH\DATA\dlh-7-193-chiral(OD,100%,1.0).D
Sample Name: dlh-7-193-chiral(OD,100%,1.0)

    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 13/05/2020 13:07:26
                                              Inj Volume : No inj
    Acq. Method     : F:\METHOD\ZK.M
    Last changed    : 13/05/2020 12:40:23 by
                     (modified after loading)
    Analysis Method : F:\METHOD\JFeng.M Last
    changed    : 19/09/2014 20:49:49 by
    Additional Info : Peak(s) manually integrated
```

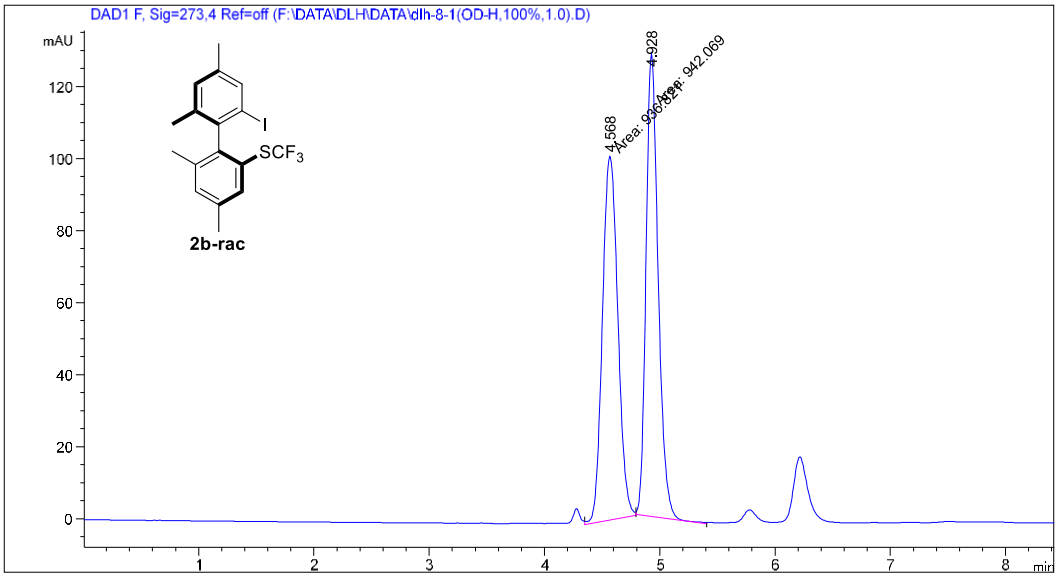



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=286,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    5.588 MM    0.0941  282.72742   50.06099   2.2568
    2    5.791 MM    0.2068 1.22449e4   986.70990  97.7432

    Totals :               1.25277e4  1036.77089


LC1260 13/05/2020 13:23:59
LC1260 13/05/2020 13:23:59                                        Page 2 of 2
```

Figure S90. HPLC spectra of **2a**.

Data File F:\DATA\DLH\DATA\dlh-8-1(OD-H,100%,1.0).D
Sample Name: dlh-8-1(OD-H,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 19/05/2020 09:44:22
                                              Inj Volume : No inj
    Acq. Method       : F:\METHOD\duanlh.M  Last
    changed    : 19/05/2020 09:35:32 by
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

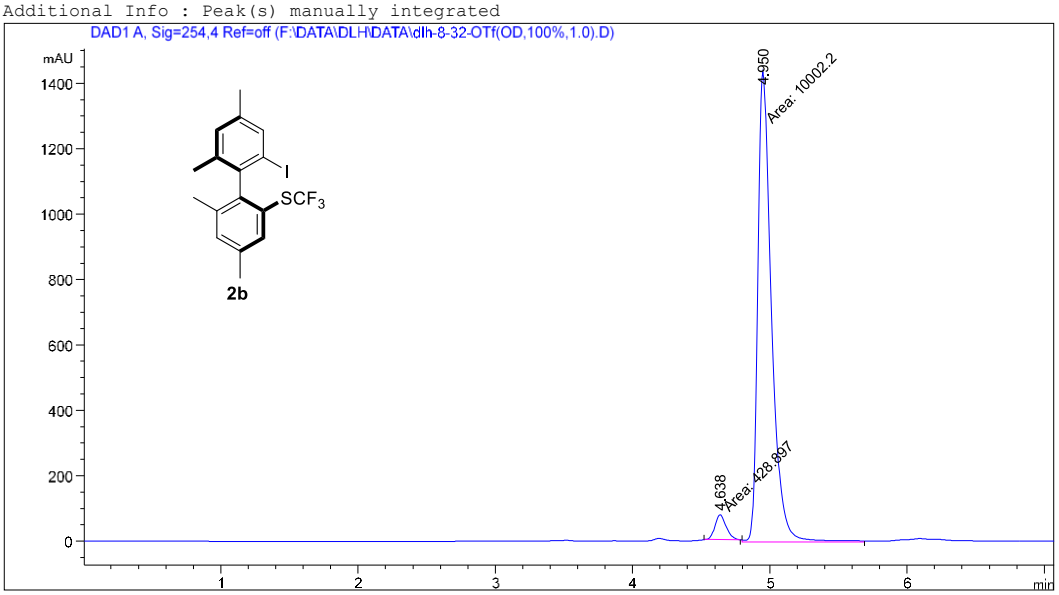



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 F, Sig=273,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    4.568 MM    0.1546  936.82080  101.01720  49.8603
    2    4.928 MM    0.1221  942.06885  128.58945  50.1397

    Totals :               1878.88965  229.60665


    ======================================================================

LC1260 19/05/2020 10:20:26
LC1260 19/05/2020 10:20:26                                    Page 2 of 2
```

Figure S91. HPLC spectra of **2b-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-32-OTf(OD,100%,1.0).D
Sample Name: dlh-8-32-OTf(OD,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 30/05/2020 15:08:26
    Acq. Method     : duanlh.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

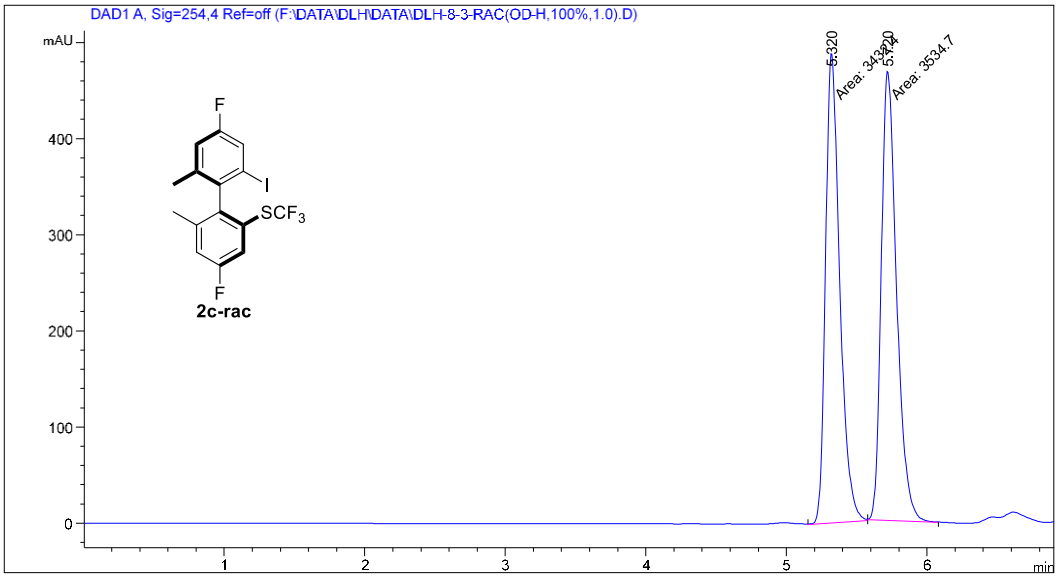



```
    ======================================================================
                         Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    4.638 MM    0.0938  428.89728   76.20920   4.1117
    2    4.950 MM    0.1159 1.00022e4  1438.71667  95.8883

    Totals :               1.04311e4  1514.92587


    ======================================================================
    *** End of Report ***


LC1260 30/06/2020 09:07:45
                                                          Page 1 of 1
```

Figure S92. HPLC spectra of **2b**.

Data File F:\DATA\DLH\DATA\DLH-8-3-RAC(OD-H,100%,1.0).D
Sample Name: DLH-8-3-RAC(OD-H,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 02/07/2020 20:42:58
                                              Inj Volume : No inj
    Acq. Method     : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 02/07/2020 20:39:56 by
                     (modified after loading)
    Analysis Method : F:\METHOD\ZK.M
    Last changed    : 14/07/2019 15:34:15 by
    Additional Info : Peak(s) manually integrated
```

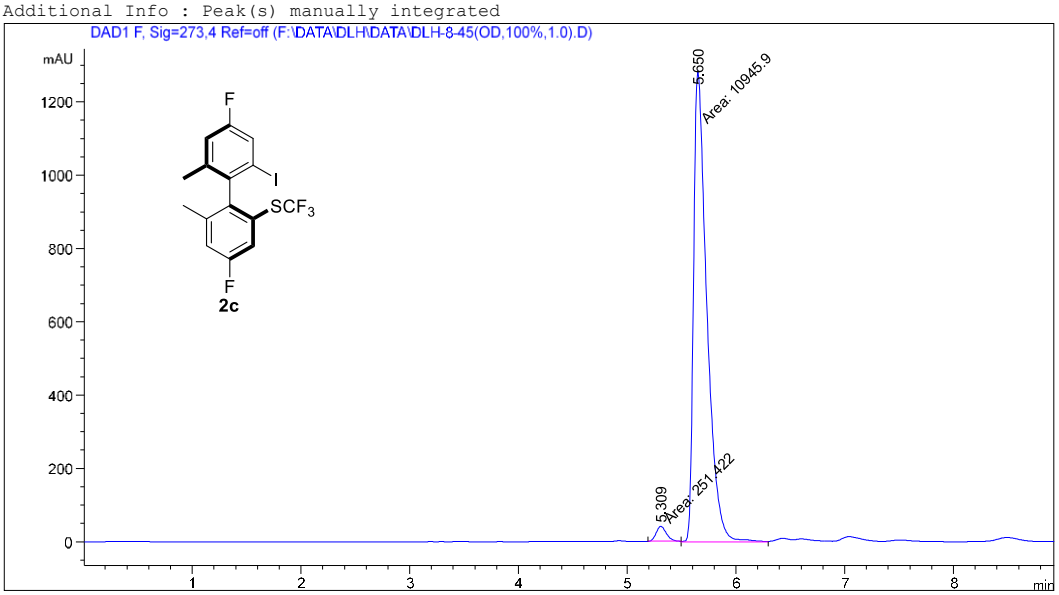



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    5.320 MM    0.1168 3432.39673  489.94940  49.2658
    2    5.720 MM    0.1259 3534.70337  468.03012  50.7342

    Totals :               6967.10010  957.97952


LC1260 02/07/2020 21:42:55
LC1260 02/07/2020 21:42:55                                    Page 2 of 2
```

Figure S93. HPLC spectra of **2c-rac**.

Data File F:\DATA\DLH\DATA\DLH-8-45(OD,100%,1.0).D
Sample Name: DLH-8-45(OD,100%,1.0)

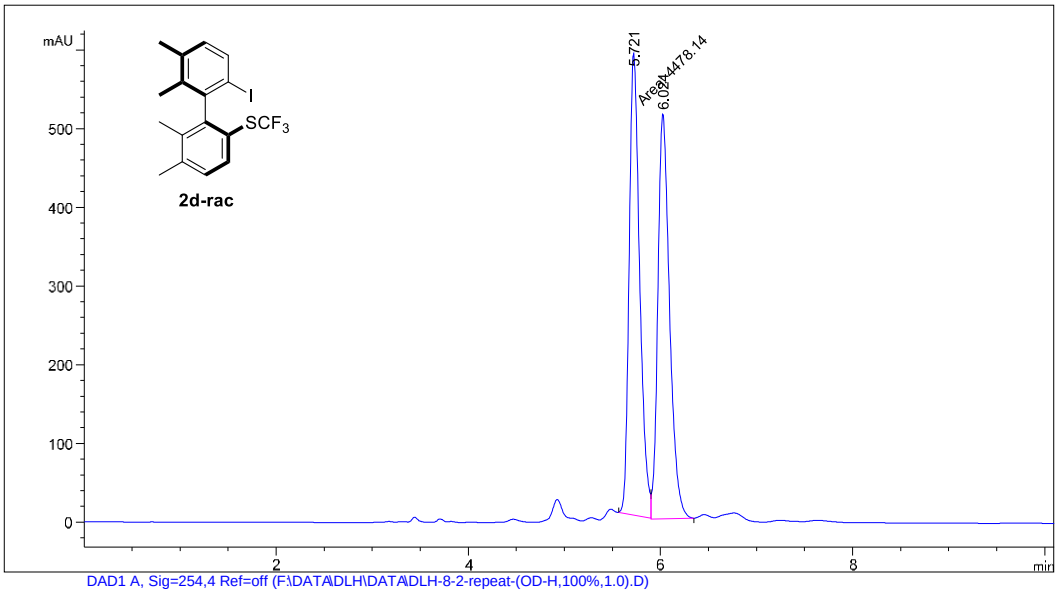
```
    ======================================================================
    Acq. Operator   :
                                          Location :  1
    Injection Date  : 06/06/2020 09:43:10
    Acq. Method     : DEF_LC.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 F, Sig=273,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    5.309 MM    0.1049  251.42212   39.96317   2.2454
    2    5.650 MM    0.1421 1.09459e4  1283.58850  97.7546

    Totals :               1.11973e4  1323.55167


    ======================================================================
    *** End of Report ***


LC1260 06/06/2020 09:59:18
                                                          Page 1 of 1
```

Figure S94. HPLC spectra of **2c**.

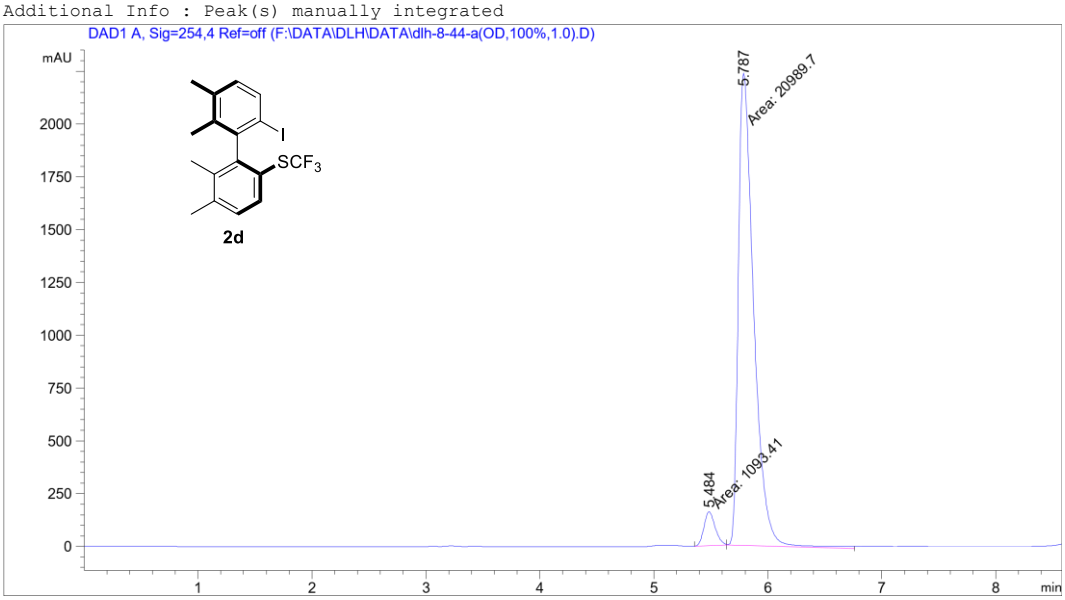
```
Data File F:\DATA\DLH\DATA\DLH-8-2-repeat-(OD-H,100%,1.0).D
Sample Name: DLH-8-2-repeat-(OD-H,100%,1.0)

    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 01/07/2020 21:35:49
                                              Inj Volume : No inj
    Acq. Method     : F:\METHOD\duanlh.M Last
    changed     : 01/07/2020 20:49:53 by
                  (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```




```
DAD1 A, Sig=254,4 Ref=off (F:\DATA\DLH\DATA\DLH-8-2-repeat-(OD-H,100%,1.0).D)
======================================================================
                      Area Percent Report
======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    5.721 MM    0.1272 4478.14307  586.78729  50.6756
    2    6.024 VB    0.1288 4358.73682  514.75287  49.3244

    Totals :               8836.87988 1101.54016


LC1260 01/07/2020 21:48:20
```

Figure S95. HPLC spectra of **2d-rac**.

```
Data File F:\DATA\DLH\DATA\dlh-8-44-a(OD,100%,1.0).D
Sample Name: dlh-8-44-a(OD,100%,1.0)

    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :   1
    Injection Date  : 06/06/2020 09:19:57
                                              Inj Volume : No inj
    Acq. Method     : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 06/06/2020 09:16:41 by
                     (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

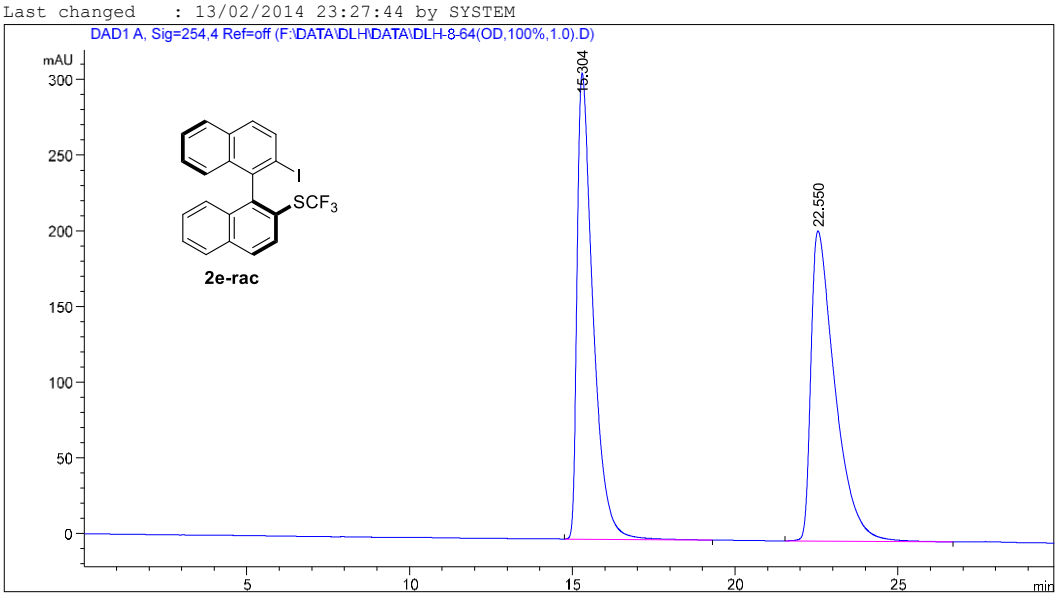



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    5.484 MM    0.1136 1093.40833  160.44019   4.9513
    2    5.787 MM    0.1564 2.09897e4  2236.69507  95.0487

    Totals :               2.20831e4  2397.13525


LC1260 30/06/2020 09:09:56
    ======================================================================
```

Figure S96. HPLC spectra of **2d**.

Data File F:\DATA\DLH\DATA\DLH-8-64(OD,100%,1.0).D
Sample Name: DLH-8-64(OD,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 16/06/2020 09:30:17
    Acq. Method     : duanlh.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
```

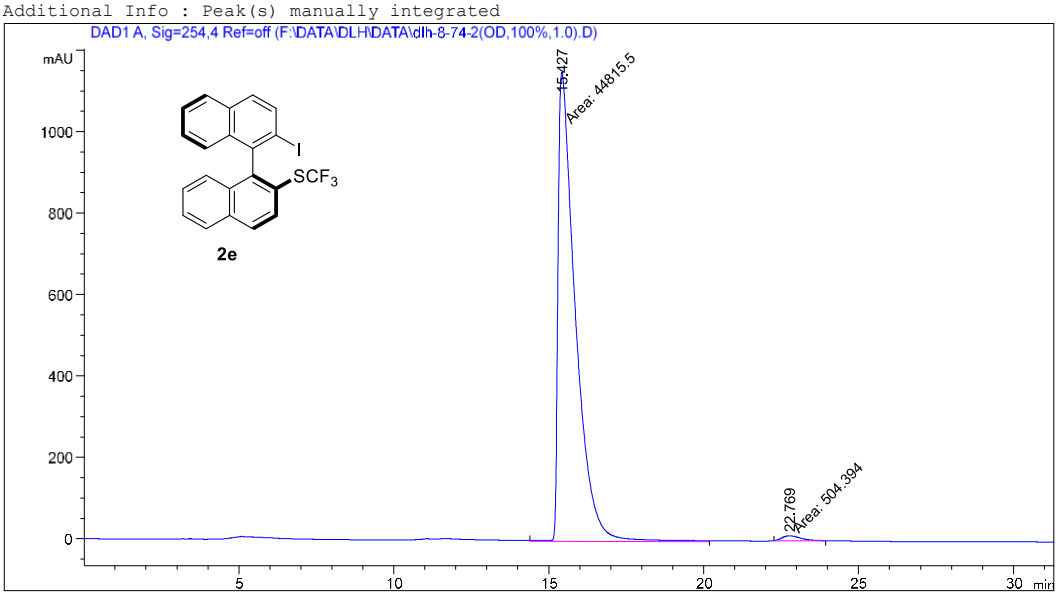



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    15.304 BB    0.5041 1.04498e4   307.77316  49.8528
    2    22.550 BB    0.7588 1.05115e4   204.78799  50.1472

    Totals :               2.09614e4   512.56116


    ======================================================================
    *** End of Report ***



LC1260 30/06/2020 09:32:31
                                                          Page 1 of 1
```

Figure S97. HPLC spectra of **2e-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-74-2(OD,100%,1.0).D
Sample Name: dlh-8-74-2(OD,100%,1.0)

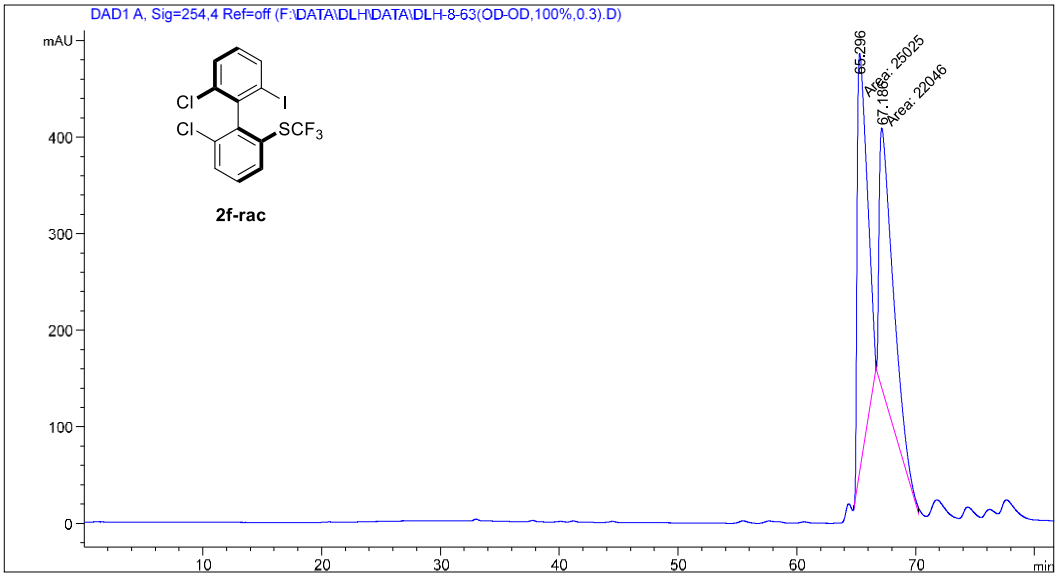
```
    ======================================================================
    Acq. Operator   :
                                          Location :  1
    Injection Date  : 22/06/2020 21:40:50
    Acq. Method     : duanlh.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    15.427 MM    0.6478 4.48155e4  1153.00928  98.8870
    2    22.769 MM    0.6929  504.39377   12.13327   1.1130

    Totals :               4.53199e4  1165.14255


    ======================================================================
    *** End of Report ***


LC1260 30/06/2020 09:33:56
                                                          Page 1 of 1
```

Figure S98. HPLC spectra of **2e**.

```
Data File F:\DATA\DLH\DATA\DLH-8-63(OD-OD,100%,0.3).D
Sample Name: DLH-8-63(OD-OD,100%,0.3)

    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 17/06/2020 14:35:26
                                              Inj Volume : No inj
    Acq. Method     : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 17/06/2020 14:34:59 by
                     (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

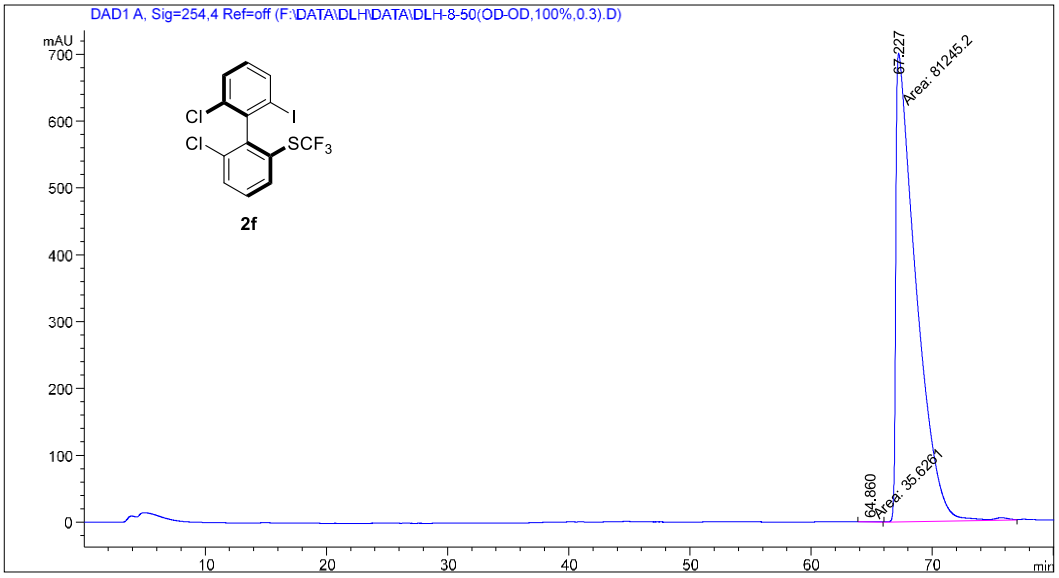



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    65.296 MM    0.9620 2.50250e4   433.55460  53.1644
    2    67.186 MM    1.3649 2.20460e4   269.19702  46.8356

    Totals :               4.70711e4   702.75162


LC1260 30/06/2020 09:30:39
LC1260 30/06/2020 09:30:39                                    Page 2 of 2
```

Figure S99. HPLC spectra of **2f-rac**.

Data File F:\DATA\DLH\DATA\DLH-8-50(OD-OD,100%,0.3).D
Sample Name: DLH-8-50(OD-OD,100%,0.3)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 17/06/2020 15:59:39
                                              Inj Volume : No inj
    Acq. Method     : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 17/06/2020 15:59:00 by
                     (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

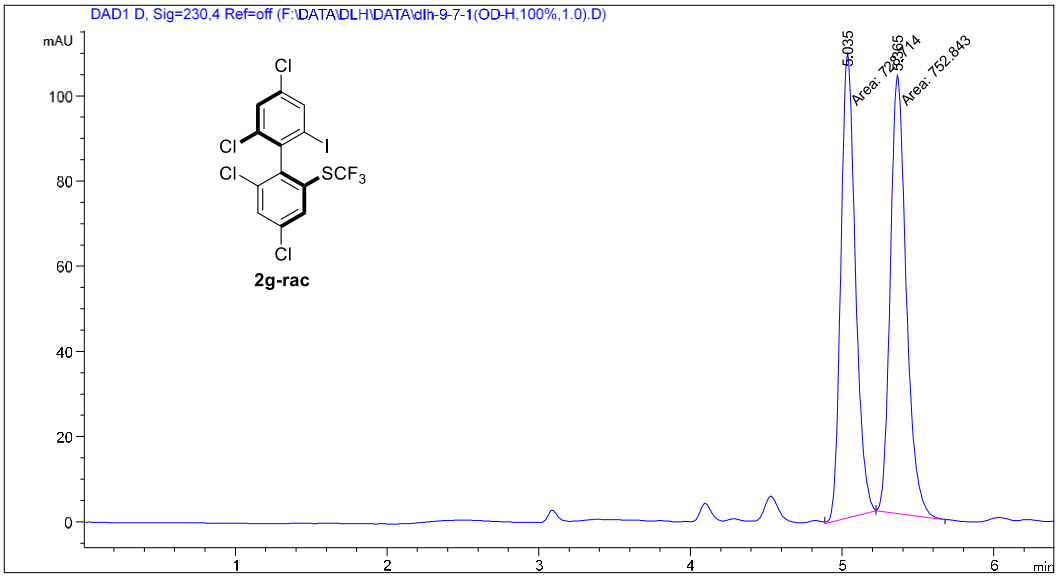



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    64.860 MM    1.3523   35.62613 4.39074e-1   0.0438
    2    67.227 MM    1.9323 8.12452e4   700.77673  99.9562

    Totals :               8.12808e4   701.21581


LC1260 30/06/2020 09:31:39
LC1260 30/06/2020 09:31:39                                    Page 2 of 2
```

Figure S100. HPLC spectra of **2f**.

Data File F:\DATA\DLH\DATA\dlh-9-7-1(OD-H,100%,1.0).D
Sample Name: dlh-9-7-1(OD-H,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 07/09/2020 16:41:25
                                              Inj Volume : No inj
    Acq. Method     : F:\METHOD\duanlh.M Last
    changed    : 07/09/2020 16:39:20 by
                 (modified after loading)
    Analysis Method : F:\METHOD\ZK.M
    Last changed    : 14/07/2019 15:34:15 by
    Additional Info : Peak(s) manually integrated
```

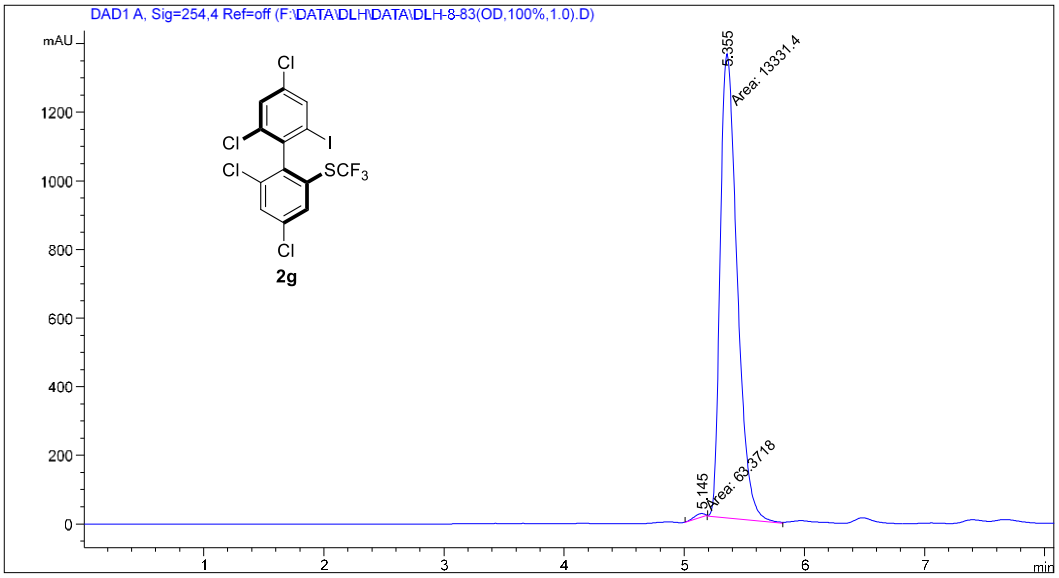



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=230,4 Ref=off

    Peak RetTime Type  Width     Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    5.035 MM    0.1113  728.71393  109.12567  49.1857
    2    5.365 MM    0.1220  752.84296  102.88705  50.8143

    Totals :               1481.55688  212.01273


LC1260 07/09/2020 16:50:46
LC1260 07/09/2020 16:50:46                                    Page 2 of 2
```

Figure S101. HPLC spectra of **2g-rac**.

Data File F:\DATA\DLH\DATA\DLH-8-83(OD,100%,1.0).D
Sample Name: DLH-8-83(OD,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 27/06/2020 18:56:30
                                              Inj Volume : No inj
    Acq. Method     : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 27/06/2020 18:53:18 by
                     (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

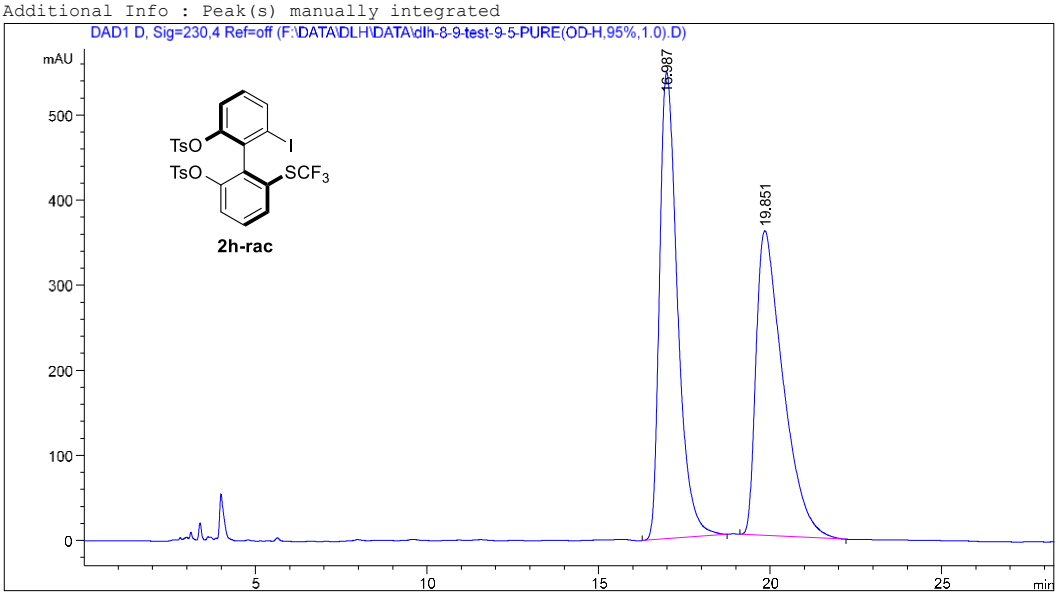



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    5.145 MM    0.1032   63.37177   10.23065   0.4731
    2    5.355 MM    0.1641 1.33314e4  1354.37061  99.5269

    Totals :               1.33947e4  1364.60125


LC1260 30/06/2020 09:37:19
LC1260 30/06/2020 09:37:19                                    Page 2 of 2
```

Figure S102. HPLC spectra of **2g**.

Data File F:\DATA\DLH\DATA\dlh-8-9-test-9-5-PURE(OD-H,95%,1.0).D
Sample Name: dlh-8-9-test-9-5-PURE(OD-H,95%,1.0)

```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 05/09/2020 14:41:22
    Acq. Method     : duanlh.M
    Analysis Method : F:\METHOD\ZK.M
    Last changed    : 14/07/2019 15:34:15 by
    Additional Info : Peak(s) manually integrated
```

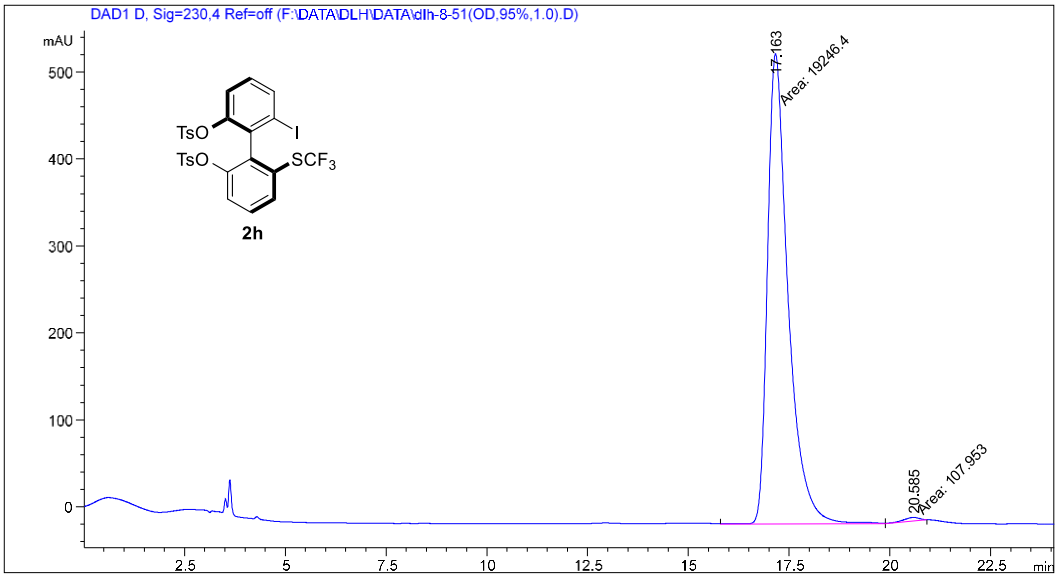



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=230,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1   16.987 BB    0.5633 1.99907e4   548.38898  50.5774
    2   19.851 BB    0.7866 1.95343e4   358.01654  49.4226

    Totals :               3.95249e4   906.40552


    ======================================================================
    *** End of Report ***


LC1260 05/09/2020 15:11:44
                                                          Page 1 of 1
```

Figure S103. HPLC spectra of **2h-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-51(OD,95%,1.0).D
Sample Name: dlh-8-51(OD,95%,1.0)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 11/06/2020 21:18:46
                                              Inj Volume : No inj
    Acq. Method     : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 11/06/2020 20:29:49 by
                     (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

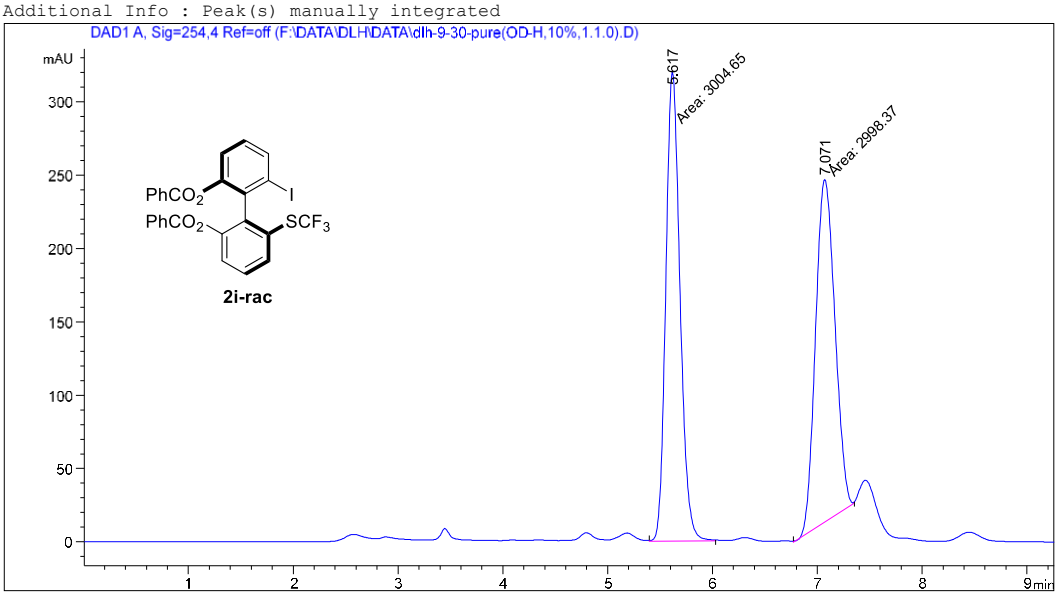



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=230,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1   17.163 MM    0.5936 1.92464e4   540.37152  99.4422
    2   20.585 MM    0.4427  107.95306    4.06392   0.5578

    Totals :               1.93543e4   544.43544


LC1260 08/08/2020 09:32:16
LC1260 08/08/2020 09:32:16                                    Page 2 of 2
```

Figure S104. HPLC spectra of **2h**.

Data File F:\DATA\DLH\DATA\dlh-9-30-pure(OD-H,10%,1.1.0).D
Sample Name: dlh-9-30-pure(OD-H,10%,1.1.0)

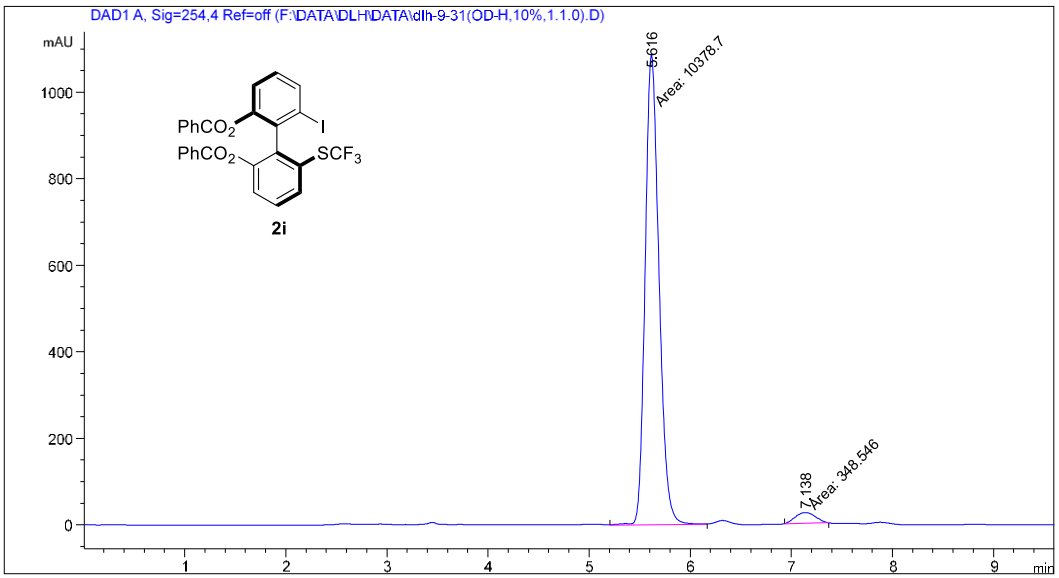
```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 23/09/2020 16:36:48
    Acq. Method     : DEF_LC.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    5.617 MM    0.1565 3004.65430  319.97919  50.0523
    2    7.071 MM    0.2138 2998.37134  233.71091  49.9477

    Totals :               6003.02563  553.69009


    ======================================================================
    *** End of Report ***


LC1260 23/09/2020 16:47:53
                                                          Page 1 of 1
```

Figure S105. HPLC spectra of **2i-rac**.

```
Data File F:\DATA\DLH\DATA\dlh-9-31(OD-H,10%,1.1.0).D
Sample Name: dlh-9-31(OD-H,10%,1.1.0)

    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 23/09/2020 15:01:17
                                              Inj Volume : No inj
    Acq. Method     : F:\METHOD\duanlh.M Last
    changed    : 23/09/2020 14:36:56 by
                 (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

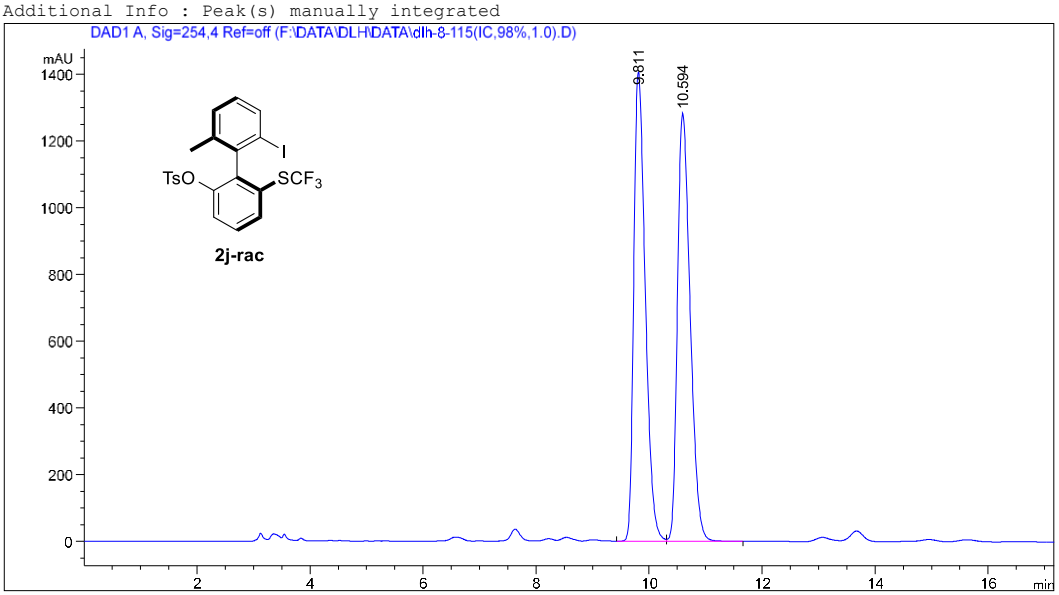



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    5.616 MM    0.1591 1.03787e4  1086.95300  96.7508
    2    7.138 MM    0.2328  348.54553   24.95789   3.2492

    Totals :               1.07273e4  1111.91090


LC1260 23/09/2020 15:12:38
LC1260 23/09/2020 15:12:38                                    Page 2 of 2
```

Figure S106. HPLC spectra of **2i**.

Data File F:\DATA\DLH\DATA\dlh-8-115(IC,98%,1.0).D
Sample Name: dlh-8-115(IC,98%,1.0)

```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 25/07/2020 21:07:38
    Acq. Method     : duanlh.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

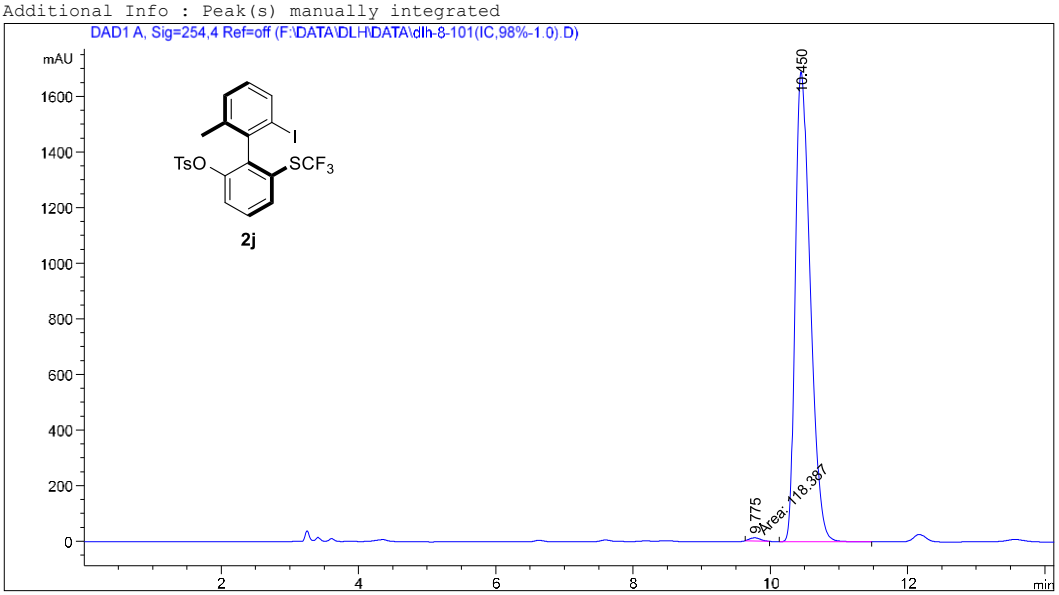



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1     9.811 BV    0.2190 1.99018e4  1407.00195  49.8409
    2    10.594 VB    0.2420 2.00288e4  1283.66345  50.1591

    Totals :               3.99306e4  2690.66541


    ======================================================================
    *** End of Report ***


LC1260 30/07/2020 15:32:40
                                                          Page 1 of 1
```

Figure S107. HPLC spectra of **2j-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-101(IC,98%-1.0).D
Sample Name: dlh-8-101(IC,98%-1.0)

```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 20/07/2020 18:12:25
    Acq. Method     : DEF_LC.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

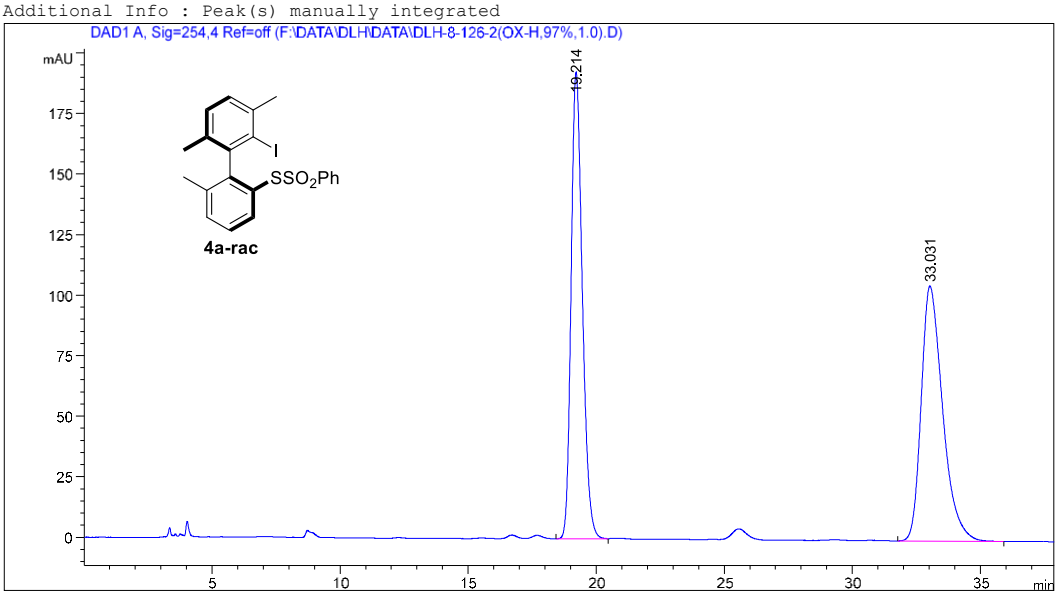



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    9.775 MM    0.1775  118.38702   11.11497   0.4584
    2    10.450 BB    0.2355 2.57104e4  1689.75989  99.5416

    Totals :               2.58288e4  1700.87486


    ======================================================================
    *** End of Report ***


LC1260 30/07/2020 15:34:18
                                                          Page 1 of 1
```

Figure S108. HPLC spectra of **2j**.

Data File F:\DATA\DLH\DATA\DLH-8-126-2(OX-H,97%,1.0).D
Sample Name: DLH-8-126-2(OX-H,97%,1.0)

```
    ====================================================================
    Acq. Operator   :
                                          Location :  1
    Injection Date  : 26/10/2020 20:34:56
    Acq. Method     : duanlh.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

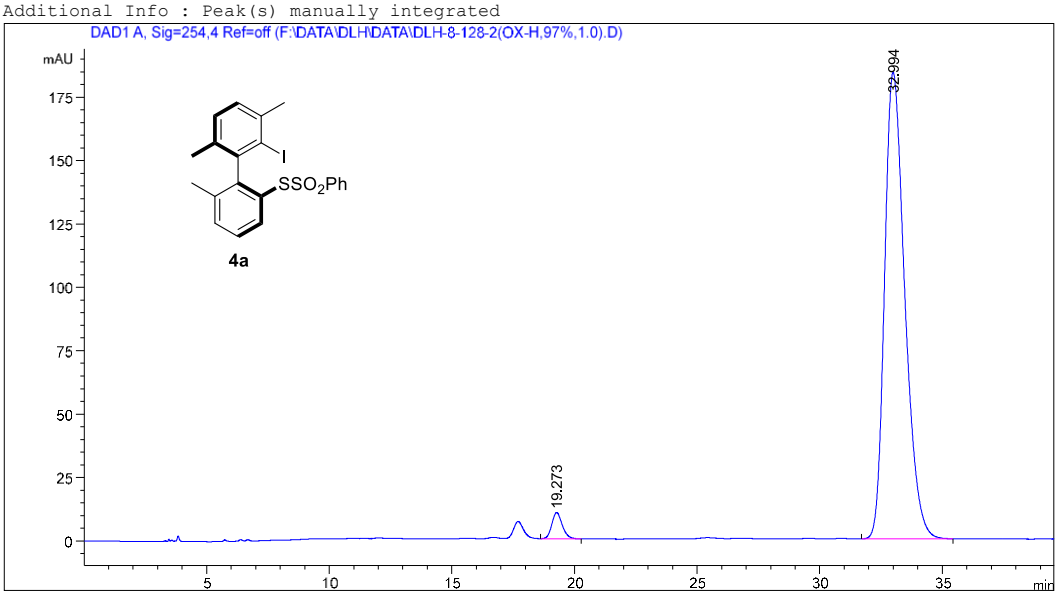



```
    ====================================================================
                         Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]    [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    19.214 BB    0.4687 5856.54297  192.65427  48.8543
    2    33.031 BB    0.8990 6131.23975  105.34064  51.1457

    Totals :               1.19878e4   297.99491


    ====================================================================
    *** End of Report ***


LC1260 26/10/2020 21:14:41
                                                          Page 1 of 1
```

Figure S109. HPLC spectra of **4a-rac**.

Data File F:\DATA\DLH\DATA\DLH-8-128-2(OX-H,97%,1.0).D
Sample Name: DLH-8-128-2(OX-H,97%,1.0)

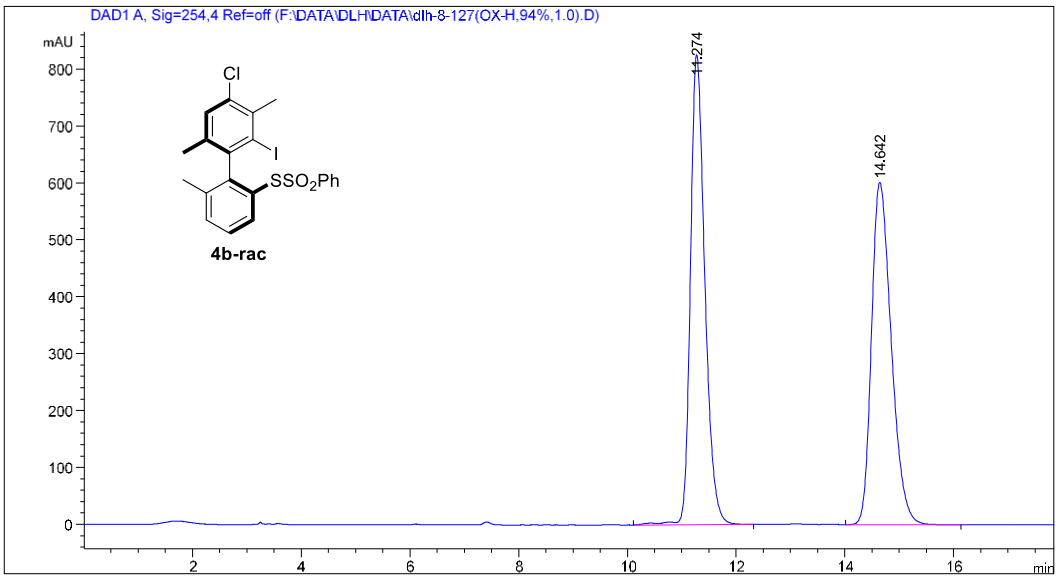
```
    ====================================================================
    Acq. Operator   :
                                          Location :  1
    Injection Date  : 26/10/2020 19:52:56
    Acq. Method     : duanlh.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                         Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    19.273 BB    0.4516  303.99725   10.32105   2.8086
    2    32.994 BB    0.8749 1.05198e4   184.04108  97.1914

    Totals :               1.08238e4   194.36212


    ====================================================================
    *** End of Report ***


LC1260 26/10/2020 21:14:02
                                                          Page 1 of 1
```

Figure S110. HPLC spectra of **4a**.

```
Data File F:\DATA\DLH\DATA\dlh-8-127(OX-H,94%,1.0).D
Sample Name: dlh-8-127(OX-H,94%,1.0)

    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 28/07/2020 15:02:19
                                              Inj Volume : No inj
    Acq. Method     : F:\METHOD\duanlh.M Last
    changed    : 28/07/2020 14:41:49 by
                 (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

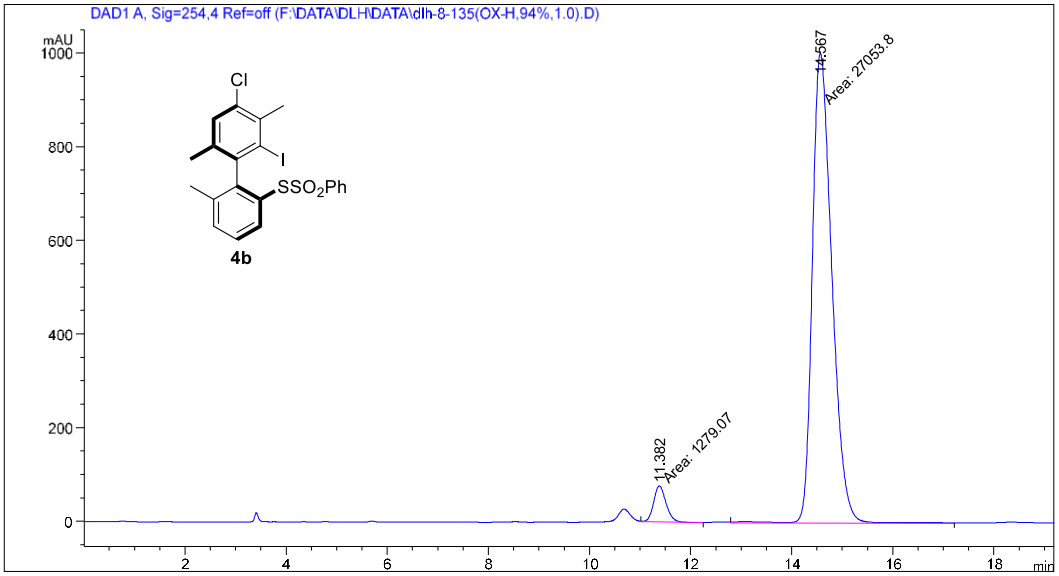



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    11.274 VB R  0.2817 1.52435e4   825.15546  50.0942
    2    14.642 BB    0.3907 1.51862e4   601.23993  49.9058

    Totals :               3.04297e4  1426.39539


LC1260 26/10/2020 18:44:27
LC1260 26/10/2020 18:44:27                                    Page 2 of 2
```

Figure S111. HPLC spectra of **4b-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-135(OX-H,94%,1.0).D
Sample Name: dlh-8-135(OX-H,94%,1.0)

```
==========================================================================
Acq. Operator   :
                                          Location :  1
Injection Date  : 04/08/2020 10:42:07
Acq. Method     : duanlh.M
Analysis Method : F:\METHOD\gwj.99.5 M.M
Last changed    : 03/08/2020 12:03:22 by
Additional Info : Peak(s) manually integrated
```

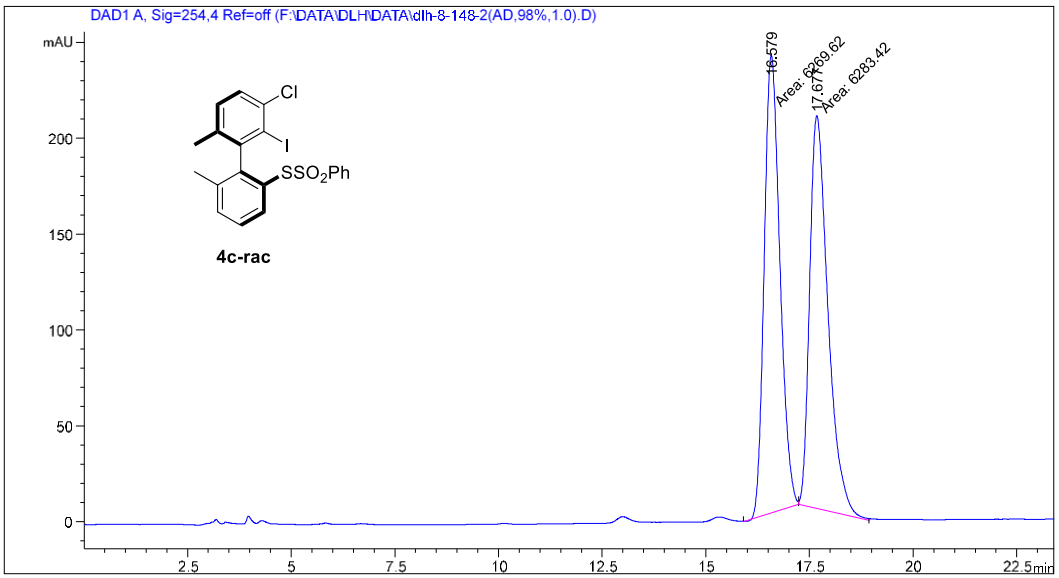



```
==========================================================================
                      Area Percent Report
==========================================================================

Sorted By             :     Signal
Multiplier            :     1.0000
Dilution              :     1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width    Area      Height    Area
  #   [min]       [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
1    11.382 MM    0.2787 1279.07239   76.48161   4.5144
2    14.567 MM    0.4492 2.70538e4  1003.72339  95.4856

Totals :               2.83329e4  1080.20500


==========================================================================
*** End of Report ***


LC1260 04/08/2020 11:03:19
                                                          Page 1 of 1
```

Figure S112. HPLC spectra of **4b**.

Data File F:\DATA\DLH\DATA\dlh-8-148-2(AD,98%,1.0).D
Sample Name: dlh-8-148-2(AD,98%,1.0)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 08/08/2020 09:12:59
                                              Inj Volume : No inj
    Acq. Method     : F:\METHOD\duanlh.M Last
    changed    : 08/08/2020 08:59:12 by
                 (modified after loading)
    Analysis Method : F:\METHOD\duanlh.M Last
    changed    : 20/05/2020 09:56:41 by
    Additional Info : Peak(s) manually integrated
```

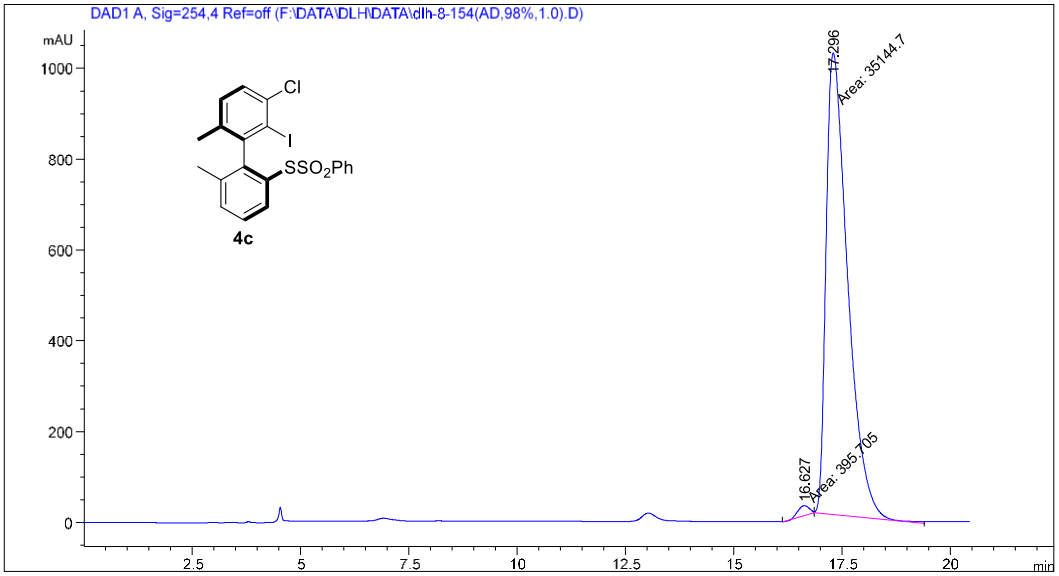



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    16.579 MM    0.4374 6269.61719  238.90573  49.9450
    2    17.677 MM    0.5114 6283.41553  204.79486  50.0550

    Totals :               1.25530e4   443.70059


LC1260 11/08/2020 15:44:22
LC1260 11/08/2020 15:44:22                                          Page 2 of 2
```

Figure S113. HPLC spectra of **4c-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-154(AD,98%,1.0).D
Sample Name: dlh-8-154(AD,98%,1.0)

```
    ======================================================================
    Acq. Operator   :
                                          Location :  1
    Injection Date  : 10/08/2020 22:39:40
    Acq. Method     : duanlh.M
    Analysis Method : F:\METHOD\duanlh.M Last
    changed    : 20/05/2020 09:56:41 by
    Additional Info : Peak(s) manually integrated
```

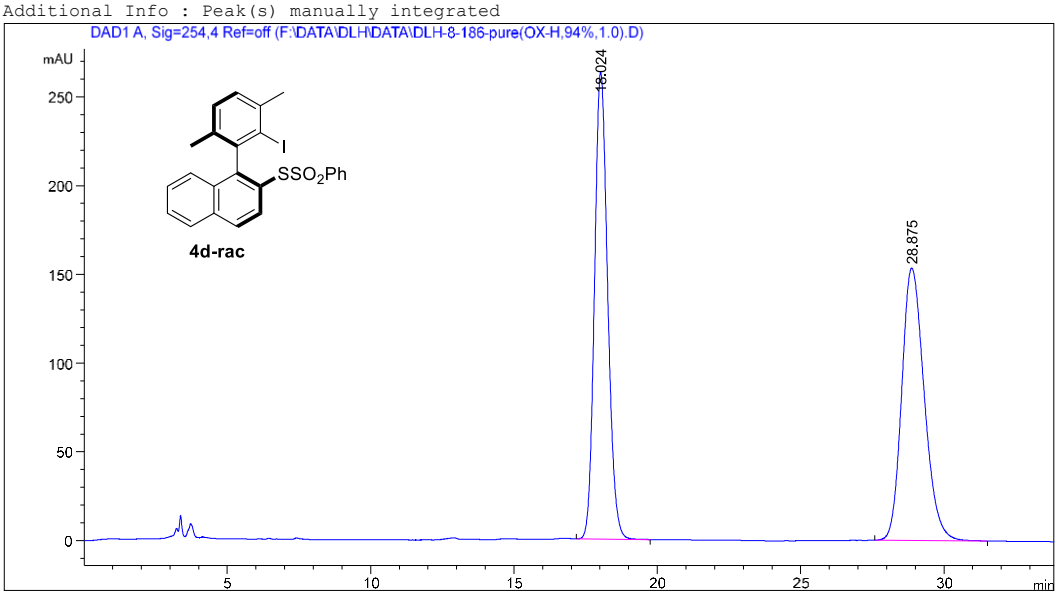



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    16.627 MM    0.3057  395.70493   21.57299   1.1134
    2    17.296 MM    0.5767 3.51447e4  1015.76196  98.8866

    Totals :               3.55404e4  1037.33496


    ======================================================================
    *** End of Report ***


LC1260 11/08/2020 15:45:34
                                                          Page 1 of 1
```

Figure S114. HPLC spectra of **4c**.

Data File F:\DATA\DLH\DATA\DLH-8-186-pure(OX-H,94%,1.0).D
Sample Name: DLH-8-186-pure(OX-H,94%,1.0)

```
    ====================================================================
    Acq. Operator   :
                                          Location :  1
    Injection Date  : 29/08/2020 20:56:22
    Acq. Method     : DEF_LC.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                         Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    18.024 BB    0.4892 8369.33398  263.06116  49.9297
    2    28.875 BB    0.8421 8392.89844  153.45613  50.0703

    Totals :               1.67622e4   416.51729


    ====================================================================
    *** End of Report ***


LC1260 29/08/2020 21:31:40
                                                          Page 1 of 1
```

Figure S115. HPLC spectra of **4d-rac**.

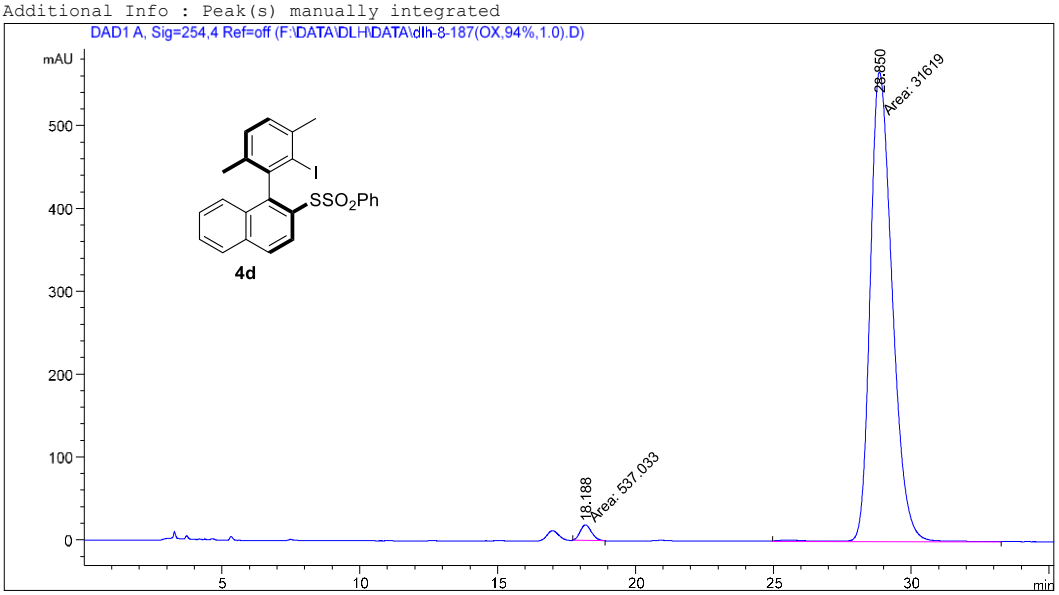
Data File F:\DATA\DLH\DATA\dlh-8-187(OX,94%,1.0).D
Sample Name: dlh-8-187(OX,94%,1.0)

==========

Acq. Operator :

Location : 1

Injection Date : 28/08/2020 09:57:47
Acq. Method : duanlh.M
Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
Last changed : 13/02/2014 23:27:44 by SYSTEM
Additional Info : Peak(s) manually integrated



==========

Area Percent Report

==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.188	MM	0.4755	537.03345	18.82492	1.6701
2	28.850	MM	0.9296	3.16190e4	566.90204	98.3299
Totals :				3.21561e4	585.72696	

==========

*** End of Report ***

LC1260 28/08/2020 10:36:41

Figure S116. HPLC spectra of **4d**.

Data File F:\DATA\DLH\DATA\DLH-8-195(OX-H,90%,1.0).D
Sample Name: DLH-8-195(OX-H,90%,1.0)

==========

Acq. Operator :

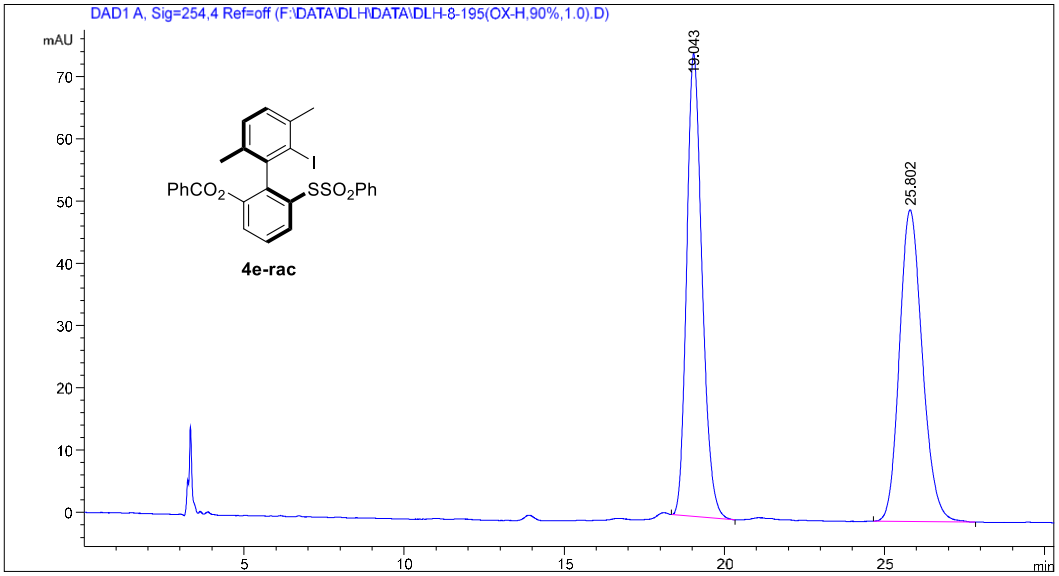
Location : 1

Injection Date : 31/08/2020 16:16:42

Acq. Method : duanlh.M

Analysis Method : F:\METHOD\duanlh.M Last changed : 20/05/2020 09:56:41 by

Additional Info : Peak(s) manually integrated



==========

Area Percent Report

==========

Sorted By : Signal

Multiplier : 1.0000

Dilution : 1.0000

Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.043	BB	0.5160	2486.39258	74.37334	49.9347
2	25.802	BB	0.7610	2492.89551	50.06126	50.0653
Totals :				4979.28809	124.43460	

==========

*** End of Report ***

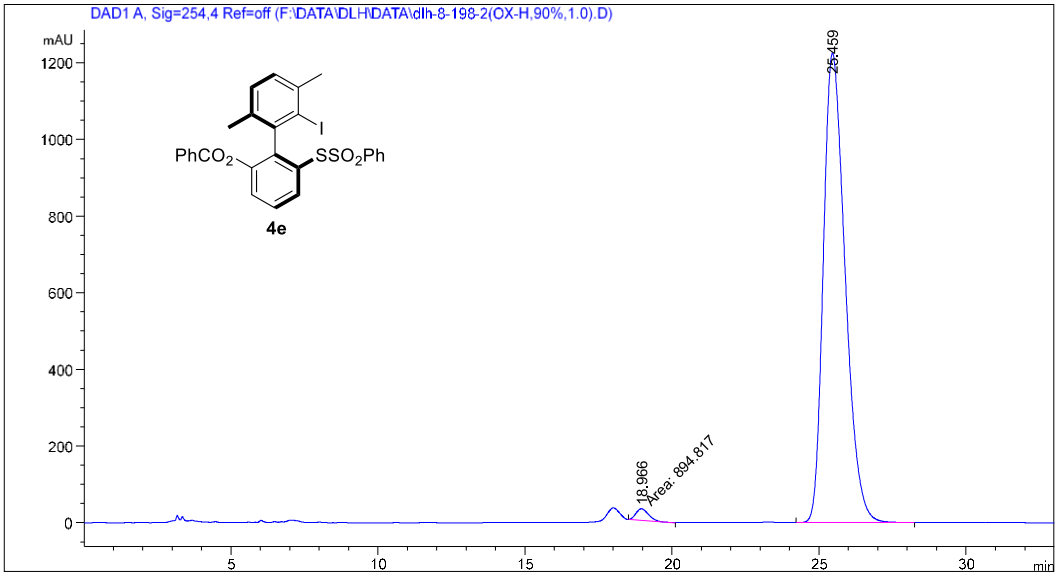
LC1260 02/09/2020 09:24:45

Page 1 of 1

Figure S117. HPLC spectra of **4e-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-198-2(OX-H,90%,1.0).D
Sample Name: dlh-8-198-2(OX-H,90%,1.0)

```
    ====================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 01/09/2020 10:13:58
    Acq. Method     : duanlh.M
    Analysis Method : F:\METHOD\duanlh.M Last
    changed    : 20/05/2020 09:56:41 by
    Additional Info : Peak(s) manually integrated
```

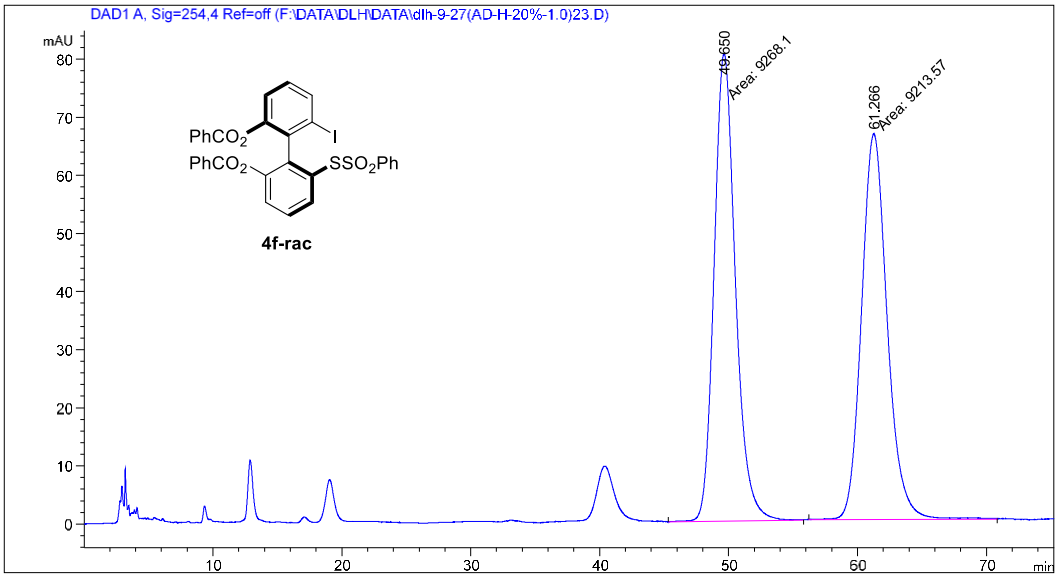



```
    ====================================================================
                         Area Percent Report
    ====================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1  18.966 MM    0.4931  894.81720   30.24434   1.4034
    2  25.459 BB    0.7988 6.28658e4  1224.78455  98.5966

    Totals :               6.37606e4  1255.02888


    ====================================================================
    *** End of Report ***


LC1260 02/09/2020 09:24:12
                                                          Page 1 of 1
```

Figure S118. HPLC spectra of **4e**.

Data File F:\DATA\DLH\DATA\dlh-9-27(AD-H-20%-1.0)23.D
Sample Name: dlh-9-27(AD-H-20%-1.0)23

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 19/09/2020 20:49:37
                                              Inj Volume : No inj
    Acq. Method     : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 19/09/2020 20:22:04 by
                     (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

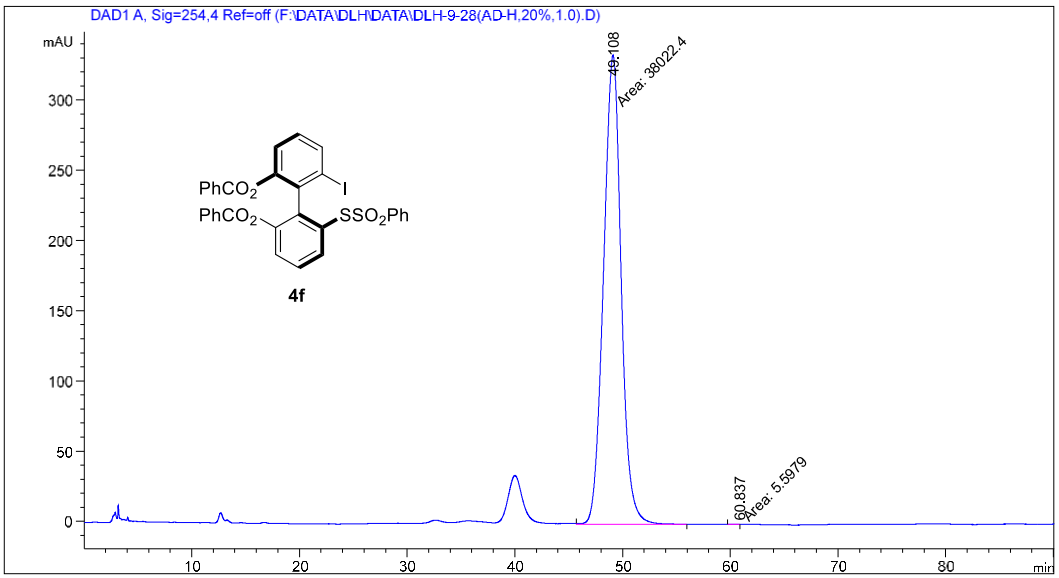



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    49.650 MM    1.9212 9268.10156   80.40347  50.1475
    2    61.266 MM    2.3125 9213.56738   66.40472  49.8525

    Totals :               1.84817e4   146.80818


LC1260 19/09/2020 22:06:16
LC1260 19/09/2020 22:06:16                                    Page 2 of 2
```

Figure S119. HPLC spectra of **4f-rac**.

Data File F:\DATA\DLH\DATA\DLH-9-28(AD-H,20%,1.0).D
Sample Name: DLH-9-28(AD-H,20%,1.0)

```
==========================================================================
Acq. Operator   :
Sample Operator :
Acq. Instrument : LC1260                      Location :  1
Injection Date  : 24/09/2020 16:08:09
                                          Inj Volume : No inj
Acq. Method     : F:\METHOD\duanlh.M Last
changed    : 24/09/2020 17:38:21 by
                (modified after loading)
Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
Last changed    : 13/02/2014 23:27:44 by SYSTEM
Additional Info : Peak(s) manually integrated
```

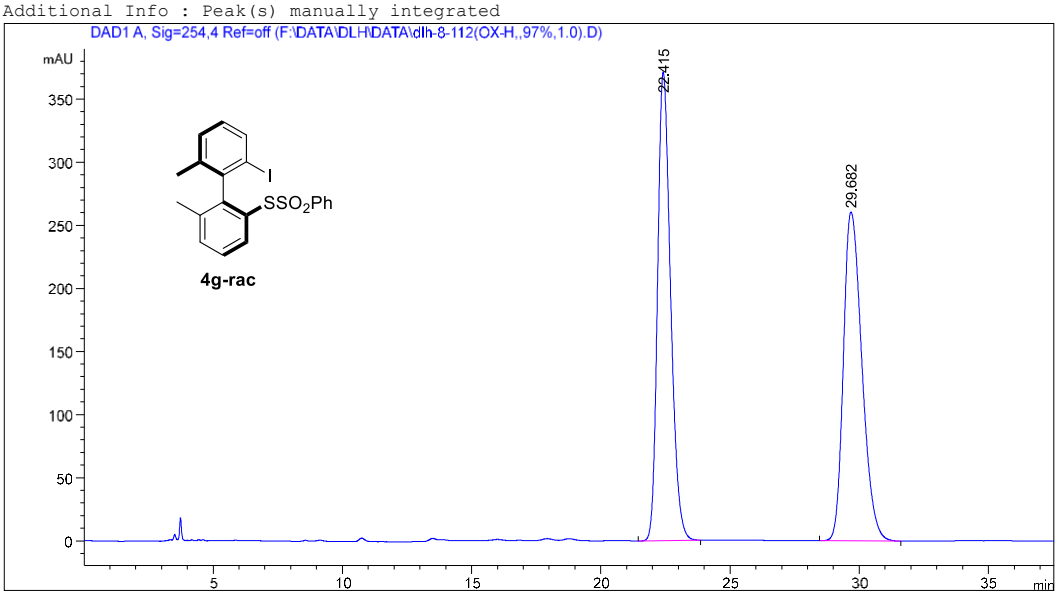



```
==========================================================================
                      Area Percent Report
==========================================================================

Sorted By             :     Signal
Multiplier            :     1.0000
Dilution              :     1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
1    49.108 MM    1.8962 3.80224e4   334.19345  99.9853
2    60.837 MM    0.7240    5.59790 1.28858e-1   0.0147

Totals :               3.80280e4   334.32231


LC1260 24/09/2020 19:18:09
LC1260 24/09/2020 19:18:09                                    Page 2 of 2
```

Figure S120. HPLC spectra of **4f**.

Data File F:\DATA\DLH\DATA\dlh-8-112(OX-H,,97%,1.0).D
Sample Name: dlh-8-112(OX-H,,97%,1.0)

```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 18/07/2020 21:20:12
    Acq. Method     : duanlh.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

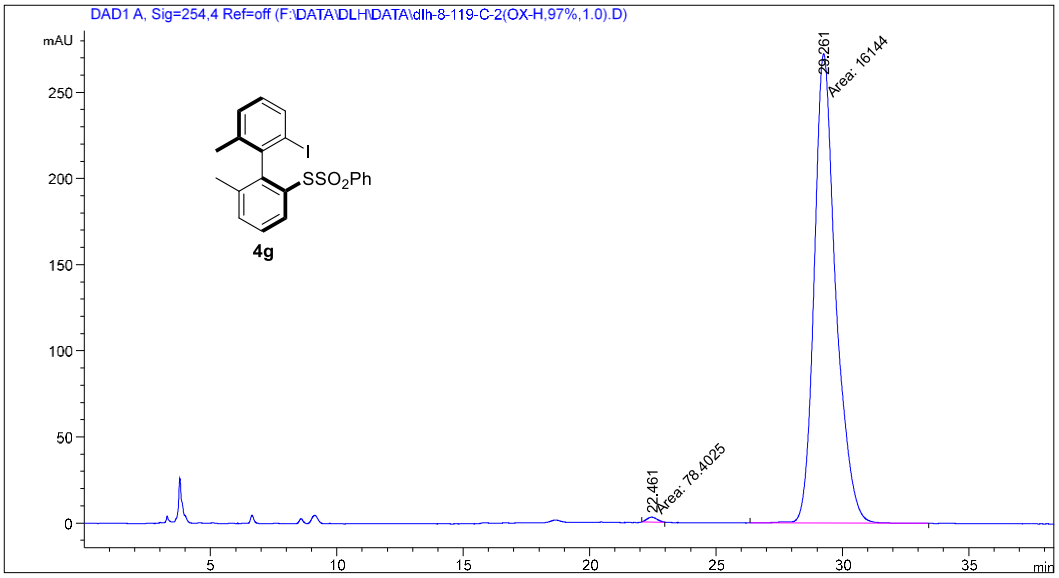



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]    [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    22.415 BB    0.5372 1.29588e4   371.26520  49.9780
    2    29.682 BB    0.7729 1.29703e4   260.49133  50.0220

    Totals :               2.59291e4   631.75653


    ======================================================================
    *** End of Report ***


LC1260 30/07/2020 15:39:17
                                                          Page 1 of 1
```

Figure S121. HPLC spectra of **4g-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-119-C-2(OX-H,97%,1.0).D
Sample Name: dlh-8-119-C-2(OX-H,97%,1.0)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 28/07/2020 16:17:41
                                              Inj Volume : No inj
    Acq. Method     : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 28/07/2020 16:07:03 by
                     (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```



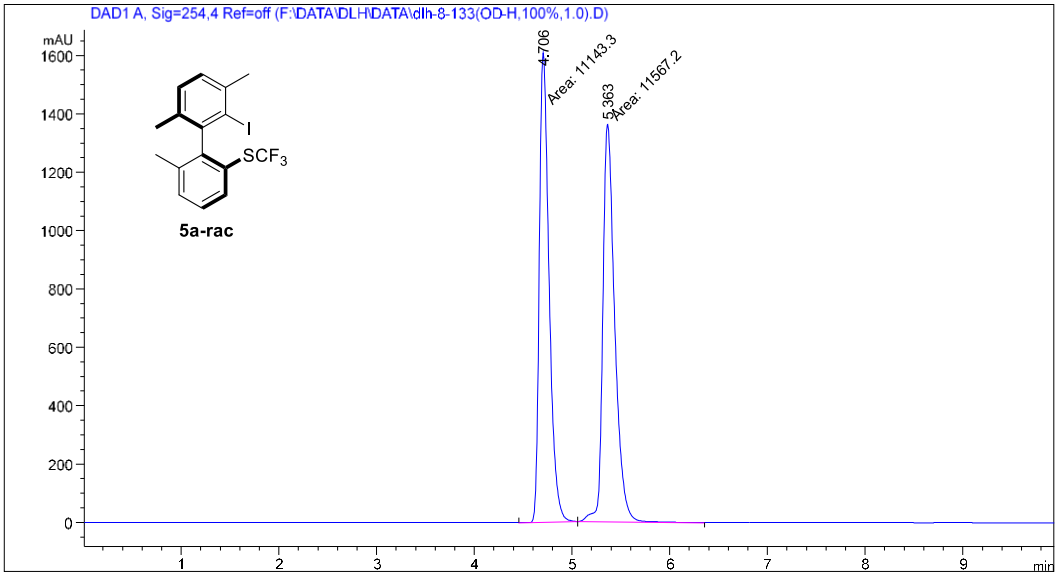

```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    22.461 MM    0.4616   78.40247    2.83080   0.4833
    2    29.261 MM    0.9878 1.61440e4   272.37766  99.5167

    Totals :               1.62224e4   275.20846


LC1260 30/07/2020 15:40:55
LC1260 30/07/2020 15:40:55                                    Page 2 of 2
```

Figure S122. HPLC spectra of **4g**.

.

Data File F:\DATA\DLH\DATA\dlh-8-133(OD-H,100%,1.0).D
Sample Name: dlh-8-133(OD-H,100%,1.0)

```
==================================================================
Acq. Operator   :
                                        Location :  1
Injection Date  : 04/08/2020 09:56:13
Acq. Method     : duanlh.M
Analysis Method : F:\METHOD\duanlh.M Last
changed    : 20/05/2020 09:56:41 by
Additional Info : Peak(s) manually integrated
```

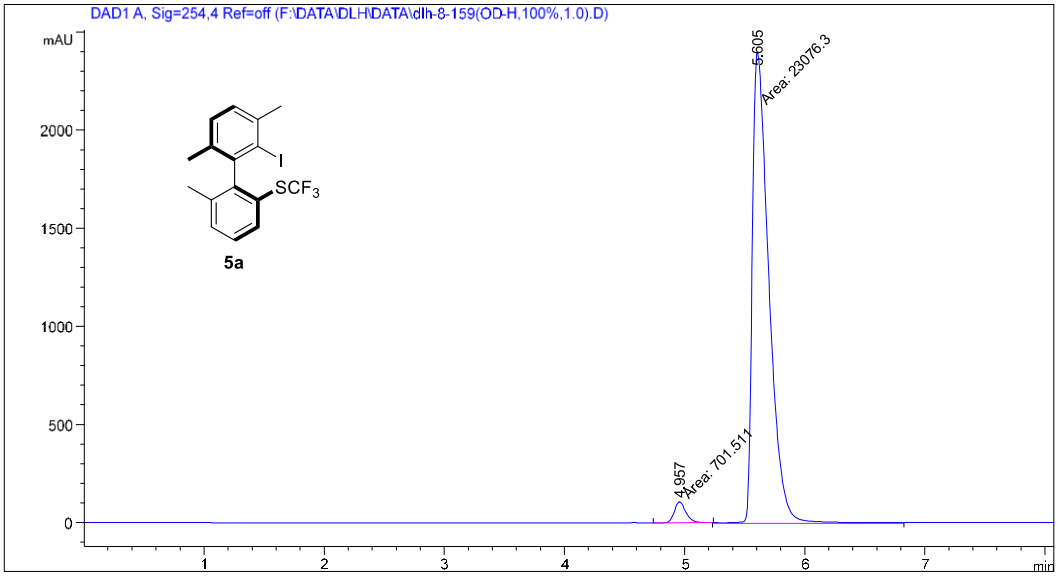



```
==================================================================
                     Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width    Area      Height    Area
  #   [min]       [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
1    4.706 MM    0.1154 1.11433e4  1609.58423  49.0669
2    5.363 MM    0.1412 1.15672e4  1365.29407  50.9331

Totals :               2.27105e4  2974.87830


==================================================================
*** End of Report ***


LC1260 11/08/2020 15:57:21
                                                    Page 1 of 1
```

Figure S123. HPLC spectra of **5a-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-159(OD-H,100%,1.0).D
Sample Name: dlh-8-159(OD-H,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
                                          Location :  1
    Injection Date  : 11/08/2020 10:56:30
    Acq. Method     : duanlh.M
    Analysis Method : F:\METHOD\duanlh.M Last
    changed    : 20/05/2020 09:56:41 by
    Additional Info : Peak(s) manually integrated
```

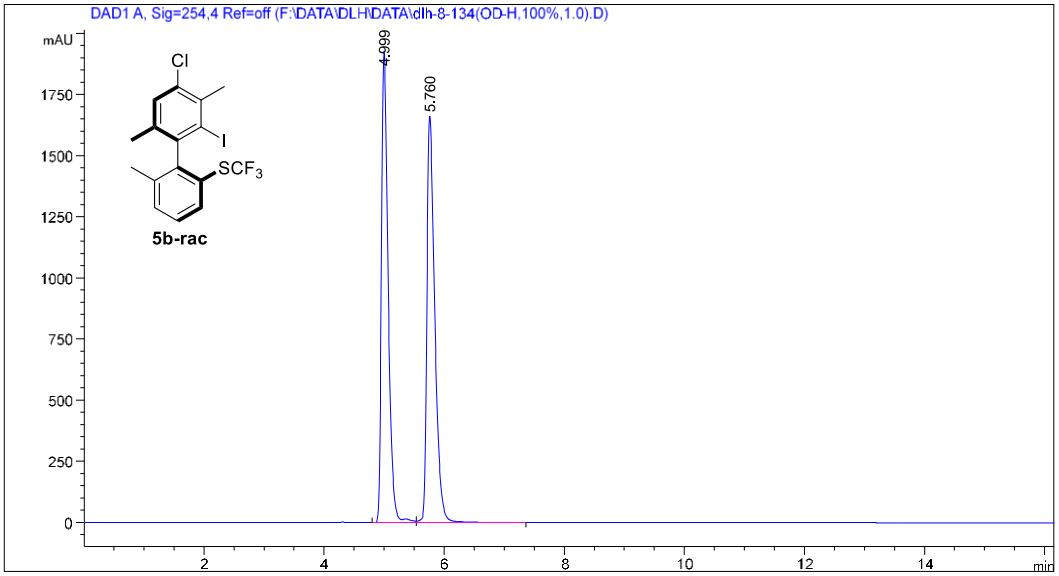



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    4.957 MM    0.1094  701.51123  106.83482   2.9503
    2    5.605 MM    0.1603 2.30763e4  2399.47119  97.0497

    Totals :               2.37778e4  2506.30602


    ======================================================================
    *** End of Report ***


LC1260 11/08/2020 11:07:22
                                                          Page 1 of 1
```

Figure S124. HPLC spectra of **5a**.

Data File F:\DATA\DLH\DATA\dlh-8-134(OD-H,100%,1.0).D
Sample Name: dlh-8-134(OD-H,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 04/08/2020 10:10:23
    Acq. Method     : duanlh.M
    Analysis Method : F:\METHOD\duanlh.M Last
    changed    : 20/05/2020 09:56:41 by
    Additional Info : Peak(s) manually integrated
```

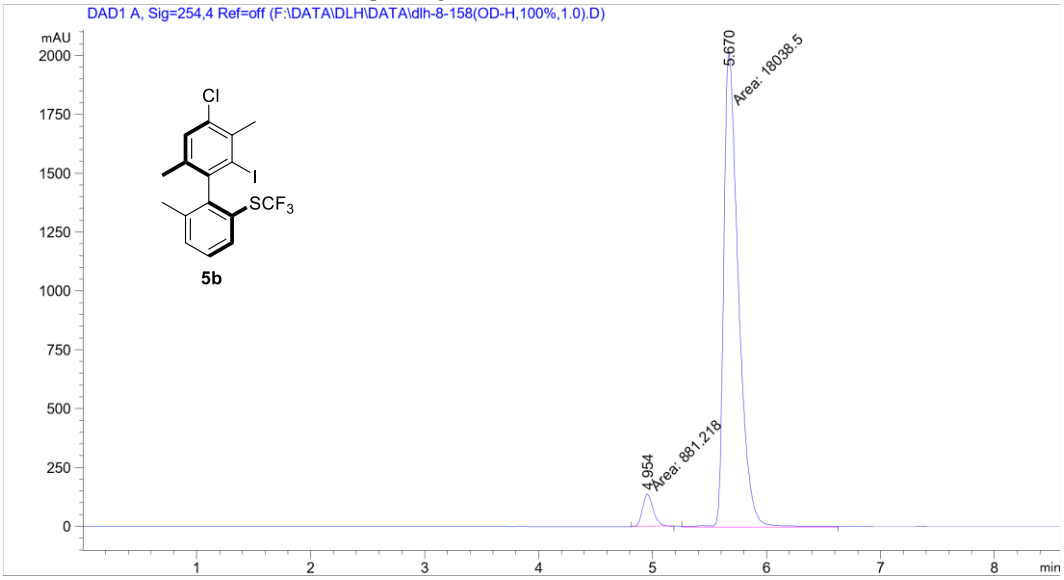



```
    ======================================================================
                         Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1     4.999 BV R  0.1177 1.49294e4  1922.34961  49.6330
    2     5.760 VB    0.1383 1.51501e4  1662.50989  50.3670

    Totals :               3.00795e4  3584.85950


    ======================================================================
    *** End of Report ***


LC1260 11/08/2020 15:48:56
                                                          Page 1 of 1
```

Figure S125. HPLC spectra of **5b-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-158(OD-H,100%,1.0).D
Sample Name: dlh-8-158(OD-H,100%,1.0)

```
==========================================================================
Acq. Operator   :
                                          Location :  1
Injection Date  : 10/08/2020 19:19:33
Acq. Method     : duanlh.M
Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
Last changed    : 13/02/2014 23:27:44 by SYSTEM
Additional Info : Peak(s) manually integrated
```

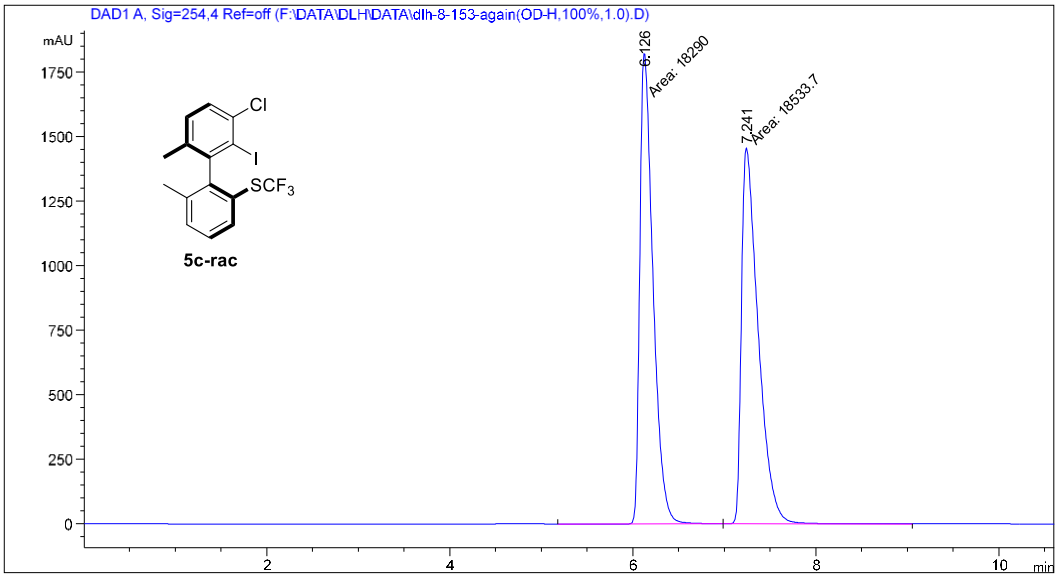



```
==========================================================================
                      Area Percent Report
==========================================================================

Sorted By             :     Signal
Multiplier            :     1.0000
Dilution              :     1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
1     4.954 MM    0.1068  881.21826  137.51082   4.6577
2     5.670 MM    0.1493 1.80385e4  2013.32617  95.3423

Totals :               1.89197e4  2150.83699


==========================================================================
*** End of Report ***


LC1260 10/08/2020 19:29:59
                                                          Page 1 of 1
```

Figure S126. HPLC spectra of **5b**.

Data File F:\DATA\DLH\DATA\dlh-8-153-again(OD-H,100%,1.0).D
Sample Name: dlh-8-153-again(OD-H,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 08/08/2020 21:34:16
                                              Inj Volume : No inj
    Acq. Method     : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 08/08/2020 21:11:42 by
                     (modified after loading)
    Analysis Method : F:\METHOD\duanlh.M Last
    changed    : 20/05/2020 09:56:41 by
    Additional Info : Peak(s) manually integrated
```

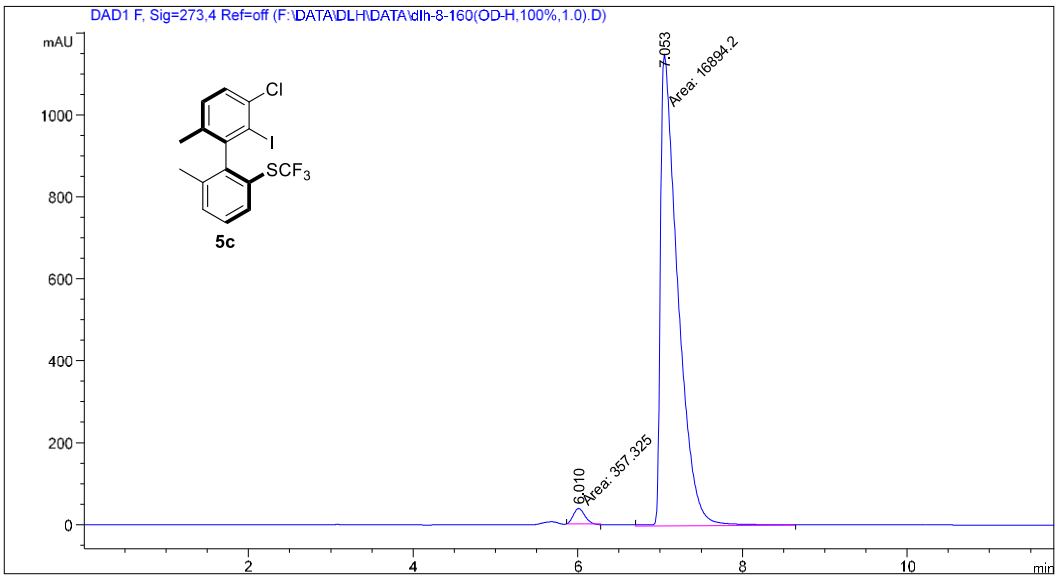



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1     6.126 MM    0.1672 1.82900e4  1823.03101  49.6690
    2     7.241 MM    0.2121 1.85337e4  1456.27991  50.3310

    Totals :               3.68237e4  3279.31091


LC1260 11/08/2020 15:42:35
LC1260 11/08/2020 15:42:35                                    Page 2 of 2
```

Figure S127. HPLC spectra of **5c-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-160(OD-H,100%,1.0).D
Sample Name: dlh-8-160(OD-H,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 12/08/2020 16:44:05
                                              Inj Volume : No inj
    Acq. Method     : F:\METHOD\duanlh.M Last
    changed    : 12/08/2020 16:16:47 by
                 (modified after loading)
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

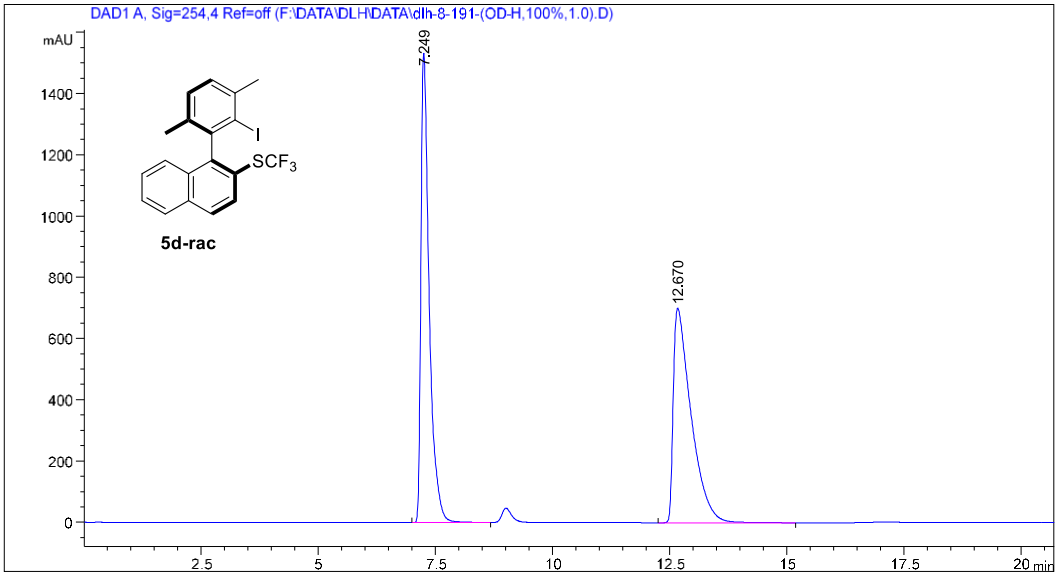



```
    ======================================================================
                          Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 F, Sig=273,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    6.010 MM    0.1582  357.32495   37.63663   2.0713
    2    7.053 MM    0.2446 1.68942e4  1151.18860  97.9287

    Totals :               1.72515e4  1188.82523


LC1260 26/10/2020 18:41:34
LC1260 26/10/2020 18:41:34                                    Page 2 of 2
```

Figure S128. HPLC spectra of **5c**.

Data File F:\DATA\DLH\DATA\dlh-8-191-(OD-H,100%,1.0).D
Sample Name: dlh-8-191-(OD-H,100%,1.0)

```
    ======================================================================
    Acq. Operator   :
                                          Location :  1
    Injection Date  : 29/08/2020 15:37:56
    Acq. Method     : duanlh.M
    Analysis Method : F:\METHOD\duanlh.M Last
    changed    : 20/05/2020 09:56:41 by
    Additional Info : Peak(s) manually integrated
```

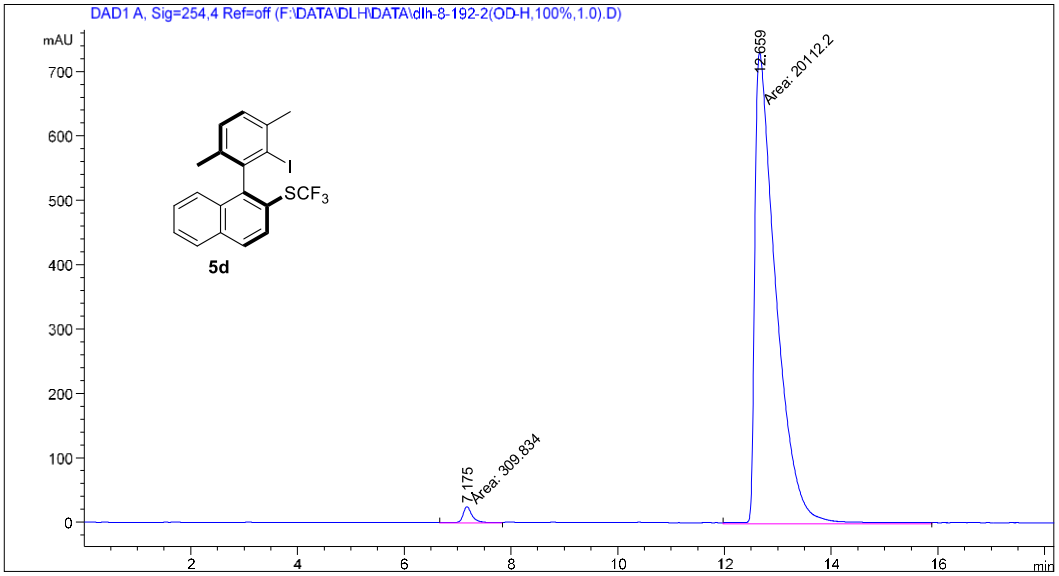



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1     7.249 BB    0.1816 1.88746e4  1533.82813  50.4883
    2    12.670 BB    0.3823 1.85094e4   700.49731  49.5117

    Totals :               3.73840e4  2234.32544


    ======================================================================
    *** End of Report ***


LC1260 02/09/2020 09:27:12
                                                          Page 1 of 1
```

Figure S129. HPLC spectra of **5d-rac**.

Data File F:\DATA\DLH\DATA\dlh-8-192-2(OD-H,100%,1.0).D
Sample Name: dlh-8-192-2(OD-H,100%,1.0)

```
    ====================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 02/09/2020 10:20:03
    Acq. Method     : duanlh.M
    Analysis Method : F:\METHOD\duanlh.M Last
    changed    : 20/05/2020 09:56:41 by
    Additional Info : Peak(s) manually integrated
```

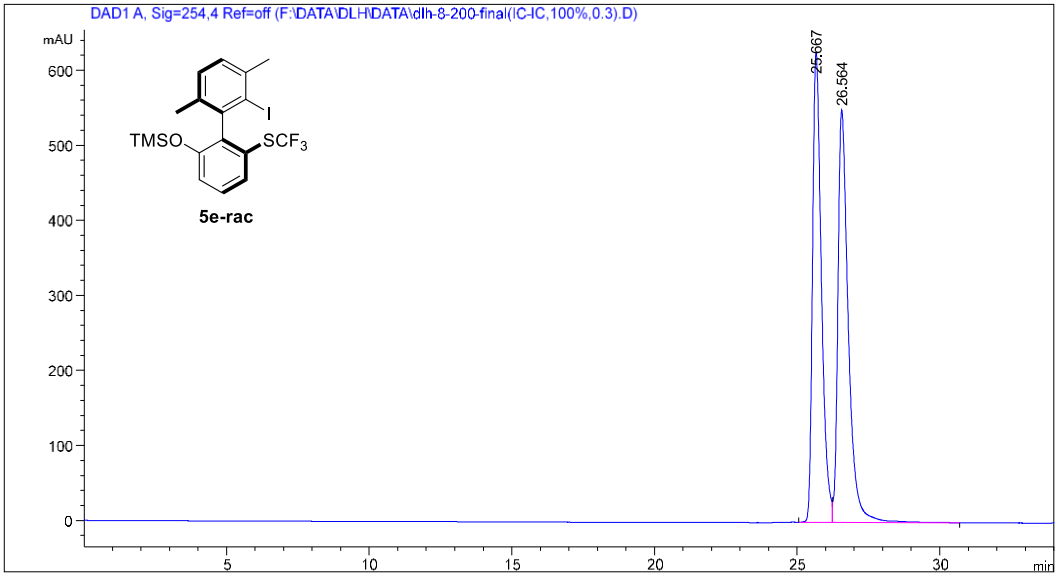



```
    ====================================================================
                         Area Percent Report
    ====================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1     7.175 MM    0.2064  309.83359   25.02227   1.5172
    2    12.659 MM    0.4587 2.01122e4   730.82196  98.4828

    Totals :               2.04220e4   755.84423


    ====================================================================
    *** End of Report ***


LC1260 02/09/2020 10:40:21
                                                          Page 1 of 1
```

Figure S130. HPLC spectra of **5d**.

Data File F:\DATA\DLH\DATA\dlh-8-200-final(IC-IC,100%,0.3).D
Sample Name: dlh-8-200-final(IC-IC,100%,0.3)

```
    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 08/10/2020 19:30:02
                                              Inj Volume : No inj
    Acq. Method     : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 08/10/2020 19:29:16 by
                     (modified after loading)
    Analysis Method : F:\METHOD\duanlh.M
    Last changed    : 20/05/2020 09:56:41 by
```

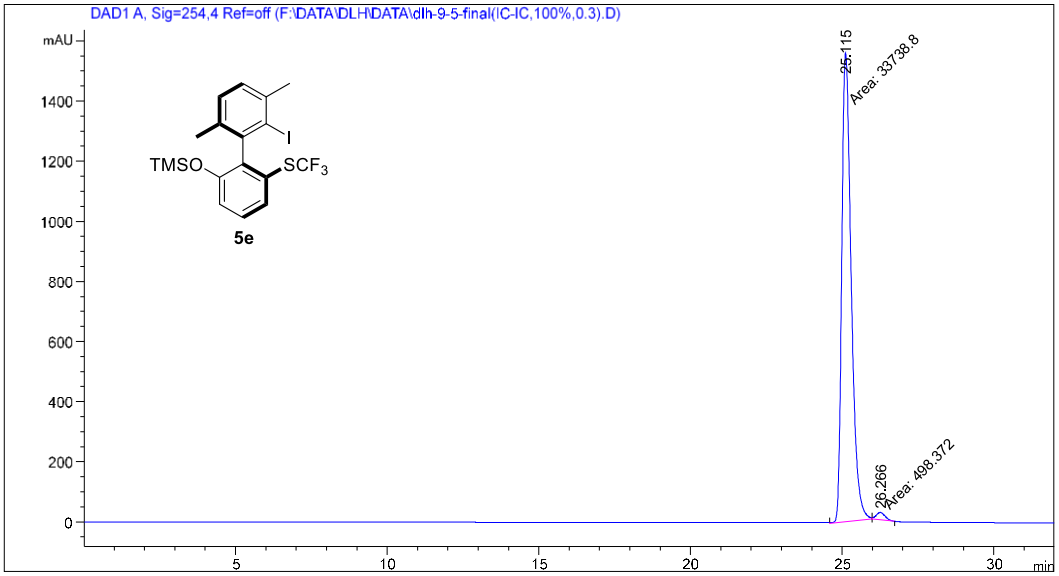



```
    ======================================================================
                         Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    25.667 BV    0.3301 1.35190e4   625.52332  49.1865
    2    26.564 VB    0.3804 1.39662e4   549.69641  50.8135

    Totals :               2.74853e4  1175.21973


    ======================================================================

LC1260 08/10/2020 20:06:04
LC1260 08/10/2020 20:06:04                                    Page 2 of 2
```

Figure S131. HPLC spectra of **5e-rac**.

Data File F:\DATA\DLH\DATA\dlh-9-5-final(IC-IC,100%,0.3).D
Sample Name: dlh-9-5-final(IC-IC,100%,0.3)

```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 08/10/2020 16:07:49
    Acq. Method     : duanlh.M
    Analysis Method : F:\METHOD\duanlh.M Last
    changed    : 20/05/2020 09:56:41 by
    Additional Info : Peak(s) manually integrated
```

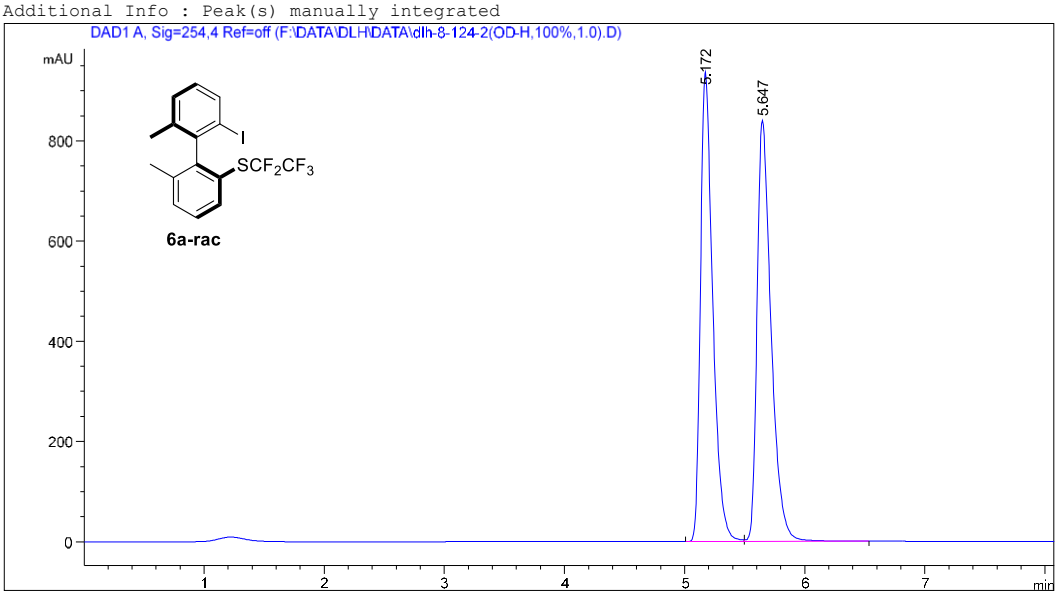



```
    ======================================================================
                         Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    25.115 MM    0.3607 3.37388e4  1559.10449  98.5444
    2    26.266 MM    0.3368  498.37244   24.65848   1.4556

    Totals :               3.42372e4  1583.76297


    ======================================================================
    *** End of Report ***


LC1260 08/10/2020 20:06:51
                                                          Page 1 of 1
```

Figure S132. HPLC spectra of **5e**.

Data File F:\DATA\DLH\DATA\dlh-8-124-2(OD-H,100%,1.0).D
Sample Name: dlh-8-124-2(OD-H,100%,1.0)

```
=====================================================================
Acq. Operator   :
                                        Location :  1
Injection Date  : 04/09/2020 09:35:52
Acq. Method     : duanlh.M
Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
Last changed    : 13/02/2014 23:27:44 by SYSTEM
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :     Signal
Multiplier            :     1.0000
Dilution              :     1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width    Area      Height    Area
  #   [min]       [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
1     5.172 BV    0.1068 6654.72900  938.14410  49.4430
2     5.647 VB    0.1204 6804.68018  840.62762  50.5570

Totals :               1.34594e4  1778.77173


=====================================================================
*** End of Report ***


LC1260 04/09/2020 09:44:41
                                                        Page 1 of 1
```

Figure S133. HPLC spectra of **6a-rac**.

Data File F:\DATA\DLH\DATA\dlh-9-2(OD-H,100%,1.0).D
Sample Name: dlh-9-2(OD-H,100%,1.0)

==========

Acq. Operator :

Location : 1

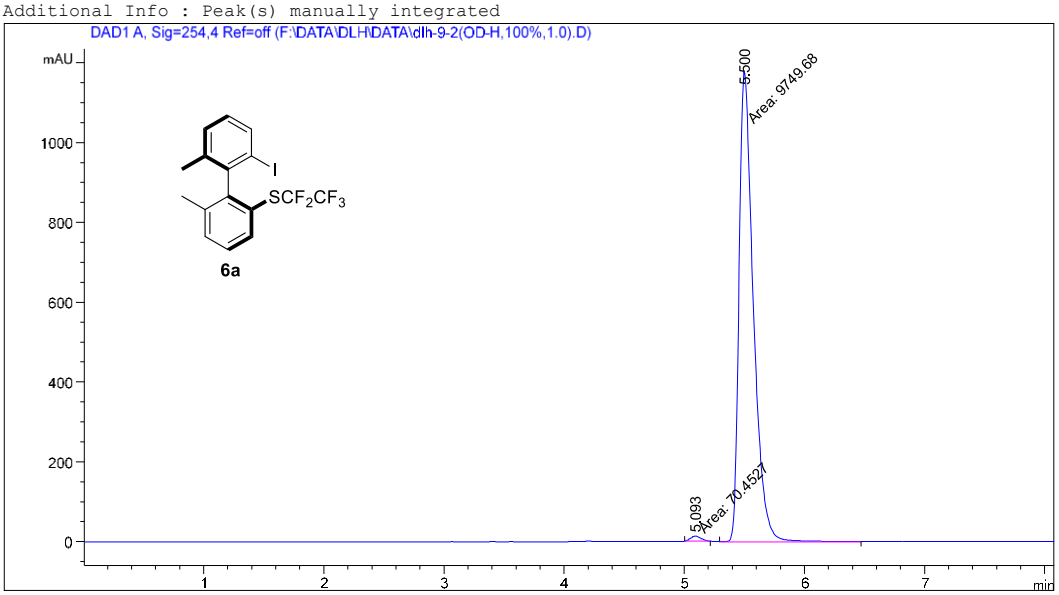
Injection Date : 04/09/2020 09:24:20

Acq. Method : duanlh.M

Analysis Method : C:\Chem32\1\Methods\DEF_LC.M

Last changed : 13/02/2014 23:27:44 by SYSTEM

Additional Info : Peak(s) manually integrated



==========

Area Percent Report

==========

Sorted By : Signal

Multiplier : 1.0000

Dilution : 1.0000

Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.093	MM	0.0957	70.45274	12.26942	0.7174
2	5.500	MM	0.1377	9749.67871	1179.95972	99.2826
Totals :				9820.13145	1192.22914	

==========

*** End of Report ***

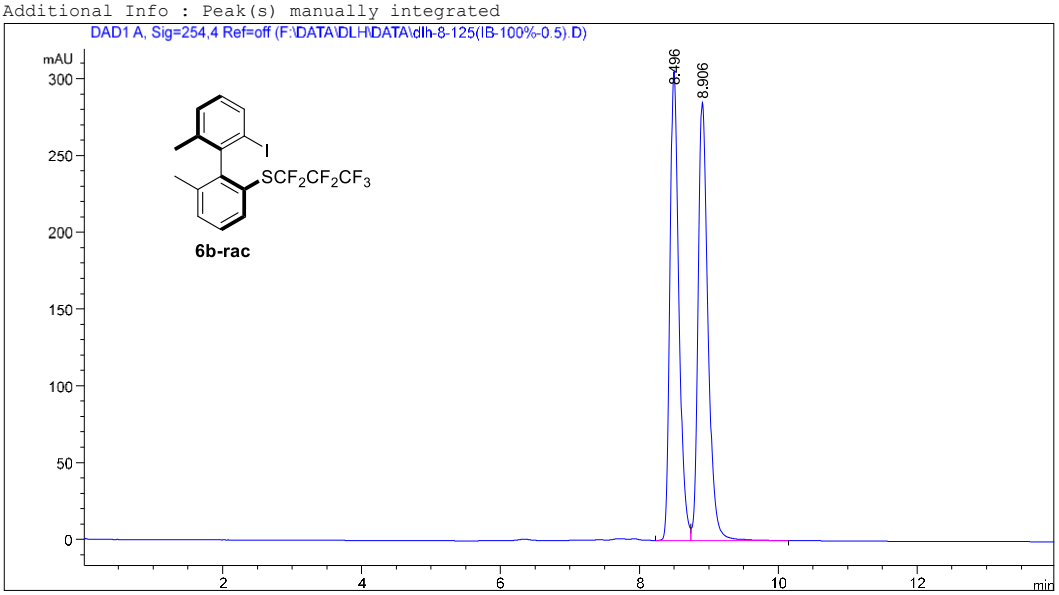
LC1260 04/09/2020 09:43:15

Page 1 of 1

Figure S134. HPLC spectra of **6a**.

Data File F:\DATA\DLH\DATA\dlh-8-125(IB-100%-0.5).D
Sample Name: dlh-8-125(IB-100%-0.5)

==========
Acq. Operator :
Location : 1
Injection Date : 05/10/2020 20:04:20
Acq. Method : duanlh.M
Analysis Method : F:\METHOD\ZK.M
Last changed : 14/07/2019 15:34:15 by
Additional Info : Peak(s) manually integrated



==========
Area Percent Report
==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.496	BV	0.1373	2753.81982	305.10529	49.2794
2	8.906	VB	0.1499	2834.35425	285.25726	50.7206

Totals : 5588.17407 590.36255

==========
*** End of Report ***

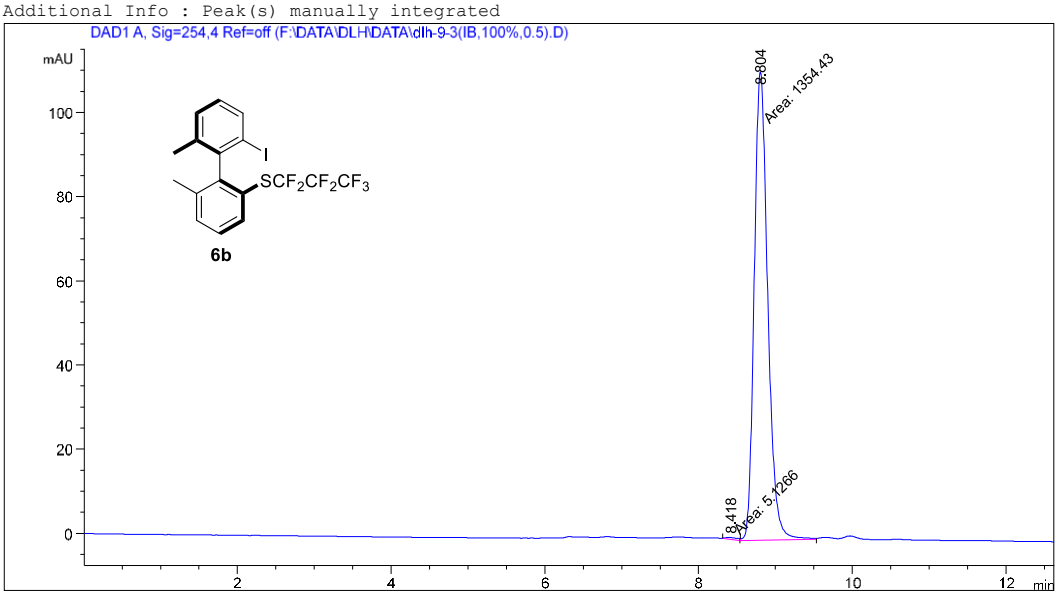
LC1260 07/10/2020 20:38:39

Page 1 of 1

Figure S135. HPLC spectra of **6b-rac**.

Data File F:\DATA\DLH\DATA\dlh-9-3(IB,100%,0.5).D
Sample Name: dlh-9-3(IB,100%,0.5)

```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 07/10/2020 20:25:36
    Acq. Method     : duanlh.M
    Analysis Method : F:\METHOD\ZK.M
    Last changed    : 14/07/2019 15:34:15 by
    Additional Info : Peak(s) manually integrated
```

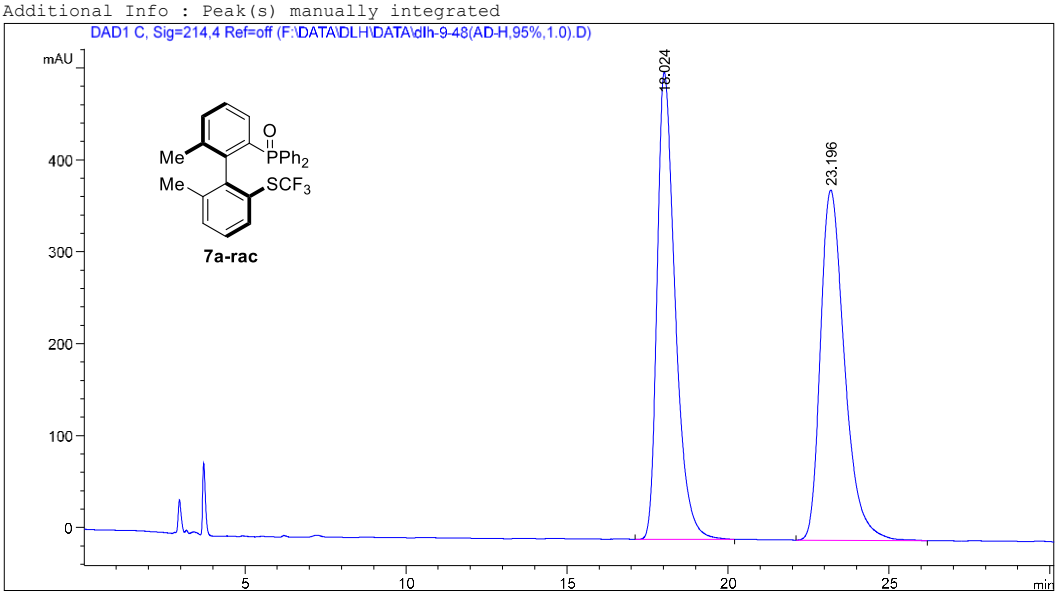



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    8.418 MM    0.1873    5.12660 4.56266e-1   0.3771
    2    8.804 MM    0.2030 1354.43445  111.21605  99.6229

    Totals :               1359.56105  111.67232


    ======================================================================
    *** End of Report ***


LC1260 07/10/2020 20:42:28
```


Figure S136. HPLC spectra of **6b**

Data File F:\DATA\DLH\DATA\dlh-9-48(AD-H,95%,1.0).D
Sample Name: dlh-9-48(AD-H,95%,1.0)

```
    ======================================================================
    Acq. Operator   :
                                          Location :  1
    Injection Date  : 12/10/2020 19:26:17
    Acq. Method     : duanlh.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

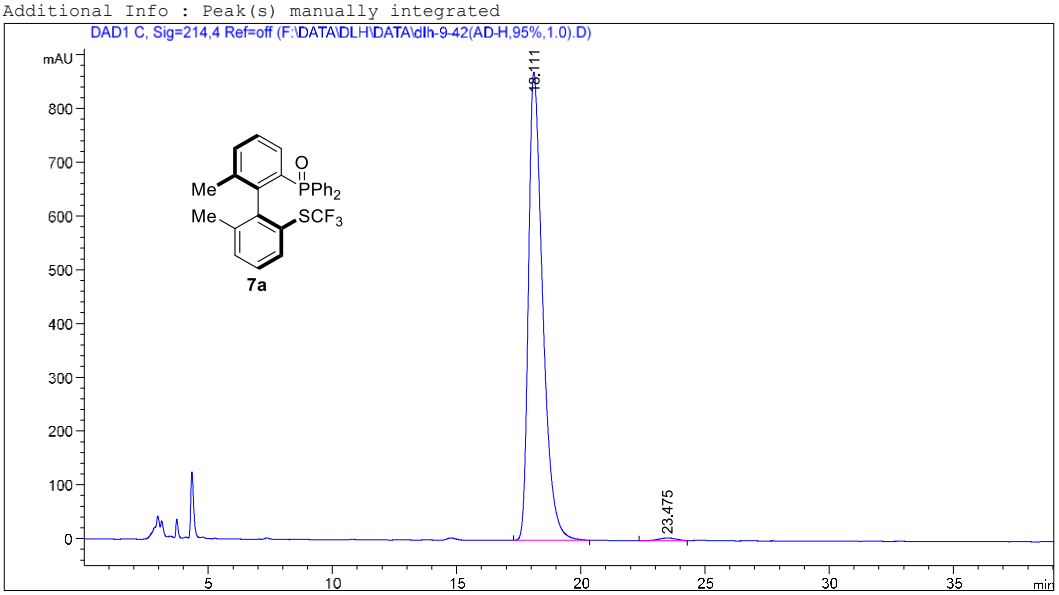



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=214,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]    [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    18.024 BB    0.5900 1.97934e4   508.61966  49.9077
    2    23.196 BB    0.8021 1.98666e4   381.17178  50.0923

    Totals :               3.96599e4   889.79144


    ======================================================================
    *** End of Report ***


LC1260 26/11/2020 19:19:40
                                                          Page 1 of 1
```

Figure S137. HPLC spectra of **7a-rac.**

Data File F:\DATA\DLH\DATA\dlh-9-42(AD-H,95%,1.0).D
Sample Name: dlh-9-42(AD-H,95%,1.0)

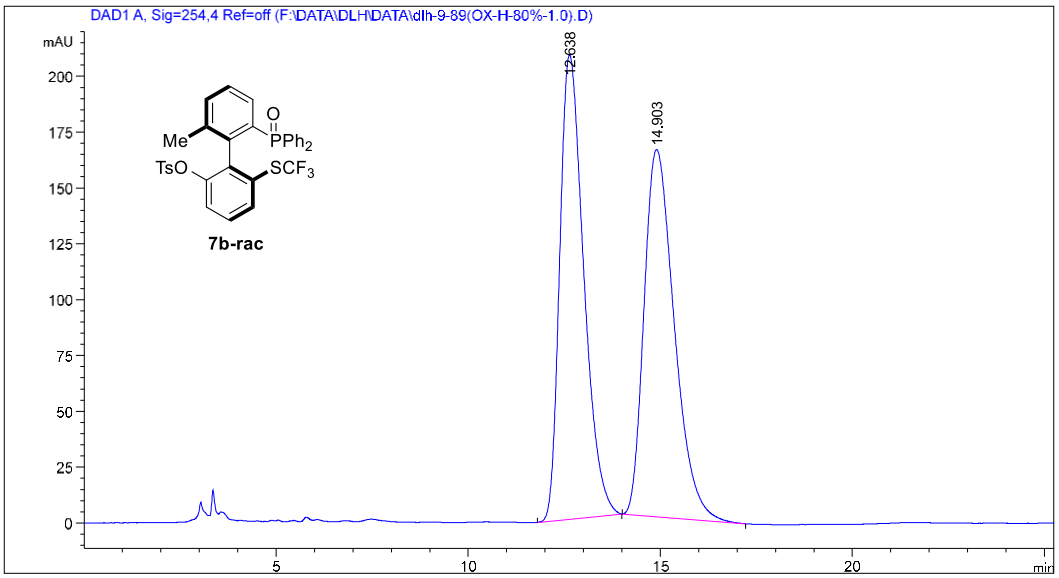
```
==========================================================================
Acq. Operator   :
                                          Location :  1
Injection Date  : 12/10/2020 19:59:06
Acq. Method     : duanlh.M
Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
Last changed    : 13/02/2014 23:27:44 by SYSTEM
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                      Area Percent Report
==========================================================================

Sorted By             :     Signal
Multiplier            :     1.0000
Dilution              :     1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=214,4 Ref=off

Peak RetTime Type  Width    Area      Height    Area
  #   [min]       [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
1    18.111 BB    0.6059 3.46350e4   871.04572  99.2227
2    23.475 BB    0.6249  271.34299    5.33954   0.7773

Totals :               3.49064e4   876.38525


==========================================================================
*** End of Report ***


LC1260 26/11/2020 19:22:25
                                                          Page 1 of 1
```

Figure S138. HPLC spectra of **7a.**

```
Data File F:\DATA\DLH\DATA\dlh-9-89(OX-H-80%-1.0).D
Sample Name: dlh-9-89(OX-H-80%-1.0)

    ======================================================================
    Acq. Operator   :
    Sample Operator :
    Acq. Instrument : LC1260                    Location :  1
    Injection Date  : 01/12/2020 09:51:28
                                              Inj Volume : No inj
    Acq. Method     : F:\METHOD\duanlh.M Last
    changed    : 01/12/2020 09:33:05 by
                 (modified after loading)
    Analysis Method : F:\METHOD\duanlh.M Last
    changed    : 20/05/2020 09:56:41 by
    Additional Info : Peak(s) manually integrated
```

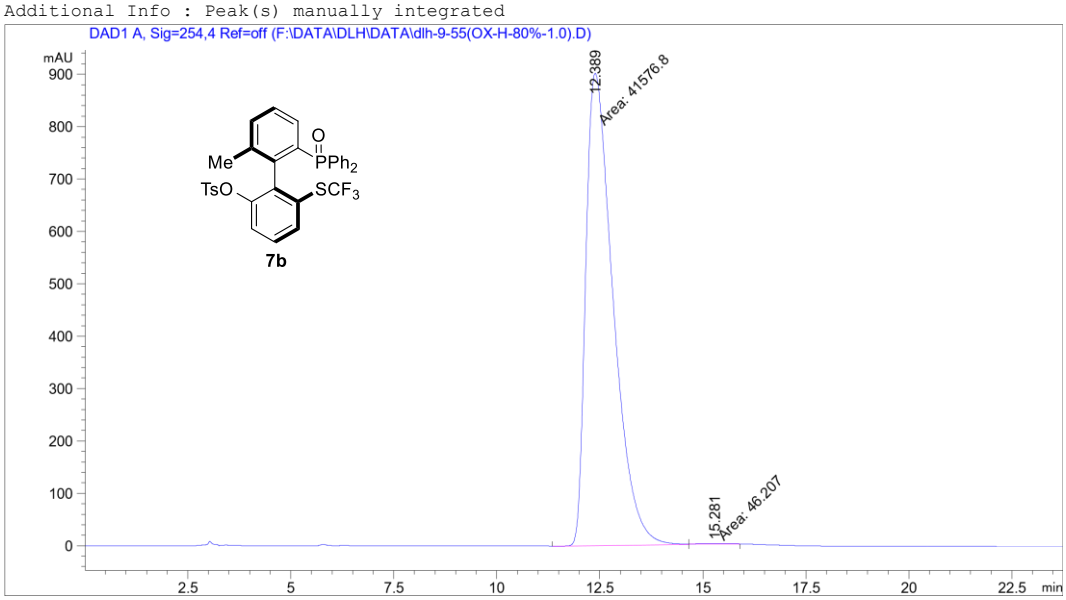



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]     [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    12.638 BB    0.6683 9022.07617  207.88490  50.0726
    2    14.903 BB    0.8424 8995.90625  164.39211  49.9274

    Totals :               1.80180e4   372.27701


LC1260 01/12/2020 10:48:48
LC1260 01/12/2020 10:48:48                                          Page 2 of 2
```

Figure S139. HPLC spectra of **7b.**

Data File F:\DATA\DLH\DATA\dlh-9-55(OX-H-80%-1.0).D
Sample Name: dlh-9-55(OX-H-80%-1.0)

```
==========================================================================
Acq. Operator   :
                                          Location :  1
Injection Date  : 01/12/2020 10:23:38
Acq. Method     : duanlh.M
Analysis Method : F:\METHOD\duanlh.M Last
changed    : 20/05/2020 09:56:41 by
Additional Info : Peak(s) manually integrated
```

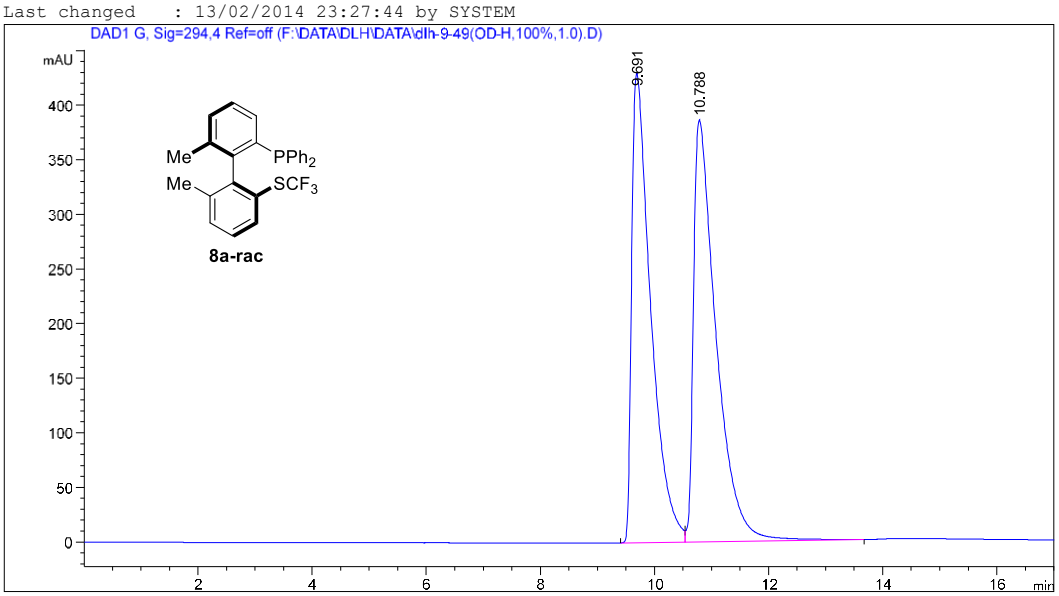



```
==========================================================================
                      Area Percent Report
==========================================================================

Sorted By             :     Signal
Multiplier            :     1.0000
Dilution              :     1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
1    12.389 MM    0.7685 4.15768e4   901.63940  99.8890
2    15.281 MM    0.8177   46.20699 9.41828e-1   0.1110

Totals :               4.16230e4   902.58123


==========================================================================
*** End of Report ***


LC1260 01/12/2020 10:50:17
                                                          Page 1 of 1
```

Figure S140. HPLC spectra of **7b.**

Data File F:\DATA\DLH\DATA\dlh-9-49(OD-H,100%,1.0).D
Sample Name: dlh-9-49(OD-H,100%,1.0)

```
==========================================================================
Acq. Operator   :
                                          Location :  1
Injection Date  : 03/12/2020 19:46:30
Acq. Method     : duanlh.M
Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
Last changed    : 13/02/2014 23:27:44 by SYSTEM
```

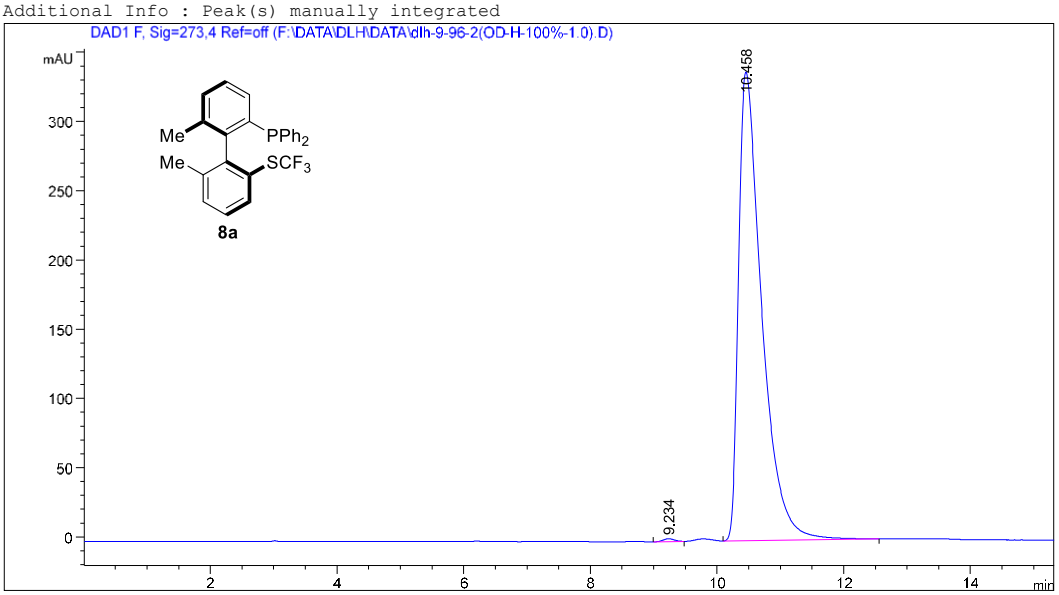



```
==========================================================================
                      Area Percent Report
==========================================================================

Sorted By             :     Signal
Multiplier            :     1.0000
Dilution              :     1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 G, Sig=294,4 Ref=off

Peak RetTime Type  Width    Area      Height    Area
  #   [min]       [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
1     9.691 BV    0.3384 9963.33105  429.92563  48.4443
2    10.788 VB    0.4002 1.06032e4   386.33618  51.5557

Totals :               2.05666e4   816.26181


==========================================================================
*** End of Report ***



LC1260 03/12/2020 20:06:58
                                                          Page 1 of 1
```

Figure S141. HPLC spectra of **8a-rac.**

Data File F:\DATA\DLH\DATA\dlh-9-96-2(OD-H-100%-1.0).D
Sample Name: dlh-9-96-2(OD-H-100%-1.0)

```
    ======================================================================
    Acq. Operator   :
                                           Location :  1
    Injection Date  : 09/12/2020 15:59:05
    Acq. Method     : duanlh.M
    Analysis Method : C:\Chem32\1\Methods\DEF_LC.M
    Last changed    : 13/02/2014 23:27:44 by SYSTEM
    Additional Info : Peak(s) manually integrated
```

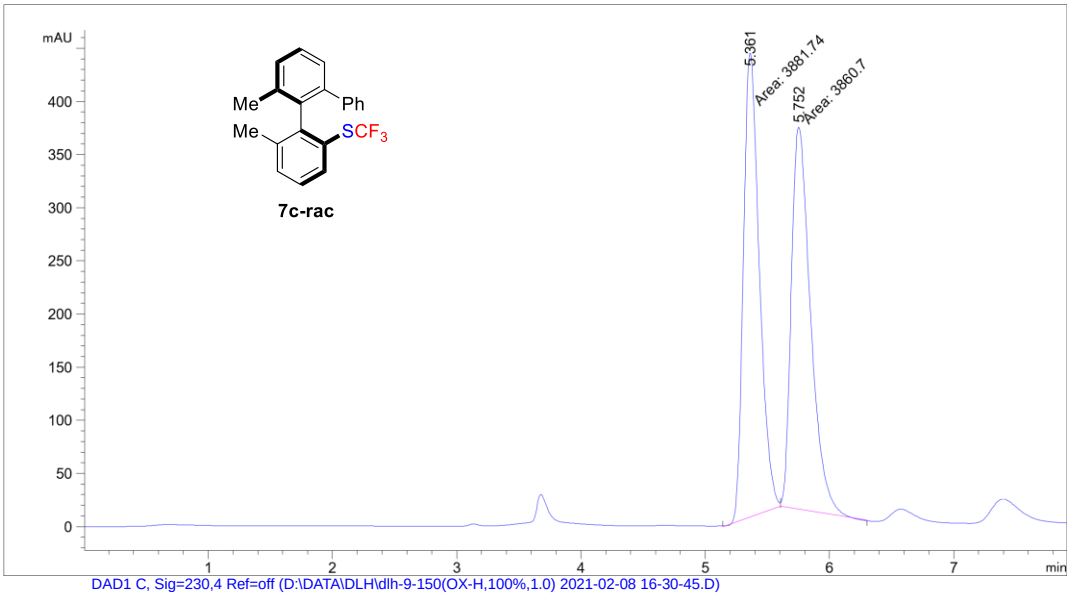



```
    ======================================================================
                        Area Percent Report
    ======================================================================

    Sorted By             :     Signal
    Multiplier            :     1.0000
    Dilution              :     1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 F, Sig=273,4 Ref=off

    Peak RetTime Type  Width    Area      Height    Area
      #   [min]       [min]   [mAU*s]    [mAU]      %
    ----|-------|----|-------|----------|----------|--------|
    1    9.234 BB    0.1809   24.11418    2.02472   0.2792
    2    10.458 BB    0.3790 8612.77930  338.34811  99.7208

    Totals :               8636.89348  340.37283


    ======================================================================
    *** End of Report ***


LC1260 09/12/2020 16:27:39
                                                          Page 1 of 1
```

Figure S142. HPLC spectra of **8a.**

Data File D:\DATA\DLH\dlh-9-150(OX-H,100%,1.0) 2021-02-08 16-30-45.D
Sample Name: dlh-9-150(OX-H,100%,1.0)

```
==========================================================================
Acq. Operator   : SYSTEM
                                          Location :  1
Injection Date  : 2021-02-08 4:30:46 PM
Acq. Method     : xjw.M
Analysis Method : D:\DATA\JWXI\xjw.M
Last changed    : 2021-01-25 8:43:47 PM by SYSTEM
Additional Info : Peak(s) manually integrated
```

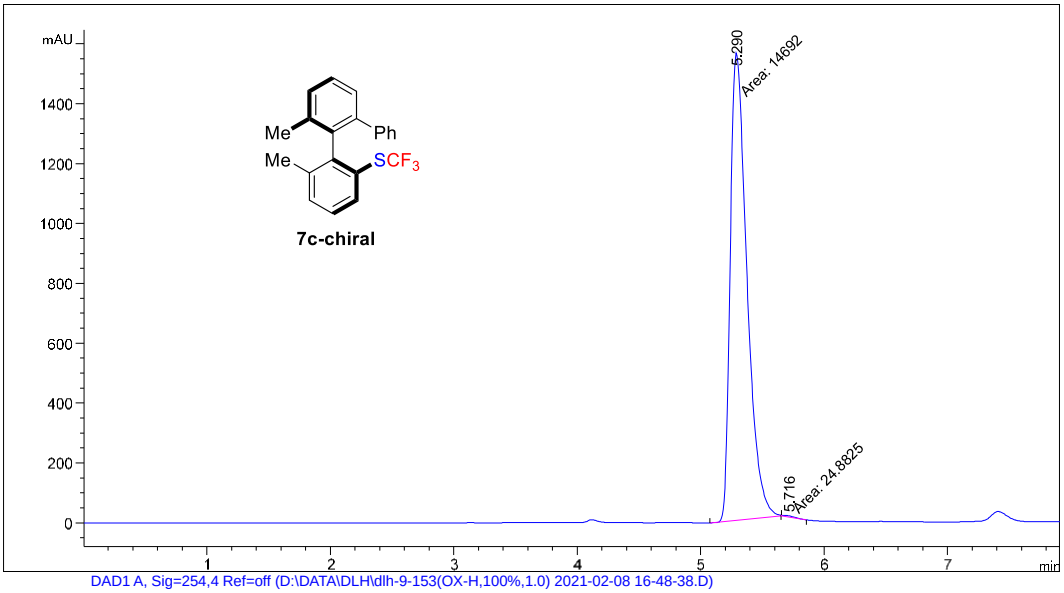


DAD1 C, Sig=230,4 Ref=off (D:\DATA\DLH\dlh-9-150(OX-H,100%,1.0) 2021-02-08 16-30-45.D)

```
==========================================================================
                      Area Percent Report
==========================================================================

Sorted By             :     Signal
Multiplier            :     1.0000
Dilution              :     1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=230,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
1     5.361 MM    0.1481 3881.73926  436.88873  50.1358
2     5.752 MM    0.1790 3860.70337  359.50961  49.8642

Totals :               7742.44263  796.39835


==========================================================================
*** End of Report ***
```

Figure S143. HPLC spectra of **7c-rac**.

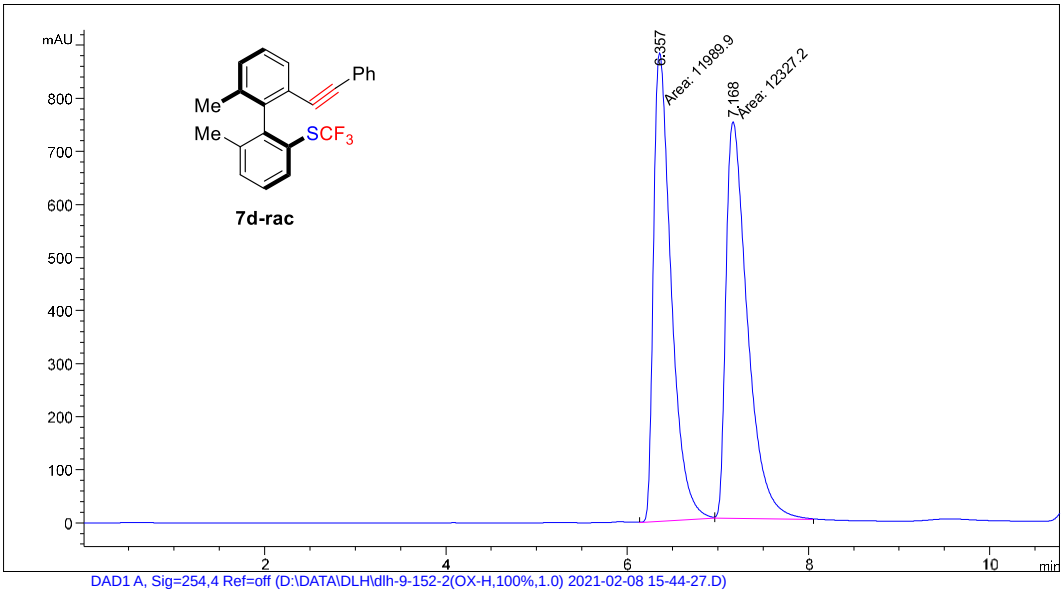
```
Data File D:\DATA\DLH\dlh-9-153(OX-H,100%,1.0) 2021-02-08 16-48-38.D
Sample Name: dlh-9-153(OX-H,100%,1.0)

    ======================================================================
    Acq. Operator   : SYSTEM
                                                      Location :   1
    Injection Date  : 2021-02-08 4:48:38 PM
    Acq. Method     : xjw.M
    Analysis Method : D:\DATA\JWXI\xjw.M
    Last changed    : 2021-01-25 8:43:47 PM by SYSTEM
    Additional Info : Peak(s) manually integrated
```




```
    DAD1 A, Sig=254,4 Ref=off (D:\DATA\DLH\dlh-9-153(OX-H,100%,1.0) 2021-02-08 16-48-38.D)
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1   5.290 MM    0.1567 1.46920e4  1562.15405  99.8309
    2   5.716 MM    0.1088   24.88251    3.81034   0.1691

    Totals :                 1.47168e4  1565.96439


    ======================================================================
    *** End of Report ***


LC-1260 2021-02-08 4:57:34 PM SYSTEM
```

Figure S144. HPLC spectra of **7c-chiral**.

```
Data File D:\DATA\DLH\dlh-9-152-2(OX-H,100%,1.0) 2021-02-08 15-44-27.D
Sample Name: dlh-9-152-2(OX-H,100%,1.0)

    ======================================================================
    Acq. Operator   : SYSTEM
                                                    Location :   1
    Injection Date  : 2021-02-08 3:44:27 PM
    Acq. Method     : xjw.M
    Analysis Method : D:\DATA\JWXI\xjw.M
    Last changed    : 2021-01-25 8:43:47 PM by SYSTEM
    Additional Info : Peak(s) manually integrated
```

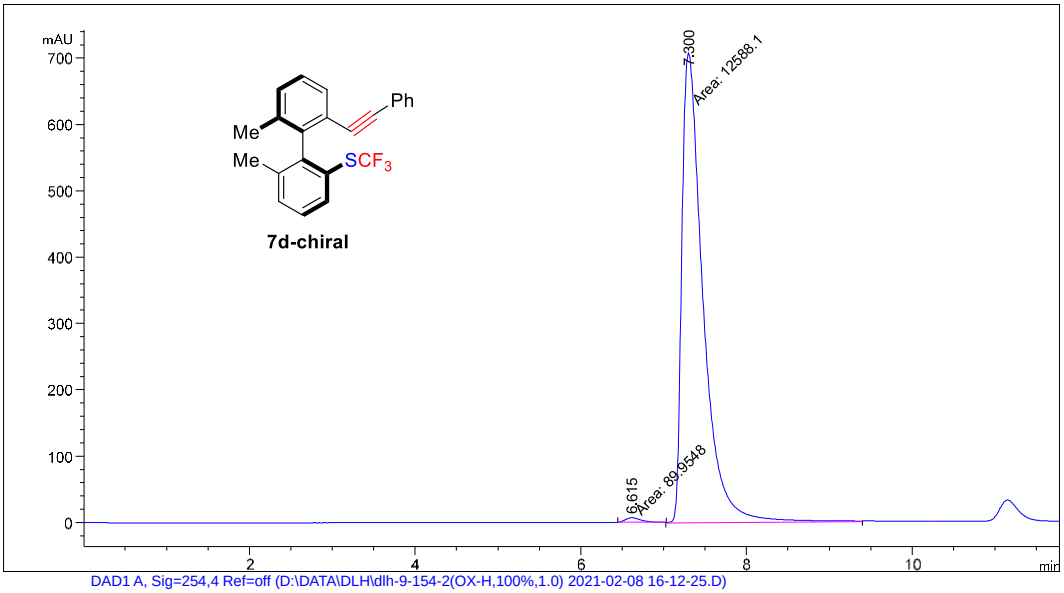



```
    DAD1 A, Sig=254,4 Ref=off (D:\DATA\DLH\dlh-9-152-2(OX-H,100%,1.0) 2021-02-08 15-44-27.D)
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
    1    6.357 MM    0.2265 1.19899e4   882.36871  49.3063
    2    7.168 MM    0.2748 1.23272e4   747.60754  50.6937

    Totals :                 2.43171e4  1629.97626


    ======================================================================
    *** End of Report ***


LC-1260 2021-02-08 4:16:15 PM SYSTEM
```

Figure S145. HPLC spectra of **7d-rac**.

Data File D:\DATA\DLH\dlh-9-154-2(OX-H,100%,1.0) 2021-02-08 16-12-25.D
Sample Name: dlh-9-154-2(OX-H,100%,1.0)

```
==========================================================================
Acq. Operator   : SYSTEM
                                                    Location :   1
Injection Date  : 2021-02-08 4:12:26 PM
Acq. Method     : xjw.M
Analysis Method : D:\DATA\JWXI\xjw.M
Last changed    : 2021-01-25 8:43:47 PM by SYSTEM
Additional Info : Peak(s) manually integrated
```



DAD1 A, Sig=254,4 Ref=off (D:\DATA\DLH\dlh-9-154-2(OX-H,100%,1.0) 2021-02-08 16-12-25.D)

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
1   6.615 MM    0.2169   89.95481    6.91076   0.7095
2   7.300 MM    0.2964 1.25881e4   707.94702  99.2905

Totals :                 1.26780e4   714.85778


==========================================================================
*** End of Report ***


LC-1260 2021-02-08 4:33:02 PM SYSTEM
```

Figure S146. HPLC spectra of **7d-chiral**.