ELECTRONIC SUPPLEMENTARY INFORMATION

Chiral Bicyclic NHC/Ir Complexes for Catalytic Asymmetric Transfer Hydrogenation of Ketones

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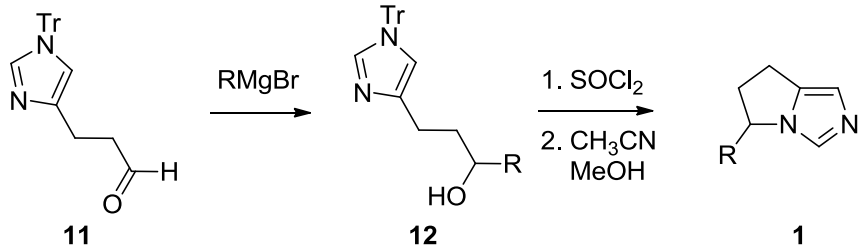
<General>

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glove box techniques under prepurified argon. NMR spectra were recorded at room temperature at 400 MHz or 500 MHz for ^{1}H and 100 MHz or 125 MHz for ^{13}C. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR and chloroform-d (δ 77.0) for ^{13}C NMR. High-resolution mass spectra were recorded on Orbitrap mass spectrometers. Single crystal X-ray diffraction data were collected at 173K on a CCD diffractometer with Mo Ka (l = 0.71073) radiation and graphite monochromator.

<Materials>

THF was distilled from sodium benzophenone-ketyl under argon prior to use. CH_2Cl_2 and 1,2-dichloroethane were distilled from CaH_2 under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. Methanol was distilled from magnesium under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. 3-(l-Trityl-1*H*-imidazol-4-yl)propionaldehyde (**11**), (*R*)-5-phenyl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazole (**1a**), and (*R*)-7-isopropyl-3-phenyl-2,3-dihydroimidazo[5,1-b]oxazole were prepared according to the reported procedures.[1] Aryl magnesium bromides in THF were prepared from magnesium and corresponding aryl bromides. Di(4-tolyl)methyl bromide and di-(4-trifluoromethylphenyl)methyl bromide were prepared from the corresponding alcohols and acetyl bromide according to the reported procedures.[2] Anhydrous CH_3CN, anhydrous *i*-PrOH, thionyl chloride, 1,2-dibromoethane, α, α'-dibromo-*p*-xylene, diphenylmethyl bromide, benzyl bromide, di(4-tolyl)methyl bromide, silver oxide, bis(1,5-cyclooctadiene)diiridium(I) dichloride, and potassium *tert*-butoxide were used as received.

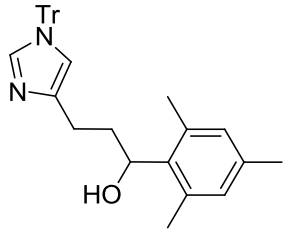
<Procedures for the Preparation of Chiral Imidazoles 1>



11 **12** **1**

General Procedure A: To a solution of 3-(1-trityl-1*H*-imidazol-4-yl)propionaldehyde (**11**) (1.0 eq.) in dry THF was added aryl magnesium bromide (1.5 eq.) in THF under N_2 atmosphere at 0 °C. The mixture was gradually warmed up to room temperature and stirred for 15 h. Then, the mixture was cooled to 0 °C and quenched by addition of saturated aqueous NH_4Cl. The aqueous layer was extracted with CH_2Cl_2 twice. Then the combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was chromatographed on silica gel to give the desired alcohol **12**.

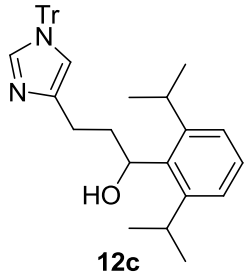
1-Mesityl-3-(1-trityl-1*H*-imidazol-4-yl)propan-1-ol (**12b**); Following the General Procedure A; The aldehyde **11** (1.80 g, 4.91 mmol) and mesitylmagnesium bromide in THF (1.00 M, 7.37 mL, 7.37 mmol) were used; purified by column chromatography (EtOAc) to give **12b** (1.85 g, 78% yield) as white solid; mp 189-191 °C; ^{1}H NMR ($CDCl_3$) δ 1.89 (dtd, *J* = 14.4, 7.2, 3.6 Hz, 1H), 2.22 (s, 3H), 2.20-2.31 (m, 1H), 2.36 (s, 6H), 2.76 (t, *J* = 6.8 Hz, 2H), 4.03 (br s, 1H), 5.15 (dd, *J* = 10.0, 4.0 Hz 1H), 6.57 (d, *J* = 1.2 Hz, 1H), 6.78 (s, 2H), 7.12-7.16 (m, 6H), 7.31-7.34 (m, 9H), 7.36 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.7, 25.7, 35.2, 70.7, 75.1, 117.9, 128.0, 129.7, 129.9, 135.8, 136.0, 137.4, 138.1, 141.1, 142.5; HRMS (ESI) calcd for $C_{34}H_{35}N_2O$ (M^++H) 487.2744, found 487.2724.



12b

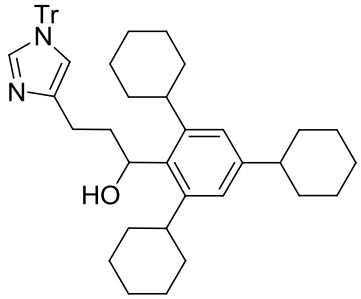
1-(2,6-Diisopropylphenyl)-3-(1-trityl-1*H*-imidazol-4-yl)propan-1-ol (**12c**); Following the General Procedure A; The aldehyde **11** (3.02 g, 8.21 mmol) and 2,6-diisopropylphenylmagnesium bromide in THF (1.00 M, 12.3 mL, 12.3 mmol) were used; purified by column chromatography (EtOAc) to give **12c** (3.17 g, 73% yield) as white solid; mp 190-191 °C; ^{1}H NMR ($CDCl_3$) δ 1.20 (d, *J* = 7.2 Hz, 12H), 1.93 (dtd, *J* = 14.4, 7.2, 3.6 Hz, 1H), 2.33 (ddt, *J* = 14.4, 10.0, 7.2 Hz, 1H), 2.79 (t, *J* = 7.2 Hz, 2H), 3.16 (br s, 1H), 3.98 (br s, 1H), 4.22 (br s, 1H), 5.37 (dd, *J* = 10.0, 3.6 Hz, 1H), 6.58 (d, *J* = 1.2 Hz, 1H), 7.13-7.20 (m, 9H), 7.31-7.35 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 24.7, 25.9, 29.1, 37.3, 69.3,

75.1, 117.9, 127.2, 128.0, 129.7, 138.2, 138.3, 141.0, 142.5; HRMS (ESI) calcd for $C_{37}H_{41}N_2O$ (M^++H) 529.3213, found 529.3202.



12c

1-(2,4,6-Tricyclohexylphenyl)-3-(1-trityl-1*H*-imidazol-4-yl)propan-1-ol (**12d**); Following the General Procedure A; The aldehyde **11** (2.00 g, 5.46 mmol) and tricyclohexylphenylmagnesium bromide in THF (1.00 M, 8.19 mL, 8.19 mmol) were used; purified by column chromatography (EtOAc) to give **12d** (2.46 g, 65% yield) as white solid; mp 216-220 °C; ^{1}H NMR ($CDCl_3$) δ 1.19-1.52 (m, 15H), 1.64-1.91 (m, 15H), 1.98 (dtd, *J* = 14.4, 7.6, 4.4 Hz, 1H), 2.27 (ddt, *J* = 13.6, 10.0, 6.8 Hz, 1H), 2.42 (tt, *J* =11.2, 2.8 Hz, 1H), 2.74 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.79 (dq, *J* =14.4, 7.2 Hz, 1H), 2.79 (br s, 1H), 3.56 (br s, 1H), 3.58 (br s, 1H), 5.31 (dd, *J* = 10.0, 4.8 Hz, 1H), 6.58 (s, 1H), 6.94 (br s, 2H), 7.12-7.17 (m, 6H), 7.30-7.34 (m, 9H), 7.37 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.0, 26.3, 26.5, 27.1, 27.3, 27.3, 34.5, 34.8, 35.3, 37.4, 40.2, 44.6, 69.6, 75.2, 117.9, 128.0, 129.8, 136.0, 138.3, 141.5, 142.7, 146.1; HRMS (ESI) calcd for $C_{49}H_{59}N_2O$ (M^++H) 691.4622, found 691.4601.

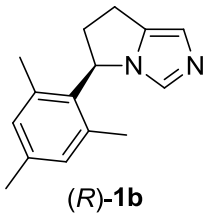


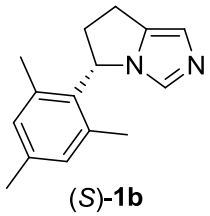
12d

General Procedure B: To a solution of alcohol **12** (1.0 eq.) in CH_2Cl_2 was added thionyl chloride (3.5 eq.). The resulting mixture was heated to 40 °C and stirred for 1 h. Then the mixture was cooled to 0 °C and quenched by addition of saturated aqueous $NaHCO_3$. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude product. The product was dissolved in 30 mL of CH_3CN and refluxed for 20 h. Then, the mixture was cooled to room temperature, added 30 mL of MeOH, and refluxed for an additional 11 h. After concentration, the residue was partitioned between Et_2O and H_2O. The organic layer was extracted with 1N HCl (10 mL) twice. The combined aqueous extracts were adjusted to pH = 8 by addition of NaOH solution

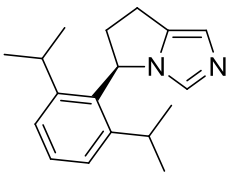
and extracted with CH_2Cl_2 three times. The organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was chromatographed on silica gel to give racemic **1**.

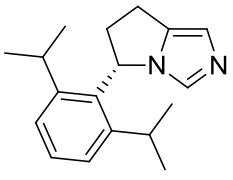
(+)- and (–)-5-Mesityl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazole (**1b**); Following the General Procedure B; The alcohol **12b** (1.75 g, 3.6 mmol) was used; purified by column chromatography ($CHCl_3$/MeOH) to give racemic **1b** (575 mg, 71% yield) as white solid; ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3H), 2.27 (s, 3H), 2.43 (s, 3H), 2.65-2.76 (m, 1H), 2.91-3.08 (m, 3H), 5.71 (t, *J* = 8.4 Hz, 1H), 6.76 (s, 1H), 6.83 (s, 1H), 6.89 (s, 1H), 7.18 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.5, 20.7, 21.7, 36.2, 56.0, 119.4, 129.3, 130.1, 131.6, 131.8, 136.4, 136.6, 136.7, 137.7; HRMS (ESI) calcd for $C_{15}H_{19}N_2$ (M^++H) 227.1543, found 227.1537; Enantiomerically pure (*R*)-**1b** and (*S*)-**1b** were obtained as clear oil by separation using preparative HPLC: Daicel Chiralcel OD-H, 2 cm × 25 cm, hexane/*i*-PrOH = 9/1, 5.0 mL/min; t_+ = 26.2 min [(+)-**1b** $[\alpha]_D^{22}$ +137.6 (*c* 1.00, $CHCl_3$)], t_- = 43.4 min [(–)-**1b**].


(*R*)-**1b**

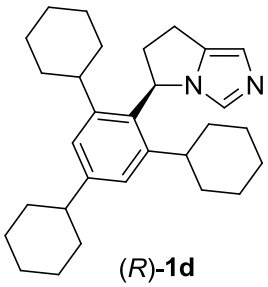

(*S*)-**1b**

(*R*)-(+)- and (*S*)-(–)-5-(2,6-Diisopropylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazole (**1c**); Following the General Procedure B; The alcohol **12c** (3.17 g, 6.00 mmol) was used; purified by column chromatography ($CHCl_3$/MeOH) to give racemic **1c** (950 mg, 59% yield) as white solid; ^{1}H NMR ($CDCl_3$) δ 0.87 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.31 (d, *J* = 6.8 Hz, 3H), 1.33 (d, *J* = 6.4 Hz, 3H), 2.47 (sept, *J* = 6.8 Hz, 1H), 2.70-2.84 (m, 1H), 2.95–3.12 (m, 3H), 3.33 (sept, *J* = 6.8 Hz, 1H), 5.87 (t, *J* = 8.8 Hz, 1H), 6.78 (s, 1H), 7.12 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 23.9, 24.1, 24.7, 28.1, 29.9, 38.1, 54.8, 120.1, 122.7, 126.0, 128.7, 129.8, 131.7, 136.1, 147.1, 149.2; HRMS (ESI) calcd for $C_{18}H_{25}N_2$ (M^++H) 269.2012, found 269.2010; Enantiomerically pure (*R*)-(+)-**1c** and (*S*)-(–)-**1c** were obtained as white solid by separation using preparative HPLC: Daicel Chiralcel OD-H, 2 cm × 25 cm, hexane/*i*-PrOH = 9/1, 5.0 mL/min; t_R = 18.9 min [(*R*)-(+)-**1c** $[\alpha]_D^{18}$ +113.6 (*c* 1.00, $CHCl_3$), mp 100-102 °C], t_S = 29.8 min [(*S*)-(–)-**1c**]; The absolute configuration was determined by anomalous dispersion effects in X-ray diffraction measurements on **8cv**.

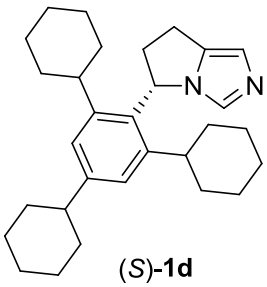

(*R*)-(+)-**1c**


(*S*)-(–)-**1c**

(+)- and (–)-5-(2,4,6-Tricyclohexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazole (**1d**); Following the General Procedure B; The alcohol **12d** (2.46 g, 3.56 mmol) was used; purified by column chromatography ($CHCl_3$/MeOH) to give racemic **1d** (1.15 g, 75% yield) as white solid; ^{1}H NMR ($CDCl_3$) δ 0.75 (qt, *J* = 10.4, 3.2 Hz, 1H), 1.07-1.62 (m, 17H), 1.67-1.92 (m, 12H), 2.02 (tt, *J* = 11.0, 3.5 Hz, 1H), 2.46 (tt, *J* = 11.5, 3.5 Hz, 1H), 2.68-2.78 (m, 1H), 2.81 (tt, *J* = 11.5, 2.5 Hz, 1H), 2.95-3.12 (m, 3H), 5.78 (t, *J* = 8.5 Hz, 1H), 6.78 (s, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.99 (d, *J* = 1.5 Hz, 1H), 7.12 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 26.08, 26.14, 26.2, 26.88, 26.95, 27.18, 27.21, 27.5, 34.3, 34.5, 34.9, 35.0, 35.5, 38.4, 39.4, 41.1, 44.5, 54.7, 120.0, 121.9, 125.1, 129.6, 130.1, 136.3, 146.0, 147.6, 147.8; HRMS (ESI) calcd for $C_{30}H_{43}N_2$ (M^++H) 431.3421, found 431.3419; Enantiomerically pure (*R*)-**1d** and (*S*)-**1d** were obtained as white solid by separation using preparative HPLC: Daicel Chiralcel OD-H, 2 cm × 25 cm, hexane/*i*-PrOH = 9/1, 5.0 mL/min; t_+ = 11.5 min [(+)-**1d** $[\alpha]_D^{22}$ +44.1 (*c* 1.00, $CHCl_3$), mp 218-220 °C], t_- = 55.0 min [(–)-**1d**].

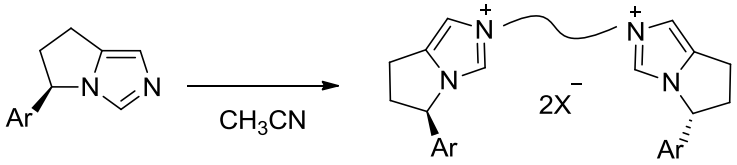


(*R*)-**1d**



(*S*)-**1d**

<Procedures for the Preparation of Bisimidazolium Salts 3>

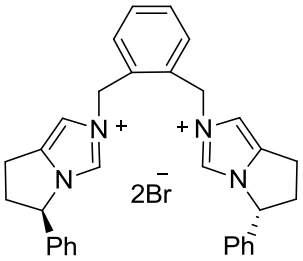


1 **3**

General Procedure C: A mixture of **1** (2.2 eq.) and linking reagent (1 eq.) in dry CH_3CN was heated to 90 °C and stirred for 3 days. After cooling to room temperature, the mixture was concentrated under reduced pressure and purified by reprecipitation to give the desired bisimidazolium salts **3**.

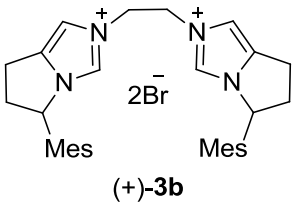
(*R*,*R*)-(+)-2,2'-(1,2-Phenylenebis(methylene))bis(5-phenyl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ium) dibromide ((*R*,*R*)-(+)-**3a**); Following the General Procedure C; (*R*)-**1a** (130 mg, 0.71 mmol) and α,α'-dibromo-*p*-xylene (84.7 mg, 0.32 mmol) were used; purified by reprecipitation (CH_2Cl_2/ether) to give (*R*,*R*)-(+)-**3a** (201 mg, 99% yield) as light brown solid; mp 98-99 °C; $[\alpha]_D^{22}$ +122.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.54-2.68 (m, 2H), 3.07-3.27 (m, 6H), 5.96 (t, *J* = 6.4,

2H), 6.21 (s, 4H), 7.09 (t, J = 4.2 Hz, 2H), 7.20-7.43 (m, 12H), 7.61 (s, 2H), 9.07 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 22.8, 37.6, 51.9, 64.5, 115.5, 126.4, 129.0, 129.4, 129.5, 130.8, 132.8, 136.6, 139.0; HRMS (ESI) calcd for $C_{32}H_{32}BrN_4$ (M^+–Br) 551.1805, found 551.1791.



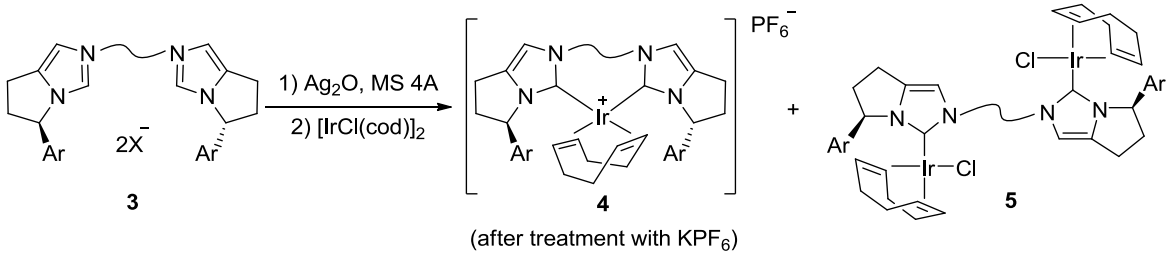
(*R,R*)-(+)-**3a**

(+)-2,2'-(Ethane-1,2-diyl)bis(5-mesityl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ium) dibromide ((+)-**3b**); Following the General Procedure C; (+)-**1b** (120 mg, 0.53 mmol) and 1,2-dibromoethane (45.3 mg, 0.24 mmol) were used; purified by reprecipitation (CH_2Cl_2/ether) to give (+)-**3b** (132.2 mg, 86% yield) as light brown solid; mp 156-157 °C; $[\alpha]_D^{22}$ +143.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 6H), 2.26 (s, 6H), 2.44 (s, 6H), 2.64-2.75 (m, 2H), 2.91-3.29 (m, 6H), 5.11-5.33 (m, 4H), 6.00 (t, J = 8.8 Hz, 2H), 6.83 (s, 2H), 6.90 (s, 2H), 8.73 (s, 2H), 9.31 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 19.0, 20.7, 22.7, 34.4, 48.9, 60.3, 117.3, 128.3, 130.1, 131.1, 132.1, 134.9, 136.8, 137.8, 139.2; HRMS (ESI) calcd for $C_{32}H_{40}BrN_4$ (M^+–Br) 559.2431, found 559.2415.



(+)-**3b**

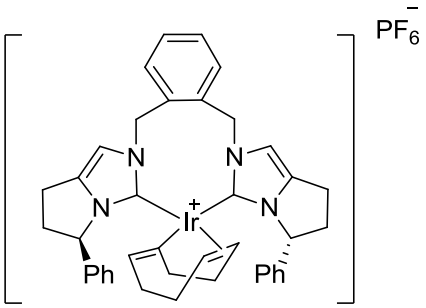
<Procedures for the Preparation of Ir Complexes 4 and 5>



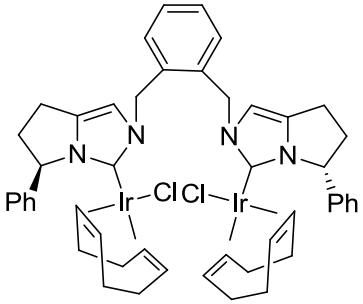
General Procedure D: A mixture of bisimidazolium salt **3** (1.0 eq.), Ag_2O (5.0 eq.), and powderous 4A molecular sieves in 1,2-dichloroethane was refluxed with stirring overnight in dark. After cooling to room temperature, the mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. The resulting silver complex was dissolved in dichloromethane

under N_2, and then added a solution of $[IrCl(cod)]_2$ (1.0 eq.) in CH_2Cl_2. The reaction mixture was stirred overnight in dark at room temperature. To remove insoluble silver salts, the suspension was filtered through Celite and the resulting solution was concentrated under reduced pressure. The crude solid was then purified by gradient column chromatography (SiO_2, first CH_2Cl_2 to give **5**; then CH_2Cl_2/acetone with KPF_6 (2.0 eq.) to give **4**).

[(*R*,*R*)-(+)-2,2'-(1,2-Phenylenebis(methylene)bis(5-mesityl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene)](1,5-cyclooctadiene)iridium hexafluorophosphate ((*R*,*R*)-(+)-**4a**); Following the General Procedure D; (*R,R*)-(+)-**3a** (101 mg, 0.15 mmol) was used; purified by recrystallization (THF/hexane) to give (*R,R*)-(+)-**4a** (68.4 mg, 51% yield) as red solid; mp 184-186 °C; $[\alpha]_D^{24}$ = +182.7 (*c* 0.50, THF); ^{1}H NMR ($CDCl_3$) δ 1.18-1.24 (s, 2H), 1.67-1.74 (m, 1H), 1.88 (dq, *J* = 13.2, 9.6 Hz, 1H), 1.98-2.08 (m, 2H), 2.12-2.33 (m, 5H), 2.54 (dd, *J* = 16.4, 9.2 Hz, 1H), 2.67-2.83 (m, 3H), 2.91- 3.01 (m, 1H), 3.21 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.58 (dd, *J* = 12.8, 7.6 Hz, 1H), 3.84 (td, *J* = 6.4, 1.2 Hz, 2H), 5.00- 5.12 (m, 3H), 5.65 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 14.0 Hz, 1H), 6.50 (d, *J* = 14.4 Hz, 1H), 6.78-6.82 (m, 2H), 6.87- 6.91 (m, 2H), 7.02-7.04 (m, 2H), 7.20-7.41 (m, 6H), 7.45-7.49 (m, 2H), 7.66-7.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.3, 20.7, 28.9, 29.1, 33.2, 33.3, 37.7, 39.9, 51.6, 51.9, 61.7, 62.4, 75.7, 75.9, 76.0, 79.5, 112.1, 113.8, 125.1, 125.8, 127.5, 128.3, 128.4, 128.9, 129.2, 129.6, 129.65, 129.75, 130.8, 131.9, 134.9, 135.1, 138.4, 138.7, 141.0, 142.2, 172.6, 173.3; HRMS (ESI) calcd for $C_{40}H_{42}IrN_4$ (M^+–PF_6) 771.3033, found 771.3010. **(*R*,*R*)-(+)-2,2'-(1,2-Phenylenebis(methylene)bis((5-phenyl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene)(1,5-cyclooctadiene)iridiumchloride)** ((*R*,*R*)-(+)-**5a**); (*R*,*R*)-(+)-**5a** (42.8 mg, 25% yield) was obtained as yellow solid; mp 163-164 °C; ^{1}H NMR spectra of **5a** indicated that conformational isomers derived from the restricted rotation around the carbene–Ir bond axis exist in a 2:1:1 ratio; The following data are for a mixture of the isomers ^{1}H NMR ($CDCl_3$) δ 0.84-0.98 (m, 2.0H), 1.02-2.21 (m, 16.0H), 2.32-2.49 (m, 2.0H), 2.74-3.10 (m, 8.0H), 4.07-4.55 (m, 4.0H), 5.40 (dd, *J* = 8.4, 6.4 Hz, 0.5H), 5.54 (d, *J* = 15.6 Hz, 1.0H), 5.60 (d, *J* = 15.2 Hz, 0.5H), 5.77-5.83 (m, 1.5H), 5.85 (s, 1.0H), 5.92 (d, *J* = 15.6 Hz, 0.5H), 6.04 (d, *J* = 15.2 Hz, 1.0H), 6.42 (s, 1.0H), 6.51 (s, 0.5H), 6.62 (s, 0.5H), 7.21-7.43 (m, 14.0H); ^{13}C NMR ($CDCl_3$) δ 21.5, 22.2, 27.3, 28.3, 28.5, 29.5, 29.7, 30.3, 31.0, 31.8, 32.0, 34.6, 34.7, 36.0, 37.5, 39.5, 48.0, 50.9, 51.9, 52.1, 52.2, 52.5, 52.8, 62.2, 64.0, 81.9, 82.4, 82.9, 84.6, 84.9, 126.7, 126.8, 127.8, 128.2, 128.2, 128.6, 128.7, 128.8, 129.0, 129.5, 129.6, 133.9, 134.6, 135.3, 137.3, 137.5, 137.7, 139.5, 142.48, 142.53, 176.0, 176.2, 176.5; $[\alpha]_D^{22}$ +89.7 (*c* 0.50, THF); HRMS (ESI) calcd for $C_{32}H_{31}ClIrN_4$ (M^+–IrCl(cod)–cod+H) 699.1861, found 699.1880.



(*R*,*R*)-(+)-**4a**



(*R*,*R*)-(+)-**5a**

The crystal structure (Fig. S1) and the ^{1}H and ^{13}C NMR spectra of (*R*,*R*)-(+)-**4a** demonstrated that *cis*-chelating bis-NHC ligand adopted the C_1 symmetric coordination mode toward the Ir center instead of the C_2 symmetric mode. The NMR spectrum measured at higher temperature (50 °C) in $CDCl_3$ remained uncharged (The complex is not enough soluble in toluene-d_8).

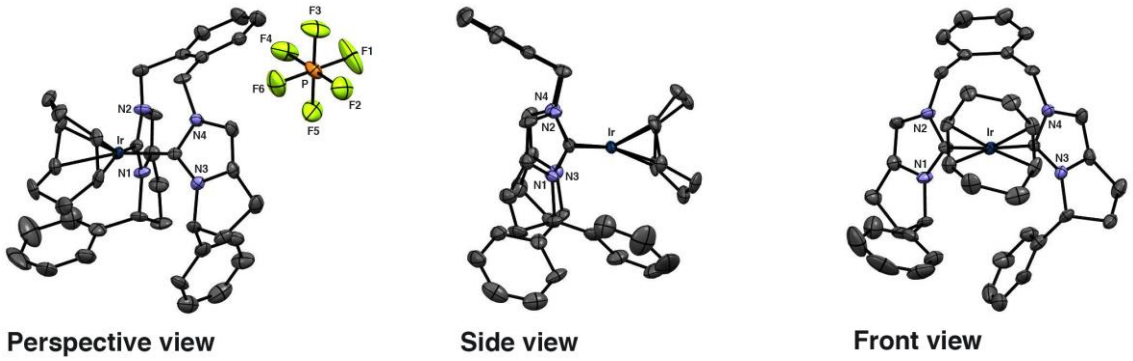
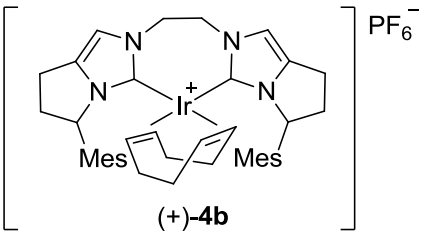


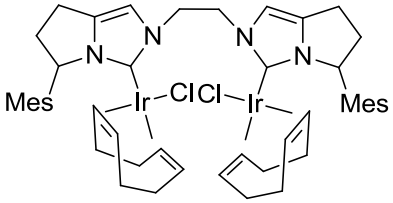
Fig. S1 Crystal Structure of **4a**: Hydrogen atoms are omitted for clarity (perspective view). Hydrogen atoms and PF_6^- anion are omitted for clarity (side and front views).

[(+)-2,2'-(Ethane-1,2-diyl)bis(5-mesityl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene)](1,5-cyclooctadiene)iridium hexafluorophosphate ((+)-**4b**); Following the General Procedure D: (+)-**3b** (103 mg, 0.16 mmol) was used; purified by recrystallization (THF/hexane) to give (+)-**4b** (32.5 mg, 22% yield) as red solid; mp 174-175 °C; $[\alpha]_D^{24}$ +161.3 (*c* 0.50, THF); ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 3H), 1.16-1.22 (m, 2H), 1.31-1.41 (m, 1H), 1.54 (s, 3H), 1.77-1.89 (m, 3H), 1.95 (s, 3H), 1.98-2.09 (m, 1H), 2.20 (s, 3H), 2.21-2.29 (m, 3H), 2.32 (s, 3H), 2.47 (s, 3H), 2.68 (q, *J* = 6.8 Hz, 1H), 2.88-3.02 (m, 6H), 3.61-3.67 (m, 1H), 4.06 (td, *J* = 7.2, 2.0 Hz, 1H), 4.16 (td, *J* = 7.2, 1.6 Hz, 1H), 4.50-4.67 (m, 2H), 4.79 (dt, *J* = 14.4, 4.8 Hz, 1H), 4.96-5.00 (m, 1H), 5.71-5.85 (m, 2H), 6.67 (s, 1H), 6.77 (s, 1H), 6.81 (s, 1H), 6.86 (s, 1H), 6.99 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 18.3, 18.8, 20.5, 20.6, 21.0, 21.1, 21.9, 22.3, 28.9, 29.2, 32.9, 33.6, 35.7, 37.1, 47.3, 49.4, 53.7, 58.9, 59.5, 70.5, 73.4, 74.1, 114.3, 116.4, 129.7, 130.2, 131.2, 132.3, 133.7, 134.1, 134.8, 135.3, 135.6, 137.3, 137.9, 138.7, 170.4, 171.2; HRMS (ESI) calcd for $C_{40}H_{50}IrN_4$ (M^+–PF_6) 779.3659, found 779.3663.

[(+)-2,2'-(Ethane-1,2-diyl)bis((5-phenyl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene)(1,5-cyclooctadiene)iridiumchloride) ((+)-**5b**); (+)-**5b** (51.7 mg, 35% yield) was obtained as yellow solid; mp 163-164 °C; $[\alpha]_D^{24}$ +128.5 (*c* 0.50, THF); ^{1}H NMR ($CDCl_3$) δ 0.78-0.96 (m, 4H), 1.18-1.33 (m, 4H), 1.61-1.72 (m, 2H), 1.70 (s, 6H), 1.79-1.96 (m, 6H), 2.10 (td, *J* = 7.6, 4.4 Hz, 2H), 2.30(s, 6H), 2.37-2.47 (m, 2H), 2.74 (s, 6H), 2.76-2.85 (m, 2H), 2.90-3.25 (m, 6H), 4.36-4.45 (m, 4H), 4.68 (d, *J* = 10.0 Hz, 2H), 4.96 (d, *J* = 10.0 Hz, 2H), 5.99 (dd, *J* = 10.0, 6.8 Hz, 2H), 6.81 (s, 4H), 6.96 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 19.1, 20.8, 21.4, 22.5, 27.6, 29.9, 31.0, 33.7, 35.8, 51.6, 51.9, 53.3, 57.4, 81.6, 84.9, 115.1, 129.6, 131.3, 134.7, 136.0, 137.5, 137.6, 174.1; HRMS (ESI) calcd for $C_{48}H_{62}ClIr_2N_4$ (M^+–Cl) 1115.3916, found 1115.3906.

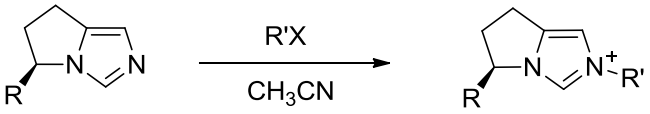


(+)-**4b**



(+)-**5b**

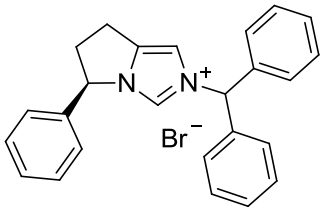
<Procedures for the Preparation of Imidazolium Salts 2>



1 **2**

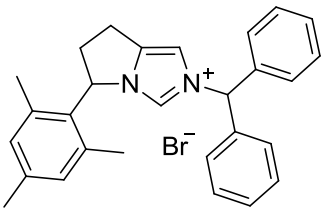
General Procedure E: A mixture of **1** (1 eq.) and alkylhalide (1.2 eq.) in dry acetonitrile was heated to 70 °C and stirred for 3 days. After cooling to room temperature, the mixture was concentrated under reduced pressure and purified by reprecipitation to give **2**.

(*R*)-(+)-2-Benzhydryl-5-phenyl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ium bromide ((*R*)-(+)-**2av**): Following the General Procedure E: (*R*)-**1a** (220 mg, 1.19 mmol) and diphenylmethyl bromide (353 mg, 1.43 mmol) were used; purified by reprecipitation (CH_2Cl_2/Et_2O) to give (*R*)-(+)-**2av** (488 mg, 95% yield) as light brown solid; mp 87-89 °C; $[\alpha]_D^{22}$ +68.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.61-2.66 (m, 1H), 3.12-3.17 (m, 3H), 6.03 (t, *J* = 5.6 Hz, 1H), 7.01 (s, 1H), 7.25-7.39 (m, 15H), 7.54 (s, 1H), 8.97 (s, 1H);^{13}C NMR ($CDCl_3$) δ 22.8, 37.6, 64.5, 67.3, 114.1, 126.4, 127.4, 127.9, 128.8, 129.0, 129.2, 129.27, 129.30, 129.4, 129.5, 131.6, 136.2, 136.7, 138.8; HRMS (ESI) calcd for $C_{25}H_{23}N_2$ (M^+–Br): 351.1856, found 351.1848.



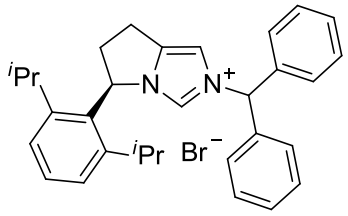
(*R*)-(+)-**2av**

(+)-2-Benzhydryl-5-mesityl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ium bromide ((+)-**2bv**); Following the General Procedure E: (+)-**1b** (100 mg, 0.442 mmol) and diphenylmethyl bromide (131 mg, 0.531 mmol) were used; purified by reprecipitation (CH_2Cl_2/Et_2O) to give (+)-**2bv** (132 mg, 71% yield) as light brown solid; mp 96-97 °C; $[\alpha]_D^{24}$ +88.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 3H), 2.23 (s, 3H), 2.50 (s, 3H), 2.62-2.73 (dq, *J* = 13.2, 10.0 Hz, 1H), 3.03-3.11 (m, 1H), 3.20-3.30 (m, 2H), 6.31 (t, *J* = 9.2 Hz, 1H), 6.79 (s, 1H), 6.88 (s, 1H), 7.01 (s, 1H), 7.24-7.38 (m, 10H), 7.58 (s, 1H), 8.59 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.2, 20.7, 21.1, 23.0, 34.4, 60.8, 66.9, 114.4, 127.7, 128.5, 128.6, 128.9, 129.0, 129.16, 129.18, 129.24, 130.0, 130.9, 131.7, 134.9, 136.2, 136.8, 137.8, 138.4, 138.9; HRMS (ESI) calcd for $C_{28}H_{29}N_2$ (M^+–Br) 393.2325, found 393.2307.



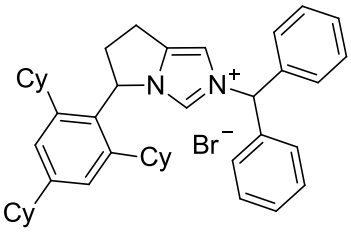
(+)-**2bv**

(*R*)-(+)-2-Benzhydryl-5-(2,6-diisopropylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ium bromide ((*R*)-(+)-**2cv**); Following the General Procedure E: (*R*)-(+)-**1c** (100 mg, 0.372 mmol) and diphenylmethyl bromide (110 mg, 0.446 mmol) were used; purified by reprecipitation (CH_2Cl_2/Et_2O) to give (*R*)-(+)-**2cv** (155 mg, 81% yield) as light brown solid; mp 124-126 °C; $[\alpha]_D^{24}$ +107.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.69 (d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.39 (d, *J* = 6.8 Hz, 3H), 2.29 (sept, *J* = 6.8 Hz, 1H), 2.74 (dq, *J* = 13.6, 9.6 Hz, 1H), 3.11 (dtd, *J* = 9.6, 6.8, 2.0 Hz, 1H), 3.19-3.38 (m, 2H), 3.48 (sept, *J* = 6.8 Hz, 1H), 6.44 (t, *J* = 9.2 Hz, 1H), 7.06 (s, 1H), 7.14 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.21 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.27-7.44 (m, 11H), 7.66 (s, 1H), 8.68 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 23.0, 23.9, 24.4, 24.5, 24.9, 28.8, 30.0, 36.1, 59.6, 67.0, 114.7, 123.8, 125.9, 127.8, 128.5, 128.9, 129.1, 129.2, 129.3, 130.0, 130.6, 136.1, 136.6, 138.2, 147.8, 148.7; HRMS (ESI) calcd for $C_{31}H_{35}N_2$ (M^+–Br) 435.2795, found 435.2776.



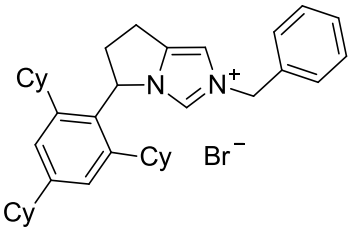
(*R*)-(+)-**2cv**

(+)-2-Benzhydryl-5-(2,4,6-tricyclohexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ium bromide ((+)-**2dv**); Following the General Procedure E: (+)-**1d** (80.0 mg, 0.186 mmol) and diphenylmethyl bromide (55.2 mg, 0.223 mmol) were used; purified by reprecipitation (CH_2Cl_2/hexane) to give (+)-**2dv** (85.7 mg, 68% yield) as white solid; mp 185-186 °C; $[\alpha]_D^{19}$ +53.6 (*c* 1.00, THF); ^{1}H NMR ($CDCl_3$) δ 0.75 (q, *J* = 13.2 Hz, 1H), 0.90 (d, *J* = 13.2 Hz, 1H), 1.07-2.04 (m, 29H), 2.38-2.48 (m, 1H), 2.72 (dq, *J* = 14.0, 9.6 Hz, 1H), 2.95-3.26 (m, 3H), 3.35 (dt, *J* = 13.2, 6.6 Hz, 1H), 6.39 (t, *J* = 9.2 Hz, 1H), 6.92 (s, 1H), 7.03 (s, 2H), 7.22-7.46 (m, 10H), 7.63 (s, 1H), 8.65 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.0, 23.4, 25.8, 26.0, 26.1, 26.8, 26.9, 27.3, 27.6, 34.1, 34.2, 34.6, 34.9, 35.7, 35.8, 40.3, 40.7, 44.5, 56.9, 59.3, 67.0, 114.4, 123.0, 125.0, 126.6, 127.4, 127.8, 128.6, 128.8, 129.1, 129.1, 129.2, 130.8, 136.2, 136.9, 141.5, 148.3, 147.8, 149.2; HRMS (ESI) calcd for $C_{43}H_{53}N_2$ (M^+–Br) 597.4203, found 597.4181.



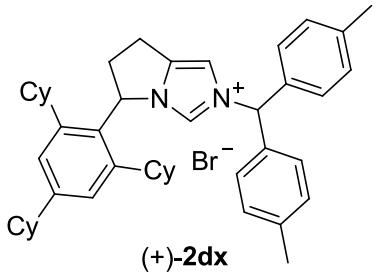
(+)-**2dv**

(+)-2-Benzyl-5-(2,4,6-tricyclohexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ium bromide ((+)-**2dw**); Following the General Procedure E; (+)-**1d** (60 mg, 0.139 mmol) and benzyl bromide (28.6 mg, 0.167 mmol) were used; purified by reprecipitation (CH_2Cl_2/hexane) to give (+)-**2dw** (78.0 mg, 93% yield) as white solid; mp 177-178 °C; $[\alpha]_D^{24}$ +4.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.28 (q, *J* = 12.4 Hz, 1H), 0.70 (d, *J* = 13.6 Hz, 1H), 0.94-2.03 (m, 29H), 2.40-2.50 (m, 1H), 2.60-2.72 (m, 1H), 2.85-2.97 (m, 1H), 3.04-3.34 (m, 3H), 5.61 (d, *J* = 14.4 Hz, 1H), 5.77 (d, *J* = 14.4 Hz, 1H), 6.22 (t, *J* = 8.8 Hz, 1H), 6.90 (s, 1H), 7.04 (s, 1H), 7.33-7.34 (m, 3H), 7.52-7.54 (m, 2H), 7.66 (s, 1H), 8.68 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.9, 25.6, 26.0, 26.1, 26.8, 26.88, 26.97, 27.04, 27.2, 34.1, 34.2, 34.5, 34.6, 35.0, 35.2, 36.2, 40.2, 40.9, 44.5, 54.0, 59.1, 115.4, 122.9, 125.2, 126.5, 129.2, 129.6, 133.6, 138.2, 146.3, 147.3, 149.2; HRMS (ESI) calcd for $C_{37}H_{49}N_2$ (M^+–Br) 521.3890, found 521.3859.



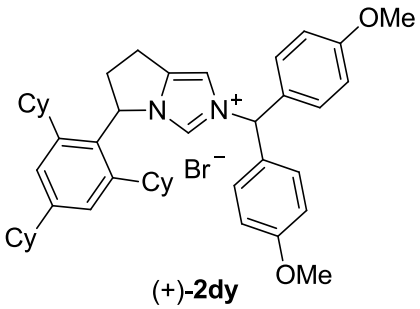
(+)-**2dw**

(+)-2-(4,4'-Dimethylphenyl)-5-(2,4,6-tricyclohexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ium bromide ((+)-**2dx**); Following the General Procedure E; (+)-**1d** (80 mg, 0.186 mmol) and di-(4-tolyl)methyl bromide (61.4 mg, 0.223 mmol) were used; purified by reprecipitation (CH_2Cl_2/hexane) to give (+)-**2dx** (85.3 mg, 65% yield) as white solid; mp 168-169 °C; $[\alpha]_D^{24}$ +77.6 (*c* 1.00, THF); ^{1}H NMR δ 0.76 (q, *J* = 13.2 Hz, 1H), 0.93 (d, *J* = 12.8 Hz, 1H), 1.07-2.06 (m, 29H), 2.31-2.33 (m, 6H), 2.40-2.50 (m, 1H), 2.70 (dq, *J* = 13.6, 9.6 Hz, 1H), 3.01-3.25 (m, 3H), 3.40 (dt, *J* = 18.4, 9.6 Hz, 1H), 6.41 (t, *J* = 9.2 Hz, 1H), 6.93 (s, 1H), 7.02 (d, *J* = 4.4 Hz, 2H), 7.11-7.16 (m, 6H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.40 (s, 1H), 8.49 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.9, 21.0, 21.1, 22.9, 23.3, 25.8, 26.0, 26.1, 26.7, 26.8, 27.3, 27.6, 34.1, 34.2, 34.5, 34.8, 35.8, 40.3, 40.6, 44.5, 59.3, 66.9, 114.4, 122.8, 125.0, 126.7, 127.2, 127.6, 129.0, 129.2, 129.6, 129.7, 130.3, 133.3, 134.0, 136.8, 138.3, 138.7, 138.7, 139.0, 146.3, 147.7, 149.0; HRMS (ESI) calcd for $C_{45}H_{57}N_2$ (M^+–Br) 625.4516, found 625.4490.



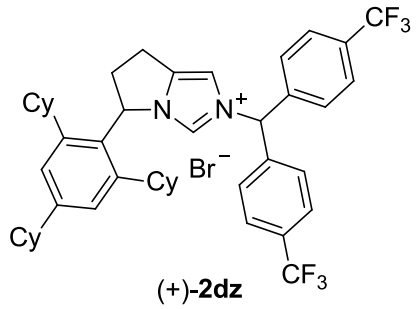
(+)-**2dx**

(+)-2-(4,4'-Di-methoxymethylphenyl)-5-(2,4,6-tricyclohexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ium bromide ((+)-**2dy**); Following the General Procedure E; (+)-**1d** (80 mg, 0.186 mmol) and di-(4-methoxymethylphenyl)methyl bromide (68.5 mg, 0.223 mmol) were used; Since this compound could not be purified by reprecipitation, the crude mixture was used without isolation for the next step (see the preparation of (+)-**8dy**).



(+)-**2dy**

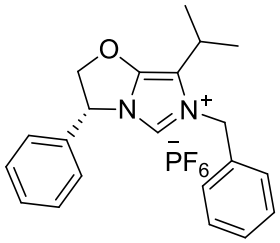
(+)-2-(4,4'-Di-trifluoromethylphenyl)-5-(2,4,6-tricyclohexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ium bromide ((+)-**2dz**); Following the General Procedure E; (+)-**1d** (80 mg, 0.186 mmol) and di-(4-trifluoromethylphenyl)methyl bromide (85.4 mg, 0.223 mmol) were used; purified by reprecipitation (CH_2Cl_2/hexane) to give (+)-**2dz** (102.9 mg, 68% yield) as light brown solid; mp 185-186 °C; $[\alpha]_D^{24}$ +135.3 (*c* 1.00, THF); ^{1}H NMR ($CDCl_3$) δ 0.60 (q, *J* = 13.2 Hz, 1H), 0.79 (d, *J* = 12.8 Hz, 1H), 1.03-1.12 (m, 1H), 1.17-1.92 (m, 27H), 1.98-2.05 (m, 1H), 2.39-2.50 (m, 1H), 2.76 (dq, *J* = 13.6, 9.6 Hz, 1H), 2.92-3.01 (m, 1H), 3.08-3.19 (m, 1H), 3.21-3.40 (m, 2H), 6.38 (t, *J* = 9.2 Hz, 1H), 6.93 (d, *J* = 1.6 Hz, 1H), 7.04 (d, *J* = 1.6 Hz, 1H), 7.18 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.60-7.65 (m, 6H), 8.33 (s, 1H), 9.02 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.9, 25.7, 25.99, 26.04, 26.7, 26.85, 26.91, 27.3, 27.6, 34.1, 34.6, 34.8, 35.6, 35.7, 40.4, 40.9, 44.5, 59.6, 65.2, 114.0, 123.1, 123.47 (q, *J* = 277 Hz), 123.51 (q, *J* = 277 Hz), 125.2, 126.13, 126.17, 126.19, 128.3, 129.8, 131.24 (q, *J* = 33.4 Hz), 131.25, 131.27 (q, *J* = 33.4 Hz), 138.6, 139.7, 140.3, 146.1, 147.6, 149.5; HRMS (ESI) calcd for $C_{45}H_{51}F_6N_2$ (M^+–Br) 733.3951, found 733.3944.



(+)-**2dz**

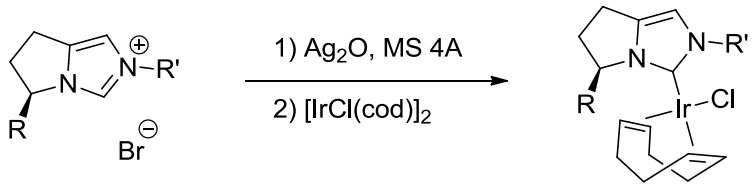
(*R*)-6-Benzyl-7-isopropyl-3-phenyl-2,3-dihydroimidazo[5,1-b]oxazol-6-ium hexafluorophosphate ((*R*)-(–)-**2ew**); Following the General Procedure E; (*R*)-7-isopropyl-3-phenyl-2,3-dihydroimidazo[5,1-b]oxazole (194 mg, 0.849 mmol) and benzyl bromide (174.0 mg, 1.02 mmol) were used; purified by reprecipitation (CH_2Cl_2/ether); Then, the bromide counter anion was converted into PF_6^-. The residue was dissolved in acetone/H_2O (1/1) and added KPF_6. After stirring at room temperature for 8 h, the mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo to give (*R*)-(–)-**2ew** (232.6 mg, 59% yield) as brown solid; mp 67-68 °C; $[\alpha]_D^{22}$ –60.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.15 (d, *J* = 7.5 Hz, 3H), 1.26 (d, *J* = 7.0 Hz, 3H), 2.84 (sept, *J* = 7.0 Hz, 1H), 4.91 (dd, *J* = 9.0, 6.0 Hz,

1H), 5.15 (d, *J* = 15.0 Hz, 1H), 5.20 (t, *J* = 15.5 Hz, 1H), 5.42 (t, *J* = 8.5 Hz, 1H), 5.96 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.22-7.43 (m, 10H), 7.86 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.8, 21.2, 23.5, 52.4, 60.8, 84.0, 113.7, 123.9, 126.7, 127.8, 129.3, 129.5, 129.8, 130.1, 132.1, 134.1, 147.5; HRMS (ESI) calcd for $C_{21}H_{23}N_2O$ (M^+–PF_6) 319.1805, found 319.1794.



((*R*)-(–)-**2ew**)

<Procedures for the Preparation of Monodentate NHC/Ir Complexes 8>

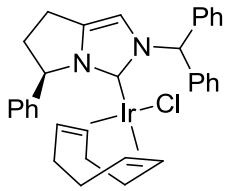


2 **8**

General Procedure F: A mixture of imidazolium salt **2** (1 eq.), Ag_2O (2.5 eq.), and powderous 4A molecular sieves in 1,2-dichloroethane was refluxed with stirring overnight in dark. After cooling to room temperature, the mixture was filtered through a pad of Celite and filtrate was concentrated under reduced pressure. The resulting silver complex was dissolved in CH_2Cl_2 under N_2, and then added a solution of $[IrCl(cod)]_2$ (0.52 eq.) in CH_2Cl_2. The reaction mixture was stirred overnight in dark at room temperature. To remove insoluble silver salts, the suspension was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was then purified by column chromatography (SiO_2) to give the desired product.

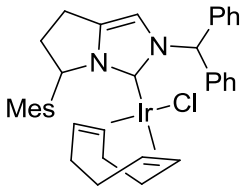
[(*R*)-(+)-2-Benzhydryl-5-phenyl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene](1,5-cyclooctadiene)iridiumchloride ((*R*)-(+)-**8av**); Following the General Procedure F: (*R*)-(+)-**2av** (100 mg, 0.237 mmol) and $[IrCl(cod)]_2$ (82.9 mg, 0.123 mmol) were used; purified by column chromatography (AcOEt/hexane = 1/1) to give (*R*)-(+)-**8av** (113.9 mg, 70% yield) as yellow solid; mp 216-220 °C; $[\alpha]_D^{21}$ +115.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR spectra of **8av** indicated that conformational isomers derived from the restricted rotation around the carbene–Ir bond axis exist in a 2:1 ratio; The following data are for a mixture of the isomers; ^{1}H NMR (CD_3Cl) δ 0.82-0.92 (m, 0.65H), 1.04-1.16 (m, 1.30H), 1.18-1.44 (m, 2.70H), 1.46-2.05 (m, 4.00H), 2.21-2.27 (m, 0.35H), 2.30-2.50 (m, 1.65H), 2.66 (td, *J* = 7.6, 2.8 Hz, 0.35H), 2.75-3.09 (m, 3H), 4.11 (td, J = 7.2, 2.8 Hz,

0.35H), 4.23-4.29 (m, 0.35H), 4.48-4.55 (m, 1.30H), 5.37 (t, J = 6.8 Hz, 0.35H), 5.79 (d, J = 7.2 Hz, 0.65H), 6.51 (s, 1.00H), 7.21-7.48 (m, 15H), 7.99 (s, 0.65H), 7.99 (s, 0.35H); ^{13}C NMR ($CDCl_3$) δ 21.5, 22.2, 28.1, 28.6, 29.4, 31.8, 32.3, 34.0, 34.4, 37.8. 39.5, 48.6, 51.7, 52.1, 52.2, 62.3, 64.0, 67.6, 67.7, 82.9, 83.3, 84.3, 111.6, 111.7, 126.3, 126.9, 127.3, 127.4, 127.5, 127.7, 127.88, 127.92, 128.0, 128.1, 128.2, 128.40, 128.46, 128.51, 128.6, 128.9, 129.5, 129.8, 130.0, 136.6, 137.6, 139.3, 139.9, 140.4, 141.0, 142.6, 176.6, 177.1; HRMS (ESI) calcd for $C_{33}H_{34}IrN_2$ (M^+–Cl) 651.2346, found 651.2343; A single crystal suitable for X-ray single-crystal structure determination was obtained by recrystallization from hot hexane.[3]



(*R*)-(+)-**8av**

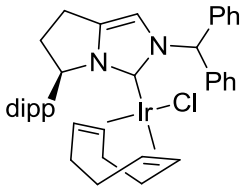
[(+)-2-Benzhydryl-5-mesityl-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene](1,5-cyclooctadiene)iridiumchloride ((+)-**8bv**); Following the General Procedure F: (+)-**2bv** (90 mg, 0.190 mmol) and [IrCl(cod)]$_2$ (66.5 mg, 0.099 mmol) were used; purified by column chromatography (CH_2Cl_2) followed by recrystallization (THF/hexane) to give (+)-**8bv** (117.6 mg, 85% yield) as yellow solid; mp 101-102 °C; $[\alpha]_D^{21}$ +82.0 (*c* 1.00, THF); ^{1}H NMR ($CDCl_3$) δ 0.70 (dtd, J = 13.2, 8.8, 4.4 Hz, 1H), 0.78-0.91 (m, 1H), 1.09-1.18 (m, 1H), 1.36-1.44 (m, 1H), 1.52-1.60 (m, 1H), 1.72-1.94 (m, 3H), 1.88 (s, 3H), 2.00 (td, J = 8.4, 4.4 Hz, 1H), 2.28 (s, 3H), 2.41-2.52 (m, 1H), 2.64 (t, J = 6.4 Hz, 1H), 2.72 (s, 3H), 2.88-3.05 (m, 3H), 4.36-4.41 (m, 1H), 4.41-4.47 (m, 1H), 6.02-6.08 (m, 1H), 6.42 (s, 1H), 6.79 (s, 1H), 6.96 (s, 1H), 7.20-7.40 (m, 10H), 8.05 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.4, 20.8, 21.5, 22.5, 27.3, 29.9, 31.0, 33.7, 35.4, 51.1, 53.1, 57.6, 67.7, 81.8, 84.8, 111.6, 126.5, 127.4, 128.0, 128.5, 128.6, 129.5, 129.7, 131.1, 134.6, 135.6, 137.4, 137.7, 138.4, 140.5, 140.7, 176.2; HRMS (ESI) calcd for $C_{36}H_{40}IrN_2$ (M^+–Cl) 693.2815, found 693.2797.



(+)-**8bv**

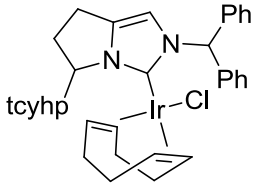
[(*R*)-(+)-2-Benzhydryl-5-(2,6-diisopropylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene](1,5-cyclooctadiene)iridiumchloride ((*R*)-(+)-**8cv**); Following the General Procedure F: (*R*)-(+)-**2cv** (80 mg, 0.155 mmol) and [IrCl(cod)]$_2$ (54.2 mg, 0.081 mmol) were used; purified by column chromatography (CH_2Cl_2) to give (*R*)-(+)-**8cv** (99.1 mg, 83% yield) as yellow solid; mp

114-116 °C; $[\alpha]_D^{21}$ +121.6 (*c* 1.00, THF); ^{1}H NMR ($CDCl_3$) δ 0.74 (d, *J* = 6.4 Hz, 3H), 0.82-0.90 (m, 1H), 1.02-1.11 (m, 2H), 1.18 (d, *J* = 7.2 Hz, 3H), 1.23 (d, *J* = 7.2 Hz, 3H), 1.21-1.33 (m, 1H), 1.38-1.48 (m, 1H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.58-1.70 (m, 1H), 1.78 (dddd, *J* = 14.0, 10.8, 7.6, 6.0 Hz, 1H), 2.01 (dddd, *J* = 14.0, 10.0, 7.6, 6.4 Hz, 1H), 2.14 (td, *J* = 7.8, 3.2 Hz, 1H), 2.41 (td, *J* = 7.6, 3.2 Hz, 1H), 2.51-2.60 (m, 1H), 2.68 (sept, *J* = 6.4 Hz, 1H), 2.94-3.17 (m, 3H), 4.05 (sept, *J* = 6.8 Hz, 1H), 4.18 (td, *J* = 8.0, 4.0 Hz, 1H), 4.65 (td, *J* = 8.0, 4.0 Hz, 1H), 6.20 (dd, *J* = 10.4, 6.8 Hz, 1H), 6.44 (s, 1H), 7.16 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21-7.39 (m, 12H), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.0, 22.5, 23.3, 24.8, 26.4, 28.0, 28.4, 29.8, 33.0, 33.5, 35.4, 51.3, 53.3, 56.0, 67.9, 81.1, 83.6, 112.2, 123.2, 125.5, 126.8, 127.4, 128.0, 128.4, 128.5, 129.5, 136.1, 138.1, 140.3, 140.8, 147.3, 147.8, 176.5; HRMS (ESI) calcd for $C_{39}H_{46}IrN_2$ (M^+–Cl) 735.3285, found 735.3264; A single crystal suitable for X-ray single-crystal structure determination was obtained by slow diffusion of pentane into a solution of (*S*)-(–)-**8cv** in CH_2Cl_2.



(*R*)-(+)-**8cv**

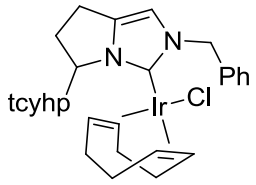
[(+)-2-Benzhydryl-5-(2,4,6-trihexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene](1,5-cyclooctadiene)iridiumchloride ((+)-**8dv**); Following the General Procedure F: (+)-**2dv** (106 mg, 0.157 mmol) and $[IrCl(cod)]_2$ (54.8 mg, 0.082 mmol) were used; purified by column chromatography (EtOAc/hexane = 1/9) to give (+)-**8dv** (117.3 mg, 80% yield) as yellow solid; mp 186-187 °C; $[\alpha]_D^{21}$ +114.6 (*c* 1.00, THF); ^{1}H NMR ($CDCl_3$) δ 0.86-0.98 (m, 4H), 1.05-1.94 (m, 32H), 2.02-2.16 (m, 1H), 2.18-2.24 (m, 1H), 2.28-2.40 (m, 3H), 2.41-2.58 (m, 2H), 2.92-3.14 (m, 3H), 3.70-3.78 (m, 1H), 4.01 (td, *J* = 7.8, 4.4 Hz, 1H), 4.75 (td, *J* = 7.6, 2.4 Hz, 1H), 6.12 (dd, *J* = 9.6, 6.8 Hz, 1H), 6.40 (s, 1H), 6.96 (d, *J* = 1.2 Hz ,1H), 7.08 (d, *J* = 1.6 Hz, 1H), 7.21-7.39 (m, 10H), 8.51 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.2, 26.17, 26.22, 26.6, 26.87, 26.94, 27.0, 27.3, 27.7, 27.8, 31.1, 31.8, 33.3, 33.6, 34.39, 34.44, 34.8, 35.0, 35.5, 37.6, 39.3, 40.4, 44.7, 50.6, 54.2, 55.8, 68.0, 79.6, 84.3, 112.0, 122.6, 124.7, 126.8, 127.3, 127.9, 128.4, 128.5, 129.5, 133.6, 138.2, 140.6, 140.8, 145.9, 147.0, 147.4, 176.8; HRMS (ESI) calcd for $C_{51}H_{64}IrN_2$ (M^+–Cl) 897.4693, found 897.4676.



(+)-**8dv**

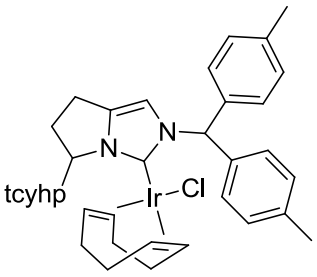
[(+)-2-Benzyl-5-(2,4,6-trihexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene](1,5-cy

clooctadiene)iridiumchloride ((+)-**8dw**); Following the General Procedure F: (+)-**2dw** (45 mg, 0.075 mmol) and [IrCl(cod)]$_2$ (26.1 mg, 0.039 mmol) were used; purified by column chromatography (EtOAc/hexane = 1/9) to give (+)-**8dw** (57.8 mg, 90% yield) as yellow solid; mp 154-156 °C; $[\alpha]_D^{21}$ +68.3 (*c* 1.00, THF); ^{1}H NMR ($CDCl_3$) δ 0.83-1.04 (m, 4H), 1.13-1.95 (m, 32H), 2.04 (ddt, *J* = 15.2, 10.4, 7.6 Hz, 1H), 2.24-2.33 (m, 2H), 2.35-2.42 (m, 1H), 2.45-2.58 (m, 2H), 2.75 (td, *J* = 11.2, 3.2 Hz, 1H), 3.02-3.14 (m, 3H), 3.67-3.76 (m, 1H), 4.05 (td, *J* = 8.0, 4.0 Hz, 1H), 4.64 (td, *J* = 7.6, 3.2 Hz, 1H), 5.47 (d, *J* = 15.6 Hz, 1H), 6.09-6.15 (m, 1H), 6.17 (d, *J* = 16.0 Hz, 1H), 6.47 (s, 1H), 6.99 (d, *J* = 1.2 Hz, 1H), 7.10 (d, *J* = 1.2Hz, 1H), 7.24-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 22.2, 26.1, 26.2, 26.5, 26.9, 27.0, 27.5, 27.7, 27.8, 29.7, 30.4, 32.5, 33.3, 33.9, 34.27, 34.35, 34.5, 34.9, 35.6, 37.6, 39.3, 40.4, 44.7, 50.8, 53.3, 55.1, 55.7, 80.4, 83.8, 112.3, 122.5, 124.6, 127.1, 127.6, 128.7, 133.7, 137.7, 138.6, 145.8, 147.0, 147.4, 176.2; HRMS (ESI) calcd for $C_{37}H_{48}ClIrN_2Na$ (M^+–cod+Na) 771.3027, found 771.3052.



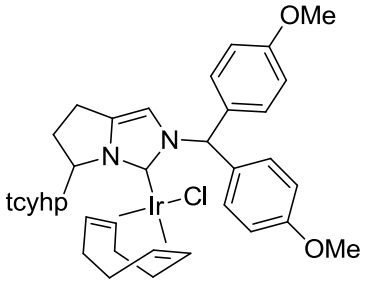
(+)-**8dw**

[(+)-2-(4,4'-Dimethylbenzhydryl)-5-(2,4,6-trihexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene](1,5-cyclooctadiene)iridiumchloride ((+)-**8dx**); Following the General Procedure F: (+)-**2dx** (40 mg, 0.056 mmol) and [IrCl(cod)]$_2$ (19.6 mg, 0.030 mmol) were used; purified by column chromatography (EtOAc/hexane = 1/9) to give (+)-**8dx** (44 mg, 81% yield) as yellow solid; mp 170-171 °C; $[\alpha]_D^{19}$ +118.3 (*c* 0.50, THF); ^{1}H NMR ($CDCl_3$) δ 0.86-0.96 (m, 4H), 1.06-1.94 (m, 32H), 2.04-2.16 (m, 1H), 2.18-2.24 (m, 1H), 2.31 (s, 3H), 2.34 (s, 3H), 2.30-2.40 (m, 3H), 2.41-2.57 (m, 2H), 2.92-3.14 (m, 3H), 3.72-3.80 (m, 1H), 3.99 (td, *J* = 7.8, 4.4 Hz, 1H), 4.74 (td, *J* = 7.6, 2.4 Hz, 1H), 6.11 (dd, *J* = 9.6, 6.8 Hz, 1H), 6.4 (s, 1H), 6.96 (d, *J* = 1.6 Hz, 1H), 7.06-7.14 (m, 7H), 7.25 (d, *J* = 8.0 Hz, 2H), 8.40 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.1, 21.4, 22.3, 26.18, 26.23, 26.6, 26.9, 27.0, 27.3, 27.7, 27.8, 29.7, 31.1, 31.9, 33.2, 33.6, 34.4, 34.9, 35.0, 35.5, 37.6, 39.3, 40.4, 50.6, 54.1, 55.8, 67.6, 79.4, 84.1, 111.9, 122.6, 124.6, 126.6, 129.0, 129.1, 129.4, 133.7, 136.8, 137.6, 137.8, 138.0, 138.1, 145.9, 147.0, 147.3, 176.4; HRMS (ESI) calcd for $C_{53}H_{68}IrN_2$ (M^+–Cl) 925.5006, found 925.4985.



(+)-**8dx**

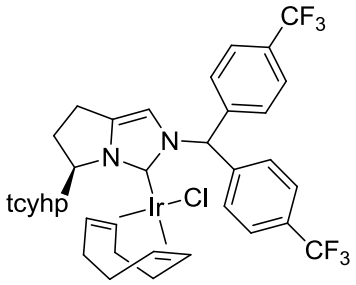
[(+)-2-(4,4'-Methoxybenzhydryl)-5-(2,4,6-trihexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene](1,5-cyclooctadiene)iridiumchloride ((+)-**8dy**); Following the General Procedure F: The crude mixture of (+)-**2dy** and $[IrCl(cod)]_2$ (65.0 mg, 0.097 mmol) were used; purified by column chromatography (EtOAc/hexane = 1/9) to give (+)-**8dy** (62.8 mg, 34% yield (2 steps)) as yellow solid; mp 174-175 °C; $[\alpha]_D^{20}$ +135.3 (*c* 0.50, THF); ^{1}H NMR ($CDCl_3$) δ 0.88-1.95 (m, 36H), 2.06-2.16 (m, 1H), 2.19-2.25 (m, 1H), 2.30-2.66 (m, 5H), 2.92-3.14 (m, 3H), 3.71-3.80 (m, 1H), 3.77 (s, 3H), 3.81 (s, 3H), 4.00 (td, *J* = 8.4, 4.0 Hz, 1H), 4.73 (td, *J* = 7.2, 2.0 Hz, 1H), 6.10 (dd, *J* = 10.0, 6.8 Hz, 1H), 6.44 (s, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 1.6 Hz, 1H), 7.08 (d, *J* = 1.2 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 8.37 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.3, 26.18, 26.23, 26.6, 26.9, 27.0, 27.4, 27.7, 27.8, 31.1, 32.0, 33.3, 33.6, 34.4, 34.5, 34.8, 35.0, 35.6, 37.6, 39.3, 40.4, 44.7, 50.7, 54.1, 55.2, 55.8, 67.0, 79.5, 84.0, 111.8, 113.7, 113.8, 122.6, 124.6, 127.8, 130.6, 133.0, 133.4, 133.7, 138.1, 145.9, 147.0, 147.4, 158.7, 159.1, 176.4; HRMS (ESI) calcd for $C_{53}H_{68}IrN_2O_2$ (M^+-Cl) 957.4905, found 957.4871.



(+)-**8dy**

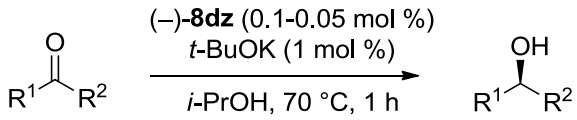
[(+)-2-(4,4'-Trifluoromethylbenzhydryl)-5-(2,4,6-trihexylphenyl)-6,7-dihydro-5*H*-pyrrolo[1,2-c]imidazol-2-ylidene](1,5-cyclooctadiene)iridiumchloride ((+)-**8dz**); (+)-**2dz** (60 mg, 0.074 mmol) and $[IrCl(cod)]_2$ (25.8 mg, 0.038 mmol) were used; purified by column chromatography (EtOAc/hexane = 1/9) to give (+)-**8dz** (51.5 mg, 65% yield) as yellow solid; mp 178-180 °C; $[\alpha]_D^{20}$ +112.5 (*c* 1.00, THF); ^{1}H NMR δ 0.83-1.96 (m, 36H), 2.06 (ddt, *J* = 15.2, 10.4, 7.6 Hz, 1H), 2.17-2.24 (m, 2H), 2.28-2.40 (m, 2H), 2.43-2.61 (m, 2H), 2.96-3.18 (m, 3H), 3.65-3.73 (m, 1H), 4.07 (td, *J* = 8.0, 4.0 Hz, 1H), 4.78 (td, *J* = 7.6, 3.2 Hz, 1H), 6.12 (dd, *J* = 9.6, 6.8 Hz, 1H), 6.42 (s, 1H), 6.97 (d, *J* = 1.2 Hz, 1H), 7.10 (d, *J* = 1.2 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 8.74 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.3, 26.16,

26.5, 26.87, 26.93, 27.0, 27.3, 27.76, 27.81, 31.0, 32.1, 33.3, 33.6, 34.40, 34.43, 34.6, 34.9, 35.4, 37.6, 39.5, 40.5, 44.7, 50.8, 54.5, 56.0, 67.1, 80.7, 85.1, 111.3, 122.7, 123.9 (q, J = 276 Hz), 124.7, 125.7, 127.1, 129.8, 130.2 (q, J = 33.3 Hz), 133.2, 139.2, 143.7, 143.8, 145.7, 147.0, 147.7, 177.7; HRMS (ESI) calcd for $C_{53}H_{62}F_6IrN_2$ (M^+-Cl) 1033.4441, found 1033.4438. Anal. calcd for $C_{53}H_{62}ClF_6IrN_2$ C, 59.56; H, 5.85, found C, 59.10; H, 5.76.



(+)-**8dz**

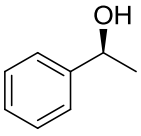
<Procedures for the Asymmetric Transfer Hydrogenation of Ketones>



6 **7**

General Procedure G: (–)-**8dz** (0.20 μmol, 0.1 or 0.05 mol %) was weighed into a flask. To this were added a solution of *t*-BuOK in *i*-PrOH (10 or 20 mL, 2 mM, 1 mol %) and aryl ketone **6** (2.00 or 4.00 mmol, 1.0 eq.), then the mixture was stirred at 70 °C for 1 h. After cooling to ambient temperature, the mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (ether/hexane) to give **7**. The enantiomeric excess of the product was determined by HPLC analysis with chiral stationary phase column (Daicel Chiralcel; OD-H, OB-H, or AD-H).

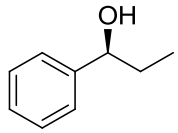
(*S*)-1-Phenylethanol ((*S*)-**7a**); Following the General Procedure G; 88% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[4] Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95/5, 1.0 mL/min, t_R = 8.6 min (minor), t_S = 10.1 min (major); 97% ee; $[\alpha]_D^{20}$ –54.8 (*c* 1.00, $CHCl_3$).



(*S*)-**7a**

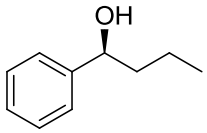
(*S*)-1-Phenylpropanol ((*S*)-**7b**); Following the General Procedure G; 93% yield; this product was

characterized by comparison of the spectroscopic data with those reported previously;[4] Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98/2, 1.0 mL/min, t_R = 11.8 min (minor), t_S = 12.6 min (major); 97% ee; $[\alpha]_D^{20}$ –45.3 (*c* 1.00, $CHCl_3$).



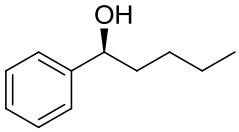
(*S*)-**7b**

(*S*)-1-Phenylbutanol ((*S*)-**7c**); Following the General Procedure G; 79% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[4] Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98/2, 0.8 mL/min, t_R = 16.1 min (minor), t_S = 17.9 min (major); 97% ee; $[\alpha]_D^{23}$ –54.4 (*c* 1.00, $CHCl_3$).



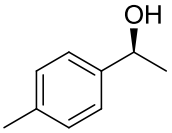
(*S*)-**7c**

(*S*)-1-Phenylpentanol ((*S*)-**7d**); Following the General Procedure G; 15% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[4] Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98/2, 1.0 mL/min, t_R = 12.5 min (minor), t_S = 13.7 min (major); 97% ee; $[\alpha]_D^{23}$ –39.4 (*c* 1.00, $CHCl_3$).



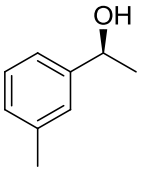
(*S*)-**7d**

(*S*)-1-(*p*-Tolyl)ethanol ((*S*)-**7e**); Following the General Procedure G; 86% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[5] Daicel Chiralcel AD-H, hexane/*i*-PrOH = 95/5, 1.0 mL/min, t_R = 12.3 min (minor), t_S = 12.9 min (major); 92% ee; $[\alpha]_D^{23}$ –49.7 (*c* 1.00, $CHCl_3$).



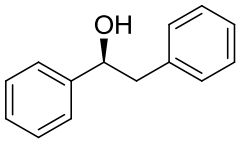
(*S*)-**7e**

(*S*)-1-(*m*-Tolyl)ethanol ((*S*)-**7f**); Following the General Procedure G; 20% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[5] Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98/2, 1.0 mL/min, t_R = 11.8 min (minor), t_S = 16.4 min (major); 83% ee; $[\alpha]_D^{23}$ –45.3 (*c* 1.00, $CHCl_3$).



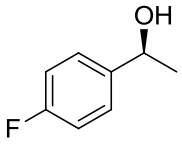
(*S*)-**7f**

(*S*)-1,2-Diphenyl-1-ethanol ((*S*)-**7g**); Following the General Procedure G; 66% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[4] Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95/5, 1.0 mL/min, t_R = 12.6 min (minor), t_S = 15.2 min (major); 98% ee; $[\alpha]_D^{22}$ –12.4 (*c* 1.00, $CHCl_3$).



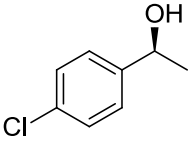
(*S*)-**7g**

(*S*)-1-(*p*-Furuorophenyl)ethanol ((*S*)-**7h**); Following the General Procedure G; 90% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[5] Daicel Chiralcel OB-H, hexane/*i*-PrOH = 95/5, 0.8 mL/min, t_S = 9.7 min (major), t_R = 10.9 min (minor); 92% ee; $[\alpha]_D^{23}$ –45.6 (*c* 1.00, $CHCl_3$).



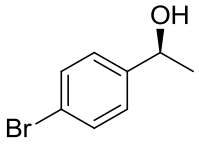
(*S*)-**7h**

(*S*)-1-(*p*-Chlorophenyl)ethanol ((*S*)-**7i**); Following the General Procedure G; 91% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[5] Daicel Chiralcel OB-H, hexane/*i*-PrOH = 95/5, 0.8 mL/min, t_R = 9.5 min (major), t_S = 11.3 min (minor); 95% ee; $[\alpha]_D^{22}$ –36.9 (*c* 1.00, $CHCl_3$).



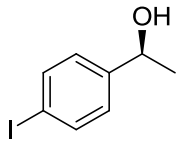
(*S*)-**7i**

(*S*)-1-(*p*-Bromophenyl)ethanol ((*S*)-**7j**); Following the General Procedure G; 91% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[5] Daicel Chiralcel OB-H, hexane/*i*-PrOH = 95/5, 0.8 mL/min, t_S = 10.0 min (major), t_R = 12.3 min (minor); 93% ee; $[\alpha]_D^{21}$ –37.3 (*c* 1.00, $CHCl_3$).



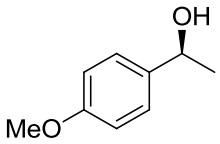
(*S*)-**7j**

***(S)*-1-(*p*-Iodophenyl)ethanol** ((*S*)-**7k**); Following the General Procedure G; 60% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[5] Daicel Chiralcel OB-H, hexane/*i*-PrOH = 95/5, 0.8 mL/min, t_S = 10.4 min (major), t_R = 12.6 min (minor); 95% ee; $[\alpha]_D^{22}$ –30.9 (*c* 1.00, $CHCl_3$).



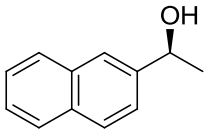
(*S*)-**7k**

(*S*)-1-(*p*-Methoxyphenyl)-ethanol ((*S*)-**7l**); Following the General Procedure G; 55% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[5] Daicel Chiralcel OD-H, hexane/*i*-PrOH = 98/2, 1.0 mL/min, t_R = 18.0 min (minor), t_S = 19.8 min (major); 94% ee; $[\alpha]_D^{23}$ –45.2 (*c* 1.00, $CHCl_3$).



(*S*)-**7l**

(*S*)-1-(2-Naphtyl)-1-ethanol ((*S*)-**7m**); Following the General Procedure G; 37% yield; this product was characterized by comparison of the spectroscopic data with those reported previously;[5] Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95/5, 1.0 mL/min, t_S = 16.6 min (major), t_R = 18.6 min (minor); 83% ee; $[\alpha]_D^{23}$ –39.4 (*c* 1.00, $CHCl_3$).



(*S*)-**7m**

<Notes and References>

1 K. Yoshida, S. Horiuchi, T. Takeichi, H. Shida, T. Imamoto and A. Yanagisawa, *Org. Lett.*, 2010, **12**, 1764–1767.

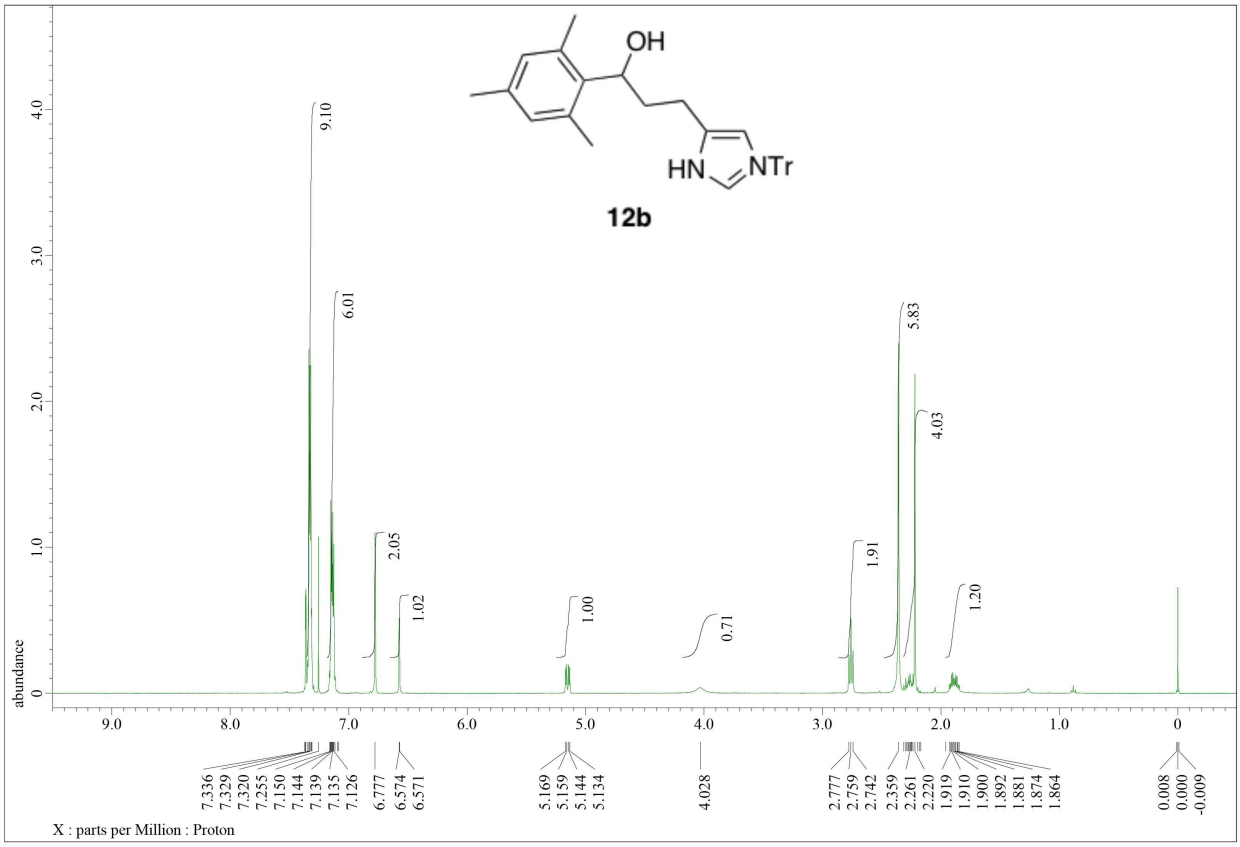
2 C. Nolte, J. Ammer and H. Mayr, *J. Org. Chem.*, 2012, **77**, 3325–3335.

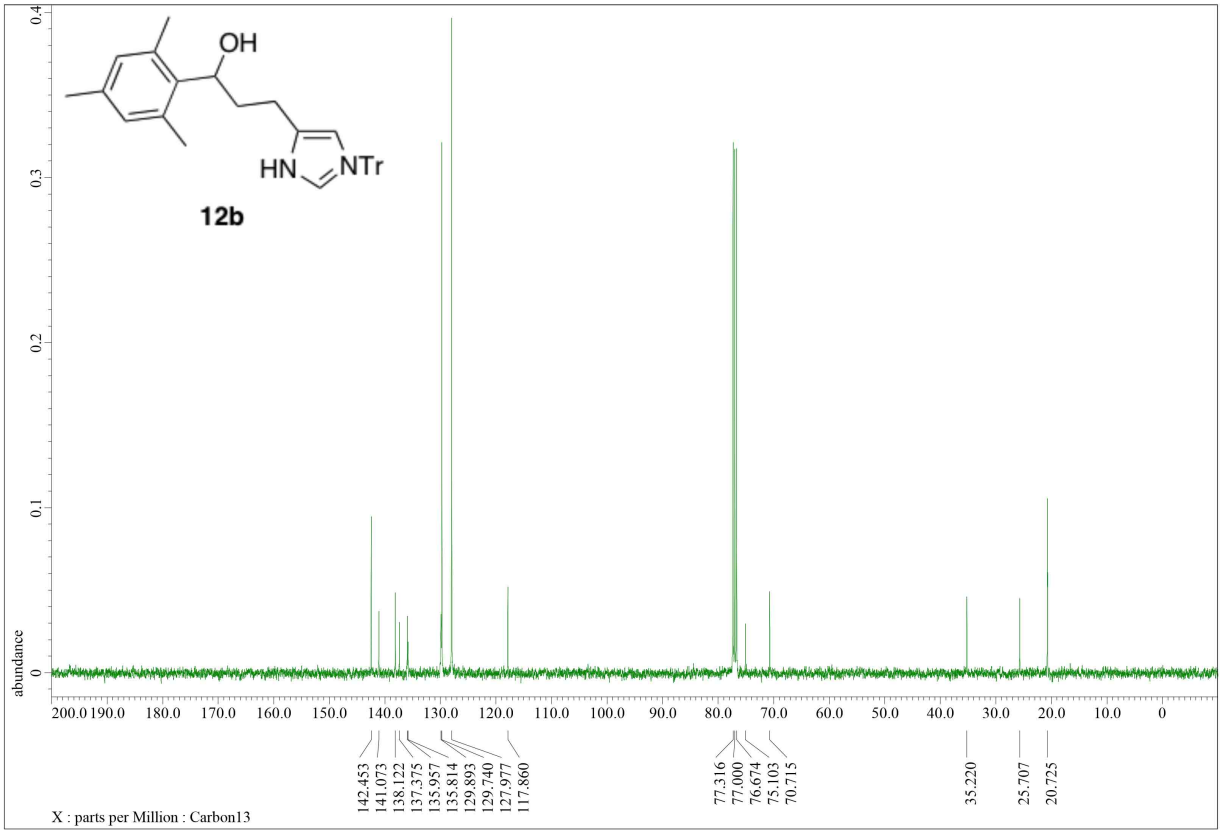
3 The crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre; deposition no. 1059389 ((*S*)-(–)-**8av**) and 1059390 ((*S*)-(–)-**8cv**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK; fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

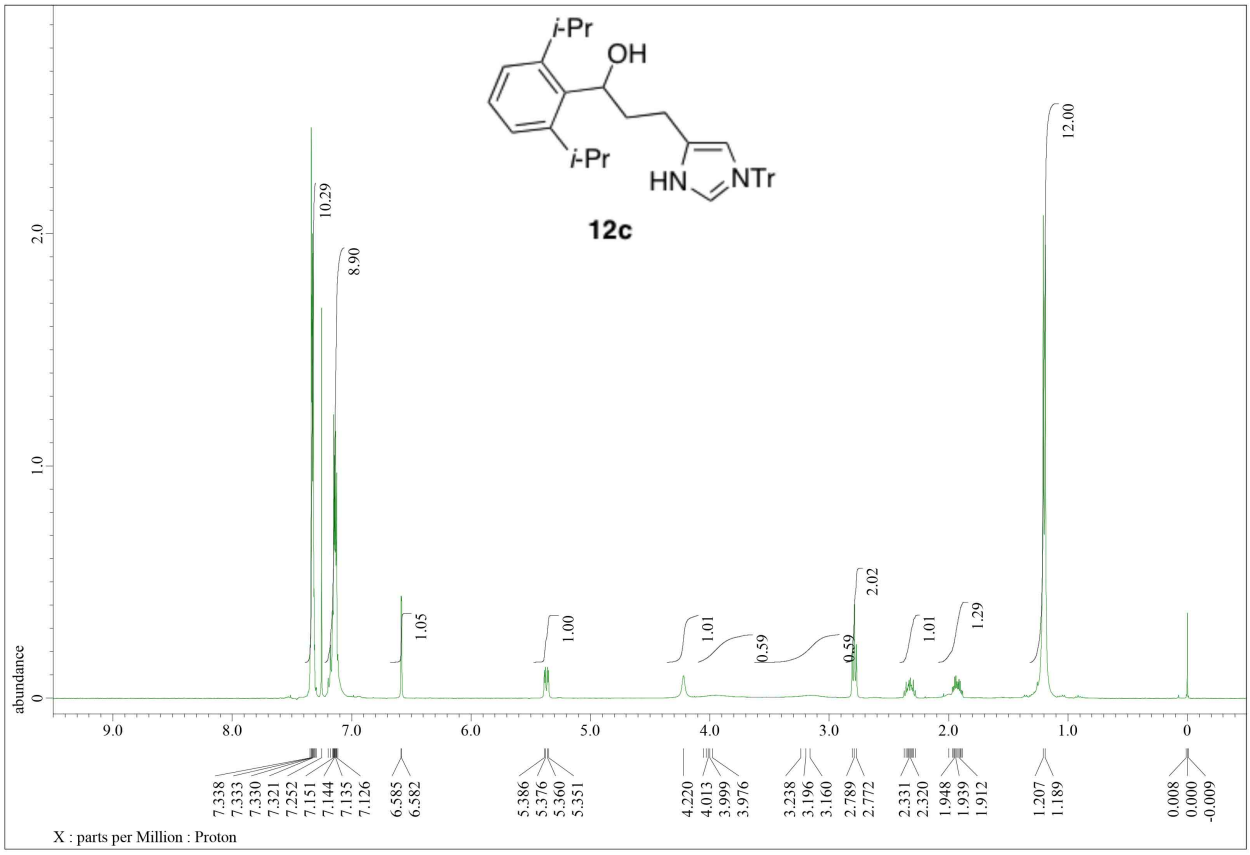
4 N. A. Salvi and S. Chattopadhyay, *Tetrahedron*, 2001, **57**, 2833-2839.

5 Y. Li, S. Yu, X. Wu, J. Xiao, W. Shen, Z. Dong and J. Gao, *J. Am. Chem. Soc.*, 2014, **136**, 4031–4039.

<^{1}H and ^{13}C NMR Spectra of New Compounds>



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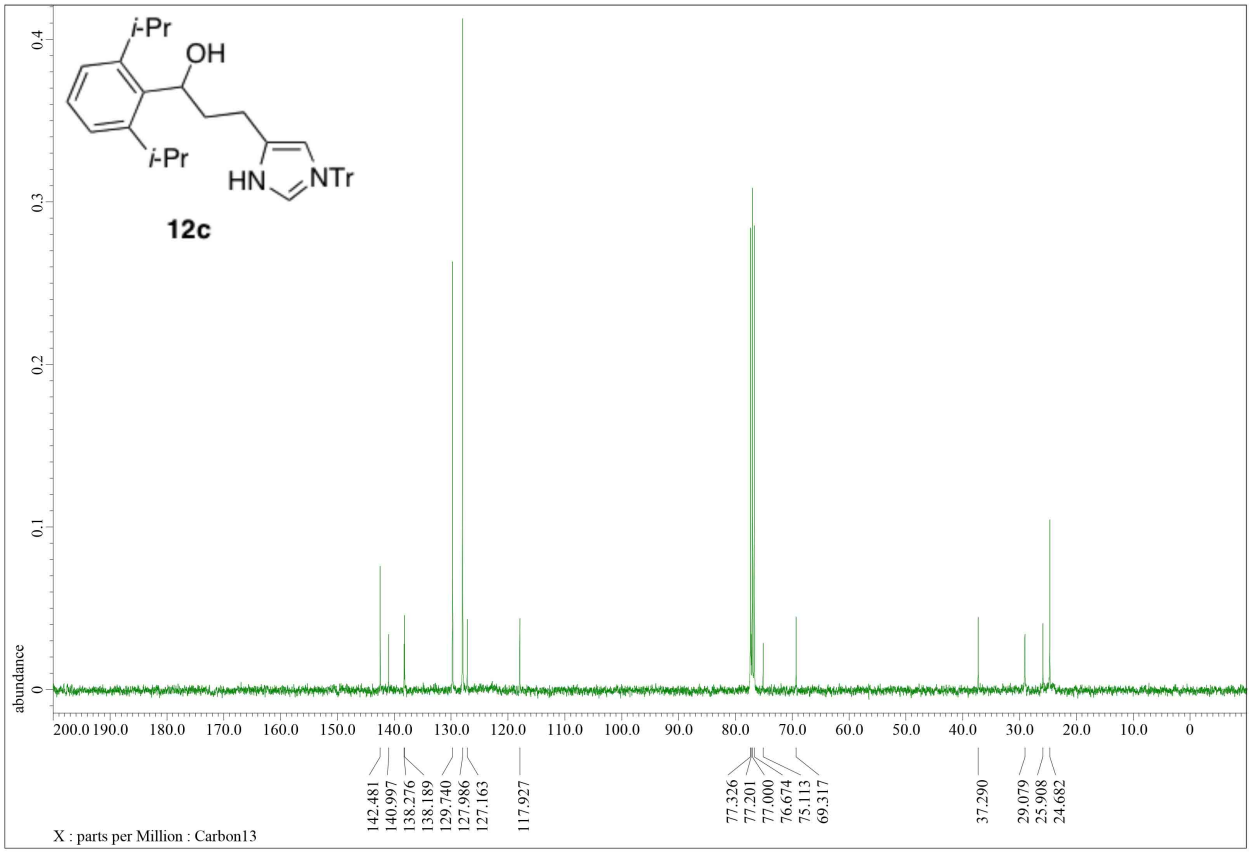
HN
NTr
12c
abundance
X : parts per Million : Proton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abundance
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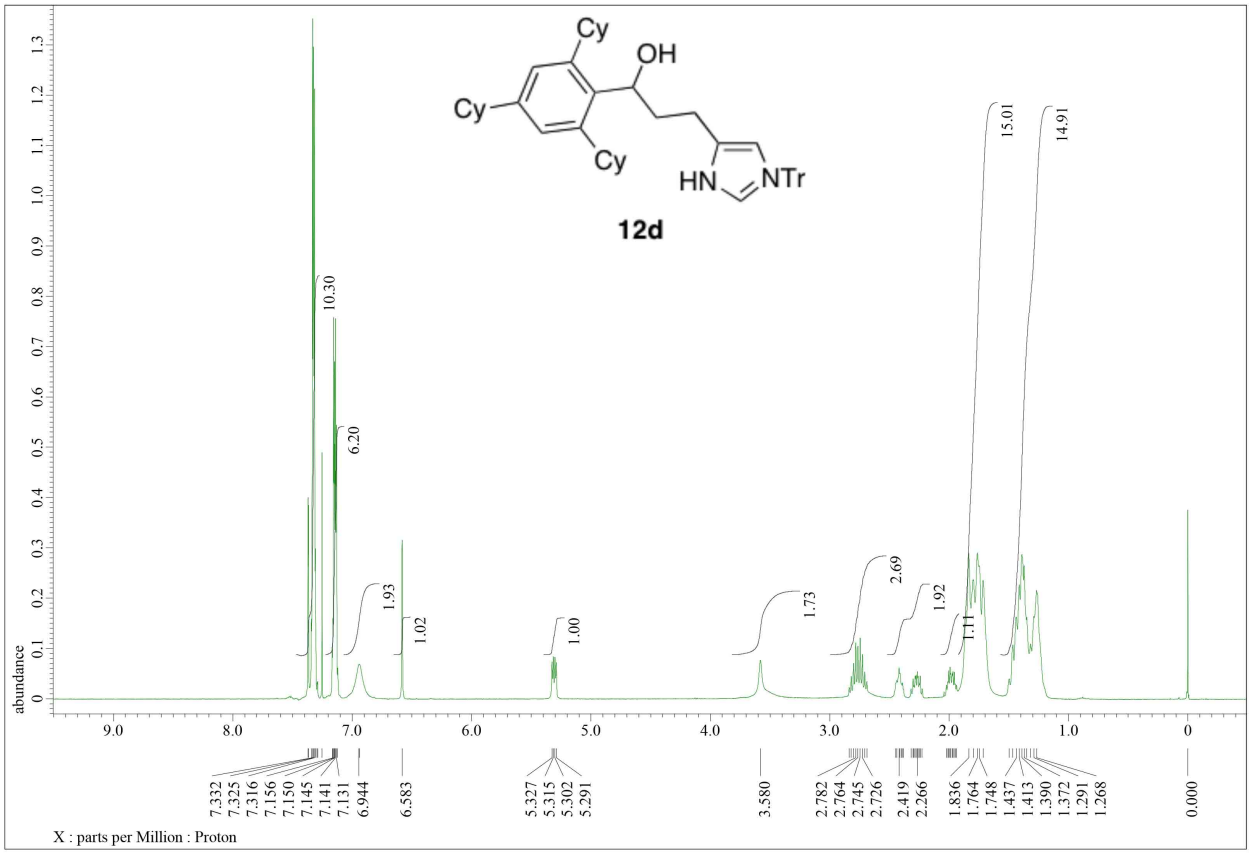
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Cy
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1.11
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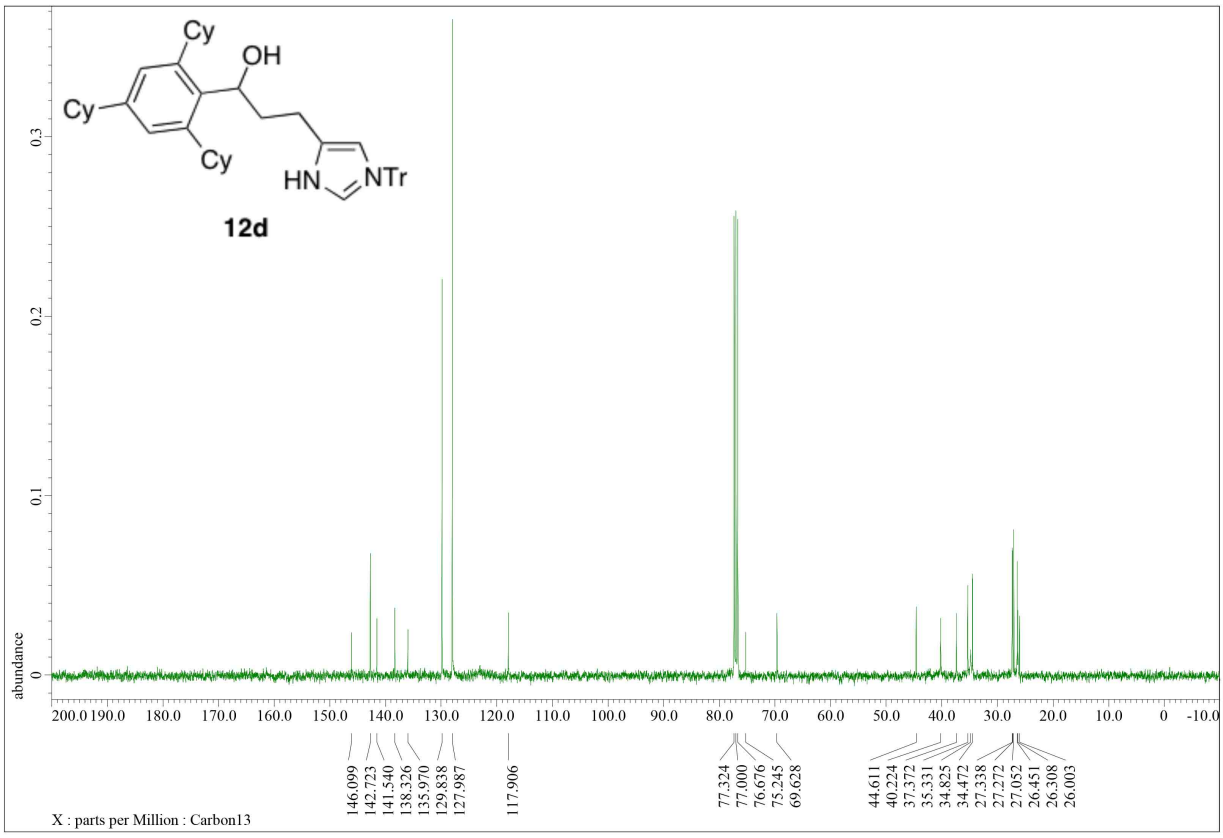
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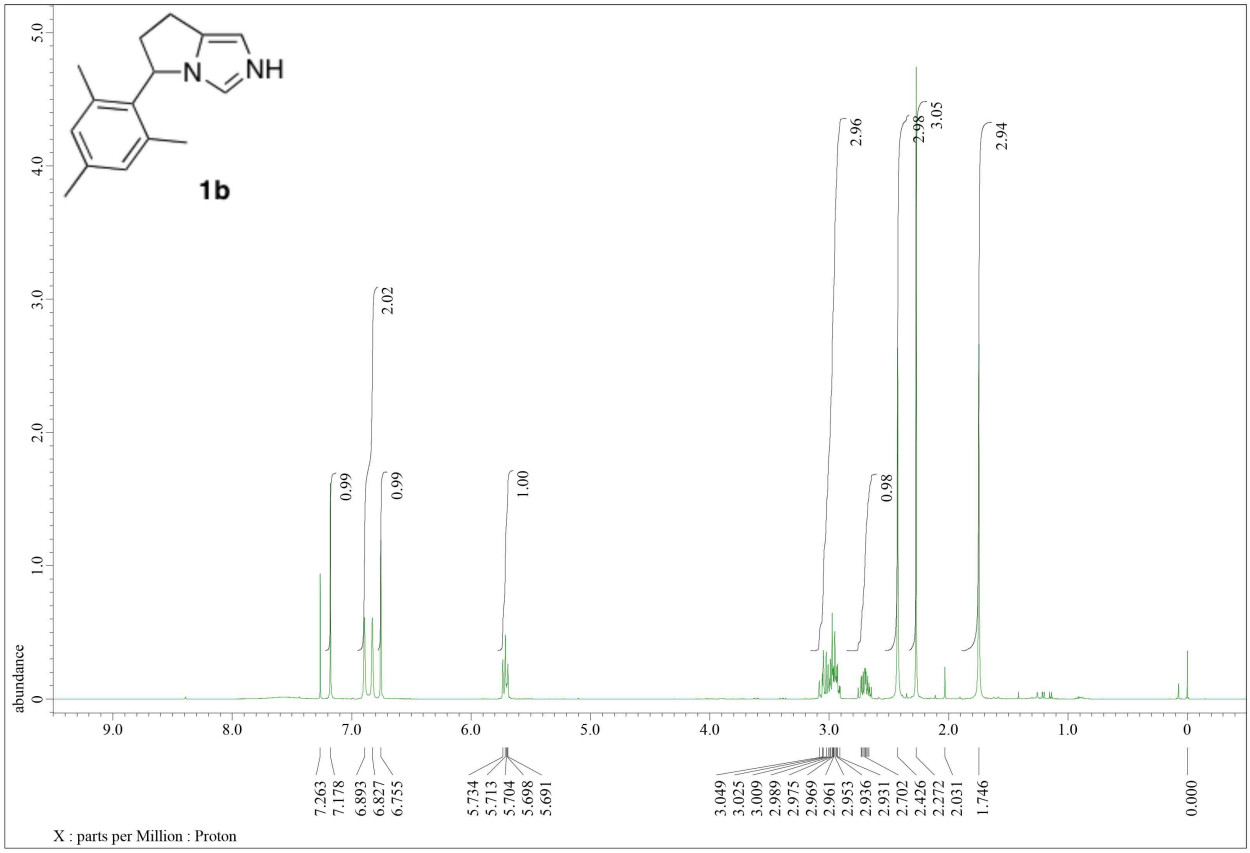
1b
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NH
abundance
X : parts per Million : Proton
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0.99
1.00
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6.893
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6.755
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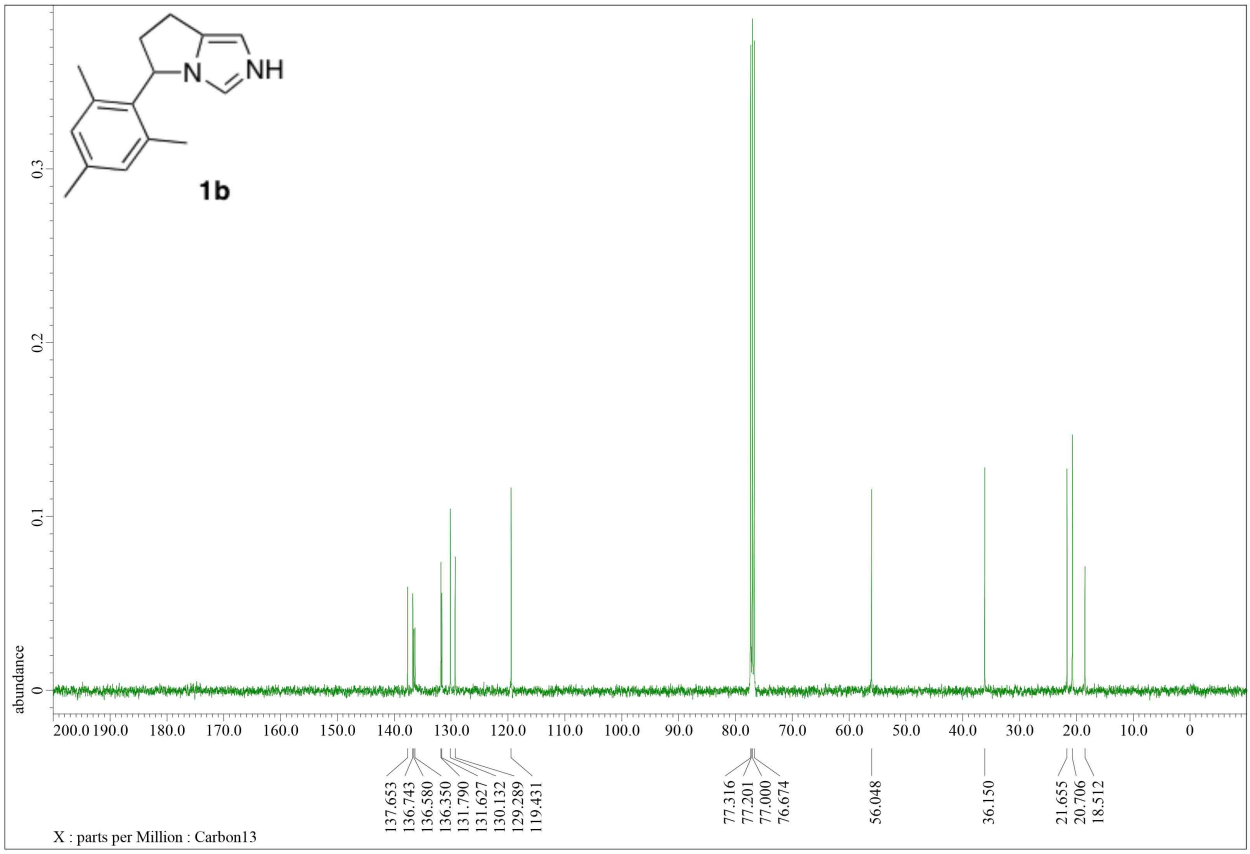
1b
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NH
abundance
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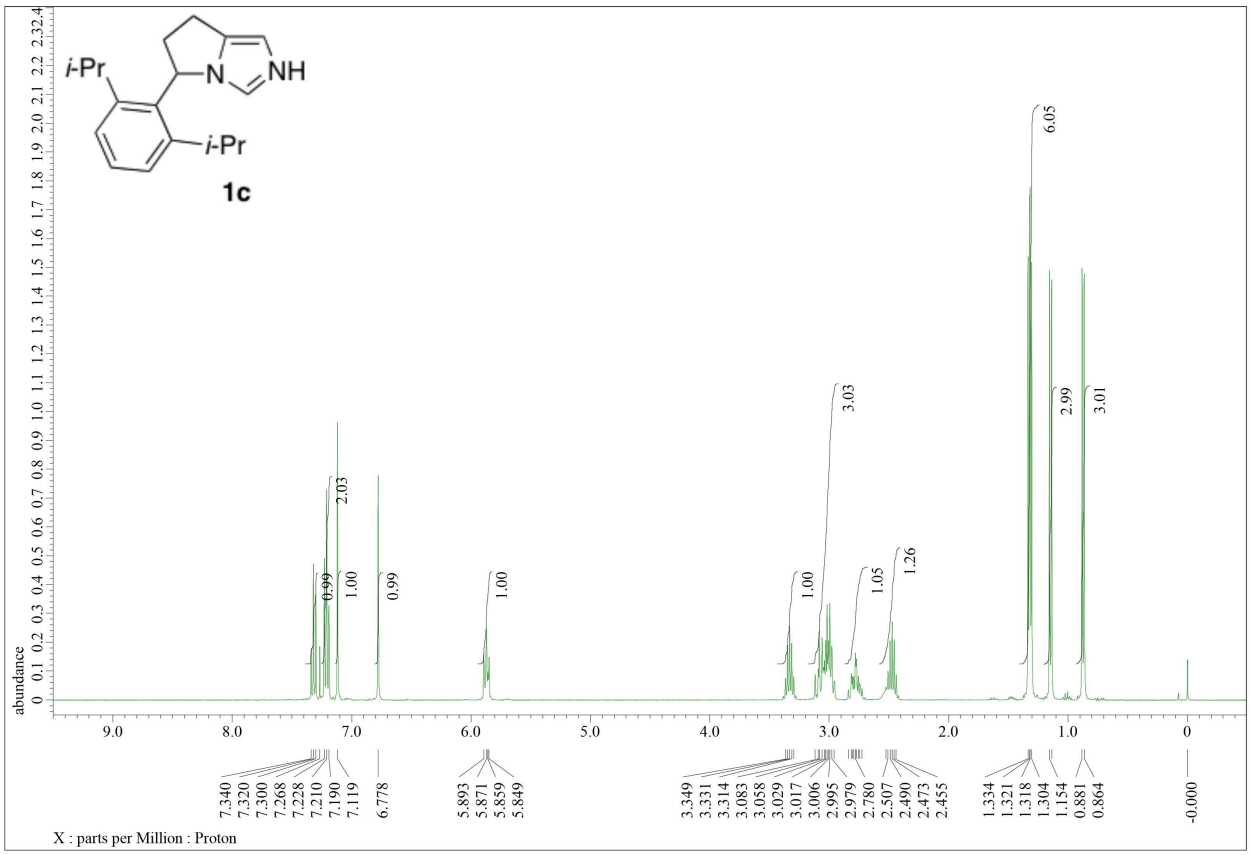
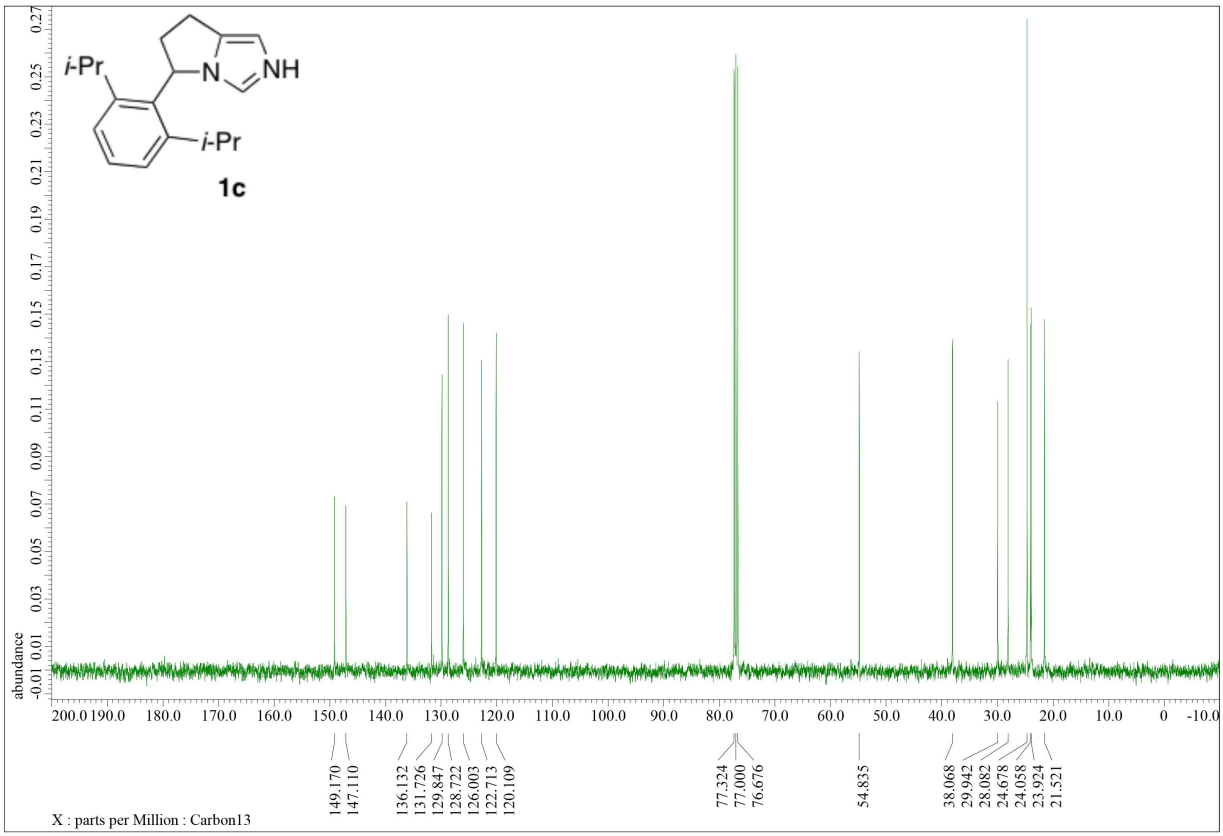
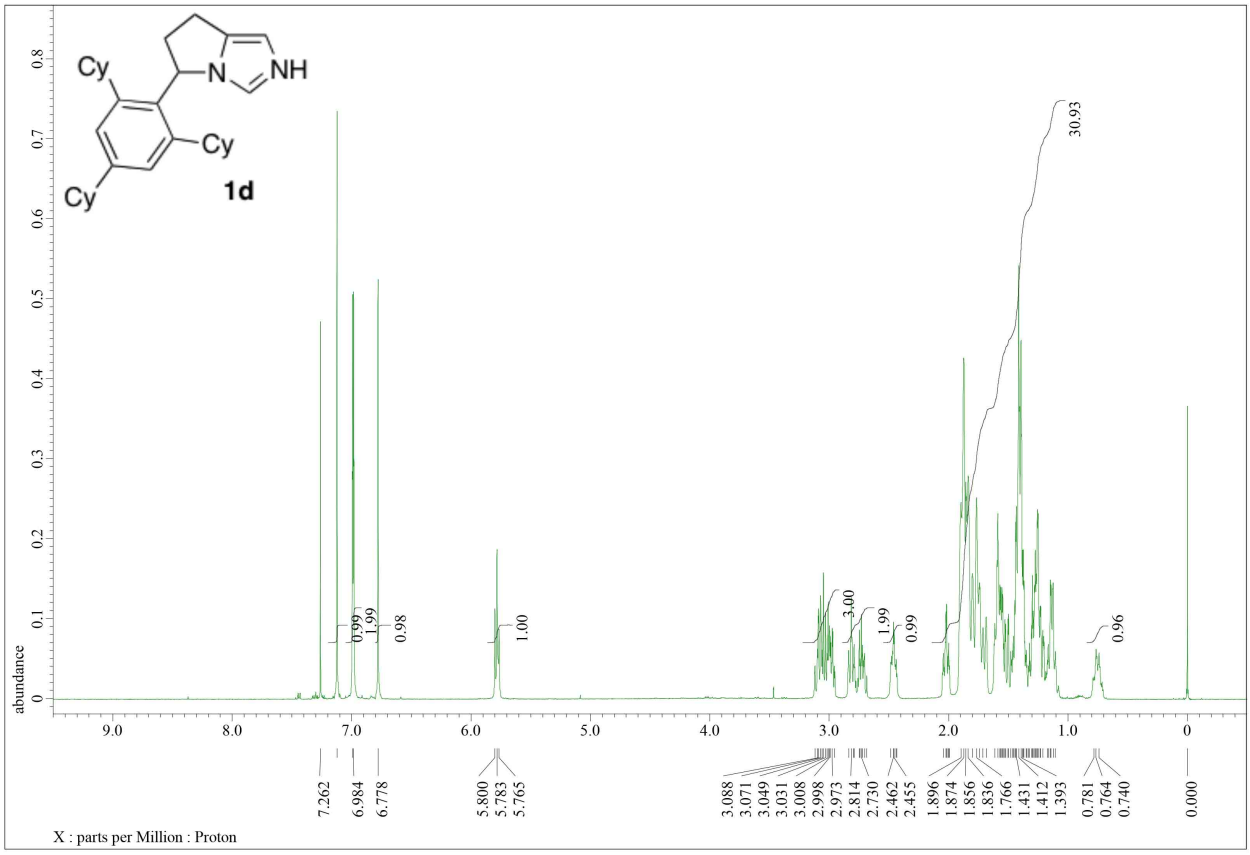
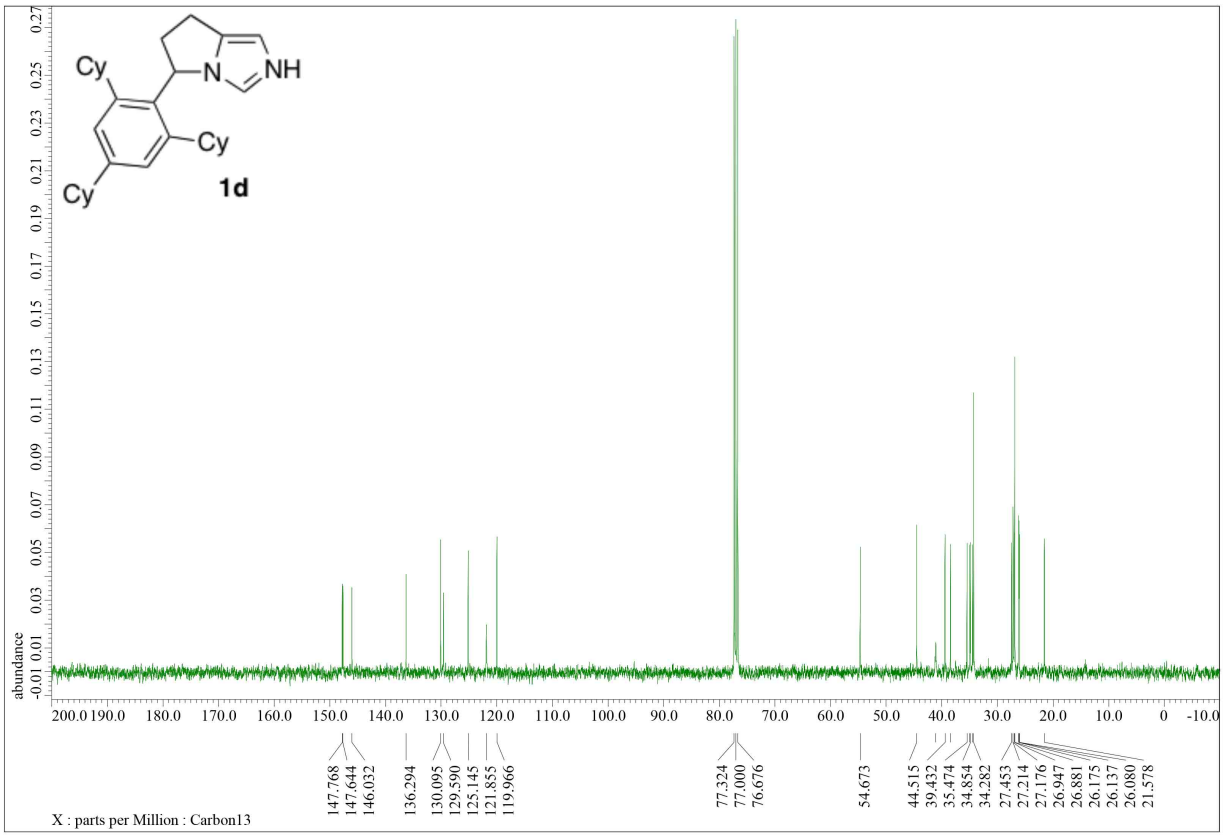
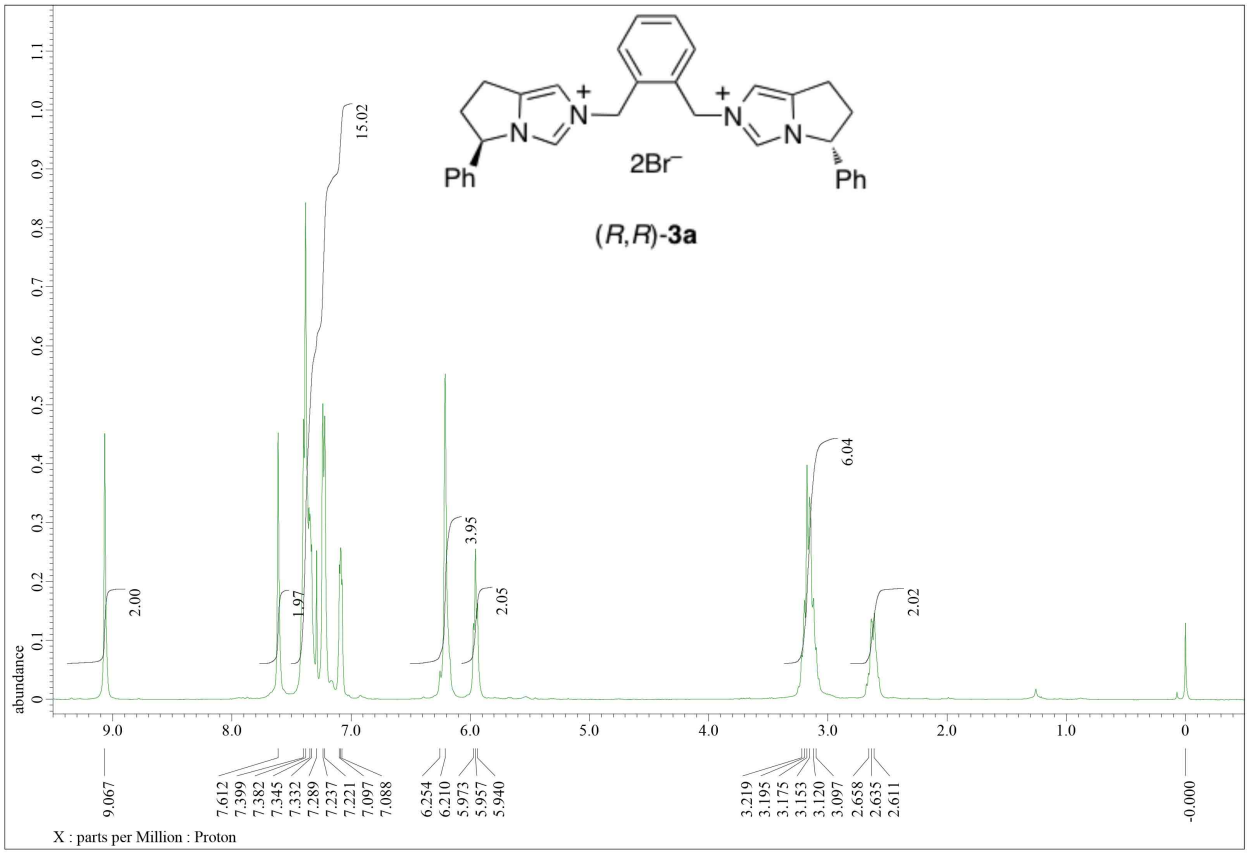
77.201
77.000
76.674
56.048
36.150
21.655
20.706
18.512

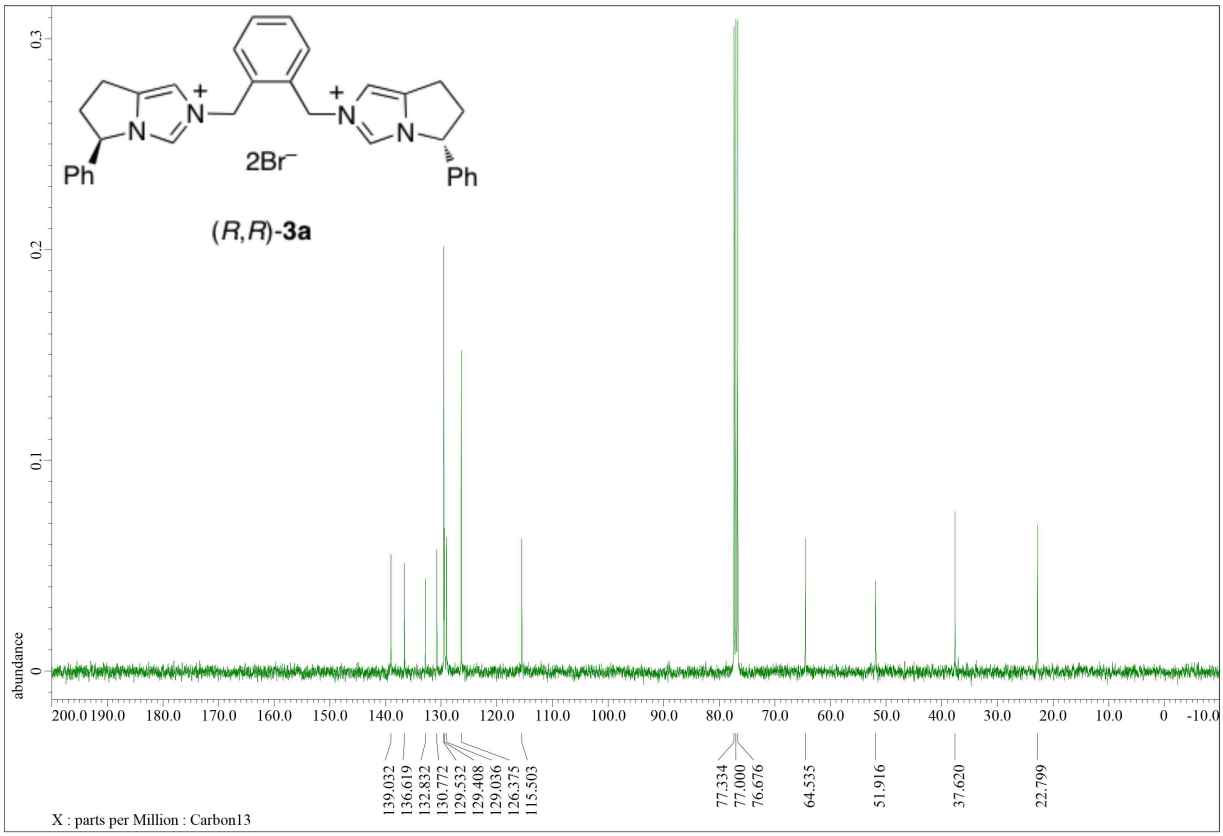

i-Pr
N
NH
i-Pr
1c
abundance
6.05
3.03
2.99
3.01
2.03
1.00
0.99
1.00
0.99
1.00
1.00
1.05
1.26
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.340
7.320
7.300
7.268
7.228
7.210
7.190
7.119
6.778
5.893
5.871
5.859
5.849
3.349
3.331
3.314
3.083
3.058
3.029
3.017
3.006
2.995
2.979
2.780
2.507
2.490
2.473
2.455
1.334
1.321
1.318
1.304
1.154
0.881
0.864
-0.000
X : parts per Million : Proton

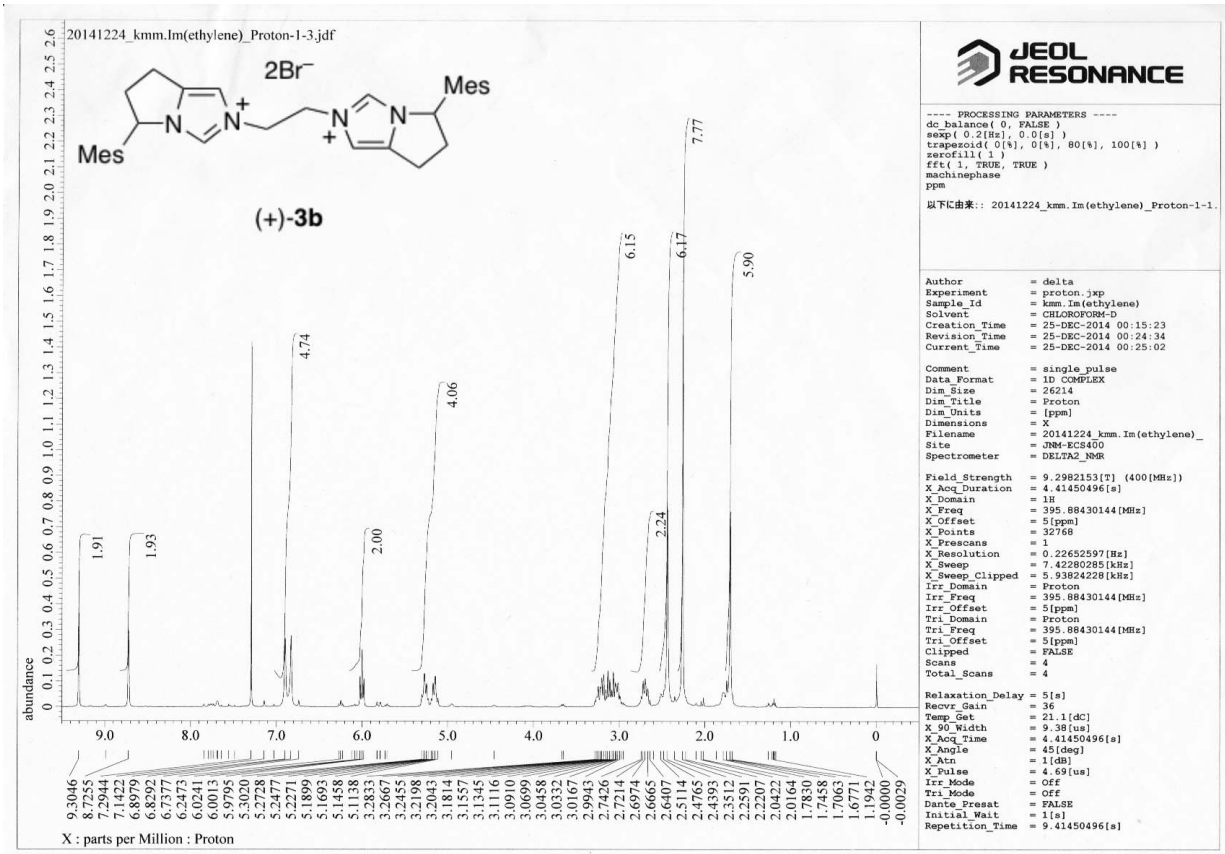

i-Pr
N
NH
i-Pr
1c
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
149.170
147.110
136.132
131.726
129.847
128.722
126.003
122.713
120.109
77.324
77.000
76.676
54.835
38.068
29.942
28.082
24.678
24.058
23.924
21.521
X : parts per Million : Carbon13

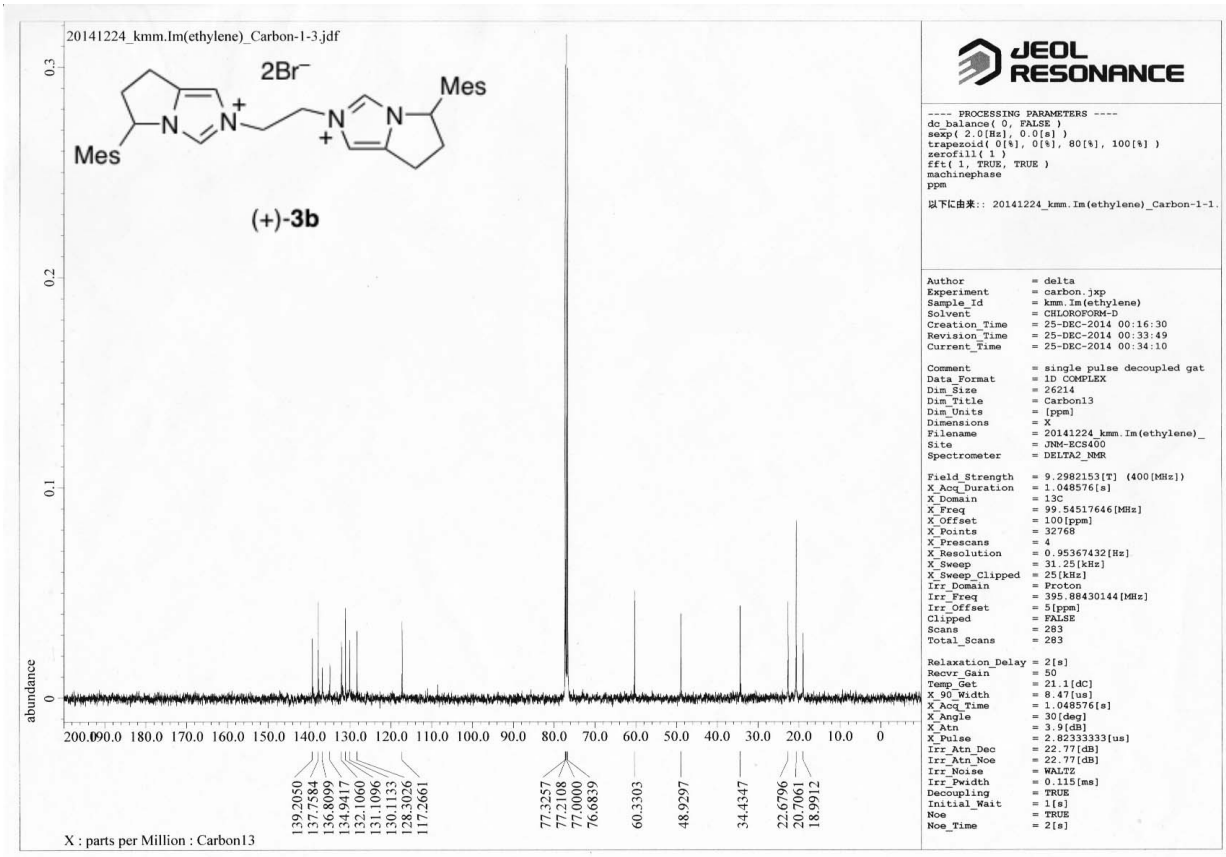

Cy
Cy
Cy
NH
N
1d
abundance
X : parts per Million : Proton
30.93
0.99
1.99
0.98
1.00
3.00
1.99
0.99
0.96
7.262
6.984
6.778
5.800
5.783
5.765
3.088
3.071
3.049
3.031
3.008
2.998
2.973
2.814
2.730
2.462
2.455
1.896
1.874
1.856
1.836
1.766
1.431
1.412
1.393
0.781
0.764
0.740
0.000

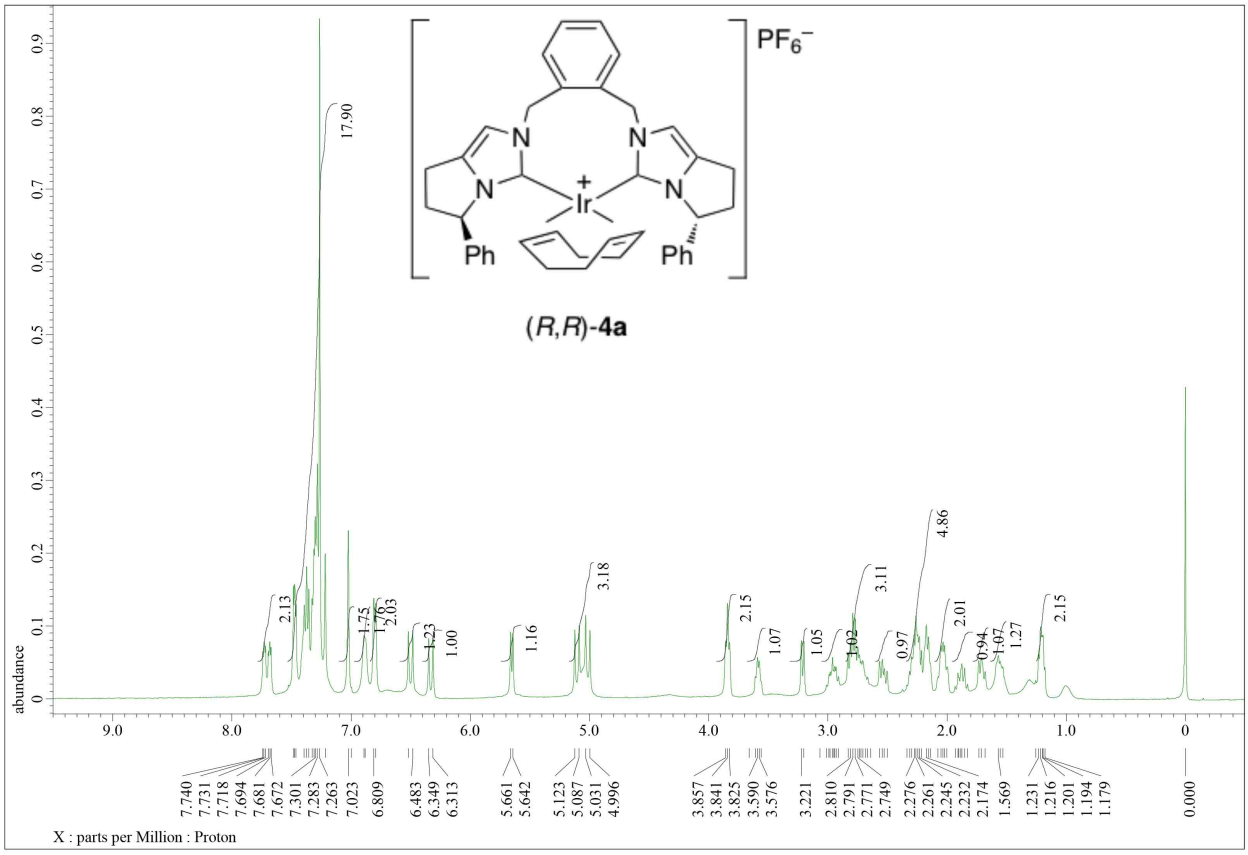

Cy
Cy
Cy
NH
N
1d
abundance
X : parts per Million : Carbon13
147.768
147.644
146.032
136.294
130.095
129.590
125.145
121.855
119.966
77.324
77.000
76.676
54.673
44.515
39.432
35.474
34.854
34.282
27.453
27.214
27.176
26.947
26.881
26.175
26.137
26.080
21.578

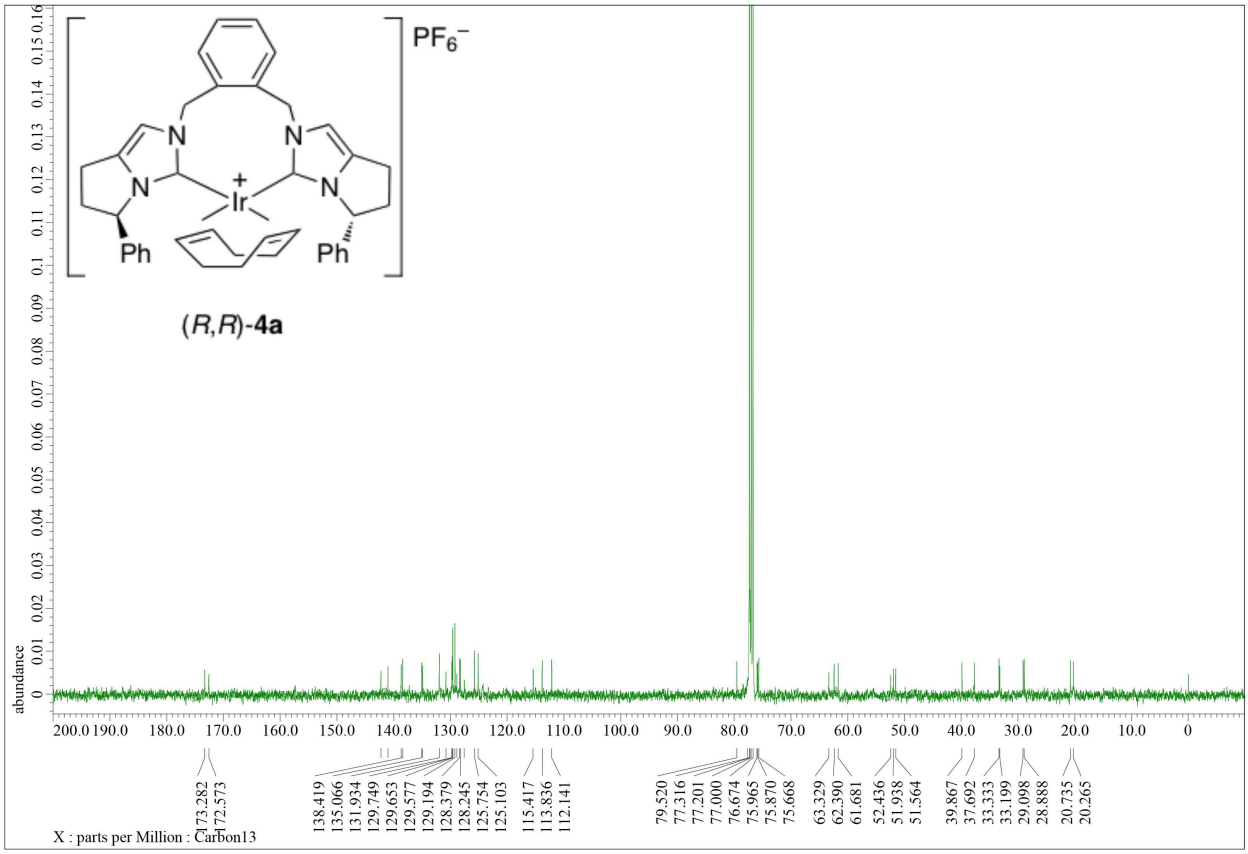

Ph
2Br⁻
Ph
(R,R)-3a
abundance
X : parts per Million : Proton

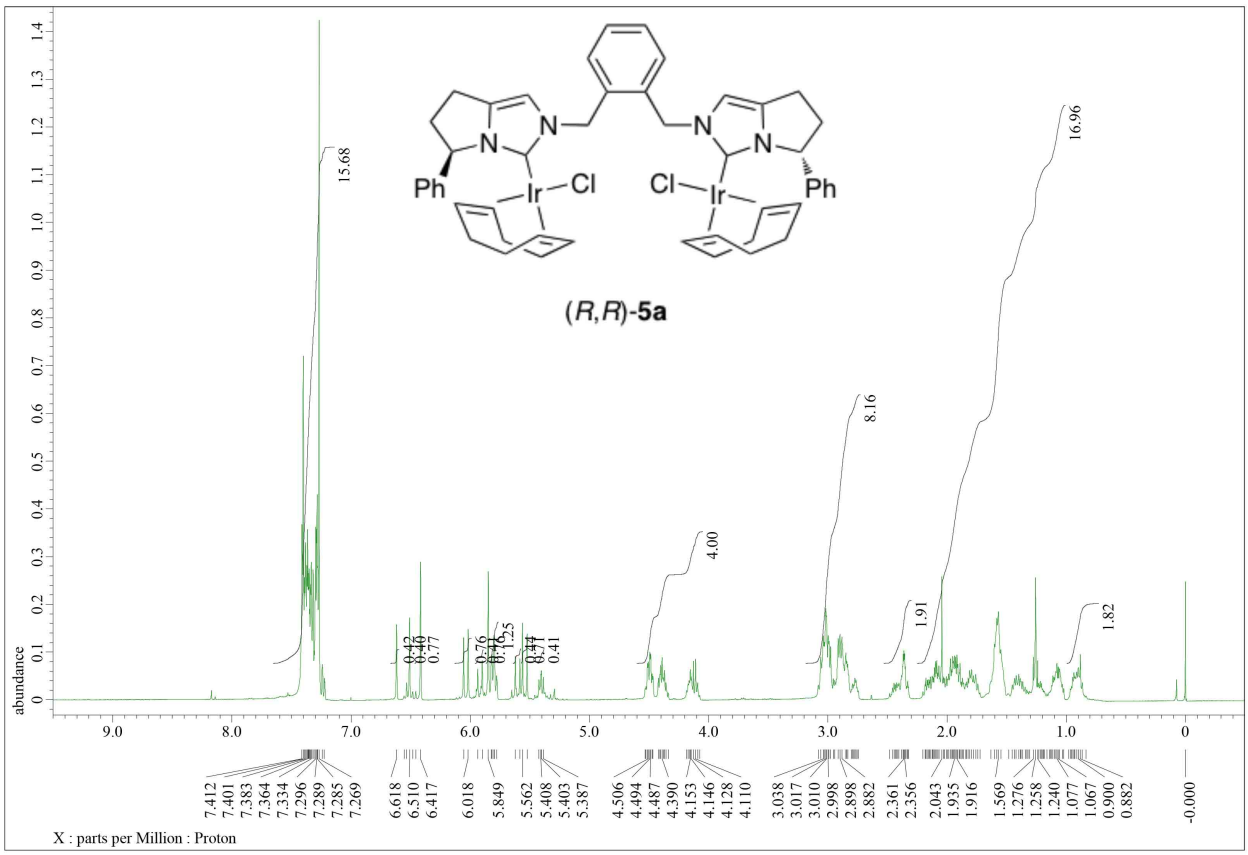

Ph
2Br⁻
Ph
(R,R)-3a
abundance
X : parts per Million : Carbon13

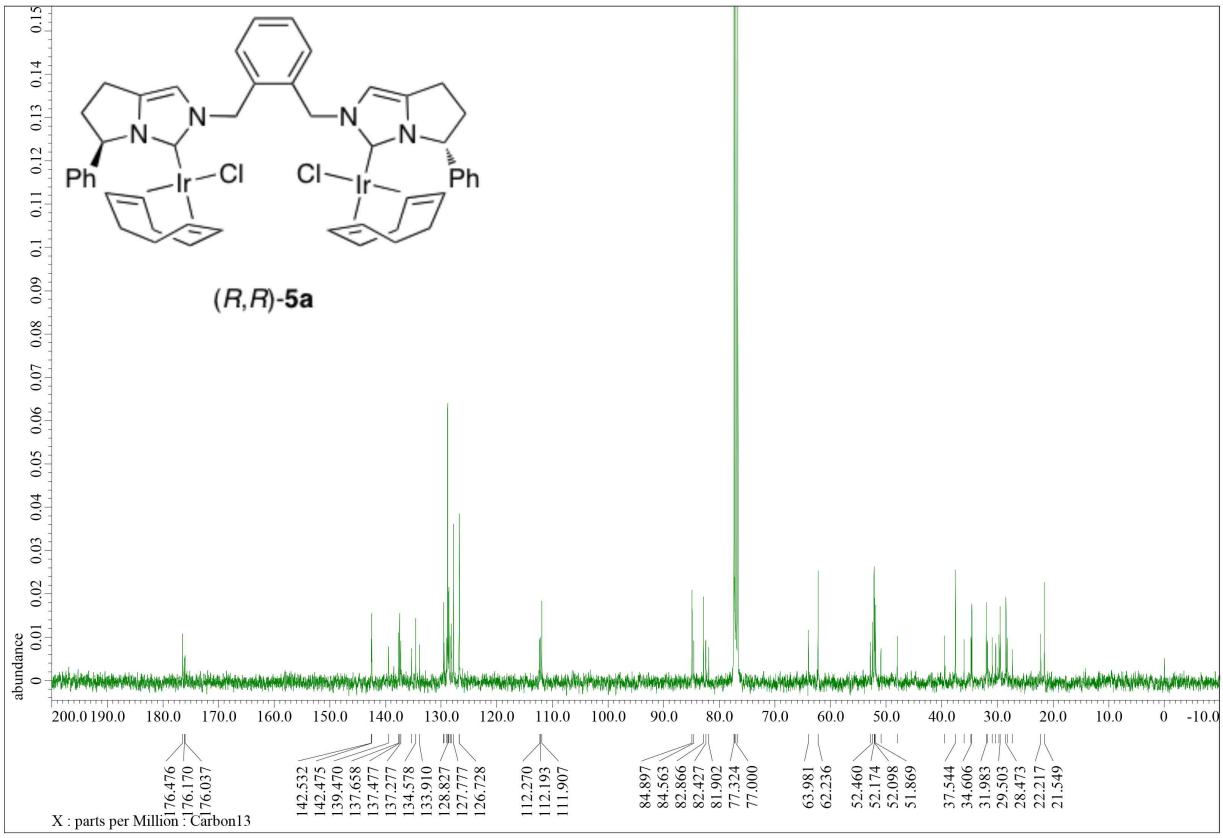

20141224_kmm.Im(ethylene)_Proton-1-3.jdf
2Br⁻
Mes
Mes
(+)-3b
1.91
1.93
2.00
4.06
4.74
6.15
6.17
2.24
7.77
5.90
abundance
X : parts per Million : Proton
JEOL RESONANCE
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
以下に由来:: 20141224_kmm.Im(ethylene)_Proton-1-1.
Author = delta
Experiment = proton.jxp
Sample_Id = kmm.Im(ethylene)
Solvent = CHLOROFORM-D
Creation_Time = 25-DEC-2014 00:15:23
Revision_Time = 25-DEC-2014 00:24:34
Current_Time = 25-DEC-2014 00:25:02
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Filename = 20141224_kmm.Im(ethylene)_
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.2982153[T] (400[MHz])
X_Acq_Duration = 4.41450496[s]
X_Domain = 1H
X_Freq = 395.88430144[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 1
X_Resolution = 0.22652597[Hz]
X_Sweep = 7.42280285[kHz]
X_Sweep_Clipped = 5.93824228[kHz]
Irr_Domain = Proton
Irr_Freq = 395.88430144[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 395.88430144[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 4
Total_Scans = 4
Relaxation_Delay = 5[s]
Recvr_Gain = 36
Temp_Get = 21.1[dC]
X_90_Width = 9.38[us]
X_Acq_Time = 4.41450496[s]
X_Angle = 45[deg]
X_Atn = 1[dB]
X_Pulse = 4.69[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE
Initial_Wait = 1[s]
Repetition_Time = 9.41450496[s]

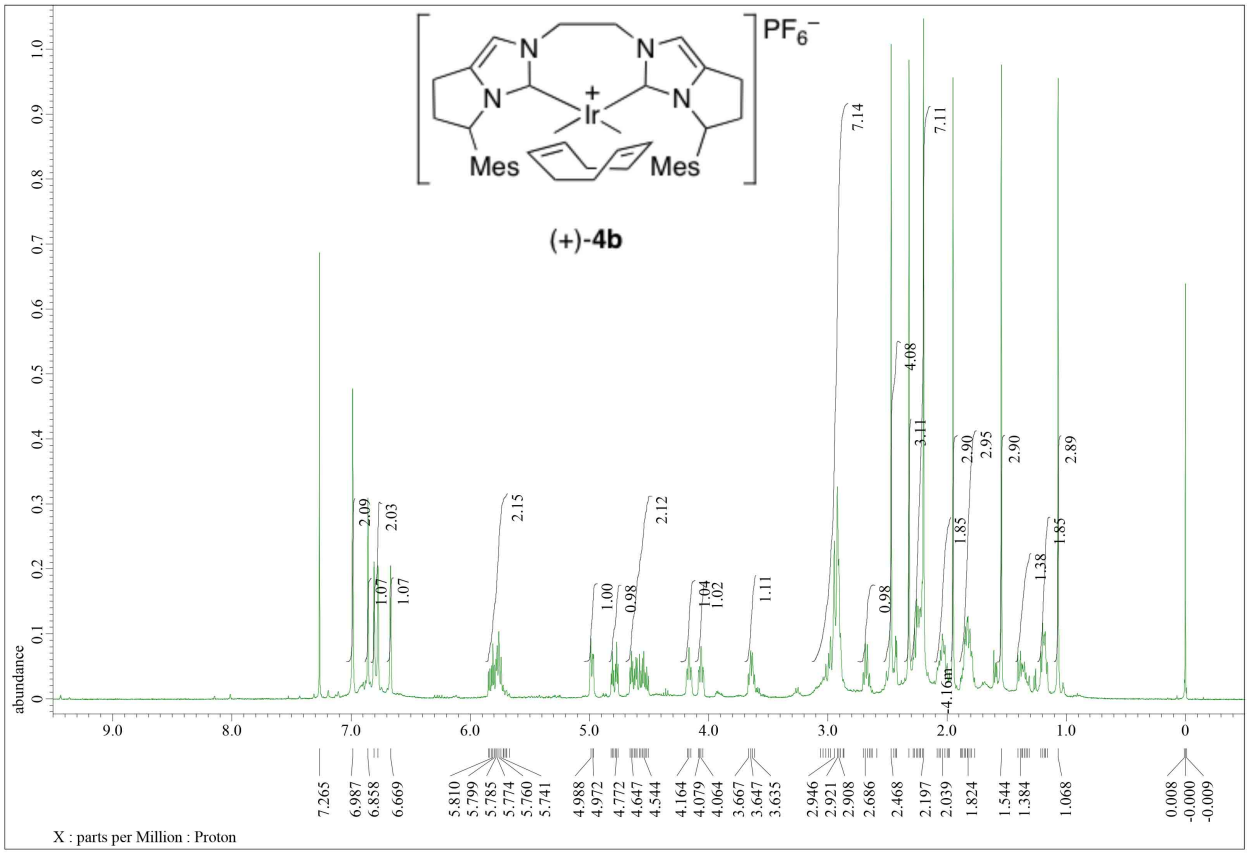

20141224_kmm.Im(ethylene)_Carbon-1-3.jdf
2Br⁻
Mes
Mes
(+)-3b
139.2050
137.7584
136.8099
134.9417
132.1060
131.1096
130.1133
128.3026
117.2661
77.3257
77.2108
77.0000
76.6839
60.3303
48.9297
34.4347
22.6796
20.7061
18.9912
abundance
X : parts per Million : Carbon13
JEOL RESONANCE
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
以下に由来:: 20141224_kmm.Im(ethylene)_Carbon-1-1.
Author = delta
Experiment = carbon.jxp
Sample_Id = kmm.Im(ethylene)
Solvent = CHLOROFORM-D
Creation_Time = 25-DEC-2014 00:16:30
Revision_Time = 25-DEC-2014 00:33:49
Current_Time = 25-DEC-2014 00:34:10
Comment = single pulse decoupled gat
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Filename = 20141224_kmm.Im(ethylene)_
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.2982153[T] (400[MHz])
X_Acq_Duration = 1.048576[s]
X_Domain = 13C
X_Freq = 99.54517646[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95367432[Hz]
X_Sweep = 31.25[kHz]
X_Sweep_Clipped = 25[kHz]
Irr_Domain = Proton
Irr_Freq = 395.88430144[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 283
Total_Scans = 283
Relaxation_Delay = 2[s]
Recvr_Gain = 50
Temp_Get = 21.1[dC]
X_90_Width = 8.47[us]
X_Acq_Time = 1.048576[s]
X_Angle = 30[deg]
X_Atn = 3.9[dB]
X_Pulse = 2.82333333[us]
Irr_Atn_Dec = 22.77[dB]
Irr_Atn_Noe = 22.77[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]

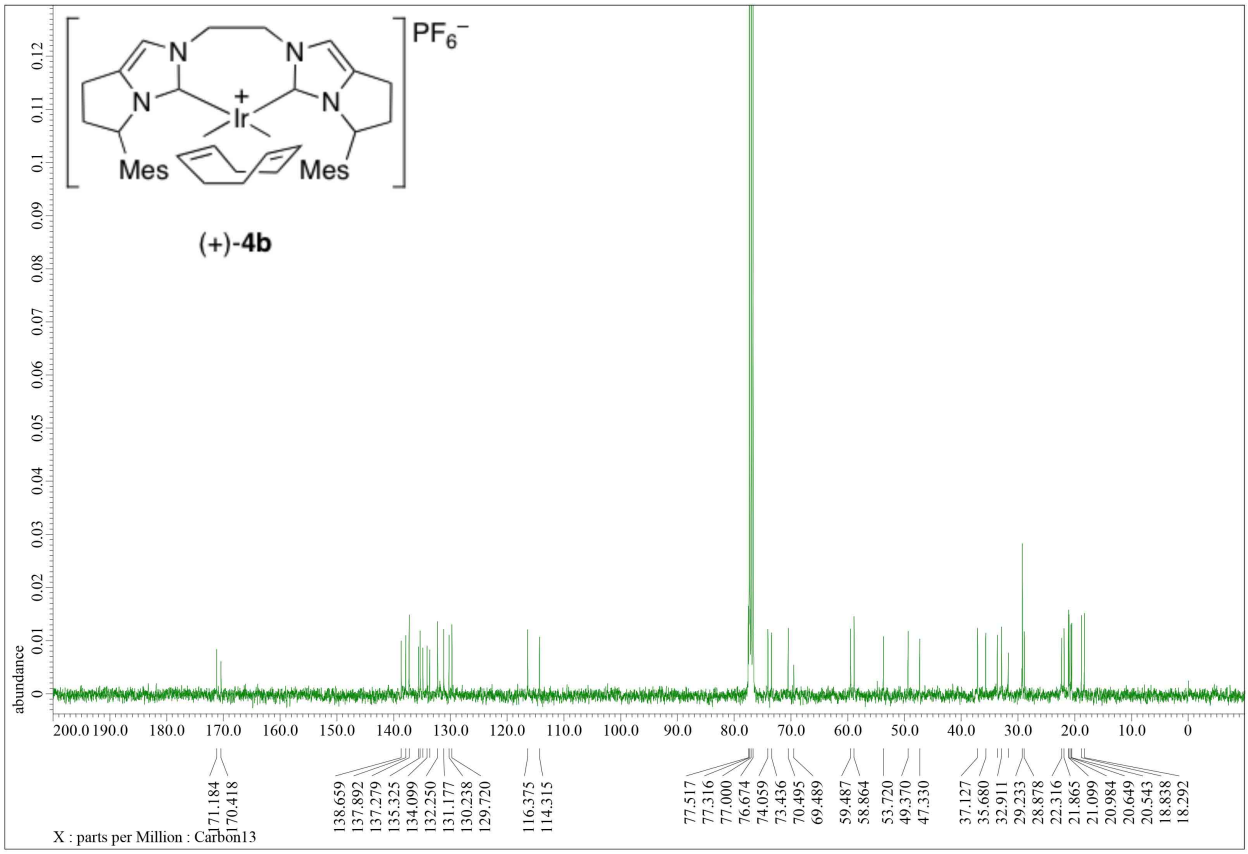

PF6−
(R,R)-4a
abundance
X : parts per Million : Proton

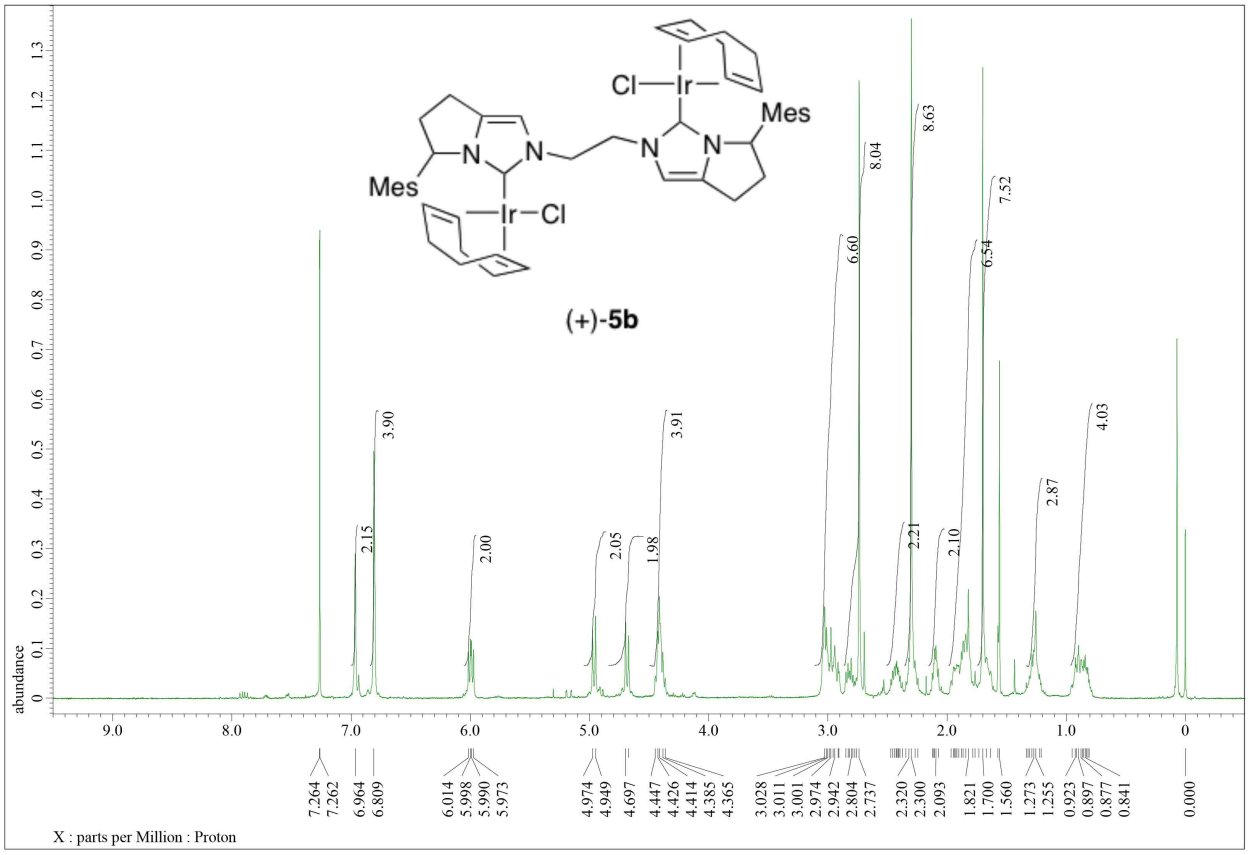

PF6−
(R,R)-4a
abundance
X : parts per Million : Carbon13

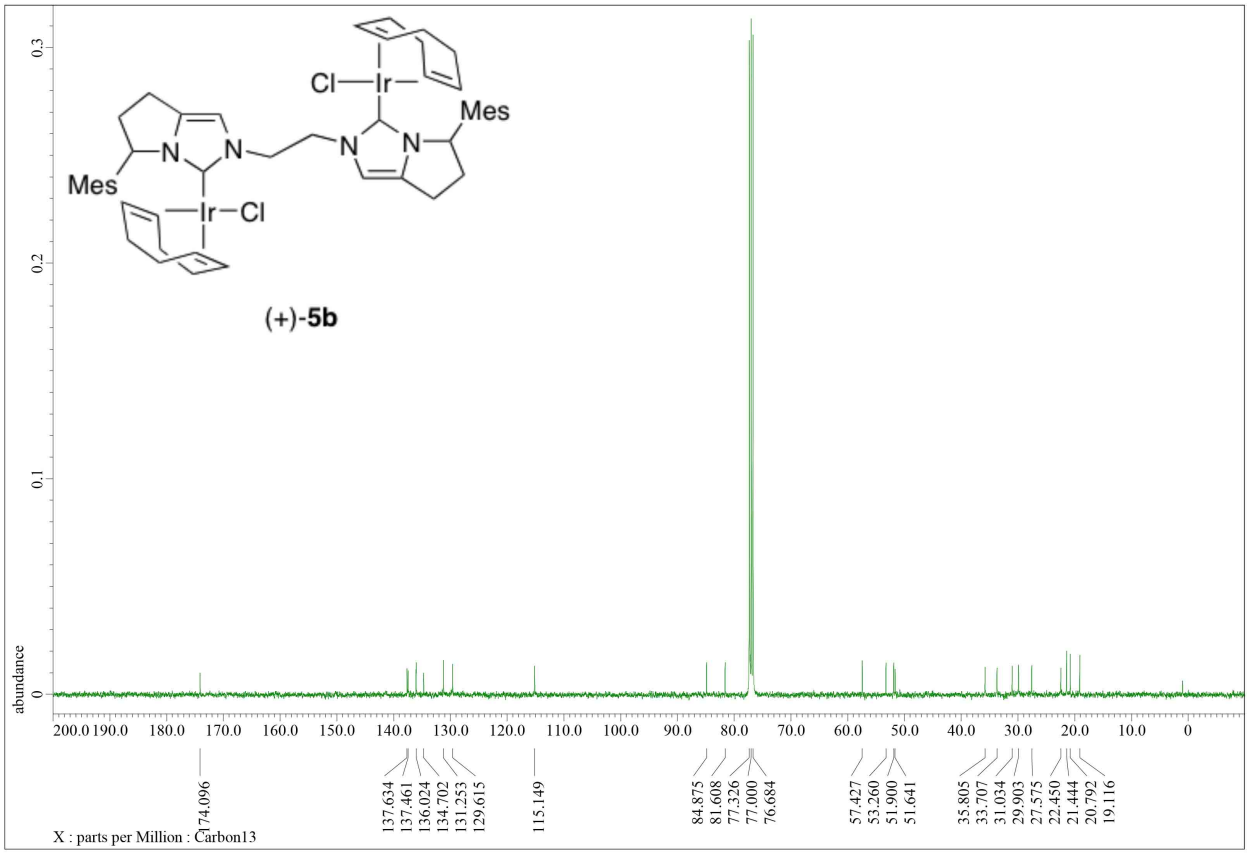

(R,R)-5a
15.68
8.16
16.96
4.00
1.91
1.82
abundance
X : parts per Million : Proton

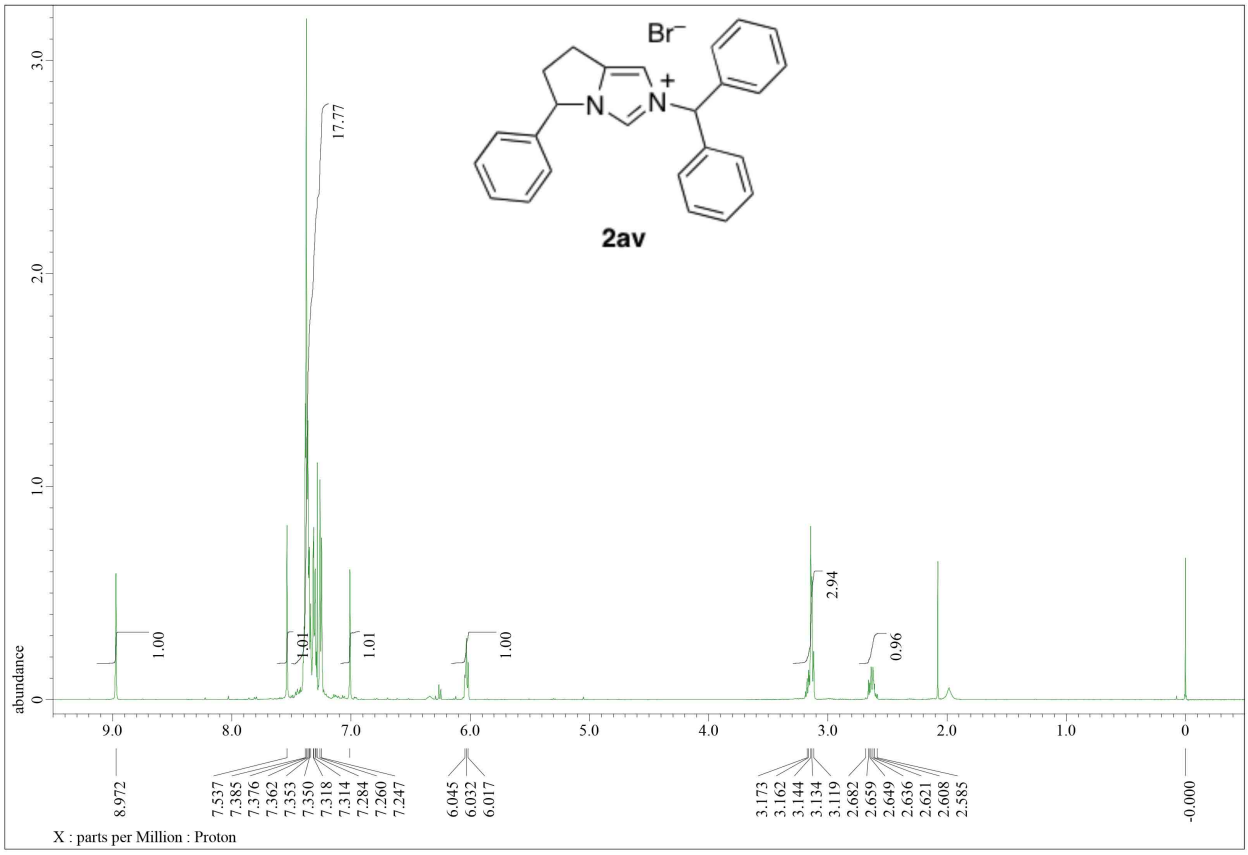

(R,R)-5a
abundance
X : parts per Million : Carbon13

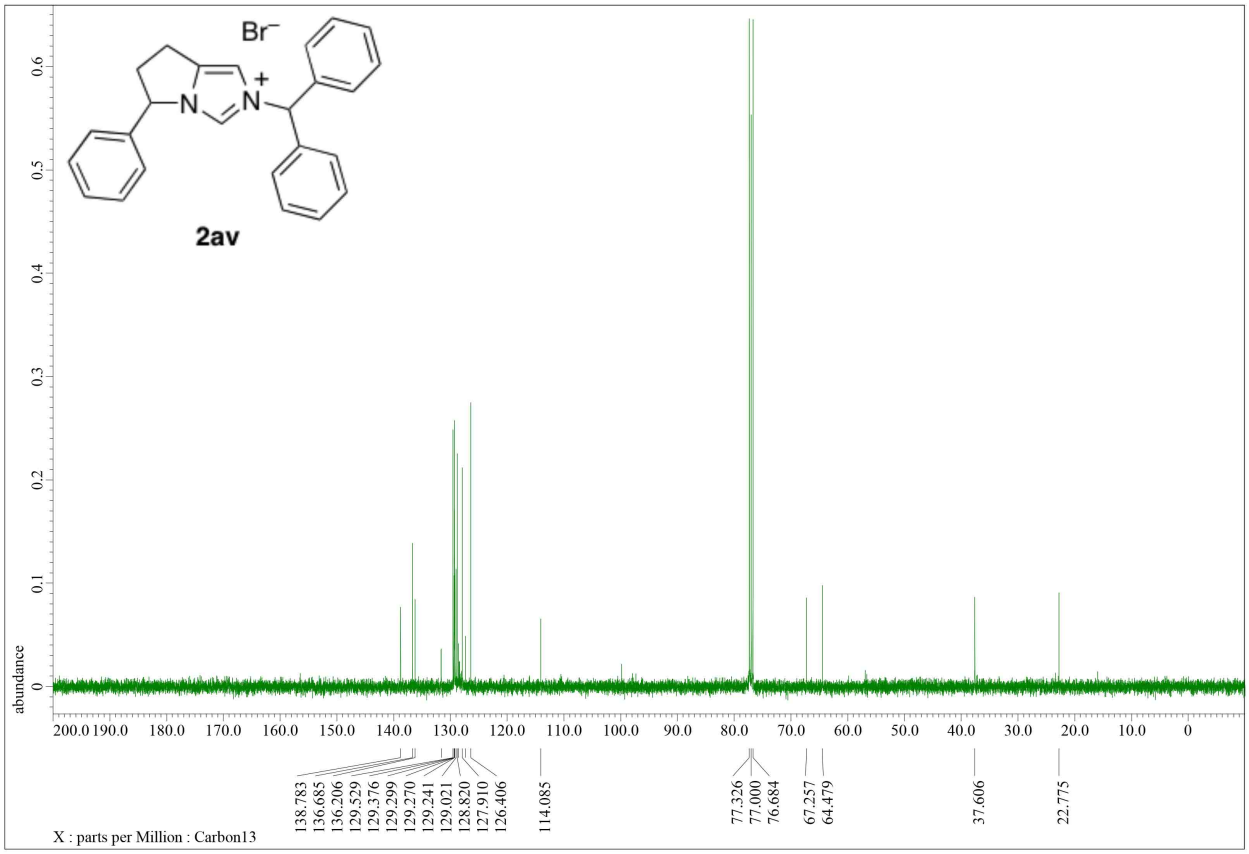

PF6−
Mes
Mes
Ir
(+)-4b
abundance
X : parts per Million : Proton

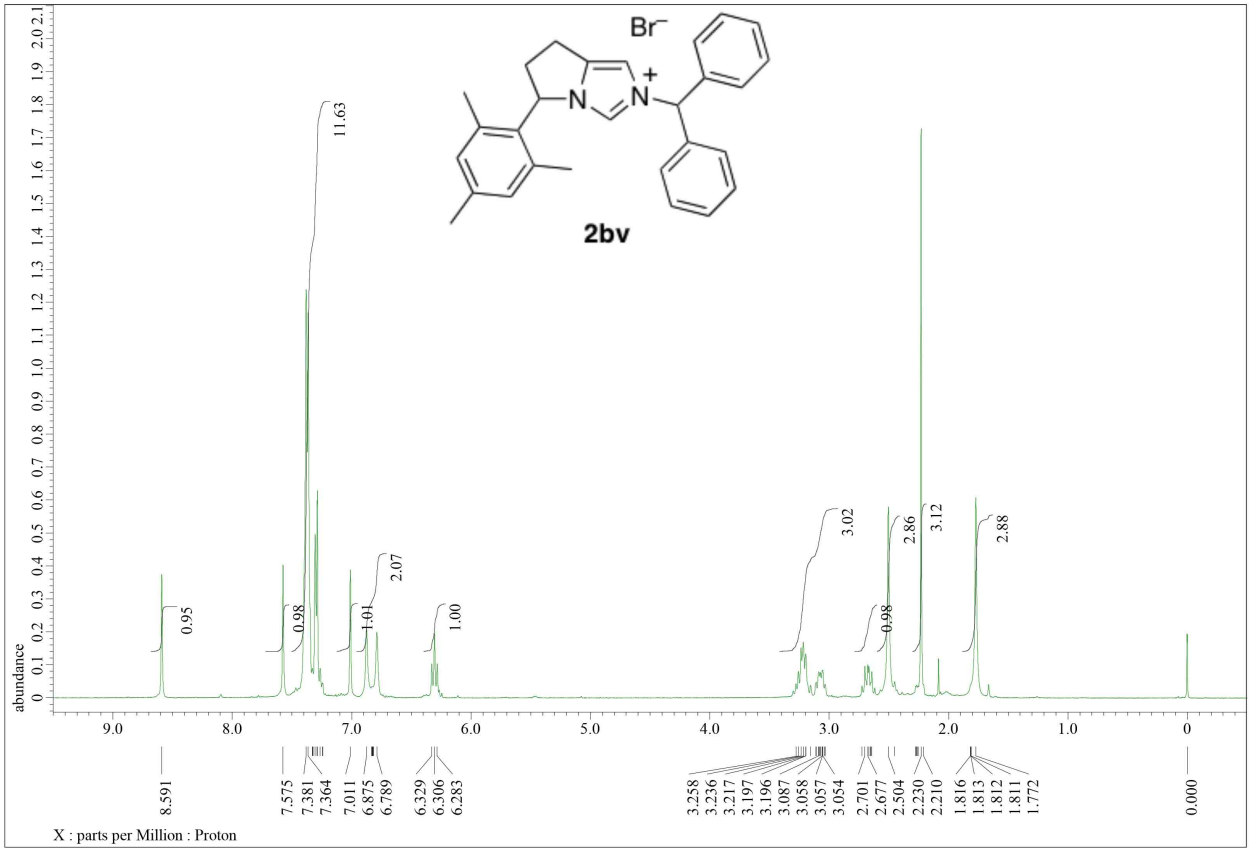

PF6−
Mes
Mes
Ir
(+)-4b
abundance
X : parts per Million : Carbon13

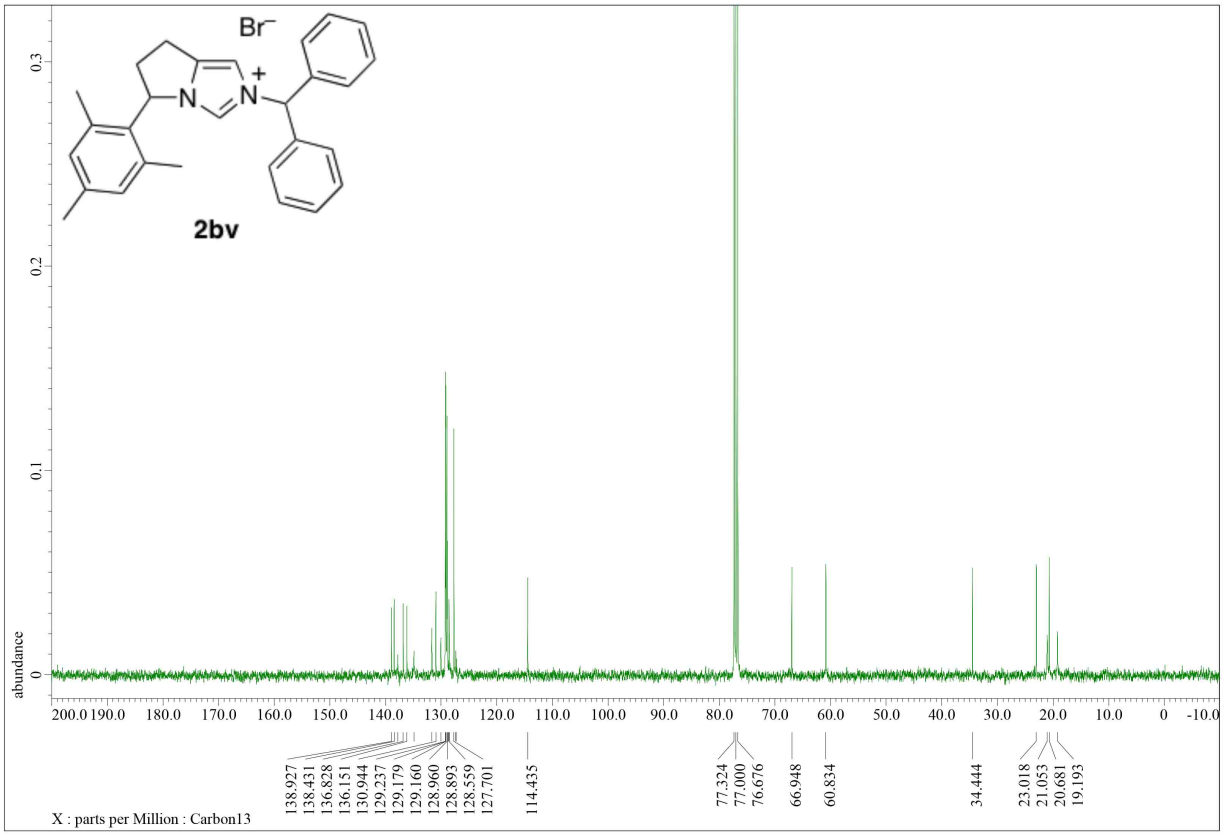

Cl—Ir
Mes
Mes
Ir—Cl
(+)-5b
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.264
7.262
6.964
6.809
6.014
5.998
5.990
5.973
4.974
4.949
4.697
4.447
4.426
4.414
4.385
4.365
3.028
3.011
3.001
2.974
2.942
2.804
2.737
2.320
2.300
2.093
1.821
1.700
1.560
1.273
1.255
0.923
0.897
0.877
0.841
0.000
X : parts per Million : Proton

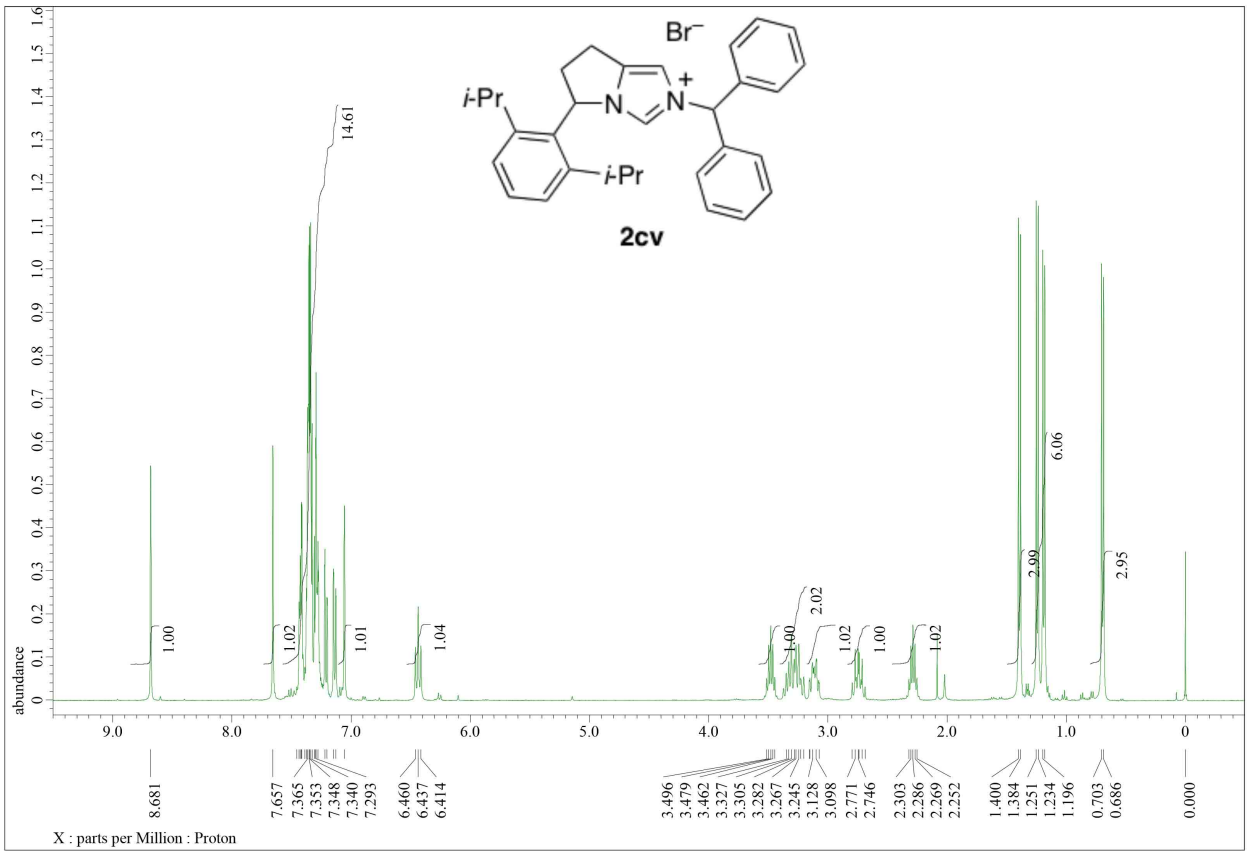

Cl—Ir
Mes
Mes
Ir—Cl
(+)-5b
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
174.096
137.634
137.461
136.024
134.702
131.253
129.615
115.149
84.875
81.608
77.326
77.000
76.684
57.427
53.260
51.900
51.641
35.805
33.707
31.034
29.903
27.575
22.450
21.444
20.792
19.116
X : parts per Million : Carbon13

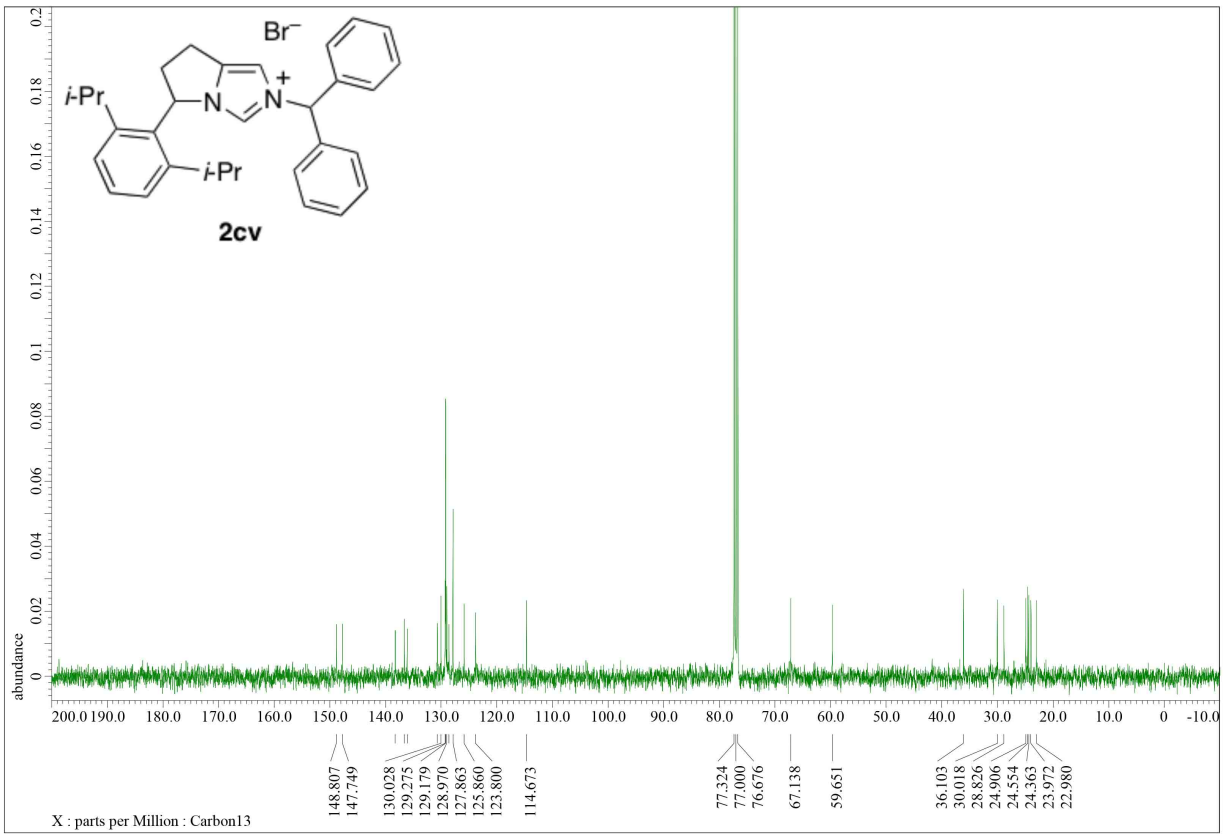

Br⁻
2av
abundance
X : parts per Million : Proton

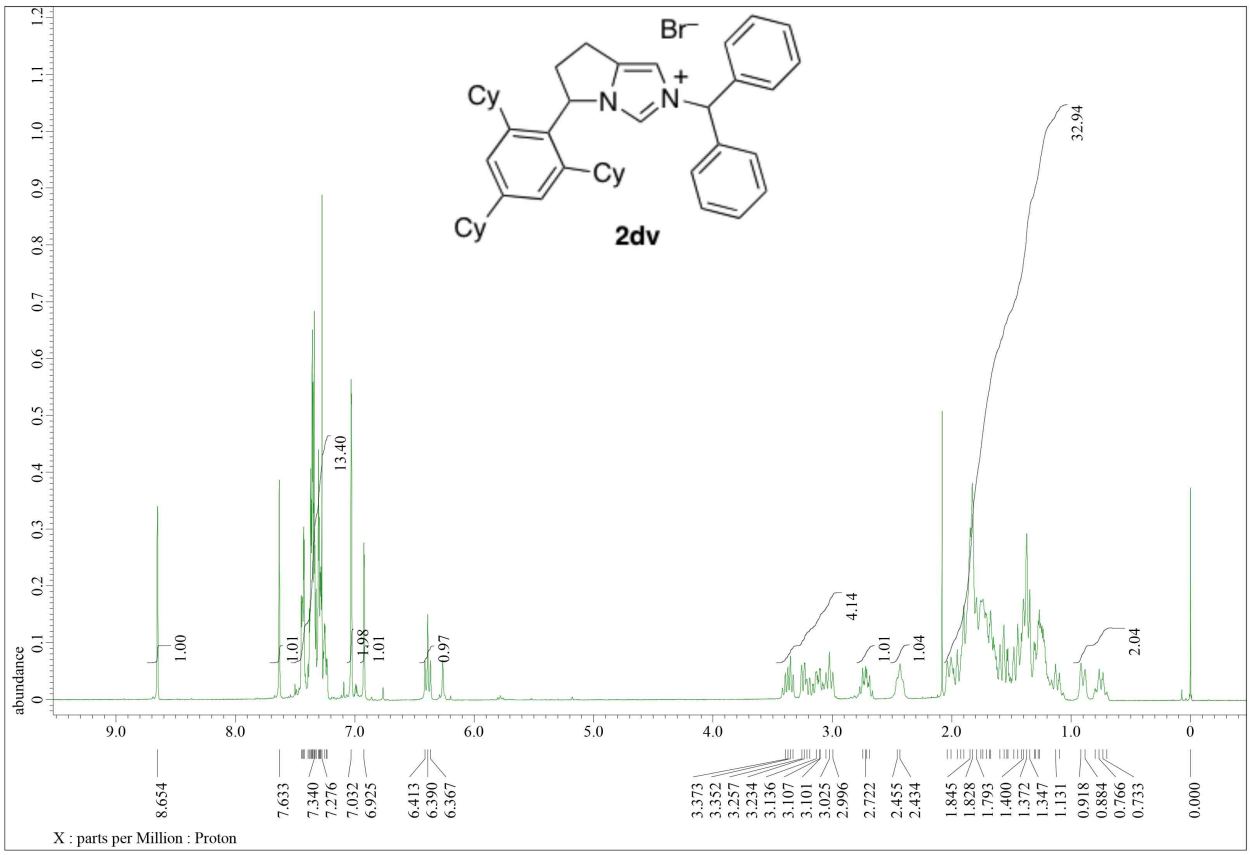

Br⁻
2av
abundance
X : parts per Million : Carbon13

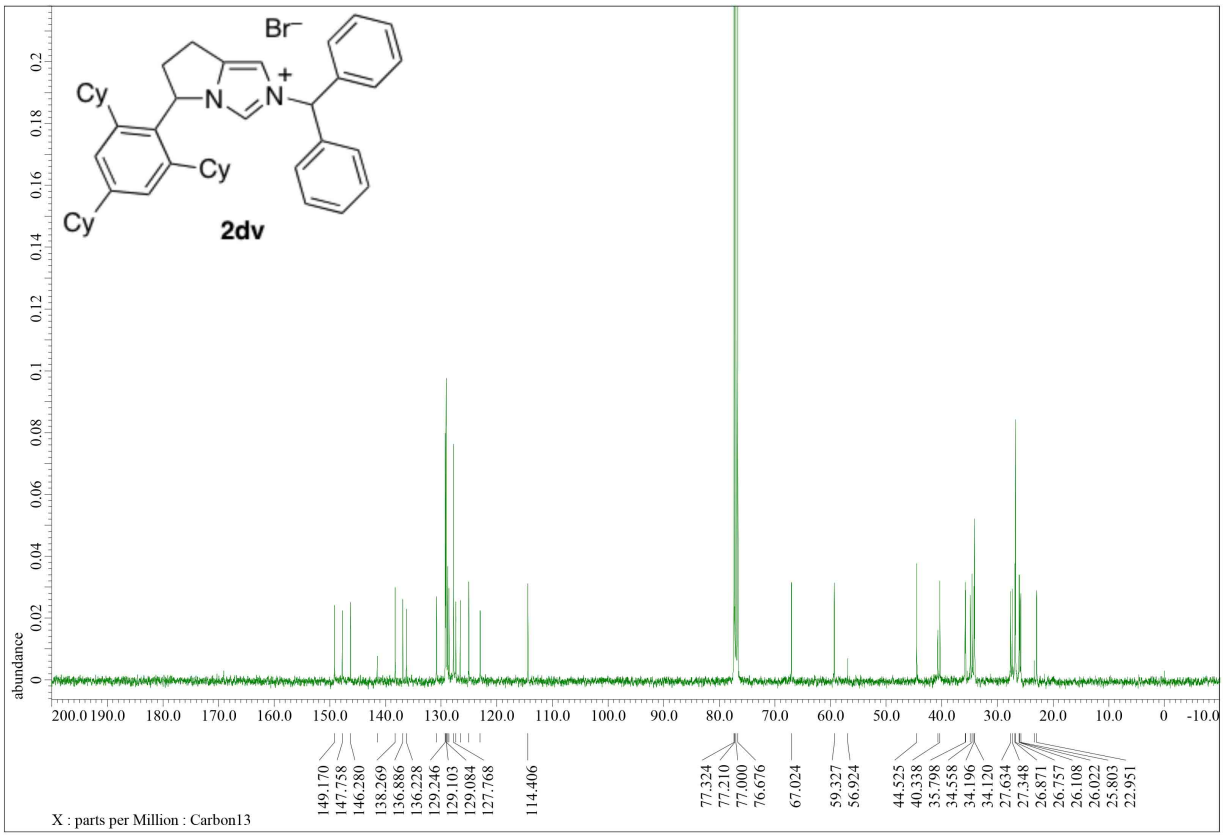

Br⁻
2bv
abundance
X : parts per Million : Proton

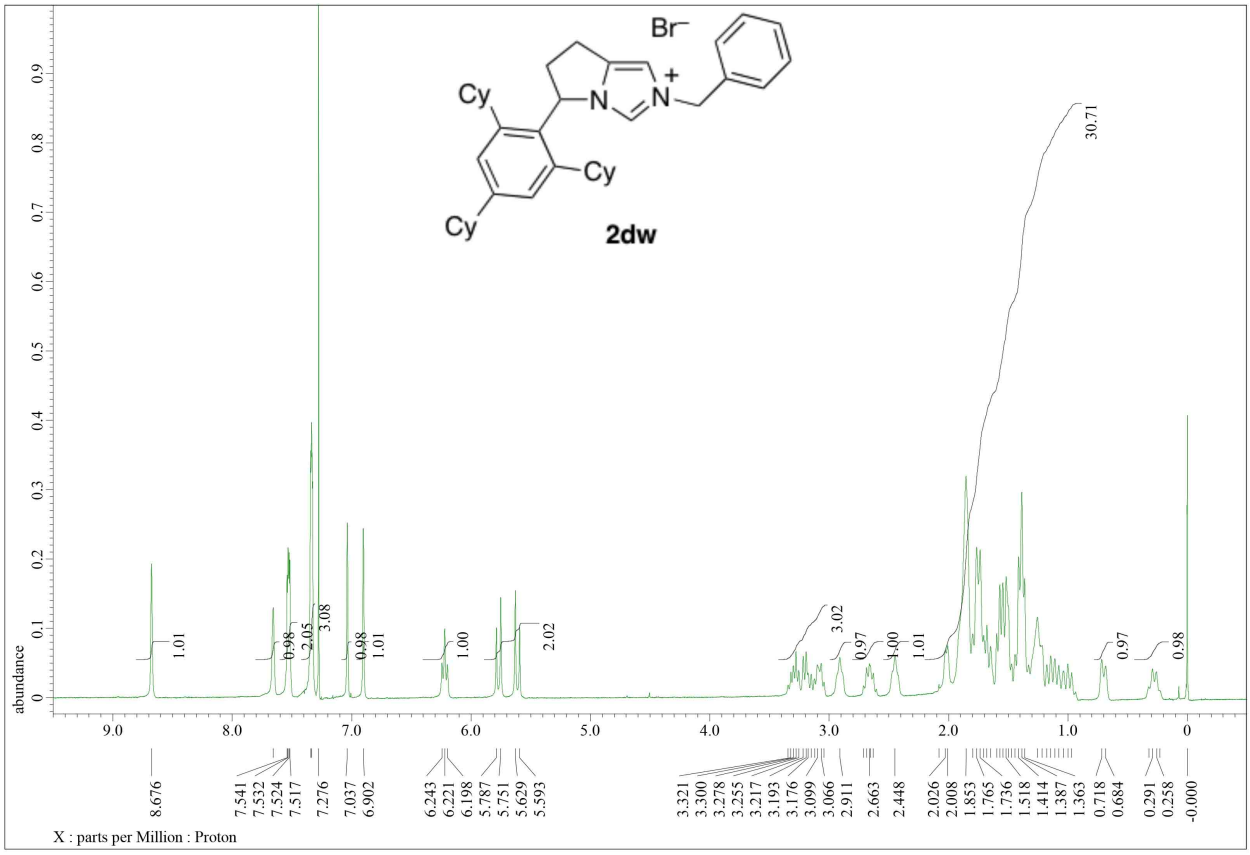

Br⁻
2bv
abundance
X : parts per Million : Carbon13

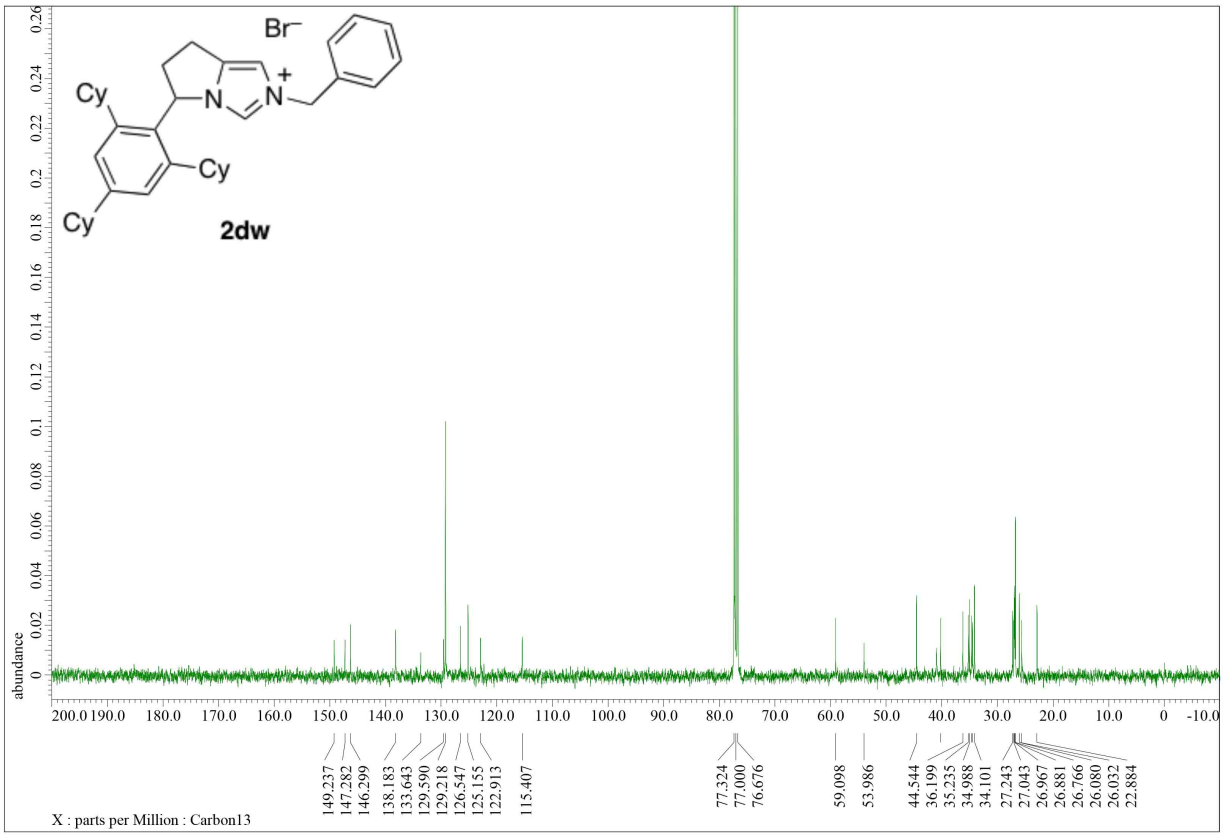

Br⁻
i-Pr
i-Pr
2cv
abundance
X : parts per Million : Proton

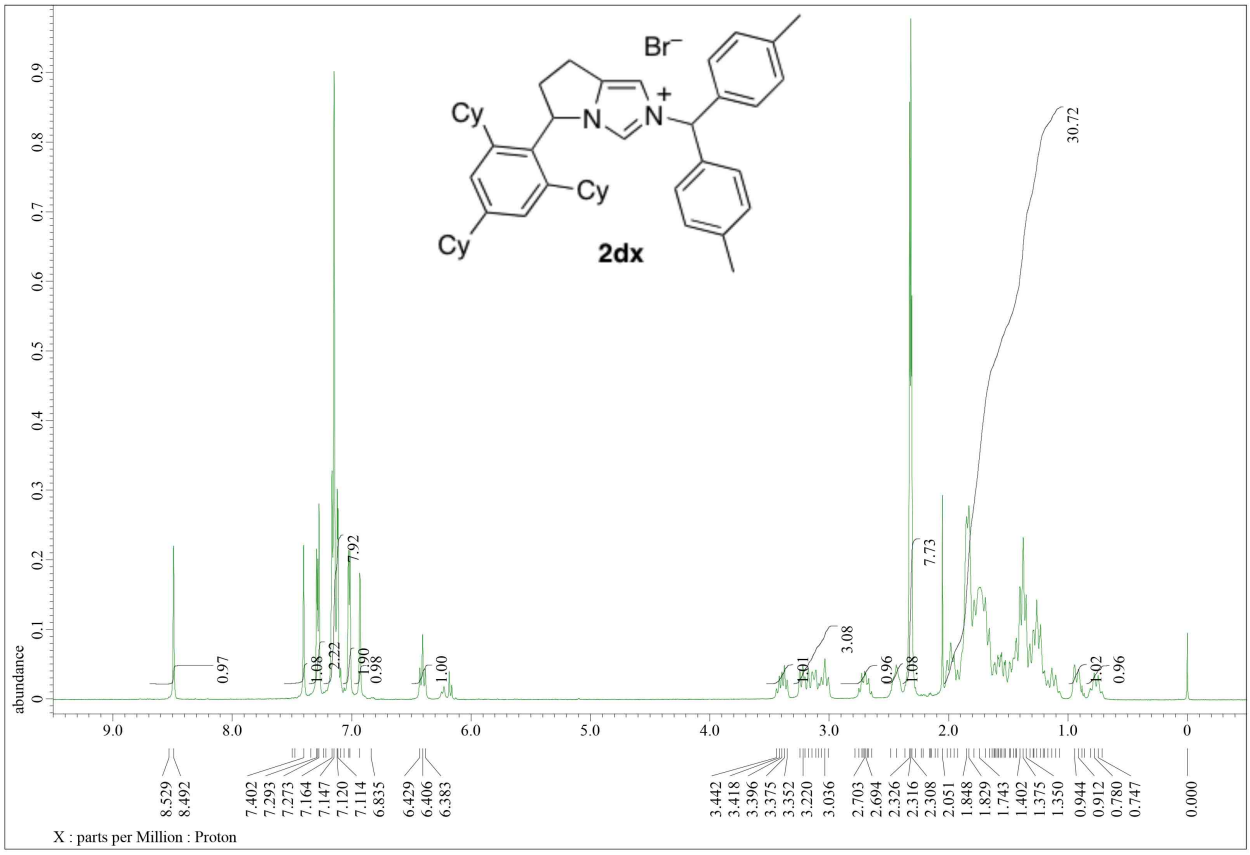

Br⁻
i-Pr
i-Pr
2cv
abundance
X : parts per Million : Carbon13

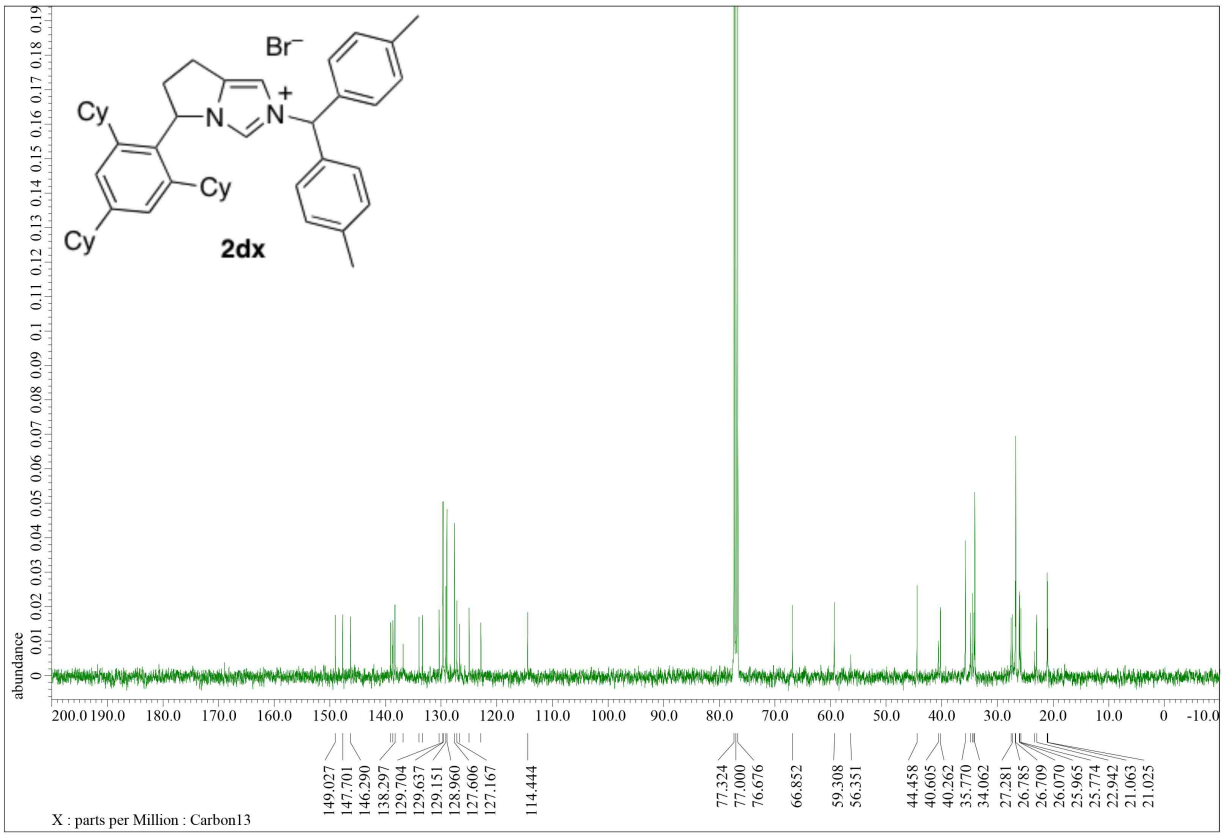

Br⁻
Cy
Cy
Cy
2dv
abundance
1.00
1.01
13.40
1.98
1.01
0.97
4.14
1.01
1.04
32.94
2.04
X : parts per Million : Proton

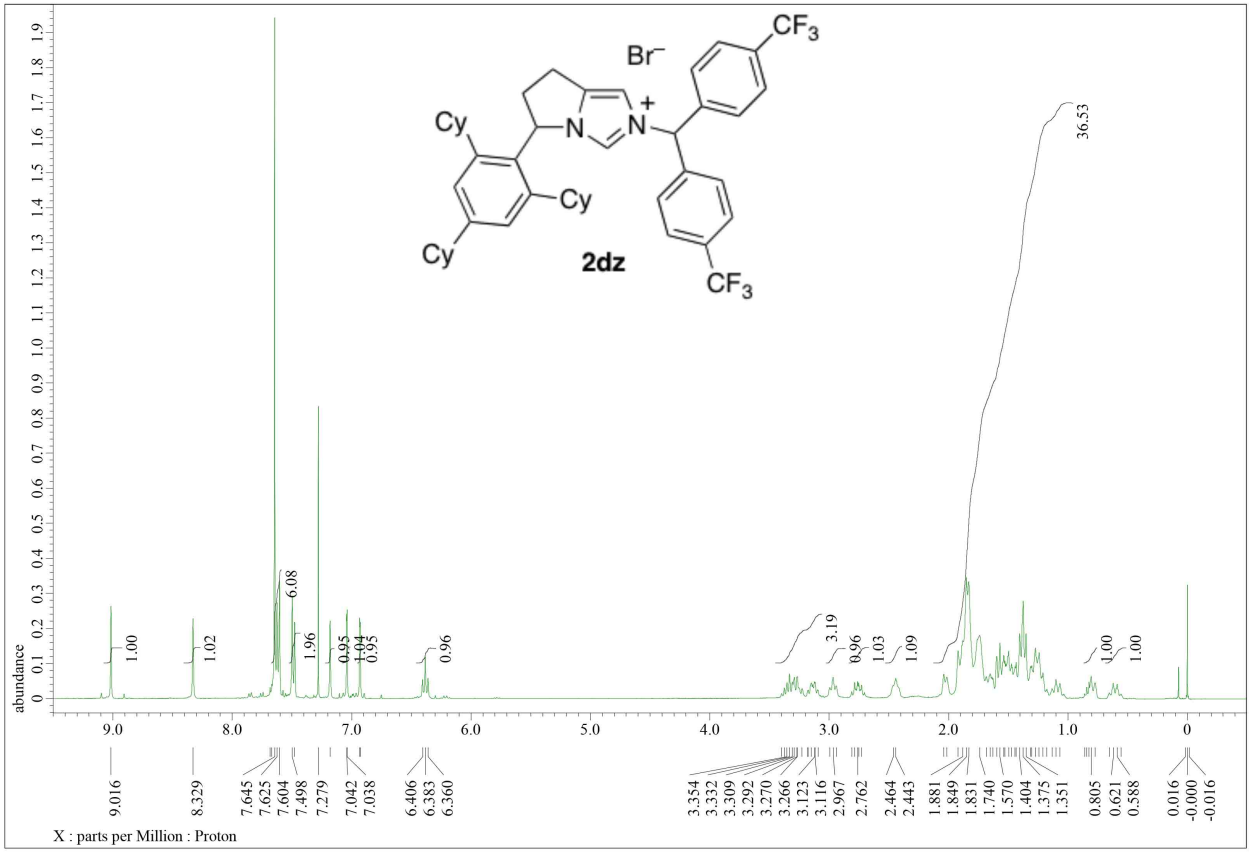

Br⁻
Cy
Cy
Cy
2dv
abundance
X : parts per Million : Carbon13

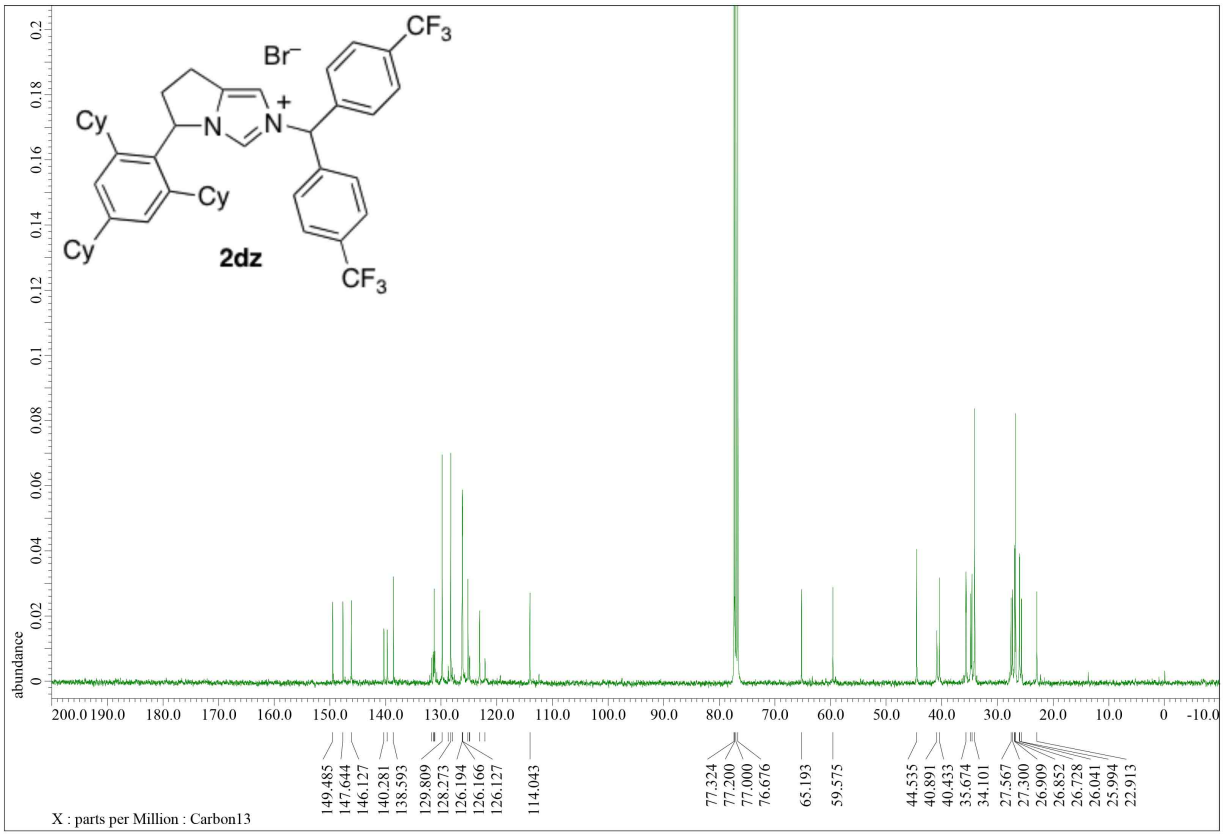

Br⁻
Cy
Cy
Cy
2dw
abundance
X : parts per Million : Proton

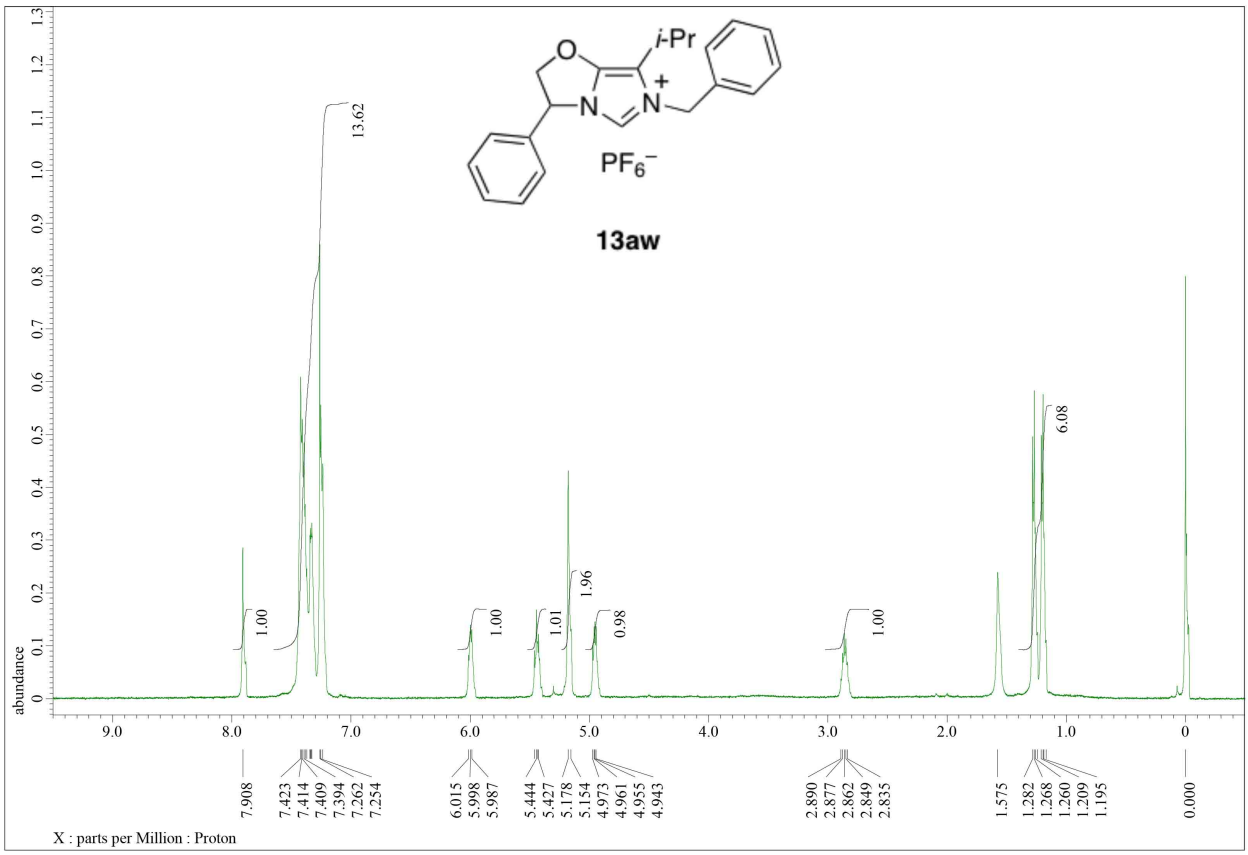

Br⁻
Cy
Cy
Cy
2dw
abundance
X : parts per Million : Carbon13

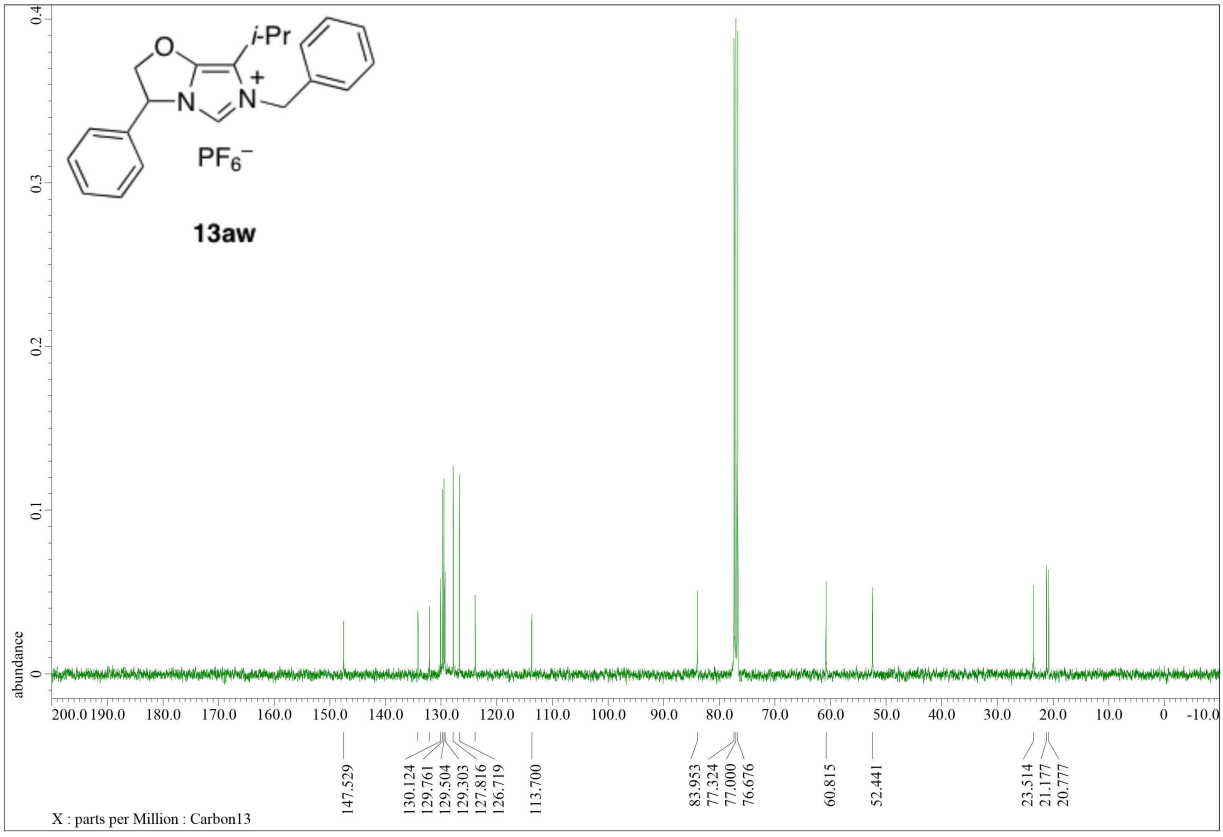

Br⁻
Cy
Cy
Cy
N
N
+
2dx
abundance
X : parts per Million : Proton

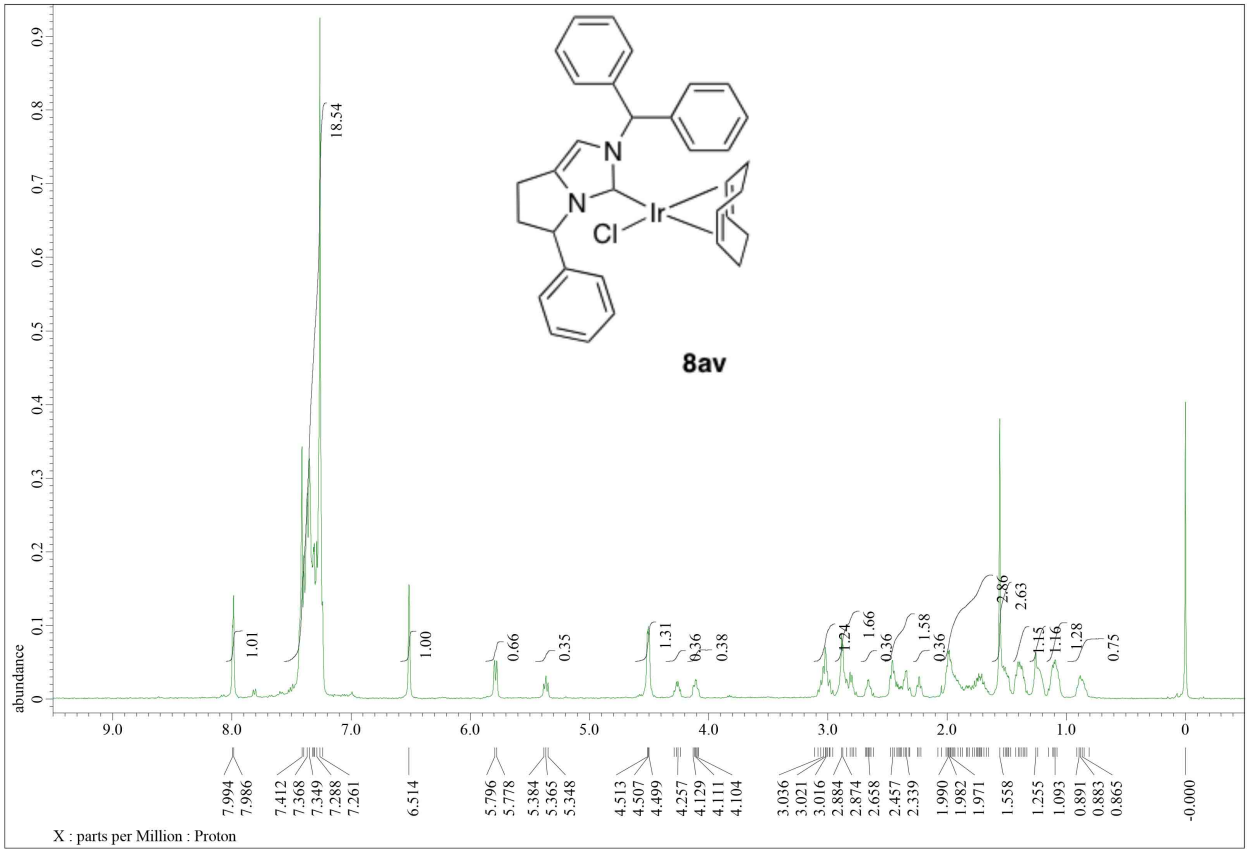

Br⁻
Cy
Cy
Cy
N
N
+
2dx
abundance
X : parts per Million : Carbon13

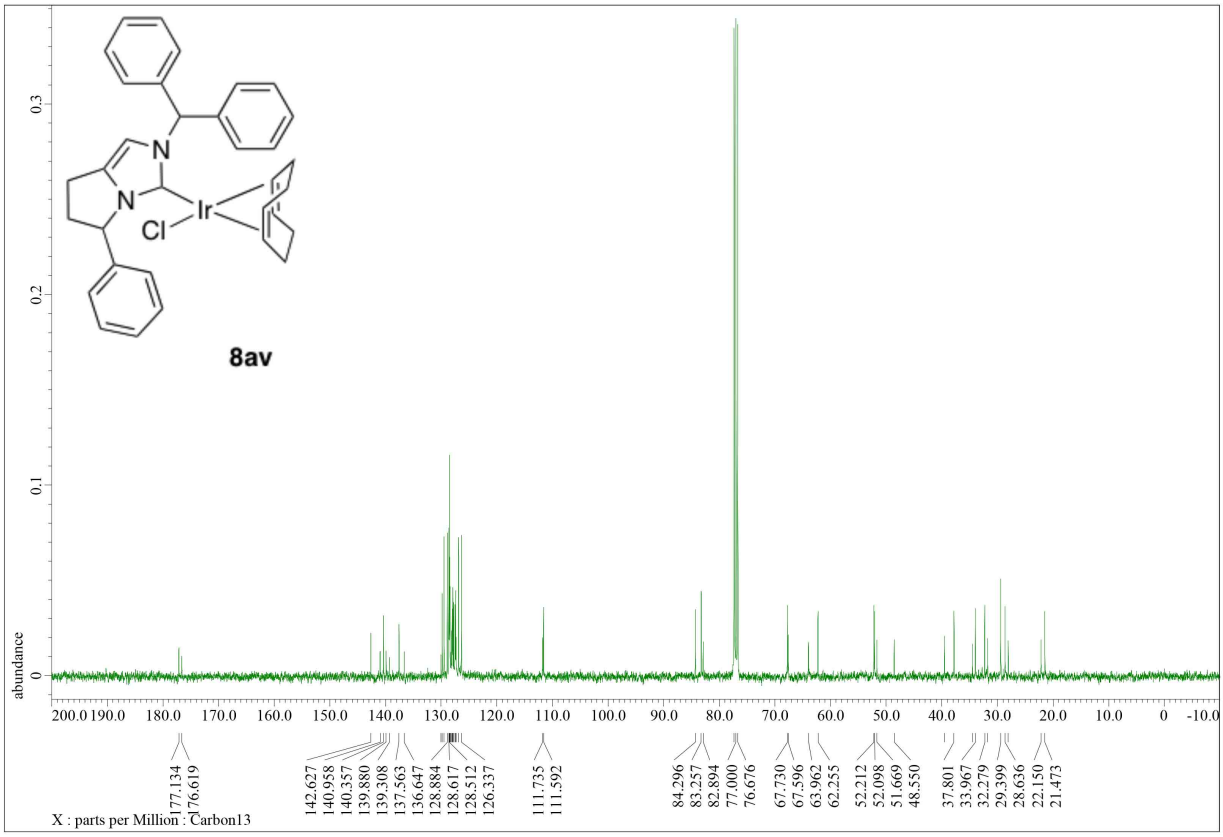

Br⁻
CF3
Cy
Cy
Cy
2dz
CF3
abundance
X : parts per Million : Proton

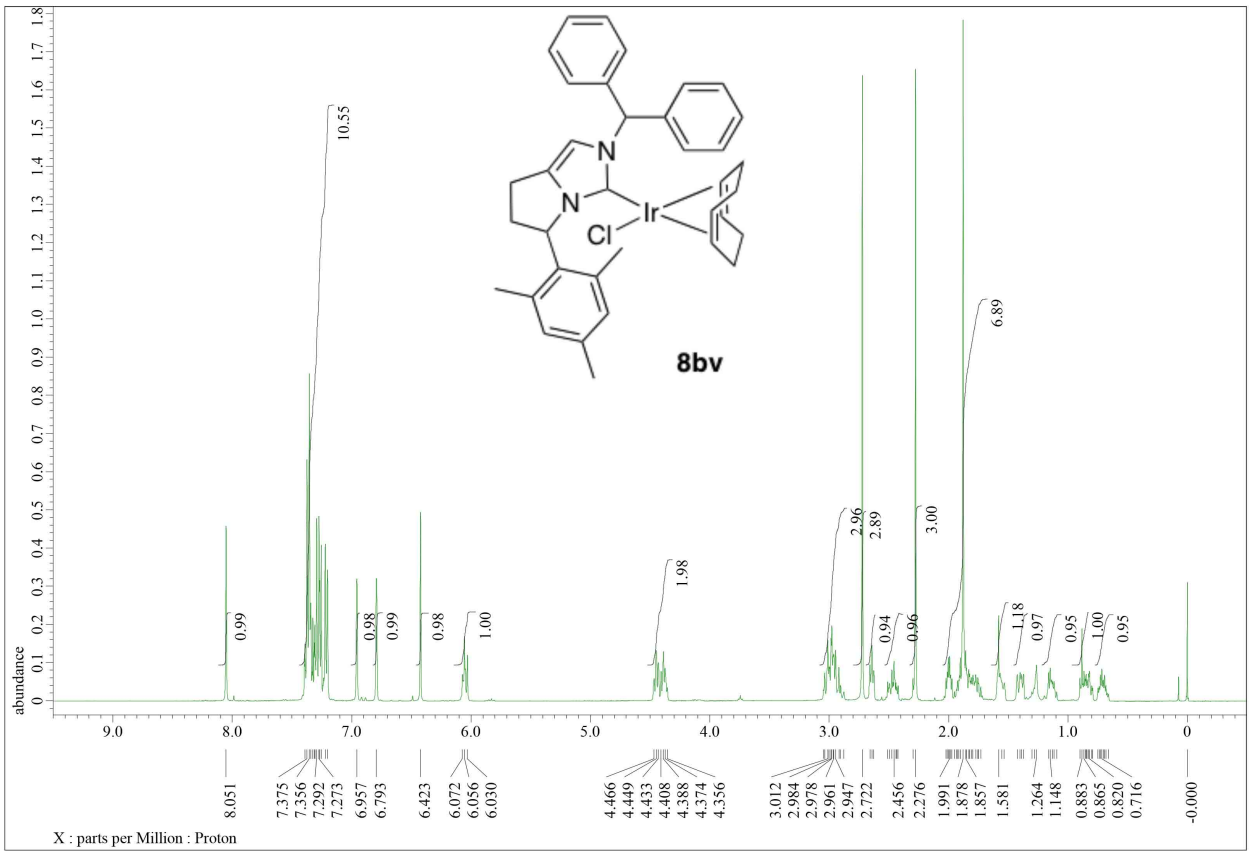

Br⁻
CF3
Cy
Cy
Cy
2dz
CF3
abundance
X : parts per Million : Carbon13

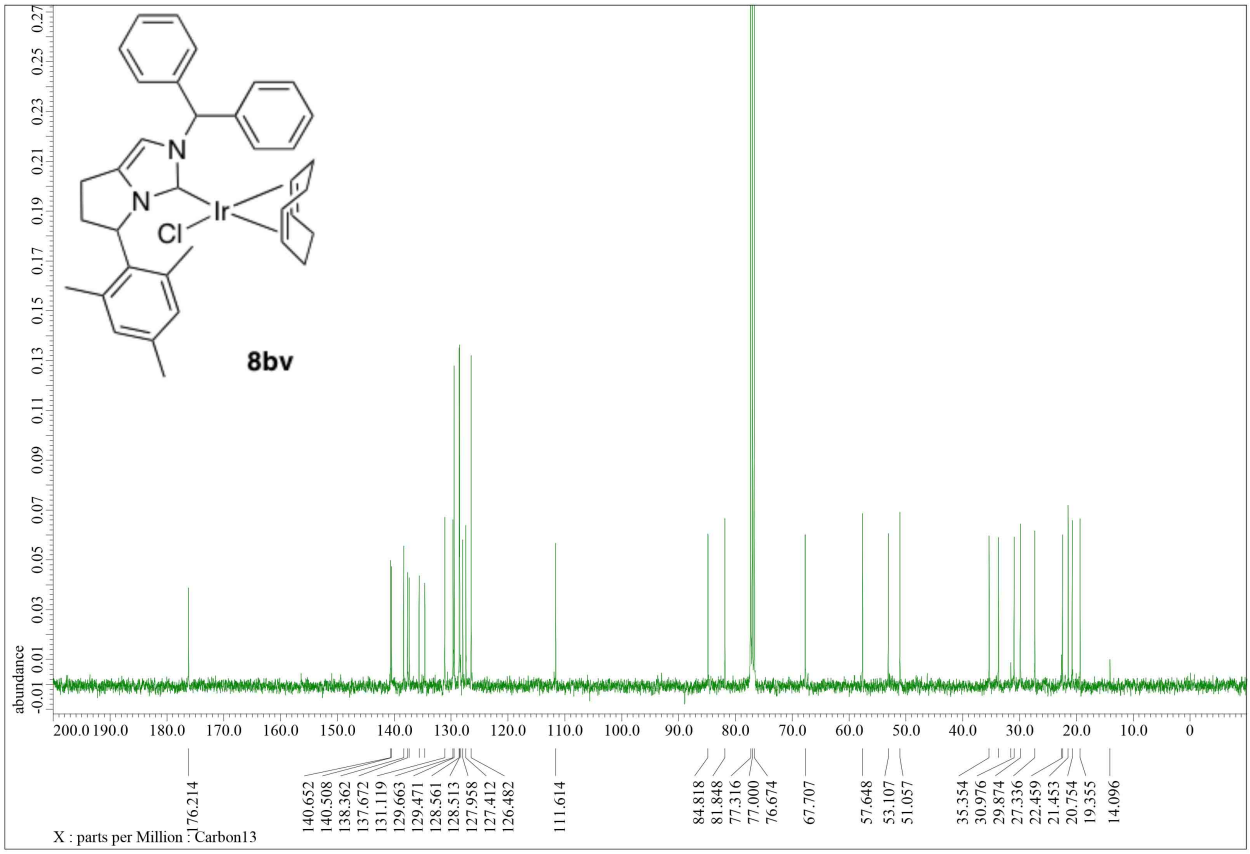

i-Pr
PF6−
13aw
13.62
6.08
1.00
1.00
1.01
1.96
0.98
1.00
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.908
7.423
7.414
7.409
7.394
7.262
7.254
6.015
5.998
5.987
5.444
5.427
5.178
5.154
4.973
4.961
4.955
4.943
2.890
2.877
2.862
2.849
2.835
1.575
1.282
1.268
1.260
1.209
1.195
0.000
X : parts per Million : Proton

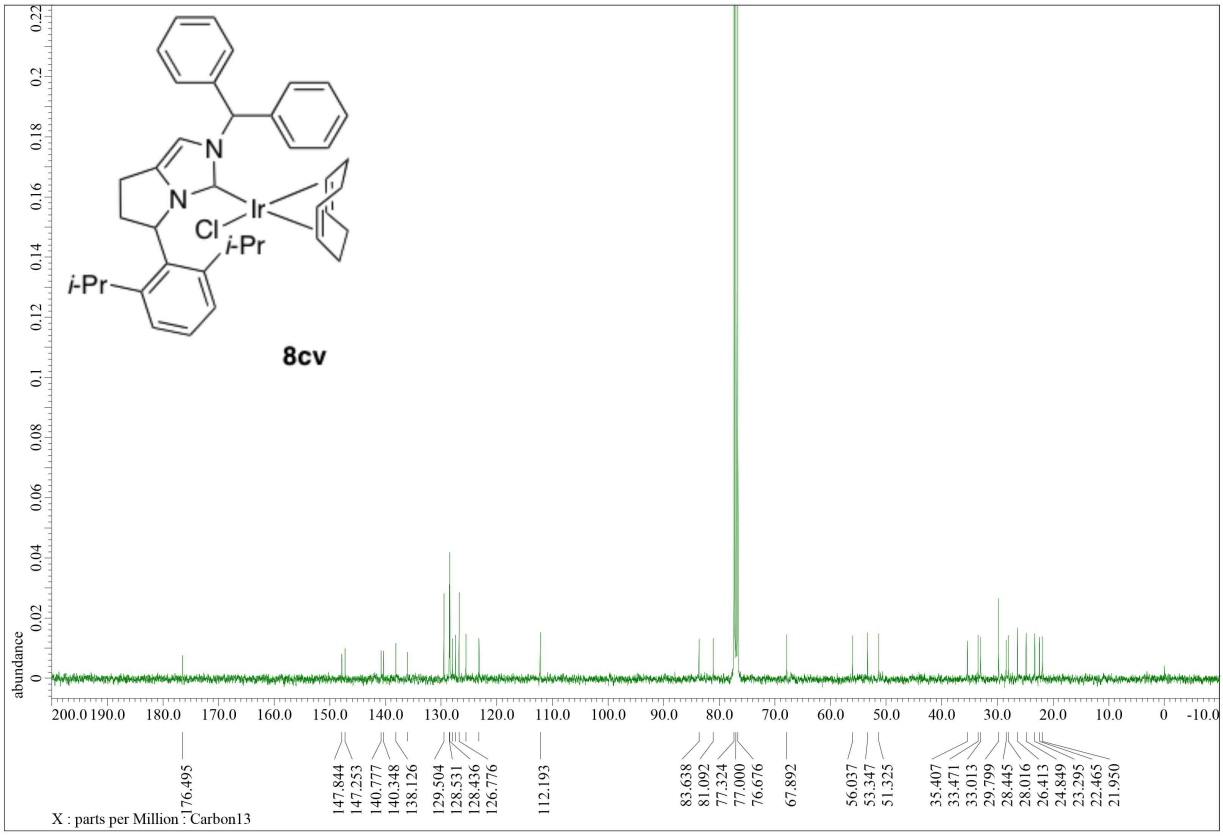

i-Pr
PF6−
13aw
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
147.529
130.124
129.761
129.504
129.303
127.816
126.719
113.700
83.953
77.324
77.000
76.676
60.815
52.441
23.514
21.177
20.777
X : parts per Million : Carbon13

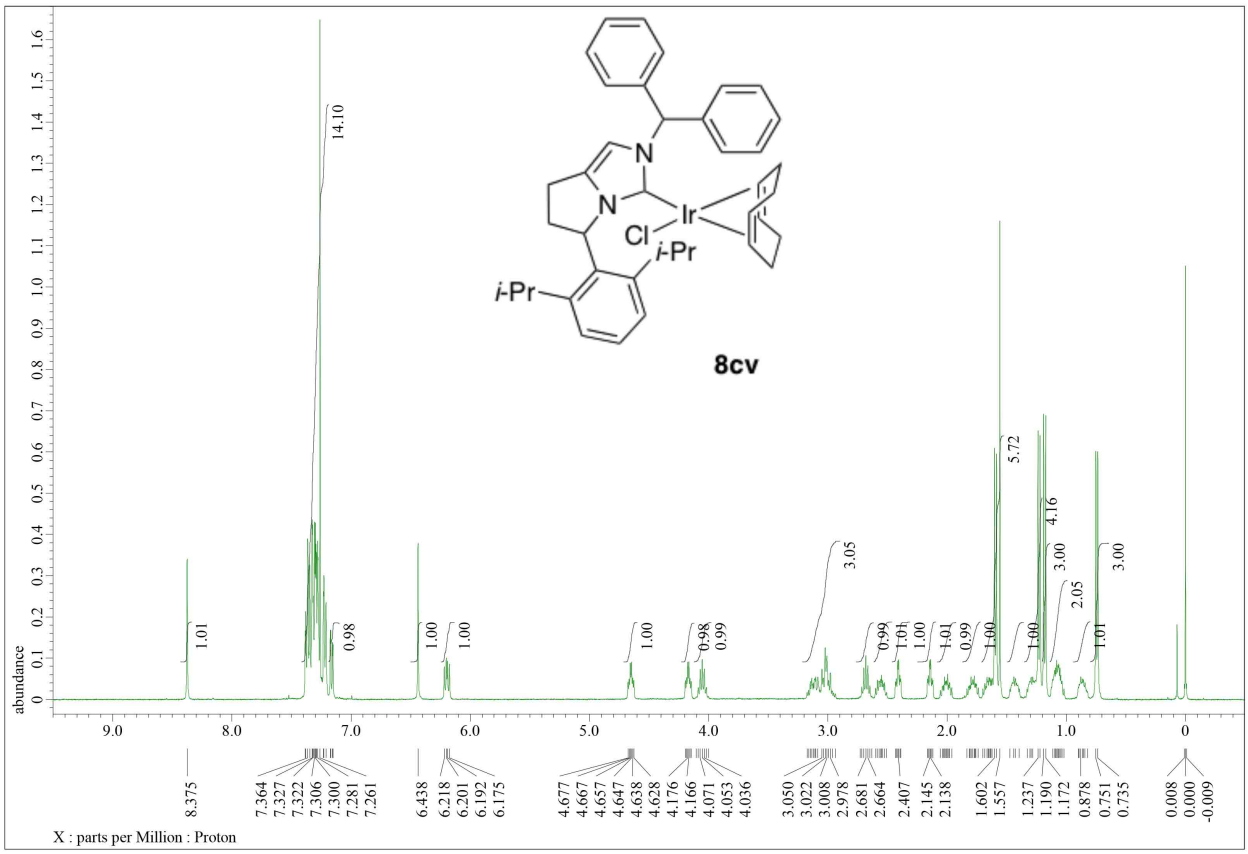

8av
abundance
X : parts per Million : Proton

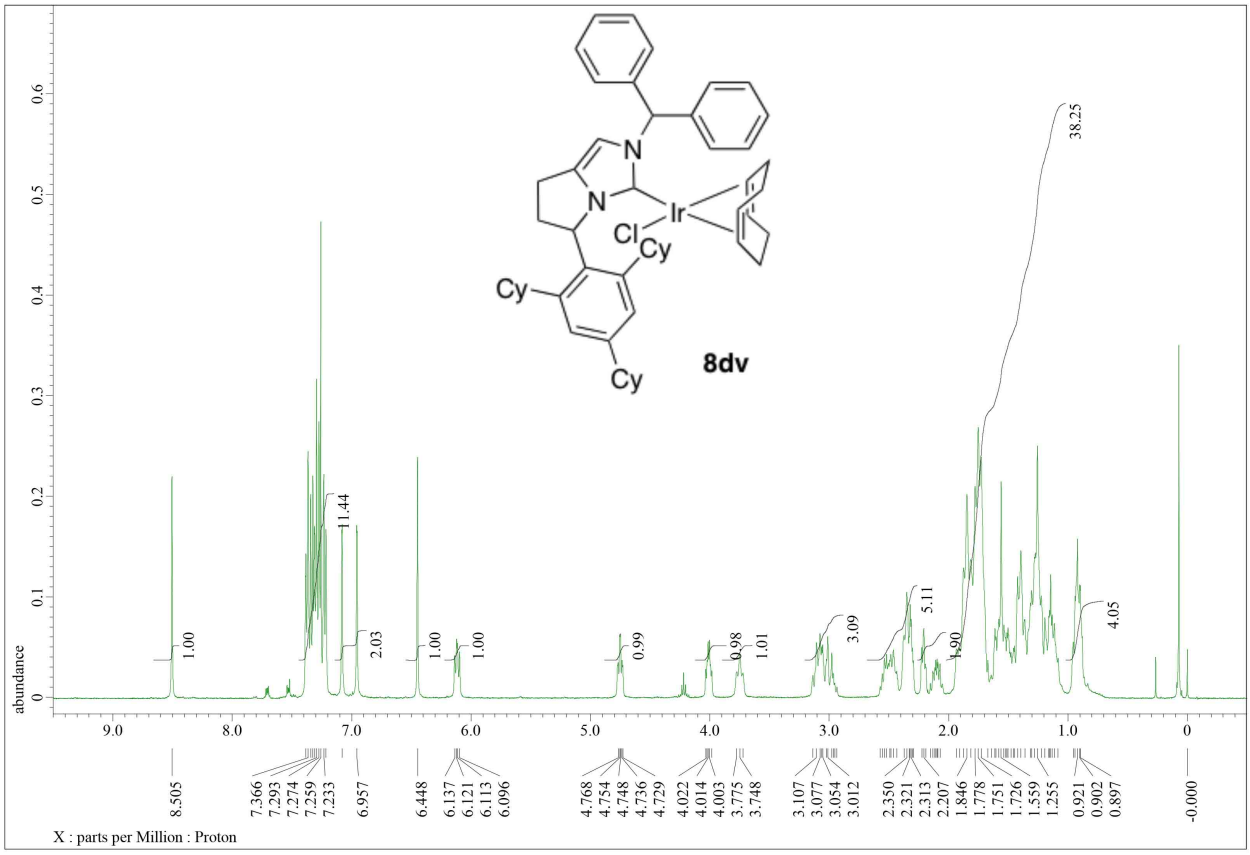

8av
abundance
X : parts per Million : Carbon13

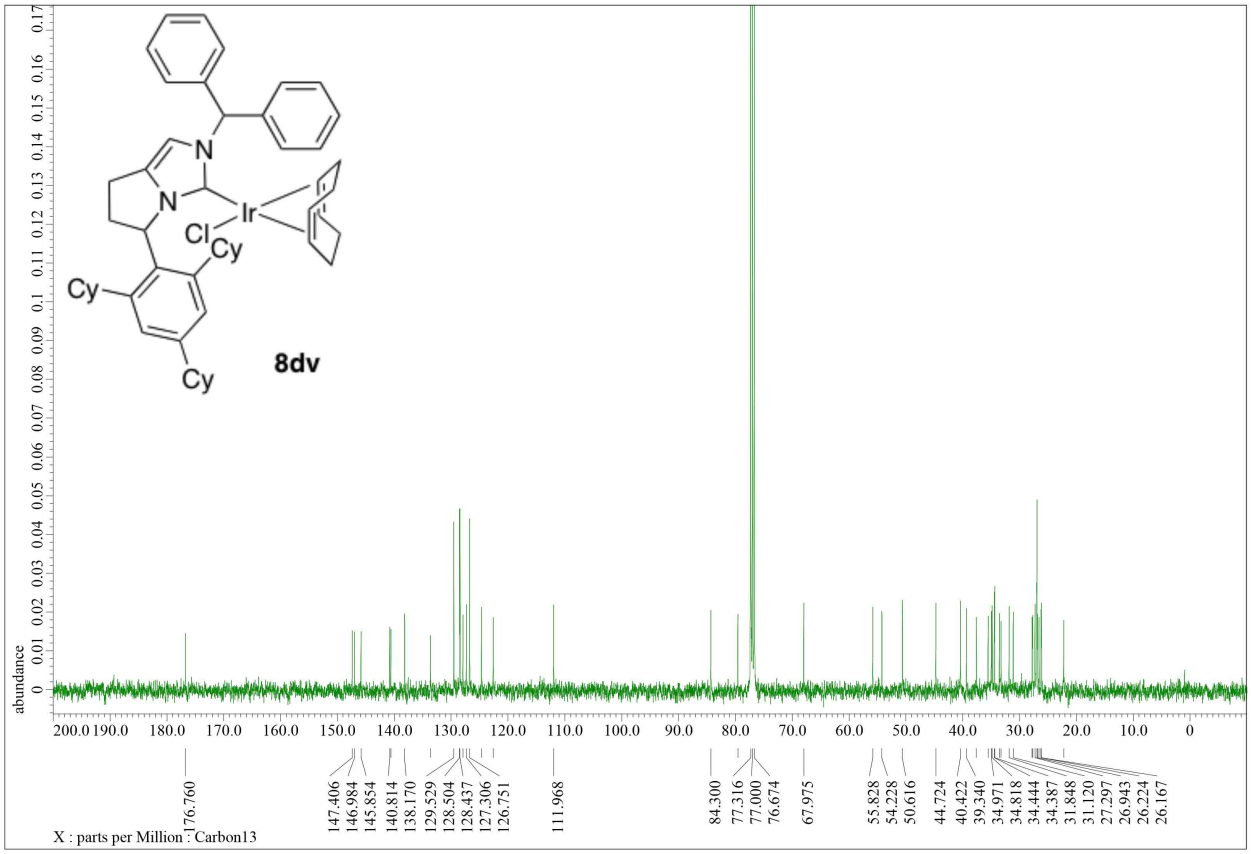

8bv
abundance
X : parts per Million : Proton

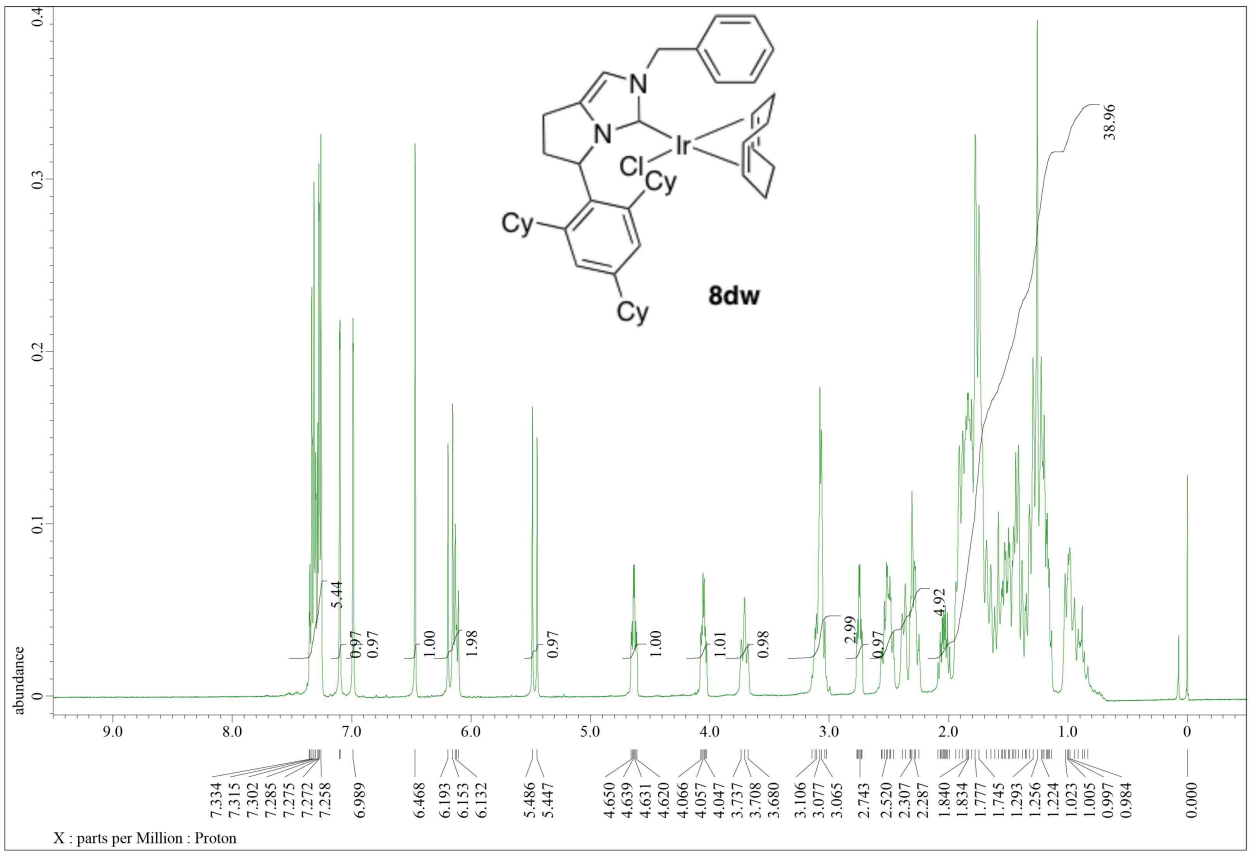

8bv
abundance
X : parts per Million : Carbon13

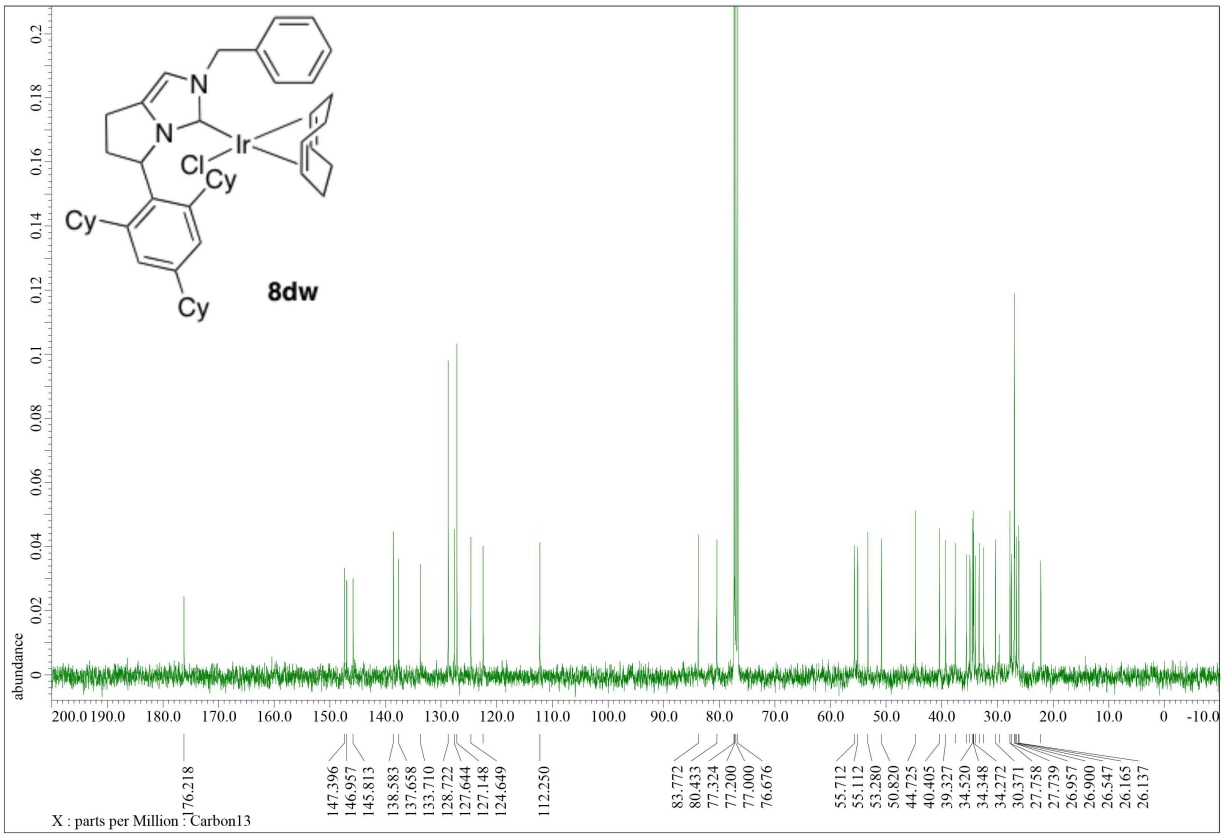

8cv
abundance
X : parts per Million : Carbon13

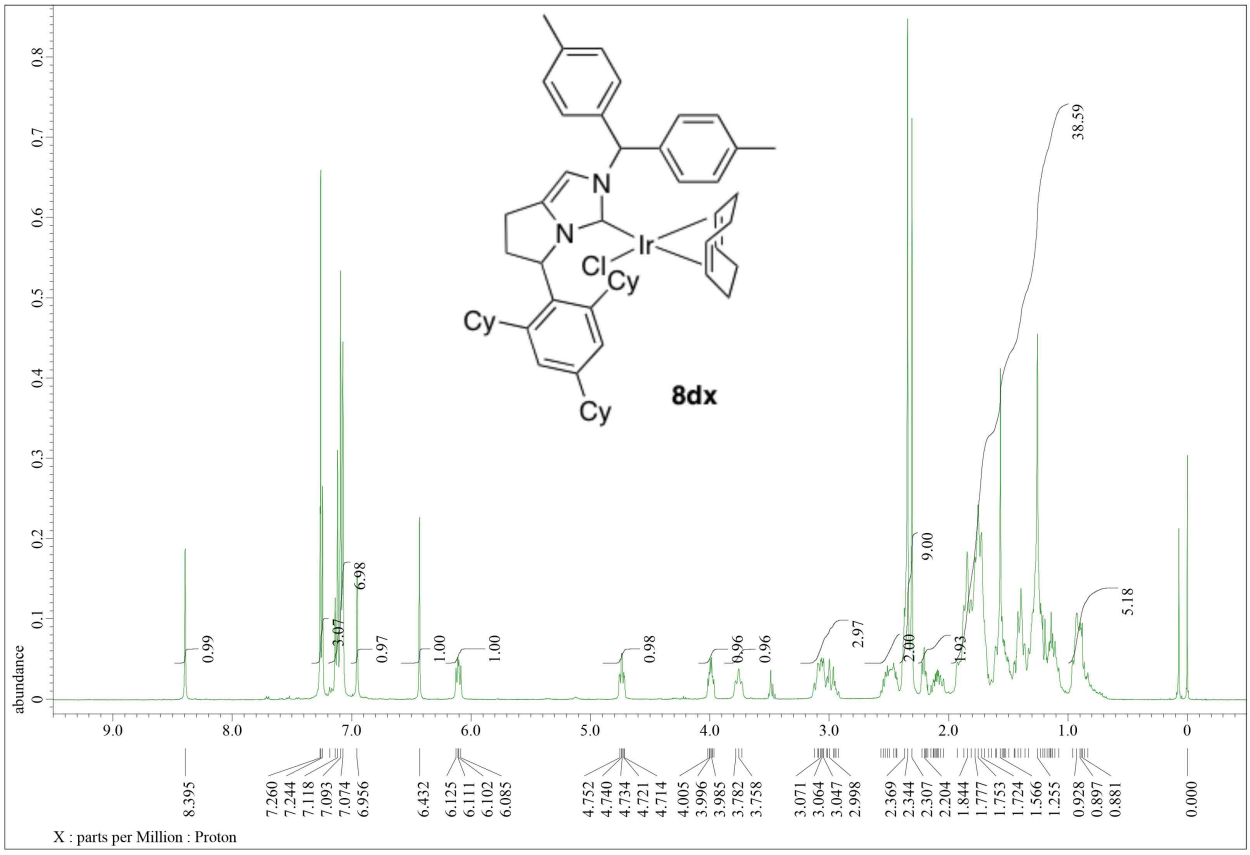

8cv
abundance
X : parts per Million : Proton

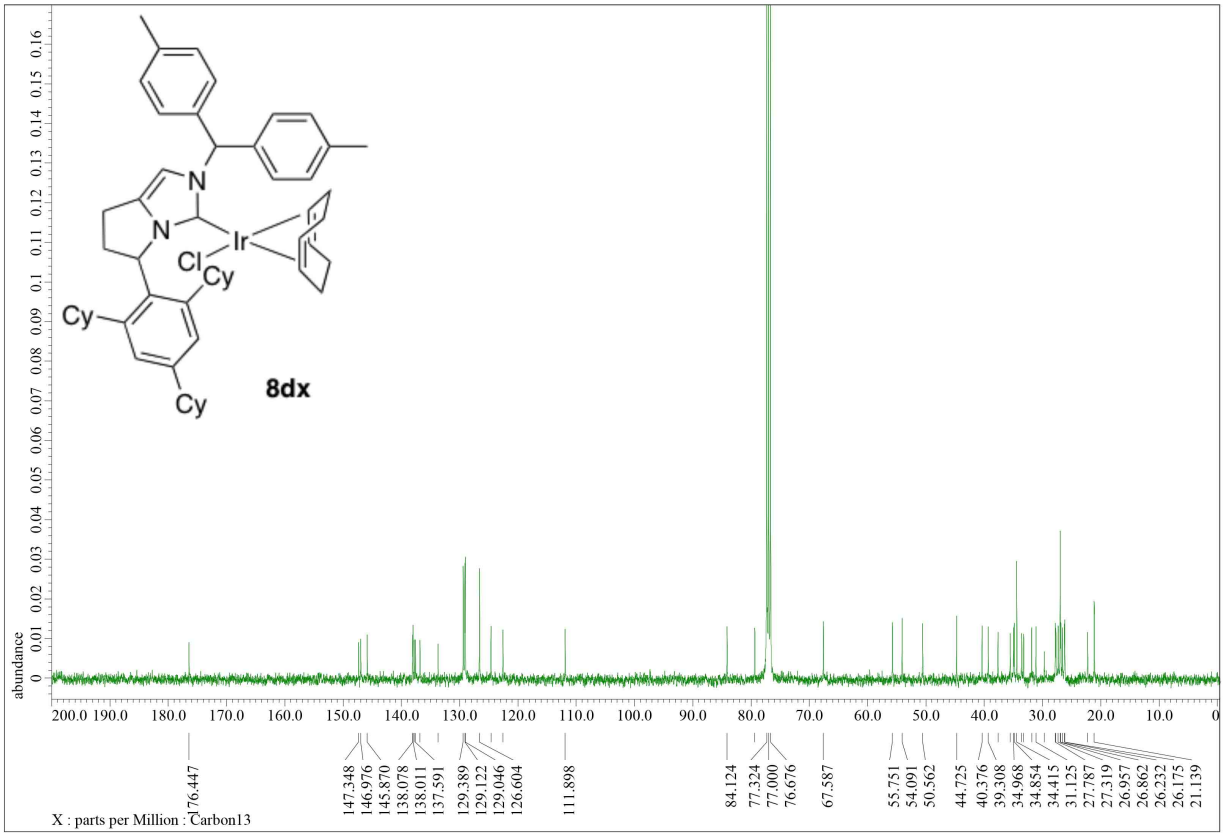

N
N
Ir
Cl
Cy
Cy
Cy
8dv
abundance
X : parts per Million : Proton

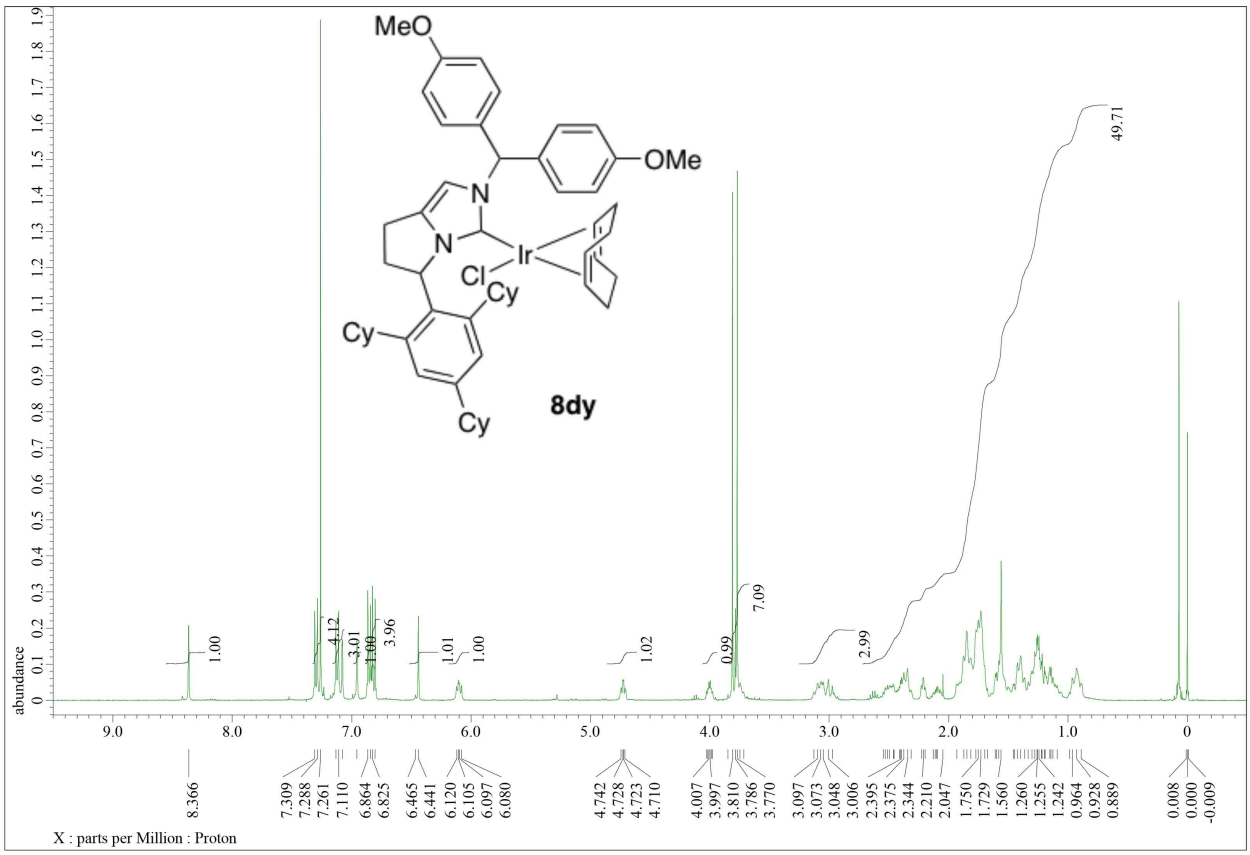

N
N
Ir
Cl
Cy
Cy
Cy
8dv
abundance
X : parts per Million : Carbon13

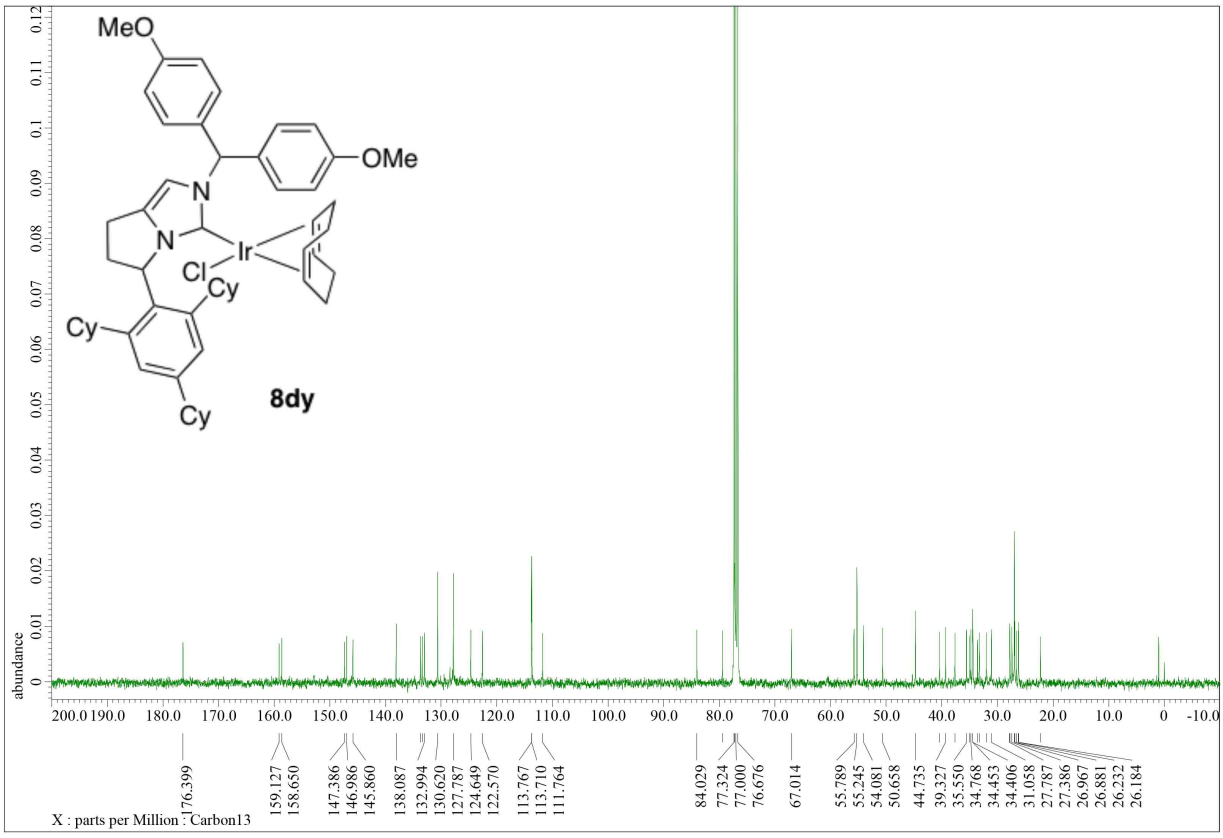

8dw
abundance
X : parts per Million : Proton

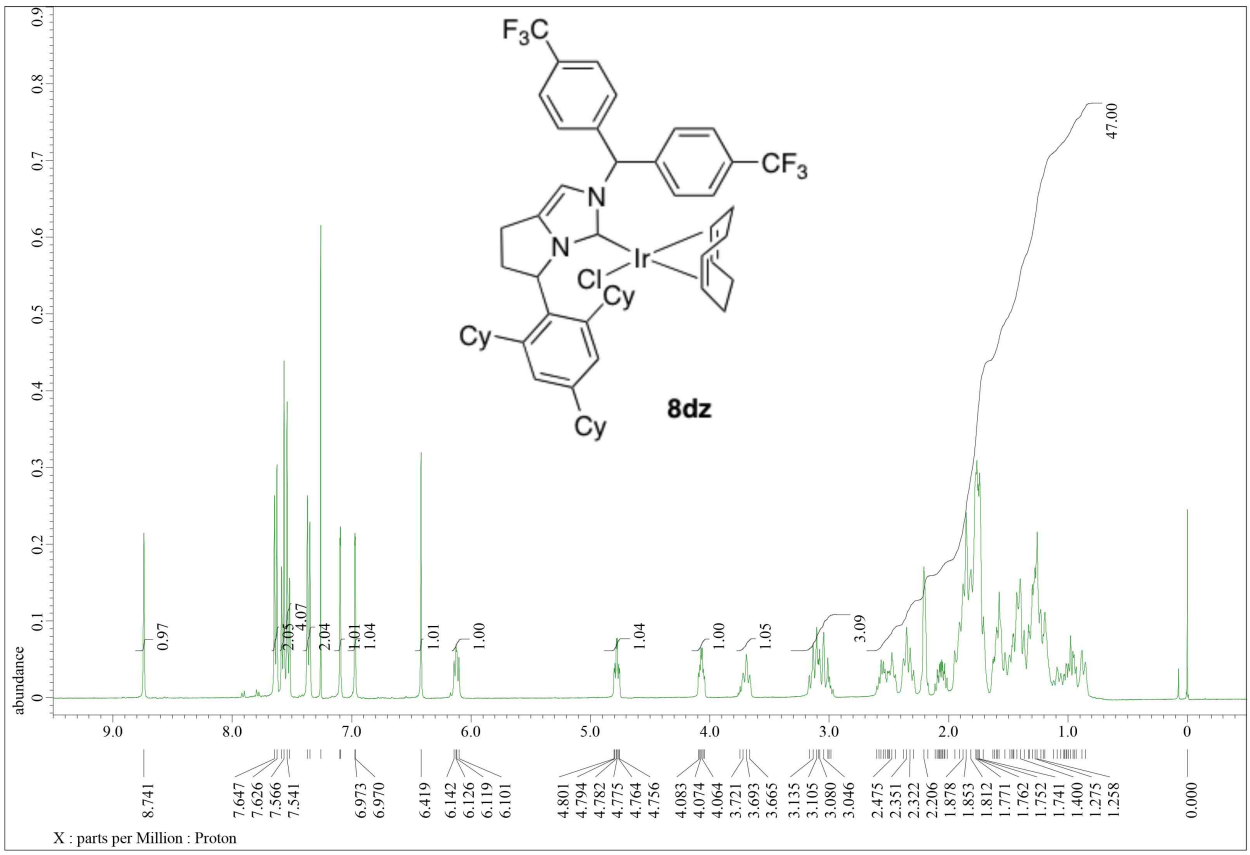

8dw
abundance
X : parts per Million : Carbon13

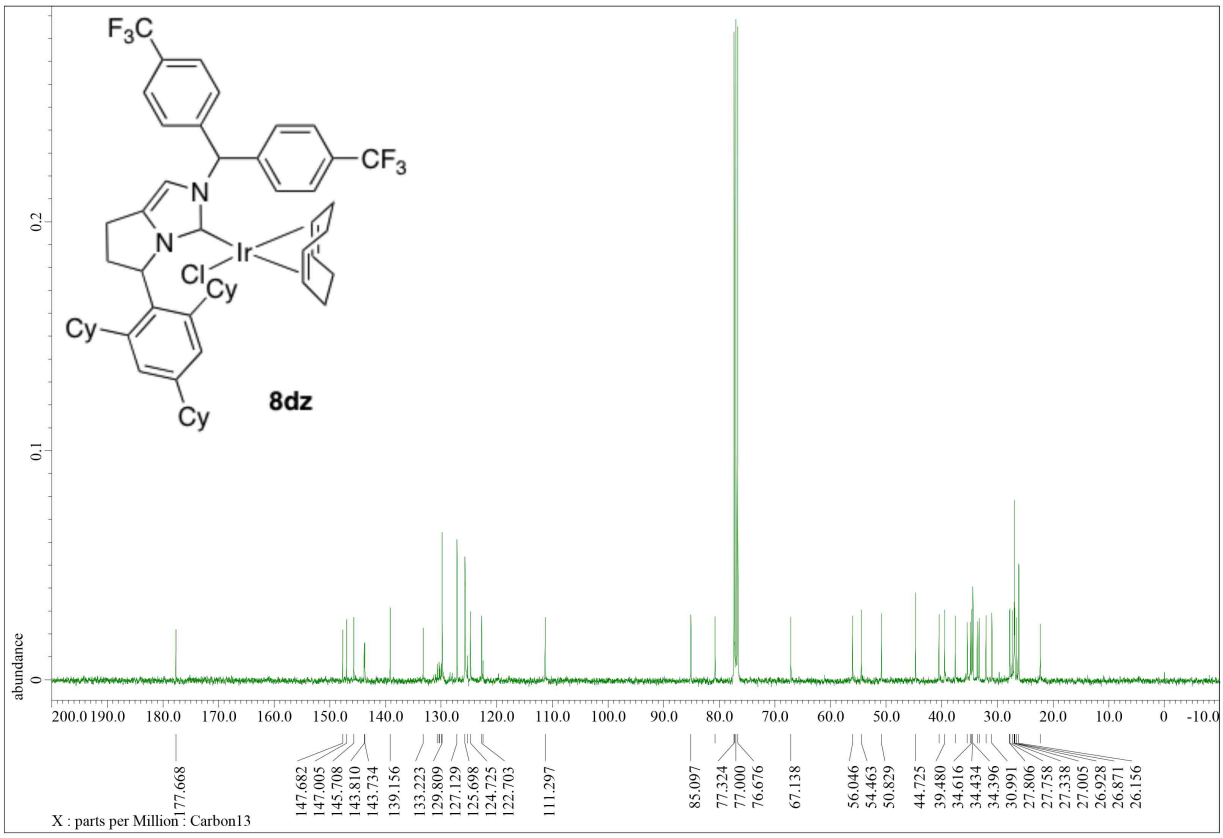

8dx
abundance
X : parts per Million : Proton


8dx
abundance
X : parts per Million : Carbon13

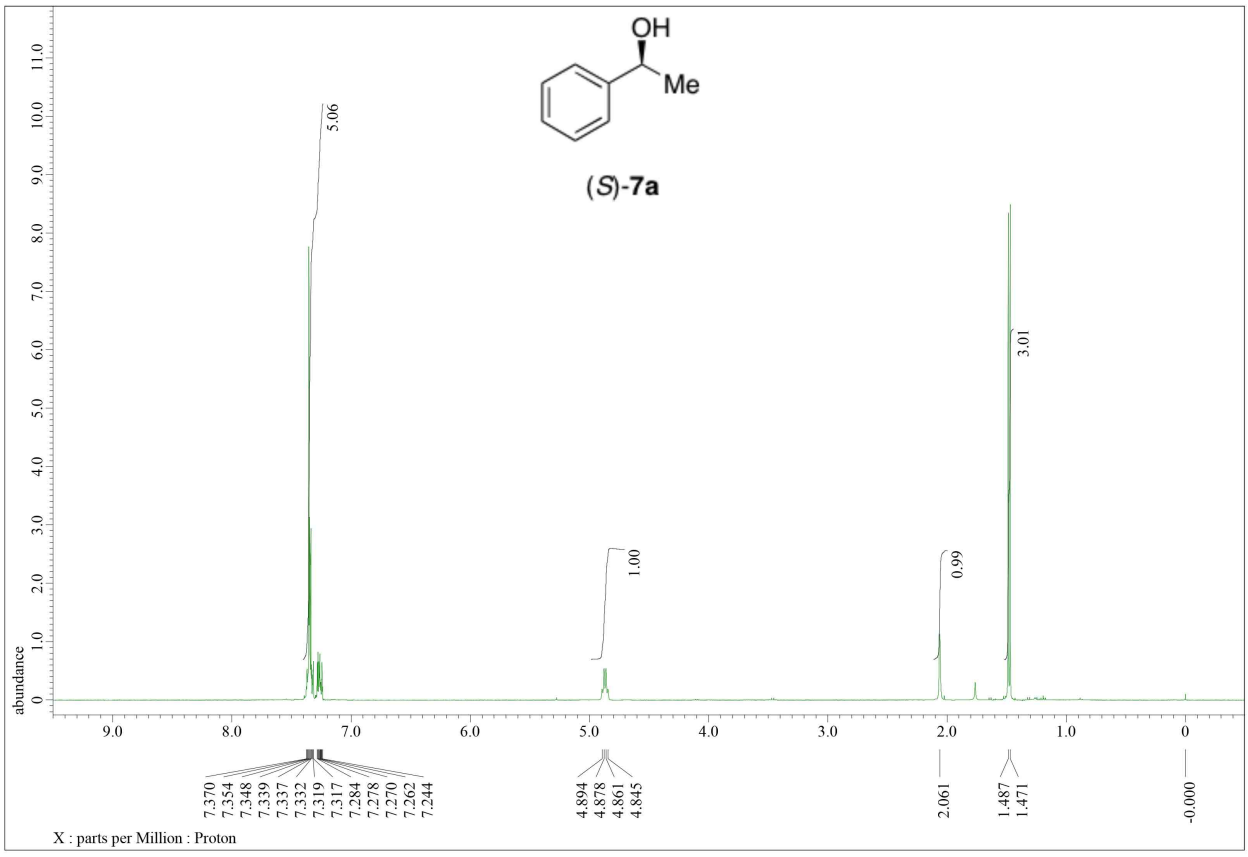

MeO
OMe
N
N
Ir
Cl
Cy
Cy
Cy
8dy
abundance
X : parts per Million : Proton

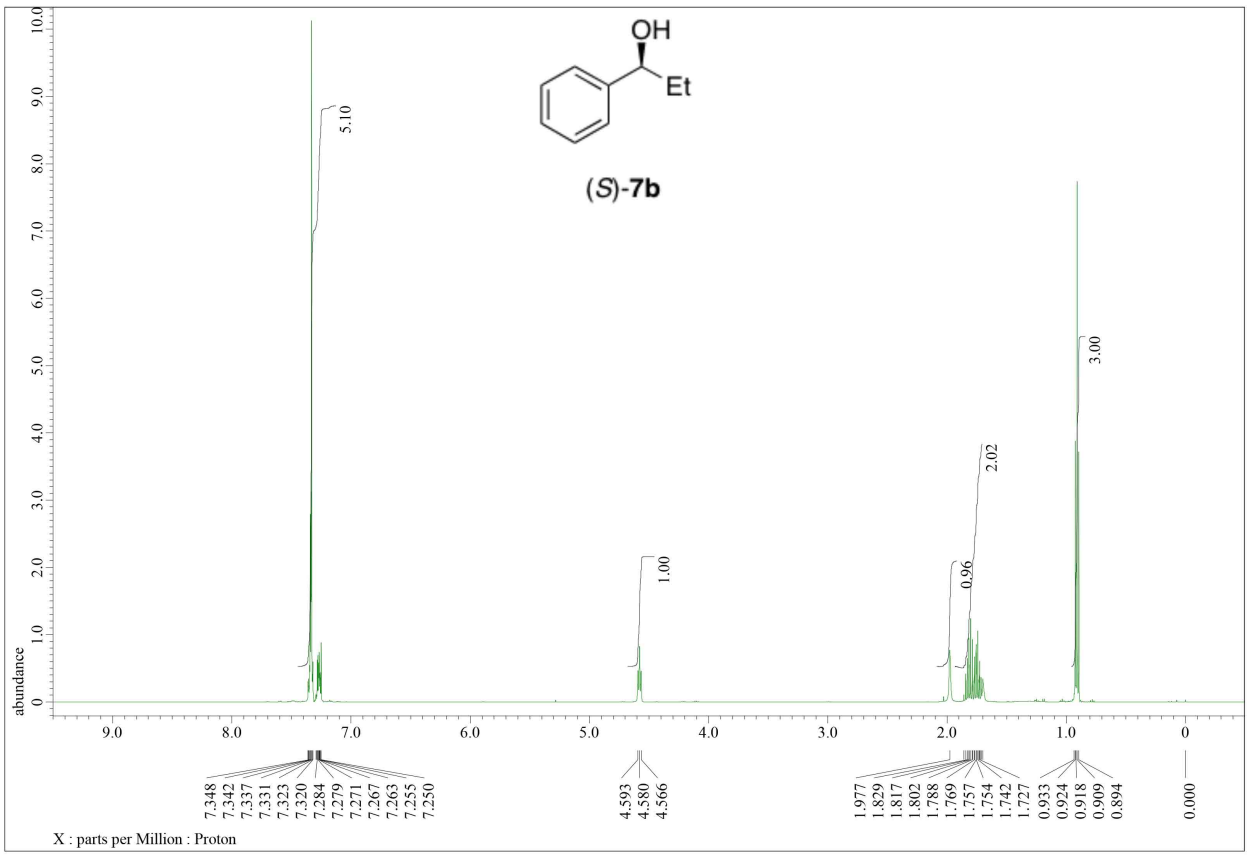

MeO
OMe
N
N
Ir
Cl
Cy
Cy
Cy
8dy
abundance
X : parts per Million : Carbon13

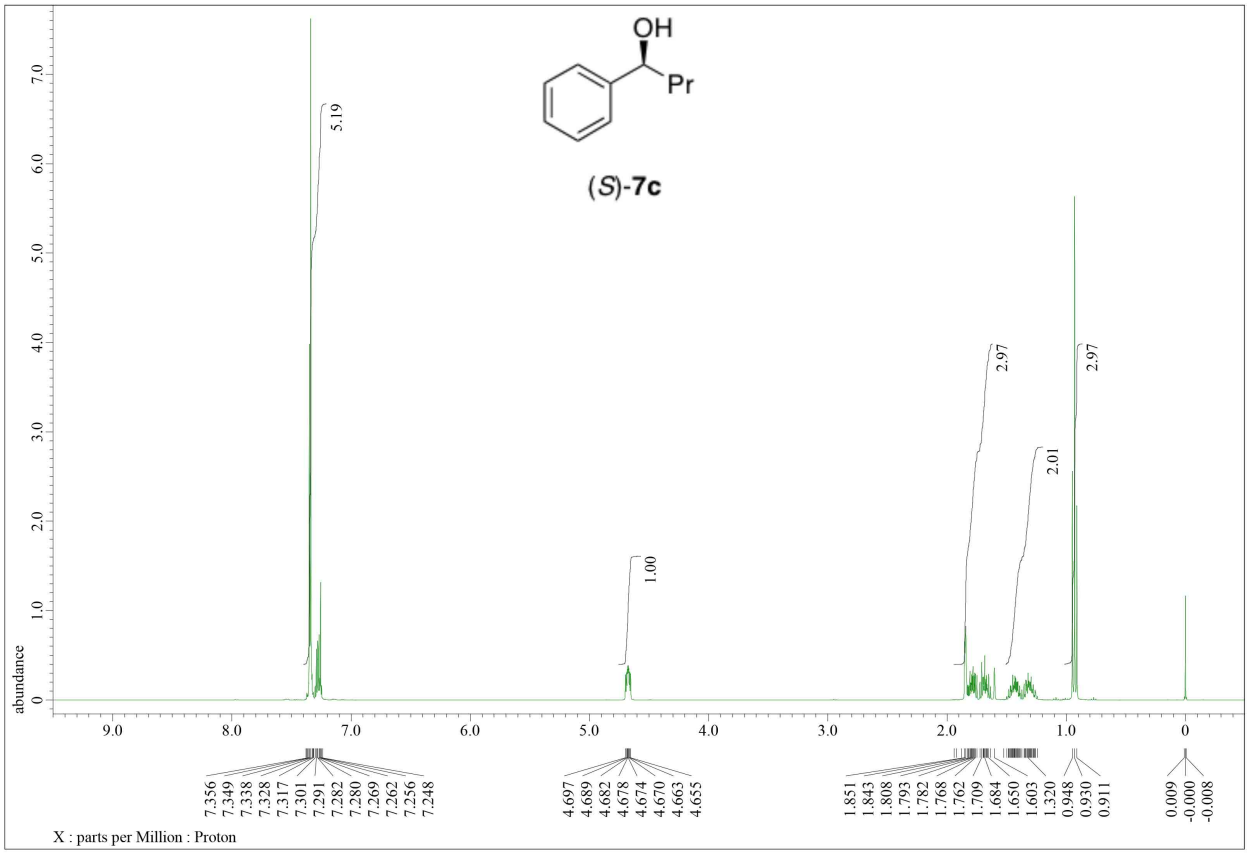

F3C
CF3
N
N
Ir
Cl
Cy
Cy
Cy
8dz
47.00
0.97
2.05
4.07
2.04
1.01
1.04
1.01
1.00
1.04
1.00
1.05
3.09
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.741
7.647
7.626
7.566
7.541
6.973
6.970
6.419
6.142
6.126
6.119
6.101
4.801
4.794
4.782
4.775
4.764
4.756
4.083
4.074
4.064
3.721
3.693
3.665
3.135
3.105
3.080
3.046
2.475
2.351
2.322
2.206
1.878
1.853
1.812
1.771
1.762
1.752
1.741
1.400
1.275
1.258
0.000
X : parts per Million : Proton

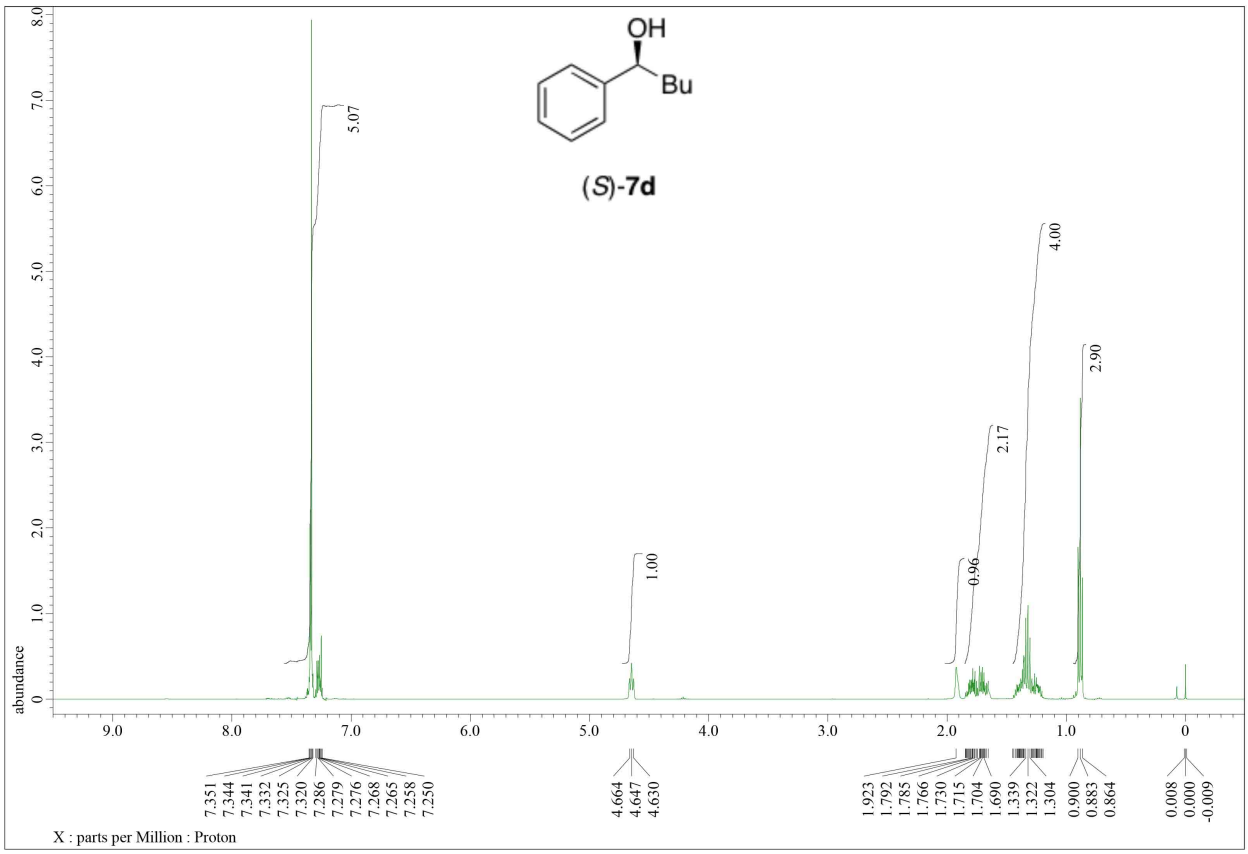

F3C
CF3
N
N
Ir
Cl
Cy
Cy
Cy
8dz
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
177.668
147.682
147.005
145.708
143.810
143.734
139.156
133.223
129.809
127.129
125.698
124.725
122.703
111.297
85.097
77.324
77.000
76.676
67.138
56.046
54.463
50.829
44.725
39.480
34.616
34.434
34.396
30.991
27.806
27.758
27.338
27.005
26.928
26.871
26.156
X : parts per Million : Carbon13

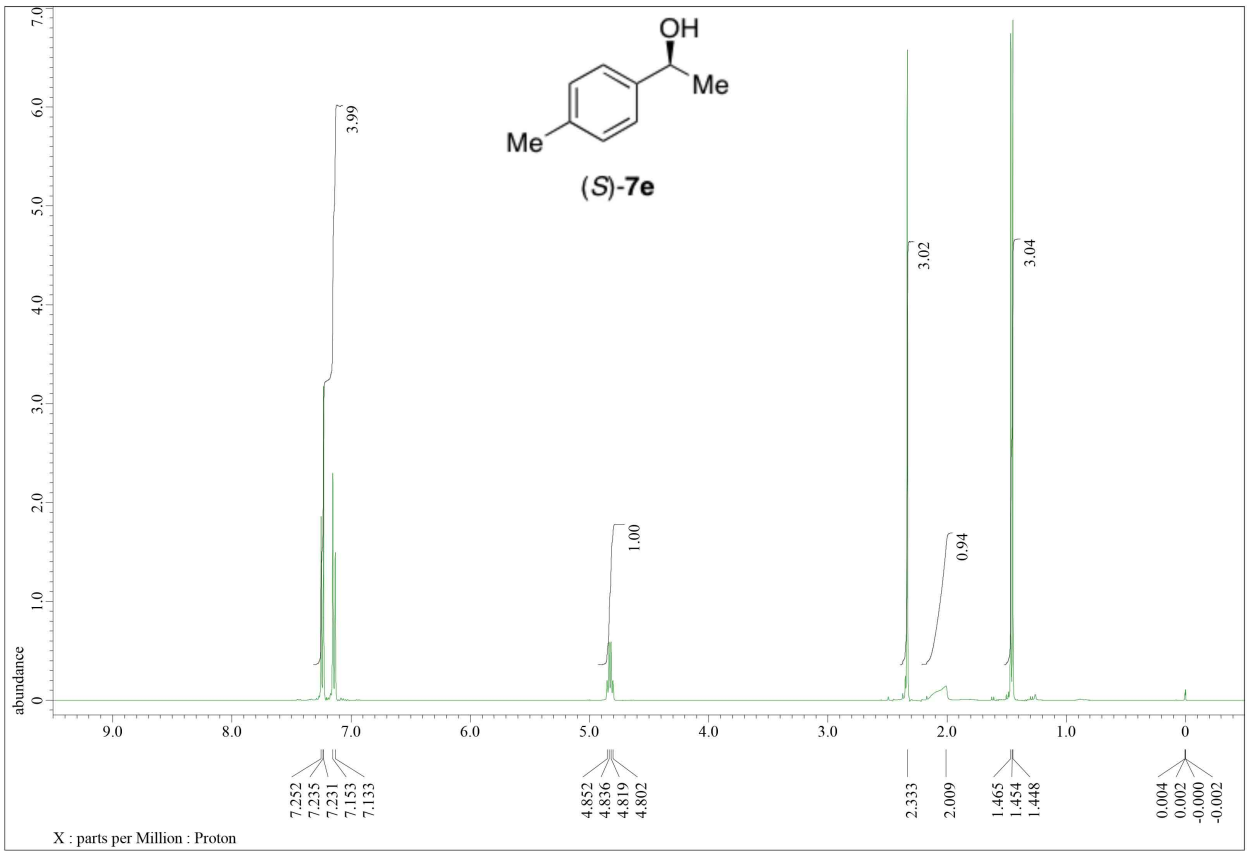
<^{1}H NMR Spectra of Known Compounds>

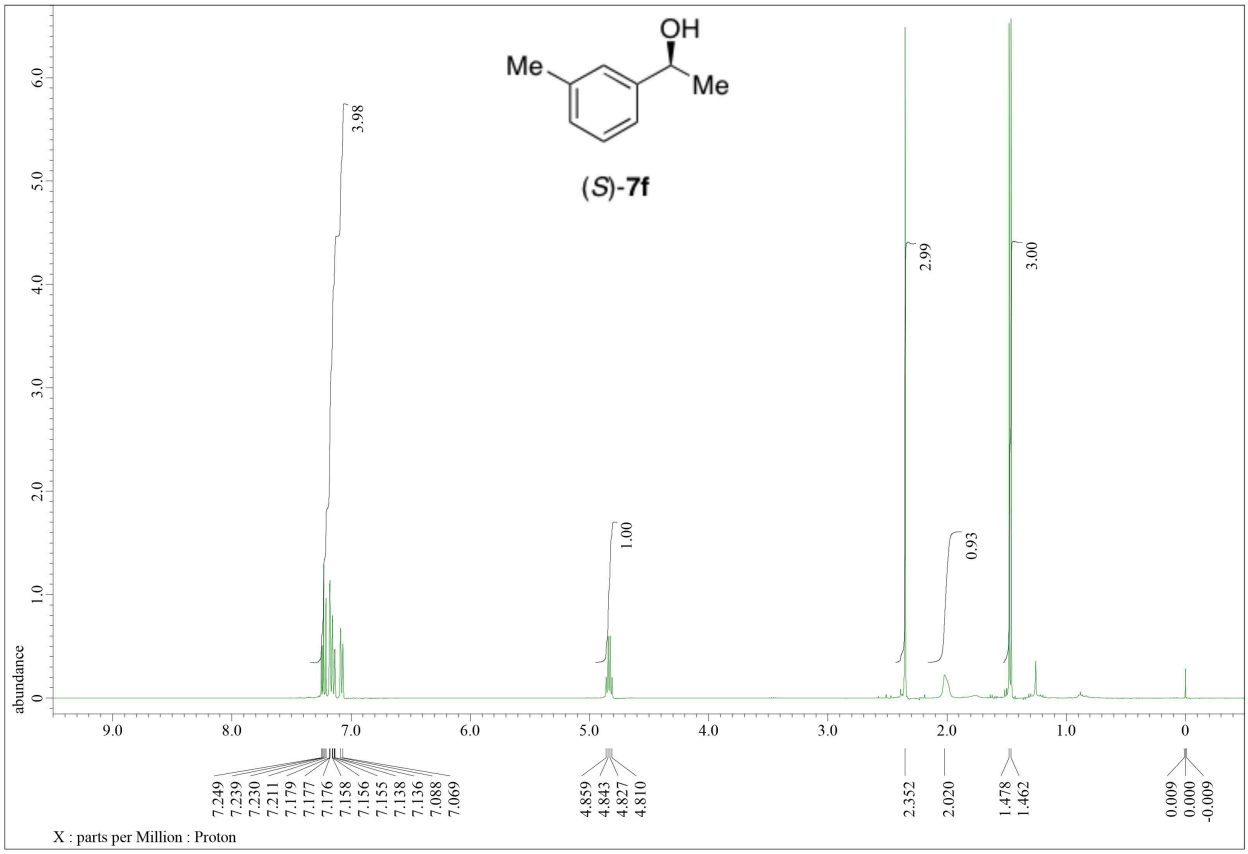


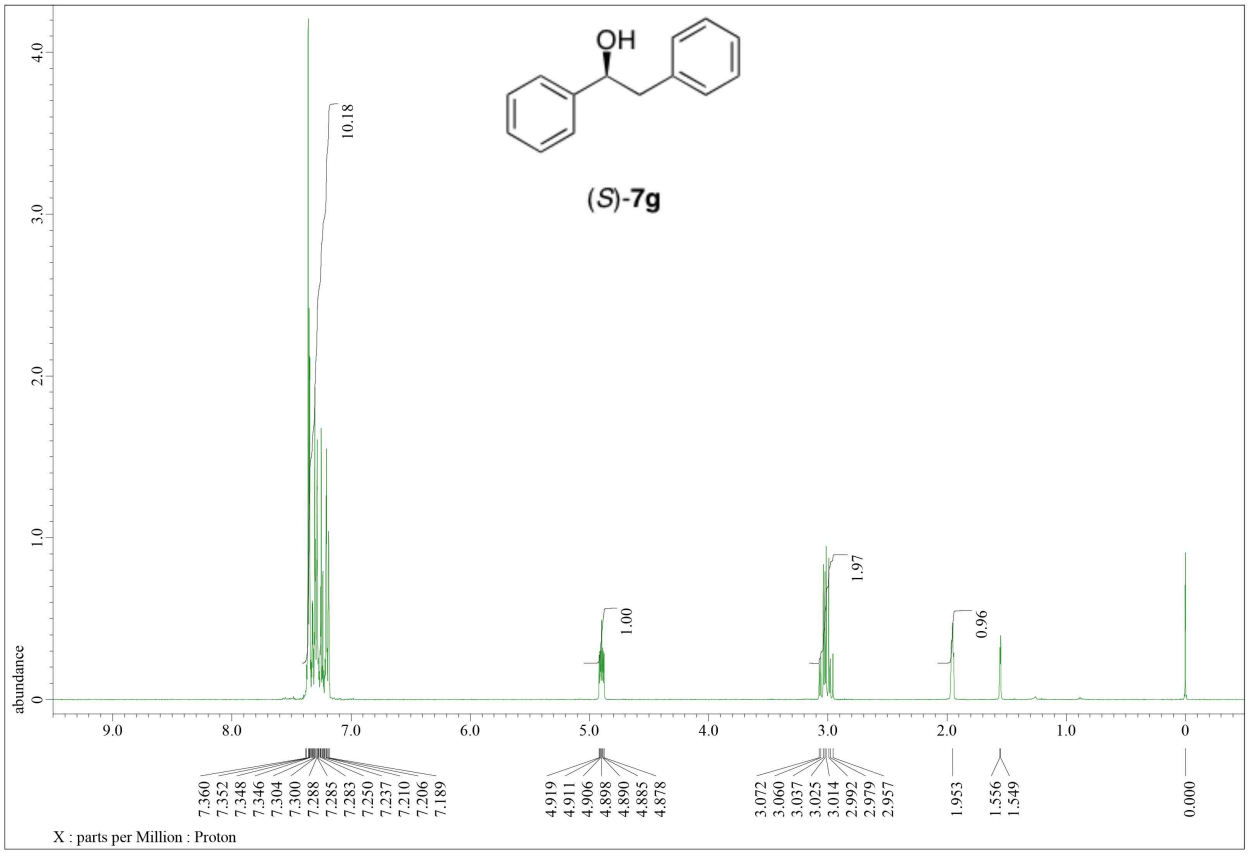


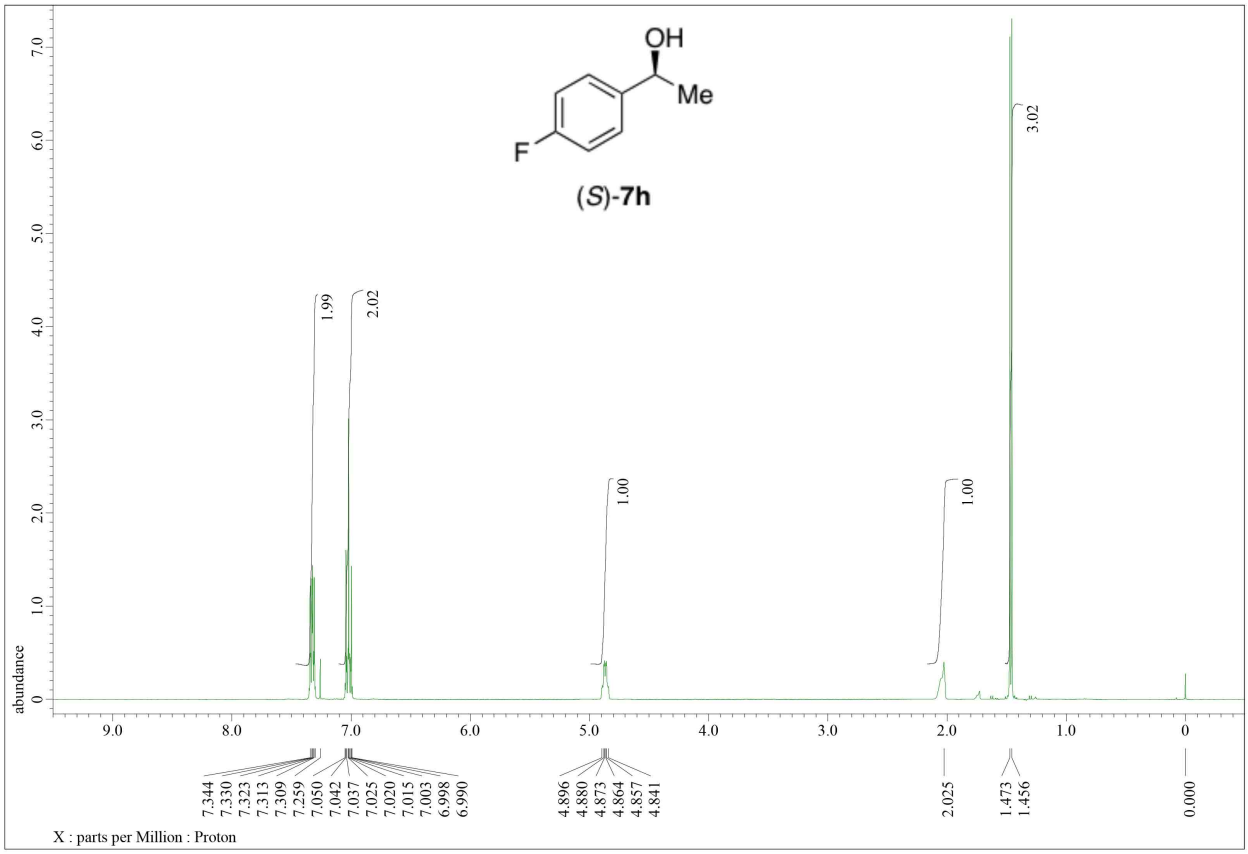

OH
Pr
(S)-7c
5.19
1.00
2.97
2.01
2.97
abundance
X : parts per Million : Proton

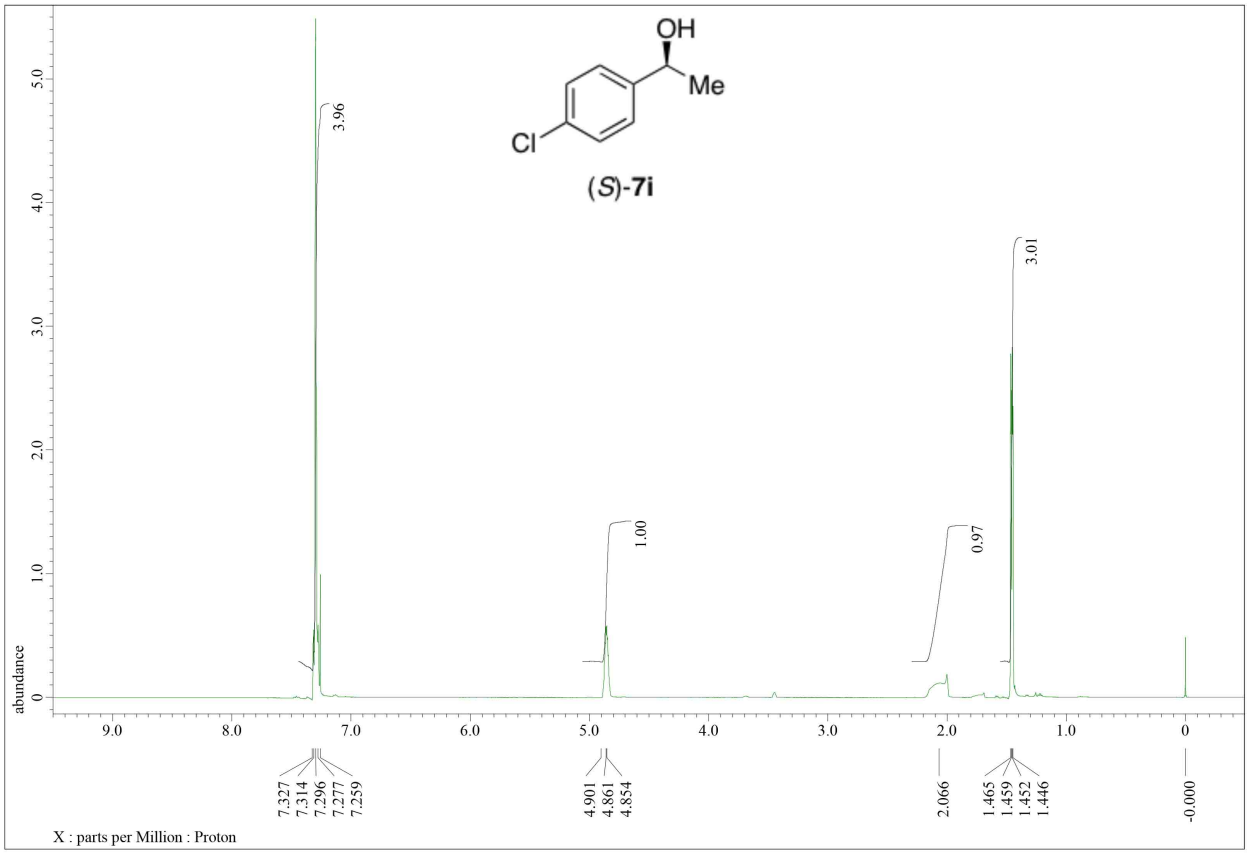

OH
Bu
(S)-7d
5.07
1.00
0.96
2.17
4.00
2.90
abundance
X : parts per Million : Proton

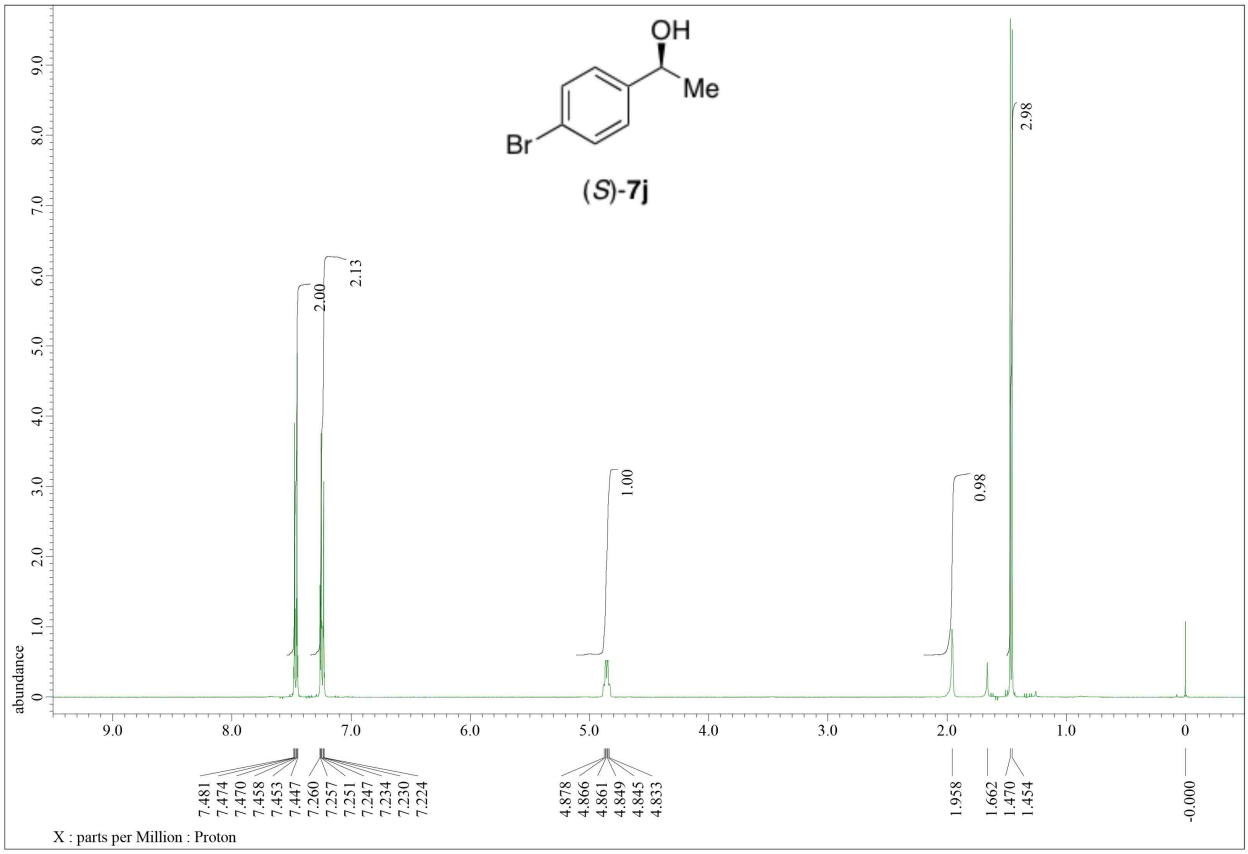

OH
Me
Me
(S)-7e
3.99
3.02
3.04
1.00
0.94
abundance
X : parts per Million : Proton
7.252
7.235
7.231
7.153
7.133
4.852
4.836
4.819
4.802
2.333
2.009
1.465
1.454
1.448
0.004
0.002
-0.000
-0.002

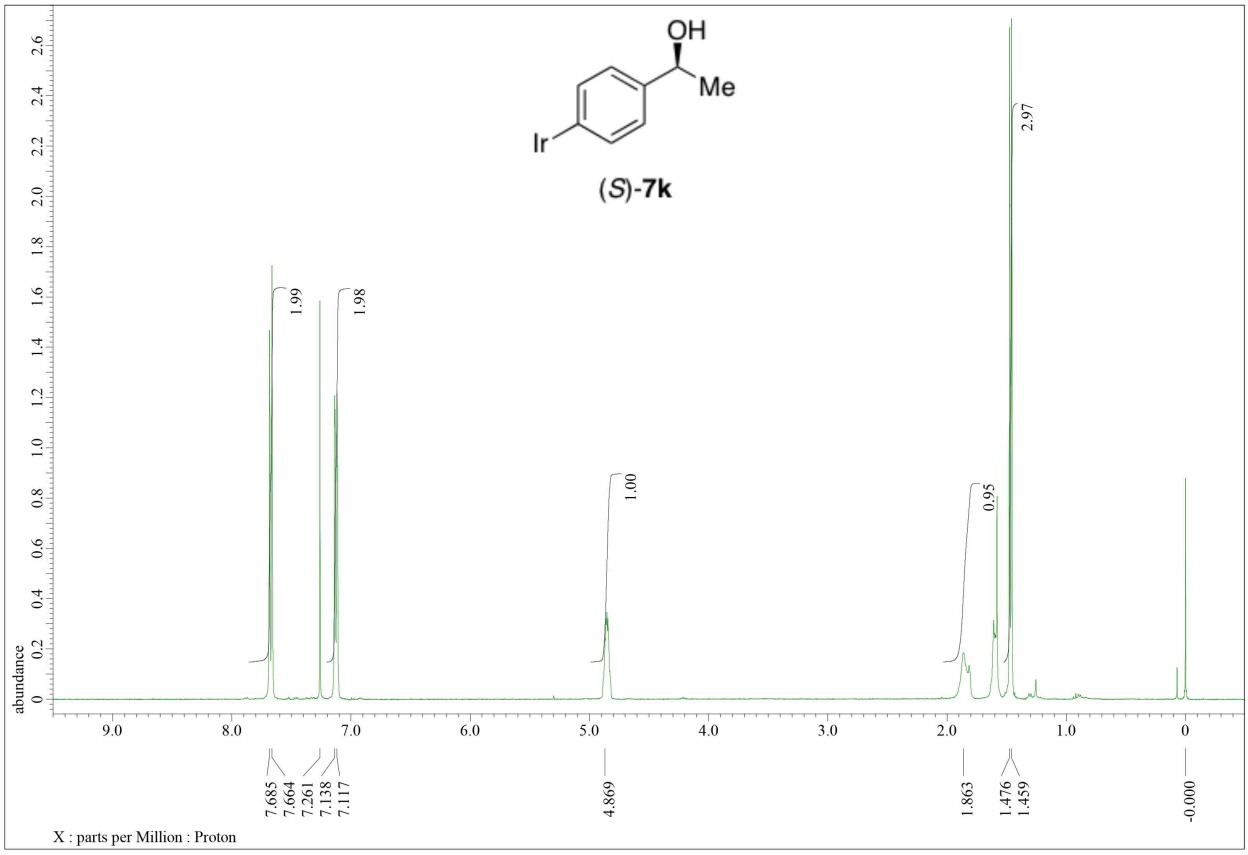

OH
Me
Me
(S)-7f
3.98
2.99
3.00
1.00
0.93
abundance
X : parts per Million : Proton
7.249
7.239
7.230
7.211
7.179
7.177
7.176
7.158
7.156
7.155
7.138
7.136
7.088
7.069
4.859
4.843
4.827
4.810
2.352
2.020
1.478
1.462
0.009
0.000
-0.009

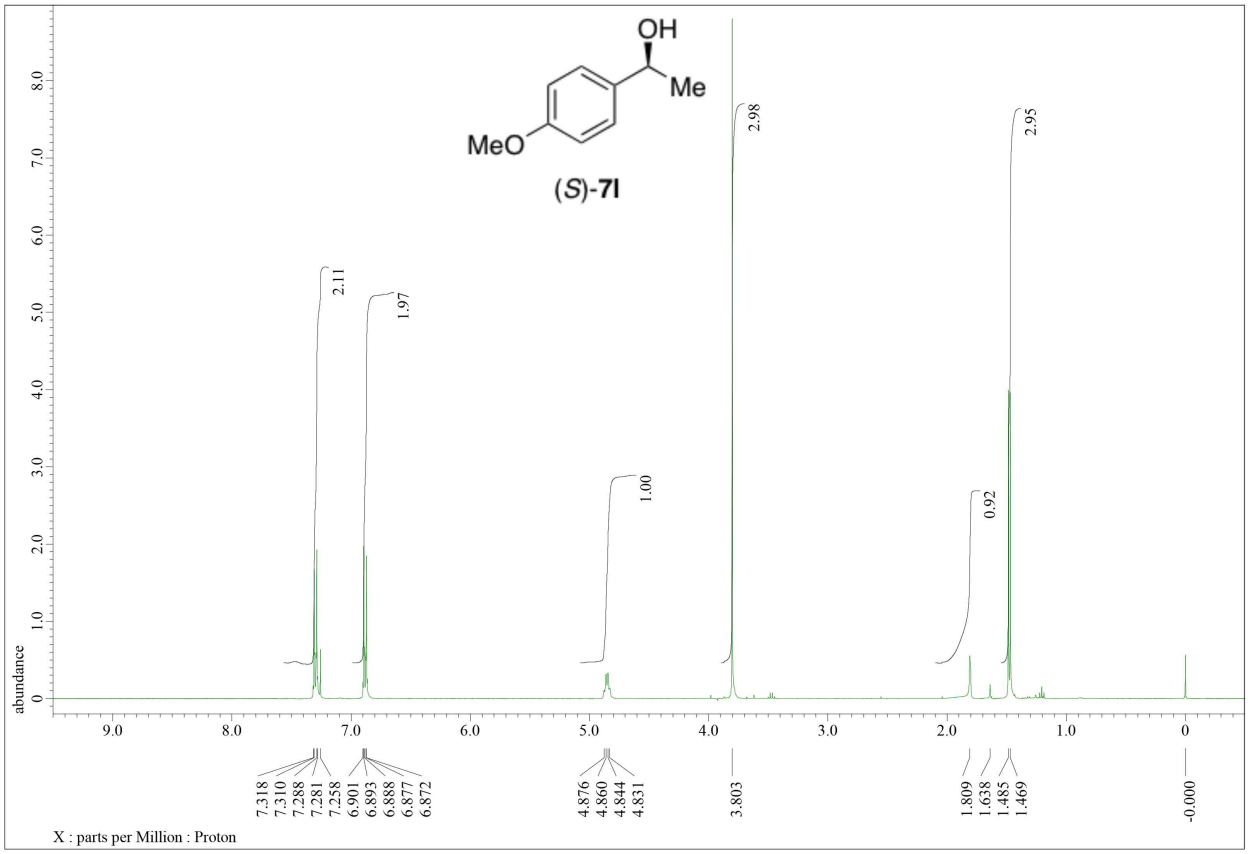

OH
(S)-7g
10.18
1.00
1.97
0.96
abundance
X : parts per Million : Proton


OH
Me
F
(S)-7h
1.99
2.02
1.00
1.00
3.02
abundance
X : parts per Million : Proton


OH
Me
Cl
(S)-7i
3.96
3.01
1.00
0.97
abundance
X : parts per Million : Proton


OH
Me
Br
(S)-7j
2.98
2.13
2.00
1.00
0.98
abundance
X : parts per Million : Proton


OH
Me
Ir
(S)-7k
abundance
X : parts per Million : Proton
1.99
1.98
1.00
2.97
0.95
7.685
7.664
7.261
7.138
7.117
4.869
1.863
1.476
1.459
-0.000


OH
Me
MeO
(S)-7l
abundance
X : parts per Million : Proton
2.11
1.97
1.00
2.98
2.95
0.92
7.318
7.310
7.288
7.281
7.258
6.901
6.893
6.888
6.877
6.872
4.876
4.860
4.844
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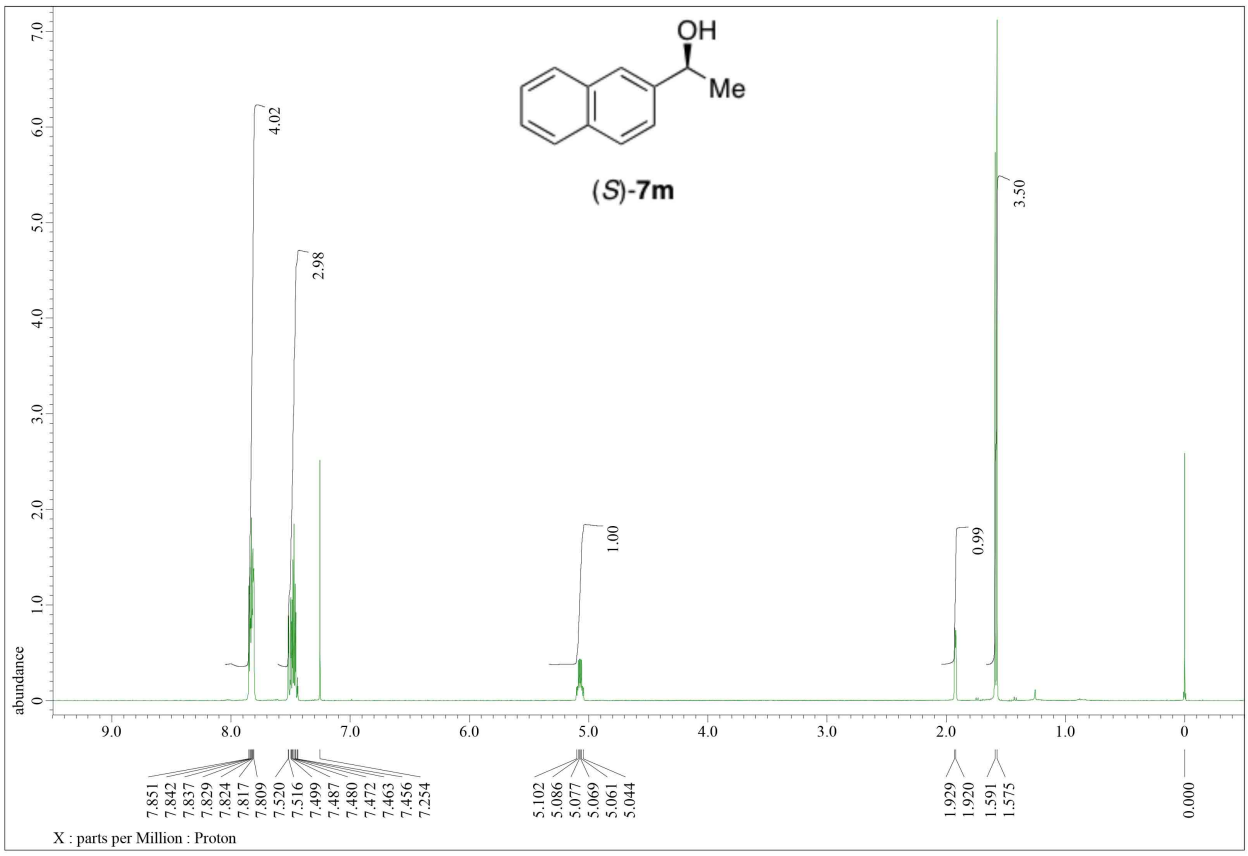
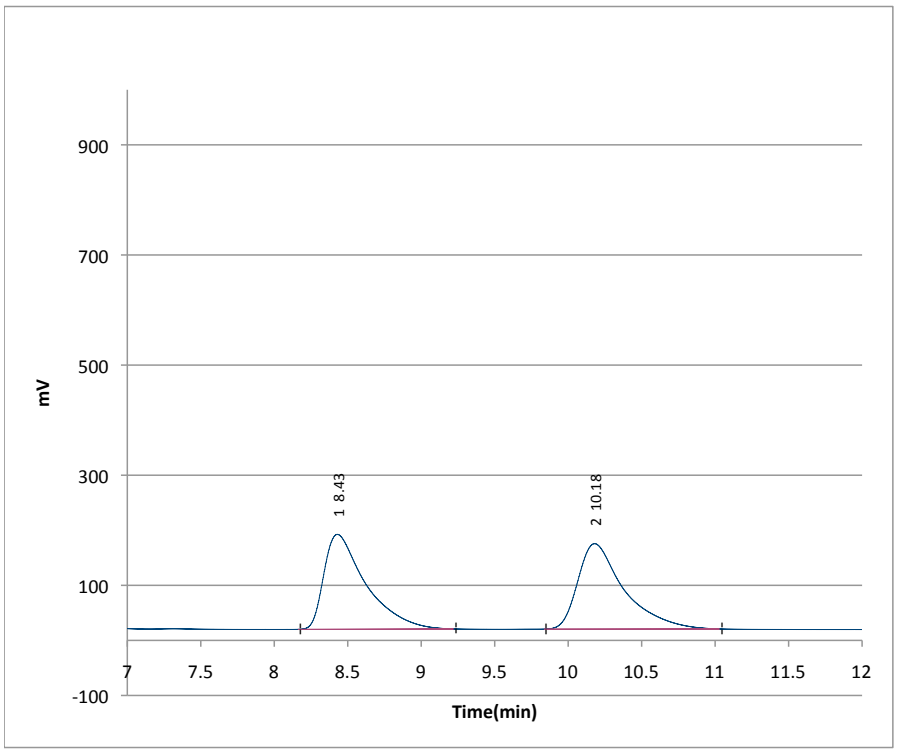
3.803
1.809
1.638
1.485
1.469
-0.000


OH
Me
(S)-7m
4.02
2.98
1.00
0.99
3.50
abundance
X : parts per Million : Proton
7.851
7.842
7.837
7.829
7.824
7.817
7.809
7.520
7.516
7.499
7.487
7.480
7.472
7.463
7.456
7.254
5.102
5.086
5.077
5.069
5.061
5.044
1.929
1.920
1.591
1.575
0.000

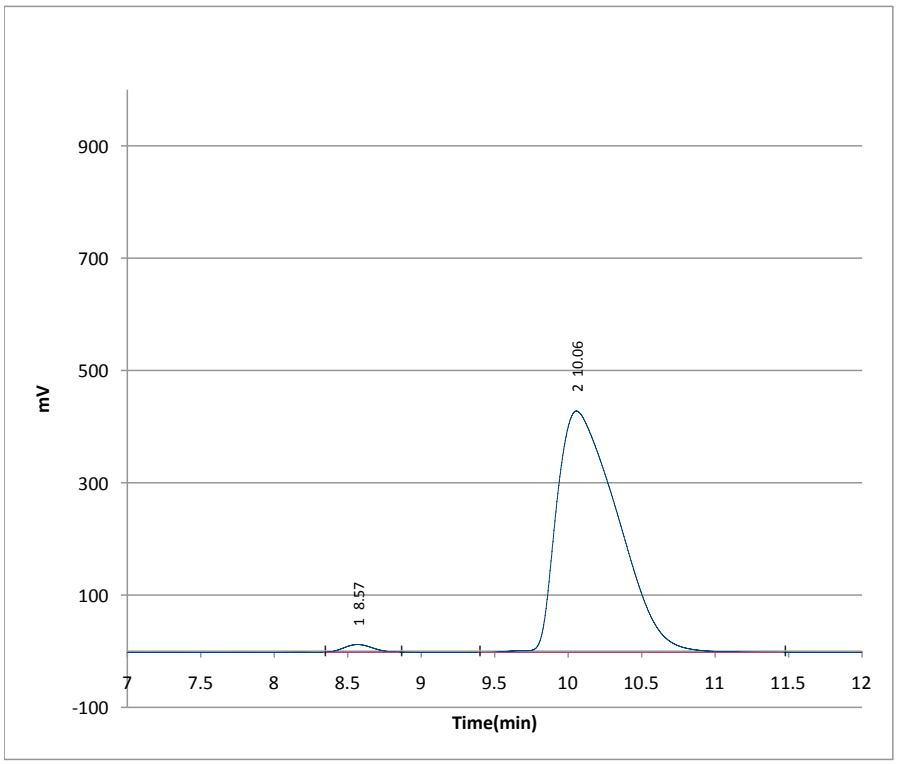
<HPLC Analysis Data of Alcohols 7>

(Table 3, entry 13)

Chiral Column: OD-H, 254 nm, 1.0 mL/min, Hex/iPrOH = 95/5



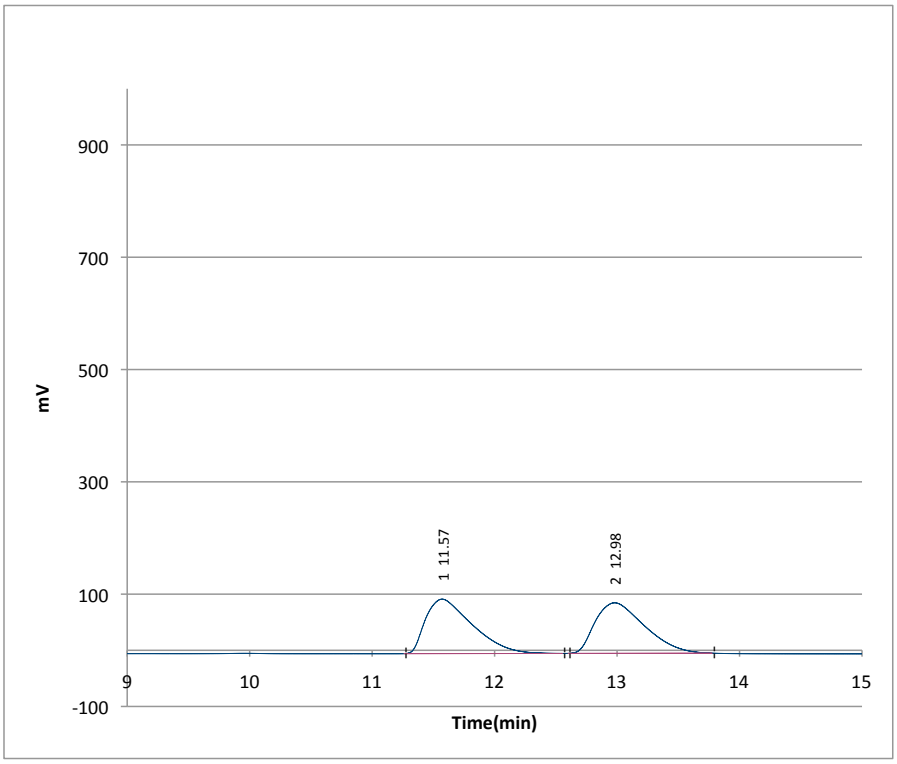
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	8.43	(R)-isomer	3402408	50.1644	172321	3446.8	1.989	2.88
2	10.18	(S)-isomer	3380102	49.8356	155232	4034.9	1.728	-----



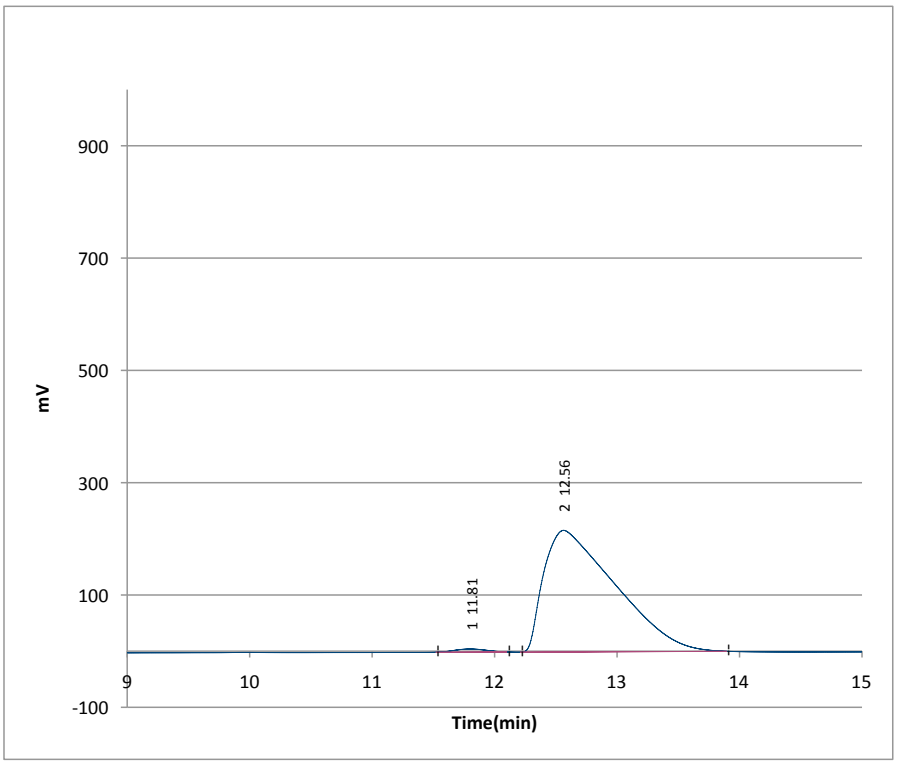
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	8.57	(R)-isomer	187468.8	1.4994	13808	9136.2	1.108	2.722
2	10.06	(S)-isomer	12315170	98.5006	429990	2985	1.768	-----

(Table 4, entry 2)

Chiral Column: OD-H, 254 nm, 1.0 mL/min, Hex/iPrOH = 98/2



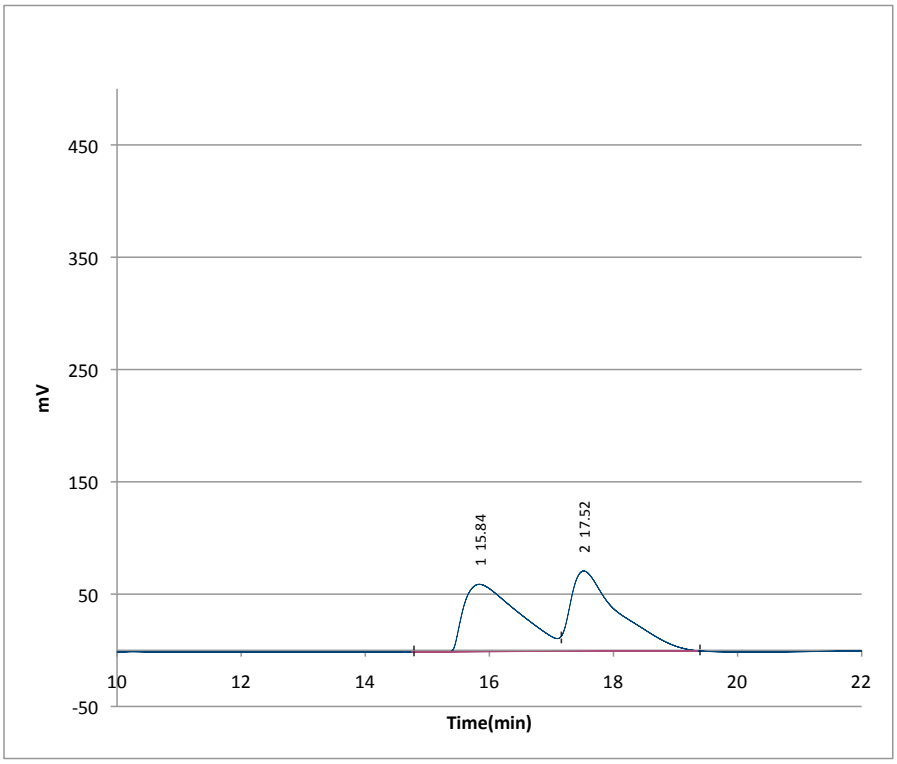
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	11.57	(R)-isomer	2567029	50.3844	96952	4182.5	1.754	1.92
2	12.98	(S)-isomer	2527864	49.6156	90020	4802.8	1.514	-----



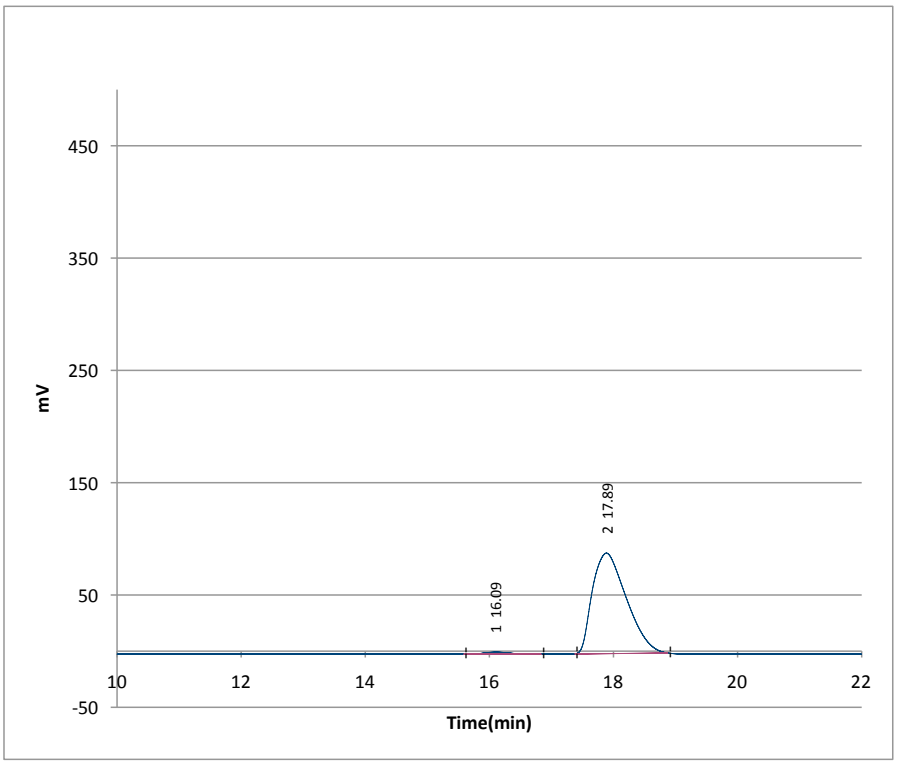
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	11.81	(R)-isomer	99393.8	1.1204	5540	10420.8	1.022	0.972
2	12.56	(S)-isomer	8771908	98.8796	216623	2109.8	2.267	-----

(Table 4, entry 4)

Chiral Column: OD-H, 254 nm, 0.8 mL/min, Hex/*i*-PrOH = 98/2



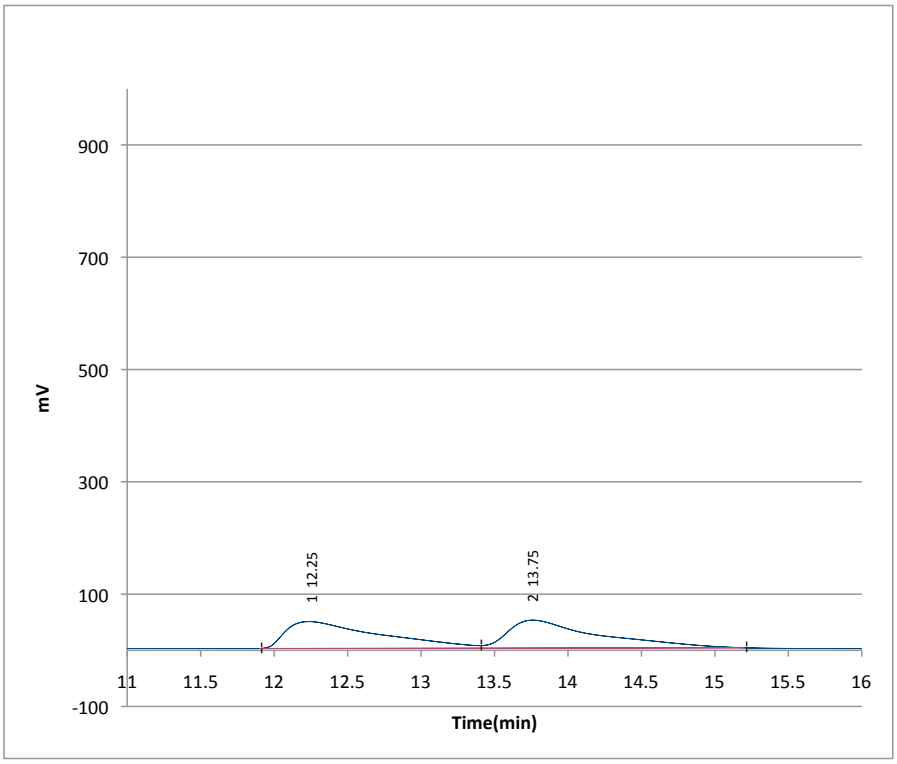
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	15.84	(R)-isomer	3711331	48.9923	59977	1482.2	-----	1.089
2	17.52	(S)-isomer	3863999	51.0077	71451	2374.1	-----	-----



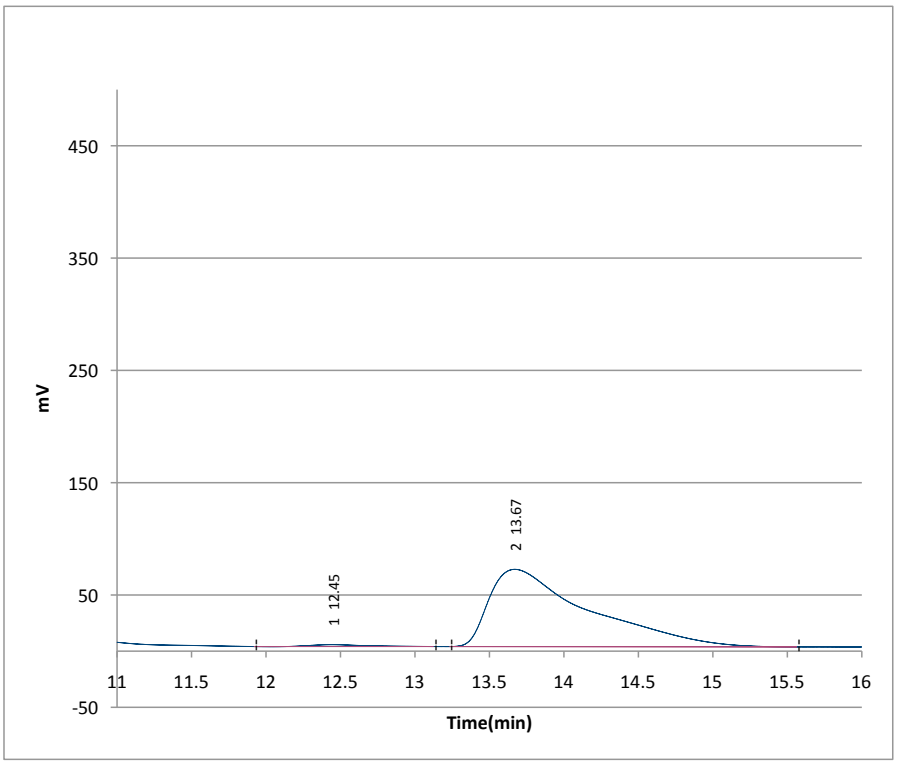
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	16.09	(R)-isomer	49397.4	1.4307	1786	7919.1	1.159	2.087
2	17.89	(S)-isomer	3403339	98.5693	89480	5099.2	1.44	-----

(Table 4, entry 6)

Chiral Column: OD-H, 254 nm, 1.0 mL/min, Hex/*i*-PrOH = 98/2



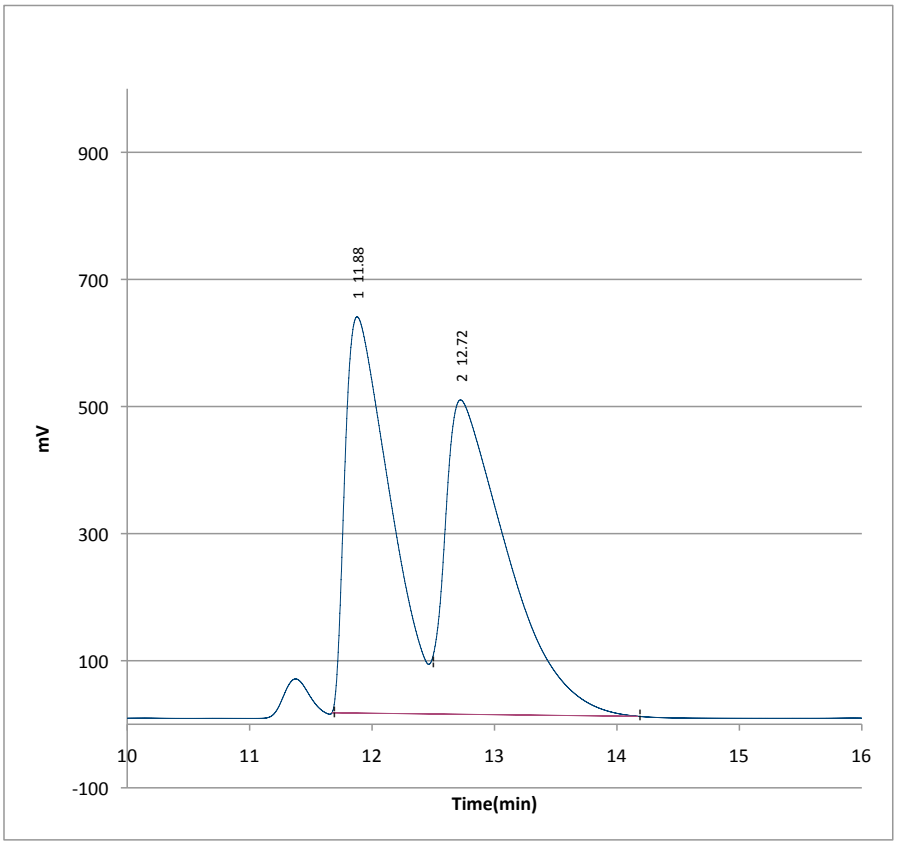
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	12.25	(R)-isomer	2116952	49.9618	47823	1731.3	-----	1.305
2	13.75	(S)-isomer	2120192	50.0382	49826	2363	-----	-----



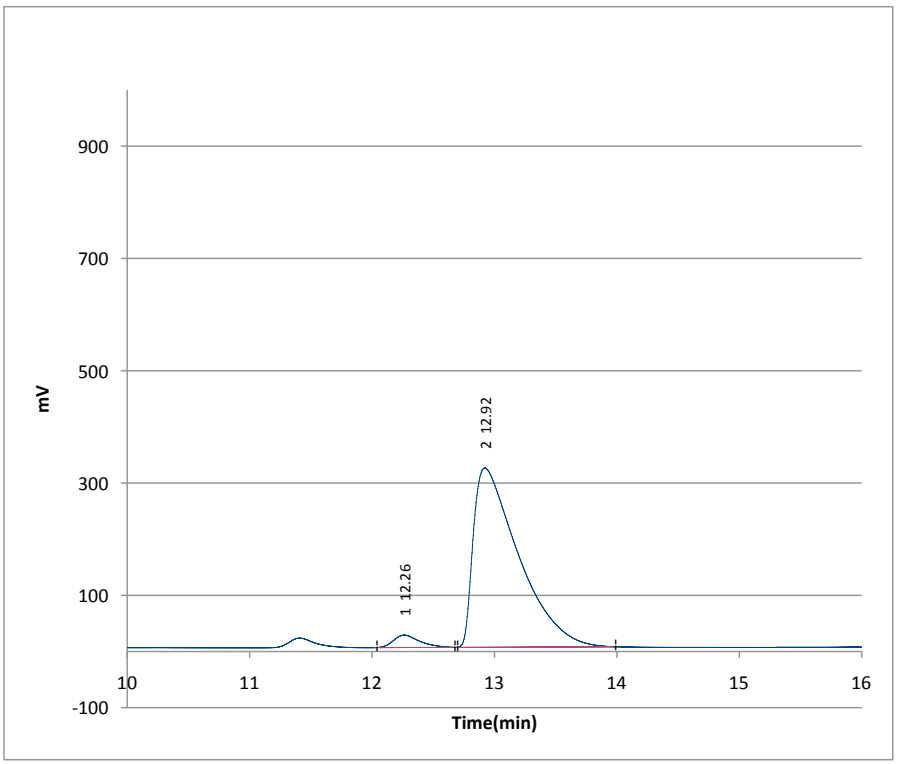
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	12.45	(R)-isomer	41044.3	1.2777	1698	4559.7	1.546	1.152
2	13.67	(S)-isomer	3171402	98.7223	68826	1555.3	2.603	-----

(Table 4, entry 8)

Chiral Column: AD-H, 254 nm, 0.8 mL/min, Hex/*i*-PrOH = 98/2



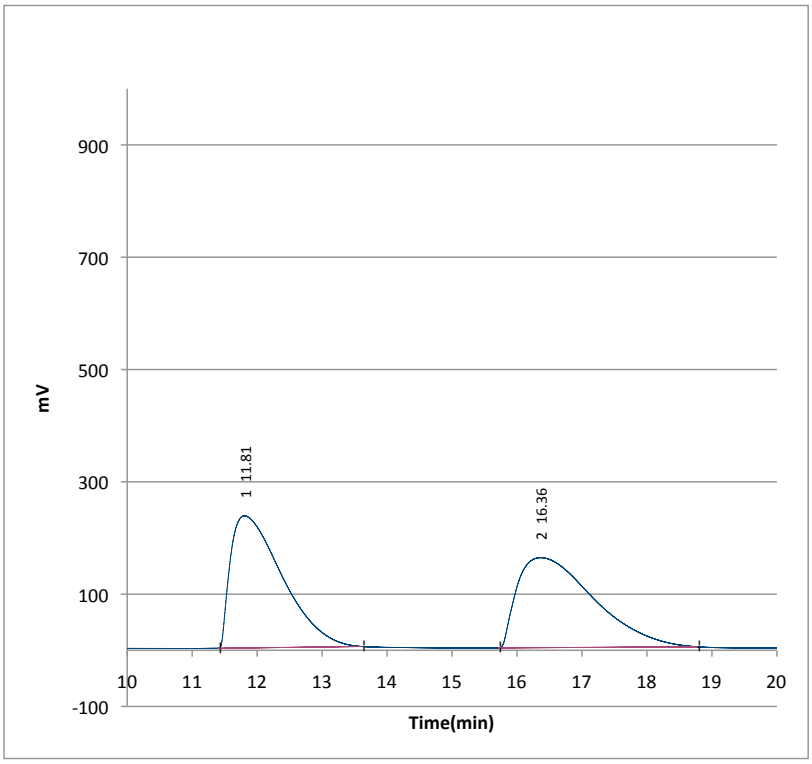
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	11.88		15858662	47.5367	623646	4934.2	-----	1.047
2	12.72		17502217	52.4633	494659	2924.9	-----	-----



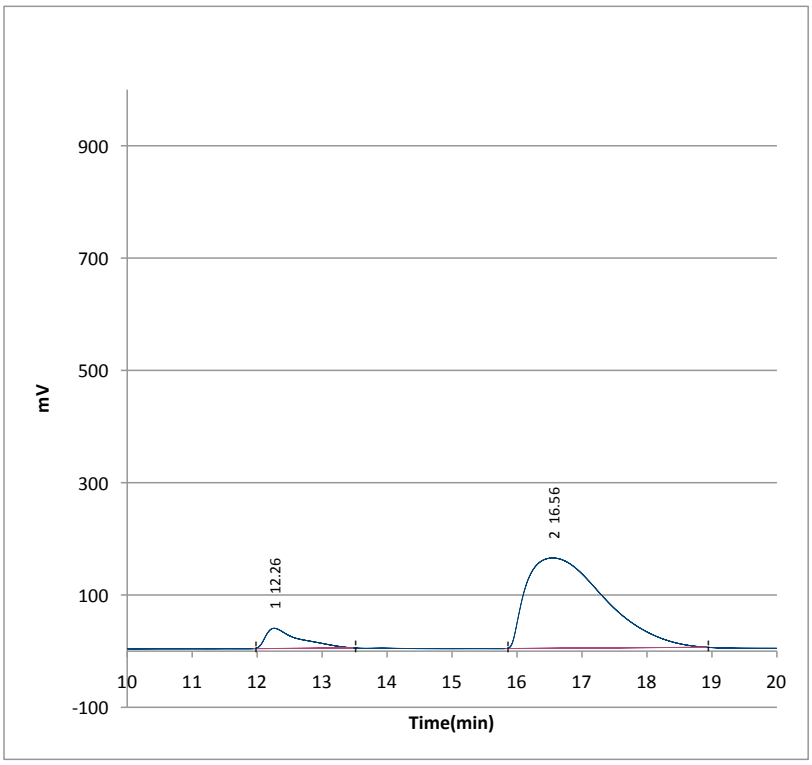
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	12.26	(R)-isomer	327506.6	3.8466	22184	13710.5	1.393	1.16
2	12.92	(S)-isomer	8186695	96.1534	319381	5170.9	2.647	-----

(Table 4, entry 10)

Chiral Column: OD-H, 254 nm, 1.0 mL/min, Hex/*i*-PrOH = 98/2



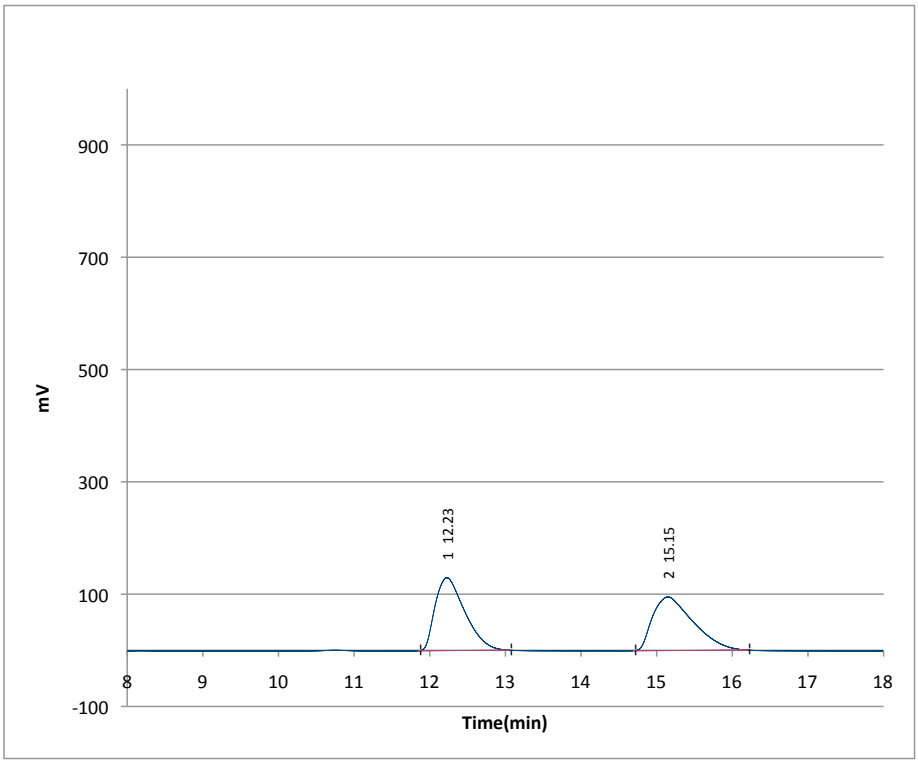
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	11.81	(*R*)-isomer	12980433	49.7812	235283	1041.9	2.476	2.528
2	16.36	(*S*)-isomer	13094540	50.2188	160257	934.4	2.197	----



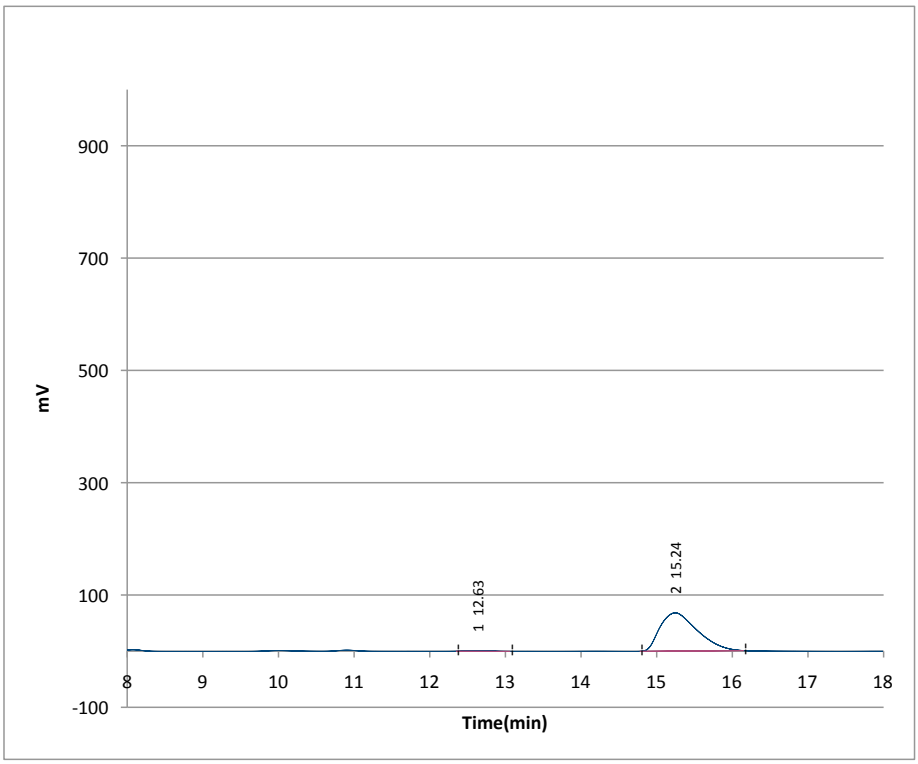
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	12.26	(*R*)-isomer	1288723	8.7141	36004	1915.9	2.634	2.622
2	16.56	(*S*)-isomer	13500170	91.2859	160767	942.4	1.988	----

(Table 4, entry 12)

Chiral Column: OD-H, 254 nm, 1.0 mL/min, Hex/*i*-PrOH = 95/5



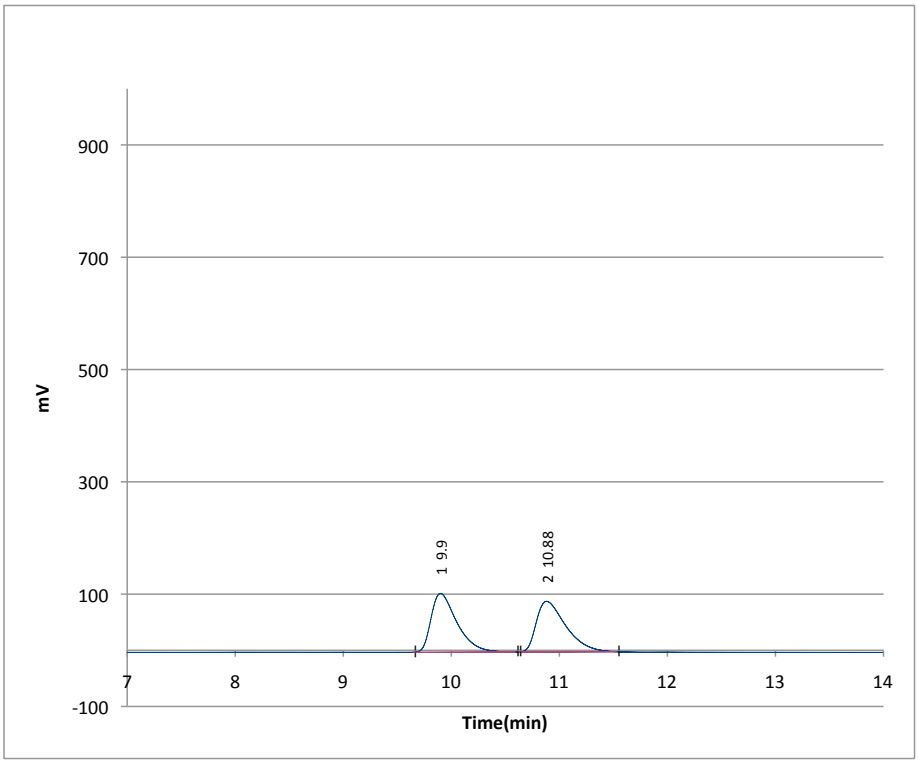
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	12.23	(*R*)-isomer	3537587	49.9746	129802	4459.6	1.529	3.372
2	15.15	(*S*)-isomer	3541190	50.0254	95441	3659.3	1.632	----



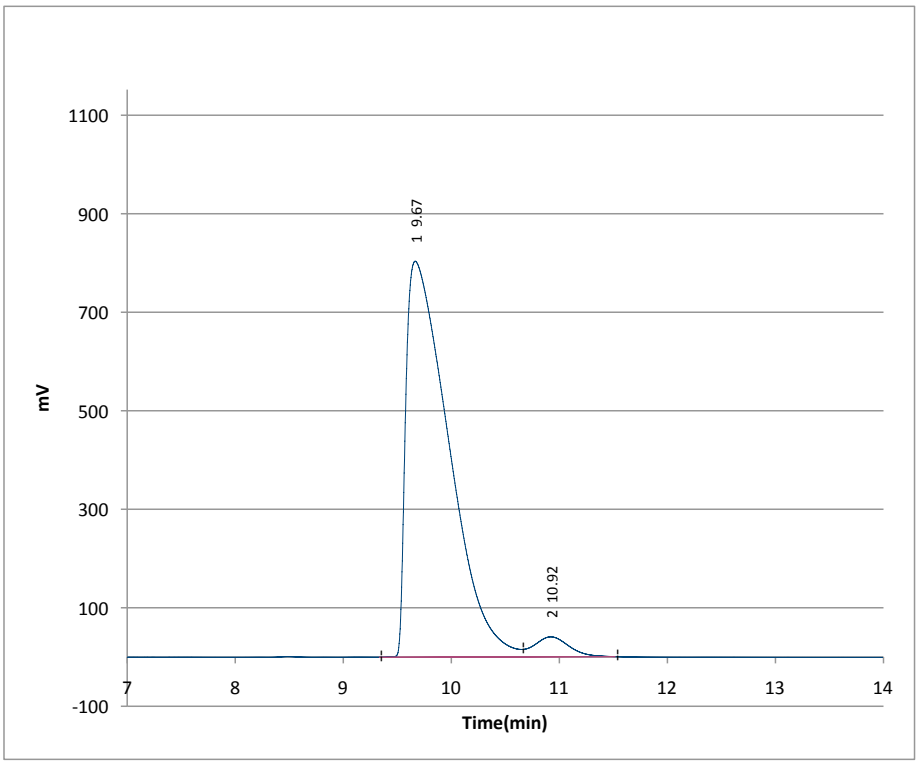
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	12.63	(*R*)-isomer	26233.4	1.1129	1300	9094.4	1.169	3.622
2	15.24	(*S*)-isomer	2330930	98.8871	68221	4439.8	1.474	----

(Table 4, entry 14)

Chiral Column: OB-H, 254 nm, 0.8 mL/min, Hex/iPrOH = 98/2



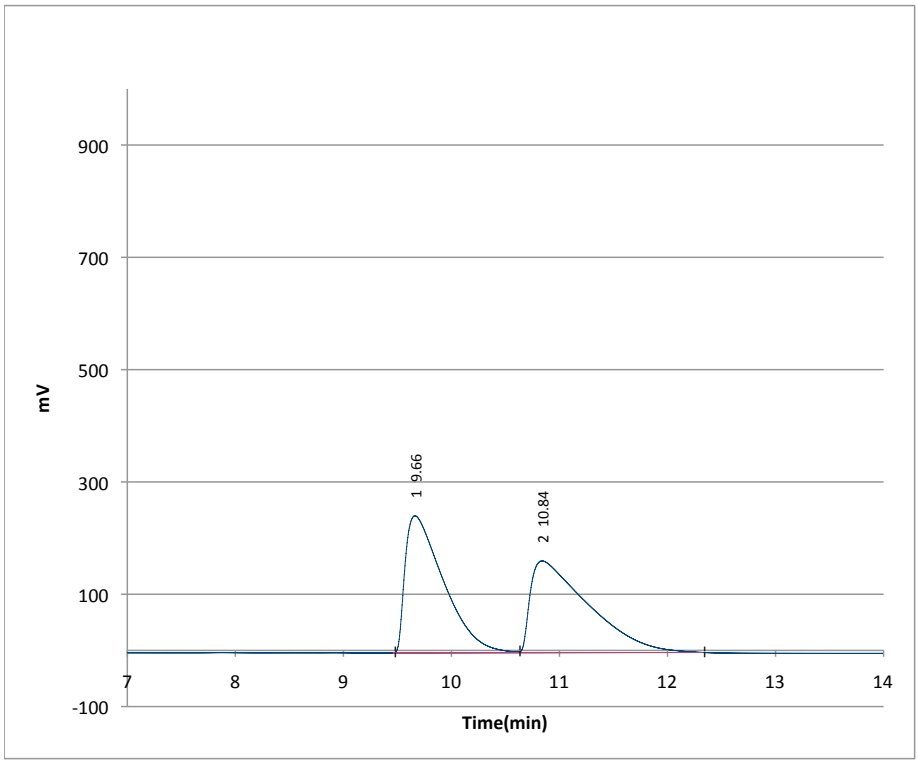
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	9.9	(*S*)-isomer	1742118	50.5146	104728	7517.9	1.65	2.012
2	10.88	(*R*)-isomer	1706625	49.4854	90178	6984.5	1.722	----



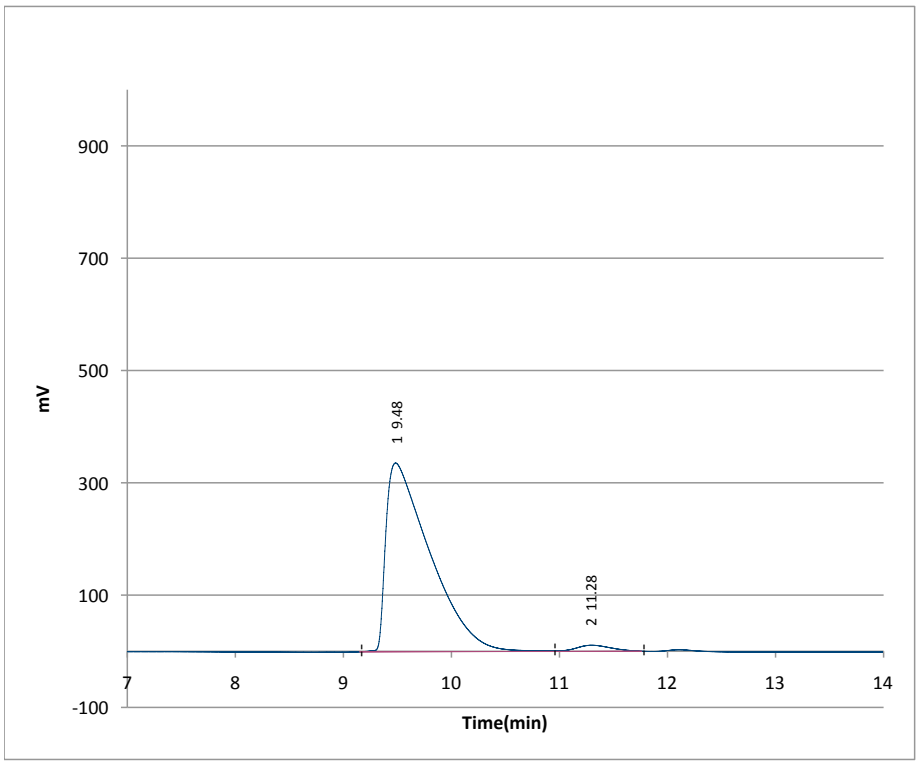
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	9.67	(*S*)-isomer	22075007	95.9744	803868	2802.9	3.114	1.88
2	10.92	(*R*)-isomer	925921.9	4.0256	40616	5193.2	----	----

(Table 4, entry 15)

Chiral Column: OB-H, 254 nm, 0.8 mL/min, Hex/*i*-PrOH = 98/2



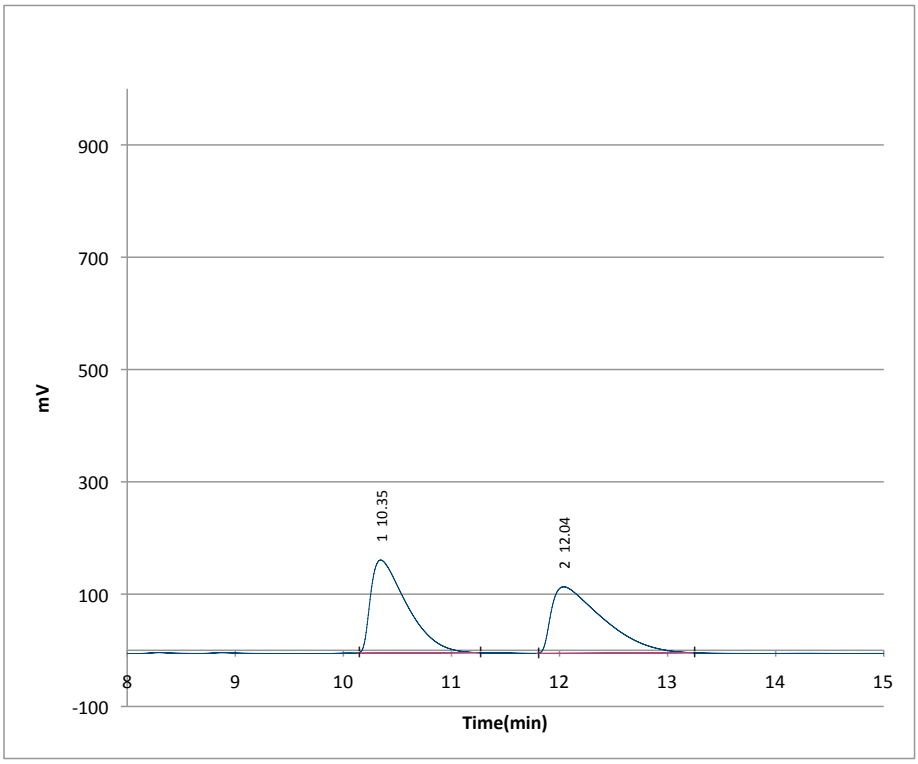
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	9.66	(*S*)-isomer	6020833	49.8336	244261	3476.4	2.642	1.434
2	10.84	(*R*)-isomer	6061029	50.1664	163490	1933.9	3.459	----



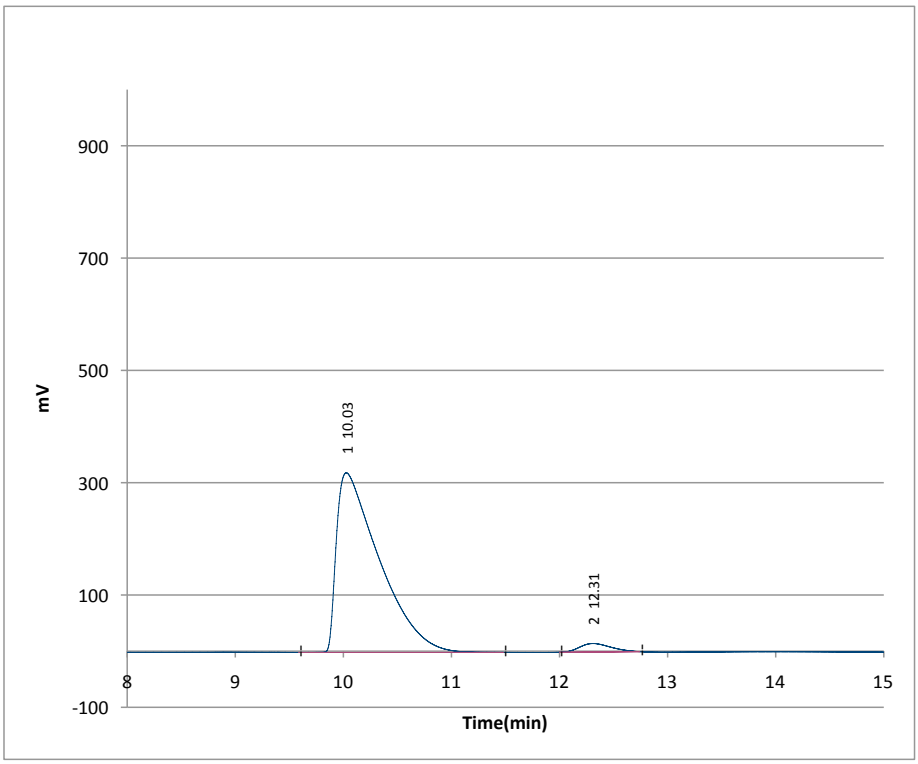
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	9.48	(*S*)-isomer	9518005	97.504	336051	2535.8	3.096	2.676
2	11.28	(*R*)-isomer	243655.8	2.496	10942	5807.6	----	----

(Table 4, entry 18)

Chiral Column: OB-H, 254 nm, 0.8 mL/min, Hex/*i*-PrOH = 98/2



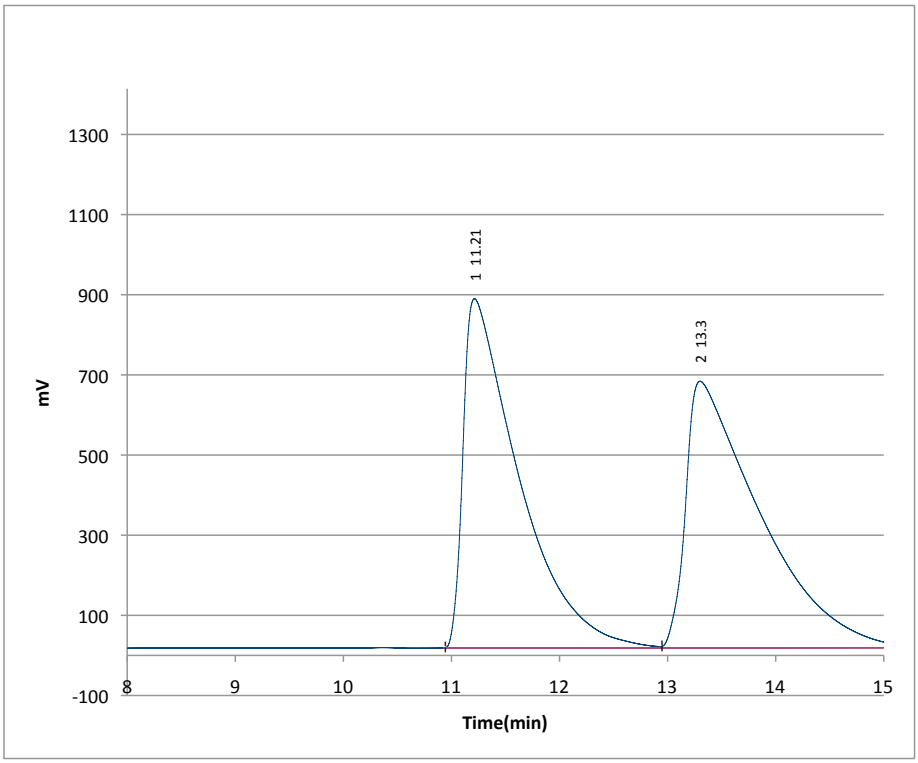
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	10.35	(S)-isomer	3851702	49.7781	165594	4186.6	2.368	2.182
2	12.04	(R)-isomer	3886047	50.2219	118401	2804.8	2.873	----



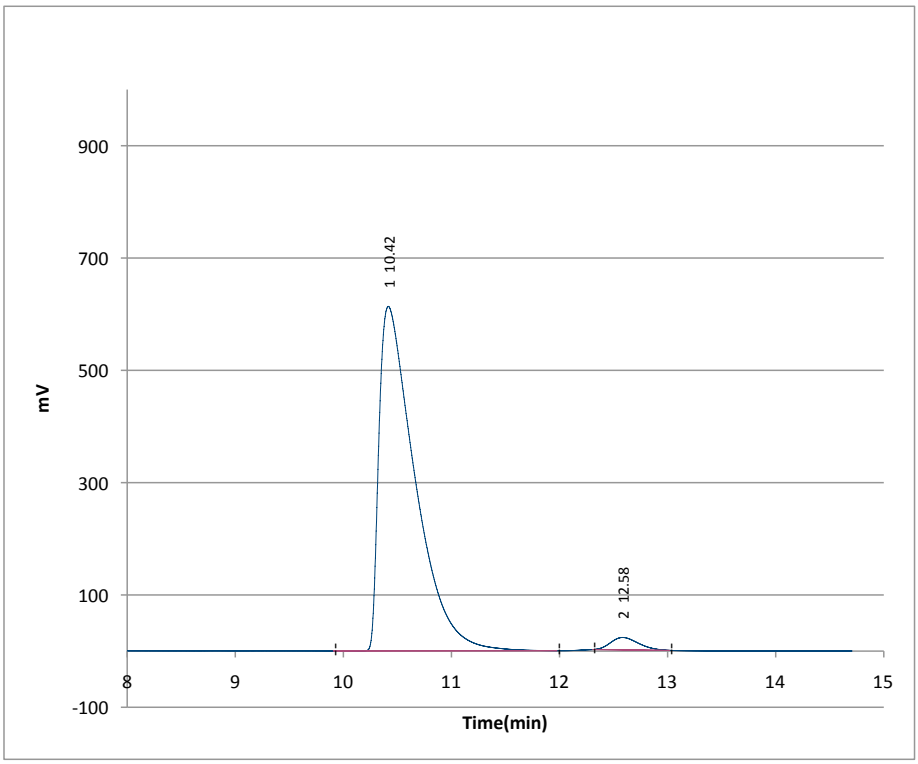
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	10.03	(S)-isomer	8809076	96.6523	319853	2697.1	2.98	3.468
2	12.31	(R)-isomer	305118.5	3.3477	15167	8228.3	1.28	----

(Table 4, entry 20)

Chiral Column: OB-H, 254 nm, 0.8 mL/min, Hex/*i*-PrOH = 98/2



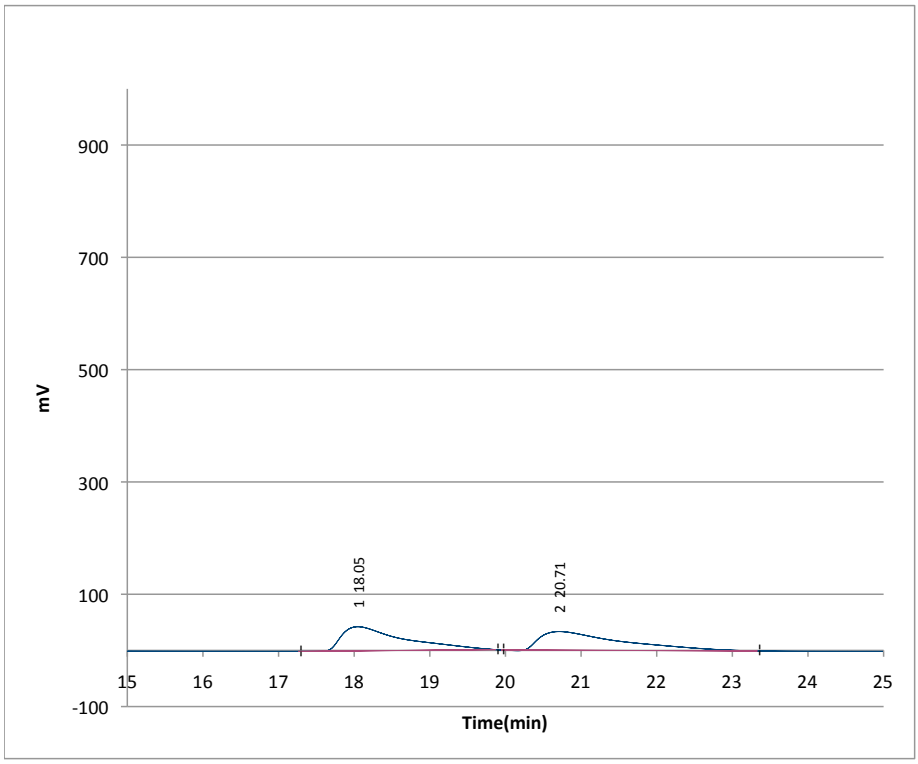
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	11.21	(S)-isomer	31129394	49.5465	871525	2229.3	3.214	1.883
2	13.3	(R)-isomer	31699305	50.4535	665461	1763.3	3.074	----



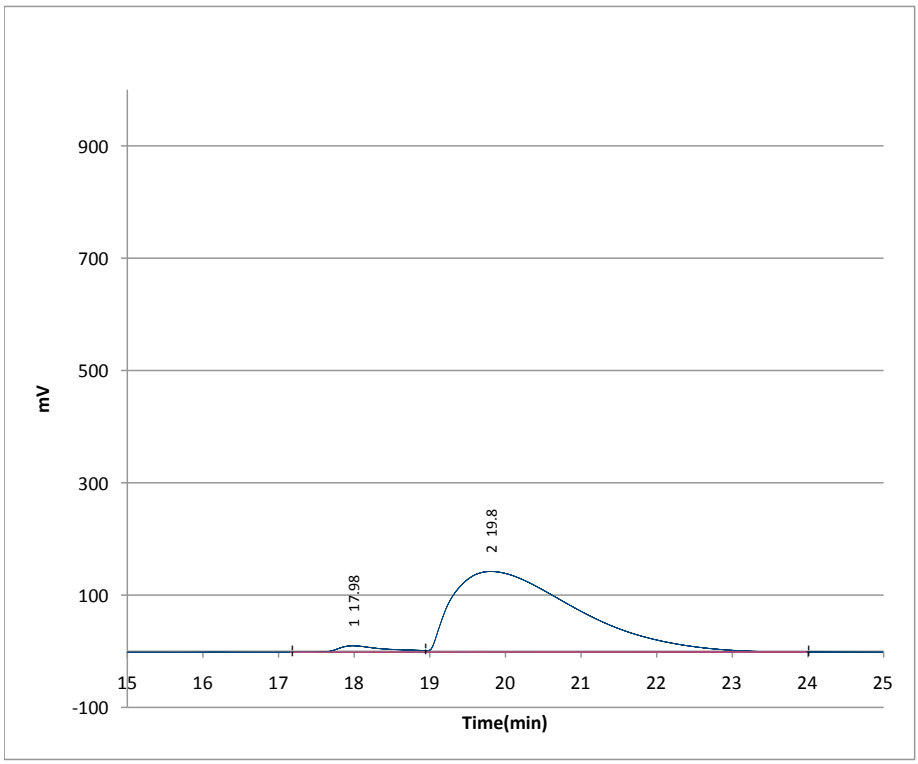
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	10.42		14153649	97.2822	613439	4344.2	2.63	3.887
2	12.58		395419.9	2.7178	22113	10876.2	1.256	----

(Table 4, entry 22)

Chiral Column: OD-H, 254 nm, 1.0 mL/min, Hex/*i*-PrOH = 98/2



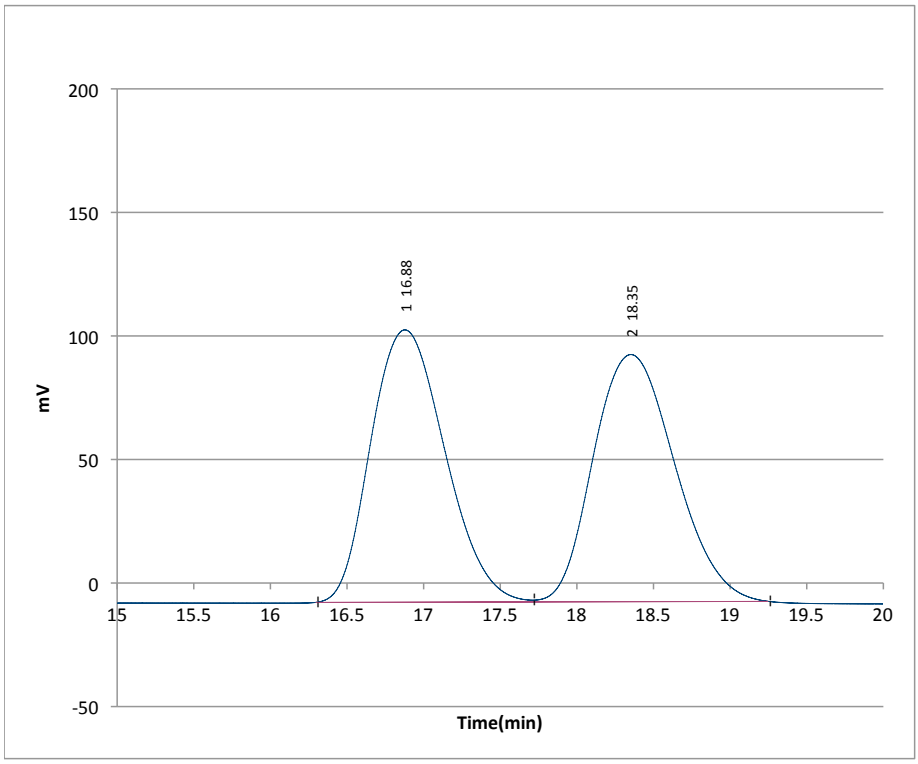
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	18.05	(*R*)-isomer	2446734	49.8297	43031	1720.3	2.685	1.348
2	20.71	(*S*)-isomer	2463456	50.1703	33233	1408	3.052	----



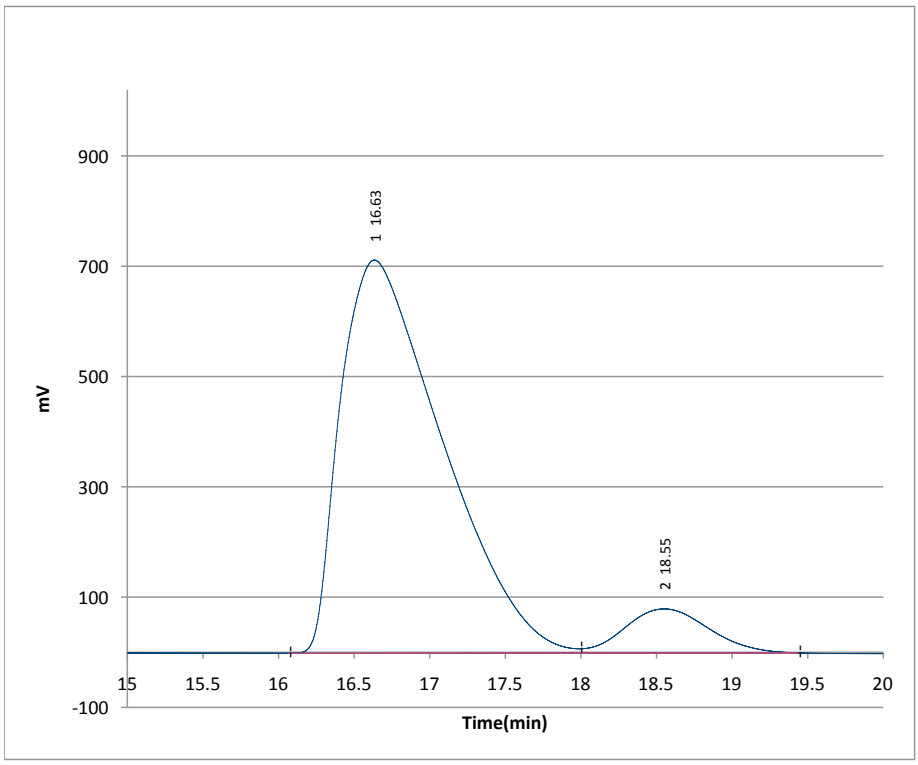
No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	17.98	(*R*)-isomer	498330.9	2.9411	11581	3949.3	----	0.871
2	19.8	(*S*)-isomer	16445253	97.0589	143785	678.1	2.329	----

(Table 4, entry 24)

Chiral Column: OD-H, 254 nm, 1.0 mL/min, Hex/*i*-PrOH = 95/5



No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	16.88	(*S*)-isomer	3698477	50.0614	110238	5723.6	1.198	1.577
2	18.35	(*R*)-isomer	3689403	49.9386	100041	5602.2	1.186	----



No.	Rt	Peak Name	Area	Area(%)	Height	NTP	Tf	Resolution
1	16.63	(*S*)-isomer	33299514	91.5274	712778	2867.3	1.879	1.69
2	18.55	(*R*)-isomer	3082498	8.4726	79978	5239.7	----	----