Supporting Information

An *N*-Heterocyclic Carbene Iridium Catalyst with Metal-Centered Chirality for Enantioselective Transfer Hydrogenation of Imines

Yanjun Li,[a] Meng Lei,[a] Wei Yuan,[a] Eric Meggers[a,b] and Lei Gong*[a]

[a]College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China

[b]Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, 35043 Marburg, Germany

Email: gongl@xmu.edu.cn

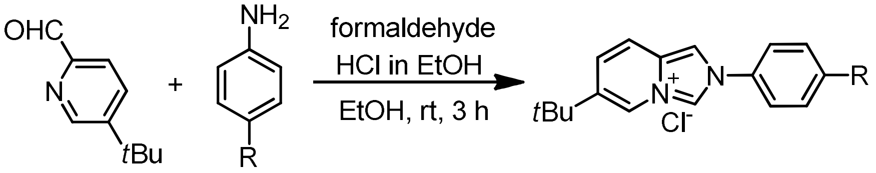
Contents

1. General Information

Synthesis of the iridium complexes were carried out under an atmosphere of argon with magnetic stirring. Catalytic reactions were performed in air. Solvents were distilled under argon from calcium hydride (CH_3CN and CH_2Cl_2) or sodium/benzophenone (THF). Iridium complexes **Δ-IrO**, **Δ-IrS**,[1] *N*-sulfonylamides **S1a-b**,[2] **S1d-i**,[3] and *N*-sulfonylimine substrates **4a-b**,[4] **4l-x**[5,6] were prepared according to published procedures. All other reagents were purchased from commercial suppliers (TCI, Adamas-beta®, Alfa and J&K) and used without further purification. Column chromatography was performed with silica gel from Huanghai Chemical Reagent (300–400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM (500 or 600 MHz) spectrometer at ambient temperature. NMR standards were used as follows: (^1H NMR) $CDCl_3$ = 7.26 ppm, (^1H NMR) CD_2Cl_2 = 5.32 ppm; (^{13}C NMR) $CDCl_3$ = 77.1 ppm, (^{13}C NMR) CD_2Cl_2 = 53.8 ppm. IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer. Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system. CD spectra were recorded on a JASCO J-810 CD spectropolarimeter (600–200 nm, 1 nm band width, 50 nm/min scanning speed). High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0T FT-MS instrument using ESI technique. Optical rotations were measured on an Anton Paar MCP 500 polarimeter at concentrations of 1.0 g/100 mL or 0.2 g/100 mL. Enantiomeric excess (ee) values of the products were determined by HPLC on chiral phase.

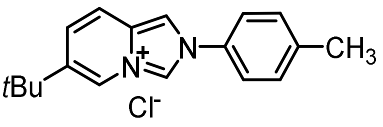
2. Synthesis of the Iridium Catalysts

2.1 Synthesis of the NHC Precursors L1a and L1b



L1a (R = Me), 99% yield
L1b (R = OMe), 99% yield

Scheme S1. Synthetic route to the NHC precursors.



L1a

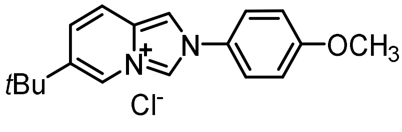
A solution of 5-(*tert*-butyl)picolinaldehyde (770 mg, 4.72 mmol), *p*-toluidine (506 mg, 4.72 mmol), formaldehyde (37% solution in water, 530 μL, 7.13 mmol), and HCl (2.0 M in EtOH, 2.36 mL, 4.72 mmol) in EtOH (8 mL) was stirred at room temperature for 3 h. The reaction mixture was concentrated and dried in *vacuo* to afford **L1a** as an white solid (1.41 g, 4.69 mmol, 99% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 12.13 (s, 1H), 9.32 (s, 1H), 7.76 (s, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 9.8 Hz, 1H), 7.40 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 9.7 Hz, 1H), 2.45 (s, 3H), 1.39 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 141.4, 141.0, 132.6, 131.38, 131.35, 129.4, 127.0, 122.2, 120.9, 116.2, 108.9, 34.4, 29.9, 21.3.

IR(film): ν (cm^{-1}) 3053, 2963, 2870, 1723, 1659, 1596, 1550, 1515, 1438, 1273, 1122, 1019, 820, 732, 543.

HRMS (ESI, m/z) calcd for $C_{18}H_{21}N_2$ (M-Cl)$^+$: 265.1699, found: 265.1695.



L1b

A solution of 5-(*tert*-butyl)picolinaldehyde (676 mg, 4.14 mmol), *p*-anisidine (510 mg, 4.14 mmol), formaldehyde (37% solution in water, 465 μL, 6.25 mmol), and HCl (2.0 M in EtOH, 2.07 mL, 4.14 mmol) in EtOH (6 mL) was stirred at room temperature for 3 h. The reaction mixture was then concentrated and dried in *vacuo* to afford **L1b** as an white solid (1.30g, 4.10 mmol, 99% yield).

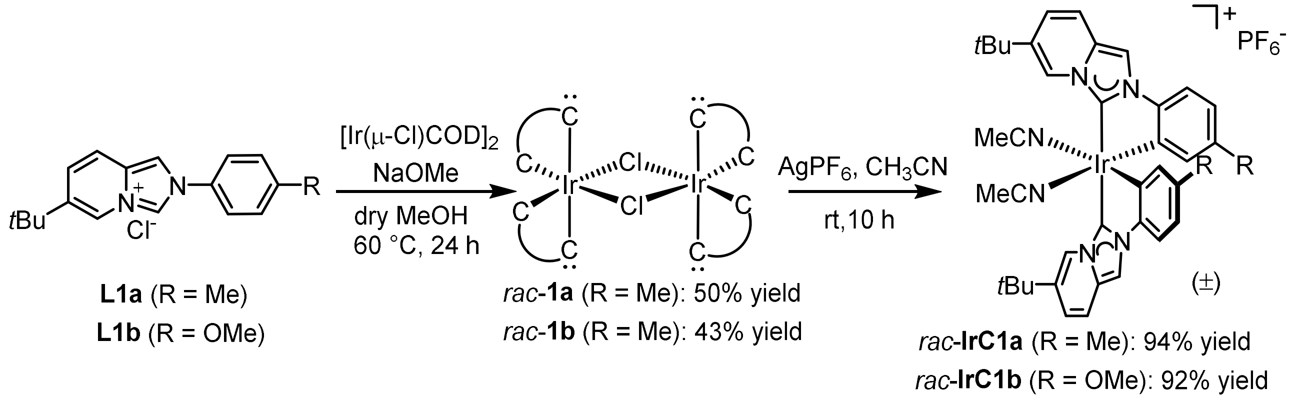
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 11.90 (d, J = 1.1 Hz, 1H), 9.15 (s, 1H), 7.87 (s, 1H), 7.78 (d, J = 9.0 Hz, 2H), 7.57 (d, J = 9.8 Hz, 1H), 7.30 (dd, J = 9.8, 1.3 Hz, 1H), 7.06 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 161.2, 141.0, 129.3, 127.8, 126.7, 123.8, 120.45, 120.4, 116.4, 115.8, 109.4, 55.9, 34.3, 29.9.

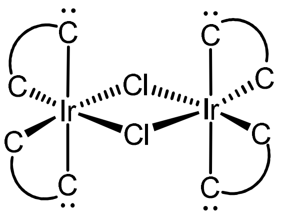
IR(film): ν (cm^{-1}) 3364, 3063, 2958, 2919, 2255, 1659, 1634, 1536, 1518, 1459, 1400, 1294, 1261, 1028, 841, 832, 819, 622, 528, 441.

HRMS (ESI, *m/z*) calcd for $C_{18}H_{21}N_2O$ (M-Cl)$^+$: 281.1648, found: 281.1649.

2.2 Synthesis of the Racemic Iridium NHC Catalysts *Rac*-IrC1a and *Rac*-IrC1b



Scheme S2. Synthetic route to the racemic iridium NHC catalysts *rac*-**IrC1a** and *rac*-**IrC1b**.

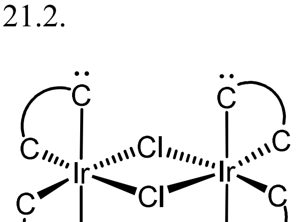


rac-**1a** $\mathrm{C}^\wedge\ddot{\mathrm{C}}$ = [**L1a**-HCl]

A mixture of [Ir(μ-Cl)(COD)]$_2$ (403 mg, 0.60 mmol) and NaOMe (270 mg, 5.00 mmol) in MeOH (20 mL) was stirred for 0.5 h at 60 °C under an argon atmosphere. The solution turned from orange to pale yellow, into which NHC precursor **L1a** (602 mg, 2.00 mmol) was added. After stirring at 60 °C for 24 h, the reaction mixture was concentrated in *vacuo*. The residue was subjected to flash chromatography on silica gel (CH$_2$Cl$_2$/*n*-hexane = 1:2) to afford *rac*-**1a** as a yellow solid (377 mg, 0.25 mmol, 50% yield).

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 9.13 (s, 4H), 7.57 (s, 4H), 7.07 (d, J = 9.3, 4.6 Hz, 4H), 6.91 (d, J = 7.8 Hz, 4H), 6.73 (dd, J = 9.8, 1.4 Hz, 4H), 6.44 (dd, J = 7.8, 1.0 Hz, 4H), 5.58 (d, J = 1.4 Hz, 4H), 1.80 (s, 12H), 1.02 (s, 36H).

^{13}C NMR (126 MHz, CDCl$_3$): δ (ppm) 167.4, 144.4, 138.0, 134.1, 134.2, 131.7, 129.6, 122.0, 121.9, 121.3, 116.1, 111.2, 104.2, 33.3, 30.0, 21.2.

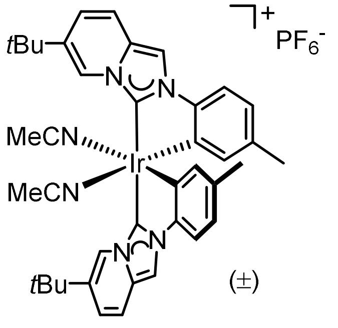


rac-**1b** $\mathrm{C}^\wedge\ddot{\mathrm{C}}$ = [**L1b**-HCl]

A mixture of [Ir(μ-Cl)(COD)]$_2$ (826 mg, 1.23 mmol) and NaOMe (443 mg, 8.20 mmol) in MeOH (40 mL) was stirred for 0.5 h at 60 °C under an argon atmosphere. The solution turned from orange to pale yellow, into which NHC precursor **L1b** (1300 mg, 4.10 mmol) was added. After stirring at 60 °C for 24 h, the reaction mixture was concentrated in *vacuo*. The residue was subjected to flash chromatography on silica gel (CH$_2$Cl$_2$/*n*-hexane = 1:2) to afford *rac*-**1b** as a yellow solid (693 mg, 0.44 mmol, 43% yield).

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) (s, 4H), 7.55 (d, J = 11.3 Hz, 4H), 7.07 (dd, J = 10.2, 0.7 Hz, 4H), 6.95 (d, J = 8.5 Hz, 4H), 6.72 (dd, J = 9.8, 1.4 Hz, 4H), 6.25 (dd, 4H), 5.28 (d, J = 2.6 Hz, 4H), 3.18 (s, 12H), 1.01 (s, 36H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 165.8, 156.8, 140.3, 134.3, 133.1, 129.6, 122.1, 121.9, 120.7, 116.1, 112.1, 107.1, 104.3, 54.6, 33.3, 29.9.



rac-**IrC1a**

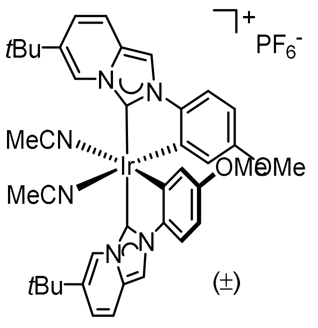
To a solution of dimeric complex *rac*-**1a** (340 mg, 0.23 mmol) in CH_3CN (20 mL) was added $AgPF_6$ (142 mg, 0.56 mmol). The mixture was stirred at room temperature for 10 h, then evaporated to dryness. The residue was subjected to column chromatograph on silica gel (CH_2Cl_2 to CH_2Cl_2/CH_3CN = 30:1) to afford *rac*-**IrC1a** as a pale brown solid (428 mg, 0.43 mmol, 94% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (s, 2H), 7.76 (s, 2H), 7.42 (d, J = 9.8 Hz, 2H), 7.13–7.05 (m, 4H), 6.66 (d, J = 7.1 Hz, 2H), 5.75 (s, 2H), 2.35 (s, 6H), 1.95 (s, 6H), 1.38 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 159.5, 144.3, 138.3, 137.0, 135.6, 129.9, 128.6, 123.20, 123.21 120.5, 125.6, 117.5, 112.1, 104.6, 33.6, 29.9, 21.3, 3.9.

IR (film): ν (cm^{-1}) 3156, 2961, 2872, 1651, 1587, 1475, 1404, 1369, 1331, 1263, 1095, 845, 802, 738, 675.

HRMS (ESI, *m*/*z*) calcd for $C_{40}H_{44}IrN_6$ $(M-PF_6)^+$: 801.3251, found: 801.3258.



rac-**IrC1b**

To a solution of *rac*-**1b** (400 mg, 0.25 mmol) in CH_3CN (15 mL) was added $AgPF_6$ (158 mg, 0.62 mmol). The mixture was stirred at room temperature for 10 h, then evaporated to dryness. The residue was subjected to column chromatograph on silica gel (CH_2Cl_2 to CH_2Cl_2/CH_3CN = 30:1) to afford *rac*-**IrC1b** as a pale brown solid (470 mg, 0.46 mmol, 92% yield).

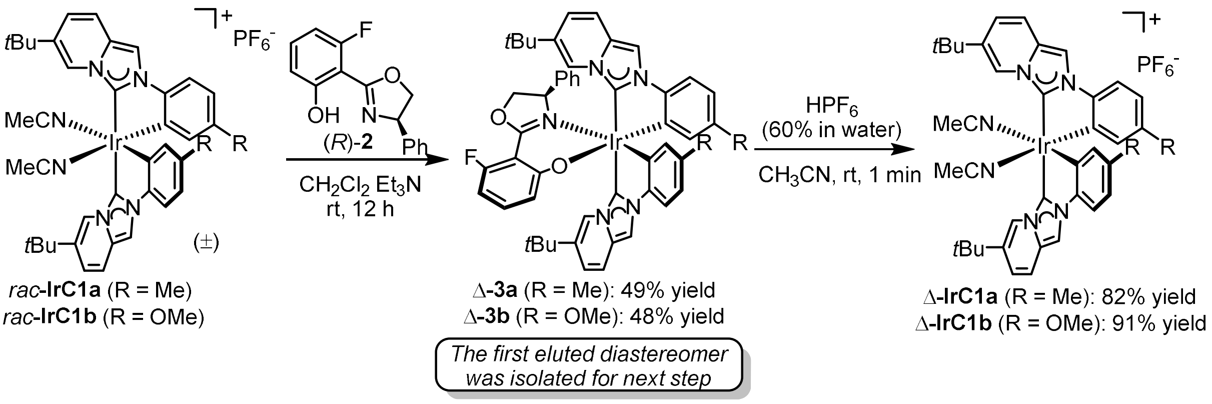
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (s, 2H), 7.71 (s, 2H), 7.38 (d, J = 9.1 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 7.05 (dd, J = 9.8, 1.2 Hz, 2H), 6.40 (dd, J = 8.5, 2.7 Hz, 2H), 5.53 (d, J = 2.6 Hz, 2H), 3.45 (s, 6H), 2.37 (s, 6H), 1.38 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 165.8, 156.8, 140.3, 134.3, 133.0, 129.6, 122.1, 121.8, 120.6, 116.1, 112.1, 107.1, 104.2, 100.1, 54.6, 33.30, 29.9, 3.8.

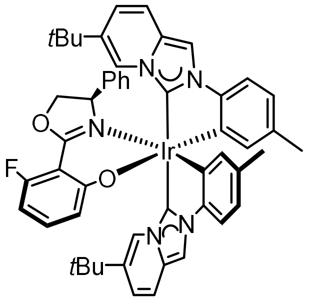
IR (film): ν (cm^{-1}) 3140, 2959, 2926, 1657, 1572, 1466, 1435, 1369, 1267, 1043, 845, 802, 558, 457.

HRMS (ESI, *m*/*z*) calcd for $C_{40}H_{44}IrN_6O_2$ $(M-PF_6)^+$: 833.3150, found: 833.3150.

2.3 Synthesis of the Nonracemic Iridium NHC Catalysts Δ-IrC1a and Δ-IrC1b



Scheme S3. Synthetic route to the nonracemic iridium NHC catalysts Δ-**IrC1a** and Δ-**IrC1b**.



Δ-3a

A solution of *rac*-**IrC1a** (220 mg, 0.22 mmol), Et_3N (224 mg, 2.20 mmol) and (*R*)-**2** (72.0 mg, 0.26 mmol) in CH_2Cl_2 (5 mL) was stirred for 12 h at room temperature, then evaporated to dryness. The produced two diastereomers were separated by preparative TLC (CH_2Cl_2/*n*-hexane = 5:2). The less polar fraction was collected as a yellow solid and identified to be **Δ-3a** (105 mg, 0.108 mmol, 49% yield), which was used for further synthesis of the nonracemic catalyst Δ-**IrC1a**.

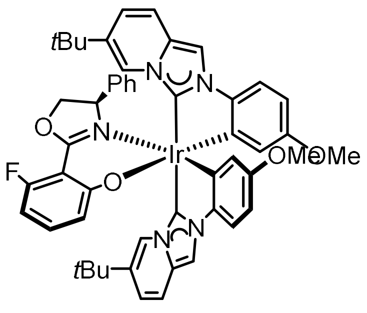
^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) 8.71 (s, 1H), 8.11 (s, 1H), 7.65 (s, 1H), 7.28 (d, *J* = 9.8 Hz, 1H), 7.06 (d, *J* = 2.7 Hz, 2H), 7.04 (d, *J* = 1.9 Hz, 1H), 6.96–6.84 (m, 5H), 6.61 (dd, *J* = 17.4, 7.7 Hz, 6H), 6.30 (d, *J* = 8.7 Hz, 1H), 6.21 (s, 1H), 5.94 (dd, *J* = 12.1, 7.9 Hz, 1H), 5.45 (s, 1H), 4.67 (t, *J* = 9.0 Hz, 1H), 4.62 (dd, *J* = 9.4, 3.5 Hz, 1H), 4.04 (dd, *J* = 8.4, 3.5 Hz, 1H), 2.04 (s, 3H), 1.92 (s, 3H), 1.40 (s, 9H), 1.28 (s, 9H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ (ppm) 176.4 (d, *J* = 3.4 Hz), 168.2, 164.95, 164.3, 162.2, 161.6 (d, *J* = 2.6 Hz), 145.9, 145.5, 140.7, 139.8, 139.0, 138.3, 136.1, 135.1 (d, *J* = 8.8 Hz), 134.8, 132.8, 132.7, 131.0, 129.6, 129.4, 128.2, 127.0, 122.1 (d, *J* = 2.3 Hz), 121.9, 121.7, 121.1, 120.3, 119.7 (d, *J* = 2.5 Hz), 117.8, 117.0, 112.3, 112.0, 104.9, 103.9, 102.6 (d, *J* = 7.4 Hz), 99.4, 99.2, 75.4, 70.0, 33.7, 33.5, 30.1, 29.9, 21.4, 21.3.

IR (film): ν (cm^{-1}) 3028, 2963, 2918, 2867, 1620, 1599, 1530, 1468, 1447, 1368, 1261, 1221, 1098, 1036, 794, 696, 615, 531.

HRMS (ESI, *m/z*) calcd for $C_{51}H_{49}FIrN_5NaO_2$ $(M+Na)^+$: 998.3392, found: 998.3394.

CD (CH_2Cl_2): λ, nm (Δε, $M^{-1}cm^{-1}$) 276 (+8), 256 (-3), 242 (+16), 218 (-29).



Δ-**3b**

A solution of *rac*-**IrC1b** (100 mg, 0.10 mmol), Et_3N (101 mg, 1.00 mmol) and (*R*)-**2** (33.0 mg, 0.12 mmol) in CH_2Cl_2 (2 mL) was stirred for 12 h at room temperature, then evaporated to dryness. The produced two diastereomers were separated by preparative TLC (CH_2Cl_2/*n*-hexane = 5:1). The less polar fraction was collected as yellow solid and identified to be Δ-**3b** (48.0 mg, 0.0476 mmol, 48% yield), which was used for further synthesis of the nonracemic catalyst Δ-**IrC1b**.

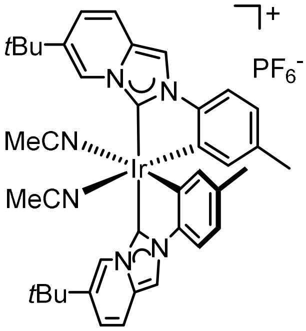
^1H NMR (500 MHz, CD_2Cl_2): δ (ppm) 8.70 (s, 1H), 8.11 (s, 1H), 7.62 (s, 1H), 7.28 (d, *J* = 9.7 Hz, 1H), 7.09–7.01 (m, 3H), 6.94–6.82 (m, 5H), 6.69 (s, 2H), 6.58–6.25 (m, 5H), 5.94 (dd, *J* = 12.2, 7.8 Hz, 1H), 5.87 (d, *J* = 2.6 Hz, 1H), 5.10 (d, *J* = 2.7 Hz, 1H), 4.70–4.62 (m, 2H), 4.04 (d, *J* = 5.4 Hz, 1H), 3.48 (s, 3H), 3.36 (s, 3H), 1.39 (s, 9H), 1.27 (s, 9H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ (ppm) 176.3, 166.9, 164.3, 164.0, 162.3, 161.6, 157.6, 157.2, 142.0, 141.6, 140.7, 140.0, 136.2, 135.3, 132.9 (d, *J* = 4.7 Hz), 132.8, 129.6, 129.5, 128.1, 127.0, 124.3, 123.2, 122.2 (d, *J* = 11.1 Hz), 121.8, 120.2, 119.7, 117.8, 116.9, 112.9, 112.6, 105.5, 104.9, 104.7, 103.9, 102.6 (d, *J* = 7.5 Hz), 99.5, 99.3, 75.4, 70.1, 54.92, 54.86, 33.7, 33.5, 30.15, 29.9.

IR (film): ν (cm^{-1}) 3077, 2962, 2926, 2855, 1621, 1597, 1567, 1530, 1447, 1409, 1367, 1261, 1221, 1098, 1037, 795, 736, 697, 434.

HRMS (ESI, *m/z*) calcd for $C_{51}H_{50}FIrN_5O_4$ $(M+H)^+$: 1008.3471, found: 1008.3479.

CD (CH_2Cl_2): λ, nm (Δε, $M^{-1}cm^{-1}$) 280 (+3), 261 (-1), 245 (+9), 217 (-16).



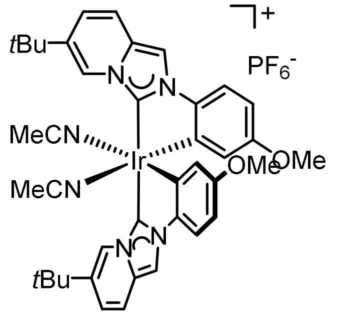
Δ-**IrC1a**

A solution of Δ-**3a** (75.0 mg, 0.077 mmol) and HPF_6 (60% in water, 18.0 µL, 0.085 mmol) in CH_3CN (4 mL) was stirred at room temperature for 1 min, then evaporated to dryness. The residue was subjected to silica gel chromatography (CH_2Cl_2/CH_3CN = 30:1) to afford Δ-**IrC1a** as a pale brown solid (62.0 mg, 0.063 mmol, 82% yield).

^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (s, 2H), 7.76 (s, 2H), 7.42 (d, *J* = 9.8 Hz, 2H), 7.12–7.05 (m, 4H), 6.67 (d, *J* = 7.0 Hz, 2H), 5.75 (s, 2H), 2.35 (s, 6H), 1.95 (s, 6H), 1.38 (s, 18H).

CD (CH_2Cl_2): λ, nm (Δε, $M^{-1}cm^{-1}$) 279 (+1), 268 (-9), 249 (+12), 225 (-64).

All other spectroscopic data of Δ-**IrC1a** were in agreement with the *rac*-**IrC1a**.



Δ-**IrC1b**

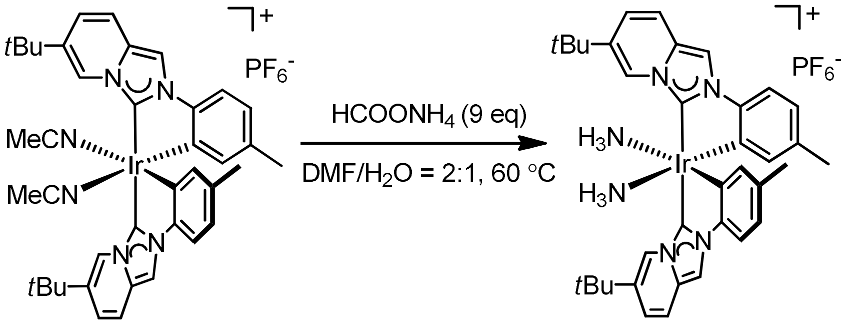
A solution of Δ-**3b** (43.0 mg, 0.043 mmol) and HPF_6 (60% in water, 10.0 μL, 0.047 mmol,) in CH_3CN (3 mL) was stirred at room temperature for 1 min, then evaporated to dryness. The residue was subjected to silica gel chromatography (CH_2Cl_2/CH_3CN = 30:1) to afford **Δ-IrC1b** as a pale brown solid (40.0 mg, 0.039 mmol, 91% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (s, 2H), 7.71 (s, 2H), 7.39 (d, J = 9.8 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 9.6 Hz, 2H), 6.40 (dd, J = 8.5, 2.6 Hz, 2H), 5.53 (d, J = 2.6 Hz, 2H), 3.45 (s, 6H), 2.36 (s, 6H), 1.38 (s, 18H).

CD (CH_2Cl_2): λ, nm (Δε, $M^{-1}cm^{-1}$) 383 (+1), 273 (-3), 257 (+21), 226 (-109).

All other spectroscopic data of **Δ-IrC1b** were in agreement with the *rac*-**IrC1b.**

2.4 Synthesis of the Bis-ammonia Complex Δ-6



Δ-**IrC1a** Δ-**6**

Scheme S4. Synthetic route to bis-ammonia complex Δ-**6**.

Compound Δ-6. A solution of HCO_2NH_4 (35.0 mg, 0.55 mmol) and **Δ-IrC1a** (60.0 mg, 0.060 mmol) in DMF/H_2O (200 μL/100 μL) was stirred at 60 °C for 3 h, cooled down to room temperature, then dried in high vacuum. The residue was washed with CH_2Cl_2/*n*-Hexane (1:10, v/v, 6 mL x 3), redissolved in CH_2Cl_2 (3 mL), washed with water (2 mL x 3), then dried over Na_2SO_4. The organic layers were combined and concentrated to dryness to afford Δ-**6** as a pale brown solid (21.0 mg, 0.020 mmol, 33% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.76 (s, 2H), 7.68 (s, 2H), 7.41 (d, J = 9.8 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 7.05 (dd, J = 9.8, 1.2 Hz, 2H), 6.64 (dd, J = 7.8, 1.0 Hz, 2H), 5.93 (d, J = 1.2 Hz, 2H), 2.74 (s, 6H), 1.98 (s, 6H), 1.35 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 162.1, 144.5, 139.0, 137.4, 136.0, 132.4, 130.1, 122.9, 122.7, 119.0, 118.0, 112.3, 105.1, 33.6, 29.7, 21.3.

IR (film): ν (cm^{-1}) 3373, 3291, 3158, 2961, 2869, 1664, 1620, 1584, 1471, 1399, 1367, 1329, 1261, 1196, 1092, 846, 801, 737, 558.

HRMS (ESI, m/z) calcd for $C_{36}H_{44}IrN_6$ $(M-PF_6)^+$: 753.3251, found: 753.3251.

2.5 CD Spectra of the Nonracemic Iridium complexes

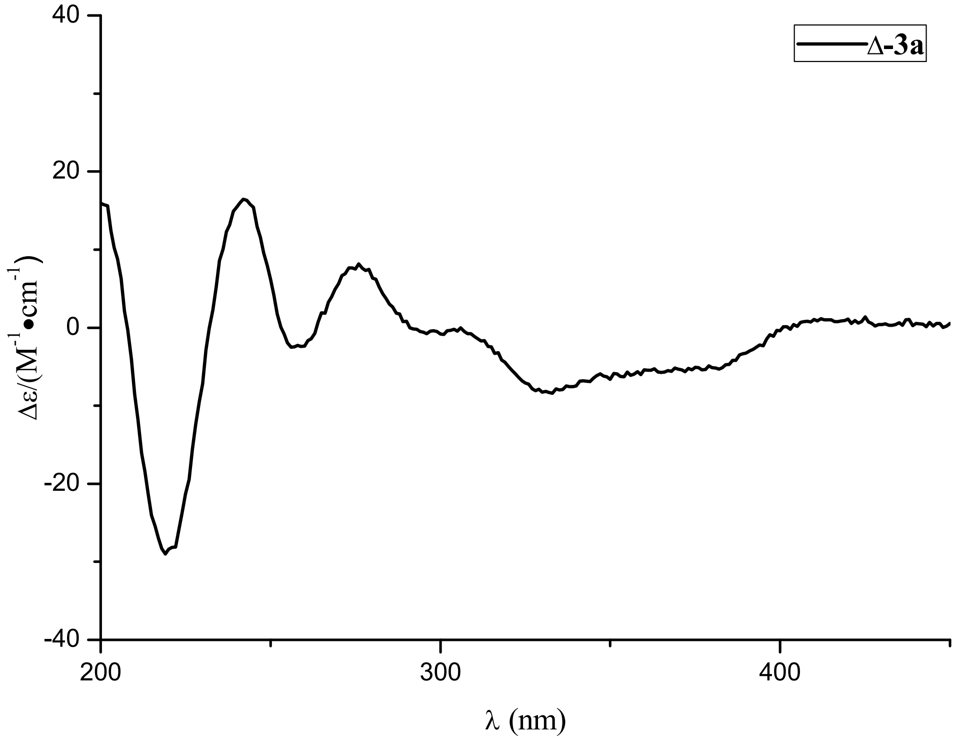


Figure S1. CD spectrum of compound **Δ-3a** recorded in MeOH (0.20 mM)

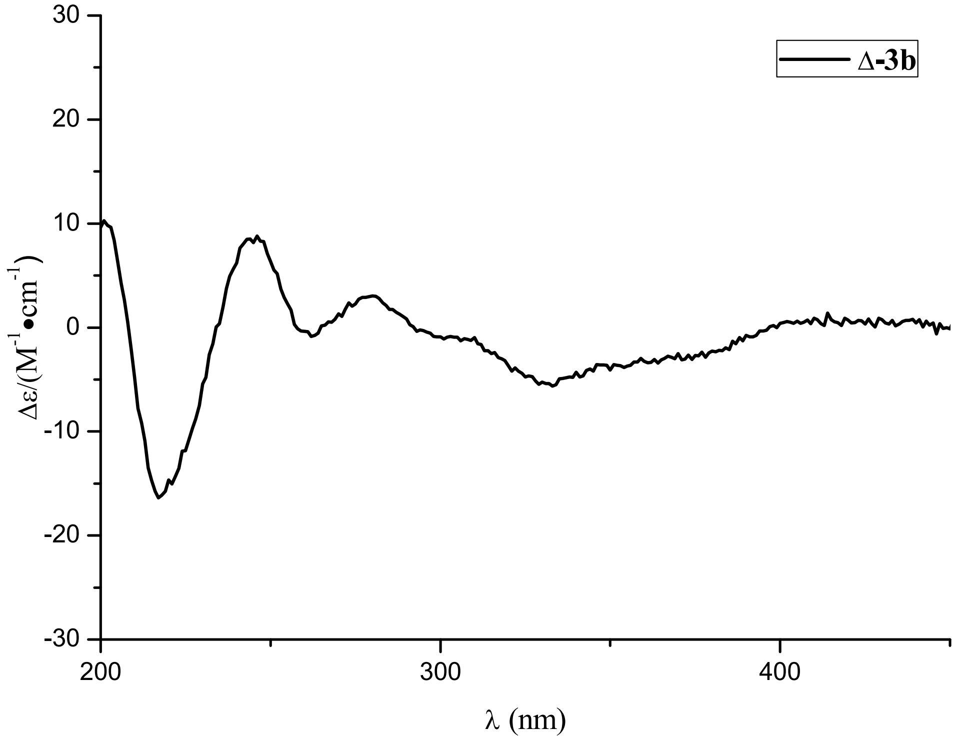


Figure S2. CD spectrum of complex **Δ-3b** recorded in MeOH (0.20 mM).

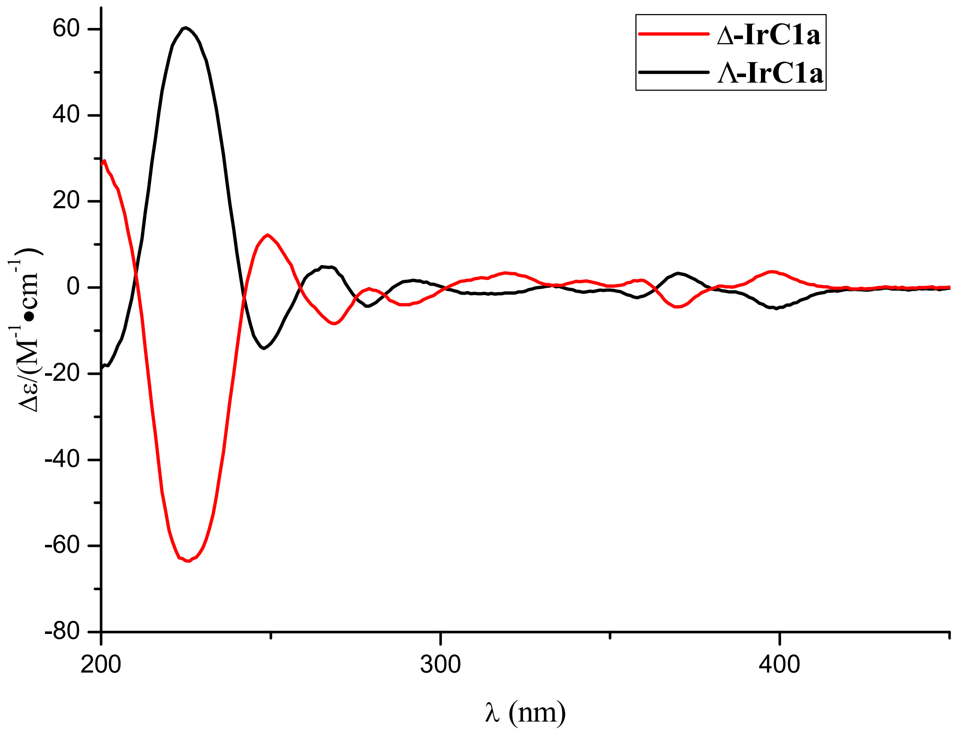


Figure S3. CD spectrum of compound Δ-**IrC1a** and Λ-**IrC1a** recorded in MeOH (0.20 mM)

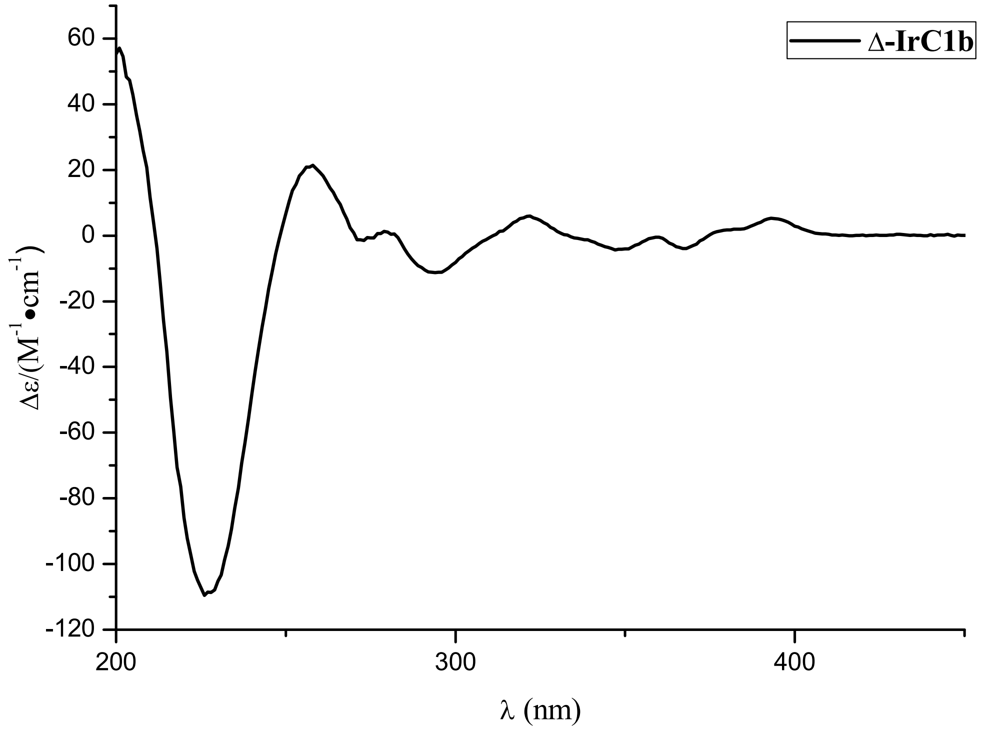


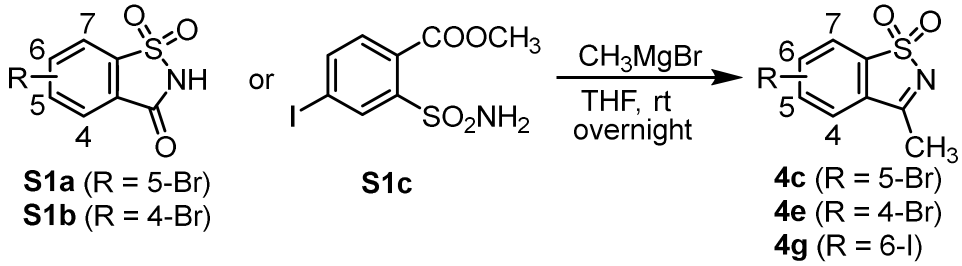
Figure S4. CD spectrum of complex Δ-**IrC1b** recorded in MeOH (0.20 mM).

3. Synthesis of the Substrates and Racemic Reference Products

3.1 Synthesis of the Substrates

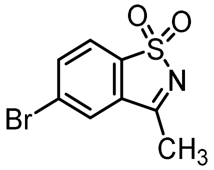
Cyclic *N*-sulfonylimines **4a-b**[4] and **4l-x**[5,6] were prepared according to published procedures, **4c-k** were synthesized by modified methods **A-C**.[7]

Method A



Scheme S5. Synthetic route to cyclic *N*-sulfonylimines **4c**, **4e** and **4g**.

General procedure. A solution of **S1a-c**[2] in THF (0.1 M) was treated with CH_3MgBr (3.0 eq, 3.0 M in THF) at 0 °C. The mixture was stirred at room temperature overnight, then quenched with water and extracted with EtOAc (100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford pure product **4c**, **4e** or **4g**.



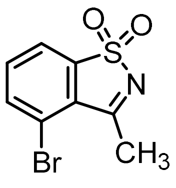
4c

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.88 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.81 (d, *J* = 1.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 2.66 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 172.0, 138.5, 136.4, 133.4, 128.7, 127.5, 123.6, 17.7.

IR (film): ν (cm^{-1}) 3419, 3087, 1611, 1551, 1377, 1325, 1284, 1171, 1145, 1065, 1022, 880, 832, 801, 706, 607, 558, 542.

HRMS (ESI, m/z) calcd for $C_8H_6BrNNaO_2S$ $(M+Na)^+$: 281.9195, found: 281.9197.



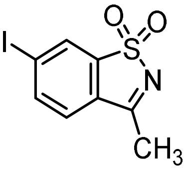
4e

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.89 (dd, *J* = 3.1, 0.8 Hz, 1H), 7.88–7.86 (m, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 2.92 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 172.6, 142.6, 139.6, 134.8, 130.12, 121.7, 120.5, 22.7.

IR (film): ν (cm^{-1}) 3437, 1958, 1633, 1591, 1572, 1548, 1438, 1405, 1325, 1173, 1017, 827, 777, 730, 597, 560, 532, 434.

HRMS (ESI, m/z) calcd for $C_8H_6BrNNaO_2S$ $(M+Na)^+$: 281.9195, found: 281.9197.



4g

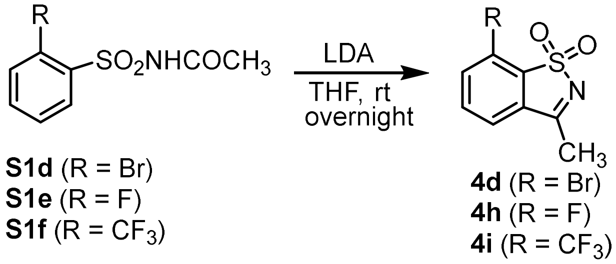
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.24 (d, *J* = 0.8 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 2.64 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 172.7, 143.1, 141.2, 131.6, 131.0, 125.1, 101.4, 17.6.

IR (film): ν (cm^{-1}) 3074, 2961, 2915, 2849, 1727, 1650, 1613, 1573, 1546, 1415, 1327, 1261, 1170, 1020, 802, 561.

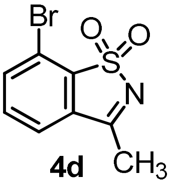
HRMS (ESI, m/z) calcd for $C_8H_6INNaO_2S$ $(M+Na)^+$: 329.9056, found: 329.9057.

Method B



Scheme S6. Synthetic route to cyclic *N*-sulfonylimines **4d**, **4h** and **4i**.

General procedure. To a solution of diisopropylamine (2.2 eq) in THF (0.1 M) at -78 °C was added dropwise *n*-BuLi (2.0 eq, 2.4 M in hexane). After stirring for 1.5 h at -78 °C, **S1d-f**[3] in THF (1.0 M) was added. The reaction was allowed to warm to room temperature slowly, then stirred overnight. The reaction was quenched with water and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford pure product **4d**, **4h** or **4i.**



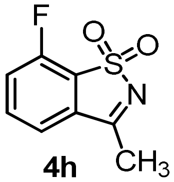
4d

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.86–7.81 (m, 1H), 7.60 (dt, *J* = 15.2, 4.1 Hz, 2H), 2.66 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 171.7, 139.5, 137.2, 135.3, 133.7, 122.8, 117.7, 17.6.

IR (film): ν (cm^{-1}) 3464, 3067, 1958, 1604, 1552, 1323, 831, 780, 721, 593, 556, 530, 483.

HRMS (ESI, m/z) calcd for $C_8H_6BrNNaO_2S$ $(M+Na)^+$: 281.9195, found: 281.9197.



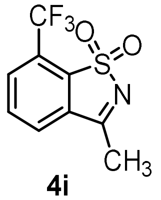
4h

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.76 (ddd, *J* = 8.2, 7.7, 4.6 Hz, 1H), 7.51–7.47 (m, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 2.67 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 172.1, 158.0, 155.9, 137.1 (d, J = 6.8 Hz), 134.6, 121.7 (d, J = 20.2 Hz), 120.0 (d, J = 3.6 Hz), 17.7.

IR (film): ν (cm^{-1}) 3083, 2923, 1959, 1572, 1471, 1441, 1417, 1332, 1290, 1177, 830, 560, 522.

HRMS (ESI, m/z) calcd for $C_8H_6FNNaO_2S$ $(M+Na)^+$: 221.9995, found: 221.9997.



4i

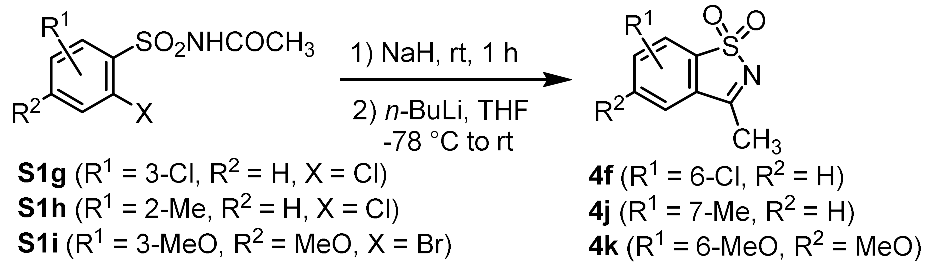
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.03–7.82 (m, 3H), 2.70 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 171.7, 137.3, 135.0, 133.0, 130.7 (q, J = 4.0 Hz), 127.5, 123.2, 121.1, 17.7.

IR (film): ν (cm^{-1}) 3436, 1575, 1421, 1343, 1285, 1219, 1172, 1131, 831, 737, 560, 533.

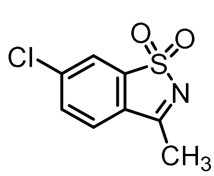
HRMS (ESI, m/z) calcd for $C_9H_6F_3NNaO_2S$ $(M+Na)^+$: 271.9964, found: 271.9964.

Method C



Scheme S7. Synthetic route to cyclic *N*-sulfonylimines **4f**, **4j** and **4k**.

General procedure. To a solution of NaH (2.0 eq, 60% dispersion in mineral oil) in THF (0.10 M) at room temperature 2-chlorobenzenesulfonamide **S1g-i**[3] in THF (1.0 M) was added dropwise. The reaction mixture was allowed to stir for 30 min at room temperature, then cooled to -78 °C. *n*-BuLi (1.5 eq, 2.4 M in hexane) was added dropwise over 10 min. The reaction mixture was stirred for 1 h at -78 °C, allowed to warm to 0 °C in an ice bath over a period of 1 h, and finally warmed to room temperature over 1 h. The reaction was quenched with water and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **4f**, **4j** or **4k**.



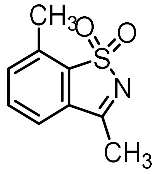
4f

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.85–7.81 (m, 1H), 7.71–7.65 (m, 2H), 2.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 171.1, 141.5, 135.0, 133.9, 131.5, 127.3, 120.1, 21.6.

IR (film): ν (cm^{-1}) 3270, 3066, 2960, 2920, 1721, 1592, 1575, 1552, 1446, 1372, 1332, 1265, 1174, 829, 800, 735, 595, 563, 487.

HRMS (ESI, m/z) calcd for $C_8H_6ClNNaO_2S$ $(M+Na)^+$: 220.0403, found: 220.0405.



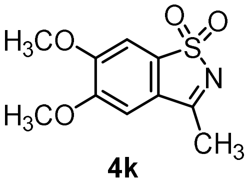
4j

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.59 (t, J = 7.6 Hz, 1H), 7.54–7.43 (m, 2H), 2.69 (s, 3H), 2.62 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$): δ (ppm) 173.5, 137.8, 135.6, 135.3, 134.0, 131.7, 121.6, 17.7, 17.3.

IR (film): ν (cm^{-1}) 2962, 2920, 2851, 1726, 1564, 1464, 1415, 1318, 1290, 1261, 1170, 1098, 1019, 830, 794, 611, 556, 538, 489.

HRMS (ESI, m/z) calcd for $C_9H_9NNaO_2S$ $(M+Na)^+$: 220.0403, found: 220.0405.



4k

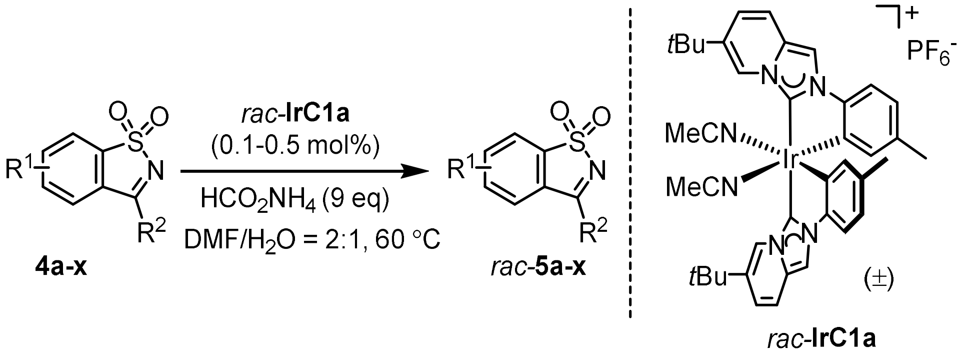
^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.36 (s, 1H), 7.01 (s, 1H), 4.00 (d, J = 4.1 Hz, 6H), 2.62 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$): δ (ppm) 173.2, 153.9, 153.5, 133.4, 124.8, 105.3, 104.8, 56.9, 56.7, 17.7.

IR (film): ν (cm^{-1}) 2961, 1958, 1611, 1576, 1537, 1502, 1459, 1406, 1310, 1257, 1155, 1015, 847, 792, 562.

HRMS (ESI, m/z) calcd for $C_{10}H_{11}NNaO_4S$ $(M+Na)^+$: 264.0301, found: 264.0306.

3.2 Synthesis of the Racemic Reference Products



Scheme S8. Synthesis of racemic reference compounds *rac*-**5a-x**.

General procedure for synthesis of the racemic reference products catalyzed by rac-IrC1a. A solution of cyclic *N*-sulfonylimines **4a-x** (0.10 mmol), HCO_2NH_4 (56.8 mg, 0.90 mmol) and *rac*-**IrC1a** (0.1–0.5 mol%) in DMF/H_2O (133 μL/67 μL) was stirred at 60 °C until it was complete, which was monitored by TLC analysis. Afterwards, the reaction mixture was dried in *vacuo* and purified by column chromatograph on silica gel (CH_2Cl_2 or EtOAc) to afford *rac*-**5a-x** as HPLC reference for the determination of enantiomeric excess.

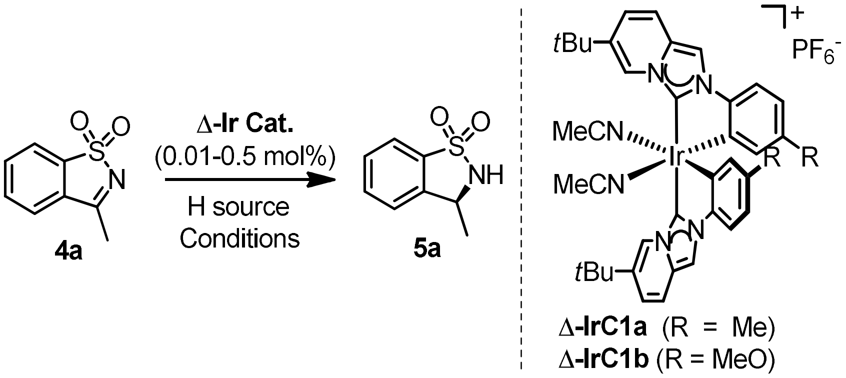
4. ATH of Cyclic *N*-Sulfonylimines by the Iridium Catalysts

4.1 Optimization of the Reaction Conditions

Note: For the low loading catalysis, all the catalysts were used as a freshly prepared stock solution.

Preparation of the stock solutions. A stock solution of Δ-**IrC1a** in DMF (2.5 mM): **Δ-IrC1a** (2.50 mg, 2.5 μmol) was dissolved in DMF (1000 μL); A stock solution of Δ-**IrC1a** in DMF (1.0 mM): **Δ-IrC1a** (2.50 mg, 2.5 μmol) was dissolved in DMF (2500 μL); A stock solution of Δ-**IrC1b** in DMF (2.5 mM): Δ-**IrC1b** (2.53 mg, 2.5 μmol) was dissolved in DMF (1000 μL); A stock solution of **Δ-IrO** in DMF (2.5 mM): **Δ-IrO**[1] (2.48 mg, 2.5 μmol) was dissolved in DMF (1000 μL); A stock solution of Δ-**IrS** in DMF (2.5 mM): **Δ-IrS**[1] (2.50 mg, 2.5 μmol) was dissolved in DMF (1000 μL); A stock solution of Δ-**6** in DMF (2.5 mM): Δ-**6** (2.25 mg, 2.5 μmol) was dissolved in DMF (1000 μL).

Table S1. Optimization of reaction conditions for the ATH reactions of cyclic *N*-sulfonylimine **4a**.



Entry	catalyst(mol%)	H source	conc. (M)	solvent	T (°C)	t (h)	conv. (%)	ee (%)
1	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	THF/H_2O (1:1)	50	6	64	93
2	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	*i*PrOH/H_2O(1:1)	50	6	55	97
3	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	DCE/H_2O (1:1)	50	6	86	86
4	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	CH_3CN/H_2O(1:1)	50	6	13	97
5	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	DMF/H_2O (1:1)	50	3.5	98	98
6	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	TFE/H_2O (1:1)	50	6	trace	n.d.
7	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	50	2.5	93	99
8	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	DMF/H_2O (4:1)	50	2.5	90	97
9	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	DMF/H_2O (6:1)	50	2.5	71	98
10	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	DMF/H_2O (8:1)	50	2.5	70	97
11	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	DMF	50	2.5	67	91
12	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	DMF/H_2O (1:2)	50	2.5	48	96
13	**Δ-IrC1a** (0.5)	HCO_2NH_4	0.5	DMF/H_2O (1:4)	50	2.5	9	n.d.
14	**Δ-IrC1a** (0.2)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	50	5	90	99
15	**Δ-IrC1a** (0.1)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	50	5	62	98
16	**Δ-IrC1a** (0.05)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	50	11	90	97
17	**Δ-IrC1a** (0.05)	HCO_2NH_4	1.0	DMF/H_2O (2:1)	50	2.5	93	97
18	**Δ-IrC1a** (0.05)	HCO_2NH_4	0.2	DMF/H_2O (2:1)	50	2.5	92	96
19	**Δ-IrC1a** (0.05)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	40	36	89	96
20	**Δ-IrC1a** (0.05)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	60	5	91	98
21	**Δ-IrC1a** (0.02)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	60	12	88	94

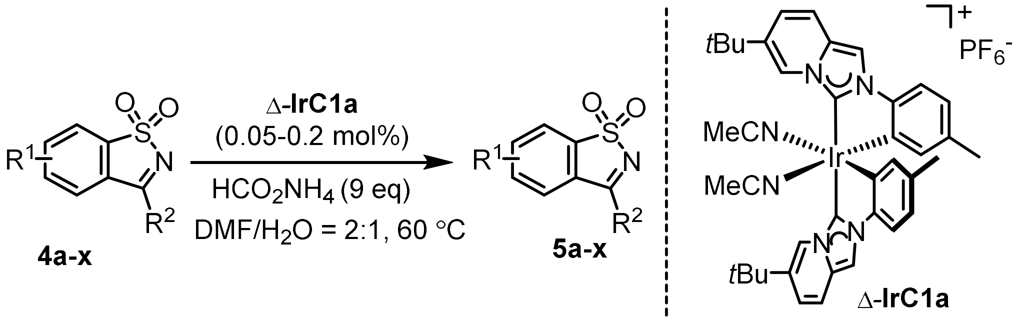
22	Δ-**IrC1a** (0.01)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	60	17	82	90
23	Δ-**IrC1b** (0.05)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	60	5	70	92
24	Δ-**IrO** (0.05)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	60	5	trace	n.d.
25	Δ-**IrS** (0.05)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	60	5	17	94
26	Δ-**IrC1a** (0.05)	HCO_2Na	0.5	DMF/H_2O (2:1)	60	5	12	15
27	Δ-**IrC1a** (0.05)	HCO_2H/Et_3N (5:2)	0.5	DMF/H_2O (2:1)	60	5	94	67
28	Δ-**6** (0.05)	HCO_2NH_4	0.5	DMF/H_2O (2:1)	60	5	98	94

General Procedure.

For entries 1-22: A solution of **4a** (18.1 mg, 0.10 mmol), HCO_2NH_4 (56.8 mg, 0.90 mmol), and Δ-**IrC1a** (0.01–0.5 mol%) in the indicated solvent was stirred at 40–60 °C for 2.5–36 h. The conversion was determined by ^{1}H NMR analysis of the crude product, and ee values were determined by chiral HPLC chromatography using a Daicel Chiralpak OD-H column.

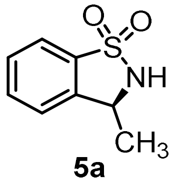
For entries 23-28: A solution of **4a** (18.1 mg, 0.10 mmol), the indicated hydrogen source (0.90 mmol), and indicated catalyst (0.050 μmol, 20 μL of a 2.5 mM stock solution of indicated catalyst in DMF) in DMF/H_2O (113 μL/67 μL) was stirred at 60 °C for 5 h. The conversion was determined by ^{1}H NMR analysis of the crude product, and ee values were determined by chiral HPLC chromatography using a Daicel Chiralpak OD-H column.

4.2 Substrate Scope



Scheme S9. Substrate scope of the ATH reaction of cyclic *N*-sulfonylimines catalyzed by Δ-**IrC1a**.

General Procedure. A solution of cyclic *N*-sulfonylimines **4a-x** (0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and Δ-**IrC1a** (0.05–0.2 mol%) in DMF/H_2O was stirred at 60 °C for indicated time until complete disappearance of the starting material, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2 or EtOAc) to afford product **5a-x**. Enantiomeric excess was established by HPLC analysis. Absolute configuration of the products were assigned as *S* by comparing their optical rotation with the literature.[6]



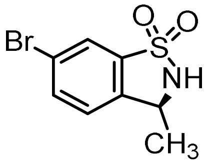
5a

A solution of cyclic *N*-sulfonylimine **4a** (36.2 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and Δ-**IrC1a** (0.10 μmol, 40 μL of a 2.5 mM stock solution of Δ-**IrC1a** in DMF) in DMF/H_2O (227 μL/133 μL) was stirred at 60 °C for 6 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5a** as a white solid (36.2 mg, 0.197 mmol, yield: 99%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-

H column, ee = 98% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 80:20, flow rate 0.7 mL/min, 30 °C, t_r(major) = 15.3 min, t_r(minor) = 19.6 min. $[\alpha]_D^{25}$ = -25.5° (*c* = 1.0, $CHCl_3$).

^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.77 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 4.83−4.75 (m, 1H), 4.68 (br, 1H), 1.62 (d, *J* = 6.5 Hz, 3H).

Other analytic data of **5a** are consistent with the literature.[6]

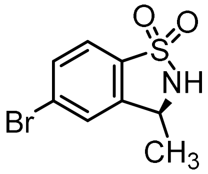


5b

A solution of cyclic *N*-sulfonylimine **4b** (52.0 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.10 µmol, 40 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (227 µL/133 µL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5b** as a white solid (51.4 mg, 0.196 mmol, yield: 98%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 0.7 mL/min, 30 °C, t_r(major) = 11.5 min, t_r(minor) = 14.3 min. $[\alpha]_D^{25}$ = -22.9° (*c* = 1.0, $CHCl_3$).

^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 1.2 Hz, 1H), 7.73 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 4.81–4.68 (m, 2H), 1.61 (d, *J* = 6.5 Hz, 3H).

Other analytic data of **5b** are consistent with the literature.[8]

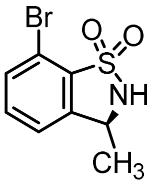


5c

A solution of cyclic *N*-sulfonylimine **4c** (52.0 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.10 µmol, 40 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (227 µL/133 µL) was stirred at 60 °C for 5 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5c** as a white solid (49.8 mg, 0.190 mmol, yield: 95%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 0.7 mL/min, 30 °C, t_r(major) = 13.3 min, t_r(minor) = 17.0 min. $[\alpha]_D^{25}$ = -26.6° (*c* = 0.2, $CHCl_3$).

^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.69–7.60 (m, 2H), 7.55 (s, 1H), 4.89–4.60 (m, 2H), 1.62 (d, *J* = 6.5 Hz, 3H).

Other analytic data of **5c** are consistent with the literature.[8]



5d

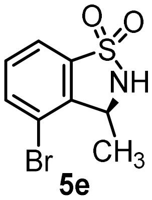
A solution of cyclic *N*-sulfonylimine **4d** (52.0 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.10 µmol, 40 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (227 µL/133 μL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5d** as a white solid (51.7 mg, 0.197 mmol, yield: 99%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 95% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate 0.8 mL/min, 30 °C, t_r(major) = 57.7 min, t_r(minor) = 64.5 min. $[\alpha]_D^{25}$ = -2.4° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.62 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 4.85 (s, 1H), 4.72 (dd, *J* = 13.2, 6.5 Hz, 1H), 1.61 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 144.8, 135.8, 134.4, 133.3, 122.9, 116.0, 52.1, 21.4.

IR (film): ν (cm^{-1}) 3240, 2989, 2962, 1958, 1588, 1454, 1392, 1321, 1262, 1163, 1089, 1027, 829, 744, 560, 526.

HRMS (ESI, m/z) calcd for $C_8H_8BrNNaO_2S$ $(M+Na)^+$: 283.9351, found: 283.9354.



5e

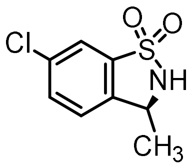
A solution of cyclic *N*-sulfonylimine **4e** (52.0 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.10 μmol, 40 μL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (227 μL/133 μL) was stirred at 60 °C for 5 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5e** as a white solid (48.8 mg, 0.186 mmol, yield: 93%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 94% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 0.8 mL/min, 30 °C, t_r(major) = 22.2 min, t_r(minor) = 25.4 min. $[\alpha]_D^{25}$ = -44.8° (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.74 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 5.10 (s, 1H), 4.73 (q, *J* = 6.7 Hz, 1H), 1.69 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 141.5, 137.6, 136.8, 131.1, 120.5, 119.3, 54.7, 20.4.

IR (film): ν (cm^{-1}) 3260, 3079, 2962, 2923, 2851, 1589, 1444, 1288, 1261, 1142, 1075, 1018, 793, 573, 535.

HRMS (ESI, m/z) calcd for $C_8H_8BrNNaO_2S$ $(M+Na)^+$: 283.9351, found: 283.9356.



5f

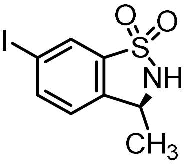
A solution of cyclic *N*-sulfonylimine **4f** (43.1 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.10 μmol, 40 μL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (227 μL/133 μL) was stirred at 60 °C for 4.5 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5f** as a white solid (41.8 mg, 0.192 mmol, yield: 96%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 95:5, flow rate 0.8 mL/min, 30 °C, t_r(major) = 35.8 min, t_r(minor) = 38.9 min. $[\alpha]_D^{25}$ = -35.9° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 4.92–4.76 (m, 2H), 1.71 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 139.5, 137.8, 133.7, 131.1, 130.8, 120.0, 53.4, 20.5.

IR (film): ν (cm^{-1}) 3533, 3264, 3081, 2962, 2927, 2854, 1721, 1574, 1446, 1372, 1293, 1262, 1168, 1148, 100, 809, 731, 661, 576, 557, 436.

HRMS (ESI, m/z) calcd for $C_8H_8ClNNaO_2S$ $(M+Na)^+$: 239.9856, found: 239.9860.



5g

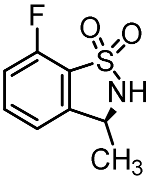
A solution of cyclic *N*-sulfonylimine **4g** (61.4 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.40 µmol, 160 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (107 µL/133 µL) was stirred at 60 °C for 5 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5g** as a white solid (50.7 mg, 0.164 mmol, yield: 82%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 80:20, flow rate 0.7 mL/min, 30 °C, t_r(major) = 13.0 min, t_r(minor) = 16.5 min. $[\alpha]_D^{25}$ = -16.3° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.07 (d, *J* = 1.1 Hz, 1H), 7.92 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 4.76–4.67 (m, 2H), 1.60 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 142.2, 141.4, 137.7, 130.2, 125.7, 93.7, 53.3, 21.3.

IR (film): ν (cm^{-1}) 3258, 2963, 2925, 2852, 1715, 1659, 1587, 1465, 1394, 1287, 1263, 1162, 1072, 1021, 823, 797, 591, 540, 503.

HRMS (ESI, m/z) calcd for $C_8H_8INNaO_2S$ $(M+Na)^+$: 331.9213, found: 331.9215.



5h

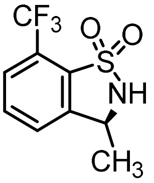
A solution of cyclic *N*-sulfonylimine **4h** (39.8 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.10 µmol, 40 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (227 µL/133 µL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5h** as a white solid (38.6 mg, 0.192 mmol, yield: 96%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 95% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate 0.8 mL/min, 30 °C, t_r(major) = 25.7 min, t_r(minor) = 30.1 min. $[\alpha]_D^{25}$ = -16.9° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.61 (td, *J* = 8.0, 4.9 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 2H), 4.86 (s, 1H), 4.82–4.75 (m, 1H), 1.63 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 157.3, 155.3, 145.5, 135.9 (d, *J* = 7.2 Hz), 119.6 (d, *J* = 4.1 Hz), 116.1 (d, *J* = 18.7 Hz), 53.5, 21.3.

IR (film): ν (cm^{-1}) 3263, 2959, 2925, 2854, 1611, 1590, 1466, 1377, 1261, 1160, 1097, 1021, 798, 525.

HRMS (ESI, m/z) calcd for $C_8H_8FNNaO_2S$ $(M+Na)^+$: 224.0152, found: 224.0152.



5i

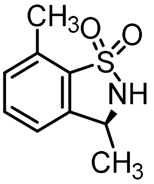
A solution of cyclic *N*-sulfonylimine **4i** (49.8 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.10 µmol, 40 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (227 µL/133 µL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5i** as a white solid (47.7 mg, 0.190 mmol, yield: 95%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 94% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 90:10, flow rate 0.8 mL/min, 30 °C, t_r(major) = 8.8 min, t_r(minor) = 10.1 min. $[\alpha]_D^{25}$ = -15.1° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.79–7.71 (m, 2H), 7.64–7.57 (m, 1H), 4.89 (s, 1H), 4.77 (p, *J* = 6.6 Hz, 1H), 1.66 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 143.8, 132.4, 126.8, 125.8 (d, *J* = 4.8 Hz), 124.8, 122.4, 120.3, 51.7, 19.8.

IR (film): ν (cm^{-1}) 3244, 2915, 1602, 1439, 1395, 1260, 1058, 1018, 796, 713, 671, 636, 562, 516, 474.

HRMS (ESI, m/z) calcd for $C_9H_8F_3NNaO_2S$ $(M+Na)^+$: 274.0120, found: 274.0120.



5j

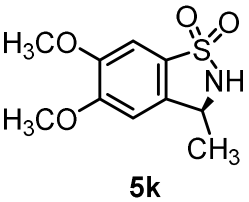
A solution of cyclic *N*-sulfonylimine **4j** (39.1 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.10 µmol, 40 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (227 µL/133 µL) was stirred at 60 °C for 6 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5j** as a white solid (38.7 mg, 0.196 mmol, yield: 98%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: AD-H, 220 nm, *n*-hexane/isopropanol = 92:8, flow rate 0.8 mL/min, 30 °C, t_r(major) = 22.4 min, t_r(minor) = 25.2 min. $[\alpha]_D^{25}$ = -15.9 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.49 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 4.82–4.68 (m, 2H), 2.63 (s, 3H), 1.59 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 142.0, 134.3, 134.1, 133.3, 130.7, 121.2, 52.9, 21.7, 17.0.

IR (film): ν (cm^{-1}) 3251, 2963, 2925, 1601, 1473, 1373, 1261, 1155, 1102, 829, 798, 763, 560.

HRMS (ESI, m/z) calcd for $C_9H_{11}NNaO_2S$ $(M+Na)^+$: 220.0403, found: 220.0405.



5k

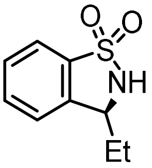
A solution of cyclic *N*-sulfonylimine **4k** (48.3 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.10 µmol, 40 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (227 µL/133 μL) was stirred at 60 °C for 7.5 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5k** as a white solid (47.7 mg, 0.196 mmol, yield: 98%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254nm, *n*-hexane/isopropanol = 80:20, flow rate 0.7 mL/min, 30 °C, t_r(major) = 23.1 min, t_r(minor) = 30.6 min. $[\alpha]_D^{25}$ = -15.3° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.17 (s, 1H), 6.73 (s, 1H), 4.76–4.66 (m, 1H), 4.58 (s, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 1.60 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 153.9, 150.5, 135.0, 127.1, 105.0, 102.5, 56.45, 56.47, 53.2, 21.9.

IR (film): ν (cm^{-1}) 3298, 2962, 2918, 2849, 1593, 1502, 1410, 1375, 1262, 1178, 1052, 800, 515, 493.

HRMS (ESI, m/z) calcd for $C_{10}H_{13}NNaO_4S$ $(M+Na)^+$: 266.0457, found: 266.0461.

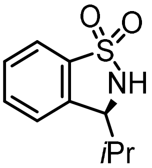


5l

A solution of cyclic *N*-sulfonylimine **4l** (39.1 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.10 μmol, 40 μL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (227 μL/133 μL) was stirred at 60 °C for 7 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5l** as a white solid (39.1 mg, 0.198 mmol, yield: 99%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 0.8 mL/min, 30 °C, t_r(major) = 11.8 min, t_r(minor) = 19.7 min. $[\alpha]_D^{25}$ = -46.7° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.78 (d, *J* = 7.8 Hz, 1H), 7.63 (td, *J* = 7.7, 1.0 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 4.75–4.62 (m, 2H), 2.01–2.12 (m, 1H), 1.88–1.77 (m, 1H), 1.04 (t, *J* = 7.4 Hz, 3H).

Other analytic data of **5l** are consistent with the literature.[9]

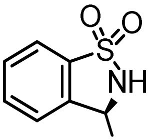


5m

A solution of cyclic *N*-sulfonylimine **4m** (41.9 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.40 μmol, 160 μL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (107 μL/133 μL) was stirred at 60 °C for 8 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5m** as a white solid (41.8 mg, 0.198 mmol, yield: 99%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 94% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 0.8 mL/min, 30 °C, t_r(major) = 9.7 min, t_r(minor) = 23.4 min. $[\alpha]_D^{25}$ = -61.9° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.79 (d, *J* = 7.8 Hz, 1H), 7.63 (td, *J* = 7.7, 0.9 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 4.71–4.66 (m, 1H), 4.62 (s, 1H), 2.36–2.22 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H).

Other analytic data of **5m** are consistent with the literature.[9]

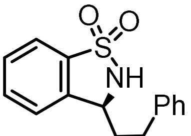


5n

A solution of cyclic *N*-sulfonylimine **4n** (44.7 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.40 µmol, 160 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (107 µL/133 µL) was stirred at 60 °C for 3 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5n** as a white solid (44.6 mg, 0.198 mmol, yield: 99%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 0.8 mL/min, 30 °C, t_r(major) = 9.5 min, t_r(minor) = 17.7 min. $[\alpha]_D^{25}$ = -46.3° (*c* = 1.0, $CHCl_3$).

^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.71 (d, *J* = 7.8 Hz, 1H), 7.59–7.51 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 4.62–4.72 (m, 2H), 2.02–1.86 (m, 1H), 1.93–2.09 (m, 1H), 1.73–1.82 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H).

Other analytic data of **5n** are consistent with the literature.[7]

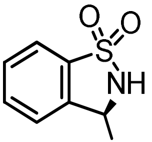


5o

A solution of cyclic *N*-sulfonylimine **4o** (54.7 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.40 µmol, 160 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (107 µL/133 µL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5o** as a white solid (53.6 mg, 0.196 mmol, yield: 98%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 80:20, flow rate 0.7 mL/min, 30 °C, t_r(major) = 24.8 min, t_r(minor) = 45.9 min. $[\alpha]_D^{20}$ = -33.0° (*c* = 1.0, $CHCl_3$).

^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.80–7.75 (m, 1H), 7.61 (td, *J* = 7.6, 1.1 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.33–7.28 (m, 2H), 7.24–7.18 (m, 3H), 4.82 (s, 1H), 4.73–4.65 (m, 1H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.34–2.24 (m, 1H), 2.15–2.05 (m, 1H).

Other analytic data of **5o** are consistent with the literature.[5d]

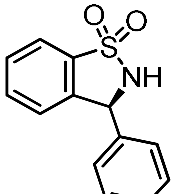


5p

A solution of cyclic *N*-sulfonylimine **4p** (33.2 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.40 µmol, 160 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (107 µL/133 µL) was stirred at 60 °C for 9 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5p** as a white solid (33.0 mg, 0.196 mmol, yield: 98%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 0.7 mL/min, 30 °C, t_r(major) = 11.2 min, t_r(minor) = 33.0 min. $[\alpha]_D^{25}$ = -48.6° (*c* = 1.0, $CHCl_3$).

^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.78 (d, *J* = 7.8 Hz, 1H), 7.65–7.60 (m, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 4.63 (br, 2H), 1.93–1.65 (m, 2H), 1.28–1.12 (m, 6H).

Other analytic data of **5p** are consistent with the literature.[9]

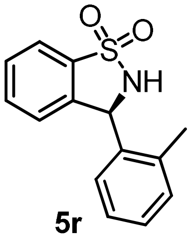


5q

A solution of cyclic *N*-sulfonylimine **4q** (48.7 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and Δ-**IrC1a** (0.40 µmol, 160 µL of a 2.5 mM stock solution of Δ-**IrC1a** in DMF) in DMF/H_2O (107 µL/133 µL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5q** as a white solid (47.6 mg, 0.194 mmol, yield: 97%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 30 °C, t_r(major) = 16.5 min, t_r(minor) = 18.6 min. $[\alpha]_D^{25}$ = 84.8° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.86–7.82 (m, 1H), 7.59–7.51 (m, 2H), 7.44–7.35 (m, 5H), 7.16–7.13 (m, 1H), 5.72 (d, *J* = 3.8 Hz, 1H), 4.89 (br, 1H).

Other analytic data of **5q** are consistent with the literature.[6]

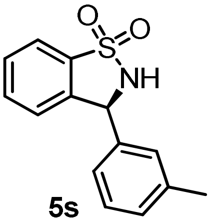


5r

A solution of cyclic *N*-sulfonylimine **4r** (51.5 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and Δ-**IrC1a** (0.40 µmol, 160 µL of a 2.5 mM stock solution of Δ-**IrC1a** in DMF) in DMF/H_2O (107 µL/133 µL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5r** as a white solid (50.3 mg, 0.194 mmol, yield: 97%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 30 °C, t_r(major) = 12.7 min, t_r(minor) = 15.1 min. $[\alpha]_D^{25}$ = 7.9° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.88–7.84 (m, 1H), 7.61–7.54 (m, 2H), 7.30–7.26 (m, 1H), 7.22–7.16 (m, 1H), 7.15–7.09 (m, 2H), 6.00 (d, *J* = 4.4 Hz, 1H), 4.70 (br, 1H), 2.46 (s, 3H).

Other analytic data of **5r** are consistent with the literature.[6]

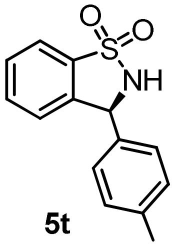


5s

A solution of cyclic *N*-sulfonylimine **4s** (51.5 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and Δ-**IrC1a** (0.40 µmol, 160 µL of a 2.5 mM stock solution of Δ-**IrC1a** in DMF) in DMF/H_2O (107 µL/133 µL) was stirred at 60 °C for 3 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5s** as a white solid (49.3 mg, 0.190 mmol, yield: 95%). Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 97% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 0.8 mL/min, 30 °C, t_r(minor) = 25.2 min, t_r(major) = 29.6 min. $[\alpha]_D^{25}$ = 77.7° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.89–7.80 (m, 1H), 7.59–7.51 (m, 2H), 7.33–7.27 (m, 1H), 7.22–7.10 (m, 4H), 5.68 (d, *J* = 4.0 Hz, 1H), 4.81 (br, 1H), 2.35 (s, 3H).

Other analytic data of **5s** are consistent with the literature.[6]

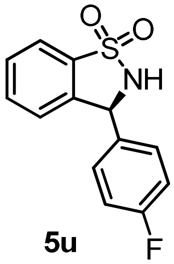


5t

A solution of cyclic *N*-sulfonylimine **4t** (51.5 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.40 μmol, 160 μL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (107 μL/133 μL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5t** as a white solid (50.4 mg, 0.194 mmol, yield: 97%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 30 °C, t_r(minor) = 19.7 min, t_r(major) = 24.5 min. $[\alpha]_D^{25}$ = 68.5° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.85–7.81 (m, 1H), 7.58–7.51 (m, 2H), 7.26–7.22 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.15–7.11 (m, 1H), 5.68 (d, *J* = 4.1 Hz, 1H), 4.84 (br, 1H), 2.36 (s, 3H).

Other analytic data of **5t** are consistent with the literature.[6]

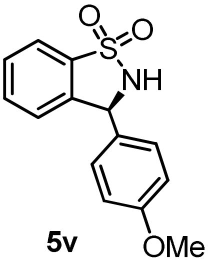


5u

A solution of cyclic *N*-sulfonylimine **4u** (52.3 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.40 μmol, 160 μL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (107 μL/133 μL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5u** as a white solid (51.6 mg, 0.196 mmol, yield: 97%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 30 °C, t_r(major) = 11.4 min, t_r(minor) = 17.6 min. $[\alpha]_D^{25}$ = 87.9° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.87–7.82 (m, 1H), 7.62–7.51 (m, 2H), 7.39–7.32 (m, 2H), 7.17–7.03 (m, 3H), 5.72 (d, *J* = 4.2 Hz, 1H), 4.93 (br, 1H).

Other analytic data of **5u** are consistent with the literature.[6]

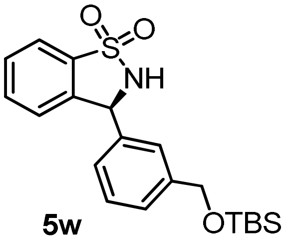


5v

A solution of cyclic *N*-sulfonylimine **4v** (54.7 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.40 µmol, 160 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (107 µL/133 µL) was stirred at 60 °C for 3 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **5v** as a white solid (53.4 mg, 0.194 mmol, yield: 97%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 30 °C, t_r(major) = 22.1 min, t_r(minor) = 30.9 min. $[\alpha]_D^{25}$ = 56.5° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.86–7.81 (m, 1H), 7.60–7.51 (m, 2H), 7.29–7.26 (m, 1H), 7.26–7.24 (m, 1H), 7.16–7.11 (m, 1H), 6.95–6.86 (m, 2H), 5.68 (d, *J* = 4.0 Hz, 1H), 4.79 (d, *J* = 3.3 Hz, 1H), 3.81 (s, 3H).

Other analytic data of **5v** are consistent with the literature.[5d]

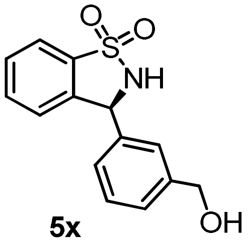


5w

A solution of cyclic *N*-sulfonylimine **4w** (77.8 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.40 µmol, 160 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (107 µL/133 µL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (EtOAc) to afford product **5w** as a white solid (77.2 mg, 0.198 mmol, yield: 99%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 30 °C, t_r(major) = 7.3 min, t_r(minor) = 8.2 min. $[\alpha]_D^{25}$ = 60.6° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.86–7.81 (m, 1H), 7.57–7.53 (m, 2H), 7.40–7.29 (m, 3H), 7.25–7.22 (m, 1H), 7.16–7.09 (m, 1H), 5.72 (d, *J* = 4.1 Hz, 1H), 4.88 (d, *J* = 3.9 Hz, 1H), 4.73 (s, 2H), 0.91 (s, 9H), 0.08 (s, 6H).

Other analytic data of **5w** are consistent with the literature.[6]



5x

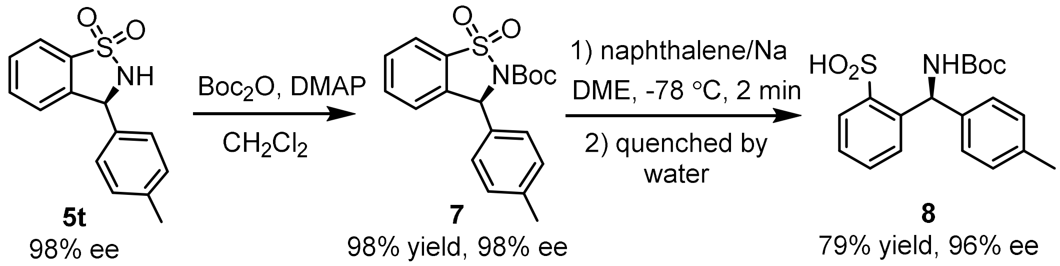
A solution of cyclic *N*-sulfonylimine **4x** (54.7 mg, 0.20 mmol), HCO_2NH_4 (113.5 mg, 1.80 mmol), and **Δ-IrC1a** (0.40 µmol, 160 µL of a 2.5 mM stock solution of **Δ-IrC1a** in DMF) in DMF/H_2O (107 µL/133 µL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (EtOAc) to afford product **5x** as a white solid (54.0 mg, 0.196 mmol, yield: 98%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 30 °C, t_r(major) = 16.3 min, t_r(minor) = 26.4 min. $[\alpha]_D^{25}$ = 84.0° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.87–7.81 (m, 1H), 7.60–7.51 (m, 2H), 7.43–7.35 (m, 3H), 7.32–7.28 (m, 1H), 7.18–7.12 (m, 1H), 5.73 (s, 1H), 4.92 (br, 1H), 4.71 (s, 2H), 1.80 (br, 1H).

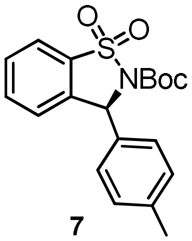
Other analytic data of **5x** are consistent with the literature.[6]

5. Synthetic Utility of the Method

5.1 Conversion to the Chiral Diarylmethylamine 8



Scheme S10. Preparation of the chiral diaryl amine **8**.



7

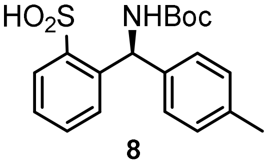
A solution of **5t** (100 mg, 0.39 mmol, 98% ee), 4-dimethylaminopyridine (9.4 mg, 0.077 mmol) in CH_2Cl_2 (4 mL) was added di-*tert*-butyl dicarbonate (Boc_2O, 168 mg, 0.77 mmol) at room temperature. The mixture was stirred for 5 h. The solvent was removed under reduced pressure and the residue was was purified by flash chromatography on silica gel (CH_2Cl_2) to afford product **7** as a white solid (137 mg, 0.381 mmol, yield: 98%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 30 °C, t_r(major) = 5.8 min, t_r(minor) = 6.3 min. $[\alpha]_D^{25}$ = 145.4° (*c* = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) 7.81 (dd, *J* = 9.0, 7.6 Hz, 1H), 7.62–7.53 (m, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 3H), 6.01 (s, 1H), 2.34 (s, 3H), 1.43 (s, 9H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ (ppm) 149.4, 138.9, 136.7, 135.9, 134.3, 133.6, 130.1, 130.0, 127.0, 125.8, 121.6, 84.9, 63.4, 28.1, 21.2.

IR (film): ν (cm^{-1}) 3077, 2979, 2922, 1723, 1587, 1488, 1329, 1195, 1181, 1021, 838, 702, 564.

HRMS (ESI, m/z) calcd for $C_{19}H_{21}NNaO_4S$ $(M+Na)^+$: 382.1083, found: 382.1091.



8

To a solution of **7** (75 mg, 0.21 mmol) in dimethoxyethane (DME, 4 mL) at -78 °C was added dropwise Sodium naphthalide (0.5 M in DME, 4.2 mL, 2.1 mmol). After stirring for 2 min at -78 °C, the reaction was diluted with CH_2Cl_2 (5 mL), then quenched with water (0.5 mL). The organic solvents were collected and evaporated. The residue was purified by flash chromatography on silica gel (CH_2Cl_2/MeOH = 30/1 to 10/1) to give the product **8** as a white solid (59.8 mg, 0.165 mmol, yield: 79%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 96% (HPLC: IC, 220 nm, 0.1% TFA/CH_3CN = 50:50, flow rate 0.5 mL/min, 30 °C, t_r(minor) = 9.7 min, t_r(major) = 11.5 min. $[\alpha]_D^{25}$ = -44.6° (*c* = 1.0, $CHCl_3$).

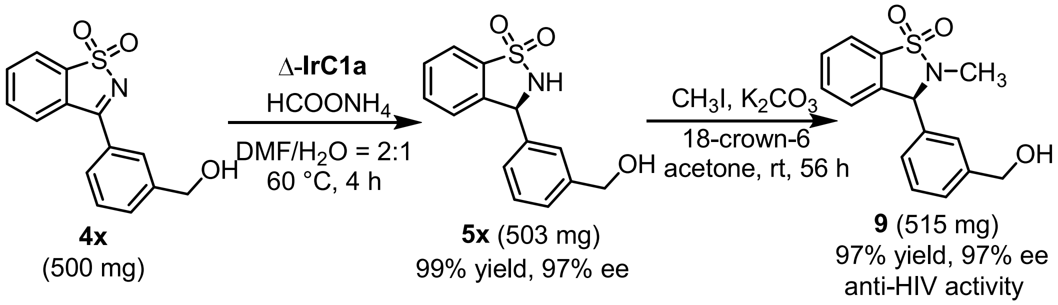
^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) 7.75 (s, 1H), 7.28 (s, 2H), 7.04 (dd, *J* = 44.0, 7.1 Hz, 6H), 6.70 (s, 1H), 5.60 (s, 1H), 2.25 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (151 MHz, CD_2Cl_2): δ (ppm) 155.9, 142.0, 140.5, 139.2, 136.9, 131.0, 129.1, 128.5, 128.3, 127.7, 127.4, 81.1, 30.1, 28.4, 21.1.

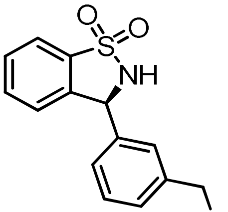
IR (film): ν (cm^{-1}) 3428, 2975, 2925, 2853, 1699, 1501, 1167, 1021, 760, 616, 572.

HRMS (ESI, m/z) calcd for $C_{19}H_{23}NNaO_4S$ $(M+Na)^+$: 384.1240, found: 384.1250.

5.2 Half-a-Gram Synthesis of the Bioactive Sultam 9

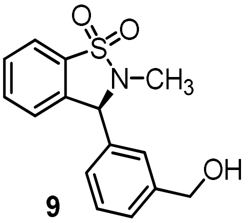


Scheme S11. Preparation of bioactive sultam **9** at half a gram-scale.



5x

A solution of cyclic *N*-sulfonylimine **4x** (500 mg, 1.83 mmol), HCO_2NH_4 (1.04 g, 16.46 mmol), and **Δ-IrC1a** (9.1 mg, 0.00915 mmol) in DMF/H_2O (2.44 mL/1.22 mL) was stirred at 60 °C for 4 h, cooled down to room temperature, then dried in *vacuo*. The residue was purified by flash chromatography on silica gel (EtOAc) to afford product **5x** as a white solid (503 mg, 1.827 mmol, yield: 99%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 30 °C, t_r(major) = 15.7 min, t_r(minor) = 24.4 min.



9

Methylation of the chiral sultam was preformed by a literature procedure. [6] Accordingly, a mixture of **5x** (503 mg, 1.827 mg), iodomethane (312 mg, 2.20 mmol), dried potassium carbonate (329 mg, 2.38 mmol), and 18-crown-6 (48.0 mg, 0.18 mmol) in dry acetone (18 mL) was stirred at room temperature under nitrogen for 56 h. The mixture was evaporated to dryness and purified by flash chromatography on silica gel (EtOAc) to afford product **9** as a white solid (515 mg, 1.78 mmol, yield: 97%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 220 nm, *n*-hexane/isopropanol = 70:30, flow rate 0.8 mL/min, 30 °C, t_r(major) = 9.5 min, t_r(minor) = 12.1 min. $[\alpha]_D^{23}$ = 96.9° (*c* = 1.0, $CHCl_3$).

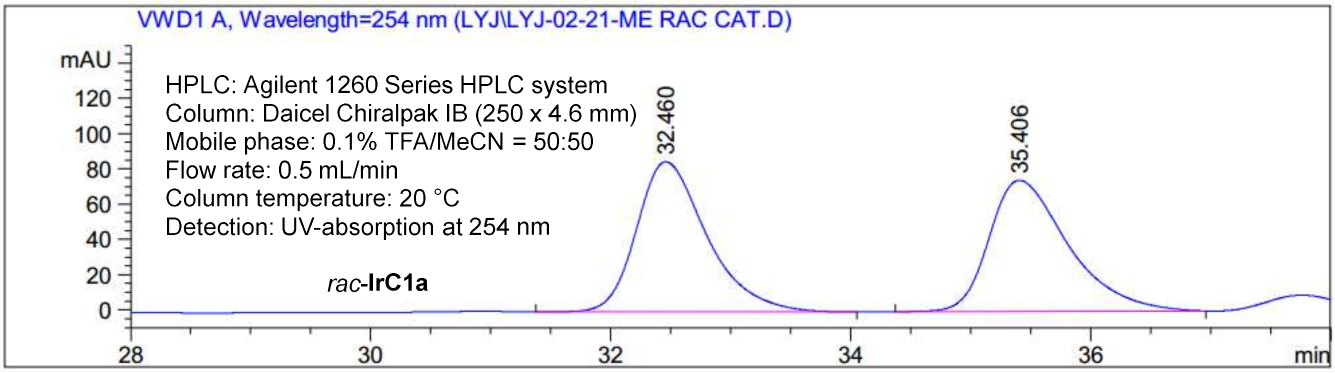
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.89–7.83 (m, 1H), 7.57–7.48 (m, 2H), 7.44–7.38 (m, 2H), 7.33 (s, 1H), 7.29–7.26 (m, 1H), 7.06–7.02 (m, 1H), 5.20 (br, 1H), 4.72 (s, 2H), 2.78 (s, 3H), 1.80 (br, 1H).

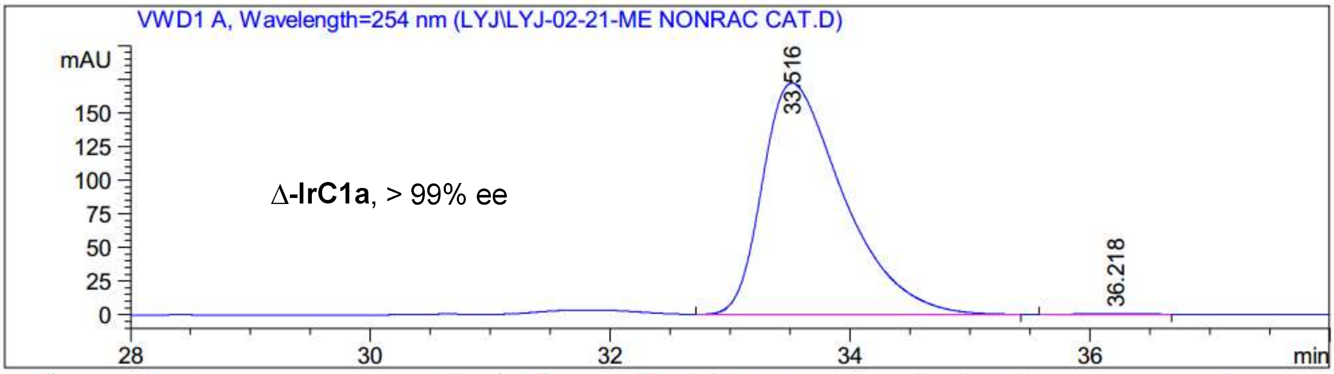
Other analytic data of **9** are consistent with the literature.[6]

6. Chiral Chromatography

6.1 Determination of Enantiopurities of the Iridium NHC Catalysts

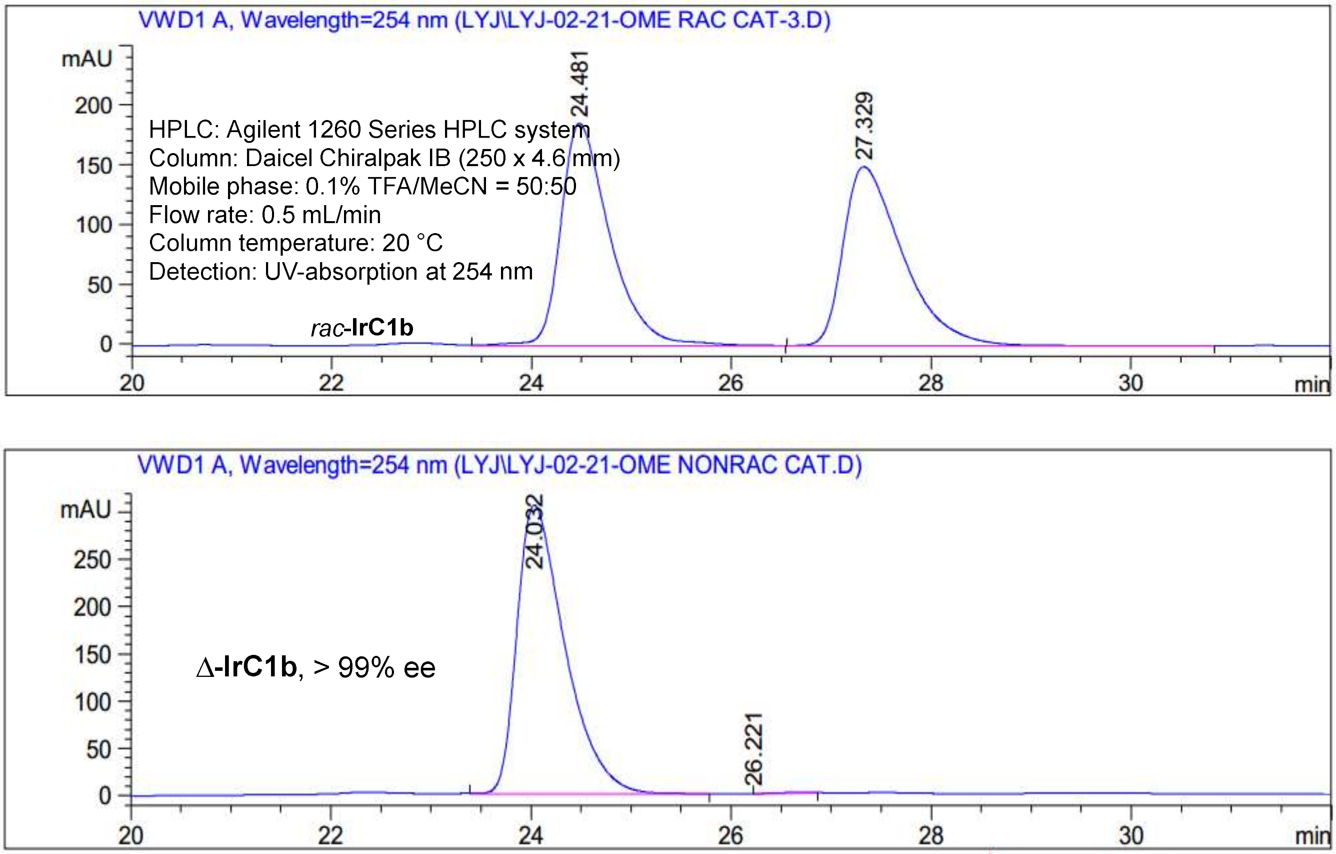
The analysis was performed with a Daicel Chiralpak IB (250 x 4.6 mm) HPLC column on an Agilent 1260 Series HPLC System. The column temperature was 20 °C and UV-absorption was measured at 254 nm.





```
 #    [min]            [min]    [mAU*s]        [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1   33.516 MM R   0.7835 8083.82324   171.95824   99.7575
  2   36.218 MM R   0.6218   19.65223 5.26744e-1    0.2425
```

Figure S5. HPLC trace for the racemic reference *rac*-**IrC1a**, and **Δ-IrC1a.**



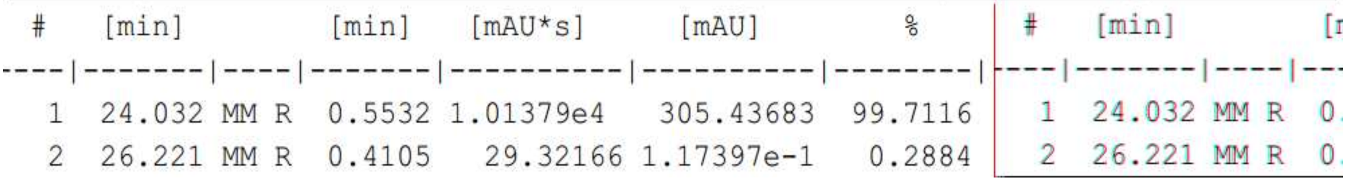
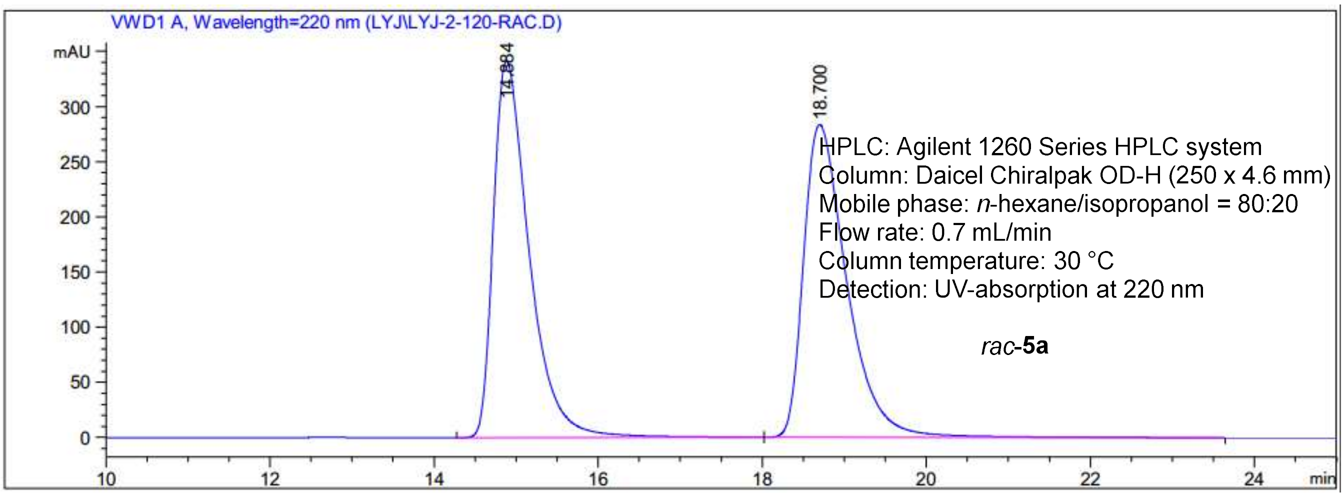

```
  #   [min]          [min]   [mAU*s]      [mAU]        %       #   [min]         [r
----|-------|----|-------|----------|----------|--------|----|-------|----|--
  1  24.032 MM R  0.5532 1.01379e4   305.43683  99.7116    1  24.032 MM R  0.
  2  26.221 MM R  0.4105   29.32166 1.17397e-1   0.2884    2  26.221 MM R  0.
```

Figure S6. HPLC trace for the racemic reference *rac*-**IrC1b**, and **Δ-IrC1b.**

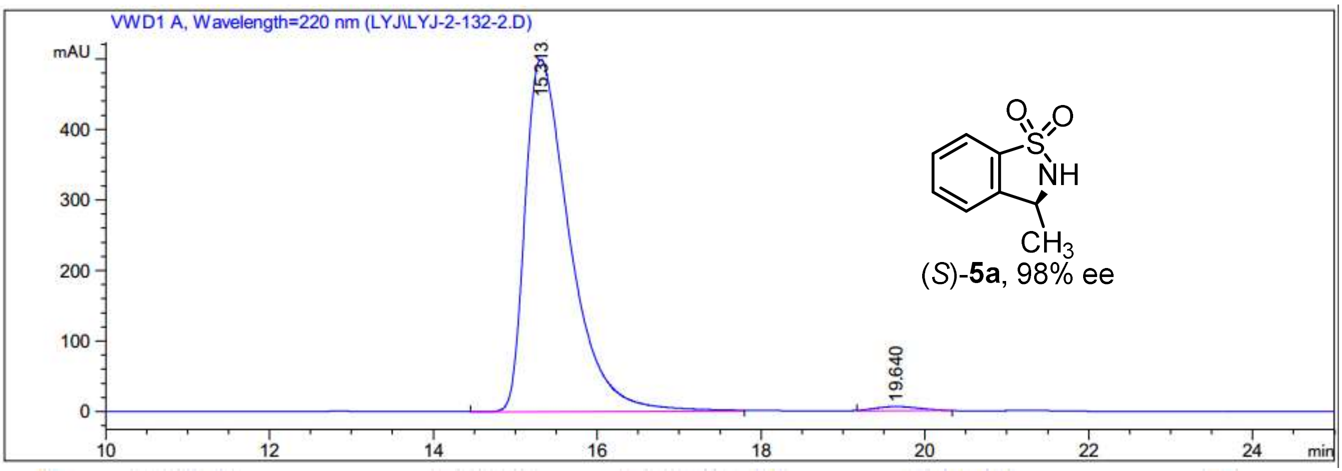
6.2 Determination of Enantioselectivities of the ATH of Cyclic *N*-Sulfonylimines

Optical purities of the compounds **5a-x** were determined with a Daicel Chiralpak OD-H or AD-H HPLC column on an Agilent 1260 Series HPLC System. The column temperature was 30 °C and UV-absorption was measured at 220 nm or 254 nm.

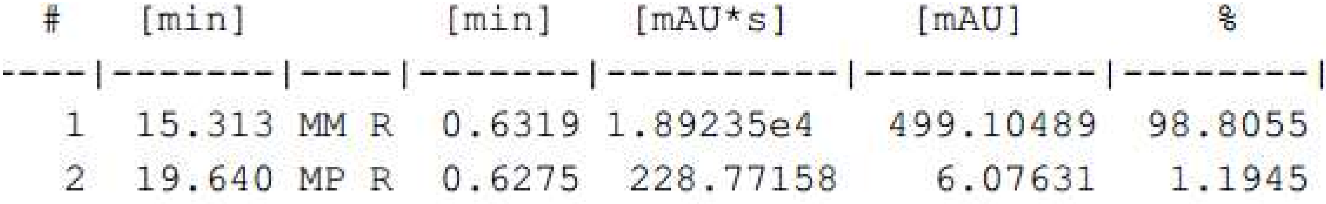


HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate: 0.7 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 220 nm

rac-**5a**

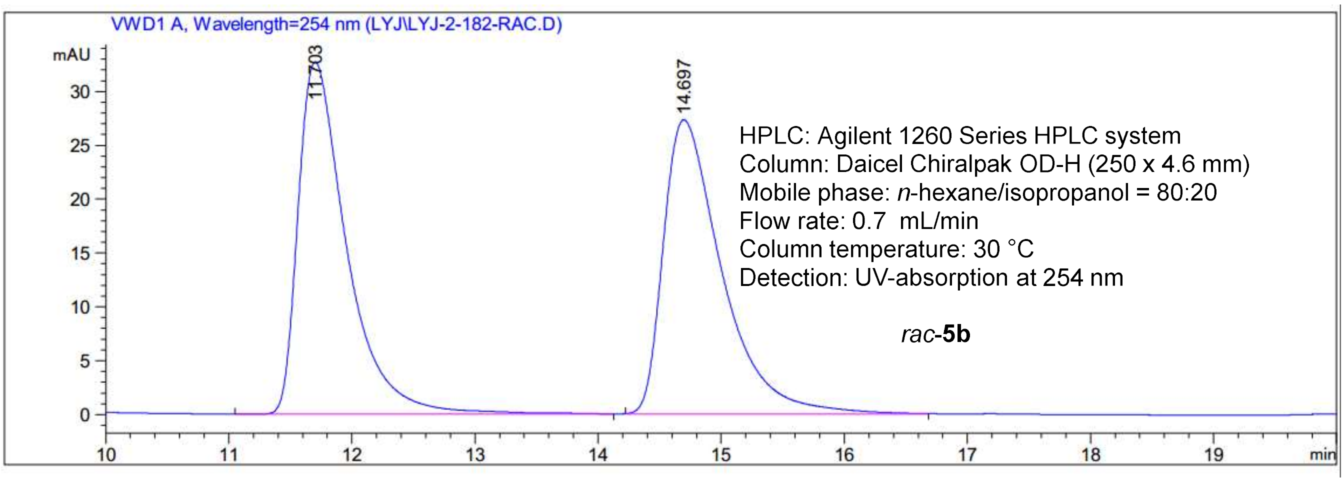


(*S*)-**5a**, 98% ee



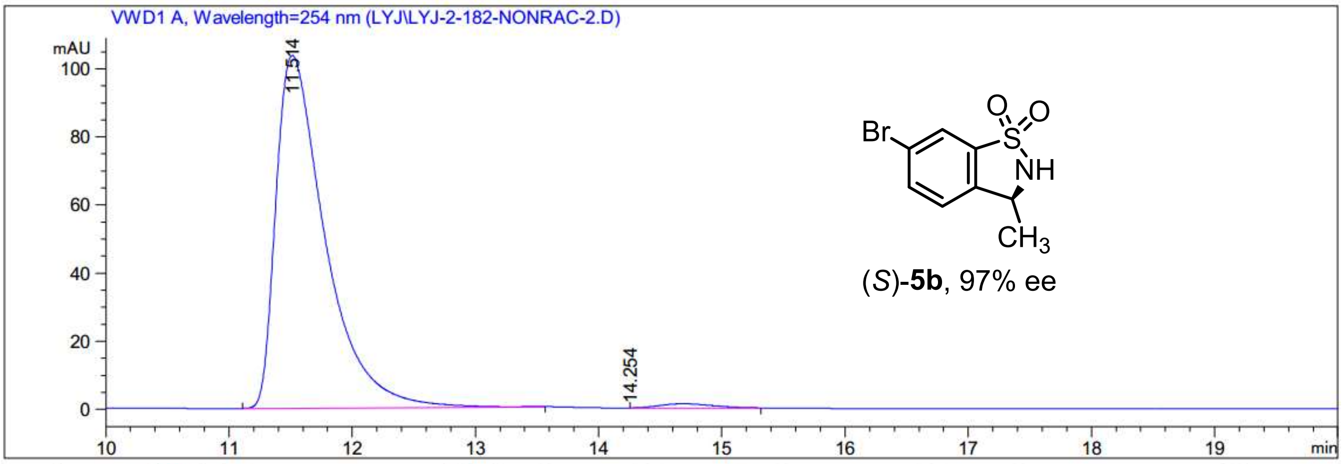
```
 #     [min]              [min]     [mAU*s]          [mAU]            %
----|-------|----|-------|----------|----------|--------|
   1  15.313 MM R  0.6319 1.89235e4    499.10489   98.8055
   2  19.640 MP R  0.6275  228.77158     6.07631    1.1945
```

Figure S7. HPLC trace for the racemic reference *rac*-**5a**, and non-racemic product (*S*)-**5a** generated from the asymmetric reaction catalyzed by Δ-**IrC1a**.

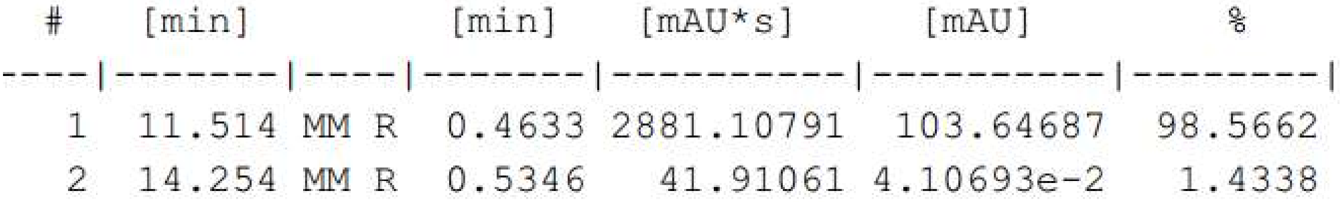


HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate: 0.7 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

rac-**5b**

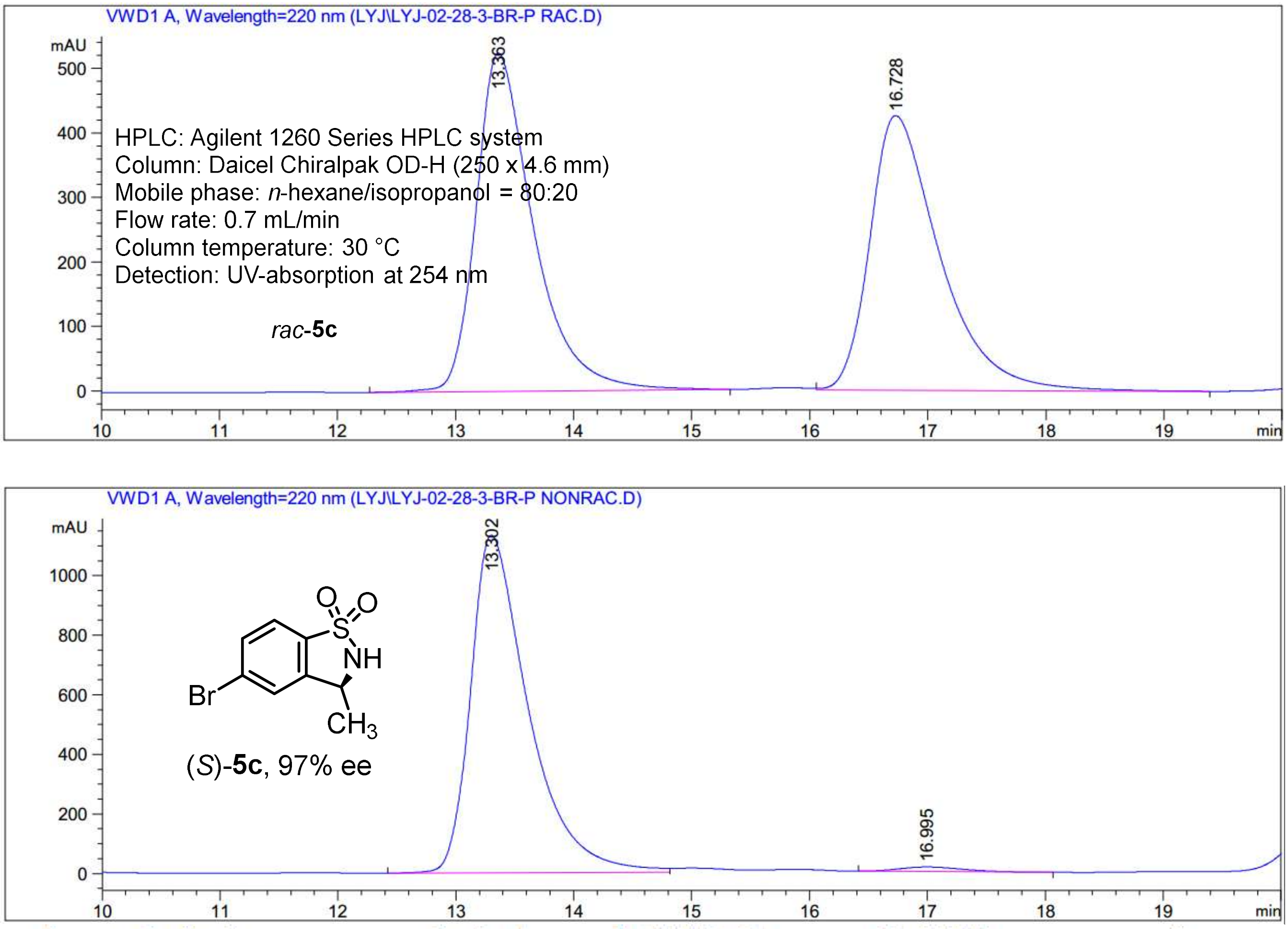


(*S*)-**5b**, 97% ee



```
  #     [min]            [min]    [mAU*s]       [mAU]          %
----|-------|----|-------|----------|----------|--------|
   1  11.514 MM R  0.4633 2881.10791  103.64687  98.5662
   2  14.254 MM R  0.5346   41.91061 4.10693e-2   1.4338
```

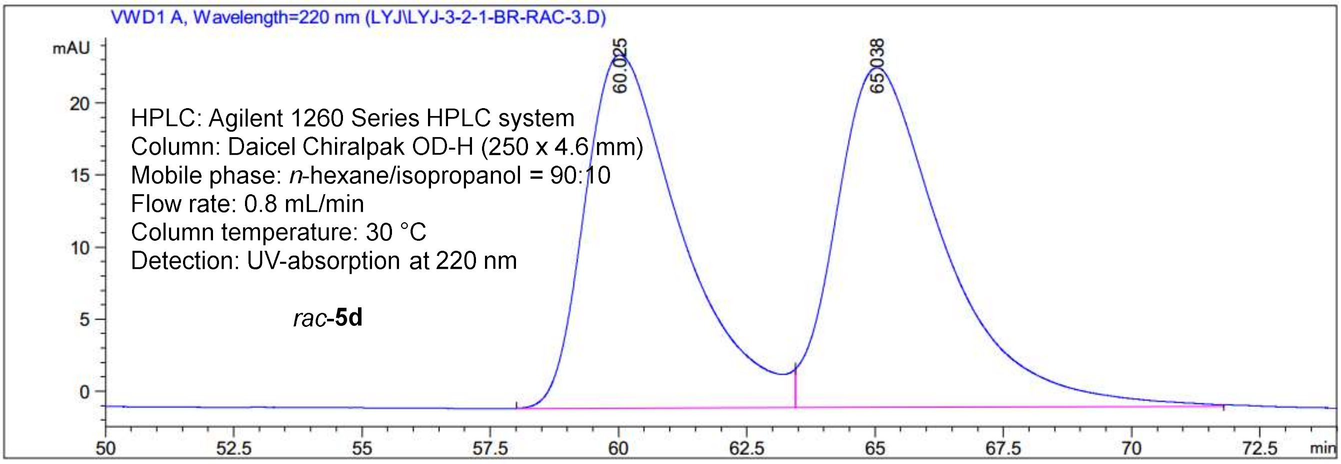
Figure S8. HPLC trace for the racemic reference *rac*-**5b**, and non-racemic product (*S*)-**5b** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.

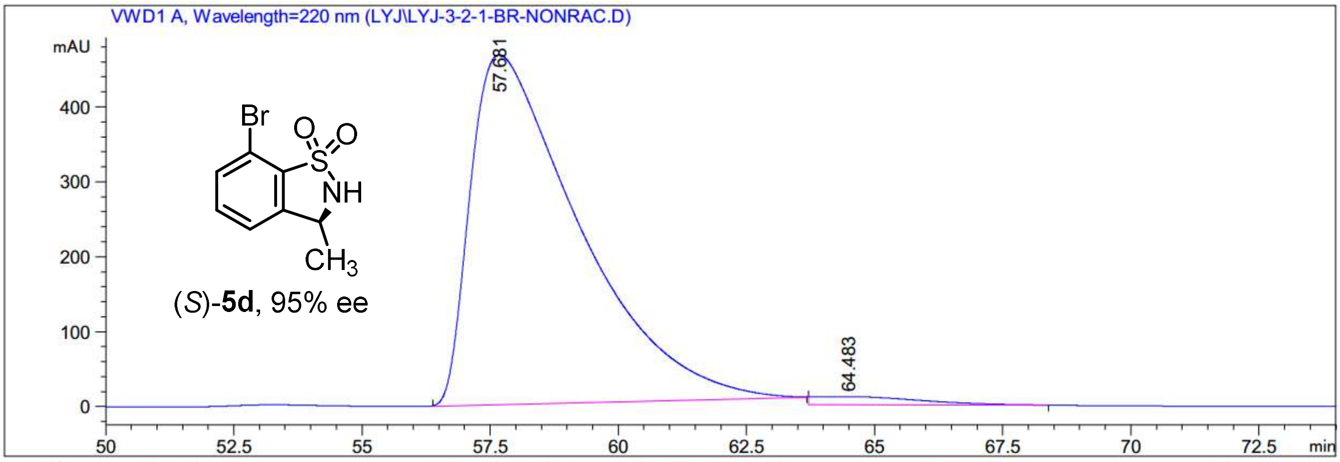


HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate: 0.7 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

```
 #     [min]             [min]     [mAU*s]       [mAU]          %
----|-------|----|-------|----------|----------|--------|
  1  13.302 BV     0.5034 3.85992e4  1133.19946  98.4780
  2  16.995 BB     0.5848  596.55634   15.78827   1.5220
```

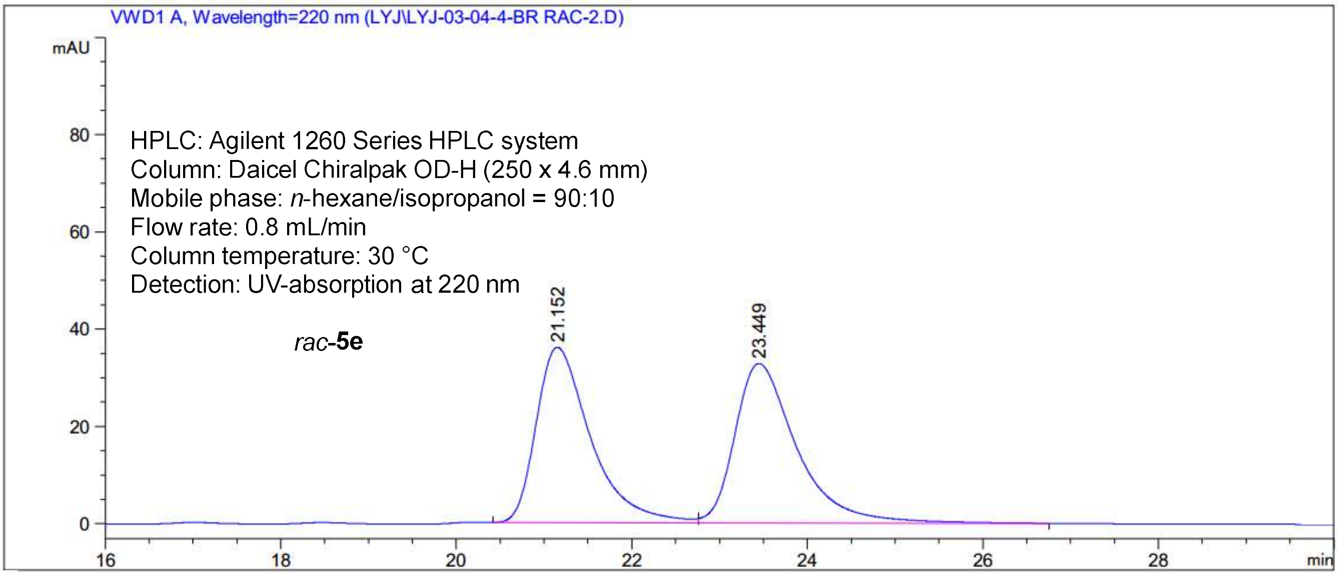
Figure S9. HPLC trace for the racemic reference *rac*-**5c**, and non-racemic product (*S*)-**5c** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.



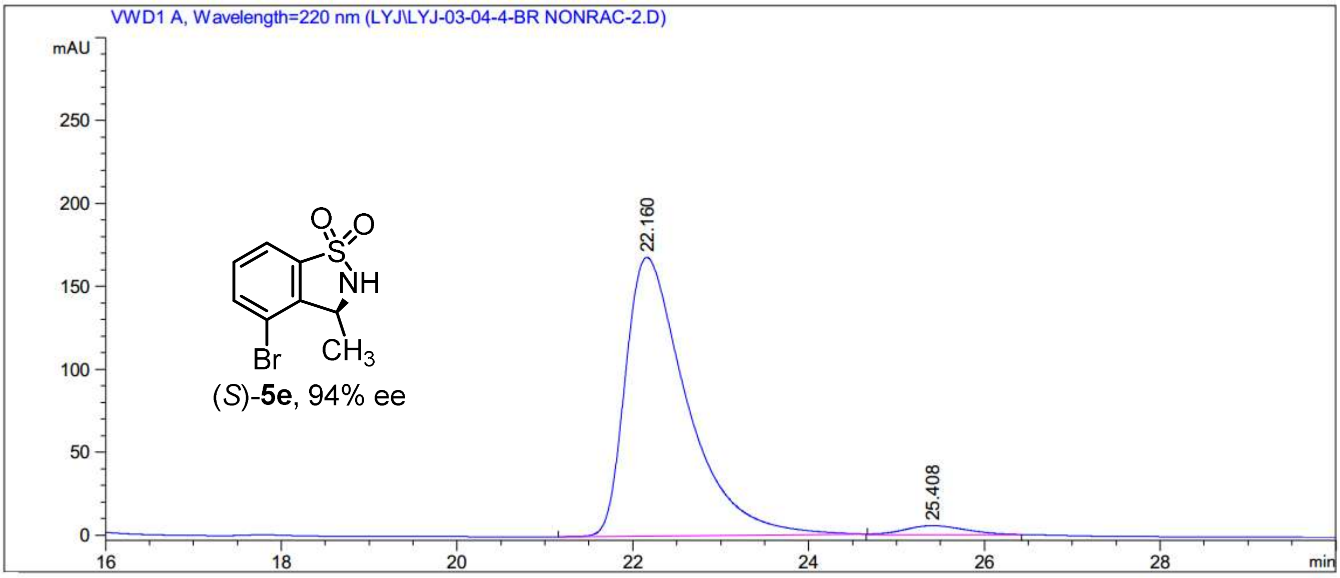


```
  #     [min]            [min]    [mAU*s]        [mAU]            %
----|--------|----|-------|-----------|-----------|---------|
   1  57.681 MM R  2.4632 6.90088e4    466.93390   97.6357
   2  64.483 MM R  2.4917 1671.08569    11.17776    2.3643
```

Figure S10. HPLC trace for the racemic reference *rac*-**5d**, and non-racemic product (*S*)-**5d** generated from the asymmetric reaction catalyzed by Δ-**IrC1a**.

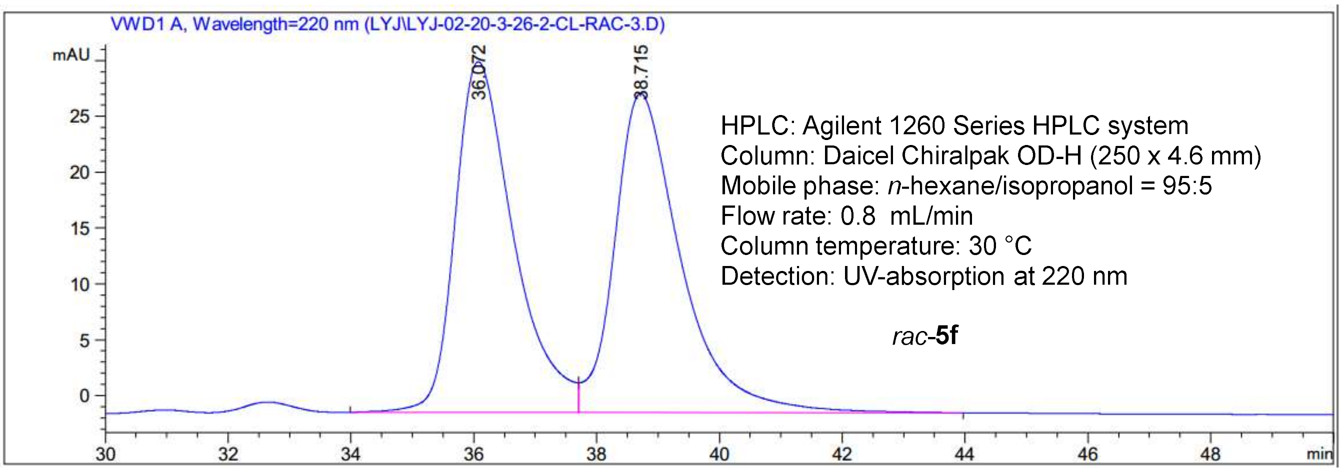


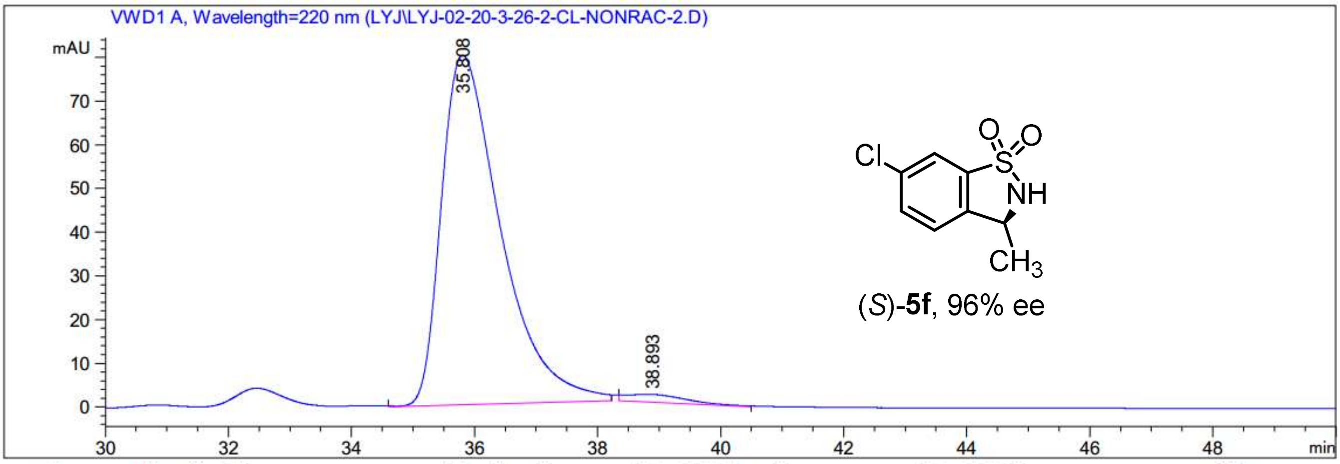
HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 90:10
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 220 nm

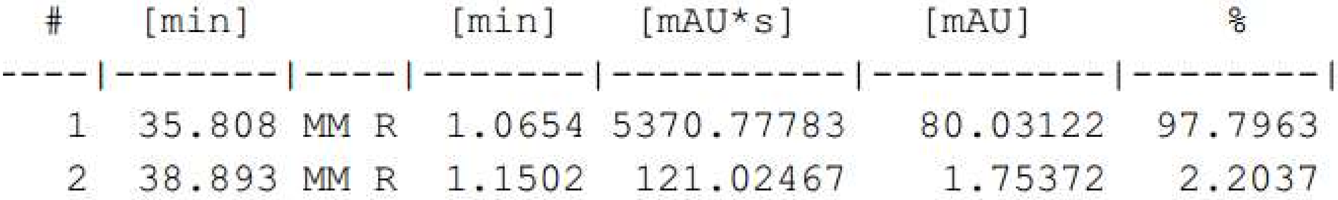


```
  #     [min]            [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   22.160 MM R   0.6195 8211.78125  168.21872  96.8768
   2   25.408 MM R   0.8108  264.73770    5.44164   3.1232
```

Figure S11. HPLC trace for the racemic reference *rac*-**5e**, and non-racemic product (*S*)-**5e** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.

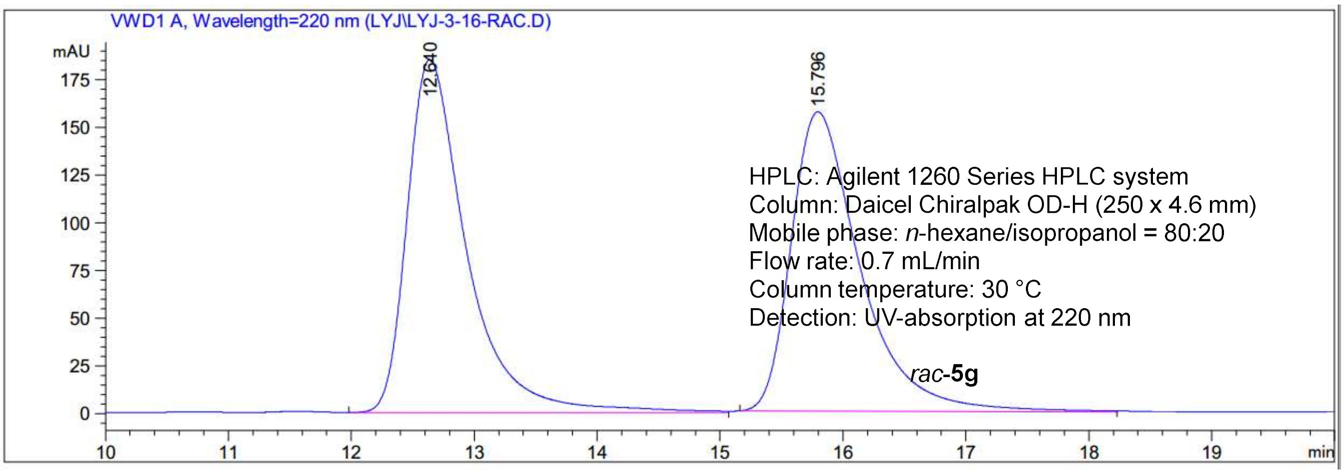




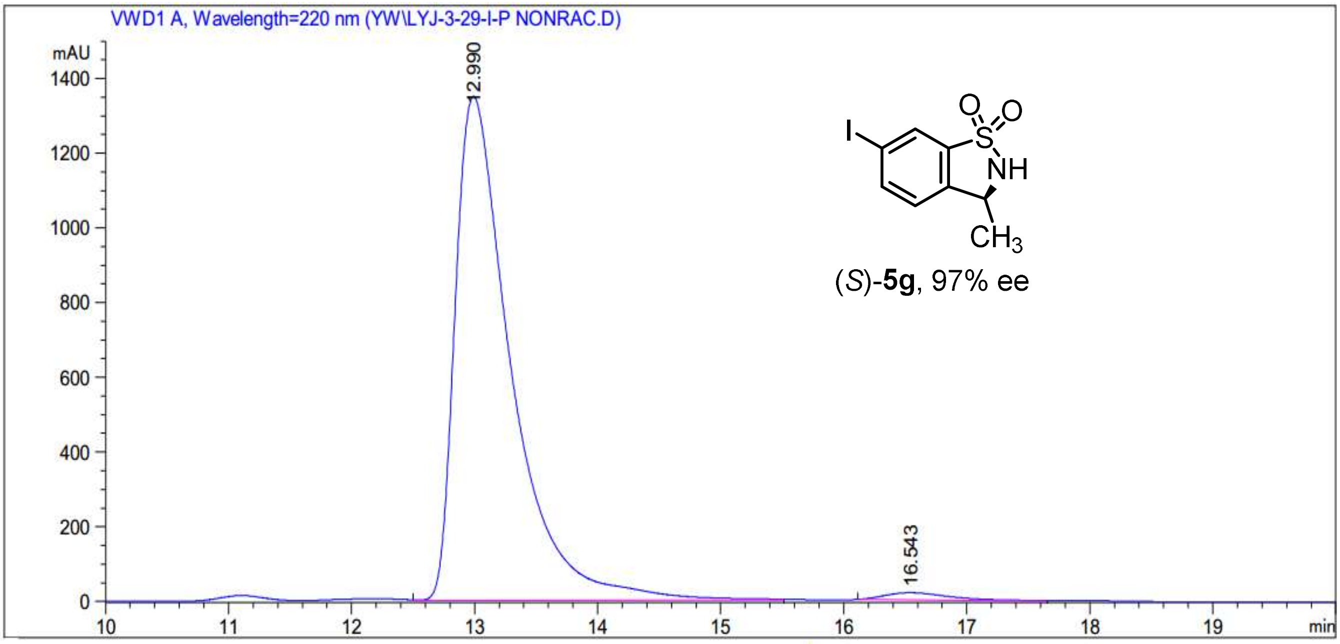


```
 #    [min]            [min]    [mAU*s]        [mAU]         %
----|-------|----|-------|----------|----------|--------|
   1  35.808 MM R   1.0654 5370.77783   80.03122  97.7963
   2  38.893 MM R   1.1502  121.02467    1.75372   2.2037
```

Figure S12. HPLC trace for the racemic reference *rac*-**5f**, and non-racemic product (*S*)-**5f** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.



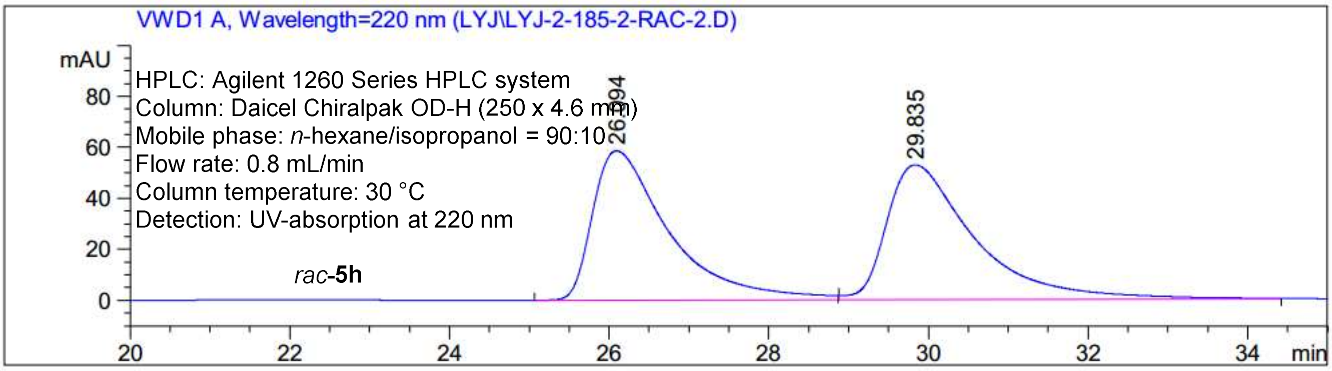
HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate: 0.7 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 220 nm



(*S*)-**5g**, 97% ee

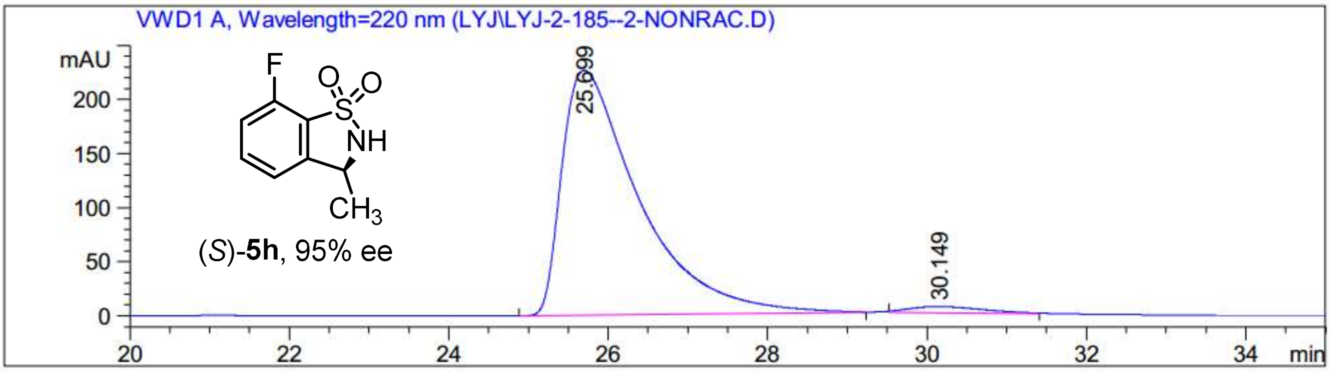
```
 #   [min]        [min]  [mAU*s]     [mAU]        %      |  #   [min]        [min]  [mAU*s]
----|-------|----|-------|----------|----------|--------|  ----|-------|----|-------|----------|-
  1  12.990 MM R  0.5255 4.25511e4  1349.64233  98.2918     1  12.990 MM R  0.5255 4.25511e4  1
  2  16.543 MM R  0.6277  739.48041   19.63378   1.7082     2  16.543 MM R  0.6277  739.48041
```

Figure S13. HPLC trace for the racemic reference *rac*-**5g**, and non-racemic product (*S*)-**5g** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 90:10
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 220 nm

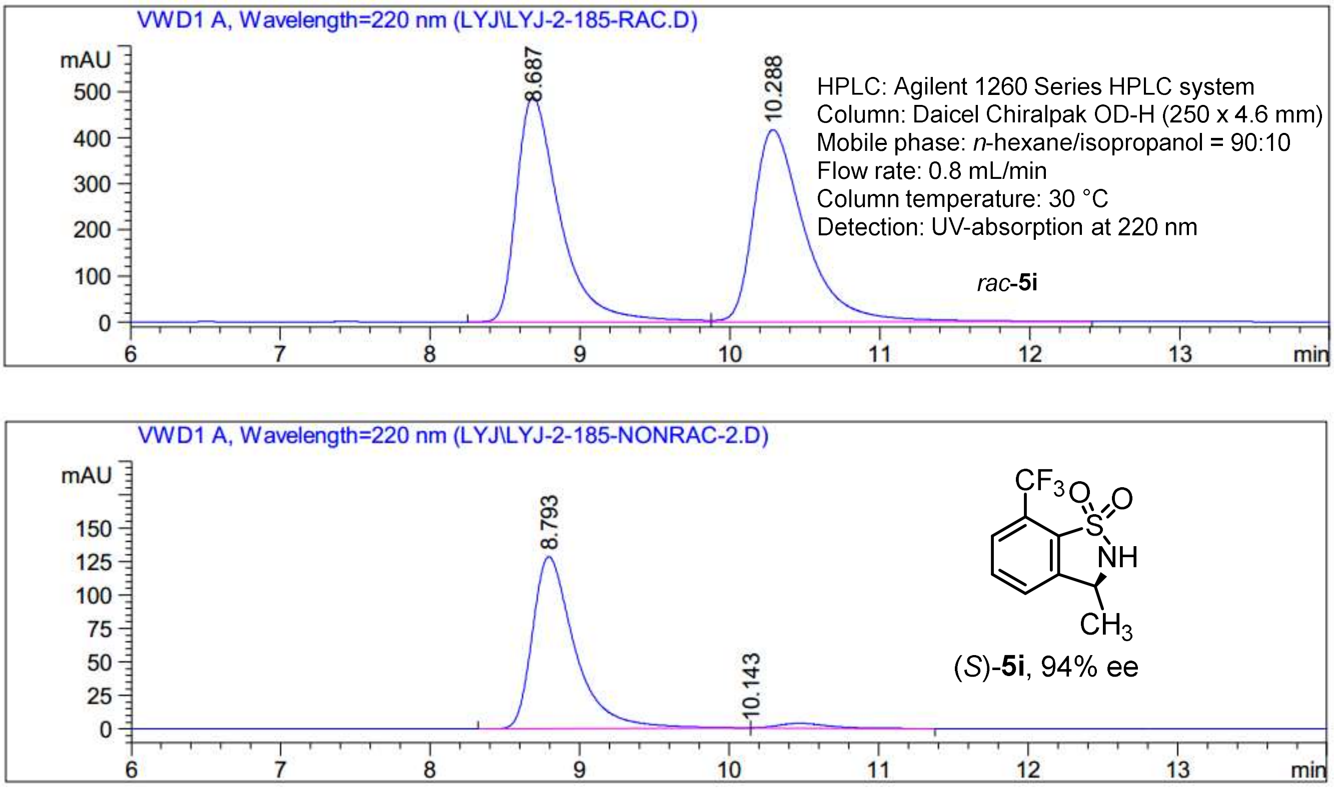
rac-**5h**



(*S*)-**5h**, 95% ee

```
 #    [min]          [min]   [mAU*s]       [mAU]          %
----|-------|----|-------|----------|----------|--------|
  1  25.699 MP R  1.1189 1.51907e4   226.27385  97.6515
  2  30.149 MM R  1.0804  365.33963    5.63574   2.3485
```

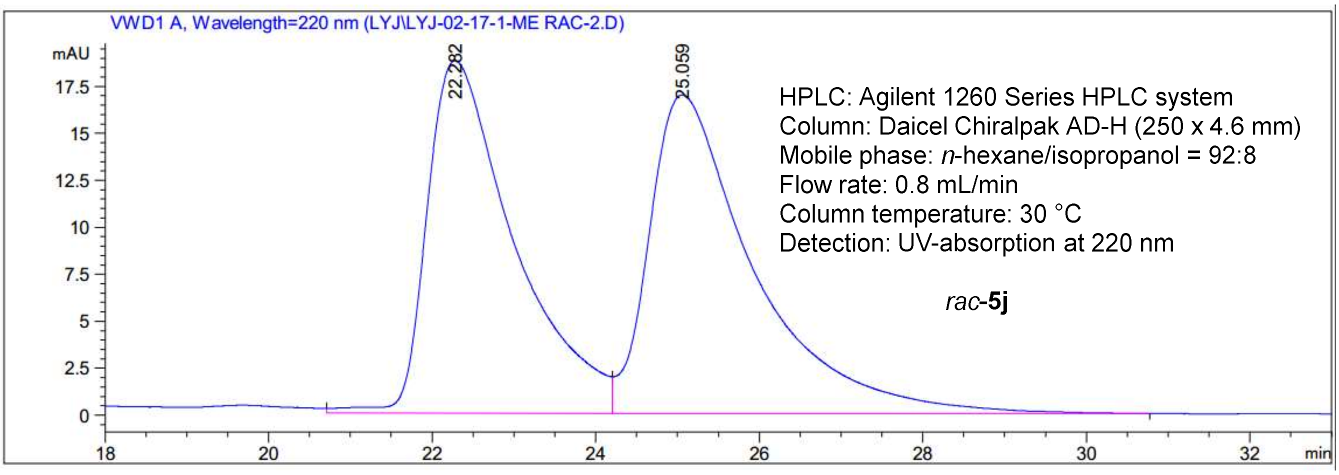
Figure S14. HPLC trace for the racemic reference *rac*-**5h**, and non-racemic product (*S*)-**5h** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 90:10
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 220 nm

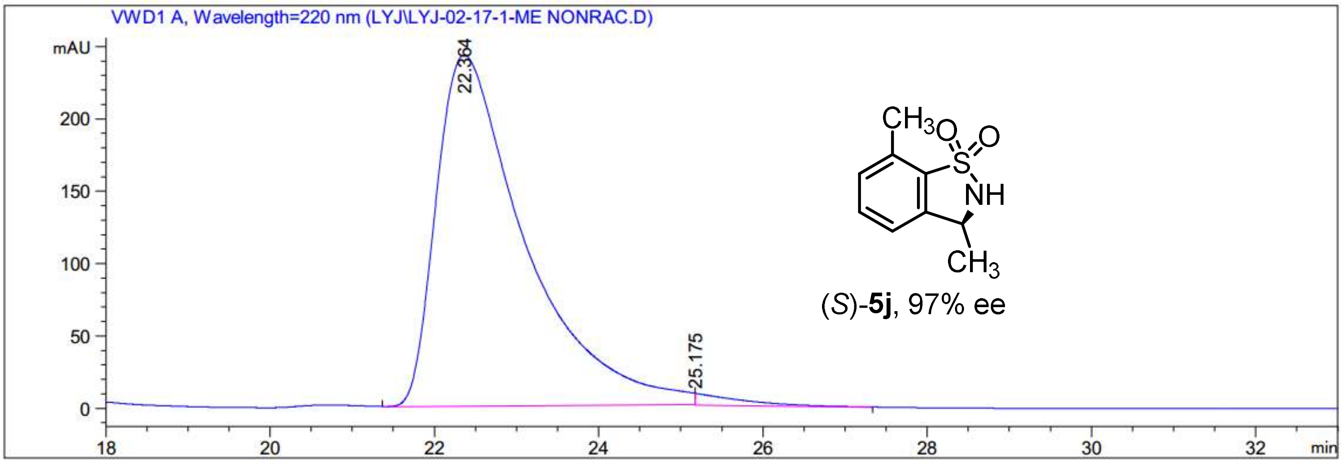
```
 #    [min]              [min]    [mAU*s]        [mAU]           %
----|-------|----|-------|----------|----------|--------|
  1    8.793 MM R   0.3300 2542.23486  128.41049   96.8249
  2   10.143 MM R   0.3836   83.36668 9.79327e-2    3.1751
```

Figure S15. HPLC trace for the racemic reference *rac*-**5i**, and non-racemic product (*S*)-**5i** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak AD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 92:8
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 220 nm

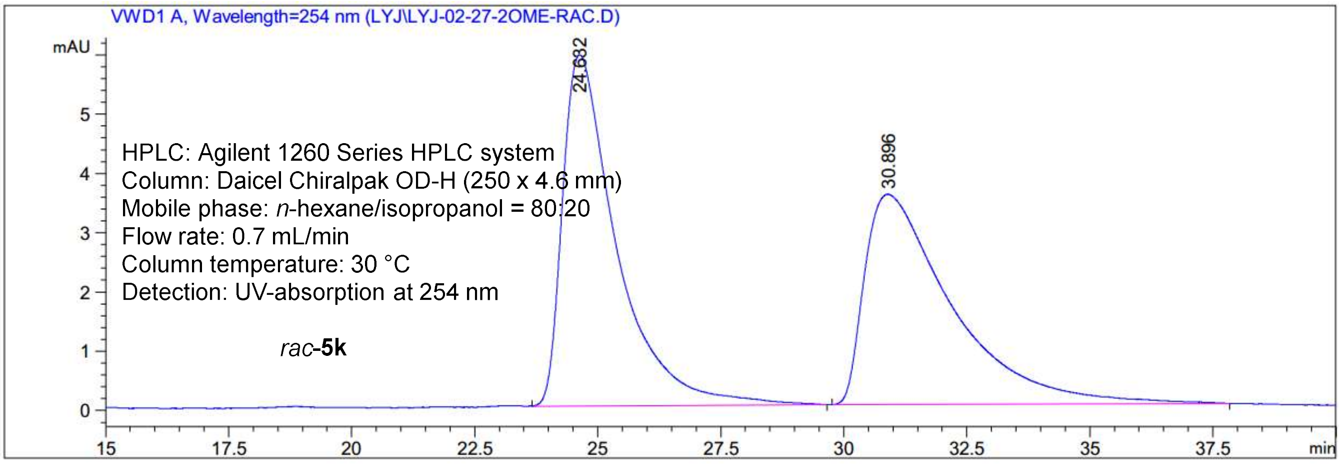
rac-**5j**



(*S*)-**5j**, 97% ee

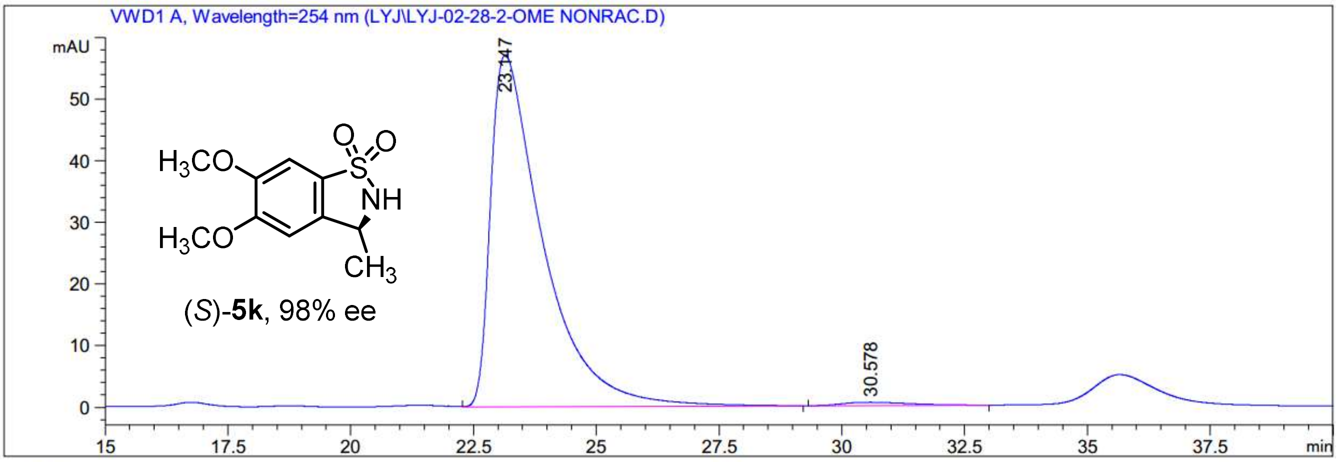
```
 #     [min]            [min]    [mAU*s]         [mAU]          %
----|-------|----|-------|----------|----------|--------|
   1   22.364 MM R   1.2573 1.83176e4    242.80940   98.4077
   2   25.175 MM R   0.6161  296.38535     8.01753    1.5923
```

Figure S16. HPLC trace for the racemic reference *rac*-**5j**, and non-racemic product (*S*)-**5j** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.

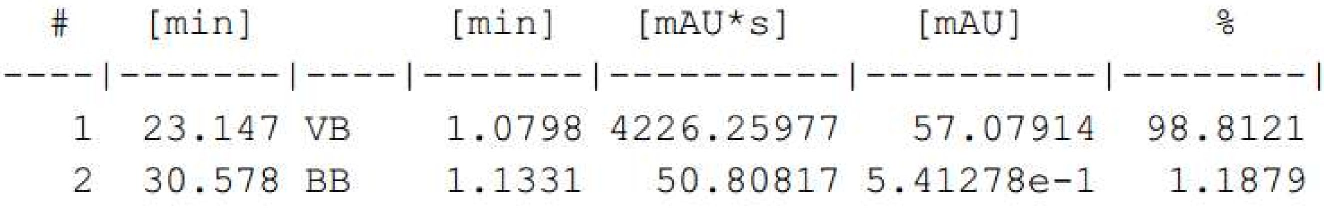


HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate: 0.7 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

rac-**5k**

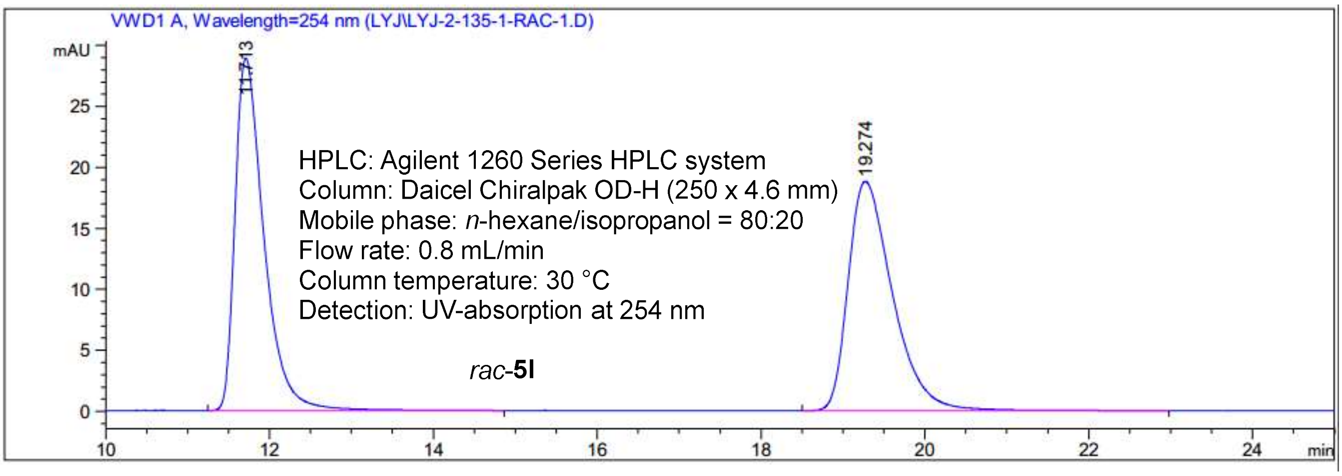


(*S*)-**5k**, 98% ee



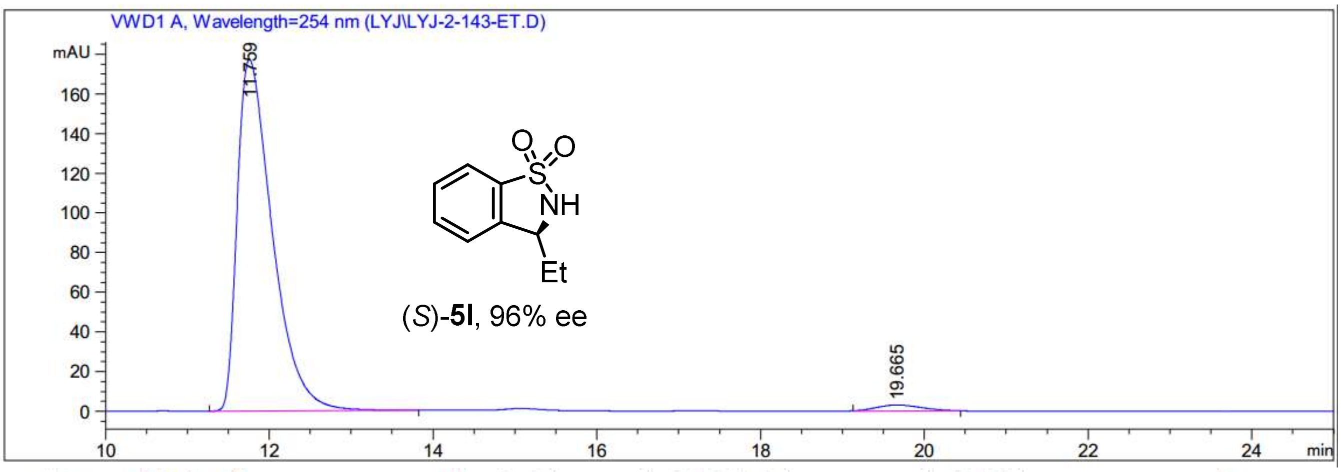
```
  #    [min]           [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.147 VB     1.0798 4226.25977   57.07914   98.8121
   2  30.578 BB     1.1331   50.80817 5.41278e-1   1.1879
```

Figure S17. HPLC trace for the racemic reference *rac*-**5k**, and non-racemic product (*S*)-**5k** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.

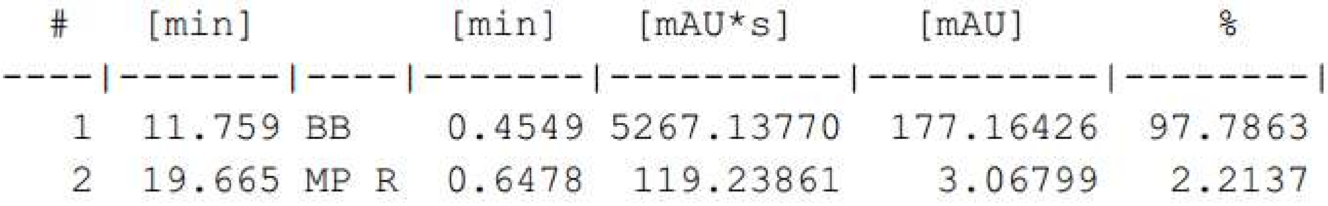


HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

rac-**5l**

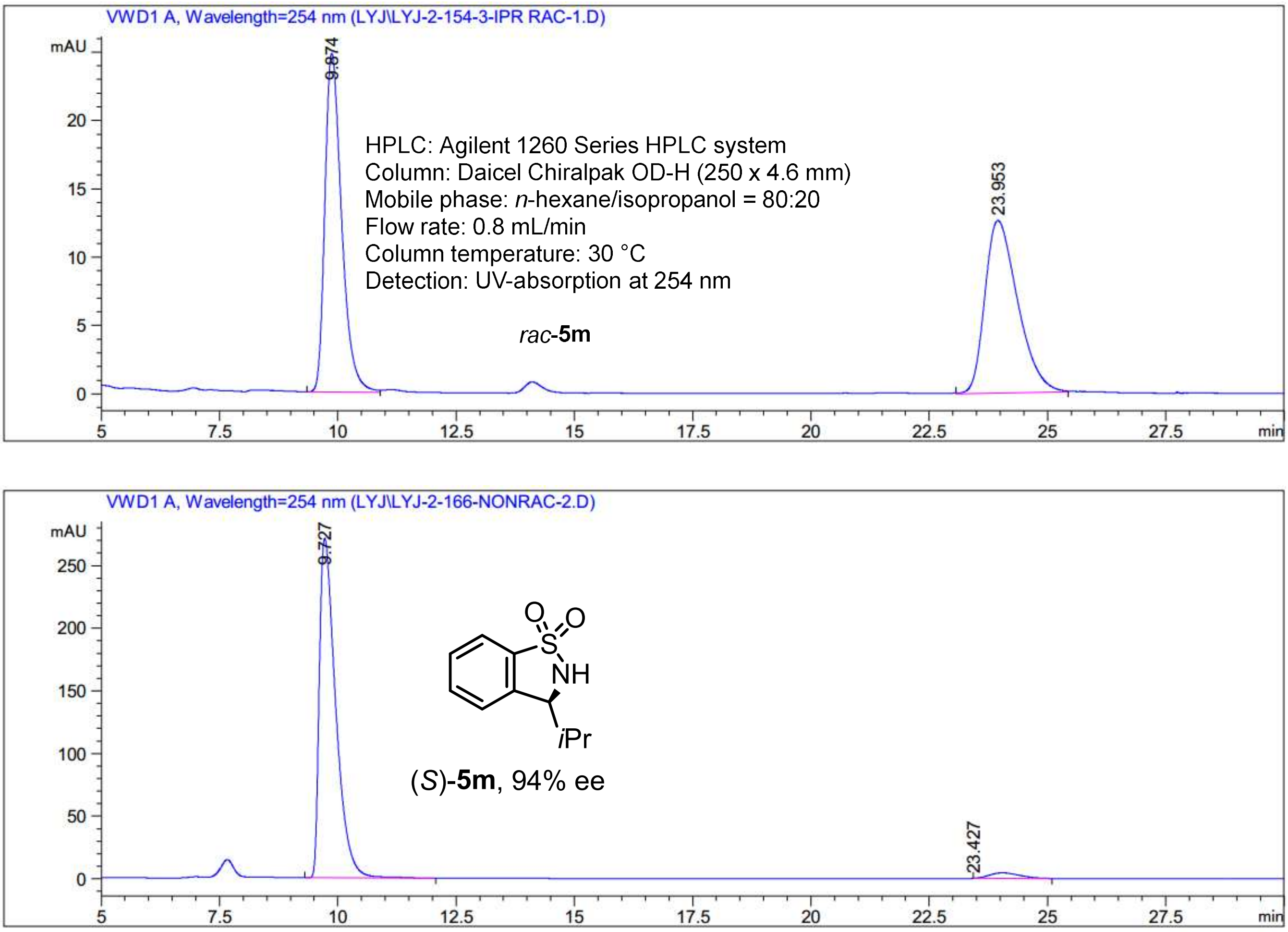


(*S*)-**5l**, 96% ee



```
  #    [min]            [min]    [mAU*s]       [mAU]         %
----|-------|----|-------|----------|----------|--------|
   1  11.759 BB     0.4549 5267.13770  177.16426  97.7863
   2  19.665 MP R   0.6478  119.23861    3.06799   2.2137
```

Figure S18. HPLC trace for the racemic reference *rac*-**5l**, and non-racemic product (*S*)-**5l** generated from the asymmetric reaction catalyzed by Δ-**IrC1a**.



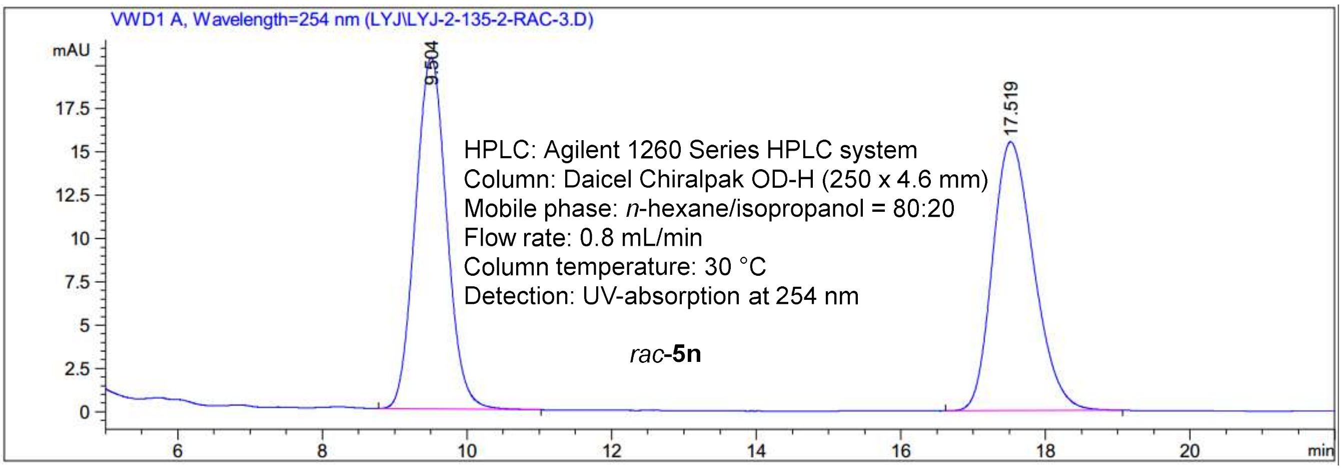
HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

rac-**5m**

(*S*)-**5m**, 94% ee

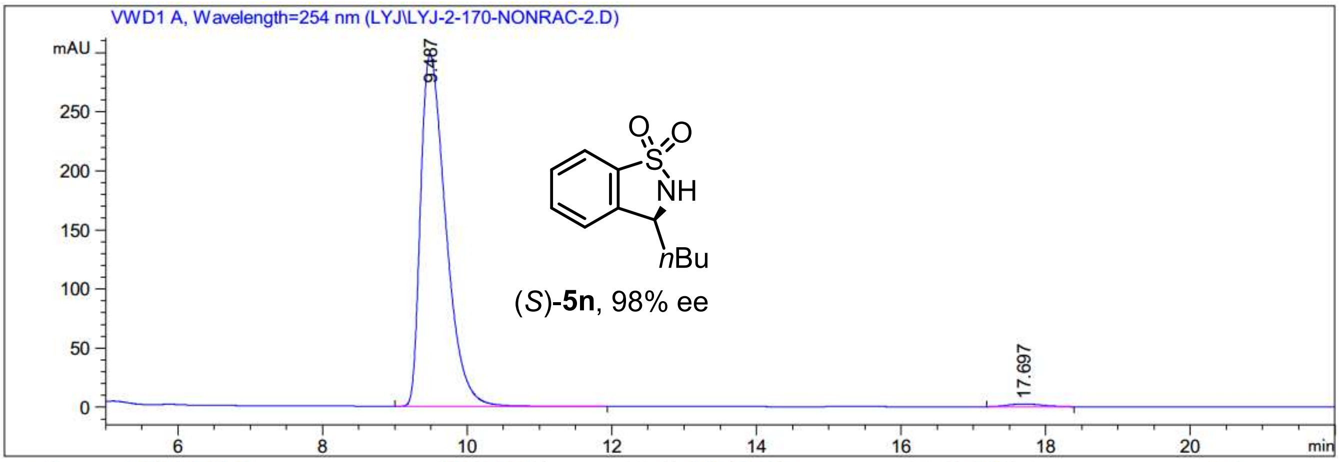
```
 #     [min]          [min]    [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1    9.727 BV    0.3652 6534.90527  271.15738  97.0041
  2   23.427 PM R  0.7518  201.82614    0.00000   2.9959
```

Figure S19. HPLC trace for the racemic reference *rac*-**5m**, and non-racemic product (*S*)-**5m** generated from the asymmetric reaction catalyzed by Δ-**IrC1a**.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

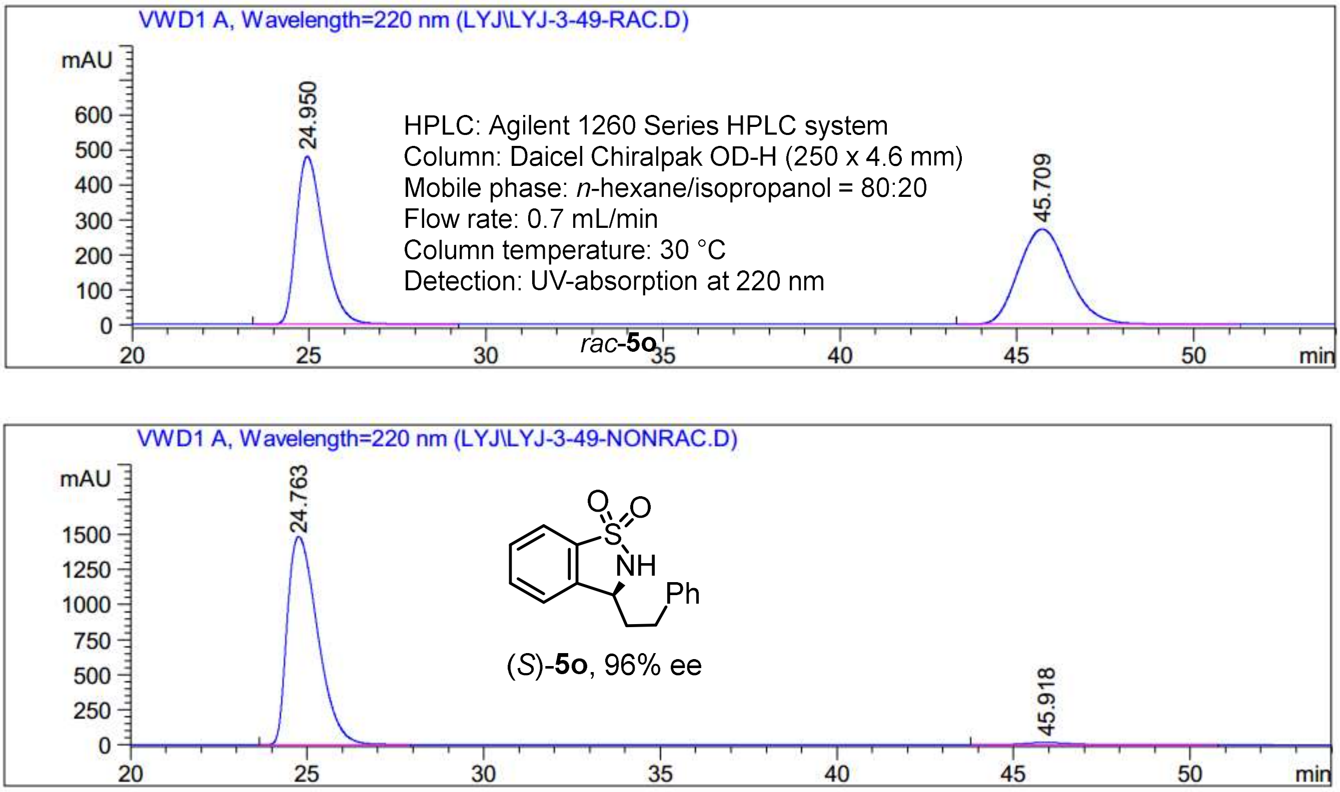
rac-**5n**



(*S*)-**5n**, 98% ee

```
 #     [min]           [min]    [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1    9.487 BB     0.3768 7205.05176  297.27289   98.7959
  2   17.697 MM R   0.5934   87.81587    2.46645    1.2041
```

Figure S20. HPLC trace for the racemic reference *rac*-**5n**, and non-racemic product (*S*)-**5n** generated from the asymmetric reaction catalyzed by Δ-**IrC1a**.



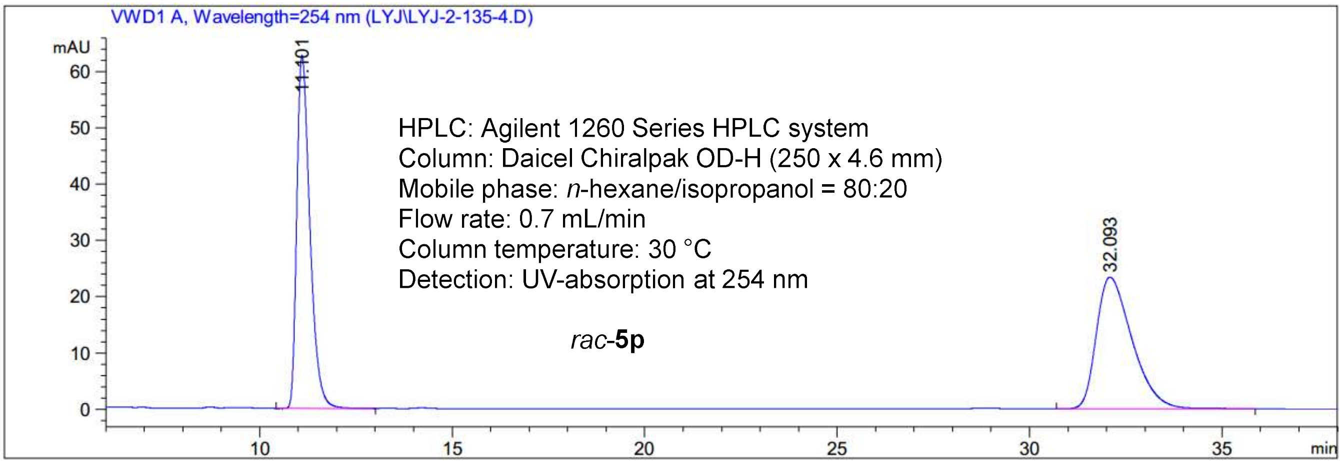
HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate: 0.7 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 220 nm

rac-**5o**

(*S*)-**5o**, 96% ee

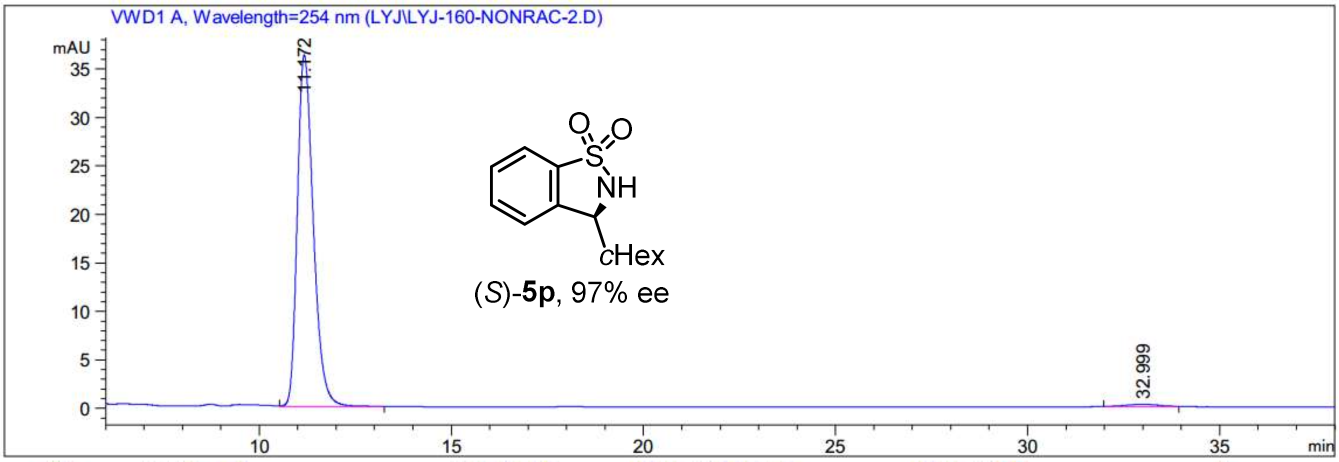
```
  #    [min]          [min]    [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
   1  24.763 BV    0.9488 8.91635e4 1484.28430  98.1834
   2  45.918 BB    1.5089 1649.71960   16.98875   1.8166
```

Figure S21. HPLC trace for the racemic reference *rac*-**5o**, and non-racemic product (*S*)-**5o** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate: 0.7 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

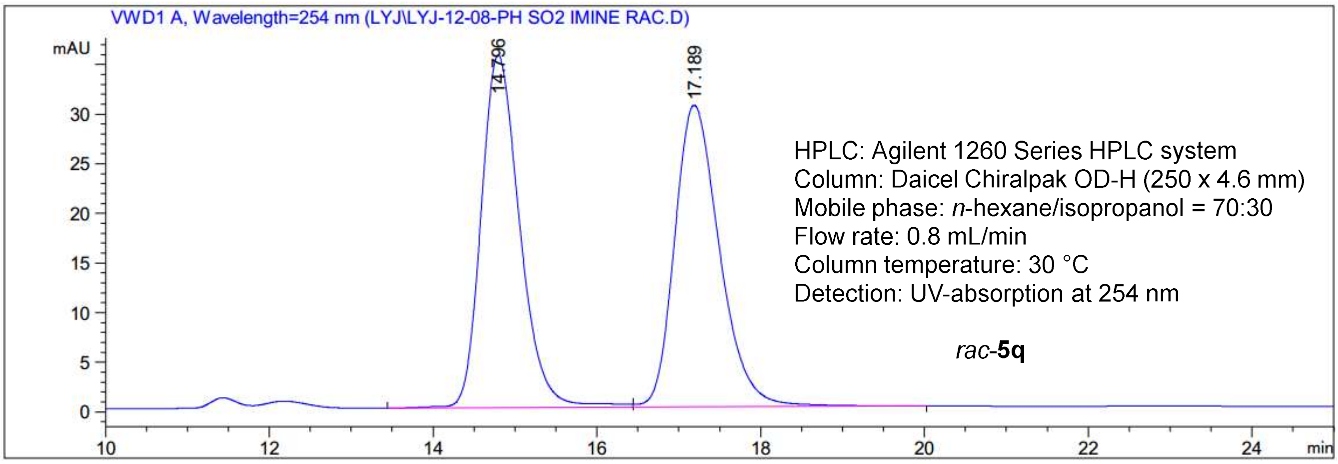
rac-**5p**



(*S*)-**5p**, 97% ee

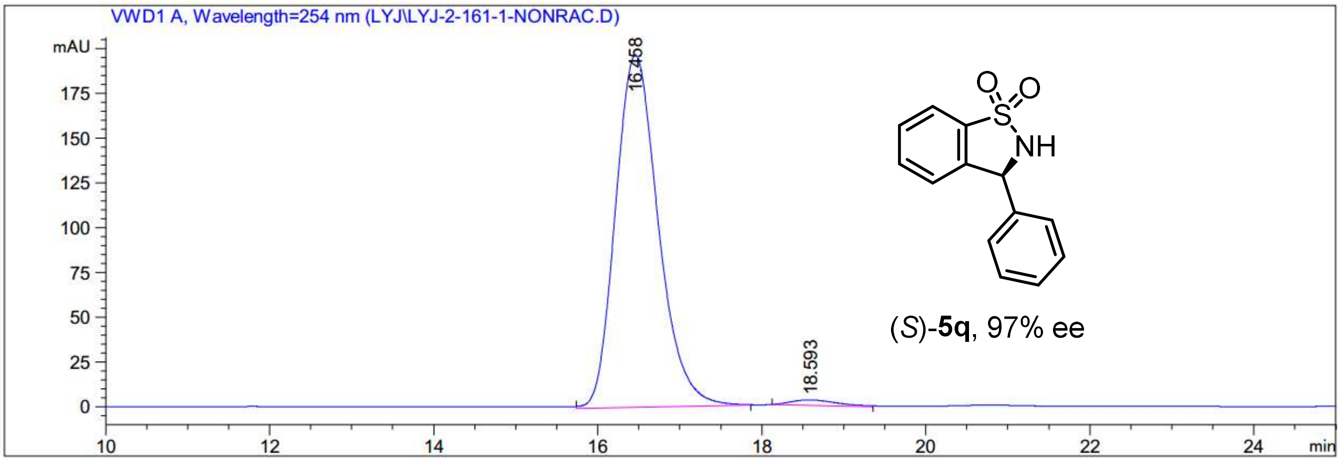
```
  #     [min]            [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.172 VB     0.4491 1046.99487   36.23561  98.5694
   2  32.999 MM R   1.0173   15.19528 2.48938e-1   1.4306
```

Figure S22. HPLC trace for the racemic reference *rac*-**5p**, and non-racemic product (*S*)-**5p** generated from the asymmetric reaction catalyzed by Δ-**IrC1a**.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 70:30
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

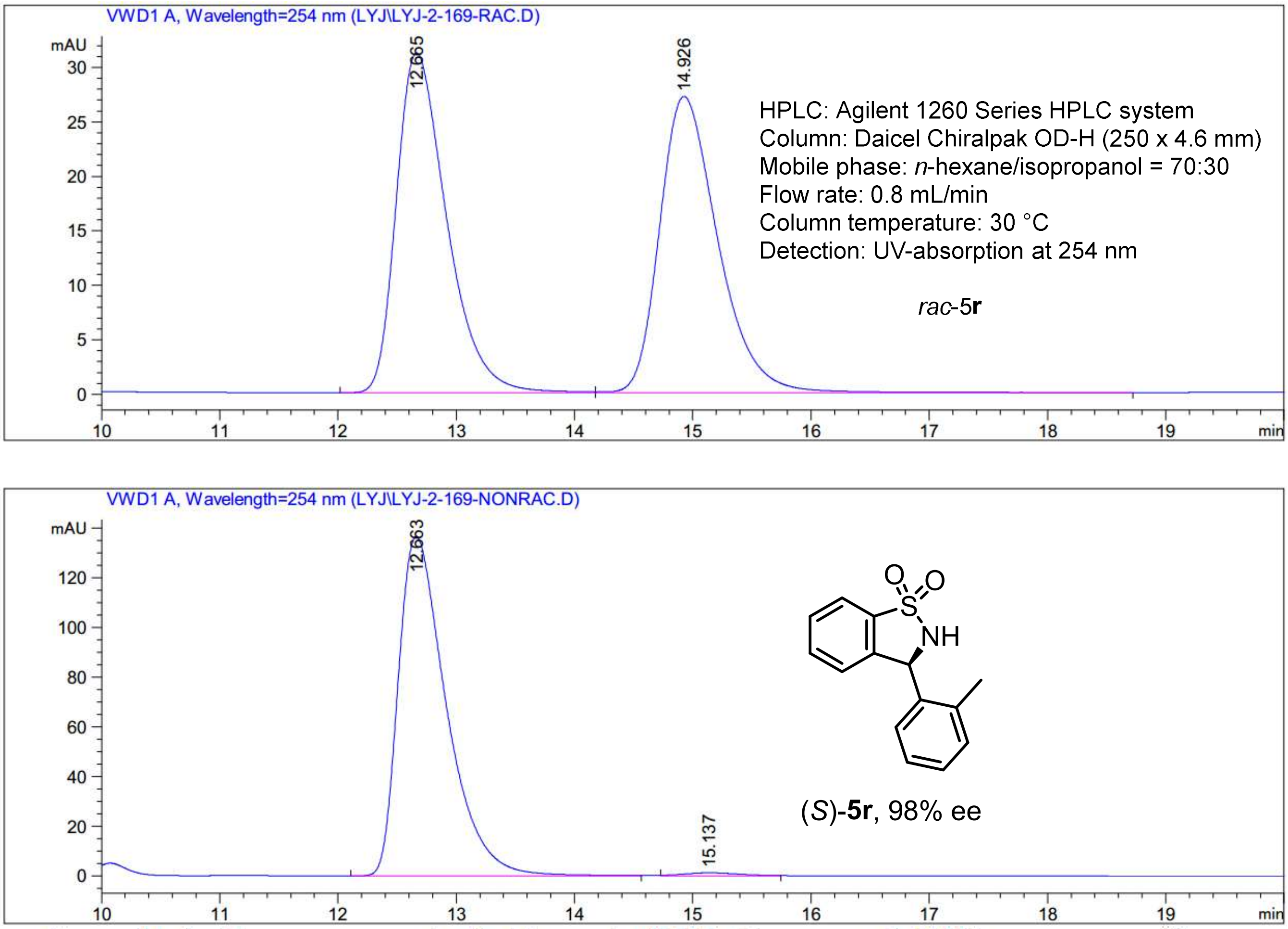
rac-**5q**



(*S*)-**5q**, 97% ee

```
  #     [min]             [min]    [mAU*s]        [mAU]           %
----|-------|----|-------|----------|----------|--------|
   1  16.458 MM R  0.6044 7140.60059  196.91640  98.3548
   2  18.593 MM R  0.6495  119.44384    3.06493   1.6452
```

Figure S23. HPLC trace for the racemic reference *rac*-**5q**, and non-racemic product (*S*)-**5q** generated from the asymmetric reaction catalyzed by Δ-**IrC1a**.



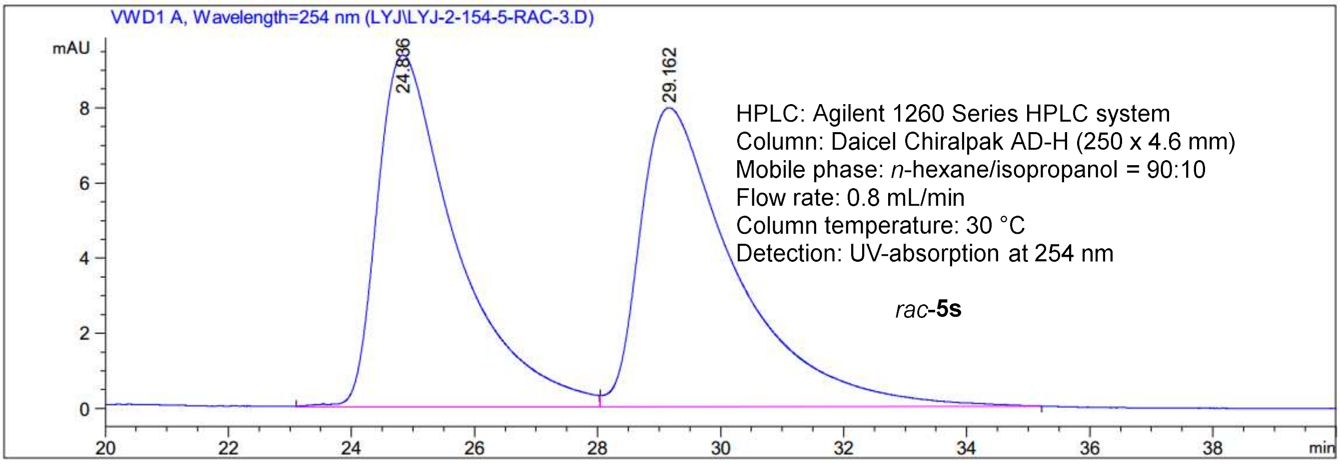
HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 70:30
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

rac-5**r**

(*S*)-**5r**, 98% ee

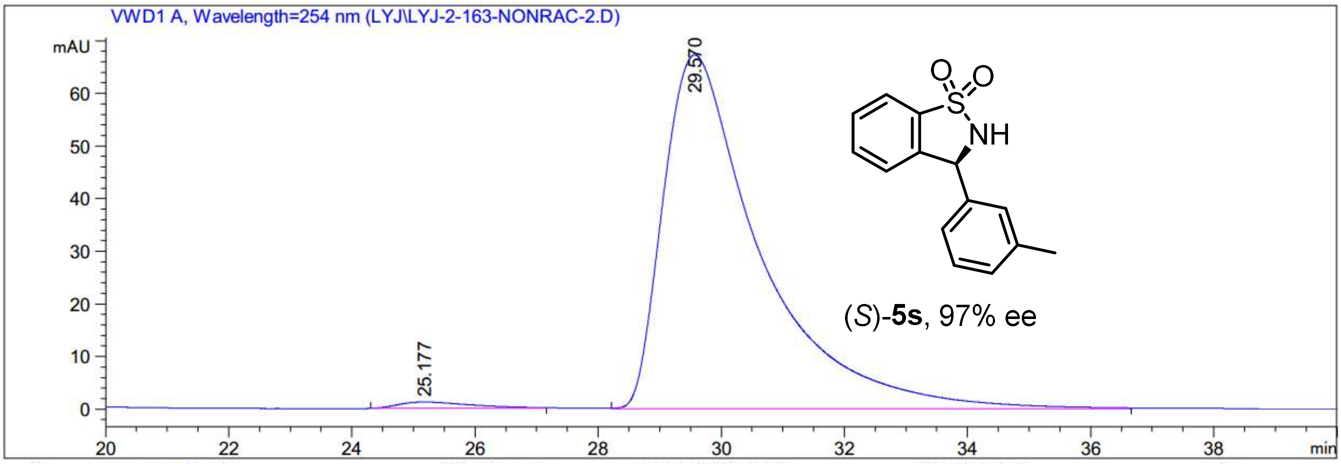
```
 #     [min]            [min]    [mAU*s]       [mAU]          %
----|-------|----|-------|----------|----------|--------|
  1  12.663 BV     0.4328 3850.97412  136.65947  99.0375
  2  15.137 MM R   0.5300   37.42450    1.17676   0.9625
```

Figure S24. HPLC trace for the racemic reference *rac*-**5r**, and non-racemic product (*S*)-**5r** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.

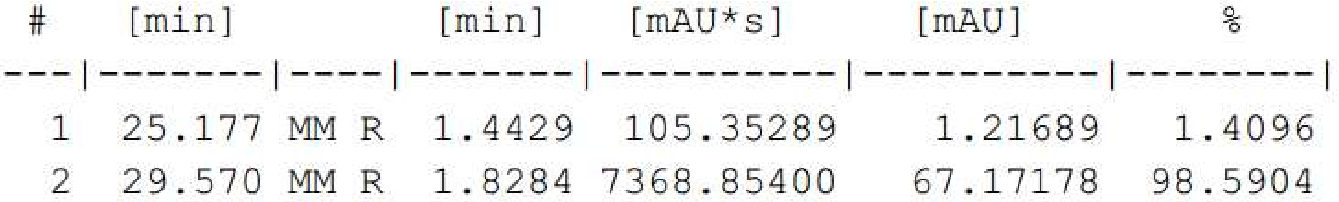


HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak AD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 90:10
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

rac-**5s**

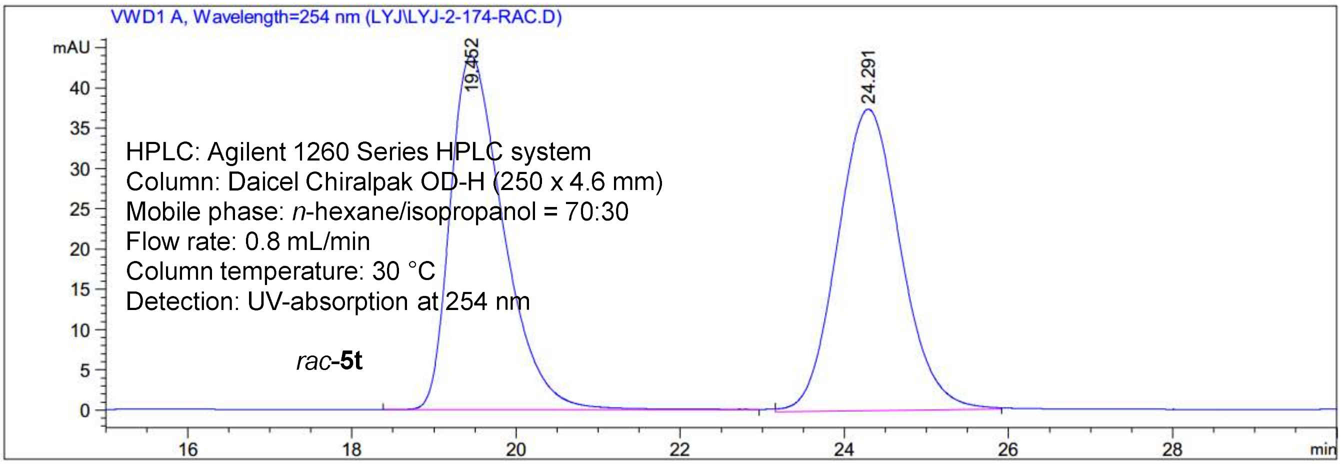


(*S*)-**5s**, 97% ee



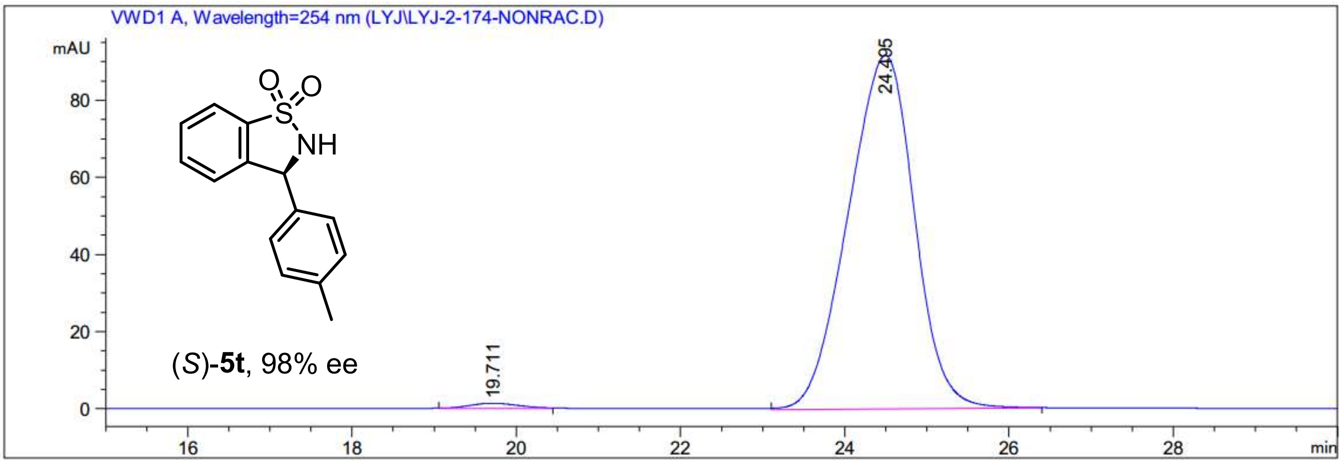
```
 #    [min]          [min]   [mAU*s]     [mAU]       %
---|-------|----|-------|----------|----------|--------|
  1  25.177 MM R  1.4429  105.35289    1.21689   1.4096
  2  29.570 MM R  1.8284 7368.85400   67.17178  98.5904
```

Figure S25. HPLC trace for the racemic reference *rac*-**5s**, and non-racemic product (*S*)-**5s** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.

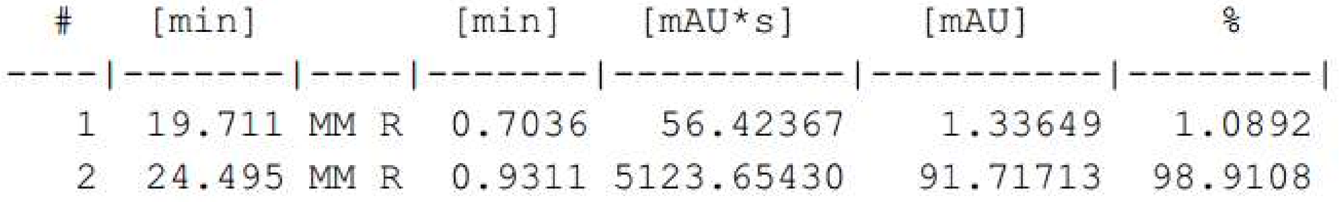


HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 70:30
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

rac-**5t**

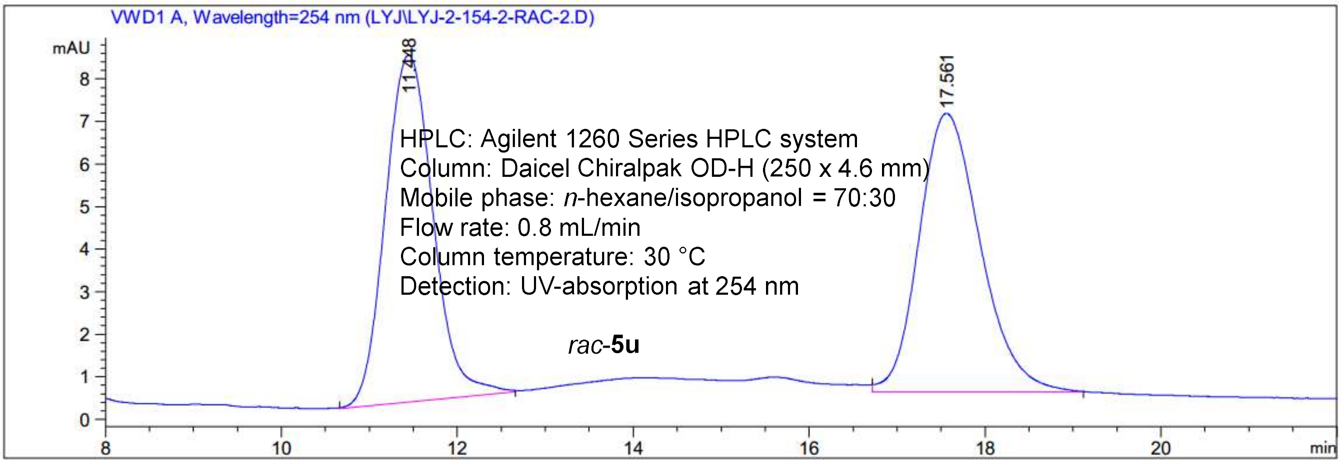


(*S*)-**5t**, 98% ee



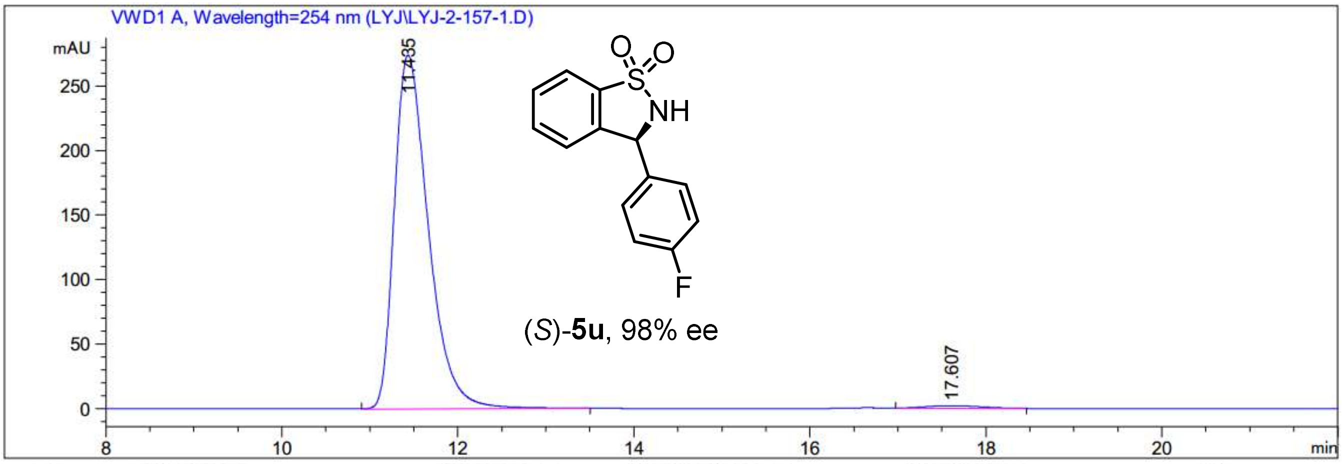
```
 #    [min]             [min]    [mAU*s]       [mAU]         %
----|-------|----|-------|----------|----------|---------|
   1  19.711 MM R  0.7036   56.42367     1.33649   1.0892
   2  24.495 MM R  0.9311 5123.65430    91.71713  98.9108
```

Figure S26. HPLC trace for the racemic reference *rac*-**5t**, and non-racemic product (*S*)-**5t** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 70:30
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

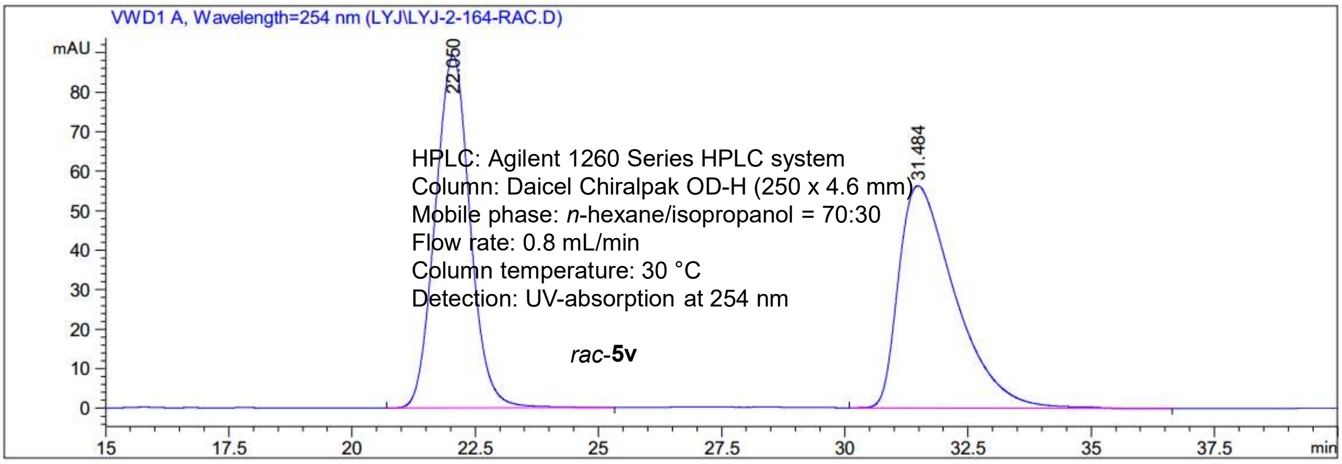
rac-**5u**

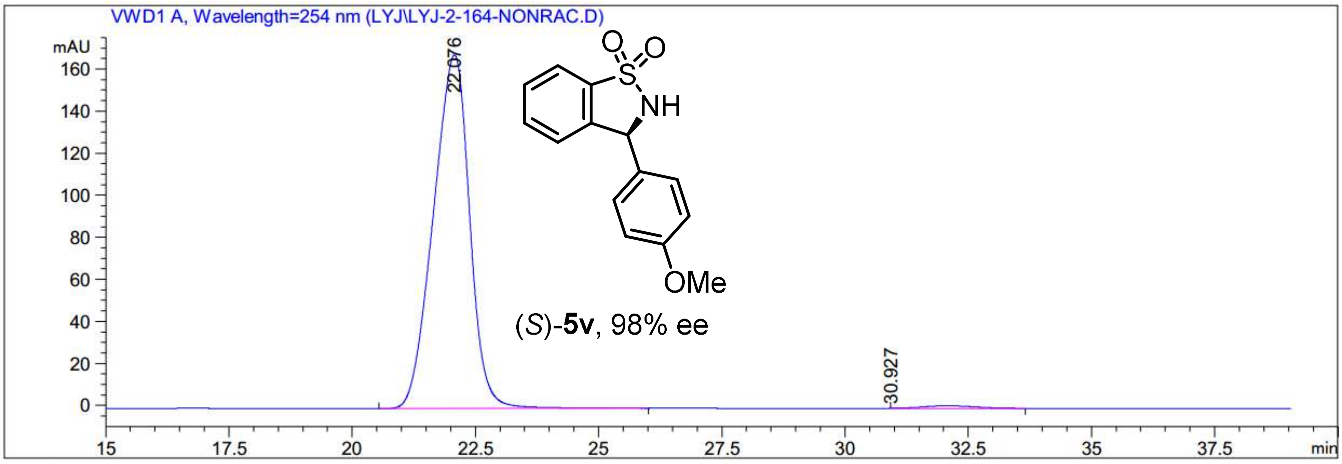


(*S*)-**5u**, 98% ee

```
  #    [min]          [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  11.435 MM R  0.4483 7368.42871  273.92953  98.8165
  2  17.607 MM R  0.7164   88.24976    2.05320   1.1835
```

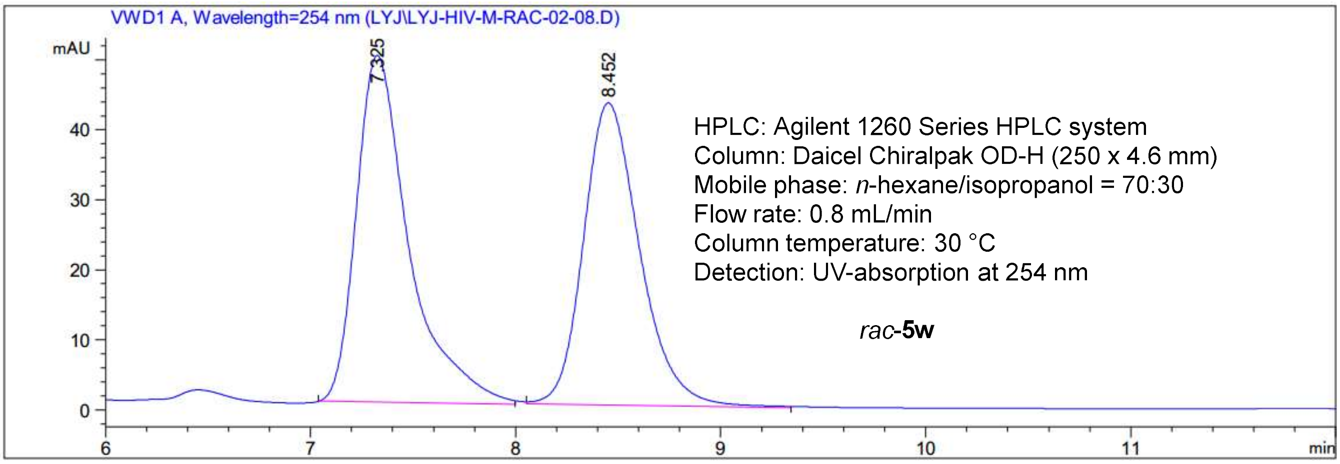
Figure S27. HPLC trace for the racemic reference *rac*-**5u**, and non-racemic product (*S*)-**5u** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.





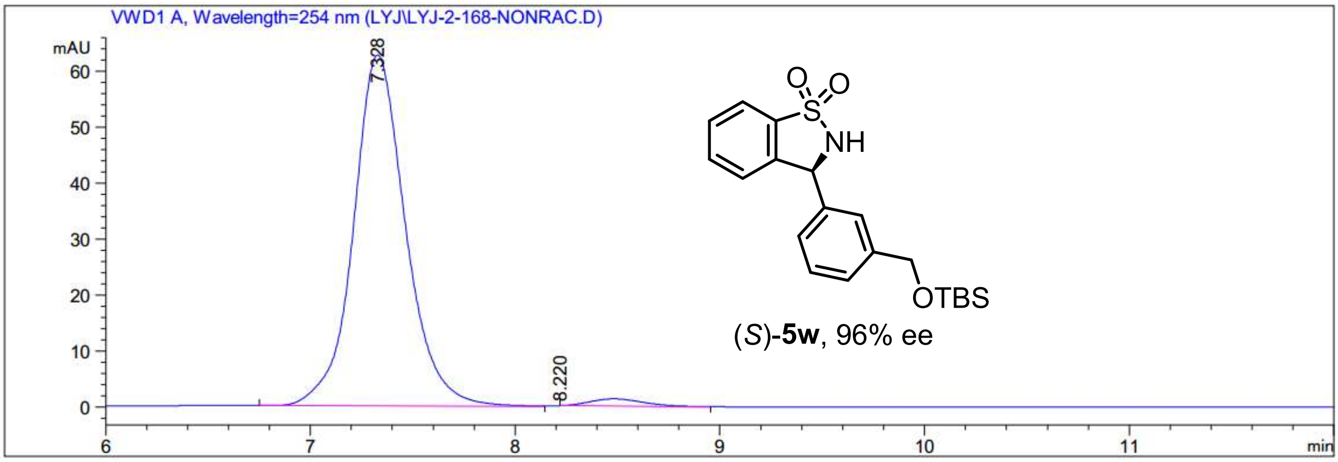
```
#    [min]            [min]    [mAU*s]        [mAU]          %
----|-------|----|-------|----------|----------|--------|
  1  22.076 BV     0.7990 8604.29102  168.14764  98.9326
  2  30.927 MM R   1.2344   92.83033 2.06865e-2   1.0674
```

Figure S28. HPLC trace for the racemic reference *rac*-**5v**, and non-racemic product (*S*)-**5v** generated from the asymmetric reaction catalyzed by Δ-**IrC1a**.

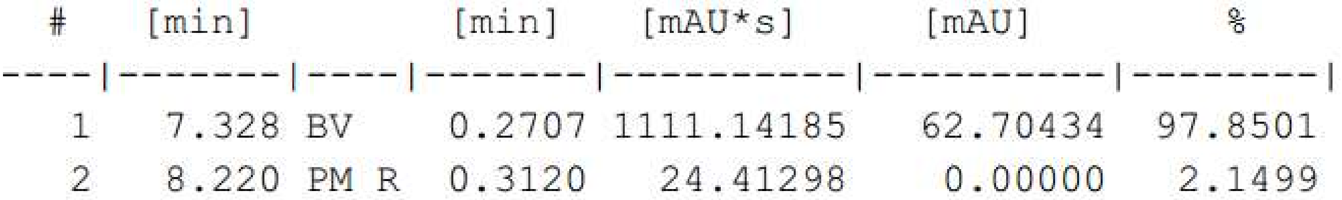


HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 70:30
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

rac-**5w**

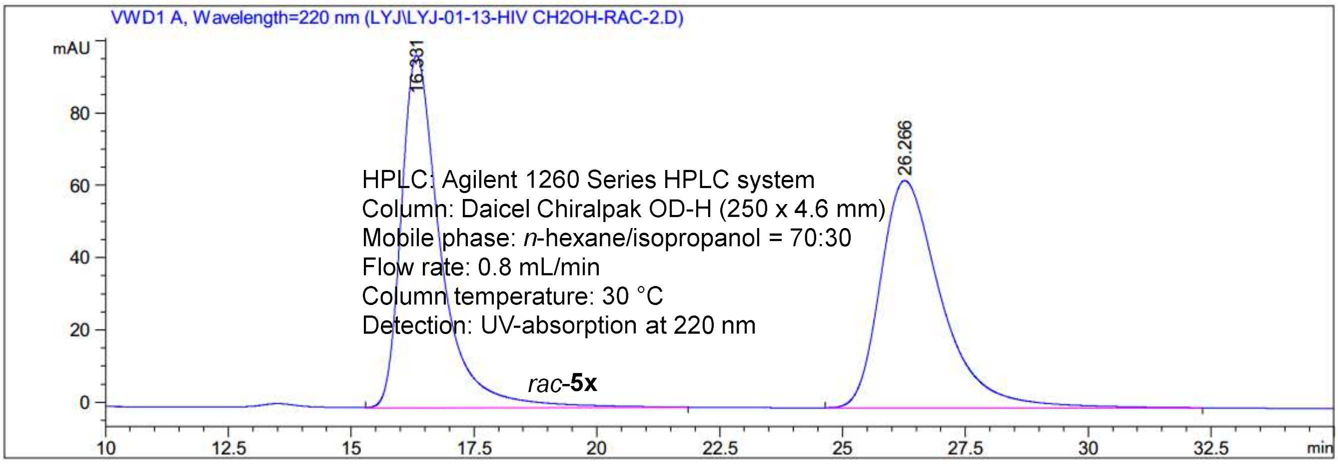


(*S*)-**5w**, 96% ee



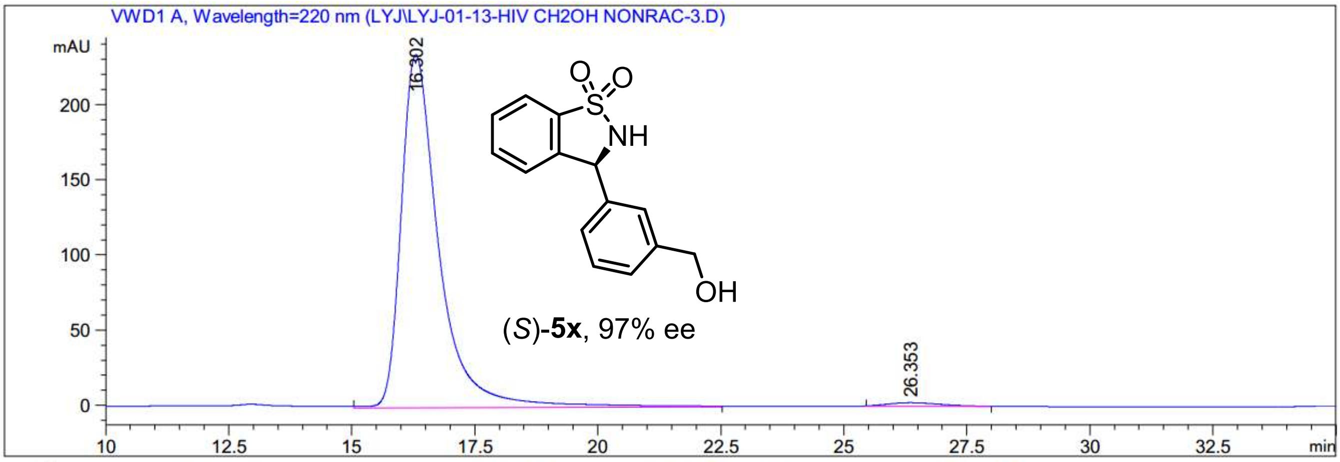
```
  #     [min]          [min]    [mAU*s]        [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1    7.328 BV     0.2707 1111.14185   62.70434   97.8501
  2    8.220 PM R   0.3120   24.41298    0.00000    2.1499
```

Figure S29. HPLC trace for the racemic reference *rac*-**5w**, and non-racemic product (*S*)-**5w** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 70:30
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 220 nm

rac-**5x**



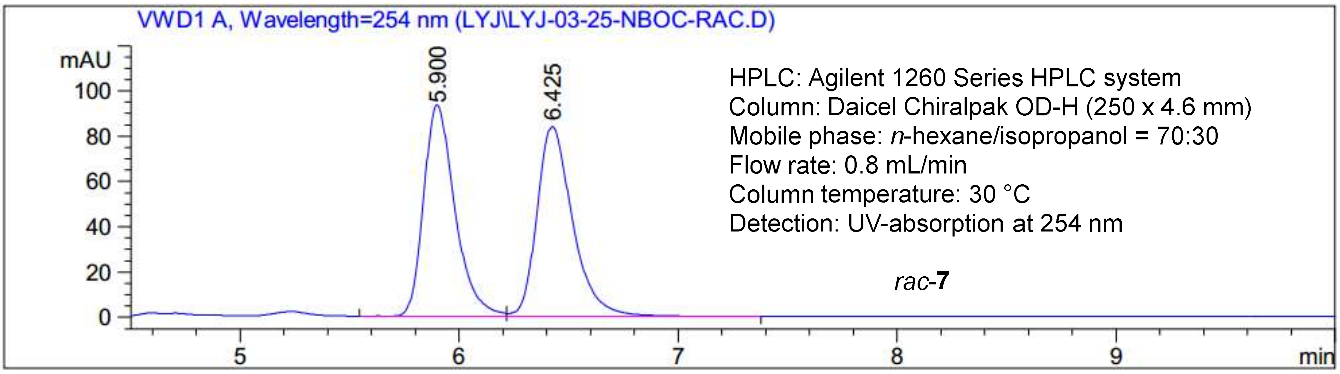
(*S*)-**5x**, 97% ee

```
 #     [min]            [min]    [mAU*s]         [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1  16.302 MM R  0.8935 1.25718e4    234.50563  98.5858
  2  26.353 MP R  1.2448  180.33557     2.41455   1.4142
```

Figure S30. HPLC trace for the racemic reference *rac*-**5x**, and non-racemic product (*S*)-**5x** generated from the asymmetric reaction catalyzed by **Δ-IrC1a**.

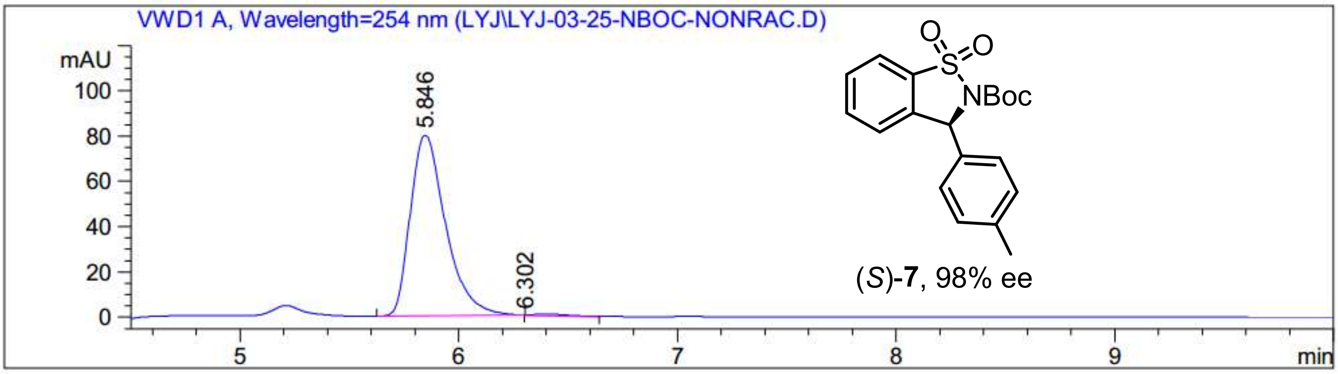
6.3 Determination of Enantiopurities of the Transformation Products

Optical purities of the compounds **5x** and **7-9** were determined with a Daicel Chiralpak OD-H or IC HPLC column on an Agilent 1260 Series HPLC System. The column temperature was 30 °C and UV-absorption was measured at 254 or 220 nm.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 70:30
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

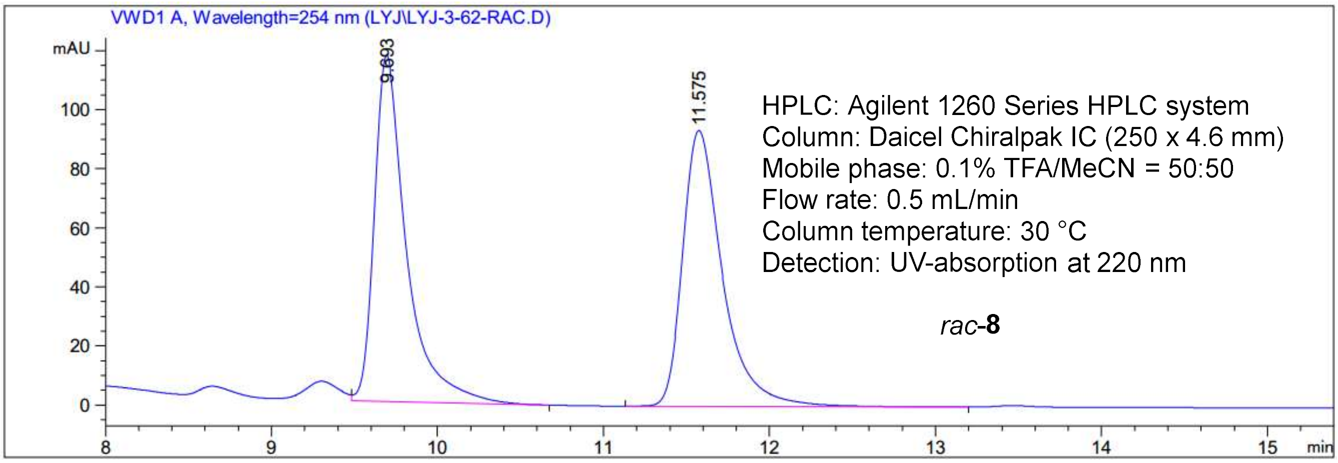
rac-**7**



(*S*)-**7**, 98% ee

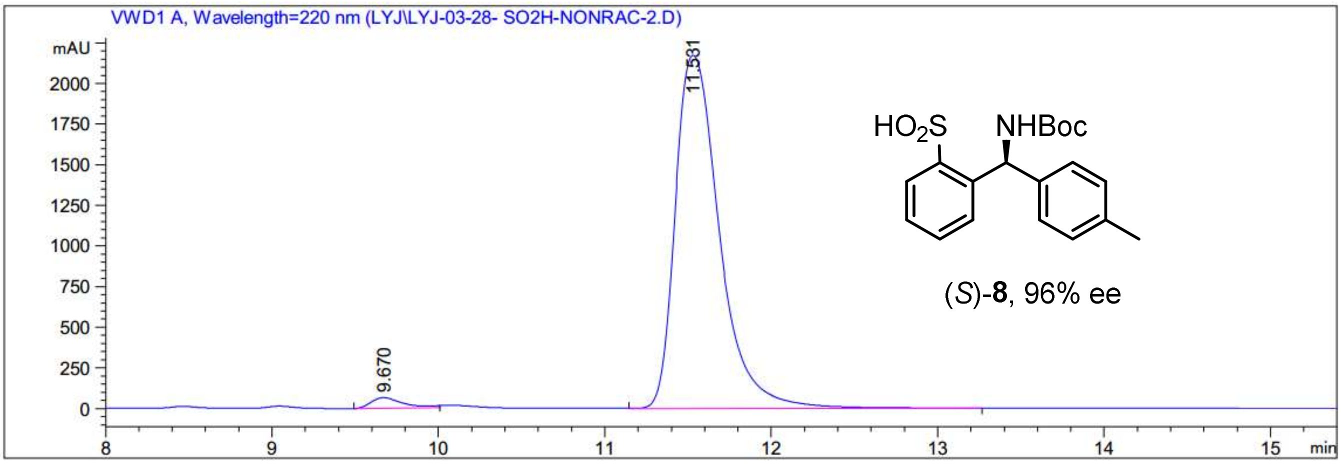
```
  #    [min]            [min]    [mAU*s]         [mAU]          %
----|-------|----|-------|----------|----------|--------|
   1    5.846 MM R   0.1872   897.65936    79.92964   98.8175
   2    6.302 MM R   0.1938    10.74202 4.47064e-1    1.1825
```

Figure S31. HPLC trace for the racemic reference *rac*-**7**, and non-racemic product (*S*)-**7**.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak IC (250 x 4.6 mm)
Mobile phase: 0.1% TFA/MeCN = 50:50
Flow rate: 0.5 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 220 nm

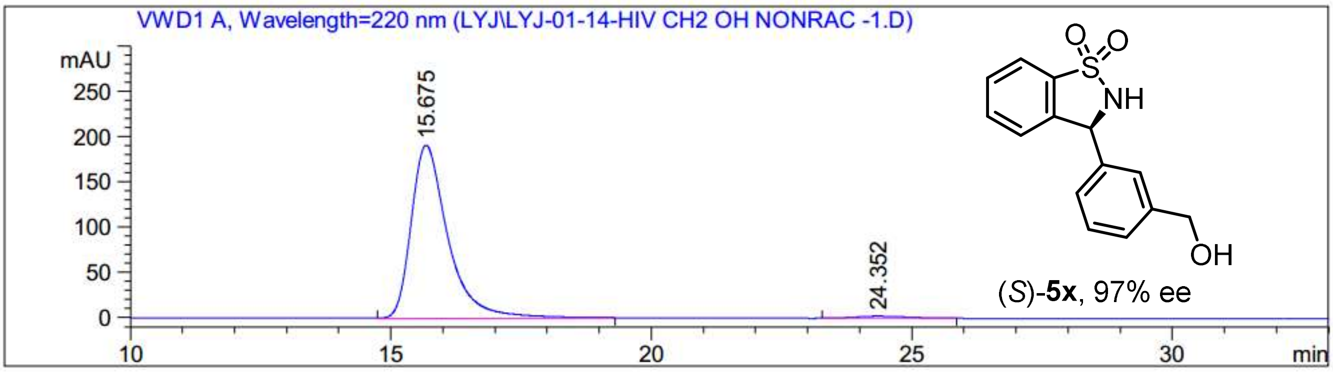
rac-**8**



(*S*)-**8**, 96% ee

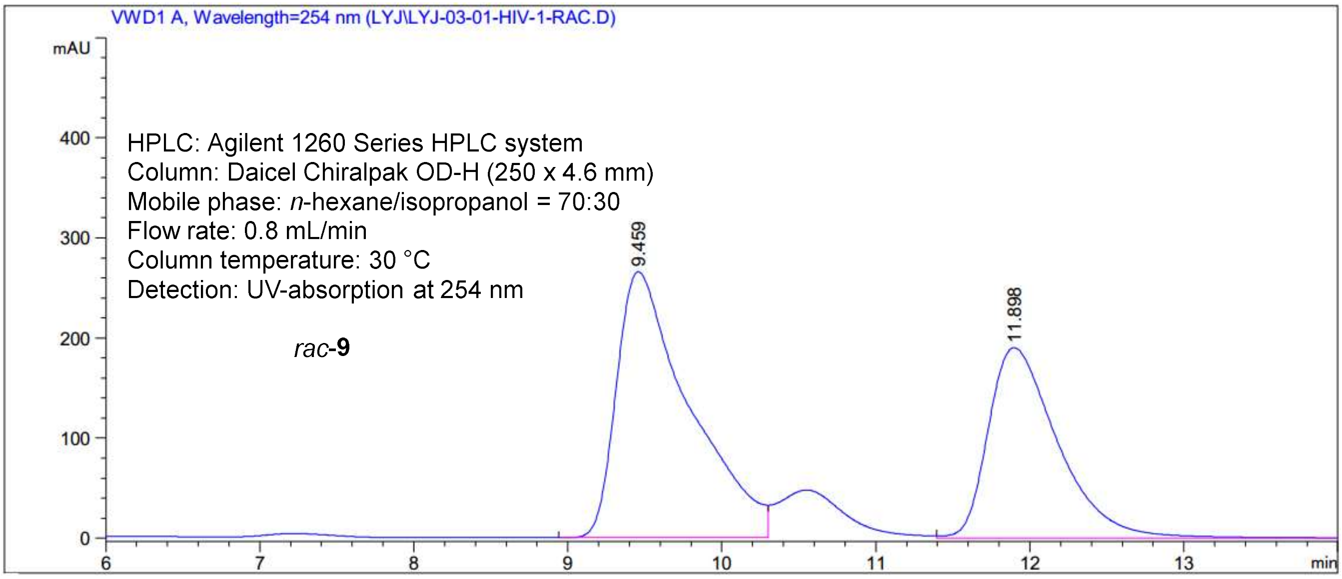
```
 #     [min]            [min]     [mAU*s]       [mAU]          %
----|-------|----|-------|----------|----------|--------|
   1    9.670 PM R  0.2217  856.84320   64.42195   2.0872
   2   11.531 MM R  0.3081 4.01955e4 2174.59497  97.9128
```

Figure S32. HPLC trace for the racemic reference *rac*-**8**, and non-racemic product (*S*)-**8**.



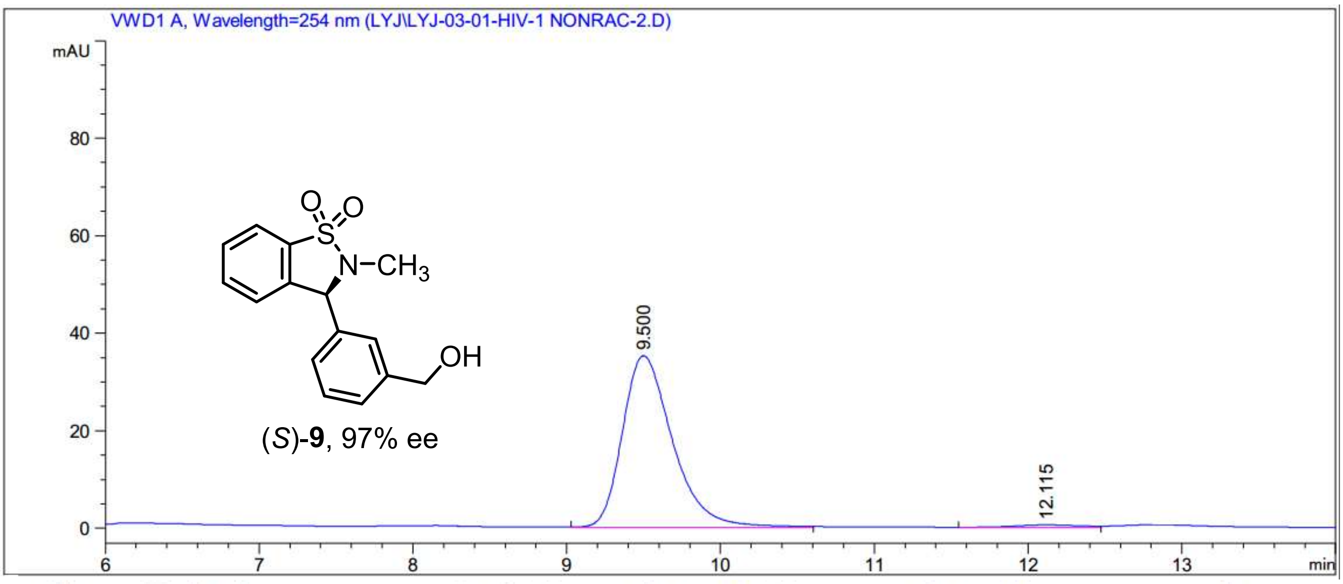
```
  #    [min]          [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  15.675 MM R  0.8262 9489.67871  191.43466  98.3484
  2  24.352 PM R  1.1527  159.36311    2.30424   1.6516
```

Figure S33. HPLC trace for non-racemic product (*S*)-**5x** at half a gram-scale generated from the asymmetric reaction catalyzed by Δ-**IrC1a**.



HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OD-H (250 x 4.6 mm)
Mobile phase: *n*-hexane/isopropanol = 70:30
Flow rate: 0.8 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

rac-**9**



(*S*)-**9**, 97% ee

```
#     [min]              [min]    [mAU*s]       [mAU]          %
----|-------|----|-------|----------|----------|--------|
   1    9.500 MM R   0.3334   806.16553   35.28566   98.2560
   2   12.115 BV     0.4103    14.30922 4.99348e-1   1.7440
```

Figure S34. HPLC trace for the racemic reference *rac*-**9**, and non-racemic product (*S*)-**9**.

7. X-Ray Diffraction of *Rac*-IrC1a

Crystallography of compound *rac*-IrC1a: Single crystals of *rac*-**IrC1a** were obtained by slow diffusion from the solution in dichloroethane layered with *n*-hexane at room temperature. Data was collected on a Bruker Smart Apex CCD area detector employing graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) at 173 K. The structure was solved by SHELXL-97.[10] Refinement was done by full-matrix least squares based on F2 data of one twin domain using SHELXL-97. The structure is shown on Figure S35. Crystallographic data for *rac*-**IrC1a** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1538578.

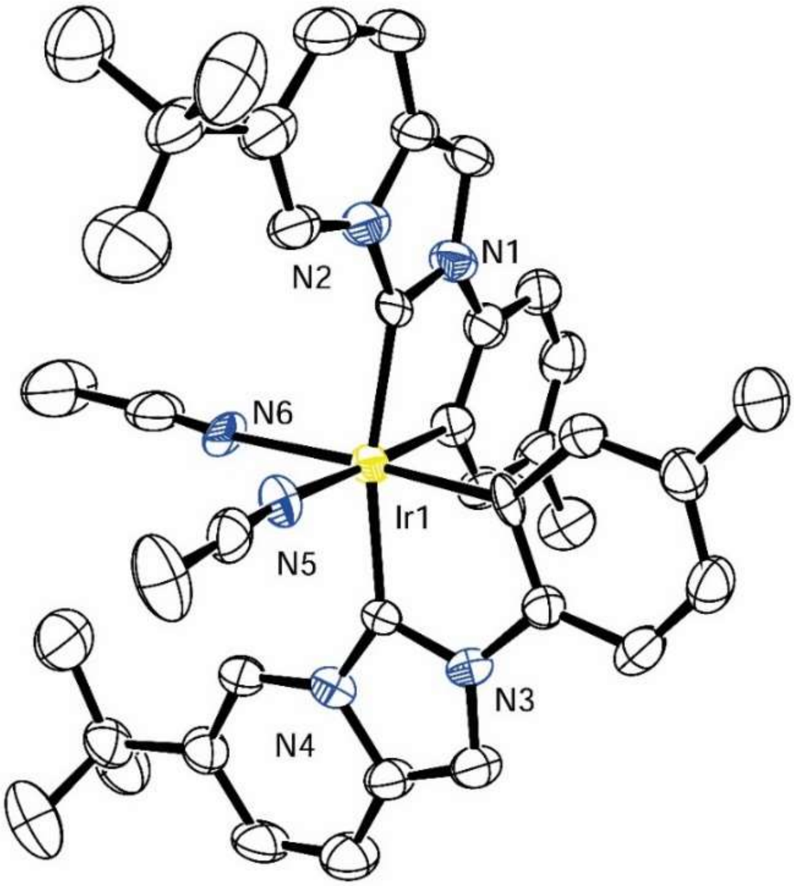


Figure S35. Crystal structure of compound *rac*-**IrC1a**.

Table S2. Crystal data and structure refinement for compound *rac*-**IrC1a**.

Identification code	lyjm	
Empirical formula	C42 H48 Cl2 F6 Ir1 P1	
Formula weight	1044.93	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 9.2337(17) Å	a= 90°
	b = 28.914(5) Å	b=102.310(3)°
	c = 16.672(3) Å	g = 90°
Volume	4348.7(14) Å^3	
Z	4	
Density (calculated)	1.596 Mg/m^3	

Absorption coefficient	3.293 mm^{-1}
F(000)	2088
Crystal size	0.32 x 0.23 x 0.15 mm^3
Theta range for data collection	1.41 to 25.99°.
Index ranges	-11<=h<=11, -35<=k<=34, -20<=l<=20
Reflections collected	16283
Independent reflections	8171 [R(int) = 0.0219]
Completeness to theta = 26.00°	99.1 %
Absorption correction	Empirical
Max. and min. transmission	0.6379 and 0.4188
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8171 / 2 / 523
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0910
R indices (all data)	R1 = 0.0364, wR2 = 0.0920
Absolute structure parameter	0.00
Largest diff. peak and hole	1.201 and -0.634 e.Å^{-3}

8. References

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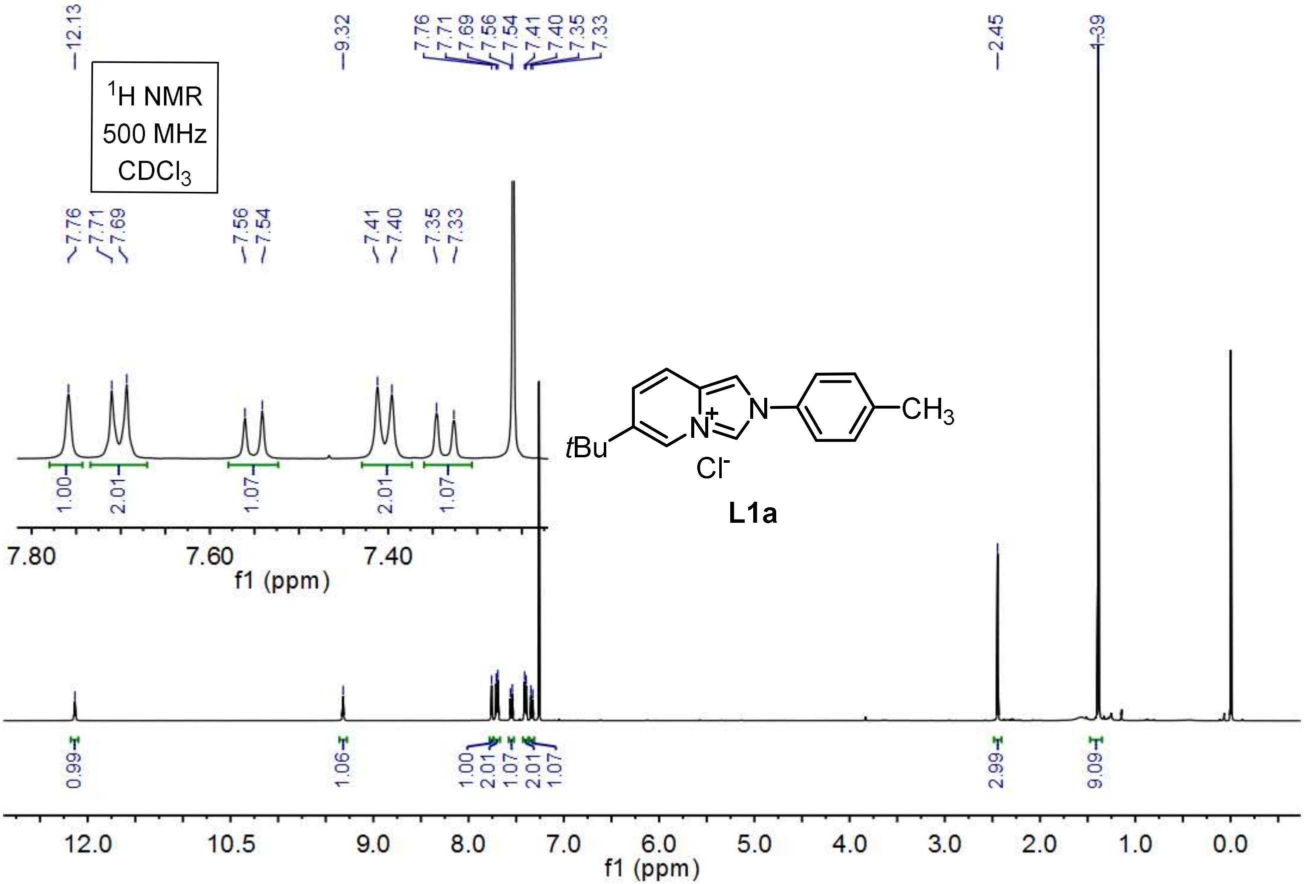
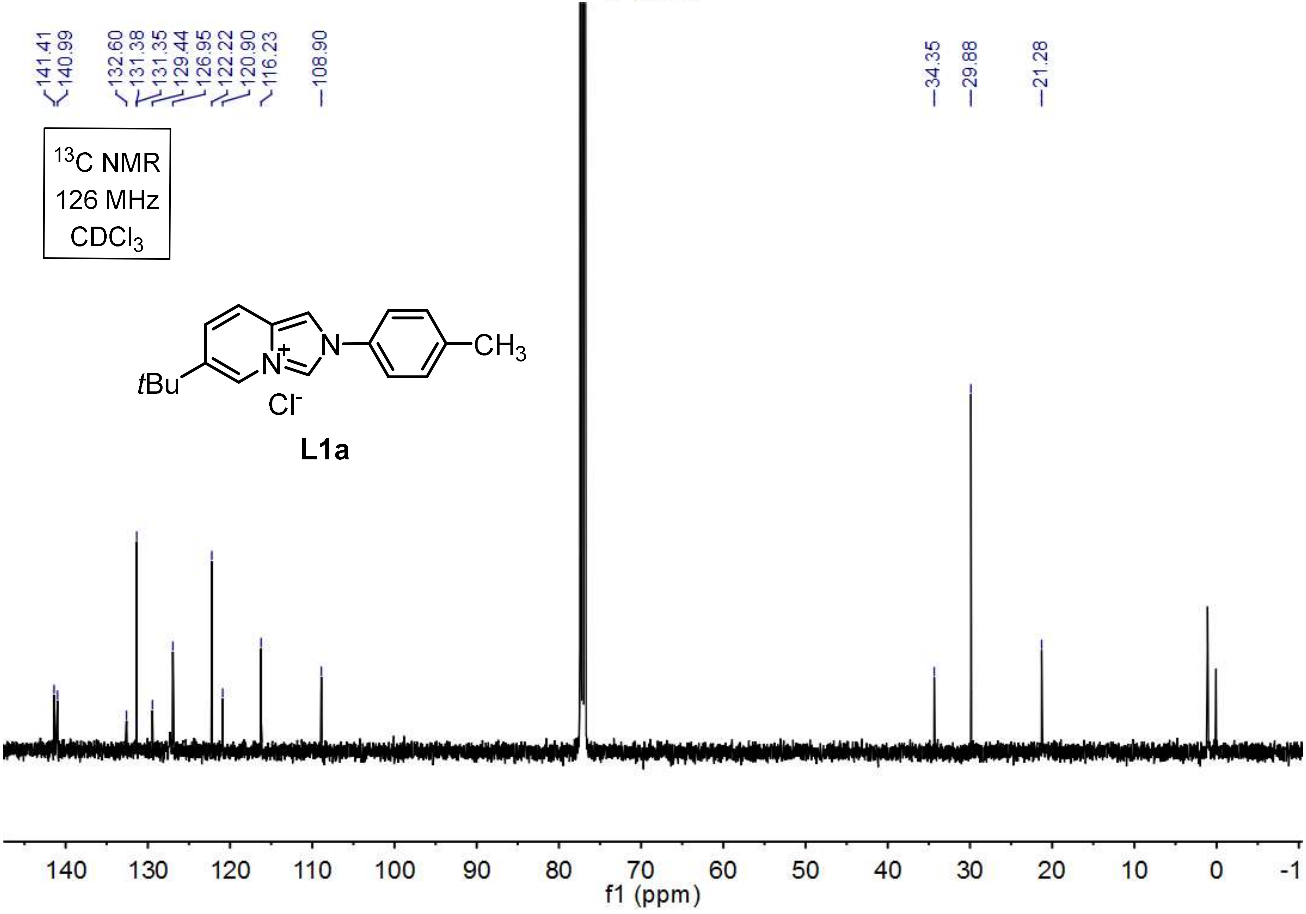
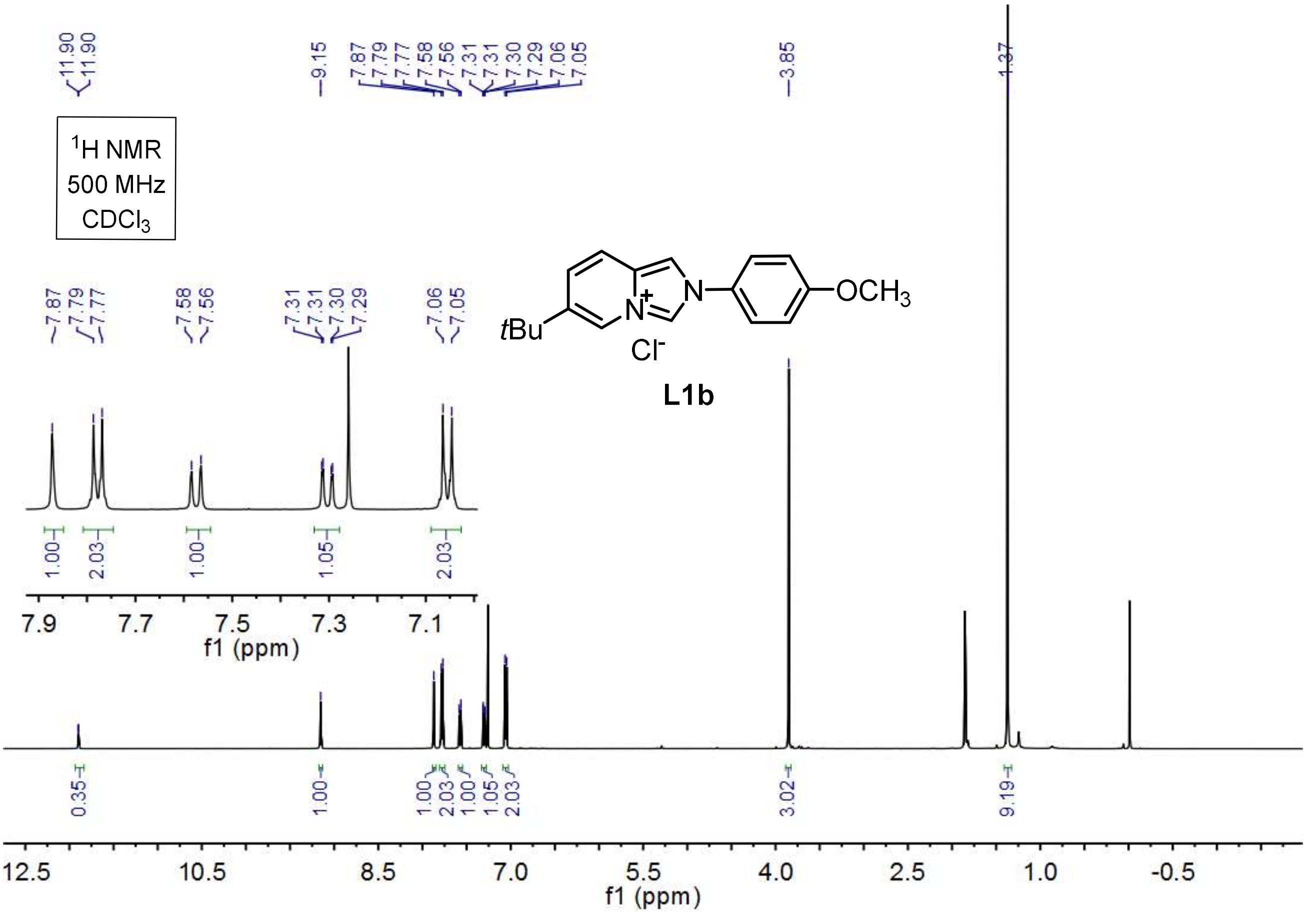
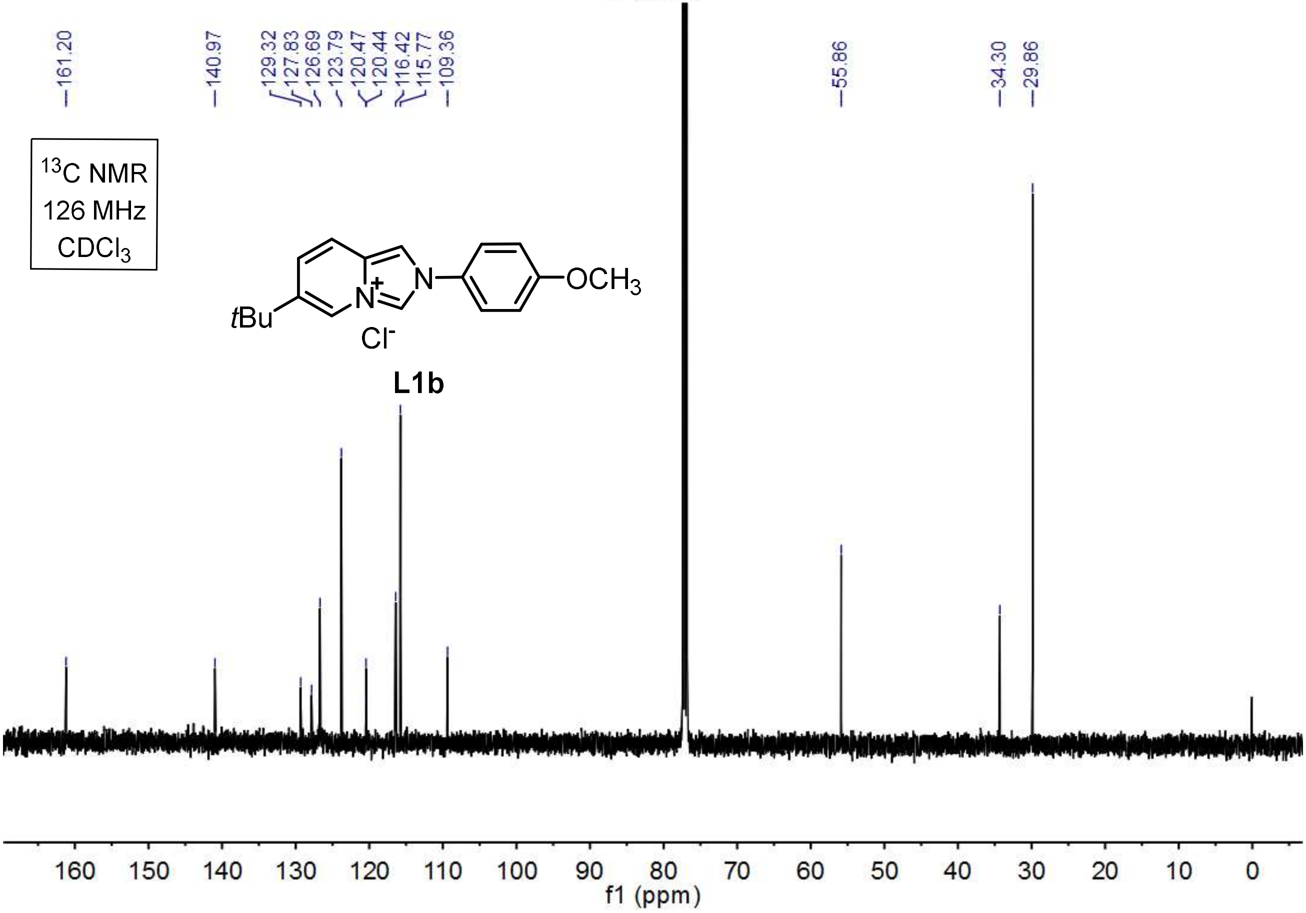
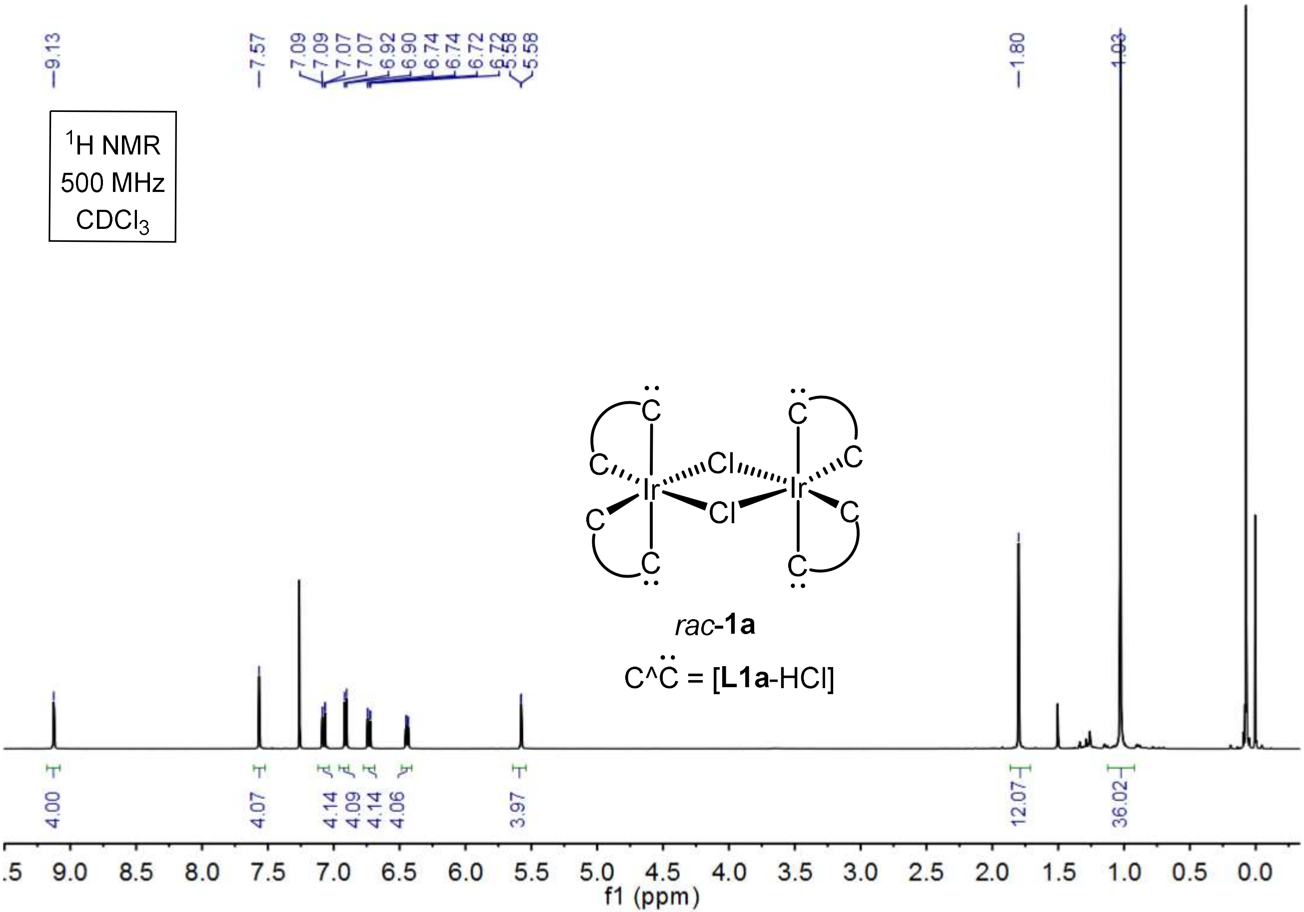
9. ^{1}H and ^{13}C NMR Spectrum





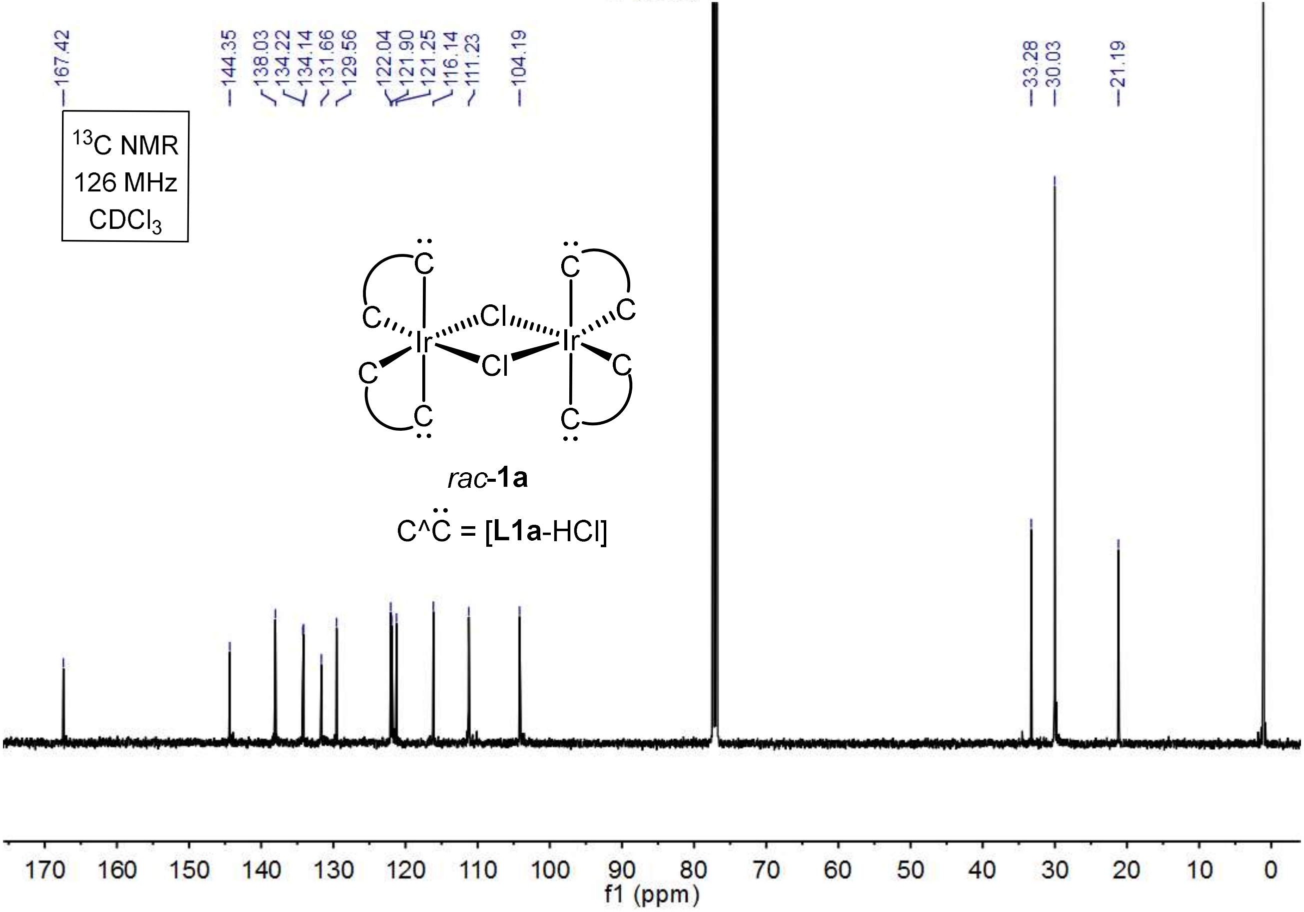

11.90
11.90
9.15
7.87
7.79
7.77
7.58
7.56
7.31
7.31
7.30
7.29
7.06
7.05
3.85
1.37
^{1}H NMR
500 MHz
$CDCl_3$
tBu
N
N
OCH_3
Cl$^-$
L1b
1.00
2.03
1.00
1.05
2.03
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
0.35
1.00
1.00
2.03
1.00
1.05
2.03
3.02
9.19
12.5
10.5
8.5
7.0
5.5
4.0
2.5
1.0
-0.5
f1 (ppm)


161.20
140.97
129.32
127.83
126.69
123.79
120.47
120.44
116.42
115.77
109.36
55.86
34.30
29.86
^{13}C NMR
126 MHz
$CDCl_3$
tBu
N
N
OCH_3
Cl$^-$
L1b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



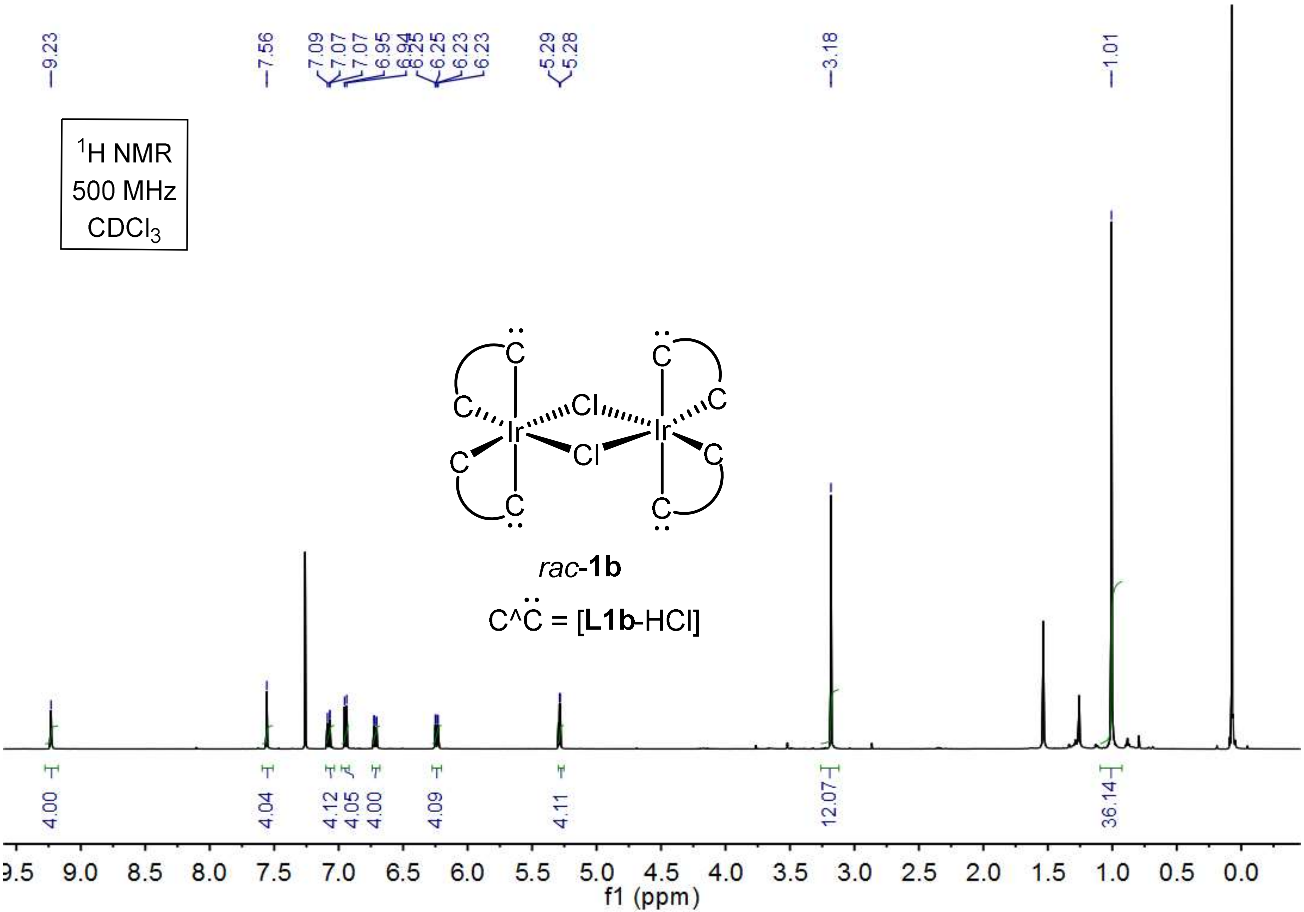
rac-**1a**

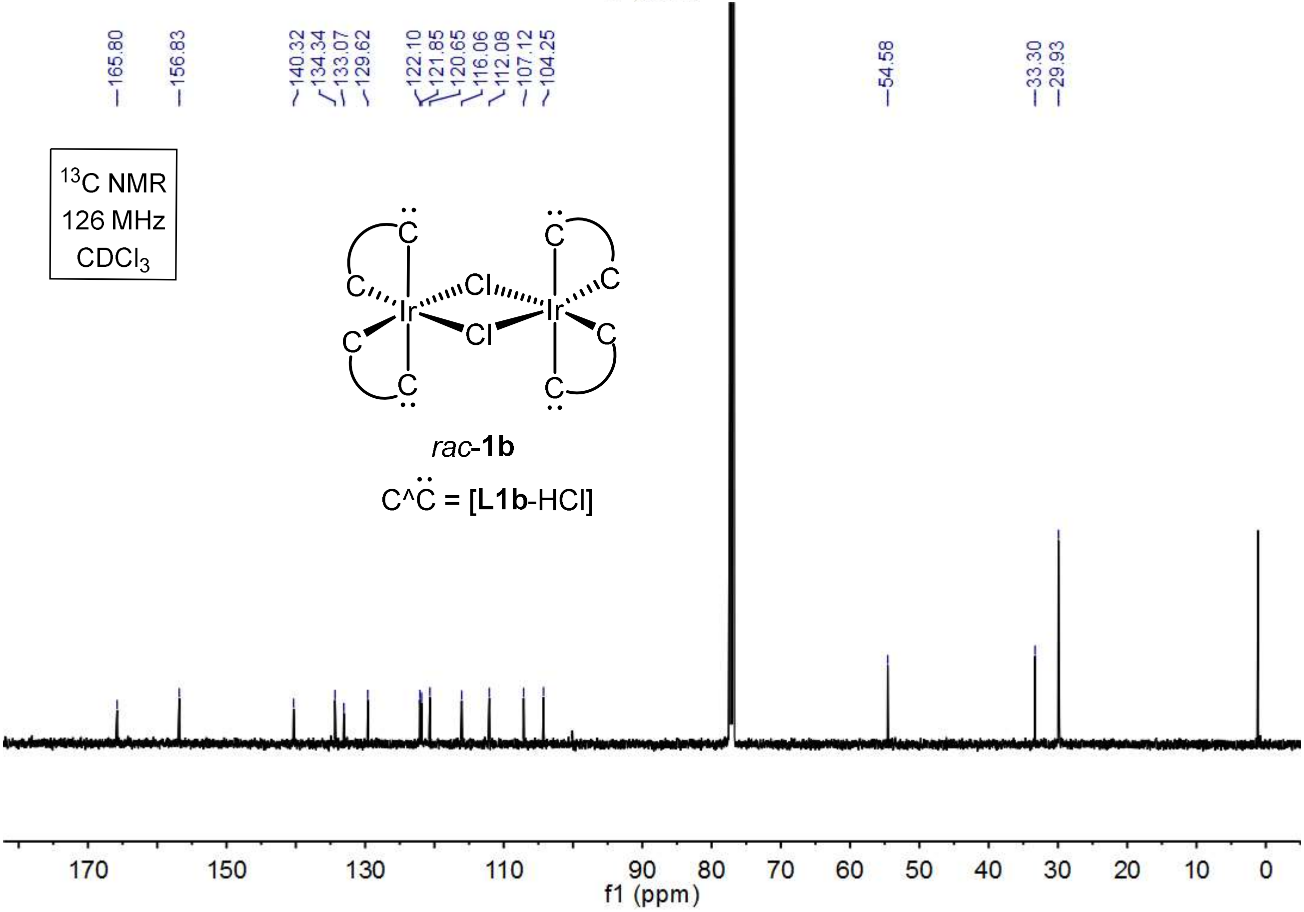
C^C̈ = [**L1a**-HCl]

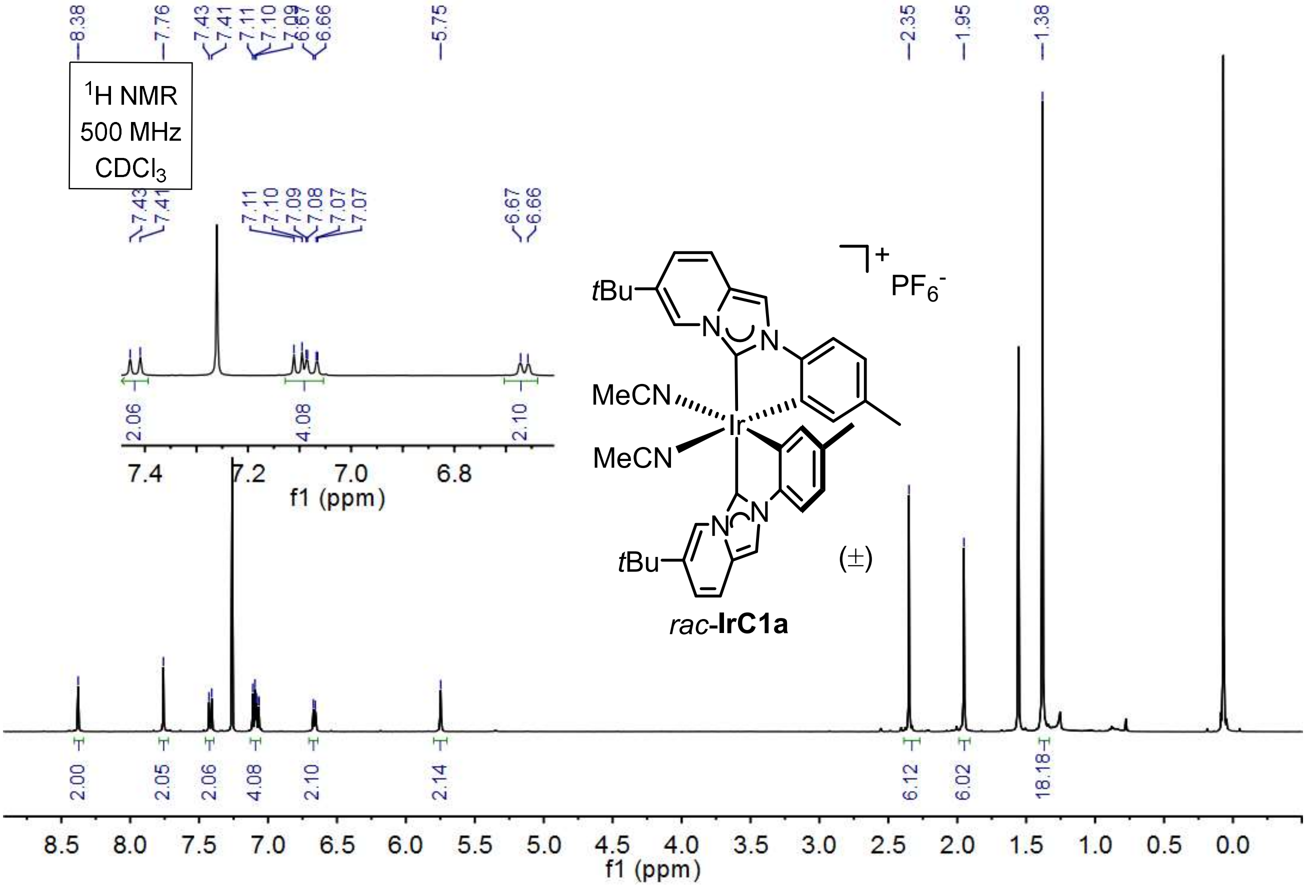


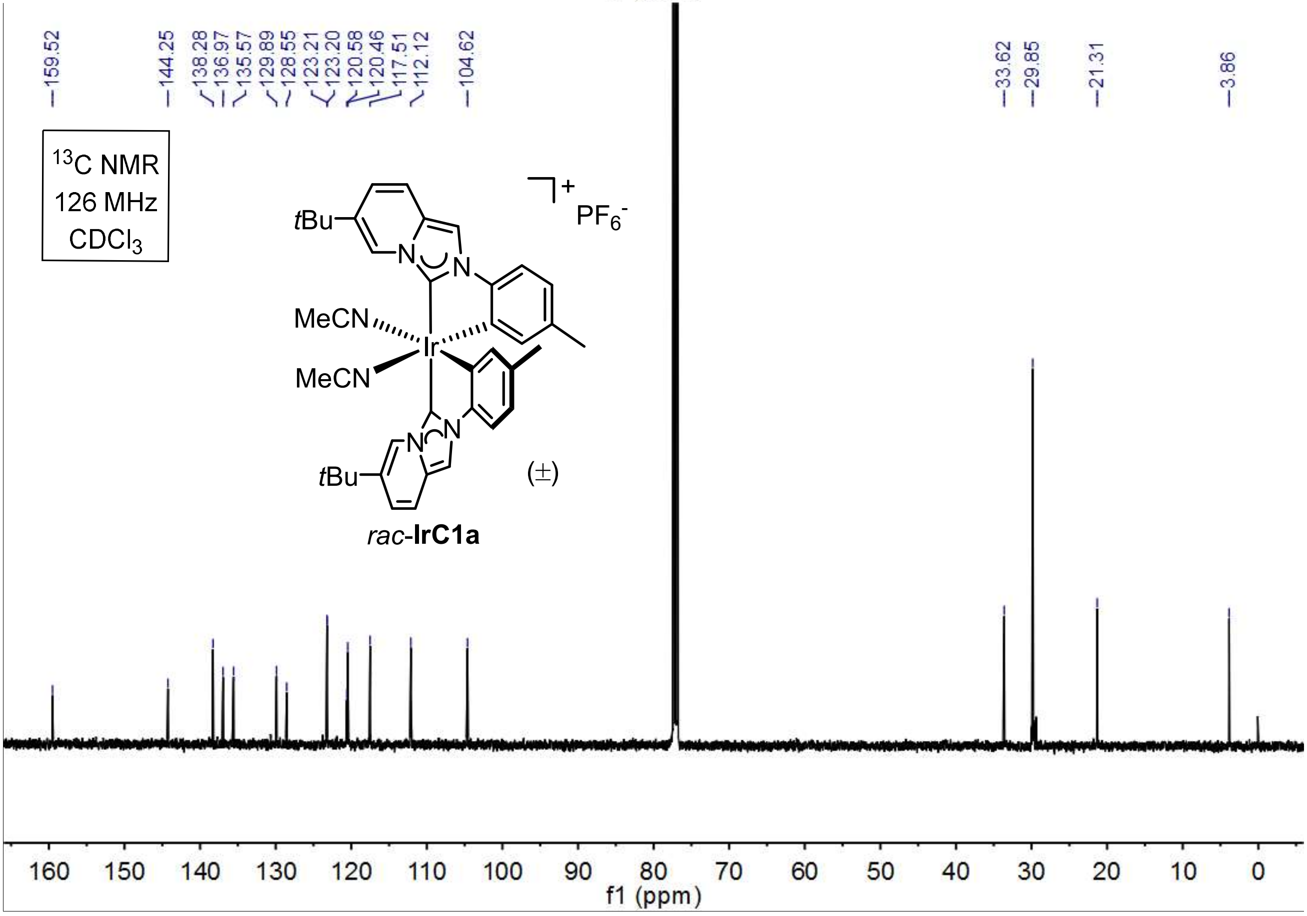
rac-**1a**

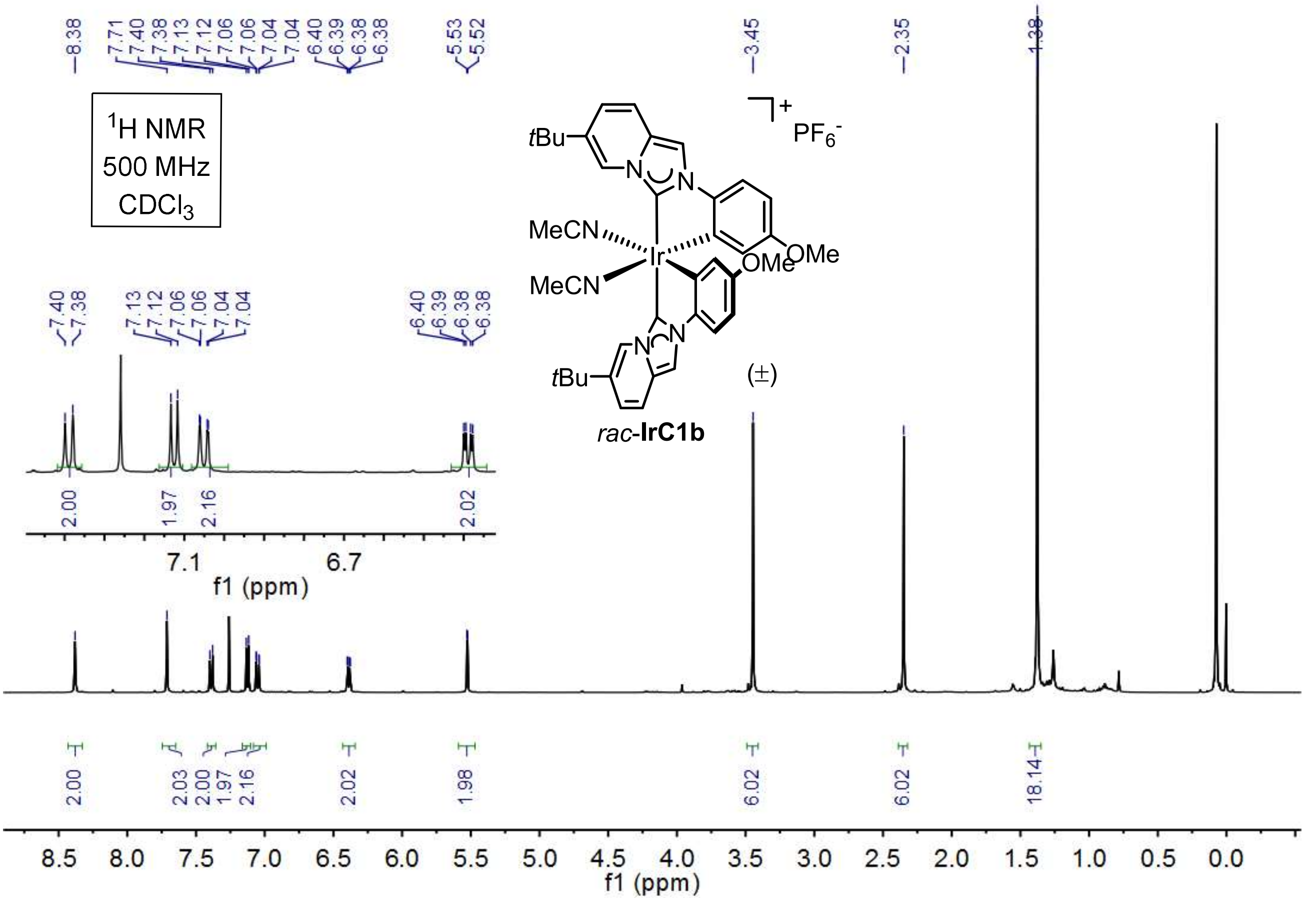
C^C̈ = [**L1a**-HCl]

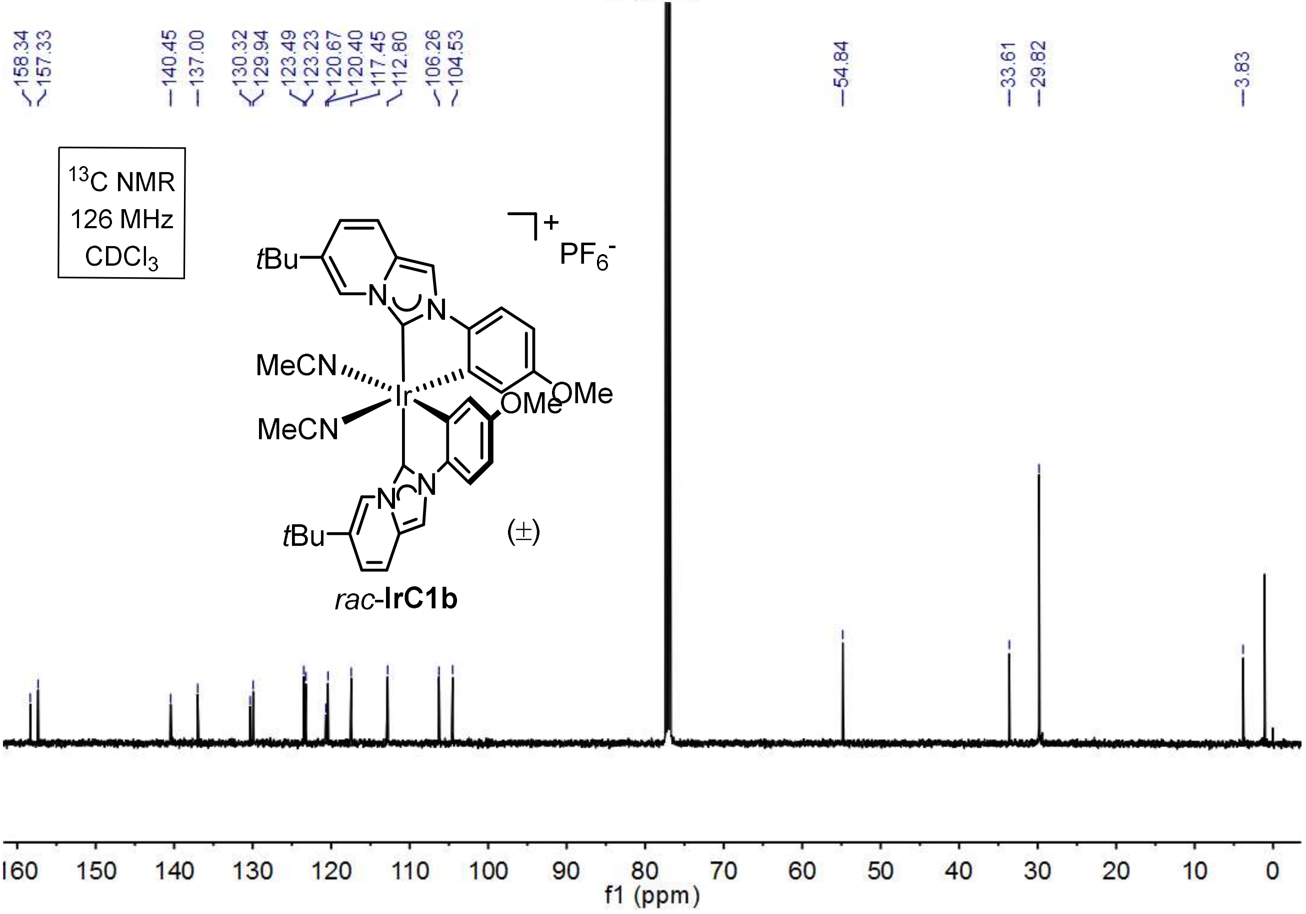

9.23
7.56
7.09
7.07
7.07
6.95
6.94
6.25
6.25
6.23
6.23
5.29
5.28
3.18
1.01
^{1}H NMR
500 MHz
CDCl$_3$
C
Cl
Ir
rac-1b
C^C̈ = [L1b-HCl]
4.00
4.04
4.12
4.05
4.00
4.09
4.11
12.07
36.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

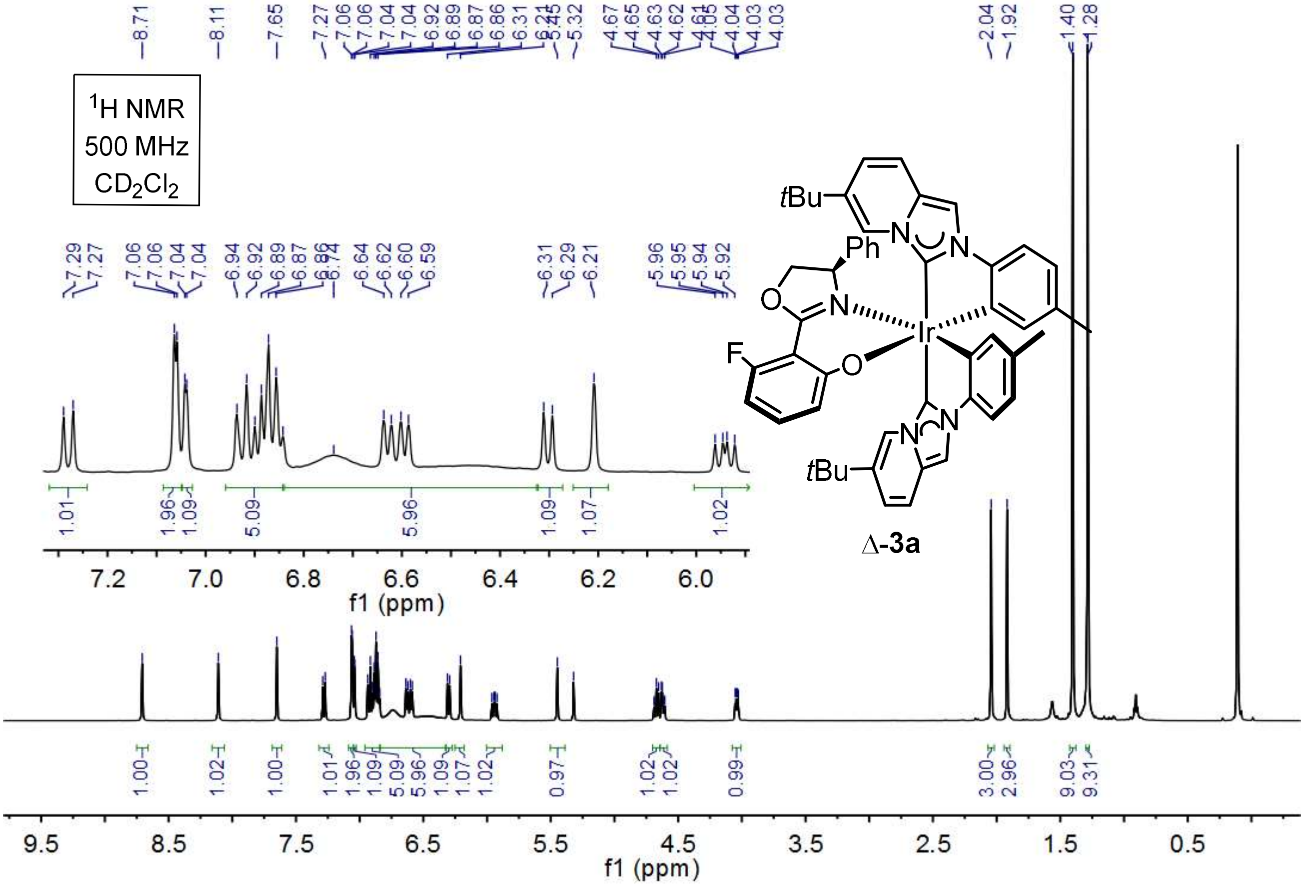

165.80
156.83
140.32
134.34
133.07
129.62
122.10
121.85
120.65
116.06
112.08
107.12
104.25
54.58
33.30
29.93
^{13}C NMR
126 MHz
CDCl$_3$
C
Cl
Ir
rac-1b
C^C̈ = [L1b-HCl]
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

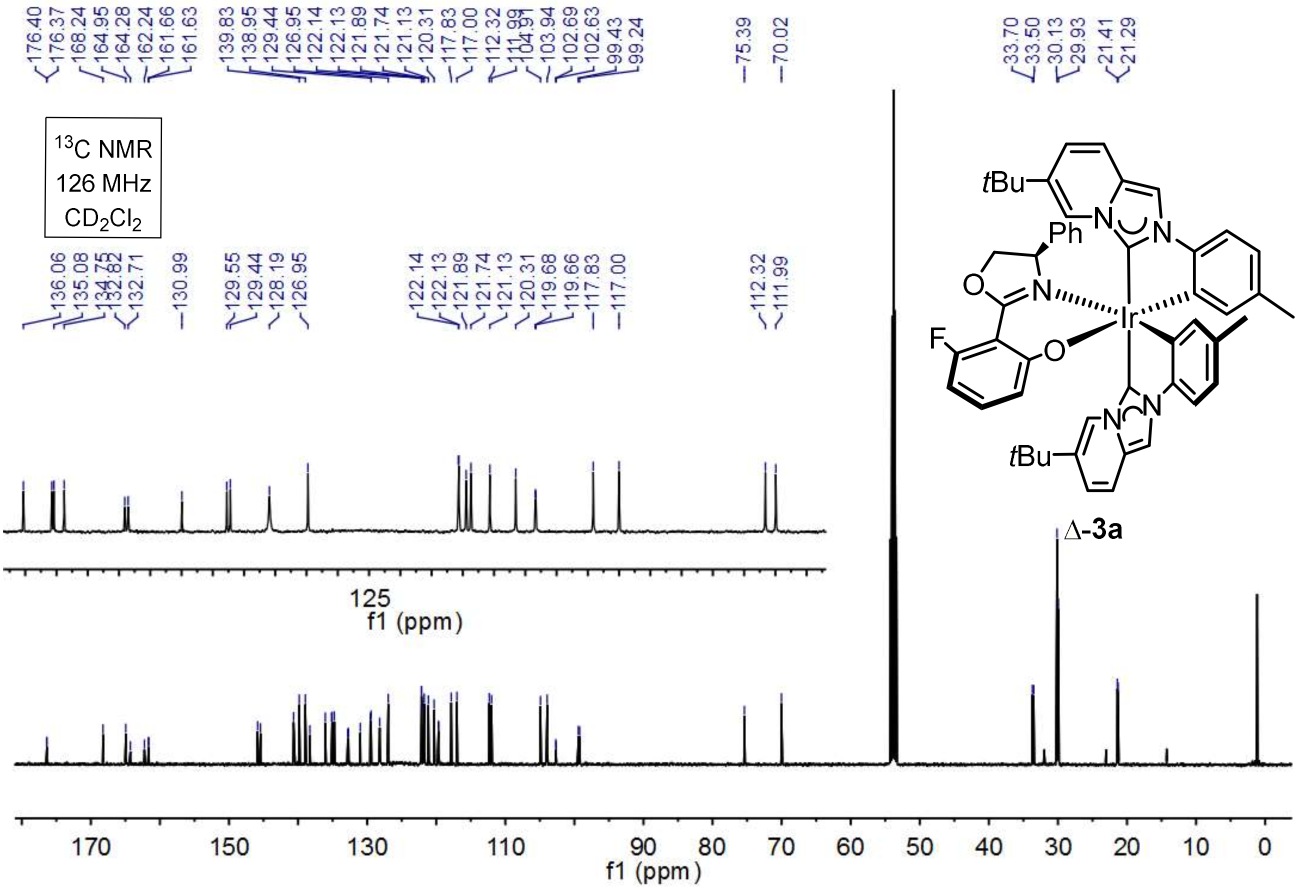

8.38
7.76
7.43
7.41
7.11
7.10
7.09
6.67
6.66
5.75
2.35
1.95
1.38
^{1}H NMR
500 MHz
$CDCl_3$
7.43
7.41
7.11
7.10
7.09
7.08
7.07
7.07
6.67
6.66
2.06
4.08
2.10
7.4
7.2
7.0
6.8
f1 (ppm)
tBu
tBu
N
N
MeCN
MeCN
Ir
+
PF_6^-
(±)
rac-IrC1a
2.00
2.05
2.06
4.08
2.10
2.14
6.12
6.02
18.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

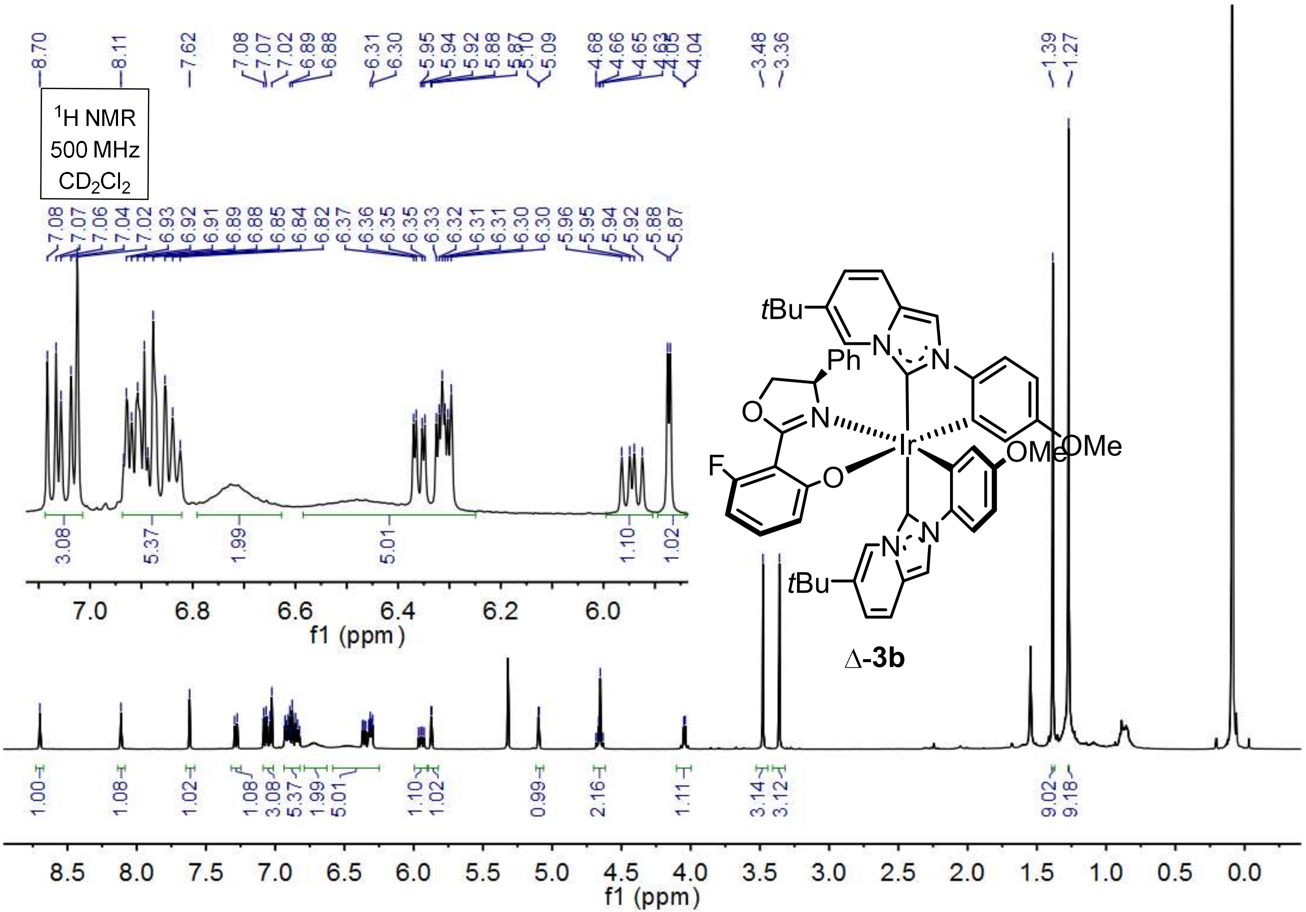

159.52
144.25
138.28
136.97
135.57
129.89
128.55
123.21
123.20
120.58
120.46
117.51
112.12
104.62
33.62
29.85
21.31
3.86
^{13}C NMR
126 MHz
$CDCl_3$
tBu
tBu
N
N
MeCN
MeCN
Ir
+
PF_6^-
(±)
rac-IrC1a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.38
7.71
7.40
7.38
7.13
7.12
7.06
7.06
7.04
7.04
6.40
6.39
6.38
6.38
5.53
5.52
3.45
2.35
1.38
1H NMR
500 MHz
CDCl3
tBu
PF6-
+
MeCN
MeCN
Ir
OMe
OMe
N
N
tBu
(±)
rac-IrC1b
2.00
1.97
2.16
2.02
7.1
6.7
f1 (ppm)
2.00
2.03
2.00
1.97
2.16
2.02
1.98
6.02
6.02
18.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.34
157.33
140.45
137.00
130.32
129.94
123.49
123.23
120.67
120.40
117.45
112.80
106.26
104.53
54.84
33.61
29.82
3.83
13C NMR
126 MHz
CDCl3
tBu
PF6-
+
MeCN
MeCN
Ir
OMe
OMe
N
N
tBu
(±)
rac-IrC1b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

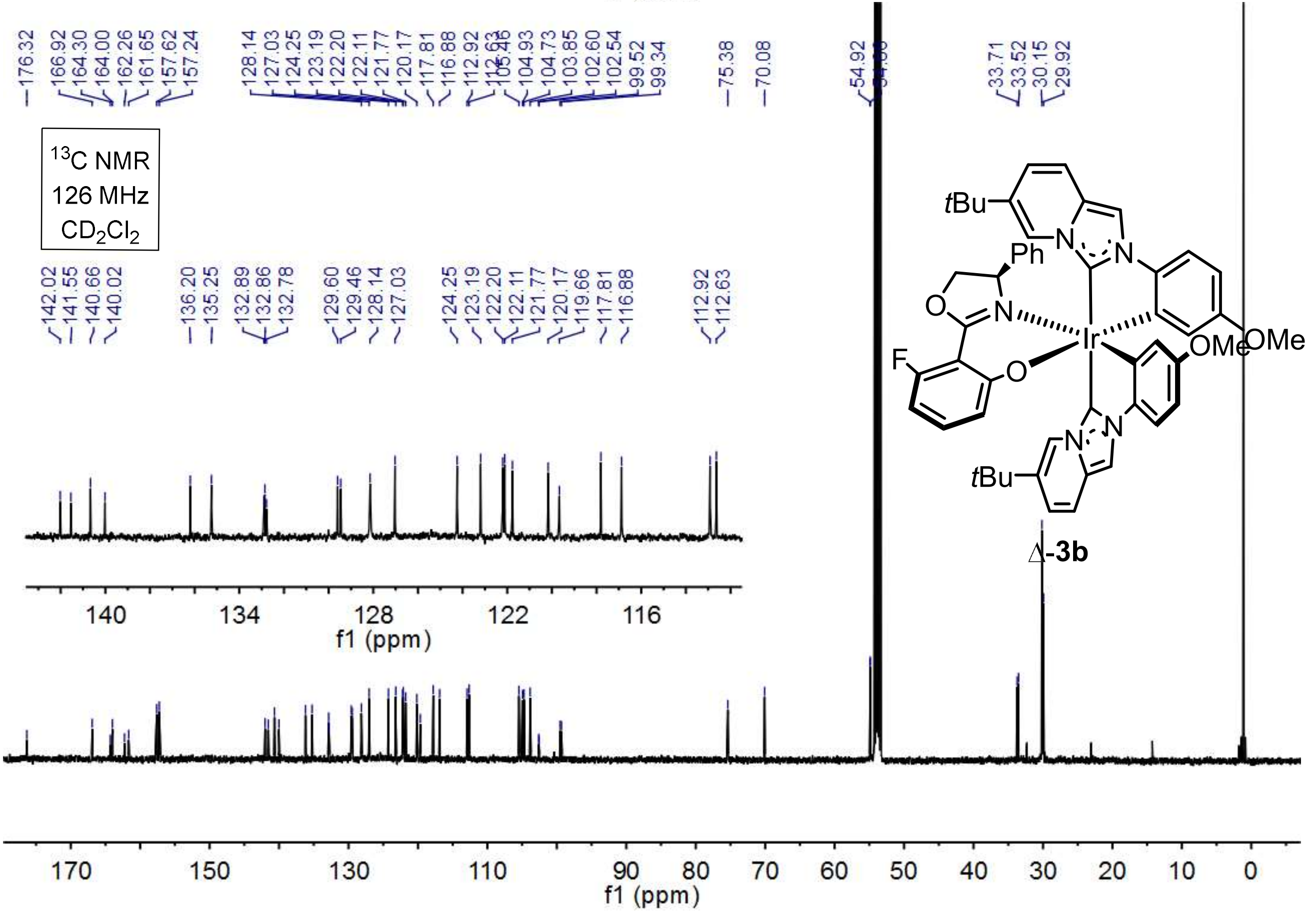

8.71
8.11
7.65
7.27
7.06
7.06
7.04
7.04
6.92
6.89
6.87
6.86
6.31
6.21
5.45
5.32
4.67
4.65
4.63
4.62
4.61
4.05
4.04
4.03
4.03
2.04
1.92
1.40
1.28
1H NMR
500 MHz
CD2Cl2
7.29
7.27
7.06
7.06
7.04
7.04
6.94
6.92
6.89
6.87
6.86
6.74
6.64
6.62
6.60
6.59
6.31
6.29
6.21
5.96
5.95
5.94
5.92
1.01
1.96
1.09
5.09
5.96
1.09
1.07
1.02
7.2
7.0
6.8
6.6
6.4
6.2
6.0
f1 (ppm)
tBu
Ph
N
N
O
N
Ir
F
O
N
N
tBu
Δ-3a
1.00
1.02
1.00
1.01
1.96
1.09
5.09
5.96
1.09
1.07
1.02
0.97
1.02
1.02
0.99
3.00
2.96
9.03
9.31
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


176.40
176.37
168.24
164.95
164.28
162.24
161.66
161.63
139.83
138.95
129.44
126.95
122.14
122.13
121.89
121.74
121.13
120.31
117.83
117.00
112.32
111.99
104.91
103.94
102.69
102.63
99.43
99.24
75.39
70.02
33.70
33.50
30.13
29.93
21.41
21.29
13C NMR
126 MHz
CD2Cl2
136.06
135.08
134.75
132.82
132.71
130.99
129.55
129.44
128.19
126.95
122.14
122.13
121.89
121.74
121.13
120.31
119.68
119.66
117.83
117.00
112.32
111.99
125
f1 (ppm)
tBu
Ph
N
N
O
N
Ir
F
O
N
N
tBu
Δ-3a
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



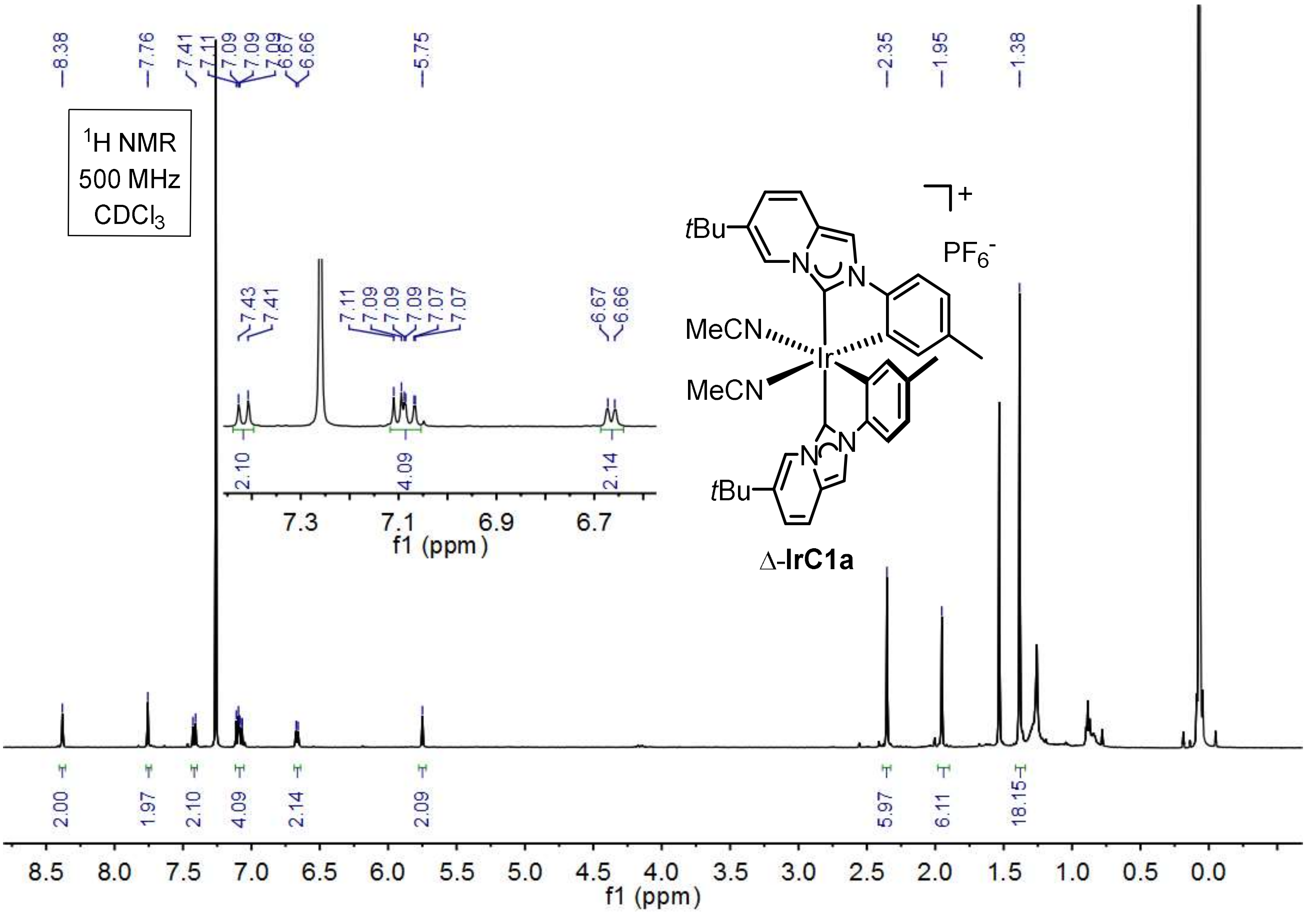
Δ-3b

^{1}H NMR
500 MHz
CD_2Cl_2
8.70 8.11 7.62 7.08 7.07 7.02 6.89 6.88 6.31 6.30 5.95 5.94 5.92 5.88 5.87 5.10 5.09 4.68 4.66 4.65 4.63 4.05 4.04 3.48 3.36 1.39 1.27
7.08 7.07 7.06 7.04 7.02 6.93 6.92 6.91 6.89 6.88 6.85 6.84 6.82 6.37 6.36 6.35 6.35 6.33 6.32 6.31 6.31 6.30 6.30 5.96 5.95 5.94 5.92 5.88 5.87
3.08 5.37 1.99 5.01 1.10 1.02
7.0 6.8 6.6 6.4 6.2 6.0
f1 (ppm)
tBu
Ph
N
N
O
N
Ir
F
O
OMe
OMe
N
N
tBu
1.00 1.08 1.02 1.08 3.08 5.37 1.99 5.01 1.10 1.02 0.99 2.16 1.11 3.14 3.12 9.02 9.18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

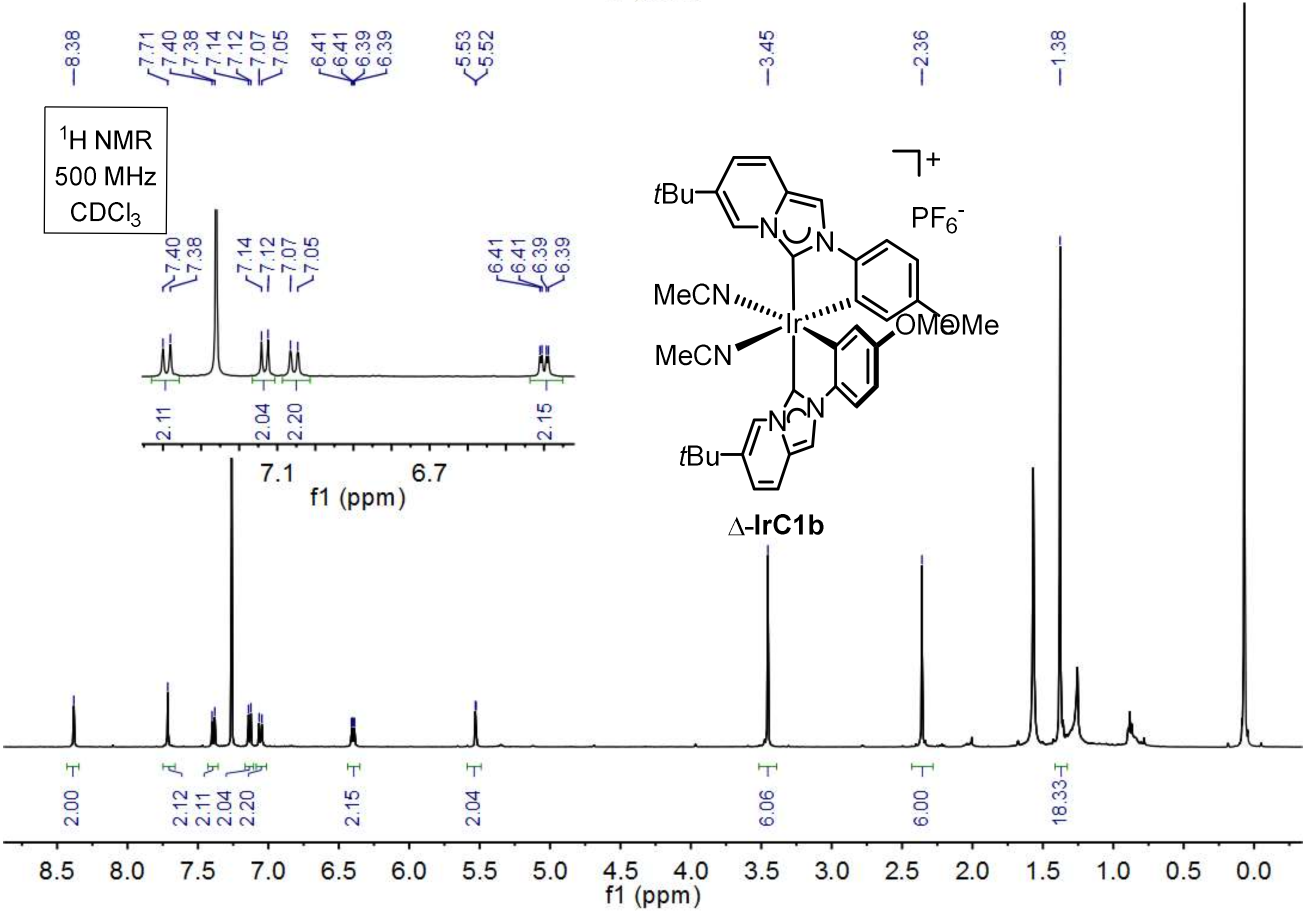


Δ-3b

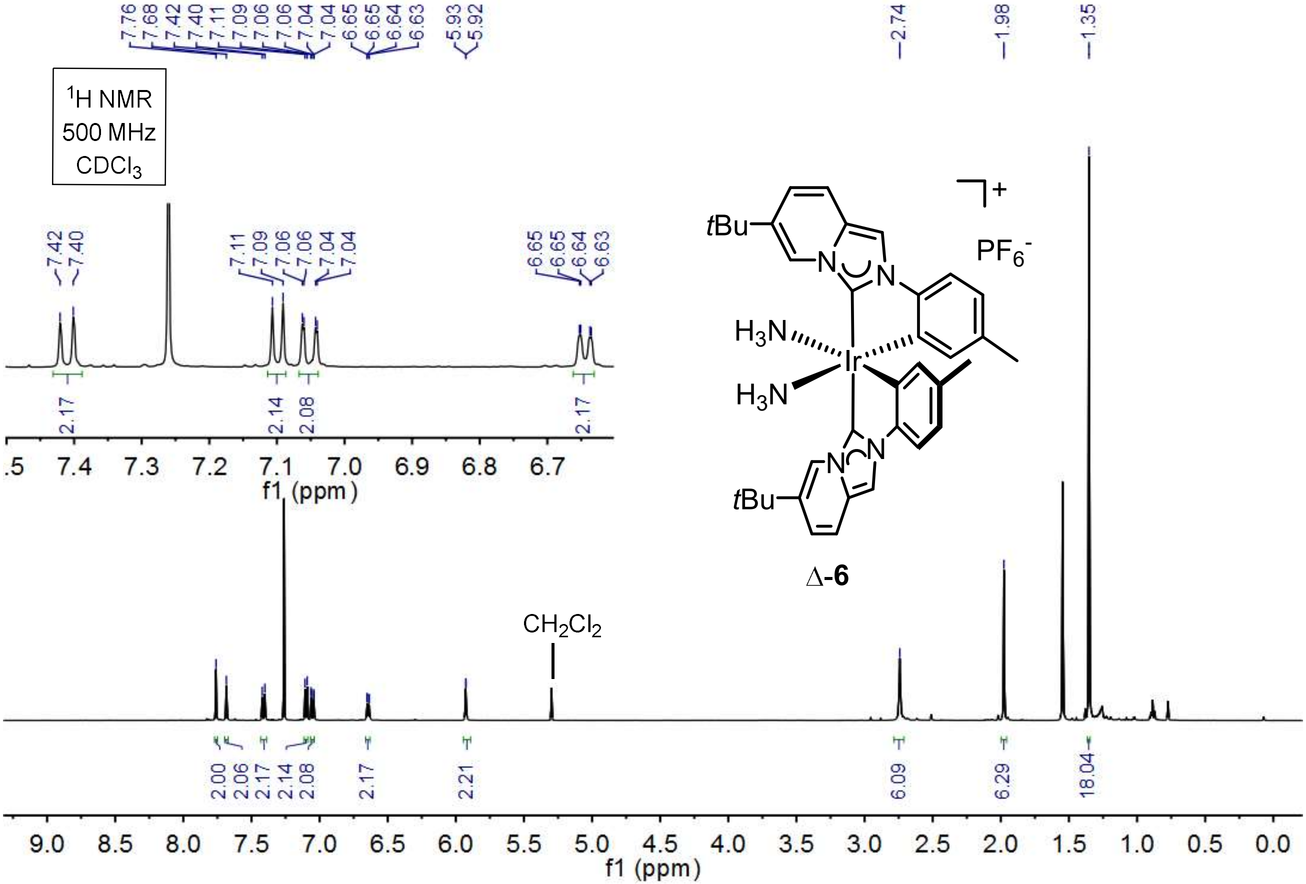
176.32 166.92 164.30 164.00 162.26 161.65 157.62 157.24 128.14 127.03 124.25 123.19 122.20 122.11 121.77 120.17 117.81 116.88 112.92 112.63 105.46 104.93 104.73 103.85 102.60 102.54 99.52 99.34 75.38 70.08 54.92 33.71 33.52 30.15 29.92
^{13}C NMR
126 MHz
CD_2Cl_2
142.02 141.55 140.66 140.02 136.20 135.25 132.89 132.86 132.78 129.60 129.46 128.14 127.03 124.25 123.19 122.20 122.11 121.77 120.17 119.66 117.81 116.88 112.92 112.63
140 134 128 122 116
f1 (ppm)
tBu
Ph
N
N
O
N
Ir
F
O
OMe
OMe
N
N
tBu
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

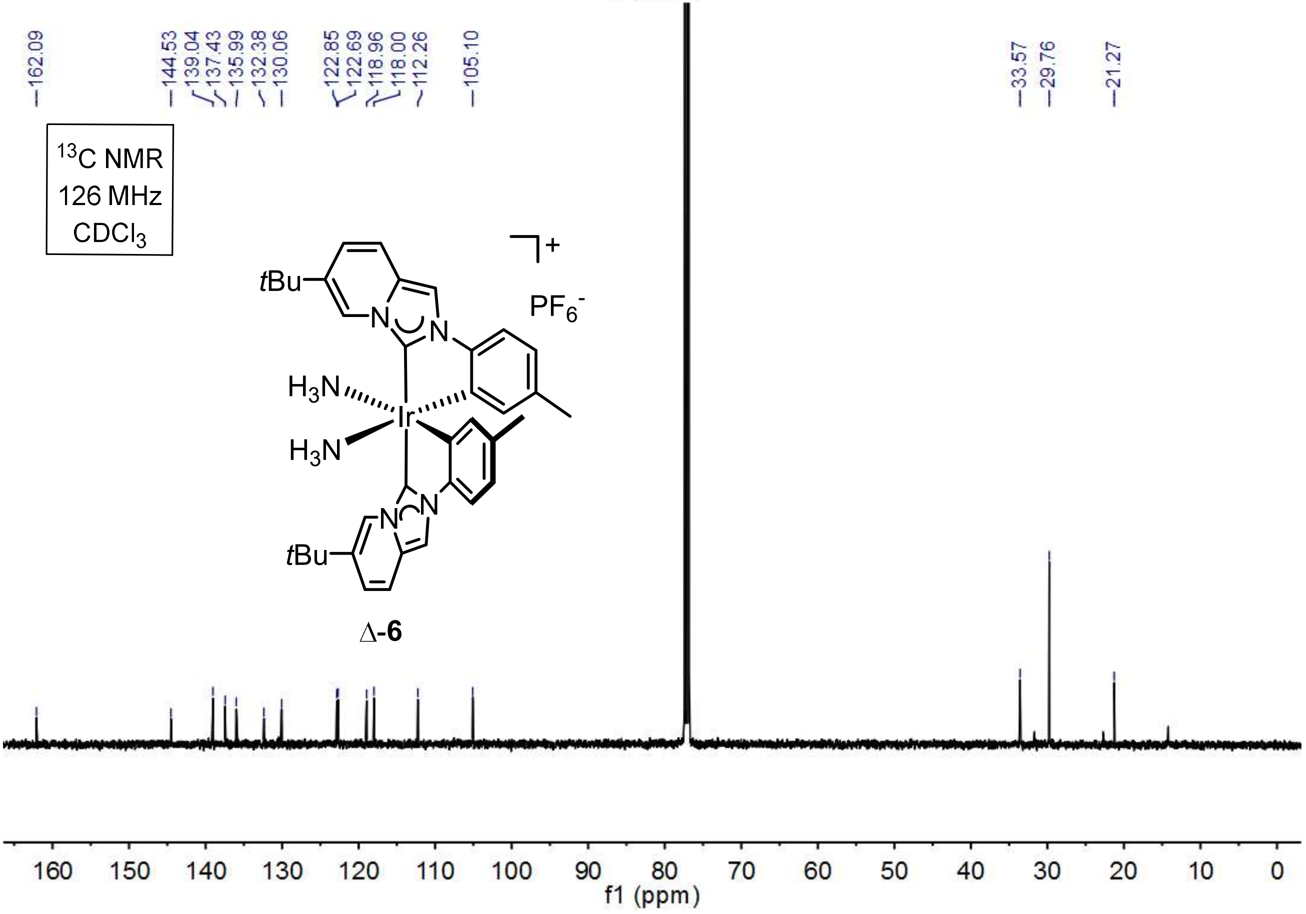


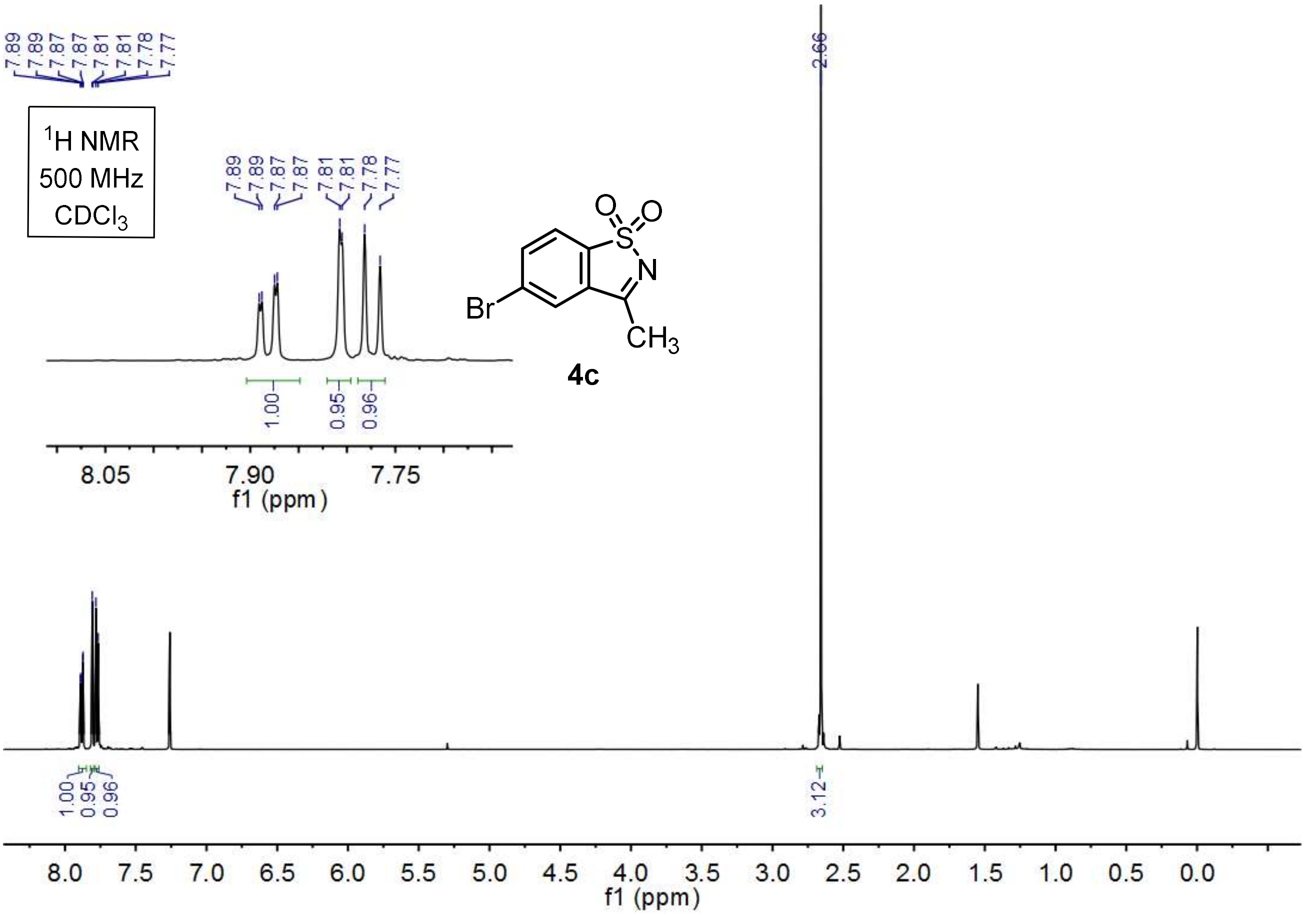
Δ-IrC1a

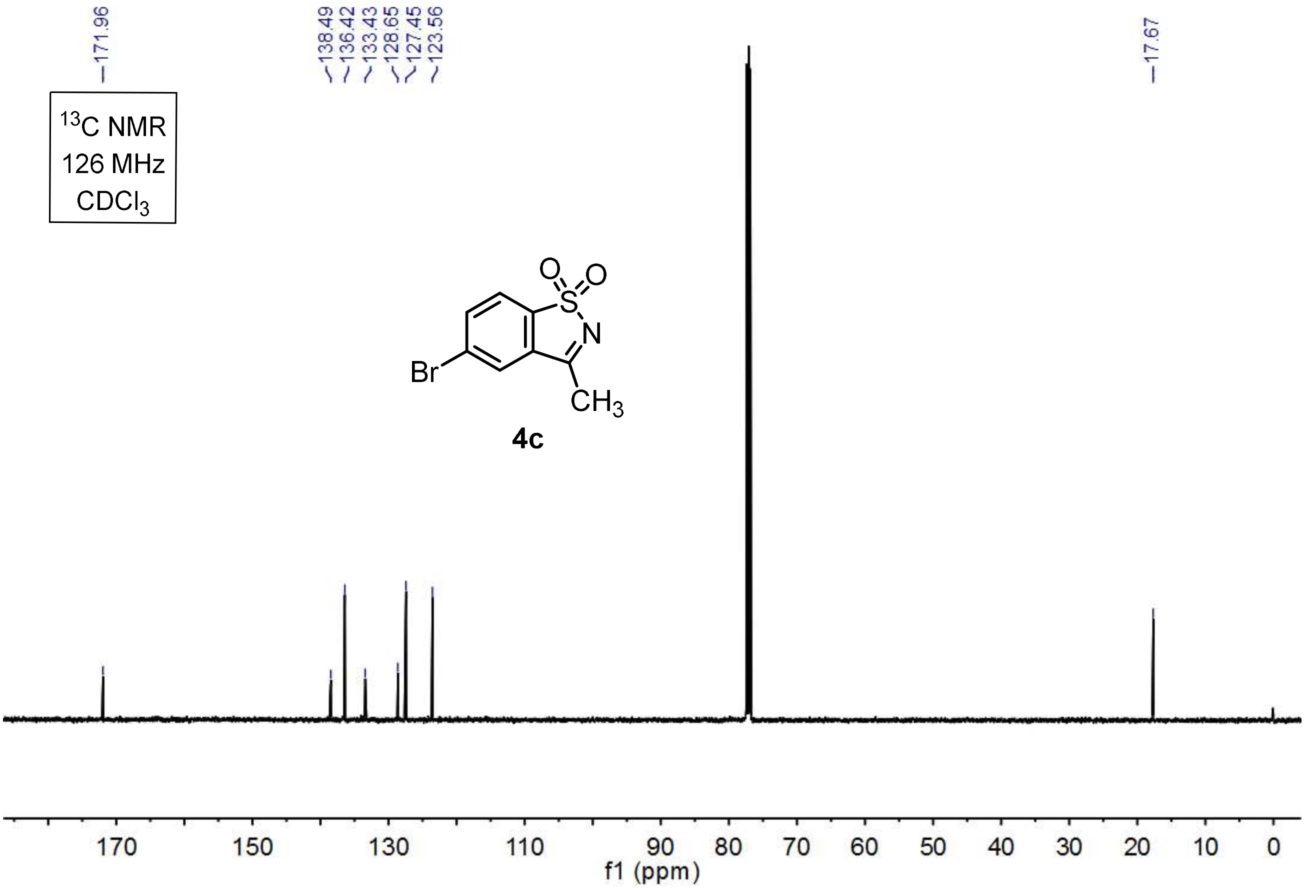


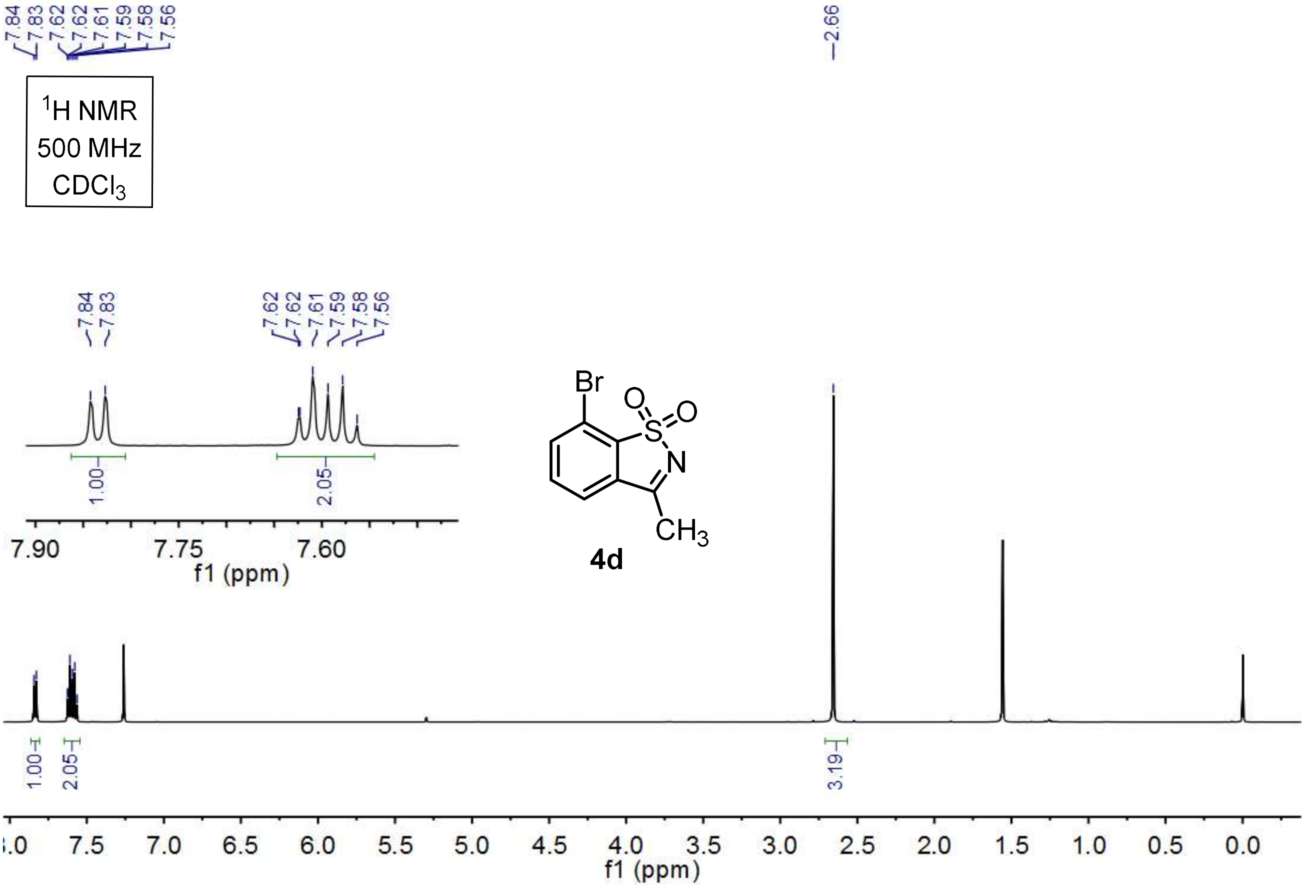
Δ-IrC1b

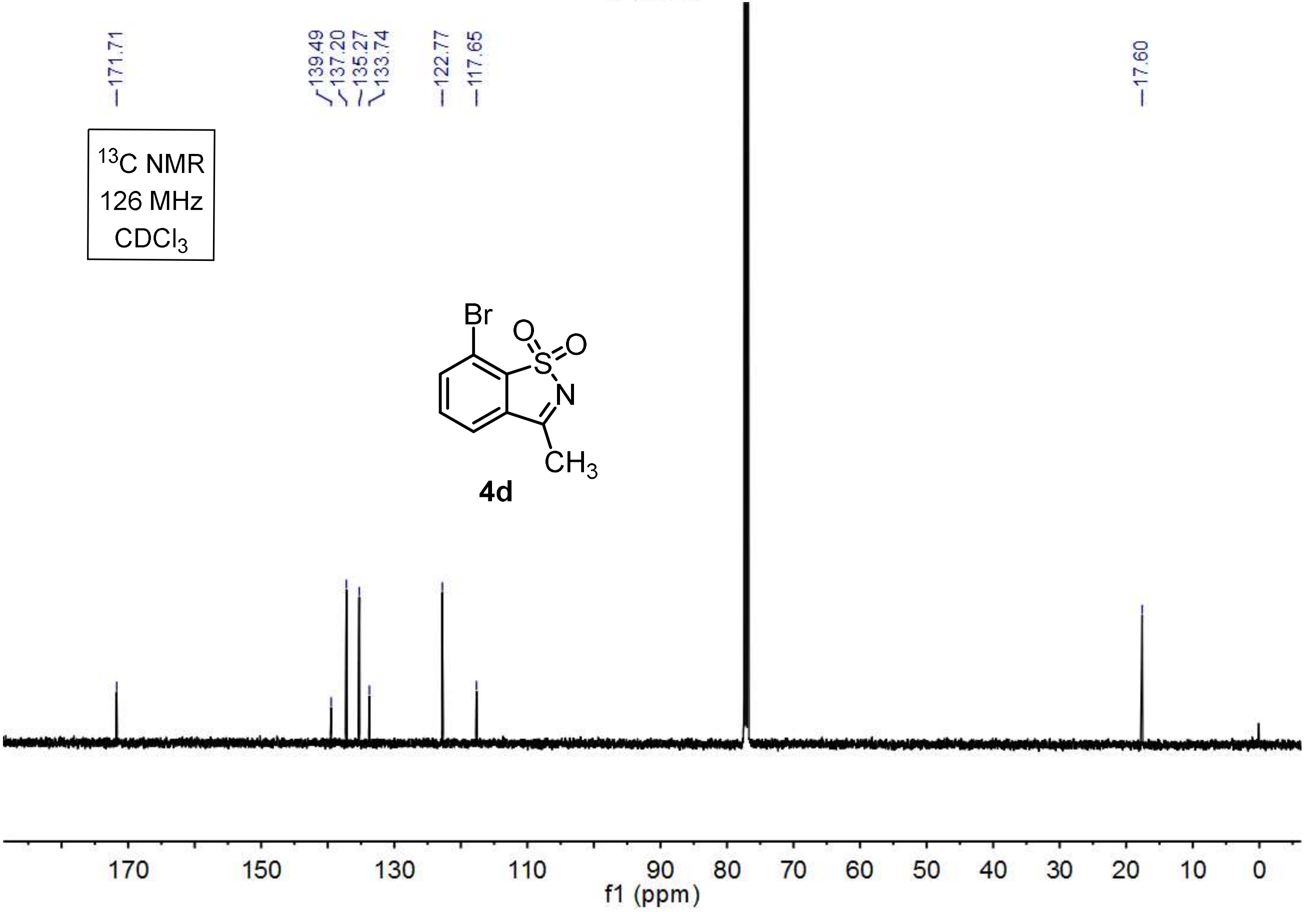

7.76
7.68
7.42
7.40
7.11
7.09
7.06
7.06
7.04
7.04
6.65
6.65
6.64
6.63
5.93
5.92
2.74
1.98
1.35
¹H NMR
500 MHz
CDCl₃
7.42
7.40
7.11
7.09
7.06
7.06
7.04
7.04
6.65
6.65
6.64
6.63
2.17
2.14
2.08
2.17
.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
tBu
N
N
PF₆⁻
+
H₃N
Ir
H₃N
N
N
tBu
Δ-6
CH₂Cl₂
2.00
2.06
2.17
2.14
2.08
2.17
2.21
6.09
6.29
18.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

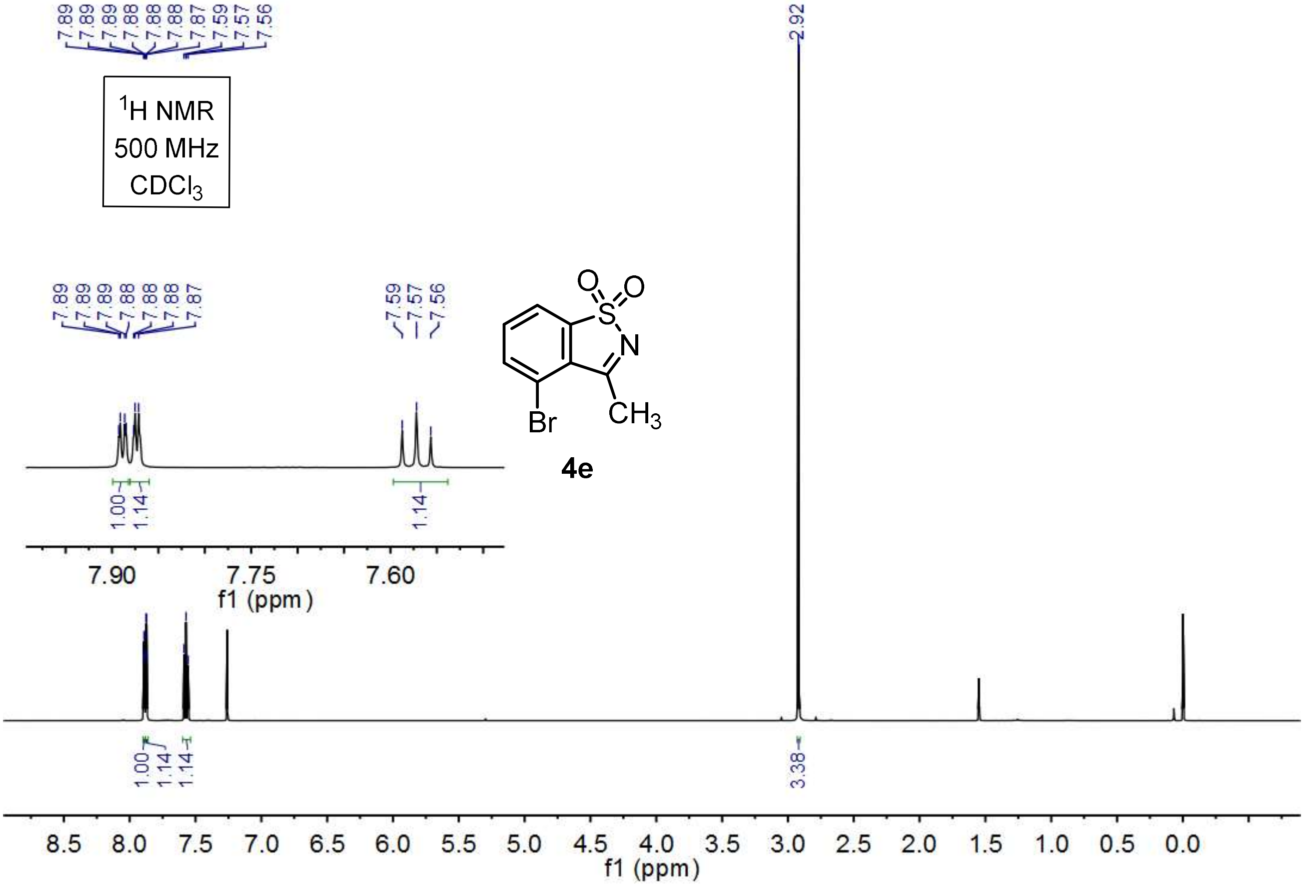

162.09
144.53
139.04
137.43
135.99
132.38
130.06
122.85
122.69
118.96
118.00
112.26
105.10
33.57
29.76
21.27
¹³C NMR
126 MHz
CDCl₃
tBu
N
N
PF₆⁻
+
H₃N
Ir
H₃N
N
N
tBu
Δ-6
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

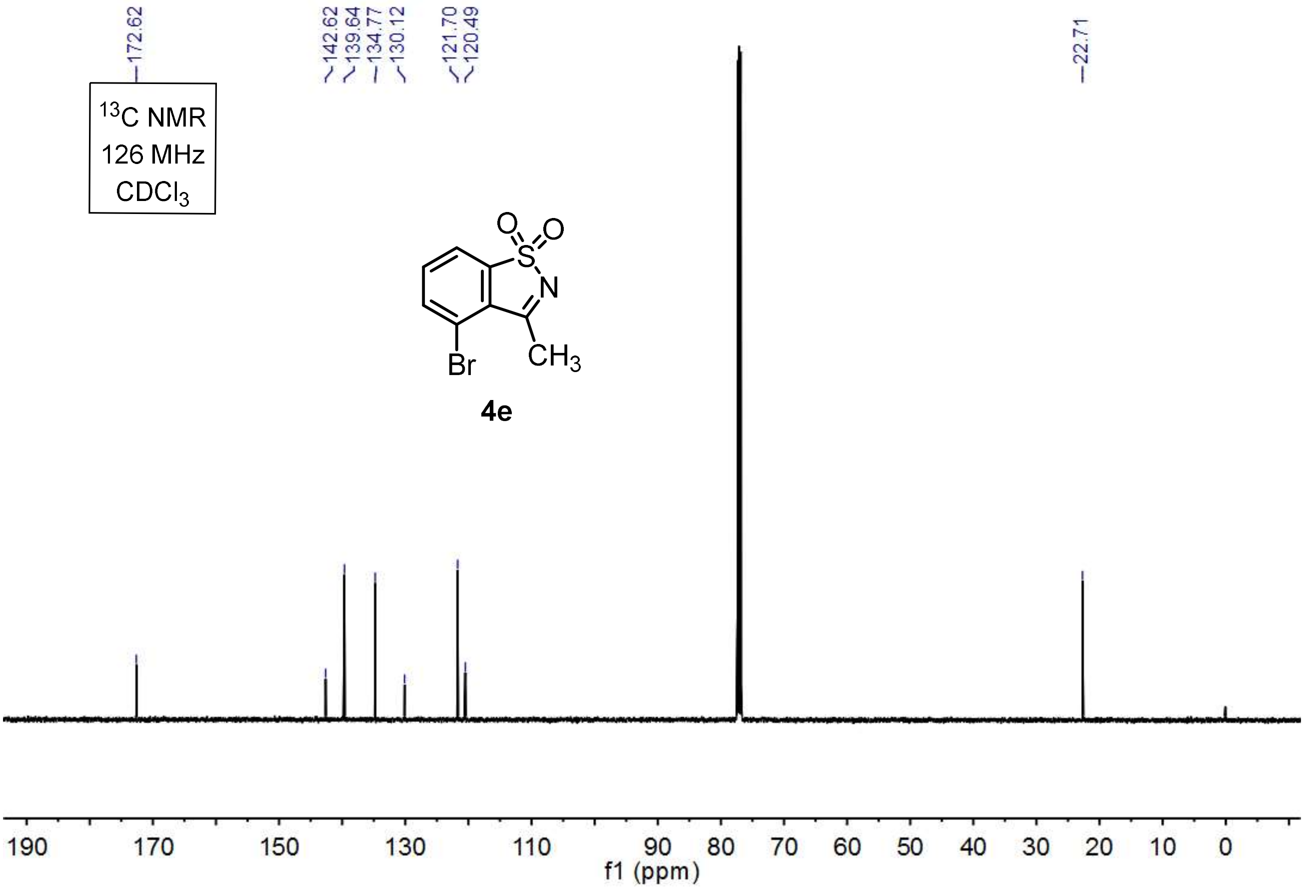

7.89
7.89
7.87
7.87
7.81
7.81
7.78
7.77
2.66
^{1}H NMR
500 MHz
$CDCl_3$
O
O
S
N
Br
CH_3
4c
1.00
0.95
0.96
3.12
8.05
7.90
7.75
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

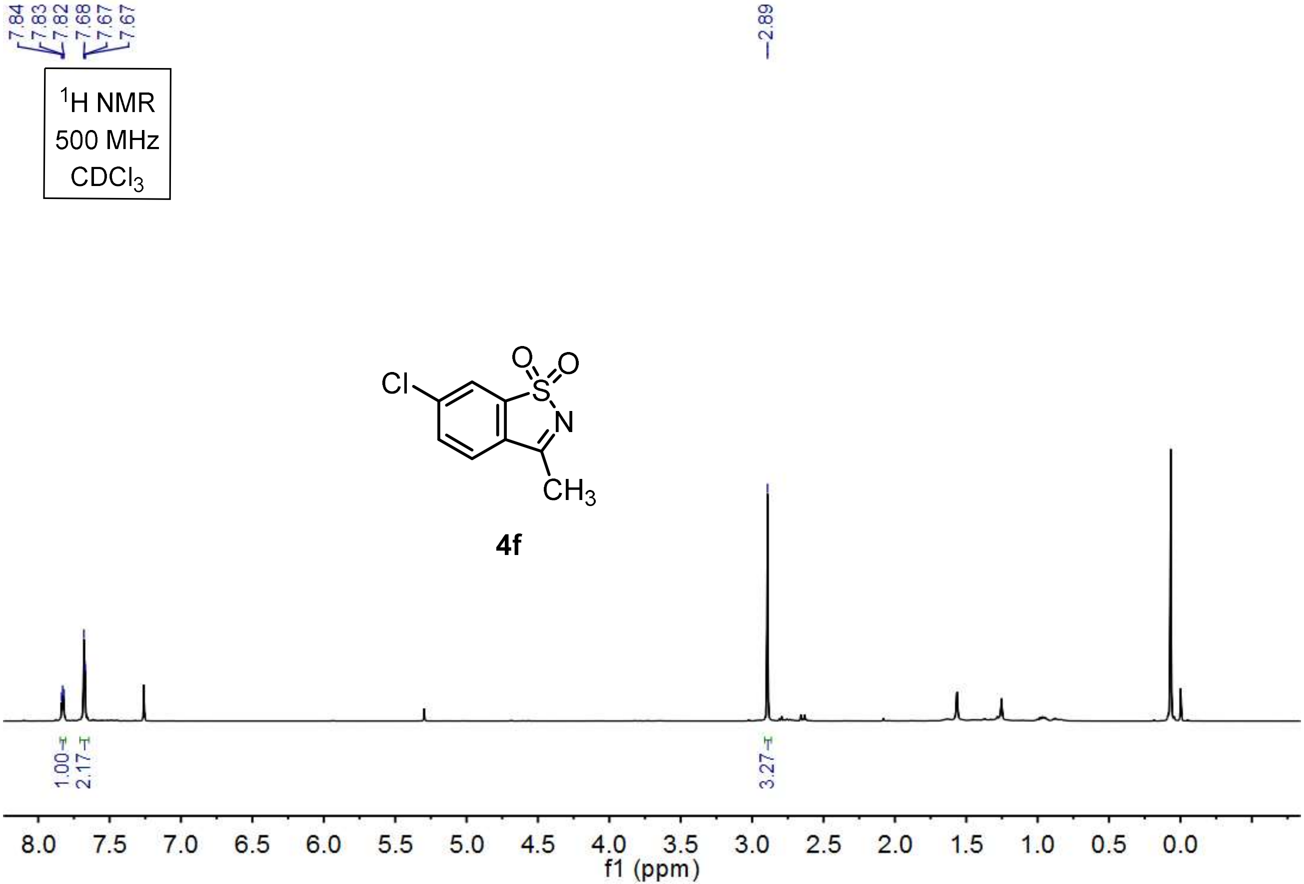

171.96
138.49
136.42
133.43
128.65
127.45
123.56
17.67
^{13}C NMR
126 MHz
$CDCl_3$
O
O
S
N
Br
CH_3
4c
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.84
7.83
7.62
7.62
7.61
7.59
7.58
7.56
2.66
^{1}H NMR
500 MHz
$CDCl_3$
1.00
2.05
7.90
7.75
7.60
f1 (ppm)
Br
O
S
O
N
CH_3
4d
1.00
2.05
3.19
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

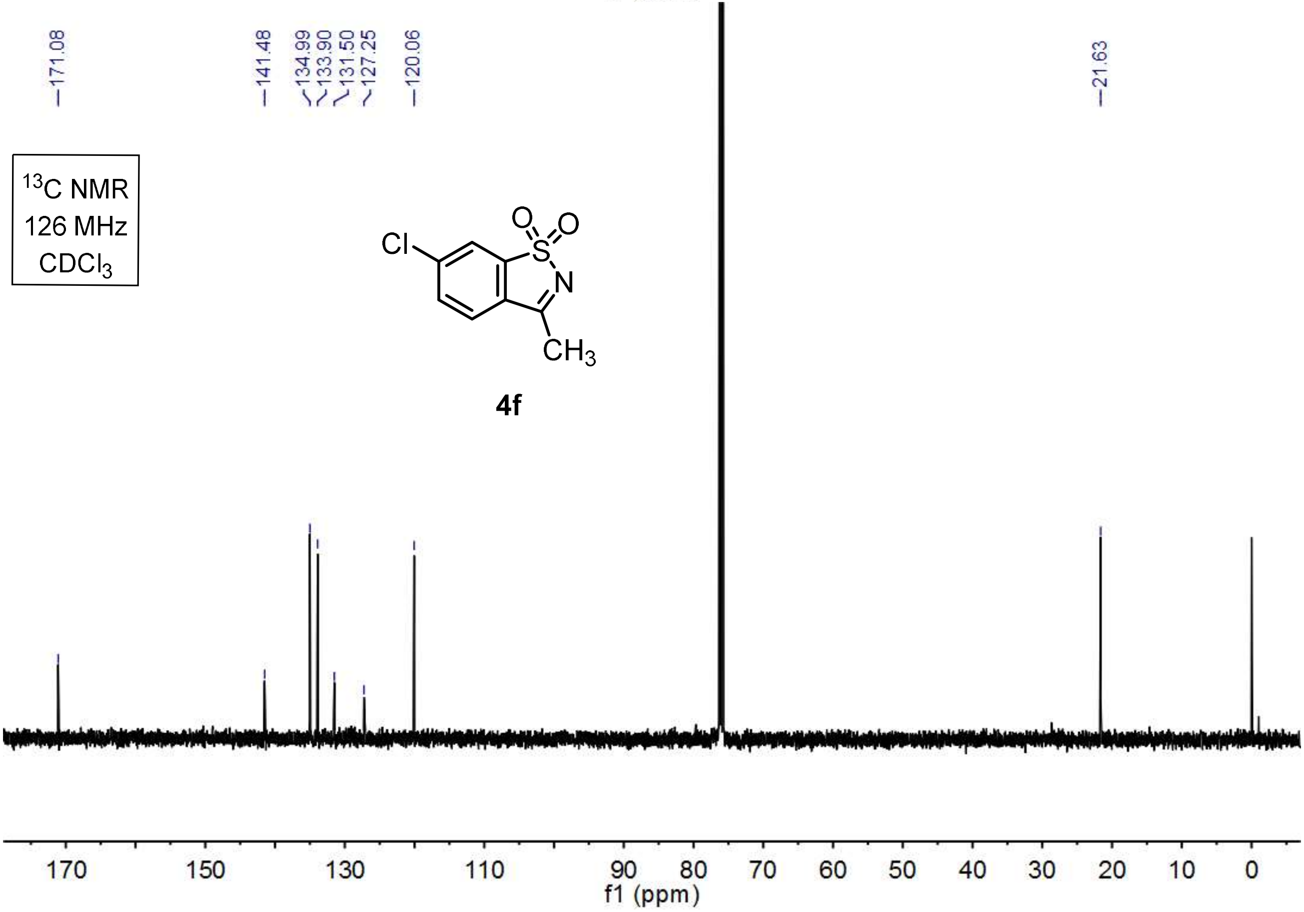

171.71
139.49
137.20
135.27
133.74
122.77
117.65
17.60
^{13}C NMR
126 MHz
$CDCl_3$
Br
O
S
O
N
CH_3
4d
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.89
7.89
7.89
7.88
7.88
7.88
7.87
7.59
7.57
7.56
2.92
^{1}H NMR
500 MHz
$CDCl_3$
4e
Br
CH_3
O
S
O
N
1.00
1.14
1.14
3.38
7.90
7.75
7.60
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

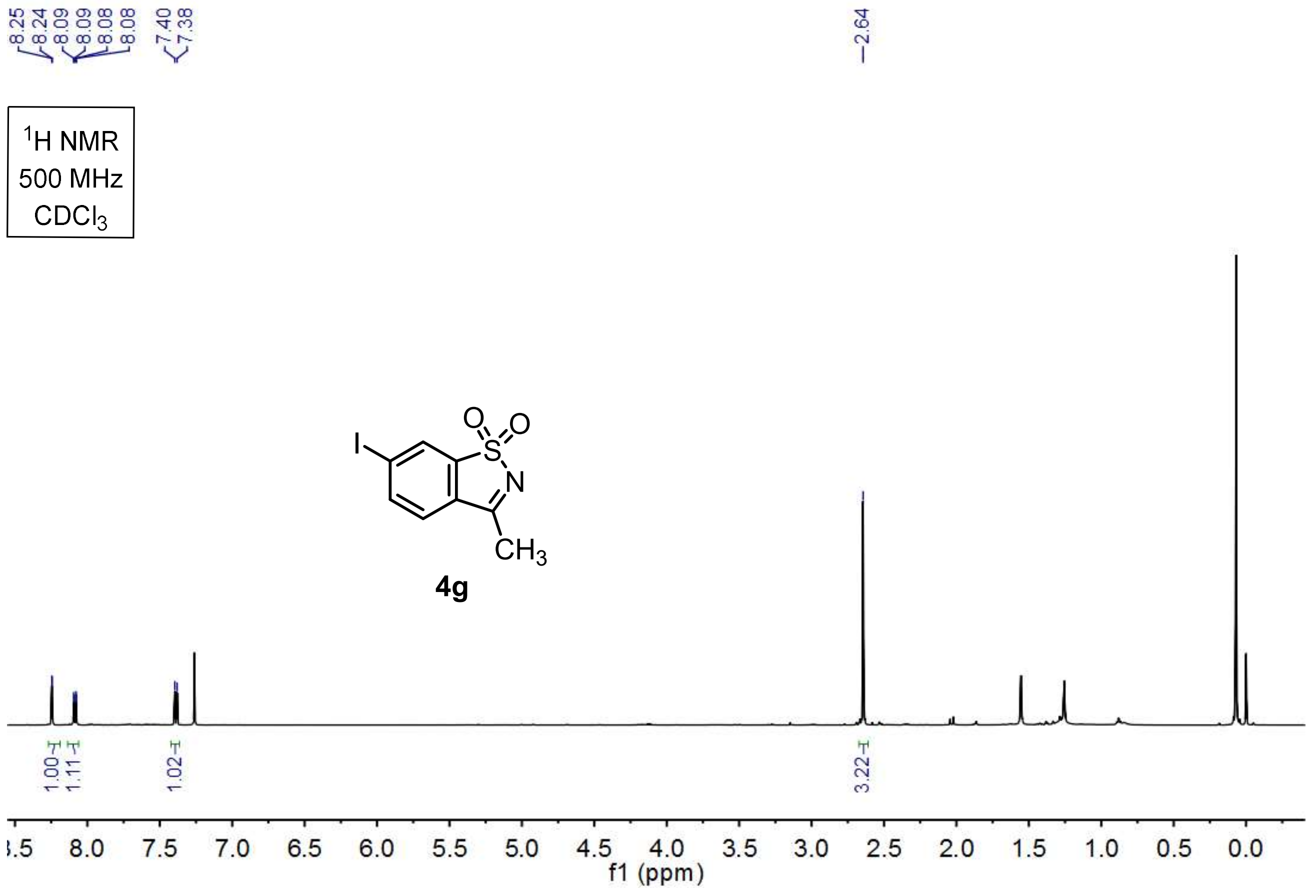

172.62
142.62
139.64
134.77
130.12
121.70
120.49
22.71
^{13}C NMR
126 MHz
$CDCl_3$
4e
Br
CH_3
O
S
O
N
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

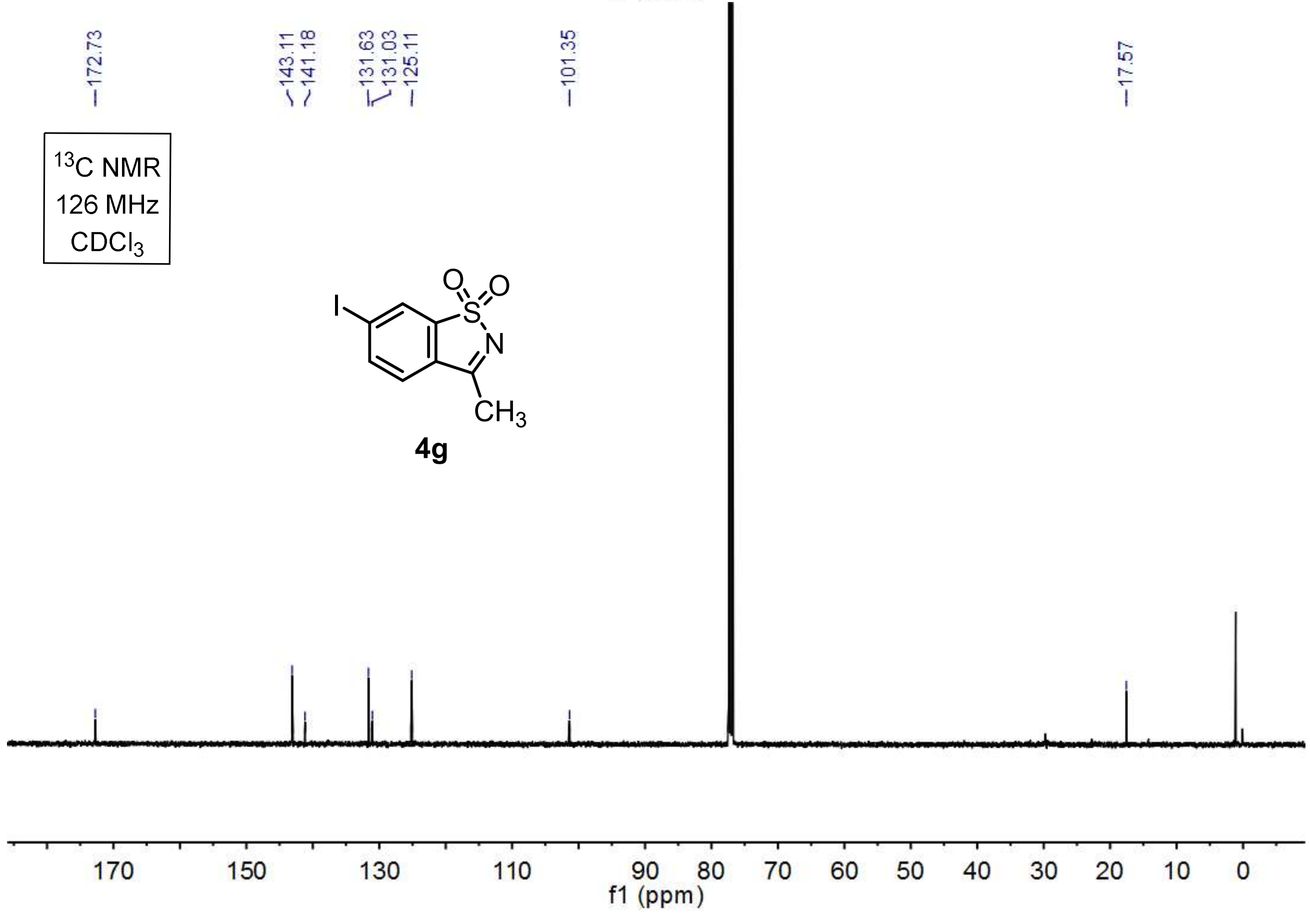

7.84
7.83
7.82
7.68
7.67
7.67
2.89
^{1}H NMR
500 MHz
CDCl$_3$
Cl
O
O
S
N
CH$_3$
1.00
2.17
3.27
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

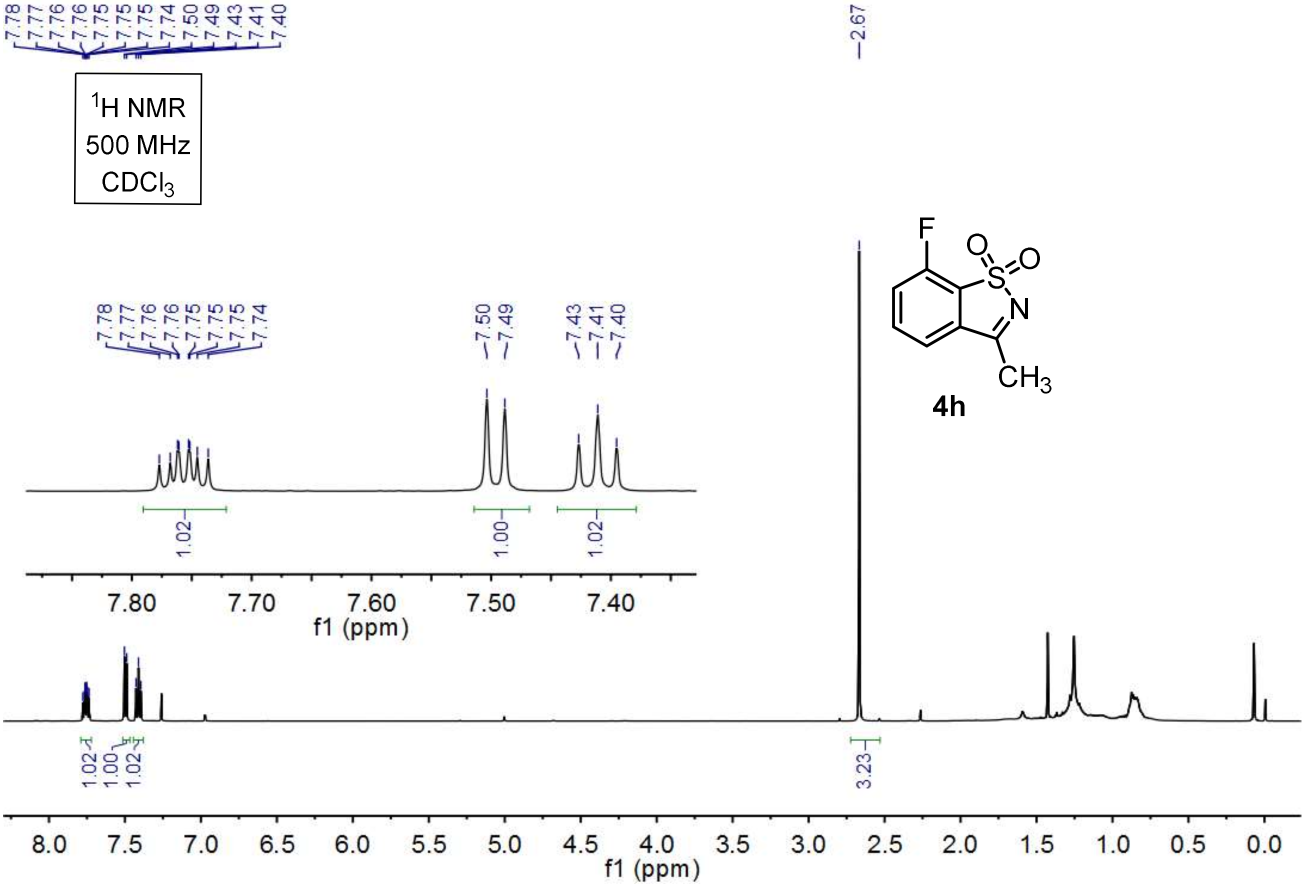
4f

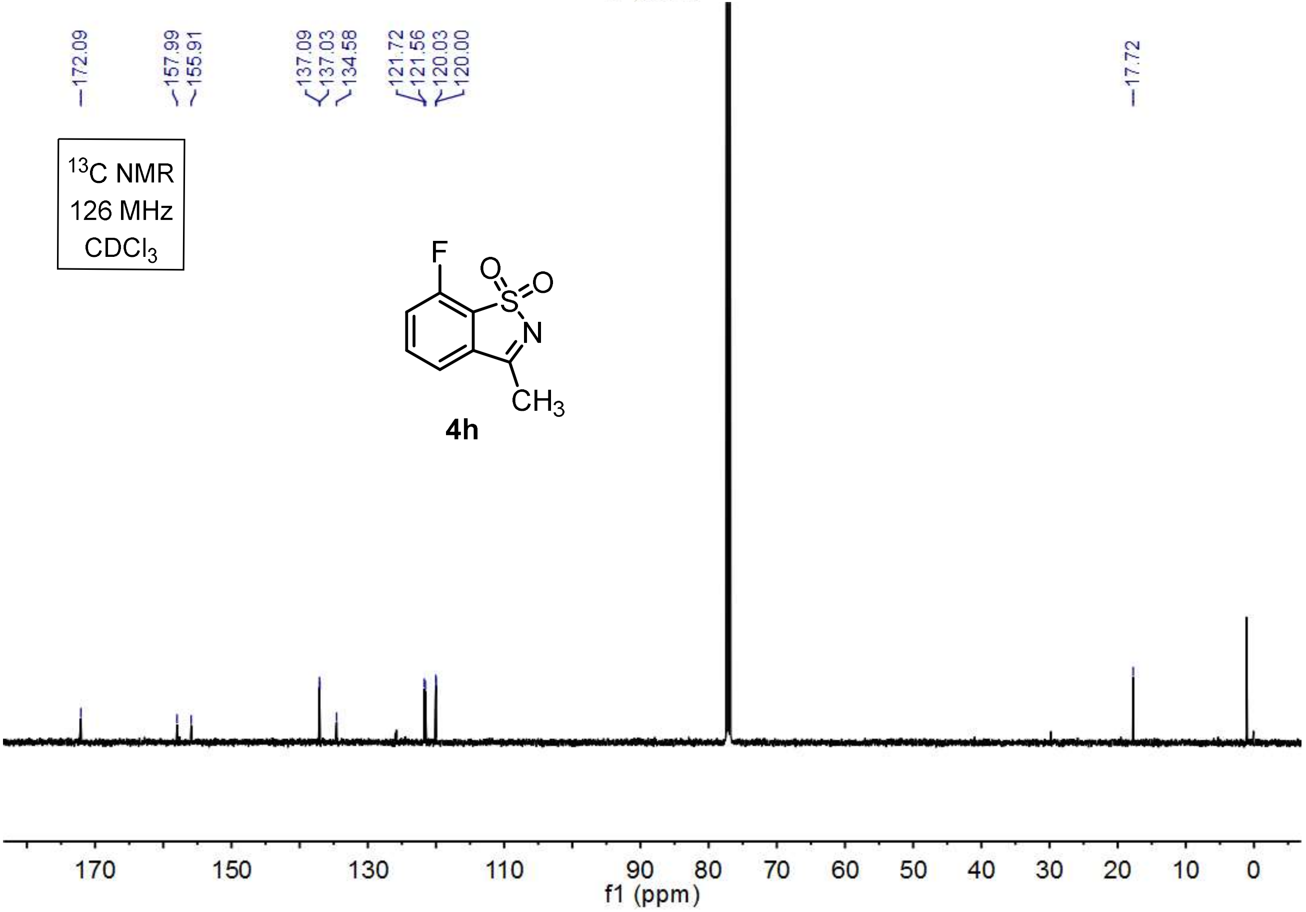

171.08
141.48
134.99
133.90
131.50
127.25
120.06
21.63
^{13}C NMR
126 MHz
CDCl$_3$
Cl
O
O
S
N
CH$_3$
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

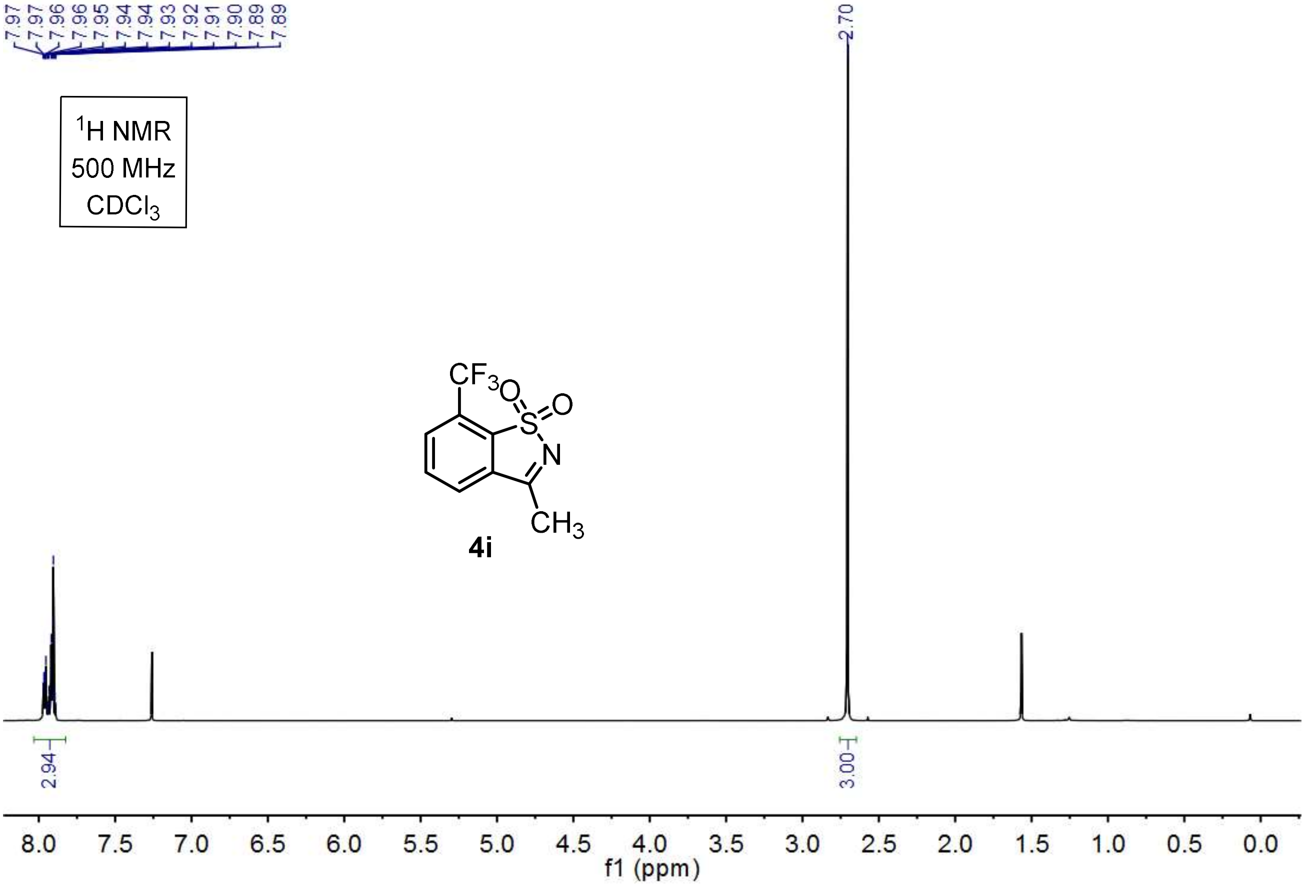
4f

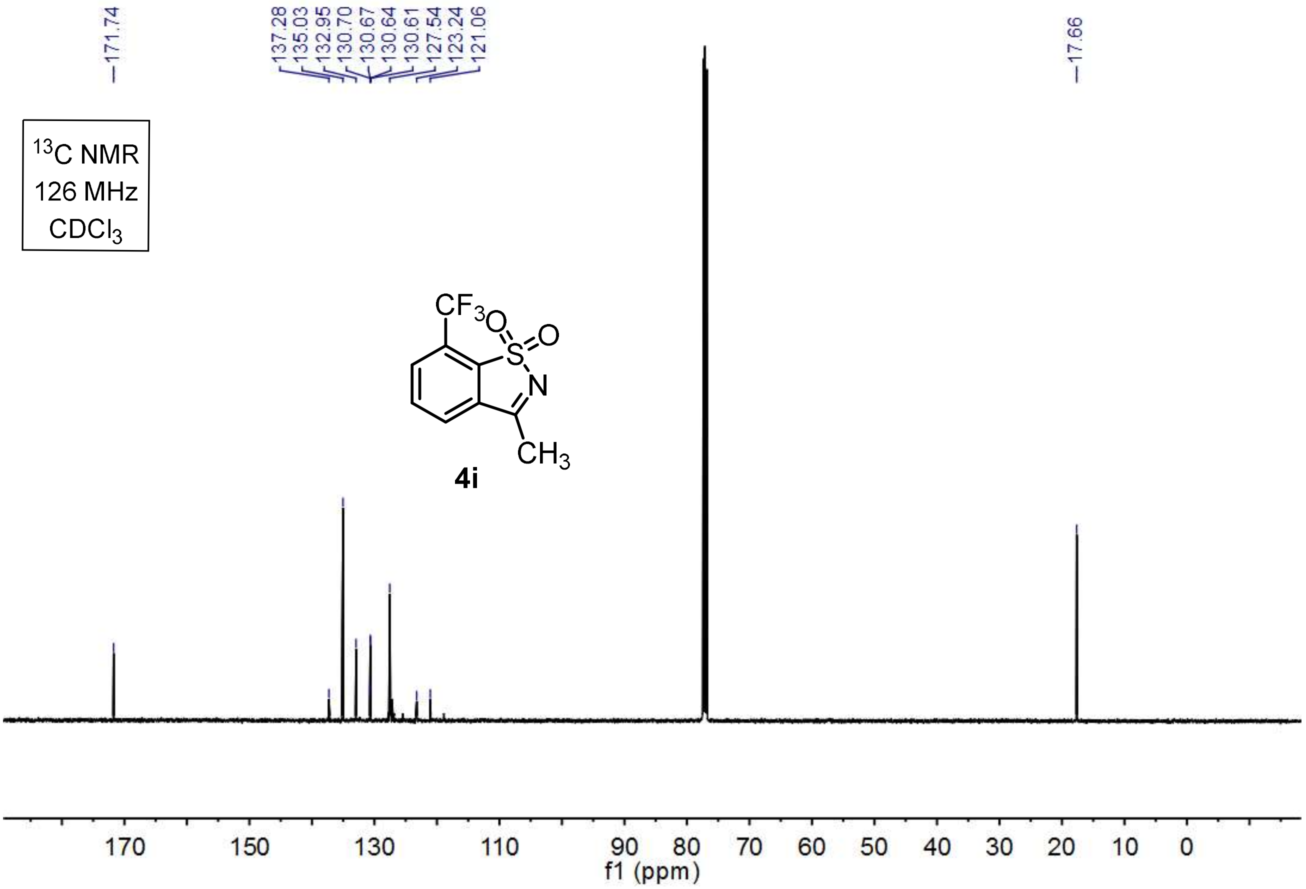

8.25
8.24
8.09
8.09
8.08
8.08
7.40
7.38
2.64
^{1}H NMR
500 MHz
$CDCl_3$
I
O
O
S
N
CH_3
4g
1.00
1.11
1.02
3.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

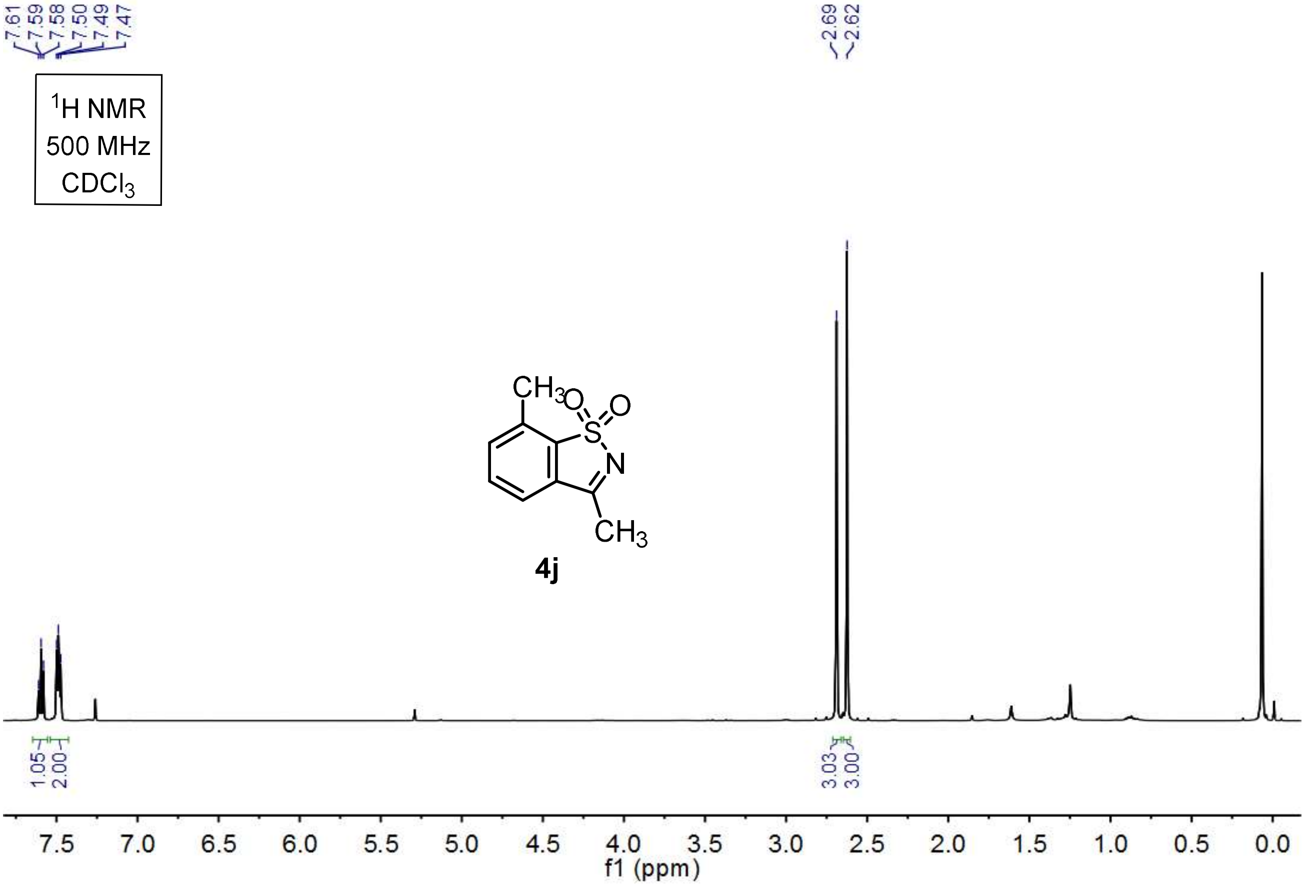

172.73
143.11
141.18
131.63
131.03
125.11
101.35
17.57
^{13}C NMR
126 MHz
$CDCl_3$
I
O
O
S
N
CH_3
4g
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

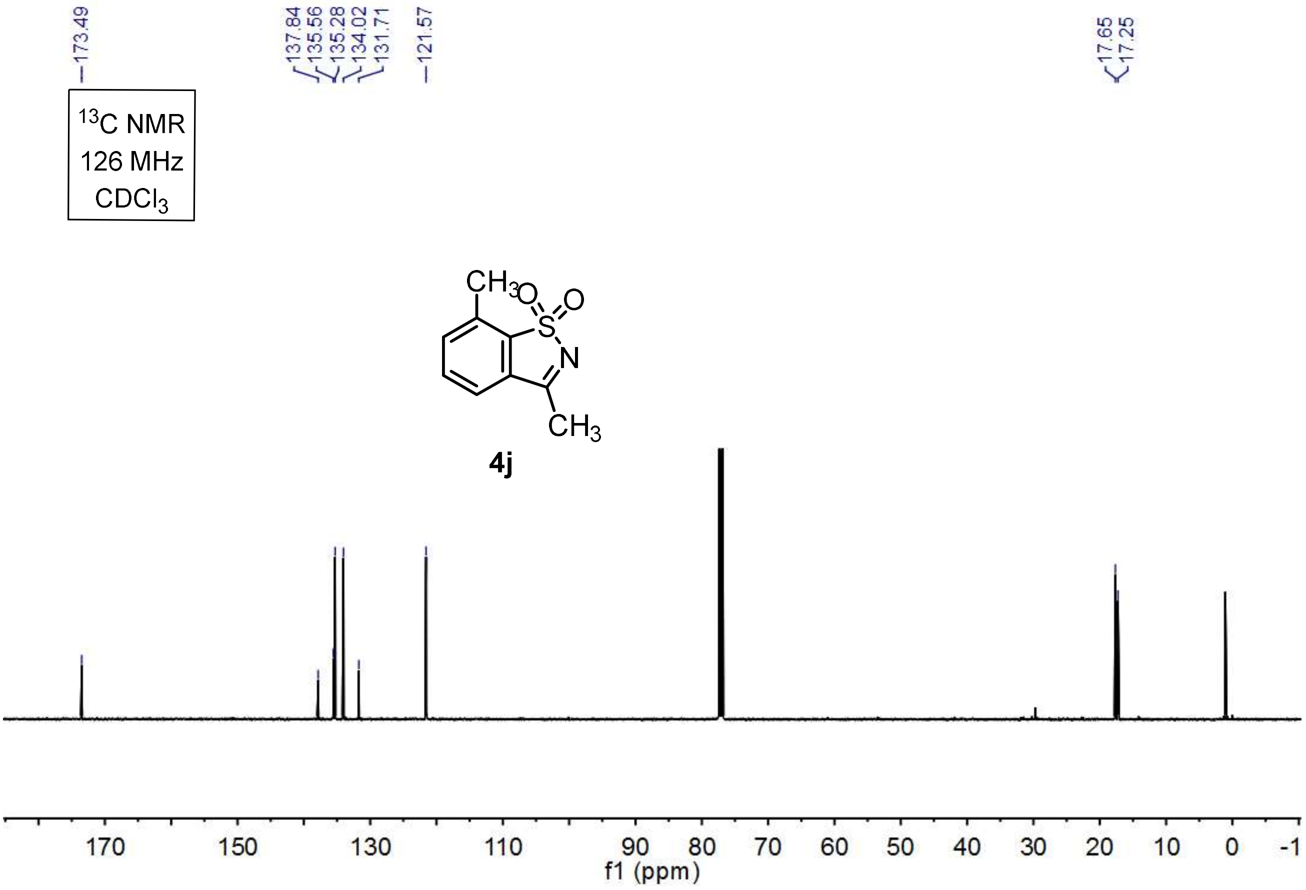

7.78
7.77
7.76
7.76
7.75
7.75
7.75
7.74
7.50
7.49
7.43
7.41
7.40
2.67
^{1}H NMR
500 MHz
CDCl$_3$
F
O
S
O
N
CH$_3$
4h
7.78
7.77
7.76
7.76
7.75
7.75
7.75
7.74
7.50
7.49
7.43
7.41
7.40
1.02
1.00
1.02
7.80
7.70
7.60
7.50
7.40
f1 (ppm)
1.02
1.00
1.02
3.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

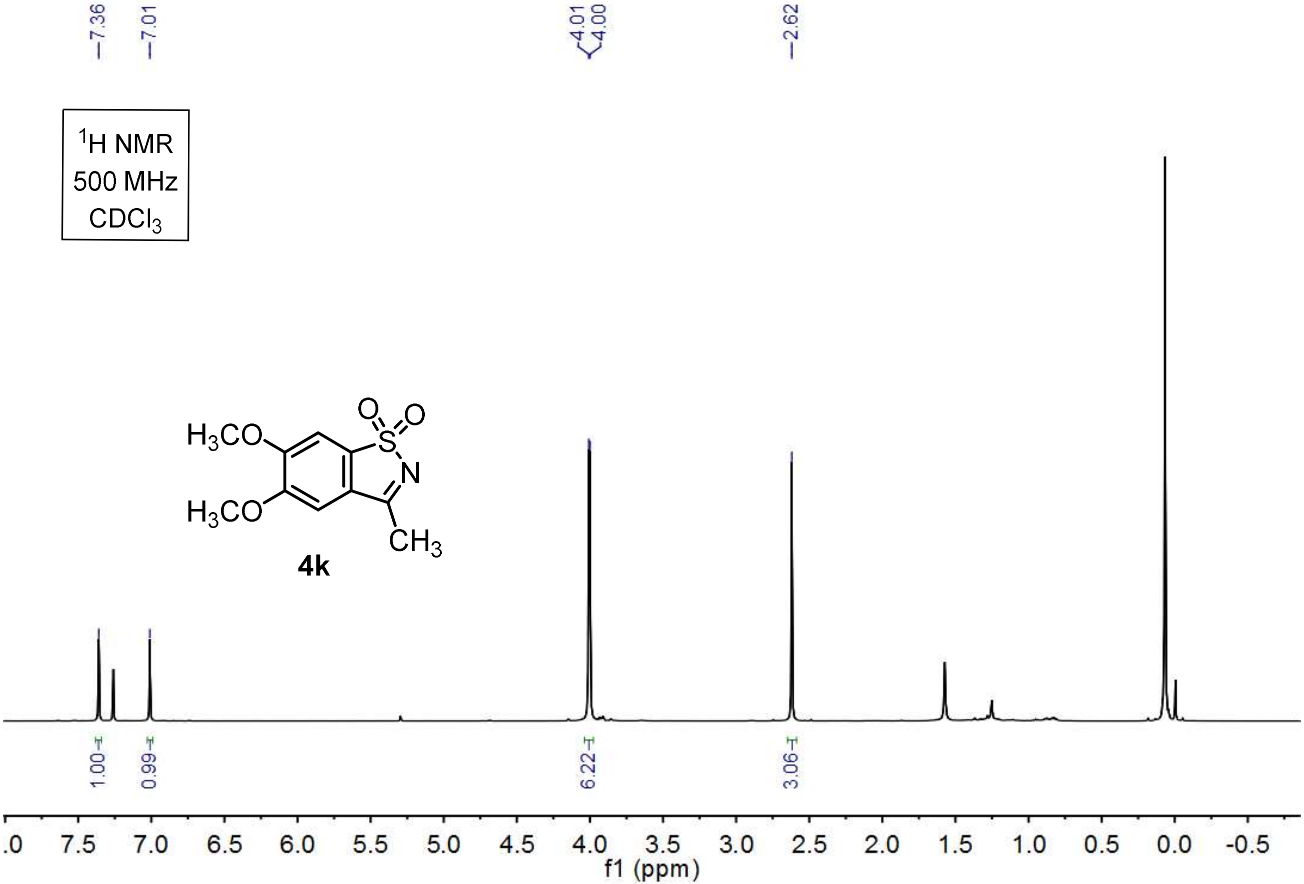

172.09
157.99
155.91
137.09
137.03
134.58
121.72
121.56
120.03
120.00
17.72
^{13}C NMR
126 MHz
CDCl$_3$
F
O
S
O
N
CH$_3$
4h
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

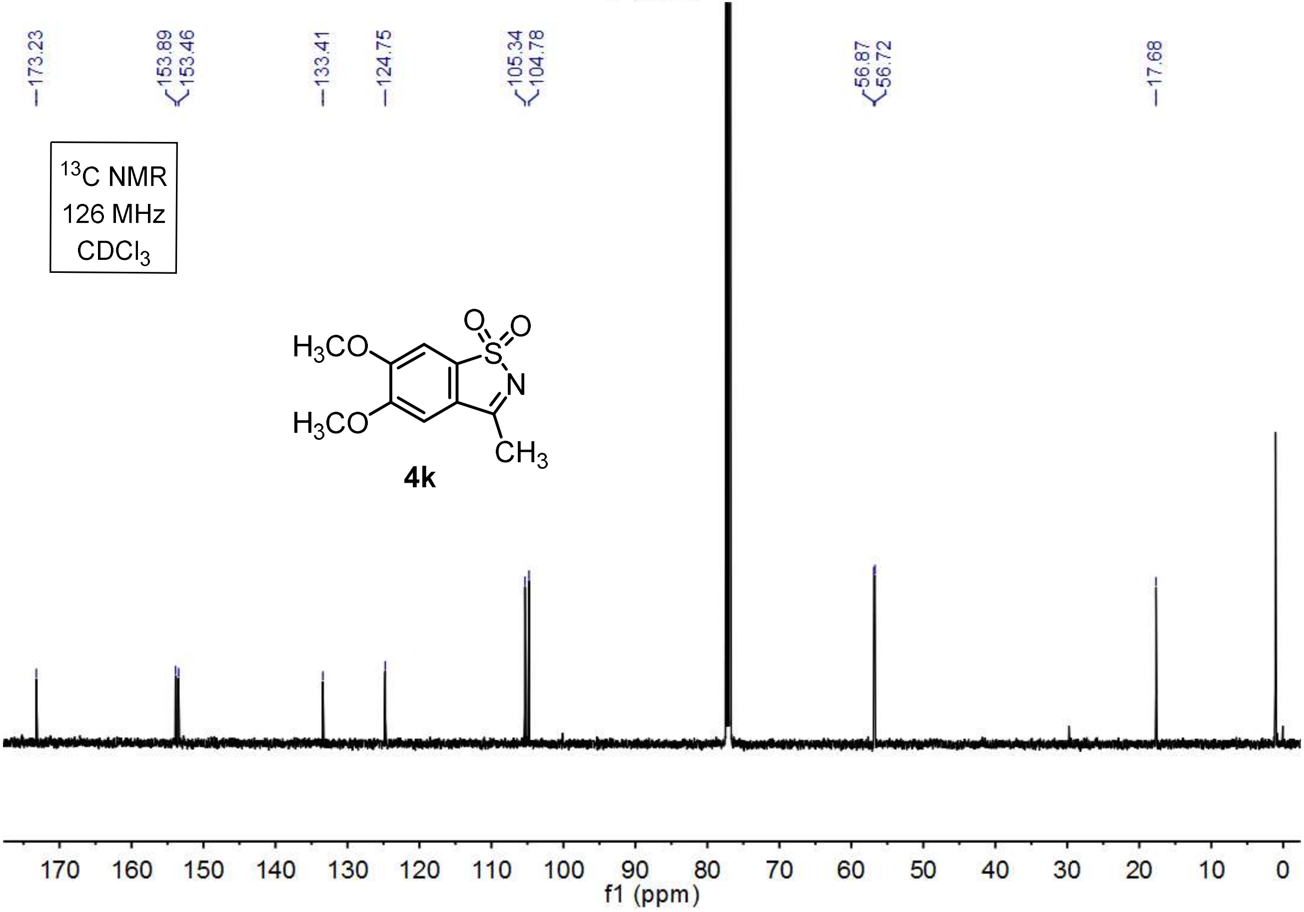

7.97
7.97
7.96
7.96
7.95
7.94
7.94
7.93
7.92
7.91
7.90
7.89
7.89
2.70
^{1}H NMR
500 MHz
$CDCl_3$
CF_3
O
S
O
N
CH_3
4i
2.94
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

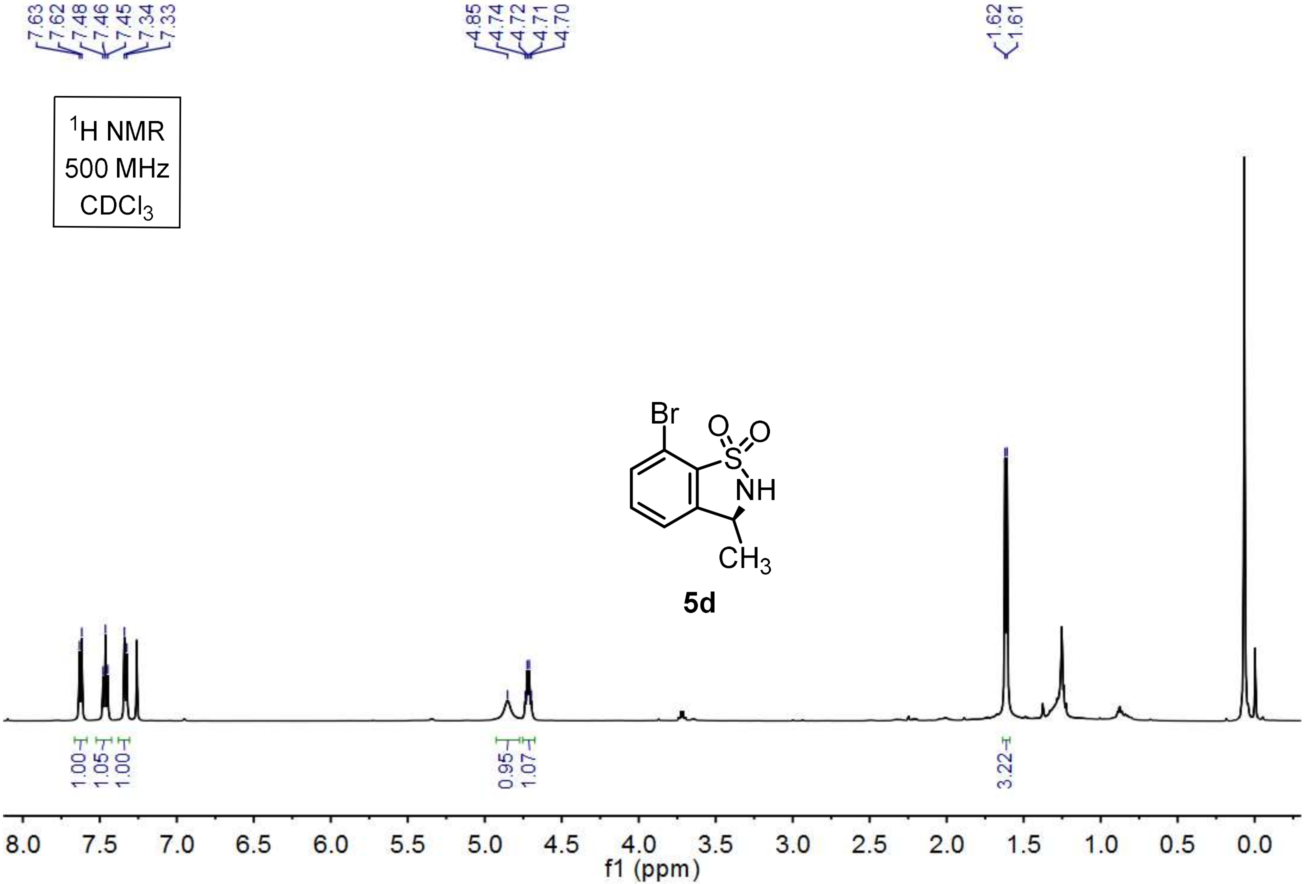

171.74
137.28
135.03
132.95
130.70
130.67
130.64
130.61
127.54
123.24
121.06
17.66
^{13}C NMR
126 MHz
$CDCl_3$
CF_3
O
S
O
N
CH_3
4i
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

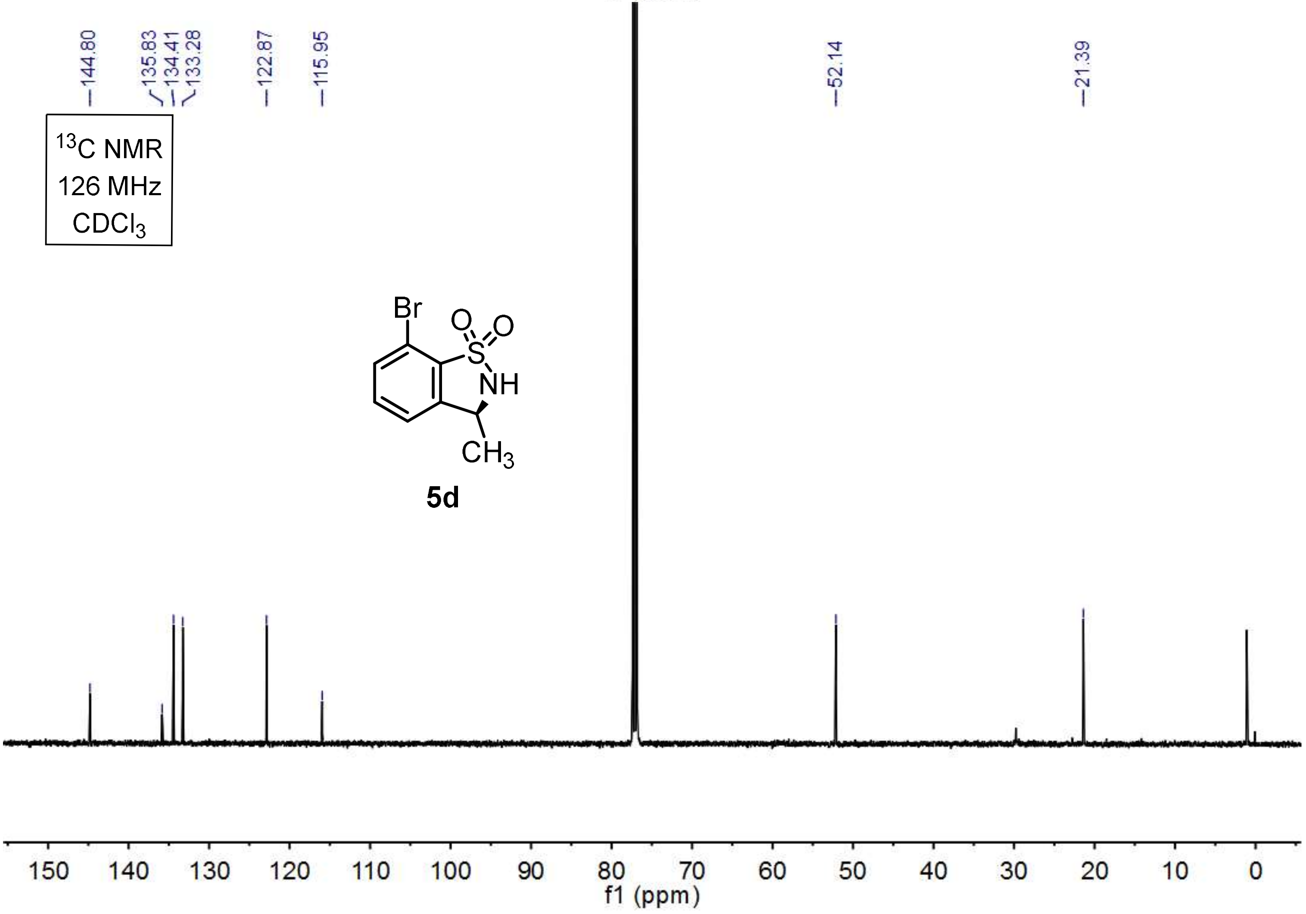

7.61
7.59
7.58
7.50
7.49
7.47
2.69
2.62
^{1}H NMR
500 MHz
$CDCl_3$
CH_3
O
O
S
N
CH_3
4j
1.05
2.00
3.03
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

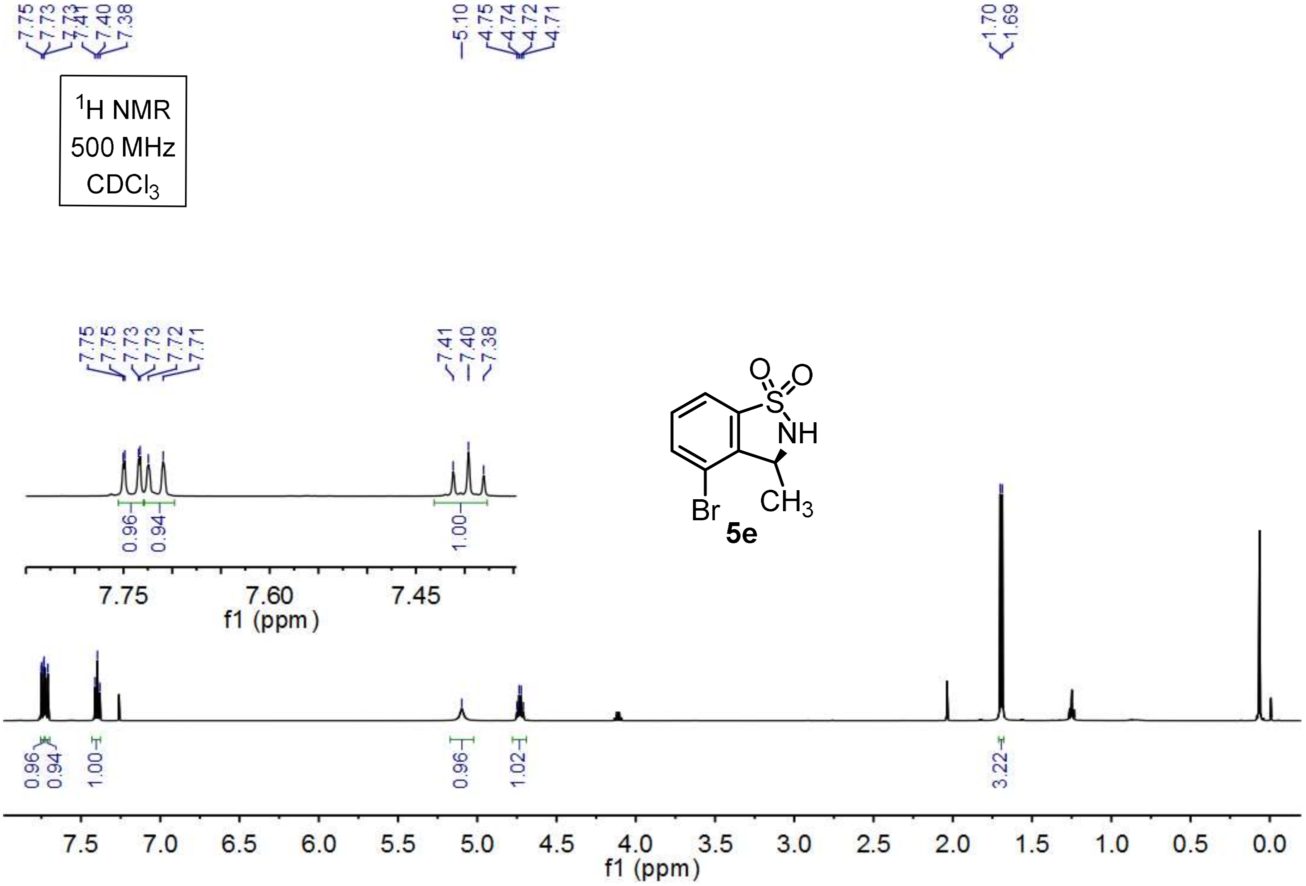

173.49
137.84
135.56
135.28
134.02
131.71
121.57
17.65
17.25
^{13}C NMR
126 MHz
$CDCl_3$
CH_3
O
O
S
N
CH_3
4j
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

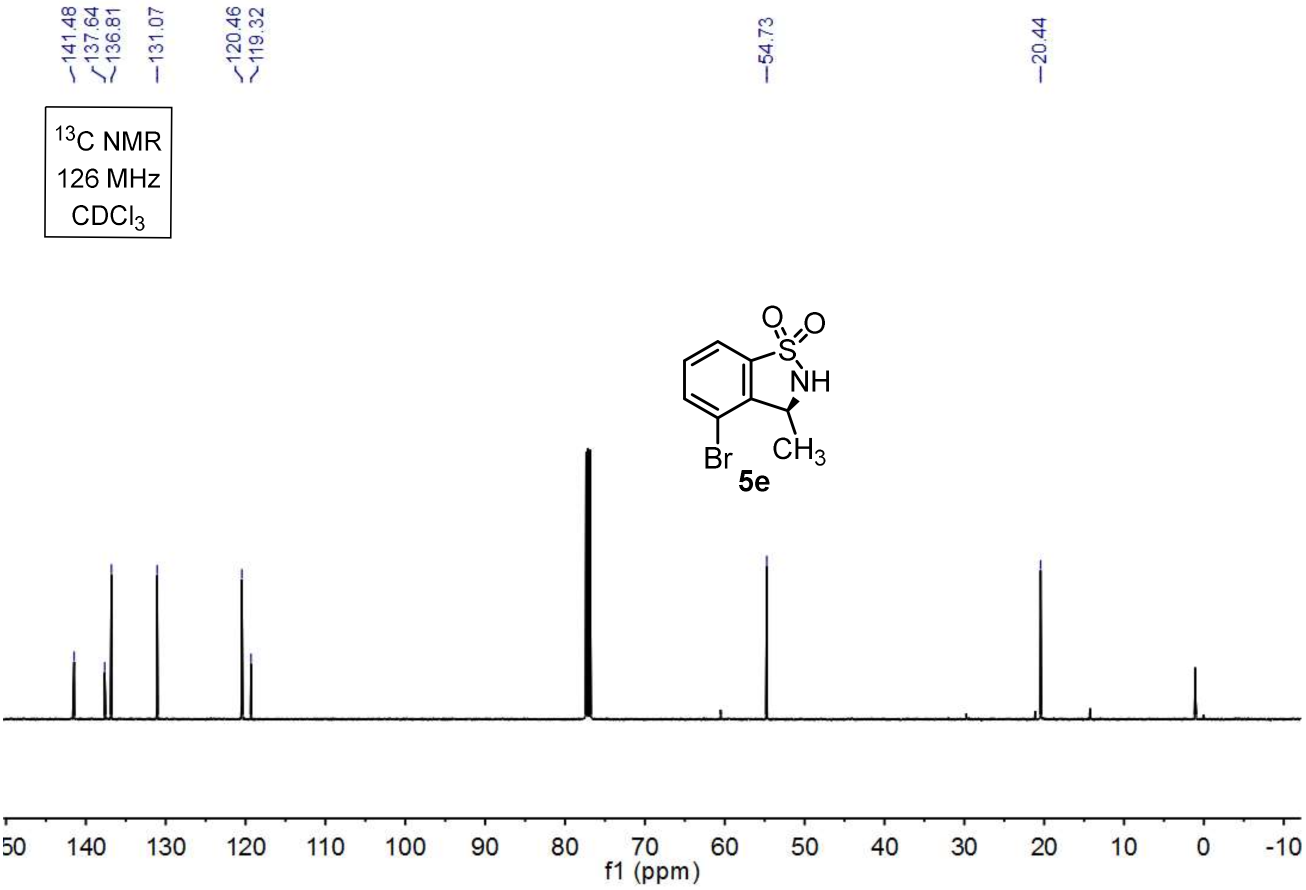

7.36
7.01
4.01
4.00
2.62
^{1}H NMR
500 MHz
CDCl$_3$
H$_3$CO
H$_3$CO
O
O
S
N
CH$_3$
4k
1.00
0.99
6.22
3.06
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

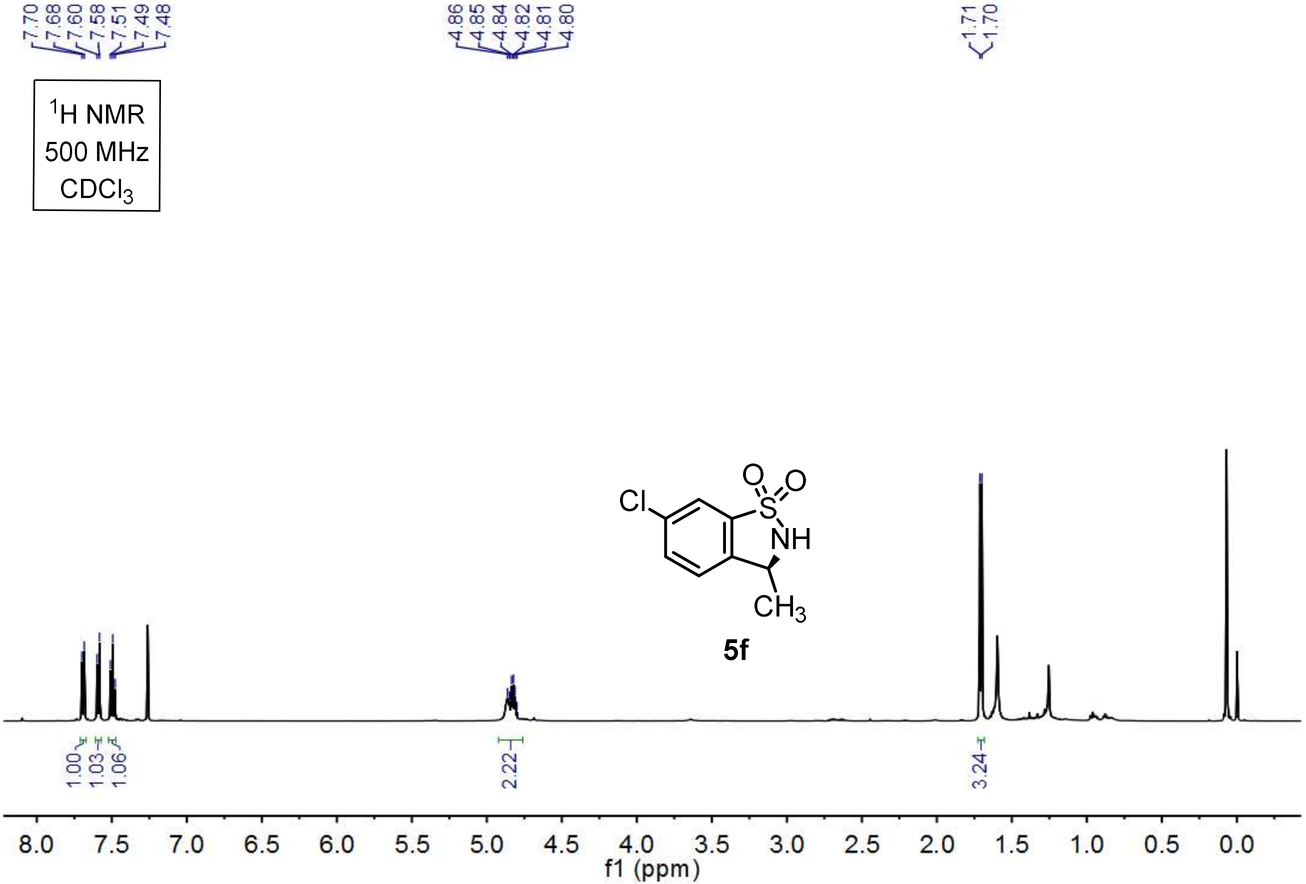

173.23
153.89
153.46
133.41
124.75
105.34
104.78
56.87
56.72
17.68
^{13}C NMR
126 MHz
CDCl$_3$
H$_3$CO
H$_3$CO
O
O
S
N
CH$_3$
4k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

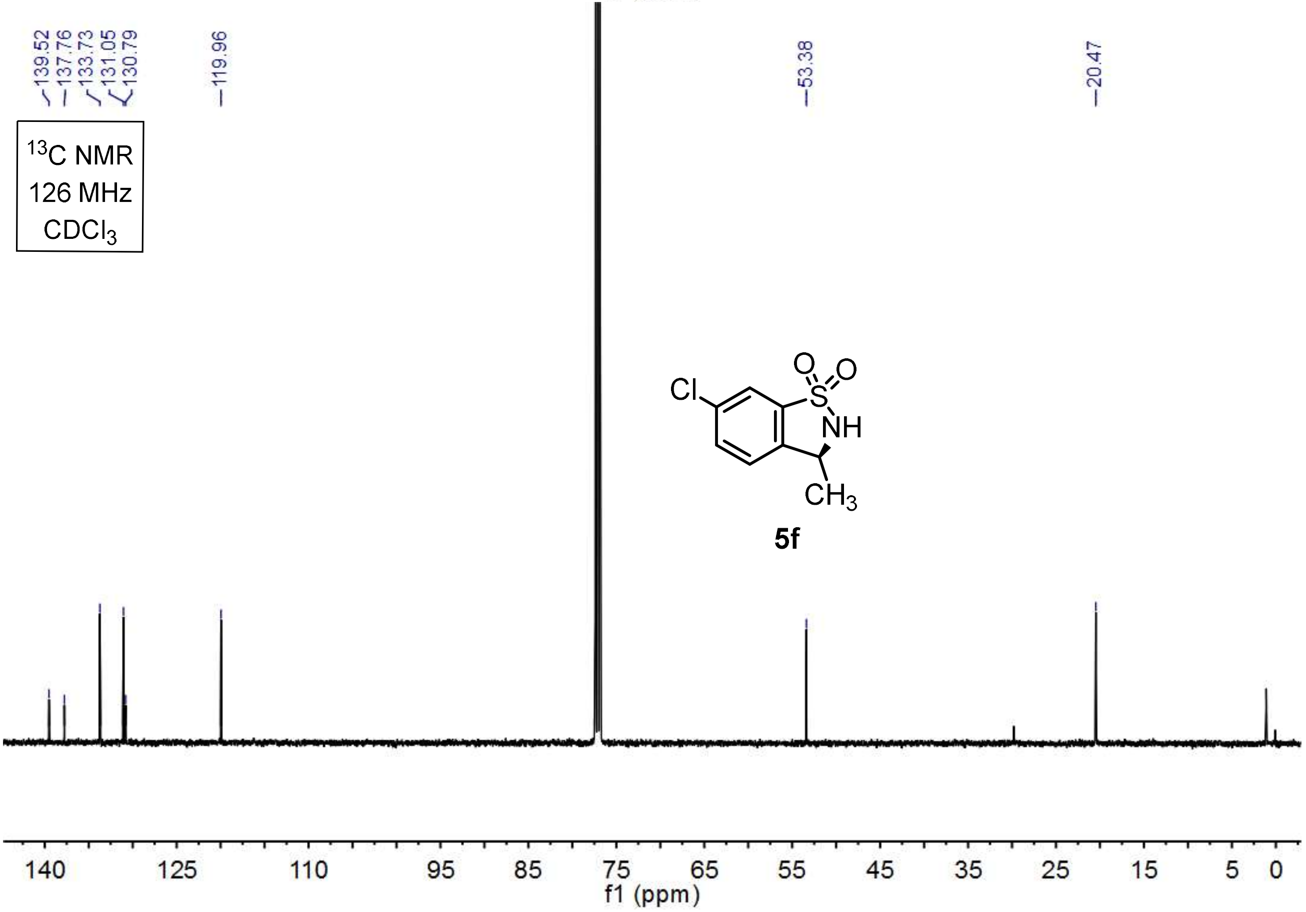

7.63
7.62
7.48
7.46
7.45
7.34
7.33
4.85
4.74
4.72
4.71
4.70
1.62
1.61
^{1}H NMR
500 MHz
$CDCl_3$
Br
O
S
O
NH
CH_3
5d
1.00
1.05
1.00
0.95
1.07
3.22
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

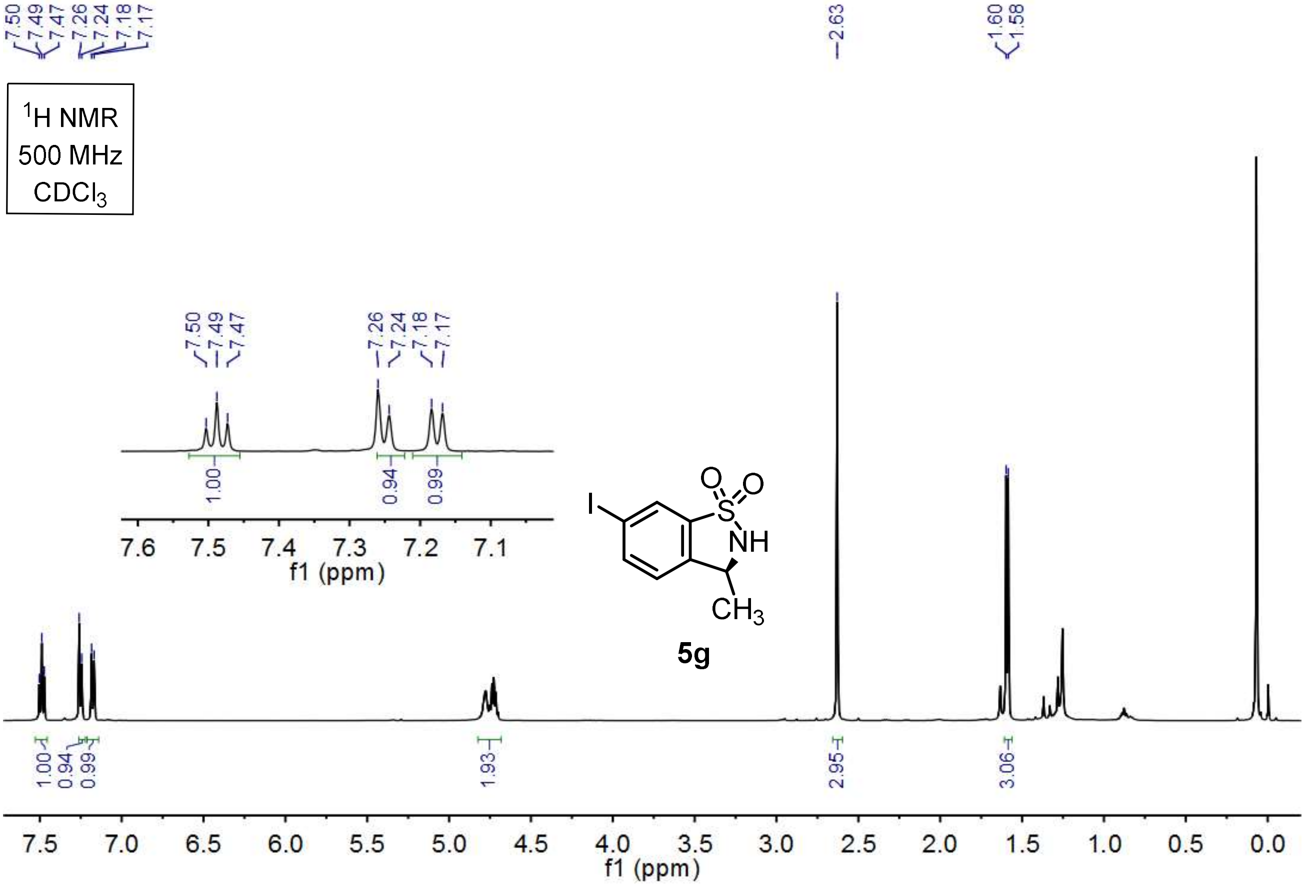

144.80
135.83
134.41
133.28
122.87
115.95
52.14
21.39
^{13}C NMR
126 MHz
$CDCl_3$
Br
O
S
O
NH
CH_3
5d
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

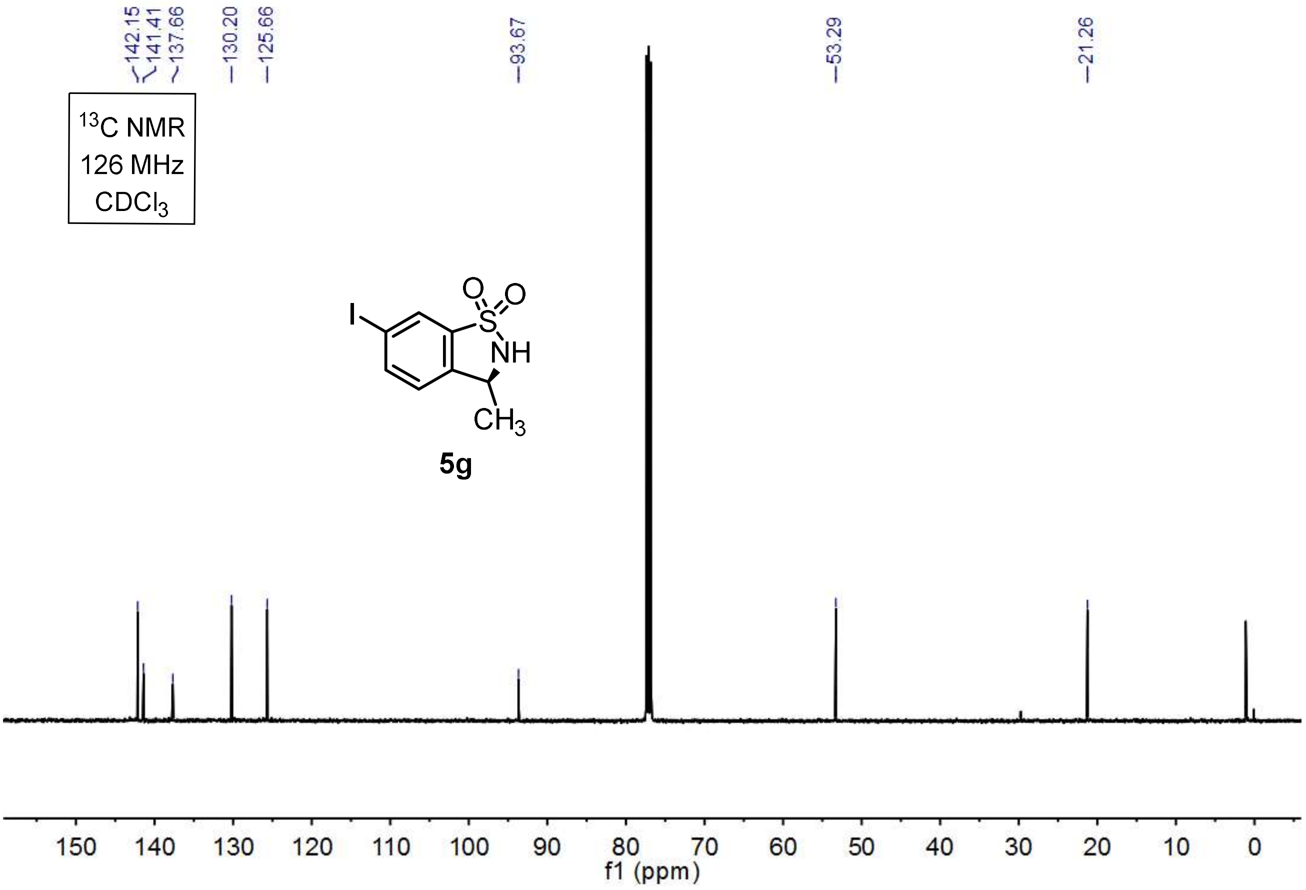

7.75
7.73
7.73
7.41
7.40
7.38
5.10
4.75
4.74
4.72
4.71
1.70
1.69
^{1}H NMR
500 MHz
CDCl$_3$
7.75
7.75
7.73
7.73
7.72
7.71
7.41
7.40
7.38
0.96
0.94
1.00
7.75
7.60
7.45
f1 (ppm)
O
O
S
NH
CH$_3$
Br
5e
0.96
0.94
1.00
0.96
1.02
3.22
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

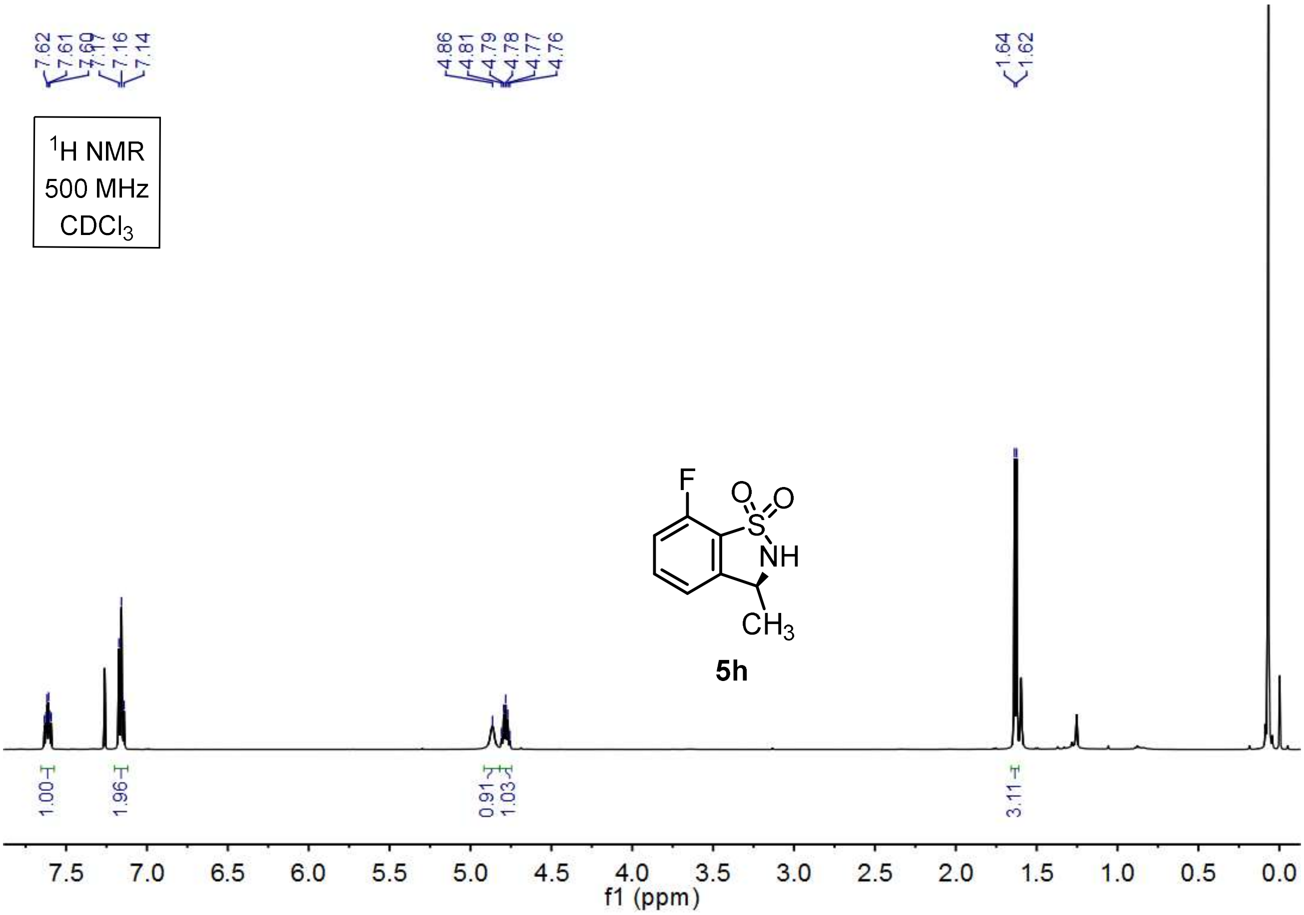

141.48
137.64
136.81
131.07
120.46
119.32
54.73
20.44
^{13}C NMR
126 MHz
CDCl$_3$
O
O
S
NH
CH$_3$
Br
5e
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.70
7.68
7.60
7.58
7.51
7.49
7.48
4.86
4.85
4.84
4.82
4.81
4.80
1.71
1.70
^{1}H NMR
500 MHz
CDCl$_3$
Cl
O
O
S
NH
CH$_3$
5f
1.00
1.03
1.06
2.22
3.24
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

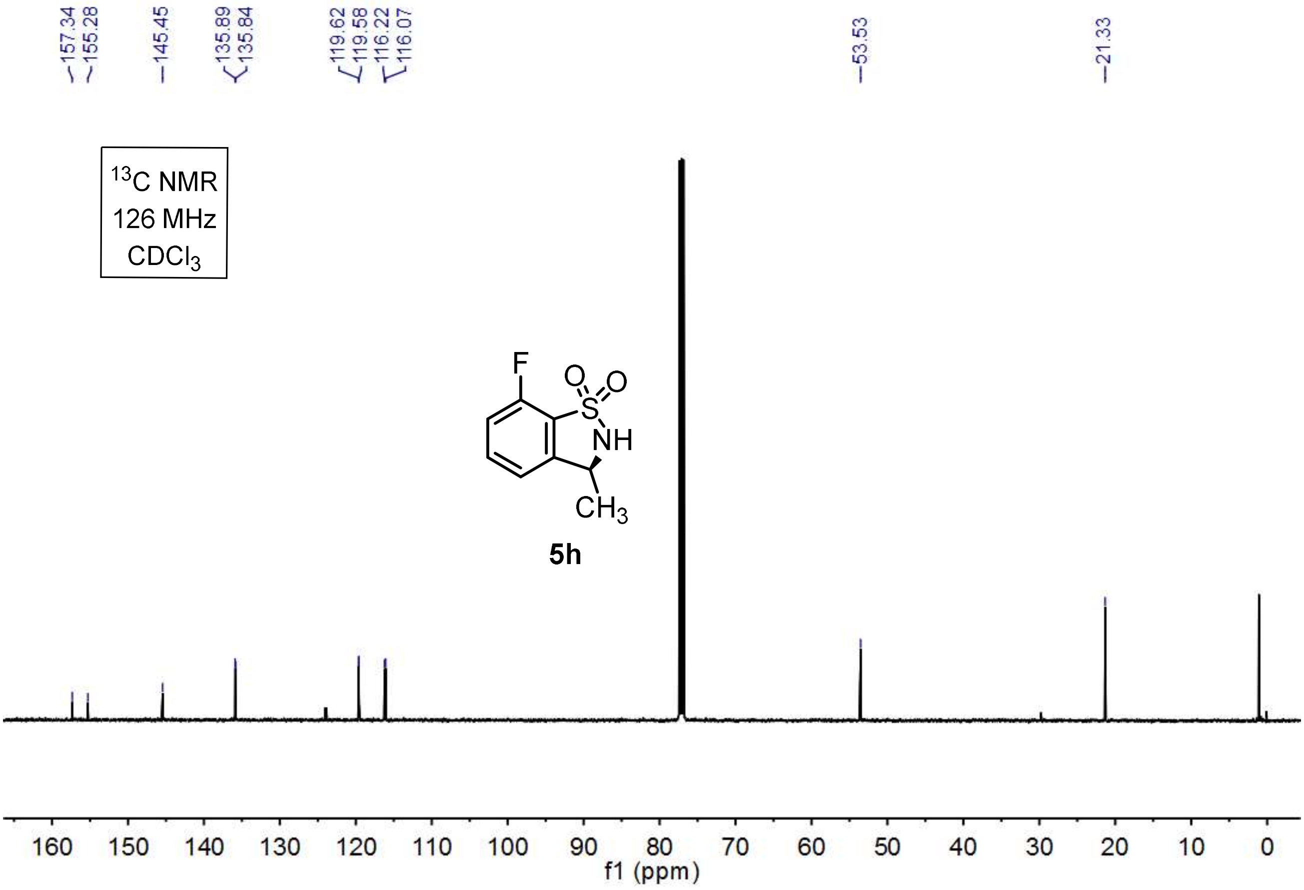

139.52
137.76
133.73
131.05
130.79
119.96
53.38
20.47
^{13}C NMR
126 MHz
CDCl$_3$
Cl
O
O
S
NH
CH$_3$
5f
140 125 110 95 85 75 65 55 45 35 25 15 5 0
f1 (ppm)


7.50
7.49
7.47
7.26
7.24
7.18
7.17
2.63
1.60
1.58
^{1}H NMR
500 MHz
$CDCl_3$
1.00
0.94
0.99
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
I
O
O
S
NH
CH_3
5g
1.00
0.94
0.99
1.93
2.95
3.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

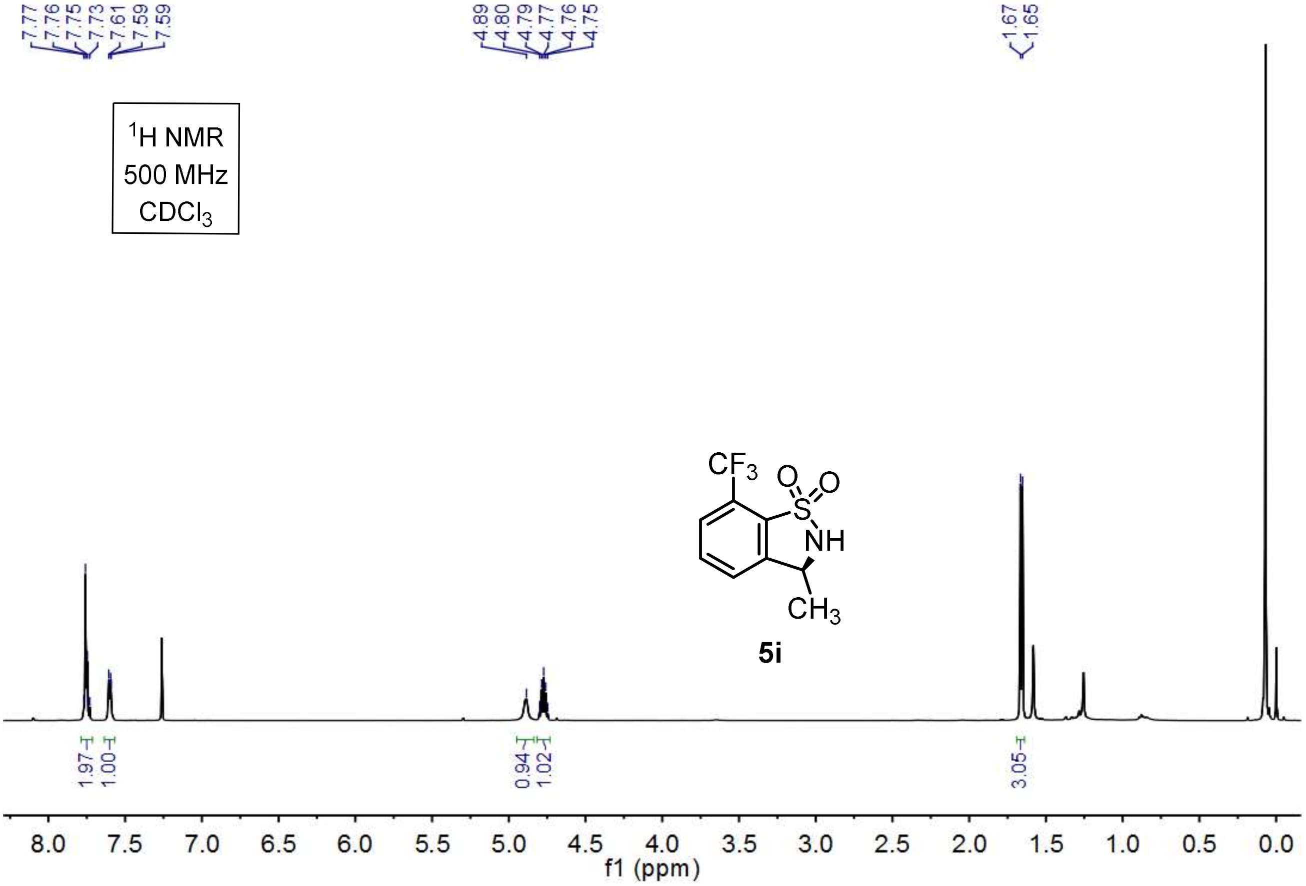

142.15
141.41
137.66
130.20
125.66
93.67
53.29
21.26
^{13}C NMR
126 MHz
$CDCl_3$
I
O
O
S
NH
CH_3
5g
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

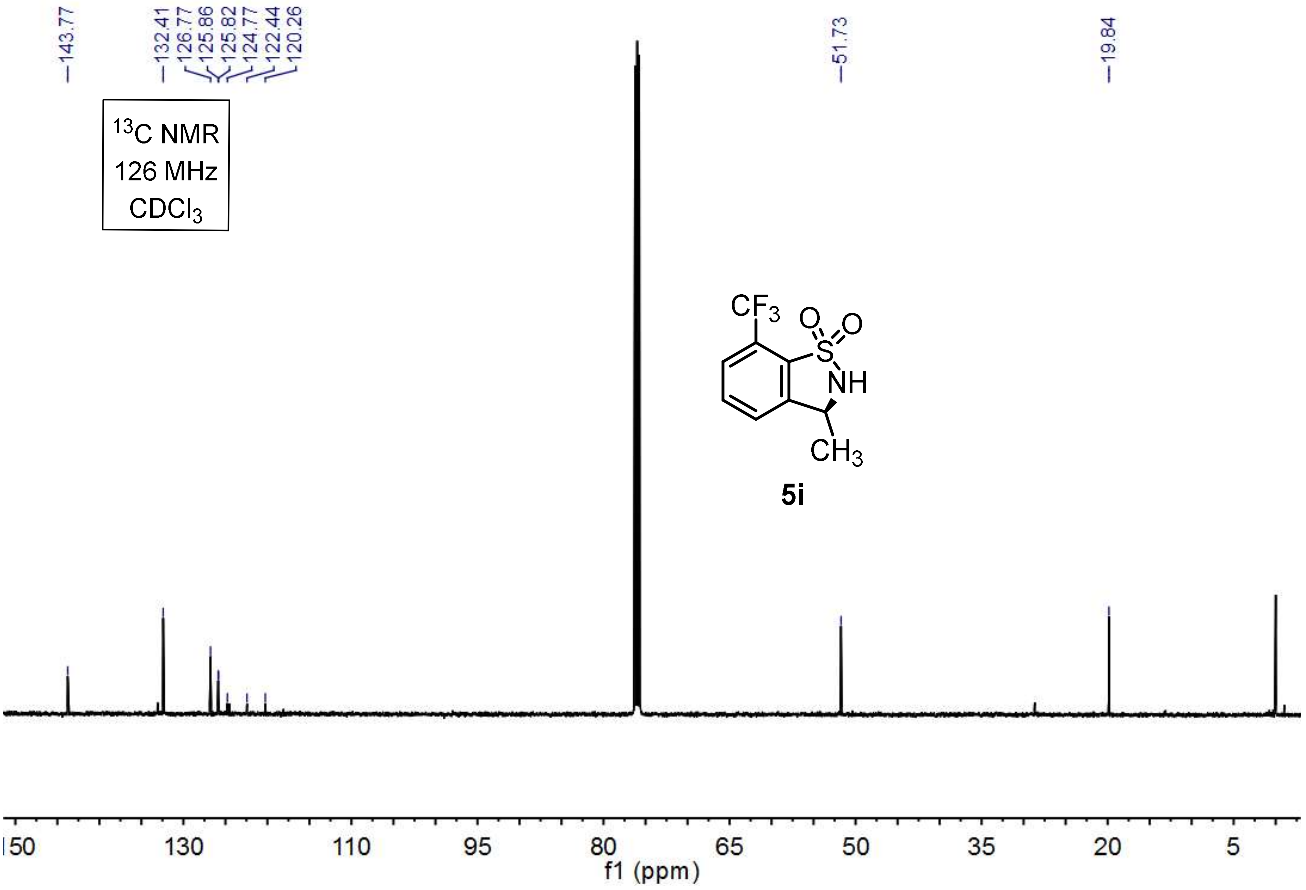

7.62
7.61
7.60
7.17
7.16
7.14
4.86
4.81
4.79
4.78
4.77
4.76
1.64
1.62
^{1}H NMR
500 MHz
CDCl$_3$
F
O
O
S
NH
CH$_3$
1.00
1.96
0.91
1.03
3.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

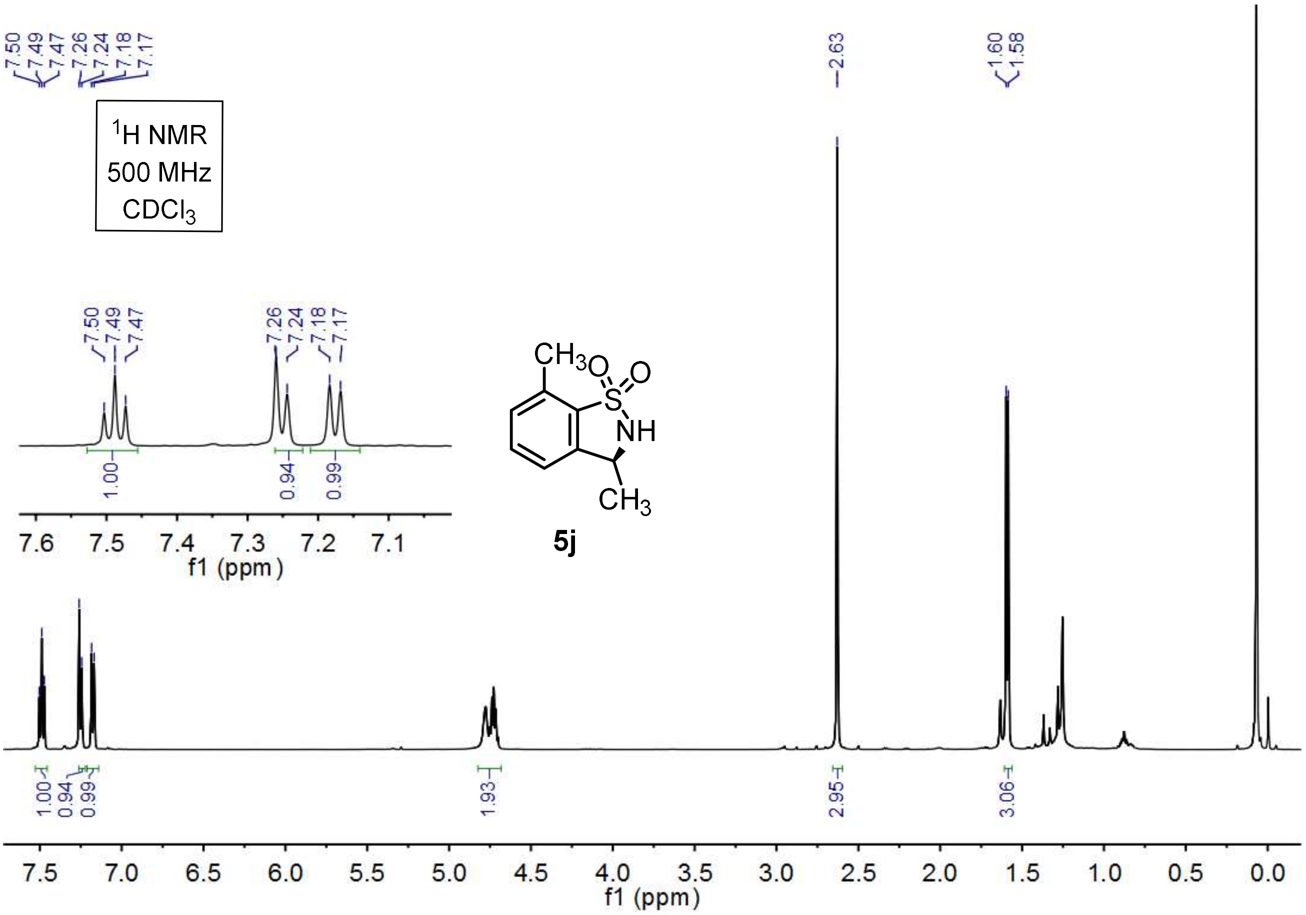
5h

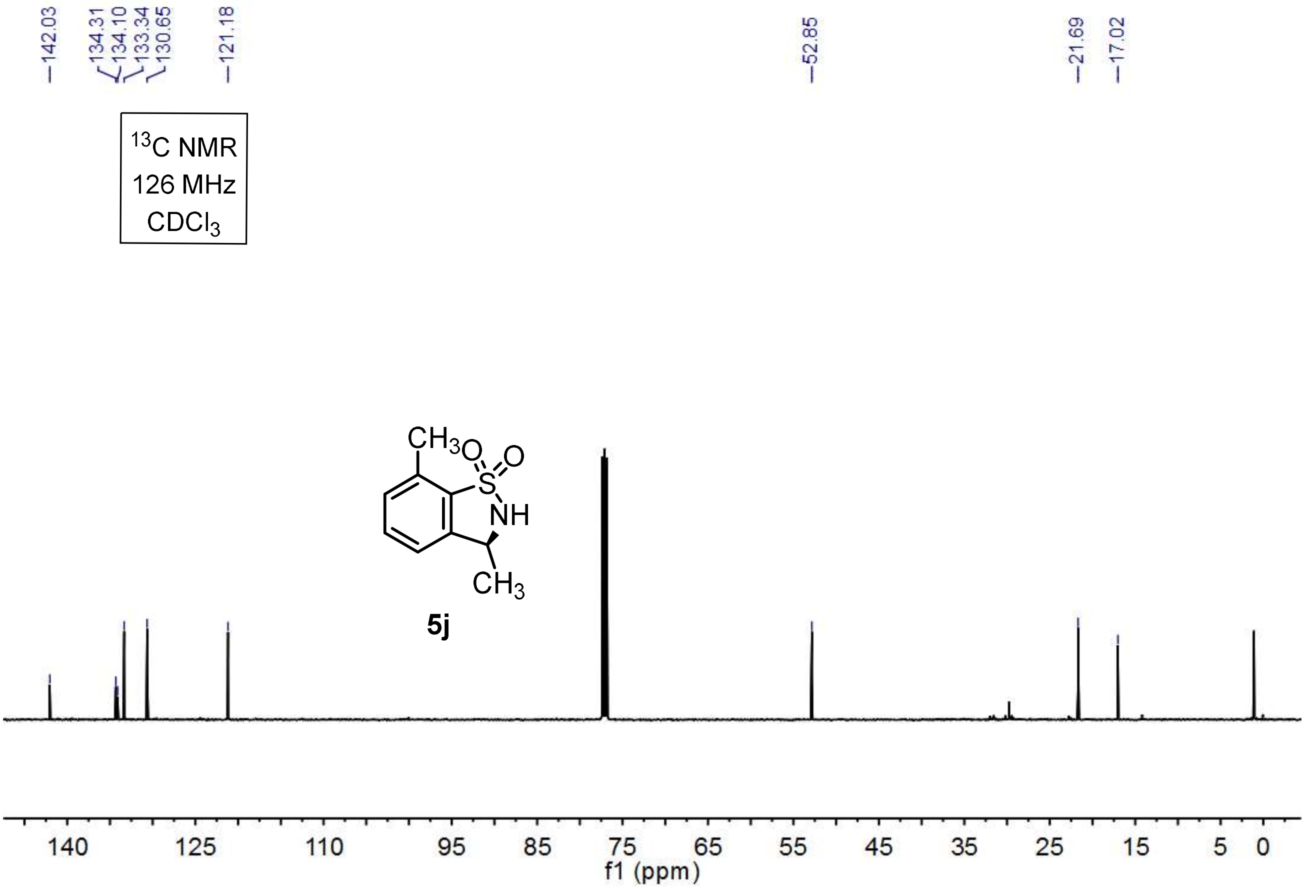

157.34
155.28
145.45
135.89
135.84
119.62
119.58
116.22
116.07
53.53
21.33
^{13}C NMR
126 MHz
CDCl$_3$
F
O
O
S
NH
CH$_3$
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

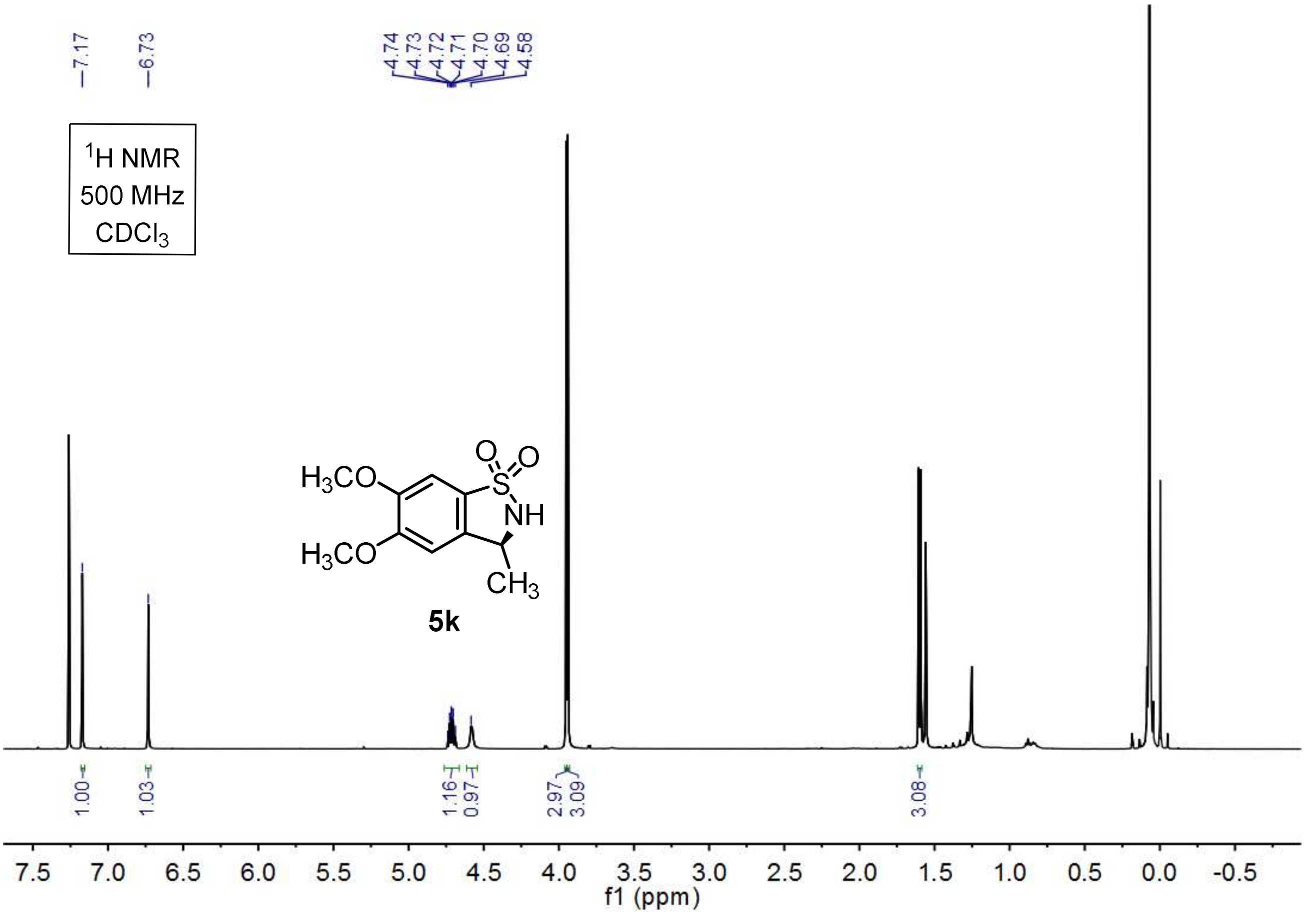
5h

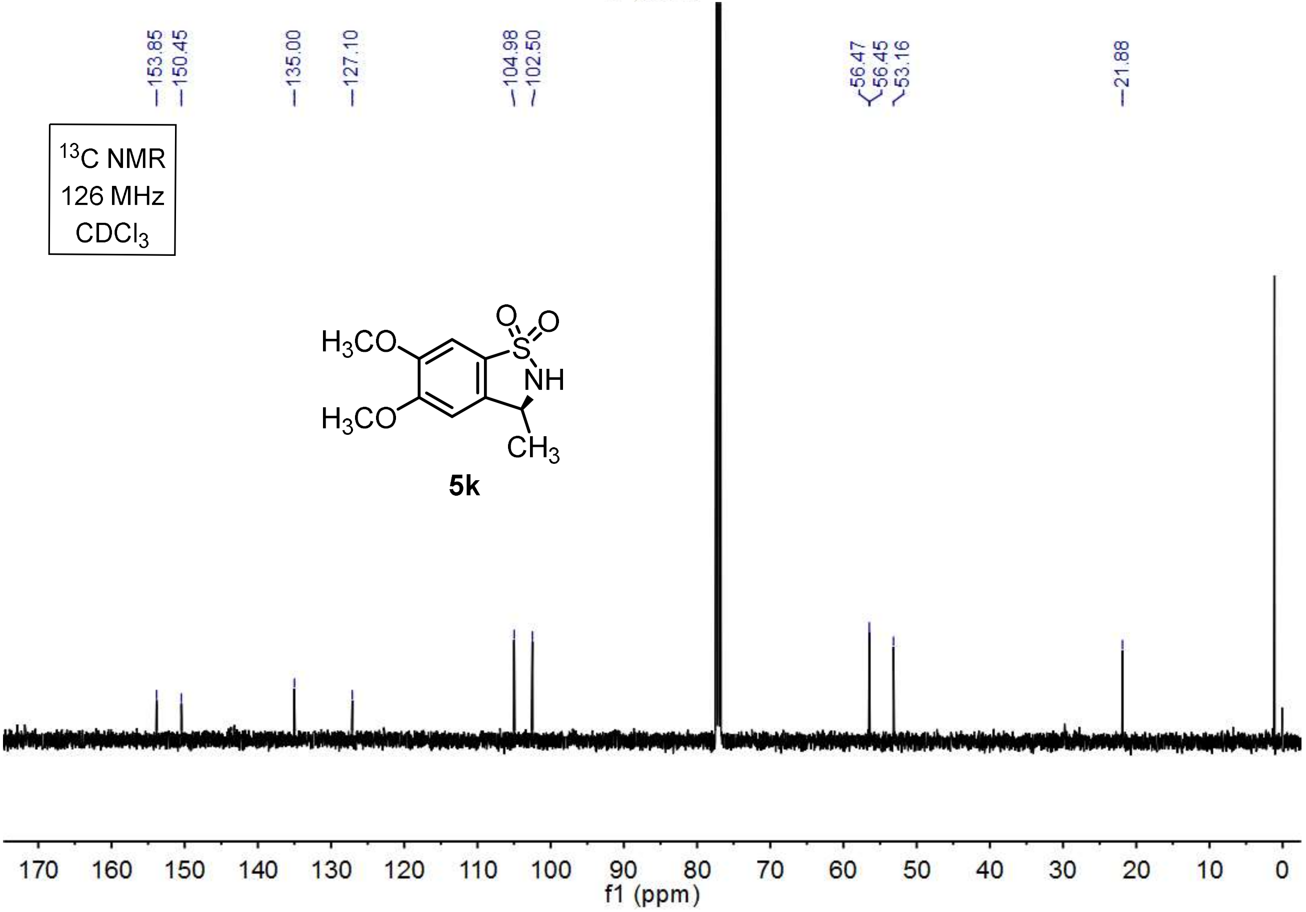

7.77
7.76
7.75
7.73
7.61
7.59
7.59
4.89
4.80
4.79
4.77
4.76
4.75
1.67
1.65
¹H NMR
500 MHz
CDCl₃
CF₃
O
O
S
NH
CH₃
5i
1.97
1.00
0.94
1.02
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

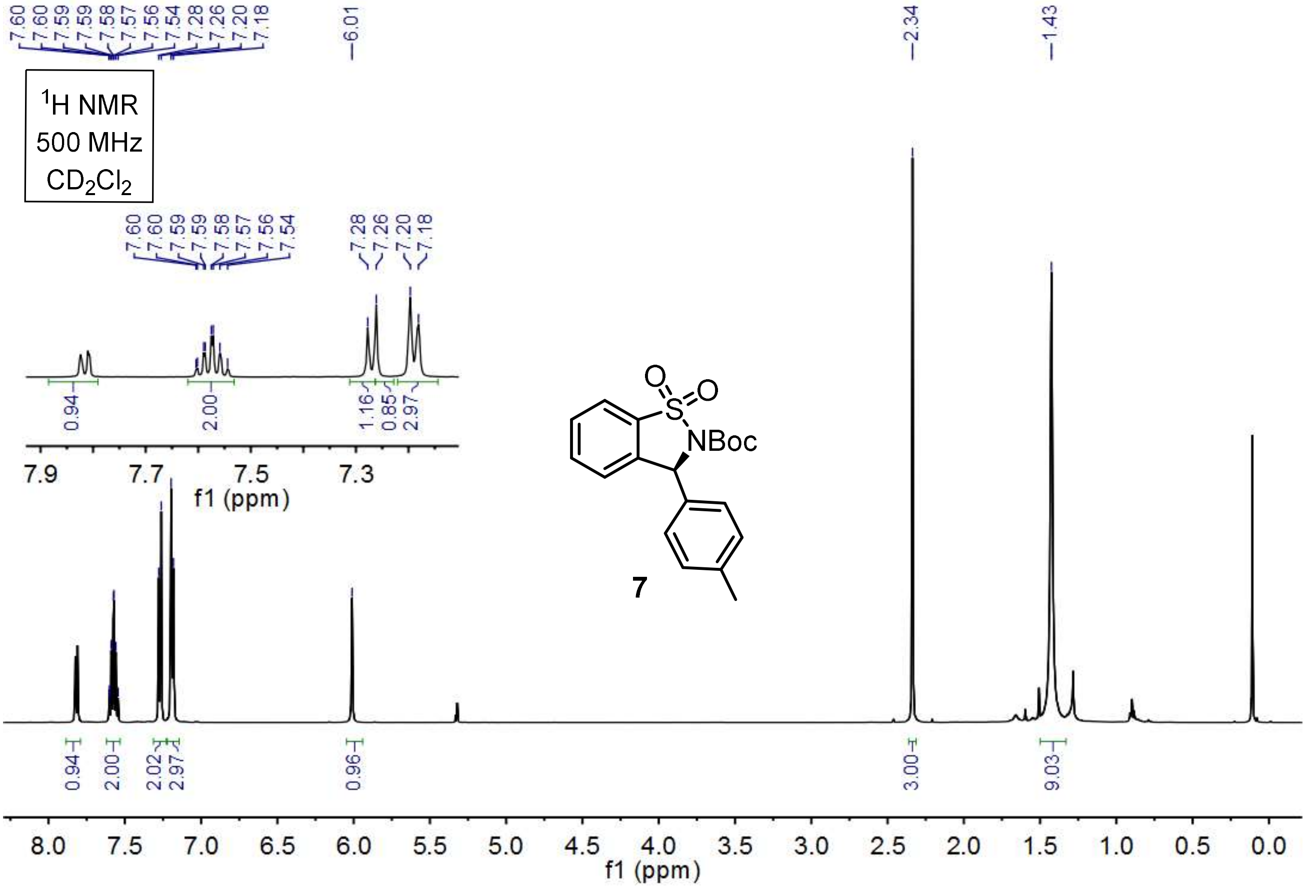

143.77
132.41
126.77
125.86
125.82
124.77
122.44
120.26
51.73
19.84
¹³C NMR
126 MHz
CDCl₃
CF₃
O
O
S
NH
CH₃
5i
150
130
110
95
80
65
50
35
20
5
f1 (ppm)

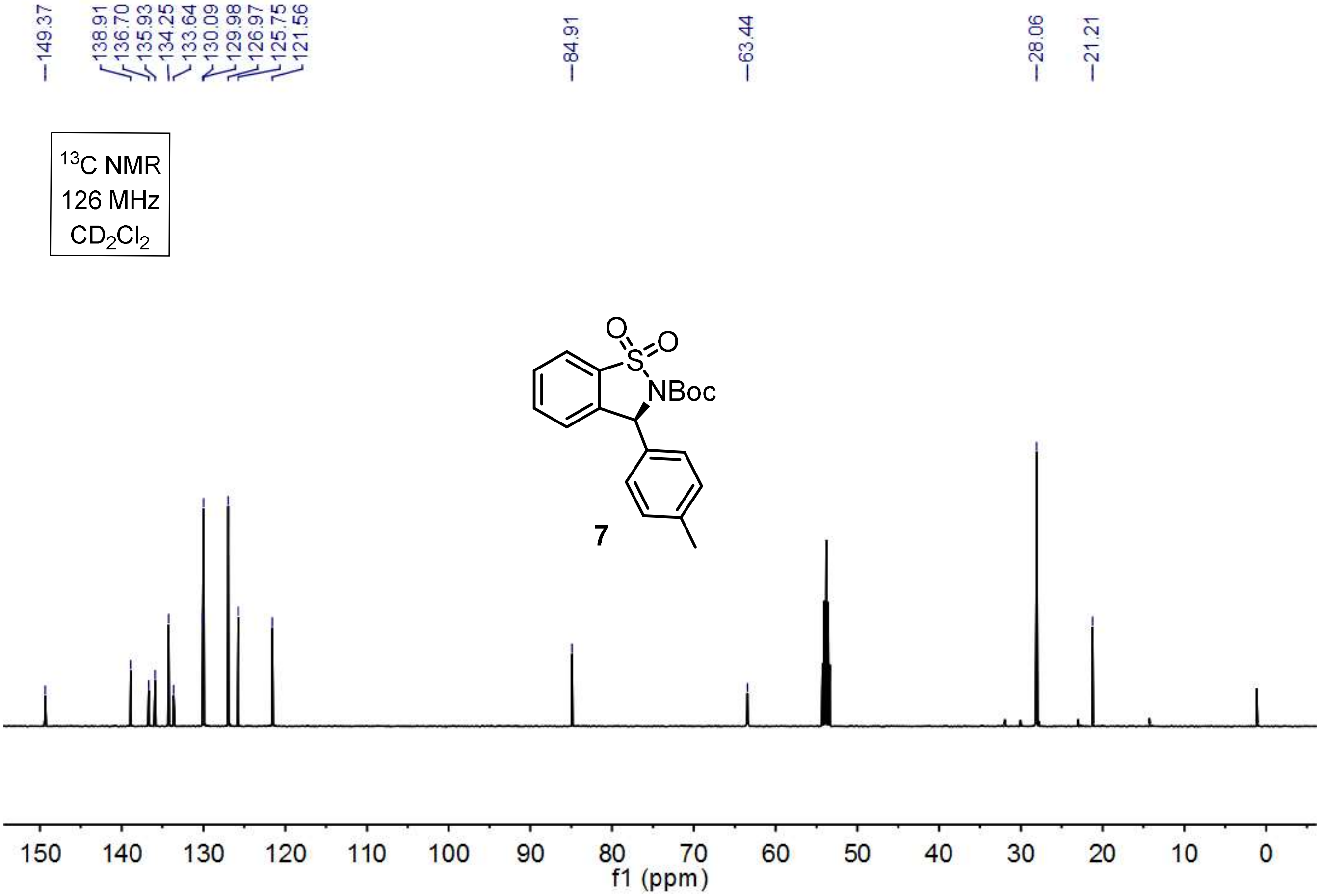

7.50
7.49
7.47
7.26
7.24
7.18
7.17
2.63
1.60
1.58
^{1}H NMR
500 MHz
CDCl$_3$
1.00
0.94
0.99
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
CH$_3$
O
O
S
NH
CH$_3$
5j
1.00
0.94
0.99
1.93
2.95
3.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

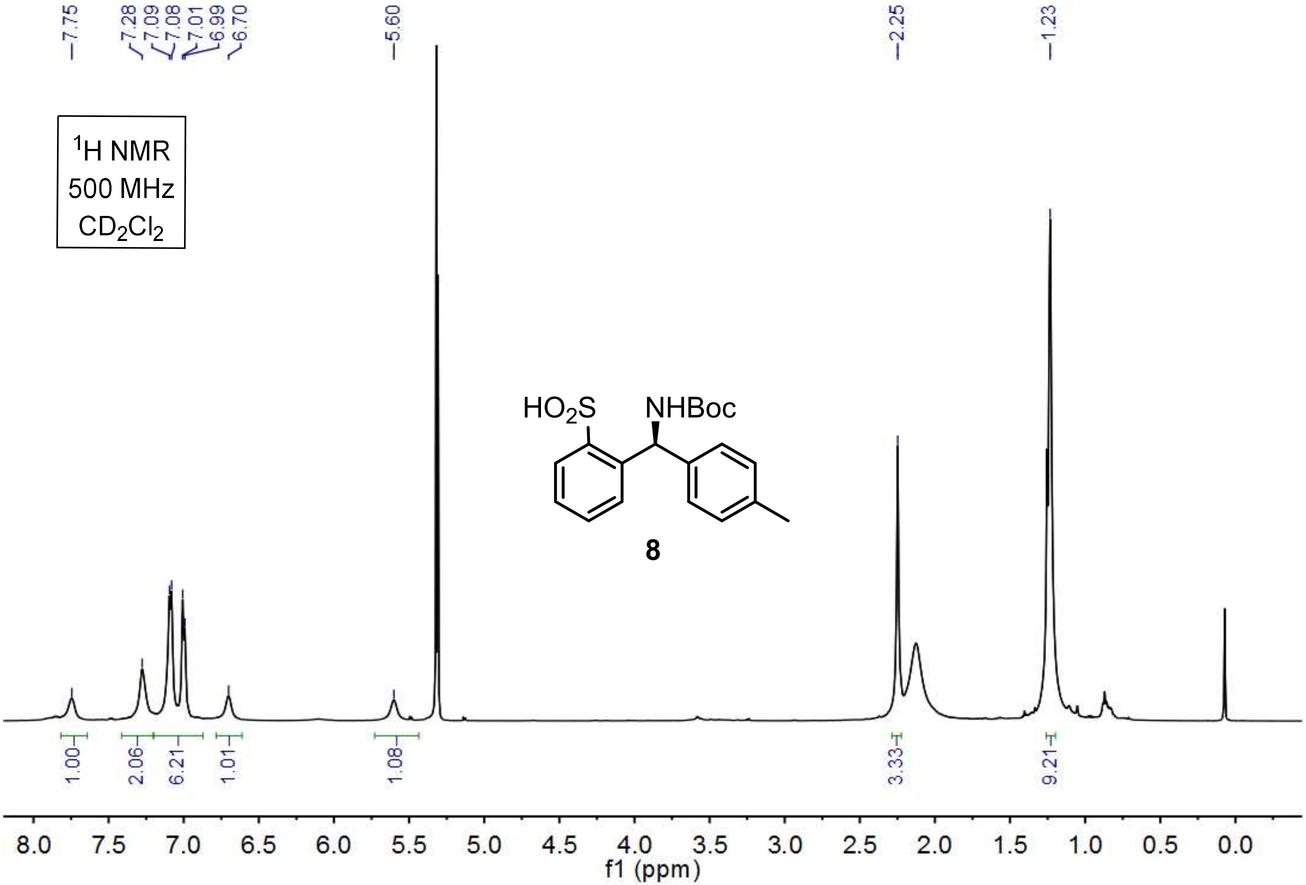

142.03
134.31
134.10
133.34
130.65
121.18
52.85
21.69
17.02
^{13}C NMR
126 MHz
CDCl$_3$
CH$_3$
O
O
S
NH
CH$_3$
5j
140
125
110
95
85
75
65
55
45
35
25
15
5
0
f1 (ppm)

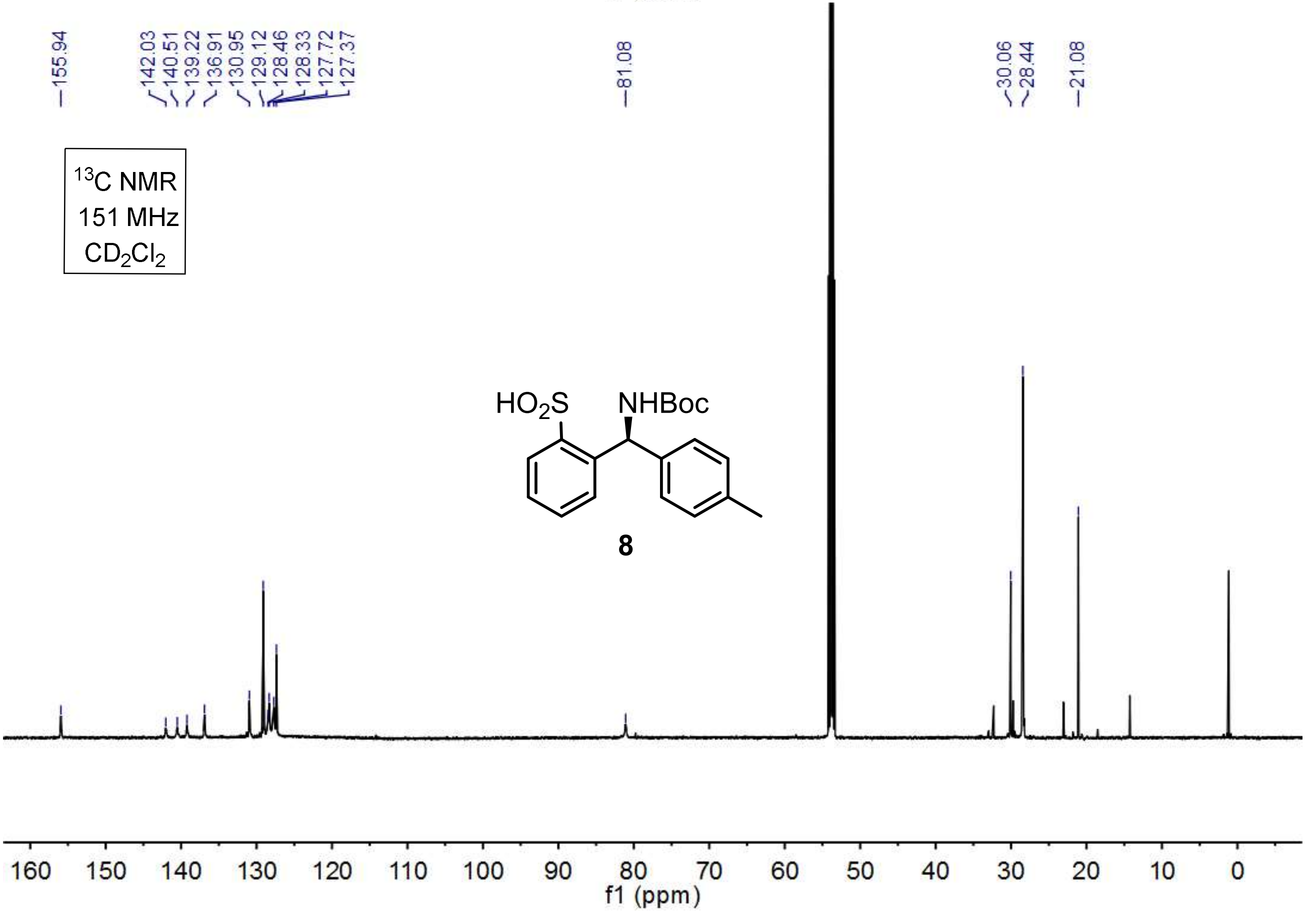

7.17
6.73
4.74
4.73
4.72
4.71
4.70
4.69
4.58
^{1}H NMR
500 MHz
$CDCl_3$
H_3CO
H_3CO
O
O
S
NH
CH_3
5k
1.00
1.03
1.16
0.97
2.97
3.09
3.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


153.85
150.45
135.00
127.10
104.98
102.50
56.47
56.45
53.16
21.88
^{13}C NMR
126 MHz
$CDCl_3$
H_3CO
H_3CO
O
O
S
NH
CH_3
5k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.60
7.60
7.59
7.59
7.58
7.57
7.56
7.54
7.28
7.26
7.20
7.18
6.01
2.34
1.43
^{1}H NMR
500 MHz
CD_2Cl_2
0.94
2.00
1.16
0.85
2.97
7.9
7.7
7.5
7.3
f1 (ppm)
O
O
S
NBoc
7
0.94
2.00
2.02
2.97
0.96
3.00
9.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.37
138.91
136.70
135.93
134.25
133.64
130.09
129.98
126.97
125.75
121.56
84.91
63.44
28.06
21.21
^{13}C NMR
126 MHz
CD_2Cl_2
O
O
S
NBoc
7
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.75
7.28
7.09
7.08
7.01
6.99
6.70
5.60
2.25
1.23
^{1}H NMR
500 MHz
CD_2Cl_2
HO_2S
NHBoc
8
1.00
2.06
6.21
1.01
1.08
3.33
9.21
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.94
142.03
140.51
139.22
136.91
130.95
129.12
128.46
128.33
127.72
127.37
81.08
30.06
28.44
21.08
^{13}C NMR
151 MHz
CD_2Cl_2
HO_2S
NHBoc
8
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)