Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Highly *cis*-Selective Synthesis of Iodo-Aziridines using Diiodomethyllithium and *in situ* Generated *N*-Boc-Imines.

James A Bull*, Tom Boultwood and Thomas A Taylor

Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, UK

E-mail: j.bull@imperial.ac.uk

General Experimental Conditions

All non-aqueous reactions were run under an inert atmosphere (argon) with flame-dried glassware using standard techniques. Anhydrous solvents were obtained by filtration through drying columns (THF, diethyl ether, CH_2Cl_2).

Flash column chromatography was performed using 230-400 mesh silica with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm), or aqueous potassium permanganate stain.

Infrared spectra (FTIR) were recorded in reciprocal centimeters (cm^{-1}).

Nuclear magnetic resonance spectra were recorded on a 400 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ = 7.27 ppm). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz, integration]. ^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard ($^{13}CDCl_3$: 77.0 ppm and $^{13}CD_3OD$: 49.00 ppm). ^{19}F NMR spectra were recorded with complete proton decoupling . Chemical shifts are reported in parts per million referenced to the standard monofluorobenzene: −113.5 ppm.

Melting points are uncorrected.

Reagents: Commercial reagents were used as supplied or purified by standard techniques where necessary.

Compound Handling/Purification/Storage:

During all handling, exposure of iodoaziridines to light should be minimized. Iodoaziridines can be stored at −20 °C, as a solution in CH_2Cl_2 or $CHCl_3$ to prevent decomposition. For example, compound **3a** was stored in a CH_2Cl_2 solution for >4 weeks without displaying noticable decomposition.

Note on Assignment of Stereochemistry:

Iodoaziridines were assigned as *cis*-iodoaziridines on the basis of the magnitude of the coupling constant between the coupling of the CHAr and CHI protons (J = 5.4 Hz). *trans*-Iodoaziridines were observed in small amounts, where stated, with coupling constants of 2.3 Hz. These assignments are consistent with the coupling constants observed for *cis*- and *trans*-bromoaziridines by Ziegler and co-workers.[1,2,3]

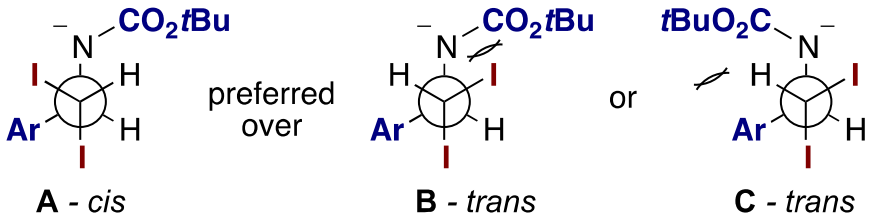
---

[1] F. E. Ziegler and M. Belema, *J. Org. Chem.* 1994, **59,** 7962
[2] F. E. Ziegler and M. Belema, *J. Org. Chem.* 1997, **62,** 1083
[3] F. E. Ziegler and M. Berlin, *Tetrahedron Lett.* 1998, **39,** 2455

Further Discussion on the Origin of *cis*-Selectivity

Our initial proposal for the stereoselectivity in the cyclisation to iodoaziridines **3** is based on subtle steric effects, illustrated below by consideration of the possible Newman projections of the intermediate anionic diiodide.

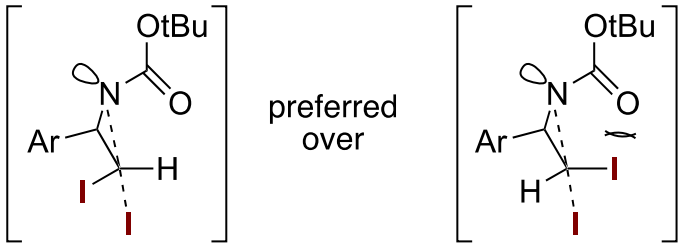
The aryl and Boc groups are likely to adopt an *anti*-periplanar orientation preferentially thus providing two potential reactive conformations, with N and I in an *anti*-periplanar arrangement appropriate for cyclisation (conformations A and B). We propose that an unfavourable interaction between the non-displaced iodide with the Boc group is dominant. Hence in the cyclisation TS, as the *N*-atom becomes sp^3 hybridised, the non-displaced iodine prefers to adopt a position away from the bulk of the Boc group and so gauche to the Ph group, resulting in the *cis*-aziridine configuration.



A - *cis* **B** - *trans* **C** - *trans*

In considering the steric bias for cyclisation it is important to consider the hybridisation at nitrogen in the *transition state* of the cyclisation. The geometry at nitrogen in aziridines is pyramidal (sp^3 hybridisation). In the transition state, the N-hybridisation will approach sp^3 as required for the bond formation and for progression to the product. This places the electron density on N, rather than conjugated into the carbonyl.

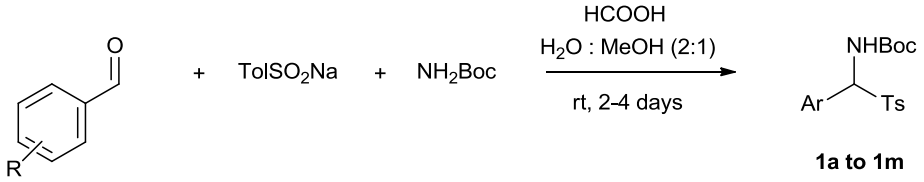
Given the large size of the iodine atom (radius I = 1.33 Å) a *cis*-substituent on N would provide a steric conflict. Furthermore, it is likely that the tBu group will be oriented into space, which will orient the C=O towards the relevant CHI_2 centre. It is on this basis that we propose the *trans*-aziridine would be dis-favoured.



A - *cis* **B** - *trans*

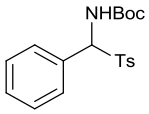
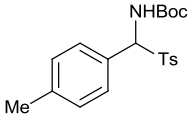
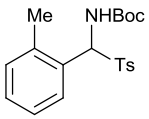
We thank a referee for suggesting a dipole minimisation argument, due to a dipole in the CHI_2 unit, that could reinforce the above stereochemical outcome.

Synthesis of *N*-Boc Imine-*p*-Toluenesulfinic Acid Adducts 1a to 1m

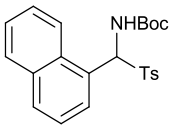
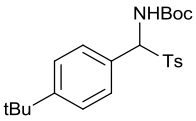
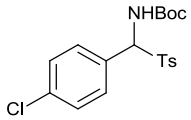
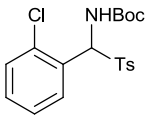
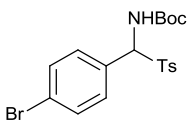


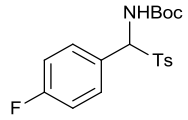
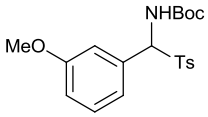
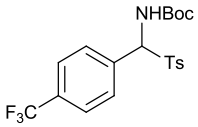
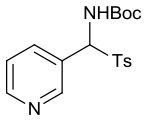
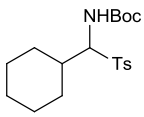
General Procedure[4]

Benzaldehyde (3.91 mL, 38.4 mmol, 1.50 equiv) was added to a suspension of *tert*-butyl carbamate (3.00 g, 25.6 mmol, 1.00 equiv) and sodium *p*-toluenesulfinate (9.11 g, 51.2 mmol, 2.0 equiv) in methanol and water (1:2, 75 mL), followed by formic acid (98%, 2.0 mL). The resulting mixture was stirred for rt for 2-4 days, during which time the product precipitated as a white solid. The precipitate was collected by filtration, then purified by trituration with diethyl ether and dried *in vacuo* to afford *N*-Boc imine–*p*-toluenesulfinic acid adduct **1a** as a white solid (8.38 g, 91%).

Compound Number	Structure	Yield (%)	NMR Data
1a		**91**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.1 Hz, 2 H, 2 × SO_2Tol-H), 7.47–7.42 (m, 5 H, 5 × Ph-H), 7.35 (d, *J* = 8.1 Hz, 2 H, 2 × SO_2Tol-H), 5.90 (d, *J* = 10.8 Hz, 1 H, NH), 5.73 (d, *J* = 10.8 Hz, 1 H, CHN), 2.45 (s, 3 H, SO_2Tol-CH_3), 1.29 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.5 (C=O), 145.0 (TolC-SO_2 quat), 133.7 (SO_2Tol*C*-CH_3 quat.), 130.0 (Ph*C*-CH quat.), 129.7 (2 × Ph-C), 129.6 (2 × SO_2Tol-C), 129.5 (2 × SO_2Tol-C), 128.9 (Ph-C), 128.7 (2 × Ph-C), 81.1 ($C(CH_3)_3$), 73.8 (HC-NH), 27.9 ($C(CH_3)_3$), 21.6 (SO_2Tol-CH_3).
1b		**79**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.2 Hz, 2 H, 2 × SO_2Tol-H), 7.33 (d, *J* = 8.1 Hz, 4 H, 2 × SO_2Tol-H and 2 × Tol-H), 7.23 (d, *J* = 8.0 Hz, 2 H, 2 × Tol-H), 5.85 (d, *J* = 10.8 Hz, 1 H, NH), 5.68 (d, *J* = 10.8 Hz, 1 H, CHN), 2.44 (s, 3 H, SO_2Tol-CH_3), 2.38 (s, 3 H, Tol-CH_3), 1.27 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.4 (C=O), 144.8 (TolC-SO_2 quat.), 139.8 (Tol*C*-CH_3 quat.), 133.8 (SO_2Tol*C*-CH_3 quat.), 129.6 (2 × SO_2Tol-C), 129.4 (2 × SO_2Tol-C), 129.3 (2 × Tol-C), 128.7 (2 × Tol-C), 126.8 (Tol*C*-CH quat.), 80.9 ($C(CH_3)_3$), 73.6 (HC-NH), 27.9 ($C(CH_3)_3$), 21.6 (SO_2Tol-CH_3), 21.2 (Tol-CH_3).
1c		**25**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 7.9 Hz, 2 H, 2 × SO_2Tol-H), 7.48–7.41 (m, 1 H, Tol-H), 7.37–7.29 (m, 5 H, 3 × Tol-H and 2 × SO_2Tol-H), 6.20 (d, 1 H, *J* = 10.8 Hz, NH), 5.75 (d, *J* = 10.8 Hz, 1 H, CHN), 2.44 (s, 3 H, SO_2Tol-CH_3), 2.43 (s, 3 H, Tol-CH_3), 1.26 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.6 (C=O), 144.9 (TolC-SO_2 quat.), 138.1 (Tol*C*-CH_3 quat.), 134.2 (SO_2Tol*C*-CH_3 quat.), 130.7 (Tol*C*-CH quat.), 129.6 (2 × SO_2Tol-C), 129.5 (2 × SO_2Tol-C), 129.3 (2 × Tol-C), 127.5 (Tol-C), 126.4 (Tol-C), 81.0 ($C(CH_3)_3$), 69.8 (CHN), 28.0 ($C(CH_3)_3$), 21.7 (SO_2Tol-CH_3), 19.8 (Tol-CH_3).

[4] A. G. Wenzel and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2002, **124**, 12964

1d		**62**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 8.4 Hz, 1 H, napthyl-H), 7.94 (d, *J* = 8.1 Hz, 1 H, napthyl-H), 7.91−7.84 (m, 3 H, napthyl-H and 2 × SO_2Tol-H), 7.77 (d, *J* = 7.3 Hz, 1 H, napthyl-H), 7.61−7.49 (m, 3 H, 3 × napthyl-H), 7.34 (d, *J* = 8.0 Hz, 2 H, 2 × SO_2Tol-H), 6.82 (d, *J* = 10.5 Hz, 1 H, NH), 5.87 (d, *J* = 10.5 Hz, 1 H, CHN), 2.43 (s, 3 H, SO_2Tol-CH_3), 1.28 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.6 (C=O), 145.0 (TolC-SO_2 quat.), 134.2 (napthyl*C*-CH quat.), 133.6 (SO_2Tol*C*-CH_3 quat.), 131.7 (napthyl-C quat.), 130.4 (napthyl-C), 129.7 (2 × SO_2Tol-C), 129.4 (2 × SO_2Tol-C), 128.8 (napthyl-C), 127.1 (napthyl-C), 126.5 (napthyl-C), 126.0 (napthyl-C), 125.0 (napthyl-C), 122.9 (napthyl-C), 122.9 (napthyl-C), 81.1 (*C*$(CH_3)_3$ quat.), 69.0 (HC-NH), 27.9 (C(*C*$H_3)_3$), 21.6 (SO_2Tol-CH_3).
1e		**59**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.2 Hz, 2 H, 2 × SO_2Tol-H), 7.45 (d, *J* = 8.5 Hz, 2 H, 2 × *t*BuAr-H), 7.39 (d, *J* = 8.5 Hz, 2 H, 2 × *t*BuAr-H), 7.34 (d, *J* = 8.2 Hz, 2 H, 2 × SO_2Tol-H), 5.87 (d, *J* = 10.8 Hz, 1 H, NH), 5.71 (d, *J* = 10.8 Hz, 1 H, CHN), 2.43 (s, 3 H, SO_2Tol-CH_3), 1.33 (s, 9 H, $OC(CH_3)_3$), 1.25 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.4 (C=O), 152.9 (Ar*C*-*t*Bu quat.), 144.8 (TolC-SO_2 quat.), 133.9 (SO_2Tol*C*-CH_3 quat.), 129.6 (2 × SO_2Tol-C), 129.5 (2 × SO_2Tol-C), 128.6 (*t*BuCAr-*C*), 126.8 (*t*BuAr*C*-CH quat.), 125.7 (*t*BuAr-*C*), 80.9 (O*C*$(CH_3)_3$), 73.6 (HC-NH), 34.7 (ArC-*C*$(CH_3)_3$), 31.2 (ArC-C(*C*$H_3)_3$, 27.9 (OC(*C*$H_3)_3$), 21.6 (SO_2Tol-CH_3).
1f		**26**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 7.8 Hz, 2 H, 2 × SO_2Tol-H), 7.40–7.37 (m, 4 H, 4 × ClAr-H), 7.34 (d, *J* = 8.0 Hz, 2 H, 2 × SO_2Tol-H), 5.89 (d, *J* = 10.6 Hz, 1 H, NH), 5.81 (d, *J* = 10.6 Hz, 1 H, CHN), 2.44 (s, 3 H, SO_2Tol-CH_3), 1.26 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.4 (C=O), 145.2 (TolC-SO_2 quat.), 135.9 (ArC-Cl quat.), 133.5 (SO_2Tol*C*-CH_3 quat.), 130.2 (2 × ClAr-C), 129.7 (2 × SO_2Tol-C), 129.5 (2 × SO_2Tol-C), 128.9 (2 × ClAr-C), 128.6 (ClAr*C*-CH quat.), 81.3 (*C*$(CH_3)_3$), 73.1 (HC-NH), 27.9 (C(*C*$H_3)_3$), 21.6 (SO_2Tol-CH_3).
1g		**57**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.0 Hz, 2 H, SO_2Tol-H), 7.59–7.53 (m, 1 H, ClAr-H), 7.40–7.31 (m, 5 H, 3 × ClAr-H and 2 × SO_2Tol-H), 6.57 (d, *J* = 10.9 Hz, 1 H, NH), 5.82 (d, 1 H, *J* = 10.8 Hz, CHN), 2.44 (s, 3 H, SO_2Tol-CH_3), 1.30 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101MHz, $CDCl_3$)** δ 153.5 (C=O), 145.2 (TolC-SO_2 quat.), 135.3 (Cl-CAr quat.), 133.9 (SO_2Tol*C*-CH_3 quat.), 130.8 (ClAr-C), 129.8 (ClAr-C), 129.7 (2 × SO_2Tol-C), 129.3 (2 × SO_2Tol-C and ClAr-C), 129.0 (ClAr*C*-CH quat.), 127.2 (ClAr-C), 81.2 (*C*$(CH_3)_3$), 70.0 (HC-NH), 27.9 (C(*C*$H_3)_3$), 21.6 (SO_2Tol-CH_3).
1h		**84**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.1 Hz, 2 H, 2 × SO_2Tol-H), 7.56 (d, *J* = 8.5 Hz, 2 H, 2 × BrAr-H), 7.35 (d, *J* = 8.1 Hz, 2 H, 2 × SO_2Tol-H), 7.32 (d, *J* = 8.5 Hz, 2 H, 2 × BrAr-H), 5.85 (d, *J* = 10.5 Hz, 1 H, NH), 5.66 (d, *J* = 10.5 Hz, 1 H, CHN), 2.44 (s, 3 H, SO_2Tol-CH_3), 1.27 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.4 (C=O), 145.3 (TolC-SO_2 quat.), 133.4 (SO_2Tol*C*-CH_3 quat.), 131.9 (2 × BrAr-C), 130.4 (2 × BrAr-C), 129.8 (2 × SO_2Tol-C), 129.5 (2 × SO_2Tol-C), 129.1 (BrAr*C*-CH quat.), 124.1 (ArC-Br – quat.), 81.3 (*C*$(CH_3)_3$), 73.1 (HC-NH), 27.9 (C(*C*$H_3)_3$), 21.6 (SO_2Tol-CH_3).

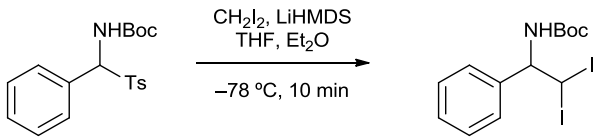
1i		**56**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.1 Hz, 2 H, 2 × SO_2Tol-H), 7.47−7.39 (m, 2 H, FAr-H), 7.35 (d, *J* = 8.1 Hz, 2 H, SO_2Tol-H), 7.16−7.07 (m, 2 H, 2 × FAr-H), 5.87 (d, *J* = 10.8 Hz, 1 H, NH), 5.67 (d, *J* = 10.8 Hz, 1 H, CHN), 2.44 (s, 3 H, SO_2Tol-CH_3), 1.27 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.5 (d, *J* = 249.5 Hz, Ar-CF quat.), 153.5 (C=O), 145.1 (TolC-SO_2), 133.5 (SO_2Tol*C*-CH_3 quat.), 130.8 (d, *J* = 8.2 Hz, 2 × FAr-C), 129.7 (2 × SO_2Tol-C), 129.4 (2 × SO_2Tol-C), 125.9 (d, *J* = 3.0 Hz, FAr*C*-CH quat.), 115.8 (d, *J* = 21.7 Hz, 2 × FAr-C), 81.2 (*C*$(CH_3)_3$ quat.), 73.1 (CHN), 27.9 ($C(CH_3)_3$), 21.6 (SO_2Tol-CH_3).
1j		**84**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.2 Hz, 2 H, 2 × SO_2Tol-H), 7.33 (m, 3 H, 2 × SO_2Tol-H and MeOAr-H), 7.02 (d, *J* = 7.7 Hz, 1 H, MeOAr-H), 6.97 (m, 2 H, 2 × MeOAr-H), 5.85 (d, *J* = 10.5 Hz, 1 H, NH), 5.69 (d, *J* = 10.7 Hz, 1 H, CHN), 3.82 (s, 3 H, Ar-OCH_3), 2.44 (s, 3 H, SO_2Tol-CH_3), 1.28 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.6 (Ar*C*-OCH_3 quat.), 153.5 (C=O), 145.0 (TolC-SO_2 quat.), 133.8 (SO_2Tol*C*-CH_3 quat.), 131.4 (MeOAr*C*-CH), 129.7 (MeOAr-C), 129.6 (2 × SO_2Tol-C), 129.5 (2 × SO_2Tol-C), 121.1 (MeOAr-C), 115.5 (MeOAr-C), 114.4 (MeOAr-C), 81.1 (*C*$(CH_3)_3$), 73.8 (HC-NH), 55.3 (ArC-O*C*H_3), 27.9 ($C(CH_3)_3$), 21.6 (SO_2Tol-CH_3).
1k		**59**	**^{1}H NMR (400 MHz, $CDCl_3$)** 7.80 (d, *J* = 8.2 Hz, 2 H, 2 × SO_2Tol-H), 7.68 (d, *J* = 8.3 Hz, 2 H, 2 × F_3CAr-H), 7.59 (d, *J* = 8.3 Hz, 2 H, 2 × F_3CAr-H), 7.36 (d, *J* = 8.2 Hz, 2 H, 2 × SO_2Tol-H), 5.96 (d, *J* = 10.8 Hz, 1 H, NH), 5.83 (d, *J* = 10.8 Hz, 1 H, CHN), 2.45 (s, 3 H, SO_2Tol-CH_3), 1.27 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.4 (C=O), 145.5 (Tol*C*-SO_2 quat.), 134.0 (F_3CAr*C*-CH quat.), 133.4 (SO_2Tol*C*-CH_3 quat.), 131.8 (q, *J* = 32.8 Hz, F_3C-*C*Ar quat.), 129.8 (2 × F_3CAr-C), 129.5 (2 × SO_2Tol-C), 129.4 (2 × SO_2Tol-C), 125.6 (q, *J* = 3.1 Hz, 2 × F_3CAr-C), 124.8 (q, *J* = 272.7 Hz, F_3*C*-CAr), 81.5 (*C*$(CH_3)_3$), 73.2 (HC-NH), 27.9 ($C(CH_3)_3$), 21.7 (SO_2Tol-CH_3).
1l		**43**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.68 (dd, *J* = 4.8, 1.4 Hz, 1 H, pyr-H), 8.67-8.63 (m, 1 H, pyr-H), 7.89-7.83 (m, 1 H, pyr-H), 7.80 (d, *J* = 8.2 Hz, 2 H, 2 × SO_2Tol-H), 7.43-7.32 (m, 3 H, pyr-H and 2 × SO_2Tol-H), 6.02-5.79 (m, 2 H, NH and CHN), 2.45 (s, 3 H, SO_2Tol-CH_3), 1.28 (s, 9 H, $C(CH_3)_3$). **^{13}C NMR (101MHz, $CDCl_3$)** δ 153.6 (C=O), 150.6 (pyr-C), 149.9 (pyr-C), 145.5 (Tol*C*-SO_2 quat.), 136.3 (pyr*C*-CH quat.), 133.2 (SO_2Tol*C*-CH_3 quat.), 129.8 (2 × SO_2Tol-C), 129.5 (2 × SO_2Tol-C), 126.6 (pyr-C), 123.5 (pyr-C), 81.4 (*C*$(CH_3)_3$), 71.9 (HC-NH), 27.9 ($C(CH_3)_3$), 21.6 (SO_2Tol-CH_3).
1m		**74**	**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2 H, 2 × SO_2Tol-H), 7.31 (d, *J* = 8.2 Hz, 2 H, 2 × SO_2Tol-H), 5.18 (d, 1 H, *J* = 11.2 Hz, NH), 4.67 (dd, *J* = 11.2, 3.6 Hz, 1 H, CHN), 2.40 (s, 3 H, SO_2Tol-CH_3), 2.13 (d, *J* = 12.4 Hz, 1 H, Cy-H), 1.82-1.64 (m, 5 H, 5 × Cy-H), 1.41-1.32 (m, 2 H, 2 × Cy-H), 1.23 (s, 9 H, $C(CH_3)_3$), 1.14 (m, 3 H, 3 × Cy-H). **^{13}C NMR (101MHz, $CDCl_3$)** δ 154.0 (C=O), 144.5 (Tol*C*-SO_2 quat.), 134.9 (SO_2Tol*C*-CH_3 quat.), 129.5 (2 × SO_2Tol-C), 128.9 (2 × SO_2Tol-C), 80.4 (*C*$(CH_3)_3$), 74.3 (HC-NH), 36.2 (CyC-CH), 30.5 (Cy-C), 27.8 ($C(CH_3)_3$), 27.4 (Cy-C), 27.2 (Cy-C), 25.9 (Cy-C), 25.6 (Cy-C), 25.5 (Cy-C), 21.4 (SO_2Tol-CH_3).

Compounds **1a**,[5] **1b**,[5] **1f**,[5] **1j**,[5] and **1m**,[5] are previously reported without NMR characterisation data. Compound **1c** is previously reported and the above data is consistent with that in the literature.[6]

[5] E. Bernacka, A. Klepacz and A. Zwierzak, *Tetrahedron Lett.* 2001, **42**, 5093.
[6] L. Huang and W. D. Wulff, *J. Am. Chem. Soc.* 2011, **133**, 8892.

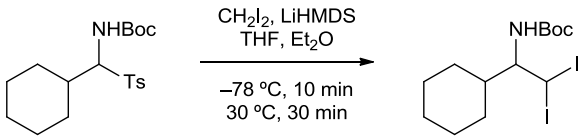
Synthesis of amino-*gem*-diiodides

(2,2-Diiodo-1-phenyl-ethyl)-*tert*-butylcarbamate (2a)



Diiodomethane (145 µL, 1.80 mmol, 3.0 equiv.) in THF (1.6 mL) was added dropwise to a solution of LiHMDS (1 M solution in THF, 1.56 mL, 1.56 mmol, 2.6 equiv.) in THF (6.0 mL) and diethyl ether (3.0 mL) at –78 °C in the dark. After 20 minutes at −78 °C, a solution of the imine-toluene sulfinic acid adduct **1a** (217 mg, 0.60 mmol, 1.0 equiv.) in THF (3 mL) was added dropwise to the reaction mixture. After a further 10 minutes at −78 °C, the reaction was quenched by the addition of saturated aqueous sodium bicarbonate solution (40 mL). The aqueous solution was extracted with CH_2Cl_2 (3 × 30 mL) and the organic extracts were combined, dried (Na_2SO_4), filtered and solvent removed *in vacuo*. Purification by flash chromatography (10% diethyl ether/hexanes) afforded amino-*gem*-diiodide **2a** (232 mg, 80%) as a white solid. R_f 0.10 (10% diethyl ether/hexanes). ν_{max} (film)/cm^{-1} 2980, 1699 (C=O), 1490, 1366, 1244, 1160, 1047. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.35 (m, 5 H, Ph-H), 5.46 (br s, 1 H, CHI_2), 5.37 (br s, 1 H, NH), 4.90 (br s, 1 H, CHPh), 1.51 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (C=O), 138.7 (Ph-C quat.), 128.6 (Ph-C), 128.3 (2 × Ph-C), 126.7 (2 × Ph-C), 80.5 ($C(CH_3)_3$), 62.2 (CHN), 28.3 ($C(CH_3)_3$), −14.7 (CHI_2). HRMS (ESI) *m/z* Calculated for $C_9H_{10}I_2NO_2^+$ [M-*t*Bu+2H]$^+$: 417.8795; Found: 417.8794.

(2,2-Diiodo-1-cyclohexyl-ethyl)-*tert*-butylcarbamate (2m)

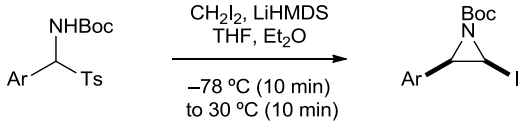


Diiodomethane (145 µL, 1.80 mmol, 3.0 equiv.) in THF (1.6 mL) was added dropwise to a solution of LiHMDS (1 M solution in THF, 1.56 mL, 1.56 mmol, 2.6 equiv.) in THF (6.0 mL) and diethyl ether (3.0 mL) at –78 °C in the dark. After 20 minutes at −78 °C, a solution of the imine-toluene sulfinic acid adduct **1m** (222 mg, 0.60 mmol, 1.0 equiv.) in THF (3.0 mL) was added dropwise to the reaction mixture. After 10 minutes at −78 °C, the reaction was then transferred to warm in a water bath at 30 °C for 30 minutes and then was then quenched by the addition of saturated aqueous sodium bicarbonate solution (40 mL). The aqueous mixture was extracted with CH_2Cl_2 (3 × 40 mL). The organic extracts were then combined, dried (Na_2SO_4), filtered and solvent removed *in vacuo*. Purification by flash chromatography (10% ethyl acetate/hexane) afforded amino-*gem*-diiodide **2m** (83 mg, 29%) as a colourless oil. R_f 0.33 (10% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2979, 2925, 2853, 1706 (C=O), 1495, 1366, 1240, 1163, 1056, 1017. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 (1 H, d, *J* = 2.7 Hz, CHI), 4.76 (1 H, d, *J* = 10.3 Hz, NH), 3.20 (1 H, ddd, *J* = 10.3, 8.9, 2.7 Hz, CHN), 1.88-1.61 (4 H, m, 4 × Cy-H), 1.49 (9 H, s, $C(CH_3)_3$), 1.33−0.86 (6 H, m, 6 × Cy-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6 (C=O), 79.7 ($C(CH_3)_3$ quat.), 63.1 (CHN), 43.8 (Cy*C*-CH), 29.7 (Cy-C), 28.9, 28.4 ($C(CH_3)_3$), 25.8(3) (Cy-C), 25.7(9) (Cy-C), 25.6 (Cy-C), −15.1 (CHI_2).

Note: Rotamers observed for CHN, NH and CHI_2 protons. Peaks given for major rotamer.

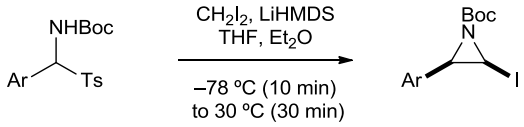
Synthesis of Iodoaziridines 3a-l

General Procedures:



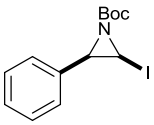
General Procedure A

Diiodomethane (145 µL, 1.80 mmol, 3.0 equiv.) in THF (1.6 mL) was added dropwise to a solution of LiHMDS (1 M solution in THF, 1.56 mL, 1.56 mmol, 2.6 equiv.) in THF (6.0 mL) and diethyl ether (3.0 mL) at –78 °C in the dark. After 20 minutes at −78 °C, a solution of the imine-toluene sulfinic acid adduct (0.60 mmol, 1.0 equiv.) in THF (2.0 mL) was added dropwise to the reaction mixture. After 10 minutes at −78 °C, the reaction flask was transferred to a water bath at 30 °C for 10 minutes and then quenched by the addition of saturated aqueous sodium bicarbonate solution (30 mL). The aqueous mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were combined, dried (Na_2SO_4), filtered and solvent removed *in vacuo*. Purification by flash chromatography (10% diethyl ether/hexane) afforded the *cis*-iodoaziridine.



General Procedure B

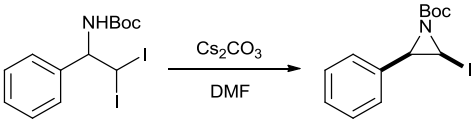
Same as **General Procedure A**, but the reaction was warmed to 30 °C for 30 minutes.



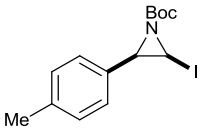
***cis*-(±)-2-Iodo-3-phenyl-1-*tert*-butoxycarbonylaziridine (3a)**

Prepared according to the **General Procedure A** described above starting from imine-HO_2STol adduct **1a** (217 mg, 0.60 mmol). Purification by flash chromatography (10% diethyl ether/hexane) afforded *cis*-iodoaziridine **3a** (172 mg, 83%) as a colourless oil. R_f 0.37 (20% diethyl ether/hexane). ν_{max} (film)/cm^{-1} 2981, 1724 (C=O), 1610, 1496, 1478, 1458, 1399, 1372, 1320, 1306, 1285, 1258, 1230, 1147, 1078, 1029. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.34 (m, 5 H, Ph-H), 4.72 (d, J = 5.4 Hz, 1 H, CHI), 3.59 (d, J = 5.4 Hz, 1 H, CHPh), 1.51 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6 (C=O), 134.8 (Ph-C quat.), 128.4 (Ph-C), 128.0 (2 × Ph-C), 127.5 (2 × Ph-C), 82.9 ($C(CH_3)_3$), 43.1 (PhCHN), 27.9 ($C(CH_3)_3$), 18.2 (CHI). HRMS (ESI) *m/z* Calculated for $C_{13}H_{17}INO_2^+$ $[M+H]^+$: 346.0298; Found: 346.0295.

Alternative procedure from diiodide (**2a**)

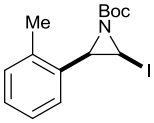


Ceasium carbonate (299 mg, 0.85 mmol, 2.0 equiv.) was added to a solution of diiodide **2a** (200 mg, 0.42 mmol) in *N,N*-dimethylformamide (10 mL) at rt, monitoring reaction progress *via* thin layer chromatography. After 15 h at rt, diethyl ether (50 mL) was added to the reaction mixture. The reaction mixture was then washed with water (50 mL) and brine (50 mL). The organic layer was then dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. Purification by flash chromatography (10% ethyl acetate/hexanes) afforded *cis*-iodoaziridine **3a** (83 mg, 54%) as a colourless oil.



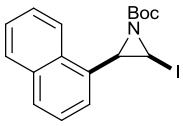
***cis*-(±)-2-Iodo-3-(4-tolyl)-1-*tert*-butoxycarbonylaziridine (3b)**

Prepared according to the **General Procedure A** described above starting from imine-HO_2STol adduct **1b** (226 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded *cis*-iodoaziridine **3b** (208 mg, 96%) as a colourless oil. R_f 0.45 (20% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2981, 1724 (C=O), 1525, 1455, 1391, 1368, 1315, 1298, 1280, 1253, 1149, 1082, 974, 862. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.3 Hz, 2 H, 2 × Tol-H), 7.20 (d, J = 8.3 Hz, 2 H, 2 × Tol-H), 4.71 (d, J = 5.4 Hz, 1 H, CHI), 3.55 (d, J = 5.4 Hz, 1 H, CHTol), 2.38 (s, 3 H, Tol-CH_3), 1.51 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (C=O), 138.3 (Tol-C quat.), 131.8 (Tol-C quat.), 128.8 (2 × Tol-C), 127.4 (2 × Tol-C), 82.9 ($C(CH_3)_3$), 43.2 (TolCHN), 27.9 ($C(CH_3)_3$), 21.3 (Tol-CH_3), 18.7 (CHI). HRMS (ESI) *m/z* Calculated for $C_{17}H_{19}NO_2^+$ $[M-I+H]^{+\cdot}$: 233.1410; Found: 233.1435.



***cis*-(±)-2-Iodo-3-(2-tolyl)-1-*tert*-butoxycarbonylaziridine (3c)**

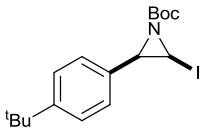
Prepared according to the **General Procedure B** described above starting from imine-HO_2STol adduct **1c** (226 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded *cis*-iodoaziridine **3c** (192 mg, 89%) as a colourless oil. R_f 0.14 (10% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2981, 1723 (C=O), 1494, 1480, 1462, 1392, 1304, 1282, 1252, 1235, 1204, 1148, 1082, 970, 788. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, 1 H, J = 7.6 Hz, Tol-H), 7.33–7.20 (m, 3 H, 3 × Tol-H), 4.76 (d, J = 5.3 Hz, 1 H, CHI, 3.59 (d, J = 5.3 Hz, 1 H, CHTol), 2.36 (s, 3 H, Tol-CH_3), 1.54 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (C=O), 136.0 (Tol-C quat.), 133.6 (Tol-C quat.) , 129.6 (Tol-C), 128.2 (Tol-C), 127.7 (Tol-C), 125.7 (Tol-C), 82.8 ($C(CH_3)_3$), 42.5 (TolCHN), 27.9 ($C(CH_3)_3$), 18.9 (Tol-CH_3), 17.0 (CHI). HRMS (ESI) *m/z* Calculated for $C_{14}H_{19}INO_2^+$ $[M+H]^+$: 360.0455; Found: 360.0471.



cis-(±)-2-Iodo-3-(2-napthenyl)-1-_tert_-butoxycarbonylaziridine (3d)

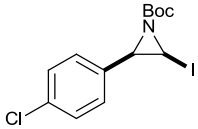
Prepared according to the **General Procedure A** described above starting from imine-HO_2STol adduct **1d** (247 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded *cis*-iodoaziridine **3d** (219 mg, 92%) as a colourless oil. R_f 0.46 (20% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2981, 1722 (C=O), 1511, 1483, 1369, 1347, 1291, 1249, 1205, 1149, 1092, 1047, 967, 802. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.01 (1 H, m, napthyl-H), 7.96-7.94 (1 H, m, napthyl-H), 7.91 (1 H, d, *J* = 8.3 Hz, napthyl-H), 7.65–7.50 (m, 4 H, 4 × napthyl-H), 4.93 (d, *J* = 5.4 Hz, 1 H, CHI), 4.09 (d, *J* = 5.4 Hz, 1 H, CHAr), 1.57 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (C=O), 133.2 (napthyl-C quat.), 131.2 (napthyl-C quat.), 131.0 (napthyl-C quat.), 128.8 (napthyl-C), 128.7 (napthyl-C), 126.4 (napthyl-C), 126.1 (napthyl-C), 126.0 (napthyl-C), 125.3 (napthyl-C), 122.7 (napthyl-C), 83.0 ($C(CH_3)_3$), 42.4 (ArCHN), 28.0 ($C(CH_3)_3$), 16.8 (CHI). HRMS (ESI) *m/z* Calculated for $C_{17}H_{19}NO_2^+$ $[M\text{-}I+H]^{+\cdot}$: 269.1410; Found: 269.1423.

.



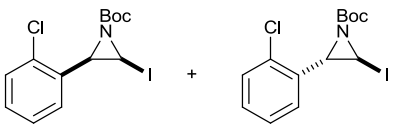
cis-(±)-2-Iodo-3-(4-_tert_-butylbenzene)-1-_tert_-butoxycarbonylaziridine (3e)

Prepared according to the **General Procedure A** described above starting from imine-HO_2STol adduct **1e** (251 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded *cis*-iodoaziridine **3e** (160 mg, 67%) as a colourless oil. R_f 0.34 (10% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2965, 1725 (C=O), 1391, 1368, 1280, 1253, 1148, 844. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2 H, *t*BuAr-H), 7.29 (d, J = 8.3 Hz, 2 H, 2 × *t*BuAr-H), 4.73 (d, *J* = 5.4 Hz, 1 H, CHI), 3.56 (d, *J* = 5.4 Hz, 1 H, CHAr), 1.51 (s, 9 H, $C(CH_3)_3$), 1.36 (s, 9 H, $ArC(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (C=O), 151.3 (*t*BuAr*C*-$C(CH_3)_3$ quat.), 131.7 (*t*BuAr*C*-CH quat.), 127.1 (2 × *t*BuAr-C), 124.9 (2 × *t*BuAr-C), 82.7 ($OC(CH_3)_3$), 43.1 (ArCHN), 34.6 (Ar-$C(CH_3)_3$), 31.3 (Ar-$C(CH_3)_3$), 27.9 ($OC(CH_3)_3$), 18.6 (CHI). HRMS (ESI) *m/z* Calculated for $C_{17}H_{27}NO_2^+$ $[M\text{-}I+H]^{+\cdot}$ 275.1880; Found: 275.1879.



cis-(±)-2-Iodo-3-(4-chlorobenzene)-1-_tert_-butoxycarbonylaziridine (3f)

Prepared according to the **General Procedure A** described above starting from imine-HO_2STol adduct **1f** (237 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded *cis*-iodoaziridine **3f** (117 mg, 51%) as a colourless oil. R_f 0.20 (10% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2984, 1724 (C=O), 1494, 1598, 1420, 1392, 1369, 1308, 1289, 1276, 1252, 1146, 1089 , 1015, 970, 842. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2 H, 2 × ClAr-H), 7.28 (d, *J* = 8.4 Hz, 2 H, 2 × ClAr-H), 4.70 (d, *J* = 5.4 Hz, 1 H, CHI), 3.55 (d, *J* = 5.4 Hz, 1 H, CHAr), 1.51 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3 (C=O), 134.2 (ClAr-C quat.), 133.4 (ClAr-C quat.), 128.8 (2 × ClAr-C), 128.3 (2 × ClAr-C), 83.1 ($C(CH_3)_3$), 42.4 (ArCHN), 27.9 ($C(CH_3)_3$), 17.8 (CHI). HRMS (ESI) *m/z* Calculated for $C_{13}H_{16}ClINO_2^+$ $[M+H]^+$: 379.9909; Found: 379.9923.



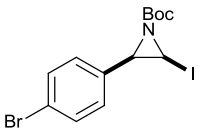
cis-(±)-2-Iodo-3-(2-chlorobenzene)-1-_tert_-butoxycarbonylaziridine and _trans_-(±)-2-Iodo-3-(2-chlorobenzene)-1-_tert_-butoxycarbonylaziridine (3g)

Prepared according to the **General Procedure B** described above starting from imine-HO_2STol adduct **1g** (238 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/petroleum ether) afforded a 88:12 mixture of *cis*-iodoaziridine ***cis*-3g** and *trans*-iodoaziridine ***trans*-3g** (118 mg, 52%) as a colourless oil. R_f 0.31 (10% ethyl acetate/petroleum ether). ν_{max} (film)/cm^{-1} 2984, 1726 (C=O), 1483, 1441, 1396, 1369, 1301, 1290, 1276, 1253, 1224, 1147, 1054, 967, 851, 750.

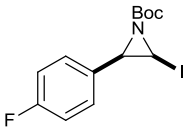
***cis*-aziridine** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.34 (m, 4 H, 4 × ClAr-H), 4.77 (d, *J* = 5.4 Hz, 1 H, CHI), 3.80 (d, *J* = 5.4 Hz, 1 H, CHAr), 1.54 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 159.4 (C=O), 133.4 (ClAr-C quat.), 133.3 (ClAr-C quat.) , 130.0 (ClAr-C), 129.5 (ClAr-C), 129.0 (ClAr-C), 126.5 (ClAr-C), 83.0 ($C(CH_3)_3$), 42.2 (ArCHN), 27.9 ($C(CH_3)_3$), 16.3 (CHI).

***trans*-aziridine** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 4 H, 4 × Ar-H), 4.01 (d, *J* = 2.3 Hz, 1 H, CHI), 3.84 (d, *J* = 2.3 Hz, 1 H, CHAr), 1.56 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.2 (C=O), 134.3 (ClAr-C quat.), 133.8 (ClAr-C quat.) , 129.3 (ClAr-C), 129.2(5) (ClAr-C), 127.0 (ClAr-C), 126.9 (ClAr-C), 83.3 ($C(CH_3)_3$), 46.1 (ArCHN), 28.0 ($C(CH_3)_3$), 10.2 (CHI).

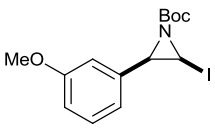
HRMS (ESI) *m/z* Calculated for $C_{13}H_{16}ClINO_2^+$ $[M+H]^+$: 379.9909; Found: 379.9907.



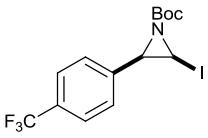
***cis*-(±)-2-Iodo-3-(4-bromobenzene)-1-*tert*-butoxycarbonylaziridine (3h)**
Prepared according to the **General Procedure A** described above starting from imine-HO_2STol adduct **1h** (264 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded *cis*-iodoaziridine **3h** (100 mg, 42%) as a colourless oil. R_f 0.39 (20% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2984, 1725 (C=O), 1490, 1424, 1369, 1307, 1290, 1276, 1253, 1149, 1069 , 1011, 974, 842. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2 H, 2 × BrAr-H), 7.22 (d, *J* = 8.4 Hz, 2 H, 2 × BrAr-H), 4.69 (d, *J* = 5.4 Hz, 1 H, CHI), 3.53 (d, *J* = 5.4 Hz, 1 H, CHAr), 1.50 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3 (C=O), 134.0 (Br-CAr quat.), 131.2 (2 × BrAr-C), 129.2 (2 × BrAr-C), 122.5 (BrAr*C*-CH quat.), 83.1 ($C(CH_3)_3$), 42.5 (ArCHN), 27.9 ($C(CH_3)_3$), 17.7 (CHI). HRMS (ESI) *m/z* Calculated for $C_{13}H_{16}{}^{79}BrINO_2^+$ $[M+H]^+$: 423.9404; Found: 423.9420.



***cis*-(±)-2-Iodo-3-(4-fluorobenzene)-1-*tert*-butoxycarbonylaziridine (3i)**
Prepared according to the **General Procedure A** described above starting from imine-HO_2STol adduct **1i** (228 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) afforded *cis*-iodoaziridine **3i** (165 mg, 76%) as a colourless oil. R_f 0.14 (10% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2984, 1724 (C=O), 1609, 1512, 1483, 1462, 1427, 1396, 1369, 1308, 1281, 1254, 1146, 1099, 1078, 1015, 970. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 2 H, 2 × FAr-H), 7.13–7.03 (m, 2 H, 2 × FAr-H), 4.70 (d, *J* = 5.2 Hz, 1 H, CHI), 3.56 (d, *J* = 5.2 Hz, 1 H, CHAr), 1.51 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247.1 Hz, Ar-CF quat.), 159.4 (C=O), 130.6 (d, *J* = 3.1 Hz, FAr-C quat.), 129.2 (d, *J* = 8.4 Hz, 2 × FAr-C), 115.0 (d, *J* = 21.9 Hz, 2 × FAr-C), 83.0 ($C(CH_3)_3$), 42.4 (ArCHN), 27.8 ($C(CH_3)_3$), 18.2 (CHI). ^{19}F NMR (377 MHz, $CDCl_3$) δ −113.3 (C-F). HRMS (ESI) *m/z* Calculated for $C_{13}H_{16}FINO_2^+$ $[M+H]^+$: 364.0204; Found: 364.0228.

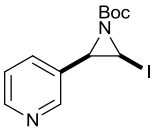


***cis*-(±)-2-Iodo-3-(3-methoxybenzene)-1-*tert*-butoxycarbonylaziridine (3j)**
Prepared according to the **General Procedure A** described above starting from imine-HO_2STol adduct **1j** (235 mg, 0.60 mmol). Purification by flash chromatography (10% ethyl acetate/hexane) on neutral alumina afforded *cis*-iodoaziridine **3j** (174 mg, 77%) as a colourless oil. R_f 0.45 (10% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2980, 1723 (C=O), 1392, 1369, 1279, 1252, 1145, 1043, 840. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 1 H, MeOAr-H), 6.96–6.88 (m, 3 H, 3 × MeOAr-H), 4.71 (d, *J* = 5.4 Hz, 1 H, CHI), 3.84 (s, 3 H, OMe), 3.57 (d, *J* = 5.4 Hz, 1 H, CHAr), 1.51 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 159.5 (C=O), 159.3 (Ar*C*-OCH_3 quat.), 136.3 (Ar*C*-CH quat.), 129.1 (MeOAr-C), 119.8 (MeOAr-C), 114.2 (MeOAr-C), 112.6 (MeOAr-C), 82.8 ($C(CH_3)_3$), 55.2 (Ar-OCH_3), 43.0 (ArCHN), 27.8 ($C(CH_3)_3$), 18.0 (CHI). HRMS (ESI) *m/z* Calculated for $C_{14}H_{19}INO_3^+$ $[M+H]^+$: 376.0404; Found: 376.0415.



***cis*-(±)-2-Iodo-3-(4-trifluoromethylbenzene)-1-*tert*-butoxycarbonylaziridine (3k)**

Prepared according to the **General Procedure A** described above starting from imine-HO_2STol adduct **1k** (258 mg, 0.60 mmol). Purification by flash chromatography (5% ethyl acetate/hexane) afforded *cis*-iodoaziridine **3k** (30 mg, 13%) as a colourless oil. R_f 0.19 (10% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2984, 1729 (C=O), 1323, 1285, 1151, 1128, 1128, 1066, 855. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2 H, 2 × F_3CAr-H), 7.47 (d, *J* = 8.4 Hz, 2 H, 2 × F_3CAr-H), 4.72 (d, *J* = 5.4 Hz, 1 H, CHI), 3.63 (d, *J* = 5.4 Hz, 1 H, CHAr), 1.52 (s, 9 H, $C(CH_3)_3$).^{13}C NMR (500 MHz, $CDCl_3$) δ 159.2 (C=O), 138.8 (F_3CAr*C*-CHN quat.), 130.5 (q, *J* = 32.5 Hz, F_3C-*C*Ar quat.), 127.9 (2 × F_3CAr-C), 125.1 (q, *J* = 3.6 Hz, 2 × F_3CAr-C), 124.1 (q, *J* = 272.2 Hz, F_3*C*-CAr), 83.3 (*C*$(CH_3)_3$ quat.), 42.5 (F_3CAr-*C*HN), 27.9 (C(*C*$H_3)_3$), 17.0 (CHI). ^{19}F NMR (470 MHz, $CDCl_3$) δ −62.7 (ArC-CF_3). HRMS (ESI) *m/z* Calculated for $C_{14}H_{16}F_3INO_2^+$ $[M+H]^+$: 414.0172; Found: 414.0183.

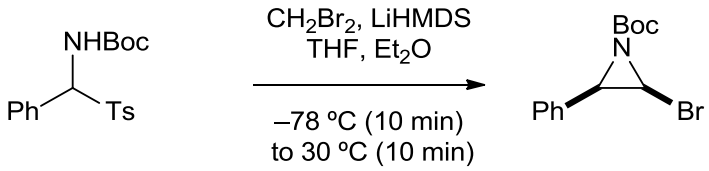


***cis*-(±)-2-Iodo-3-(3-pyridyl)-1-*tert*-butoxycarbonylaziridine (3l)**

Prepared according to the General Procedure A described above starting from imine-HO_2STol adduct **1l** (219 mg, 0.60 mmol). Purification by flash chromatography (40% ethyl acetate/hexane) afforded *cis*-iodoaziridine **3l** (101 mg, 49%) as a yellow oil. R_f 0.16 (40% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2981, 1729 (C=O), 1370, 1293, 1252, 1152, 755. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (br s, 2 H, 2 × pyr-H), 7.66 (d, *J* = 7.7 Hz, 1 H, pyr-H), 7.35 (br s, 1 H, pyr-H), 4.72 (d, *J* = 5.4 Hz, 1 H, CHI), 3.61 (d, *J* = 5.4 Hz, 1 H, CHAr), 1.49 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1 (C=O), 149.3 (pyr-C), 148.8 (pyr-C), 135.4 (pyr*C*-CH quat.), 131.0, (pyr-C) 123.0 (pyr-C), 83.3 (*C*$(CH_3)_3$ quat.), 40.8 (pyr-CHN), 27.8 (C(*C*$H_3)_3$), 17.1 (CHI). HRMS (ESI) *m/z* Calculated for $C_{12}H_{16}IN_2O_2^+$ $[M+H]^+$: 374.0251; Found: 347.0261.

Synthesis of Bromoaziridine

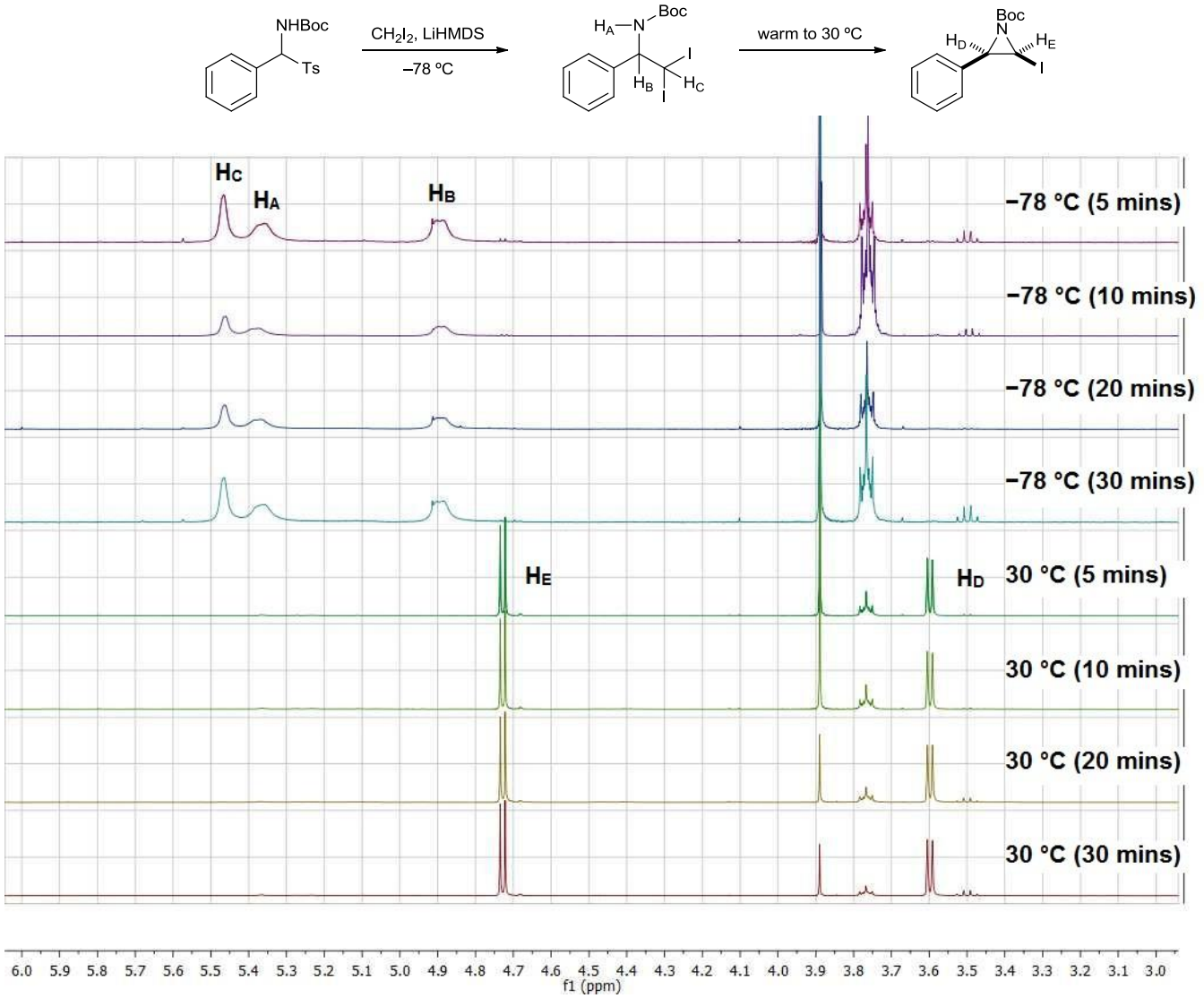
cis-(±)-2-Bromo-3-phenyl-1-*tert*-butoxycarbonylaziridine (5)



Dibromomethane (126 µL, 1.80 mmol, 3.0 equiv.) in THF (1.6 mL) was added dropwise to a solution of LiHMDS (1 M solution in THF, 1.56 mL, 1.56 mmol, 2.6 equiv.) in THF (6.0 mL) and diethyl ether (3.0 mL) at –78 °C in the dark. After 20 minutes at −78 °C, a solution of imine-toluene sulfinic acid adduct **1a** (0.60 mmol, 1.0 equiv.) in THF (2.0 mL) was added dropwise to the reaction mixture. After 10 minutes at −78 °C, the reaction flask was transferred to a water bath at 30 °C for 10 minutes and then quenched by the addition of saturated aqueous sodium bicarbonate solution (30 mL). The aqueous mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were combined, dried (Na_2SO_4), filtered and solvent removed *in vacuo*. Purification by flash chromatography (10% diethyl ether/hexane) afforded *cis*-bromoaziridine **5** (53 mg, 30%) as a colourless oil. R_f 0.25 (10% ethyl acetate/hexane). ν_{max} (film)/cm^{-1} 2982, 1726 (C=O), 1303, 1279, 1257, 1233, 1156, 907, 730, 698. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.35 (m, 5 H, Ph-H), 4.87 (d, *J* = 5.1 Hz, 1 H, CHBr), 3.75 (d, *J* = 5.1 Hz, 1 H, CHPh), 1.52 (s, 9 H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3 (C=O), 133.2 (Ph-C quat.), 128.4 (Ph-C), 128.0 (2 × Ph-C), 127.8 (2 × Ph-C), 83.0 ($C(CH_3)_3$ quat.), 44.7 (CHBr), 44.1 (CHPh), 27.9 ($C(CH_3)_3$). HRMS (CI) *m/z* Calculated for $C_{13}H_{17}NO_2{}^{79}Br^+$ $[M+H]^+$: 298.0437; Found: 298.0450.

Reaction Sampling

Sampling of Ph example:



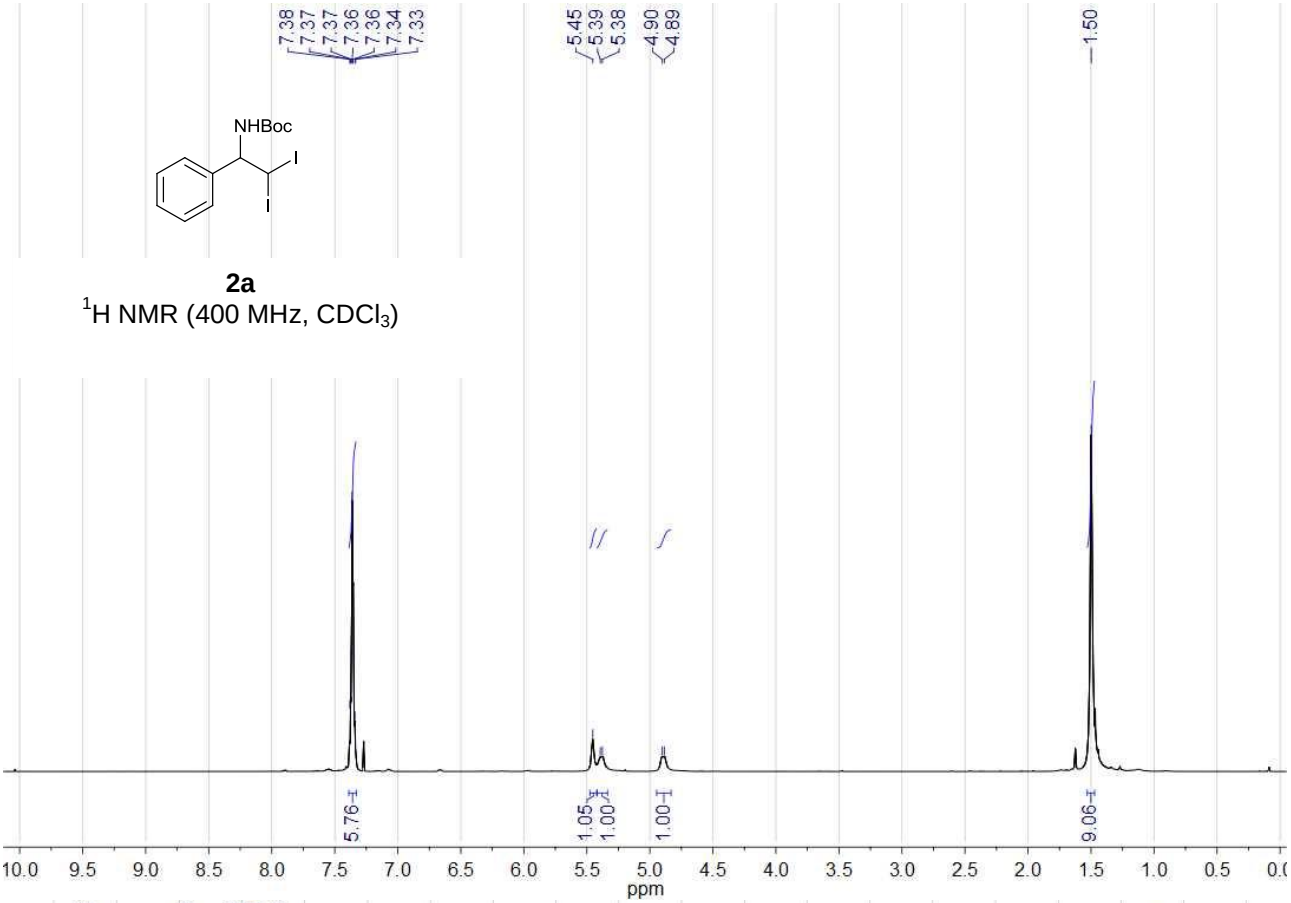
Sampling was carried out at low temperature (−78 °C) and at the elevated temperature (30 °C) after the addition of the imine toluene sulfinic acid adduct to the reaction mixture. Aliquots of the reaction mixture were quenched by addition to a saturated aqueous sodium bicarbonate solution. The aqueous layer was then extracted with diethyl ether to give a sample for ^{1}H NMR analysis.

After 30 min at −78 °C, it is evident from the ^{1}H NMR spectra that the amino *gem*-diiodoide was the only product obtained from the low temperature quench. According to the general procedure, the reaction vessel was transfered to a warm water bath at 30 °C. Sampling the reaction mixture after 5 min at 30 °C, it was evident that the *cis*-iodoaziridine was the only product from the elevated temperature quench. The *cis*-iodoaziridine was stable at 30 min at 30 °C, with the sample showing no degradation products.

This further supports our mechanistic hypothesis of addition followed by cyclisation at elevated temperatures, rather than an alternative *via* diiodocarbene. Low temperature is required for the initial addition for the stability of $LiCHI_2$.

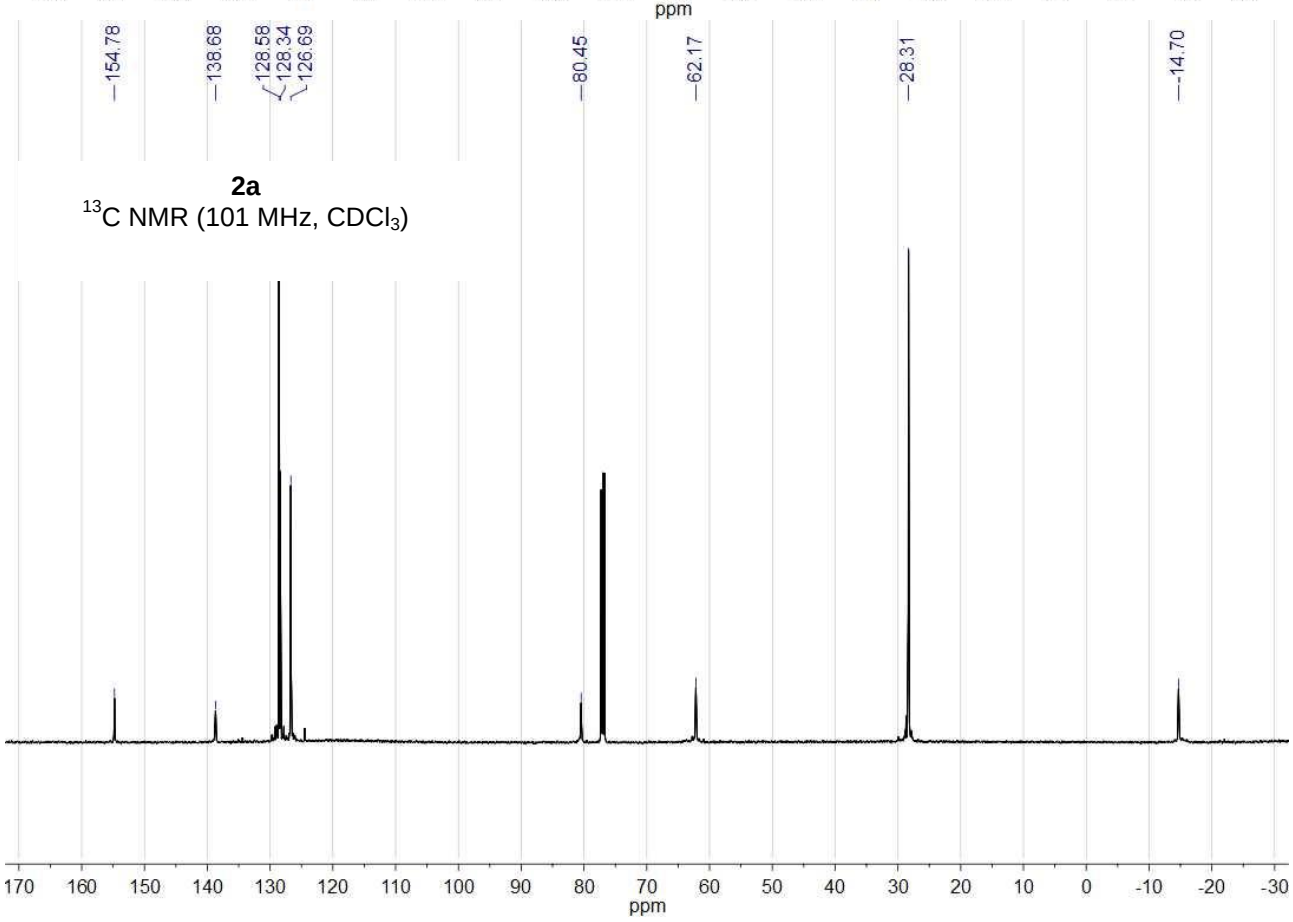
Electronic Supplementary Material (ESI) for Chemical Communications

^{1}H and ^{13}C NMR spectra of selected compounds



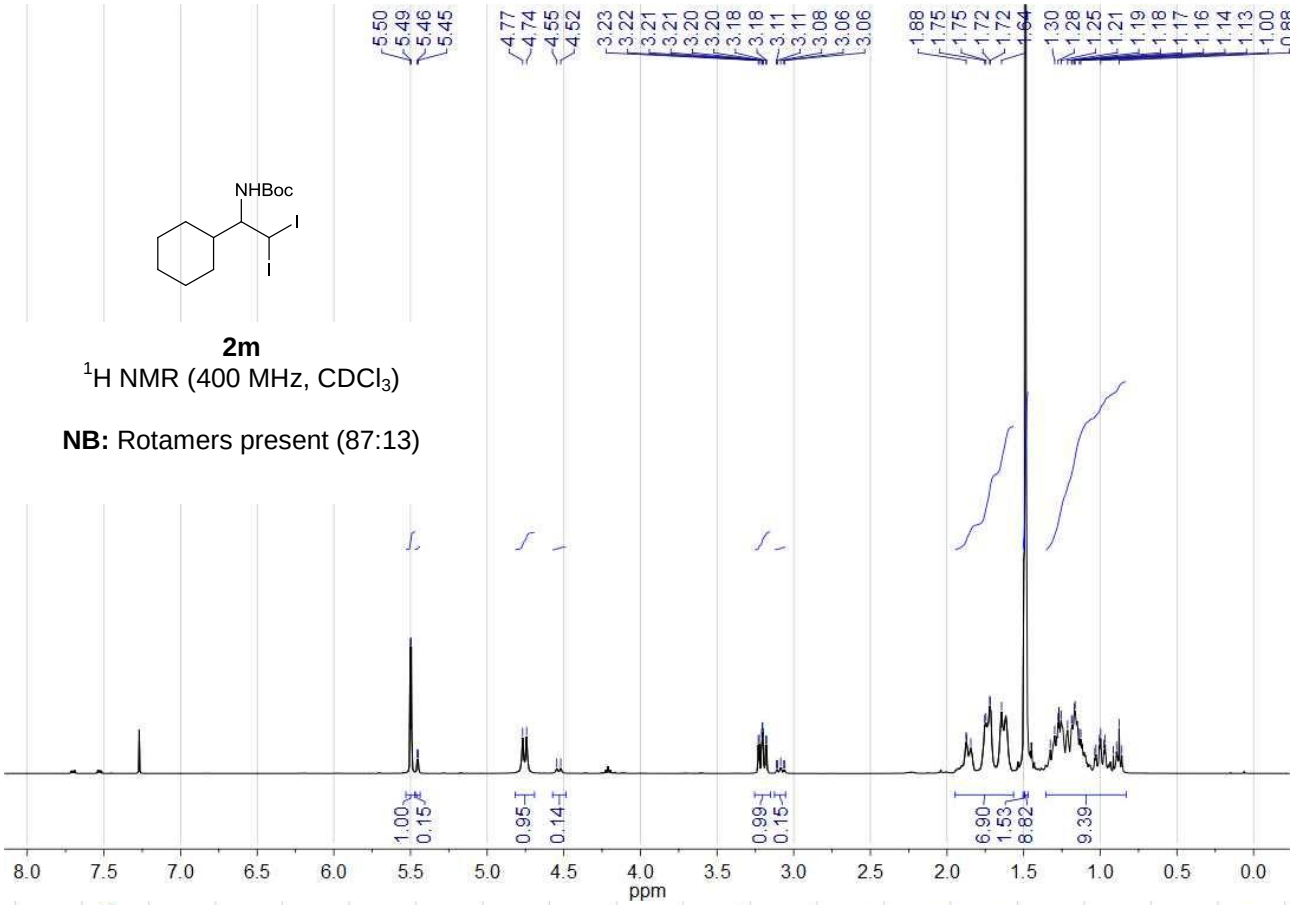
2a

^{1}H NMR (400 MHz, $CDCl_3$)



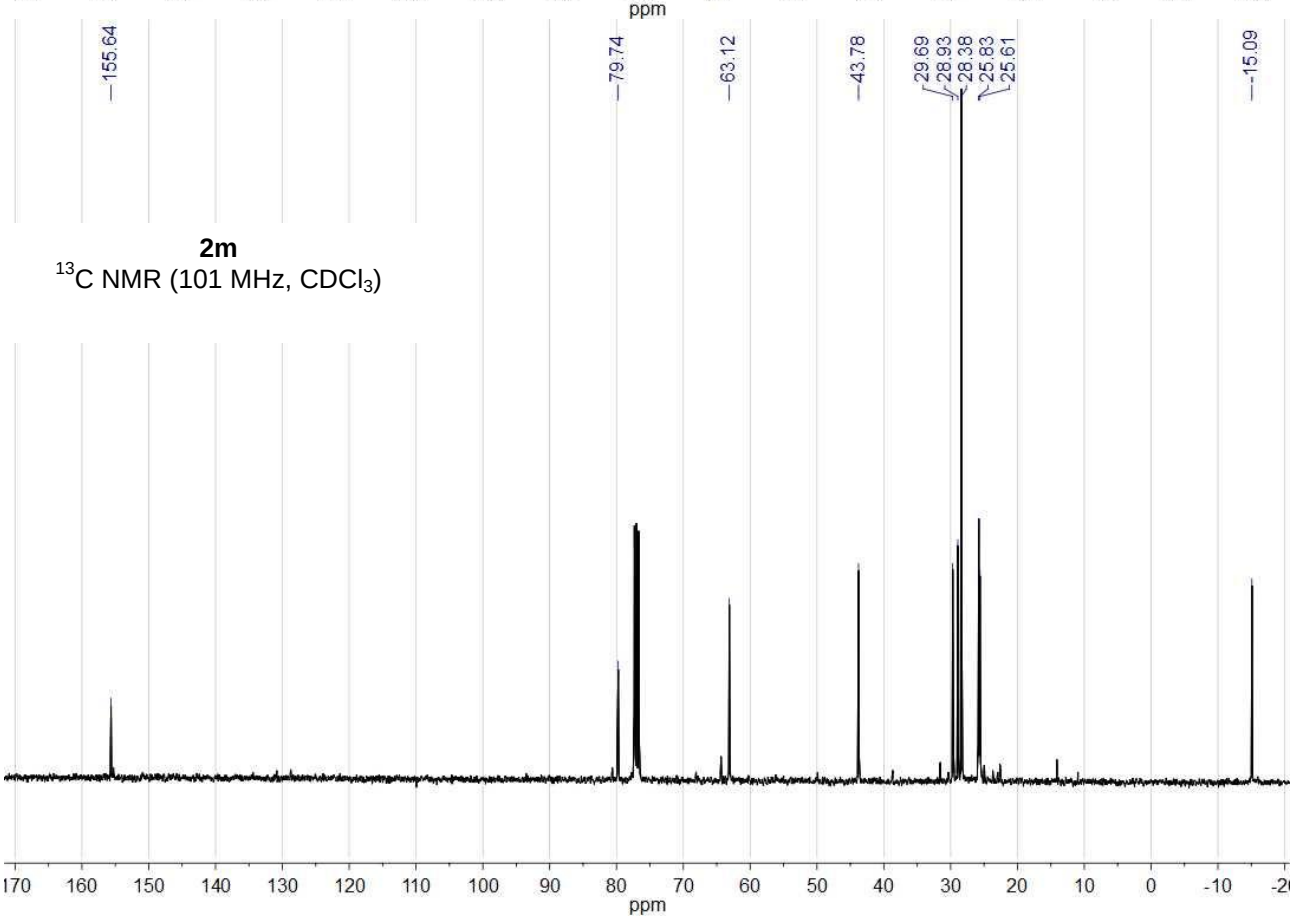
2a

^{13}C NMR (101 MHz, $CDCl_3$)

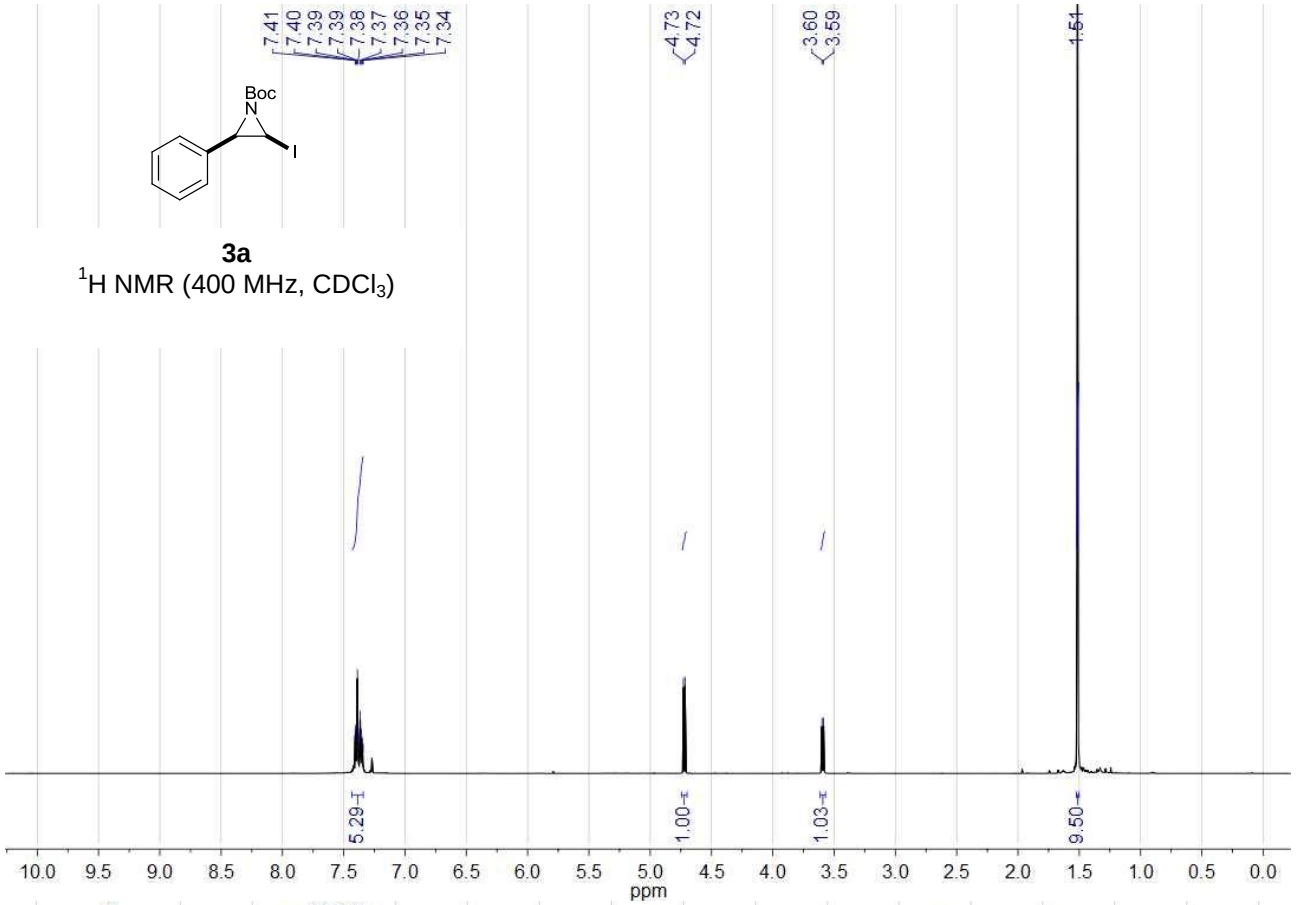


2m
^{1}H NMR (400 MHz, $CDCl_3$)

NB: Rotamers present (87:13)

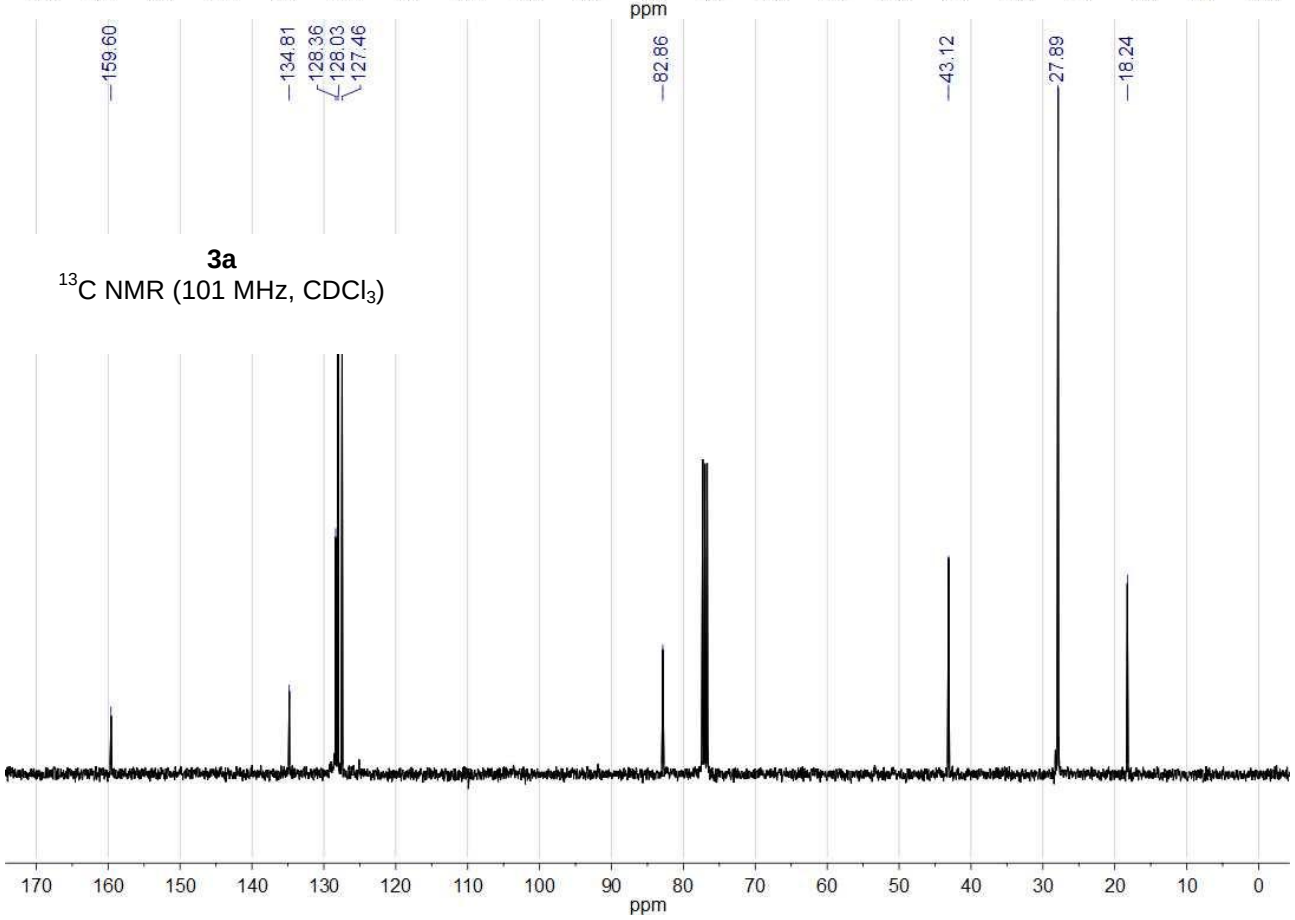


2m
^{13}C NMR (101 MHz, $CDCl_3$)



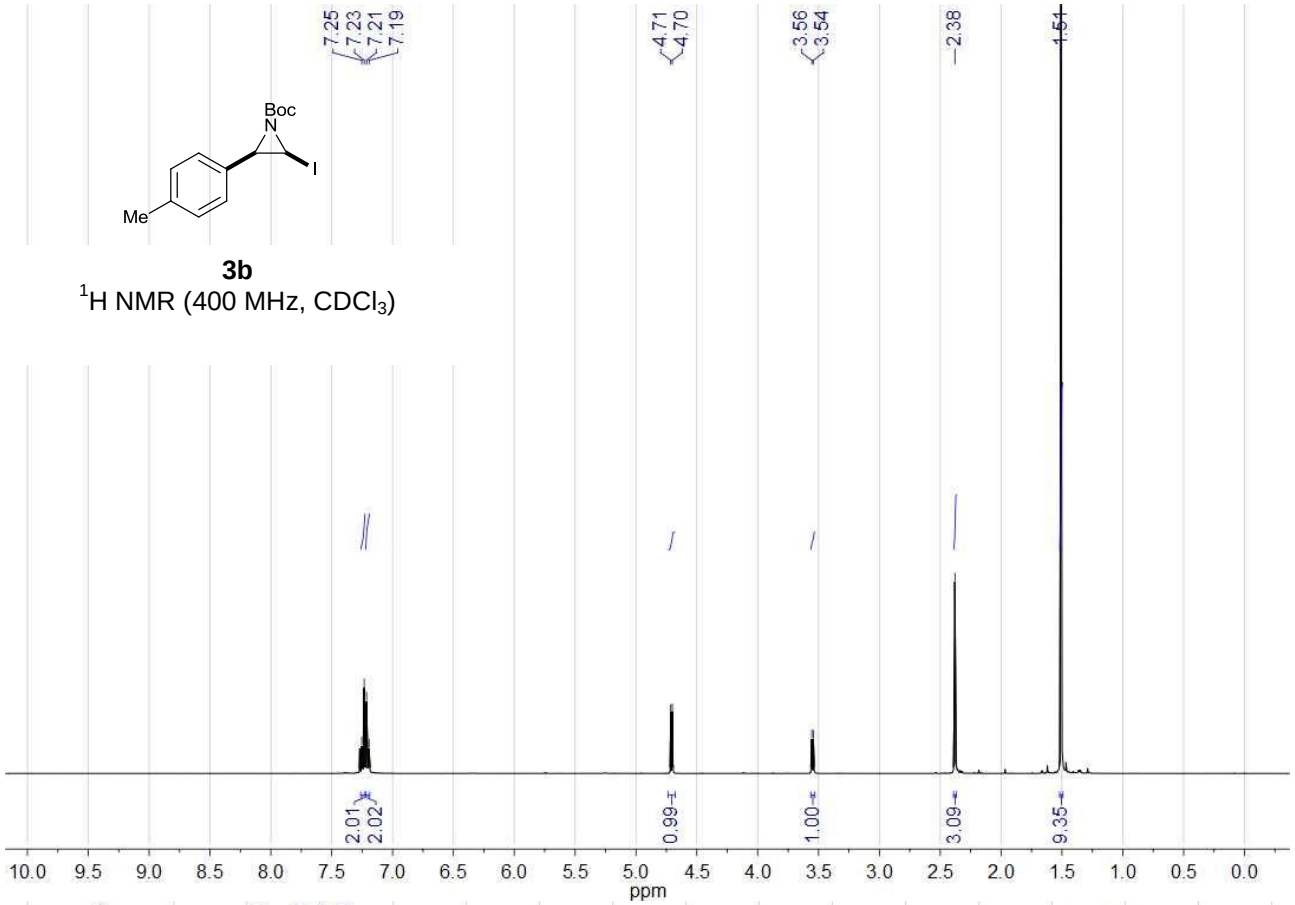
3a

^{1}H NMR (400 MHz, $CDCl_3$)



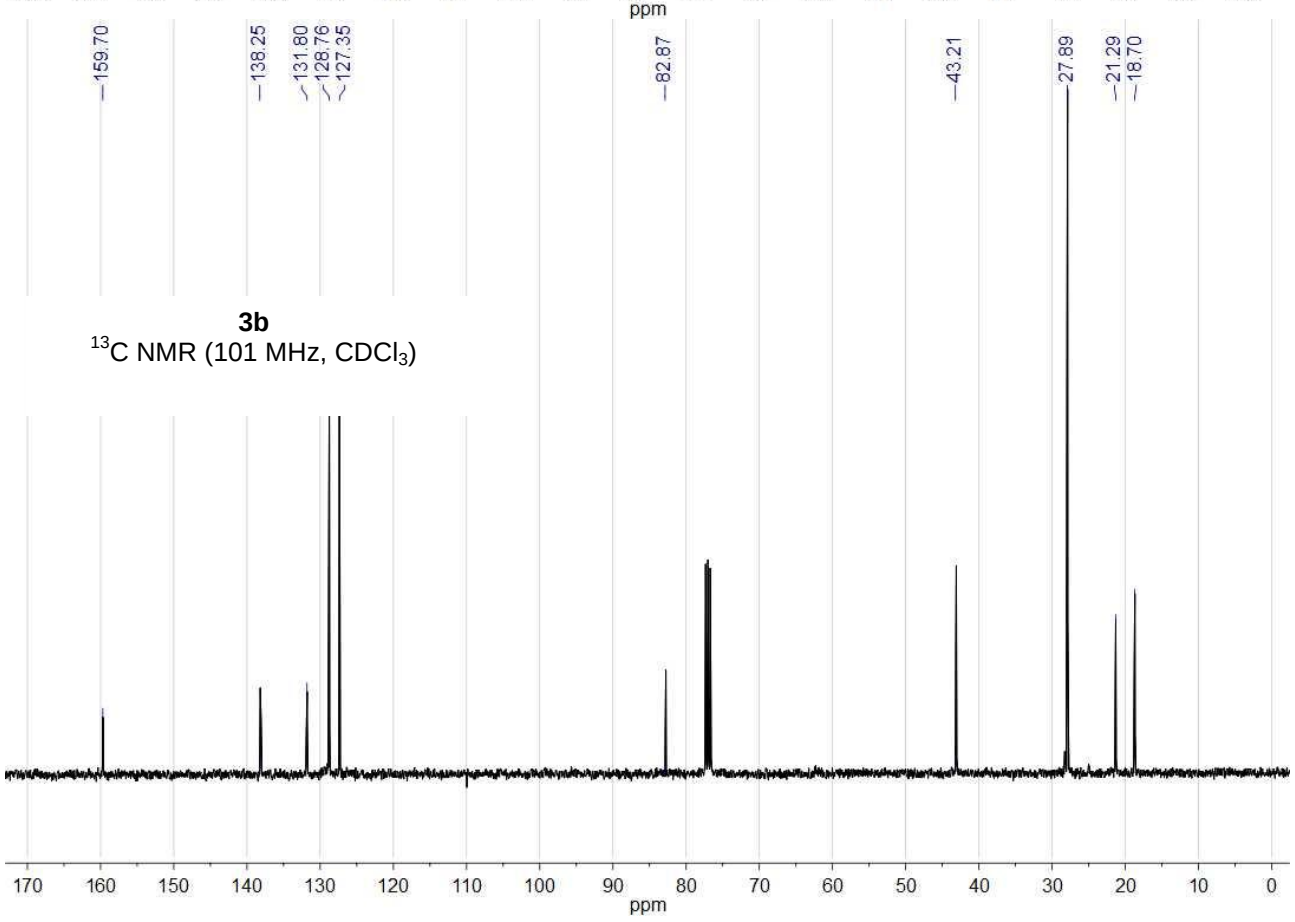
3a

^{13}C NMR (101 MHz, $CDCl_3$)



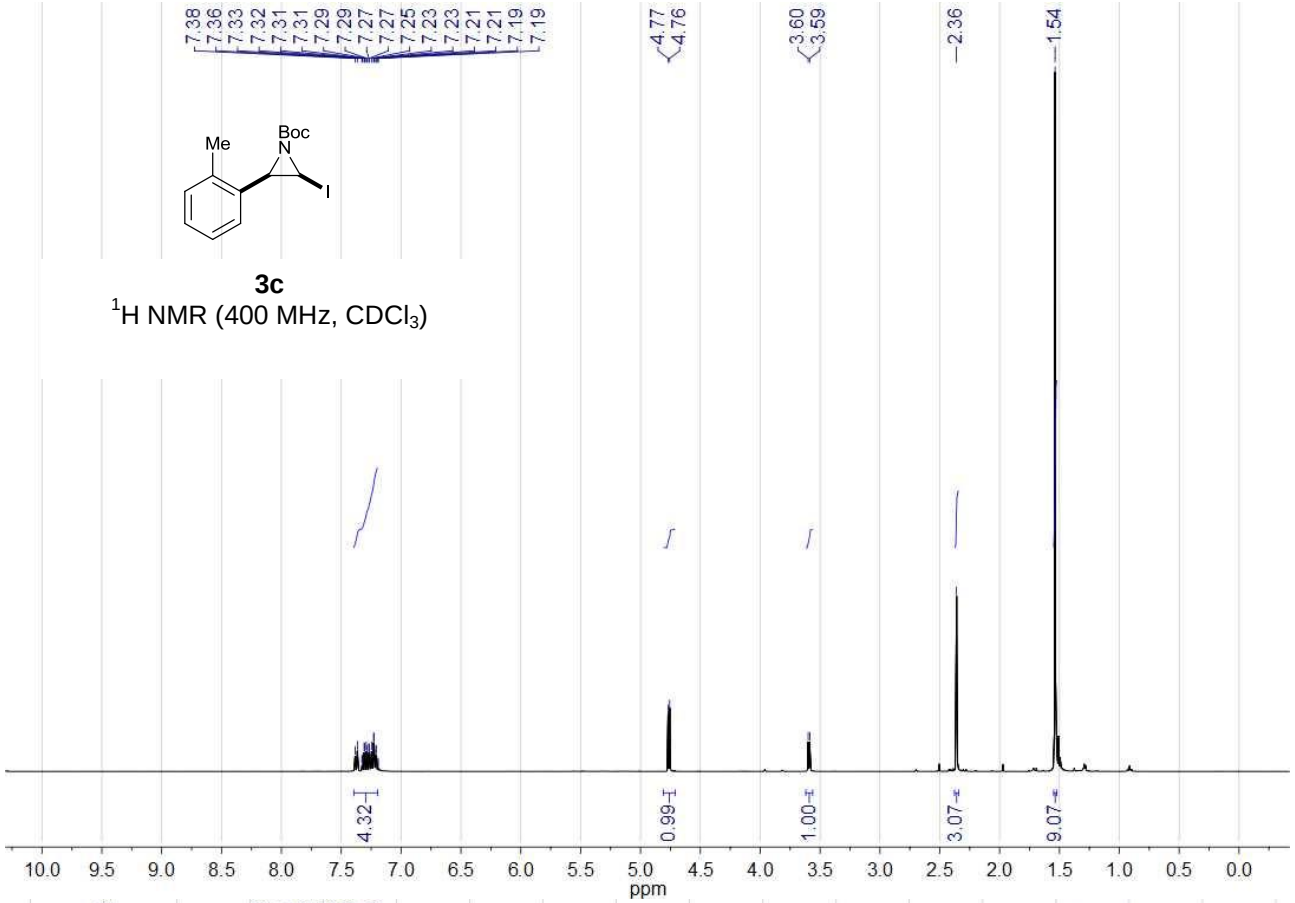
3b

^{1}H NMR (400 MHz, $CDCl_3$)

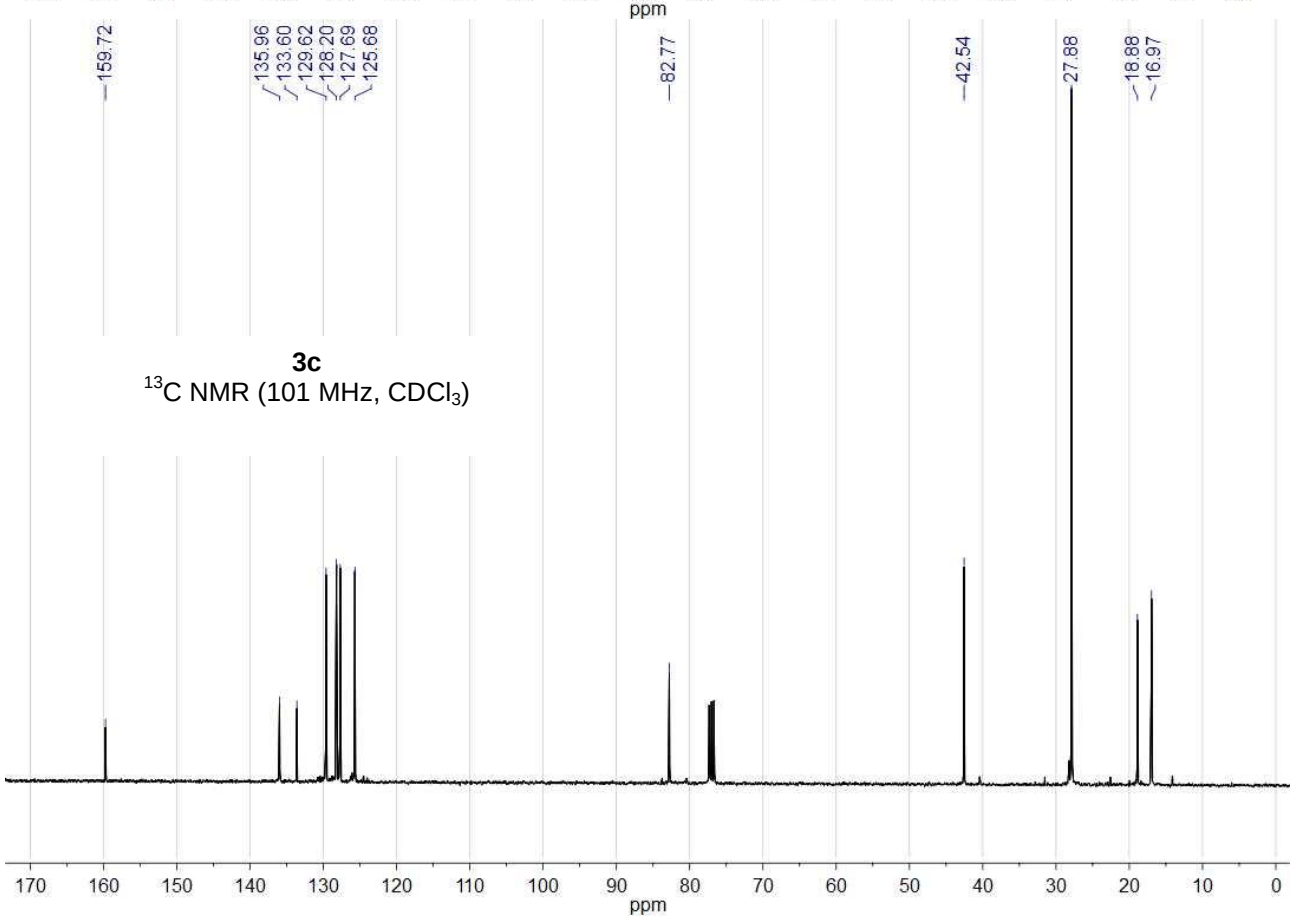


3b

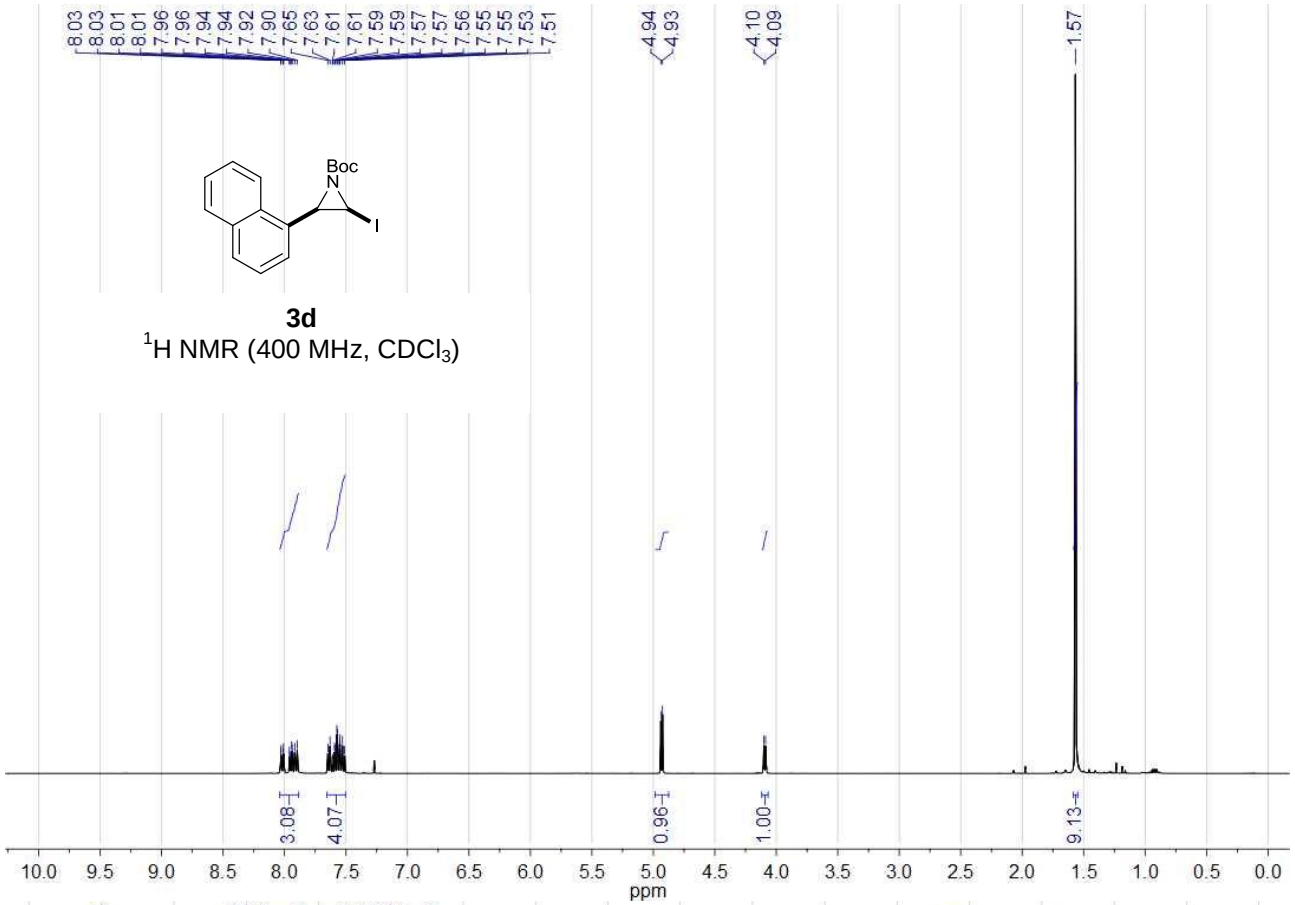
^{13}C NMR (101 MHz, $CDCl_3$)



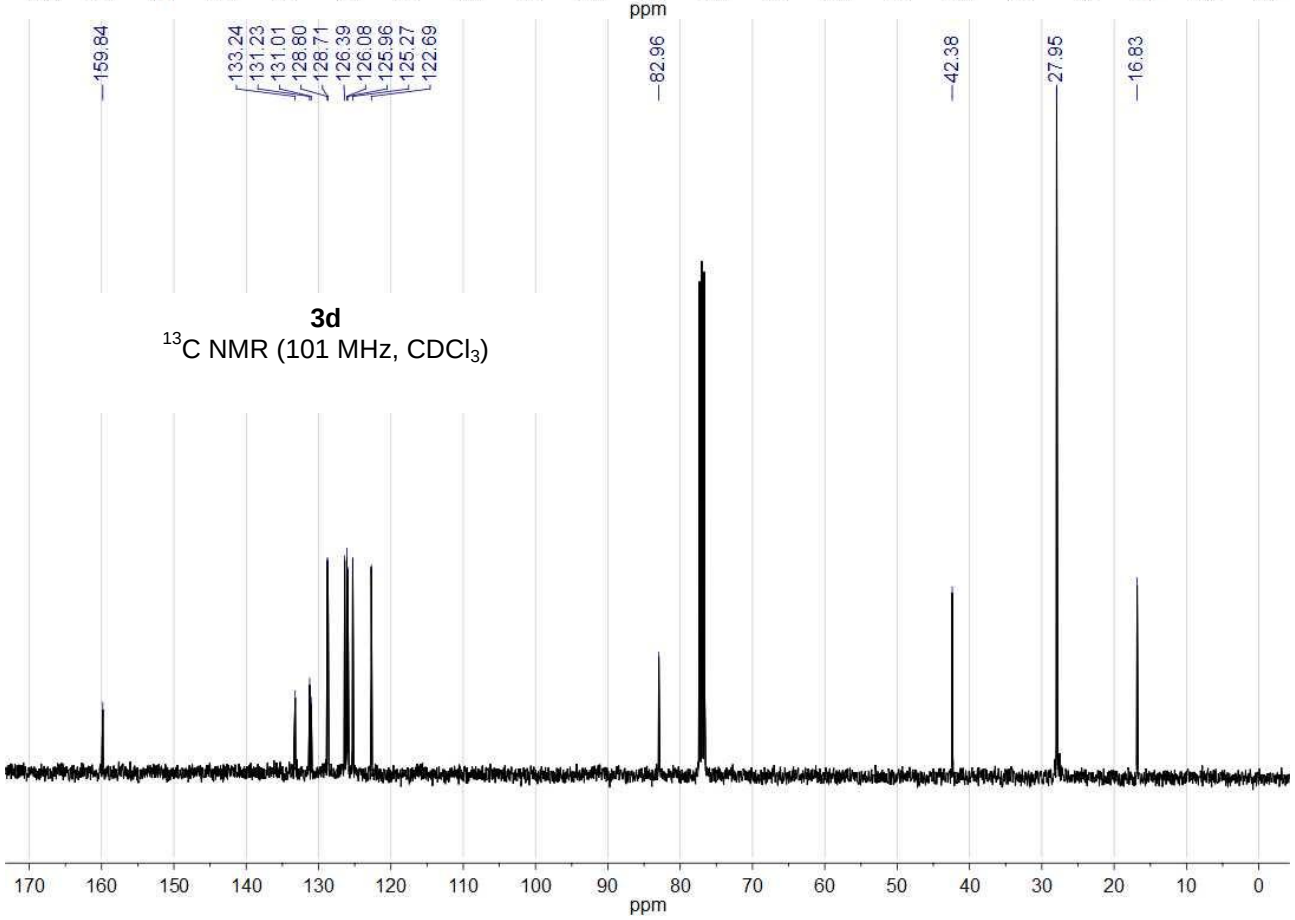
3c
^{1}H NMR (400 MHz, $CDCl_3$)



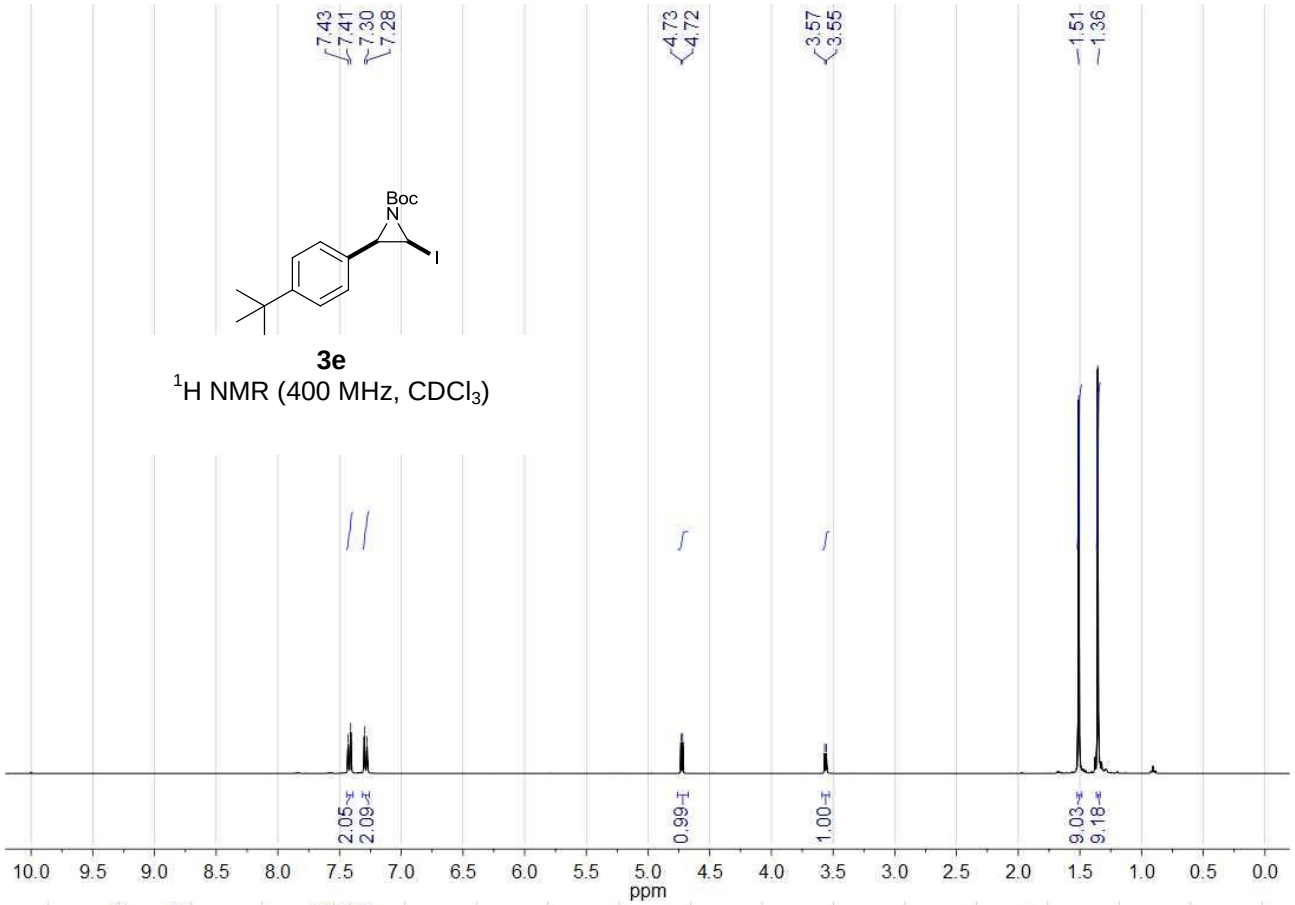
3c
^{13}C NMR (101 MHz, $CDCl_3$)



3d
^{1}H NMR (400 MHz, $CDCl_3$)

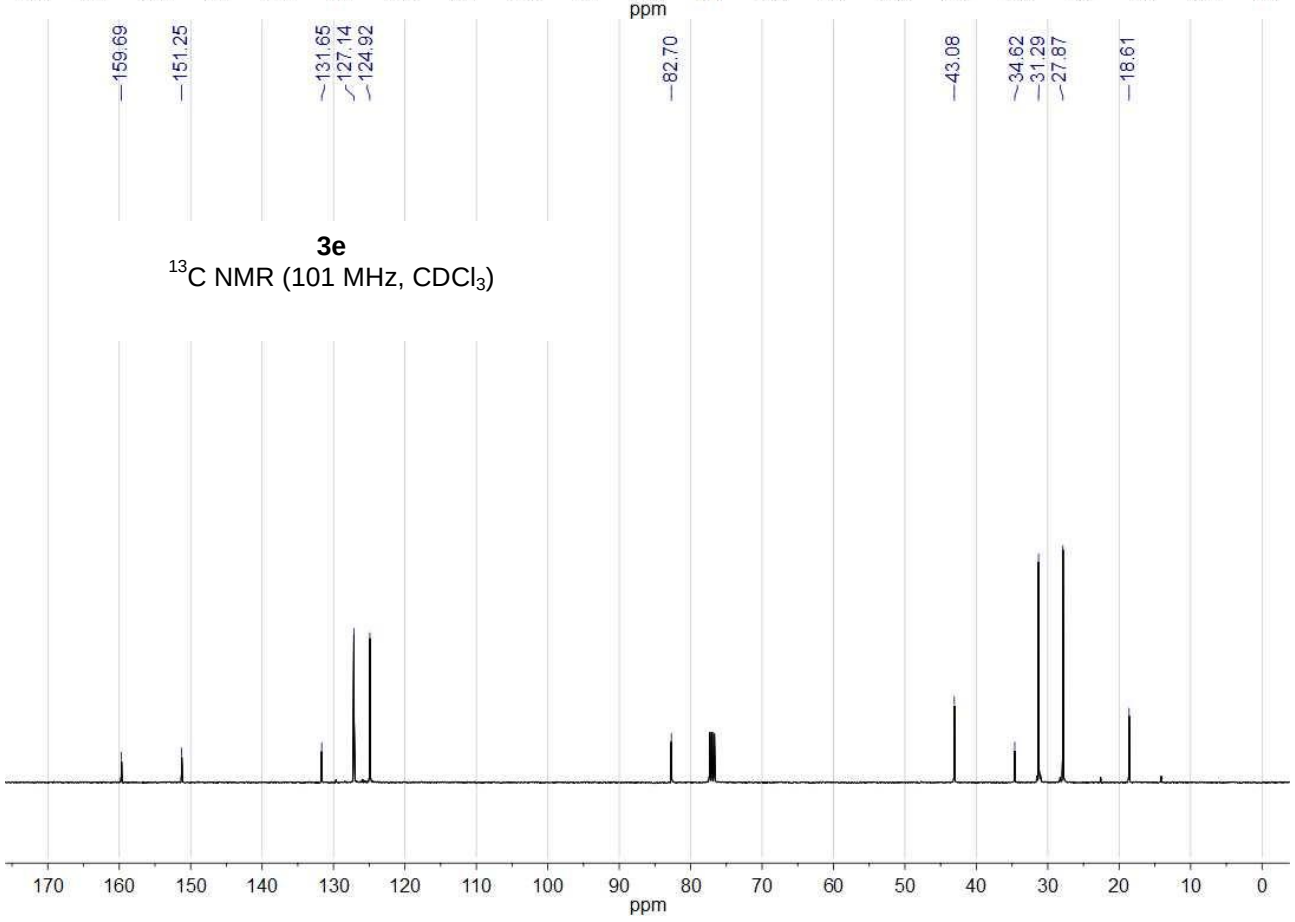


3d
^{13}C NMR (101 MHz, $CDCl_3$)



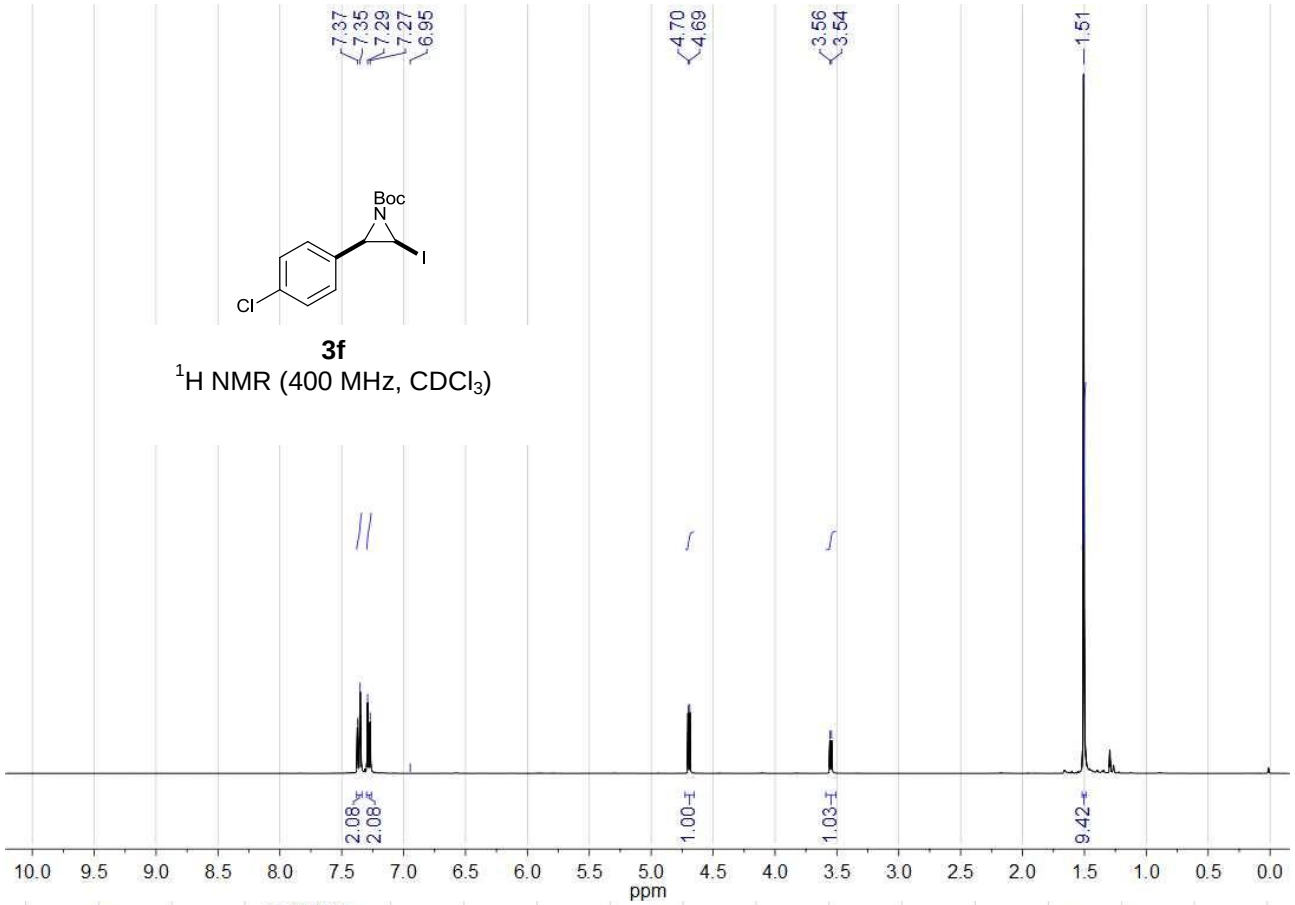
3e

^{1}H NMR (400 MHz, $CDCl_3$)



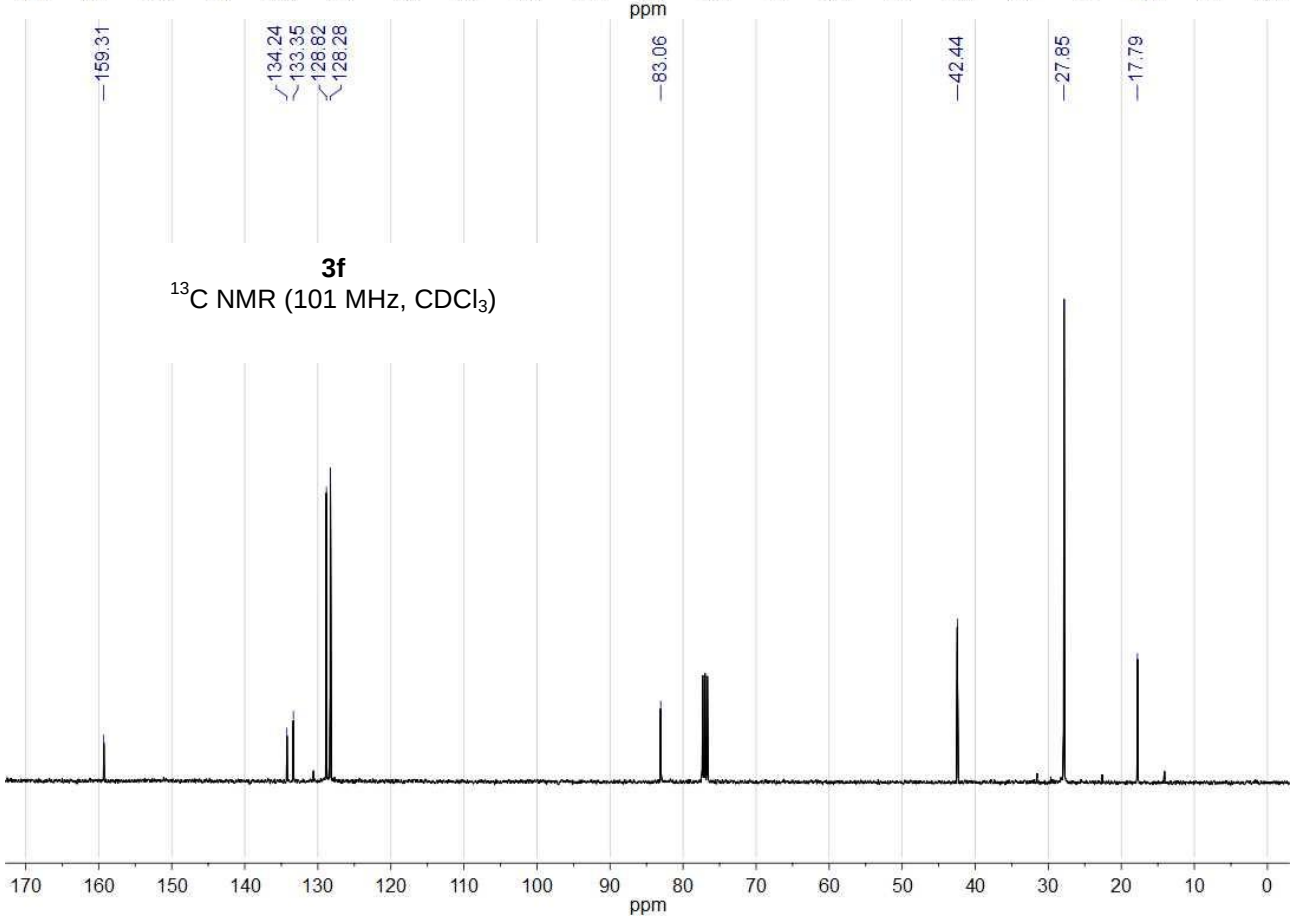
3e

^{13}C NMR (101 MHz, $CDCl_3$)



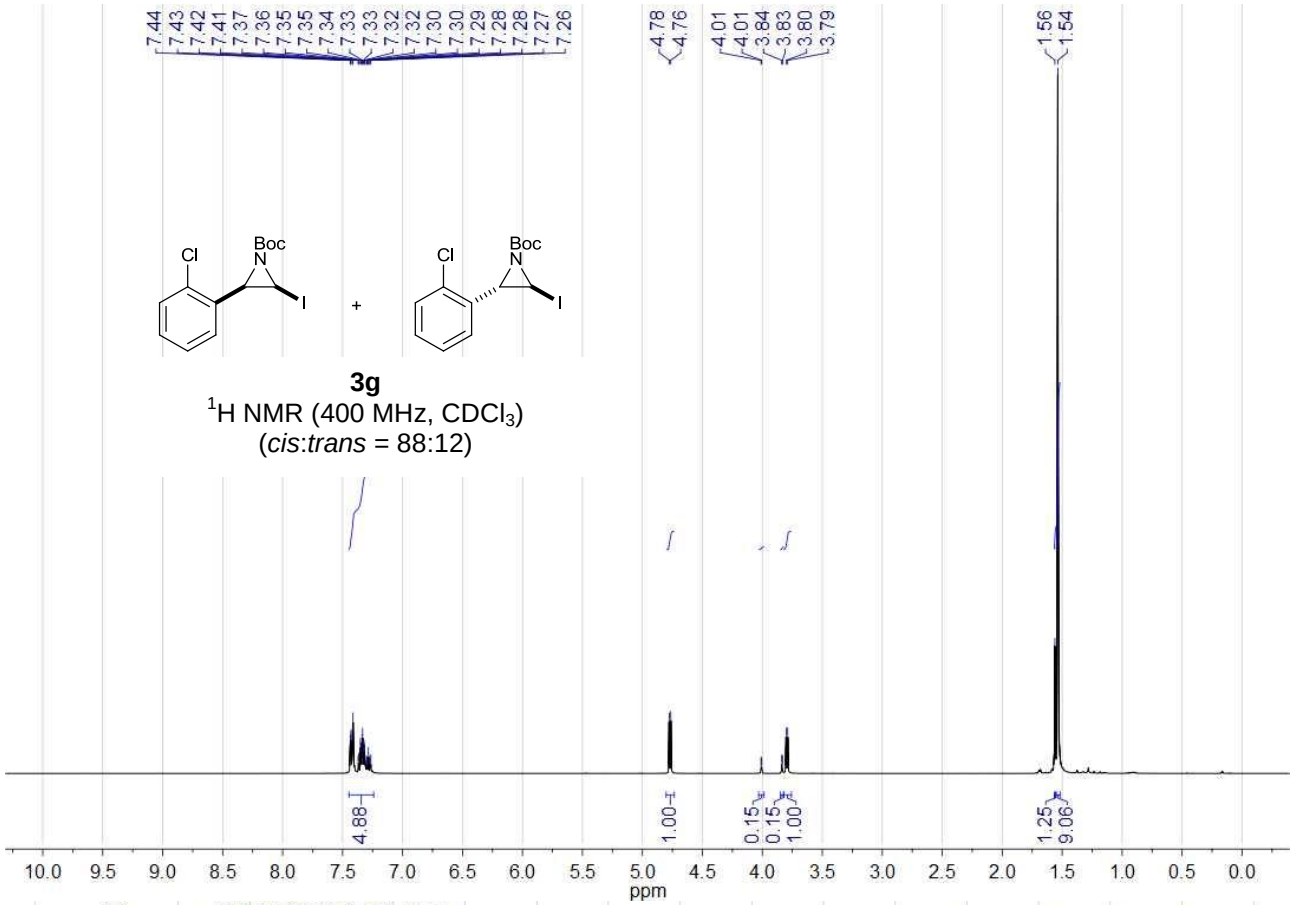
3f

^{1}H NMR (400 MHz, $CDCl_3$)

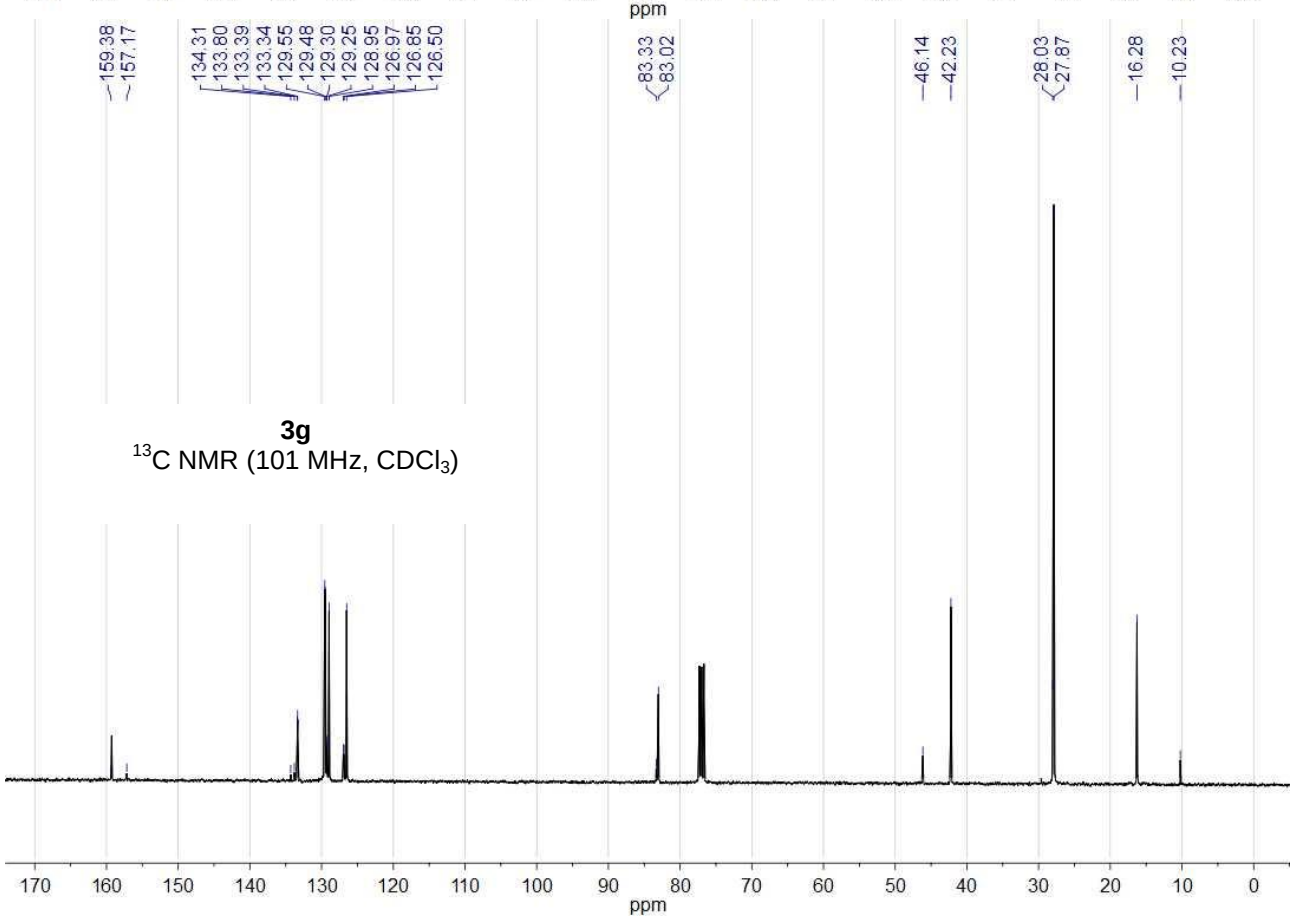


3f

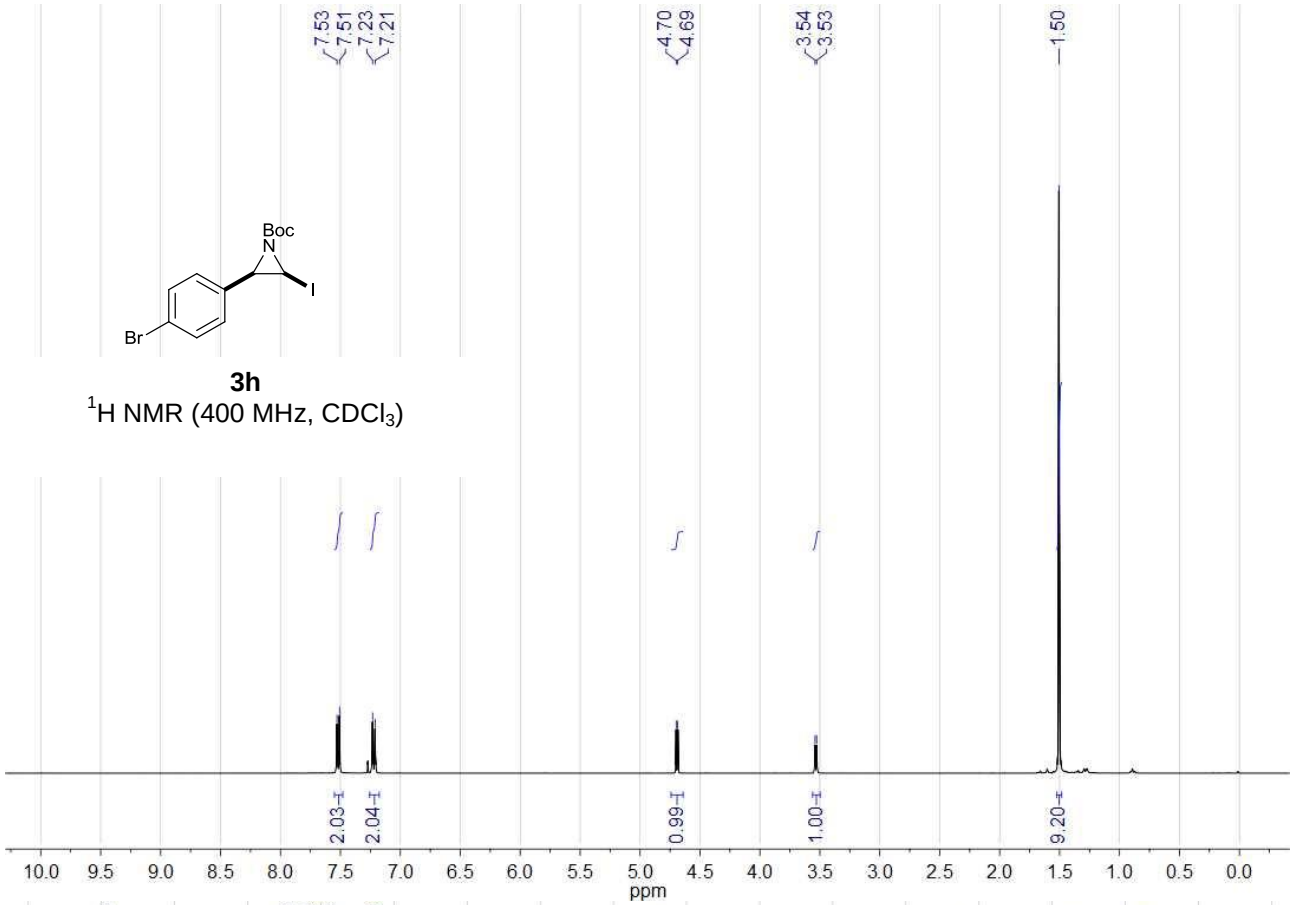
^{13}C NMR (101 MHz, $CDCl_3$)



3g
^{1}H NMR (400 MHz, $CDCl_3$)
(*cis*:*trans* = 88:12)

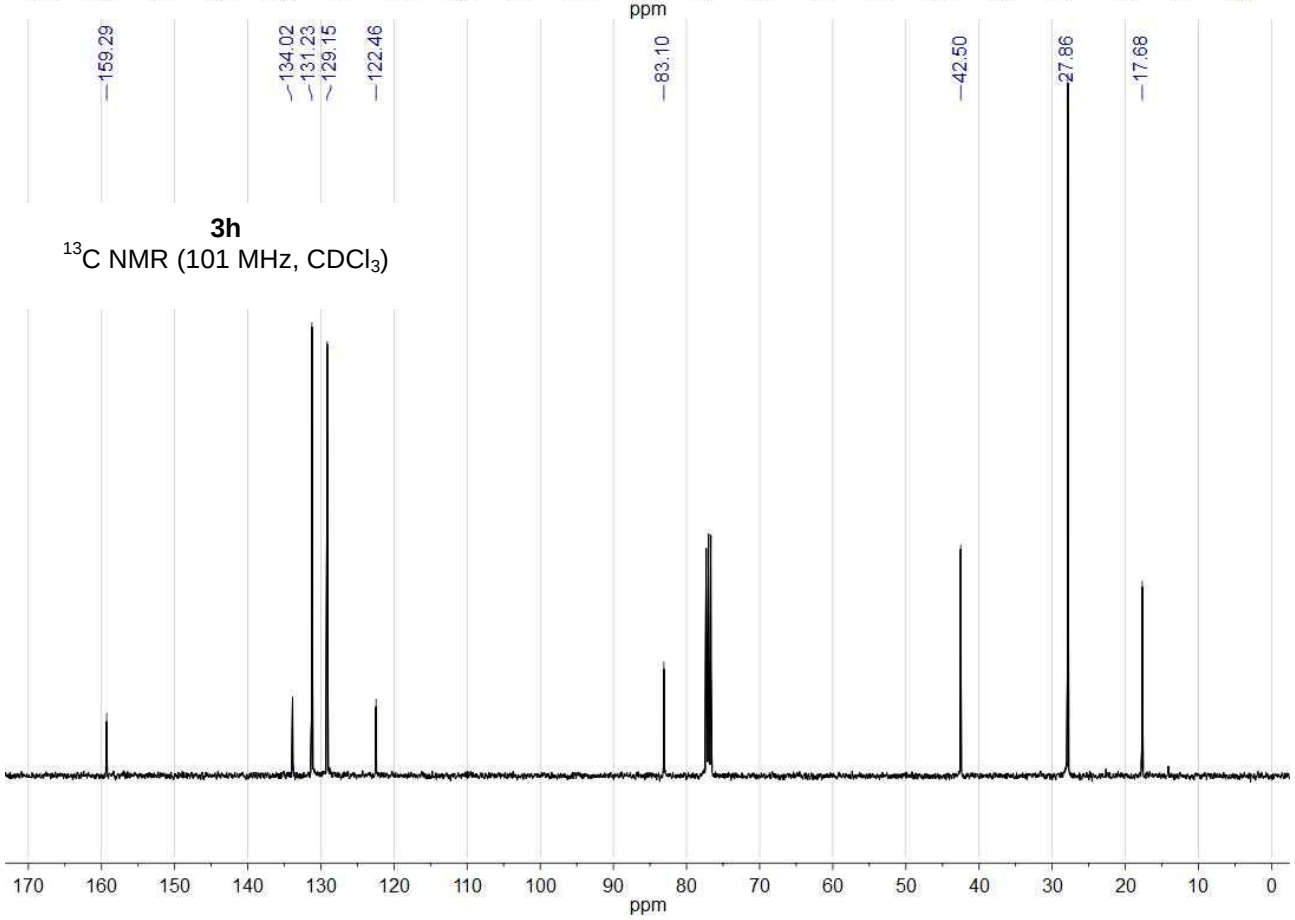


3g
^{13}C NMR (101 MHz, $CDCl_3$)



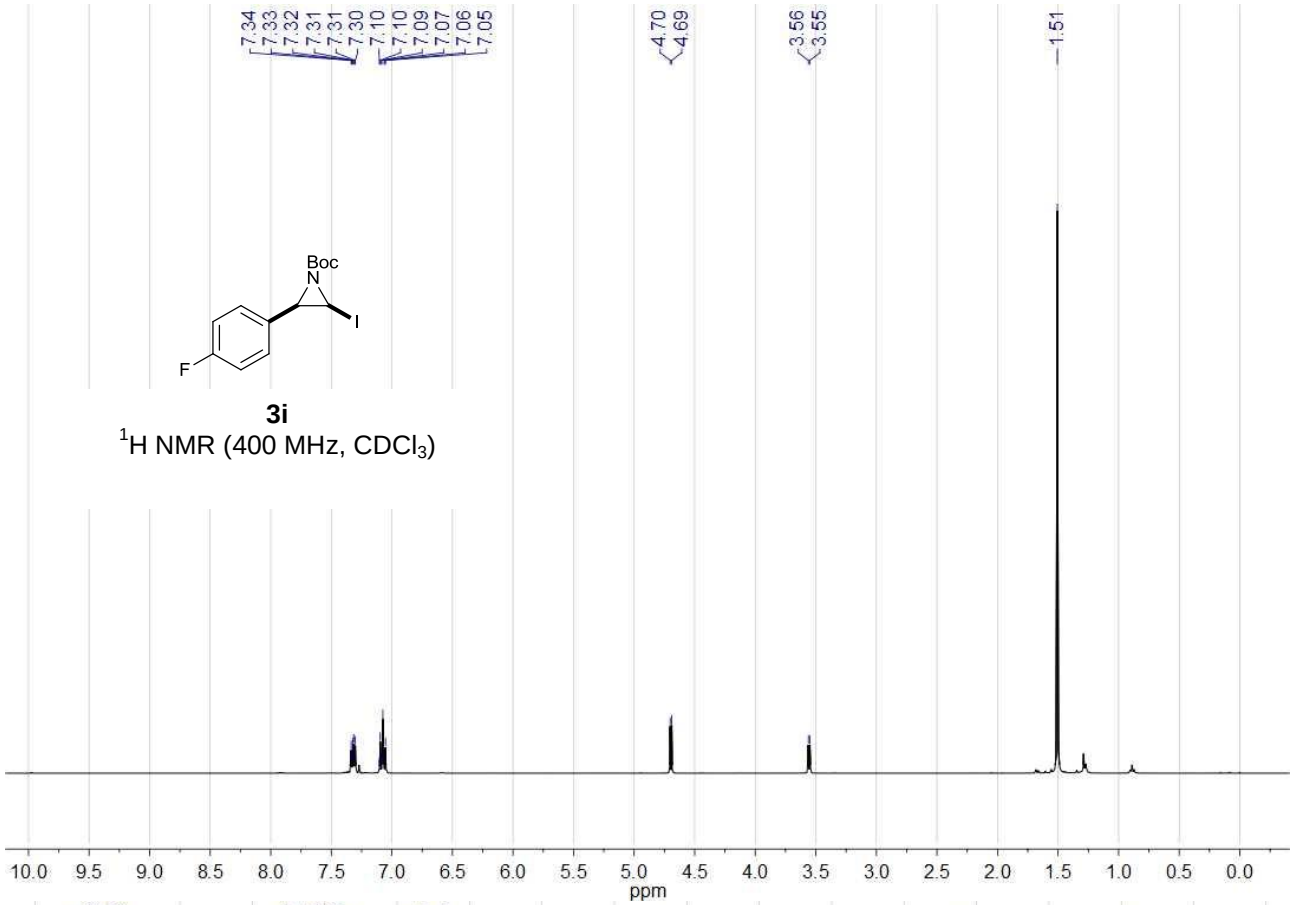
3h

^{1}H NMR (400 MHz, $CDCl_3$)



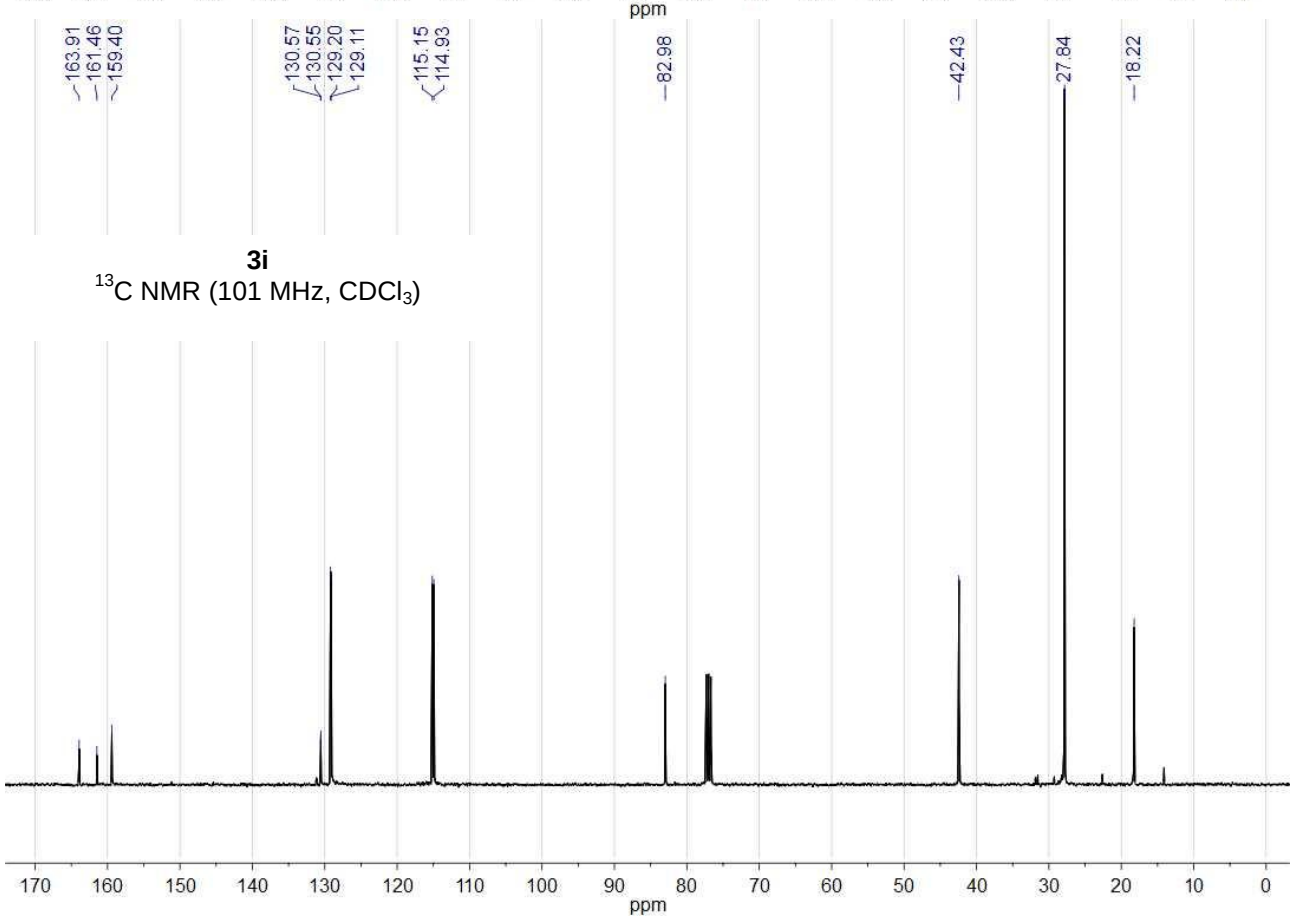
3h

^{13}C NMR (101 MHz, $CDCl_3$)



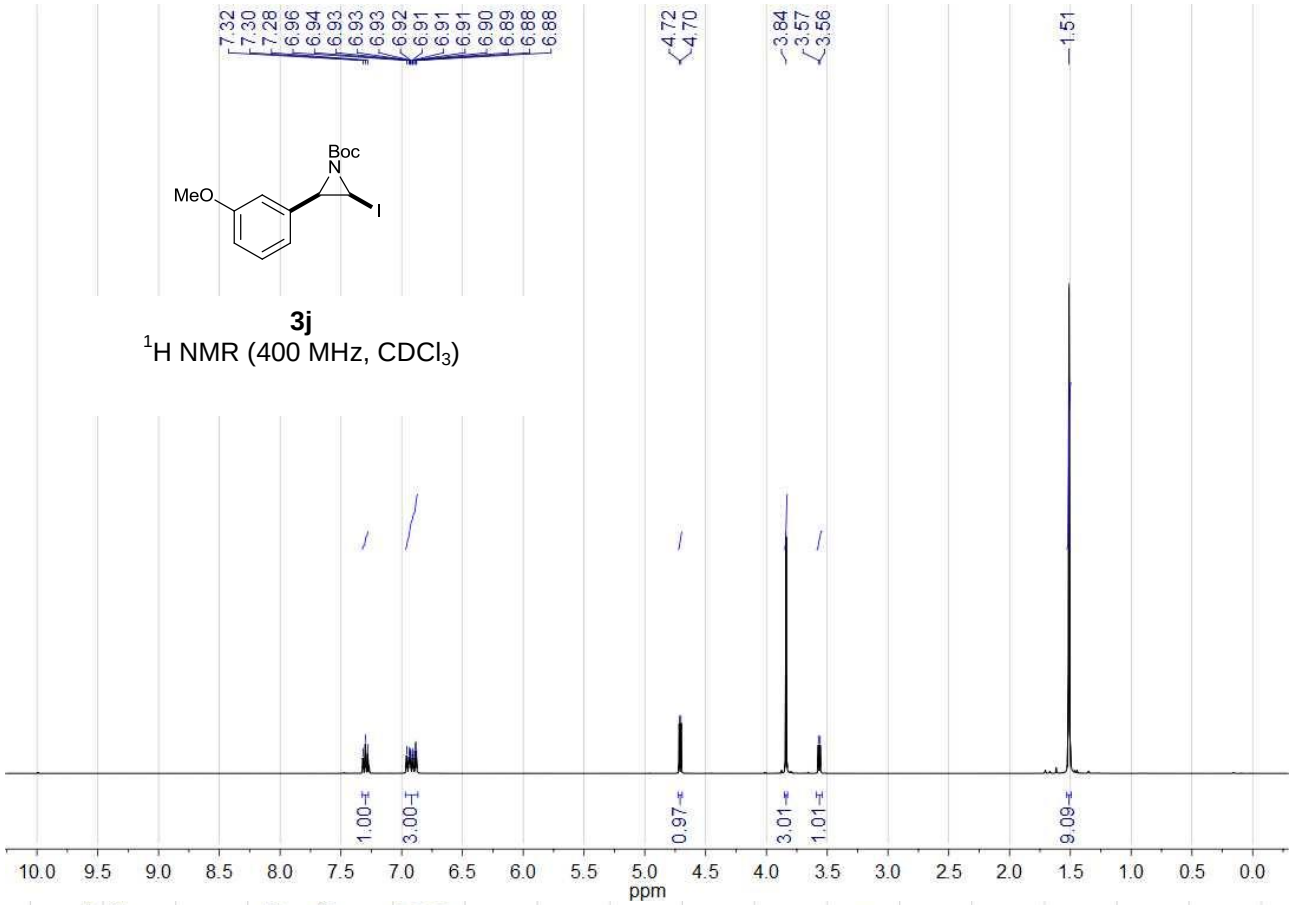
3i

^{1}H NMR (400 MHz, $CDCl_3$)

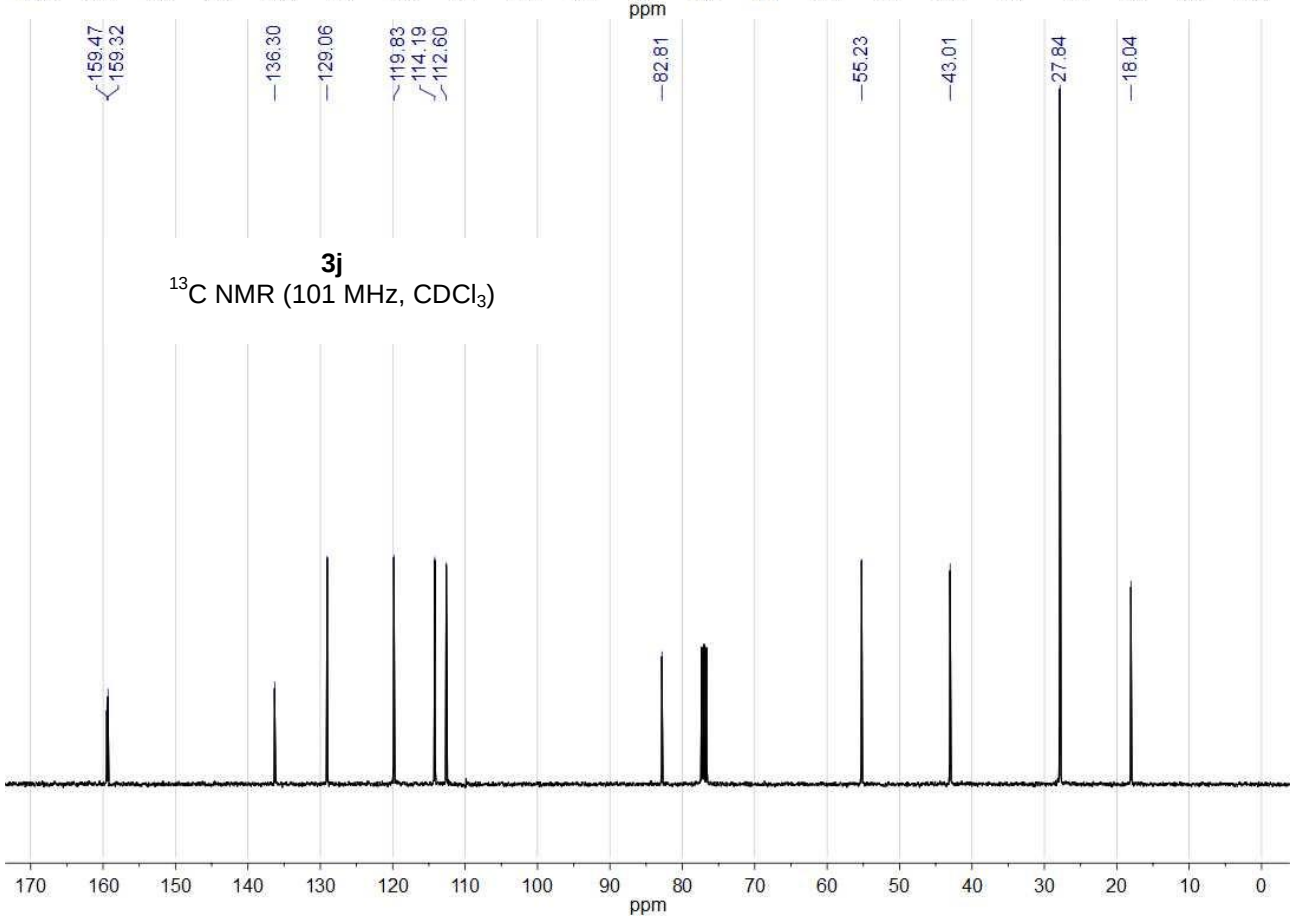


3i

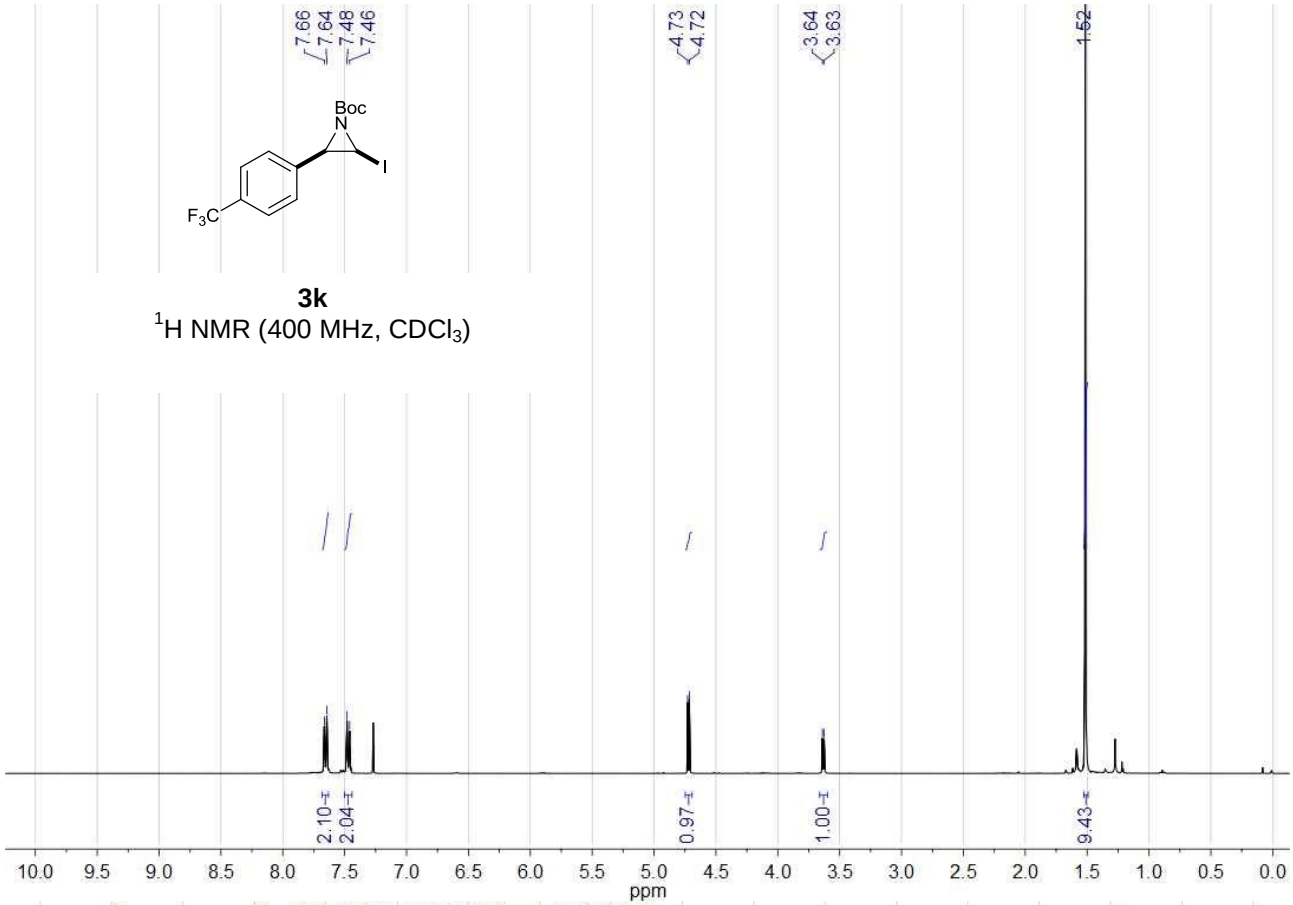
^{13}C NMR (101 MHz, $CDCl_3$)



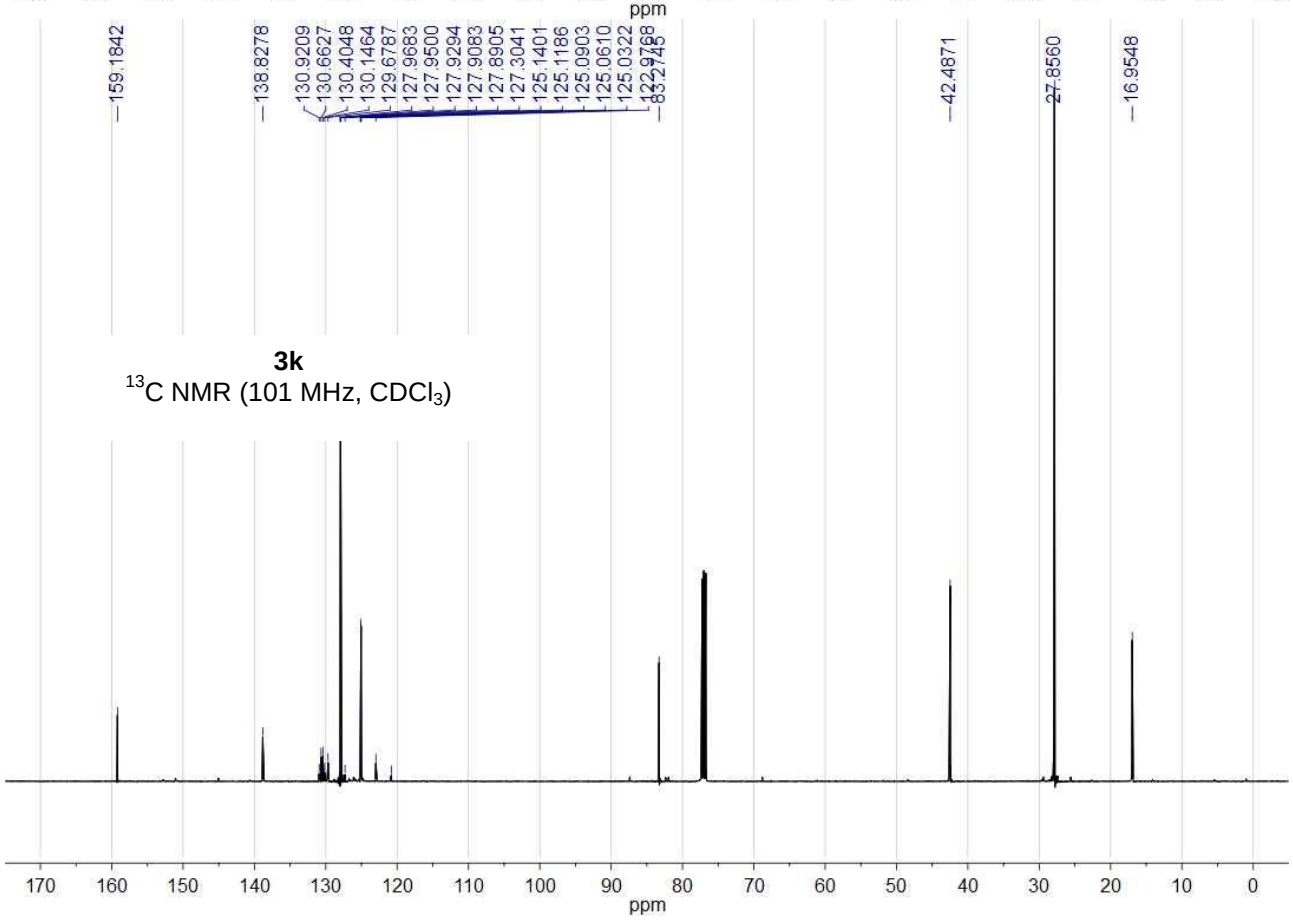
3j
^{1}H NMR (400 MHz, $CDCl_3$)



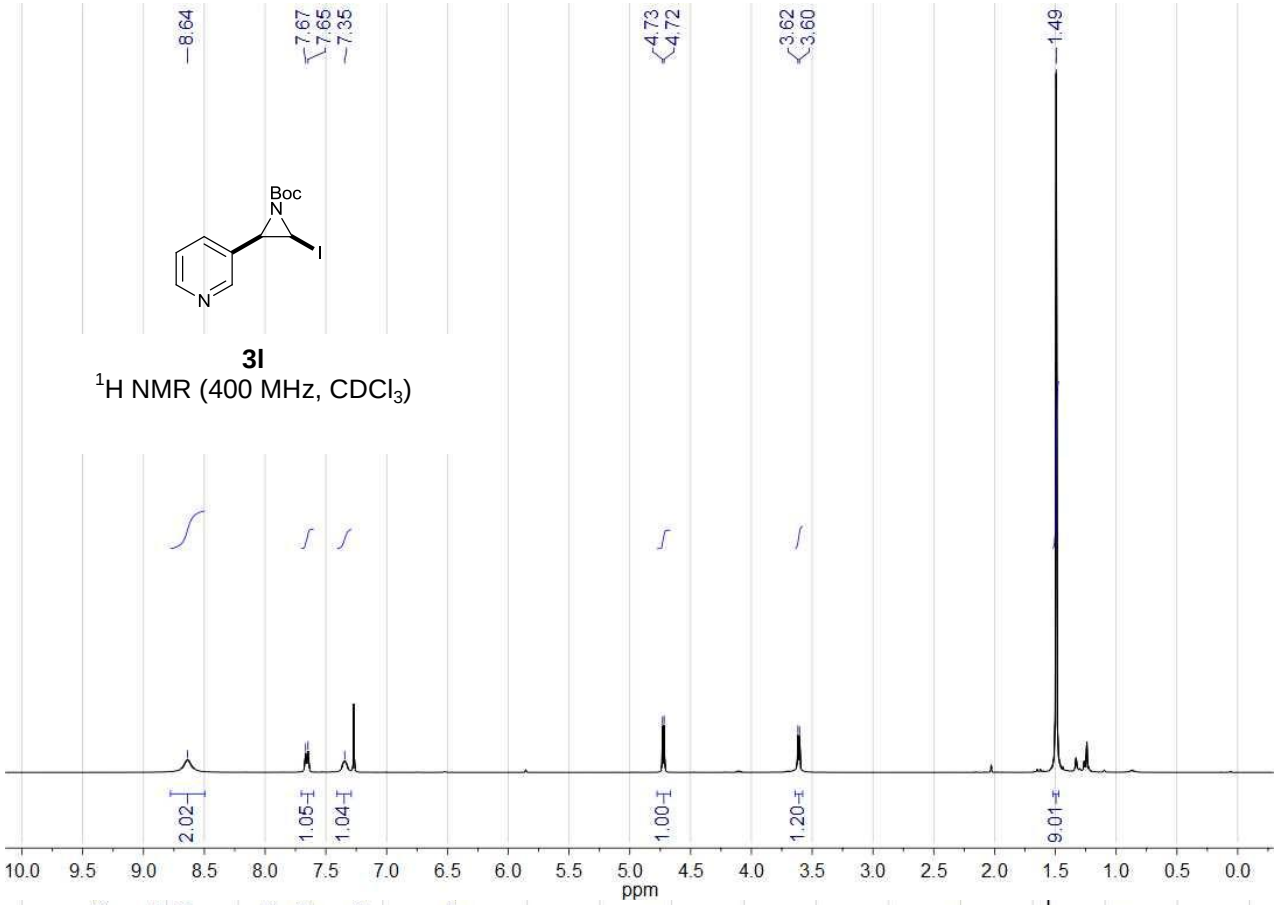
3j
^{13}C NMR (101 MHz, $CDCl_3$)



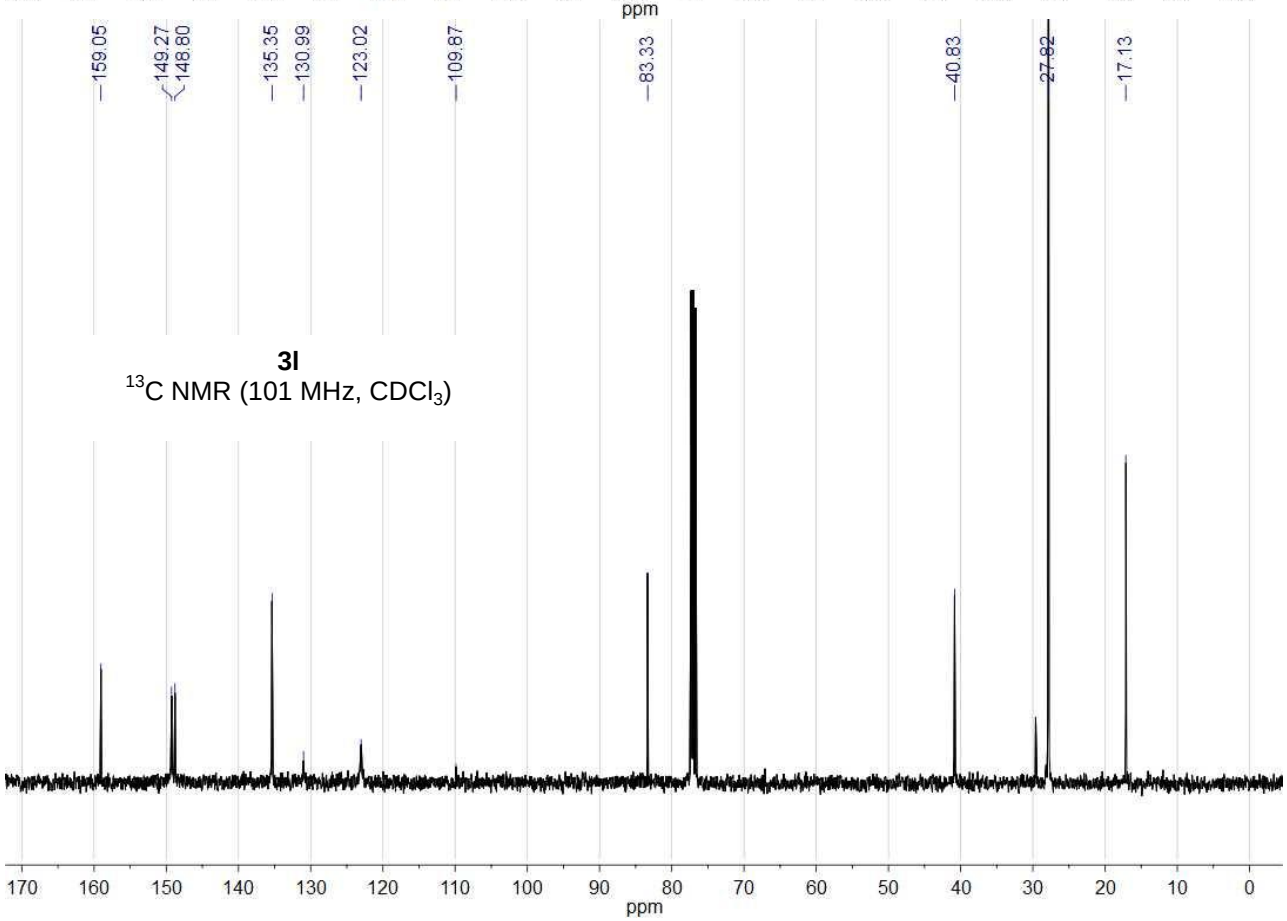
3k
^{1}H NMR (400 MHz, $CDCl_3$)



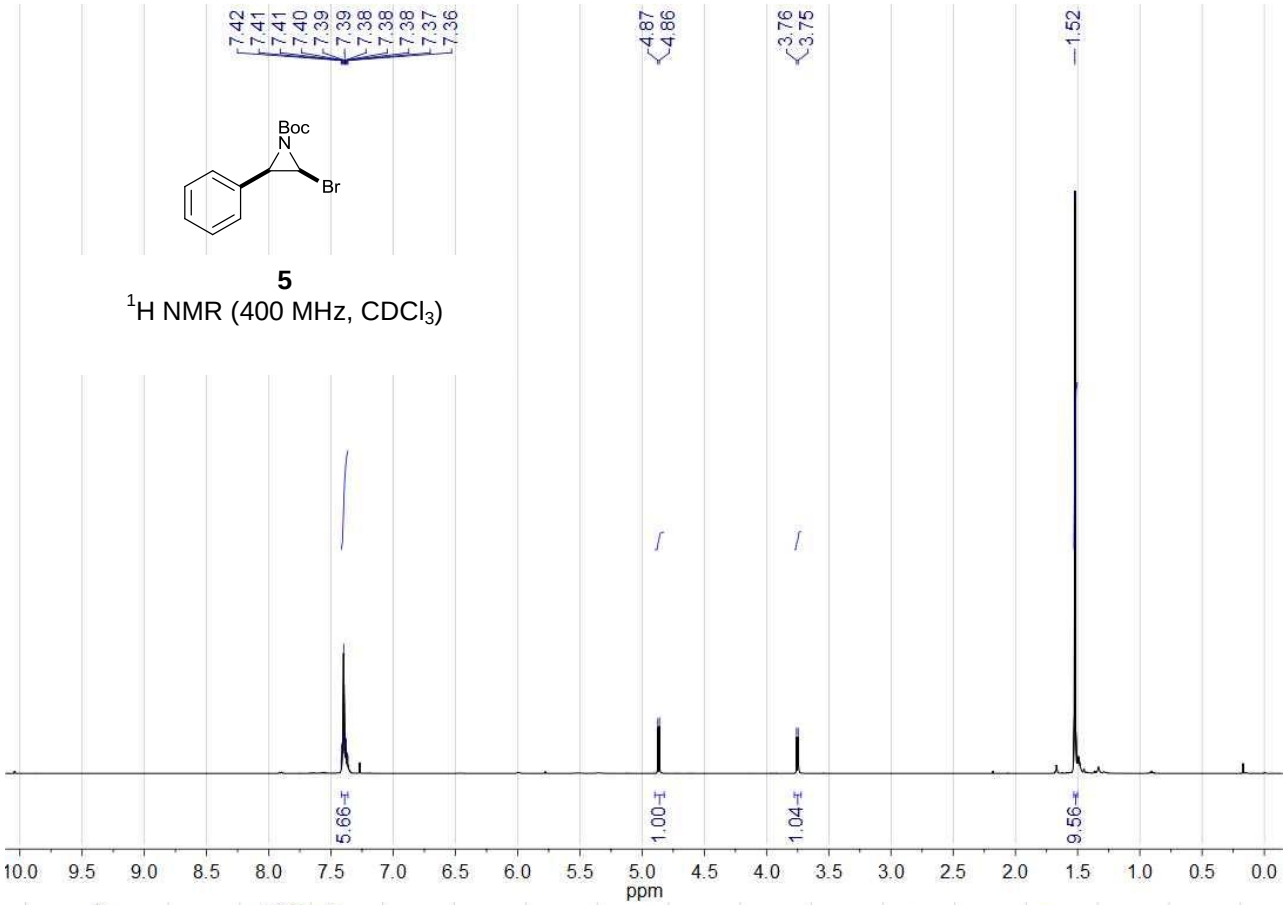
3k
^{13}C NMR (101 MHz, $CDCl_3$)



3l
^{1}H NMR (400 MHz, $CDCl_3$)

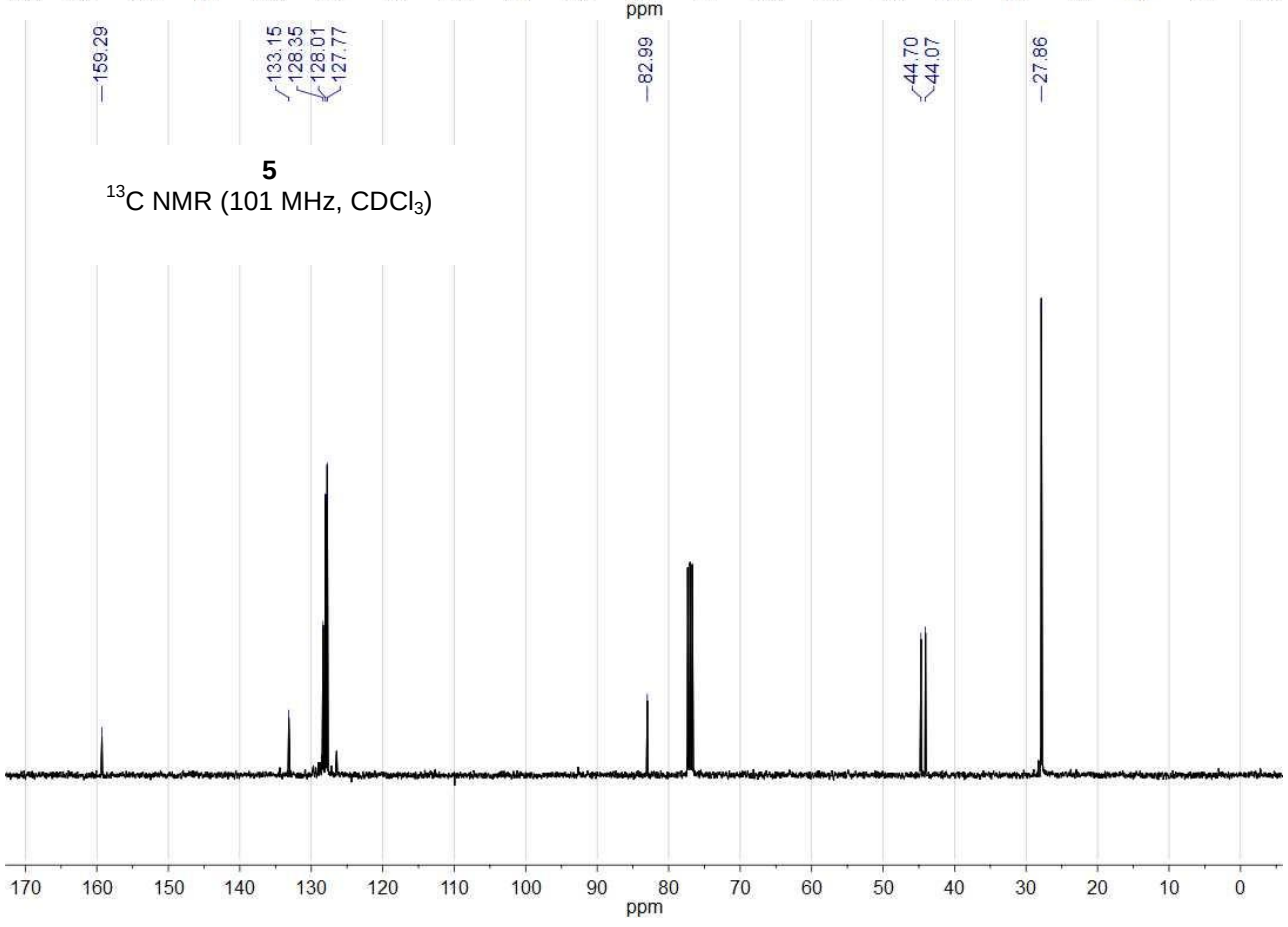


3l
^{13}C NMR (101 MHz, $CDCl_3$)



5

^{1}H NMR (400 MHz, $CDCl_3$)



5

^{13}C NMR (101 MHz, $CDCl_3$)