Supporting Information

Mild and Regioselective $Pd(OAc)_2$-Catalyzed C–H Arylation of Tryptophans by $[ArN_2]X$, Promoted by Tosic Acid

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1. General Experimental Details

Commercially-sourced solvents and reagents were purchased from Acros Organics, Alfa Aesar, Fisher Scientific, Fluorochem, Sigma-Aldrich or VWR and used as received unless otherwise noted. Petrol refers to the fraction of petroleum ether boiling in the range of 40–60 °C. Room temperature (RT) refers to reactions where no thermostatic control was applied and was recorded as 16–23 °C.

Thin layer chromatography (TLC) analysis was performed using Merck 5554 aluminium backed silica plates. Spots were visualised by the quenching of ultraviolet light (λ_{max} = 254 nm). Retention factors (R_f) are quoted to two decimal places and reported along with the solvent system used in parentheses. All flash column chromatography was performed using either Merck 60 or Fluorochem 60 Å silica gel (particle size 40–63 μm) and the solvent system used is reported in parentheses.

Optical rotations were recorded using a digital polarimeter at 20 °C (using the sodium D line, 259 nm) with a path length of 100 mm, with the solvent and concentration used indicated in the text. The appropriate solvent was used as a background with ten readings taken for each sample and the average $[\alpha]_D$ values in units of 10^{-1} deg cm^3 g^{-1} quoted to one decimal place.

Melting points were recorded using a Stuart digital SMP3 machine using a temperature ramp of 3 °C min^{-1} and are quoted to the nearest whole number. Where applicable, decomposition (dec.) is noted.

All NMR spectra were recorded on either Jeol ECS400, Jeol ECX400 or Bruker Avance 500 spectrometers (typically at 298 K). Chemical shifts are reported in parts per million (ppm) of tetramethylsilane. Coupling constants (J) are reported in Hz and quoted to ±0.5 Hz. Multiplicities are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), sextet, (sext), heptet (hept), multiplet (m), apparent (app) and broad (br). Spectra were processed using MestReNova. NMR spectra are representative of the compounds prepared.

Proton (^{1}H) spectra were typically recorded at 400 MHz. Chemical shifts are internally referenced to residual non-deuterated solvent ($CHCl_3$ δ_H = 7.26 ppm), given to two decimal places.

Carbon-13 (^{13}C) spectra were recorded at 101 MHz. Chemical shifts are internally referenced to residual solvent ($CDCl_3$ δ_C = 77.16 ppm) and given to one decimal place.

Boron-11 (^{11}B) spectra were recorded at 128 MHz and obtained with ^{1}H decoupling. Chemical shifts are externally referenced to $BF_3{\cdot}OEt_2$ and given to one decimal place.

Fluorine-19 (^{19}F) spectra were recorded at 376 MHz and obtained with ^{1}H decoupling. Chemical shifts are externally referenced to $CFCl_3$ and given to one decimal place.

Electrospray ionisation (ESI) mass spectrometry was performed using a Bruker Daltronics micrOTOF spectrometer. Electron impact (EI) mass spectrometry was performed using a Waters GCT Premier mass spectrometer. Mass to charge ratios (m/z) are reported in Daltons with percentage abundance in parentheses along with the corresponding fragment ion, where known. Where complex isotope patterns were observed, the most abundant ion is reported. High resolution mass spectra (HRMS) are reported with less than 5 ppm error.

Infrared spectra were recorded using a Bruker Alpha FT-IR spectrometer and were carried out as ATR. Absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}) to the nearest whole number and described as weak (w), medium (m), strong (s) or broad (br).

UV–visible spectroscopy was performed on a Jasco V-560 spectrometer, with a background taken in the appropriate solvent prior to recording spectra, using a quartz cell with a path length of 1 cm. The wavelength of maximum absorption (λ_{max}) is reported in nm along with the extinction coefficient (ε) in mol dm^{-3} cm^{-1}.

Diffraction data were collected at 110 K on an Agilent SuperNova diffractometer MoKα radiation (λ = 0.71073 Å). Data collection, unit cell determination and frame integration were carried out with CrysalisPro. Absorption coefficients were applied using face indexing and the ABSPACK absorption correction software within CrysalisPro. Structures were solved and refined using Olex2[1] implementing SHELX algorithms and the Superflip[2] structure solution program. Structures were solved by charge flipping, Patterson or direct methods and refined with the ShelXL[3] package using full-matrix least squares minimisation. All non-hydrogen atoms were refined anisotropically. Where applicable, absolute configurations were established by anomalous dispersion.

Transmission electron microscopy was performed at the Department of Biology Technology Facility, University of York, using an FEI Technai 12 G2 BioTWIN microscope operating at 120 kV, and images were captured using an SIS Megaview III camera. Samples were prepared by suspending *ca.* 1 mg of material in reagent grade ethanol with vigorous shaking, applying a small amount to a TEM grid, and allowing the solvent to evaporate. The grids used were 200 mesh copper grids with a Formvar/carbon support film. The resulting images were enlarged and particle sizes measured manually.

2. General Procedures

General Procedure A: Synthesis of aryldiazonium tetrafluoroborates[4]

The appropriate aniline (1 eq.) was dissolved in ethanol and HBF_4 (50 wt% in H_2O, 2 eq.) before being cooled to 0 °C with stirring. A 90% solution of *tert*-butylnitrite (2 eq.) was then added dropwise and the mixture was allowed to warm to room temperature with stirring for 1 h. After 1 h Et_2O was added to precipitate the aryldiazonium tetrafluoroborate which was collected by filtration through a glass sinter and washed with further Et_2O until the filtrate ran clear, then dried *in vacuo* to afford the desired compound, which was subsequently stored at −18 °C.

General Procedure B: Direct arylation of tryptophan with $Pd(OAc)_2$

To a microwave tube was added tryptophan **1** (50 mg, 0.192 mmol, 1 eq.), the appropriate aryldiazonium salt (0.192 mmol, 1 eq.), $Pd(OAc)_2$ (2 mg, 9.6 μmol, 5 mol%) and EtOAc (5 mL). The reaction mixture was stirred at RT for 16 h. After 16 h the resulting brown reaction mixture was filtered through Celite then washed with sat. aq. $NaHCO_3$. The organic layer was collected and dried over $MgSO_4$, filtered and evaporated to give a brown solid. When purification was required, it was performed using dry-loaded flash column chromatography with a SiO_2 stationary phase and the solvent system specified for each compound.

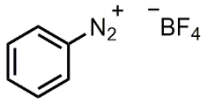
General Procedure C: Direct arylation of tryptophan with $Pd(OTs)_2(MeCN)_2$

As in general procedure B except using $Pd(OTs)_2(MeCN)_2$ (5.1 mg, 9.6 μmol, 5 mol%) in place of $Pd(OAc)_2$.

3. Synthetic Procedures and Compound Data

The synthesis of methyl (2*S*)-2-amino-3-(1*H*-indol-3-yl)propanoate hydrochloride and methyl (2*S*)-2-acetamido-3-(1*H*-indol-3-yl)propanoate (**1**) have been previously reported.[5]

Benzenediazonium tetrafluoroborate (2a)

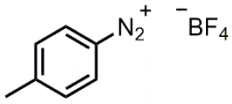


Synthesised using general procedure A from phenylamine (0.91 mL, 931 mg, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (1.92 g, quant.).

M.P. 103–105 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.67 (dd, *J* = 8.5, 1.0 Hz, 2H), 8.26 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.98 (ddt, *J* = 9.5, 8.0, 2.0 Hz); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 140.8, 132.7, 131.2, 116.1; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 105 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 105.0480 $[M-BF_4]^+$ ($C_6H_5N_2$ requires 105.0447).

The analytical data obtained was in accordance with the literature.[6]

4-Methylbenzene-1-diazonium tetrafluoroborate (2b)

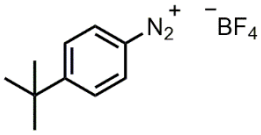


Synthesised using general procedure A from 4-amino-1-methylbenzene (1.07 g, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (1.78 g, 86%).

M.P. 106–107 °C (lit.[8] 101–102 °C); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.58–8.51 (m, 2H), 7.83–7.75 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 153.94, 132.7, 131.8, 112.0, 22.4; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 119 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 119.0603 $[M-BF_4]^+$ ($C_7H_7N_2$ requires 119.0604).

The analytical data obtained was in accordance with the literature.[7]

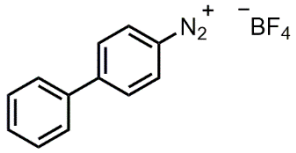
4-*tert*-butylbenzene-1-diazonium tetrafluoroborate (2c)



Synthesised using general procedure A from 4-*tert*-butylaniline (0.8 mL, 746 mg, 5 mmol, 1 eq.) in EtOH (1.5 mL) to afford the *title compound* as a white solid (963 mg, 78%).

M.P. 93–94 °C (lit.[9] 91 °C); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.62–8.56 (m, 2H), 8.06–8.00 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 165.5, 132.8, 128.5, 112.2, 36.5, 30.2; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 161 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 161.1070 $[M-BF_4]^+$ ($C_{10}H_{13}N_2$ requires 161.1073). The analytical data obtained was in accordance with the literature.[8]

4-Phenylbenzene-1-diazonium tetrafluoroborate (2d)

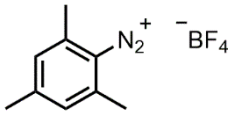


Synthesised using general procedure A from 4-phenylaniline (846 mg, 5 mmol, 1 eq.) in EtOH (1.5 mL) to afford the *title compound* as a brown solid (870 mg, 65%).

M.P. 118–119 °C (lit.[9] 111–112 °C); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.76–8.70 (m, 2H), 8.36–8.29 (m, 2H), 7.95–7.88 (m, 2H), 7.65–7.56 (m, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 151.5, 136.4, 133.5, 130.8, 129.6, 129.0, 128.0, 113.3; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); EI-MS *m/z* (ion, %): 154 ($[M-BF_4-N_2]^+$, 100); EI-HRMS *m/z*: 154.0782 $[M-BF_4-N_2]^+$ ($C_{12}H_{10}$ requires 154.0783).

The analytical data obtained was in accordance with the literature.[9]

2,4,6-Trimethylbenzene-1-diazonium tetrafluoroborate (2e)

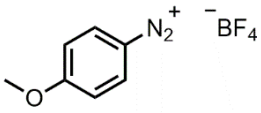


Synthesised using general procedure A from 2,4,6-trimethylphenylamine (1.4 mL, 1.35 g, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (2.34 g, quant.).

M.P. 84–85 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 7.40 (s, 2H), 2.57 (s, 6H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 153.4, 143.7, 130.7, 112.0, 22.1, 18.1; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 147 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 147.0916 $[M-BF_4]^+$ ($C_9H_{11}N_2$ requires 147.0917).

The analytical data obtained was in accordance with the literature.[10]

4-Methoxybenzene-1-diazonium tetrafluoroborate (2f)

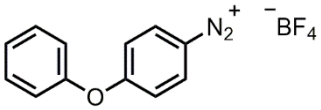


Synthesised using general procedure A from 4-methoxyaniline (1.23 g, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (2.16 g, 98%).

M.P. 145–147 °C (lit.[11] 143 °C); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.64–8.58 (m, 2H), 7.51–7.45 (m, 2H), 4.04 (s, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 168.8, 136.2, 117.3, 103.4, 57.5; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 135 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 135.0548 $[M-BF_4]^+$ ($C_7H_7N_2O$ requires 135.0553).

The analytical data obtained was in accordance with the literature.[6,11]

4-Phenoxybenzene-1-diazonium tetrafluoroborate (2g)

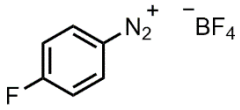


Synthesised using general procedure A from 4-phenoxyaniline (1.85 g, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as an off-white solid (2.71 g, 95%).

M.P. 167–170 °C (lit.[7] 177–178 °C); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.67–8.60 (m, 2H), 7.61–7.54 (m, 2H), 7.45–7.37 (m, 3H), 7.33–7.27 (m, 2H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 167.1, 152.7, 136.6, 131.0, 126.9, 121.0, 118.7, 106.0; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 197 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 197.0706 $[M-BF_4]^+$ ($C_{12}H_9N_2O$ requires 197.0709).

The analytical data obtained was in accordance with the literature.[7]

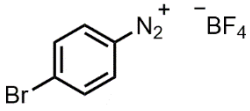
4-Fluorobenzene-1-diazonium tetrafluoroborate (2h)



Synthesised using general procedure A from 4-aminofluorobenzene (0.95 mL, 1.11 g, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (2.05 g, 98%).

M.P. 164–165 °C (lit.[6] 161–162 °C); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.83–8.77 (m, 2H), 7.93–7.85 (m, 2H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 168.4 (d, *J* = 267.0 Hz), 137.0 (d, *J* = 12.0 Hz), 119.4 (d, *J* = 25 .0 Hz), 111.9 (d, *J* = 3.0 Hz); ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −87.1, −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 123 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 123.0353 $[M-BF_4]^+$ ($C_6H_4FN_2$ requires 123.0353). The analytical data obtained was in accordance with the literature.[6]

4-Bromobenzene-1-diazonium tetrafluoroborate (2i)

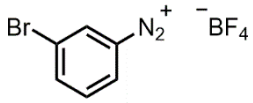


Synthesised using general procedure A from 4-aminobromobenzene (1.72 g, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (2.52 g, 93%).

M.P. 138–140 °C (lit.[7] 138 °C dec.); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.60–8.55 (m, 2H), 8.29–8.24 (m, 2H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 136.6, 134.5, 134.0, 115.2; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 183 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 182.9556 $[M-BF_4]^+$ ($C_6H_4BrN_2$ requires 182.9552).

The analytical data obtained was in accordance with the literature.[7]

3-Bromobenzene-1-diazonium tetrafluoroborate (2j)

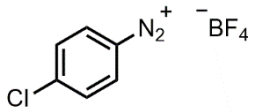


Synthesised using general procedure A from 3-aminobromobenzene (1.09 mL, 1.72 g, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (2.71 g, quant.).

M.P. 140–142 °C (lit.[7] 145 °C); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.96 (t, *J* = 2.0 Hz, 1H), 8.69 (ddd, *J* = 8.5, 2.0, 1.0 Hz, 1H), 8.49 (ddd, *J* = 8.5, 2.0, 1.0 Hz, 1H), 7.92 (t, *J* = 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 143.8, 134.3, 132.8, 131.9, 122.3, 117.8; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 183 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 182.9548 $[M-BF_4]^+$ ($C_6H_4BrN_2$ requires 182.9552).

The analytical data obtained was in accordance with the literature.[7]

4-Chlorobenzene-1-diazonium tetrafluoroborate (2k)

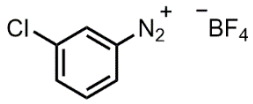


Synthesised using general procedure A from 4-aminochlorobenzene (1.28 g, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (2.15 g, 95%).

M.P. 138–139 °C (lit.[6] 134 °C dec.); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.73–8.64 (m, 2H), 8.15–8.07 (m, 2H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 146.5, 134.4, 131.6, 114.8; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 139 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 139.0054 $[M-BF_4]^+$ ($C_6H_4ClN_2$ requires 139.0058).

The analytical data obtained was in accordance with the literature.[9]

3-Chlorobenzene-1-diazonium tetrafluoroborate (2l)

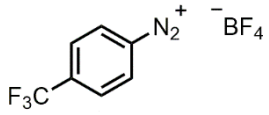


Synthesised using general procedure A from 3-aminochlorobenzene (1.10 mL, 1.28 g, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (2.26 g, quant.).

M.P. 147–148 °C (lit.[10] 148 °C dec.); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.85 (t, *J* = 2.0 Hz, 1H), 8.67 (ddd, *J* = 8.5, 2.0, 1.0 Hz, 1H), 8.37 (ddd, *J* = 8.5, 2.0, 1.0 Hz, 1H), 8.01 (t, *J* = 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 141.1, 134.6, 132.9, 131.7, 131.6, 117.8; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 139 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 139.0055 $[M-BF_4]^+$ ($C_6H_4ClN_2$ requires 139.0058).

The analytical data obtained was in accordance with the literature.[10]

4-(Trifluoromethyl)benzene-1-diazonium tetrafluoroborate (2m)

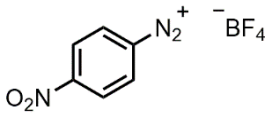


Synthesised using general procedure A from 4-aminobenzotrifluoride (1.26 mL, 1.61 mg, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (2.38 g, 92%).

M.P. 118–119 °C (lit.[12] 105–106 °C); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.91 (d, *J* = 8.5 Hz, 2H), 8.42 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 113.8, 128.3, 122.3 (q, *J* = 274.0 Hz), 121.3, 110.5; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −62.5, −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 173 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 173.0325 $[M-BF_4]^+$ ($C_7H_4F_3N_2$ requires 173.0321).

The analytical data obtained was in accordance with the literature.[12]

4-Nitrobenzene-1-diazonium tetrafluoroborate (2n)

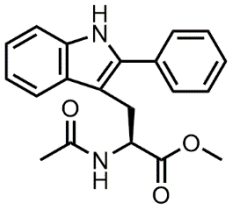


Synthesised using general procedure A from 4-nitroaniline (1.38 g, 10 mmol, 1 eq.) in EtOH (3 mL) to afford the *title compound* as a white solid (2.24 g, 95%).

M.P. 148–151 °C (lit.[6] 155 °C dec.); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, δ): 8.95–8.90 (m, 2H), 8.75–8.69 (m, 2H); ^{13}C NMR (101 MHz, $(CD_3)_2SO$, δ): 153.3, 134.6, 126.1, 121.9; ^{11}B NMR (128 MHz, $(CD_3)_2SO$, δ): −2.3; ^{19}F NMR (376 MHz, $(CD_3)_2SO$, δ): −148.1 (m, $^{1}J_{F-^{10}B}$, 4F), −148.1 (m, $^{1}J_{F-^{11}B}$, 4F); ESI-MS *m/z* (ion, %): 150 ($[M-BF_4]^+$, 100); ESI-HRMS *m/z*: 150.0304 $[M-BF_4]^+$ ($C_6H_4N_3O_2$ requires 150.0298).

The analytical data obtained was in accordance with the literature.[6]

Methyl (2*S*)-2-acetamido-3-(2-phenyl-1*H*-indol-3-yl)propanoate (3a)



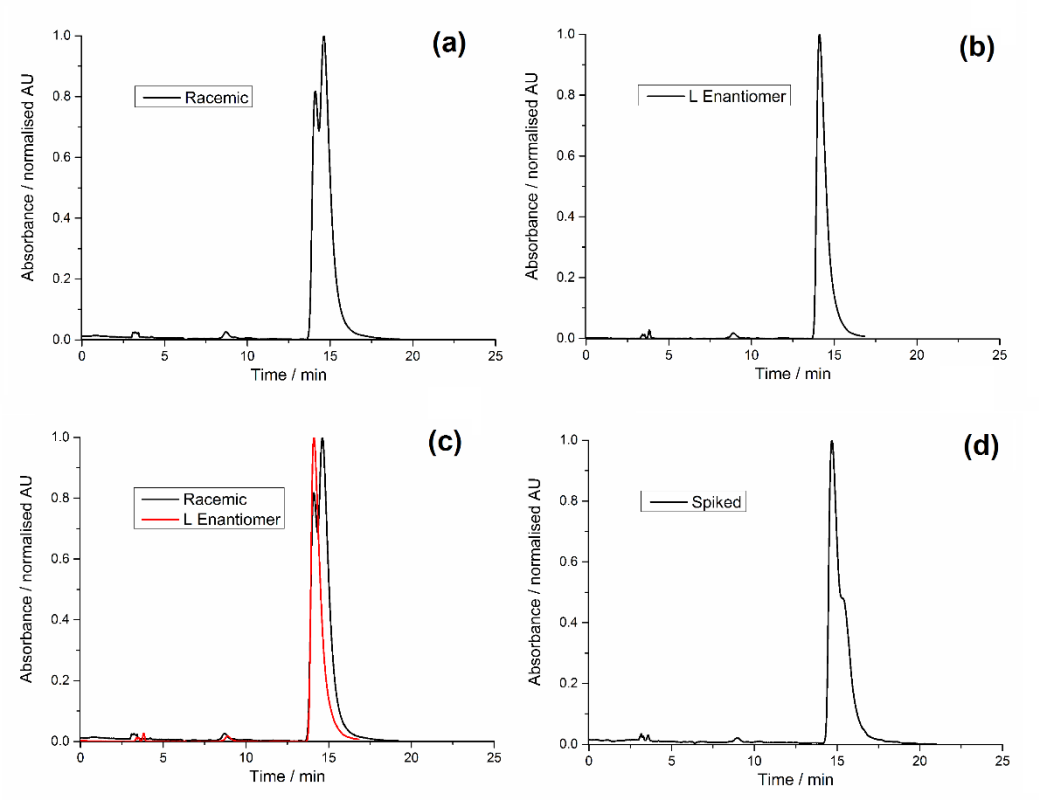
Method A: Synthesised using general procedure B with aryldiazonium salt **2a** (37 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as an off-white solid (64 mg, quant.).

Method B: Synthesised using general procedure C with aryldiazonium salt **2a** (37 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as an off-white solid (64 mg, quant.).

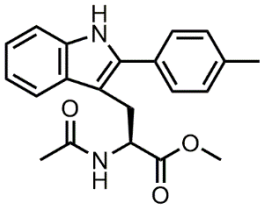
Rf 0.25 (EtOAc/petrol, 1:1, v/v); $[\alpha]_D$ = +49.1 (*c* 0.42, $CHCl_3$ – lit.[13a] +47.3, *c* 0.1, $CHCl_3$); M.P. 82–83 °C (lit.[14] 85–86 °C); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.43 (s, 1H), 7.59–7.52 (m, 3H), 7.45 (d, *J* = 15.1 Hz, 2H), 7.39–7.32 (m, 2H), 7.22–7.17 (m, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 5.81 (d, *J* = 8 Hz, 1H), 4.89–4.76 (dt, *J* = 8.0, 5.0 Hz, 1H), 3.54 (d, *J* = 5.5 Hz, 2H), 3.29 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.3, 169.8, 136.1, 135.8, 133.3, 129.5, 129.3, 128.4, 128.2, 122.6, 120.1, 119.0, 111.1, 106.8, 52.9, 52.1, 26.7, 23.0.

Crystals suitable for X-ray diffraction were grown by slow diffusion from a solution of hexane/Et_2O (1:3, *v/v*).The analytical data obtained was in accordance with the literature.[13,14]

A racemic sample of **3a** was prepared from racemic-**1** allowing *L*-**3a** to be compared by chiral HPLC analysis (using Chiralpak IB column eluting with 81:19 Hexane:IPA on an Agilent 1200 series chromatograph – the raw data was reprocessed in Origin 2016. The figure below shows (±)-**3a** (**a**) and *L*-**3a** (**b**), the overlaid chromatograms (**c**) (offset for *L*-**3a** by 0.23 mins for the overlay) and a spiked sample of (±)-**3a** with *L*-**3a** (*ca.* 1:1) (**d**), which confirms the overlay given in (**c**).



Methyl (2*S*)-3-[2-(4-methylphenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3b)



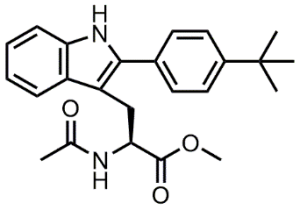
Method A: Synthesised using general procedure B with aryldiazonium salt **2b** (40 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (67 mg, quant.).

Method B: Synthesised using general procedure C with aryldiazonium salt **2b** (40 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (67 mg, quant.).

R_f 0.32 (petrol/EtOAc, 1:1, *v/v*); M.P. 97–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.14 (br s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.49–7.43 (m, 2H), 7.38–7.33 (m, 1H), 7.31–7.27 (m, 2H), 7.20 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 5.77 (d, *J* = 8.0 Hz, 1H), 4.82 (dt, *J* = 8.0, 5.5 Hz, 1H), 3.54 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.52 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.33 (s, 3H), 2.41 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.4, 169.7, 138.2, 136.2, 135.7, 130.3, 130.0, 129.6, 128.3, 122.5, 120.1, 118.9, 111.0, 106.6, 52.9, 52.2, 26.8, 23.0, 21.4.

The analytical data obtained was in accordance with the literature.[15]

Methyl (2*S*)-3-[2-(4-*tert*-butylphenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3c)

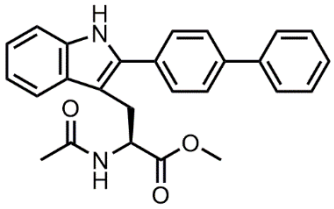


Method A: Synthesised using general procedure B with aryldiazonium salt **2c** (48 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (75 mg, quant.).

Method B: Synthesised using general procedure C with aryldiazonium salt **2c** (48 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (75 mg, quant.).

R_f 0.30 (petrol/EtOAc, 1:1.5, *v/v*); $[\alpha]_D$ = +68.6 (*c* 0.10, $CHCl_3$); M.P. 153–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.14 (br s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 4H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.19 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 5.77 (d, *J* = 8.0 Hz, 1H), 4.84 (dt, *J* = 8.0, 5.5 Hz, 1H), 3.56 (app d, *J* = 5.5 Hz, 2H), 3.28 (s, 3H), 1.64 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.3, 169.7, 151.3, 136.1, 135.7, 130.4, 129.6, 128.1, 126.2, 122.5, 120.1, 118.9, 111.0, 106.5, 52.9, 52.1, 34.9, 31.4, 26.6, 23.0; ESI–MS *m/z* (ion, %): 393 ($[M+H]^+$, 10), 415 ($[M+Na]^+$, 100); ESI–HRMS *m/z*: 393.2169 $[M+Na]^+$ ($C_{24}H_{29}N_2O_3$ requires 393.2173); IR (solid-state ATR, cm^{-1}): 3282 (w, br), 2960 (m), 1738 (m), 1660 (m), 1518 (m), 1436 (m), 1372 (m), 1260 (m), 1214 (m), 1013 (m), 837 (m), 799 (m), 741 (s), 588 (m).

Methyl (2*S*)-2-acetamido-3-[2-(4-phenylphenyl)-1*H*-indol-3-yl]propanoate (3d)

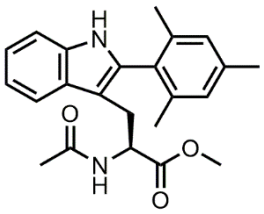


Method A: Synthesised using general procedure B with aryldiazonium salt **2d** (52 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (79 mg, quant.).

Method B: Synthesised using general procedure C with aryldiazonium salt **2d** (52 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (79 mg, quant.).

R_f 0.27 (petrol/EtOAc, 1:1.5, *v/v*); $[\alpha]_D$ = +94.8 (*c* 0.10, $CHCl_3$); M.P. 205–206 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.32 (br s, 1H), 7.74–7.67 (m, 2H), 7.66–7.61 (m, 4H), 7.60–7.56 (m, 1H), 7.52–7.44 (m, 2H), 7.43–7.35 (m, 2H), 7.21 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.15 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 5.84 (d, *J* = 8.0 Hz, 1H), 4.87 (dt, *J* = 8.0, 5.5 Hz, 1H), 3.62 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.59 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.32 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.3, 169.7, 140.9, 140.3, 135.9, 135.7, 132.2, 129.7, 129.1, 128.7, 127.9, 127.1, 122.8, 120.2, 119.0, 111.1, 107.2, 100.1, 53.0, 52.2, 26.8, 23.0; ESI–MS *m/z* (ion, %): 413 ($[M+H]^+$, 10), 435 ($[M+Na]^+$, 100); ESI–HRMS *m/z*: 413.1871 $[M+H]^+$ ($C_{26}H_{25}N_2O_3$ requires 413.1860); IR (solid-state, ATR, cm^{-1}): 3406 (w), 3378 (w), 1746 (m), 1655 (s), 1460 (m), 1449 (m), 1374 (m), 1314 (m), 1184 (m), 1008 (w), 982 (w), 842 (w), 767 (m), 743 (s), 734 (m), 697 (m), 535 (s), 512 (m).

Methyl (2*S*)-2-acetamido-3-[2-(2,4,6-trimethylphenyl)-1*H*-indol-3-yl]propanoate (3e)



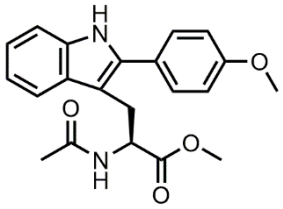
Method A: Synthesised using general procedure B (with a reaction time of 24 h) with aryldiazonium salt **2e** (45 mg, 0.192 mmol, 1 eq.). Purification by dry-loaded flash column chromatography (SiO_2, petrol/EtOAc, 1:1, *v/v*) afforded the *title compound* as an off-white solid (60 mg, 76%).

Method B: Synthesised using general procedure C with aryldiazonium salt **2e** (45 mg, 0.192 mmol, 1 eq.). Purification by dry-loaded flash column chromatography (SiO_2, petrol/EtOAc, 1:1, *v/v*) afforded the *title compound* as an off-white solid (60 mg, 75%).

R_f 0.31 (petrol/EtOAc, 1:1, *v/v*); $[\alpha]_D$ = +22.2 (*c* 0.20, $CHCl_3$; lit.[13a] +35.2 *c* 0.10, $CHCl_3$); M.P. 157–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.98 (br s, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.20 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.15 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H), 6.99 (m, 2H), 5.64 (d, *J* = 7.5 Hz, 1H), 4.72 (dt, *J* = 7.0, 5.0 Hz, 1H), 3.47 (s, 3H), 3.17 (dd, *J* = 15.0, 5.0 Hz, 1H), 3.02 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.35 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.5, 169.9, 138.9, 138.2, 138.2, 135.8, 134.7, 128.8, 122.1, 119.8, 118.8, 110.9, 108.0, 53.1, 52.3, 27.2, 23.1, 21.3, 20.4, 20.3.

Crystals suitable for X-ray diffraction were grown by overnight diffusion from a solution of CH_2Cl_2.

Methyl (2*S*)-2-acetamido-3-[2-(4-methoxyphenyl)-1*H*-indol-3-yl]propanoate (3f)



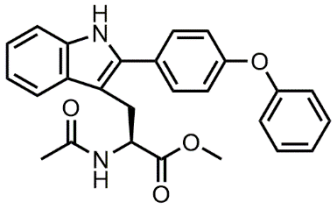
Method A: Synthesised using general procedure B (with a reaction time of 24 h) with aryldiazonium salt **2f** (43 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (70 mg, quant.).

Method B: Synthesised using general procedure C with aryldiazonium salt **2f** (43 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (70 mg, quant.).

R_f 0.15 (petrol/EtOAc, 1:1, *v/v*); $[\alpha]_D$ = +35.1 (*c* 0.10, $CHCl_3$; lit.[13a] 34.9 *c* 0.10, $CHCl_3$); M.P. 200–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.41 (br s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.50–7.40 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.17 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.12 (ddd, *J* = 8.5, 8.0, 1.0 Hz, 1H), 7.01–6.91 (m, 2H), 5.85 (d, *J* = 8.0 Hz, 1H), 4.82 (dt, *J* = 8.0, 5.5 Hz, 1H), 3.83 (s, 3H), 3.49 (d, *J* = 5.5 Hz, 2H), 3.34 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.4, 169.8, 159.5, 136.1, 135.7, 129.7, 129.5, 125.6, 122.3, 120.0, 118.7, 114.6, 111.0, 106.0, 55.5, 53.0, 52.2, 26.8, 23.0.

The analytical data obtained was in accordance with the literature.[13]

Methyl (2*S*)-2-acetamido-3-[2-(4-phenoxyphenyl)-1*H*-indol-3-yl]propanoate (3g)

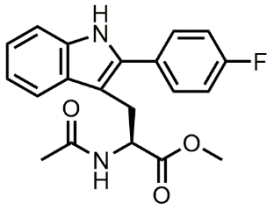


Method A: Synthesised using general procedure B with aryldiazonium salt **2g** (55 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (82 mg, quant.).

Method B: Synthesised using general procedure C with aryldiazonium salt **2g** (55 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (82 mg, quant.).

R_f 0.29 (petrol/EtOAc, 1:1.5, *v/v*); $[\alpha]_D$ = +85.3 (*c* 0.10, $CHCl_3$); M.P. 72–74 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.32 (br s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.52–7.47 (m, 2H), 7.42–7.36 (m, 2H), 7.35–7.32 (m, 1H), 7.22–7.16 (m, 2H), 7.15–7.11 (m, 1H), 7.10–7.04 (m, 4H), 5.85 (d, *J* = 8.0 Hz, 1H), 4.84 (dt, *J* = 8.0, 5.5 Hz, 1H), 3.52 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.49 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.38 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.4, 169.7, 157.6, 156.5, 135.8, 135.7, 130.1, 129.8, 129.5, 127.9, 124.1, 122.6, 120.1, 119.6, 119.0, 118.9, 111.1, 106.6, 53.0, 52.2, 26.8, 23.1; ESI–MS *m/z* (ion, %): 429 ($[M+H]^+$, 20), 451 ($[M+Na]^+$, 100); ESI–HRMS *m/z*: 451.1622 $[M+Na]^+$ ($C_{26}H_{24}N_2NaO_4$ requires 451.1628); IR (solid-state, ATR, cm^{-1}): 3266 (w, br), 2961 (w), 1736 (m), 1654 (m), 1588 (w), 1487 (s), 1458 (m), 1436 (m), 1372 (w), 1229 (s), 1012 (m), 869 (m), 840 (m), 795 (m), 743 (s), 692 (m), 486 (w).

Methyl (2*S*)-3-[2-(4-fluorophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3h)



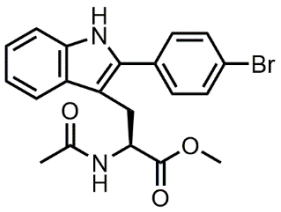
Method A: Synthesised using general procedure B with aryldiazonium salt **2h** (40 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (68 mg, quant.).

Method B: Synthesised using general procedure C with aryldiazonium salt **2h** (40 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (68 mg, quant.).

R_f 0.23 (petrol/EtOAc, 1:1, *v/v*); $[\alpha]_D$ = +43.1* (*c* 0.11, $CHCl_3$; lit.[13a] 54.4 *c* 0.10, $CHCl_3$); M.P. 212–216 °C dec.; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.17 (br s, 1H), 7.59–7.50 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.24–7.12 (m, 4H), 5.82 (d, *J* = 8.0 Hz, 1H), 4.84 (dt, *J* = 8.0, 5.5 Hz, 1H), 3.50 (m, 2H), 3.33 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.3, 169.7, 162.6 (d, $^1J_{C–F}$ = 249.0 Hz), 135.8, 135.1, 130.2 (d, $^3J_{C–F}$ = 8.0 Hz), 129.5, 129.4 (d, $^4J_{C–F}$ = 3.5 Hz), 122.8, 120.3, 119.0, 116.3 (d, $^2J_{C–F}$ = 21.5 Hz), 111.1, 107.0, 52.9, 52.2, 26.8, 23.1; ^{19}F NMR (376 MHz, $CDCl_3$, δ): −112.8–−112.9 (m).

The analytical data obtained was in accordance with the literature.[13,15]

Methyl (2*S*)-3-[2-(4-bromophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3i)



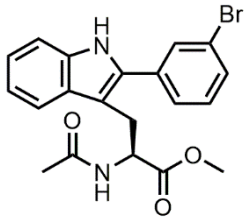
Method A: Synthesised using general procedure B with aryldiazonium salt **2i** (52 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (80 mg, quant.).

Method B: Synthesised using general procedure C with aryldiazonium salt **2i** (52 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (80 mg, quant.).

R_f 0.31 (petrol/EtOAc, 1:1, *v/v*); $[\alpha]_D$ = +44.0 (*c* 0.10, $CHCl_3$); M.P. 74–75 °C dec.; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.36 (br s, 1H), 7.60–7.54 (m, 3H), 7.44–7.39 (m, 2H), 7.34 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.21 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 5.85 (d, *J* = 8.0 Hz, 1H), 4.83 (dt, *J* = 8.0, 5.5 Hz, 1H), 3.52 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.47 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.33 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.3, 169.8, 135.9, 134.8, 132.4, 132.2, 129.9, 129.5, 123.0, 122.2, 120.3, 119.1, 111.2, 107.4, 53.0, 52.2, 26.9, 23.1; ESI–MS *m/z* (ion, %): 415 ([M+H]$^+$, 30), 437 ([M+Na]$^+$, 100); ESI–HRMS *m/z*: 437.0474 [M+Na]$^+$ ($C_{20}H_{19}BrN_2NaO_3$ requires 437.0471).

The analytical data obtained was in accordance with the literature.[15]

Methyl (2*S*)-3-[2-(3-bromophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3j)

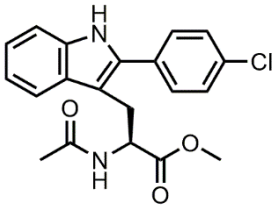


Method A: Synthesised using general procedure B with aryldiazonium salt **2j** (43 mg, 0.192 mmol, 1 eq.) to afford the *title compound* as a brown solid (80 mg, quant.).

Method B: Synthesised using general procedure C with aryldiazonium salt **2j** (43 mg, 0.192 mmol, 1 eq.). Purification by dry-loaded flash column chromatography (SiO_2, petrol/EtOAc, 1:1, *v/v*) afforded the *title compound* as a brown solid (55 mg, 69%).

R_f 0.28 (petrol/EtOAc, 1:1, *v/v*); $[\alpha]_D$ = +50.5 (*c* 0.10, $CHCl_3$); M.P. 82–84 °C dec.; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.27 (br s, 1H), 7.71 (t, *J* = 1.5 Hz, 1H), 7.58 (ddt, *J* = 8.0, 1.5, 1.0 Hz, 1H), 7.53–7.48 (m, 2H), 7.38–7.32 (m, 2H), 7.22 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.15 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 5.84 (d, *J* = 8.0 Hz, 1H), 4.85 (dt, *J* = 8.0, 5.5 Hz, 1H), 3.53 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.48 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.34 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 172.3, 169.7, 135.9, 135.3, 134.4, 131.2, 131.1, 130.8, 129.4, 127.1, 123.2, 123.1, 120.4, 119.2, 111.2, 107.9, 52.9, 52.2, 26.8, 23.1; ESI–MS *m/z* (ion, %): 415 ($[M+H]^+$, 50), 437 ($[M+Na]^+$, 100); ESI–HRMS *m/z*: 415.0658 $[M+H]^+$ ($C_{20}H_{20}BrN_2O_3$ requires 415.0652); IR (solid-state, ATR, cm^{-1}): 3264 (w, br), 3057 (w), 2951 (w), 2924 (w), 2850 (w), 1732 (m), 1651 (s), 1596 (m), 1518 (m), 1435 (s), 1372 (m), 1261 (m), 1214 (s), 1010 (m), 787 (m), 741 (s), 687 (s), 594 (m), 507 (m), 437 (m); UV–vis (DMSO, nm): λ_{max} 312 (ε = 19398 mol dm^{-3} cm^{-1}).

Methyl (2*S*)-3-[2-(4-chlorophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3k)



Method A: Synthesised using general procedure B with aryldiazonium salt **2k** (43 mg, 0.192 mmol, 1 eq.). Purification by dry-loaded flash column chromatography (SiO_2, petrol/EtOAc, 1:1, *v/v*) afforded the *title compound* as a brown solid (52 mg, 73%).

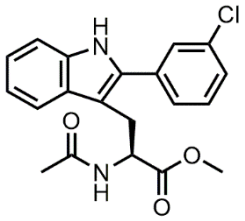
Method B: Synthesised using general procedure C with aryldiazonium salt **2k** (43 mg, 0.192 mmol, 1 eq.). Purification by dry-loaded flash column chromatography (SiO_2, petrol/EtOAc, 1:1, *v/v*) afforded the *title compound* as a brown solid (57 mg, 80%).

R_f 0.39 (petrol/EtOAc, 1:1, *v/v*); $[\alpha]_D$ = +45.6 (*c* 0.10, $CHCl_3$); M.P. 202 °C dec.; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.19 (br s, 1H), 7.57 (dt, *J* = 8.0, 1.0, 1.0 Hz, 1H), 7.53–7.48 (m, 2H), 7.47–7.43 (m, 2H), 7.38–7.33 (m, 1H), 7.22 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.15 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 5.82 (d, *J* = 8.0 Hz, 1H), 4.84 (dt, *J* = 8.0, 5.5 Hz, 1H), 3.51 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.46 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.33 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.3, 169.7, 135.9, 134.8, 134.2, 131.7, 129.6, 129.5, 123.0, 120.4, 119.1, 111.2, 107.5, 53.0, 52.2, 26.9, 23.1; ESI–MS *m/z* (ion, %): 371 ($[M+H]^+$, 30), 393 ($[M+Na]^+$, 100); ESI–HRMS *m/z*: 371.1166 $[M+H]^+$ ($C_{20}H_{20}ClN_2O_3$ requires 371.1157).

Crystals suitable for X-ray diffraction were grown by slow diffusion from a solution of CH_2Cl_2.

The analytical data obtained was in accordance with the literature.[15]

Methyl (2*S*)-3-[2-(3-chlorophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3l)

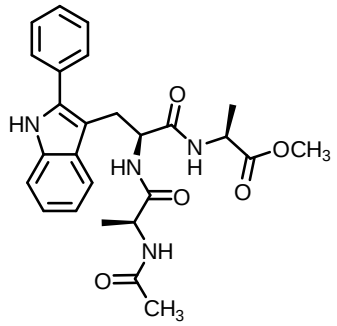


Method A: Synthesised using general procedure B with aryldiazonium salt **2l** (43 mg, 0.192 mmol, 1 eq.). Purification by dry-loaded flash column chromatography (SiO_2, petrol/EtOAc, 1:1, *v/v*) afforded the *title compound* as a brown solid (45 mg, 63%).

Method B: Synthesised using general procedure C with aryldiazonium salt **2l** (43 mg, 0.192 mmol, 1 eq.). Purification by dry-loaded flash column chromatography (SiO_2, petrol/EtOAc, 1:1, *v/v*) afforded the *title compound* as a brown solid (57 mg, 80%).

R_f 0.26 (petrol/EtOAc, 1:1, *v/v*); $[\alpha]_D$ = +54.4 (*c* 0.10, $CHCl_3$); M.P. 78–79 °C dec.; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.19 (br s, 1H), 7.61–7.54 (m, 2H), 7.47 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.45–7.39 (m, 1H), 7.36 (ddd, *J* = 7.5, 2.5, 1.5 Hz, 2H), 7.22 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.15 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 5.83 (d, *J* = 8.0 Hz, 1H), 4.85 (dt, *J* = 8.0, 5.5 Hz, 1H), 3.54 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.51 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.34 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, ($CDCl_3$, δ): 172.3, 169.7, 135.9, 135.2, 135.1, 134.5, 130.6, 129.5, 128.3, 128.2, 126.6, 123.2, 120.4, 119.3, 111.2, 107.9, 52.9, 52.2, 26.9, 23.1; ESI–MS *m/z* (ion, %): 371 ([M+H]$^+$, 90), 393 ([M+Na]$^+$, 100); ESI–HRMS *m/z*: 393.0963 [M+Na]$^+$ ($C_{20}H_{19}ClN_2NaO_3$ requires 393.0976); IR (solid-state, ATR, cm^{-1}): 3271 (w, br), 3059 (w), 2952 (w), 2852 (w), 1733 (m), 1651 (s), 1597 (m), 1520 (m), 1436 (m), 1372 (s), 1214 (s), 788 (s), 737 (s), 688 (m); UV–Vis (DMSO, nm): λ_{max} 312 (ε = 15639 mol dm^{-3} cm^{-1}).

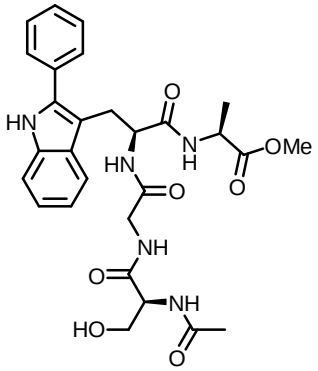
Ac-AlaTrpPhAla-OMe (5)



To a microwave tube was added peptide **4** (20 mg, 0.052 mmol, 1 eq.), benzenediazonium tetrafluoroborate **2a** (11 mg, 0.0572 mmol, 1.1 eq.), $Pd(OAc)_2$ (2.4 mg, 0.0104 mmol, 20 mol%) and MeOH (2 mL), which was stirred at RT for 24 h. The resulting brown reaction mixture was filtered through Celite with MeOH (5 mL) and the solvent removed under reduced pressure to give the product as a brown residue.

λ_{max} 300 nm, $[\alpha]_D$: +23.1 (*c* 0.0017, MeOH; $[\alpha]_D$ of peptide **4** = +20.3, *c* 0.005, MeOH), v_{max}/cm^{-1} (ATR) 3270.5, 3055.5, 2981.1, 2466.8, 2419.4, 2074.33, 1751.03, 1625.91, 1546.9, 1452.9, 1205.27, 973.5, 745.9, 698.0, 609.6, 489.6; ^{1}H NMR (500 MHz, CD_3OD, δ): 7.67 (d, *J* = 7.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.37-7.34 (m, 2H), 7.11 (app t, *J* = 7.5 Hz, 1H), 7.03 (app t, *J* = 7.5 Hz, 1H), 4.68 (app t, *J* = 7.5 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 1H), 3.54 (s, 3H), 3.48 (dd, *J* = 14.5, 7.5 Hz, 1H), 3.35 (3H, s), 1.89 (s, 3H), 1.22 (d, *J* = 7.5 Hz, 3H), 1.13 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, CD_3OD, δ) 174.5, 173.9, 173.6, 173.2, 137.7, 137.3, 134.5, 130.5, 129.9, 129.3, 128.6, 122.9, 120.2, 119.9, 112.0, 107.7, 55.4, 52.7, 50.9, 49.9, 28.3, 22.3, 17.7, 17.4; ESI–MS *m/z* (ion, %): $[(M+H)^+]$ 479.11, $[(M+Na)^+]$ 501.11; R_f = 0.44 (6% $MeOH/CH_2Cl_2$).

Ac-SerGlyTrpPhAla-OMe (7)

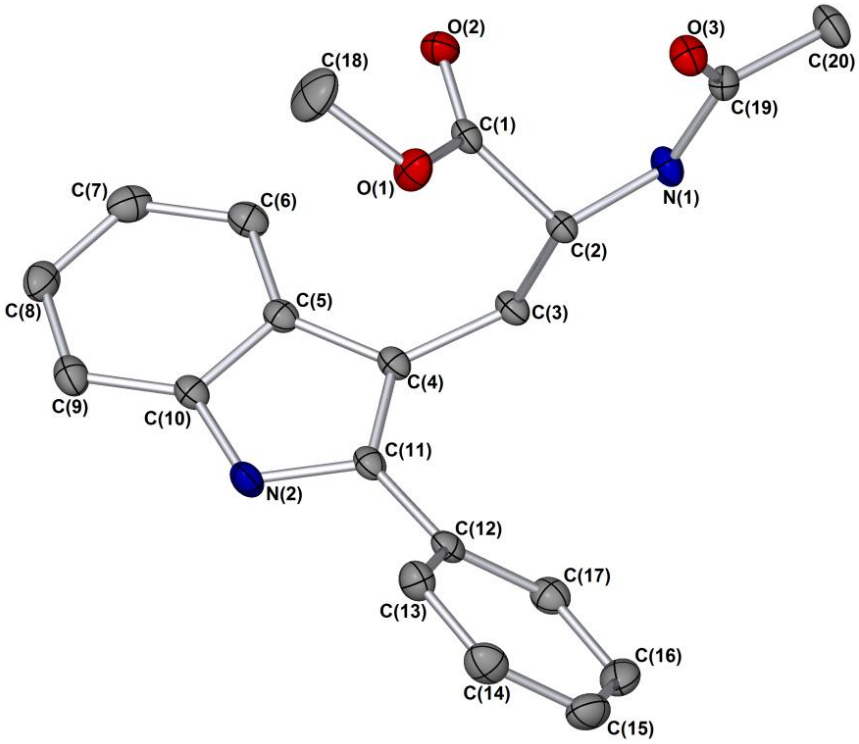


To a microwave tube was added peptide **6** (20 mg, 0.0433 mmol, 1 eq.), benzenediazonium tetrafluoroborate **2a** (9.2 mg, 0.0476 mmol, 1.1 eq.), $Pd(OAc)_2$ (2 mg, 0.0087 mmol, 20 mol%) and MeOH (2 mL), which was stirred at 37 °C for 8 h. The resulting brown reaction mixture was filtered through Celite with MeOH (5 mL) and the solvent removed under reduced pressure. This crude mixture was purified by preparative TLC (6% $MeOH/CH_2Cl_2$) to give an off white solid (10.8 mg, 45%).

λ_{max} 304 nm, $[\alpha]_D$: +33.1 (*c* 0.005, MeOH; $[\alpha]_D$ of peptide **6** = +28.5, *c* 0.005, MeOH), v_{max}/cm^{-1} (ATR) 3821.64, 1734.6, 1637.0, 1528.4, 1451.8, 1375.0, 1340.8, 1305.3, 1222.1, 1154.4, 1057.8, 745.0, 697.4; ^{1}H NMR (500 MHz, CD_3OD, δ): 7.70-7.67 (m, 2H), 7.64 (ddd, *J* = 8.0, 1.0, 1.0 Hz, 1H), 7.52-7.47 (m, 2H), 7.40-7.35 (m, 2H), 7.12 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.04 (8.0, 7.0, 1.0 Hz, 1H), 4.73 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.36 (t, *J* = 5.5 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 1H), 3.85-3.73 (m, 3H), 3.66 (d, *J* = 16.5 Hz, 1H), 3.54 (s, 3H), 3.51 (dd, *J* = 14.5, 8.0 Hz, 1H), 3.28 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.03 (s, 3H), 1.24 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, CD_3OD, δ): 173.9, 173.7, 173.4, 173.0, 171.0, 137.7, 137.2, 134.7, 130.5, 129.9, 129.4, 128.5, 122.8, 120.1, 119.8, 112.0, 107.9, 62.9, 57.1, 55.8, 52.7, 48.5, 43.7, 28.7, 22.6, 17.7; ESI–MS *m/z* (ion, %): $[(M+H)^+]$ 522.2476, $[(M+Na)^+]$ 574.2289; R_f = 0.13 (6% $MeOH/CH_2Cl_2$).

4. X-Ray Crystallographic Data

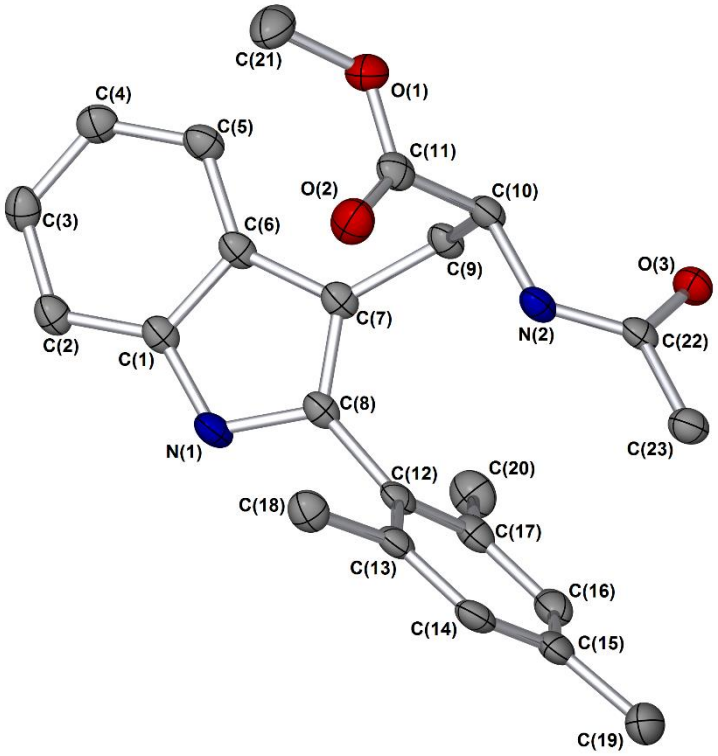
Methyl (2*S*)-2-acetamido-3-(2-phenyl-1*H*-indol-3-yl) propanoate (3a)



Compound reference	ijsf1413
Chemical formula	$C_{20}H_{20}N_2O_3$
Formula mass	336.38
Crystal system	Trigonal
a / Å	21.2602(5)
b / Å	21.2602(5)
c / Å	10.1814(3)
α / º	90
β / º	90
γ / º	120
Unit cell volume / Å^3	3985.4(2)
Temperature / K	110.05(10)
Space group	R3
No. of formula units per unit cell, Z	9
No. of reflections measured	6369
No. of independent reflections	4199
R_{int}	0.0191
Final R_1 values (I > 2σ(I))	0.0363
Final wR(F^2) values (I > 2σ(I))	0.0863
Final R_1 values (all data)	0.0404
Final wR(F^2) values (all data)	0.0901

CCDC number: 1053549 (compound 3a)

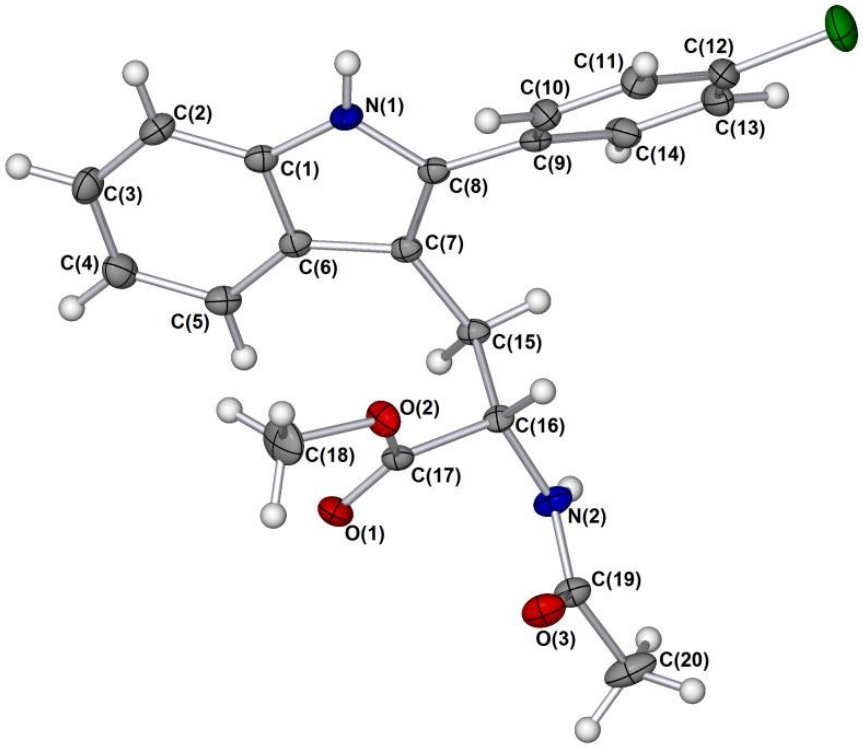
Methyl (2*S*)-2-acetamido-3-[2-(2,4,6-trimethylphenyl)-1*H*-indol-3-yl]propanoate (3e)



Compound reference	ijsf1488
Chemical formula	$C_{23}H_{26}N_2O_3$
Formula mass	378.46
Crystal system	Monoclinic
a / Å	8.7152(3)
b / Å	13.5902(4)
c / Å	8.7625(3)
α / º	90
β / º	100.507(3)
γ / º	90
Unit cell volume / Å^3	1020.44(6)
Temperature / K	110.05(10)
Space group	$P2_1$
No. of formula units per unit cell, Z	2
No. of reflections measured	6691
No. of independent reflections	3634
R_{int}	0.0256
Final R_1 values (I > 2σ(I))	0.0334
Final wR(F^2) values (I > 2σ(I))	0.0865
Final R_1 values (all data)	0.0350
Final wR(F^2) values (all data)	0.0882

CCDC number: 1053551 (compound 3e)

Methyl (2*S*)-3-[2-(4-chlorophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3k)



Compound reference	ijsf1487
Chemical formula	$C_{20}H_{19}ClN_2O_3$
Formula mass	370.82
Crystal system	Trigonal
a / Å	20.7806(2)
b / Å	20.7806(2)
c / Å	11.18107(13)
α / º	90
β / º	90
γ / º	120
Unit cell volume / Å^3	4181.48(10)
Temperature / K	110.05(10)
Space group	R3
No. of formula units per unit cell, Z	9
No. of reflections measured	19066
No. of independent reflections	3300
R_{int}	0.0214
Final R_1 values (I > 2σ(I))	0.0217
Final wR(F^2) values (I > 2σ(I))	0.0550
Final R_1 values (all data)	0.0219
Final wR(F^2) values (all data)	0.0552

CCDC number: 1053550 (compound 3k)

5. Green Metrics Data

All metrics were calculated using the Chem21 unified green metrics toolkit.[16]

In addition to the reagent quantities stated in the experimental section in this publication and our previous publications,[13] the following values for workup reagents/solvents were used in all cases:

Ethyl acetate: 10 mL

Celite: 10 g

Sat. aq. $NaHCO_3$: 10 mL

$MgSO_4$: 5 g

Where purification by column chromatography was performed (Conditions A–C), the following additional values were used:

Ethyl acetate: 115 mL

Petroleum ether (40–60): 125 mL

Silica gel: 25 g

Conditions	**A**	**B**	**C**	**D**
Reagents[a]	$PhI(OAc)_2$ / $PhB(OH)_2$	$PhB(OH)_2$ with Cu^{II}	[PhMesI]OTf	$[PhN_2]BF_4$
Yield / %	56	93	85	100
Temp. / °C	40	40	25	RT (*ca.* 20)
Solvent	AcOH	AcOH	EtOAc	EtOAc
AE	48	88	46	74
RME	16	62	24	74
OE	33	70	52	100
MI: Total	6902	4139	4504	602
MI: Reaction	152	89	86	71
MI: Reaction chemicals	6	2	4	1
MI: Reaction solvents	146	87	82	70
MI: Workup	6750	4050	4418	531
MI: Workup chemicals	1389	833	909	391
MI: Workup solvents	5361	3217	3509	140

[a] **Conditions D** (current work) compared with previously reported reaction conditions (**A**-**C**) – see Introduction section of paper.

6. Kinetic Curves Using UV–Visible Spectroscopic Data

General procedure for kinetic measurements with $Pd(OAc)_2$

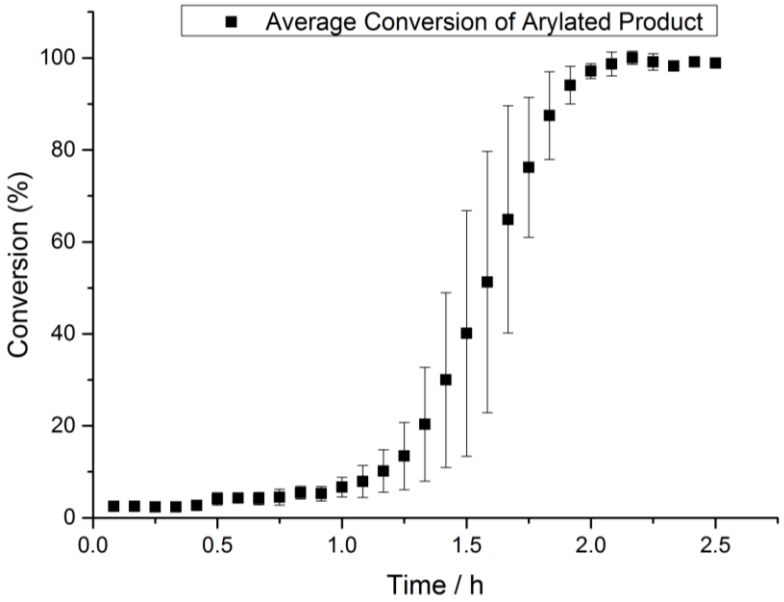
To a microwave tube was added tryptophan **1** (50 mg, 0.192 mmol, 1 eq.), aryldiazonium salt **2a** (37 mg, 0.192 mmol, 1 eq.), $Pd(OAc)_2$ (2 mg, 9.6 µmol, 5 mol%) and EtOAc (5 mL). The reaction mixture was stirred at 37 °C, with aliquots of 100 µL taken every 5 min. The stirring was stopped for 10–15 s before each aliquot was taken. The aliquots were prepared for UV–visible spectroscopy by filtration through a Celite plug and dilution to 100 mL in EtOAc (1000-fold dilution). A UV–visible spectrum was then recorded, scanning between 400–256 nm. After the reaction had reached completion (or ceased as a result of catalyst poisoning), the resulting brown reaction mixture was filtered through Celite then washed with sat. aq. $NaHCO_3$. The organic layer was collected and dried over $MgSO_4$, filtered and evaporated to give a brown solid. ^1H NMR spectroscopic analysis of the crude material confirmed product conversion (**3**).

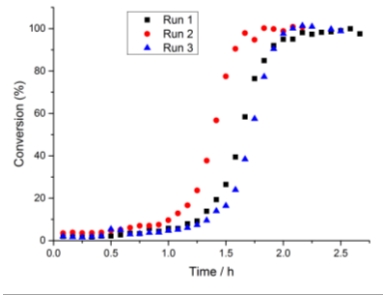
Catalyst poisoning tests

The general procedure above was followed, with addition of either PVPy (202 mg, 1.92 mmol, 10 eq., 200 eq. wrt Pd) or Hg (28 µL, 385 mg, 1.92 mmol, 10 eq., 200 eq. wrt Pd) to the reaction after 90 min. Alternatively, the reaction mixture was filtered through a pre-heated (*ca*. 37 °C) Celite™ plug after 90 min then recharged to a microwave vial and reaction continued.

Analysis of errors in kinetic measurements

The reaction between tryptophan **1** and aryldiazonium salt **2a** was performed three times to evaluate the errors associated with each measurement. This indicated that the key source of error was irregularity in the length of the induction period (subsequently confirmed to be due to water – see studies by *in situ* IR in the main paper), which resulted in the data spread of k_{obs} seen in the figure below.



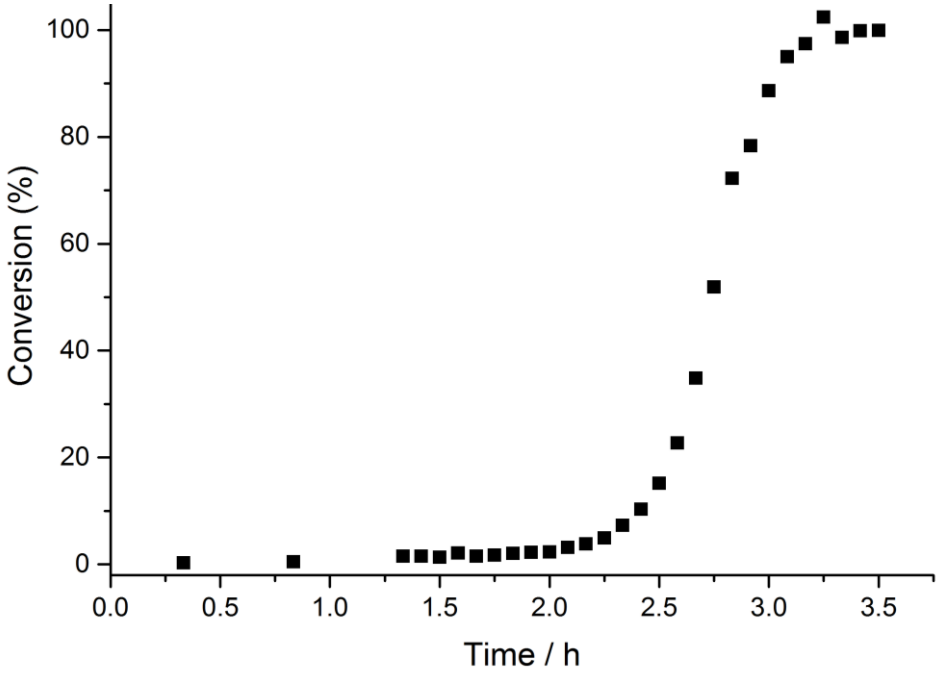


k_{obs} / 10^{-5} mol dm^{-3} s^{-1}	k_{obs} / 10^{-5} mol dm^{-3} s^{-1}	k_{obs} / 10^{-5} mol dm^{-3} s^{-1}
1.86	2.13	2.15

The figure above shows the errors between three different runs, with associated k_{obs} values.

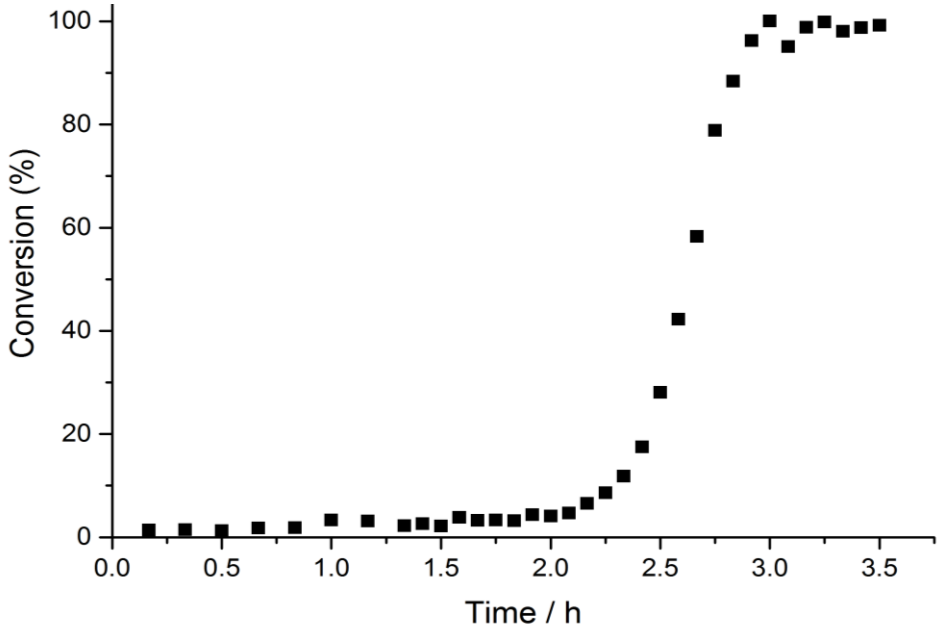
Removal of tryptophan 1 for duration of induction period

To a microwave tube was added aryldiazonium salt **2a** (37 mg, 0.192 mmol, 1 eq.), $Pd(OAc)_2$ (2 mg, 9.6 µmol, 5 mol%) and EtOAc (5 mL). The reaction was then stirred for 100 min, before addition of tryptophan **1** (50 mg, 0.192 mmol, 1 eq.). The reaction was monitored by UV-vis spectroscopic analysis as described in the general procedure.



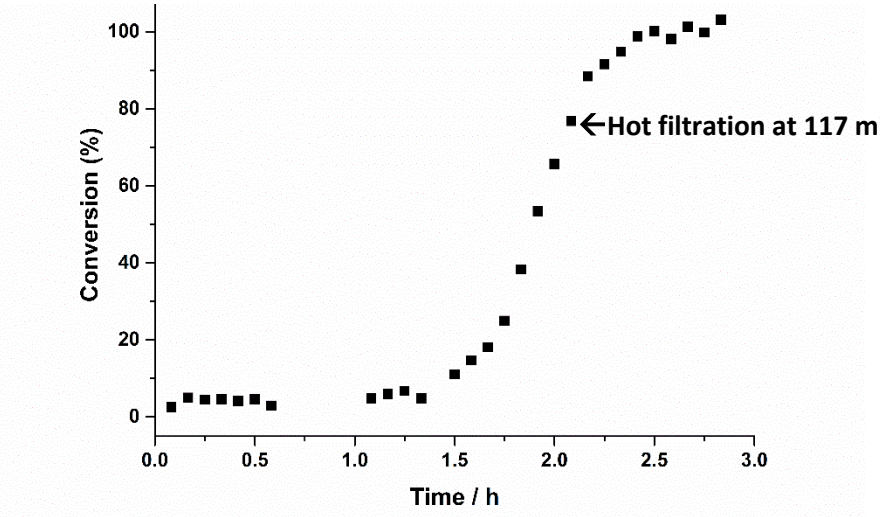
Removal of aryldiazonium 2a for duration of induction period

To a microwave tube was added tryptophan **1** (50 mg, 0.192 mmol, 1 eq.), $Pd(OAc)_2$ (2 mg, 9.6 µmol, 5 mol%) and EtOAc (5 mL). The reaction was then stirred for 100 min, before addition of aryldiazonium salt **2a** (37 mg, 0.192 mmol, 1 eq.). The reaction was monitored by UV-vis spectroscopic analysis as described in the general procedure.



Results of the hot filtration experiment

The general procedure was followed using tryptophan (50 mg, 0.192 mmol, 1 eq.), $[PhN_2]BF_4$ (37 mg, 0.192 mmol, 1 eq.), $Pd(OAc)_2$ (2 mg, 0.0096 mmol, 5 mol%) and EtOAc (5 ml). The reaction mixture was filtered through a pre-heated Celite plug after 117 mins.



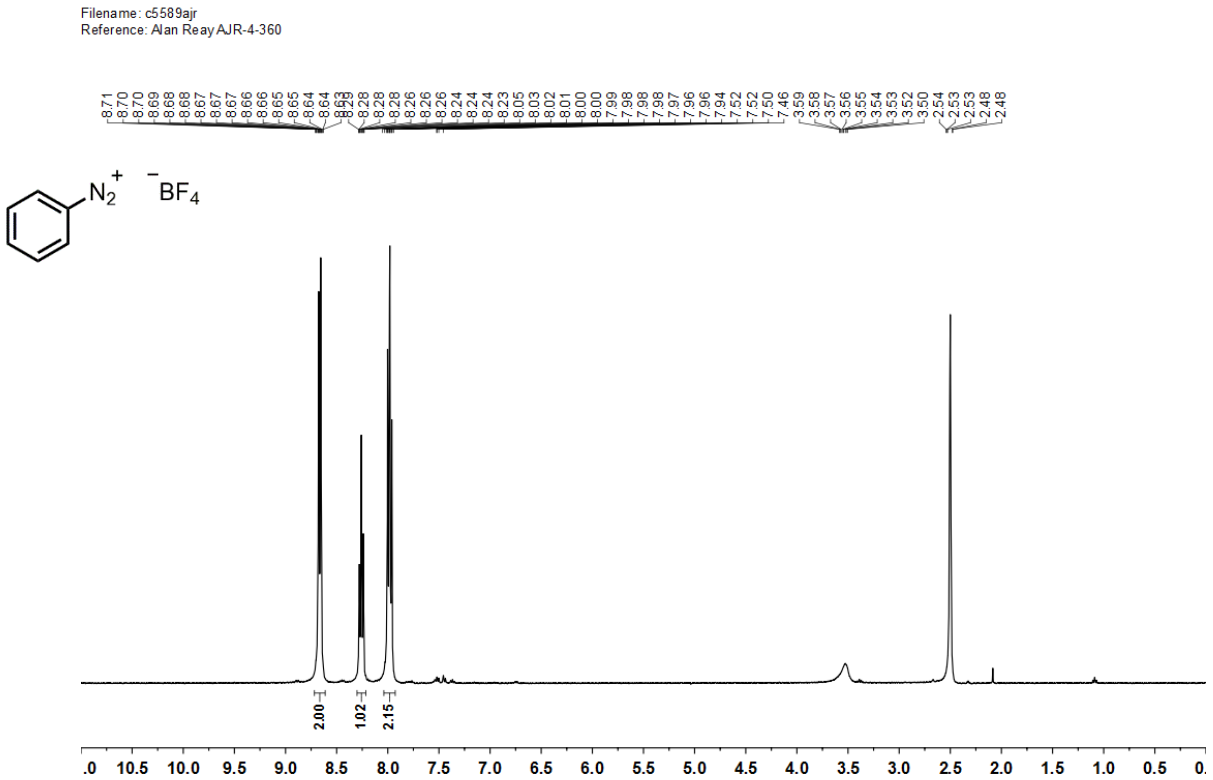
Procedure for the additional tosic acid (5 mol%) experiment

The general procedure was followed using tryptophan (50 mg, 0.192 mmol, 1 eq.), $[PhN_2]BF_4$ (37 mg, 0.192 mmol, 1 eq.), $Pd(OAc)_2$ (2 mg, 0.0096 mmol, 5 mol%), tosic acid (1.7 mg, 0.0096 mmol, 5 mol%) and EtOAc (5 ml). The reaction was monitored by UV-vis spectroscopic analysis as described in the general procedure.

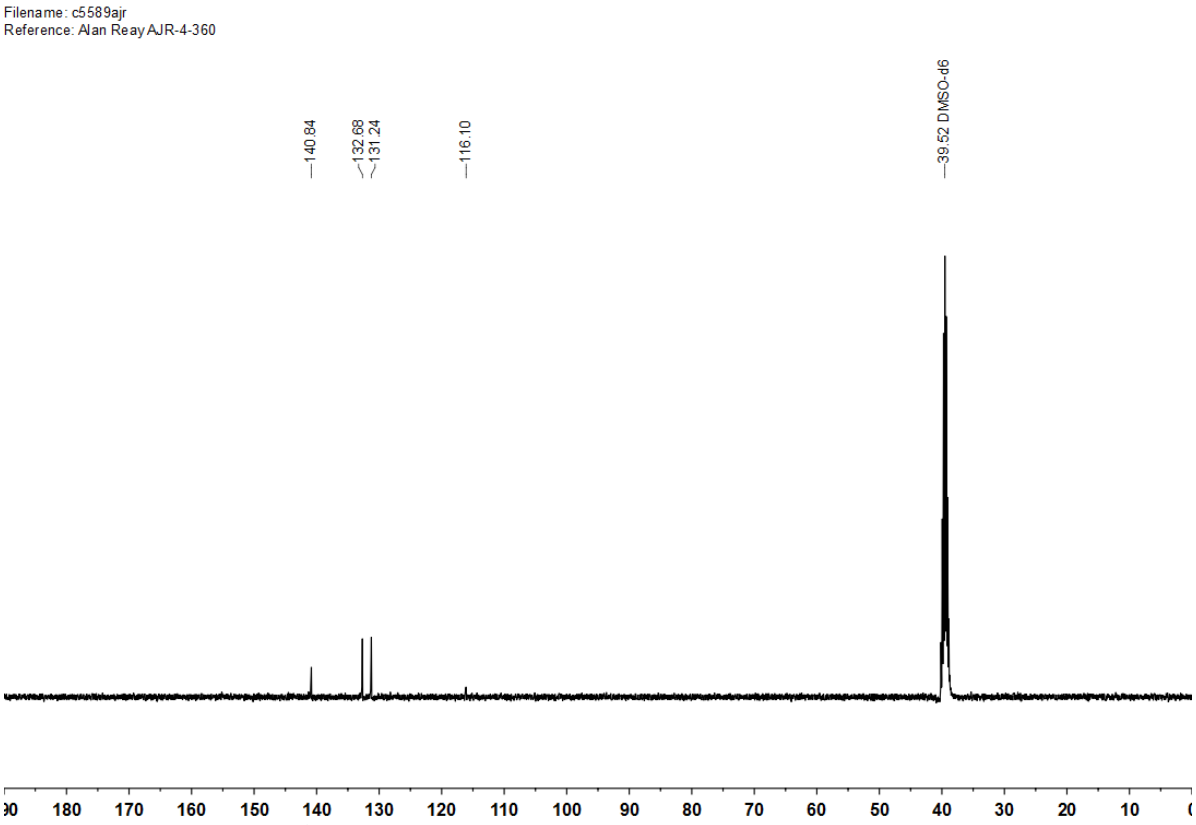
Kinetic studies employing $Pd(OTs)_2(CH_3CN)_2$ simply involved substituting the $Pd(OAc)_2$ within the general procedure.

7. Representative NMR Spectroscopic Data

Benzenediazonium tetrafluoroborate (2a)

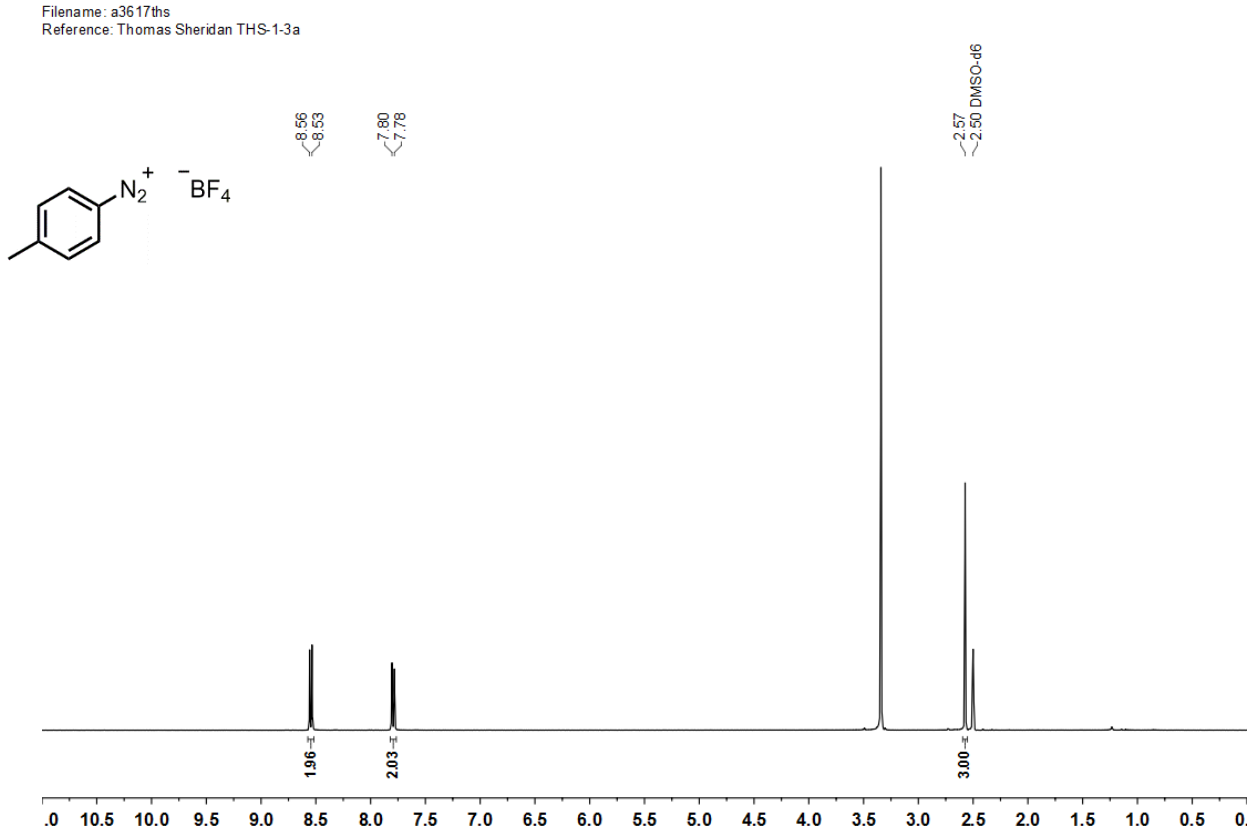


^{1}H NMR spectrum of **2a** (400 MHz, $(CD_3)_2SO$).

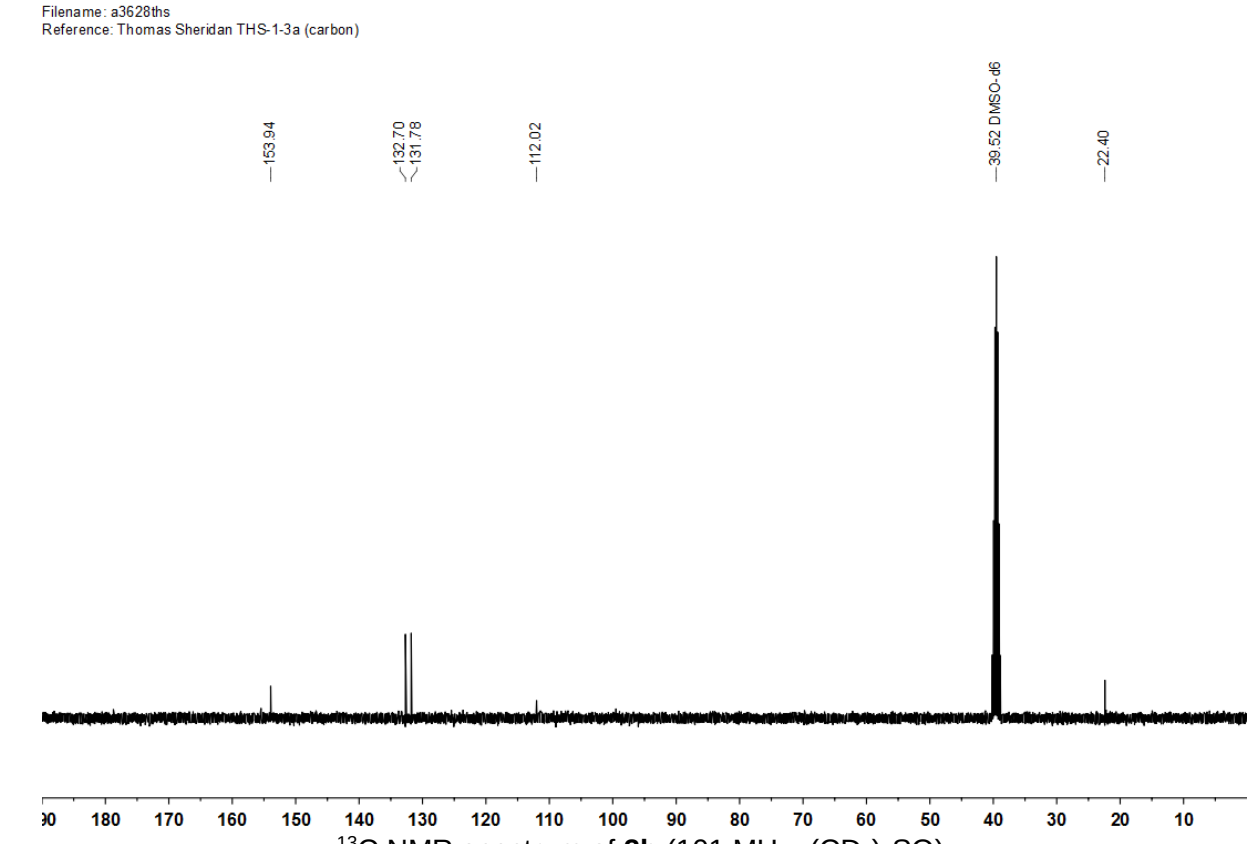


^{13}C NMR spectrum of **2a** (101 MHz, $(CD_3)_2SO$).

4-Methylbenzene-1-diazonium tetrafluoroborate (2b)

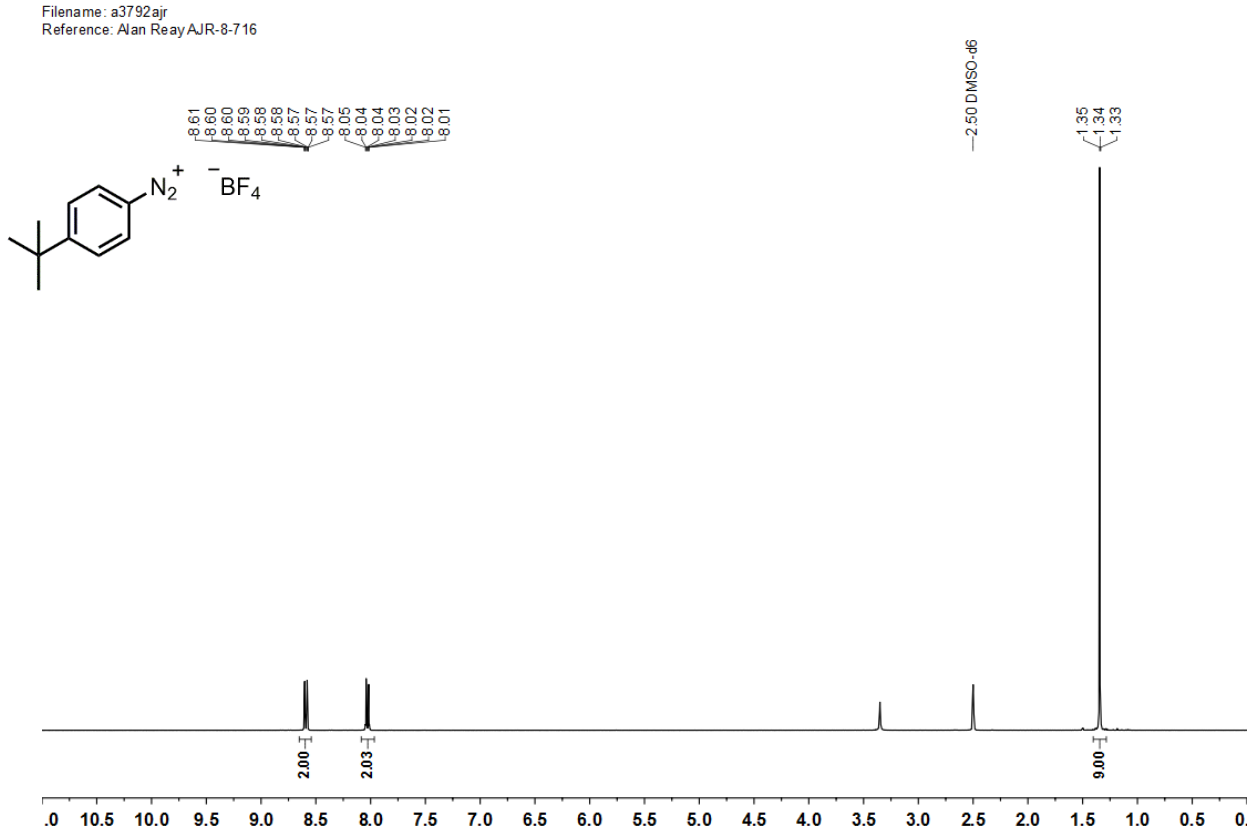


^{1}H NMR spectrum of **2b** (400 MHz, $(CD_3)_2SO$).

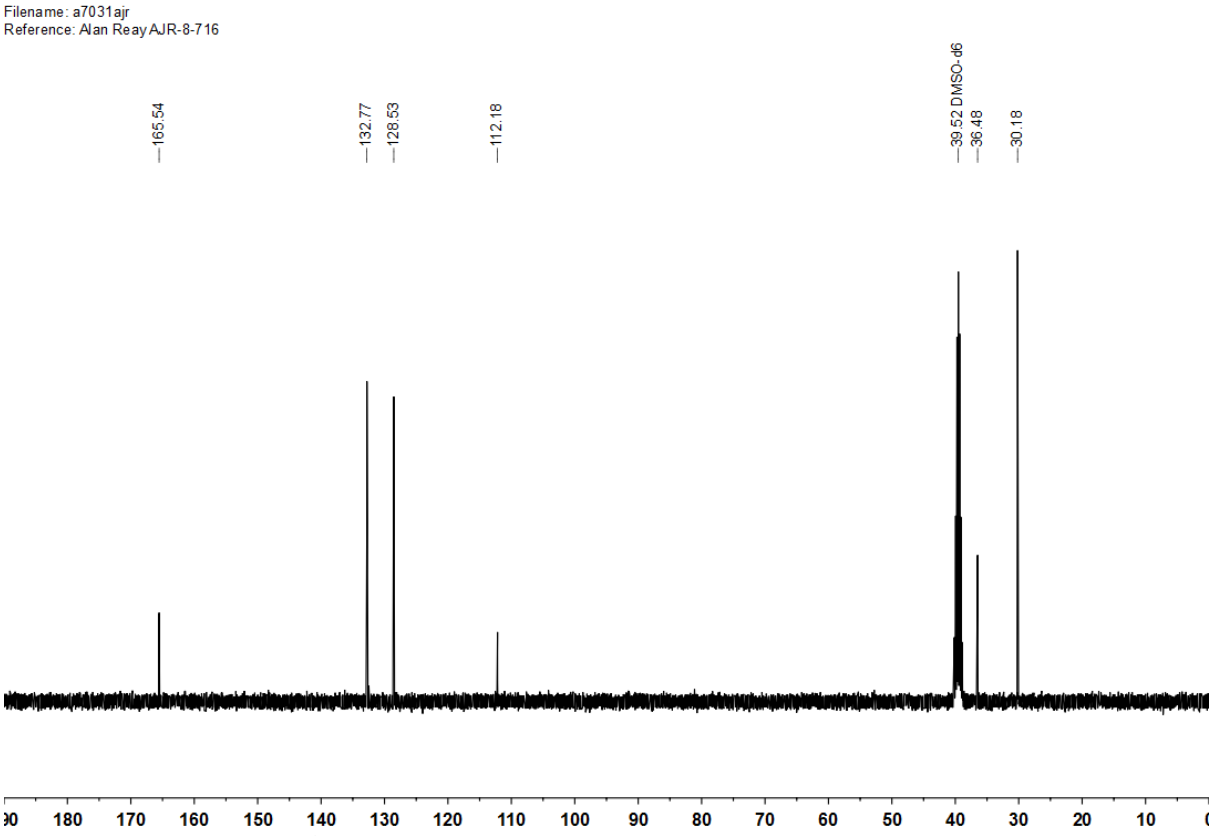


^{13}C NMR spectrum of **2b** (101 MHz, $(CD_3)_2SO$).

4-*tert*-butylbenzene-1-diazonium tetrafluoroborate (2c)

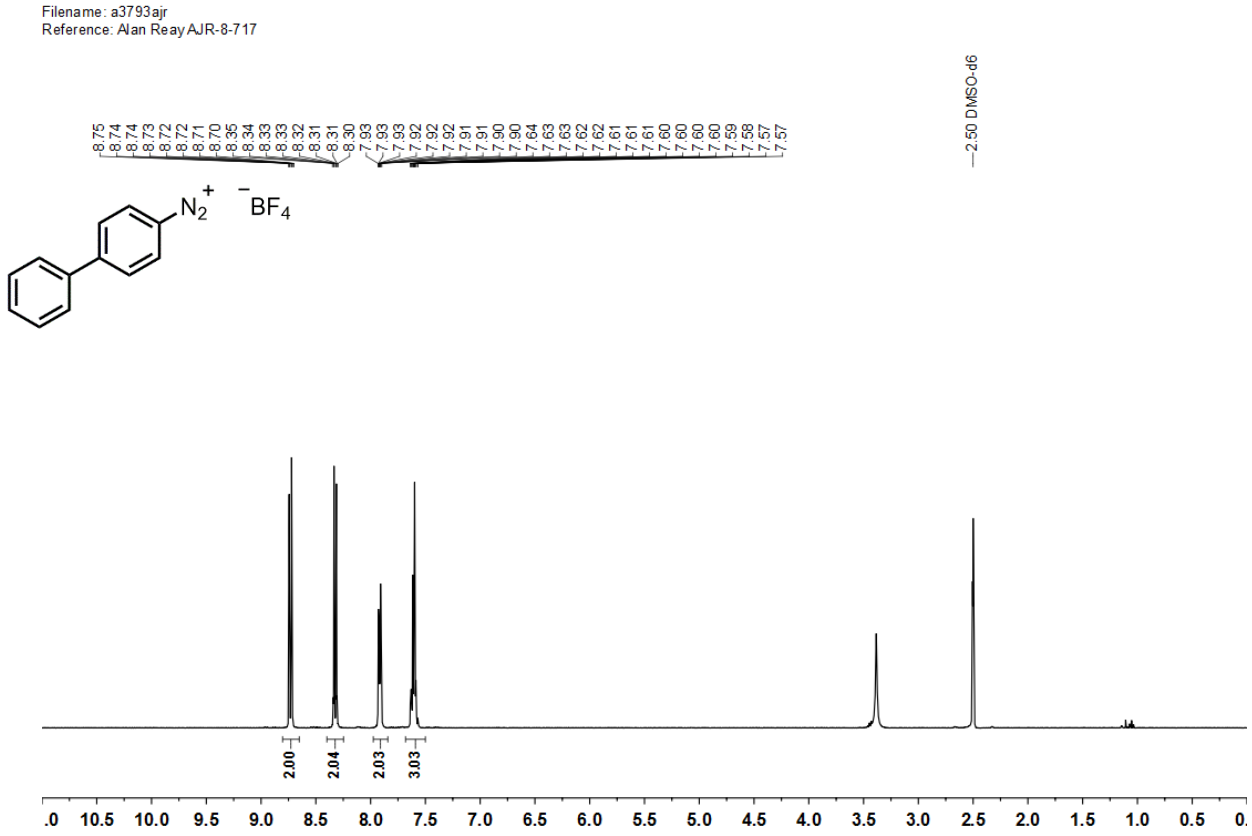


^{1}H NMR spectrum of **2c** (400 MHz, $(CD_3)_2SO$).

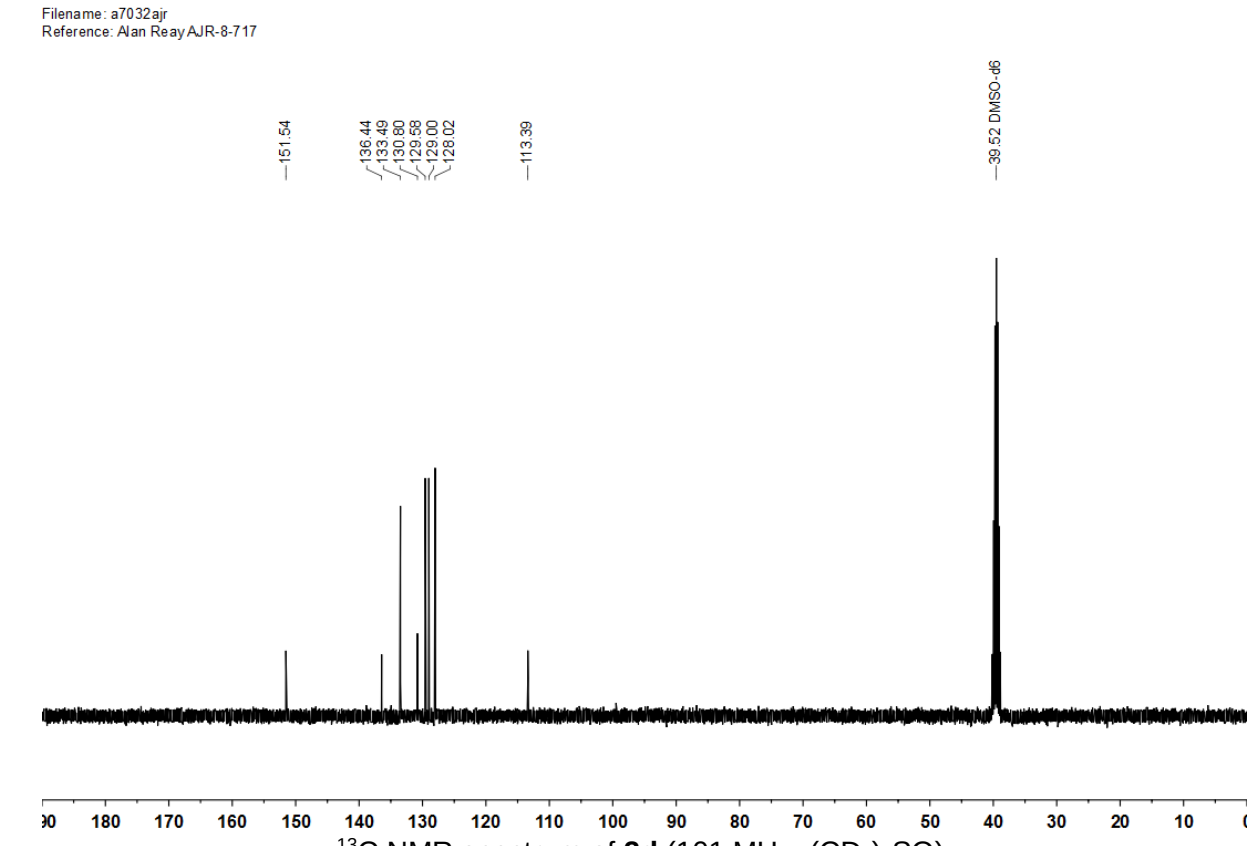


^{13}C NMR spectrum of **2c** (101 MHz, $(CD_3)_2SO$).

4-Phenylbenzene-1-diazonium tetrafluoroborate (2d)

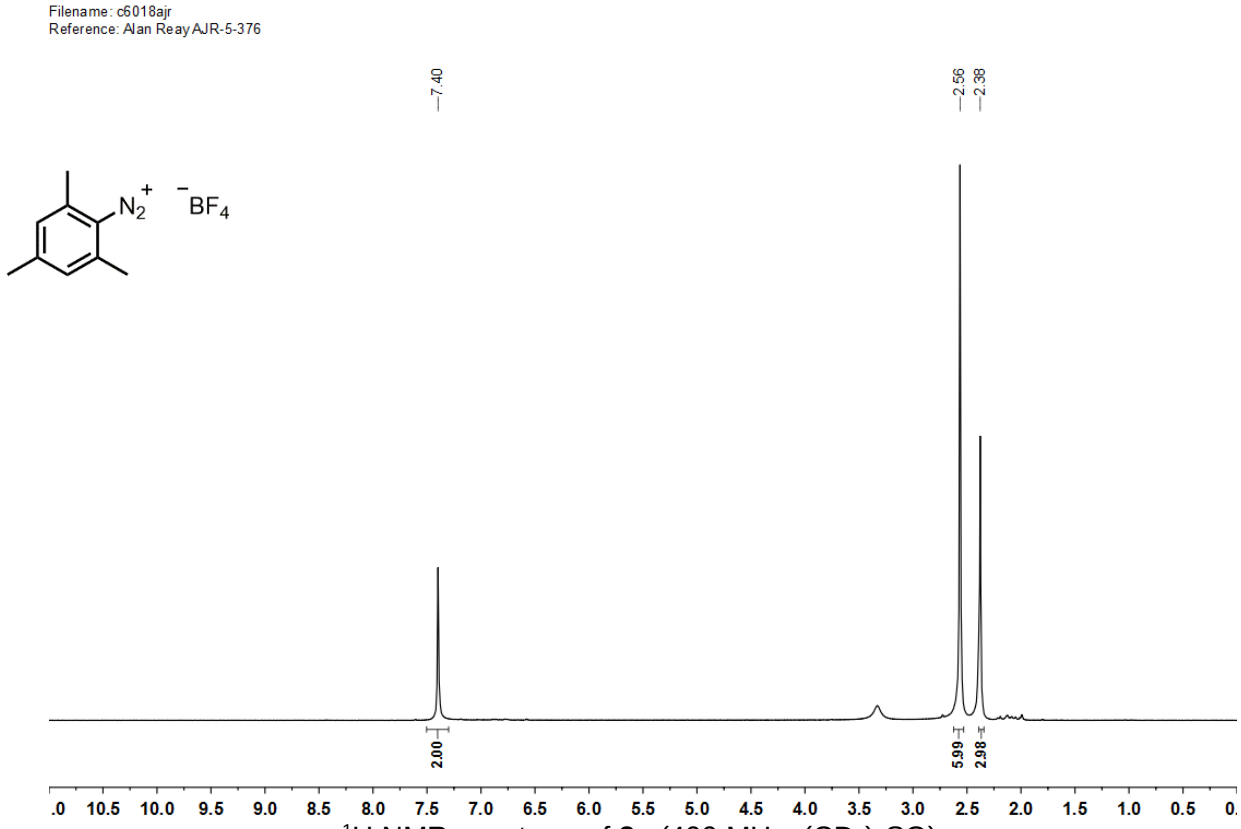


^{1}H NMR spectrum of **2d** (400 MHz, $(CD_3)_2SO$).

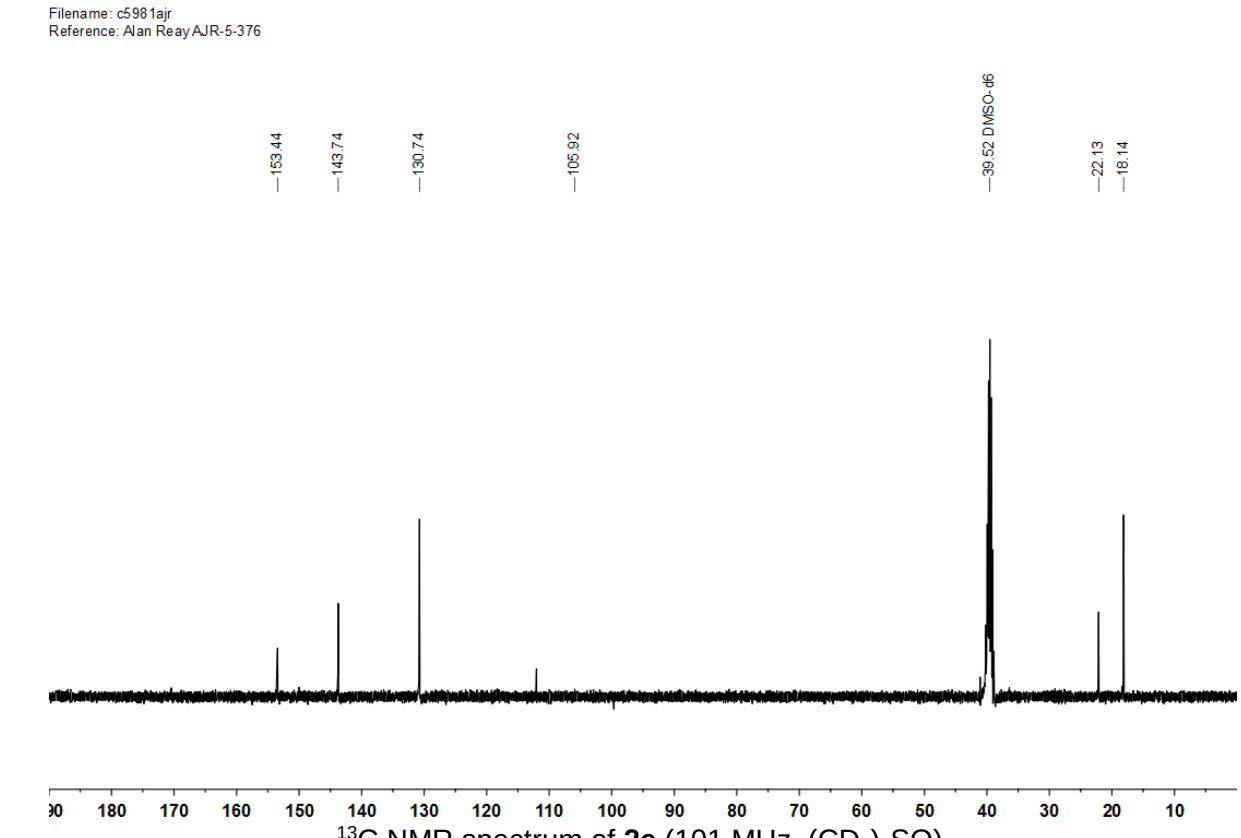


^{13}C NMR spectrum of **2d** (101 MHz, $(CD_3)_2SO$).

2,4,6-Trimethylbenzene-1-diazonium tetrafluoroborate (2e)

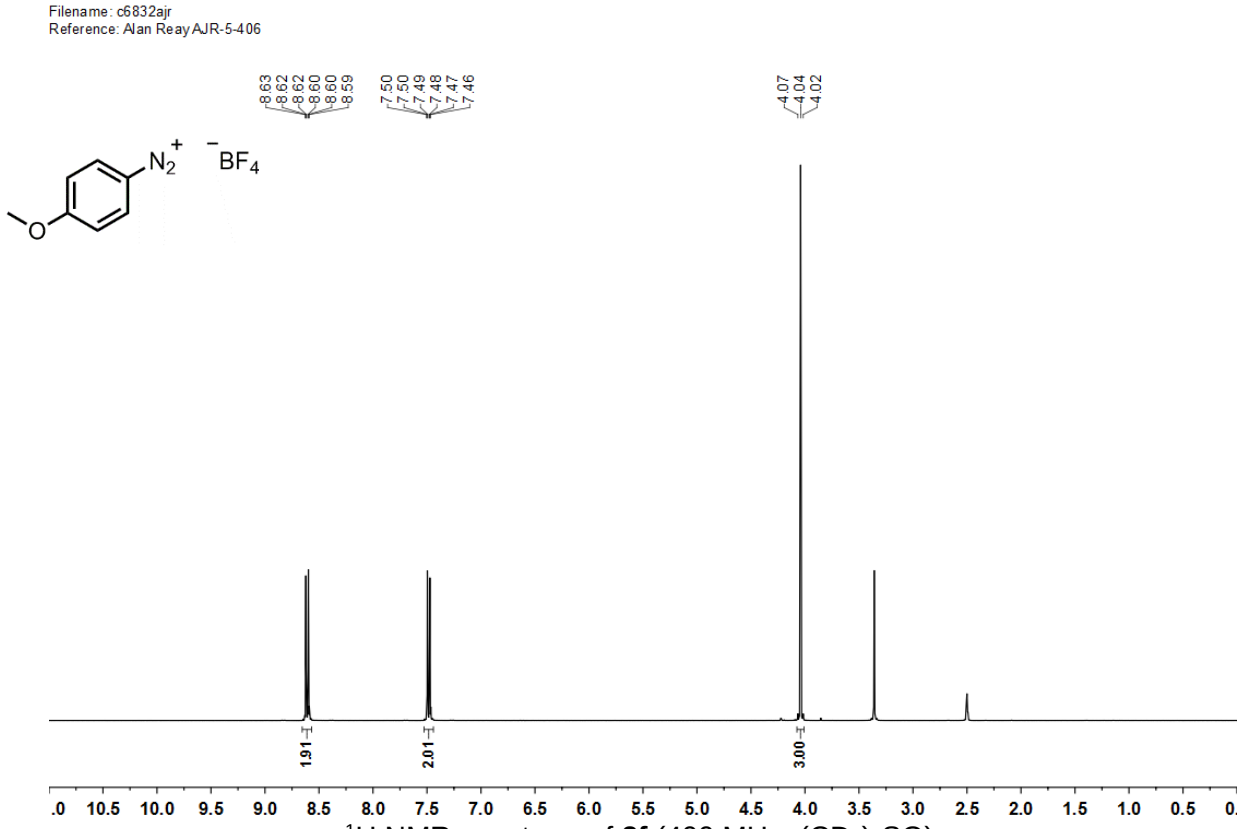


^{1}H NMR spectrum of **2e** (400 MHz, $(CD_3)_2SO$).

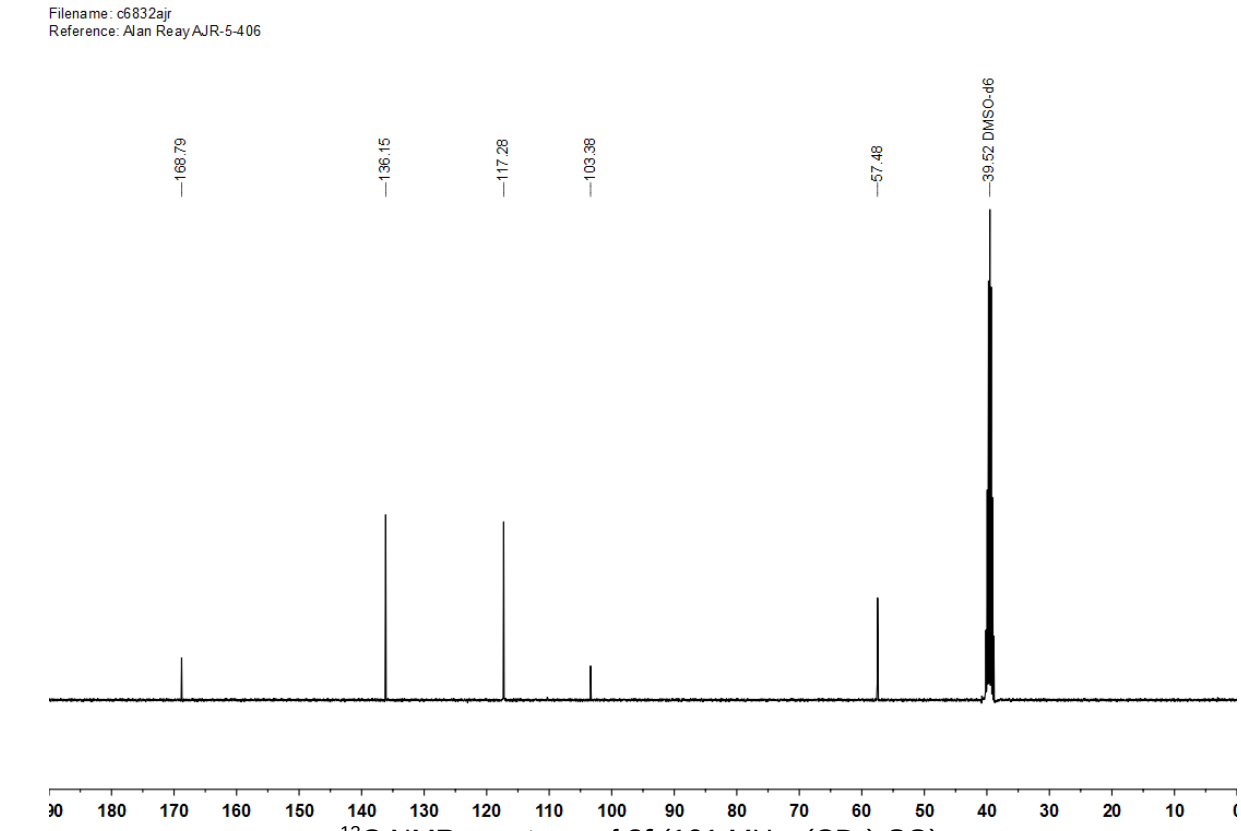


^{13}C NMR spectrum of **2e** (101 MHz, $(CD_3)_2SO$).

4-Methoxybenzene-1-diazonium tetrafluoroborate (2f)

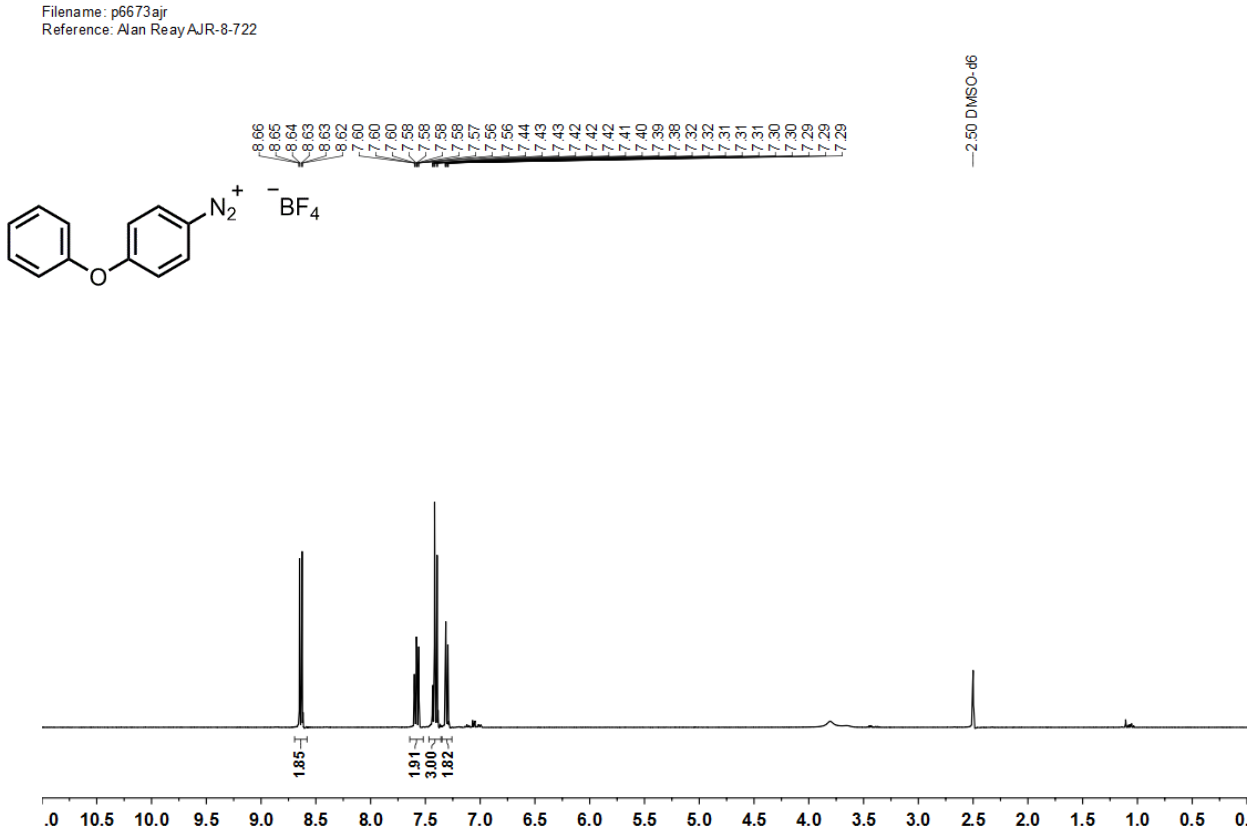


^{1}H NMR spectrum of **2f** (400 MHz, $(CD_3)_2SO$).

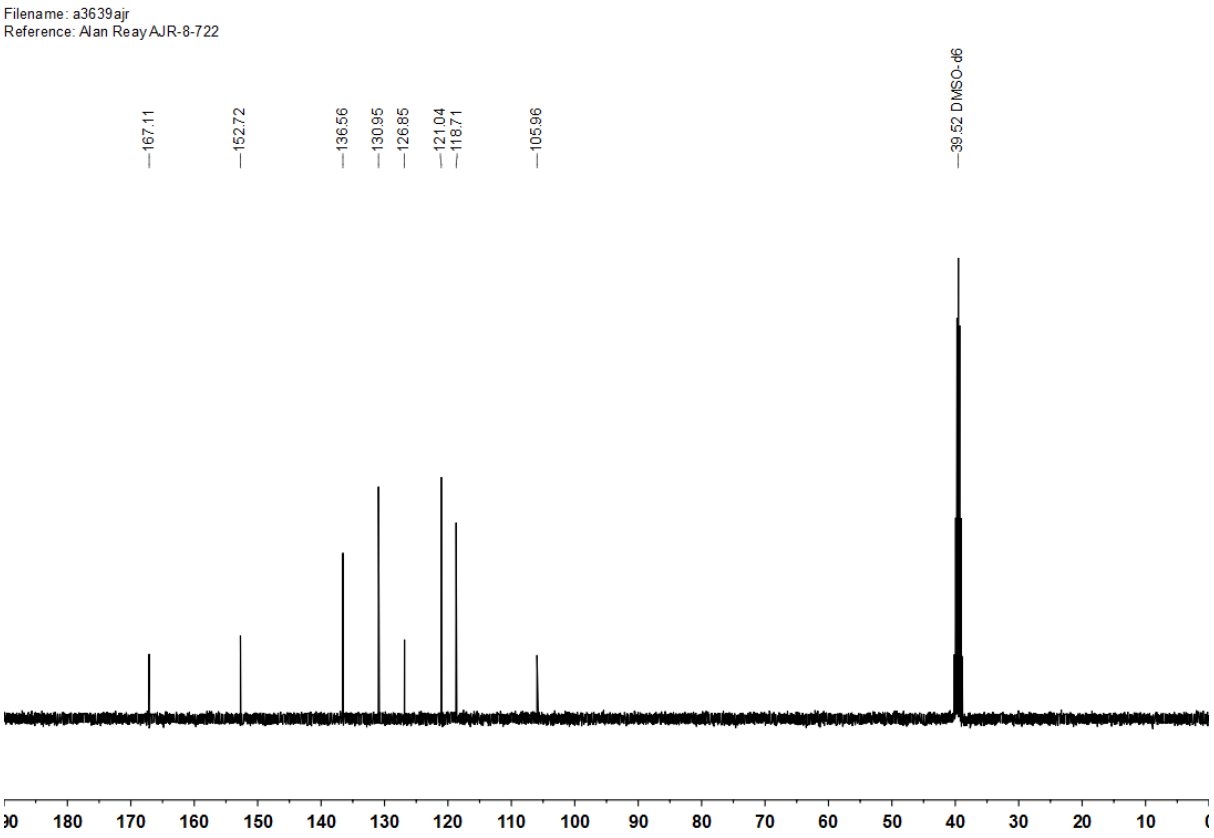


^{13}C NMR spectrum of **2f** (101 MHz, $(CD_3)_2SO$).

4-Phenoxybenzene-1-diazonium tetrafluoroborate (2g)

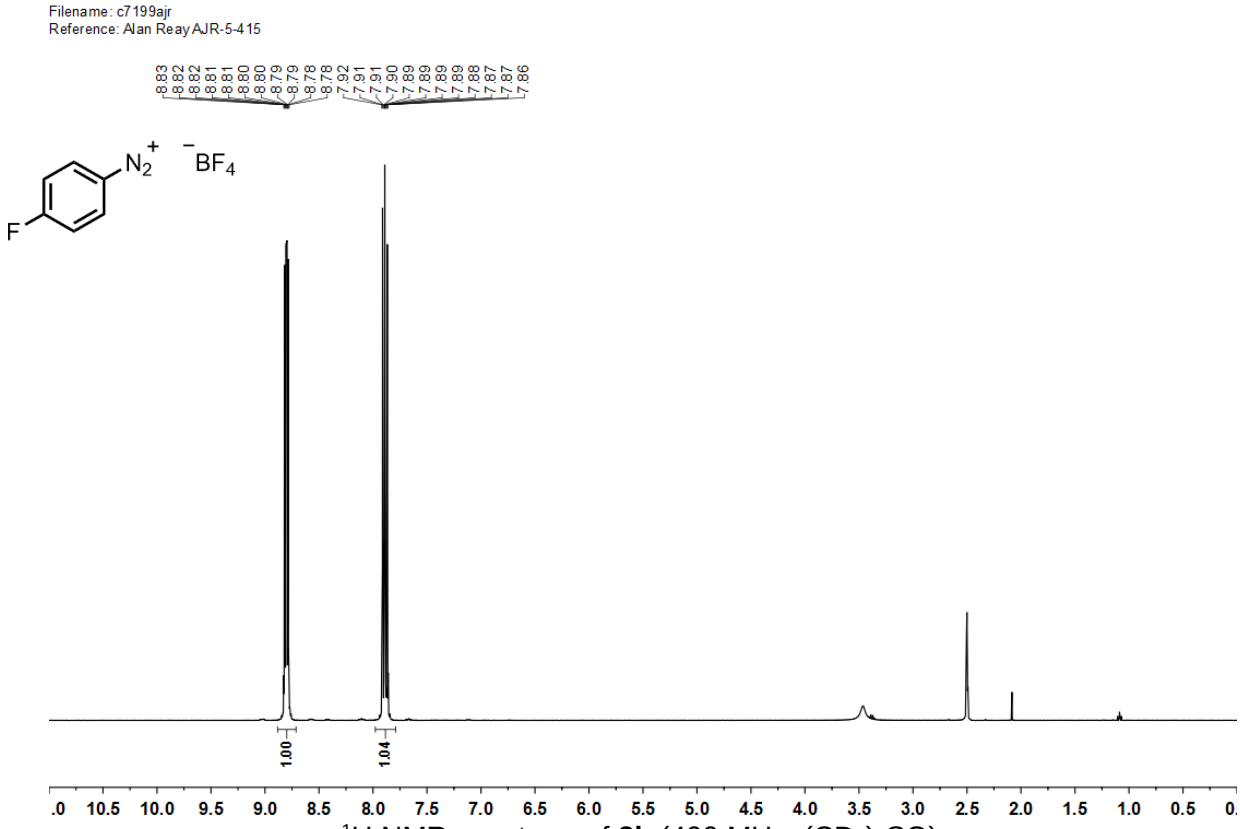


^{1}H NMR spectrum of **2g** (400 MHz, $(CD_3)_2SO$).

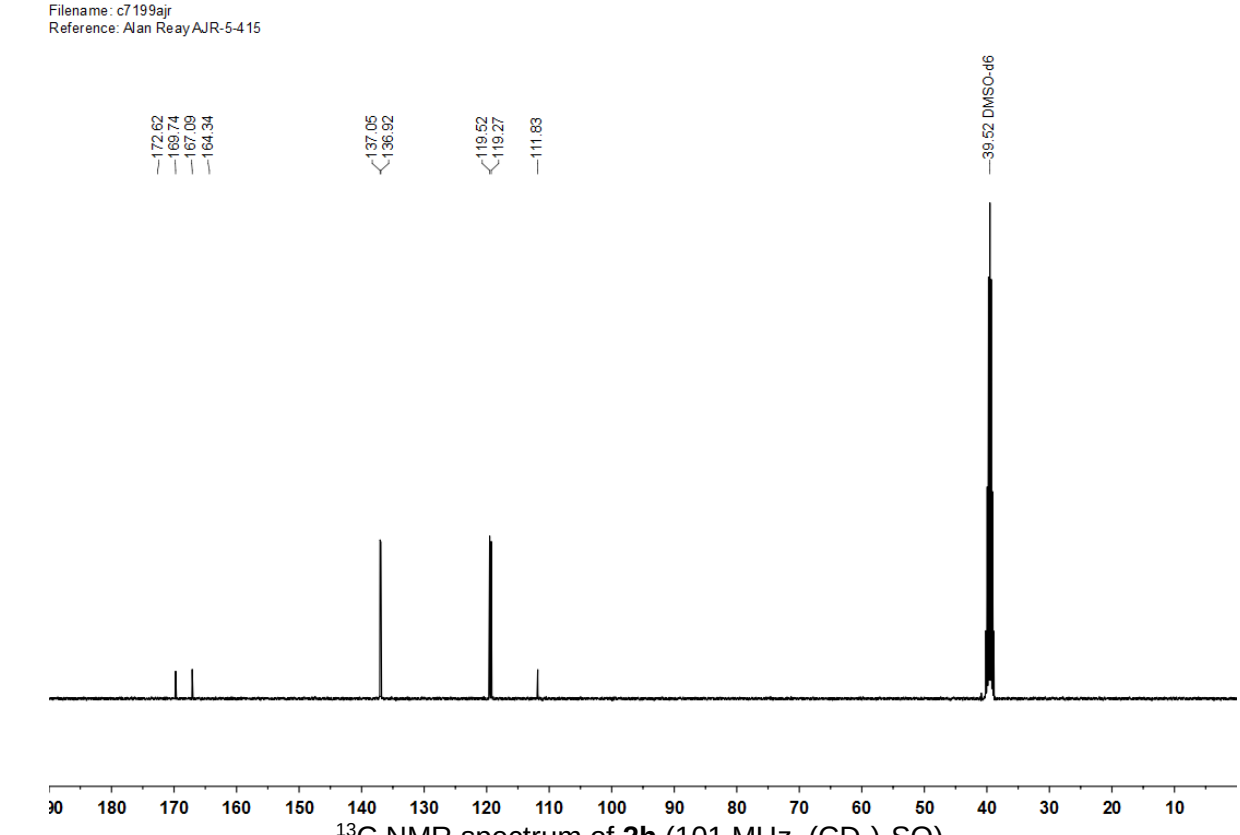


^{13}C NMR spectrum of **2g** (101 MHz, $(CD_3)_2SO$).

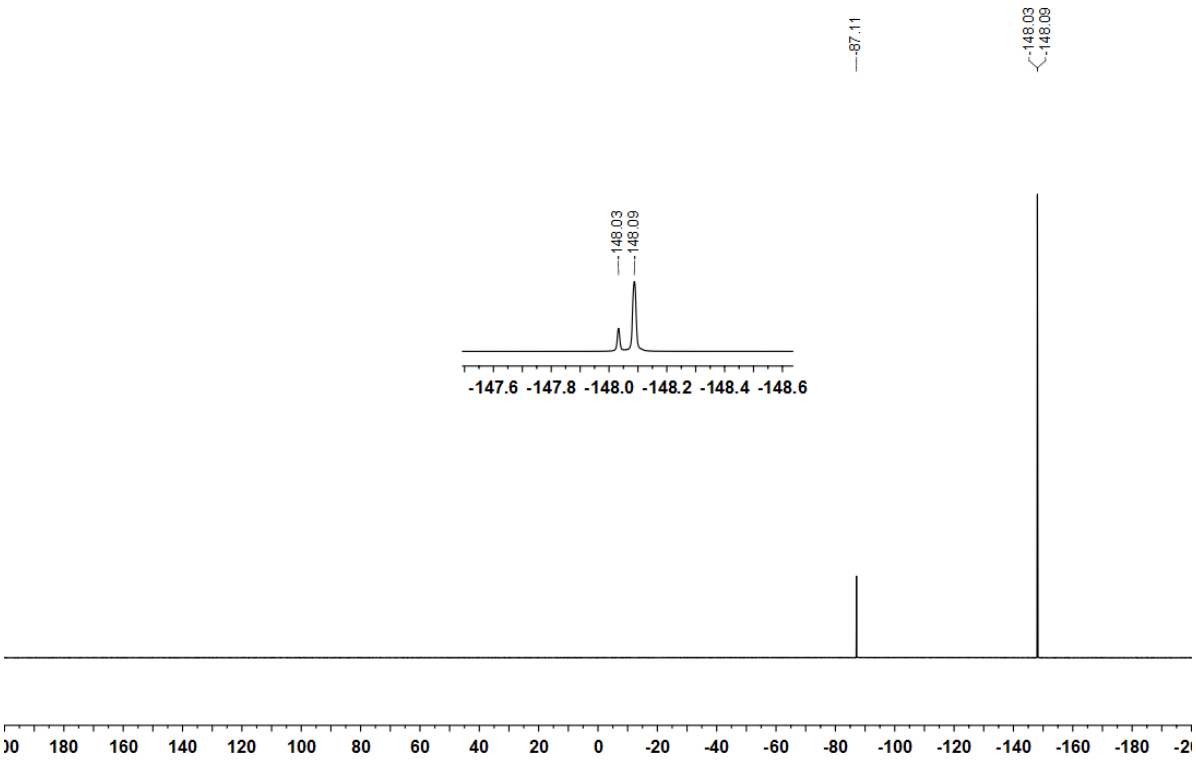
4-Fluorobenzene-1-diazonium tetrafluoroborate (2h)



^{1}H NMR spectrum of **2h** (400 MHz, $(CD_3)_2SO$).

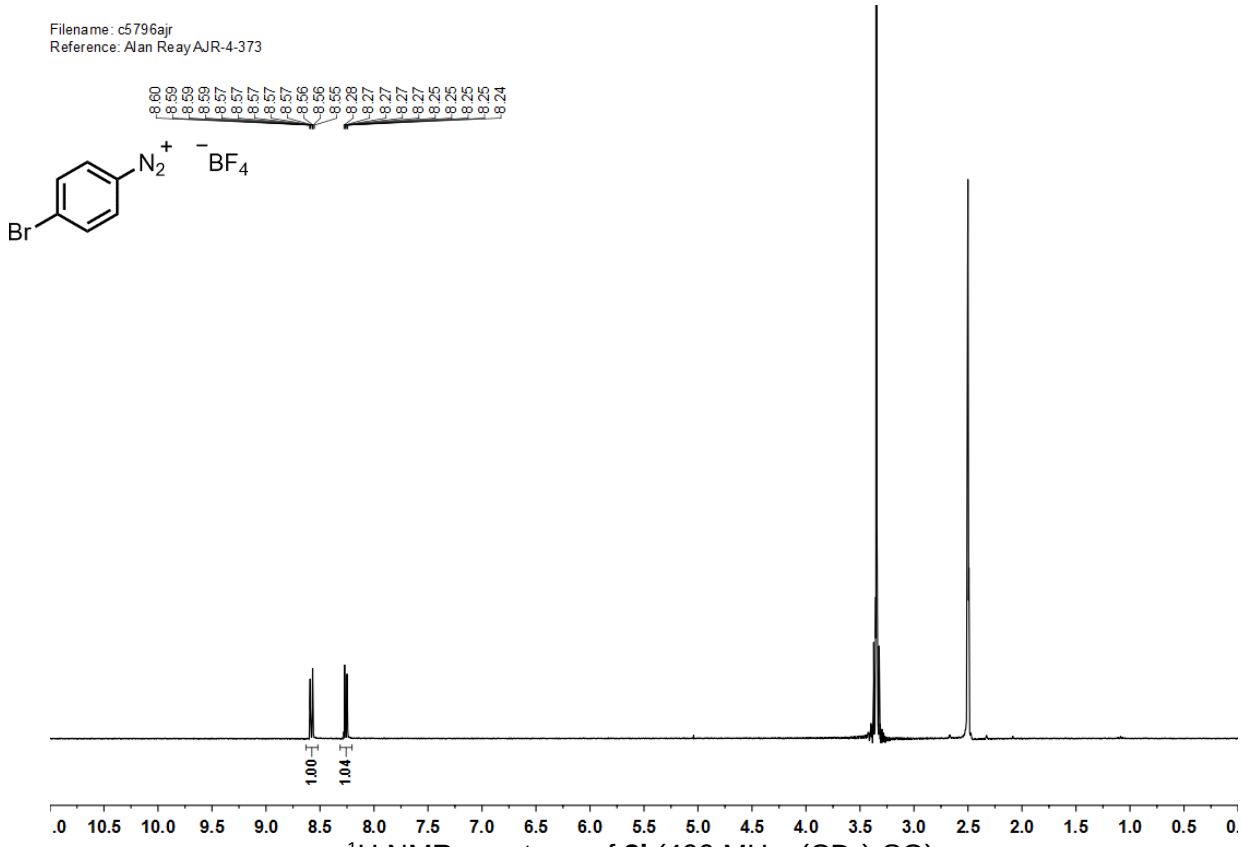


^{13}C NMR spectrum of **2h** (101 MHz, $(CD_3)_2SO$).

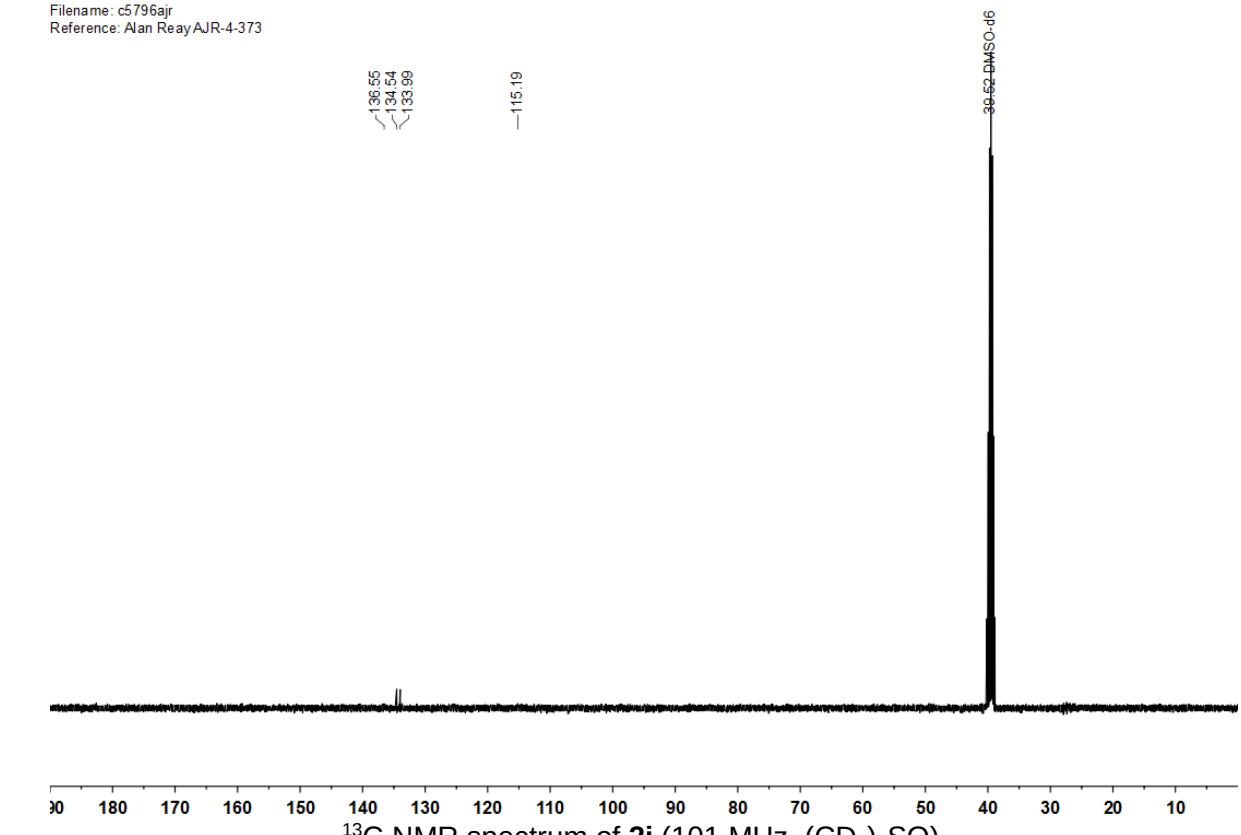


^{19}F NMR spectrum of **2h** (376 MHz, $(CD_3)_2SO$).

4-Bromobenzene-1-diazonium tetrafluoroborate (2i)

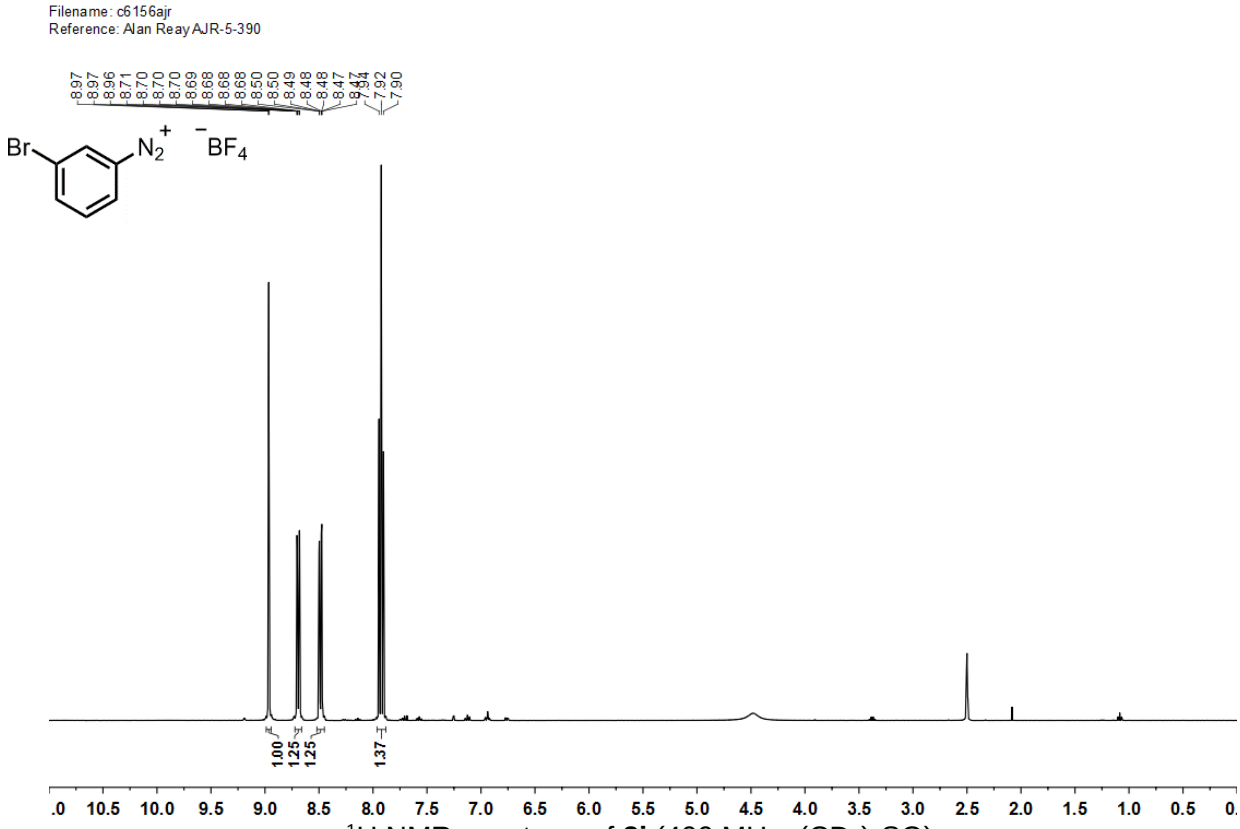


^{1}H NMR spectrum of **2i** (400 MHz, $(CD_3)_2SO$).

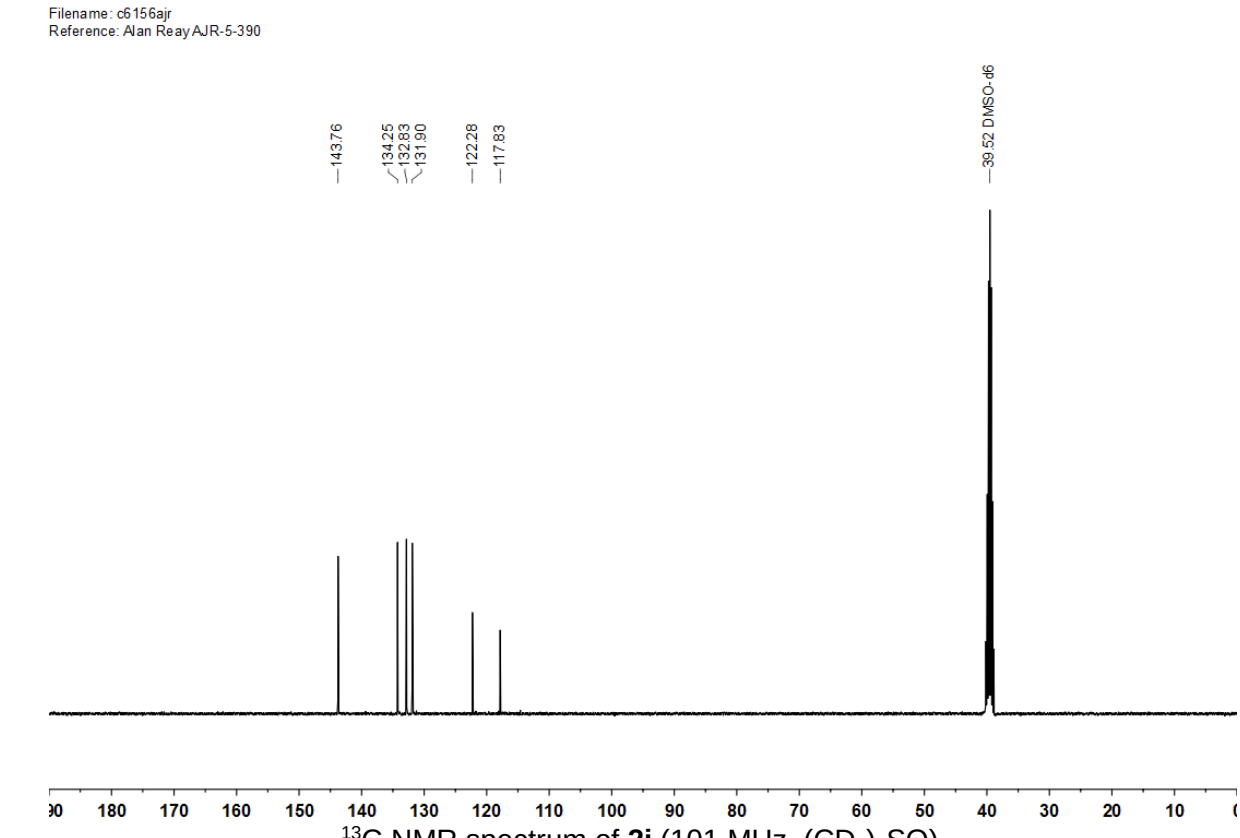


^{13}C NMR spectrum of **2i** (101 MHz, $(CD_3)_2SO$).

3-Bromobenzene-1-diazonium tetrafluoroborate (2j)

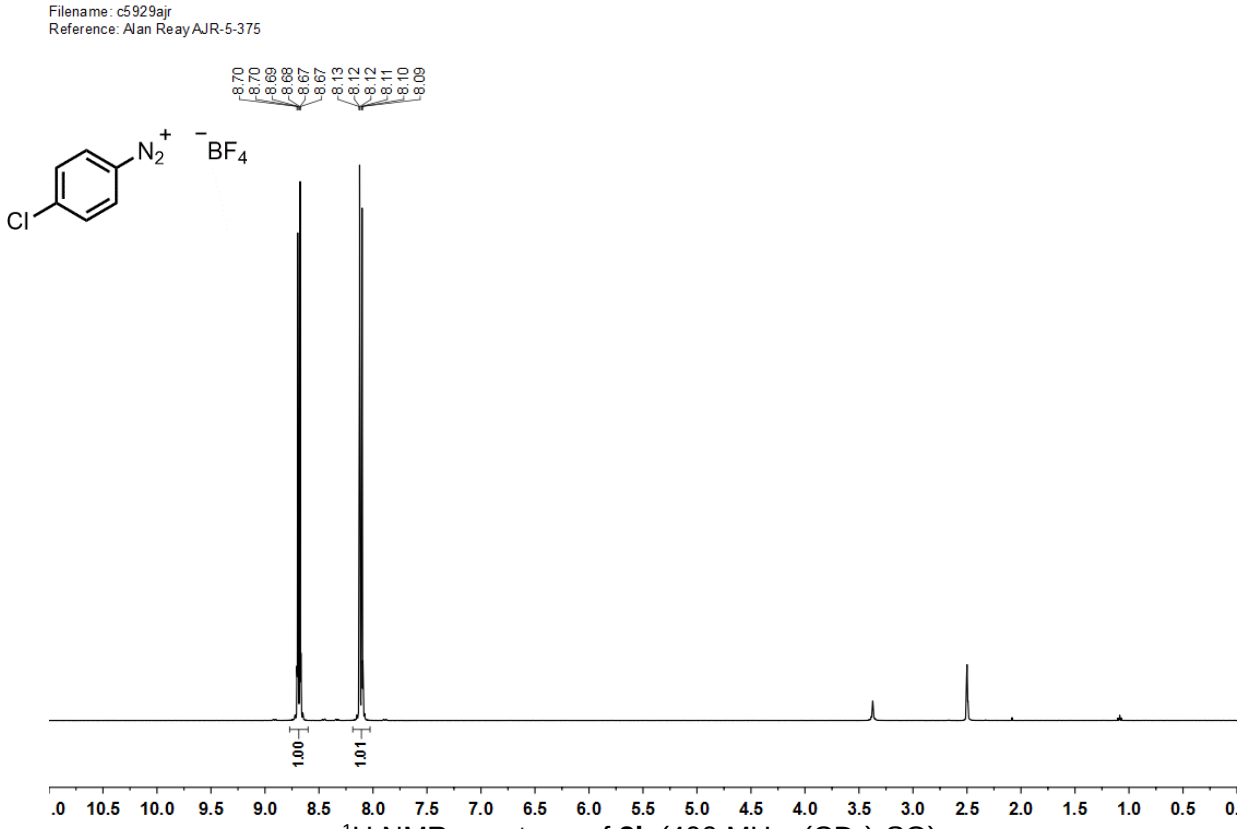


^{1}H NMR spectrum of **2j** (400 MHz, $(CD_3)_2SO$).

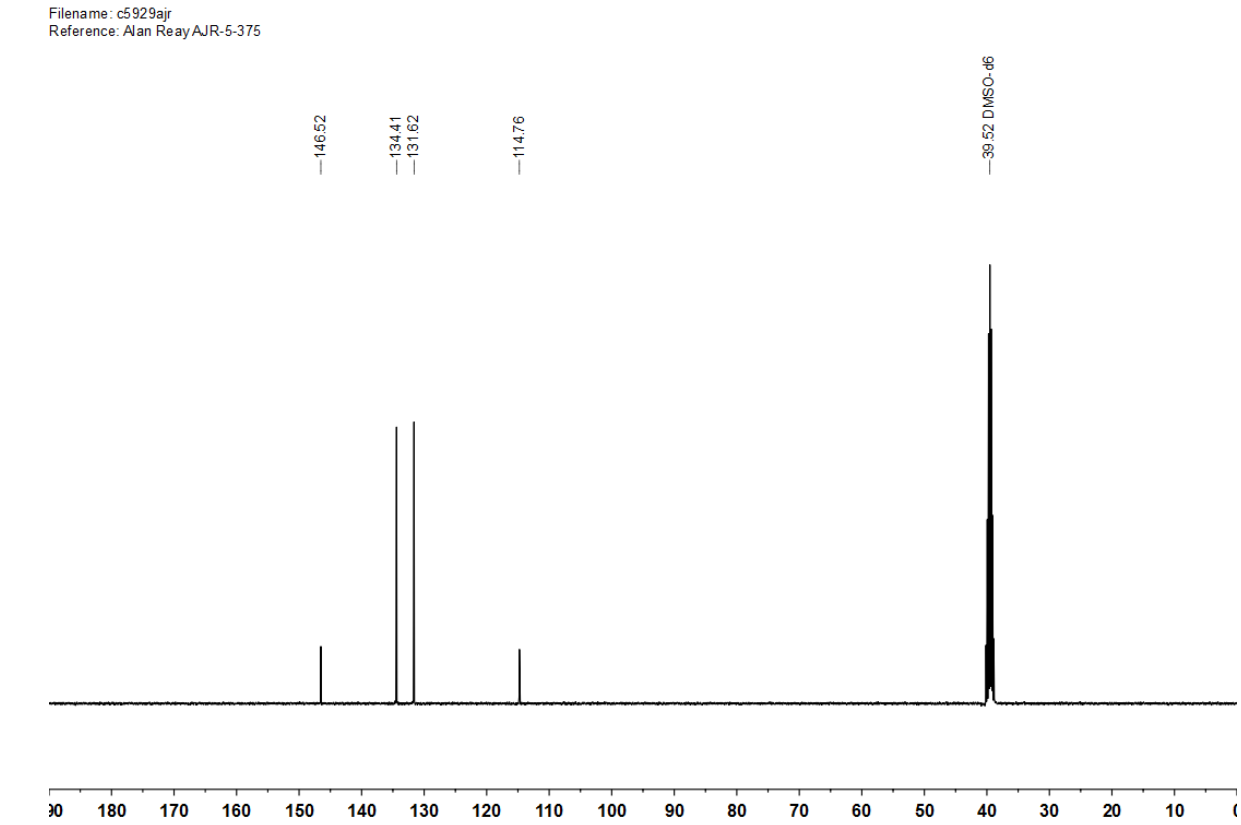


^{13}C NMR spectrum of **2j** (101 MHz, $(CD_3)_2SO$).

4-Chlorobenzene-1-diazonium tetrafluoroborate (2k)

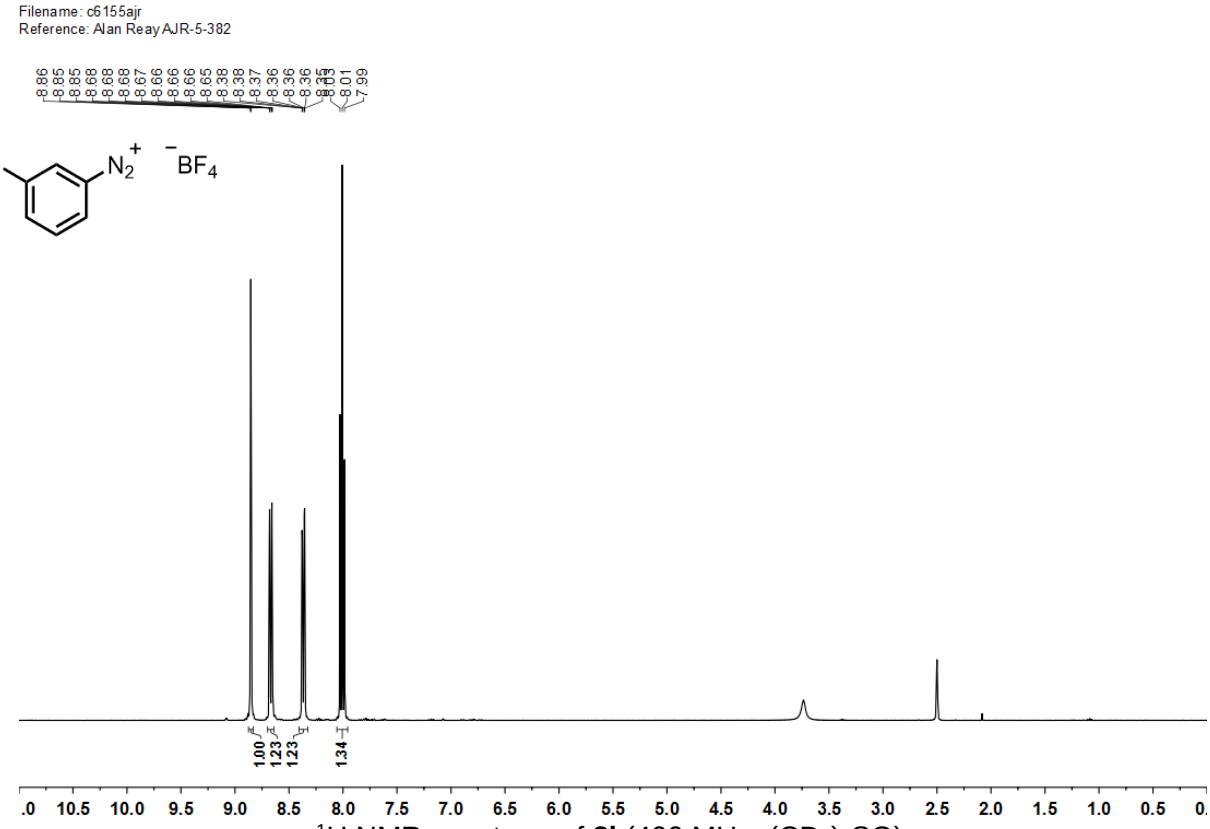


^{1}H NMR spectrum of **2k** (400 MHz, $(CD_3)_2SO$).

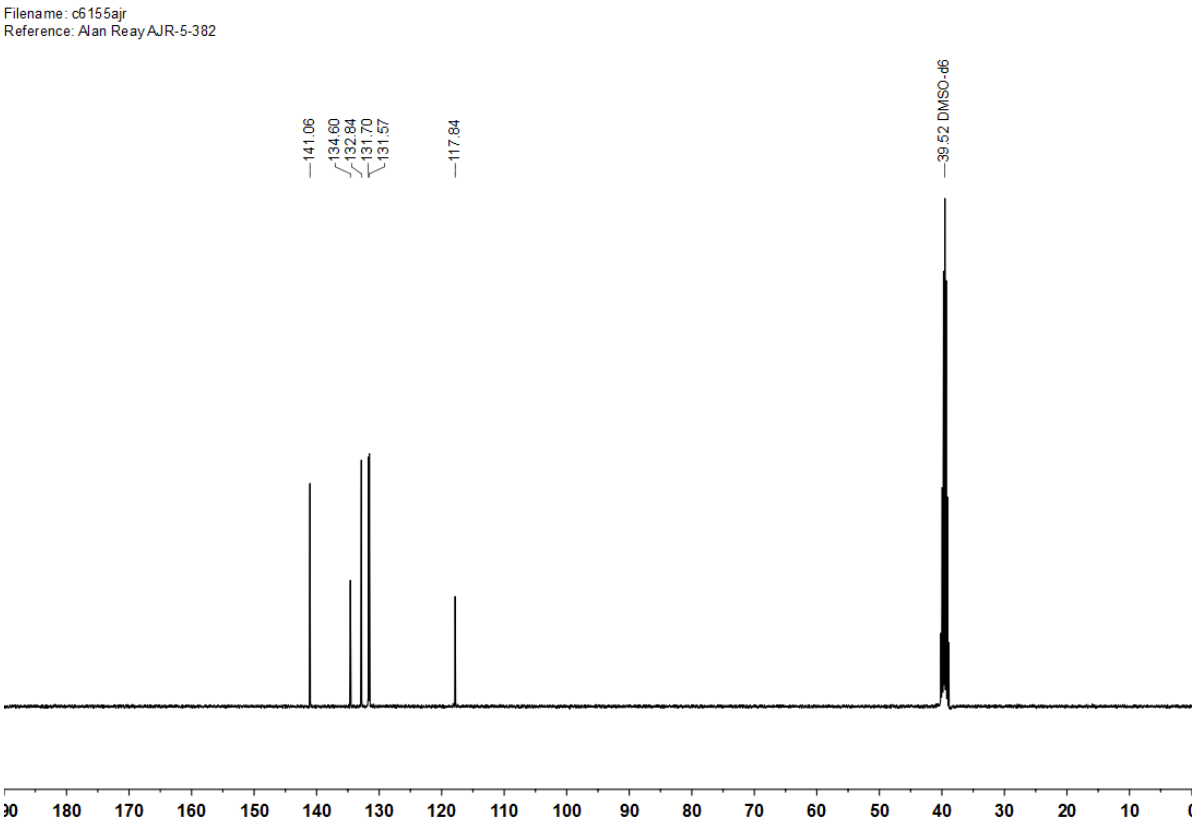


^{13}C NMR spectrum of **2k** (101 MHz, $(CD_3)_2SO$).

3-Chlorobenzene-1-diazonium tetrafluoroborate (2l)

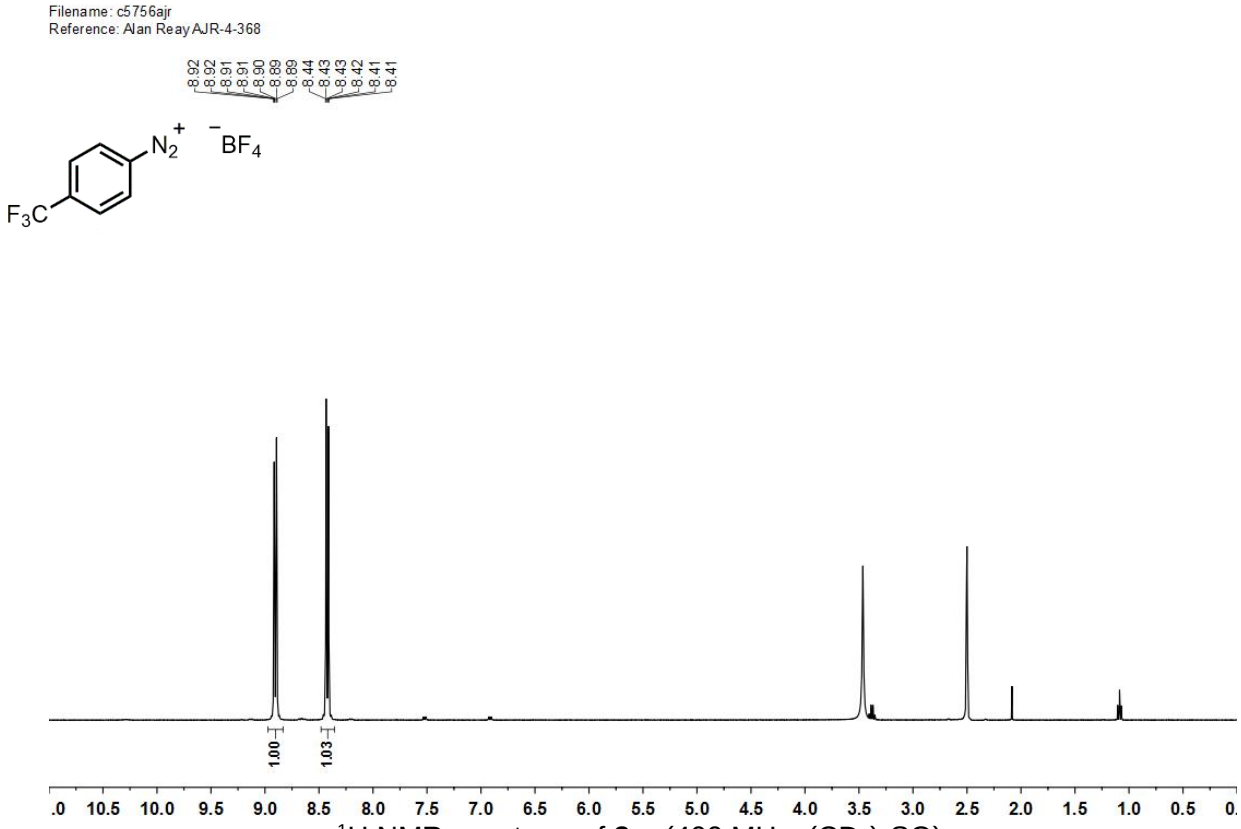


^{1}H NMR spectrum of **2l** (400 MHz, $(CD_3)_2SO$).

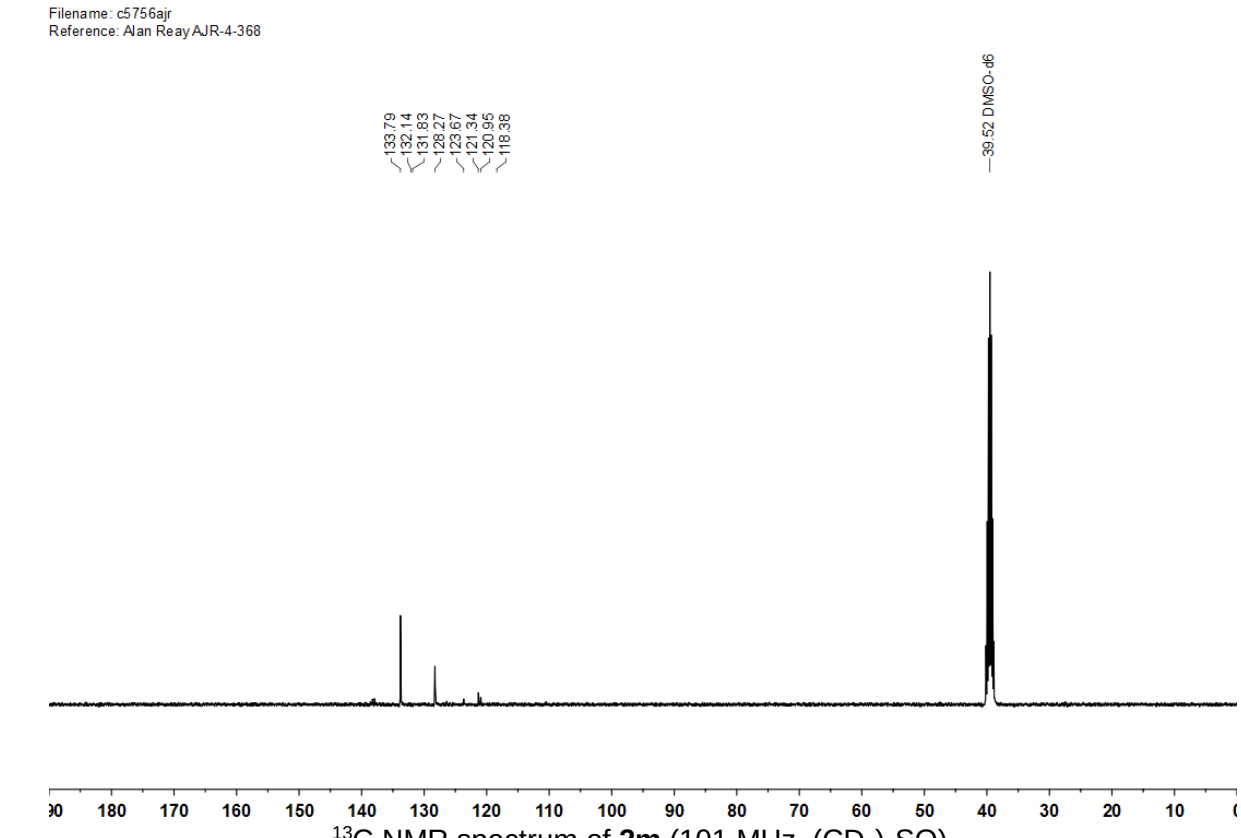


^{13}C NMR spectrum of **2l** (101 MHz, $(CD_3)_2SO$).

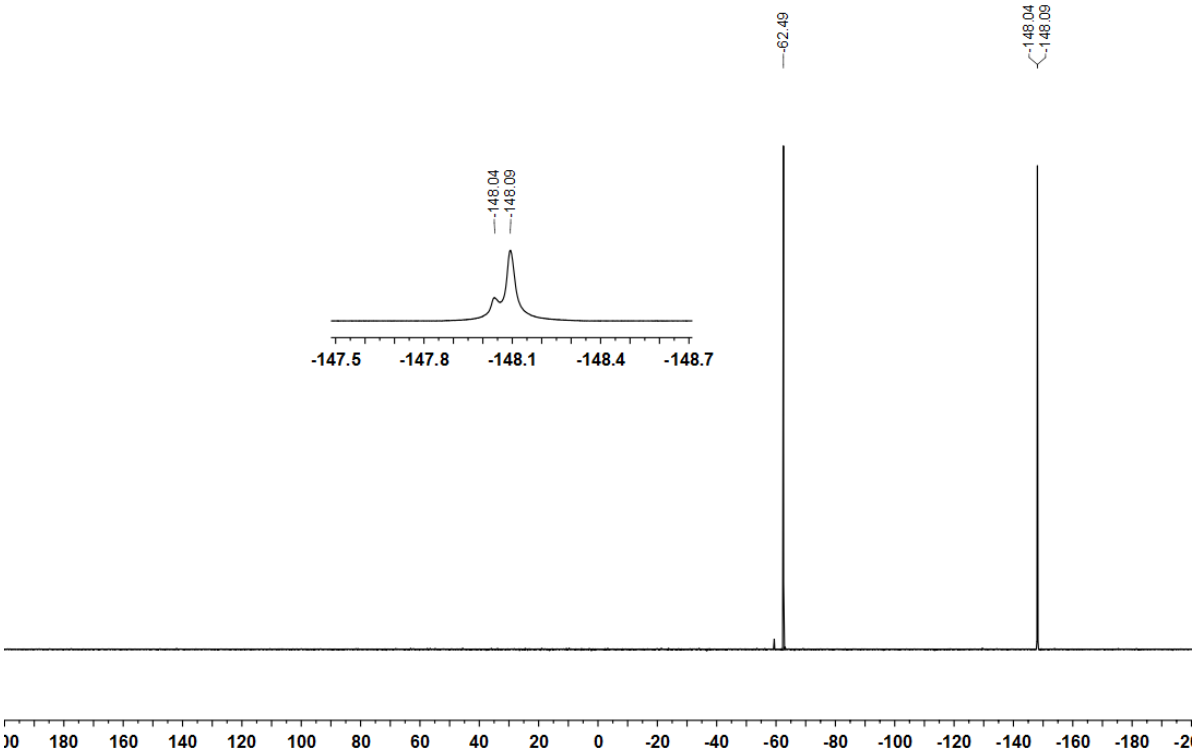
4-(Trifluoromethyl)benzene-1-diazonium tetrafluoroborate (2m)



^{1}H NMR spectrum of **2m** (400 MHz, $(CD_3)_2SO$).

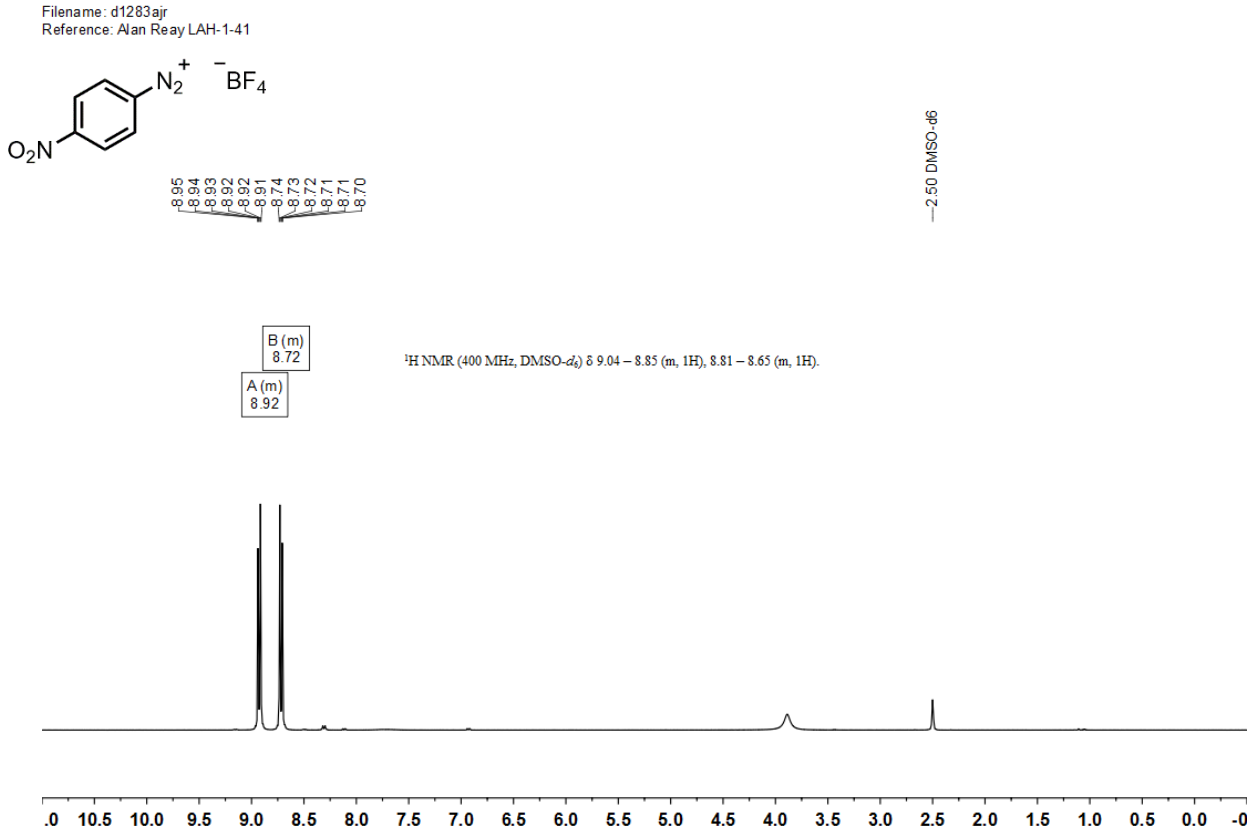


^{13}C NMR spectrum of **2m** (101 MHz, $(CD_3)_2SO$).

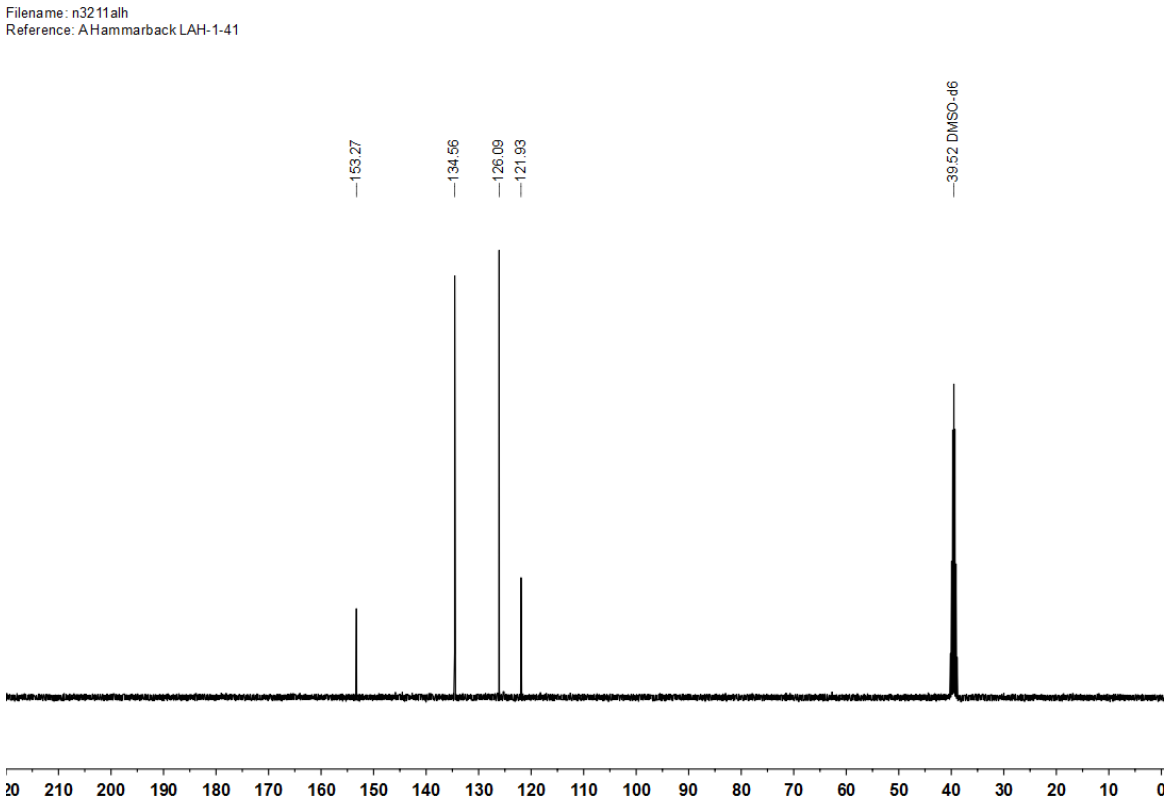


^{19}F NMR spectrum of **2m** (376 MHz, $(CD_3)_2SO$).

4-Nitrobenzene-1-diazonium tetrafluoroborate (2n)

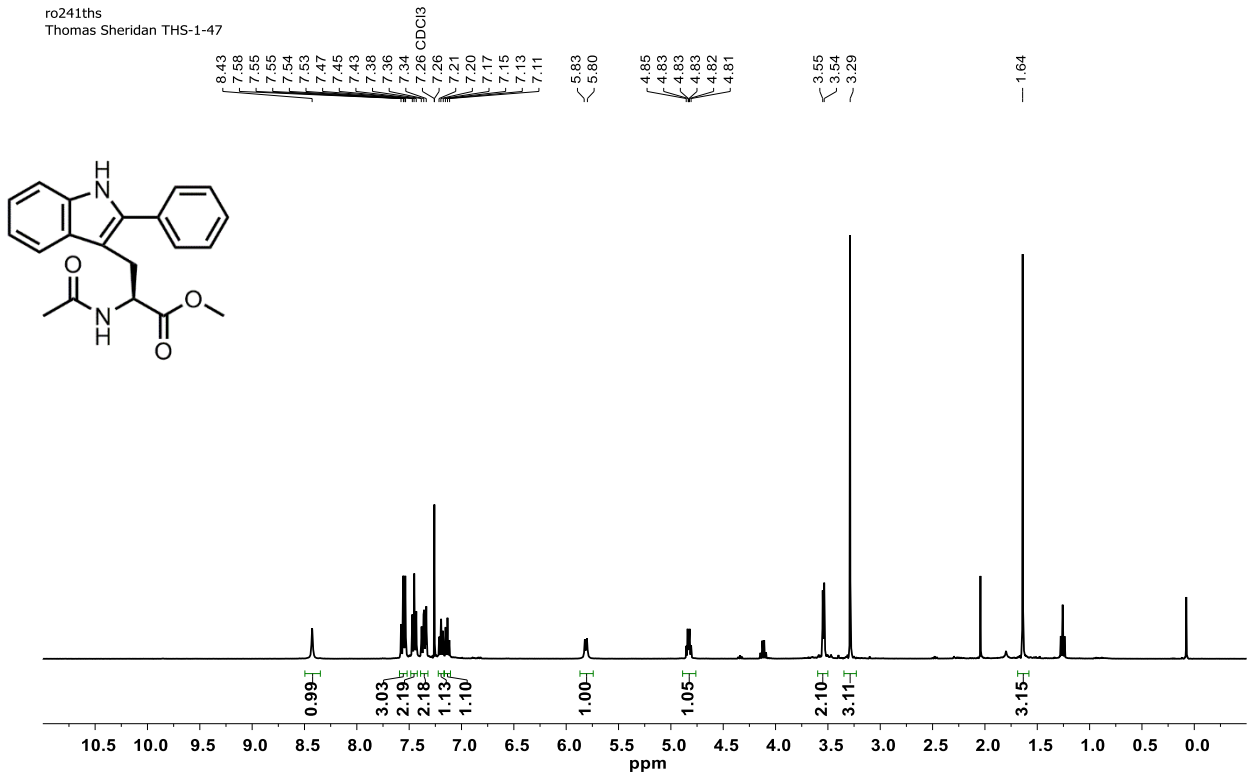


^{1}H NMR spectrum of **2n** (400 MHz, $(CD_3)_2SO$).

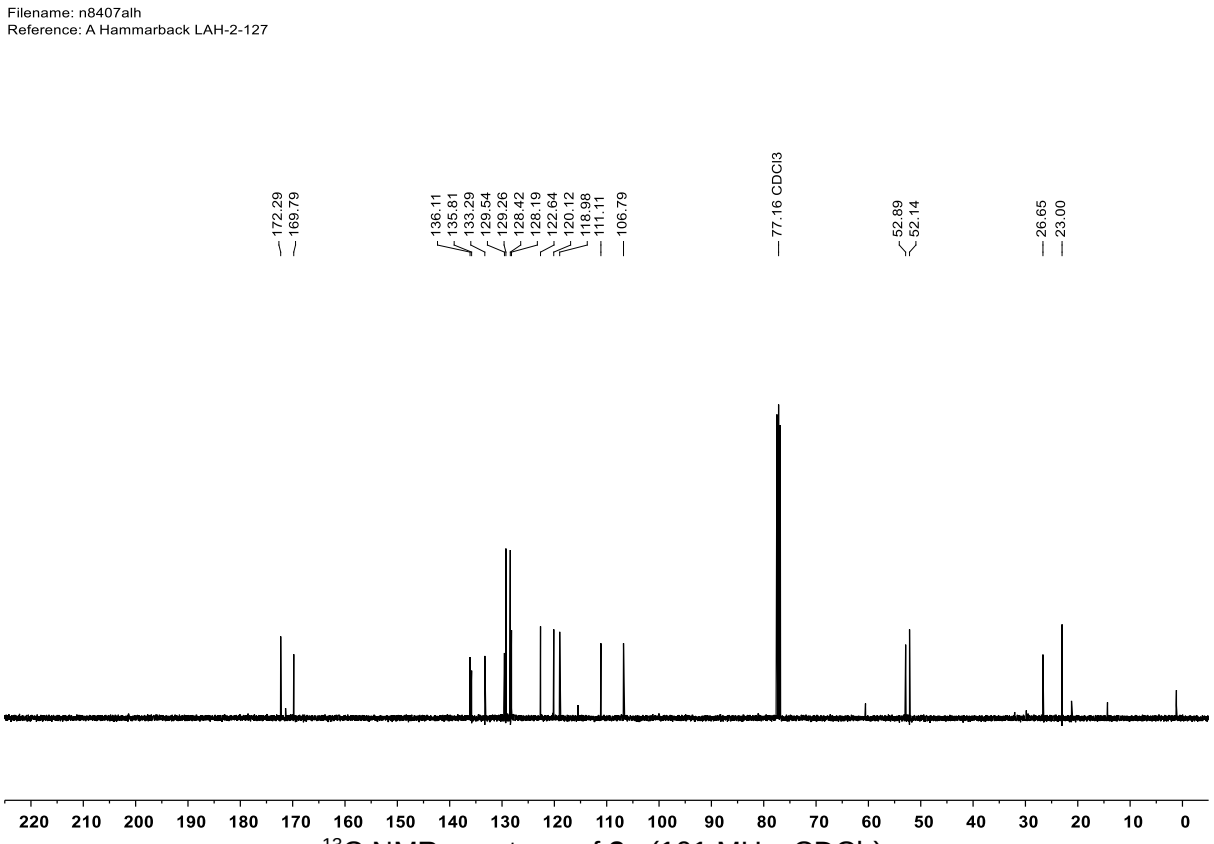


^{13}C NMR spectrum of **2n** (101 MHz, $(CD_3)_2SO$).

Methyl (2*S*)-2-acetamido-3-(2-phenyl-1*H*-indol-3-yl)propanoate (3a)

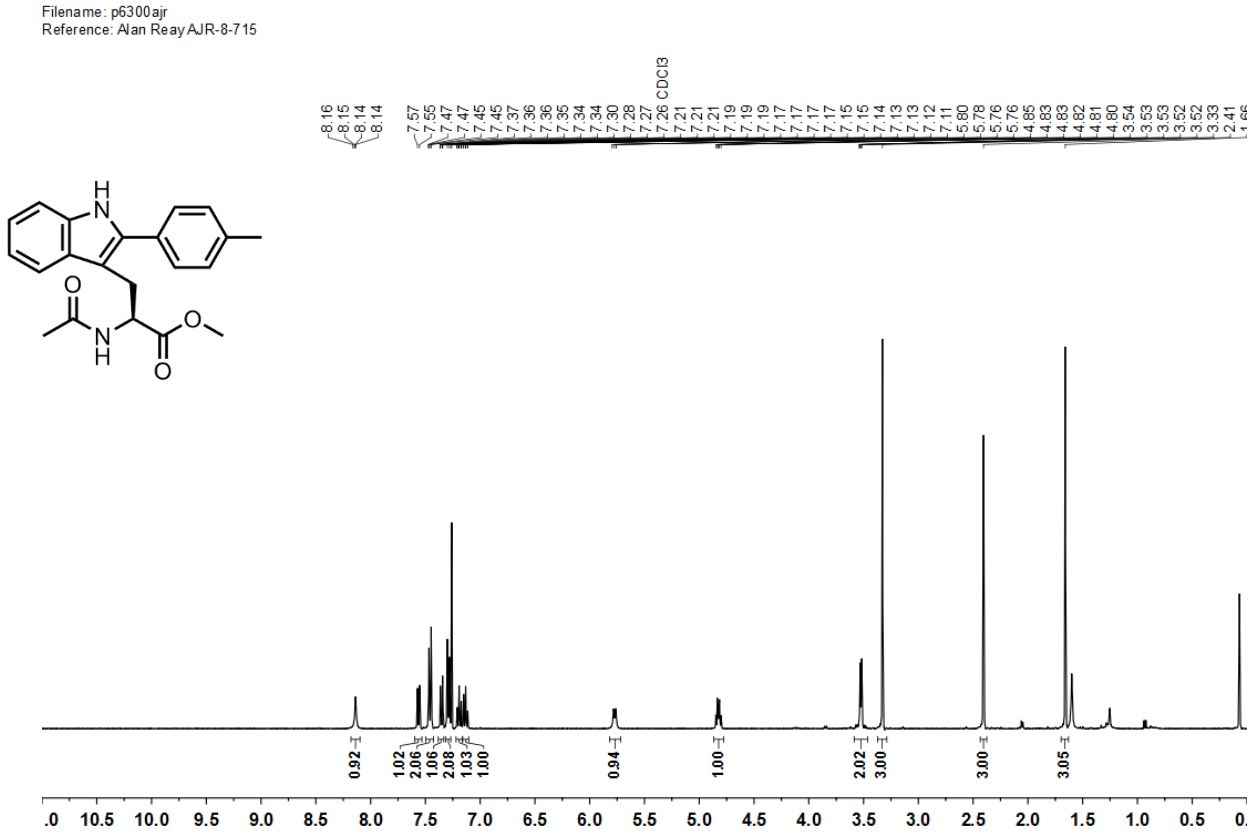


^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$) *residual EtOAc present.

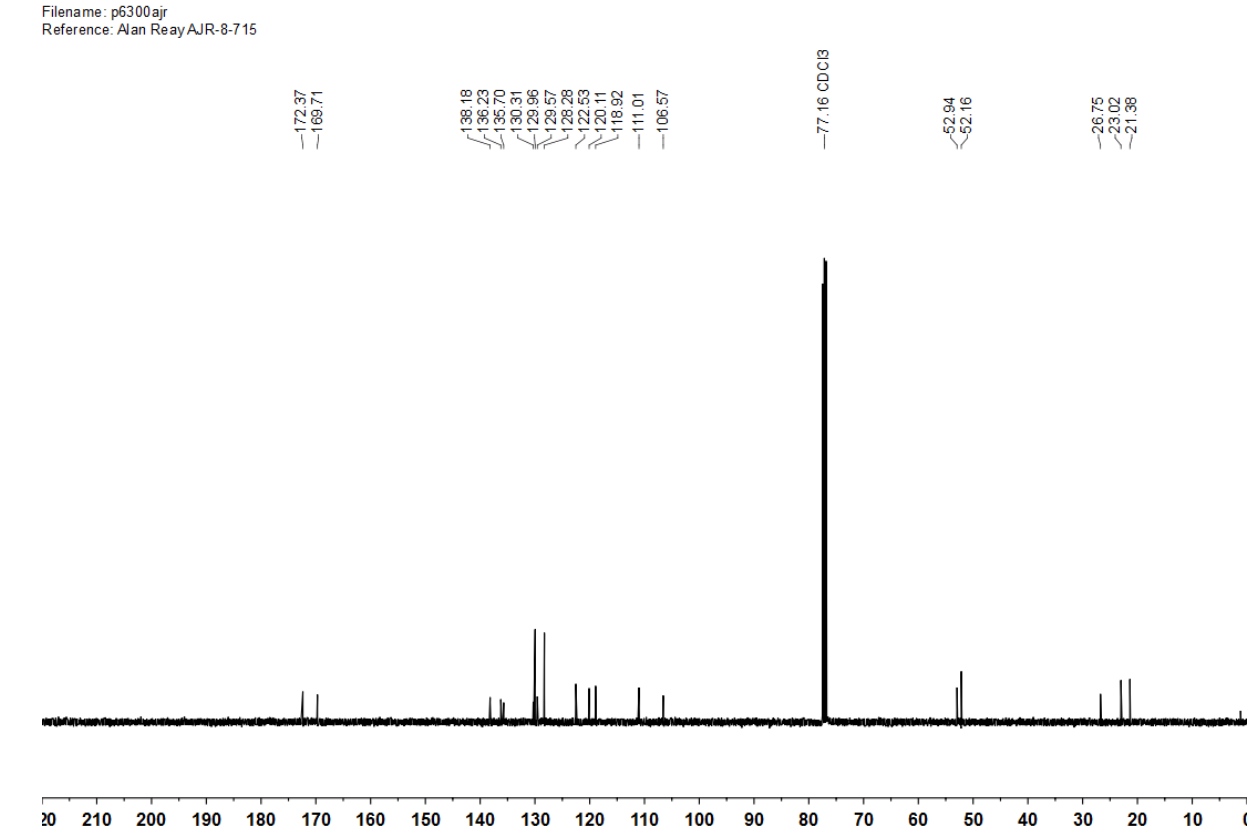


^{13}C NMR spectrum of **3a** (101 MHz, $CDCl_3$).

Methyl (2*S*)-3-[2-(4-methylphenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3b)

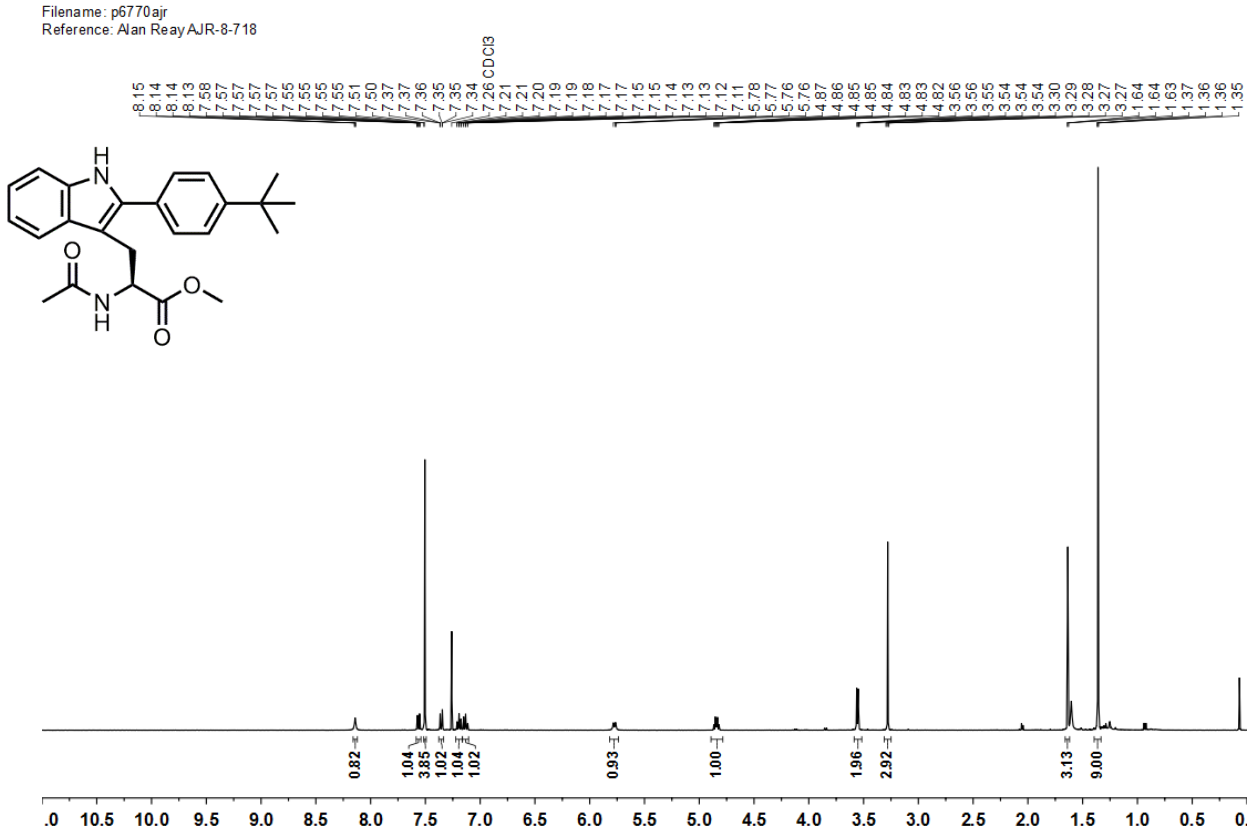


^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$).

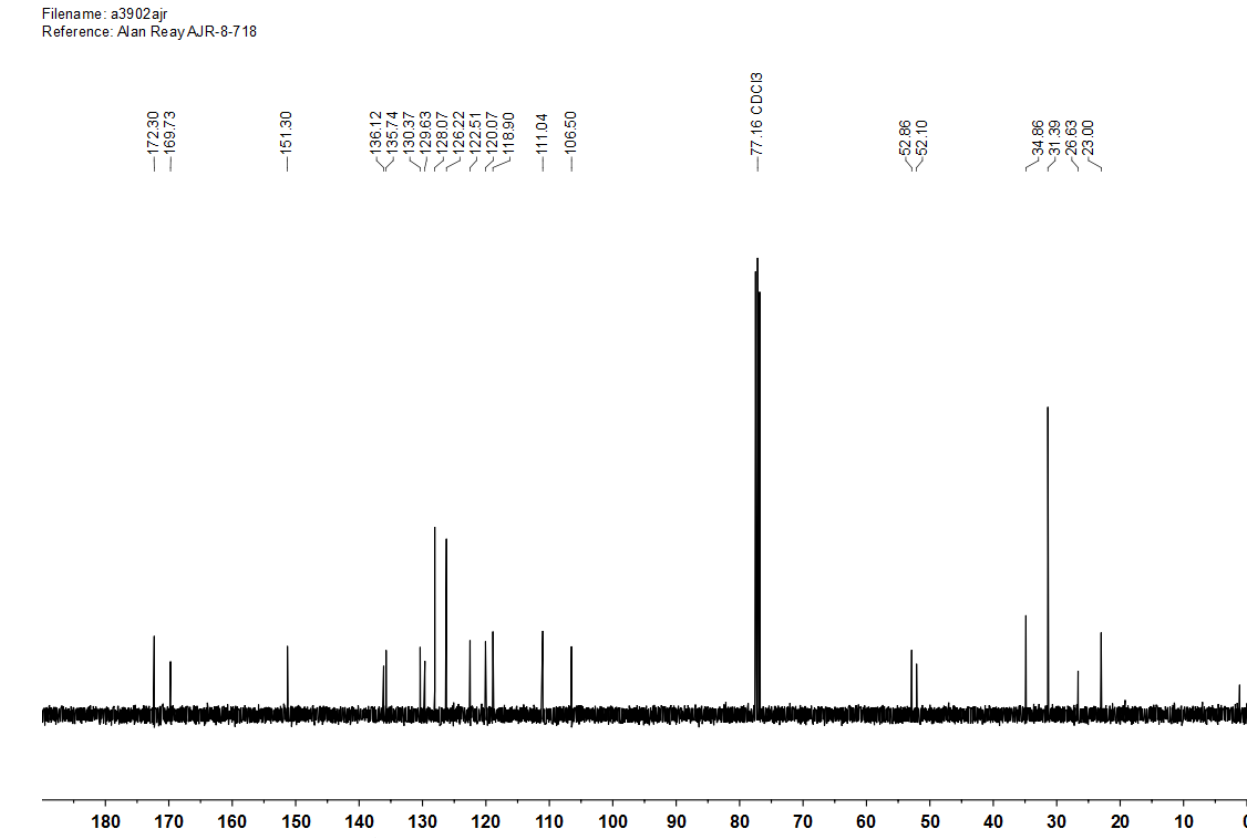


^{13}C NMR spectrum of **3b** (101 MHz, $CDCl_3$).

Methyl (2*S*)-3-[2-(4-*tert*-butylphenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3c)

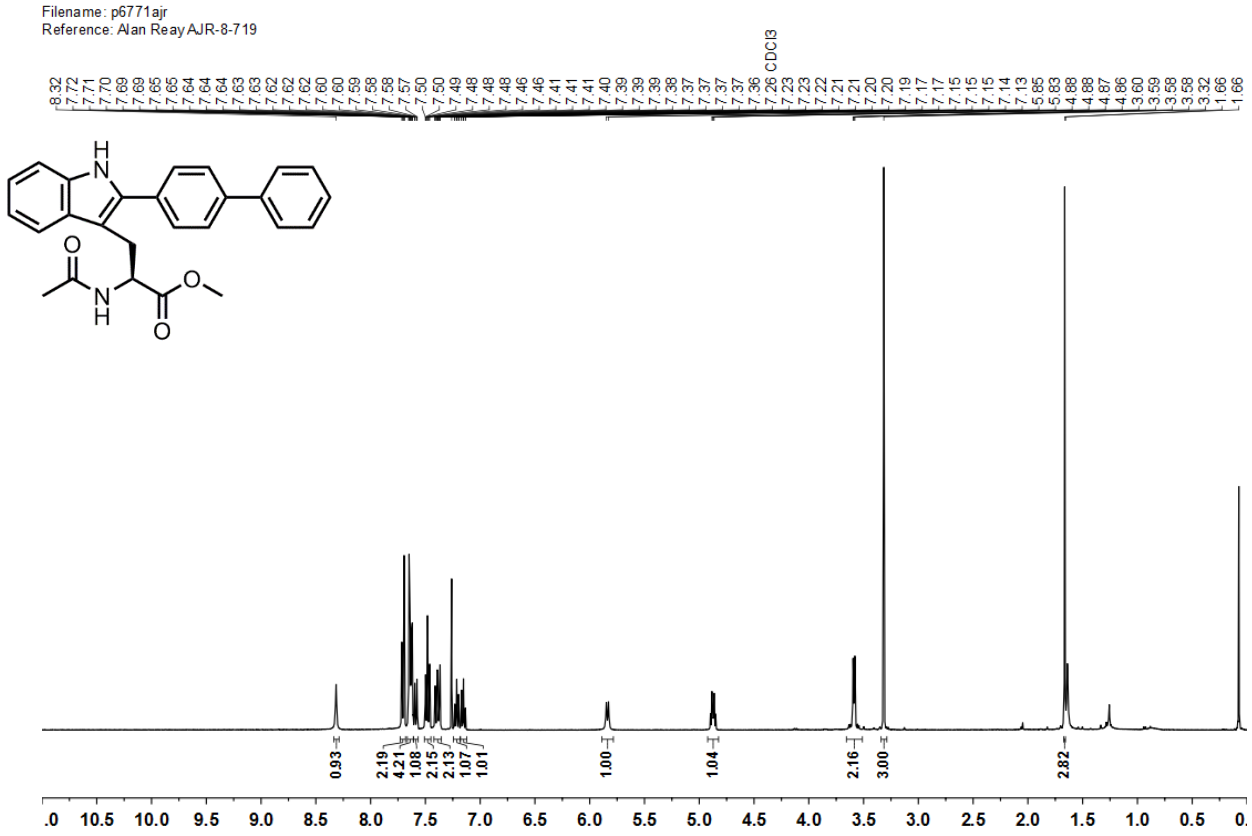


^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$).

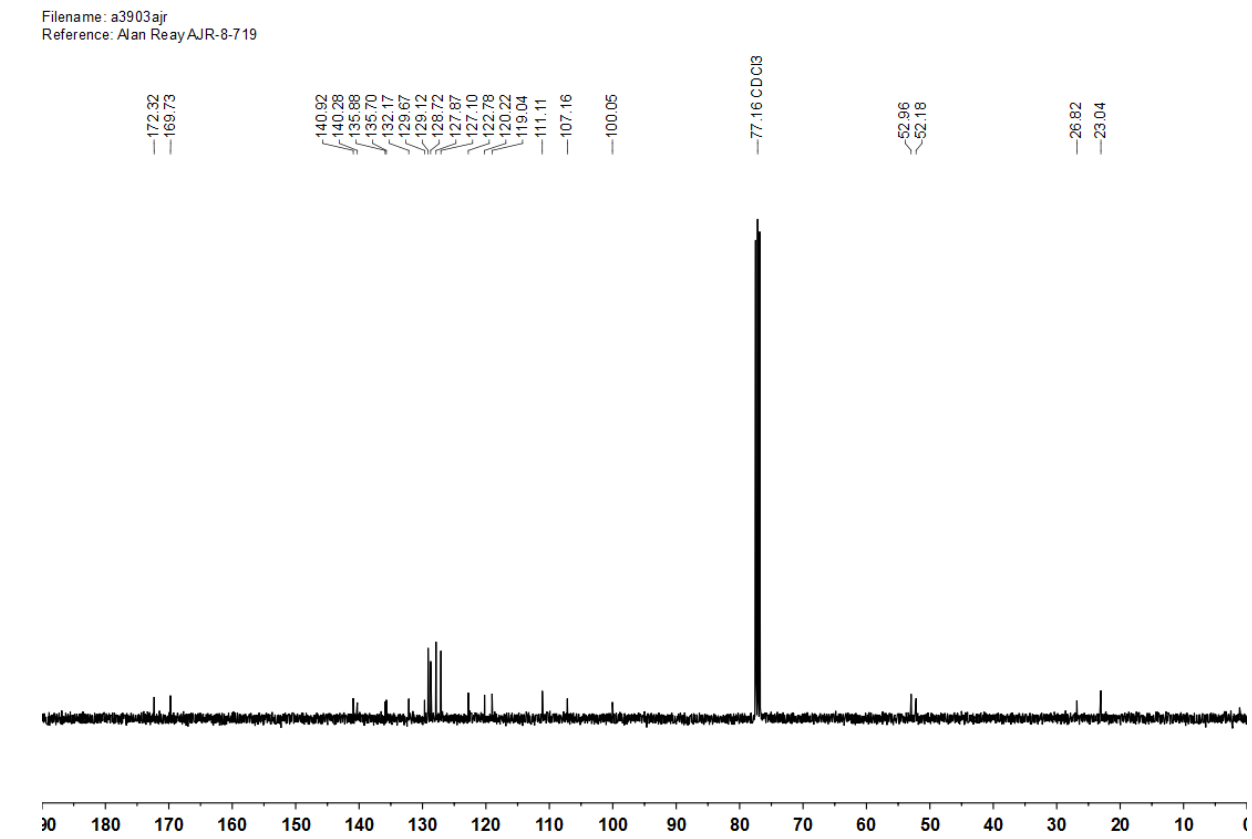


^{13}C NMR spectrum of **3c** (101 MHz, $CDCl_3$).

Methyl (2*S*)-2-acetamido-3-[2-(4-phenylphenyl)-1*H*-indol-3-yl]propanoate (3d)

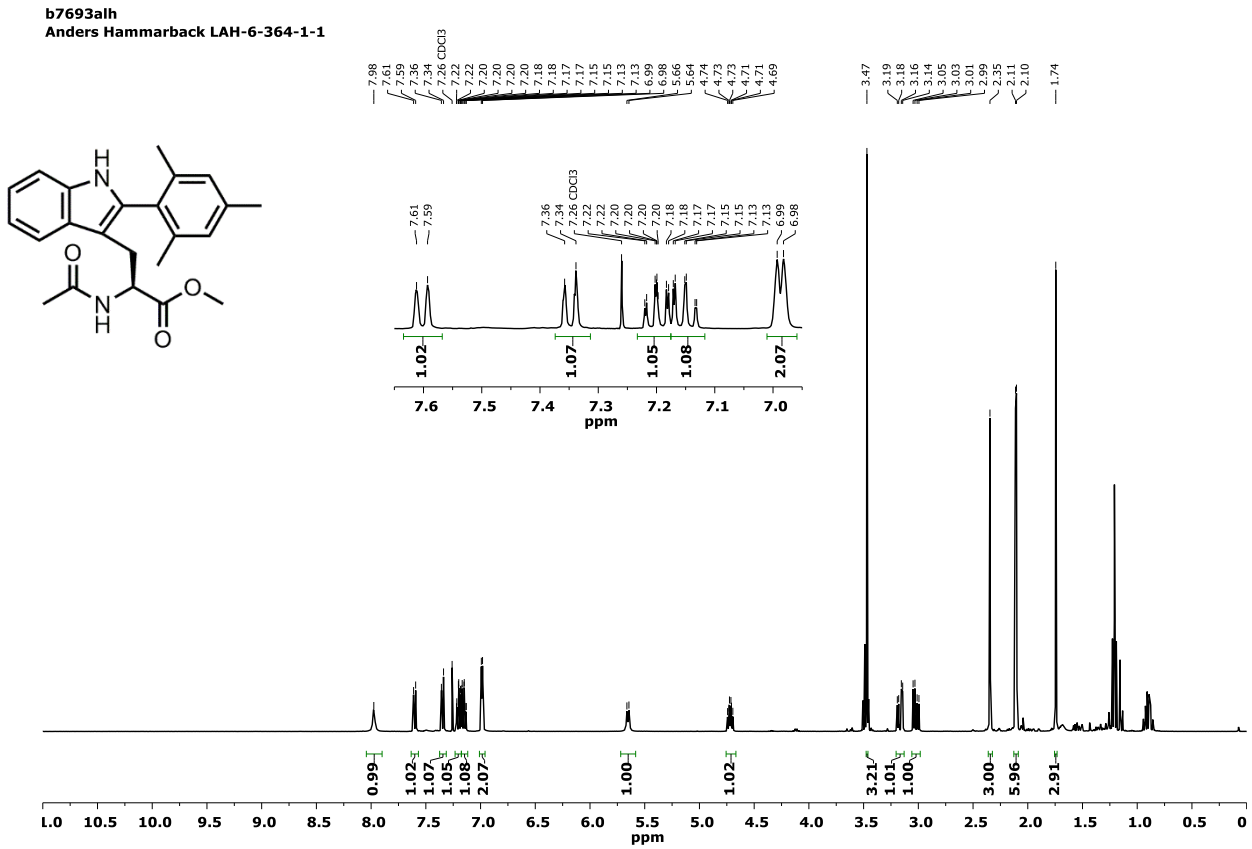


^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$).

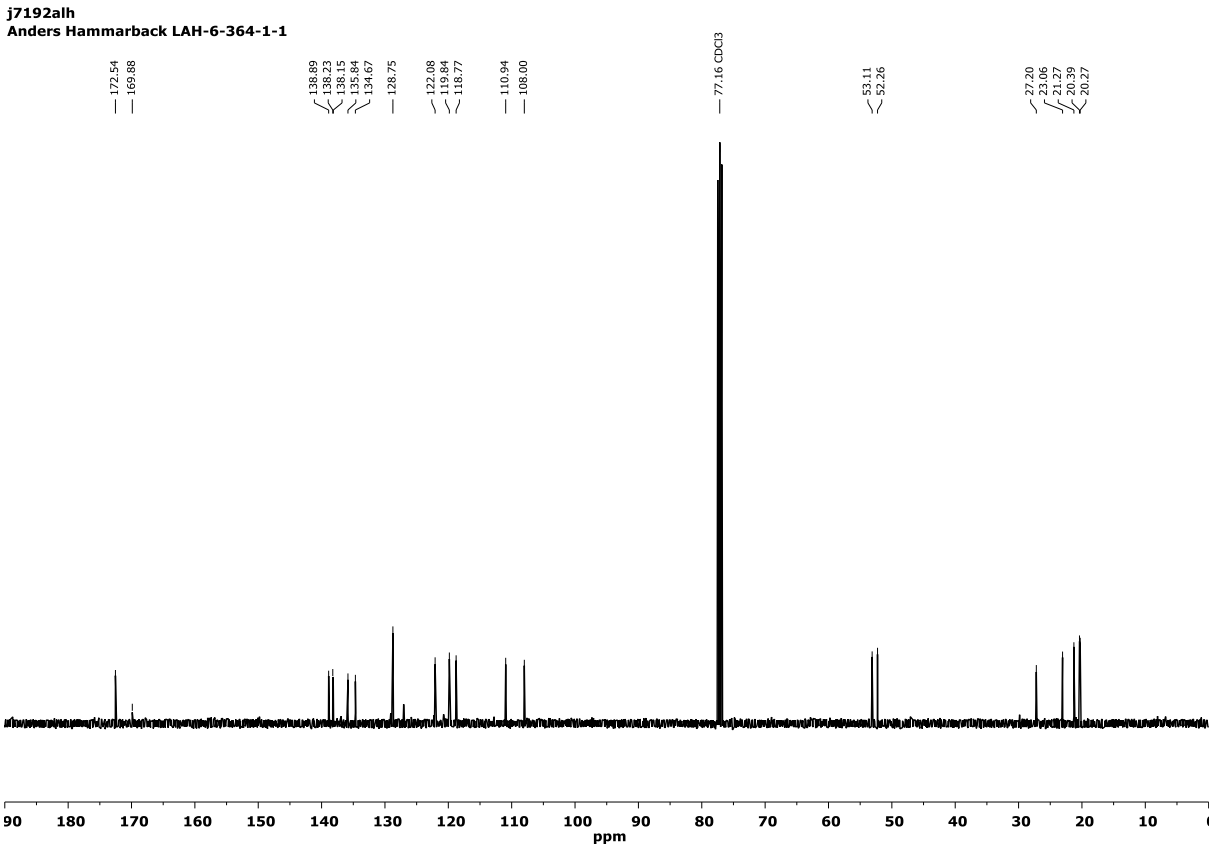


^{13}C NMR spectrum of **3d** (101 MHz, $CDCl_3$).

Methyl (2*S*)-2-acetamido-3-[2-(2,4,6-trimethylphenyl)-1*H*-indol-3-yl]propanoate (3e)

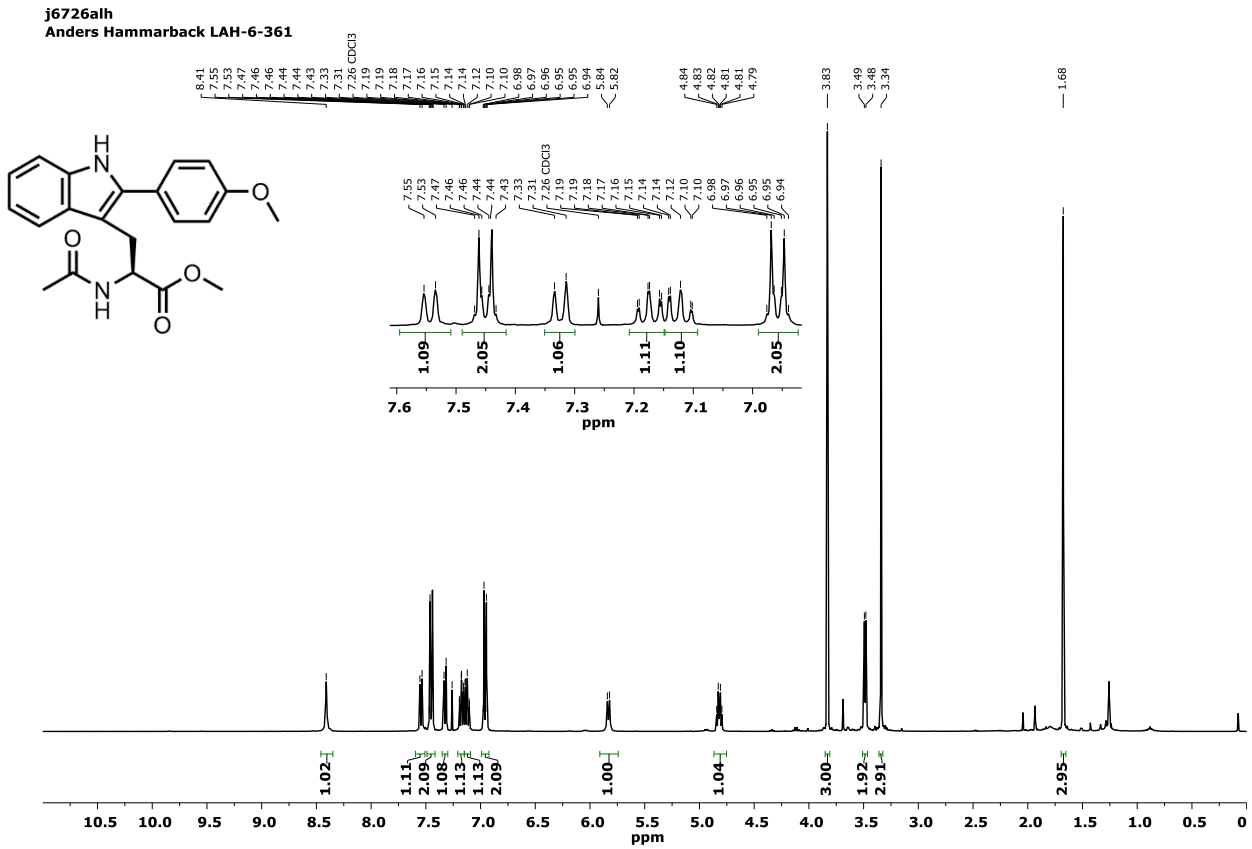


^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$).

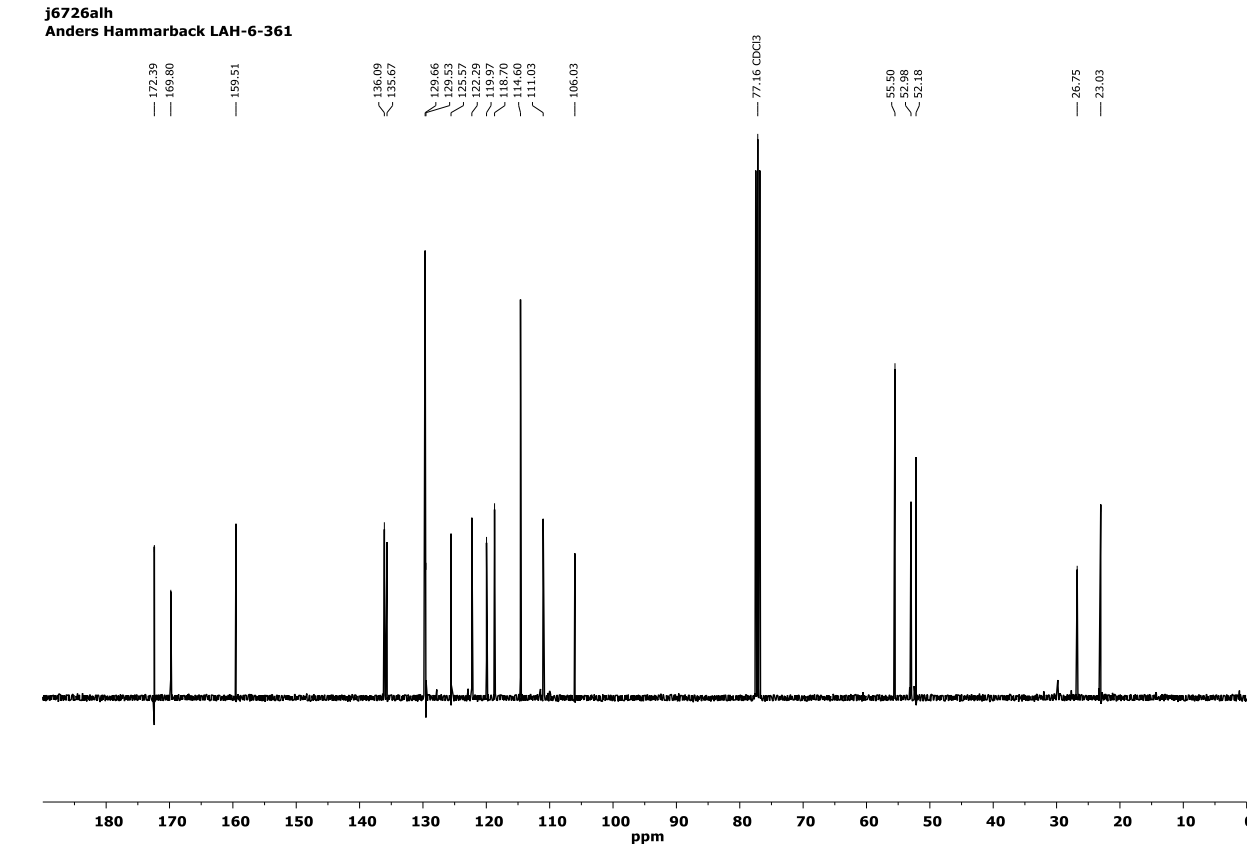


^{13}C NMR spectrum of **3e** (101 MHz, $CDCl_3$).

Methyl (2*S*)-2-acetamido-3-[2-(4-methoxyphenyl)-1*H*-indol-3-yl]propanoate (3f)

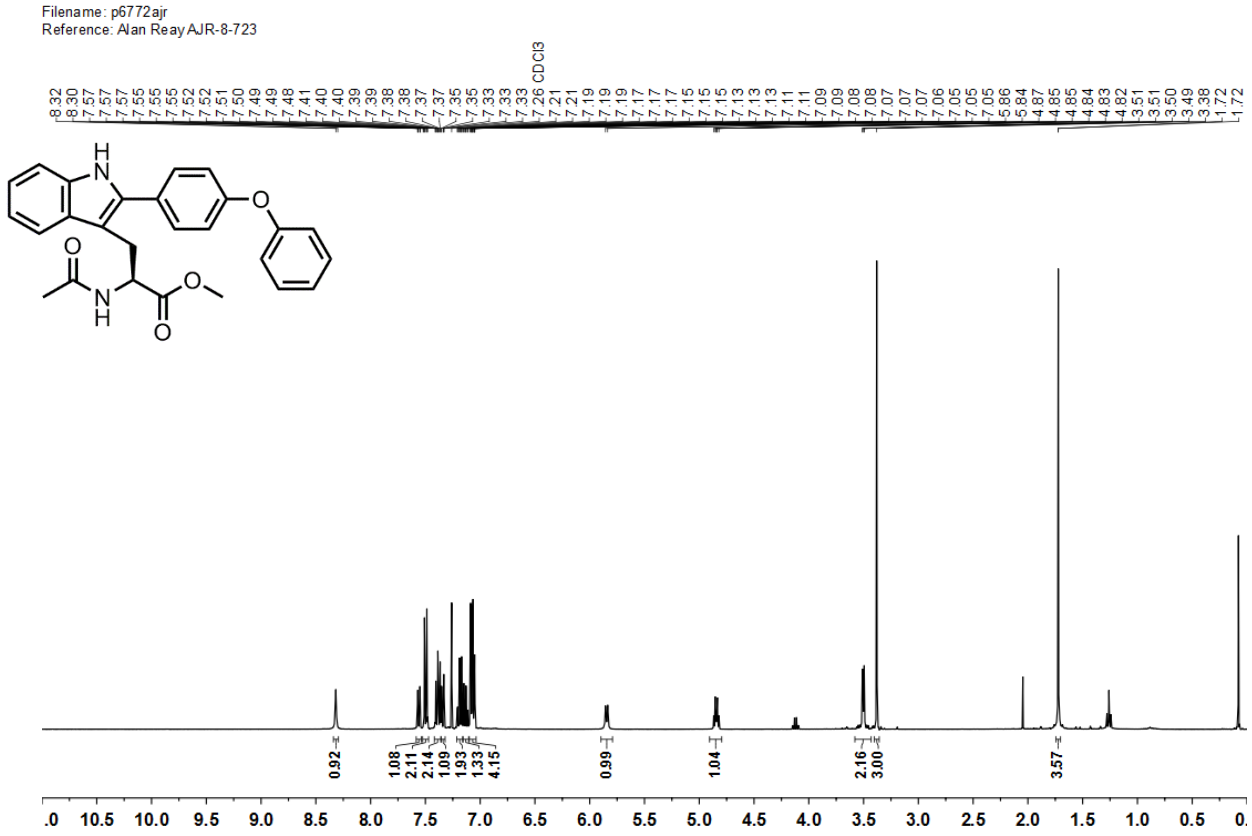


^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$).

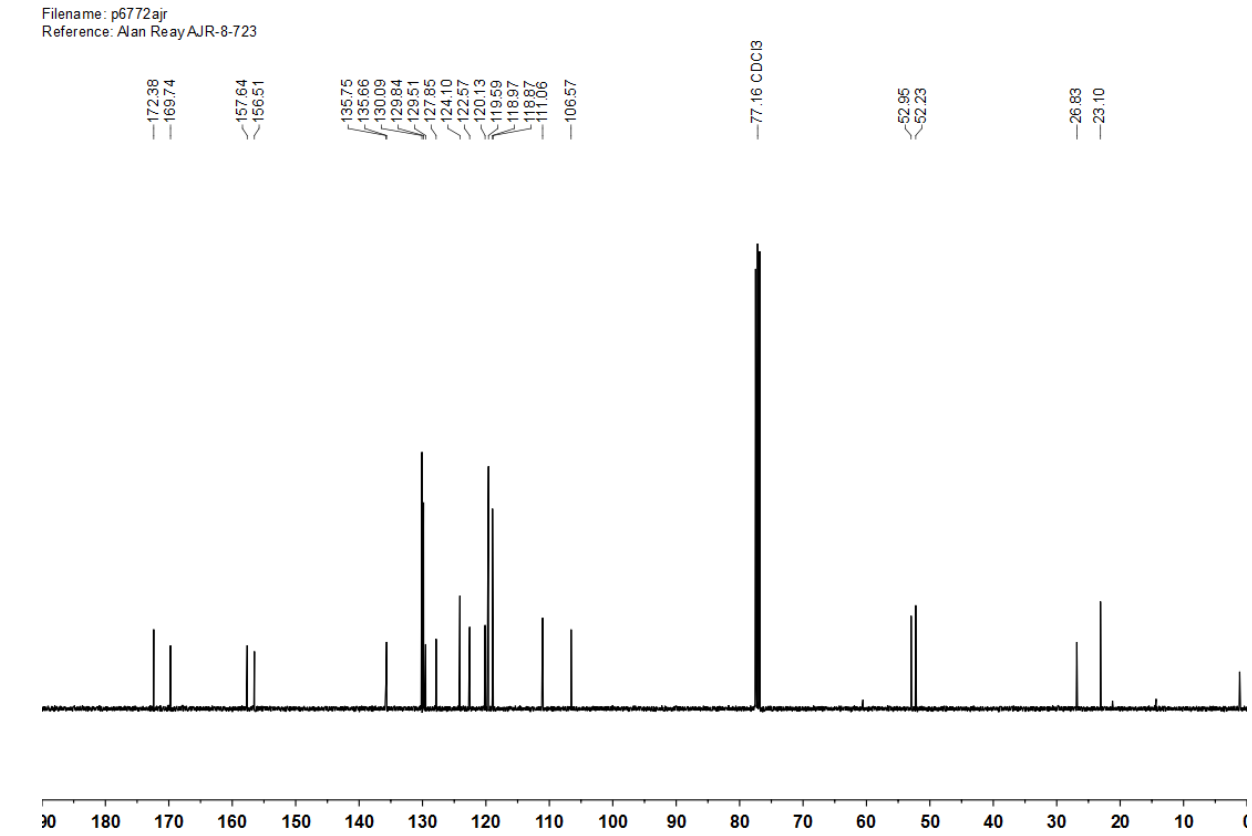


^{13}C NMR spectrum of **3f** (101 MHz, $CDCl_3$).

Methyl (2*S*)-2-acetamido-3-[2-(4-phenoxyphenyl)-1*H*-indol-3-yl]propanoate (3g)

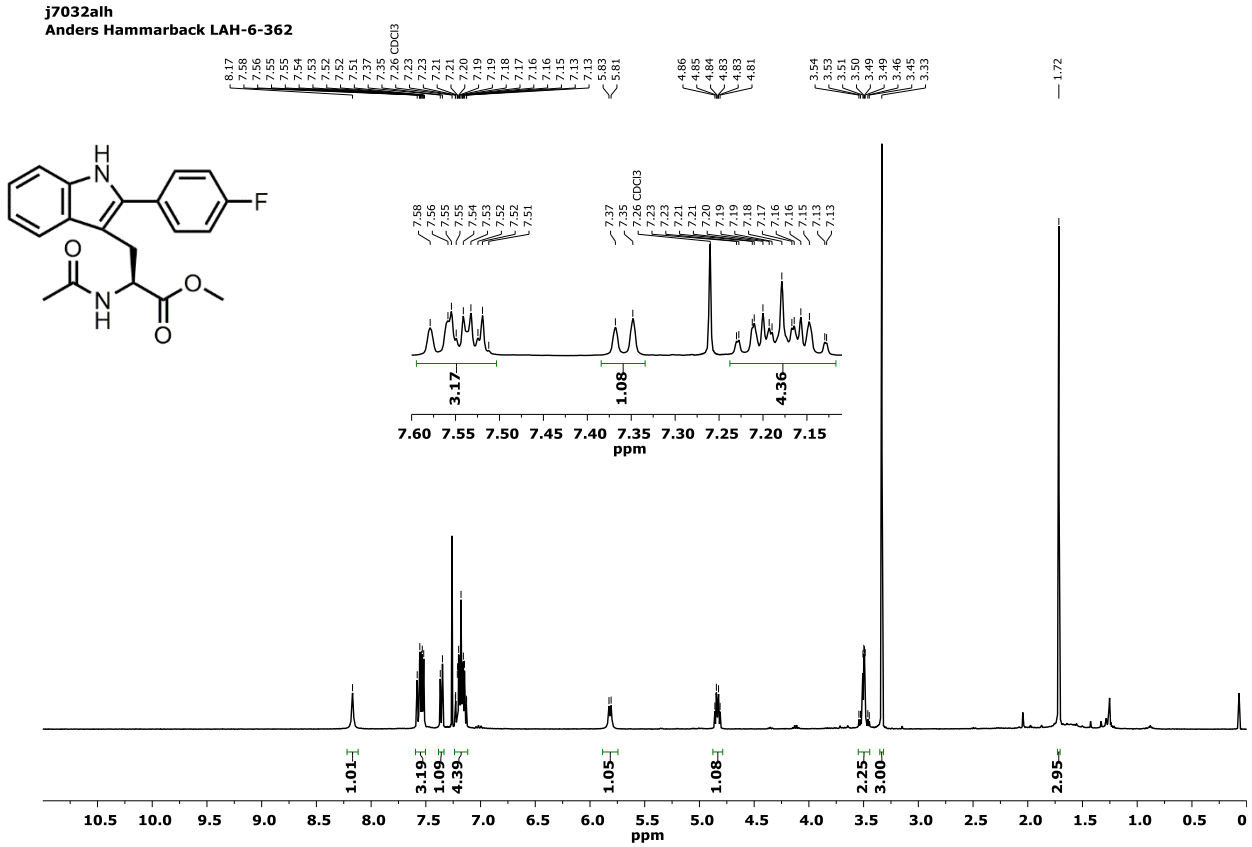


^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$).

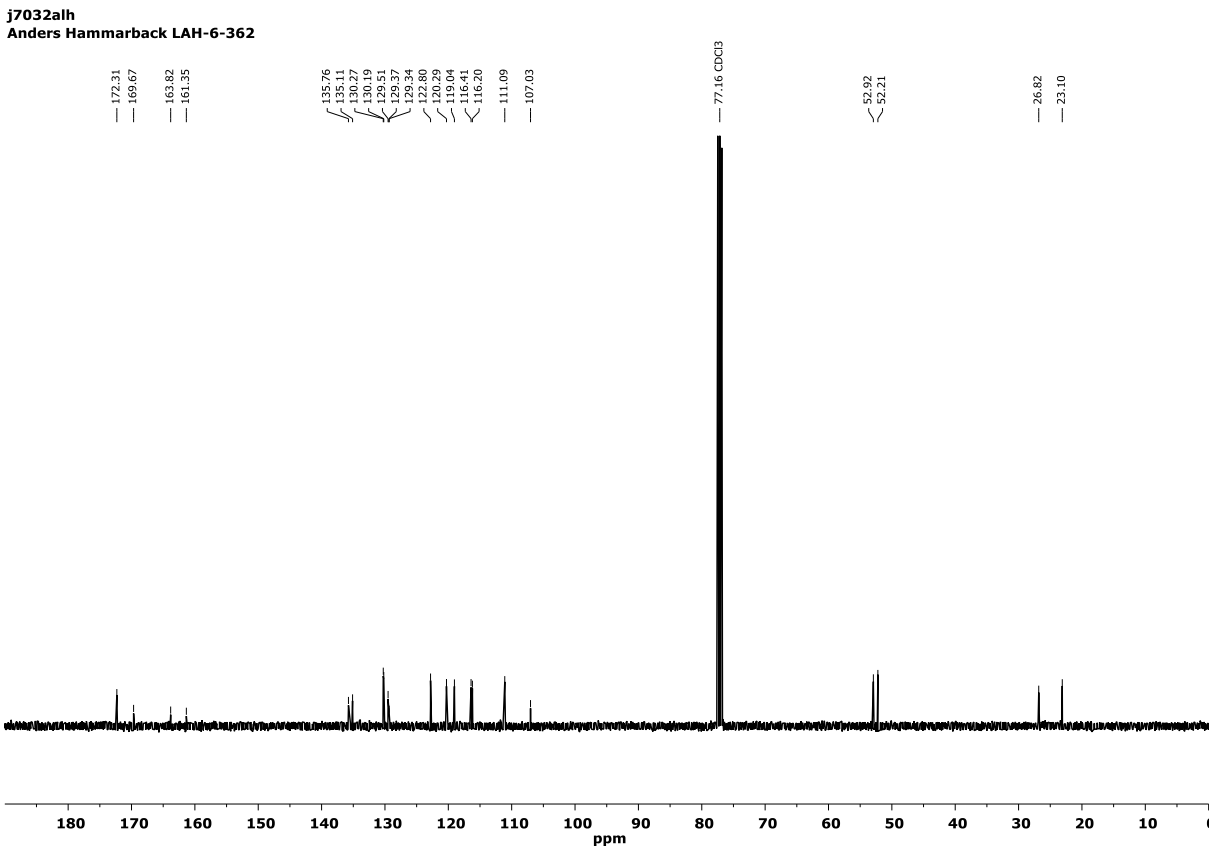


^{13}C NMR spectrum of **3g** (101 MHz, $CDCl_3$).

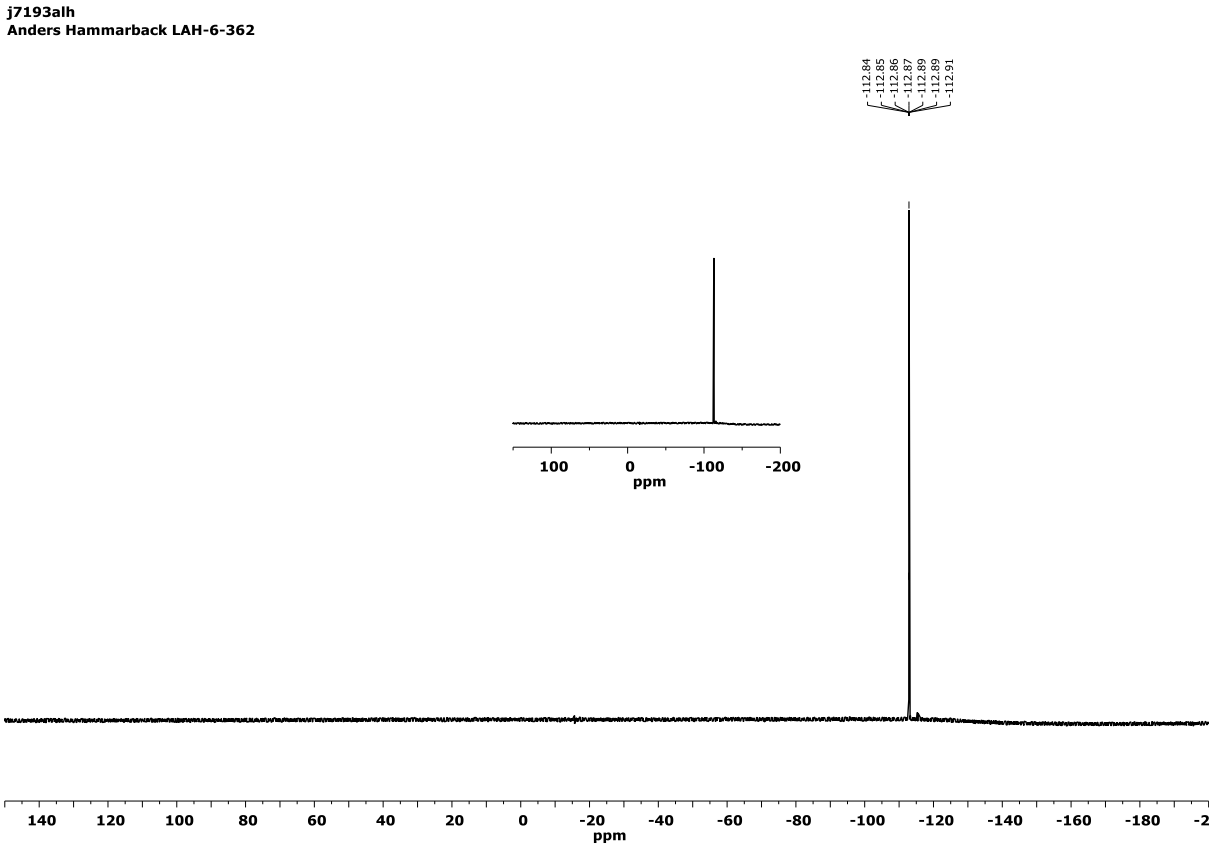
Methyl (2*S*)-3-[2-(4-fluorophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3h)



^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$).

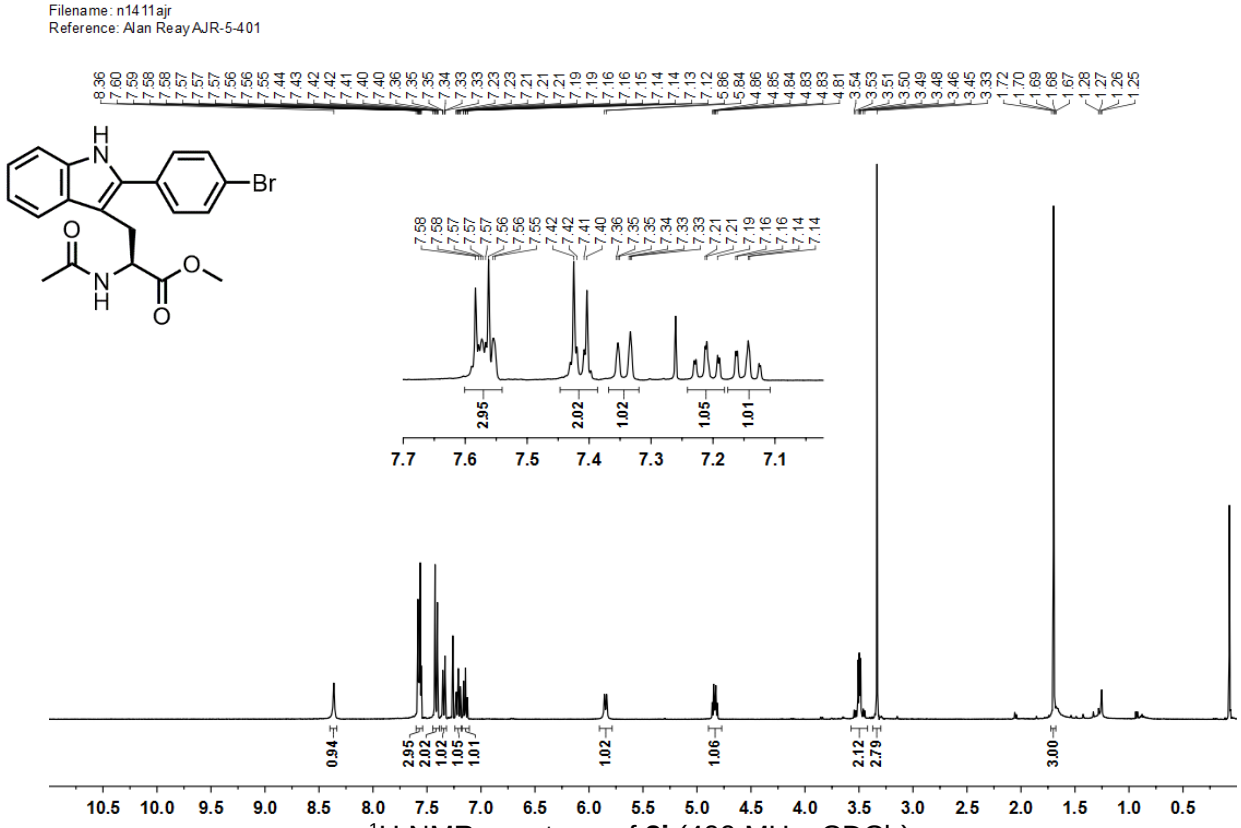


^{13}C NMR spectrum of **3h** (101 MHz, $CDCl_3$).

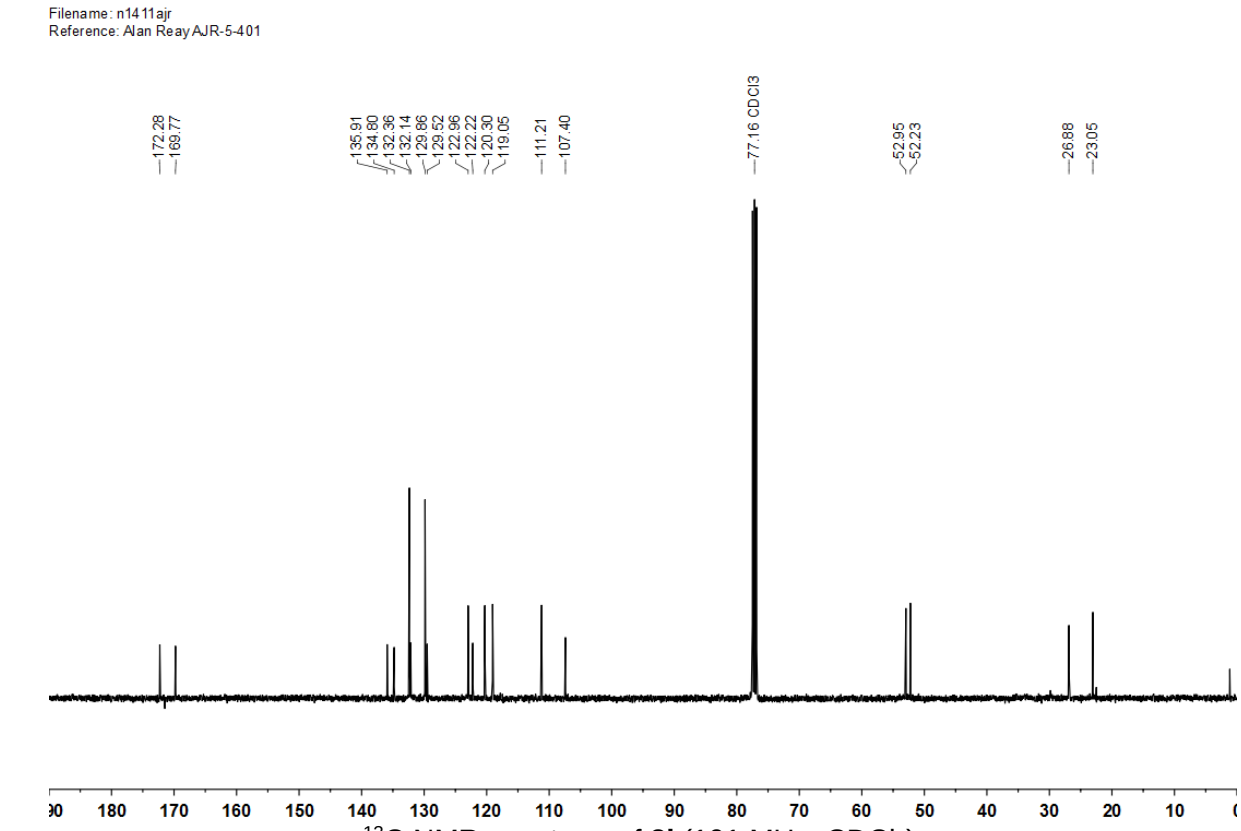


^{19}F NMR spectrum of **3h** (376 MHz, $(CD_3)_2SO$).

Methyl (2*S*)-3-[2-(4-bromophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3i)

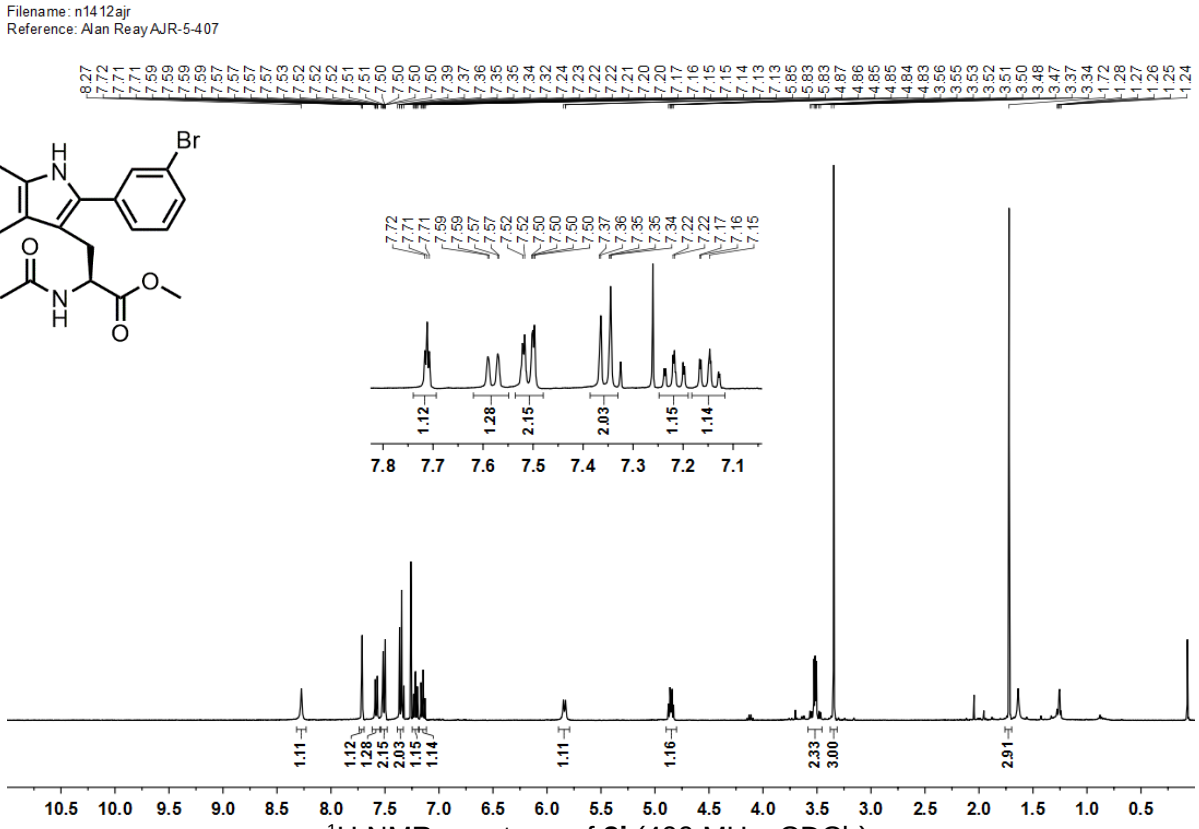


^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$).

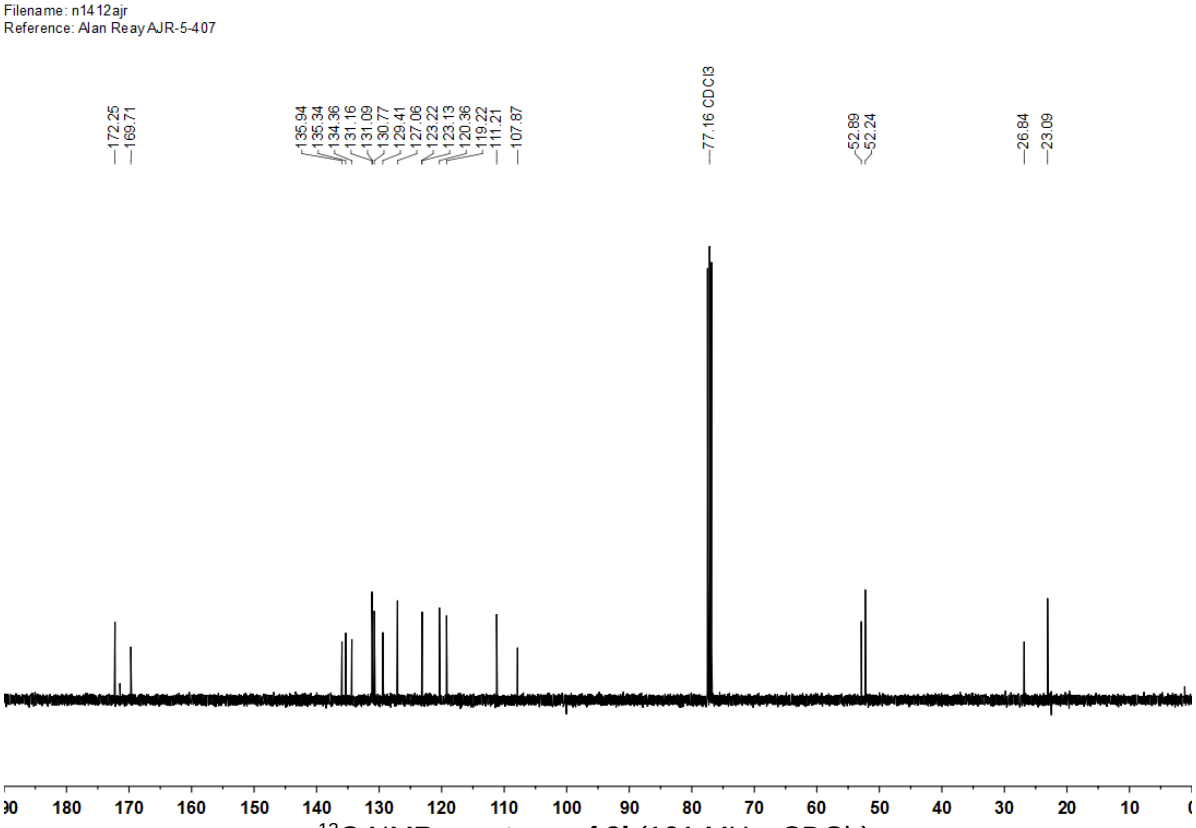


^{13}C NMR spectrum of **3i** (101 MHz, $CDCl_3$).

Methyl (2*S*)-3-[2-(3-bromophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3j)

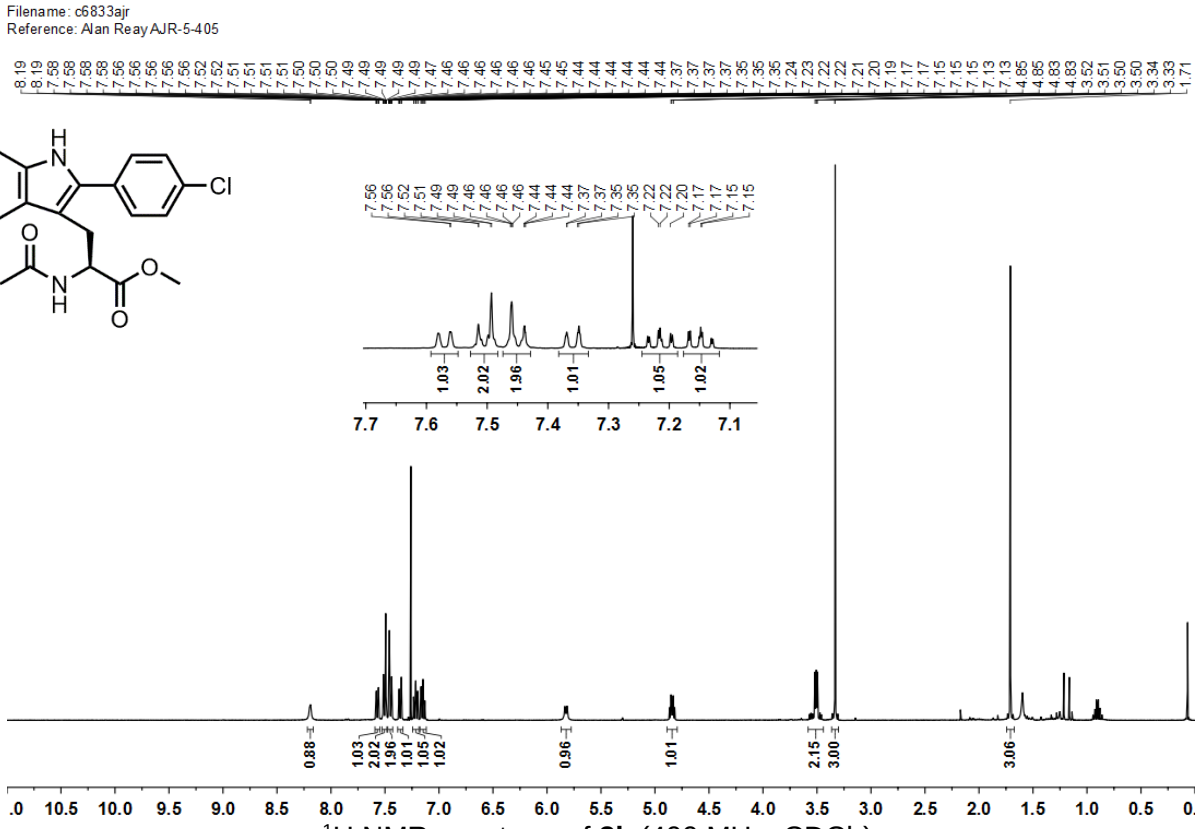


^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$).

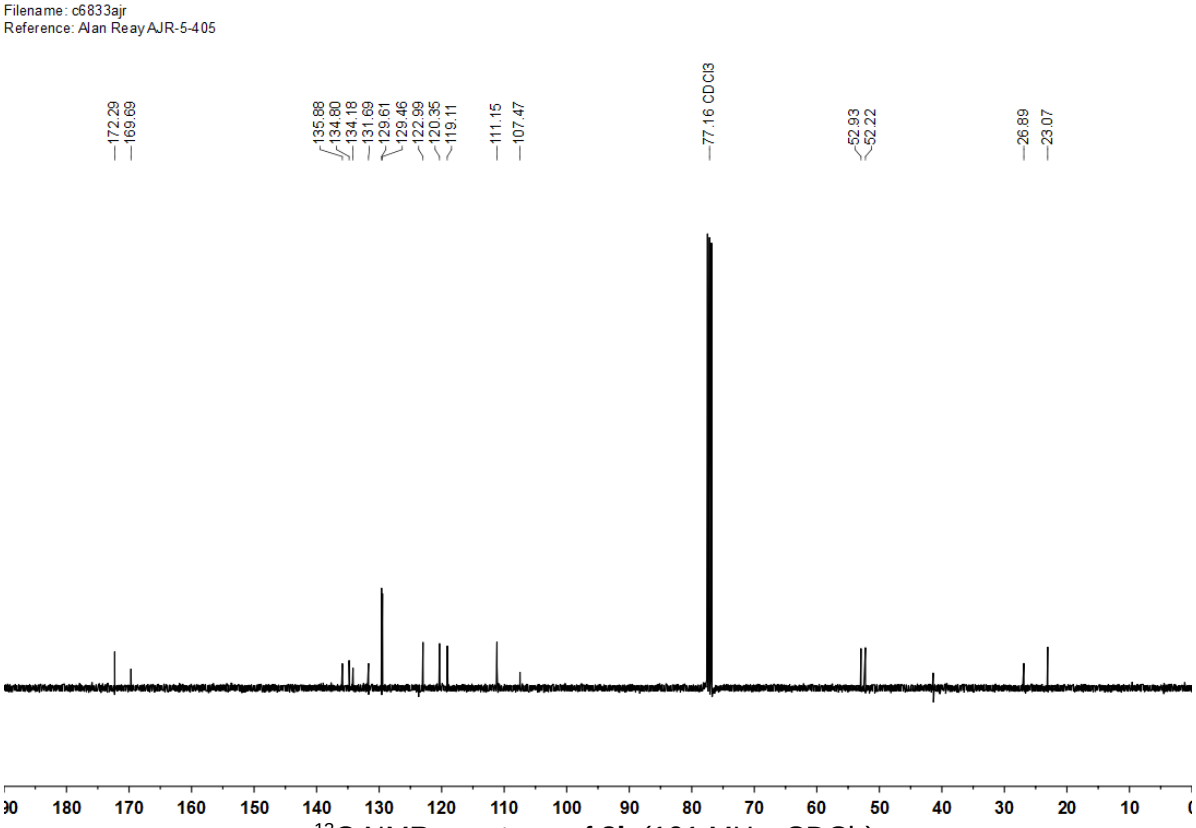


^{13}C NMR spectrum of **3j** (101 MHz, $CDCl_3$).

Methyl (2*S*)-3-[2-(4-chlorophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3k)

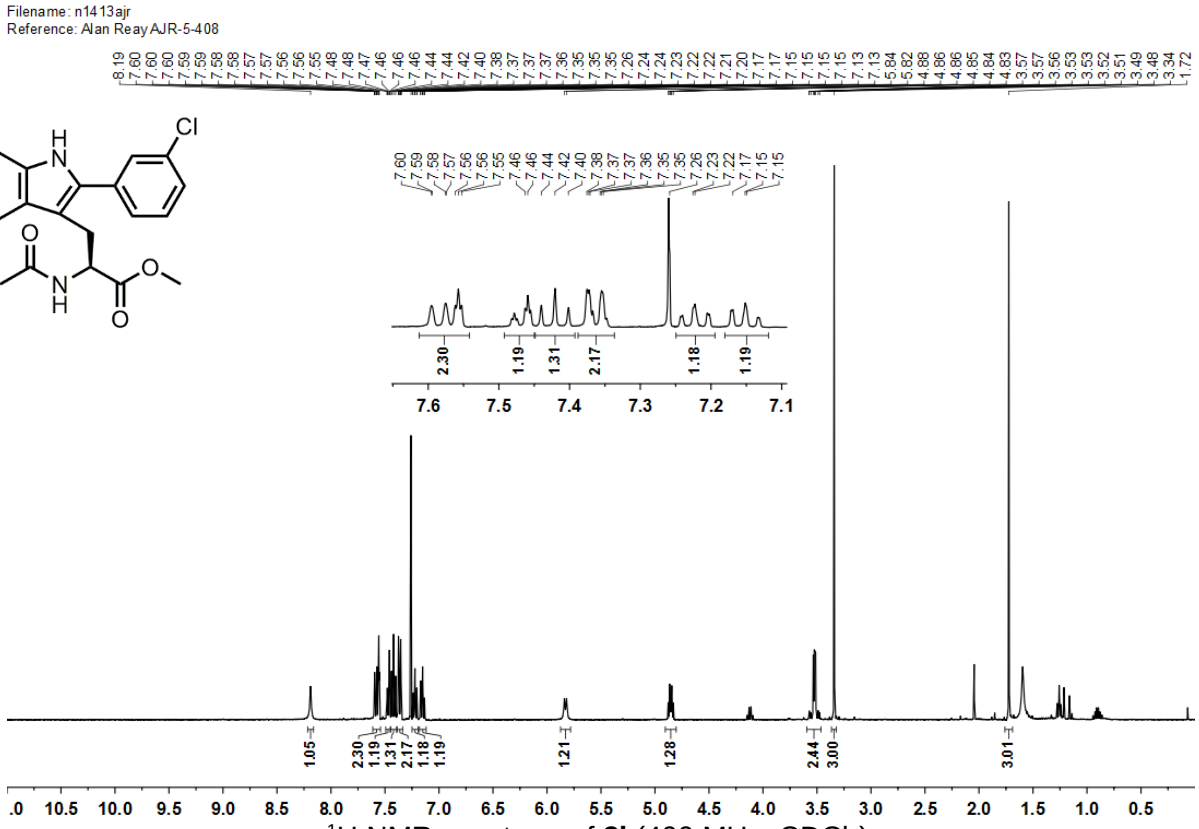


^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$).

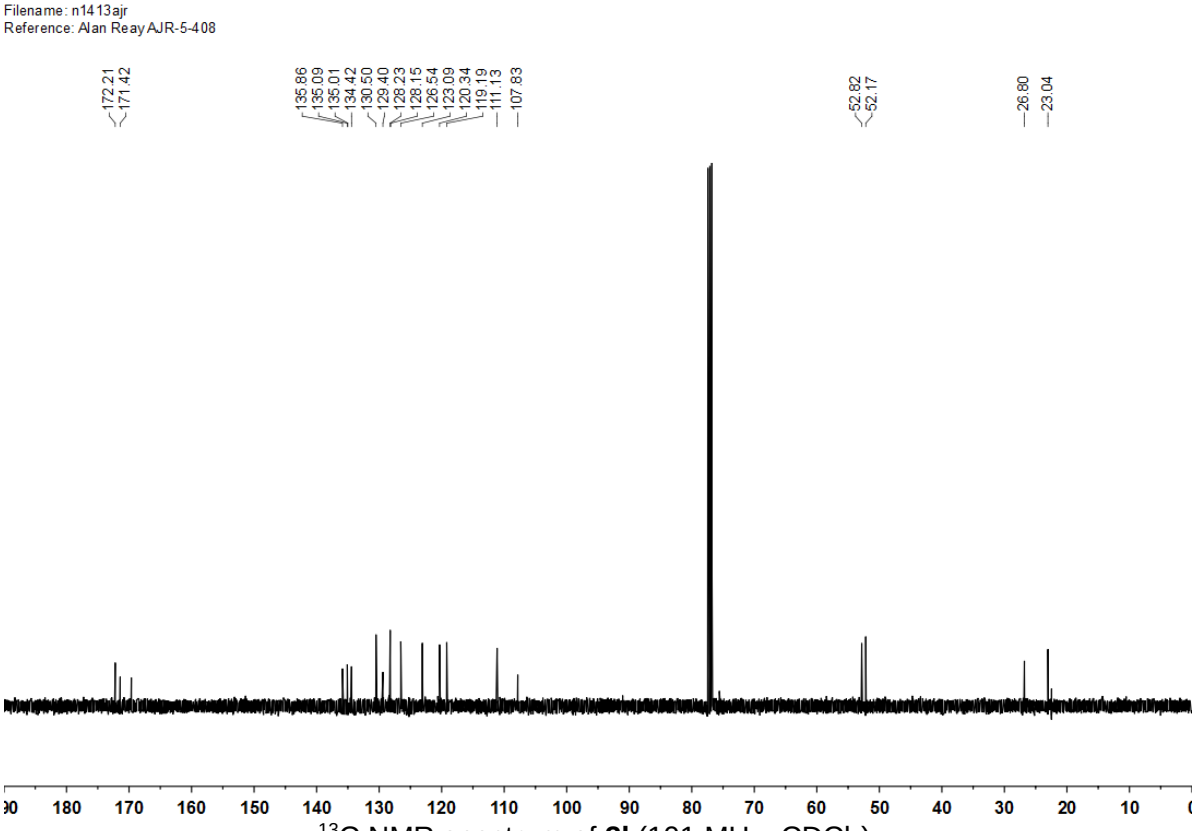


^{13}C NMR spectrum of **3k** (101 MHz, $CDCl_3$).

Methyl (2*S*)-3-[2-(3-chlorophenyl)-1*H*-indol-3-yl]-2-acetamidopropanoate (3l)

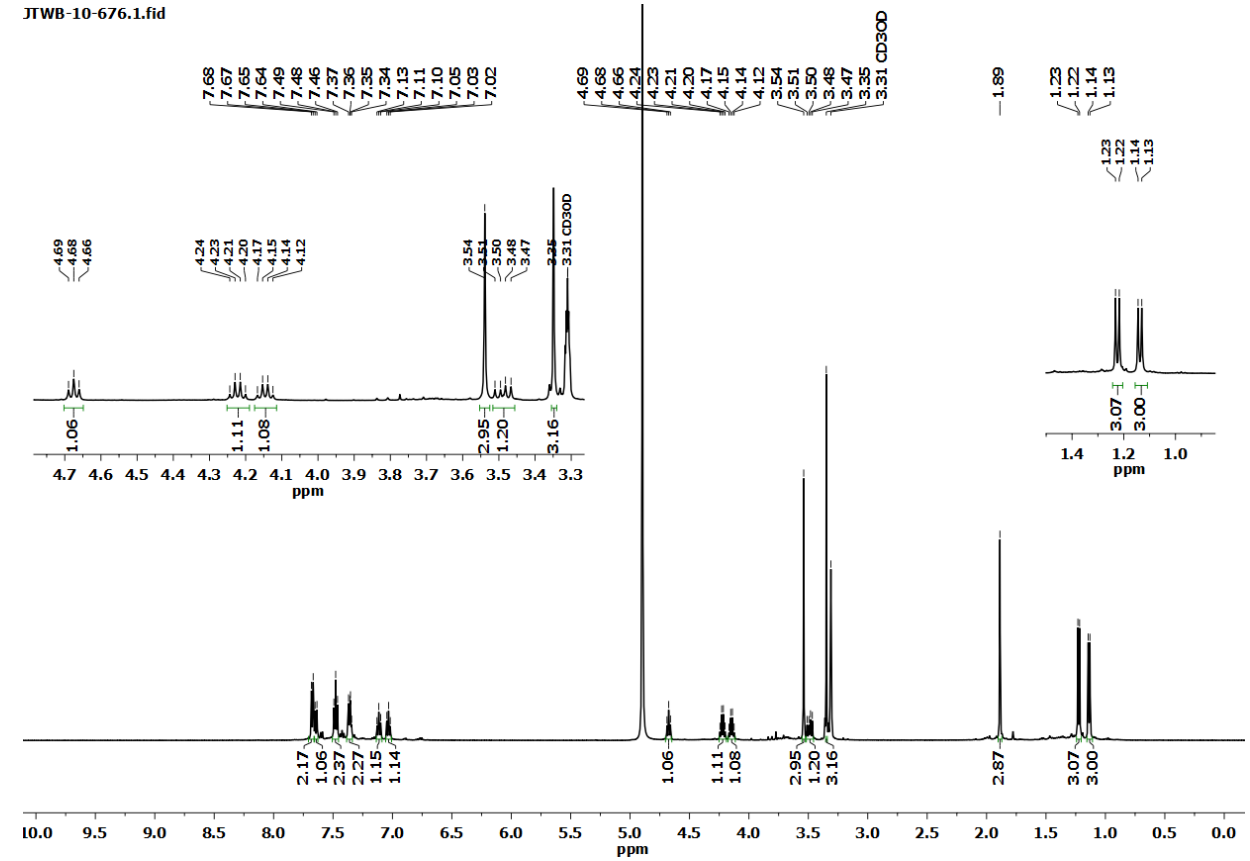


^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$).

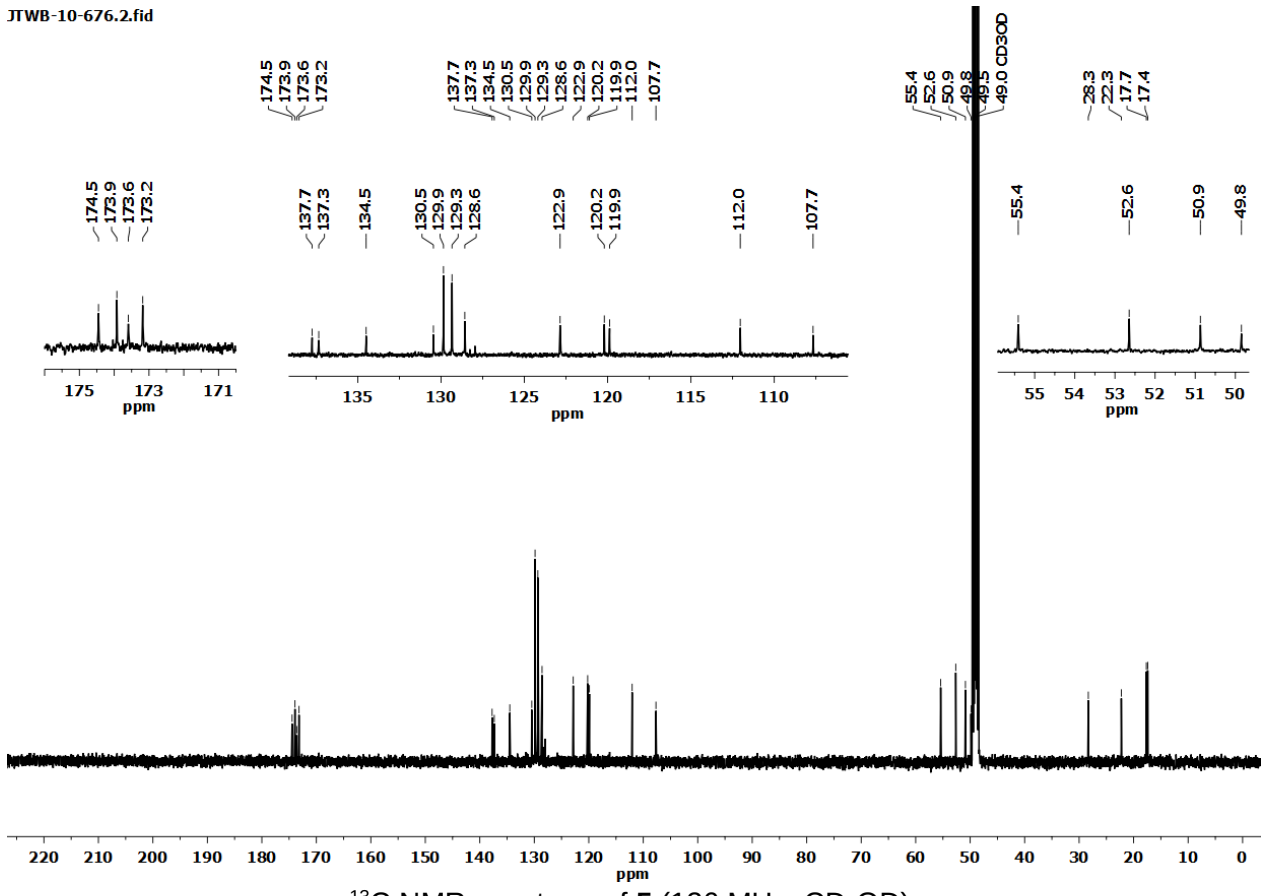


^{13}C NMR spectrum of **3l** (101 MHz, $CDCl_3$).

Ac-AlaTrpPhAla-OMe (5)

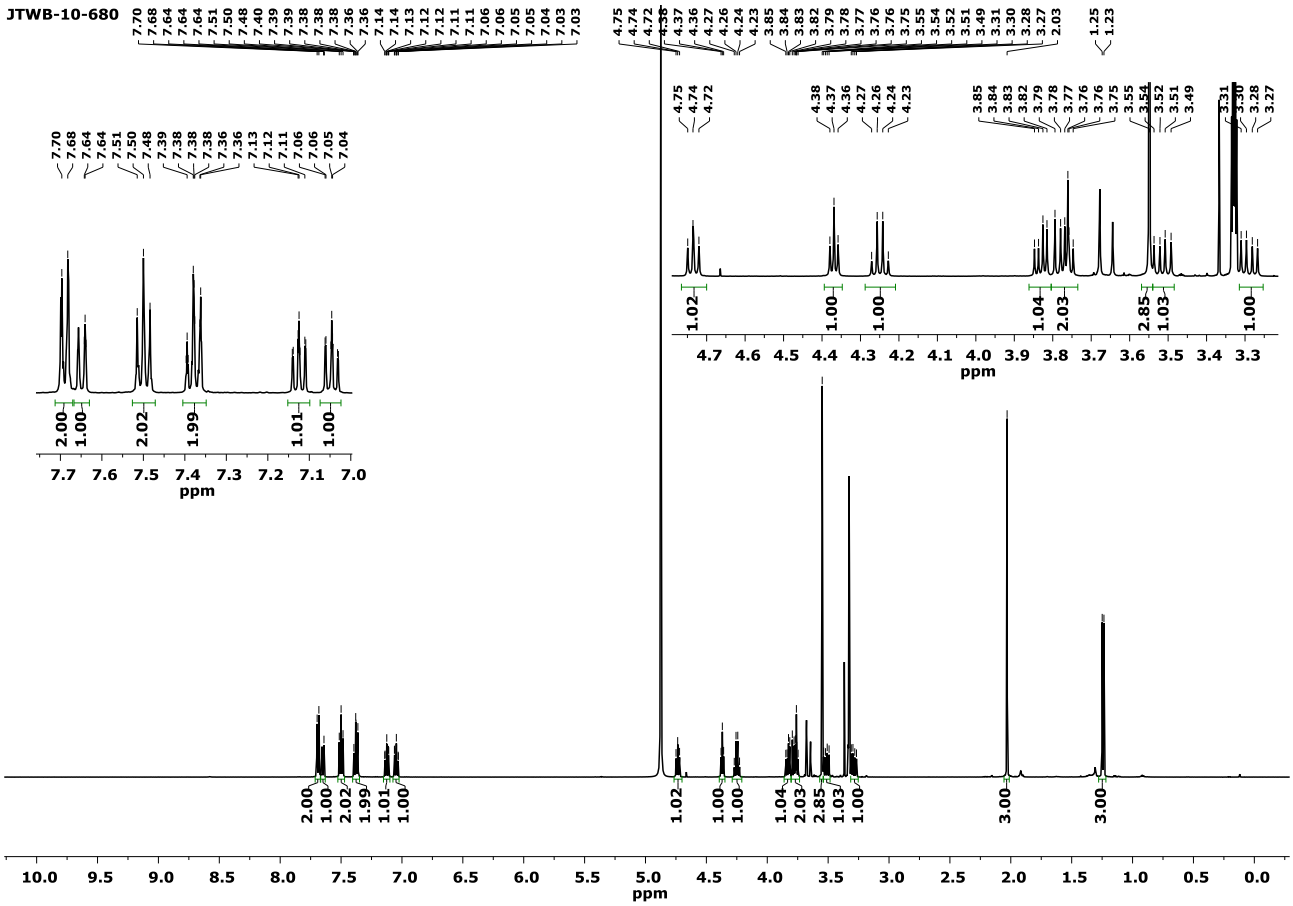


^{1}H NMR spectrum of **5** (500 MHz, CD_3OD).

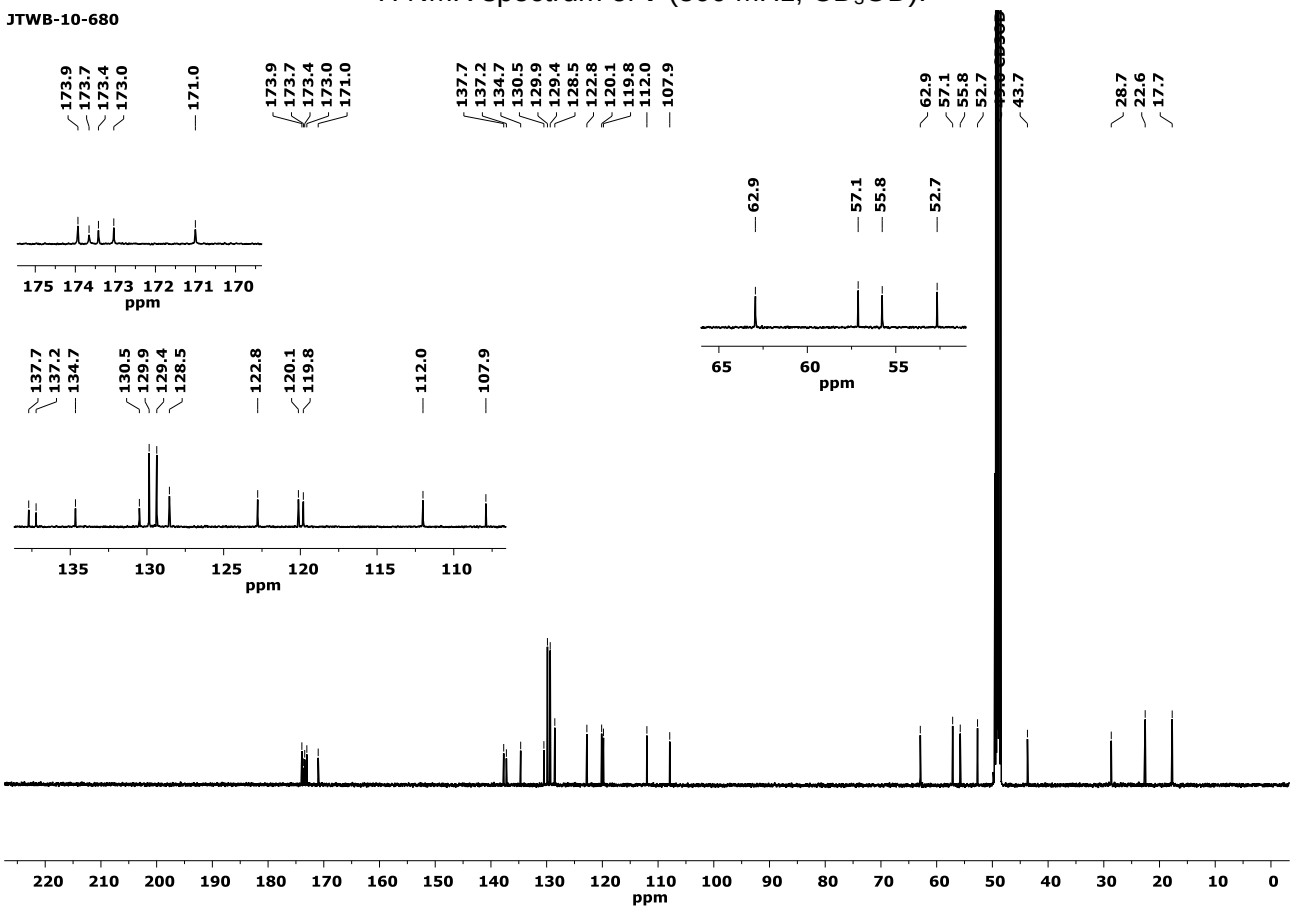


^{13}C NMR spectrum of **5** (126 MHz, CD_3OD).

Ac-SerGlyTrpPhAla-OMe (7)



^{1}H NMR spectrum of **7** (500 MHz, CD_3OD).



^{13}C NMR spectrum of **7** (126 MHz, CD_3OD).

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