Supporting Information

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

Alan J. Reay, L. Anders. Hammarback, Joshua T. W. Bray, Thomas Sheridan, David Turnbull, Adrian C. Whitwood and Ian J. S. Fairlamb*

Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.

* Email: ian.fairlamb@york.ac.uk; Tel: +0044 (0)1904 324091.

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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 (Rf) 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 [α]_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 (^1H) 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 (^13C) 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 (^11B) spectra were recorded at 128 MHz and obtained with ^1H decoupling. Chemical shifts are externally referenced to BF_3·OEt_2 and given to one decimal place.

Fluorine-19 (^19F) spectra were recorded at 376 MHz and obtained with ^1H 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\(_2\)O, 2 eq.) before being cooled to 0 °C with stirring. A 90% solution of tert-butyl nitrite (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\(_2\)O was added to precipitate the aryldiazonium tetrafluoroborate which was collected by filtration through a glass sinter and washed with further Et\(_2\)O 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 (2S)-2-amino-3-(1H-indol-3-yl)propanoate hydrochloride and methyl (2S)-2-acetamido-3-(1H-indol-3-yl)propanoate (1) have been previously reported.

Benzenediazonium tetrafluoroborate (2a)

![Image of 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\(_3\))\(_2\)SO, 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\(_3\))\(_2\)SO, δ): 140.8, 132.7, 131.2, 116.1; \(^{11}\)B NMR (128 MHz, (CD\(_3\))\(_2\)SO, δ): −2.3; \(^{19}\)F NMR (376 MHz, (CD\(_3\))\(_2\)SO, δ): −148.1 (m, \(^1J_{F-10B}, 4F\)), −148.1 (m, \(^1J_{F-11B}, 4F\)); ESI-MS m/z (ion, %): 105 ([M−BF\(_4^−\)], 100); ESI-HRMS m/z: 105.0480 [M−BF\(_4^−\)] (C\(_6\)H\(_5\)N\(_2\) requires 105.0447).

The analytical data obtained was in accordance with the literature.

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

![Image of 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.\(^6\) 101–102 °C); \(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO, δ): 8.58–8.51 (m, 2H), 7.83–7.75 (m, 2H), 2.57 (s, 3H); \(^13\)C NMR (101 MHz, (CD\(_3\))\(_2\)SO, δ): 153.94, 132.7, 131.8, 112.0, 22.4; \(^{11}\)B NMR (128 MHz, (CD\(_3\))\(_2\)SO, δ): −2.3; \(^{19}\)F NMR (376 MHz, (CD\(_3\))\(_2\)SO, δ): −148.1 (m, \(^1J_{F-10B}, 4F\)), −148.1 (m, \(^1J_{F-11B}, 4F\)); ESI-MS m/z (ion, %): 119 ([M−BF\(_4^−\)], 100); ESI-HRMS m/z: 119.0603 [M−BF\(_4^−\)] (C\(_7\)H\(_7\)N\(_2\) requires 119.0604).

The analytical data obtained was in accordance with the literature.

4-tert-butybenzene-1-diazonium tetrafluoroborate (2c)

![Image of 4-tert-butybenzene-1-diazonium tetrafluoroborate (2c)]

Synthesised using general procedure A from 4-tert-butyIaniline (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.\(^5\) 91 °C); \(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO, δ): 8.62–8.56 (m, 2H), 8.06–8.00 (m, 2H), 1.35 (s, 9H); \(^13\)C NMR (101 MHz, (CD\(_3\))\(_2\)SO, δ): 165.5, 132.8, 128.5, 112.2, 36.5, 30.2; \(^{11}\)B NMR (128 MHz, (CD\(_3\))\(_2\)SO, δ): −2.3; \(^{19}\)F NMR (376 MHz, (CD\(_3\))\(_2\)SO, δ): −148.1 (m, \(^1J_{F-10B}, 4F\)), −148.1 (m, \(^1J_{F-11B}, 4F\)); ESI-MS m/z (ion, %): 161 ([M−BF\(_4^−\)], 100); ESI-HRMS m/z: 161.0603 [M−BF\(_4^−\)] (C\(_{10}\)H\(_{13}\)N\(_2\) requires 161.0604). The analytical data obtained was in accordance with the literature.\(^7\)
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); ¹H NMR (400 MHz, (CD₃)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); ¹³C NMR (101 MHz, (CD₃)₂SO, δ): 151.5, 136.4, 133.5, 130.8, 129.6, 129.0, 128.0, 113.3; ¹¹B NMR (128 MHz, (CD₃)₂SO, δ): −2.3; ¹⁹F NMR (376 MHz, (CD₃)₂SO, δ): −148.1 (m, ¹J_F−¹⁰B, 4F), −148.1 (m, ¹J_F−¹¹B, 4F); EI-MS m/z (ion, %): 154 ([M−BF₄−N₂]⁺, 100); EI-HRMS m/z: 154.0782 [M−BF₄−N₂]⁺ (C₁₂H₁₀N₂ 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; ¹H NMR (400 MHz, (CD₃)₂SO, δ): 7.40 (s, 2H), 2.57 (s, 6H), 2.39 (s, 3H); ¹³C NMR (101 MHz, (CD₃)₂SO, δ): 153.4, 143.7, 130.7, 112.0, 22.1, 18.1; ¹¹B NMR (128 MHz, (CD₃)₂SO, δ): −2.3; ¹⁹F NMR (376 MHz, (CD₃)₂SO, δ): −148.1 (m, ¹J_F−¹⁰B, 4F), −148.1 (m, ¹J_F−¹¹B, 4F); ESI-MS m/z (ion, %): 147 ([M−BF₄]⁺, 100); ESI-HRMS m/z: 147.0916 [M−BF₄]⁺ (C₉H₁₁N₂ 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); ¹H NMR (400 MHz, (CD₃)₂SO, δ): 8.64–8.58 (m, 2H), 7.51–7.45 (m, 2H), 4.04 (s, 3H); ¹³C NMR (101 MHz, (CD₃)₂SO, δ): 168.8, 136.2, 117.3, 103.4, 57.5; ¹¹B NMR (128 MHz, (CD₃)₂SO, δ): −2.3; ¹⁹F NMR (376 MHz, (CD₃)₂SO, δ): −148.1 (m, ¹J_F−¹⁰B, 4F), −148.1 (m, ¹J_F−¹¹B, 4F); ESI-MS m/z (ion, %): 135 ([M−BF₄]⁺, 100); ESI-HRMS m/z: 135.0548 [M−BF₄]⁺ (C₇H₇N₂O requires 135.0553).

The analytical data obtained was in accordance with the literature.⁶,¹¹
4-Phenoxybenzene-1-diazonium tetrafluoroborate (2g)

![Chemical Structure]

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); ¹H NMR (400 MHz, (CD₃)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); ¹³C NMR (101 MHz, (CD₃)₂SO, δ): 167.1, 152.7, 136.6, 131.0, 126.9, 121.0, 118.7, 106.0; ¹¹B NMR (128 MHz, (CD₃)₂SO, δ): −2.3; ¹⁹F NMR (376 MHz, (CD₃)₂SO, δ): −148.1 (m, J_F–¹⁰B, 4F), −148.1 (m, J_F–¹¹B, 4F); ESI-MS m/z (ion, %): 197 ([M–BF₄]⁺, 100); ESI-HRMS m/z: 197.0706 [M–BF₄]⁺ (C₁₂H₉N₂O requires 197.0709).

The analytical data obtained was in accordance with the literature.

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

![Chemical Structure]

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); ¹H NMR (400 MHz, (CD₃)₂SO, δ): 8.83–8.77 (m, 2H), 7.93–7.85 (m, 2H); ¹³C NMR (101 MHz, (CD₃)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); ¹¹B NMR (128 MHz, (CD₃)₂SO, δ): −2.3; ¹⁹F NMR (376 MHz, (CD₃)₂SO, δ): −87.1, −148.1 (m, J_F–¹⁰B, 4F), −148.1 (m, J_F–¹¹B, 4F); ESI-MS m/z (ion, %): 123 ([M–BF₄]⁺, 100); ESI-HRMS m/z: 123.0353 [M–BF₄]⁺ (C₆H₄FN₂ requires 123.0353). The analytical data obtained was in accordance with the literature.

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

![Chemical Structure]

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.); ¹H NMR (400 MHz, (CD₃)₂SO, δ): 8.60–8.55 (m, 2H), 8.29–8.24 (m, 2H); ¹³C NMR (101 MHz, (CD₃)₂SO, δ): 136.6, 134.5, 134.0, 115.2; ¹¹B NMR (128 MHz, (CD₃)₂SO, δ): −2.3; ¹⁹F NMR (376 MHz, (CD₃)₂SO, δ): −148.1 (m, J_F–¹⁰B, 4F), −148.1 (m, J_F–¹¹B, 4F); ESI-MS m/z (ion, %): 183 ([M–BF₄]⁺, 100); ESI-HRMS m/z: 182.9556 [M–BF₄]⁺ (C₆H₄BrN₂ requires 182.9552).

The analytical data obtained was in accordance with the literature.
3-Bromobenzene-1-diazonium tetrafluoroborate (2j)

\[
\text{Br} \quad \text{N}_2^+ \quad \text{BF}_4^- 
\]

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\(_3\))\(_2\)SO, \(\delta\)): 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); \(^1^C\) NMR (101 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): 143.8, 134.3, 132.8, 131.9, 122.3, 117.8; \(^1^B\) NMR (128 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): −2.3; \(^1^9^F\) NMR (376 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): −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\(_6\)H\(_4\)BrN\(_2\) requires 182.9552).

The analytical data obtained was in accordance with the literature.\(^7\)

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

\[
\text{Cl} \quad \text{N}_2^+ \quad \text{BF}_4^- 
\]

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\(_3\))\(_2\)SO, \(\delta\)): 8.73–8.64 (m, 2H), 8.15–8.07 (m, 2H); \(^1^C\) NMR (101 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): 146.5, 134.4, 131.6, 114.8; \(^1^B\) NMR (128 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): −2.3; \(^1^9^F\) NMR (376 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): −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\(_6\)H\(_4\)ClN\(_2\) requires 139.0058).

The analytical data obtained was in accordance with the literature.\(^9\)

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

\[
\text{Cl} \quad \text{N}_2^+ \quad \text{BF}_4^- 
\]

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\(_3\))\(_2\)SO, \(\delta\)): 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); \(^1^C\) NMR (101 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): 141.1, 134.6, 132.9, 131.7, 131.6, 117.8; \(^1^B\) NMR (128 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): −2.3; \(^1^9^F\) NMR (376 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): −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\(_6\)H\(_4\)ClN\(_2\) 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-aminobenzotri fluoride (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.\textsuperscript{12} 105–106 °C); \textsuperscript{1}H NMR (400 MHz, (CD\textsubscript{3})\textsubscript{2}SO, δ): 8.91 (d, J = 8.5 Hz, 2H), 8.42 (d, J = 8.5 Hz, 2H); \textsuperscript{13}C NMR (101 MHz, (CD\textsubscript{3})\textsubscript{2}SO, δ): 113.8, 128.3, 122.3 (q, J = 274.0 Hz), 121.3, 110.5; \textsuperscript{11}B NMR (128 MHz, (CD\textsubscript{3})\textsubscript{2}SO, δ): −2.3; \textsuperscript{19}F NMR (376 MHz, (CD\textsubscript{3})\textsubscript{2}SO, δ): −148.1 (m, J\textsubscript{F–10B}, 4F), 148.1 (m, J\textsubscript{F–11B}, 4F); ESI-MS m/z (ion, %): 173 ([M−BF\textsubscript{4}]\textsuperscript{+}, 100); ESI-HRMS m/z: 173.0325 [M−BF\textsubscript{4}]\textsuperscript{+} (C\textsubscript{7}H\textsubscript{4}F\textsubscript{3}N\textsubscript{2} requires 173.0321).

The analytical data obtained was in accordance with the literature.\textsuperscript{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.\textsuperscript{6} 155 °C dec.); \textsuperscript{1}H NMR (400 MHz, (CD\textsubscript{3})\textsubscript{2}SO, δ): 8.95–8.90 (m, 2H), 8.75–8.69 (m, 2H); \textsuperscript{13}C NMR (101 MHz, (CD\textsubscript{3})\textsubscript{2}SO, δ): 153.3, 134.6, 126.1, 121.9; \textsuperscript{11}B NMR (128 MHz, (CD\textsubscript{3})\textsubscript{2}SO, δ): −2.3; \textsuperscript{19}F NMR (376 MHz, (CD\textsubscript{3})\textsubscript{2}SO, δ): −148.1 (m, J\textsubscript{F–10B}, 4F), −148.1 (m, J\textsubscript{F–11B}, 4F); ESI-MS m/z (ion, %): 150 ([M−BF\textsubscript{4}]\textsuperscript{+}, 100); ESI-HRMS m/z: 150.0304 [M−BF\textsubscript{4}]\textsuperscript{+} (C\textsubscript{6}H\textsubscript{4}N\textsubscript{3}O\textsubscript{2} requires 150.0298).

The analytical data obtained was in accordance with the literature.\textsuperscript{6}
Methyl (2S)-2-acetamido-3-(2-phenyl-1H-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); [α]_D = +49.1 (c 0.42, CHCl₃ – lit.¹³a +47.3, c 0.1, CHCl₃); M.P. 82–83 ºC (lit.¹⁴ 85–86 ºC); ¹H NMR (400 MHz, CDCl₃, 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). ¹³C NMR (101 MHz, CDCl₃, 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/Et₂O (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 (2S)-3-[2-(4-methylphenyl)-1H-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), 3.33 (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.

Methyl (2S)-3-[2-(4-tert-butylphenyl)-1H-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, v/v); $[α]_D = +68.6$ (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$_2$O$_3$ 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 $(2S)$-2-acetamido-3-[2-(4-phenylphenyl)-1H-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); $[\alpha]_D^\circ = +94.8$ (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$_2$O$_3$ requires 413.1860); IR (solid-state, ATR, cm$^{-1}$): 3406 (w), 3378 (w), 1746 (m), 1655 (s), 1460 (m), 1450 (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 $(2S)$-2-acetamido-3-[2-(2,4,6-trimethylphenyl)-1H-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); $[\alpha]_D^\circ = +22.2$ (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$_2$Cl$_2$. 
Methyl (2S)-2-acetamido-3-[2-(4-methoxyphenyl)-1H-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.).

RF 0.15 (petrol/EtOAc, 1:1, v/v); [α]D = +35.1 (c 0.10, CHCl3); lit.13a 34.9 c 0.10, CHCl3; M.P. 200–203 °C; 1H NMR (400 MHz, CDCl3, 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); 13C NMR (101 MHz, CDCl3, 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 (2S)-2-acetamido-3-[2-(4-phenoxyphenyl)-1H-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.).

RF 0.29 (petrol/EtOAc, 1:1.5, v/v); [α]D = +85.3 (c 0.10, CHCl3); M.P. 72–74 °C; 1H NMR (400 MHz, CDCl3, 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); 13C NMR (101 MHz, CDCl3, 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]+ (C26H24N2O4 requires 451.1628); IR (solid-state, ATR, cm–1): 3266 (w, br), 3257 (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 (2S)-3-[2-(4-fluorophenyl)-1H-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.).

Rf 0.23 (petrol/EtOAc, 1:1, v/v); [α]D = +43.1° (c 0.11, CHCl3; lit.13a 54.4 c 0.10, CHCl3); M.P. 212–216 °C dec.; 1H NMR (400 MHz, CDCl3, 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); 13C NMR (101 MHz, CDCl3, δ): 172.3, 169.7, 162.6 (d, 1JCF = 249.0 Hz), 135.8, 135.1, 130.2 (d, 3JCF = 8.0 Hz), 129.5, 129.4 (d, 4JCF = 3.5 Hz), 122.8, 120.3, 119.0, 116.3 (d, 2JCF = 21.5 Hz), 111.1, 107.0, 52.9, 52.2, 26.8, 23.1; 19F NMR (376 MHz, CDCl3, δ): −112.8—112.9 (m).

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

Methyl (2S)-3-[2-(4-bromophenyl)-1H-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.).

Rf 0.31 (petrol/EtOAc, 1:1, v/v); [α]D = +44.0° (c 0.10, CHCl3); M.P. 74–75 °C dec.; 1H NMR (400 MHz, CDCl3, 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); 13C NMR (101 MHz, CDCl3, 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]+ (C20H19BrN2O3 requires 437.0471).

The analytical data obtained was in accordance with the literature.15
Methyl (2S)-3-[2-(3-bromophenyl)-1H-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 (SiO₂, petrol/EtOAc, 1:1, v/v) afforded the title compound as a brown solid (55 mg, 69%).

Rf 0.28 (petrol/EtOAc, 1:1, v/v); [α]₀ = +50.5 (c 0.10, CHCl₃); M.P. 82–84 °C dec.; ¹H NMR (400 MHz, CDCl₃, δ): 8.27 (br s, 1H), 7.71 (t, J = 1.5 Hz, 1H), 7.58 (ddd, 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 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); ¹³C NMR (101 MHz, CDCl₃, 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]+ (C₂₀H₂₀BrN₂O₃ 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), 1010 (m), 787 (m), 741 (s), 687 (s), 594 (m), 507 (m), 437 (m); UV–vis (DMSO, nm): λmax 312 (ε = 19398 mol dm⁻³ cm⁻¹).

Methyl (2S)-3-[2-(4-chlorophenyl)-1H-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 (SiO₂, 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 (SiO₂, petrol/EtOAc, 1:1, v/v) afforded the title compound as a brown solid (57 mg, 80%).

Rf 0.39 (petrol/EtOAc, 1:1, v/v); [α]₀ = +45.6 (c 0.10, CHCl₃); M.P. 202 °C dec.; ¹H NMR (400 MHz, CDCl₃, δ): 8.19 (br s, 1H), 7.57 (dt, J = 8.0, 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); ¹³C NMR (101 MHz, CDCl₃, 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]+ (C₂₀H₂₀ClN₂O₃ requires 371.1157).
Crystals suitable for X-ray diffraction were grown by slow diffusion from a solution of CH$_2$Cl$_2$.

The analytical data obtained was in accordance with the literature.$^{15}$

**Methyl (2S)-3-[2-(3-chlorophenyl)-1H-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%).

$^1$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, $J = 8.0, 5.5$ 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$_2$NaO$_3$ requires 393.0976); IR (solid-state, ATR, cm$^{-1}$): 3271 (w), 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): $\lambda_{\text{max}}$ 312 ($\epsilon = 15639$ mol dm$^{-1}$ 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\textsubscript{max} 300 nm, [\alpha]_D: +23.1 (c 0.0017, MeOH; [\alpha]_D of peptide 4 = +20.3, c 0.005, MeOH), ν\textsubscript{max}/cm\(^{-1}\) (ATR) 3270.5, 3055.5, 2981.1, 2466.8, 2419.4, 2074.33, 1751.03, 1546.9, 1452.9, 1205.27, 973.5, 745.9, 698.0, 609.6, 489.6; \(^1\)H NMR (500 MHz, CD\textsubscript{3}OD, 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), 1.13 (d, J = 7.0 Hz, 3H); \(^{13}\)C NMR (126 MHz, CD\textsubscript{3}OD, 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\textsubscript{f} = 0.44 (6% MeOH/CH\textsubscript{2}Cl\textsubscript{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)\textsubscript{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\textsubscript{2}Cl\textsubscript{2}) to give an off white solid (10.8 mg, 45%).

λ\textsubscript{max} 304 nm, [\alpha]_D: +33.1 (c 0.005, MeOH; [\alpha]_D of peptide 6 = +28.5, c 0.005, MeOH), ν\textsubscript{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\textsubscript{3}OD, δ): 7.70-7.67 (m, 2H), 7.64 (dd, J = 8.0, 1.0, 1.0 Hz, 1H), 7.52-7.47 (m, 2H), 7.40-7.35 (m, 2H), 7.40 (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\textsubscript{3}OD, δ) 174.5, 173.9, 173.6, 173.2, 137.9, 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\textsubscript{f} = 0.13 (6% MeOH/CH\textsubscript{2}Cl\textsubscript{2}).
4. X-Ray Crystallographic Data

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

| Compound reference     | ijsf1413 |
|------------------------|----------|
| Chemical formula       | C_{20}H_{20}N_{2}O_{3} |
| Formula mass           | 336.38   |
| Crystal system         | Trigonal |
| a / Å                  | 21.2602(5) |
| b / Å                  | 21.2602(5) |
| c / Å                  | 10.1814(3) |
| α / °                  | 90        |
| β / °                  | 90        |
| γ / °                  | 120       |
| Unit cell volume / Å³  | 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 R₁ values (I > 2σ(I)) | 0.0363 |
| Final wR(F²) values (I > 2σ(I)) | 0.0863 |
| Final R₁ values (all data) | 0.0404 |
| Final wR(F²) values (all data) | 0.0901 |

CCDC number: 1053549 (compound 3a)
Methyl (2S)-2-acetamido-3-[2-(2,4,6-trimethylphenyl)-1H-indol-3-yl]propanoate (3e)

| Compound reference | ijsf1488 |
|--------------------|----------|
| Chemical formula   | C₂₃H₂₆N₂O₃ |
| Formula mass       | 378.46   |
| Crystal system     | Monoclinic |
| a / Å              | 8.7152(3) |
| b / Å              | 13.5902(4) |
| c / Å              | 8.7625(3) |
| α / °              | 90       |
| β / °              | 100.507(3) |
| γ / °              | 90       |
| Unit cell volume / Å³ | 1020.44(6) |
| Temperature / K    | 110.05(10) |
| Space group        | P2₁      |
| No. of formula units per unit cell, Z | 2 |
| No. of reflections measured | 6691 |
| No. of independent reflections | 3634 |
| R₁ values (I > 2σ(I)) | 0.0256 |
| Final R₁ values (all data) | 0.0334 |
| Final wR(F²) values (I > 2σ(I)) | 0.0865 |
| Final wR(F²) values (all data) | 0.0350 |
| Final wR(F²) values (all data) | 0.0882 |

CCDC number: 1053551 (compound 3e)
Methyl (2S)-3-[2-(4-chlorophenyl)-1H-indol-3-yl]-2-acetamidopropanoate (3k)

| Compound reference       | ijsf1487                        |
|--------------------------|---------------------------------|
| Chemical formula         | C_{20}H_{19}ClN_{2}O_{3}        |
| Formula mass             | 370.82                          |
| Crystal system           | Trigonal                        |
| a / Å                    | 20.7806(2)                      |
| b / Å                    | 20.7806(2)                      |
| c / Å                    | 11.18107(13)                    |
| α / °                    | 90                              |
| β / °                    | 90                              |
| γ / °                    | 120                             |
| Unit cell volume / Å³    | 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.\textsuperscript{16}

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

Ethyl acetate: 10 mL

Celite: 10 g

Sat. aq. NaHCO\textsubscript{3}: 10 mL

MgSO\textsubscript{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\textsuperscript{a} | PhI(OAc)\textsubscript{2} / PhB(OH)\textsubscript{2} with Cu\textsuperscript{II} | [PhMesI]OTf | [PhN\textsubscript{2}]BF\textsubscript{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 |

\textsuperscript{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. $^1$H 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.

![Average Conversion of Arylated Product](image)

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

| $k_{obs}$ / 10$^{-5}$ | Run 1 | Run 2 | Run 3 |
|----------------------|-------|-------|-------|
| mol dm$^3$ s$^{-1}$   | 1.86  | 2.13  | 2.15  |
| mol dm$^{-3}$ s$^{-1}$ | 1.86  | 2.13  | 2.15  |
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.

![Conversion vs Time](image)

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$_3$CN)$_2$ simply involved substituting the Pd(OAc)$_2$ within the general procedure.
7. Representative NMR Spectroscopic Data

Benzenediazonium tetrafluoroborate (2a)

\[
\text{N}_2^+ \cdot \text{BF}_4
\]

\[1^H\text{ NMR spectrum of 2a (400 MHz, (CD}_3\text{)}_2\text{SO).}\]

\[13^C\text{ NMR spectrum of 2a (101 MHz, (CD}_3\text{)}_2\text{SO).}\]
4-Methylbenzene-1-diazonium tetrafluoroborate (2b)

$\text{H NMR spectrum of 2b (400 MHz, (CD}_3)_2\text{SO).}$

$\text{C NMR spectrum of 2b (101 MHz, (CD}_3)_2\text{SO).}$
4-tert-butylbenzene-1-diazonium tetrafluoroborate (2c)

$\text{H NMR spectrum of 2c (400 MHz, (CD}_3\text{)}_2\text{SO).}$

$\text{C NMR spectrum of 2c (101 MHz, (CD}_3\text{)}_2\text{SO).}$
4-Phenylbenzene-1-diazonium tetrafluoroborate (2d)

$\text{Ph}^+ \text{N}_2^- \text{BF}_4^-$

$^1\text{H}$ NMR spectrum of 2d (400 MHz, (CD$_3$)$_2$SO).

$^1\text{C}$ NMR spectrum of 2d (101 MHz, (CD$_3$)$_2$SO).
2,4,6-Trimethylbenzene-1-diazonium tetrafluoroborate (2e)

$\text{H NMR spectrum of 2e (400 MHz, (CD}_3\text{)_2SO).}$

$\text{C NMR spectrum of 2e (101 MHz, (CD}_3\text{)_2SO).}$
4-Methoxybenzene-1-diazonium tetrafluoroborate (2f)

H NMR spectrum of 2f (400 MHz, (CD₃)₂SO).

C NMR spectrum of 2f (101 MHz, (CD₃)₂SO).
4-Phenoxybenzene-1-diazonium tetrafluoroborate (2g)

\[ \text{H NMR spectrum of 2g (400 MHz, (CD}_3\text{)}_2\text{SO).} \]

\[ \text{^13C NMR spectrum of 2g (101 MHz, (CD}_3\text{)}_2\text{SO).} \]

Reference: Alan Reay AJR 87:22
4-Fluorobenzene-1-diazonium tetrafluoroborate (2h)

$\text{H NMR spectrum of 2h (400 MHz, (CD}_3\text{)}_2\text{SO).}$

$\text{C NMR spectrum of 2h (101 MHz, (CD}_3\text{)}_2\text{SO).}$
$^{19}$F NMR spectrum of 2h (376 MHz, (CD$_3$)$_2$SO).
4-Bromobenzene-1-diazonium tetrafluoroborate (2i)

\[ \text{Br} \quad \text{N}_2^+ \quad \text{BF}_4^- \]

\(^1\text{H NMR spectrum of } 2i \) (400 MHz, (CD\(_3\))\(_2\)SO).

\(^{13}\text{C NMR spectrum of } 2i \) (101 MHz, (CD\(_3\))\(_2\)SO).
3-Bromobenzene-1-diazonium tetrafluoroborate (2j)

$\text{Br} \begin{array}{c} \text{N}_2^+ \\ \text{BF}_4^- \end{array} \quad \text{H NMR spectrum of } 2j \ (400 \text{ MHz, } (\text{CD}_3)_2\text{SO}).$

$\text{C NMR spectrum of } 2j \ (101 \text{ MHz, } (\text{CD}_3)_2\text{SO}).$
4-Chlorobenzene-1-diazonium tetrafluoroborate (2k)

$\text{H NMR spectrum of } 2k (400 \text{ MHz, (CD}_3\text{)}_2\text{SO}).$

$\text{C NMR spectrum of } 2k (101 \text{ MHz, (CD}_3\text{)}_2\text{SO}).$
3-Chlorobenzene-1-diazonium tetrafluoroborate (2I)

\[
\begin{align*}
\text{Cl} & \quad \text{N}_2^+ \quad \text{BF}_4^- \\
\end{align*}
\]

\[\text{H NMR spectrum of 2I (400 MHz, (CD}_3\text{)$_2$SO).}\]

\[\text{C NMR spectrum of 2I (101 MHz, (CD}_3\text{)$_2$SO).}\]
4-(Trifluoromethyl)benzene-1-diazonium tetrafluoroborate (2m)

$\text{N}_2^+ \text{BF}_4^-$

$\text{H}^1 \text{NMR spectrum of } 2\text{m} \ (400 \text{ MHz}, \ (\text{CD}_3)_2\text{SO})$.

$\text{C}^{13} \text{NMR spectrum of } 2\text{m} \ (101 \text{ MHz}, \ (\text{CD}_3)_2\text{SO})$. 

Reference: Author, Reference AJR-4-368
$^{19}$F NMR spectrum of 2m (376 MHz, (CD$_3$)$_2$SO).
4-Nitrobenzene-1-diazonium tetrafluoroborate (2n)

$\text{H NMR spectrum of } 2n \ (400 \text{ MHz, (CD}_3\text{)}_2\text{SO}).$

$\text{C NMR spectrum of } 2n \ (101 \text{ MHz, (CD}_3\text{)}_2\text{SO}).$
Methyl (2S)-2-acetamido-3-(2-phenyl-1H-indol-3-yl)propanoate (3a)

1H NMR spectrum of 3a (400 MHz, CDCl₃) *residual EtOAc present.

13C NMR spectrum of 3a (101 MHz, CDCl₃).

Filename: m8467a.pdf
Reference: A Hammarbeck LAH-2-127
Methyl \((2S)-3-[2-(4\text{-methylphenyl})-1H\text{-indol-3-yl}]\text{-2-acetamidopropanoate}\) (3b)

\[\text{\textsuperscript{1}H NMR spectrum of 3b (400 MHz, CDCl}_3\text{).}\]

\[\text{\textsuperscript{13}C NMR spectrum of 3b (101 MHz, CDCl}_3\text{).}\]
Methyl (2S)-3-[2-(4-tert-butylphenyl)-1H-indol-3-yl]-2-acetamidopropanoate (3c)

\[ \text{H NMR spectrum of 3c (400 MHz, CDCl}_3\text{).} \]

\[ \text{C NMR spectrum of 3c (101 MHz, CDCl}_3\text{).} \]
Methyl (2S)-2-acetamido-3-[2-(4-phenylphenyl)-1H-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 (2S)-2-acetamido-3-[2-(2,4,6-trimethylphenyl)-1H-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 (2S)-2-acetamido-3-[2-(4-methoxyphenyl)-1H-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 (2S)-2-acetamido-3-[2-(4-phenoxyphenyl)-1H-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 (2S)-3-[2-(4-fluorophenyl)-1H-indol-3-yl]-2-acetamidopropanoate (3h)

\[
\text{H NMR spectrum of 3h (400 MHz, CDCl}_3\text{).}
\]

\[
\text{C NMR spectrum of 3h (101 MHz, CDCl}_3\text{).}
\]
$^{19}$F NMR spectrum of 3h (376 MHz, (CD$_3$)$_2$SO).
Methyl (2S)-3-[2-(4-bromophenyl)-1H-indol-3-yl]-2-acetamidopropanoate (3i)
Methyl (2S)-3-[2-(3-bromophenyl)-1H-indol-3-yl]-2-acetamidopropanoate (3j)

$\text{H NMR spectrum of 3j (400 MHz, CDCl}_3\text{).}$

$\text{C NMR spectrum of 3j (101 MHz, CDCl}_3\text{).}$
Methyl (2S)-3-[2-(4-chlorophenyl)-1H-indol-3-yl]-2-acetamidopropanoate (3k)
Methyl (2S)-3-[2-(3-chlorophenyl)-1H-indol-3-yl]-2-acetamidopropanoate (3I)
Ac-AlaTrpPhAla-OMe (5)

$^{1}H$ NMR spectrum of $5$ (500 MHz, CD$_3$OD).

$^{13}C$ NMR spectrum of $5$ (126 MHz, CD$_3$OD).
Ac-SerGlyTrpPhAla-OMe (7)

$^1$H NMR spectrum of 7 (500 MHz, CD$_3$OD).

$^{13}$C NMR spectrum of 7 (126 MHz, CD$_3$OD).
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