Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information:

Visible Light Photocatalytic Asymmetric Synthesis of Pyrrolo[1,2*a*]indoles via Intermolecular [3+2] Cycloaddition

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1. General Information

^{1}H and ^{13}C NMR were recorded on a *Bruker AV-300* at 300 and 75 MHz for ^{1}H and ^{13}C, respectively. The chemical shifts (δ, reported in ppm) for ^{1}H NMR are referenced to tetramethylsilane (0 ppm) or to the residual non-deuterated solvent peak ($CDCl_3$ at 7.26 ppm; DMSO-d_6 at 2.50 ppm), while for ^{13}C NMR are given in ppm relative to the residual non-deuterated solvent peak ($CDCl_3$ at 77.16 ppm; DMSO-d_6 at 39.51 ppm). Coupling constants are given in Hz. The following abbreviations were used to indicate the multiplicity: s, singlet; d, doublet; dd, double doublet; ddd, double double doublet; dt, doublet triplet; dq, doublet quartet; t, triplet; q, quartet; m, multiplet; bs, broad singlet; bt, broad triplet.

UV-Vis measurements were acquired on an *Agilent 8453 UV-Vis Spectrophotometer* controlled by *UV-Visible ChemStation Software*. HPLC grade CH_3CN solvent and a Teflon-top 10x10 mm precision cell made of quartz SUPRASIL® were used for all measurements.

Emission spectra were recorded on a *JASCO Spectrofluorometer FP-8600* equipped with a *TC-815 Peltier* thermostated single cell holder (water-cooled) controlled by *Spectra Manager Version 2.10.01*. HPLC grade CH_3CN solvent and a 10x10 mm light path quartz SUPRASIL® cuvette equipped with a silicone/PTFE septum were used for all measurements.

Emission spectra of the light sources used for the photochemical reactions were recorded on an optical spectrometer *StellarNet model Blue-Wave UV-NB50*.

Cyclic Voltammetry (CV) experiments were acquired on an *IVIUM Technologies CompactStat* controlled by *IviumSoft version 2.124* offering a compliance voltage of up to ± 100 V (available at the counter electrode), ± 10 V scan range and ± 1 A current range. HPLC grade CH_3CN solvent was used for all measurements. Tetra-*n*-butylammonium hexafluorophosphate was used as supporting electrolyte at 0.1 M concentration. All cyclic voltammetry experiments were performed using a conventional three-electrode system, containing a coiled Pt wire acting as counter electrode, an Ag/AgCl saturated solution as reference electrode and a glassy carbon working electrode (A = 0.071 cm^2) at 20 mV/s scan rate. All the electrodes were purchased from Metrohm. Redox-active species were dissolved at 1.0 mM concentration, and these solutions were thoroughly purged with At and kept under an inert atmosphere throughout the measurements.

High-Resolution Mass Spectra (HRMS) were obtained on an Agilent Technologies 6120 Quadrupole LC/MS coupled with an SFC Agilent Technologies 1260 Infinity Series instrument for the ESI-MS (Electrospray Ionization) or on an Agilent Technologies 5977B MSD coupled with an Agilent Technologies 7820A GC System for the EI-MS (Electron Ionization mass spectroscopy). MassWorks software version 4.0.0.0 (Cerno Bioscience) was used for the formula identification. MassWorks is an MS calibration software which calibrates isotope profiles to achieve high mass accuracy and enables elemental composition determination on conventional mass spectrometers of unit mass resolution allowing highly accurate comparisons between calibrated and theoretical spectra.[1]

Optical rotations were recorded on a *Perkin Elmer 241 MC Polarimeter* in a 10 cm path length cell in HPLC grade $CHCl_3$ (concentration in g/100 mL).

Enantiomeric excesses were determined in a *Supercritical Fluid Chromatography* (SFC). The chromatograms were acquired on an *Agilent Technologies 1260 Infinity Series* instrument with a SFC module and a UV-Vis detector, employing *Daicel Chiralpak* IA, IB, IC, ID and IG chiral columns. The exact conditions for the analysis are specified in each case.

Crystal of compound **4e** was obtained by slow evaporation of a solution of the corresponding compound in a MeOH/$CHCl_3$ solvent mixture. This crystal was mounted at low temperature in inert oil on a glass fibre. Data were collected on a Bruker ×8 APPEX II CCD-based diffractometer, equipped with a graphite monochromated MoKα radiation source (λ = 0.71073 Å). Data were integrated using SAINT[2] and an absorption correction was performed with the program SADABS.[3] These structures were solved by direct methods using SHELXTL[4] and refined by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were computed and refined with an overall isotropic temperature factor using a riding model.

2. Materials and Methods

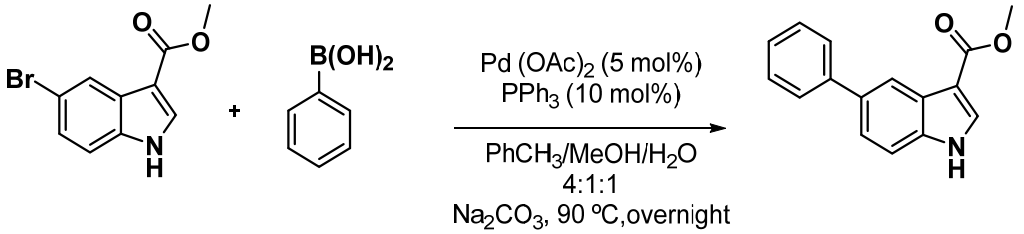
All reagents and materials were purchased from commercial sources and used without further purification while anhydrous solvents were taken from a SPS solvent dispenser. Chromatographic purification was accomplished using Flash Chromatography (FC) on Merck Geduran® Si 60 Silica Gel (40-63 μm). Thin Layer Chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 F_{254}) and a solution of $KMnO_4$, I_2 or phosphomolybdic acid was served as staining agent. Michael acceptor **2d** and ligands **L1-L5** were purchased from commercial sources and used without further purification.

The photocatalytic system used for performing the photochemical reactions was a custom-made temperature-controlled system, in which the reaction mixture was kept at room temperature by passing coolant through the metallic system employing a recirculating chiller. The irradiation was achieved with a 5000 K single white LED) located 1 cm beneath the base of the vial (Figure S1).

Figure S1: custom-made temperature-controlled photocatalytic system.

3. Synthesis of starting materials and ligands

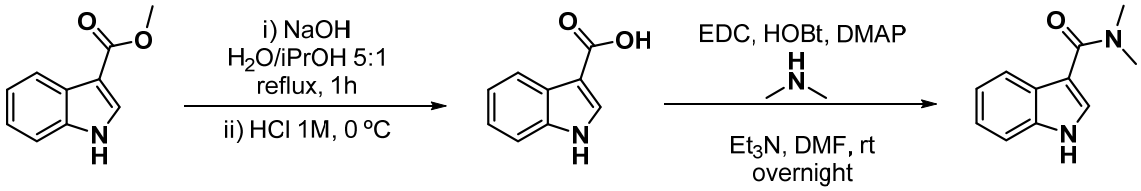
3.1. Synthesis of methyl 5-phenyl-1*H*-indole-3-carboxylate



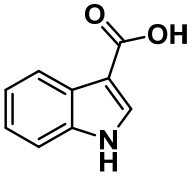
A seal glass tube was charged with methyl 5-bromo-1*H*-indole-3-carboxylate (4.4 mmol, 1.1 eq.), phenylboronic acid (4.0 mmol, 1.0 eq.), triphenylphosphine (0.4 mmol, 0.1 eq.), sodium carbonate (8.0 mmol, 2.0 eq.) and $Pd(OAc)_2$ (0.2 mmol, 0.05 eq.). Then, 20 mL of a toluene/methanol/H_2O 4:1:1 solvent mixture were added and the resulting mixture was stirred overnight at 90 ºC. Afterwards, the crude reaction mixture was extracted with diethyl ether (3x30 mL). The combined organic layers were washed with brine (40 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Finally, the crude was purified by flash chromatography (cyclohexane/ethyl acetate 70:30 as eluent) affording the desired product as a white solid (603.1 mg, 60% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (bs, 1H), 8.42 (s, 1H), 7.96 (d, J = 2.9 Hz, 1H),7.69 (d, J = 7.2 Hz, 2H), 7.57 – 7.41 (m, 4H), 7.34 (t, J = 7.3 Hz, 1H), 3.94 (s, 3H).

3.2. Synthesis of *N,N*-dimethyl-1*H*-indole-3-carboxamide



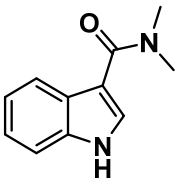
1*H*-indole-3-carboxylic acid[5]



To a solution of NaOH (36 mmol, 4.5 eq.) in 30 mL of H_2O/*iso*propanol 5:1 solvent mixture, 8.0 mmol of methyl 1*H*-indole-3-carboxylate were added. The solution was stirred at 90 ºC for 1h (until the white precipitate disappeared). Then, the solution was cooled at 0 ºC and an aqueous solution of HCl (1 M) was added until a white precipitate appears. Finally, the white solid was filtered off, washed with water and diethyl ether and dried under vacuum. 1*H*-indole-3-carboxylic acid was afforded in 85% yield (684.9 mg).

^{1}H NMR (300 MHz, DMSO-d_6): δ 11.87 (bs, 1H), 11.76 (bs, 1H), 8.05 – 7.88 (m, 2H), 7.49 – 7.36 (m, 1H), 7.20 – 7.05 (m, 2H).

***N,N*-dimethyl-1*H*-indole-3-carboxamide**[6]

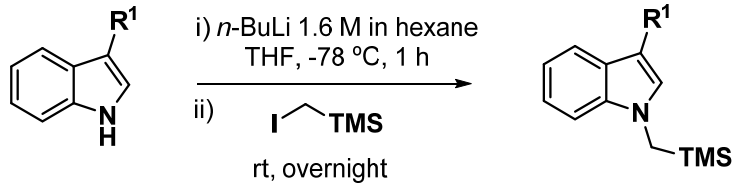


A 25 mL flask was charged with 1*H*-indole-3-carboxylate (6.0 mmol, 1.0 eq.), HOBt (6.0 mmol, 1.0 eq.) and 16 mL of DMF. Then, 6.0 mmol of EDC (1.0 eq.) and the resulting solution was stirred at room temperature. After 30 minutes, DMAP (6.0 mmol, 1.0 eq.), Dimethyl amine (6.0 mmol, 1.0 eq.) and Triethylamine (12.0 mmol, 2.0 eq.) were added and the reaction mixture stirred overnight at room temperature. The crude reaction mixture was poured into water and extracted with diethyl ether (3x40 mL). The combined organic layers were washed with brine (60 mL), dried over $MgSO_4$ and dried under reduced pressure. The crude mixture was purified by flash chromatography (cyclohexane/ethyl acetate 10:90 as eluent) affording the desired product as a white solid (790.6 mg, 70% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.03 (bs, 1H), 7.82 – 7.71 (m, 1H), 7.41 – 7.30 (m, 2H), 7.25 – 7.13 (m, 2H), 3.15 (s, 6H).

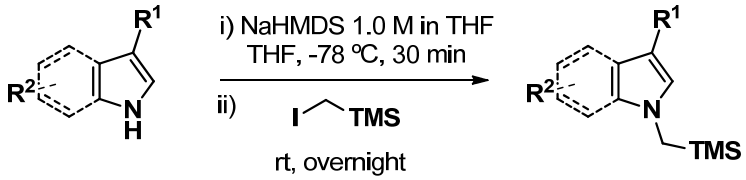
3.3. Synthesis of 1-[(trimethylsilyl)methy]indole and 1-[(trimethylsilyl)methy]pyrrole derivatives 1

General procedure A



An oven-dried 50 mL flask was charged with the corresponding indole (5.0 mmol, 1.0 eq.) and 20 mL of anhydrous THF. The solution was cooled at -78°C and treated with 3.4 mL of a 1.6 M solution of *n*-butyl lithium in hexane (5.5 mmol, 1.1 eq.) by a dropwise addition. The reaction mixture was stirred at this temperature for 1 hour and 1.5 mL of (iodomethyl)trimethylsilane (10.0 mmol, 2.0 eq.) were added dropwise. The solution was allowed to warm up to room temperature and stirred overnight. Then, the reaction was quenched with a saturated aqueous solution of ammonium chloride and extracted with ethyl acetate (2x15 mL). The combined organic layers were washed with a saturated aqueous solution of sodium chloride, dried over $MgSO_4$, filtered and concentrated under reduced pressure.

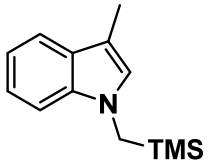
General procedure B



An oven-dried 50 mL flask was charged with the corresponding indole (5.0 mmol, 1.0 eq.) and 20 mL of anhydrous THF. The reaction flask was placed in an ice-bath and 5.5 mL of a 1.0 M solution of NaHMDS in THF (5.5 mmol, 1.1 eq.) were added dropwise. The reaction mixture was stirred at this temperature for 30 minutes and 1.5 mL of (iodomethyl)trimethylsilane (10.0 mmol, 2.0 eq.) were added dropwise. The solution was allowed to warm up to room temperature and stirred overnight. Then, the reaction was quenched with a saturated aqueous solution of ammonium chloride and extracted with

ethyl acetate (2x15 mL). The combined organic layers were washed with a saturated aqueous solution of sodium chloride, dried over $MgSO_4$, filtered and concentrated under reduced pressure.

3-Methyl-1-[(trimethylsilyl)methyl]-1*H*-indole (1a)[7]



1a

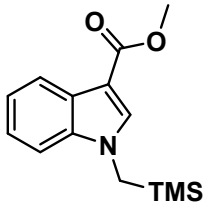
1a was prepared following the general procedure A starting from 655.4 mg (5.0 mmol) of 3-methyl-1*H*-indole. The crude was purified by flash chromatography (cyclohexane as eluent) affording indole **1a** as a colourless oil (782.6 mg, 72% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.36 - 7.34 (m, 2H), 7.25 – 7.19 (m, 1H), 6.91 (s, 1H), 3.73 (s, 2H), 2.47 (s, 3H), 0.20 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 137.0, 128.3, 126.1, 121.1, 118.8, 118.1, 109.5, 37.0, 9.8, -2.0.

HRMS (ESI): calculated for $C_{13}H_{20}NSi^+$, $[M+H]^+$ = 218.1360; found = 218.1389

Methyl 1-[(trimethylsilyl)methyl]-1*H*-indole-3-carboxylate (1b)[8]



1b

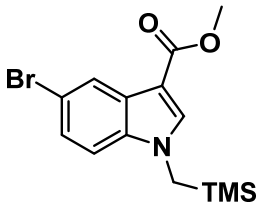
1b was prepared following the general procedure B starting from 876.0 mg (5.0 mmol) of methyl 1*H*-indole-3-carboxylate. The crude was purified by flash chromatography (cyclohexane/ethyl acetate 90:10 as eluent) affording the indole **1b** as a white solid (1.3 gr, 96% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 – 8.17 (m, 1H), 7.76 (s, 1H), 7.36 – 7.24 (m, 3H), 3.94 (s, 3H), 3.74 (s, 2H), 0.13 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 165.5, 137.2, 134.4, 126.4, 122.3, 121.49, 121.47, 110.3, 106.3, 50.8, 38.1, -2.2.

HRMS (ESI): calculated for $C_{14}H_{20}NO_2Si^+$, $[M+H]^+$ = 262.1258; found = 262.1295

Methyl 5-bromo-1-[(trimethylsilyl)methyl]-1*H*-indole-3-carboxylate (1c)



1c

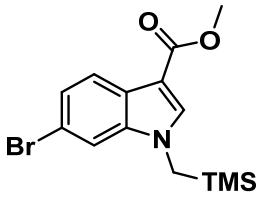
1c was prepared following the general procedure B starting from 1.27 g (5.0 mmol) of methyl 5-bromo-1*H*-indole-3-carboxylate. The crude was purified by flash chromatography (cyclohexane/ethyl acetate 90:10 as eluent) affording indole **1c** as a white solid (1.2 gr, 70% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (d, *J* = 1.9 Hz, 1H), 7.69 (s, 1H), 7.33 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 3.90 (s, 3H), 3.67 (s, 2H), 0.08 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0, 135.8, 135.1, 127.8, 125.3, 124.2, 115.2, 111.7, 106.1, 51.0, 38.5, -2.2.

HRMS (ESI): calculated for $C_{14}H_{19}NO_2BrSi^+$, $[M+H]^+$ = 340.0363; found = 340.0333

Methyl 6-bromo-1-[(trimethylsilyl)methyl]-1*H*-indole-3-carboxylate (1d)



1d

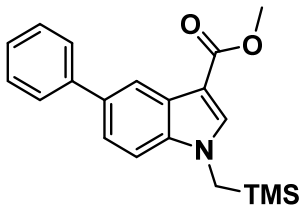
1d was prepared following the general procedure B starting from 1.27 g (5.0 mmol) of methyl 6-bromo-1*H*-indole-3-carboxylate. The crude was purified by flash chromatography (cyclohexane/ethyl acetate 90:10 as eluent) affording indole **1d** as a white solid (1.3 gr, 77% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.67 (s, 1H), 7.45 (d, *J* = 1.5 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.5 Hz, 1H), 3.90 (s, 3H), 3.65 (s, 2H), 0.11 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 138.0, 134.7, 125.2, 124.8, 122.9, 116.1, 113.3, 106.8, 51.0, 38.4, -2.2.

HRMS (ESI): calculated for $C_{14}H_{19}NO_2BrSi^+$, $[M+H]^+$ = 340.0363; found = 340.0387

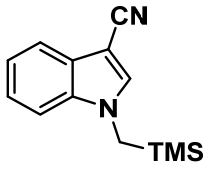
Methyl 5-phenyl-1-[(trimethylsilyl)methyl]-1*H*-indole-3-carboxylate (1e)



1e

1e was prepared following the general procedure B starting from 1.26 gr (5.0 mmol) of *N*,*N*-dimethyl-1*H*-indole-3-carboxamide. The crude was purified by flash chromatography (cyclohexane/ethyl acetate 90:10 as eluent) affording indole **1e** as a white solid (842.9 mg, 50% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, *J* = 1.7 Hz, 1H), 7.76 (s, 1H), 7.74 – 7.68 (m, 2H), 7.56 – 7.43 (m, 3H), 7.39 – 7.30 (m, 2H), 3.93 (s, 3H), 3.74 (s, 2H), 0.13 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 142.3, 136.9, 135.2, 135.0, 128.8 (2C), 127.7 (2C), 127.0, 126.7, 122.3, 120.2, 110.7, 106.9, 51.0, 38.6, -2.0.

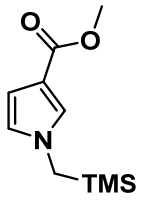
1-[(Trimethylsilyl)methyl]-1*H*-indole-3-carbonitrile (1f)



1f

1f was prepared following the general procedure B starting from 710.8 mg (5.0 mmol) of 1*H*-indole-3-carbonitrile. The crude was purified by flash chromatography (cyclohexane/ethyl acetate 90:10 as eluent) affording the indole **1f** as a white solid (673.7 mg, 59% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 – 7.62 (m, 1H), 7.42 (s, 1H), 7.31 – 7.14 (m, 3H), 3.65 (s, 2H), 0.02 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 135.9, 134.7, 127.6, 123.3, 121.6, 119.9, 116.2, 110.9, 84.6, 38.5, -2.3.
HRMS (ESI): calculated for $C_{13}H_{17}N_2Si^+$, $[M+H]^+$ = 229.1156; found = 229.1180

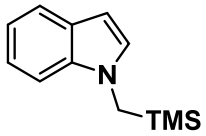
Methyl 1-[(trimethylsilyl)methyl]-1*H*-pyrrole-3-carboxylate (1g)



1g

1g was prepared following the general procedure B starting from 625.7 mg (5.0 mmol) of methyl 1*H*-pyrrole-3-carboxylate. The crude was purified by flash chromatography (cyclohexane/ethyl acetate 90:10 as eluent) affording the pyrrole **1g** as a white solid (770.5 mg, 73% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13 (t, *J* =1.9 Hz, 1H), 6.53 (dd, *J* =2.7, 1.7 Hz, 1H), 6.44 (t, *J* = 2.5 Hz, 1H), 3.77 (s, 3H), 3.47 (s, 2H), 0.07 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2, 126.3, 122.5, 115.1, 109.8, 50.7, 42.1, -2.8.
HRMS (ESI): calculated for $C_{10}H_{18}NO_2Si^+$, $[M+H]^+$ = 212.1101; found = 212.1080

1-[(Trimethylsilyl)methyl]-1*H*-indole (1h)[7]



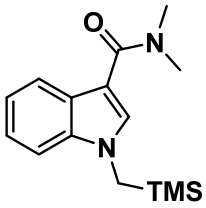
1h

1h was prepared following the general procedure A starting from 585.8 mg (5.0 mmol) of 1*H*-indole. The crude was purified by flash chromatography (cyclohexane as eluent) affording indole **1h** as a colourless oil (681.5 mg, 67% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 7.9 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.22 – 7.13 (m, 1H), 7.10 (d, J = 3.0 Hz, 1H), 6.58 (d, J = 2.3 Hz, 1H), 3.76 (s, 2H), 0.18 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 128.24, 128.18, 121.1, 120.8, 118.8, 109.7, 100.6, 37.4, -1.9.

***N*,*N*-dimethyl-1-[(trimethylsilyl)methyl]-1*H*-indole-3-carboxamide (1i)**



1i

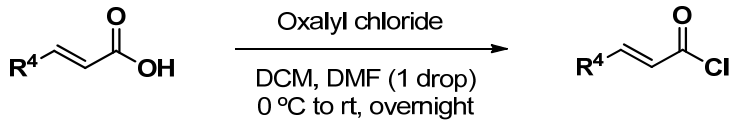
1i was prepared following the general procedure B starting from 1.07 gr (5.0 mmol) of *N*,*N*-dimethyl-1*H*-indole-3-carboxamide. The crude was purified by flash chromatography (cyclohexane/ethyl acetate 75:25 as eluent) affording indole **1i** as a white solid (1.2 gr, 91% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 1H), 7.24 (s, 1H), 7.21 – 7.17 (m, 1H), 7.16 – 7.02 (m, 2H), 3.59 (s, 2H), 3.06 (s, 6H), -0.00 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 136.5, 130.5, 126.5, 122.0, 121.3, 120.4, 110.03, 109.96, 37.8, 37.7, 37.6 -2.0.

3.4. Synthesis of Michael acceptors 2 and 3

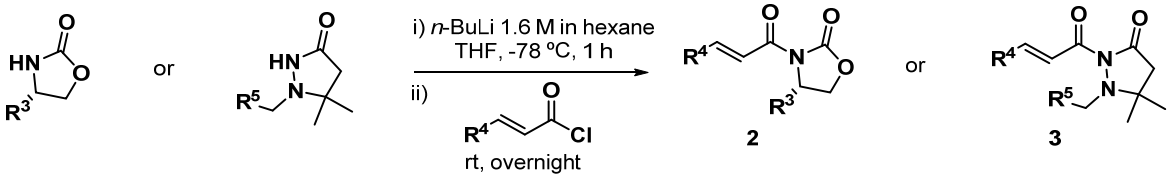
General procedure for the synthesis of α,β-unsaturated acid chlorides



To an oven-dried flask, the corresponding α,β-unsaturated carboxylic acid (5.0 mmol) and 30 mL of dichloromethane were added. The mixture was stirred at 0 °C under nitrogen atmosphere and 846 μL of oxalyl chloride (10.0 mmol, 2 eq.) were added dropwise, followed by a drop of *N,N*-dimethylformamide. The reaction mixture was allowed to warm up to room temperature and stirred overnight. Then, the solvent and residual oxalyl chloride were removed under reduced pressure, affording the

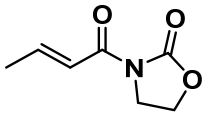
corresponding acid chloride. The acid chloride was used subsequently in the next step without further purification.

General procedure for the synthesis of Michael acceptors 2 and 3



To an oven-dried flask, the corresponding oxazolidinone or pyrazolidinone (5.0 mmol, 1.0 eq.) and 20 mL of anhydrous THF were added. The solution was cooled at -78°C and treated with 3.4 mL of a 1.6 M solution of *n*-butyllithium in hexane (5.5 mmol, 1.1 eq.) by a dropwise addition. The reaction mixture was stirred at that temperature for 1 hour and a solution of the corresponding acid chloride (5.5 mmol, 1.1 eq.) in 5 mL of anhydrous THF was slowly added. The reaction mixture was allowed to warm up to room temperature and stirred overnight. Then, the reaction was quenched with a saturated aqueous solution of ammonium chloride and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with a saturated aqueous solution of sodium chloride, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude reaction mixture was purified by flash chromatography (eluent specified in each case).

(*E*)-3-(But-2-enoyl)oxazolidin-2-one (2a)[9]



2a

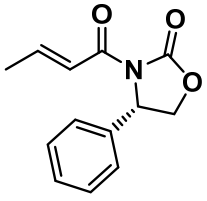
2a was prepared following the general procedure starting from crotonoyl chloride (527.0 µL, 5.5 mmol) and oxazolidin-2-one (435.4 mg, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 70:30 as eluent) affording the Michael acceptor **2a** as a white solid (496.2 mg, 64% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 – 7.08 (m, 2H), 4.43 (t, *J* = 7.9 Hz, 2H), 4.07 (t, *J* = 7.9 Hz, 2H), 1.96 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 153.4, 146.3, 121.3, 62.0, 42.5, 18.3.

HRMS (ESI): calculated for $C_7H_{10}NO_3^+$, $[M+H]^+$ = 156.0655; found = 156.0657

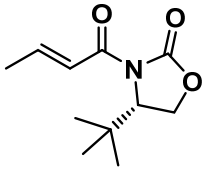
(*S*,*E*)-3-(But-2-enoyl)-4-phenyloxazolidin-2-one (2b)[10]



2b

2b was prepared following the general procedure starting from crotonoyl chloride (527.0 μL, 5.5 mmol) and (*S*)-4-phenyloxazolidin-2-one (815.9 mg, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording the Michael acceptor **2b** as a white solid (983.9 mg, 70% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.25 (m, 6H), 7.10 (dq, *J* = 15.2, 6.8 Hz, 1H), 5.49 (dd, *J* = 8.7, 3.9 Hz, 1H), 4.70 (t, *J* = 8.8 Hz, 1H), 4.28 (dd, *J* = 8.9, 3.9 Hz, 1H), 1.94 (dd, *J* = 6.8, 1.5 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 164.6, 153.8, 147.3, 139.3, 129.3, 128.7, 126.0, 121.9, 70.1, 57.8, 18.6.
HRMS (ESI): calculated for $C_{13}H_{14}NO_3^+$, $[M+H]^+$ = 232.0968; found = 232.0975
$[\alpha]^{20}_D$ = + 89.5 (c = 1.000, $CHCl_3$); {lit.[9] $[\alpha]^{22}_D$ = + 111.8 (c = 1.100, $CHCl_3$)}.

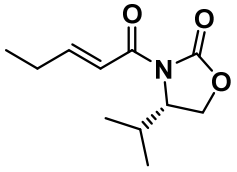
(*S*,*E*)-3-(But-2-enoyl)-4-(*tert*-butyl)oxazolidin-2-one (2c)[10]



2c

2c was prepared following the general procedure starting from crotonoyl chloride (527.0 μL, 5.5 mmol) and (*S*)-4-(*tert*-butyl)oxazolidin-2-one (716.0 mg, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 85:15 as eluent) affording the Michael acceptor **2c** as a white solid (971.8 mg, 92% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (dq, *J* = 15.3, 1.3 Hz, 1H), 7.13 (dq, *J* = 15.3, 6.6 Hz, 1H), 4.50 (dd, *J* = 7.2, 2.1 Hz, 1H), 4.31 – 4.19 (m, 2H), 1.95 (dd, *J* = 6.6, 1.4 Hz, 3H), 0.93 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 165.6, 154.9, 147.0, 122.2, 65.4, 61.0, 36.1, 25.9, 18.7.
HRMS (ESI): calculated for $C_{11}H_{18}NO_3^+$, $[M+H]^+$ = 212.1281; found = 212.1284
$[\alpha]^{20}_D$ = + 90.5 (c = 0.790, $CHCl_3$); {lit.[10] $[\alpha]^{22}_D$ = + 101.2 (c = 1.100, $CHCl_3$)}.

(*S*,*E*)-4-Isopropyl-3-(pent-2-enoyl)oxazolidin-2-one (2e)

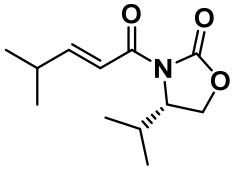


2e

2e was prepared following the general procedure starting from (*E*)-pent-2-enoyl chloride (652.1 mg, 5.5 mmol) and (*S*)-4-isopropyloxazolidin-2-one (645.8 mg, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 85:15 as eluent) affording the Michael acceptor **2e** as a yellowish oil (750.0 mg, 71% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 – 7.12 (m, 2H), 4.53 – 4.46 (m, 1H), 4.33 – 4.18 (m, 2H), 2.48 – 2.25 (m, 3H), 1.11 (t, *J* = 7.4 Hz, 3H), 0.93 (d, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 165.1, 154.0, 152.5, 120.0, 63.3, 58.5, 28.5, 25.7, 17.9, 14.6, 12.2.
HRMS (ESI): calculated for $C_{11}H_{18}NO_3^+$, $[M+H]^+$ = 212.1281; found = 212.1305
$[\alpha]^{20}_D$ = + 83.5 (c = 1.000, $CHCl_3$)

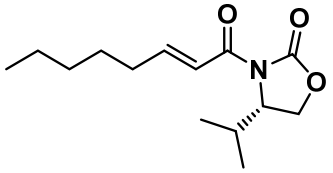
(*S*,*E*)-4-Isopropyl-3-(4-methylpent-2-enoyl)oxazolidin-2-one (2f)



2f

2f was prepared following the general procedure starting from (*E*)-4-methylpent-2-enoyl chloride (729.2 mg, 5.5 mmol) and (*S*)-4-isopropyloxazolidin-2-one (645.8 mg, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 90:10 as eluent) affording the Michael acceptor **2f** as a colourless oil (731.7 mg, 65% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 – 7.06 (m, 2H), 4.53 – 4.46 (m, 1H), 4.32 – 4.18 (m, 2H), 2.63 – 2.48 (m, 1H), 2.47 – 2.35 (m, 1H), 1.10 (d, *J* = 6.8 Hz, 6H), 0.93 (d, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2, 157.2, 154.0, 117.8, 63.3, 58.4, 31.3, 28.4, 21.20, 21.16, 17.9, 14.6.
HRMS (ESI): calculated for $C_{12}H_{20}NO_3^+$, $[M+H]^+$ = 226.1438; found = 226.1403
$[\alpha]^{20}_D$ = + 90.5 (c = 1.090, $CHCl_3$).

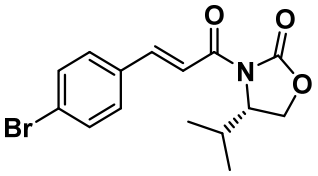
(*S*,*E*)-4-Isopropyl-3-(oct-2-enoyl)oxazolidin-2-one (2g)



2g

2g was prepared following the general procedure starting from (*E*)-oct-2-enoyl chloride (883.5 mg, 5.5 mmol) and (*S*)-4-isopropyloxazolidin-2-one (645.8 mg, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 85:15 as eluent) affording the Michael acceptor **2g** as a yellowish oil (1.0 gr, 82% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 – 7.22 (m, 1H), 7.14 (dt, *J* = 15.3, 6.6 Hz, 1H), 4.49 (dt, *J* = 7.9, 3.6 Hz, 1H), 4.32 – 4.18 (m, 2H), 2.47 – 2.35 (m, 1H), 2.32 – 2.23 (m, 2H), 1.56 – 1.44 (m, 2H), 1.37 – 1.27 (m, 4H), 0.96 – 0.86 (m, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 153.9, 151.2, 120.3, 63.2, 58.4, 32.4, 31.2, 28.4, 27.6, 22.2, 17.8, 14.5, 13.8.
HRMS (ESI): calculated for $C_{14}H_{24}NO_3^+$, $[M+H]^+$ = 254.1751; found = 254.1744
$[\alpha]^{20}_D$ = + 64.9 (c = 1.000, $CHCl_3$)

(*S*,*E*)-3-[3-(4-Bromophenyl)acryloyl]-4-isopropyloxazolidin-2-one (2h)



2h

2h was prepared following the general procedure starting from (*E*)-3-(4-bromophenyl)acryloyl chloride (1.35 g, 5.5 mmol) and (*S*)-4-isopropyloxazolidin-2-one (645.8 mg, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording the Michael acceptor **2h** as a colourless oil (1.5 gr, 87% yield).

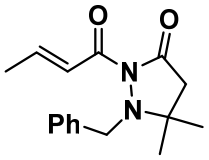
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, *J* = 15.7 Hz, 1H), 7.76 (d, *J* = 15.7 Hz, 1H), 7.56 – 7.44 (m, 4H), 4.60 – 4.50 (m, 1H), 4.37 – 4.20 (m, 2H), 2.52 – 2.39 (m, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 154.1, 144.7, 133.5, 132.1 (2C), 129.9 (2C), 124.9, 117.8, 63.5, 58.7, 28.5, 18.0, 14.7.

HRMS (ESI): calculated for $C_{15}H_{17}NO_3Br^+$, $[M+H]^+$ = 338.0386; found = 338.0484

$[\alpha]^{20}_D$ = + 71.3 (c = 1.000, $CHCl_3$)

(*E*)-1-Benzyl-2-(but-2-enoyl)-5,5-dimethylpyrazolidin-3-one (3a)[11]



3a

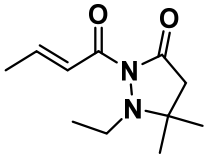
3a was prepared following the general procedure starting from crotonoyl chloride (527.0 μL, 5.5 mmol) and 1-benzyl-5,5-dimethylpyrazolidin-3-one (1.02 gr, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording the Michael acceptor **3a** as a white solid (762.6 mg, 56% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 2H), 7.34 – 7.24 (m, 3H), 7.04 – 6.90 (m, 1H), 6.84 (d, *J* = 15.5 Hz, 1H), 4.08 (s, 2H), 2.56 (s, 2H), 1.86 (d, *J* = 6.5 Hz, 3H), 1.30 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 174.1, 163.0, 145.0, 136.9, 129.4, 128.1, 127.3, 122.7, 60.7, 56.8, 43.4, 25.8, 18.1.

HRMS (ESI): calculated for $C_{16}H_{21}N_2O_2^+$, $[M+H]^+$ = 273.1598; found = 273.1550

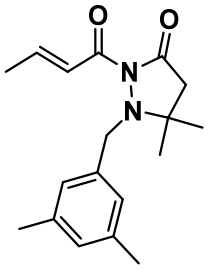
(*E*)-1-Ethyl-2-(but-2-enoyl)-5,5-dimethylpyrazolidin-3-one (3b)[11]



3b

3b was prepared following the general procedure starting from crotonoyl chloride (527.0 μL, 5.5 mmol) and 1-ethyl-5,5-dimethylpyrazolidin-3-one (711.0 mg, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording the Michael acceptor **3b** as a colourless oil (672.9 gr, 64% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16 (dq, *J* = 15.2, 6.6 Hz, 1H), 7.08 – 6.99 (m, 1H), 2.99 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 2H), 1.94 (dd, *J* = 6.6, 1.3 Hz, 3H), 1.31 (s, 6H), 1.07 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 175.0, 163.9, 146.0, 122.9, 60.5, 47.2, 43.9, 25.6, 18.3, 12.7.
HRMS (ESI): calculated for $C_{11}H_{19}N_2O_2^+$, $[M+H]^+$ = 211.1441; found = 211.1444

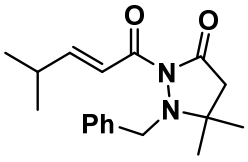
(*E*)-2-(But-2-enoyl)-1-(3,5-dimethylbenzyl)-5,5-dimethylpyrazolidin-3-one (3c)



3c

3c was prepared following the general procedure starting from crotonoyl chloride (527.0 μL, 5.5 mmol) and 1-(3,5-dimethylbenzyl)-5,5-dimethylpyrazolidin-3-one (1.16 g, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording the Michael acceptor **3c** as a white solid (796.1 mg, 53% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98 – 6.71 (m, 5H), 3.96 (s, 2H), 2.53 (s, 2H), 2.26 (s, 6H), 1.82 (d, *J* = 6.5 Hz, 3H), 1.29 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 163.0, 144.5, 137.4, 136.5, 128.8, 127.4, 122.7, 60.6, 56.7, 43.3, 25.8, 21.0, 18.0.
HRMS (ESI): calculated for $C_{18}H_{25}N_2O_2^+$, $[M+H]^+$ = 301.1911; found = 301.1936

(*E*)-1-Benzyl-5,5-dimethyl-2-(4-methylpent-2-enoyl)pyrazolidin-3-one (3d)[12]



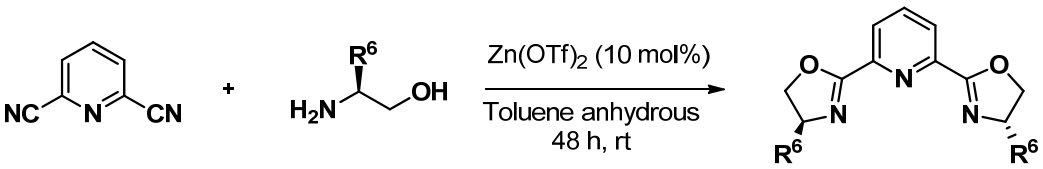
3d

3d was prepared following the general procedure starting from (*E*)-4-methylpent-2-enoyl chloride (729.2 mg, 5.5 mmol) and 1-benzyl-5,5-dimethylpyrazolidin-3-one (1.02 g, 5.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording the Michael acceptor **3d** as a colourless oil (916.2 mg, 61% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 2H), 7.24 – 7.13 (m, 3H), 6.87 (dd, *J* = 15.5, 6.5 Hz, 1H), 6.68 (dd, *J* = 15.5, 1.0 Hz, 1H), 3.99 (s, 2H), 2.48 (s, 2H), 2.21 – 2.28 (m, 1H), 1.21 (s, 6H), 0.95 (d, *J* = 6.8 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 174.4, 163.8, 156.7, 137.3, 129.7, 128.5, 127.7, 118.8, 61.0, 57.2, 43.9, 31.4, 26.2, 21.4.
HRMS (ESI): calculated for $C_{18}H_{25}N_2O_2^+$, $[M+H]^+$ = 301.1911; found = 301.1939

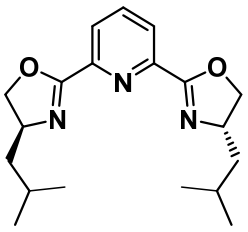
3.5. Synthesis of PyBOX-type ligands L8-L11

3.5.1. General procedure for the synthesis of PyBOX-type ligands L8 and L9



An oven-dried Schlenk was charged with 54.5 mg of flame-dried zinc trifluoromethanesulfonate (0.15 mmol, 0.1 eq.). Then, 193.7 mg of pyridine-2,6-dicarbonitrile (1.5 mmol, 1.0 eq.) and 12 mL of toluene anhydrous were added to the Schlenk under nitrogen atmosphere. The reaction mixture was stirred over 10 min and the corresponding β-amino alcohol (3.0 mmol, 2.0 eq.) was slowly added. The mixture was stirred at room temperature and under nitrogen atmosphere. After 48 hours, the reaction was quenched by the addition of a saturated aqueous solution of ammonium chloride (8 mL) and the crude was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with a saturated aqueous solution of sodium chloride (10 mL), dried over magnesium sulfate, filtered and concentrated under reduced pressure.

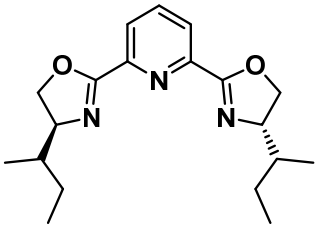
2,6-Bis((*S*)-4-isobutyl-4,5-dihydrooxazol-2-yl)pyridine (L8)[13]



L8

L8 was prepared following the general procedure starting from (*S*)-(+)-leucinol (351.6 mg, 3.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 50:50 as eluent) affording the ligand **L8** as a white solid (276.5 mg, 56% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.85 (t, *J* = 7.8 Hz, 1H), 4.60 (dd, *J* = 9.4, 8.2 Hz, 2H), 4.43 – 4.31 (m, 2H), 4.08 (t, *J* = 8.2 Hz, 2H), 1.92 – 1.66 (m, 4H), 1.44 – 1.33 (m, 2H), 0.98 (d, *J* = 5.4 Hz, 6H), 0.96 (d, *J* = 5.4 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 162.3, 147.1, 137.3, 125.8, 74.0, 65.6, 45.6, 25.6, 22.93, 22.85.
HRMS (ESI): calculated for $C_{19}H_{28}N_3O_2^+$, $[M+H]^+$ = 330.2176; found = 330.2178
$[\alpha]^{20}_D$ = - 147.9 (c = 1.000, $CHCl_3$); {lit.[13] $[\alpha]^{22}_D$ = + 119.5 (c = 0.960, CH_2Cl_2)}.

2,6-Bis[(*S*)-4-((*S*)-*sec*-butyl)-4,5-dihydrooxazol-2-yl]pyridine (L9)[14]

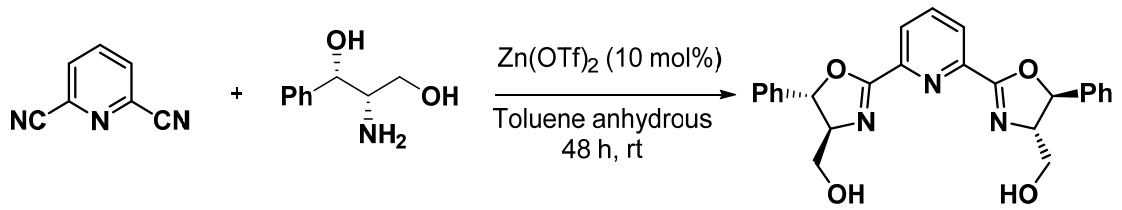


L9

L9 was prepared following the general procedure starting from (*S*)-(+)-isoleucinol (351.6 mg, 3.0 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 50:50 as eluent) affording the ligand **L9** as a white solid (242.0 mg, 49% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.8 Hz, 2H), 7.83 (t, *J* = 7.8 Hz, 1H), 4.55 – 4.42 (m, 2H), 4.30 – 4.17 (m, 4H), 1.78 – 1.55 (m, 4H), 1.31 – 1.15 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 6H), 0.86 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 161.9, 146.7, 136.9, 125.5, 71.3, 70.3, 38.9, 25.9, 14.3, 11.3.
HRMS (ESI): calculated for $C_{19}H_{28}N_3O_2^+$, $[M+H]^+$ = 330.2176; found = 330.2166
$[\alpha]^{20}_D$ = - 138.2 (c = 1.000, $CHCl_3$); {lit.[14] $[\alpha]^{22}_D$ = - 105.5 (c = 1.240, CH_2Cl_2)}.

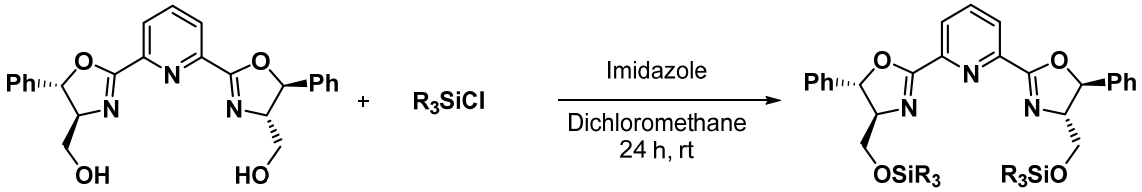
3.5.2. General procedure for the synthesis of alcohol-protected PyBOX-type ligands L10 and L11

Synthesis of [(4*S*,4'*S*,5*S*,5'*S*)-pyridine-2,6-diylbis(5-phenyl-4,5-dihydrooxazole-2,4-diyl)]dimethanol[15]



((4*S*,4'*S*,5*S*,5'*S*)-pyridine-2,6-diylbis(5-phenyl-4,5-dihydrooxazole-2,4-diyl))dimethanol was synthesized following the procedure described in section 3.3.1. using (1*S*,2*S*)-2-amino-1-phenylpropane-1,3-diol (501.6 mg, 3.0 mmol). The product was used subsequently in the next step without further purification.

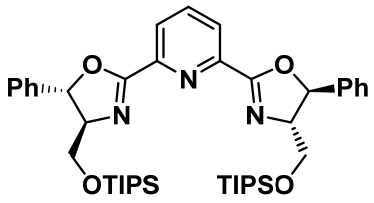
General procedure for the protection of [(4*S*,4'*S*,5*S*,5'*S*)-pyridine-2,6-diylbis(5-phenyl-4,5-dihydrooxazole-2,4-diyl)]dimethanol[15]



To a suspension of ((4*S*,4'*S*,5*S*,5'*S*)-pyridine-2,6-diylbis(5-phenyl-4,5-dihydrooxazole-2,4-diyl))dimethanol (415.9 mg, 1.5 mmol, 1.0 eq.) in dichloromethane (12 mL), 612.1 mg of imidazole (9.0 mmol, 6.0 eq.) were added. Then, the corresponding silyl chloride (3.3 mmol, 2.2 eq.) was added dropwise and the reaction mixture was stirred overnight at room temperature. Finally, the reaction mixture was concentrated under reduced pressure.

The crude reaction mixture was purified by flash chromatography (eluent specified in each case).

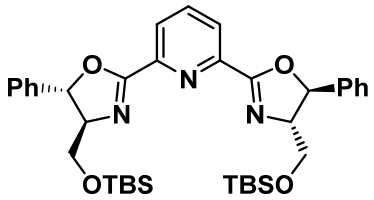
2,6-Bis{(4*S*,5*S*)-5-phenyl-4-[((triisopropylsilyl)oxy)methyl]-4,5-dihydrooxazol-2-yl}pyridine (L10)[15]



L10

L10 was prepared following the general procedure using triisopropylsilyl chloride (706.1 μL, 3.3 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 70:30 as eluent) affording the ligand **L10** as a white solid (946.3 mg, 85% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, *J* = 7.8 Hz, 2H), 7.90 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.24 (m, 10H), 5.73 (d, *J* = 6.4 Hz, 2H), 4.43 – 4.33 (m, 2H), 4.18 (dd, *J* = 9.8, 4.1 Hz, 2H), 3.81 (dd, *J* = 9.5, 8.5 Hz, 2H), 1.16 – 1.00 (m, 42H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0, 147.3, 141.0, 137.3, 128.6, 128.1, 126.0, 125.9, 85.1, 77.1, 65.7, 18.1, 12.0.
HRMS (ESI): calculated for $C_{43}H_{64}N_3O_4Si_2^+$, $[M+H]^+$ = 742.4430; found = 742.4429
$[\alpha]^{20}_D$ = + 60.2 (c = 1.000, $CHCl_3$); {lit.[15] $[\alpha]^{22}_D$ = + 160.0 (c = 1.000, $CHCl_3$)}.

2,6-Bis{(4*S*,5*S*)-4-[((*tert*-butyldimethylsilyl)oxy)methyl]-5-phenyl-4,5-dihydrooxazol-2-yl}pyridine (L11)[15]



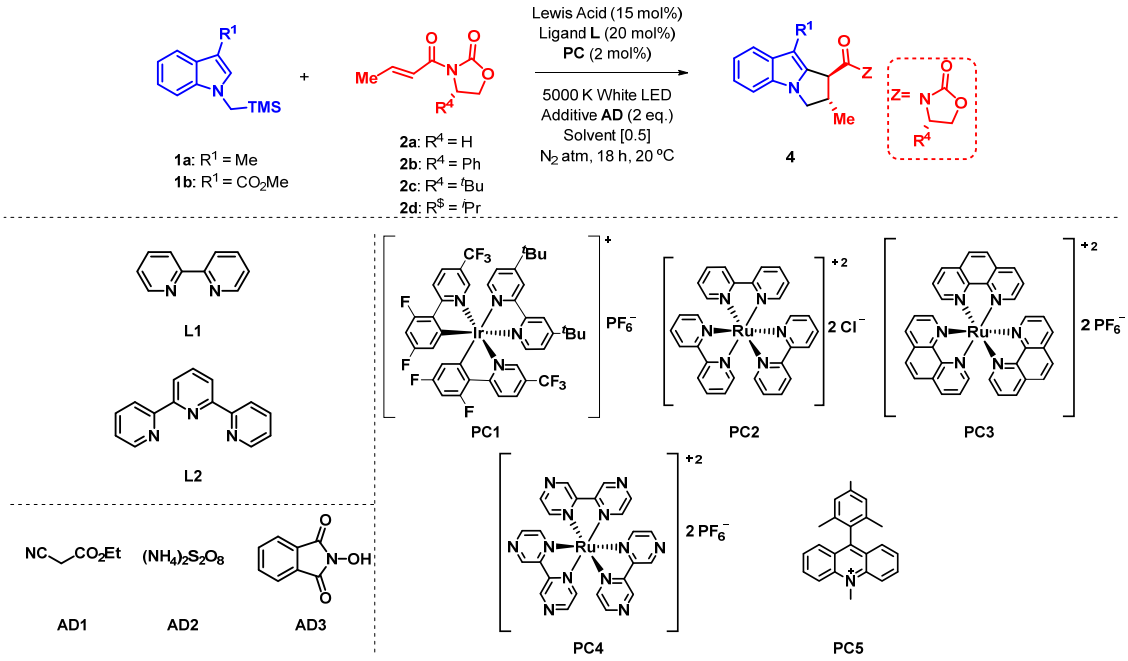
L11

L11 was prepared following the general procedure using *tert*-butyldimethylsilyl chloride (497.4 mg, 3.3 mmol). The crude was purified by flash chromatography (cyclohexane/ethyl acetate 70:30 as eluent) affording the ligand **L11** as a white solid (878.4 mg, 89% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.9 Hz, 2H), 7.90 (t, *J* = 7.9 Hz, 1H), 7.40 – 7.24 (m, 10H), 5.66 (d, *J* = 6.6 Hz, 2H), 4.39 – 4.30 (m, 2H), 4.07 (dd, *J* = 10.1, 4.1 Hz, 2H), 3.75 (dd, *J* = 10.1, 7.8 Hz, 2H), 0.88 (s, 18H), 0.07 (s, 12H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 162.8, 147.1, 140.8, 137.1, 128.5, 127.9, 125.9, 125.8, 84.8, 76.9, 65.1, 25.8, 18.2, -5.4.
HRMS (ESI): calculated for $C_{37}H_{52}N_3O_4Si_2^+$, $[M+H]^+$ = 658.3491; found = 658.3490
$[\alpha]^{20}_D$ = + 76.2 (c = 1.000, $CHCl_3$); {lit.[15] $[\alpha]^{22}_D$ = + 194.2 (c = 1.090, $CHCl_3$)}.

4. Optimization Studies

4.1. Optimization of the diastereoselective photocatalytic [3+2] cyclization

Table S1: Optimization of reaction conditions for the diastereoselective version[a]



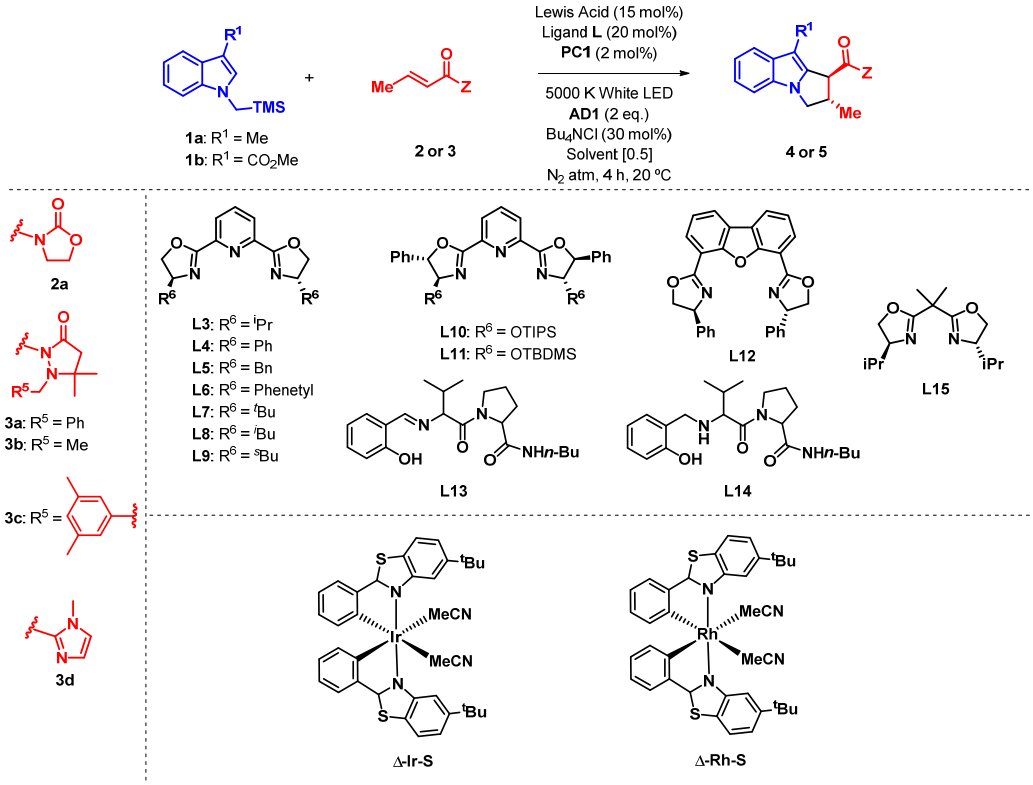
Entry	1	2	Lewis Acid	Ligand	PC	Solvent	Additive	*d.r.*[b]	Yield (%)[c]
1	**1a**	**2a**	$Yb(OTf)_3$	-	**PC2**	MeCN	**AD1**	95:5	30
2	**1a**	**2a**	$Yb(OTf)_3$	-	**PC2**	MeCN	**AD2**	-	<5
3	**1a**	**2a**	$Yb(OTf)_3$	-	**PC2**	MeCN	**AD3**	95:5	7
4	**1a**	**2a**	$Yb(OTf)_3$	-	**PC1**	MeCN	**AD1**	95:5	35
5	**1a**	**2a**	$Yb(OTf)_3$	-	**PC3**	MeCN	**AD1**	95:5	32
6	**1a**	**2a**	$Yb(OTf)_3$	-	**PC4**	MeCN	**AD1**	95:5	14
7	**1a**	**2a**	$Yb(OTf)_3$	-	**PC5**	MeCN	**AD1**	-	<5
8	**1a**	**2a**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	44
9[d]	**1a**	**2a**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	18
10	**1a**	**2a**	$Sc(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	20
11	**1a**	**2a**	$Cu(OTf)_2$	**L1**	**PC1**	MeCN	**AD1**	-	<5
12[e]	**1a**	**2a**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	70
13[e]	**1a**	**2a**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	-	95:5	19
14[e]	**1a**	**2a**	-	-	**PC1**	MeCN	**AD1**	95:5	10
15[e]	**1a**	**2a**	$Yb(OTf)_3$	**L1**	-	MeCN	**AD1**	-	<5
16[e,f]	**1a**	**2a**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	-	<5
17[e,g]	**1a**	**2a**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	-	<5
18[e]	**1a**	**2b**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	60:40	70[h]
19[e]	**1a**	**2c**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	25[h]
20[e]	**1a**	**2d**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	65[h]
21[e]	**1b**	**2a**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	76[h]

22[e]	**1b**	**2b**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	79:21	17[h]
23[e]	**1b**	**2c**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	20[h]
24[e]	**1b**	**2d**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	57[h]
25[e]	**1b**	**2d**	$Yb(OTf)_3$	**L1**	**PC1**	DCE	**AD1**	92:8	50[h]
26[e]	**1b**	**2d**	$Yb(OTf)_3$	**L1**	**PC1**	THF	**AD1**	88:12	38[h]
27[e]	**1b**	**2d**	$Yb(OTf)_3$	**L1**	**PC1**	DMF	**AD1**	95:5	10[h]
28[e]	**1b**	**2d**	$Yb(OTf)_3$	**L2**	**PC1**	MeCN	**AD1**	95:5	43[h]
29[e,i]	**1b**	**2d**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	33[h]
30[e,j]	**1b**	**2d**	$Yb(OTf)_3$	**L1**	**PC1**	MeCN	**AD1**	95:5	32[h]

[a] The corresponding indole derivative **1** (0.1 mmol, 1.0 eq.), Michael acceptor **2** (0.2 mmol, 2.0 eq.), photocatalyst **PC** (0.002 mmol, 2 mol%), Lewis acid (0.015 mmol, 15 mol%), ligand **L** (0.02 mmol, 20 mol%), additive **AD** (0.2 mmol, 2.0 eq.) and 2 mL of the solvent were added to an oven-dried vial. The vial was closed with a PTFE/rubber septum and the reaction mixture was degassed by three freeze-pump-thaw cycles. Afterwards, the reaction mixture was stirred and irradiated using a 5000K white LED (see Figure S1) at 20 °C for 18 h. [b] Measured by NMR. [c] NMR yield using 9-bromophenantrene as internal standard. [d] 0.25 M of concentration. [e] 2.0 equivalent of **1** and 1.0 equivalents of **2** were used. [f] The reaction was carried out in the darkness. [g] The reaction was carried out in presence of O_2. [h] Isolated yield. [i] A 420 nm LED was used as irradiation source. [j] A 450 nm LED was used as irradiation source.

4.2. Optimization of the enantioselective photocatalytic [3+2] cyclization

Table S2: Optimization of reaction conditions for the enantioselective version[a]



Entry	1	2	Lewis Acid	Ligand	Solvent	*e.r.*[b]
1	**1b**	**2a**	$Sc(OTf)_3$	**L3**	MeCN	53:47
2	**1b**	**2a**	$Yb(OTf)_3$	**L3**	MeCN	54:46
3	**1b**	**2a**	$Yb(OTf)_3$	**L5**	MeCN	56:44
4	**1b**	**2a**	$Yb(OTf)_3$	**L6**	MeCN	53:47

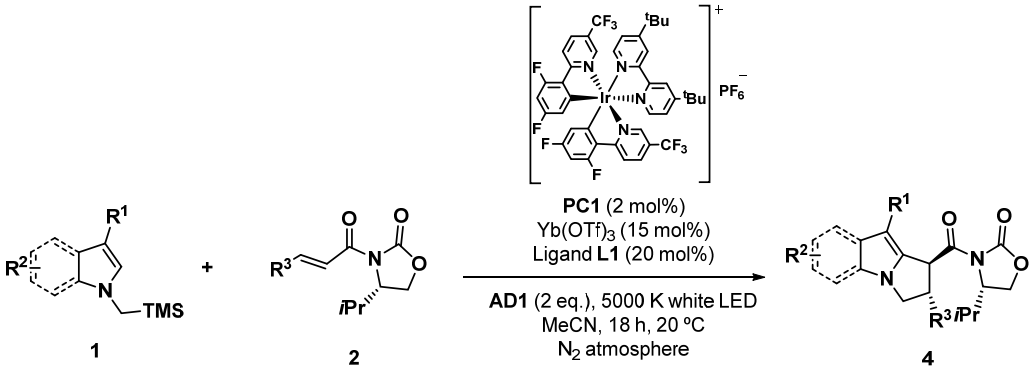
5	**1b**	**2a**	$Yb(OTf)_3$	**L7**	MeCN	56:44
6	**1b**	**2a**	$Yb(OTf)_3$	**L8**	MeCN	58:42
7	**1b**	**3a**	$Yb(OTf)_3$	**L5**	MeCN	70:30
8	**1b**	**3b**	$Yb(OTf)_3$	**L5**	MeCN	58:42
9	**1b**	**3c**	$Yb(OTf)_3$	**L5**	MeCN	56:44
10[c]	**1b**	**3d**	$Yb(OTf)_3$	**L5**	MeCN	-
11	**1b**	**3a**	$Yb(OTf)_3$	**L3**	MeCN	70:30
12	**1b**	**3a**	$Yb(OTf)_3$	**L6**	MeCN	50:50
13	**1b**	**3a**	$Yb(OTf)_3$	**L7**	MeCN	50:50
14	**1b**	**3a**	$Yb(OTf)_3$	**L10**	MeCN	55:45
15	**1b**	**3a**	$Yb(OTf)_3$	**L11**	MeCN	50:50
16	**1a**	**3a**	$Yb(OTf)_3$	**L3**	MeCN	85:15
17	**1a**	**3a**	$Yb(OTf)_3$	**L4**	MeCN	59:41
18	**1a**	**3a**	$Yb(OTf)_3$	**L5**	MeCN	73:27
19	**1a**	**3a**	$Yb(OTf)_3$	**L6**	MeCN	53:47
20	**1a**	**3a**	$Yb(OTf)_3$	**L7**	MeCN	77:23
21	**1a**	**3a**	$Yb(OTf)_3$	**L8**	MeCN	75:25
22	**1a**	**3a**	$Yb(OTf)_3$	**L9**	MeCN	77:23
23	**1a**	**3a**	$Yb(OTf)_3$	**L10**	MeCN	63:37
24	**1a**	**3a**	$Yb(OTf)_3$	**L11**	MeCN	52:48
25	**1a**	**3a**	$Yb(OTf)_3$	**L12**	MeCN	55:45
26	**1a**	**3a**	$Yb(OTf)_3$	**L13**	MeCN	47:53
27	**1a**	**3a**	$Yb(OTf)_3$	**L14**	MeCN	50:50
28	**1a**	**3a**	$Sc(OTf)_3$	**L3**	MeCN	76:24
29	**1a**	**3a**	$Ni(OTf)_2$	**L15**	MeCN	53:47
30	**1a**	**3a**	**Δ-Ir-S**	**-**	MeCN	n. r.
31	**1a**	**3a**	**Δ-Rh-S**	**-**	MeCN	74:26
32	**1a**	**3a**	$Yb(OTf)_3$	**L3**	DCM	70:30
33	**1a**	**3a**	$Yb(OTf)_3$	**L3**	THF	46:54
34	**1a**	**3a**	$Yb(OTf)_3$	**L3**	1,4-Dioxane	44:56
35	**1a**	**3a**	$Yb(OTf)_3$	**L3**	DMF	61:39
36[d]	**1a**	**3a**	$Yb(OTf)_3$	**L3**	MeCN	63:37
37[e]	**1a**	**3a**	$Yb(OTf)_3$	**L3**	MeCN	80:20
38[f]	**1a**	**3a**	$Yb(OTf)_3$	**L3**	MeCN	84:16
39[g]	**1a**	**3a**	$Yb(OTf)_3$	**L3**	MeCN	71:29
40[h]	**1a**	**3a**	$Yb(OTf)_3$	**L3**	MeCN	60:40
41[i]	**1a**	**3a**	$Yb(OTf)_3$	**L3**	MeCN	84:16
42[j]	**1a**	**3a**	$Yb(OTf)_3$	**L3**	MeCN	81:19

[a] The corresponding indole derivative **1** (0.2 mmol, 2.0 eq.), Michael acceptor **2 or 3** (0.1 mmol, 1.0 eq.), photocatalyst **PC1** (0.002 mmol, 2 mol%), Lewis acid (0.015 mmol, 15 mol%), ligand **L** (0.02 mmol, 20 mol%), additive **AD1** (0.2 mmol, 2.0 eq.) and 2 mL of the solvent were added to an oven-dried vial. The vial was closed with a PTFE/rubber septum and the reaction mixture was degassed by three freeze-pump-thaw cycles. Afterwards, the reaction mixture was stirred and irradiated using a 5000 K white LED (see Figure S1) at 20 °C for 4 h. [b] Determined by SFC-LC using quiral columns. [c] Giese-product was obtained. [d] MeCN (with 237 ppm of water) was used. [e] 0.25 M of

concentration. [f] 1.0 M of concentration. [g] 1.5 equivalents of indole were used. [h] 30 mol% of ligand **L3** were used. [i] Reaction carried out at -5 °C. [j] A 420 nm LED was used as irradiation source.

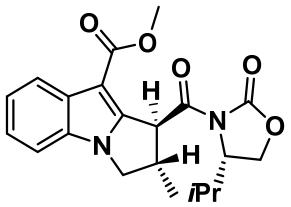
5. Experimental procedure for the photocatalytic [3+2] cyclization

5.1. General procedure for the diastereoselective photocatalytic [3+2] cyclization



An oven-dried glass vial equipped with a magnetic stirrer was charged with the corresponding indole derivative **1** (0.2 mmol, 2.0 eq.), Michael acceptor **2** (0.1 mmol, 1.0 eq.), photocatalyst **PC1** (0.002 mmol, 2 mol%), Ytterbium(III) trifluoromethanesulfonate (0.015 mmol, 15 mol%) and ligand **L1** (0.02 mmol, 20 mol%). Then, 2 mL of anhydrous acetonitrile and additive **AD1** (0.2 mmol, 2.0 eq.) were sequentially added to the vial. The vial was closed with a PTFE/rubber septum and the reaction mixture was degassed by three freeze-pump-thaw cycles. Afterwards, the reaction mixture was stirred and irradiated (a 5000 K white LED in a custom-made temperature-controlled system was used, see Figure S1) at 20 °C. After 18 hours, the crude was filter over Celite® and concentrated under reduced pressure. The filtered crude was purified by flash chromatography on silica gel to afford the final pyrrolo[1,2*a*]indoles **4**. The absolute configuration of the pyrrolo[1,2*a*]indoles **4** was determined by X-ray of one of the compounds (**4e**, see section 12).

Methyl (1*S*,2*S*)-1-((*S*)-4-isopropyl-2-oxooxazolidine-3-carbonyl)-2-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (4a)



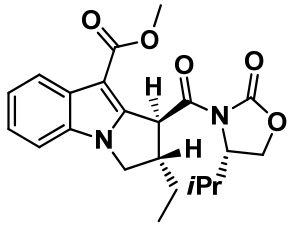
4a

4a was prepared following the general procedure starting from indole **1b** (52.3 mg, 0.2 mmol) and Michael acceptor **2d** (19.7 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **4a** as a colourless oil (21.9 mg, 57% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 – 8.00 (m, 1H), 7.30 – 7.17 (m, 3H), 5.62 (d, *J* = 5.5 Hz, 1H), 4.54 (ddd, *J* = 8.1, 4.2, 2.4 Hz, 1H), 4.49 – 4.39 (m, 2H), 4.28 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.84 (s, 3H), 3.77 (dd, *J* = 10.1, 5.7 Hz, 1H), 3.39 – 3.24 (m, 1H), 2.43 – 2.30 (m, 1H), 1.44 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 2.9 Hz, 3H), 0.94 (d, *J* = 2.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 166.6, 154.8, 149.6, 132.9, 130.2, 122.4, 122.1, 121.9, 110.2, 100.3, 64.2, 59.3, 51.3, 50.9, 49.4, 43.6, 29.3, 19.1, 18.1, 15.4.
HRMS (ESI): calculated for $C_{21}H_{25}N_2O_5^+$, $[M+H]^+$ = 385.1758; found = 385.1736
$[\alpha]^{20}_D$ = + 77.1 (c = 1.000, $CHCl_3$)
The enantiomeric excess of **4a** was determined by SFC on a *Daicel Chiralpak ID-3* column: CO_2/MeOH gradient from 95:5 to 60:40, flow rate 2.0 mL/min, τ_{major} = 3.9 min, τ_{minor} = 3.5 min. *e.r.* > 99:1.

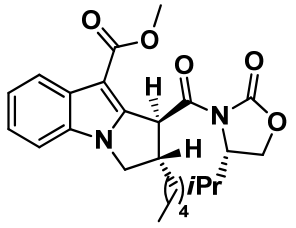
Methyl (1*S*,2*S*)-2-ethyl-1-((*S*)-4-isopropyl-2-oxooxazolidine-3-carbonyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (4b)



4b

4b was prepared following the general procedure starting from indole **1b** (52.3 mg, 0.2 mmol) and Michael acceptor **2e** (21.1 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **4b** as a white solid (19.1 mg, 48% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 – 7.99 (m, 1H), 7.30 – 7.19 (m, 3H), 5.77 (d, *J* = 6.3 Hz, 1H), 4.55 (ddd, *J* = 8.1, 4.1, 2.2 Hz, 1H), 4.51 – 4.40 (m, 2H), 4.28 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.88 – 3.78 (m, 4H), 3.32 – 3.18 (m, 1H), 2.41 – 2.26 (m, 1H), 1.97 – 1.69 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 172.5, 166.7, 155.0, 149.9, 132.8, 130.1, 122.3, 122.1, 121.9, 110.1, 100.0, 64.3, 59.4, 50.9, 50.6, 49.4, 47.4, 29.5, 26.8, 18.2, 15.6, 12.1.
HRMS (ESI): calculated for $C_{22}H_{27}N_2O_5^+$, $[M+H]^+$ = 399.1914; found = 399.1900
$[\alpha]^{20}_D$ = + 55.6 (c = 0.730, $CHCl_3$)

Methyl (1*S*,2*S*)-1-((*S*)-4-isopropyl-2-oxooxazolidine-3-carbonyl)-2-pentyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (4c)

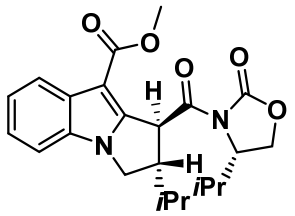


4c

4c was prepared following the general procedure starting from indole **1b** (52.3 mg, 0.2 mmol) and Michael acceptor **2g** (25.3 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **4c** as a colourless oil (21.6 mg, 49% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 – 7.99 (m, 1H), 7.31 – 7.19 (m, 3H), 5.77 (d, *J* = 6.6 Hz, 1H), 4.55 (dd, *J* = 4.1, 2.2 Hz, 1H), 4.53 – 4.39 (m, 2H), 4.28 (dd, *J* = 8.4, 2.2 Hz, 1H), 3.86 – 3.76 (m, 4H), 3.40 – 3.23 (m, 1H), 2.41 – 2.27 (m, 1H), 1.96 – 1.64 (m, 2H), 1.53 – 1.38 (m, 2H), 1.38 – 1.25 (m, 4H), 0.96 (d, *J* = 6.9 Hz, 6H), 0.93 – 0.86 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 172.5, 165.7, 155.0, 149.9, 132.7, 130.0, 122.3, 122.1, 121.9, 110.1, 100.0, 64.2, 59.4, 50.9, 49.7, 49.1, 47.6, 33.8, 31.9, 29.5, 27.6, 22.6, 16.1, 15.5, 14.1.
HRMS (ESI): calculated for $C_{25}H_{33}N_2O_5^+$, $[M+H]^+$ = 441.2384; found = 441.2394
$[\alpha]^{20}_D$ = + 54.0 (c = 1.000, $CHCl_3$)

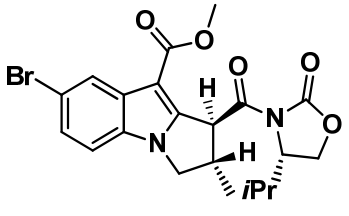
Methyl (1*S*,2*S*)-2-isopropyl-1-((*S*)-4-isopropyl-2-oxooxazolidine-3-carbonyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (4d)



4d

4d was prepared following the general procedure starting from indole **1b** (52.3 mg, 0.2 mmol) and Michael acceptor **2f** (22.5 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **4d** as a colourless oil (11.5 mg, 28% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 – 8.00 (m, 1H), 7.33 – 7.21 (m, 3H), 5.96 (d, *J* = 7.4 Hz, 1H), 4.64 – 4.50 (m, 2H), 4.45 (dd, *J* = 10.2, 8.5 Hz, 1H), 4.30 (dd, *J* = 7.9, 1.6 Hz, 1H), 3.92 – 3.84 (m, 4H), 3.37 – 3.26 (m, 1H), 2.42 – 2.27 (m, 1H), 2.19 – 2.04 (m, 1H), 1.12 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 1.7 Hz, 3H), 0.98 (d, *J* = 1.7 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 173.1, 165.8, 155.3, 150.3, 132.6, 130.0, 122.3, 122.1, 122.0, 110.1, 99.9, 64.3, 59.5, 55.9, 50.9, 47.9, 45.4, 31.9, 29.8, 20.6, 20.4, 18.2, 15.7.
HRMS (ESI): calculated for $C_{23}H_{29}N_2O_5^+$, $[M+H]^+$ = 413.2071; found = 413.2023
$[\alpha]^{20}_D$ = + 43.6 (c = 1.000, $CHCl_3$)

Methyl (1*S*,2*S*)-7-bromo-1-((*S*)-4-isopropyl-2-oxooxazolidine-3-carbonyl)-2-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (4e)



4e

4e was prepared following the general procedure starting from indole **1c** (68.1 mg, 0.2 mmol) and Michael acceptor **2d** (19.7 mg, 0.1 mmol). The crude was filtered over Celite®

and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **4e** as a white solid (33.8 mg, 73% yield).

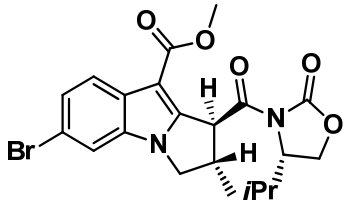
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, *J* = 1.8 Hz, 1H), 7.32 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 5.62 (d, *J* = 5.7 Hz, 1H), 4.53 (dd, *J* = 7.3, 4.7 Hz, 1H), 4.50 – 4.37 (m, 2H), 4.28 (dd, *J* = 8.7, 2.2 Hz, 1H), 3.84 (s, 3H), 3.76 (dd, *J* = 10.2, 5.9 Hz, 1H), 3.40 – 3.25 (m, 1H), 2.43 – 2.29 (m, 1H), 1.44 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 165.1, 154.8, 150.6, 131.6, 131.5, 125.3, 124.7, 115.6, 111.5, 100.1, 64.3, 59.3, 51.5, 51.1, 49.4, 43.6, 29.3, 18.9, 18.1, 15.5.

HRMS (ESI): calculated for $C_{21}H_{24}N_2O_5Br^+$, $[M+H]^+$ = 463.0863; found = 463.0865

$[\alpha]^{20}_D$ = + 63.5 (c = 0.880, $CHCl_3$)

Methyl (1*S*,2*S*)-6-bromo-1-((*S*)-4-isopropyl-2-oxooxazolidine-3-carbonyl)-2-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (4f)



4f

4f was prepared following the general procedure starting from indole **1d** (68.1 mg, 0.2 mmol) and Michael acceptor **2d** (19.7 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **4f** as a white solid (26.4 mg, 57% yield).

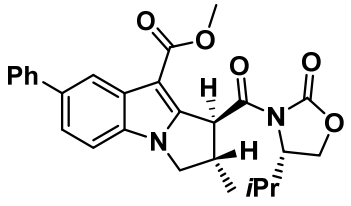
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.6 Hz, 1H), 7.42 (d, *J* = 1.7 Hz, 1H), 7.32 (dd, *J* = 8.6, 1.7 Hz, 1H), 5.60 (d, *J* = 5.6 Hz, 1H), 4.53 (ddd, *J* = 8.1, 4.2, 2.4 Hz, 1H), 4.48 – 4.35 (m, 2H), 4.28 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.83 (s, 3H), 3.74 (dd, *J* = 10.2, 5.7 Hz, 1H), 3.38 – 3.23 (m, 1H), 2.42 – 2.28 (m, 1H), 1.43 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 1.7 Hz, 3H), 0.94 (d, *J* = 1.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 166.2, 154.7, 150.1, 133.6, 128.9, 125.2, 123.3, 115.8, 113.3, 100.7, 64.3, 59.3, 51.4, 51.0, 49.3, 43.6, 29.3, 19.0, 18.1, 15.4.

HRMS (ESI): calculated for $C_{21}H_{24}N_2O_5Br^+$, $[M+H]^+$ = 463.0863; found = 463.0855

$[\alpha]^{20}_D$ = + 62.1 (c = 1.000, $CHCl_3$)

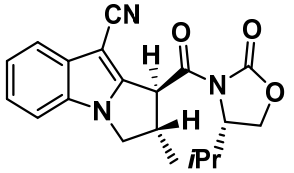
(1*S*,2*S*)-Methyl 1-((*S*)-4-isopropyl-2-oxooxazolidine-3-carbonyl)-2-methyl-7-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (4g)



4g

4g was prepared following the general procedure starting from indole **1e** (33.7 mg, 0.1 mmol) and Michael acceptor **2d** (9.9 mg, 0.05 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **4g** as a white solid (10.1 mg, 44% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.3 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.52 – 7.40 (m, 3H), 7.36 – 7.29 (m, 2H), 5.63 (d, *J* = 5.5 Hz, 1H), 4.56 – 4.51 (m, 1H), 4.49 – 4.42 (m, 2H), 4.29 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.86 (s, 3H), 3.77 (dd, *J* = 10.2, 4.7 Hz, 1H), 3.39 – 3.27 (m, 1H), 2.43 – 2.31 (m, 1H), 1.46 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 2.6 Hz, 3H), 0.95 (d, *J* = 2.7 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 165.4, 154.6, 150.0, 142.4, 135.4, 132.3, 130.5, 128.6 (2C), 127.6 (2C), 126.6, 122.1, 120.5, 110.2, 100.6, 64.1, 59.1, 51.3, 50.8, 49.3, 43.4, 29.2, 19.0, 18.0, 15.3.
$[\alpha]^{20}_D$ = + 78.6 (c = 0.500, $CHCl_3$)

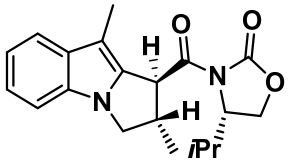
(1*S*,2*S*)-1-((*S*)-4-Isopropyl-2-oxooxazolidine-3-carbonyl)-2-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (4h)



4h

4h was prepared following the general procedure starting from indole **1f** (45.6 mg, 0.2 mmol) and Michael acceptor **2d** (19.7 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **4h** as a colourless oil (13.0 mg, 37% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 – 7.65 (m, 1H), 7.31 – 7.21 (m, 3H), 5.52 (d, *J* = 6.9 Hz, 1H), 4.59 – 4.49 (m, 2H), 4.42 (dd, *J* = 10.2, 7.6 Hz, 1H), 4.34 – 4.25 (m, 1H), 3.81 (dd, *J* = 10.2, 6.9 Hz, 1H), 3.64 – 3.50 (m, 1H), 2.51 – 2.38 (m, 1H), 1.40 (d, *J* = 6.9 Hz, 3H), 0.97 (d, *J* = 2.2 Hz, 3H), 0.95 (d, *J* = 2.2 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 154.5, 148.4, 132.2, 131.6, 123.5, 122.2, 120.1, 115.6, 110.7, 79.1, 64.2, 59.6, 51.3, 49.6, 42.0, 28.9, 18.21, 18.19, 15.2.
HRMS (ESI): calculated for $C_{20}H_{22}N_3O_3^+$, $[M+H]^+$ = 352.1656; found = 352.1660
$[\alpha]^{20}_D$ = + 42.1 (c = 1.000, $CHCl_3$)

(*S*)-3-((1*S*,2*S*)-2,9-Dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-1-carbonyl)-4-isopropyloxooxazolidin-2-one (4i)



4i

4i was prepared following the general procedure starting from indole **1a** (43.5 mg, 0.2 mmol) and Michael acceptor **2d** (19.7 mg, 0.1 mmol). The crude was filtered over Celite®

and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **4i** as a colourless oil (21.4 mg, 63% yield).

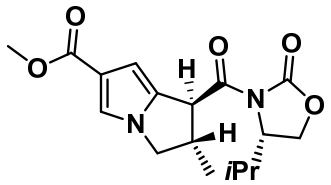
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.02 (m, 3H), 5.21 (d, *J* = 4.0 Hz, 1H), 4.53 – 4.43 (m, 1H), 4.39 – 4.25 (m, 3H), 3,71 (dd, *J* = 9.6, 4.0 Hz, 1H), 3.32 – 3.19 (m, 1H), 2.48 – 2.35 (m, 1H), 2.19 (s, 3H), 1.34 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 3.3 Hz, 3H), 0.93 (d, *J* = 3.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 154.3, 137.4, 132.9, 132.7, 121.0, 119.0, 118.6, 109.4, 103.2, 63.8, 59.2, 50.4, 48.0, 43.7, 28.8, 19.9, 18.1, 15.0, 6.9.

HRMS (ESI): calculated for $C_{20}H_{25}N_2O_3^+$, $[M+H]^+$ = 341.1860; found = 341.1914

$[\alpha]^{20}_D$ = + 18.1 (c = 0.960, $CHCl_3$)

Methyl (1*S*,2*S*)-1-((*S*)-4-isopropyl-2-oxooxazolidine-3-carbonyl)-2-methyl-2,3-dihydro-1*H*-pyrrolizine-6-carboxylate (4j)



4j

4j was prepared following the general procedure starting from pyrrole **1g** (42.3 mg, 0.2 mmol) and Michael acceptor **2d** (19.7 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **4j** as a colourless oil (4.7 mg, 14% yield).

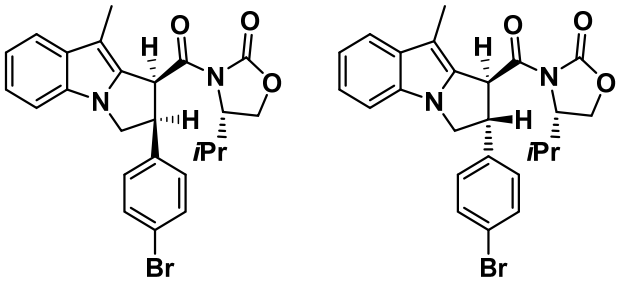
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.60 (d, *J* = 2.8 Hz, 1H), 6.56 (d, *J* = 2.8 Hz, 1H), 5.38 (d, *J* = 5.6 Hz, 1H), 4.57 – 4.51 (m, 1H), 4.45 (t, *J* = 8.4 Hz, 1H), 4.30 – 4.23 (m, 2H), 3.74 (s, 3H), 3.64 (dd, *J* = 10.4, 6.0 Hz, 1H), 3.29 - 3.18 (m, 1H), 2.44 – 2.31 (m, 1H), 1.38 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.6, 165.1, 154.7, 141.0, 115.4, 113.7, 108.1, 64.1, 59.3, 53.6, 50.9, 48.8, 43.7, 29.3, 18.8, 18.1, 15.4.

HRMS (ESI): calculated for $C_{17}H_{23}N_2O_5^+$, $[M+H]^+$ = 335.1601; found = 335.1599

$[\alpha]^{20}_D$ = + 55.8 (c = 0.820, $CHCl_3$)

(*S*)-3-[(1*S*,2*S*)-2-(4-bromophenyl)-9-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-1-carbonyl]-4-isopropyloxazolidin-2-one (4k mayor) and (*S*)-3-[(1*S*,2*R*)-2-(4-bromophenyl)-9-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-1-carbonyl]-4-isopropyloxazolidin-2-one (4k minor)



4k major **4k minor**

4k was prepared following the general procedure starting from indole **1a** (43.5 mg, 0.2 mmol) and Michael acceptor **2h** (33.8 mg, 0.1 mmol). The crude was filtered over Celite ® and purified by flash chromatography (cyclohexane/ethyl acetate 90:10 as eluent) affording product **4k major** followed by product **4k minor** as white solids (29.4 mg, 61% combined yield).

Major diastereosimer:

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.40 - 7.34 (m, 2H), 7.25 - 7.07 (m, 3H), 6.95 - 6.89 (m, 2H), 5.70 (d, *J* = 3.3 Hz, 1H), 4.70 (dd, *J* = 9.8, 7.2 Hz, 1H), 4.49 (dt, *J* = 7.9, 3.8 Hz, 1H), 4.36 - 4.21 (m, 3H), 4.04 (dd, *J* = 9.8, 3.6 Hz, 1H), 2.36 - 2.22 (m, 4H), 0.88 (d, *J* = 3.9 Hz, 3H), 0.85 (d, *J* = 3.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 154.1, 141.6, 137.0, 133.2, 133.0, 132.2 (2C), 128.7 (2C), 121.54, 121.45, 119.4, 119.0, 109.7, 104.2, 63.6, 59.0, 52.3, 51.1, 48.1, 28.5, 18.2, 14.8, 9.0.

HRMS (ESI): calculated for for $C_{25}H_{26}N_2O_3Br^+$, $[M+H]^+$ = 481.1121; found = 481.1100

$[\alpha]^{20}_D$ = + 73.6 (c = 0.850, $CHCl_3$)

Minor diastereosimer:

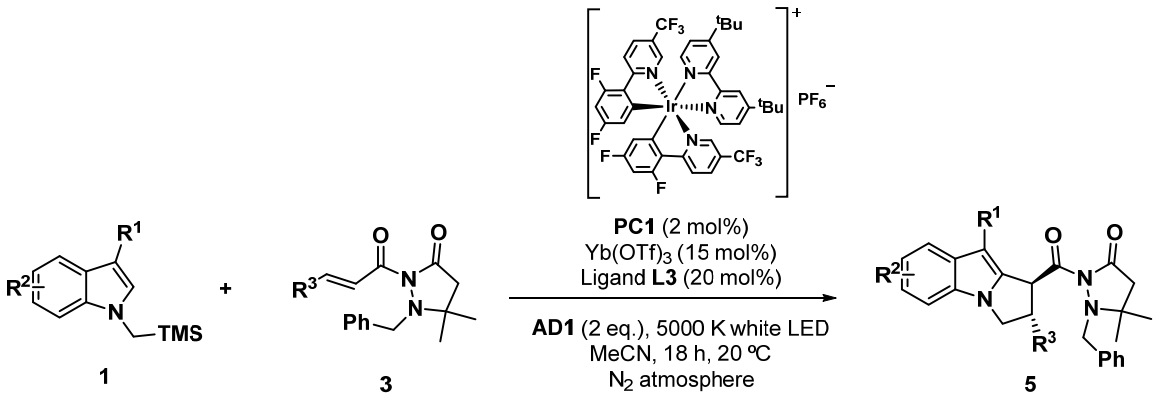
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.44 -7.38 (m, 2H), 7.23 – 7.02 (m, 5H), 5.74 (d, *J* = 5.3 Hz, 1H), 4.63 (dd, *J* = 9.8, 7.4 Hz, 1H), 4.53 – 4.45 (m, 1H), 4.39 – 4.21 (m, 3H), 4.05 (dd, *J* = 9.8, 5.3 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.20 (s, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 154.0, 140.2, 136.9, 132.9, 132.8, 132.2 (2C), 129.0 (2C), 121.6, 121.5, 119.2, 119.0, 109.6, 103.5, 63.6, 59.2, 53.1, 50.6, 48.1, 28.6, 18.1, 14.7, 8.8.

HRMS (ESI): calculated for for $C_{25}H_{26}N_2O_3Br^+$, $[M+H]^+$ = 481.1121; found = 481.1120

$[\alpha]^{20}_D$ = + 9.1 (c = 1.000, $CHCl_3$)

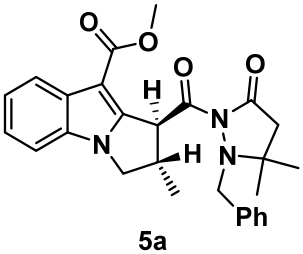
5.2. General procedure for the enantioselective photocatalytic [3+2] cyclization



1 3 5

An oven-dried glass vial equipped with a magnetic stirrer was charged with the corresponding indole derivative **1** (0.2 mmol, 2.0 eq.), Michael acceptor **3** (0.1 mmol, 1.0 eq.), photocatalyst **PC1** (0.002 mmol, 2 mol%), Ytterbium(III) trifluoromethanesulphonate (0.015 mmol, 15 mol%) and chiral ligand **L3** (0.02 mmol, 20 mol%). Then, 2 mL of anhydrous acetonitrile and the additive **AD1** (0.2 mmol, 2.0 eq.) were sequentially added to the vial. The vial was closed with a PTFE/rubber septum and the reaction mixture was degassed by three freeze-pump-thaw cycles. Afterwards, the reaction mixture was stirred and irradiated (a 5000 K white LED in a custom-made temperature-controlled system was used, Figure S1) at 20 °C. After 18 hours, the crude was filter over Celite® and concentrated under reduced pressure. The filtered crude was purified by flash chromatography on silica gel to afford the final pyrrolo[1,2-*a*]indoles **5**, which was further analyzed by SFC on chiral columns. The absolute configuration of the pyrrolo[1,2.*a*]indoles **5** was determined by comparison of the optical rotation of the corresponding derivatized products of **4a** and **5a** through a reduction (see section 6.1).

Methyl (1*S*,2*S*)-1-(2-benzyl-3,3-dimethyl-5-oxopyrazolidine-1-carbonyl)-2-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5a)



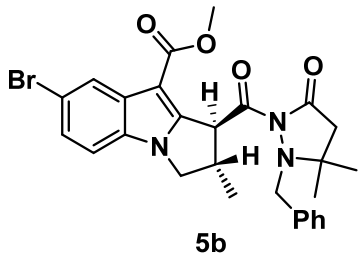
5a

5a was prepared following the general procedure starting from indole **1b** (52.3 mg, 0.2 mmol) and Michael acceptor **3a** (27.2 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **5a** as a white solid (27.6 mg, 60% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 – 8.01 (m, 1H), 7.53 – 7.46 (m, 2H), 7.31 – 7.18 (m, 6H), 5.44 (d, *J* = 3.3 Hz, 1H), 4.31 (dd, *J* = 10.2, 7.0 Hz, 1H), 4.24 (d, *J* = 14.1 Hz, 1H), 4.07 (d, *J* = 14.1 Hz, 1H), 3.82 (s, 3H), 3.74 (dd, *J* = 10.2, 3.5 Hz, 1H), 3.01 (ddd, *J* = 10.2, 7.0, 3.5 Hz, 1H), 2.79 (d, *J* = 17.2 Hz, 1H), 2.71 (d, *J* = 17.2 Hz, 1H), 1.37 (d, *J* =7.1 Hz, 3H), 1.30 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 175.0, 168.3, 165.5, 149.4, 138.2, 133.0, 130.4, 129.0 (2C), 128.3 (2C), 127.4, 122.2, 122.0, 121.8, 110.2, 100.5, 60.7, 57.0, 51.4, 51.0, 50.9, 43.9, 43.0, 26.3 (2C), 20.4.
HRMS (ESI): calculated for $C_{27}H_{30}N_3O_4^+$, $[M+H]^+$ = 460.2231; found = 460.2238
$[\alpha]^{20}_D$ = - 2.4 (c = 0.900, $CHCl_3$)
The enantiomeric excess of **5a** was determined by SFC on a *Daicel Chiralpak IB-3* column: CO_2/MeOH gradient from 95:5 to 70:30, flow rate 2.0 mL/min, τ_{major} = 2.9 min, τ_{minor} = 2.7 min. *e.r.* = 70:30.
Optical rotation of the derivatized product **6a**: $[\alpha]^{20}_D$ = - 4.8 (c = 0.667, $CHCl_3$).

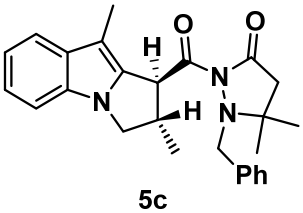
Methyl (1*S*,2*S*)-1-(2-benzyl-3,3-dimethyl-5-oxopyrazolidine-1-carbonyl)-7-bromo-2-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (5b)



5b

5b was prepared following the general procedure starting from indole **1c** (68.1 mg, 0.2 mmol) and Michael acceptor **3a** (27.2 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **5b** as a white solid (24.2 mg, 45% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, *J* = 1.9 Hz, 1H), 7.50 (d, *J* = 6.6 Hz, 2H), 7.33 – 7.22 (m, 4H), 7.12 (d, *J* = 8.6 Hz, 1H), 5.45 (d, *J* = 3.4 Hz, 1H), 4.33 – 4.21 (m, 2H), 4.06 (d, *J* = 14.0 Hz, 1H), 3.82 (s, 3H), 3.72 (dd, *J* = 10.2, 3.8 Hz, 1H), 3.08 – 2.95 (m, 1H), 2.80 (d, *J* = 17.1 Hz, 1H), 2.72 (d, *J* =17.1 Hz, 1H), 1.37 (d, *J* = 7.1 Hz, 3H), 1.31 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 175.1, 168.0, 165.0, 150.5, 138.2, 131.8, 131.7, 129.0 (2C), 128.4 (2C), 127.5, 125.2, 124.6, 115.5, 111.6, 100.3, 60.8, 57.0, 51.6, 51.1, 51.0, 43.9, 43.1, 26.4, 26.3, 20.2.
HRMS (ESI): calculated for $C_{27}H_{29}N_3O_4Br^+$, $[M+H]^+$ = 538.1336; found = 538.1341
$[\alpha]^{20}_D$ = - 11.1 (c = 1.000, $CHCl_3$)
The enantiomeric excess of **5b** was determined by SFC on a *Daicel Chiralpak IB-3* column: CO_2/MeOH gradient from 95:5 to 70:30, flow rate 2.0 mL/min, τ_{major} = 4.0 min, τ_{minor} = 4.3 min. *e.r.* = 70:30.

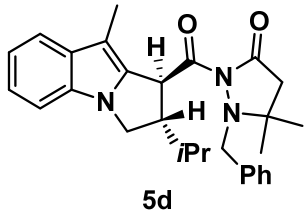
1-Benzyl-2-((1*S*,2*S*)-2,9-dimethyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-1-carbonyl)-5,5-dimethylpyrazolidin-3-one (5c)



5c

5c was prepared following the general procedure starting from indole **1a** (43.5 mg, 0.2 mmol) and Michael acceptor **3a** (27.2 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **5c** as a colourless oil (33.2 mg, 80% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.43 (m, 3H), 7.31 – 7.00 (m, 6H), 5.12 (d, *J* = 3.3 Hz, 1H), 4.34 (dd, *J* = 9.4, 6.8 Hz, 1H), 4.09 (s, 2H), 3.65 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.14 (ddd, *J* = 10.3, 6.8, 3.4 Hz, 1H), 2.72 (s, 2H), 2.21 (s, 3H), 1.37 – 1.19 (m, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 175.0, 169.2, 137.9, 137.8, 133.0, 132.8, 128.9 (2C), 128.4 (2C), 127.5, 120.9, 119.0, 118.5, 109.4, 103.0, 60.6, 57.0, 50.6, 49.1, 44.1, 43.3, 26.5, 26.3, 20.1, 9.1.
HRMS (ESI): calculated for $C_{26}H_{30}N_3O_2^+$, $[M+H]^+$ = 416.2333; found = 416.2374
$[\alpha]^{20}_D$ = - 37.3 (c = 0.810, $CHCl_3$)
The enantiomeric excess of **5c** was determined by SFC on a *Daicel Chiralpak IA-3* column: CO_2/MeOH gradient from 95:5 to 60:40, flow rate 3.0 mL/min, τ_{major} = 4.7 min, τ_{minor} = 4.5 min. *e.r.* = 85:15.

1-Benzyl-2-((1*S*,2*S*)-2-isopropyl-9-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-1-carbonyl)-5,5-dimethylpyrazolidin-3-one (5d)

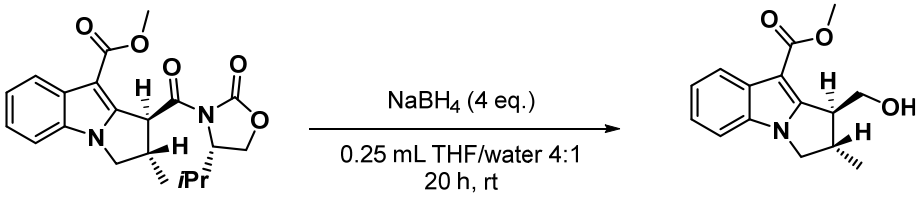


5d

5d was prepared following the general procedure starting from indole **1a** (43.5 mg, 0.2 mmol) and Michael acceptor **3d** (30.0 mg, 0.1 mmol). The crude was filtered over Celite® and purified by flash chromatography (cyclohexane/ethyl acetate 80:20 as eluent) affording product **5d** as a colourless oil (23.1 mg, 52% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, *J* = 6.7 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.16 (m, 4H), 7.14 – 7.07 (m, 1H), 7.07 – 6.99 (m, 1H), 5.46 (d, *J* = 5.1 Hz, 1H), 4.35 (dd, *J* = 9.7, 8.0 Hz, 1H), 4.11 (s, 2H), 3.78 (dd, *J* = 9.8, 5.8 Hz, 1H), 3.28 – 3.15 (m, 1H), 2.84 (d, *J* = 17.1 Hz, 1H), 2.70 (d, *J* = 17.1 Hz, 1H), 2.21 (s, 3H), 1.99 – 1.84 (m, 1H), 1.25 (s, 3H), 1.22 (s, 3H), 0.95 (m, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 174.9, 169.8, 138.8, 138.5, 132.9, 132.7, 128.6 (2C), 128.4 (2C), 127.4, 120.8, 118.9, 118.6, 109.5, 101.7, 60.4, 56.8, 55.0, 46.9, 45.8, 44.2, 32.2, 26.9, 26.1, 20.6, 20.0, 9.0.
HRMS (ESI): calculated for $C_{28}H_{34}N_3O_2^+$, $[M+H]^+$ = 444.2646; found = 444.2627
$[\alpha]^{20}_D$ = - 15.2 (c =1.000, $CHCl_3$)
The enantiomeric excess of **5d** was determined by SFC on a *Daicel Chiralpak ID-3* column: CO_2/MeOH gradient from 95:5 to 60:40, flow rate 2.0 mL/min, τ_{major} = 4.1 min, τ_{minor} = 3.7 min. *e.r.* = 72:28.

6. Derivatization of final products 4

6.1. General procedure for the reductive derivatization of 4[16]



4a **6a**

Sodium borohydride (7.6 mg, 0.2 mmol, 4.0 eq.) was added to a solution of **4a** (19.2 mg, 0.05 mmol, 1.0 eq.) in a 0.25 mL of THF/water 4:1 solvent mixture. The reaction mixture was stirred at room temperature. After 20 hours, the reaction was quenched with an 1N aqueous solution of HCl (5 mL) and extracted with ethyl acetate (2 x 8 mL). The combined organic layers were washed with a saturated aqueous solution of sodium chloride (10 mL), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Finally, the crude was purified by flash chromatography (cyclohexane/ethyl acetate 50:50 as eluent) to afford the final product **6a** as a white solid (10.4 mg, 80% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 – 8.02 (m, 1H), 7.28 – 7.21 (m, 3H), 4.32 (dd, *J* = 10.4, 7.6 Hz, 1H), 4.19 (bt, *J* = 5.8 Hz, 1H), 4.08 – 3.98 (m, 1H), 3.95 (s, 3H), 3.94 – 3.87 (m, 1H), 3.67 (dd, *J* = 10.4, 5.3 Hz, 1H), 3.41 – 3.34 (m, 1H), 2.91 – 2.75 (m, 1H), 1.33 (d, *J* = 7.0 Hz, 3H).

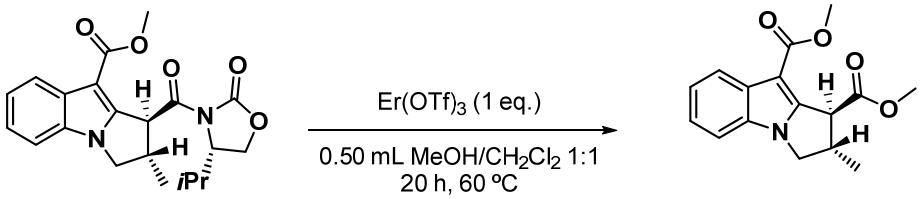
^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 152.9, 132.6, 130.3, 122.3, 122.0 (2C), 110.0, 100.4, 64.4, 51.3, 51.1, 50.9, 39.9, 19,5.

HRMS (ESI): calculated for $C_{15}H_{18}NO_3^+$, $[M+H]^+$ = 260.1281; found = 260.1282

$[\alpha]^{20}_D$ = - 11.7 (c = 0.720, $CHCl_3$)

The enantiomeric excess of **6a** was determined by SFC on a *Daicel Chiralpak IB-3* column: CO_2/MeOH gradient from 95:5 to 70:30, flow rate 2.0 mL/min, τ_{major} = 3.3 min, τ_{minor} = 3.1 min. *e.r.* > 99:1.

6.2. General procedure for the esterification of 4[17]



4a **7a**

Erbium(III) trifluoromethanesulfonate (30.7 mg, 0.05 mmol, 1.0 eq.) was added to a solution of **4a** (19.2 mg, 0.05 mmol, 1.0 eq.) in a 0.50 mL of a 1:1 mixture of MeOH/CH_2Cl_2. The reaction mixture was stirred at 60 °C. After 20 hours, the reaction was quenched with water (5 mL) and extracted with ethyl acetate (2 x 8 mL). The combined organic layers were washed with a saturated aqueous solution of sodium chloride (10 mL), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Finally, the crude was purified by flash chromatography (cyclohexane/ethyl

acetate 80:20 as eluent) to afford the final product **7a** as a white solid (12.1 mg, 84% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 – 8.08 (m, 1H), 7.31 – 7.20 (m, 3H), 4.45 (dd, *J* = 10.2, 7.7 Hz, 1H), 4.01 (d, *J* = 6.0 Hz, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 3.72 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.36 – 3.20 (m, 1H), 1.40 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 165.2, 148.1, 132.8, 130.5, 122.6, 122.1, 122.0, 110.2, 100.7, 52.6, 52.5, 51.3, 50.9, 42.5, 19.4.

HRMS (ESI): calculated for $C_{16}H_{18}NO_4^+$, $[M+H]^+$ = 288.1230; found = 288.1198

$[\alpha]^{20}_D$ = + 19.4 (c = 0.690, $CHCl_3$)

The enantiomeric excess of **7a** was determined by SFC on a *Daicel Chiralpak IA-3* column: CO_2/MeOH gradient from 95:5 to 60:40, flow rate 3.0 mL/min, τ_{major} = 4.2 min, τ_{minor} = 4.0 min. *e.r.* > 99:1.

7. Cyclic Voltammetry Measurements

Cyclic Voltammetry of indole **1a** and additive **AD1** are presented.

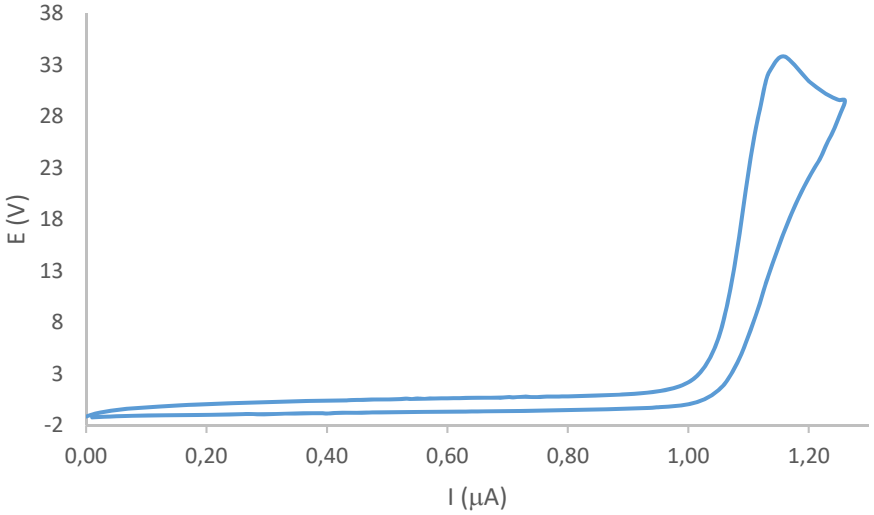


*Figure S2: Cyclic voltammetry of indole **1a**, E^p_{ox} = 1.16 V vs Ag/AgCl*

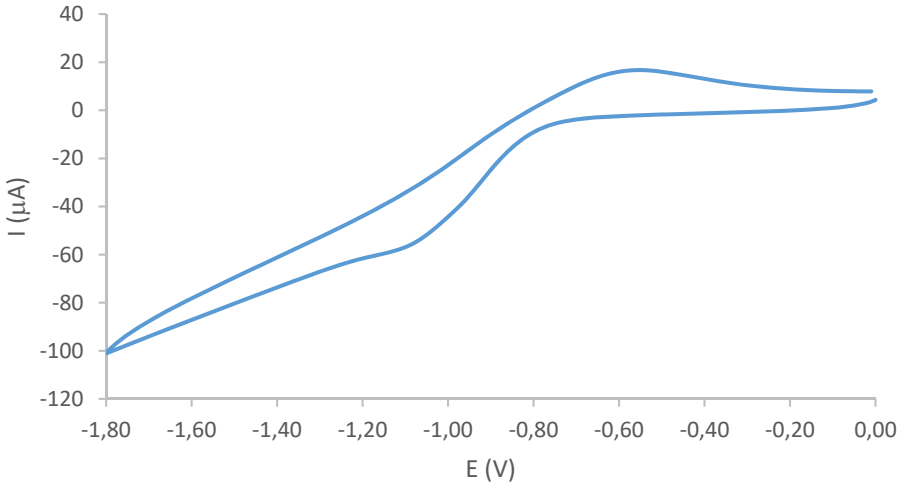


*Figure S3: Cyclic voltammetry of **AD1**, E^p_{red} = -1.07 V vs Ag/AgCl*

8. Quenching Study

Stern-Volmer studies were carried out using indole **1a**, Michael acceptor **2a** and additive **AD1** as quenchers. For the measurements, a 30 mM solution of iridium complex **PC1** was mixed with the required amount of quencher in a total volume of 3 mL of dry CH_3CN in a 10x10 mm light path quartz cuvette equipped with a silicone/PTFE septum. Then, the samples were bubbled with nitrogen for 5 minutes prior to the emission measurements. The excitation wavelength was fixed at 385 nm and the emission spectrum was recorded from 450 nm to 650 nm.

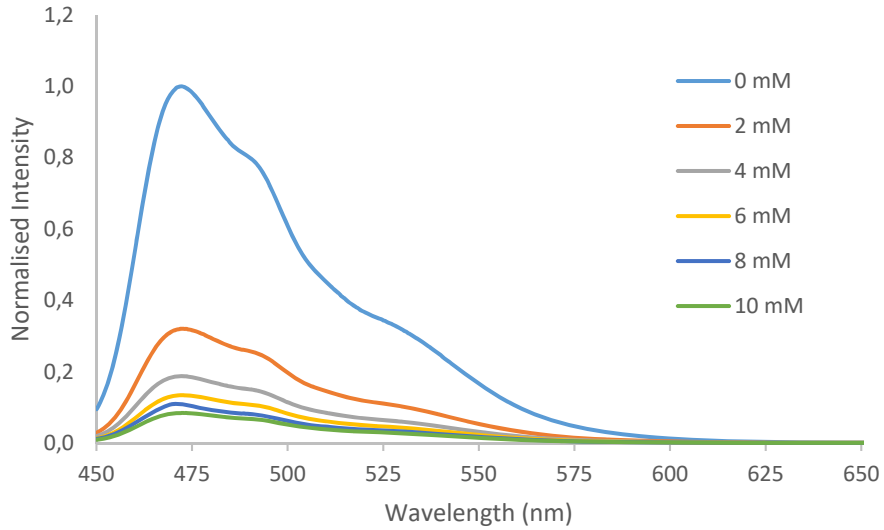


*Figure S4: Emission spectra of **PC1** using indole **1a** as quencher.*

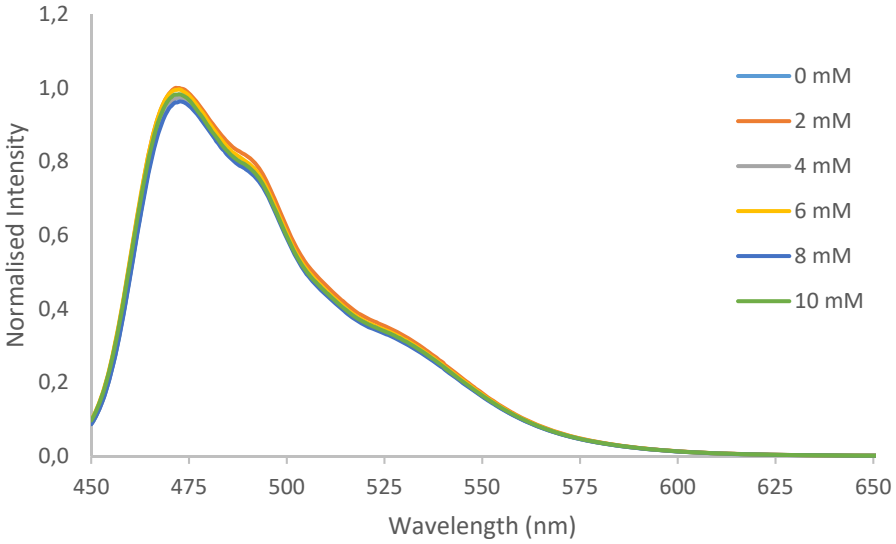


*Figure S5: Emission spectra of **PC1** using Michael acceptor **2a** as quencher.*

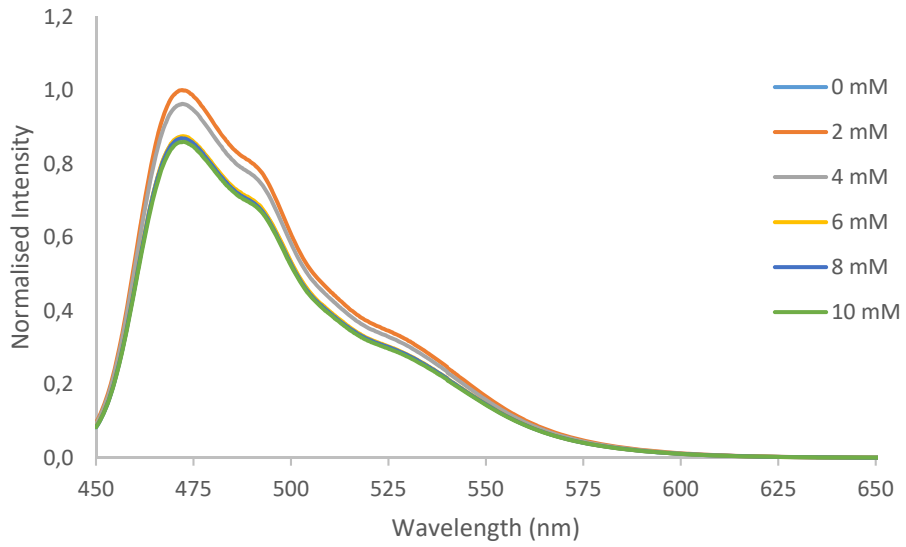


*Figure S6: Emission spectra of **PC1** using additive **AD1** as quencher.*

The Stern-Volmer plot shows a linear correlation between the amounts of quencher and the ratio I_0/I (equation [1]). Stern-Volmer quenching constant was calculated for indole **1a** (K_{SV} = 1.06 mM^{-1}). In the cases of Michael acceptor **2a** and additive **AD1**, the above-mentioned constants were not calculated due to the lack of quenching.

$$I_0/I = 1 + K_{SV} \cdot [Q] \qquad [1]$$

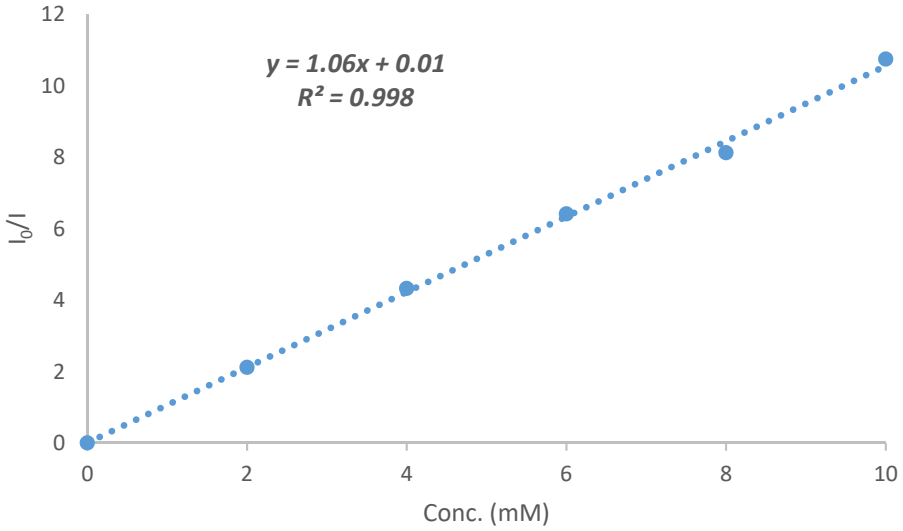


*Figure S7: Stern-Volmer quenching plot of **PC1** using indole **1a** as quencher*

9. SFC Traces

SFC chromatograms of enantioenriched products are presented.

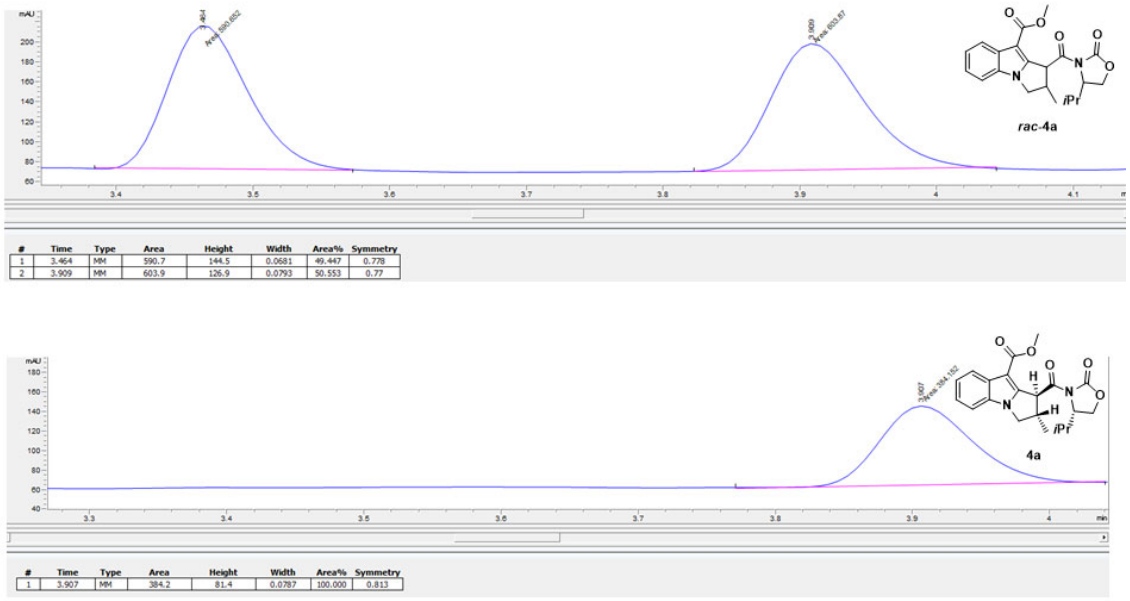


*Figure S8: SFC chromatograms for **4a***

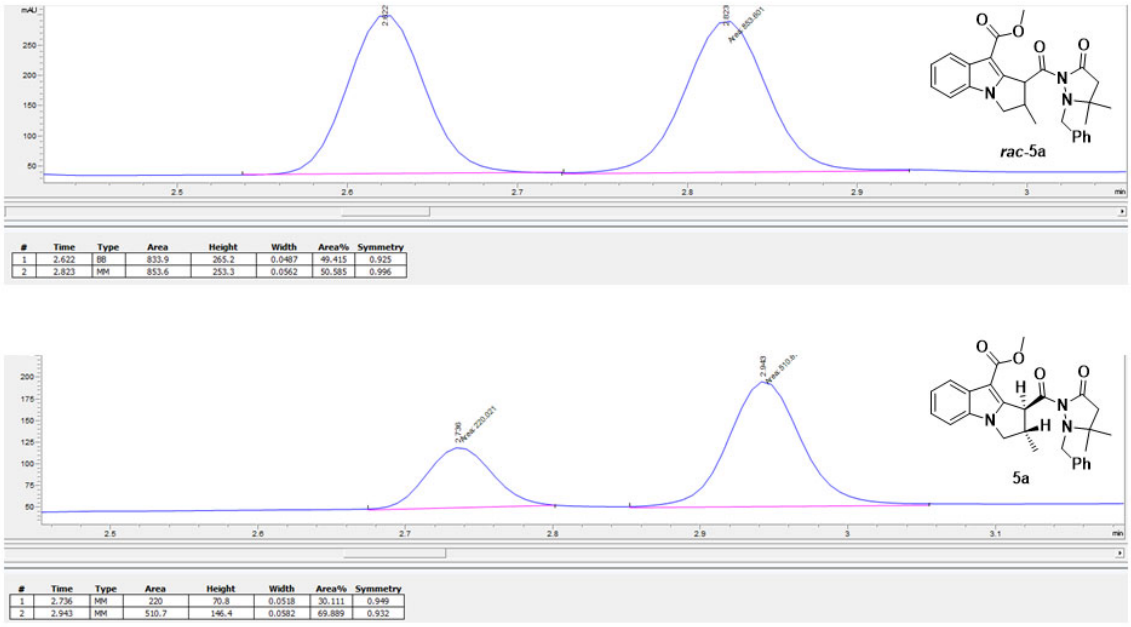
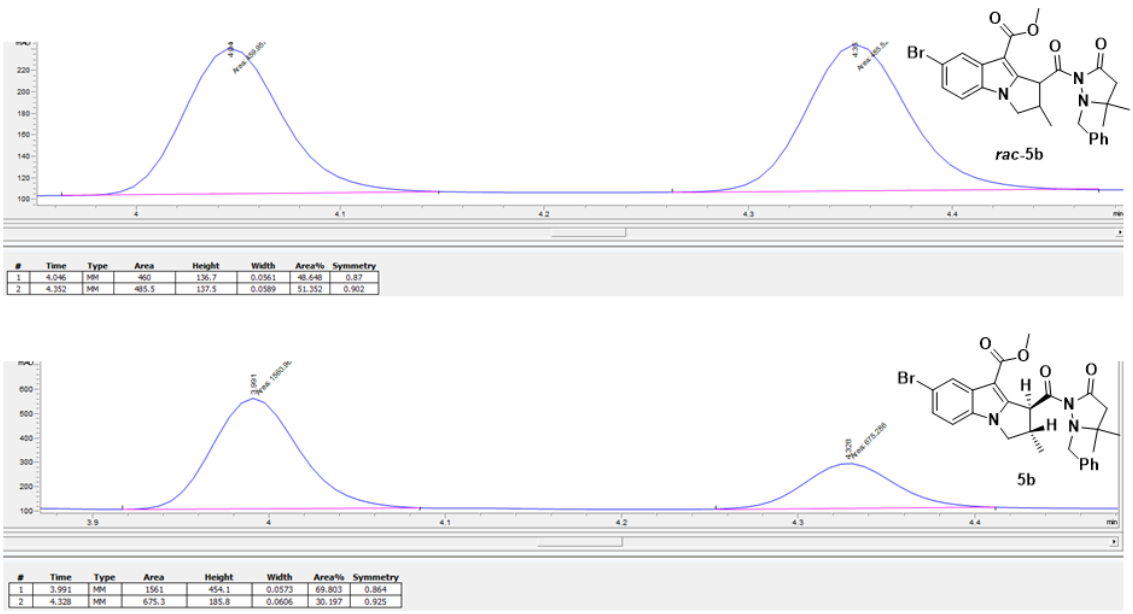


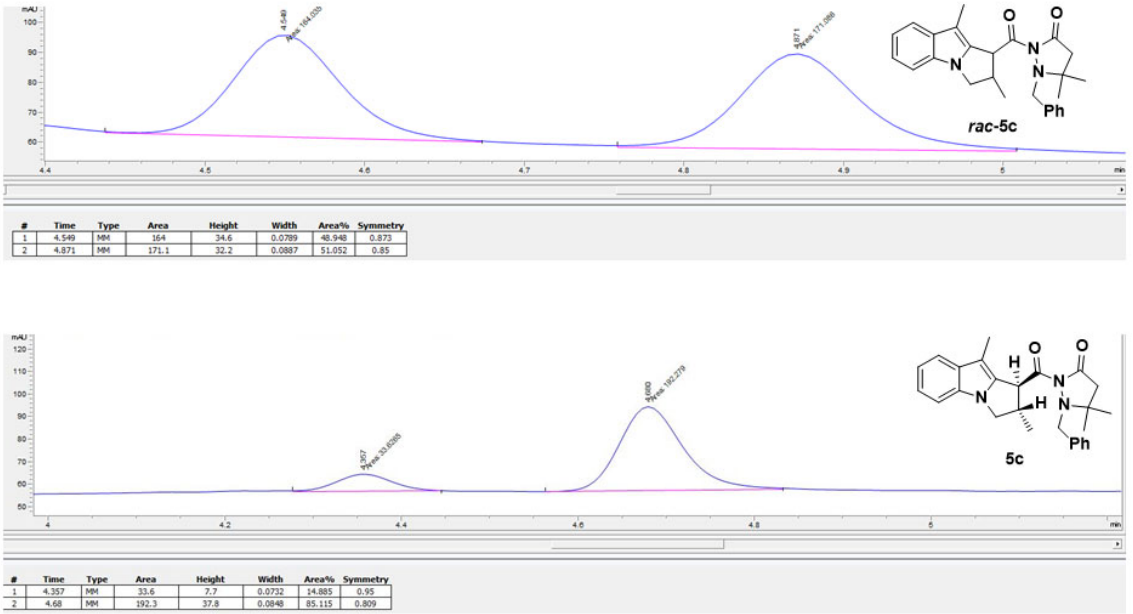
*Figure S9: SFC chromatograms for **5a***



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.046	MM	460	136.7	0.0561	48.648	0.87
2	4.352	MM	485.5	137.5	0.0589	51.352	0.902

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.991	MM	1561	454.1	0.0573	69.803	0.864
2	4.328	MM	675.3	185.8	0.0606	30.197	0.925

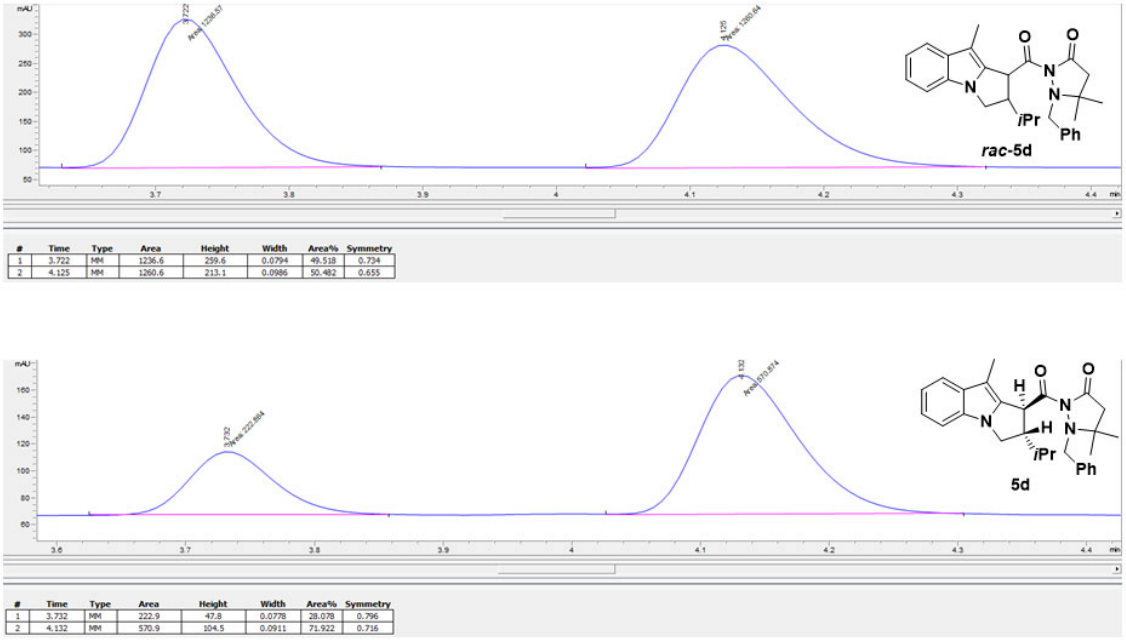
Figure S10: SFC chromatograms for ***5b***



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.549	MM	164	34.6	0.0789	48.948	0.873
2	4.871	MM	171.1	32.2	0.0887	51.052	0.85

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.357	MM	33.6	7.7	0.0732	14.885	0.95
2	4.68	MM	192.3	37.8	0.0848	85.115	0.809

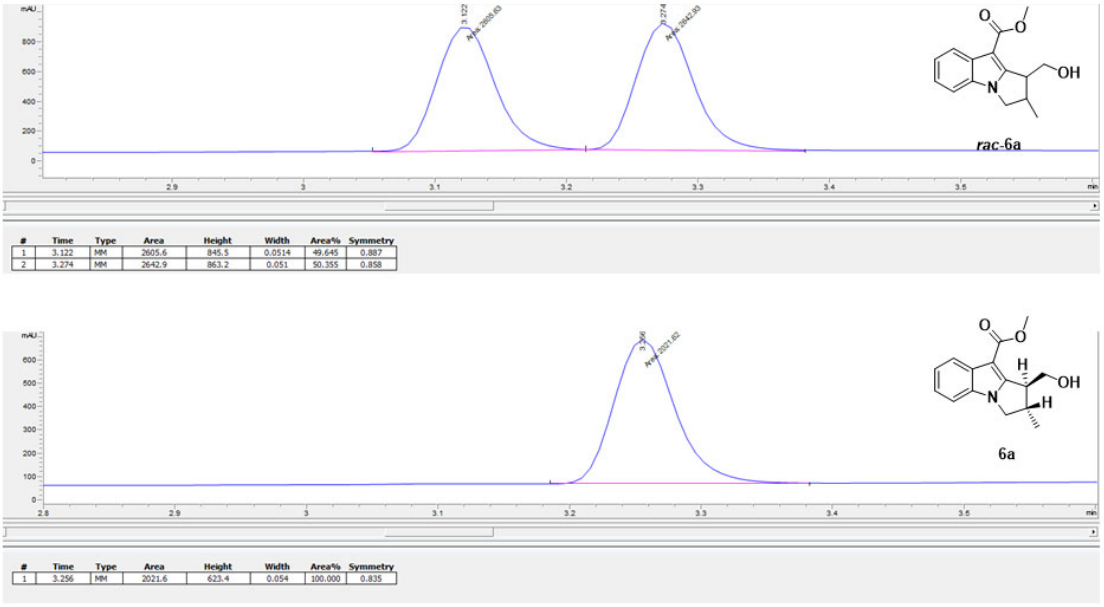
Figure S11: SFC chromatograms for ***5c***



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.722	MM	1236.6	259.6	0.0794	49.518	0.734
2	4.125	MM	1260.6	213.1	0.0986	50.482	0.655

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.732	MM	222.9	47.8	0.0778	28.078	0.796
2	4.132	MM	570.9	104.5	0.0911	71.922	0.716

*Figure S12: SFC chromatograms for **5d***



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.122	MM	2605.6	845.5	0.0514	49.645	0.887
2	3.274	MM	2642.9	863.2	0.051	50.355	0.858

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.256	MM	2021.6	623.4	0.054	100.000	0.835

*Figure S13: SFC chromatograms for **6a***

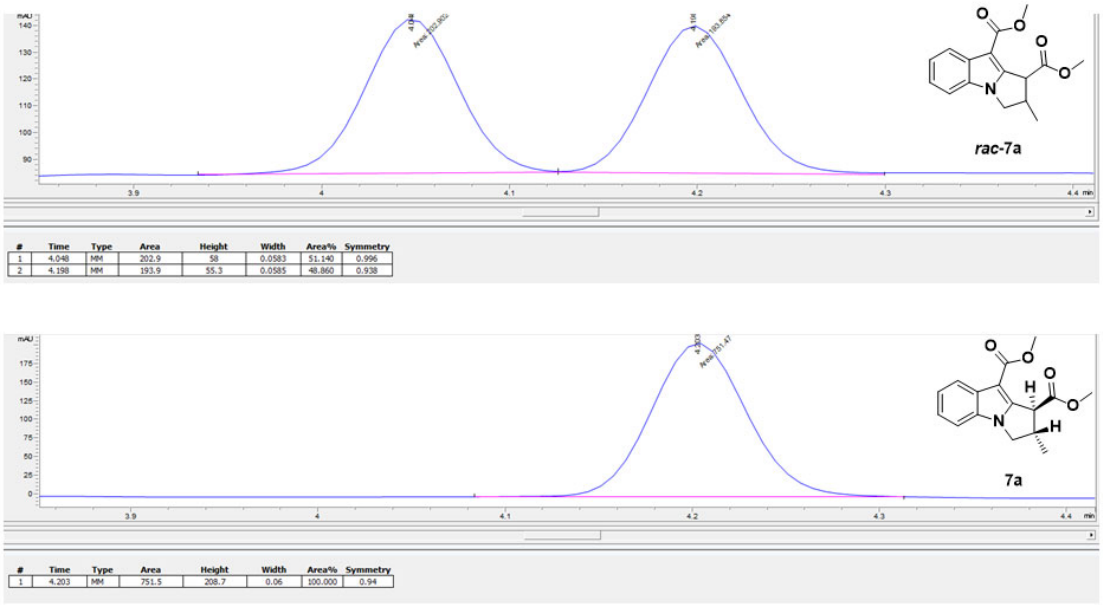


*Figure S14: SFC chromatograms for **7a***

10. Emission spectra of light sources

Emission spectra of light sources used for carrying out the photochemical reactions are presented.

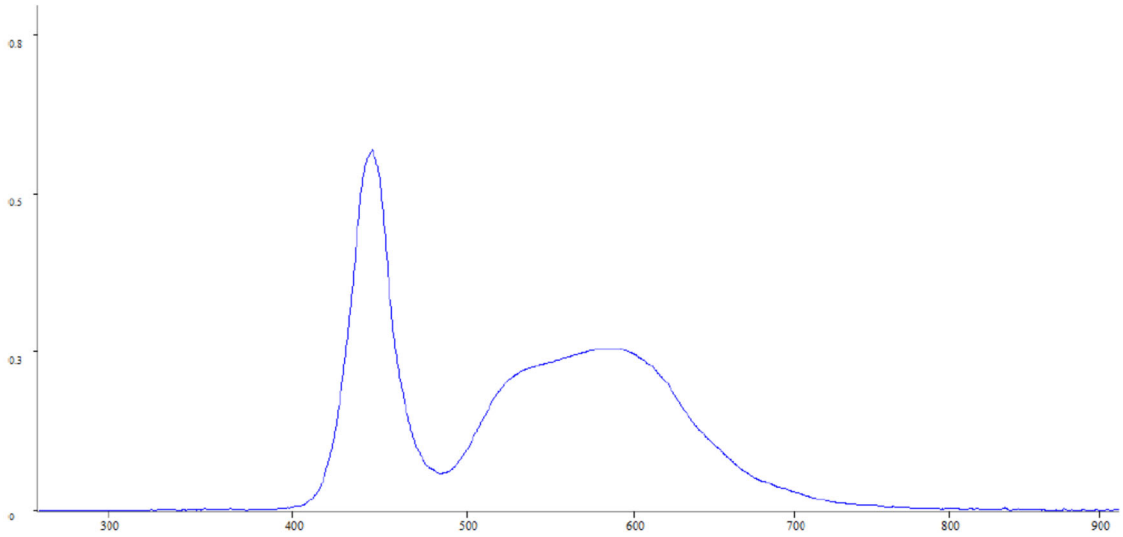


Figure S15: Emission spectrum of 5000 K White LED of the custom-made temperature-controlled system

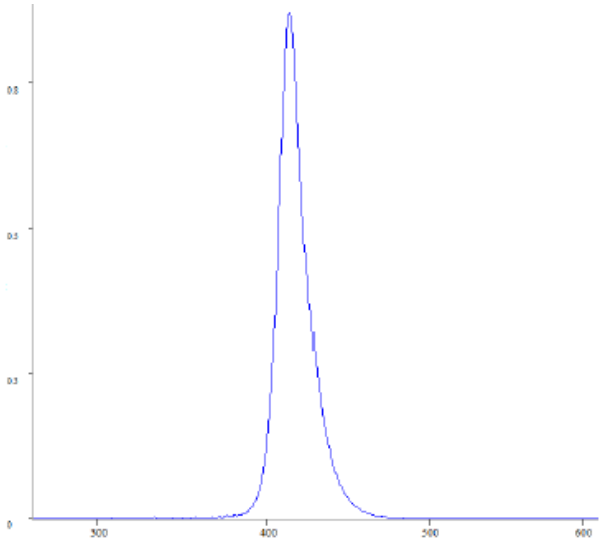


Figure S16: Emission spectrum of 420 nm LED of the custom-made temperature-controlled system (350 mW)

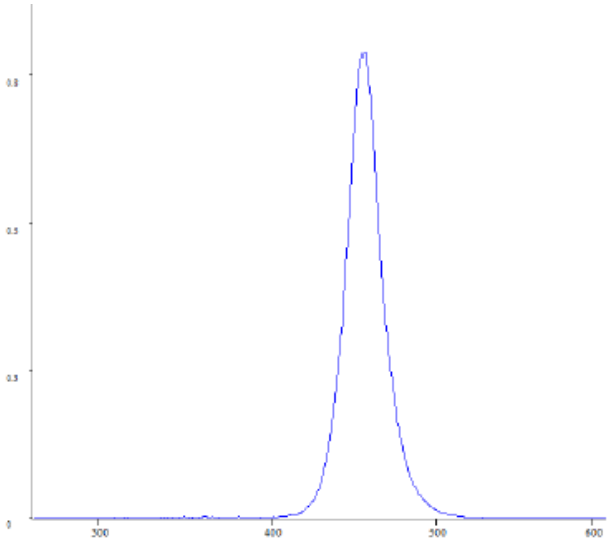


Figure S17: Emission spectrum of 450 nm LED of the custom-made temperature-controlled system (350 mW)

11. NMR Spectra

11.1. NMR spectra of indole derivatives 1

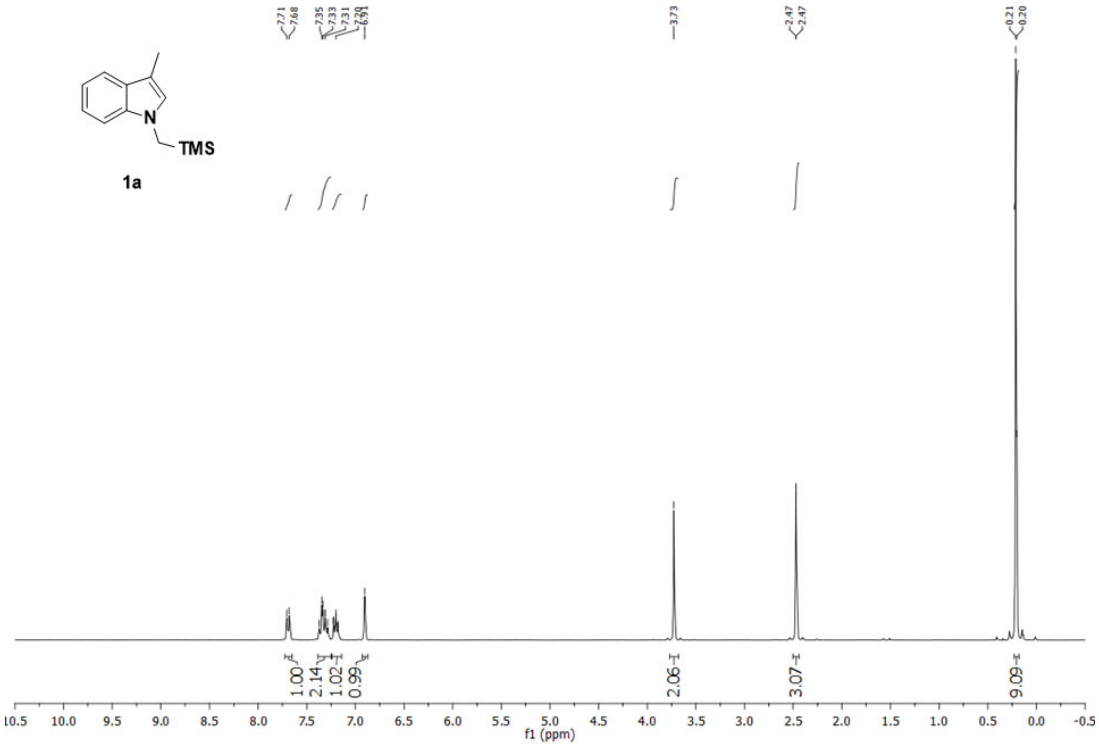


*Figure S18: ^{1}H NMR spectrum of indole **1a** ($CDCl_3$, 298 K)*

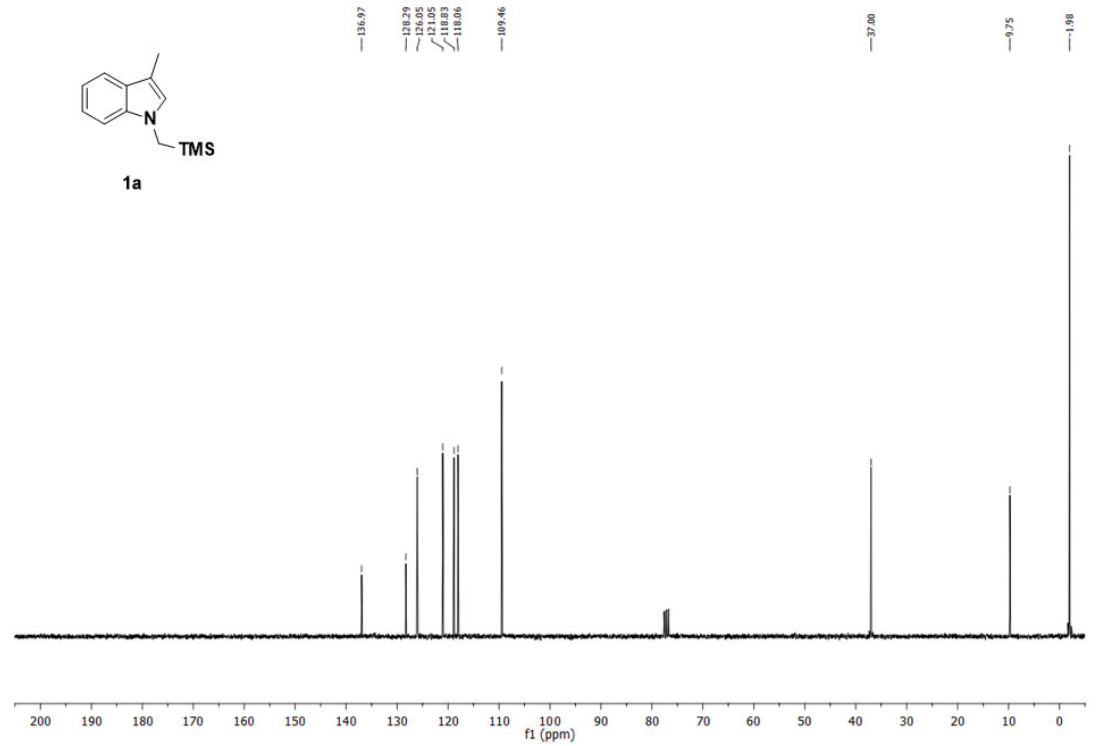


*Figure S19: ^{13}C NMR spectrum of indole **1a** ($CDCl_3$, 298 K)*

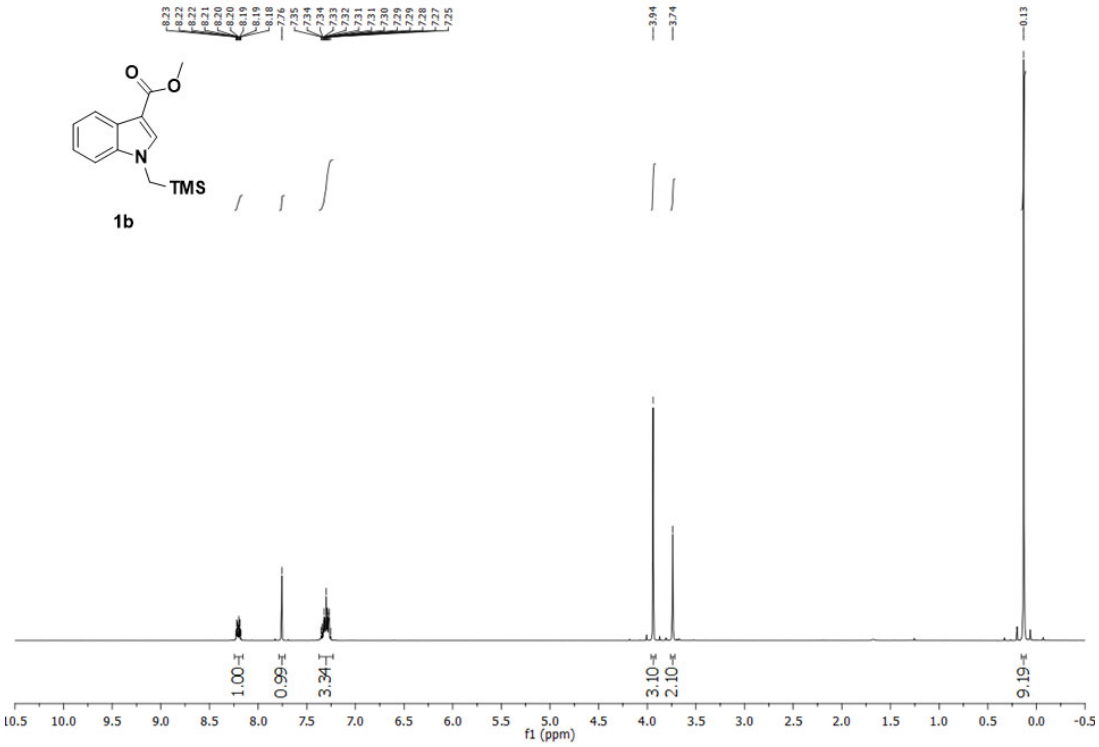


*Figure S20: ^{1}H NMR spectrum of indole **1b** ($CDCl_3$, 298 K)*

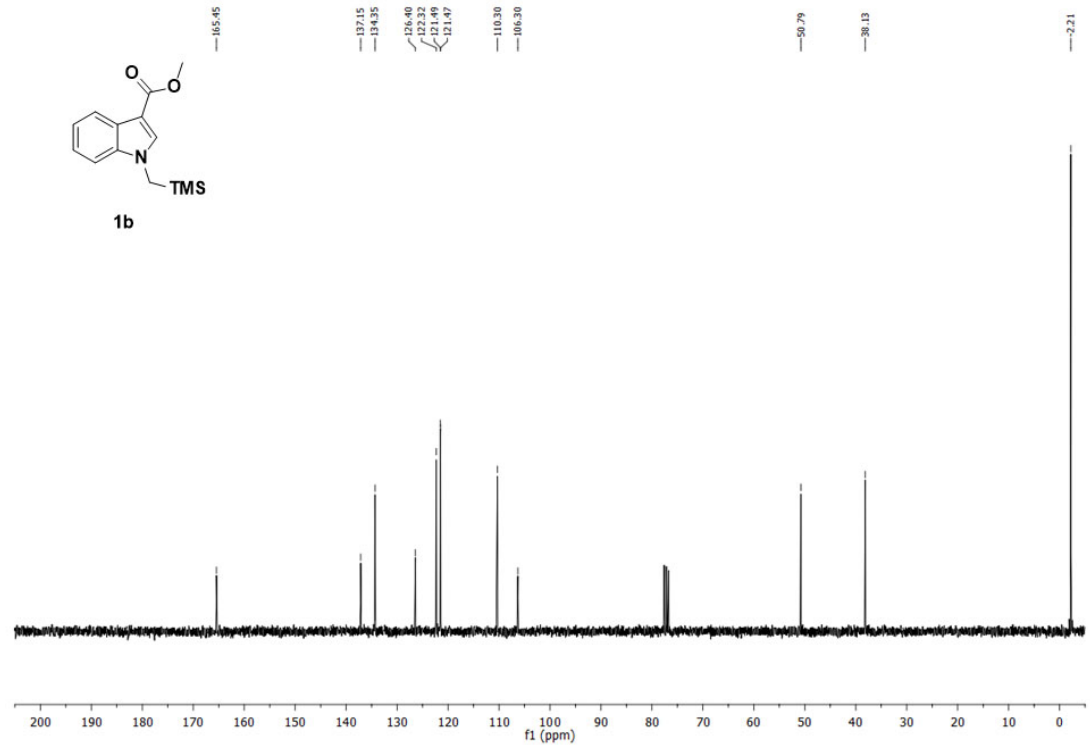


*Figure S21: ^{13}C NMR spectrum of indole **1b** ($CDCl_3$, 298 K)*

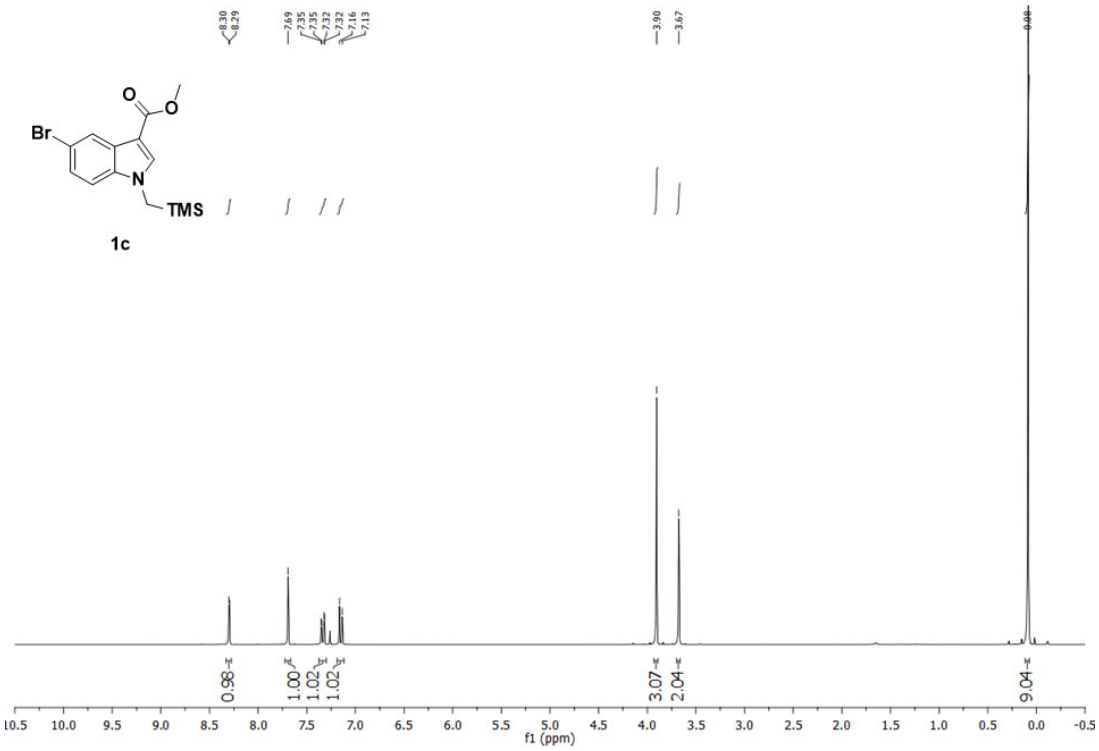


*Figure S22: ^{1}H NMR spectrum of indole **1c** ($CDCl_3$, 298 K)*

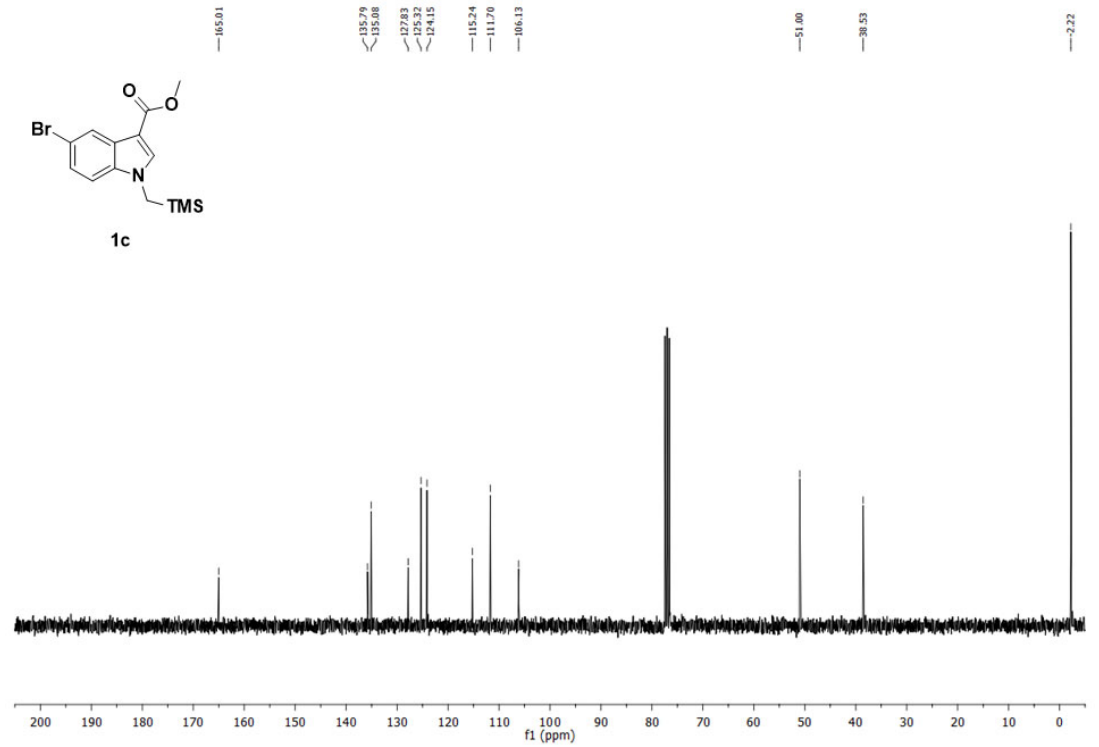


*Figure S23: ^{13}C NMR spectrum of indole **1c** ($CDCl_3$, 298 K)*

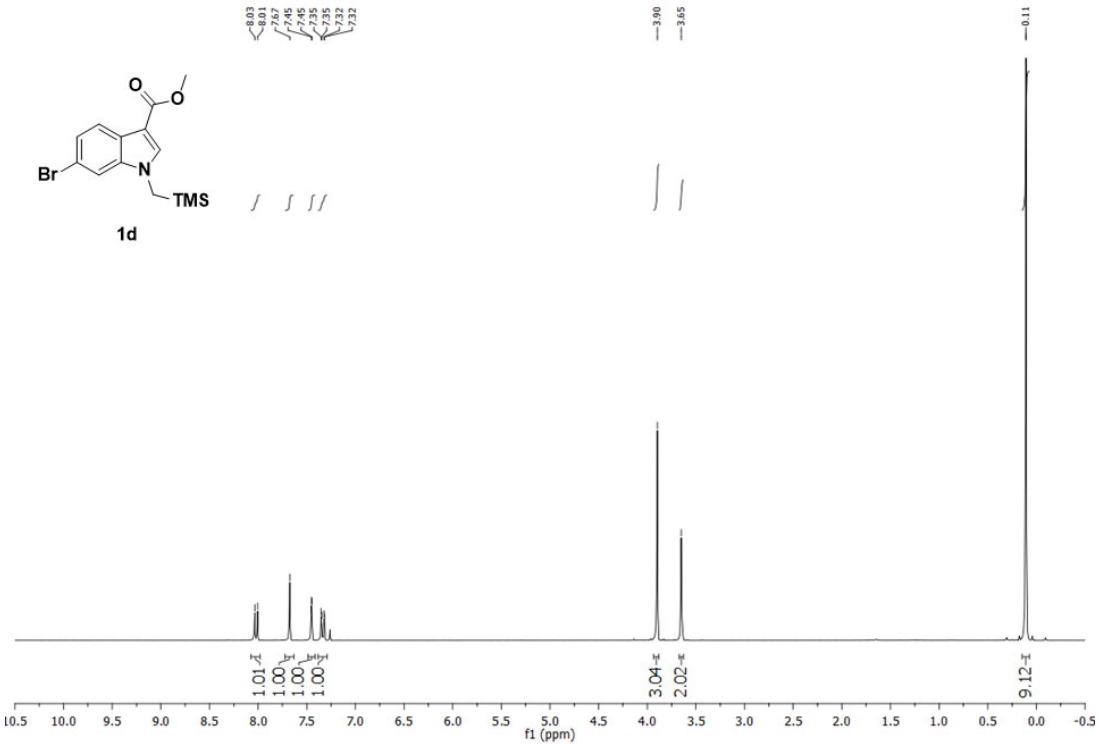


*Figure S24: ^{1}H NMR spectrum of indole **1d** ($CDCl_3$, 298 K)*

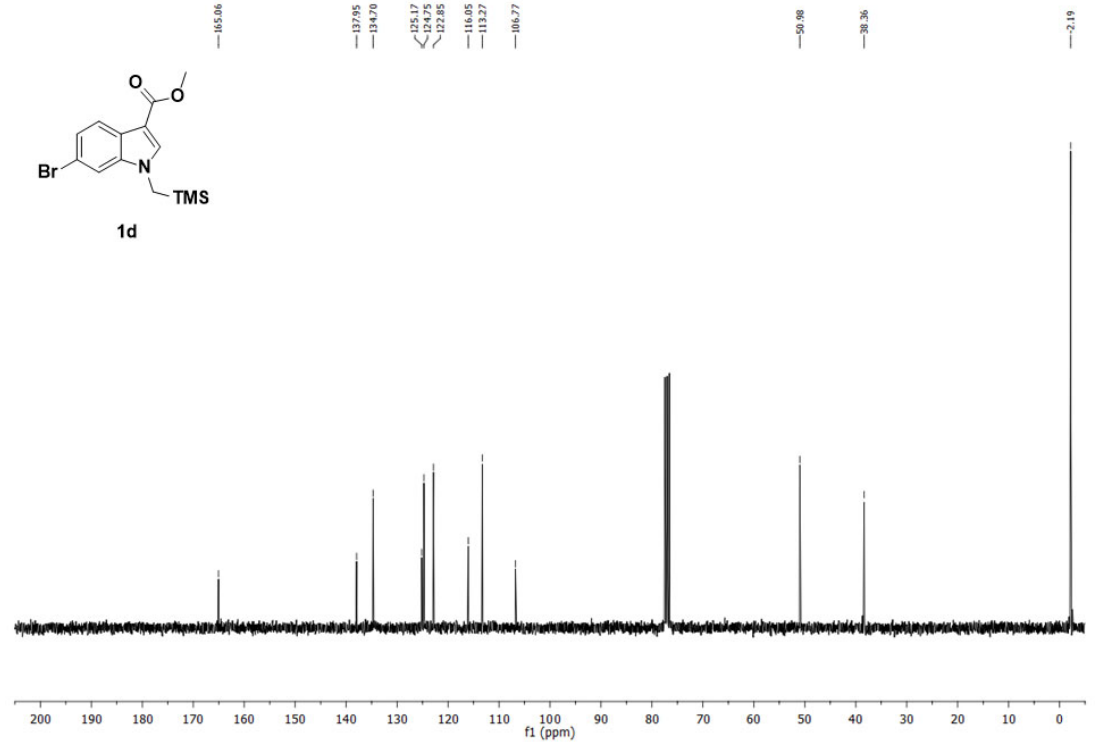


*Figure S25: ^{13}C NMR spectrum of indole **1d** ($CDCl_3$, 298 K)*

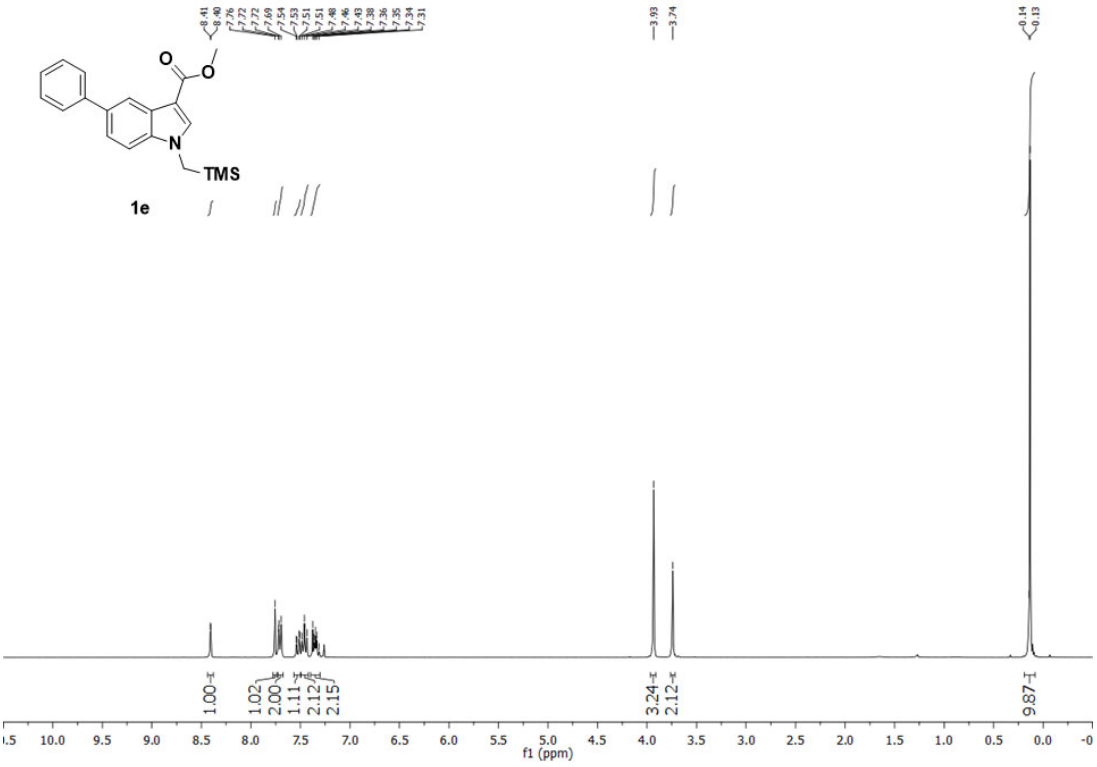


*Figure S26: ^{1}H NMR spectrum of indole **1e** ($CDCl_3$, 298 K)*

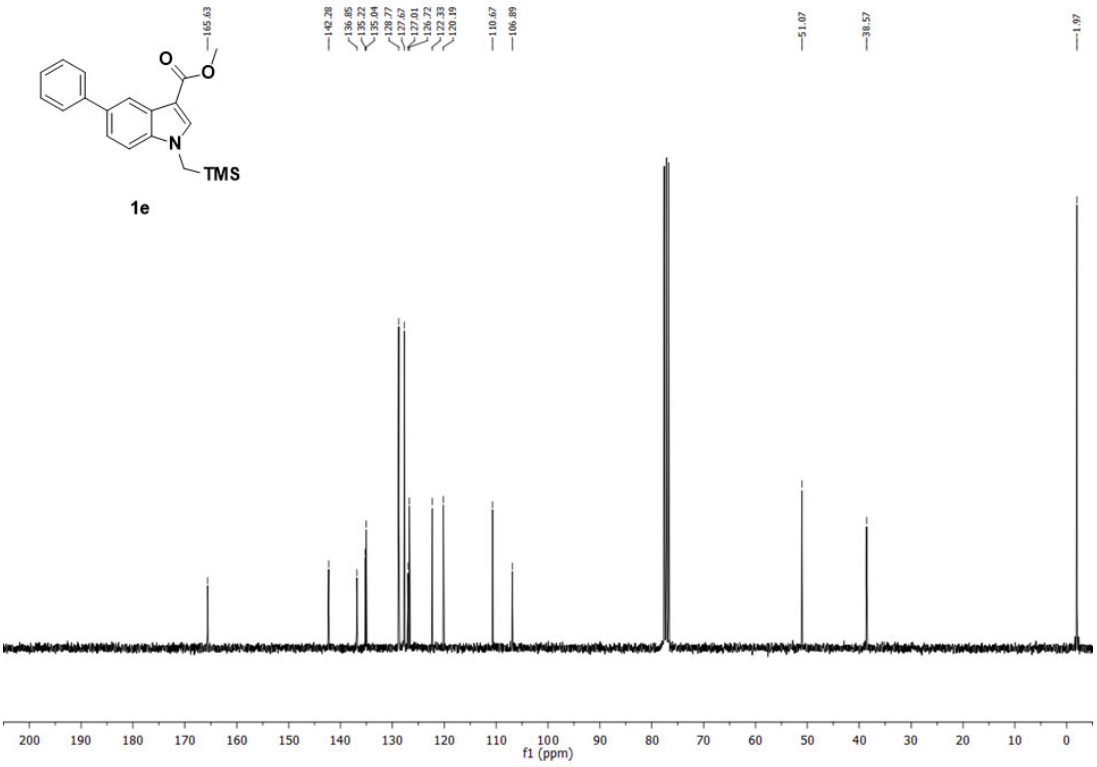


*Figure S27: ^{13}C NMR spectrum of indole **1e** ($CDCl_3$, 298 K)*

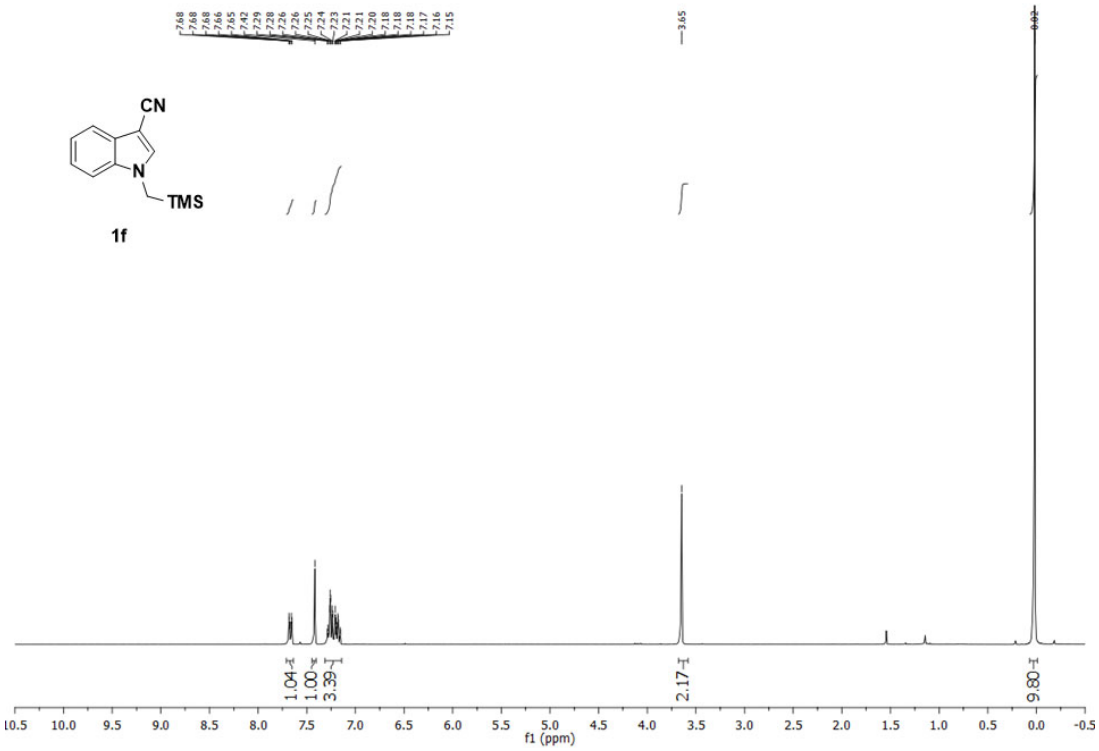


*Figure S28: ^{1}H NMR spectrum of indole **1f** ($CDCl_3$, 298 K)*

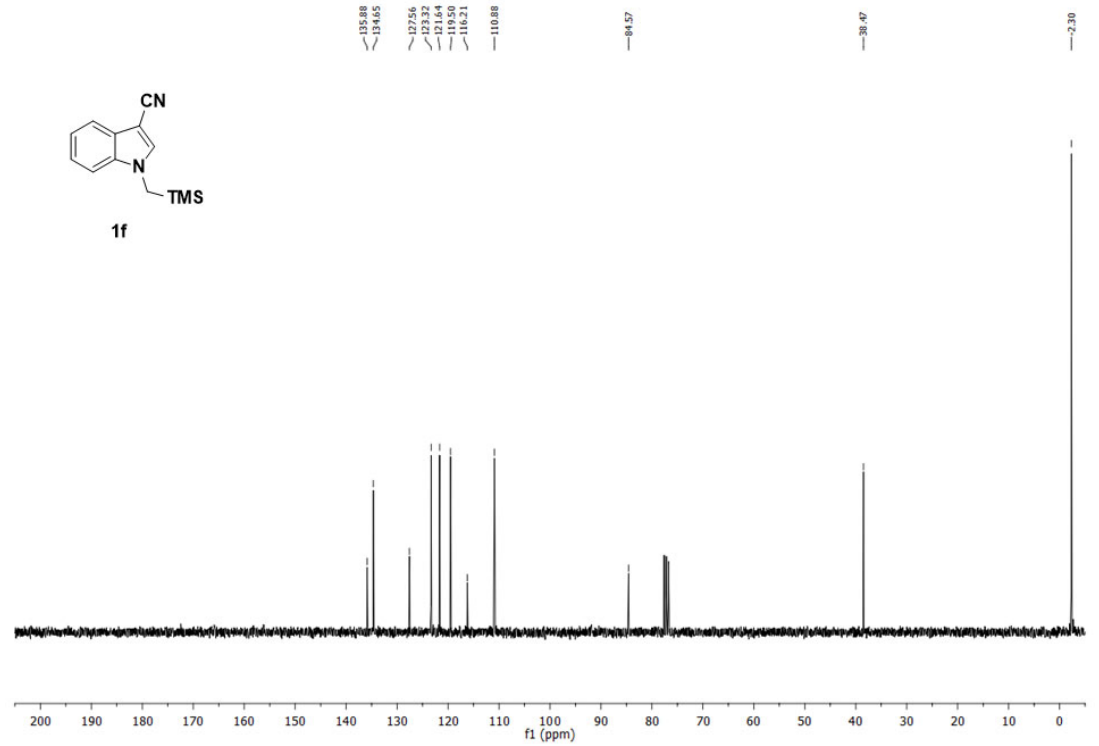


*Figure S29: ^{13}C NMR spectrum of indole **1f** ($CDCl_3$, 298 K)*

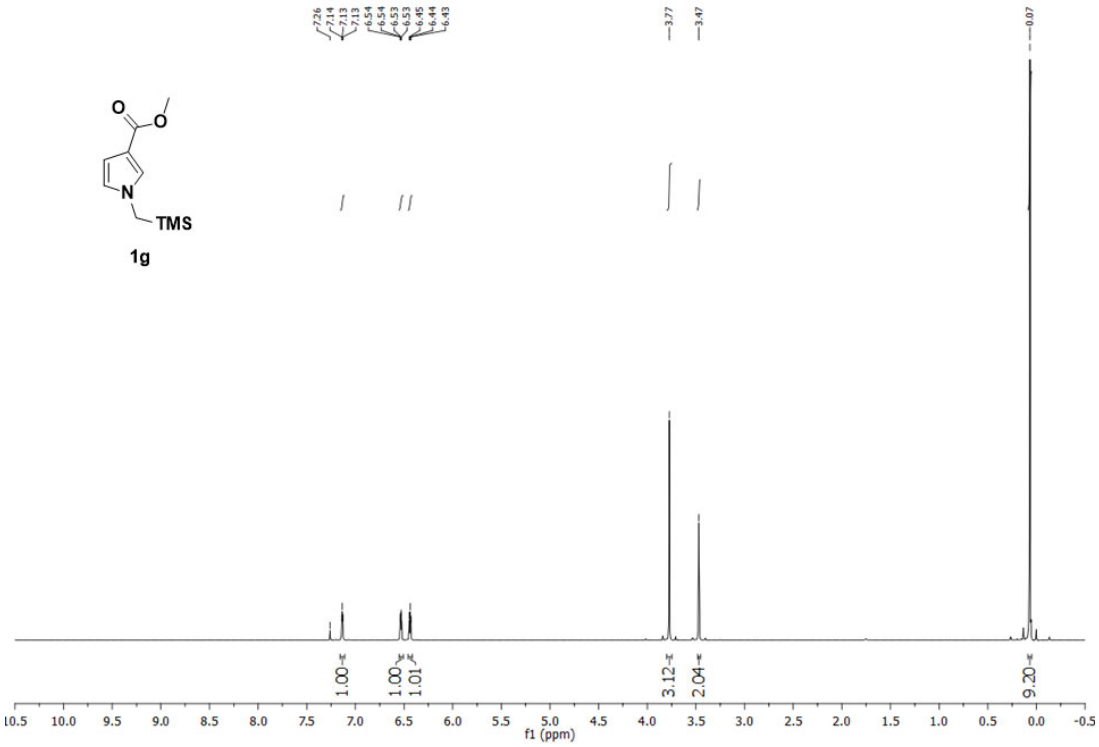


*Figure S30: ^{1}H NMR spectrum of indole **1g** ($CDCl_3$, 298 K)*

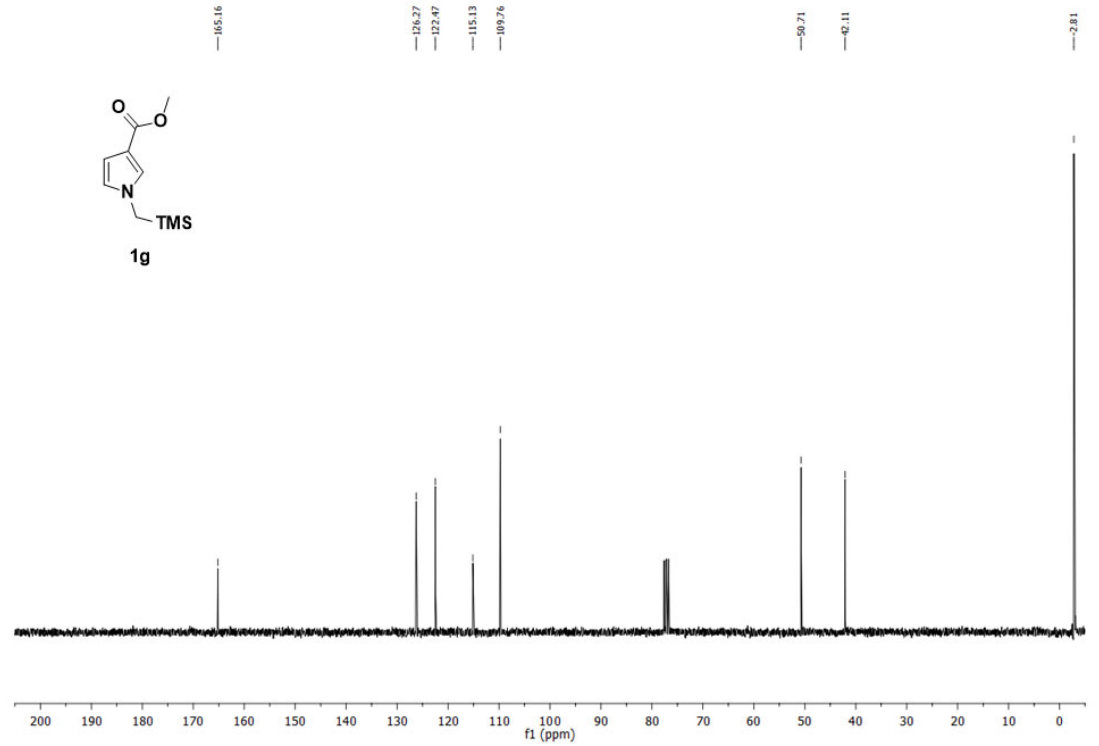


*Figure S31: ^{13}C NMR spectrum of indole **1g** ($CDCl_3$, 298 K)*

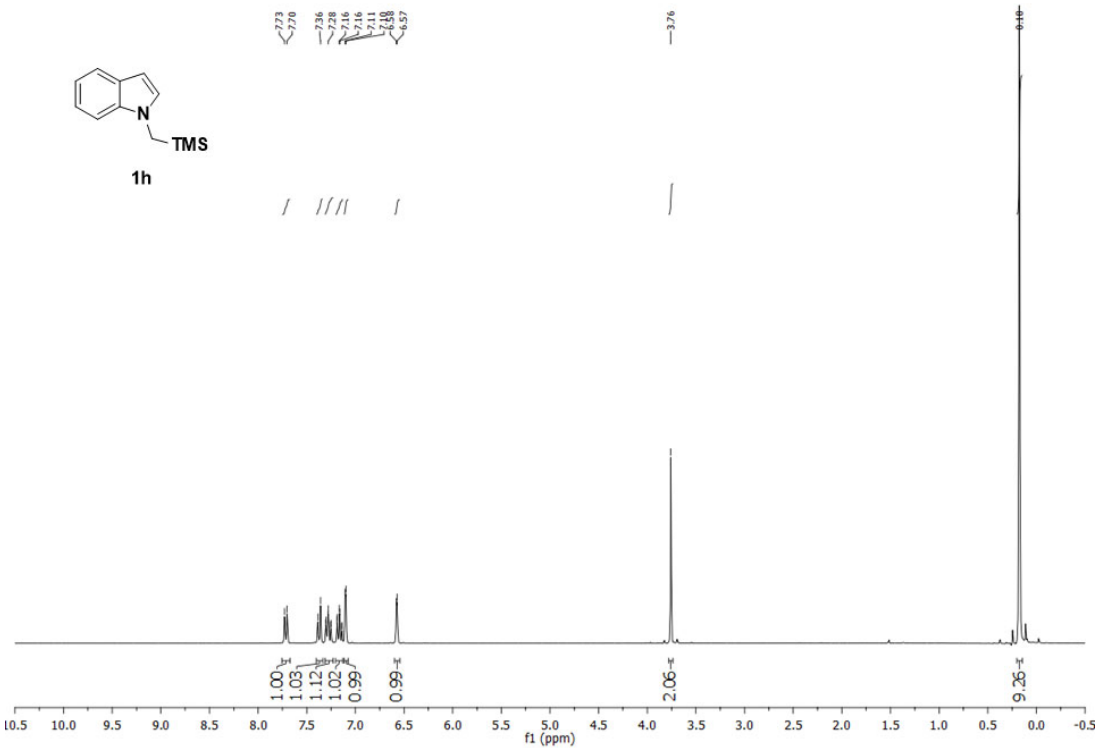


*Figure S32: ^{1}H NMR spectrum of indole **1h** ($CDCl_3$, 298 K)*

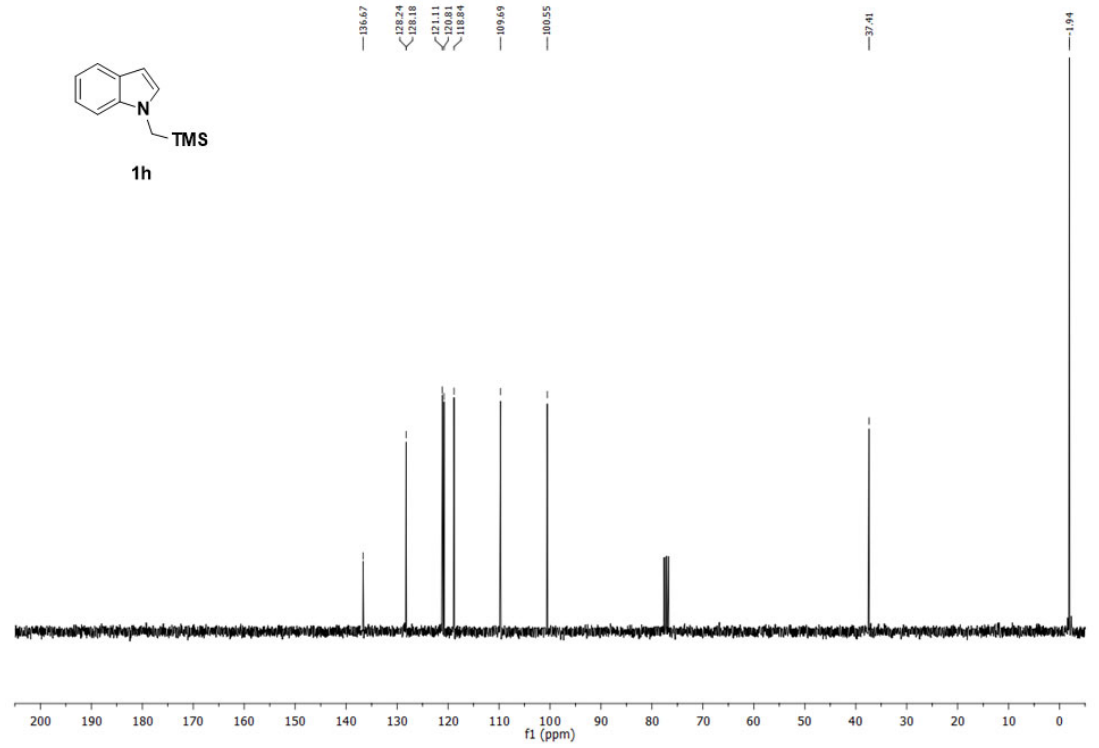


*Figure S33: ^{13}C NMR spectrum of indole **1h** ($CDCl_3$, 298 K)*

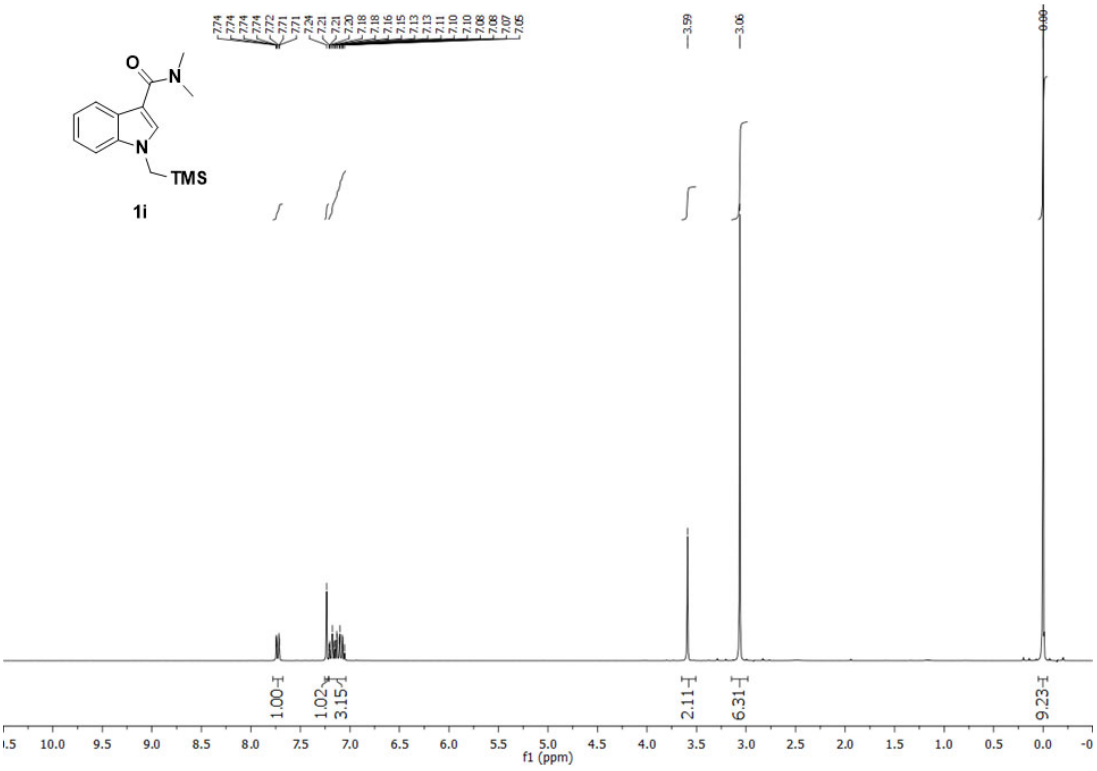


*Figure S34: ^{1}H NMR spectrum of indole **1i** ($CDCl_3$, 298 K)*

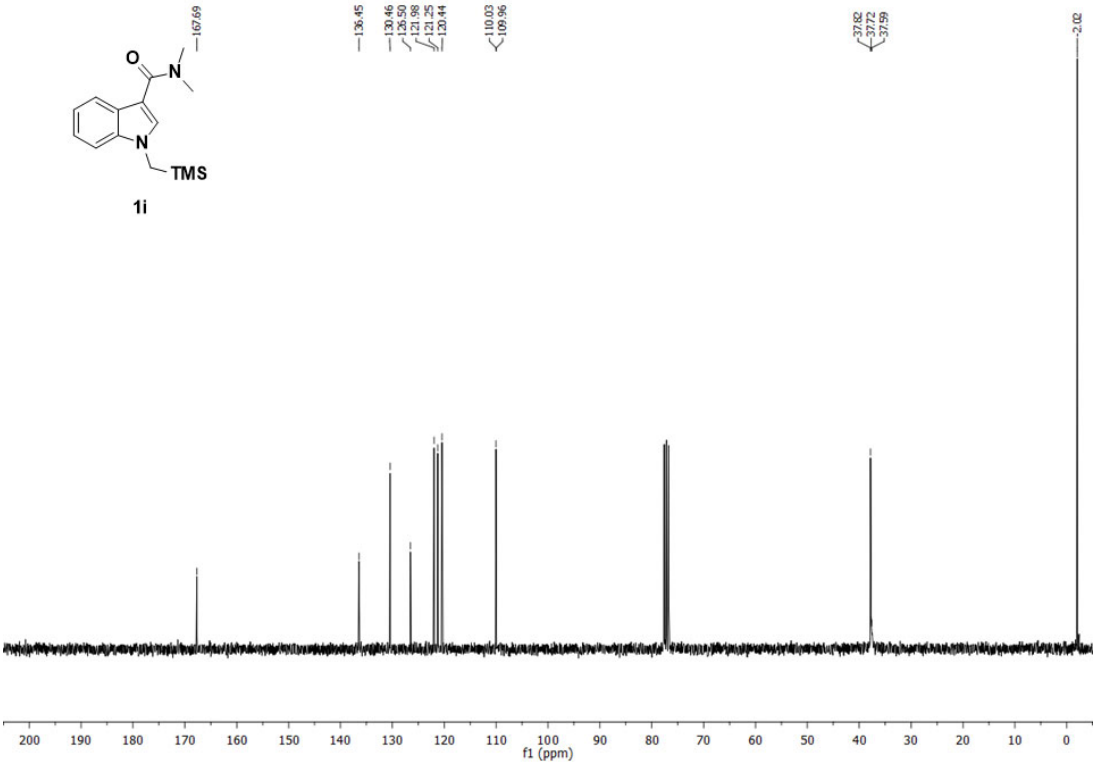


*Figure S35: ^{13}C NMR spectrum of indole **1i** ($CDCl_3$, 298 K)*

11.2. NMR spectra of Michael acceptors 2 and 3

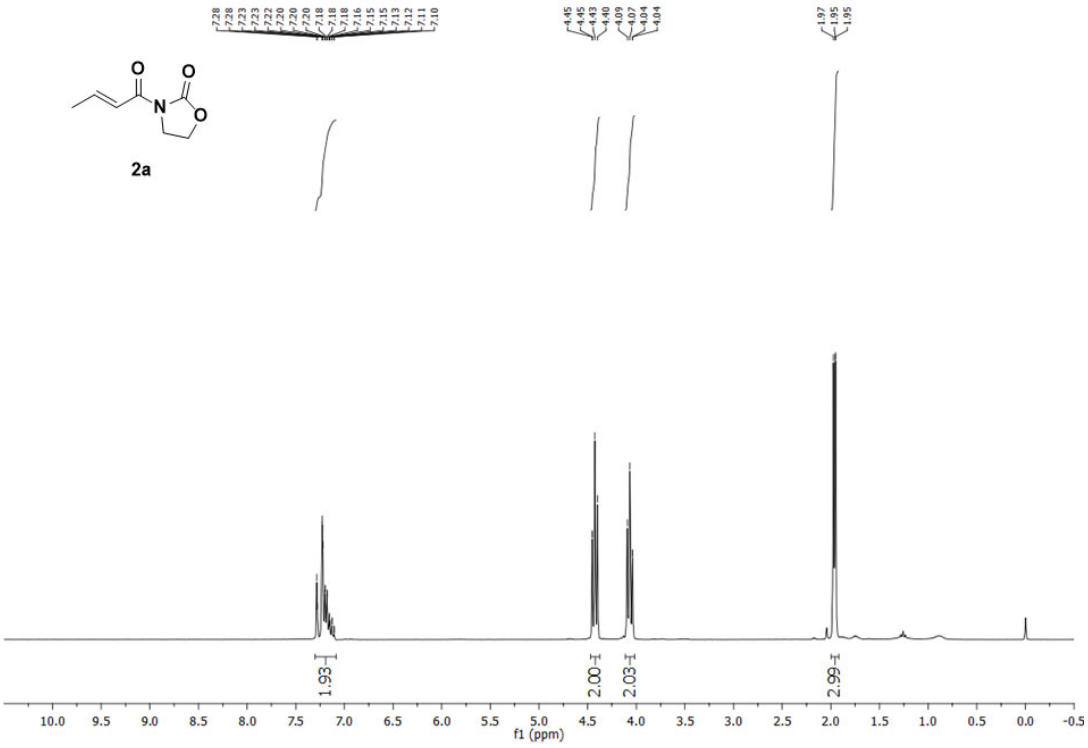


*Figure S36: ^{1}H NMR spectrum of Michael acceptor **2a** ($CDCl_3$, 298 K)*

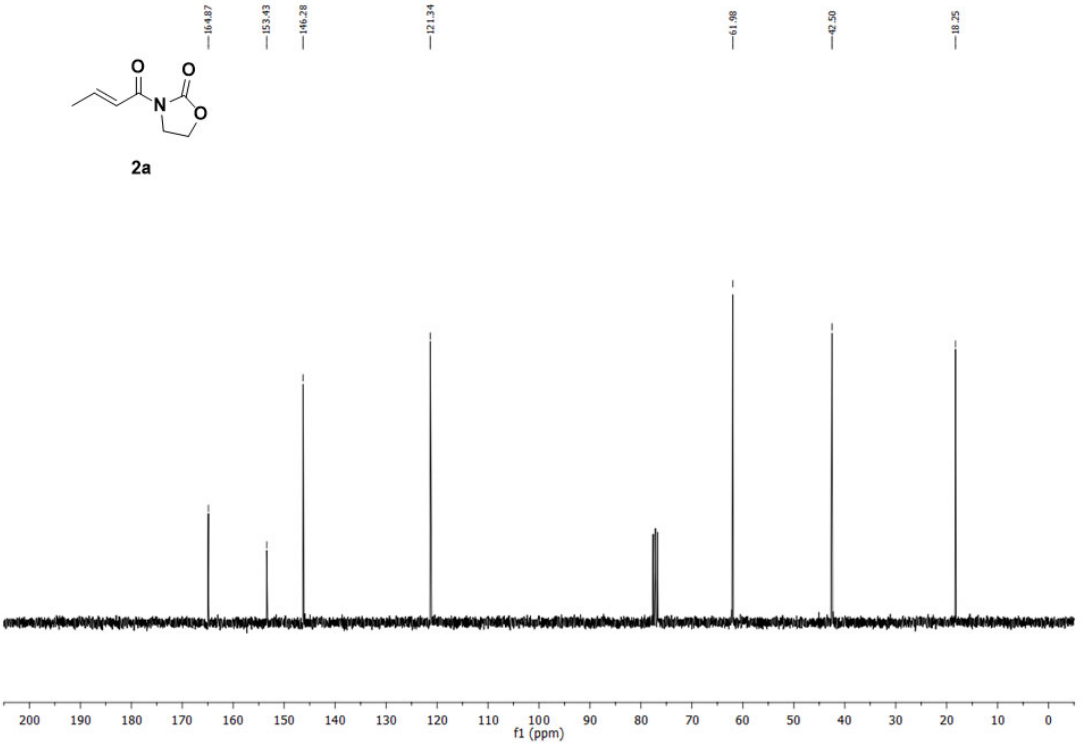


*Figure S37: ^{13}C NMR spectrum of Michael acceptor **2a** ($CDCl_3$, 298 K)*

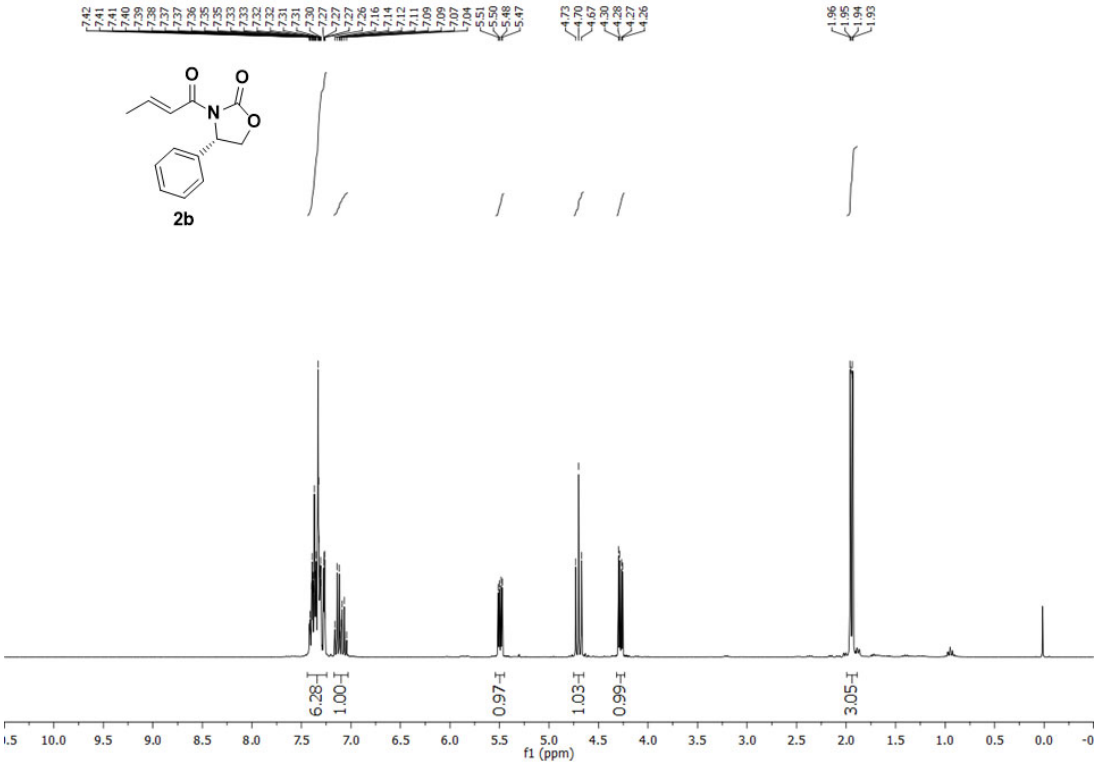


*Figure S38: ^{1}H NMR spectrum of Michael acceptor **2b** ($CDCl_3$, 298 K)*

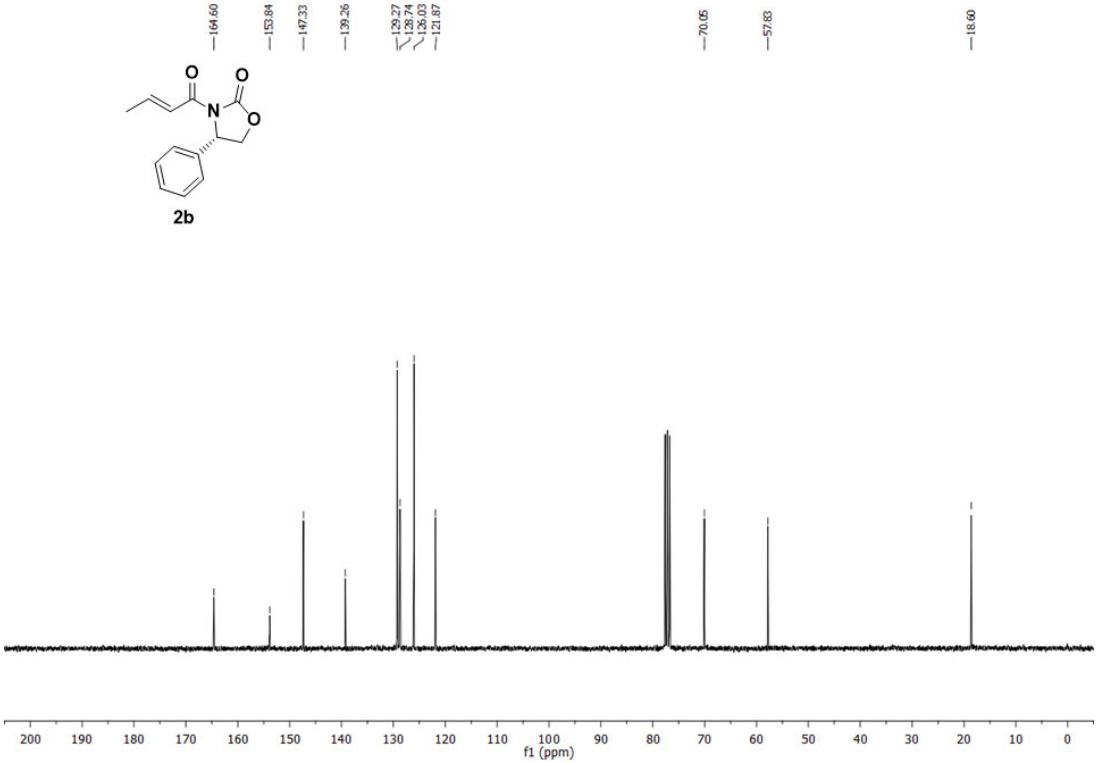


*Figure S39: ^{13}C NMR spectrum of Michael acceptor **2b** ($CDCl_3$, 298 K)*

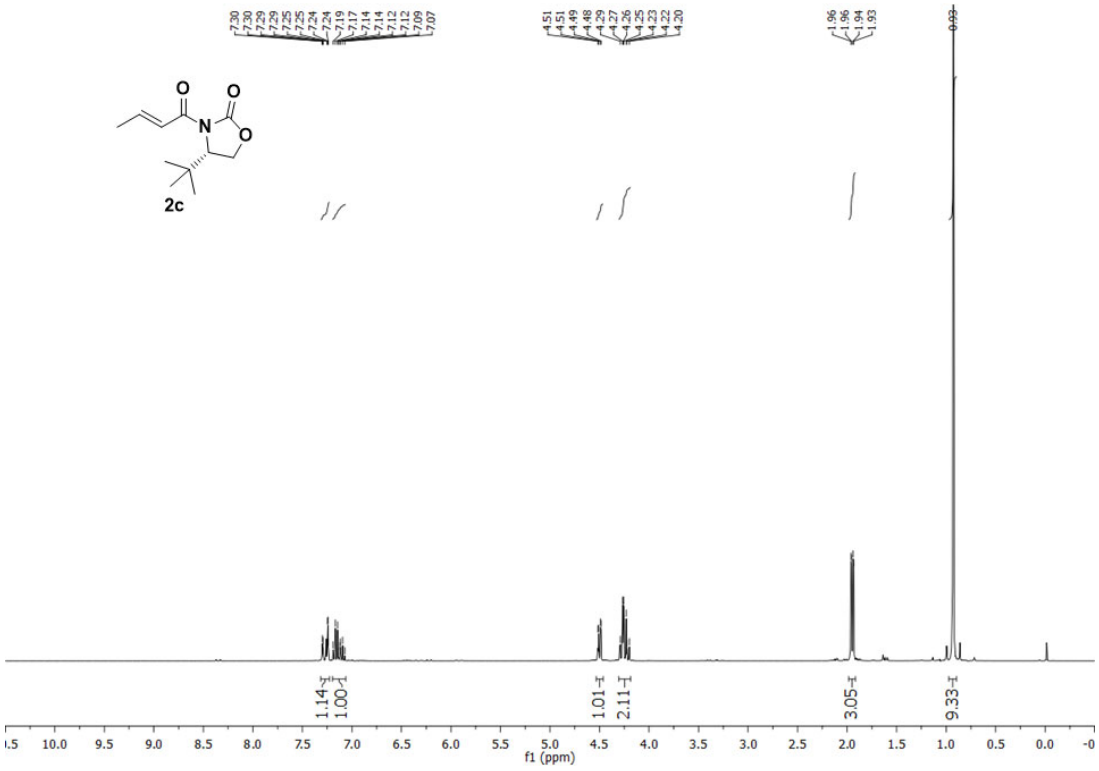


*Figure S40: [1]H NMR spectrum of Michael acceptor **2c** ($CDCl_3$, 298 K)*

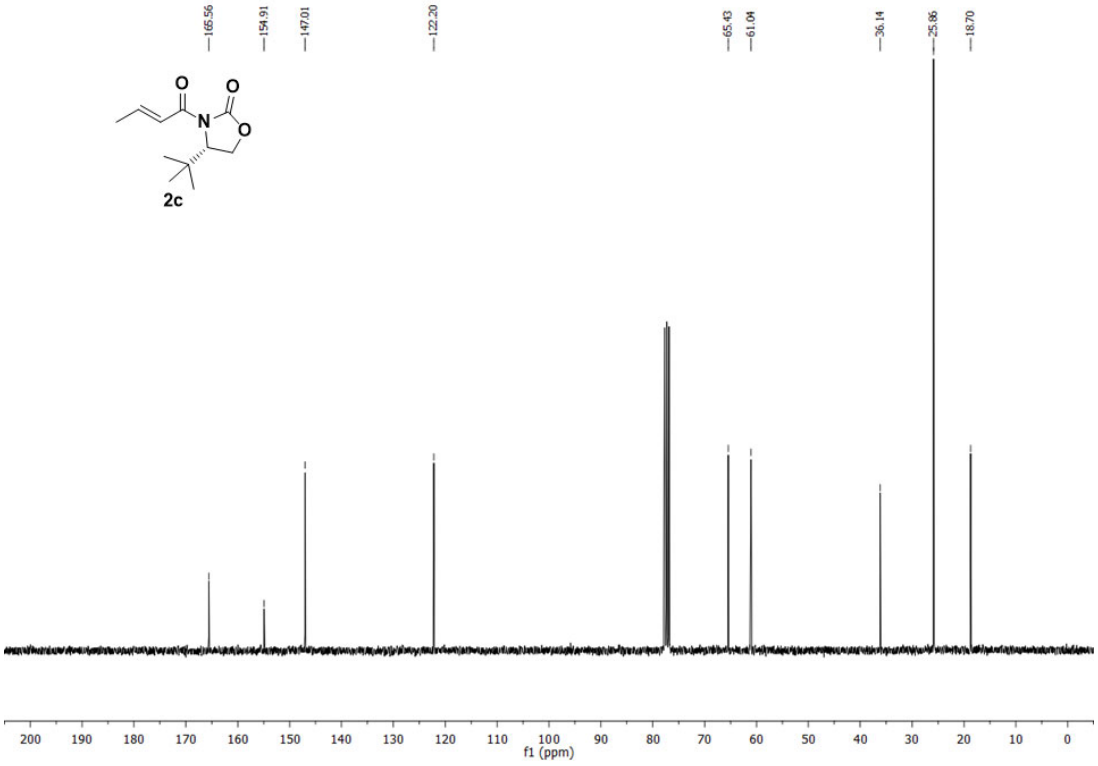


*Figure S41: [13]C NMR spectrum of Michael acceptor **2c** ($CDCl_3$, 298 K)*

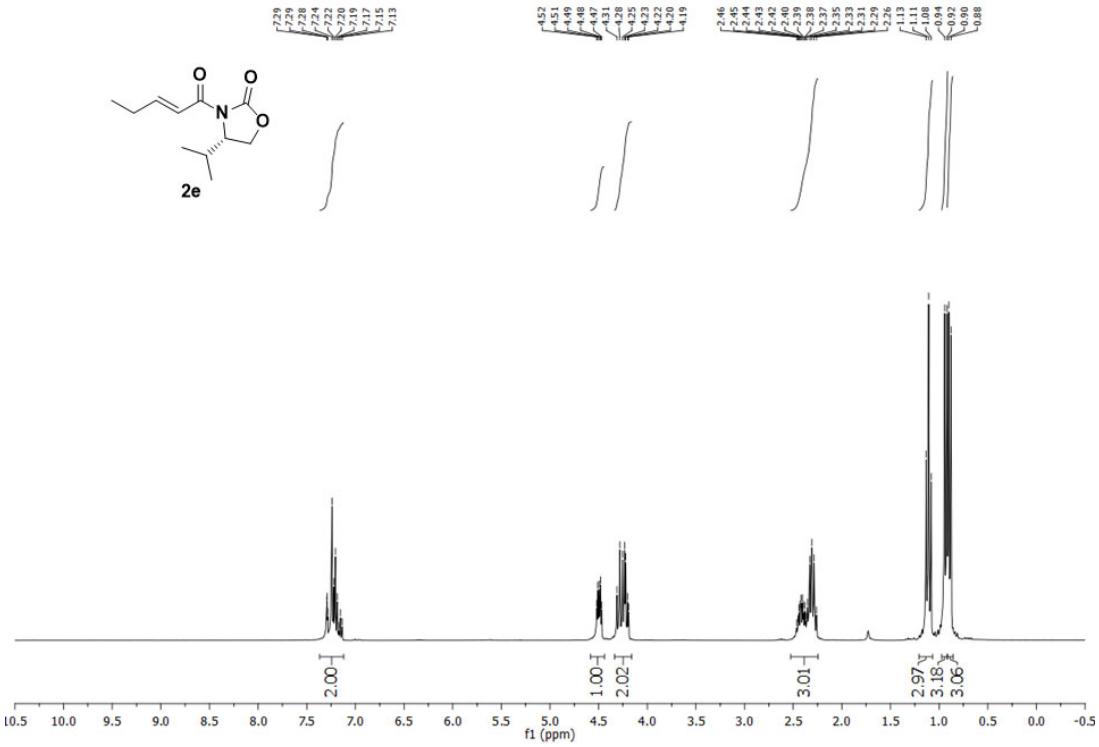


*Figure S42: ^{1}H NMR spectrum of Michael acceptor **2e** ($CDCl_3$, 298 K)*

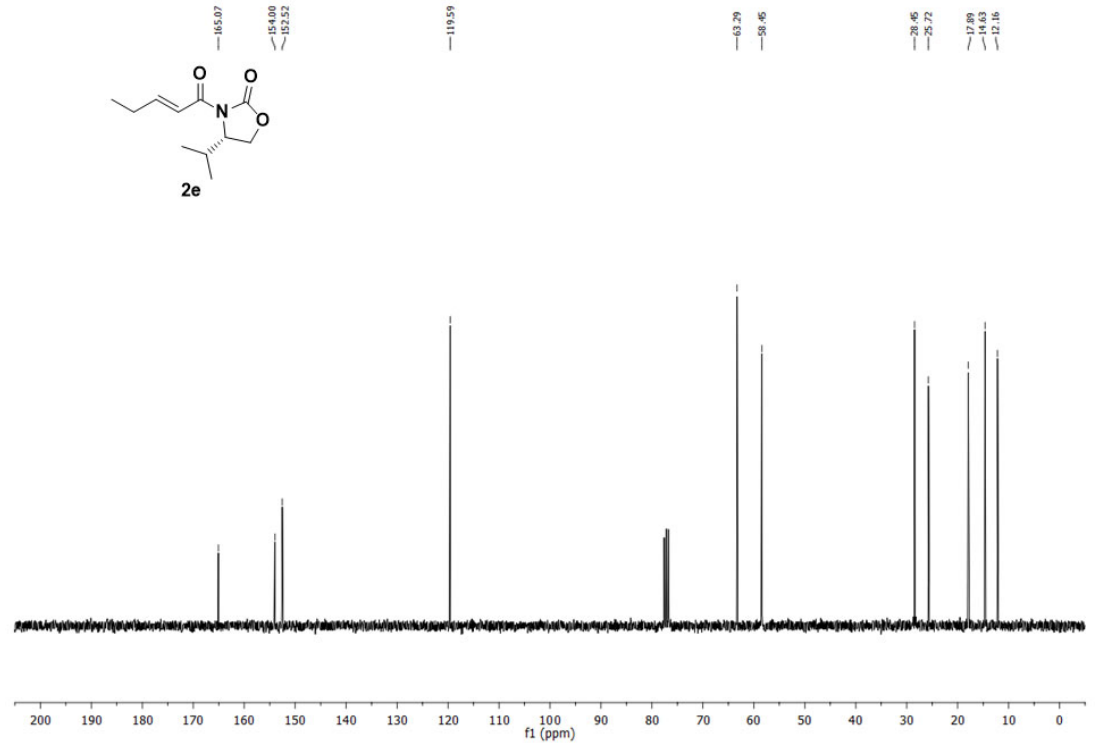


*Figure S43: ^{13}C NMR spectrum of Michael acceptor **2e** ($CDCl_3$, 298 K)*

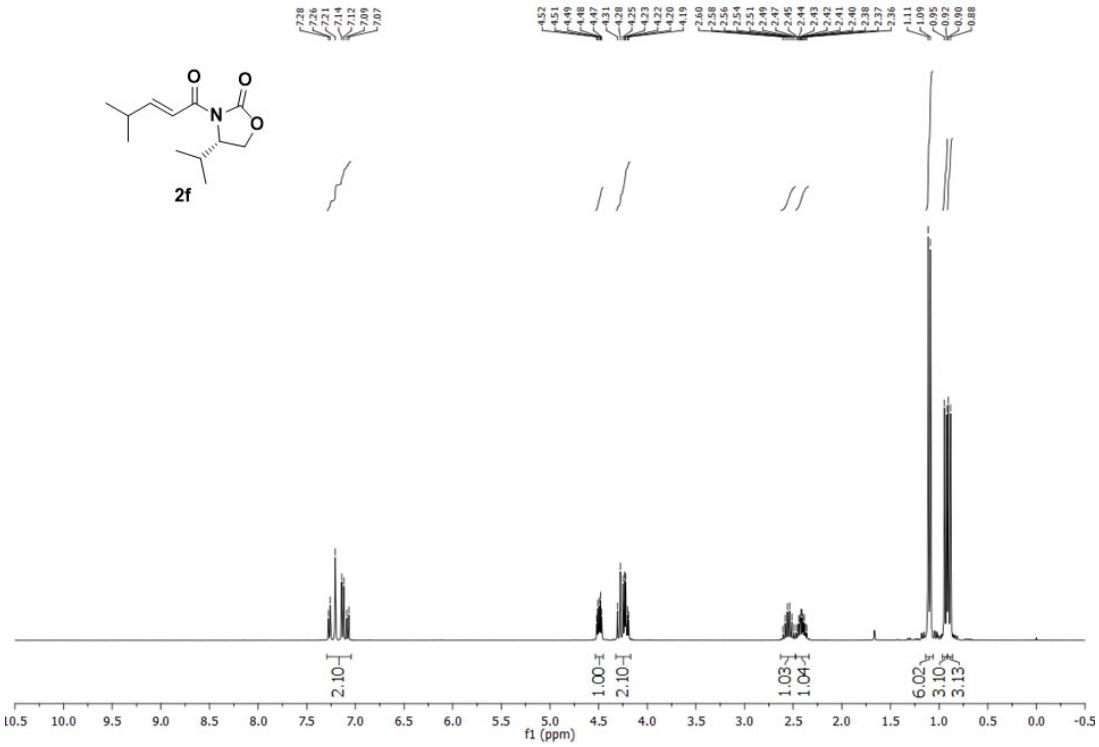


*Figure S44: ^{1}H NMR spectrum of Michael acceptor **2f** ($CDCl_3$, 298 K)*

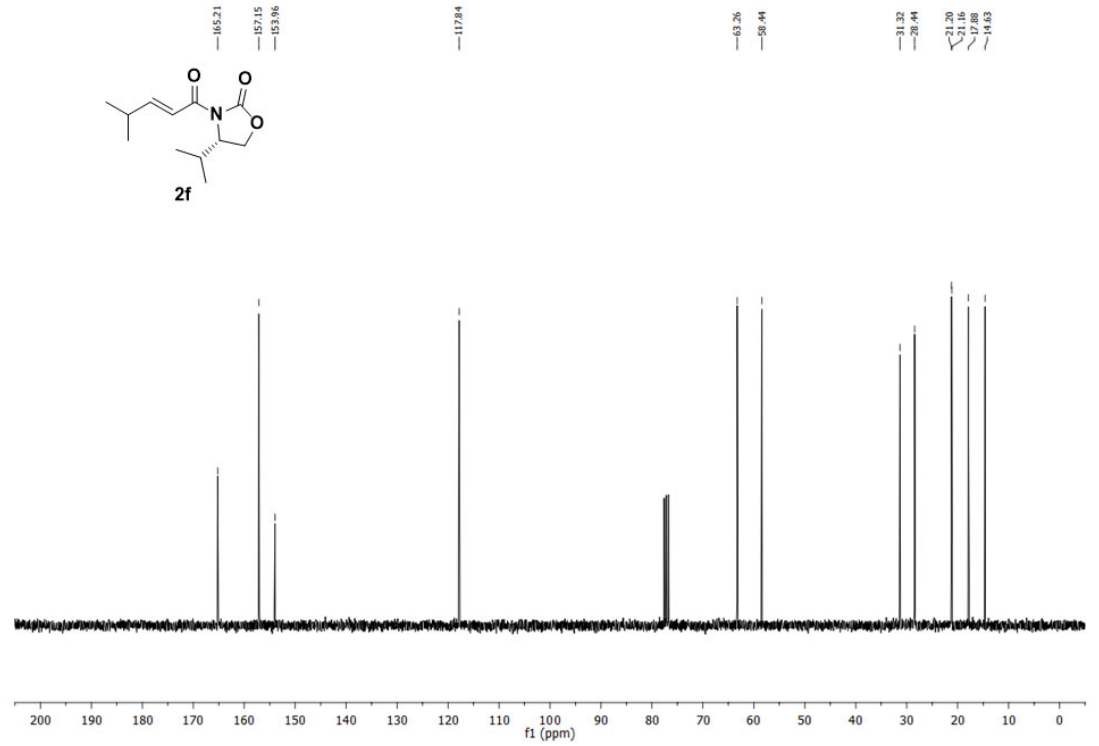


*Figure S45: ^{13}C NMR spectrum of Michael acceptor **2f** ($CDCl_3$, 298 K)*

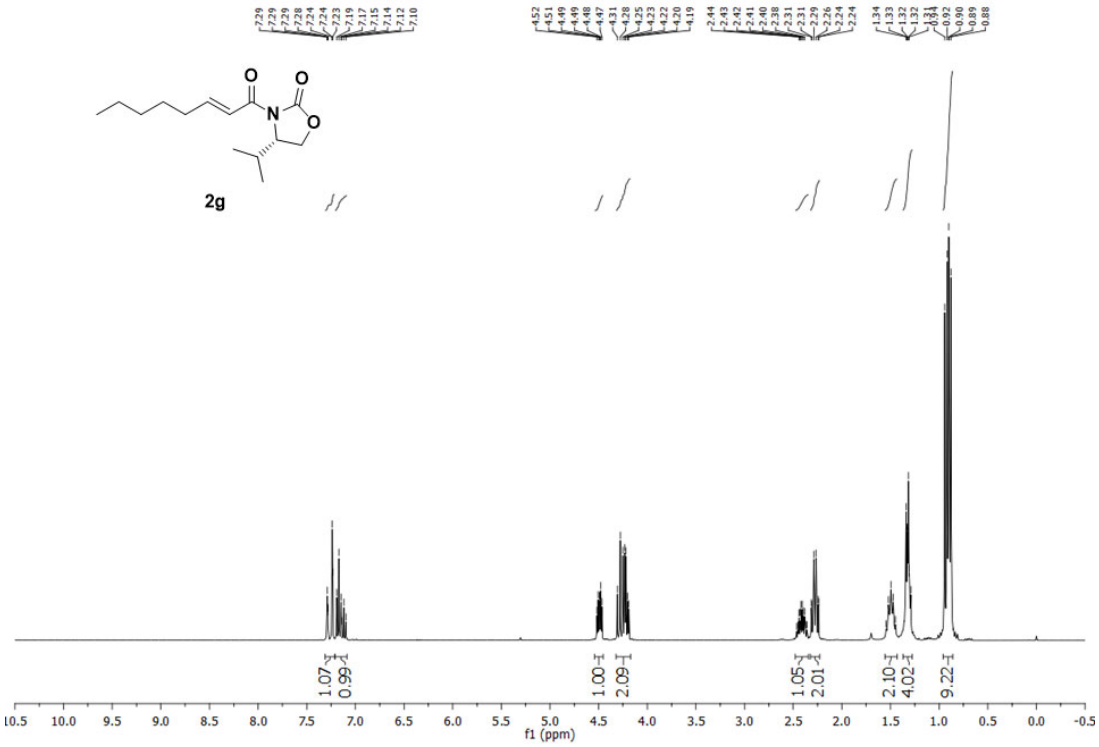


*Figure S46: ^{1}H NMR spectrum of Michael acceptor **2g** ($CDCl_3$, 298 K)*

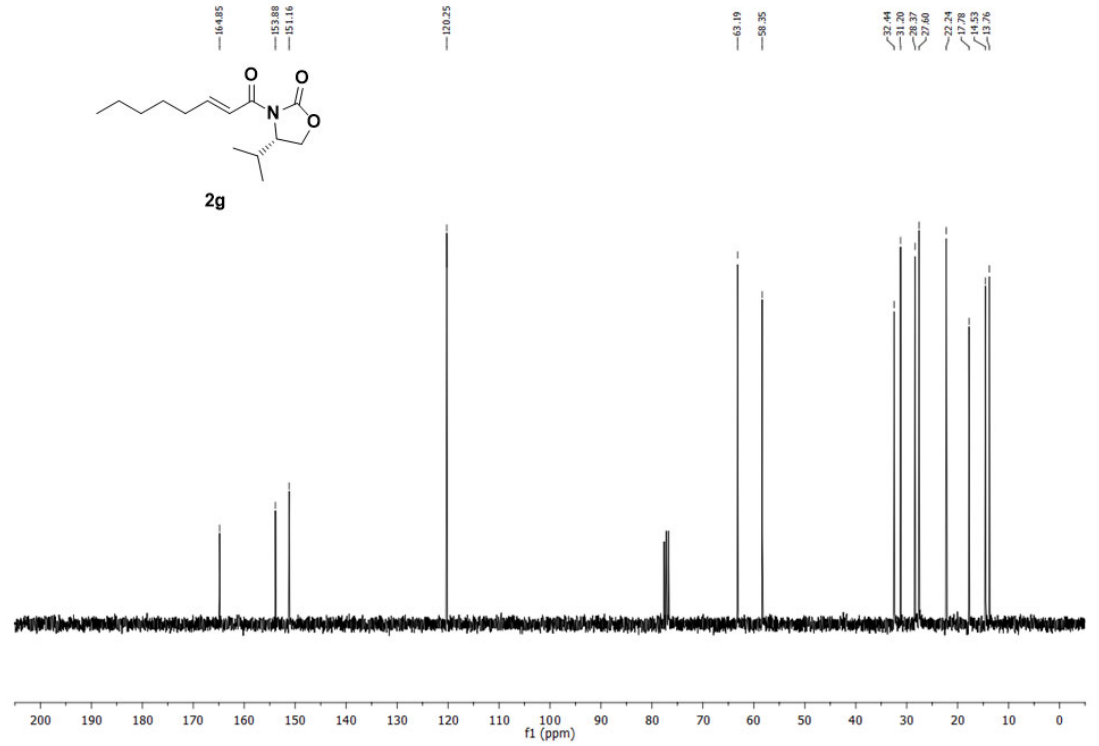


*Figure S47: ^{13}C NMR spectrum of Michael acceptor **2g** ($CDCl_3$, 298 K)*

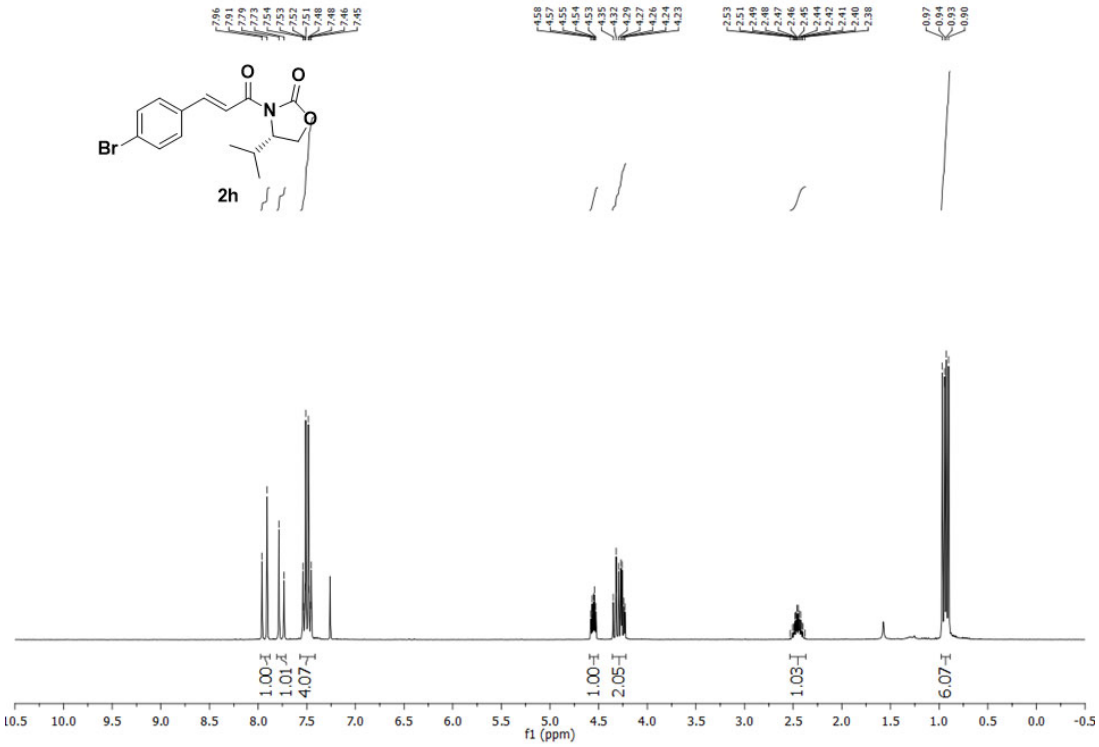


*Figure S48: ^{1}H NMR spectrum of Michael acceptor **2h** ($CDCl_3$, 298 K)*

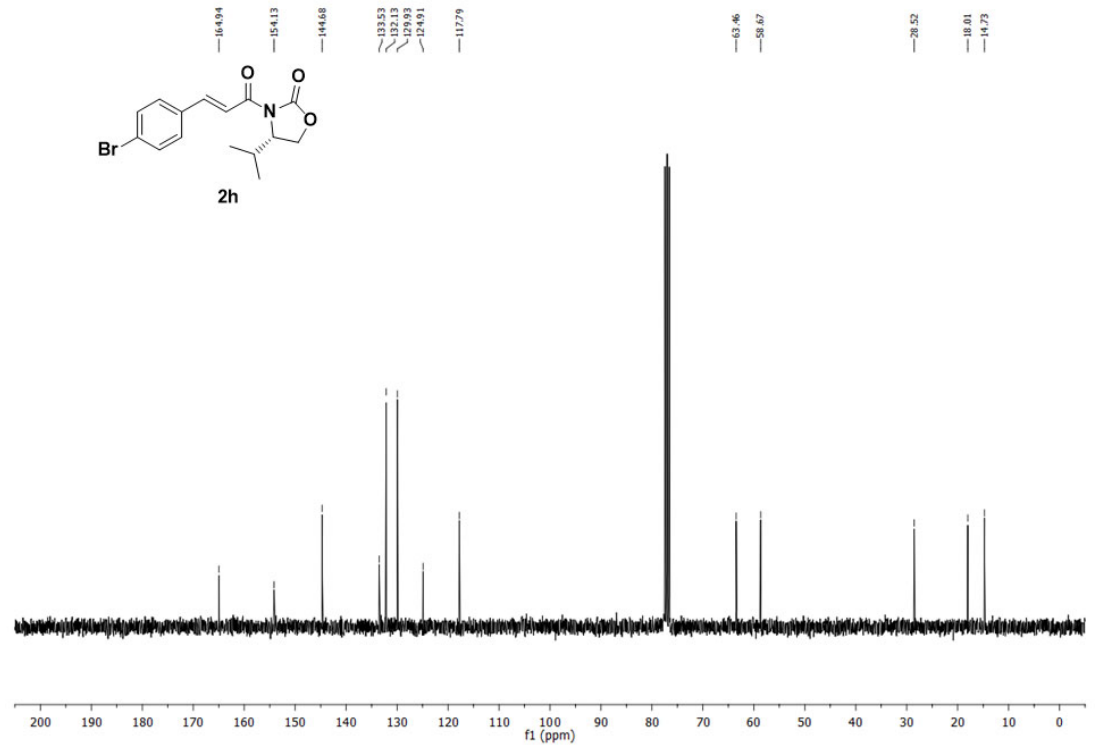


*Figure S49: ^{13}C NMR spectrum of Michael acceptor **2h** ($CDCl_3$, 298 K)*

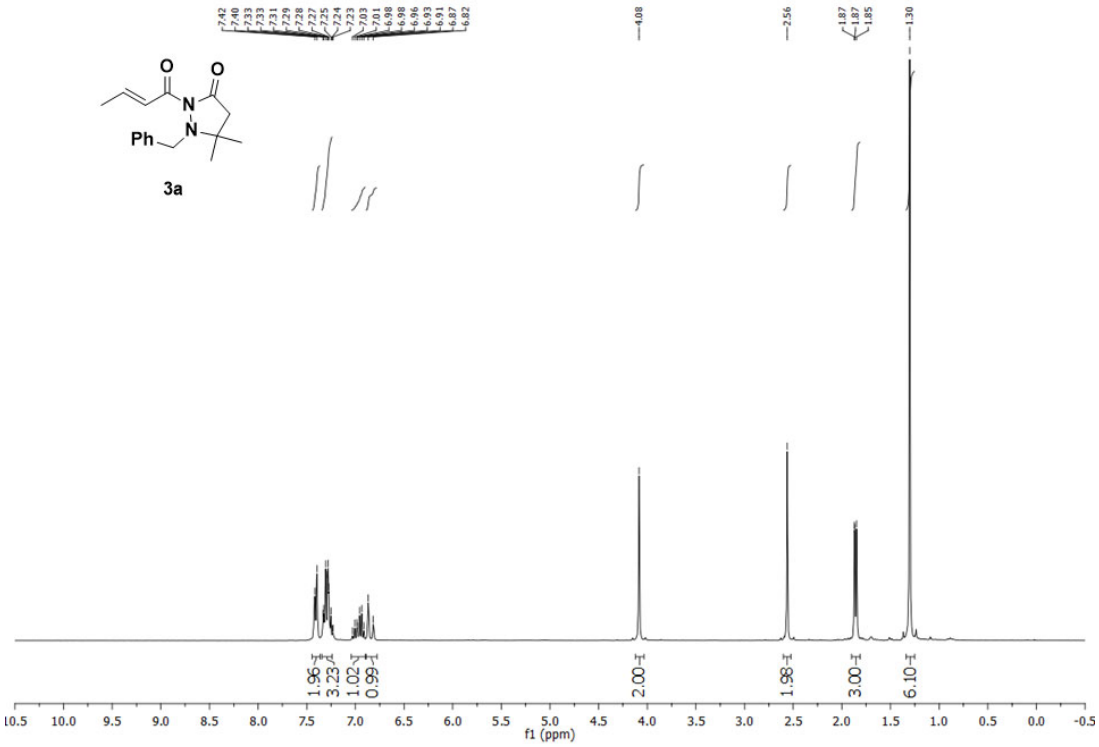


*Figure S50: [1]H NMR spectrum of Michael acceptor **3a** ($CDCl_3$, 298 K)*

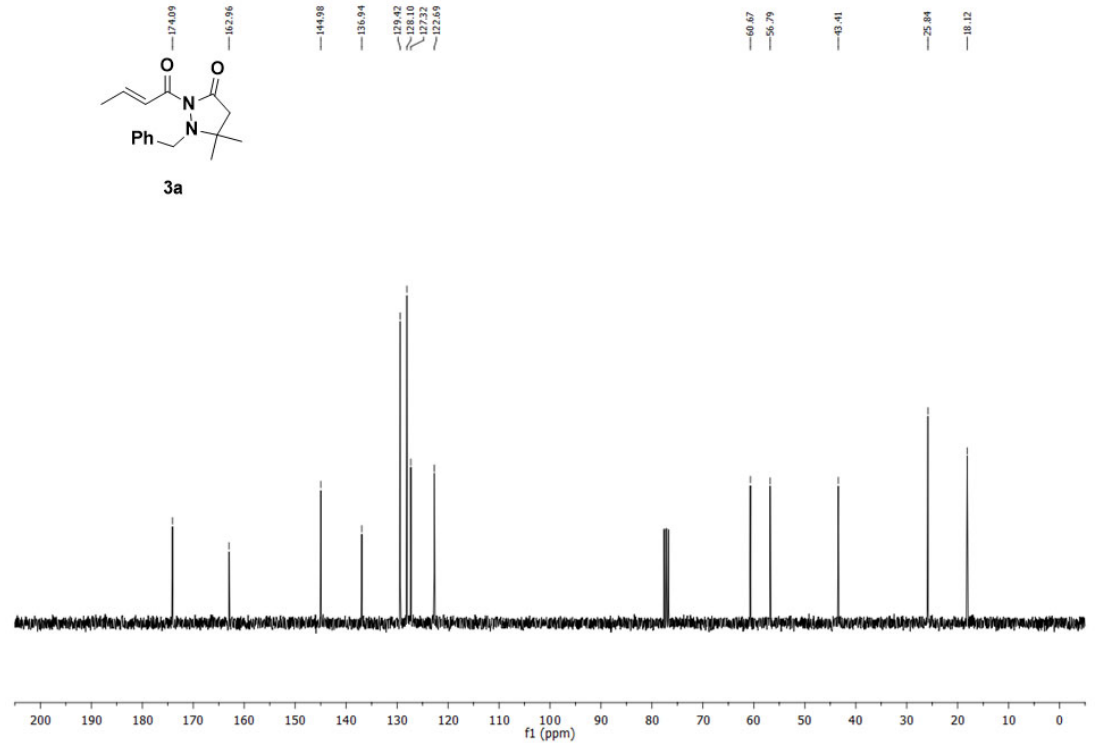


*Figure S51: [13]C NMR spectrum of Michael acceptor **3a** ($CDCl_3$, 298 K)*

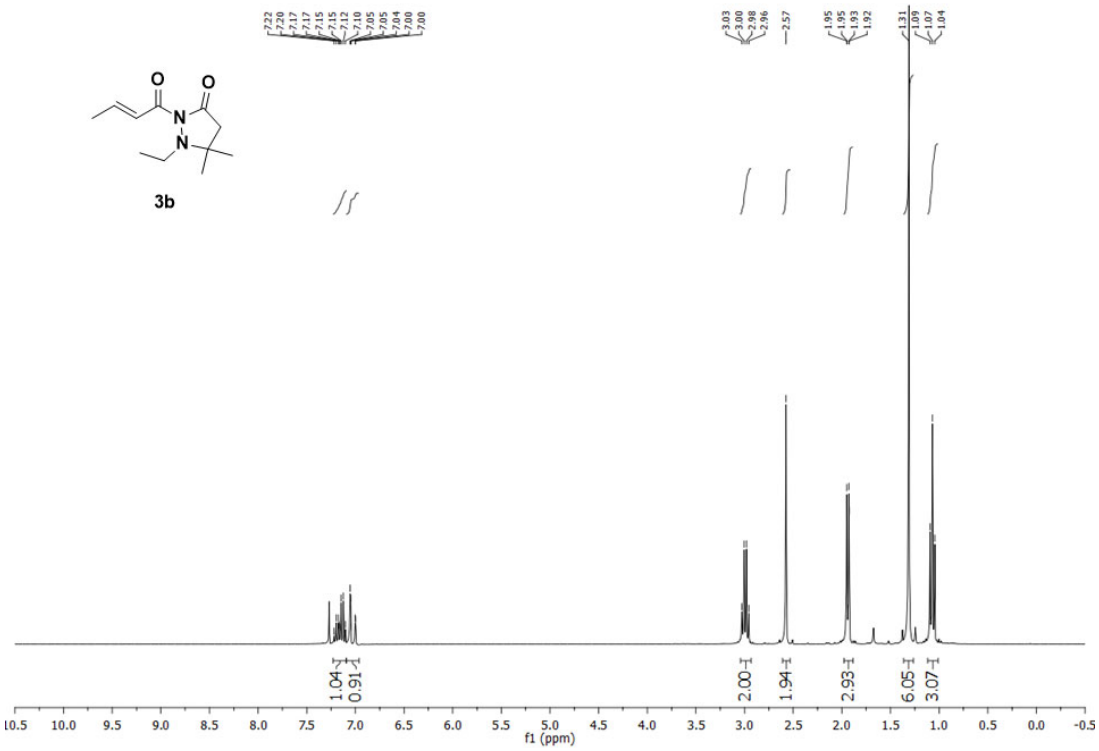


*Figure S52: [1]H NMR spectrum of Michael acceptor **3b** ($CDCl_3$, 298 K)*

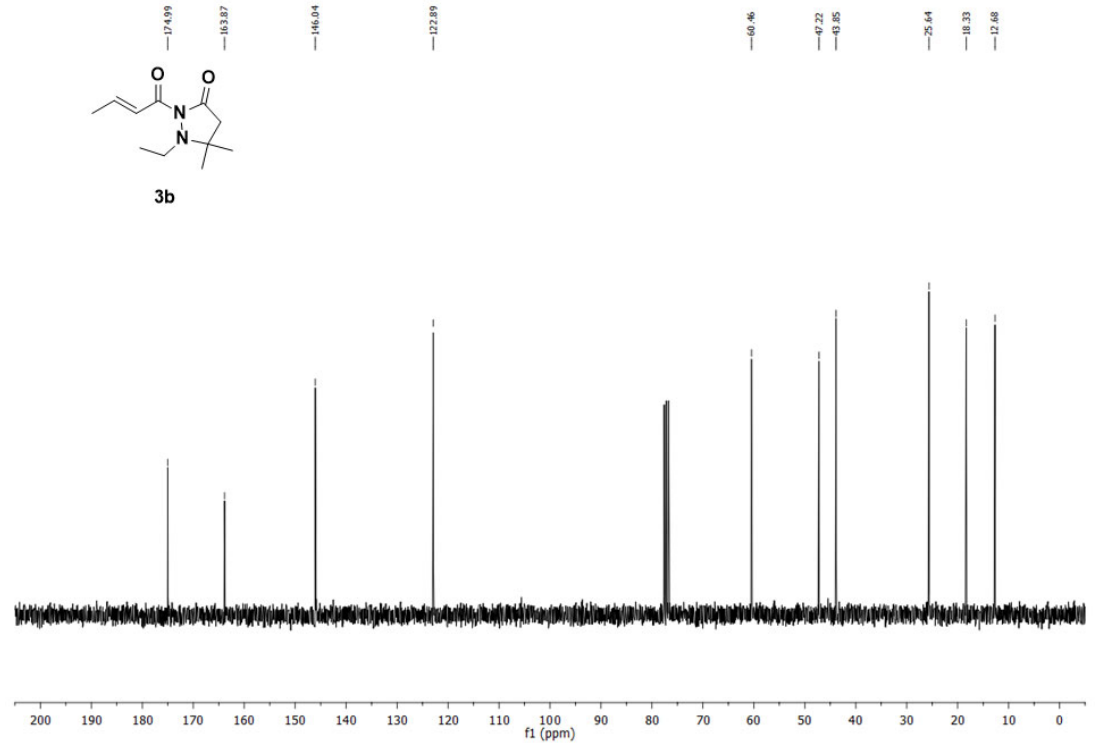


*Figure S53: [13]C NMR spectrum of Michael acceptor **3b** ($CDCl_3$, 298 K)*

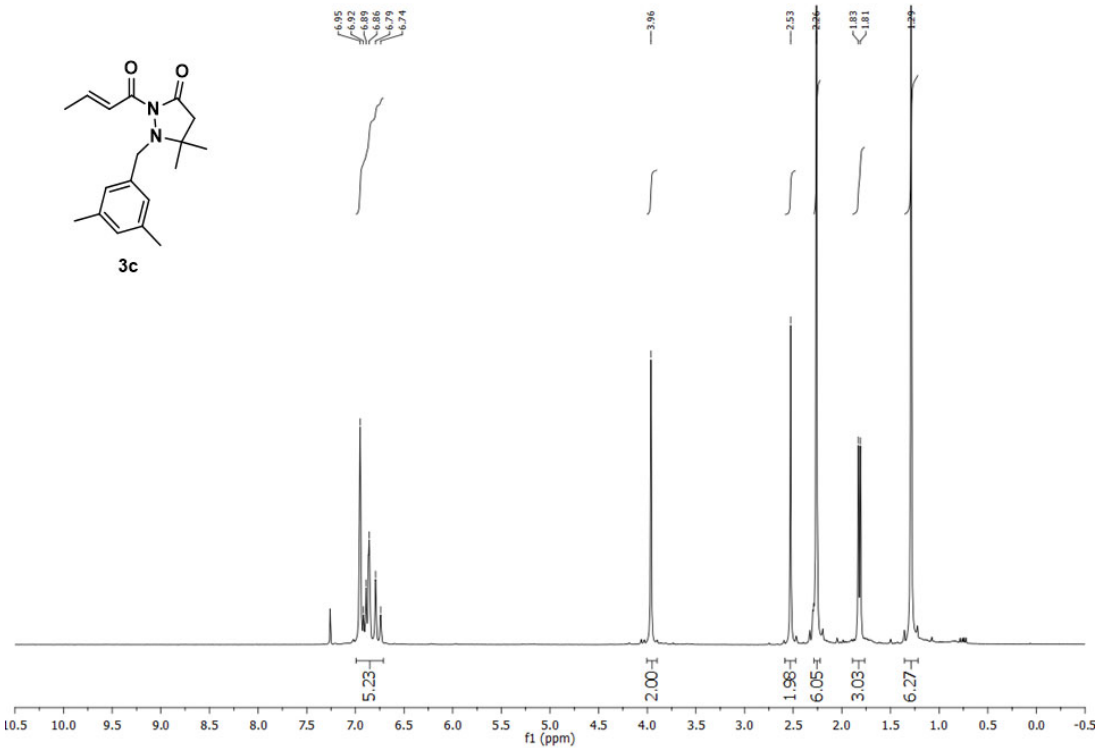


*Figure S54: ^{1}H NMR spectrum of Michael acceptor **3c** ($CDCl_3$, 298 K)*

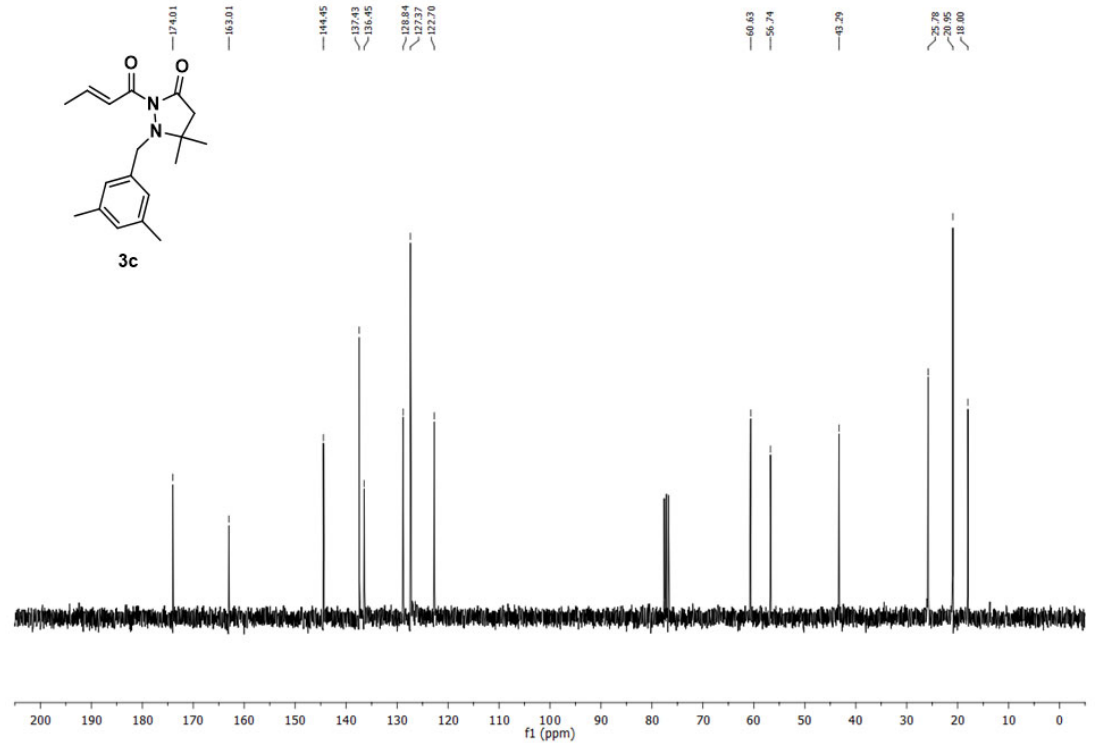


*Figure S55: ^{13}C NMR spectrum of Michael acceptor **3c** ($CDCl_3$, 298 K)*

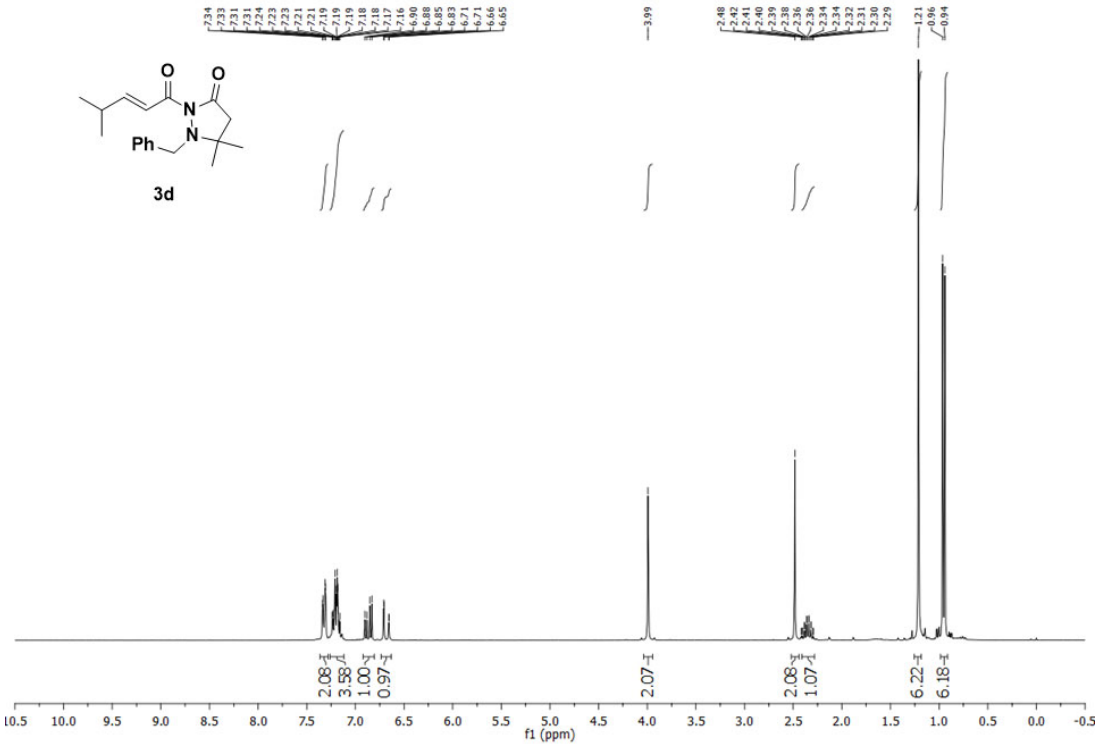


*Figure S56: ^{1}H NMR spectrum of Michael acceptor **3d** ($CDCl_3$, 298 K)*

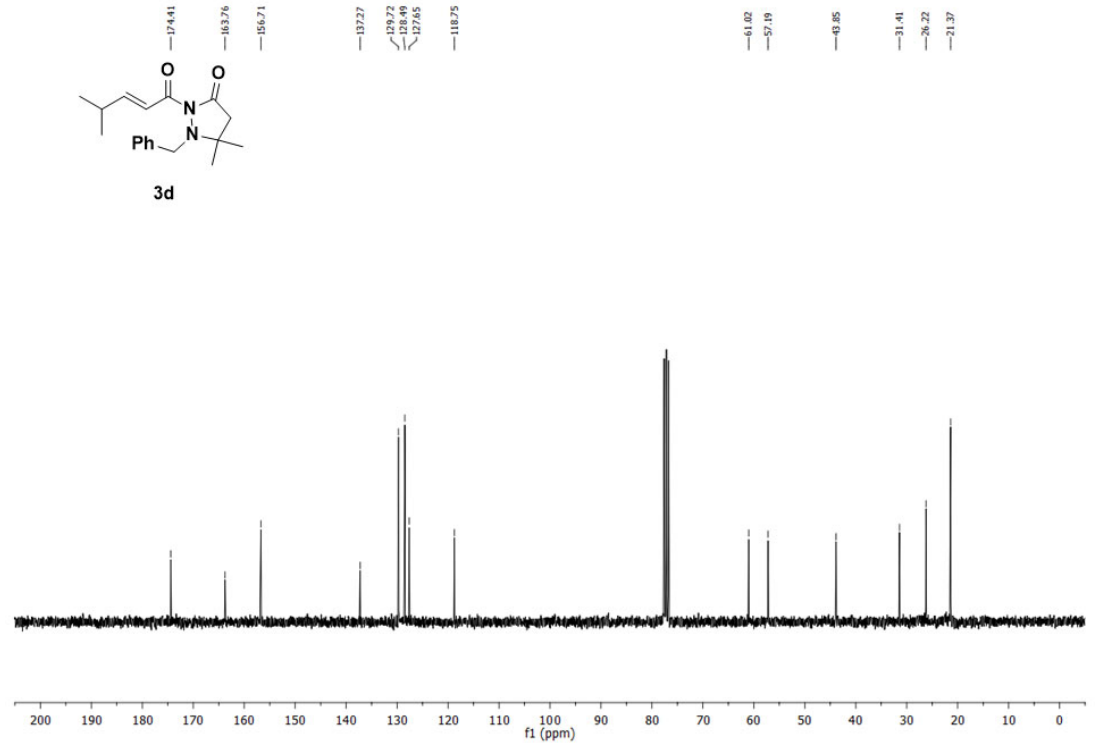


*Figure S57: ^{13}C NMR spectrum of Michael acceptor **3d** ($CDCl_3$, 298 K)*

11.3. NMR spectra of ligands L8-L11

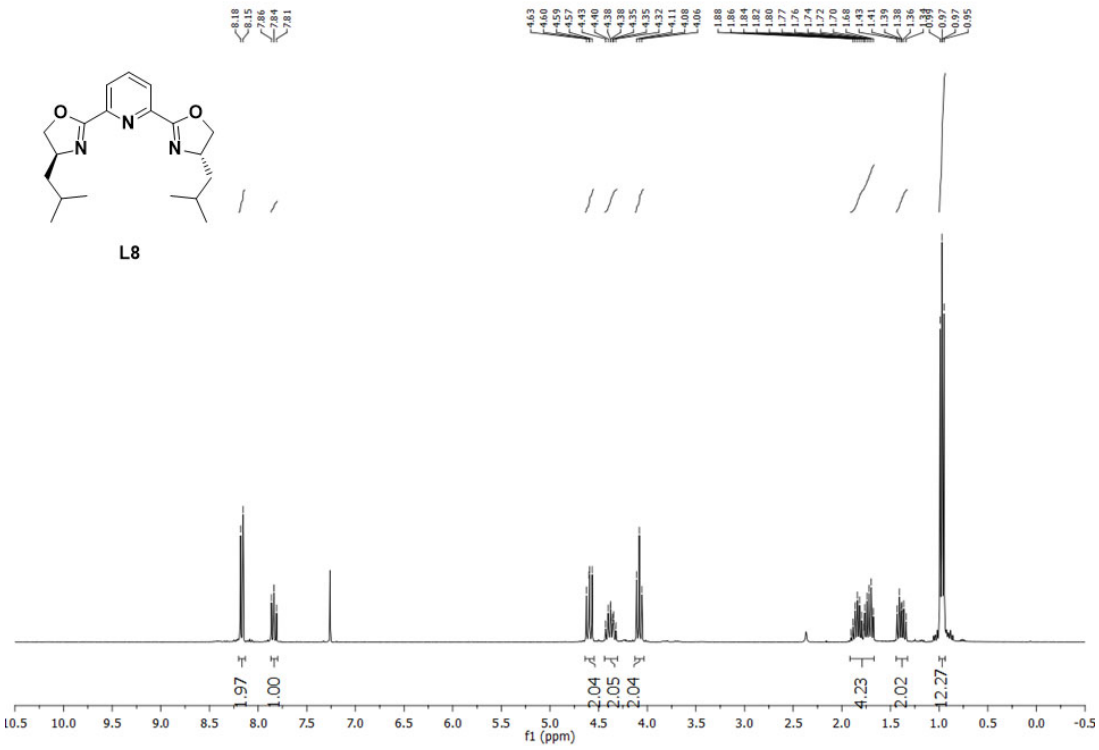


*Figure S58: ^{1}H NMR spectrum of ligand **L8** ($CDCl_3$, 298 K)*

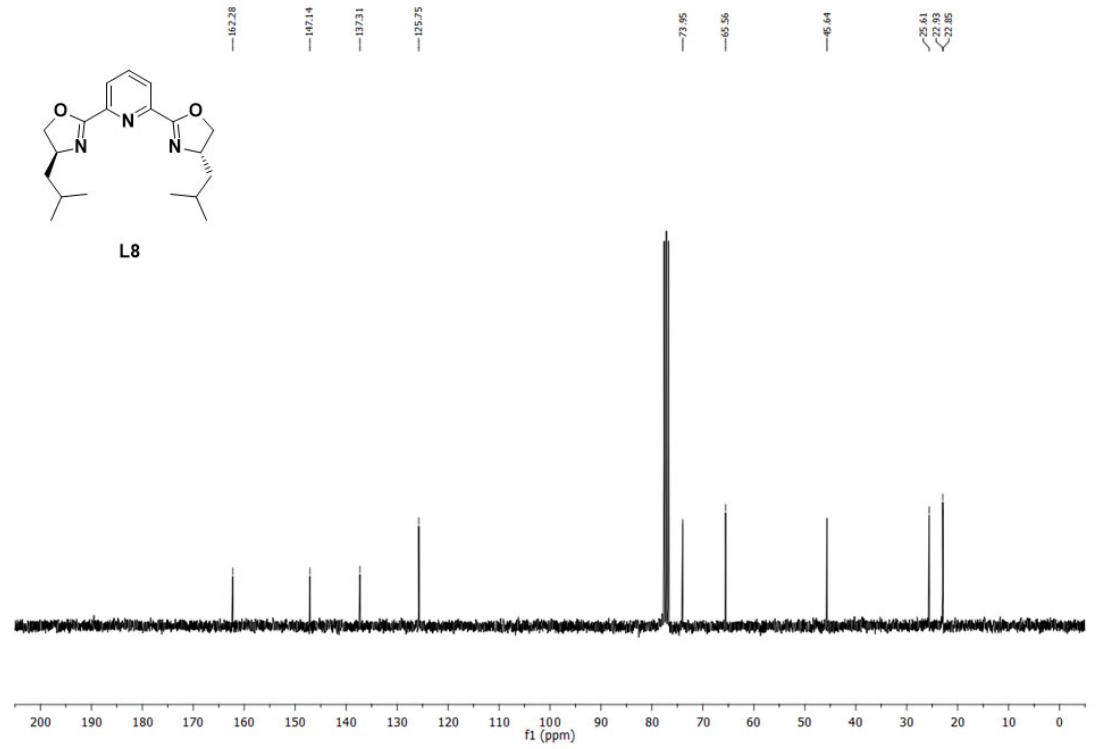


*Figure S59: ^{13}C NMR spectrum of ligand **L8** ($CDCl_3$, 298 K)*

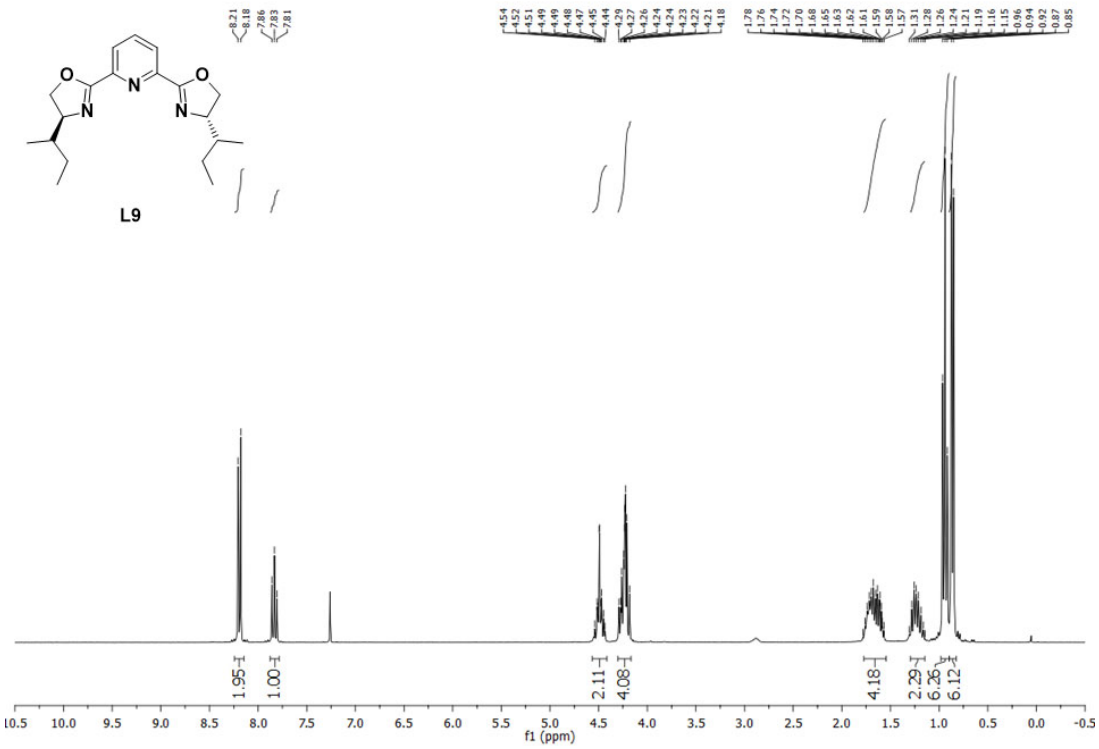


*Figure S60: ^{1}H NMR spectrum of ligand **L9** ($CDCl_3$, 298 K)*

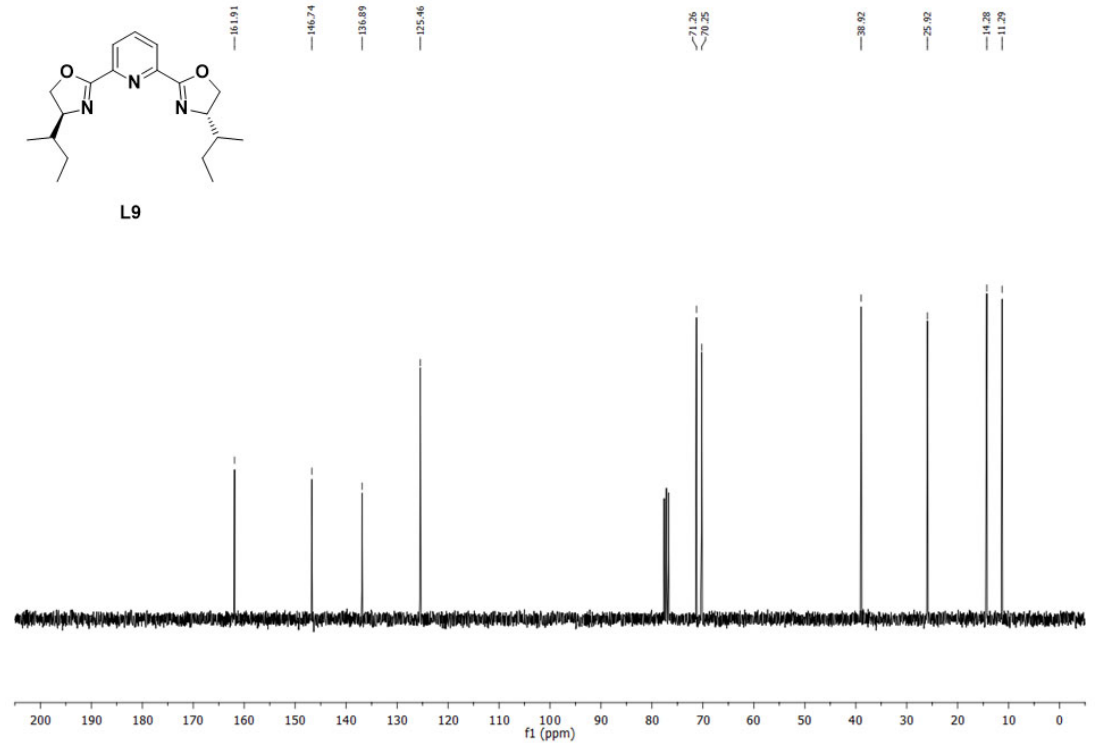


*Figure S61: ^{13}C NMR spectrum of ligand **L9** ($CDCl_3$, 298 K)*

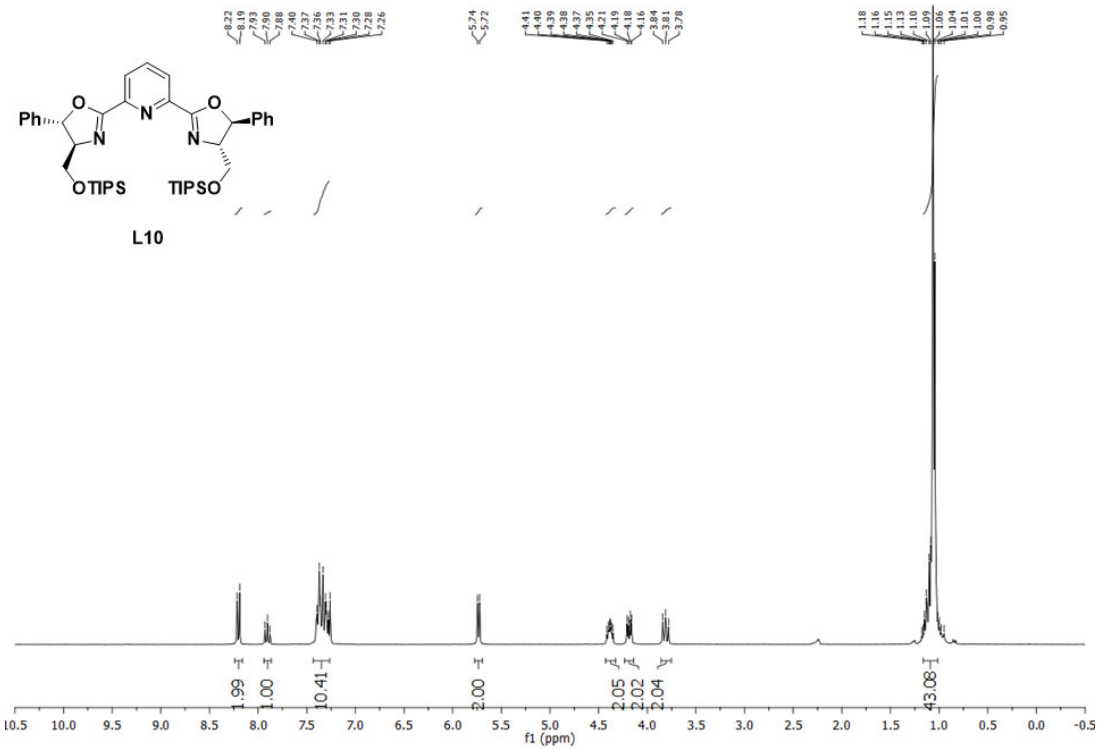


*Figure S62: ^{1}H NMR spectrum of ligand **L10** ($CDCl_3$, 298 K)*

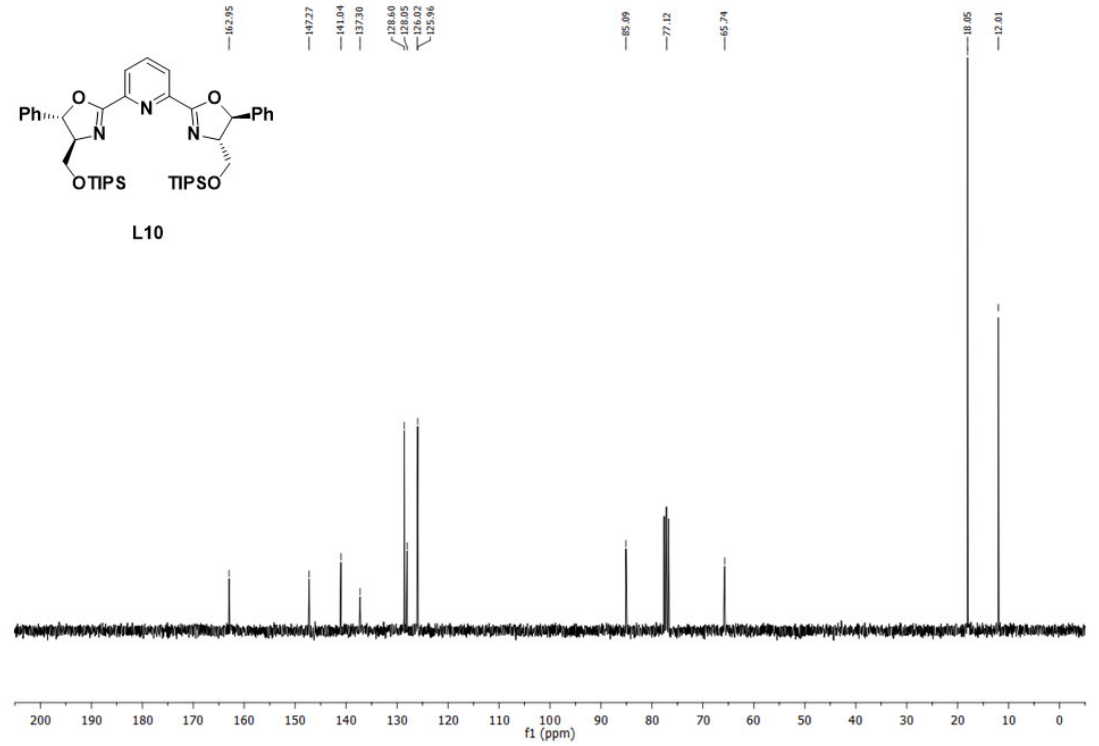


*Figure S63: ^{13}C NMR spectrum of ligand **L10** ($CDCl_3$, 298 K)*

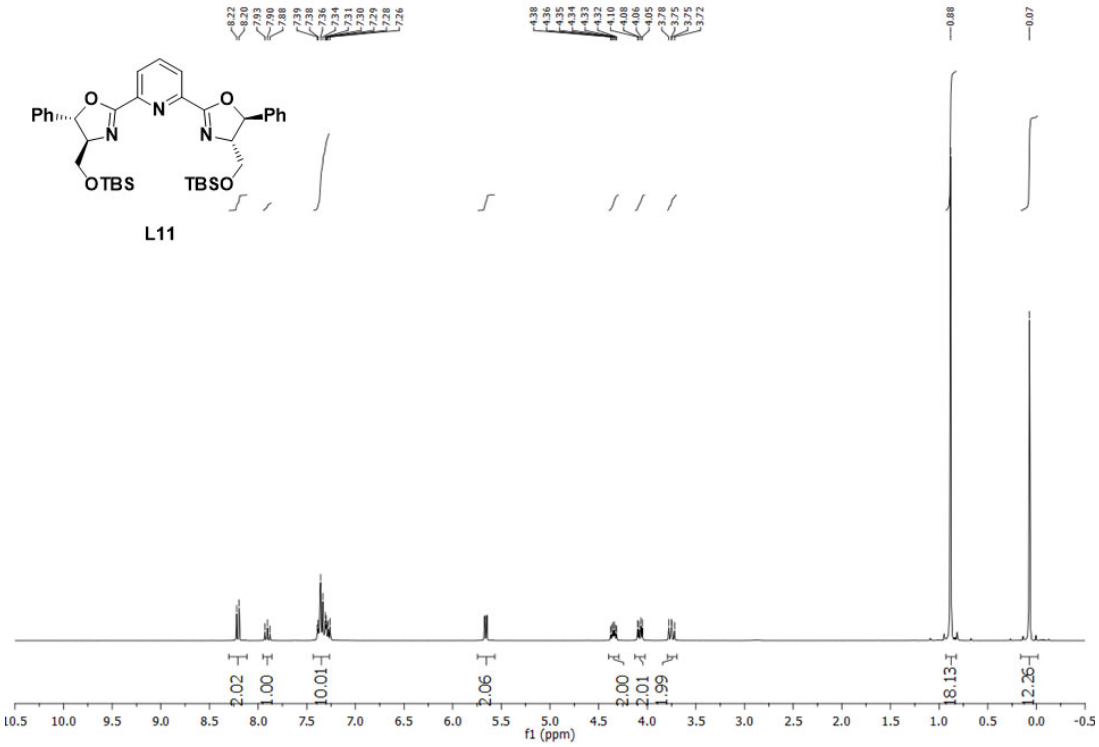


*Figure S64: ^{1}H NMR spectrum of ligand **L11** ($CDCl_3$, 298 K)*

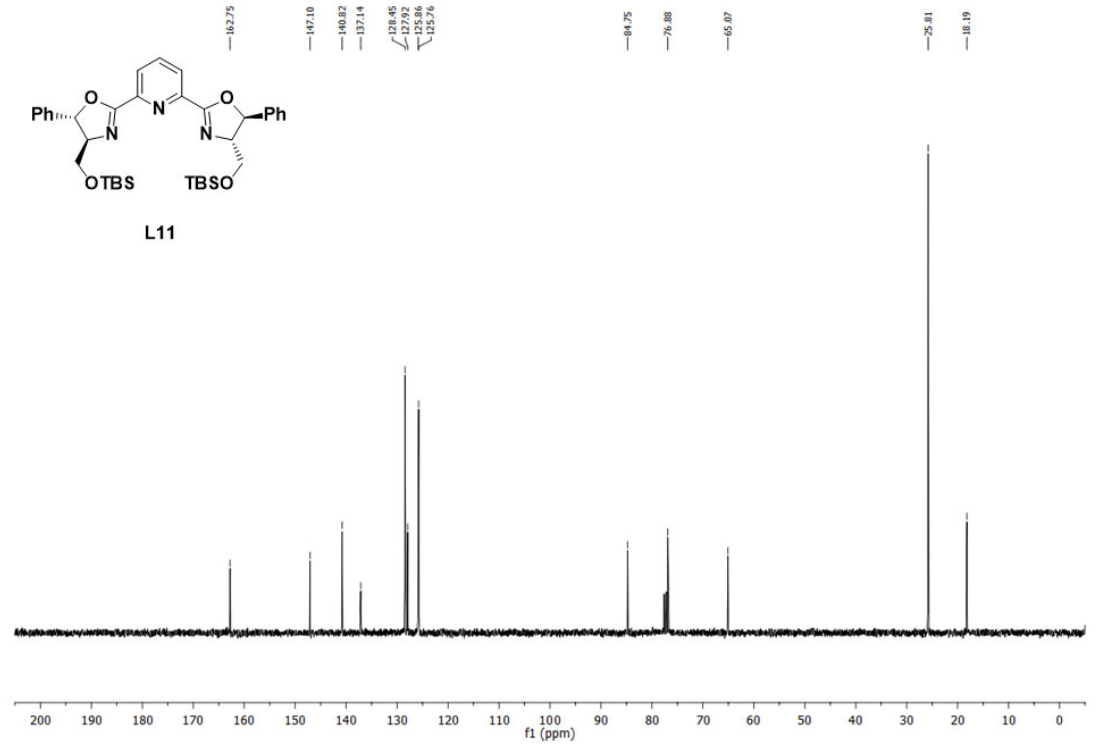


*Figure S65: ^{13}C NMR spectrum of ligand **L11** ($CDCl_3$, 298 K)*

11.4. NMR spectra of final products 4

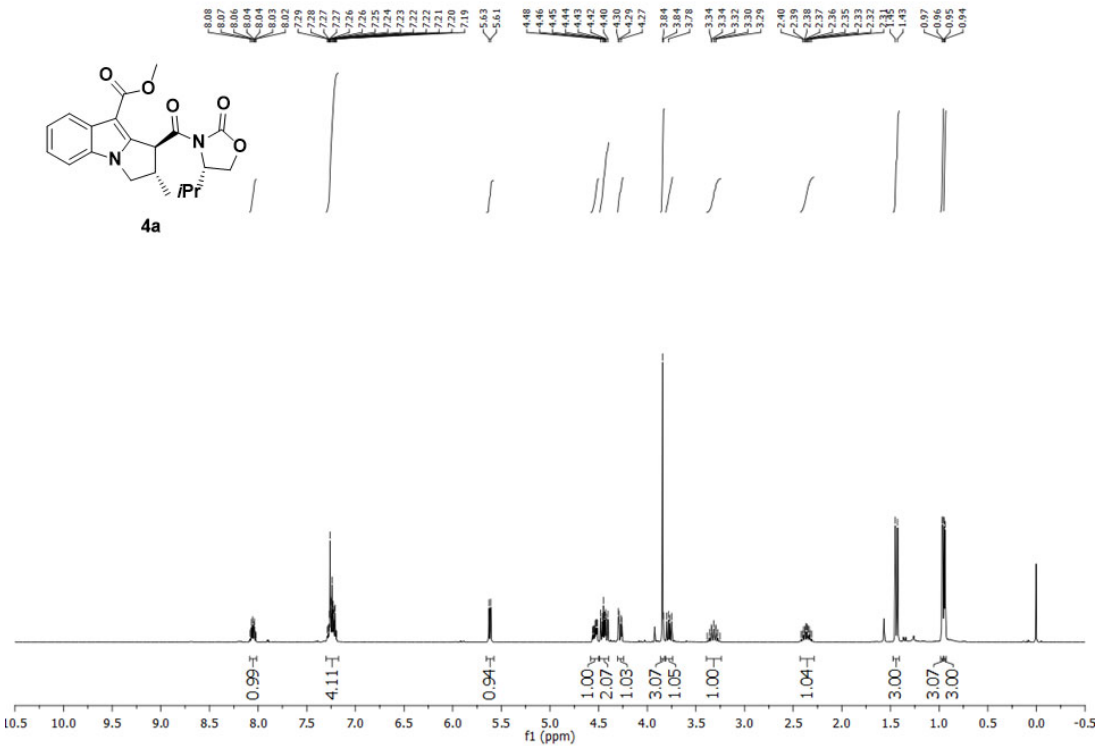


*Figure S66: ^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 298 K)*

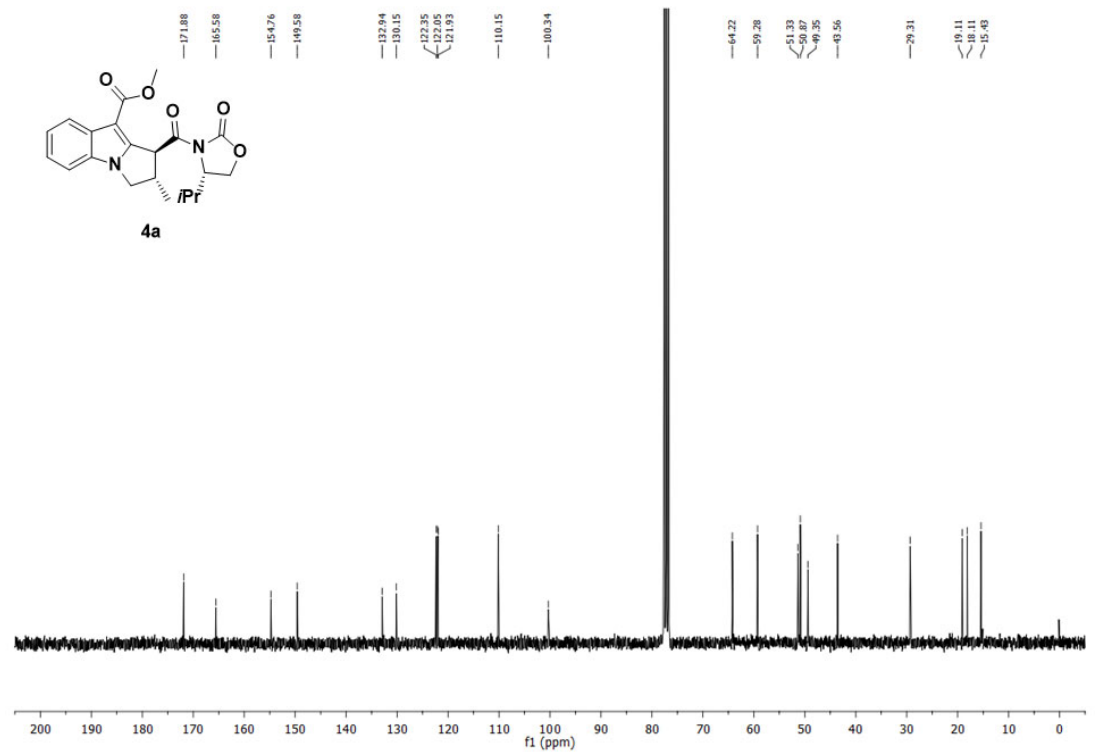


*Figure S67: ^{13}C NMR spectrum of compound **4a** ($CDCl_3$, 298 K)*

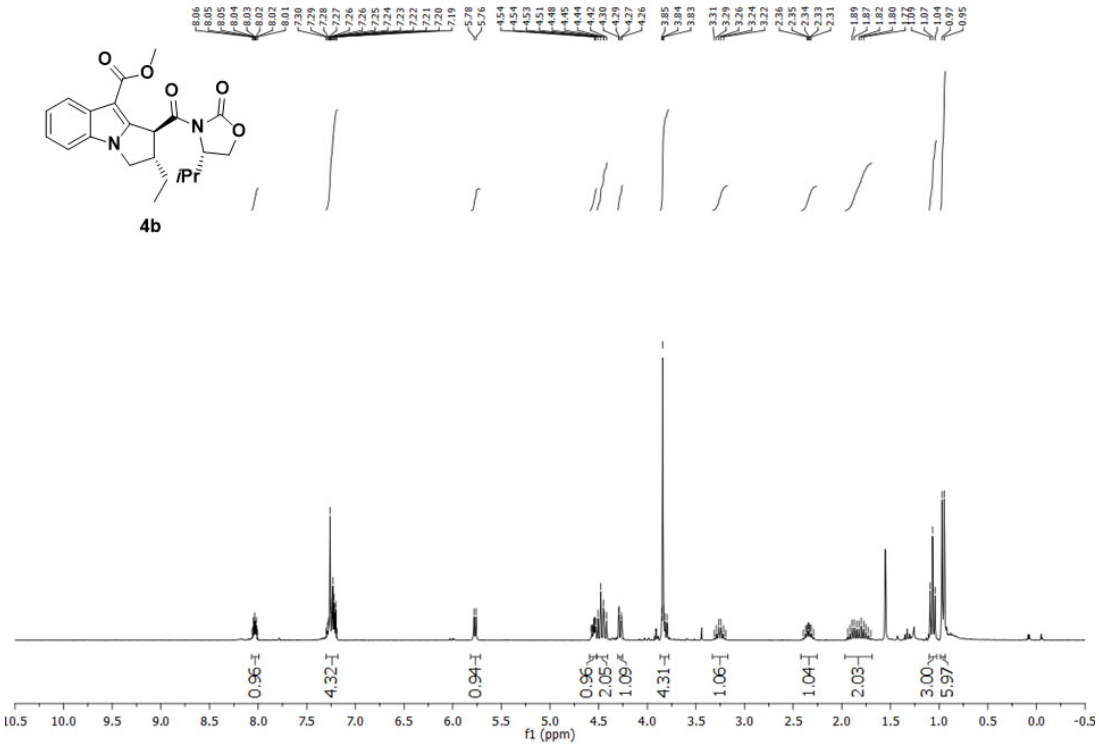


*Figure S68: ^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 298 K)*

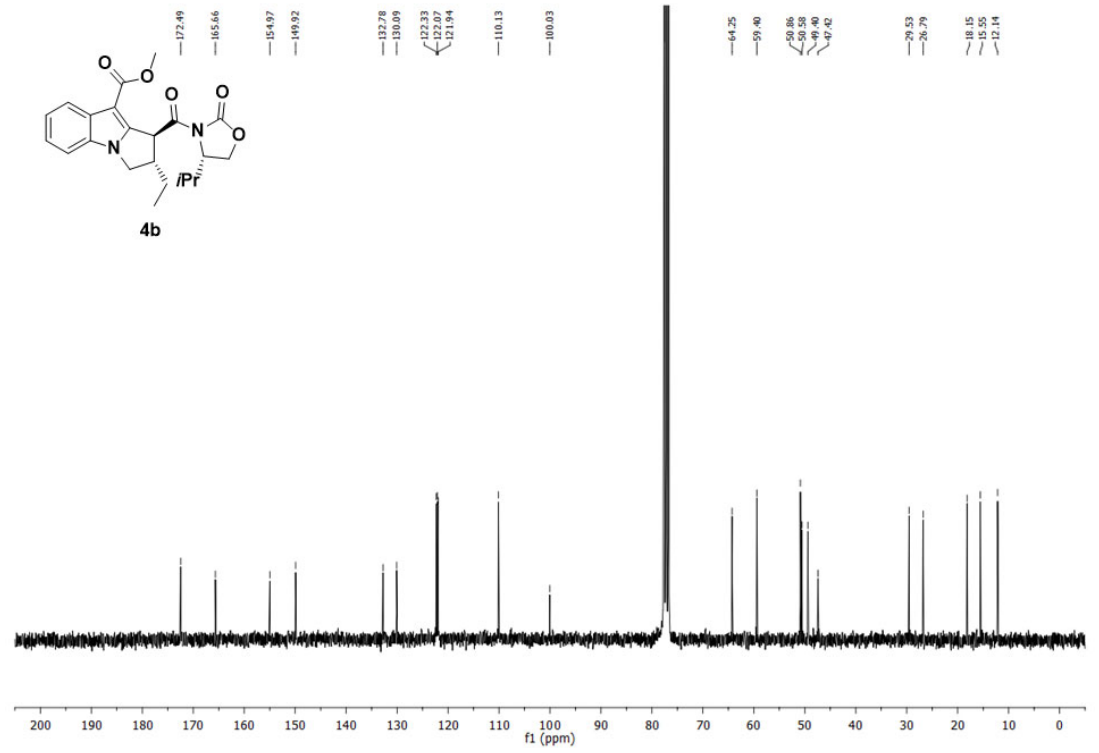


*Figure S69: ^{13}C NMR spectrum of compound **4b** ($CDCl_3$, 298 K)*

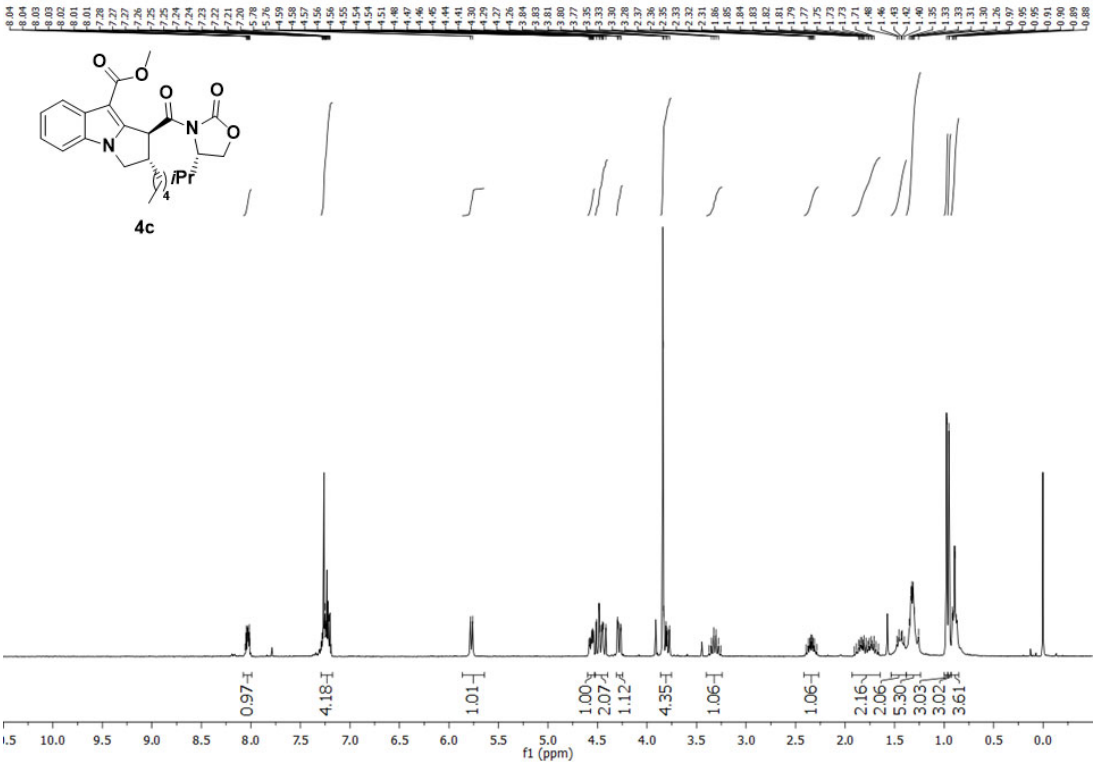


*Figure S70: [1]H NMR spectrum of compound **4c** ($CDCl_3$, 298 K)*

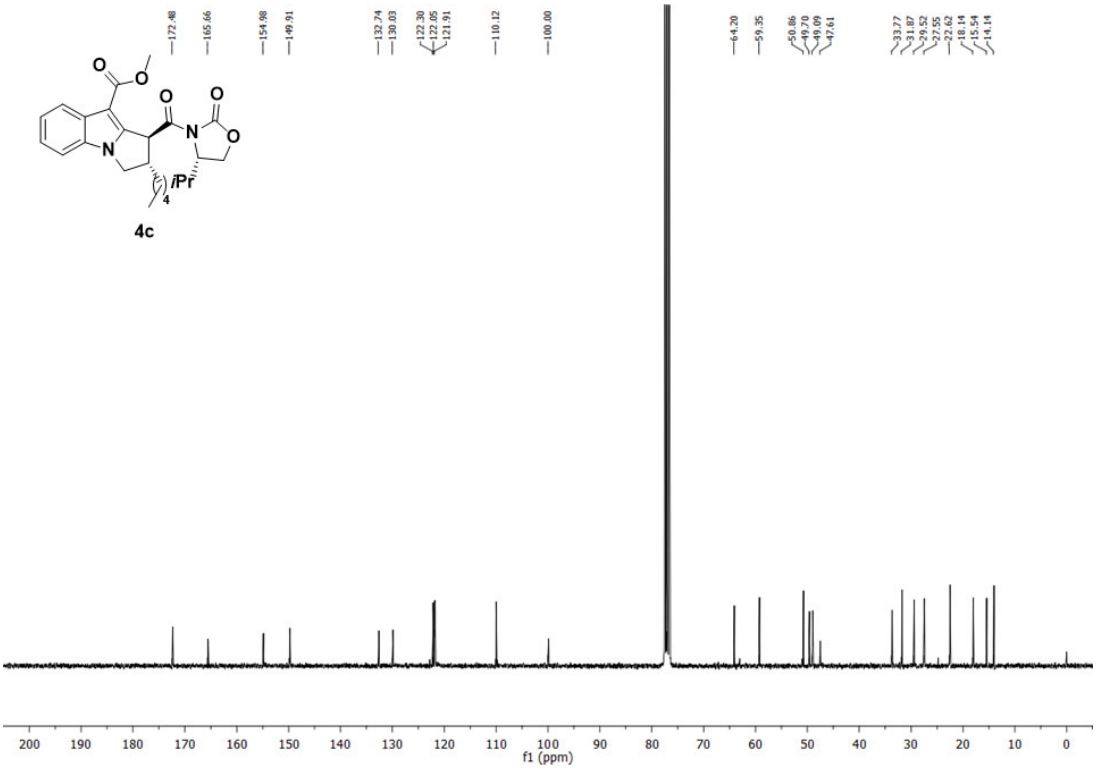


*Figure S71: [13]C NMR spectrum of compound **4c** ($CDCl_3$, 298 K)*

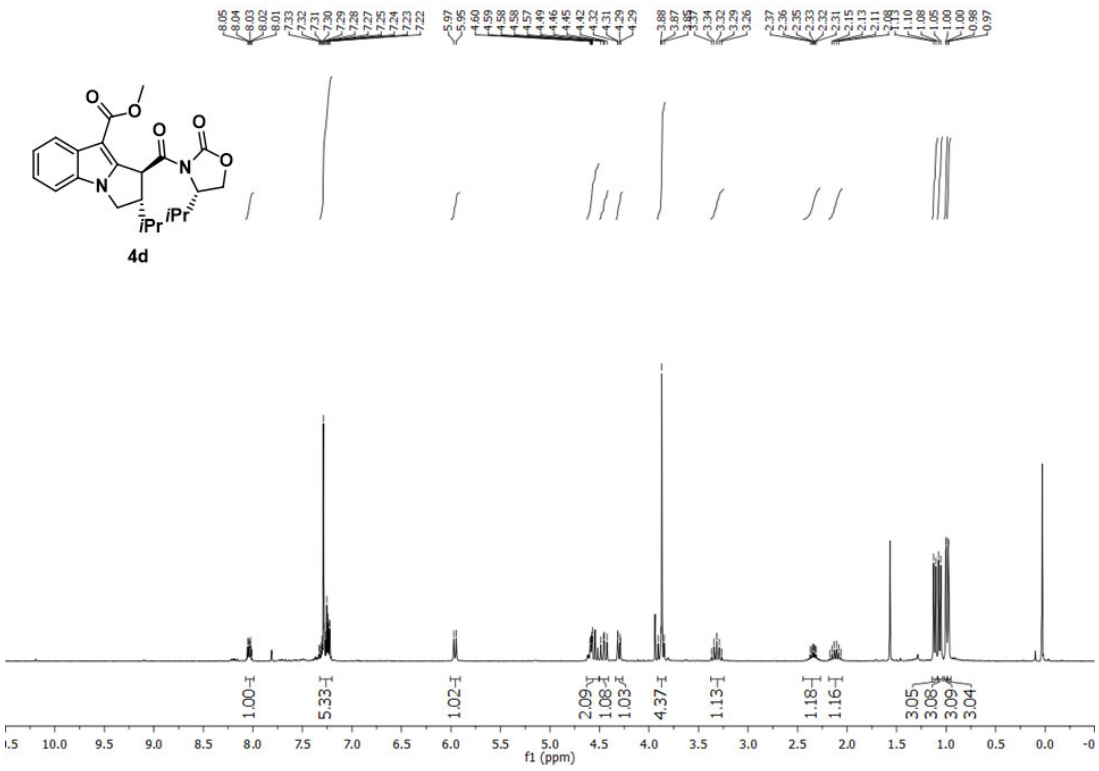


*Figure S72: [1]H NMR spectrum of compound **4d** ($CDCl_3$, 298 K)*

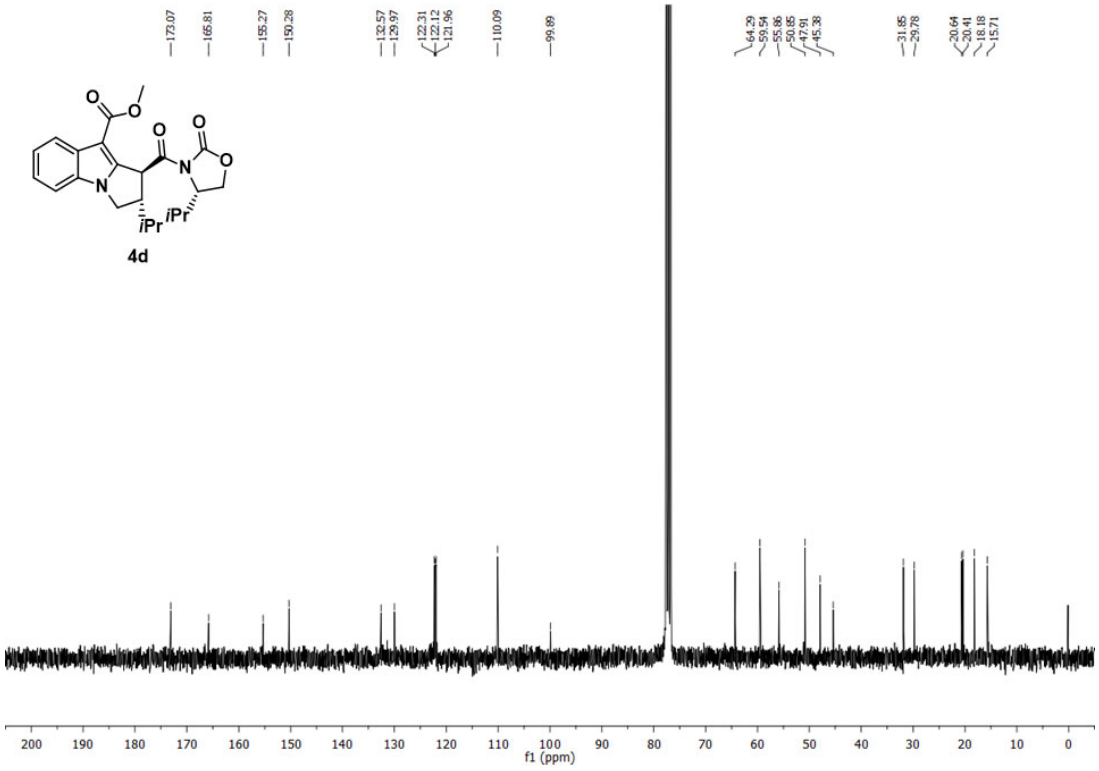


*Figure S73: [13]C NMR spectrum of compound **4d** ($CDCl_3$, 298 K)*

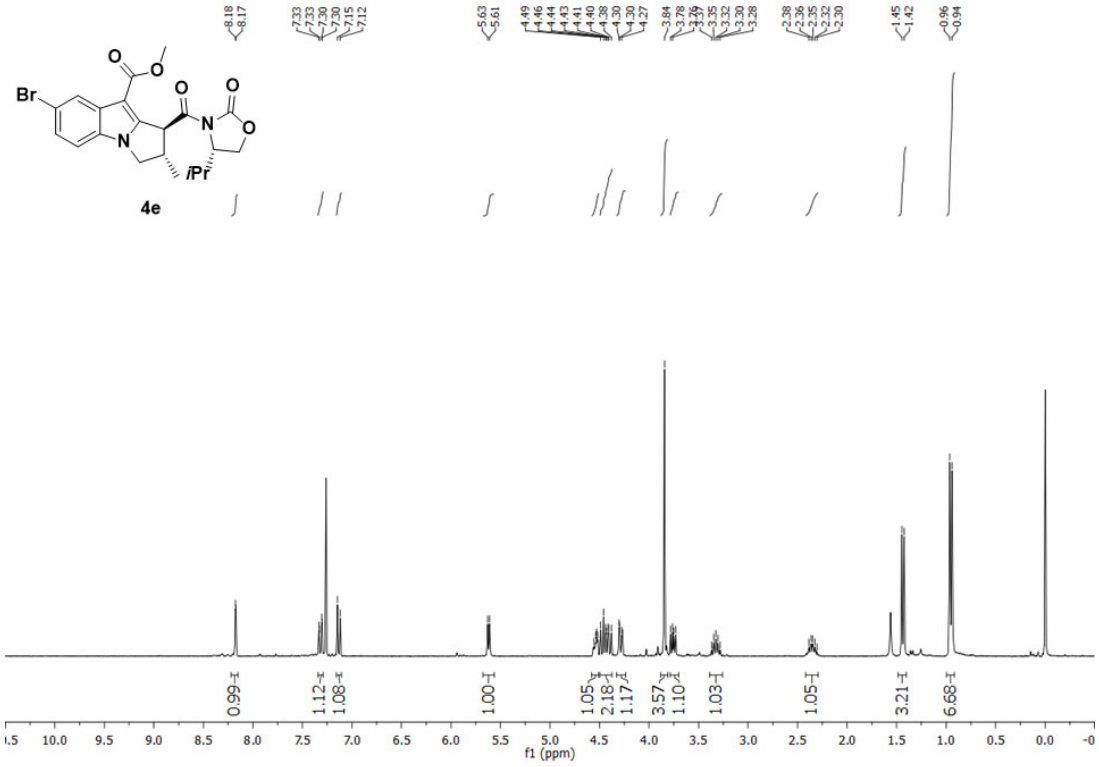


*Figure S74: [1]H NMR spectrum of compound **4e** ($CDCl_3$, 298 K)*

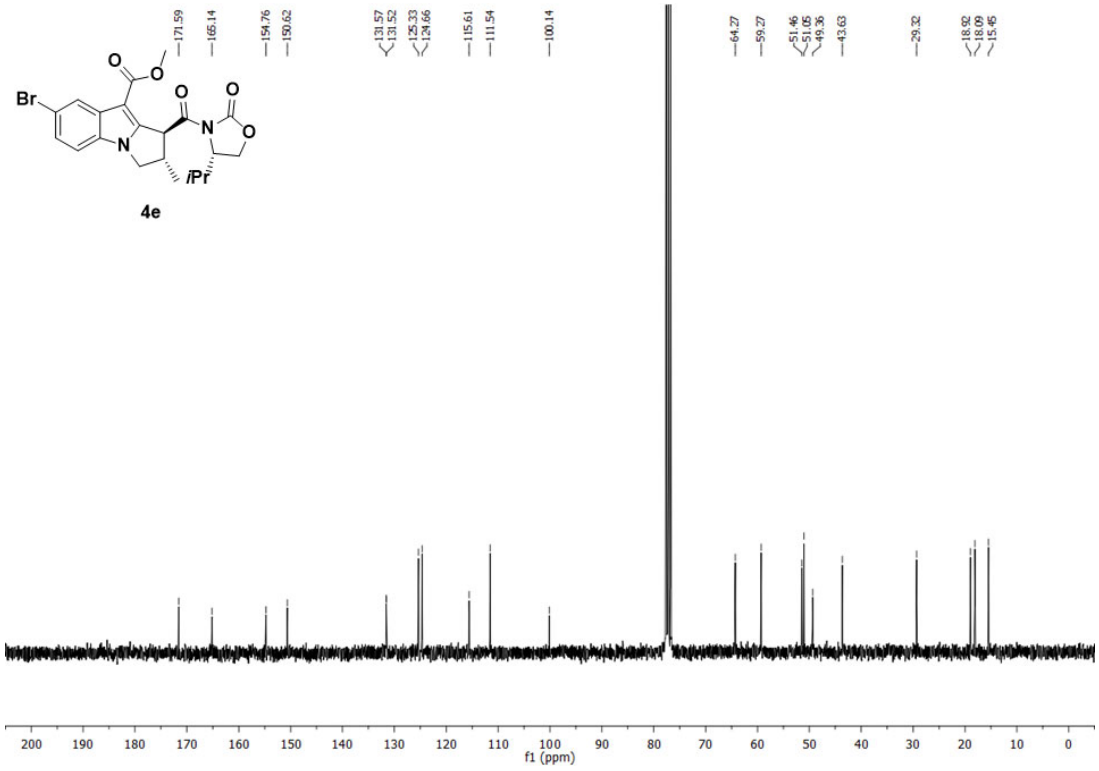


*Figure S75: [13]C NMR spectrum of compound **4e** ($CDCl_3$, 298 K)*

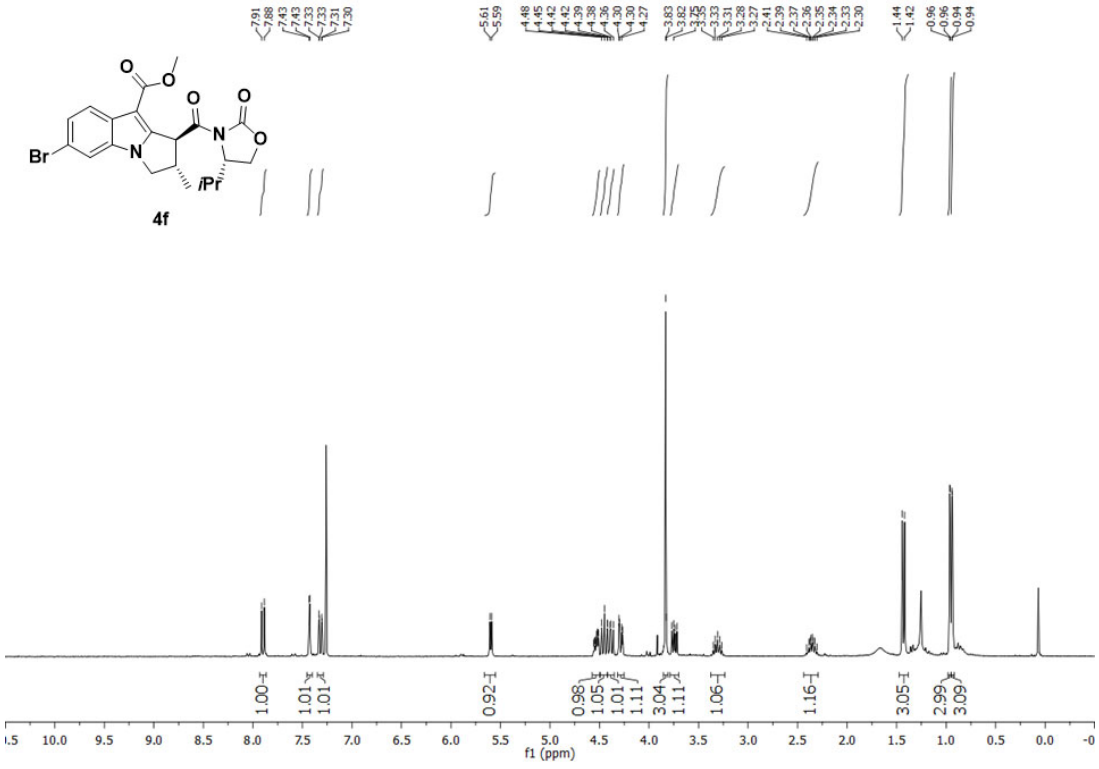


*Figure S76: ^{1}H NMR spectrum of compound **4f** ($CDCl_3$, 298 K)*

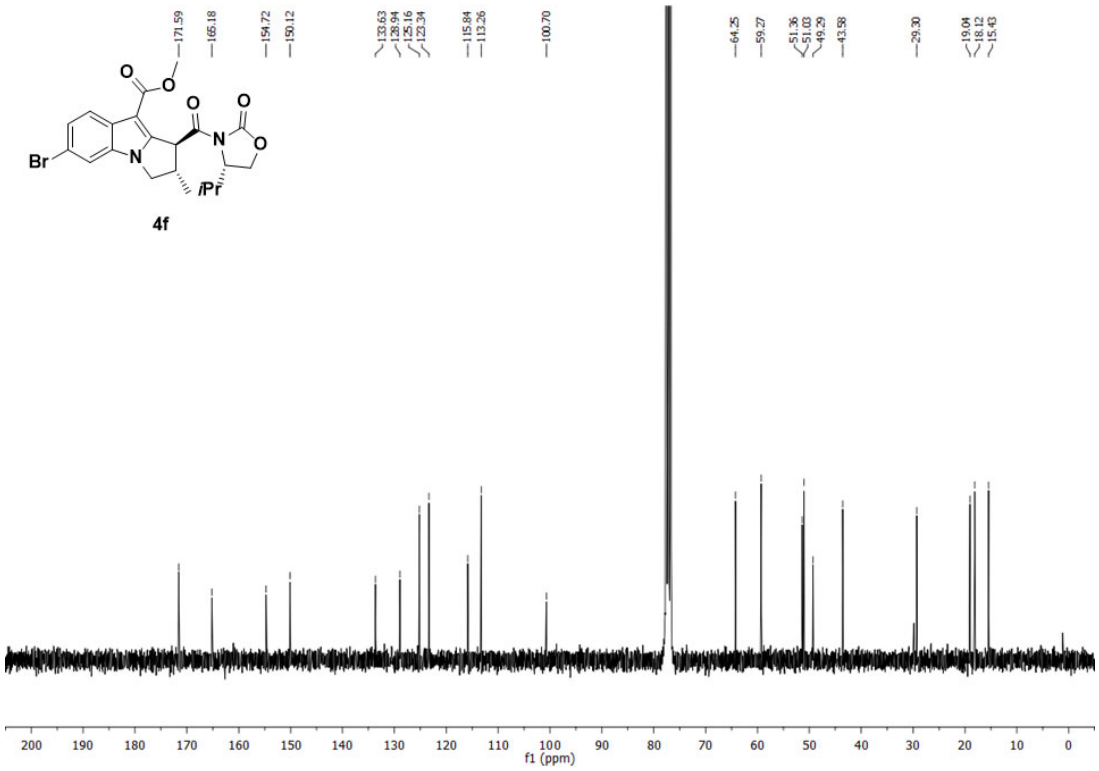


*Figure S77: ^{13}C NMR spectrum of compound **4f** ($CDCl_3$, 298 K)*

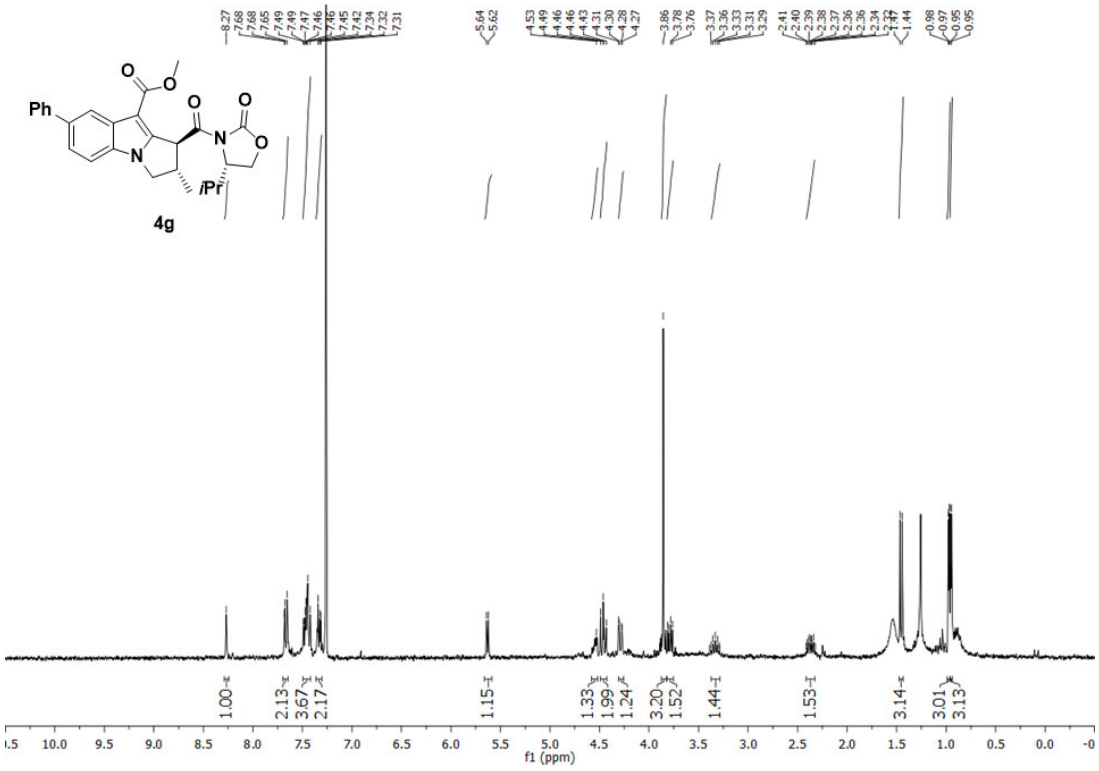


*Figure S78: ^{1}H NMR spectrum of compound **4g** ($CDCl_3$, 298 K)*

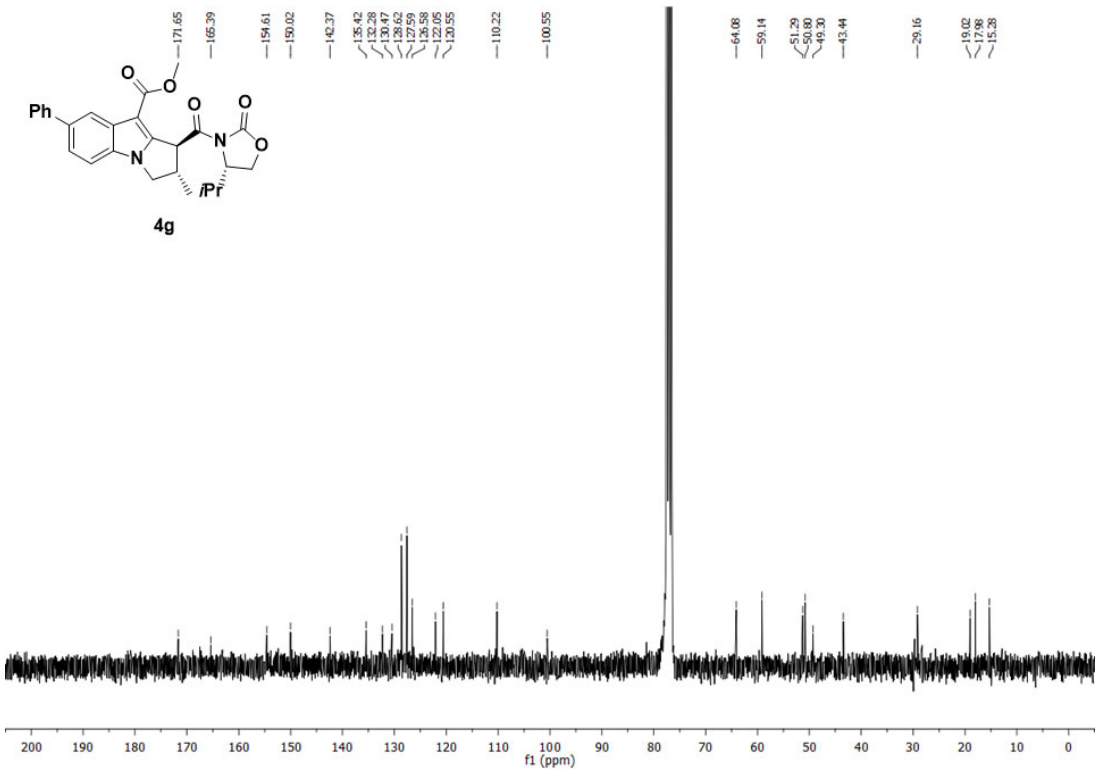


*Figure S79: ^{13}C NMR spectrum of compound **4g** ($CDCl_3$, 298 K)*

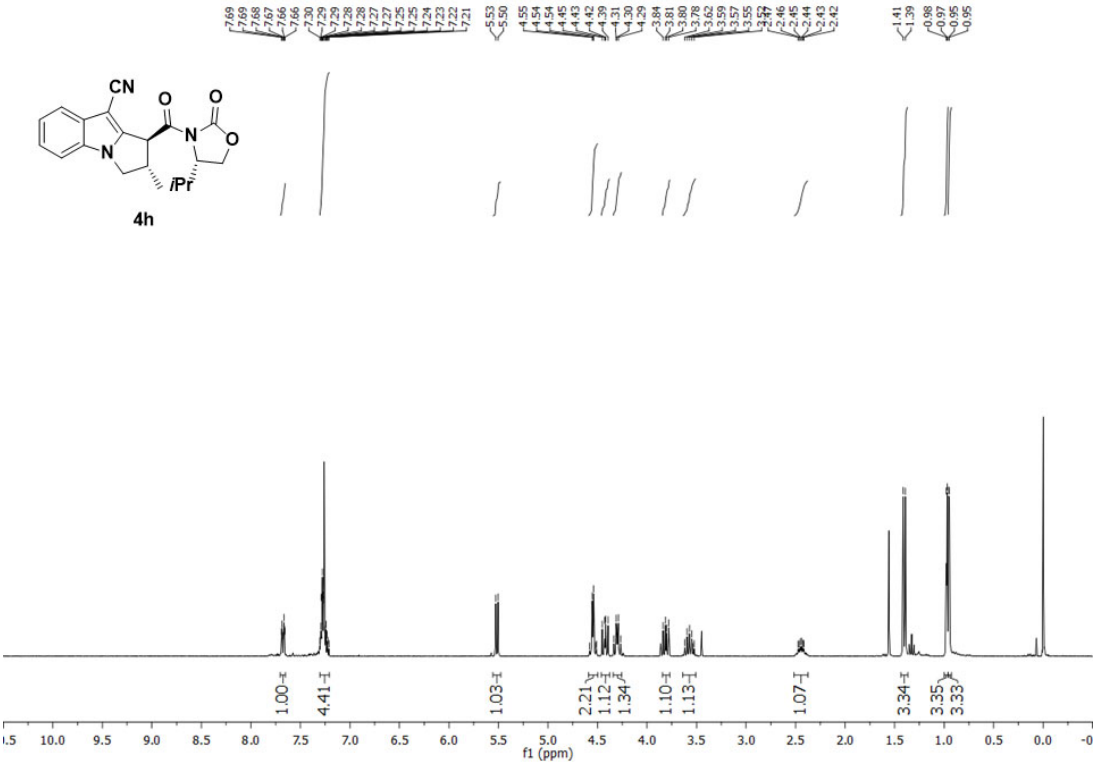


*Figure S80: [1]H NMR spectrum of compound **4h** ($CDCl_3$, 298 K)*

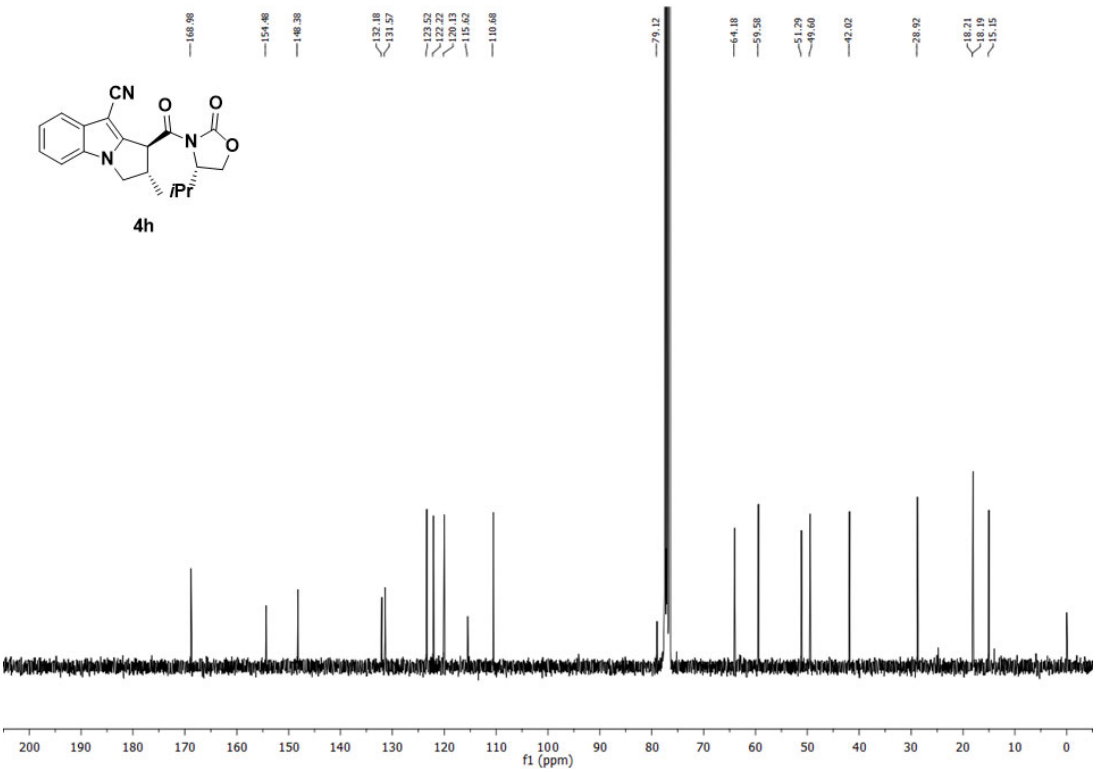


*Figure S81: [13]C NMR spectrum of compound **4h** ($CDCl_3$, 298 K)*

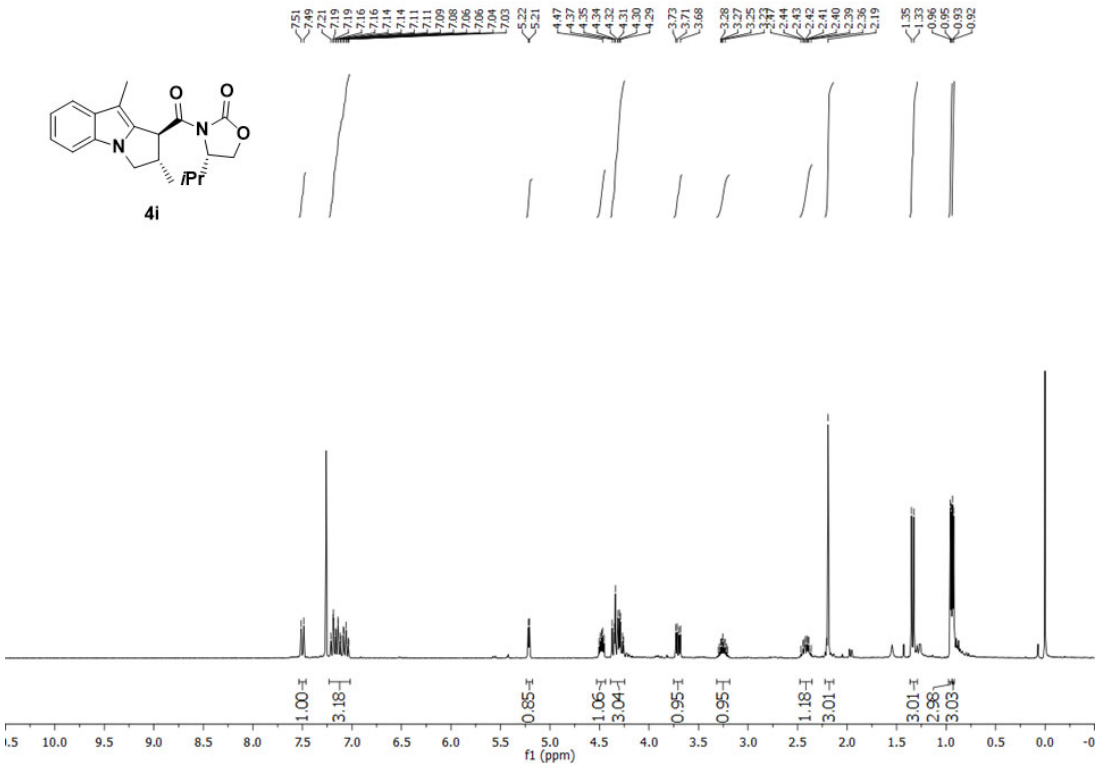


*Figure S82: ^{1}H NMR spectrum of compound **4i** ($CDCl_3$, 298 K)*

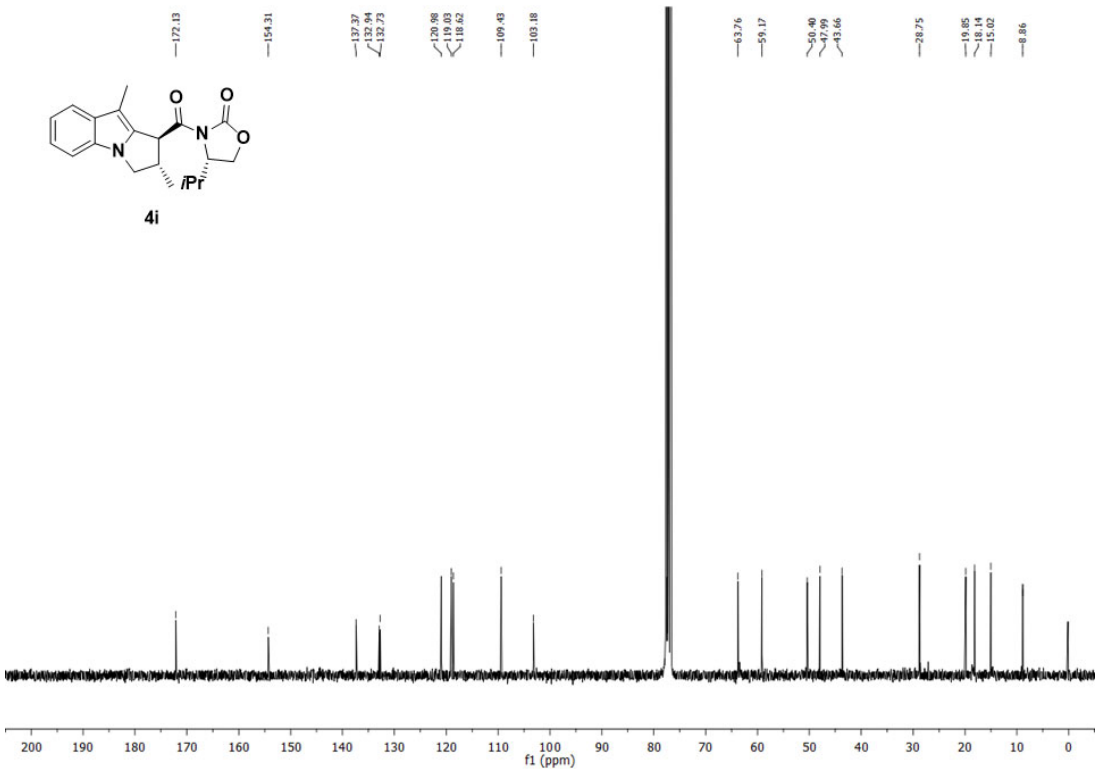


*Figure S83: ^{13}C NMR spectrum of compound **4i** ($CDCl_3$, 298 K)*

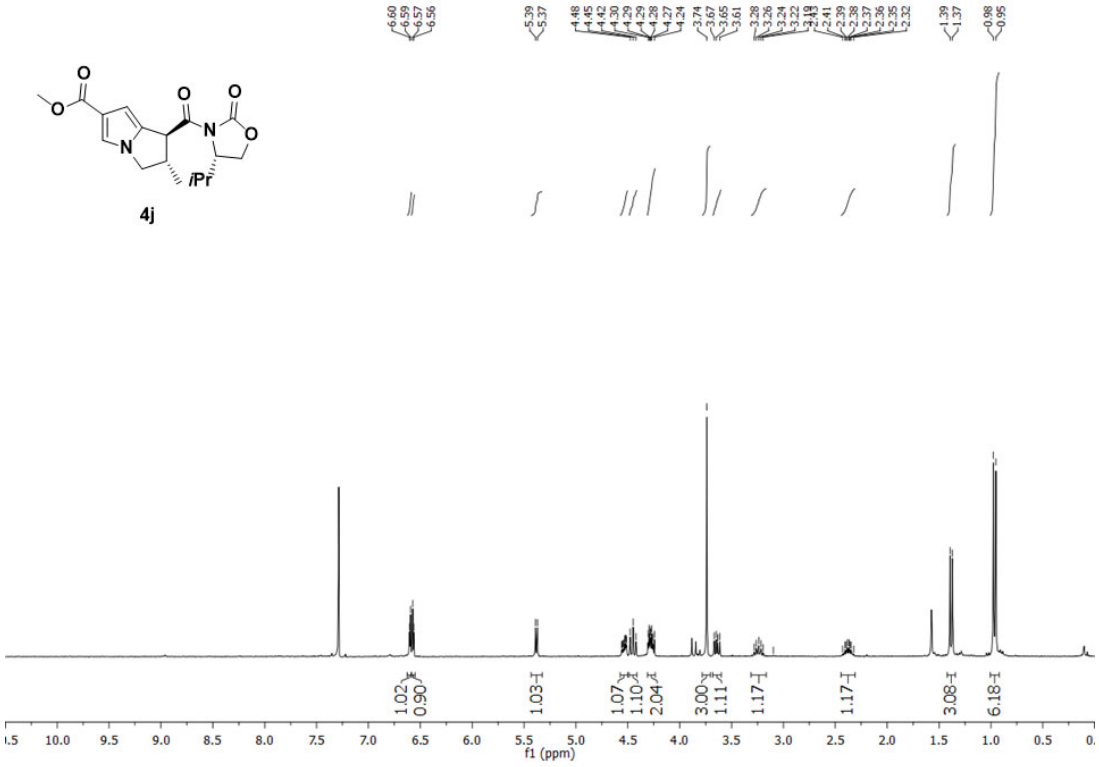


*Figure S84: ^{1}H NMR spectrum of compound **4j** ($CDCl_3$, 298 K)*

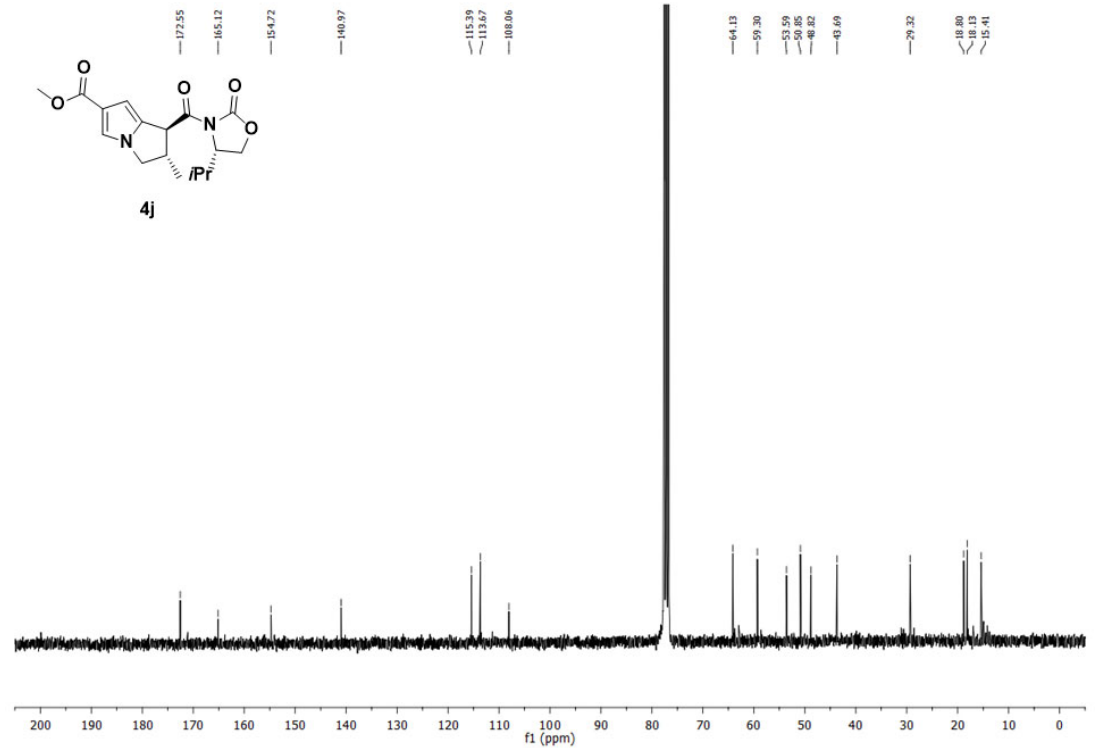


*Figure S85: ^{13}C NMR spectrum of compound **4j** ($CDCl_3$, 298 K)*

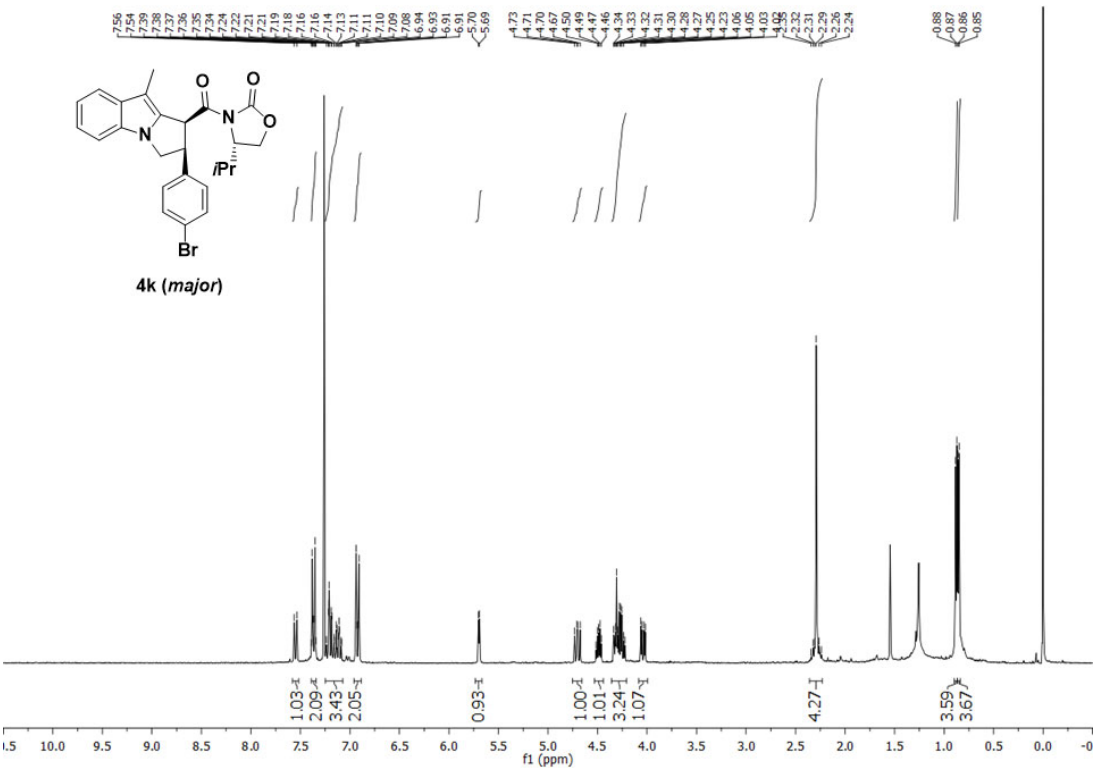


*Figure S86: ^{1}H NMR spectrum of compound **4k major** ($CDCl_3$, 298 K)*

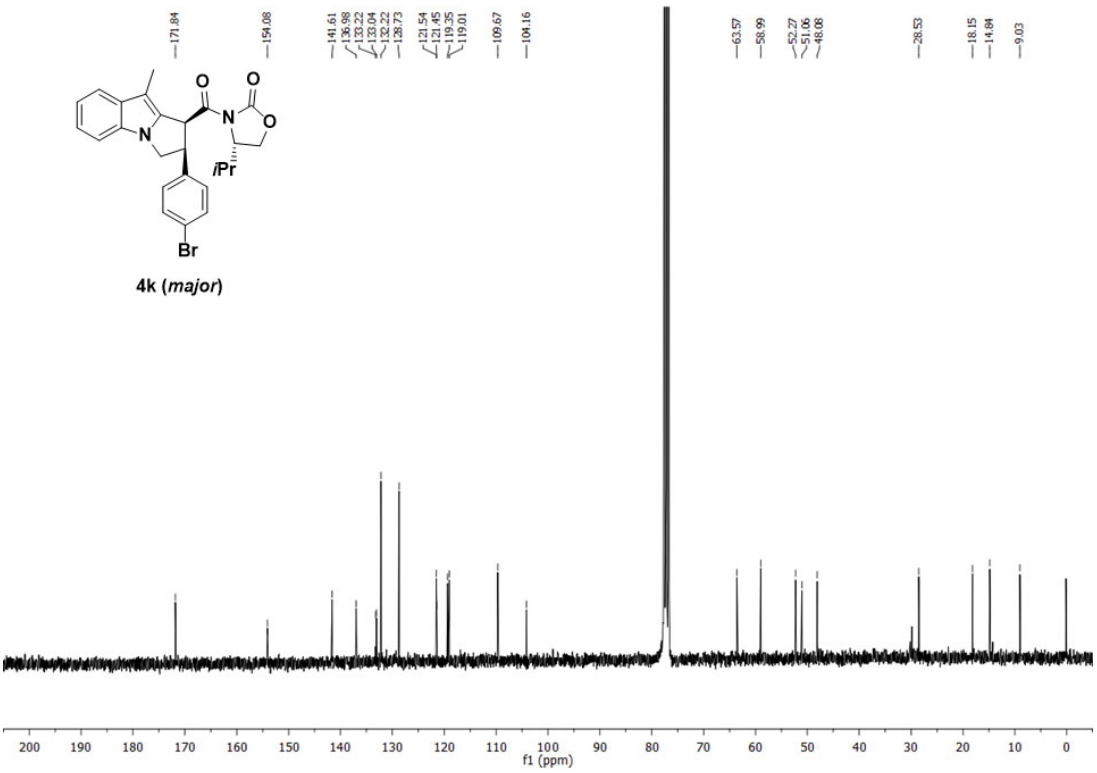


*Figure S87: ^{13}C NMR spectrum of compound **4k major** ($CDCl_3$, 298 K)*

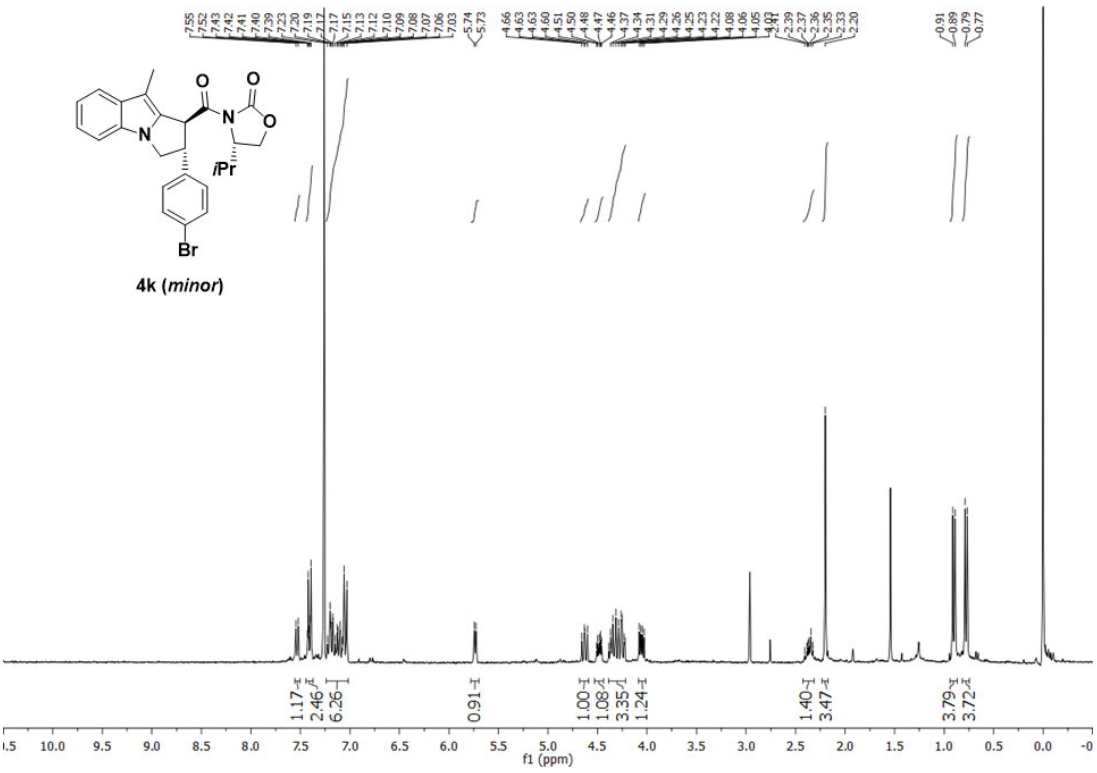


*Figure S88: ^{1}H NMR spectrum of compound **4k minor** ($CDCl_3$, 298 K)*

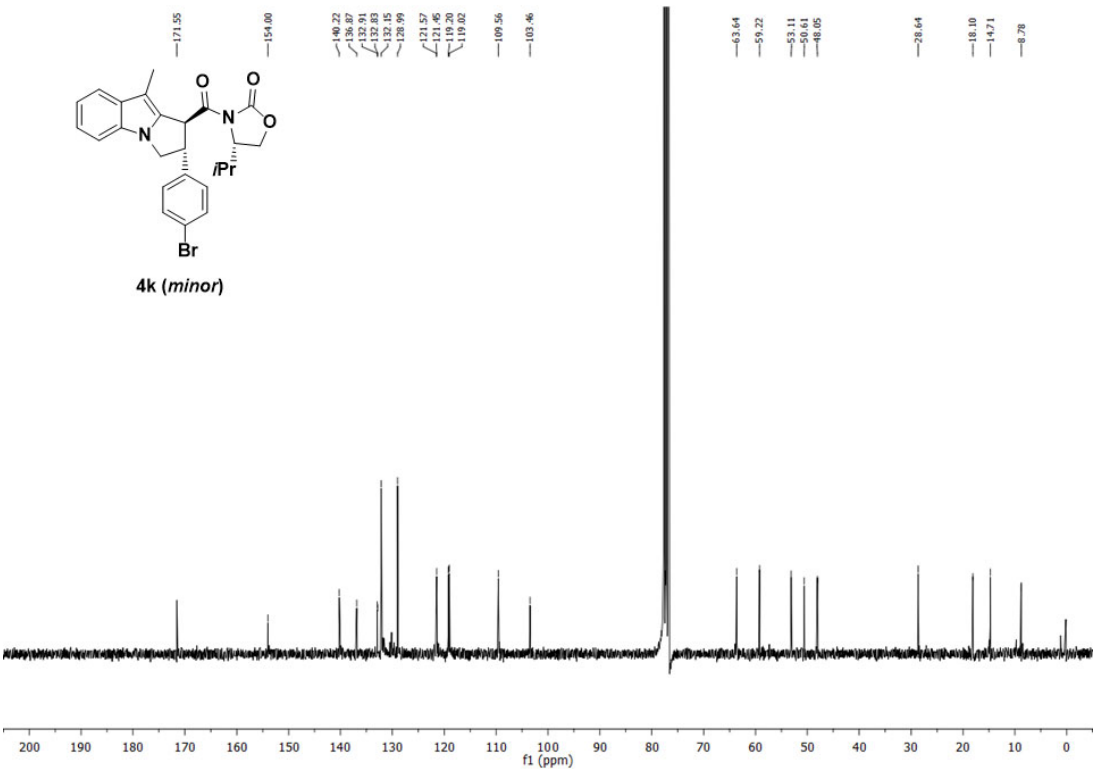


*Figure S89: ^{13}C NMR spectrum of compound **4k minor** ($CDCl_3$, 298 K)*

11.5. NMR spectra of final products 5

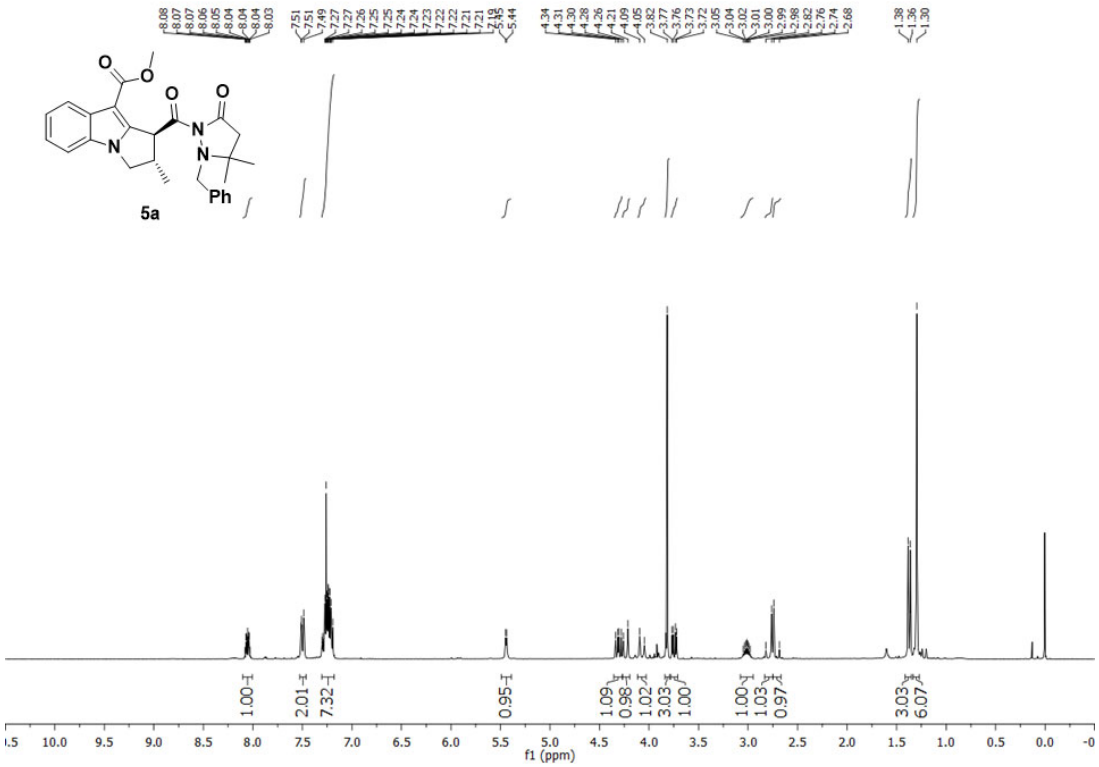


*Figure S90: [1]H NMR spectrum of compound **5a** ($CDCl_3$, 298 K)*

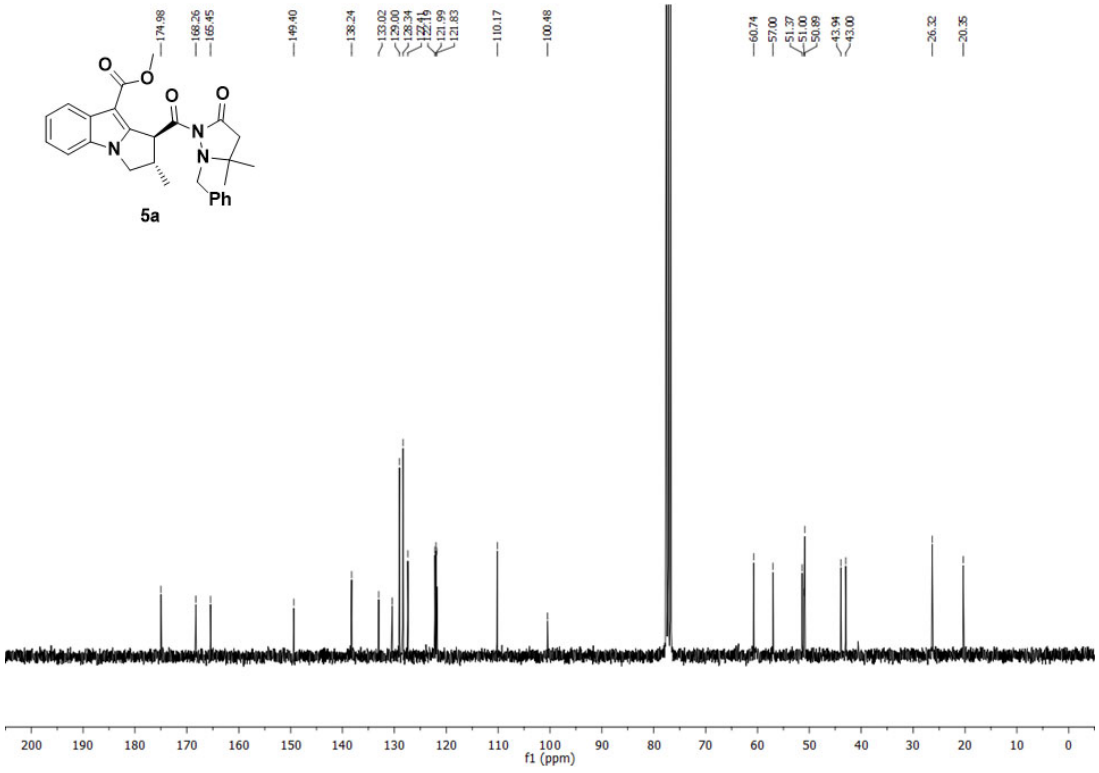


*Figure S91: [13]C NMR spectrum of compound **5a** ($CDCl_3$, 298 K)*

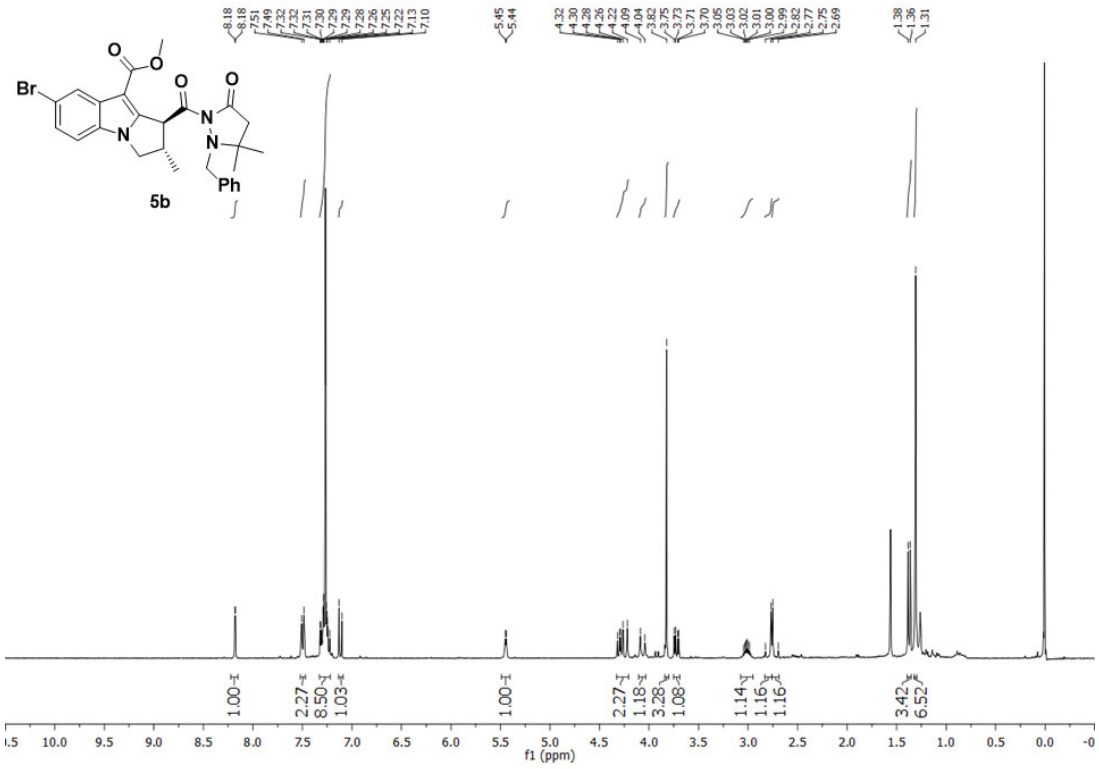


*Figure S92: [1]H NMR spectrum of compound **5b** ($CDCl_3$, 298 K)*

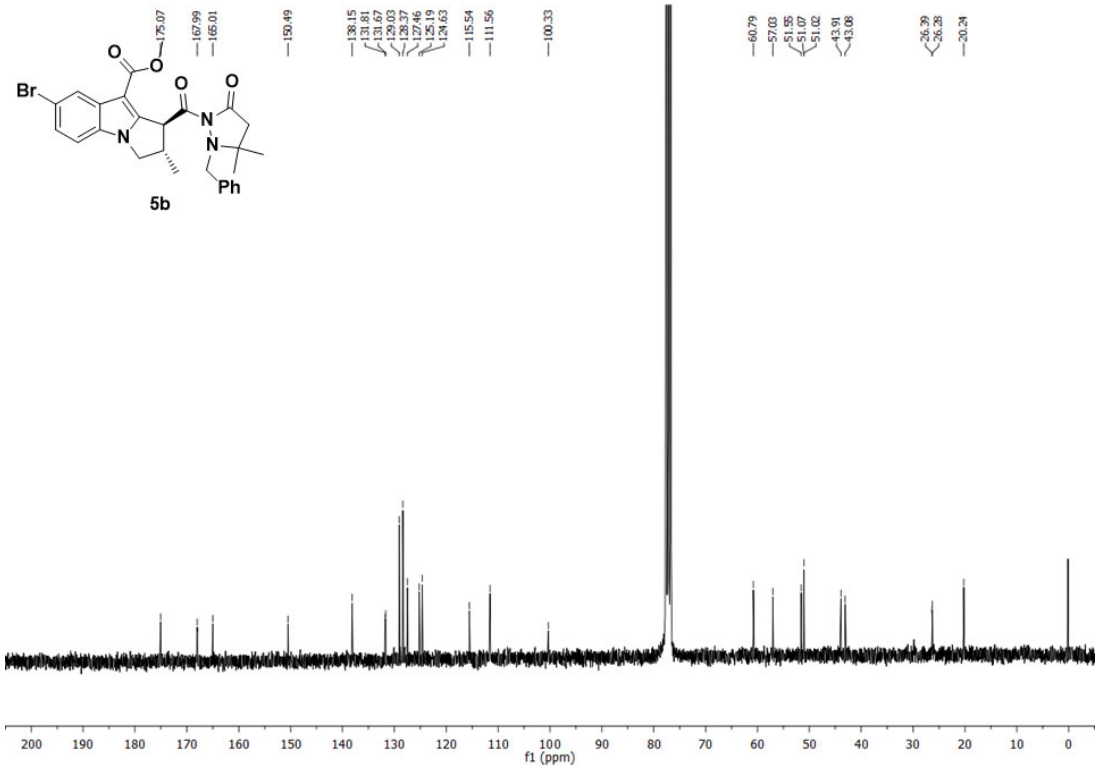


*Figure S93: [13]C NMR spectrum of compound **5b** ($CDCl_3$, 298 K)*

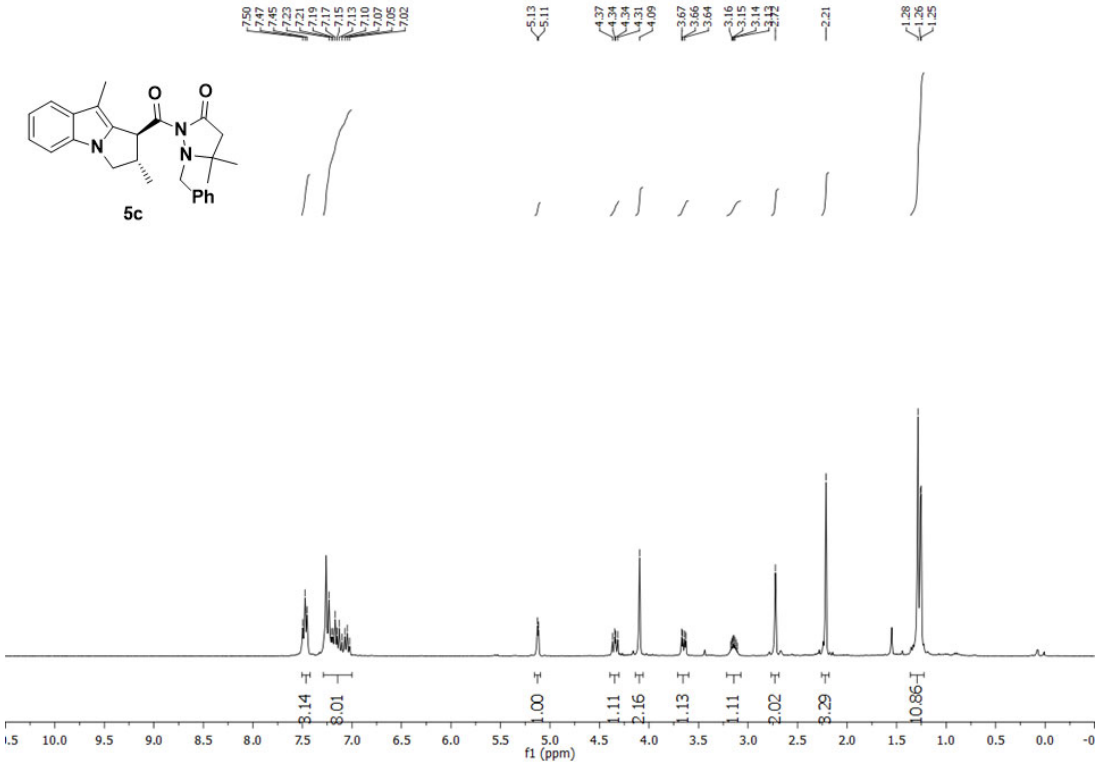


*Figure S94: [1]H NMR spectrum of compound **5c** ($CDCl_3$, 298 K)*

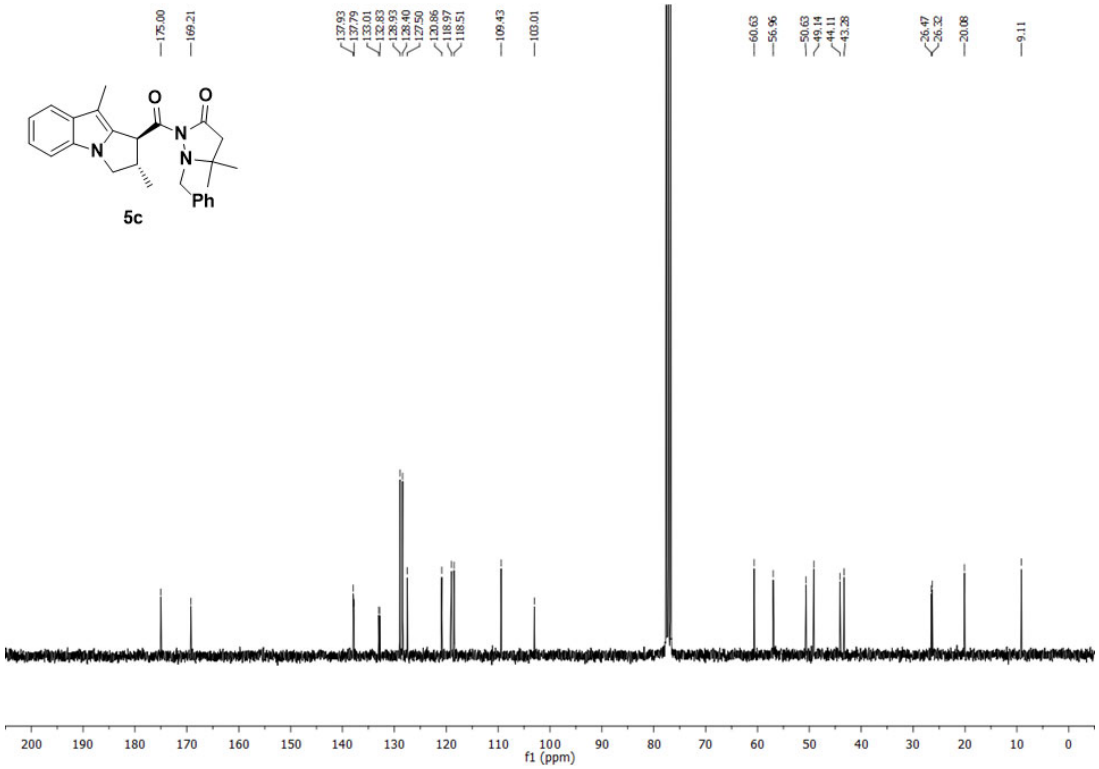


*Figure S95: [13]C NMR spectrum of compound **5c** ($CDCl_3$, 298 K)*

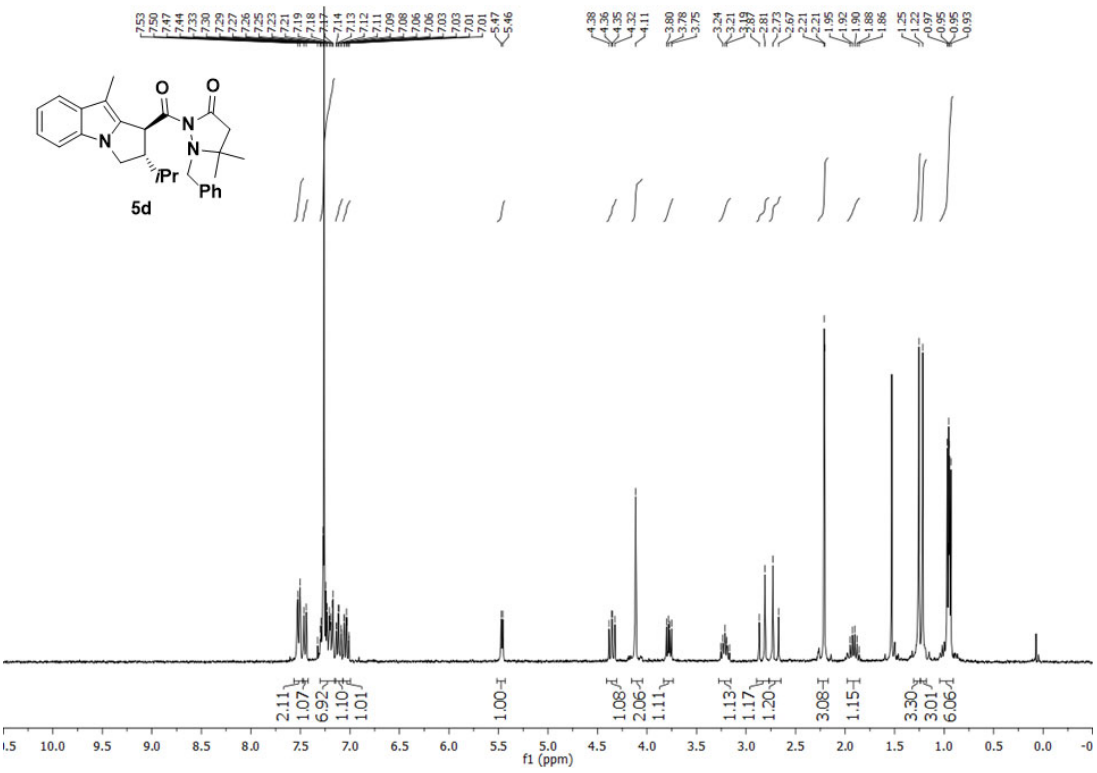


*Figure S96: [1]H NMR spectrum of compound **5d** ($CDCl_3$, 298 K)*

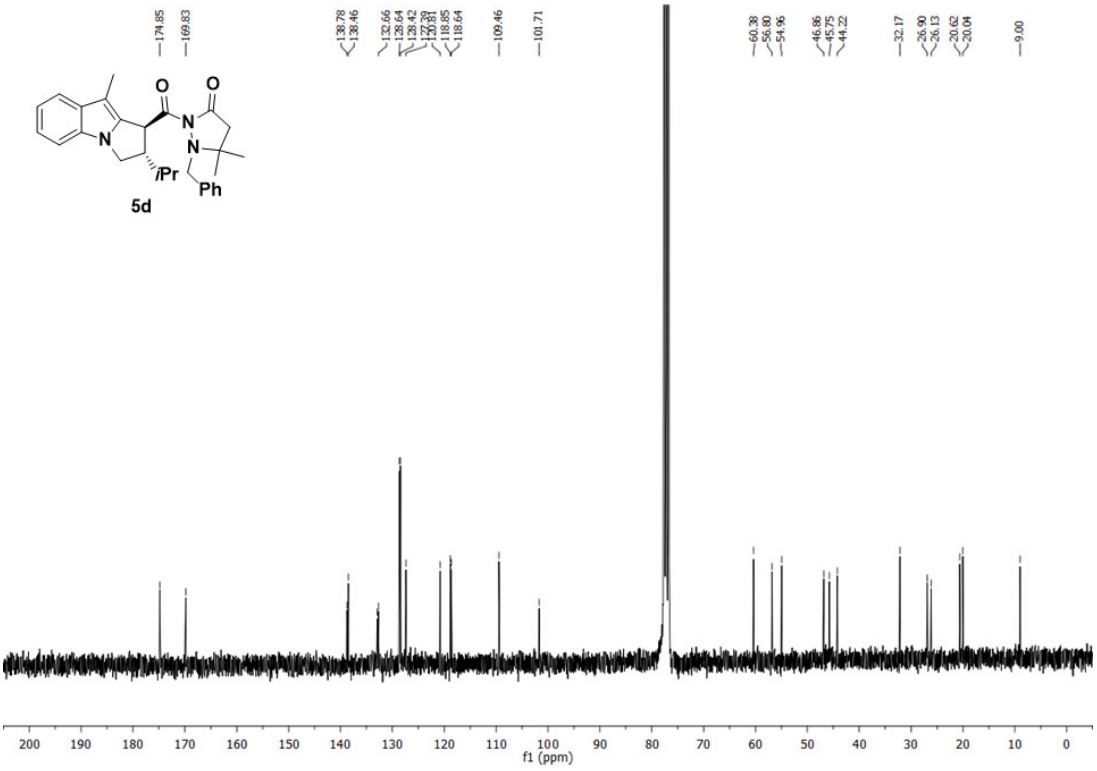


*Figure S97: [13]C NMR spectrum of compound **5d** ($CDCl_3$, 298 K)*

11.6. NMR spectra of derivatized product 6a

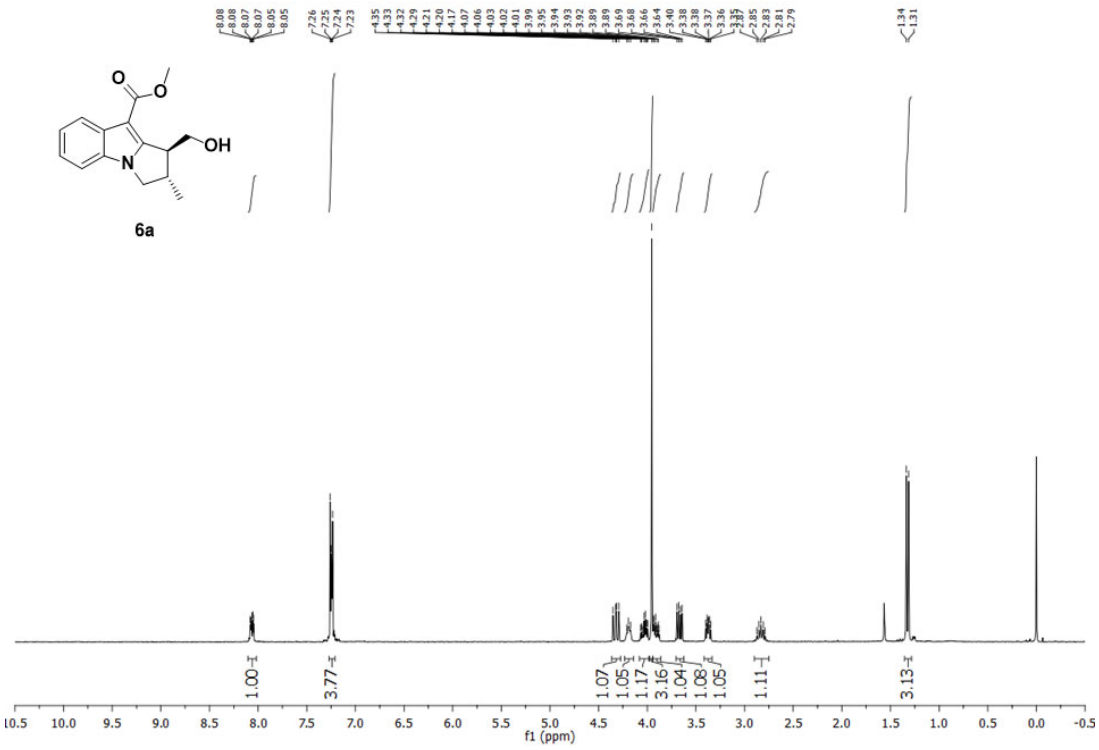


*Figure S98: ^{1}H NMR spectrum of compound **6a** ($CDCl_3$, 298 K)*

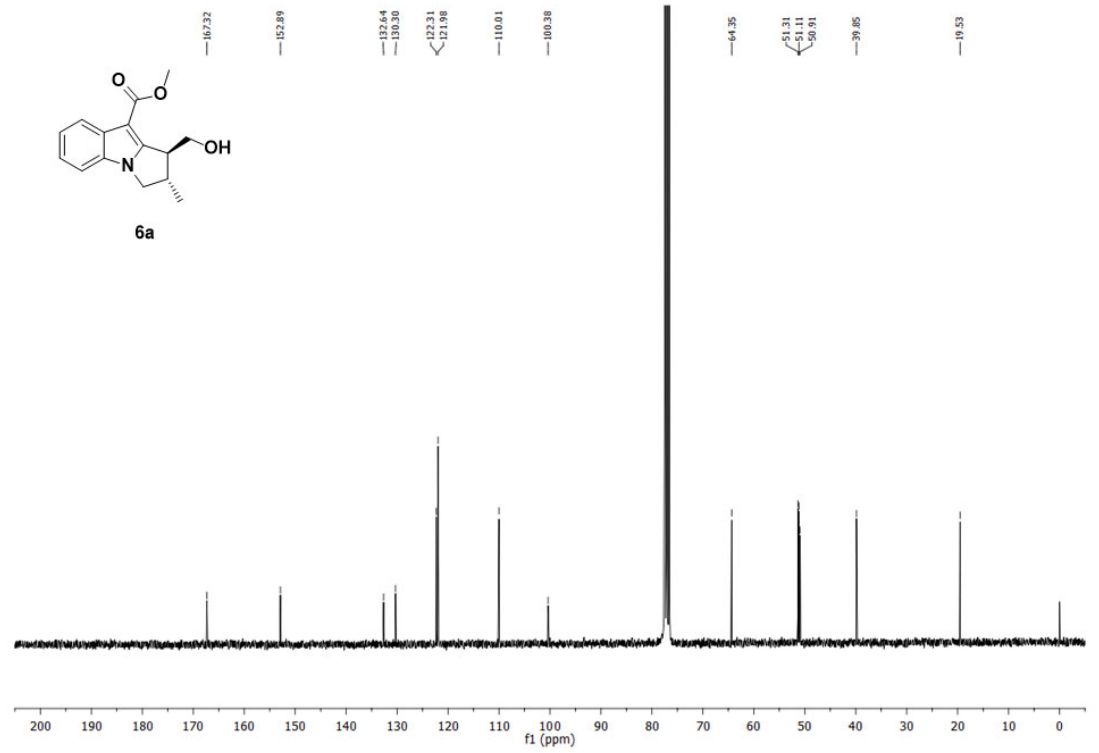


*Figure S99: ^{13}C NMR spectrum of compound **6a** ($CDCl_3$, 298 K)*

11.7. NMR spectra of derivatized product 7a

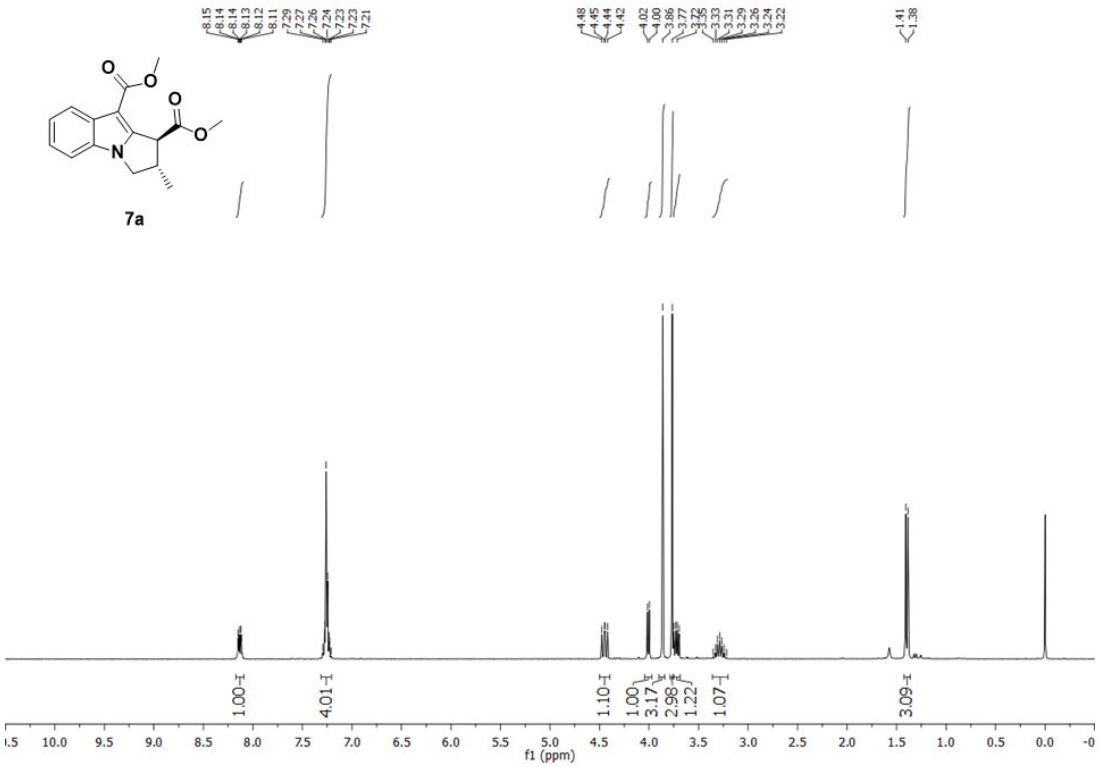


*Figure S100: ^{1}H NMR spectrum of compound **7a** ($CDCl_3$, 298 K)*

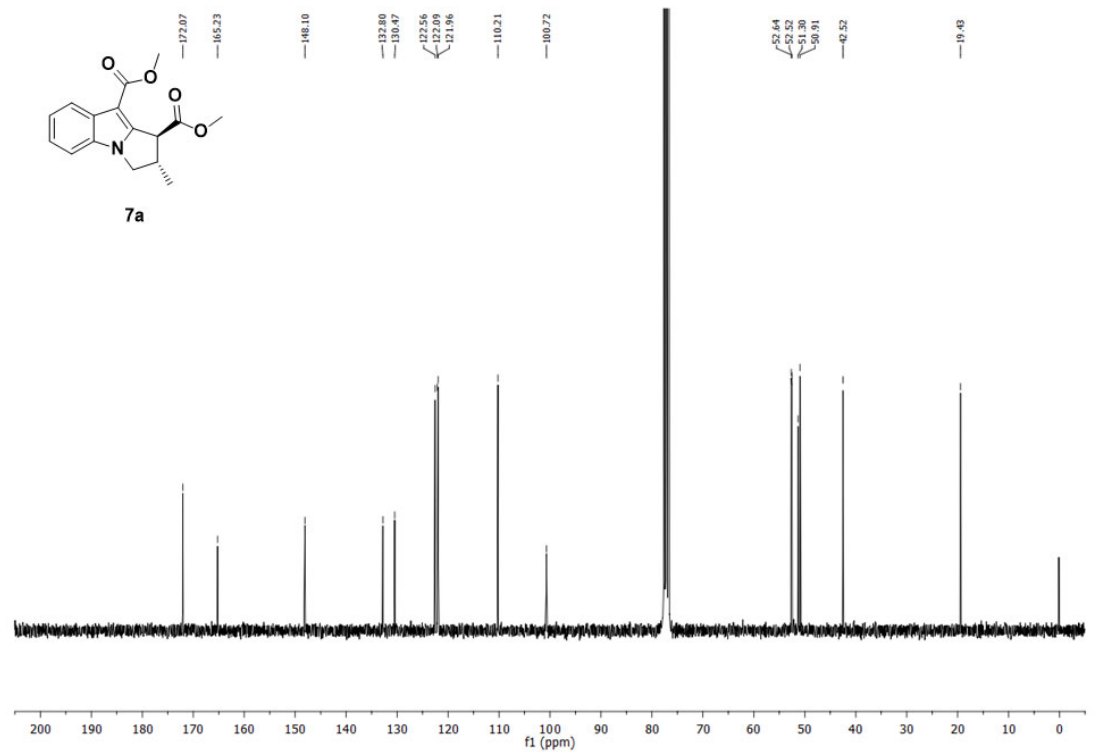


*Figure S101: ^{13}C NMR spectrum of compound **7a** ($CDCl_3$, 298 K)*

12. X Ray Data of product 4e

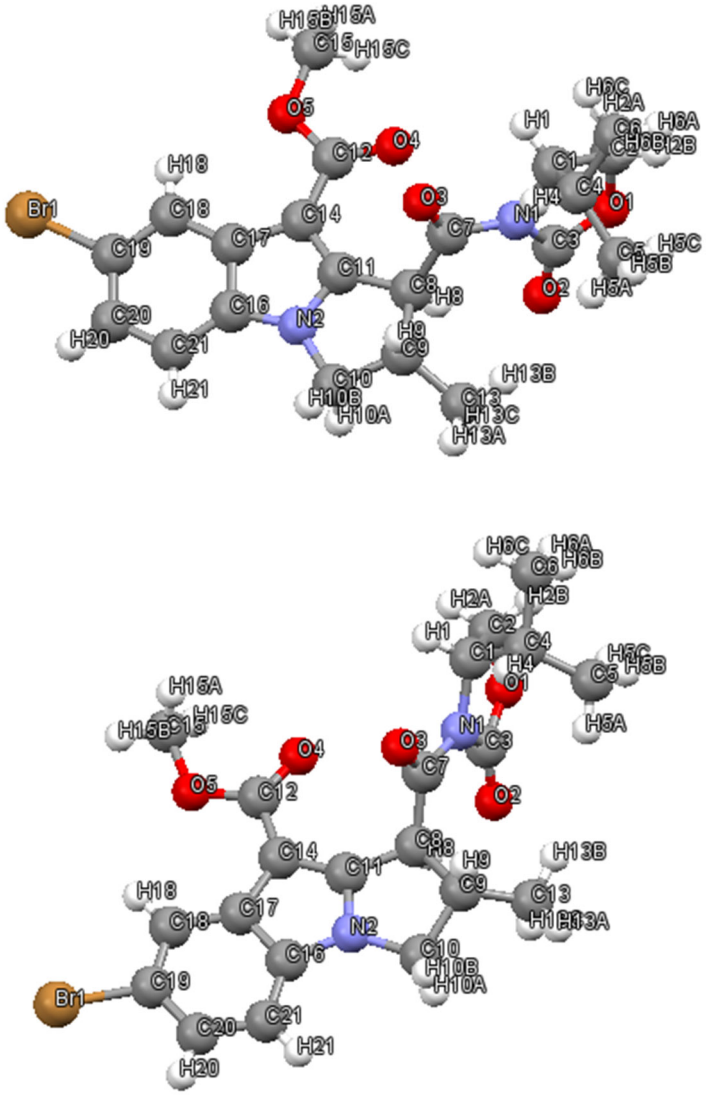


*Figure S102: X Ray structure of **4e***

*Table S3: Sample and crystal data of **4e***

Chemical formula	$C_{21}H_{23}BrN_2O_5$
Formula weight	463.32 g/mol
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal size	0.071 x 0.211 x 0.247 mm
Crystal habit	clear colourless plate
Crystal system	monoclinic
Space group	C 1 2 1

Unit cell dimensions	a = 20.4515(7) Å	α = 90°
	b = 6.59020(10) Å	β = 115.8079(14)°
	c = 16.4904(5) Å	γ = 90°
Volume	2000.89(10) $Å^3$	
Z	4	
Density (calculated)	1.538 g/cm^3	
Absorption coefficient	2.091 mm^{-1}	
F(000)	952	

*Table S4: Data collection and structure refinement of **4e***

Theta range for data collection	1.37 to 25.35°	
Index ranges	-24<=h<=24, -7<=k<=7, -19<=l<=19	
Reflections collected	18040	
Independent reflections	3650 [R(int) = 0.0441]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3650 / 1 / 266	
Goodness-of-fit on F^2	1.102	
Δ/σ_{max}	0.001	
Final R indices	3296 data; I>2σ(I)	R1 = 0.0266, wR2 = 0.0496
	all data	R1 = 0.0334, wR2 = 0.0622
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0121P)^2+3.7850P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.0(0)	
Largest diff. peak and hole	0.250 and -0.256 $eÅ^{-3}$	
R.M.S. deviation from mean	0.062 $eÅ^{-3}$	

*Table S5: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) of **4e***

	x/a	y/b	z/c	U(eq)
Br1	0.55221(2)	0.37799(8)	0.72960(3)	0.02520(13)
O4	0.29691(17)	0.7242(5)	0.2817(2)	0.0237(8)
O2	0.0790(2)	0.5880(6)	0.1625(2)	0.0330(9)
O5	0.40109(19)	0.7590(5)	0.4089(2)	0.0232(8)
O3	0.26738(17)	0.2998(5)	0.1754(2)	0.0246(8)
C16	0.3355(2)	0.2096(7)	0.4884(3)	0.0180(10)
C1	0.1752(3)	0.5217(7)	0.0314(3)	0.0201(11)
C17	0.3718(2)	0.3868(10)	0.4832(2)	0.0169(9)
C7	0.2168(2)	0.3735(10)	0.1843(2)	0.0179(8)
C8	0.2036(2)	0.3366(7)	0.2665(3)	0.0180(12)
C11	0.2715(2)	0.3487(9)	0.3529(3)	0.0159(11)
C20	0.4245(2)	0.1422(7)	0.6370(3)	0.0204(11)
O1	0.0830(2)	0.7240(6)	0.0413(2)	0.0360(10)
C3	0.1072(3)	0.5992(8)	0.1126(3)	0.0255(12)
N1	0.1658(2)	0.4891(6)	0.1142(2)	0.0182(9)
C15	0.4163(3)	0.9399(7)	0.3708(4)	0.0300(14)
C12	0.3395(2)	0.6620(7)	0.3553(3)	0.0183(10)
C5	0.0764(3)	0.2639(9)	0.9454(4)	0.0343(14)
N2	0.2750(2)	0.1899(6)	0.4064(2)	0.0179(9)
C10	0.2127(3)	0.0522(7)	0.3676(3)	0.0217(11)
C19	0.4610(2)	0.3152(7)	0.6309(3)	0.0197(12)
C14	0.3293(2)	0.4771(7)	0.3956(3)	0.0174(10)
C2	0.1262(3)	0.7073(8)	0.9928(3)	0.0317(13)
C9	0.1792(2)	0.1107(7)	0.2676(3)	0.0221(11)
C13	0.0981(3)	0.0810(8)	0.2191(4)	0.0305(13)
C6	0.1651(3)	0.3783(13)	0.8864(3)	0.0354(11)
C4	0.1537(2)	0.3347(7)	0.9705(3)	0.0218(13)
C18	0.4372(2)	0.4401(6)	0.5570(3)	0.0178(11)
C21	0.3605(3)	0.0869(7)	0.5645(3)	0.0211(11)

*Table S6: Bond lengths (Å) of **4e***

Br1-C19	1.912(4)	O4-C12	1.217(5)
O2-C3	1.194(6)	O5-C12	1.344(5)

O5-C15	1.443(5)	O3-C7	1.208(5)
C16-N2	1.385(5)	C16-C21	1.390(6)
C16-C17	1.406(8)	C1-N1	1.474(6)
C1-C4	1.529(6)	C1-C2	1.534(7)
C1-H1	1.0	C17-C18	1.404(6)
C17-C14	1.450(6)	C7-N1	1.398(6)
C7-C8	1.512(6)	C8-C11	1.497(6)
C8-C9	1.573(6)	C8-H8	1.0
C11-N2	1.351(6)	C11-C14	1.374(6)
C20-C21	1.383(6)	C20-C19	1.391(6)
C20-H20	0.95	O1-C3	1.341(6)
O1-C2	1.431(6)	C3-N1	1.392(6)
C15-H15A	0.98	C15-H15B	0.98
C15-H15C	0.98	C12-C14	1.445(6)
C5-C4	1.524(7)	C5-H5A	0.98
C5-H5B	0.98	C5-H5C	0.98
N2-C10	1.465(6)	C10-C9	1.534(7)
C10-H10A	0.99	C10-H10B	0.99
C19-C18	1.372(6)	C2-H2A	0.99
C2-H2B	0.99	C9-C13	1.508(6)
C9-H9	1.0	C13-H13A	0.98
C13-H13B	0.98	C13-H13C	0.98
C6-C4	1.530(6)	C6-H6A	0.98
C6-H6B	0.98	C6-H6C	0.98
C4-H4	1.0	C18-H18	0.95
C21-H21	0.95		

*Table S7: Bond angles (°) of **4e***

C12-O5-C15	115.1(4)	N2-C16-C21	130.4(4)
N2-C16-C17	106.9(4)	C21-C16-C17	122.8(4)
N1-C1-C4	112.0(4)	N1-C1-C2	100.1(4)
C4-C1-C2	114.9(4)	N1-C1-H1	109.8
C4-C1-H1	109.8	C2-C1-H1	109.8
C18-C17-C16	118.9(4)	C18-C17-C14	133.7(5)
C16-C17-C14	107.3(4)	O3-C7-N1	119.3(4)

O3-C7-C8	122.7(4)	N1-C7-C8	118.0(4)
C11-C8-C7	113.1(4)	C11-C8-C9	101.9(4)
C7-C8-C9	110.2(4)	C11-C8-H8	110.5
C7-C8-H8	110.5	C9-C8-H8	110.5
N2-C11-C14	110.7(4)	N2-C11-C8	110.2(4)
C14-C11-C8	139.1(5)	C21-C20-C19	119.3(4)
C21-C20-H20	120.3	C19-C20-H20	120.3
C3-O1-C2	111.1(4)	O2-C3-O1	122.4(5)
O2-C3-N1	128.7(5)	O1-C3-N1	108.8(4)
C3-N1-C7	128.8(4)	C3-N1-C1	111.4(4)
C7-N1-C1	119.6(4)	O5-C15-H15A	109.5
O5-C15-H15B	109.5	H15A-C15-H15B	109.5
O5-C15-H15C	109.5	H15A-C15-H15C	109.5
H15B-C15-H15C	109.5	O4-C12-O5	123.7(4)
O4-C12-C14	124.0(4)	O5-C12-C14	112.4(4)
C4-C5-H5A	109.5	C4-C5-H5B	109.5
H5A-C5-H5B	109.5	C4-C5-H5C	109.5
H5A-C5-H5C	109.5	H5B-C5-H5C	109.5
C11-N2-C16	109.6(4)	C11-N2-C10	113.9(4)
C16-N2-C10	136.2(4)	N2-C10-C9	102.1(4)
N2-C10-H10A	111.3	C9-C10-H10A	111.3
N2-C10-H10B	111.3	C9-C10-H10B	111.3
H10A-C10-H10B	109.2	C18-C19-C20	124.2(4)
C18-C19-Br1	117.7(3)	C20-C19-Br1	118.1(3)
C11-C14-C12	123.2(4)	C11-C14-C17	105.5(4)
C12-C14-C17	131.3(4)	O1-C2-C1	106.3(4)
O1-C2-H2A	110.5	C1-C2-H2A	110.5
O1-C2-H2B	110.5	C1-C2-H2B	110.5
H2A-C2-H2B	108.7	C13-C9-C10	114.2(4)
C13-C9-C8	113.4(4)	C10-C9-C8	104.8(4)
C13-C9-H9	108.0	C10-C9-H9	108.0
C8-C9-H9	108.0	C9-C13-H13A	109.5
C9-C13-H13B	109.5	H13A-C13-H13B	109.5
C9-C13-H13C	109.5	H13A-C13-H13C	109.5
H13B-C13-H13C	109.5	C4-C6-H6A	109.5

C4-C6-H6B	109.5	H6A-C6-H6B	109.5
C4-C6-H6C	109.5	H6A-C6-H6C	109.5
H6B-C6-H6C	109.5	C5-C4-C1	113.1(4)
C5-C4-C6	111.1(4)	C1-C4-C6	109.3(5)
C5-C4-H4	107.7	C1-C4-H4	107.7
C6-C4-H4	107.7	C19-C18-C17	117.1(4)
C19-C18-H18	121.5	C17-C18-H18	121.5
C20-C21-C16	117.7(4)	C20-C21-H21	121.1
C16-C21-H21	121.1		

*Table S8: Torsion angles (°) of **4e***

N2-C16-C17-C18	-177.9(4)	C21-C16-C17-C18	1.7(7)
N2-C16-C17-C14	1.8(5)	C21-C16-C17-C14	-178.6(4)
O3-C7-C8-C11	43.4(7)	N1-C7-C8-C11	-140.1(5)
O3-C7-C8-C9	-69.8(6)	N1-C7-C8-C9	106.7(5)
C7-C8-C11-N2	-133.6(5)	C9-C8-C11-N2	-15.4(5)
C7-C8-C11-C14	50.3(8)	C9-C8-C11-C14	168.5(6)
C2-O1-C3-O2	-179.9(5)	C2-O1-C3-N1	-1.8(6)
O2-C3-N1-C7	-16.4(9)	O1-C3-N1-C7	165.7(5)
O2-C3-N1-C1	169.5(5)	O1-C3-N1-C1	-8.5(5)
O3-C7-N1-C3	-174.7(5)	C8-C7-N1-C3	8.7(8)
O3-C7-N1-C1	-1.0(7)	C8-C7-N1-C1	-177.6(4)
C4-C1-N1-C3	-108.4(4)	C2-C1-N1-C3	13.9(5)
C4-C1-N1-C7	76.8(5)	C2-C1-N1-C7	-160.9(4)
C15-O5-C12-O4	-3.6(6)	C15-O5-C12-C14	177.2(4)
C14-C11-N2-C16	1.1(5)	C8-C11-N2-C16	-176.2(4)
C14-C11-N2-C10	176.5(4)	C8-C11-N2-C10	-0.8(5)
C21-C16-N2-C11	178.6(5)	C17-C16-N2-C11	-1.8(5)
C21-C16-N2-C10	4.7(9)	C17-C16-N2-C10	-175.7(5)
C11-N2-C10-C9	17.1(5)	C16-N2-C10-C9	-169.2(5)
C21-C20-C19-C18	1.2(7)	C21-C20-C19-Br1	-176.3(3)
N2-C11-C14-C12	-179.1(4)	C8-C11-C14-C12	-3.0(9)
N2-C11-C14-C17	0.1(5)	C8-C11-C14-C17	176.2(5)
O4-C12-C14-C11	2.6(7)	O5-C12-C14-C11	-178.1(4)
O4-C12-C14-C17	-176.3(5)	O5-C12-C14-C17	3.0(7)

C18-C17-C14-C11	178.4(5)	C16-C17-C14-C11	-1.2(5)
C18-C17-C14-C12	-2.5(9)	C16-C17-C14-C12	177.9(5)
C3-O1-C2-C1	10.6(6)	N1-C1-C2-O1	-14.2(5)
C4-C1-C2-O1	106.0(5)	N2-C10-C9-C13	-150.0(4)
N2-C10-C9-C8	-25.3(5)	C11-C8-C9-C13	150.3(4)
C7-C8-C9-C13	-89.5(5)	C11-C8-C9-C10	25.0(5)
C7-C8-C9-C10	145.2(4)	N1-C1-C4-C5	55.8(5)
C2-C1-C4-C5	-57.5(6)	N1-C1-C4-C6	-179.8(4)
C2-C1-C4-C6	66.8(5)	C20-C19-C18-C17	-0.5(7)
Br1-C19-C18-C17	177.0(3)	C16-C17-C18-C19	-0.9(7)
C14-C17-C18-C19	179.5(5)	C19-C20-C21-C16	-0.4(7)
N2-C16-C21-C20	178.5(5)	C17-C16-C21-C20	-1.0(7)

Table S9: Anisotropic atomic displacement parameters (Å²) of ***4e***

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	0.0214(2)	0.0326(2)	0.0168(2)	0.0001(3)	0.00375(16)	0.0015(3)
O4	0.0255(19)	0.0240(19)	0.0195(18)	0.0076(15)	0.0079(15)	0.0003(15)
O2	0.033(2)	0.042(2)	0.028(2)	0.0036(17)	0.0167(18)	0.0131(17)
O5	0.028(2)	0.0217(19)	0.0179(18)	0.0023(15)	0.0082(16)	-0.0088(15)
O3	0.0200(18)	0.035(2)	0.0191(18)	0.0023(13)	0.0090(15)	0.0070(14)
C16	0.020(2)	0.019(2)	0.016(2)	0.000(2)	0.009(2)	0.000(2)
C1	0.021(3)	0.023(3)	0.013(2)	0.004(2)	0.004(2)	-0.004(2)
C17	0.0199(19)	0.019(2)	0.0143(19)	-0.002(3)	0.0098(16)	-0.001(3)
C7	0.0176(19)	0.018(2)	0.0155(19)	-0.001(3)	0.0051(16)	-0.002(3)
C8	0.017(2)	0.020(3)	0.017(2)	0.0018(19)	0.0070(18)	0.0005(19)
C11	0.020(2)	0.017(3)	0.0125(19)	-0.002(2)	0.0094(17)	-0.001(2)
C20	0.024(3)	0.024(3)	0.015(2)	0.007(2)	0.010(2)	0.006(2)
O1	0.047(2)	0.035(2)	0.028(2)	0.0120(18)	0.0177(18)	0.0222(18)
C3	0.028(3)	0.027(3)	0.017(3)	0.000(2)	0.005(2)	0.005(2)
N1	0.021(2)	0.020(2)	0.013(2)	0.0002(16)	0.0070(17)	0.0020(16)
C15	0.035(3)	0.026(3)	0.030(3)	0.002(2)	0.015(2)	-0.011(2)
C12	0.023(3)	0.020(3)	0.018(2)	-0.003(2)	0.015(2)	0.000(2)
C5	0.030(3)	0.035(3)	0.033(3)	-0.012(3)	0.008(3)	-0.003(2)
N2	0.019(2)	0.018(2)	0.0145(19)	0.0009(17)	0.0056(16)	-0.0040(16)
C10	0.022(3)	0.022(3)	0.021(3)	-0.001(2)	0.010(2)	-0.005(2)

C19	0.016(2)	0.028(3)	0.015(2)	-0.0019(18)	0.0067(19)	0.0030(18)
C14	0.022(3)	0.018(2)	0.015(2)	0.0030(19)	0.012(2)	0.0017(19)
C2	0.045(3)	0.025(3)	0.025(3)	0.005(2)	0.015(3)	0.005(2)
C9	0.022(3)	0.022(3)	0.021(3)	0.000(2)	0.008(2)	-0.003(2)
C13	0.023(3)	0.031(3)	0.030(3)	0.001(2)	0.005(2)	-0.006(2)
C6	0.045(3)	0.043(3)	0.018(2)	-0.002(4)	0.013(2)	0.008(4)
C4	0.023(2)	0.024(4)	0.016(2)	0.000(2)	0.0059(19)	0.004(2)
C18	0.020(2)	0.019(3)	0.018(2)	-0.0031(17)	0.012(2)	-0.0026(17)
C21	0.026(3)	0.021(3)	0.020(3)	0.003(2)	0.013(2)	-0.001(2)

*Table S10: Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) of **4e***

	x/a	y/b	z/c	U (eq)
H1	0.2268	0.5587	0.0475	0.024
H8	0.1662	0.4327	0.2675	0.022
H20	0.4433	0.0629	0.6904	0.024
H15A	0.4341	0.9019	0.3266	0.045
H15B	0.4533	1.0206	0.4189	0.045
H15C	0.3717	1.0201	0.3412	0.045
H5A	0.0716	0.2275	0.0002	0.052
H5B	0.0655	0.1452	-0.0942	0.052
H5C	0.0423	0.3734	-0.0860	0.052
H10A	0.1781	0.0754	0.3940	0.026
H10B	0.2284	-0.0915	0.3766	0.026
H2A	0.1558	0.8311	0.0011	0.038
H2B	0.0948	0.6889	-0.0723	0.038
H9	0.2023	0.0246	0.2372	0.027
H13A	0.0866	-0.0627	0.2210	0.046
H13B	0.0807	0.1244	0.1563	0.046
H13C	0.0745	0.1622	0.2485	0.046
H6A	0.1300	0.4808	-0.1505	0.053
H6B	0.1580	0.2532	-0.1486	0.053
H6C	0.2145	0.4289	-0.0957	0.053
H4	0.1873	0.2219	0.0041	0.026
H18	0.4637	0.5576	0.5558	0.021
H21	0.3346	-0.0310	0.5666	0.025

*Table S11: Hydrogen bond sistances (Å²) and angles (°) of **4e***

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
C8-H8···O2	1.00	2.13	2.894(6)	131.9
C20-H20···O2	0.95	2.66	3.358(6)	130.6
C9-H9···O4	1.00	2.64	3.442(6)	137.2
C4-H4···O3	1.00	2.63	3.168(5)	114.0
C18-H18···O5	0.95	2.56	3.059(5)	112.8

13. Stereochemical outcome

Based on the previous stereochemical model from Sibi´s work,[18] we propose an equilibrium between monocoordinated (**B**) and bicoordinated (**A**) Yb complexes. In order to justify the observed stereochemistry, we suggest an monocoordinated model (**B**), which is attacked by the radical indole derivative. In Sibi´s work, they employed 2 equivalents of Yb, while in our work we used 15 mol%. The lower energetic barrier in the attack of the indole radical species to complex **B** and the lower number of equivalents of Yb could be the reasons for our observed stereochemical outcome.

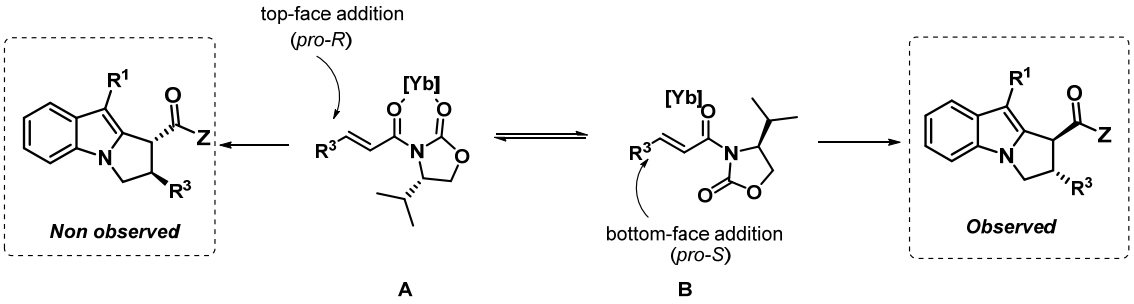


Figure S103: Stereochemical outcome for the [3+2] cycloaddition

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