Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Photocatalytic (3+2) Dipolar Cycloadditions of Aziridines Driven by Visible-Light

Daniele Mazzarella,[a‡] Tommaso Bortolato,[a‡] Giorgio Pelosi[b] and Luca Dell'Amico [a]*

[a]Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131, Padova (Italy).

[b] Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17, 43124 Parma, Italy.

‡These authors contributed equally.

Table of Contents

A. General Information

All reactions were carried out in anhydrous solvents purchased from commercial suppliers over molecular sieves in a sealed bottle which were used without further purification. Chemicals were purchased from commercial sources (Sigma–Aldrich, Alfa Aesar, Fluorochem or TCI) and used without further purification.

NMR spectra were collected on a Bruker AC-300 spectrometer fitted with a Bruker PABBO BB/19F-1H/D probe head, Bruker 200 equipped with a QNP probehead, Bruker 400 Avance III HD spectrometer equipped with a BBI-z grad probehead, Bruker 500 Avance III equipped with a BBI-ATM-z grad probehead and Bruker Neo 600 equipped with a Prodigy probehead operating at the denoted spectrometer frequency given in MHz for the specified nucleus. Reported coupling constants and chemicals shifts were based on a first order analysis. The internal reference for ^{1}H NMR was the residual peak of $CDCl_3$ (7.26 ppm) and the central peak of $CDCl_3$ (77.16 ppm) for ^{13}C NMR spectra. The external reference of ^{19}F NMR is α,α,α-trifluorotoluene (-63.72 ppm) All coupling constants (*J*) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quadruplet, m = multiplet, br = broad. High resolution mass spectrometry (HRMS) was recorded on a Xevo G2-XS QToF in the Department of Pharmaceutical Sciences – University of Padova.

Thin-layer chromatography (TLC) analysis was performed on pre-coated Merck TLC plates (silica gel 60G F254, 0.25 mm). Visualization of the developed purification was performed by checking UV absorbance (254 nm) as well as with ethanolic phosphomolybdic acid and potassium permanganate solutions. Chromatographic purification of the products was accomplished using flash chromatography on silica gel (SiO_2, 0.04-0.0063 mm) purchased from Sigma-Aldrich, with the indicated solvent system according to the standard techniques, or with pre-coated Merck preparative TLC plates (silica gel 60G F254, 20x20 cm). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

Steady-state absorption spectroscopy studies were performed at room temperature on a Varian Cary 50 UV-vis; 10 mm path length Hellma Analytics 100 QS quartz cuvettes were used.

Steady-state emission spectroscopy studies were performed at room temperature on a Varian Cary Eclipse Fluorescence spectrophotometer; 10 mm path length Hellma Analytics 117.100F QS quartz cuvettes were used.

The electrochemical characterizations were carried out in acetonitrile (MeCN)/0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) at room temperature, on an BASi EC Epsilon potentiostat-galvanostat in a glass cell. All the cyclic voltammograms were recorded in a typical three-electrode cell, which was composed of a glassy carbon (GC) working electrode (3 mm diameter), a platinum wire as counter electrode and a Ag/AgCl reference electrode. The glass electrochemical cell was kept closed with a stopper connected to the potentiostat. Oxygen was removed by purging the solvent with high-purity Nitrogen (N_2), introduced from a line into the cell by means of a glass pipe.

The Kessil lamps PR160L (50W) were purchased from Kessil webpage: www.kessil.com/science/PR160L.php.

B. Light sources emission spectra

Kessil lights

In Figure S1 the emission spectra of Kessil LED PR160L lights are reported. The image can be found on the Kessil website. (More info at: www.kessil.com/science/PR160L.php)

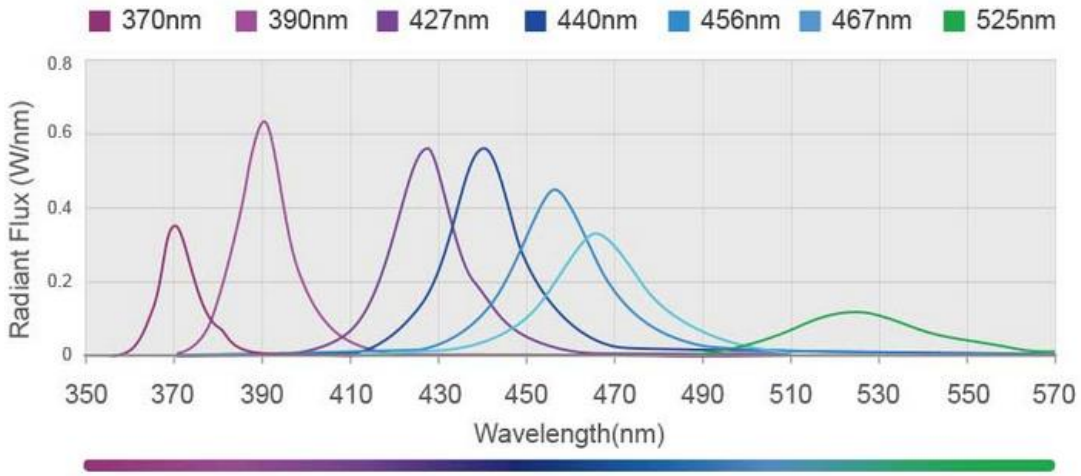


Figure S1: Emission spectra of the Kessil lights used in this work

C. Experimental setup for light irradiation

Reaction setup with Kessil LED PR160L

Figure S2 shows the general setup of a reaction performed under Kessil 427 nm LED PR160L light irradiation. The reaction mixture is placed at a fixed distance (about 5 cm) from the light source and stirred vigorously. A maximum of three reaction vessels were irradiated at the same time placing them following the lines of homogeneous irradiance provided by the producer. To maintain a stable reaction temperature one fan was placed above the irradiated vials.

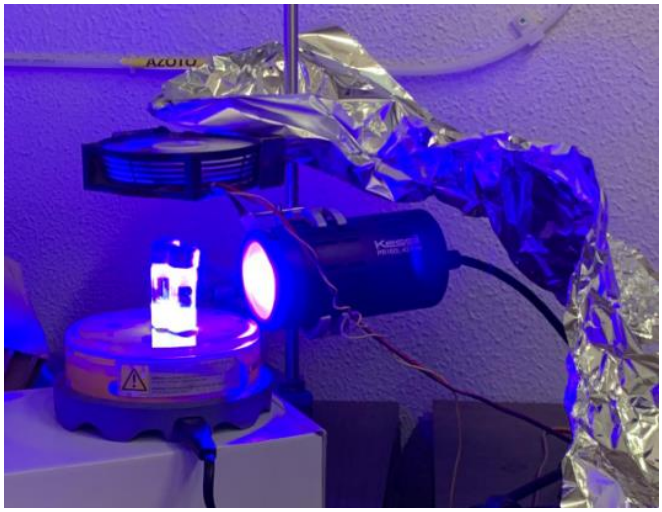


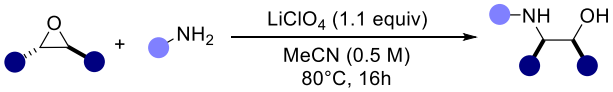
Figure S2: General setup of the reaction performed under Kessil 427 nm LED PR160L light irradiation

D. Synthetic procedures and characterizations

General procedures for the synthesis of aziridines

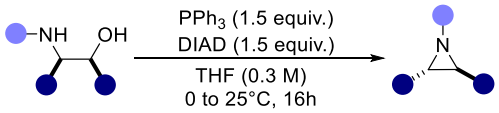
The synthetic procedures were adapted from the literature.[1]

General procedure A, for epoxides ring-opening



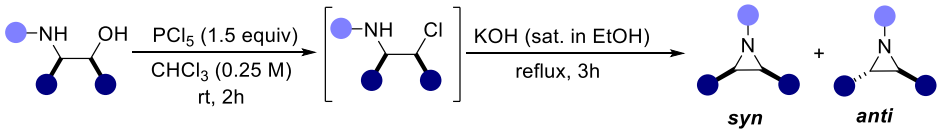
A tube equipped with a stirbar was charged with the desired epoxide (1 equiv.) and $LiClO_4$ (1.1 equiv), and the content dissolved in MeCN to obtain a 0.5 M concentration. The required amine (1.5 equiv.) was then added at room temperature under stirring. The tube was sealed by a screw cap and the content stirred at 80°C. After 16h, the tube was allowed to cool to room temperature. If a solid precipitated, it was vacuum filtered and washed with hexane. If no precipitate was observed, the solvent was evaporated under reduced pressure and the residue vacuum filtered and washed with hexane. The obtained solid was dissolved in EtOAc and filtered through a short plug of silica. The solvent was removed under reduced pressure to obtain the crude amino alcohol, which was used in the subsequent step without further purification.

General procedure B, for *anti* aziridines synthesis



A round-bottom flask equipped with a stirbar was charged with the desired amino alcohol (1 equiv.) and PPh_3 (1.5 equiv.) under a nitrogen atmosphere. Dry THF was added until complete dissolution of the solids was observed (a concentration of 0.3 M was generally obtained). The reaction mixture was cooled to 0°C and DIAD (1.5 equiv.) was added dropwise under stirring. The reaction mixture was then allowed to warm to room temperature and the content stirred for 16h. In case full conversion of the amino alcohol was not detected by TLC analysis after 16h, the reaction mixture was further stirred at 40°C for 2h. The crude reaction mixture was then filtered and the solid washed with 1:1 hexane:Et_2O. The filtrate was concentrated under reduced pressure and the crude residue purified by flash column chromatography to obtain the desired aziridine.

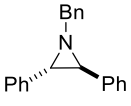
General procedure C, for syn and *anti* aziridines synthesis



This procedure affords both *syn*- and *anti*-aziridine, with the *syn*-aziridine being the major product. The desired amino alcohol (1 equiv.) was dissolved in dry $CHCl_3$ (0.25 M) under a nitrogen atmosphere. PCl_5 (1.5 equiv.) was added portionwise over 10 min under stirring at room temperature. After 2h, TLC analysis revealed complete conversion of the starting material. The reaction mixture was concentrated under reduced pressure, quenched by the addition of 10% aqueous NaOH until basic pH and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and filtered on paper. The solvent was removed under reduced pressure and the crude residue was dissolved in EtOH saturated with KOH (0.5 M). The resulting mixture was heated to reflux under stirring for 3h, after which the solvent was evaporated under reduced pressure. The crude residue was dissolved in EtOAc and the

organic layer washed with water and brine, dried over Na_2SO_4 and filtered on paper. The solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography to obtain the desired aziridines.

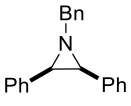
anti-1-benzyl-2,3-diphenylaziridine



7

The starting amino alcohol was obtained according to a literature procedure.[2] According to General Procedure B, *anti*-1-benzyl-2,3-diphenylaziridine was obtained in 98% yield (1.02 g, 3.57 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 90:10). The spectral data are in agreement with those reported in the literature.[3] **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.48 – 7.30 (m, 10H), 7.27 – 7.16 (m, 5H), 3.68 (d, *J* = 14.2 Hz, 1H), 3.43 (br s, 1H), 3.37 (d, *J* = 14.2 Hz, 1H), 3.22 (br s, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 140.0, 139.8, 134.1, 133.8, 130.3, 129.3, 128.7, 128.4, 128.3, 128.1, 128.0, 127.2, 126.8, 126.5, 56.3, 51.1, 45.8 ppm. **HRMS (ESI+):** Calculated for $C_{21}H_{20}N^+$ $[M+H]^+$: 286.1590 *m/z*. Found: 286.1632 *m/z*.

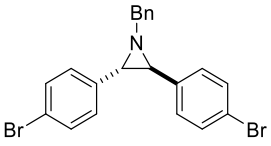
syn-1-benzyl-2,3-diphenylaziridine



7

The starting amino alcohol was obtained according to a literature procedure.[2] According to General Procedure C, *syn*-1-benzyl-2,3-diphenylaziridine was obtained in 33% yield (414 mg, 1.45 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 95:5 to 90:10). The spectral data are in agreement with those reported in the literature.[4] **^{1}H NMR (200 MHz, $CDCl_3$)** δ 7.55 – 7.43 (m, 2H), 7.42 – 7.24 (m, 3H), 7.22 – 7.02 (m, 10H), 3.91 (s, 2H), 3.09 (s, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 139.3, 136.6, 128.6, 128.3, 128.2, 127.8, 127.3, 126.7, 65.1, 49.5 ppm. **HRMS (ESI+):** Calculated for $C_{21}H_{20}N^+$ $[M+H]^+$: 286.1590 *m/z*. Found: 286.1632 *m/z*.

anti-1-benzyl-2,3-bis(4-bromophenyl)aziridine

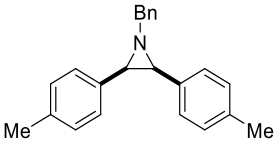


According to General Procedure A, the ring-opening was performed on 764 mg (2.16 mmol) of epoxide and provided 812 mg of crude amino alcohol. According to General Procedure B, *anti*-1-benzyl-2,3-bis(4-bromophenyl)aziridine was obtained in 58% yield (556 mg, 1.25 mmol) over two steps after purification by flash column chromatography on silica gel (hexane:EtOAc 90:10). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 – 7.44 (m, 4H), 7.28 – 7.22 (m, 6H), 7.21 – 7.17 (m, 3H), 3.60 (d, *J* = 14.2 Hz, 1H), 3.33 (d, *J* = 14.2 Hz, 1H), 3.29 (br s, 1H), 3.10 (br s, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.2, 138.8, 136.0, 132.8, 132.0, 131.8, 131.6, 128.4, 128.3, 128.2, 127.8, 127.0, 56.2, 50.6, 45.2 ppm. **HRMS (ESI+):** Calculated for $C_{21}H_{18}Br_2N^+$ $[M+H]^+$: 441.9801 *m/z*. Found: 441.9800 *m/z*.

1-benzyl-2,3-di-_p_-tolylaziridines

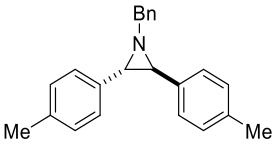
According to General Procedure A, the ring-opening was performed on 1.04 g (4.6 mmol) of epoxide and provided 1.22 g of crude amino alcohol. According to General Procedure C, *syn*-1-benzyl-2,3-di-*p*-tolylaziridine was obtained in 28% yield (405 mg, 1.29 mmol) over three steps and *anti*-1-benzyl-2,3-di-*p*-tolylaziridine was obtained in 18% yield (265 mg, 0.84 mmol) over three steps after purification by flash column chromatography on silica gel (hexane:EtOAc 95:5 to 90:10).

syn-1-benzyl-2,3-di-_p_-tolylaziridine



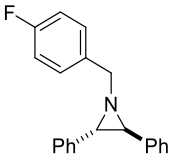
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.4 Hz, 2H), 7.34 (dt, *J* = 23.4, 7.2 Hz, 3H), 7.13 (d, *J* = 7.7 Hz, 4H), 7.00 (d, *J* = 7.7 Hz, 4H), 3.92 (s, 2H), 3.05 (s, 2H), 2.28 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 139.4, 136.0, 133.6, 128.48, 128.46, 128.1, 128.0, 127.1, 65.1, 49.3, 21.2 ppm. **HRMS (ESI+):** Calculated for $C_{23}H_{24}N^+$ $[M+H]^+$: 314.1903 *m/z*. Found: 314.1947 *m/z*.

***anti*-1-benzyl-2,3-di-*p*-tolylaziridine**



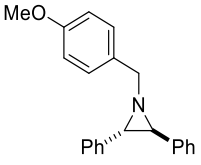
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.25 – 7.22 (m, 4H), 7.22 – 7.14 (m, 5H), 3.68 (d, *J* = 14.3 Hz, 1H), 3.38 (br s, 1H), 3.31 (d, *J* = 14.3 Hz, 1H), 3.14 (br s, 1H), 2.39 (s, 3H), 2.36 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.9, 137.7, 137.1, 136.7, 131.1, 130.2, 129.2, 129.1, 128.3, 127.9, 126.7, 126.4, 56.3, 50.7, 45.7, 21.3 ppm. **HRMS (ESI+):** Calculated for $C_{23}H_{24}N^+$ $[M+H]^+$: 314.1903 *m/z*. Found: 314.1947 *m/z*.

***anti*-1-(4-fluorobenzyl)-2,3-diphenylaziridine**



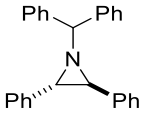
According to General Procedure A, the ring-opening was performed on 588 mg (3 mmol) of epoxide and provided 760 mg of crude amino alcohol. According to General Procedure B, *anti*-1-(4-fluorobenzyl)-2,3-diphenylaziridine was obtained in 51% yield (462 mg, 1.52 mmol) over two steps after purification by flash column chromatography on silica gel (hexane:EtOAc 90:10). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.27 (m, 10H), 7.21 – 7.14 (m, 2H), 6.96 – 6.88 (m, 2H), 3.60 (d, *J* = 14.1 Hz, 1H), 3.43 (br s, 1H), 3.36 (d, *J* = 14.1 Hz, 1H), 3.20 (br s, 1H) ppm. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -116.42 ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.9 (d, *J* = 244.2 Hz), 139.8, 135.4 (d, *J* = 3.1 Hz), 133.9, 130.3, 129.4 (d, *J* = 8.0 Hz), 128.5, 128.4, 128.1, 127.3, 126.5, 115.1 (d, *J* = 21.1 Hz), 55.5, 51.1, 45.6 ppm. **HRMS (ESI+):** Calculated for $C_{21}H_{19}FN^+$ $[M+H]^+$: 304.1496 *m/z*. Found: 304.1540 *m/z*.

***anti* -1-(4-methoxybenzyl)-2,3-diphenylaziridine**



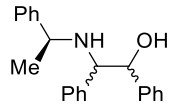
According to General Procedure A, the ring-opening was performed on 588 mg (3 mmol) of epoxide and provided 910 mg of crude amino alcohol. According to General Procedure B, *anti*-1-(4-methoxybenzyl)-2,3-diphenylaziridine was obtained oil in 63% yield (596 mg, 1.89 mmol) over two steps after purification by flash column chromatography on silica gel (hexane:EtOAc 95:5 to 80:20). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 17.2 Hz, 10H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 3.63 (d, *J* = 13.9 Hz, 1H), 3.44 (br s, 1H), 3.32 (d, *J* = 13.9 Hz, 1H), 3.22 (br s, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5, 140.1, 134.2, 131.8, 130.3, 129.1, 128.4, 128.3, 128.0, 127.1, 126.5, 113.7, 55.7, 55.3, 51.1, 45.6 ppm. **HRMS (ESI+):** Calculated for $C_{14}H_{12}N^+$ $[M+H]^+$: 316.1696 *m/z*. Found: 316.1759 *m/z*.

***anti* -1-benzhydryl-2,3-diphenylaziridine**



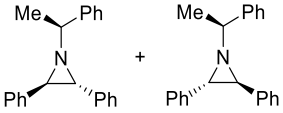
The epoxide ring-opening was performed according to a modification of General Procedure A. A tube equipped with a stirbar was charged with *trans*-stilbene oxide (588 mg, 3 mmol, 1 equiv.) and $LiClO_4$ (351 mg, 3.3 mmol, 1.1 equiv), and the content dissolved in 6 mL of MeCN. Benzhydryl amine (724 µl, 4.5 mmol, 1.5 equiv.) was then added at room temperature under stirring. The tube was sealed by a screw cap and the content stirred at 80°C. After 16h, the tube was allowed to cool to room temperature, the solvent was evaporated under reduced pressure and the residue was and filtered on a short plug of silica using hexane:EtOAc 60:40 as the eluent. The solvent was removed under reduced pressure to obtain a white solid, which was vacuum filtered and washed with hexane. The resulting solid (510 mg) was used in the subsequent step without further purification. According to General Procedure B, *anti*-1-benzhydryl-2,3-diphenylaziridine was obtained in 26% yield (278 mg, 0.77 mmol) over two steps after purification by flash column chromatography on silica gel (hexane:EtOAc 95:5). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.26 (m, 7H), 7.26 – 7.21 (m, 3H), 7.22 – 7.07 (m, 10H), 4.12 (s, 1H), 3.49 (d, *J* = 2.8 Hz, 1H), 3.31 (d, *J* = 2.8 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.1, 143.9, 140.2, 133.8, 130.5, 128.43, 128.41, 128.0, 127.9 (2C), 127.64, 127.60, 127.0, 126.9, 126.7, 126.6, 68.9, 52.1, 44.3 ppm. **HRMS (ESI+):** Calculated for $C_{27}H_{24}N^+$ $[M+H]^+$: 362.1903 *m/z*. Found: 362.1901 *m/z*.

(S)-1,2-diphenyl-2-((1-phenylethyl)amino)ethan-1-ol



According to General Procedure A, the ring-opening was performed on 981 mg (5 mmol) of epoxide with 909 mg of (S)-(−)-α-methylbenzylamine. After heating for 32h, the solvent was evaporated under reduced pressure and (S)-1,2-diphenyl-2-((1-phenylethyl)amino)ethan-1-ol was obtained in 52% yield (830 mg, 2.61 mmol) as an inseparable mixture of diastereomers after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.25 (m), 7.22 (dt, *J* = 4.7, 2.8 Hz), 7.20 – 7.16 (m), 7.15 – 7.05 (m), 7.04 – 6.95 (m), 4.97 (d, *J* = 4.9 Hz, 1H, *minor di*), 4.69 (d, *J* = 6.3 Hz, 1H, *major di*), 4.01 (d, *J* = 4.9 Hz, 1H, *minor di*), 3.78 (q, *J* = 6.5 Hz, 1H, *minor di*), 3.66 (d, *J* = 6.3 Hz, 1H, *major di*), 3.52 (q, *J* = 6.6 Hz, 1H, *major di*), 1.91 (br s, 4H, *major and minor di*), 1.36 (d, *J* = 6.5 Hz, 3H, *minor di*), 1.26 (d, *J* = 6.7 Hz, 3H, *major di*) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.51 (*minor di*), 144.93 (*major di*), 140.64 (*major di*), 140.59 (*minor di*), 139.74 (*major di*), 139.20 (*minor di*), 128.65 (*minor di*), 128.55 (*major di*), 128.44 (*major di*), 128.37 (*major di*), 128.25 (*minor di*), 128.10 (*minor di*), 128.09 (*major di*), 127.83 (*minor di*), 127.82 (*major di*), 127.66 (*major di*), 127.50 (*minor di*), 127.34 (*minor di*), 127.19 (*minor di*), 127.15 (*major di*), 127.08 (*major di*), 126.71 (*major di*), 126.66 (*minor di*), 126.52 (*minor di*), 77.32 (*major di*), 75.38 (*minor di*), 65.82 (*major di*), 65.64 (*minor di*), 54.90 (*major di*), 54.59 (*minor di*), 24.84 (*major di*), 23.01 (*minor di*) ppm.

2,3-diphenyl-1-((S)-1-phenylethyl)aziridine

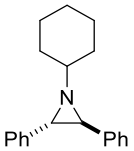


According to General Procedure B, the two diastereomeric 2,3-diphenyl-1-((S)-1-phenylethyl)aziridines were obtained and separated by flash column chromatography on silica gel (hexane:EtOAc 98:2 to 90:10). Structural assignment is not possible based on the NMR data.

The less polar diastereomer was obtained in 25% yield (380 mg, 1.27 mmol). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (s, 2H), 7.41 – 7.28 (m, 4H), 7.24 – 7.12 (m, 6H), 7.12 – 7.02 (m, 3H), 3.29 (s, 2H), 3.06 (q, *J* = 6.5 Hz, 1H), 1.41 (d, *J* = 6.6 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.2, 134.0, 133.8, 130.4, 128.8, 128.7, 128.6, 128.5, 127.9, 127.7, 127.0, 126.6, 60.3, 51.3, 44.2, 24.6 ppm.

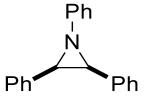
The more polar diastereomer was obtained in 22% yield (330 mg, 1.10 mmol). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (s, 2H), 7.46 – 7.38 (m, 3H), 7.37 – 7.33 (m, 2H), 7.30 – 7.16 (m, 8H), 3.50 (s, 1H), 3.18 (q, *J* = 6.4 Hz, 2H), 1.15 (d, *J* = 6.4 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.3, 140.0, 133.7, 130.4, 128.41, 128.35, 128.1, 127.2, 127.0, 126.6, 60.1, 51.5, 44.0, 23.6 ppm.

***anti* -1-cyclohexyl-2,3-diphenylaziridine**



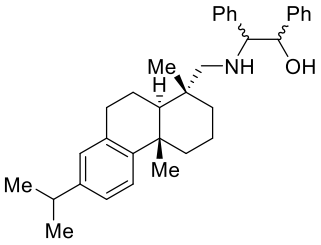
According to General Procedure A, the ring-opening was performed on 588 mg (3 mmol) of epoxide and provided 230 mg of crude amino alcohol. According to General Procedure B, *anti*-1-cyclohexyl-2,3-diphenylaziridine was obtained in 17% yield (141 mg, 0.51 mmol) over two steps after purification by flash column chromatography on silica gel (hexane:EtOAc 95:5 to 90:10). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 7.3 Hz, 4H), 7.34 (t, *J* = 7.1 Hz, 4H), 7.28 (br s, 2H), 3.31 (s, 1H), 3.19 (s, 1H), 1.94 – 1.79 (m, 2H), 1.78 – 1.70 (m, 1H), 1.58 – 1.42 (m, 3H), 1.42 – 1.33 (m, 1H), 1.29 – 1.08 (m, 3H), 0.90 – 0.76 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.7, 134.3, 130.1, 128.3, 127.6, 127.4, 127.1, 126.8, 58.8, 50.3, 43.6, 33.3, 32.4, 26.1, 25.0, 24.5 ppm. **HRMS (ESI+):** Calculated for $C_{20}H_{24}N^+$ $[M+H]^+$: 278.1903 *m/z*. Found: 278.1903 *m/z*.

***syn*-1,2,3-triphenylaziridine**



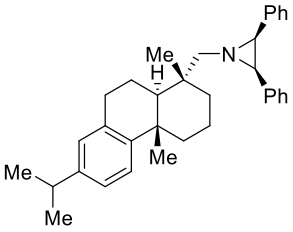
syn-1,2,3-triphenylaziridine was prepared according to a literature procedure.[5] The spectral data are in agreement with those reported. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.28 (m, 6H), 7.25 – 7.13 (m, 8H), 7.09 – 7.02 (m, 1H), 3.67 (s, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.7, 136.0, 129.3, 128.0, 127.9, 127.1, 122.8, 120.0, 49.2 ppm. **HRMS (ESI+):** Calculated for $C_{20}H_{18}N^+$ $[M+H]^+$: 272.1434 *m/z*. Found: 272.1435 *m/z*.

2-((7-isopropyl-1,4a-dimethyl-octahydrophenanthren-1-yl)methyl)amino)-1,2-diphenylethan-1-ol



The compound was synthesized according to a modified General Procedure A. A tube equipped with a stirbar was charged with 981 mg of *trans*-stilbene oxide (5 mmol, 1 equiv.), 3.57 g of (+)-dehydroabietylamine (technical grade, 60% purity) and 532 mg of $LiClO_4$ (5 mmol, 1 equiv). The content was dissolved in MeCN (10 mL). The tube was sealed by a screw cap and the content stirred at 80°C. After 16h, the tube was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (hexane:EtOAc 90:10 to 80:20) and the target compound was isolated in 93% yield (2.26 g, 4.67 mmol, inseparable mixture of diastereomers). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.17 (m, 15H), 7.17 – 7.09 (m, 4H), 7.09 – 6.98 (m, 5H), 6.91 (d, *J* = 4.4 Hz, 2H), 4.85 – 4.71 (m, 2H), 3.91 – 3.75 (m, 2H), 3.32 (br s, 1H), 3.11 (br s, 1H), 2.91 – 2.77 (m, 3H), 2.72 – 2.60 (m, 1H), 2.49 – 2.36 (m, 2H), 2.36 – 2.24 (m, 2H), 2.22 – 2.00 (m, 3H), 1.88 – 1.70 (m, 4H), 1.68 – 1.57 (m, 6H), 1.47 – 1.30 (m, 8H), 1.26 (m, 9H), 1.20 (s, 4H), 1.05 – 0.90 (m, 4H), 0.88 (s, 3H), 0.84 (s, 4H), 0.79 – 0.69 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.57, 147.55, 145.62, 145.57, 140.6, 140.5, 140.0, 139.9, 134.92, 134.88, 128.3, 128.24, 128.17, 128.12, 128.11, 128.0, 127.7, 127.6, 127.60 (2C), 127.02, 126.95, 126.9, 126.8, 124.45 (2C), 124.0, 123.9, 76.6, 76.5, 69.7, 69.6, 59.2, 58.8, 45.5, 45.0, 38.64, 38.62, 37.59, 37.58, 37.2, 37.1, 36.3, 36.2, 33.59, 33.58, 30.42, 30.41, 25.61, 25.59, 24.19, 24.15, 24.12 (2C), 19.7, 19.5, 18.97, 18.96, 18.88, 18.87 ppm. **HRMS (ESI+):** Calculated for $C_{34}H_{44}NO^+$ $[M+H]^+$: 482.3417 *m/z*. Found: 482.3402 *m/z*.

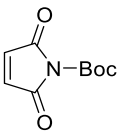
***syn*-1-((7-isopropyl-1,4a-dimethyl-octahydrophenanthren-1-yl)methyl)-2,3-diphenylaziridine**



According to General procedure C, *syn*-1-((7-isopropyl-1,4a-dimethyl-octahydrophenanthren-1-yl)methyl)-2,3-diphenylaziridine was obtained starting from 2.17 g of amino alcohol (4.5 mmol, 1 equiv.) in 39% yield (822 mg, 1.77 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 99:1 to 95:5). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.22 – 7.14 (m, 5H), 7.13 – 6.98 (m, 7H), 6.87 (s, 1H), 2.90 (s, 3H), 2.95 – 2.79 (m, 2H), 2.61 (d, *J* = 12.0 Hz, 1H), 2.50 (d, *J* = 12.1 Hz, 1H), 2.29 (dt, *J* = 12.5, 2.9 Hz, 1H), 1.99 – 1.90 (m, 2H), 1.82 – 1.71 (m, 2H), 1.69 – 1.62 (m, 2H), 1.64 – 1.57 (m, 1H), 1.42 (td, *J* = 12.9, 3.1 Hz, 1H), 1.25 (s, 3H), 1.25 (s, 3H), 1.24 (s, 3H), 1.07 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.7, 145.4, 136.8, 135.0, 128.0, 127.9, 127.7, 127.6, 127.0, 126.44, 126.42, 124.4, 123.8, 73.9, 50.9, 49.9, 46.6, 38.8, 38.5, 37.8, 37.2, 33.6, 30.6, 25.8, 24.2, 24.1, 19.3, 19.2, 19.1 ppm. **HRMS (ESI+):** Calculated for $C_{34}H_{42}N^+$ $[M+H]^+$: 464.3312 *m/z*. Found: 464.3408 *m/z*.

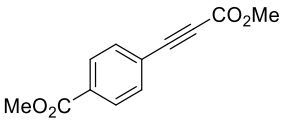
Synthesis of other starting materials

***N*-Boc-maleimide**



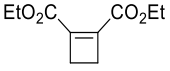
N-Boc-maleimide was synthesised according to a literature procedure.[6] The spectral data are in agreement with those reported.

methyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)benzoate



methyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)benzoate was synthesised according to a literature procedure.[7] The spectral data are in agreement with those reported.

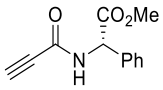
diethyl cyclobut-1-ene-1,2-dicarboxylate



To a solution of diethyl α,α'-dibromo-adipate (2000 mg, 5.55 mmol, 1 equiv) in 14 ml of dry DMF, sodium hydride 60% wt (470 mg, 11.66 mmol, 2.1 equiv) was added at 0

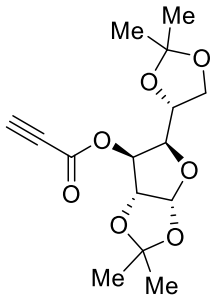
°C. The solution was then warmed up to room temperature and kept stirring for 4 hours. To the crude solution, 100 mL of Et_2O was added and then the solids were removed by filtration on a pad of silica. The solution was then washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporation. Finally, the crude was purified by flash column chromatography (hexane:Et_2O 9:1). The target compound was obtained in 62% yield (681 mg, 3.4 mmol). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.24 (q, *J* = 7.1 Hz, 4H), 2.65 (s, 4H), 1.31 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.5, 142.6, 61.0, 27.2, 14.3 ppm. **HRMS (ESI+):** Calculated for $C_{10}H_{15}O_4^+$ $[M+H]^+$: 199.0965 *m/z*. Found: 199.0973 *m/z*.

methyl (*S*)-2-phenyl-2-propiolamidoacetate



Methyl (*S*)-2-phenyl-2-propiolamidoacetate was synthesised by adapting a literature procedure.[8] (*S*)-2-phenylglycine methyl ester hydrochloride (605 mg, 3 mmol, 1 equiv) and *N,N*-dicyclo-hexylcarbodiimide (619 mg, 3 mmol, 1 equiv) were dissolved in 10 mL of DCM and the mixture cooled to 0°C. Propiolic acid (210 mg, 3 mmol, 1 equiv) and triethylamine (268 mg, 3 mmol, 1 equiv) were then added and the reaction stirred at room temperature for 20 h. The precipitated dicyclohexylurea was filtered off and the filtrate was washed with 1 M HCl, 1 M $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4 and filtered on paper. The solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography (hexane:EtOAc 9:1). The target compound was obtained in 49% yield (319 mg, 1.47 mmol). $[\alpha]_D^{25}$= 158.60 (c = 0.47, $CHCl_3$). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (s, 5H), 6.89 (br s, 1H), 5.60 (d, *J* = 7.3 Hz, 1H), 3.75 (s, 3H), 2.83 (s, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.7, 151.2, 135.7, 129.2, 129.0, 127.4, 76.9, 74.3, 56.7, 53.2 ppm. **HRMS (ESI+):** Calculated for $C_{12}H_{12}NO_3^+$ $[M+H]^+$: 218.0812 *m/z*. Found: 218.0806 *m/z*.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl propiolate



A solution of DMAP (61 mg, 0.50 mmol, 0.1 equiv) and DCC (1031 mg, 5 mmol, 1 equiv) in CH_2Cl_2 (8 mL) was added slowly over 1 h to a solution of propiolic acid (311 µL, 5 mmol, 1 equiv) and 1,2:5,6-di-*O*-isopropylidene-α-*D*-glucofuranose (1431 mg, 5.5 mmol, 1.1 equiv) in CH_2Cl_2 (8 mL) at 0 °C. The mixture was allowed to stir at room temperature until the acid was consumed (determined by TLC). Upon completion, the mixture was filtered through a layer of Celite, the filtrate was concentrated by rotary evaporation, and the residue was purified by flash column chromatography (hexane:EtOAc 9:1). The target compound was obtained in 14% yield (220 mg, 0.7 mmol). $[\alpha]_D^{25}$= -43.30 (c = 0.72, $CHCl_3$). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.91 (d, *J* = 3.5 Hz, 1H), 5.34 (s, 1H), 4.53 (d, *J* = 3.5 Hz, 1H), 4.27 – 4.17 (m, 2H), 4.10 (dd, *J* = 8.4, 5.5 Hz, 1H), 4.01 (dd, *J* = 8.6, 4.2 Hz, 1H), 2.96 (s, 1H), 1.51 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.3, 112.6, 109.6, 105.2, 83.1, 79.7, 77.8, 76.2, 74.1, 72.4, 67.3, 27.0, 26.8, 26.3, 25.3 ppm. **HRMS (ESI+):** Calculated for $C_{15}H_{20}NaO_7$ $[M+Na]^+$: 335.1107 *m/z*. Found: 335.1128 *m/z*.

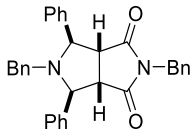
General procedures for the photochemical reactions

General procedure D, for pyrrolidines synthesis

An 8 mL vial was charged with a stirbar, the desired aziridine (0.2 mmol, 1 equiv.), 9,10-dicyanoanthracene (2.3 mg, 0.01 mmol, 0.05 equiv.) and the desired alkene (0.24 mmol, 1.2 equiv.) if solid. The vial was closed with a screwcap equipped with a septum and purged with nitrogen. Dry

acetonitrile (4 mL, 0.05 M) was finally added, followed by the desired alkene (0.24 mmol, 1.2 equiv.) if liquid. The reaction mixture was degassed by nitrogen bubbling for 5 minutes. The desired alkene (0.24 mmol, 1.2 equiv.) was added after nitrogen bubbling if liquid and volatile. The vial was then secured with parafilm and irradiated under stirring for 90 min with a Kessil 427 nm lamp set at 50% of its maximum output power according to the experimental setup shown in Section C. Trichloroethylene (18 µL, 0.2 mmol, 1 equiv.) or CH_2Br_2 (14 µL, 0.2 mmol, 1 equiv.) was added as the internal standard and a sample was taken for ^{1}H NMR yield determination. The solvent was then evaporated under reduced pressure and the crude reaction mixture purified by flash column chromatography.

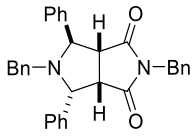
syn-2,5-dibenzyl-4,6-diphenyltetrahydropyrrolo[3,4-_c_]pyrrole-1,3(2_H_,3a_H_)-dione



syn-**9**

According to General procedure D, the product was obtained starting from *syn*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and *N*-benzylmaleimide (44.9 mg, 0.24 mmol, 1.2 equiv.) in 42% yield (39.7 mg, 0.084 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). The *anti*-diastereomer was also isolated in 34% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 – 7.56 (m, 4H), 7.51 – 7.42 (m, 4H), 7.41 – 7.34 (m, 2H), 7.25 – 7.16 (m, 9H), 6.87 – 6.78 (m, 2H), 4.57 (s, 2H), 3.72 (dd, *J* = 5.1, 2.0 Hz, 2H), 3.58 (s, 2H), 3.20 (dd, *J* = 4.9, 2.0 Hz, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 176.6, 140.4, 135.8, 132.8, 130.6, 129.2, 128.8, 128.34, 128.30, 128.1, 128.0, 127.9, 127.5, 67.1, 52.5, 50.2, 42.2 ppm. **HRMS (ESI+):** Calculated for $C_{25}H_{22}N_2NaO_2^+$ [M-C_7H_6+Na]$^+$: 405.1573 *m/z*. Found: 405.1564 *m/z*.

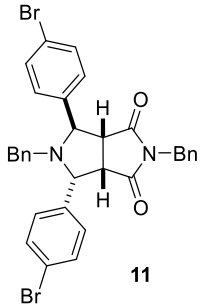
anti-2,5-dibenzyl-4,6-diphenyltetrahydropyrrolo[3,4-_c_]pyrrole-1,3(2_H_,3a_H_)-dione



anti-**9**

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and *N*-benzylmaleimide (44.9 mg, 0.24 mmol, 1.2 equiv.) in 94% yield (88.8 mg, 0.188 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.55 – 7.47 (m, 2H), 7.46 – 7.14 (m, 10H), 7.12 – 7.00 (m, 4H), 6.97 (m, 4H), 4.77 (s, 1H), 4.70 (d, *J* = 13.7 Hz, 1H), 4.57 (d, *J* = 13.7 Hz, 1H), 4.38 (d, *J* = 8.9 Hz, 1H), 3.72 (t, *J* = 8.4 Hz, 1H), 3.44 (d, *J* = 7.7 Hz, 1H), 3.41 (d, *J* = 15.3 Hz, 1H), 2.76 (d, *J* = 14.8 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 178.1, 175.5, 138.5, 136.9, 136.5, 136.2, 129.8, 129.0, 128.7, 128.57, 128.55 (2C), 128.3, 128.21 (3C), 127.7, 127.0, 67.1, 64.8, 50.8, 50.7, 50.2, 42.8 ppm. **HRMS (ESI+):** Calculated for $C_{32}H_{29}N_2O_2^+$ [M+H]$^+$: 473.2224 *m/z*. Found: 473.2266 *m/z*.

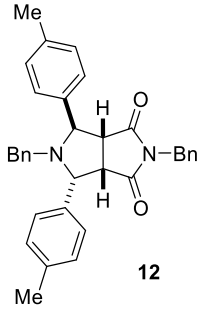
anti-2,5-dibenzyl-4,6-bis(4-bromophenyl)tetrahydropyrrolo[3,4-_c_]pyrrole-1,3(2_H_,3a_H_)-dione



11

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-bis(4-bromophenyl)aziridine (88.6 mg, 0.2 mmol, 1 equiv.) and *N*-benzylmaleimide (44.9 mg, 0.24 mmol, 1.2 equiv.) in 66% yield (83.1 mg, 0.132 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 85:15 to 80:20). The relative configuration is assigned in analogy with **13**. *Note: the reaction mixture was irradiated for only 45 min. Longer reaction times led to lower yields as determined by ^{1}H NMR analysis of the crude reaction mixtures.* **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.48 (m, 4H), 7.44 (q, *J* = 8.3, 7.3 Hz, 3H), 7.31 (q, *J* = 7.0 Hz, 3H), 7.17 (d, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 7.3 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 6.1 Hz, 1H), 4.74 (t, *J* = 6.9 Hz, 2H), 4.56 (d, *J* = 13.7 Hz, 1H), 4.30 (d, *J* = 8.9 Hz, 1H), 3.71 (t, *J* = 8.4 Hz, 1H), 3.42 (d, *J* = 7.9 Hz, 1H), 3.35 (d, *J* = 14.9 Hz, 1H), 2.73 (d, *J* = 14.8 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.6, 175.1, 137.8, 136.1, 135.7, 135.3, 131.8, 130.5, 129.9, 129.8, 128.81, 128.77, 128.7, 128.5, 127.6, 127.2, 122.4, 122.1, 66.5, 64.3, 50.5, 50.4, 50.2, 42.9 ppm. **HRMS (ESI+):** Calculated for $C_{32}H_{27}Br_2N_2O_2^+$ [M+H]$^+$: 629.0434 *m/z*. Found: 629.0430 *m/z*.

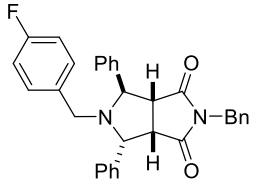
anti-2,5-dibenzyl-4,6-di-_p_-tolyltetrahydropyrrolo[3,4-_c_]pyrrole-1,3(2_H_,3a_H_)-dione



12

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-di-*p*-tolylaziridine (62.7 mg, 0.2 mmol, 1 equiv.) and *N*-benzylmaleimide (44.9 mg, 0.24 mmol, 1.2 equiv.) in 70% yield (70.1 mg, 0.140 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 85:15). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (dt, *J* = 8.0, 1.7 Hz, 2H), 7.48 – 7.37 (m, 3H), 7.35 – 7.29 (m, 2H), 7.28 – 7.23 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.4 Hz, 2H), 6.94 – 6.84 (m, 6H), 4.75 (s, 1H), 4.68 (dd, *J* = 43.7, 14.2 Hz, 2H), 4.35 (d, *J* = 8.9 Hz, 1H), 3.72 (t, *J* = 8.4 Hz, 1H), 3.44 (d, *J* = 7.9 Hz, 1H), 3.40 (d, *J* = 14.6 Hz, 1H), 2.76 (d, *J* = 14.8 Hz, 1H), 2.38 (s, 3H), 2.28 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.3, 175.7, 138.7, 137.9, 137.7, 136.2, 133.8, 133.4, 129.8, 129.3, 129.2, 128.9, 128.6, 128.5, 128.24, 128.16, 127.7, 126.8, 66.8, 64.4, 50.8, 50.7, 50.1, 42.8, 21.4, 21.2 ppm. **HRMS (ESI+):** Calculated for $C_{34}H_{33}N_2O_2^+$ $[M+H]^+$: 501.2537 *m/z*. Found: 501.2583 *m/z*.

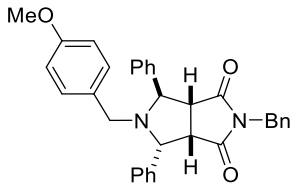
anti-2-benzyl-5-(4-fluorobenzyl)-4,6-diphenyltetrahydropyrrolo[3,4-_c_]pyrrole-1,3(2_H_,3a_H_)-dione



13

According to General procedure D, the product was obtained starting from *anti*-1-(4-fluorobenzyl)-2,3-diphenylaziridine (60.7 mg, 0.2 mmol, 1 equiv.) and *N*-benzylmaleimide (44.9 mg, 0.24 mmol, 1.2 equiv.) in 61% yield (59.9 mg, 0.122 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20 to 70:30). The relative configuration is assigned based on single-crystal X-ray diffraction (vide infra). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 6.6 Hz, 2H), 7.48 – 7.34 (m, 7H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 2H), 7.06 – 6.93 (m, 8H), 4.74 (s, 1H), 4.66 (dd, *J* = 42.7, 14.0 Hz, 2H), 4.41 (d, *J* = 9.0 Hz, 1H), 3.75 (t, *J* = 8.4 Hz, 1H), 3.46 (d, *J* = 7.8 Hz, 1H), 3.35 (d, *J* = 14.6 Hz, 1H), 2.77 (d, *J* = 14.6 Hz, 1H) ppm. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -115.96 (dq, *J* = 12.5, 6.2 Hz) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.1, 175.4, 161.9 (d, *J* = 244.7 Hz), 136.8, 136.4, 136.2, 134.1 (d, *J* = 3.0 Hz), 129.9, 129.1 (d, *J* = 8.0 Hz), 128.9, 128.65, 128.61, 128.60 (2C), 128.32, 128.28, 128.2, 115.4 (d, *J* = 21.1 Hz), 67.1, 64.8, 50.7, 50.7, 49.4, 42.8 ppm. **HRMS (ESI+):** Calculated for $C_{32}H_{28}FN_2O_2^+$ $[M+H]^+$: 491.2129 *m/z*. Found: 491.2129 *m/z*.

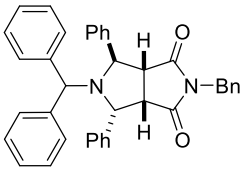
anti-2-benzyl-5-(4-methoxybenzyl)-4,6-diphenyltetrahydropyrrolo[3,4-_c_]pyrrole-1,3(2_H_,3a_H_)-dione



14

According to General procedure D, the product was obtained starting from *anti*-1-(4-methoxybenzyl)-2,3-diphenylaziridine (63.1 mg, 0.2 mmol, 1 equiv.) and *N*-benzylmaleimide (44.9 mg, 0.24 mmol, 1.2 equiv.) in 66% yield (66.3 mg, 0.132 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20 to 70:30). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 6.8 Hz, 3H), 7.49 – 7.35 (m, 6H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 6.3 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 4H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.79 (s, 1H), 4.72 (d, *J* = 13.7 Hz, 1H), 4.60 (d, *J* = 13.7 Hz, 1H), 4.41 (d, *J* = 8.9 Hz, 1H), 3.86 (s, 3H), 3.75 (t, *J* = 8.4 Hz, 1H), 3.45 (d, *J* = 7.9 Hz, 1H), 3.37 (d, *J* = 14.5 Hz, 1H), 2.73 (d, *J* = 14.5 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.2, 175.5, 158.6, 137.0, 136.6, 136.2, 130.4, 129.8, 128.9, 128.7, 128.6, 128.52, 128.49, 128.2, 128.14, 128.13, 113.9, 67.0, 64.7, 55.4, 50.8, 50.7, 49.5, 42.8 ppm. **HRMS (ESI+):** Calculated for $C33H31N2O3^+$ $[M+H]^+$: 503.2329 *m/z*. Found: 503.2370 *m/z*.

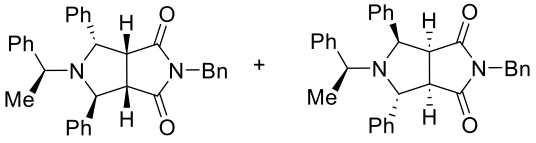
***anti*-5-benzhydryl-2-benzyl-4,6-diphenyltetrahydropyrrolo[3,4-*c*]pyrrole-1,3(2*H*,3a*H*)-dione**



15

According to General procedure D, the product was obtained starting from *anti*-1-benzhydryl-2,3-diphenylaziridine (72.3 mg, 0.2 mmol, 1 equiv.) and *N*-benzylmaleimide (44.9 mg, 0.24 mmol, 1.2 equiv.) in 85% yield (93.1 mg, 0.170 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 85:15 to 80:20). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.36 – 7.28 (m, 6H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 6.9 Hz, 1H), 7.12 (d, *J* = 6.9 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.83 (t, *J* = 7.7 Hz, 2H), 6.78 (d, *J* = 7.3 Hz, 1H), 6.74 – 6.65 (m, 4H), 6.56 (d, *J* = 7.4 Hz, 2H), 5.01 (s, 1H), 4.75 (d, *J* = 10.0 Hz, 1H), 4.71 (s, 1H), 4.54 (d, *J* = 14.0 Hz, 1H), 4.41 (d, *J* = 13.9 Hz, 1H), 3.95 – 3.84 (m, 1H), 3.34 (d, *J* = 8.4 Hz, 1H) ppm. . **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.0, 175.4, 141.6, 141.4, 139.8, 139.6, 135.8, 130.3, 129.6, 128.8, 128.7, 128.4, 128.2 (2C), 128.1, 127.84, 127.82, 127.80, 127.2, 127.0, 126.9, 126.8, 67.6, 67.3, 67.0, 53.2, 51.2, 42.7 ppm. **HRMS (ESI+):** Calculated for $C_{38}H33N_2O_2^+$ $[M+H]^+$: 549.2537 *m/z*. Found: 549.2545 *m/z*.

***anti*-2-benzyl-4,6-diphenyl-5-((*R*)-1-phenylethyl)tetrahydropyrrolo[3,4-*c*]pyrrole-1,3(2*H*,3a*H*)-dione**



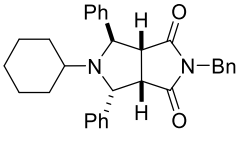
16 major **16** minor

According to General procedure D, the product was obtained starting from *anti*-2,3-diphenyl-1-((S)-1-phenylethyl)aziridine (59.8 mg, 0.2 mmol, 1 equiv.) and *N*-benzylmaleimide (44.9 mg, 0.24 mmol, 1.2 equiv.). The reaction outcome is independent of which diastereoisomer of the starting aziridine is used. The product was obtained with 60:40 dr based on ^{1}H NMR analysis of the crude reaction mixture and the two diastereomers could be separated by flash column chromatography. The absolute configuration of the major diastereomer is assigned based on single-crystal X-ray diffraction and by an unchanging stereocentre in the synthetic procedure (vide infra).

Major diastereomer: the major diastereomer was obtained in 49% yield (47.6 mg, 0.098 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 90:10). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.24 (m, 8H), 7.18 (dd, *J* = 5.2, 1.9 Hz, 4H), 7.14 – 7.05 (m, 6H), 6.96 – 6.87 (m, 2H), 4.91 (s, 1H), 4.87 (d, *J* = 9.9 Hz, 1H), 4.49 (d, *J* = 14.0 Hz, 1H), 4.38 (d, *J* = 13.9 Hz, 1H), 3.88 (dd, *J* = 9.9, 8.3 Hz, 1H), 3.67 (q, *J* = 7.1 Hz, 1H), 3.21 (d, *J* = 8.2 Hz, 1H), 0.84 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.0, 175.5, 144.4, 141.8, 140.5, 135.8, 129.5, 128.7, 128.6, 128.3, 128.2, 128.0, 127.8, 127.8, 127.3, 126.7, 67.0, 67.0, 58.6, 53.2, 51.4, 42.6, 24.0.

Minor diastereomer: the minor diastereomer was obtained in 33% yield (32.1 mg, 0.066 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 90:10). $[\alpha]_D^{25}$= -7.51 (c = 0.71, $CHCl_3$).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 – 7.50 (m, 2H), 7.49 – 7.26 (m, 8H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 4H), 7.06 – 6.94 (m, 4H), 4.92 (d, *J* = 9.1 Hz, 1H), 4.68 (d, *J* = 13.7 Hz, 1H), 4.62 – 4.52 (m, 2H), 3.88 – 3.77 (m, 2H), 3.23 (d, *J* = 7.9 Hz, 1H), 0.51 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.0, 175.8, 142.8, 141.8, 136.8, 136.2, 129.9, 128.7, 128.7, 128.6, 128.5, 128.3, 128.2, 128.2, 128.0, 127.7, 127.0, 64.8, 63.6, 52.3, 52.2, 51.0, 42.8, 11.1.

***anti*-2-benzyl-5-cyclohexyl-4,6-diphenyltetrahydropyrrolo[3,4-*c*]pyrrole-1,3(2*H*,3a*H*)-dione**

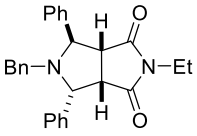


17

According to General procedure D, the product was obtained starting from *anti*-1-cyclohexyl-2,3-diphenylaziridine (45.5 mg, 0.2 mmol, 1 equiv.) and *N*-benzylmaleimide (44.9 mg, 0.24 mmol, 1.2 equiv.) in 57% yield (52.8 mg, 0.114 mmol) after filtering the crude reaction mixture and washing the resulting solid with hexane. The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.28 (m, 10H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.4

Hz, 2H), 7.00 (d, *J* = 7.2 Hz, 2H), 5.04 (s, 1H), 5.00 (d, *J* = 9.6 Hz, 1H), 4.54 – 4.38 (m, 2H), 3.80 (dd, *J* = 9.5, 8.2 Hz, 1H), 3.22 (d, *J* = 8.1 Hz, 1H), 2.40 (tt, *J* = 11.8, 3.1 Hz, 1H), 1.60 – 1.51 (m, 2H), 1.44 (d, *J* = 12.8 Hz, 1H), 1.30 (ddd, *J* = 20.0, 9.9, 6.6 Hz, 3H), 1.00 – 0.86 (m, 1H), 0.77 – 0.57 (m, 2H), 0.27 (qd, *J* = 12.3, 3.1 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.4, 175.8, 143.8, 138.8, 135.9, 129.5, 128.9, 128.6, 128.4, 128.1, 128.05, 128.01, 128.97, 127.9, 65.3, 65.0, 56.4, 53.4, 50.9, 42.7, 32.3, 28.7, 26.5, 26.0, 25.8 ppm. **HRMS (ESI+):** Calculated for $C_{31}H_{33}N_2O_2^+$ $[M+H]^+$: 465.2537 *m/z*. Found: 465.2574 *m/z*.

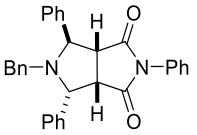
anti-5-benzyl-2-ethyl-4,6-diphenyltetrahydropyrrolo[3,4-*c*]pyrrole-1,3(2*H*,3a*H*)-dione



18

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and N-ethylmaleimide (30.0 mg, 0.24 mmol, 1.2 equiv.) in 53% yield (43.5 mg, 0.106 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.22 (m, 11H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.06 – 7.00 (m, 2H), 4.86 (s, 1H), 4.50 (d, *J* = 9.2 Hz, 1H), 3.85 – 3.73 (m, 1H), 3.60 (d, *J* = 15.7 Hz, 1H), 3.60 – 3.47 (m, 2H), 3.43 (d, *J* = 7.9 Hz, 1H), 2.90 (d, *J* = 14.9 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.2, 175.9, 138.5, 137.4, 136.8, 128.9, 128.7, 128.65, 128.59, 128.5, 128.2, 128.0, 127.7, 127.0, 67.1, 64.70, 51.1, 50.9, 50.6, 34.2, 13.4 ppm. **HRMS (ESI+):** Calculated for $C_{27}H_{27}N_2O_2^+$ $[M+H]^+$: 411.2067 *m/z*. Found: 411.2091 *m/z*.

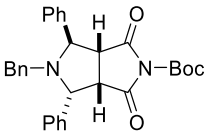
anti-5-benzyl-2,4,6-triphenyltetrahydropyrrolo[3,4-*c*]pyrrole-1,3(2*H*,3a*H*)-dione



19

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and N-phenylmaleimide (41.6 mg, 0.24 mmol, 1.2 equiv.) in 81% yield (74.3 mg, 0.162 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 – 7.42 (m, 4H), 7.43 – 7.27 (m, 9H), 7.28 – 7.18 (m, 5H), 7.07 (d, *J* = 6.1 Hz, 2H), 4.99 (s, 1H), 4.60 (d, *J* = 9.4 Hz, 1H), 4.02 – 3.95 (m, 1H), 3.66 (d, *J* = 15.0 Hz, 1H), 3.62 (d, *J* = 8.2 Hz, 2H), 2.97 (d, *J* = 14.8 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.3, 174.9, 138.4, 137.5, 136.8, 132.1, 129.2, 128.9, 128.8, 128.70, 128.67, 128.66, 128.5, 128.3, 127.8, 127.1, 126.2, 67.6, 65.0, 51.6, 50.9, 50.8 ppm. **HRMS (ESI+):** Calculated for $C_{31}H_{27}N_2O_2^+$ $[M+H]^+$: 459.2067 *m/z*. Found: 459.2109 *m/z*.

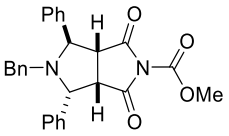
anti-tert-butyl 5-benzyl-1,3-dioxo-4,6-diphenylhexahydropyrrolo[3,4-*c*]pyrrole-2(1*H*)-carboxylate



20

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and *N*-Boc-maleimide (49.3 mg, 0.24 mmol, 1.2 equiv.) in 62% yield (59.8 mg, 0.124 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.26 (m, 11H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 4.90 (s, 1H), 4.49 (d, *J* = 9.4 Hz, 1H), 3.85 (t, *J* = 8.7 Hz, 1H), 3.59 (d, *J* = 14.7 Hz, 1H), 3.49 (d, *J* = 8.0 Hz, 1H), 2.90 (d, *J* = 14.7 Hz, 1H), 1.57 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.4, 171.8, 146.4, 138.3, 137.0, 136.2, 128.9, 128.8, 128.70 (3C), 128.4, 128.1, 127.8, 127.1, 86.2, 67.8, 65.2, 51.43, 51.35, 50.7, 27.9 ppm. **HRMS (ESI+):** Calculated for $C_{30}H_{31}N_2O_4^+$ $[M+H]^+$: 483.2278 *m/z*. Found: 483.2298 *m/z*.

anti-methyl 5-benzyl-1,3-dioxo-4,6-diphenylhexahydropyrrolo[3,4-*c*]pyrrole-2(1*H*)-carboxylate

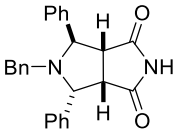


21

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and *N*-methoxycarbonylmaleimide (37.2 mg, 0.24 mmol, 1.2 equiv.) in 64% yield (56.0 mg, 0.127 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20 to 70:30). The relative configuration is assigned in analogy

with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.27 (m, 11H), 7.19 (d, *J* = 7.5 Hz, 2H), 6.99 (dd, *J* = 7.2, 2.0 Hz, 2H), 4.91 (s, 1H), 4.51 (d, *J* = 9.5 Hz, 1H), 3.98 (s, 3H), 3.93 – 3.86 (m, 1H), 3.59 (d, *J* = 14.8 Hz, 1H), 3.54 (d, *J* = 8.2 Hz, 1H), 2.89 (d, *J* = 14.7 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.0, 171.5, 148.8, 138.2, 136.7, 136.0, 129.0, 128.9, 128.8, 128.74, 128.72, 128.5, 128.0, 127.8, 127.2, 67.8, 65.3, 55.2, 51.5, 51.3, 50.8 ppm. **HRMS (ESI+):** Calculated for $C_{27}H_{25}N_2O_4^+$ $[M+H]^+$: 441.1809 *m/z*. Found: 441.1811 *m/z*.

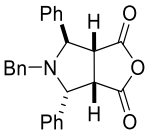
***anti*-5-benzyl-4,6-diphenyltetrahydropyrrolo[3,4-*c*]pyrrole-1,3(2*H*,3a*H*)-dione**



22

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and maleimide (23.3 mg, 0.24 mmol, 1.2 equiv.) in 80% yield (61.2 mg, 0.160 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.31 (td, *J* = 15.6, 14.5, 7.0 Hz, 8H), 7.23 – 7.17 (m, 3H), 6.97 (dd, *J* = 7.5, 1.7 Hz, 2H), 4.81 (s, 1H), 4.47 (d, *J* = 9.3 Hz, 1H), 3.86 – 3.72 (m, 1H), 3.57 (d, *J* = 14.8 Hz, 1H), 3.48 (d, *J* = 8.0 Hz, 1H), 2.86 (d, *J* = 14.7 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.4, 176.3, 138.4, 137.3, 136.5, 128.85, 128.84, 128.65, 128.62, 128.57, 128.3, 128.0, 127.8, 127.1, 67.2, 64.6, 52.27, 52.26, 50.6 ppm. **HRMS (ESI+):** Calculated for $C_{25}H_{23}N_2O_2^+$ $[M+H]^+$: 383.1754 *m/z*. Found: 383.1790 *m/z*.

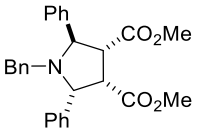
***anti*-5-benzyl-4,6-diphenyltetrahydro-1H-furo[3,4-c]pyrrole-1,3(3a*H*)-dione**



23

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and maleic anhydride (23.5 mg, 0.24 mmol, 1.2 equiv.) in 58% yield (44.3 mg, 0.116 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.27 (m, 11H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.03 – 6.92 (m, 2H), 4.91 (s, 1H), 4.54 (d, *J* = 9.2 Hz, 1H), 4.06 (t, *J* = 8.8 Hz, 1H), 3.76 (d, *J* = 8.4 Hz, 1H), 3.61 (d, *J* = 14.8 Hz, 1H), 2.88 (d, *J* = 14.7 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 169.6, 137.9, 136.2, 135.1, 129.22, 129.15, 128.85, 128.82, 128.77, 128.75, 127.8, 127.3, 67.8, 65.9, 51.8, 51.4, 50.5 ppm. **HRMS (ESI+):** Calculated for $C_{25}H_{22}NO_3^+$ $[M+H]^+$: 384.1594 *m/z*. Found: 384.1583 *m/z*.

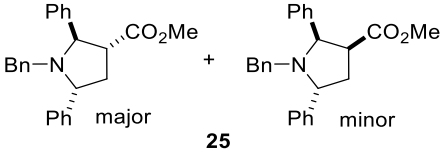
***anti*-dimethyl-1-benzyl-2,5-diphenylpyrrolidine-3,4-dicarboxylate**



24

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and dimethyl maleate (34.6 mg, 0.24 mmol, 1.2 equiv.) in 71% yield (61.0 mg, 0.142 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). The relative configuration is assigned according to a literature report.[3] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.22 – 7.11 (m, 5H), 7.03 (d, *J* = 7.0 Hz, 2H), 5.04 (d, *J* = 7.7 Hz, 1H), 4.85 (d, *J* = 6.8 Hz, 1H), 3.82 (dd, *J* = 8.3, 6.8 Hz, 1H), 3.67 (d, *J* = 14.6 Hz, 1H), 3.62 (s, 3H), 3.47 (t, *J* = 8.2 Hz, 1H), 3.26 (s, 3H), 3.14 (d, *J* = 14.6 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.1, 171.5, 141.6, 139.1, 138.4, 128.9, 128.3, 128.26, 128.25, 128.08, 128.06, 128.0, 127.5, 126.5, 69.5, 65.3, 54.2, 52.6, 52.1, 51.5, 50.4 ppm. **HRMS (ESI+):** Calculated for $C_{27}H_{28}NO_4^+$ $[M+H]^+$: 430.2013 *m/z*. Found: 430.2078 *m/z*.

***anti*-methyl 1-benzyl-2,5-diphenylpyrrolidine-3-carboxylate**



25

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and methyl acrylate (20.7 mg, 0.24 mmol, 1.2 equiv.) in 82% yield (60.9 mg, 0.164 mmol) after purification by

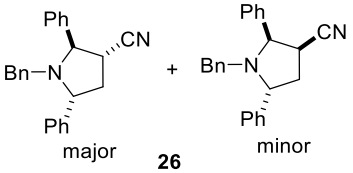
flash column chromatography on silica gel (hexane:EtOAc 90:10). The product was obtained with 78:22 dr based on ^{1}H NMR analysis of the crude reaction mixture and was isolated as the mixture of the two diastereomers. The relative configuration is assigned based on a literature report.[9]

Major diastereomer. The spectral data matched with those reported in the literature.[9] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.17 (m, 13H), 7.11 (d, *J* = 7.1 Hz, 2H), 4.60 (d, *J* = 8.4 Hz, 1H), 4.48 (dd, *J* = 9.2, 3.7 Hz, 1H), 3.79 (q, *J* = 9.2 Hz, 1H), 3.64 (d, *J* = 13.7 Hz, 1H), 3.25 (s, 3H), 3.16 (d, *J* = 47.5 Hz, 1H), 3.16 – 3.11 (m, 1H), 2.12 (ddd, *J* = 13.4, 9.5, 3.8 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 144.3, 139.4, 138.9, 129.0, 128.61, 128.56, 128.11, 128.05, 127.7, 127.6, 127.3, 126.7, 67.3, 65.4, 51.40, 51.36, 47.91, 35.13 ppm.

Minor diastereomer. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.17 (m, 13H), 7.14 (d, *J* = 7.4 Hz, 2H), 4.62 (d, *J* = 6.4 Hz, 1H), 4.35 (t, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 3.62 (d, *J* = 9.8 Hz, 1H), 3.54 (d, *J* = 14.5 Hz, 1H), 2.99 (d, *J* = 14.4 Hz, 1H), 2.90 – 2.80 (m, 1H), 2.42 (dt, *J* = 13.8, 6.9 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.1, 142.8, 141.0, 139.6, 130.6, 128.5, 128.44, 128.39, 128.2, 128.1, 127.6, 127.4, 126.5, 68.0, 65.1, 52.0, 50.8, 50.5, 37.5 ppm.

HRMS (ESI+): Calculated for $C_{25}H_{26}NO_2^+$ $[M+H]^+$: 372.1998 *m/z*. Found: 372.1998 *m/z*.

***anti*-1-benzyl-2,5-diphenylpyrrolidine-3-carbonitrile**



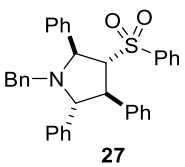
26

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and acrylonitrile (12.7 mg, 0.24 mmol, 1.2 equiv.). The product was obtained with 75:25 dr based on ^{1}H NMR analysis of the crude reaction mixture and the two diastereomers could be separated by flash column chromatography. The relative configuration is assigned in analogy with **25**.

Major diastereomer: the major diastereomer was obtained in 49% yield (33.6 mg, 0.098 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.20 (m, 13H), 7.06 (d, *J* = 6.4 Hz, 2H), 4.54 – 4.46 (m, 2H), 3.71 – 3.61 (m, 2H), 3.23 (d, *J* = 13.8 Hz, 1H), 2.91 (dt, *J* = 13.5, 8.8 Hz, 1H), 2.41 (ddd, *J* = 13.6, 9.4, 4.3 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.6, 138.7, 137.3, 128.81, 128.76, 128.7, 128.6, 128.5, 128.3, 127.8 (2C), 127.1, 120.1, 66.8, 64.2, 51.1, 37.8, 33.8 ppm. **HRMS (ESI+):** Calculated for $C_{24}H_{23}N_2^+$ $[M+H]^+$: 339.1856 *m/z*. Found: 339.1876 *m/z*.

Minor diastereomer: the major diastereomer was obtained in 24% yield (16.5 mg, 0.048 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.19 (m, 13H), 7.13 (d, *J* = 7.4 Hz, 2H), 4.50 (d, *J* = 5.5 Hz, 1H), 4.35 (dd, *J* = 8.1, 5.6 Hz, 1H), 3.57 (d, *J* = 14.3 Hz, 1H), 3.17 (dt, *J* = 10.1, 6.0 Hz, 1H), 3.05 – 2.93 (m, 2H), 2.45 – 2.36 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.2, 138.8, 138.7, 129.0, 128.7, 128.6, 128.5, 128.3, 128.2, 128.99, 127.95, 127.0, 122.0, 69.1, 64.3, 50.3, 37.6, 35.8 ppm. **HRMS (ESI+):** Calculated for $C_{24}H_{23}N_2^+$ $[M+H]^+$: 339.1856 *m/z*. Found: 339.1876 *m/z*.

***anti*-1-benzyl-2,3,5-triphenyl-4-(phenylsulfonyl)pyrrolidine**

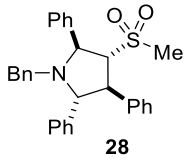


27

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and *anti*-(2-(phenylsulfonyl)vinyl)benzene (58.6 mg, 0.24 mmol, 1.2 equiv.) in 77% yield (81.6 mg, 0.154 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). The relative configuration is assigned based on single-crystal X-ray diffraction (vide infra). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 – 7.65 (m, 2H), 7.48 (td, *J* = 5.1, 3.1 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.27 (m, 6H), 7.25 – 7.17 (m, 6H), 7.15 – 7.09 (m, 5H), 7.08 – 7.04 (m, 2H), 7.01 – 6.97 (m, 2H), 4.95 (d, *J* = 4.8 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.18 (dd, *J* = 8.5, 4.9 Hz, 1H), 3.86 (t, *J* = 8.1 Hz, 1H), 3.57 (d, *J* = 14.2 Hz, 1H), 3.10 (d, *J* = 14.2 Hz, 1H) ppm. **^{13}C NMR (101 MHz,**

$CDCl_3$) δ 140.9, 140.3, 139.6, 138.4, 138.3, 133.6, 129.0, 128.8, 128.69, 128.67, 128.59, 128.57, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.0, 126.8, 76.7, 75.7, 64.8, 55.2, 50.3 ppm. **HRMS (ESI+):** Calculated for $C_{35}H_{32}NO_2S^+$ $[M+H]^+$: 530.2148 *m/z*. Found: 530.2159 *m/z*.

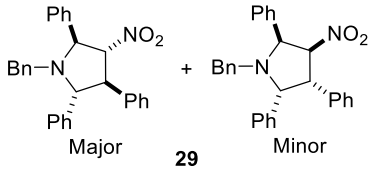
***anti*-1-benzyl-3-(methylsulfonyl)-2,4,5-triphenylpyrrolidine**



28

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and *trans*-(2-(methylsulfonyl)vinyl)benzene (43.7 mg, 0.24 mmol, 1.2 equiv.) in 80% yield (74.8 mg, 0.160 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). The relative configuration is assigned in analogy with **27**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.14 (m, 18H), 7.07 (d, *J* = 7.1 Hz, 2H), 4.95 (d, *J* = 5.6 Hz, 1H), 4.52 (d, *J* = 7.3 Hz, 1H), 4.04 (dd, *J* = 8.5, 5.7 Hz, 1H), 3.93 (t, *J* = 8.1 Hz, 1H), 3.60 (d, *J* = 14.1 Hz, 1H), 3.10 (d, *J* = 14.1 Hz, 1H), 2.45 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 140.8, 139.90, 139.88, 138.3, 129.1, 128.9, 128.6, 128.5, 128.24, 128.16, 127.9, 127.7, 126.9, 76.1, 75.4, 64.6, 54.8, 50.4, 40.9 ppm. **HRMS (ESI+):** Calculated for $C_{30}H_{30}NO_2S^+$ $[M+H]^+$: 468.1992 *m/z*. Found: 468.2006 *m/z*.

***anti*-1-benzyl-3-nitro-2,4,5-triphenylpyrrolidine**



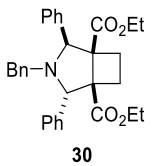
29

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and *trans*-β-nitrostyrene (35.8 mg, 0.24 mmol, 1.2 equiv.). The product was obtained with 72:28 dr based on ^{1}H NMR analysis of the crude reaction mixture and the two diastereomers could be separated by flash column chromatography with a minor impurity. The relative configuration is assigned in analogy with **27**.

Major diastereomer: the major diastereomer was obtained in 49% yield (42.8 mg, 0.098 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.53 (m, 2H), 7.47 – 7.37 (m, 3H), 7.28 – 7.25 (m, 3H), 7.23 – 7.19 (m, 3H), 7.10 – 7.03 (m, 5H), 6.94 – 6.89 (m, 2H), 6.89 – 6.83 (m, 2H), 6.02 (dd, J = 11.0, 9.5 Hz, 1H), 5.18 (d, J = 9.4 Hz, 1H), 4.89 (dd, J = 11.1, 8.2 Hz, 1H), 4.78 (d, J = 8.2 Hz, 1H), 3.79 (d, J = 13.3 Hz, 1H), 3.62 (d, J = 13.2 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.0, 137.9, 136.9, 135.3, 129.03, 129.00, 128.95, 128.9, 128.6, 128.33, 128.29, 128.28, 128.2, 127.5, 127.3, 127.2, 91.2, 68.6, 68.5, 51.8, 50.9 ppm. **HRMS (ESI+):** Calculated for $C_{29}H_{27}N_2O_2^+$ $[M+H]^+$: 435.2067 *m/z*. Found: 435.2076 *m/z*.

Minor diastereomer: the minor diastereomer was obtained in 15% yield (12.8 mg, 0.030 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.26 (m, 15H), 7.23 (d, J = 7.3 Hz, 2H), 7.14 (d, J = 6.7 Hz, 1H), 7.07 (d, J = 7.1 Hz, 2H), 5.30 – 5.22 (m, 1H), 4.96 (d, J = 6.5 Hz, 1H), 4.53 (d, J = 6.8 Hz, 1H), 4.25 – 4.17 (m, 1H), 3.62 (d, J = 14.2 Hz, 1H), 3.10 (d, J = 14.2 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.8, 139.2, 138.6, 138.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.4, 128.3, 128.23, 128.20, 127.9, 127.6, 127.0, 98.3, 72.6, 70.4, 57.9, 50.5 ppm. **HRMS (ESI+):** Calculated for $C_{29}H_{27}N_2O_2^+$ $[M+H]^+$: 435.2067*m/z*. Found: 435.2076 *m/z*.

***anti*-dimethyl 3-benzyl-2,4-diphenyl-3-azabicyclo[3.2.0]heptane-1,5-dicarboxylate**

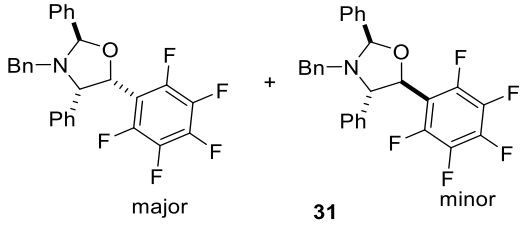


30

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and diethyl cyclobut-1-ene-1,2-dicarboxylate (47.6 mg, 0.24 mmol, 1.2 equiv.) in 57% yield (51.9 mg, 0.114 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 7H), 7.30 – 7.21 (m, 6H), 5.27 (s, 1H), 4.37 (dddd, *J* = 17.9, 10.8, 7.1, 3.6 Hz, 2H), 4.30 (s, 1H), 3.79 (d, *J* = 14.6 Hz, 1H), 3.68 (ddq, *J* = 42.5, 10.8, 6.9 Hz, 2H), 2.89

(d, *J* = 14.7 Hz, 1H), 2.58 – 2.38 (m, 3H), 2.11 – 2.01 (m, 1H), 1.41 (t, *J* = 7.1 Hz, 3H), 0.64 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.8, 172.0, 139.4, 137.6, 137.4, 128.5, 128.42, 128.40, 128.2, 127.9, 127.7, 127.5, 126.8, 114.3, 72.6, 70.9, 61.5, 60.5, 60.4, 57.3, 50.8, 29.4, 18.4, 14.4, 13.5 ppm. **HRMS (ESI+):** Calculated for $C_{31}H_{34}NO_4^+$ $[M+H]^+$: 484.2482 *m/z*. Found: 484.2453 *m/z*.

***anti*-3-benzyl-5-(perfluorophenyl)-2,4-diphenyloxazolidine**



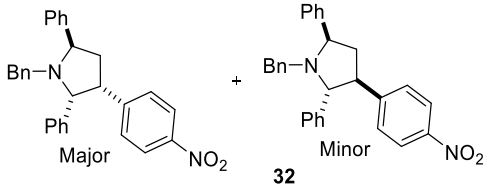
31

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and pentafluorobenzaldehyde (47.0 mg, 0.24 mmol, 1.2 equiv.). The product was obtained with 67:33 dr based on ^{1}H NMR analysis of the crude reaction mixture and the two diastereomers could be separated by crystallization. The relative configuration is assigned based on single-crystal X-ray diffraction of the major diastereomer (vide infra).

Major diastereomer: the major diastereomer was obtained as colourless crystals in 45% yield (43.3 mg, 0.090 mmol) after freezing the crude reaction mixture at -20°C for 72 h. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.35 – 7.28 (m, 4H), 7.28 – 7.16 (m, 8H), 6.12 (d, *J* = 6.9 Hz, 1H), 6.07 (s, 1H), 4.81 (d, *J* = 6.9 Hz, 1H), 3.76 (d, *J* = 14.6 Hz, 1H), 3.12 (d, *J* = 14.6 Hz, 1H) ppm. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -141.48 (dd, *J* = 22.0, 7.4 Hz, 2H), -155.28 (t, *J* = 21.2 Hz, 1H), -163.06 (td, *J* = 21.8, 7.6 Hz, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.8, 143.3, 141.5, 138.5, 138.3, 135.9, 129.0, 128.53, 128.46, 128.37, 128.3, 128.0 (2C), 127.9, 127.1, 114.0, 94.8, 76.9, 67.8, 50.2 ppm. (*Note: due to the numerous C-F couplings, a thorough analysis of the signal multiplicities in the ^{13}C NMR spectrum was not possible*) **HRMS (ESI+):** Calculated for $C_{28}H_{21}F_5NO^+$ $[M+H]^+$: 482.1538 *m/z*. Found: 482.1551 *m/z*.

Minor diastereomer: The compound could not be fully purified by flash column chromatography on silica gel (hexane:EtOAc 95:5) and was obtained in 17% yield (16.8 mg, 0.035 mmol) containing 26% of the major diastereomer as the only impurity. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 6.3 Hz, 2H), 7.43 – 7.38 (m, 5H), 7.37 – 7.33 (m, 3H), 7.16 – 7.11 (m, 3H), 6.97 – 6.89 (m, 2H), 5.43 (s, 1H), 5.36 (d, *J* = 8.8 Hz, 1H), 4.13 (d, *J* = 8.8 Hz, 1H), 3.71 (s, 2H) ppm. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -141.18 (dd, *J* = 22.5, 8.0 Hz, 2F), -153.76 (t, *J* = 21.2 Hz, 1F), -161.90 (td, *J* = 22.2, 8.0 Hz, 2F) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.6, 144.1, 142.5, 138.7, 136.4, 134.8, 129.9, 129.6, 129.1, 128.8, 128.7, 128.6, 128.1, 128.0, 127.3, 112.9, 95.9, 77.6, 70.7, 51.8 ppm. (*Note: due to the numerous C-F couplings, a thorough analysis of the signal multiplicities in the ^{13}C NMR spectrum was not possible*) **HRMS (ESI+):** Calculated for $C_{28}H_{21}F_5NO^+$ $[M+H]^+$: 482.1538 *m/z*. Found: 482.1551 *m/z*.

***anti*-1-benzyl-3-(4-nitrophenyl)-2,5-diphenylpyrrolidine**

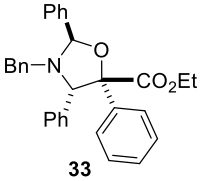


32

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and 4-nitrostyrene (35.8 mg, 0.24 mmol, 1.2 equiv.) in 76% yield (66.0 mg, 0.152 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). The product was obtained with 77:23 dr based on 1H NMR analysis of the crude reaction mixture and was isolated as the mixture of the two diastereomers. The relative configuration is assigned in analogy with **31**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.7 Hz, 2H, minor *di*), 7.91 (d, *J* = 8.8 Hz, 2H, major *di*), 7.50 (d, *J* = 7.1 Hz, major and minor *di*), 7.46 – 7.37 (m, major and minor *di*), 7.38 – 7.28 (m, major and minor *di*), 7.23 (t, *J* = 7.3 Hz, major and minor *di*), 7.19 – 7.11 (m, major and minor *di*), 7.10 – 7.03 (m, major and minor *di*), 6.91 (d, *J* = 5.9 Hz, 2H, major *di*), 4.70 (dd, *J* = 9.6, 2.7 Hz, 1H, major *di*), 4.62 (d, *J* = 7.1 Hz, 1H, major *di*), 4.52 (t, *J* = 7.7 Hz, 1H, minor *di*), 4.36 (d, *J* = 5.6 Hz, 1H, minor *di*), 4.14 (q, *J* = 7.9 Hz, 1H, major *di*), 3.78 (d, *J* = 13.5 Hz, 1H, major *di*), 3.70 – 3.59 (m, 2H, minor *di*), 3.51 (d, *J* = 13.5 Hz, 1H, major *di*), 3.11 (d, *J*

= 14.1 Hz, 1H, minor *di*), 3.08 – 2.95 (m, 1H, major and minor *di*), 2.33 (ddd, *J* = 13.0, 8.1, 3.0 Hz, 1H, major *di*), 2.22 (dt, *J* = 13.3, 8.6 Hz, 1H, minor *di*) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.7 (minor *di*), 148.73 (major *di*), 146.69 (minor *di*), 146.3 (major *di*), 145.1 (major *di*), 143.2 (minor *di*), 141.0 (minor *di*), 139.44 (minor *di*), 139.42 (major *di*), 138.7 (major *di*), 129.4 (major *di*), 128.9 (major *di*), 128.78 (major *di*), 128.77 (minor *di*), 128.65 (minor *di*), 128.57 (major *di*), 128.4 (minor *di*), 128.34 (minor *di*), 128.28 (minor *di*), 128.14 (major *di*), 128.09 (major *di*), 128.07 (minor *di*), 127.71 (minor *di*), 127.69 (major *di*), 127.6 (minor *di*), 127.3 (major *di*), 127.2 (major *di*), 126.9 (minor *di*), 126.8 (major *di*), 126.6 (minor *di*), 123.9 (minor *di*), 122.9 (major *di*), 73.2 (minor *di*), 70.2 (major *di*), 66.4 (minor *di*), 65.7 (major *di*), 52.3 (minor *di*), 51.7 (major *di*), 50.9 (minor *di*), 48.3 (major *di*), 44.1 (minor *di*), 38.6 (major *di*) ppm. **HRMS (ESI+):** Calculated for $C_{29}H_{27}N_2O_2^+$ $[M+H]^+$: 435.2067 *m/z*. Found: 435.2076 *m/z*.

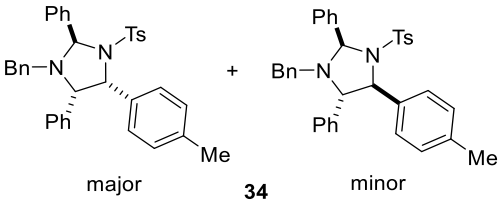
***anti*-3-benzyl-5-ethoxy-2,4,5-triphenyloxazolidine**



33

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and ethyl benzoylformate (42.8 mg, 0.24 mmol, 1.2 equiv.). The product was obtained with 88:12 dr and in 44% yield based on ^{1}H NMR analysis of the crude reaction mixture but coeluted with the unreacted ethyl benzoylformate and could not be purified by flash column chromatography. The major diastereomer could be isolated in 15% yield (13.5 mg, 0.031 mmol) after freezing the crude reaction mixture at -20°C for 72 h, while the minor diastereomer could not be isolated. The relative configuration is assigned in analogy with **31**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 – 7.61 (m, 2H), 7.40 – 7.34 (m, 6H), 7.34 – 7.30 (m, 4H), 7.32 – 7.21 (m, 6H), 7.04 – 6.97 (m, 2H), 5.85 (s, 1H), 4.95 (s, 1H), 3.83 – 3.63 (m, 2H), 3.40 (d, *J* = 14.1 Hz, 1H), 2.99 (d, *J* = 14.1 Hz, 1H), 0.69 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.4, 141.4, 138.14, 138.08, 135.8, 129.6, 129.4, 129.3, 128.4, 128.32, 128.26, 128.20, 128.16, 128.1, 128.0, 127.1, 126.7, 95.8, 89.6, 70.4, 61.1, 49.0, 13.5 ppm. **HRMS (ESI+):** Calculated for $C_{31}H_{30}NO_3^+$ $[M+H]^+$: 464.2220 *m/z*. Found: 464.2263 *m/z*.

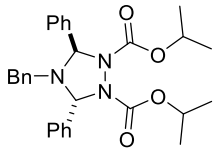
***anti*-1-benzyl-2,5-diphenyl-4-(p-tolyl)-3-tosylimidazolidine**



34

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and 4-methyl-*N*-(4-methylbenzylidene) benzenesulfonamide (62.2 mg, 0.24 mmol, 1.2 equiv.) in 79% yield (88.6 mg, 0.158 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 90:10). The product was obtained with 62:38 dr based on ^{1}H NMR analysis of the crude reaction mixture and was isolated as the mixture of the two diastereomers. The relative configuration is assigned in analogy with **31**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 8.2 Hz, 2H, minor *di*), 7.37 – 6.86 (m, major and minor *di*), 6.82 – 6.73 (m, 2H, major *di*), 5.95 (s, 1H, major *di*), 5.71 (s, 1H, minor *di*), 5.25 (d, *J* = 6.5 Hz, 1H, major *di*), 4.93 (d, *J* = 6.3 Hz, 2H, major *di*), 4.91 (d, *J* = 6.8 Hz, 1H, minor *di*), 4.33 (d, *J* = 7.3 Hz, 1H, minor *di*), 3.64 (d, *J* = 14.9 Hz, 1H, major *di*), 3.35 (d, *J* = 14.1 Hz, 1H, minor *di*), 2.91 (d, *J* = 14.1 Hz, 1H, minor *di*), 2.72 (d, *J* = 14.9 Hz, 1H, major *di*), 2.50 (s, 3H, minor *di*), 2.33 (s, 3H, major *di*), 2.25 (s, 3H, minor *di*), 2.17 (s, 3H, major *di*) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.6, 142.4, 138.54, 138.51, 138.2, 137.94, 137.90, 137.3, 137.0, 136.6, 136.2, 135.6, 135.3, 135.1, 129.6, 129.4, 129.1, 129.0, 128.9, 128.83, 128.79, 128.51, 128.49, 128.41, 128.38, 128.34, 128.30, 128.29, 128.2, 128.1, 128.0, 127.9, 127.84, 127.81, 127.7, 127.4, 127.3, 127.22, 127.15, 127.0, 80.3, 79.0, 73.0, 70.0, 69.3, 68.0, 49.7, 31.1, 21.8, 21.5, 21.3, 21.2 ppm. **HRMS (ESI+):** Calculated for $C_{36}H_{34}KN_2O_2S^+$ $[M+K]^+$: 597.1973 *m/z*. Found: 597.1942 *m/z*.

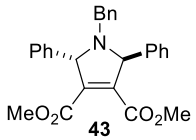
***anti*-diisopropyl 4-benzyl-3,5-diphenyl-1,2,4-triazolidine-1,2-dicarboxylate**



35

According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and diisopropyl azodicarboxylate (48.5 mg, 0.24 mmol, 1.2 equiv.) in 48% yield (46.8 mg, 0.096 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 7.0 Hz, 4H), 7.38 – 7.27 (m, 10H), 7.24 – 7.18 (m, 1H), 5.84 (s, 2H), 5.05 (hept, *J* = 6.2 Hz, 2H), 3.34 (d, *J* = 13.4 Hz, 1H), 3.20 (d, *J* = 13.5 Hz, 1H), 1.31 (d, *J* = 6.2 Hz, 6H), 1.27 (d, *J* = 6.2 Hz, 6H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.7 (2C), 138.4, 136.1 (2C), 129.0, 128.60, 128.56 (2C), 128.55 (2C), 127.7 (2C), 127.5, 80.6 (2C), 70.4 (2C), 52.6, 22.12, 22.11 ppm. **HRMS (ESI+):** Calculated for $C_{29}H_{34}N_3O_4^+$ $[M+H]^+$: 488.2544 *m/z*. Found: 488.2590 *m/z*.

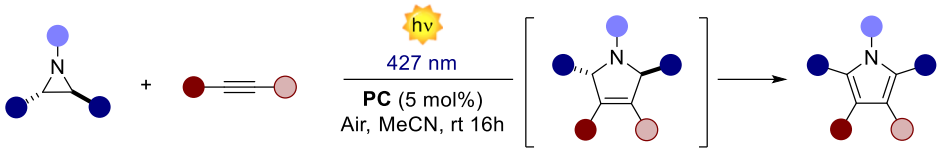
***anti*-dimethyl 1-benzyl-2,5-diphenyl-2,5-dihydro-1H-pyrrole-3,4-dicarboxylate**



43

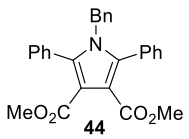
According to General procedure D, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol, 1.2 equiv.) in 72% yield (61.6 mg, 0.144 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20 to 75:25). The relative configuration is assigned in analogy with **13**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.30 (m, 6H), 7.27 (dd, *J* = 5.9, 1.8 Hz, 4H), 7.21 (d, *J* = 7.1 Hz, 3H), 6.99 (d, *J* = 6.0 Hz, 2H), 5.33 (s, 2H), 3.67 (d, *J* = 13.7 Hz, 1H), 3.62 (s, 6H), 3.21 (d, *J* = 14.0 Hz, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.9, 140.5, 138.8, 137.9, 128.8, 128.5, 128.42, 128.37, 128.1, 126.9, 72.5, 52.2, 50.3 ppm. **HRMS (ESI+):** Calculated for $C_{27}H_{26}NO_4^+$ $[M+H]^+$: 428.1856 *m/z*. Found: 428.1838 *m/z*.

General procedure E, for pyrroles synthesis



An 8 mL vial was charged with a stirbar, the desired aziridine (0.2 mmol, 1 equiv.), 9,10-dicyanoanthracene (2.3 mg, 0.01 mmol, 0.05 equiv.) and the desired alkyne (0.24 mmol, 1.2 equiv.) if solid. Dry acetonitrile (4 mL, 0.05 M) was finally added. The desired alkyne (0.24 mmol, 1.2 equiv.) was added at this stage if liquid. The vial was closed with a screwcap equipped with a septum and a needle was inserted in the septum to ensure contact between the reaction mixture and the ambient atmosphere. The resulting mixture in the vial was irradiated under stirring for 16h with a Kessil 427 nm lamp set at 50% of its maximum output power according to the experimental setup shown in Section C. Trichloroethylene (18 µL, 0.2 mmol, 1 equiv.) was added as the internal standard and a sample was taken for ^{1}H NMR yield determination. The solvent was then evaporated under reduced pressure and the crude reaction mixture purified by flash column chromatography.

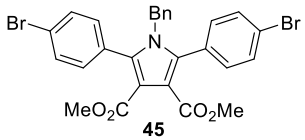
dimethyl 1-benzyl-2,5-diphenyl-1*H*-pyrrole-3,4-dicarboxylate



44

According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol, 1.2 equiv.) in 83% yield (70.6 mg, 0.166 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (200 MHz, $CDCl_3$)** δ 7.31 – 7.11 (m, 10H), 7.05 – 6.93 (m, 3H), 6.45 (dd, *J* = 6.6, 2.8 Hz, 2H), 4.81 (s, 2H), 3.57 (s, 6H) ppm. **^{13}C NMR (50 MHz, $CDCl_3$)** δ 165.4, 137.3, 137.2, 130.7, 130.7, 128.8, 128.4, 128.2, 127.4, 126.2, 115.0, 51.7, 48.6 ppm. **HRMS (ESI+):** Calculated for $C_{27}H_{24}NO_4^+$ $[M+H]^+$: 426.1700 *m/z*. Found: 426.1730 *m/z*.

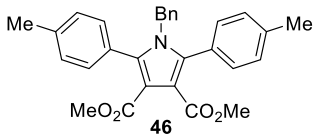
dimethyl 1-benzyl-2,5-bis(4-bromophenyl)-1*H*-pyrrole-3,4-dicarboxylate



45

According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-bis(4-bromophenyl)aziridine (88.6 mg, 0.2 mmol, 1 equiv.) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol, 1.2 equiv.) in 82% yield (95.7 mg, 0.164 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). *Two rotamers observed*. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.27 (m, 4H), 7.16 – 7.09 (m, 5H), 6.56 (dd, *J* = 6.6, 2.7 Hz, 2H), 4.88 (s, 2H), 3.67 (s, 3H), 3.66 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.4, 165.2, 137.5, 137.0, 136.0, 132.3, 131.5, 130.6, 130.5, 129.7, 129.0, 128.6, 128.3, 127.5, 126.1, 123.4, 115.2, 115.1, 51.8, 48.7 ppm. **HRMS (ESI+):** Calculated for $C_{27}H_{22}Br_2NO_4^+$ $[M+H]^+$: 581.9910 *m/z*. Found: 581.9910 *m/z*.

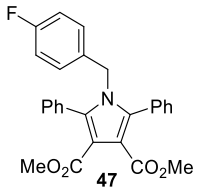
dimethyl 1-benzyl-2,5-di-*p*-tolyl-1*H*-pyrrole-3,4-dicarboxylate



46

According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-di-*p*-tolylaziridine (62.7 mg, 0.2 mmol, 1 equiv.) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol, 1.2 equiv.) in 95% yield (86.2 mg, 0.190 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.21 – 7.04 (m, 11H), 6.58 (dd, *J* = 6.8, 2.9 Hz, 2H), 4.90 (s, 2H), 3.67 (s, 6H), 2.34 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.6, 138.7, 137.5, 137.3, 130.6, 129.0, 128.4, 127.8, 127.3, 126.2, 114.8, 51.7, 48.5, 21.5 ppm. **HRMS (ESI+):** Calculated for $C_{29}H_{28}NO_4^+$ $[M+H]^+$: 454.2013 *m/z*. Found: 454.2010 *m/z*.

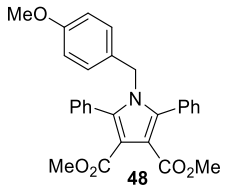
dimethyl 1-(4-fluorobenzyl)-2,5-diphenyl-1*H*-pyrrole-3,4-dicarboxylate



47

According to General procedure E, the product was obtained starting from *anti*-1-(4-fluorobenzyl)-2,3-diphenylaziridine (60.6 mg, 0.2 mmol, 1 equiv.) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol, 1.2 equiv.) in 56% yield (49.7 mg, 0.112 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.32 (m, 6H), 7.32 – 7.27 (m, 4H), 6.76 (t, *J* = 8.6 Hz, 2H), 6.47 (dd, *J* = 8.5, 5.3 Hz, 2H), 4.88 (s, 2H), 3.66 (s, 6H) ppm. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -114.80 (td, *J* = 8.7, 4.5 Hz) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.3, 162.0 (d, *J* = 246.2 Hz), 137.1, 132.8 (d, *J* = 3.2 Hz), 130.6, 128.9, 128.3, 128.0 (d, *J* = 8.0 Hz), 115.3 (d, *J* = 21.4 Hz), 115.0, 51.7, 47.9 ppm. **HRMS (ESI+):** Calculated for $C_{27}H_{22}FNNaO_4^+$ $[M+Na]^+$: 466.1425 *m/z*. Found: 466.1411 *m/z*.

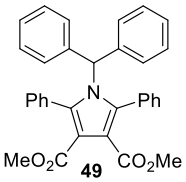
dimethyl 1-(4-methoxybenzyl)-2,5-diphenyl-1*H*-pyrrole-3,4-dicarboxylate



48

According to General procedure E, the product was obtained starting from *anti* -1-(4-methoxybenzyl)-2,3-diphenylaziridine (63.1 mg, 0.2 mmol, 1 equiv.) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol, 1.2 equiv.) in 81% yield (73.8 mg, 0.162 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.30 – 7.24 (m, 6H), 7.24 – 7.18 (m, 4H), 6.53 (d, *J* = 8.7 Hz, 2H), 6.35 (d, *J* = 8.7 Hz, 2H), 4.77 (s, 2H), 3.64 (s, 3H), 3.58 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.5, 158.9, 137.2, 130.9, 130.8, 129.3, 128.8, 128.3, 127.6, 114.9, 113.8, 55.3, 51.7, 48.1 ppm. **HRMS (ESI+):** Calculated for $C_{28}H_{26}NO_5^+$ $[M+H]^+$: 456.1805 *m/z*. Found: 456.1806 *m/z*.

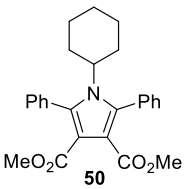
dimethyl 1-benzhydryl-2,5-diphenyl-1*H*-pyrrole-3,4-dicarboxylate



49

According to General procedure E, the product was obtained starting from *anti* -1-benzhydryl-2,3-diphenylaziridine (72.3 mg, 0.2 mmol, 1 equiv.) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol, 1.2 equiv.) in 57% yield (57.2 mg, 0.114 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 – 7.07 (m, 13H), 7.02 (d, *J* = 7.1 Hz, 4H), 6.83 – 6.72 (m, 4H), 6.53 (s, 1H), 3.60 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.4, 138.4, 137.4, 131.2, 131.0, 128.6, 128.4, 128.1, 127.8, 127.5, 115.5, 64.1, 51.6 ppm. **HRMS (ESI+):** Calculated for $C_{33}H_{28}NO_4^+$ $[M+H]^+$: 502.2013 *m/z*. Found: 502.2015 *m/z*.

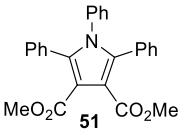
dimethyl 1-cyclohexyl-2,5-diphenyl-1*H*-pyrrole-3,4-dicarboxylate



50

According to General procedure E, the product was obtained starting from *anti* -1-cyclohexyl-2,3-diphenylaziridine (55.5 mg, 0.2 mmol, 1 equiv.) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol, 1.2 equiv.) in 93% yield (77.7 mg, 0.186 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.46 – 7.37 (m, 10H), 3.74 (ddt, *J* = 12.1, 7.4, 3.4 Hz, 1H), 3.59 (s, 6H), 1.71 (dd, *J* = 12.4, 3.6 Hz, 2H), 1.59 – 1.48 (m, 2H), 1.43 (dd, *J* = 12.4, 3.5 Hz, 2H), 1.38 – 1.32 (m, 1H), 0.96 – 0.79 (m, 2H), 0.72 – 0.54 (m, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.6, 136.6, 132.1, 131.4, 128.9, 128.0, 128.0, 59.3, 51.6, 33.7, 26.3, 25.1 ppm. **HRMS (ESI+):** Calculated for $C_{26}H_{28}NO_4^+$ $[M+H]^+$: 418.2013 *m/z*. Found: 418.2014 *m/z*.

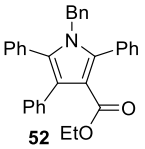
dimethyl 1,2,5-triphenyl-1*H*-pyrrole-3,4-dicarboxylate



51

According to General procedure E, the product was obtained starting from *syn*-1,2,3-triphenylaziridine (54.3 mg, 0.2 mmol, 1 equiv.) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol, 1.2 equiv.) in 79% yield (65.0 mg, 0.158 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.40 – 7.20 (m, 11H), 6.96 (t, *J* = 7.8 Hz, 2H), 6.54 (t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 8.1 Hz, 2H), 6.27 (s, 2H), 3.66 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.7, 137.1, 136.9, 130.9, 130.5, 129.0, 128.7, 128.2, 128.0, 127.7, 115.0, 51.9 ppm. **HRMS (ESI+):** Calculated for $C_{26}H_{22}NO_4^+$ $[M+H]^+$: 412.1543 *m/z*. Found: 412.1551 *m/z*.

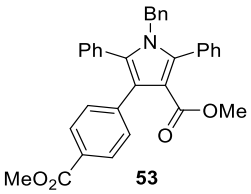
ethyl 1-benzyl-2,4,5-triphenyl-1*H*-pyrrole-3-carboxylate



52

According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and ethyl 3-phenylpropiolate (28.8 mg, 0.24 mmol, 1.2 equiv.) in 84% yield (76.9 mg, 0.168 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.23 – 6.98 (m, 18H), 6.57 – 6.51 (m, 2H), 4.88 (s, 2H), 3.84 (q, *J* = 7.1 Hz, 2H), 0.72 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.3, 138.8, 138.2, 135.4, 132.9, 132.5, 131.9, 131.5, 131.0, 130.9, 128.3, 128.2, 128.1, 128.0, 127.8, 127.3, 127.1, 126.3, 126.0, 124.8, 113.7, 59.5, 48.7, 13.7 ppm. **HRMS (ESI+):** Calculated for $C_{32}H_{28}NO_2^+$ $[M+H]^+$: 458.2115 *m/z*. Found: 458.2142 *m/z*.

methyl 1-benzyl-4-(4-(methoxycarbonyl)phenyl)-2,5-diphenyl-1*H*-pyrrole-3-carboxylate

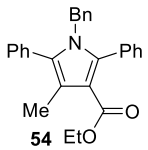


53

According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and methyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)benzoate (52.4 mg, 0.24 mmol, 1.2 equiv.) in 56% yield (56.2 mg, 0.112 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 95:5 to 80:20). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.35 (s, 5H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.14 (m, 3H), 7.14 – 7.10 (m, 3H), 7.09 – 7.05 (m, 2H), 6.61 (dd, *J* = 6.4, 2.8 Hz, 2H), 4.96 (s, 2H), 3.87 (s, 3H), 3.44 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.4, 165.5, 140.6, 139.4, 137.9, 133.4, 132.0, 131.4,

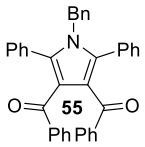
131.3, 130.8, 130.7, 128.7, 128.6, 128.4, 128.3, 128.1, 128.0, 127.6, 127.2, 126.2, 123.6, 113.1, 52.0, 50.8, 48.7 ppm. **HRMS (ESI+):** Calculated for $C_{33}H_{28}NO_4^+$ [M+H]$^+$: 502.2013 *m/z*. Found: 502.2045 *m/z*.

ethyl 1-benzyl-4-methyl-2,5-diphenyl-1*H*-pyrrole-3-carboxylate



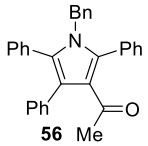
According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and ethyl but-2-ynoate (26.9 mg, 0.24 mmol, 1.2 equiv.) in 81% yield (64.1 mg, 0.162 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.34 – 7.18 (m, 10H), 7.14 – 7.03 (m, 3H), 6.58 – 6.48 (m, 2H), 4.87 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.24 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.8, 139.2, 138.4, 133.1, 132.2, 131.2, 131.0, 129.9, 128.4, 128.2, 128.1, 127.8, 127.0, 126.3, 126.2, 119.3, 113.4, 59.2, 48.6, 14.1, 11.8 ppm. **HRMS (ESI+):** Calculated for $C_{27}H_{26}NO_2^+$ [M+H]$^+$: 396.1958 *m/z*. Found: 396.1957 *m/z*.

(1-benzyl-2,5-diphenyl-1*H*-pyrrole-3,4-diyl)bis(phenylmethanone)



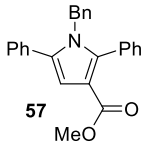
According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and 1,4-diphenylbut-2-yne-1,4-dione (56.2 mg, 0.24 mmol, 1.2 equiv.) in 76% yield (78.7 mg, 0.152 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.52 – 7.44 (m, 4H), 7.31 (m, 4H), 7.24 (m, 8H), 7.17 – 7.07 (m, 7H), 6.71 – 6.63 (m, 2H), 5.10 (s, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 192.4, 139.5, 137.7, 137.4, 131.8, 131.1, 130.5, 129.0, 128.7, 128.6, 128.2, 127.9, 127.4, 126.2, 124.1, 48.7 ppm. **HRMS (ESI+):** Calculated for $C_{37}H_{28}NO_2^+$ [M+H]$^+$: 518.2115 *m/z*. Found: 518.2151 *m/z*.

1-(1-benzyl-2,4,5-triphenyl-1*H*-pyrrol-3-yl)ethan-1-one



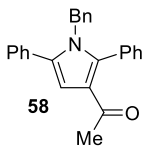
According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and 4-phenylbut-3-yn-2-one (34.6 mg, 0.24 mmol, 1.2 equiv.) in 87% yield (74.4 mg, 0.174 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 (s, 6H), 7.23 – 7.14 (m, 9H), 7.14 – 7.08 (m, 5H), 6.66 – 6.54 (m, 2H), 4.94 (s, 2H), 1.89 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.8, 138.1, 137.5, 135.6, 133.0, 132.4, 131.7, 131.5, 131.1, 130.8, 128.7, 128.4, 128.2, 127.8, 127.7, 127.1, 126.3, 126.2, 124.2, 124.0, 48.6, 31.3 ppm. **HRMS (ESI+):** Calculated for $C_{31}H_{26}NO^+$ [M+H]$^+$: 428.2009 *m/z*. Found: 428.2008 *m/z*.

methyl 1-benzyl-2,5-diphenyl-1*H*-pyrrole-3-carboxylate



According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and methyl propiolate (20.2 mg, 0.24 mmol, 1.2 equiv.) in 84% yield (61.7 mg, 0.168 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 70:30). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.31 – 7.12 (m, 10H), 7.06 – 6.97 (m, 3H), 6.71 (s, 1H), 6.58 – 6.45 (m, 2H), 4.95 (s, 2H), 3.58 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.2, 140.3, 138.2, 135.4, 132.7, 132.0, 130.8, 129.4, 128.5, 128.4, 128.4, 128.0, 127.8, 127.1, 126.0, 113.9, 110.9, 51.0, 48.6 ppm. **HRMS (ESI+):** Calculated for $C_{25}H_{22}NO_2^+$ [M+H]$^+$: 368.1645 *m/z*. Found: 368.1660 *m/z*.

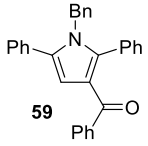
1-(1-benzyl-2,5-diphenyl-1*H*-pyrrol-3-yl)ethan-1-one



According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and 3-butyn-2-one (16.3 mg, 0.24 mmol, 1.2 equiv.) in 89% yield (62.6 mg, 0.178 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (m, 8H), 7.27 – 7.22 (m, 2H), 7.16 – 7.09 (m, 3H), 6.82 (s, 1H), 6.66 – 6.56 (m, 2H),

4.99 (s, 2H), 2.05 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 194.5, 139.4, 138.2, 135.5, 132.6, 132.5, 130.9, 129.4, 129.0, 128.6, 128.5, 128.4, 127.9, 127.2, 126.1, 124.5, 110.3, 48.6, 29.1 ppm. **HRMS (ESI+):** Calculated for $C_{25}H_{22}NO^+$ $[M+H]^+$: 352.1696 *m/z*. Found: 352.1701 *m/z*.

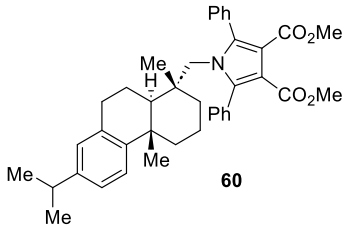
(1-benzyl-2,5-diphenyl-1*H*-pyrrol-3-yl)(phenyl)methanone



59

According to General procedure E, the product was obtained starting from *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.) and benzoylacetylene (31.2 mg, 0.24 mmol, 1.2 equiv.) in 74% yield (61.2 mg, 0.148 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 80:20). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.77 – 7.67 (m, 2H), 7.38 – 7.20 (m, 9H), 7.19 – 7.16 (m, 4H), 7.12 – 7.06 (m, 3H), 6.70 (s, 1H), 6.64 – 6.56 (m, 2H), 5.11 (s, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 192.1, 139.8, 138.1, 135.5, 132.7, 131.9, 131.3, 130.9, 129.9, 129.6, 129.5, 128.6, 128.5, 128.3, 128.1, 127.9, 127.8, 127.2, 126.3, 126.2, 112.7, 48.8 ppm. **HRMS (ESI+):** Calculated for $C_{30}H_{24}NO^+$ $[M+H]^+$: 414.1852 *m/z*. Found: 414.1906 *m/z*.

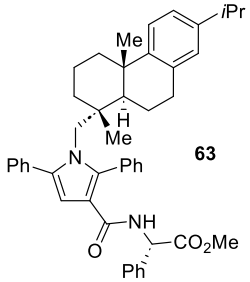
dimethyl 1-((7-isopropyl-1,4a-dimethyl-octahydrophenanthren-1-yl)methyl)-2,5-diphenyl-1H-pyrrole-3,4-dicarboxylate



60

According to General procedure E, the product was obtained starting from *syn*-1-((7-isopropyl-1,4a-dimethyl-octahydrophenanthren-1-yl)methyl)-2,3-diphenylaziridine (92.7 mg, 0.2 mmol, 1 equiv.) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol, 1.2 equiv.) in 55% yield (66.7 mg, 0.110 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 75:25). $[\alpha]_D^{25}$= 6.46 (c = 0.48, $CHCl_3$). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.27 (m, 10H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.80 – 6.75 (m, 1H), 4.31 (d, *J* = 14.5 Hz, 1H), 3.83 (d, *J* = 14.5 Hz, 1H), 3.66 (s, 6H), 2.78 (hept, *J* = 6.8 Hz, 1H), 2.68 (dd, *J* = 17.3, 6.7 Hz, 1H), 2.49 (ddd, *J* = 17.8, 10.6, 8.2 Hz, 1H), 2.02 (d, *J* = 12.8 Hz, 1H), 1.39 – 1.22 (m, 4H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.08 – 0.97 (m, 2H), 0.95 (s, 3H), 0.87 – 0.80 (m, 1H), 0.36 (s, 3H), 0.27 (td, *J* = 12.9, 4.6 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.8, 165.7, 147.3, 145.7, 138.4, 137.8, 134.4, 131.8, 131.5, 128.6, 128.2, 126.8, 123.8, 123.7, 55.5, 51.8, 47.0, 40.1, 37.9, 37.7, 37.6, 33.6, 29.7, 25.3, 24.14, 24.07, 19.0, 18.4, 18.1 ppm. **HRMS (ESI+):** Calculated for $C_{40}H_{46}NO_4^+$ $[M+H]^+$: 604.3421 *m/z*. Found: 604.3480 *m/z*.

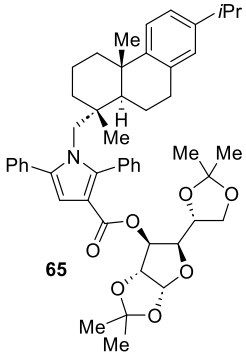
methyl (S)-2-(1-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-2,5-diphenyl-1H-pyrrole-3-carboxamido)-2-phenylacetate



63

According to General procedure E, the product was obtained starting from *syn*-1-((7-isopropyl-1,4a-dimethyl-octahydrophenanthren-1-yl)methyl)-2,3-diphenylaziridine (47 mg, 0.1 mmol, 1 equiv.) and methyl (*S*)-2-phenyl-2-propiolamidoacetate (32.5 mg, 0.15 mmol, 1.5 equiv.) in 48% yield (32 mg, 0.048 mmol) after purification by flash column chromatography on silica gel (hexane:EtOAc 90:10). $[\alpha]_D^{25}$= 30.67 (c = 0.65, $CHCl_3$). Two rotamers observed. In ^{1}H NMR, only diagnostic peaks are listed. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.16 (m, 11H), 7.09 (d, *J* = 8.5 Hz, 3H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.78 (s, 1H), 6.70 (s, 1H), 6.16 (d, *J* = 5.5 Hz, 1H), 5.59 (dd, *J* = 35.9, 4.7 Hz, 1H), 4.21 (dd, *J* = 206.3, 15.1 Hz, 1H), 3.96 (dd, *J* = 187.0, 12.8 Hz, 1H), 3.64 (d, *J* = 19.6 Hz, 4H), 2.79 (dt, *J* = 13.5, 6.6 Hz, 2H), 2.02 (d, *J* = 12.2 Hz, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.6, 171.4, 164.6, 164.4, 147.4, 145.7, 137.2, 136.9, 136.8, 136.6, 134.6, 134.4, 132.3, 129.7, 129.2, 129.1, 128.8, 128.7, 128.4, 128.3, 127.4, 127.2, 126.8, 123.8, 123.7, 117.8, 117.5, 111.8, 111.4, 56.8, 56.3, 55.6, 55.5, 52.6, 47.3, 46.6, 40.5, 40.3, 38.1, 38.0, 37.5, 37.4, 33.5, 32.1, 30.3, 29.8, 29.7, 29.5, 25.3, 24.14, 24.07, 22.8, 22.1, 19.1, 19.0, 18.6, 18.1, 14.3 ppm. **HRMS (ESI+):** Calculated for $C_{46}H_{51}N_2O_3^+$ $[M+H]^+$: 679.3894 *m/z*. Found: 679.3878 *m/z*.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 1-(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-2,5-diphenyl-1*H*-pyrrole-3-carboxylate

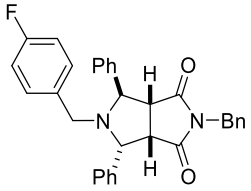


65

According to General procedure E, the product was obtained starting from *syn*-1-((7-isopropyl-1,4a-dimethyl-octahydrophenanthren-1-yl)methyl)-2,3-diphenylaziridine (47 mg, 0.1 mmol, 1 equiv.) and (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl propiolate (47 mg, 0.15 mmol, 1.5 equiv.) in 43% yield (33 mg, 0.043 mmol) after purification by flash column chromatography on silica gel (hexane:Et_2O 80:20). $[\alpha]_D^{25}$= -26.16 (c = 0.45, $CHCl_3$). Rotamers observed. In ^{1}H NMR, only diagnostic peaks are listed. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 – 7.27 (m, 10H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.83 – 6.63 (m, 2H), 5.71 (s, 1H), 5.26 (s, 1H), 4.49 (m, 1H), 4.33 – 4.20 (m, 1H), 4.15 (d, *J* = 4.3 Hz, 1H), 3.93 (d, *J* = 14.2 Hz, 1H), 3.88 – 3.76 (m, 2H), 3.57 – 3.47 (m, 1H), 2.79 (dt, *J* = 13.7, 6.9 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.59 – 2.41 (m, 1H), 2.03 (d, *J* = 11.7 Hz, 1H), 1.86 – 1.59 (m, 3H), 1.49 (s, 3H), 1.46 – 1.38 (m, 2H), 1.36 (s, 3H), 1.27 (d, *J* = 4.7 Hz, 6H), 1.20 (d, *J* = 6.8 Hz, 6H), 1.09 – 0.99 (m, 2H), 0.96 (s, 3H), 0.37 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.5, 147.4, 145.7, 141.6, 136.9, 134.5, 134.3, 134.1, 132.8, 129.8, 129.2, 128.8, 128.7, 128.4, 128.1, 128.0, 127.9, 127.7, 127.6, 126.8, 126.4, 123.8, 123.7, 121.0, 113.2, 112.6, 112.5, 112.2, 111.7, 109.5, 109.1, 105.2, 105.1, 83.4, 79.9, 75.4, 75.3, 72.8, 72.5, 72.4, 72.2, 67.4, 67.3, 67.0, 66.8, 55.5, 47.2, 46.7, 40.6, 40.4, 38.4, 38.2, 37.9, 37.6, 33.6, 32.1, 30.5, 29.8, 29.7, 27.0, 26.93, 26.86, 26.4, 25.5, 25.3, 24.14, 24.07, 22.8, 19.0, 18.6, 18.2, 18.1, 14.3 ppm. **HRMS (ESI+):** Calculated for $C_{49}H_{58}NO_7Na^+$ [M+Na]$^+$: 796.4189 *m/z*. Found: 796.4160 *m/z*.

E. Crystallographic analyses

Crystal structure of 13



13 was crystallized by slow evaporation of a solution of 40 mg in 2 mL of DCM:MeCN 1:1.

Crystal data for 13:

$C_{32}H_{27}FN_2O_2$, monoclinic, C2/c, a = 31.6910(6) Å, b = 6.6329(1) Å, c = 25.7816(5) Å, β = 112.057(1)°, V = 5022.73(16) Å^3; Z = 8; dcalc = 1.297 mg/cm^3, F(000) = 2064, CuKα radiation (λ = 1.54178), mu = 0.692, Tot. refl. = 34917, hkl range = -38<h<38, -7<k<8, -31<l<29; Theta range 3.01 - 72.22, unique reflections = 4942, number of parameters = 442, GooF = 1.044, R = 0.041, wR2 = 0.094, CSD 2285592

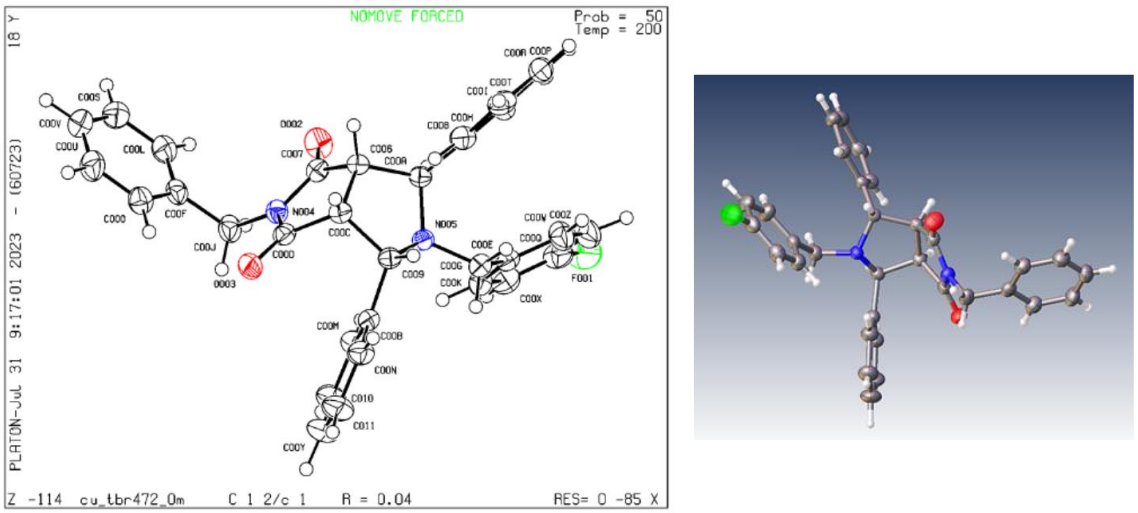
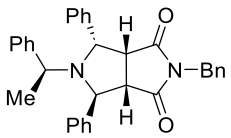


*Figure S3: ORTEP representation of **13***

Crystal structure of *major*-16



16 major

***Major*-16** was crystallized by slow evaporation of a solution of 47 mg in 1 mL of Heptane:DCM 1:1.

Crystal data for major-16:

$C_{33}H_{30}N_2O_2$, triclinic, P1, a = 6.8195(6) Å, b = 19.5313 (9) Å, c = 20.532(2) Å, α = 96.793(5) , β = 95.640(7), γ = 99.888(5)°, V = 2655.5(3) Å^3; Z = 1; dcalc = 1.217 mg/cm^3, F(000) = 1033, CuKα radiation (λ = 1.54178), mu = 0.594, Tot. refl. = 19166, hkl range = -7<h<8, -23<k<23, -25<l<24; Theta range 2.18 - 70.07, unique reflections = 8169, number of parameters = 1481, GooF = 1.005, R = 0.126, wR2 = 0.306, CSD 2300984

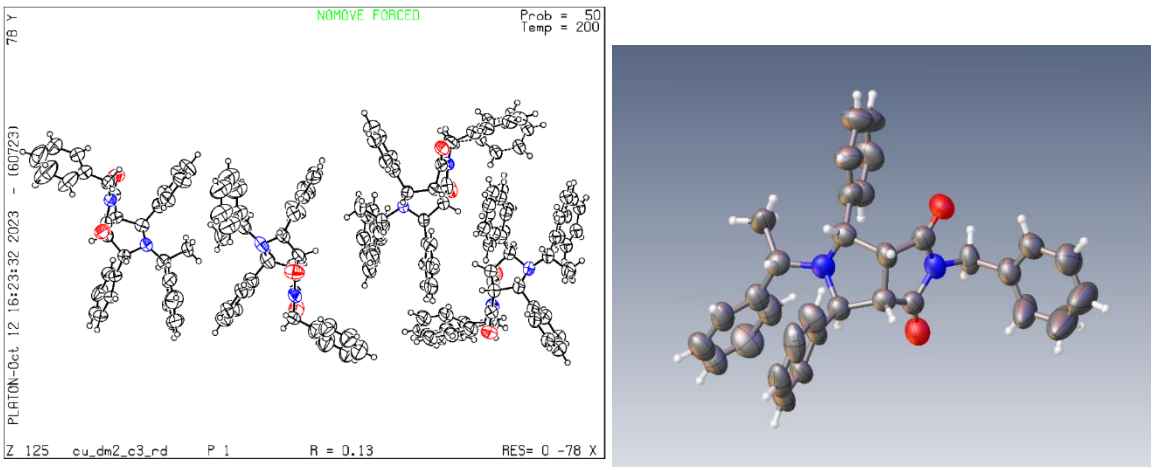
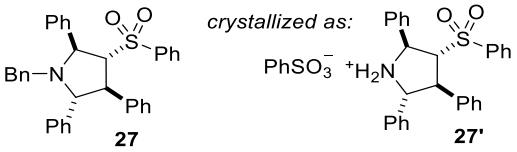


*Figure S4: ORTEP representation of **major-16***

Crystal structure of 27'



A solution of 20 mg of **27** in 2 mL of DCM:MeCN 1:1 was slowly evaporated. A small fraction of **27** underwent debenzylation and crystallized as the benzenesulfonate salt **27'**. Although a mechanism accounting for the observed phenomenon cannot be proposed, the relative configuration of the carbon atoms of the pyrrolidine ring must be preserved during the crystallization. Therefore, the relative configuration of **27** can be deduced from the relative configuration of **27'**.

Crystal data for 27':

$C_{34}H_{31}NO_5S_2$, monoclinic, Pn, a = 12.5078(10) Å, b = 5.9193(1) Å, c = 19.787(2) Å, β = 96.743(5)°, V = 1454.8(2) Å^3; Z = 2; dcalc = 1.364 mg/cm^3, F(000)= 628, CuKα radiation (λ = 1.54178), mu = 2.022, Tot. refl. = 26136, hkl range = -15<h<15, -7<k<7, -22<l<24; Theta range 3.98 - 70.32, unique reflections = 5344, number of parameters = 414, GooF = 1.022, R = 0.053, wR2 = 0.128, Flack parameter = 0.065(18), CSD 2286152

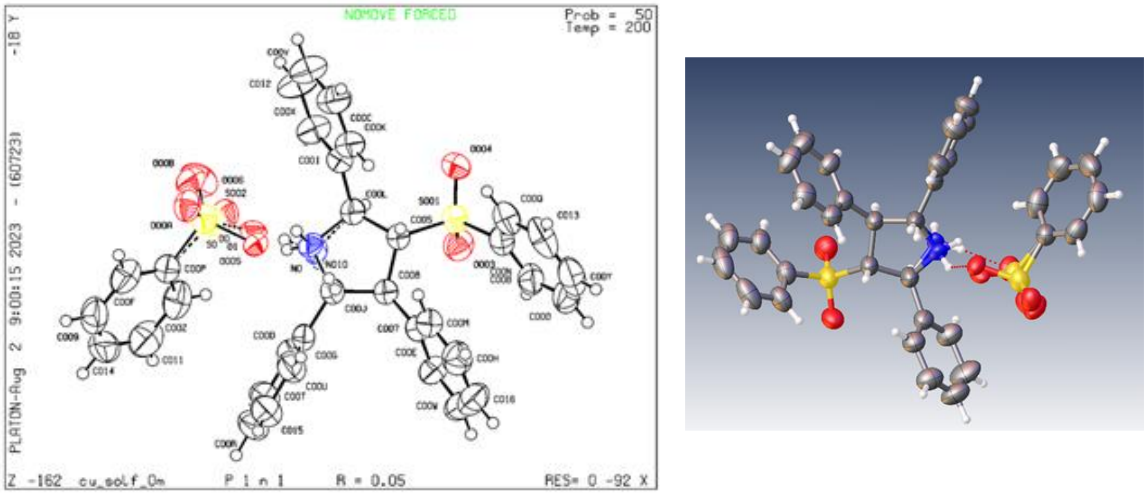
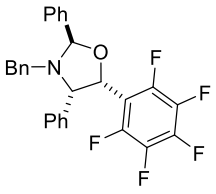


*Figure S5: ORTEP representation of **27'***

Crystal structure of 31



31 was crystallized by storing the crude reaction mixture at -20 °C for 72h.

Crystal data for 21:

$C_{28}H_{20}F_5NO$, C_2H_3N, monoclinic, P21/c, a = 10.5292(2) Å, b = 12.5977(2) Å, c = 20.0573(4) Å, β = 103.635(1)°, V = 2585.49(8) Å^3; Z = 4; dcalc = 1.342 mg/cm^3 , F(000) = 1080, CuKα radiation (λ = 1.54178), mu = 0.905, Tot. refl. = 21770, hkl range = -13<h<11, -15<k<14, -24<l<24; Theta range 4.18 -

72.54, unique reflections = 5100, number of parameters = 342, GooF = 1.021, R = 0.073, wR2 = 0.1918, CSD 2285593

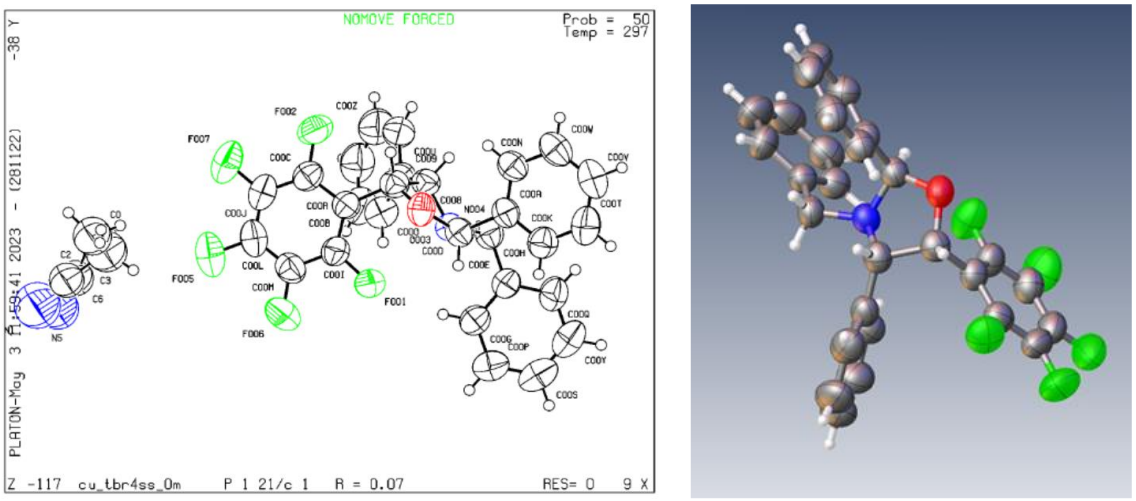


*Figure S6: ORTEP representation of **31***

F. Mechanistic experiments

Stereospecificity of the reaction

The following experiments were performed according to General procedure D. At the end of the reaction, the solvent was evaporated and the yields and diastereomeric ratios were inferred by ^{1}H NMR analysis of the crude reaction mixtures using pyrazine as the internal standard. The structural assignment was done according to a literature report.[3]

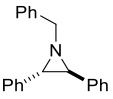
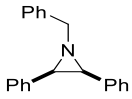
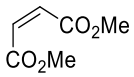
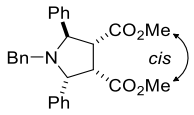
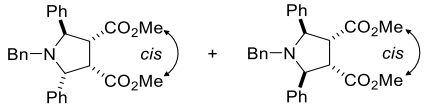
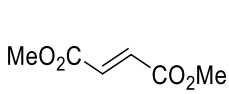
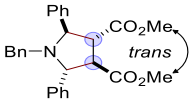
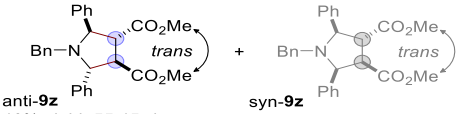
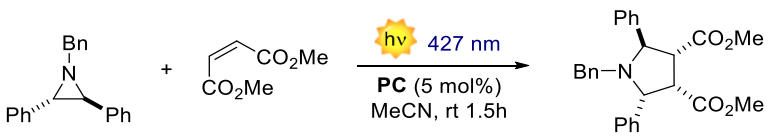
Alkene \ Aziridine		
	 **anti** 73% yield, >95:5 *dr*	 **anti** 52% yield, >95:5 *dr* **syn** 16% yield, >95:5 *dr* *anti* : *syn* 77 : 23
	 **anti** 88% yield, 60:40 *dr*	 anti-**9z** 46% yield, 55:45 *dr* syn-**9z** *not detected*

Table S1: results of the reaction stereospecificity investigation

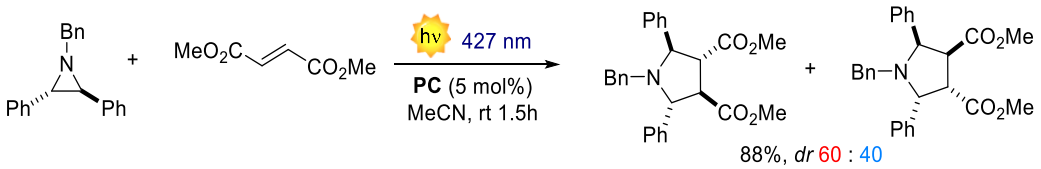
NMR spectra of the crude reaction mixtures and characteristic peaks

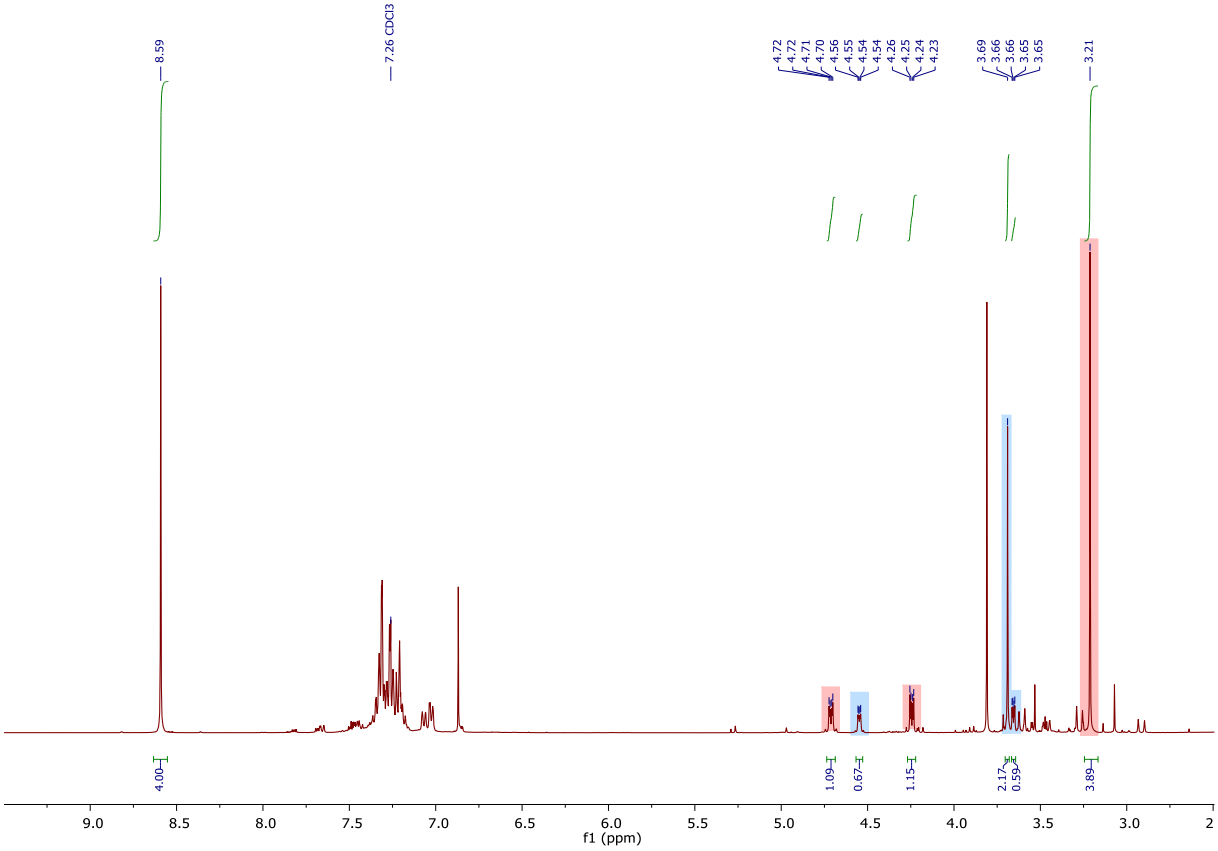
anti aziridine with dimethyl maleate



The compound was isolated and fully characterized (see above).

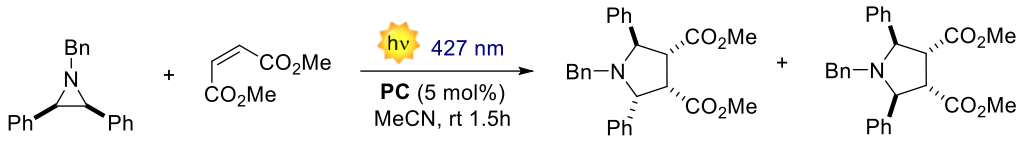
***anti* aziridine with dimethyl fumarate**



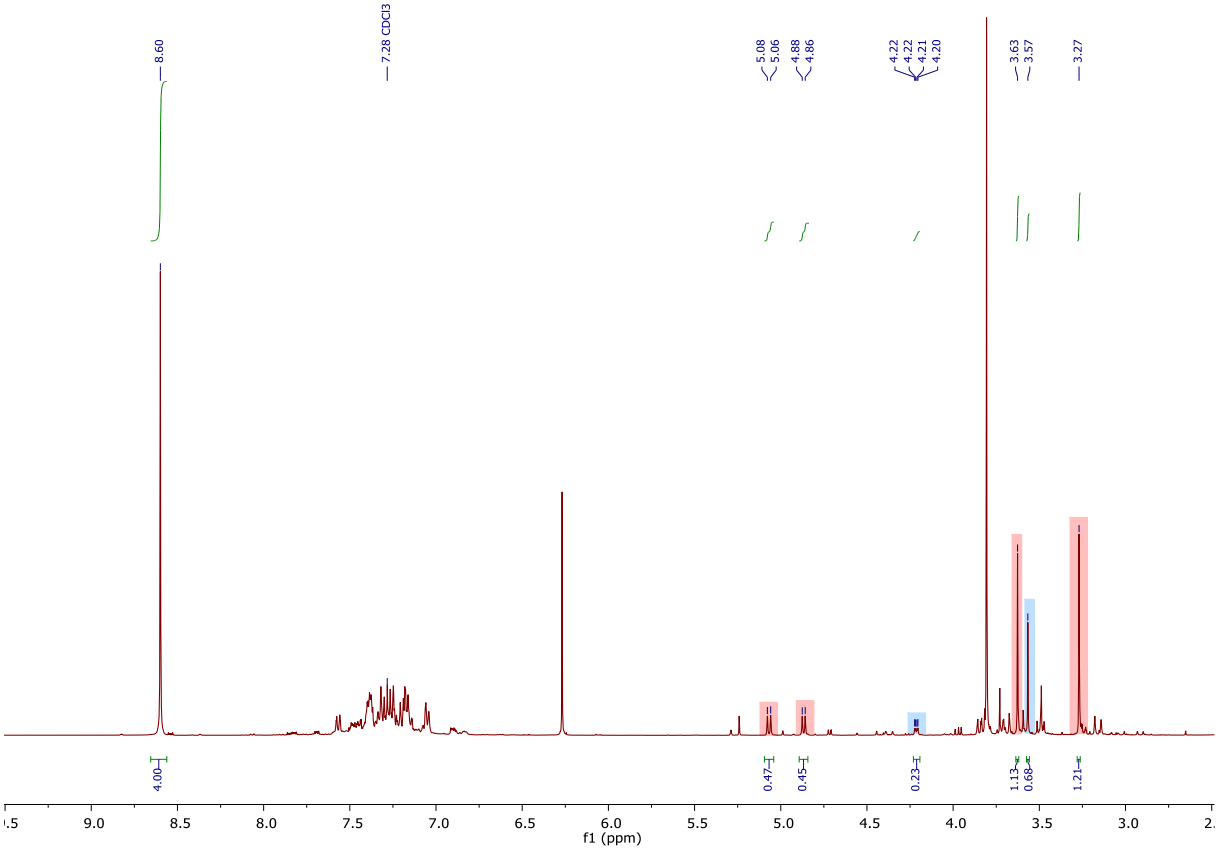


Diagnostic peaks for the major diastereomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.71 (dd, J = 6.3, 2.4 Hz, 2H), 4.24 (dd, J = 6.3, 2.5 Hz, 2H), 3.21 (s, 6H) ppm. Diagnostic peaks for the minor diastereomer: **^{1}H NMR (400 MHz, $CDCl_3$)** 4.55 (dd, J = 4.3, 1.9 Hz, 2H), 3.69 (s, 6H), 3.66 (dd, J = 4.4, 1.9 Hz, 2H) ppm.

***syn* aziridine with dimethyl maleate**

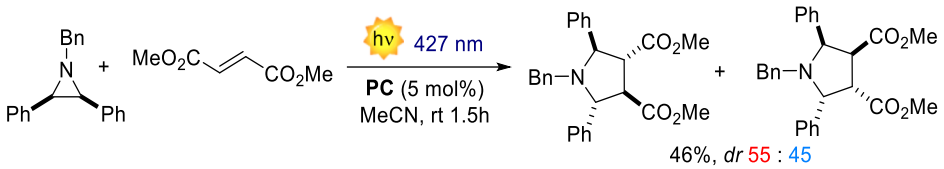


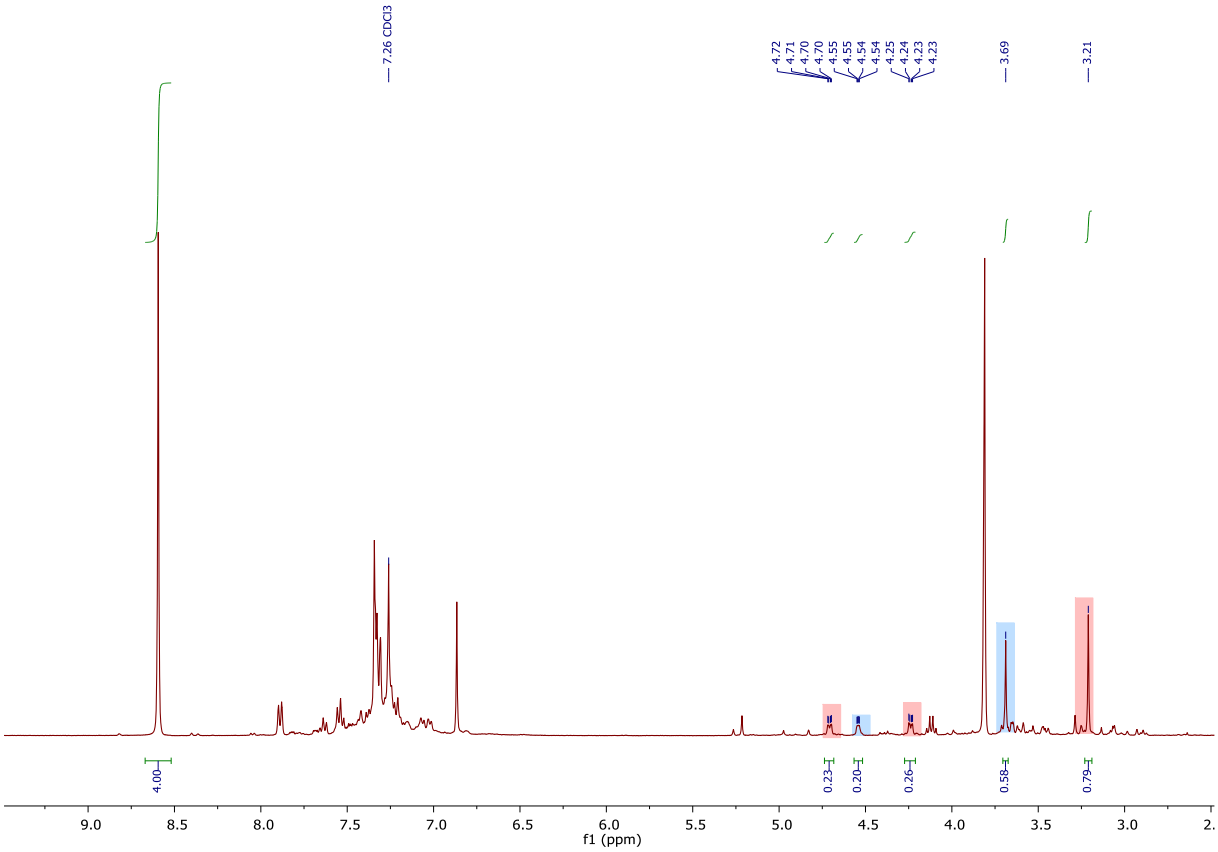
68%, *anti:syn* 77 : 23



Diagnostic peaks for the major diastereomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.07 (d, *J* = 7.7 Hz, 1H), 4.87 (d, *J* = 6.8 Hz, 1H), 3.63 (s, 3H), 3.27 (s, 3H) ppm. Diagnostic peaks for the minor diastereomer: **^{1}H NMR (400 MHz, $CDCl_3$)** 4.21 (dd, *J* = 5.3, 2.2 Hz, 2H), 3.57 (s, 6H) ppm.

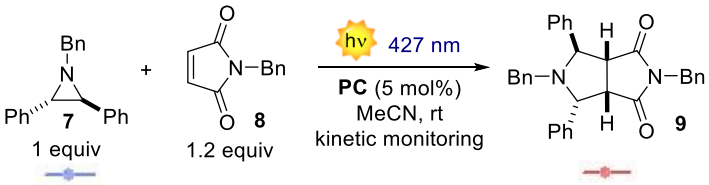
***syn* aziridine with dimethyl fumarate**





Diagnostic peaks for the major diastereomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.71 (dd, J = 6.3, 2.4 Hz, 2H), 4.24 (dd, J = 6.3, 2.5 Hz, 2H), 3.21 (s, 6H) ppm. Diagnostic peaks for the minor diastereomer: **^{1}H NMR (400 MHz, $CDCl_3$)** 4.55 (dd, J = 4.3, 1.9 Hz, 2H), 3.69 (s, 6H), 3.66 (dd, J = 4.4, 1.9 Hz, 2H) ppm.

Reaction monitoring



A 4 mL vial was charged with a stirbar, *anti*-1-benzyl-2,3-diphenylaziridine **7** (28.5 mg, 0.1 mmol, 1 equiv.), *N*-benzylmaleimide **8** (22.5 mg, 0.12 mmol, 1.2 equiv.) and 9,10-dicyanoanthracene (1.1 mg, 0.005 mmol, 0.05 equiv.). The vial was closed with a screwcap equipped with a septum and purged with nitrogen. Dry acetonitrile (2 mL, 0.05 M) was finally added. The reaction mixture was degassed by nitrogen bubbling for 2 minutes. The vial was then secured with parafilm and irradiated under stirring with a Kessil 427 nm lamp set at 50% of its maximum output power according to the experimental setup shown in Section C. 100 µL of the reaction mixture were taken after 5, 10, 15, 30, 60 and 90 minutes and analysed by ^{1}H NMR with CH_2Br_2 as the internal standard to determine yield and conversion of the aziridine over time.

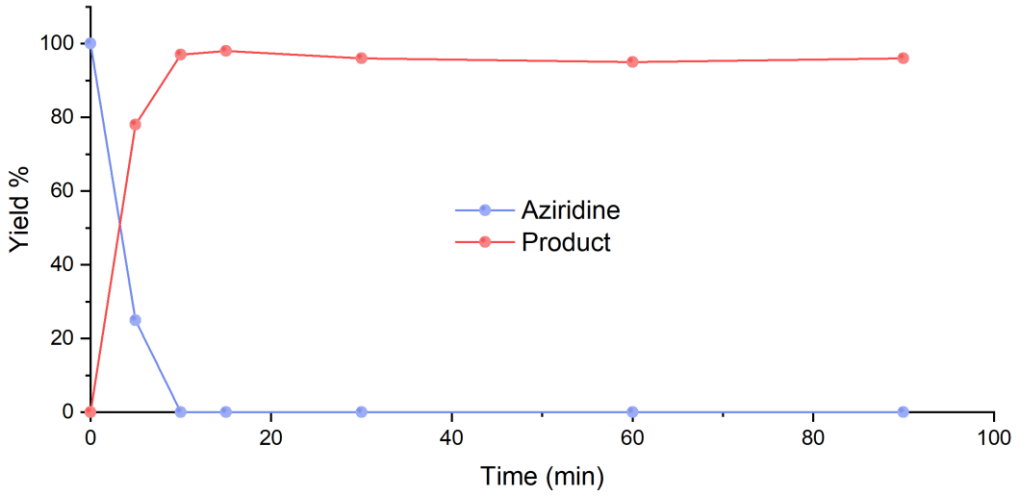
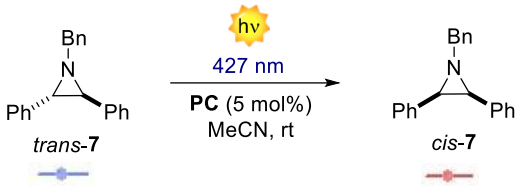


Figure S7: Kinetic trace of the reaction mixture

Aziridine isomerization under photoredox conditions



A 4 mL vial was charged with a stirbar, anti-aziridine *anti*-**7** (0.1 mmol, 1 equiv.) and 9,10-dicyanoanthracene (1.1 mg, 0.005 mmol, 0.05 equiv.). The vial was closed with a screwcap equipped with a septum and purged with nitrogen. Dry acetonitrile (2 mL, 0.05 M) was finally added. The reaction mixture was degassed by nitrogen bubbling for 2 minutes. The vial was then secured with parafilm and irradiated under stirring with a Kessil 427 nm lamp set at 50% of its maximum output power. The vial was placed at a distance of 5 cm from the light source and a fan was placed above the irradiated vial to maintain a stable reaction temperature. After 10 min, the stirring was continued for 50 minutes in the dark. Aliquots of the reaction mixture were taken after 5, 10, 15, 20, 30 and 60 minutes since the beginning of the irradiation and analysed by ^{1}H NMR wit CH_2Br_2 as the internal standard to determine the amount of the identifiable compounds.

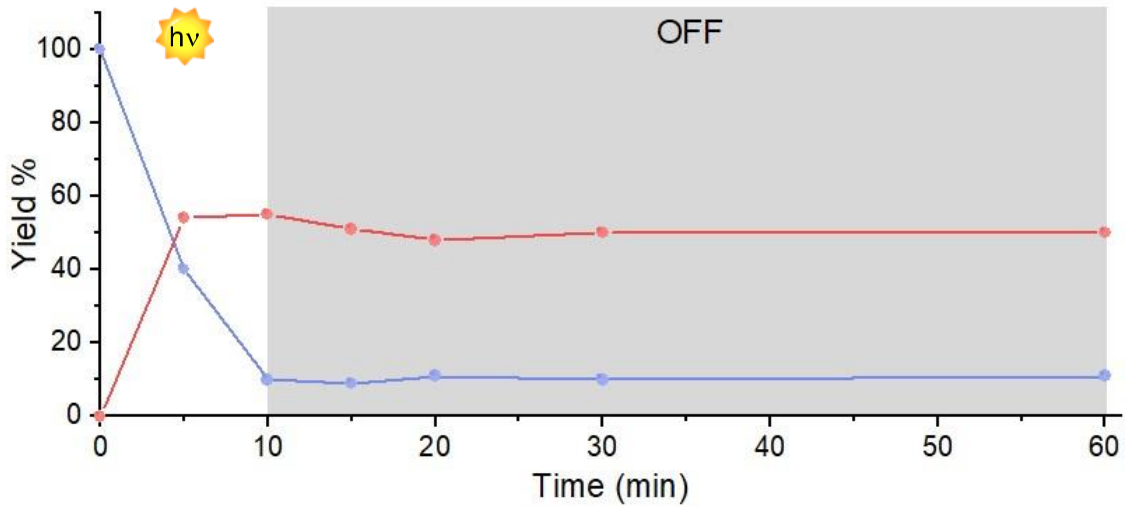
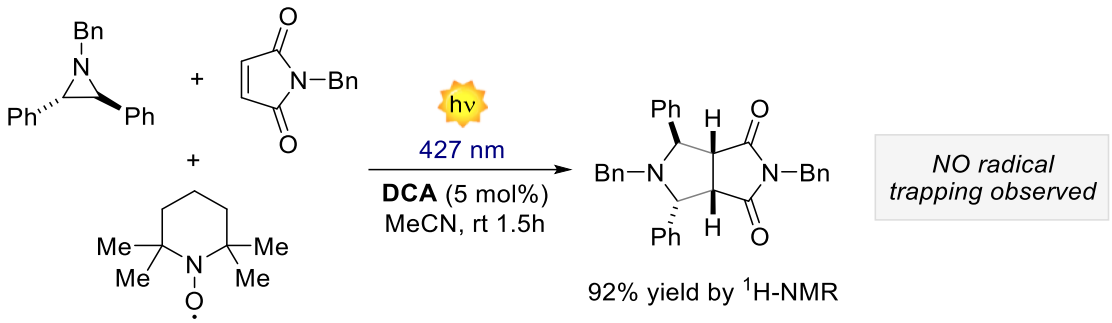


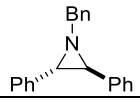
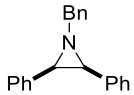
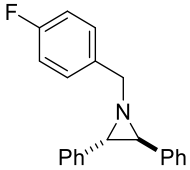
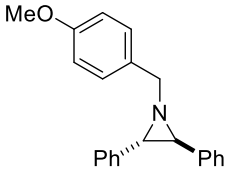
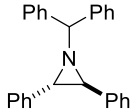
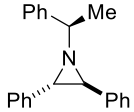
*Figure S8: Conversion of anti-aziridine anti-**7** to syn-aziridine syn-**7** under the optimized conditions in the absence of a dipolarophile.*

Tempo trapping



An 8 mL vial was charged with a stirbar, *anti*-1-benzyl-2,3-diphenylaziridine (57.1 mg, 0.2 mmol, 1 equiv.), *N*-benzylmaleimide (44.9 mg, 0.24 mmol, 1.2 equiv.), (2,2,6,6-tetramethylpiperidin-1-yl)oxy (62.6 mg, 0.4 mmol, 2 equiv.), and 9,10-dicyanoanthracene (2.3 mg, 0.01 mmol, 0.05 equiv.). The vial was closed with a screwcap equipped with a septum and purged with nitrogen. Dry acetonitrile (4 mL, 0.05 M) was added, and the reaction mixture was sparged with nitrogen for 5 minutes. The vial was then secured with parafilm and irradiated under stirring for 90 min with a Kessil 427 nm lamp set at 50% of its maximum output power according to the experimental setup shown in Section C. Trichloroethylene (18 µL, 0.2 mmol, 1 equiv.) was added as the internal standard and a sample was taken for ^{1}H NMR yield determination. Both NMR and UPC^2 analyses revealed the sole formation of the cycloaddition product (92% yield by ^{1}H NMR).

G. Cyclic Voltammetry

Compound	E_{ox} (vs Ag/AgCl)
	1.54 V
	1.62 V
	1.56 V
	1.43 V
	1.62 V
	1.60 V

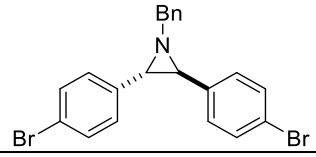
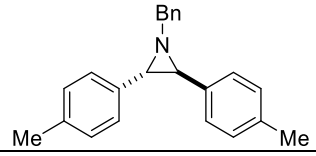
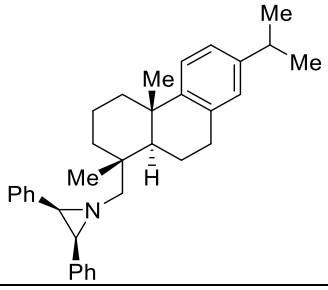
	1.59 V
	1.41 V
	1.57 V

Table S2: Summary of the redox potential of the aziridines used in this work.

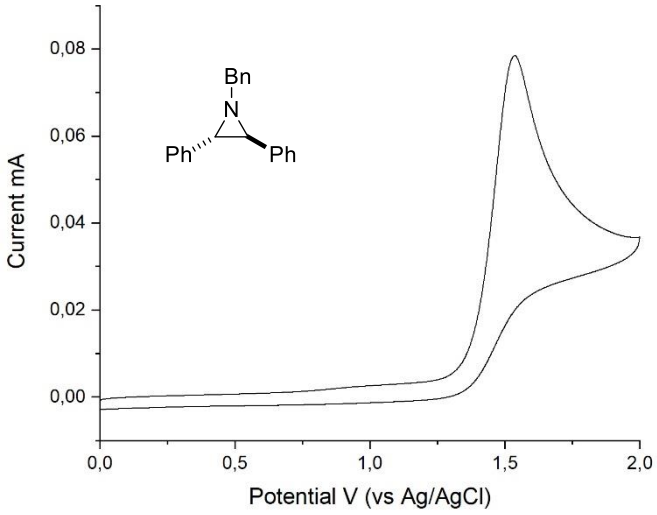


Figure S9. Cyclic voltammogram in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (NaCl 3.5 M) reference electrode, Pt wire auxiliary electrode.

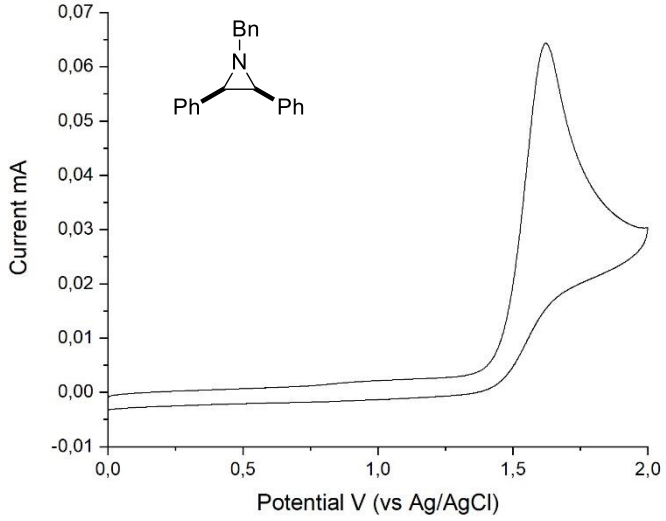


Figure S10. Cyclic voltammogram in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (NaCl 3.5 M) reference electrode, Pt wire auxiliary electrode.

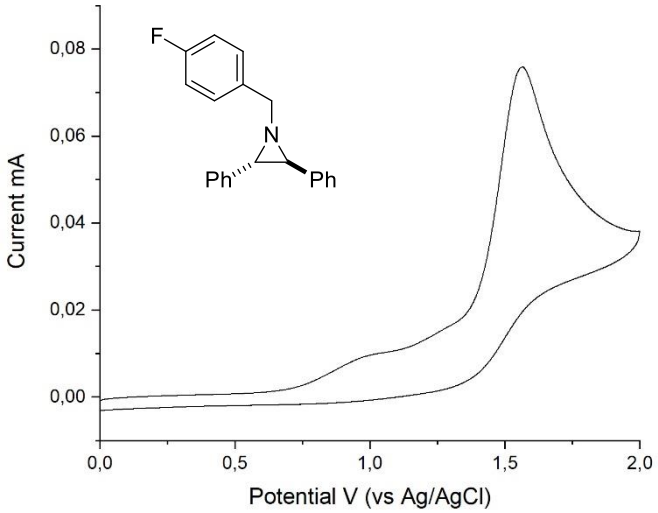


Figure S11. Cyclic voltammogram in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (NaCl 3.5 M) reference electrode, Pt wire auxiliary electrode.

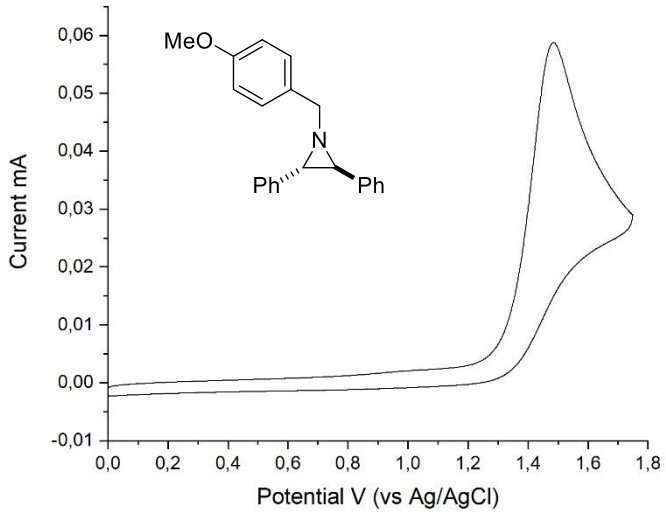


Figure S12. Cyclic voltammogram in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (NaCl 3.5 M) reference electrode, Pt wire auxiliary electrode.

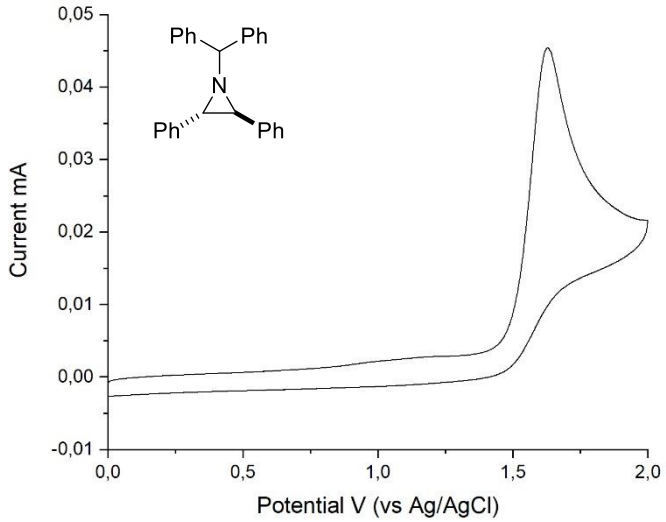


Figure S13. Cyclic voltammogram in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (NaCl 3.5 M) reference electrode, Pt wire auxiliary electrode.

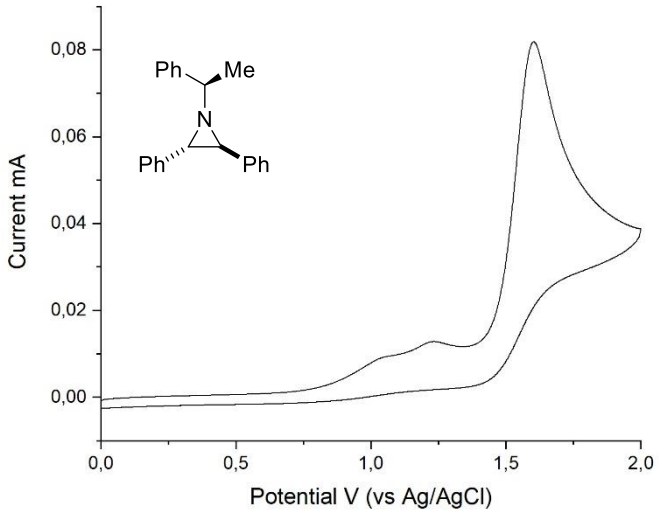


Figure S14. Cyclic voltammogram in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (NaCl 3.5 M) reference electrode, Pt wire auxiliary electrode.

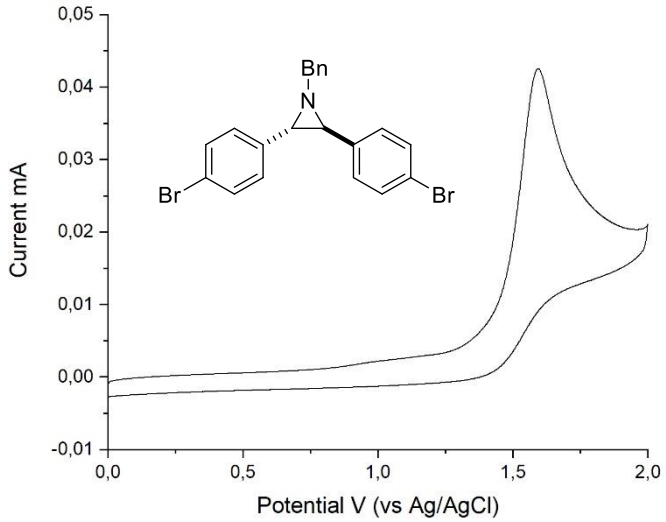


Figure S15. Cyclic voltammogram in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (NaCl 3.5 M) reference electrode, Pt wire auxiliary electrode.

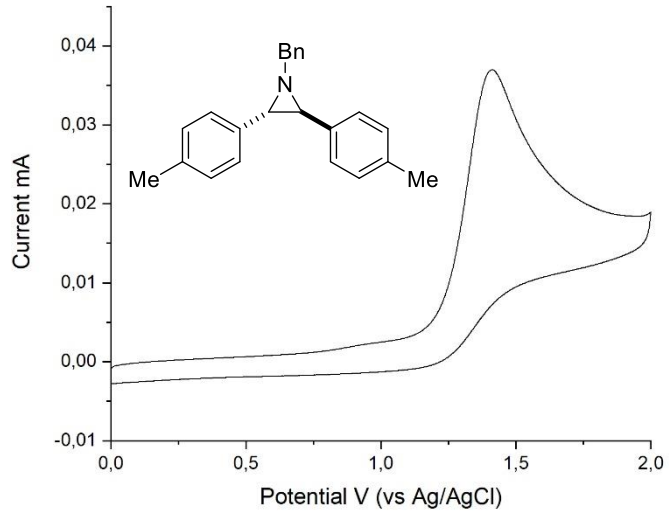


Figure S16. Cyclic voltammogram in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (NaCl 3.5 M) reference electrode, Pt wire auxiliary electrode.

.

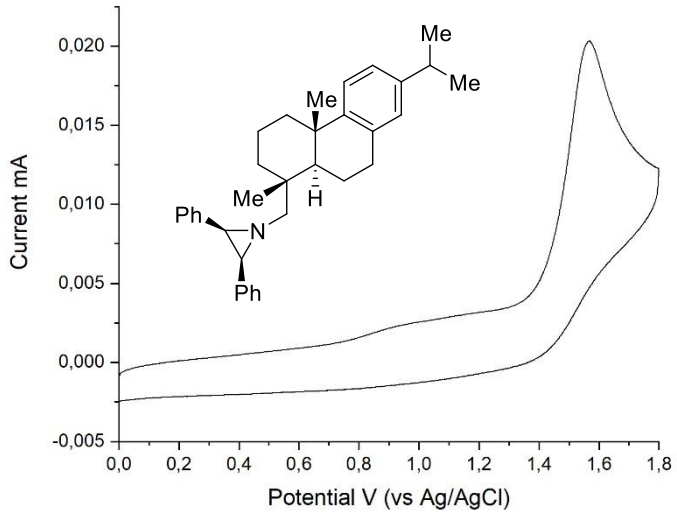


Figure S17. Cyclic voltammogram in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (NaCl 3.5 M) reference electrode, Pt wire auxiliary electrode.

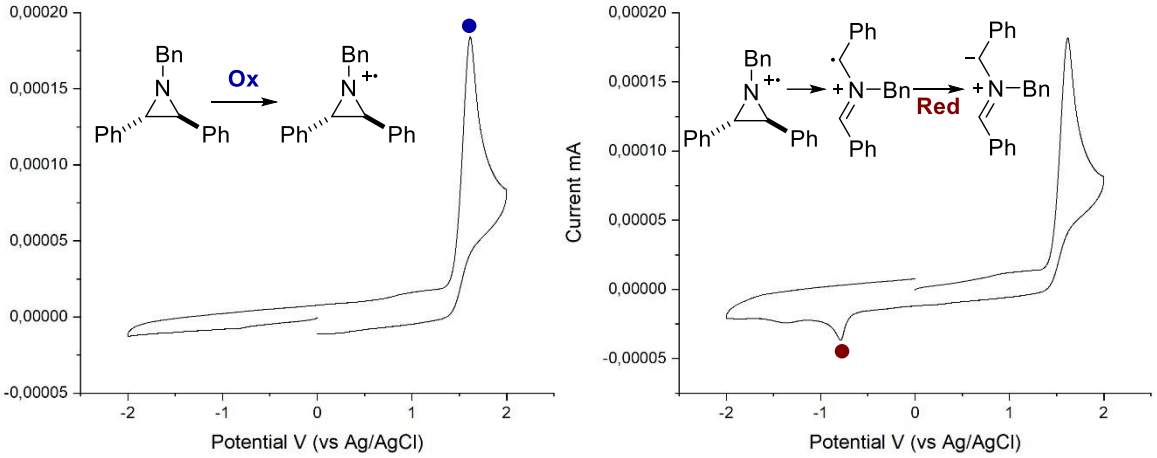


*Figure S18. Cyclic voltammogram of aziridine **7** in [0.1 M] TBAPF6 in CH3CN. Sweep rate: 400 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (NaCl 3.5 M) reference electrode, Pt wire auxiliary electrode.*

H. UV-Vis and emission spectra

Stern-Volmer Studies

A screw-capped vial, fitted with a rubber septum, was charged with a 0.01 mM solution of DCA in CH_3CN. The mixture was degassed with argon and used to record the emission spectrum of the photocatalyst. To this mixture, either aziridine **7** (Figure S19) or maleimide **8** (Figure S20) were added and the emission spectrum of the title solution was recorded. This was repeated 4 times. The excitation wavelength was fixed at 390 nm and the emission lights was acquired from 410 to 520 nm. A solvent blank was subtracted from all the measurements.

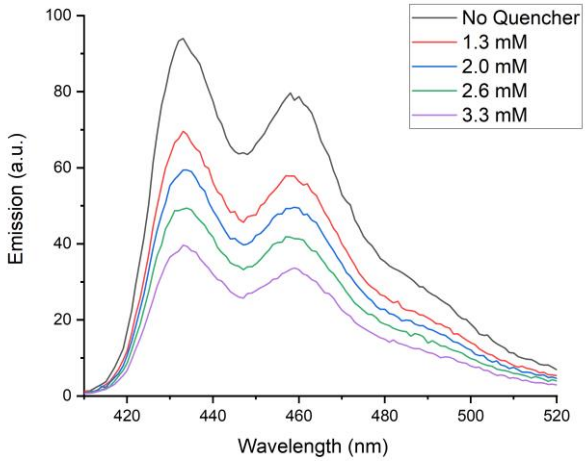


*Figure S19. Quenching of the emission of a 0.01 mM solution of DCA by increasing amounts of aziridine **7**. λ_{exc} = 390 nm. Emission was acquired from 410 to 520 nm.*

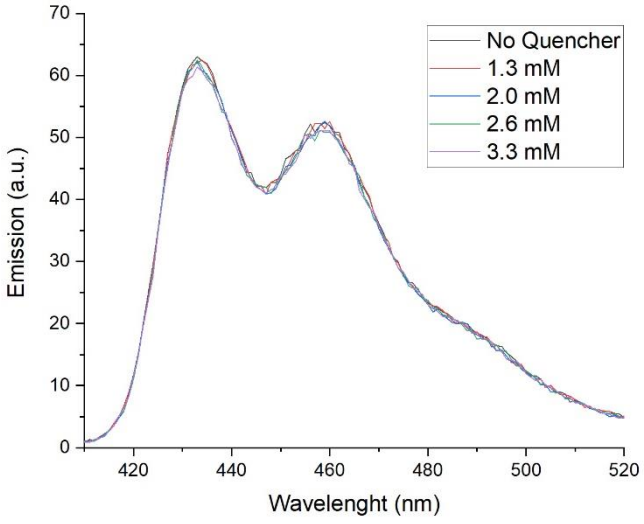


*Figure S20. Quenching of the emission of a 0.01 mM solution of DCA by increasing amounts of maleimide **8**. λ_{exc} = 390 nm. Emission was acquired from 410 to 520 nm.*

The Stern-Volmer plot, reported in Figure S21, shows a linear correlation between the increasing amounts of aziridine **7** and the ratio I_0/I. Based on these values, we calculated a Stern-Volmer quenching constant of 368 M^{-1}

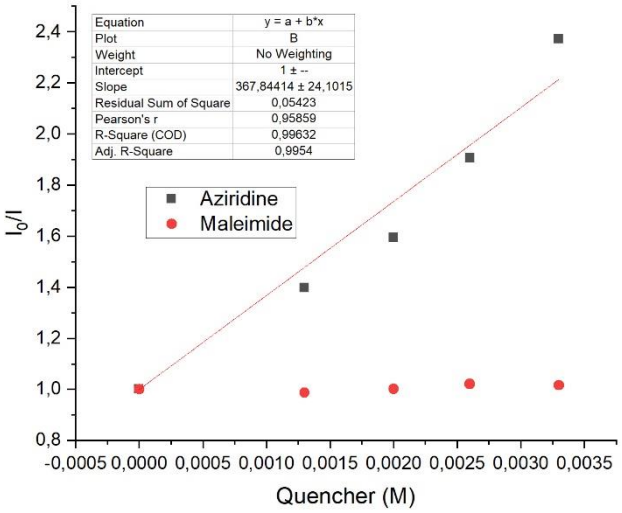


Figure S21. Stern-Volmer plot of the emission quenching reported in Figures S19-S20.

EDA Complex evaluation

Uv-Vis studies were carried out in order to evaluate the formation of an electron donor-acceptor complex (EDA) between electron-rich aziridine **7** and electron-poor maleimide **8**. The spectroscopic analysis revealed no formation of a new absorption band upon mixing the two reaction components, ruling out the formation of the EDA complex.

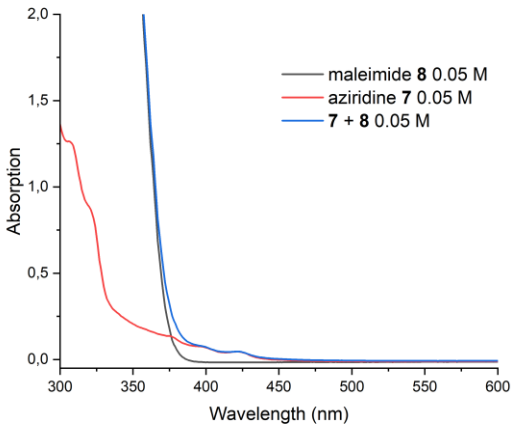


*Figure S22. Absorption spectra of maleimide **8** (0.05 M), aziridine **7** (0.05 M) and an equimolar mixture of **7** and **8** (0.05 M) in MeCN.*

Absorption and Emission Profiles of Starting Materials and Products

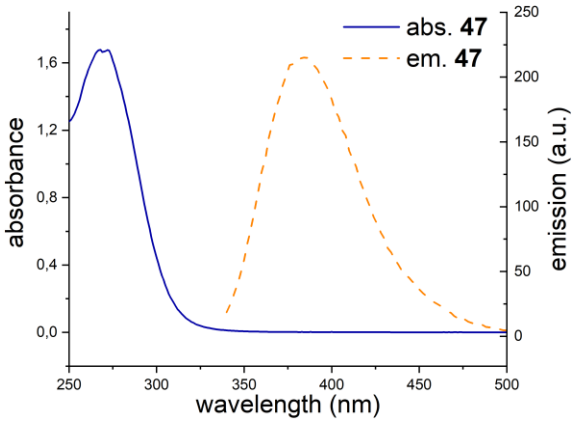


*Figure S23. Absorption and emission spectra of **47.** The absorption spectrum was recorded on a 10^{-3} M solution of **47** in MeCN. The emission spectrum was recorded on a 10^{-5} M solution of **47** in MeCN (λ_{exc} = 310 nm).*

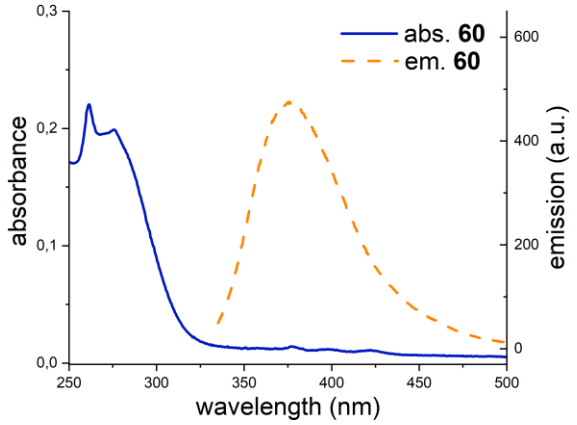


*Figure S24. Absorption and emission spectra of **60.** The absorption spectrum was recorded on a 10^{-5} M solution of **60** in MeCN. The emission spectrum was recorded on a 10^{-5} M solution of **60** in MeCN (λ_{exc} = 310 nm).*

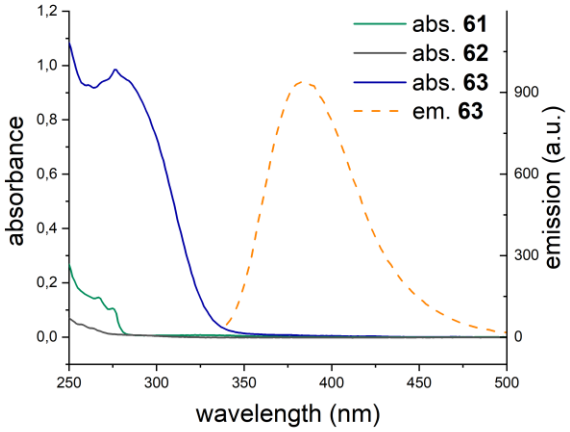


*Figure S25. Absorption spectra of **61**, **62** and **63** and emission spectrum of **63.** The absorption spectra were recorded on a 10^{-3} M solution of **61**, **62** and **63** in MeCN. The emission spectrum was recorded on a 10^{-5} M solution of **63** in MeCN (λ_{exc} = 310 nm).*

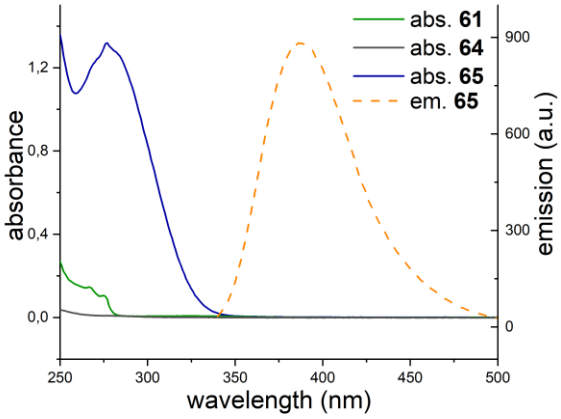
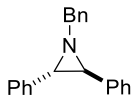


*Figure S26. Absorption spectra of **61**, **64** and **65** and emission spectrum of **65.** The absorption spectra were recorded on a 10^{-3} M solution of **61**, **64** and **65** in MeCN. The emission spectrum was recorded on a 10^{-5} M solution of **65** in MeCN (λ_{exc} = 320 nm).*

I. References

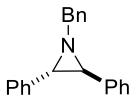
1. (a) Watson, I. D. G.; Yudin, A. K., Ring-Opening Reactions of Nonactivated Aziridines Catalyzed by Tris(pentafluorophenyl)borane. *J. Org. Chem.* **2003,** *68* (13), 5160-5167. (b) Pfister, J. R., A One-Pot Synthesis of Aziridines from 2-Aminoethanols. *Synthesis* **1984,** *1984* (11), 969-970.
2. Lutz, R. E.; Freek, J. A.; Murphey, R. S., Secondary and Tertiary Amino Ketones and Alcohols Derived from Desoxybenzoin and 1,2-Diphenylethanol. Ring-Chain Tautomerism of the α-(β-Hydroxyethylamino) Ketones. *J. Am. Chem. Soc.* **1948,** *70* (6), 2015-2023.
3. Huisgen, R.; Matsumoto, K.; Ross, C. H., Cycloadditions of 1-Substituted cis- and trans-2,3-Diphenylaziridines via Azomethine Ylides. *Heterocycles* **1981,** *15* (2), 1131-1136.
4. Mayer, M. F.; Hossain, M. M., Catalytic Preparation of Aziridines with an Iron Lewis Acid. *J. Org. Chem.* **1998,** *63* (20), 6839-6844.
5. Fan, G.; Liu, Y., Titanium-mediated cross-coupling reactions of imines with ketones or aldehydes: an efficient route for the synthesis of 1,2-amino alcohols. *Tetrahedron Lett.* **2012,** *53* (38), 5084-5087.
6. Sengoku, T.; Murata, Y.; Aso, Y.; Kawakami, A.; Inuzuka, T.; Sakamoto, M.; Takahashi, M.; Yoda, H., Indium-Catalyzed Amide Allylation of N-Carbonyl Imides: Formation of Azaspiro-γ-lactones via Ring Opening–Reclosure. *Org. Lett.* **2015,** *17* (23), 5846-5849.
7. Zhu, Y.; Chen, F.; Zhao, X.; Yan, D.; Yong, W.; Zhao, J., Cobalt(III)-Catalyzed Intermolecular Carboamination of Propiolates and Bicyclic Alkenes via Non-Annulative Redox-Neutral Coupling. *Org. Lett.* **2019,** *21* (15), 5884-5888.
8. Papanastassiou, Z. B.; Bruni, R. J.; White V, E. V., Potential Carcinolytic Agents.1,2 V. Enamine Mustards. *J. Med. Chem.* **1967,** *10* (4), 701-706.
9. Wittland, C.; Arend, M.; Risch, N., Synthesis of 2,4,5-Triphenyl-Substituted Oxazolidine and 2,5-Diphenyl-Substituted Pyrrolidine Derivatives. *Synthesis* **1996,** *1996* (03), 367-371.

J. NMR spectra



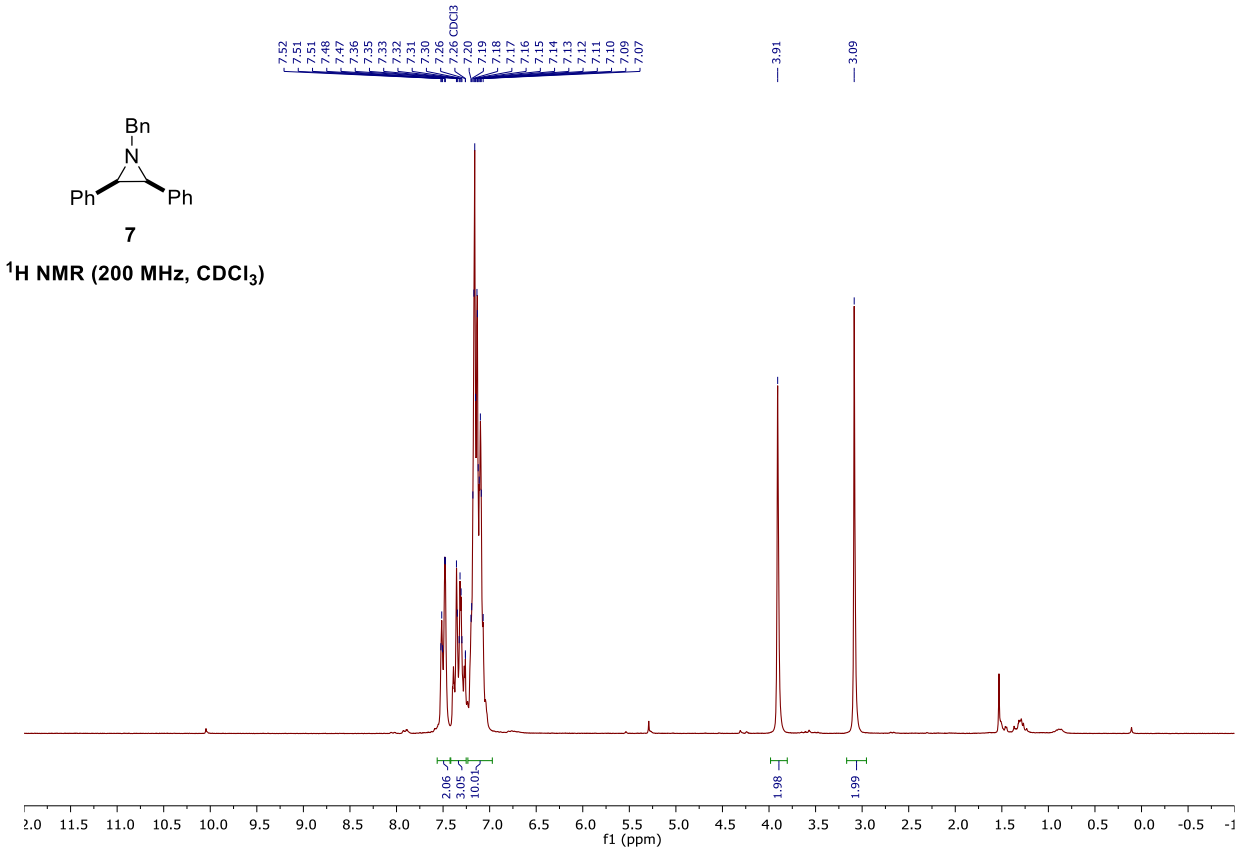
7

^{1}H NMR (300 MHz, $CDCl_3$)



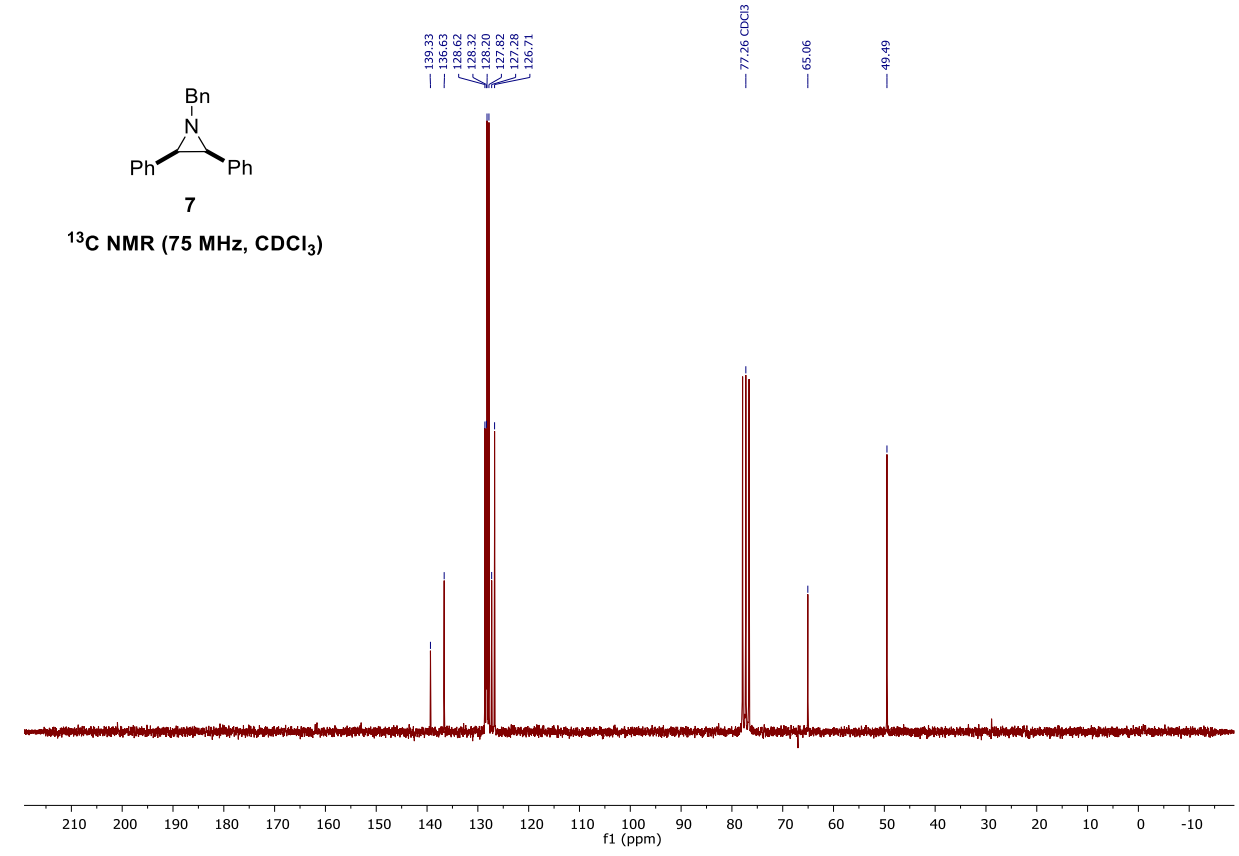
7

^{13}C NMR (75 MHz, $CDCl_3$)



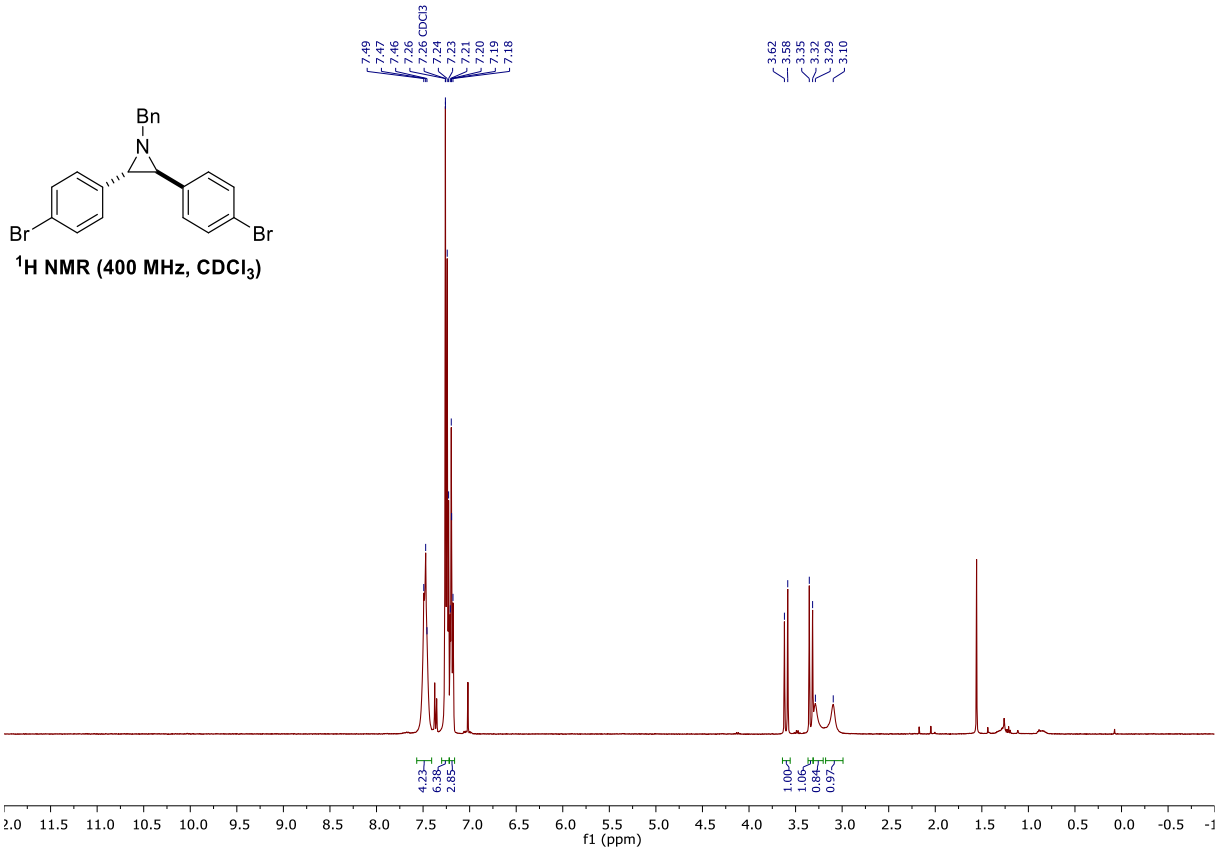
7

^{1}H NMR (200 MHz, $CDCl_3$)

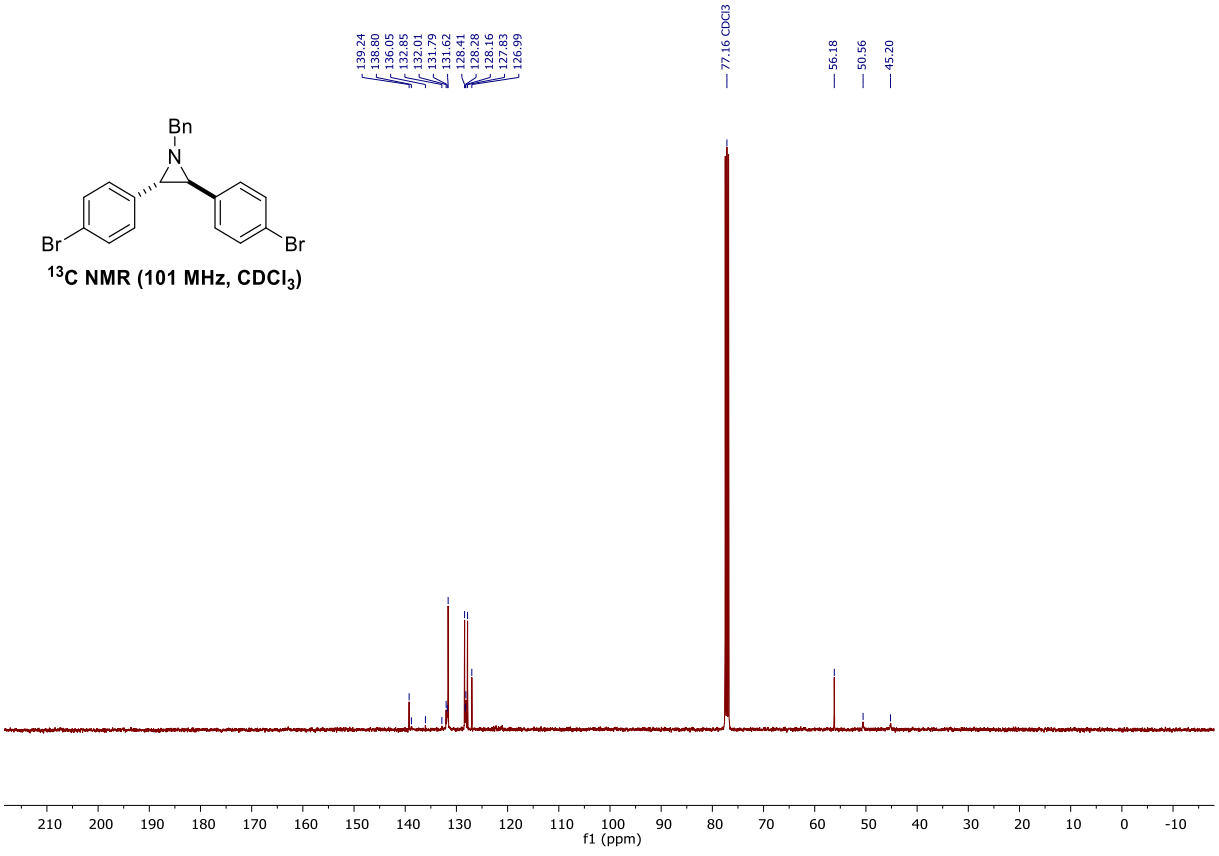


7

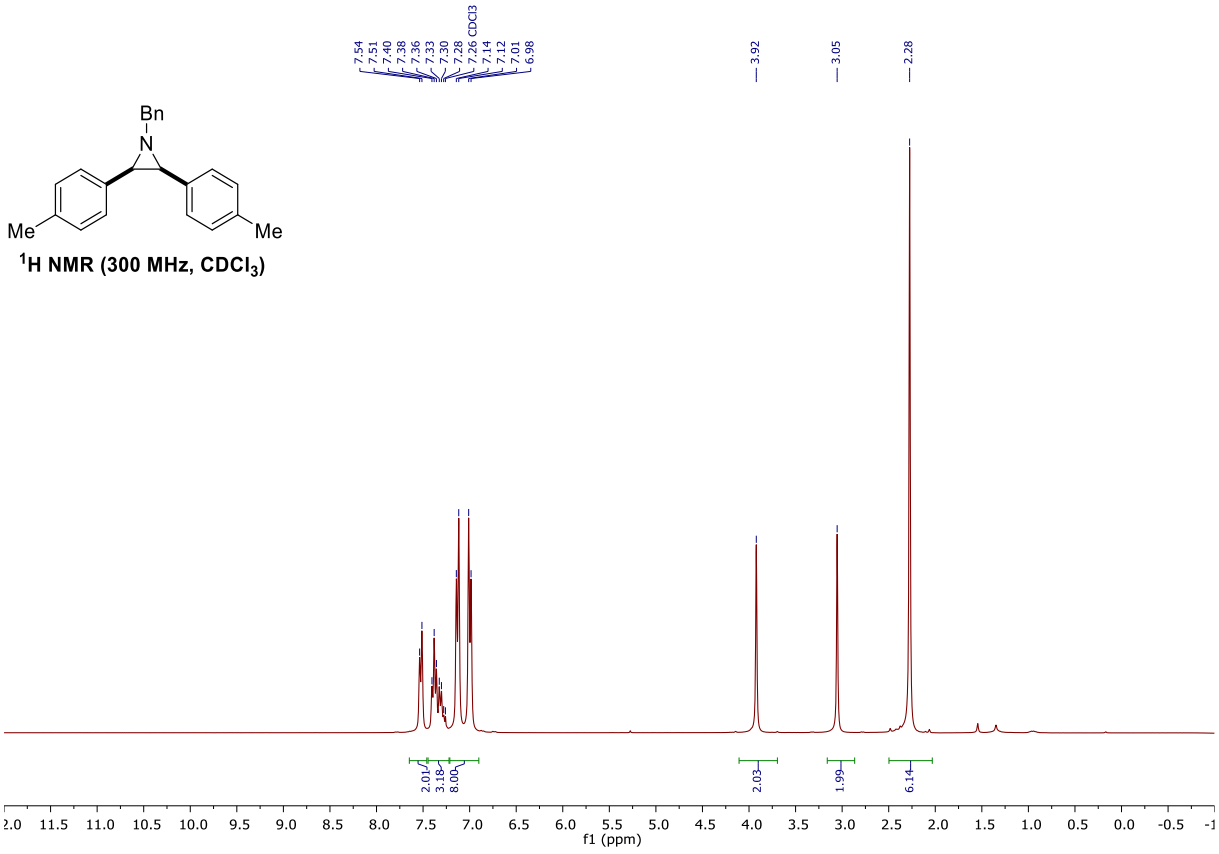
^{13}C NMR (75 MHz, $CDCl_3$)



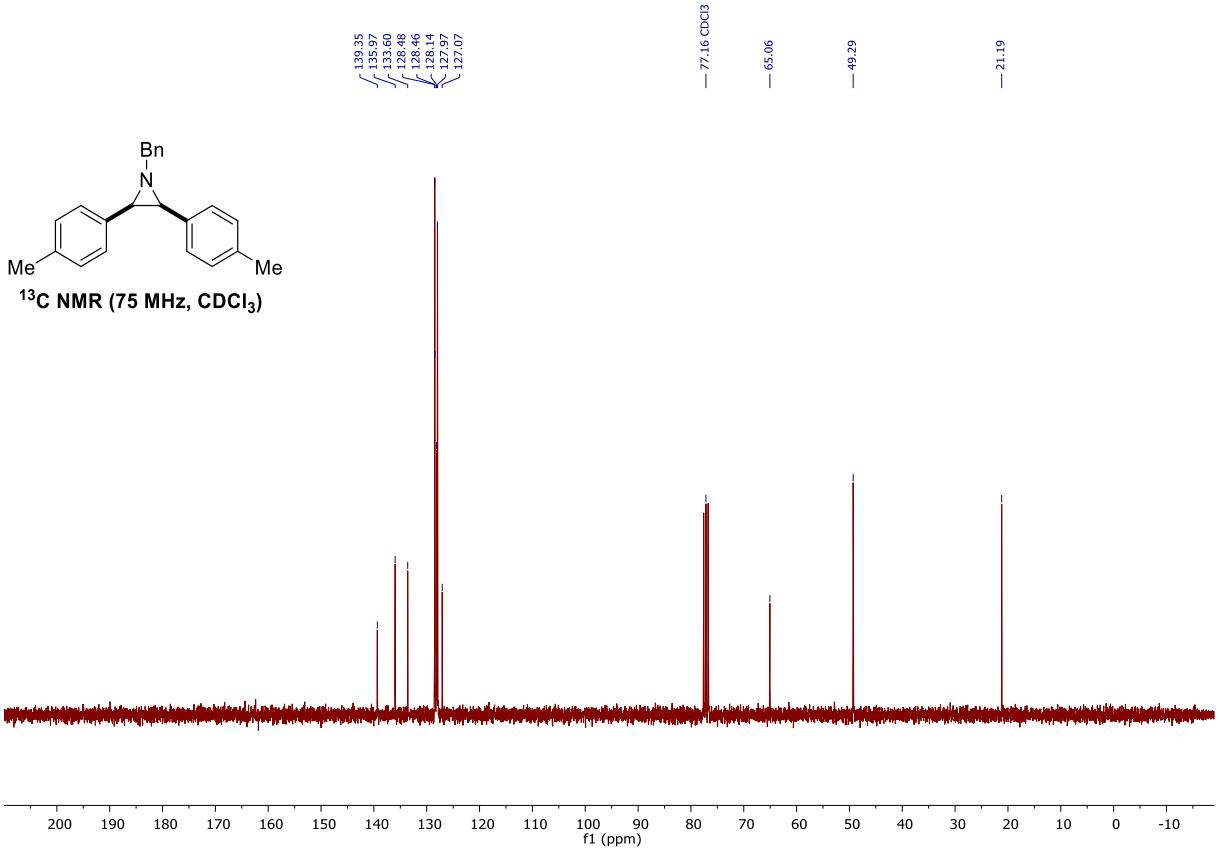
^{1}H NMR (400 MHz, $CDCl_3$)



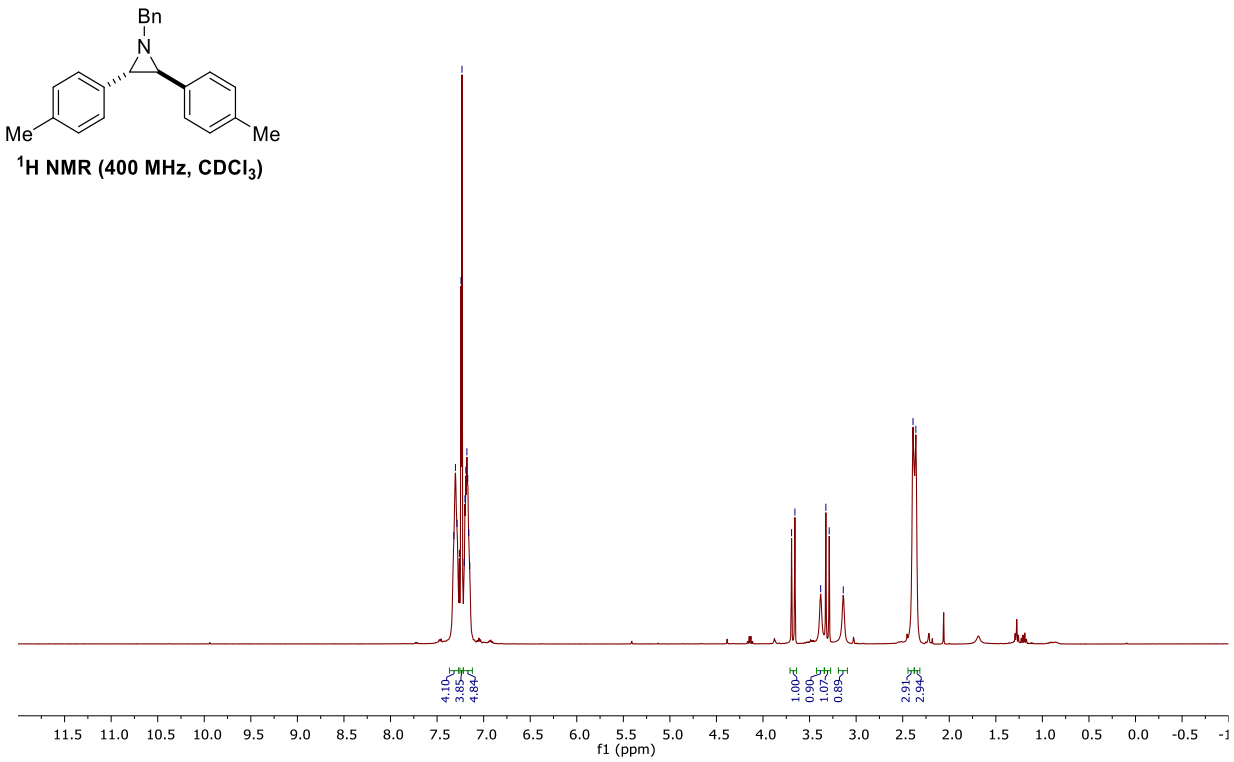
^{13}C NMR (101 MHz, $CDCl_3$)



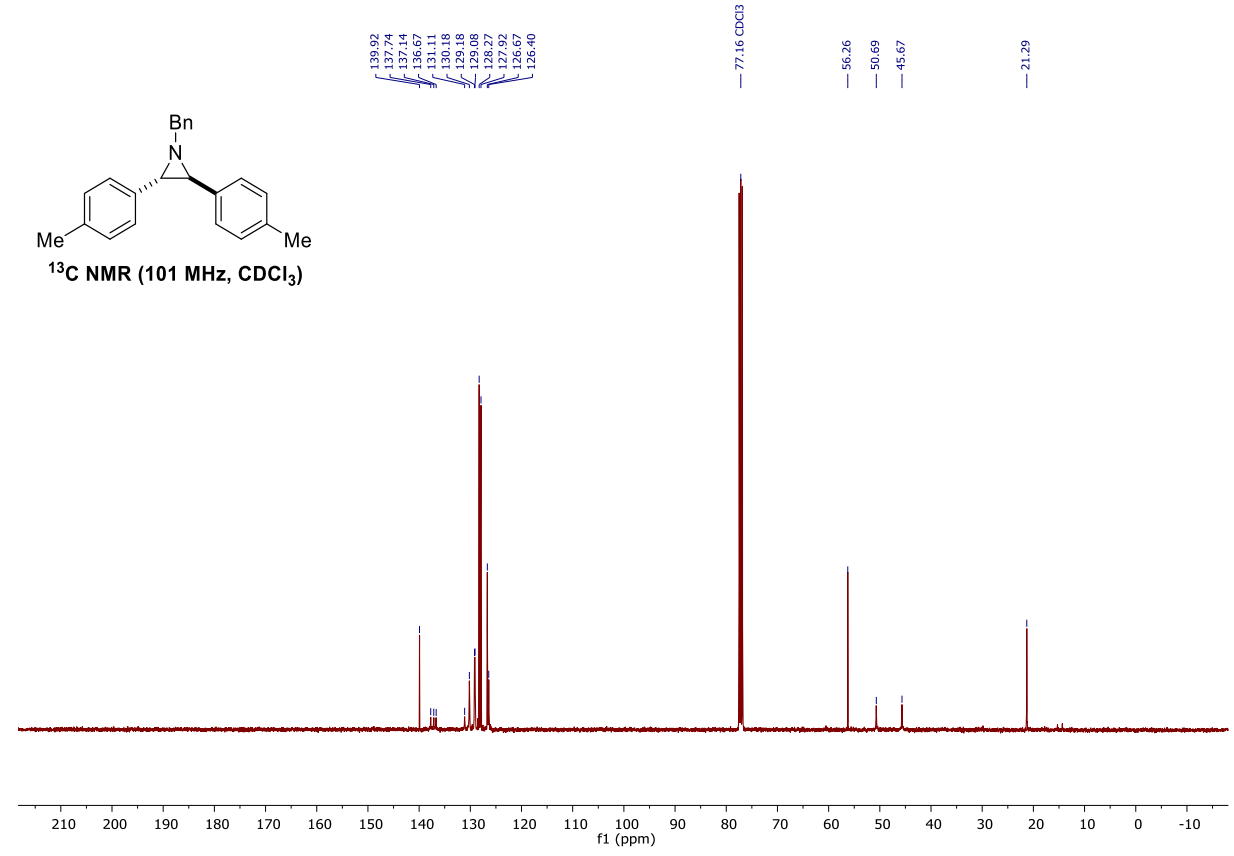
^{1}H NMR (300 MHz, $CDCl_3$)



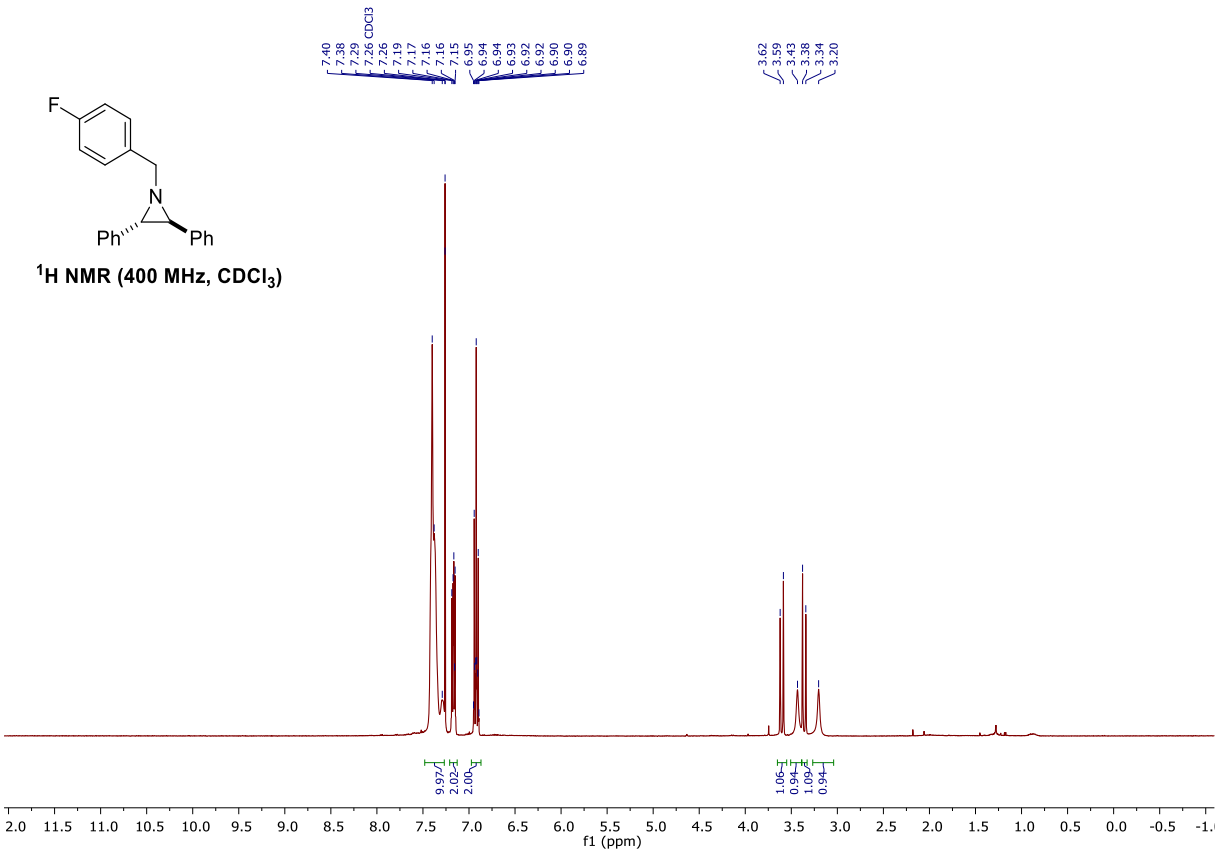
^{13}C NMR (75 MHz, $CDCl_3$)



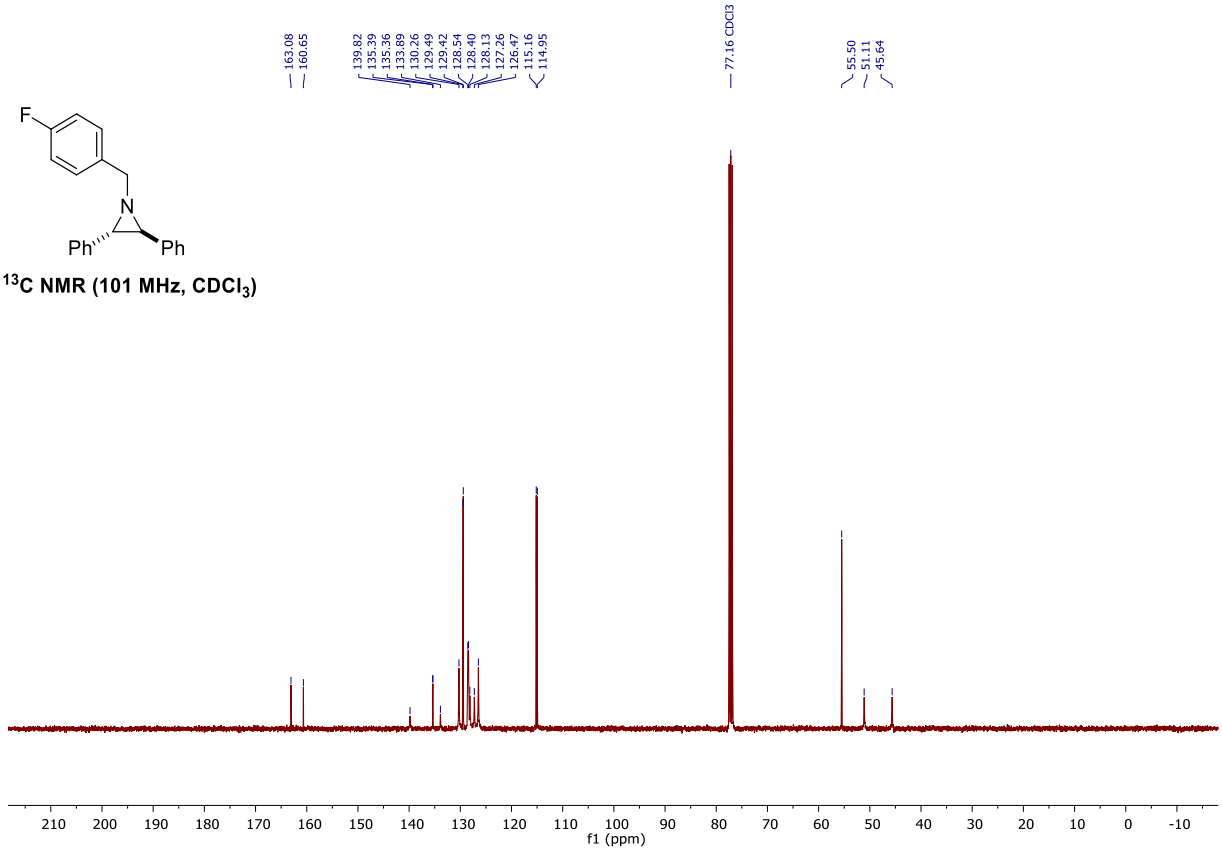
^{1}H NMR (400 MHz, $CDCl_3$)



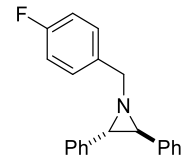
^{13}C NMR (101 MHz, $CDCl_3$)



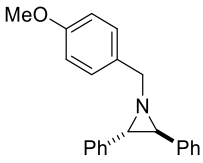
^{1}H NMR (400 MHz, $CDCl_3$)



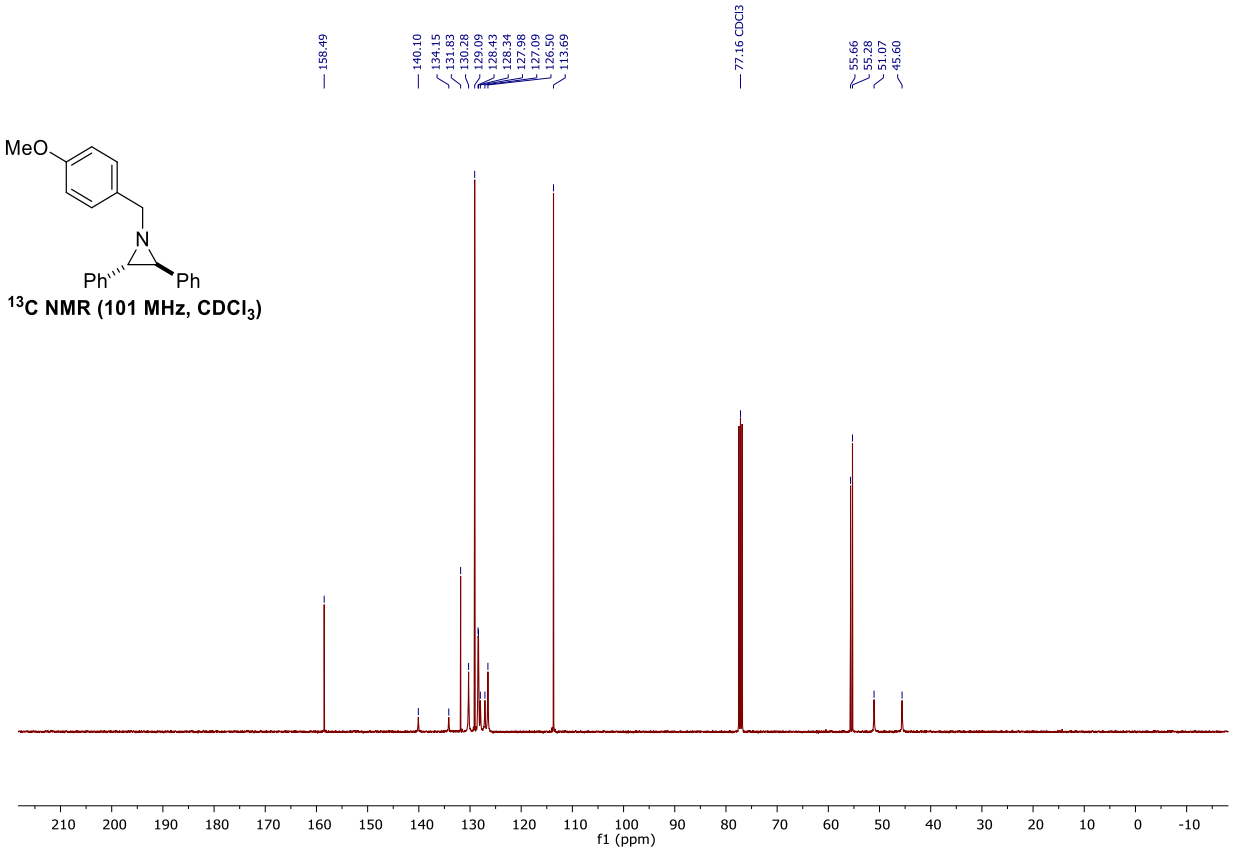
^{13}C NMR (101 MHz, $CDCl_3$)



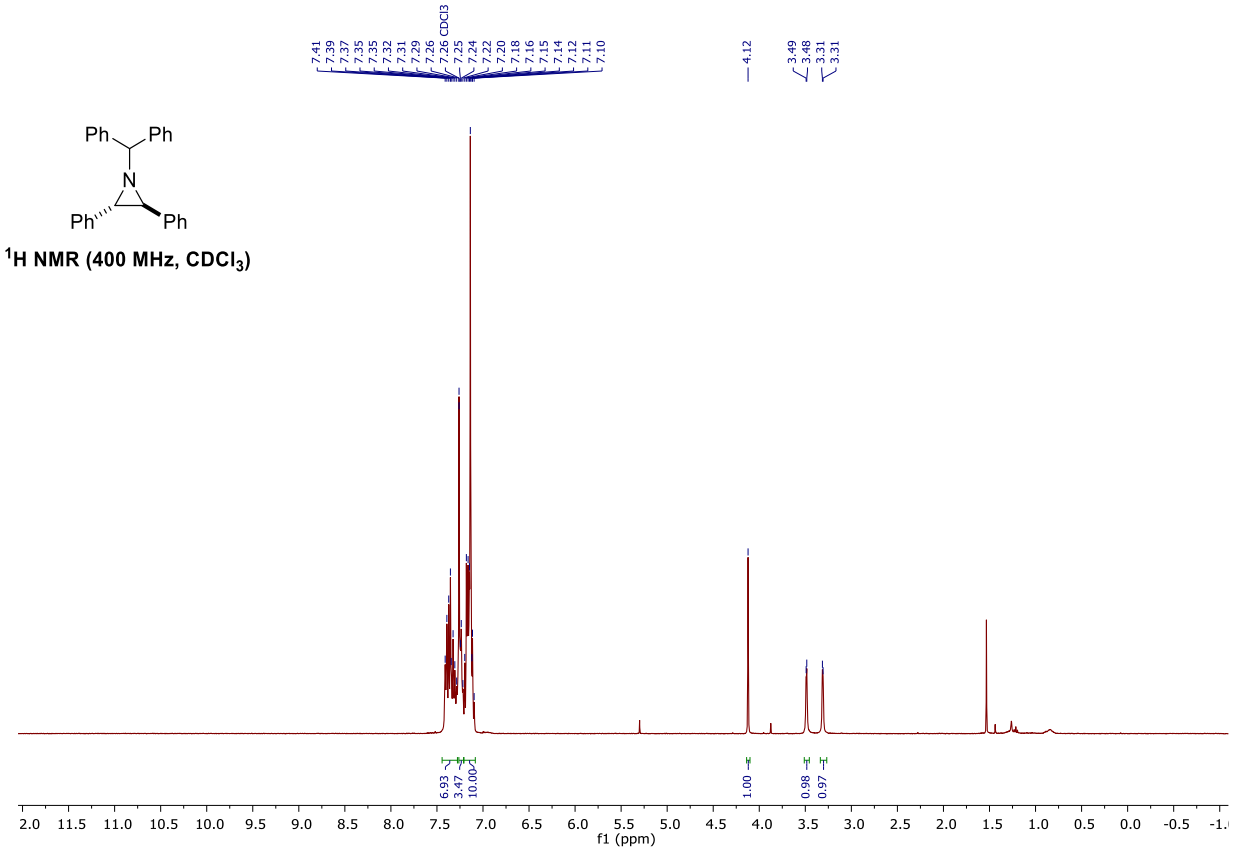
^{19}F NMR (377 MHz, $CDCl_3$)



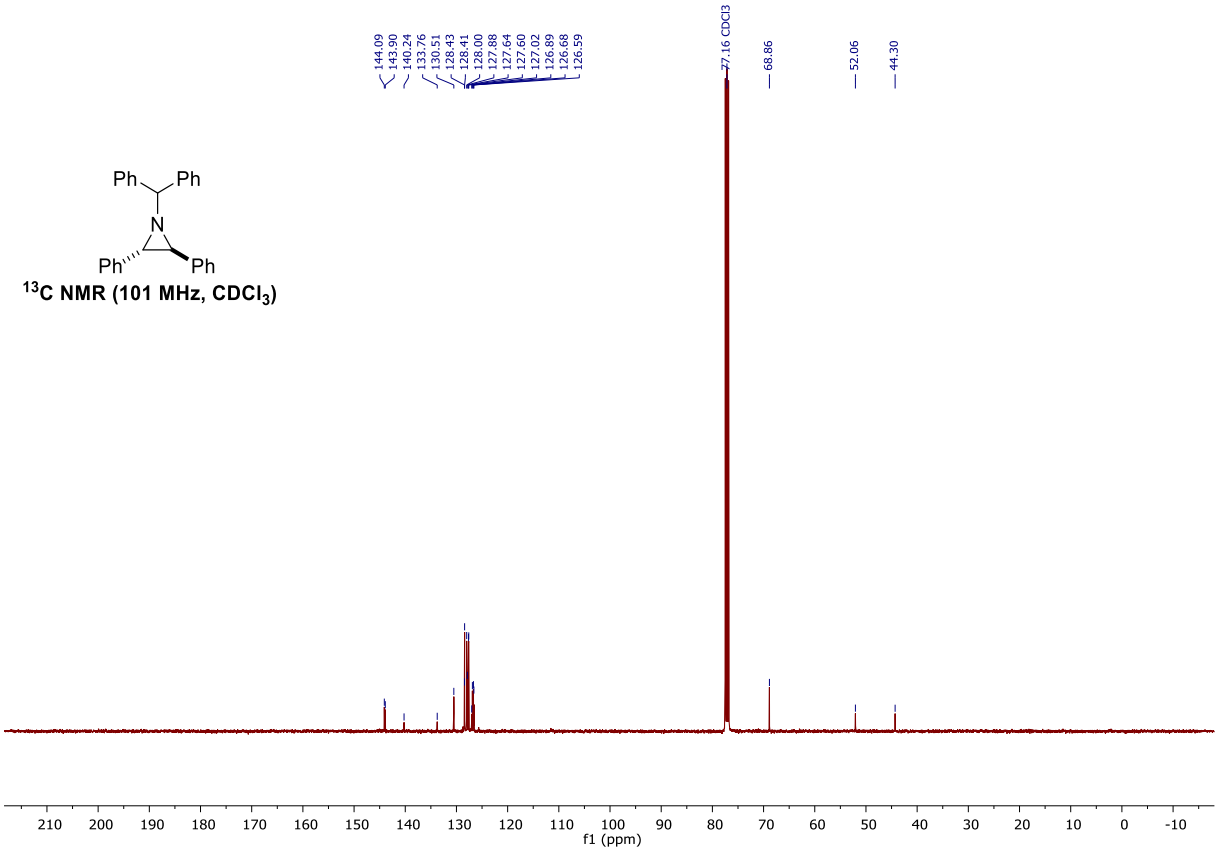
^{1}H NMR (400 MHz, $CDCl_3$)



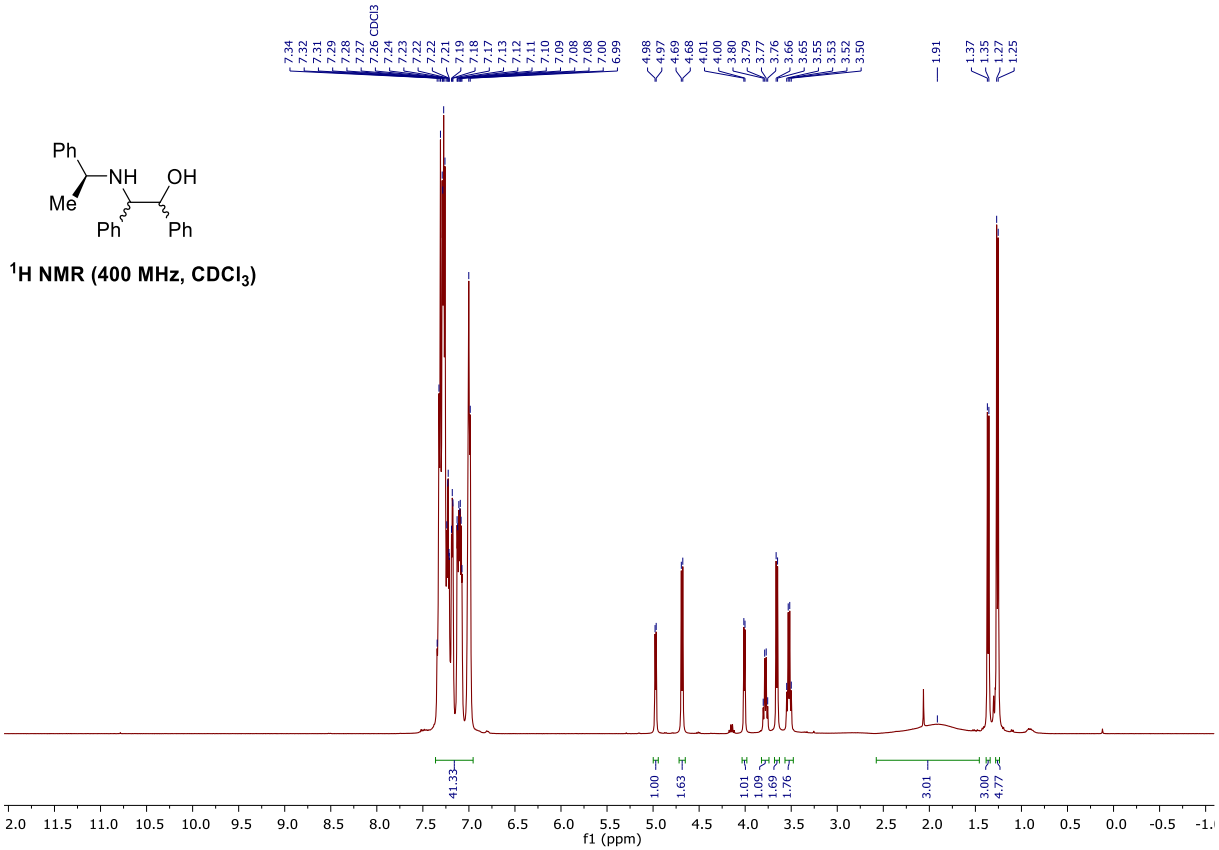
^{13}C NMR (101 MHz, $CDCl_3$)



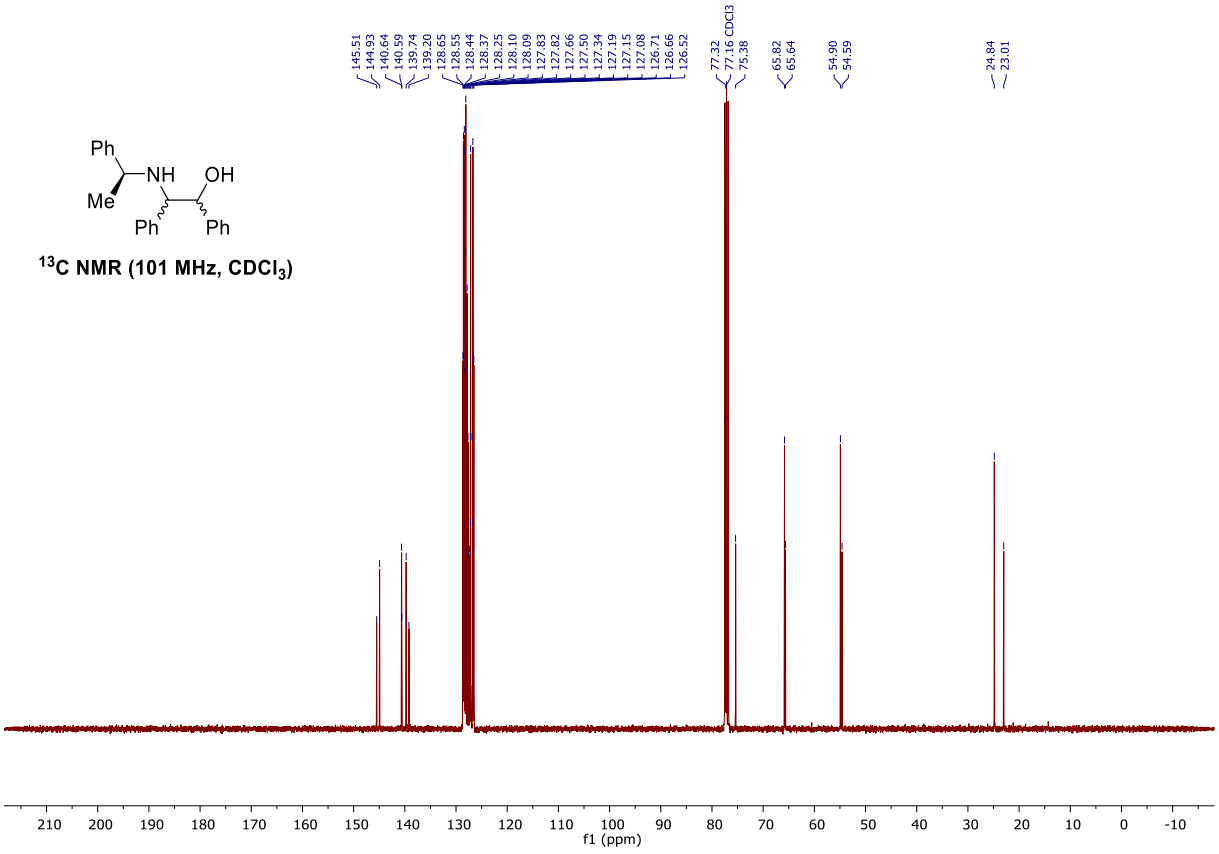
^{1}H NMR (400 MHz, $CDCl_3$)



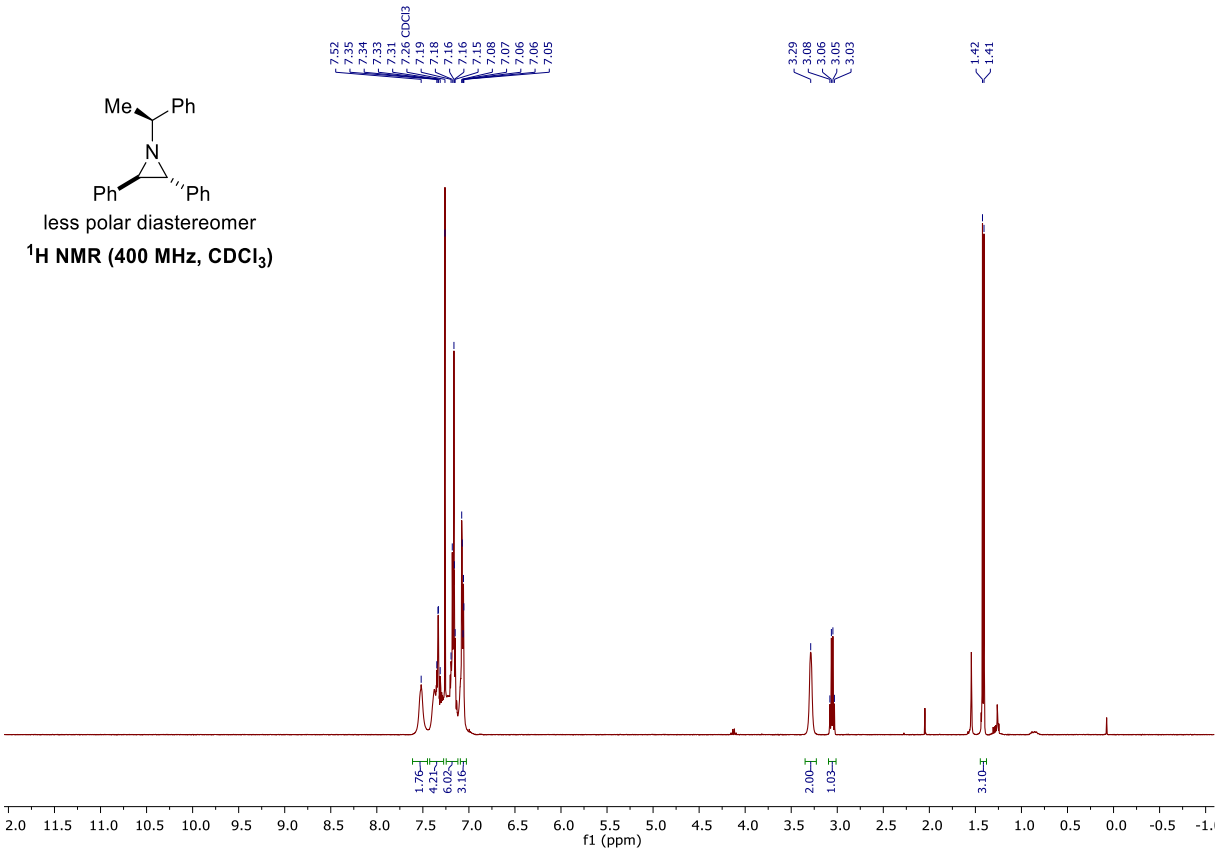
^{13}C NMR (101 MHz, $CDCl_3$)



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

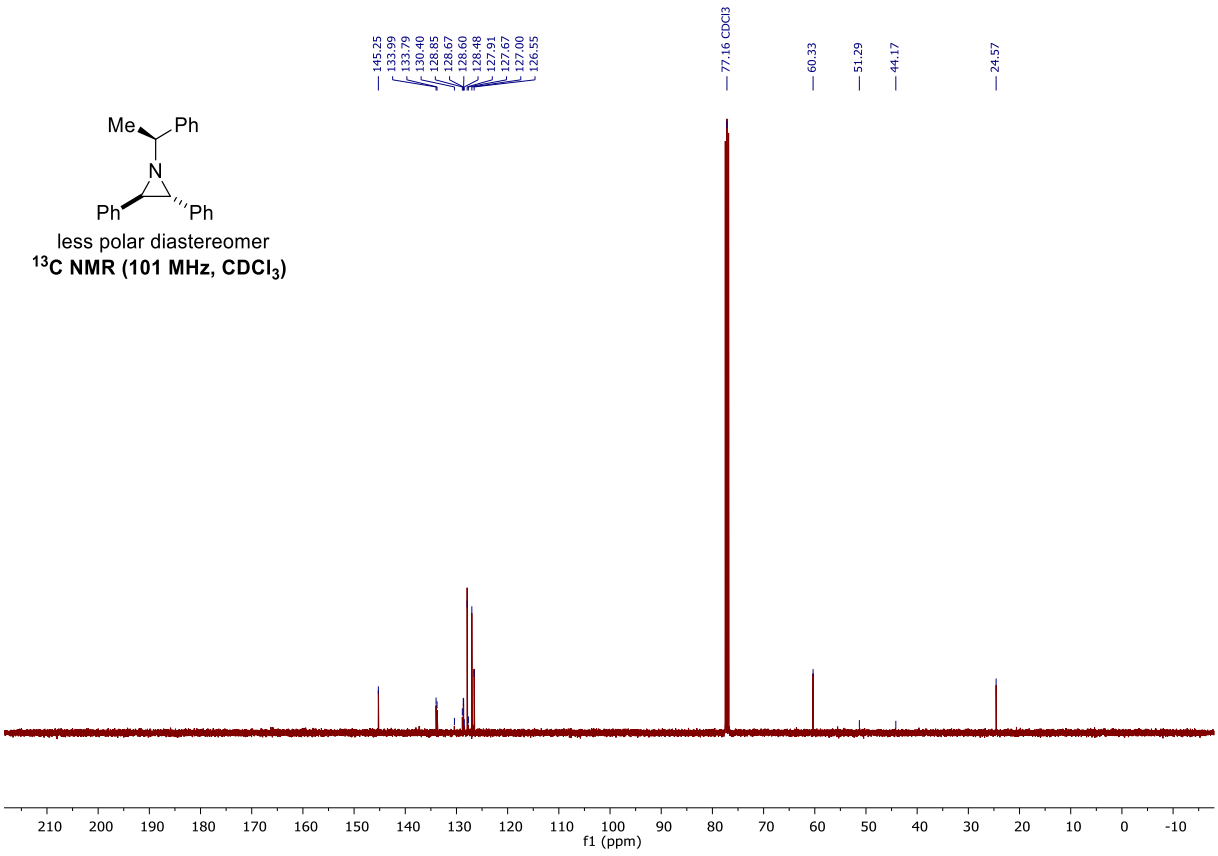


^{13}C NMR (101 MHz, $CDCl_3$)



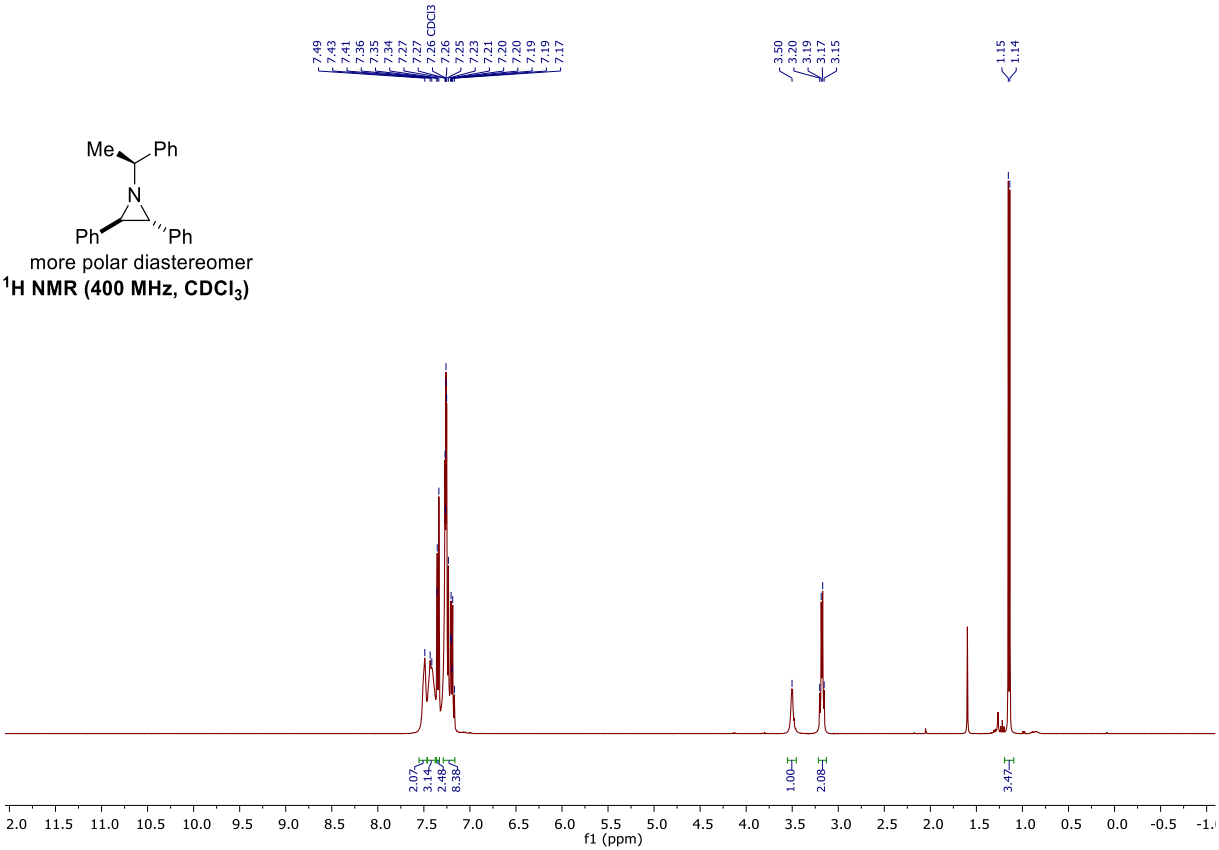
less polar diastereomer

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



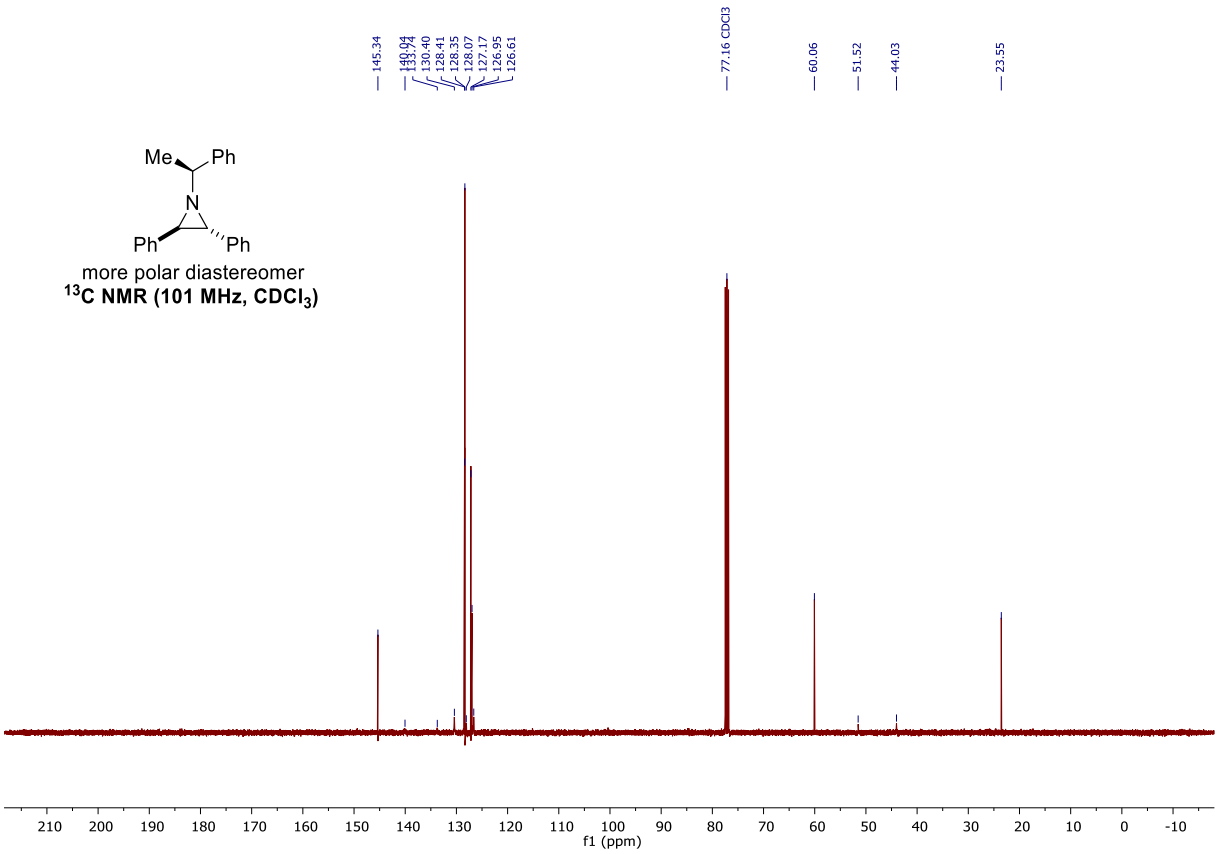
less polar diastereomer

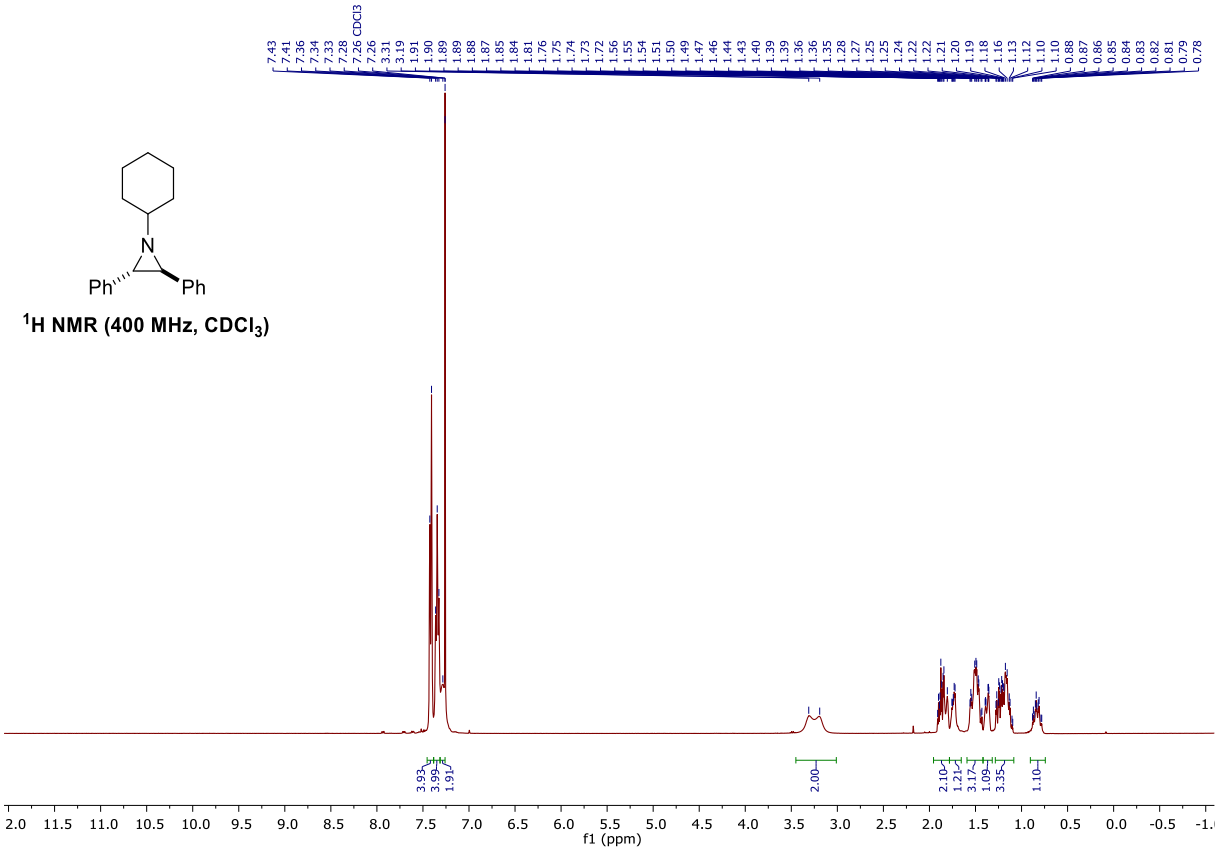
^{13}C NMR (101 MHz, $CDCl_3$)

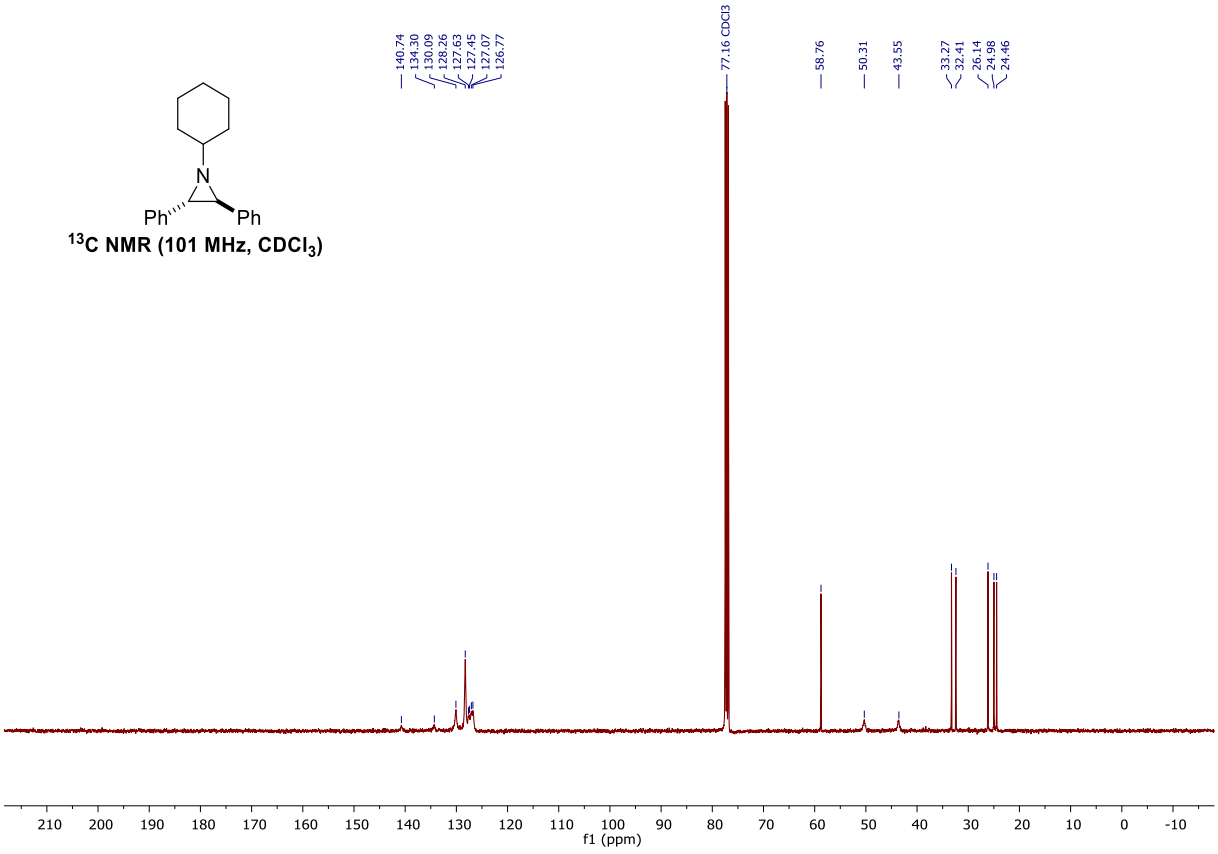


more polar diastereomer

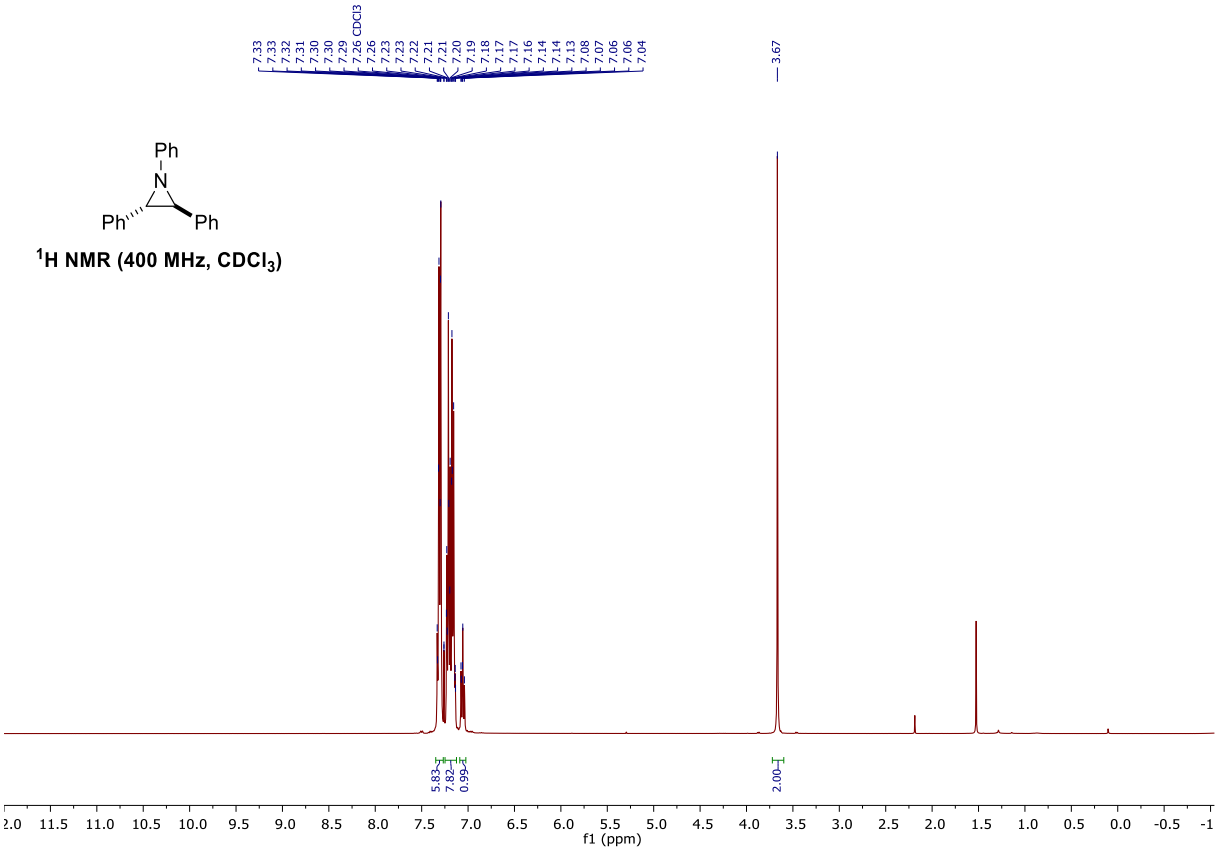
^{1}H NMR (400 MHz, $CDCl_3$)


Me
Ph
N
Ph
Ph
more polar diastereomer
13C NMR (101 MHz, CDCl3)
145.34
140.04
133.74
130.40
128.41
128.35
128.07
127.17
126.95
126.61
77.16 CDCl3
60.06
51.52
44.03
23.55
f1 (ppm)

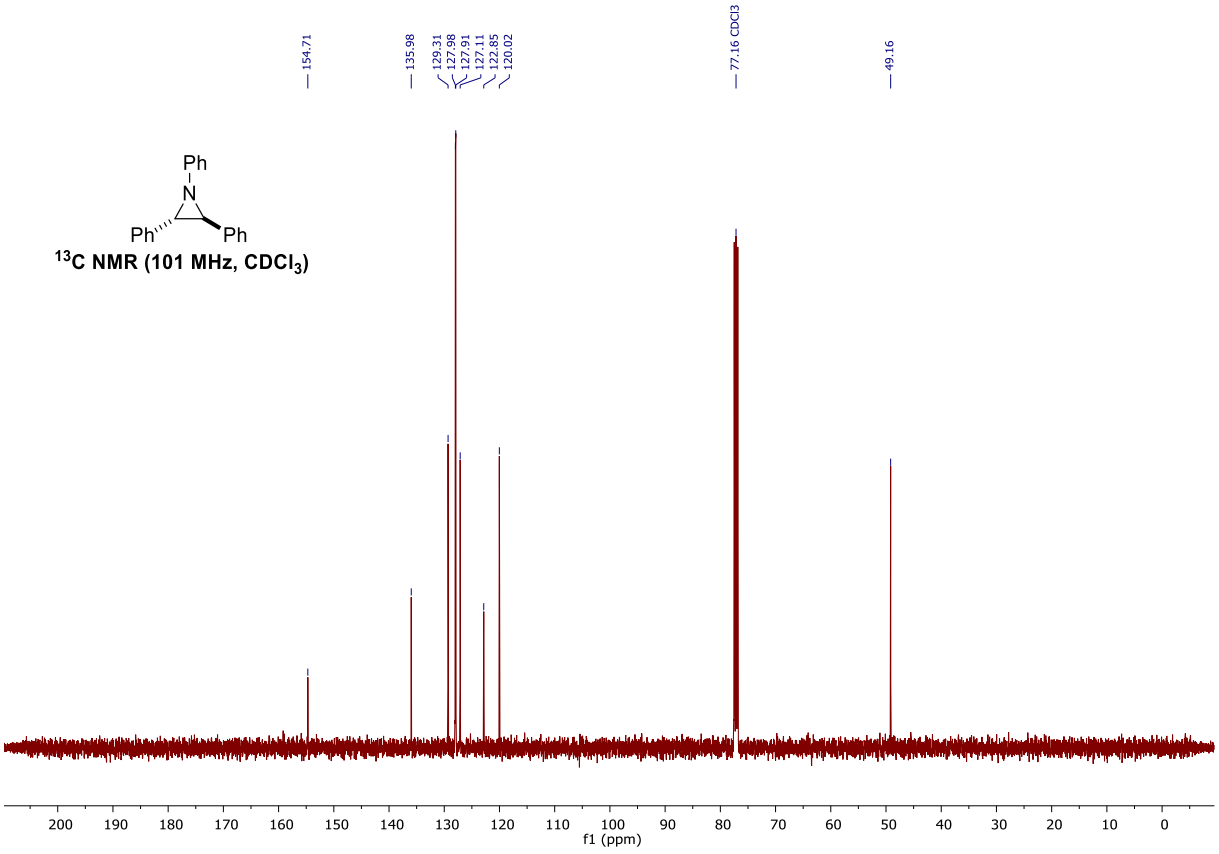

N
Ph
Ph
1H NMR (400 MHz, CDCl3)
7.26 CDCl3
3.93
3.99
1.91
2.00
2.10
1.21
3.17
1.09
3.35
1.10
f1 (ppm)

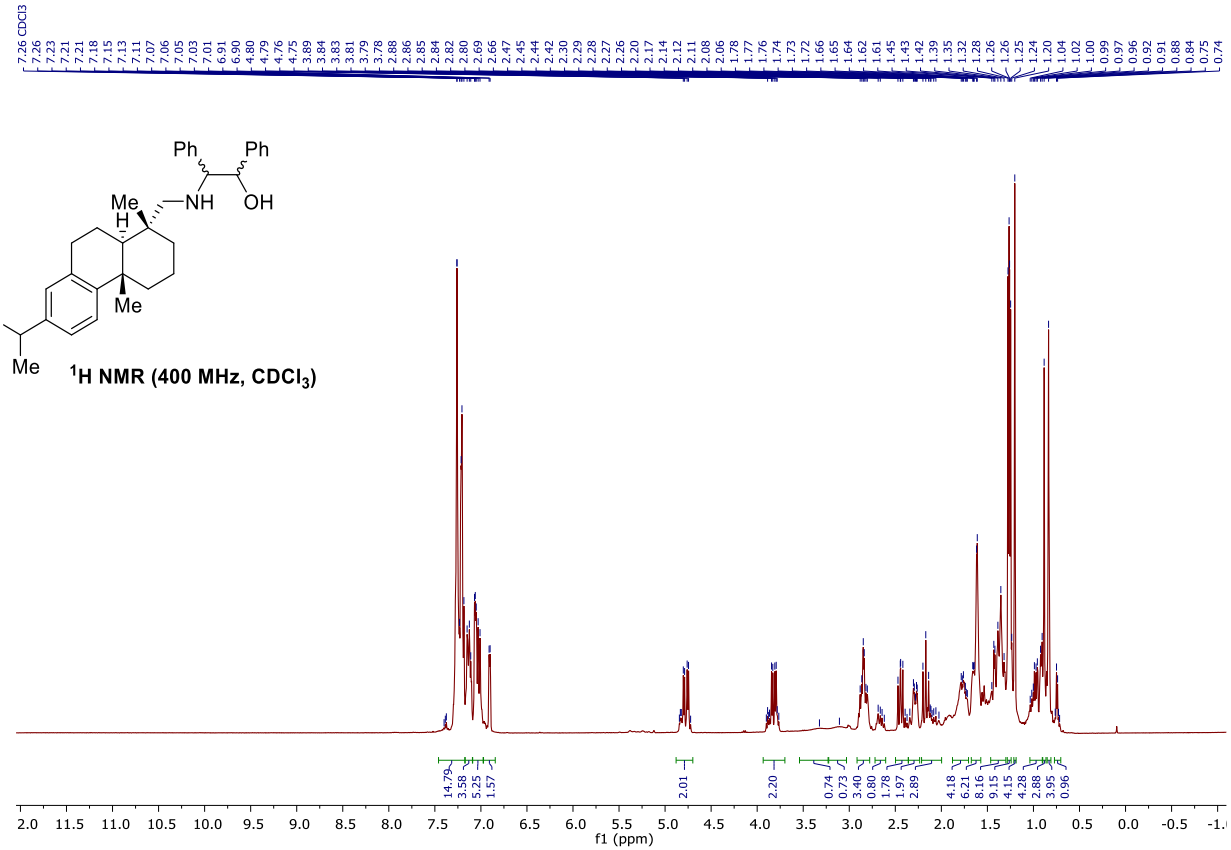


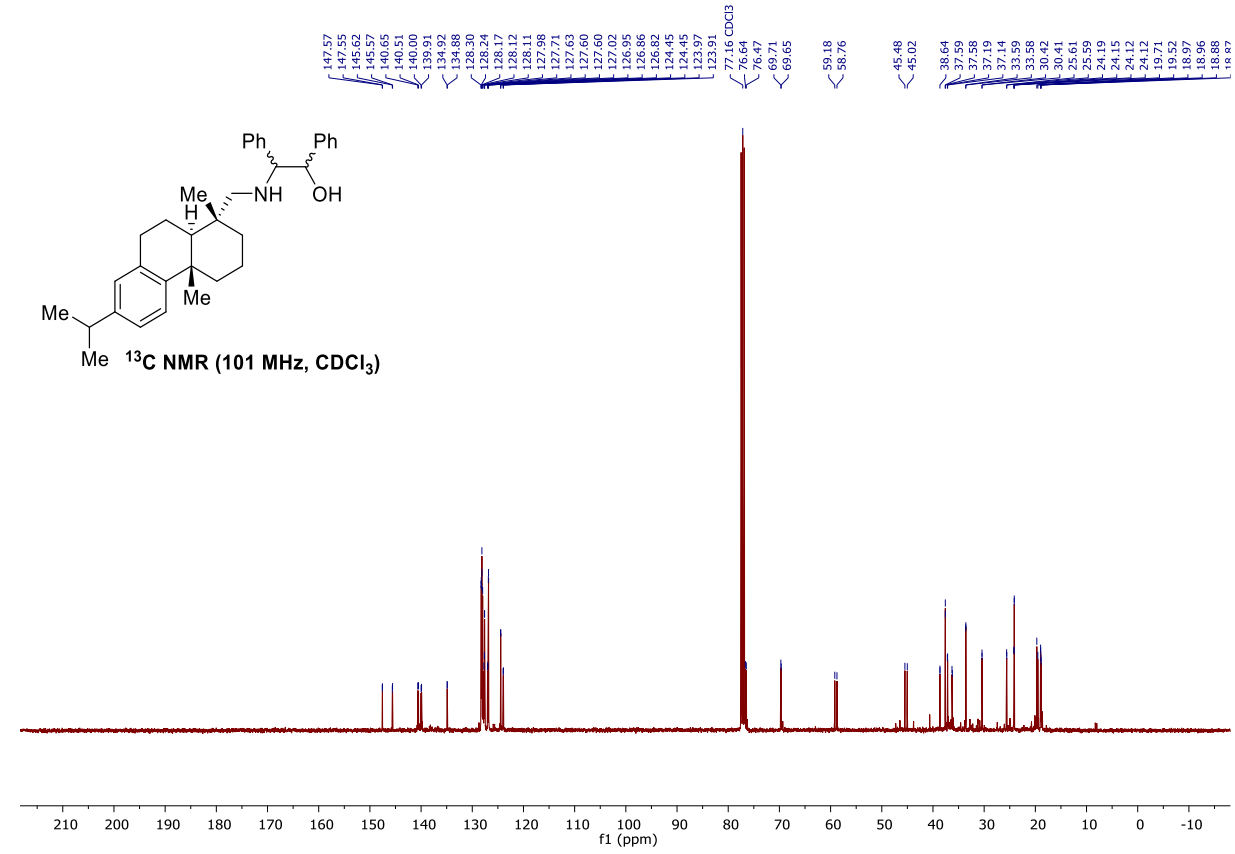
^{13}C NMR (101 MHz, $CDCl_3$)

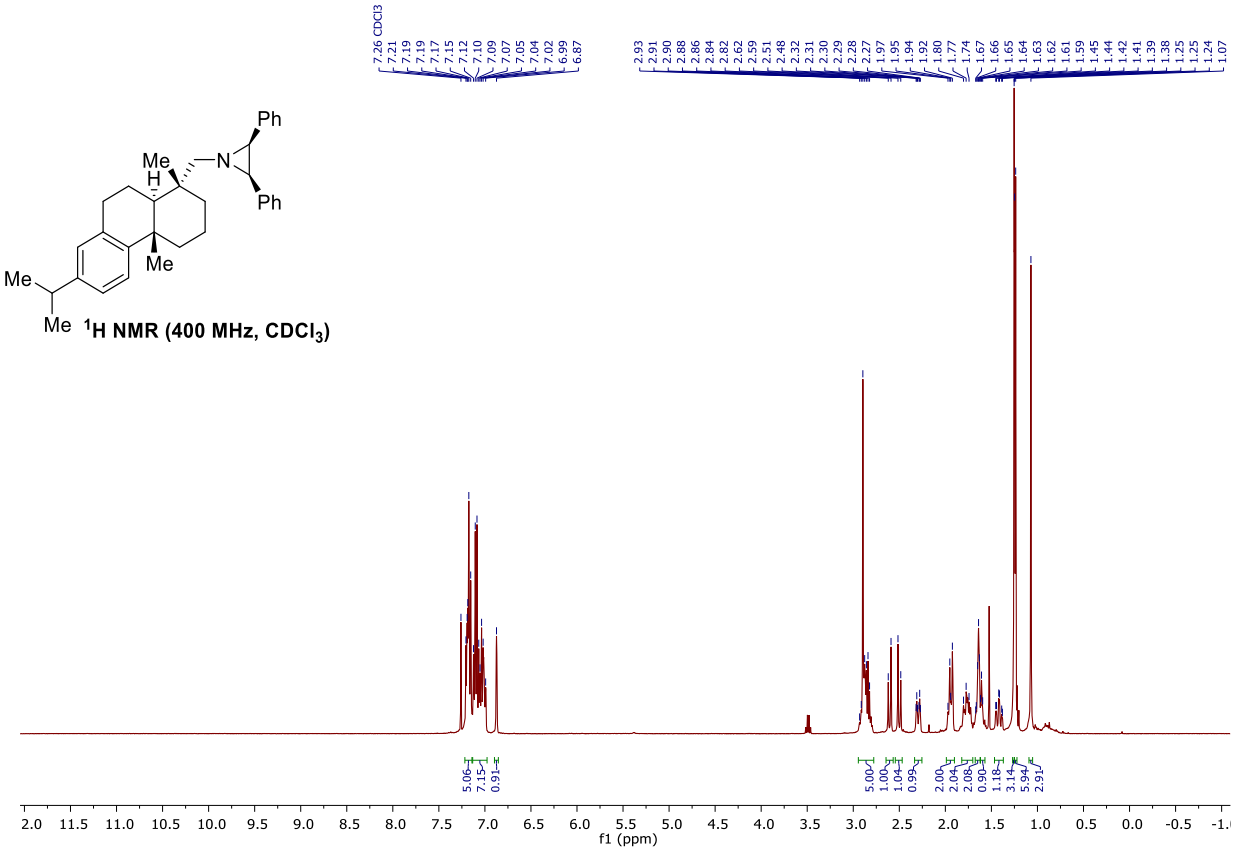


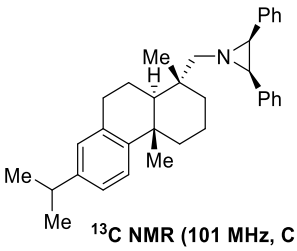
^{1}H NMR (400 MHz, $CDCl_3$)


154.71
135.98
129.31
127.98
127.91
127.11
122.85
120.02
77.16 CDCl3
49.16
Ph
N
Ph
Ph
13C NMR (101 MHz, CDCl3)
f1 (ppm)

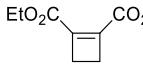

Ph
Ph
Me
NH
OH
H
Me
Me
Me
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Ph
Ph
Me
NH
OH
H
Me
Me
Me
Me
13C NMR (101 MHz, CDCl3)
f1 (ppm)

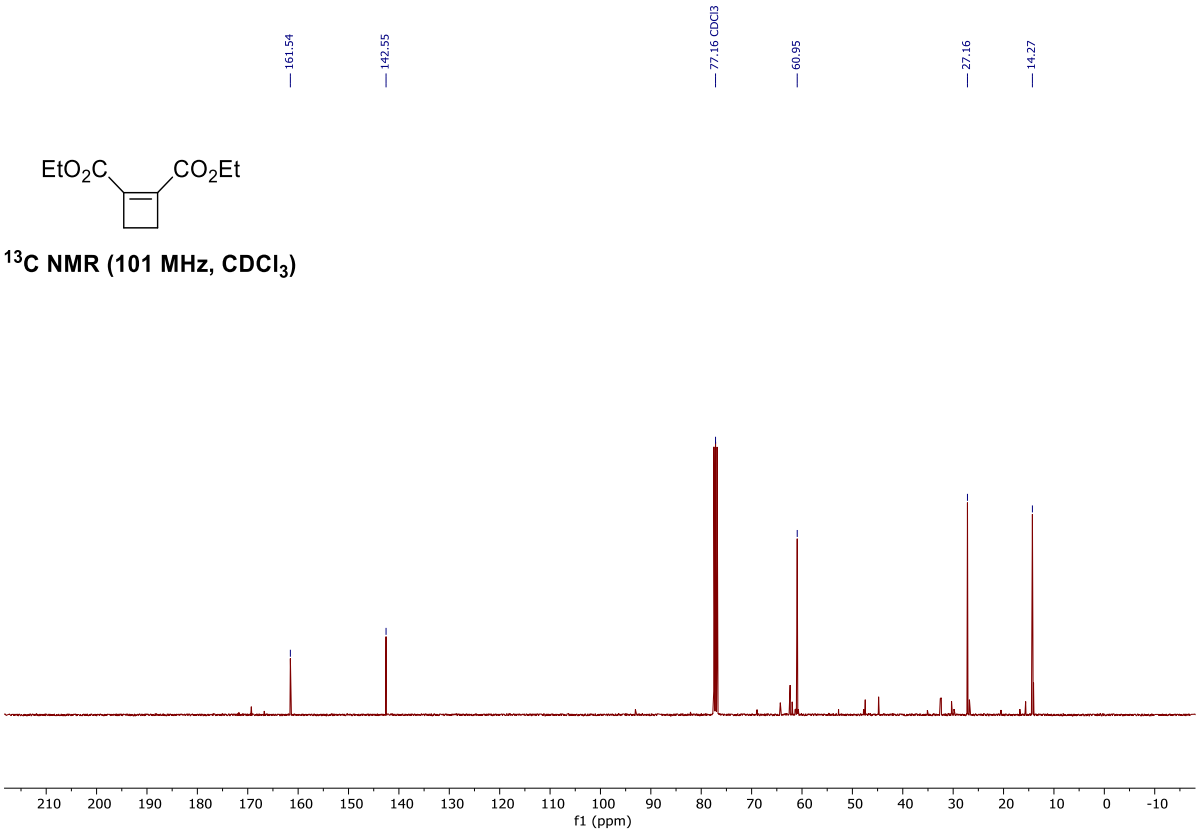

Ph
Me
N
H
Ph
Me
Me
Me
1H NMR (400 MHz, CDCl3)
f1 (ppm)

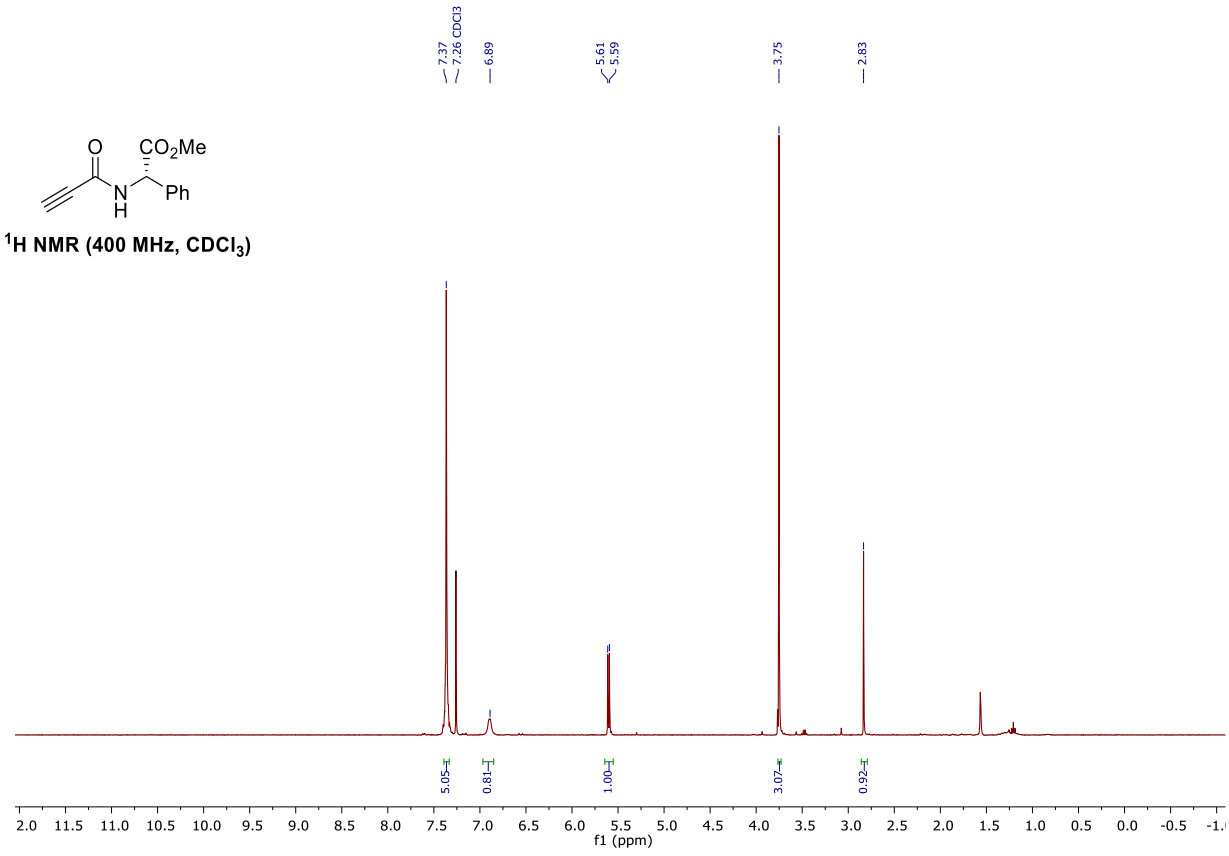


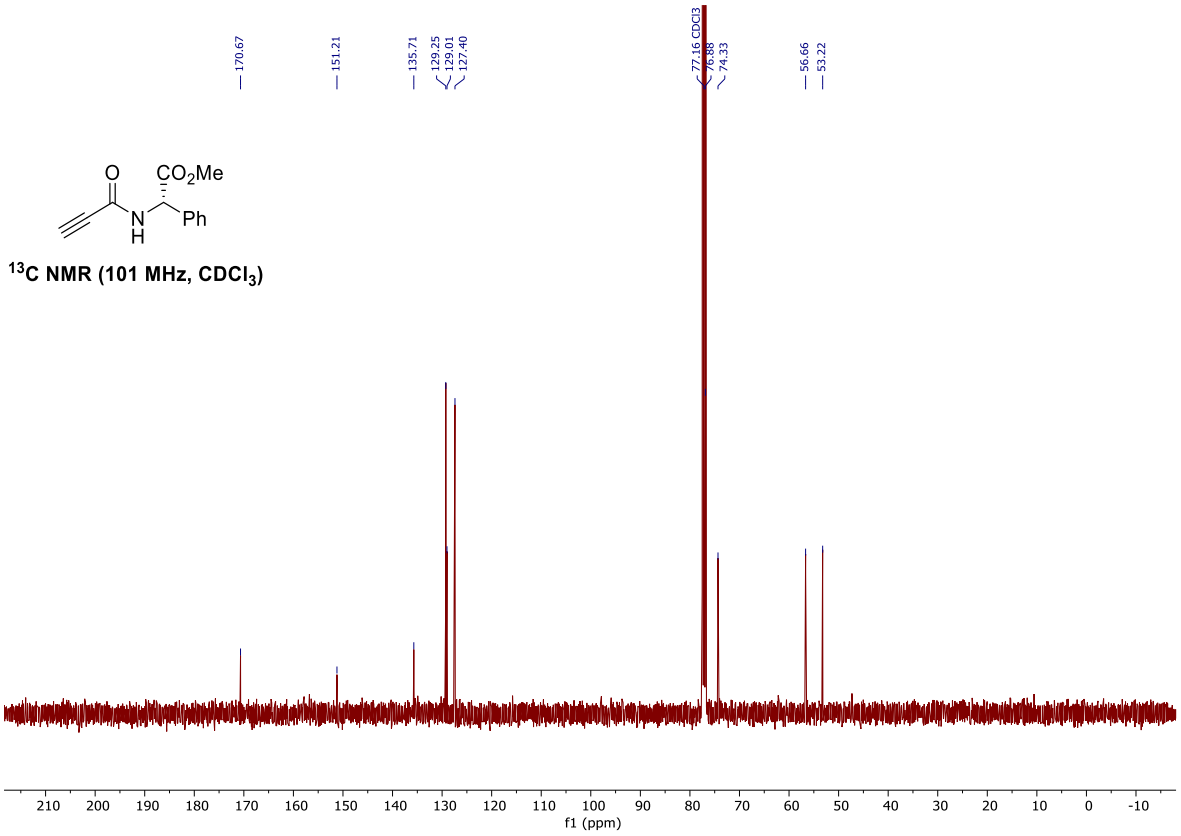
^{13}C NMR (101 MHz, $CDCl_3$)



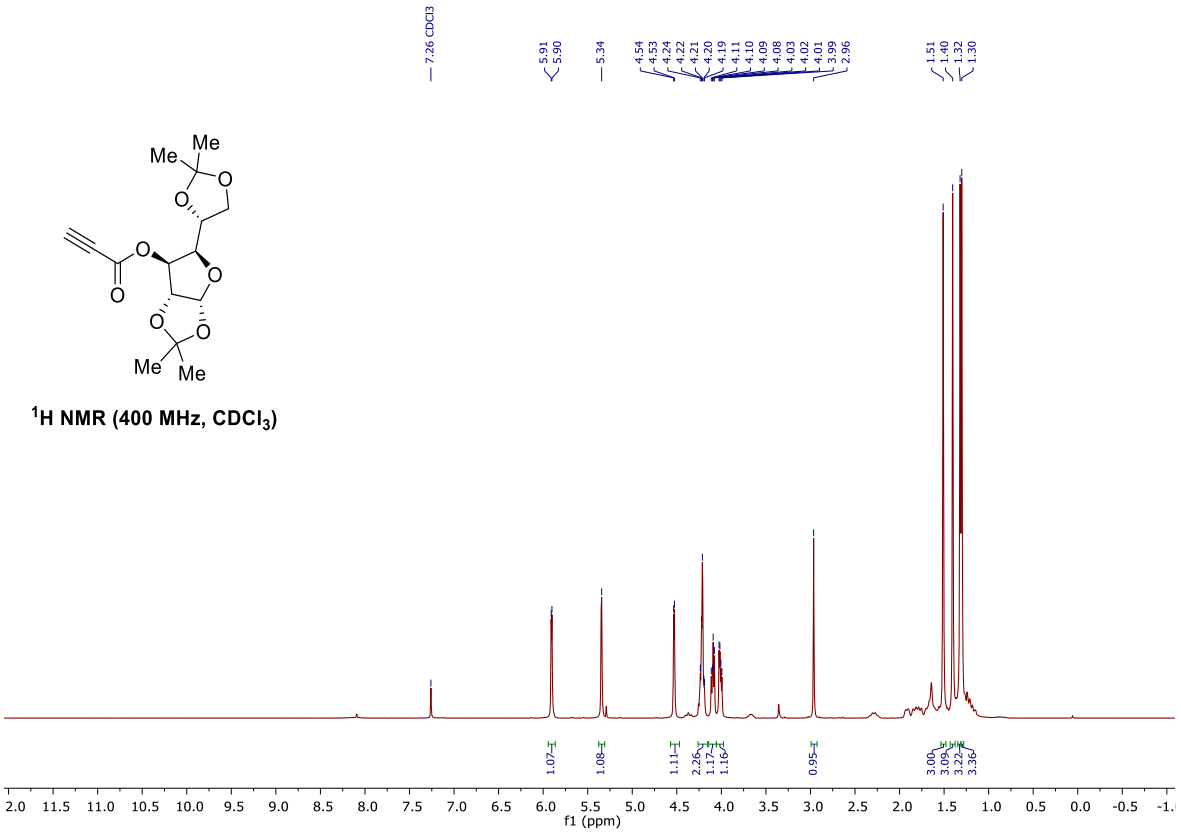
^{1}H NMR (400 MHz, $CDCl_3$)


161.54
142.55
77.16 CDCl3
60.95
27.16
14.27
EtO2C
CO2Et
13C NMR (101 MHz, CDCl3)
f1 (ppm)

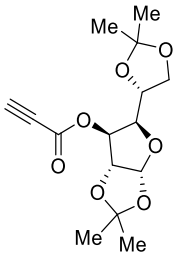

7.37
7.26 CDCl3
6.89
5.61
5.59
3.75
2.83
O
CO2Me
N
H
Ph
1H NMR (400 MHz, CDCl3)
5.05
0.81
1.00
3.07
0.92
f1 (ppm)



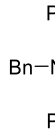
^{13}C NMR (101 MHz, $CDCl_3$)



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

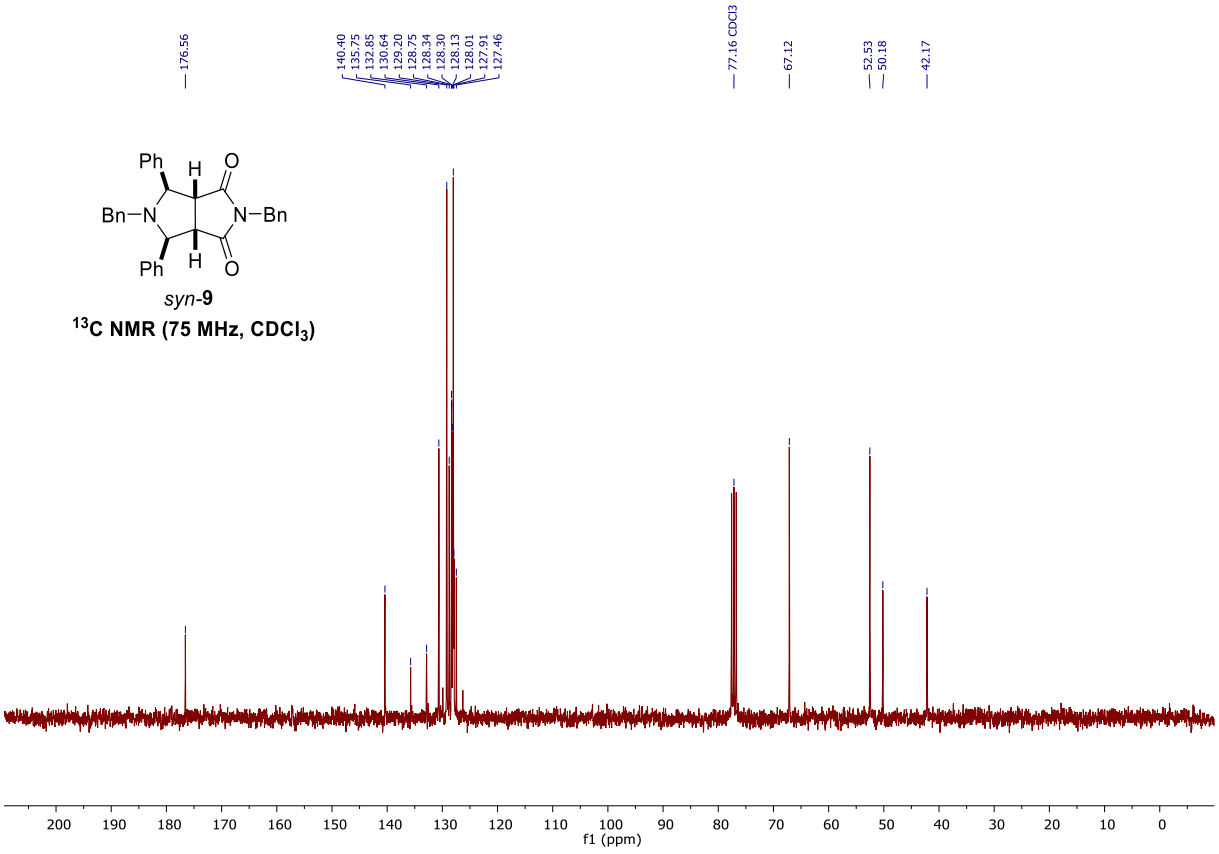


^{13}C NMR (101 MHz, $CDCl_3$)



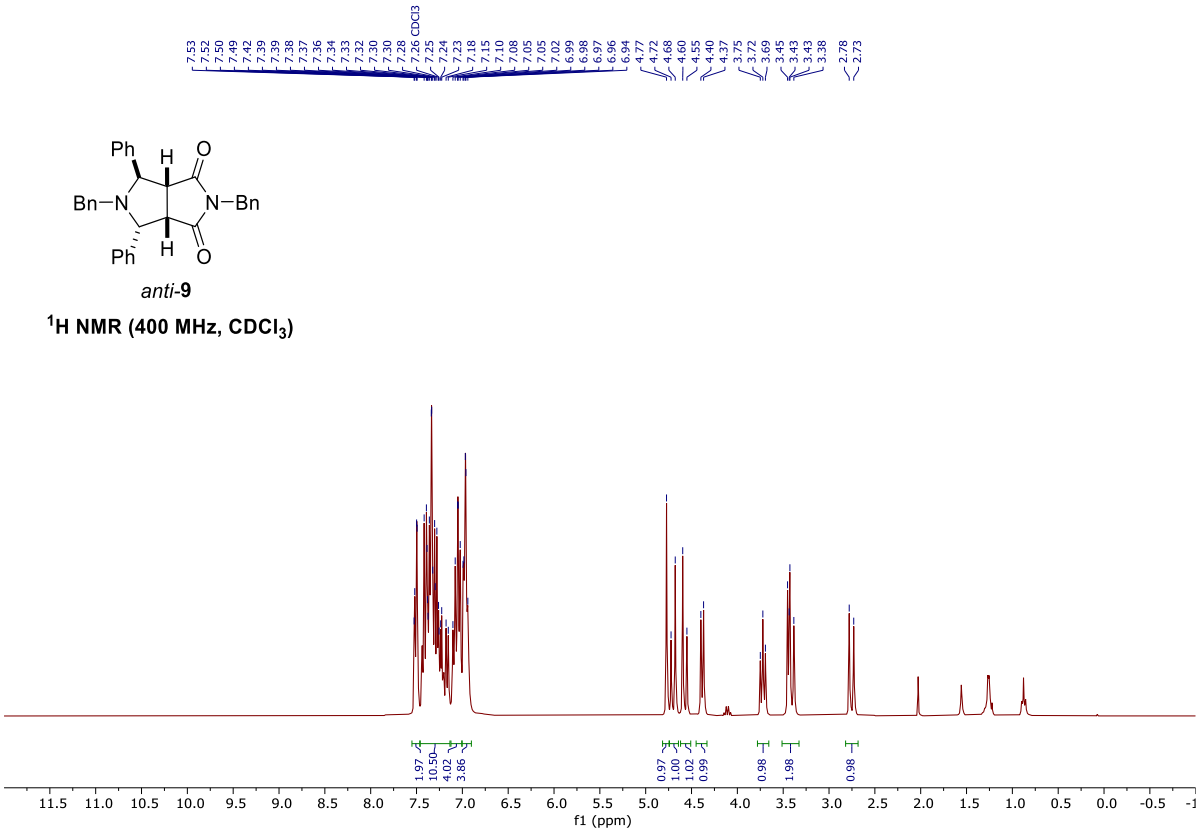
syn-**9**

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



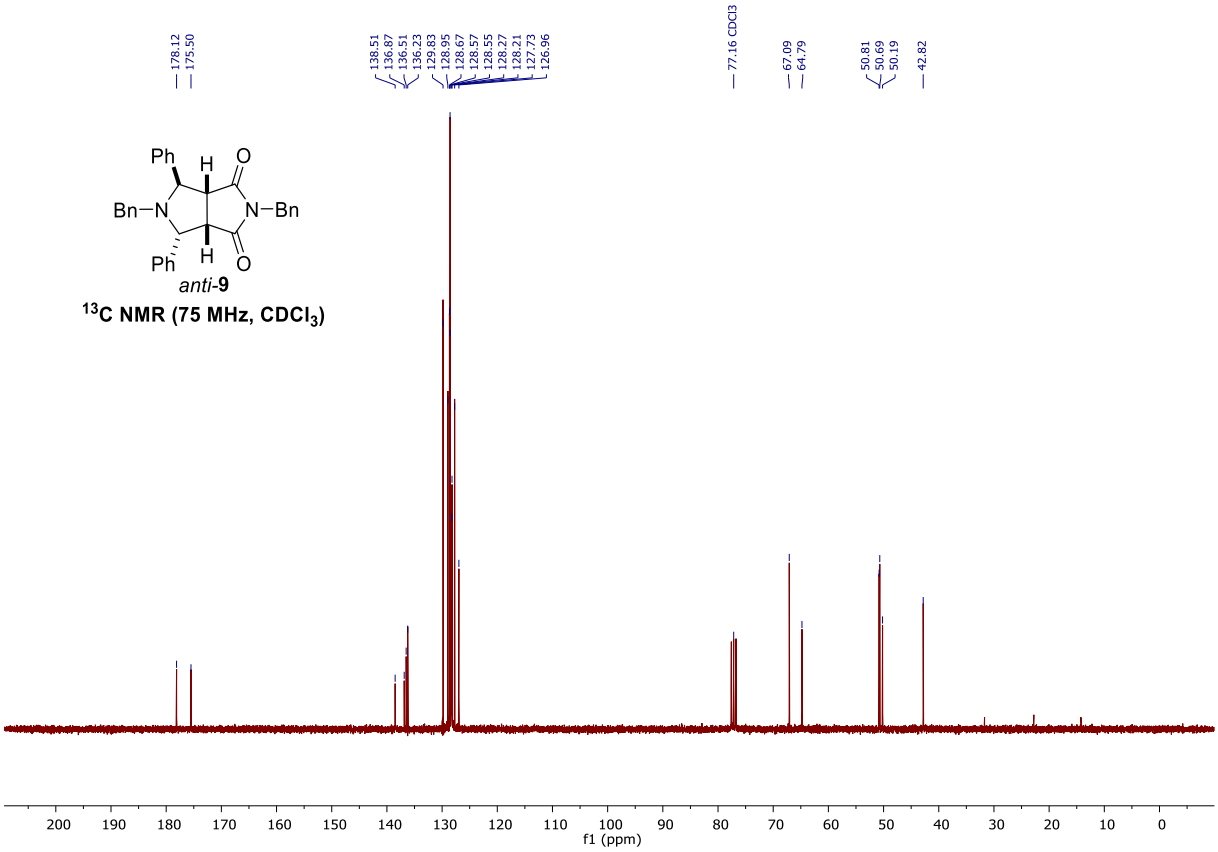
syn-**9**

^{13}C NMR (75 MHz, $CDCl_3$)



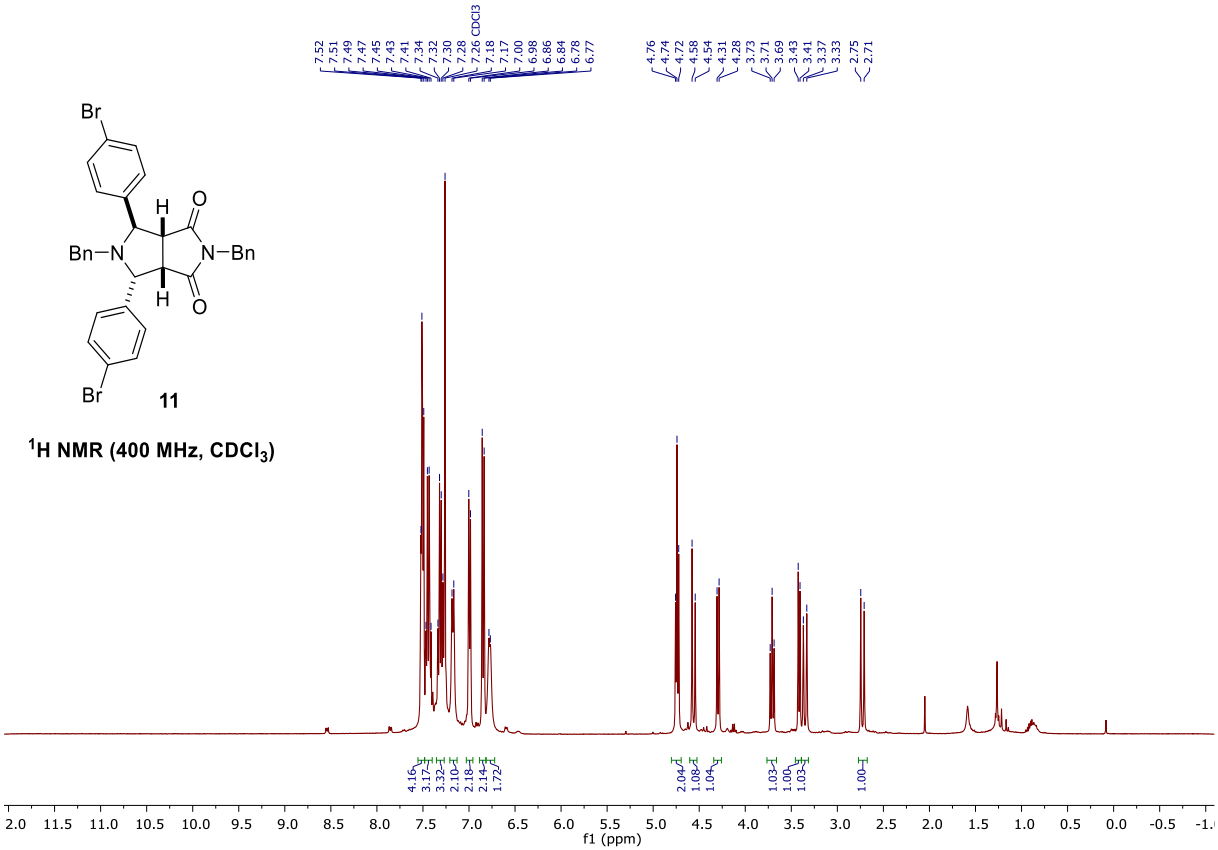
anti-**9**

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



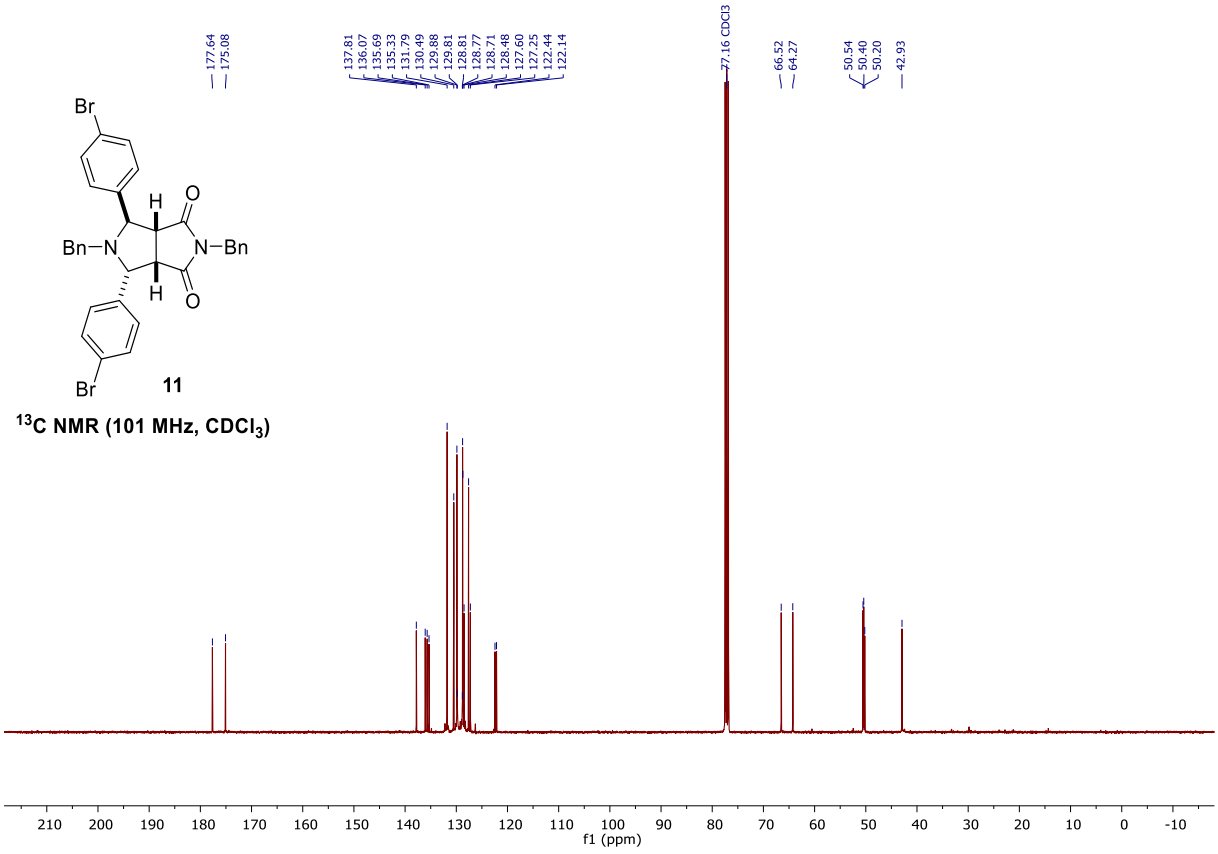
anti-**9**

^{13}C NMR (75 MHz, $CDCl_3$)

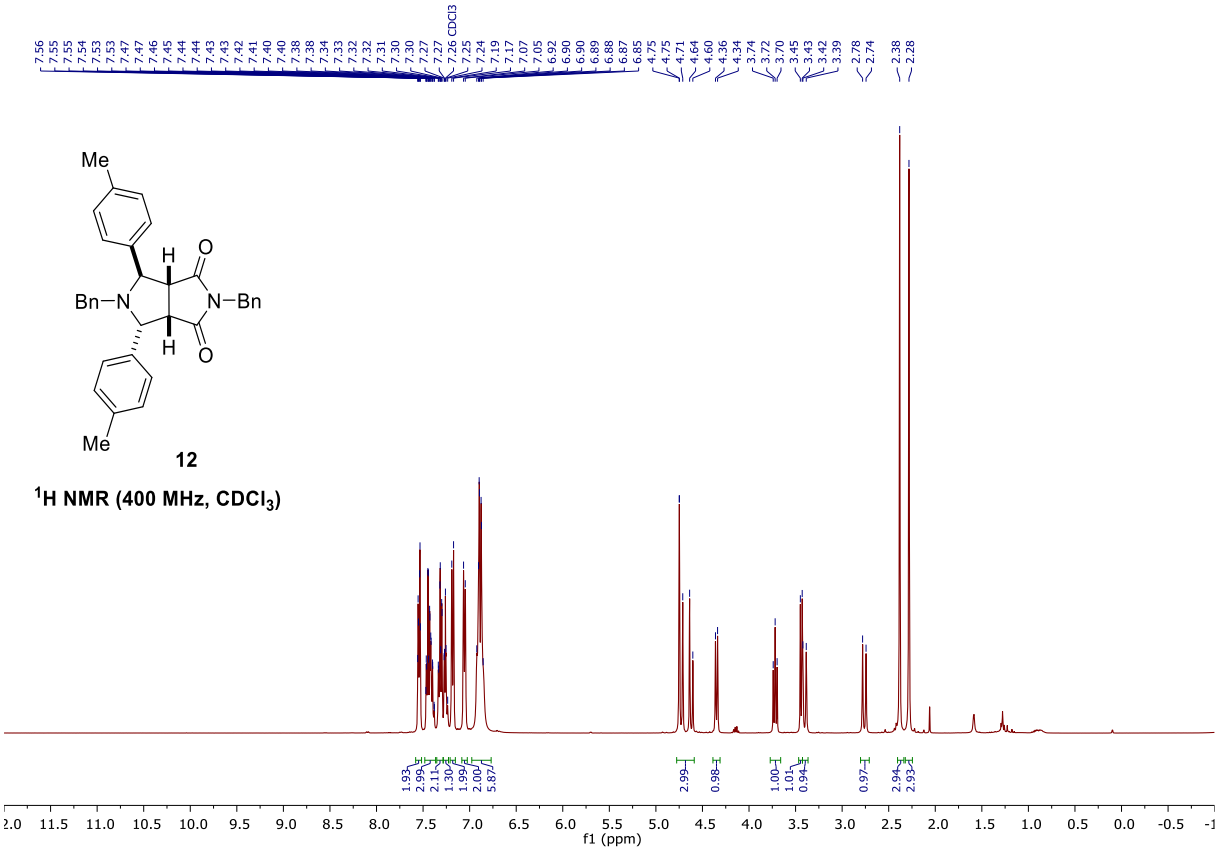


11

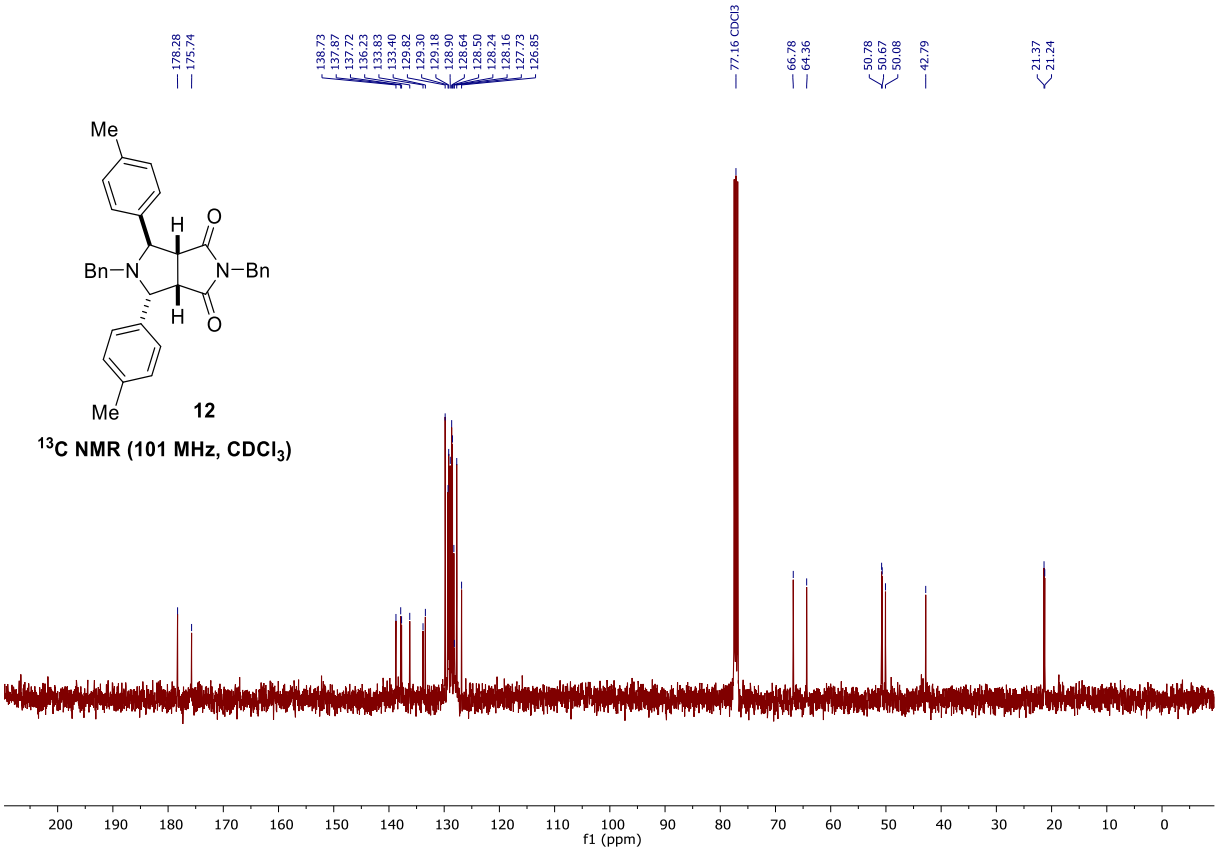
^{1}H NMR (400 MHz, $CDCl_3$)



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

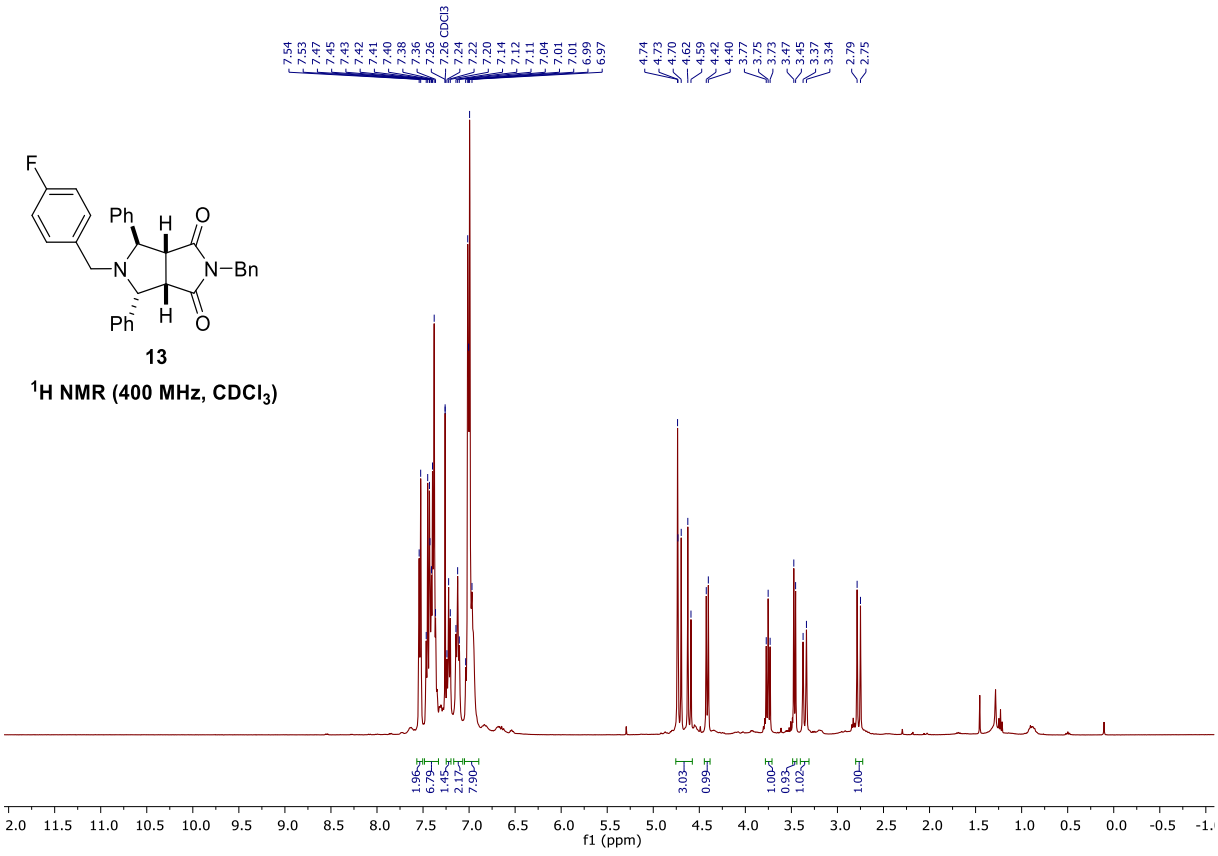


^{1}H NMR (400 MHz, $CDCl_3$)



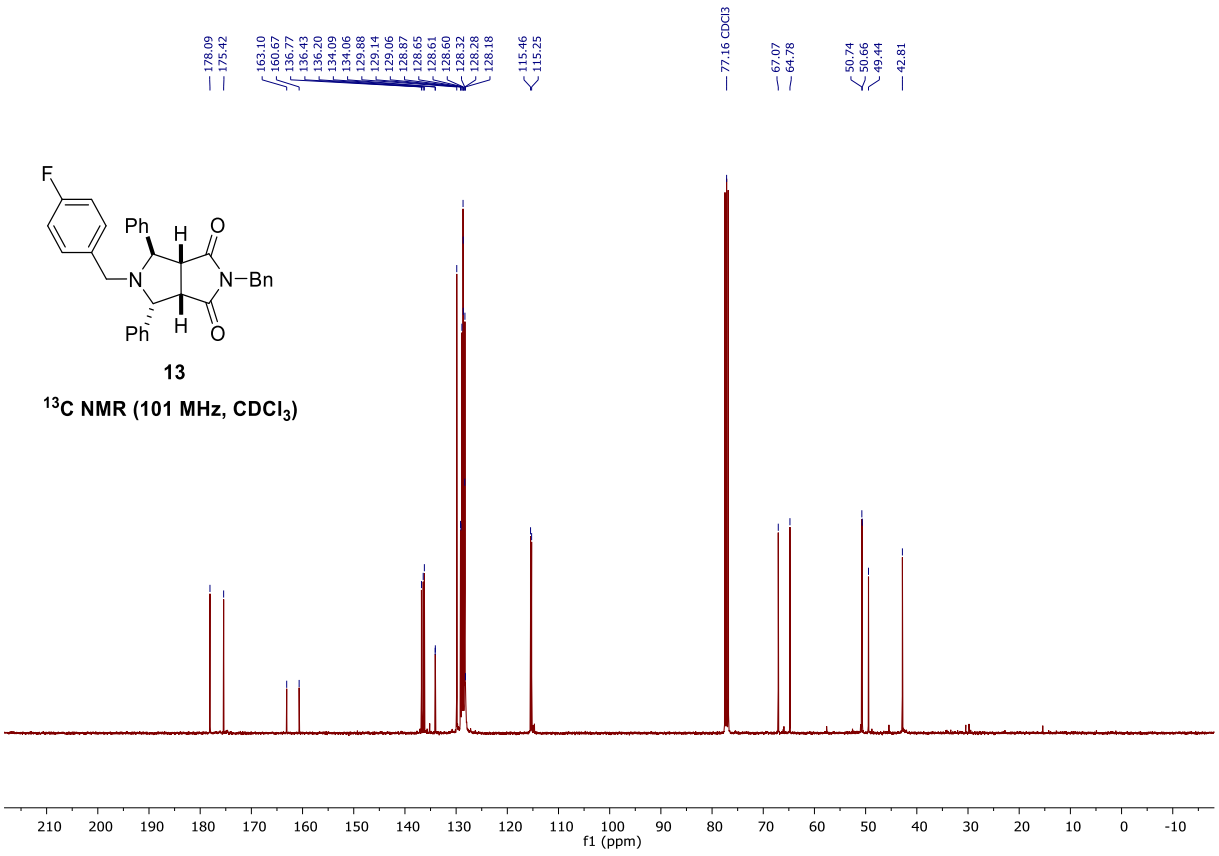
12

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



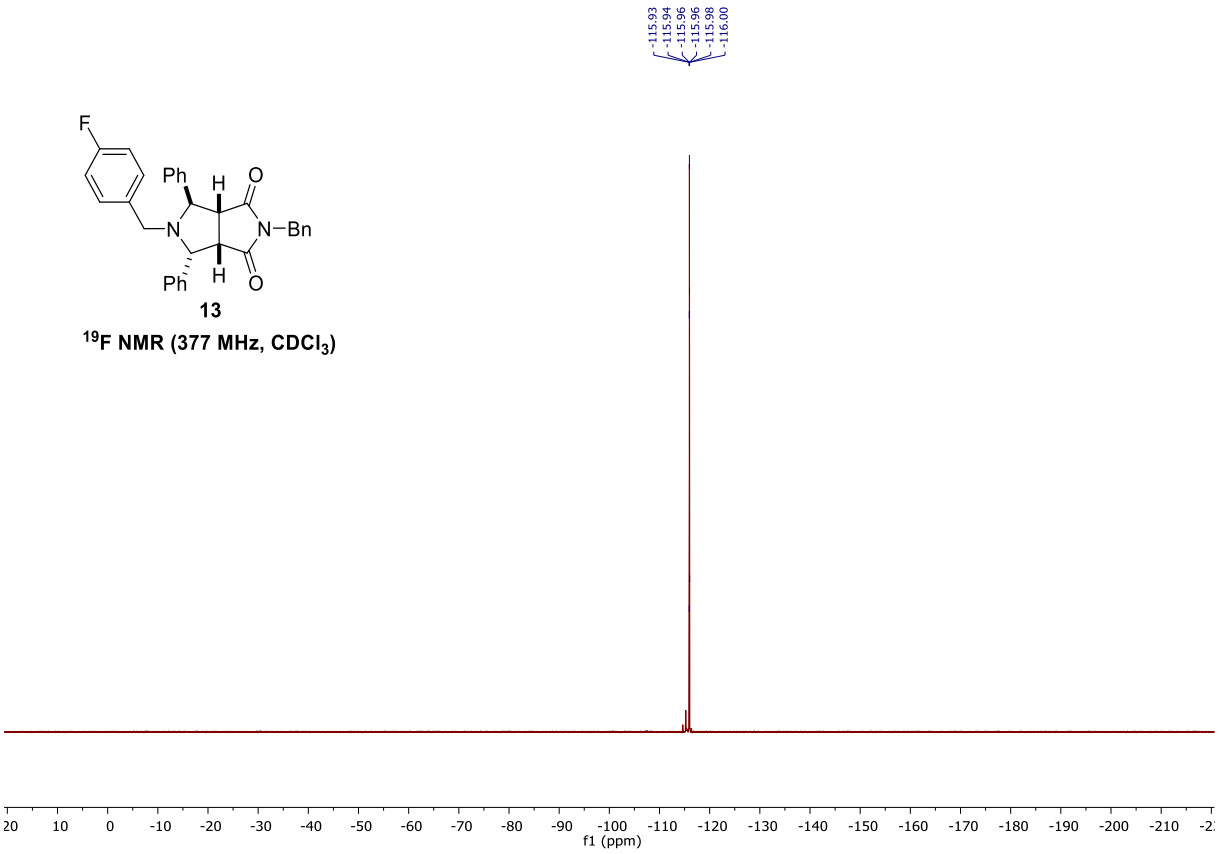
13

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



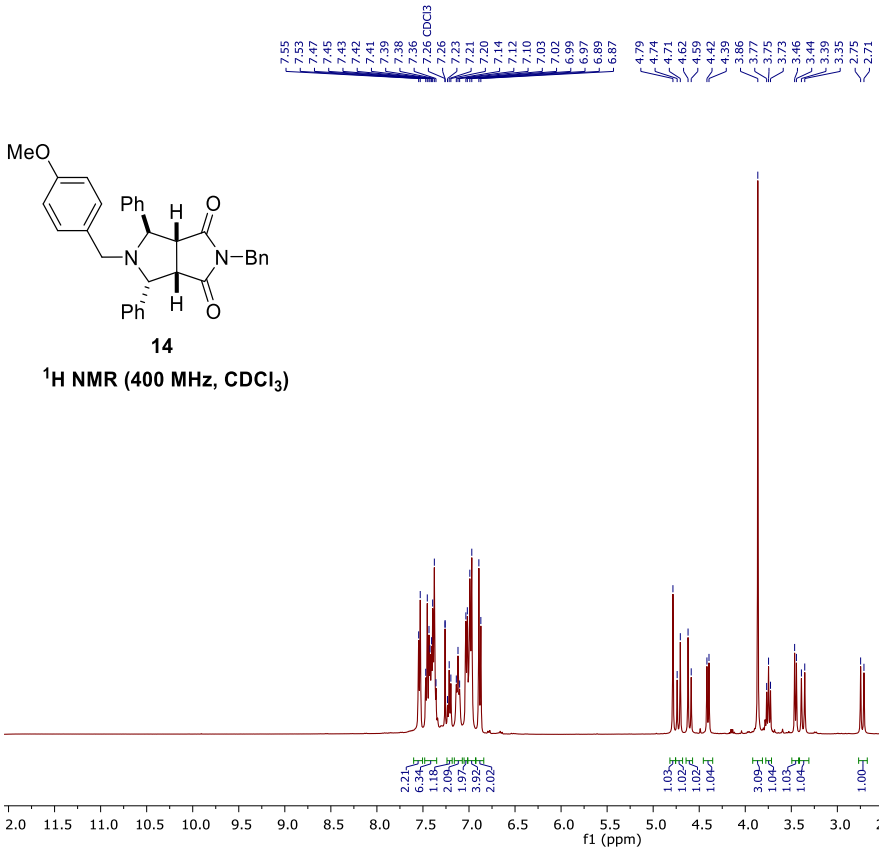
13

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



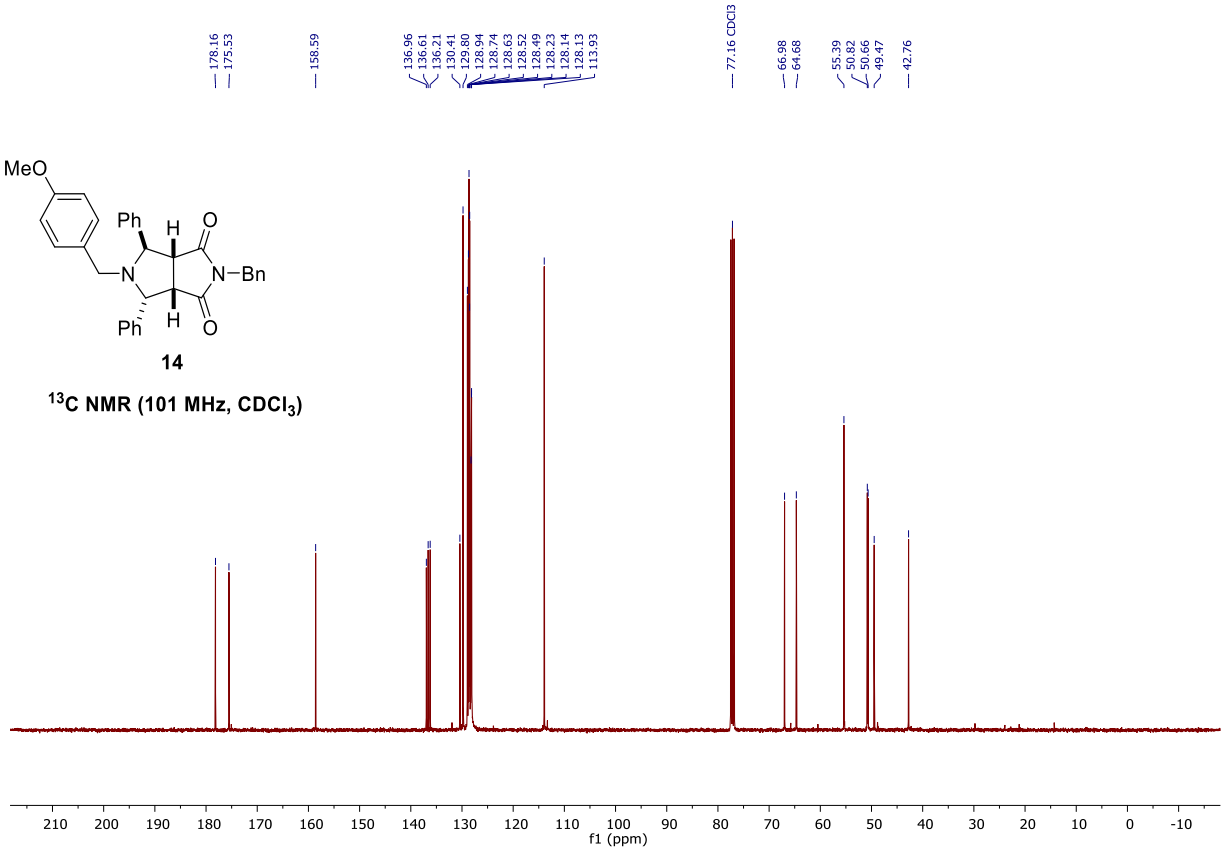
13

^{19}F NMR (377 MHz, $CDCl_3$)



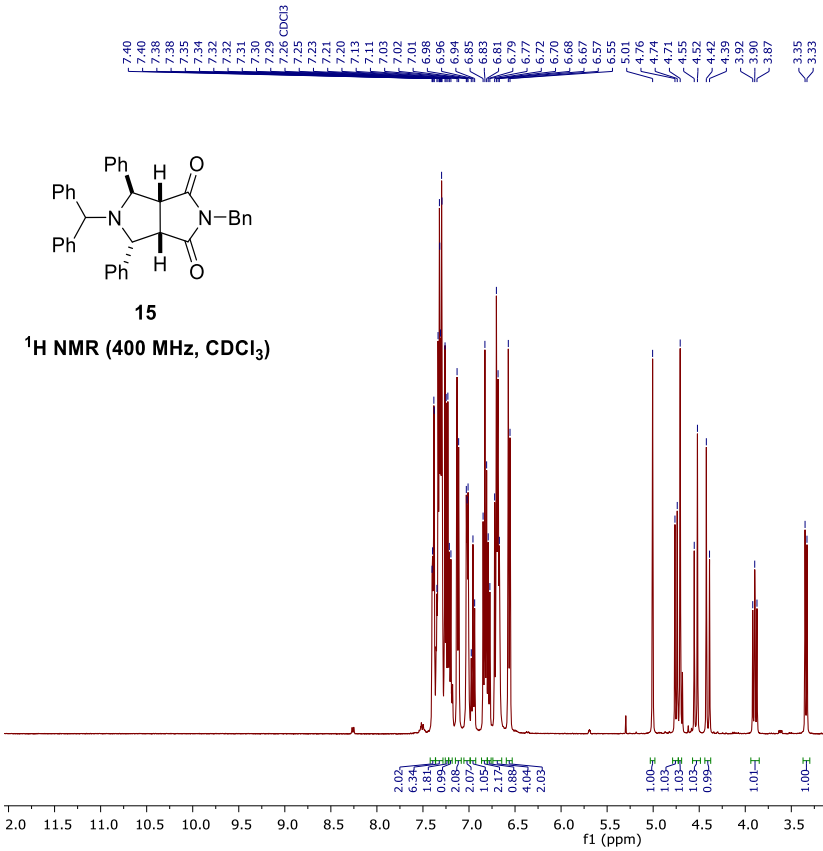
14

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



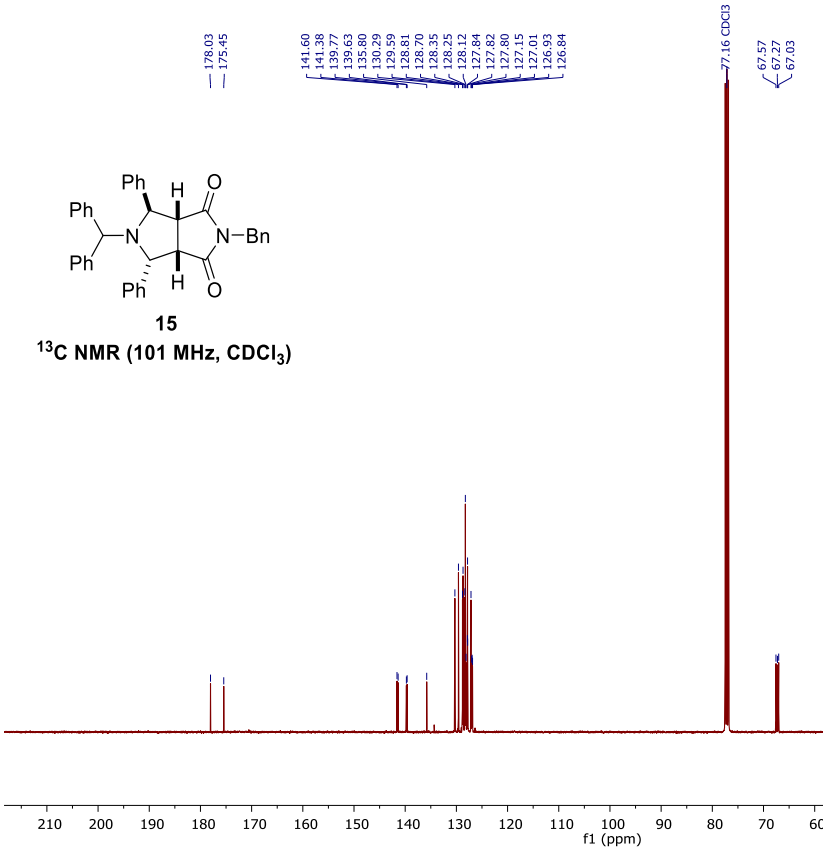
14

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



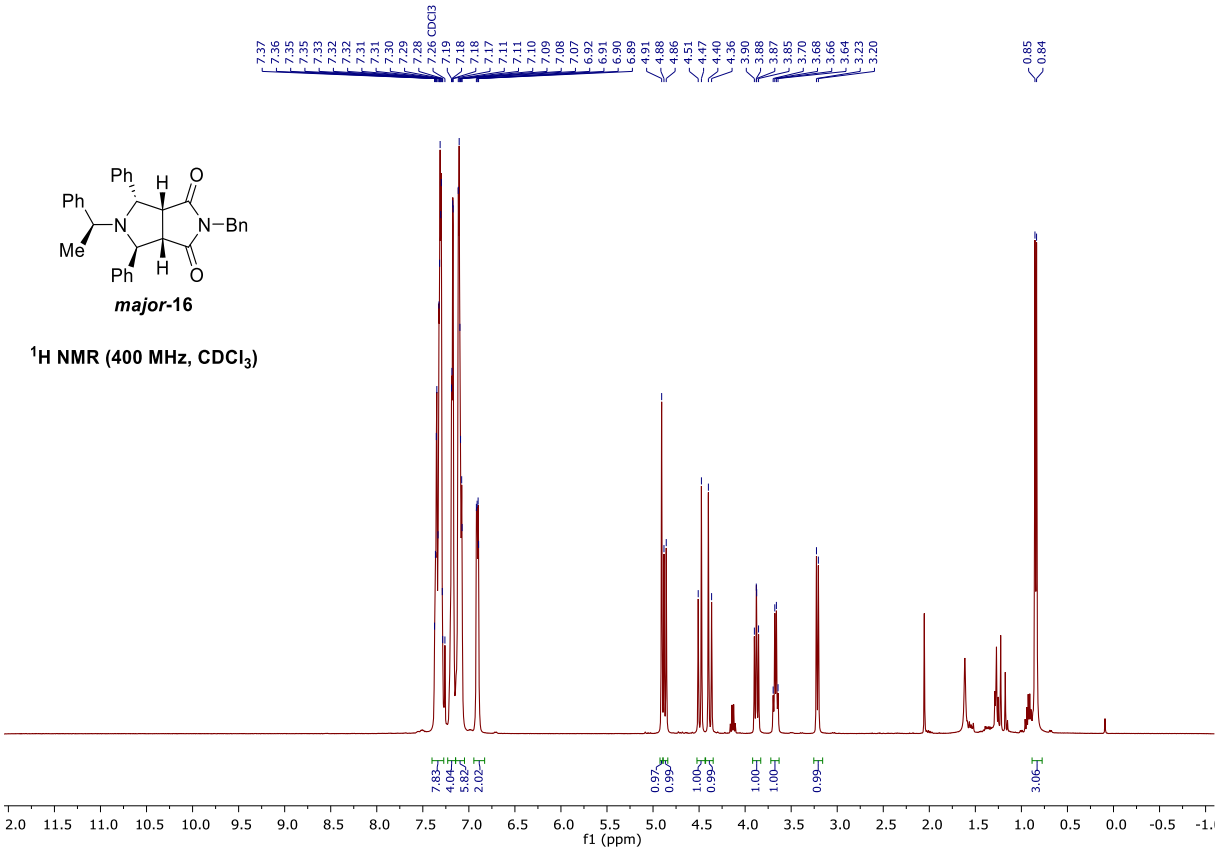
15

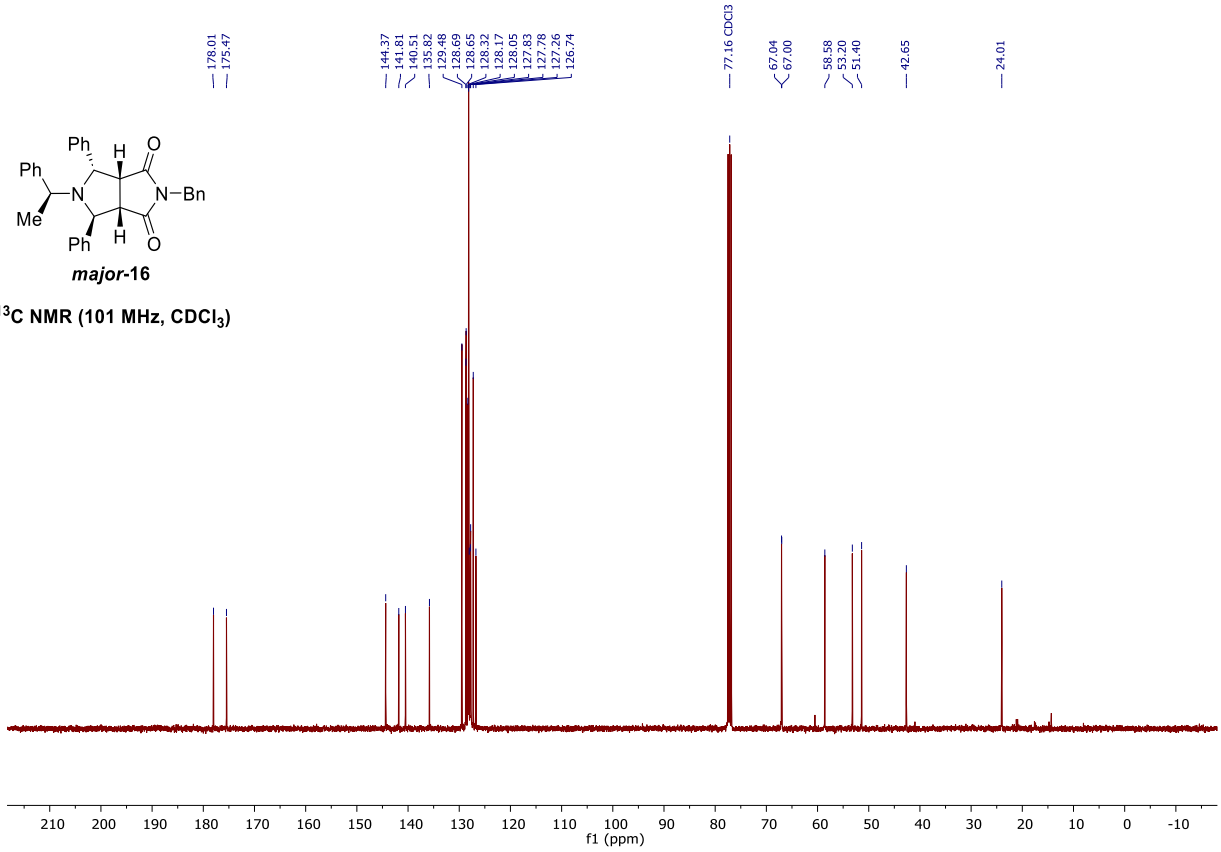
^{1}H NMR (400 MHz, $CDCl_3$)

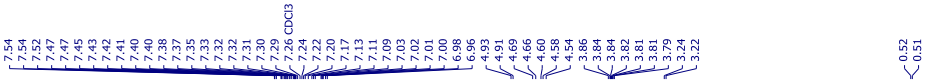


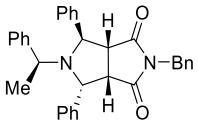
15

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


major-16
1H NMR (400 MHz, CDCl3)
f1 (ppm)

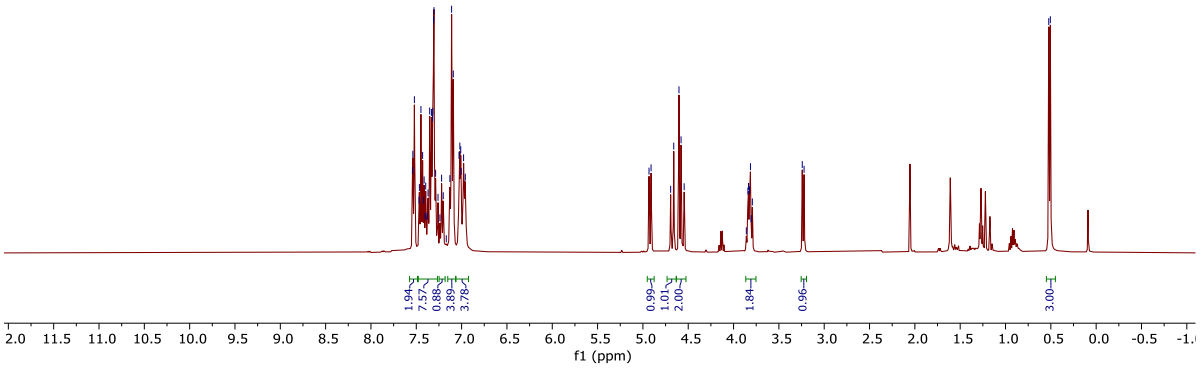

major-16
13C NMR (101 MHz, CDCl3)
f1 (ppm)

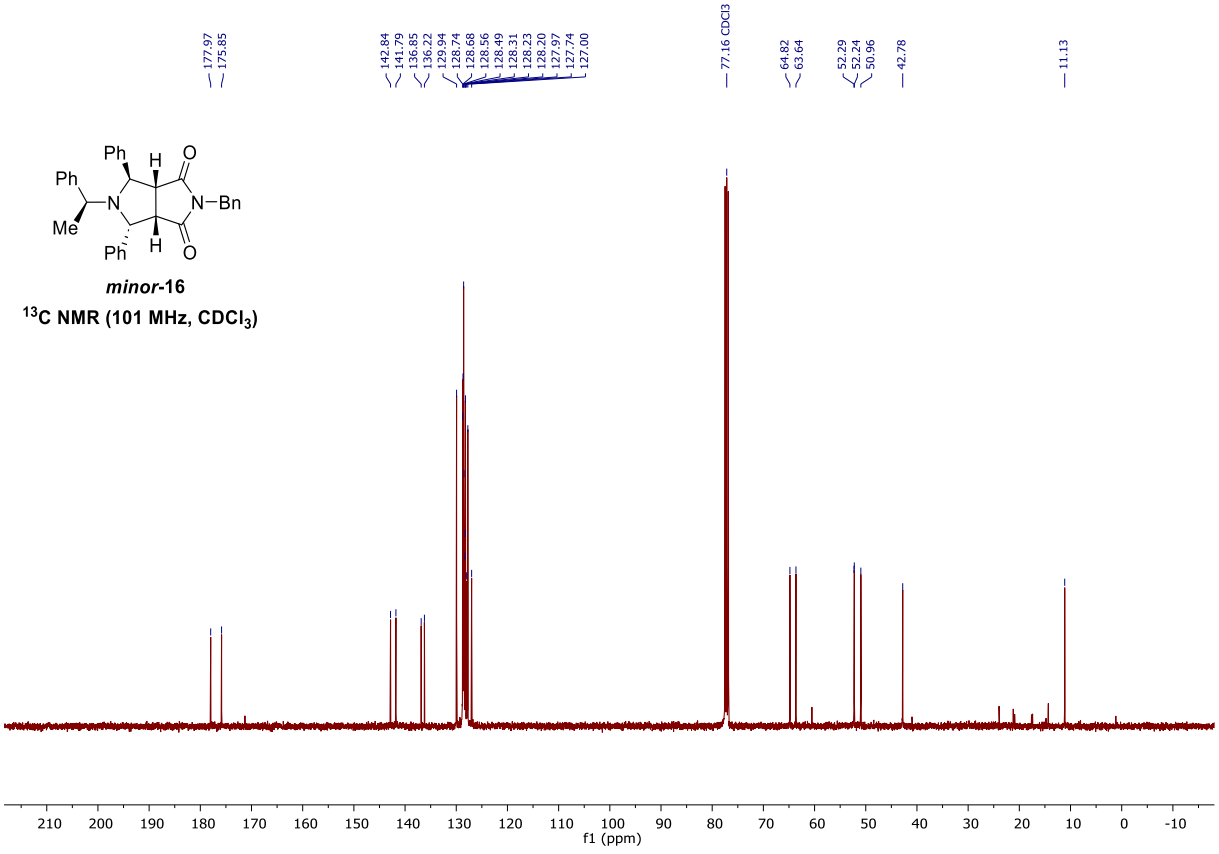




***minor*-16**

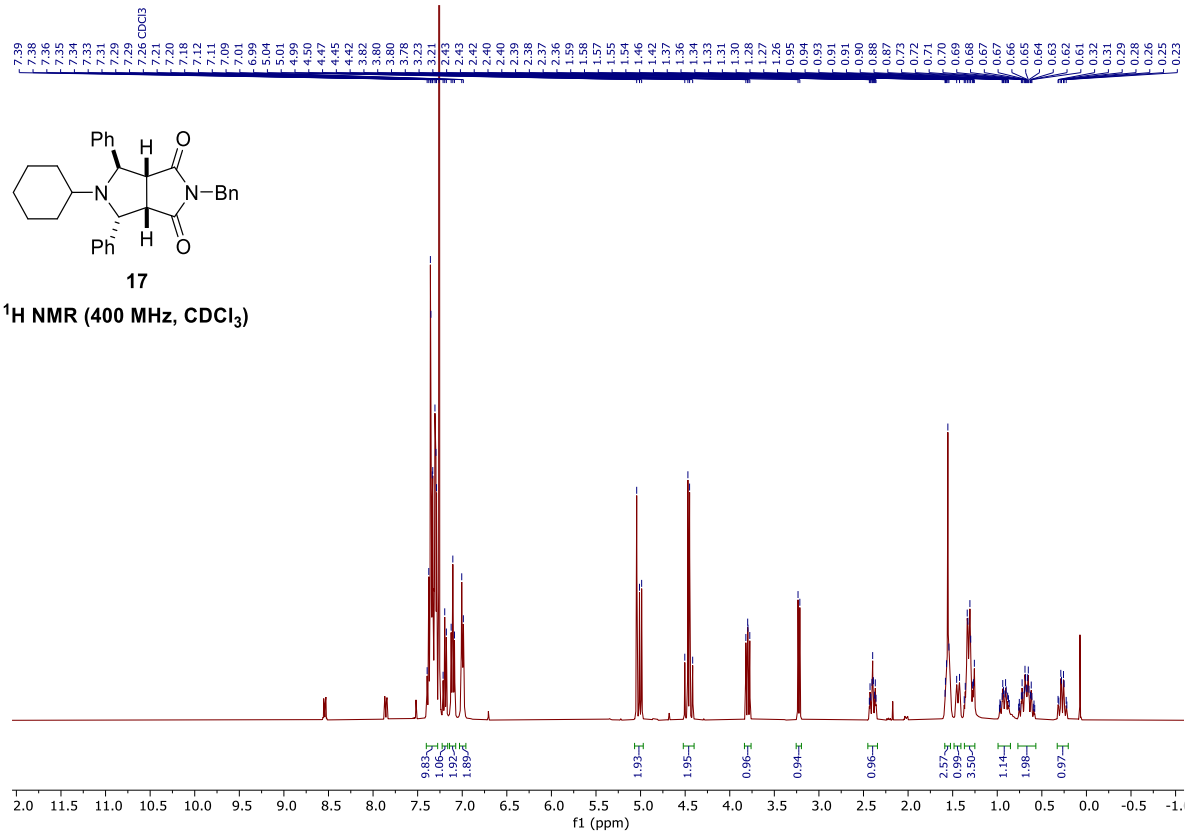
^{1}H NMR (400 MHz, $CDCl_3$)





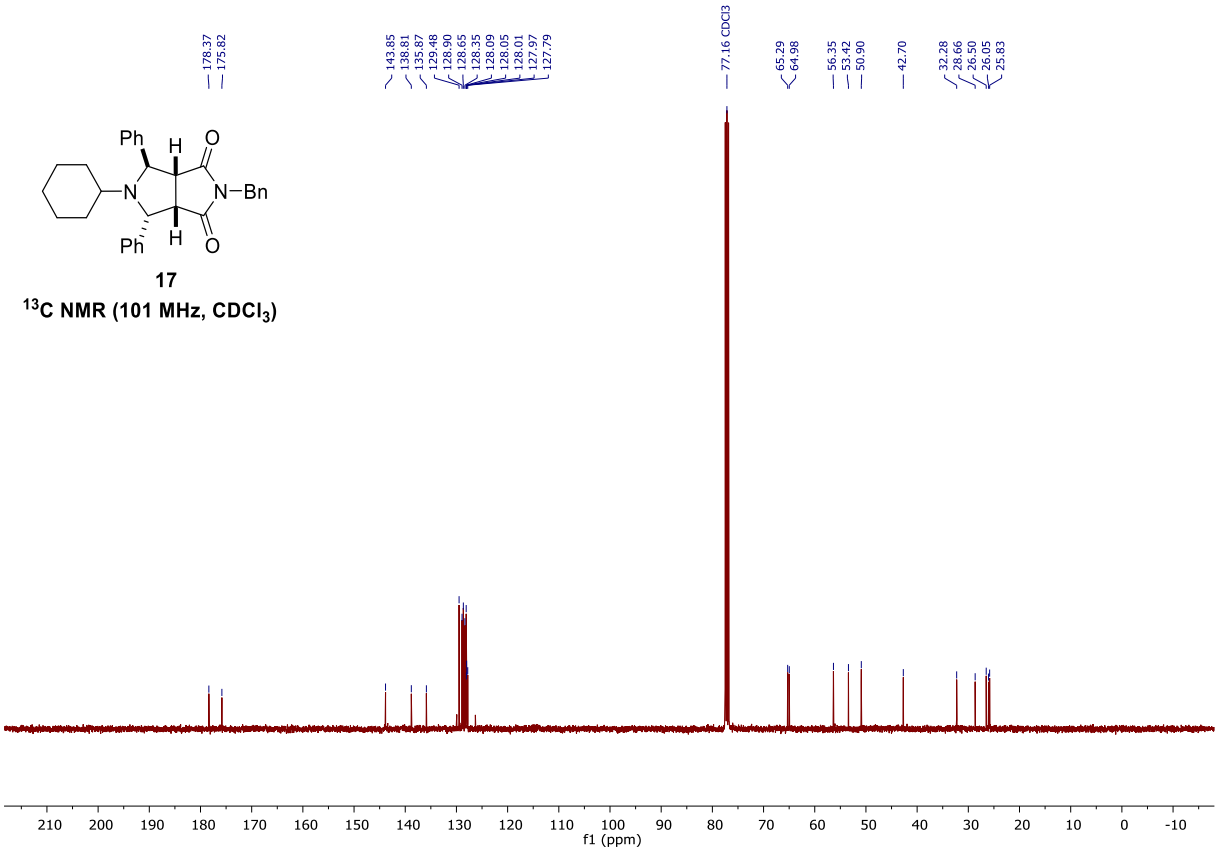
***minor*-16**

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



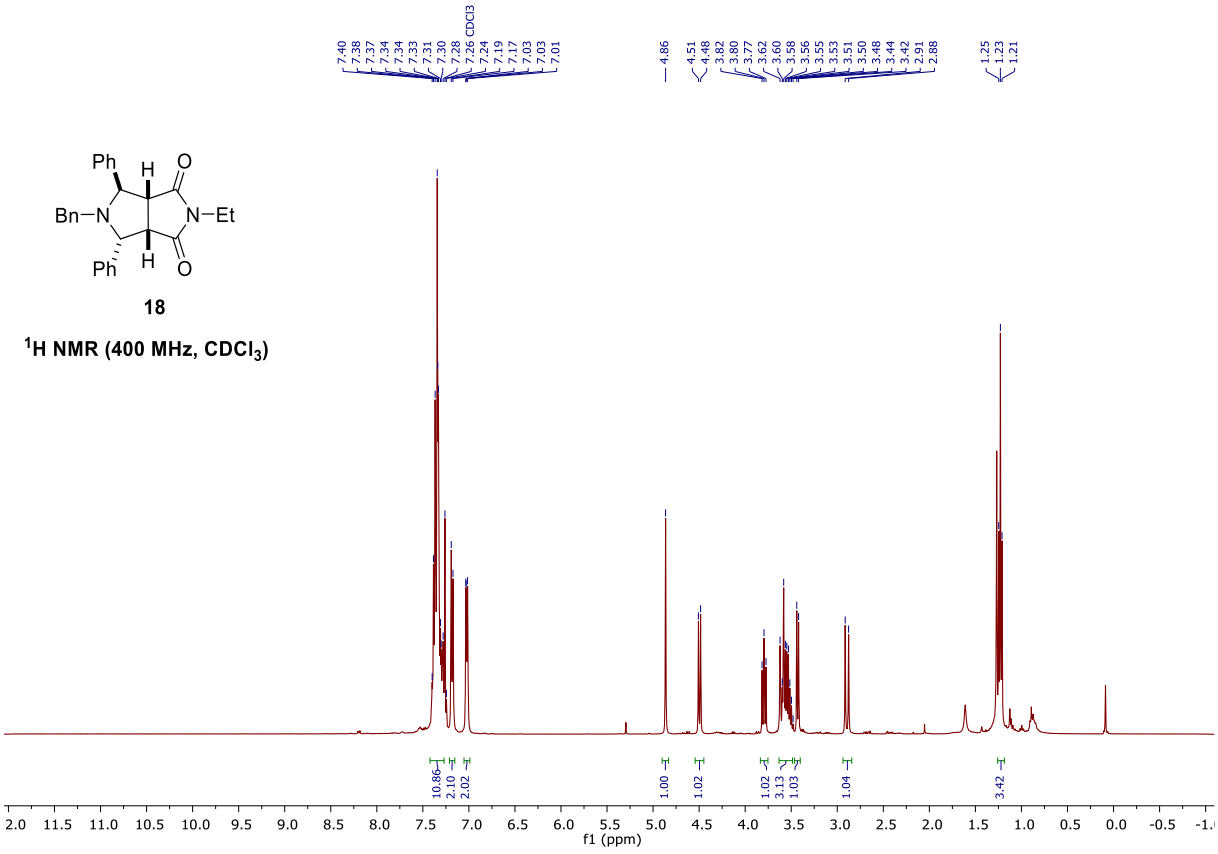
17

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



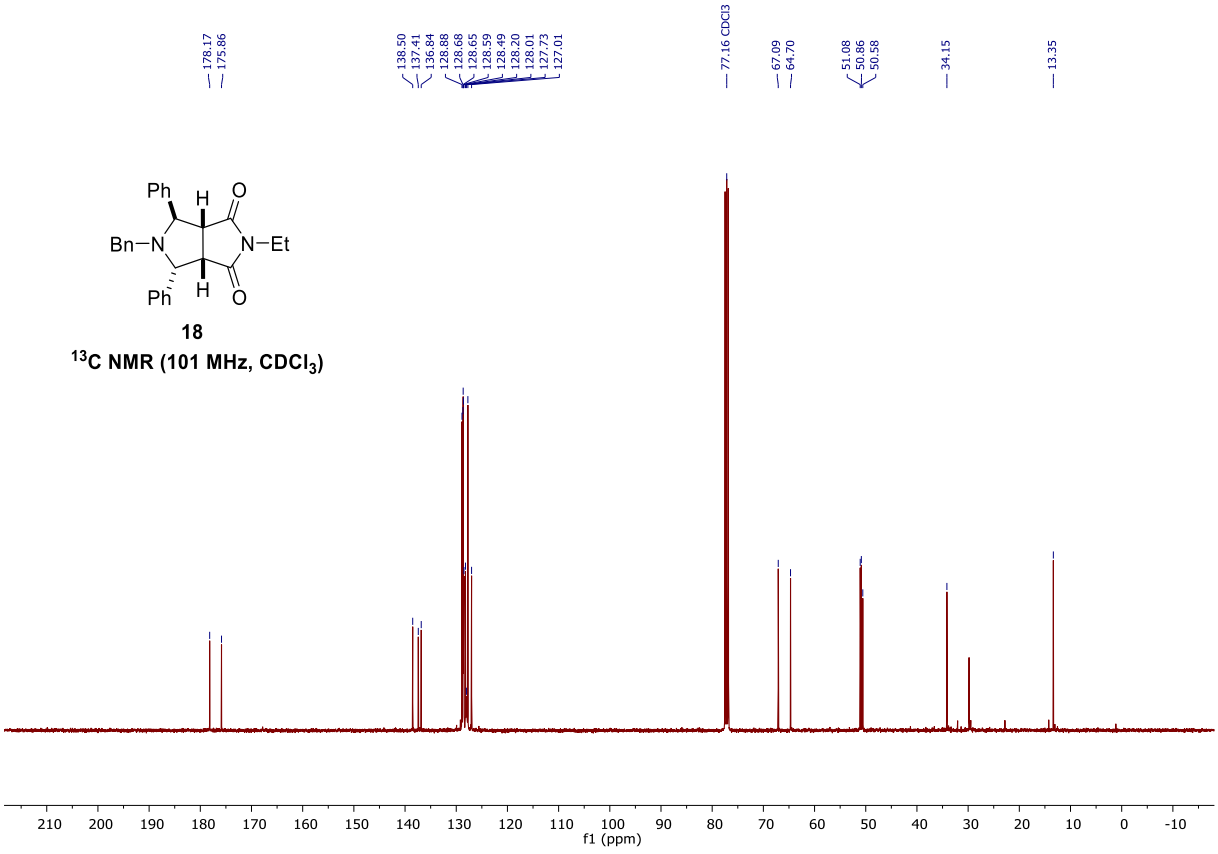
17

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



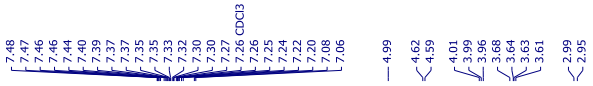
18

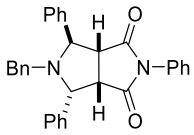
^{1}H NMR (400 MHz, $CDCl_3$)



18

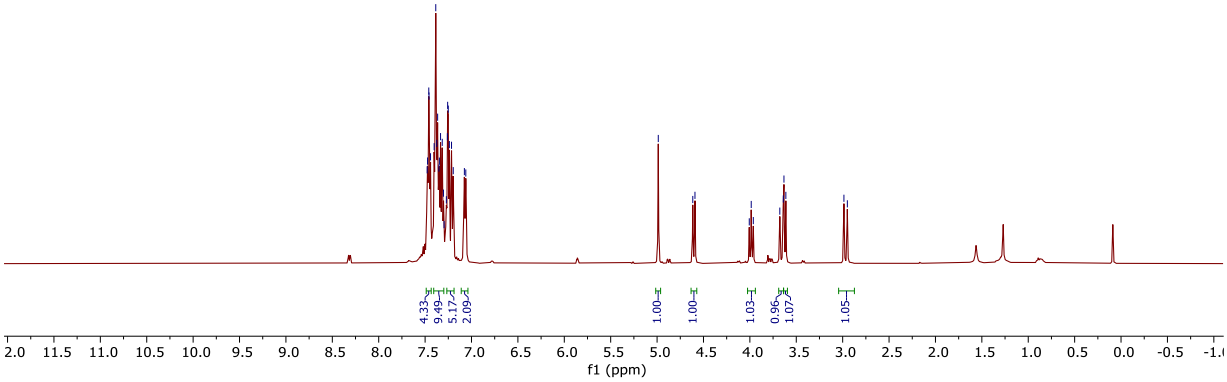
^{13}C NMR (101 MHz, $CDCl_3$)

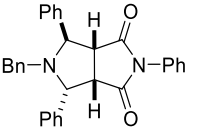




19

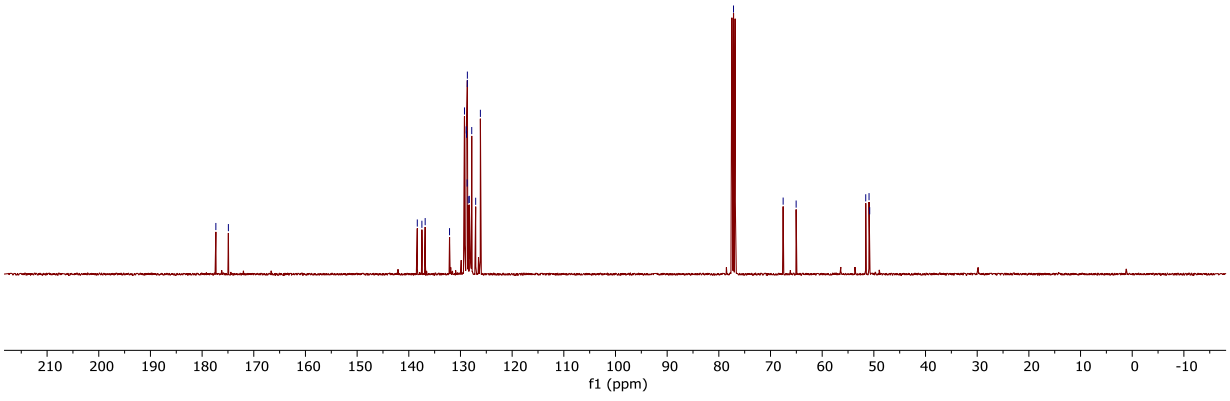
^{1}H NMR (400 MHz, $CDCl_3$)

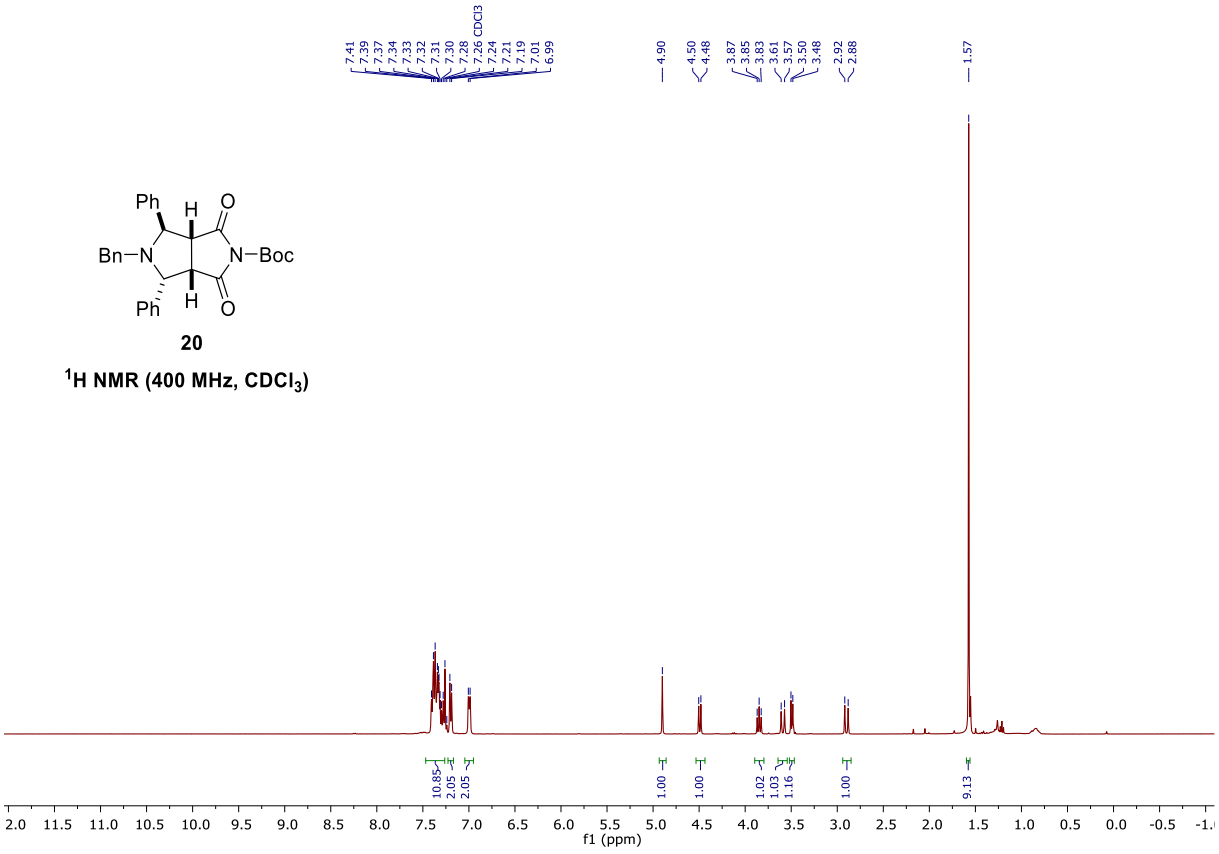




19

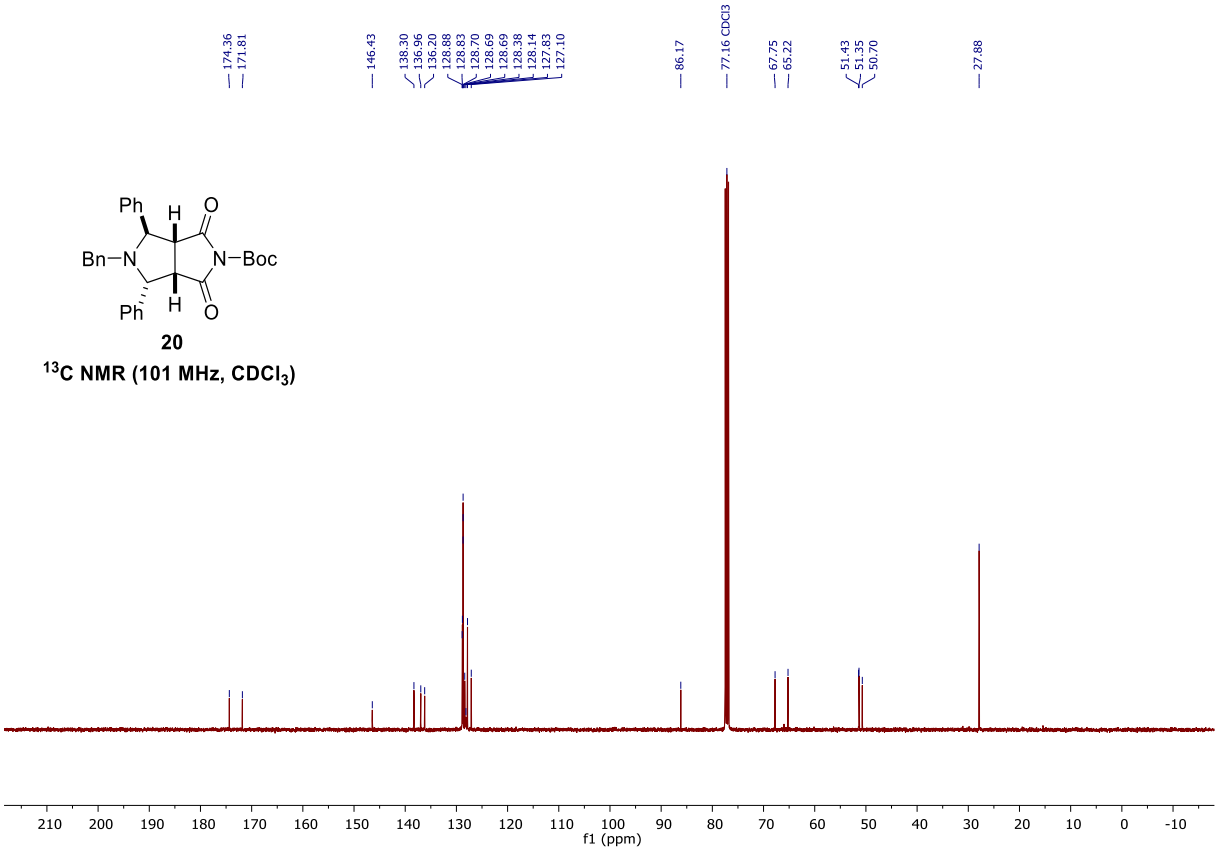
^{13}C NMR (101 MHz, $CDCl_3$)





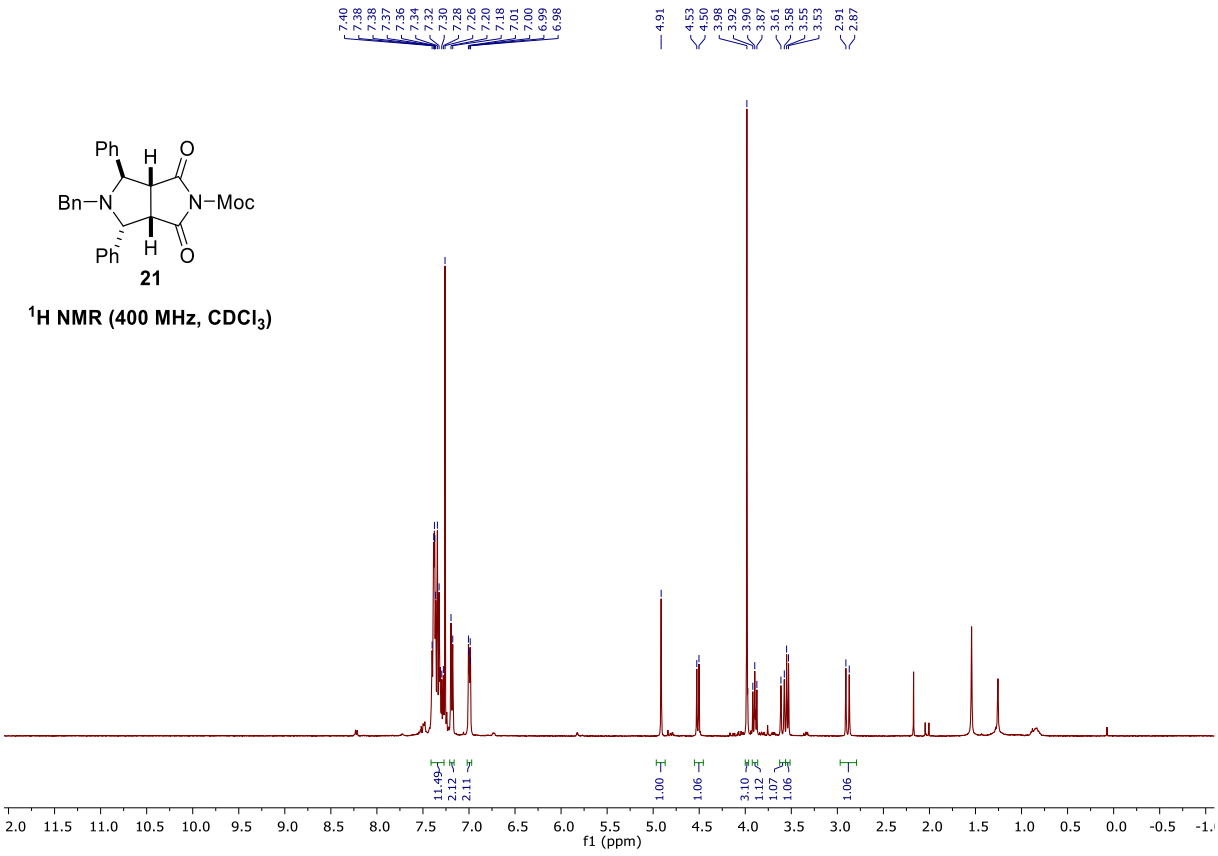
20

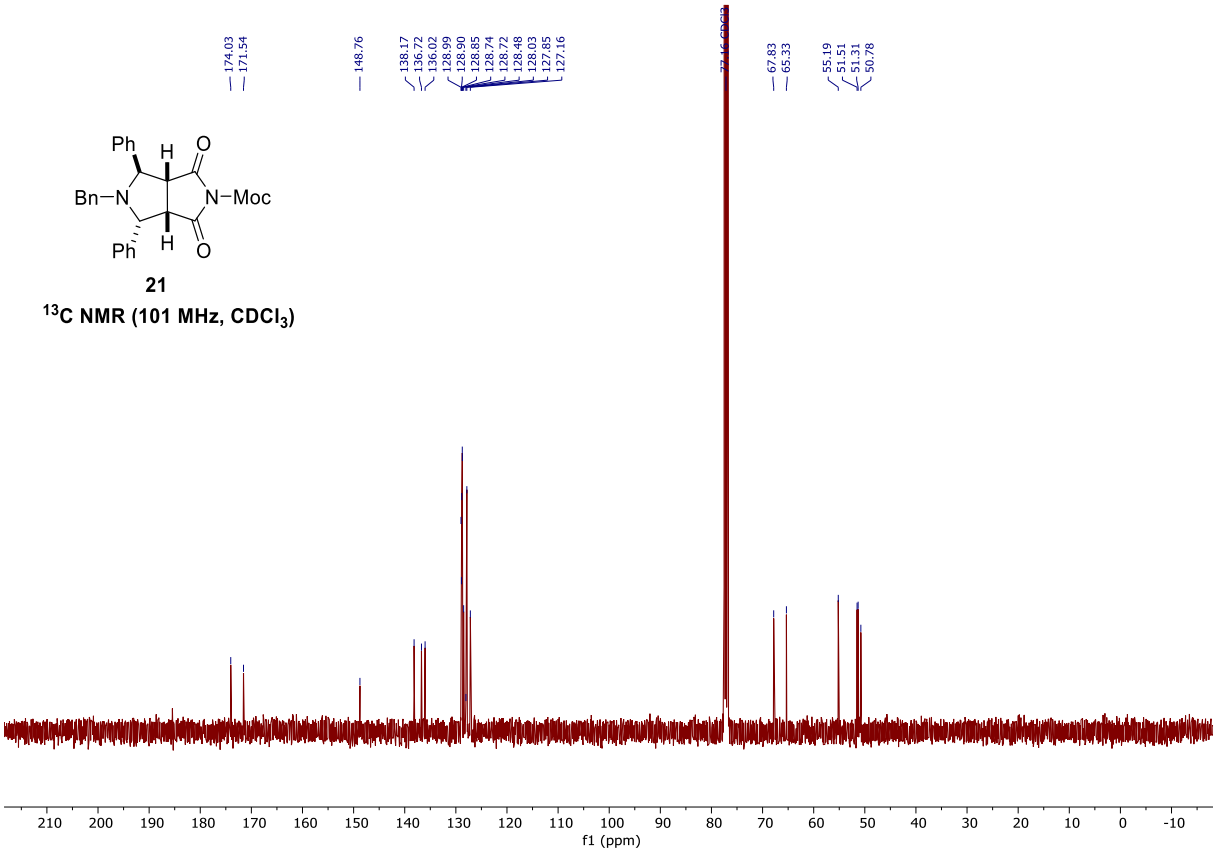
^{1}H NMR (400 MHz, $CDCl_3$)

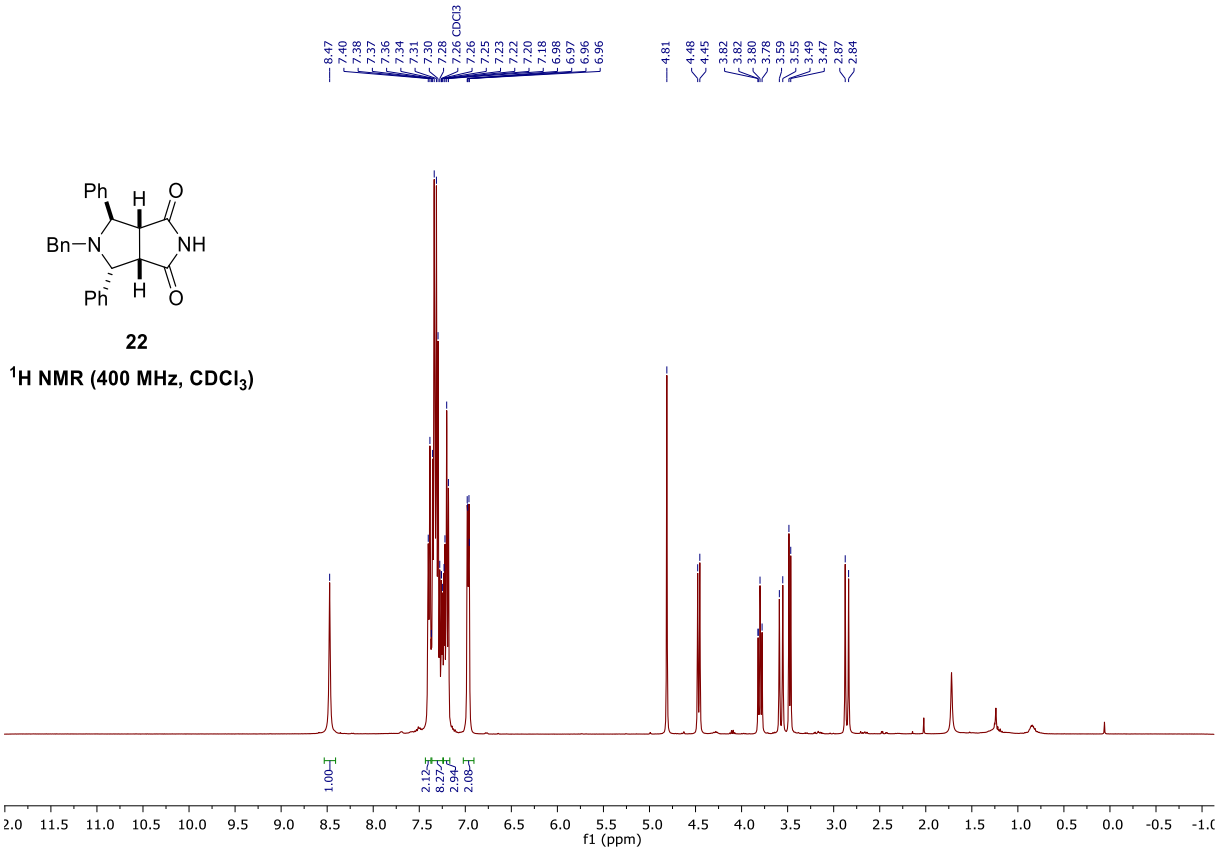


20

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

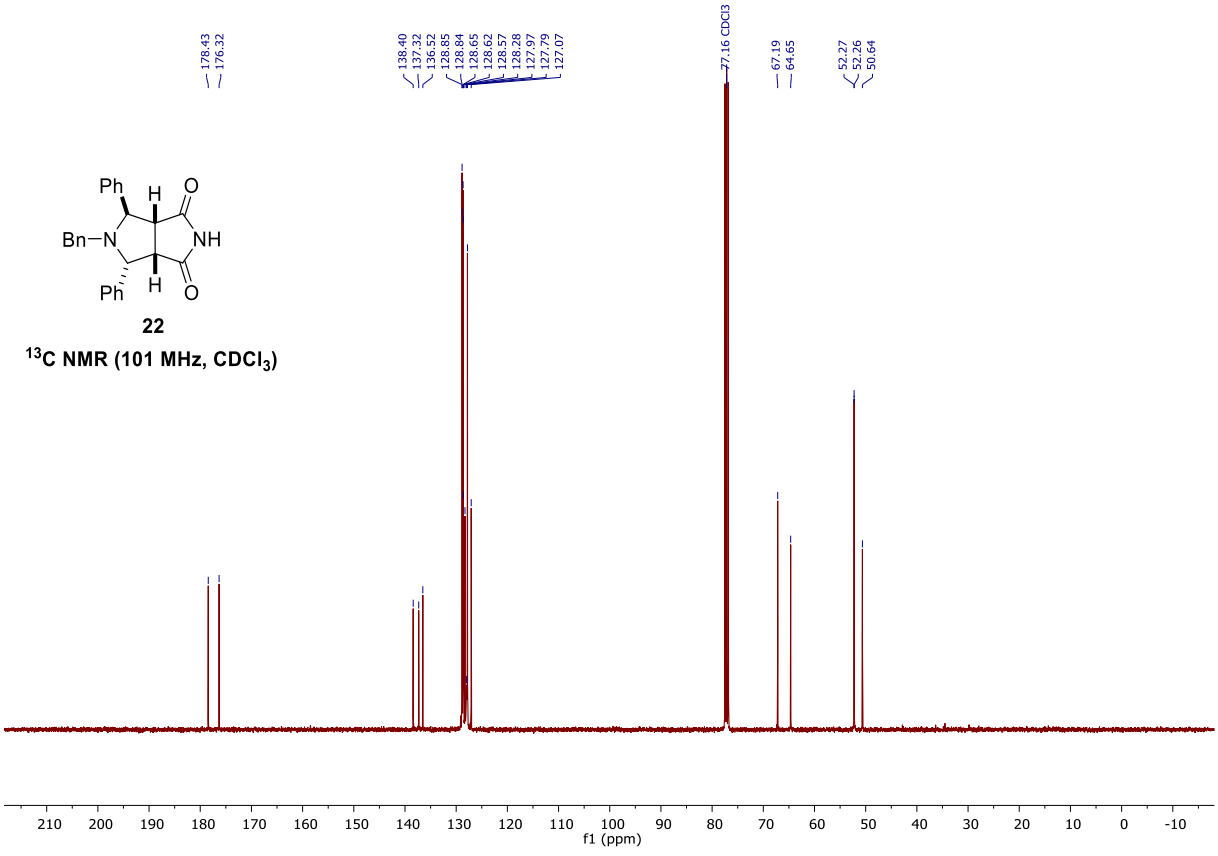

Ph
H
O
Bn–N
N–Moc
Ph
H
O
21
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


Ph
H
O
Bn–N
N–Moc
Ph
H
O
21
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)



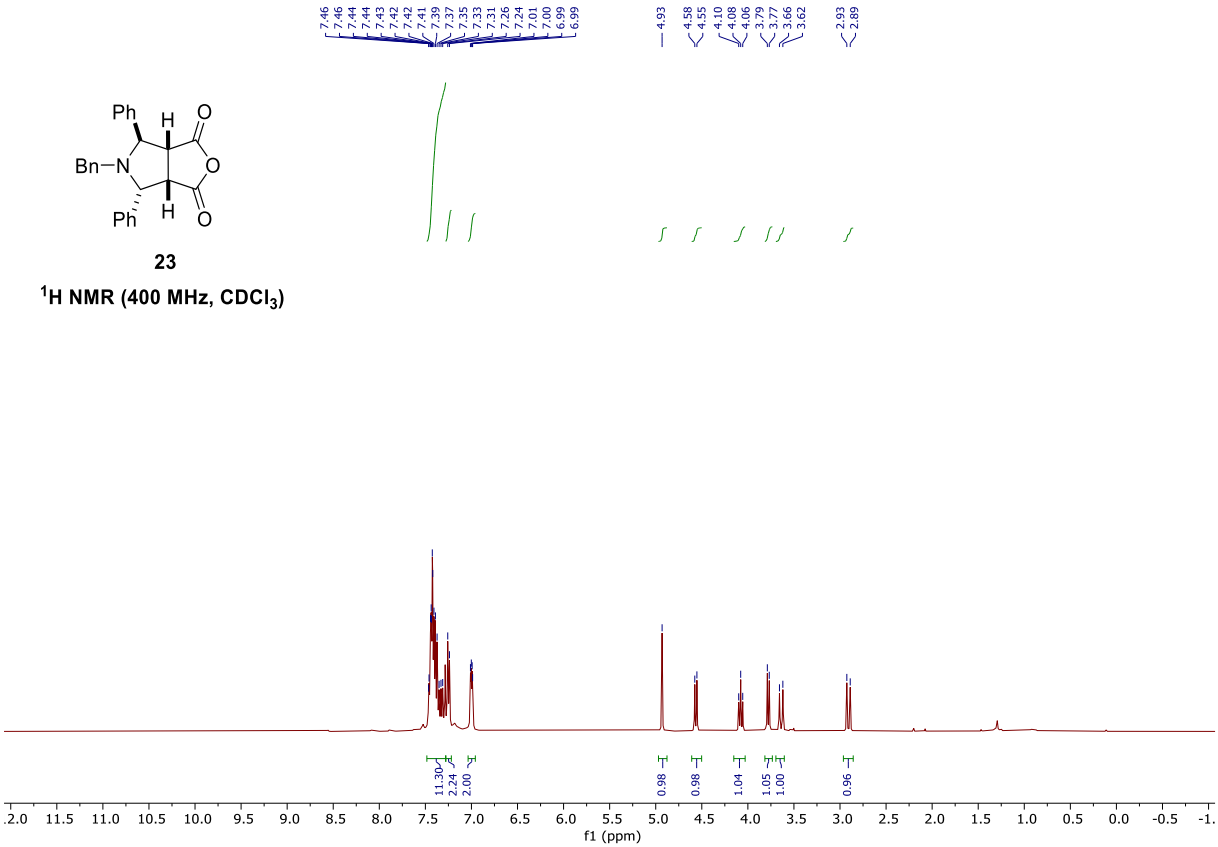
22

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



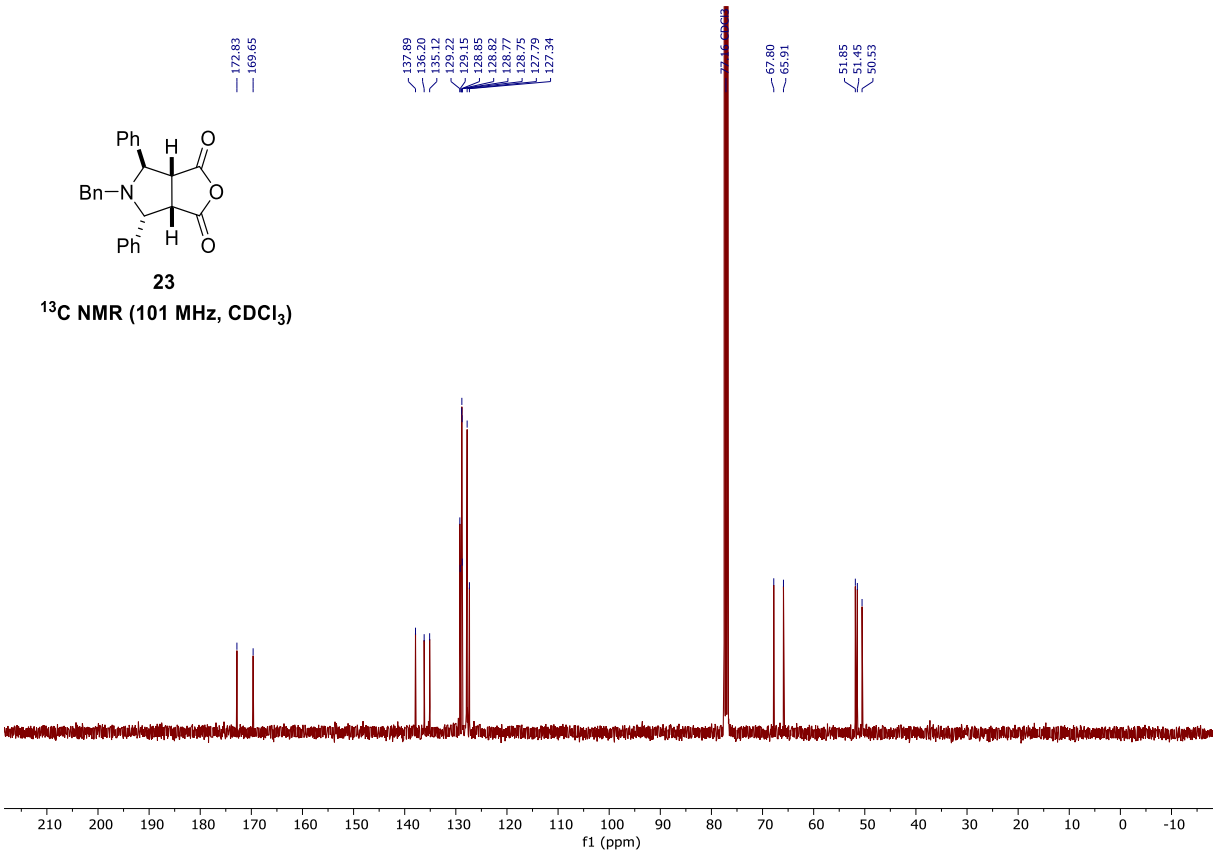
22

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



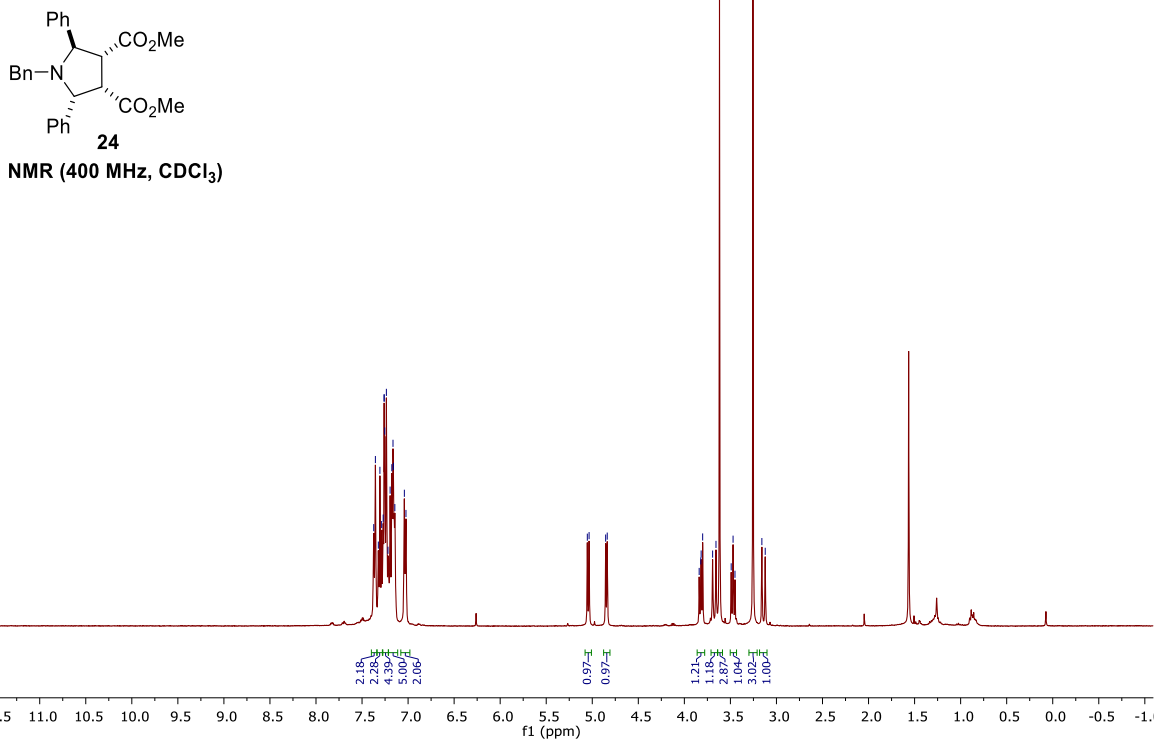
23

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



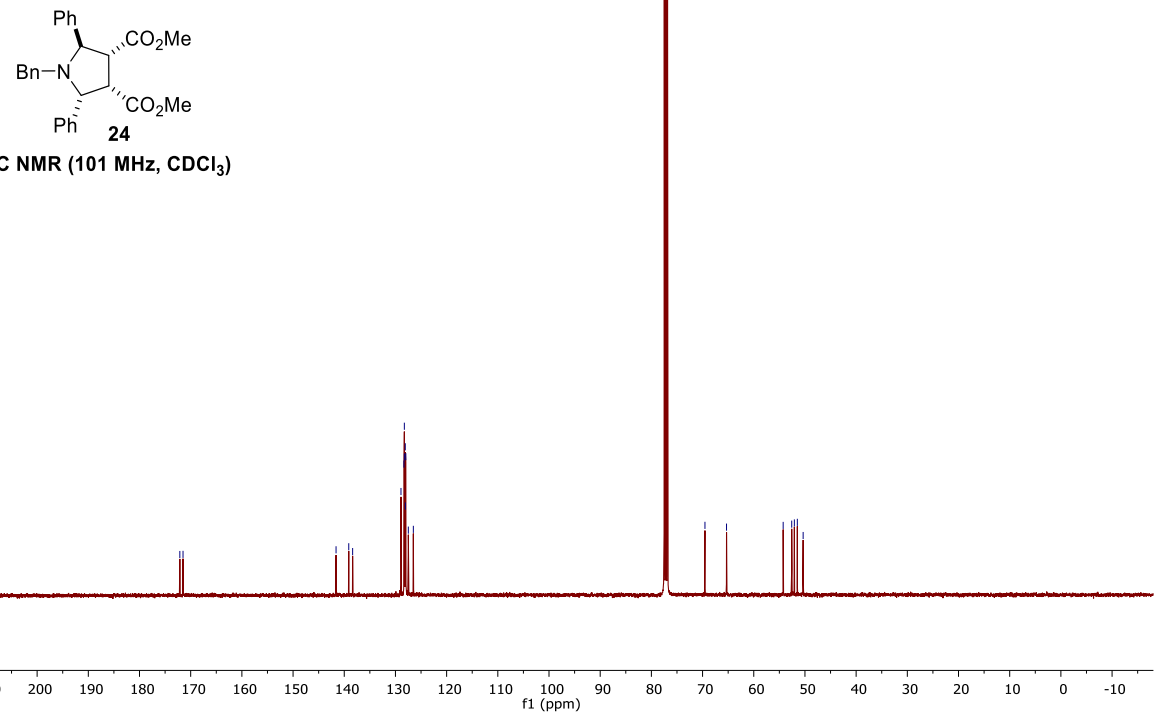
23

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



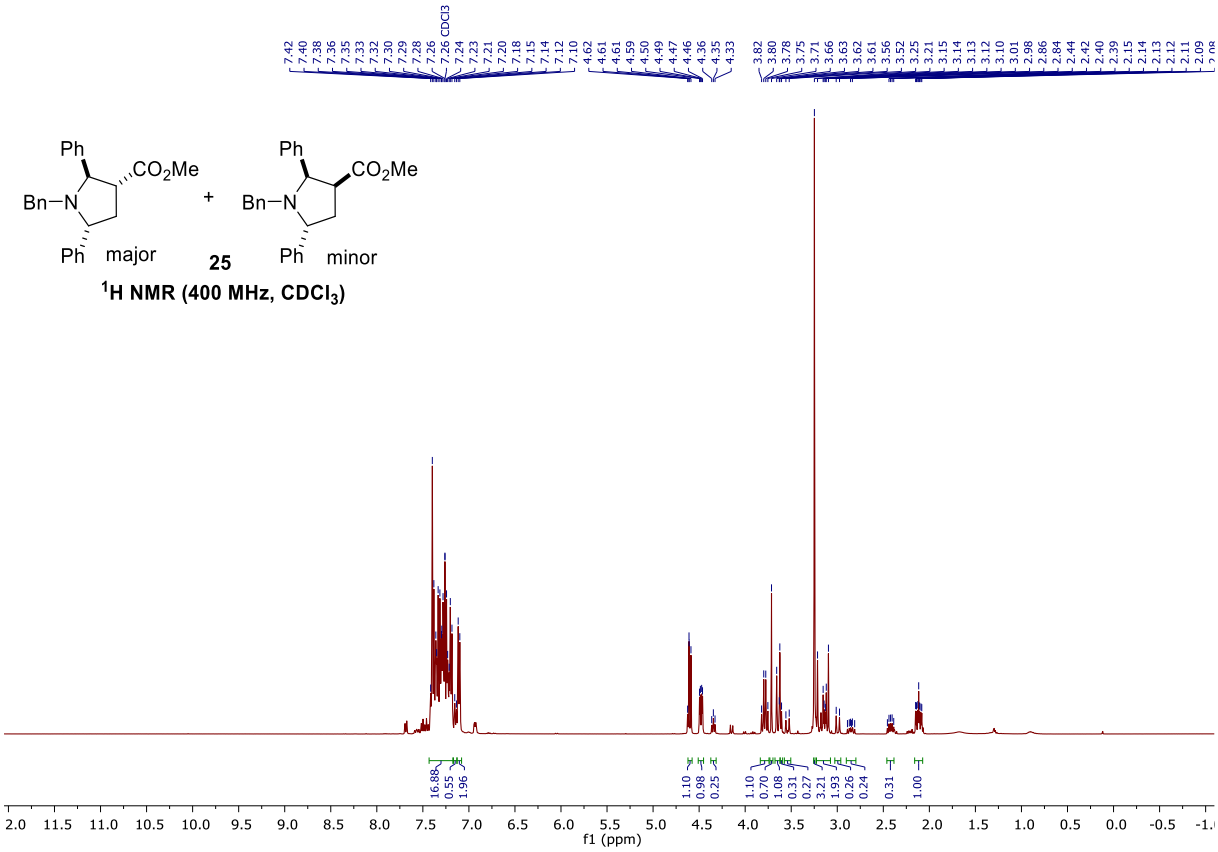
24

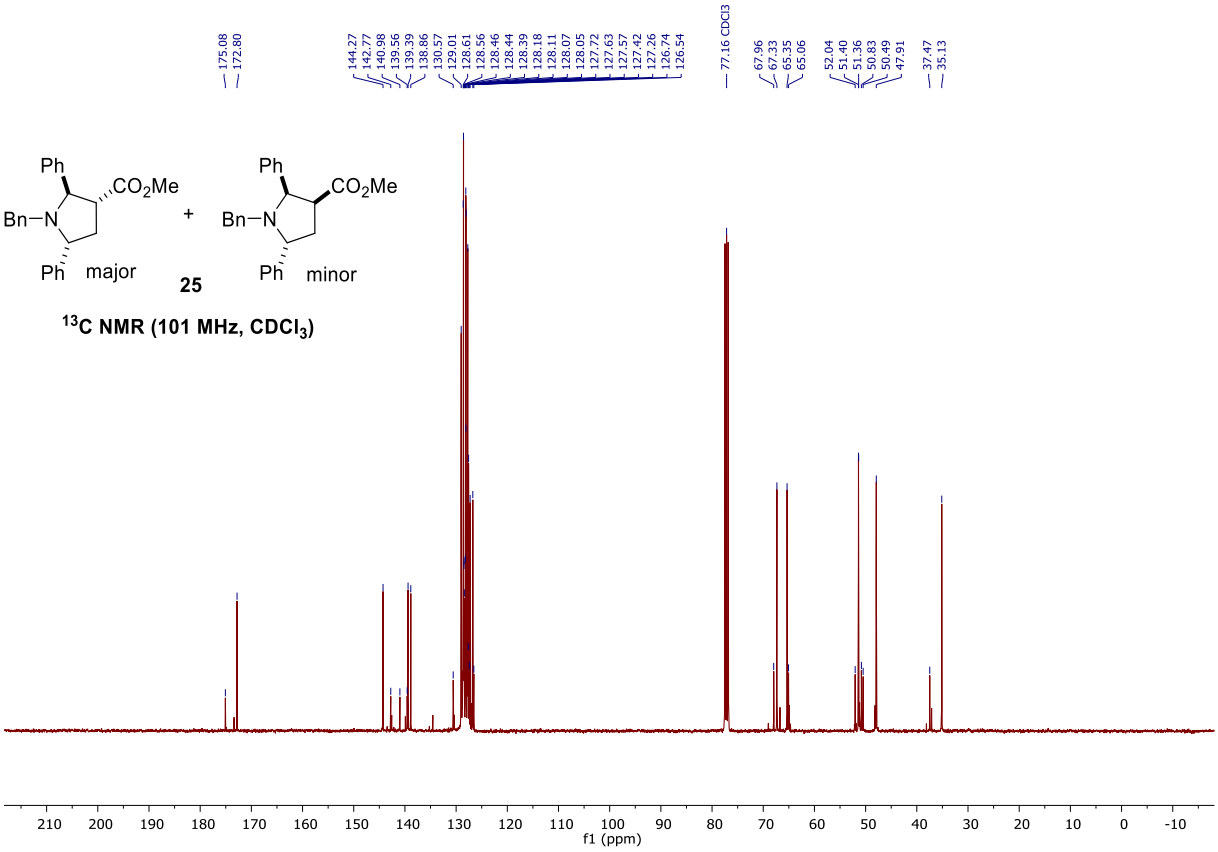
^{1}H NMR (400 MHz, $CDCl_3$)

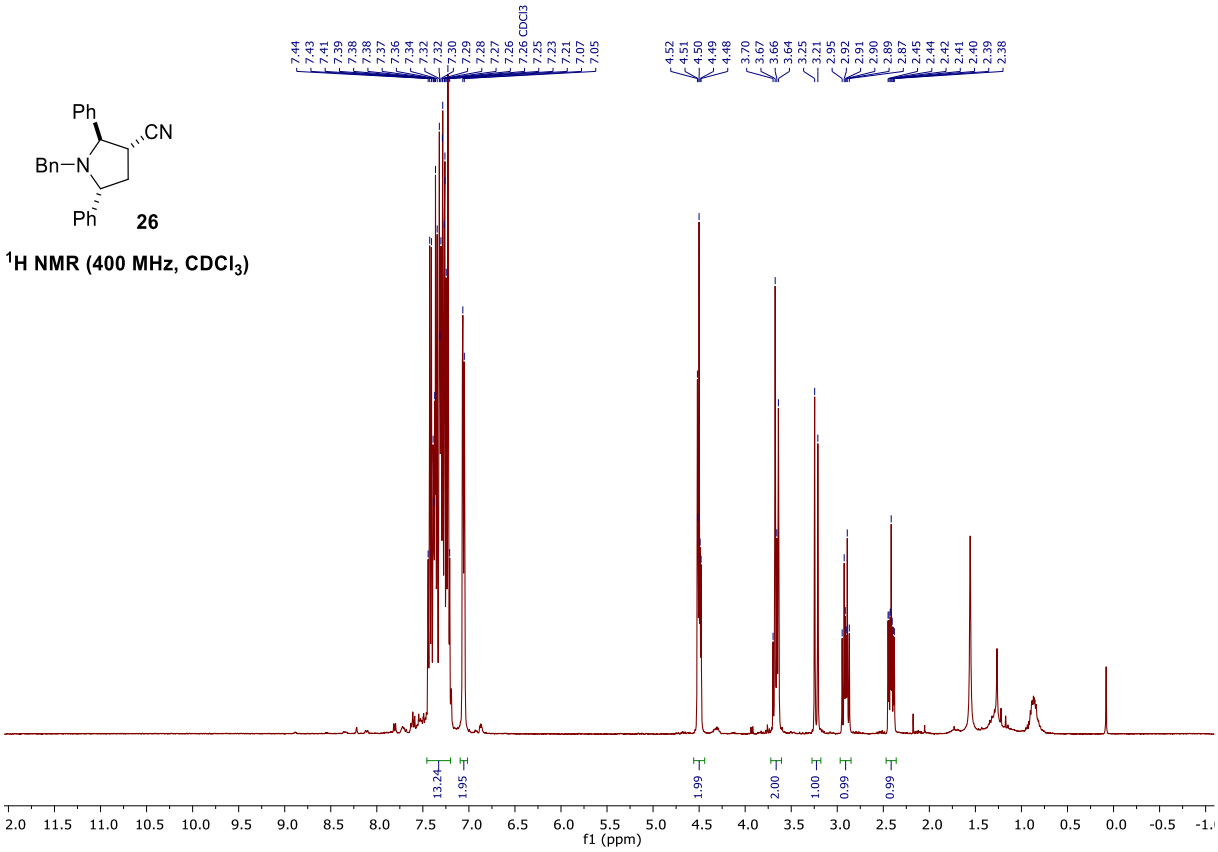


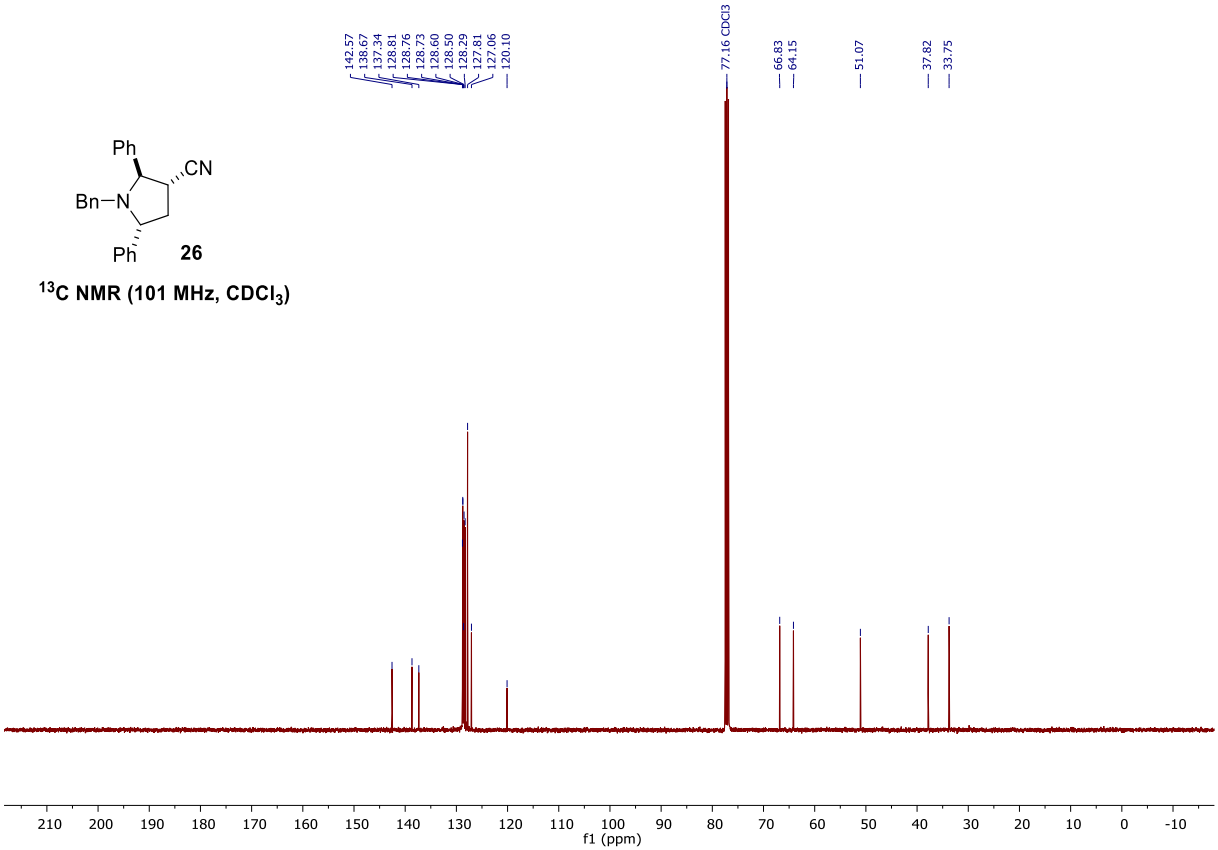
24

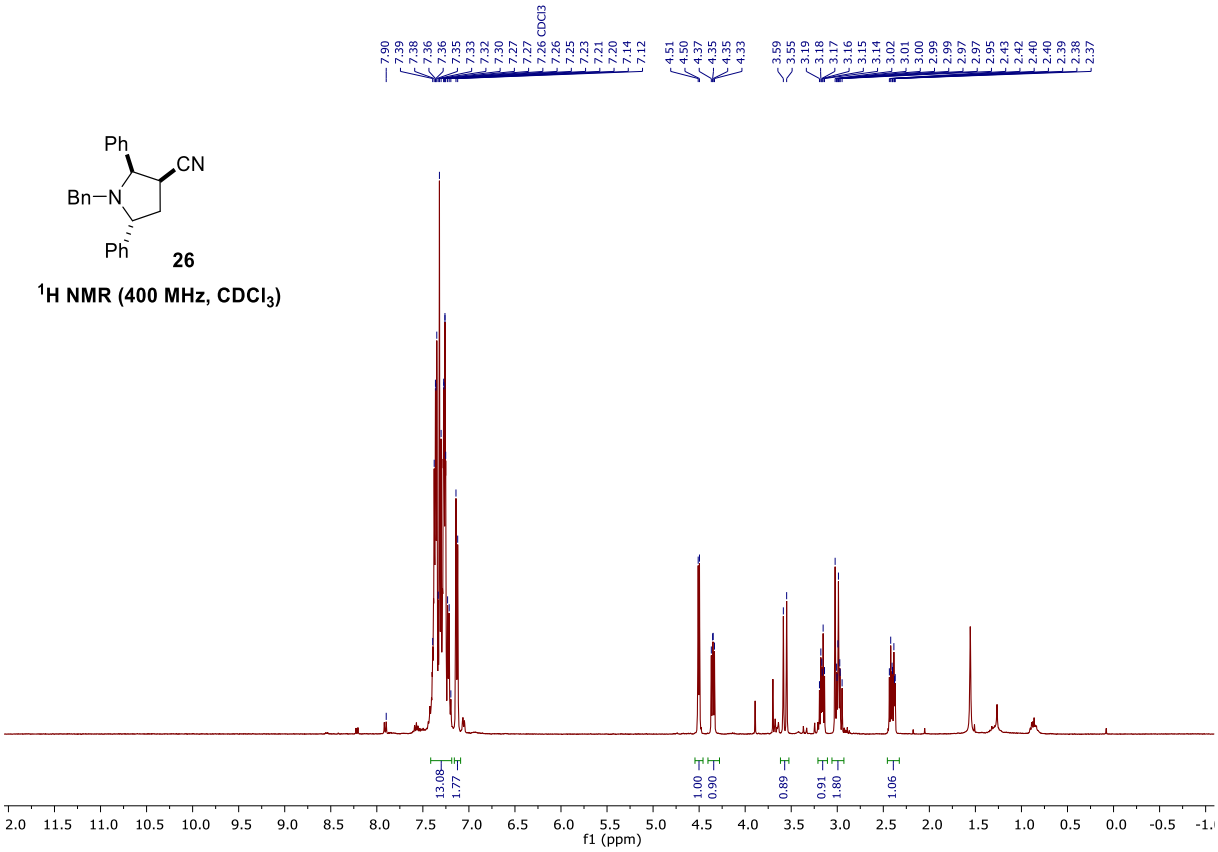
^{13}C NMR (101 MHz, $CDCl_3$)

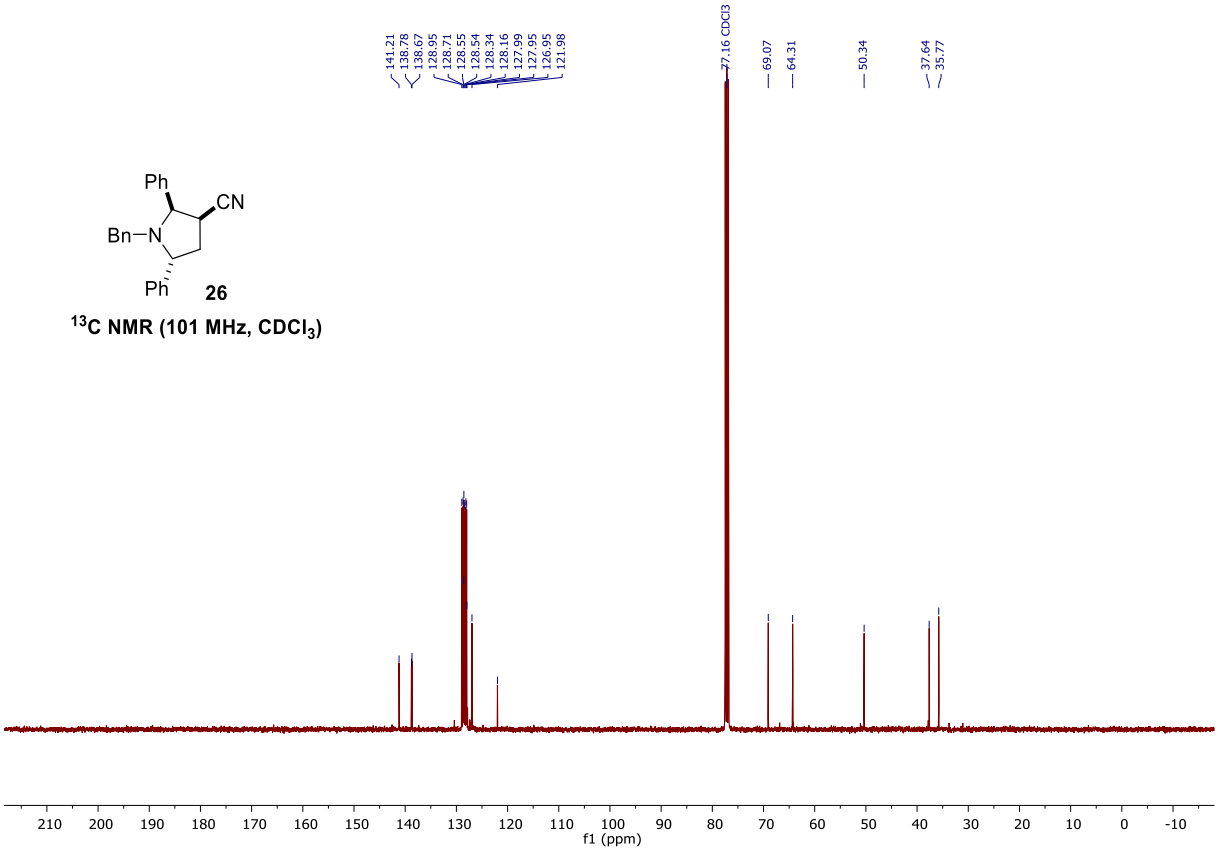

Ph
CO2Me
Bn–N
Ph
major
+
Ph
CO2Me
Bn–N
Ph
minor
25
1H NMR (400 MHz, CDCl3)
f1 (ppm)

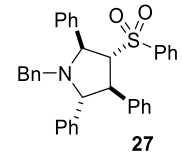

Ph
CO2Me
Bn–N
Ph
major
+
Ph
CO2Me
Bn–N
Ph
minor
25
13C NMR (101 MHz, CDCl3)
f1 (ppm)


Ph
CN
Bn—N
Ph
26
^{1}H NMR (400 MHz, CDCl$_3$)
7.44 7.43 7.41 7.39 7.38 7.38 7.37 7.36 7.34 7.32 7.32 7.30 7.29 7.28 7.27 7.26 CDCl3 7.25 7.23 7.21 7.07 7.05
4.52 4.51 4.50 4.49 4.48
3.70 3.67 3.66 3.64 3.25 3.21 2.95 2.92 2.91 2.90 2.89 2.87 2.45 2.44 2.42 2.41 2.40 2.39 2.38
13.24 1.95 1.99 2.00 1.00 0.99 0.99
f1 (ppm)


Ph
CN
Bn—N
Ph
26
^{13}C NMR (101 MHz, CDCl$_3$)
142.57 138.67 137.34 128.81 128.76 128.73 128.60 128.50 128.29 127.81 127.06 120.10
77.16 CDCl3
66.83 64.15 51.07 37.82 33.75
f1 (ppm)

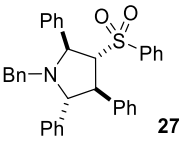

Ph
CN
Bn—N
Ph
26
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


Ph
CN
Bn—N
Ph
26
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)



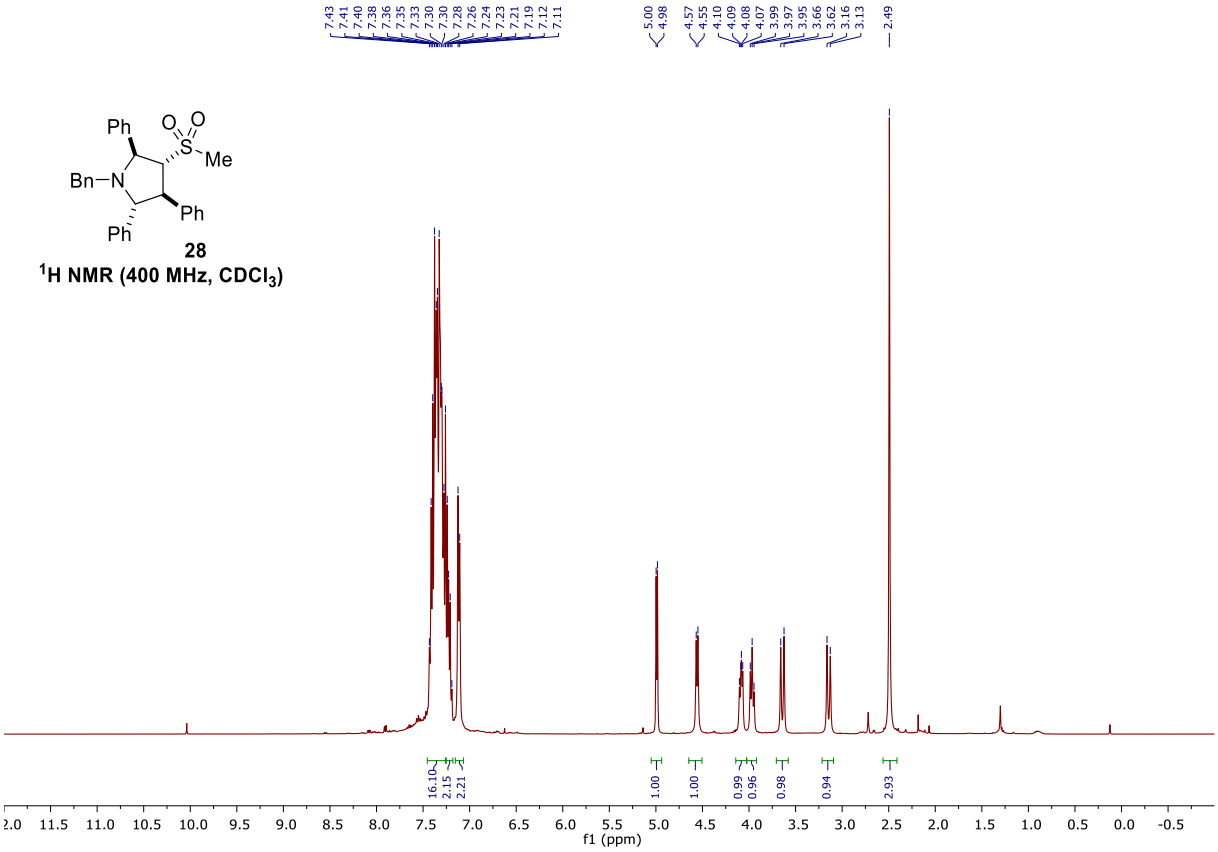
27

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



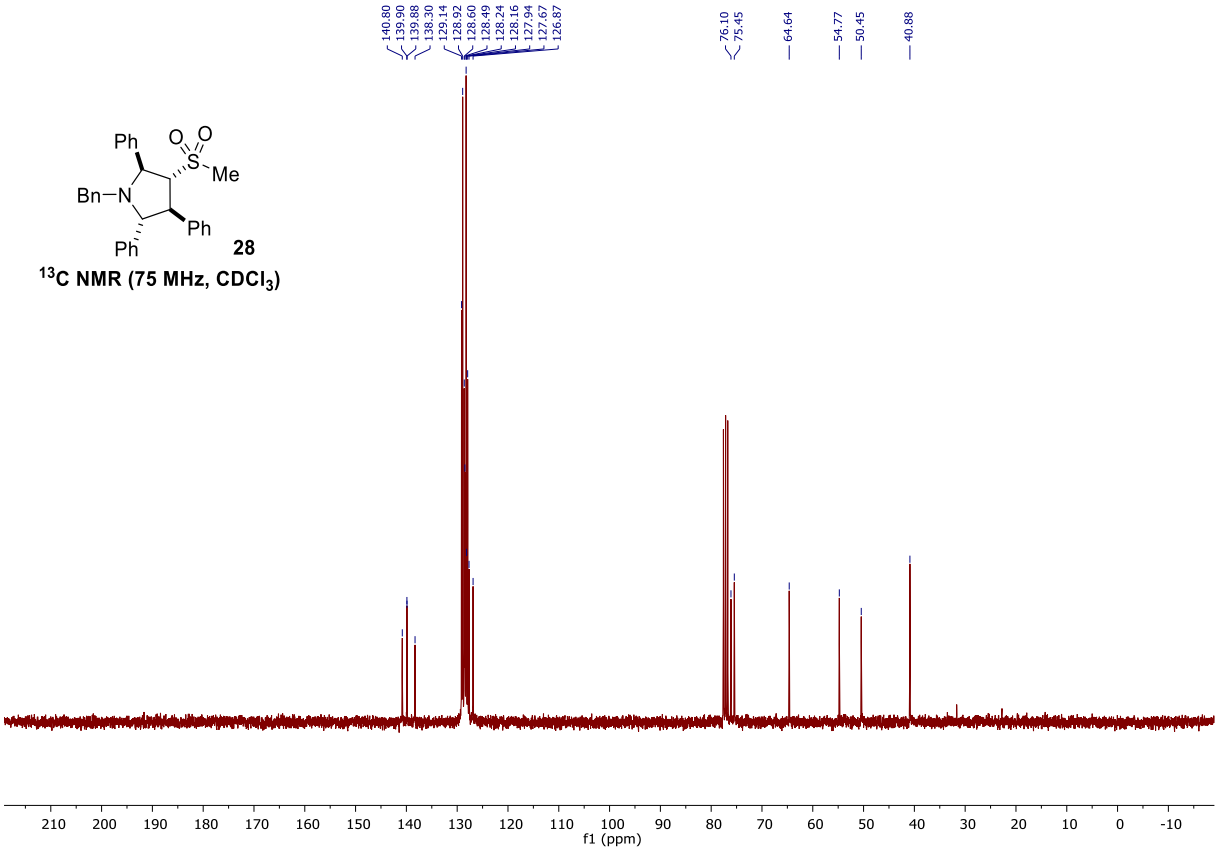
27

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



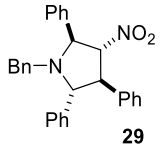
28

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



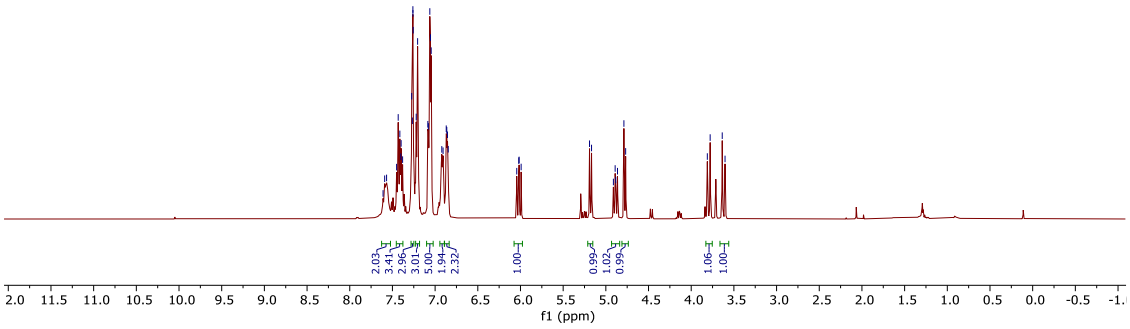
28

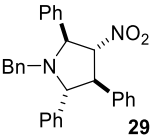
^{13}C NMR (75 MHz, $CDCl_3$)



29

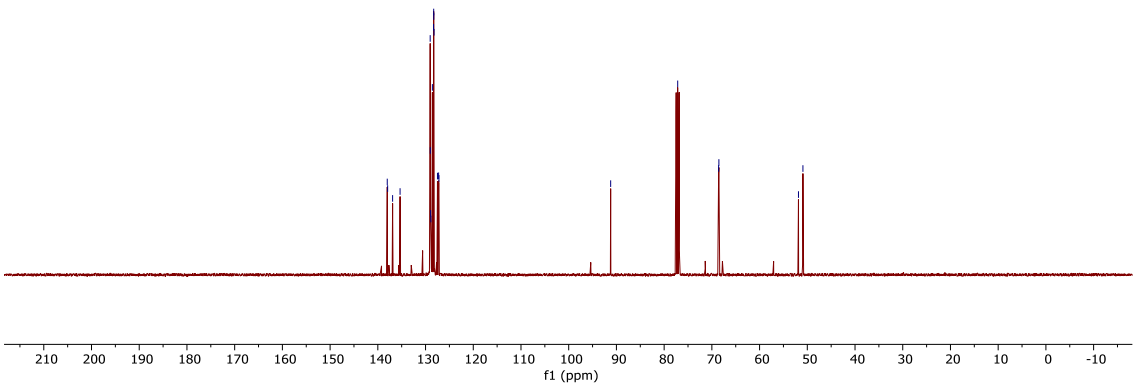
^{1}H NMR (400 MHz, $CDCl_3$)

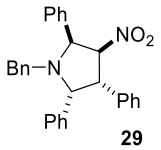




29

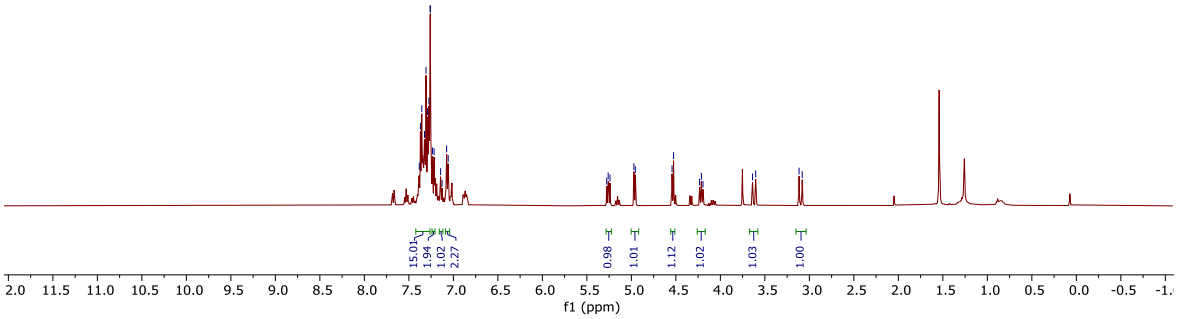
^{13}C NMR (101 MHz, $CDCl_3$)

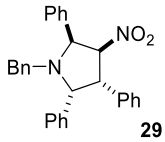




29

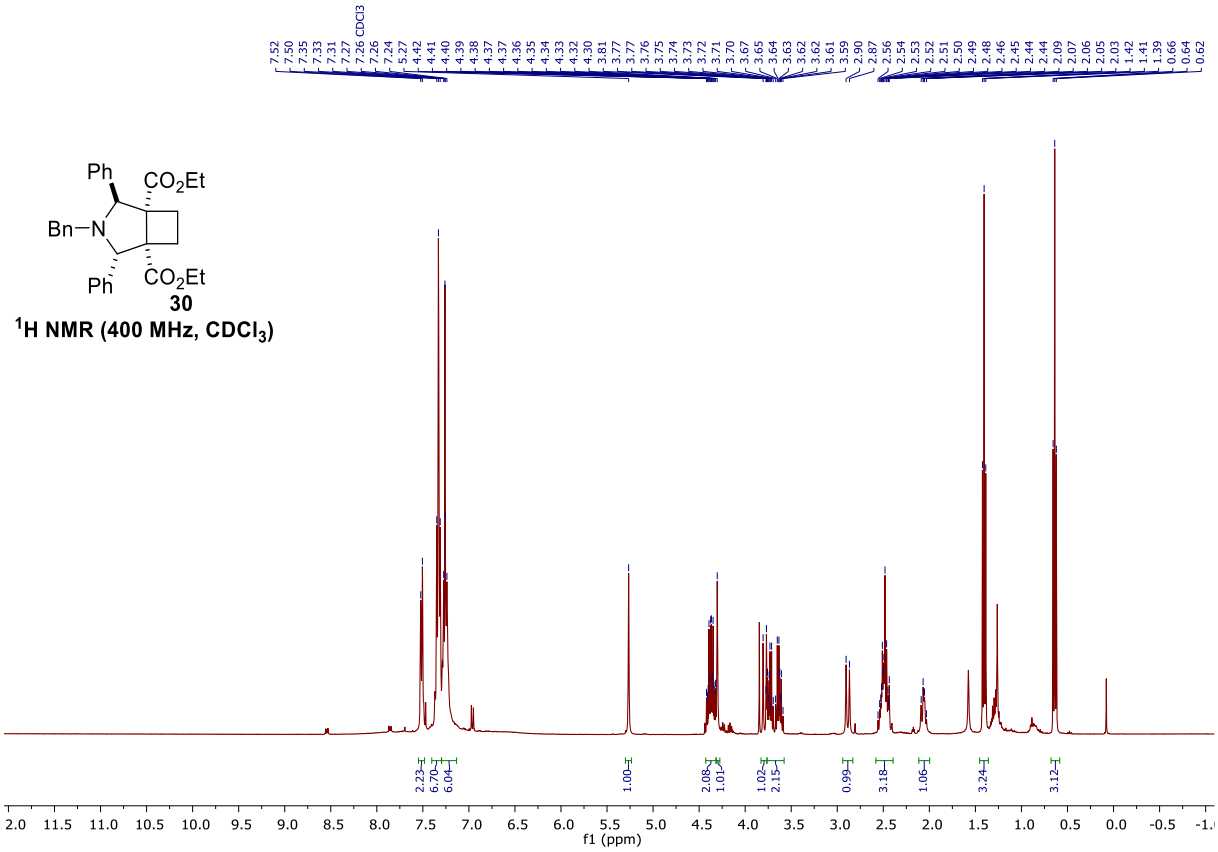
^{1}H NMR (400 MHz, $CDCl_3$)

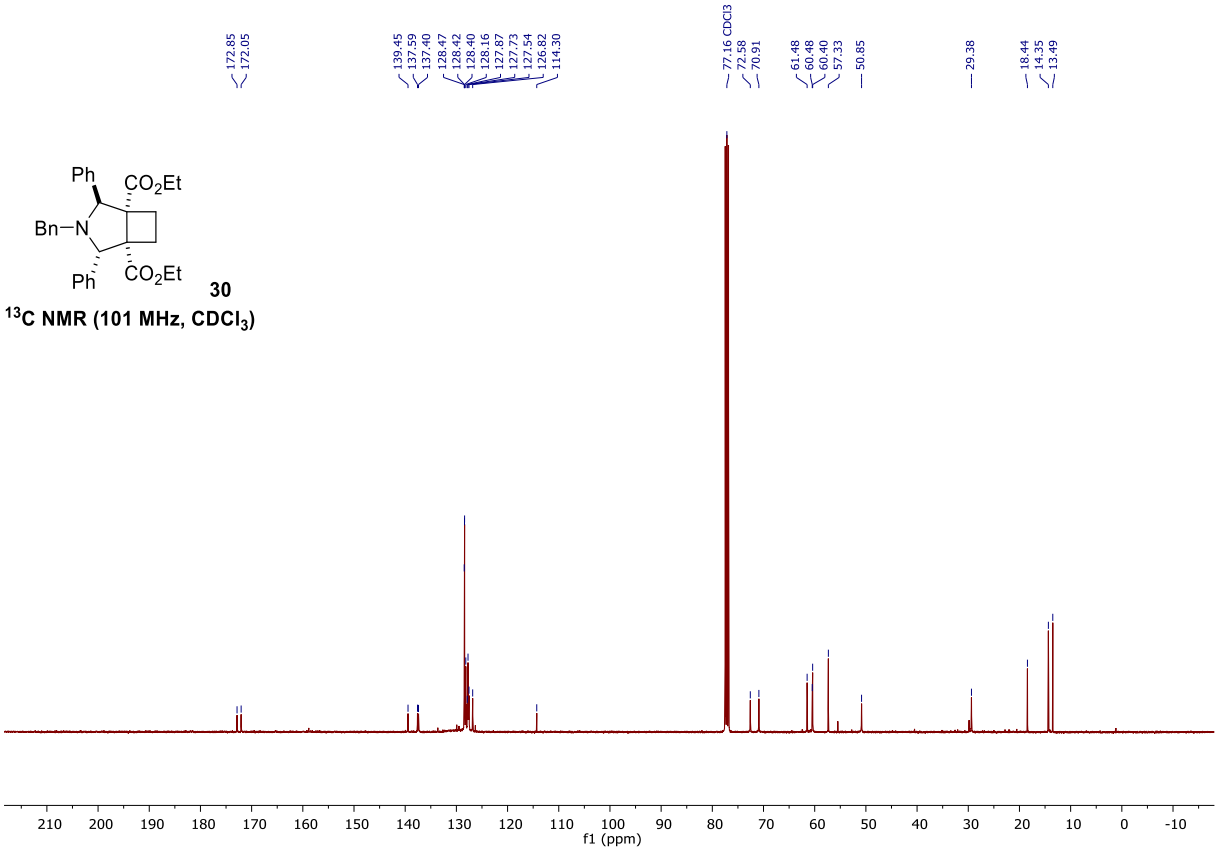


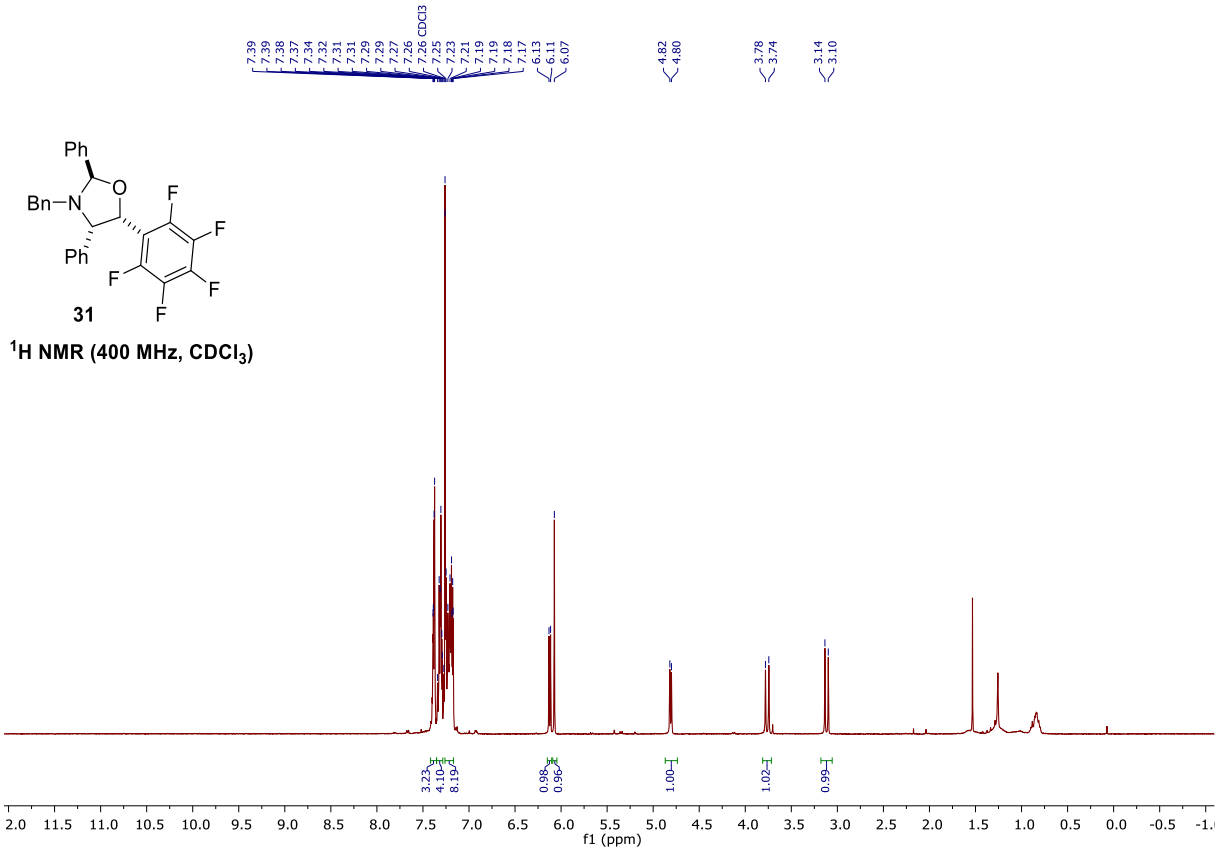


29

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

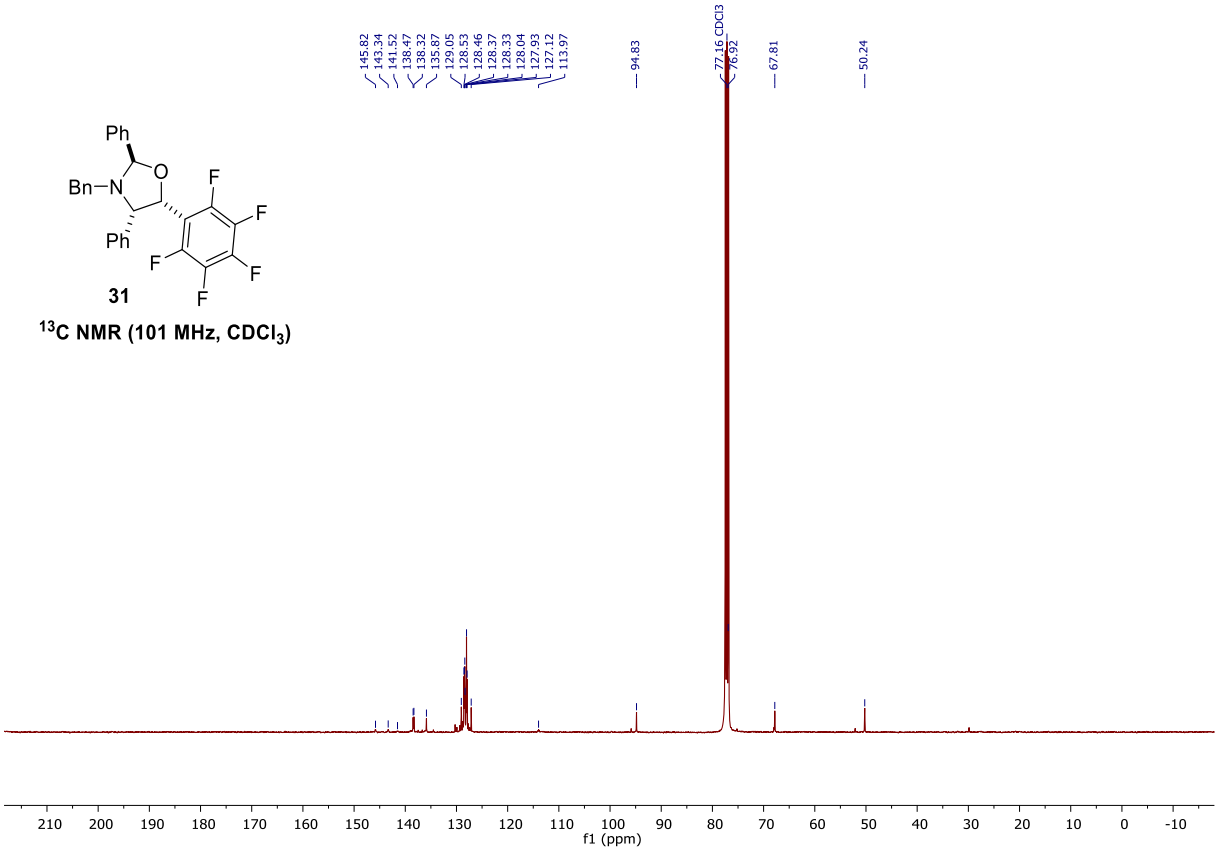

Ph
CO2Et
Bn–N
Ph
CO2Et
30
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Ph
CO2Et
Bn–N
Ph
CO2Et
30
13C NMR (101 MHz, CDCl3)
f1 (ppm)



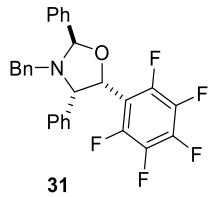
31

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



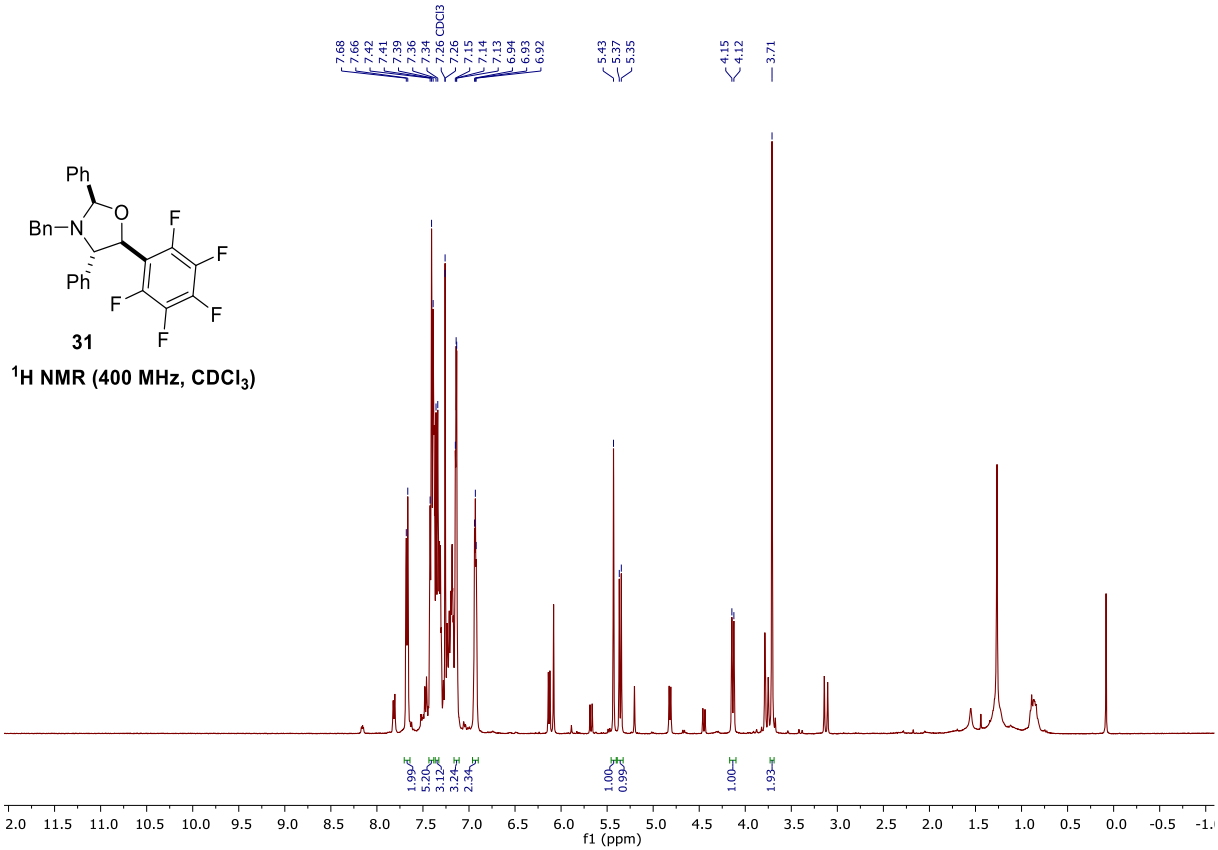
31

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



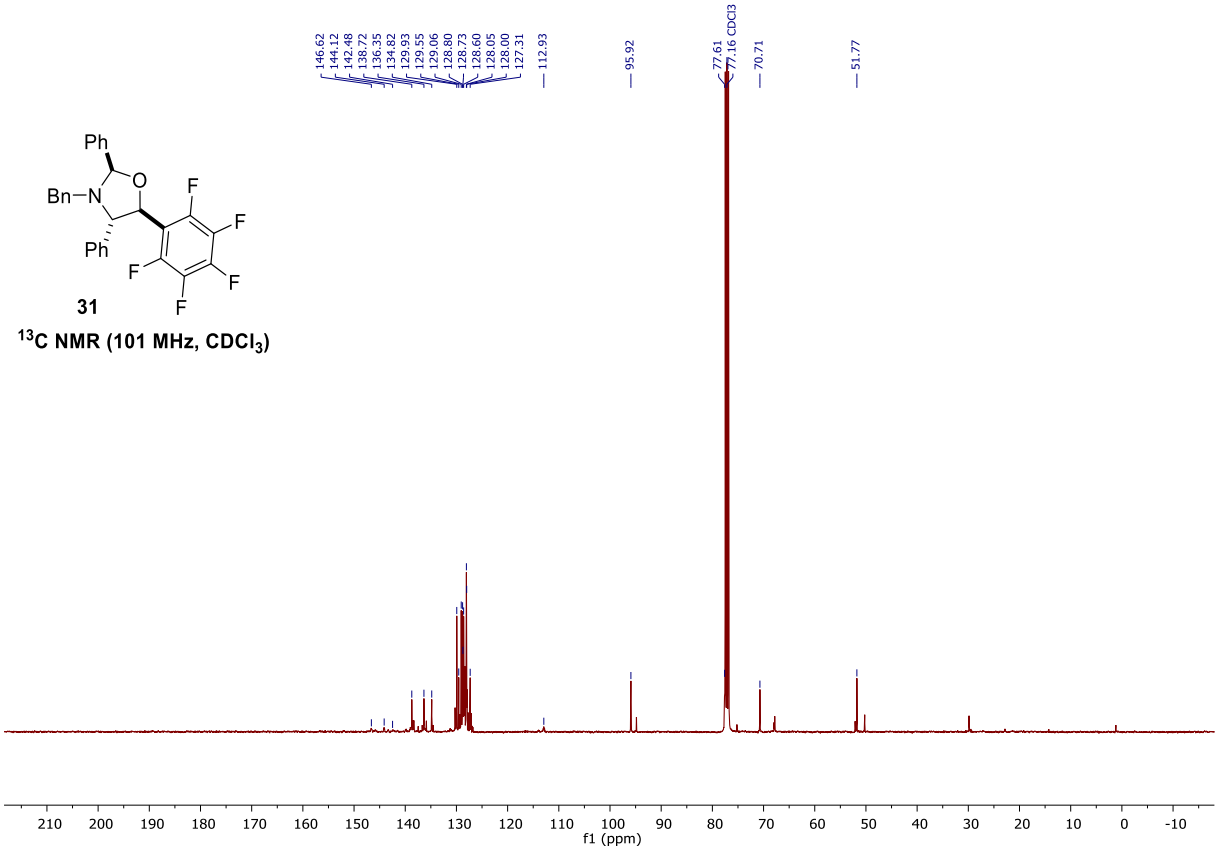
31

^{19}F NMR (377 MHz, $CDCl_3$)

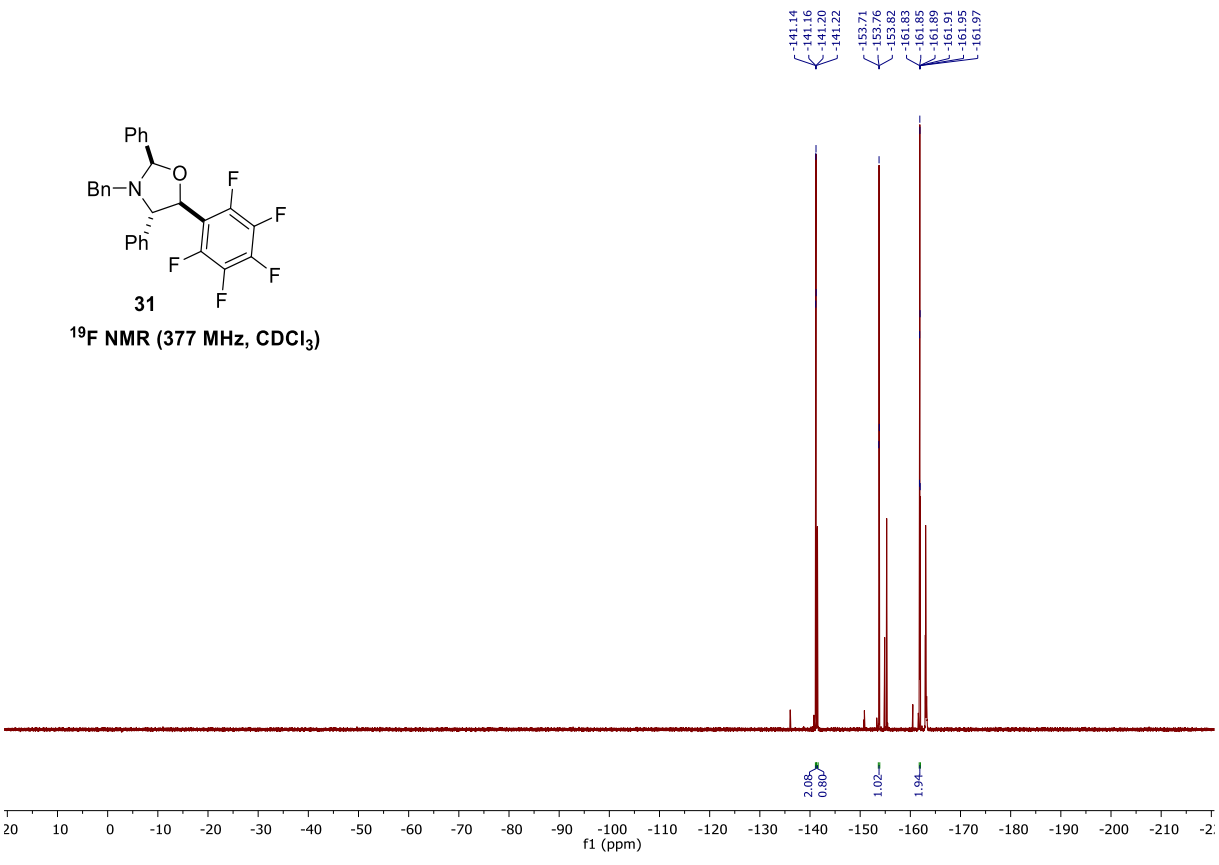


31

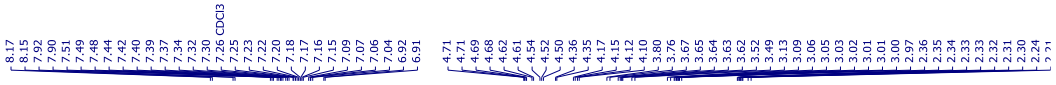
^{1}H NMR (400 MHz, $CDCl_3$)

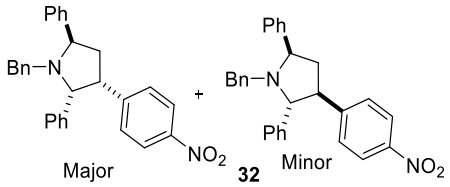


^{13}C NMR (101 MHz, $CDCl_3$)

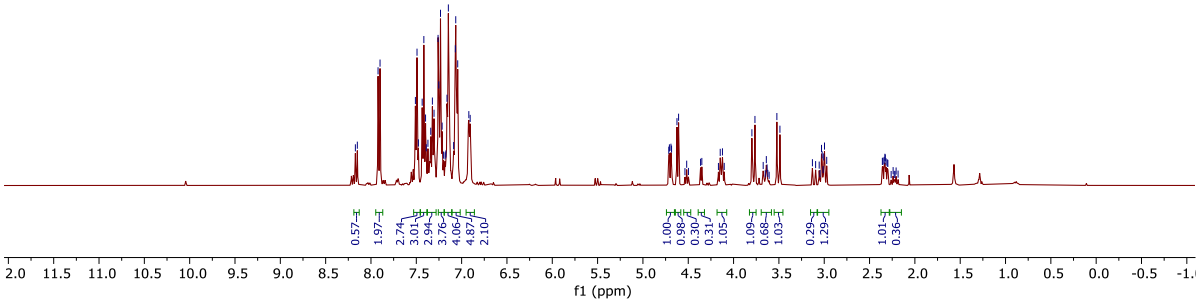


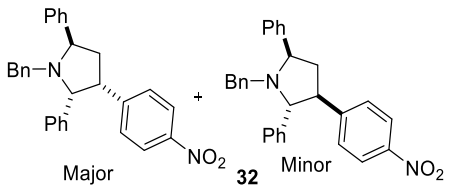
^{19}F NMR (377 MHz, $CDCl_3$)



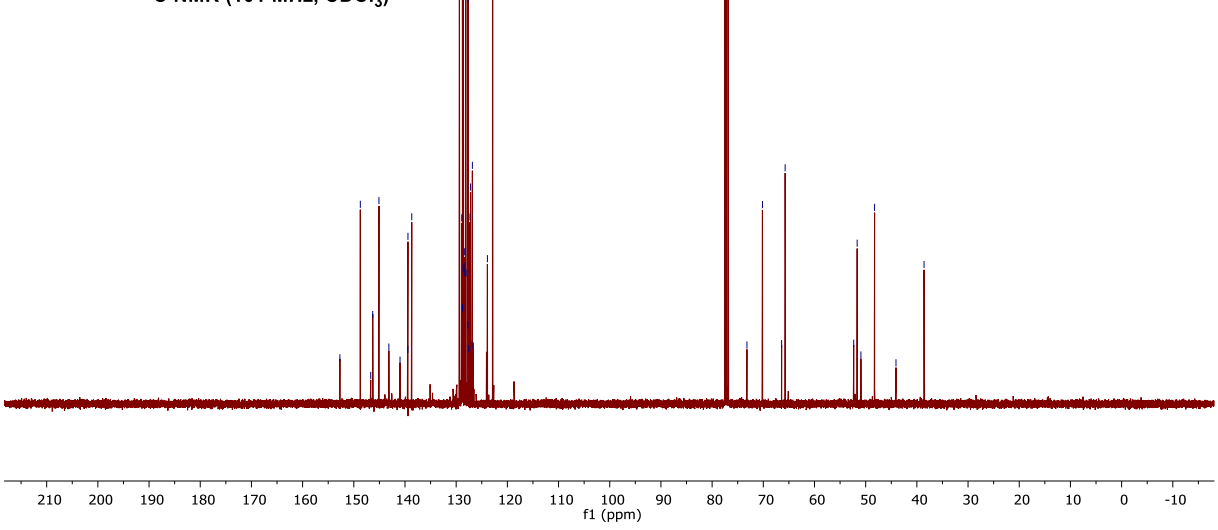


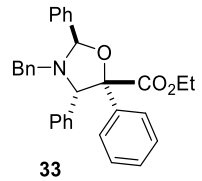
^{1}H NMR (400 MHz, $CDCl_3$)





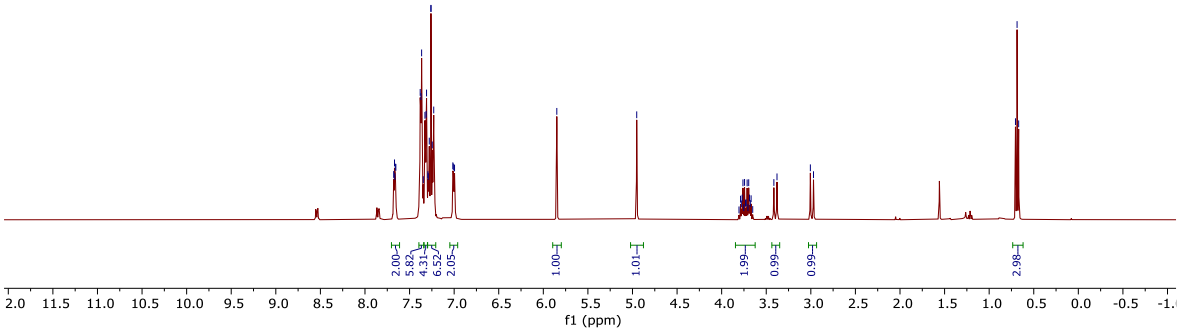
^{13}C NMR (101 MHz, $CDCl_3$)

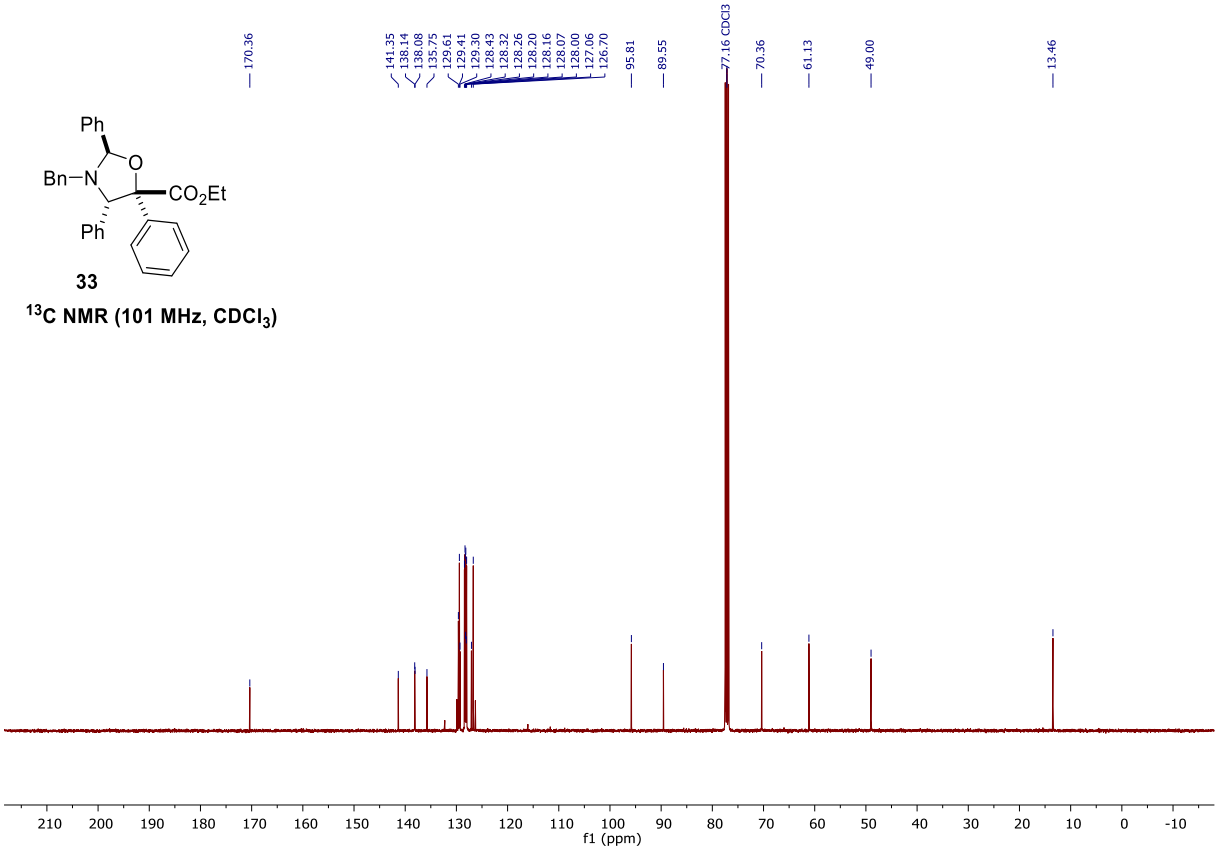




33

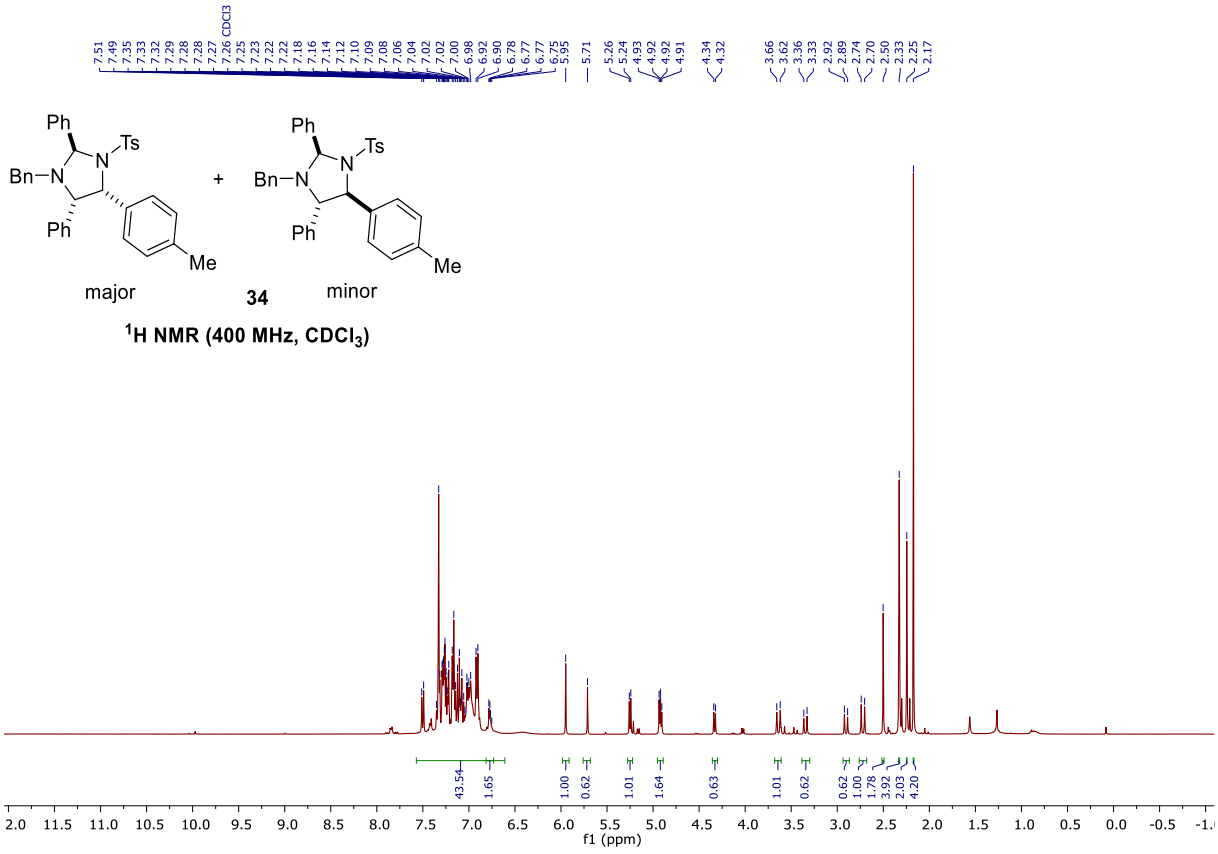
^{1}H NMR (400 MHz, $CDCl_3$)

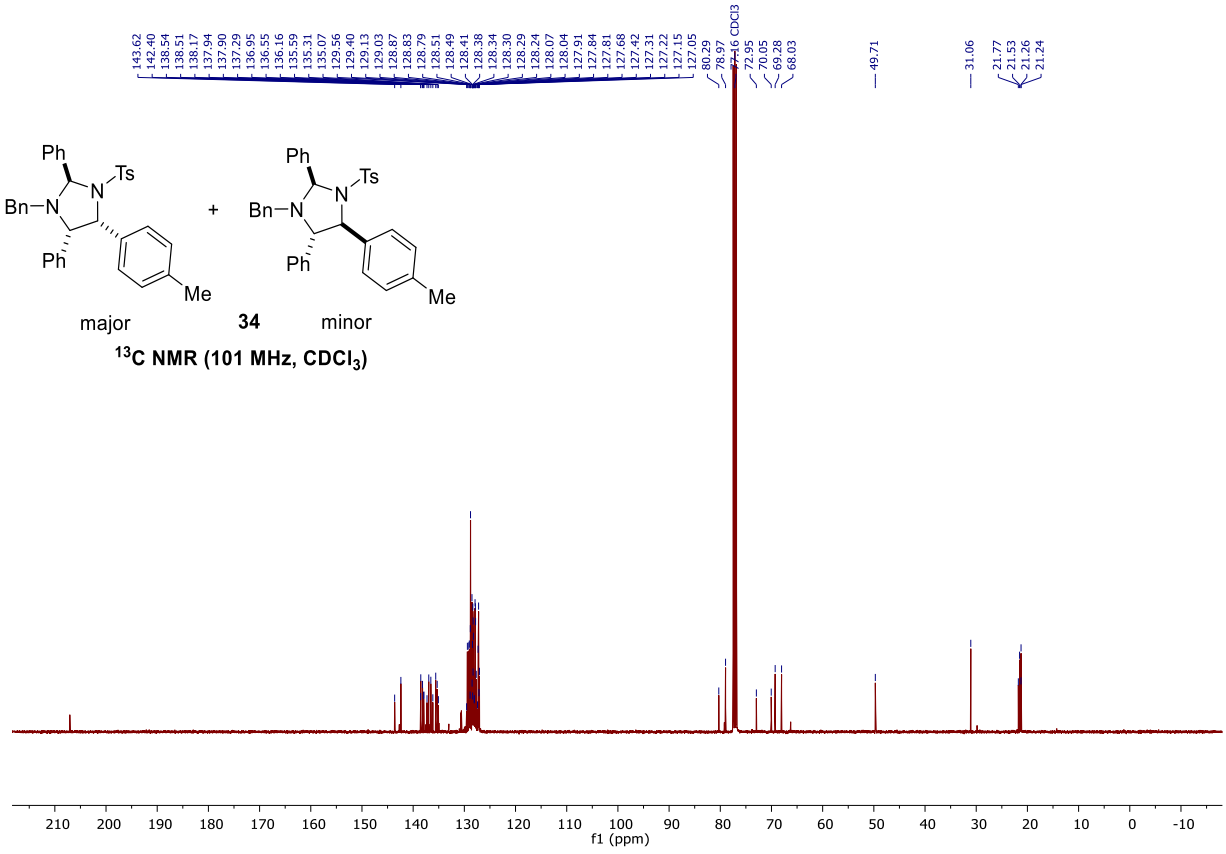


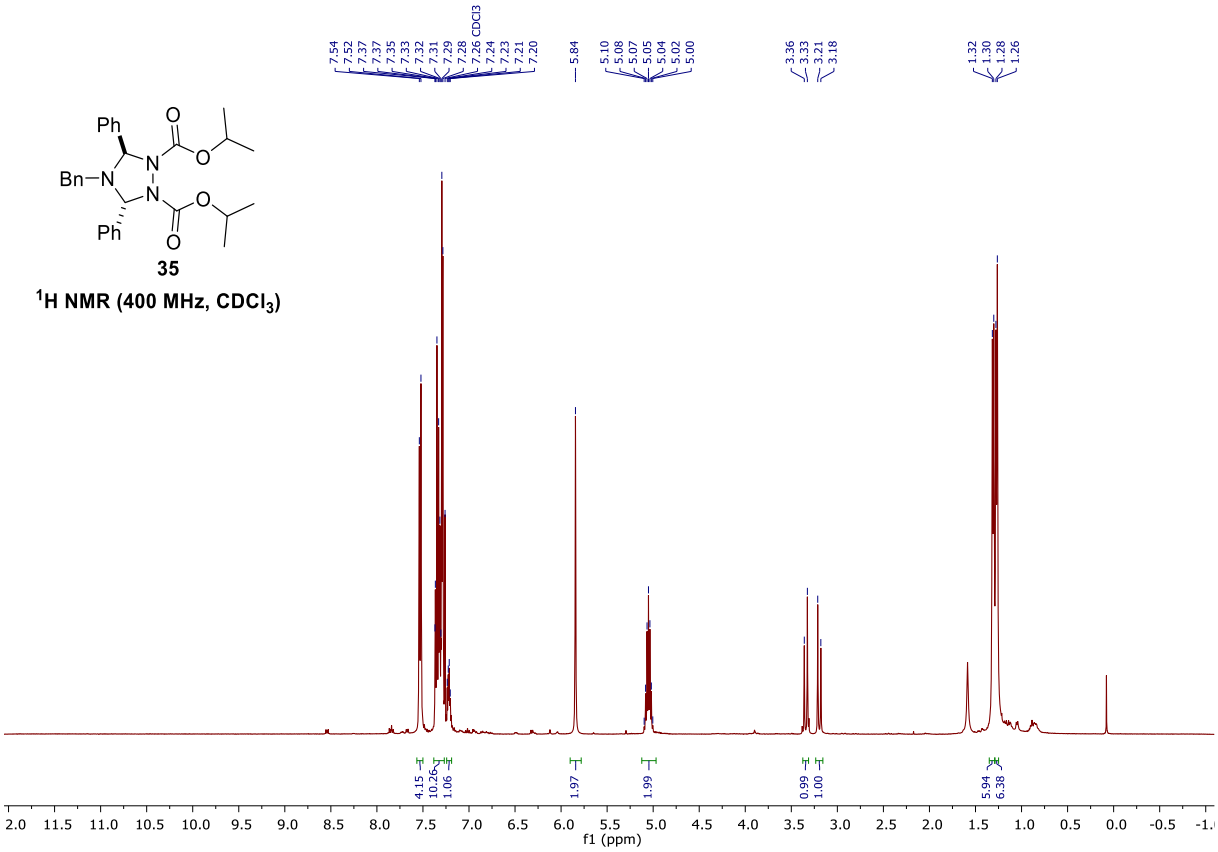


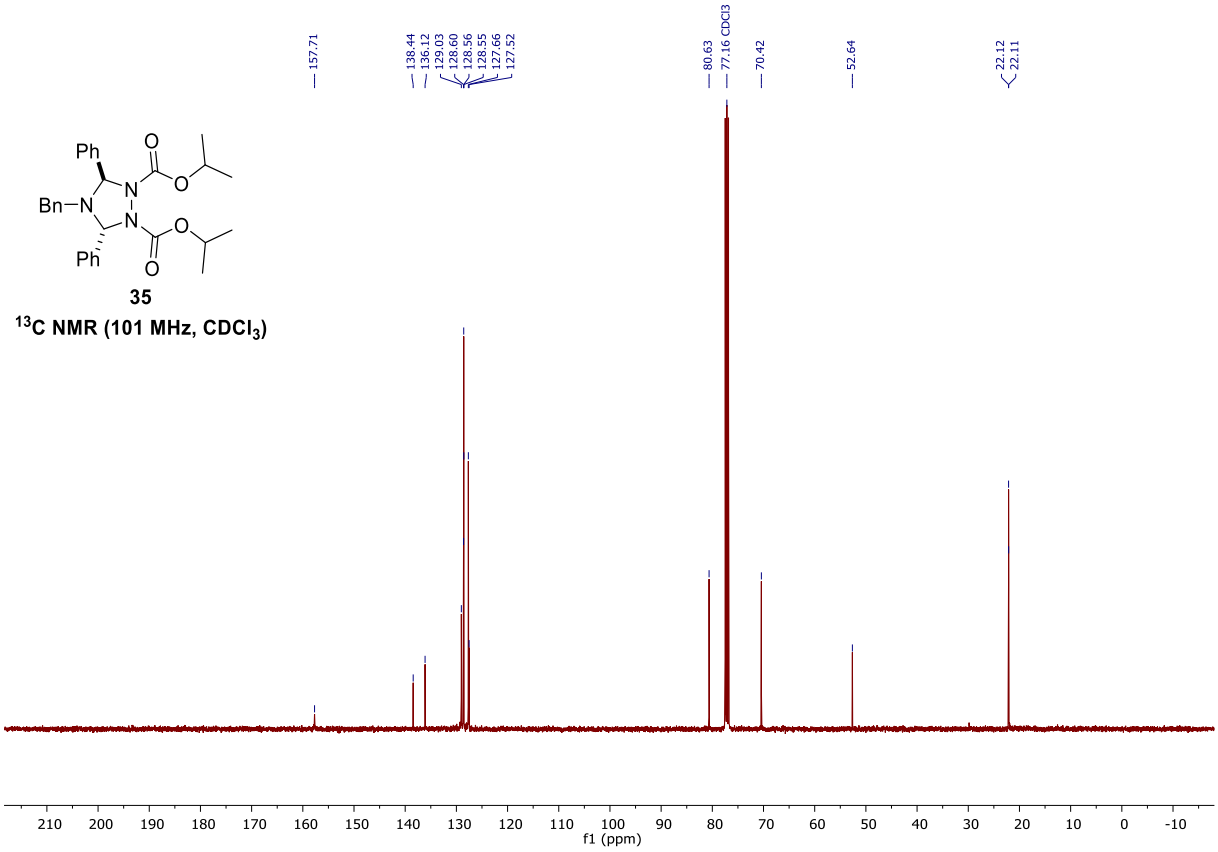
33

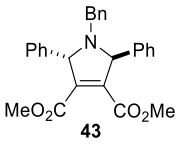
^{13}C NMR (101 MHz, $CDCl_3$)


major
34
minor
1H NMR (400 MHz, CDCl3)
f1 (ppm)


major
34
minor
13C NMR (101 MHz, CDCl3)
f1 (ppm)

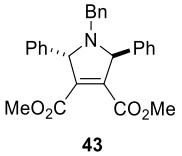

7.54
7.52
7.37
7.37
7.35
7.33
7.32
7.31
7.29
7.28
7.26 CDCl3
7.24
7.23
7.21
7.20
5.84
5.10
5.08
5.07
5.05
5.04
5.02
5.00
3.36
3.33
3.21
3.18
1.32
1.30
1.28
1.26
Ph
Bn—N
N
N
O
O
O
O
Ph
35
1H NMR (400 MHz, CDCl3)
4.15
10.26
1.06
1.97
1.99
0.99
1.00
5.94
6.38
f1 (ppm)


157.71
138.44
136.12
129.03
128.60
128.56
128.55
127.66
127.52
80.63
77.16 CDCl3
70.42
52.64
22.12
22.11
Ph
Bn—N
N
N
O
O
O
O
Ph
35
13C NMR (101 MHz, CDCl3)
f1 (ppm)



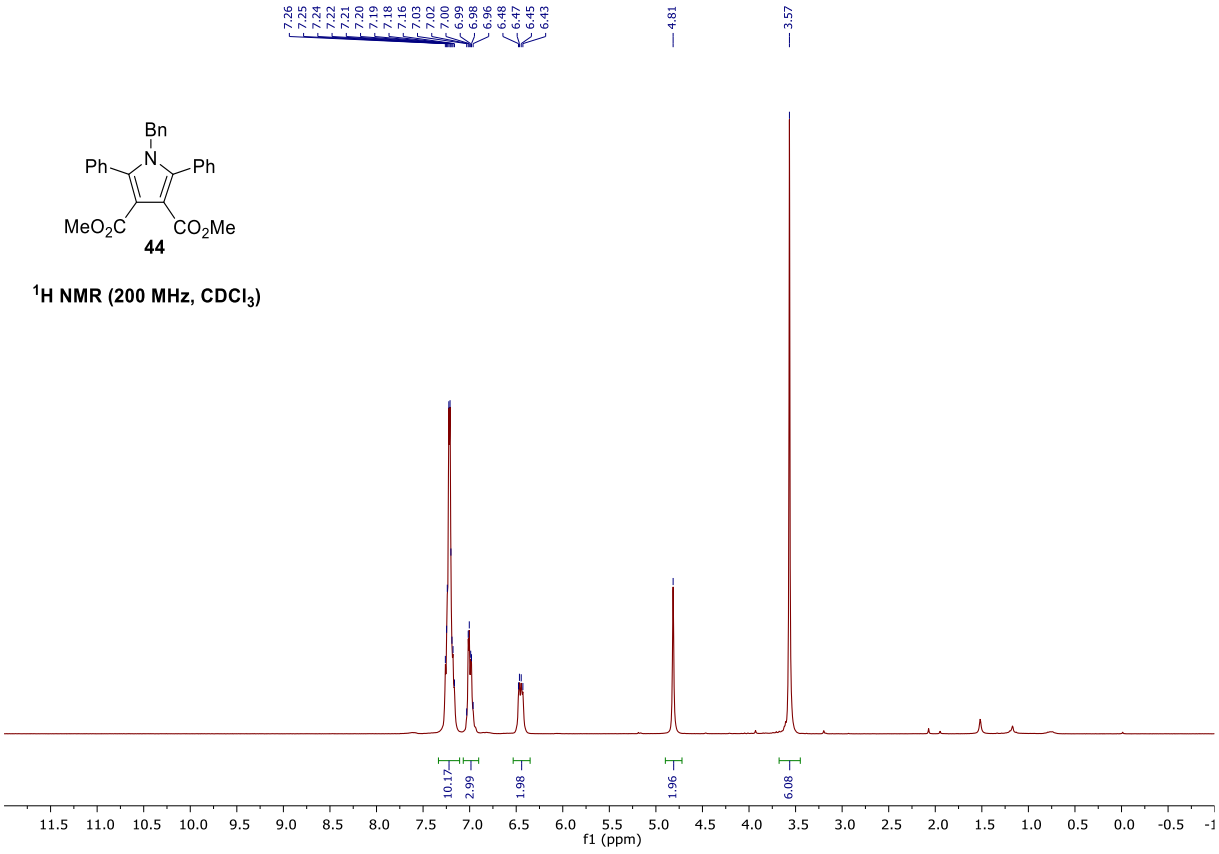
43

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

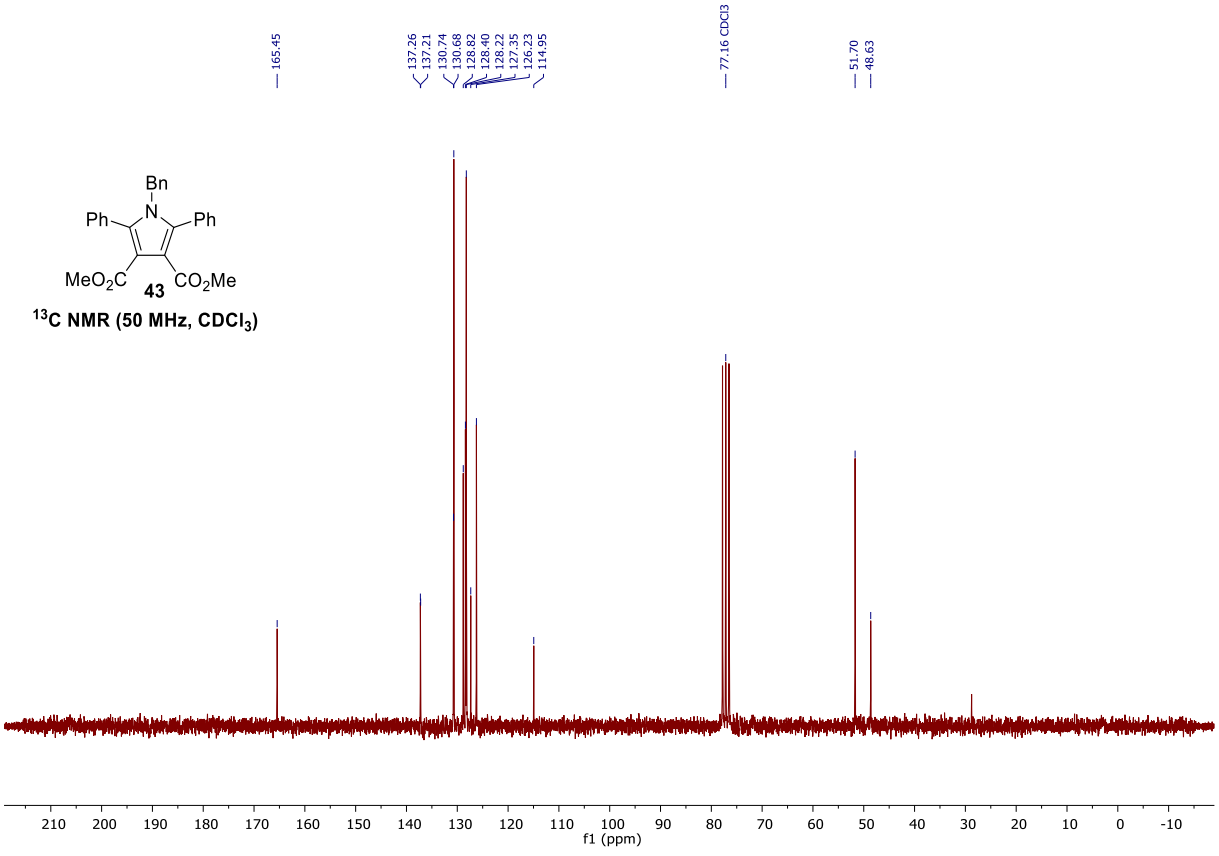


43

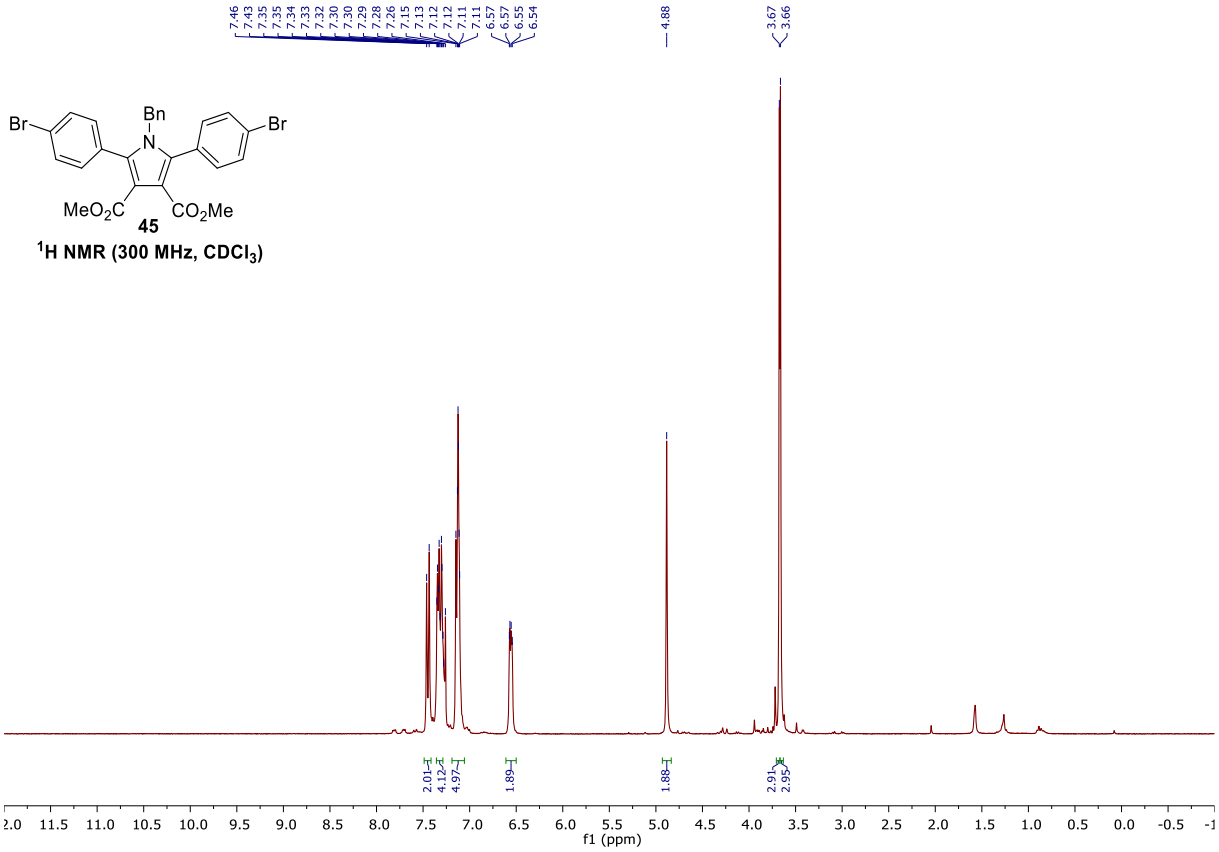
^{13}C NMR (101 MHz, $CDCl_3$)

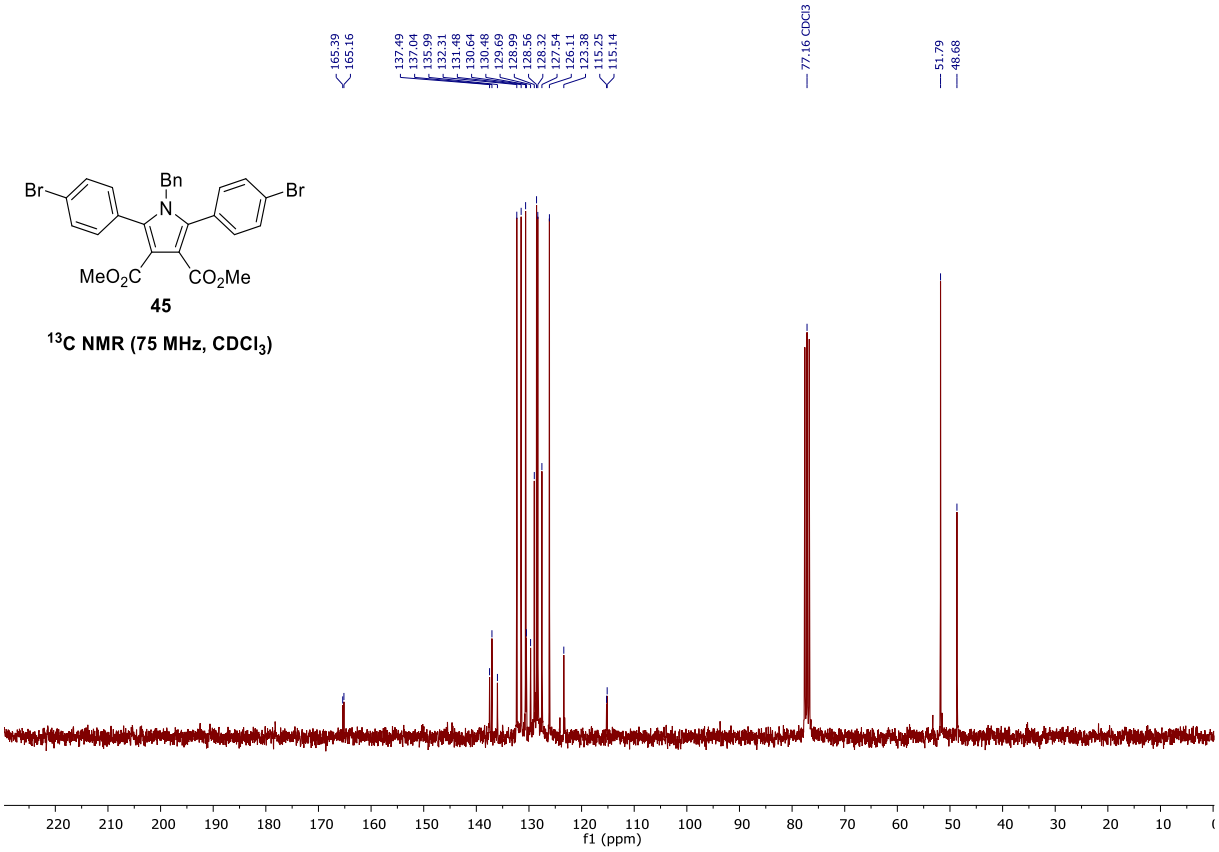


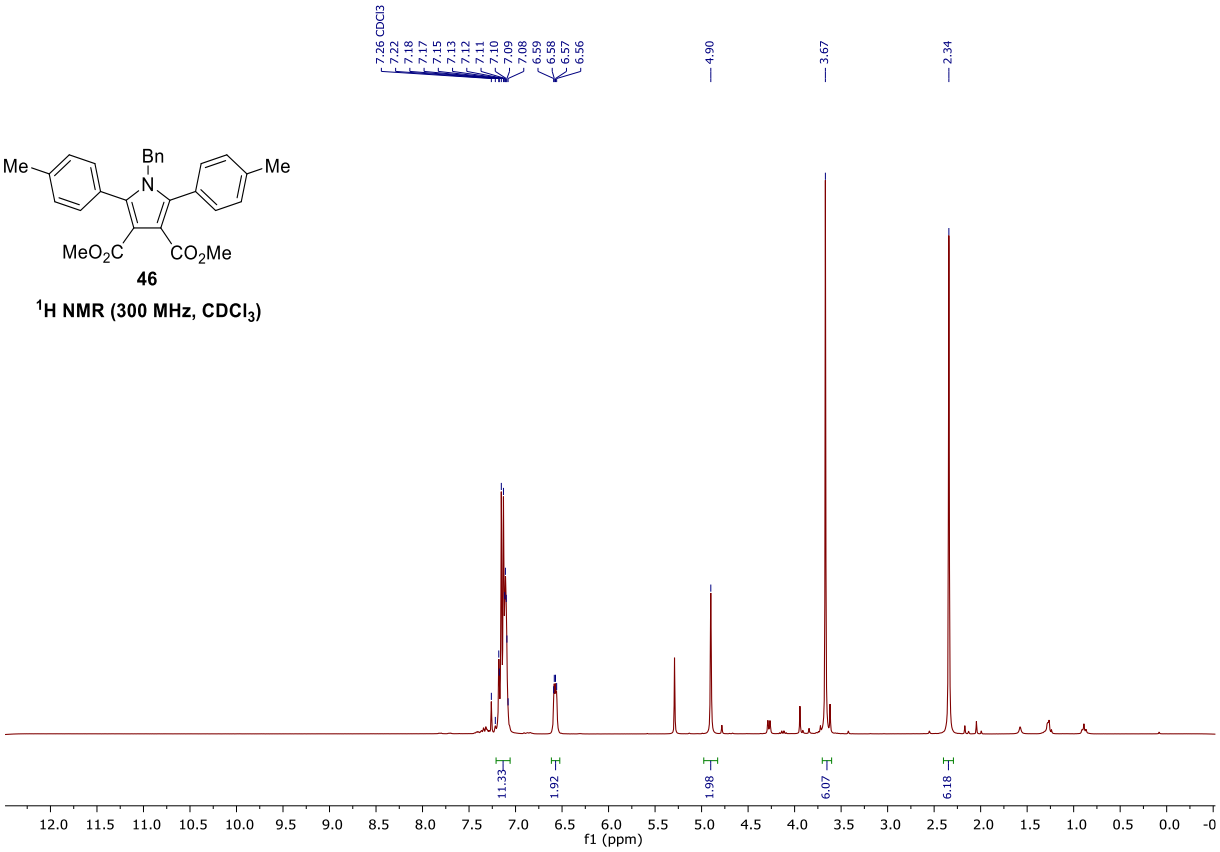
^{1}H NMR (200 MHz, $CDCl_3$)



^{13}C NMR (50 MHz, $CDCl_3$)

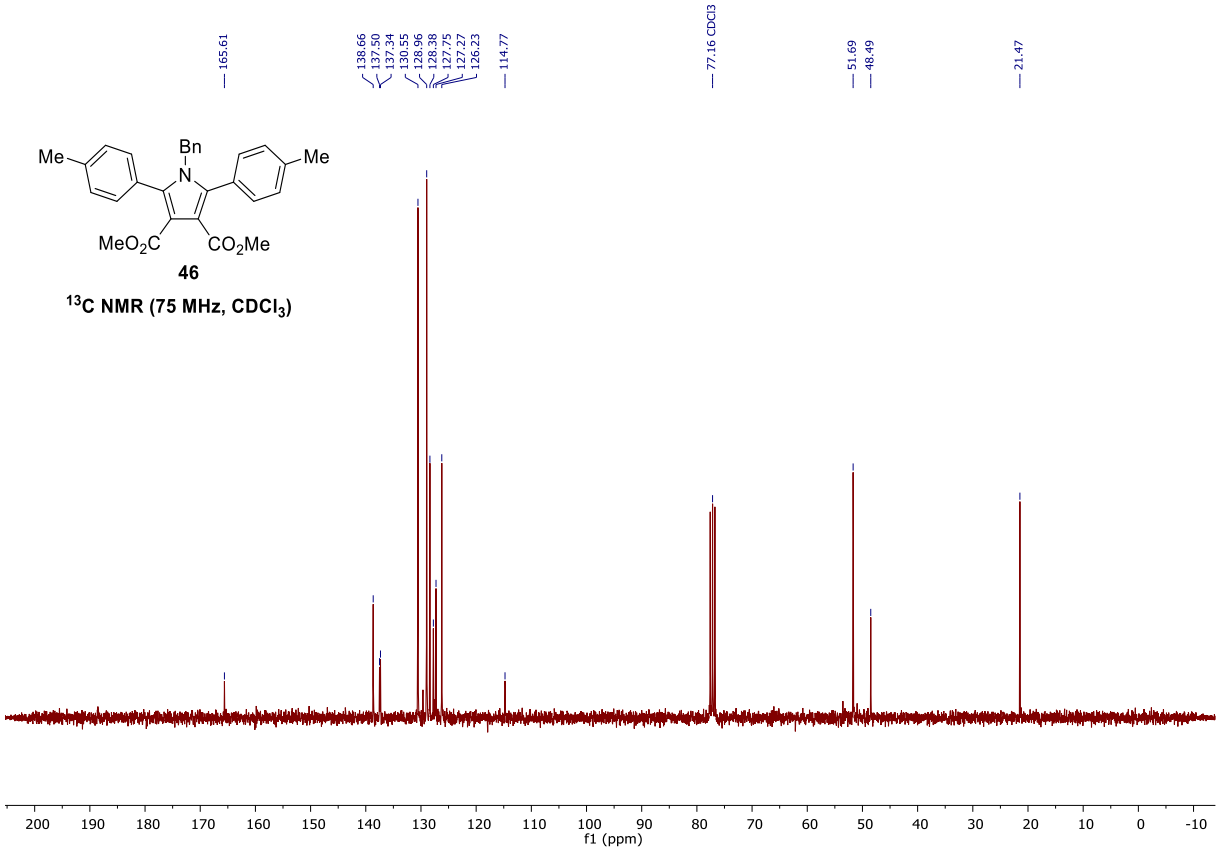

Br
Bn
N
Br
MeO2C
CO2Me
45
1H NMR (300 MHz, CDCl3)
7.46
7.43
7.35
7.34
7.33
7.32
7.30
7.30
7.29
7.28
7.26
7.15
7.13
7.12
7.12
7.11
7.11
6.57
6.57
6.55
6.54
4.88
3.67
3.66
2.01
4.12
4.97
1.89
1.88
2.91
2.95
f1 (ppm)


Br
Bn
N
Br
MeO2C
CO2Me
45
13C NMR (75 MHz, CDCl3)
165.39
165.16
137.49
137.04
135.99
132.31
131.48
130.64
130.48
129.69
128.99
128.56
128.32
127.54
126.11
123.38
115.25
115.14
77.16 CDCl3
51.79
48.68
f1 (ppm)



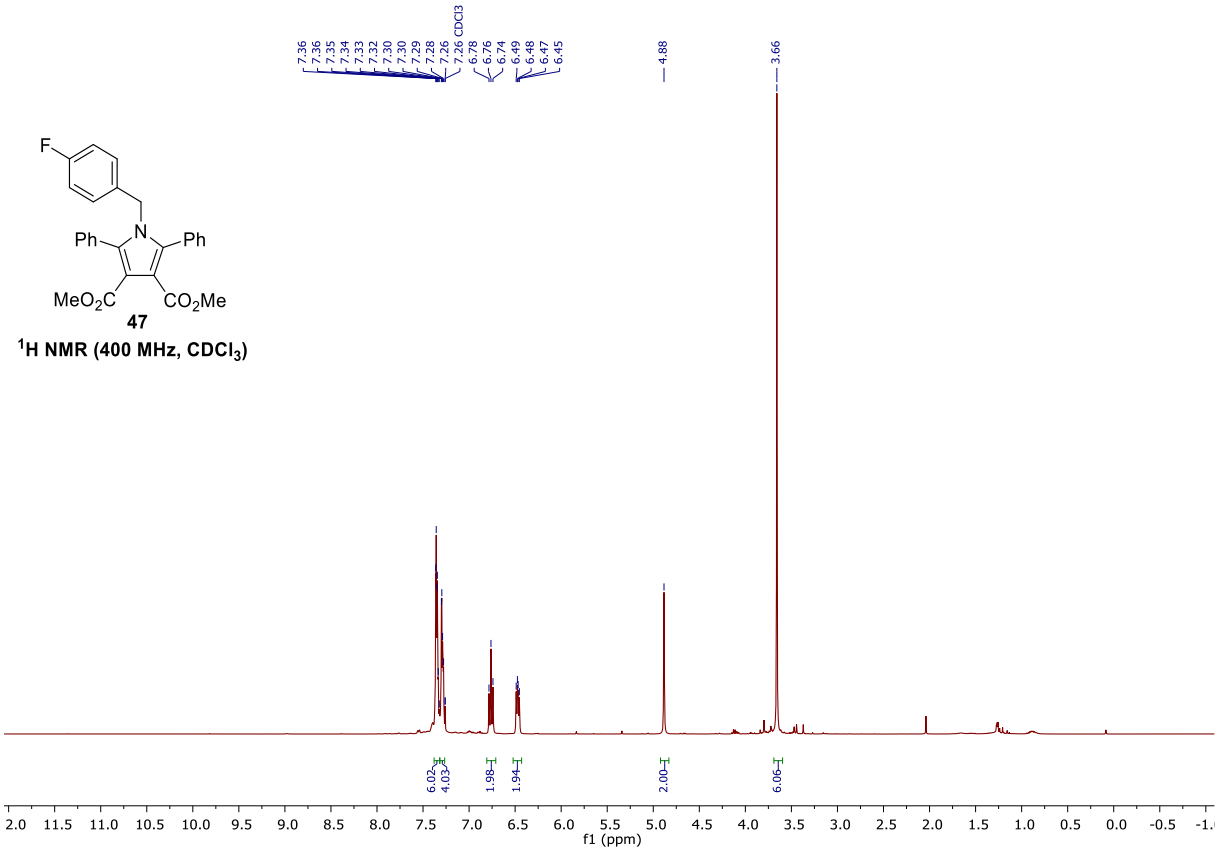
46

^{1}H NMR (300 MHz, $CDCl_3$)

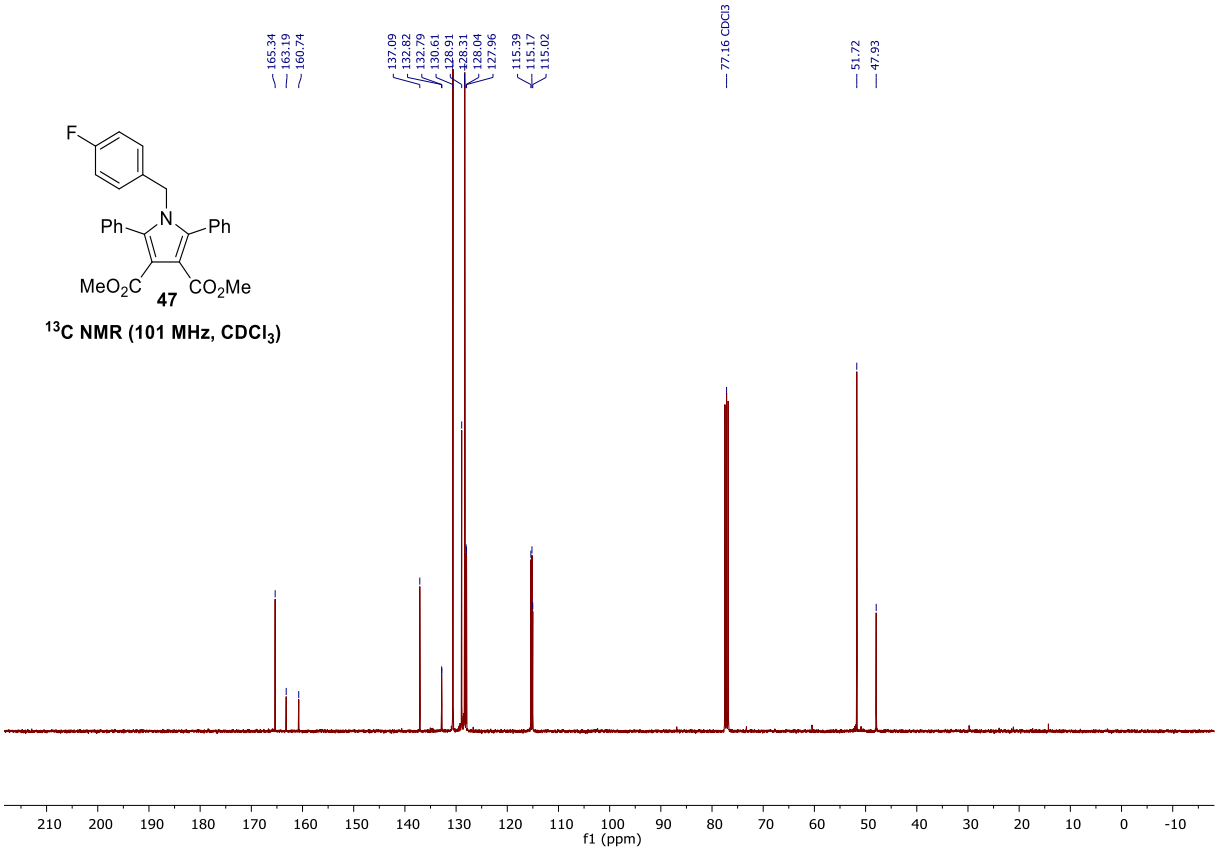


46

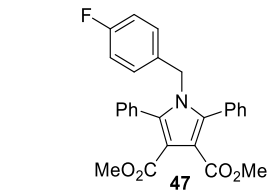
^{13}C NMR (75 MHz, $CDCl_3$)



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

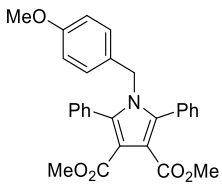


^{13}C NMR (101 MHz, $CDCl_3$)



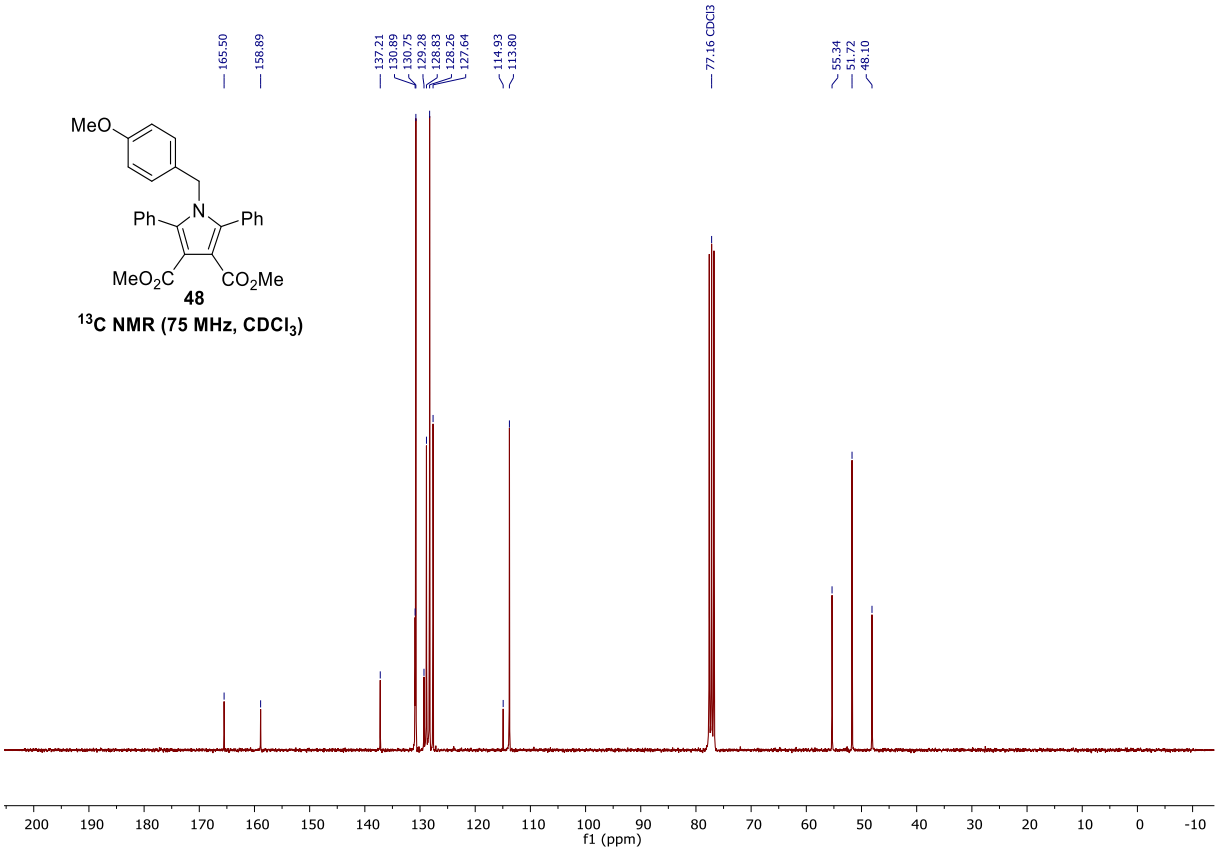
47

^{19}F NMR (377 MHz, $CDCl_3$)



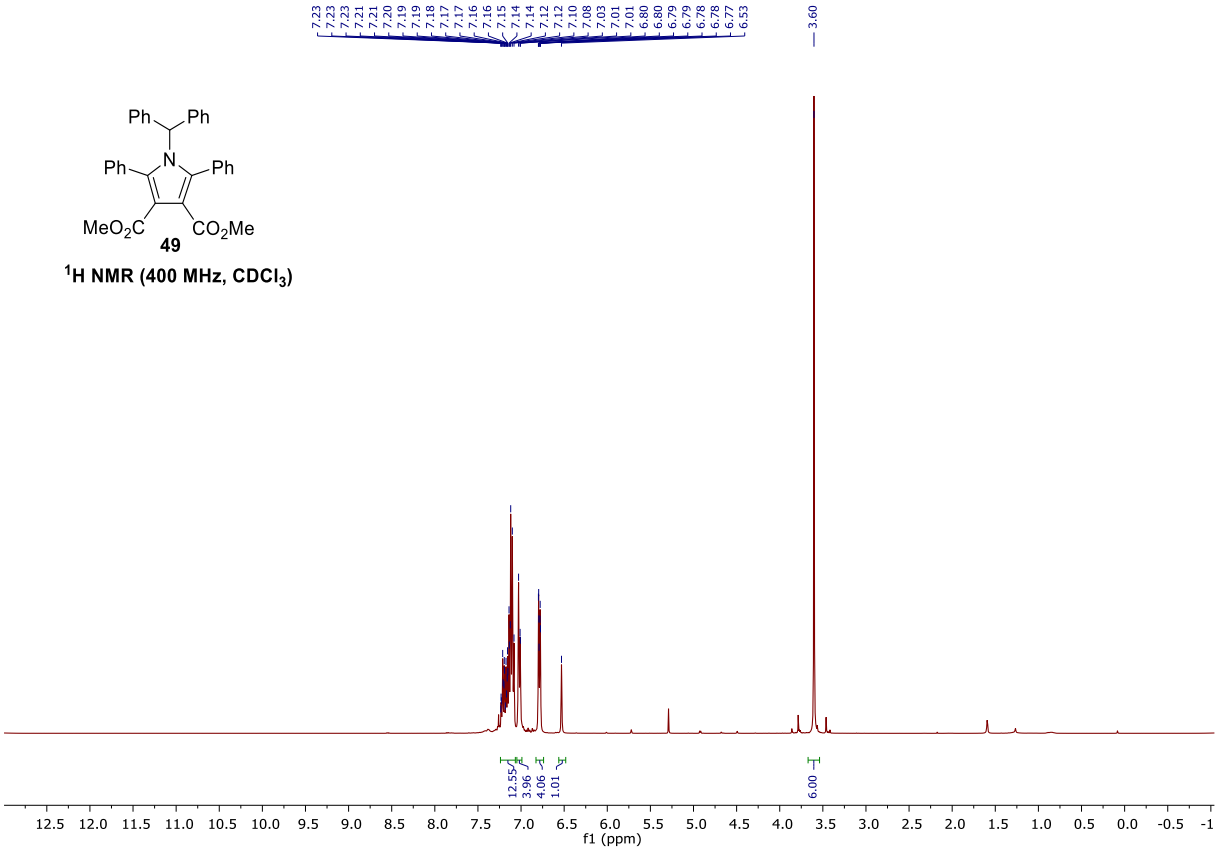
48

^{1}H NMR (300 MHz, $CDCl_3$)



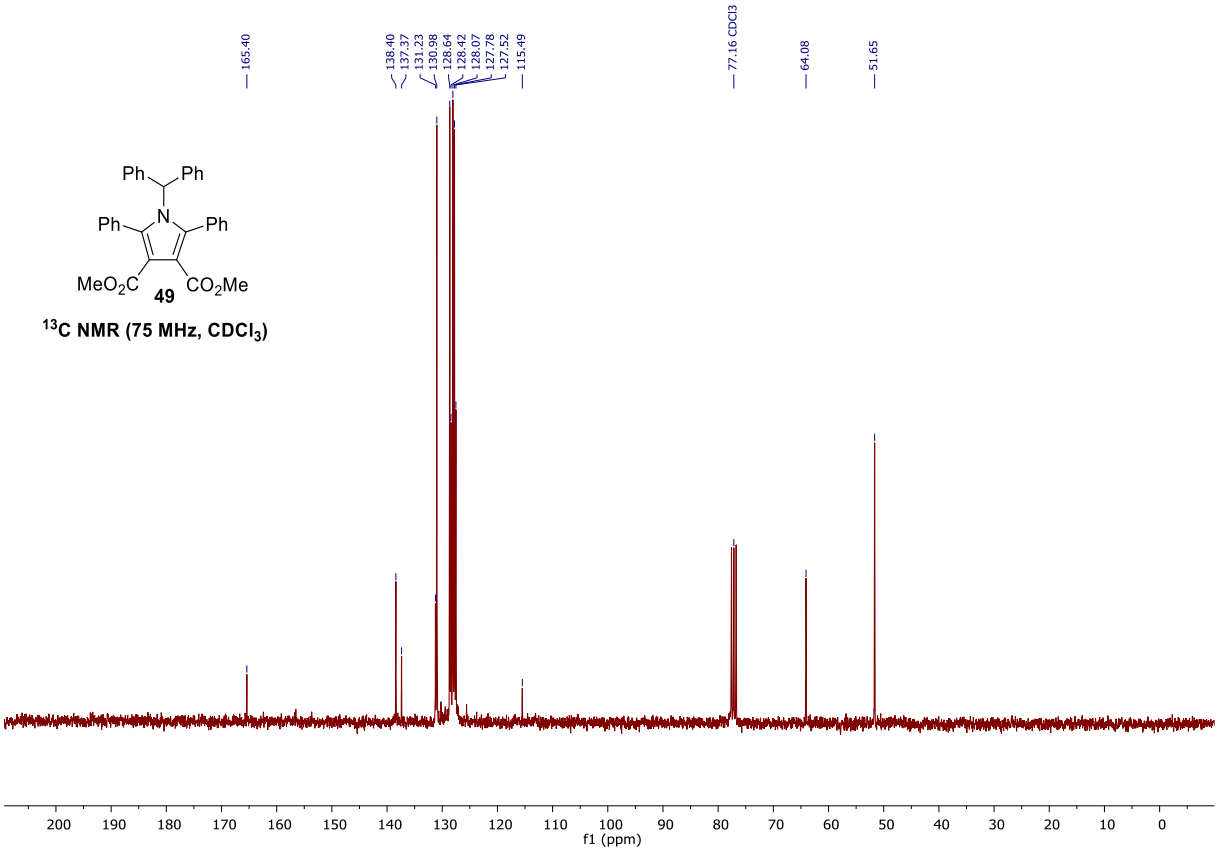
48

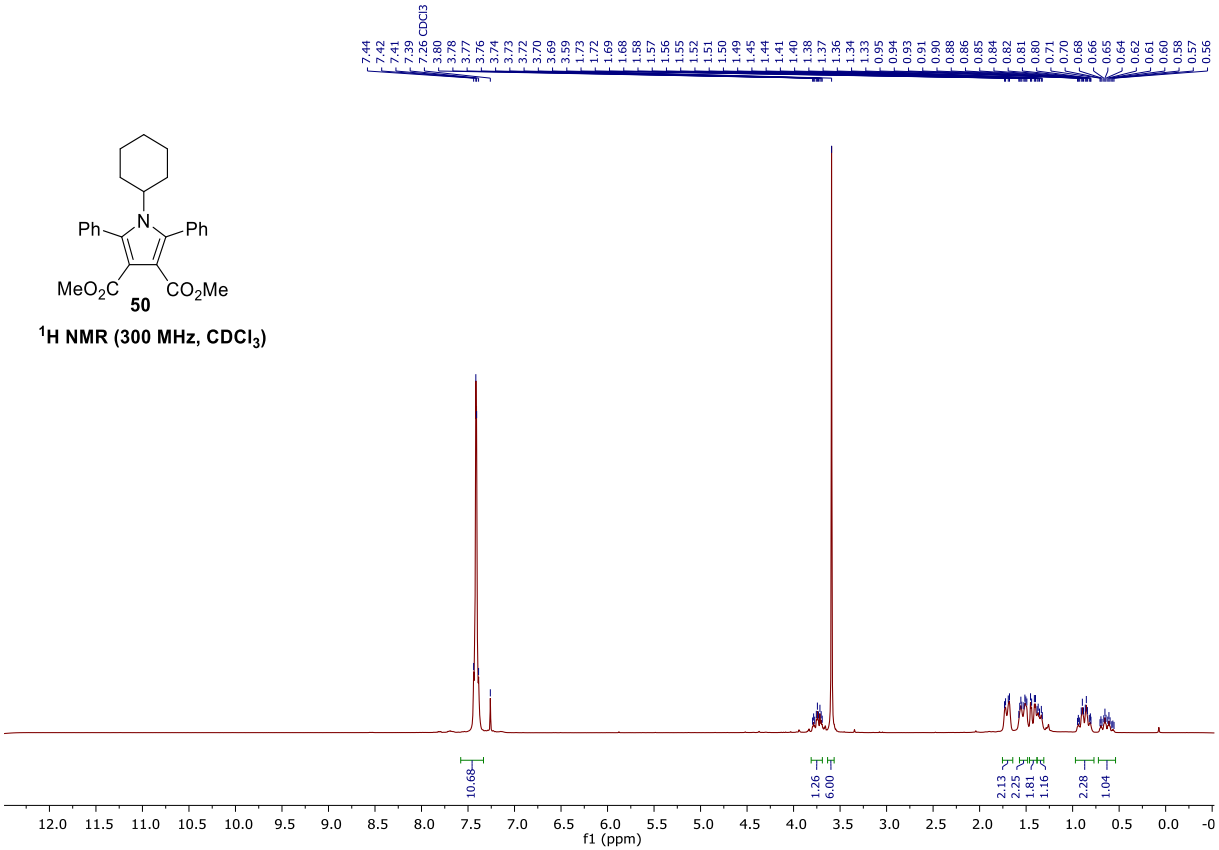
^{13}C NMR (75 MHz, $CDCl_3$)

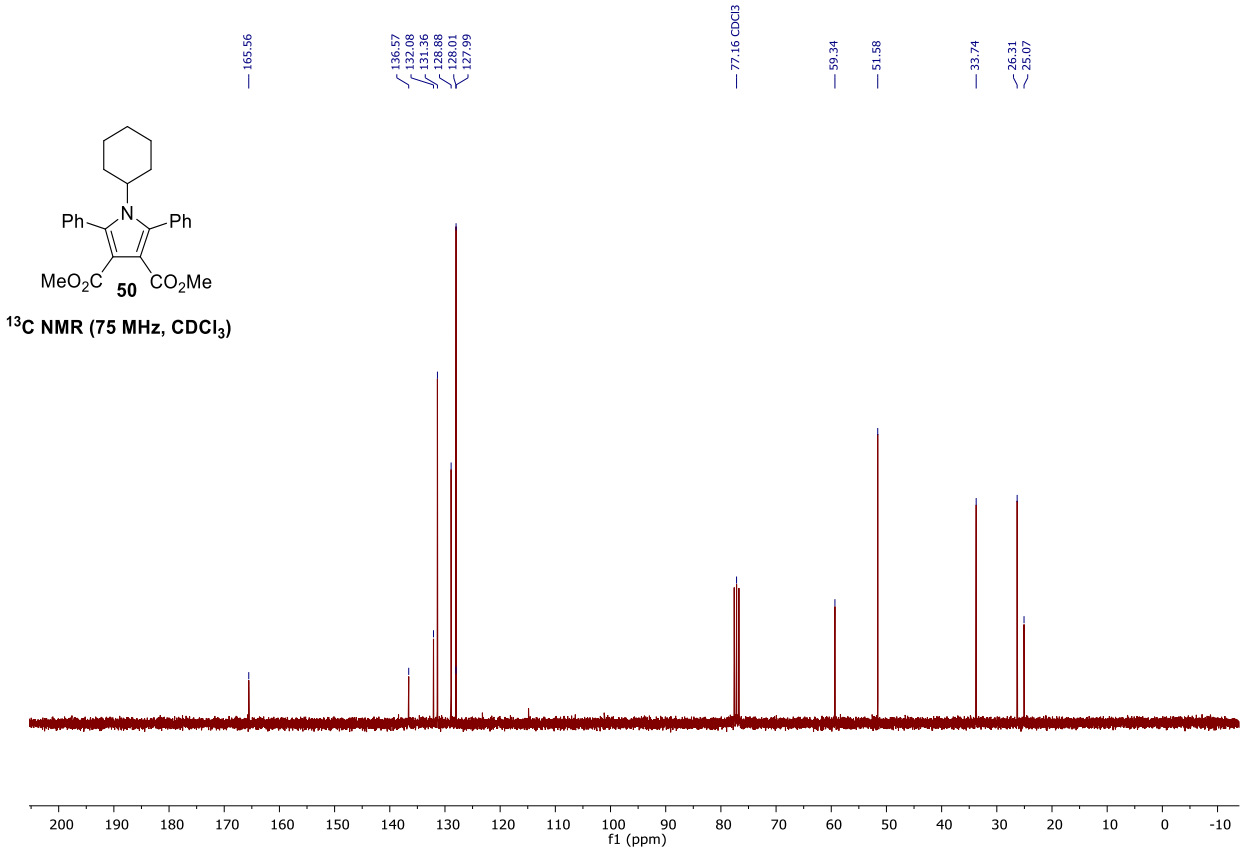


49

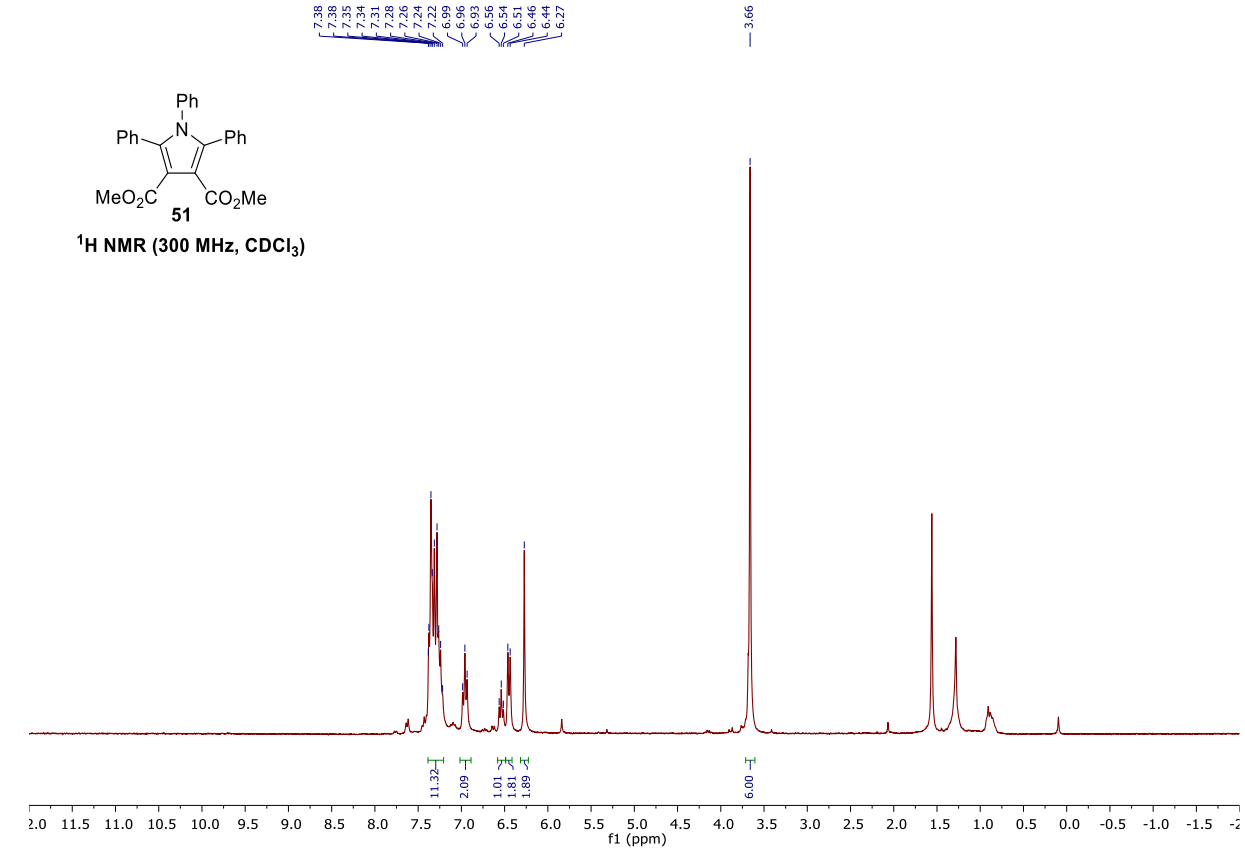
^{1}H NMR (400 MHz, $CDCl_3$)


165.40
138.40
137.37
131.23
130.98
128.64
128.42
128.07
127.78
127.52
115.49
77.16 CDCl3
64.08
51.65
Ph
Ph
N
Ph
Ph
MeO2C
CO2Me
49
13C NMR (75 MHz, CDCl3)
f1 (ppm)

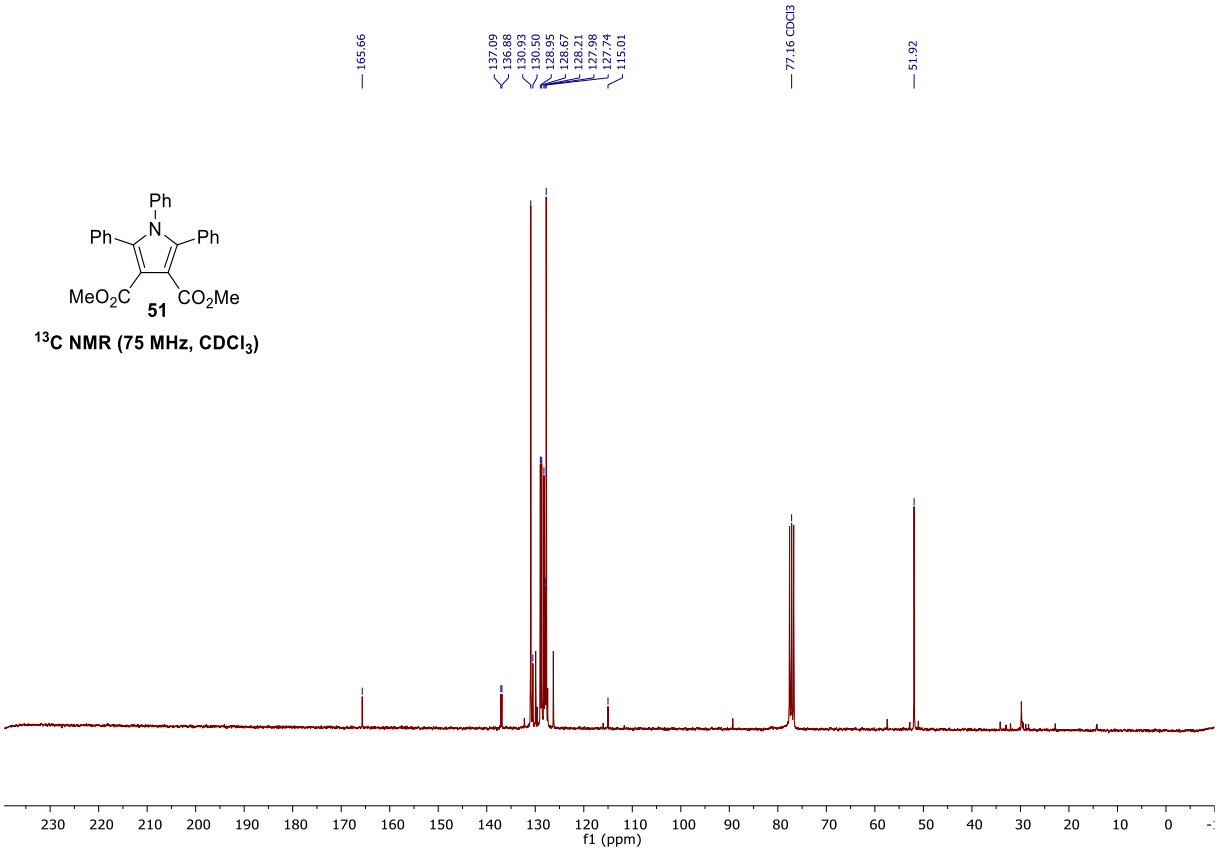

7.44
7.42
7.41
7.39
7.26 CDCl3
3.80
3.78
3.77
3.76
3.74
3.73
3.72
3.70
3.69
3.59
1.73
1.72
1.69
1.68
1.58
1.57
1.56
1.55
1.52
1.51
1.50
1.49
1.45
1.44
1.41
1.40
1.38
1.37
1.36
1.34
1.33
0.95
0.94
0.93
0.91
0.90
0.88
0.86
0.85
0.84
0.82
0.81
0.80
0.71
0.70
0.68
0.66
0.65
0.64
0.62
0.61
0.60
0.58
0.57
0.56
Ph
Ph
N
Ph
Ph
MeO2C
CO2Me
50
1H NMR (300 MHz, CDCl3)
10.68
1.26
6.00
2.13
2.25
1.81
1.16
2.28
1.04
f1 (ppm)

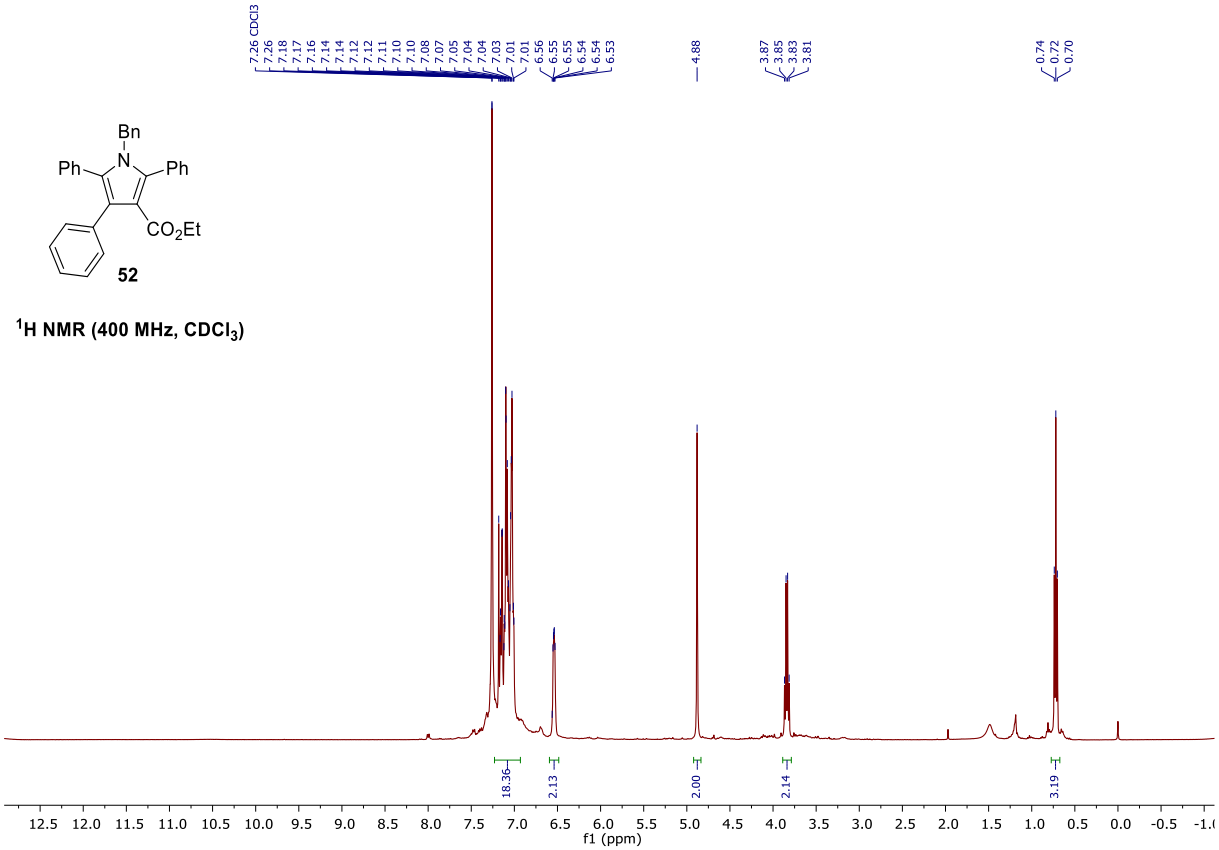


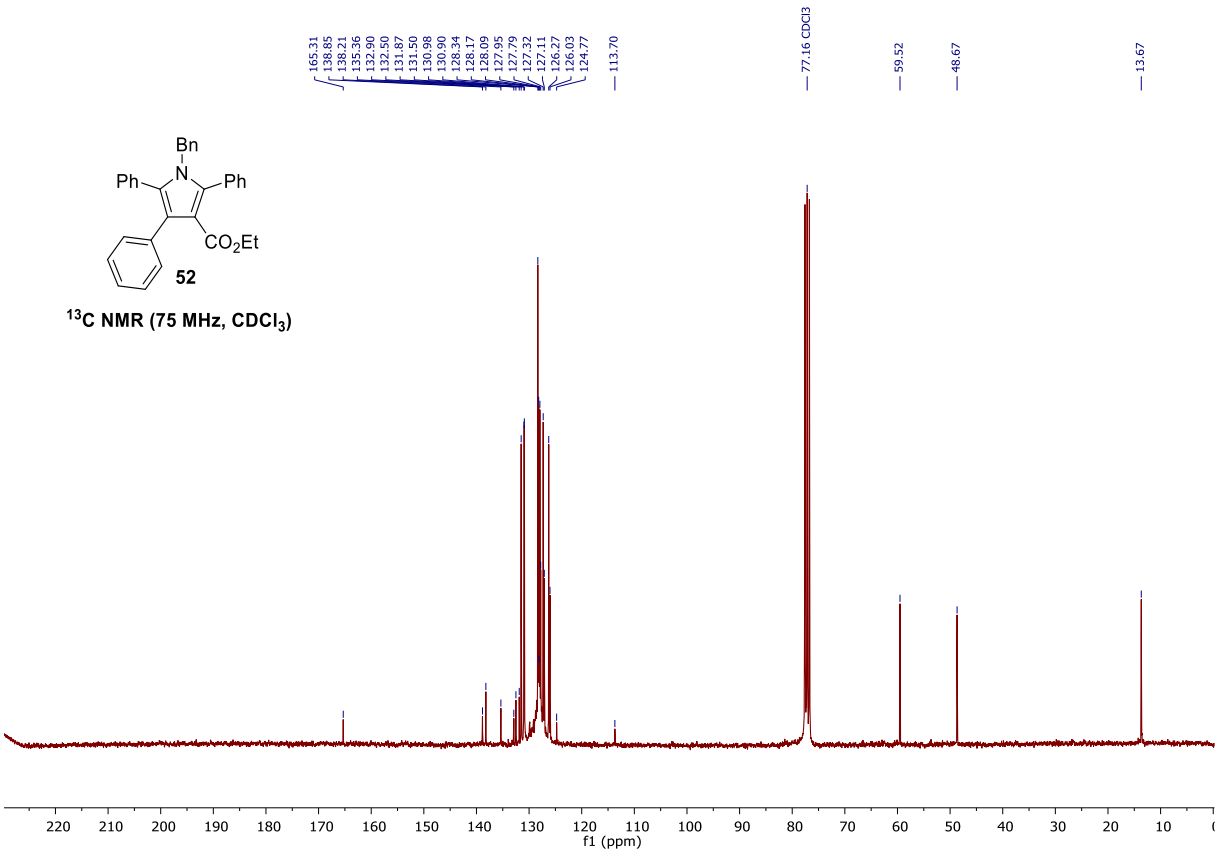
^{13}C NMR (75 MHz, $CDCl_3$)

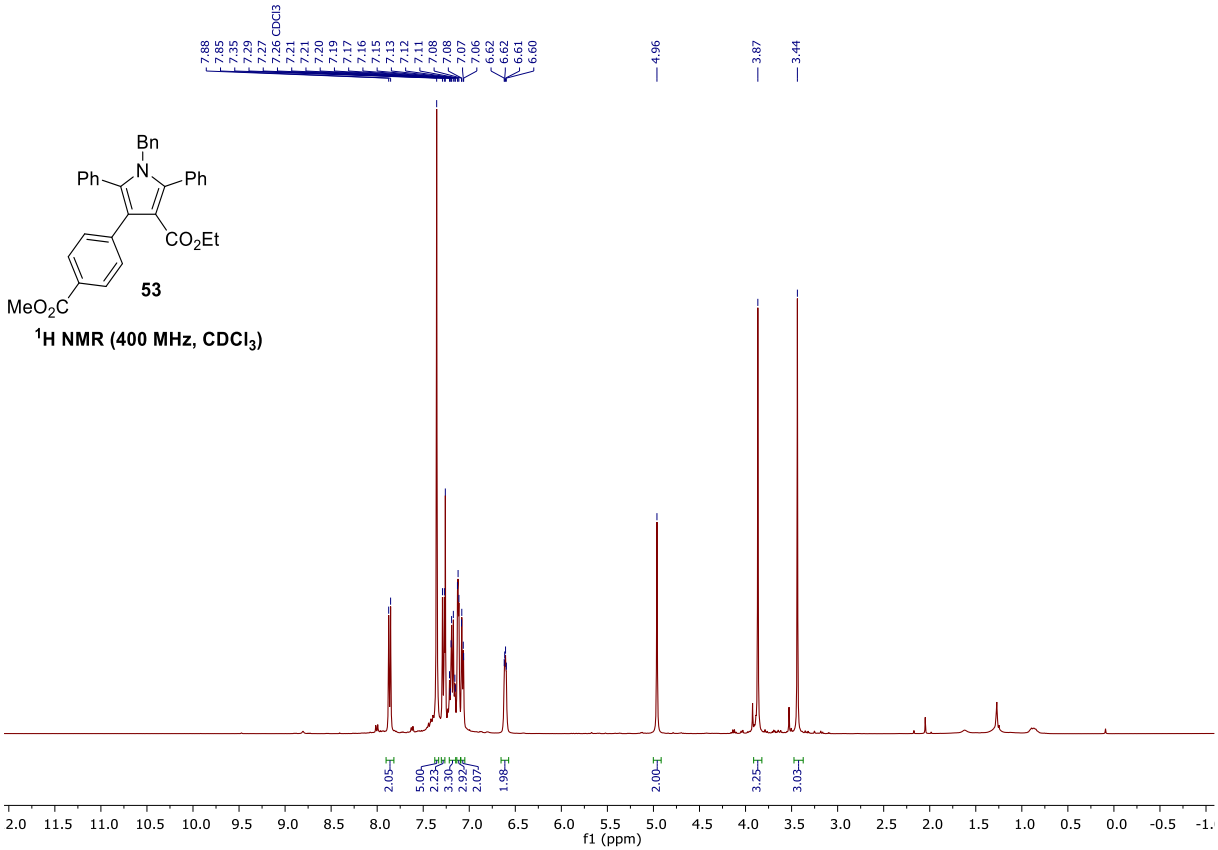


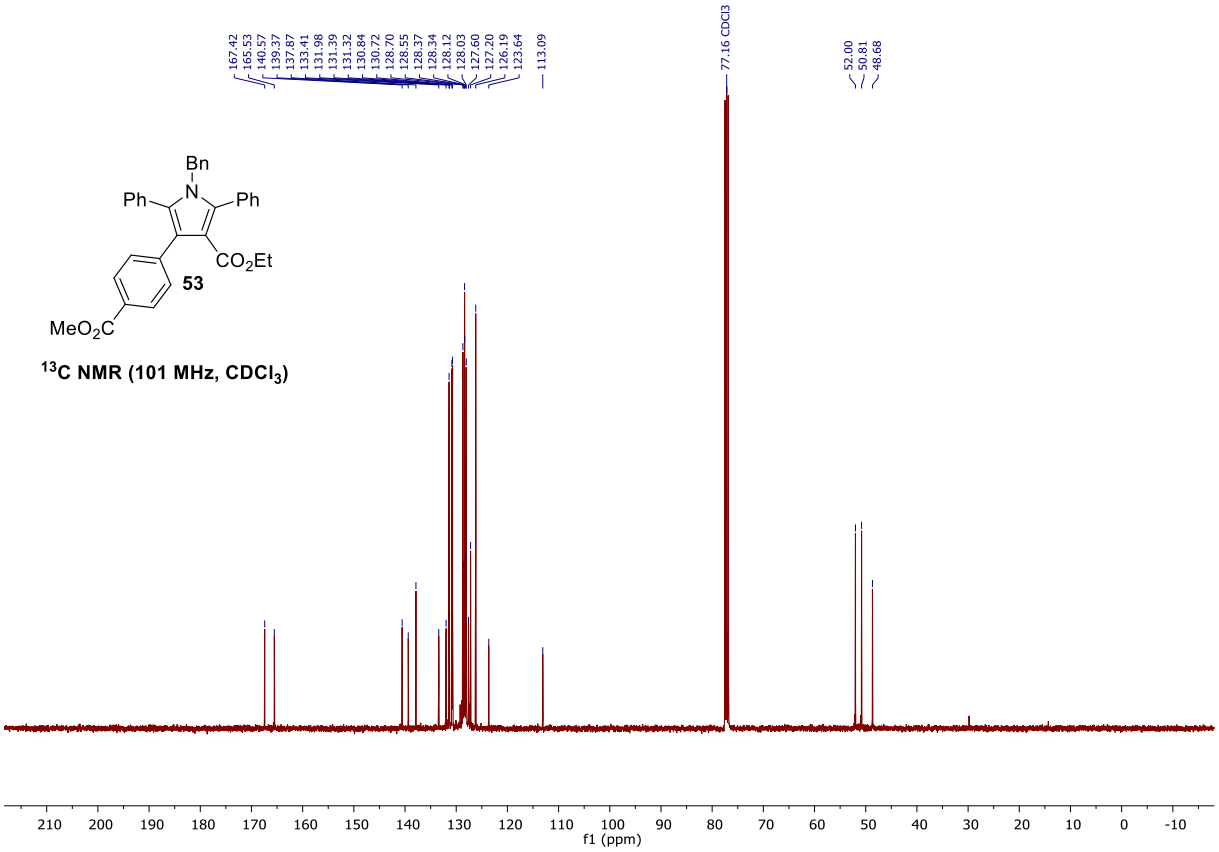
^{1}H NMR (300 MHz, $CDCl_3$)

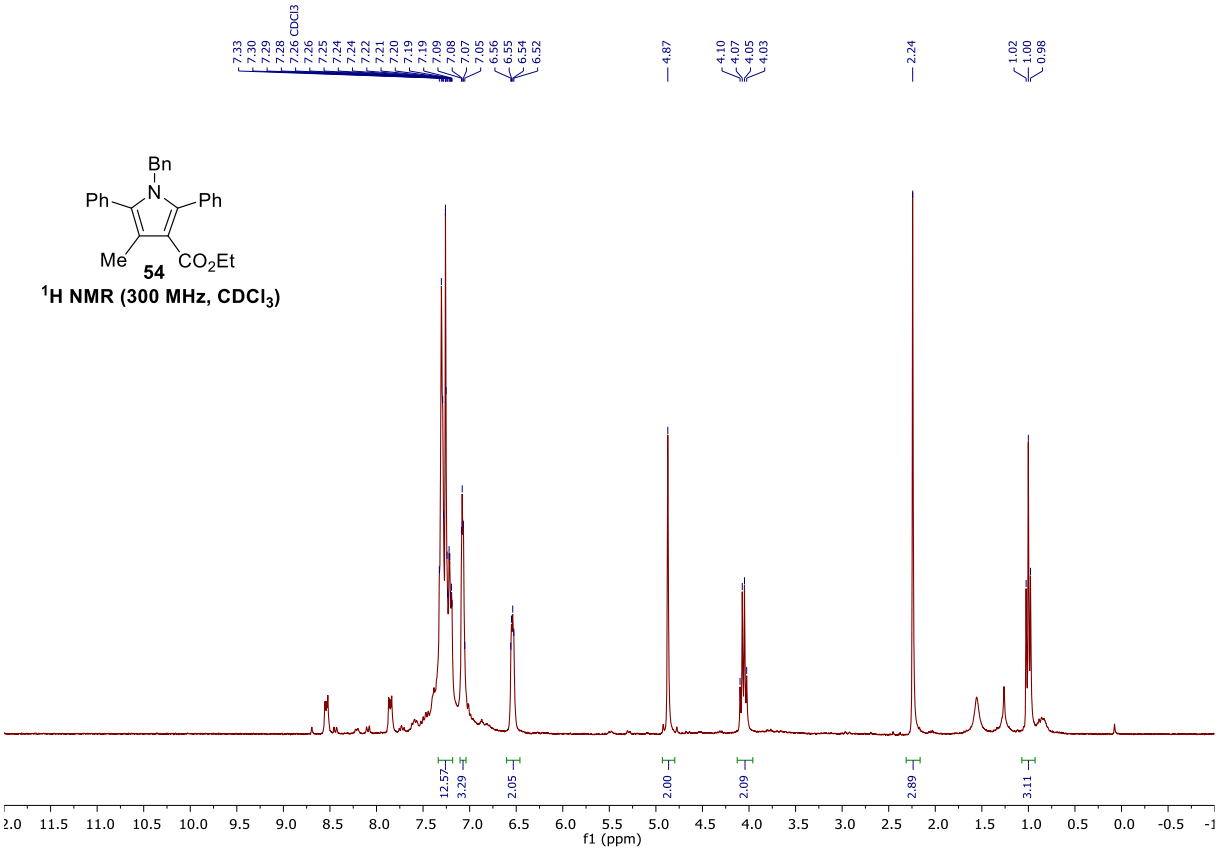

165.66
137.09
136.88
130.93
130.50
128.95
128.67
128.21
127.98
127.74
115.01
77.16 CDCl3
51.92
Ph
N
Ph
Ph
MeO2C
CO2Me
51
13C NMR (75 MHz, CDCl3)
f1 (ppm)

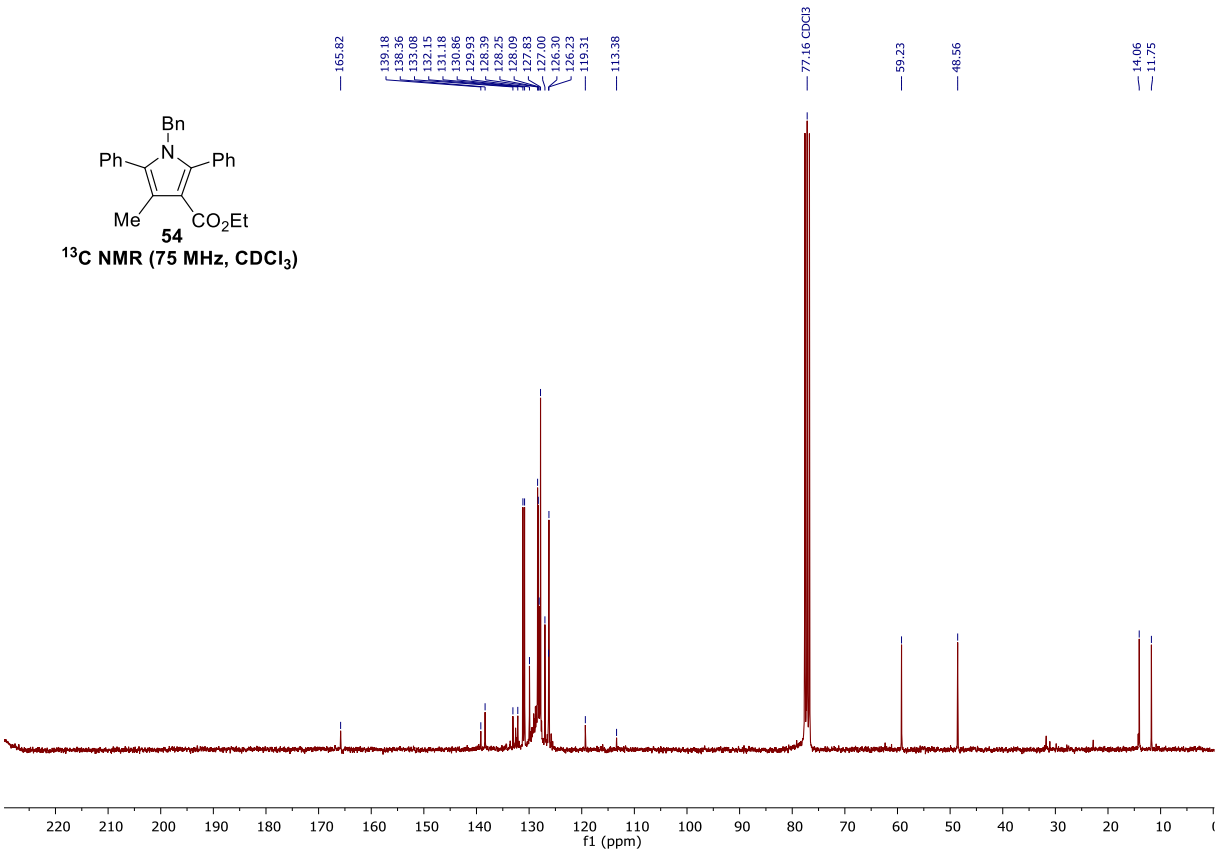

7.26 CDCl3
7.26
7.18
7.17
7.16
7.14
7.14
7.12
7.12
7.11
7.10
7.10
7.08
7.07
7.05
7.04
7.04
7.03
7.01
7.01
6.56
6.55
6.55
6.54
6.54
6.53
4.88
3.87
3.85
3.83
3.81
0.74
0.72
0.70
Bn
N
Ph
Ph
CO2Et
52
1H NMR (400 MHz, CDCl3)
18.36
2.13
2.00
2.14
3.19
f1 (ppm)

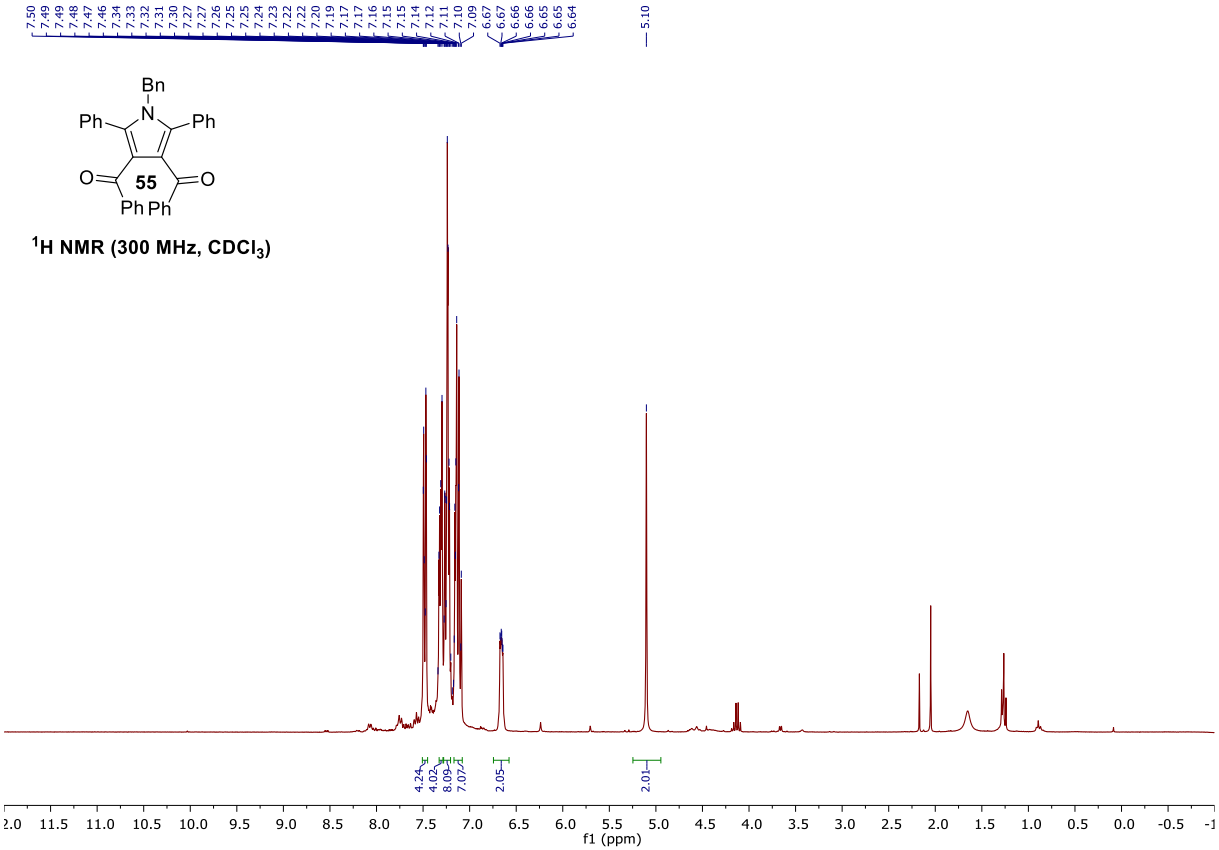

165.31
138.85
138.21
135.36
132.90
132.50
131.87
131.50
130.98
130.90
128.34
128.17
128.09
127.95
127.79
127.32
127.11
126.27
126.03
124.77
113.70
77.16 CDCl3
59.52
48.67
13.67
Bn
N
Ph
Ph
CO2Et
52
13C NMR (75 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

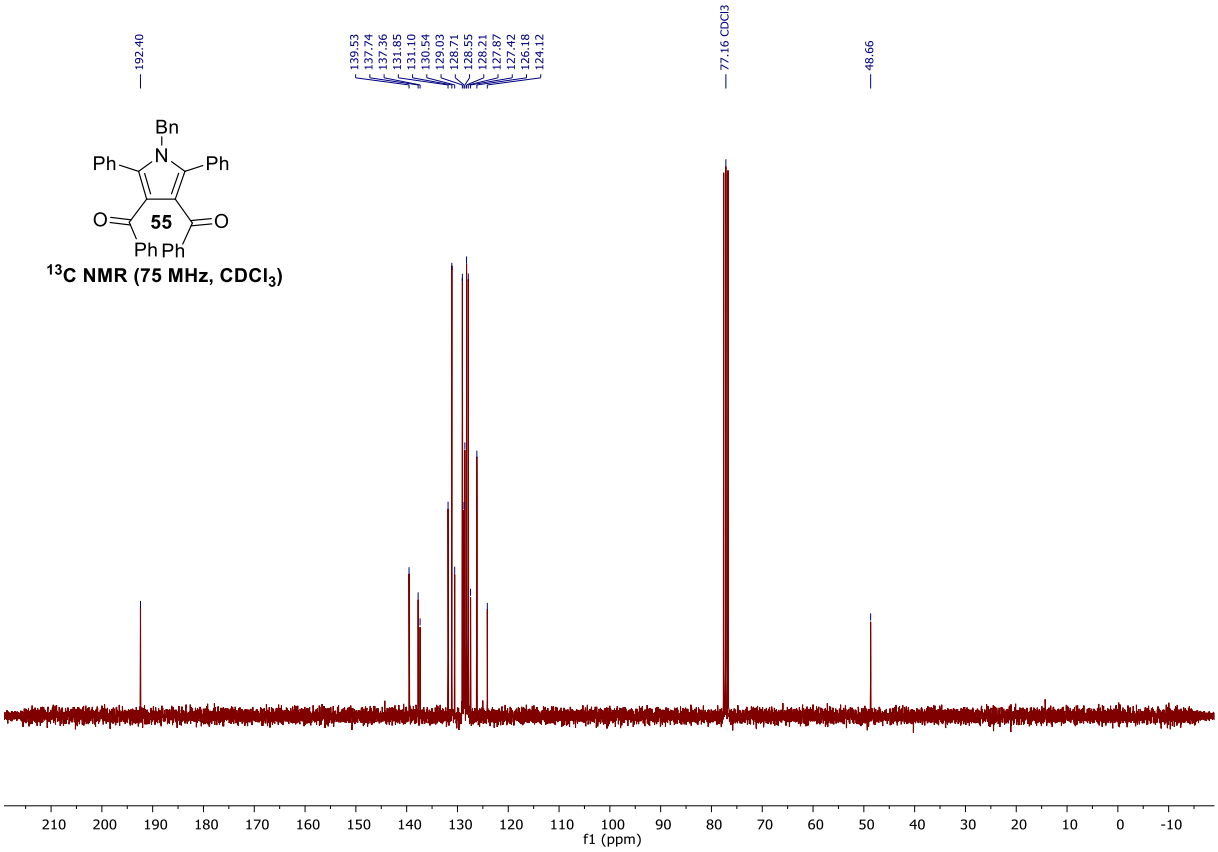

7.88
7.85
7.35
7.29
7.27
7.26 CDCl3
7.21
7.21
7.20
7.19
7.17
7.16
7.15
7.13
7.12
7.11
7.08
7.08
7.07
7.06
6.62
6.62
6.61
6.60
4.96
3.87
3.44
Bn
N
Ph
Ph
CO2Et
MeO2C
53
1H NMR (400 MHz, CDCl3)
2.05
5.00
2.23
3.30
2.92
2.07
1.98
2.00
3.25
3.03
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


167.42
165.53
140.57
139.37
137.87
133.41
131.98
131.39
131.32
130.84
130.72
128.70
128.55
128.37
128.34
128.12
128.03
127.60
127.20
126.19
123.64
113.09
77.16 CDCl3
52.00
50.81
48.68
Bn
Ph
N
Ph
CO2Et
53
MeO2C
13C NMR (101 MHz, CDCl3)
f1 (ppm)

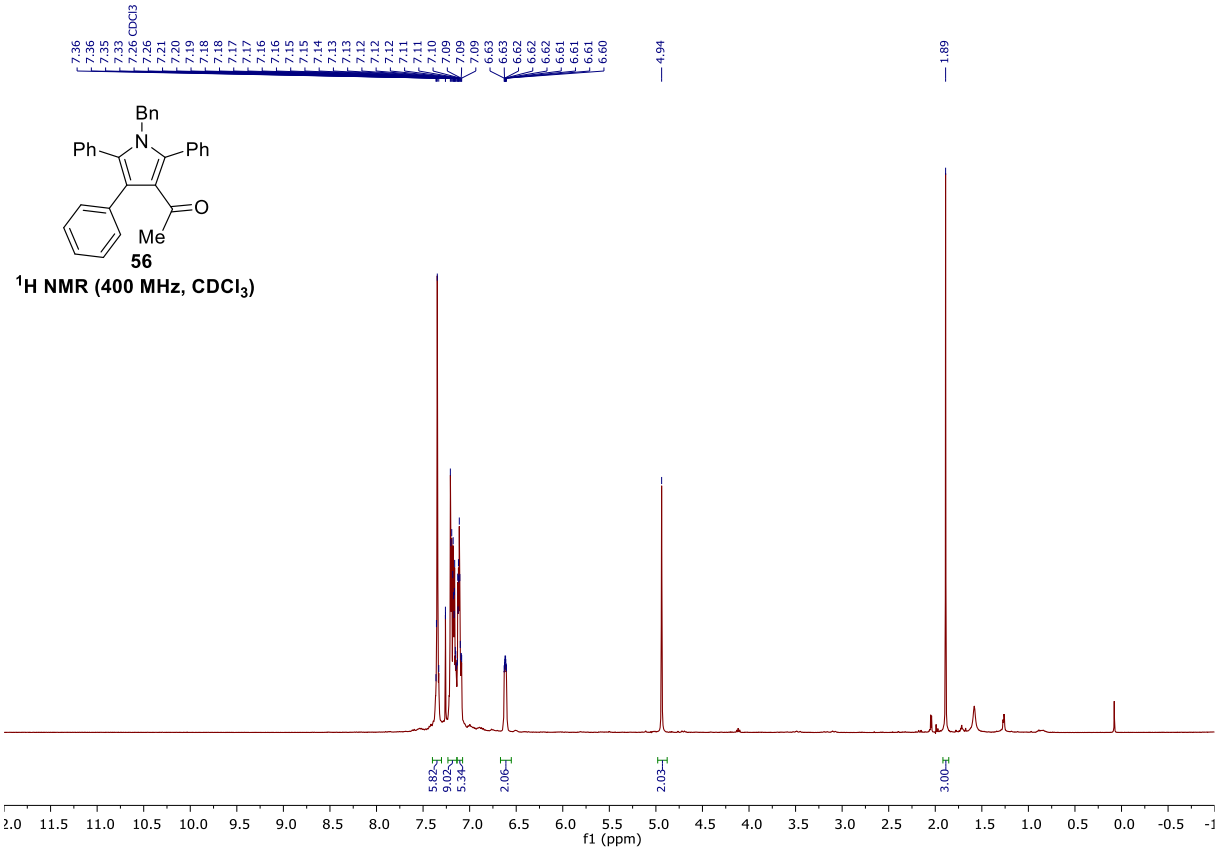

7.33
7.30
7.29
7.28
7.26 CDCl3
7.26
7.25
7.24
7.24
7.22
7.21
7.20
7.19
7.19
7.09
7.08
7.07
7.05
6.56
6.55
6.54
6.52
4.87
4.10
4.07
4.05
4.03
2.24
1.02
1.00
0.98
Bn
Ph
N
Ph
Me
CO2Et
54
1H NMR (300 MHz, CDCl3)
12.57
3.29
2.05
2.00
2.09
2.89
3.11
f1 (ppm)


Bn
N
Ph
Ph
Me
CO2Et
54
13C NMR (75 MHz, CDCl3)
165.82
139.18
138.36
133.08
132.15
131.18
130.86
129.93
128.39
128.25
128.09
127.83
127.00
126.30
126.23
119.31
113.38
77.16 CDCl3
59.23
48.56
14.06
11.75
f1 (ppm)

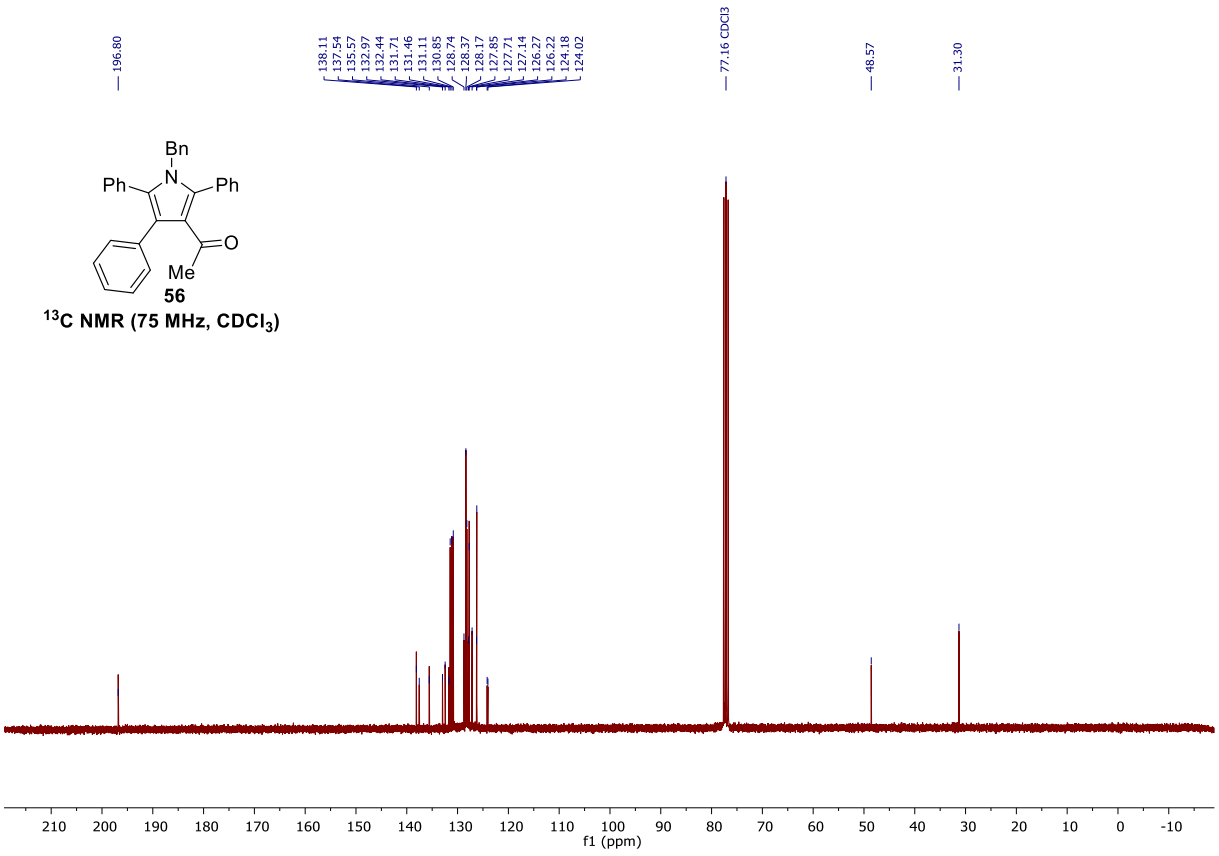

Bn
N
Ph
Ph
O
O
55
Ph Ph
1H NMR (300 MHz, CDCl3)
7.50
7.49
7.49
7.48
7.47
7.46
7.34
7.33
7.32
7.31
7.30
7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.20
7.19
7.17
7.17
7.16
7.15
7.15
7.14
7.12
7.11
7.10
7.09
6.67
6.67
6.66
6.66
6.65
6.65
6.64
5.10
4.24
4.02
8.09
7.07
2.05
2.01
f1 (ppm)



^{13}C NMR (75 MHz, $CDCl_3$)

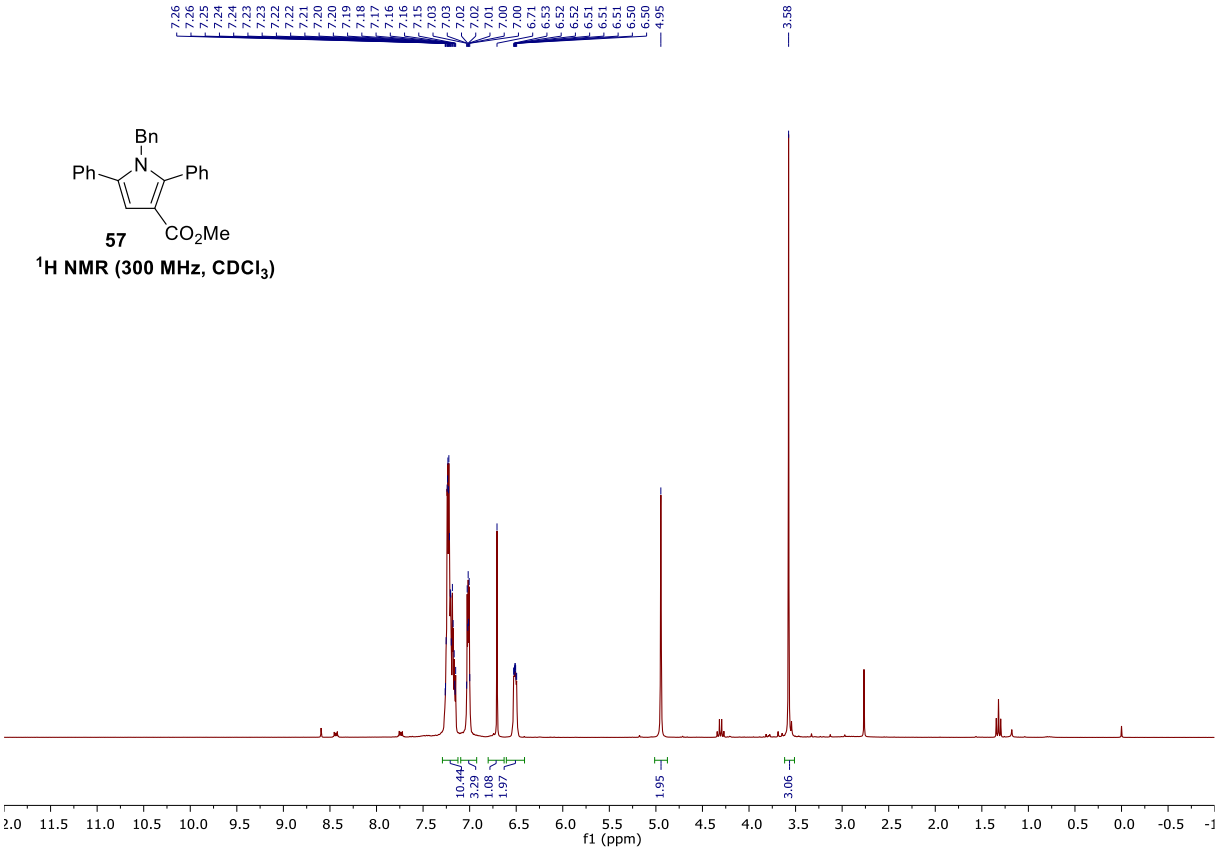


^{1}H NMR (400 MHz, $CDCl_3$)



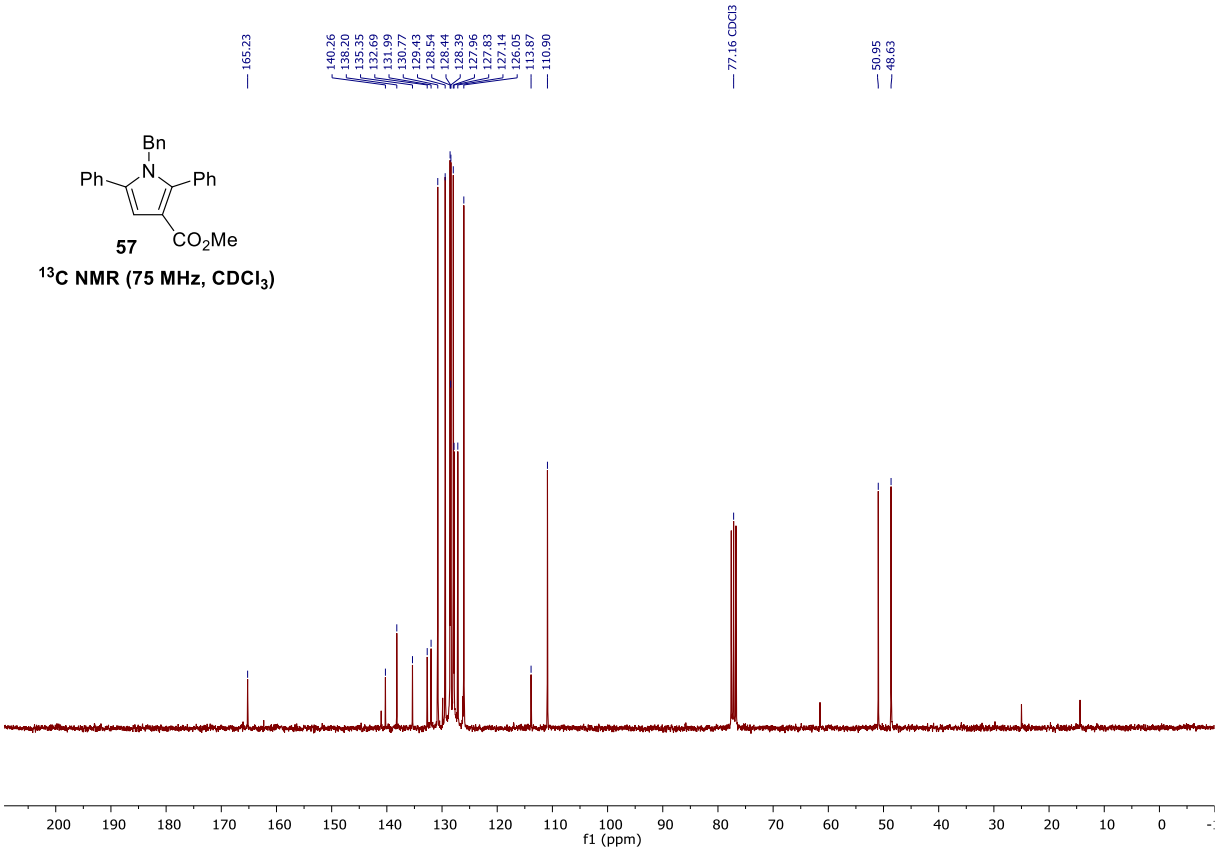
56

^{13}C NMR (75 MHz, $CDCl_3$)

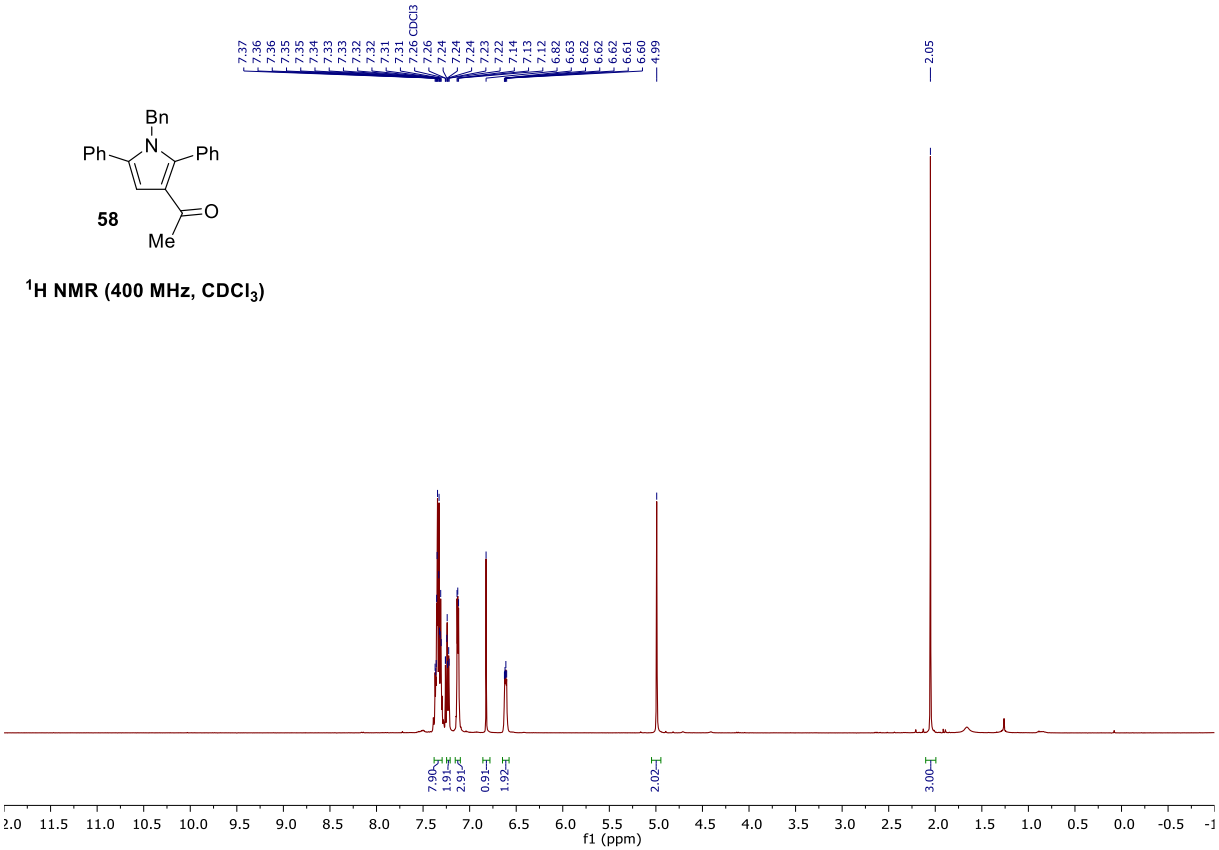


57

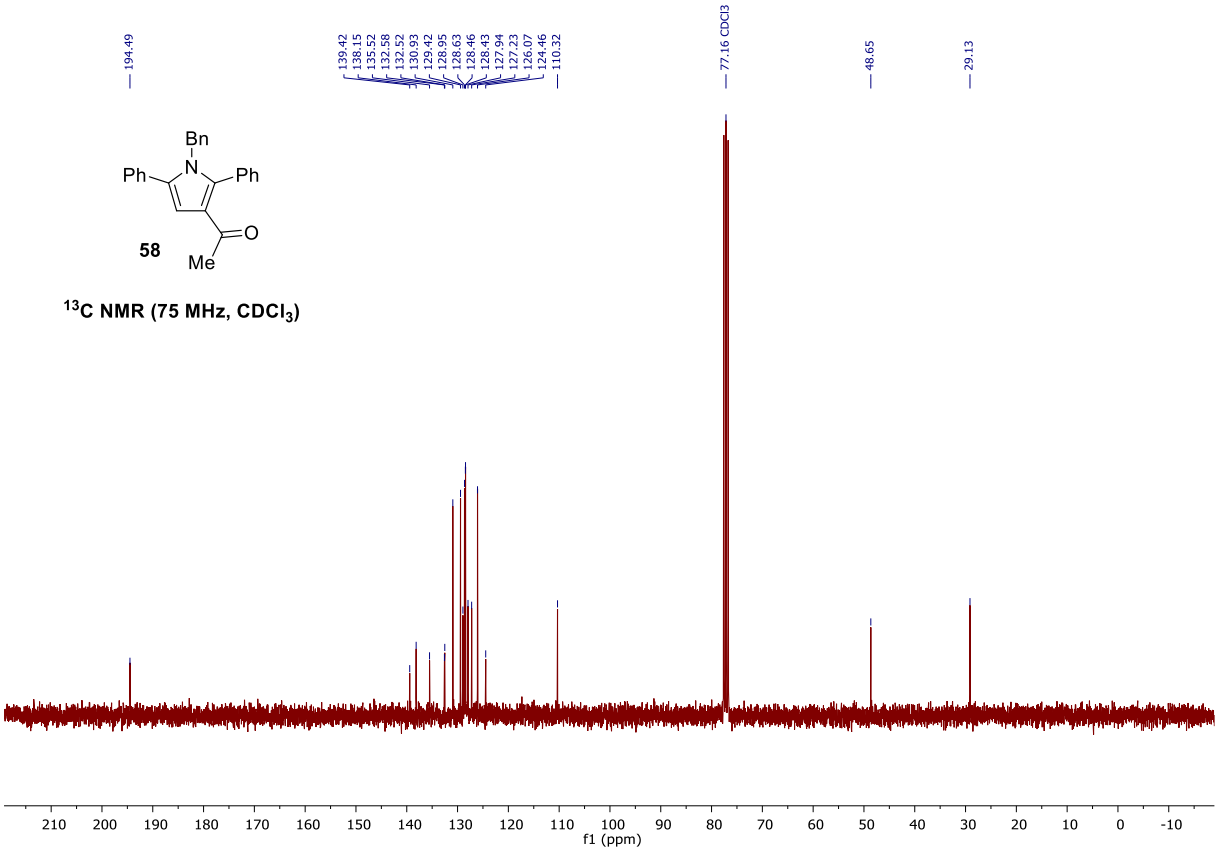
^{1}H NMR (300 MHz, $CDCl_3$)



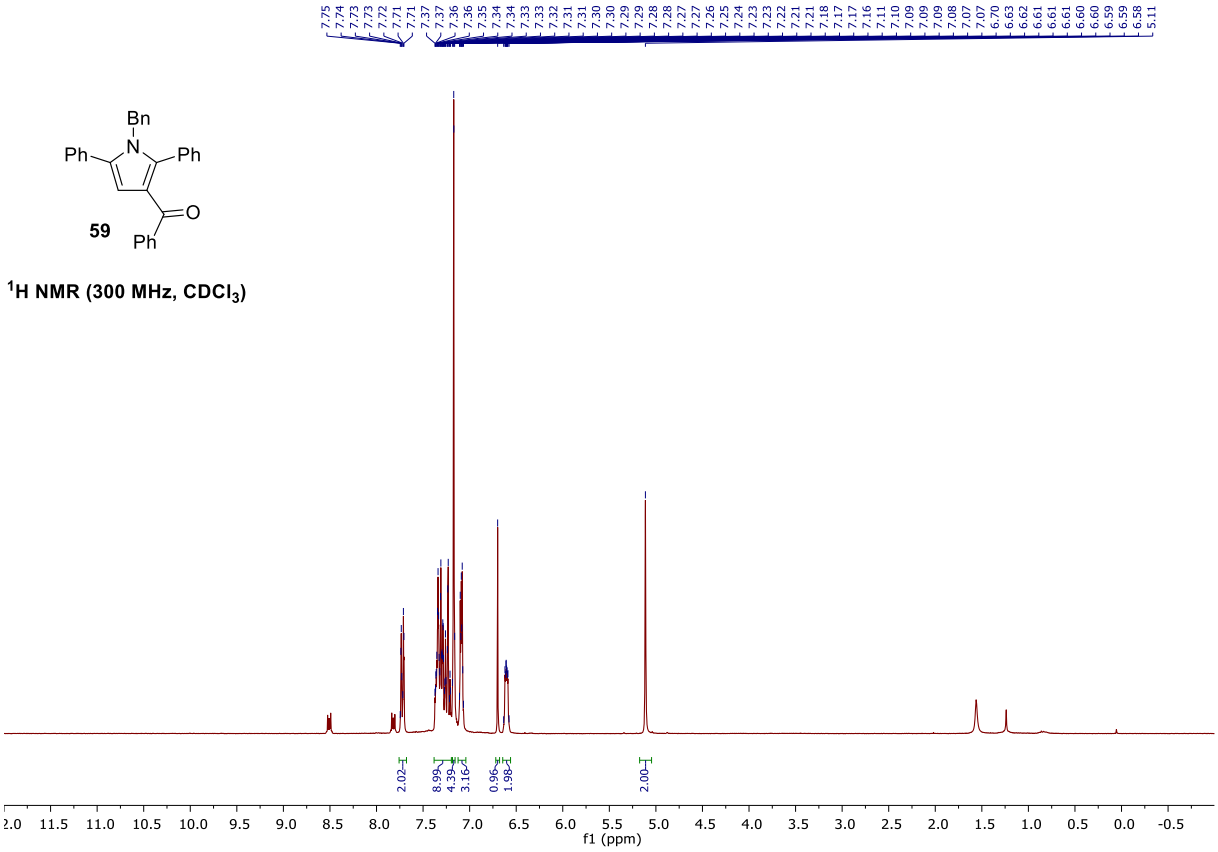
^{13}C NMR (75 MHz, $CDCl_3$)



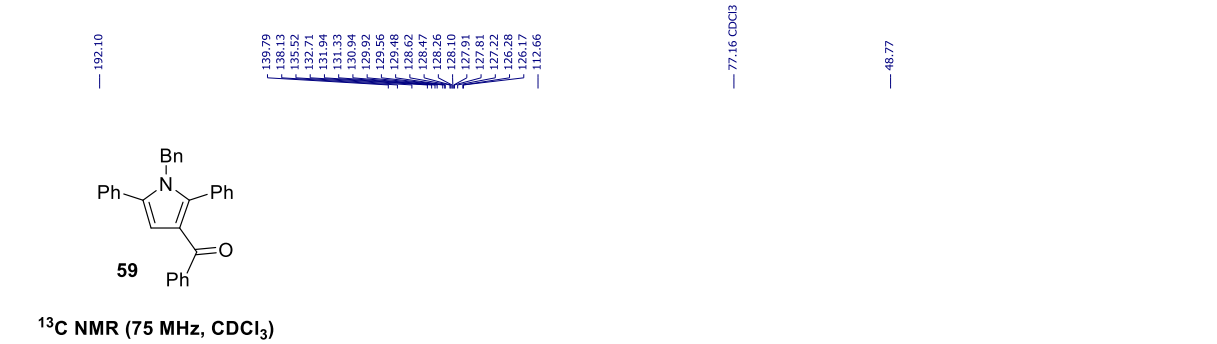
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

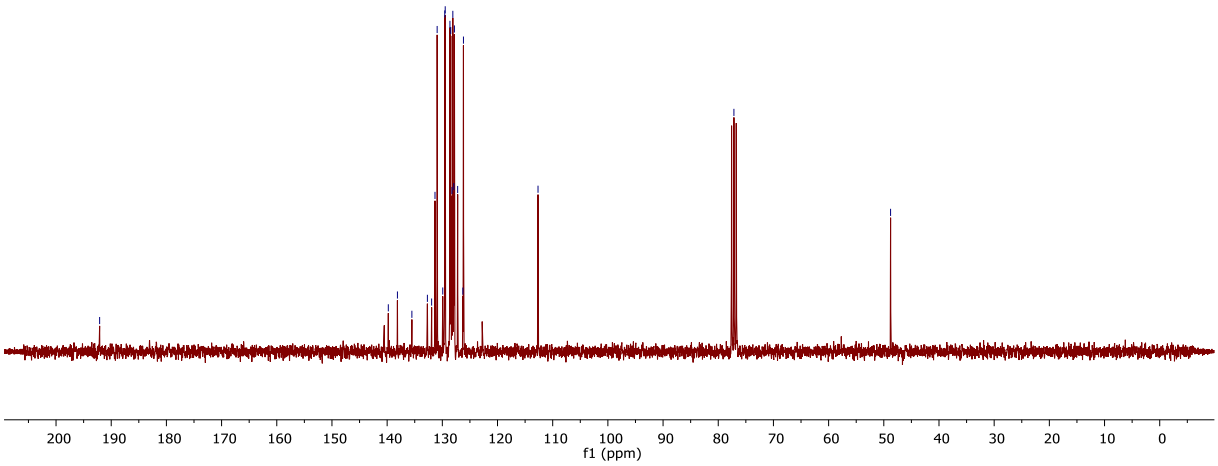


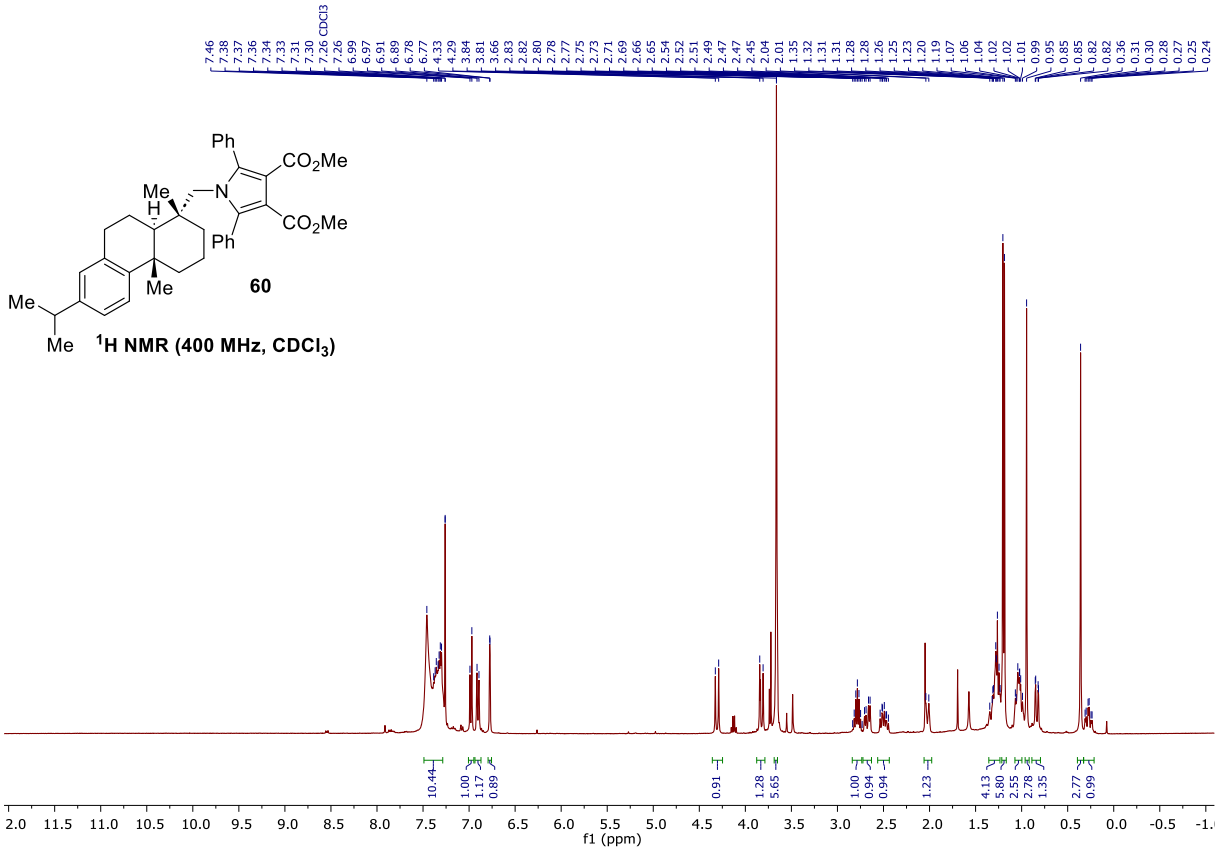
^{1}H NMR (300 MHz, $CDCl_3$)



59

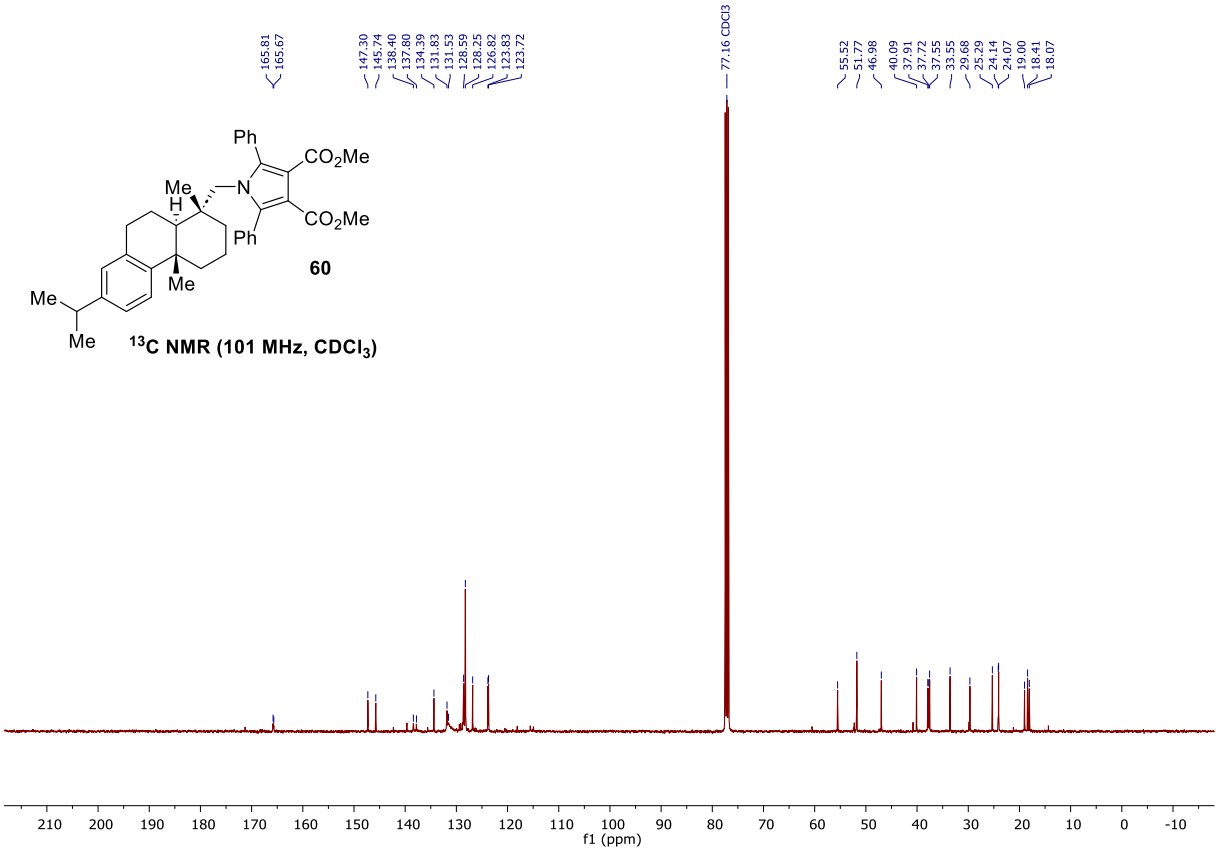
^{13}C NMR (75 MHz, $CDCl_3$)

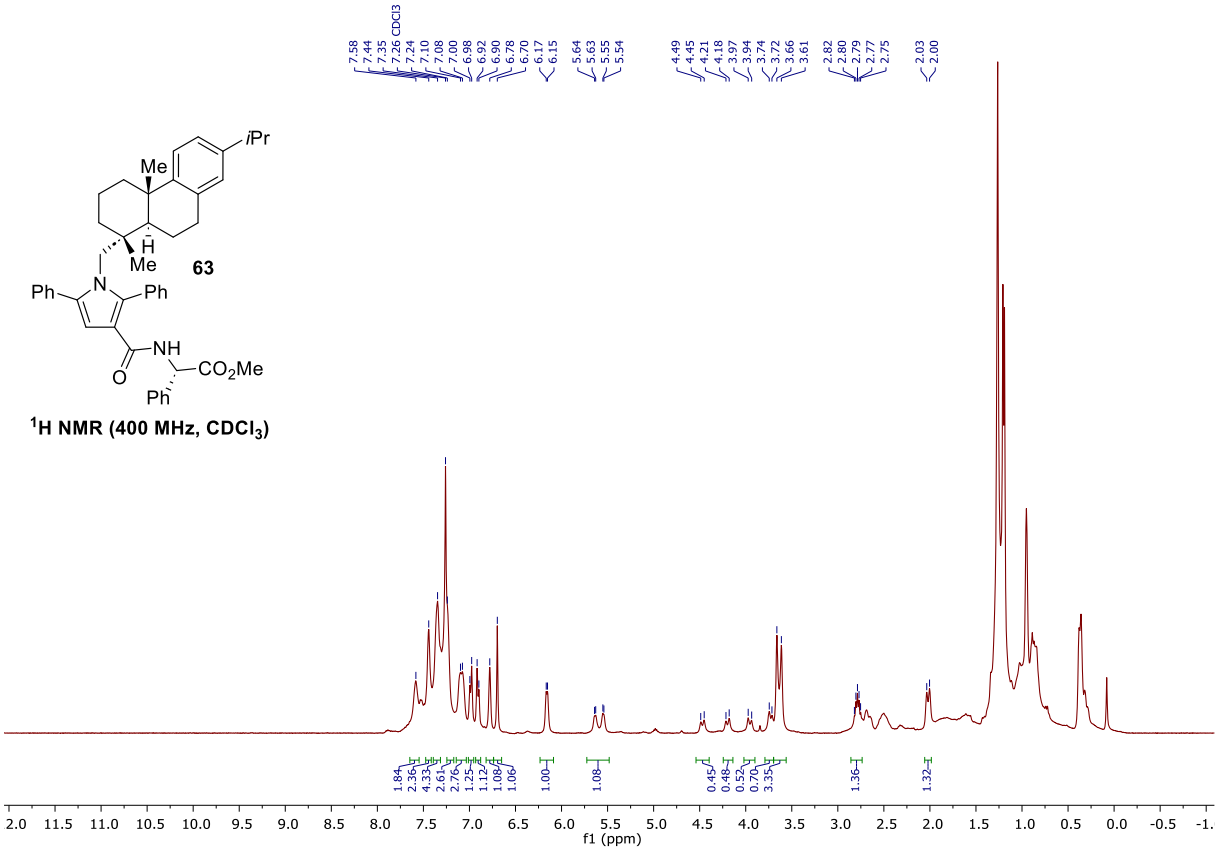


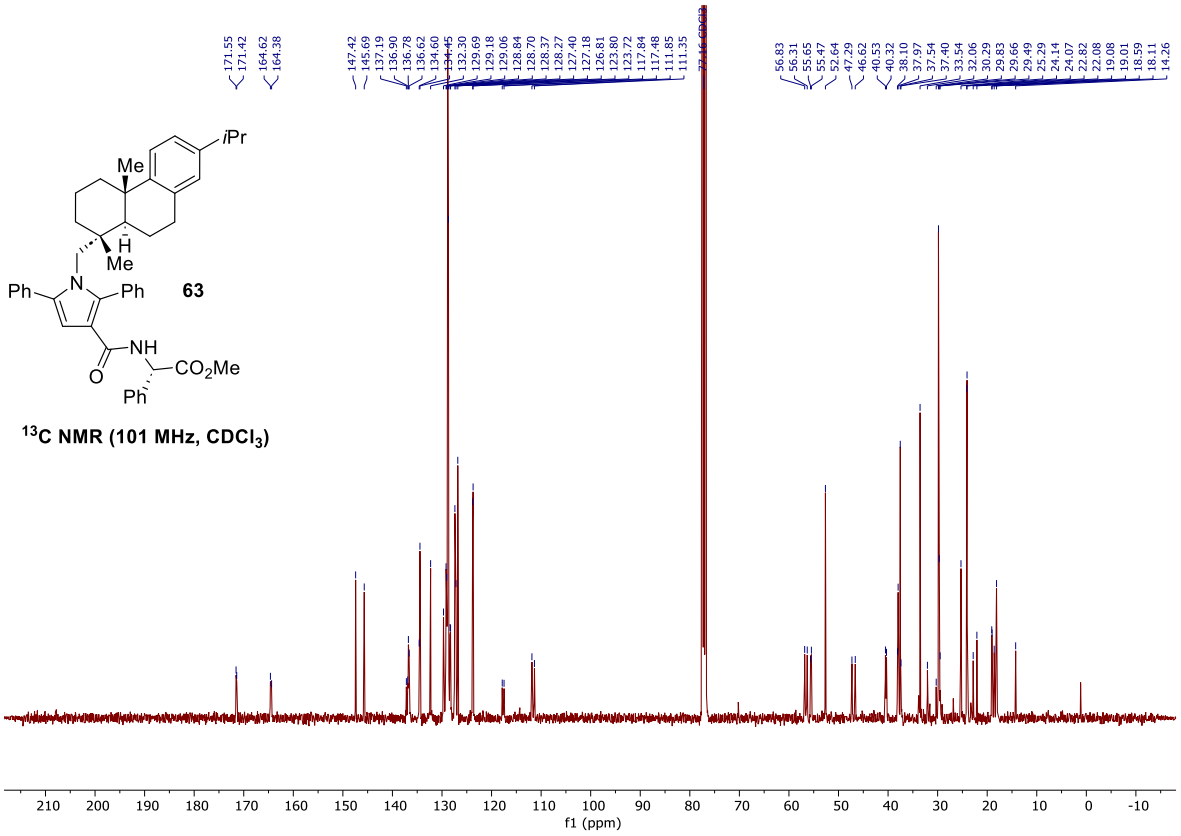


60

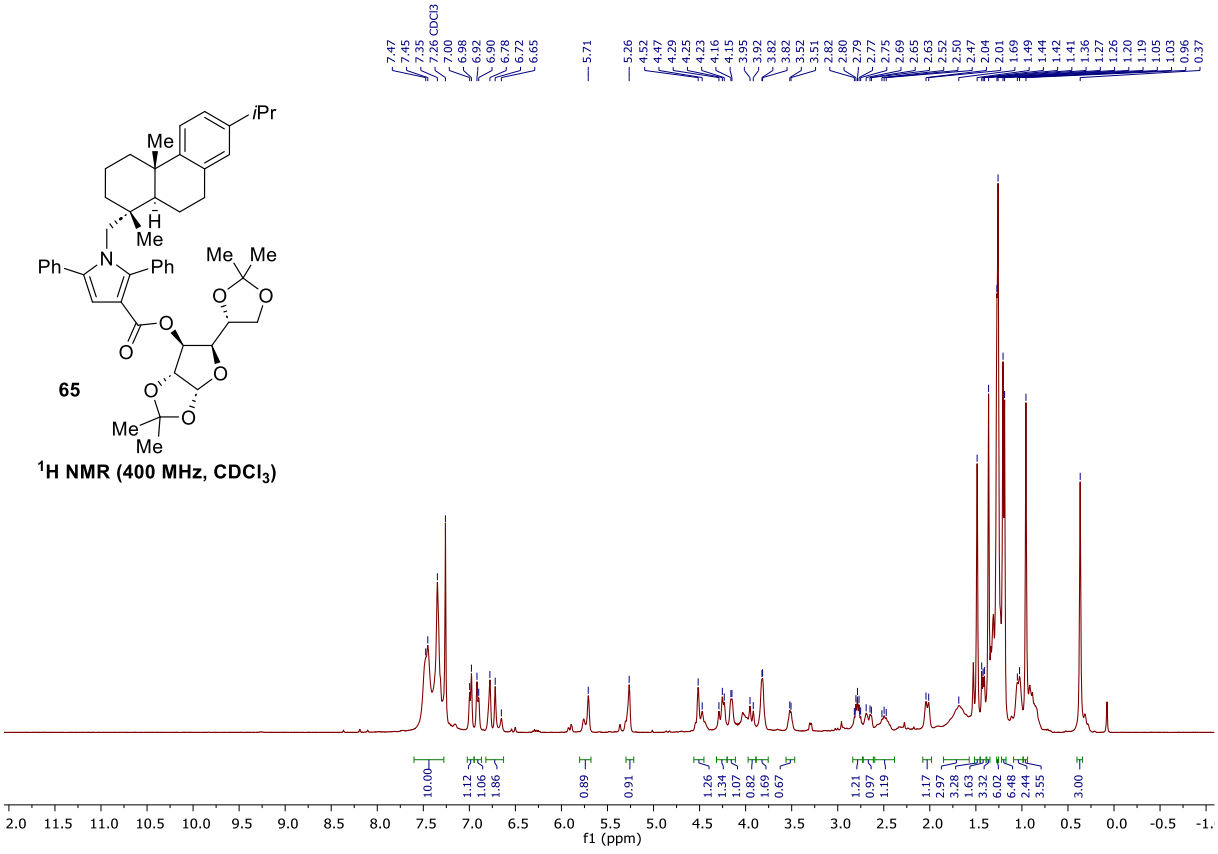
^{1}H NMR (400 MHz, $CDCl_3$)


165.81
165.67
147.30
145.74
138.40
137.80
134.39
131.83
131.53
128.59
128.25
126.82
123.83
123.72
77.16 CDCl3
55.52
51.77
46.98
40.09
37.91
37.72
37.55
33.55
29.68
25.29
24.14
24.07
19.00
18.41
18.07
Ph
CO2Me
Me
N
H
CO2Me
Ph
Me
Me
Me
60
13C NMR (101 MHz, CDCl3)
f1 (ppm)

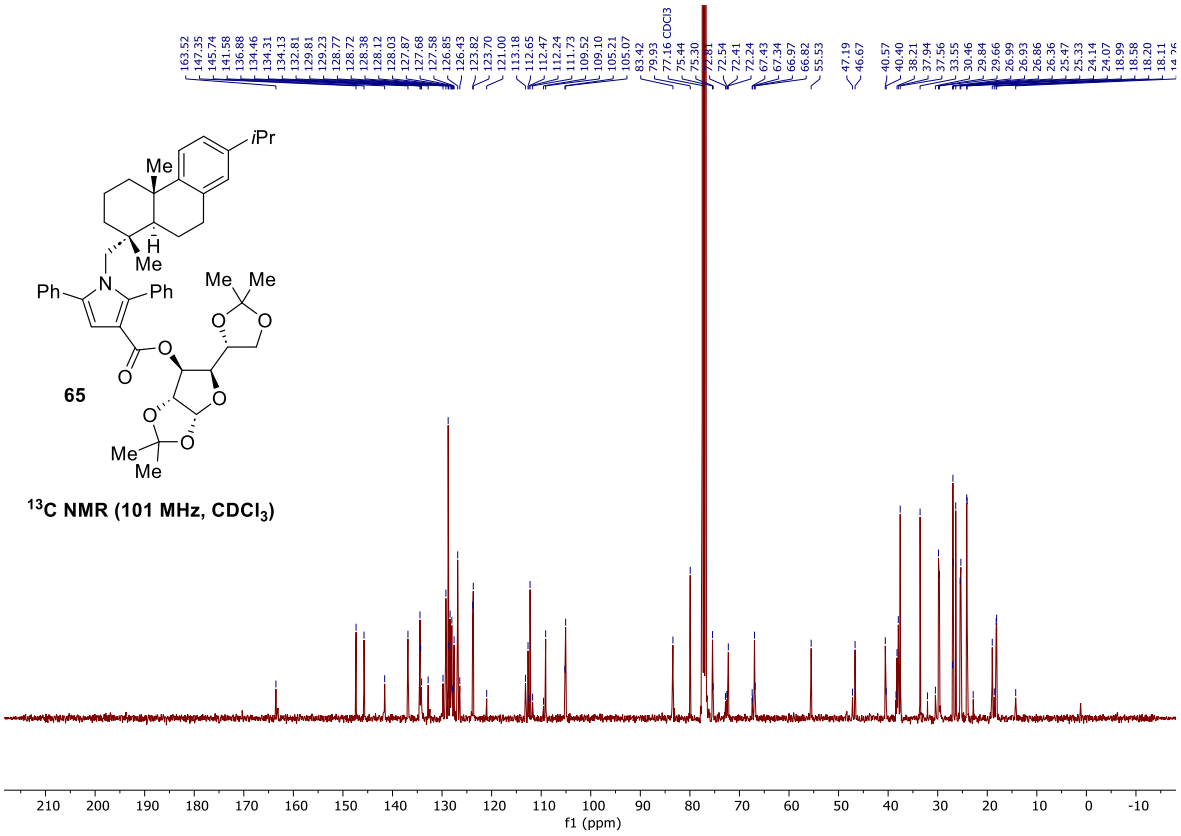

7.58
7.44
7.35
7.26 CDCl3
7.24
7.10
7.08
7.00
6.98
6.92
6.90
6.78
6.70
6.17
6.15
5.64
5.63
5.55
5.54
4.49
4.45
4.21
4.18
3.97
3.94
3.74
3.72
3.66
3.61
2.82
2.80
2.79
2.77
2.75
2.03
2.00
iPr
Me
H
Me
63
Ph
N
Ph
NH
CO2Me
O
Ph
1H NMR (400 MHz, CDCl3)
1.84
2.36
4.33
2.61
2.76
1.25
1.12
1.08
1.06
1.00
1.08
0.45
0.48
0.52
0.70
3.35
1.36
1.32
f1 (ppm)



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



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


163.52
147.35
145.74
141.58
136.88
134.46
134.31
134.13
132.81
129.81
129.23
128.77
128.72
128.38
128.12
128.03
127.87
127.68
127.58
126.85
126.43
123.82
123.70
121.00
113.18
112.65
112.47
112.24
111.73
109.52
109.10
105.21
105.07
83.42
79.93
77.16 CDCl3
75.44
75.30
72.81
72.54
72.41
72.24
67.43
67.34
66.97
66.82
55.53
47.19
46.67
40.57
40.40
38.21
37.94
37.56
33.55
30.46
29.84
29.66
26.99
26.93
26.86
26.36
25.47
25.33
24.14
24.07
18.99
18.58
18.20
18.11
iPr
Me
H
Me
N
Ph
Ph
Me
Me
O
O
O
O
O
O
O
Me
Me
65
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)