Electronic Supplementary Information

Visible-Light Paternò-Büchi Dearomatisation Process Towards the Construction of Oxeto-Indolinic Polycycles

Javier Mateos,[a] Alberto Vega-Peñaloza,[a] Pietro Franceschi,[a] Francesco Rigodanza,[a]
Philip Andreetta,[a] Xavier Companyó,[a]* Giorgio Pelosi, [b] Marcella Bonchio,[a]
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, Parco Area delle Scienze 1, 43124 Parma, Italy

E-mail: luca.dellamico@unipd.it, xavier.companyo@unipd.it

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A. GENERAL INFORMATION

NMR spectra were recorded on Bruker 400 Avance III HD equipped with a BBI-z grad probe head 5mm and Bruker 500 Avance III equipped with a BBI-ATM-z grad probehead 5mm. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. NMR yields were calculated by using trichloroethylene as internal standard.

High-Resolution Mass Spectra (HRMS) were obtained using Waters GCT gas chromatograph coupled with a time-of-flight mass spectrometer (GC/MS-TOF) with electron ionization (EI).

400 nm LED were purchased from Amazon https://www.amazon.it/gp/product/B00V4GY1UO/ref=ppx_yo_dt_b_asin_title_o07_s00?ie=UTF8&psc=1. 405 nm LED were purchased from Amazon https://www.amazon.it/JUNERAIN-Lampada-fotopolimerizzante-Stampante-fotosensibile/dp/B07KJH2ZPK. 465 nm LED strips were purchased from Amazon: https://www.amazon.it/Striscia-Decorazioni-Connettori-Connessione-Alimentatore/dp/B00HSF64E6.

Chromatographic purification of products was accomplished using flash chromatography on silica gel (SiO_2, 0.04-0.063 mm) purchased from Machery-Nagel, with the indicated solvent system according to the standard techniques. Thin-layer chromatography (TLC) analysis was performed on pre-coated Merck TLC plates (silica gel 60 GF254, 0.25 mm). Visualization of the developed chromatography was performed by checking UV absorbance (254nm) as well as with aqueous ceric ammonium molybdate and potassium permanganate solutions. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

Materials: Commercial grade reagents and solvents were purchased at the highest commercial quality from Sigma Aldrich or FluoroChem and used as received, unless otherwise stated. Indole **1a**, 2-methylindole, 2,3-dimethylindole, 2-methyl-1H-indole-3-carboxaldehyde, 2,3-dihydro-1H-cyclopentindole, 1,2,3,4-tetrahydrocarbazole, tetrahydro-ß-carboline, tryptamine, melatonin, (*L)*-tryptophan hydrochloride, benzophenone **2a**, 4,4’-dichlorobenzophenone **2b**, 3,3’-bistrifluoromethylbenzophenone **2c**, 3,3’-dichlorobenzophenone **2d**, 4,4’-dimethylbenzophenone **2e**, 4,4’-difluorobenzophenone **2f**, benzil **2g**, 4,4’-dimethylbenzil **2h**, 3,3’-dimethoxybenzil **2i** and 4,4’-difluorobenzil **2j** were purchased from Sigma-Aldrich and used as received. 6-fluoro-2-methylindole, 5-bromo-2-methylindole and 5-methoxy-2-methylindole were purchased from FluoroChem.

A.1. LIGHT SOURCES EMISSION SPECTRA

The following spectra were recorded by an AvaSpec ULS3648 high-resolution fiber-optic spectrometer which was placed at a fixed distance of 0.5 cm from the light source.

(more info at: https://www.avantes.com/products/spectrometers/starline/item/209-avaspec-uls3648-high-resolution-spectrometer).

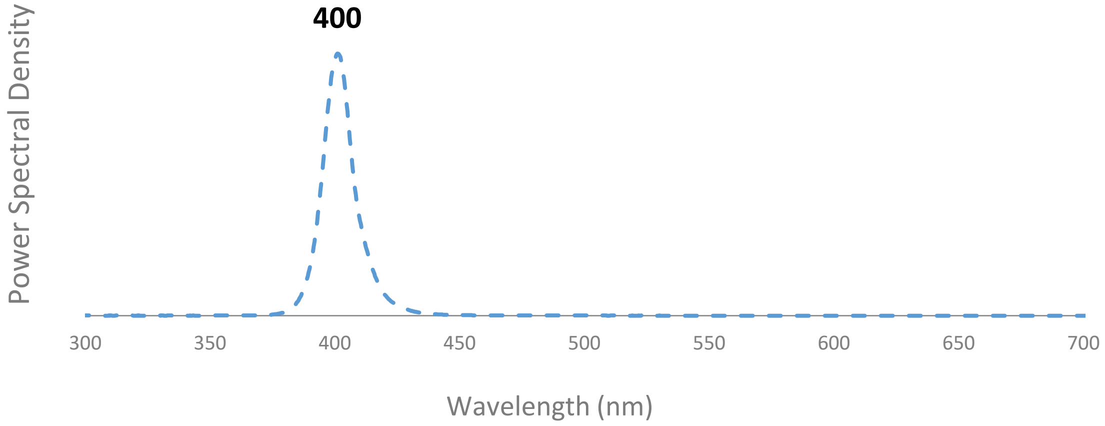


Figure S1. Emission spectra of the 400 nm LEDs used in this work.

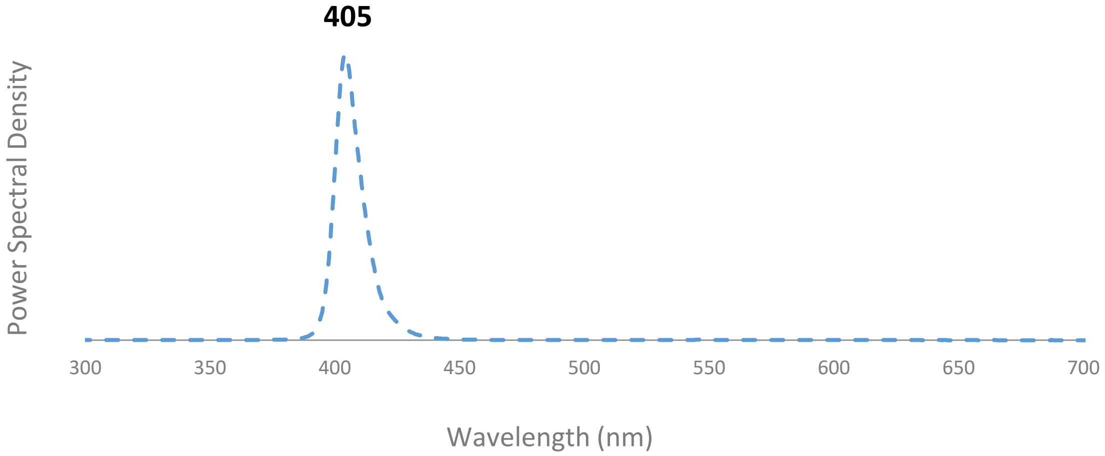


Figure S2. Emission spectra of the 405 nm LEDs used in this work.

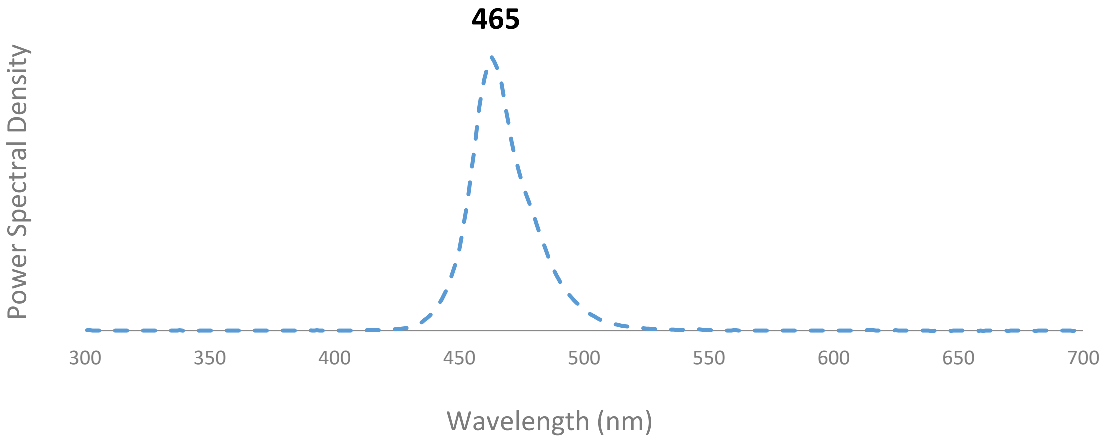


Figure S3. Emission spectra of the blue LEDs used in this work.

A.2. 405 NM REACTION SETUP

Figure S4 shows the general setup of a batch reaction under 405 nm irradiation. The reaction mixture was placed in the middle of the photoreactor (at about 1.5 cm distance from the light source). To maintain a stable reaction temperature one fan was placed close to the vials (25±2 °C) and the temperature was controlled by a thermometer.

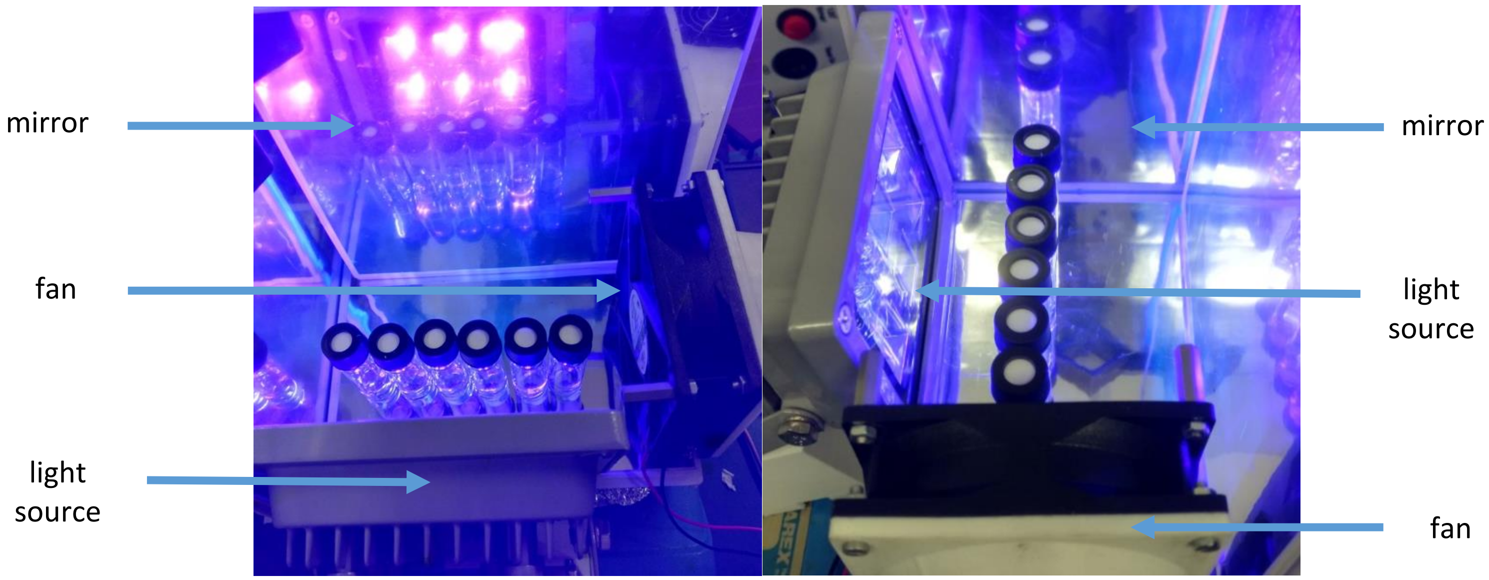


Figure S4. **Left:** top view of the photoreactor used in this work. **Right:** Side view of the photoreactor used in this work.

A.3. 465 NM REACTION SETUP

Figure S5 shows the general setup of a batch reaction under 465 nm irradiation. The reaction mixture was placed in the middle of the photoreactor (at about 1.5 cm distance from the light source. To maintain a stable reaction temperature a fan was placed close to the vials (25±2 °C) and the temperature was controlled by a thermometer.

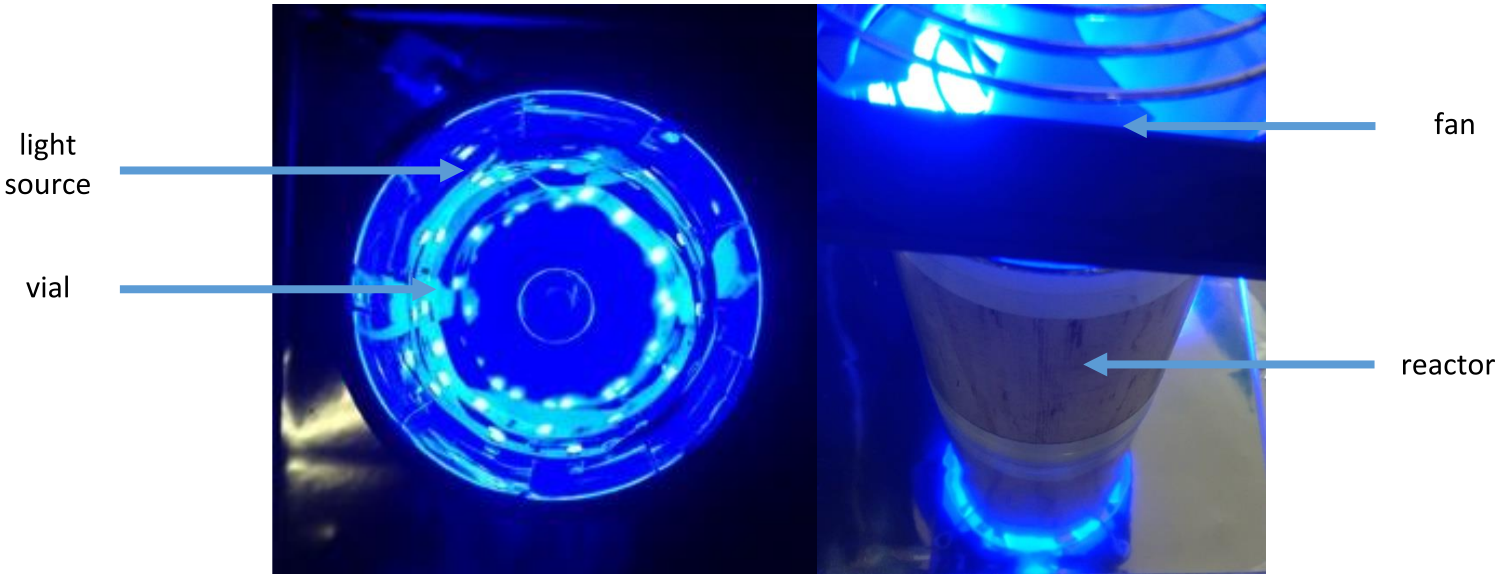
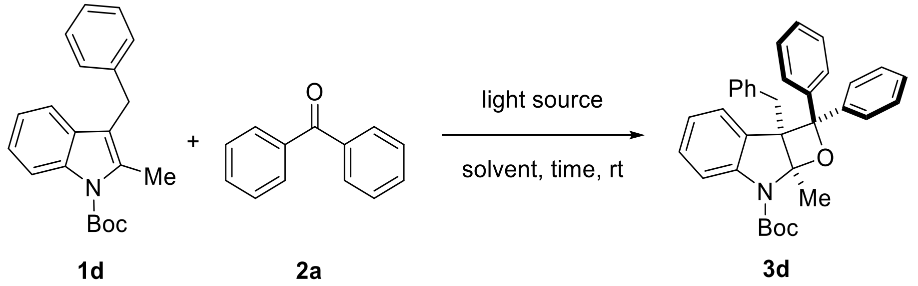


Figure S5. **Left:** top view of the photoreactor used in this work. **Right:** Front view of the photoreactor used in this work.

B. REACTION OPTIMIZATION

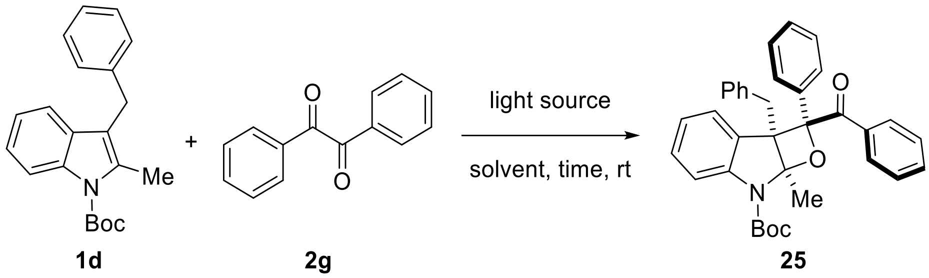
Table S1. Exploratory studies of the reaction between *N-Boc-3-benzyl-2-methylindole* ***1d*** *and benzophenone* ***2a****.*



entry	light source	solvent	1d:2a ratio	time (h)	Conversion (%)	NMR yield[a] (%)[b]
1	405 nm	toluene	1:3	16	>99	>99 (96)
2	405 nm	toluene	1:2	16	>99	>99 (97)
3	405 nm	toluene	1:1	16	>99	>99 (98)
4	405 nm	toluene	1:1	2	30	28
5	405 nm	toluene	1:1	4	58	56
6	CFL bulb	toluene	1:1	4	30	26
7	405 nm	toluene	1:1	6	75	74
8	405 nm	toluene	1:1	8	85	84
9	405 nm	CH_2Cl_2	1:1	4	nr	-
10	405 nm	ACN	1:1	4	35	-
11	405 nm	MeOH	1:1	4	39	-
12	405 nm	acetone	1:1	4	70	63 (68)
13	405 nm	acetone	1:1	7	>99	>99 (98)
14	405 nm	acetone	1:1	16	>99	>99 (98)
15	-	PhMe	1:1	16	-	-
16	-	Ace	1:1	16	-	-

[a] Inferred by ^{1}H NMR analysis of the crude mixture. NMR yield calculated using trichloroethylene as internal standard [b] Isolated yield after flash column chromatography.

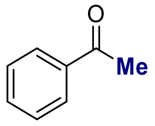
Table S2. Exploratory studies of the reaction between *N-Boc-3-benzyl-2-methylindole **1d** and benzil **2g***



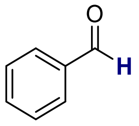
entry	light source	solvent	1d:2g ratio	time (h)	Conversion (%)	NMR yield[a] (%)[b]
1	405 nm	toluene	1:1	16	>99	>99 (93)
2	465 nm	toluene	1:1	16	>99	87 (85)
3	465 nm	acetone	1:1	16	>99	>99 (>98)
4	-	toluene	1:1	16	-	-
5	-	acetone	1:1	16	-	-

[a] Inferred by ^{1}H NMR analysis of the crude mixture. NMR yield calculated using trichloroethylene as internal standard [b] Isolated yield after flash column chromatography.

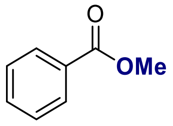
Table S3. Unreactive substrates



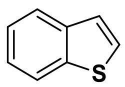
9% yield



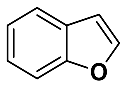
no reaction



no reaction



13% yield

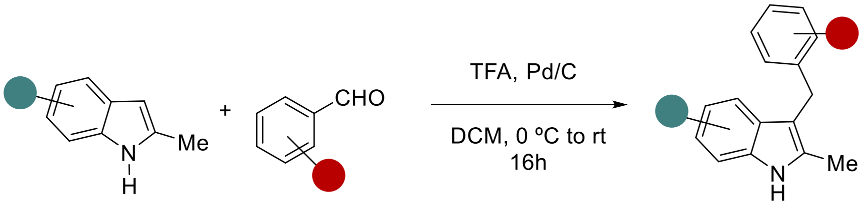


no reaction

NMR yield calculated using trichloroethylene as internal standard

C. GENERAL PROCEDURES FOR THE SYNTHESIS OF STARTING MATERIALS

C.1. PREPARATION OF 2-METHYL-3-BENZYLINDOLE DERIVATIVES AS SYNTHETIC PRECURSORS S1-S6.

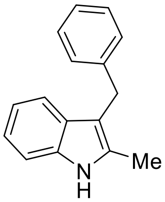


S1 - S7

3-benzyl substituted indoles were prepared using a described procedure in literature.[1]

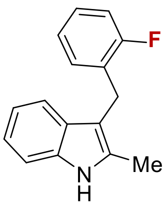
In a two-necked round bottom flask, a solution of 2-methylindole (0.66 g, 5 mmol) and benzaldehyde (765 µL ,7.5 mmol) in dichloromethane (25 mL, 0.2 M) was added to a stirring ice-cold mixture of trifluoroacetic acid (38 µL, 0.5 mmol, 10 mol%) and Pd/C (5 wt%) in DCM. This flask was filled with hydrogen and the mixture was stirred at 0 °C. After full consumption of the starting material, monitored by TLC (2% acetone in hexane), the palladium on carbon was filtered and the solvent was concentrated under reduced pressure. The crude product was purified by chromatography (9:1, hexane:EtOAc), giving 2-methyl-3-benzyl indole as a white solid that turned red overtime (1.04 g, 94% yield).

3-benzyl-2-methyl-1*H*-indole (S1).



^{1}H-NMR (400 MHz, CDCl$_3$): δ: 7.73 (*br* s, 1H, NH), 7.38 (d, *J* = 8.0 Hz, 1H, Ar), 7.27 — 7.20 (m, 5H, Ar), 7.16 —7.07 (m, 2H, Ar), 7.03 —7.00 (m, 1H, Ar), 4.06 (s, 2H, CH$_2$), 2.37 (s, 3H, CH$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 141.6, 135.3, 131.6, 128.9, 128.2, 125.6, 121.0, 119.2, 118.4, 110.6, 110.1, 30.1, 11.8. ppm. *These data matched with the previously reported in literature.*[1]

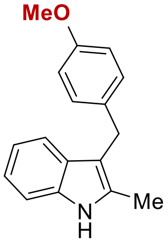
3-(2-fluorobenzyl)-2-methyl-1*H*-indole (S2).



Synthesized following the described procedure *i)* using 1 equivalent of 2-methylindole (0.66 g, 5 mmol) and 1.5 equivalents of 2-fluorobenzaldehyde (788 µL, 7.5 mmol) in 25 mL of dichloromethane**.** After flash column chromatography on silica gel (9:1 Hexane/EtOAc) yielding pure **S2** (white solid), in 69% yield, (824 mg, 3.4 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.81 (*br* s, 1H, NH), 7.46 (d, *J* = 8.0 Hz, 1H, Ar), 7.31 (d, *J* = 8.0 Hz, 1H, Ar), 7.16 — 6.96 (m, 6H, Ar), 4.10 (s, 2H, CH$_2$), 2.43 (s, 3H, CH$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 162.2, 159.7, 150.8, 135.3, 131.9, 130.4 (d, *J* = 4.5 Hz), 128.8, 128.4 (d, *J* = 8.0 Hz), 127.4 (d, *J* = 16.4 Hz), 123.9 (d, *J* = 3.6 Hz), 121.1, 119.3, 118.3, 115.1 (d, *J* = 22.9 Hz), 110.2, 109.1, 22.8 (d, *J* = 4.1 Hz), 11.8 ppm. **^{19}F-NMR (376 MHz, CDCl$_3$)**: δ -118.56 (q, *J* = 6.8 Hz, 1F, C-F Ar) ppm. **HRMS(ESI-MS)** calculated for $C_{16}H_{15}FN^+$ [M+H$^+$] 140.1110, found 240.1109.

3-(4-methoxybenzyl)-2-methyl-1*H*-indole (S3).

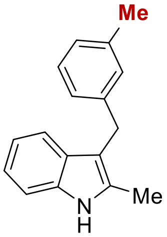


Synthesized following the described procedure *i)* using 1 equivalent of 2-methylindole (0.66 g, 5 mmol) and 1.5 equivalents of *p*-anisaldehyde (911 µL, 7.5 mmol) in 25 mL of dichloromethane**.** After flash column chromatography on silica gel (9:1 Hexane/EtOAc) yielding pure **S3** (white solid that turns red overtime), in 56% yield, (703 mg, 2.8 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.61 (*br* s, 1H, NH), 7.44 (d, *J* = 8.0 Hz, 1H, Ar), 7.29 — 7.24 (m, 5H, Ar), 7.17 —7.14 (m, 1H, Ar), 7.10 —7.07 (m, 1H, Ar), 4.11 (s, 2H, CH$_2$), 2.34 (s, 3H, CH$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 141.8, 135.4, 131.8, 129.0, 128.4 (x2), 128.4 (x2), 125.8, 121.1, 119.3, 118.5, 110.7, 110.4, 30.2, 11.8 ppm.

These data matched with the previously reported in literature.[2]

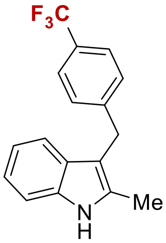
3-(3-methylbenzyl)-2-methyl-1*H*-indole (S4).



Synthesized following the described procedure *i)* using 1 equivalent of 2-methylindole (0.66 g, 5 mmol) and 1.5 equivalents of *m*-tolualdehyde (883 µL, 7.5 mmol) in 25 mL of dichloromethane**.** After flash column chromatography on silica gel (9:1 Hexane/EtOAc) yielding pure **S4** (white solid that turns red overtime), in 67% yield, (789 mg, 3.35 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.77 (*br* s, 1H, NH), 7.31 (d, *J* = 8.0 Hz, 1H, Ar), 7.20 — 7.01 (m, 6H, Ar), 7.17 —7.14 (m, 1H, Ar), 7.10 —7.07 (m, 1H, Ar), 4.09 (s, 2H, CH$_2$), 2.43 (s, 3H, CH$_3$), 2.33 (s, 3H, CH$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 141.6, 137.8, 135.3, 131.6, 129.1, 129.0, 128.2, 126.5, 125.4, 121.0, 119.3, 118.5, 110.7, 110.2, 30.1, 21.5, 11.9 ppm. **HRMS(ESI-MS)** calculated for $C_{17}H_{18}N^+$ [M+H$^+$] 236.1361, found 236.1370.

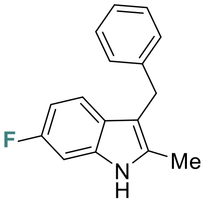
3-(4-trifluoromethylbenzyl)-2-methyl-1*H*-indole (S5).



Synthesized following the described procedure *i)* using 1 equivalent of 2-methylindole (0.66 g, 5 mmol) and 1.5 equivalents of 4-trifluoromethylbenzaldehyde (1.02 mL, 7.5 mmol) in 25 mL of dichloromethane**.** After flash column chromatography on silica gel (9:1 Hexane/EtOAc) yielding pure **S5** (white solid that turns orange overtime), in 72% yield, (1.04 g, 3.6 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.87 (*br* s, 1H, NH), 7.48 (d, *J* = 8.0 Hz, 2H, Ar), 7.38 — 7.31 (m, 4H, Ar), 7.38 — 7.31 (m, 4H, Ar), 7.12 (t, *J* = 6.4 Hz), 7.06 (t, *J* = 6.4 Hz, Ar), 4.14 (s, 2H, CH$_2$), 2.42 (s, 3H, CH$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 145.8, 135.3, 131.9, 128.6, 128.5 (x2), 125.2 (q, *J*= 3.8 Hz), 121.3, 119.5, 118.1, 110.3, 109.6, 30.0, 11.8 ppm. **^{19}F-NMR (376 MHz, CDCl$_3$)**: δ -62.66 (s, 3F, CF$_3$) ppm. **HRMS(ESI-MS)** calculated for $C_{17}H_{15}F_3N^+$ [M+H$^+$] 290.1078, found 290.1081.

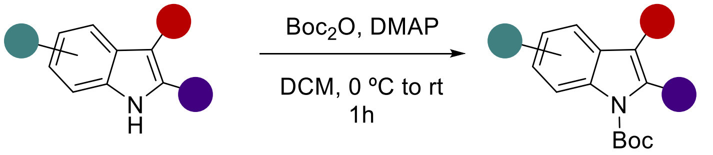
6-fluoro-2-methyl-1*H*-indole (S6).



Synthesized following the described procedure *i)* using 1 equivalent of 6-fluoro-2-methylindole (300 mg, 2 mmol) and 2 equivalents of benzaldehyde (410 µL, 4 mmol) in 10 mL of dichloromethane**.** After flash column chromatography on silica gel (9:1 Hexane/EtOAc) yielding pure **S6** (pink solid), in 55% yield, (263 mg, 1.1 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.75 (*br* s, 1H, NH), 7.30 — 7.24 (m, 6H, Ar), 6.98 (dd, *J* = 9.6, 2.3 Hz, 1H, Ar), 6.81 (ddd, *J* = 9.8, 8.6, 2.3 Hz, 1H, Ar), 4.07 (s, 2H, CH$_2$), 2.40 (s, 3H, CH$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 159.5 (d, *J* = 236.1 Hz), 141.4, 135.1 (d, *J* = 12.4 Hz), 131.8 (d, *J* = 3.7 Hz), 128.4 (x2), 128.2 (x2), 125.8, 125.4, 118.9 (d, *J* = 24.0 Hz), 110.6, 107.8 (d, *J* = 26.0 Hz), 96.7 (d, *J* = 26.0 Hz), 30.1, 11.8 ppm. **^{19}F-NMR (376 MHz, CDCl$_3$)**: δ -123.08— -123.15 (m, 1F, C-F Ar) ppm. **HRMS(ESI-MS)** calculated for $C_{16}H_{15}FN^+$ [M+H$^+$] 240.1110, found 240.1093.

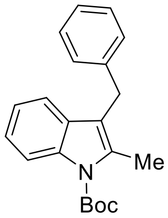
C.2. *N*-BOC PROTECTION OF INDOLE DERIVATIVES 1D – 1I, 1K, 1L, 1O, 1T, 1U.



1d - 1l, 1k, 1l, 1o, 1t, 1u

3-benzyl-2-methylindole (221.3 mg, 1 mmol, 1.0 equiv.) and DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) were dissolved in dichloromethane (5 mL, 0.2 M). Subsequently, di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) were added dropwise at 0 °C. After full consumption of the starting material, monitored by TLC (5% ethyl acetate in hexane), the reaction was quenched with 10 mL of HCl 4M. The organic layer was washed with 1x10 mL of HCl 4M, 1x10 mL of a saturated $NaHCO_3$ solution and 1x10 mL brine solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by chromatography (95:5, hexane:EtOAc), giving *N*-Boc-3-benzyl-2-methylindole as a white solid (306 mg, 95% yield).

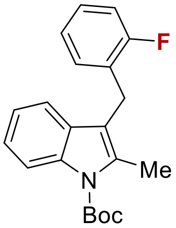
tert-butyl 3-benzyl-2-methyl-1*H*-indole-1-carboxylate (1d).



^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.14 (d, *J* = 8.5 Hz, 1H, Ar), 7.37 (d, *J* = 8.0 Hz, 1H, Ar), 7.27—7.14 (m, 7H, Ar), 4.05 (s, 2H, CH_2), 2.60 (s, 3H, CH_3), 1.70 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 150.8, 140.3, 135.8, 134.0, 130.1, 128.4 (× 2), 128.1 (× 2), 125.9, 123.3, 122.4, 118.2, 116.8, 115.3, 83.5, 29.8, 28.3 (× 3), 14.1 ppm.

These data matched with the previously reported in literature. [3]

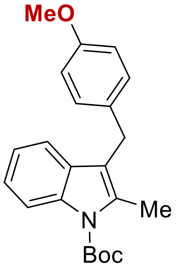
***tert*-butyl 3-(2-fluorobenzyl)-2-methyl-1*H*-indole-1-carboxylate (1e).**



Synthesized following the described procedure using 1 equivalent of the corresponding indole derivative **S2** (239.3 mg, 1.0 mmol), 1.5 equivalents of di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) and 0.1 equivalents of DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) in 5 mL of dichloromethane**. 1e** was obtained after flash column chromatography on silica gel (95:5 Hexane/EtOAc) as a white solid, in 65% yield, (220.6 mg, 0.65 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.14 (d, *J* = 8.5 Hz, 1H, Ar), 7.39 (d, *J* = 8.1 Hz, 1H, Ar), 7.26—7.16 (m, 3H, Ar), 7.08—6.97 (m, 3H, Ar), 4.07 (s, 2H, CH$_2$), 2.61 (s, 3H, CH$_3$), 1.72 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 162.1, 159.7, 150.8, 135.8, 134.5, 130.0 (d, *J* = 4.5 Hz), 130.0, 127.6 (d, *J* = 8.0 Hz), 127.0 (d, *J* = 16.4 Hz), 124.0 (d, *J* = 3.6 Hz), 123.4, 122.5, 118.1, 115.5, 115.4, 115.2, 115.0, 83.6, 28.3 (× 3), 27.4, 22.5 (d, *J* = 4.1 Hz), 14.1 ppm. **^{19}F-NMR (376 MHz, CDCl$_3$)**: δ -118.21 (q, *J* = 7.1 Hz, 1F, C-F Ar) ppm. **HRMS(ESI-MS)** calculated for $C_{21}H_{23}FNO_2^+$ [M+H$^+$] 340.1635, found 340.1632.

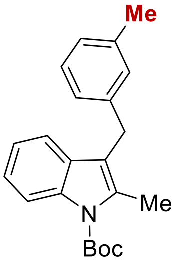
***tert*-butyl 3-(4-methoxybenzyl)-2-methyl-1*H*-indole-1-carboxylate (1f).**



Synthesized following the described procedure using 1 equivalent of the corresponding indole derivative **S3** (251 mg, 1.0 mmol), 1.5 equivalents of di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) and 0.1 equivalents of DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) in 5 mL of dichloromethane**. 1f** was obtained after flash column chromatography on silica gel (95:5 Hexane/EtOAc) as a white solid, in 89% yield, (316 mg, 0.89 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.10 (d, *J* = 8.5 Hz, 1H, Ar), 7.33 (d, *J* = 8.1 Hz, 1H, Ar), 7.20—7.09 (m, 4H, Ar), 6.78 (d, *J* = 8.2 Hz, 2H, Ar), 3.98 (s, 2H, CH$_2$), 3.75 (s, 3H, OCH$_3$), 2.58 (s, 3H, CH$_3$), 1.69 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 157.9, 150.9, 135.8, 133.9, 132.4, 130.1, 129.0 (× 2), 123.3, 122.4, 118.3, 117.3, 115.4, 113.8 (x2), 83.5, 29.0, 28.3 (× 3), 14.1 ppm. **HRMS(ESI-MS)** calculated for $C_{22}H_{26}NO_3^+$ [M+H$^+$] 351.1934, found 351.1930.

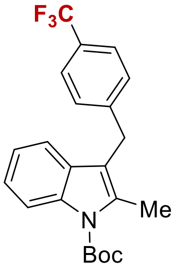
***tert*-butyl 3-(3-methylbenzyl)-2-methyl-1*H*-indole-1-carboxylate (1g).**



Synthesized following the described procedure using 1 equivalent of the corresponding indole derivative **S4** (235.1 mg, 1.0 mmol), 1.5 equivalents of di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) and 0.1 equivalents of DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) in 5 mL of dichloromethane**. 1g** was obtained after flash column chromatography on silica gel (95:5 Hexane/EtOAc) as a white solid, in 72% yield, (241.5 mg, 0.72 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.15 (d, *J* = 8.5 Hz, 1H, Ar), 7.39 (d, *J* = 8.1 Hz, 1H, Ar), 7.27—7.23 (m, 1H, Ar), 7.20—7.15 (m, 2H, Ar), 7.04—7.00 (m, 3H, Ar), 4.04 (s, 2H, CH$_2$), 2.62 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$), 1.73 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 150.9, 140.3, 138.0, 135.8, 134.1, 130.2, 128.9, 128.3, 126.8, 125.2, 123.3, 122.5, 118.3, 117.0, 115.4, 83.5, 29.8, 28.4 (×3), 21.5, 14.2 ppm. **HRMS(ESI-MS)** calculated for $C_{22}H_{26}NO_2^+$ [M+H$^+$] 336.1885, found 336.1880.

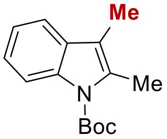
***tert*-butyl 3-(4-trifluoromethylbenzyl)-2-methyl-1*H*-indole-1-carboxylate (1h).**



Synthesized following the described procedure using 1 equivalent of the corresponding indole derivative **S5** (289.3 mg, 1.0 mmol), 1.5 equivalents of di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) and 0.1 equivalents of DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) in 5 mL of dichloromethane**. 1h** was obtained after flash column chromatography on silica gel (95:5 Hexane/EtOAc) as a white solid, in 92% yield, (358.3 mg, 0.65 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.14 (d, *J* = 8.5 Hz, 1H, Ar), 7.51 (d, *J* = 8.1 Hz, 2H, Ar), 7.34—7.15 (m, 5H, Ar), 7.20—7.15 (m, 2H, Ar), 7.04—7.00 (m, 3H, Ar), 4.12 (s, 2H, CH$_2$), 2.60 (s, 3H, CH$_3$), 1.72 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 150.8, 144.5, 135.8, 134.4, 129.8, 128.4 (x2), 125.3 (q, *J*= 3.8 Hz), 123.6, 122.6, 118.0, 115.9, 115.5, 83.8, 29.8, 28.3 (× 3), 14.2 ppm. **^{19}F-NMR (376 MHz, CDCl$_3$)**: δ -62.75 (s, 3F, CF$_3$) ppm. **HRMS(ESI-MS)** calculated for $C_{22}H_{23}F_3NO_2^+$ [M+H$^+$] 390.1603, found 390.1605.

***tert*-butyl 2,3-dimethyl-1*H*-indole-1-carboxylate (1i).**

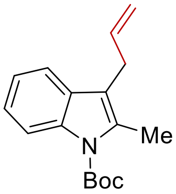


Synthesized following the described procedure using 1 equivalent of 2,3-dimethylindole (145.2 mg, 1.0 mmol), 1.5 equivalents of di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) and 0.1 equivalents of DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) in 5 mL of dichloromethane**. 1i** was obtained after flash column chromatography on silica gel (95:5 Hexane/EtOAc) as a white solid, in 95% yield, (233.0 mg, 0.95 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.11 — 8.03 (m, 1H, Ar), 7.43 — 7.34 (m, 1H, Ar), 7.23 — 7.15 (m, 2H, Ar), 2.51 (s, 3H, CH$_3$), 2.17 (s, 3H, CH$_3$), 1.66 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 150.8, 135.6, 132.8, 130.8, 123.2, 122.3, 117.7, 115.3, 113.7, 83.2, 28.3, 13.9, 8.7 ppm.

These data matched with the previously reported in literature.[4]

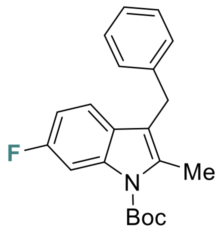
***tert*-butyl 3-allyl-2-methyl-1*H*-indole-1-carboxylate (1k).**



Synthesized following the described procedure using 1 equivalent of 3-allyl-2-methylindole (171.2 mg, 1.0 mmol), 1.5 equivalents of di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) and 0.1 equivalents of DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) in 5 mL of dichloromethane. **1k** was obtained after flash column chromatography on silica gel (95:5 Hexane/EtOAc) as a white solid, in 35% yield, (94.9 mg, 0.35 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$ δ 8.12 (d, *J* = 8.0 Hz, 1H, Ar), 7.46 (d, *J* = 8.2 Hz, 1H, Ar), 7.28 — 7.21 (m, 2H, Ar), 5.96 (ddt, *J* = 17.0, 10.0, 5.9 Hz, 1H, Csp^2-H), 5.09 — 5.03 (m, 2H, Csp^2-H$_2$), 3.45 (d, *J* = 6.0 Hz, 2H, CH$_2$), 2.56 (s, 3H, CH$_3$), 1.71 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 150.8, 136.0, 135.8, 133.7, 130.0, 123.3, 122.3, 118.0, 115.7, 115.4, 115.1, 83.4, 28.3 (x3), 28.3, 13.9 ppm. **HRMS(ESI-MS)** calculated for $C_{17}H_{22}NO_2^+$ [M+H$^+$] 272.1572, found 272.1569.

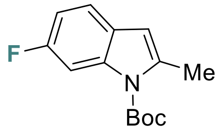
tert-butyl 3-benzyl-6-fluoro-2-methyl-1_H_-indole-1-carboxylate (1l).



Synthesized following the described procedure using 1 equivalent of the corresponding indole derivative **S6** (239.3 mg, 1.0 mmol), 1.5 equivalents of di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) and 0.1 equivalents of DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) in 5 mL of dichloromethane**. 1l** was obtained after flash column chromatography on silica gel (95:5 Hexane/EtOAc) as a white solid, in 98% yield, (332.6 mg, 0.98 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.96 (d, *J* = 8.0 Hz, 1H, Ar), 7.34 — 7.24 (m, 6H, Ar), 5.96 (dt, *J* = 8.8, 2.3 Hz, 1H, Ar), 4.08 (s, 2H, CH$_2$), 2.66 (s, 3H, CH$_3$), 1.77 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 160.5 (d, *J* = 236.1 Hz), 150.6, 140.2, 136.1 (d, *J* = 12.4 Hz), 134.2 (d, *J* = 3.7 Hz), 128.5 (x2), 128.2 (x2), 126.4, 126.2, 118.7 (d, *J* = 24.0 Hz), 116.7, 110.5 (d, *J* = 26.0 Hz), 103.1 (d, *J* = 26.0 Hz), 84.0, 29.9, 28.3 (x3), 14.3 ppm. **^{19}F-NMR (376 MHz, CDCl$_3$)**: δ -119.51— -119.58 (m, 1F, C-F Ar) ppm. **HRMS(ESI-MS)** calculated for $C_{21}H_{22}FNO_2^+$ [M+H$^+$] 340.1635, found 340.1633.

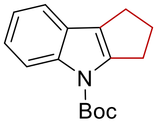
tert-butyl 6-fluoro-2-methyl-1_H_-indole-1-carboxylate (1o).



Synthesized following the described procedure using 1 equivalent of 6-fluoro-2-methylindole (149.2 mg, 1.0 mmol), 1.5 equivalents of di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) and 0.1 equivalents of DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) in 5 mL of dichloromethane. **1o** was obtained after flash column chromatography on silica gel (95:5 Hexane/EtOAc) as a white solid, in 90% yield, (224.4 mg, 0.90 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.84 (dd, *J* = 8.0, 2.3 Hz, 1H, Ar), 7.36 — 7.26 (m, 1H, Ar), 6.93 (dt, *J* = 8.2, 2.3 Hz, 1H, Ar), 6.27 (s, 1H, CH), 2.57 (s, 3H, CH$_3$), 1.68 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 162.2, 157.4, 146.3, 137.7 (d, *J* = 3.9 Hz), 125.1 (d, *J* = 1.6 Hz), 150.6, 140.2, 136.1 (d, *J* = 12.4 Hz), 134.2 (d, *J* = 3.7 Hz), 119.3 (d, *J* = 9.8 Hz), 110.2 (d, *J* = 24.0 Hz), 107.1 (d, *J* = 1.1 Hz), 102.6 (d, *J* = 29.0 Hz), 84.8, 27.0 (x3), 16.7 ppm. **^{19}F-NMR (376 MHz, CDCl$_3$)**: δ -119.65— -119.72 (m, 1F, C-F Ar) ppm. **HRMS(ESI-MS)** calculated for $C_{14}H_{17}FNO_2^+$ [M+H$^+$] 250.1238, found 250.1244.

tert-butyl 2,3-dihydrocyclopenta[_b_]indole-4-carboxylate (1t).

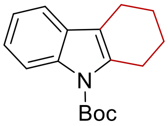


Synthesized following the described procedure using 1 equivalent of the corresponding indole 2,3-dihydrocyclopenta[*b*]indole (157.1 mg, 1.0 mmol), 1.5 equivalents of di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) and 0.1 equivalents of DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) in 5 mL of dichloromethane**. 1t** was obtained after flash column chromatography on silica gel (95:5 Hexane/EtOAc) as a white solid, in 63% yield, (162.0 mg, 0.63 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.15 (s, 1H, Ar), 7.34 (d, *J* = 7.2 Hz, 1H, Ar), 7.17 — 7.22 (m, 2H, Ar), 3.06 (t, *J* = 7.6 Hz, 2H, CH$_2$), 2.73 — 2.76 (m, 2H, CH$_2$), 2.44—2.49 (m, 2H, CH$_2$), 1.63 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 149.9, 143.9, 140.1, 126.7, 124.4, 122.8, 122.5, 118.4, 115.7, 82.9, 29.1, 28.2, 27.3 (x3), 24.0 ppm.

These data matched with the previously reported in literature.[5]

tert-butyl 1,2,3,4-tetrahydro-9_H_-carbazole-9-carboxylate (1u).

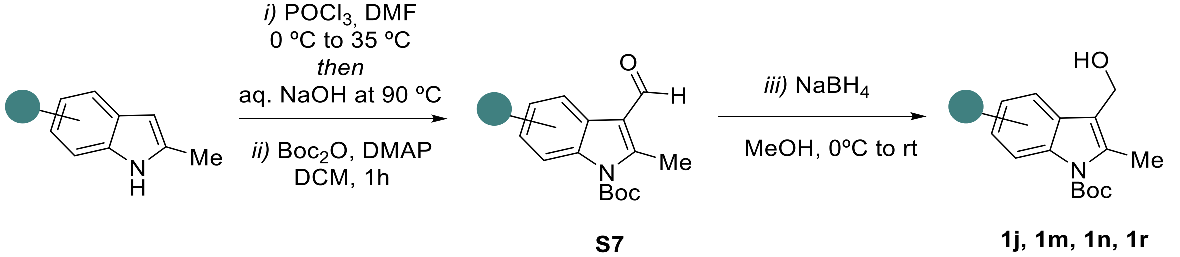


Synthesized following the described procedure using 1 equivalent of the corresponding indole derivative (171.1 mg, 1.0 mmol), 1.5 equivalents of di-*tert*-butyl dicarbonate (334 µL, 1.5 mmol, 1.5 equiv.) and 0.1 equivalents of DMAP (12.2 mg, 0.1 mmol, 0.1 equiv.) in 5 mL of dichloromethane**. 1u** was obtained after flash column chromatography on silica gel (95:5 Hexane/EtOAc) as a white solid, in 91% yield, (246.7 mg, 0.91 mmol).

^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.12 (m, 1H, Ar), 7.37 (m, 1H, Ar), 7.20 (m, 2H, Ar), 2.98 (m, 2H, CH$_3$), 2.63 (m, 2H, CH$_2$), 1.85 (m, 4H, 2xCH$_2$), 1.65 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 150.7, 135.8, 135.6, 129.9, 123.3, 122.3, 117.4, 116.7, 115.4, 83.1, 28.3 (x3), 25.6 (x2), 22.3, 21.1 ppm.

These data matched with the previously reported in literature.[6]

C.3. PREPARATION OF 3-HYDROXYMETHYL-SUBSTITUTED INDOLES 1J, 1M, 1N, 1R.



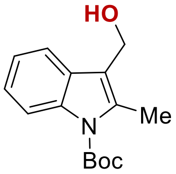
i) The reaction was performed following the previously reported in literature Vilsmeier formylation of indoles.[7]

$POCl_3$ (1.73 mL, 18.6 mmol) was added dropwise to DMF (5 mL) at 0 °C. The reaction mixture was stirred at this temperature for 30 min. Then, a solution of 2-methylindole (2.03 g, 15.5 mmol) in 5 mL of DMF (3.1 M) was added slowly. The resulting reaction mixture was allowed to warm up to 35 °C and kept at this temperature for 40 min. The reaction was allowed to cool down to room temperature and 10 g of ice were added followed by 30 mL of a 5M NaOH solution. The reaction mixture was heated at 90 °C for 30 min and allowed to cool down to room temperature again. An additional 10 g of ice were added and stirred for 30 min. The precipitate was filtered and washed with water. **1a** was used without further purification steps.

ii) The crude product was protected following the procedure described in section C.2 and used without further purification steps.

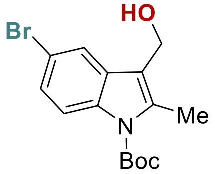
iii) **S7** (1.16 g, 4.5 mmol) was dissolved in 20 mL of MeOH (0.23M). Then, 1.5 equivalents of $NaBH_4$ (253 mg, 6.75 mmol) were added portionwise at 0 °C. After full consumption of the starting material, monitored by TLC, the reaction was quenched with 20 mL of water. The reaction mixture was extracted with 3x15 mL of EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by chromatography (8:2, hexane:EtOAc), furnishing **1j** as a yellowish solid in 91% overall yield (1.05 g, 4.1 mmol) after three consecutive steps.

***tert*-butyl 3-(3-hydroxymethyl)-2-methyl-1*H*-indole-1-carboxylate (1j).**



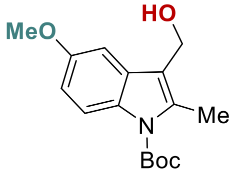
Synthesized following the described procedure *ii)* and *iii)*, obtaining **1j** as a yellowish solid in 91% overall yield after two consecutive steps. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.13—8.12 (m, 1H, Ar), 7.65—7.62 (m, 1H, Ar), 7.29—7.24 (m, 2H, Ar), 4.83 (s, 2H, CH_2), 2.65 (s, 3H, CH_3), 1.71 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$)**: δ 150.7, 135.8, 135.7, 128.9, 123.7, 122.8, 118.0, 117.6, 115.5, 83.9, 55.5, 28.3 (×3), 14.0 ppm. **HRMS(ESI-MS)** calculated for $C_{15}H_{19}NO_3^+$ [M+H$^+$] 262.1365, found 262.1367.

tert-butyl 3-(3-hydroxymethyl)-5-bromo-2-methyl-1*H*-indole-1-carboxylate (1m).



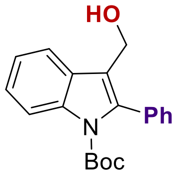
Synthesized following the described procedure starting from 5-bromo-2-methylindole (210 g, 1.0 mmol) and obtaining **1m** as a white solid in 19% overall yield (64.6 mg, 0.19 mmol) after three consecutive steps. **^{1}H-NMR (400 MHz, Acetone-d$_6$):** δ 8.04 (d, *J* = 8.2 Hz, 1H, Ar), 7.79 (s, 1H, Ar), 7.36 (dd, *J* = 8.9, 2.5 Hz, 1H, Ar), 4.71 (d, *J* = 6.2 Hz, 2H, CH$_2$), 3.93 (t, *J* = 4.9 Hz, 1H, OH), 2.59 (s, 3H, CH$_3$), 1.69 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 150.2, 136.1, 134.6, 131.6, 125.7, 121.3, 118.0, 116.8, 115.2, 84.1, 54.0, 27.4 (x3), 13.2 ppm. **HRMS(ESI-MS)** calculated for $C_{15}H_{19}BrNO_3^+$ [M+H$^+$] 340.0470, found 340.0472.

tert-butyl 3-(3-hydroxymethyl)-5-methoxy-2-methyl-1*H*-indole-1-carboxylate (1n).



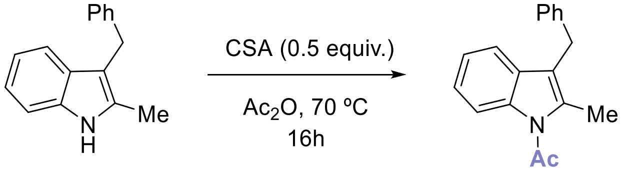
Synthesized following the described procedure starting from 5-methoxy-2-methylindole (806 mg, 5.0 mmol) and obtaining **1n** as a white solid in 81% overall yield (1.18 g, 4.1 mmol) after three consecutive steps. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 7.97 (d, *J* = 8.2 Hz, 1H, Ar), 7.06 (d, *J* = 2.6 Hz, 1H, Ar), 6.85 (dd, *J* = 8.9, 2.5 Hz, 1H, Ar), 4.76 (s, 2H, CH$_2$), 3.85 (s, 3H, OCH$_3$), 2.58 (s, 3H, CH$_3$), 1.67 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 156.0, 150.6, 136.3, 130.4, 117.5, 116.3, 112.2, 100.9, 83.8, 55.7, 55.5, 28.3 (x3), 14.0 ppm. **HRMS(ESI-MS)** calculated for $C_{16}H_{22}NO_4^+$ [M+H$^+$] 292.1471, found 292.1472.

tert-butyl 3-(3-hydroxymethyl)-2-phenyl-1*H*-indole-1-carboxylate (1r).



Synthesized following the described procedure starting from 2-phenylindole-3-carboxaldehyde (1.1 g, 5.0 mmol) and obtaining **1r** as a yellowish solid in 91% overall yield (1.47 g, 4.5 mmol) after two consecutive steps. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 8.29 (d, *J* = 8.2 Hz, 1H, Ar), 7.77 (d, *J* = 8.1 Hz, 1H, Ar), 7.46—7.33 (m, 7H, Ar), 7.20—7.15 (m, 2H, Ar), 7.04—7.00 (m, 3H, Ar), 4.65 (s, 2H, CH$_2$), 1.27 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 150.1, 137.7, 136.7, 133.4, 129.8 (x2), 128.7, 128.0, 128.0 (x2), 124.9, 123.1, 119.6, 119.1, 115.3, 83.4, 55.9, 27.5 (x3) ppm. **HRMS(ESI-MS)** calculated for $C_{20}H_{22}NO_3^+$ [M+H$^+$] 324.1521, found 324.1521.

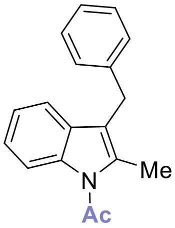
C.4. *N*-AC PROTECTION OF INDOLE DERIVATIVES 1P.



S1 **1p**

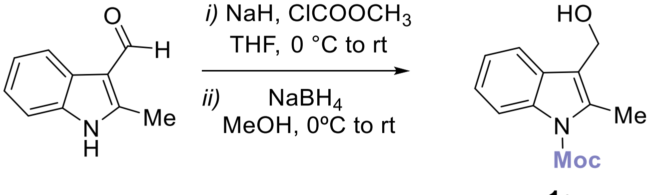
3-benzyl-2-methylindole (0.68 mmol, 150 mg) and 10-camphorsulfonic acid (0.34 mmol, 8.0 mg) were dissolved in acetic anhydride (1.5 mL, 0.45 M) at 0 ºC. The reaction was heated at 70 ºC and stirred vigorously for for 16h. After full consumption of the starting material, monitored by TLC, the reaction was quenched with 5 mL of brine. 10 mL of EtOAc were added and the organic layer was washed with 3x10 mL of a saturated $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by chromatography (95:5, hexane:EtOAc), giving *N*-Ac-3-benzyl-2-methylindole as a yellowish solid in 30% yield (90 mg, 0.2 mmol).

1-(3-benzyl-2-methyl-1*H*-indol-1-yl)ethan-1-one (1p).



^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.98 (d, *J* = 8.5 Hz, 1H, Ar), 7.40 (d, *J* = 8.0 Hz, 1H, Ar), 7.27—7.19 (m, 7H, Ar), 4.08 (s, 2H, CH_2), 2.79 (s, 3H, $COCH_3$), 2.64 (s, 3H, CH_3) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 170.3, 139.9, 135.8, 133.9, 130.6, 128.5 (x2), 128.2 (x2), 126.1, 123.8, 123.0, 118.7, 118.4, 115.0, 29.9, 27.7, 14.6 ppm. **HRMS(ESI-MS)** calculated for $C_{18}H_{18}NO^+$ [M+H$^+$] 264.1310, found 264.1318.

C.5. *N*-MOC PROTECTION OF INDOLE DERIVATIVES 1Q.

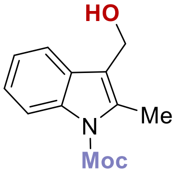


1q

i) 2-methylindole-3-carboxaldehyde (715 mg, 4.5 mmol) were dissolved in 10 mL of anhydrous THF. Subsequently, 2.5 equivalents of NaH 60% in mineral oil (410 mg, 10.3 mmol) were added portionwise at 0 °C. After 10 min, methyl chloroformate (420 µL, 1.2 equivalents) were added at 0°C dropwise. After full consumption of the starting material, monitored by TLC, the reaction was quenched with 20 mL of brine and extracted with 3x15 mL of EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was used without further purification steps.

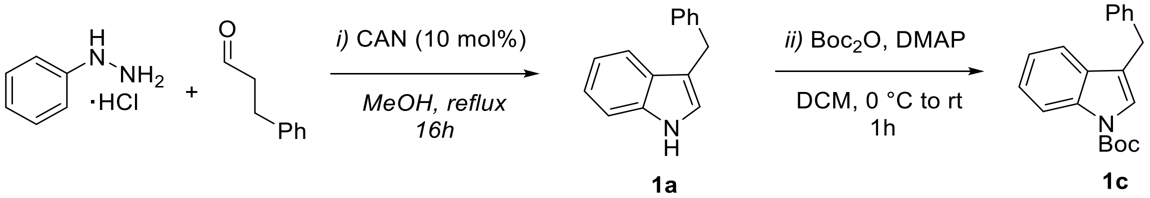
ii) The crude product was dissolved in 20 mL of MeOH (0.23M). Then, 1.5 equivalents of $NaBH_4$ (253 mg, 6.75 mmol) were added portionwise at 0 °C. After full consumption of the starting material, monitored by TLC, the reaction was quenched with 20 mL of water. The reaction mixture was extracted with 3x15 mL of EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by chromatography (7:3, hexane:EtOAc), furnishing **1q** as a yellowish solid in 45% overall yield (438 mg, 2.0 mmol) after two steps.

methyl 3-(hydroxymethyl)-2-methyl-*1H*-indole-1-carboxylate (1q).



^{1}H-NMR (500 MHz, CDCl$_3$): δ 8.09—8.07 (m, 1H, Ar), 7.63—7.61 (m, 1H, Ar), 7.31—7.25 (m, 2H, Ar), 4.80 (s, 2H, CH_2), 4.05 (s, 3H, $COCH_3$), 2.61 (s, 3H, CH_3) ppm. **^{13}C-NMR (125 MHz, CDCl$_3$)**: δ 152.9, 135.7, 135.7, 129.3, 124.1, 123.3, 118.3, 118.3, 115.6, 55.5, 53.7, 13.7 ppm. **HRMS(ESI-MS)** calculated for $C_{12}H_{14}NO_3^+$ [M+H$^+$] 220.0968, found 220.0972.

C.6. PREPARATION OF 1C.

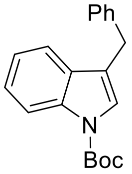


i) The reaction was performed following the previously reported in literature oxidative Fischer indole synthesis.[8]

Phenyl hydrazine hydrochloride (1.44 g, 10 mmol, 1.0 equivalent) and cerium ammonium nitrate (1.1 g, 2 mmol, 0.2 equivalents) were dissolved in 20 mL of MeOH (0.5 M). Subsequently, hydrocinnamaldehyde (1.3 mL, 10 mmol, 1.0 equivalents) were added dropwise and the mixture was heated to reflux and stirred for 16 h. The reaction was cooled to room temperature and quenched with 20 mL of water. Then, extracted with 3x20 mL of EtOAc. The combined organic layers were washed 3x15 mL of brine and the organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by chromatography (9:1, hexane:EtOAc), furnishing **1a** as a yellow solid in 60% overall yield (1.2 g, 6.0 mmol).

*ii) The crude product was N-Boc protected following the procedure described in section C.3 and purified by column chromatography (95:5, hexane:EtOAc) furnishing **1c** in 92% yield.*

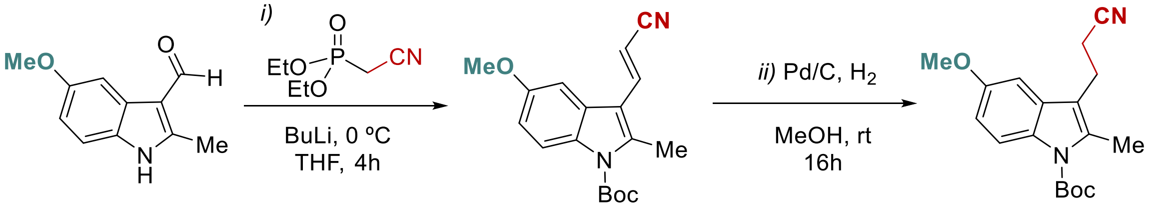
***tert*-butyl 3-benzyl-1*H*-indole-1-carboxylate (1c).**



^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.18 (br, 1H, Ar), 7.48 (d, *J* = 7.4 Hz, 1H, Ar), 7.41 (br, 1H, Ar), 7.36 – 7.32 (m, 5H, Ar), 7.26 – 7.21 (m, 2H, Ar), 4.08 (s, 2H, CH_2), 1.70 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (125 MHz, $CDCl_3$)**: δ 149.8, 139.6, 135.6, 130.5, 128.6 (x2), 128.4 (x2), 126.2, 124.3, 123.5, 123.3, 120.0, 119.3, 115.2, 83.4, 31.3, 28.1 (x3) ppm

These data matched with the previously reported in literature.[3]

C.7. PREPARATION OF 1S.



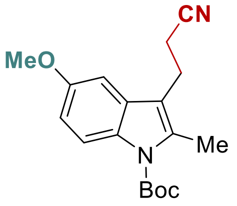
1s

i) The reaction was performed following the previously reported procedure in literature. [9]

To a solution of diethylcyanomethyl phosphonate (842 µL, 5.2 mmol, 1.3 equiv.) in anhydrous THF (10 mL) at 0°C, BuLi (192 µL, 4.8 mmol, 2.5M in hexanes, 1.2 equiv.) was added dropwise and the mixture was stirred for 1h at the same temperature. A solution of 5-methoxyindole-3-carboxaldeyde (1.15 g, 4.0 mmol, 1 equiv.) in anhydrous THF (7 mL) was prepared, the solution of the Wittig reagent was added dropwise via cannula. After the addition, the reaction mixture was stirred at 0°C for 4h. The reaction was then concentrated, and the product was used without further purification.

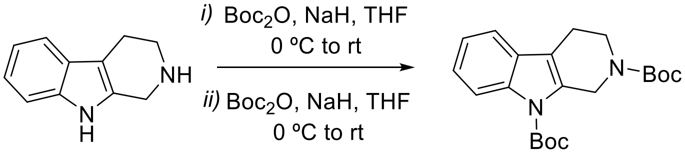
ii) The crude was dissolved in 20 mL of MeOH (0.2 M). Then, the round-bottom flask was back-filled three times with H_2. After 16h, the reaction was filtered through a pad of celite and concentrated under reduced pressure. The crude product was purified by chromatography (9:1, hexane:EtOAc), furnishing **1s** as a yellow solid in 45% overall yield (254.3 g, 1.8 mmol) after two steps.

***tert*-butyl 3-(2-cyanoethyl)-5-methoxy-2-methyl-1*H*-indole-1-carboxylate (1s).**



^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 8.03 (d, *J* = 8.2 Hz, 1H, Ar), 7.13 (d, *J* = 2.6 Hz, 1H, Ar), 6.88 (dd, *J* = 8.9, 2.5 Hz, 1H, Ar), 3.85 (s, 3H, OCH_3), 3.08 (t, *J* = 7.2 Hz, 2H, CH_2), 2.74 (t, *J* = 7.2 Hz, 2H, CH_2), 2.60 (s, 3H, CH_3), 1.70 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 156.1, 150.3, 135.0, 130.3, 130.0, 119.5, 116.1, 115.2, 111.8, 100.7, 83.4, 55.0, 27.5 (x3), 19.9, 17.2, 13.5 ppm. **HRMS(ESI-MS)** calculated for $C_{18}H_{23}N_2O_3^+$ [M+H$^+$] 315.1630, found 315.1632.

C.8. PREPARATION OF 1V.



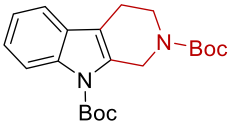
1v

The reaction was performed following the previously reported procedure in literature.[10] *Two identical steps were performed in order to obtain* ***1v****.*

Tetrahydro-β-carboline (861 mg, 5.0 mmol, 1.0 equiv.) was dissolved in THF. Then, NaH (240 mg, 60 wt % mineral oil suspension, 6 mmol, 1.2 equiv.), was added portionwise at 0 °C. The mixture was warmed to room temperature, and di-*tert*-butyl dicarbonate (1.7 mL, 7.5 mmol, 1.5 equiv.) was added and stirred overnight at room temperature. After full consumption of the starting material, monitored by TLC, water was added, and the mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was used without further purification and subjected to the same procedure.

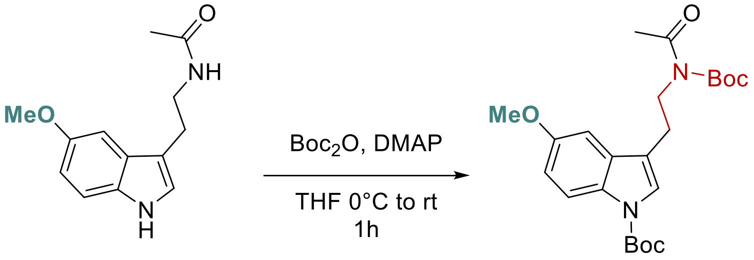
The crude product was purified by chromatography (9:1, hexane:EtOAc), furnishing **1v** as a yellow solid in 73% overall yield (1.35 g, 3.7 mmol) after two consecutive steps.

di-*tert*-butyl 2,3,4,9-tetrahydrol-1*H*-β-carboline-2,9-dicarboxylate (1v).



^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.21 (d, *J* = 8.1 Hz, 1H, Ar), 7.43 (d, *J* = 8.0 Hz, 1H, Ar), 7.35 — 7.22 (m, 2H, Ar), 4.84 (br, 2H, CH_2), 3.76 (br, 2H, CH_2), 2.76 (br, 2H, CH_2), 1.70 (s, 9H, $C(CH_3)_3$), 1.53 (s, 9H, $C(CH_3)_3$) ppm.
^{13}C-NMR (101 MHz, CDCl$_3$): δ 155.0, 150.0, 135.9, 128.9, 124.0, 122.7, 117.7, 115.4, 83.9, 80.0, 44.4, 40.2, 28.5 (x3), 28.3 (x3), 21.2 ppm.
These data matched with the previously reported in literature. [10]

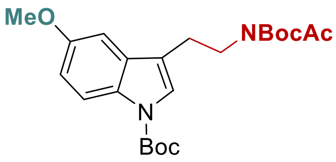
C.9. PREPARATION OF 1W.



1w

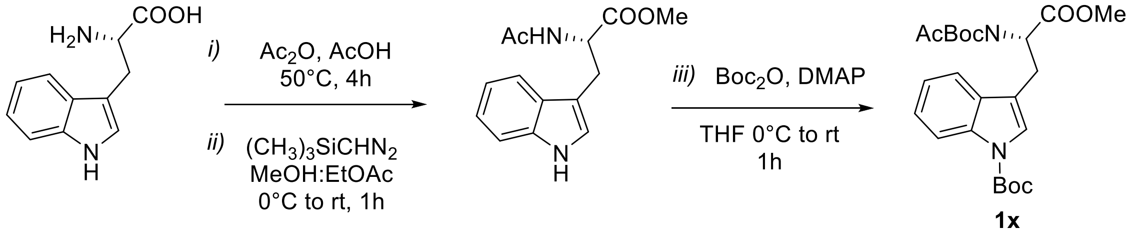
Melatonin (500 mg, 2.1 mmol, 1.0 equiv.) was dissolved in anhydrous THF (21.5 mL, 0.1 M) and DMAP (14.0 mg, 0.1 mmol, 0.05 equiv.) was added. Subsequently, di-*tert*-butyl dicarbonate (1.12 mL, 5.0 mmol, 2.4 equiv.) were added dropwise at 0 °C. After full consumption of the starting material, monitored by TLC (5% ethyl acetate in hexane), the reaction was quenched with 15 mL of HCl 4M. The organic layer was washed with 1x10 mL of HCl 4M, 1x10 mL of a saturated $NaHCO_3$ solution and 1x10 mL brine solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by chromatography (95:5, hexane:EtOAc), giving **1w** as a transparent oil (729.3 mg, 83% yield).

***tert*-butyl-3-(2-(*N*-(*tert*-butoxycarbonyl)acetamido)ethyl)-5-methoxy-1*H*-indole-1-carboxylate (1w).**



^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.01 (br, 1H, Ar), 7.38 (s, 1H, Ar), 7.15 (s, 1H, Ar), 6.94 (dd, *J* = 8.9, 2.5 Hz, 1H, Ar), 3.98 (t, *J* = 8.6 Hz, 1H, CH_2), 3.90 (s, 3H, OCH_3), 2.90 (t, *J* = 8.6 Hz, 1H, CH_2), 2.53 (s, 3H, $COCH_3$), 1.67 (s, 9H, $C(CH_3)_3$), 1.47 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$)**: δ 173.0, 155.9, 153.1, 123.8, 116.0, 113.1, 101.9, 83.2, 83.1, 55.8, 44.3, 28.2 (x3), 27.9 (x3), 27.1, 24.3 ppm. **HRMS(ESI-MS)** calculated for $C_{23}H_{33}N_2O_6^+$ [$M+H^+$] 433.2260, found 433.2254.

C.10. PREPARATION OF 1X.



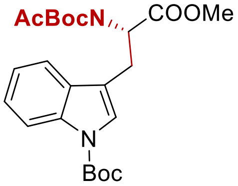
1x

i) (*L*)-Tryptophan (1.02 g, 5.0 mmol, 1.0 equiv.) was added portion wise to acetic acid (2 mL, 2M). Subsequently, acetic anhydride (4.5 mL, 47.5 mmol, 9.5 equiv.) was added. The mixture was stirred for 4h at 50 °C. The reaction mixture was poured into 10 g of ice. Then, extracted with 2x20 mL of EtOAc, the combined organic layers were washed with 10 mL of a 2M NaOH solution and 10 mL of brine. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was used without further purification steps.

ii) The crude was dissolved in MeOH:EtOAc, (3:7, 45 mL, 0.1 M). Subsequently, trimethylsilyldiazomethane (6.5 mL, 13 mmol, 2.0 M in Et_2O, 2.6 equiv.) was added dropwise at 0 °C. The mixture was stirred for 1h at room temperature. Then, acetic acid (1.14 mL, 20 mmol, 4.0 equiv.) was added dropwise and stirred for additional 5 min. The reaction was extracted with 3x10 mL of EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The reaction crude product was used without further purification steps.

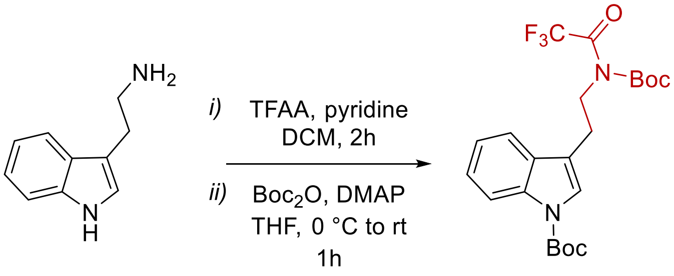
iii) The crude was dissolved in anhydrous THF (10 mL, 0.5 M) and DMAP (610.8 mg, 5.0 mmol, 1.0 equiv.) was added. Subsequently, di-*tert*-butyl dicarbonate (5.6 mL, 25.0 mmol, 5.0 equiv.) were added dropwise at 0 °C. After full consumption of the starting material, monitored by TLC (5% ethyl acetate in hexane), the reaction was quenched with 15 mL of HCl 4M. The organic layer was washed with 1x10 mL of HCl 4M, 1x10 mL of a saturated $NaHCO_3$ solution and 1x10 mL brine solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by chromatography (95:5, hexane:EtOAc), giving **1x** as a yellowish oil (874.9 mg, 38% yield) after three consecutive steps.

tert-butyl (_R_)-3-(2-(_N_-(_tert_-butoxycarbonyl)acetamido)-3-methoxy-3-oxopropyl)-1_H_-indole-1-carboxylate (1x).



^{1}H-NMR (400 MHz, CDCl$_3$): δ 8.12 (d, _J_ = 8.2 Hz, 1H, Ar), 7.52 (d, _J_ = 7.7 Hz, 1H, Ar), 7.38 (s, 1H, Ar), 7.31—7.24 (m, 2H, Ar), 5.47 (dd, _J_ = 9.7, 5.1 Hz, 1H, CH), 3.76 (s, 3H, COOCH$_3$), 3.55 (dd, _J_ = 14.8, 4.9 Hz, 1H, CH$_2$α), 3.31 (dd, _J_ = 14.8, 9.6 Hz, 1H, CH$_2$β), 2.38 (s, 3H, COCH$_3$), 1.67 (s, 9H, C(CH$_3$)$_3$), 1.33 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, CDCl$_3$)**: δ 172.8, 170.6, 152.0, 149.6, 130.4, 124.4, 124.1, 122.5, 118.8, 116.6, 115.3, 84.0, 83.5, 55.4, 52.3, 28.2 (x3), 27.6 (x3), 26.6, 25.0 ppm. **HRMS(ESI-MS)** calculated for $C_{24}H_{33}N_2O_7^+$ [M+H$^+$] 461.2210, found 461.2218.

C.11. PREPARATION OF 1Y.

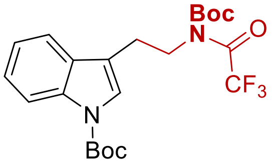


1y

i) Tryptamine (3.2 g, 20 mmol, 1.0 equiv.) was dissolved in anhydrous DCM (150 mL). Subsequently, pyridine (18 mL) was added. The solution was cooled at 0 °C and trifluoroacetic anhydride (3.1 mL, 22 mmol, 1.1 equiv.) was added dropwise, the mixture was stirred at this temperature for 5 min. The ice bath was removed, and the mixture was stirred for another 2h at room temperature. After addition of 150 mL saturated $NaHCO_3$, the phases were separated, and the organic layer washed with 50 mL of a saturated NH_4Cl solution and 50 mL of water. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was used without further purification.

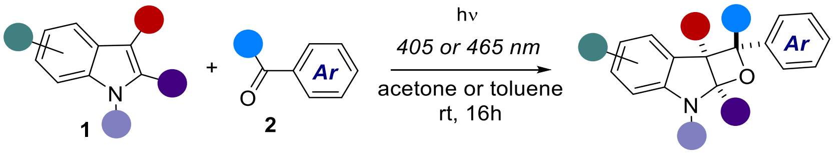
ii) As reported before in section C.2., The crude product was purified by chromatography (95:5, hexane:EtOAc), giving **1y** as a transparent oil (6.9 g, 76% yield).

***tert*-butyl-3-(2-(*N*-(*tert*-butoxycarbonyl)-2,2,2-trifluoroacetamido)ethyl)-1*H*-indole-1-carboxylate (1y).**



^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.15 (br, 1H, Ar), 7.65 (d, *J* = 8.5 Hz, 1H, Ar), 7.45 (s, 1H, Ar), 7.38—7.28 (m, 2H, Ar), 4.03 (t, *J* = 8.6 Hz, 1H, CH_2), 3.05 (t, *J* = 8.6 Hz, 1H, CH_2), 1.69 (s, 9H, $C(CH_3)_3$), 1.47 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$)**: δ 159.7 (q, *J* = 40.5 Hz), 150.8, 149.6, 135.6, 130.2, 124.6, 123.7, 122.7, 118.9, 116.3 (q, *J* = 110.9 Hz), 115.5, 85.9, 83.6, 46.7, 28.3 (x3), 27.4 (x3), 23.8 ppm. **^{19}F-NMR (376 MHz, $CDCl_3$)**: δ -69.63 (s, 3F, $COCF_3$) ppm. **HRMS(ESI-MS)** calculated for $C_{22}H_{28}F_3N_2O_5^+$ [M+H$^+$] 457.1872, found 457.1865.

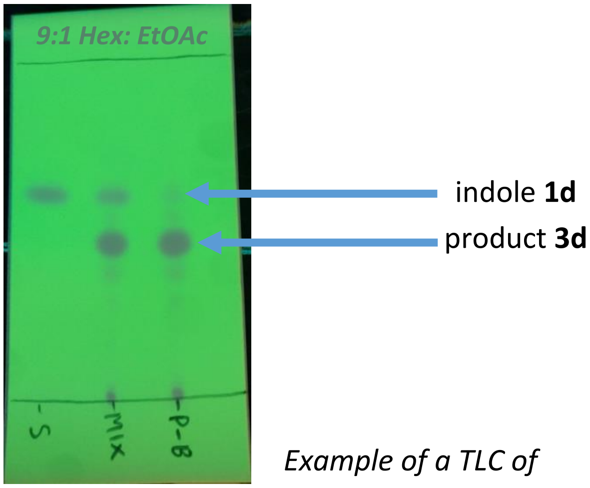
D. GENERAL PROCEDURE FOR THE VISIBLE LIGHT PATERNÒ-BÜCHI REACTION



In a 4 mL vial, indole (0.1 mmol, 1.0 equiv.) and the benzophenone derivative (0.1 mmol, 1.0 equiv.) were added. The two reagents were dissolved in acetone or toluene (1 mL, 0.1 M) and the reaction mixture was bubbled with N_2 for one minute. Then, the vial was placed in front of the selected light source (as described in section A.2 and A.3.), and irradiated for 16 h. The crude product was purified by chromatography (95:5, hexane:EtOAc) if needed or directly evaporated, giving the oxetane products **3c, 3d, 5-33** in the stated yields and diastereomeric ratio.

Note:

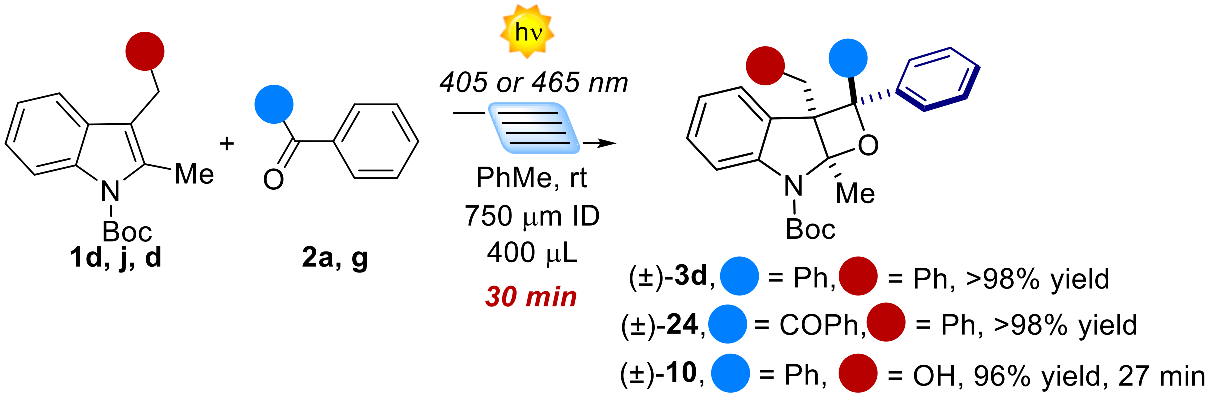
*Direct evaporation of the crude reaction mixture delivered the pure product. **3d**, **5**, **8**, and **24.***



*Example of a TLC of the crude product **3d** after 16 h of irradiation at 405 nm.*

Figure S6. Photoreaction performed under natural sun-light irradiation in a partially cloudy day (31/01/2020 from 11:00 until 17:00). On the roof-top of the Department of Chemical Sciences of the Padova University (Italy).

Implementation of the reaction into a microfluidic photoreactor.



In this setup, the solution containing **1d** or **1j** (0.1 M in Toluene) and **2a** or **2g** (1 equiv.) was firstly degassed by bubbling Nitrogen for 1 min. Subsequently, the solution under was introduced in continuous-flow into the micro-photoreactor via a double syringe pump (Syrris Atlas). The microfluidic reactor consists of a transparent TFE capillary (BGB®; internal diameter: 750 µm; inner volume: 400 µL), passed to a plastic support (Figure S7, left) covered by aluminum foil. This was placed in front (ca 1 cm) of the light-source, 405 nm LED 10W x 2 (Figure S7 right). Aluminium foil was used to avoid undesired irradiation of the tubing. To maintain a stable reaction temperature, a fan was placed in close proximity to the reactor and the temperature was controlled by a thermometer (25±2 °C).

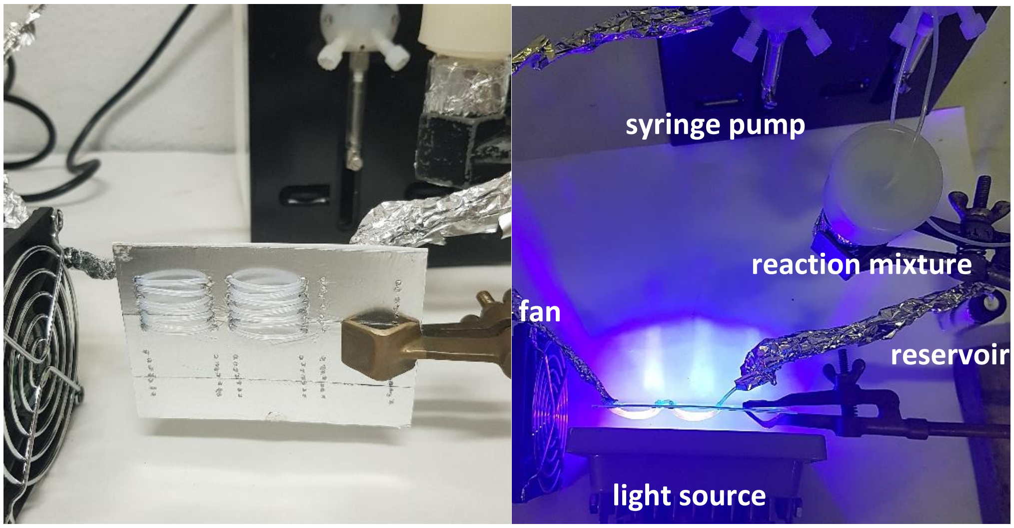
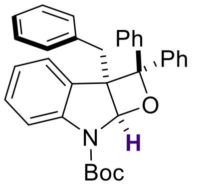


Figure S7. Microfluidic photoreactor used in this study. Zoom of the reactor (left) and assembled system at work (right).

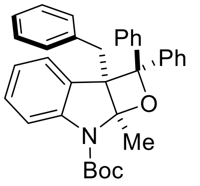
***tert*-butyl-2a-benzyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (3c).**



Synthesized following the described procedure, using 1 equivalent of **1c** (30.7 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **3c** (white solid), in 50% yield (24.5 mg, 0.050 mmol). *Yield in toluene: 48%.*

^{1}H-NMR (200 MHz, Acetone-d$_6$): δ 7.96 (dd, *J* = 8.4, 2.2 Hz, 2H, Ar), 7.58 – 7.54 (m, 3H, Ar), 7.53 – 7.50 (m, 3H, Ar), 7.38 – 7.34 (m, 1H, Ar), 7.15 (t, *J* = 7.8 Hz, 2H, Ar), 7.04 – 6.95 (m, 5H, Ar), 6.86 – 6.82 (m, 3H, Ar), 6.67 (br, 1H, CH), 3.53 (d, *J* = 16.7 Hz, 1H, CHα), 3.15 (d, *J* = 16.7 Hz, 1H, CHβ), 1.54 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (50 MHz, Acetone-d$_6$)**: δ 143.5, 143.4, 136.5, 129.4 (x2), 128.3 (x2), 127.9, 127.8 (x2), 127.3, 127.2 (x2), 126.4, 126.2 (x2), 126.2, 125.5 (x2), 121.9, 114.9, 94.6, 91.9, 39.0, 27.5 (x3). ppm. **HRMS(ESI-MS)** calculated for $C_{33}H_{32}NO_3^+$ [M+H$^+$] 490.6225, found 490.6230

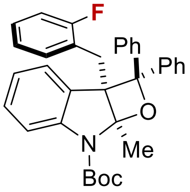
***tert*-butyl-2a-benzyl-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(2*H*)-carboxylate (3d).**



Synthesized following the described procedure, using 1 equivalent of **1d** (32.1 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **3d** (white foam), in 98% yield (49.3 mg, 0.098 mmol). *Yield in toluene: 98%*.

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.91 (d, *J* = 8.3 Hz, 2H, Ar), 7.57 (d, *J* = 8.2 Hz, 1H, Ar), 7.52 (d, *J* = 8.5 Hz, 2H, Ar), 7.45 (q, *J* = 6.9 Hz, 3H, Ar), 7.32—7.13 (m, 1H, Ar), 7.05—6.90 (m, 7H, Ar), 6.81—6.78 (m, 3H, Ar), 3.87 (d, *J* = 15.7 Hz, 1H, CH$_2$α), 3.21 (d, *J* = 15.7 Hz, 1H, CH$_2$β), 1.88 (s, 3H, CH$_3$), 1.62 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 151.5, 145.2, 144.0, 143.3, 137.2, 130.5, 129.7 (x3), 128.1, 128.0 (x3), 127.8 (x3), 127.1 (x3), 126.9, 126.1 (x3), 126.0, 125.7, 121.8, 115.2, 81.0, 62.8, 36.9, 27.7 (x3), 23.4 ppm. **HRMS(ESI-MS)** calculated for $C_{34}H_{34}NO_3^+$ [M+H$^+$] 504.2460, found 504.2453.

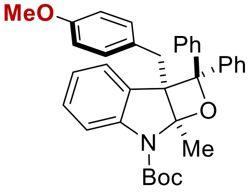
***tert*-butyl-2a-(2-fluorobenzyl)-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (5).**



Synthesized following the described procedure, using 1 equivalent of **1e** (33.9 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **5** (white foam), in >98% yield (52.0 mg, 0.099 mmol). *Yield in acetone: 40%.*

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.91 (d, *J* = 7.9 Hz, 2H, Ar), 7.59 (d, *J* = 8.2 Hz, 1H, Ar), 7.53 (d, *J* = 7.9 Hz, 2H, Ar), 7.45 (q, *J* = 7.3 Hz, 3H, Ar), 7.32 (t, *J* = 7.3 Hz, 1H, Ar), 7.11–6.92 (m, 6H, Ar), 6.81 (t, *J* = 7.5 Hz, 1H, Ar), 6.72 (t, *J* = 7.6 Hz, 1H, Ar), 6.46 (t, *J* = 7.8 Hz, 1H, Ar)., 3.70 (d, *J* = 17.0 Hz, 1H, $CH_2\alpha$), 3.34 (d, *J* = 17.0 Hz, 1H, $CH_2\beta$), 1.87 (s, 3H, CH_3), 1.63 (s, 9H, $C(CH_3)$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 162.01 (d, *J* = 243.3 Hz), 152.4, 146.2, 144.7, 144.0, 131.2, 130.7 (d, *J* = 3.5 Hz), 129.2, 129.0 (x2), 128.7 (d, *J* = 8.7 Hz), 128.0, 127.9 (x2), 127.2 (d, *J* = 22.1 Hz), 126.9 (x2), 126.6 (x2), 125.3 (d, *J* = 13.8 Hz), 124.5, 124.4, 122.9, 116.1, 115.7 (d, *J* = 23.3 Hz), 101.7, 93.0, 82.0, 63.1, 30.6, 28.6 (x3), 23.3 ppm. **^{19}F-NMR (376 MHz, Acetone-d$_6$)**: δ -117.10 (q, *J* = 7.4 Hz, 1F, C-F Ar) ppm. **HRMS(ESI-MS)** calculated for $C_{34}H_{33}FNO_3^+$ [M+H$^+$] 522.2439, found 522.2440.

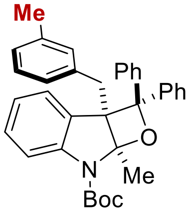
***tert*-butyl-2a-(4-methoxybenzyl)-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(2*H*)-carboxylate (6).**



Synthesized following the described procedure, using 1 equivalent of **1f** (35.1 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **6** (white foam), in 78% yield (41.6 mg, 0.078 mmol). *Yield in acetone: 44%.*

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.90 (d, *J* = 8.3 Hz, 2H, Ar), 7.58 (d, *J* = 8.3 Hz, 1H, Ar), 7.52 (d, *J* = 8.4 Hz, 2H, Ar), 7.45 (t *J* = 7.9 Hz, 3H, Ar), 7.31 (t, *J* = 7.3 Hz, 1H, Ar), 7.06—6.91 (m, 4H, Ar), 6.81 (t, *J* = 8.1 Hz, 1H, Ar), 6.69 (d, *J* = 8.2 Hz, 2H, Ar), 6.56 (d, *J* = 8.1 Hz, 2H, Ar) 3.78 (d, *J* = 15.7 Hz, 1H, $CH_2\alpha$), 3.63 (s, 3H, OCH_3), 3.14 (d, *J* = 15.7 Hz, 1H, $CH_2\beta$), 1.88 (s, 3H, CH_3), 1.62 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 158.9, 152.4, 146.1, 144.9, 144.3, 131.6 (x2), 131.5, 129.6, 129.0, 128.9 (x2), 127.9 (x2), 127.8, 127.0 (x2), 126.9, 126.6 (x2), 122.6, 116.0, 114.0, 101.9, 93.0, 81.9, 63.8, 55.2, 36.9, 30.6, 28.6 (x3), 24.1ppm. **HRMS(ESI-MS)** calculated for $C_{35}H_{36}NO_4^+$ [M+H$^+$] 534.2566, found 534.2571.

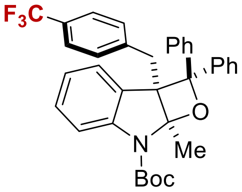
***tert*-butyl-2a-(3-methylbenzyl)-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(2*H*)-carboxylate (7).**



Synthesized following the described procedure, using 1 equivalent of **1g** (33.5 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **7** (white foam), in 72% yield (37.2 mg, 0.072 mmol).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.91 (d, *J* = 8.3 Hz, 2H, Ar), 7.60—7.41 (m, 6H, Ar), 7.32 (t, *J* = 7.8 Hz, 1H, Ar), 7.07—6.92 (m, 4H, Ar), 6.88—6.78 (m, 3H, Ar), 6.65 (s, 1H, Ar), 6.51 (d, *J* = 7.9 Hz, 1H, Ar), 3.84 (d, *J* = 15.7 Hz, 1H, CH$_2$α), 3.18 (d, *J* = 15.7 Hz, 1H, CH$_2$β), 2.07 (s, 3H, CH$_3$), 1.88 (s, 3H, CH$_3$), 1.62 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 152.4, 146.1, 144.8, 144.2, 137.9, 137.9, 133.3, 131.6, 131.5, 130.6, 129.3, 128.9 (x2), 128.5, 127.9 (x2), 127.8, 127.4, 127.3, 127.0 (x2), 126.6 (x2), 122.6, 116.0, 101.9, 93.0, 81.9, 63.7, 37.7, 28.6 (x3), 24.1, 21.3ppm. **HRMS(ESI-MS)** calculated for $C_{35}H_{36}NO_3^+$ [M+H$^+$] 518.2617, found 518.2622.

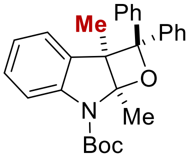
***tert*-butyl 2a-(4-trifluoromethylbenzyl)-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(2*H*)-carboxylate (8).**



Synthesized following the described procedure, using 1 equivalent of **1h** (38.9 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **8** (white foam), in >98% yield (57.0 mg, 0.099 mmol).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.93 (d, *J* = 8.3 Hz, 2H, Ar), 7.59 (d, *J* = 8.3 Hz, 1H, Ar), 7.53 (d, *J* = 8.4 Hz, 2H, Ar), 7.48—7.44 (m, 3H, Ar), 7.38—7.31 (m, 3H, Ar), 7.07—6.93 (m, 6H, Ar), 6.80 (t, *J* = 8.1 Hz, 1H, Ar), 3.98 (d, *J* = 15.7 Hz, 1H, CH$_2$α), 3.34 (d, *J* = 15.7 Hz, 1H, CH$_2$β), 1.93 (s, 3H, CH$_3$), 1.63 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 152.4, 146.1, 144.6, 144.0, 143.0, 131.2 (x2), 130.8, 129.2, 129.3 (q, *J*= 137.0 Hz, CF$_3$), 129.0 (x2), 128.0, 128.0 (x2), 127.6, 127.1, 127.0 (x2), 126.6 (x2), 125.4 (q, *J* = 3.7 Hz), 122.8, 116.2, 101.8, 92.9, 82.1, 63.5, 37.5, 28.6 (x3), 24.2 ppm. **^{19}F-NMR (376 MHz, Acetone-d$_6$)**: δ -63.37 (s, 3F, CF$_3$) ppm. **HRMS(ESI-MS)** calculated for $C_{35}H_{33}F_3NO_3^+$ [M+H$^+$] 572.2334, found 572.2340.

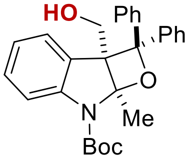
tert-butyl-2a,7a-dimethyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(2*H*)-carboxylate (9).



Synthesized following the described procedure, using 1 equivalent of **1i** (24.5 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **9** (white foam), in 82% yield (35.1 mg, 0.082 mmol).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.73 (d, *J* = 8.3 Hz, 2H, Ar), 7.47—7.37 (m, 6H, Ar), 7.25 (t, *J* = 7.8 Hz, 1H, Ar), 7.02—6.96 (m, 3H, Ar), 6.92—6.84 (m, 2H, Ar), 1.88 (s, 3H, CH_3), 1.64 (s, 9H, $C(CH_3)_3$), 1.45 (s, 3H, CH_3) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 152.2, 145.0, 144.7, 133.2, 128.9, 128.8 (x2), 127.8 (x2), 127.6 (x2), 126.9, 126.4 (x2), 126.4 (x2), 126.0, 122.9, 115.6, 102.7, 92.6, 81.6, 59.3, 28.6 (x3), 21.2, 18.0 ppm. **HRMS(ESI-MS)** calculated for $C_{28}H_{30}NO_3^+$ [M+H$^+$] 428.2197, found 428.2197.

tert-butyl-2a-(hydroxymethyl)-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (10).

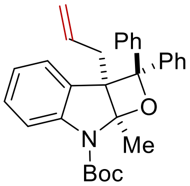


Synthesized following the described procedure, using 1 equivalent of **1j** (26.3 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (8:2 Hexane/EtOAc) yielding pure **10** (white solid), in 85% yield (37.7 mg, 0.085 mmol). *Yield in toluene: 80%.*

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.81 (d, *J* = 7.6 Hz, 2H, Ar), 7.55 (d, *J* = 8.1 Hz, 1H, Ar), 7.51 (d, *J* = 7.6 Hz, 1H, Ar), 7.45 (d, *J* = 7.6 Hz, 2H, Ar), 7.38 (t, *J* = 7.6 Hz, 2H, Ar), 7.26 (t, *J* = 7.3 Hz, 1H, Ar), 7.05—6.97 (m, 3H, Ar), 6.93 (t, *J* = 7.3 Hz, 1H, Ar), 6.84 (t, *J* = 7.3 Hz, 1H, Ar), 4.38 (dd, *J* = 11.4, 4.0 Hz, 1H, $CH_2\alpha$), 3.84 (dd, *J* = 11.4, 5.6 Hz, 1H, $CH_2\beta$), 3.78 (dd, *J* = 5.6, 4.0 Hz, 1H, OH), 2.04 (s, 3H, CH_3), 1.65 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 152.3, 146.4, 144.6, 144.1, 130.2, 128.8 (x3), 127.8 (x2), 127.8, 127.3, 126.9, 126.4 (x2), 126.3 (x2), 122.6, 115.6, 101.6, 91.3, 81.6, 63.5, 61.4, 28.6 (x3), 21.9 ppm. **HRMS(ESI-MS)** calculated for $C_{28}H_{30}NO_4^+$ [M+H$^+$] 444.2169, found 444.2169.

The reaction has been efficiently implemented into a microfluidic photoreactor (See Figure S7 and Figure 4c in the main text) in a parallel setup leading to 1.20 g of product (96% yield) in 15 h reaction time (27 min residence time).

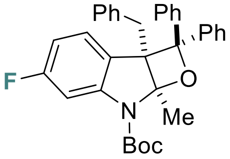
tert-butyl-2a-allyl-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(2*H*)-carboxylate (11).



Synthesized following the described procedure, using 1 equivalent of **1k** (27.1 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to a preparative TLC separation, yielding pure **11** (white foam), in 67% yield (30.4 mg, 0.067 mmol).

^{1}H-NMR (500 MHz, Acetone-d$_6$): δ 7.80 (d, *J* = 8.3 Hz, 2H, Ar), 7.55—7.53 (m, 1H, Ar), 7.45 (d, *J* = 7.8 Hz, 2H, Ar), 7.42 — 7.37 (m, 3H, Ar), 7.30 — 7.26 (m, 1H, Ar), 7.04—6.98 (m, 3H, Ar), 6.92 (t, *J* = 8.1 Hz, 1H, Ar), 6.85 (t, *J* = 7.9 Hz, 1H, Ar), 5.37 — 5.29 (m, 1H, Csp^{2}H), 5.01 (d, *J* = 16.0 Hz, 1H, (*E*)-Csp^{2}H$_2$), 4.86 (d, *J* = 11.2 Hz, 1H, (*Z*)-Csp^{2}H$_2$), 3.11 (dd, *J* = 15.0, 6.4 Hz, 1H, CH$_2\alpha$), 2.55 (dd, *J* = 16.4, 8.6 Hz, 1H, CH$_2\beta$), 1.98 (s, 3H, CH$_3$), 1.64 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (125 MHz, Acetone-d$_6$)**: δ 151.4, 145.0, 143.9, 143.2, 133.9, 129.7, 128.0, 127.9 (x2), 127.0 (x2), 126.4, 126.1, 125.8 (x2), 125.6 (x2), 122.4, 121.8, 117.8, 115.0, 101.4, 91.4, 80.9, 61.7, 36.3, 27.7 (x3), 21.9 ppm. **HRMS(ESI-MS)** calculated for $C_{30}H_{32}NO_3^+$ [M+H$^+$] 454.5820, found 454.5828.

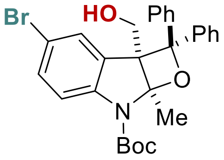
tert-butyl-2a-benzyl-5-fluoro-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (12).



Synthesized following the described procedure, using 1 equivalent of **1l** (33.9 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **12** (white foam), in 72% yield (37.5 mg, 0.072 mmol).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.91 (d, *J* = 7.6 Hz, 2H, Ar), 7.53 (d, *J* = 7.6 Hz, 2H, Ar), 7.48-7.40 (m, 3H, Ar), 7.08 (t, *J* = 7.6 Hz, 2H, Ar), 7.04-7.03 (m, 3H, Ar), 6.97 (t, *J* = 7.3 Hz, 1H, Ar), 6.84-6.81 (m, 2H, Ar), 6.55 (td, *J* = 8.7, 2.4 Hz, 1H, Ar), 3.86 (d, *J* = 16.2 Hz, 1H, CH$_2\alpha$), 3.22 (d, *J* = 16.2 Hz, 1H, CH$_2\beta$), 1.92 (s, 3H, CH$_3$), 1.63 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 163.5 (d, *J* = 241.0 Hz), 152.2, 147.4 (d, *J* = 12.7 Hz), 144.7, 143.9, 137.8, 130.6 (x2), 129.0 (x2), 128.7 (x2), 128.7 (d, *J* = 9.9 Hz), 128.0 (x3), 127.3 (d, *J* = 2.5 Hz), 127.0 (d, *J* = 23.7 Hz), 127.0 (x2), 126.5 (x2), 109.0 (d, *J* = 23.0 Hz), 103.8, 103.5, 102.7, 93.1, 82.6, 63.4, 37.5, 28.5 (x3), 24.2 ppm. **^{19}F-NMR (376 MHz, Acetone-d$_6$)**: δ -114.69 (q, *J* = 10.1 Hz, 1F, C-F Ar) ppm. **HRMS(ESI-MS)** calculated for $C_{34}H_{33}FNO_3^+$ [M+H$^+$] 522.2439, found 522.2445.

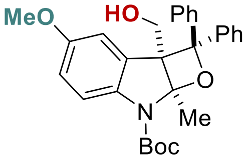
***tert*-butyl-5-bromo-2a-(hydroxymethyl)-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (13).**



Synthesized following the described procedure, using 1 equivalent of **1m** (34.0 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (9:1 Hexane/EtOAc) yielding pure **13** (white solid), in 52% yield (27.2 mg, 0.052 mmol).

^{1}H-NMR (500 MHz, Acetone-d$_6$): δ 7.82 (d, *J* = 8.0 Hz, 2H, Ar), 7.67 (d, *J* = 2.2 Hz, 1H, Ar), 7.48–7.44 (m, 3H, Ar), 7.38 (t, *J* = 8.0 Hz, 2H, Ar), 7.27 (t, *J* = 7.3 Hz, 2H, Ar), 7.12 (dd, *J* = 8.7, 2.2 Hz, 1H, Ar), 7.08 (t, *J* = 8.0 Hz, 2H, Ar), 6.97 (t, *J* = 7.3 Hz, 1H, Ar), 4.42 (dd, *J* = 11.7, 4.3 Hz, 1H, CH$_2$α), 4.04 (dd, *J* = 5.3, 4.3 Hz, 1H, OH), 3.84 (dd, *J* = 11.7, 5.3 Hz, 1H, CH$_2$β), 2.02 (s, 3H, CH$_3$), 1.64 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (125 MHz, Acetone-d$_6$)**: δ 152.0, 145.7, 144.4, 143.7, 133.1, 131.5, 130.3, 128.9 (x2), 128.0 (x2), 128.0, 127.2, 126.4 (x2), 126.3 (x2), 117.1, 114.6, 101.9, 91.3, 82.1, 63.6, 61.1. 28.6 (x3), 21.9 ppm. **HRMS(ESI-MS)** calculated for $C_{28}H_{29}BrNO_4^+$ [M+H$^+$] 522.1274, found 522.1271.

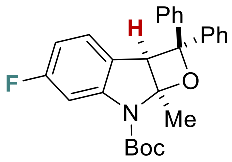
***tert*-butyl-2a-(hydroxymethyl)-4-methoxy-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (14).**



Synthesized following the described procedure, using 1 equivalent of **1n** (29.1 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (9:1 Hexane/EtOAc) yielding pure **14** (white solid), in 83% yield (39.3 mg, 0.083 mmol). *Yield in acetone: 60%.*

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.81 (d, *J* = 7.7 Hz, 2H, Ar), 7.48 (d, *J* = 7.7 Hz, 2H, Ar), 7.44 (d, *J* = 8.6 Hz, 1H, Ar), 7.38 (t, *J* = 7.7 Hz, 2H, Ar), 7.25 (t, *J* = 7.3 Hz, 1H, Ar), 7.13 (d, *J* = 2.6 Hz, 1H, Ar), 7.05 (t, *J* = 7.7 Hz, 2H, Ar), 6.94 (t, *J* = 7.3 Hz, 1H, Ar), 6.55 (dd, *J* = 8.6, 2.6 Hz, 1H, Ar), 4.40 (q, *J* = 6.6 Hz, 1H, CH$_2$α), 3.81 (m, 2H, CH$_2$β and OH overlapped), 3.70 (s, 3H, OCH$_3$), 2.01 (s, 3H, CH$_3$), 1.63 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 156.1, 152.3, 144.7, 144.2, 140.1, 131.5, 128.8 (x2), 127.9 (x2), 127.8, 127.0, 126.4 (x2), 126.3 (x2), 116.2, 114.2, 113.3, 101.7, 91.2, 81.4, 63.7, 61.5,55.9, 28.7 (x3), 22.0 ppm. **HRMS(ESI-MS)** calculated for $C_{29}H_{32}NO_5^+$ [M+H$^+$] 474.2275, found 474.2273.

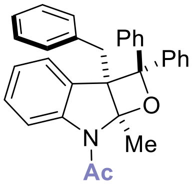
tert-butyl-5-fluoro-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (15).



Synthesized following the described procedure, using 1 equivalent of **1o** (24.9 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **15** (white foam), in 49% yield (21.0 mg, 0.049 mmol).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.65 (d, *J* = 7.7 Hz, 2H, Ar), 7.45 (t, *J* = 7.7 Hz, 2H, Ar), 7.37–7.31 (m, 2H, Ar), 7.24 (d, *J* = 7.7 Hz, 2H, Ar), 7.12 (dd, *J* = 7.7, 6.1 Hz, 1H, Ar), 7.07 (t, *J* = 7.7 Hz, 2H, Ar), 6.98 (t, *J* = 7.3 Hz, 1H, Ar), 6.49 (td, *J* = 8.8, 2.4 Hz, 1H, Ar), 4.75 (s, 1H, CH), 1.92 (s, 3H, CH$_3$), 1.65 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$):** δ 163.5 (d, *J* = 240.7 Hz), 152.2, 147.0, 143.3, 129.1 (x2), 128.4 (x2), 128.3, 128.2, 128.0, 127.5, 126.6 (x2), 126.3 (x2), 124.3 (d, *J* = 2.4 Hz), 109.2 (d, *J* = 22.9 Hz), 103.6 (d, *J* = 29.5 Hz), 100.2, 89.8, 82.5, 58.0, 30.6, 28.5 (x3), 25.7 ppm. **^{19}F-NMR (376 MHz, Acetone-d$_6$)**: δ -115.07 (q, *J* = 9.7 Hz, 1F, C-F Ar) ppm. **HRMS(ESI-MS)** calculated for $C_{27}H_{27}FNO_3^+$ [M+H$^+$] 432.1969, found 432.1972.

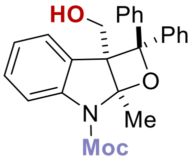
1-(2a-benzyl-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indol-7(*2H*)-yl)ethan-1-one (16).



Synthesized following the described procedure, using 1 equivalent of **1p** (26.3 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (9:1 Hexane/EtOAc) yielding pure **16** (white solid), in 71% yield (32.0 mg, 0.071 mmol).

^{1}H-NMR (500 MHz, CDCl$_3$): δ 7.85 (br s, 1H, Ar), 7.73 (d, *J* = 7.6 Hz, 2H, Ar), 7.43 (t, *J* = 7.6 Hz, 2H, Ar), 7.33–7.29 (m, 3H, Ar), 7.13 (d, *J* = 7.6 Hz, 1H, Ar), 7.08–6.95 (m, 7H, Ar), 6.91 (t, *J* = 7.6 Hz, 1H, Ar), 6.68 (d, *J* = 7.6 Hz, 2H, Ar), 3.58 (d, *J* = 16.7 Hz, 1H, CHα), 3.18 (d, *J* = 16.7 Hz, 1H, CHβ), 2.53 (s, 3H, COCH$_3$), 1.80 (s, 3H, CH$_3$) ppm. **^{13}C-NMR (125 MHz, CDCl$_3$)**: δ 170.1, 146.8, 142.6, 142.4, 136.7, 129.7 (x2), 128.9, 128.5(x2), 128.2 (x2), 127.6, 127.4 (x2), 126.7, 126.3, 126.0 (x2), 125.8 (x2), 123.4, 117.1, 93.6, 63.1, 41.0, 36.9 , 24.0 ppm. **HRMS(ESI-MS)** calculated for $C_{31}H_{28}NO_2^+$ [M+H$^+$] 446.2115, found 446.2114.

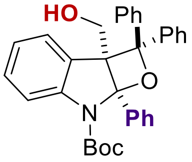
methyl-2a-(hydroxymethyl)-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (17).



Synthesized following the described procedure, using 1 equivalent of **1q** (27.9 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (7:3 Hexane/EtOAc) yielding pure **17** (white solid), in 96% yield (33.0 mg, 0.096 mmol).

^{1}H-NMR (200 MHz, Acetone-d$_6$): δ 7.89 – 7.74 (m, 2H, Ar), 7.64 – 7.47 (m, 2H, Ar), 7.45-7.32 (m, 4H, Ar), 7.31 – 7.18 (m, 1H, Ar), 7.13 – 6.78 (m, 5H, Ar), 3.89 (s, 3H, COOCH$_3$), 3.82 (dd, *J* = 6.7, 4.5 Hz, 2H, CH$_2$), 2.02 (s, 3H, CH$_3$) ppm. **^{13}C-NMR (50 MHz, Acetone-d$_6$)**: δ 143.3, 142.7, 129.1, 127.6 (x2), 127.5 (x4), 126.6 (x2), 126.6, 126.3, 125.7, 125.0 (x4), 121.7, 114.2, 60.2, 60.0, 51.4, 23.1, 20.2, 16.5 ppm. **HRMS(ESI-MS)** calculated for $C_{25}H_{24}NO_4^+$ [M+H$^+$] 402.1700, found 402.1703.

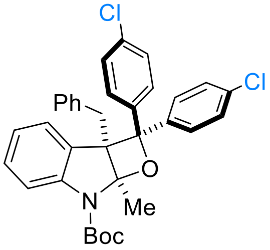
tert-butyl-2a-(hydroxymethyl)-2,2,7a-triphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (18).



Synthesized following the described procedure, using 1 equivalent of **1r** (32.3 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 60 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (9:1 Hexane/EtOAc) yielding pure **18** (white solid), in 22% yield (11.1 mg, 0.022 mmol).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 8.01 (d, *J* = 7.8 Hz, 2H, Ar), 7.69 (d, *J* = 7.8 Hz, 1H, Ar), 7.65 (d, *J* = 7.3 Hz, 1H, Ar)), 7.51–7.46 (m, 3H, Ar), 7.41 (t, *J* = 7.8 Hz, 3H, Ar)), 7.35–7.24 (m, 4H, Ar), 7.04 (q, *J* = 7.3 Hz, 3H, Ar), 6.92 (t, *J* = 7.3 Hz, 1H, Ar), 6.85 (t, *J* = 7.3 Hz, 1H, Ar), 3.97 (dd, *J* = 11.2, 4.2 Hz 1H, CH$_2$α), 3.62 (t, *J* = 4.2 Hz, 1H, OH), 3.39 (dd, *J* = 11.3, 4.2 Hz, 1H, CH$_2$β),1.22 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 151.8, 146.8, 145.0, 144.3, 140.0, 130.8, 130.1, 129.0, 128.8 (x2), 128.8, 128.7, 128.5, 128.3, 128.0 (x2), 127.8, 127.0, 126.5 (x2), 126.3 (x2),122.8, 114.6, 102.9, 93.3, 81.1, 65.0, 62.4, 28.2 (x3) ppm. **HRMS(ESI-MS)** calculated for $C_{33}H_{32}NO_4^+$ [M+H$^+$] 506.2326, found 506.2324.

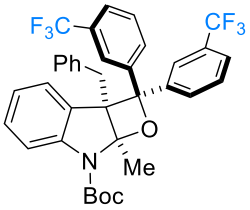
tert-butyl-2a-benzyl-2,2-bis(4-chlorophenyl)-7a-methyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (19).



Synthesized following the described procedure, using 1 equivalent of **1d** (32.1 mg, 0.1 mmol) and 1 equivalent of 4,4'-dichlorobenzophenone **2b** (25.1 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **19** (white foam), in 86% yield (49.2 mg, 0.086 mmol).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.91 (d, *J* = 8.6 Hz, 2H, Ar), 7.60 (d, *J* = 8.6 Hz, 1H, Ar), 7.51 (dd, *J* = 10.7, 8.6 Hz, 4H, Ar), 7.45 (d, *J* = 7.3 Hz, 1H, Ar), 7.09 (d, *J* = 8.6 Hz, 2H, Ar), 7.05–7.00 (m, 4H, Ar), 6.85–6.80 (m, 3H, Ar), 3.88 (d, *J* = 16.0 Hz, 1H, CH$_2$α), 3.23 (d, *J* = 16.0 Hz, 1H, CH$_2$β), 1.90 (s, 3H, CH$_3$), 1.62 (s, 9H, C(CH$_3$)$_3$). ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 152.3, 146.0, 143.4, 142.6, 137.7,133.7, 132.7, 130.9, 130.6(x2), 129.3, 129.2 (x2), 128.7 (x2), 128.7 (x2),128.3 (x2),128.1 (x2), 127.6, 126.9, 122.9, 116.1, 102.2, 92.4, 82.2, 63.8, 37.4, 28.5 (x3), 24.1 ppm. **HRMS(ESI-MS)** calculated for $C_{34}H_{32}Cl_2NO_3^+$ [M+H$^+$] 572.1754, found 572.1758.

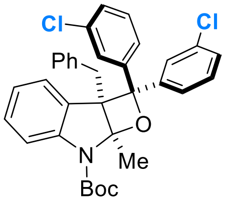
tert-butyl-2a-benzyl-7a-methyl-2,2-bis(3-(trifluoromethyl)phenyl)-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (20).



Synthesized following the described procedure, using 1 equivalent of **1d** (32.1 mg, 0.1 mmol) and 1 equivalent of 3,3'-bis(trifluoromethyl)benzophenone **2c** (31.8 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **20** (white foam), in 53% yield (33.9 mg, 0.053 mmol). *Yield in toluene: 47%.*

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 8.30 (d, *J* = 7.2 Hz, 1H, Ar), 8.26 (s, 1H, Ar), 7.90 — 7.72 (m, 5H, Ar), 7.58 — 7.55 (m, 2H, Ar), 7.34 — 7.32 (m, 2H, Ar), 7.21 (m, 2H, Ar), 7.04 — 7.00 (m, 4H, Ar), 6.84-6.80 (m, 3H, Ar), 4.06 (d, *J* = 16.0 Hz,1H, CH$_2$α), 3.23 (d, *J* = 16.0 Hz, 1H, CH$_2$β), 1.95 (s, 3H, CH$_3$), 1.63 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 152.2, 146.0, 145.5, 144.8, 137.5, 131.0, 130.6 (x2), 130.5, 130.4 130.3, 129.5, 129.1, 128.7 (x2), 127.7, 127.0, 125.3 (q), 124.2 (q), 123.4 (q), 123.0, 116.1, 102.5, 92.4, 82.4, 64.1, 37.2, 28.5 (x3), 24.1 ppm. **^{19}F-NMR (376 MHz, Acetone d$_6$)**: δ -63.32 (s, 3F, ArCF$_3$), -63.47 (s, 3F, ArCF$_3$) ppm **HRMS(ESI-MS)** calculated for $C_{36}H_{32}F_6NO_3^+$ [M+H$^+$] 640.2281, found 640.2280.

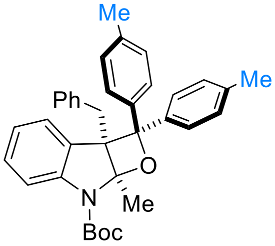
***tert*-butyl-2a-benzyl-2,2-bis(3-chlorophenyl)-7a-methyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (21).**



Synthesized following the described procedure, using 1 equivalent of **1d** (32.1 mg, 0.1 mmol) and 1 equivalent of 3,3'-dichlorobenzophenone **2d** (25.1 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **21** (white foam), in 70% yield (40.1 mg, 0.070 mmol). *Yield in toluene: 70%.*

^{1}H-NMR (500 MHz, Acetone-d$_6$): δ 7.95 – 7.88 (m, 2H, Ar), 7.61 (d, *J* = 8.5 Hz, 1H, Ar), 7.59 – 7.57 (m, 2H, Ar), 7.55 – 7.48 (m, 2H, Ar), 7.42 – 7.38 (m, 1H, Ar), 7.13 – 7.08 (m, 1H, Ar), 7.06 – 7.00 (m, 5H, Ar), 6.91 – 6.81 (m, 3H, Ar), 4.01 (d, *J* = 16.1 Hz, 1H, CH$_2$α), 3.26 (d, *J* = 16.1 Hz, 1H, CH$_2$β), 1.93 (s, 3H, CH$_3$), 1.65 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (125 MHz, Acetone-d$_6$)**: δ 151.4, 145.8, 145.1, 145.0, 136.8, 134.0, 133.0, 130.0, 129.8, 129.7 (x2), 128.9, 128.6, 127.8 (x2), 127.5, 126.8, 126.5, 126.1, 125.8, 125.7, 124.7, 124.4, 122.0, 115.3, 101.5, 91.3, 81.4, 63.0, 36.3, 27.7, 23.2 ppm. **HRMS(ESI-MS)** calculated for $C_{34}H_{32}Cl_2NO_3^+$ [M+H$^+$] 572.1754, found 572.1755.

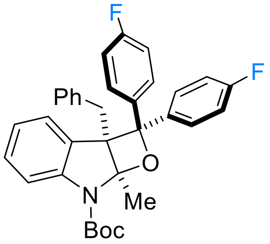
***tert*-butyl-2a-benzyl-7a-methyl-2,2-di-p-tolyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (22).**



Synthesized following the described procedure, using 1 equivalent of **1d** (32.1 mg, 0.1 mmol) and 1 equivalent of 4,4'-dimethylbenzophenone **2e** (21.0 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **22** (white foam), in 86% yield (45.7 mg, 0.086 mmol). *Yield in toluene: 73%.*

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.75 (d, *J* = 8.0 Hz, 2H, Ar), 7.59 (d, *J* = 8.0 Hz, 1H, Ar), 7.41 (d, *J* = 7.5 Hz, 1H, Ar), 7.37 (d, *J* = 8.0 Hz, 1H, Ar), 7.25 (d, *J* = 8.0 Hz, 2H, Ar), 7.01–6.97 (m, 4H, Ar), 6.85 (d, *J* = 8.0 Hz, 2H, Ar), 6.81– 6.76 (m, 3H, Ar), 3.82 (d, *J* = 16.1 Hz, 1H, CH$_2$α), 3.21 (d, *J* = 16.1 Hz, 1H, CH$_2$β), 2.33 (s, 3H, ArCH$_3$), 2.09 (s, 3H, ArCH$_3$), 1.88 (s, 3H, CH$_3$) 1.61 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 152.5, 146.1, 143.7, 142.2, 141.6, 138.2, 137.3, 136.1, 131.6, 130.7, 130.5 (x2), 129.8, 129.5, 128.9, 128.6 (x2), 128.5 (x2), 127.7, 126.9, 126.8, 126.5, 122.6, 116.1, 101.8, 93.1, 81.8, 63.5, 37.8, 28.6 (x3), 27.4, 21.0, 20.8 ppm. **HRMS(ESI-MS)** calculated for $C_{36}H_{38}NO_3^+$ [M+H$^+$] 532.2846, found 532.2840.

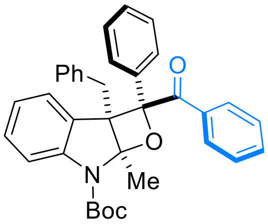
***tert*-butyl-2a-benzyl-2,2-bis(4-fluorophenyl)-7a-methyl-2a,7a-dihydrooxeto[*2,3*-*b*]indole-7(*2H*)-carboxylate (23).**



Synthesized following the described procedure, using 1 equivalent of **1d** (32.1 mg, 0.1 mmol) and 1 equivalent of 4,4'-difluorobenzophenone **2f** (21.8 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **23** (white foam), in 52% yield (28.1 mg, 0.052 mmol). *Yield in toluene: 30%.*

^{1}H-NMR (400 MHz, Acetone-d_6): δ 7.93 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar), 7.59 (d, *J* = 8.2 Hz, 1H, Ar), 7.53 (dd, *J* = 8.9, 5.4 Hz, 2H, Ar), 7.41 (d, *J* = 7.5 Hz, 1H, Ar), 7.23 (t, *J* = 8.9 Hz, 2H, Ar), 7.04–7.00 (m, 4H, Ar), 6.84–6.79 (m, 5H, Ar), 3.86 (d, *J* = 16.0 Hz, 1H, $CH_2\alpha$), 3.22 (d, *J* = 16.0 Hz, 1H, $CH_2\beta$), 1.89 (s, 3H, CH_3), 1.62 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d_6)**: δ 163.0 (d, *J* = 244.4 Hz), 160.9 (d, *J* = 244.4 Hz), 152.3, 146.1, 140.8 (d, *J* = 3.0 Hz), 140.0 (d, *J* = 3.0 Hz), 137.8, 133.5, 133.4, 131.2, 130.6 (x2),129.2, 129.1 (d, *J* = 8.0 Hz), 128.6 (d, *J* = 8.0 Hz), 128.5 (x2), 127.6, 126.9, 122.8, 116.3 (d, *J* = 22.1 Hz), 116.1, 115.8 (d, *J* = 21.5 Hz), 114.7 (d, *J* = 21.5 Hz), 102.1, 93.0, 82.1, 63.7, 37.5, 30.6, 28.6 (x3), 24.1 ppm. **^{19}F-NMR (376 MHz, Acetone-d_6)**: δ -117.51– -117.58 (m, 1F, C-F Ar), -118.43– -118.50 (m, 1F, C-F Ar) ppm. **HRMS(ESI-MS)** calculated for $C_{34}H_{32}F_2NO_3^+$ [M+H$^+$] 540.2345, found 540.2340.

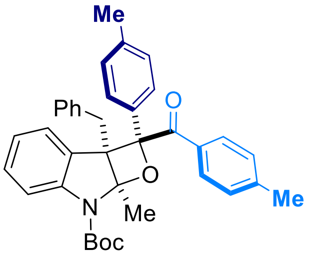
***tert*-butyl-2-benzoyl-2a-benzyl-7a-methyl-2-phenyl-2a,7a-dihydrooxeto*[2,3-b]*indole-7(*2H*)-carboxylate (24).**



Synthesized following the described procedure, using 1 equivalent of **1d** (32.1 mg, 0.1 mmol) and 1 equivalent of benzil **2g** (21.0 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 465 nm photoreactor described in **Section A.3.**. The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **24** (yellow foam), in >98% yield (52.0 mg, 0.099 mmol). *Yield in toluene: 85%.*

^{1}H-NMR (400 MHz, Acetone-d_6): δ 8.04 (d, *J* = 8.3 Hz, 2H, Ar), 7.65 (d, *J* = 7.9 Hz, 1H, Ar), 7.58—7.55 (m, 5H, Ar), 7.49—7.40 (m, 2H, Ar), 7.27 (t, *J* = 8.0 Hz, 2H, Ar), 7.21 (t, *J* = 8.1 Hz, 1H, Ar), 7.09 (t, *J* = 8.1 Hz, 1H, Ar), 7.02-7.00 (m, 3H, Ar), 6.79-6.76 (m, 2H, Ar), 3.54 (d, *J* = 15.7 Hz, 1H, $CH_2\alpha$), 2.93 (d, *J* = 15.7 Hz, 1H, $CH_2\beta$), 1.99 (s, 3H, CH_3), 1.49 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d_6)**: δ 200.8, 152.2, 145.3, 138.2, 137.1, 136.9, 133.2, 130.5 (x2), 129.8 (x2), 129.6, 129.5, 129.4 (x2), 129.3, 128.7 (x2), 128.5 (x2), 127.3 (x2), 127.0, 123.3, 116.2, 102.2, 97.1, 82.3, 64.4, 37.7, 28.4 (x3), 24.0 ppm. **HRMS(ESI-MS)** calculated for $C_{35}H_{34}NO_4^+$ [M+H$^+$] 532.6520, found 532.6514.

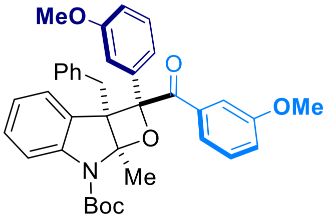
***tert*-butyl-2a-benzyl-7a-methyl-2-(4-methylbenzoyl)-2-(*p*-tolyl)-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (25).**



Synthesized following the described procedure, using 1 equivalent of **1d** (32.1 mg, 0.1 mmol) and 1 equivalent of 4,4'-dimethylbenzil **2h** (23.8 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 465 nm photoreactor described in **Section A.3.**. The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **25** (white foam), in >98% yield (54.8 mg, 0.098 mmol).

^{1}H NMR (400 MHz, Acetone-d$_6$): δ 7.88 (d, *J* = 8.0 Hz, 2H, Ar), 7.64 (d, *J* = 8.2 Hz, 1H, Ar), 7.54 (d, *J* = 8.0 Hz, 2H, Ar), 7.37 (d, *J* = 8.1 Hz, 2H, Ar), 7.21– 7.11 (m, 3H, Ar), 7.10 – 7.05 (m, 2H, Ar), 7.04 – 6.97 (m, 3H, Ar), 6.80 – 6.76 (m, 2H, Ar) 3.53 (d, *J* = 16.0 Hz, 1H, CH$_2$α), 2.96 (d, *J* = 16.0 Hz, 1H, CH$_2$β), 2.40 (s, 3H, CH$_3$), 2.27 (s, 3H, CH$_3$), 1.99 (s, 3H, CH$_3$), 1.52 (s, 9H, C(CH$_3$)$_3$) ppm.**^{13}C NMR (101 MHz, Acetone-d$_6$):** δ 199.0, 151.3, 144.4, 143.0, 138.0, 136.4, 134.4, 133.3, 129.6 (x2), 129.2 (x2), 129.1 (x2), 128.9, 128.5, 128.3 (x2), 127.8 (x2), 126.4 (x2), 126.0, 125.2, 122.3, 115.3, 101.1, 96.3, 81.3, 63.4, 36.9, 27.5 (x3), 23.1, 20.6, 20.2 ppm. **HRMS(ESI-MS)** calculated for $C_{37}H_{38}NO_4^+$ [M+H$^+$] 560.2795, found 560.2796.

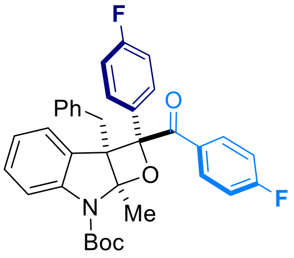
***tert*-butyl-2a-benzyl-2-(3-methoxybenzoyl)-2-(3-methoxyphenyl)-7a-methyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (26).**



Synthesized following the described procedure, using 1 equivalent of **1d** (32.1 mg, 0.1 mmol) and 1 equivalent of 3,3'-dimethoxylbenzil **2i** (27.0 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 465 nm photoreactor described in **Section A.3.**. The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **26** (white foam), in >98% yield (57.9 mg, 0.098 mmol).

^{1}H NMR (400 MHz, Acetone-d$_6$): δ 7.66 (d, *J* = 8.2 Hz, 1H, Ar), 7.58 (t, *J* = 6.8 Hz, 3H, Ar), 7.55 – 7.45 (m, 2H, Ar), 7.29 – 7.16 (m, 3H, Ar), 7.13 – 7.04 (m, 3H, Ar), 7.05 – 6.97 (m, 3H, Ar), 6.82 – 6.76 (m, 2H, Ar), 3.91 (s, 3H, OCH$_3$), 3.73 (s, 3H, OCH$_3$), 3.58 (d, *J* = 16.0 Hz, 1H, CH$_2$α), 2.99 (d, *J* = 16.0 Hz, 1H, CH$_2$β), 2.01 (s, 3H, CH$_3$), 1.50 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C NMR (101 MHz, Acetone-d$_6$):** δ 199.5, 160.0, 159.0, 151.2, 144.3, 138.8, 137.2, 136.2, 130.4, 129.6 (x3), 128.8, 128.7, 128.6, 127.7 (x2), 126.0, 122.4, 121.2, 118.6, 118.2, 115.3, 113.8, 113.4, 112.3, 101.2, 96.1, 81.3, 63.6, 54.7, 54.6, 36.7, 27.5 (x3), 23.0 ppm. **HRMS(ESI-MS)** calculated for $C_{37}H_{38}NO_6^+$ [M+H$^+$] 592.2694, found 592.2695.

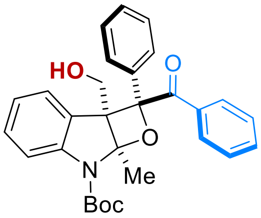
***tert*-butyl-2a-benzyl-2-(4-fluorobenzoyl)-2-(4-fluorophenyl)-7a-methyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (27).**



Synthesized following the described procedure, using 1 equivalent of **1d** (32.1 mg, 0.1 mmol) and 1 equivalent of 4,4'-difluorobenzil **2j** (24.6 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 465 nm photoreactor described in **Section A.3.**. The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **27** (white foam), in >98% yield (56.7 mg, 0.098 mmol).

^{1}H NMR (400 MHz, Acetone-d$_6$): δ 8.07 (dd, *J* = 7.9, 6.0 Hz, 2H, Ar), 7.67 (dd, *J* = 7.5, 5.9 Hz, 2H, Ar), 7.62 (d, *J* = 8.2 Hz, 1H, Ar), 7.52 (d, *J* = 7.6 Hz, 1H, Ar), 7.35 (t, *J* = 8.7 Hz, 2H, Ar), 7.19 (t, *J* = 7.8 Hz, 1H, Ar), 7.12 – 6.98 (m, 6H, Ar), 6.79 (d, *J* = 4.7 Hz, 2H, Ar), 3.55 (d, *J* = 16.0 Hz, 1H, CH$_2$$\alpha$), 2.97 (d, *J* = 16.0 Hz, 1H, CH$_2$β), 2.00 (s, 3H, CH$_3$), 1.52 (s, 9H, C(CH$_3$)$_3$) ppm.**^{13}C NMR (101 MHz, Acetone-d$_6$):** δ 198.6, 165.1 (d, *J* = 220.Hz), 162.7 (d, *J* = 220.Hz), 151.1, 144.3, 136.0, 133.1 (d, *J* = 2.9 Hz), 132.4 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 9.4 Hz, x2), 129.6 (x2), 129.2, 128.6 (d, *J* = 8.3 Hz, x2), 128.5 (d, *J* = 21.9 Hz, x2), 127.8 (x2), 126.1, 122.5, 115.3 (d, *J* = 21.0 Hz, x2), 115.2, 114.6 (d, *J* = 21.9 Hz, x2), 101.5, 95.8, 81.5, 63.5, 36.5, 27.5 (x3), 23.0 ppm. **^{19}F-NMR (376 MHz, Acetone-d$_6$)**: δ -107.85– -107.91 (m, 1F, C-F Ar), -115.89 – -115.95 (m, 1F, C-F Ar) ppm. **HRMS(ESI-MS)** calculated for $C_{35}H_{32}NO_4^+$ [M+H$^+$] 568.2294, found 568.2297.

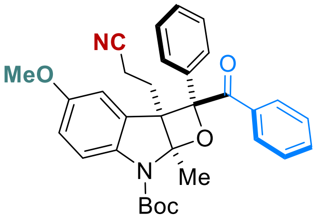
***tert*-butyl-2-benzoyl-2a-(hydroxymethyl)-7a-methyl-2-phenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (28).**



Synthesized following the described procedure, using 1 equivalent of **1j** (26.3 mg, 0.1 mmol) and 1 equivalent of benzil **2g** (21.0 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 465 nm photoreactor described in **Section A.3.**. The crude product was subjected to flash column chromatography on silica gel (8:2 Hexane/EtOAc) yielding pure **28** (white foam), in 85% yield (40.2 mg, 0.085 mmol).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.88 (d, *J* = 7.9 Hz, 2H, Ar), 7.63 (d, *J* = 7.9 Hz, 1H, Ar), 7.59 (d, *J* = 7.9 Hz, 2H, Ar), 7.52–7.47 (m, 3H, Ar), 7.40 (q, *J* = 7.2 Hz, 2H, Ar), 7.26 (t, *J* = 7.9 Hz, 2H, Ar), 7.18 (t, *J* = 7.9 Hz, 1H, Ar), 7.07 (t, *J* = 7.9 Hz, 1H, Ar), 4.08 (dd, *J* = 11.3, 3.6 Hz, 1H, CH$_2$$\alpha$), 3.70 – 3.59 (m, 2H, CH$_2$β and OH overlapped), 2.10 (s, 3H, CH$_3$), 1.48 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 199.8, 152.0, 145.6, 137.8, 136.7, 133.2, 129.9 (x2), 129.3 (x2), 129.2, 129.1, 128.5 (x2), 128.5, 126.5 (x2), 123.2, 115.7, 102.1, 95.1, 81.9, 64.1, 61.1, 41.8, 28.4 (x3), 21.9 ppm. **HRMS(ESI-MS)** calculated for $C_{29}H_{30}NO_5^+$ [M+H$^+$] 472.2118, found 472.2119.

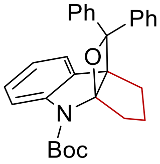
tert-butyl-2a-(2-cyanoethyl)-4-methoxy-7a-methyl-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (29).



Synthesized following the described procedure, using 1 equivalent of **1s** (31.4 mg, 0.1 mmol) and 1 equivalent of benzil **2g** (21.0 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 465 nm photoreactor described in **Section A.3.**. The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **29** (white foam), in 79% yield (41.4 mg, 0.079 mmol).

^{1}H-NMR (500 MHz, Acetone-d$_6$): δ 7.91 (d, *J* = 7.5 Hz, 2H, Ar), 7.60 — 7.57 (m, 3H, Ar), 7.53 (t, *J* = 7.5 Hz, 2H, Ar), 7.44 — 7.41 (m, 2H, Ar), 7.27 (t, *J* = 7.5 Hz, 2H, Ar), 7.19 (d, *J* = 2.7 Hz, 1H, Ar), 6.81 (dd, *J* = 9.1, 2.7 Hz, 1H, Ar), 3.87 (s, 3H, OCH_3), 2.47 (ddd, *J* = 16.8, 11.2, 5.8 Hz, 1H, CH_2), 2.11 (s, 3H, CH_3), 2.13-2.07 (m, 2H, CH_2) 1.88 (ddd, *J* = 15.7, 10.1, 5.8 Hz, 1H, CH_2), 1.48 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (125 MHz, Acetone-d$_6$)**: δ 200.0, 156.9, 152.0, 138.7, 137.6, 136.6, 133.4, 129.9 (x2), 129.5 (x2), 129.4, 129.2, 128.6 (x2), 126.9 (x2), 120.0, 117.0, 115.8, 113.9, 102.0, 95.9, 82.0, 63.7, 56.1, 28.4, 27.8 (x3), 22.2, 13.2 ppm. **HRMS(ESI-MS)** calculated for $C_{32}H_{33}N_2O_5^+$ [M+H$^+$] 525.2384, found 525.2389.

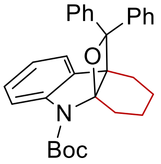
tert-butyl-9,9-diphenyl-2,3-dihydro-*1H,4H*-3a,8b-(epoxymethano)cyclopenta[*b*]indole-4-carboxylate (30).



Synthesized following the described procedure, using 1 equivalent of **1t** (25.7 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **30** (white foam), in 65% yield (28.6 mg, 0.065 mmol). *Yield in toluene: 50%.*

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.72 (d, *J* = 7.9 Hz, 2H, Ar), 7.48 (d, *J* = 7.9 Hz, 2H, Ar), 7.42 – 7.38 (m, 3H, Ar), 7.26 (t, *J* = 7.5 Hz, 1H, Ar), 7.02 – 6.92 (m, 4H, Ar), 6.89 – 6.81 (m, 2H, Ar), 2.70 – 2.61 (m, 2H, CH_2), 1.90–1.74 (m, 3H, CH_2), 1.64 (s, 9H, $C(CH_3)_3$), 1.58 – 1.46 (m, 1H, CH_2) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 152.0, 145.2, 144.4, 132.8, 129.2, 128.7 (x3), 128.6, 128.0 (x2), 127.5, 127.3, 126.9, 126.7, 126.2 (x2), 125.9 (x2), 123.2, 115.1, 91.4, 55.0, 34.1, 28.6 (x3), 28.3, 28.2 ppm. **HRMS(ESI-MS)** calculated for $C_{29}H_{30}NO_3^+$ [M+H$^+$] 440.2220, found 440.2222.

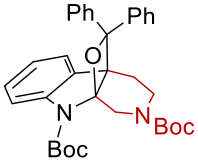
tert-butyl-11,11-diphenyl-5,6,7,8-tetrahydro-_9H_-8a,4b-(epoxymethano)carbazole-9-carboxylate (31).



Synthesized following the described procedure, using 1 equivalent of **1u** (27.1 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (95:5 Hexane/EtOAc) yielding pure **31** (white foam), in 69% yield (31.3 mg, 0.069 mmol). *Yield in acetone: 59%.*

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.64 (d, *J* = 7.9 Hz, 2H, Ar), 7.44 – 7.37 (m, 6H, Ar), 7.23 (t, *J* = 7.3 Hz, 1H, Ar), 6.97 (q, *J* = 7.3 Hz, 3H, Ar), 6.89 (q, *J* = 7.3 Hz, 2H, Ar), 2.57 – 2.51 (m, 1H, CH$_2$), 2.25 – 2.21 (m, 1H, CH$_2$), 2.18 – 2.00 (m, 2H, CH$_2$), 1.64 (s, 9H, C(CH$_3$)$_3$), 1.52 – 1.44 (m, 4H) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 152.0, 145.3, 145.1, 131.8, 129.1, 129.0 (x2), 127.7 (x2), 127.5, 126.7, 126.3 (x2), 126.0 (x2), 125.6, 122.8, 115.0, 101.3, 94.4, 81.4, 58.9, 28.7 (x3), 28.0, 19.9, 19.7 ppm. **HRMS(ESI-MS)** calculated for $C_{30}H_{32}NO_3^+$ [M+H$^+$] 454.2377, found 454.2375.

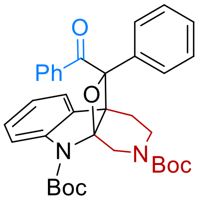
di-_tert_-butyl-11,11-diphenyl-3,4-dihydro-_9H_-9a,4a-(epoxymethano)pyrido[_3,4-b_]indole-2,9(_1H_)-dicarboxylate (32).



Synthesized following the described procedure, using 1 equivalent of **1v** (37.2 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of toluene. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (8:2 Hexane/EtOAc) yielding pure **32** (white foam), in 82% yield (45.5 mg, 0.082 mmol). *Yield in acetone: 68%.*

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ 7.69 (t, *J* = 7.1 Hz, 2H, Ar), 7.49 – 7.37 (m, 6H, Ar), 7.27 (q, *J* = 7.1 Hz, 1H, Ar), 7.03 – 6.98 (m, 3H, Ar), 6.93 – 6.86 (m, 2H, Ar), 4.44 (d, *J* = 14.1 Hz, 1H, CH$_2$α), 3.95 (d, *J* = 14.1 Hz, 1H CH$_2$β), 3.34 – 3.24 (m, 1H, CH$_2$), 2.78 – 2.70 (m, 1H, CH$_2$), 2.46 – 2.30 (m, 2H, CH$_2$), 1.68 (s, 9H, C(CH$_3$)$_3$), 1.43 (s, 4H, C(CH$_3$)$_3$), 1.28 (s, 5H, C(CH$_3$)$_3$) ppm. **^{13}C-NMR (101 MHz, Acetone-d$_6$)**: δ 155.7, 155.0, 151.7, 151.7, 144.6, 144.4, 129.4, 129.3, 129.1 (x2), 128.0, 127.9, 127.8, 127.8, 127.1 (x2), 126.2 (x2), 125.8 (x2), 123.2, 123.1, 115.2, 94.9, 82.0, 79.7, 79.6, 41.8, 40.7, 40.2, 28.7 (x3), 28.6 (x3), 28.6 (x3), 28.5 (x3), 27.3, 26.8, 24.4, 21.3, 17.8 ppm. **HRMS(ESI-MS)** calculated for $C_{34}H_{39}N_2O_5^+$ [M+H$^+$] 555.2853, found 555.2859.

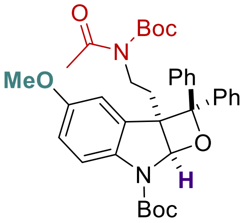
di-*tert*-butyl-11-benzoyl-11-phenyl-3,4-dihydro-9H-9a,4a-(epoxymethano)pyrido[*3,4-b*]indole-2,9(*1H*)-dicarboxylate (33).



Synthesized following the described procedure, using 1 equivalent of **1v** (37.2 mg, 0.1 mmol) and 1 equivalent of benzil **2g** (21.0 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 465 nm photoreactor described in **Section A.3.**. The crude product was subjected to flash column chromatography on silica gel (8:2 Hexane/EtOAc) yielding pure **33** (white foam), in 67% yield (39.0 mg, 0.067 mmol). *Yield in toluene: 67%.*

^{1}H NMR (400 MHz, Acetone-d$_6$): δ 7.84 (d, *J* = 7.7 Hz, 2H, Ar), 7.60 (t, *J* = 8.7 Hz, 2H, Ar), 7.52 (t, *J* = 7.2 Hz, 2H, Ar), 7.49 – 7.41 (m, 4H, Ar), 7.31 (t, *J* = 7.5 Hz, 2H, Ar), 7.24 (t, *J* = 7.8 Hz, 1H, Ar), 7.13 (t, *J* = 7.4 Hz, 1H, Ar), 4.25 (dd, *J* = 37.5, 14.3 Hz, 2H, CH$_2$), 3.20 (*br*, 1H, CH$_2$), 2.72 (m, 1H, CH$_2$), 2.19 – 2.10 (m, 2H, CH$_2$), 1.50 (s, 5H, C(CH$_3$)$_3$), 1.47 (s, 9H, C(CH$_3$)$_3$), 1.33 (s, 4H, C(CH$_3$)$_3$) ppm.**^{13}C NMR (101 MHz, Acetone-d$_6$):** δ 199.2, 137.2, 136.0, 132.3, 129.6, 128.9 (x2), 128.8 (x2), 128.7, 128.2, 128.1, 127.7 (x2), 126.7, 125.5 (x2), 123.0, 114.5, 97.6, 45.5, 39.5, 38.9, 27.7 (x3), 27.5 (x3), 26.1, 25.7, 23.5, 16.9, ppm. **HRMS(ESI-MS)** calculated for $C_{35}H_{39}N_2O_6^+$ [M+H$^+$] 583.2803, found 583.2800.

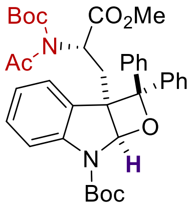
***tert*-butyl-2a-(2-(*N*-(*tert*-butoxycarbonyl)acetamido)ethyl)-4-methoxy-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (34).**



Synthesized following the described procedure, using 1 equivalent of **1w** (43.2 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 405 nm photoreactor described in **Section A.2.** The crude product was subjected to flash column chromatography on silica gel (8:2 Hexane/EtOAc) yielding pure **34** (white foam), in 42% yield (25.8 mg, 0.042 mmol). *Yield in toluene: 26%. The product was accompanied by the corresponding deacetylated by-product.*

^{1}H NMR (400 MHz, Acetone-d$_6$): δ 7.85 (d, *J* = 7.8 Hz, 2H, Ar), 7.56 (d, *J* = 7.7 Hz, 3H, Ar), 7.44 (t, *J* = 7.7 Hz, 2H, Ar), 7.30 (t, *J* = 7.3 Hz, 1H, Ar), 7.16 (t, *J* = 10.0 Hz, 2H, Ar), 7.07 (d, *J* = 2.5 Hz, 1H, Ar), 7.03 (t, *J* = 7.3 Hz, 1H, Ar), 6.66 (dd, *J* = 8.8, 2.5 Hz, 1H, Ar), 6.54 (br, 1H, CH), 3.73 (s, 3H, OCH$_3$), 3.32 (ddd, *J* = 13.3, 10.7, 5.9 Hz, 1H, CH$_2$), 3.19 – 3.12 (m, 1H, CH$_2$), 2.50 – 2.38 (m, 1H, CH$_2$), 2.27 (s, 3H, COCH$_3$), 1.96 – 1.90 (m, 1H, CH$_2$), 1.63 (s, 9H, C(CH$_3$)$_3$), 1.46 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C NMR (101 MHz, Acetone-d$_6$):** δ 171.6, 155.7, 152.6, 143.3, 128.2 (x4), 127.2 (x4), 127.2, 126.4, 125.9 (x2), 125.5 (x2), 114.1, 112.5, 94.1, 92.5, 82.5, 55.1, 40.9, 39.9, 31.7, 27.6 (x3), 27.2 (x3), 25.9, 23.5, 20.5 ppm. **HRMS(ESI-MS)** calculated for $C_{36}H_{43}N_2O_7^+$ [M+H$^+$] 615.3065, found 615.3066.

tert-butyl-2a-(2-(*N*-(*tert*-butoxycarbonyl)acetamido)-3-methoxy-3-oxopropyl)-2,2-diphenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (35).

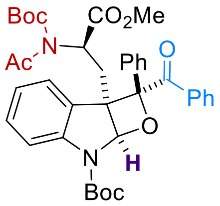


Synthesized following the described procedure, using 1 equivalent of **1x** (46.1 mg, 0.1 mmol) and 1 equivalent of benzophenone **2a** (18.2 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 465 nm photoreactor described in **Section A.2**. The crude product was subjected to flash column chromatography on silica gel (8:2 Hexane/EtOAc) yielding pure **35** (white foam), in 73% yield (46.9 mg, 0.073 mmol). *The product was accompanied by the corresponding deacetylated by-product.*

Mixture of diastereoisomers.

^{1}H NMR (400 MHz, Acetone-d$_6$): δ 7.84 (d, *J* = 7.8 Hz, 2H, Ar), 7.49 – 7.44 (m, 5H, Ar), 7.37 – 7.25 (m, 2H, Ar), 7.14 – 6.95 (m, 4H, Ar), 6.81 (t, *J* = 7.5 Hz, 1H, Ar), 6.73 (*br*, 1H, CH), 5.28 (t, *J* = 6.4 Hz, 1H, CH), 3.56 (s, 3H, COOCH$_3$), 2.86 – 2.72 (m, 2H, CH$_2$), 1.92 (s, 3H, COCH$_3$), 1.65 (s, 9H, C(CH$_3$)$_3$), 1.40 (s, 9H, C(CH$_3$)$_3$) ppm. **^{13}C NMR (101 MHz, Acetone-d$_6$):** δ 171.3, 170.4, 151.4, 143.3, 143.2, 128.1 (x4), 128.1, 127.2, 127.1, 127.0 (x4), 126.2, 126.1 (x2), 125.6 (x2), 124.2, 122.0, 95.0, 92.3, 83.5, 52.0, 51.5, 32.6, 27.6, 27.0, 25.5 ppm. **HRMS(ESI-MS)** calculated for $C_{32}H_{33}N_2O_5^+$ [M+H$^+$] 643.3014, found 643.3016. $[\alpha]_D^{20}$ = -0.043 (c=0.62, MeOH).

tert-butyl-2-benzoyl-2a-(-2-(*N*-(*tert*-butoxycarbonyl)acetamido)-3-methoxy-3-oxopropyl)-2-phenyl-2a,7a-dihydrooxeto[*2,3-b*]indole-7(*2H*)-carboxylate (36).



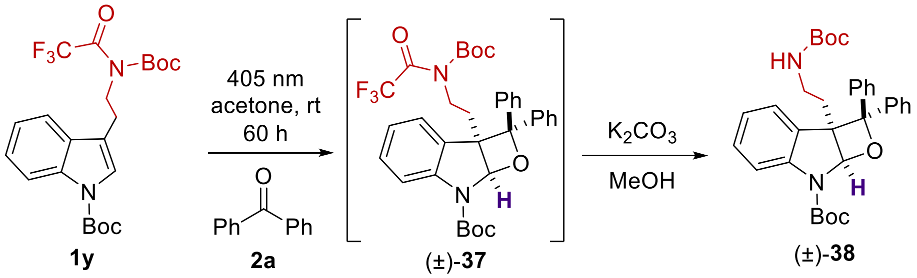
Synthesized following the described procedure, using 1 equivalent of **1x** (46.1 mg, 0.1 mmol) and 1 equivalent of benzil **2g** (21.0 mg, 0.1 mmol) in 1 mL of acetone. Irradiated for 16 h using the 465 nm photoreactor described in **Section A.3**. The crude product was subjected to flash column chromatography on silica gel (9:1 Hexane/EtOAc) yielding pure **36** (white foam), in 79% yield (53.0 mg, 0.079 mmol). *The product was accompanied by the corresponding deacetylated by-product.*

Mixture of diastereoisomers.

^{1}H NMR (400 MHz, Acetone-d$_6$): δ 7.94 (t, *J* = 7.0 Hz, 2H, Ar), 7.66 – 7.53 (m, 5H, Ar), 7.52 – 7.37 (m, 2H, Ar), 7.33 – 7.22 (m, 3H, Ar), 7.20 – 7.08 (m, 1H, Ar), 6.84 (s, 1H, CH), 5.16 (t, *J* = 6.8 Hz, 1H, CH), 3.53 (s, 3H, COOCH$_3$), 2.44 (qd, *J* = 15.1, 6.9 Hz, 2H, CH$_2$), 2.03 (s, 3H, COCH$_3$), 1.61 (s, 9H, C(CH$_3$)$_3$), 1.39 (s, 9H, C(CH$_3$)$_3$) ppm.**^{13}C NMR (101 MHz, Acetone-d$_6$):** δ 198.5, 171.2, 151.4, 137.5, 135.2, 133.0, 132.8, 129.3, 129.2, 129.1 (X2), 129.0, 128.8, 128.6, 128.0, 127.9 (x2), 125.9 (x2), 125.7, 122.8, 98.1, 92.5, 83.7, 83.5, 51.8, 51.6, 51.5, 33.0, 27.6 (x3), 27.1 (x3), 30.0, 25.5, 16.9 ppm. **HRMS(ESI-MS)** calculated for $C_{38}H_{43}N_2O_9$ [M+H$^+$] 671.2963, found 671.2970. $[\alpha]_D^{20}$ = -0.017 (c=0.38, MeOH).

E. PRODUCT MANIPULATIONS

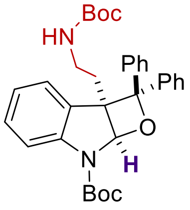
E.1. TRYPTAMINE DEPROTECTION



i) Following the procedure described in *Section F*, **1y** (45.6 mg, 0.1 mmol, 1.0 equiv.) and benzophenone **2a** (18.2 mg, 0.1 mmol, 1.0 equiv.) were dissolved in 1 mL of acetone (0.1M) and irradiated for 60 h at 405 nm.

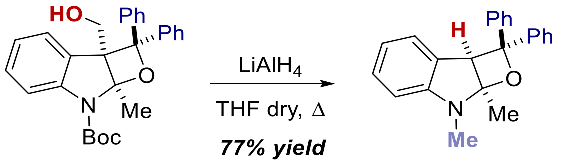
ii) The crude product solution of the Paternò-Büchi reaction was evaporated under reduced pressure and dissolved in 1mL of MeOH (0.1 M). Then K_2CO_3 (41.5 mg, 0.3 mmol, 1.5 equiv.) were added. After full consumption of the starting materials the reaction was quenched with 5 mL of a saturated NH_4Cl solution and extracted with 3x10 mL of EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (9:1 hexane:EtOAc) furnishing **38** as a white solid (25.0 mg, 46% yield).

di-*tert*-butyl 3a-(hydroxydiphenylmethyl)-2,3,3a,8a-tetrahydropyrrolo[*2,3-b*]indole-1,8-dicarboxylate (38)



^{1}H-NMR (500 MHz, Acetone-d$_6$): δ 7.83 (d, *J* = 8.0 Hz, 2H, Ar), 7.50—7.49 (m, 2H, Ar), 7.44 (t, *J* = 7.8 Hz, 2H, Ar), 7.38 (d, *J* = 8.1 Hz, 1H, Ar), 7.31 (t, *J* = 7.8 Hz, 2H, Ar), 7.13 – 7.07 (m, 4H, Ar), 7.00 (t, *J* = 7.9 Hz, 2H, Ar), 6.87 (t, *J* = 7.8 Hz, 1H, Ar), 6.55 (br, 1H, CH), 5.75 (br, 1H, NH), 2.72 – 2.64 (m, 2H, CH_2), 2.41 – 2.35 (m, 1H), 2.06 – 2.01 (m, 1H overlapped with acetone, 1.64 (s, 9H, $C(CH_3)_3$), 1.41 (s, 9H, $C(CH_3)_3$) ppm. **^{13}C-NMR (125 MHz, Acetone-d$_6$)**: δ 143.5, 143.4, 138.1, 128.1 (x2), 128.3 (x4), 127.2 (x4), 127.1 (x2), 126.7, 126.3, 126.0 (x2), 125.5 (x2), 122.3, 114.9, 94.3, 92.7, 40.9, 36.7, 33.2, 27.7 (x3), 27.6 (x3) ppm. **HRMS(ESI-MS)** calculated for $C_{33}H_{39}N_2O_5^+$ [M+H$^+$] 543.2853, found 543.2849.

E.2. LiAlH$_4$ REDUCTION OF 10

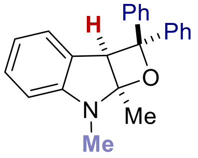


(±)-**10**
>20:1 dr

(±)-**39**
>20:1 dr

10 (100 mg, 0.225 mmol, 1 equiv.) was dissolved in 10 mL of anhydrous THF (0.025 M). Subsequently, a 1M solution of LiAlH$_4$ in THF (1.13 mL, 1.125 mmol, 5 equiv.) was added dropwise, the mixture was stirred at reflux for 4 h. Then, the reaction was quenched with 10 mL of EtOAc at 0°C, 10 mL of a saturated Rochelle salt solution was added, and the mixture was stirred for 30 min. The organic layer was washed with 2x10 mL of Rochelle salt saturated solution and 1x10 mL of a saturated NH$_4$Cl solution. The organic layer was dried over MgSO$_4$, filtered and concentrated under reduced pressure, giving **39** as a white solid in 77% yield (56.7 mg, 0.174 mmol).

7,7a-dimethyl-2,2-diphenyl-2,2a,7,7a-tetrahydrooxeto[*2,3-b*]indole (39).



^{1}**H-NMR (300 MHz, CDCl$_3$):** δ 7.56 (br, 1H, Ar), 7.39—7.36 (m, 1H, Ar), 7.29—7.26 (m, 2H, Ar), 7.23—7.11 (m, 8H, Ar), 7.04—6.90 (m, 2H, Ar), 5.71 (s, 1H, CH), 2.23 (s, 3H, NCH$_3$), 2.12 (s, 3H, CH$_3$) ppm. ^{13}**C-NMR (125 MHz, Acetone-d$_6$)**: δ 145.6 (x2), 135.8, 131.0, 129.6, 128.1 (x4), 126.8 (x2), 126.5 (x4), 120.2, 118.2, 117.4, 110.1, 105.7, 75.3, 10.5, 7.7 ppm. **HRMS(ESI-MS)** calculated for $C_{23}H_{22}NO^+$ [M+H$^+$] 328.1696, found 328.1672.

F. MECHANISTIC INSIGHTS

F.1. ΔG_{PET} CALCULATIONS

Using the Gibbs energy of PET equation:

$$\Delta G = E^{ox}(D) - E^{red}(A) - \Delta E_{exc} + \Delta E_{coul}$$

ΔG of PET processes between *N*-Boc protected indole **1d** and benzophenone **2a** or benzil **2g** has been calculated. E^{ox}(D) is the oxidation potential of the donor **1d**, and has been calculated through cyclic voltammetries reported in figure S6. E^{ox}(**1d**) = 1.40 eV. E^{red}(A) is the reduction potential of the acceptors **2a** and **2g** and has been calculated through cyclic voltammetry reported in figures S7 and S8. E^{red}(**2a**) = -2.20 eV, E^{red}(**2g**) **= -**1.10 eV. ΔE_{exc} is the excitation energy of the acceptor, reported in literature as 2.20 eV.[11] or calculated by onset emission of **2g** as 2.82 eV. ΔE_{coul} is a term that takes into account the ability of the solvent to separate the radical-ion pair, its value is reported as 0.05 eV for MeCN.[12]

ΔG_{ET} (**2a**) = 1.35 eV

ΔG_{ET} (**2g**) = -0.27 eV

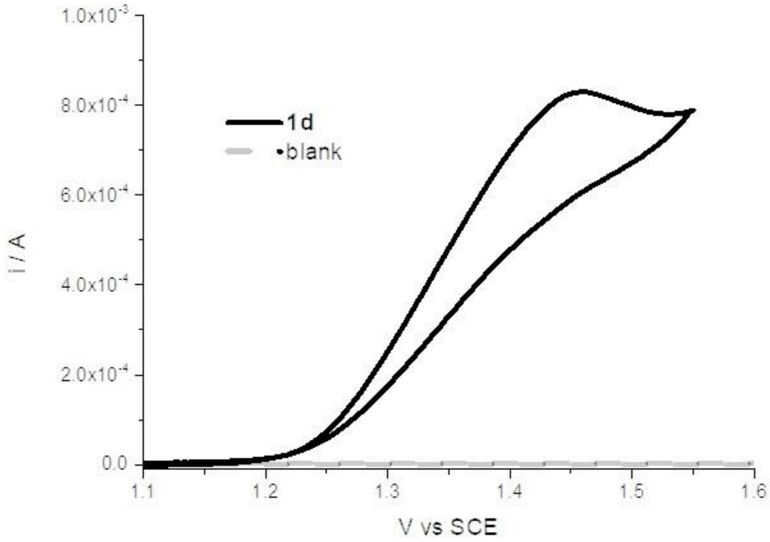


Figure S8. Anodic CV of *N*-Boc protected indole **1d** in 0.1 MTBAPF$_6$ MeCN solution. GC electrode. Scan rate: 100 mV/s, potential referred to SCE at room temperature using a platinum wire as counter electrode.

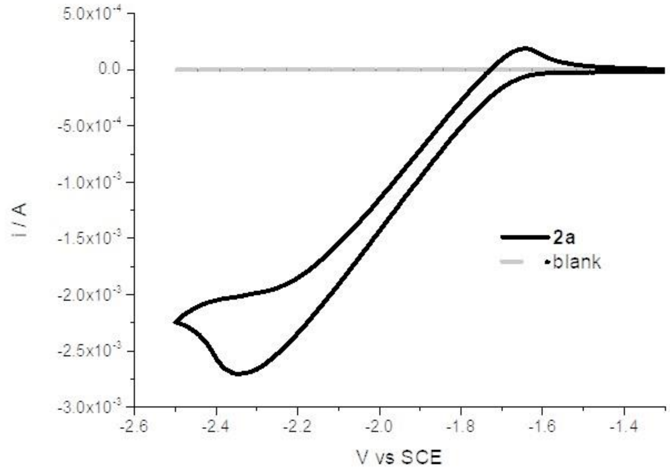


Figure S9. Cathodic CV of benzophenone (**2a**) in 0.1 M TBAPF$_6$ MeCN solution. GC electrode. Scan rate: 100 mV/s, potential referred to SCE at room temperature using a platinum wire as counter electrode.

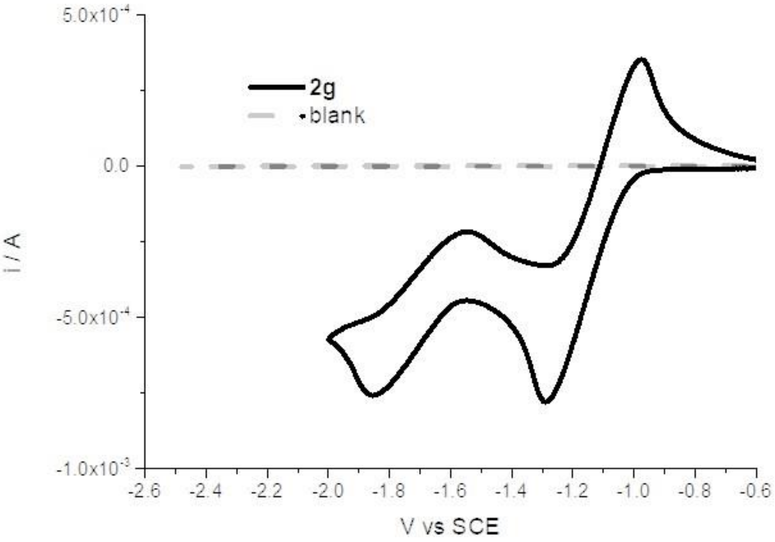


Figure S10. Cathodic CV of benzil (**2g**) in 0.1 M TBAPF$_6$ MeCN solution. GC electrode. Scan rate: 100 mV/s, potential referred to SCE at room temperature using a platinum wire as counter electrode.

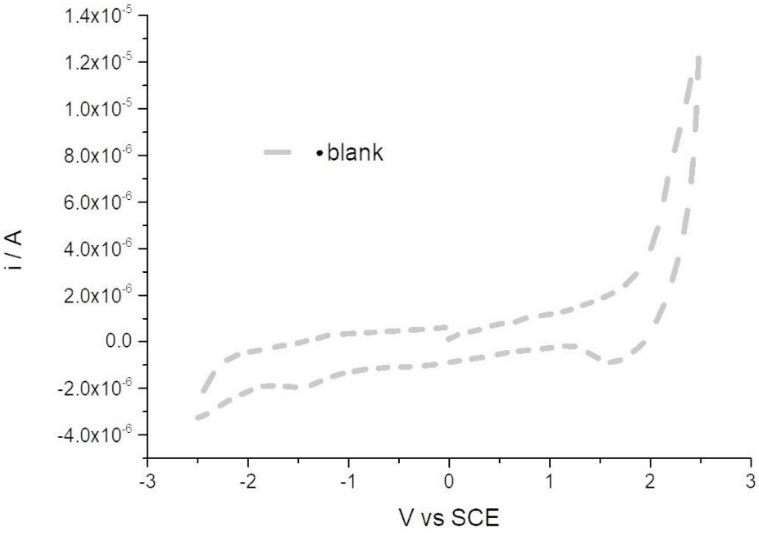


Figure S11. Blank Cathodic CV 0.1 M TBAPF$_6$ MeCN solution. GC electrode. Scan rate: 100 mV/s, potential referred to SCE at room temperature using a platinum wire as counter electrode.

F.2. PHOTOPHYSICAL STUDIES

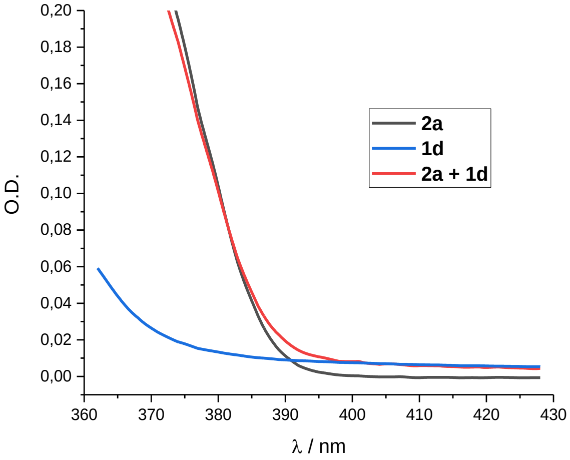


Figure S12. Absorption spectra of **2a** (black line), **1d** (blue line) and **2a + 1d** (red line) 0.01 M in MeCN, 298 K.

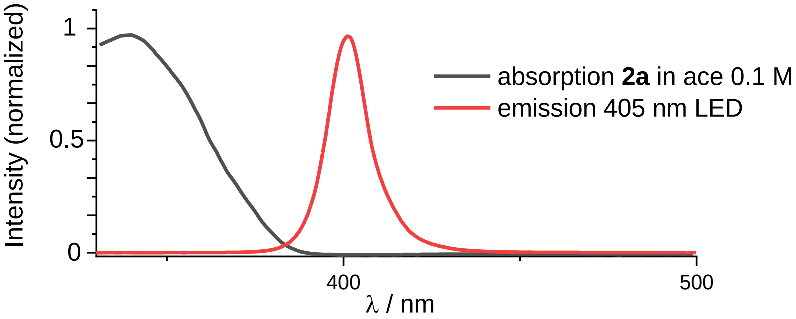


Figure S13. Absorption spectra of **2a** (black line) 0.1 M in acetone and emission of the 405 nm lamp used in this work and described in Section A.1.

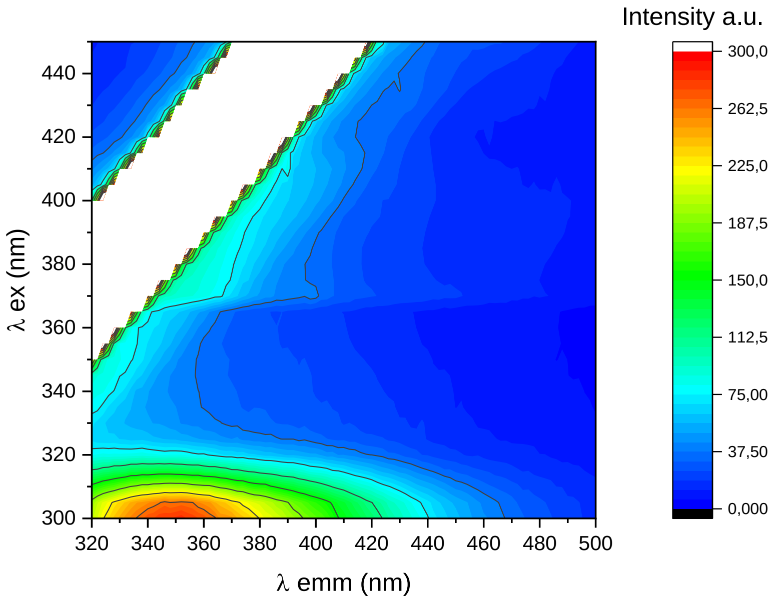


Figure S14. Fluorescence 3D matrixes of **2a** 0.01 M in Ace, 298 K.

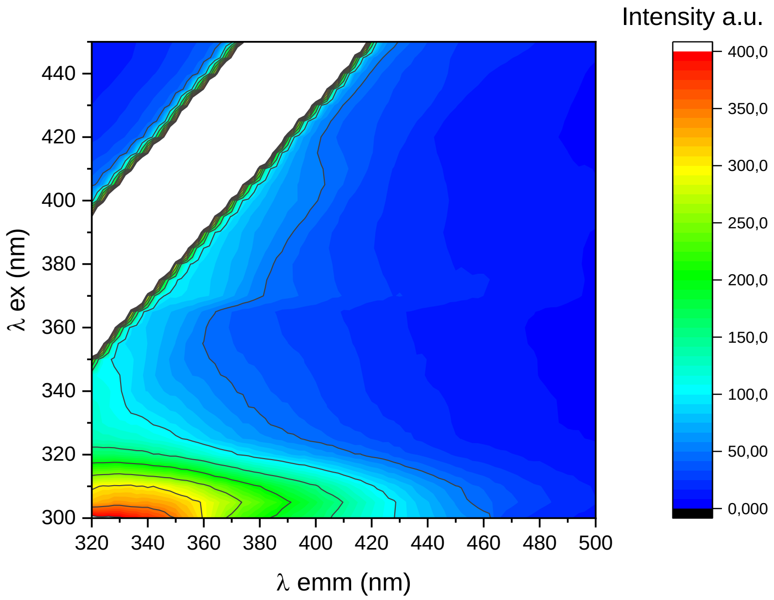


Figure S15. Fluorescence 3D matrixes of **2a** + **1d** 0.01 M in MeCN, 298 K.

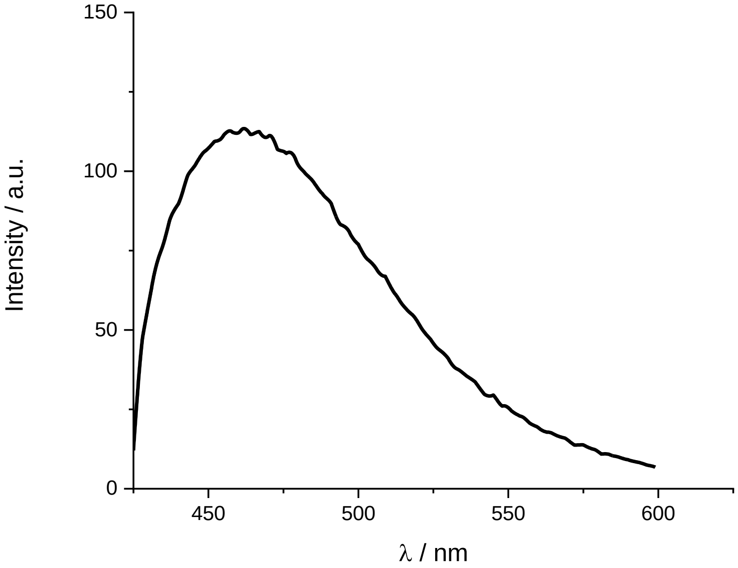


Figure S16. Emission spectrum of **2a** + **1d** 0.01 M in MeCN (λ_{ex}=405 nm).

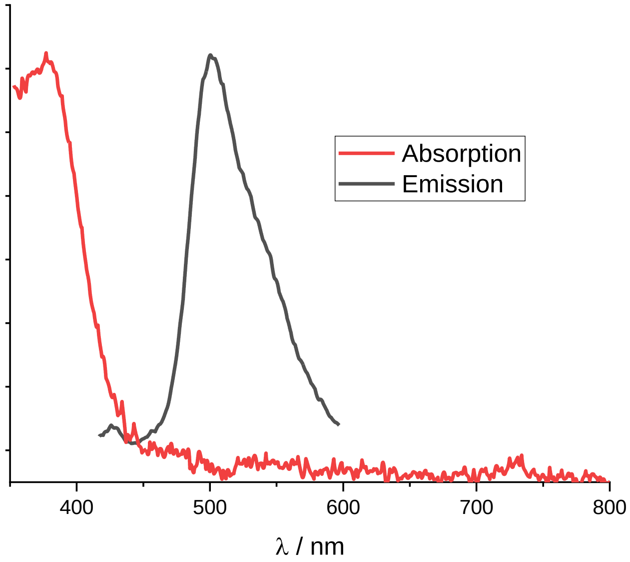
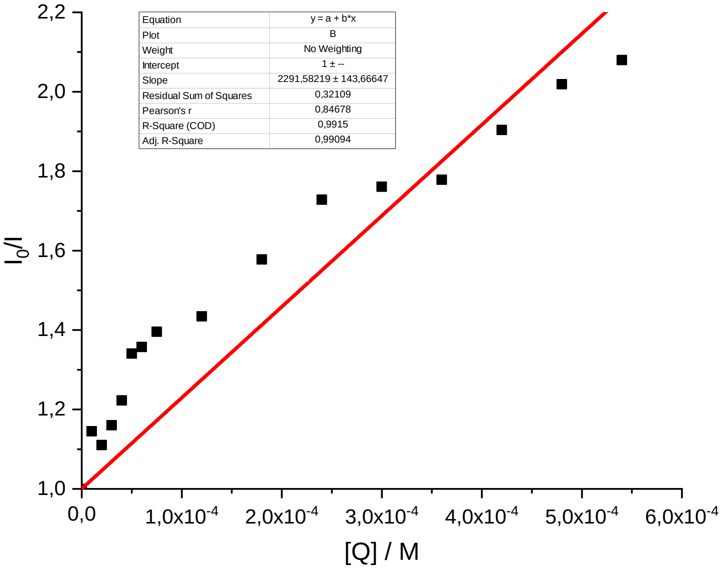


Figure S17. Absorption/emission spectra of **2g** 0.01 M in MeCN. (λ_{ex}=380 nm).



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	1 ± --
Slope	2291,58219 ± 143,66647
Residual Sum of Squares	0,32109
Pearson's r	0,84678
R-Square (COD)	0,9915
Adj. R-Square	0,99094

Figure S18. Stern-Volmer of **2a** in presence of **1d** in MeCN. (λ_{ex}=365 nm).

F.3. GRIESBECK MODELS FOR BENZOPHENONE 2A

In order to predict the high regioselectivity of the reaction, we applied the Griesbeck-type models, generally used for triplet 1,4-biradicals.[13]

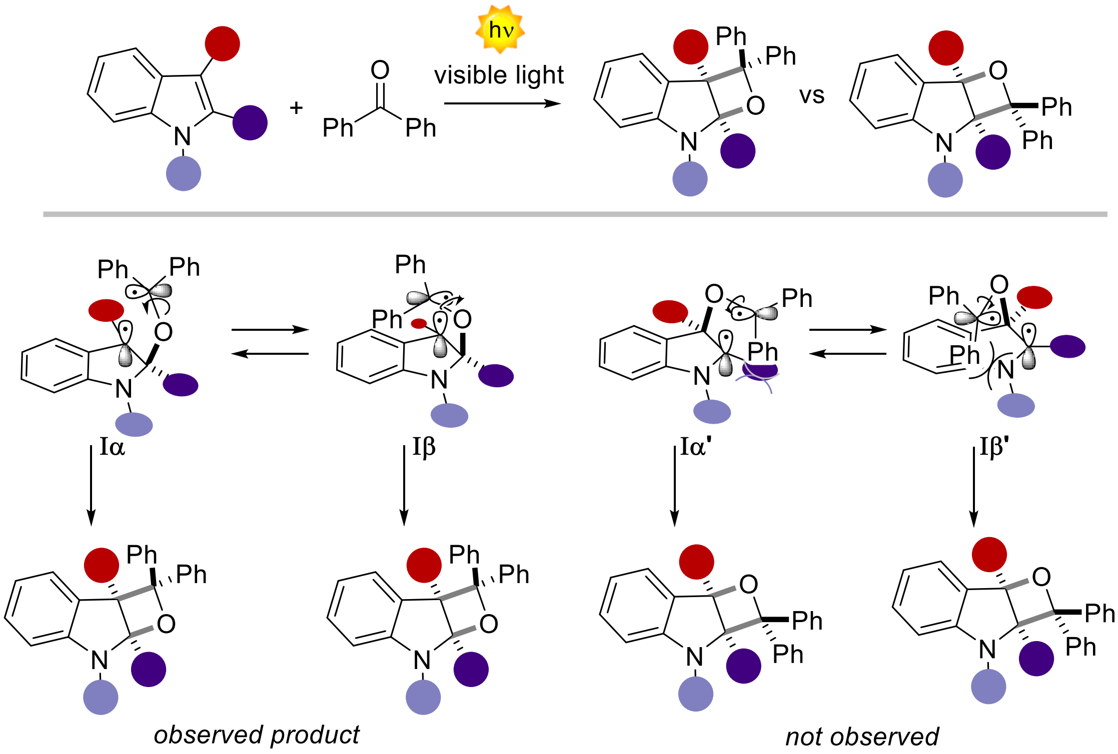


Figure S19. Proposed Griesbeck models for the photochemical addition of **2a** to an indole moiety were Iα corresponds to the most favorable 1,4-biradical for the ring closure.

F.4. GRIESBECK MODELS AND POSSIBLE REACTION MECHANISMS FOR BENZIL 2G

The ΔG = 0.15 eV value found for the reaction between indole ***1d*** *and benzil* ***2g****, led to the result that photoelectron transfer (PET) is thermodynamically feasible. In order to clarify the possible mechanisms, we depicted the different reaction pathways in figure S18.*[14]

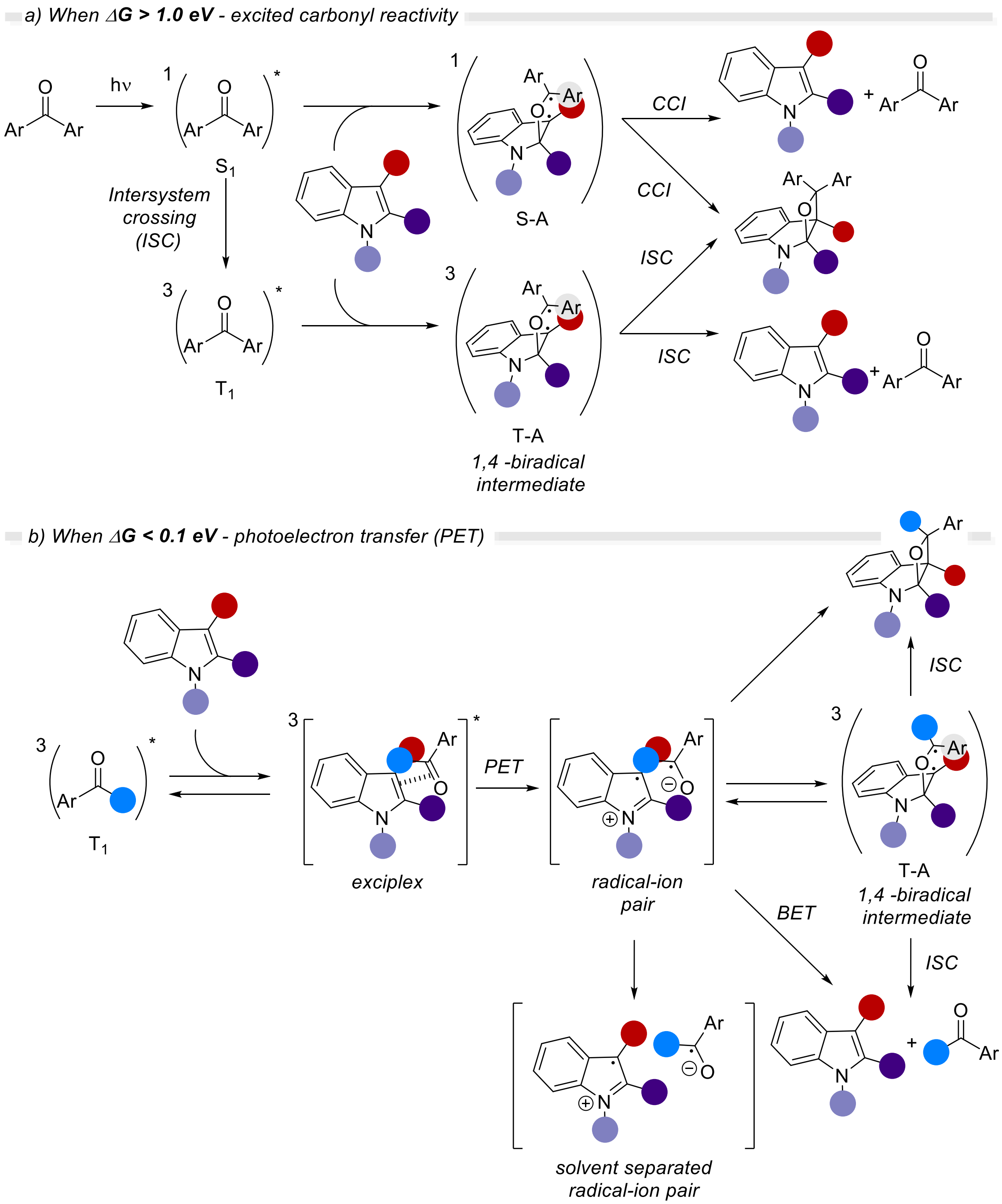
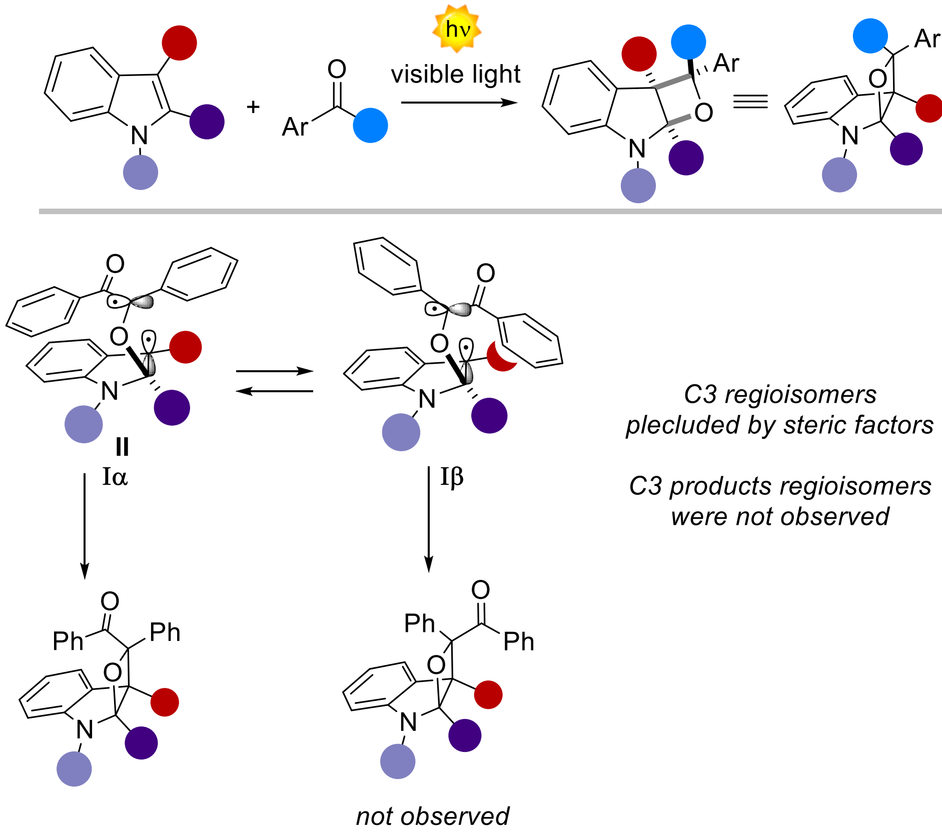


Figure S20. Possible reaction pathways depending on the ΔG of the Paaternò-Büchi reaction.

In order to predict the high stereo- and regio-selectivity of the reaction, we applied the Griesbeck models, generally used for triplet 1,4-biradicals.



C3 regioisomers plecluded by steric factors

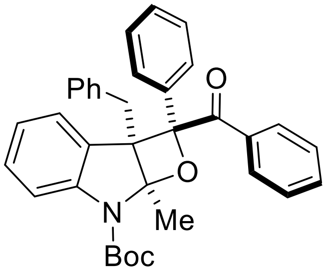
C3 products regioisomers were not observed

not observed

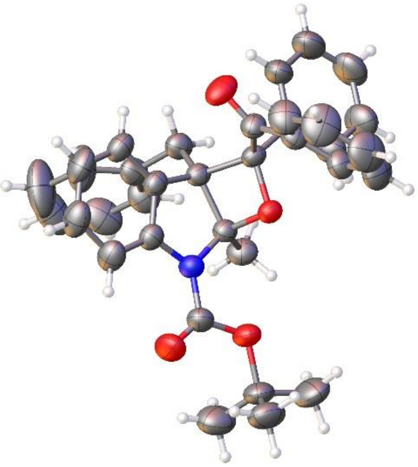
Figure S21. Proposed Griesbeck-type models for the photochemical addition of **2g** to an indole moiety were Iβ and Iγ corresponds to the most favorable 1,4-biradicals for the ring closure.

G. X-RAY CRYSTALLOGRAPHIC ANALYSIS

Compound 24



(±)-**24**



Yellow crystals of **24** were grown by slow evaporation of a diethylether solution at ambient temperature. **Mp**: 120-124 °C.

Crystal data: $C_{35}H_{33}NO_4$

Orthorhombic, *F*2dd, a=8.4764(13)Å, b=33.008(5)Å, c=40.934(6) Å, V=11453(3)Å3; Z=16; dcalc=1.233 mg/cm^3 , F(000)= 4512, mu=0.080, Tot. refl.= 34654 hkl range= -10<h<10, -41<k<41, -50<l<50; Theta max 26.5°, ref.tot.= 5881, number of parameters = 365, GooF= 1.013, R=0.0417, wR2=0.0911.

CCDC 1972525 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

H. REFERERNCES

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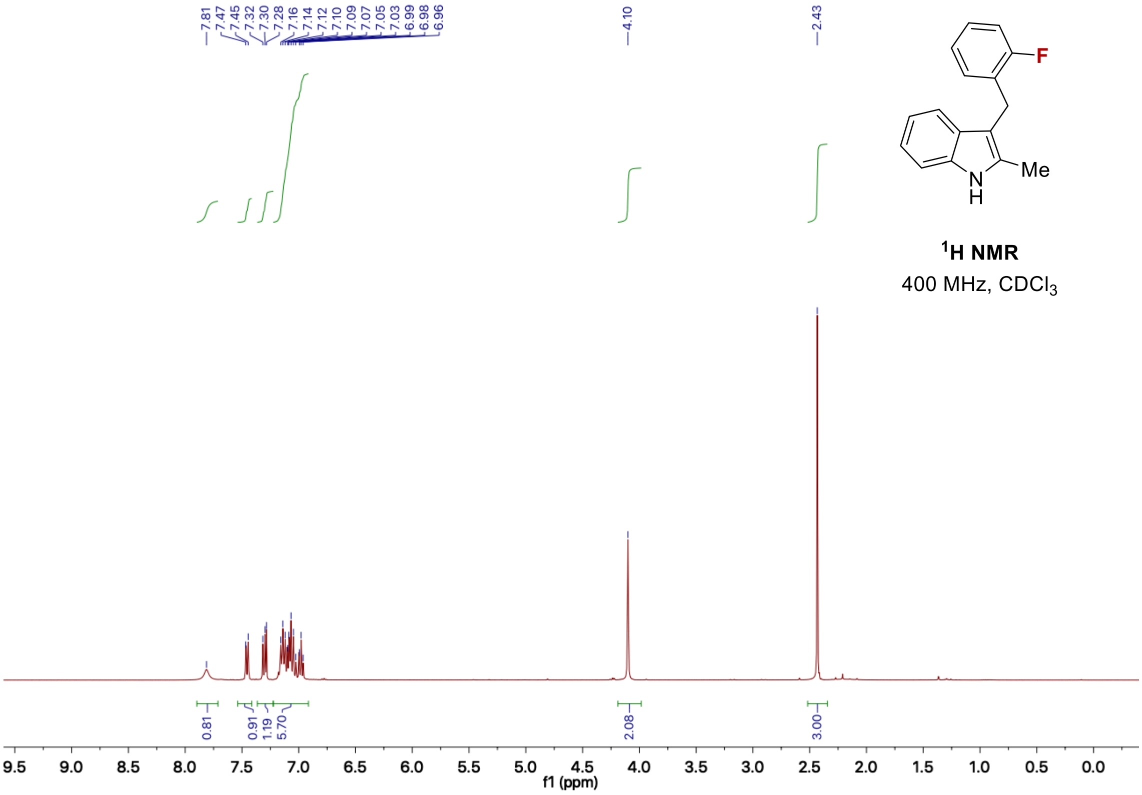
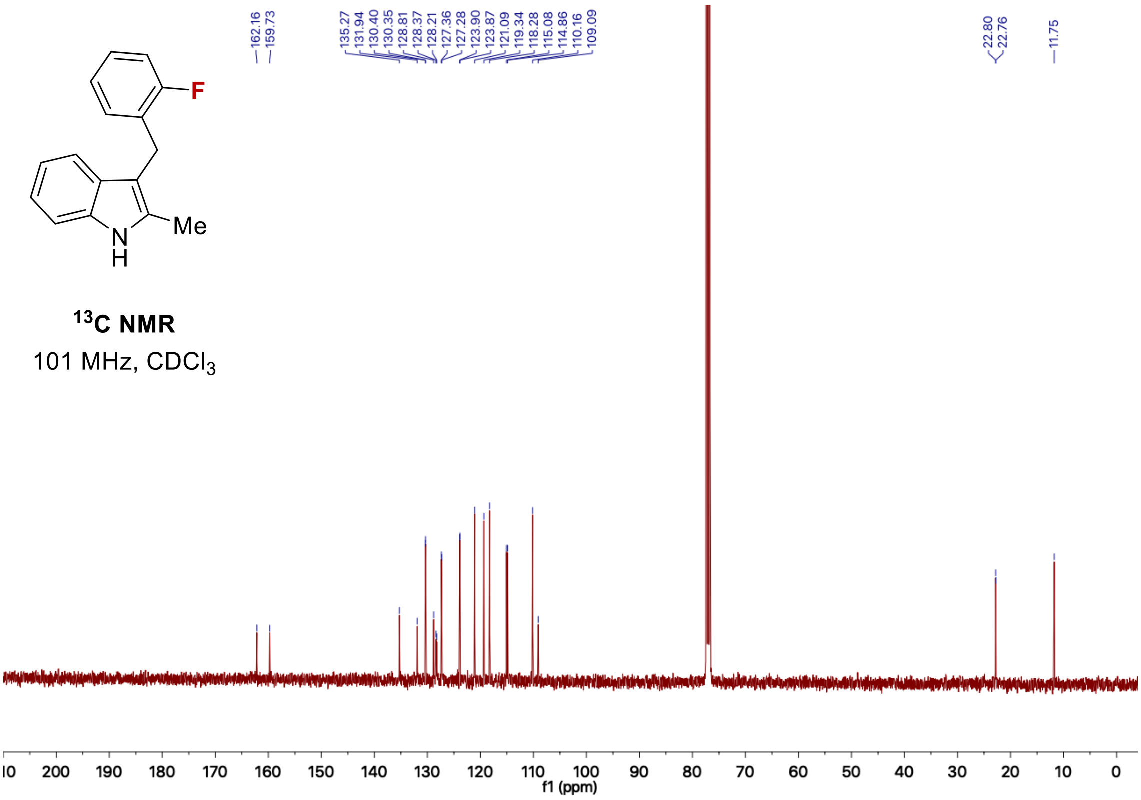
I. NMR SPECTRA OF THE STARTING MATERIALS

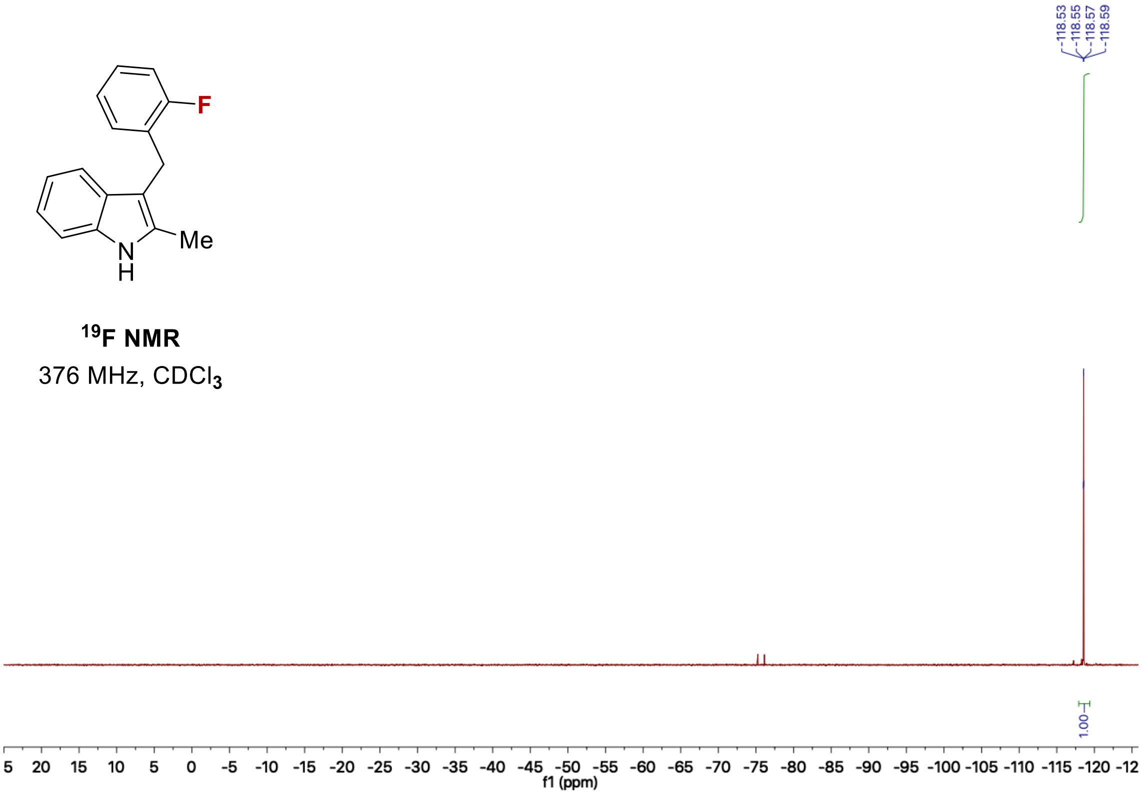
S2 - ^{1}H NMR (CDCl$_3$)



S2 - ^{13}C NMR (CDCl$_3$)



S2 - ^{19}F NMR ($CDCl_3$)



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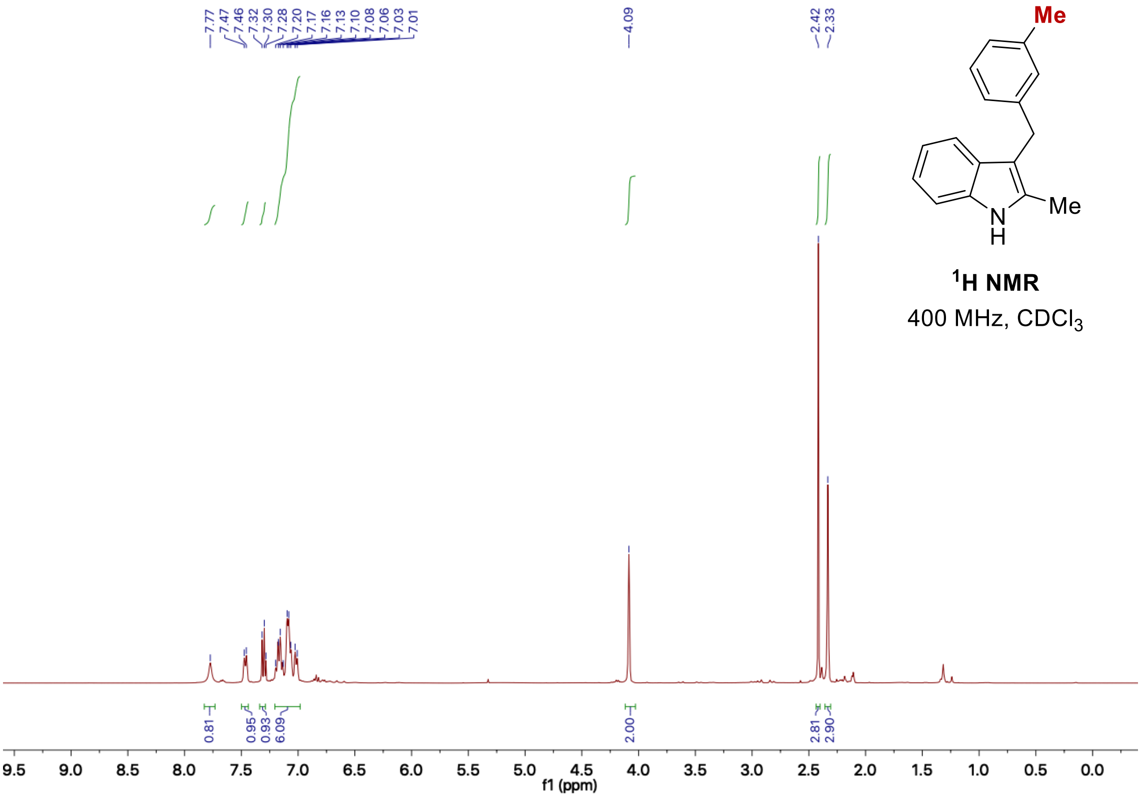

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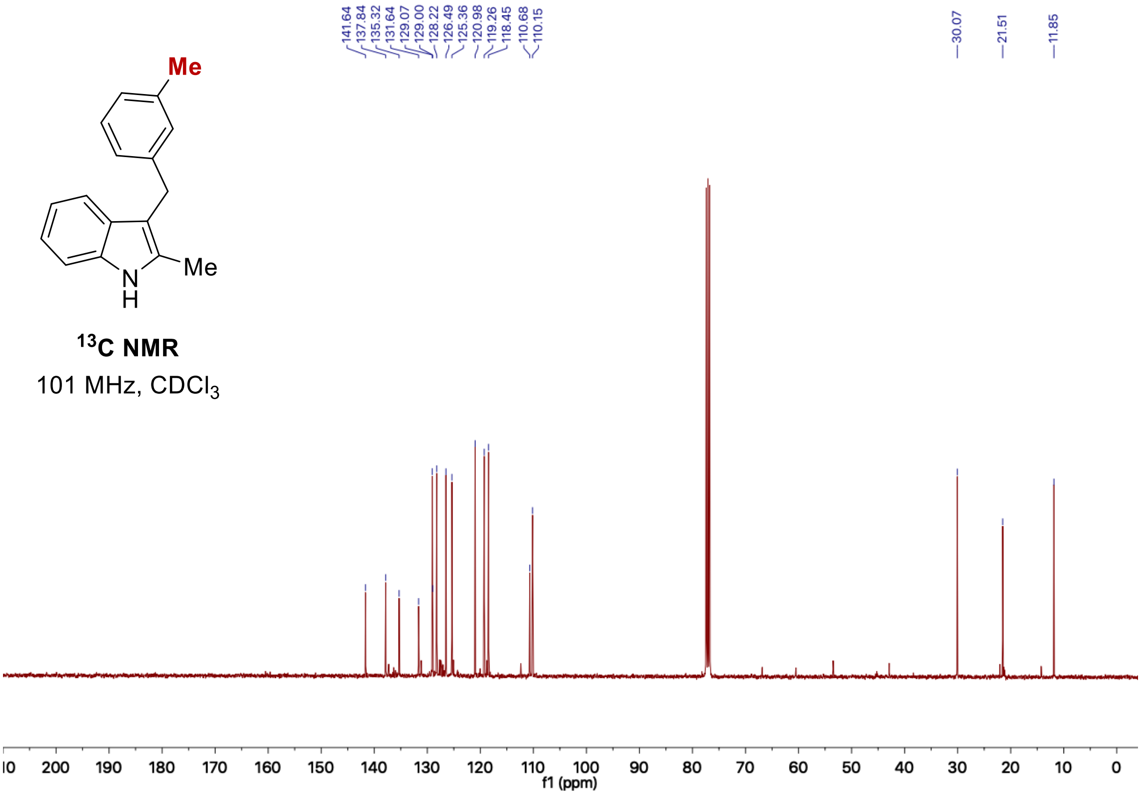

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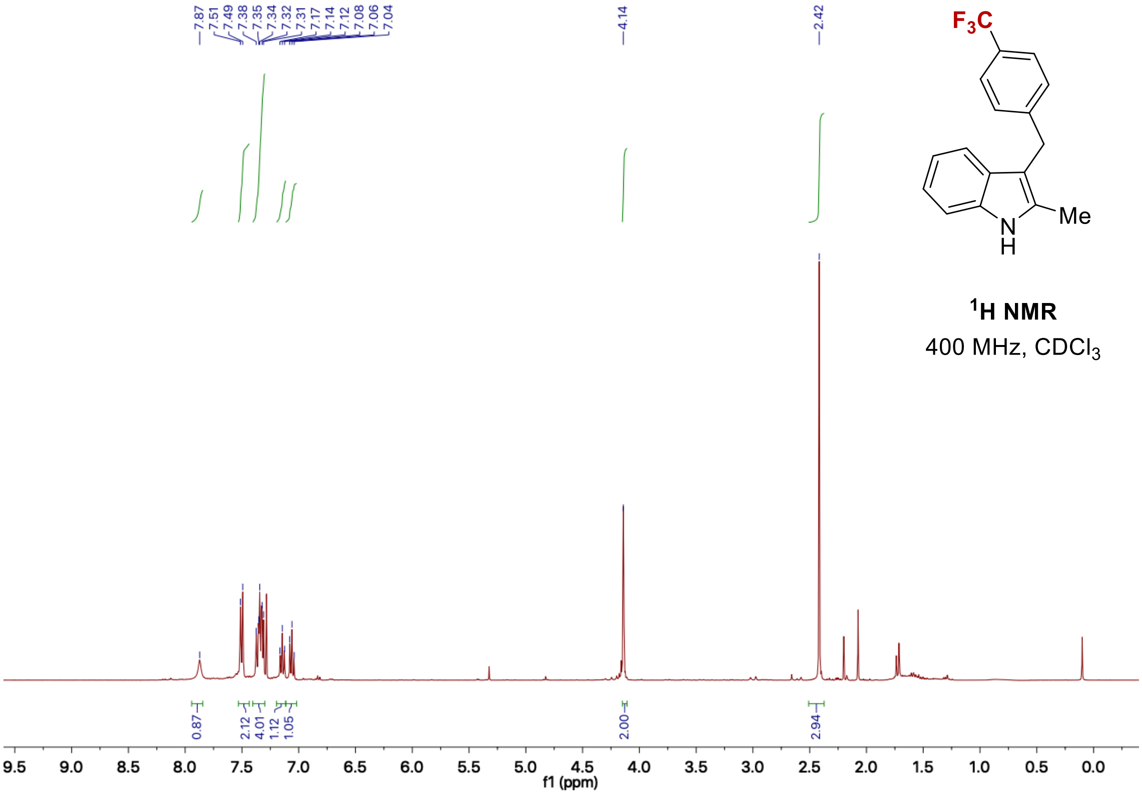

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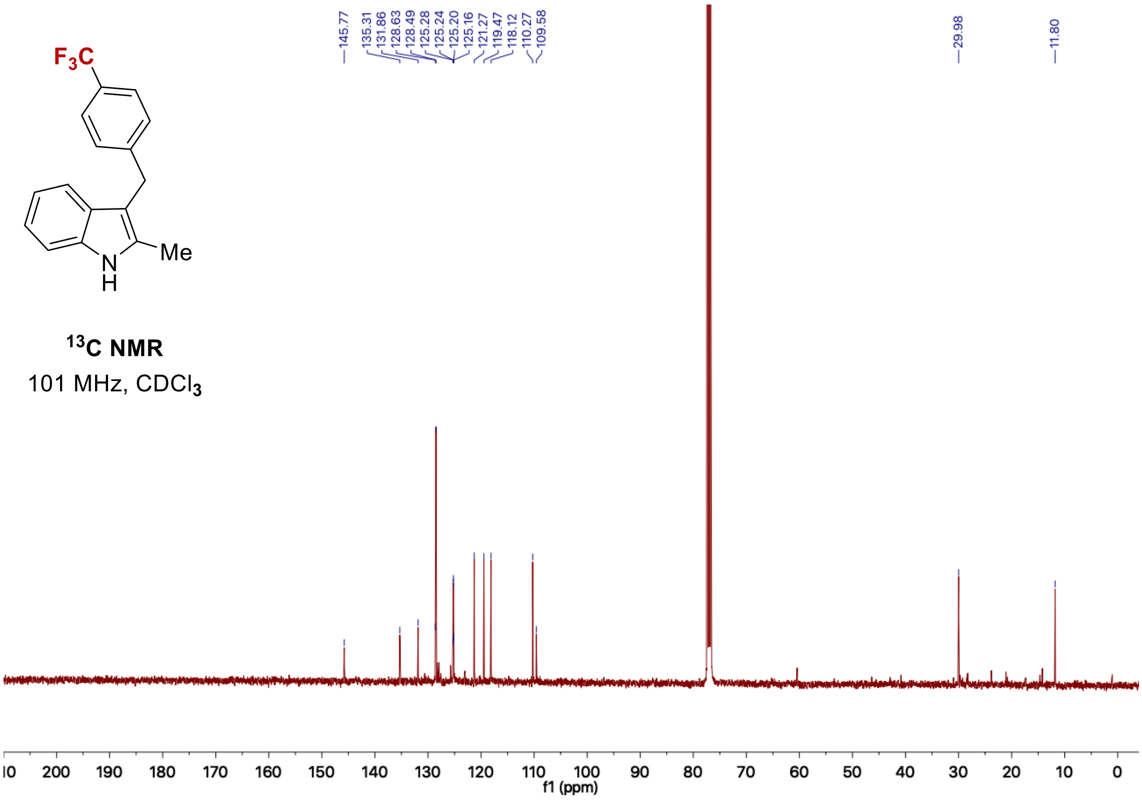

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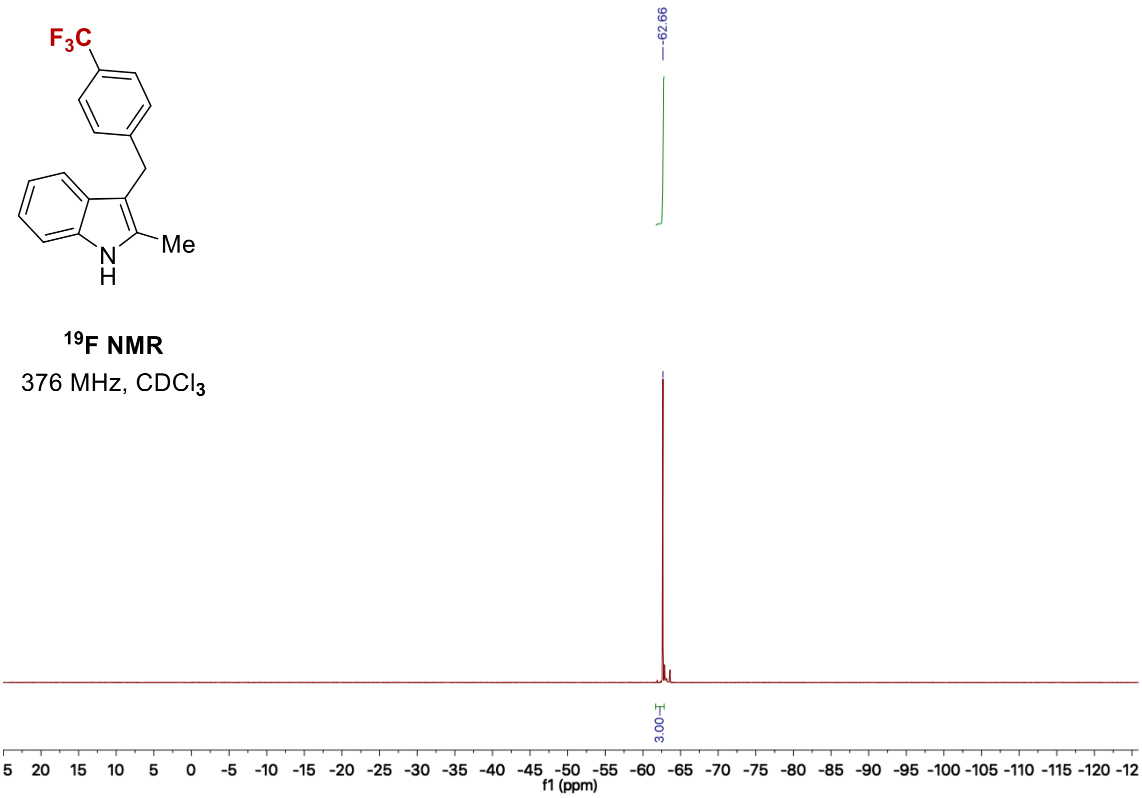
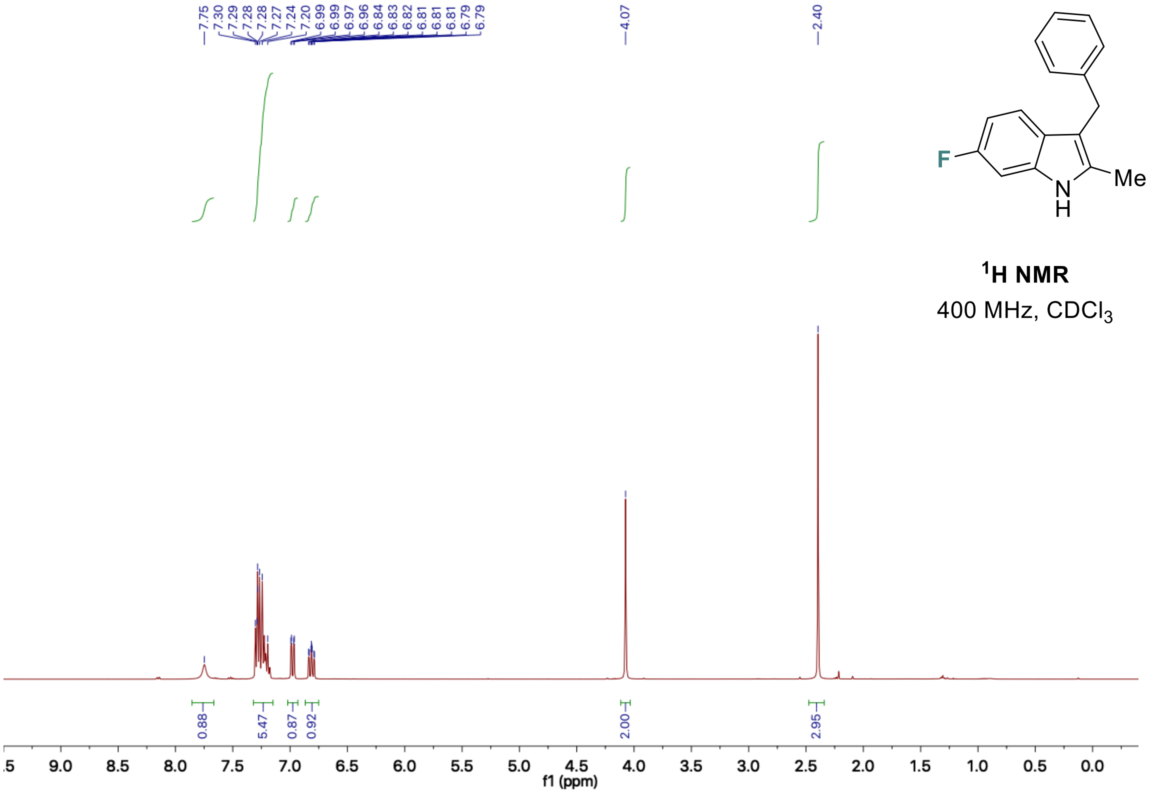


^{19}F NMR
376 MHz, $CDCl_3$

S6 - ^{1}H NMR ($CDCl_3$)



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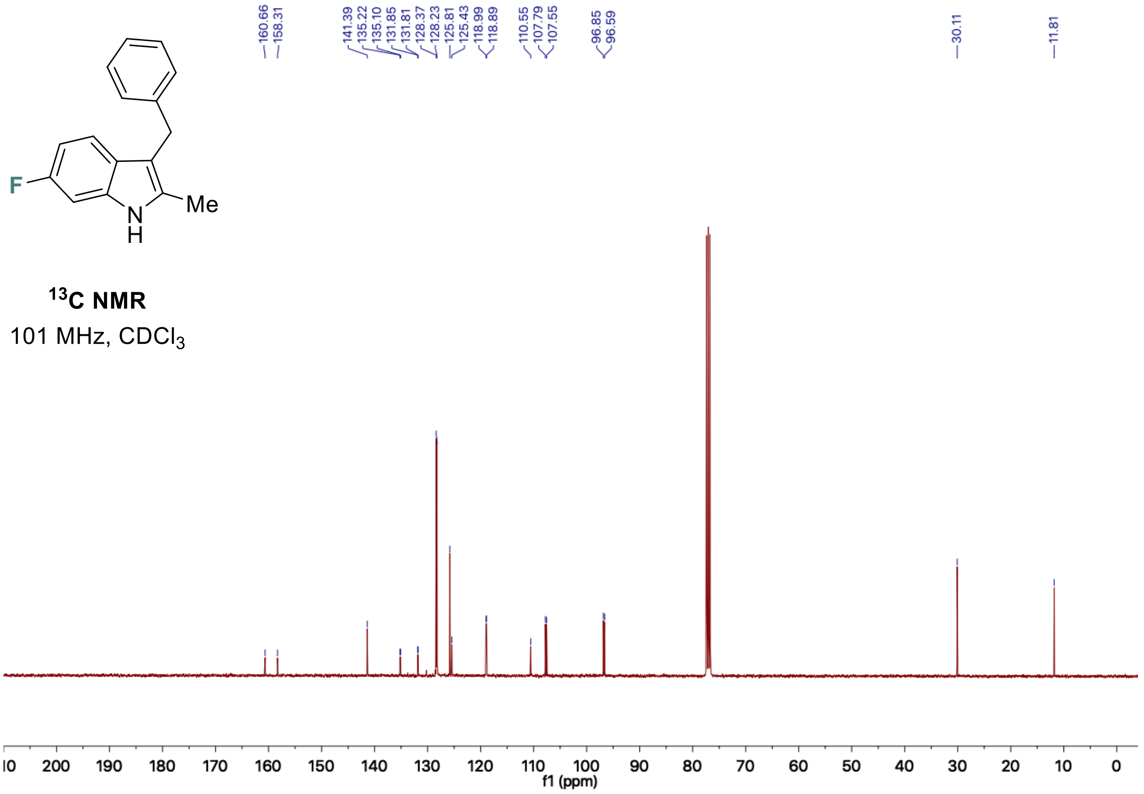

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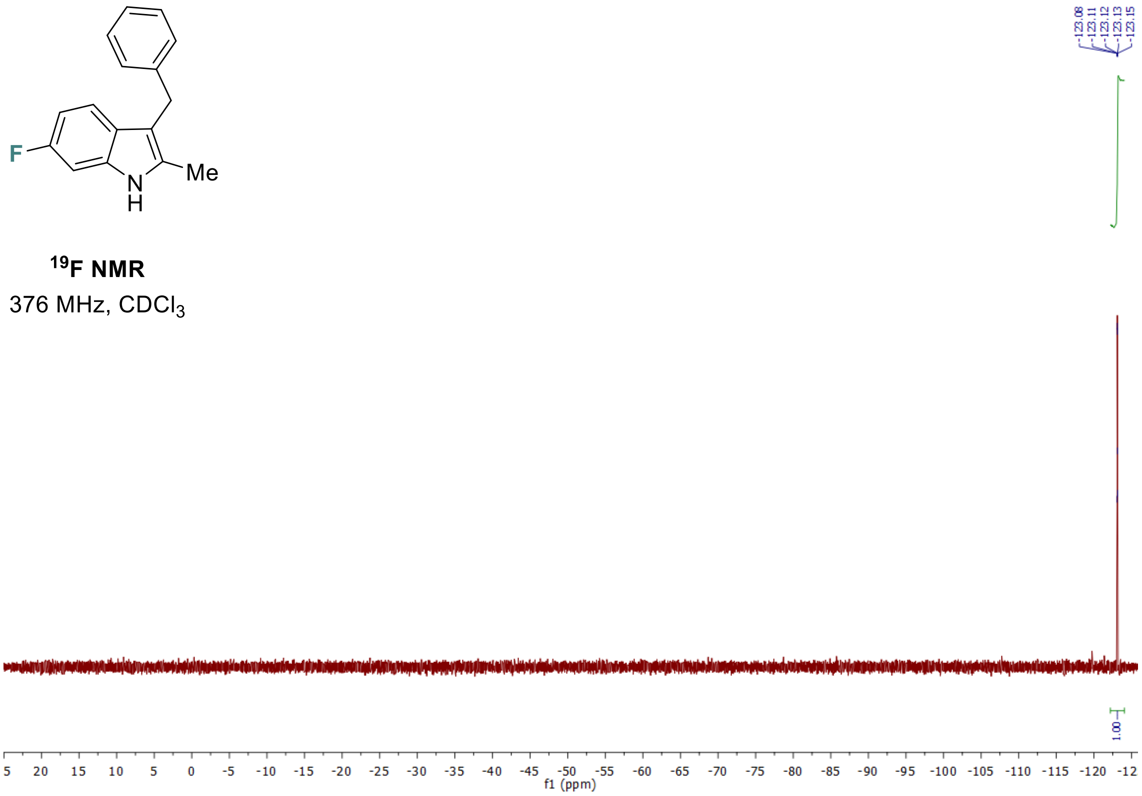

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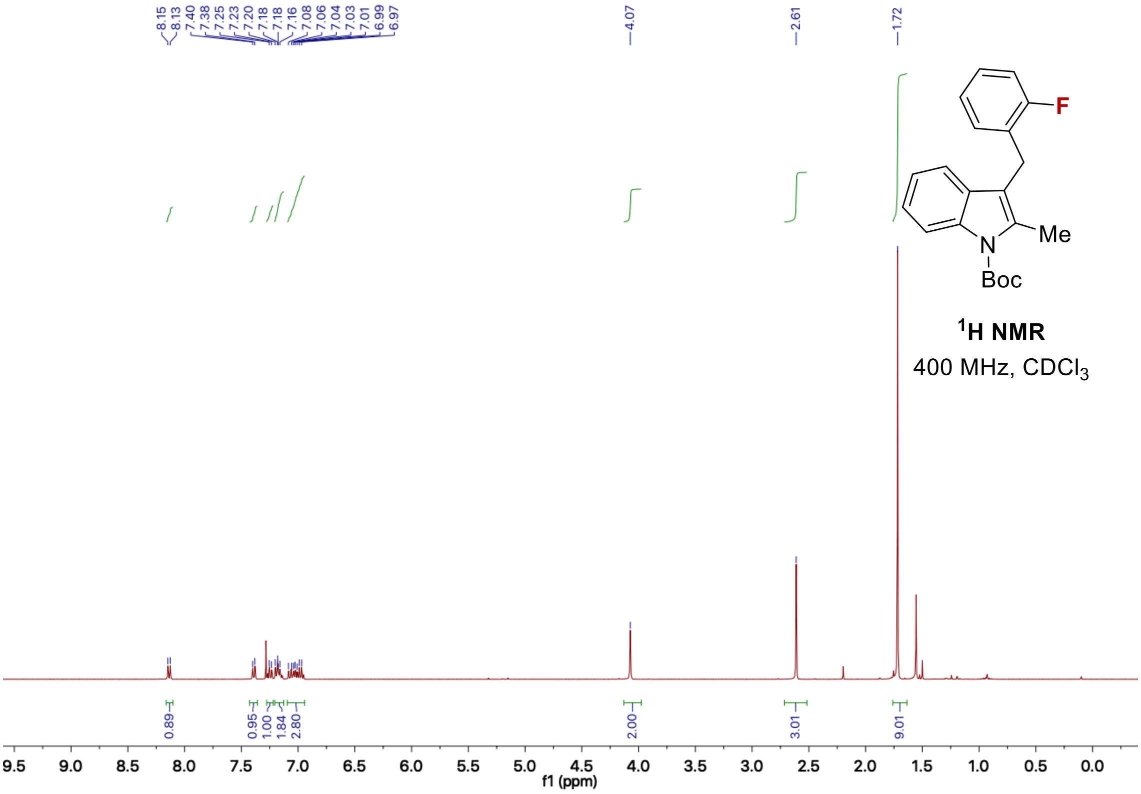

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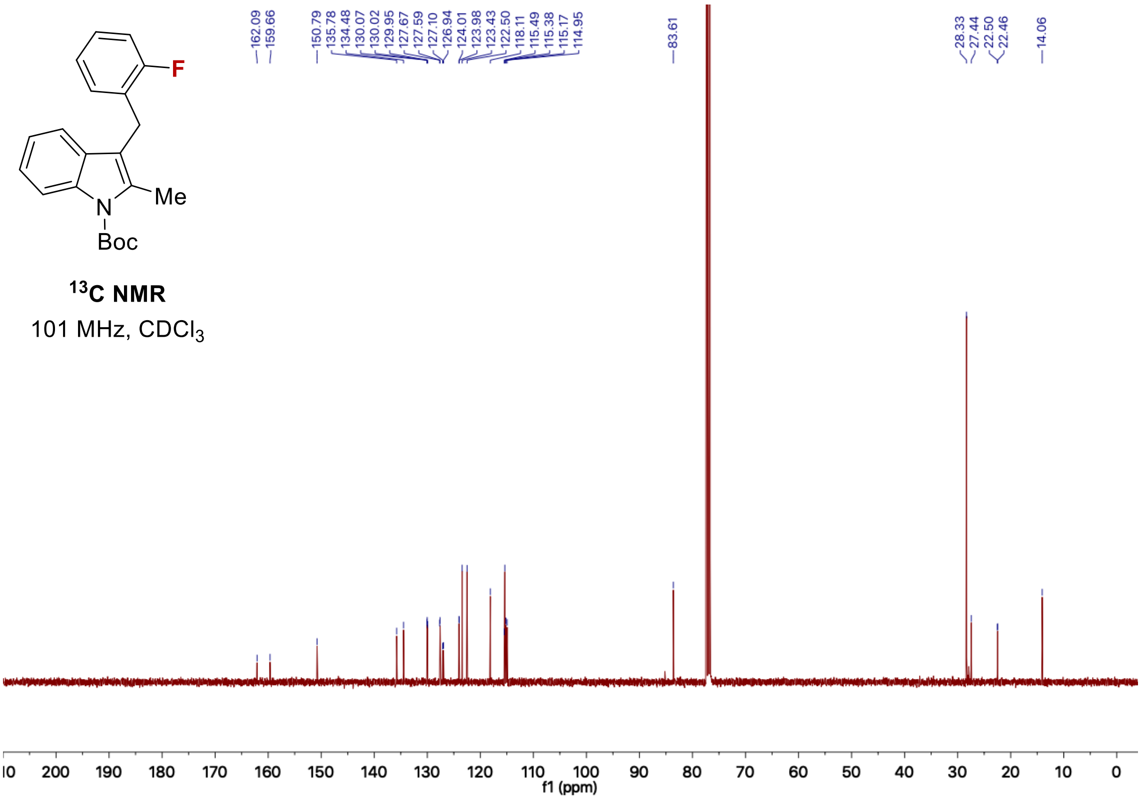

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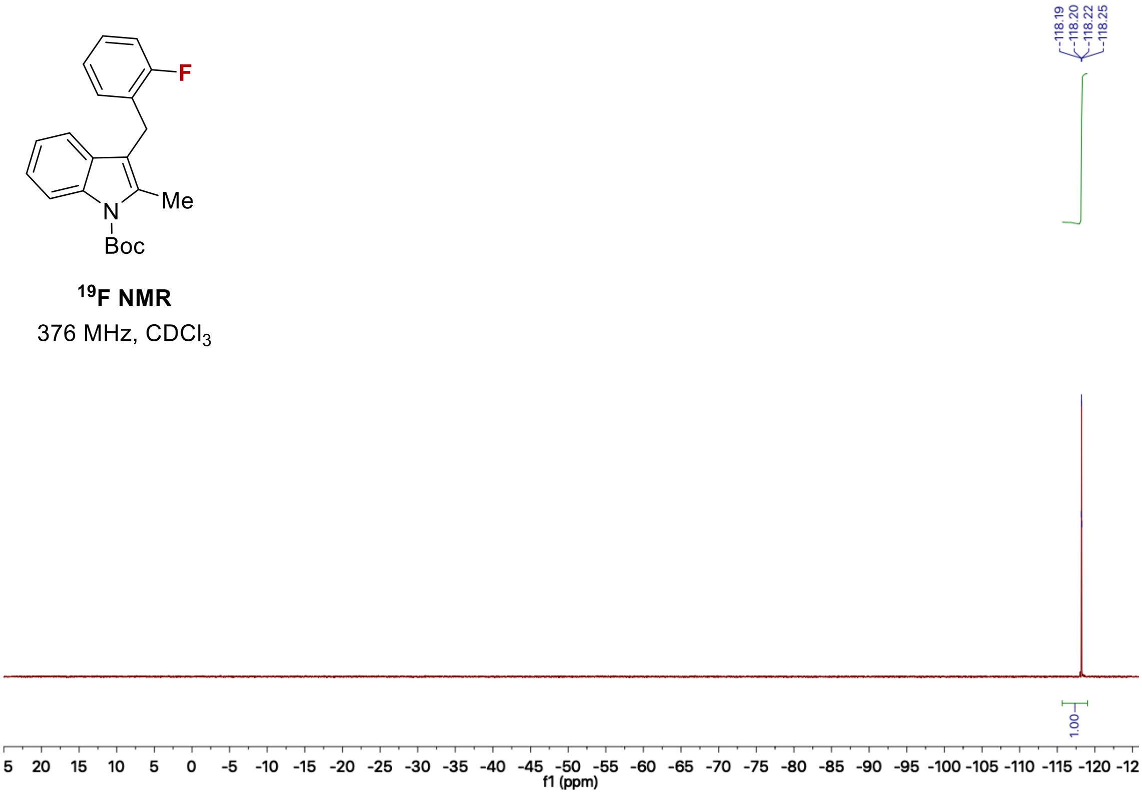

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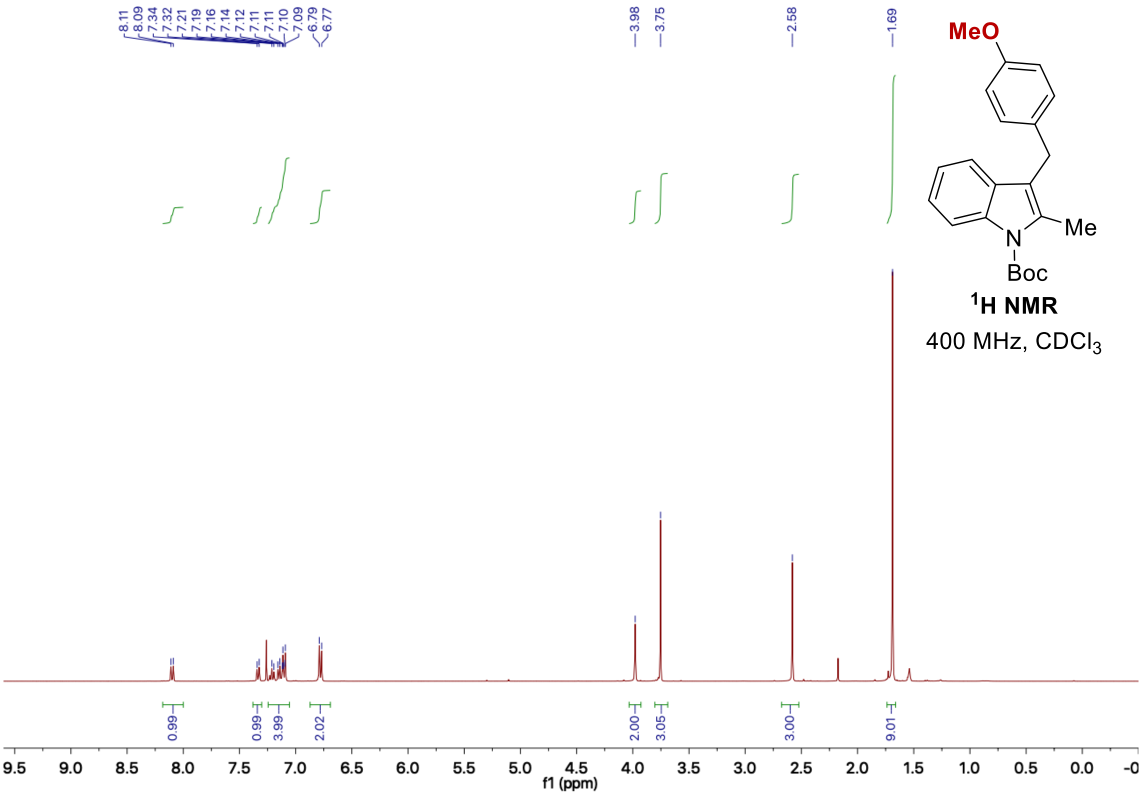

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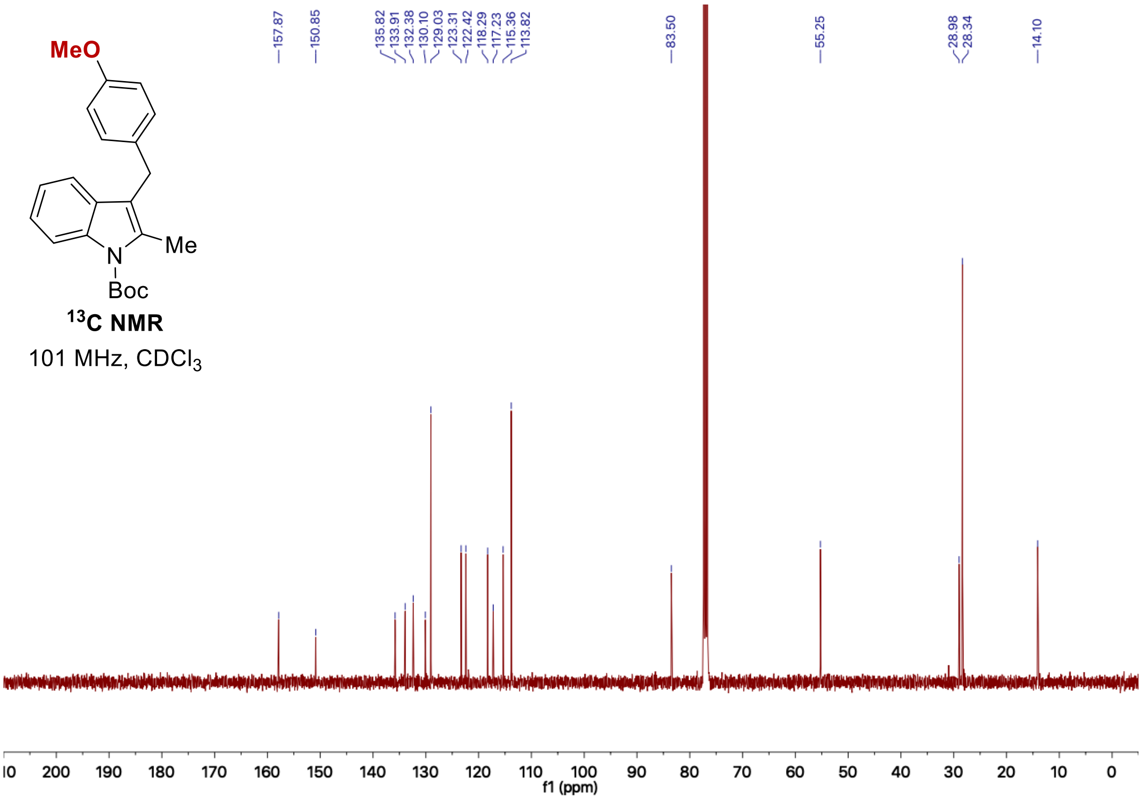

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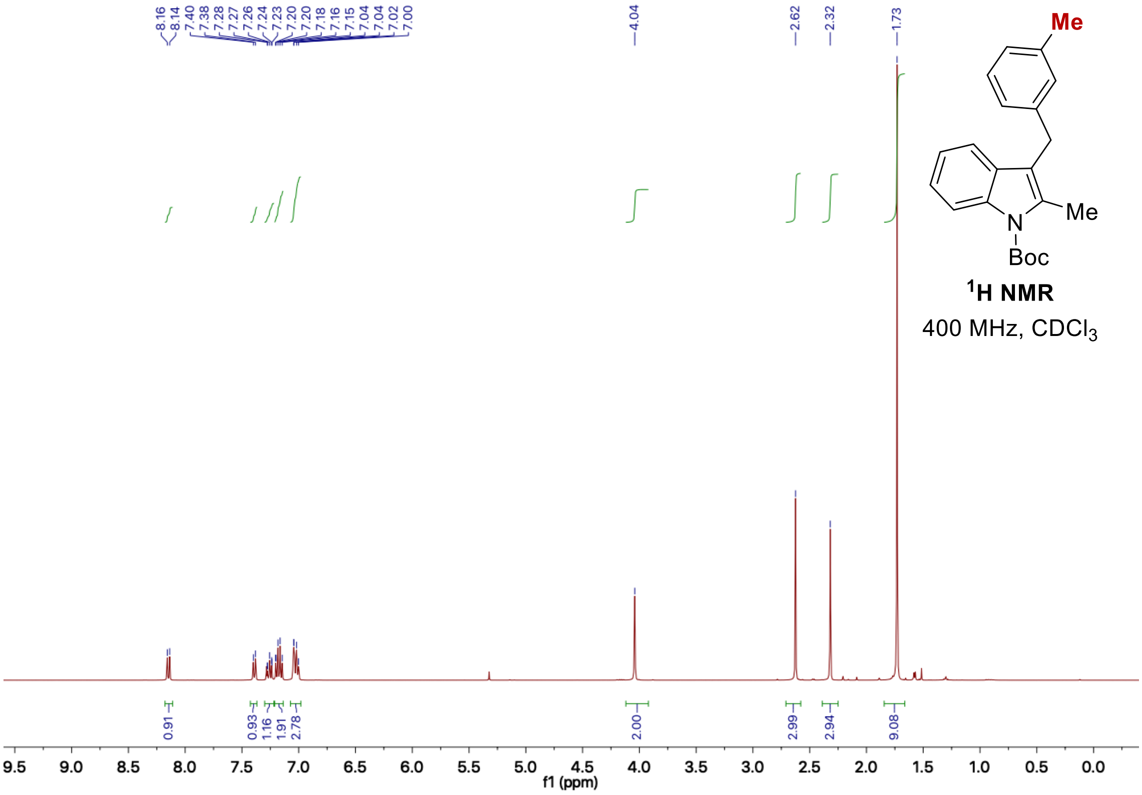

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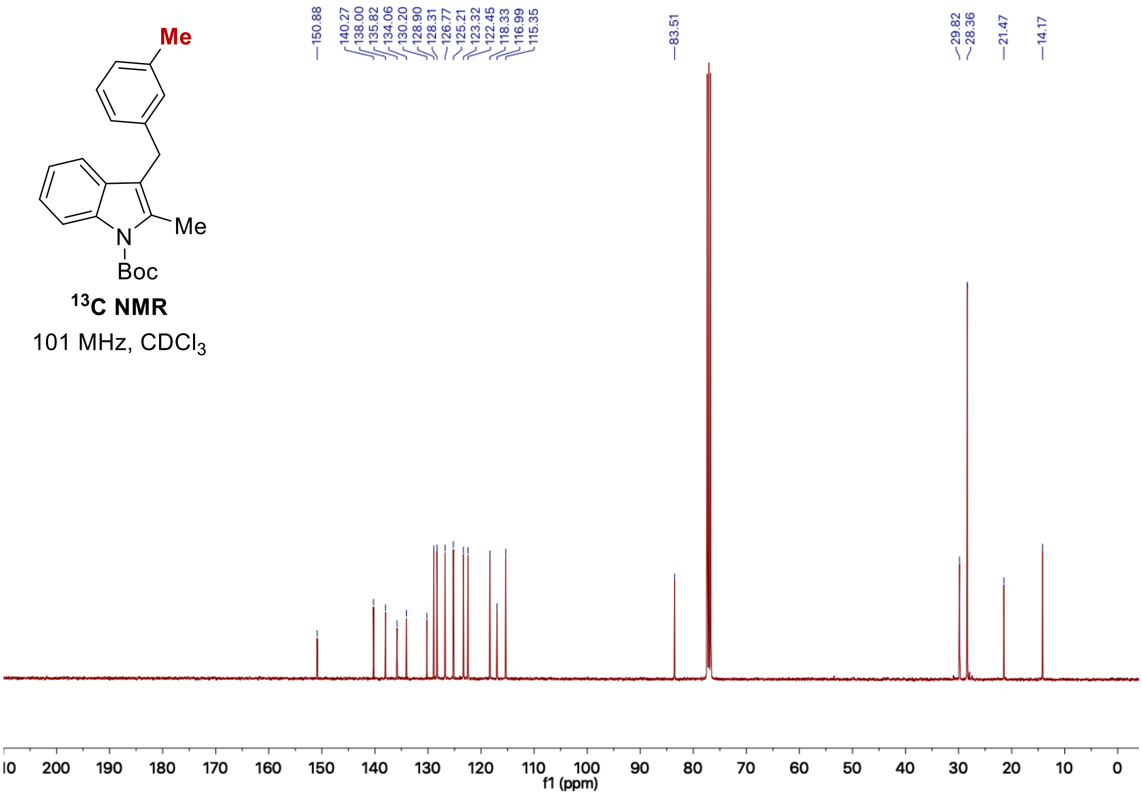

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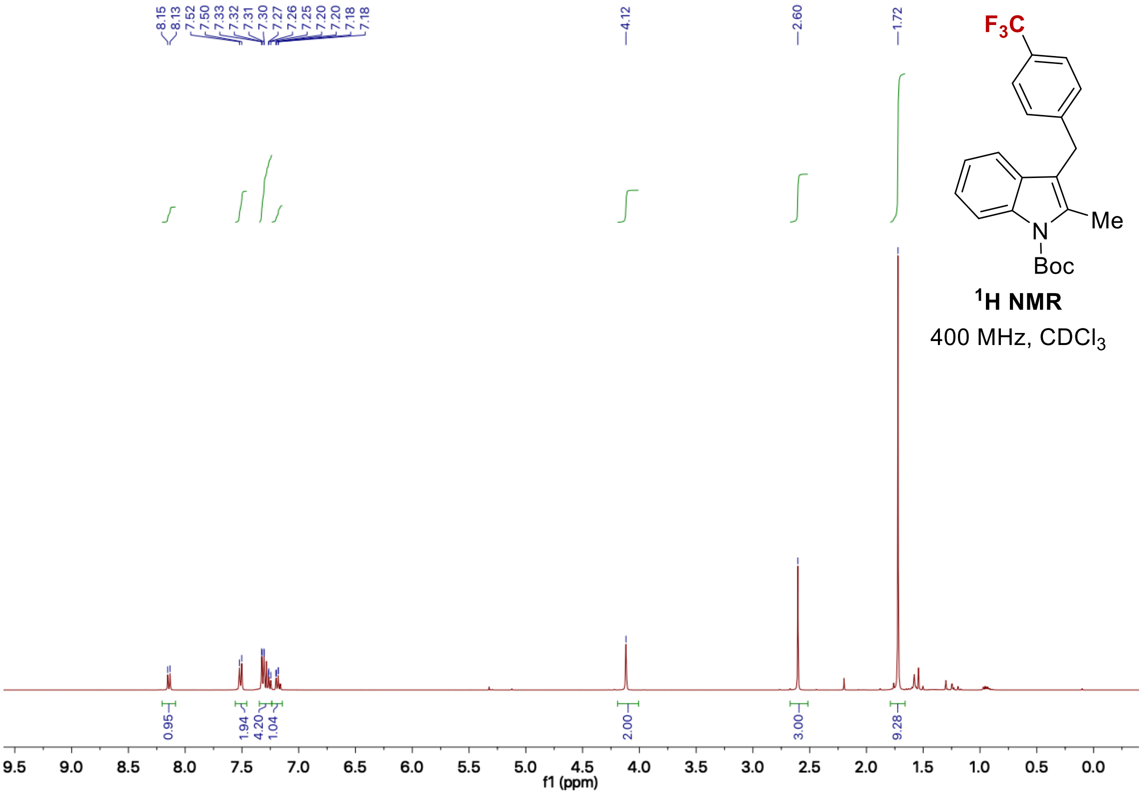

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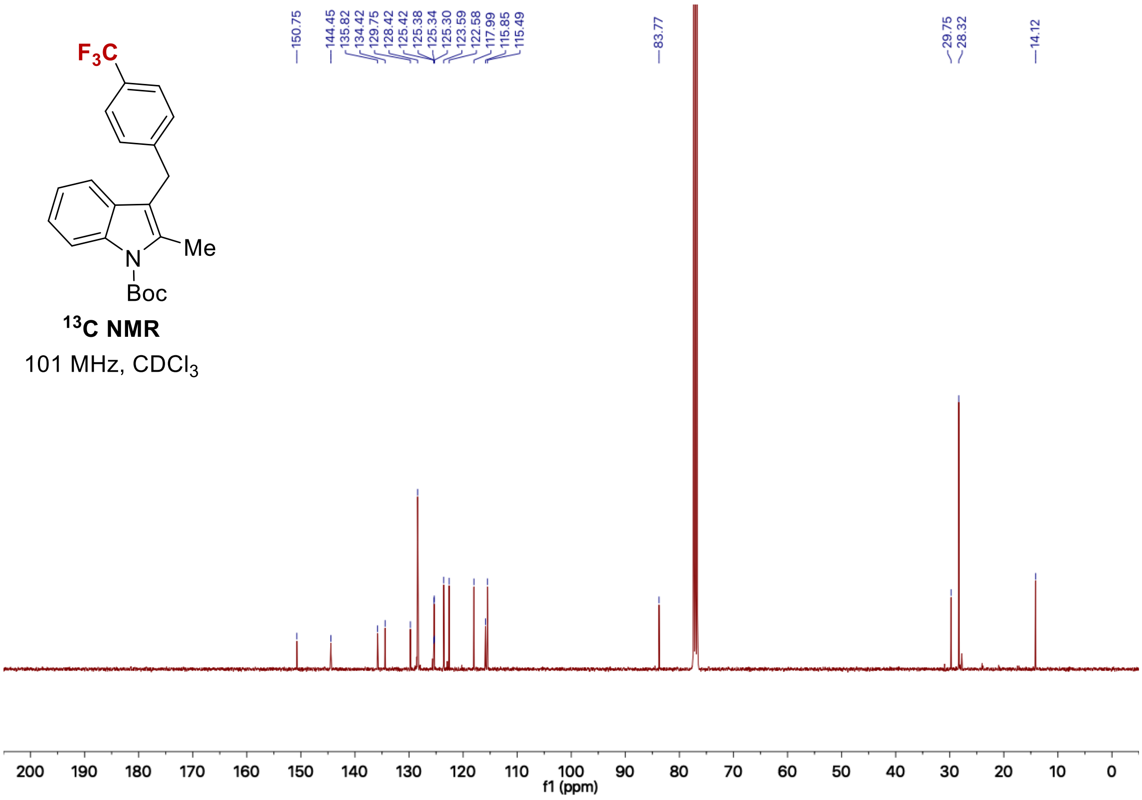

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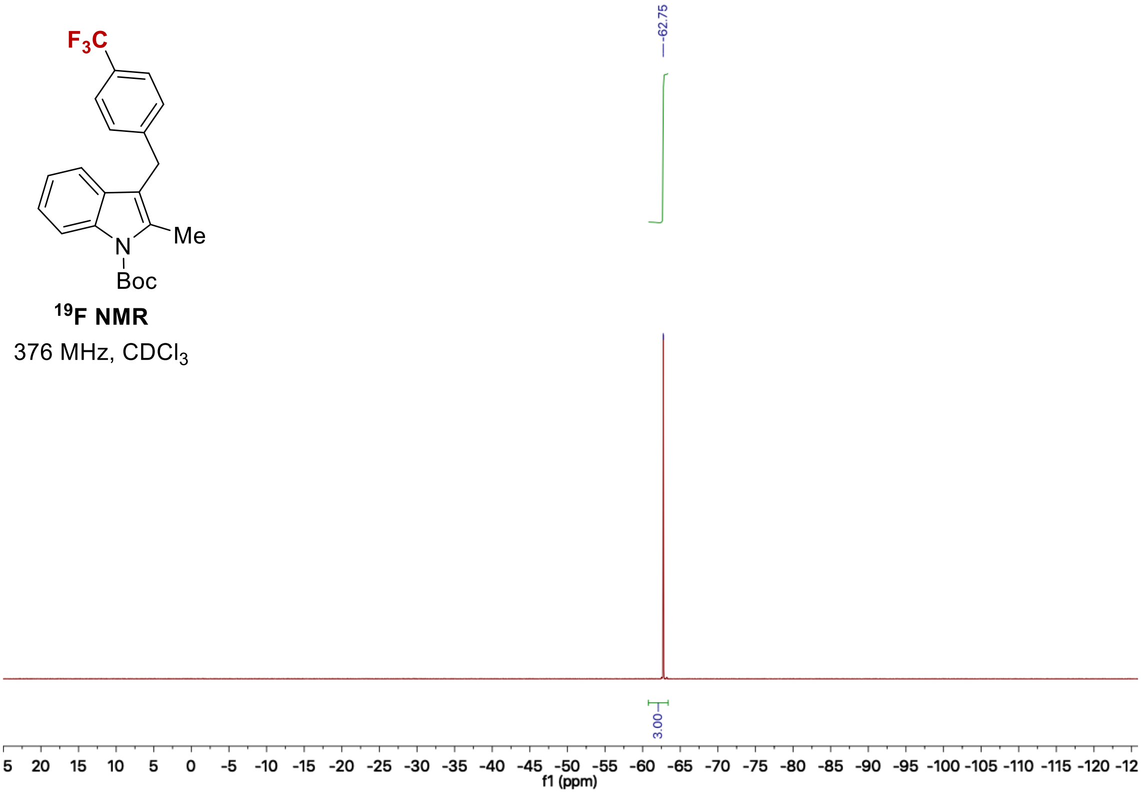

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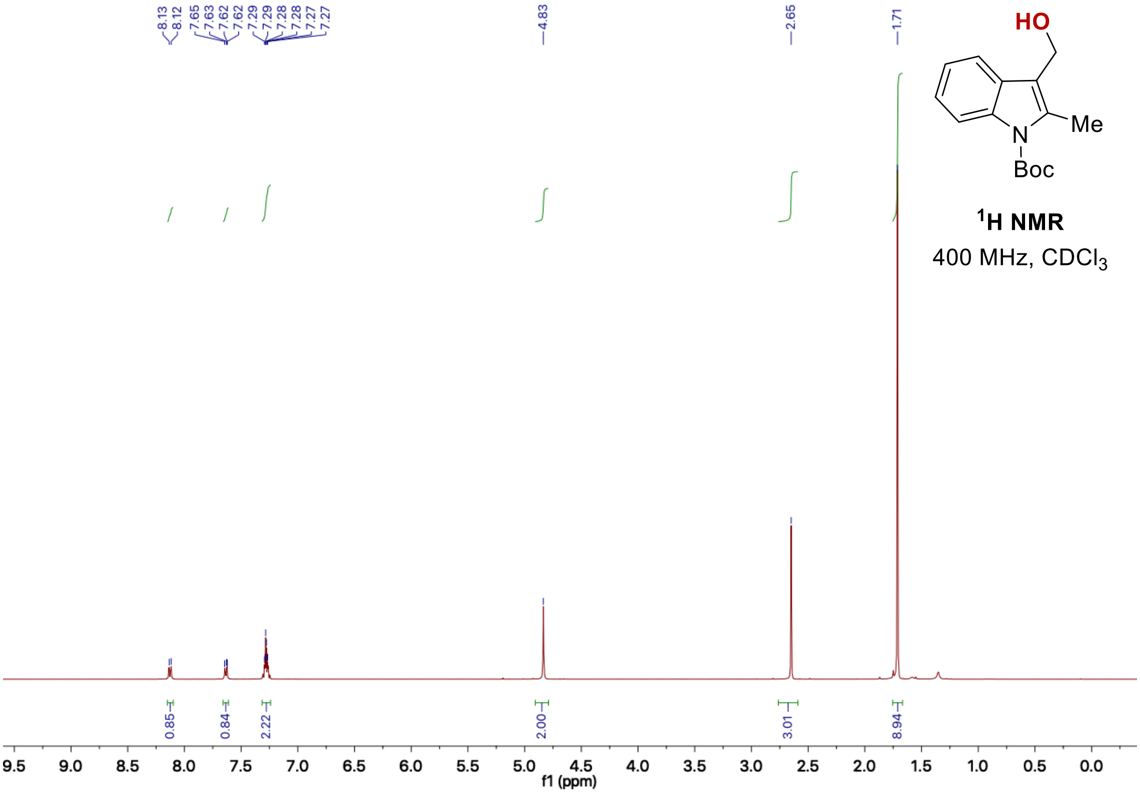

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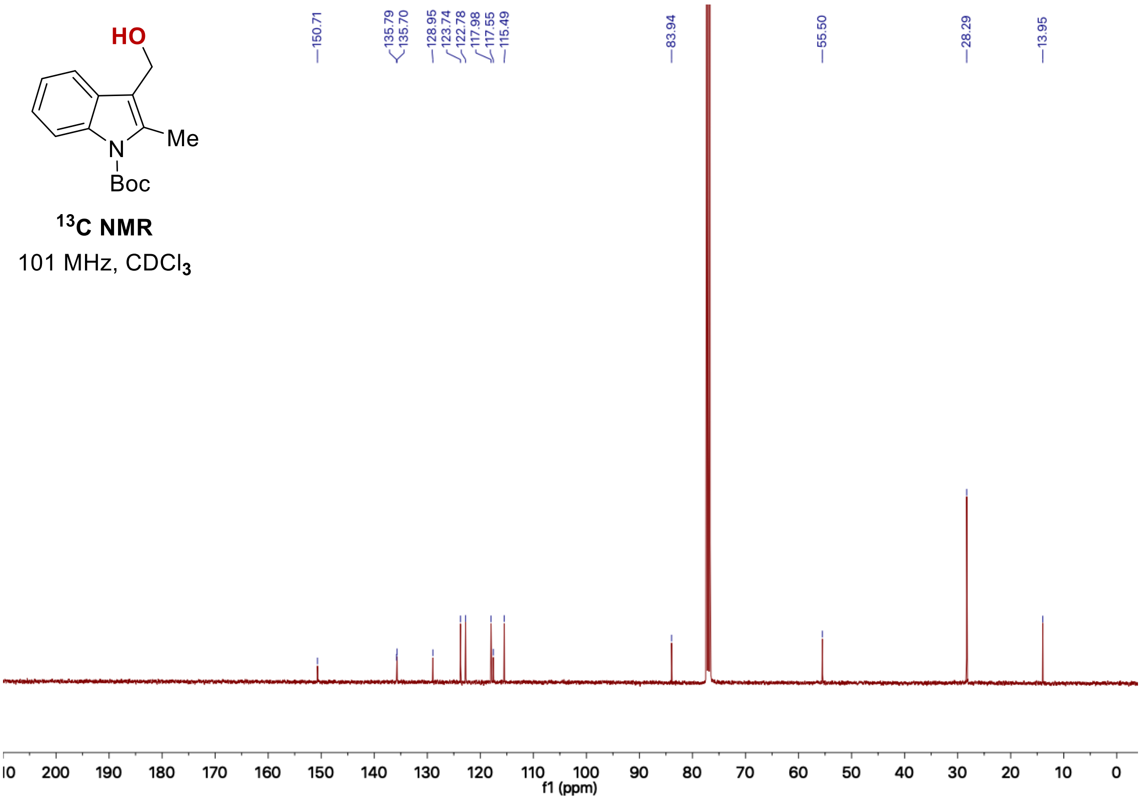

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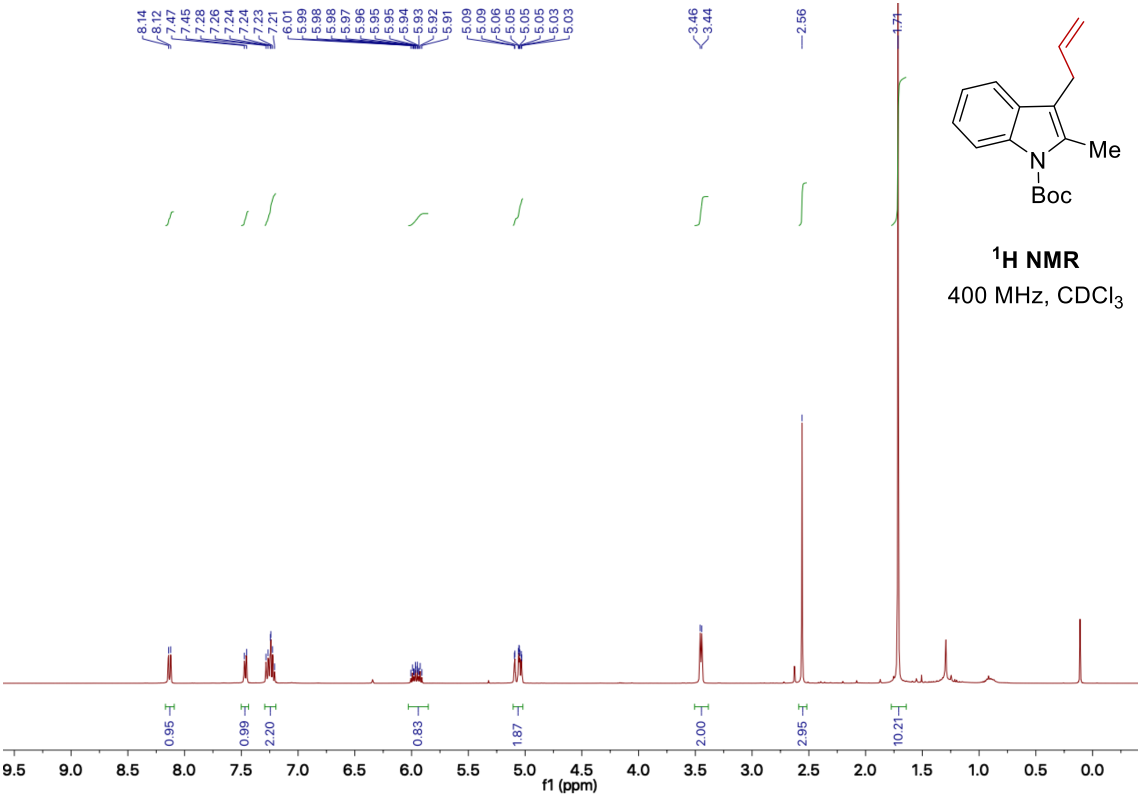

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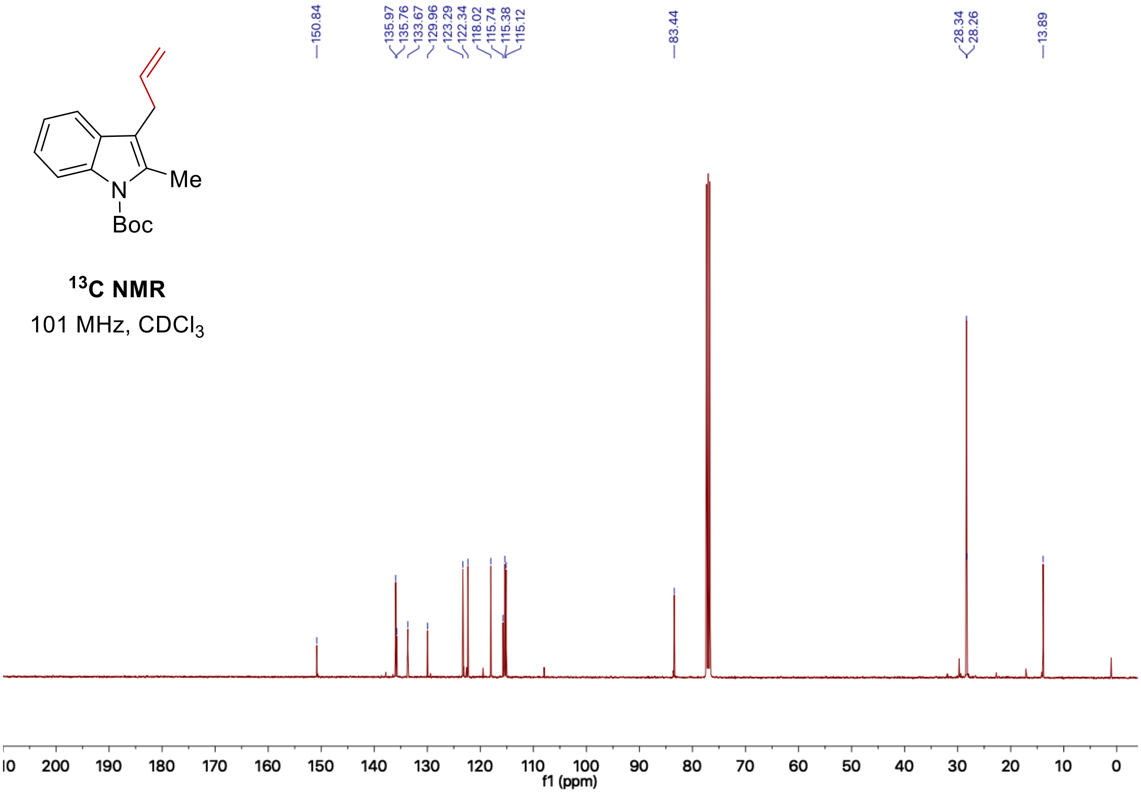

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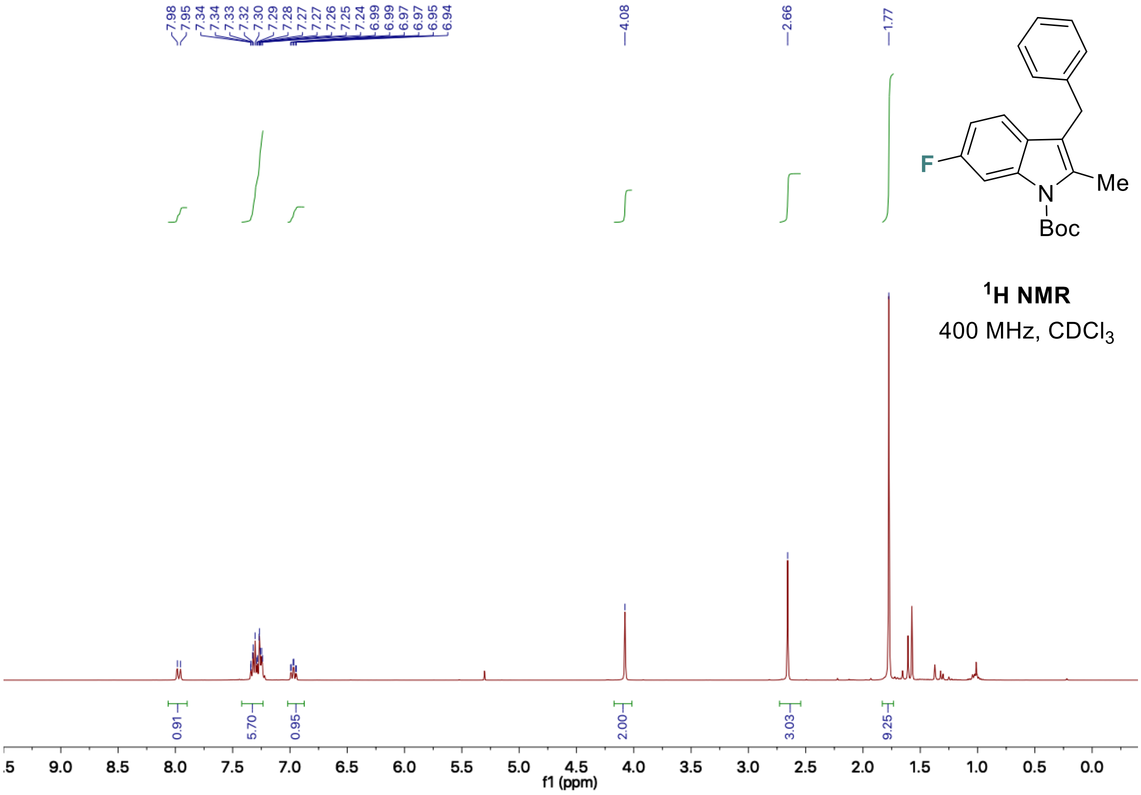

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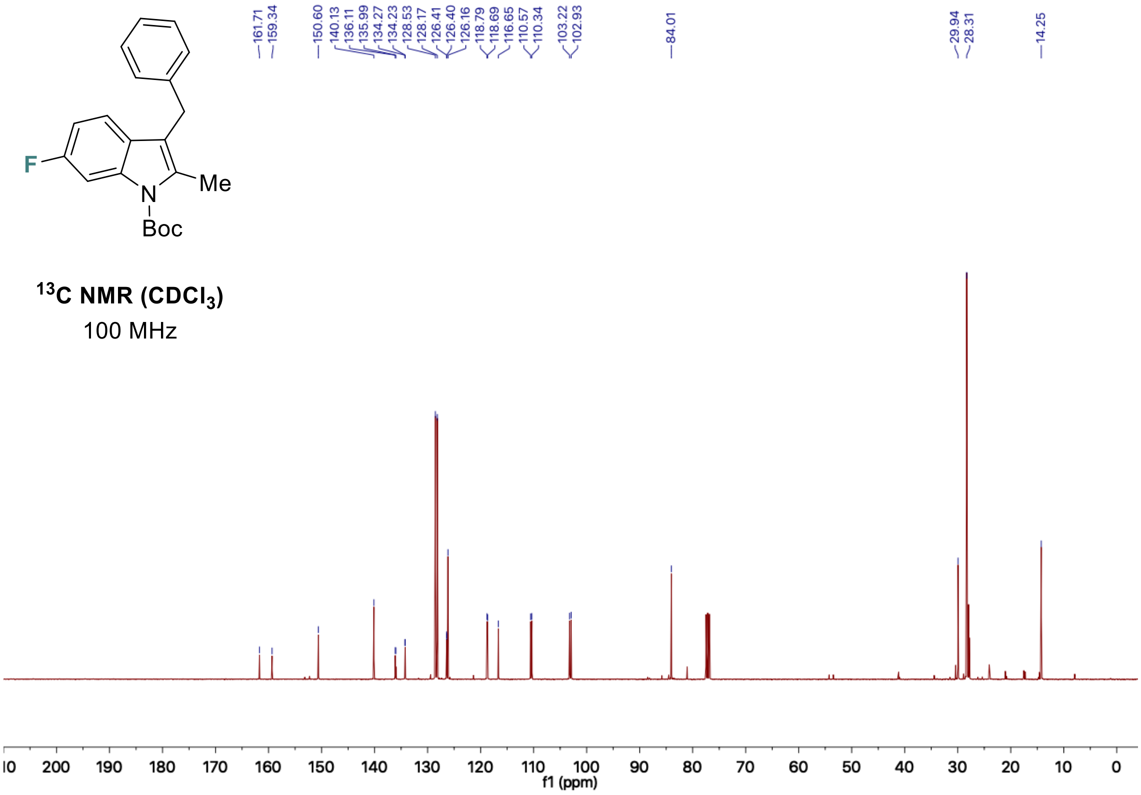

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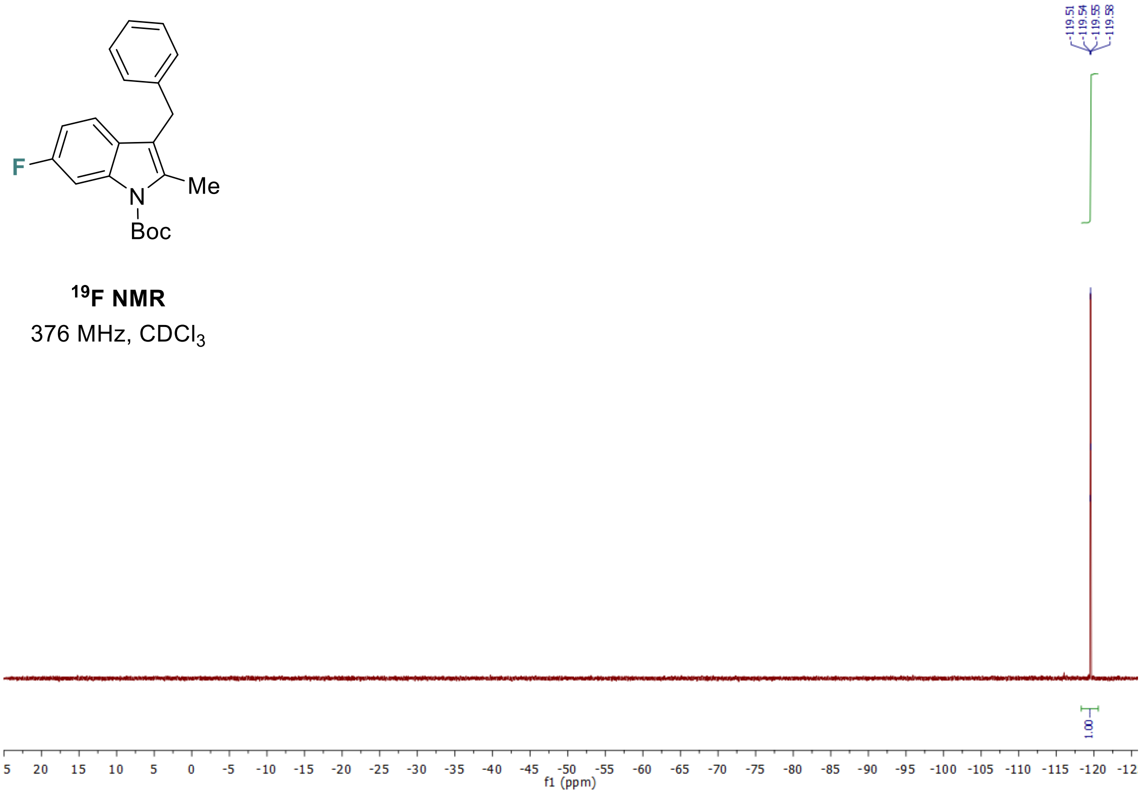
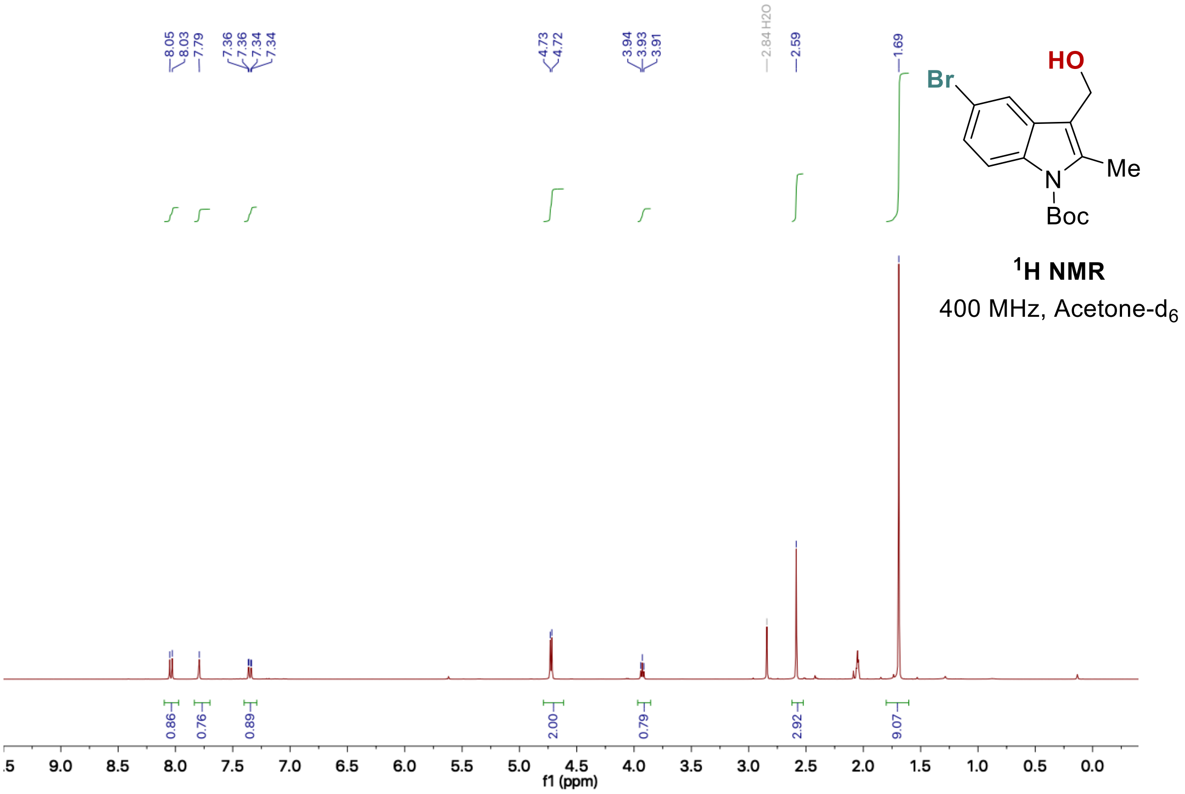


1m - ^{1}H NMR (Acetone-d_6)



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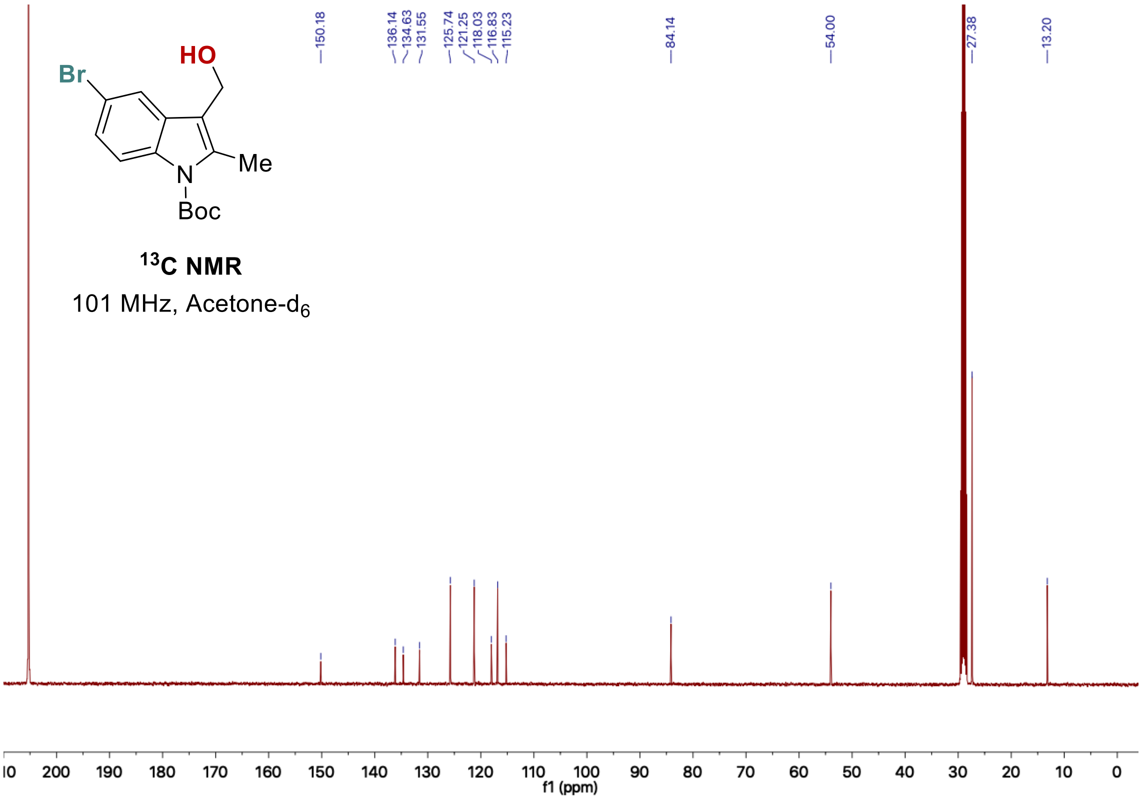

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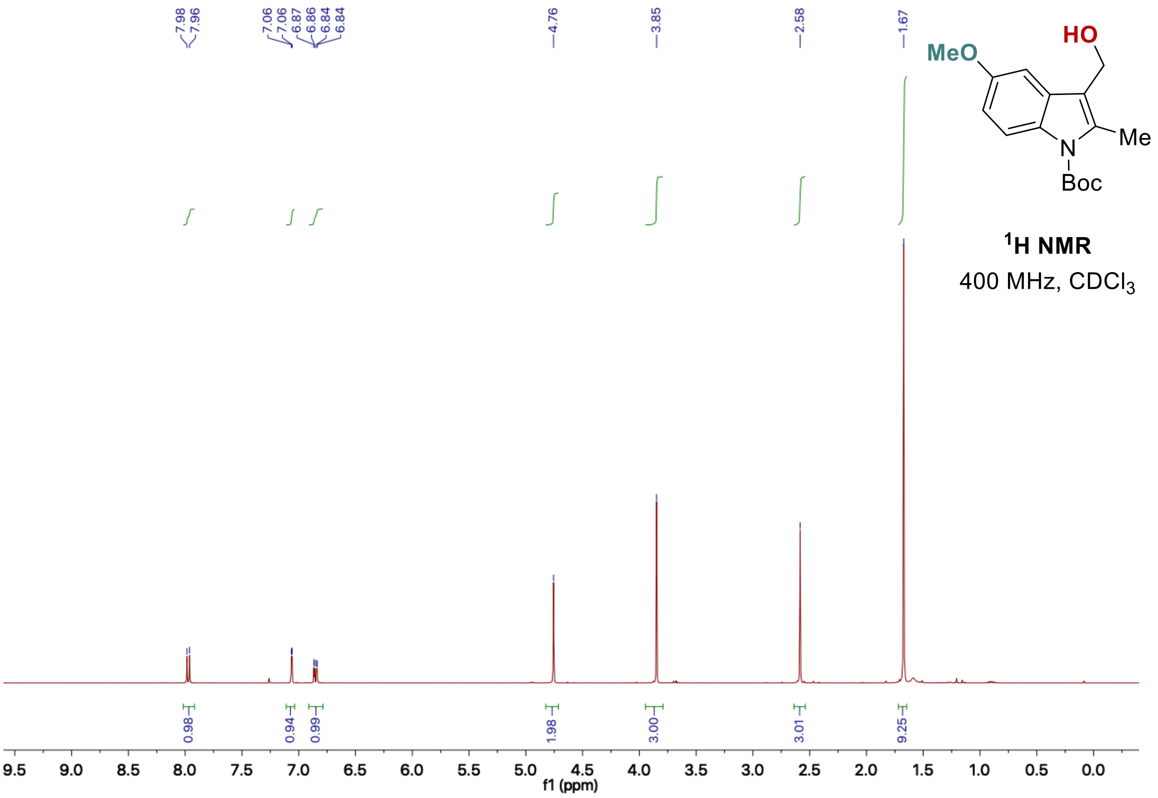

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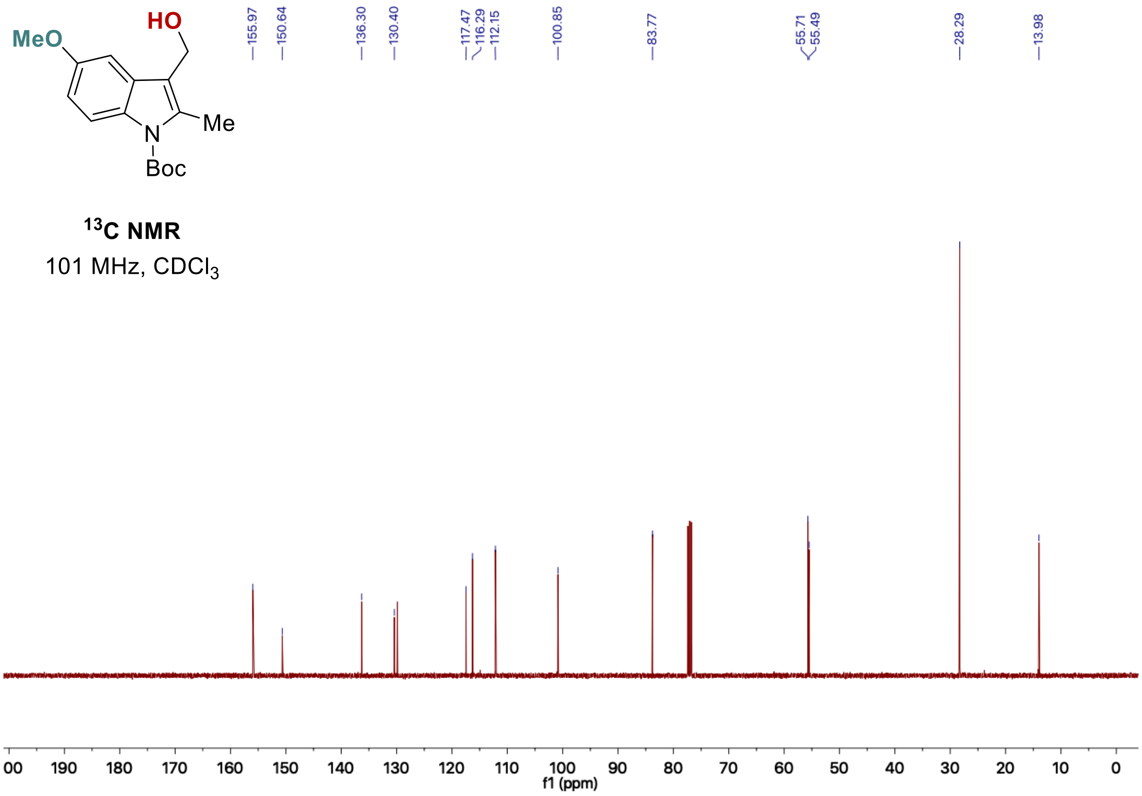
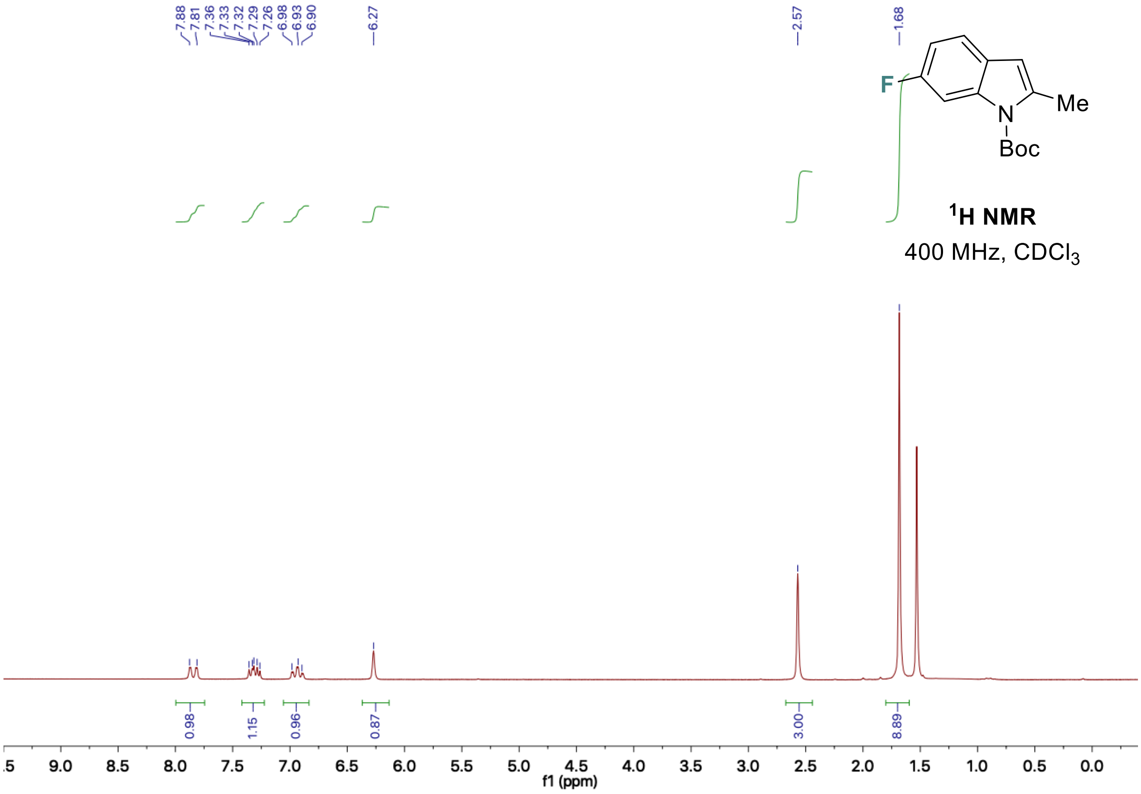
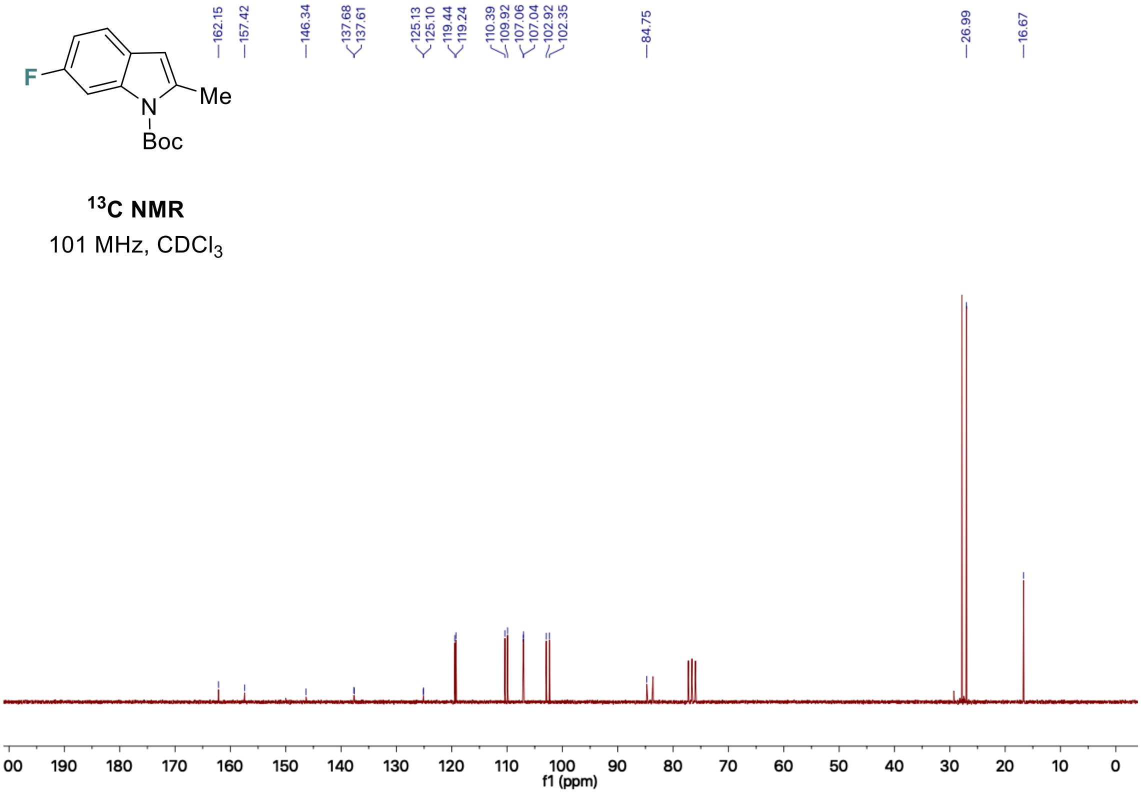


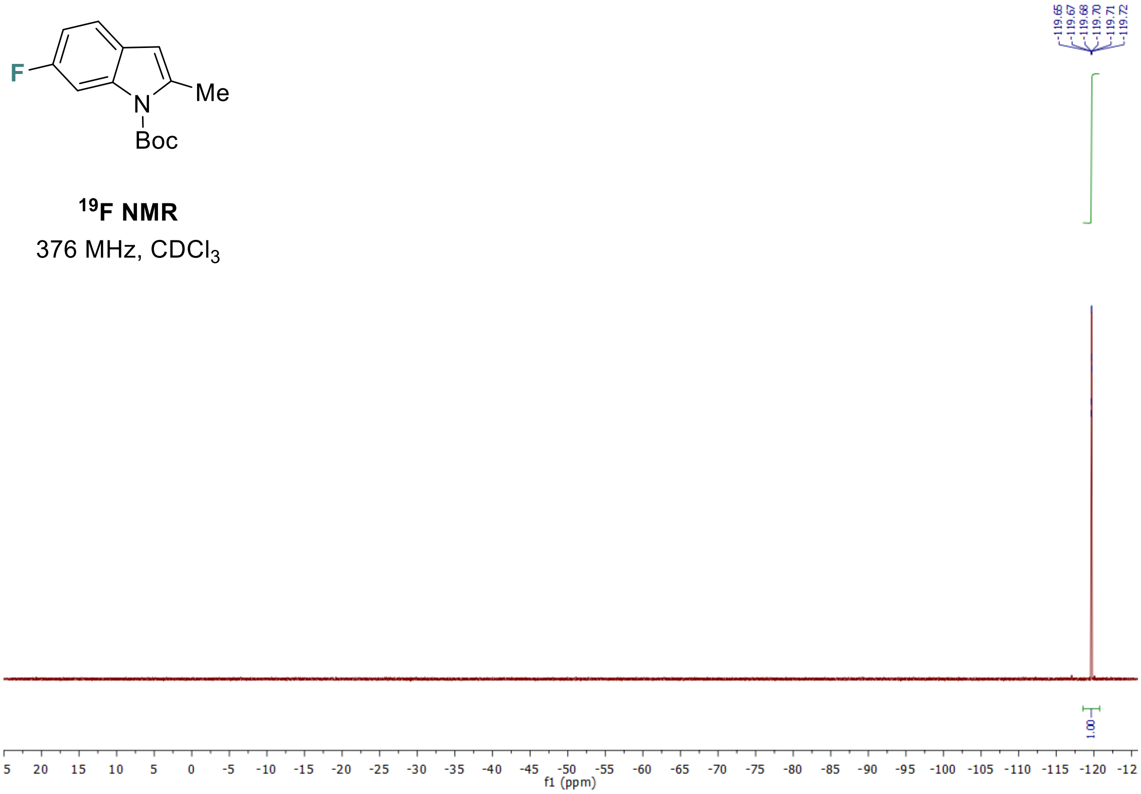
1o - ¹H NMR (CDCl₃)



1o - ¹³C NMR (CDCl₃)



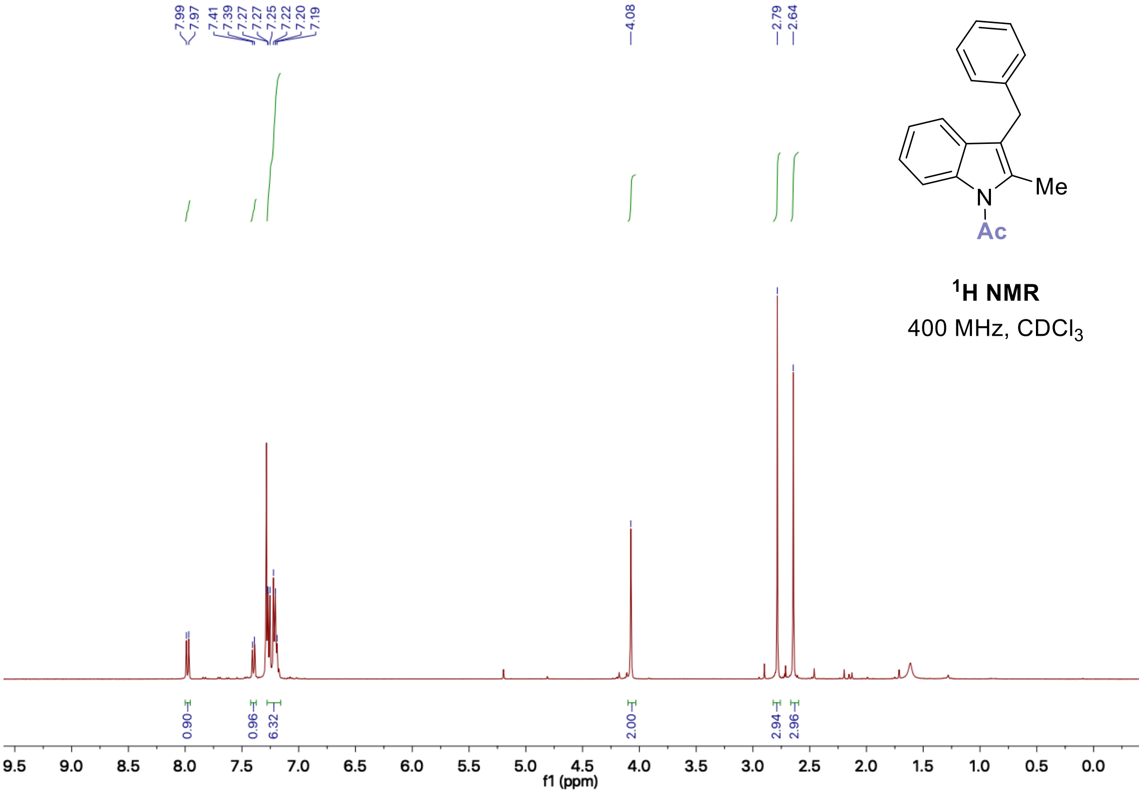
1o - ^{19}F NMR (CDCl$_3$)



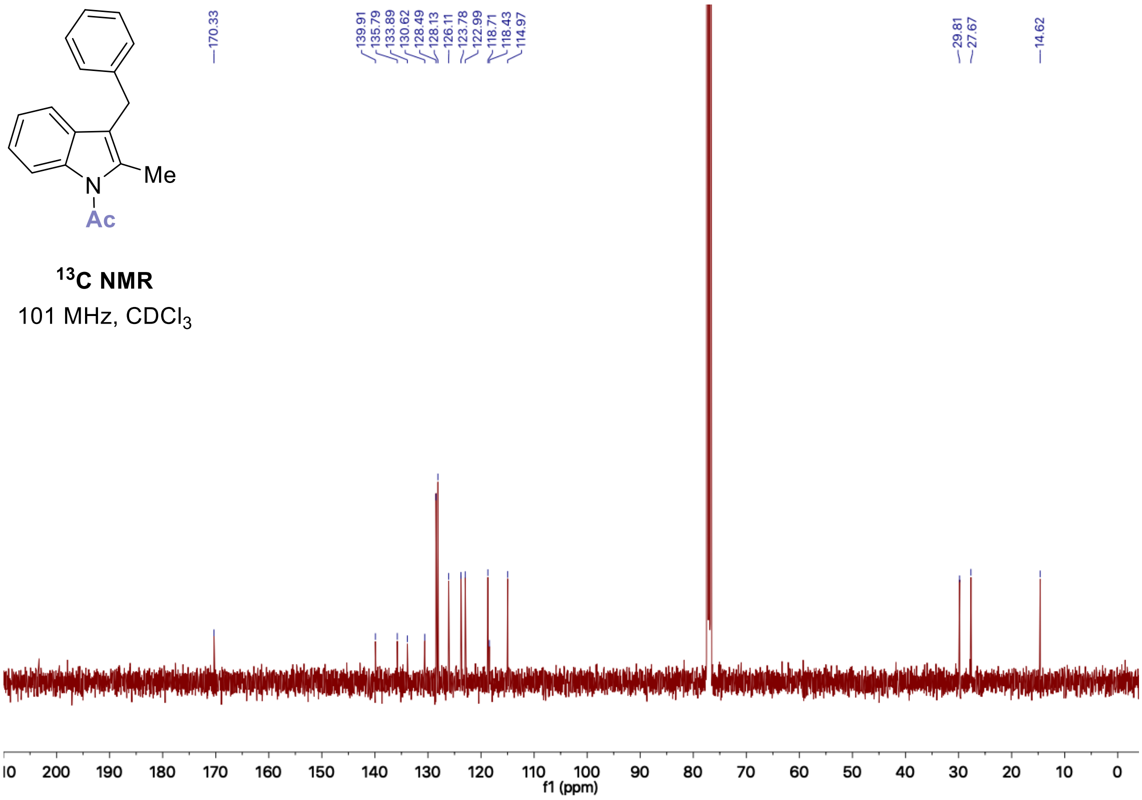
^{19}F NMR

376 MHz, CDCl$_3$

1p - ^{1}H NMR ($CDCl_3$)



1p - ^{13}C NMR ($CDCl_3$)



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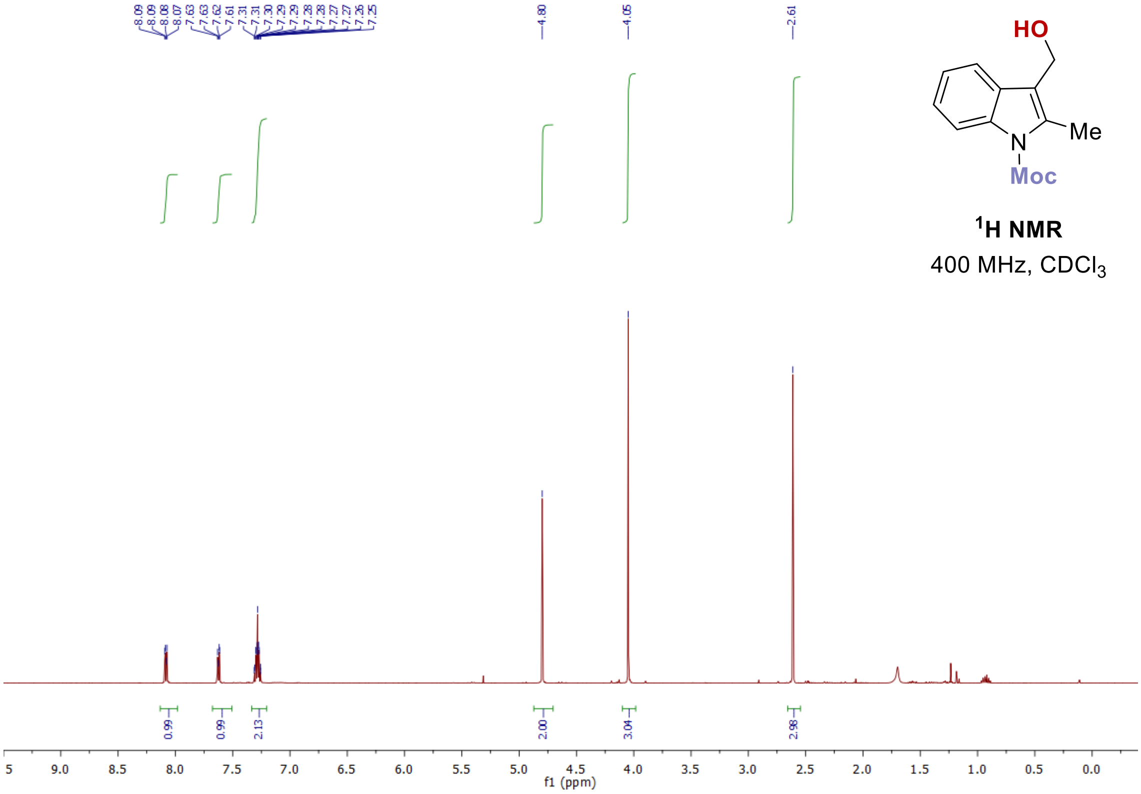
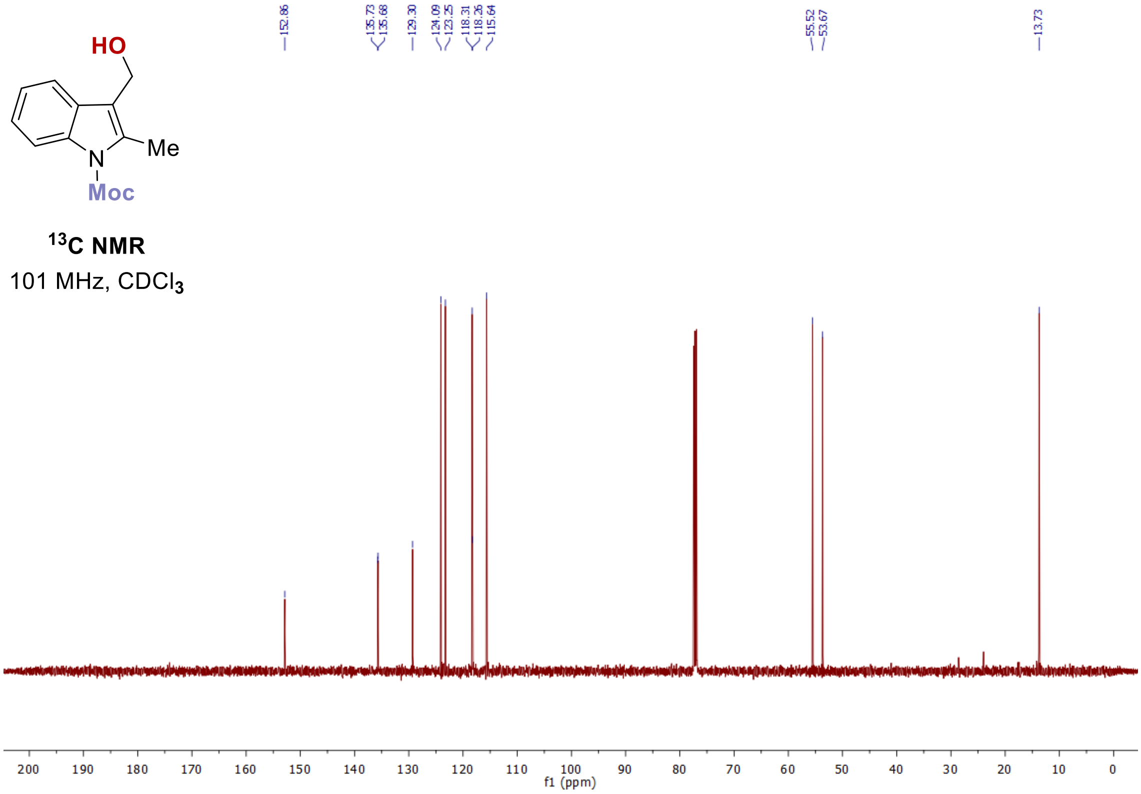


1q - ^{13}C NMR (CDCl$_3$)



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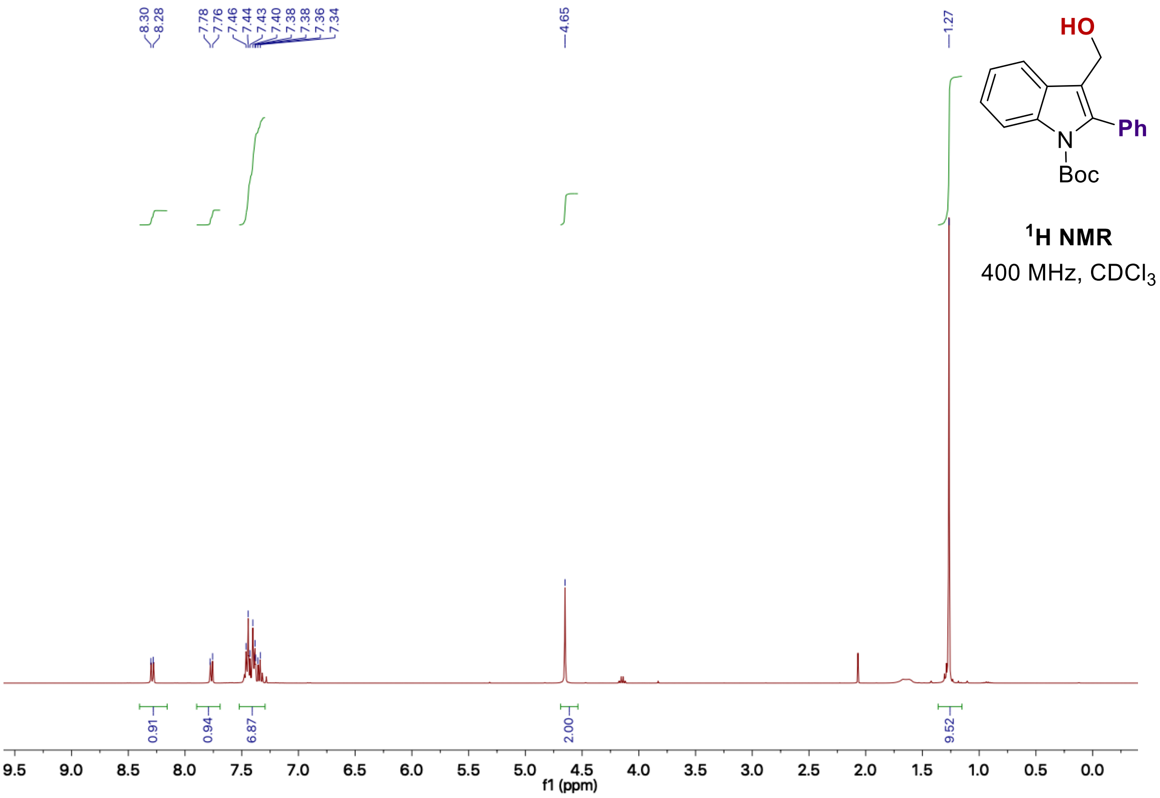

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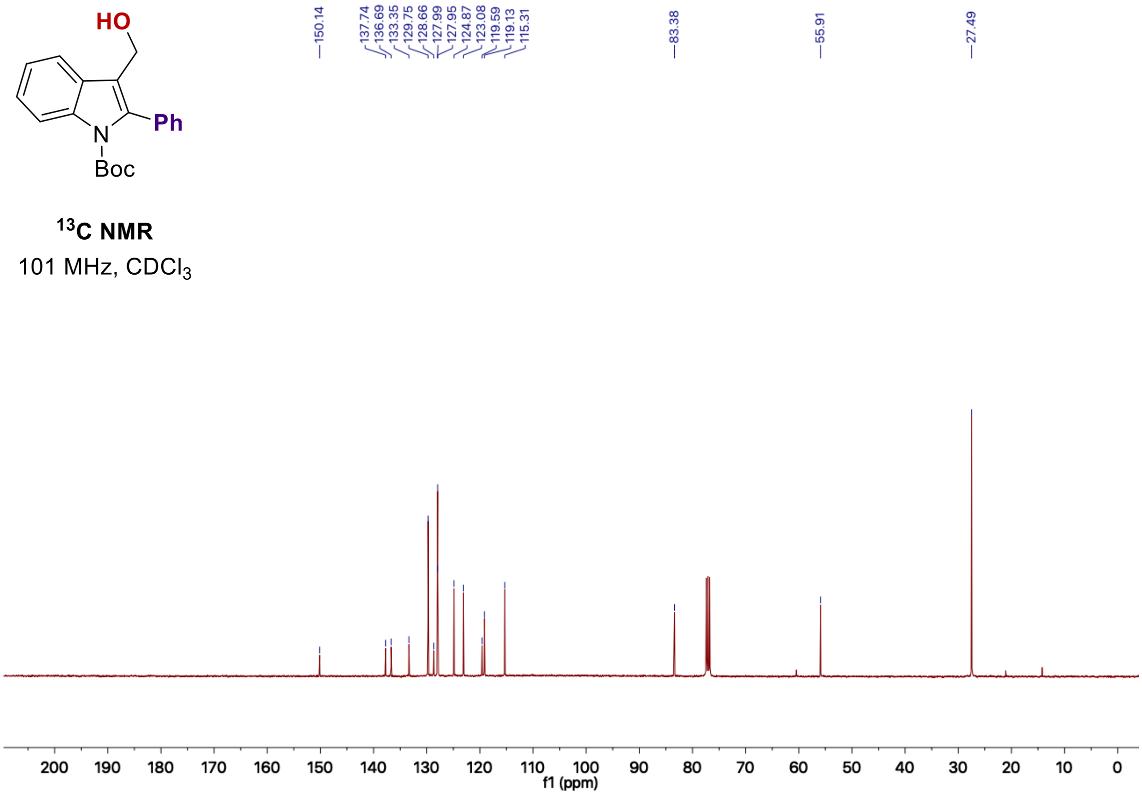
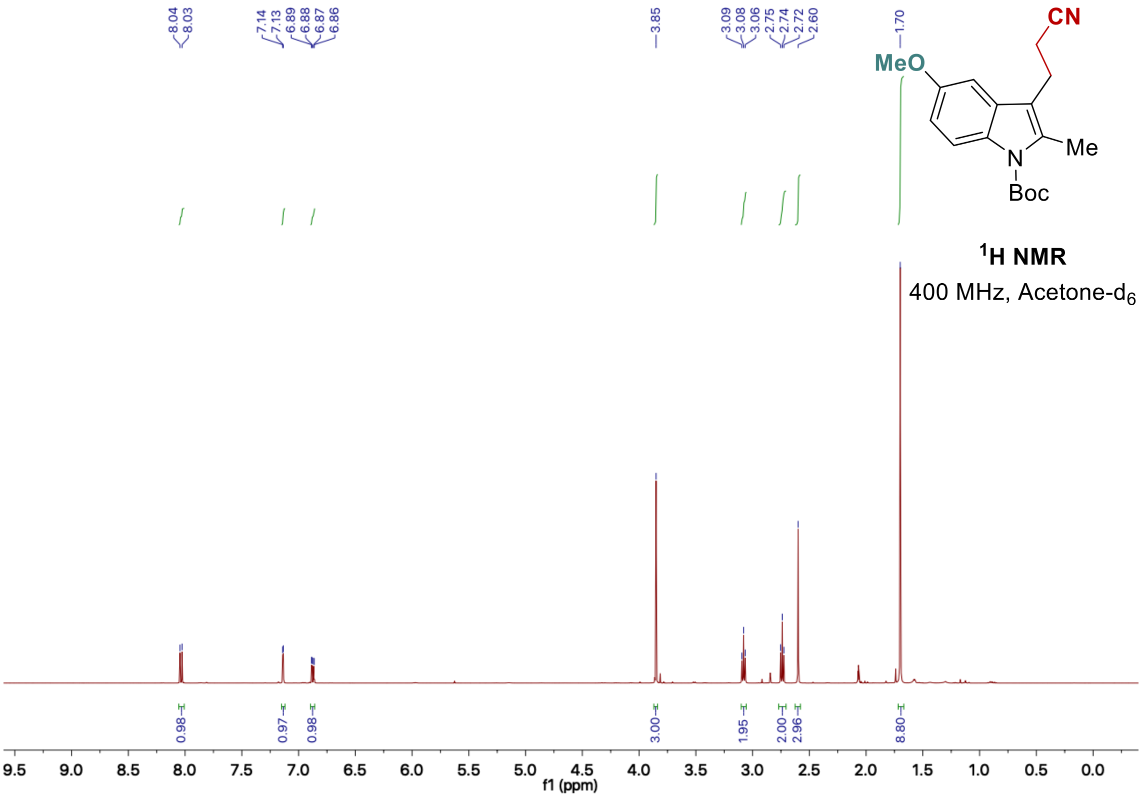


1s - ^{1}H NMR (Acetone-d_6)



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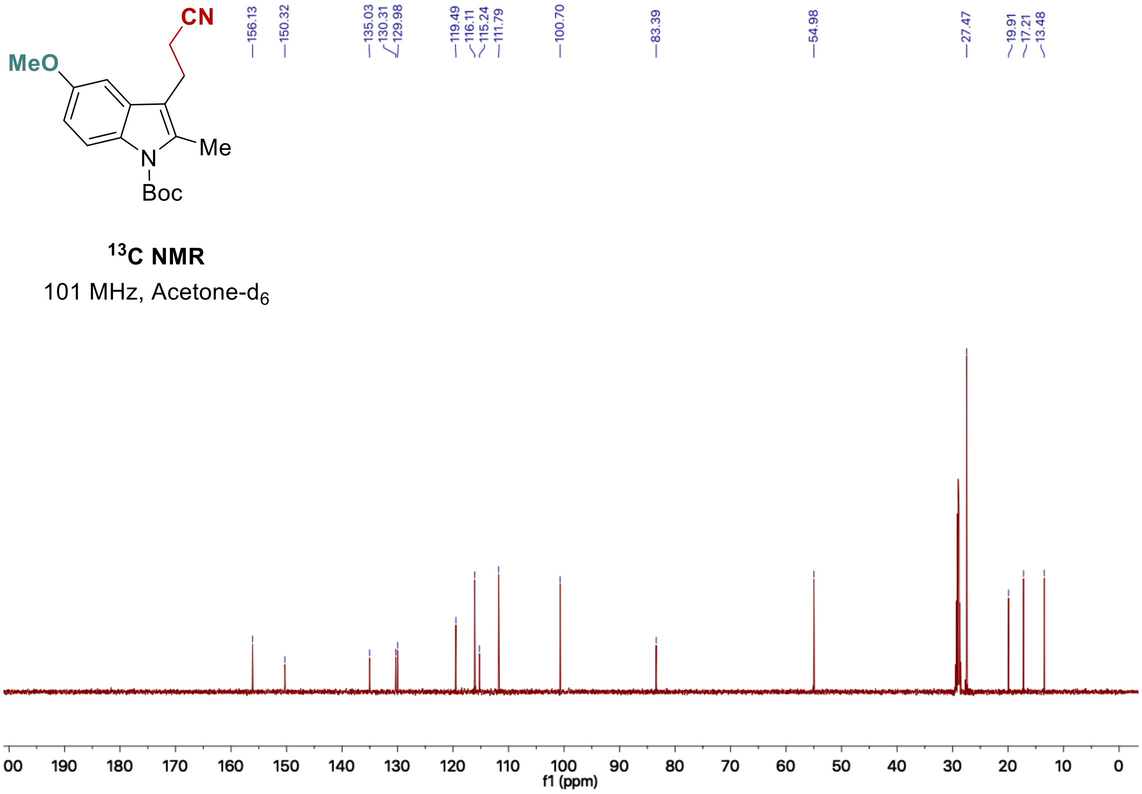

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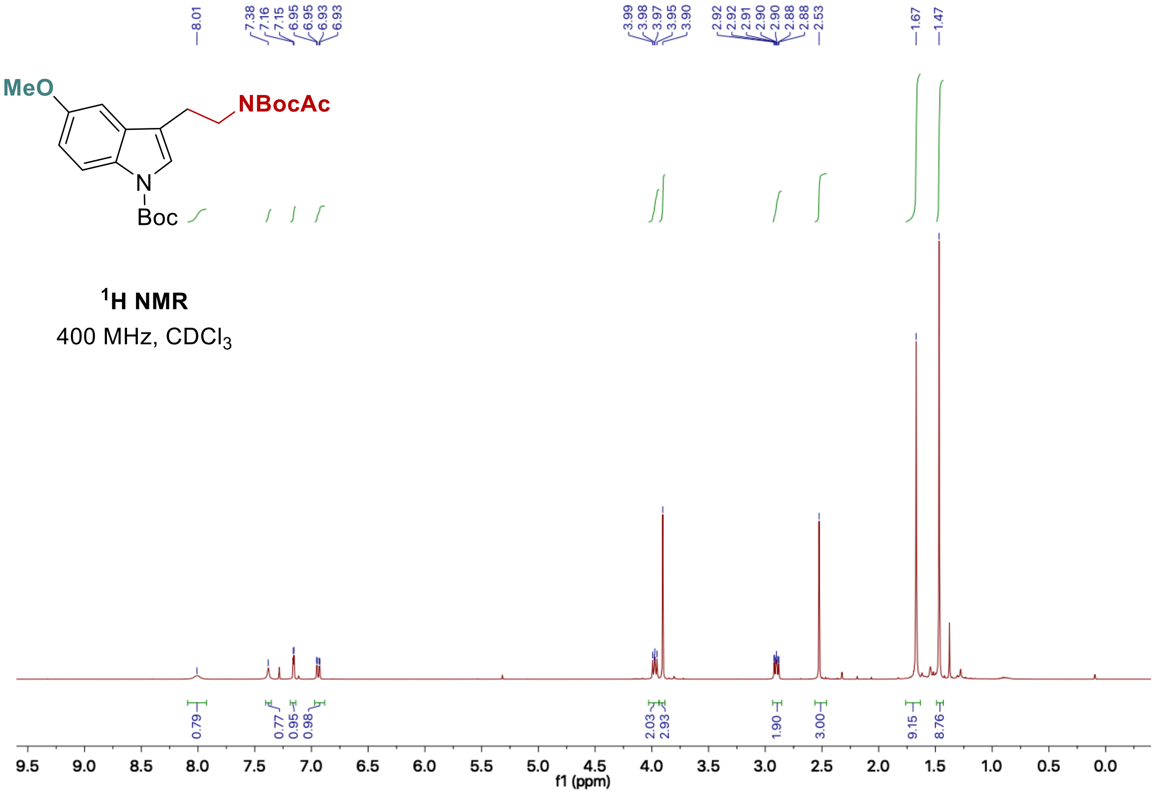

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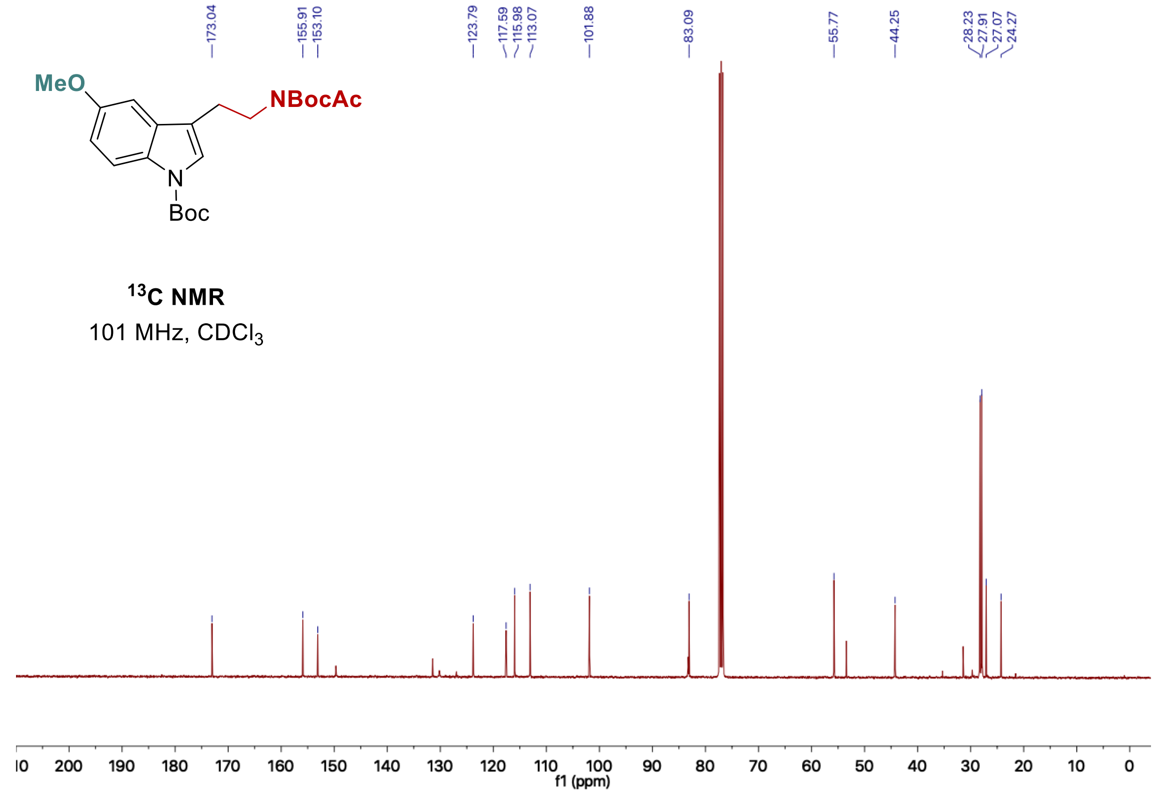
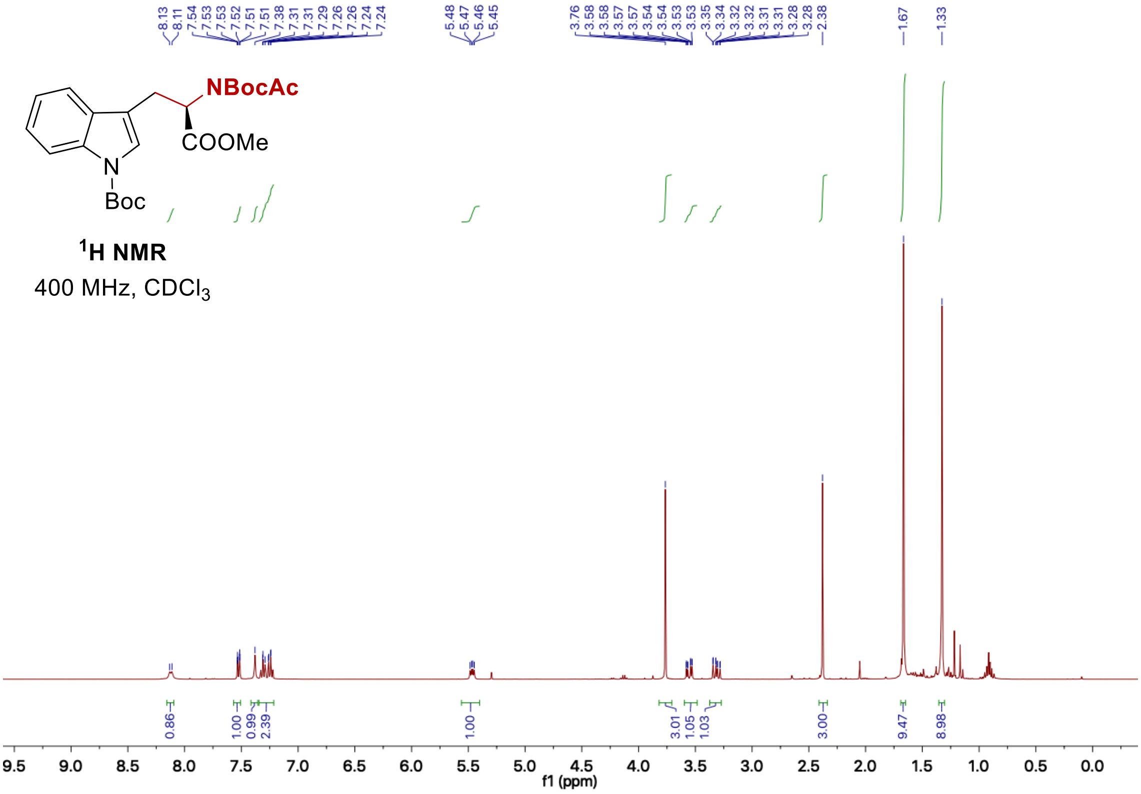


1x - ^{1}H NMR ($CDCl_3$)



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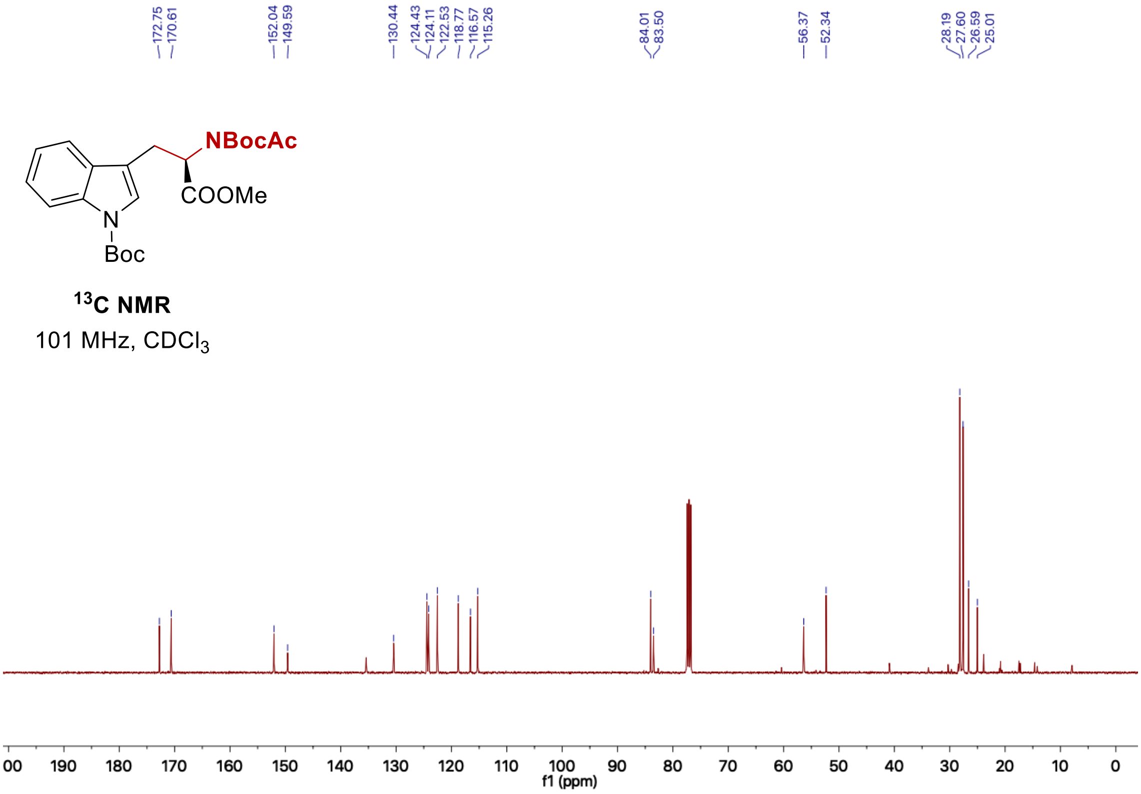

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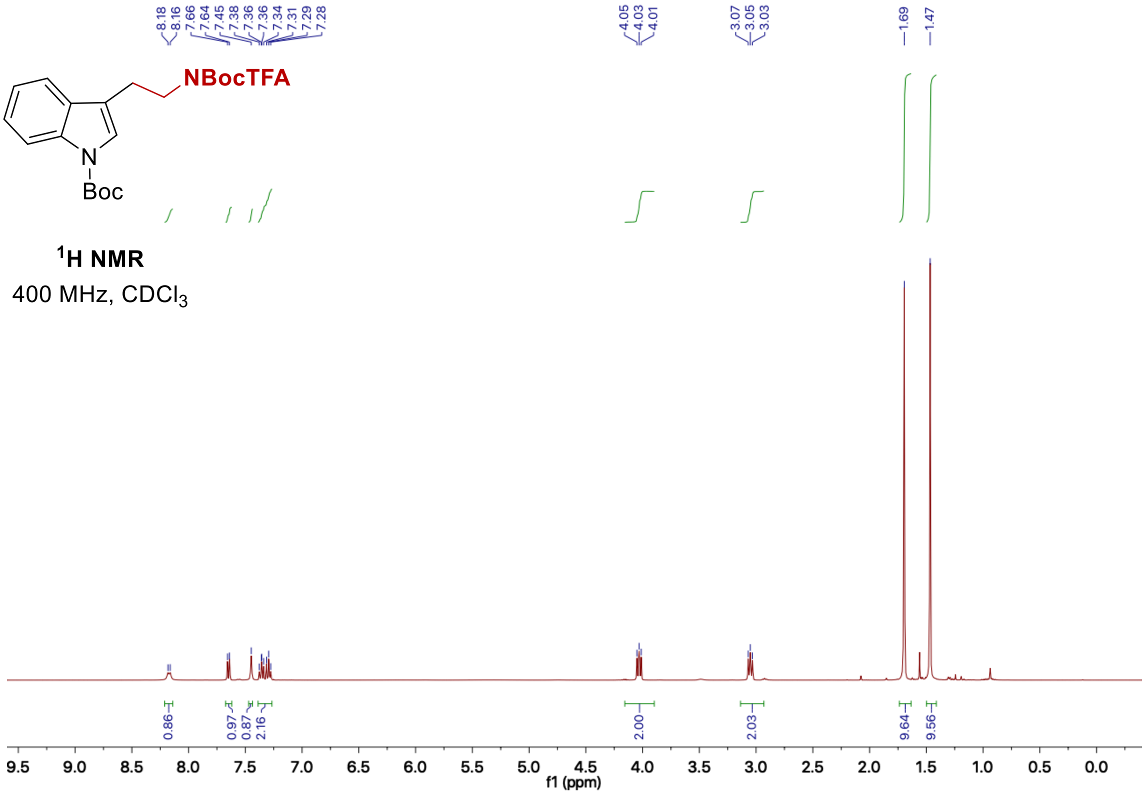

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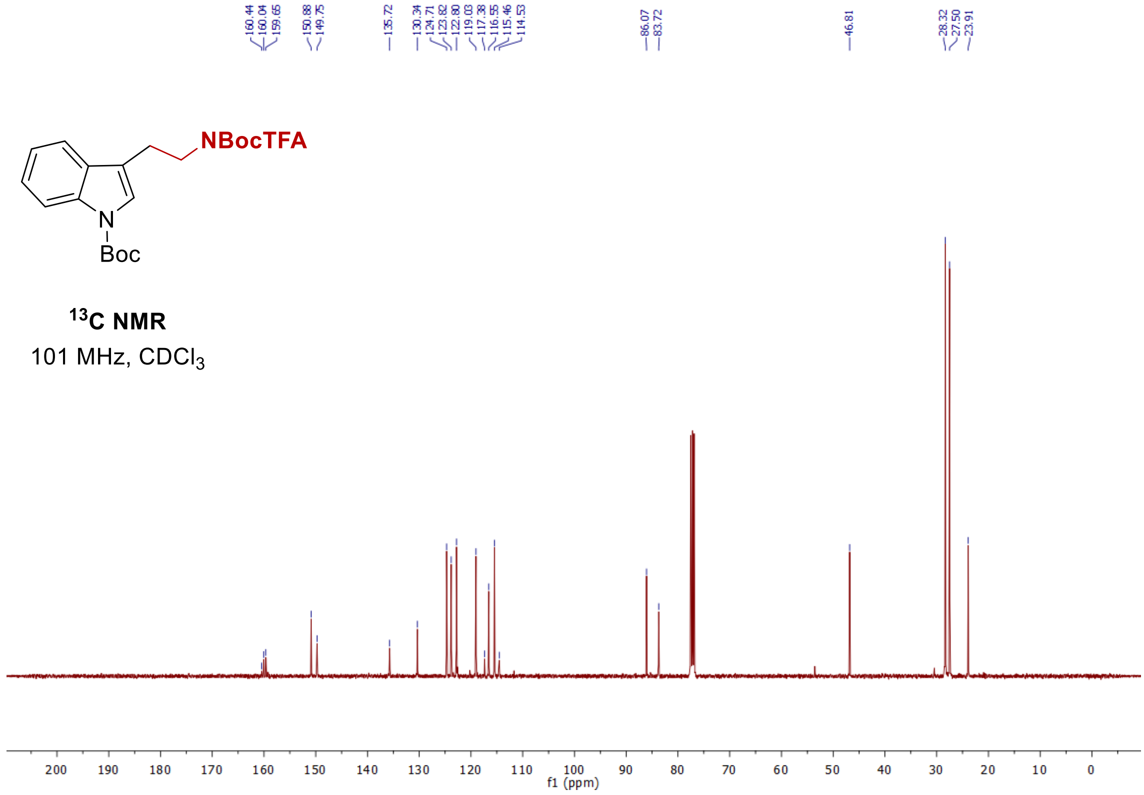
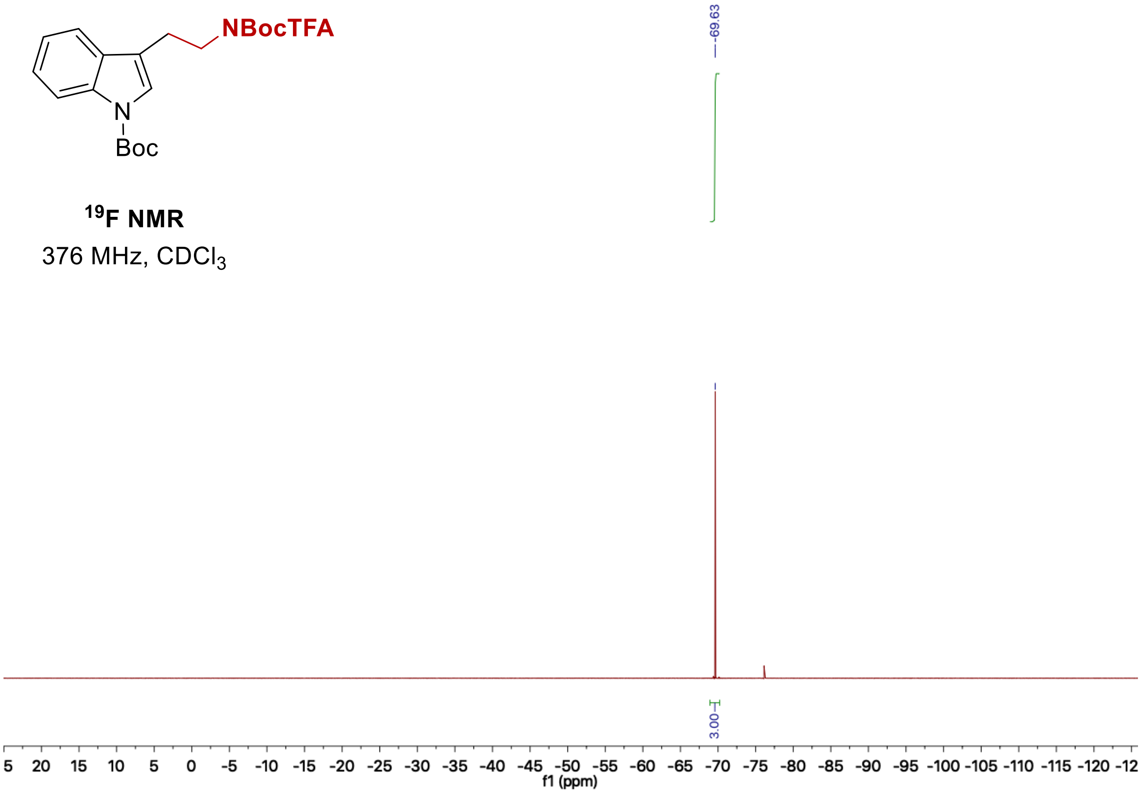


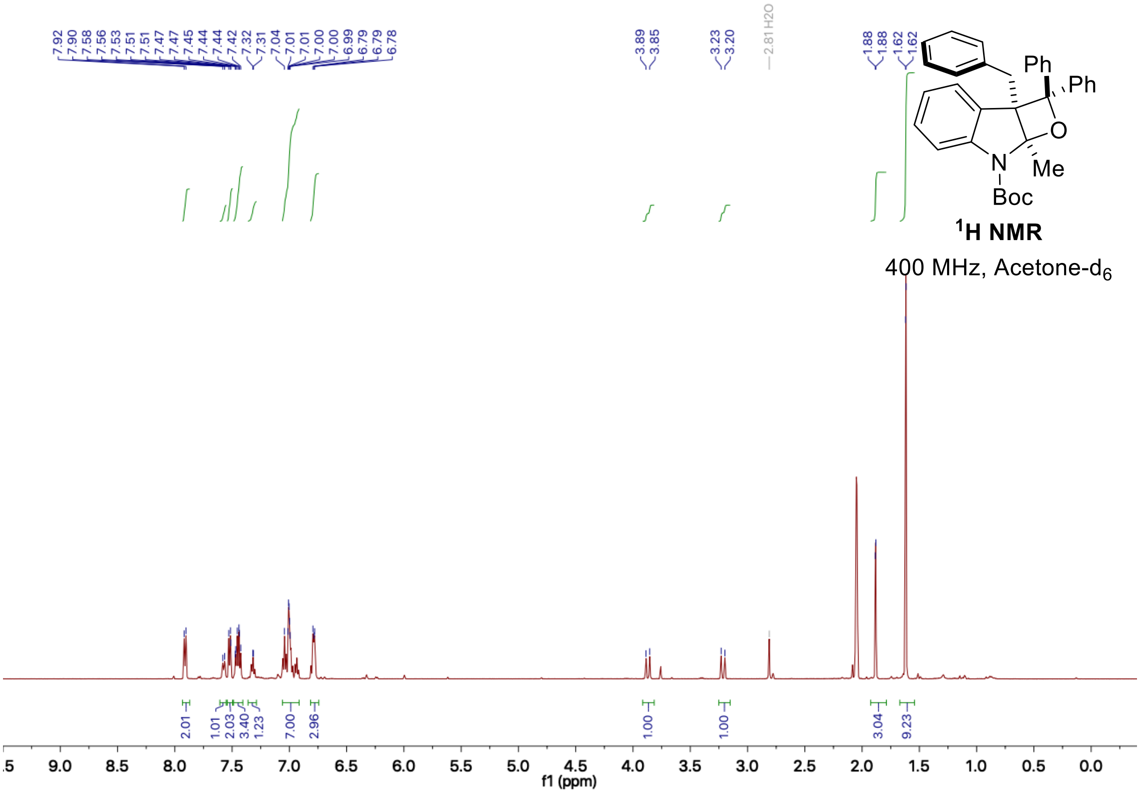
1y - ^{19}F NMR ($CDCl_3$)



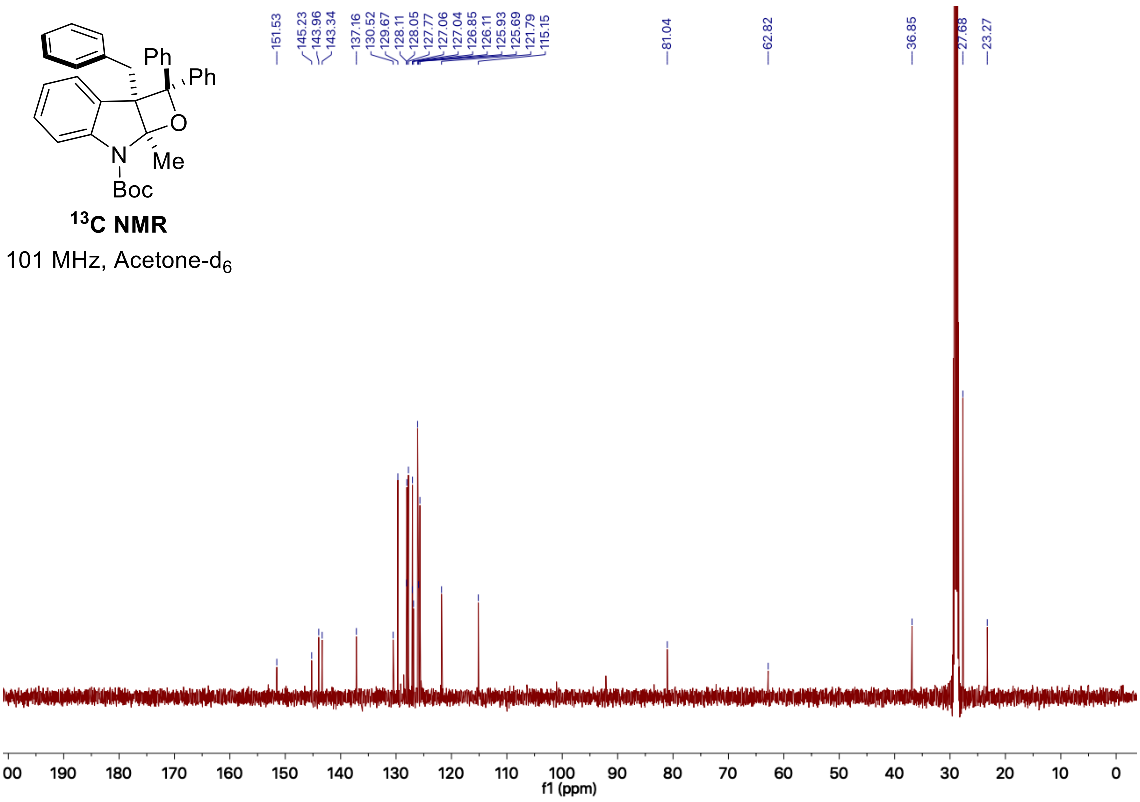
^{19}F NMR
376 MHz, $CDCl_3$

J. NMR SPECTRA OF THE PATERNÒ-BÜCHI PRODUCTS

3d - ^{1}H NMR (Acetone-d$_6$)



3d - ^{13}C NMR (Acetone-d$_6$)



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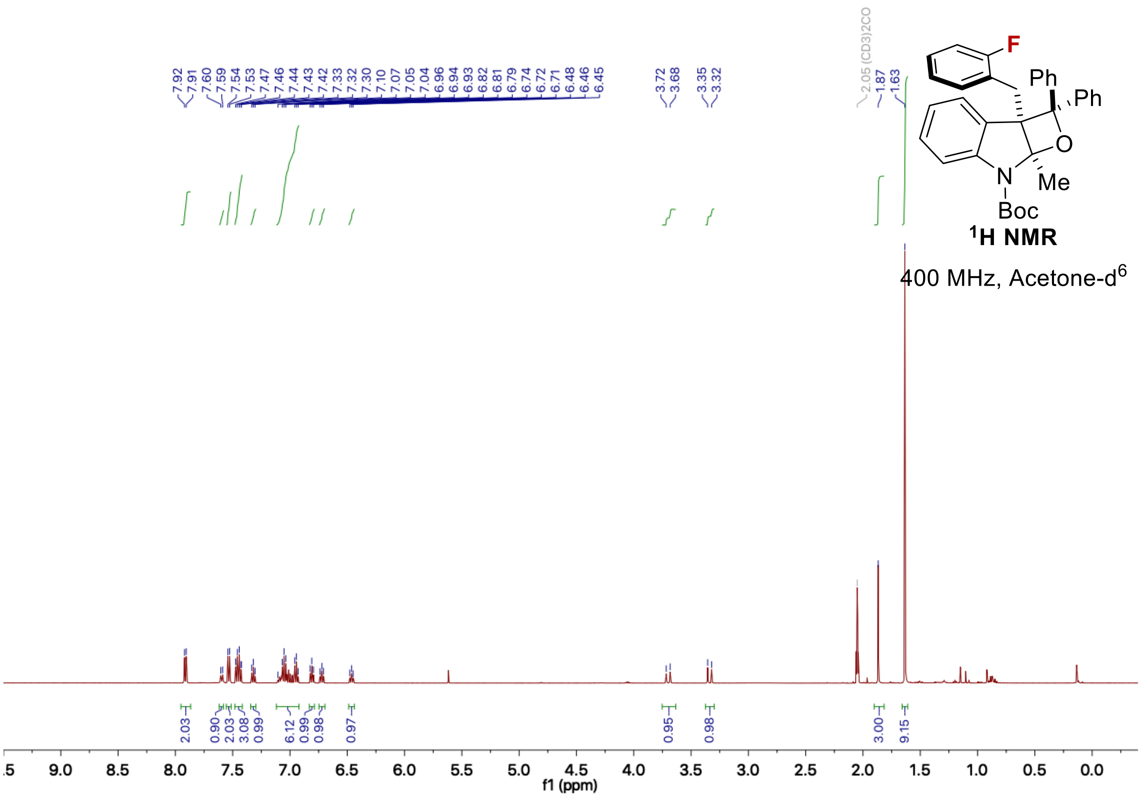

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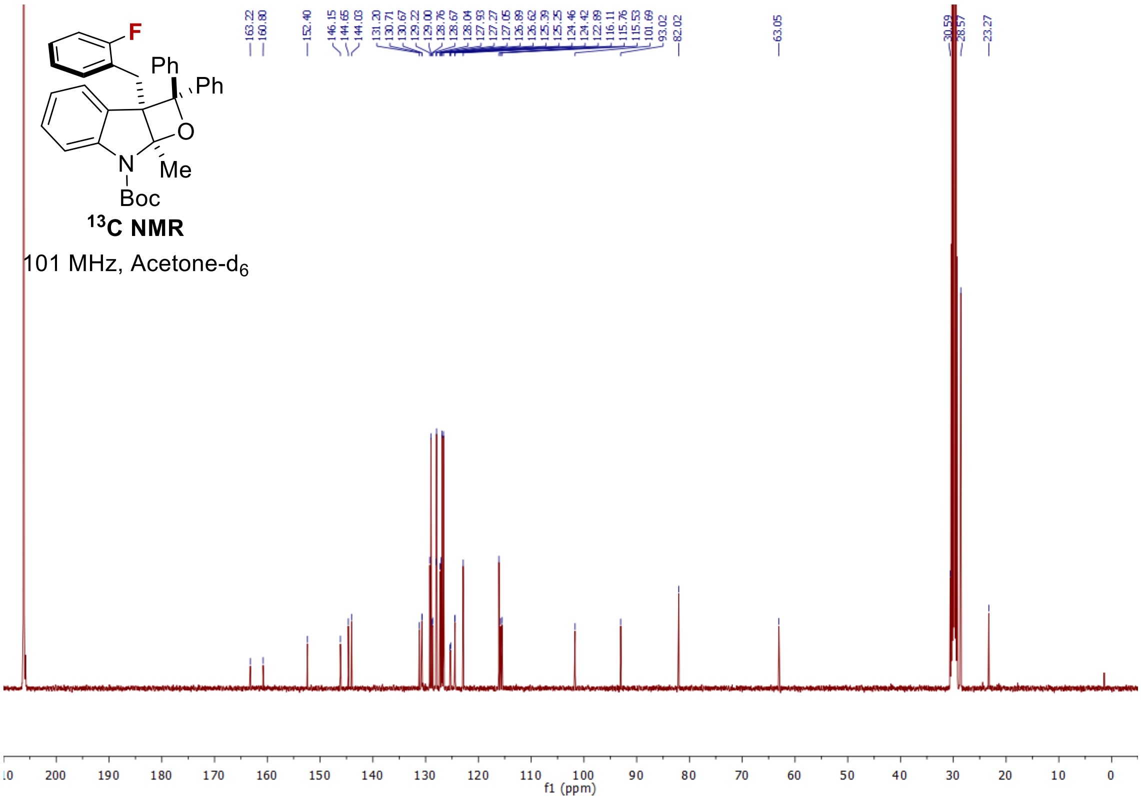

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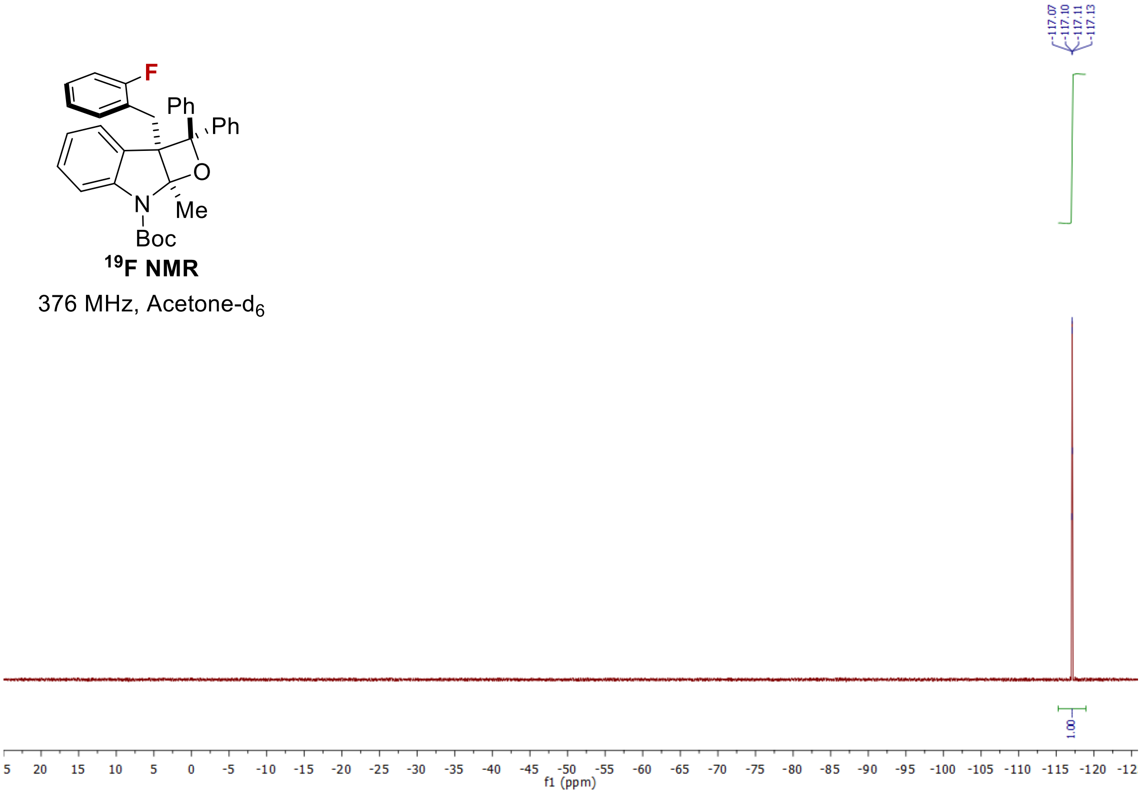

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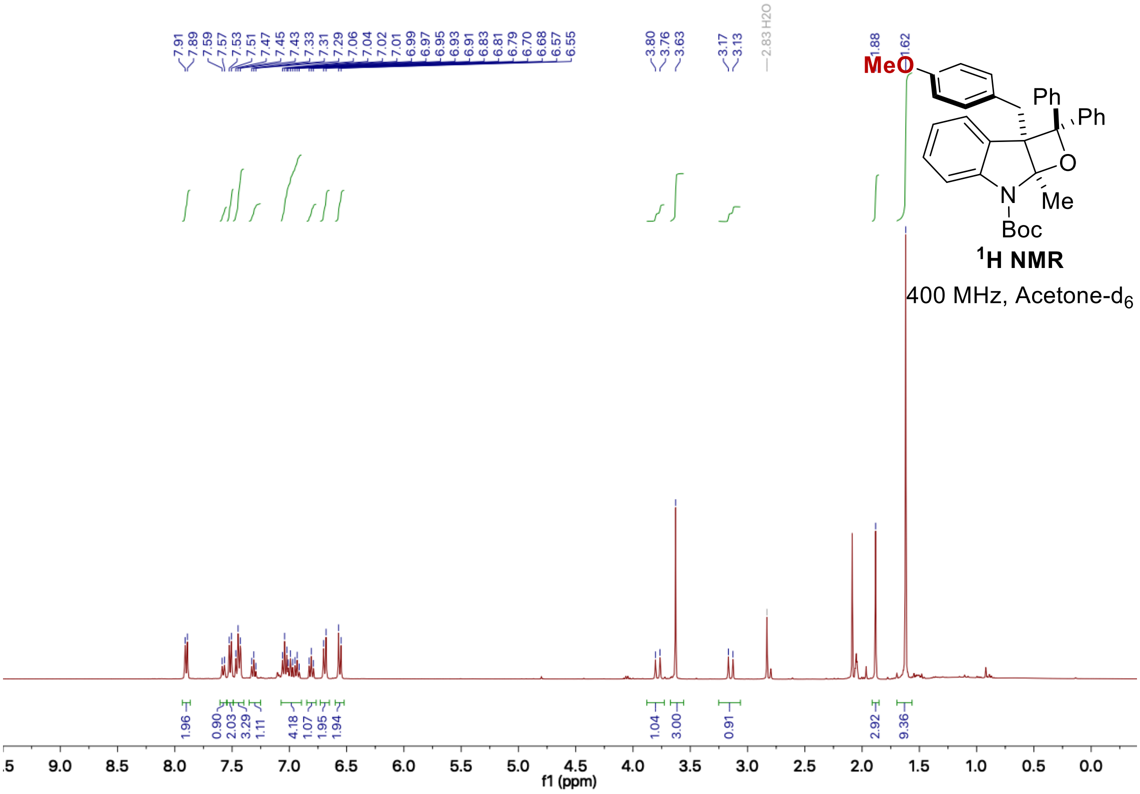

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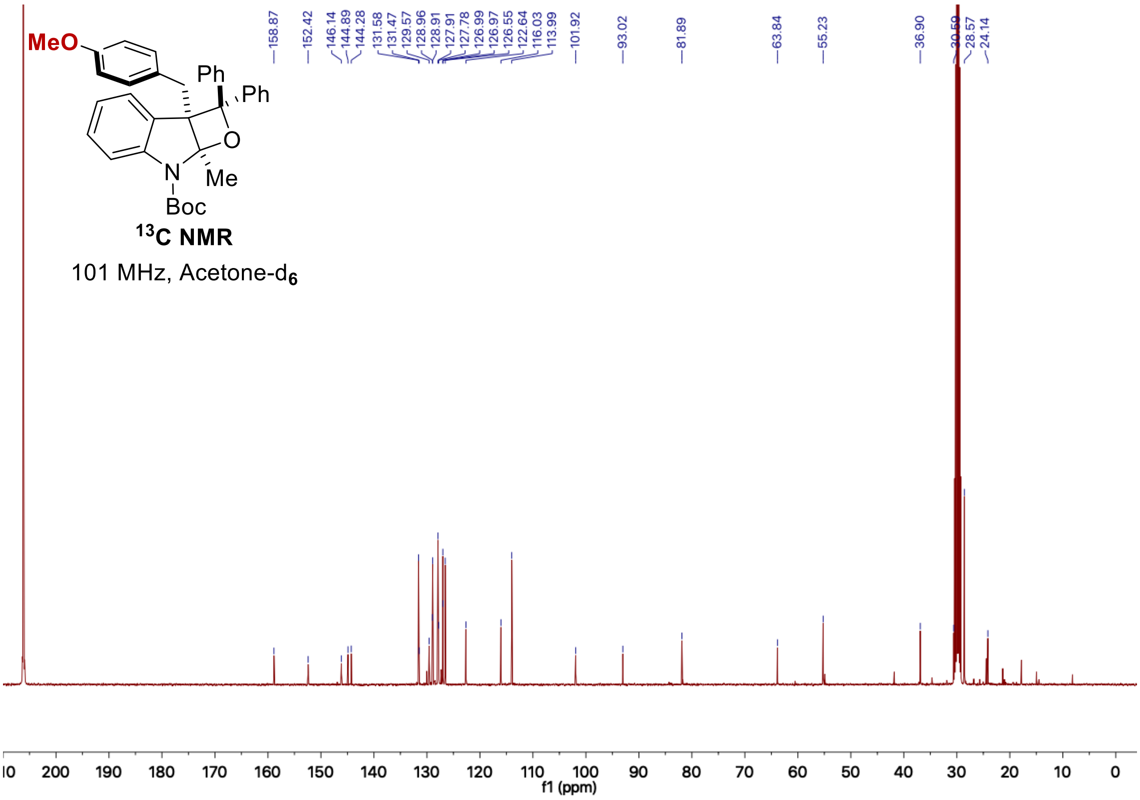
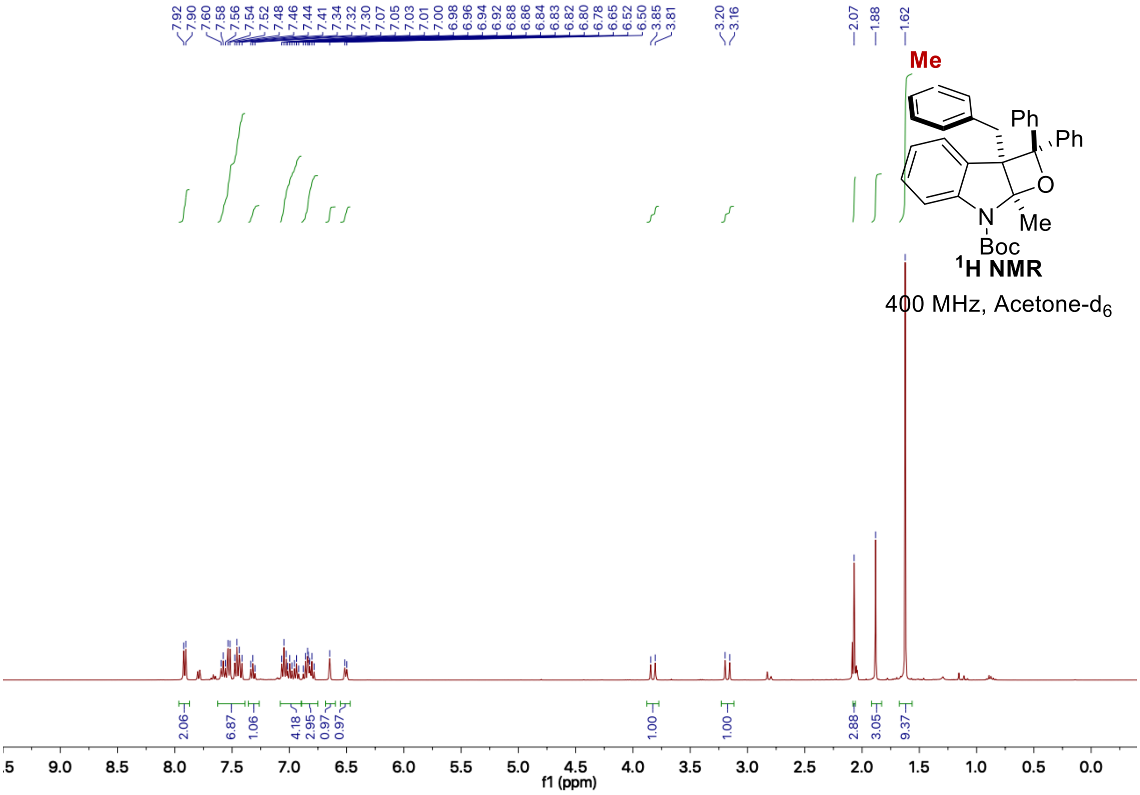
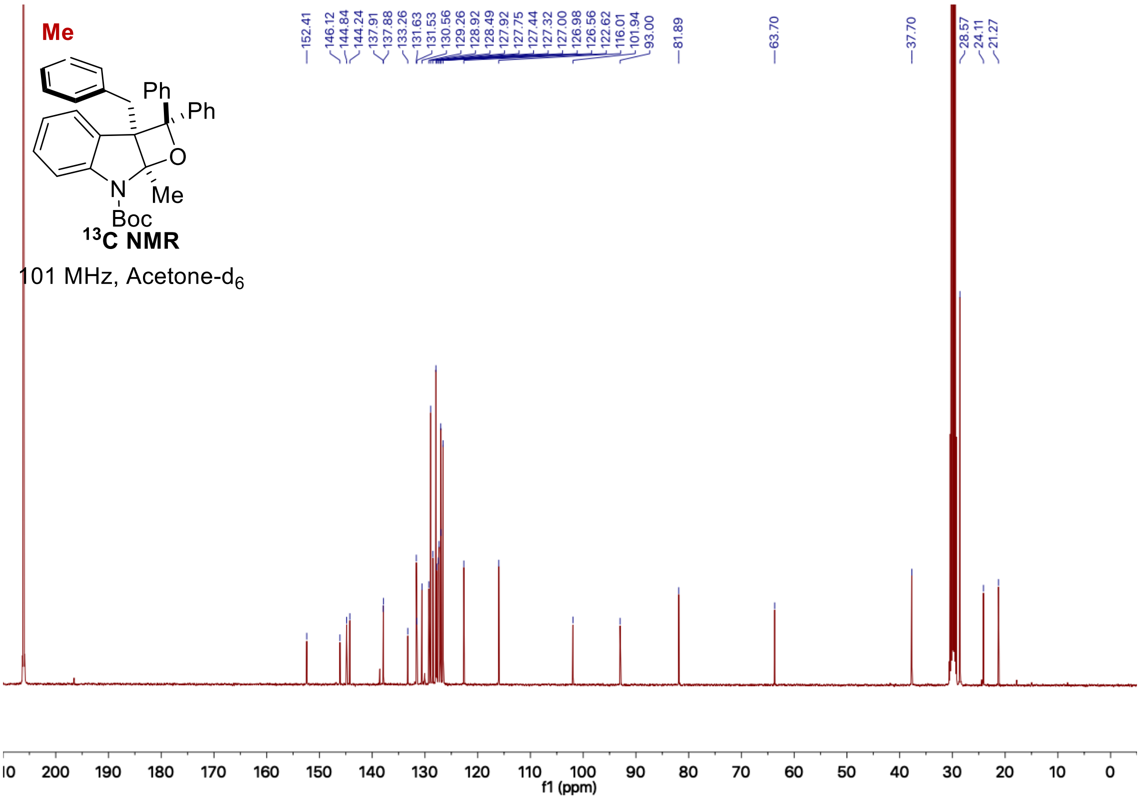


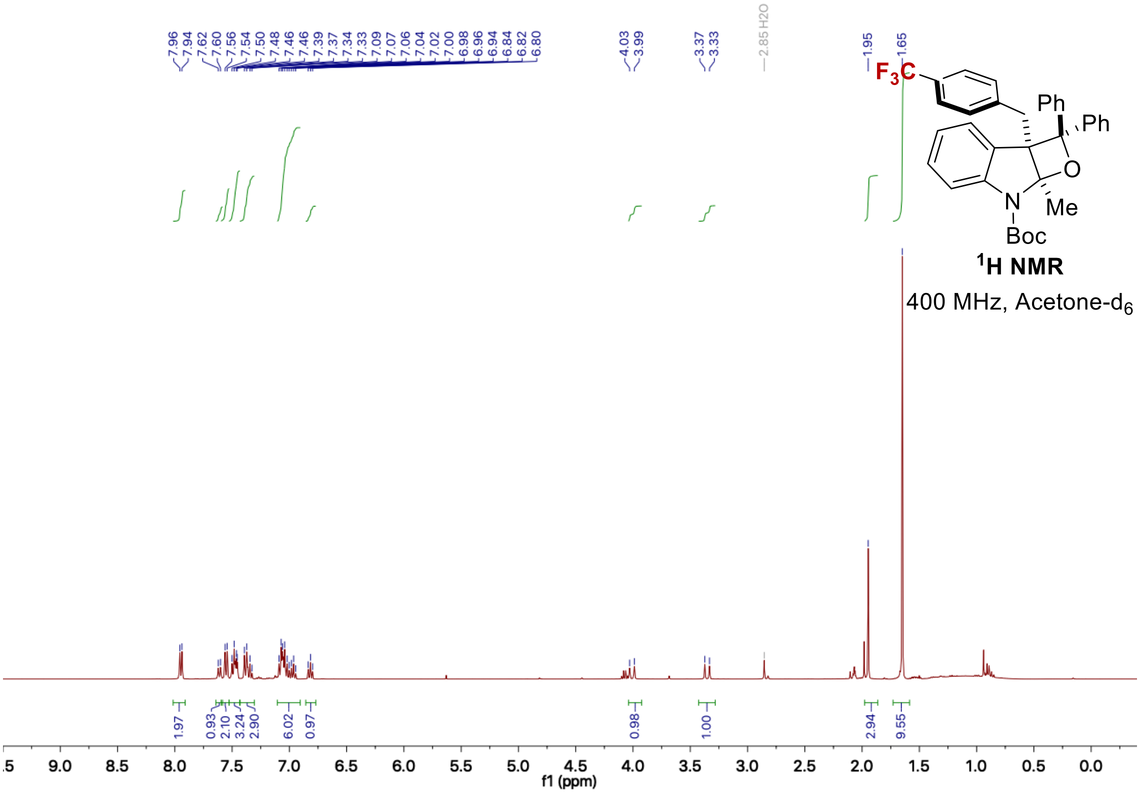
7 - ^{1}H NMR (Acetone-d$_6$)



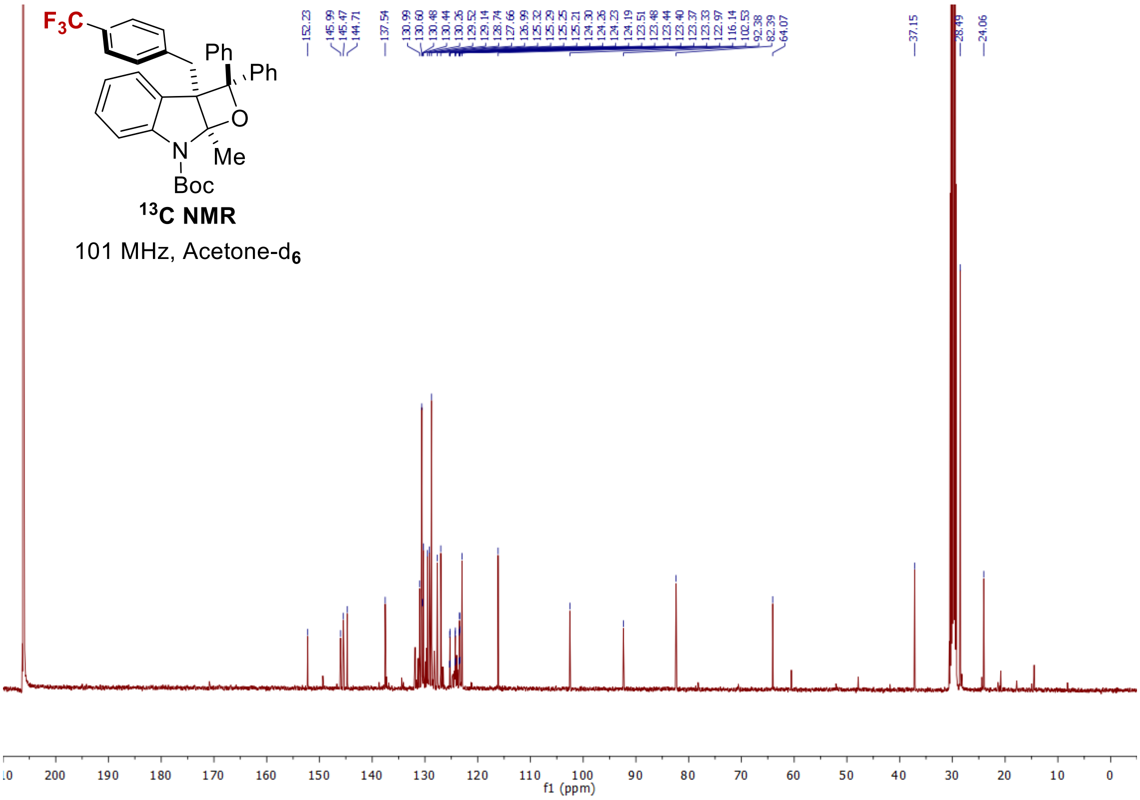
7 - ^{13}C NMR (Acetone-d$_6$)



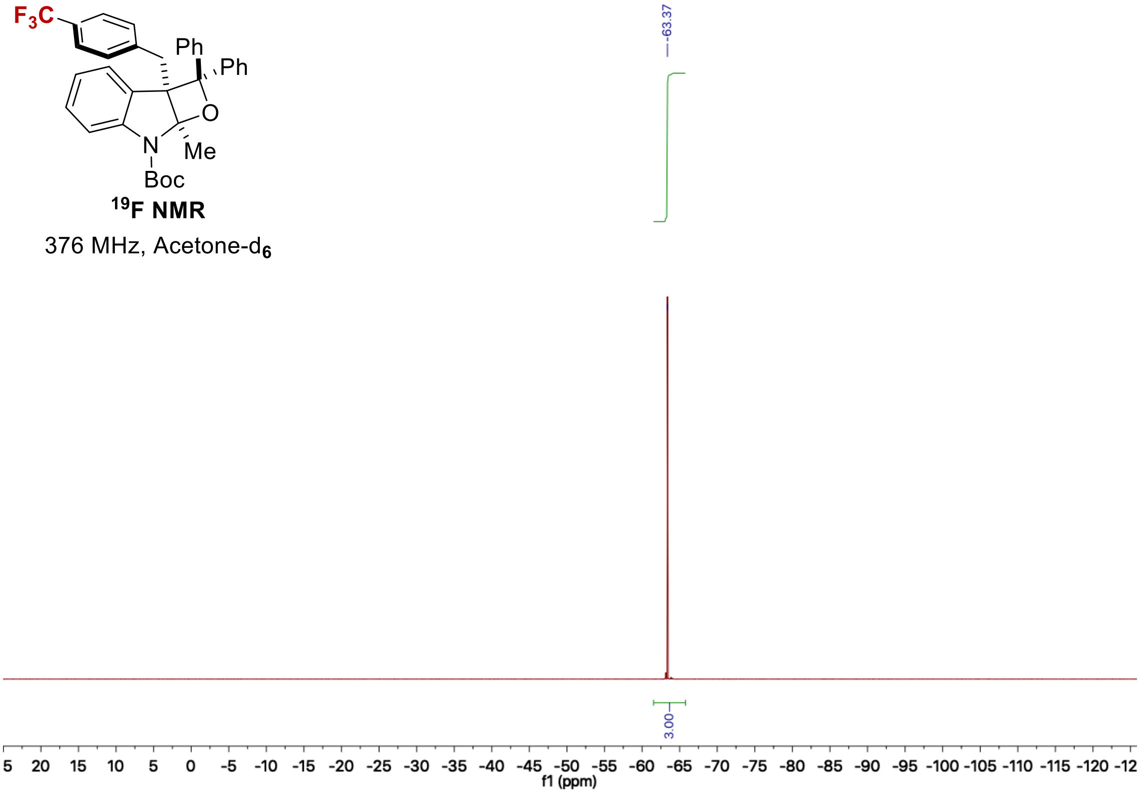
8 - ^{1}H NMR (Acetone-d$_6$)



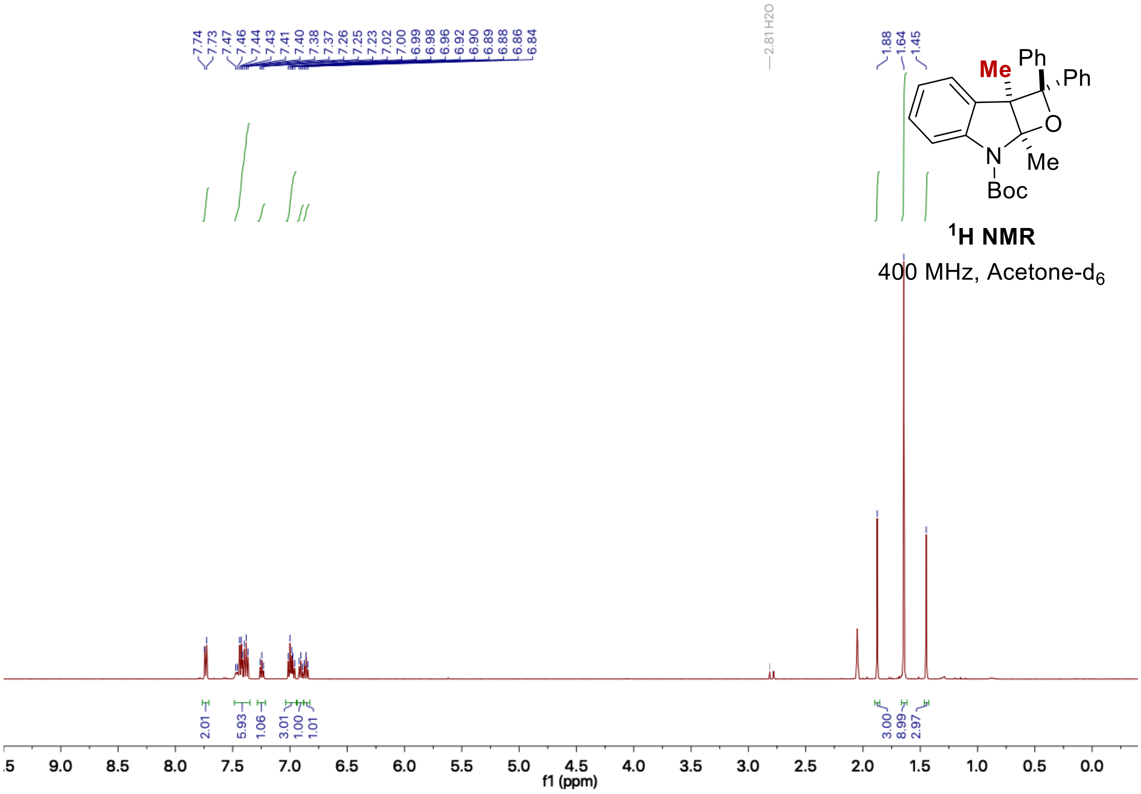
8 - ^{13}C NMR (Acetone-d$_6$)



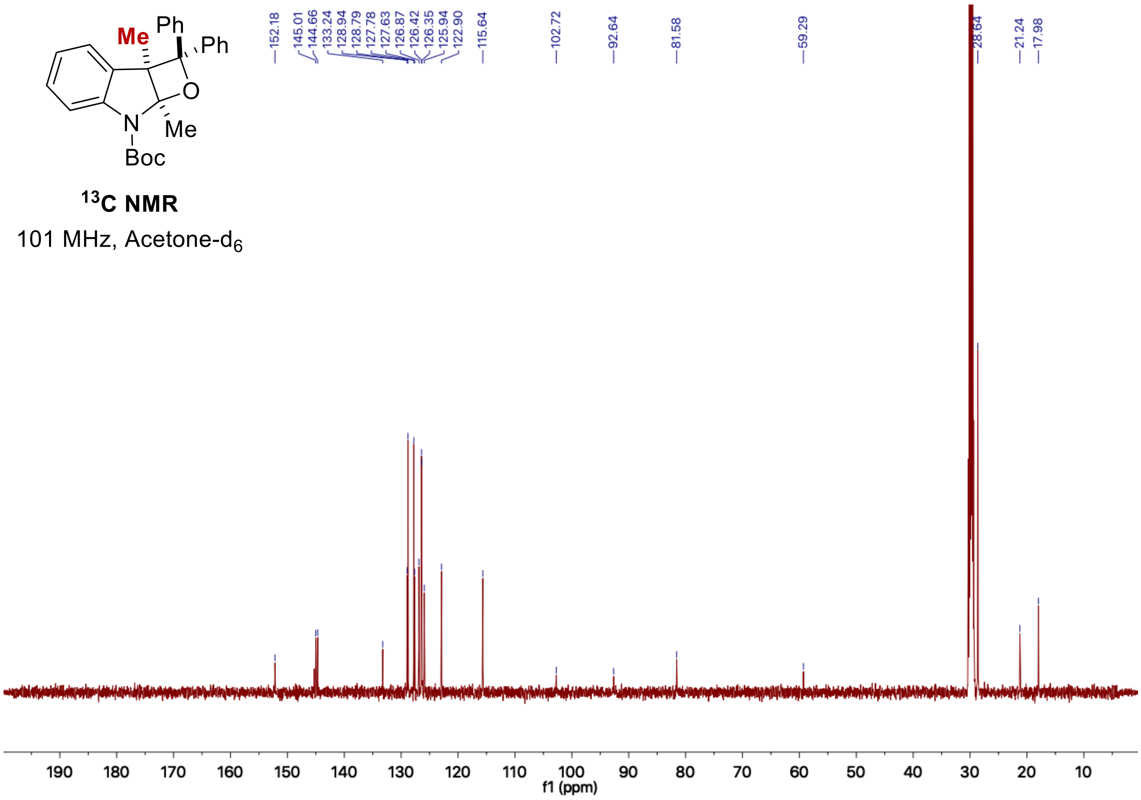
8 - ¹⁹F NMR (Acetone-d$_6$)



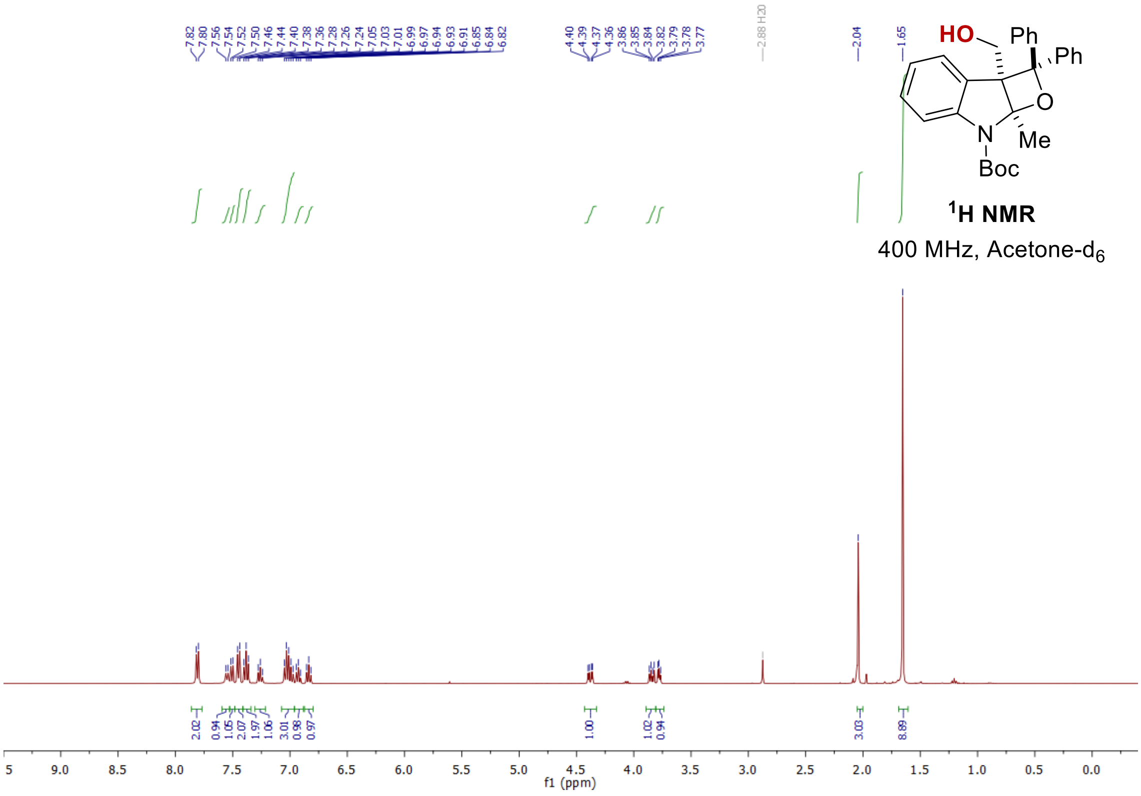
9 - ^{1}H NMR (Acetone-d_6)



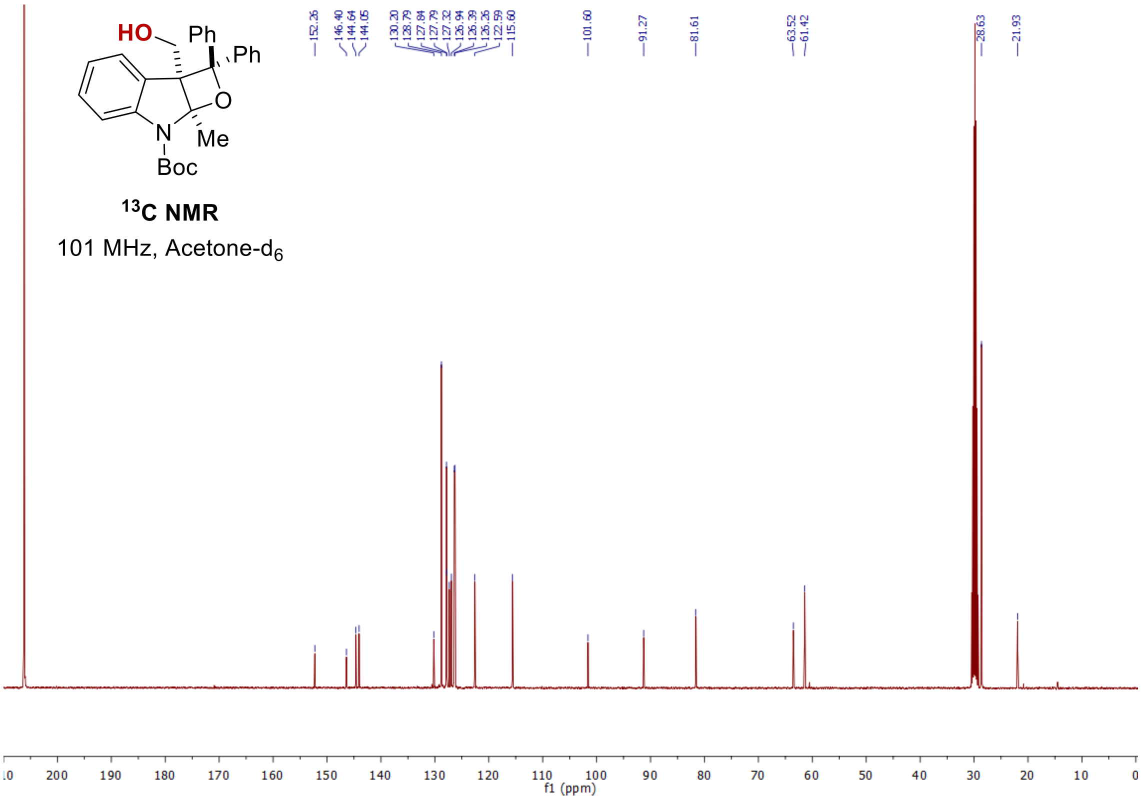
9 - ^{13}C NMR (Acetone-d_6)



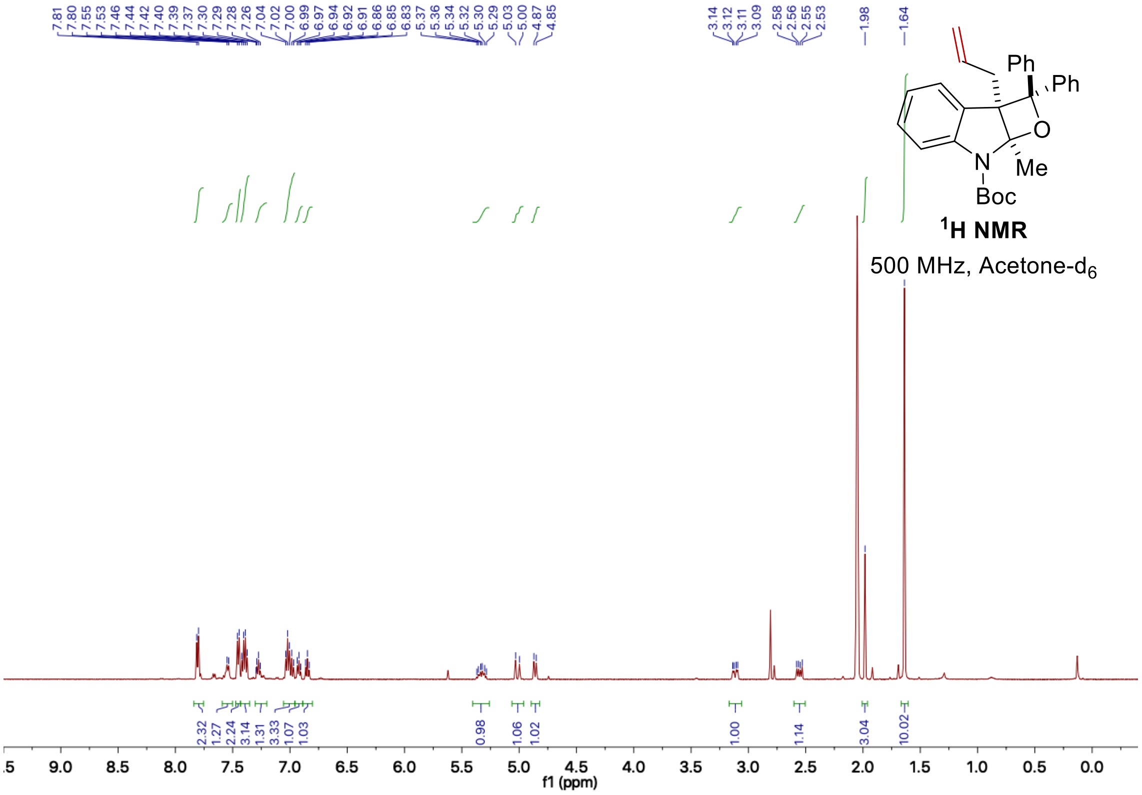
10 - ^{1}H NMR (Acetone-d$_6$)



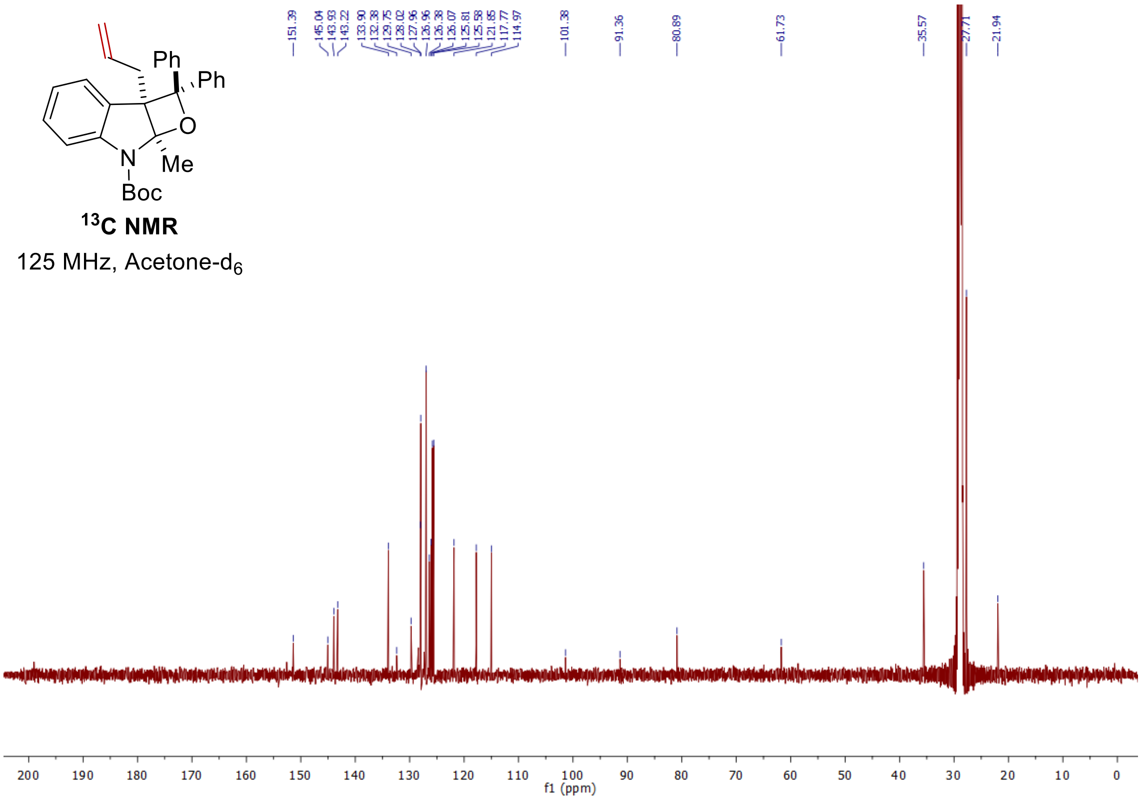
10 - ^{13}C NMR (Acetone-d$_6$)



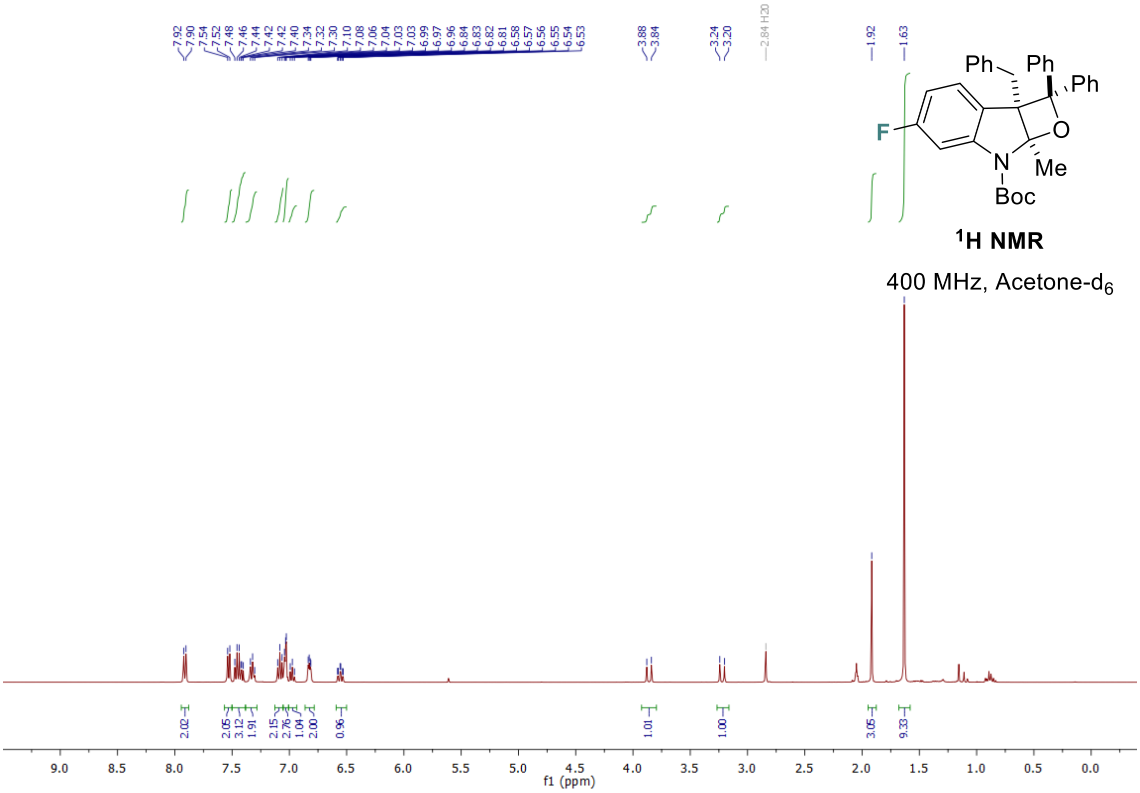
11 - ^{1}H NMR (Acetone-d$_6$)



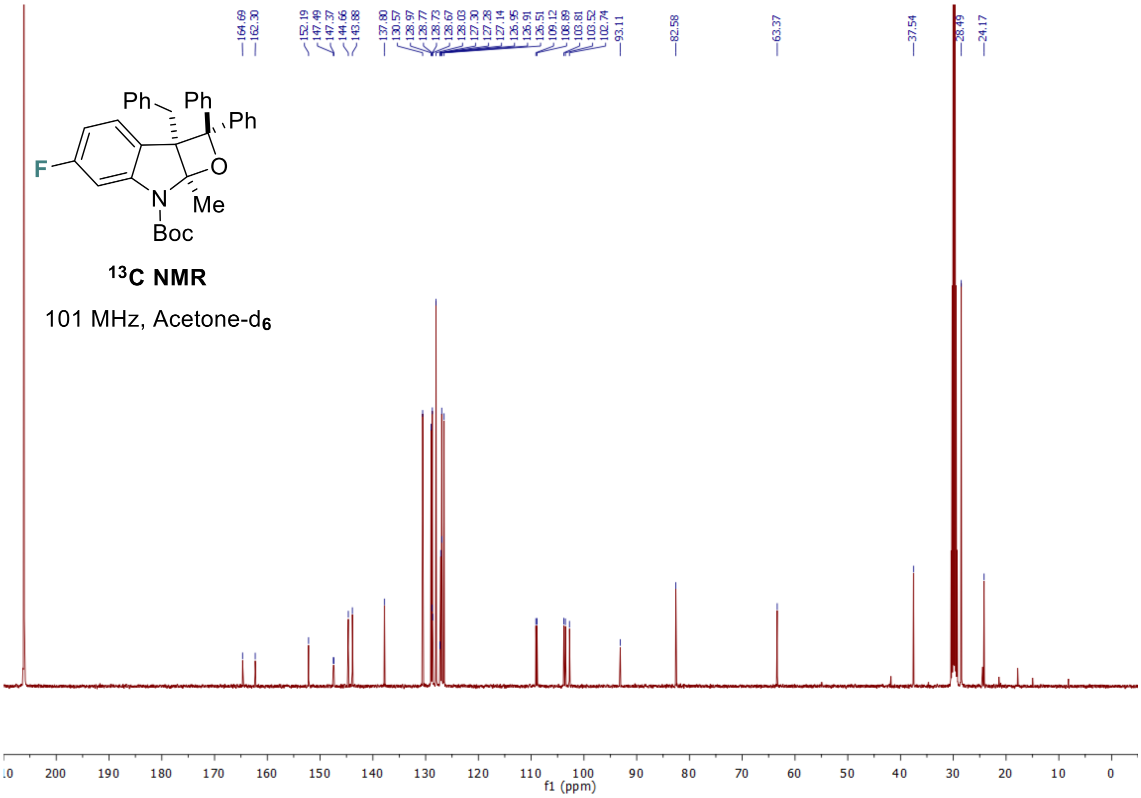
11 - ^{13}C NMR (Acetone-d$_6$)



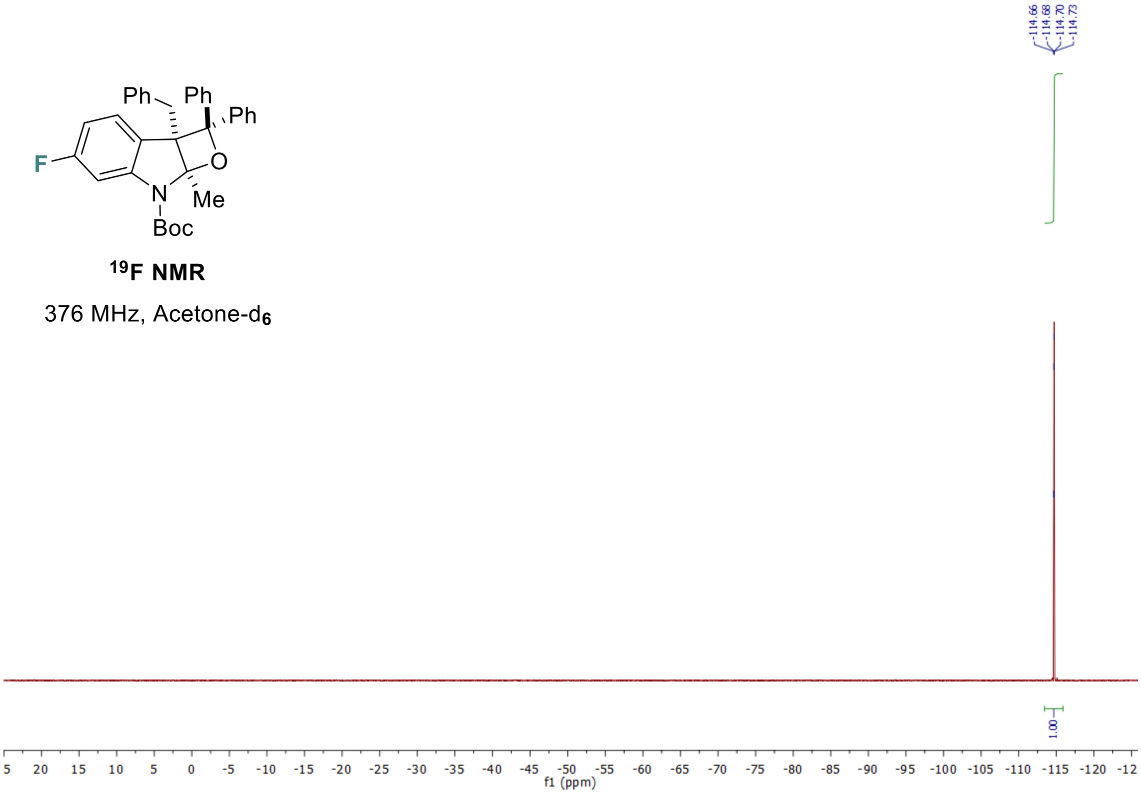
12 - ^{1}H NMR (Acetone-d$_6$)



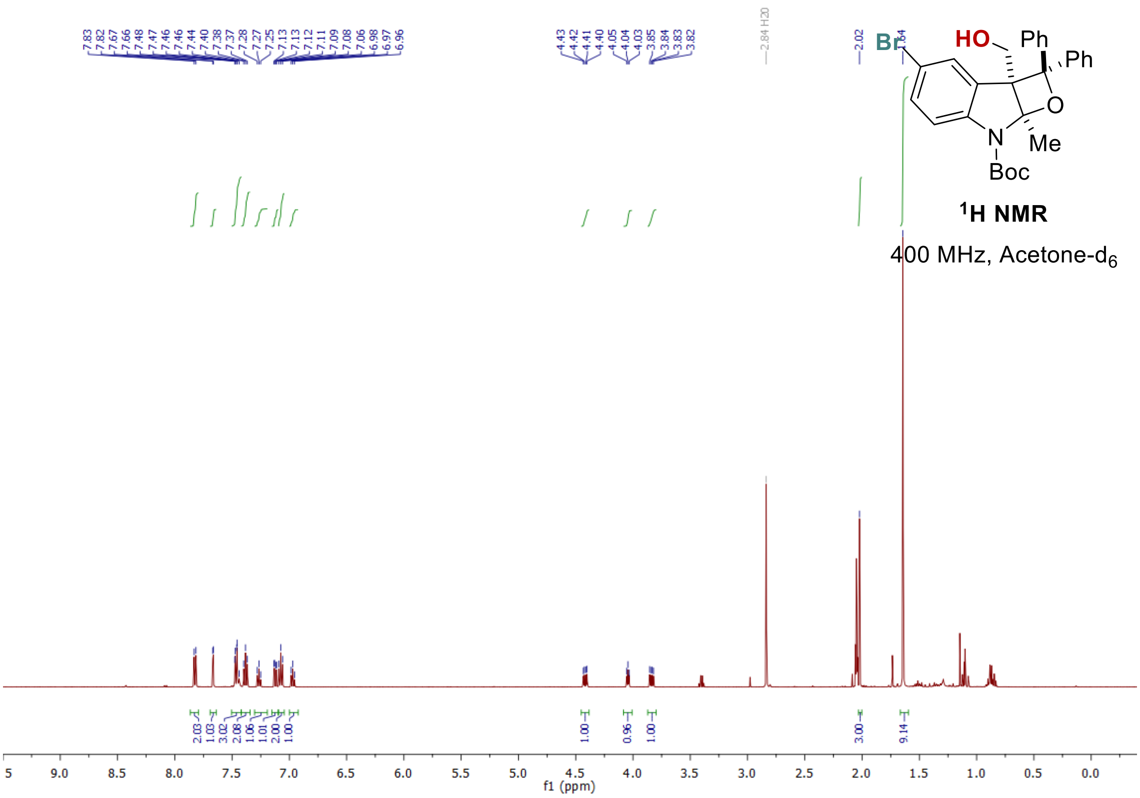
12 - ^{13}C NMR (Acetone-d$_6$)



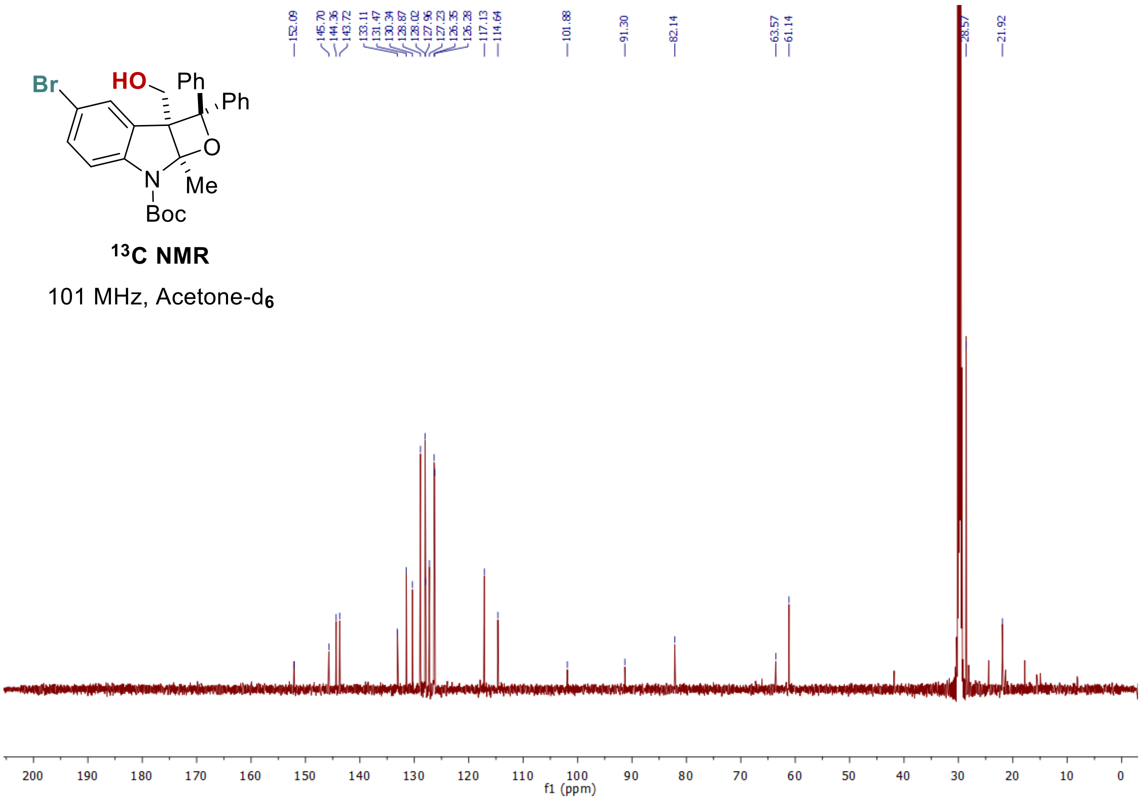
12 - ^{19}F NMR (Acetone-d$_6$)



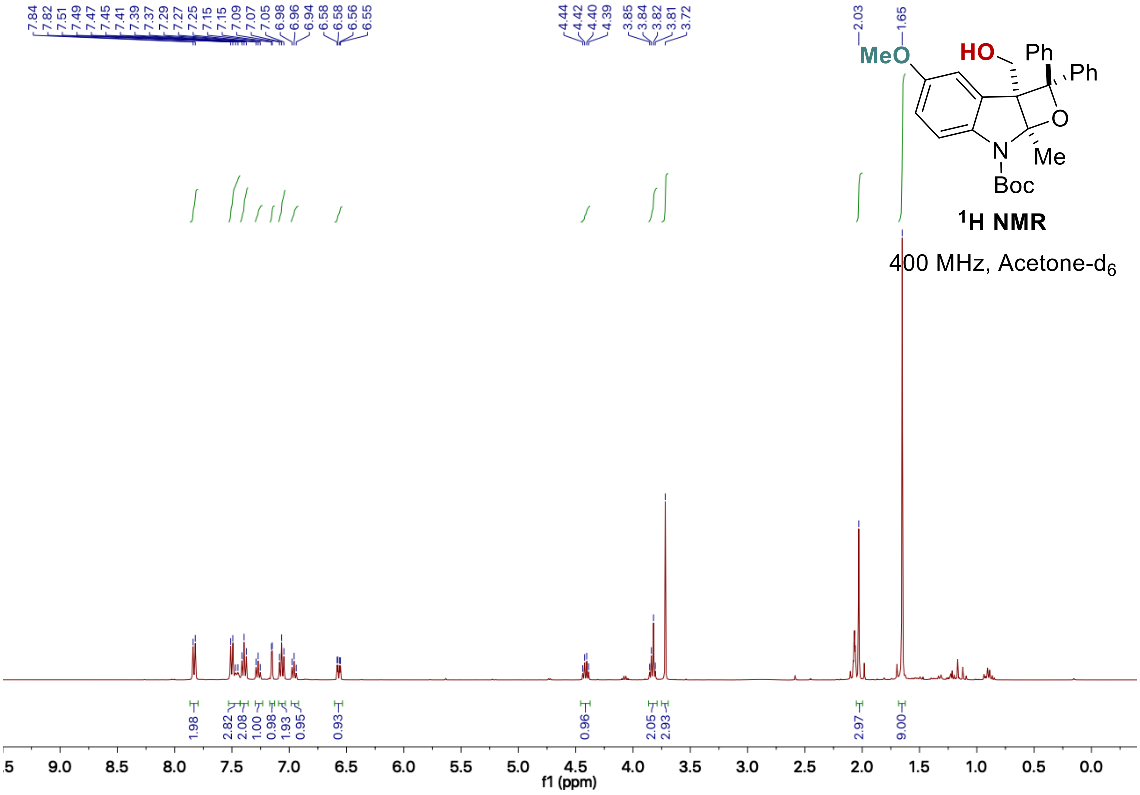
13 - ^{1}H NMR (Acetone-d$_6$)



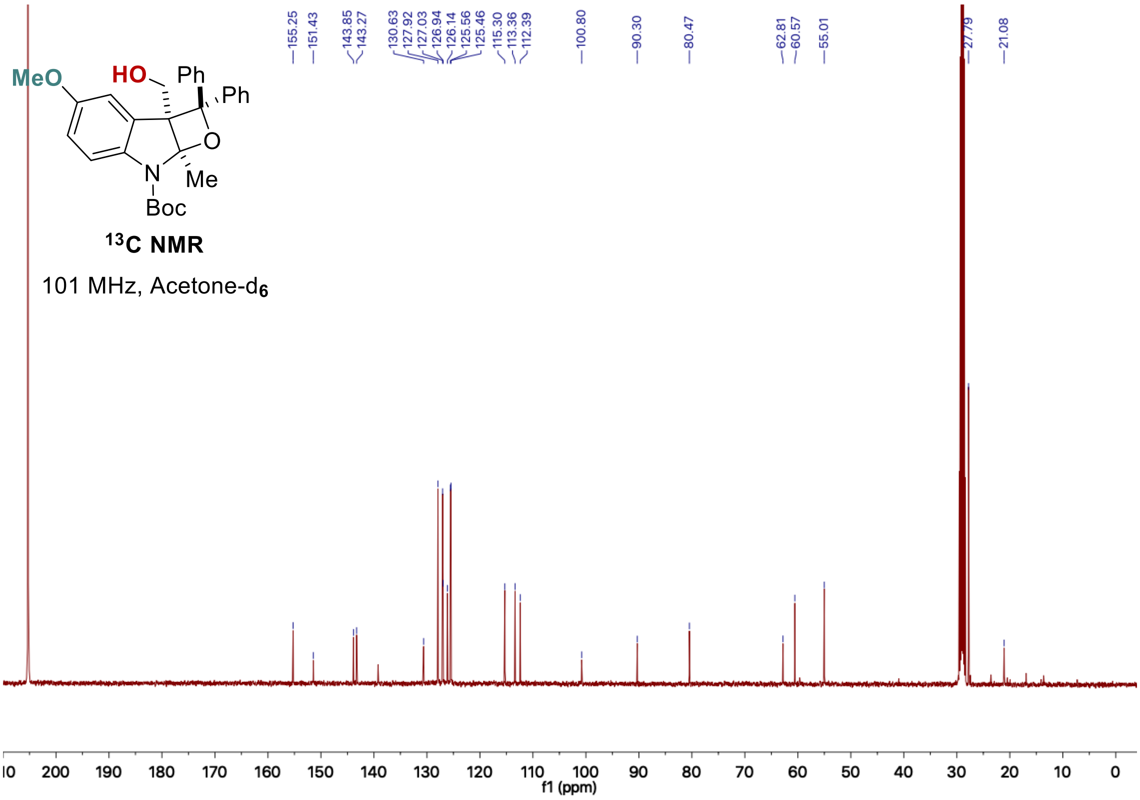
13 - ^{13}C NMR (Acetone-d$_6$)



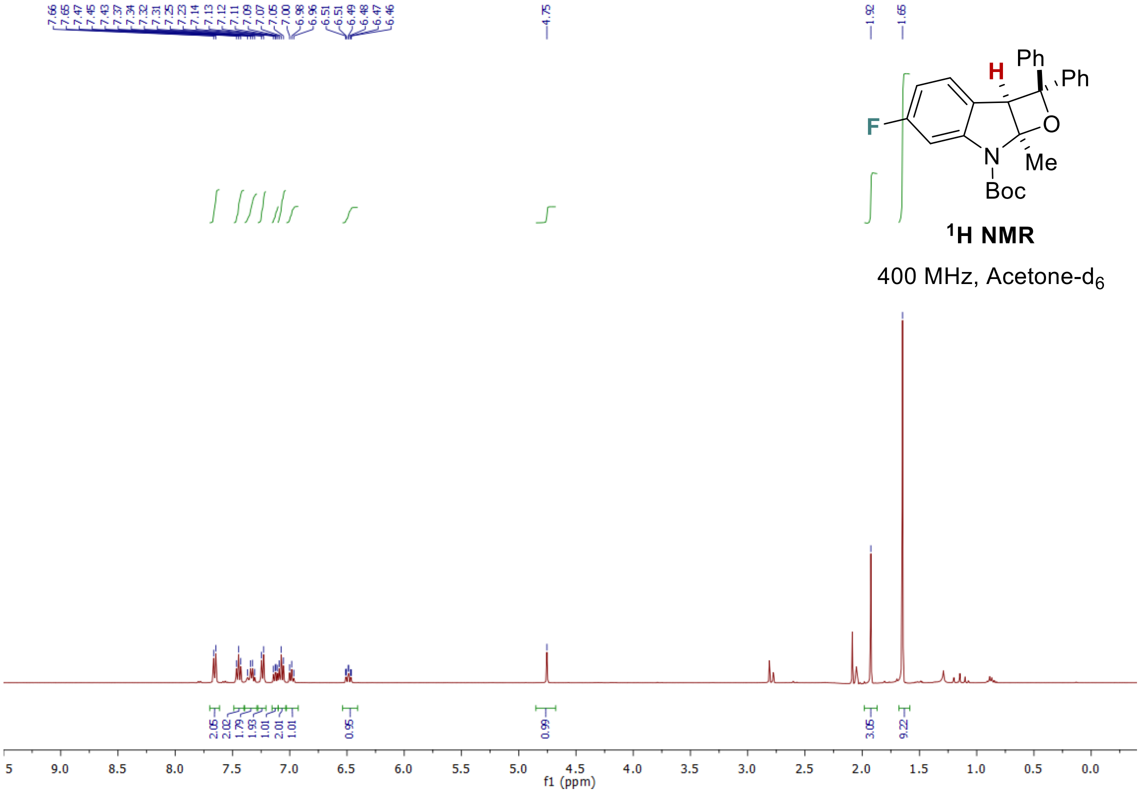
14 - ^{1}H NMR (Acetone-d$_6$)



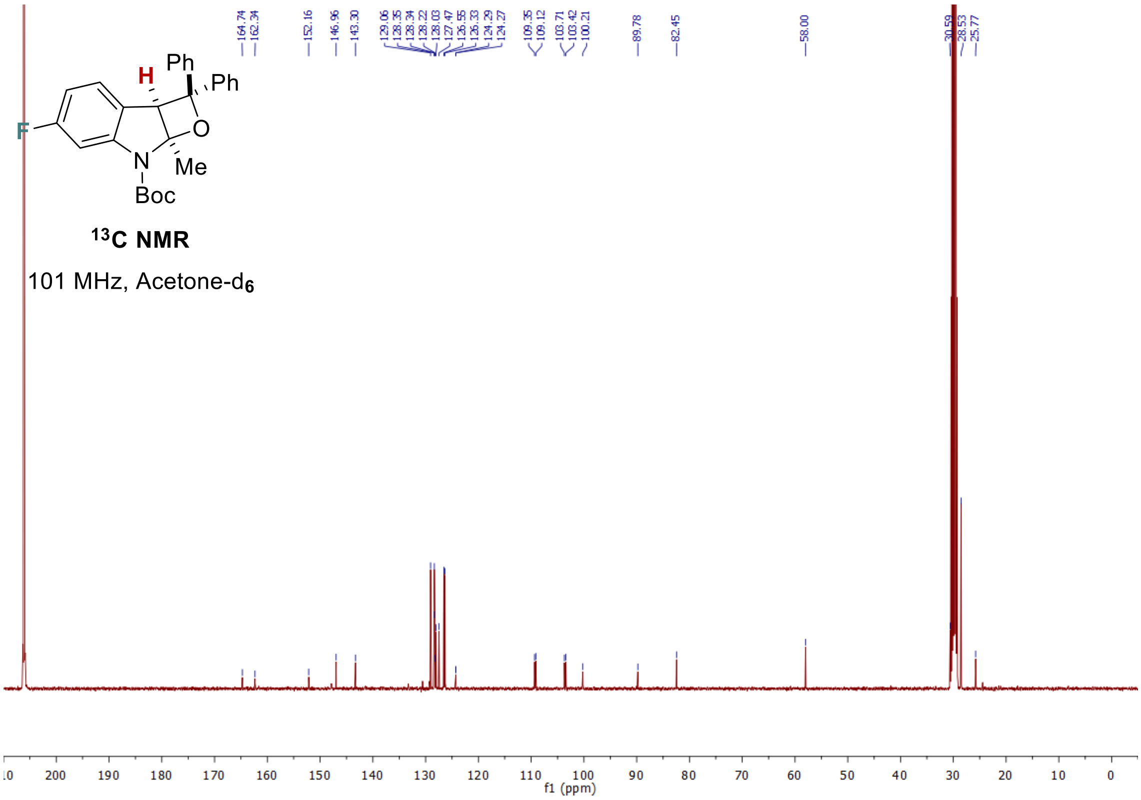
14 - ^{13}C NMR (Acetone-d$_6$)



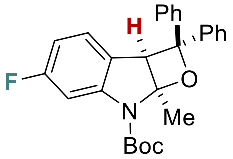
15 - ^{1}H NMR (Acetone-d_6)



15 - ^{13}C NMR (Acetone-d_6)

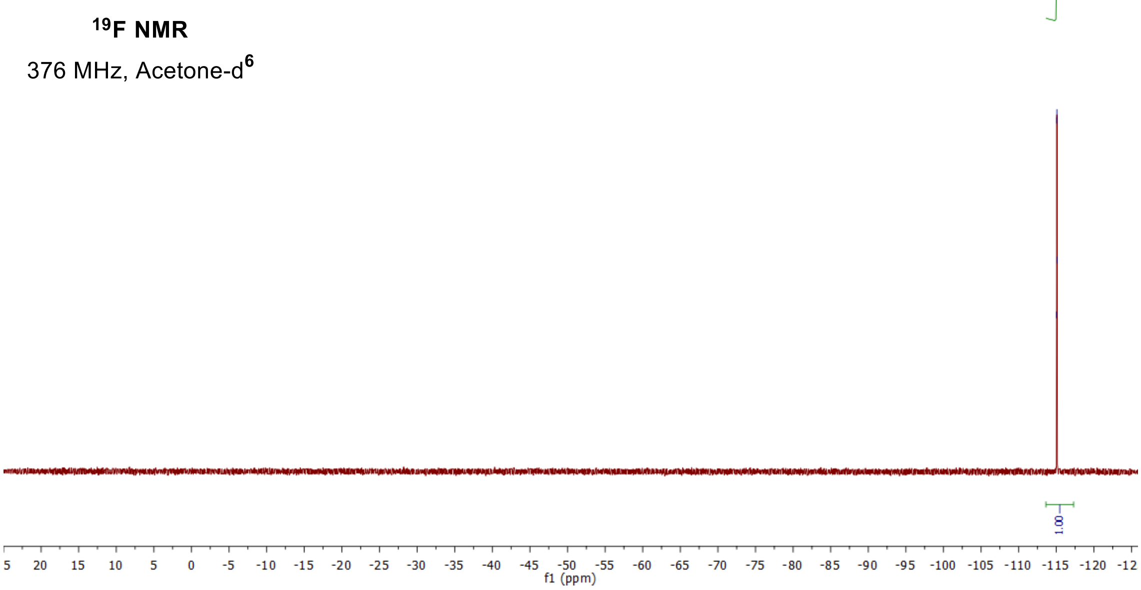


15 - ^{19}F NMR (Acetone-d$_6$)

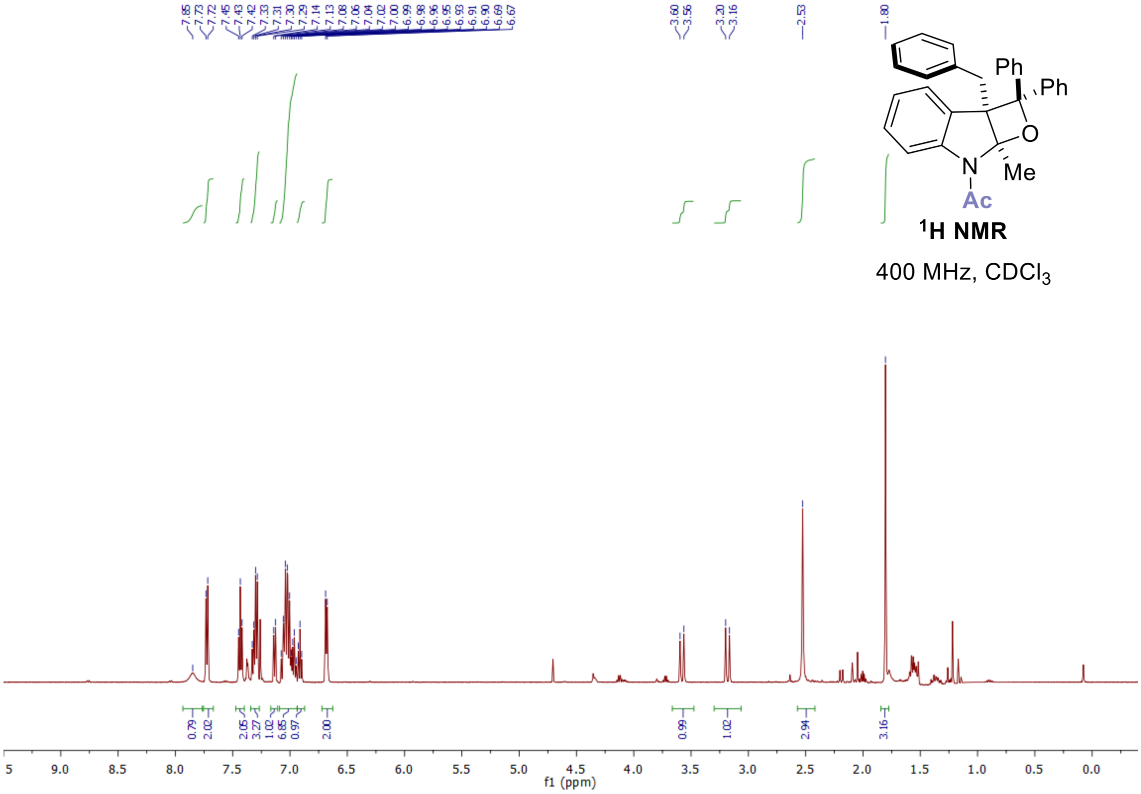


^{19}F NMR

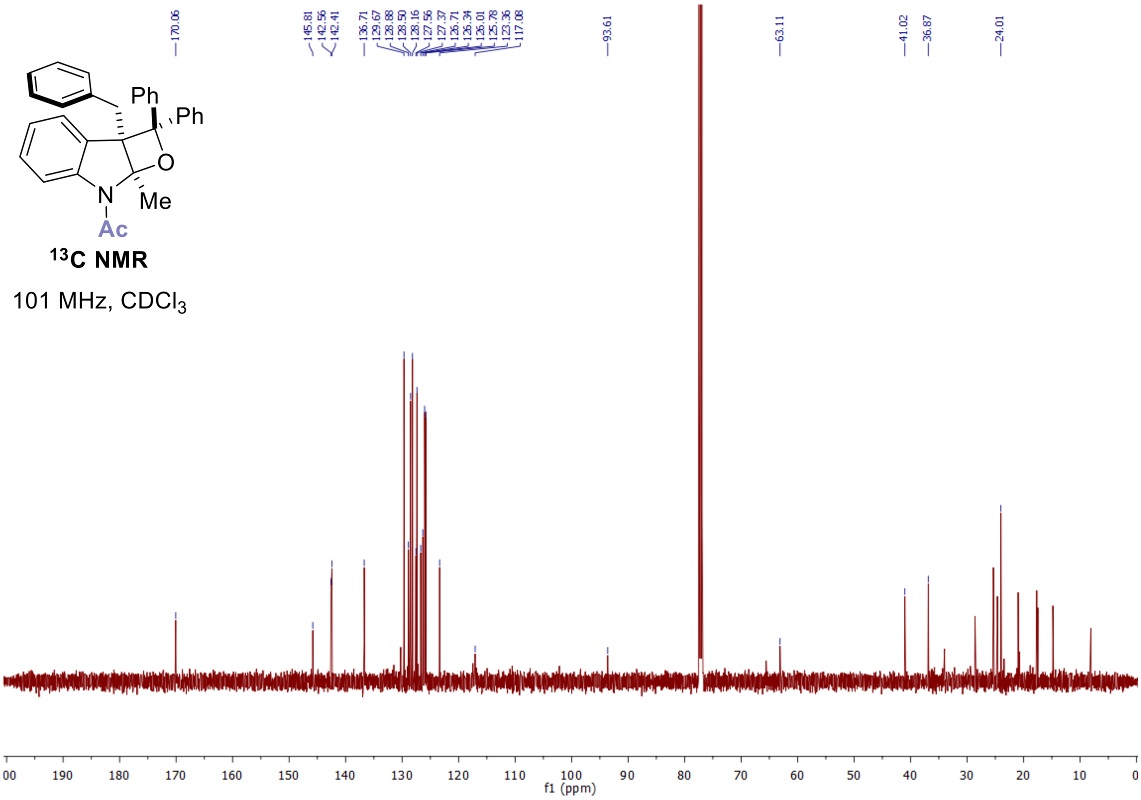
376 MHz, Acetone-d^{6}



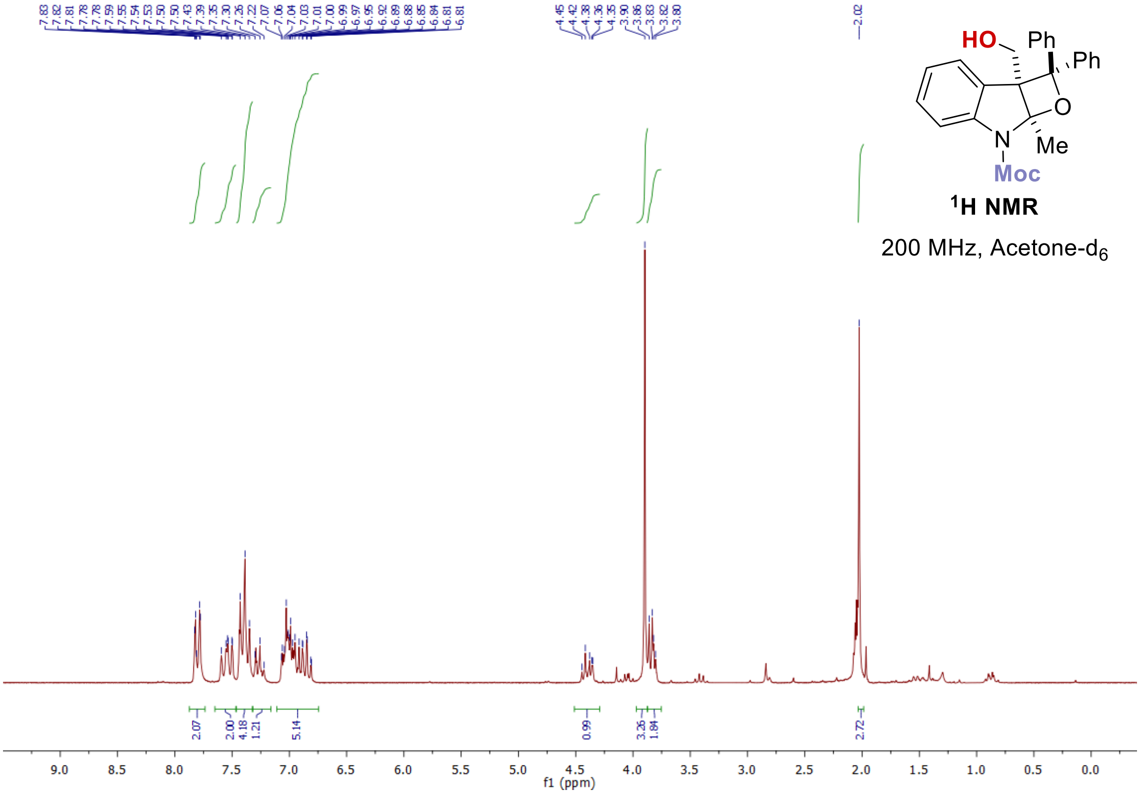
16 - ^{1}H NMR ($CDCl_3$)



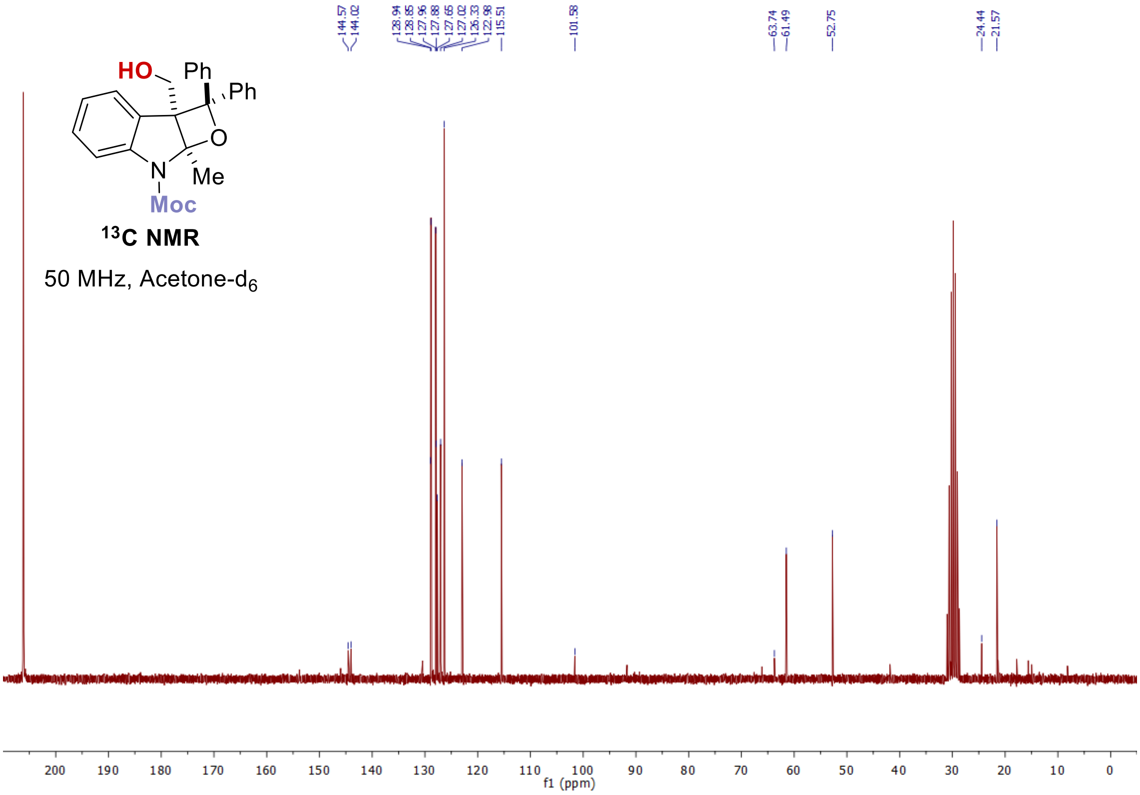
16 - ^{13}C NMR ($CDCl_3$)



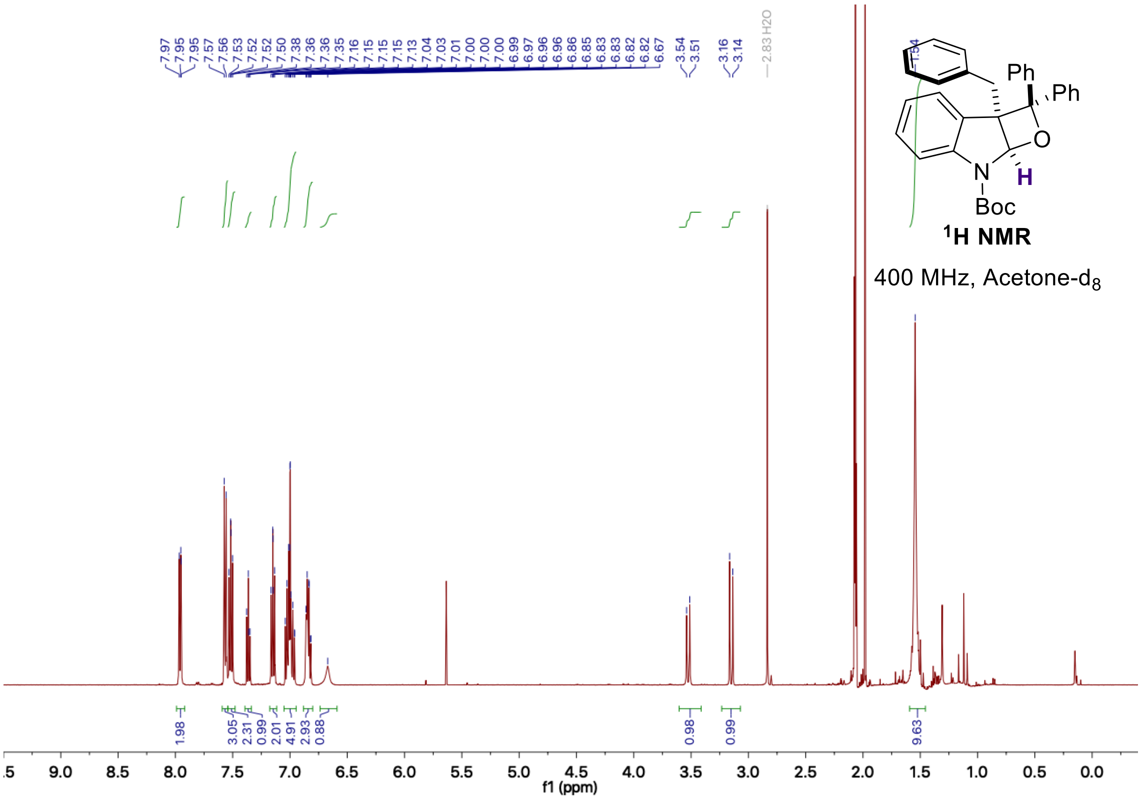
17 - ^{1}H NMR (Acetone-d_6)



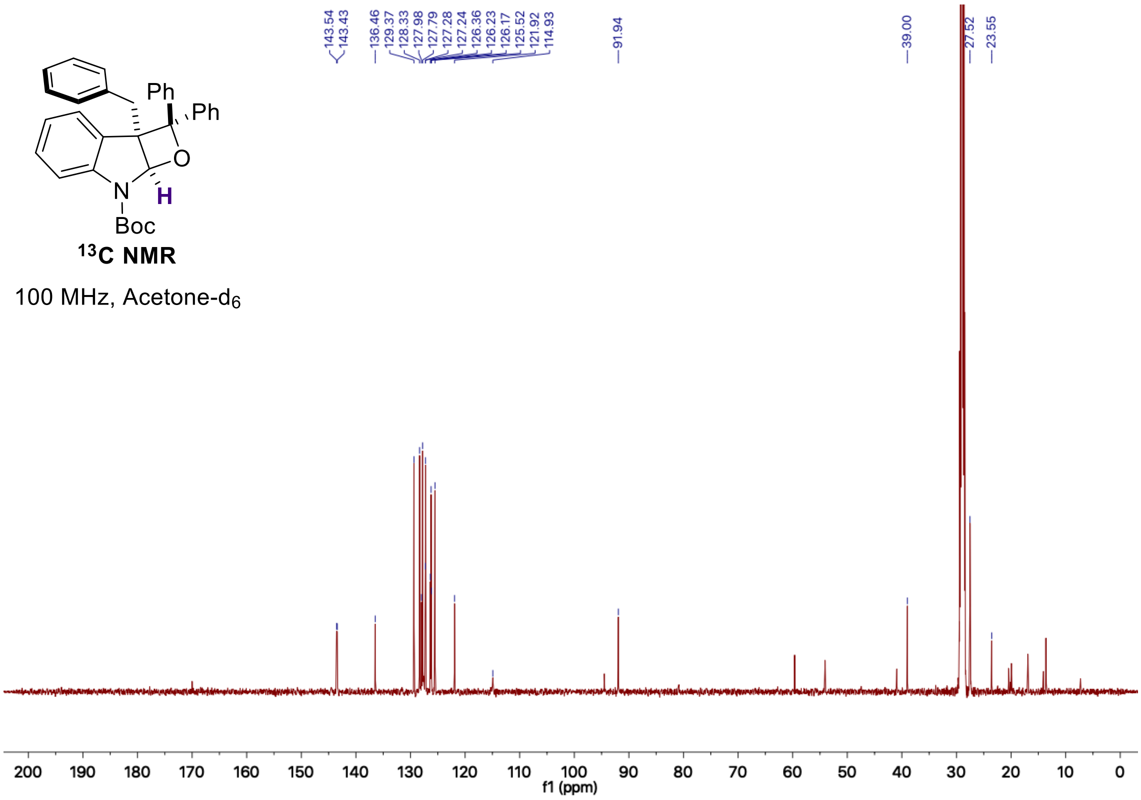
17 - ^{13}C NMR (Acetone-d_6)



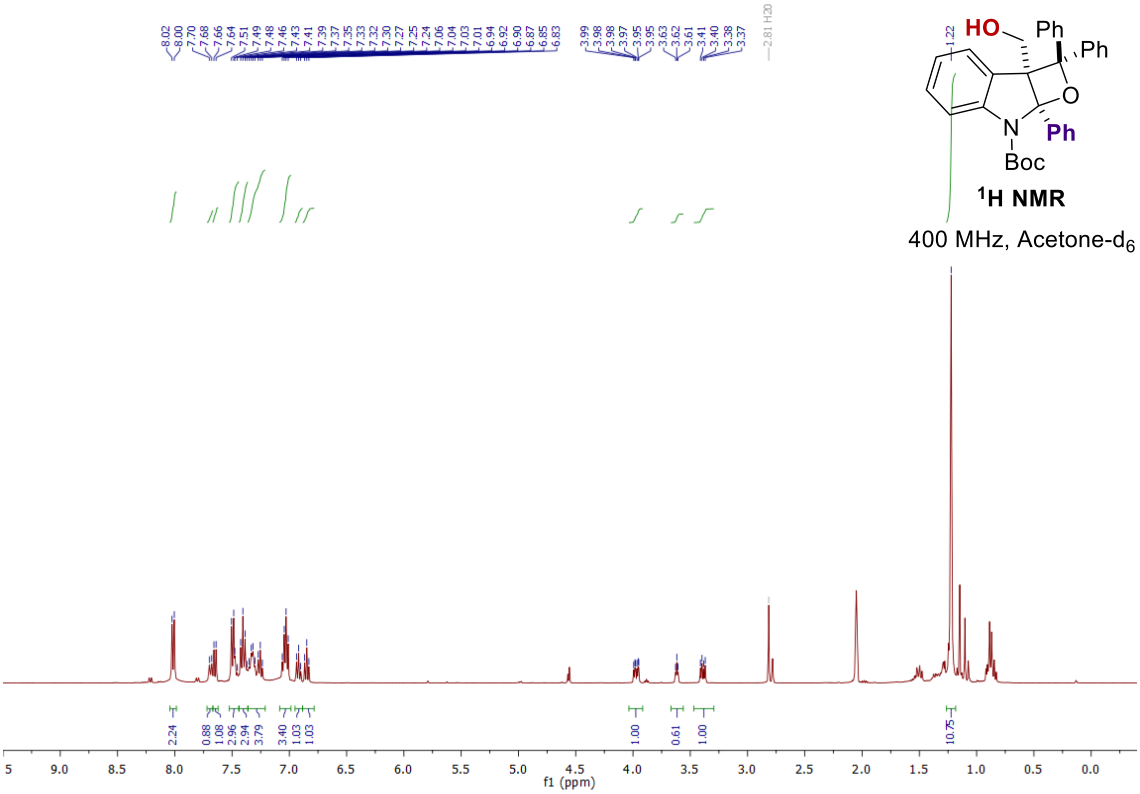
3c - ^{1}H NMR (Acetone-d_6)



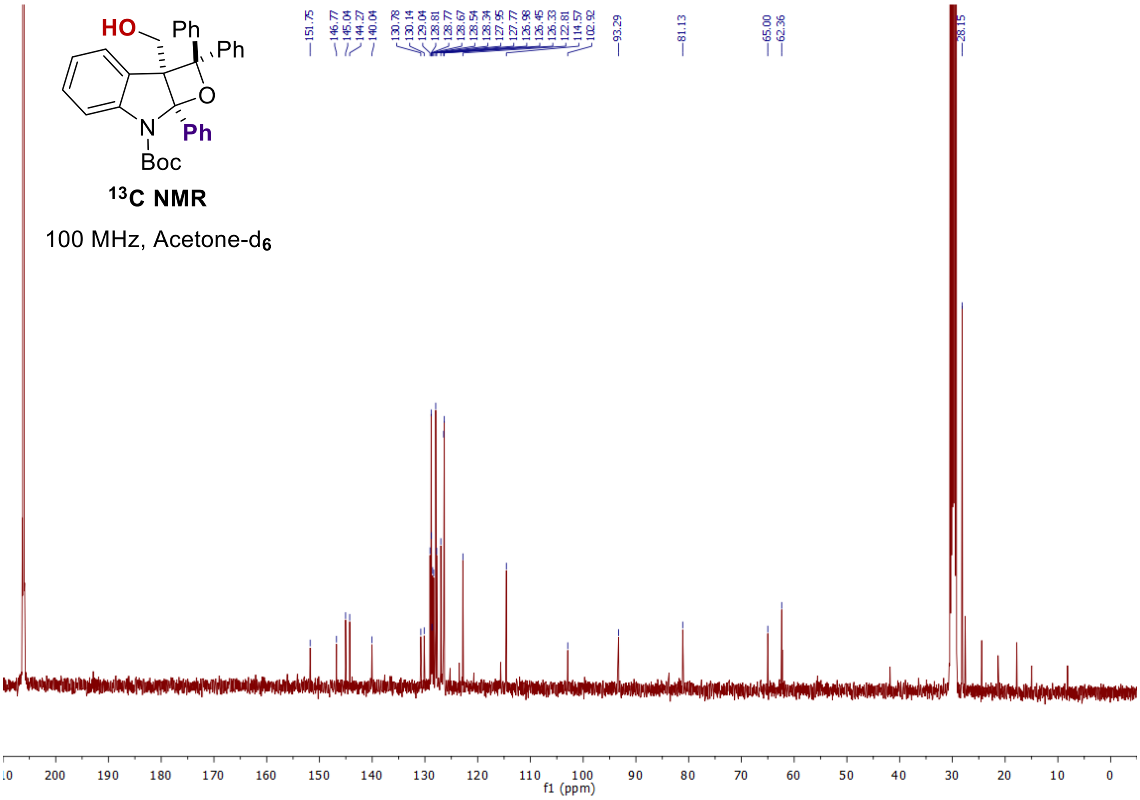
3c - ^{13}C NMR (Acetone-d_6)



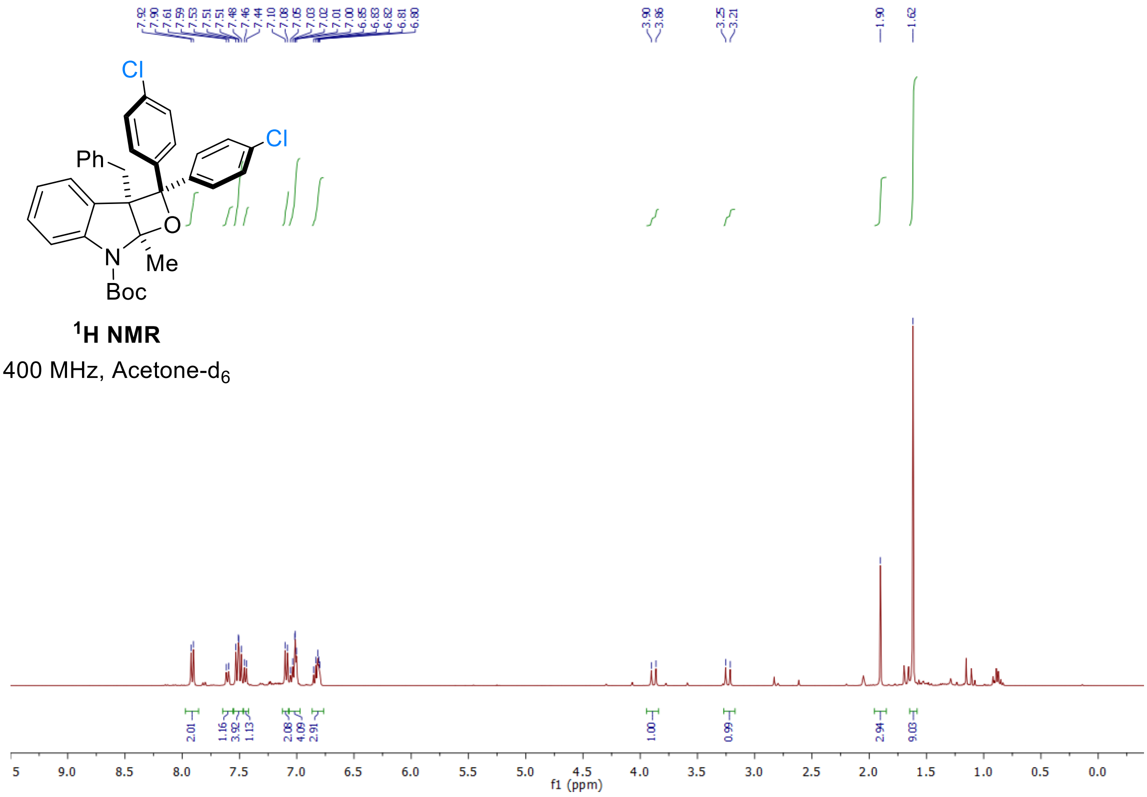
18 - ^{1}H NMR (Acetone-d$_6$)



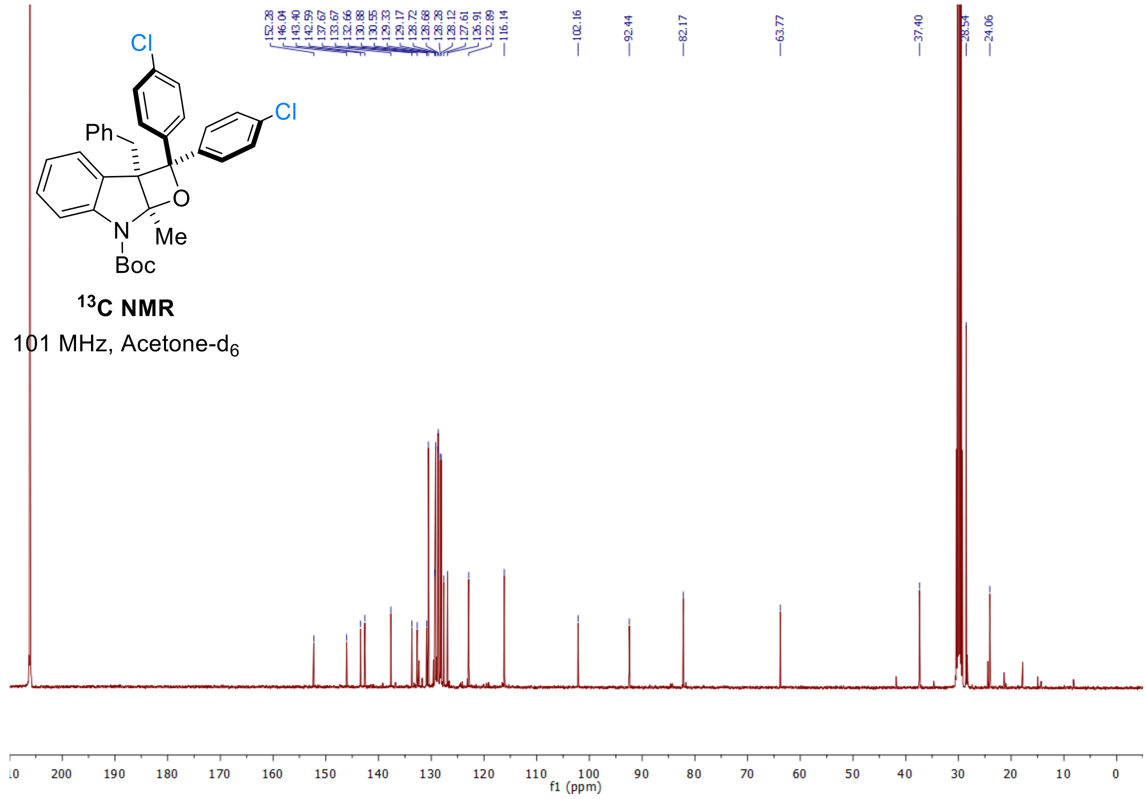
18 - ^{13}C NMR (Acetone-d$_6$)



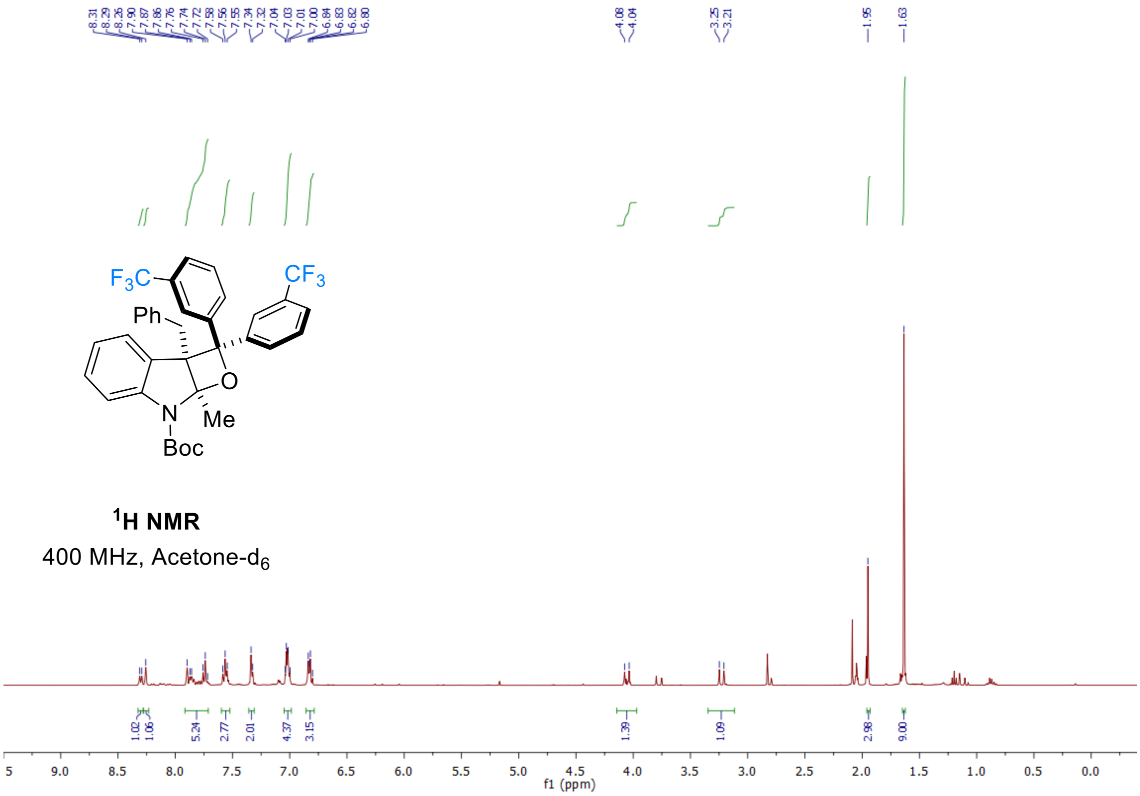
19 - ^{1}H NMR (Acetone-d$_6$)



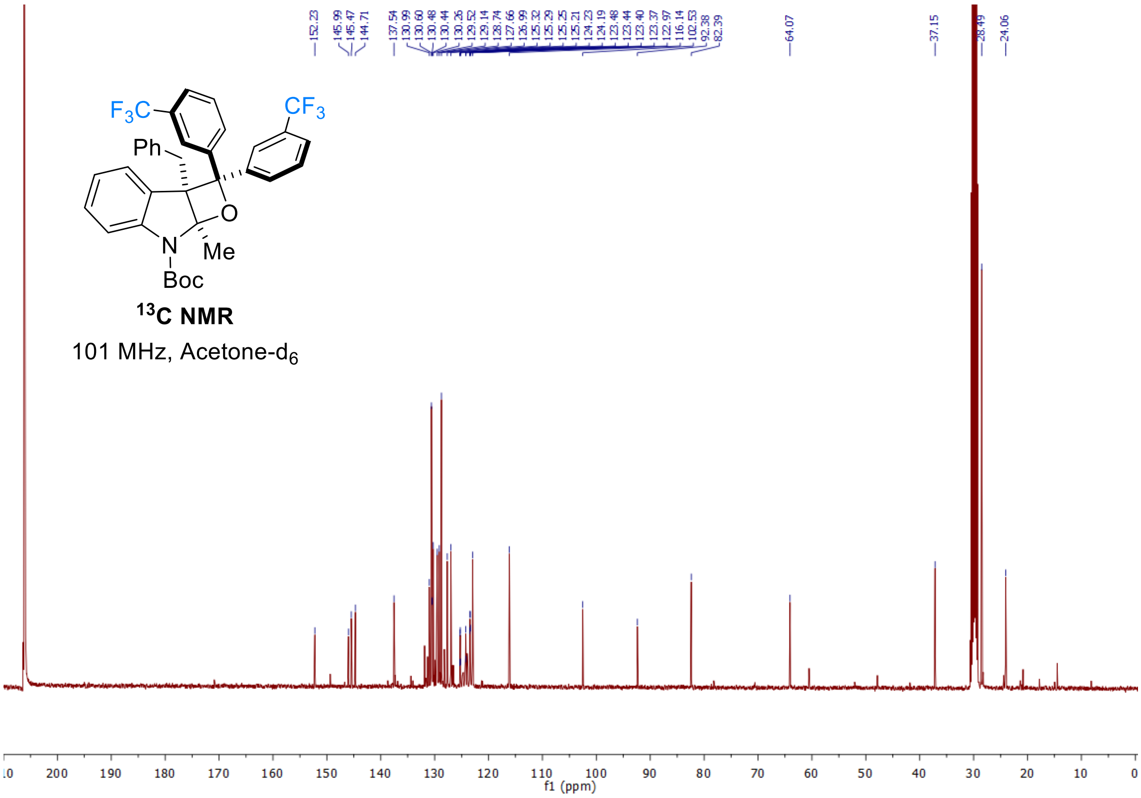
19 - ^{13}C NMR (Acetone-d$_6$)



20 - ^{1}H NMR (Acetone-d_6)



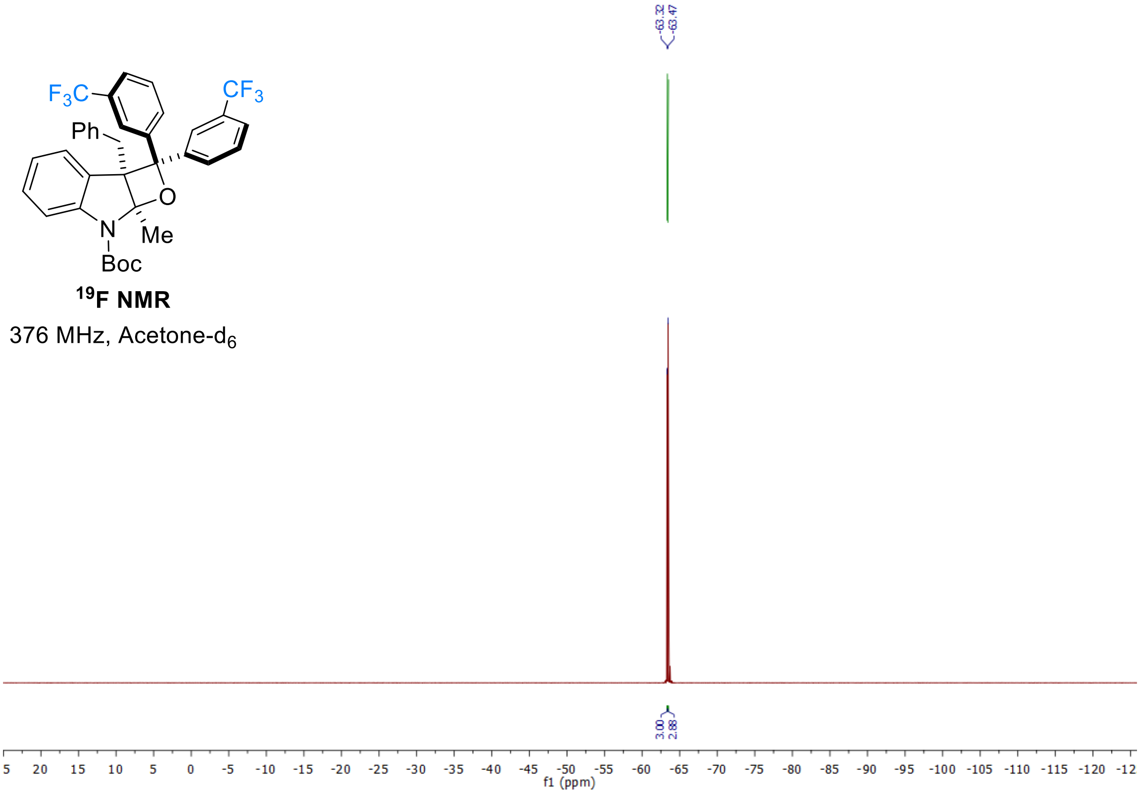
20 - ^{13}C NMR (Acetone-d_6)



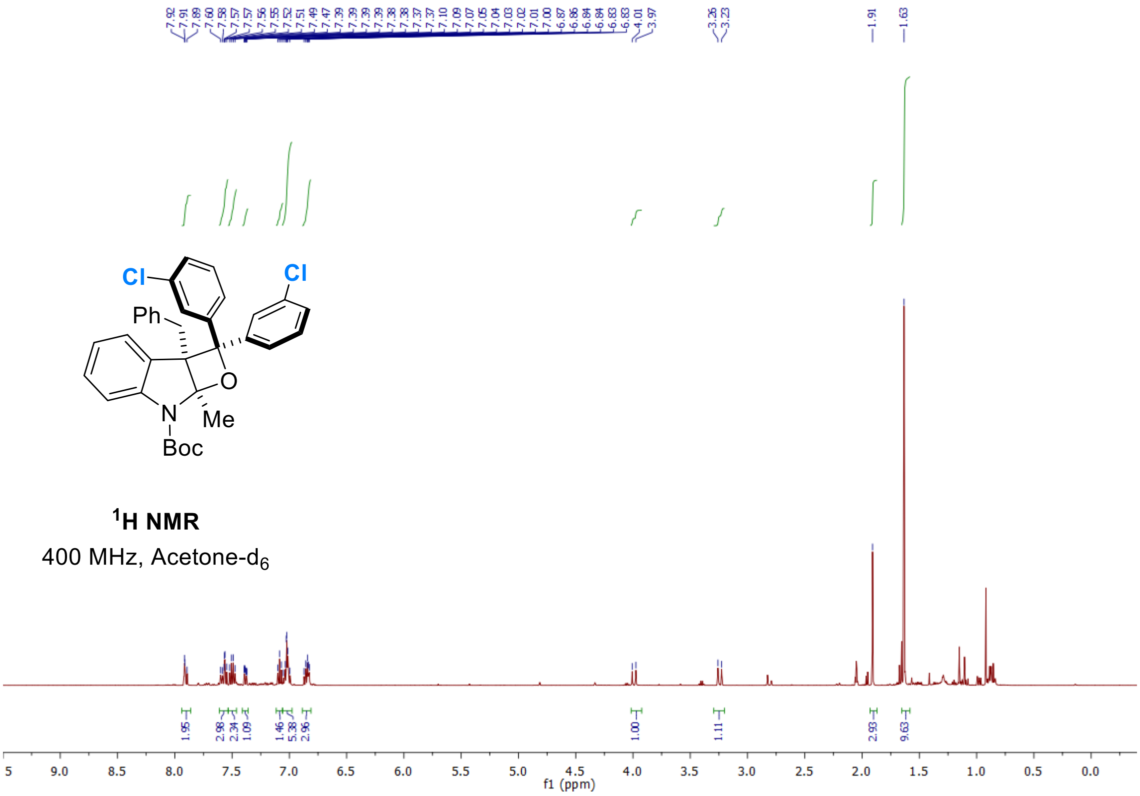
20 - ^{19}F NMR (Acetone-d$_6$)

^{19}F NMR

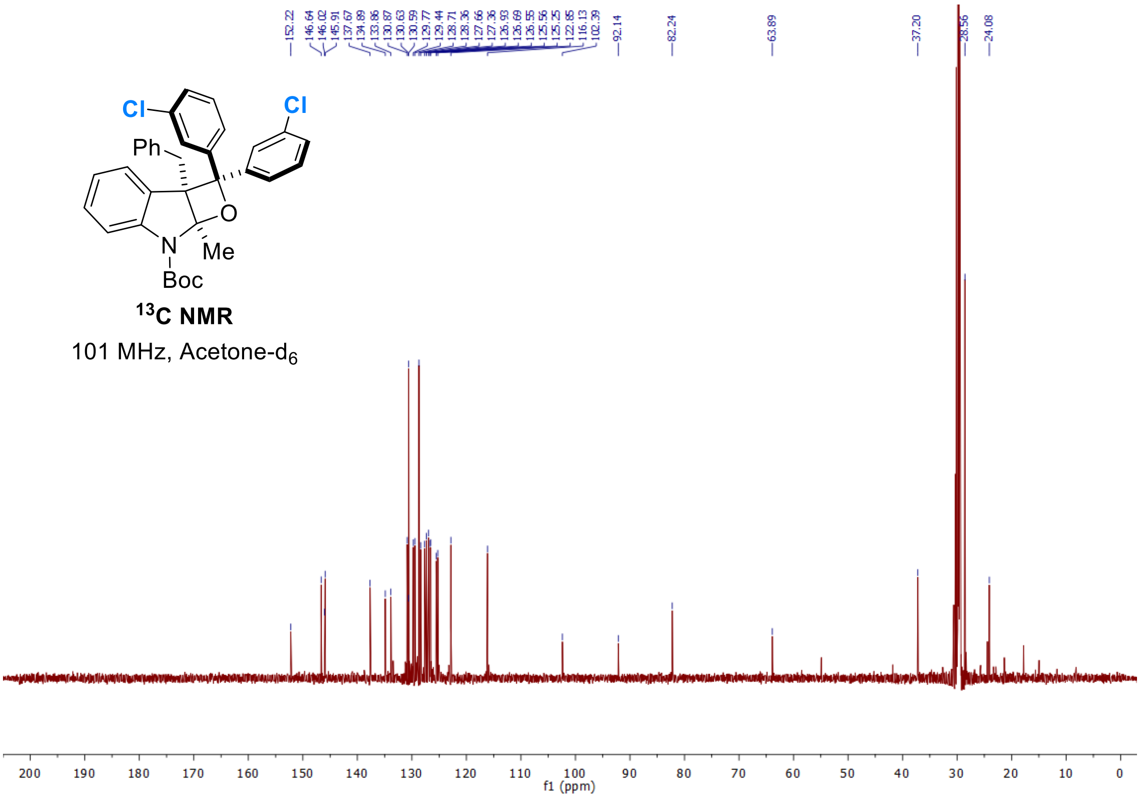
376 MHz, Acetone-d$_6$



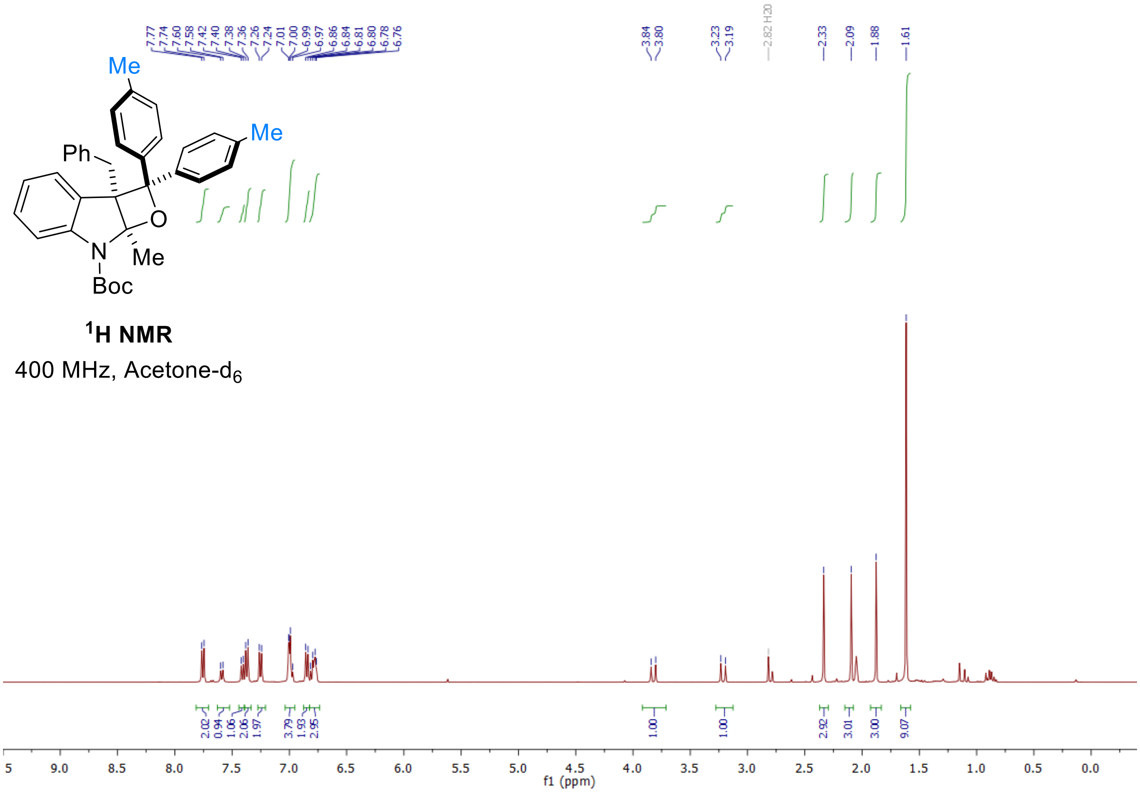
21 - ^{1}H NMR (Acetone-d$_6$)



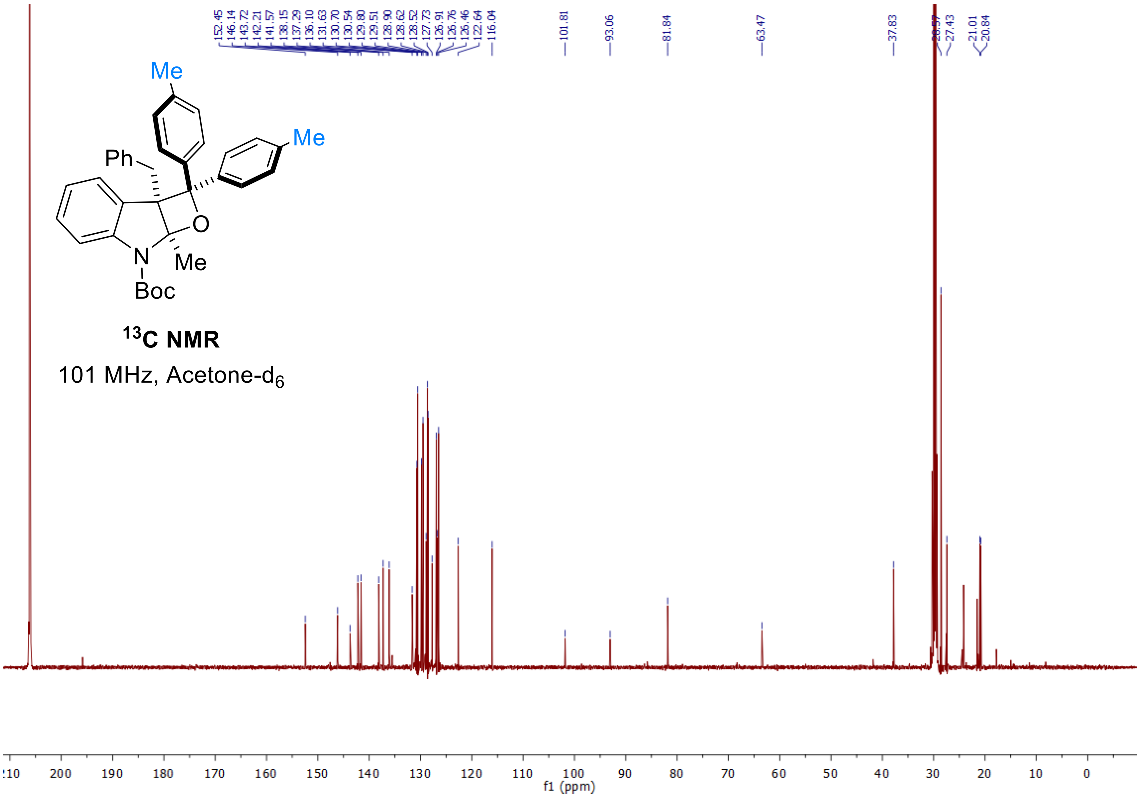
21 - ^{13}C NMR (Acetone-d$_6$)



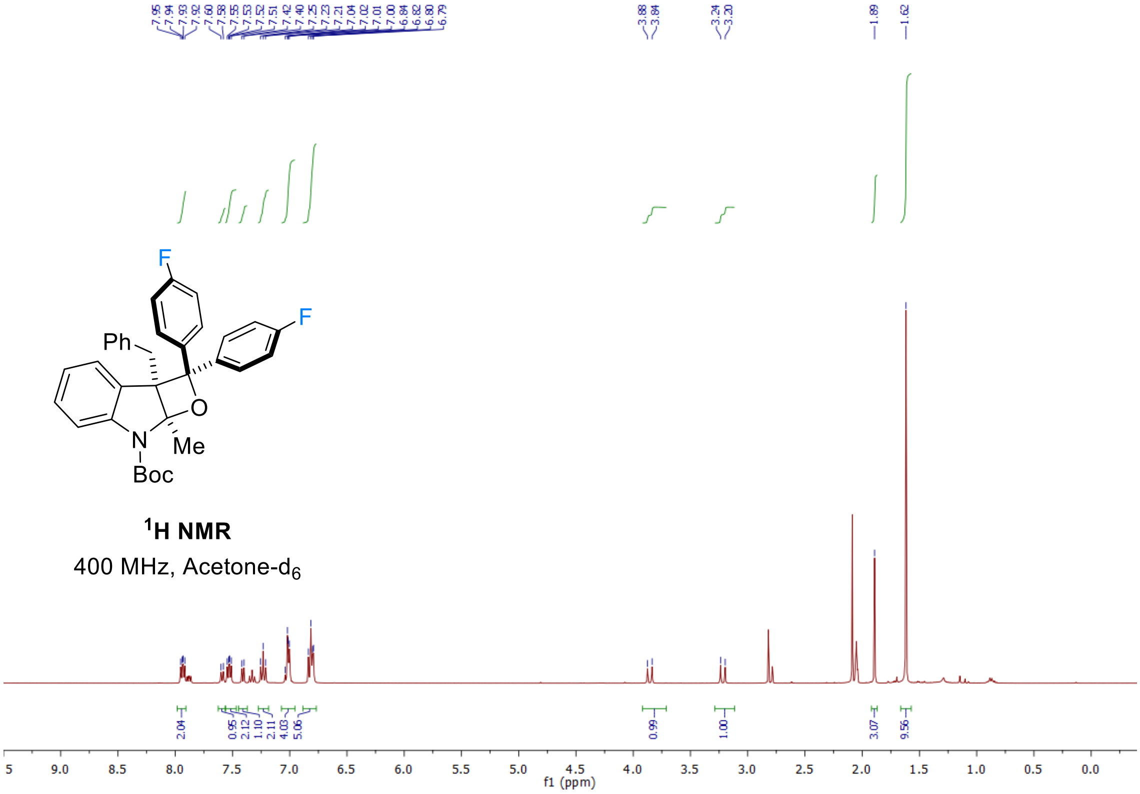
22 - ^{1}H NMR (Acetone-d$_6$)



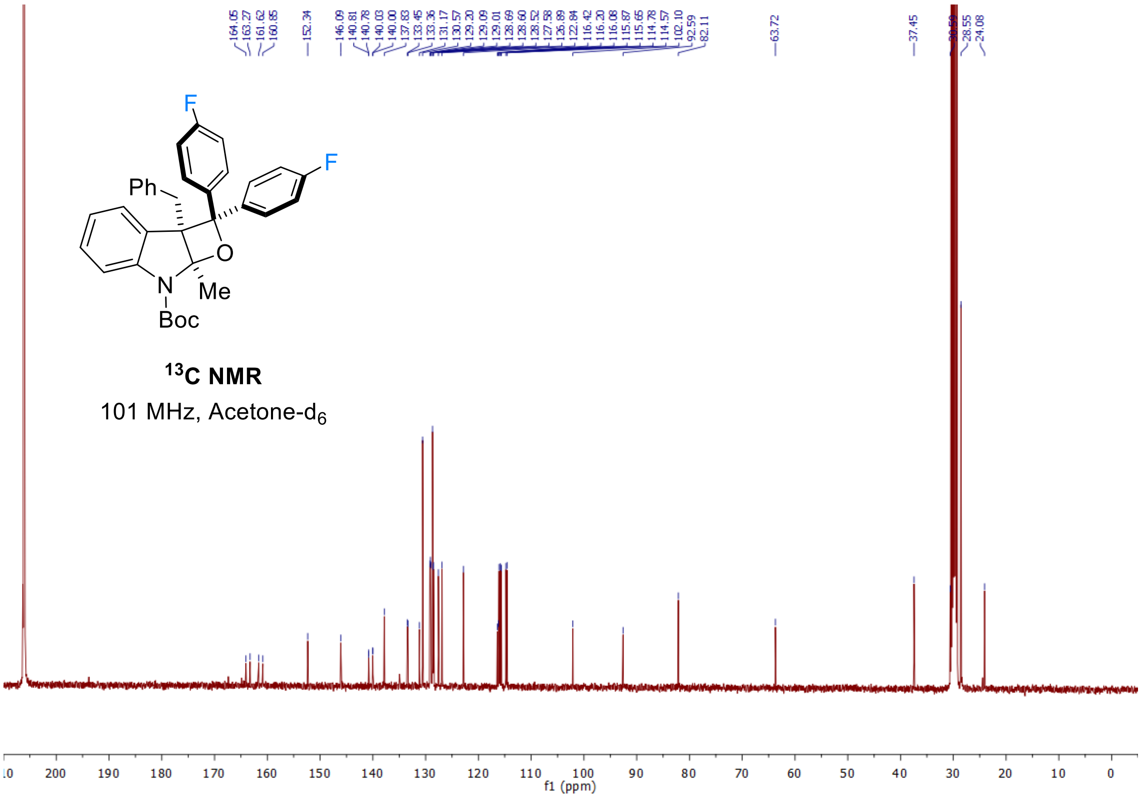
22 - ^{13}C NMR (Acetone-d$_6$)



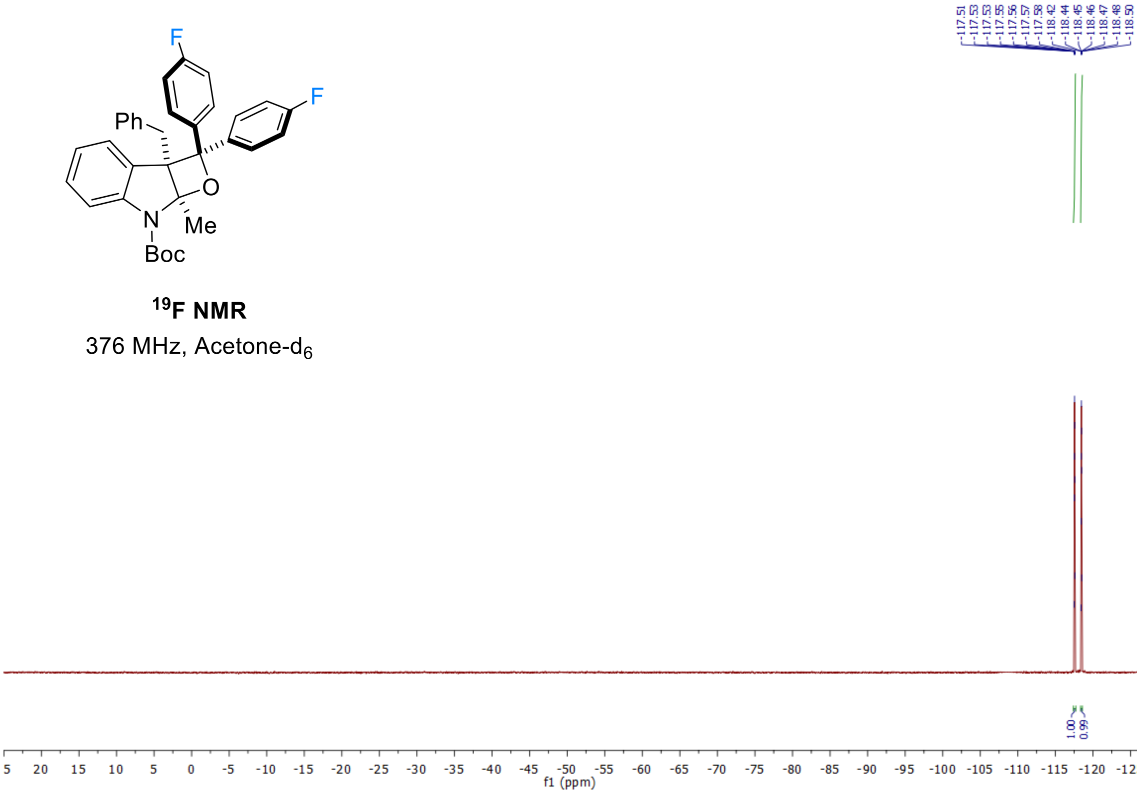
23 - ^{1}H NMR (Acetone-d^6)



23 - ^{13}C NMR (Acetone-d$_6$)



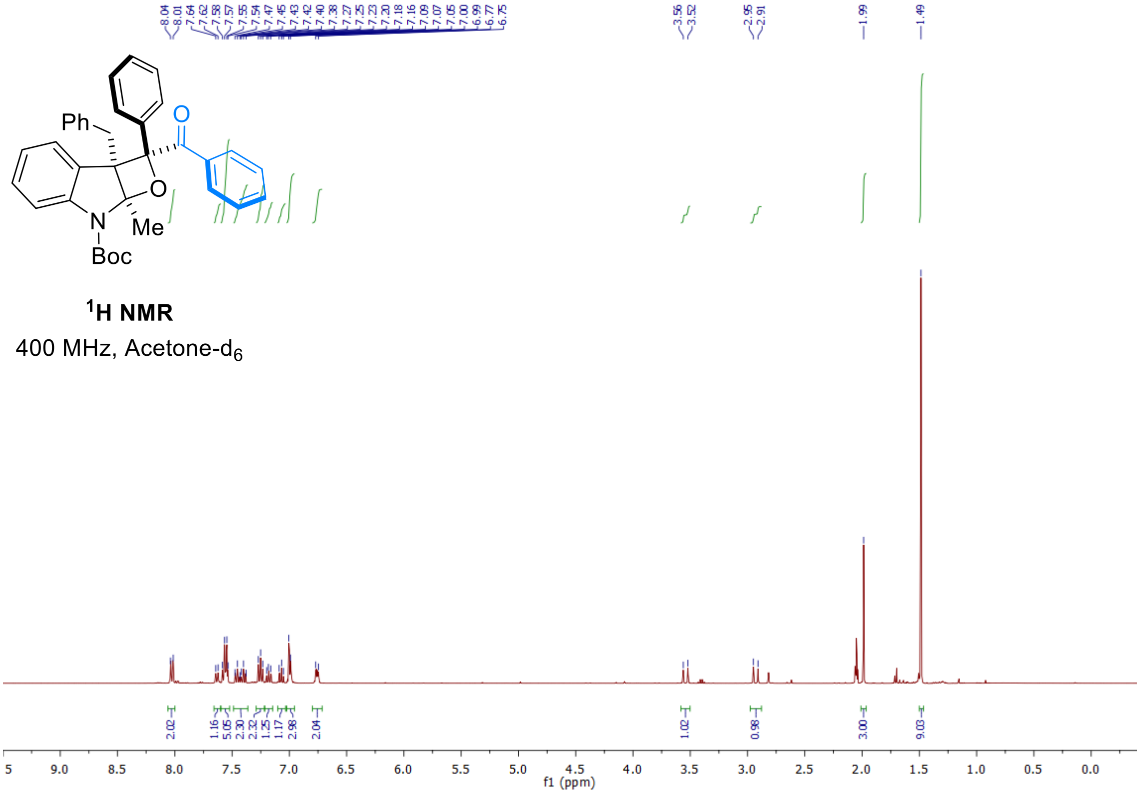
23 - ^{19}F NMR (Acetone-d_6)



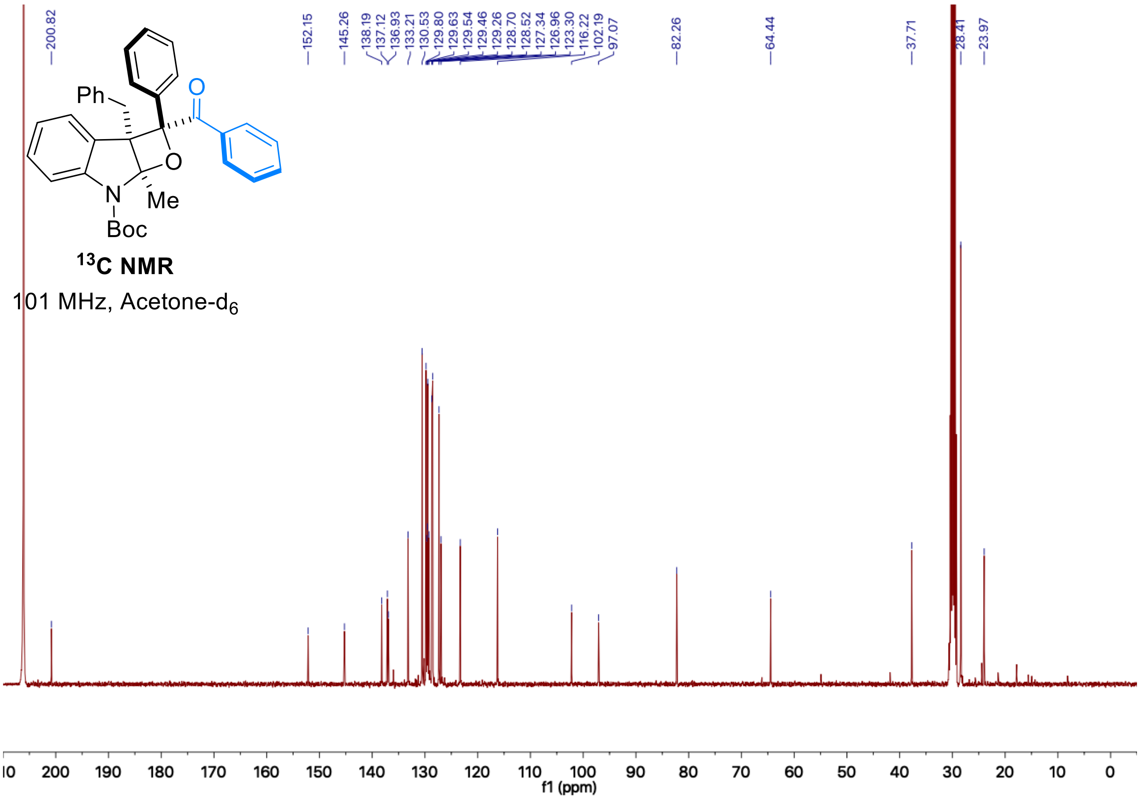
^{19}F NMR

376 MHz, Acetone-d_6

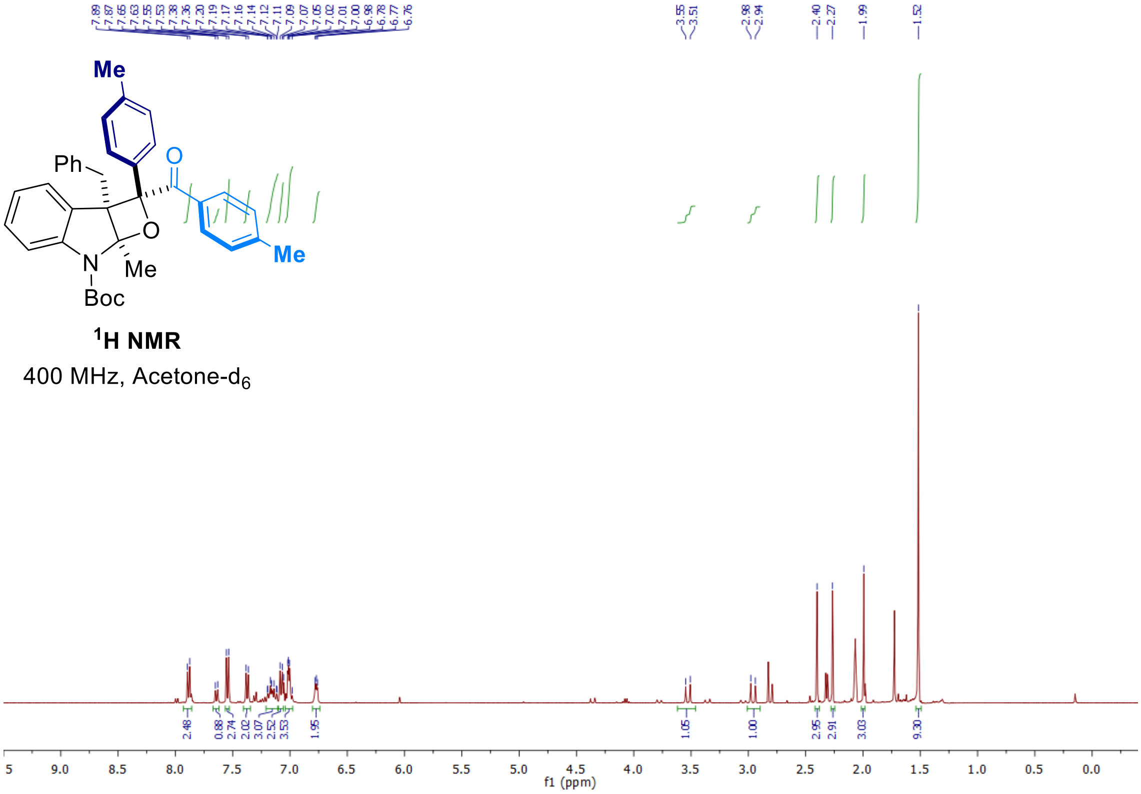
24 - ¹H NMR (Acetone-d$_6$)



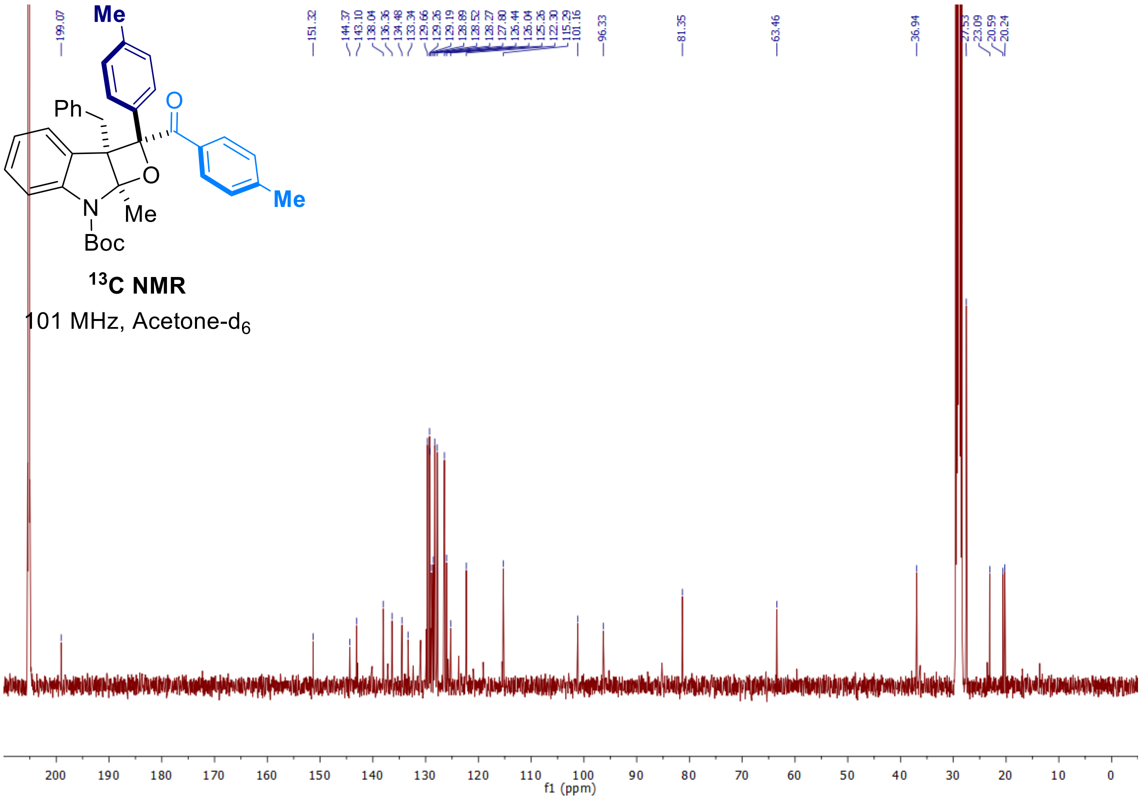
24 - ¹³C NMR (Acetone-d$_6$)



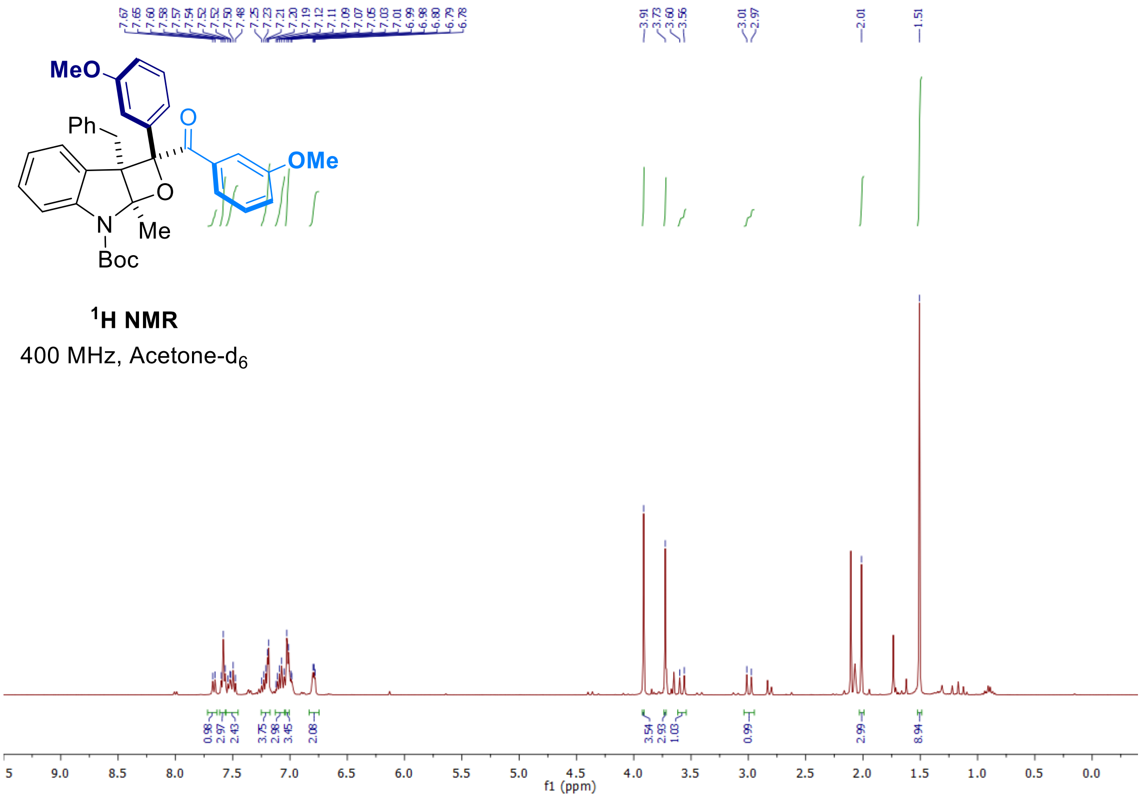
25 - ^{1}H NMR (Acetone-d_6)



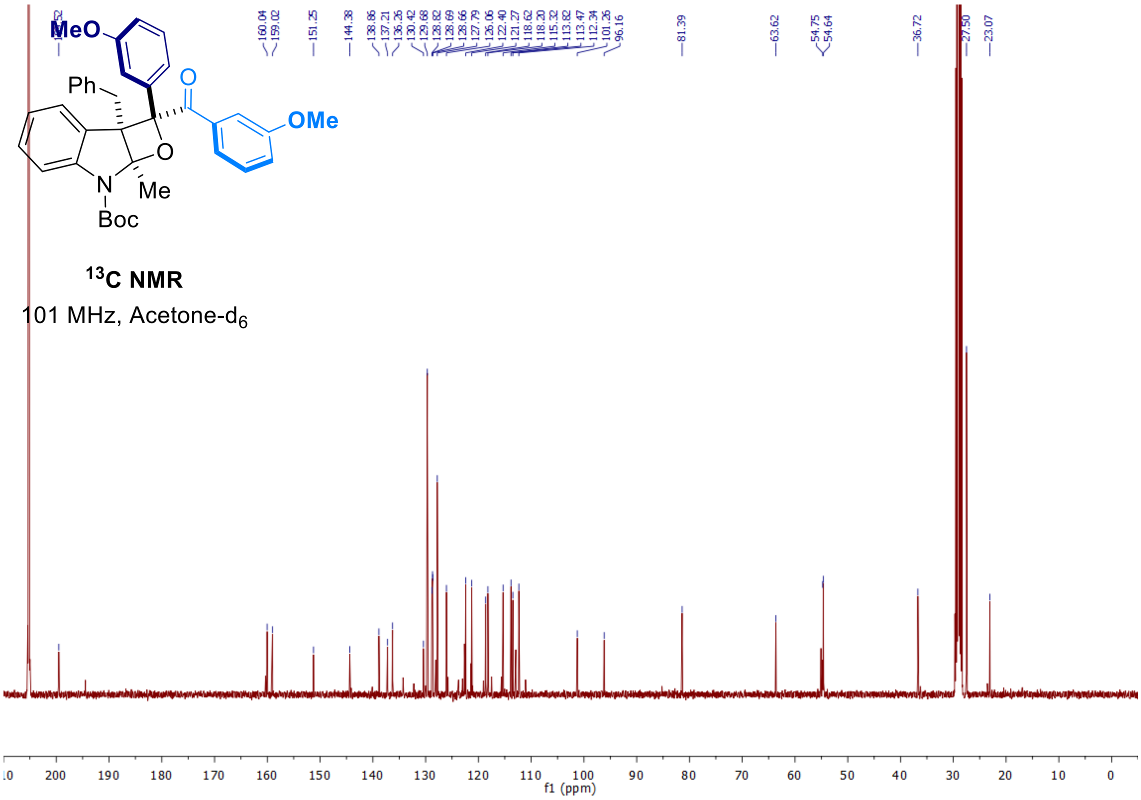
25 - ^{13}C NMR (Acetone-d_6)



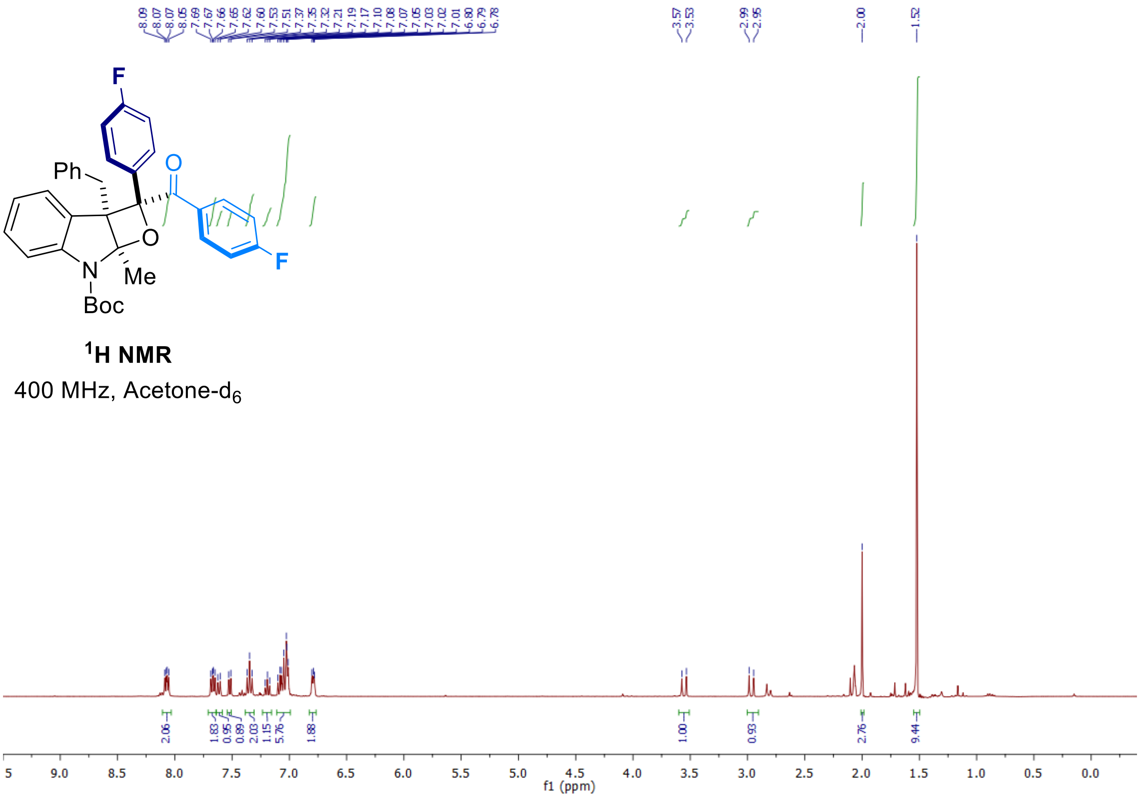
26 - ^{1}H NMR (Acetone-d$_6$)



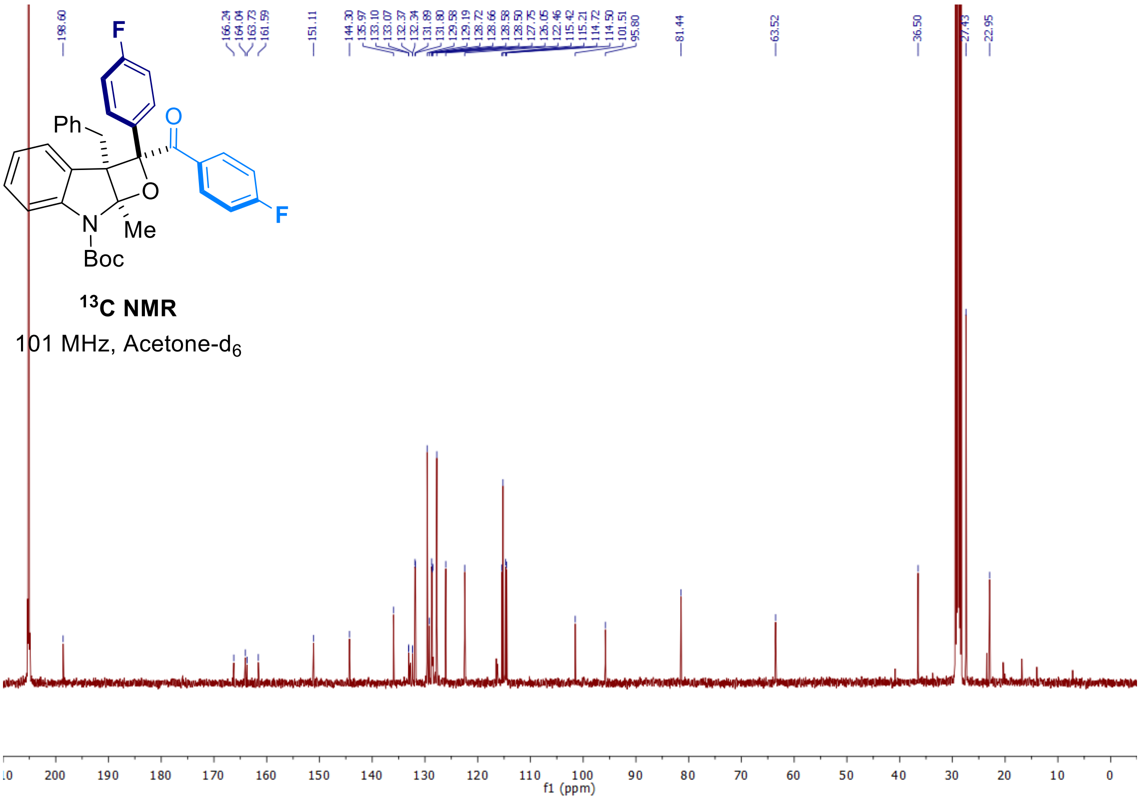
26 - ^{13}C NMR (Acetone-d$_6$)



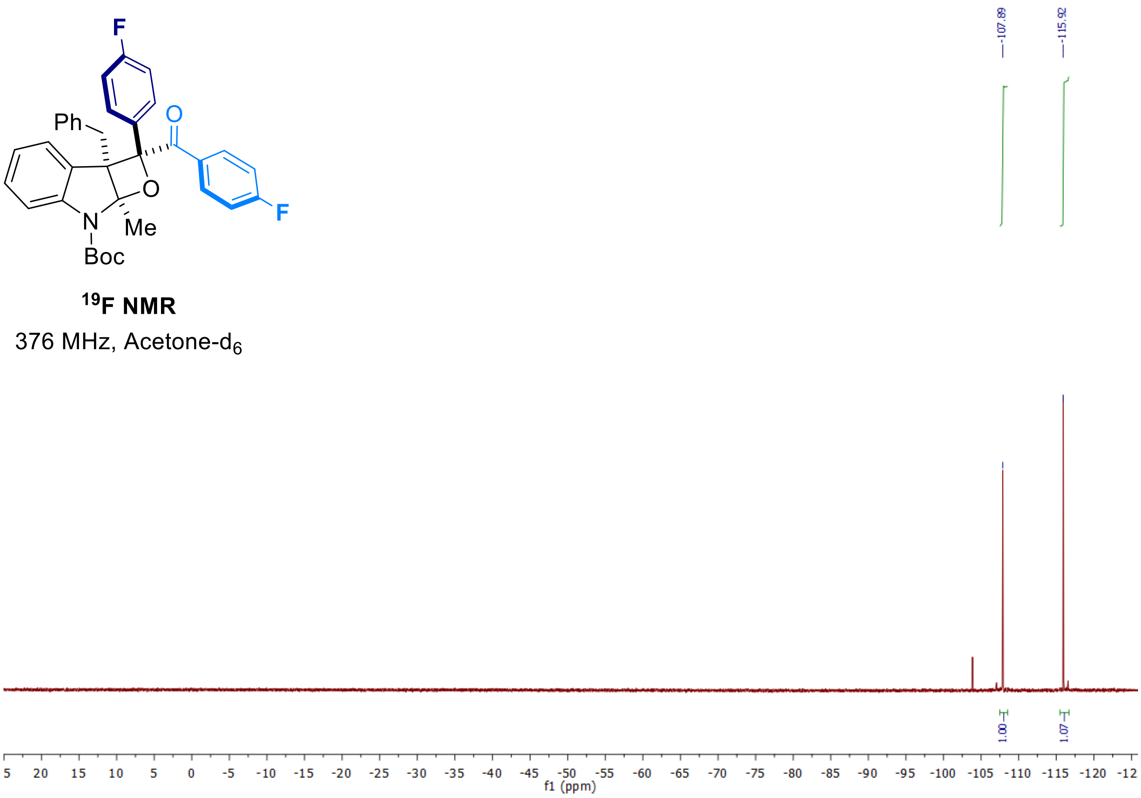
27 - ^{1}H NMR (Acetone-d$_6$)



27 - ^{13}C NMR (Acetone-d$_6$)



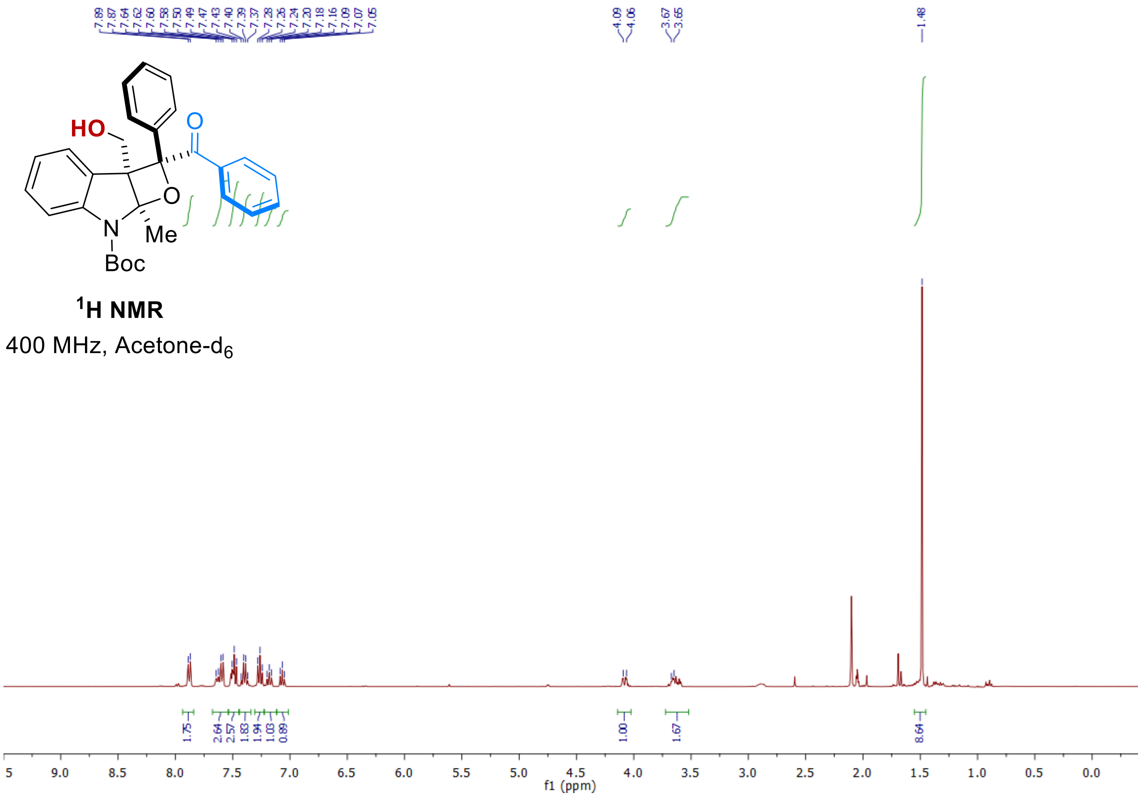
27 - ^{19}F NMR (Acetone-d_6)



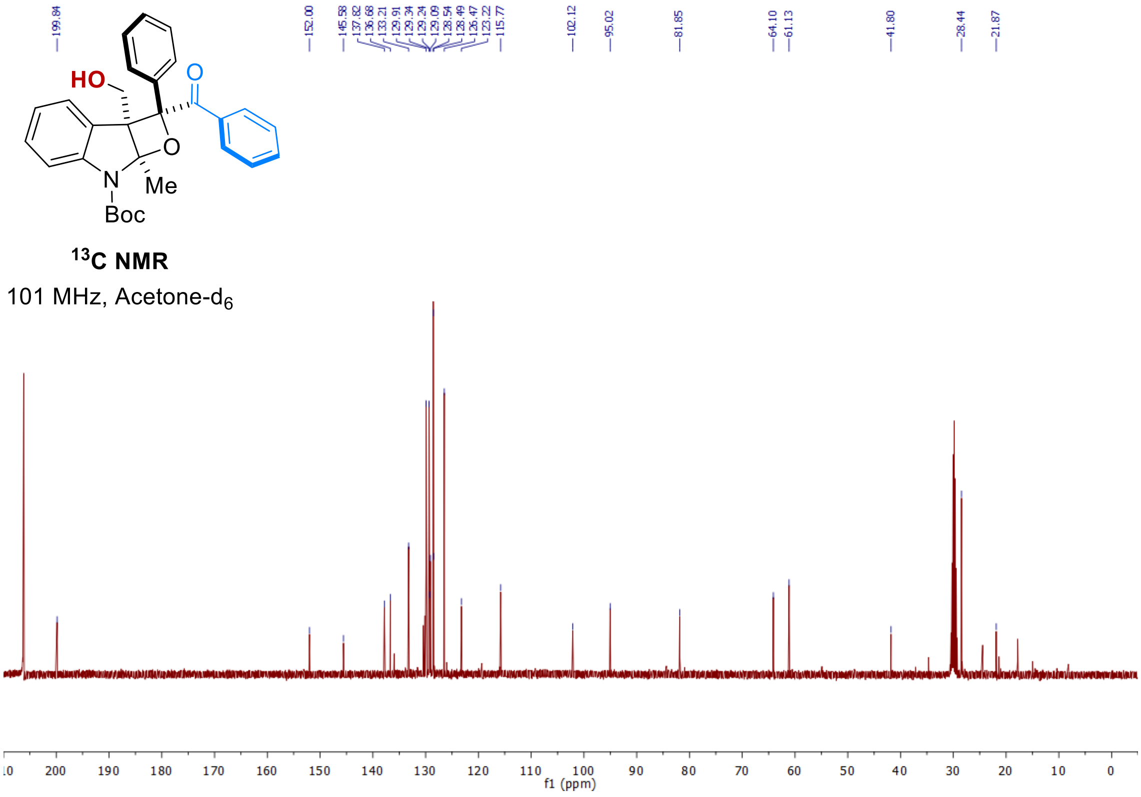
^{19}F NMR

376 MHz, Acetone-d_6

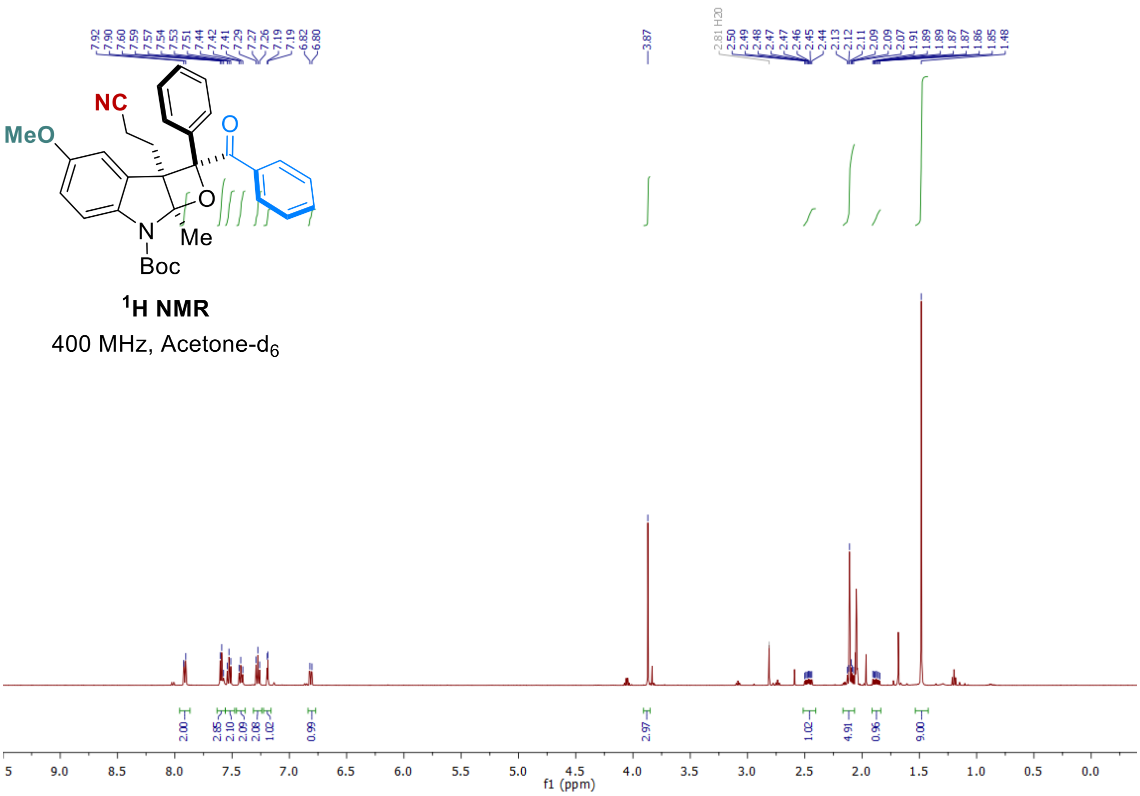
28 - ^{1}H NMR (Acetone-d$_6$)



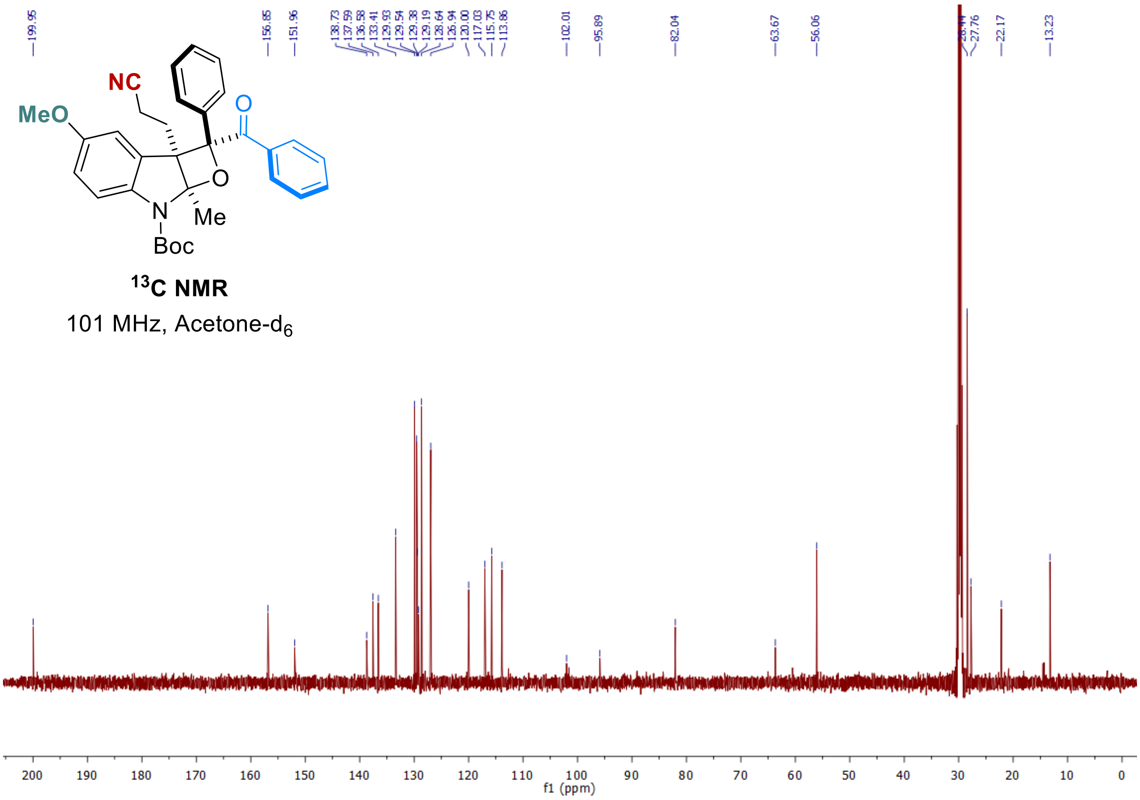
28 - ^{13}C NMR (Acetone-d$_6$)



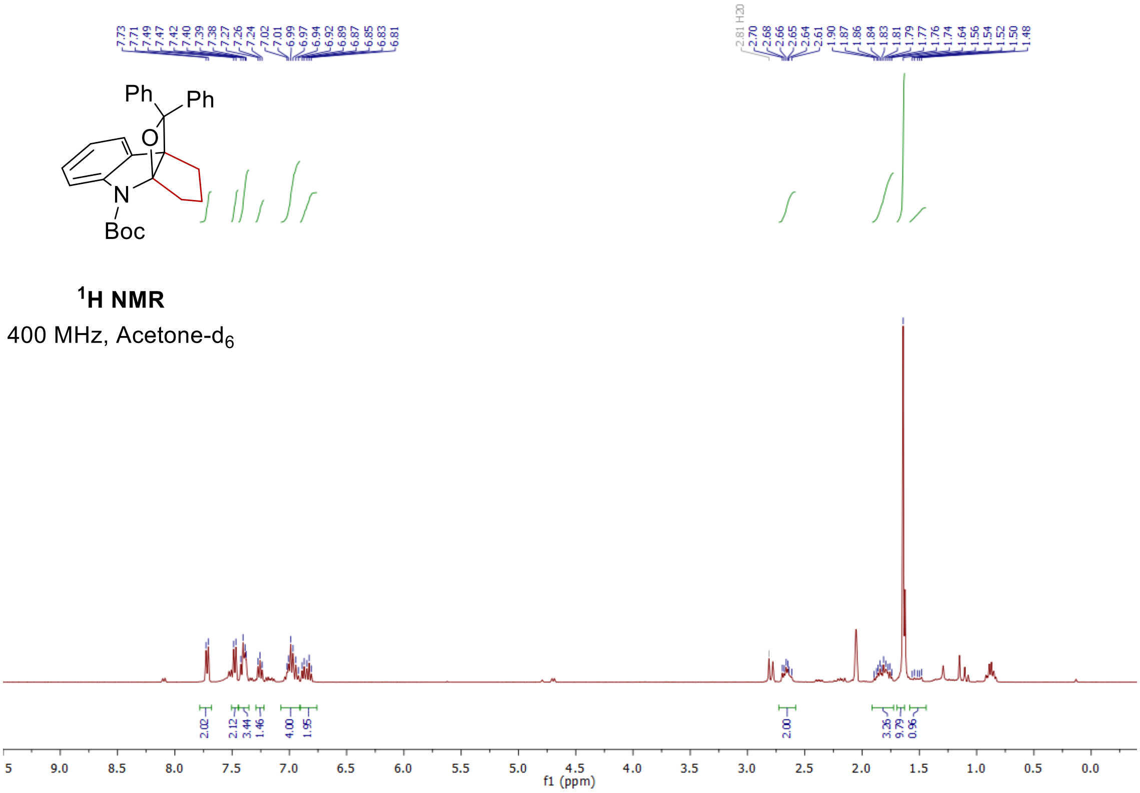
29 - ^{1}H NMR (Acetone-d$_6$)



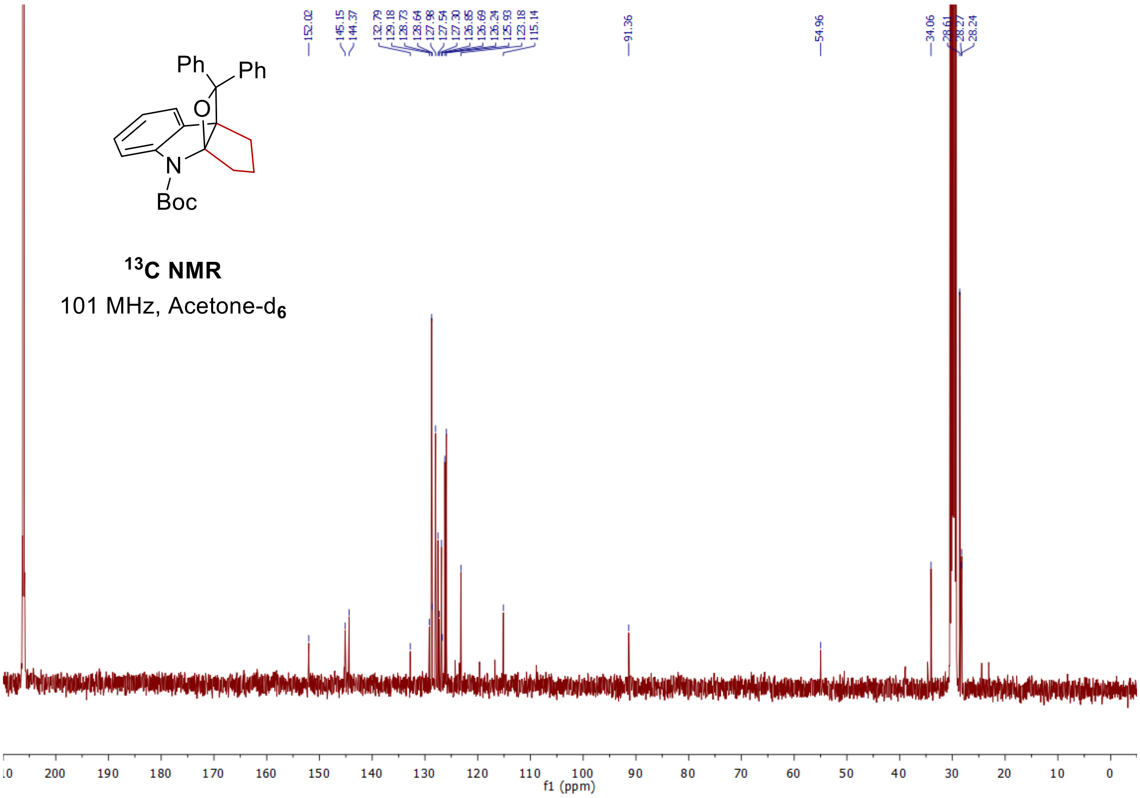
29 - ^{13}C NMR (Acetone-d$_6$)



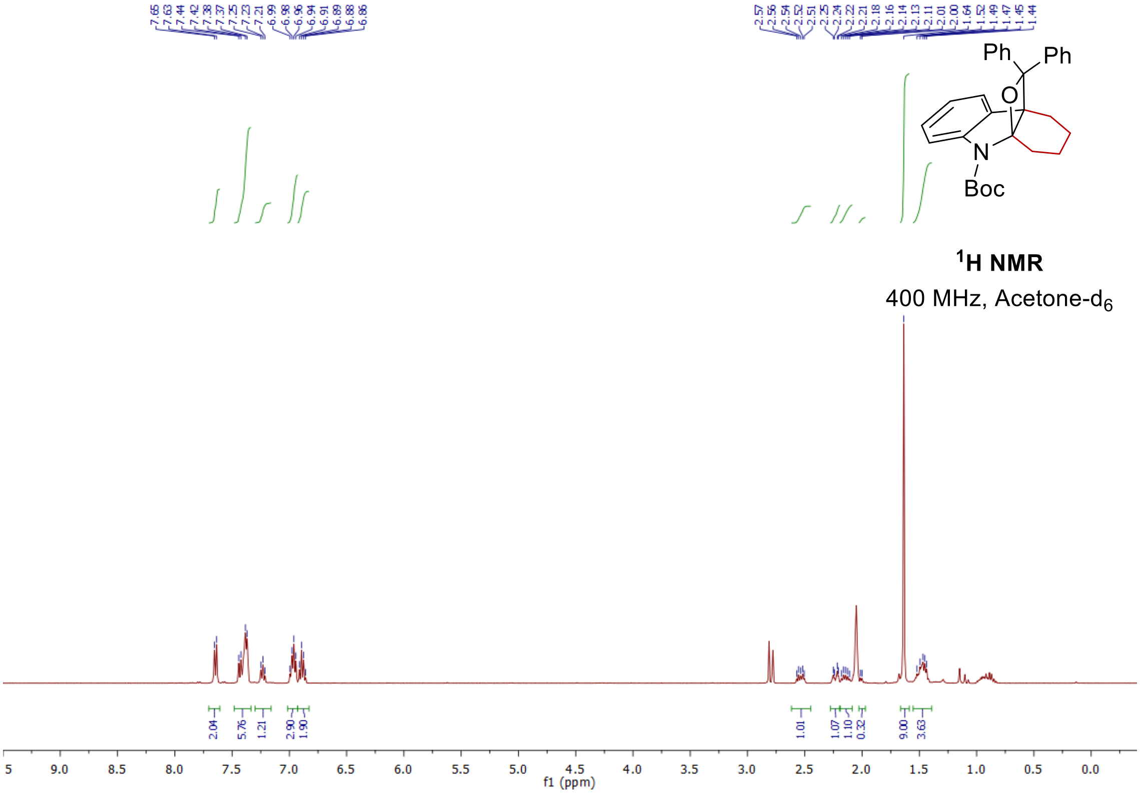
30 - ^{1}H NMR (Acetone-d$_6$)



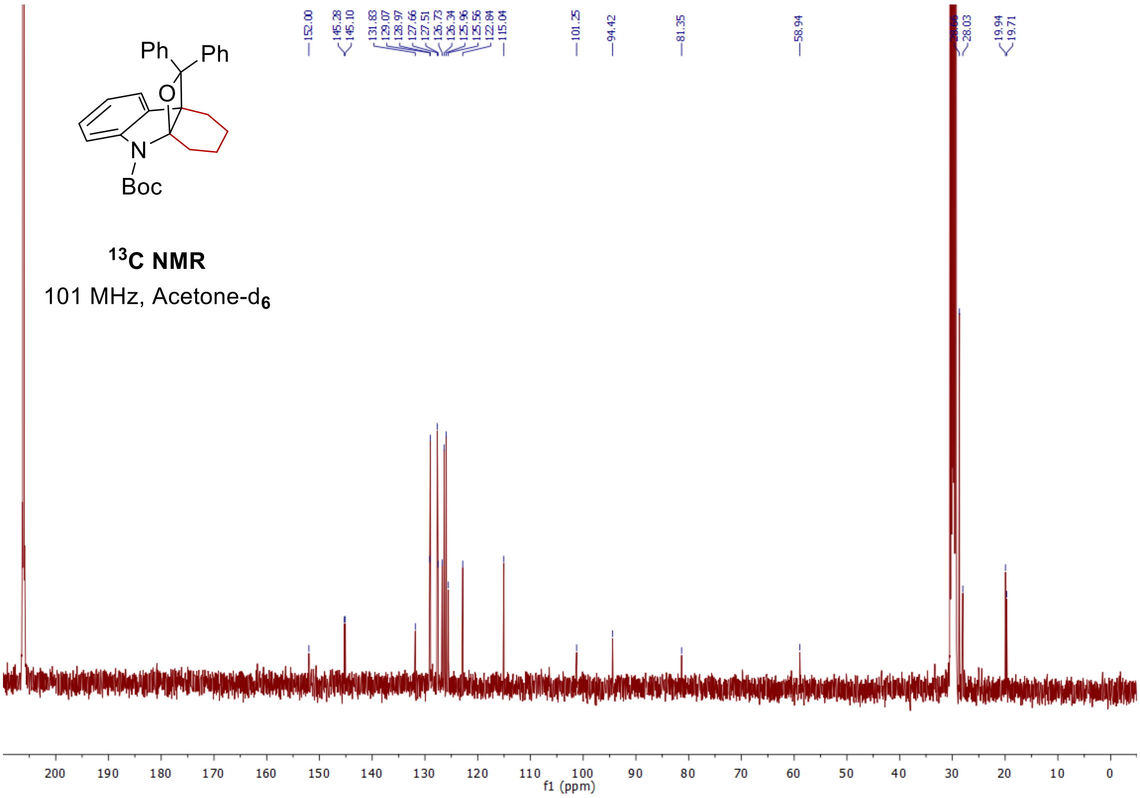
30 - ^{13}C NMR (Acetone-d$_6$)



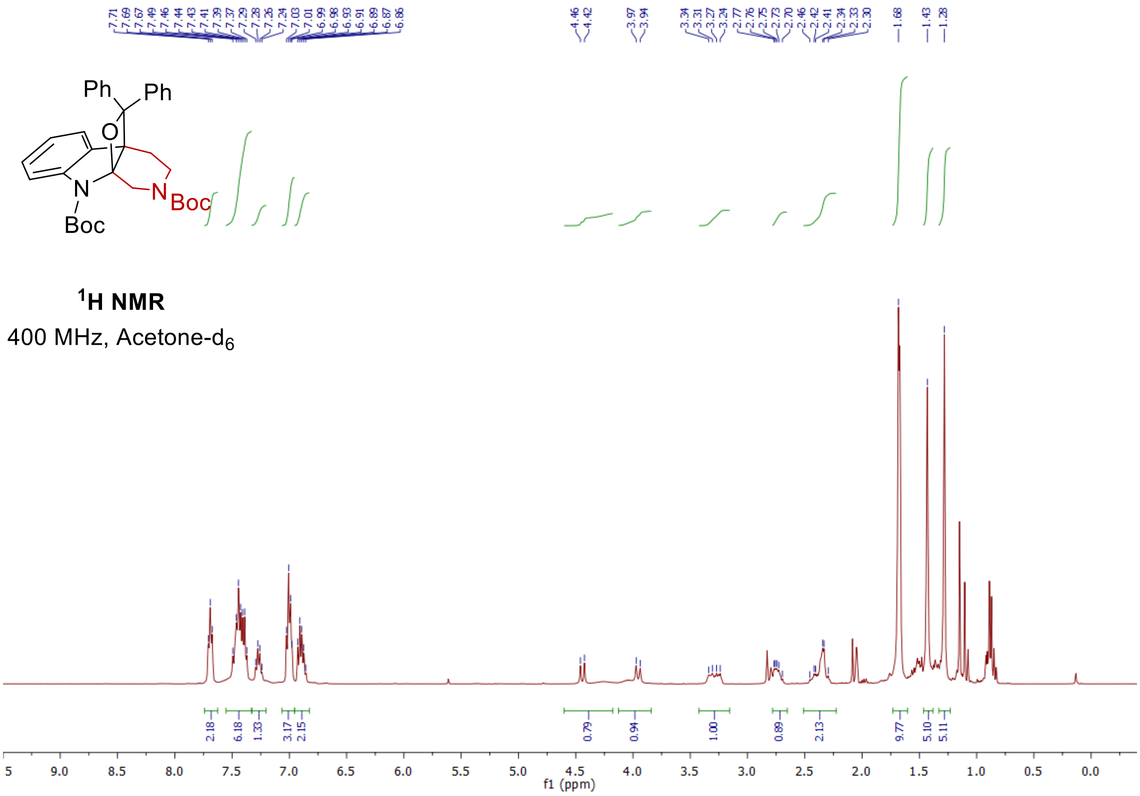
31 - ^{1}H NMR (Acetone-d$_6$)



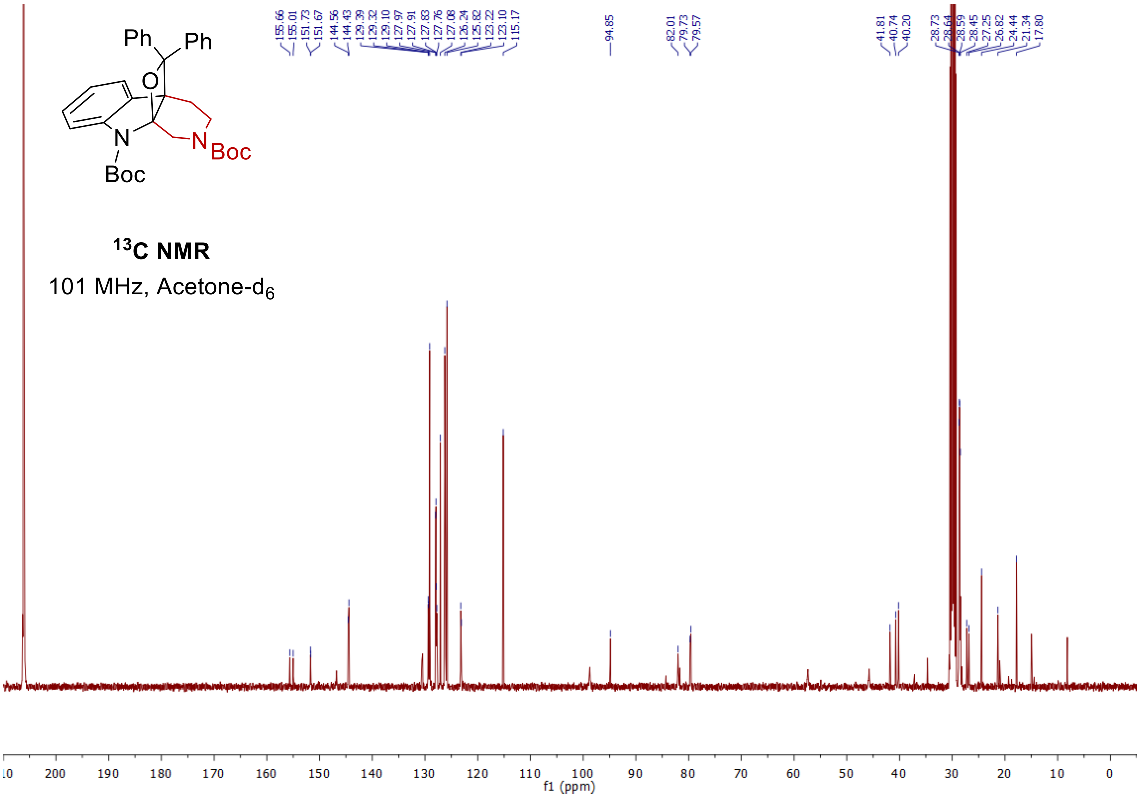
31 - ^{13}C NMR (Acetone-d$_6$)



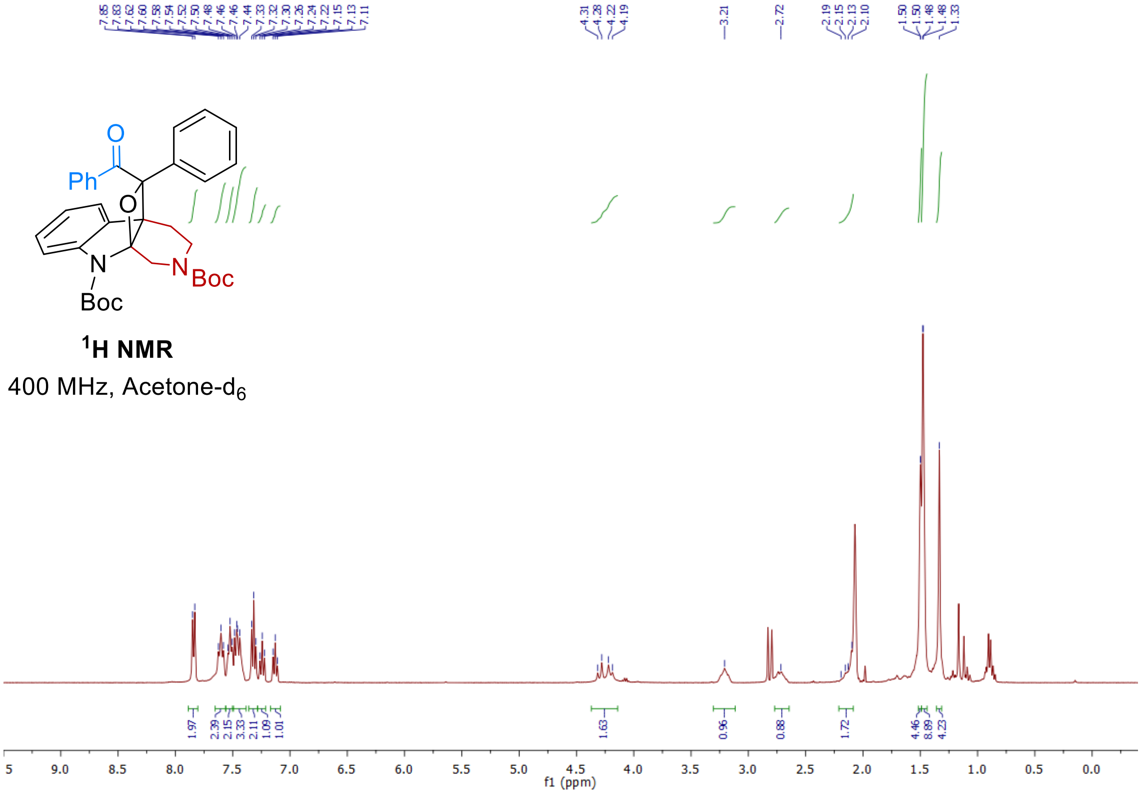
32 - ^{1}H NMR (Acetone-d$_6$)



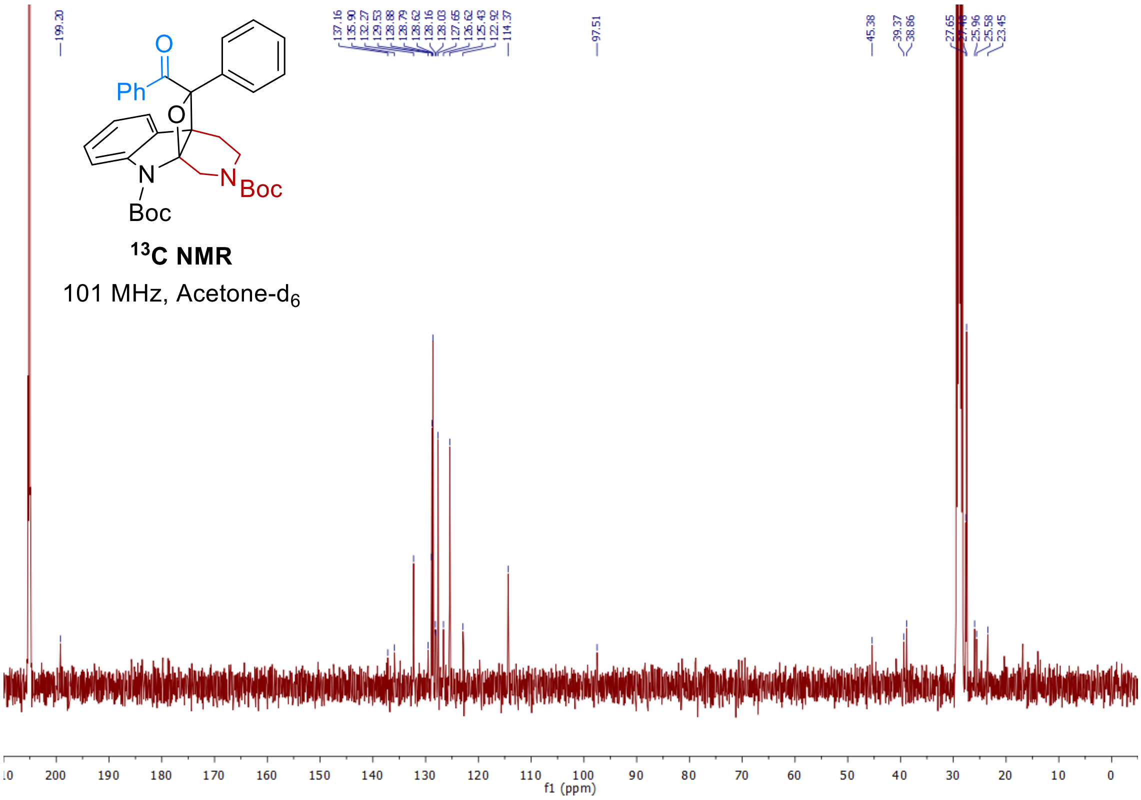
32 - ^{13}C NMR (Acetone-d$_6$)



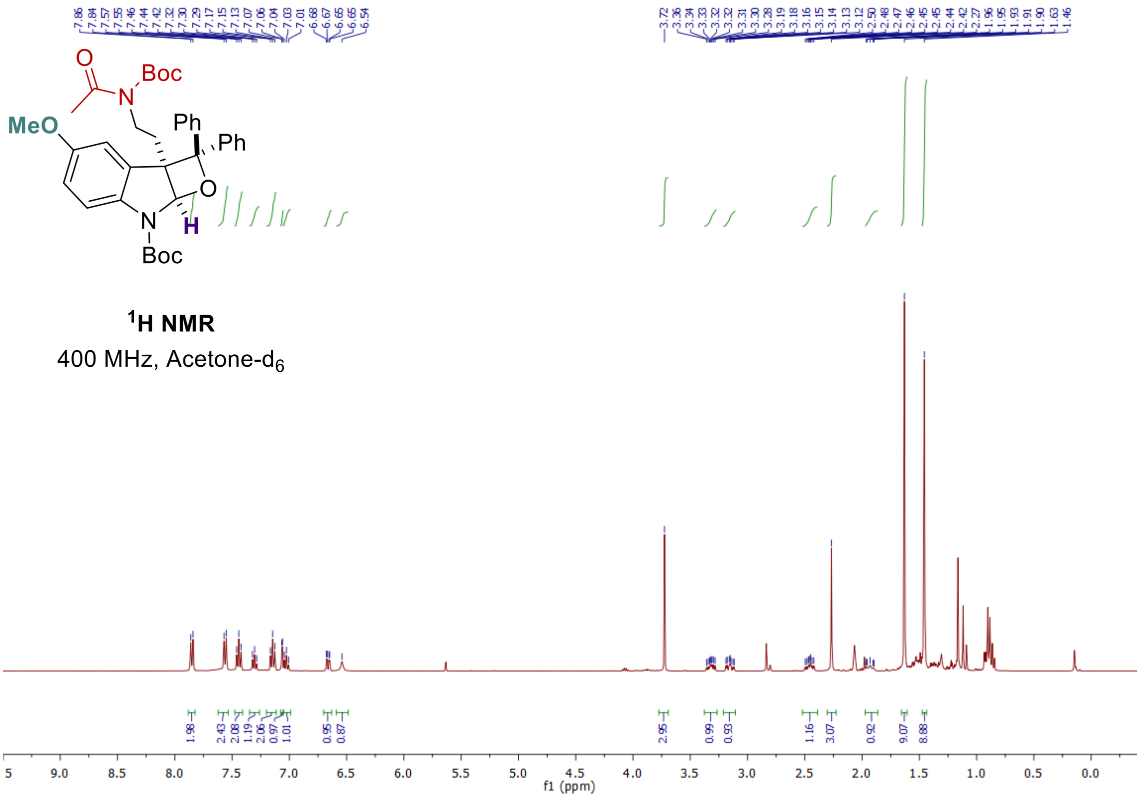
33 - ^{1}H NMR (Acetone-d$_6$)



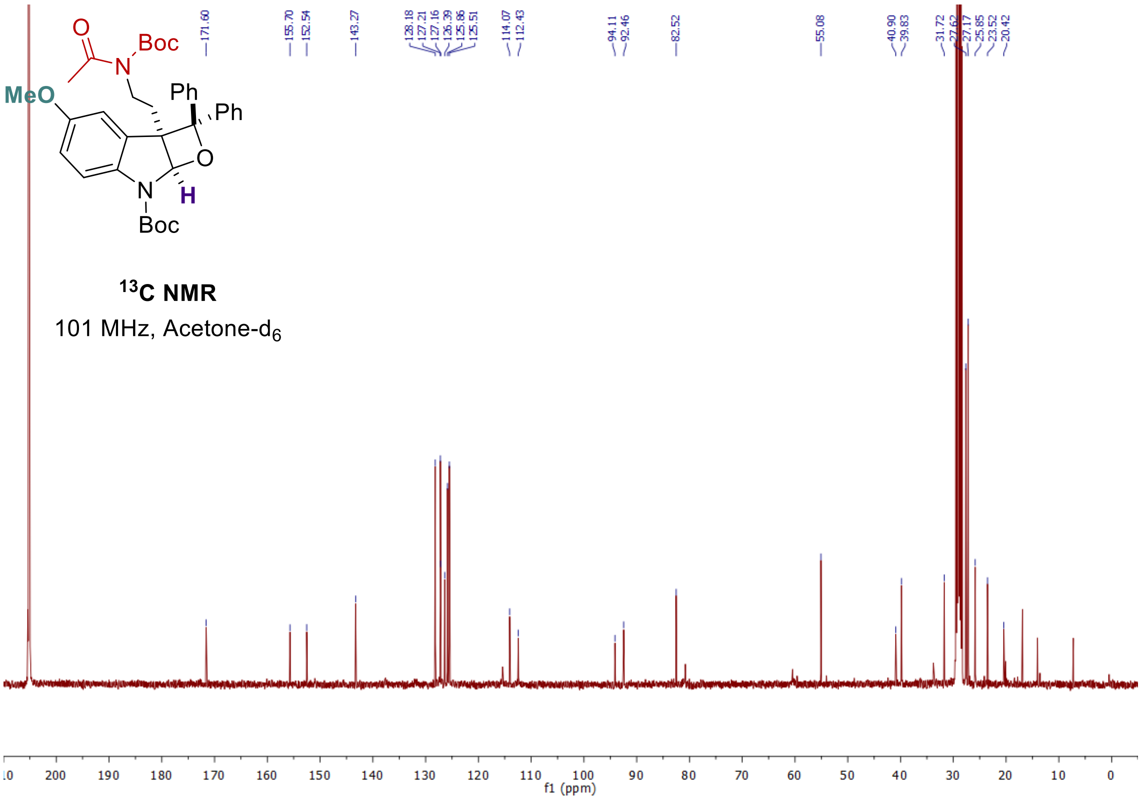
33 - ^{13}C NMR (Acetone-d$_6$)



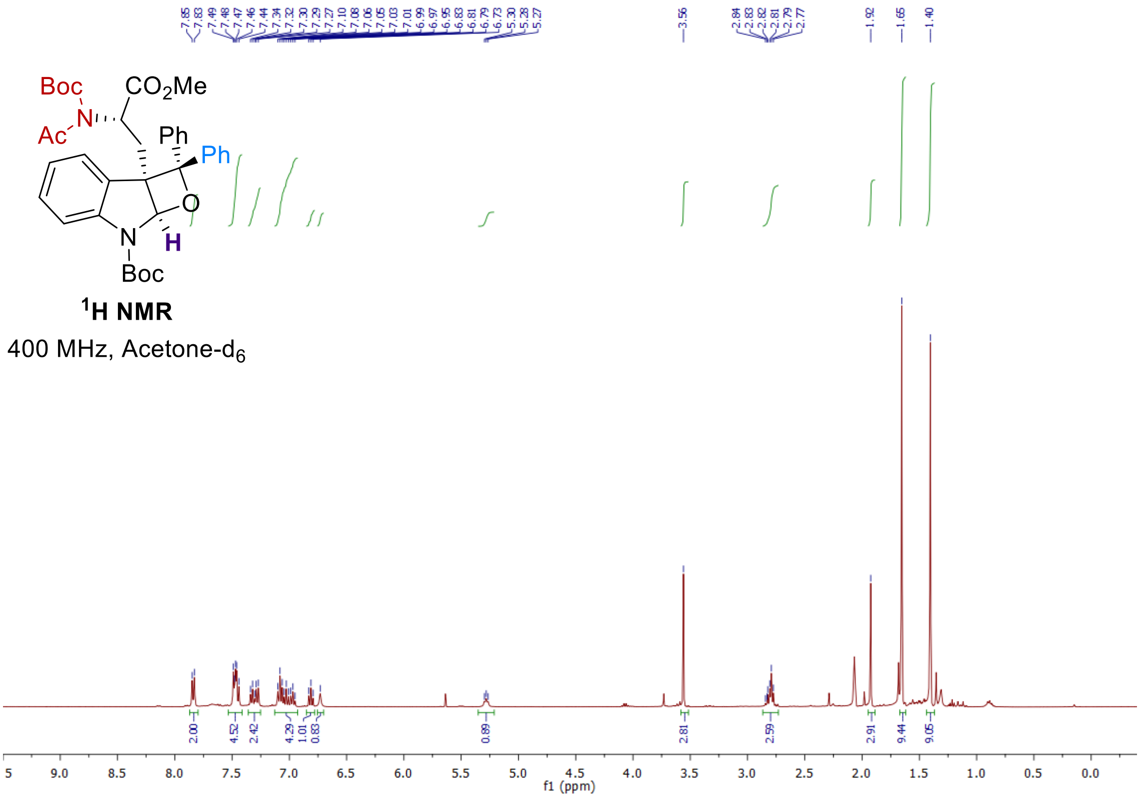
34 - ^{1}H NMR (Acetone-d$_6$)



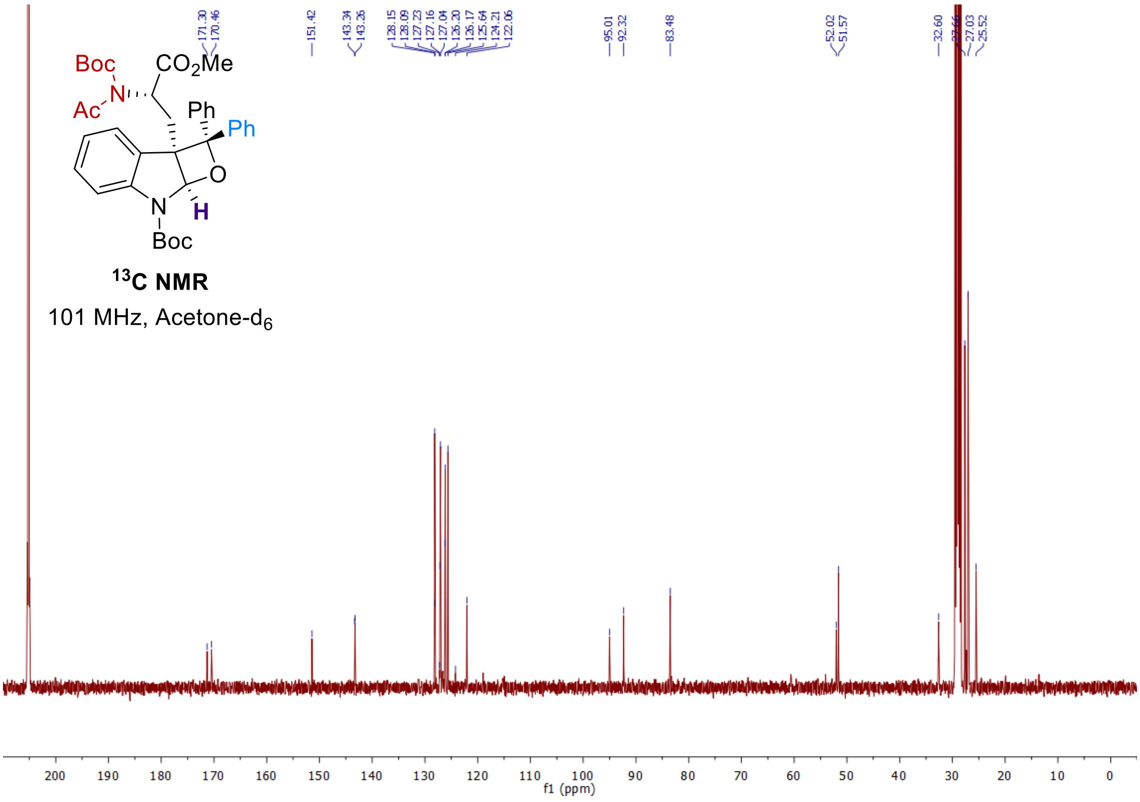
34 - ^{13}C NMR (Acetone-d$_6$)



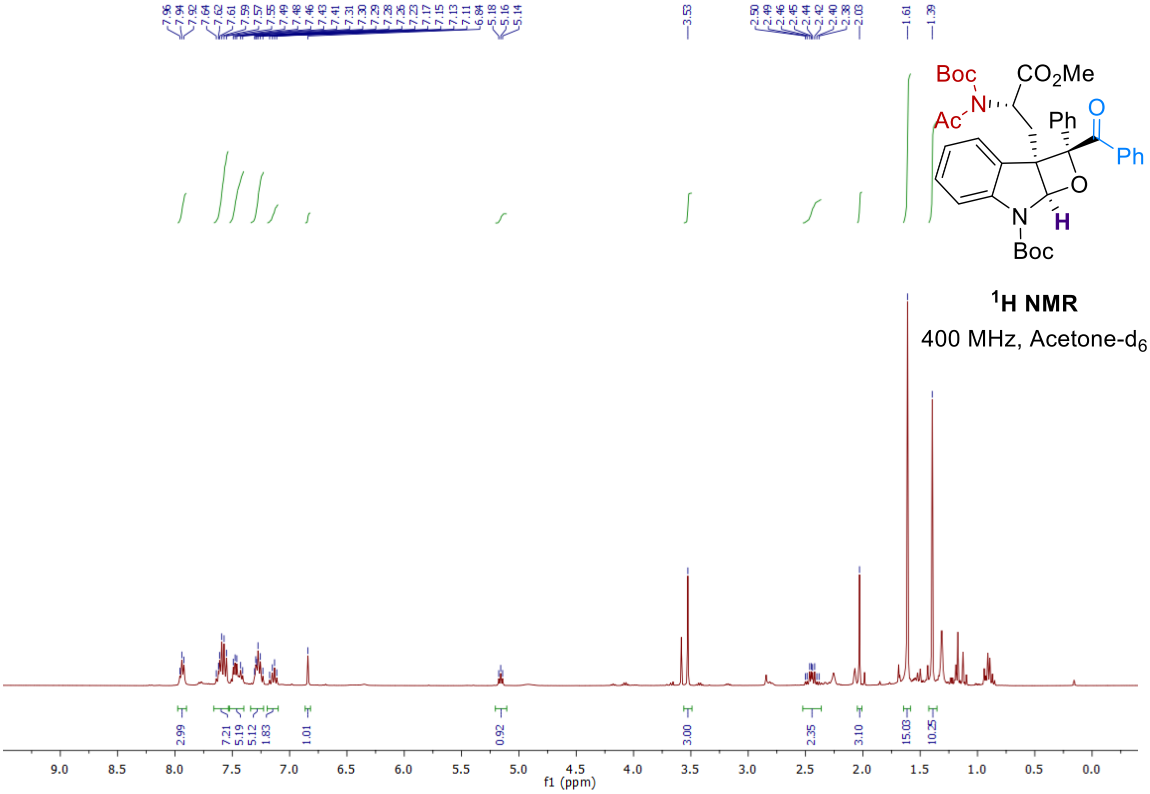
35 - ^{1}H NMR (Acetone-d$_6$)



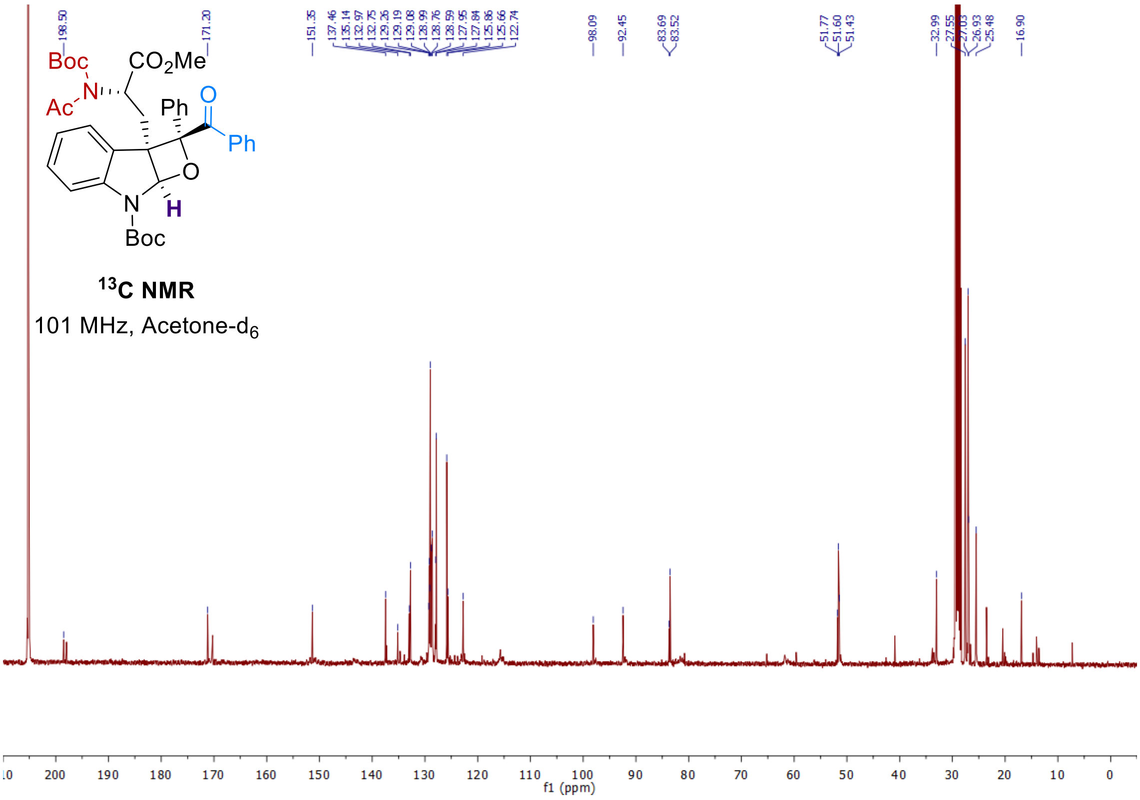
35 - ^{13}C NMR (Acetone-d$_6$)



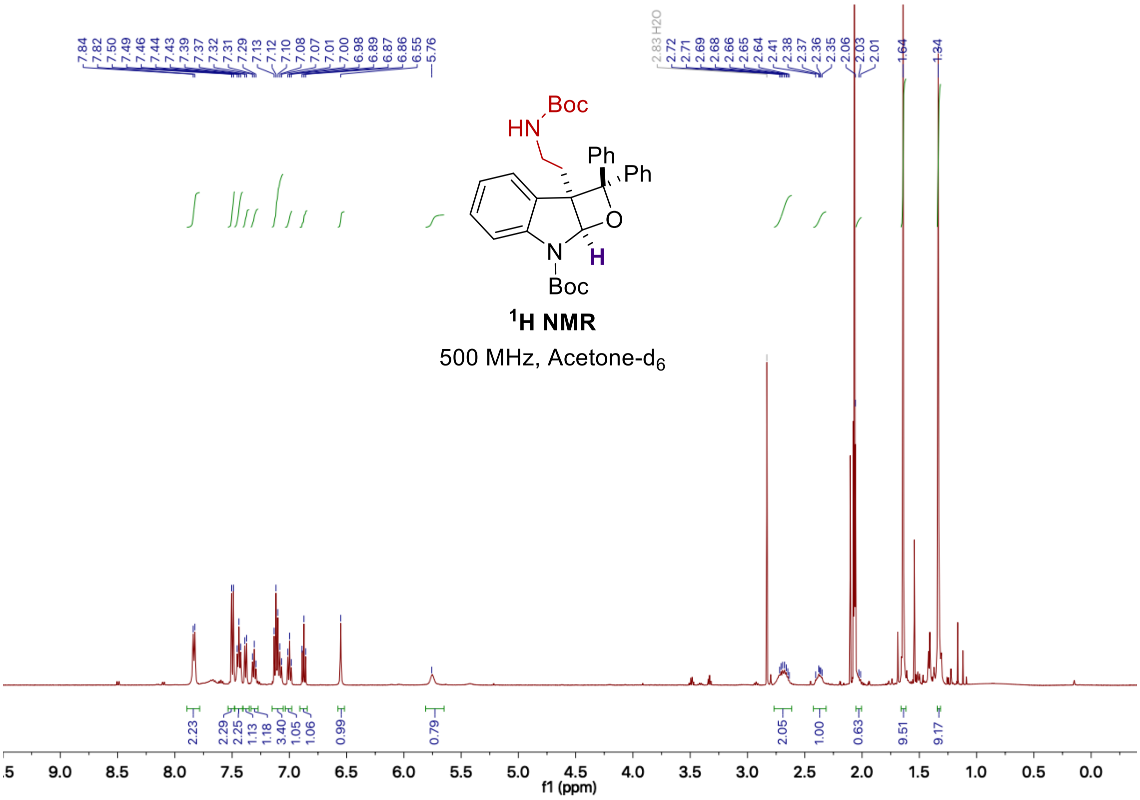
36 - ^{1}H NMR (Acetone-d$_6$)



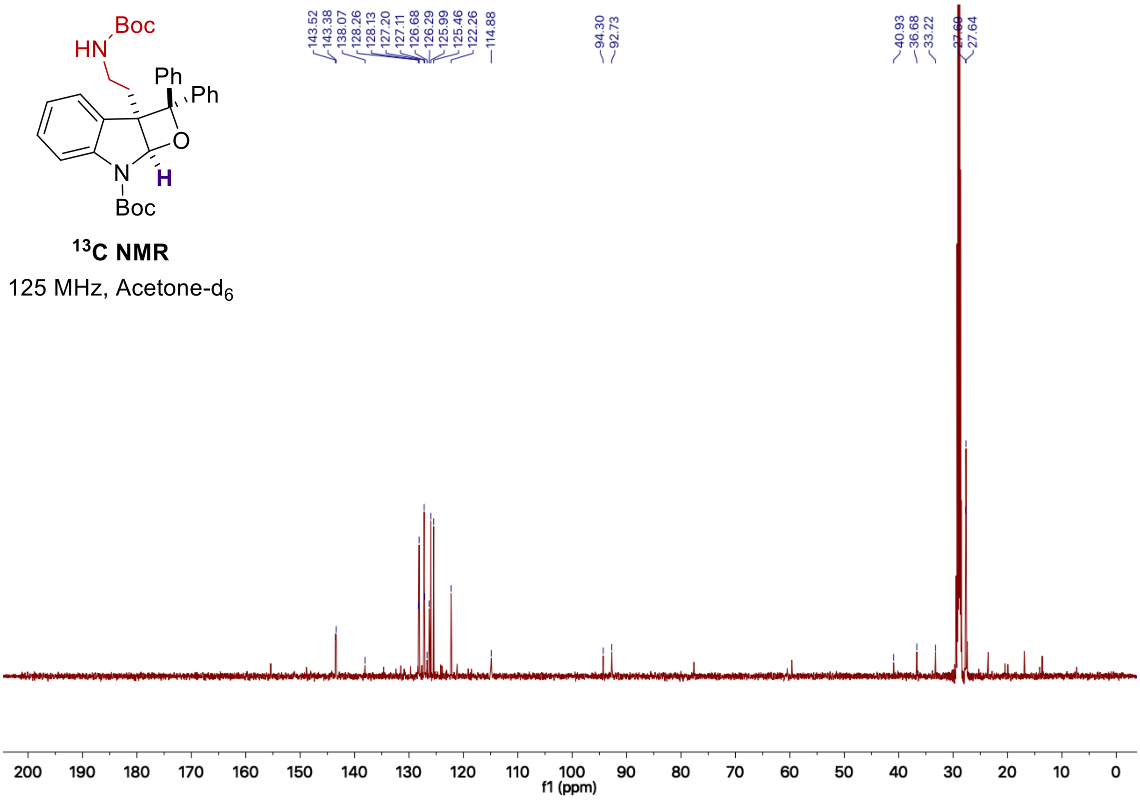
36 - ^{13}C NMR (Acetone-d$_6$)



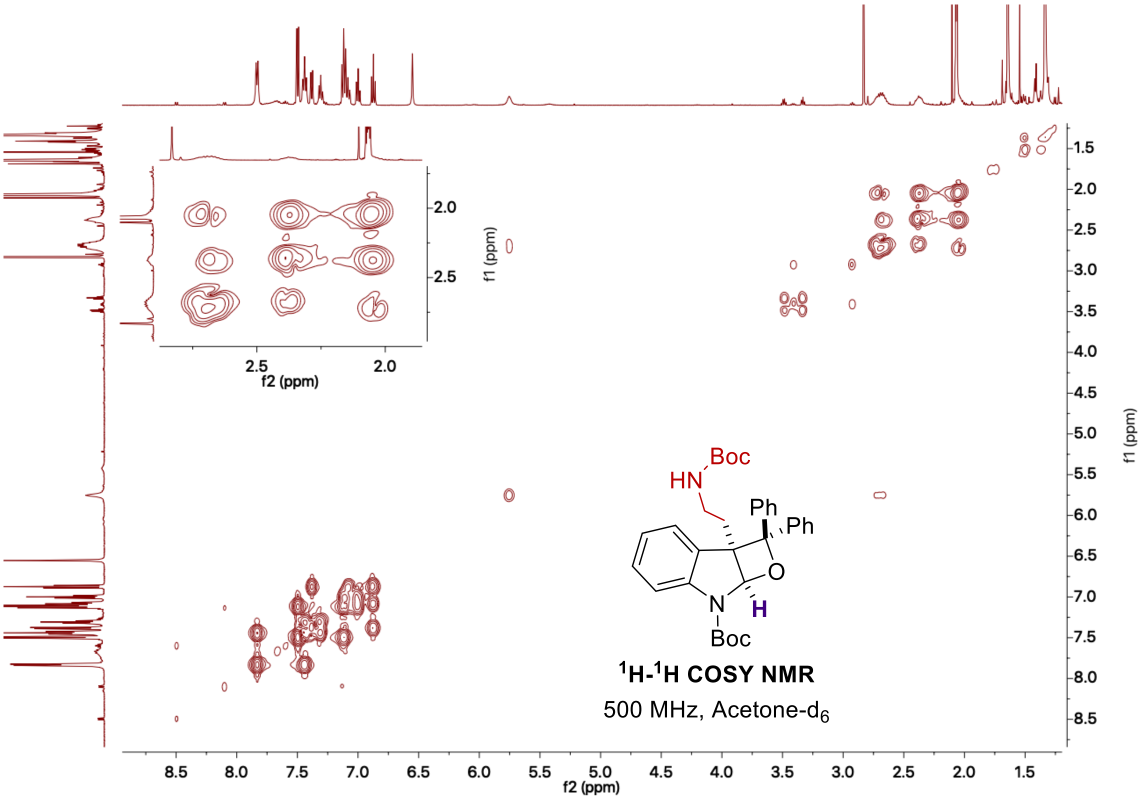
38 - ^{1}H NMR (Acetone-d$_6$)



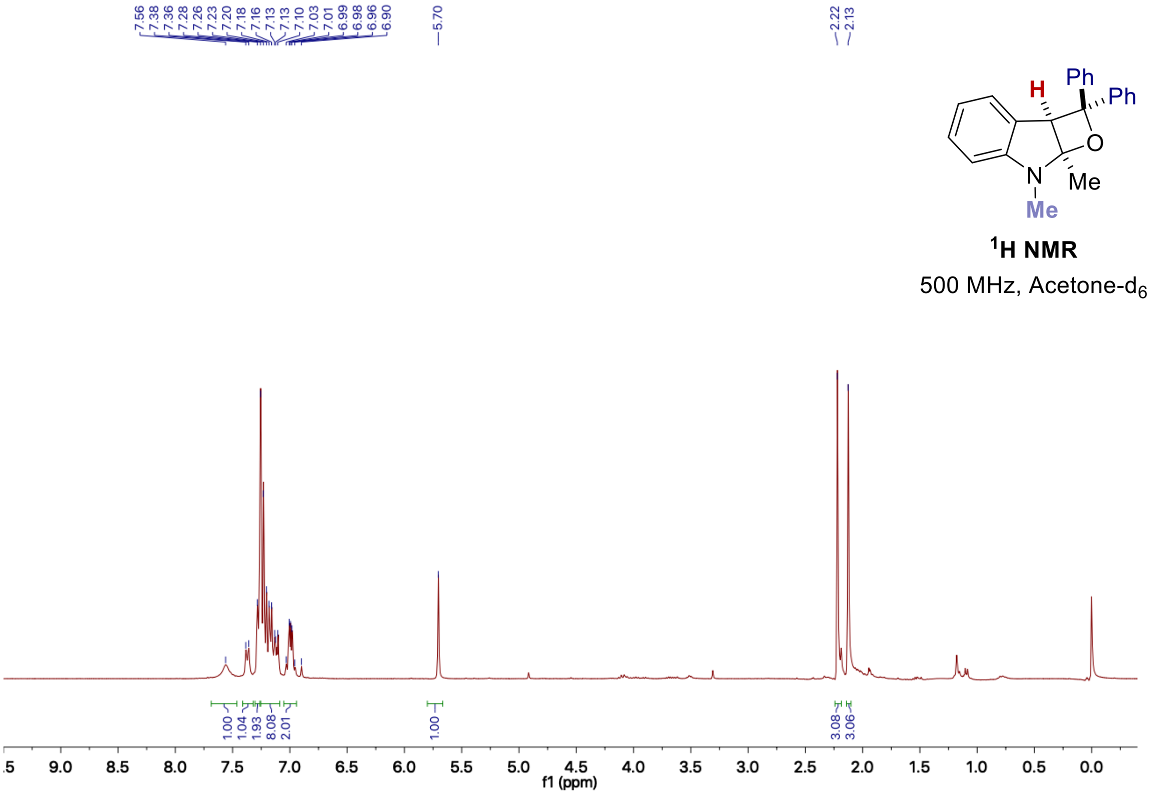
38 - ^{13}C NMR (Acetone-d$_6$)



38 - ^1H-^1H COSY NMR (Acetone-d$_6$)



39 ^{1}H NMR (CDCl$_3$)



39 ^{13}C NMR (Acetone-d$_6$)