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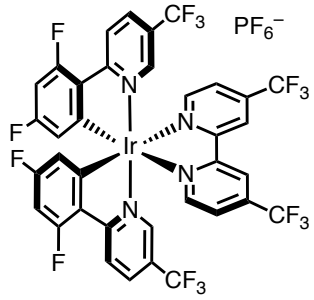
1. General Information

Commercial reagents were purified prior to use according to the guidelines of Perrin and Armarego.[1] All solvents were purified following the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator and a water bath. Chromatographic purification of isolated products was accomplished using forced-flow chromatography on automated Biotage Isolera™ Spektra or Teledyne ISCO CombiFlash™ NextGen 300+ systems using silica gel (Silicycle Silia*Sep*™ cartridges), following the general method of Still.[3] Thin-layer chromatography (TLC) was performed on Analtech 250 micron silica gel plates. Visualization of the developed chromatogram was achieved by fluorescence quenching, $KMnO_4$ stain or vanillin stain. Preparative thin-layer chromatography was performed on Analtech 250–1000 micron silica gel plates. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-II 500 (500 and 125 MHz) instrument and are internally referenced to residual protic solvent signals ($CDCl_3$ referenced to δ 7.26 and 77.16 ppm, respectively; MeCN-d_3 referenced to δ 1.94 and 118.26 ppm, respectively; acetone-d_6 referenced to δ 2.05 and 29.84, respectively, DMSO-d_6 referenced to δ 2.50 and 39.52 ppm, respectively). ^{19}F spectra were recorded on a Bruker NB300 NanoBay 300 MHz (282 MHz) instrument. Data for ^{1}H NMR are reported by chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets, dq = doublet of quartets, dp = doublet of pentets, br = broad), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity (for ^{19}F coupling), and no special nomenclature is used for equivalent carbons. Regioisomers are assigned via literature comparison or 2D ^{1}H NMR for indicated examples, with related structures assigned by analogy. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and peaks are reported in wavenumbers (cm^{-1}). High-resolution mass spectra were obtained at the Princeton University mass spectrometry facilities.

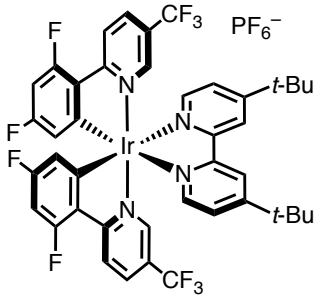
2. Synthesis and characterization of substrates, reagents and catalysts

All reagents and catalysts were purchased from commercial vendors and used as received, excluding select examples described below:

Photocatalysts Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**) and Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (**[Ir-2]**) were prepared according to literature procedures.[4-5]

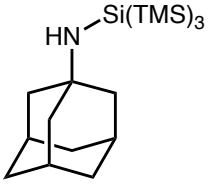


[Ir-1]



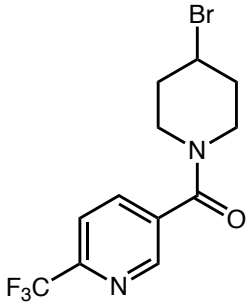
[Ir-2]

$(TMS)_3SiOH$ and $(TMS)_3SiNHAd$ were prepared following literature procedures.[6-7]



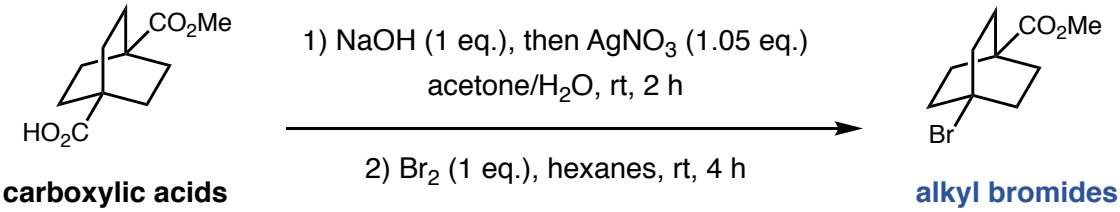
$(TMS)_3SiNHAd$

(4-bromopiperidine-1-yl)(6-(trifluoromethyl)pyridine-3-yl)methanone (**Br-1**) was prepared according to literature procedures.[8]



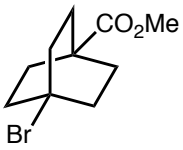
Br-1

Hunsdiecker-Borodin synthesis of alkyl bromide substrates



carboxylic acids **alkyl bromides**

Select alkyl bromides were synthesized using Hunsdiecker-Borodin bromination conditions adapted from literature procedures.[9] To a 40 mL vial equipped with a Teflon stir bar was added carboxylic acid (5.75 mmol, 1.0 equiv.) and acetone (10 mL). The contents of the vial were stirred for 1–2 minutes, after which a solution of 1 M NaOH (5.8 mL, 5.8 mmol, 1.0 equiv.) was added to the heterogeneous mixture and allowed to stir at room temperature for 10 minutes, ultimately producing a homogeneous, clear solution. A 4 M solution of $AgNO_3$ in water (1.5 mL, 6.0 mmol, 1.05 equiv.) was then added dropwise to the vial, affording a white precipitate. This mixture was allowed to stir at room temperature for an additional 2 hours, after which the resulting brown suspension was filtered and washed with water, acetone and ether (10 mL each). The remaining pale-brown solid was then collected and dried under vacuum overnight at 50 °C to afford the crude silver carboxylate salt, which was carried through the next step without further purification. This salt was then suspended in hexanes (12 mL) in a clean 40 mL vial with a Teflon stir bar, and the vial was capped and sparged with nitrogen for 10 minutes. Bromine (1.0 equiv.) was then added dropwise, and the mixture was stirred at room temperature under nitrogen for 4 hours. After 4 hours, the dark red suspension was filtered, and the remaining yellow solid washed with ether (3 x 15 mL) and $NaHCO_3$ (2 x 20 mL). The organic phase was separated, washed with brine (20 mL), dried over $MgSO_4$, and concentrated to afford the alkyl bromide as a colorless oil, which formed a pale white solid upon standing. This alkyl bromide was subsequently characterized and used without further purification.



Methyl 4-bromobicyclo[2.2.2]octane-1-carboxylate (S1)

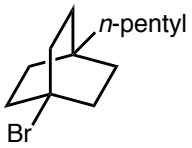
Prepared following the general procedure outlined above using 4-(methoxycarbonyl)bicyclo[2.2.2]octane-1-carboxylic acid (1.22 g, 5.75 mmol, 1.0 equiv.) to first afford the crude silver salt (1.54 g, 4.83 mmol, 84% yield). This product was subsequently exposed to bromine (247 μL, 4.83 mmol, 1.0 equiv.) to deliver the final alkyl bromide product as a white solid (769.7 mg, 3.11 mmol, 64% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.63 (s, 3H), 2.27 – 2.20 (m, 6H), 1.98 – 1.90 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.25, 62.30, 52.01, 36.98, 36.94, 31.27.

Spectral data are consistent with those previously reported in literature:[9]

Birch, A. M.; Birtles, S.; Buckett, L. K.; Kemmitt, P. D.; Smith, G. J.; Smith, T. J. D.; Turnbull, A. V.; Wang, S. J. Y. *J. Med. Chem.* **2009**, *52*, 1558.



1-bromo-4-pentylbicyclo[2.2.2]octane (S2)

Prepared following the general procedure outlined above using 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid (1.29 g, 5.75 mmol, 1.0 equiv.) to first afford the crude silver salt (1.64 g, 4.94 mmol, 86% yield). This product was subsequently exposed to bromine (253 μL, 4.94 mmol, 1.0 equiv.) to deliver the final alkyl bromide product as a clear oil (707.3 mg, 3.76 mmol, 76% yield), which formed a waxy white solid upon storage at 8 °C.

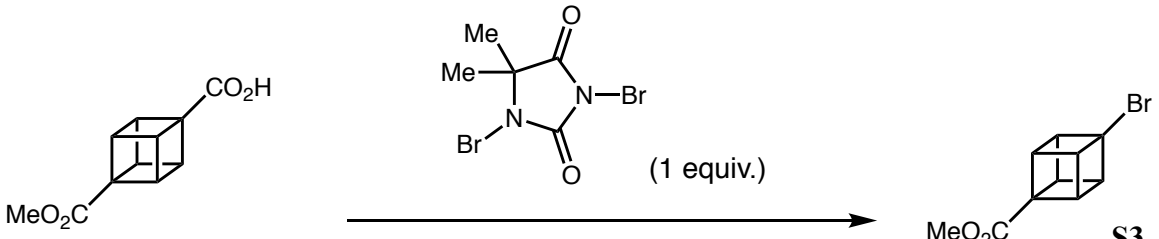
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.24 – 2.14 (m, 6H), 1.57 – 1.48 (m, 6H), 1.28 – 1.22 (m, 2H), 1.20 – 1.08 (m, 4H), 1.03 – 0.98 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 65.26, 41.20, 38.03, 34.02, 32.79, 28.79, 23.40, 22.75, 14.19.

Spectral data are consistent with those previously reported in literature:[10]

Candish, L.; Standley, E. A.; Gómez-Suárez, A.; Mukherjee, S.; Glorius, F. *Chem. Eur. J.* **2016**, *22*, 9971.

Photo-Hunsdiecker synthesis of bromocubanes



cubane carboxylic acid
1.25 mmol

Ir-2 (2 mol%), Cs_2CO_3 (1 equiv.)
PhF (0.1 M)
40 W blue LEDs, 18 h

bromocubane

Methyl 4-bromocubane-1-carboxylate (S3)

Prepared using procedures adapted from previous literature reports.[10] An oven-dried 40 mL vial equipped with Teflon stir bar was charged with 4-methoxycarbonylcubane-1-carboxylate (257.7 mg, 1.25 mmol, 1.0 equiv.), cesium carbonate (407.3 mg, 1.25 mmol, 1.0 equiv.), **[Ir-2]** (28.0 mg, 0.025 mmol, 0.02 equiv.) and 1,3-dibromo-5,5-dimethylhydantoin (357.4 mg, 1.25 mmol. 1.0 equiv.). Fluorobenzene (12.5 mL, 0.1 M) was then added to the vial, which was capped, equipped with a vent needle through the septum and sparged under nitrogen at 0° C for 5 minutes. After 5 minutes, the vial was sealed with Parafilm and irradiated with a 40 W Kessil Blue LED for 18 h, using fans to maintain equilibrated temperatures of 30–35° C. After 18 h, the reaction mixture was filtered through a silica pad and rinsed with dichloromethane (20 mL). The filtrate was concentrated *in vacuo* to obtain a crude residue (*note: product* **S3** *can be moderately volatile under reduced pressure – as an alternative procedure, the solvent(s) can be removed from the filtrate via vigorous sparging under nitrogen, at room temperature, overnight)*. The crude residue was ultimately purified by flash chromatography (100% pentane to 2:1 pentane/Et_2O) to provide bromocubane **S3** (170.6 mg, 0.708 mmol, 57% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.34 – 4.30 (m, 3H), 4.27 – 4.24 (m, 3H), 3.71 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.00, 63.26, 56.36, 54.71, 51.85, 47.85.

Spectral data are consistent with those previously reported in literature:[11]

Watanabe, A.; Koyamada, K.; Miyamoto, K.; Kanazawa, J.; Uchiyama, M. *Org. Process Res. Dev.* **2020**, *24*, 1328.

3. Reaction setup

Reactions were typically performed in the Integrated Photoreactor[12] using a 450 nm LED module. Use of the Integrated Photoreactor, in lieu of traditional blue Kessil lamp setups, allows for precise control over reaction temperature, light intensity, stir rate and irradiation time. In particular, access to light intensities greater than the measured output of standard single-lamp Kessil setups, as well as reproducible control of reaction stir rates, is critical to achieving maximum efficiency for this transformation. Integrated Photoreactor settings, while generally executed at 25% light intensity, 3500 fan rpm, 100–500 stir rpm and 4 h irradiation time for the optimized reaction, are specified for each substrate (equilibrated temperatures at the indicated fan speed are generally measured to be ~30–35 °C). Light intensities across various photoreactor/LED plate assemblies were verified using a Thorlabs PM100D Optical Power Meter with associated Thorlabs S425C Thermal Power Sensor (resolution: 100 μW; optical power range: 2 mW–10 W) to ensure standardization. For both optimization (0.05 mmol) and standard scales (0.25 mmol), appropriate chambers and vial holders for the irradiation of 8 mL or 40 mL reaction vials, respectively, were selected (both sizes of chambers and vial holders utilized for this study are displayed *vide infra*). For introduction of air to the reaction vessel, an 18G vent needle is inserted through the septum of the vial cap prior to irradiation – this procedure provides sufficient oxygen incorporation while preventing substantial changes in concentration (via solvent evaporation over the course of the reaction).

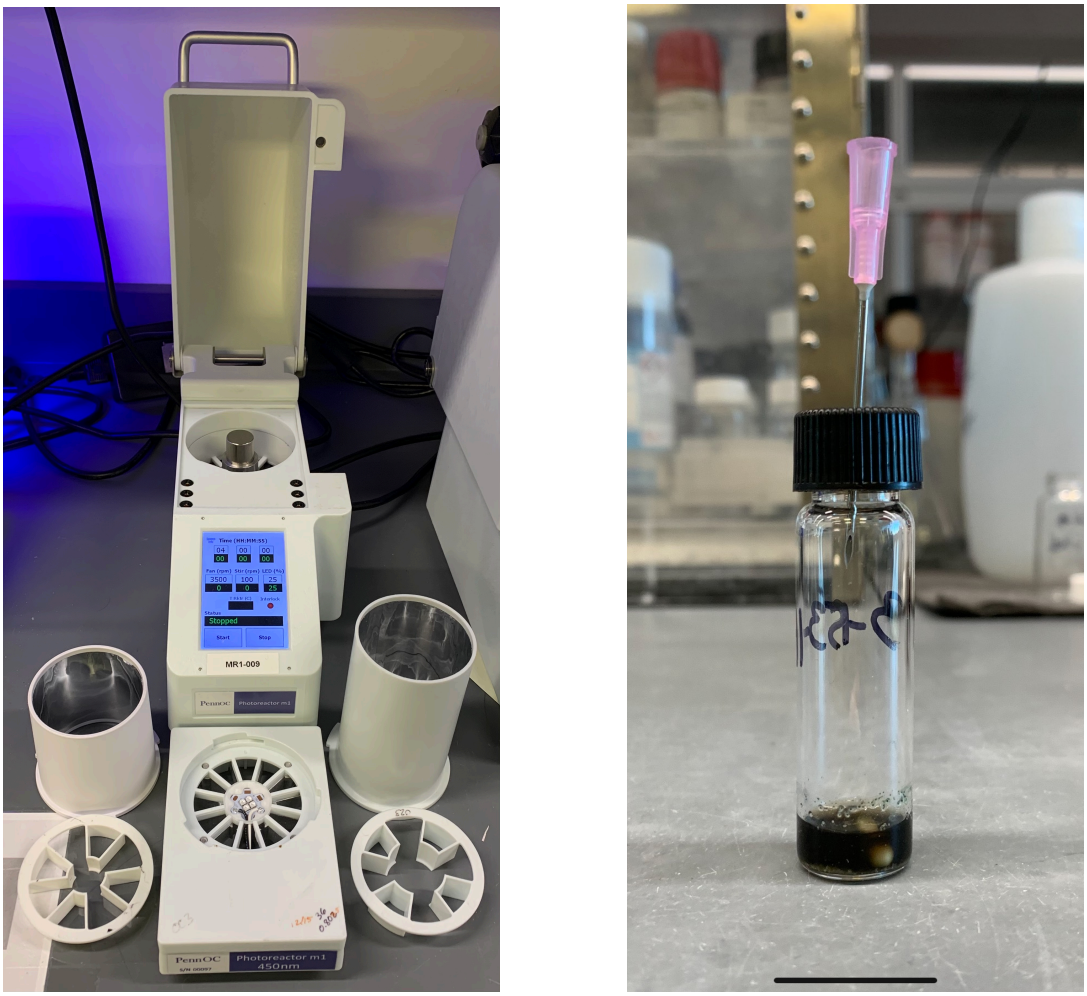
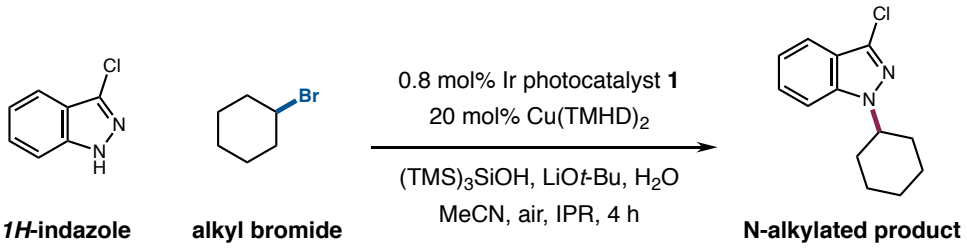


Figure S1: Components required for optimal reaction setup. a) Integrated Photoreactor and associated equipment. b) Typical 0.05 mmol scale (optimization scale) reaction setup, featuring standard vent needle assembly.

4. Optimization studies

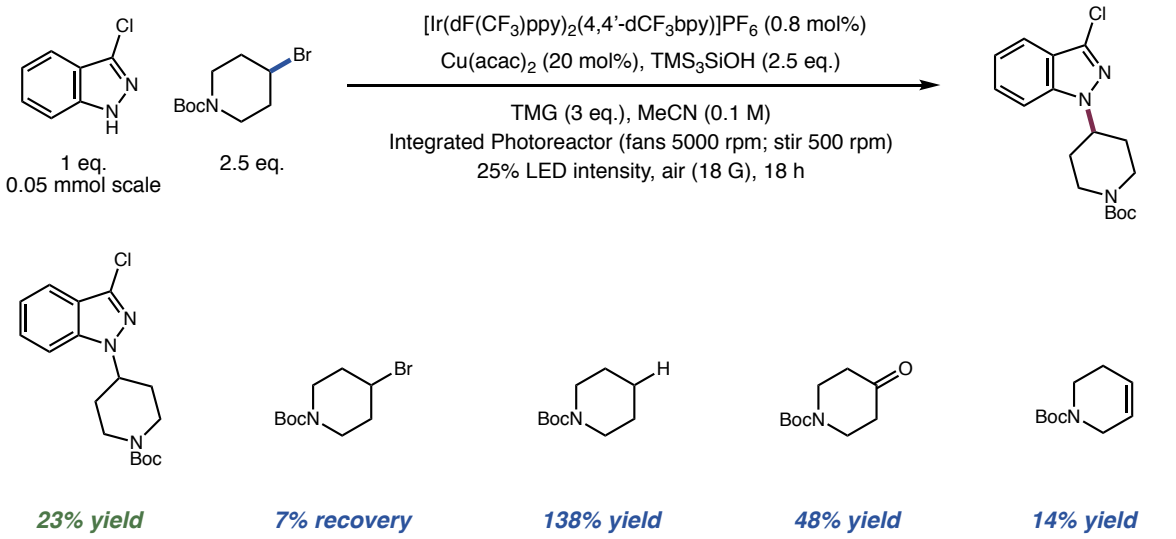
General procedure for optimization studies and control experiments: To an oven-dried 8 mL vial equipped with a Teflon stir bar was added *N*-nucleophile (0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.4 μmol, 0.008 equiv.), copper salt (0.01 mmol, 0.2 equiv.), base (0.15 mmol, 3.0 equiv.) and solvent (0.5 mL, 0.1 M). The resulting solution was stirred for 1–2 minutes under air to ensure complete ligation of the nucleophile to the copper precatalyst. Following this complexation period, alkyl halide (0.125 mmol, 2.5 equiv.), silyl radical precursor (0.125 mmol, 2.5 equiv.) and any further additives, such as H_2O (9 μL, 0.5 mmol, 10 equiv.), were added to the mixture as indicated, after which the vial was capped and an 18G vent needle was inserted through the Teflon-lined septum. Alternatively, for non-aerobic reactions employing stoichiometric oxidants, oxidant (0.10 mmol, 2.0 equiv.) was added last, after which the vial was capped, sparged under nitrogen for 10 minutes and sealed with Parafilm. For irradiated experiments, the reaction mixture was subsequently stirred within the Integrated Photoreactor (450 nm irradiation) for 4 hours using the following settings (unless otherwise specified): 25% LED intensity, 100 rpm stir rate and 3500 rpm fan speed. Alternatively, for select indicated examples, the vial was irradiated using a single 40 W Kessil blue LED for 4 hours (vial placed 2 cm away), using fans to maintain equilibrated temperatures of ~30 °C. After 4 hours, mesitylene (5 μL, 35.9 μmol, 0.72 equiv.) was added via syringe to the reaction mixture, which was stirred for an additional 1–2 minutes. An aliquot of the reaction mixture (~0.1 mL) was passed through a celite plug into an NMR tube, followed by 0.5–0.8 mL $CDCl_3$, and analyzed via ^{1}H NMR to determine the analytical yield of the desired *N*-alkylated product. Deviations to the general protocol described above, as well as specific reagent identities and stoichiometries used during optimization, are indicated within each experiment below.



***1H*-indazole** **alkyl bromide** **N-alkylated product**

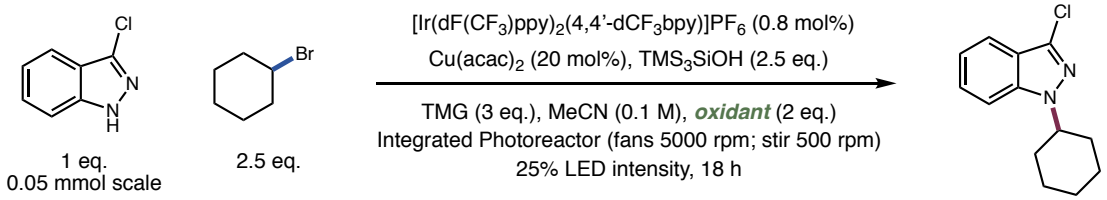
entry	*deviation*	*yield*
1	**none**	**93%**
2	no water	58%
3	TMG as base, no water	41%
4	sparged under N_2 atmosphere	8%
5	ambient light only	<1%
6	40 W Kessil Blue LEDs as light source	40%
7	no base	4%
8	no photocatalyst	<1%
9	no copper catalyst	<1%
10	no $(TMS)_3SiOH$	<1%

Figure S2: Control reactions for optimized C(sp^3)–N coupling (see Figure 1).



Analytical yields via ^{1}H NMR vs. mesitylene

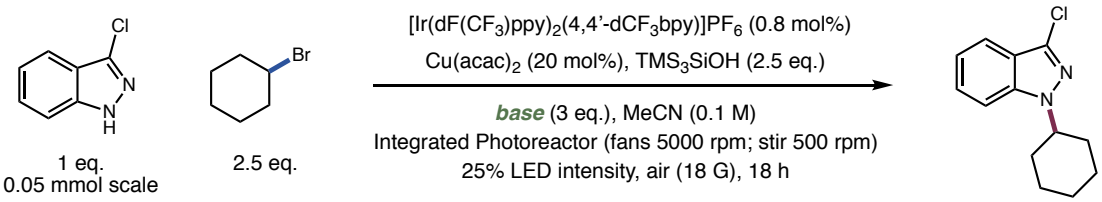
Figure S3: Optimization studies – summary of frequently observed alkyl byproducts.



Oxidant	**Yield**
Air (via 18 G needle)	***39%***
$(NH_4)_2S_2O_8$	***39%***
$Na_2S_2O_8$	***45%***
$K_2S_2O_8$	***43%***
$PhI(OAc)_2$	***0%***
$MesI(OAc)_2$	***0%***

Analytical yields via ^{1}H NMR vs. mesitylene

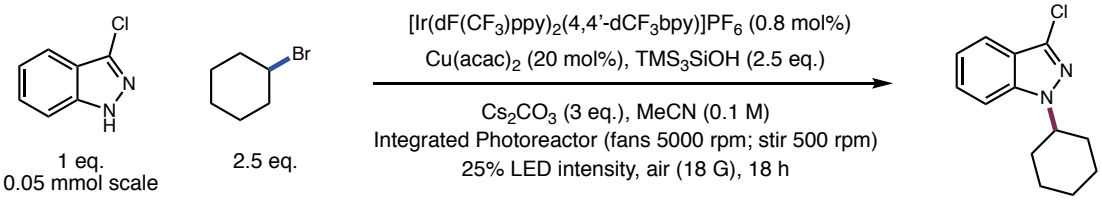
Figure S4: Optimization studies - evaluation of oxidants.



Base	**Yield**
TMG	***43%***
TMG (5 eq.)	***43%***
DBU	***<1%***
K_3PO_4	***26%***
K_2CO_3	***0%***
Cs_2CO_3	***45%***
C_2HCO_3	***0%***
$CsOH \cdot H_2O$	***0%***
LiOH	***0%***
Bu_4NOAc	***0%***

Analytical yields via ^{1}H NMR vs. mesitylene

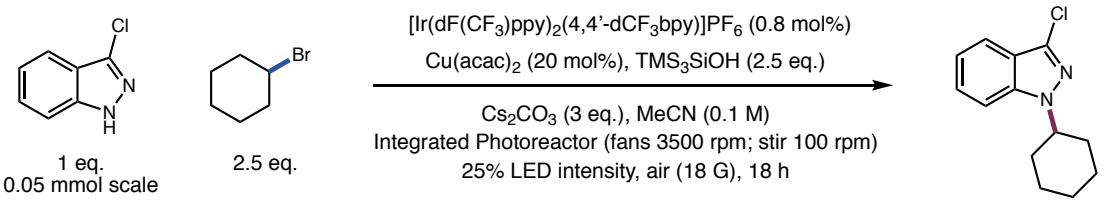
Figure S5: Optimization studies - evaluation of organic and inorganic bases.



Deviations in IPR setup	**Yield**
none	***45%***
3900 rpm fans	***54%***
2800 rpm fans	***56%***
1500 rpm stir	***35%***
1000 rpm stir	***41%***
100 rpm stir, 3500 rpms fans	***60%***

Analytical yields via ^{1}H NMR vs. mesitylene

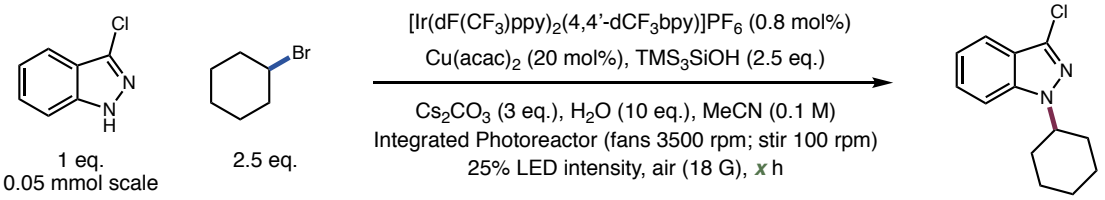
Figure S6: Optimization studies - evaluation of IPR stir rate and fan speed settings.



Additive	**Yield**
none	***59%***
10 eq. H_2O	***68%***

Analytical yields via ^{1}H NMR vs. mesitylene

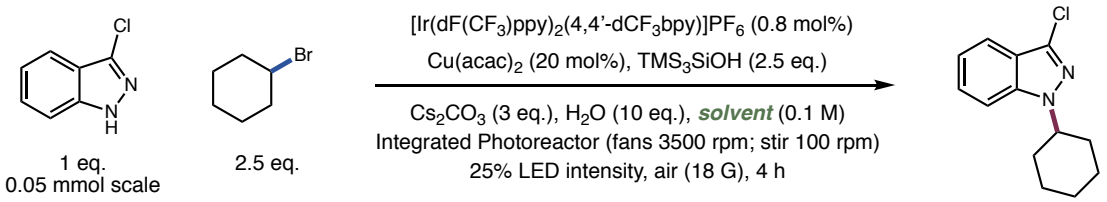
Figure S7: Optimization studies - evaluation of water as an exogenous additive.



Time elapsed	**Yield**
0 min.	***0%***
30 min.	***54%***
1 h	***58%***
2 h	***67%***
4 h	***69%***
18 h	***69%***

Analytical yields via ^{1}H NMR vs. mesitylene

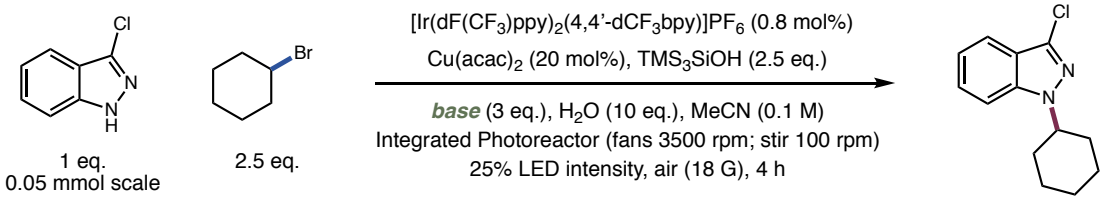
Figure S8: Optimization studies - time course using Cs_2CO_3 as base.



Solvent	**Yield**
MeCN	***58%***
DMF	***<1%***
DMSO	***<1%***
1,4-dioxane	***6%***
Acetone	***30%***
Methanol	***41%***
DME	***15%***

Analytical yields via ^{1}H NMR vs. mesitylene

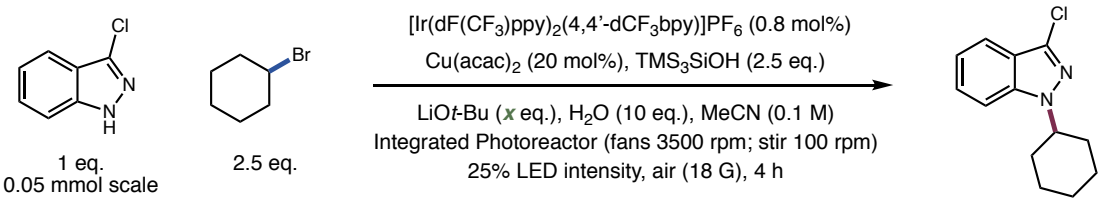
Figure S9: Optimization studies - evaluation of reaction solvents.



	LiOt-Bu	*Li_2CO_3*	*Li_3PO_4*	*NaOt-Bu*	*KOt-Bu*
no H_2O	***54% pdt*** *95% AlkBr*	***0% pdt*** *116% AlkBr*	***0% pdt*** *155% AlkBr*	-	-
10 eq. H_2O	***78% pdt*** *71% AlkBr*	***0% pdt*** *142% AlkBr*	***0% pdt*** *138% AlkBr*	***15% pdt*** *177% AlkBr*	***0% pdt*** *181% AlkBr*

Analytical yields via ^{1}H NMR vs. mesitylene

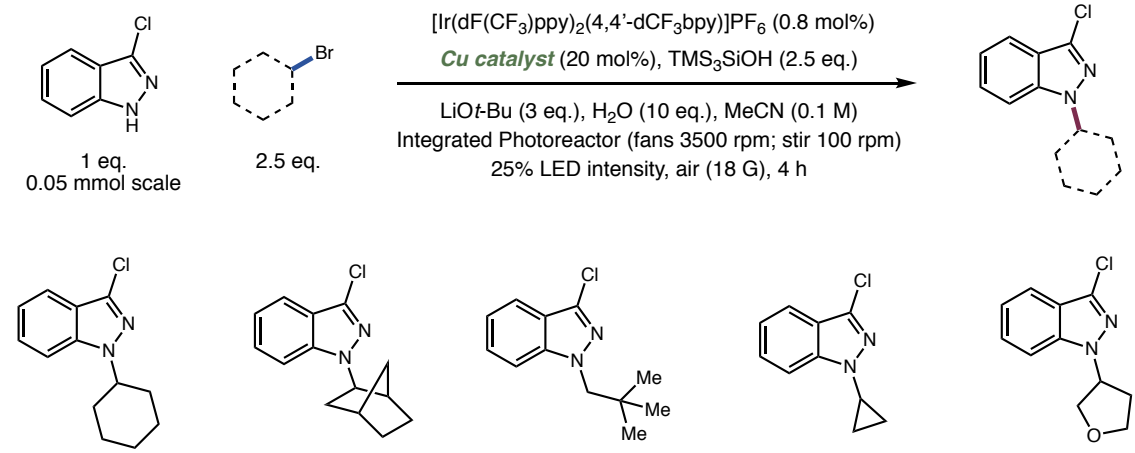
Figure S10: Optimization studies - comparison of bases with and without water as additive.



Base loading	**Yield**
0 equiv.	***0%***
1 equiv.	***45%***
1.5 equiv.	***47%***
2 equiv.	***58%***
2.5 equiv.	***78%***
3 equiv.	***80%***

Analytical yields via ^{1}H NMR vs. mesitylene

Figure S11: Optimization studies - evaluation of base loading.



Cu(acac)$_2$: 84% yield
Cu(TMHD)$_2$: 86% yield

Cu(acac)$_2$: 41% yield
Cu(TMHD)$_2$: 45% yield

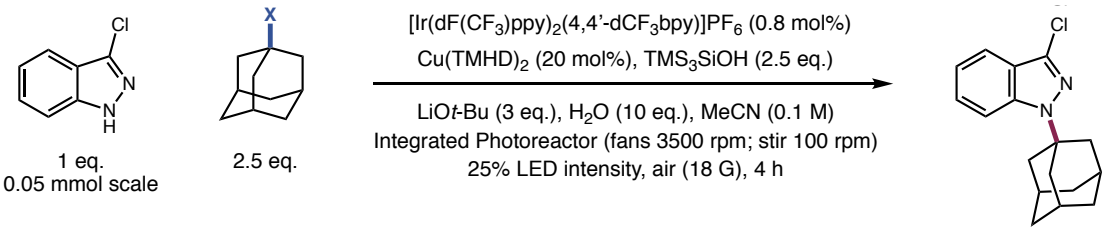
Cu(acac)$_2$: 32% yield
Cu(TMHD)$_2$: 54% yield

Cu(acac)$_2$: 65% yield
Cu(TMHD)$_2$: 80% yield

Cu(acac)$_2$: 47% yield
Cu(TMHD)$_2$: 80% yield

Analytical yields via ^{1}H NMR vs. mesitylene

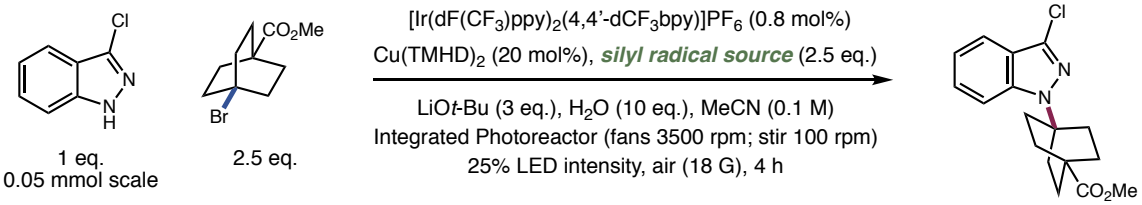
Figure S12: Optimization studies – direct comparison of copper(II) diketonate precatalysts.



Substrate + conditions	**Yield**
X = Cl	***0%***
X = Br	***56%***
X = I	***71%***
X = I, no silanol	***0%***
X = I, no photocatalyst	***0%***

Analytical yields via ^{1}H NMR vs. mesitylene

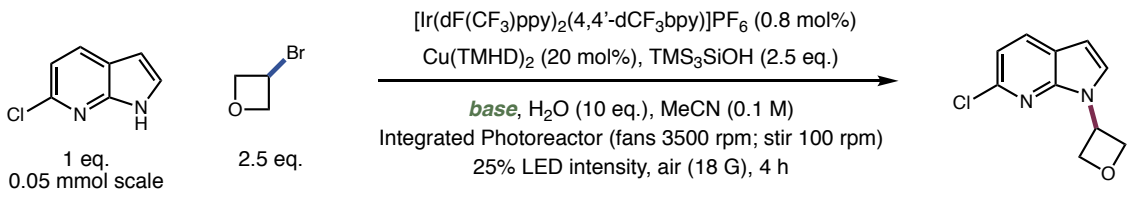
Figure S13: Optimization studies - evaluation of tertiary halides using various conditions.



Silyl radical source	**Yield**
TMS_3SiH	***3%***
TMS_3SiOH	***23%***
$TMS_3SiNH(t\text{-Bu})$	***25%***
$TMS_3SiNH(Ad)$	***40%***

Analytical yields via ^{1}H NMR vs. mesitylene

Figure S14: Optimization studies - evaluation of silyl radical precursors for tertiary substrates.



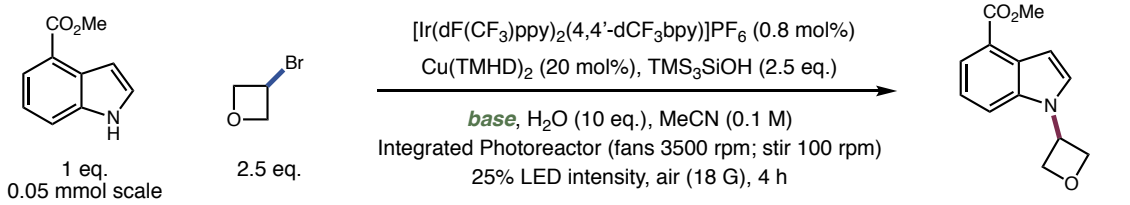
1 eq.
0.05 mmol scale

2.5 eq.

Base	Yield
LiO*t*-Bu (3 eq.)	***30%***
TMG (3 eq.)	***26%***
Cs_2CO_3 (3 eq.)	***9%***
CsOAc (3 eq.)	***11%***
K_3PO_4 (3 eq.)	***8%***
TMG (1 eq.), LiO*t*-Bu (3 eq.)	***84%***
DBN (1 eq.), LiO*t*-Bu (3 eq.)	***86%***

Analytical yields via ^{1}H NMR vs. mesitylene

Figure S15: Optimization studies - evaluation of base conditions for azaindole substrate.



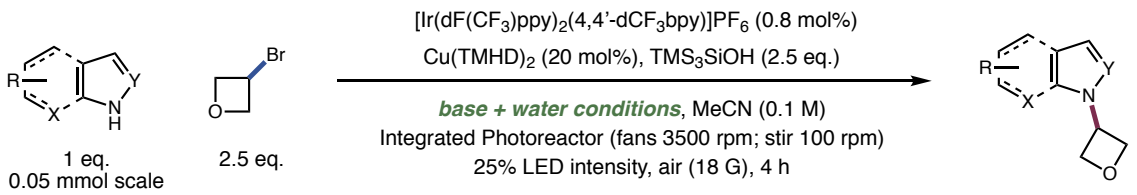
1 eq.
0.05 mmol scale

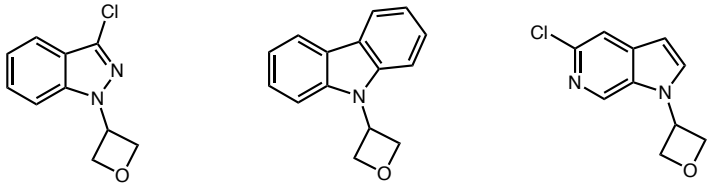
2.5 eq.

Base	Yield
TMG (1 eq.), LiO*t*-Bu (3 eq.)	***17%***
BTMG (1 eq.), LiO*t*-Bu (3 eq.)	***9%***
BTTP (1 eq.), LiO*t*-Bu (3 eq.)	***6%***
K_3PO_4 (1 eq.), LiO*t*-Bu (3 eq.)	***6%***
TBD (1 eq.), LiO*t*-Bu (3 eq.)	***18%***
DBU (1 eq.), LiO*t*-Bu (3 eq.)	***26%***
DBN (1 eq.), LiO*t*-Bu (3 eq.)	***71%***

Analytical yields via ^{1}H NMR vs. mesitylene

Figure S16: Optimization studies - evaluation of base conditions for indole substrate.

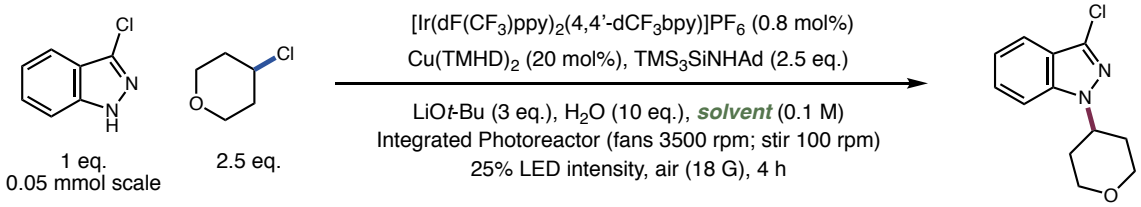




Conditions	Yield	Yield	Yield
3 eq. LiO*t*-Bu, 10 eq. H_2O	***86%***	—	—
3 eq. LiO*t*-Bu, 1 eq. DBN, 10 eq. H_2O	***87%***	***39%***	***90%***
1 eq. DBN, 10 eq. H_2O	***54%***	***35%***	***6%***
1 eq. DBN	***41%***	***32%***	***2%***
3 eq. DBN	***72%***	***41%***	***32%***

Analytical yields via ^{1}H NMR vs. mesitylene

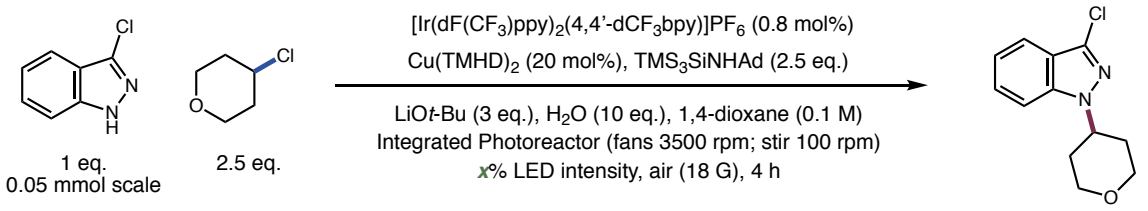
Figure S17: Optimization studies – general evaluation of base and water conditions.



Solvent	Yield
dioxane	***41%***
THF	***24%***
Et_2O	***0%***
MTBE	***0%***
DME	***11%***
MeCN	***6%***

Analytical yields via ^{1}H NMR vs. mesitylene

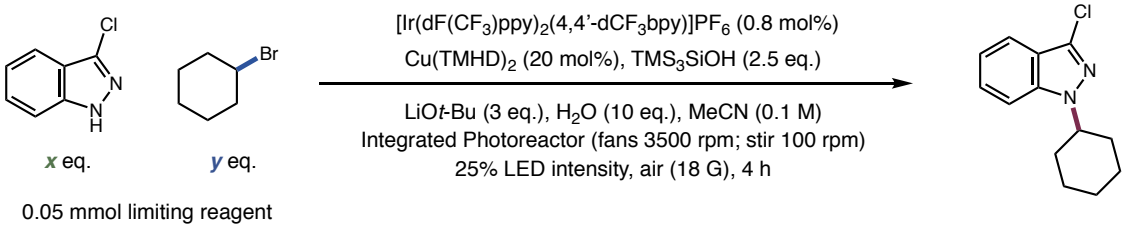
Figure S18: Optimization studies – solvent evaluation for chloride activation.



Light intensity	**Yield**
15%	***26%***
25% (standard)	***40%***
35%	***43%***
45%	***50%***
55%	***54%***
65%	***52%***
75%	***47%***
100%	***47%***

Analytical yields via ^{1}H NMR vs. mesitylene

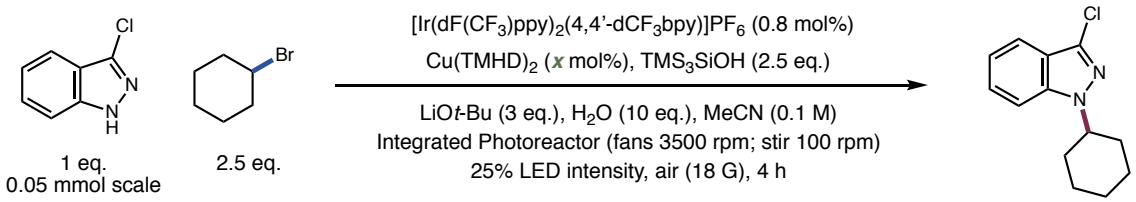
Figure S19: Optimization studies – light intensity evaluation for chloride activation.



indazole eq.	*bromide eq.*	**Pdt**	**AlkBr**
1	2.5	***93%***	***26%***
1	1.5	***60%***	***0%***
1	1	***41%***	***0%***
2	1	***41%***	***0%***

Analytical yields via ^{1}H NMR vs. mesitylene

Figure S20: Optimization studies – effect of reagent stoichiometry under standard conditions.



Copper loading	**Yield**	**TON**
no copper	***<1%***	***N/A***
5 mol%	***57%***	***11.4***
10 mol%	***66%***	***6.6***
15 mol%	***72%***	***4.8***
20 mol% (standard)	***89%***	***4.5***

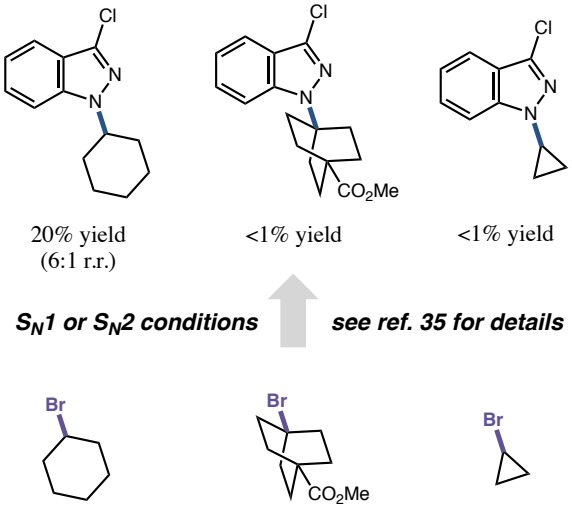
Analytical yields via ^{1}H NMR vs. mesitylene

Figure S21: Effect of lower copper loadings, with calculated turnover numbers (TONs) reported.

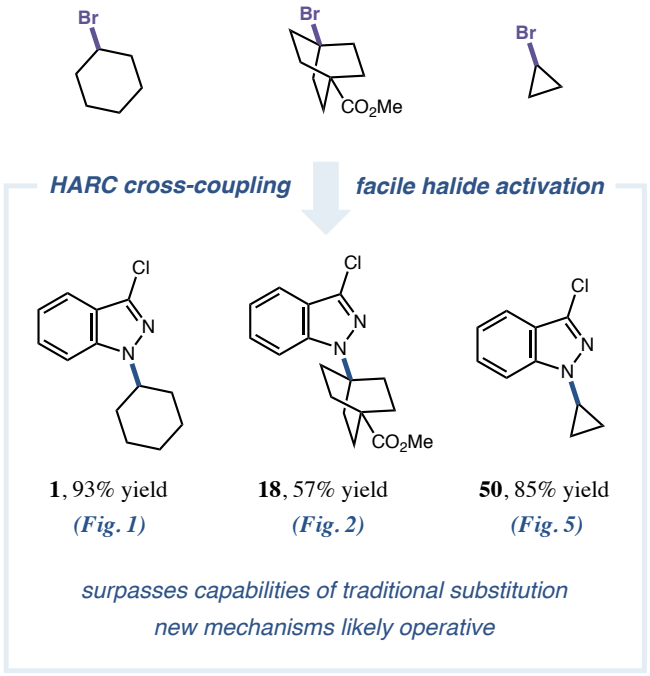
As indicated in **Figure S21**, higher TONs for the copper catalyst are generally observed at lower catalyst loadings, with TONs > 10 possible for the C–N coupling process under appropriate conditions. However, at lower copper loadings, the desired *N*-alkylated product is consistently obtained in reduced overall yield. To provide optimal yield in the desired transformation, the copper loadings employed are generally 20 mol% or greater, despite the reduced TONs under such conditions (given the status of copper as an inexpensive and earth-abundant choice of metal for homogeneous catalysis,[13] this choice is consistent with the anticipated preferences in conditions for practicing synthetic chemists).

5. Mechanistic experiments and HARC coupling vs. substitution conditions

Entries in this section pertain to the experimental details of results reported in Figure 7, which lead to the mechanistic proposal for HARC *N*-alkylation shown in Scheme 2. All experiments were conducted using 3-chloroindazole as a model nucleophile and as the limiting reagent.



Control experiments for the S_N1 or S_N2 alkylations of the three representative bromides shown above with 3-chloroindazole were previously reported in ref. 35 (*Nature* **2018**, *559*, 83),[14] and exact reaction conditions can be found in the Supporting Information of this reference. In general, conditions for these control experiments included excess halide and base, elevated reaction temperatures (typically 90 °C), and prolonged reaction times (16–40 hours) under inert atmosphere conditions,[14] consistent with reaction conditions most often successful for S_N1/S_N2 processes.[15]



Yields and regiochemical assignments (all >20:1 r.r.) for generation of products **18** and **50** via HARC coupling were obtained using isolated material from 0.25 mmol scale reactions, with data taken from the respective scope tables wherein each product is first reported (see Figures 2 and 5). The yield for optimized HARC *N*-alkylation to generate **1** was determined by ^{1}H NMR on 0.05 mmol scale, measured during the evaluation of control experiments. Product **1** was obtained following the general optimization scale procedure detailed in **Section 4**, using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF$_3$)ppy]$_2$[4,4′-d(CF$_3$)bpy]PF$_6$ (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (4.3 mg, 10 μmol, 0.20 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), bromocyclohexane (15.4 μL, 0.125 mmol, 2.5 equiv.), (TMS)$_3$SiOH (33 mg, 0.125 mmol, 2.5 equiv.), MeCN (0.5 mL, 0.1 M) and water (9 μL, 0.5 mmol, 10 equiv.) and performed in the Integrated Photoreactor under 450 nm irradiation (3500 rpm fans, 100 rpm stir, 25% light intensity) for 4 hours. Following the reaction, mesitylene (5 μL, 35.9 μmol, 0.72 equiv.) was added as an internal standard, and the yield and regioselectivity were determined via ^{1}H NMR (93% yield, >20:1 r.r.). Spectral data for product **1**, in particular the diagnostic 4.35–4.29 ppm 1H α–N multiplet, was consistent with assignments previously reported.[14]

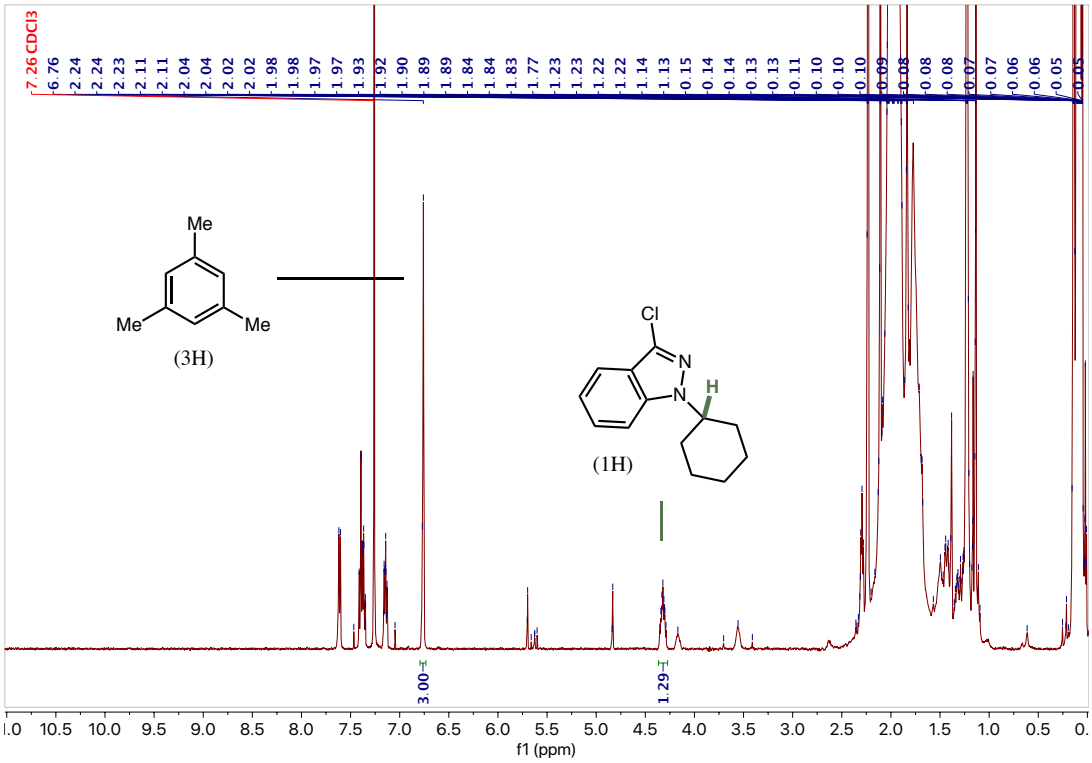
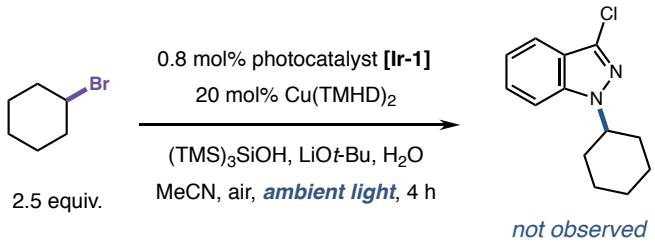


Figure S22: ^{1}H NMR assay for standard HARC formation of product **1** (500 MHz, $CDCl_3$).

[(1.29 mmol **1**/mmol Mes) * 0.0359 mmol Mes]/0.050 mmol **1** (theoretical) = *93% assay yield*



The non-photonic control experiment for generation of **1**, used to eliminate the possibility of background substitution pathways, was performed following the general optimization scale procedure detailed in **Section 4**, using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (4.3 mg, 10 μmol, 0.20 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), bromocyclohexane (15.4 μL, 0.125 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (33 mg, 0.125 mmol, 2.5 equiv.), MeCN (0.5 mL, 0.1 M) and water (9 μL, 0.5 mmol, 10 equiv.) and stirred under ambient light in a fume hood for 4 hours. Following the reaction, mesitylene (5 μL, 35.9 μmol, 0.72 equiv.) was added as an internal standard, and the resulting ^{1}H NMR spectrum displayed no signals corresponding to the desired product **1**. The lack of reactivity observed for reactions exposed only to ambient light was a general trend observed across all 13 nucleophile classes examined in this study (for additional examples, see Figure S26).

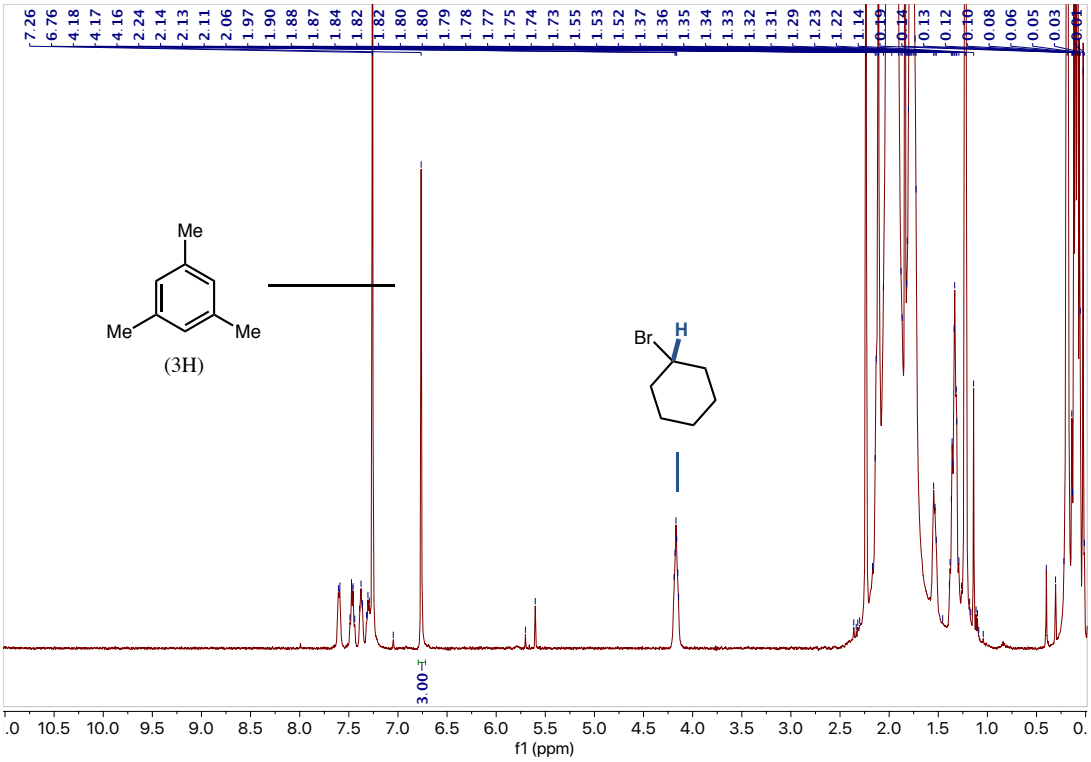
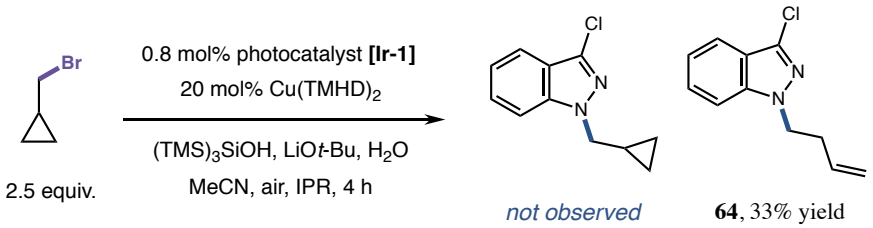
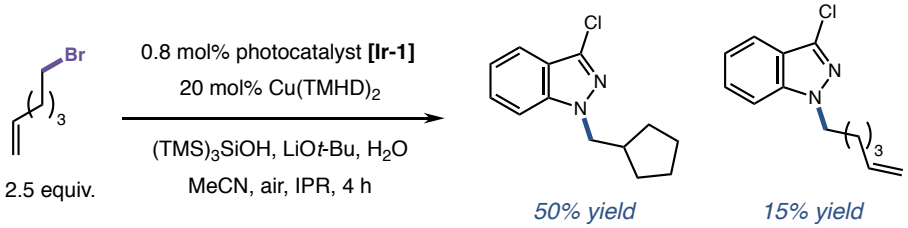


Figure S23: ^{1}H NMR assay for non-photonic generation of product **1** (500 MHz, $CDCl_3$).



Radical clock studies to generate product **64** via HARC *N*-alkylation were conducted following the general optimization scale procedure detailed in **Section 4**, using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (4.3 mg, 10 μmol, 0.20 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), (bromomethyl)cyclopropane (12.1 μL, 0.125 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (33 mg, 0.125 mmol, 2.5 equiv.), MeCN (0.5 mL, 0.1 M) and water (9 μL, 0.5 mmol, 10 equiv.) and performed in the Integrated Photoreactor under 450 nm irradiation (3500 rpm fans, 100 rpm stir, 25% light intensity) for 4 hours. Following the reaction, mesitylene (5 μL, 35.9 μmol, 0.72 equiv.) was added as an internal standard, and the yield was determined via ^{1}H NMR (33% yield). Spectral data for ring-opened homoallyl product **64**, in particular the diagnostic 4.37 ppm 2H α–N triplet, was consistent with assignments previously reported.[14] Absence of the anticipated α–N 2H doublet ruled out formation of the direct cyclopropylmethyl-coupled product, confirming that **64** is the only detectable adduct formed via HARC functionalization of 3-chloroindazole under these conditions.



Analytical yields via ^{1}H NMR vs. mesitylene

Following the same general procedure, additional radical clocks (such as 6-bromo-1-hexene) with varying rates of unimolecular rearrangement (k = 1.8 x 10^5 s^{-1} at 20 °C for 5-*exo*-trig ring-closing of the corresponding 5-hexenyl radical)[16] could also be utilized to provide further information, suggesting a preliminary rate of C–N product formation on the order of 10^5 M^{-1} s^{-1} based on competitive formation of both direct-coupling and cyclized products in the above transformation.

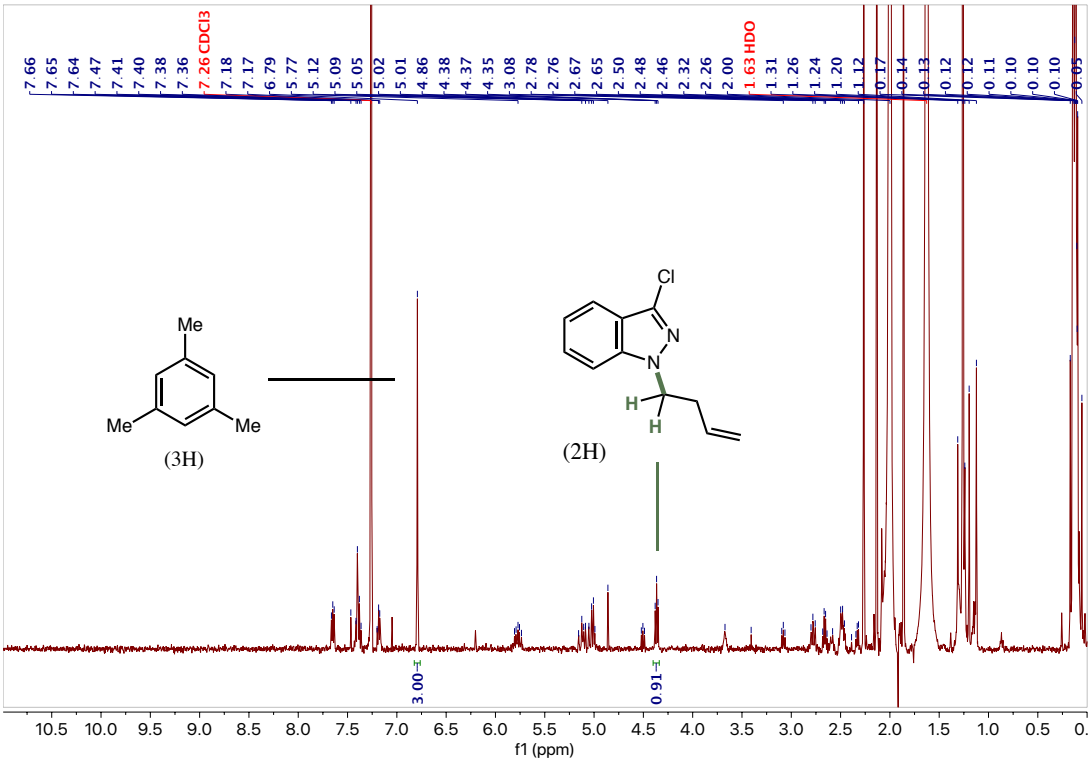
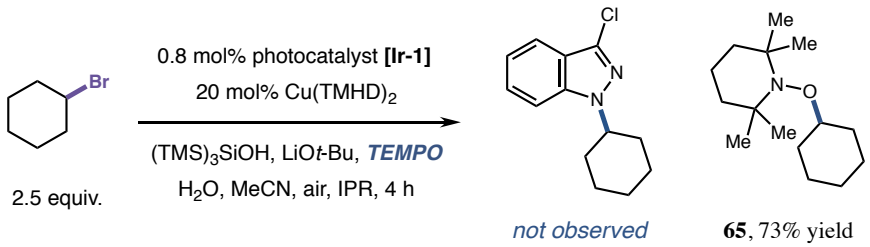


Figure S24: ^{1}H NMR assay for HARC formation of ring-opened product **64** (500 MHz, $CDCl_3$).

[(0.455 mmol **64**/mmol Mes) * 0.0359 mmol Mes]/0.050 mmol **64** (theoretical) = *33% assay yield*



TEMPO-trapping studies to generate adduct **65** via HARC coupling were conducted following the general optimization scale procedure detailed in **Section 4**, using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (4.3 mg, 10 μmol, 0.20 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), (bromomethyl)cyclopropane (12.1 μL, 0.125 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (33 mg, 0.125 mmol, 2.5 equiv.), MeCN (0.5 mL, 0.1 M) and water (9 μL, 0.5 mmol, 10 equiv.), with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 15.6 mg, 0.10 mmol, 2 equiv.) added immediately prior to 450 nm irradiation in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity) for 4 hours. Following the reaction, mesitylene (5 μL, 35.9 μmol, 0.72 equiv.) was added as an internal standard, and the resulting ^{1}H NMR spectrum displayed no signals corresponding to the desired product **1**. Instead, the yield of TEMPO-trapped adduct **65** was determined via ^{1}H NMR to be 73% yield. Spectral data for **65**, in particular the diagnostic 3.61–3.54 ppm 1H α–O multiplet, was consistent with assignments previously reported.[17]

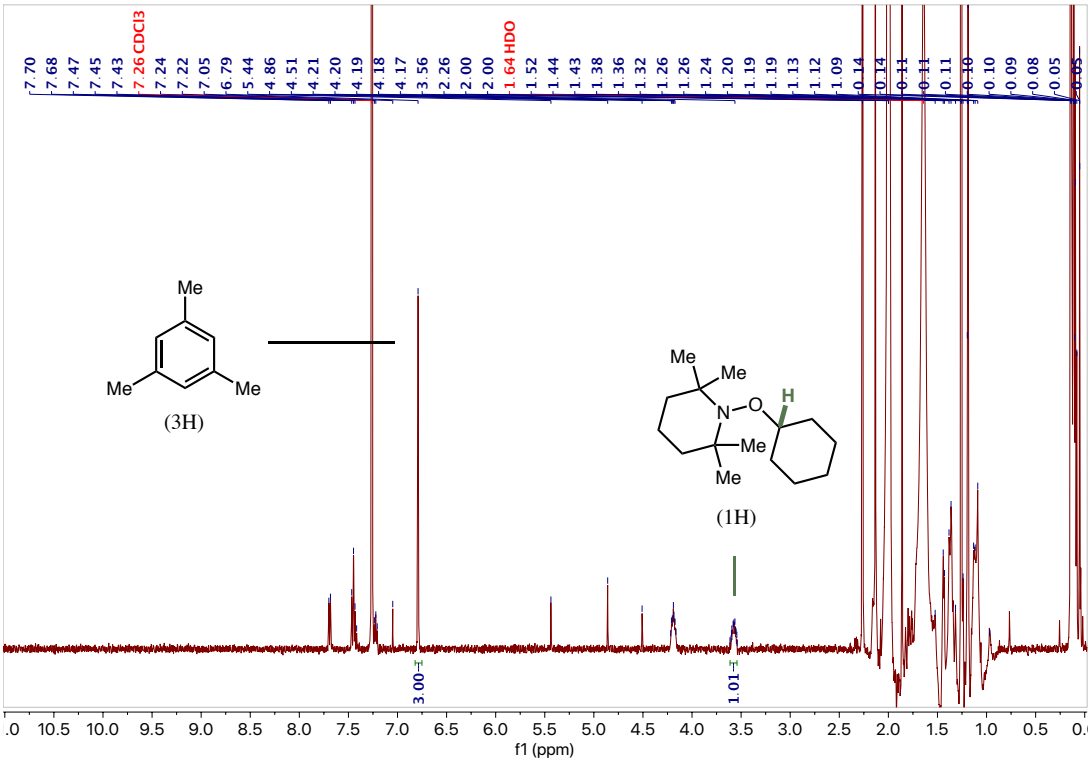
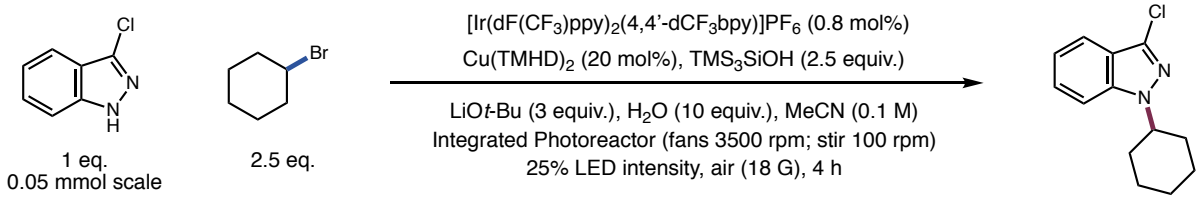


Figure S25: ^{1}H NMR assay for TEMPO-trapping studies forming adduct **65** (500 MHz, $CDCl_3$).

[(1.01 mmol **65**/mmol Mes) * 0.0359 mmol Mes]/0.050 mmol **65** (theoretical) = *73% assay yield*

6. Sensitivity of reaction to deviations from typical setup

To display the sensitivity of the optimized HARC *N*-alkylation to variations in common reaction parameters (such as temperature, LED intensity, concentration, and incorporation of water or oxygen), deviations to the standard protocol were systematically investigated and reported as % deviations on a radar diagram according the method of Glorius.[18] The control reaction (for representative yield of the standard bromocyclohexane/3-chloroindazole coupling) was performed following the general optimization scale procedure detailed in **Section 4** using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (4.3 mg, 10 μmol, 0.20 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), bromocyclohexane (15.4 μL, 0.125 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (33 mg, 0.125 mmol, 2.5 equiv.), MeCN (0.5 mL, 0.1 M) and water (9 μL, 0.5 mmol, 10 equiv.) and performed in the Integrated Photoreactor under 450 nm irradiation (3500 rpm fans, 100 rpm stir, 25% light intensity) for 4 hours. Following the reaction, mesitylene (5 μL, 35.9 μmol, 0.72 equiv.) was added as an internal standard, and the yield was determined via ^{1}H NMR (89% yield). For each subsequent experiment, the deviation from the control reaction, as well as the appropriate label for the experiment displayed on the radar diagram, is indicated, and all other components of the reaction were identical to the control experiment. All % deviations and related graphical representations were reported according to the protocol of Glorius[18] and all yields were determined via ^{1}H NMR using mesitylene as an internal standard. All deviations were selected based on practicality for manipulation within the Integrated Photoreactor, and to best represent parameters most likely to be changed by practitioners of the HARC N-alkylation protocol, in the event that conditions must be reoptimized for specific substrates not detailed within this report. As specified by Glorius,[18] all deviations were selected to impose relatively minor perturbations to the standard reaction, as more substantial perturbations that inhibit all reactivity provide relatively minimal information regarding the sensitivity of the standard reaction as designed.



entry	*deviation*	*description/label*	*yield*	*% deviation from control*
1	**none**	**control**	**89%**	**N/A**
2	0.125 M reaction (0.4 mL MeCN)	High C	81%	–9%
3	0.0833 M reaction (0.6 mL MeCN)	Low C	80%	–10%
4	anhydrous (no additional water added)	No H_2O	54%	–39%
5	100 equiv. water added	High H_2O	70%	–21%
6	sparged under N_2 atmosphere/oxygen-free	Low O_2	8%	–91%
7	uncapped vial, fully open to atmosphere	High O_2	81%	–9%
8	6800 rpm fan speed (reduced temp.)	Max fans	83%	–7%
9	1500 rpm fan speed (elevated temp.)	Min fans	87%	–2%
10	10% blue LED intensity	Low I	82%	–8%
11	40% blue LED intensity	High I	80%	–10%

Figure S26: Description of experiments and result for reaction sensitivity measurements.

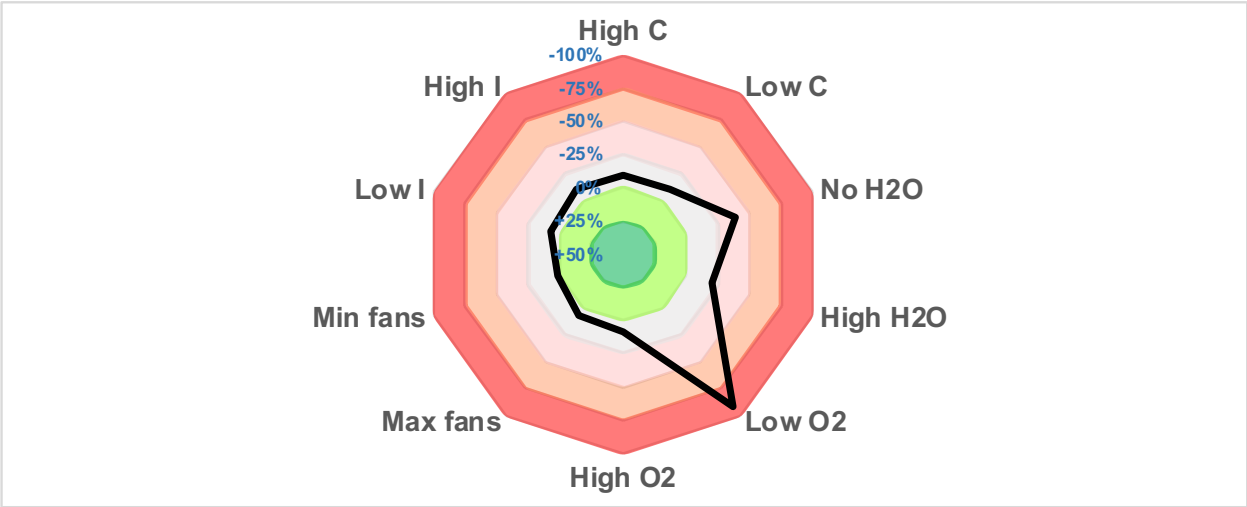


Figure S27: Radar diagram for sensitivity results reported in **Figure S26**.

As indicated in the radar diagram, positive or negative deviations to several parameters, including concentration, LED intensity and cooling fan speed (inversely correlated with temperature), have only a minor impact on the reaction and provide yields within 10% of the optimized conditions. However, the HARC *N*-alkylation is more sensitive to water loadings, as anhydrous conditions or large excesses of water (100 equiv.) are substantially detrimental (21–39% reduction in yield). Additionally, although the reaction can be performed in an open vessel (entry 7) in lieu of using a vent needle for O_2 incorporation with minimal change in yield, oxygen-free reactions performed under inert atmospheres of nitrogen are ineffective. Collectively, these experiments demonstrate a reproducible and robust performance of the HARC *N*-alkylation under most conditions, although careful consideration to the loading of water and incorporation of O_2 into the reaction mixture are recommended.

In the case of entry 7, an open vessel setup frequently causes complete evaporation of reaction solvent, which may lead to additional irreproducibility or inefficiency for other substrates. Given this observation, as well as the practical challenges associated with introducing atmospheres of gases (such as O_2) to reaction vessels within the Integrated Photoreactor, the vent needle assembly described in **Section 3** is generally recommended for introduction of O_2.

7. General procedures for the copper–HARC *N*-alkylation

General procedure A: To an oven-dried 40 mL vial equipped with a Teflon stir bar was added *N*-nucleophile (0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.0 μmol, 0.008 equiv.), bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) ($Cu(TMHD)_2$, 0.05–0.15 mmol, 0.2–0.6 equiv.), Li*O*t*-Bu (0.75 mmol, 3.0 equiv.), MeCN (2.5 mL, 0.1 M) and water (2.5 mmol, 10 equiv.). The resulting solution was stirred for 1–2 minutes under air to ensure complete ligation of the nucleophile to the copper precatalyst. Following this complexation period, alkyl halide (0.625 mmol, 2.5 equiv.) and silyl radical precursor (0.625 mmol, 2.5 equiv.) were added to the mixture, after which the vial was capped and an 18G vent needle was inserted through the Teflon-lined septum. The reaction mixture was subsequently stirred under air within the Integrated Photoreactor (450 nm irradiation) for 4 hours (settings for light intensity, fan speed and stir rate are indicated for each substrate). After 4 hours, the reaction mixture was diluted with EtOAc (5 mL), followed by the addition of KF on alumina (40 wt. % from Sigma-Aldrich, 1.0 g) and tetrabutylammonium bromide (500 mg) to the vial. This suspension was stirred under air for 2–24 hours, then filtered into a separatory funnel, using an additional 25 mL EtOAc wash to ensure complete transfer from the vial. The organic layer was subsequently washed with saturated Na_2CO_3 (10 mL), water (10 mL) and brine (10 mL), and the collected aqueous layer was extracted with EtOAc (10 mL). The combined organics were dried over $MgSO_4$ and concentrated *in vacuo* to obtain the crude product. This residue was purified by flash chromatography and/or preparative thin-layer chromatography on silica gel to afford the desired *N*-alkylated product.

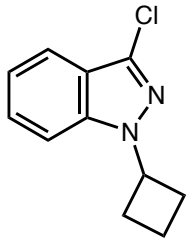
Note: This procedure is best employed for the coupling of highly acidic *N*-heterocycles, such as indazoles and pyrazoles.

General procedure B: To an oven-dried 40 mL vial equipped with a Teflon stir bar was added *N*-nucleophile (0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.0 μmol, 0.008 equiv.), MeCN (2.5 mL, 0.1 M) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 0.25 mmol, 1.0 equiv.) The resulting homogeneous solution was stirred for 5 minutes, after which Li*O*t*-Bu (0.75 mmol, 3.0 equiv.) and water (2.5 mmol, 10 equiv.) were added to the vial. This suspension was then sonicated under air for 1 minute until the mixture became homogeneous. $Cu(TMHD)_2$ (0.05–0.15 mmol, 0.2–0.6 equiv.) was then added to the vial, and the solution was stirred for 1–2 minutes under air to ensure complete ligation of the nucleophile to the copper precatalyst. Following this complexation period, alkyl halide (0.625 mmol, 2.5 equiv.) and silyl radical precursor (0.625 mmol, 2.5 equiv.) were added to the mixture, after which the vial was capped and an 18G vent needle was inserted through the Teflon-lined septum. The reaction mixture was subsequently stirred under air within the Integrated Photoreactor (450 nm irradiation) for 4 hours (settings for light intensity, fan speed and stir rate are indicated for each substrate). After 4 hours, the reaction mixture was diluted with EtOAc (5 mL), followed by the addition of KF on alumina (40 wt. %, 1.0 g) and tetrabutylammonium bromide (500 mg) to the vial. This suspension was stirred under air for 2–24 hours, then filtered into a separatory funnel, using an additional 25 mL EtOAc wash to ensure complete transfer from the vial. The organic layer was subsequently washed with saturated Na_2CO_3 (10 mL), water (10 mL) and brine (10 mL), and the collected aqueous layer was extracted with EtOAc (10 mL). The combined organics were dried over $MgSO_4$ and concentrated *in vacuo* to obtain the crude product. This residue was purified by flash chromatography and/or preparative thin-layer chromatography on silica gel to afford the desired *N*-alkylated product.

General procedure C: To an oven-dried 8 mL vial equipped with a Teflon stir bar was added *N*-nucleophile (0.05 mmol, 1.0 equiv.), photocatalyst (0.4 μmol, 0.008 equiv.) $Cu(TMHD)_2$ (0.01–0.03 mmol, 0.2–0.6 equiv.), LiO*t*-Bu (0.15 mmol, 3.0 equiv.), solvent (0.5 mL, 0.1 M) and water (0.5 mmol, 10 equiv.). The resulting solution was stirred for 1–2 minutes under air to ensure complete ligation of the nucleophile to the copper precatalyst. Following this complexation period, alkyl halide (0.125 mmol, 2.5 equiv.) and silyl radical precursor (0.125 mmol, 2.5 equiv.) were added to the mixture, after which the vial was capped and an 18G vent needle was inserted through the Teflon-lined septum. The reaction mixture was subsequently stirred under air within the Integrated Photoreactor (450 nm irradiation) for 4 hours (settings for light intensity, fan speed and stir rate are indicated for each substrate). This reaction setup was replicated five times for each *N*-nucleophile to reach a combined 0.25 mmol scale procedure. After 4 hours, the contents of the five vials were combined and diluted with EtOAc (5 mL), followed by the addition of KF on alumina (40 wt. %, 1.0 g) and tetrabutylammonium bromide (500 mg) to the vial. This suspension was stirred under air for 2–24 hours, then filtered into a separatory funnel, using an additional 25 mL EtOAc wash to ensure complete transfer from the vial. The organic layer was subsequently washed with saturated Na_2CO_3 (10 mL), water (10 mL) and brine (10 mL), and the collected aqueous layer was extracted with EtOAc (10 mL). The combined organics were dried over $MgSO_4$ and concentrated *in vacuo* to obtain the crude product. This residue was purified by flash chromatography and/or preparative thin-layer chromatography on silica gel to afford the desired *N*-alkylated product.

Note: This procedure is best employed for select halide coupling partners which encounter reduced yields when using General Procedures A or B on 0.25 mmol scale.

8. Alkyl bromide scope for alkylation of 3-chloro-1*H*-indazole



3-chloro-1-cyclobutyl-1*H*-indazole (2)

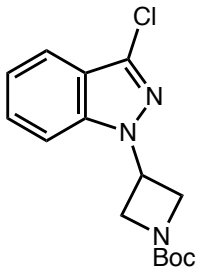
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), bromocyclobutane (59 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 300 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (44.8 mg, 87% yield, >20:1 r.r.) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.18 (dt, *J* = 7.8, 3.7 Hz, 1H), 5.01 (p, *J* = 8.3 Hz, 1H), 2.79 (pd, *J* = 9.6, 2.9 Hz, 2H), 2.53 – 2.47 (m, 2H), 2.00 – 1.85 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.32, 132.79, 127.29, 121.30, 121.27, 119.88, 109.58, 52.87, 30.11, 15.05.

Spectral data are consistent with those reported in literature:[13]

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



***tert*-butyl 3-(3-chloro-1*H*-indazol-1-yl)azetidine-1-carboxylate (3)**

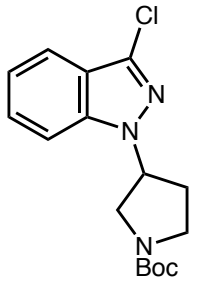
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), *tert*-butyl 3-bromoazetidine-1-carboxylate (148 mg, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 300 rpm stir, 25% light intensity). Purification by flash chromatography (4:1 hexane/EtOAc) provided the title compound (68.9 mg, 90% yield, >20:1 r.r.) as an orange-yellow oil. The regiochemical assignment of this product was verified by NOESY analysis (as indicated in the spectral data).

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.69 (t, *J* = 8.0 Hz, 2H), 7.52 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.31 – 7.28 (m, 1H), 5.69 (tt, *J* = 7.9, 5.4 Hz, 1H), 4.41 (br d, *J* = 39.9 Hz, 4H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.27, 140.78, 134.33, 128.09, 122.01, 121.88, 120.33, 109.24, 80.24, 56.08, 47.62, 28.53.

IR (film) ν_{max} 3068, 2975, 2932, 2887, 1688, 1616, 1496, 1470, 1438, 1405, 1393, 1366, 1336, 1300, 1250, 1221, 1134, 1051, 1003, 949, 896, 856, 767, 740 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{19}ClN_3O_2$ ($[M+H]^+$) 308.11603, found 308.18431.



(±)-*tert*-butyl 3-(3-chloro-1*H*-indazol-1-yl)pyrrolidine-1-carboxylate (4)

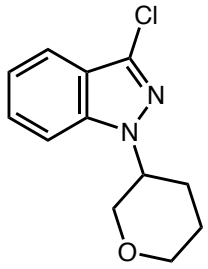
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), (±)-*tert*-butyl 3-bromopyrrolidine-1-carboxylate (156 mg, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (44.1 mg, 55% yield, >20:1 r.r., mixture of rotamers) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 5.13 (dq, *J* = 14.9, 7.1 Hz, 1H), 3.95 – 3.85 (m, 1H), 3.80 – 3.71 (m, 2H), 3.53 (q, *J* = 8.4 Hz, 1H), 2.68 – 2.53 (m, 1H), 2.41 – 2.34 (m, 1H), 1.48 & 1.46 (rotameric singlets, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.53, 140.82, 133.58, 127.80, 121.70, 121.58, 120.16, 109.25 & 109.20 (rotameric singlets), 79.84, 57.54 & 56.90 (rotameric singlets), 50.41 & 50.27 (rotameric singlets), 44.96 & 44.45 (rotameric singlets), 31.15 & 30.56 (rotameric singlets), 28.63.

IR (film) ν_{max} 3058, 2976, 2881, 1738, 1690, 1617, 1492, 1466, 1401, 1365, 1337, 1274, 1248, 1166, 1128, 990, 877, 746 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{21}ClN_3O_2$ ($[M+H]^+$) 322.13168, found 322.13642.



(±)-3-chloro-1-(tetrahydro-2*H*-pyran-3-yl)-1*H*-indazole (5)

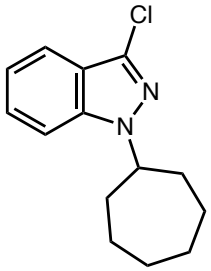
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 3-bromo-tetrahydro-2*H*-pyran (70 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 300 rpm stir, 25% light intensity). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (41.8 mg, 71% yield, >20:1 r.r.) as a waxy yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 3.9 Hz, 2H), 7.24 – 7.18 (m, 1H), 4.55 (tt, *J* = 11.1, 4.4 Hz, 1H), 4.08 – 3.99 (m, 2H), 3.79 (t, *J* = 10.8 Hz, 1H), 3.55 – 3.46 (m, 1H), 2.41 – 2.33 (m, 1H), 2.24 – 2.18 (m, 1H), 1.95 – 1.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.72, 133.30, 127.67, 121.61, 121.10, 120.03, 109.20, 70.82, 68.01, 54.71, 29.41, 25.83.

IR (film) ν_{max} 3061, 2955, 2916, 2859, 1615, 1573, 1493, 1465, 1414, 1380, 1366, 1337, 1282, 1225, 1192, 1176, 1088, 1061, 1033, 997, 964, 913, 879, 862, 835, 765, 755, 738 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{14}ClN_2O$ ($[M+H]^+$) 237.07892, found 237.07657.



3-chloro-1-cycloheptyl-1*H*-indazole (6)

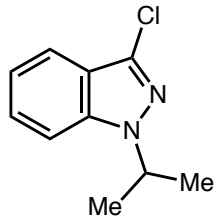
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), bromocycloheptane (86 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (37.6 mg, 60% yield, >20:1 r.r.) as a waxy yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.17 (ddd, *J* = 7.9, 5.6, 1.8 Hz, 1H), 4.55 (tt, *J* = 9.8, 4.5 Hz, 1H), 2.23 – 2.15 (m, 2H), 2.10 – 2.04 (m, 2H), 1.90 – 1.83 (m, 2H), 1.74 – 1.64 (m, 4H), 1.61 – 1.53 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.80, 132.14, 127.05, 121.06, 121.01, 119.84, 109.62, 60.89, 34.64, 27.98, 24.88.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



3-chloro-1-isopropyl-1*H*-indazole (7)

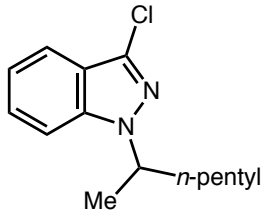
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 2-bromopropane (59 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (28.1 mg, 58% yield, >20:1 r.r.) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.18 (ddd, *J* = 7.9, 4.5, 3.2 Hz, 1H), 4.80 (p, *J* = 6.7 Hz, 1H), 1.58 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.07, 132.41, 127.20, 121.21, 121.17, 119.96, 109.48, 50.96, 22.25.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



(±)-3-chloro-1-(heptan-2-yl)-1*H*-indazole (8)

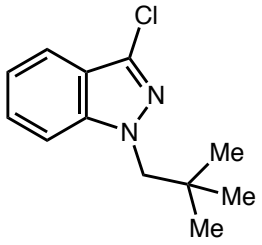
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 2-bromoheptane (98 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (47.3 mg, 75% yield, >20:1 r.r.) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.40 (d, *J* = 3.9 Hz, 2H), 7.18 (dt, *J* = 7.9, 3.8 Hz, 1H), 4.58 (tq, *J* = 8.9, 6.6 Hz, 1H), 2.15 – 2.03 (m, 1H), 1.87 – 1.76 (m, 1H), 1.55 (d, *J* = 6.6 Hz, 3H), 1.27 – 1.17 (m, 6H), 0.84 – 0.79 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.75, 132.50, 127.16, 121.08, 120.97, 119.90, 109.46, 55.46, 36.49, 31.57, 26.24, 22.55, 20.90, 14.06.

IR (film) ν_{max} 3053, 2952, 2929, 2858, 1616, 1493, 1463, 1409, 1378, 1337, 1214, 1193, 1128, 1102, 1055, 1006, 975, 767, 740 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{20}ClN_2$ ($[M+H]^+$) 251.13095, found 251.13122.



3-chloro-1-neopentyl-1*H*-indazole (9)

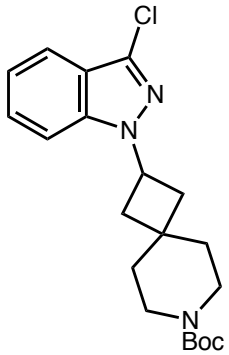
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), $Ir[dF(CF_3)ppy]_2[4,4'\text{-}d(CF_3)bpy]PF_6$ (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), $Cu(TMHD)_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), neopentyl bromide (79 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (30.0 mg, 54% yield, >20:1 r.r.) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.19 – 7.16 (m 1H), 4.11 (s, 2H), 1.02 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.97, 132.64, 127.36, 121.03, 120.88, 119.76, 110.22, 60.67, 34.37, 28.21.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



***tert*-butyl 2-(3-chloro-1*H*-indazol-1-yl)-7-azaspiro[3.5]nonane-7-carboxylate (10)**

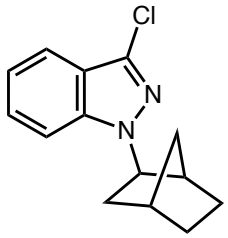
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 2-bromo-7-(*tert*-butoxycarbonyl)-7-azaspiro[3.5]nonane (190 mg, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 300 rpm stir, 25% light intensity). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (86.4 mg, 92% yield, >20:1 r.r., mixture of rotamers) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.20 – 7.17 (m, 1H), 5.02 (p, *J* = 8.3 Hz, 1H), 3.45 – 3.43 (m, 2H), 3.36 – 3.33 (m, 2H), 2.57 – 2.53 (m, 2H), 2.49 – 2.44 (m, 2H), 1.73 – 1.69 (m, 4H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.09, 140.54, 132.94, 127.38, 121.45, 121.40, 119.98, 109.49, 79.58, 48.33, 41.05 & 40.93 (rotameric singlets), 39.08 and 38.80 (rotameric singlets), 36.10, 32.46, 28.61.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



(±)-*exo*-2-(3-chloro-1*H*-indazol-1-yl)bicyclo[2.2.1]heptane (11)

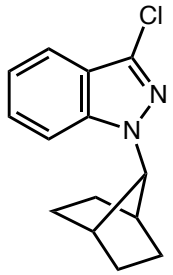
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), *exo*-2-bromonorbornane (80 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (5:1 hexane/EtOAc), provided the title compound (31.1 mg, 50% yield, >20:1 r.r., 4:1 d.r.) as a yellow oil. Assignment of the major (*exo*) and minor (*endo*) diastereomers was determined by ^{1}H NMR, showing good agreement with the *exo* and *endo* assignments of similar bicyclo[2.2.1]heptane compounds featuring nitrogen-based substituents at the C2-position.[19]

(mixture of diastereomers) **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.68 – 7.65 (m, 1H), 7.44 – 7.37 (m, 2H), 7.21 – 7.17 (m, 1H), 4.85 (dtd, *J* = 11.1, 4.4, 1.9 Hz, 0.2H, *endo*), 4.43 – 4.40 (m, 0.8H, *exo*), 2.69 – 2.68 (m, 0.2 H, *endo*) 2.49 – 2.47 (m, 2H), 2.46 – 2.40 (m, 0.8H, *exo*), 2.15 – 2.08 (m, 0.2 H, *endo*), 2.01 – 1.97 (m, 0.8H, *exo*), 1.94 – 1.84 (m, 1H), 1.69 – 1.56 (m, 2H), 1.50 – 1.47 (m, 0.2H, *endo*), 1.40 – 1.35 (m, 0.8H, *exo*), 1.31 – 1.23 (m, 2H).

(mixture of diastereomers) **^{13}C NMR (125 MHz, $CDCl_3$)** δ 141.35, 140.61, 131.68, 131.30, 127.05, 127.02, 126.42, 122.04, 121.44, 121.23, 121.22, 119.81, 110.02, 109.80, 61.64, 60.79, 43.15, 42.17, 38.93, 37.26, 36.87, 35.99, 35.94, 32.84, 29.26, 28.80, 27.37, 22.36.

IR (film) ν_{max} 3053, 2954, 2872, 1615, 1573, 1492, 1464, 1336, 1279, 1220, 1197, 1161, 1127, 1073, 1006, 988, 947, 896, 842, 769, 739 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{16}ClN_2$ ($[M+H]^+$) 247.09965, found 247.09933.



7-(3-chloro-1*H*-indazol-1-yl)bicyclo[2.2.1]heptane (12)

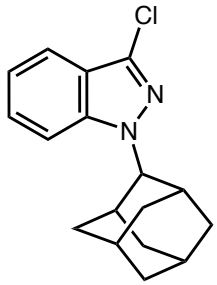
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 7-bromonorbornane (79 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (5:1 hexane/EtOAc), provided the title compound (29.1 mg, 47% yield, >20:1 r.r.) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 4.28 (s, 1H), 2.98 (s, 2H), 1.80 (dd, *J* = 38.5, 8.9 Hz, 4H), 1.42 (dd, *J* = 39.2, 6.6 Hz, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.31, 132.12, 127.19, 121.56, 121.21, 119.85, 110.67, 67.96, 40.28, 27.91, 27.62.

IR (film) ν_{max} 3058, 2955, 2911, 2873, 1615, 1573, 1492, 1465, 1372, 1338, 1226, 1208, 1184, 1128, 1080, 1030, 1008, 985, 837, 824, 767, 739 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{16}ClN_2$ ($[+H]^+$) 247.09965, found 247.09722.



3-chloro-1-(adamantan-2-yl)-1*H*-indazole (13)

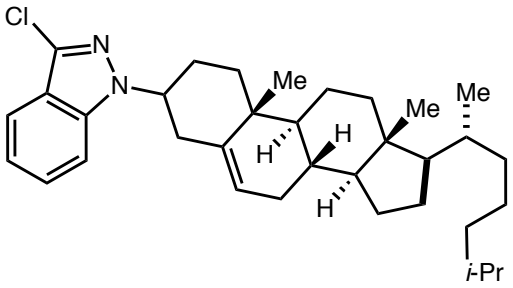
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 2-bromoadamatane (134 mg, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (38.6 mg, 54% yield, >20:1 r.r.) as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.19 (ddd, *J* = 7.9, 4.8, 2.9 Hz, 1H), 4.63 (s, 1H), 2.49 – 2.42 (m, 4H), 2.05 – 1.96 (m, 6H), 1.83 (s, 2H), 1.65 (d, J = 13.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.80, 131.71, 126.89, 121.22, 121.11, 119.87, 110.33, 63.81, 38.49, 37.90, 32.79, 32.08, 27.87, 27.47.

IR (film) ν_{max} 3053, 2903, 2854, 1615, 1492, 1464, 1397, 1365, 1345, 1337, 1284, 1267, 1222, 1200, 1180, 1131, 1101, 1085, 1058, 1039, 1008, 989, 959, 903, 834, 823, 794, 767, 740 cm^{-1}.

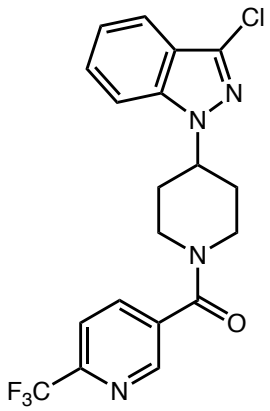
HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{20}ClN_2$ ($[M+H]^+$) 287.13095, found 287.13057.



3β-(3-chloro-1*H*-indazol-1-yl)-5-cholestene (14)

Prepared following general procedure C outlined above using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (6.5 mg, 15 μmol, 0.30 equiv.), Li*O*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), 3β-bromo-5-cholestene (56 mg, 0.125 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (33 mg, 0.125 mmol, 2.5 equiv.), MeCN (0.15 mL), toluene (0.35 mL, 0.1 M total in solvents) and water (9 μL, 0.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). *Due to challenges in the scaling of this reaction, the analytical yield was determined based on the 0.05 mmol scale reaction performed (in duplicate) according to general procedure C*. Following the reaction, mesitylene (5 μL, 35.9 μmol, 0.72 equiv.) was added as an internal standard, and the yield was determined via ^{1}H NMR (56% yield, 1:1 d.r.). Semi-pure material obtained via preparative thin-layer chromatography (10:1 hexane/EtOAc) was used for HRMS analysis and to determine the diastereomeric ratio via ^{1}H NMR (as indicated in the spectral data).

HRMS (ESI-TOF) m/z calcd. for $C_{34}H_{50}ClN_2$ ($[M+H]^+$) 521.36570, found 521.28567.



(4-(3-chloro-1*H*-indazol-1-yl)piperidin-1-yl)(6-(trifluoromethyl)pyridin-3-yl)methanone (15)

Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), (4-bromopiperidine-1-yl)(6-(trifluoromethyl)pyridine-3-yl)methanone (**Br-1**, 211 mg, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography (2:1 to 1:1.5 hexane/EtOAc) provided the title compound (89.2 mg, 87% yield, >20:1 r.r.) as a white solid.

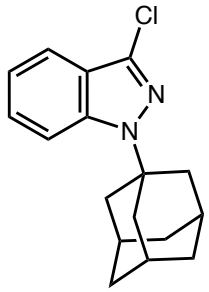
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 4.85 (br s, 1H), 4.67 (tt, *J* = 10.9, 4.3 Hz, 1H), 4.05 – 3.88 (br s, 1H), 3.25 (br d, *J* = 100.8 Hz, 2H), 2.33 (br s, 2H), 2.19 – 2.04 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.53, 149.22 (q, *J* = 35.2 Hz), 148.15, 140.26, 136.58, 134.50, 133.52, 127.81, 121.76, 121.37, 121.27 (q, *J* = 274.6 Hz), 120.66 (q, *J* = 2.8 Hz), 120.29, 108.99, 55.49, 46.95, 41.61, 32.00, 31.37.

^{19}F NMR (282 MHz, $CDCl_3$) δ -68.08 (s, 3F).

IR (film) ν_{max} 3058, 2942, 2861, 1732, 1632, 1493, 1465, 1441, 1371, 1333, 1276, 1251, 1177, 1129, 1082, 1004, 974, 943, 895, 856, 788, 742, 718 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{17}ClF_3N_4O$ ($[M+H]^+$) 409.10375, found 409.10357.



3-chloro-1-(adamantan-1-yl)-1*H*-indazole (16)

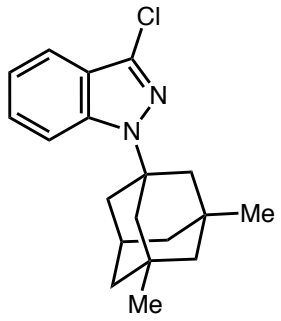
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 1-bromoadamantane (134 mg, 0.625 mmol, 2.5 equiv.), (TMS)$_3$SiNHAd (249 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (45.2 mg, 63% yield, >20:1 r.r.) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.34 (dd, *J* = 8.8, 6.8 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 2.42 (d, *J* = 3.0 Hz, 6H), 2.28 (s, 3H), 1.85 – 1.79 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.40, 131.45, 126.46, 122.43, 120.74, 120.16, 112.88, 61.56, 42.41, 36.43, 29.98.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



3-chloro-1-(3,5-dimethyladamantan-1-yl)-1*H*-indazole (17)

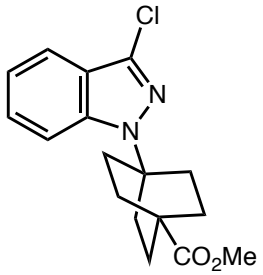
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 1-bromo-3,5-dimethyladamantane (124 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiNHAd$ (249 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (49.0 mg, 62% yield, >20:1 r.r.) as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.7 Hz, 1H), 7.66 (dt, *J* = 8.1, 1.1 Hz, 1H), 7.34 (ddd, *J* = 8.5, 6.9, 1.2 Hz, 1H), 7.18 – 7.15 (m, 1H), 2.34 (p, *J* = 3.3 Hz, 1H), 2.27 – 2.26 (m, 2H), 2.11 – 2.08 (m, 2H), 2.04 – 2.01 (m, 2H), 1.55 – 1.50 (m, 2H), 1.45 – 1.41 (m, 2H), 1.30 (dt, *J* = 8.6, 2.2 Hz, 2H), 0.96 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.47, 131.47, 126.51, 122.41, 120.77, 120.17, 112.85, 63.22, 50.66, 48.33, 42.72, 40.92, 33.11, 30.61, 30.32.

IR (film) ν_{max} 3051, 2898, 2845, 1615, 1567, 1491, 1458, 1355, 1333, 1297, 1249, 1193, 1171, 1128, 1015, 997, 968, 928, 896, 838, 767, 750, 738 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{24}ClN_2$ ($[M+H]^+$) 315.16225, found 315.15978.



Methyl 4-(3-chloro-1*H*-indazol-1-yl)bicyclo[2.2.2]octane-1-carboxylate (18)

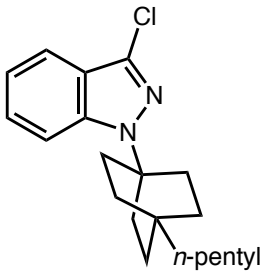
Prepared following general procedure C outlined above using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**[Ir-2]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), $Cu(TMHD)_2$ (13 mg, 30 μmol, 0.60 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), methyl 4-bromobicyclo[2.2.2]octane-1-carboxylate (31 mg, 0.125 mmol, 2.5 equiv.), $(TMS)_3SiNHAd$ (50 mg, 0.125 mmol, 2.5 equiv.), MeCN (0.5 mL, 0.1 M) and water (9 μL, 0.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification of five combined 0.05 mmol scale crude reaction vials (0.25 mmol total) by flash chromatography (10:1 hexane/EtOAc) provided the title compound (45.8 mg, 57% yield, >20:1 r.r.) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (t, *J* = 7.9 Hz, 2H), 7.35 (dd, *J* = 8.7, 6.9 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 3.69 (s, 3H), 2.37 – 2.34 (m, 6H), 2.09 – 2.05 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.51, 139.80, 131.87, 126.76, 122.60, 120.98, 120.25, 112.51, 60.87, 52.06, 38.74, 30.65, 28.94.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



3-chloro-1-(4-pentylbicyclo[2.2.2]octan-1-yl)-1*H*-indazole (19)

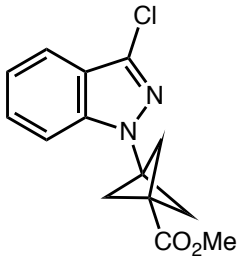
Prepared following general procedure C outlined above using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (13 mg, 30 μmol, 0.60 equiv.), Li*O*t-Bu (12 mg, 0.15 mmol, 3.0 equiv.), 1-bromo-4-pentylbicyclo[2.2.2]octane (32 mg, 0.125 mmol, 2.5 equiv.), $(TMS)_3SiNHAd$ (50 mg, 0.125 mmol, 2.5 equiv.), MeCN (0.5 mL, 0.1 M) and water (9 μL, 0.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 10% light intensity). Purification of five combined 0.05 mmol scale crude reaction vials (0.25 mmol total) by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (41.9 mg, 51% yield, >20:1 r.r.) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.33 (ddd, *J* = 8.5, 6.8, 1.2 Hz, 1H), 7.16 (dd, *J* = 8.0, 6.9 Hz, 1H), 2.31 – 2.28 (m, 6H), 1.65 – 1.62 (m, 6H), 1.34 – 1.28 (m, 2H), 1.24 – 1.20 (m, 4H), 1.17 – 1.14 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.79, 131.40, 126.44, 122.44, 120.75, 120.09, 112.77, 61.35, 41.13, 32.91, 31.50, 31.46, 30.68, 23.65, 22.84, 14.25.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



Methyl 3-(3-chloro-1*H*-indazol-1-yl)bicyclo[1.1.1]pentane-1-carboxylate (20)

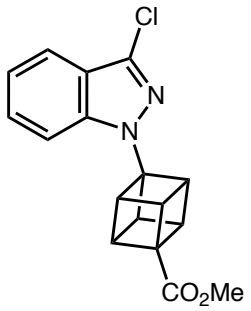
Prepared following general procedure C outlined above using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (13 mg, 30 μmol, 0.60 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), methyl 3-bromobicyclo[1.1.1]pentane-1-carboxylate (26 mg, 0.125 mmol, 2.5 equiv.), $(TMS)_3SiNHAd$ (50 mg, 0.125 mmol, 2.5 equiv.), MeCN (0.5 mL, 0.1 M) and water (9 μL, 0.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification of five combined 0.05 mmol scale crude reaction vials (0.25 mmol total) by flash chromatography (10:1 hexane/EtOAc) provided the title compound (44.4 mg, 64% yield, >20:1 r.r.) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dt, *J* = 8.2, 1.1 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.44 (ddd, *J* = 8.4, 6.8, 1.1 Hz, 1H), 7.23 (ddd, *J* = 8.0, 6.8, 0.9 Hz, 1H), 3.76 (s, 3H), 2.75 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.58, 140.69, 134.33, 128.10, 121.89, 121.83, 120.18, 110.19, 55.17, 52.26, 50.96, 35.44.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



Methyl 4-(3-chloro-1*H*-indazol-1-yl)cubane-1-carboxylate (21)

Prepared following general procedure C outlined above using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (**[Ir-2]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (13 mg, 30 μmol, 0.60 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), methyl 4-bromocubane-1-carboxylate (30 mg, 0.125 mmol, 2.5 equiv.), (TMS)$_3$SiNHAd (69 mg, 0.175 mmol, 3.5 equiv.), MeCN (0.5 mL, 0.1 M) and water (9 μL, 0.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification of five combined 0.05 mmol scale crude reaction vials (0.25 mmol total) by flash chromatography (6:1 to 4:1 hexane/EtOAc) provided the title compound (39.7 mg, 51% yield, >20:1 r.r.) as a white solid.

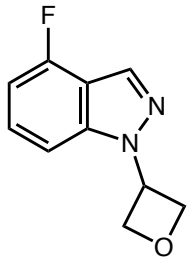
^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.71 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.31 (td, *J* = 7.3, 1.0 Hz, 1H), 4.68 – 4.64 (m, 3H), 4.37 – 4.33 (m, 3H), 3.71 (s, 3H).

^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 172.03, 140.67, 133.71, 128.61, 122.92, 122.66, 120.31, 111.58, 72.48, 57.15, 51.71, 51.25, 45.71.

IR (film) ν_{max} 3056, 3009, 2956, 2909, 2844, 1721, 1618, 1558, 1493, 1470, 1438, 1412, 1388, 1332, 1306, 1243, 1217, 1177, 1132, 1090, 1043, 1021, 1002, 951, 900, 836, 806, 765, 733 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{14}ClN_2O_2$ ($[M+H]^+$) 313.07383, found 313.02453.

9. *N*-nucleophile scope for C–N coupling of 3-bromooxetane



4-fluoro-1-(oxetan-3-yl)-1*H*-indazole (22)

Prepared following general procedure A outlined above using 4-fluoro-1*H*-indazole (34.0 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (38.8 mg, 81% yield, >20:1 r.r.) as a white solid. The regiochemical assignment of this product was verified by NOESY analysis (as indicated in the spectral data).

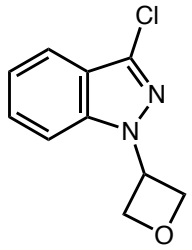
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.37 – 7.29 (m, 2H), 6.82 (dd, *J* = 10.0, 7.6 Hz, 1H), 5.78 (tt, *J* = 7.7, 6.2 Hz, 1H), 5.30 (t, *J* = 6.7 Hz, 2H), 5.14 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.12 (d, *J* = 253.2 Hz), 141.82 (d, *J* = 9.1 Hz), 130.70 (d, *J* = 2.0 Hz), 127.86 (d, *J* = 7.7 Hz), 115.07 (d, *J* = 23.3 Hz), 105.65 (d, *J* = 18.5 Hz), 105.04 (d, *J* = 4.3 Hz), 77.32, 53.20.

^{19}F NMR (282 MHz, $CDCl_3$) δ -117.38 (dd, *J* = 9.8, 4.6 Hz, 1F).

IR (film) ν_{max} 3099, 3013, 2968, 2887, 1637, 1579, 1508, 1460, 1446, 1397, 1327, 1299, 1267, 1232, 1202, 1148, 965, 869, 826, 777, 734 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{10}FN_2O$ ($[M+H]^+$) 193.07717, found 193.07176.



3-chloro-1-(oxetan-3-yl)-1*H*-indazole (23)

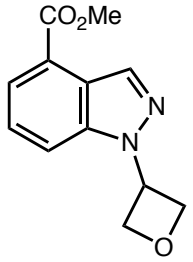
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (44.8 mg, 86% yield, >20:1 r.r.) as a white solid.

^{1}H NMR (500 MHz, CD_3CN) δ 7.69 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.54 – 7.48 (m, 1H), 7.30 – 7.26 (m, 1H), 5.90 – 5.85 (m, 1H), 5.07 (p, *J* = 6.8 Hz, 4H).

^{13}C NMR (125 MHz, CD_3CN) δ 141.80, 133.90, 128.80, 122.87, 121.93, 120.25, 110.95, 77.96, 53.44.

IR (film) ν_{max} 3058, 2956, 2922, 2881, 2851, 1617, 1497, 1468, 1436, 1368, 1337, 1294, 1220, 1168, 1120, 1060, 1026, 1006, 965, 890, 842, 767, 747 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{10}ClN_2O$ ($[M+H]^+$) 209.04762, found 209.05751.



Methyl 1-(oxetan-3-yl)-1*H*-indazole-4-carboxylate (24)

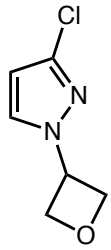
Prepared following general procedure A outlined above using methyl 1*H*-indazole-4-carboxylate (44.0 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (4:1 hexane/EtOAc) provided the title compound (38.4 mg, 66% yield, >20:1 r.r.) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.48 (dd, *J* = 8.4, 7.2 Hz, 1H), 5.83 (tt, *J* = 7.7, 6.2 Hz, 1H), 5.31 (t, *J* = 6.6 Hz, 2H), 5.16 (t, *J* = 7.3 Hz, 2H), 4.03 (s, 3H).

^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 166.95, 140.85, 135.14, 126.57, 125.06, 123.69, 123.48, 115.38, 77.67, 53.00, 52.40.

IR (film) ν_{max} 3063, 2947, 2891, 1711, 1610, 1583, 1506, 1451, 1430, 1375, 1353, 1304, 1285, 1269, 1193, 1171, 1146, 1114, 1042, 1018, 966, 942, 867, 845, 816, 775, 753, 738 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{13}N_2O_3$ ($[M+H]^+$) 233.09207, found 233.09112.



3-chloro-1-(oxetan-3-yl)-1*H*-pyrazole (25)

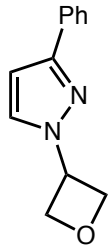
Prepared following general procedure A outlined above using 3-chloro-1*H*-pyrazole (25.6 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (3:1 to 1:1 hexane/EtOAc) provided the title compound (35.6 mg, 90% yield, >20:1 r.r.) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 2.4 Hz, 1H), 6.24 (d, *J* = 2.4 Hz, 1H), 5.37 (p, *J* = 7.1 Hz, 1H), 5.05 (t, *J* = 6.6 Hz, 2H), 5.01 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.31, 130.18, 105.97, 77.52, 56.16.

IR (film) ν_{max} 3118, 2955, 2886, 1504, 1479, 1454, 1398, 1360, 1334, 1316, 1274, 1167, 1041, 968, 904, 843, 812, 771 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_6H_8ClN_2O$ ($[M+H]^+$) 159.03197, found 159.05089.



3-phenyl-1-(oxetan-3-yl)-1*H*-pyrazole (26)

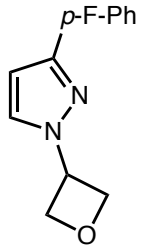
Prepared following general procedure A outlined above using 3-phenyl-1*H*-pyrazole (36.0 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (5:1 to 3:1 hexane/EtOAc) provided the title compound (35.2 mg, 70% yield, >20:1 r.r.) as a yellow oil. The regiochemical assignment of this product was verified by NOESY analysis (as indicated in the spectral data).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 2H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.30 (m, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 5.51 (tt, *J* = 7.6, 6.3 Hz, 1H), 5.14 (t, *J* = 6.6 Hz, 2H), 5.07 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.24, 133.38, 129.34, 128.79, 127.99, 125.82, 103.71, 78.01, 55.78.

IR (film) ν_{max} 3119, 3048, 2997, 2943, 2878, 1604, 1497, 1475, 1453, 1426, 1359, 1288, 1270, 1223, 1213, 1091, 1075, 1045, 980, 948, 903, 819, 785, 748, 703 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{13}N_2O$ ($[M+H]^+$) 201.10224, found 201.10167.



3-(4-fluorophenyl)-1-(oxetan-3-yl)-1*H*-pyrazole (27)

Prepared following general procedure A outlined above using 3-(4-fluorophenyl)-1*H*-pyrazole (40.5 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (22 mg, 50 μmol, 0.20 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (2:1 hexane/EtOAc) provided the title compound (31.2 mg, 57% yield, >20:1 r.r.) as a yellow oil.

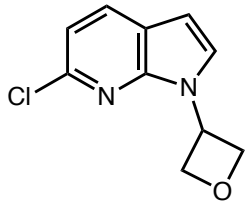
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 2.4 Hz, 1H), 5.48 (p, *J* = 7.1 Hz, 1H), 5.13 (t, *J* = 6.6 Hz, 2H), 5.06 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.72 (d, *J* = 246.5 Hz), 151.33, 129.61, 129.56, 127.45 (d, *J* = 8.0 Hz), 115.66 (d, *J* = 21.6 Hz), 103.44, 77.94, 55.71.

^{19}F NMR (282 MHz, $CDCl_3$) δ -114.44 (tt, *J* = 8.6, 5.4 Hz, 1F).

IR (film) ν_{max} 3104, 3053, 2956, 2878, 1605, 1534, 1503, 1479, 1462, 1427, 1381, 1347, 1320, 1262, 1205, 1166, 1101, 1045, 981, 963, 890, 852, 828, 810, 767, 727 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{12}FN_2O$ ($[M+H]^+$) 219.09282, found 219.09464.



6-chloro-1-(oxetan-3-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (28)

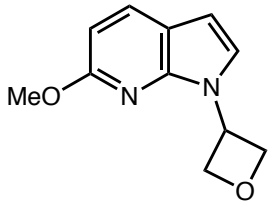
Prepared following general procedure B outlined above using 6-chloro-1*H*-pyrrolo[2,3-*b*]pyridine (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (44.6 mg, 85% yield) as a waxy yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 3.7 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 3.6 Hz, 1H), 6.11 (p, *J* = 7.4 Hz, 1H), 5.19 (t, *J* = 7.4 Hz, 2H), 4.95 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.67, 144.89, 131.53, 124.61, 119.22, 116.65, 101.96, 78.69, 48.04.

IR (film) ν_{max} 3094, 2960, 2881, 1575, 1506, 1462, 1421, 1361, 1326, 1298, 1252, 1216, 1122, 1103, 975, 914, 813, 782, 722 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{10}ClN_2O$ ($[M+H]^+$) 209.04762, found 209.04618.



6-methoxy-1-(oxetan-3-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (29)

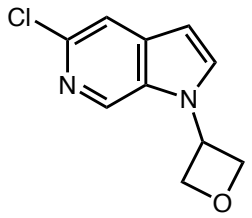
Prepared following general procedure B outlined above using 6-methoxy-1*H*-pyrrolo[2,3-*b*]pyridine (37.0 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (7:1 hexane/EtOAc) provided the title compound (27.7 mg, 54% yield) as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 3.7 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 3.6 Hz, 1H), 5.98 (p, *J* = 7.2 Hz, 1H), 5.16 – 5.09 (m, 4H), 3.98 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 160.94, 145.38, 132.00, 121.50, 114.39, 104.47, 101.62, 78.60, 53.47, 48.31.

IR (film) ν_{max} 3114, 2992, 2953, 2893, 1604, 1574, 1510, 1491, 1443, 1420, 1341, 1330, 1312, 1278, 1238, 1155, 1111, 1019, 998, 954, 886, 850, 810, 748, 715 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{13}N_2O_2$ ($[M+H]^+$) 205.09715, found 205.09689.



5-chloro-1-(oxetan-3-yl)-1*H*-pyrrolo[2,3-*c*]pyridine (30)

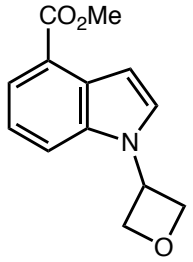
Prepared following general procedure B outlined above using 6-chloro-1*H*-pyrrolo[2,3-*c*]pyridine (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (3:1 to 1:1 hexane/EtOAc) provided the title compound (40.0 mg, 77% yield) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.63 (d, *J* = 3.4 Hz, 1H), 7.54 (s, 1H), 6.56 (d, *J* = 3.3 Hz, 1H), 5.60 (p, *J* = 6.6 Hz, 1H), 5.22 (t, *J* = 7.5 Hz, 2H), 5.02 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.10, 137.00, 132.17, 131.76, 130.75, 115.18, 102.16, 77.84, 51.48.

IR (film) ν_{max} 3139, 2962, 2922, 2876, 1597, 1559, 1505, 1461, 1435, 1415, 1372, 1335, 1291, 1273, 1235, 1207, 1121, 1104, 1055, 988, 955, 913, 895, 880, 846, 832, 788, 763, 721 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{10}ClN_2O$ ($[M+H]^+$) 209.04762, found 209.04964.



Methyl 1-(oxetan-3-yl)-1*H*-indole-4-carboxylate (31)

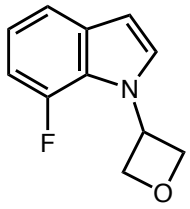
Prepared following general procedure B outlined above using methyl 1*H*-indole-4-carboxylate (43.8 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (4:1 hexane/EtOAc) provided the title compound (37.5 mg, 65% yield) as an orange solid.

^{1}H NMR (500 MHz, CD_3CN) δ 7.84 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.28 (dd, *J* = 8.2, 7.5 Hz, 1H), 7.16 (dd, *J* = 3.3, 0.8 Hz, 1H), 5.70 (tt, *J* = 7.6, 6.1 Hz, 1H), 5.10 (t, *J* = 7.4 Hz, 2H), 4.95 (t, *J* = 6.7 Hz, 2H), 3.92 (s, 3H).

^{13}C NMR (125 MHz, CD_3CN) δ 168.43, 137.51, 129.12, 128.73, 123.96, 122.61, 121.87, 115.67, 104.14, 78.38, 52.26, 51.51.

IR (film) ν_{max} 3105, 3028, 2953, 2881, 1707, 1603, 1573, 1508, 1439, 1384, 1354, 1330, 1313, 1263, 1210, 1193, 1178, 1152, 1111, 1017, 975, 909, 818, 764, 746, 730 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{14}NO_3$ ($[M+H]^+$) 232.09682, found 232.10055.



7-fluoro-1-(oxetan-3-yl)-1*H*-indole (32)

Prepared following general procedure B outlined above using 7-fluoro-1*H*-indole (33.8 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (10:1 to 7:1 hexane/EtOAc) provided the title compound (32.6 mg, 68% yield) as a yellow oil.

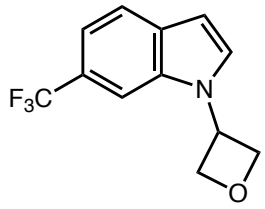
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 3.3 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.02 (td, *J* = 7.9, 4.5 Hz, 1H), 6.89 (ddd, *J* = 13.1, 7.9, 0.9 Hz, 1H), 6.66 (dd, *J* = 3.3, 2.4 Hz, 1H), 5.94 (p, *J* = 6.9 Hz, 1H), 5.15 (t, *J* = 7.2 Hz, 2H), 5.00 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.02 (d, *J* = 242.7 Hz), 132.66 (d, *J* = 5.3 Hz), 125.27, 123.92 (d, *J* = 9.2 Hz), 120.31 (d, *J* = 6.9 Hz), 117.07 (d, *J* = 3.4 Hz), 107.93 (d, *J* = 18.6 Hz), 104.05 (d, *J* = 2.0 Hz), 78.67 (d, *J* = 2.6 Hz), 51.80 (d, *J* = 6.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -135.11 (d, *J* = 12.8 Hz, 1F).

IR (film) ν_{max} 3129, 3109, 3073, 3038, 2960, 2882, 1629, 1576, 1525, 1489, 1445, 1320, 1236, 1272, 1236, 1217, 1160, 1101, 1049, 1032, 976, 895, 848, 821, 782, 714 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{11}FNO$ ($[M+H]^+$) 192.08192, found 192.08879.



6-trifluoromethyl-1-(oxetan-3-yl)-1*H*-indole (33)

Prepared following general procedure B outlined above using 6-trifluoromethyl-1*H*-indole (46.3 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (40.0 mg, 66% yield) as a yellow solid.

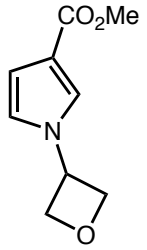
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H), 7.64 (d, *J* = 3.3 Hz, 1H), 7.38 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.69 (d, *J* = 3.3 Hz, 1H), 5.63 (tt, *J* = 7.6, 6.0 Hz, 1H), 5.22 (t, *J* = 7.4 Hz, 2H), 5.05 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (125 MHz, CD_3CN) δ 134.71, 131.29, 127.44, 125.25 (q, *J* = 271.6 Hz), 124.29 (q, *J* = 31.9 Hz), 121.82, 116.87 (q, *J* = 3.5 Hz), 106.95 (q, *J* = 4.5 Hz), 103.45, 78.10, 50.69.

^{19}F NMR (282 MHz, $CDCl_3$) δ -60.59 (s, 3F).

IR (film) ν_{max} 3114, 3102, 2967, 2891, 1507, 1461, 1419, 1341, 1312, 1269, 1238, 1212, 1148, 1131, 1106, 1059, 1050, 978, 916, 897, 861, 828, 789, 766, 738 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{11}F_3NO$ ($[M+H]^+$) 242.07873, found 242.26430.



Methyl 1-(oxetan-3-yl)-1*H*-pyrrole-3-carboxylate (34)

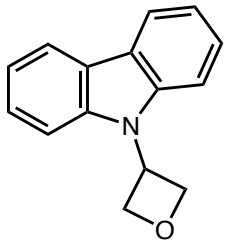
Prepared following general procedure B outlined above using methyl 1*H*-pyrrole-3-carboxylate (31.3 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (3:1 hexane/EtOAc) provided the title compound (29.0 mg, 64% yield) as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.53 (m, 1H), 6.87 (t, *J* = 2.7 Hz, 1H), 6.66 – 6.65 (m, 1H), 5.19 (p, *J* = 6.5 Hz, 1H), 5.07 (t, *J* = 7.3 Hz, 2H), 4.86 (t, *J* = 6.6 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.08, 124.38, 120.03, 117.01, 111.13, 78.64, 54.08, 51.29.

IR (film) ν_{max} 3134, 3113, 2981, 2951, 2885, 1697, 1583, 1539, 1510, 1486, 1444, 1431, 1402, 1372, 1259, 1198, 1128, 993, 960, 932, 888, 818, 792, 760, 729 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{12}NO_3$ ($[M+H]^+$) 182.08117, found 182.08209.



9-(oxetan-3-yl)-9*H*-carbazole (35)

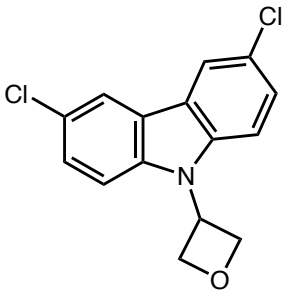
Prepared following general procedure B outlined above using carbazole (41.8 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (10 mg, 0.125 mmol, 0.5 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (6:1 hexane/EtOAc) provided the title compound (32.1 mg, 58% yield) as a white solid.

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.48 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 6.11 (tt, *J* = 8.0, 5.8 Hz, 1H), 5.36 (dd, *J* = 7.2, 5.8 Hz, 2H), 5.27 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 140.49, 126.71, 124.20, 121.17, 120.25, 110.80, 76.39, 50.18.

IR (film) ν_{max} 3053, 2944, 2880, 1596, 1485, 1450, 1349, 1325, 1241, 1225, 1214, 1162, 1083, 975, 884, 817, 750, 725 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{14}NO$ ($[M+H]^+$) 224.10699, found 224.07693.



3,6-dichloro-9-(oxetan-3-yl)-9*H*-carbazole (36)

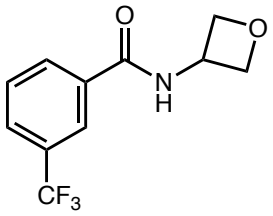
Prepared following general procedure B outlined above using 3,6-dichloro-9*H*-carbazole (59.0 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (9:1 to 5:1 hexane/EtOAc) provided the title compound (54.7 mg, 75% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.2 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.46 (dd, *J* = 8.8, 2.2 Hz, 2H), 5.77 (tt, *J* = 8.0, 5.7 Hz, 1H), 5.37 (dd, *J* = 7.6, 5.7 Hz, 2H), 5.28 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.30, 126.93, 125.76, 123.86, 120.62, 110.96, 76.12, 49.70.

IR (film) ν_{max} 3058, 2966, 2890, 1475, 1440, 1357, 1283, 1243, 1224, 1167, 1079, 1066, 1027, 973, 901, 864, 848, 811, 801, 720 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{12}Cl_2NO$ ($[M+H]^+$) 292.02905, found 292.04702.



***N*-(oxetan-3-yl)-3-(trifluoromethyl)benzamide (37)**

Prepared following general procedure B outlined above using 3-(trifluoromethyl)benzamide (47.3 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (1:1 hexane/EtOAc) provided the title compound (44.2 mg, 72% yield) as a white solid.

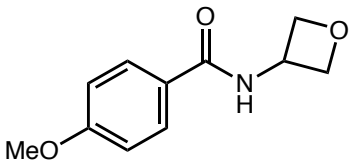
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 6.81 (br s, 1H), 5.26 (dtd, *J* = 13.3, 7.3, 6.0 Hz, 1H), 5.04 (t, *J* = 7.1 Hz, 2H), 4.63 (dd, *J* = 7.1, 6.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.75, 134.62, 131.42 (q, *J* = 32.9 Hz), 130.49 (q, *J* = 1.1 Hz), 129.56, 128.68 (q, *J* = 3.7 Hz), 124.10 (q, *J* = 3.8 Hz), 123.74 (q, *J* = 272.6 Hz), 78.48, 45.67.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.77 (s, 3F).

IR (film) ν_{max} 3269, 3084, 2958, 2887, 1646, 1548, 1483, 1434, 1401, 1372, 1317, 1280, 1162, 1119, 1092, 1071, 976, 921, 907, 870, 822, 756, 722 cm^{-1}.

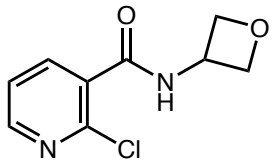
HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{11}F_3NO_2$ ($[M+H]^+$) 246.07364, found 246.07258.



***N*-(oxetan-3-yl)-4-methoxybenzamide (38)**

Prepared following general procedure B outlined above (*in duplicate*) using 4-methoxybenzamide (37.8 mg, 0.25 mmol, 1.0 equiv.), $Ir[dF(CF_3)ppy]_2[4,4'-d(CF_3)bpy]PF_6$ (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), $Cu(TMHD)_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Following the reaction, mesitylene (25 μL, 179.5 μmol, 0.72 equiv.) was added as an internal standard, and the yield was determined via ^1H NMR (78% yield). Semi-pure material obtained via flash chromatography (1:1 hexane/EtOAc to 100% EtOAc) was used for HRMS analysis and to confirm the peak assignments employed for the reported ^1H NMR yield (as indicated in the spectral data).

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{14}NO_3$ ($[M+H]^+$) 208.09682, found 208.09476.



***N*-(oxetan-3-yl)-2-chloro-nicotinamide (39)**

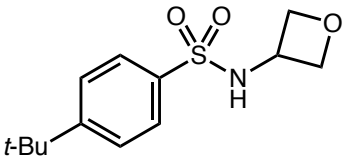
Prepared following general procedure B outlined above using 2-chloronicotinamide (39.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (19:1 CH_2Cl_2/MeOH) provided the title compound (26.1 mg, 49% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 – 8.48 (m, 1H), 8.12 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.37 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1H), 7.14 (br s, 1H), 5.25 (dqd, *J* = 7.5, 6.1, 4.8 Hz, 1H), 5.03 (t, *J* = 7.0 Hz, 2H), 4.63 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.13, 151.55, 147.19, 140.24, 130.42, 123.07, 78.24, 45.66.

IR (film) ν_{max} 3239, 3057, 2960, 2885, 1664, 1584, 1547, 1475, 1446, 1401, 1371, 1332, 1309, 1229, 1194, 1165, 1130, 1093, 1069, 974, 948, 888, 873, 860, 816, 752, 716 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_9H_{10}ClN_2O_2$ ($[M+H]^+$) 213.04253, found 213.04671.



***N*-(oxetan-3-yl)-4-*tert*-butylbenzenesulfonamide (40)**

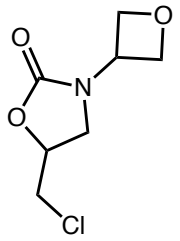
Prepared following general procedure B outlined above using 4-*tert*-butylbenzenesulfonamide (53.3 mg, 0.25 mmol, 1.0 equiv.), $Ir[dF(CF_3)ppy]_2[4,4'\text{-}d(CF_3)bpy]PF_6$ (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), $Cu(TMHD)_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*-*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (4:1 hexane/EtOAc) provided the title compound (49.5 mg, 74% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 5.09 (br d, *J* = 9.2 Hz, 1H), 4.71 (t, *J* = 7.2 Hz, 2H), 4.52 (dp, *J* = 9.3, 6.8 Hz, 1H), 4.37 (t, *J* = 6.7 Hz, 2H), 1.34 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.34, 136.99, 126.89, 126.52, 78.65, 48.05, 35.37, 31.21.

IR (film) ν_{max} 3148, 2965, 2880, 1595, 1464, 1401, 1355, 1333, 1271, 1186, 1162, 1138, 1114, 1088, 965, 891, 841, 787, 754, 704 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{20}NO_3S$ ($[M+H]^+$) 270.11584, found 270.11733.



(±)-*N*-(oxetan-3-yl)-5-(chloromethyl)-2-oxazolidinone (41)

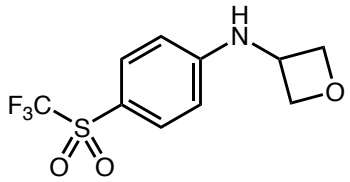
Prepared following general procedure B outlined above using (±)-5-(chloromethyl)-2-oxazolidinone (33.9 mg, 0.25 mmol, 1.0 equiv.), $Ir[dF(CF_3)ppy]_2[4,4'\text{-}d(CF_3)bpy]PF_6$ (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), $Cu(TMHD)_2$ (22 mg, 50 μmol, 0.20 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (1:1 to 1:2 hexane/EtOAc) provided the title compound (33.9 mg, 71% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.11 (tt, *J* = 7.7, 6.3 Hz, 1H), 4.88 – 4.82 (m, 3H), 4.78 (q, *J* = 7.0 Hz, 2H), 3.97 (t, *J* = 8.9 Hz, 1H), 3.79 – 3.76 (m, 1H), 3.74 – 3.70 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.19, 74.60, 71.75, 48.51, 44.88, 44.10.

IR (film) ν_{max} 2966, 2891, 1745, 1493, 1441, 1376, 1340, 1288, 1251, 1112, 1068, 1027, 996, 970, 901, 864, 836, 752, 711 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_7H_{11}ClNO_3$ ($[M+H]^+$) 192.04220, found 192.13494.



***N*-(oxetan-3-yl)-4-(trifluoromethylsulfonyl)aniline (42)**

Prepared following general procedure B outlined above using 4-(trifluoromethylsulfonyl)aniline (56.3 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (1.5:1 hexane/EtOAc) provided the title compound (40.6 mg, 58% yield) as a white solid.

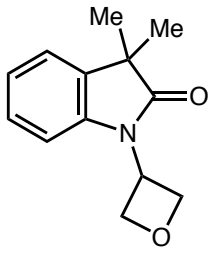
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.6 Hz, 2H), 6.60 – 6.58 (m, 2H), 5.12 – 5.03 (m, 3H), 4.72 (dp, *J* = 12.7, 6.1 Hz, 1H), 4.57 (t, *J* = 6.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.60, 133.39, 120.15 (q, *J* = 325.5 Hz), 117.73, 112.58, 78.35, 48.00.

^{19}F NMR (282 MHz, $CDCl_3$) δ -79.06 (s, 3F).

IR (film) ν_{max} 3381, 2957, 2927, 2884, 1694, 1590, 1534, 1408, 1341, 1289, 1211, 1178, 1134, 1067, 996, 965, 829, 763, 713 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{11}F_3NO_3S$ ($[M+H]^+$) 282.04062, found 282.04037.



3,3-dimethyl-1-(oxetan-3-yl)-1,3-dihydro-2*H*-indol-2-one (43)

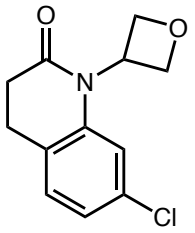
Prepared following general procedure B outlined above using 3,3-dimethyl-1,3-dihydro-2*H*-indol-2-one (40.3 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (4:1 hexane/EtOAc) provided the title compound (49.5 mg, 91% yield) as a yellow oil.

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.31 (td, *J* = 7.7, 1.3 Hz, 1H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 5.49 (tt, *J* = 8.0, 6.2 Hz, 1H), 5.10 (t, *J* = 6.6 Hz, 2H), 4.98 (dd, *J* = 8.0, 7.0 Hz, 2H), 1.30 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 181.21, 139.81, 136.02, 128.16, 123.07, 122.96, 109.88, 74.35, 45.95, 44.04, 24.71.

IR (film) ν_{max} 3058, 2961, 2922, 2881, 1716, 1697, 1609, 1487, 1454, 1384, 1365, 1332, 1303, 1237, 1214, 1188, 1160, 1123, 1073, 1025, 975, 919, 875, 812, 764, 755 cm^{-1}.

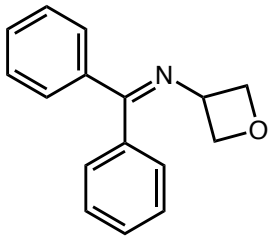
HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}NO_2$ ($[M+H]^+$) 218.11756, found 218.11735.



7-chloro-1-(oxetan-3-yl)-3,4-dihydro-2(1*H*)-quinolinone (44)

Prepared following general procedure B outlined above (*in duplicate*) using 7-chloro-3,4-dihydro-2(1*H*)-quinolinone (45.4 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Following the reaction, mesitylene (25 μL, 179.5 μmol, 0.72 equiv.) was added as an internal standard, and the yield was determined via ^{1}H NMR (56% yield). Semi-pure material obtained via preparative thin-layer chromatography (7:1 toluene/EtOAc) was used for HRMS analysis and to confirm the peak assignments employed for the reported ^{1}H NMR yield (as indicated in the spectral data).

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{13}ClNO_2$ ($[M+H]^+$) 238.06293, found 238.05785.



1,1-diphenyl-*N*-(oxetan-3-yl)-methanimine (45)

Prepared following general procedure B outlined above using benzophenone imine (42.0 μL, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (5:1 hexane/EtOAc) provided the title compound (48.5 mg, 82% yield) as a white solid.

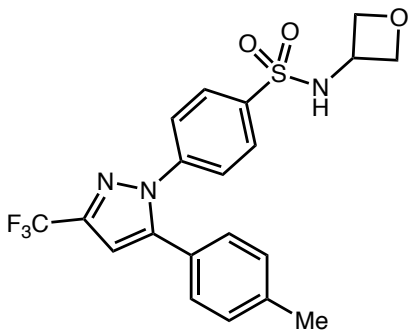
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.44 (m, 3H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.05 – 7.03 (m, 2H), 4.86 – 4.84 (m, 2H), 4.73 – 4.67 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 130.74, 129.12, 128.81, 128.34, 127.67, 79.19, 56.38.

IR (film) ν_{max} 3056, 2953, 2927, 2873, 1611, 1590, 1573, 1492, 1446, 1360, 1317, 1289, 1220, 1184, 1165, 1122, 1091, 1074, 1025, 1000, 967, 929, 914, 859, 784, 774, 742, 705 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{16}NO$ ($[M+H]^+$) 238.12264, found 238.12323.

10. Alkylation of pharmaceutical compounds



***N*-(3-oxetanyl)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (46)**

Prepared following general procedure B outlined above using Celecoxib (95.3 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (4:1 hexane/EtOAc) provided the title compound (95.2 mg, 87% yield) as a white solid.

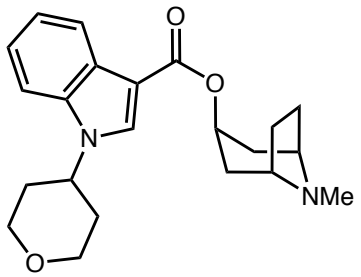
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 2H), 7.50 – 7.48 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 1H), 5.35 (d, *J* = 9.4 Hz, 1H), 4.72 (t, *J* = 7.2 Hz, 2H), 4.52 (dp, *J* = 9.5, 6.7 Hz, 1H), 4.37 (t, *J* = 6.7 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.43, 144.38 (q, *J* = 38.4 Hz), 143.02, 140.08, 139.55, 129.91, 128.84, 127.99, 125.90, 125.74, 121.12 (q, *J* = 269.3 Hz), 106.60, 78.53, 48.02, 21.48.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.50 (s, 3F).

IR (film) ν_{max} 3272, 3154, 2955, 2881, 1595, 1497, 1475, 1452, 1437, 1412, 1368, 1354, 1333, 1303, 1276, 1236, 1195, 1153, 1121, 1094, 1021, 975, 897, 837, 826, 807, 759, 743, 719 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{20}H_{19}F_3N_3O_4S$ ($[M+H]^+$) 438.10937, found 438.11140.



1-(tetrahydro-2*H*-pyran-4-yl)-(3-*endo*)-8-methyl-8-azabicyclo[3.2.1]octan-3-yl-1*H*-indole-3-carboxylate (47)

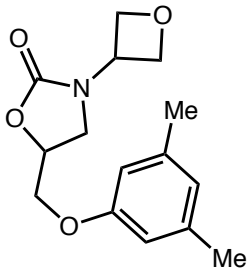
Prepared following general procedure B outlined above using Tropisetron hydrochloride (80.2 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 4-bromotetrahydro-2*H*-pyran (70 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography (9:1 CH_2Cl_2/MeOH) provided the title compound (47.5 mg, 52% yield) as a pale brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 – 8.17 (m, 1H), 7.85 (s, 1H), 7.45 – 7.43 (m, 1H), 7.29 (dt, *J* = 6.0, 2.3 Hz, 2H), 5.31 (t, *J* = 5.4 Hz, 1H), 4.51 (td, *J* = 9.3, 5.1 Hz, 1H), 4.18 (dt, *J* = 11.8, 3.3 Hz, 2H), 3.63 (ddt, *J* = 14.7, 12.0, 7.3 Hz, 2H), 3.53 – 3.50 (m, 2H), 2.70 – 2.61 (m, 2H), 2.58 – 2.56 (m, 3H), 2.35 – 2.29 (m, 2H), 2.25 – 2.20 (m, 2H), 2.13 – 2.05 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.11, 136.22, 130.50, 126.77, 123.10, 122.40, 121.71, 110.07, 107.91, 67.34, 65.37, 60.93, 53.09, 39.38, 35.44, 33.36, 25.49.

IR (film) ν_{max} 3114, 2957, 2924, 2846, 2704, 2587, 1674, 1529, 1486, 1461, 1423, 1389, 1341, 1269, 1251, 1199, 1173, 1144, 1117, 1083, 1032, 931, 879, 823, 776, 754 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{22}H_{29}N_2O_3$ ($[M+H]^+$) 369.21727, found 369.21715.



(±)-3-(oxetan-3-yl)-5-((3,5-dimethylphenoxy)methyl)oxazolidin-2-one (48)

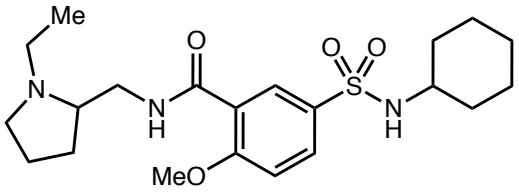
Prepared following general procedure B outlined above using (±)-Metaxalone (55.3 mg, 0.25 mmol, 1.0 equiv.), $Ir[dF(CF_3)ppy]_2[4,4'\text{-}d(CF_3)bpy]PF_6$ (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), $Cu(TMHD)_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), 3-bromooxetane (52 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (1:2 hexane/EtOAc) provided the title compound (60.5 mg, 87% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.65 (s, 1H), 6.52 (s, 2H), 5.15 (p, *J* = 7.0 Hz, 1H), 4.93 – 4.84 (m, 3H), 4.80 (t, *J* = 6.8 Hz, 2H), 4.17 – 4.11 (m, 2H), 3.97 (t, *J* = 8.7 Hz, 1H), 3.86 (dd, *J* = 8.6, 5.8 Hz, 1H), 2.29 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.17, 156.74, 139.65, 123.68, 112.46, 74.80, 74.74, 71.45, 67.96, 48.52, 43.34, 21.55.

IR (film) ν_{max} 2997, 2940, 2916, 2875, 1726, 1590, 1494, 1477, 1443, 1378, 1325, 1293, 1262, 1214, 1178, 1159, 1124, 1095, 1072, 1042, 995, 970, 951, 903, 866, 836, 779, 758, 736 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{20}NO_4$ ($[M+H]^+$) 278.13868, found 278.13826.



(±)-1-[(1-ethylpyrrolidin-2-yl)methyl]-2-methoxy-5-(*N*-cyclohexanesulfamoyl)benzamide (49)

Prepared following general procedure B outlined above using (±)-Sulpiride (85.4 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), bromocyclohexane (77 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 100 rpm stir, 25% light intensity). Purification by flash chromatography (10:1 CH_2Cl_2/MeOH) provided the title compound (77.8 mg, 73% yield) as a brown solid.

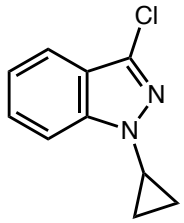
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (br s, 1H), 8.67 (d, *J* = 2.5 Hz, 1H), 7.98 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 5.19 (br s, 1H), 4.11 (s, 3H), 3.83 – 3.78 (m, 1H), 3.64 (br d, *J* = 63.6 Hz, 2H), 3.13 – 3.04 (m, 2H), 2.66 – 2.60 (m, 2H), 2.12 (br s, 1H), 2.01 – 1.92 (m, 2H), 1.80 – 1.73 (m, 3H), 1.64 – 1.60 (m, 2H), 1.50 (dt, *J* = 13.2, 4.0 Hz, 1H), 1.28 – 1.05 (m, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.06, 160.98, 134.07, 132.23, 131.44, 121.57, 111.96, 66.93, 57.06, 54.39, 52.84, 52.32, 41.84, 34.14 (d, *J* = 13.8 Hz), 28.84, 25.28, 24.81, 23.96, 10.68.

IR (film) ν_{max} 3291, 3109, 2932, 2855, 2607, 2486, 1643, 1596, 1525, 1485, 1451, 1321, 1283, 1246, 1164, 1125, 1081, 1013, 919, 887, 822, 728 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{21}H_{34}N_3O_4S$ ($[M+H]^+$) 424.22645, found 424.22643.

11. *N*-nucleophile scope for cyclopropylation using bromocyclopropane



3-chloro-1-cyclopropyl-1*H*-indazole (50)

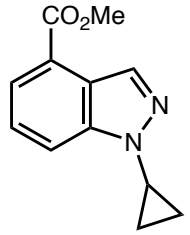
Prepared following general procedure A outlined above using 3-chloro-1*H*-indazole (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (41.1 mg, 85% yield, >20:1 r.r.) as a low-melting pale white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 3.55 (tt, *J* = 7.0, 3.6 Hz, 1H), 1.27 – 1.20 (m, 2H), 1.19 – 1.13 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.18, 132.83, 127.62, 121.67, 121.53, 119.94, 110.21, 29.70, 6.76.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



Methyl 1-cyclopropyl-1*H*-indazole-4-carboxylate (51)

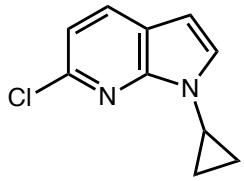
Prepared following general procedure A outlined above using methyl 1*H*-indazole-4-carboxylate (44.0 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (9:1 hexane/EtOAc) provided the title compound (35.0 mg, 65% yield, >20:1 r.r.) as a yellow-brown oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.94 (dd, *J* = 7.3, 0.9 Hz, 1H), 7.84 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.46 (dd, *J* = 8.4, 7.3 Hz, 1H), 4.01 (s, 3H), 3.65 – 3.61 (m, 1H), 1.27 – 1.18 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.94, 141.31, 133.95, 125.69, 124.62, 123.09, 122.85, 114.82, 52.30, 29.53, 6.65.

IR (film) ν_{max} 3089, 3013, 2952, 2896, 1714, 1607, 1583, 1501, 1453, 1421, 1396, 1367, 1302, 1277, 1191, 1168, 1144, 1050, 1027, 1005, 924, 846, 810, 775, 750 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{13}N_2O_2$ ($[M+H]^+$) 217.09715, found 217.09543.



6-chloro-1-cyclopropyl-1*H*-pyrrolo[2,3-*b*]pyridine (52)

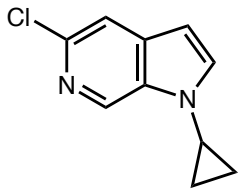
Prepared following general procedure B outlined above using 6-chloro-1*H*-pyrrolo[2,3-*b*]pyridine (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (32.3 mg, 67% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.15 (d, *J* = 3.6 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.37 (d, *J* = 3.6 Hz, 1H), 3.53 (tt, *J* = 7.4, 3.8 Hz, 1H), 1.15 – 1.09 (m, 2H), 1.05 – 1.01 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.03, 144.67, 131.09, 128.34, 119.73, 116.24, 99.76, 26.78, 6.58.

IR (film) ν_{max} 3089, 3017, 2922, 2851, 1595, 1557, 1506, 1459, 1424, 1366, 1326, 1299, 1259, 1221, 1192, 1140, 1120, 1106, 1026, 939, 912, 873, 812, 776, 716 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{10}ClN_2$ ($[M+H]^+$) 193.05270, found 193.05402.



5-chloro-1-cyclopropyl-1*H*-pyrrolo[2,3-*c*]pyridine (53)

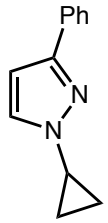
Prepared following general procedure B outlined above using 5-chloro-1*H*-pyrrolo[2,3-*c*]pyridine (38.1 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (6:1 hexane/EtOAc) provided the title compound (30.5 mg, 63% yield) as a pale brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.47 (s, 1H), 7.30 (d, *J* = 3.2 Hz, 1H), 6.36 (d, *J* = 3.2 Hz, 1H), 3.42 (tt, *J* = 7.1, 3.7 Hz, 1H), 1.15 – 1.08 (m, 2H), 1.07 – 1.01 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.90, 136.80, 133.94, 133.81, 132.50, 114.82, 100.57, 27.42, 6.58.

IR (film) ν_{max} 3093, 3018, 2957, 2916, 1597, 1557, 1498, 1460, 1424, 1406, 1382, 1367, 1288, 1270, 1239, 1210, 1195, 1126, 1058, 1021, 945, 912, 873, 850, 833, 792, 764, 728 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{10}ClN_2$ ($[M+H]^+$) 193.05270, found 193.05064.



3-phenyl-1-cyclopropyl-1*H*-pyrazole (54)

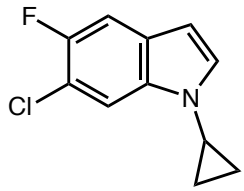
Prepared following general procedure A outlined above using 3-phenyl-1*H*-pyrazole (36.0 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (8:1 hexane/EtOAc) provided the title compound (33.3 mg, 72% yield, >20:1 r.r.) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 3.64 (tt, *J* = 7.4, 3.8 Hz, 1H), 1.19 – 1.14 (m, 2H), 1.05 (td, *J* = 7.4, 5.1 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.60, 133.64, 130.92, 128.68, 127.70, 125.79, 102.61, 32.88, 6.75.

IR (film) ν_{max} 3094, 3058, 3027, 2952, 1606, 1525, 1499, 1456, 1403, 1353, 1305, 1246, 1191, 1071, 1045, 1026, 990, 938, 842, 747 cm^{-1}.

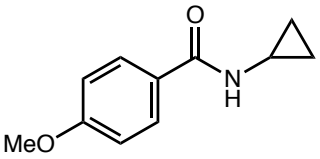
HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{13}N_2$ ($[M+H]^+$) 185.10732, found 185.10626.



6-chloro-5-fluoro-1-cyclopropyl-1*H*-indole (55)

Prepared following general procedure B outlined above (*in duplicate*) using 6-chloro-5-fluoro-1*H*-indole (42.4 mg, 0.25 mmol, 1.0 equiv.), $Ir[dF(CF_3)ppy]_2[4,4'\text{-}d(CF_3)bpy]PF_6$ (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), $Cu(TMHD)_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Following the reaction, mesitylene (25 μL, 179.5 μmol, 0.72 equiv.) was added as an internal standard, and the yield was determined via ^1H NMR (48% yield). Semi-pure material obtained via flash chromatography (10:1 hexane/CH_2Cl_2) was used for HRMS analysis and to confirm the peak assignments employed for the reported ^1H NMR yield (as indicated in the spectral data).

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{10}ClFN$ ($[M+H]^+$) 210.04803, found 210.09919.



***N*-cyclopropyl-4-methoxybenzamide (56)**

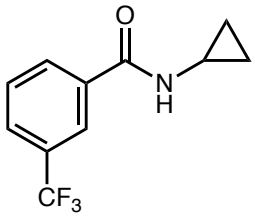
Prepared following general procedure B outlined above using 4-methoxybenzamide (37.8 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (1:1 hexane/EtOAc) provided the title compound (24.5 mg, 51% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.15 (br s, 1H), 3.84 (s, 3H), 2.89 (dp, *J* = 7.2, 3.5 Hz, 1H), 0.88 – 0.82 (m, 2H), 0.62 – 0.59 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.53, 162.34, 128.78, 126.83, 113.86, 55.55, 23.22, 6.96.

IR (film) ν_{max} 3272, 3078, 3007, 2961, 2840, 1621, 1606, 1541, 1502, 1456, 1370, 1323, 1310, 1243, 1175, 1113, 1031, 959, 865, 845, 818, 770 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{14}NO_2$ ($[M+H]^+$) 192.10191, found 192.11040.



***N*-cyclopropyl-3-(trifluoromethyl)benzamide (57)**

Prepared following general procedure B outlined above using 3-(trifluoromethyl)benzamide (47.3 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (3:1 hexane/EtOAc) provided the title compound (38.1 mg, 66% yield) as a white solid.

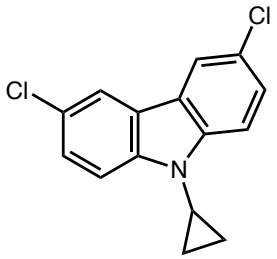
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 6.63 (br s, 1H), 2.89 (tq, *J* = 7.1, 3.6 Hz, 1H), 0.88 – 0.84 (m, 2H), 0.66 – 0.63 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.69, 135.31, 131.12 (q, *J* = 32.9 Hz), 130.41, 129.28, 128.17 (q, *J* = 3.7 Hz), 123.99 (q, *J* = 3.8 Hz), 123.81 (q, *J* = 272.5 Hz), 23.42, 6.84.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.75 (s, 3F).

IR (film) ν_{max} 3263, 3064, 1635, 1615, 1591, 1535, 1487, 1438, 1334, 1302, 1279, 1160, 1113, 1092, 1071, 1022, 964, 911, 838, 814, 780, 761 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{11}F_3NO$ ($[M+H]^+$) 230.07873, found 230.09285.



3,6-dichloro-9-cyclopropyl-9*H*-carbazole (58)

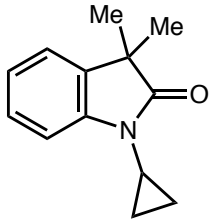
Prepared following general procedure B outlined above using 3,6-dichloro-9*H*-carbazole (59.0 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), LiO*t*-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (10:1 hexane/CH_2Cl_2) provided the title compound (35.9 mg, 52% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.42 (dd, *J* = 8.6, 2.2 Hz, 2H), 3.27 (tt, *J* = 6.9, 3.7 Hz, 1H), 1.28 – 1.22 (m, 2H), 1.08 – 1.05 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.35, 126.52, 125.26, 123.23, 120.22, 111.47, 24.22, 6.98.

IR (film) ν_{max} 3078, 3012, 2916, 2851, 1471, 1440, 1375, 1320, 1281, 1232, 1115, 1075, 1065, 1032, 874, 858, 834, 808, 783, 722 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{12}Cl_2N$ ($[M+H]^+$) 276.03413, found 276.20407.



3,3-dimethyl-1-cyclopropyl-1,3-dihydro-2*H*-indol-2-one (59)

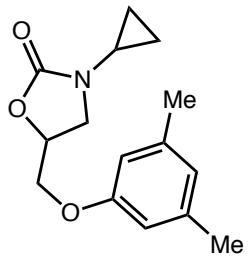
Prepared following general procedure B outlined above using 3,3-dimethyl-1,3-dihydro-2*H*-indol-2-one (40.3 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (8:1 hexane/EtOAc) provided the title compound (35.3 mg, 70% yield) as a yellow oil.

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.28 – 7.24 (m, 2H), 7.13 (d, *J* = 7.8, 1H), 7.03 (td, *J* = 7.5, 1.1 Hz, 1H), 2.65 (tt, *J* = 7.2, 3.8 Hz, 1H), 1.25 (s, 6H), 1.01 (td, *J* = 7.2, 5.1 Hz, 2H), 0.84 – 0.81 (m, 2H).

^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 181.51, 144.13, 136.03, 128.35, 122.94, 122.85, 109.94, 44.35, 24.66, 22.60, 6.36.

IR (film) ν_{max} 3048, 2968, 2927, 2866, 1716, 1611, 1488, 1458, 1385, 1338, 1301, 1211, 1127, 1028, 1008, 987, 929, 892, 848, 822, 754, 743 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}NO$ ($[M+H]^+$) 202.12264, found 202.12316.



(±)-3-cyclopropyl-5-((3,5-dimethylphenoxy)methyl)oxazolidin-2-one (60)

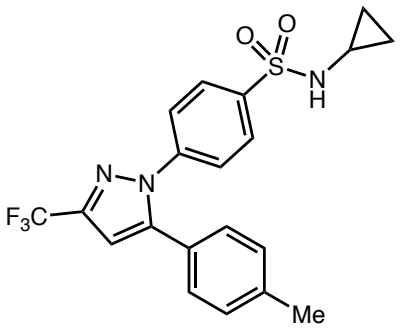
Prepared following general procedure B outlined above using (±)-Metaxalone (55.3 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (2:1 to 1:1 hexane/EtOAc) provided the title compound (55.1 mg, 84% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (s, 1H), 6.51 (s, 2H), 4.74 (dq, *J* = 9.9, 5.2 Hz, 1H), 4.13 – 4.00 (m, 2H), 3.68 (t, *J* = 8.8 Hz, 1H), 3.50 (dd, *J* = 8.8, 5.9 Hz, 1H), 2.56 (tt, *J* = 7.1, 4.1 Hz, 1H), 2.28 (s, 6H), 0.80 – 0.75 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.21, 157.75, 139.47, 123.37, 112.32, 70.90, 67.97, 48.05, 25.74, 21.48, 5.95, 5.89.

IR (film) ν_{max} 3084, 3013, 2957, 2916, 1745, 1592, 1488, 1446, 1424, 1371, 1324, 1296, 1270, 1233, 1177, 1156, 1143, 1130, 1081, 1063, 1033, 1022, 955, 910, 873, 832, 761, 701 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{15}H_{20}NO_3$ ($[M+H]^+$) 262.14377, found 262.14450.



***N*-cycloproyl-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (61)**

Prepared following general procedure B outlined above using Celecoxib (95.3 mg, 0.25 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 2.3 mg, 2.0 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (32 mg, 75 μmol, 0.30 equiv.), Li*O*t-Bu (60 mg, 0.75 mmol, 3.0 equiv.), DBN (31 μL, 0.25 mmol, 1.0 equiv.), bromocyclopropane (50 μL, 0.625 mmol, 2.5 equiv.), $(TMS)_3SiOH$ (165 mg, 0.625 mmol, 2.5 equiv.), MeCN (2.5 mL, 0.1 M) and water (45 μL, 2.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (3500 rpm fans, 500 rpm stir, 25% light intensity). Purification by flash chromatography (4:1 to 1:1 hexane/EtOAc) provided the title compound (53.9 mg, 51% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 2H), 7.50 – 7.47 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.11 – 7.09 (m, 2H), 6.75 (s, 1H), 5.03 (s, 1H), 2.38 (s, 3H), 2.27 – 2.23 (m, 1H), 0.60 – 0.58 (m, 4H).

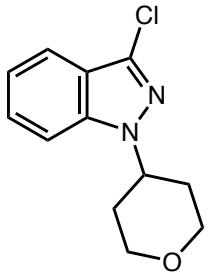
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.41, 144.22 (q, *J* = 38.6 Hz), 142.72, 139.95, 139.23, 129.87, 128.84, 128.61, 125.78, 125.66, 121.17 (q, *J* = 269.2 Hz), 106.40 (q, *J* = 2.0 Hz), 24.38, 21.45, 6.32.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.46 (s, 3F).

IR (film) ν_{max} 3310, 3149, 3094, 2957, 2924, 2860, 1596, 1496, 1472, 1452, 1409, 1365, 1320, 1271, 1234, 1153, 1125, 1094, 1052, 1027, 994, 977, 952, 887, 826, 808, 756, 742, 720 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{20}H_{19}F_3N_3O_2S$ ($[M+H]^+$) 422.11446, found 422.11650.

12. Alkyl chloride scope for *N*-alkylation



3-chloro-1-(tetrahydro-2*H*-pyran-4-yl)-1*H*-indazole (62)

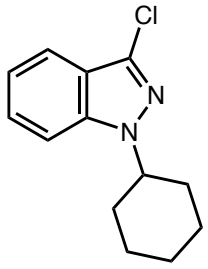
Prepared following general procedure C outlined above using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (4.3 mg, 10 μmol, 0.20 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), 4-chloro-tetrahydro-2*H*-pyran (13.5 μL, 0.125 mmol, 2.5 equiv.), $(TMS)_3SiNHAd$ (50 mg, 0.125 mmol, 2.5 equiv.), 1,4-dioxane (0.1 mL, 0.5 M) and water (9 μL, 0.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (1500 rpm fans, 100 rpm stir, 55% light intensity). Purification of five combined 0.05 mmol scale crude reaction vials (0.25 mmol total) by flash chromatography (5:1 hexane/EtOAc) provided the title compound (30.7 mg, 52% yield, >20:1 r.r.) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.21 (ddd, *J* = 7.9, 5.8, 1.8 Hz, 1H), 4.59 (tt, *J* = 11.6, 4.2 Hz, 1H), 4.17 (dd, *J* = 11.5, 4.5 Hz, 2H), 3.60 (td, *J* = 12.1, 2.1 Hz, 2H), 2.40 (dtd, *J* = 13.5, 11.9, 4.6 Hz, 2H), 1.99 – 1.94 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.10, 132.92, 127.45, 121.45, 121.40, 120.15, 109.33, 67.33, 55.80, 32.50.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



3-chloro-1-cyclohexyl-1*H*-indazole (1)

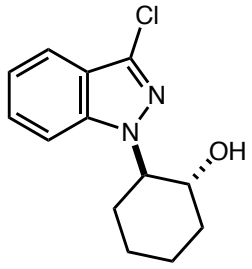
Prepared following general procedure C outlined above using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4′-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (4.3 mg, 10 μmol, 0.20 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), chlorocyclohexane (15 μL, 0.125 mmol, 2.5 equiv.), (TMS)$_3$SiNHAd (50 mg, 0.125 mmol, 2.5 equiv.), 1,4-dioxane (0.1 mL, 0.5 M) and water (9 μL, 0.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (1500 rpm fans, 100 rpm stir, 55% light intensity). Purification of five combined 0.05 mmol scale crude reaction vials (0.25 mmol total) by flash chromatography, followed by preparative thin-layer chromatography (10:1 hexane/EtOAc), provided the title compound (29.2 mg, 50% yield, >20:1 r.r.) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 4.38 – 4.32 (m, 1H), 2.05 – 2.01 (m, 4H), 1.98 – 1.93 (m, 2H), 1.78 – 1.74 (m, 1H), 1.51 – 1.42 (m, 2H), 1.37 – 1.30 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.11, 132.31, 127.10, 121.14, 121.08, 119.93, 109.54, 58.62, 32.65, 25.91, 25.44.

Spectral data are consistent with those reported in literature:

Liang, Y.; Zhang, X.; MacMillan, D. W. C. *Nature* **2018**, *559*, 83.



(±)-3-chloro-1-(tetrahydro-2*H*-pyran-3-yl)-1*H*-indazole (63)

Prepared following general procedure C outlined above using 3-chloro-1*H*-indazole (7.6 mg, 0.05 mmol, 1.0 equiv.), Ir[dF(CF_3)ppy]$_2$[4,4'-d(CF_3)bpy]PF_6 (**[Ir-1]**, 0.5 mg, 0.4 μmol, 0.008 equiv.), Cu(TMHD)$_2$ (4.3 mg, 10 μmol, 0.20 equiv.), LiO*t*-Bu (12 mg, 0.15 mmol, 3.0 equiv.), 2-chlorocyclohexanol (mixture of diastereomers) (16.8, 0.125 mmol, 2.5 equiv.), $(TMS)_3SiNHAd$ (50 mg, 0.125 mmol, 2.5 equiv.), 1,4-dioxane (0.05 mL, 1.0 M) and water (9 μL, 0.5 mmol, 10 equiv.), performed in the Integrated Photoreactor (1500 rpm fans, 100 rpm stir, 55% light intensity). Purification of five combined 0.05 mmol scale crude reaction vials (0.25 mmol total) by flash chromatography (6:1 to 4:1 hexane/EtOAc) provided the title compound (25.0 mg, 40% yield, >20:1 r.r., >20:1 d.r.) as a yellow-brown oil. The relative *trans*-stereochemistry of the title compound was confirmed via analysis of relevant ^{1}H NMR coupling constants, supplemented by 2D NMR (COSY and NOESY) analysis (as indicated in the spectral data).

^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 7.73 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 4.73 (d, *J* = 5.6 Hz, 1H), 4.31 (ddd, *J* = 11.8, 9.4, 4.5 Hz, 1H), 3.76 (tt, *J* = 10.2, 5.0 Hz, 1H), 1.99 – 1.86 (m, 3H), 1.77 – 1.71 (m, 2H), 1.45 – 1.32 (m, 3H).

^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 141.49, 130.56, 126.94, 121.26, 119.69, 118.54, 111.02, 71.56, 63.57, 34.86, 31.05, 24.66, 24.05.

IR (film) ν_{max} 3365, 3058, 2935, 2859, 1616, 1494, 1465, 1451, 1408, 1338, 1300, 1248, 1193, 1153, 1129, 1066, 1025, 992, 947, 870, 848, 808, 764, 743 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{16}ClN_2O$ ($[M+H]^+$) 251.09457, found 251.09508.

13. Additional non-photonic controls and mechanistic experiments

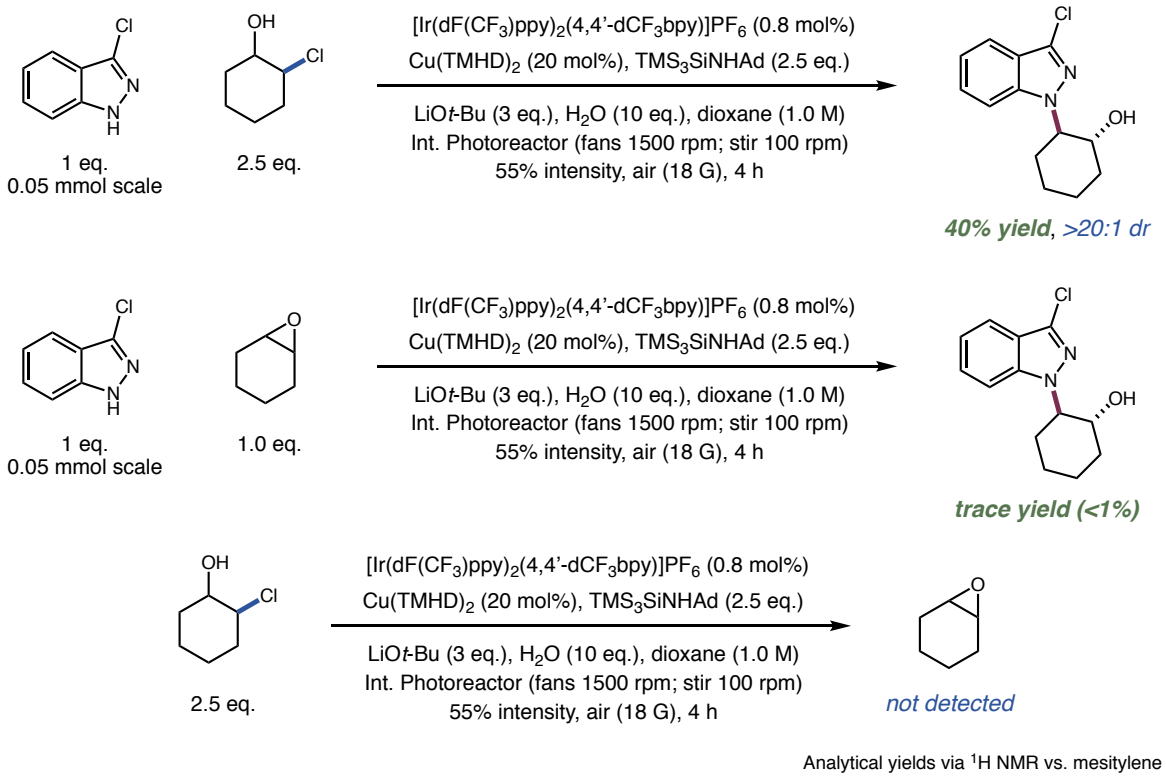


Figure S28: Control reactions for formation of **63** from *in situ*-generated epoxides.

Based on the exclusive *trans*-selectivity observed during generation of product **63** (see Figure 6), an alternative coupling pathway for this reaction could be proposed, with **63** obtained via photocatalytic formation of cyclohexene oxide *in situ*, followed by a non-photonic epoxide-opening S_N2 process. Subjecting cyclohexene oxide as the electrophile to the standard reaction conditions (in place of the alkyl chloride) leads to negligible yields of the desired *N*-alkyl product; furthermore, subjecting the chlorohydrin electrophile to the standard reaction conditions *in the absence of the 1H-indazole nucleophile* does not lead to detectable amounts of *in situ* cyclohexene oxide generation over the course of the reaction. Collectively, these control reactions suggest that **63** is obtained via a *trans*-selective HARC-based coupling pathway in line with the proposed general mechanism, rather than a background epoxide-opening process.

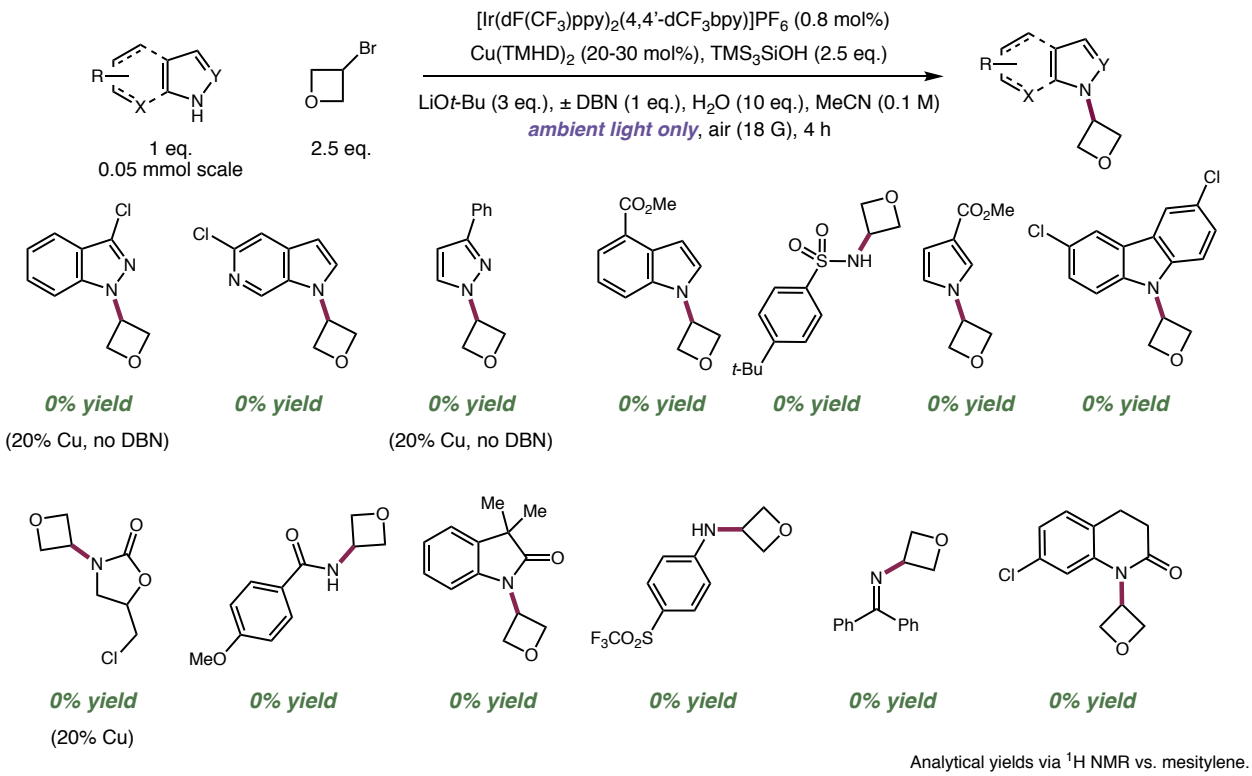


Figure S29: Non-photonic control reactions for each nucleophile class used in C–N coupling.

Reactions performed outside of the Integrated Photoreactor (i.e. exposed only to ambient light) at room temperature failed to deliver *N*-alkylated product when using any of the *N*-nucleophile substrate classes employed within the optimized C–N coupling (as indicated in Figure 7). These control reactions verify that, under the visible light-mediated conditions reported *vide supra*, background substitution reactivity (either via S_N1 or S_N2 mechanisms) is negligible and not responsible for the high efficiencies observed in the designed C–N coupling protocol.

14. Additional examples and current limitations

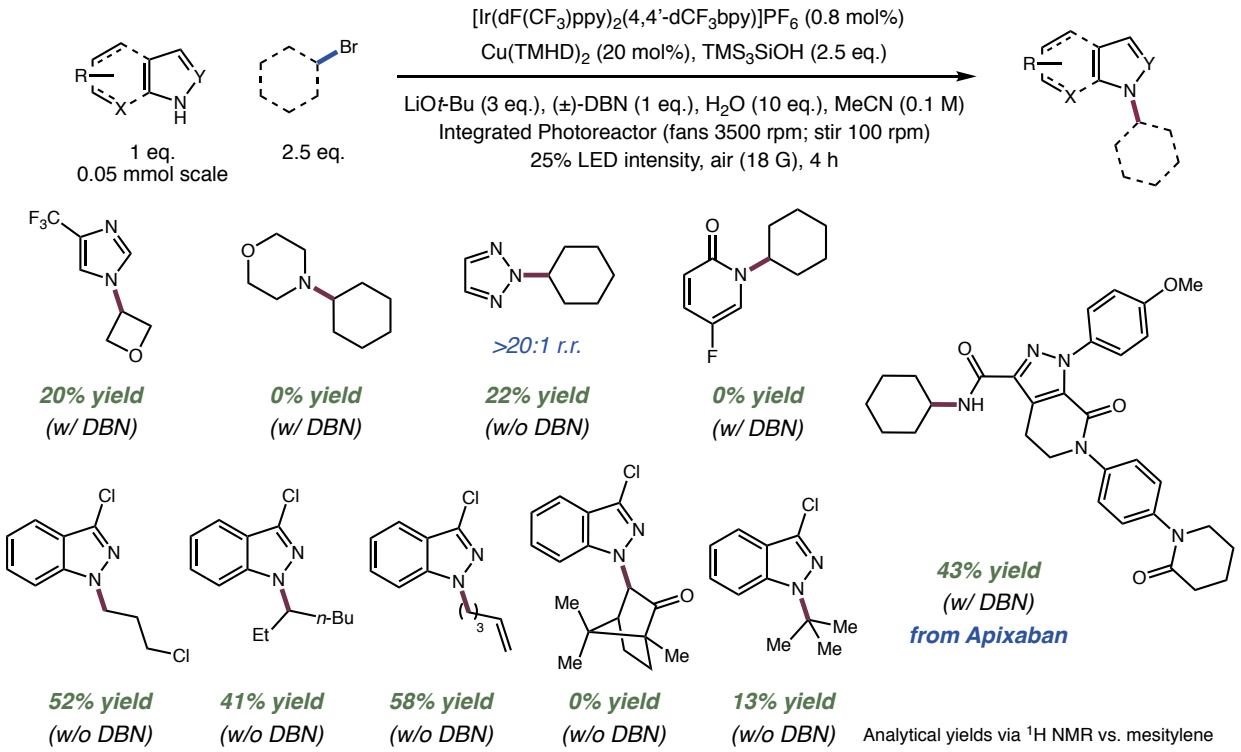


Figure S30: Additional examples using general setup for optimization studies.

While additional complex substrates such as Apixaban are competent within this HARC *N*-alkylation methodology, several classes of *N*-nucleophile and bromide coupling partners have thus far proven ineffective under a variety of conditions (the highest obtained yields for each case are displayed in **Figure S30**). For *N*-nucleophiles, highly acidic N–H heterocycles such as (benz)imidazoles or (benzo)triazoles can deliver yield of the desired *N*-alkylated products, often with high regioselectivity, although coupling yields are modest (<25% yield in all cases). Additional nucleophiles of interest, such as simple alkylamines or pyridones, are incompatible with this method, presumably due to challenges arising from minimal N–H acidity or problematic coordination behavior with the copper catalyst. For halides, simple primary bromides are competent and display high functional group tolerance for functionality such as aliphatic chlorides or distal olefins, but generally couple in modest yields compared to analogous secondary bromides. For acyclic secondary cases, more sterically hindered bromides (i.e. both alkyl substituents bulkier than Me) are compatible, but coupling yields tend to trend with steric hindrance (bulkier substituents reduce yields, see Figure 2 for additional comparisons). For more activated cases, bromides adjacent to carbonyl functionality have thus far been ineffective coupling partners. Although bridgehead tertiary bromides are competent (see Figure 2), more traditional tertiary halides, such as *tert*-butyl bromide, react in only modest yield, with elimination to isobutylene observed as a deleterious pathway under all conditions tested.

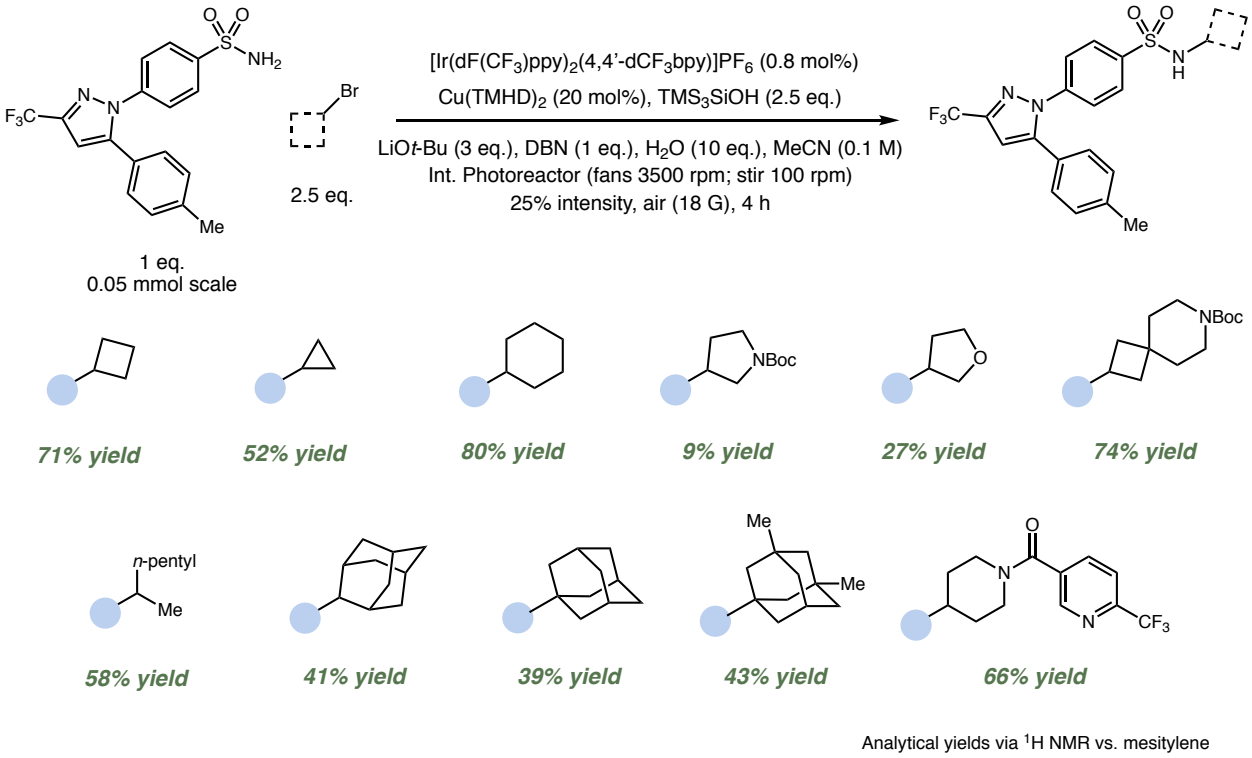


Figure S31: Initial results on optimization scale for diverse Celecoxib *N*-alkylations.

15. Spectral data for *N*-alkylation products

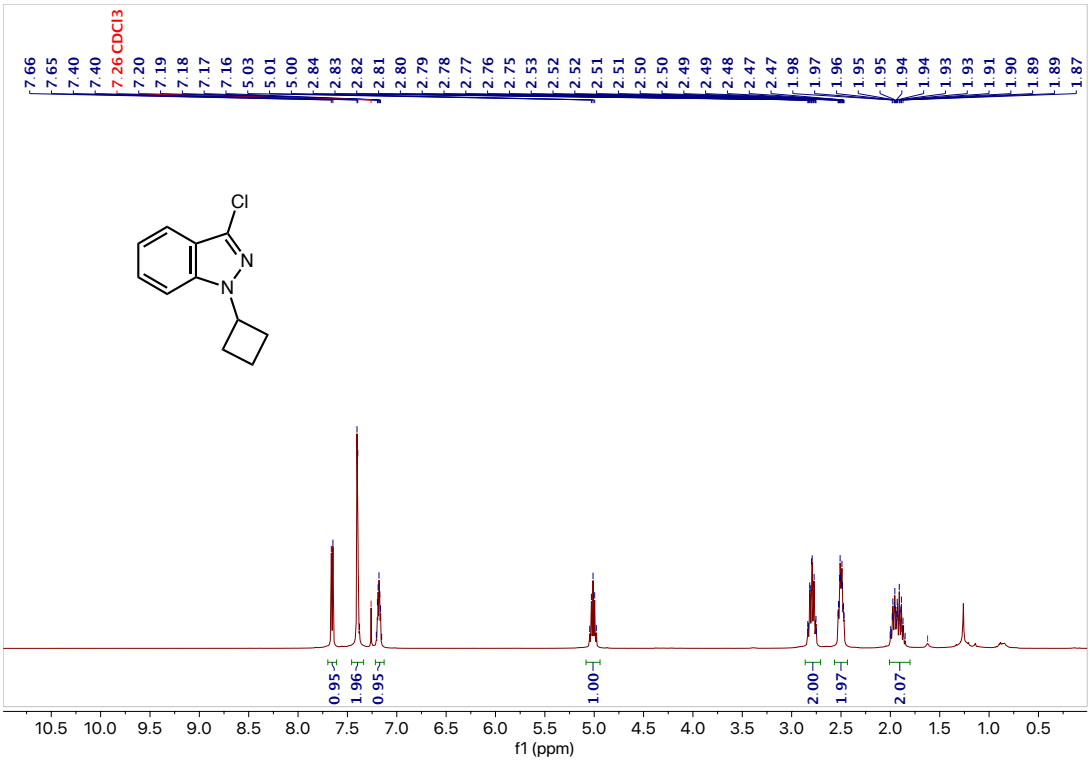


Figure S32: ^{1}H NMR spectrum of **2** (500 MHz, $CDCl_3$).

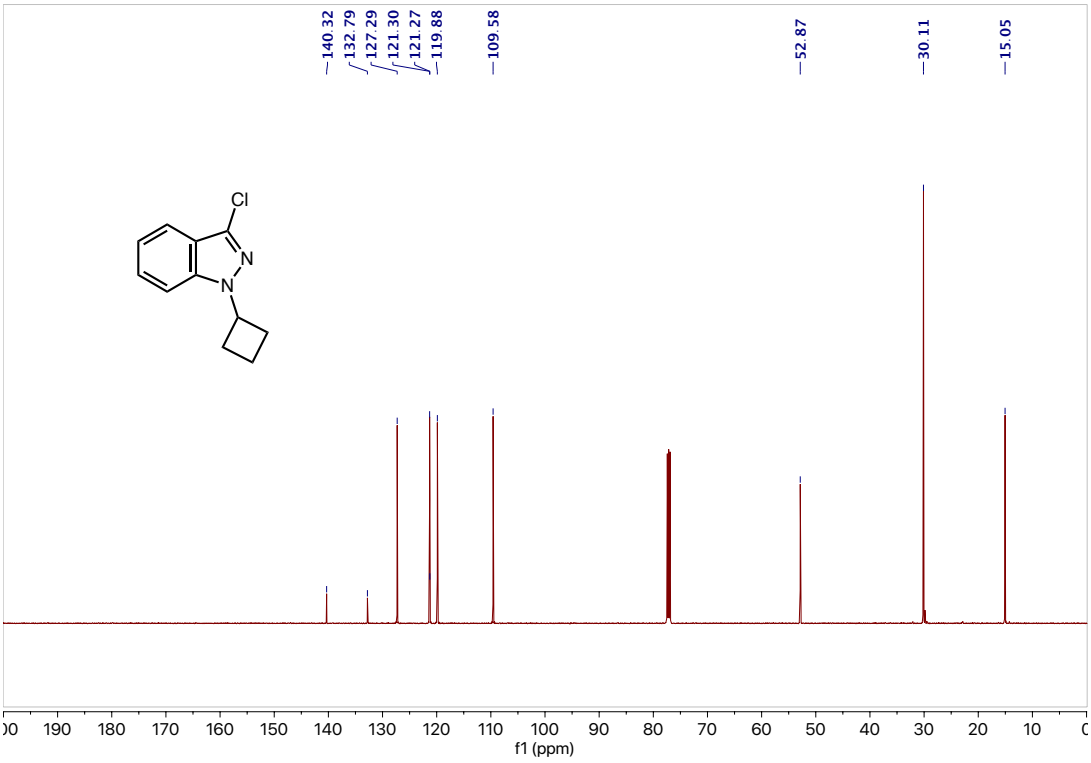


Figure S33: ^{13}C NMR spectrum of **2** (125 MHz, $CDCl_3$).

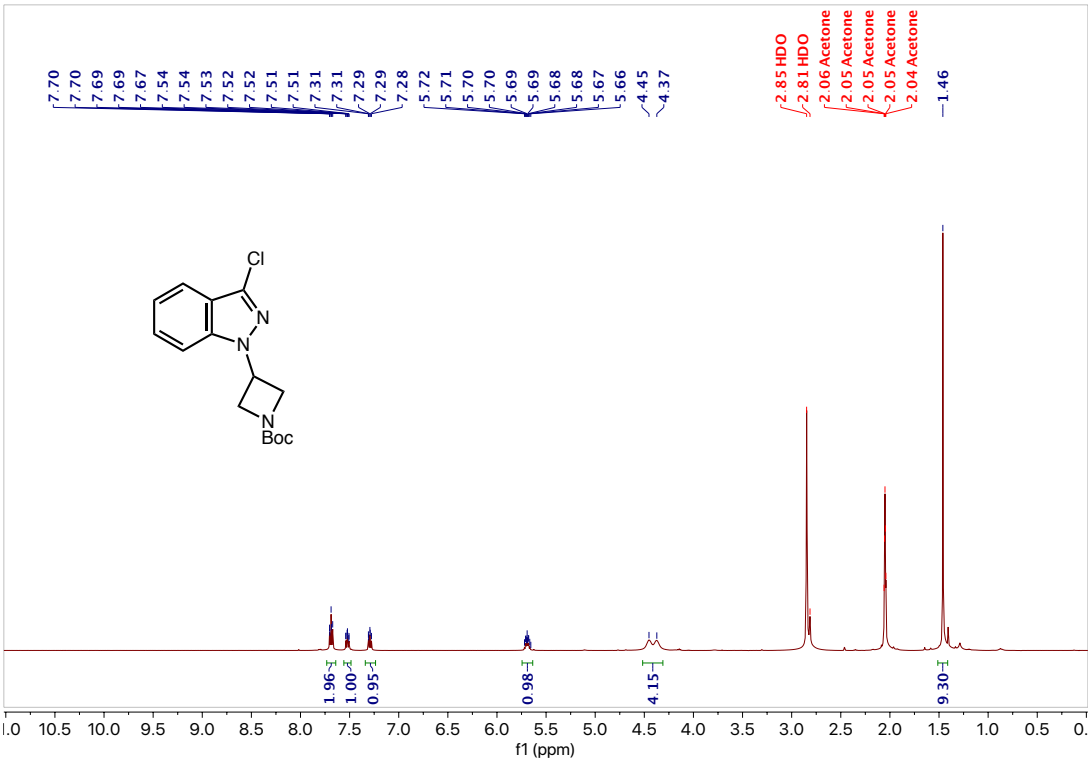


Figure S34: ^{1}H NMR spectrum of **3** (500 MHz, $(CD_3)_2CO$).

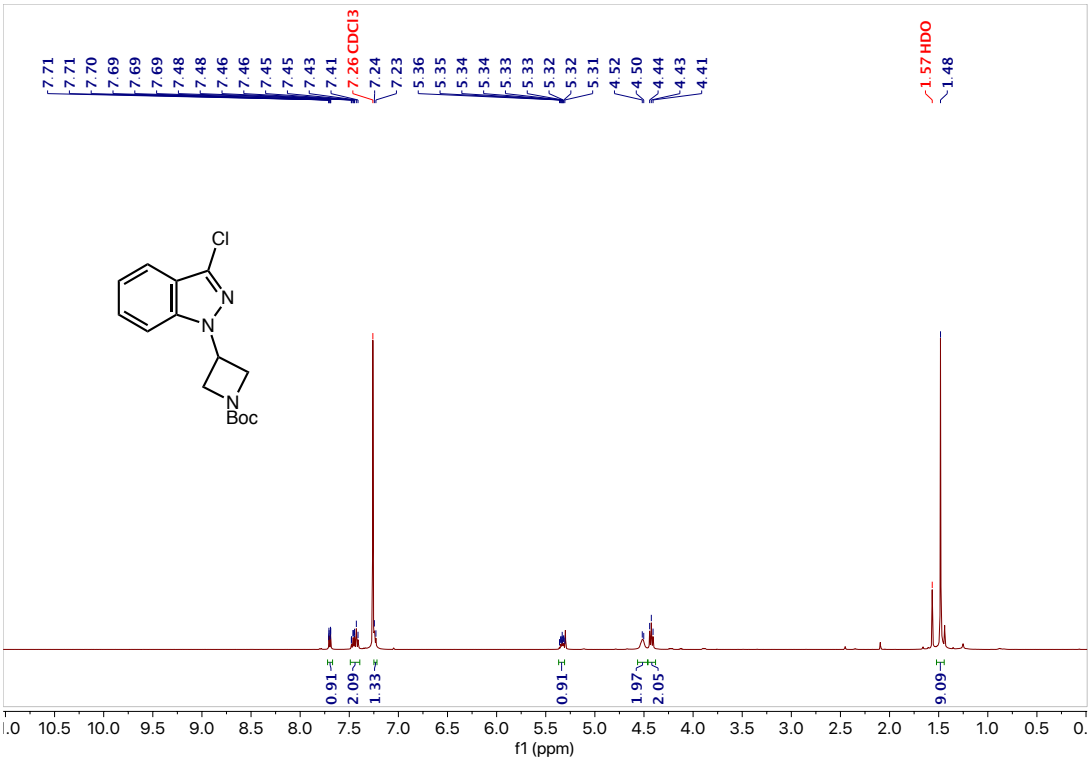


Figure S35: ^{1}H NMR spectrum of **3** (500 MHz, $CDCl_3$).

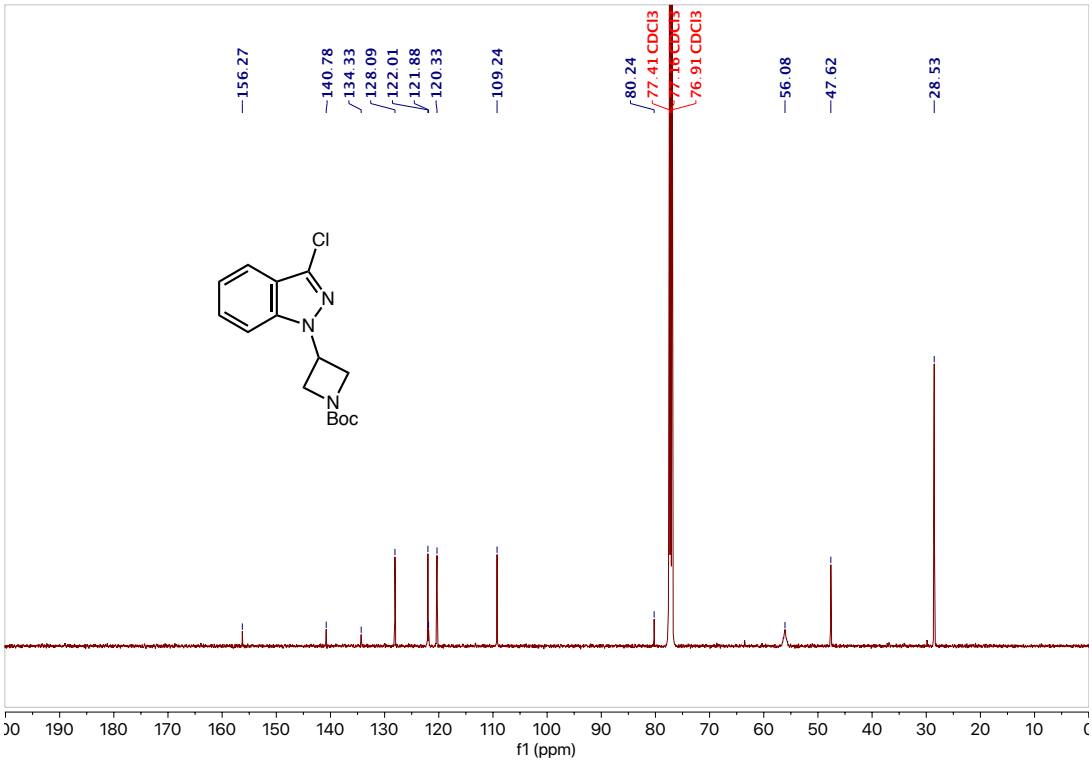


Figure S36: ^{13}C NMR spectrum of **3** (125 MHz, $CDCl_3$).

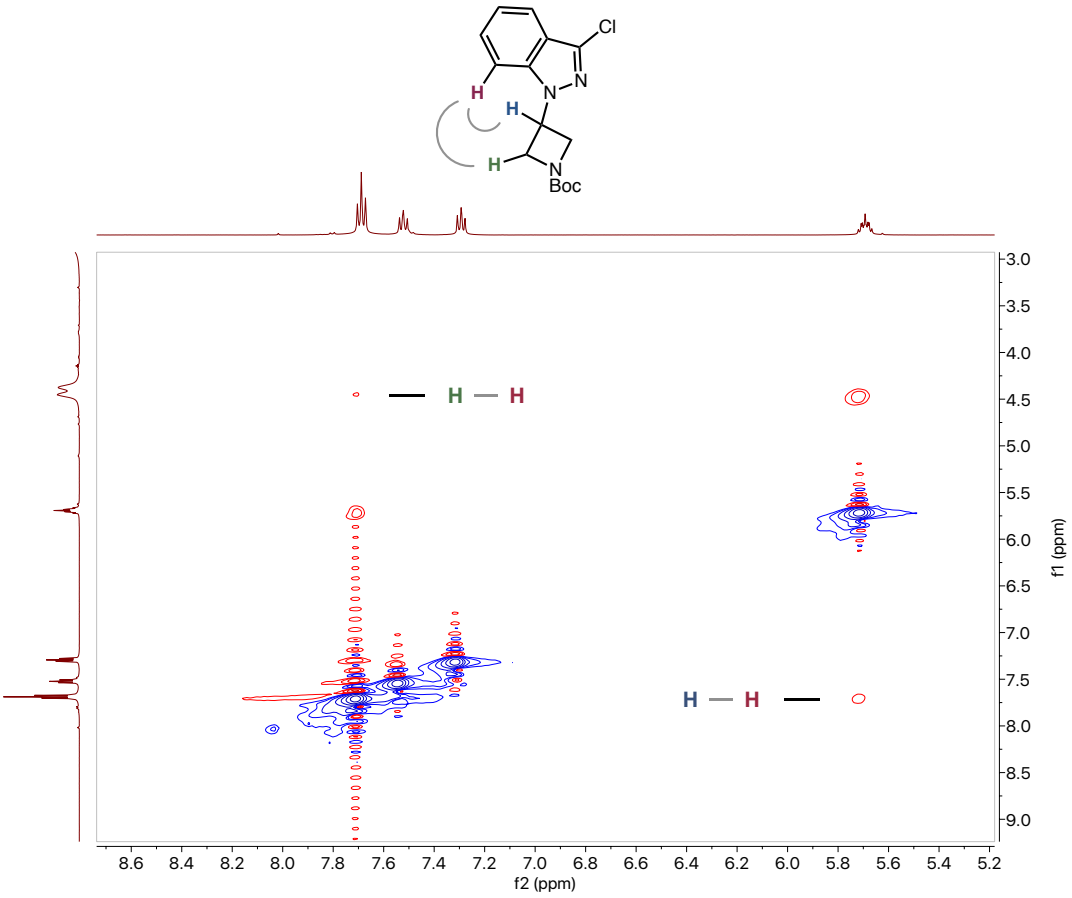


Figure S37: ^{1}H 2D NMR: NOESY spectrum of **3** (500 MHz, $(CD_3)_2CO$).

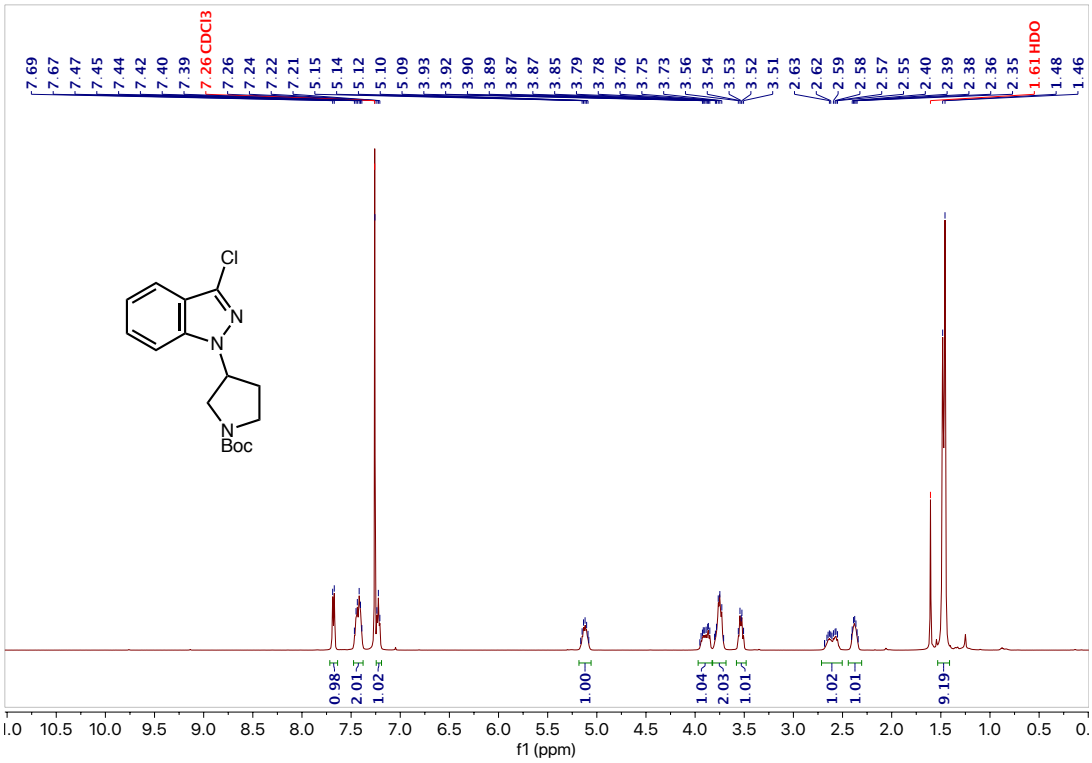


Figure S38: ^{1}H NMR spectrum of **(±)-4** (500 MHz, $CDCl_3$).

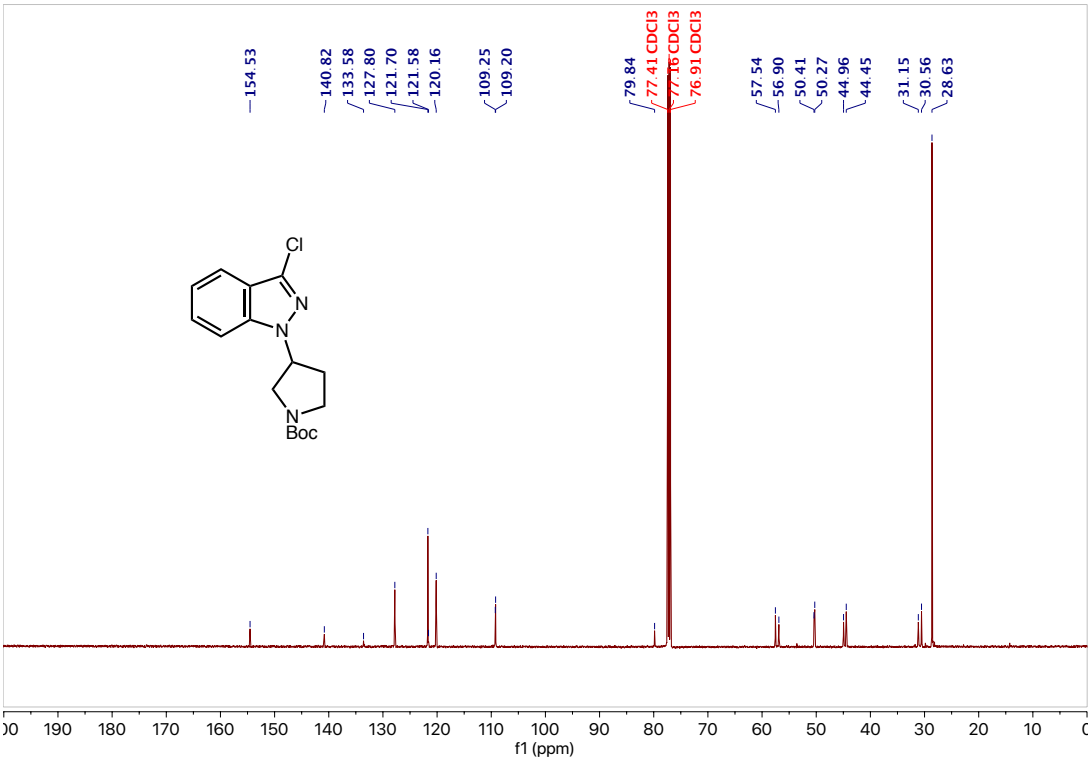


Figure S39: ^{13}C NMR spectrum of **(±)-4** (125 MHz, $CDCl_3$).

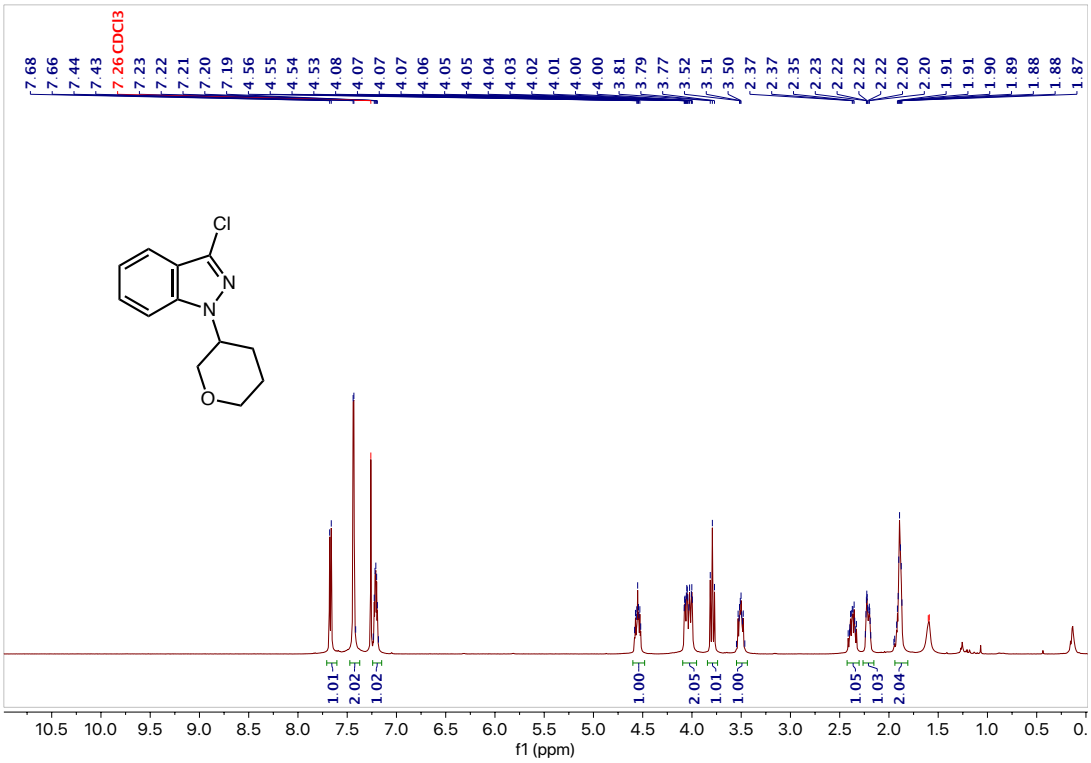


Figure S40: ^{1}H NMR spectrum of **(±)-5** (500 MHz, $CDCl_3$).

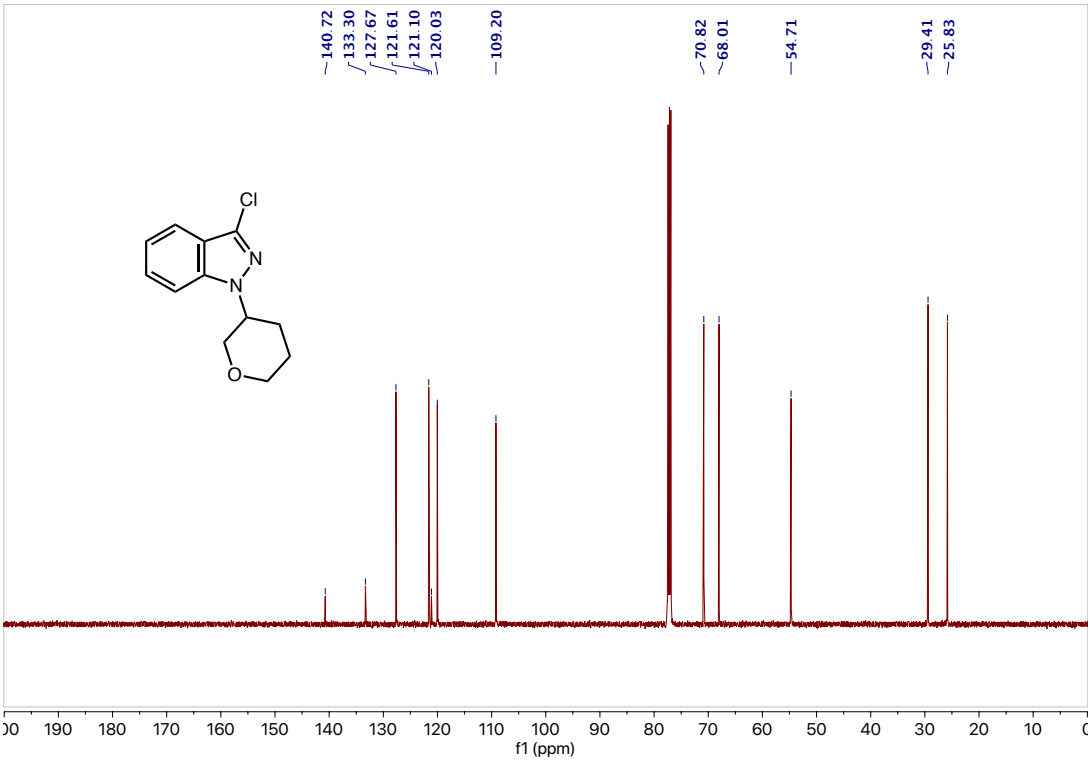


Figure S41: ^{13}C NMR spectrum of **(±)-5** (125 MHz, $CDCl_3$).

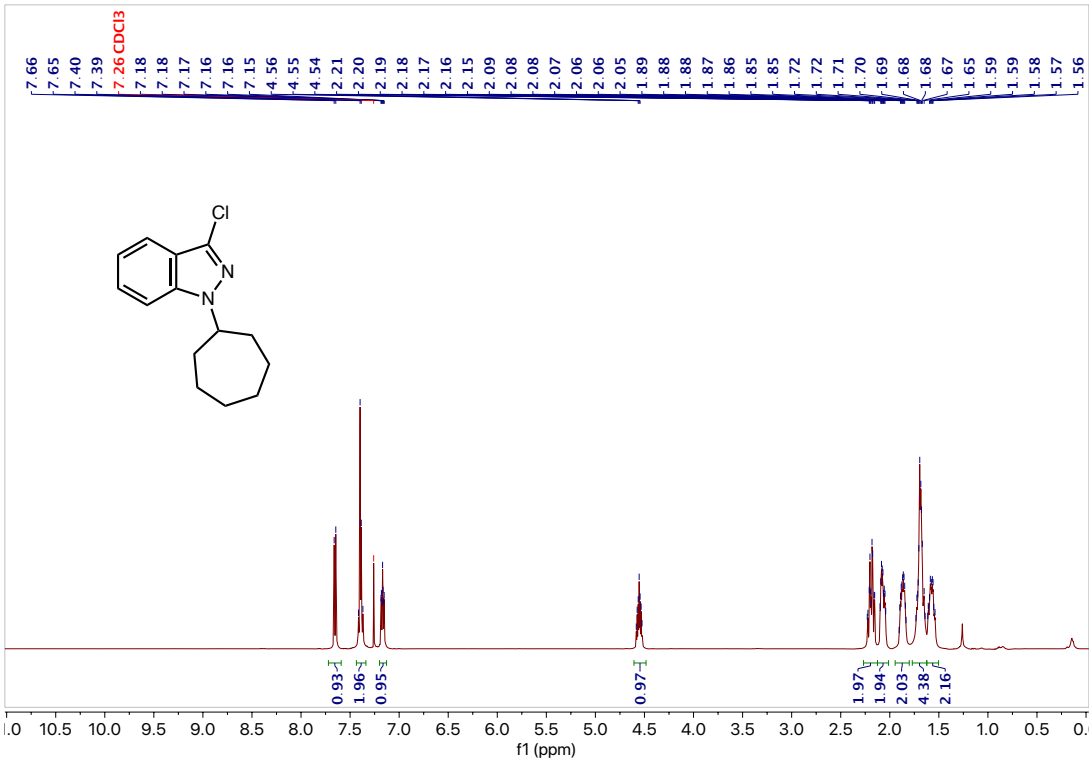


Figure S42: ^{1}H NMR spectrum of **6** (500 MHz, $CDCl_3$).

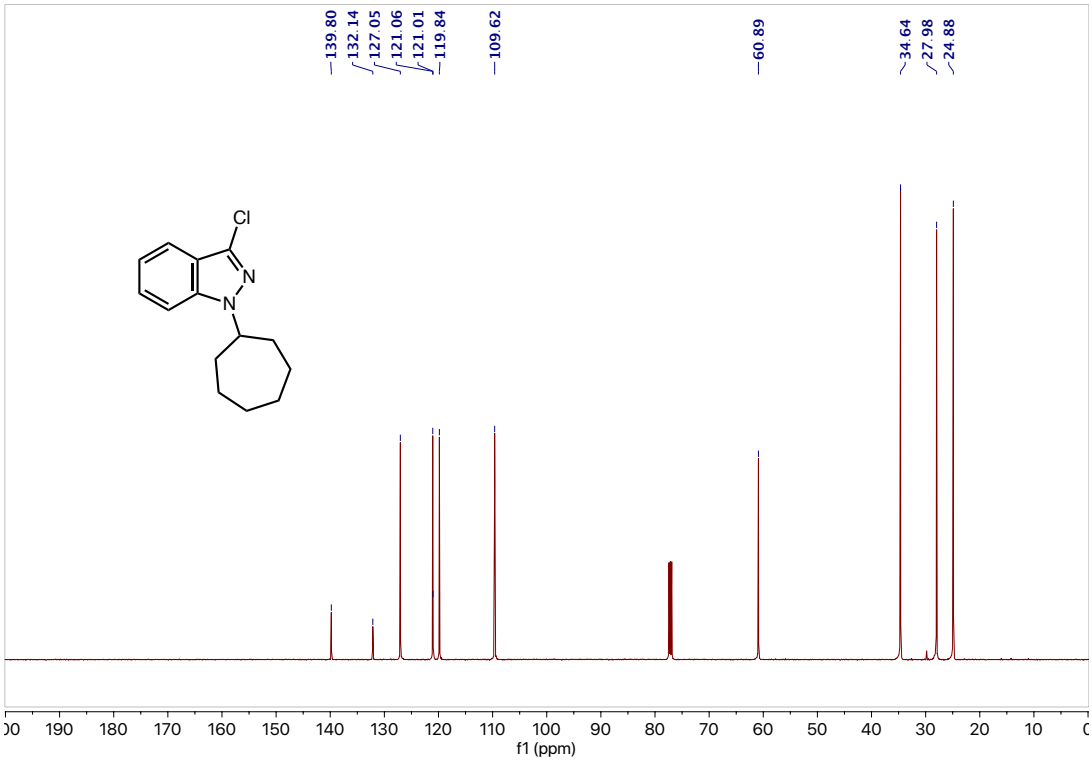


Figure S43: ^{13}C NMR spectrum of **6** (125 MHz, $CDCl_3$).

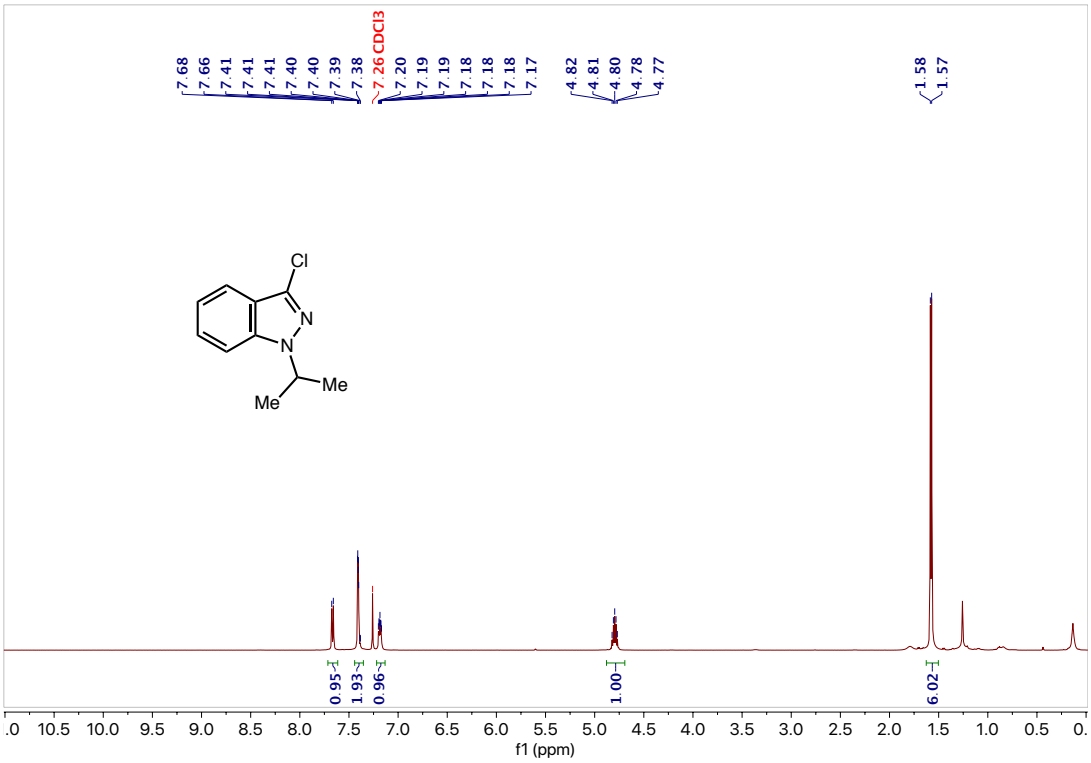


Figure S44: ^{1}H NMR spectrum of **7** (500 MHz, $CDCl_3$).

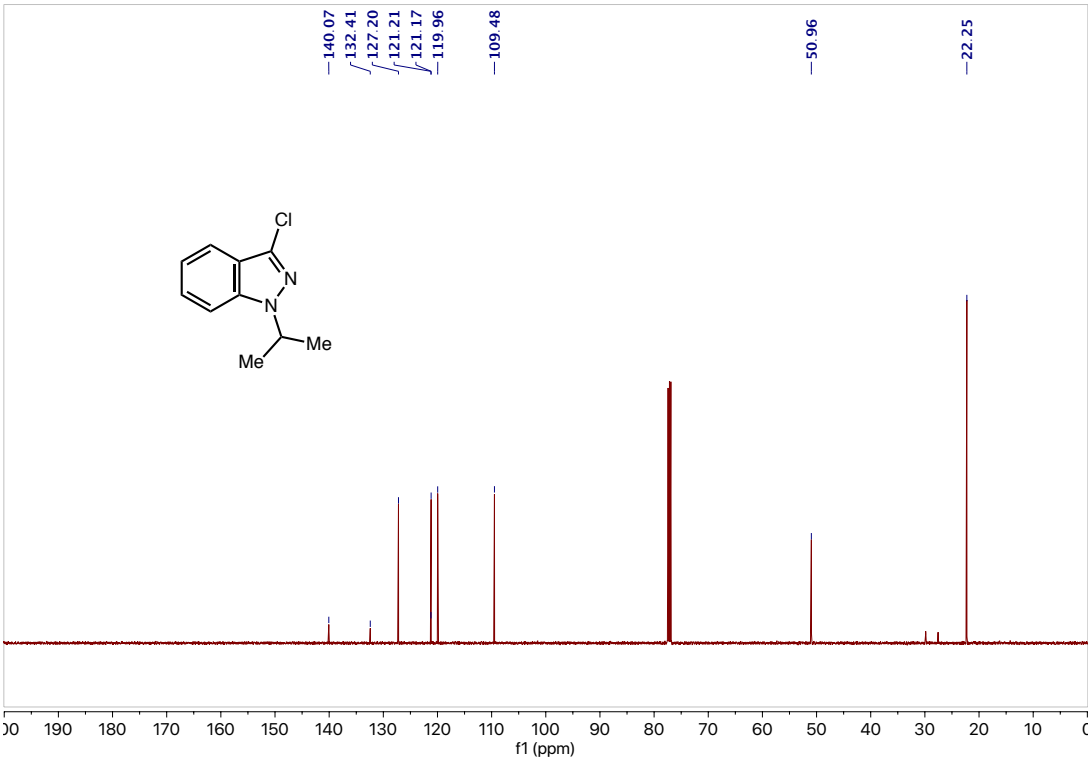


Figure S45: ^{13}C NMR spectrum of **7** (125 MHz, $CDCl_3$).

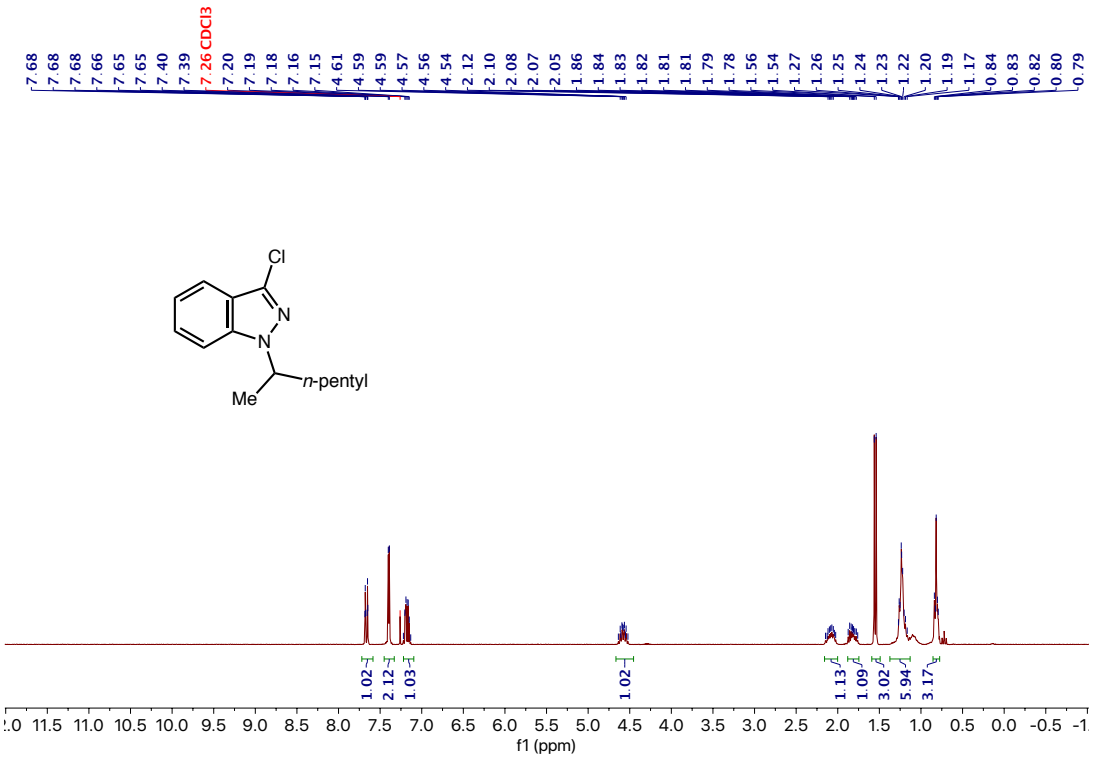


Figure S46: ^{1}H NMR spectrum of **(±)-8** (500 MHz, $CDCl_3$).

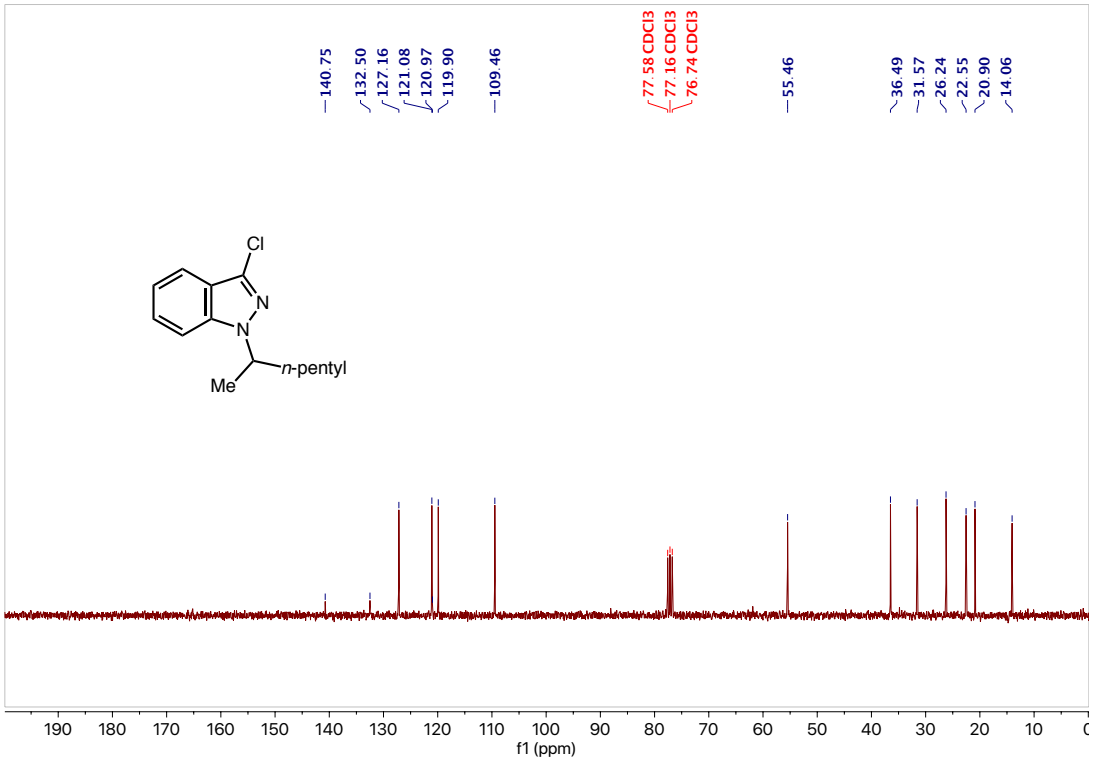


Figure S47: ^{13}C NMR spectrum of **(±)-8** (125 MHz, $CDCl_3$).

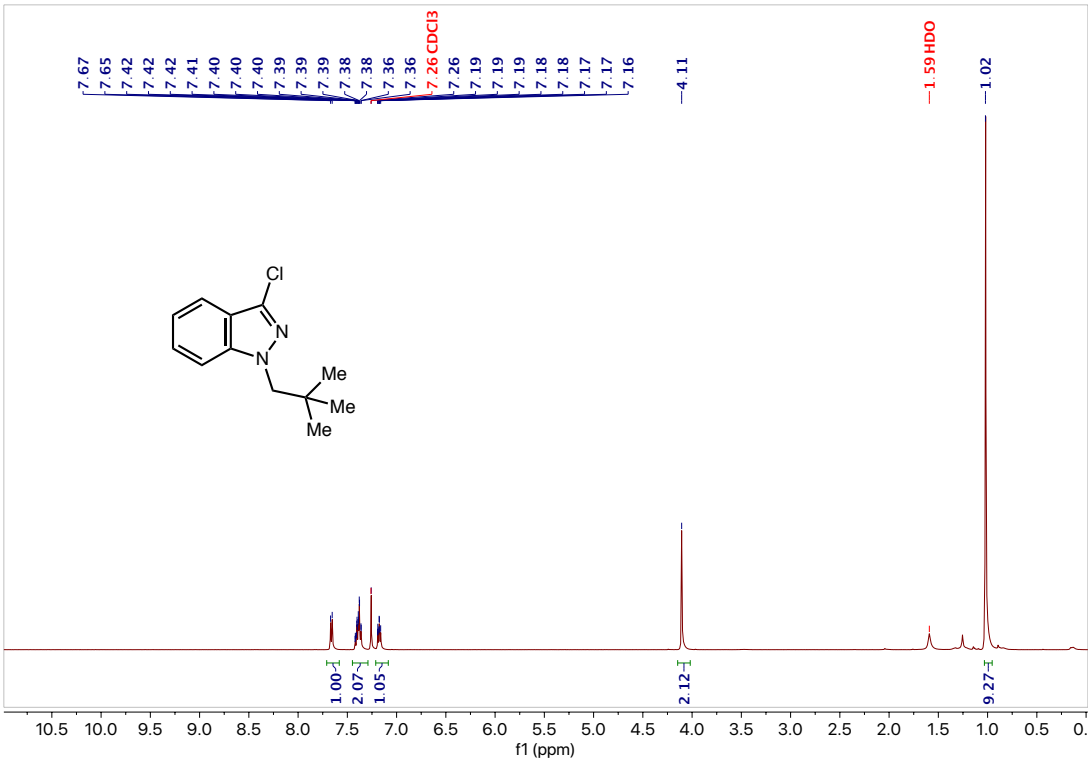


Figure S48: ^{1}H NMR spectrum of **9** (500 MHz, $CDCl_3$).

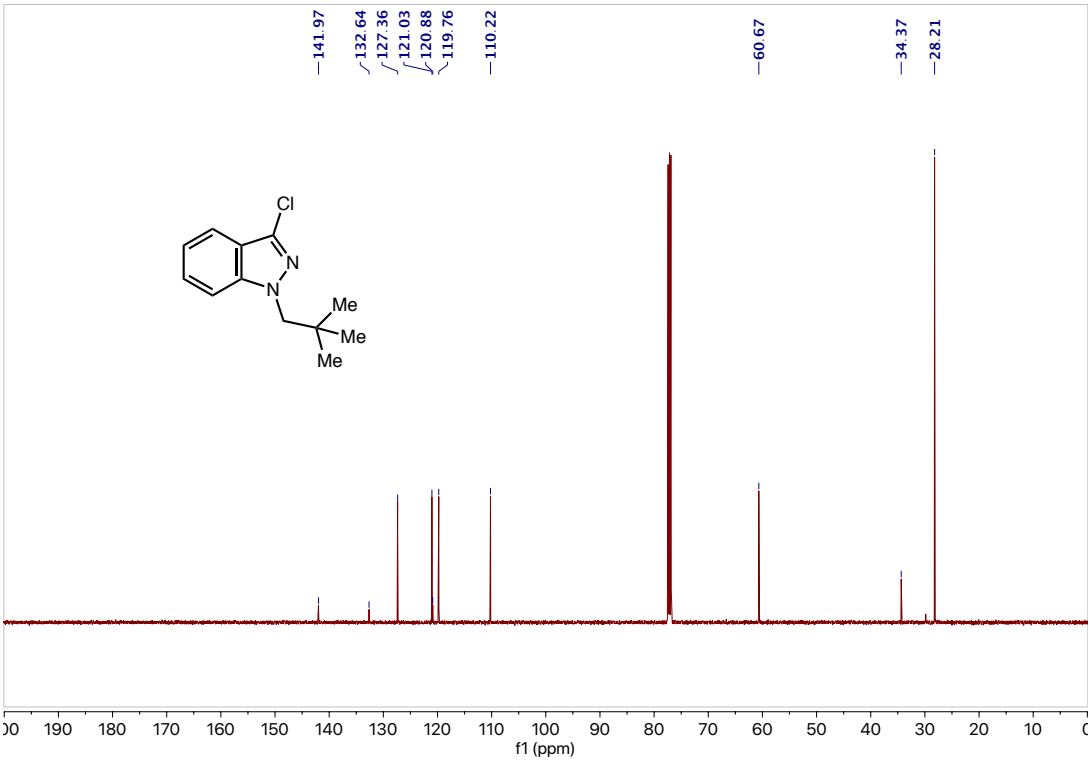


Figure S49: ^{13}C NMR spectrum of **9** (125 MHz, $CDCl_3$).

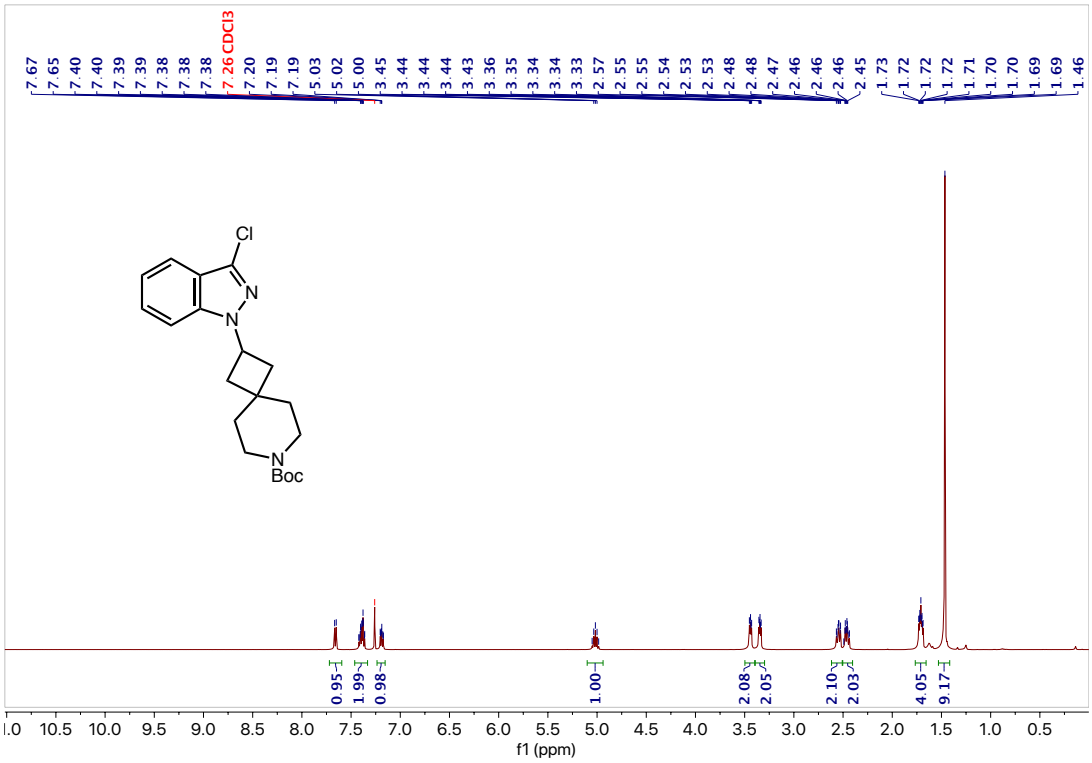


Figure S50: ^{1}H NMR spectrum of **10** (500 MHz, $CDCl_3$).

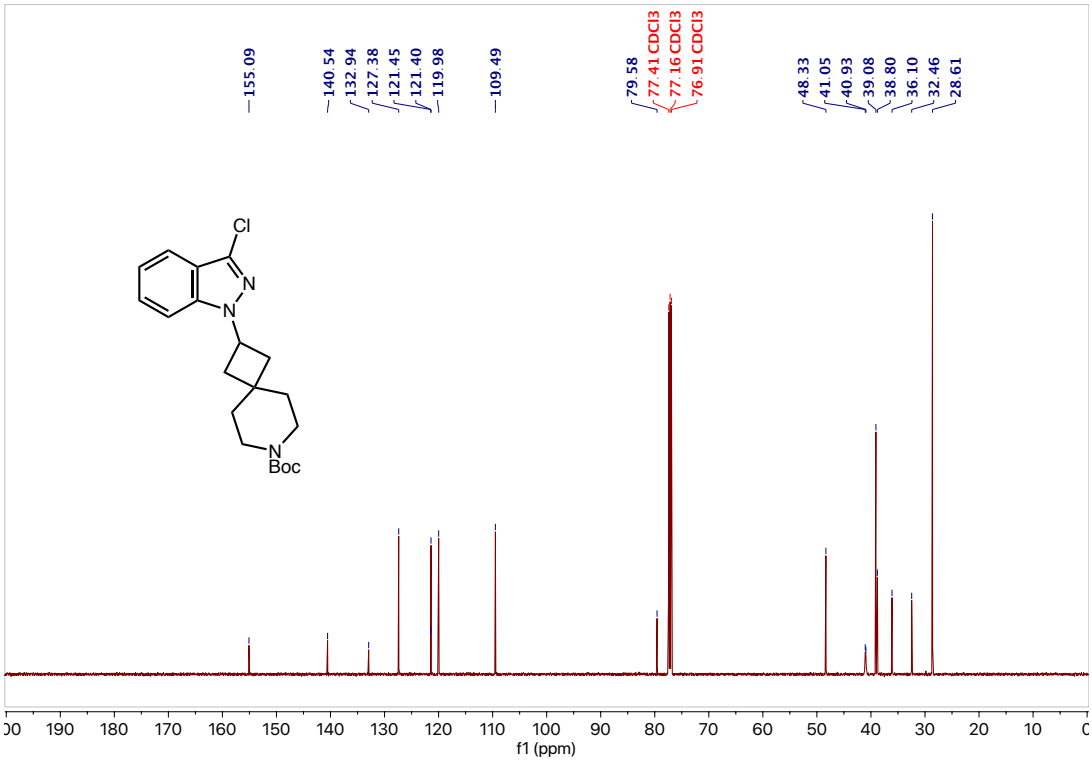


Figure S51: ^{13}C NMR spectrum of **10** (125 MHz, $CDCl_3$).

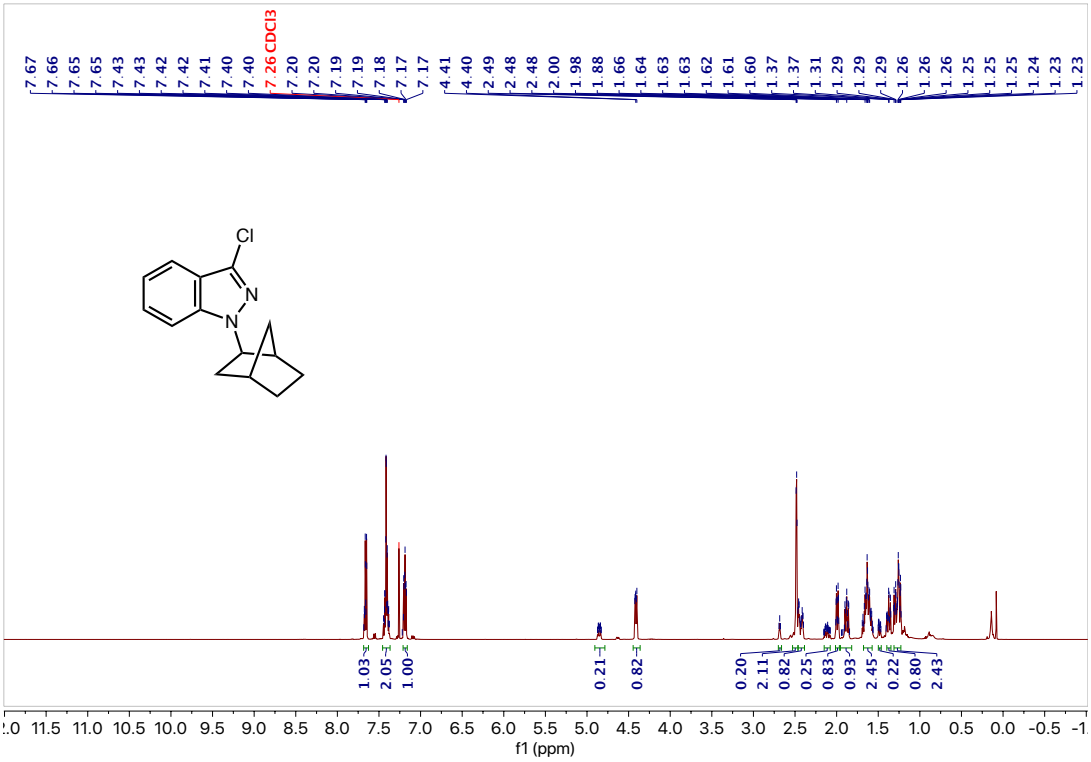


Figure S52: ^{1}H NMR spectrum of **(±)-11** (mixture of diastereomers, d.r. 4:1) (500 MHz, $CDCl_3$).

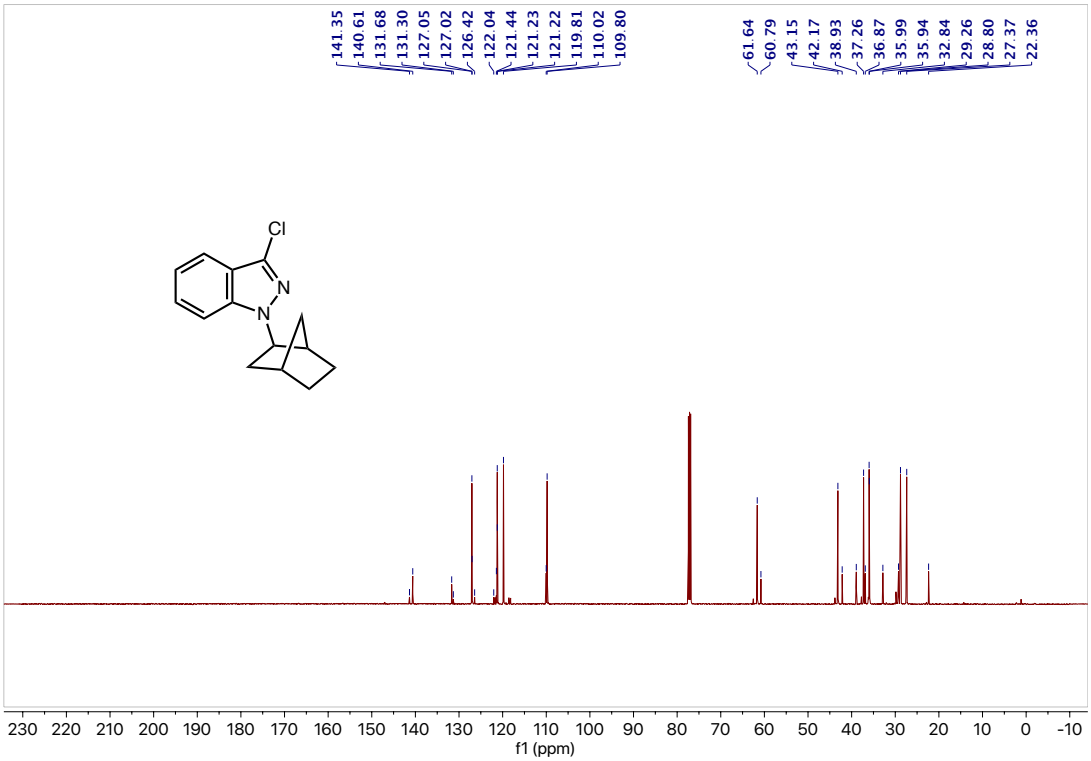


Figure S53: ^{13}C NMR spectrum of **(±)-11** (mixture of diastereomers, d.r. 4:1) (125 MHz, $CDCl_3$).

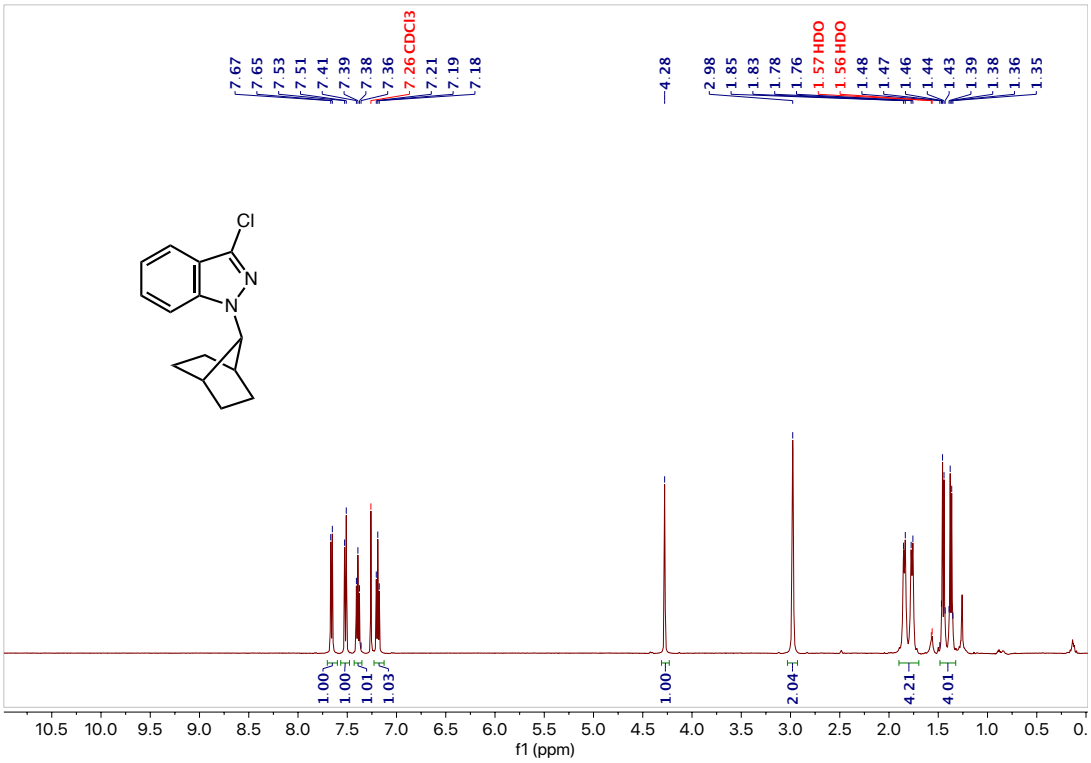


Figure S54: ^{1}H NMR spectrum of **12** (500 MHz, $CDCl_3$).

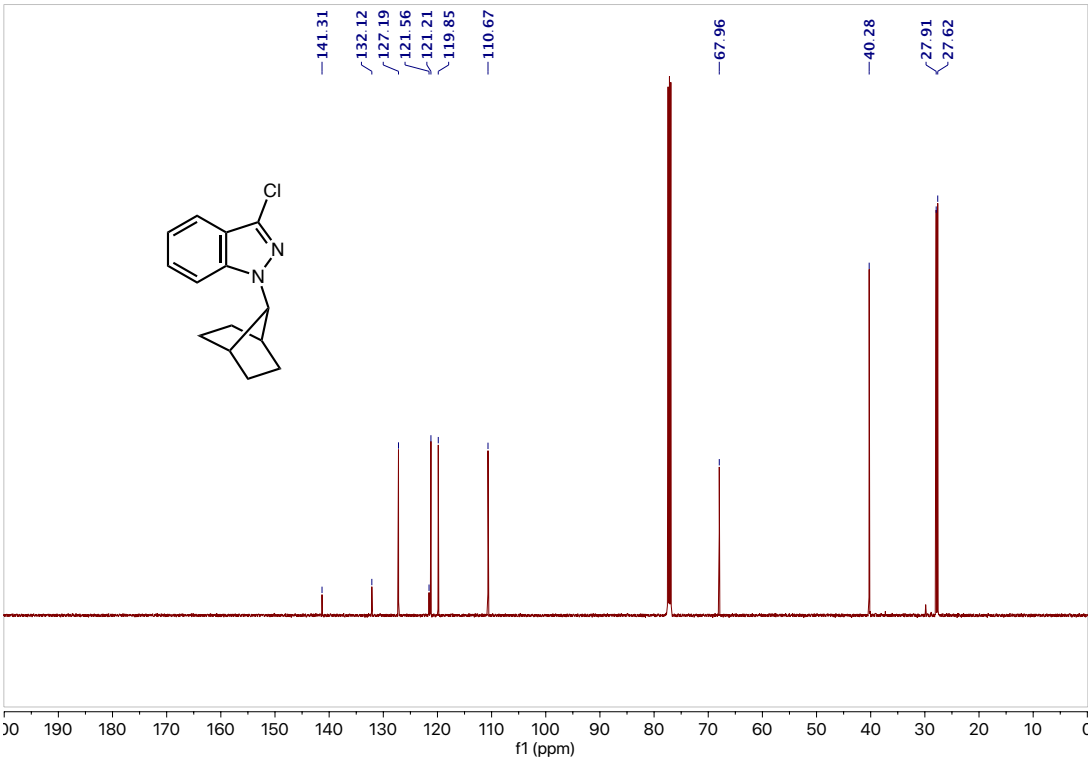


Figure S55: ^{13}C NMR spectrum of **12** (125 MHz, $CDCl_3$).

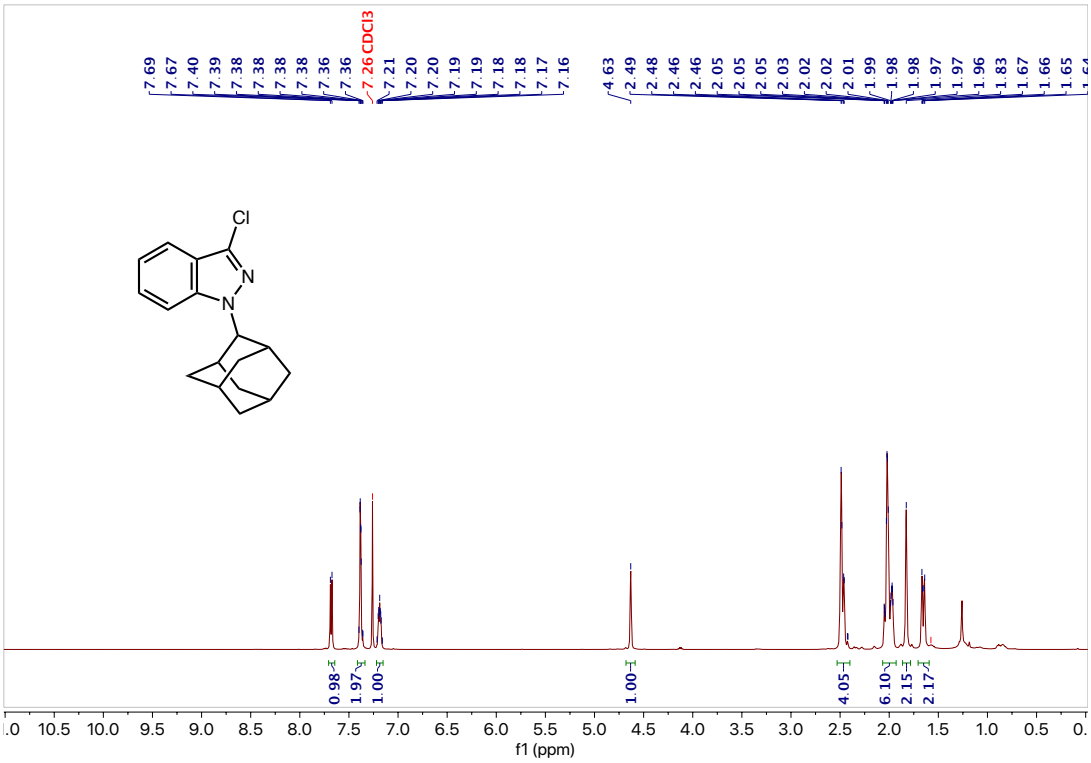


Figure S56: ^{1}H NMR spectrum of **13** (500 MHz, $CDCl_3$).

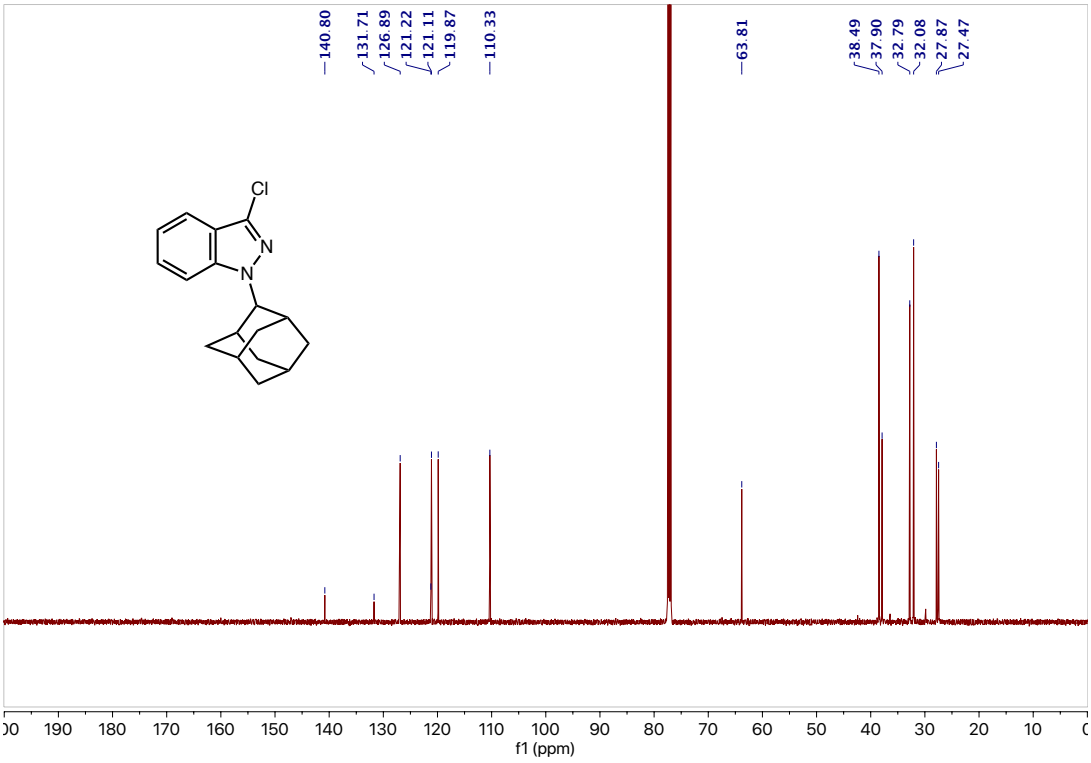


Figure S57: ^{13}C NMR spectrum of **13** (125 MHz, $CDCl_3$).

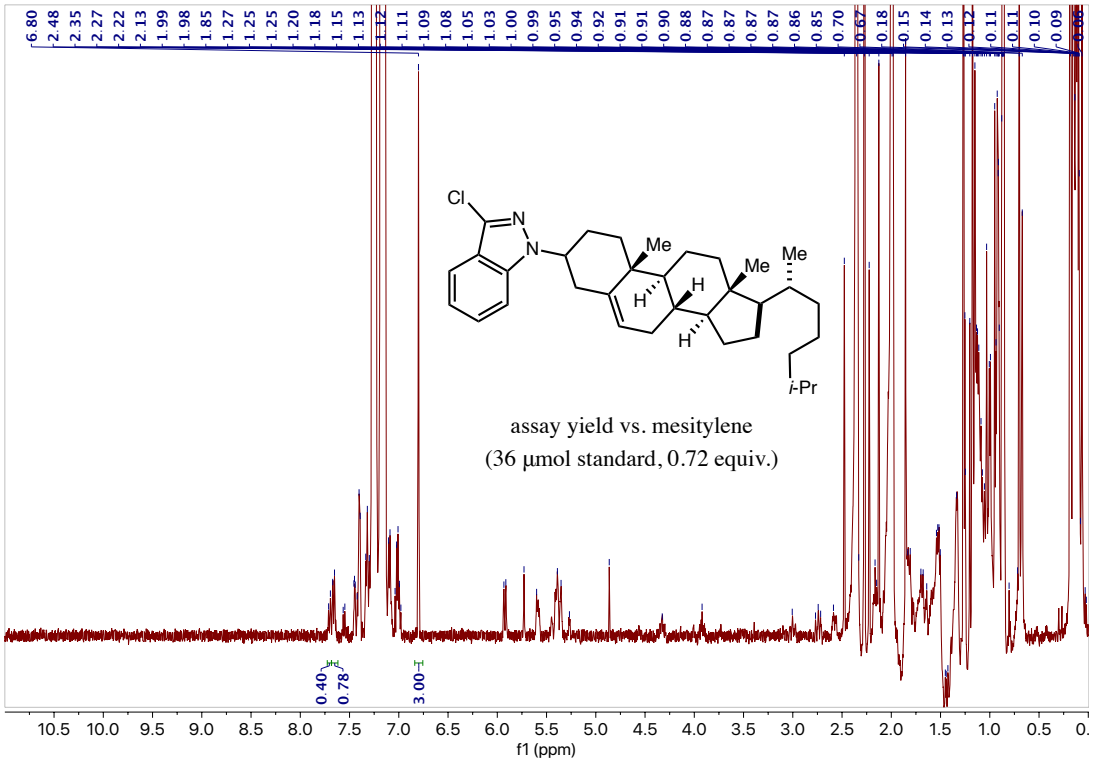


Figure S58: ^{1}H NMR assay of **14** using mesitylene as an internal standard (500 MHz, $CDCl_3$).

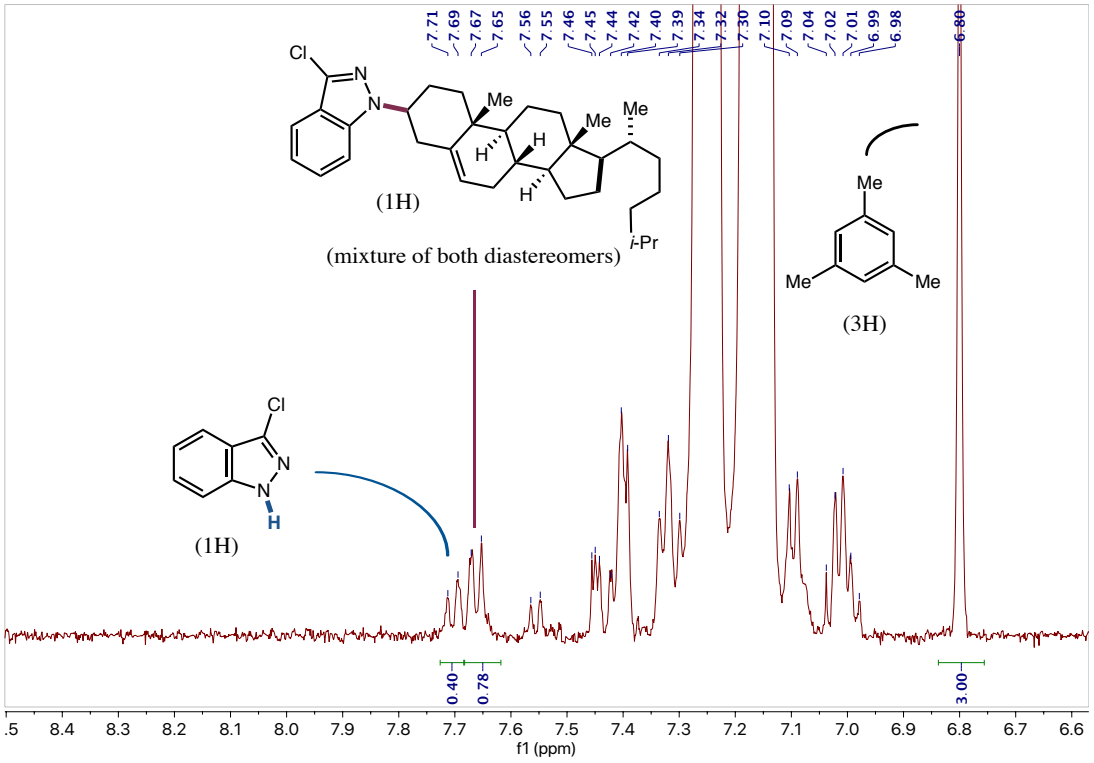


Figure S59: Assignment of **Figure S58** (500 MHz, $CDCl_3$).

[(0.78 mmol **14**/mmol Mes) * 0.0359 mmol Mes]/0.050 mmol **14** (theoretical) = *56% assay yield*

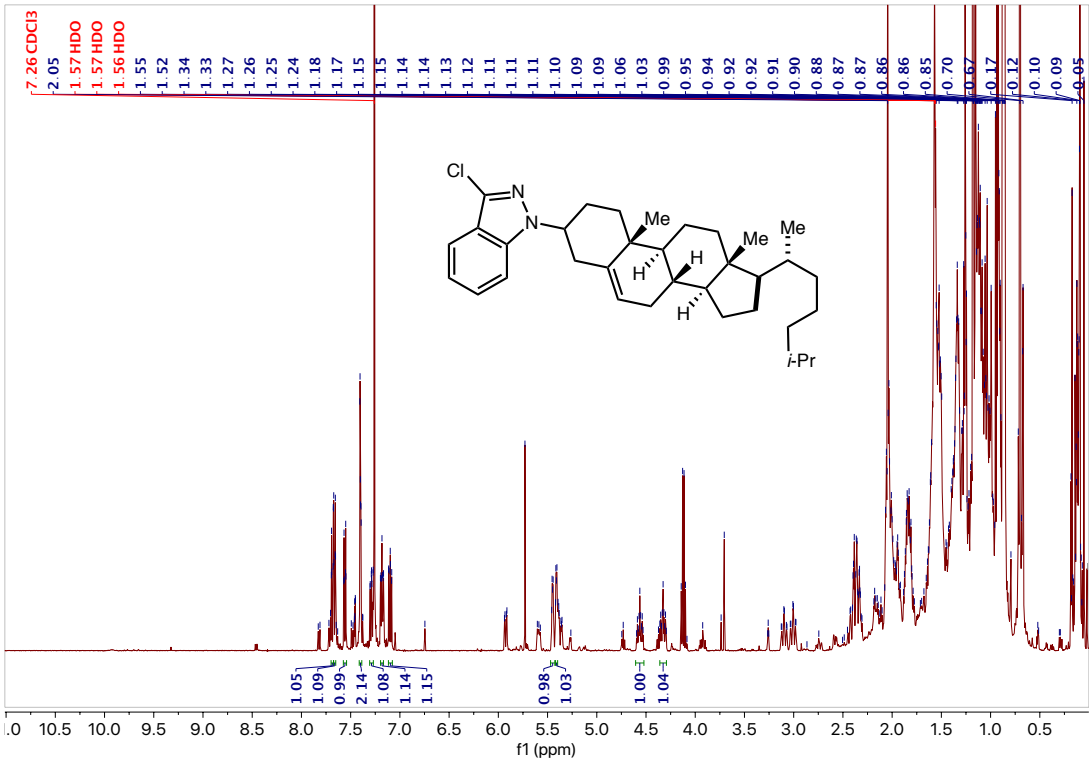


Figure S60: Diastereomeric analysis for **14** via ^{1}H NMR using semi-pure material (500 MHz, $CDCl_3$).

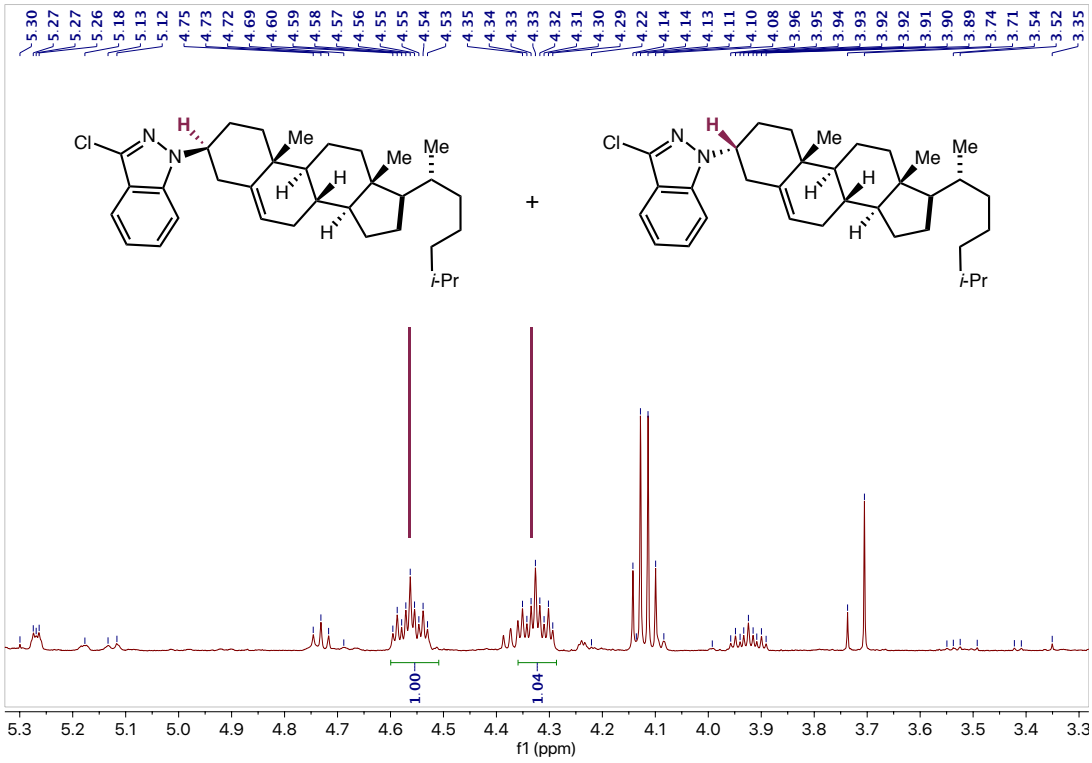


Figure S61: Assignment of **Figure S60** (500 MHz, $CDCl_3$).

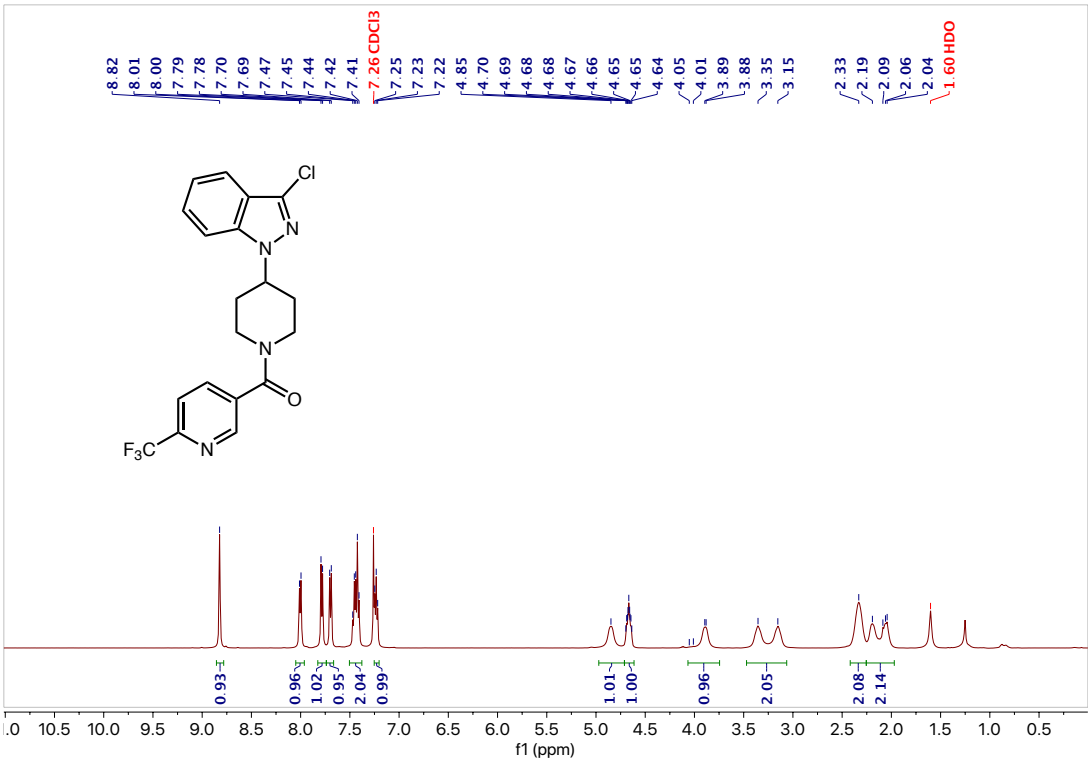


Figure S62: ^{1}H NMR spectrum of **15** (500 MHz, $CDCl_3$).

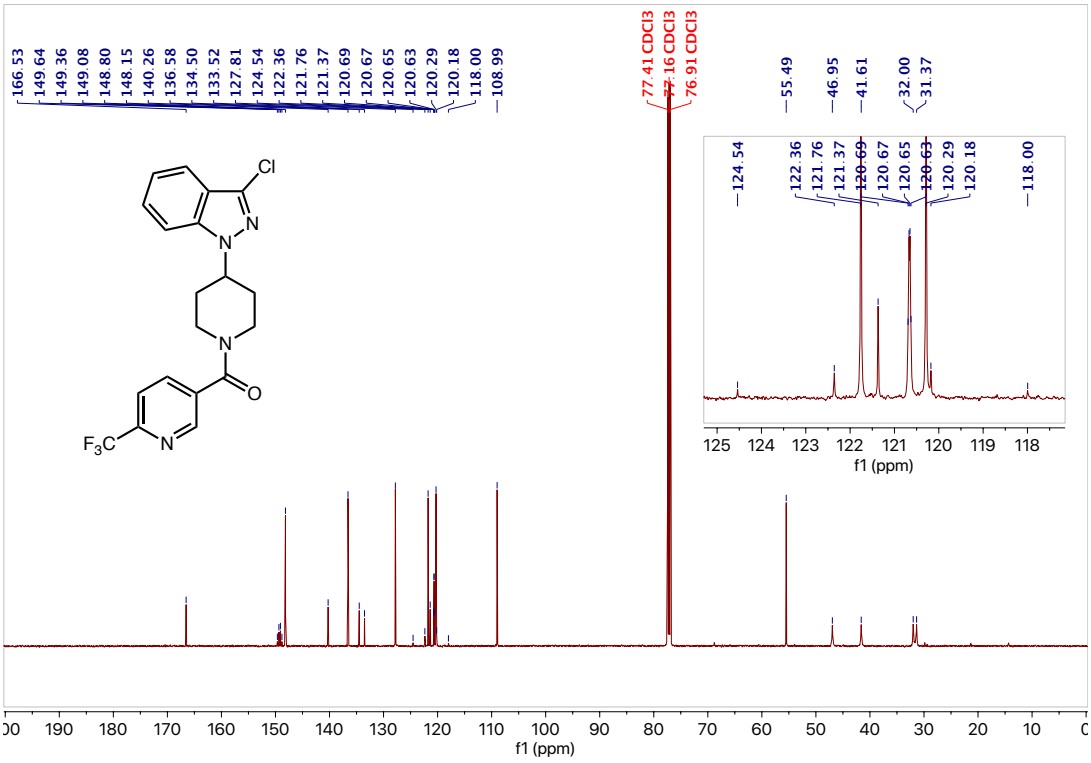


Figure S63: ^{13}C NMR spectrum of **15** (125 MHz, $CDCl_3$).

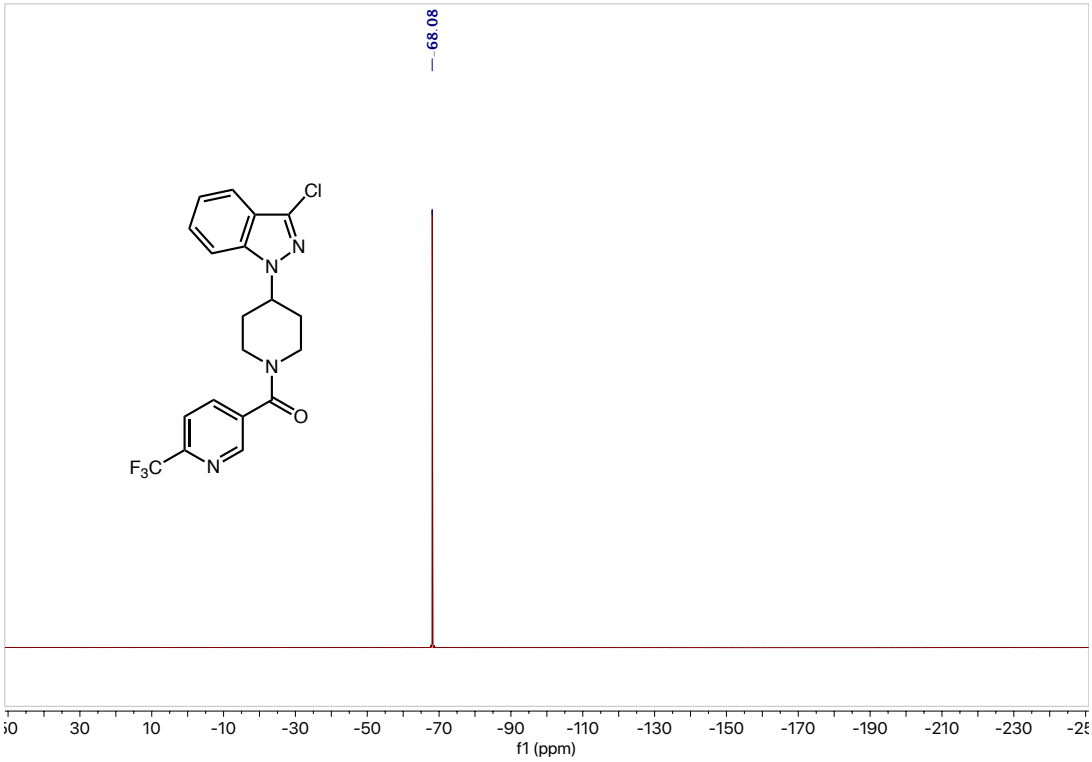


Figure S64: ^{19}F NMR spectrum of **15** (282 MHz, $CDCl_3$).

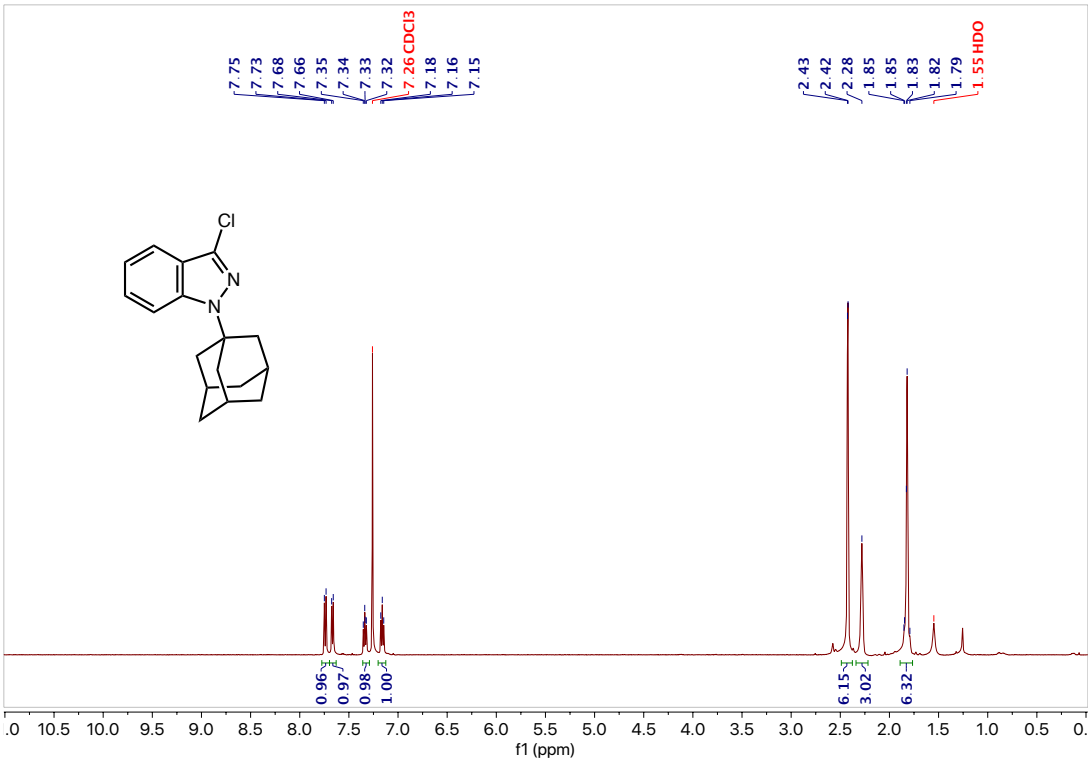


Figure S65: ^{1}H NMR spectrum of **16** (500 MHz, $CDCl_3$).

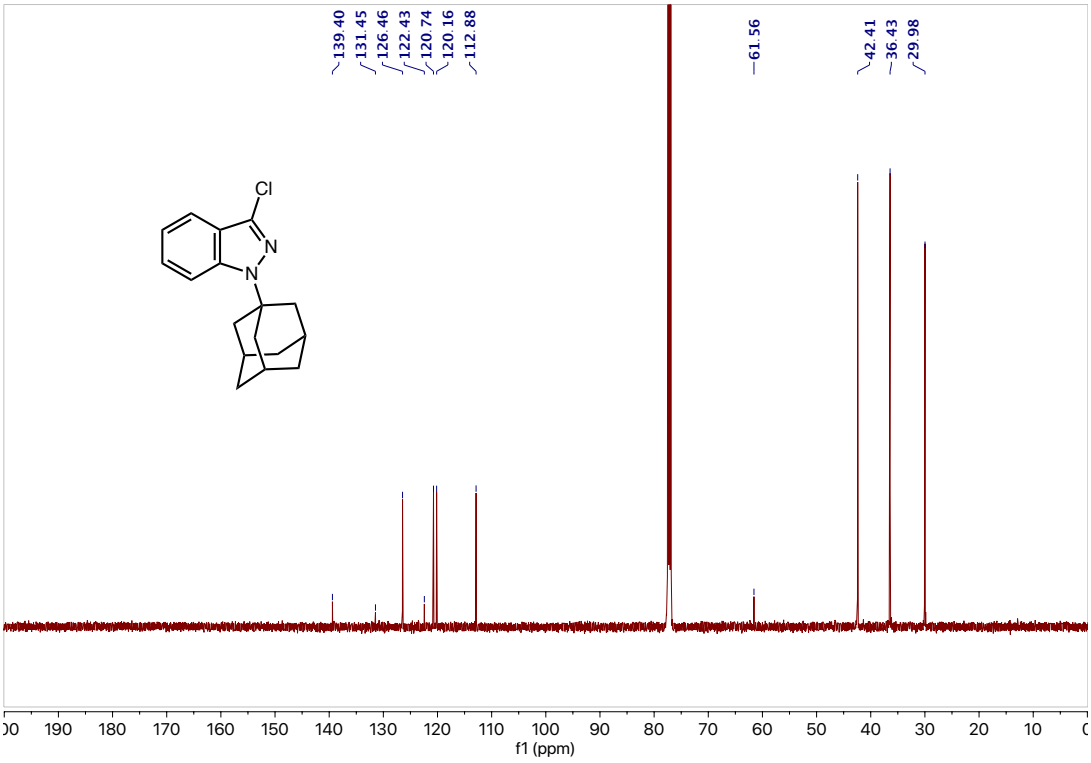


Figure S66: ^{13}C NMR spectrum of **16** (125 MHz, $CDCl_3$).

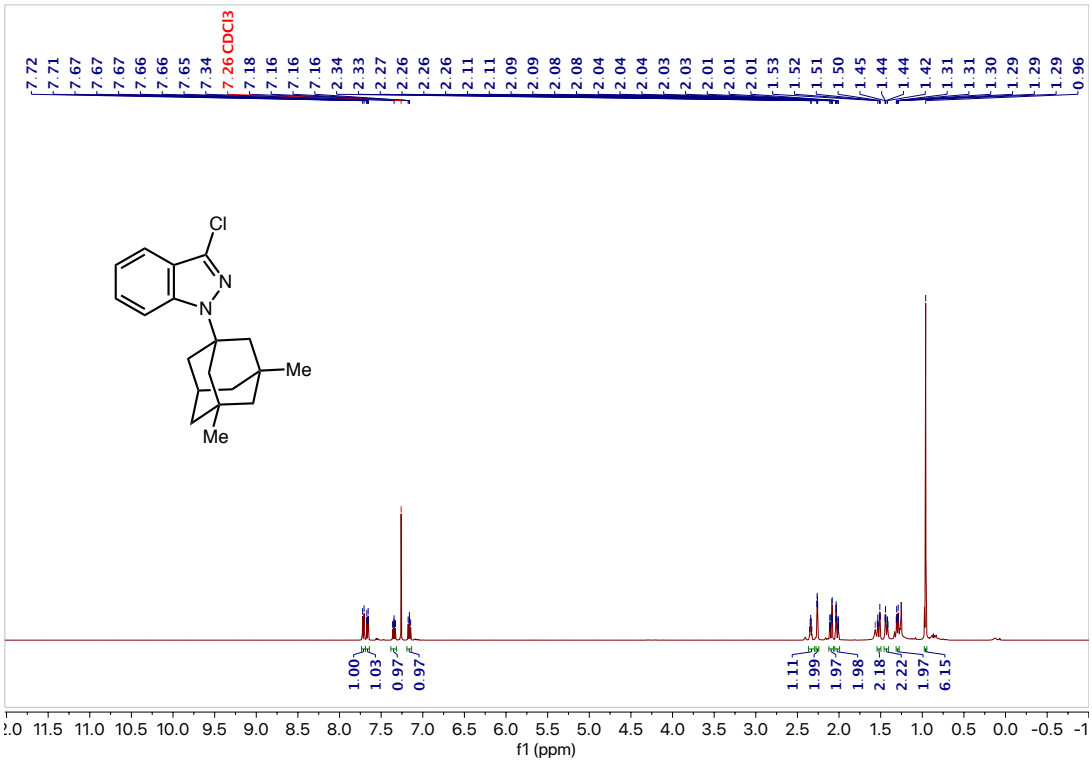


Figure S67: ^{1}H NMR spectrum of **17** (500 MHz, $CDCl_3$).

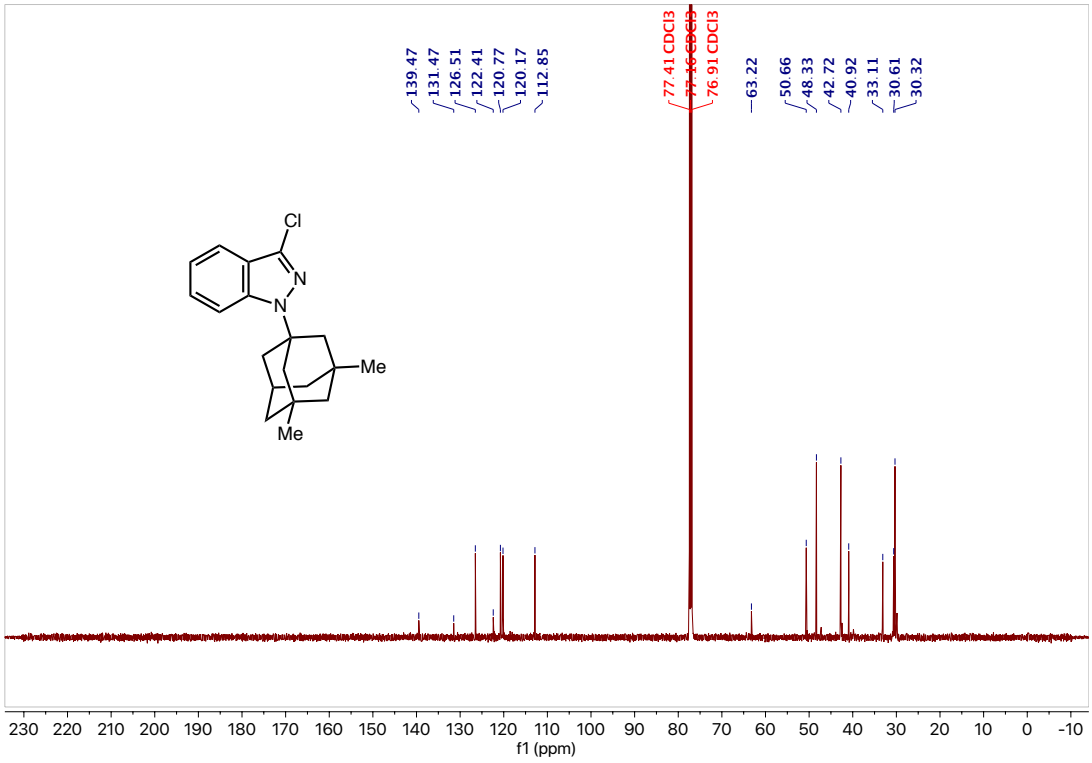


Figure S68: ^{13}C NMR spectrum of **17** (125 MHz, $CDCl_3$).

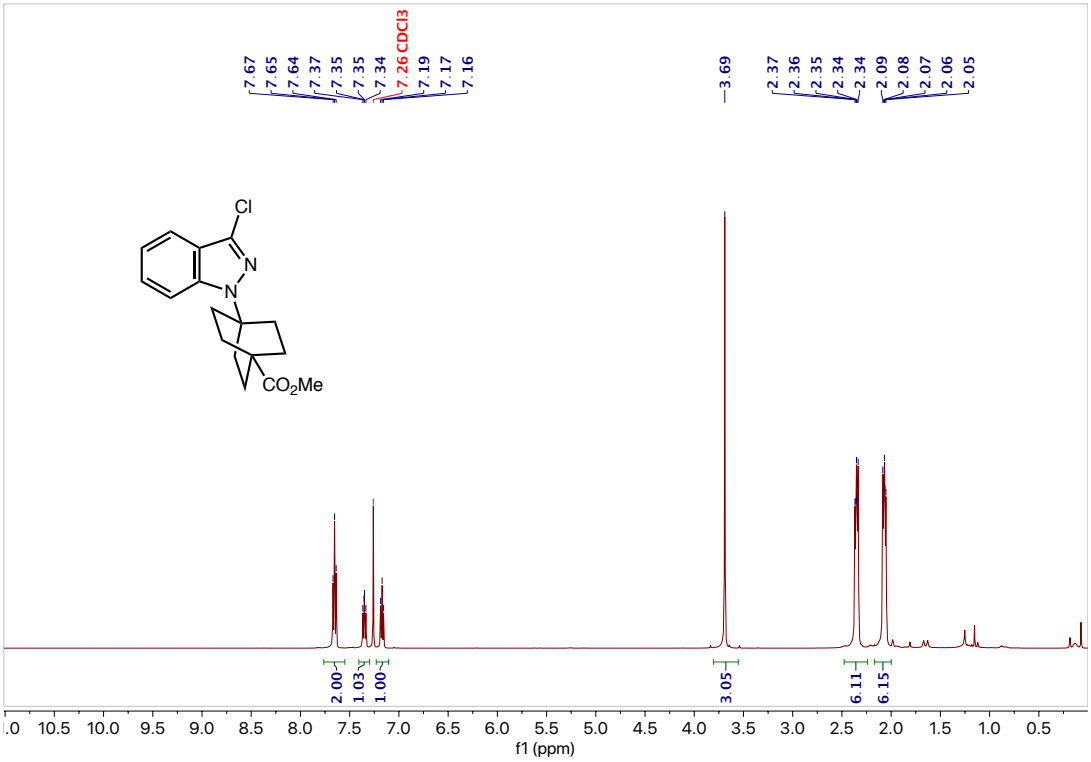


Figure S69: ^{1}H NMR spectrum of **18** (500 MHz, $CDCl_3$).

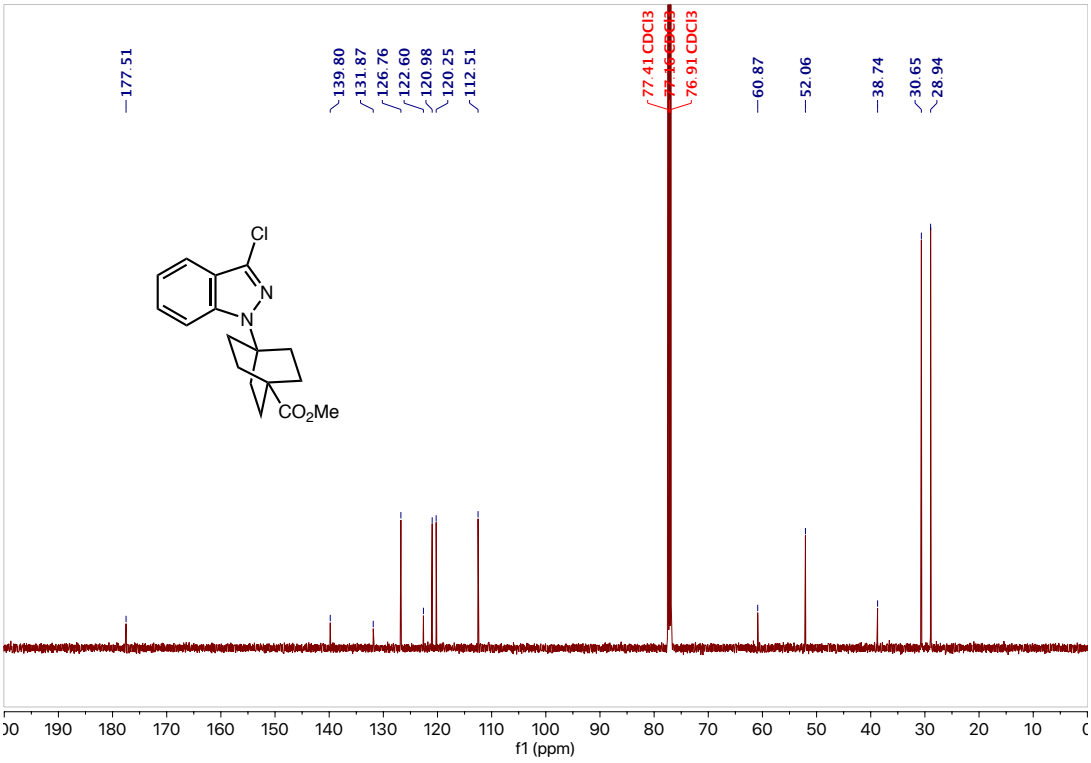


Figure S70: ^{13}C NMR spectrum of **18** (125 MHz, $CDCl_3$).

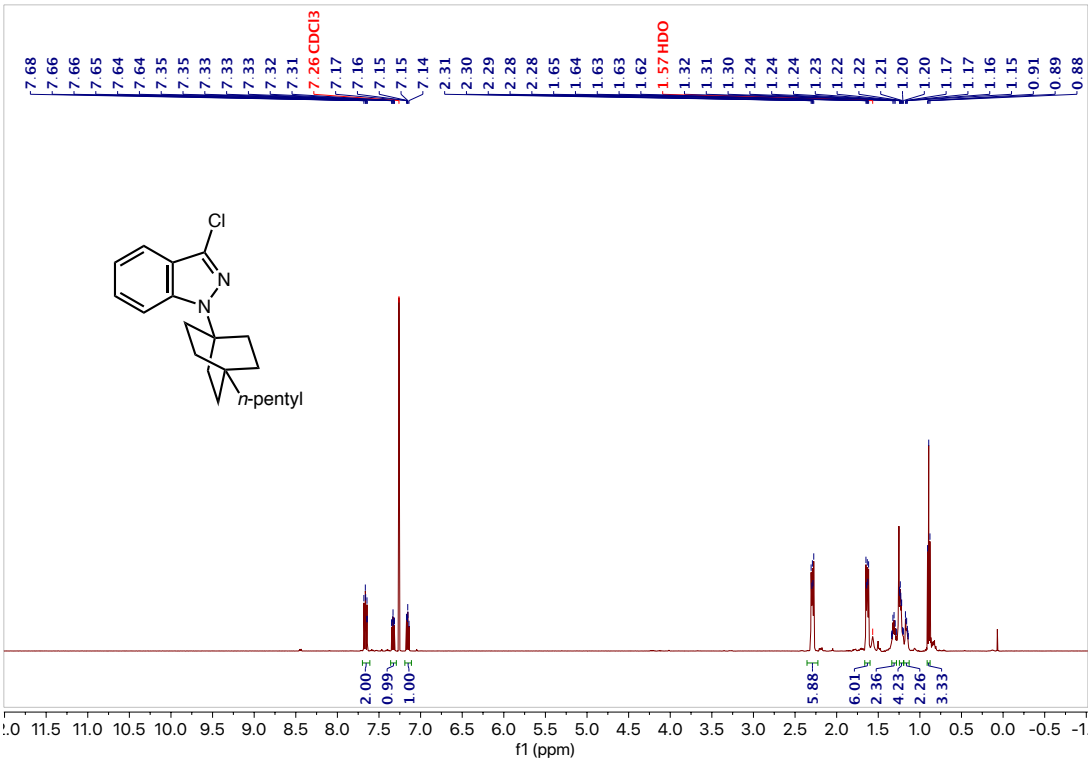


Figure S71: ^{1}H NMR spectrum of **19** (500 MHz, $CDCl_3$).

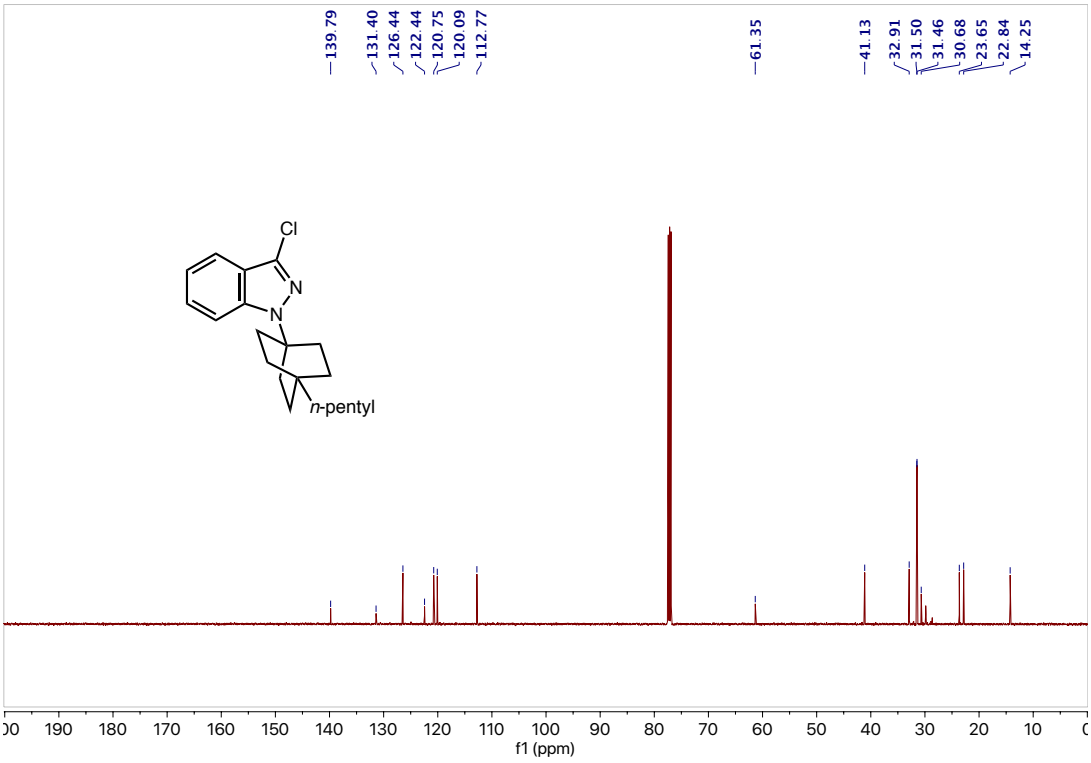


Figure S72: ^{13}C NMR spectrum of **19** (125 MHz, $CDCl_3$).

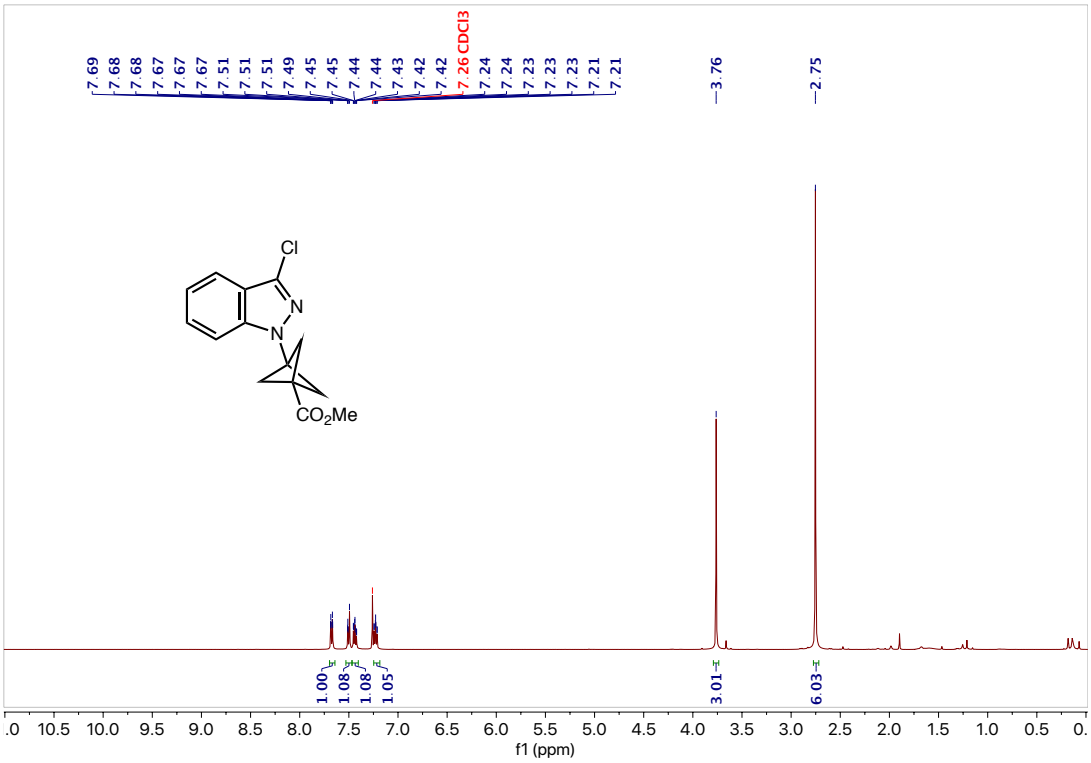


Figure S73: ^{1}H NMR spectrum of **20** (500 MHz, $CDCl_3$).

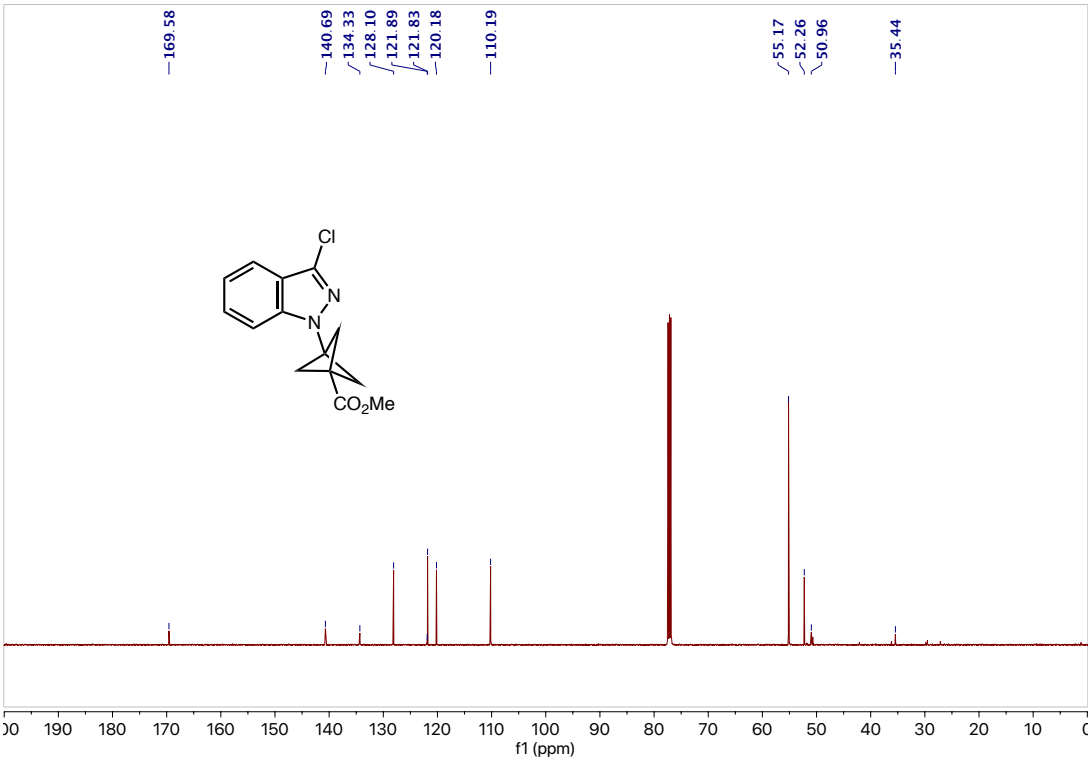


Figure S74: ^{13}C NMR spectrum of **20** (125 MHz, $CDCl_3$).

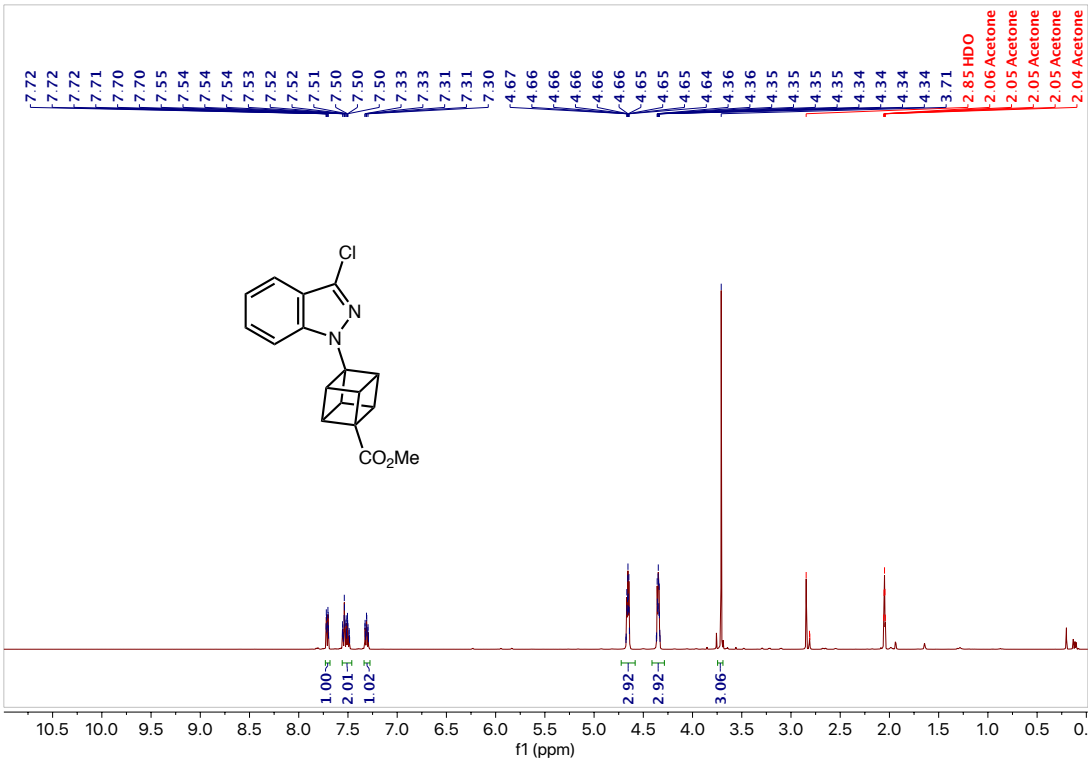


Figure S75: ^{1}H NMR spectrum of **21** (500 MHz, $(CD_3)_2CO$).

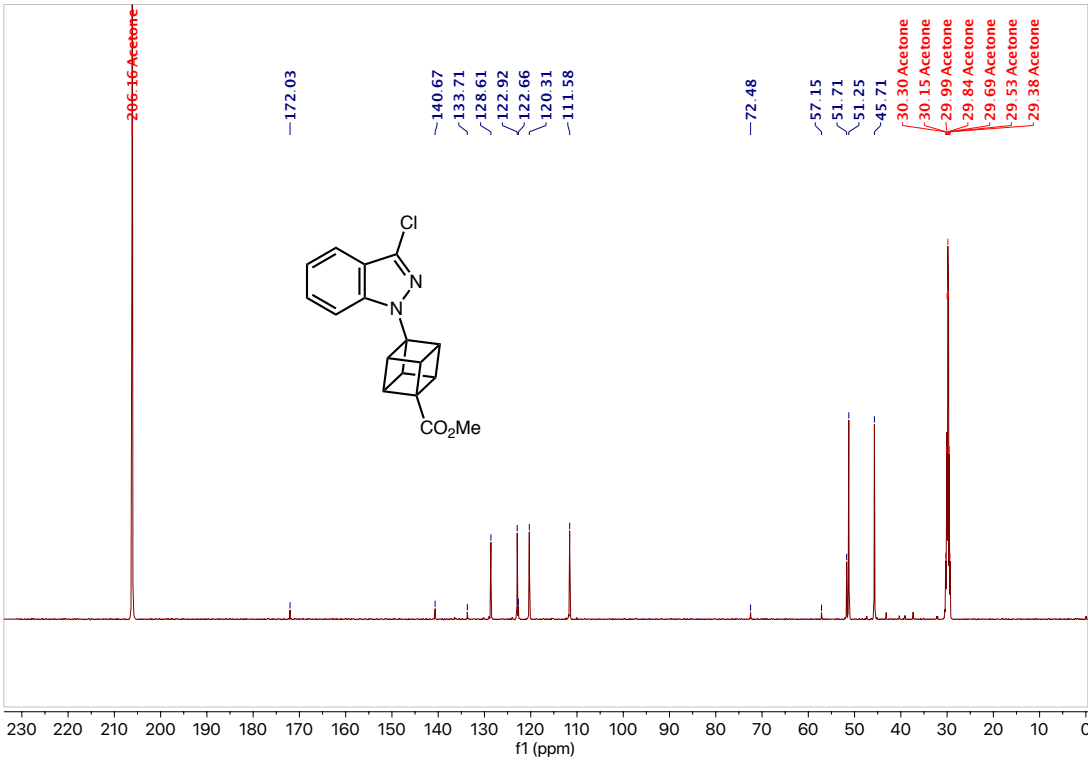


Figure S76: ^{13}C NMR spectrum of **21** (125 MHz, $(CD_3)_2CO$).

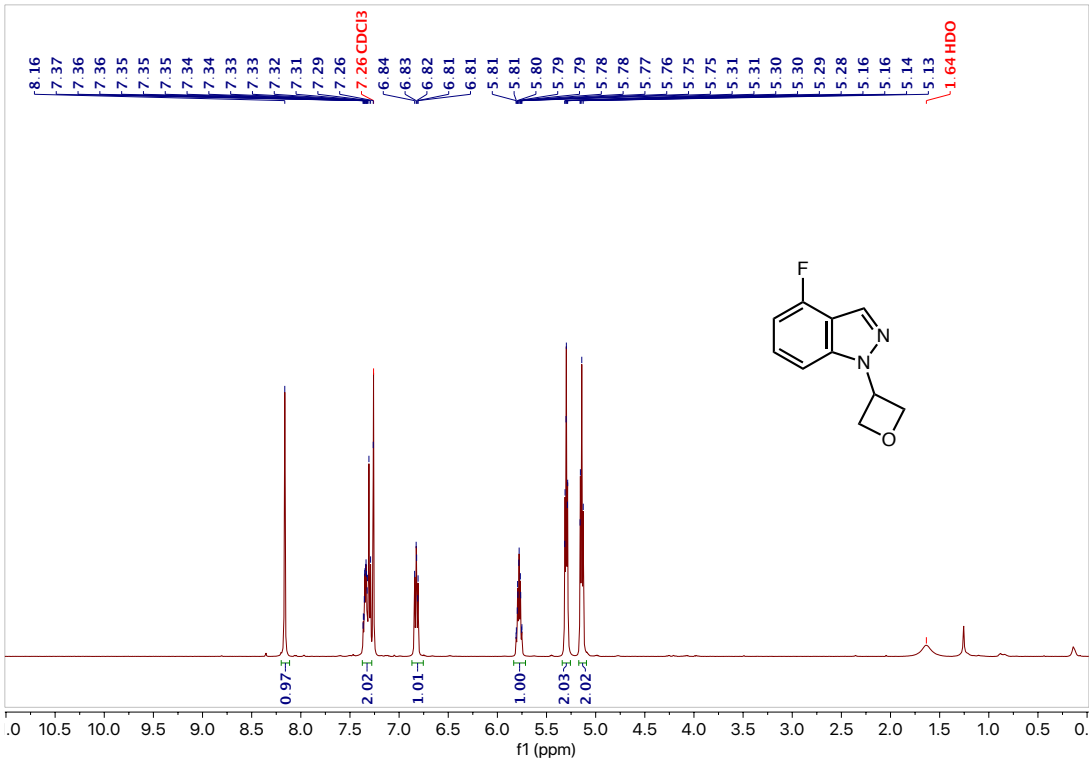


Figure S77: ^{1}H NMR spectrum of **22** (500 MHz, $CDCl_3$).

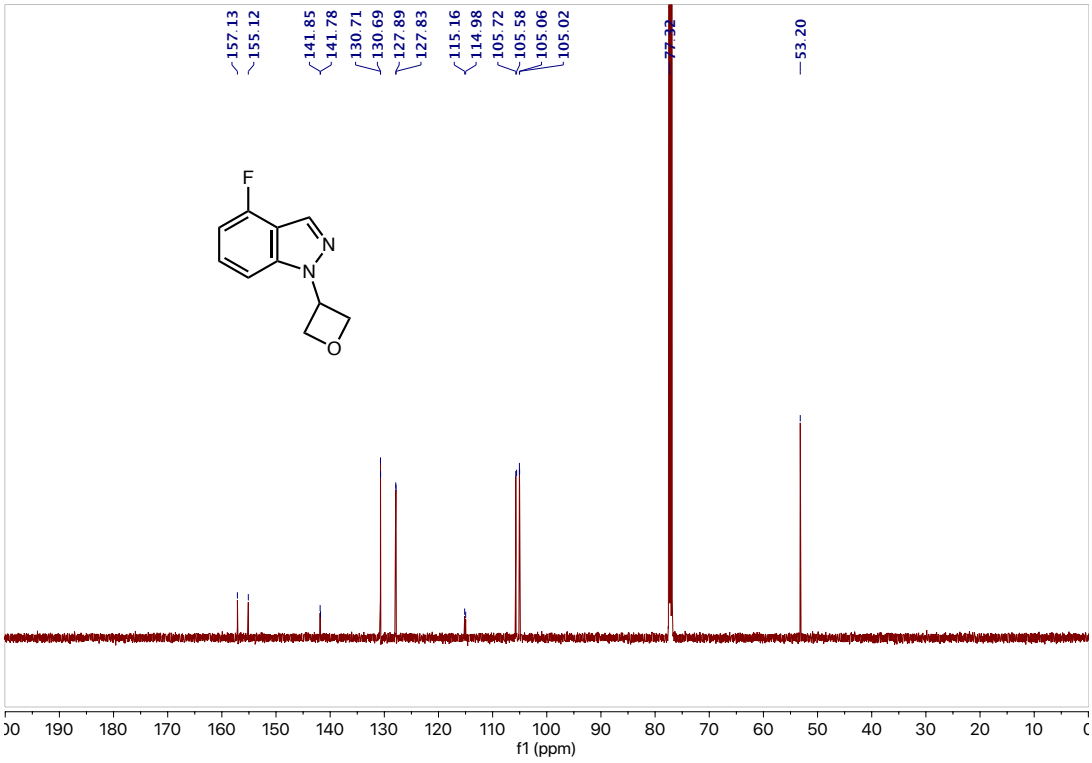


Figure S78: ^{13}C NMR spectrum of **22** (125 MHz, $CDCl_3$).

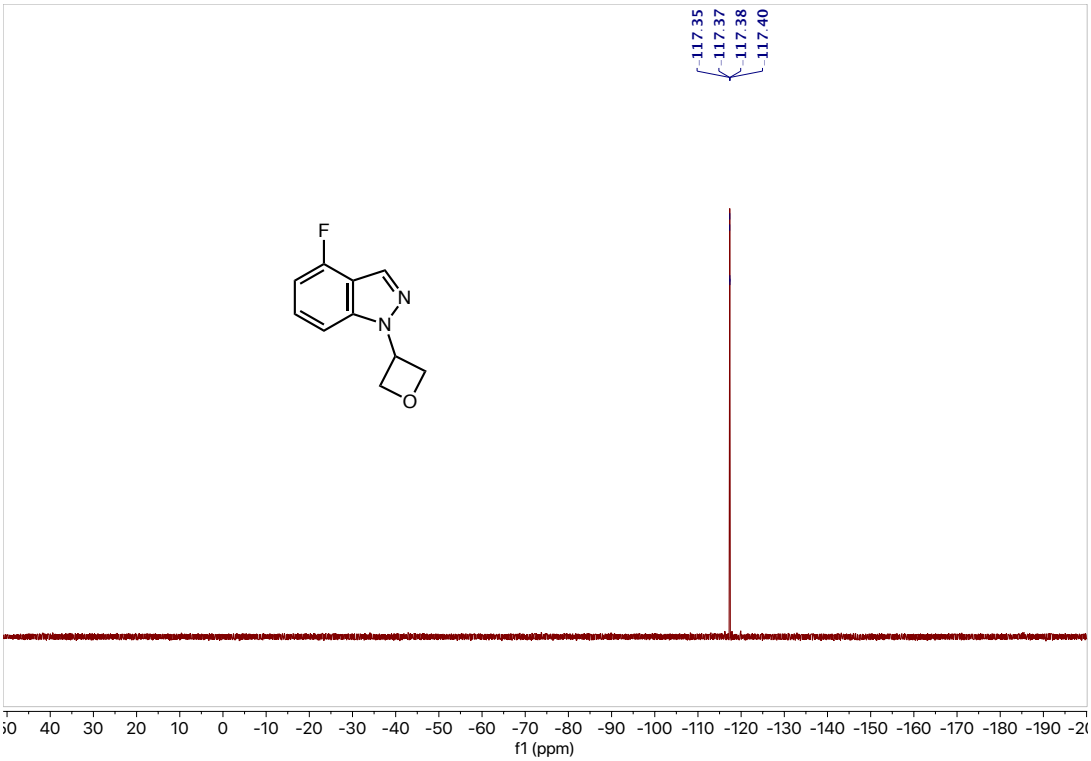


Figure S79: ^{19}F NMR spectrum of **22** (282 MHz, $CDCl_3$).

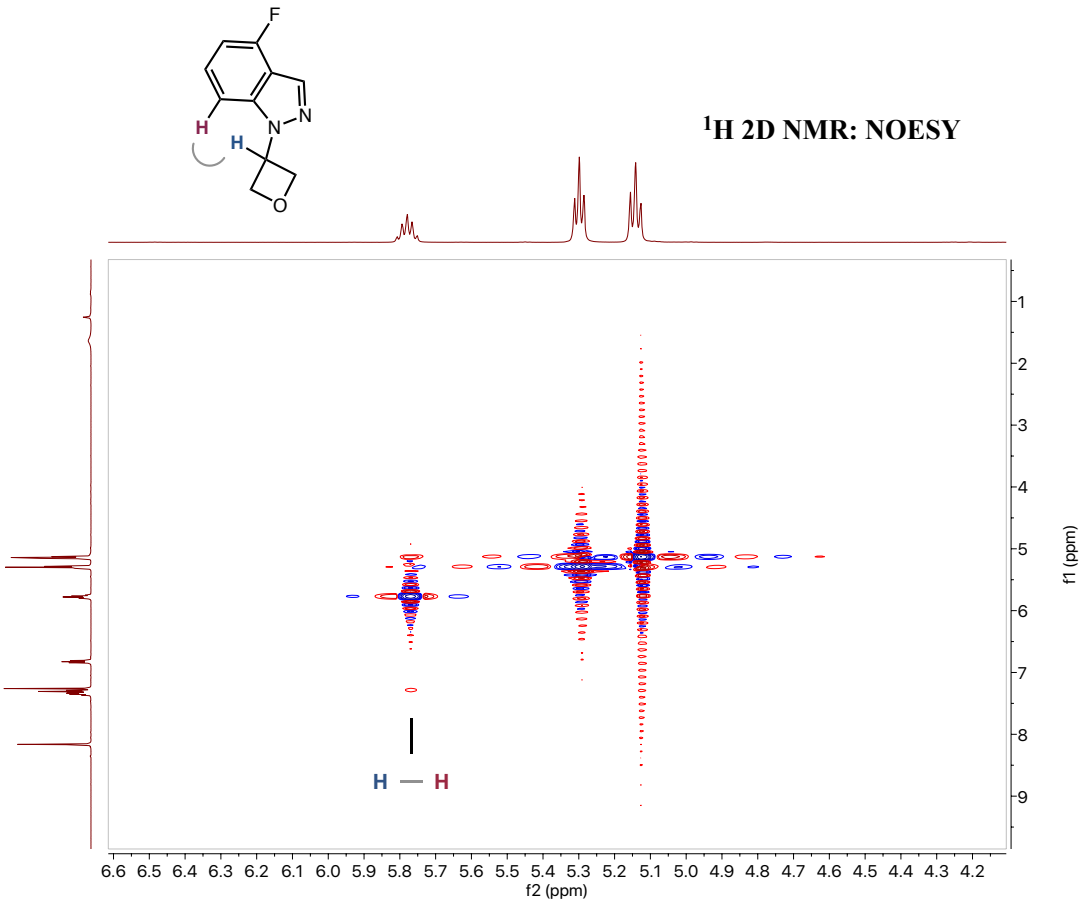


Figure S80: ^{1}H 2D NMR: NOESY spectrum of **22** (500 MHz, $CDCl_3$).

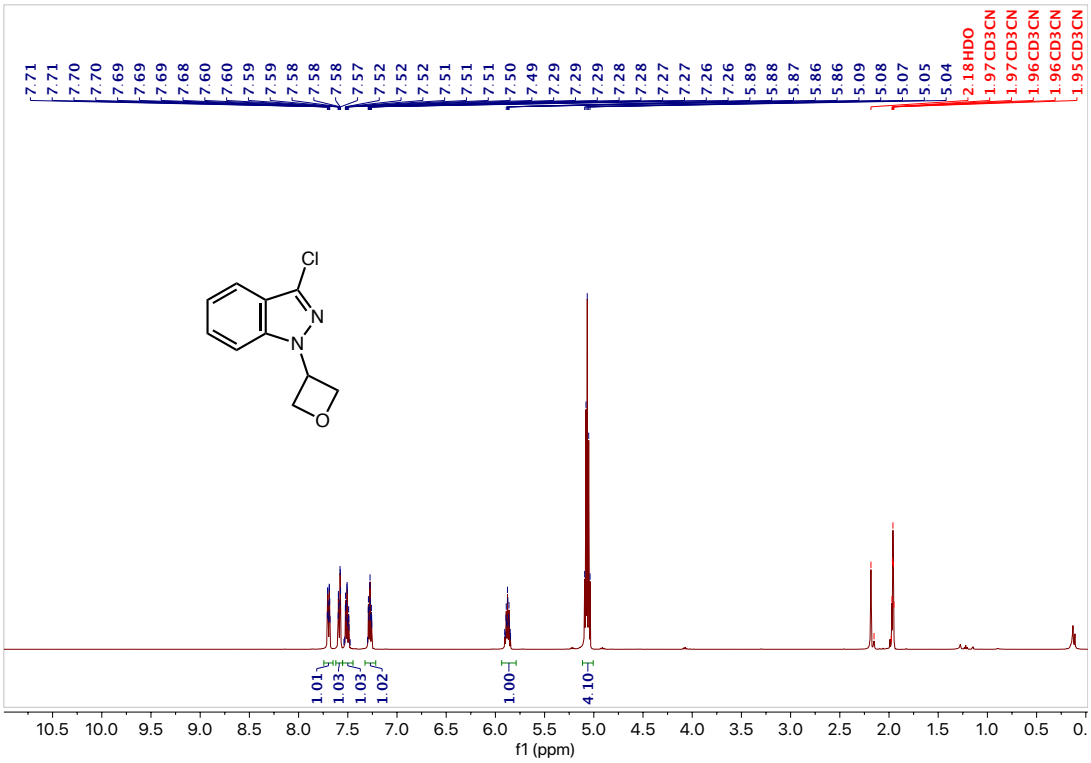


Figure S81: ^{1}H NMR spectrum of **23** (500 MHz, CD_3CN).

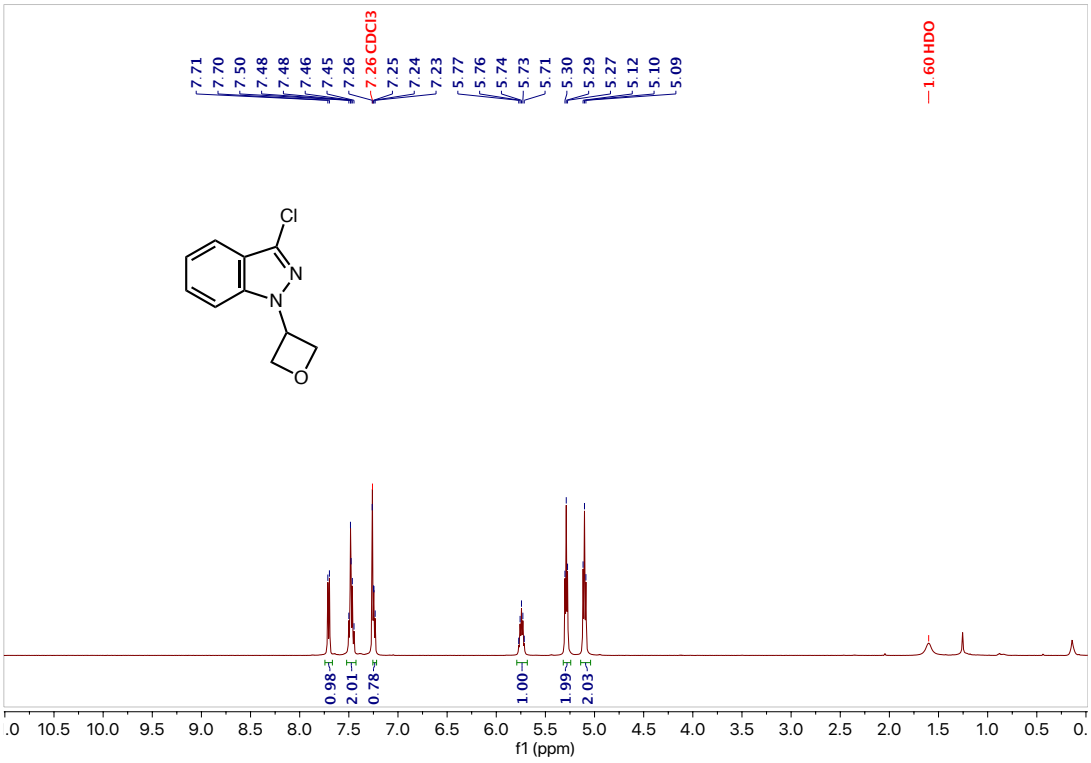


Figure S82: ^{1}H NMR spectrum of **23** (500 MHz, $CDCl_3$).

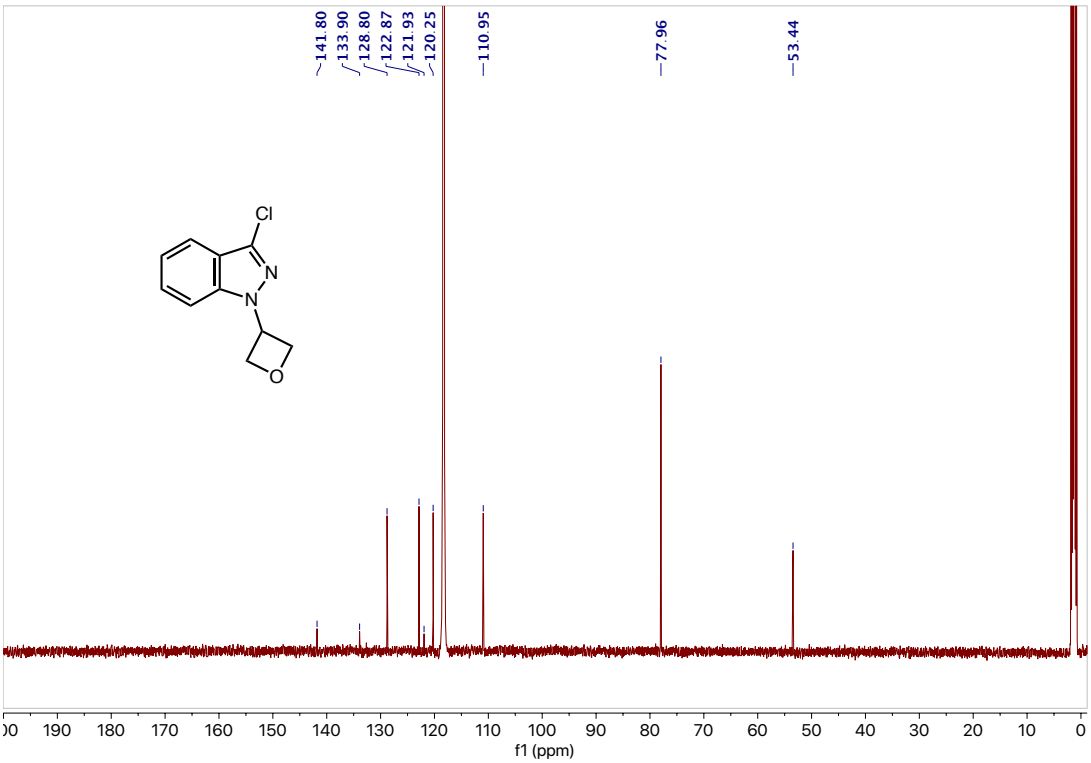


Figure S83: ^{13}C NMR spectrum of **23** (125 MHz, CD_3CN).

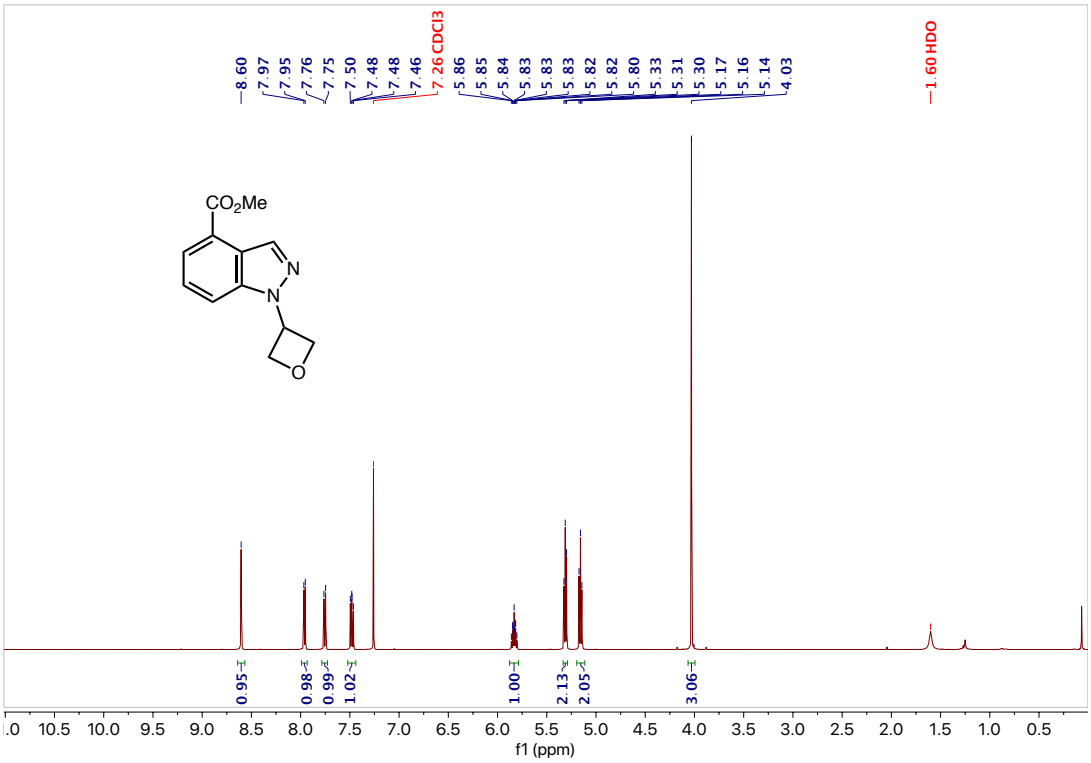


Figure S84: ^{1}H NMR spectrum of **24** (500 MHz, $CDCl_3$).

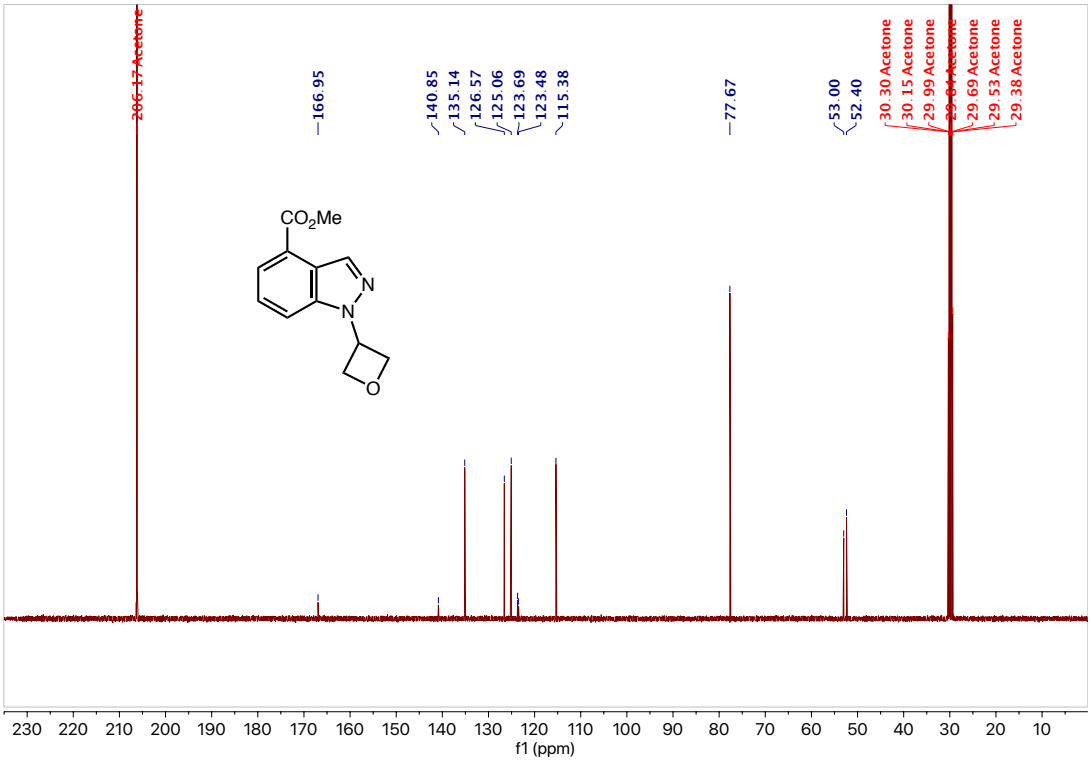


Figure S85: ^{13}C NMR spectrum of **24** (125 MHz, $CDCl_3$).

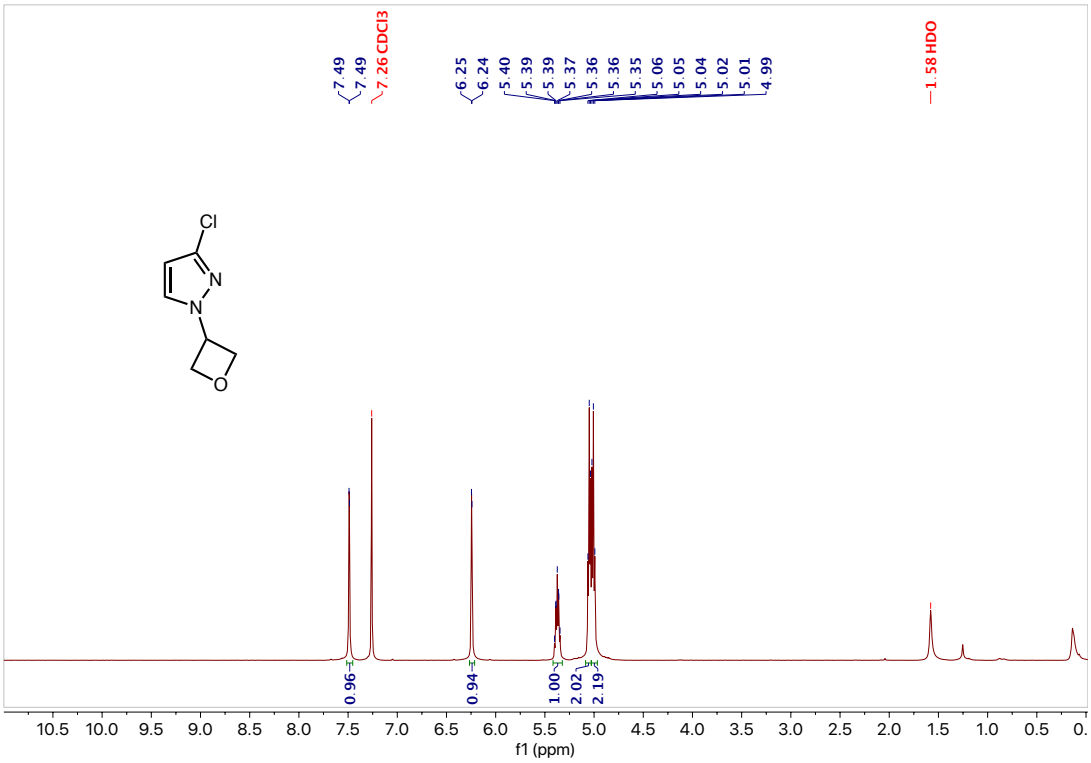


Figure S86: ^{1}H NMR spectrum of **25** (500 MHz, $CDCl_3$).

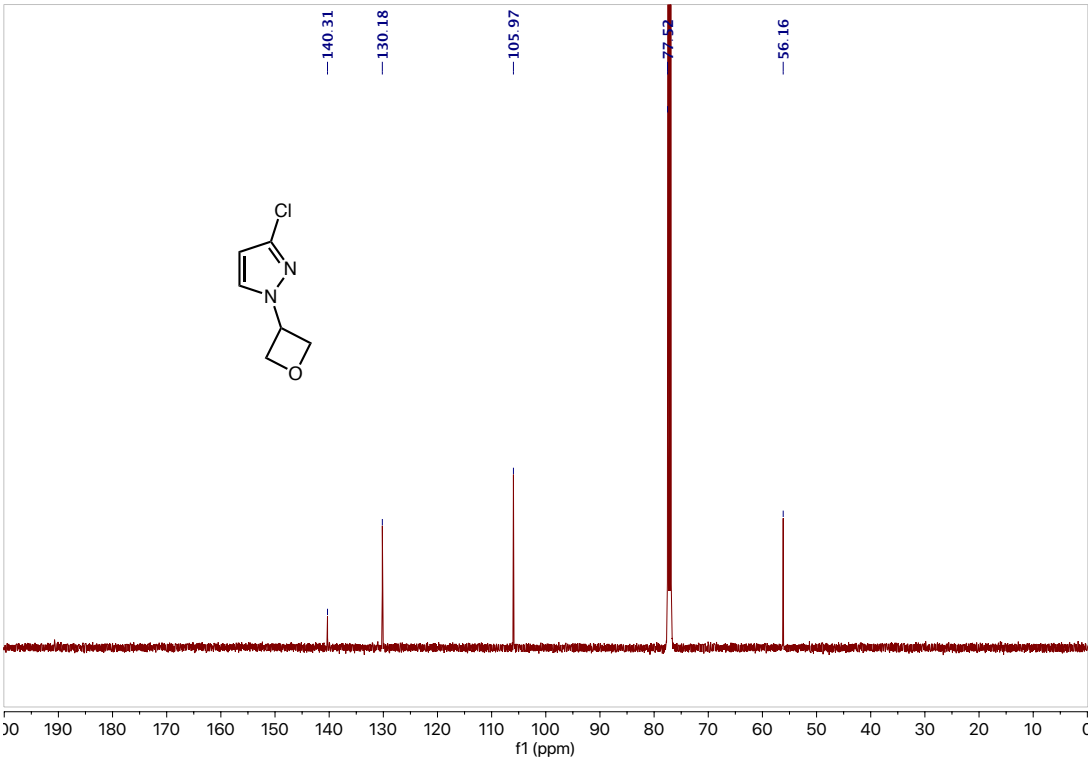


Figure S87: ^{13}C NMR spectrum of **25** (125 MHz, $CDCl_3$).

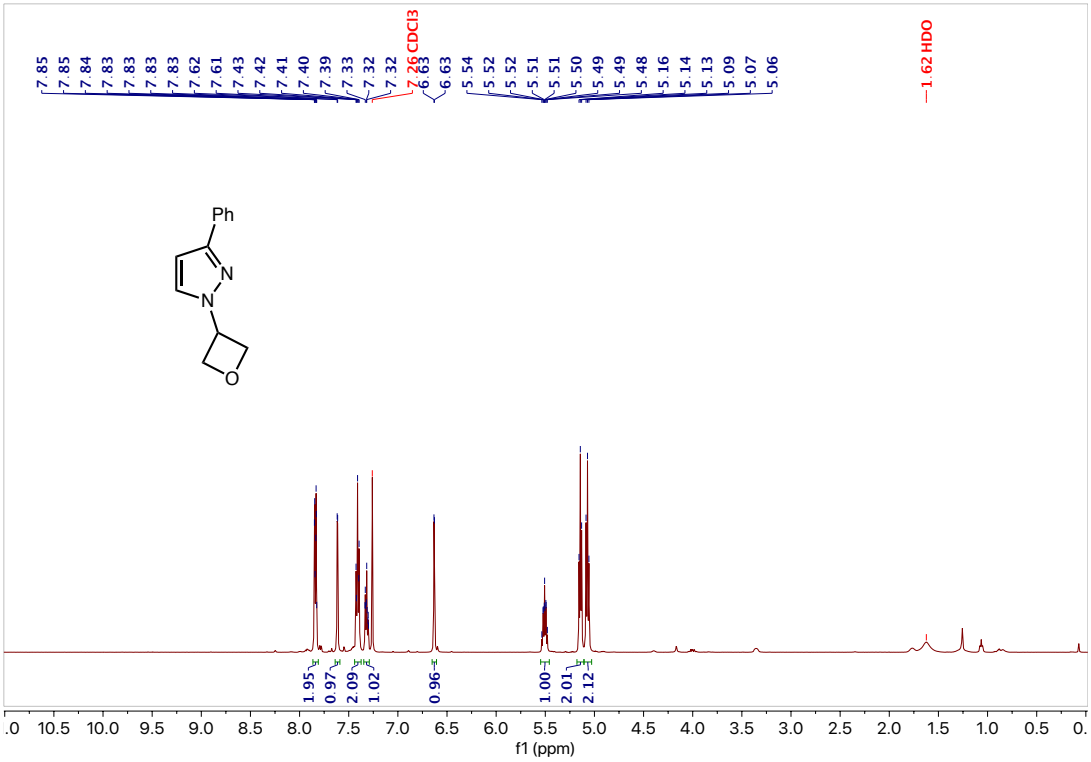


Figure S88: ^{1}H NMR spectrum of **26** (500 MHz, $CDCl_3$).

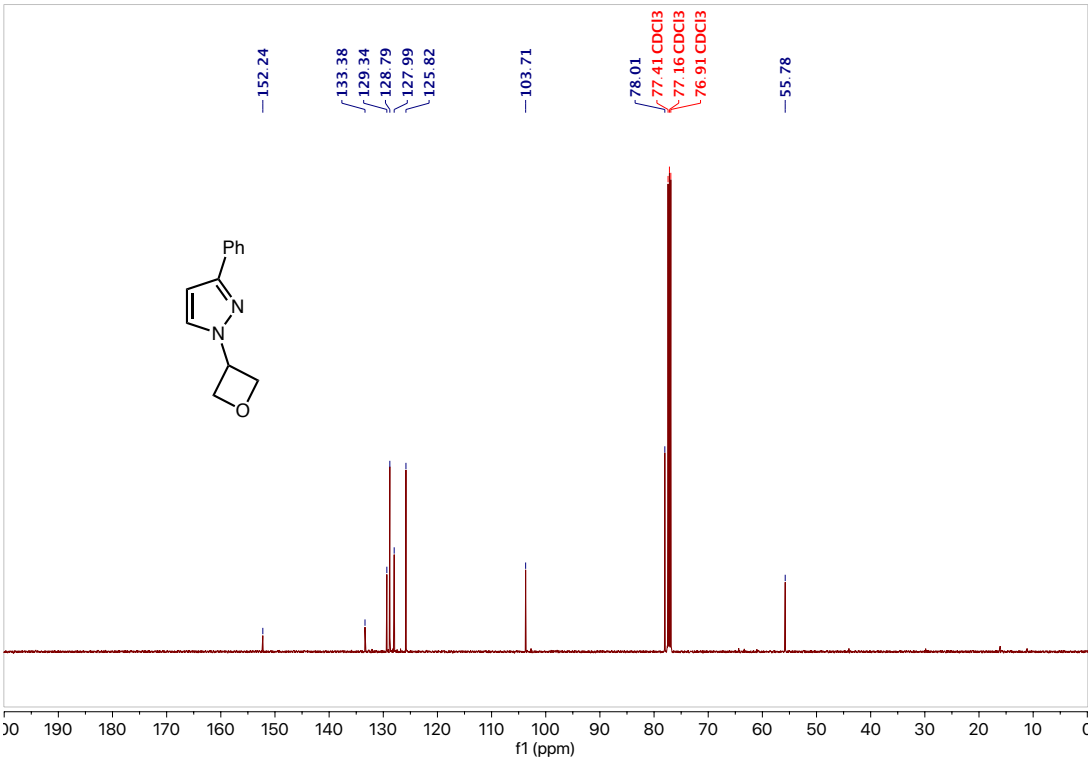


Figure S89: ^{13}C NMR spectrum of **26** (125 MHz, $CDCl_3$).

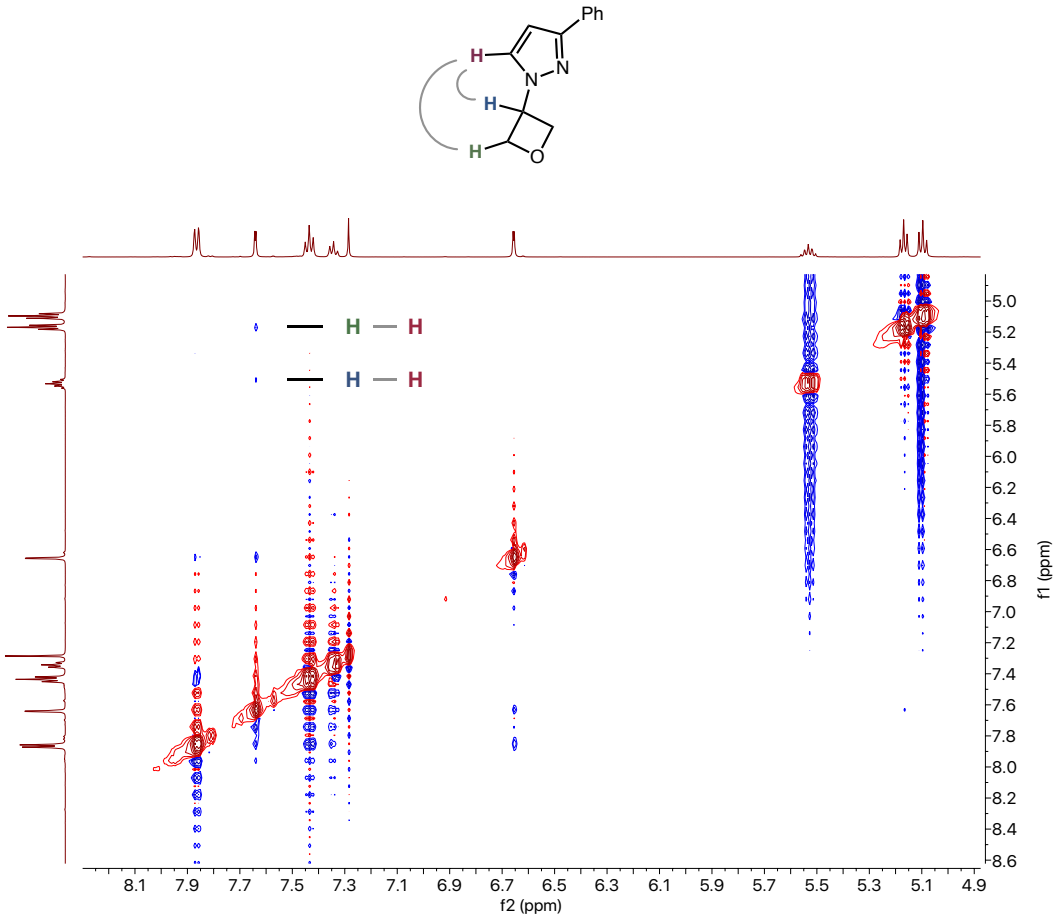


Figure S90: ^{1}H 2D NMR: NOESY spectrum of **26** (500 MHz, $CDCl_3$).

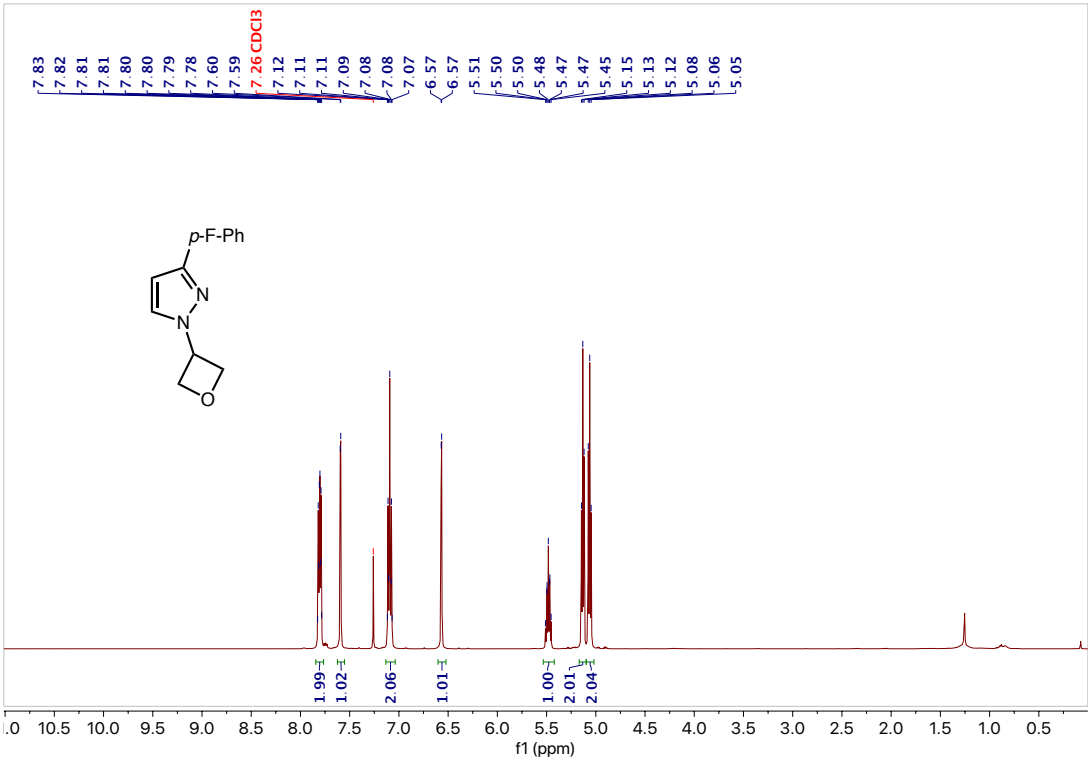


Figure S91: ^{1}H NMR spectrum of **27** (500 MHz, $CDCl_3$).

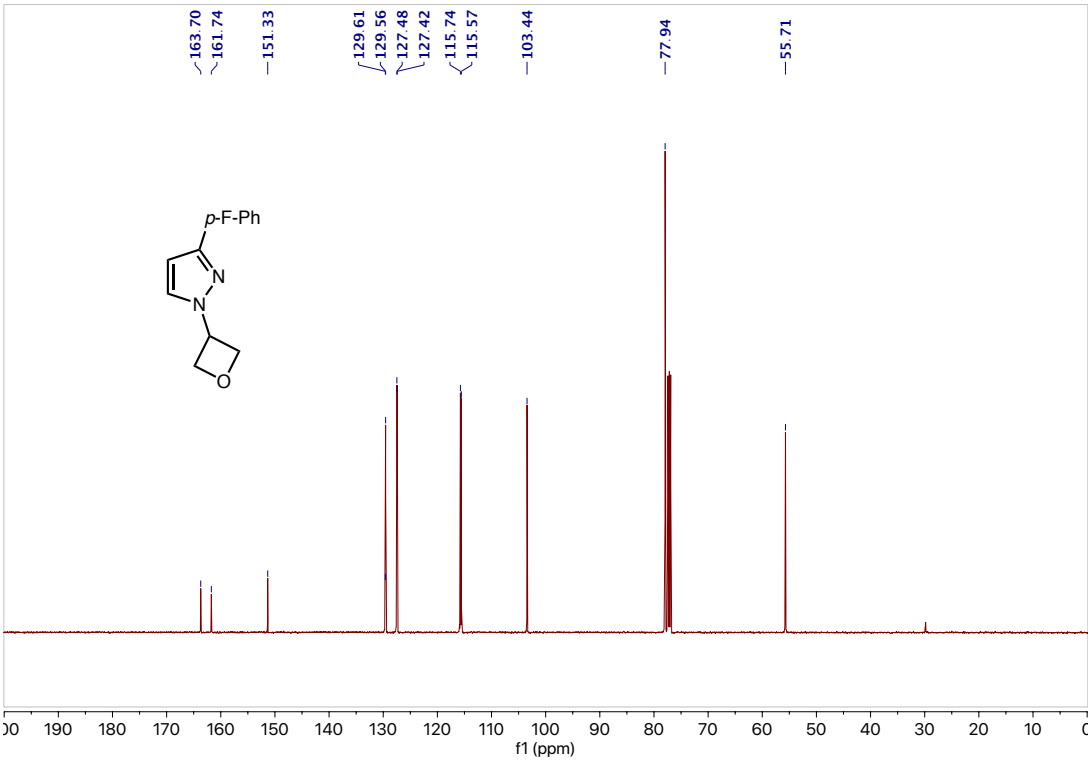


Figure S92: ^{13}C NMR spectrum of **27** (125 MHz, $CDCl_3$).

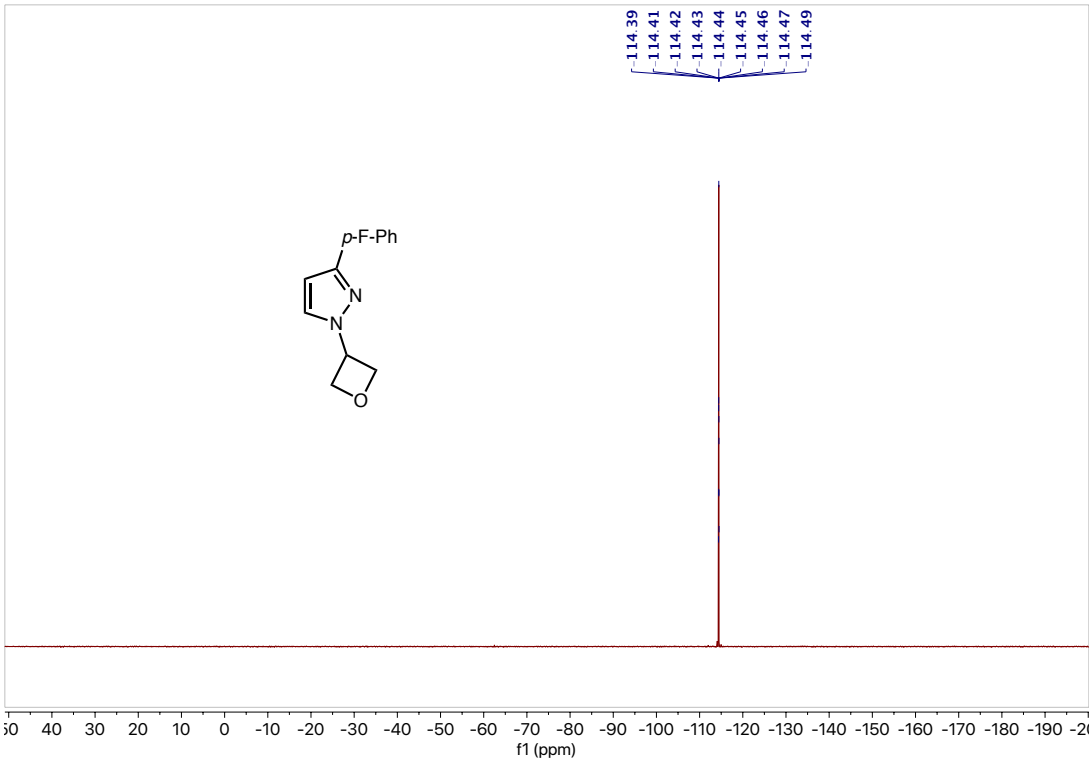


Figure S93: ^{19}F NMR spectrum of **27** (282 MHz, $CDCl_3$).

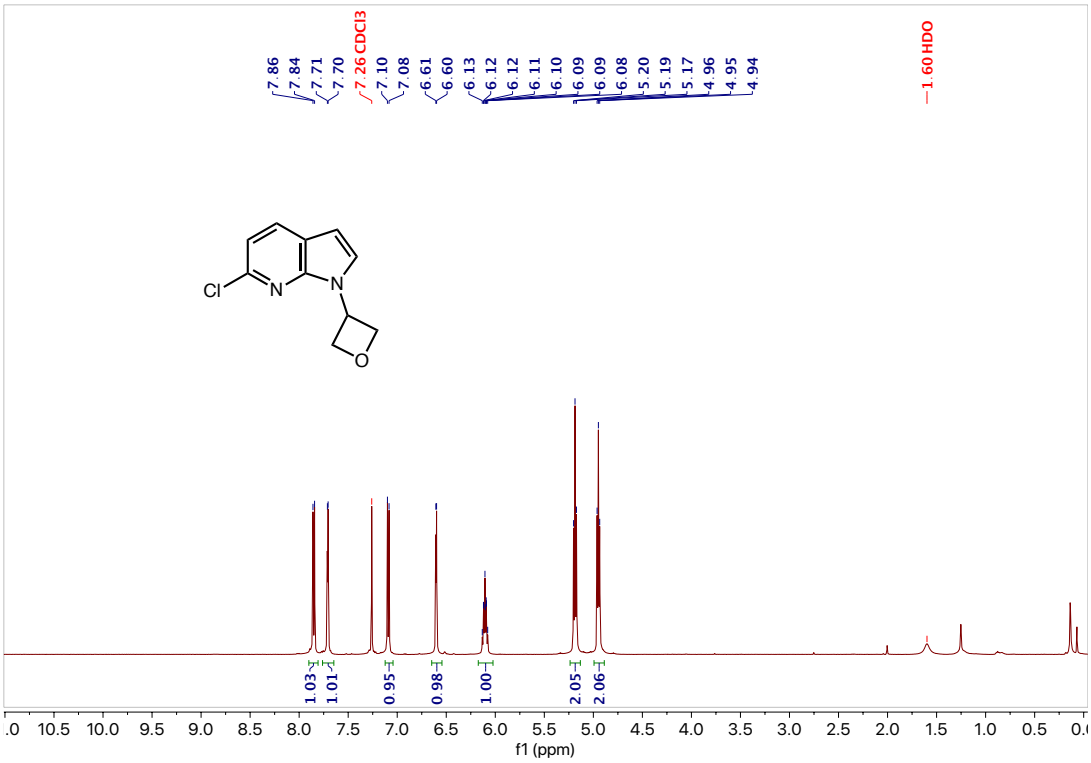


Figure S94: ^{1}H NMR spectrum of **28** (500 MHz, $CDCl_3$).

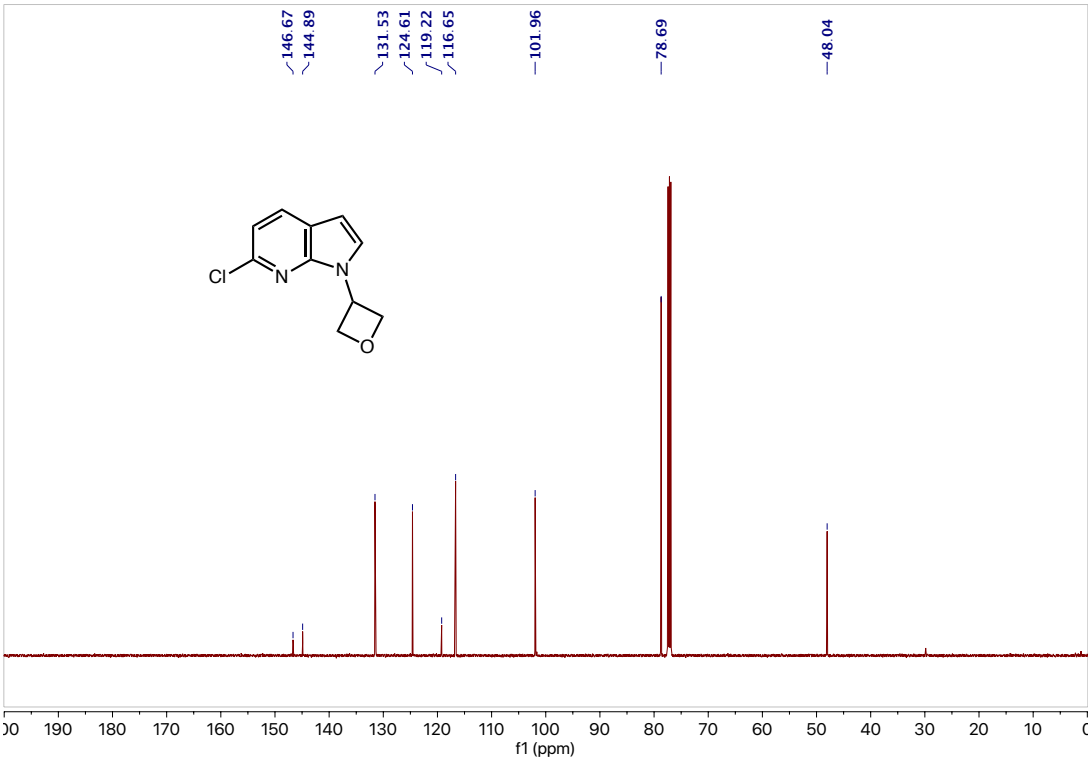


Figure S95: ^{13}C NMR spectrum of **28** (125 MHz, $CDCl_3$).

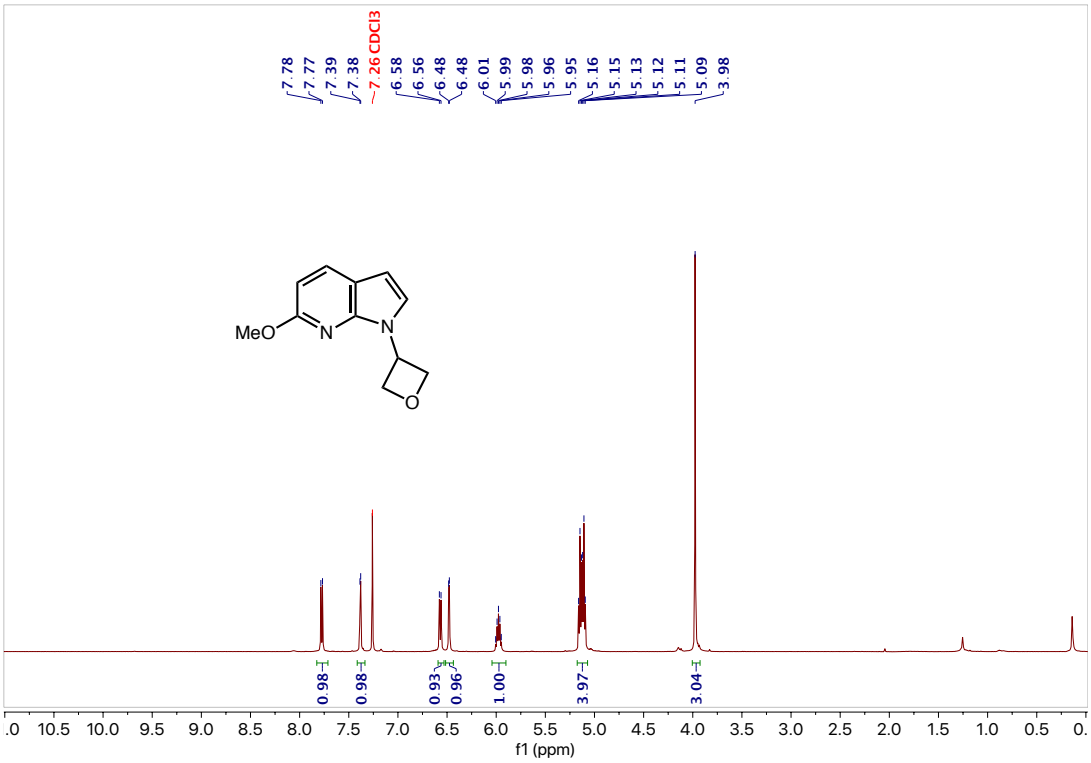


Figure S96: ^{1}H NMR spectrum of **29** (500 MHz, $CDCl_3$).

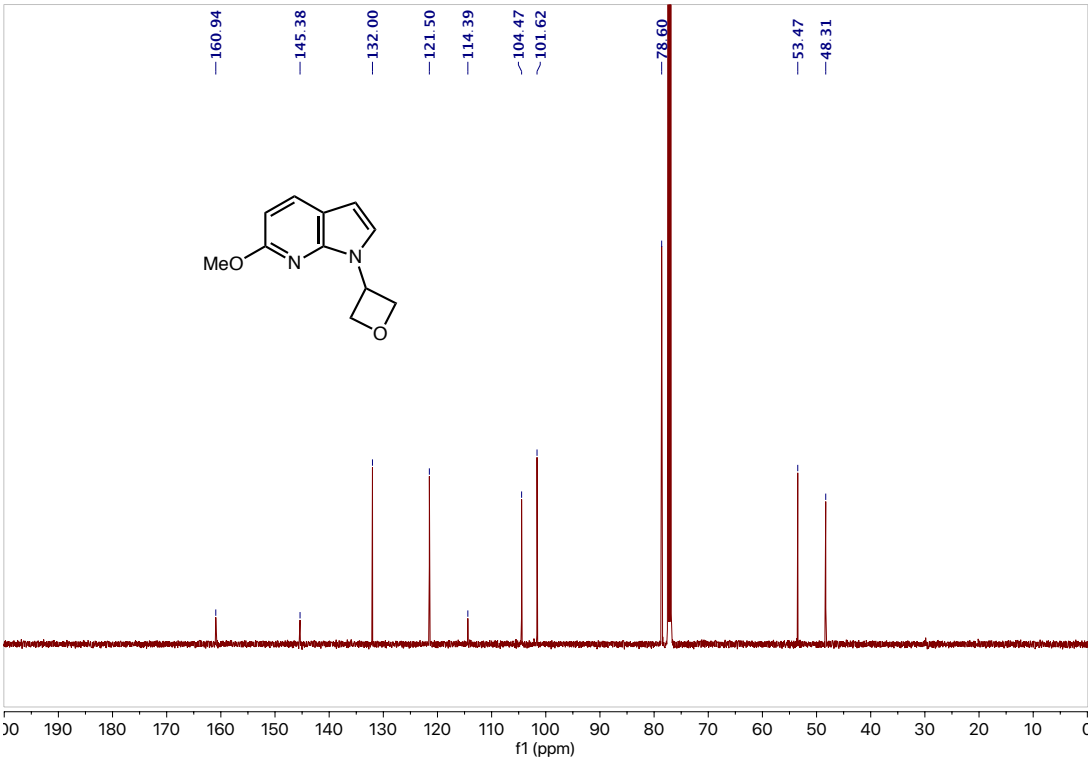


Figure S97: ^{13}C NMR spectrum of **29** (125 MHz, $CDCl_3$).

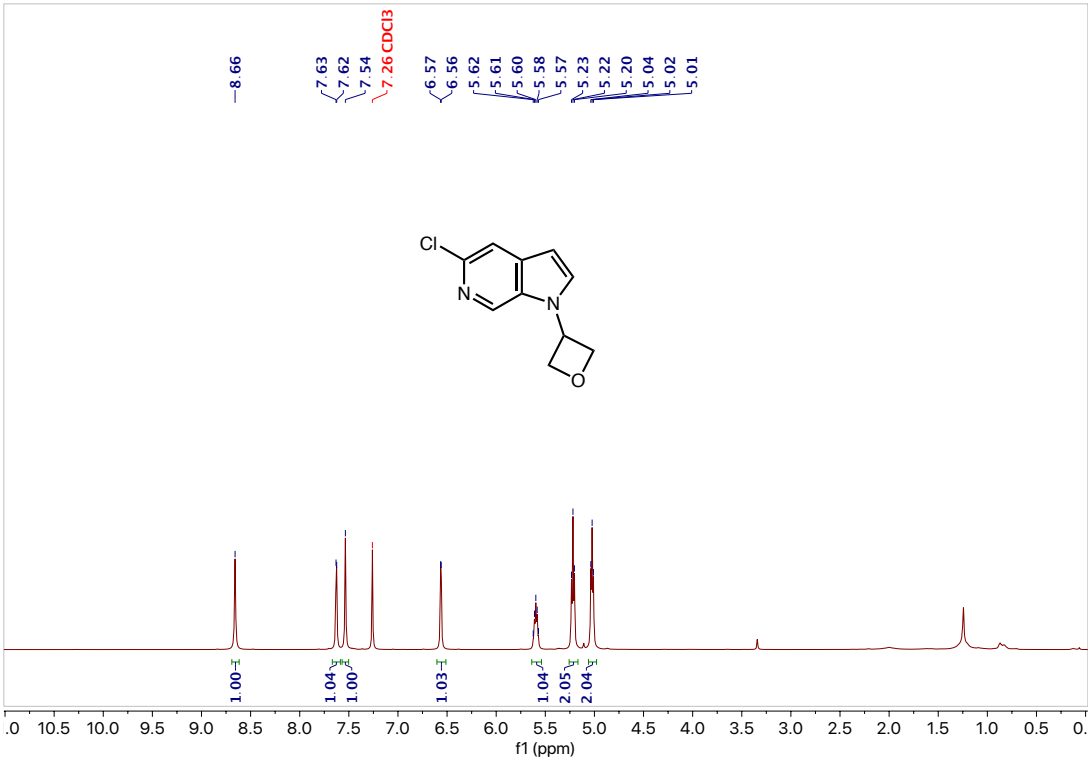


Figure S98: ^{1}H NMR spectrum of **30** (500 MHz, $CDCl_3$).

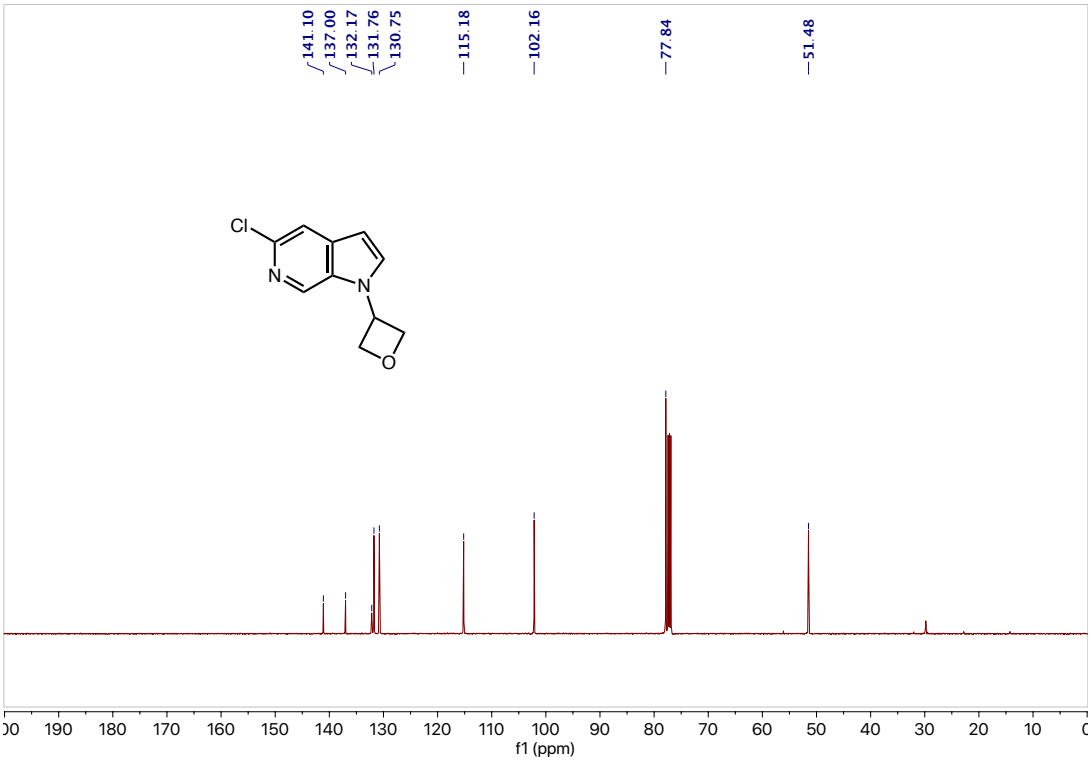


Figure S99: ^{13}C NMR spectrum of **30** (125 MHz, $CDCl_3$).

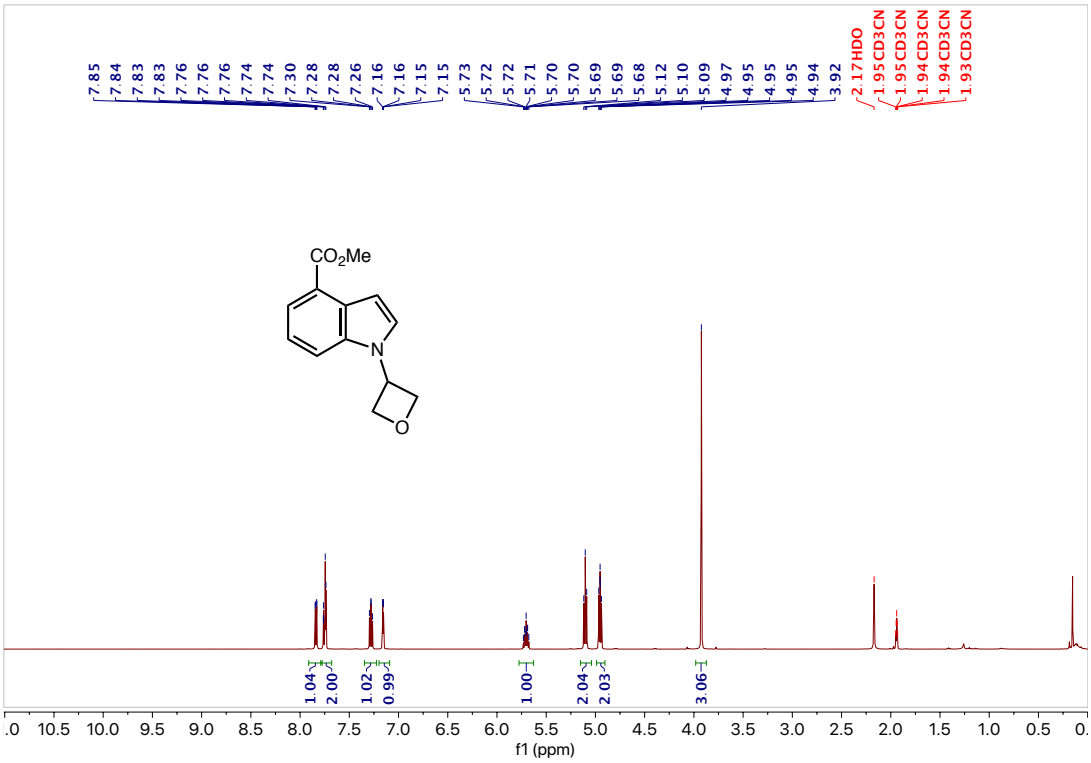


Figure S100: ^{1}H NMR spectrum of **31** (500 MHz, CD_3CN).

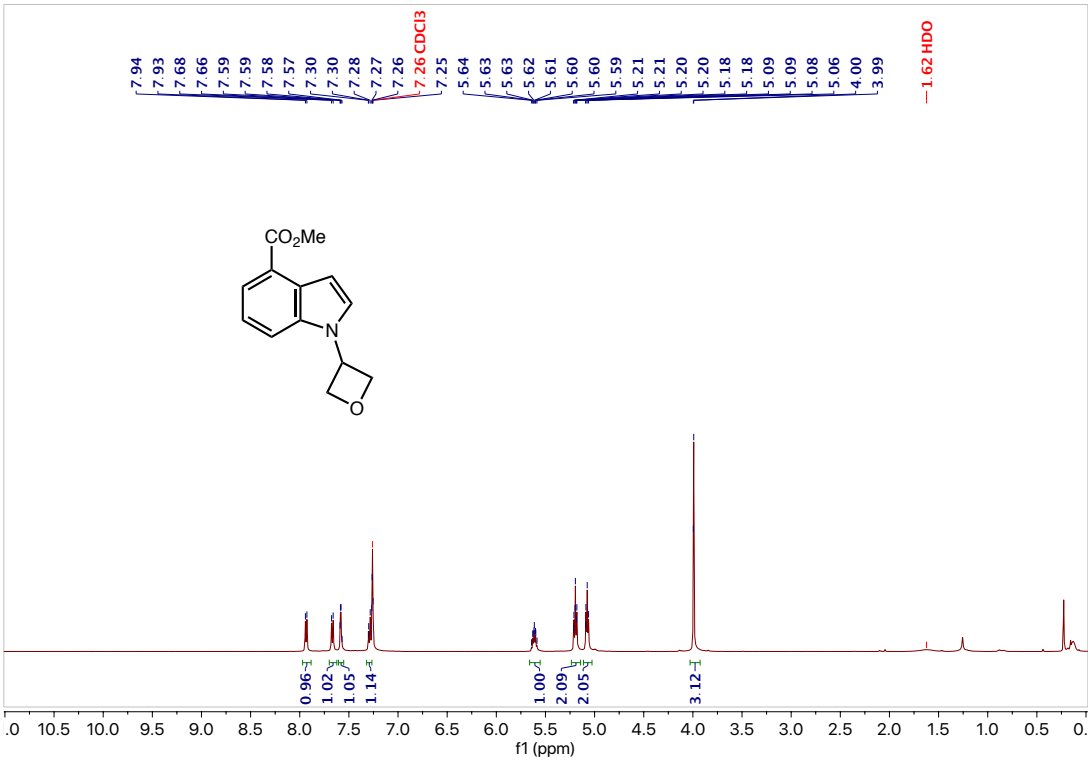


Figure S101: ^{1}H NMR spectrum of **31** (500 MHz, $CDCl_3$).

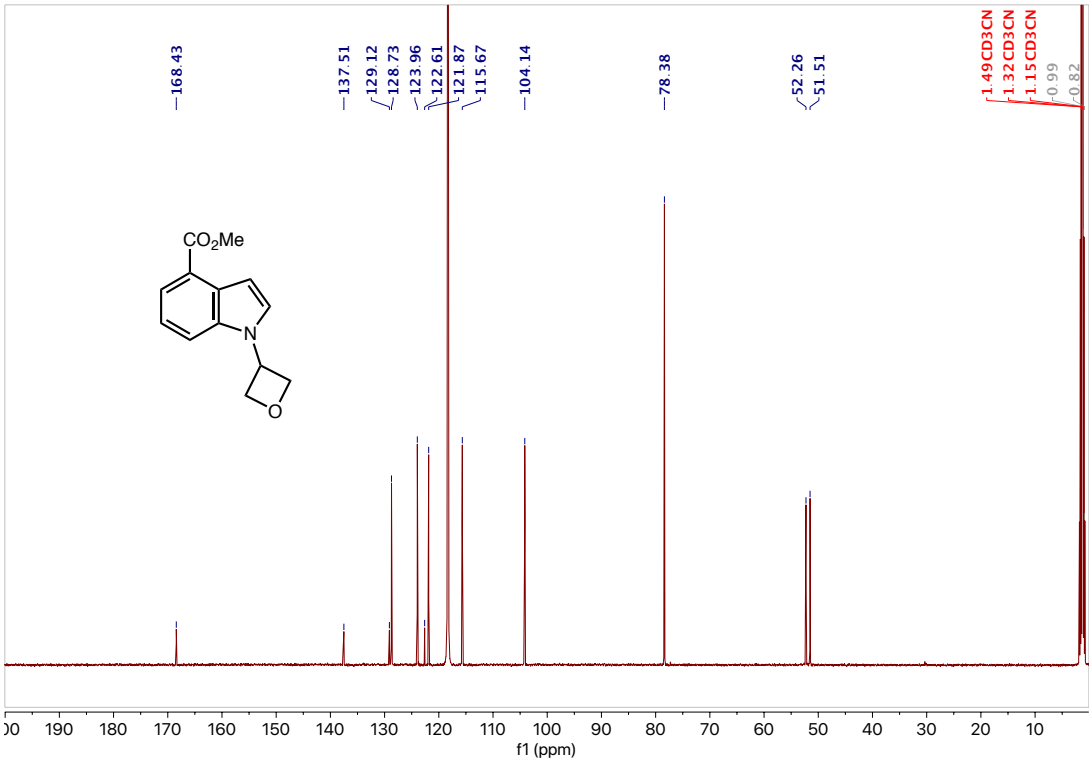


Figure S102: ^{13}C NMR spectrum of **31** (125 MHz, CD_3CN).

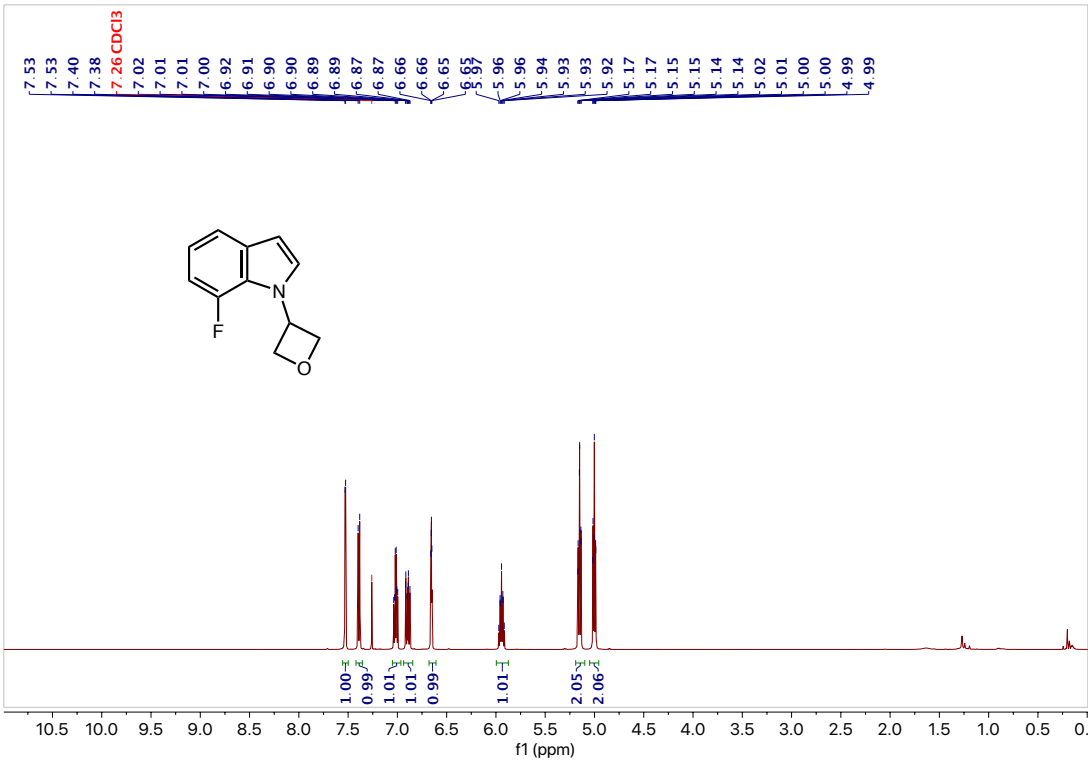


Figure S103: ^{1}H NMR spectrum of **32** (500 MHz, $CDCl_3$).

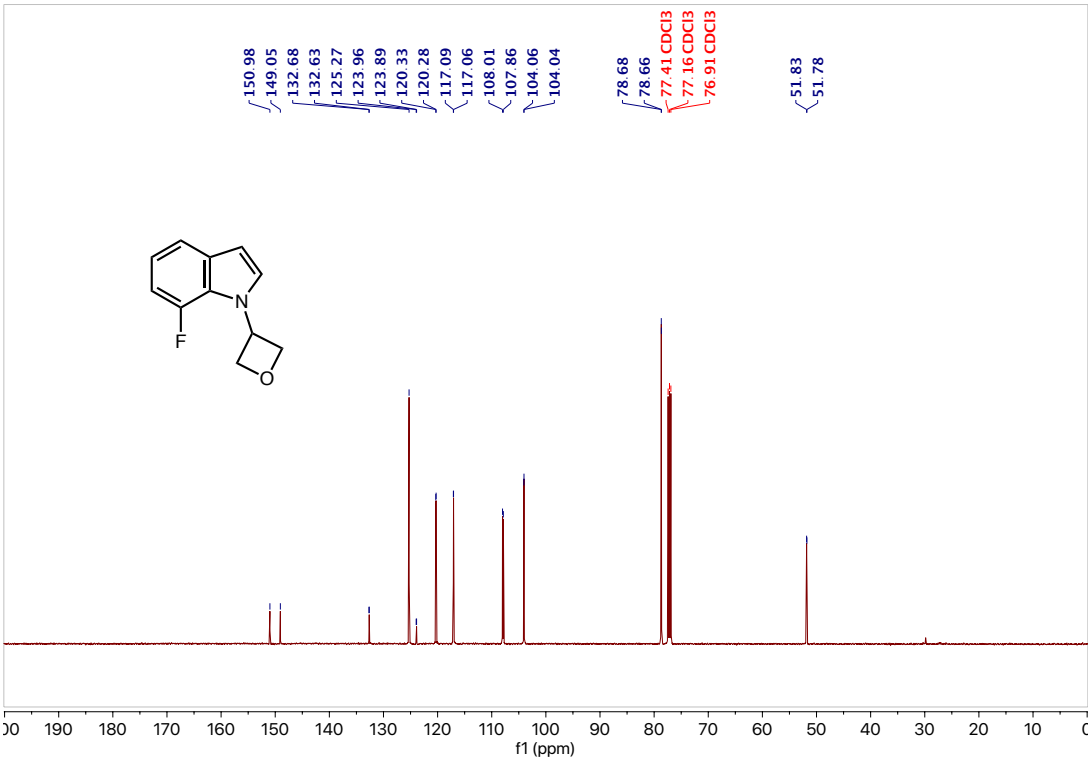


Figure S104: ^{13}C NMR spectrum of **32** (125 MHz, $CDCl_3$).

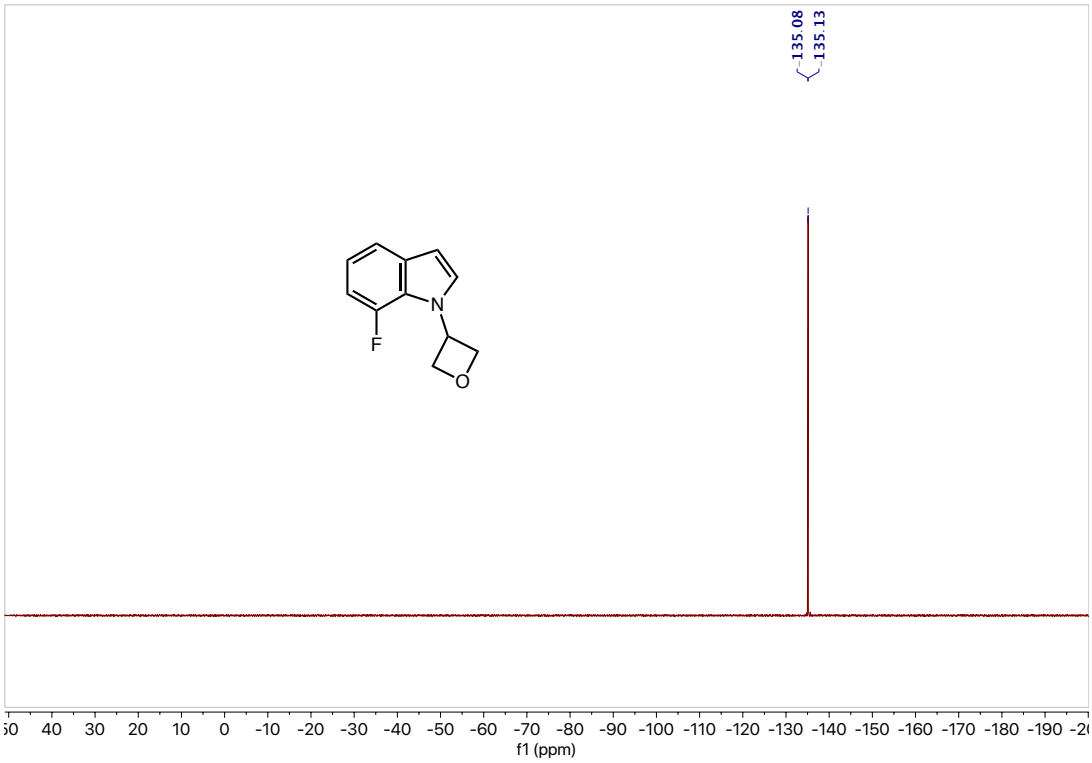


Figure S105: ^{19}F NMR spectrum of **32** (282 MHz, $CDCl_3$).

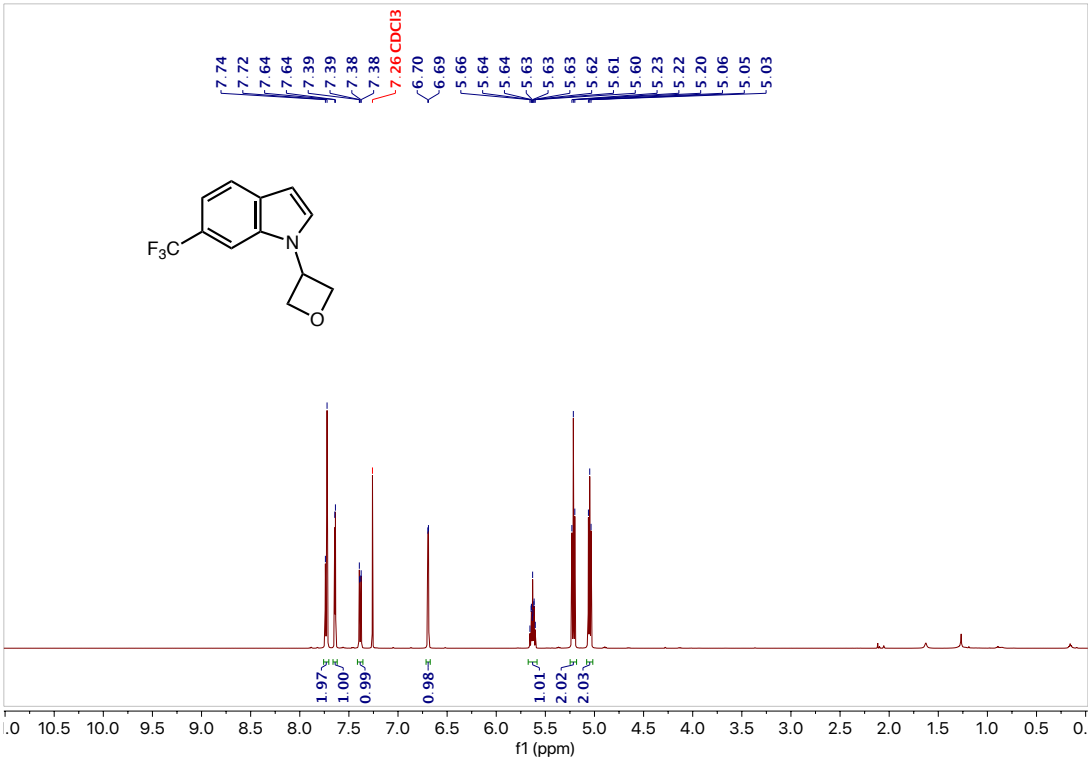


Figure S106: ^{1}H NMR spectrum of **33** (500 MHz, $CDCl_3$).

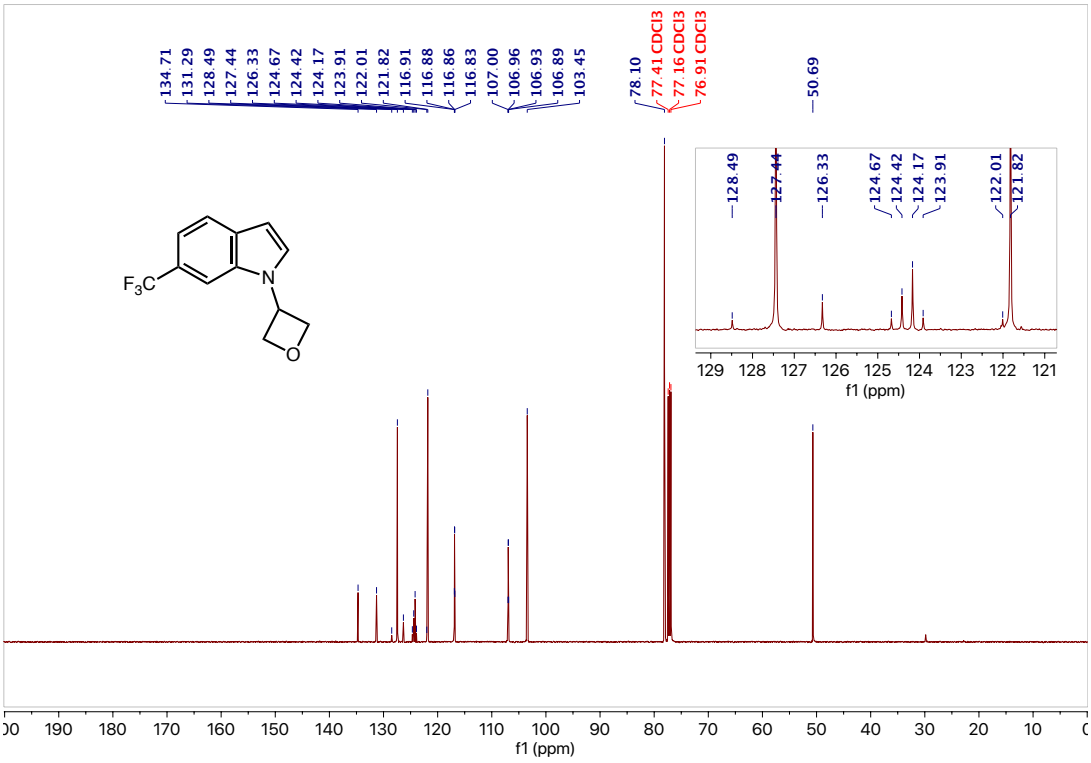


Figure S107: ^{13}C NMR spectrum of **33** (125 MHz, $CDCl_3$).

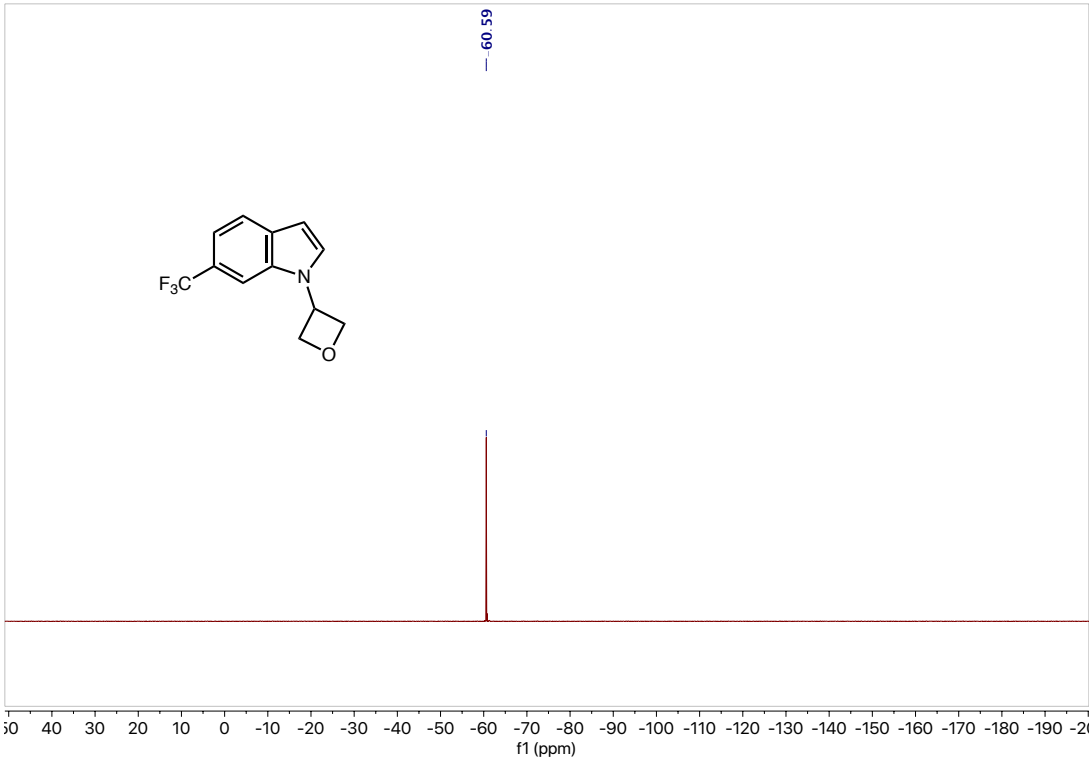


Figure S108: ^{19}F NMR spectrum of **33** (282 MHz, $CDCl_3$).

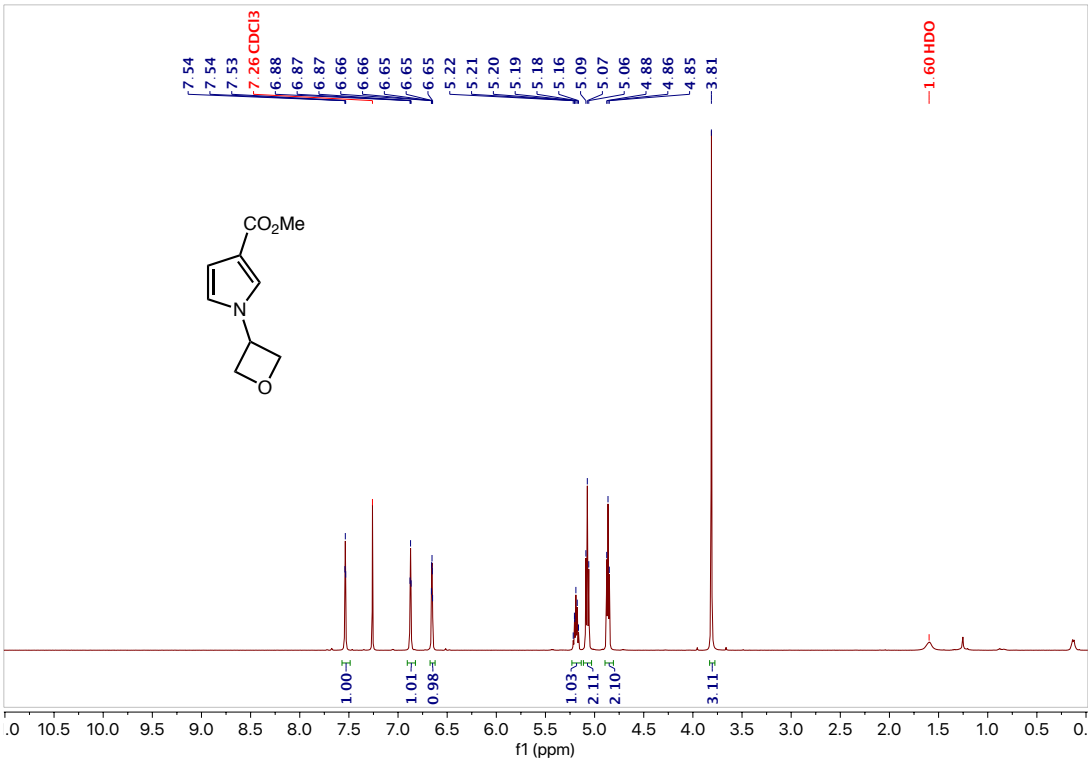


Figure S109: ^{1}H NMR spectrum of **34** (500 MHz, $CDCl_3$).

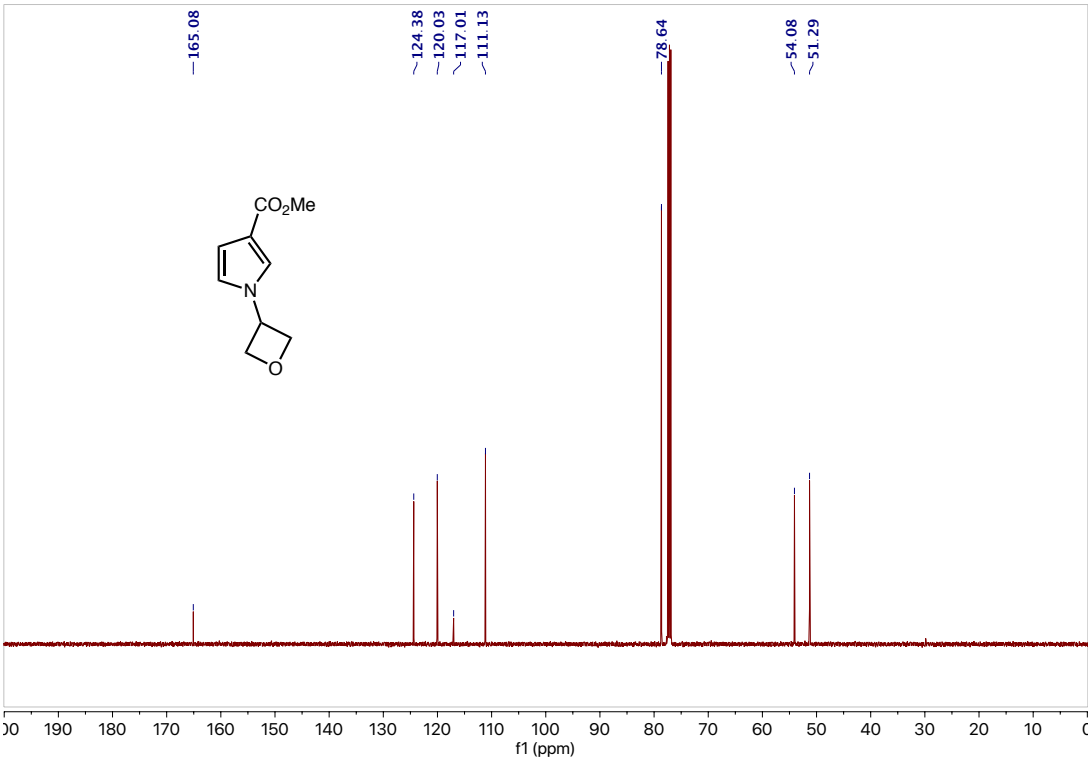


Figure S110: ^{13}C NMR spectrum of **34** (125 MHz, $CDCl_3$).

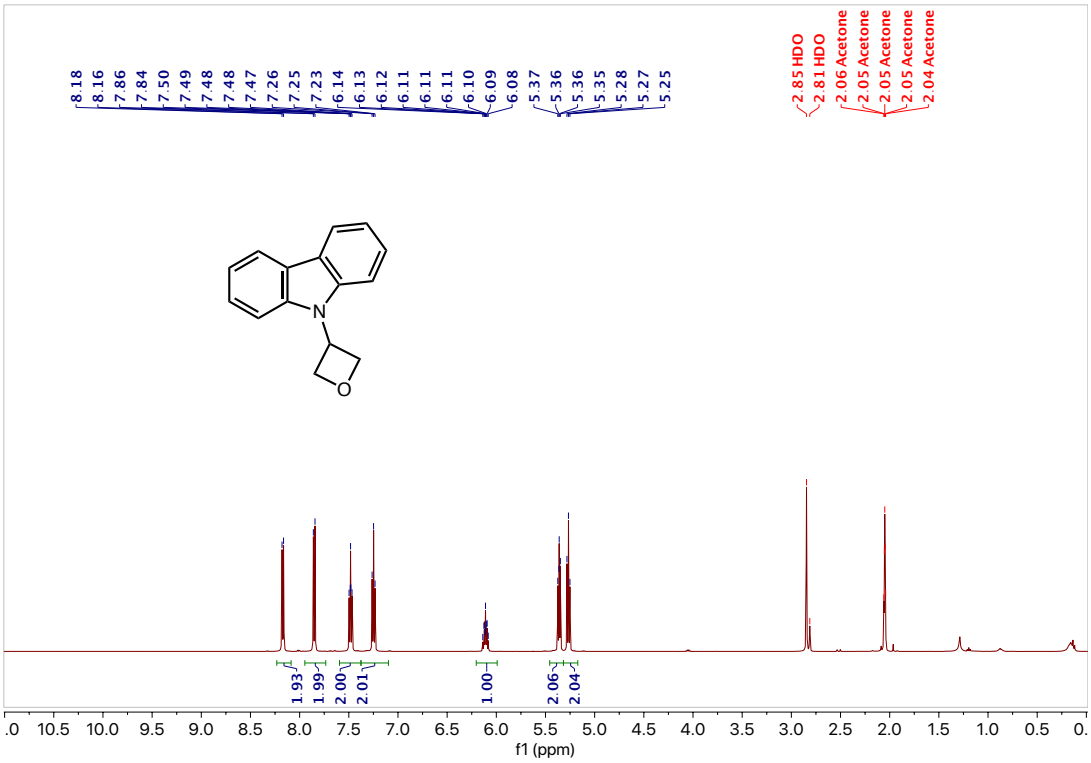


Figure S111: ^{1}H NMR spectrum of **35** (500 MHz, $(CD_3)_2CO$).

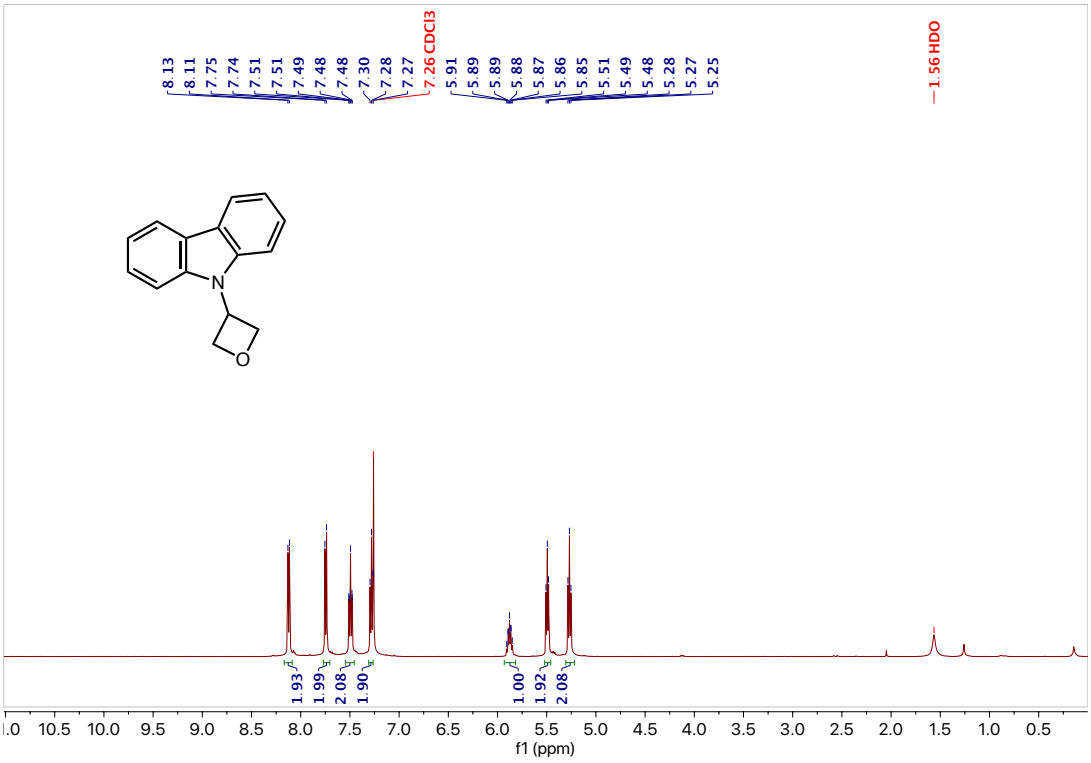


Figure S112: ^{1}H NMR spectrum of **35** (500 MHz, $CDCl_3$).

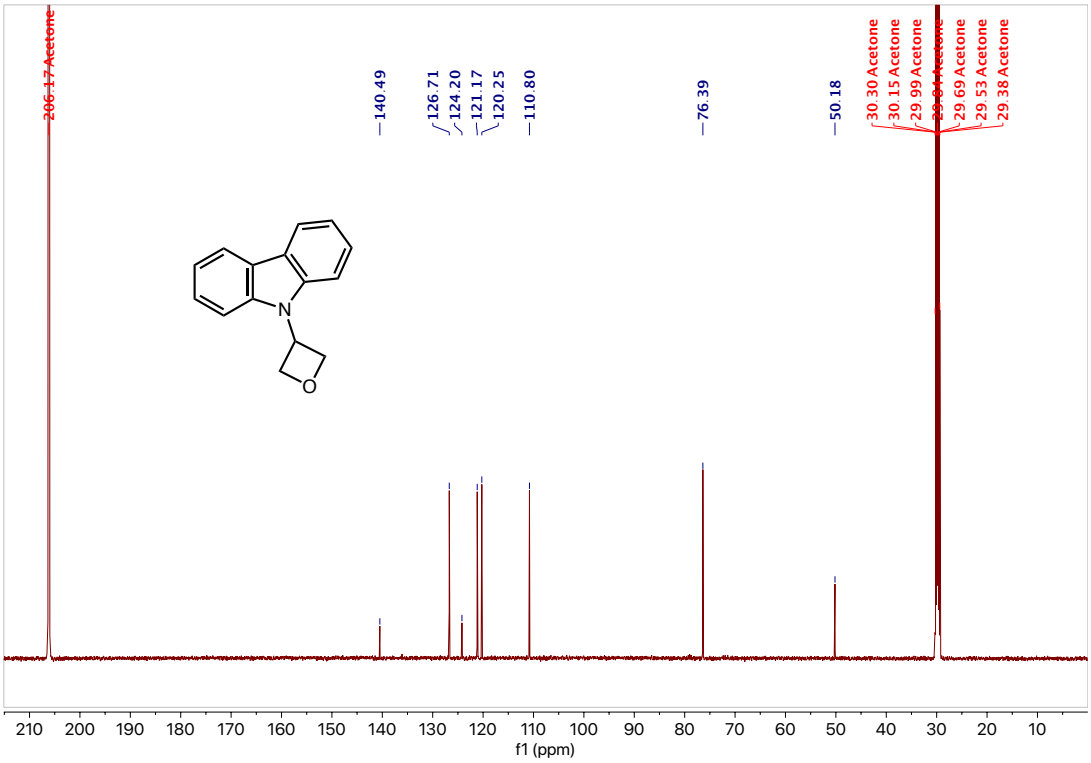


Figure S113: ^{13}C NMR spectrum of **35** (125 MHz, $(CD_3)_2CO$).

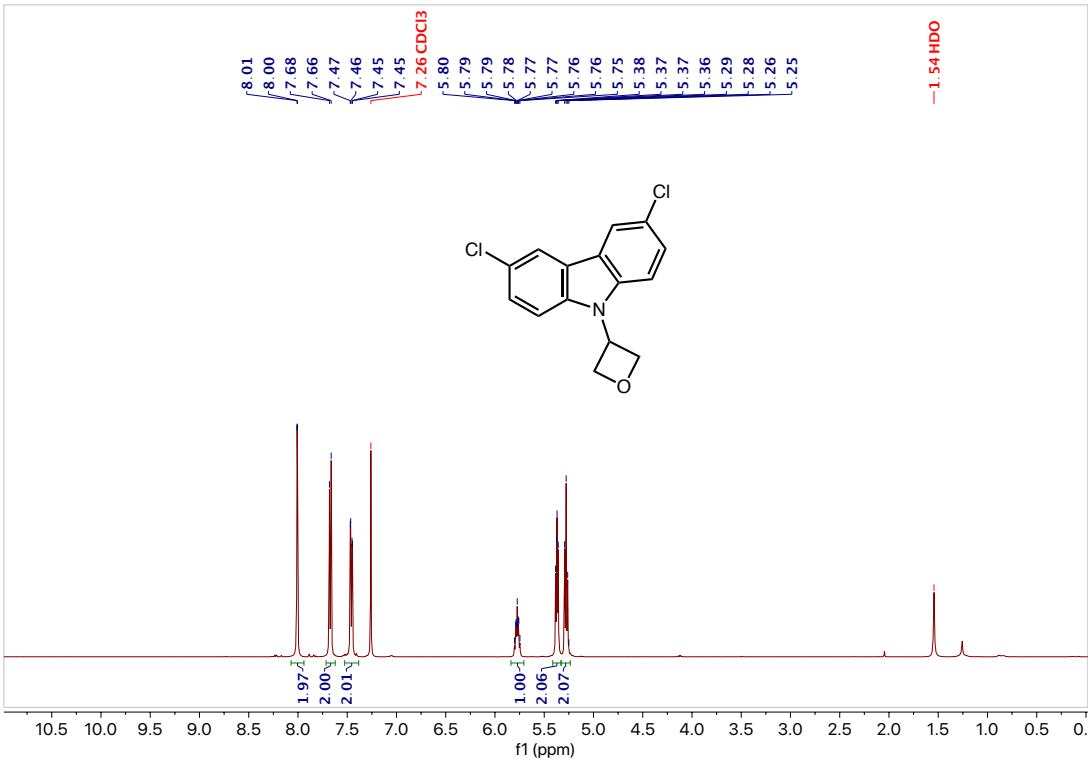


Figure S114: ^{1}H NMR spectrum of **36** (500 MHz, $CDCl_3$).

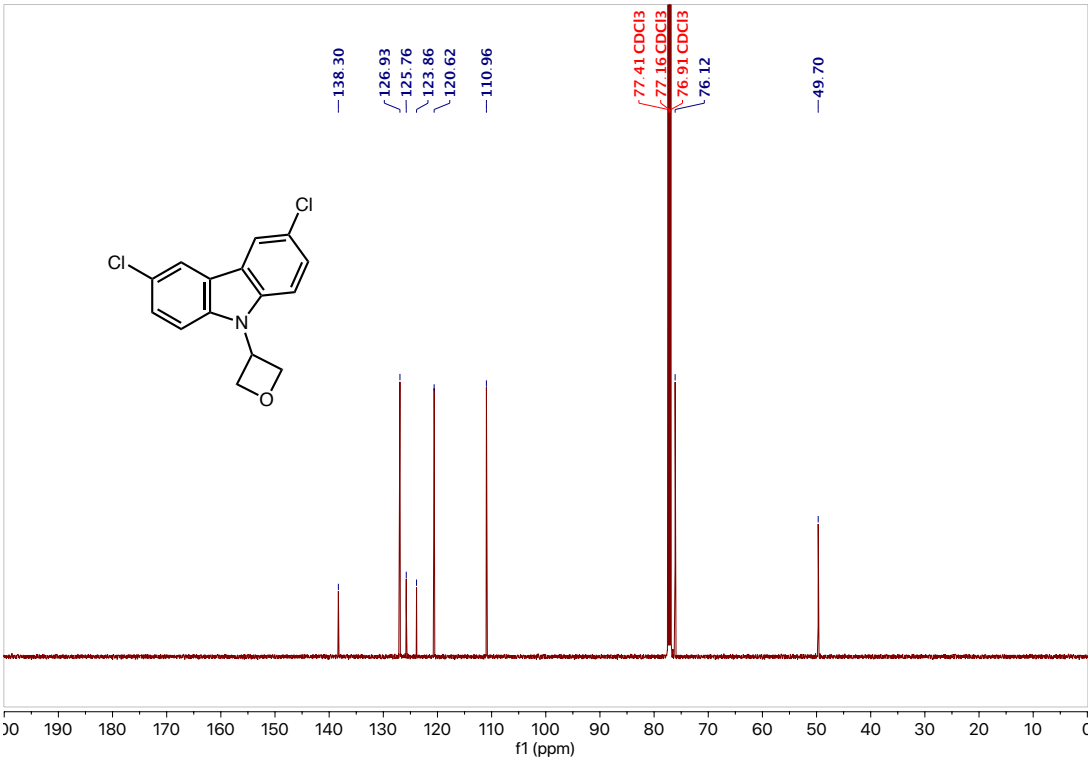


Figure S115: ^{13}C NMR spectrum of **36** (125 MHz, $CDCl_3$).

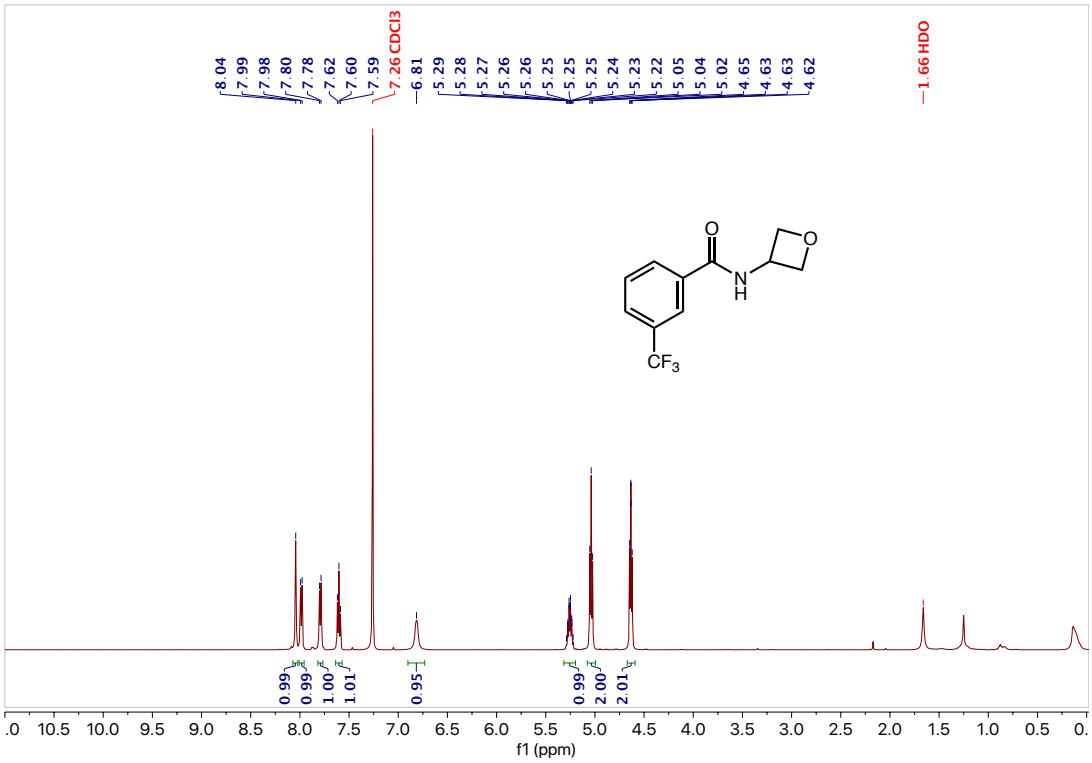


Figure S116: ^{1}H NMR spectrum of **37** (500 MHz, $CDCl_3$).

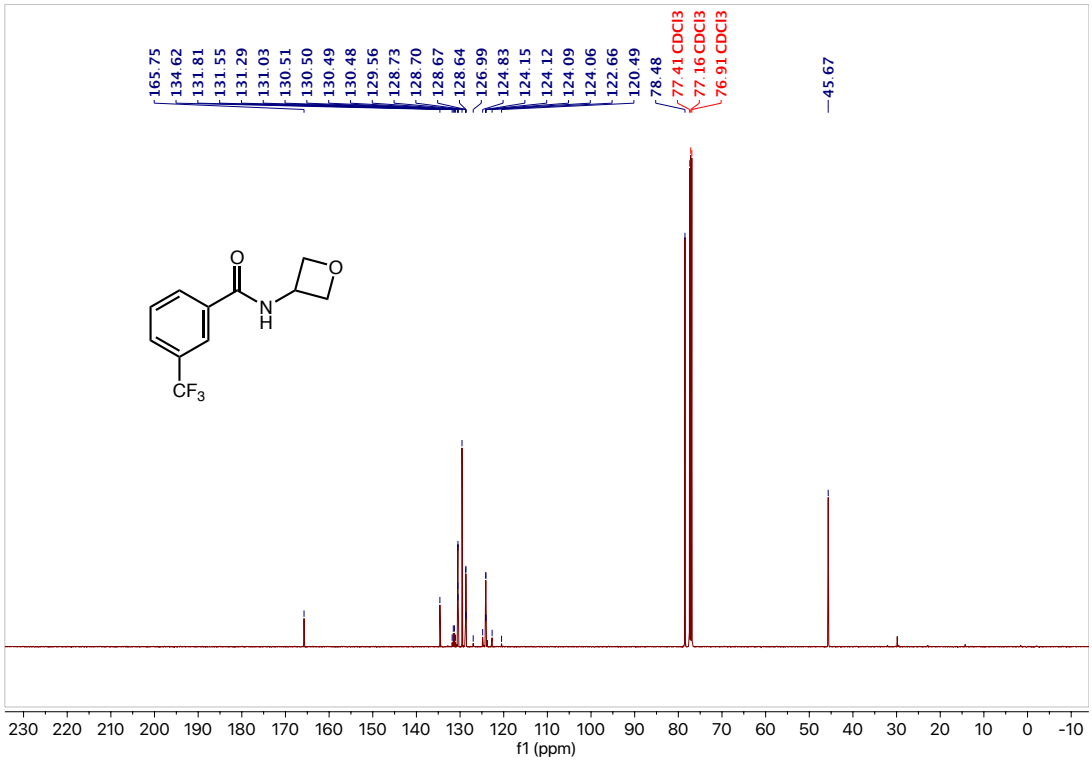


Figure S117: ^{13}C NMR spectrum of **37** (125 MHz, $CDCl_3$).

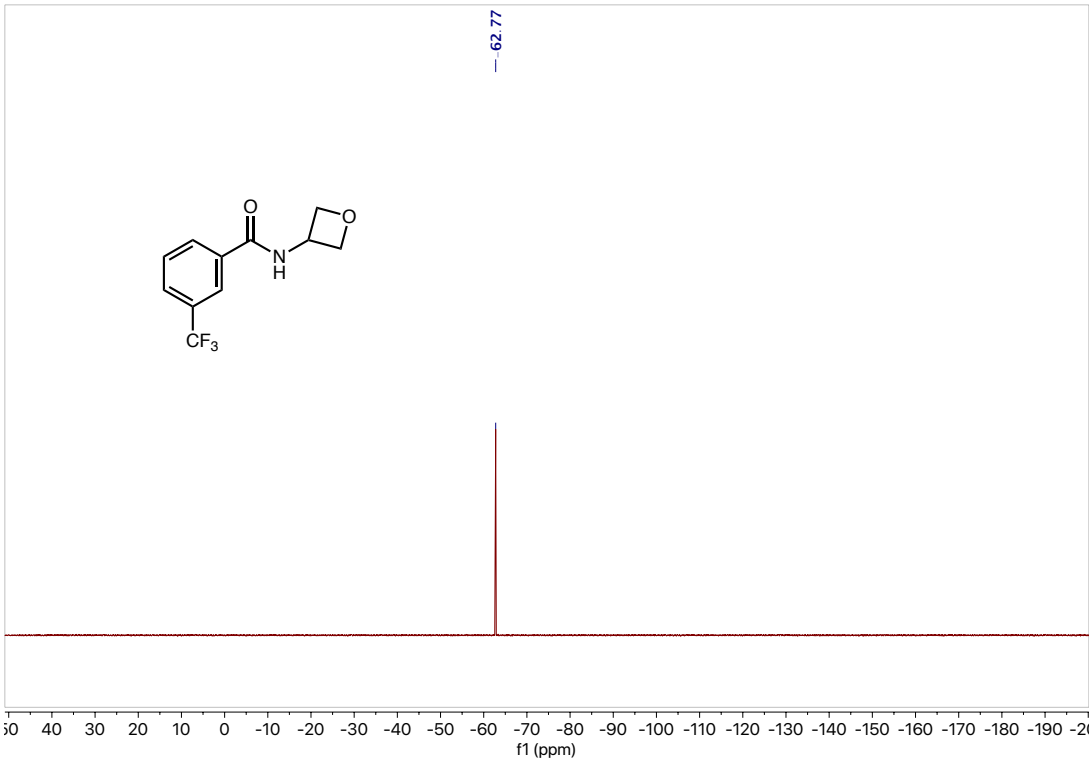


Figure S118: ^{19}F NMR spectrum of **37** (282 MHz, $CDCl_3$).

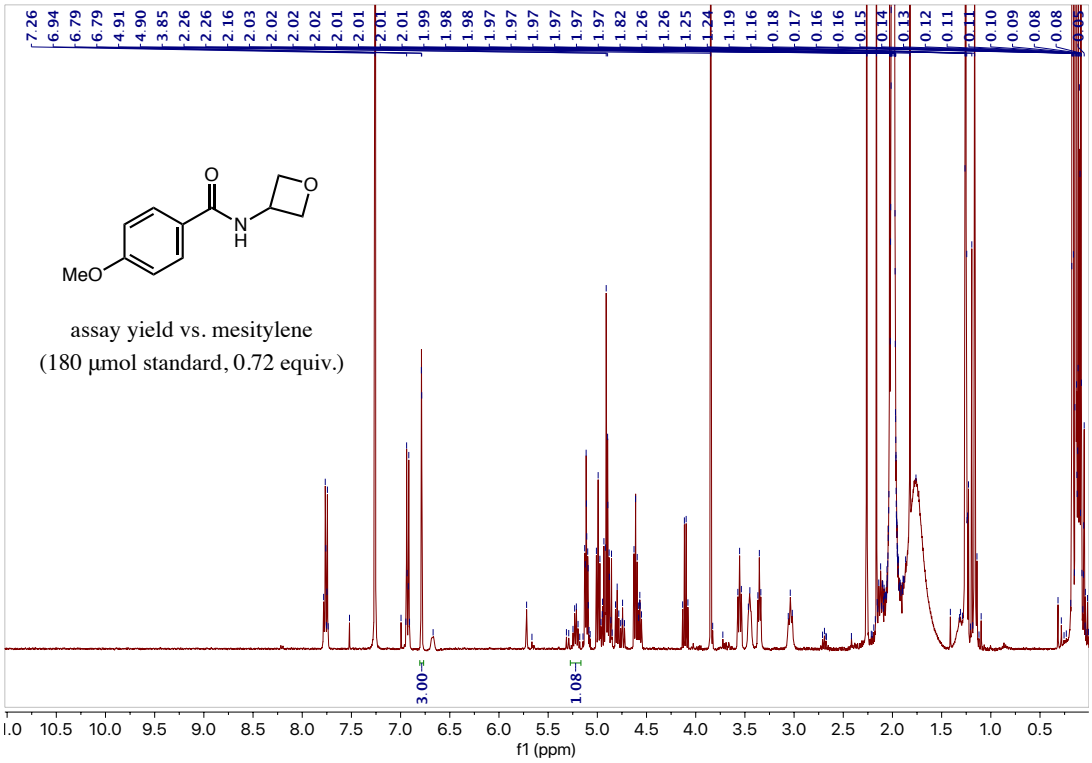


Figure S119: ^{1}H NMR assay of **38** using mesitylene as an internal standard (500 MHz, $CDCl_3$).

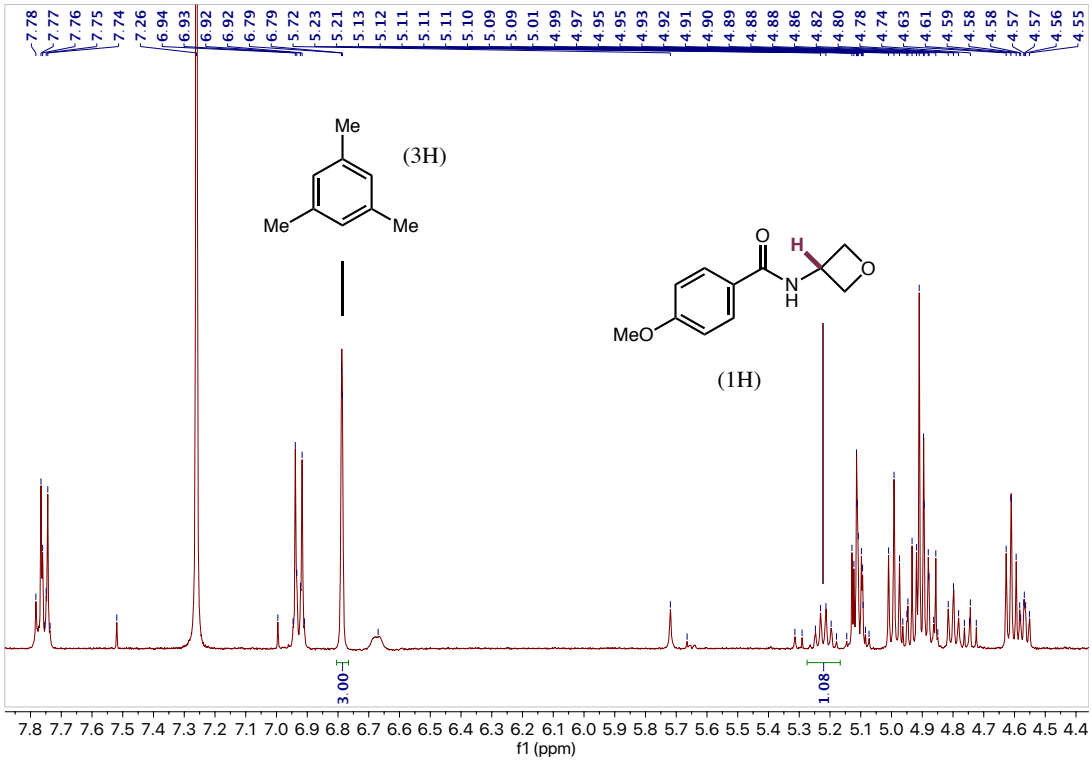


Figure S120: Assignment of **Figure S119** (500 MHz, $CDCl_3$).

[(1.08 mmol **38**/mmol Mes) * 0.180 mmol Mes]/0.250 mmol **38** (theoretical) = *78% assay yield*

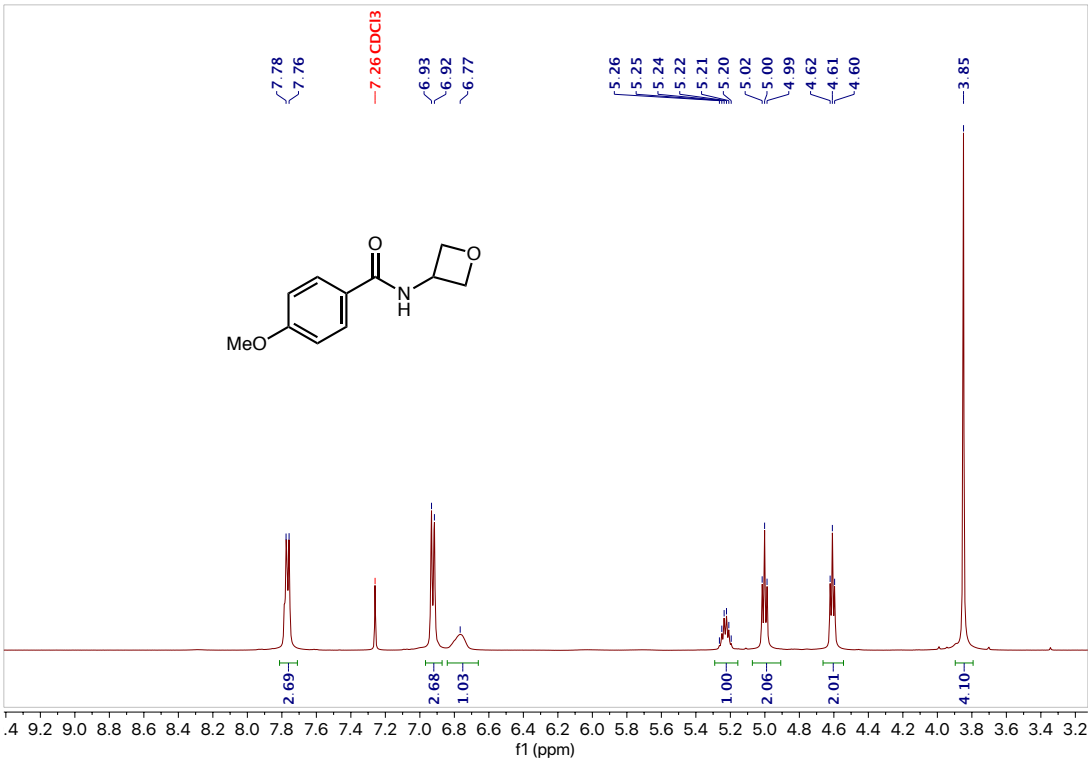


Figure S121: Confirmation of ^{1}H NMR assignments for **38** using semi-pure material (500 MHz, $CDCl_3$). (impure mixture with 4-methoxybenzamide)

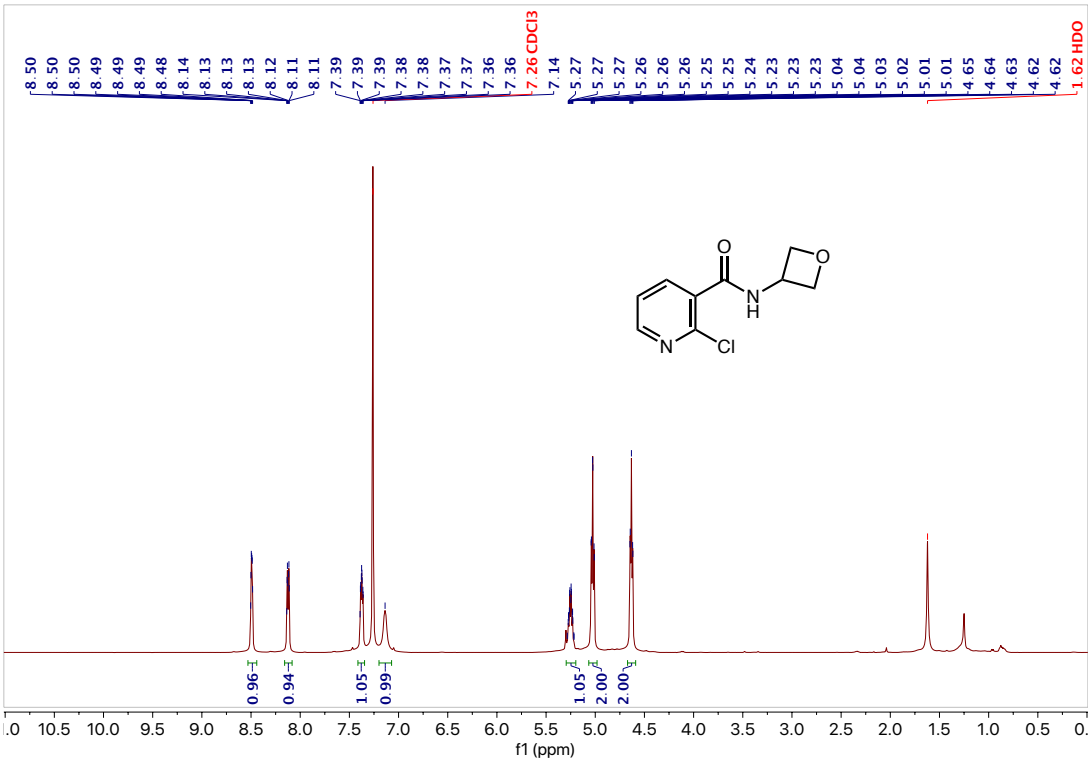


Figure S122: ^{1}H NMR spectrum of **39** (500 MHz, $CDCl_3$).

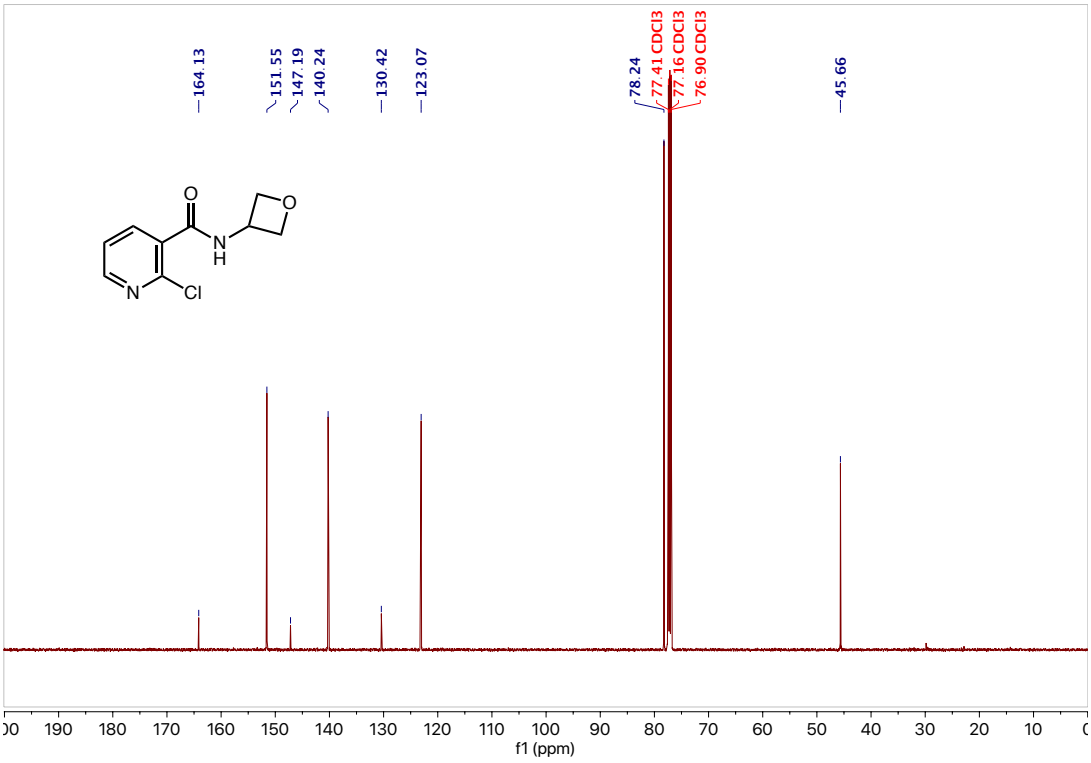


Figure S123: ^{13}C NMR spectrum of **39** (125 MHz, $CDCl_3$).

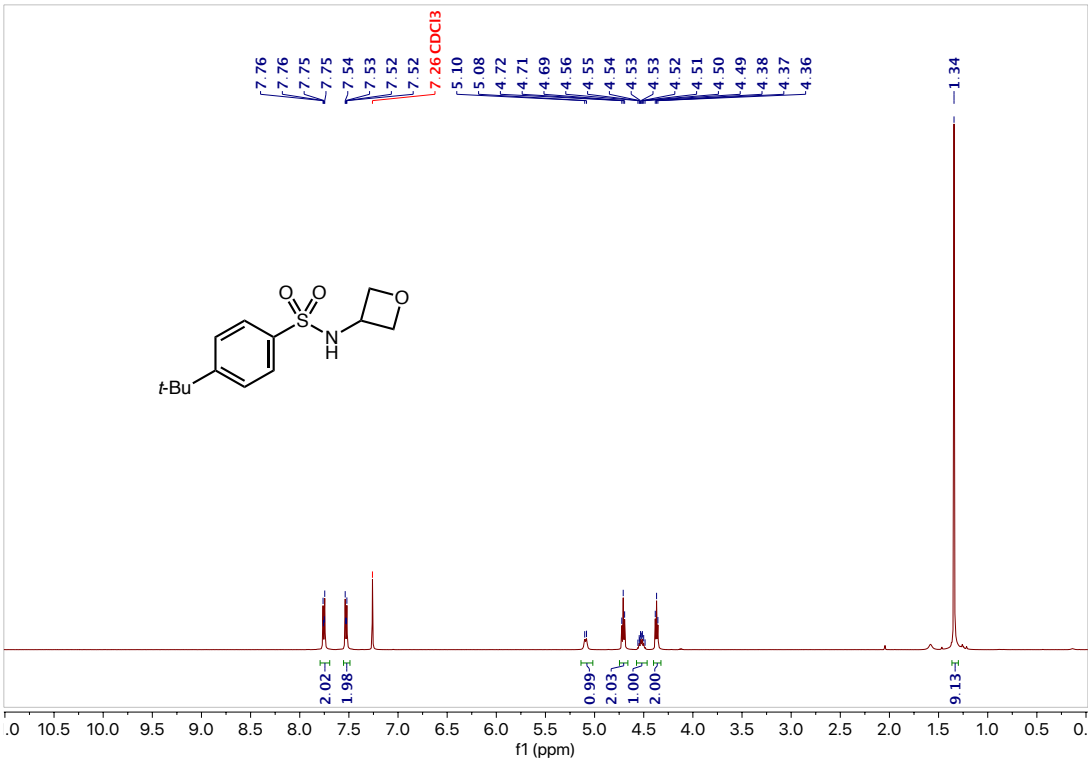


Figure S124: ^{1}H NMR spectrum of **40** (500 MHz, $CDCl_3$).

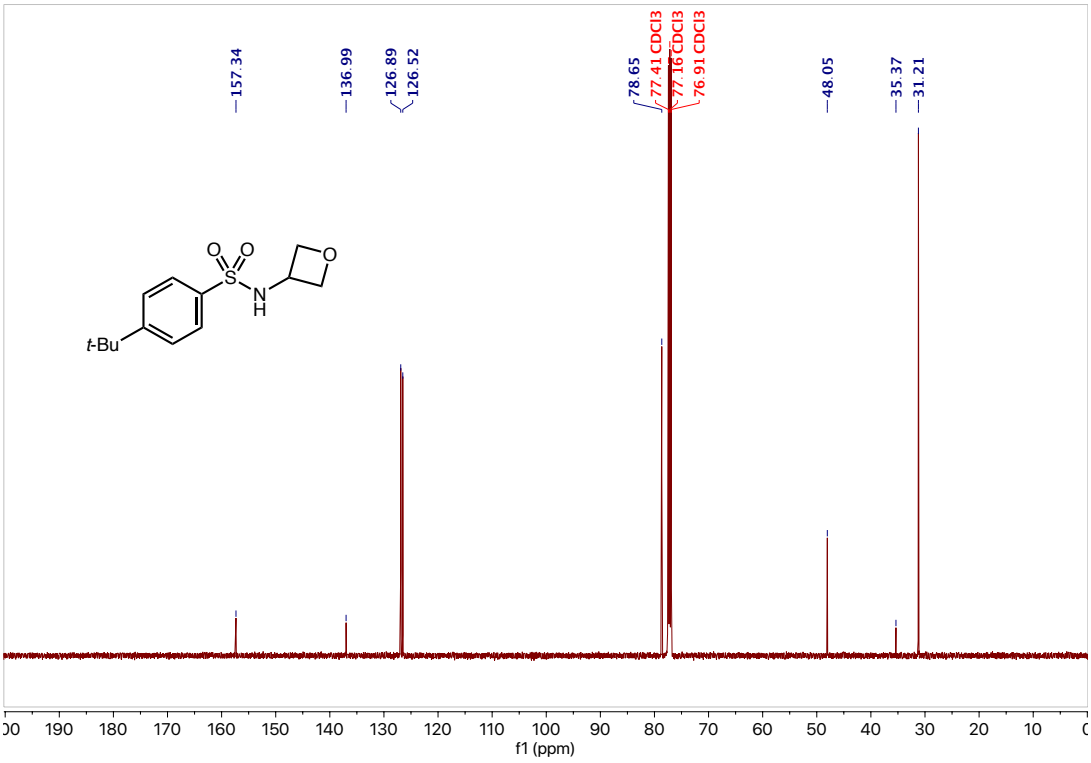


Figure S125: ^{13}C NMR spectrum of **40** (125 MHz, $CDCl_3$).

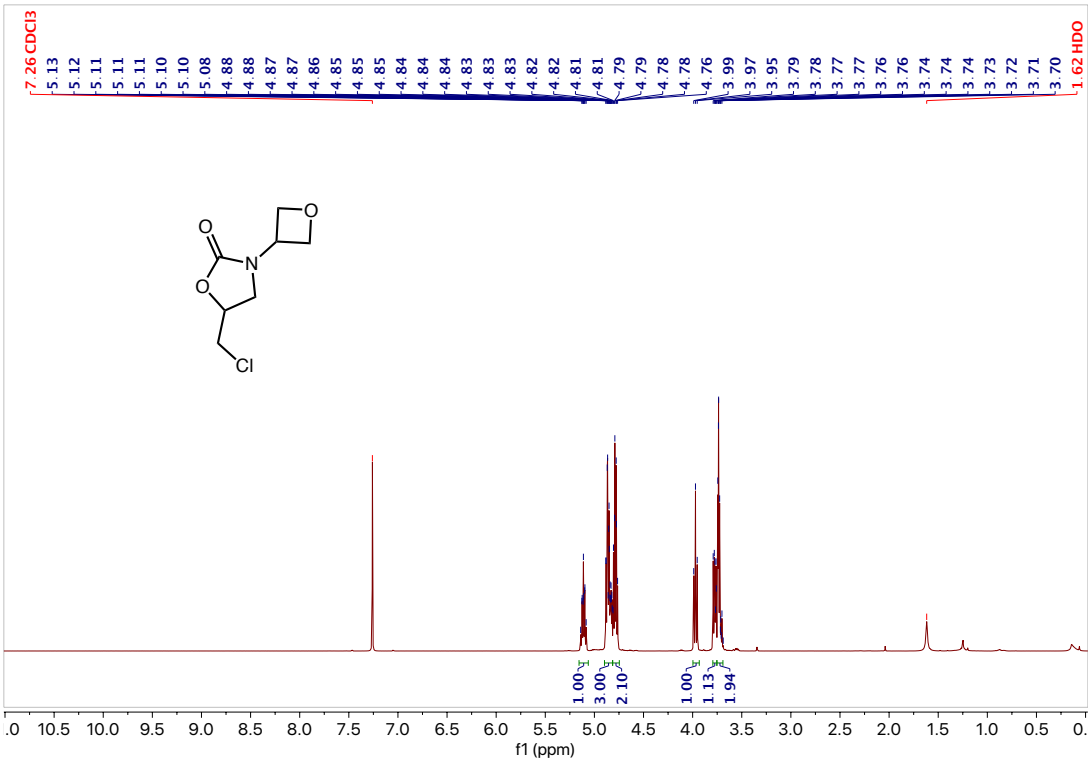


Figure S126: ^{1}H NMR spectrum of **(±)-41** (500 MHz, $CDCl_3$).

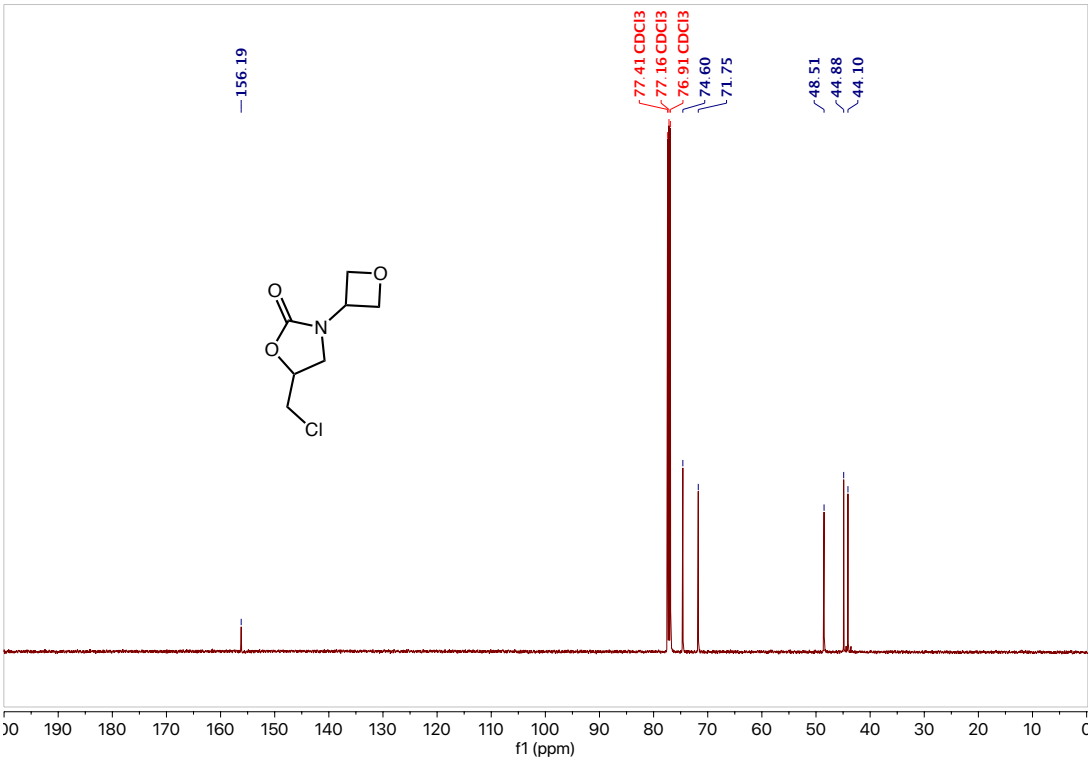


Figure S127: ^{13}C NMR spectrum of **(±)-41** (125 MHz, $CDCl_3$).

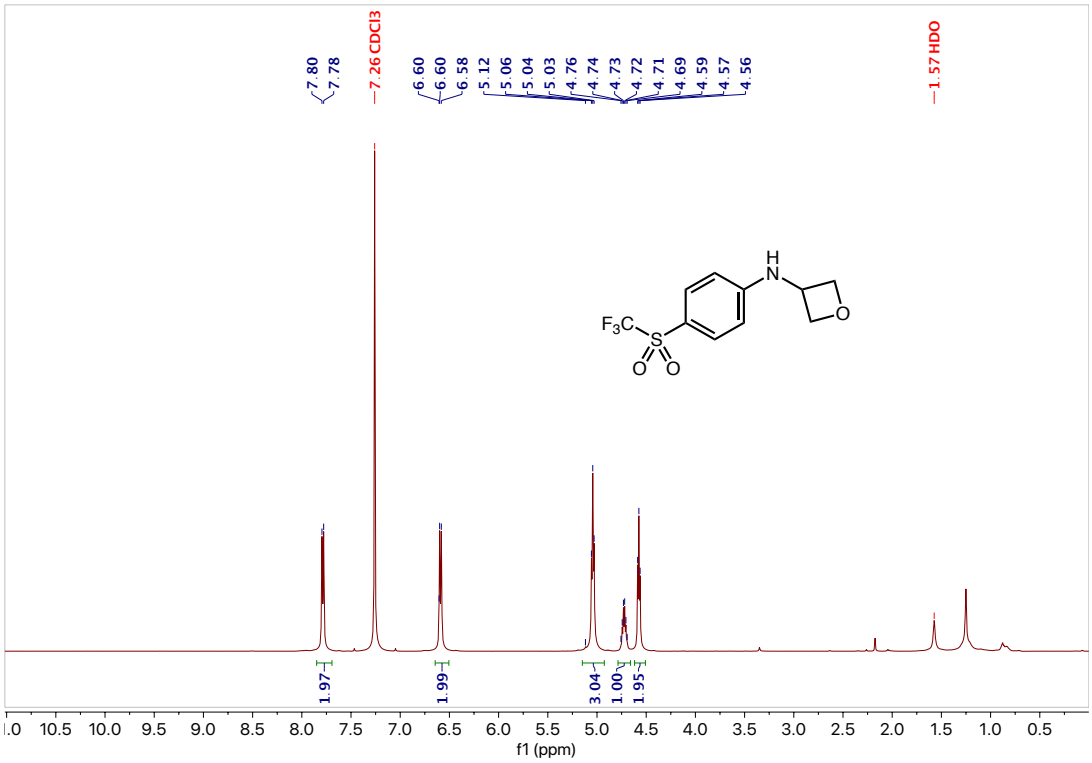


Figure S128: ^{1}H NMR spectrum of **42** (500 MHz, $CDCl_3$).

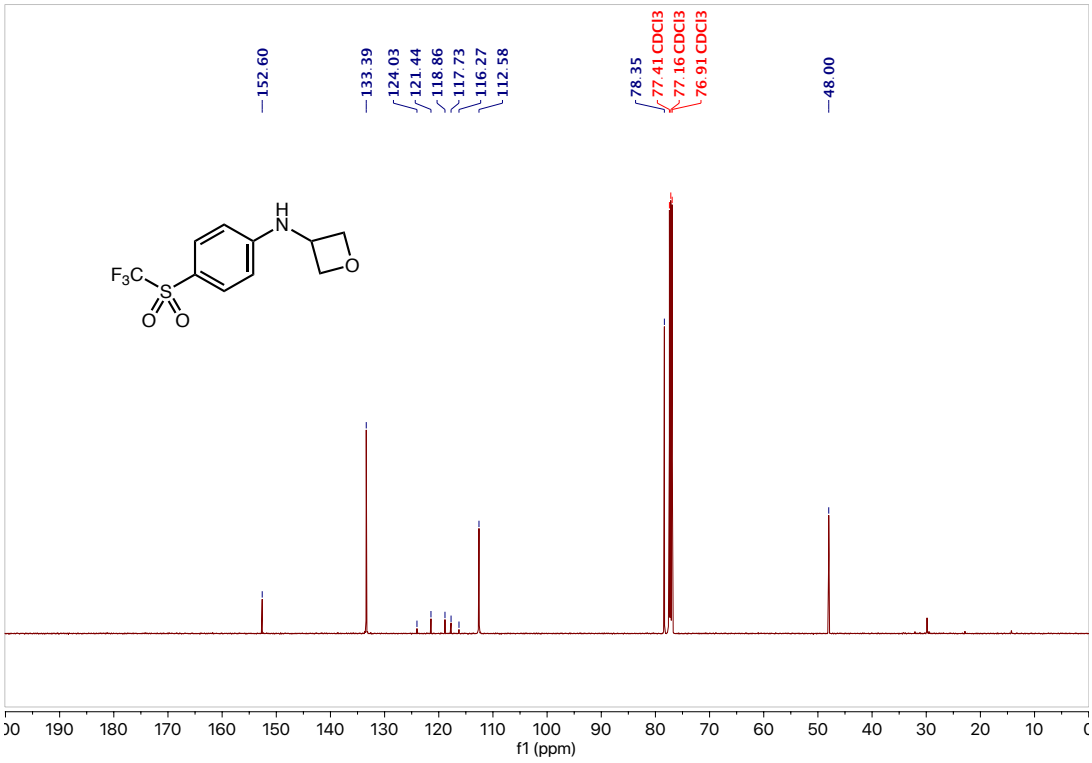


Figure S129: ^{13}C NMR spectrum of **42** (125 MHz, $CDCl_3$).

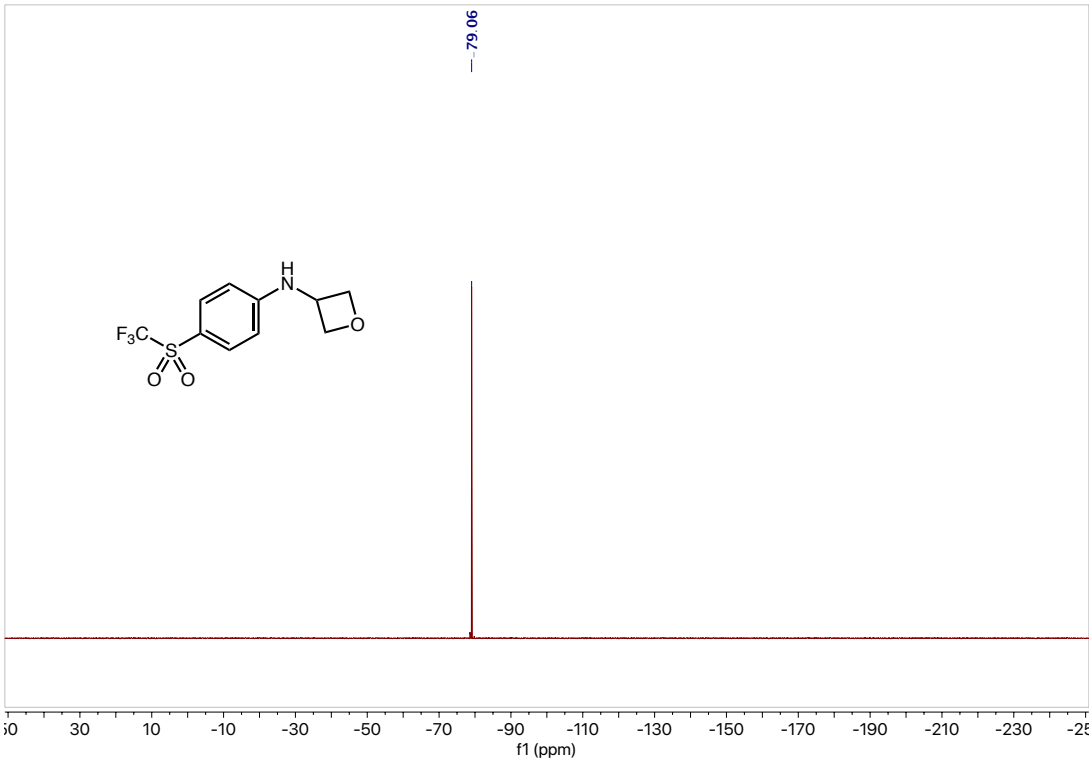


Figure S130: ^{19}F NMR spectrum of **42** (282 MHz, $CDCl_3$).

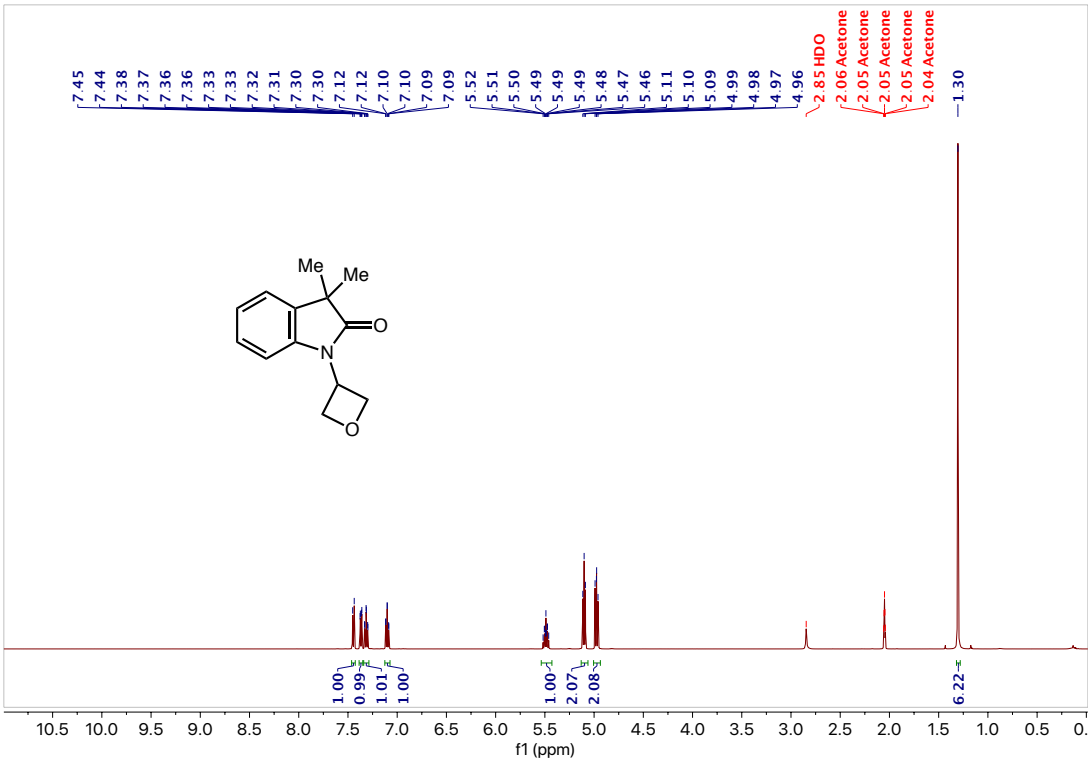


Figure S131: ^{1}H NMR spectrum of **43** (500 MHz, $(CD_3)_2CO$).

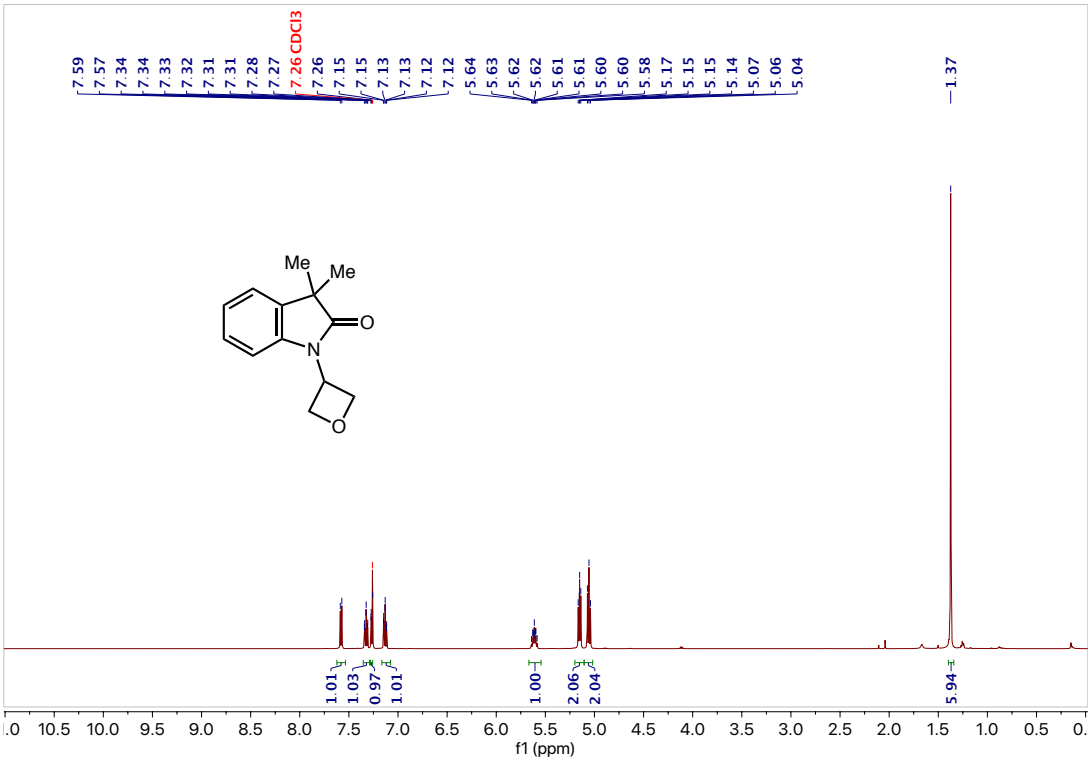


Figure S132: ^{1}H NMR spectrum of **43** (500 MHz, $CDCl_3$).

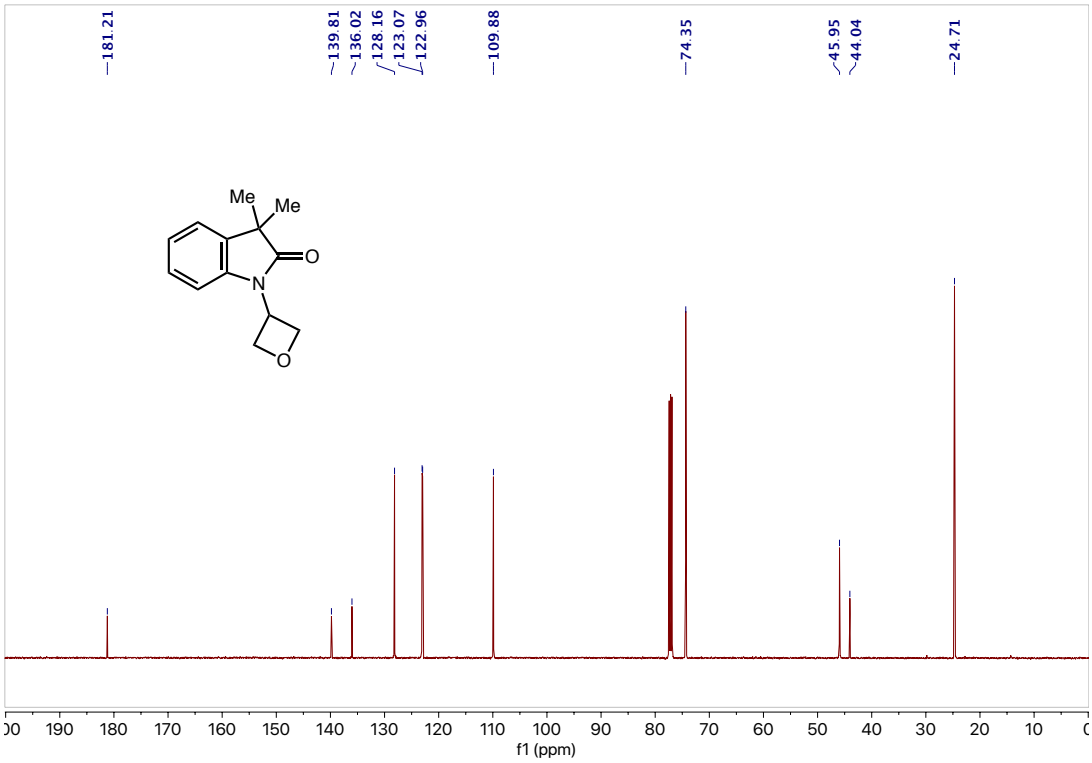


Figure S133: ^{13}C NMR spectrum of **43** (125 MHz, $CDCl_3$).

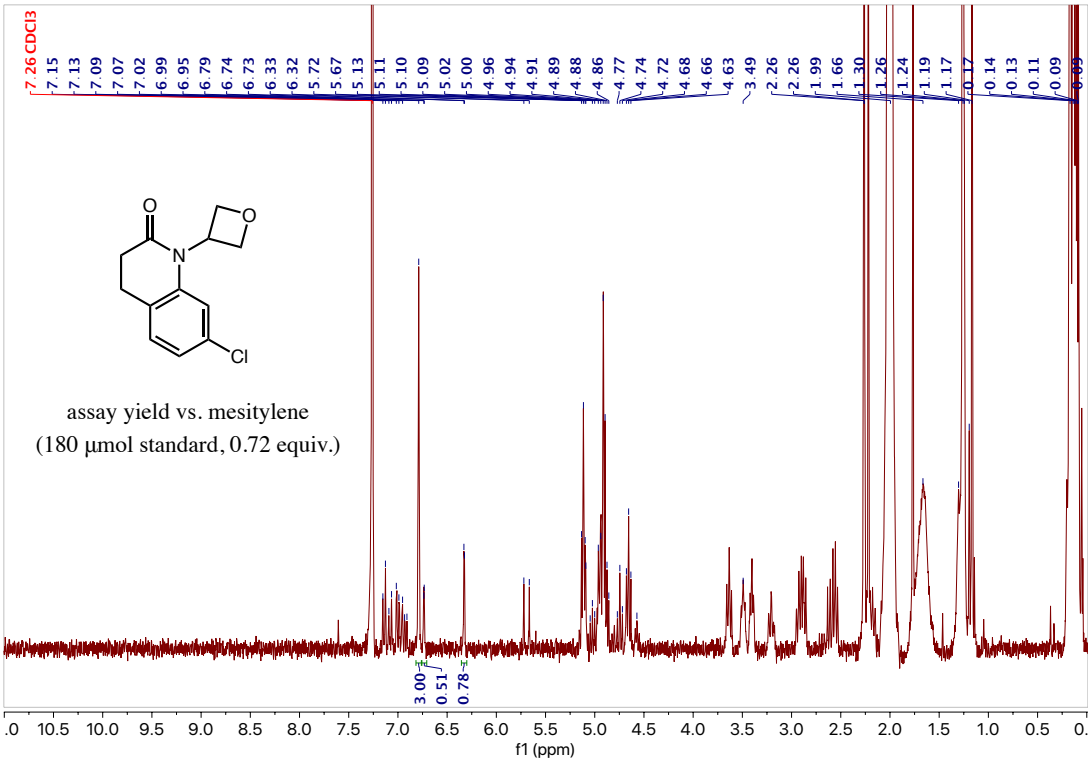


Figure S134: ^{1}H NMR assay of **44** using mesitylene as an internal standard (500 MHz, $CDCl_3$).

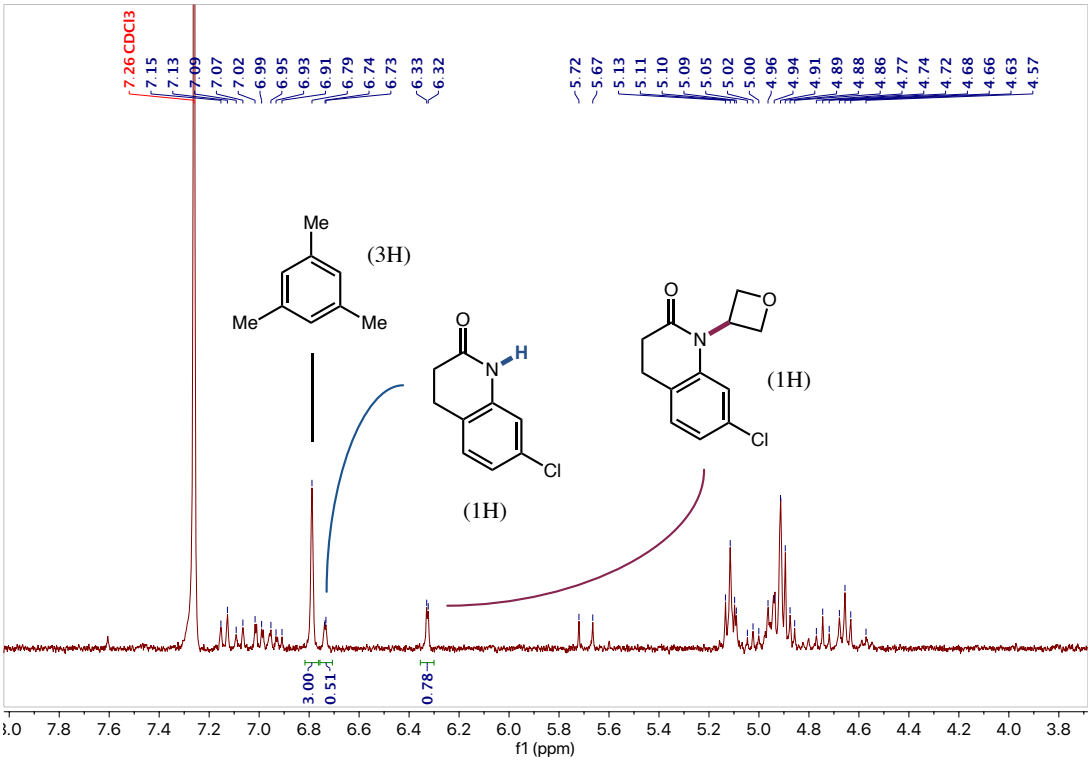


Figure S135: Assignment of **Figure S134** (500 MHz, $CDCl_3$).

[(0.78 mmol **44**/mmol Mes) * 0.180 mmol Mes]/0.250 mmol **44** (theoretical) = *56% assay yield*

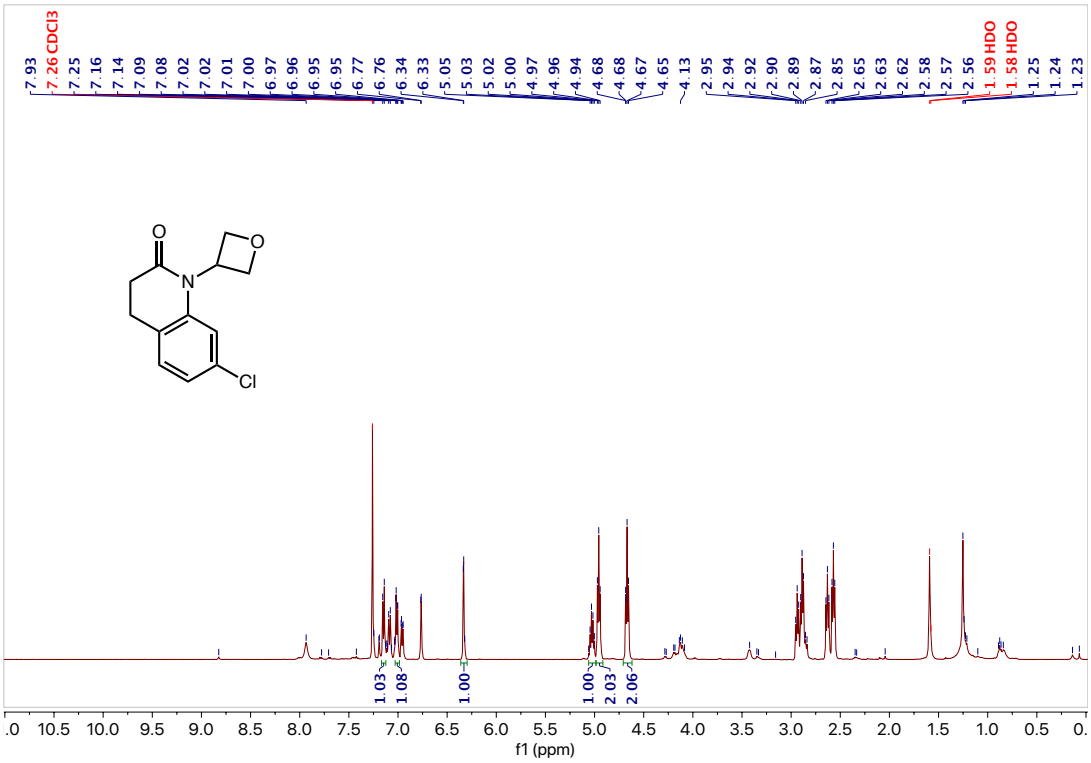


Figure S136: Confirmation of ^{1}H NMR assignments for **44** using semi-pure material (500 MHz, $CDCl_3$).

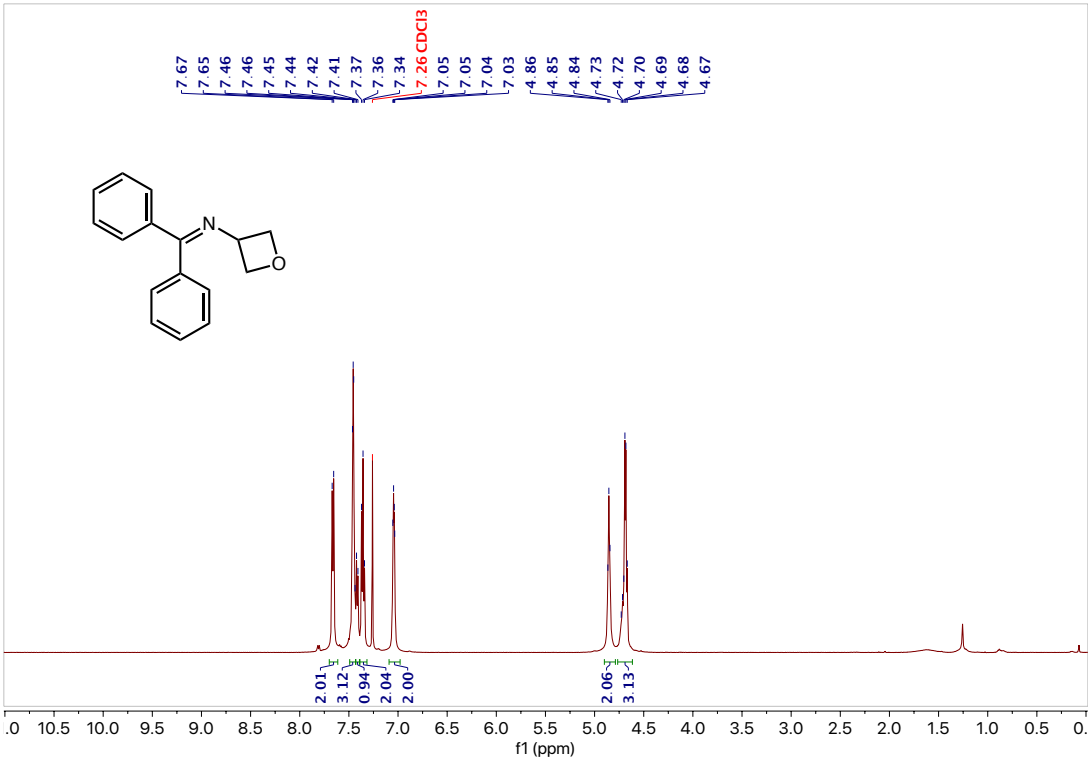


Figure S137: ^{1}H NMR spectrum of **45** (500 MHz, $CDCl_3$).

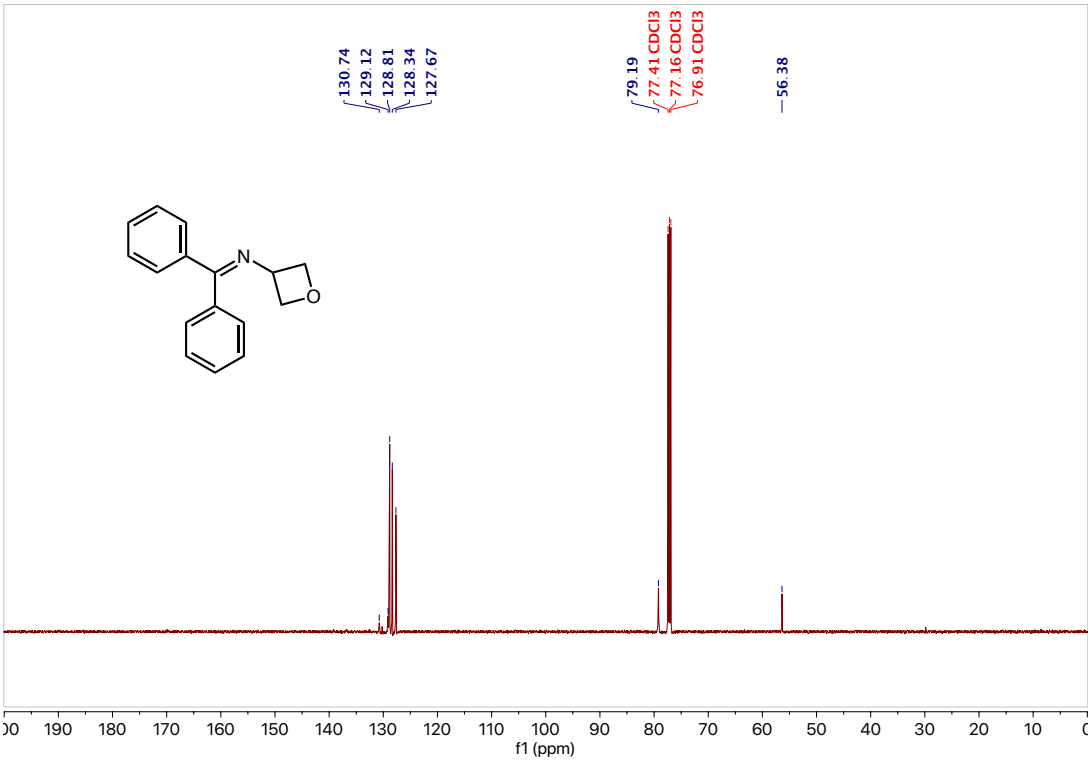


Figure S138: ^{13}C NMR spectrum of **45** (125 MHz, $CDCl_3$).

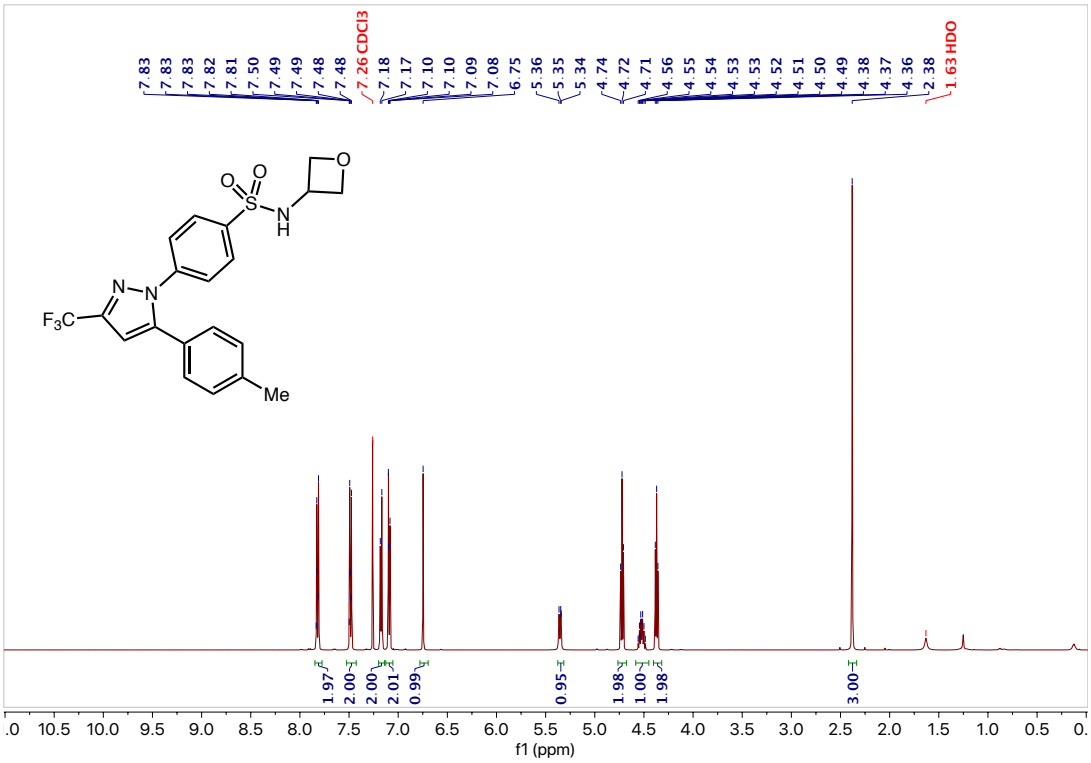


Figure S139: ^{1}H NMR spectrum of **46** (500 MHz, $CDCl_3$).

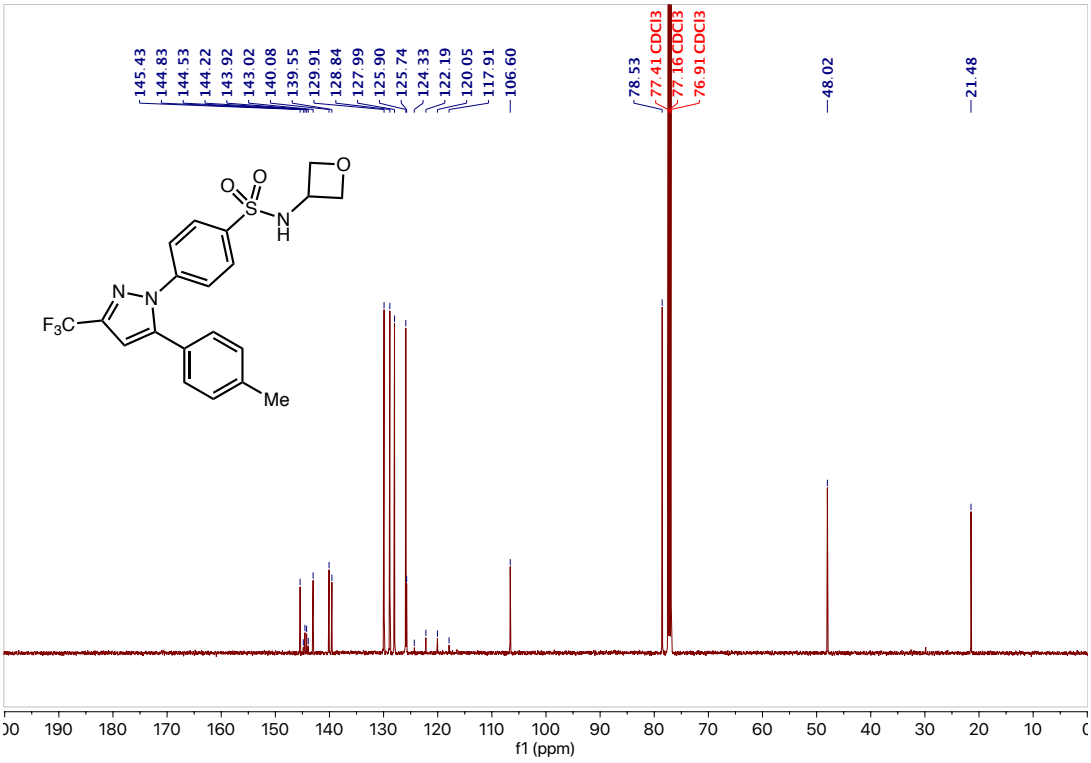


Figure S140: ^{13}C NMR spectrum of **46** (125 MHz, $CDCl_3$).

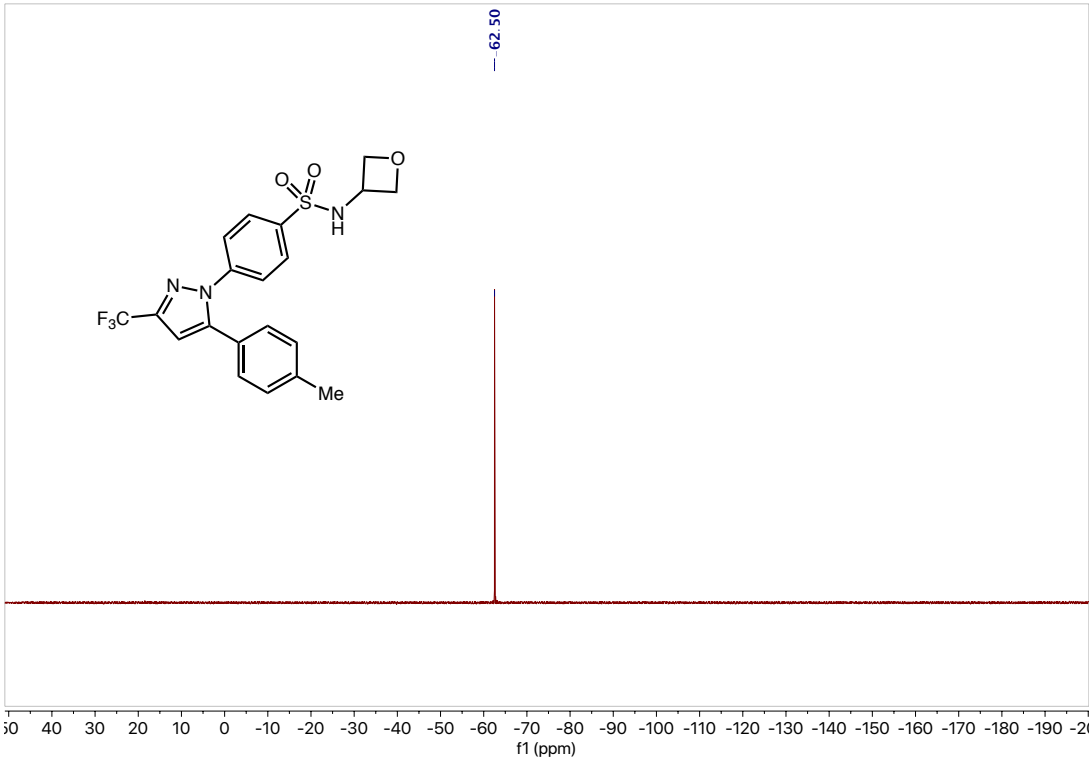


Figure S141: ^{19}F NMR spectrum of **46** (282 MHz, $CDCl_3$).

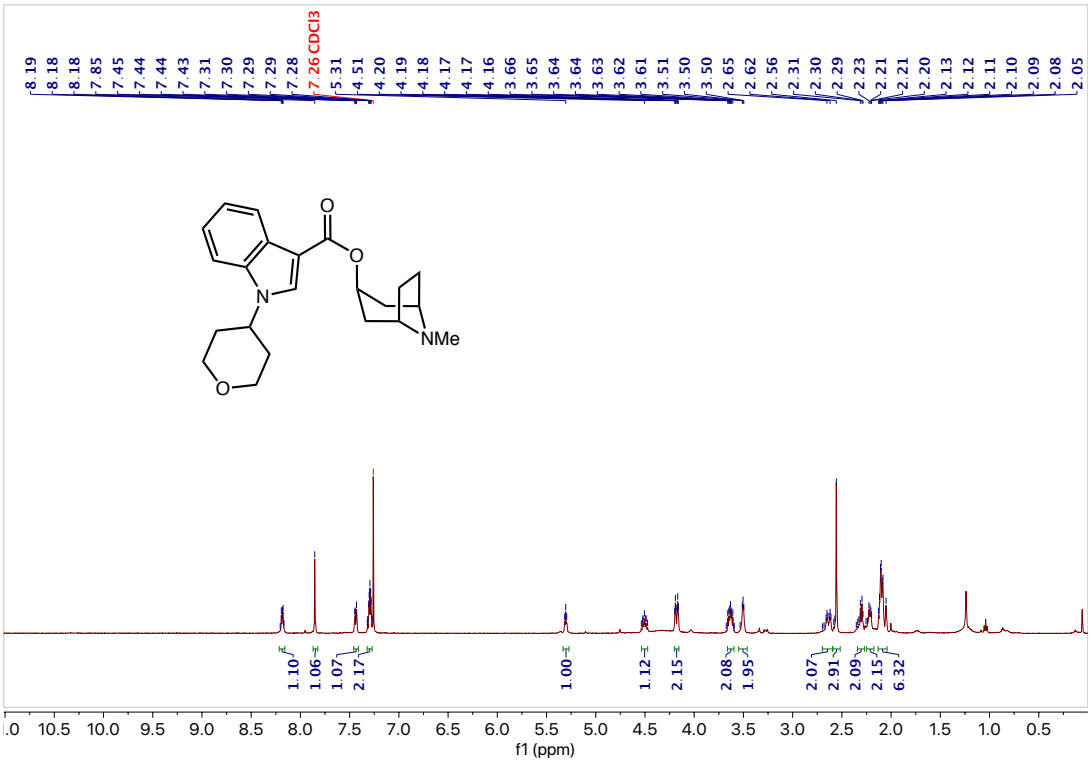


Figure S142: ^{1}H NMR spectrum of **47** (500 MHz, $CDCl_3$).

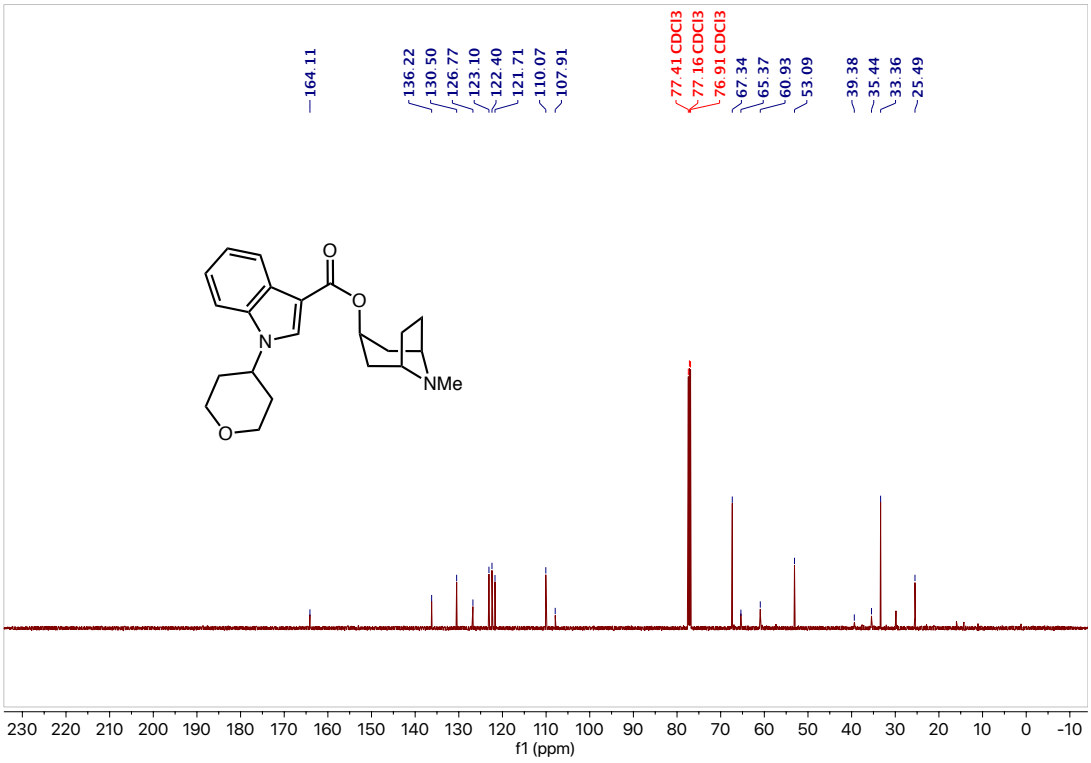


Figure S143: ^{13}C NMR spectrum of **47** (125 MHz, $CDCl_3$).

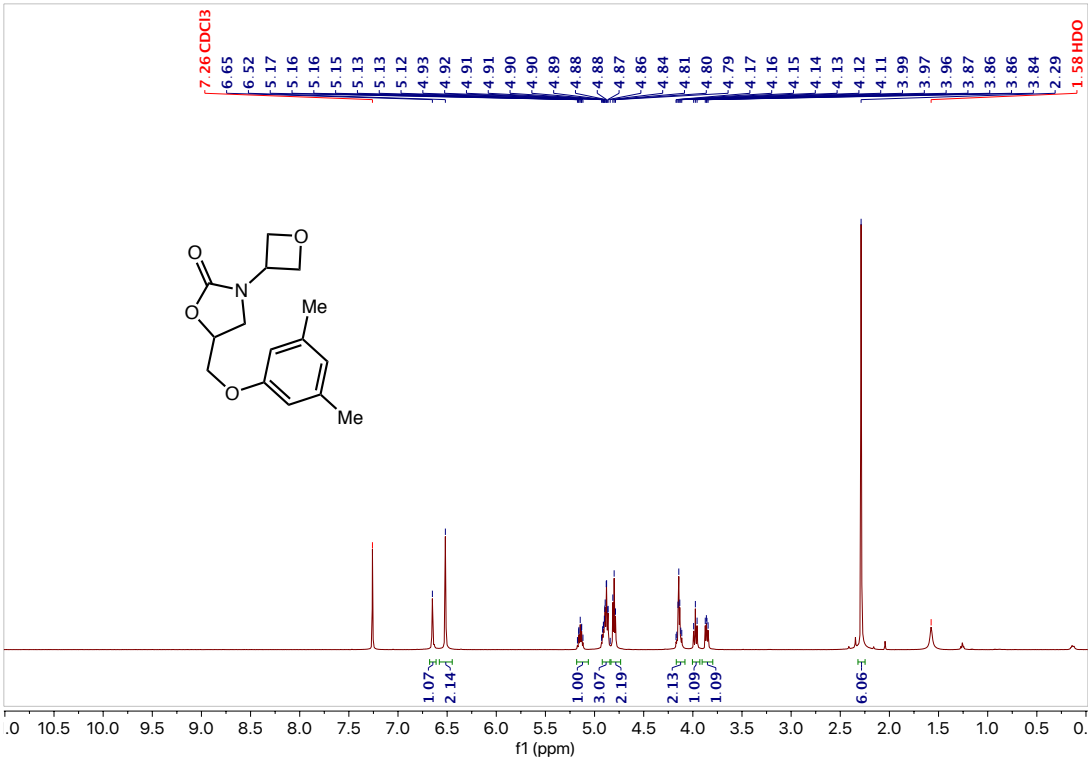


Figure S144: ^{1}H NMR spectrum of **(±)-48** (500 MHz, $CDCl_3$).

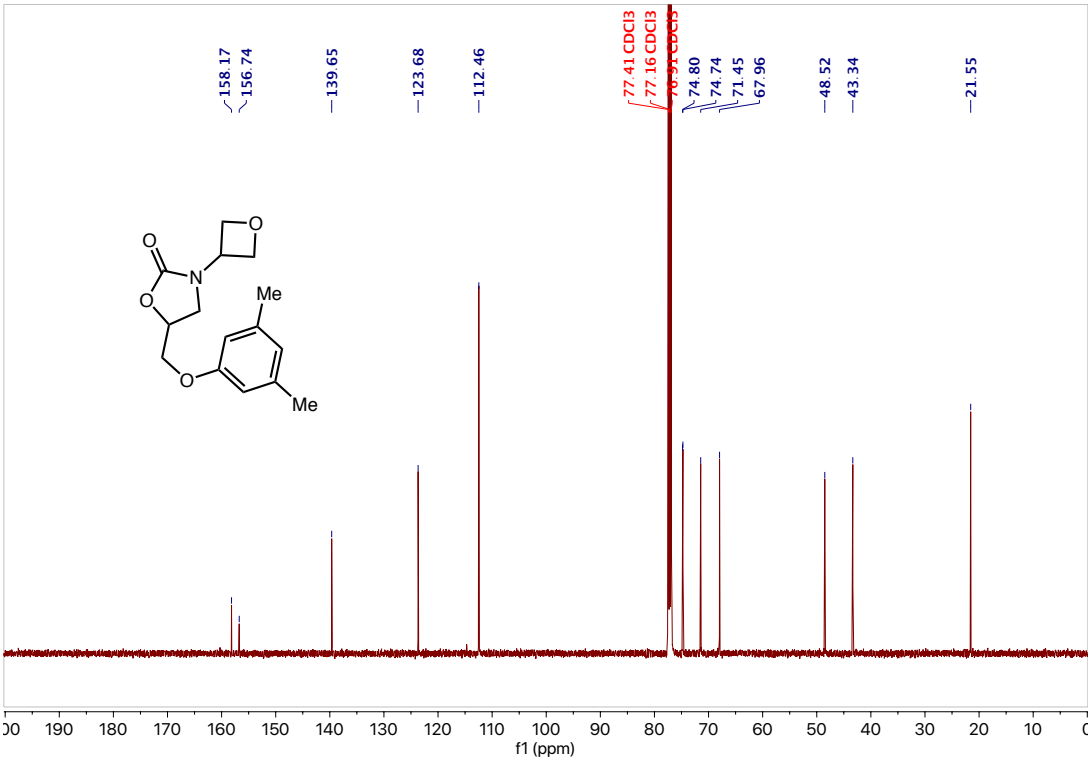


Figure S145: ^{13}C NMR spectrum of **(±)-48** (125 MHz, $CDCl_3$).

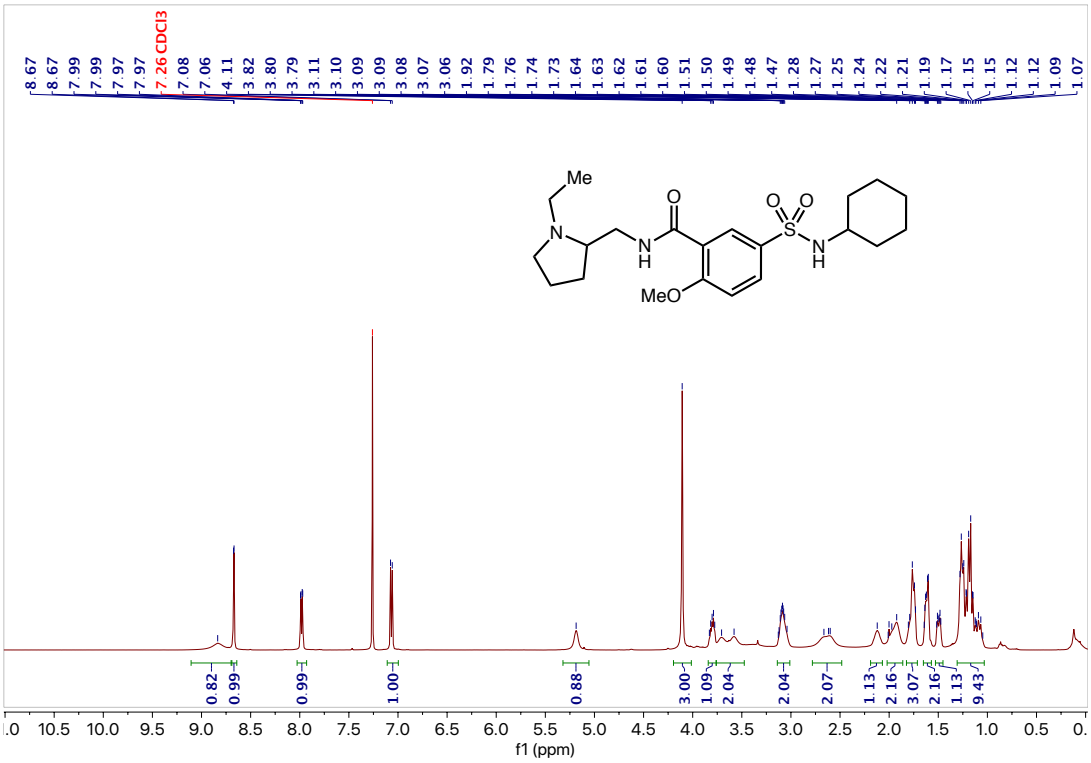


Figure S146: ^{1}H NMR spectrum of **(±)-49** (500 MHz, $CDCl_3$).

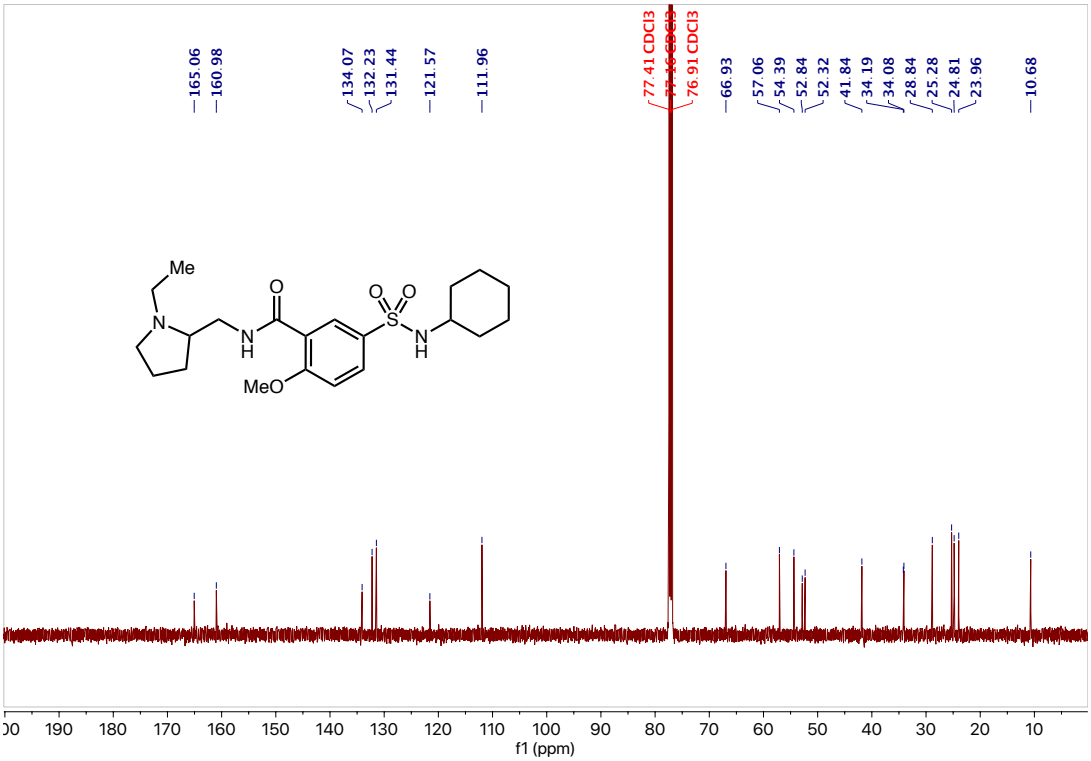


Figure S147: ^{13}C NMR spectrum of **(±)-49** (125 MHz, $CDCl_3$).

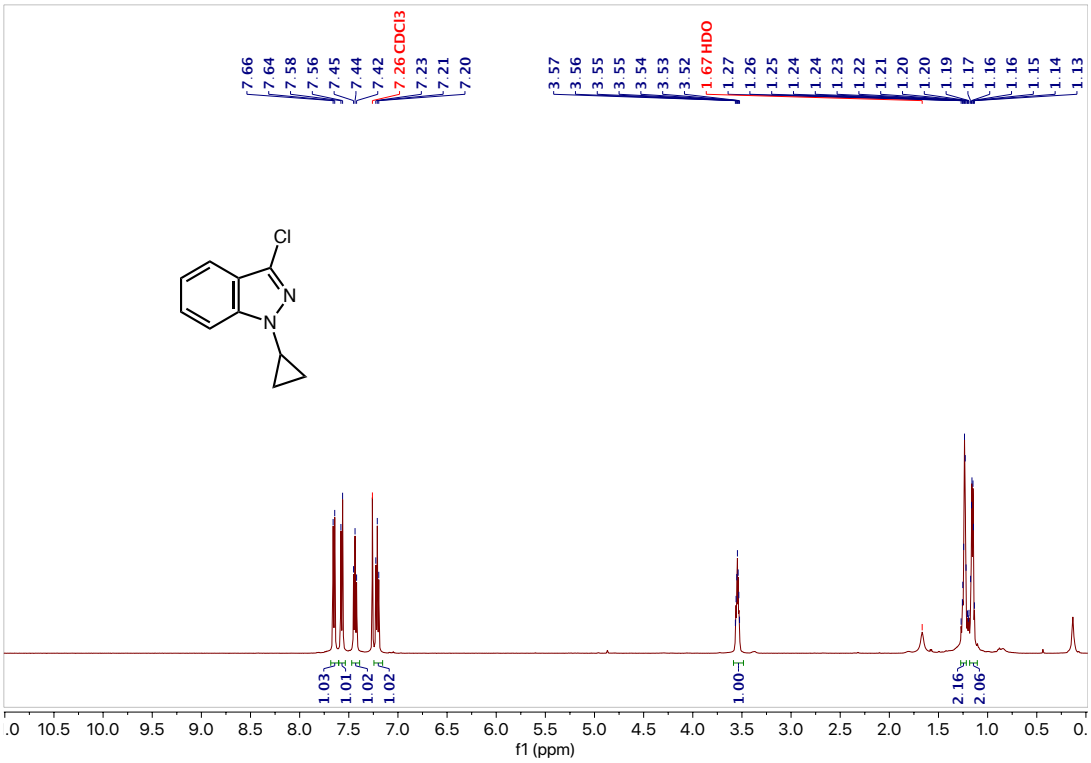


Figure S148: ^{1}H NMR spectrum of **50** (500 MHz, $CDCl_3$).

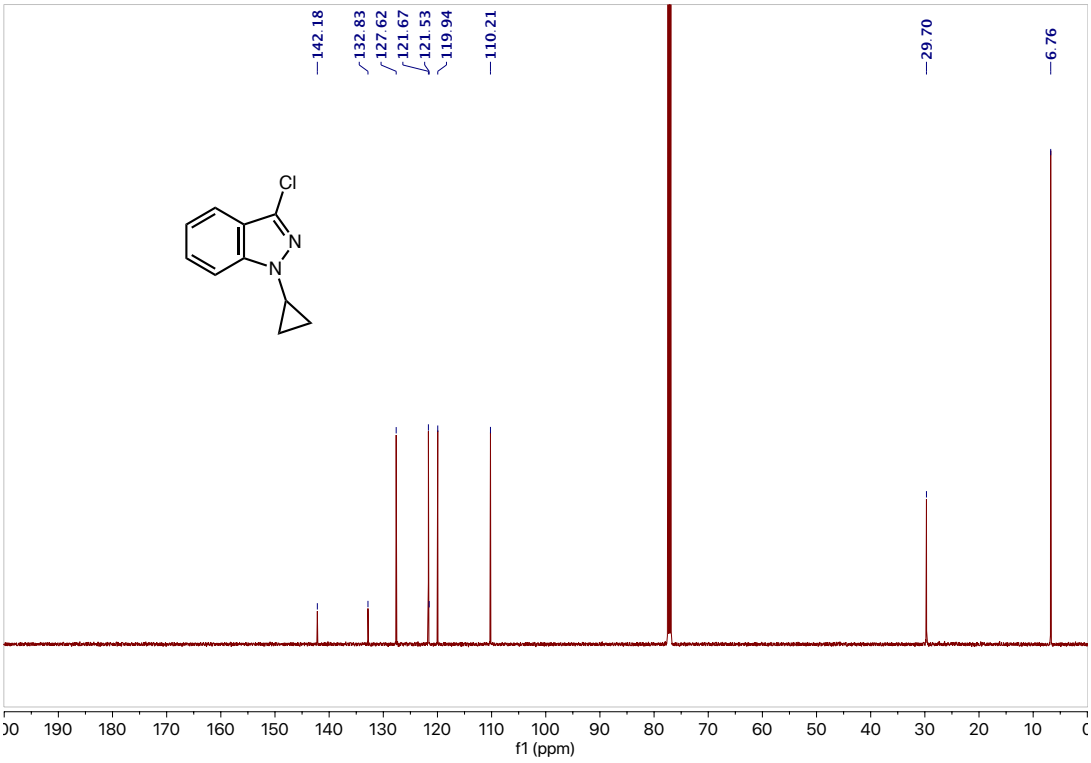


Figure S149: ^{13}C NMR spectrum of **50** (125 MHz, $CDCl_3$).

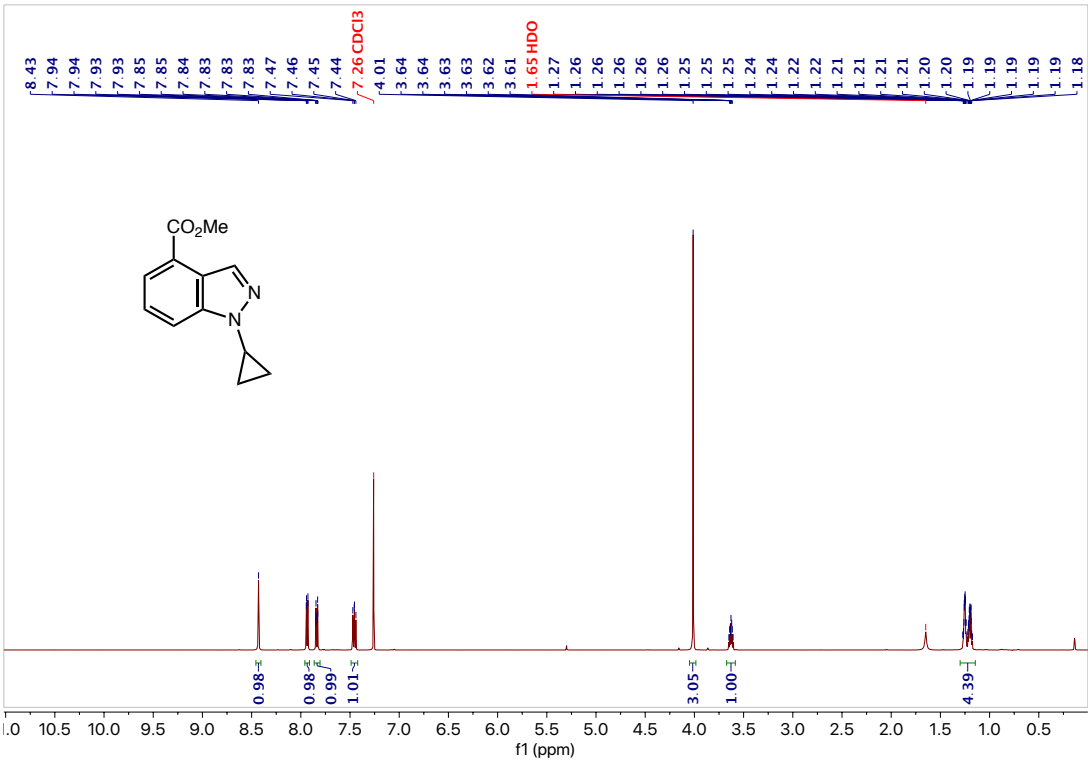


Figure S150: ^{1}H NMR spectrum of **51** (500 MHz, $CDCl_3$).

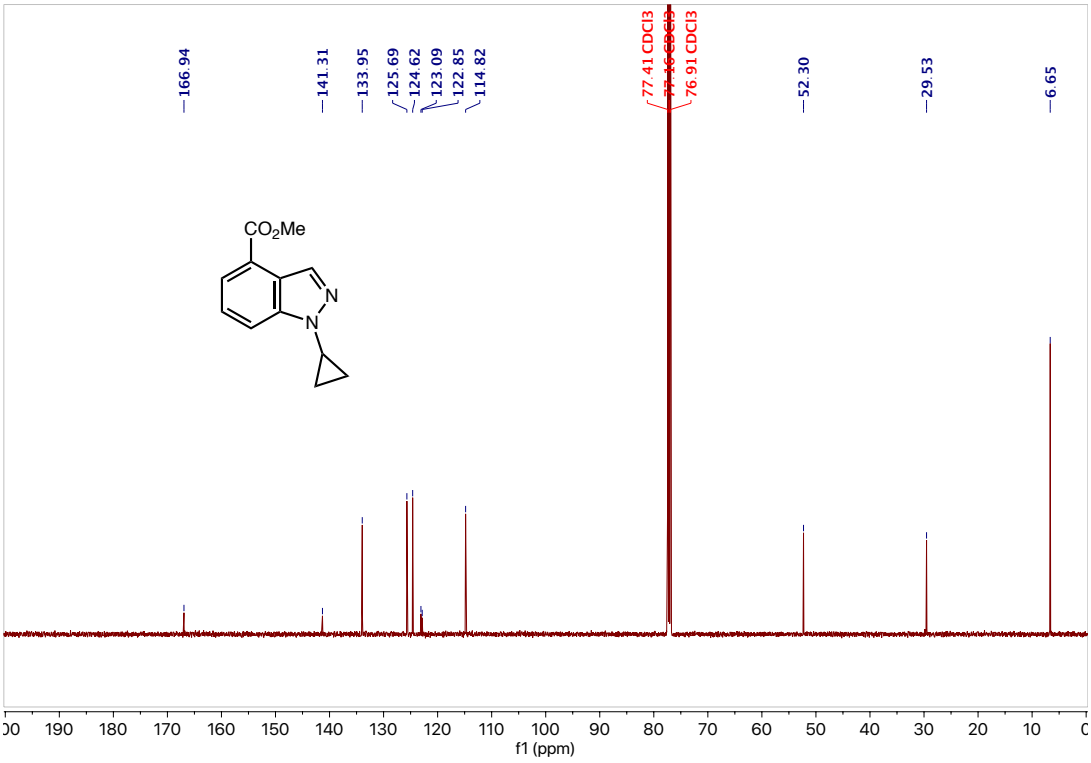


Figure S151: ^{13}C NMR spectrum of **51** (125 MHz, $CDCl_3$).

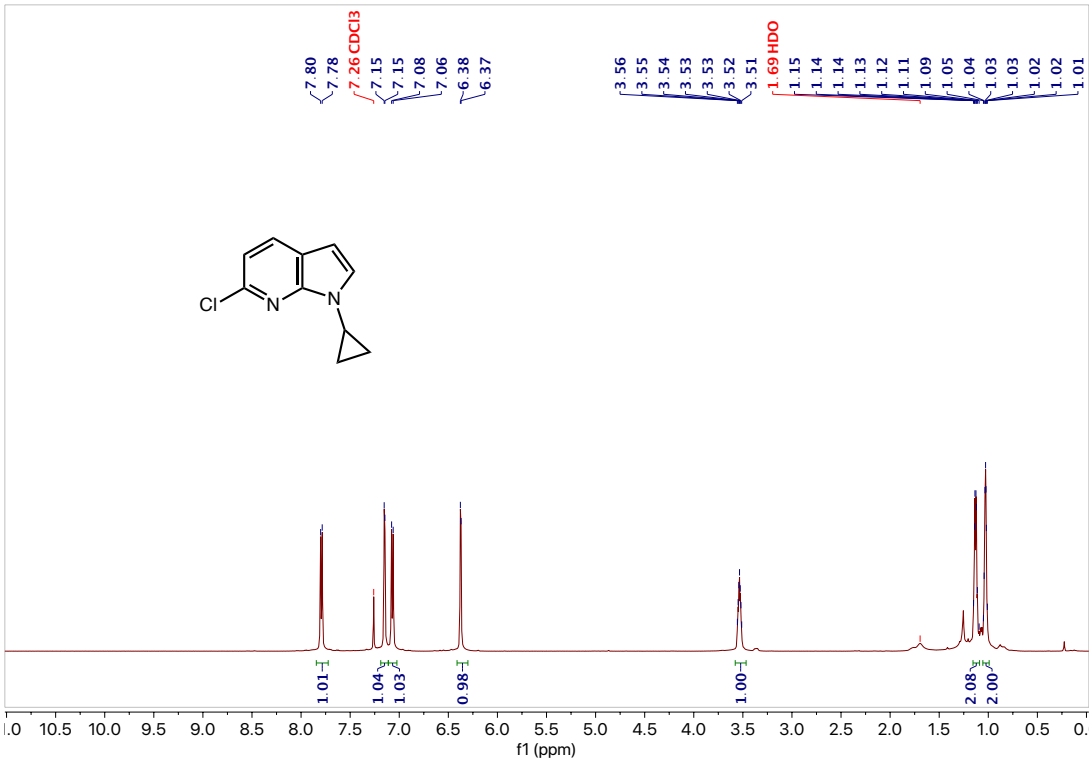


Figure S152: ^{1}H NMR spectrum of **52** (500 MHz, $CDCl_3$).

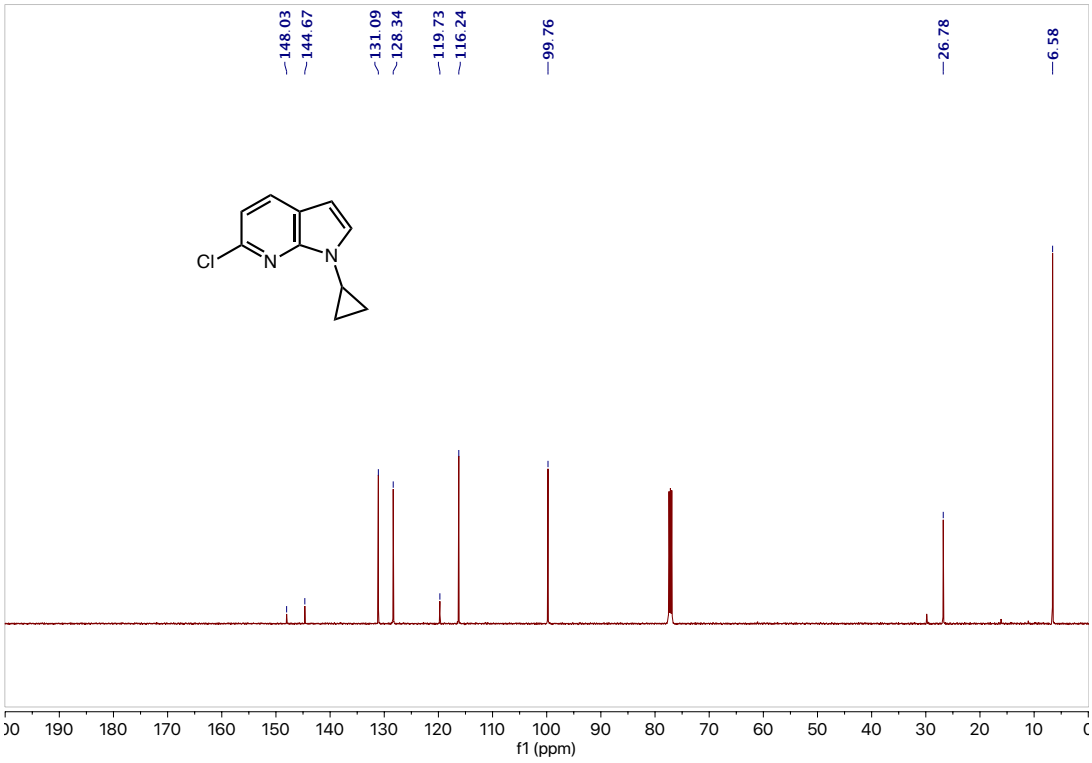


Figure S153: ^{13}C NMR spectrum of **52** (125 MHz, $CDCl_3$).

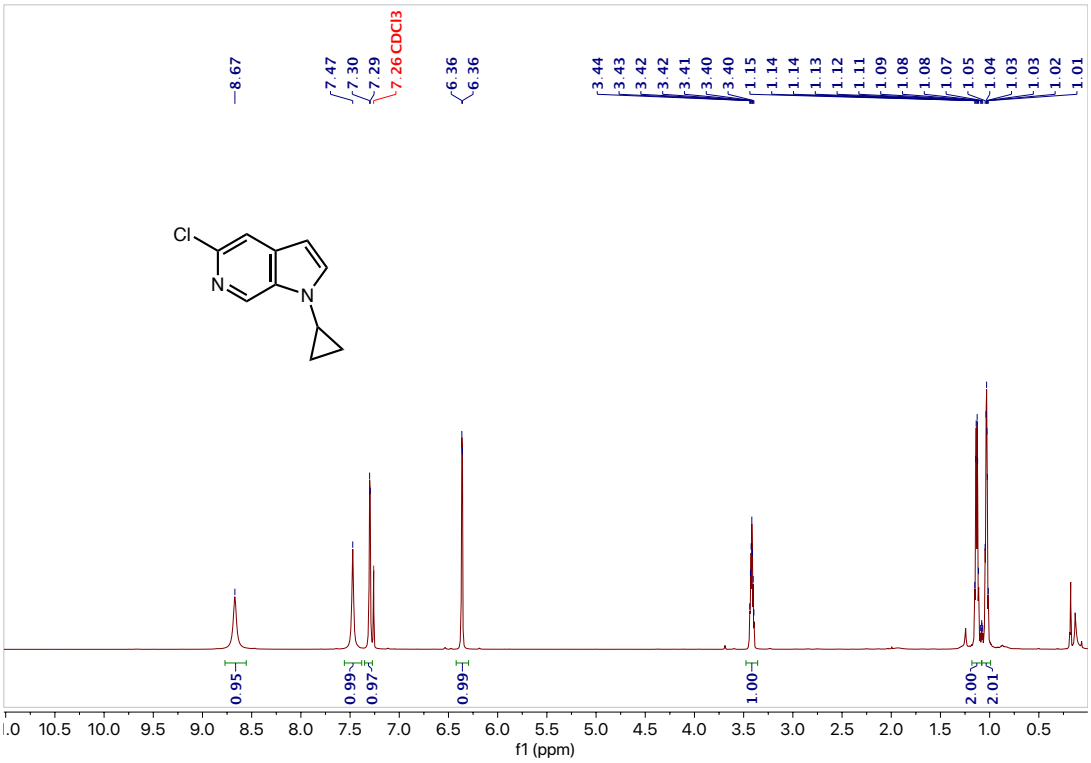


Figure S154: ^{1}H NMR spectrum of **53** (500 MHz, $CDCl_3$).

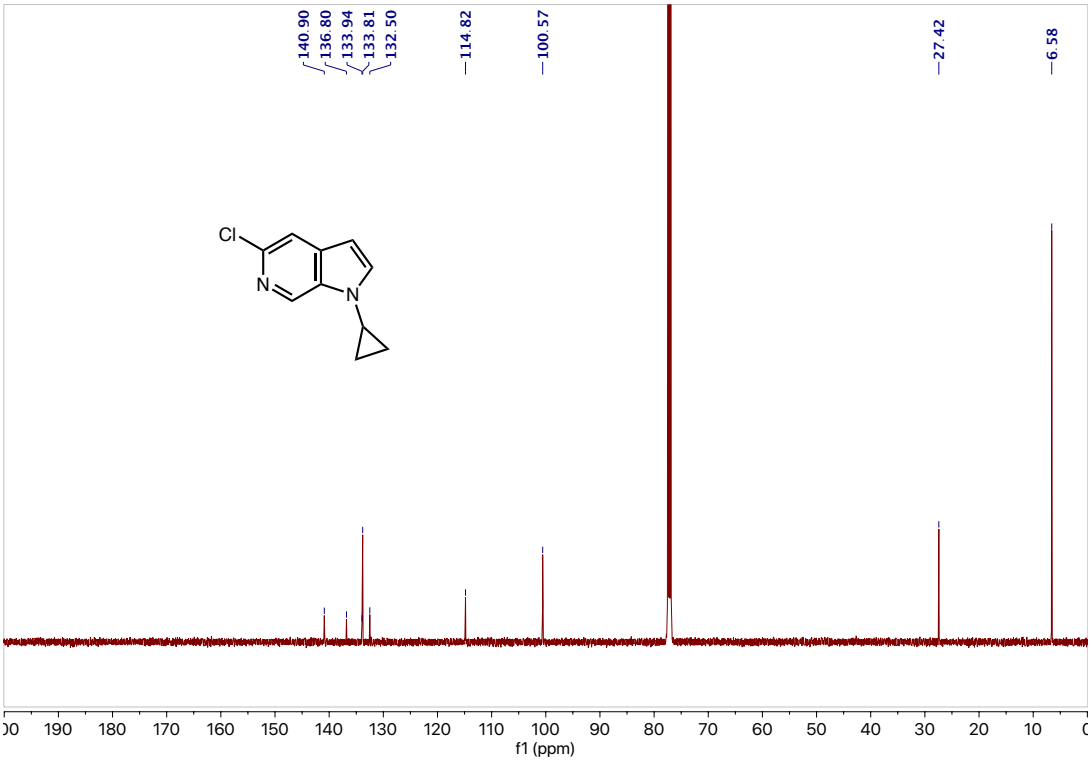


Figure S155: ^{13}C NMR spectrum of **53** (125 MHz, $CDCl_3$).

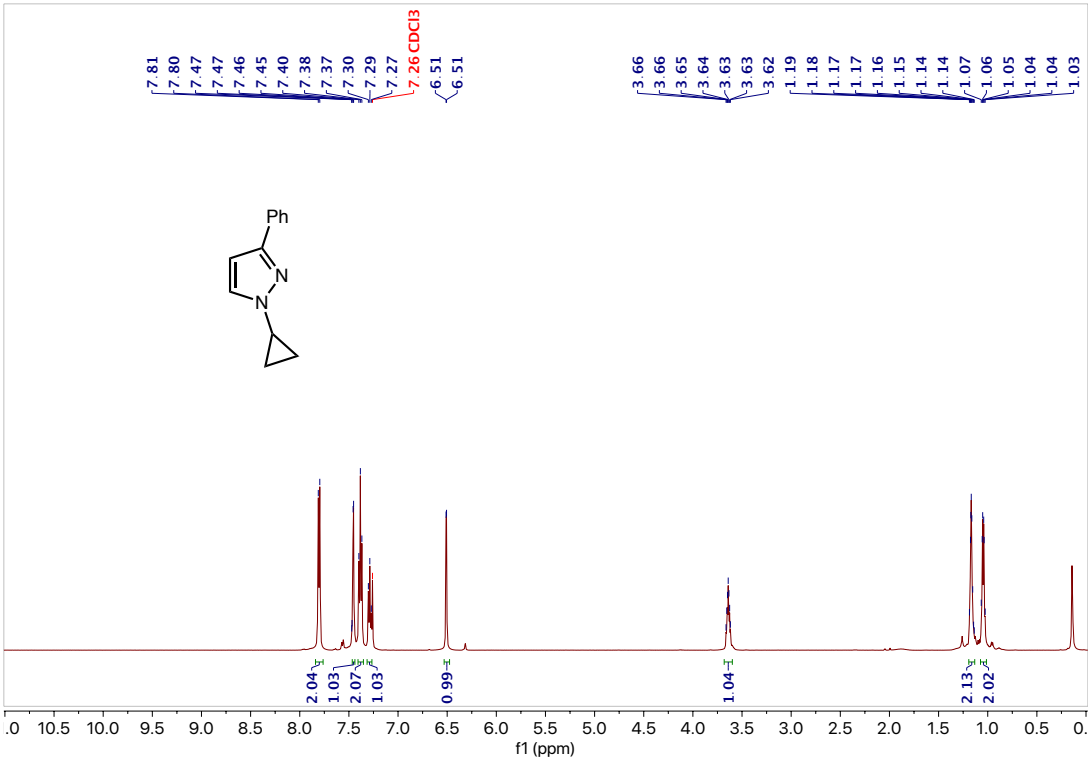


Figure S156: ^{1}H NMR spectrum of **54** (500 MHz, $CDCl_3$).

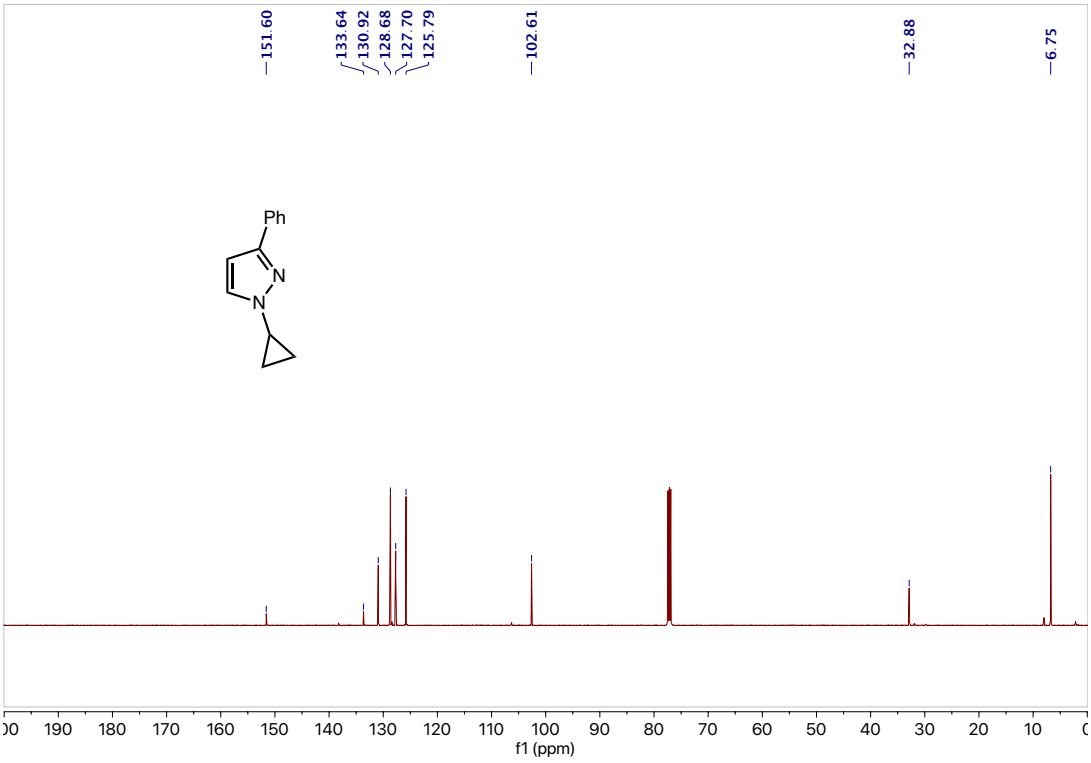


Figure S157: ^{13}C NMR spectrum of **54** (125 MHz, $CDCl_3$).

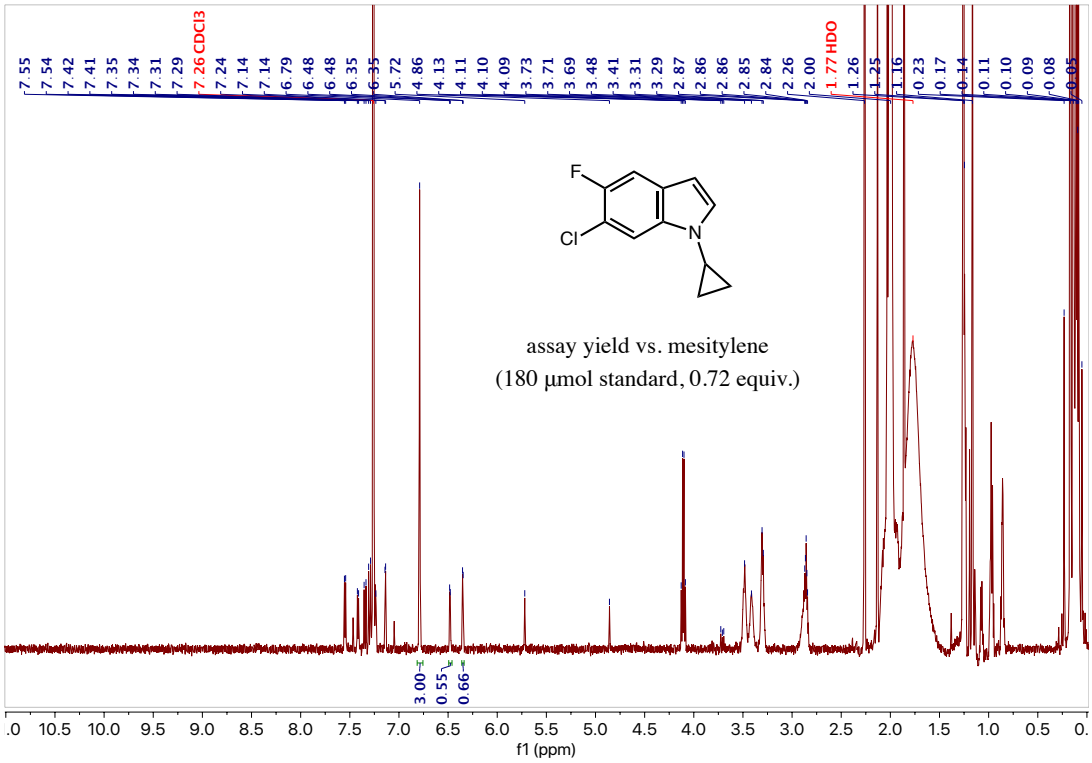


Figure S158: ^{1}H NMR assay of **55** using mesitylene as an internal standard (500 MHz, $CDCl_3$).

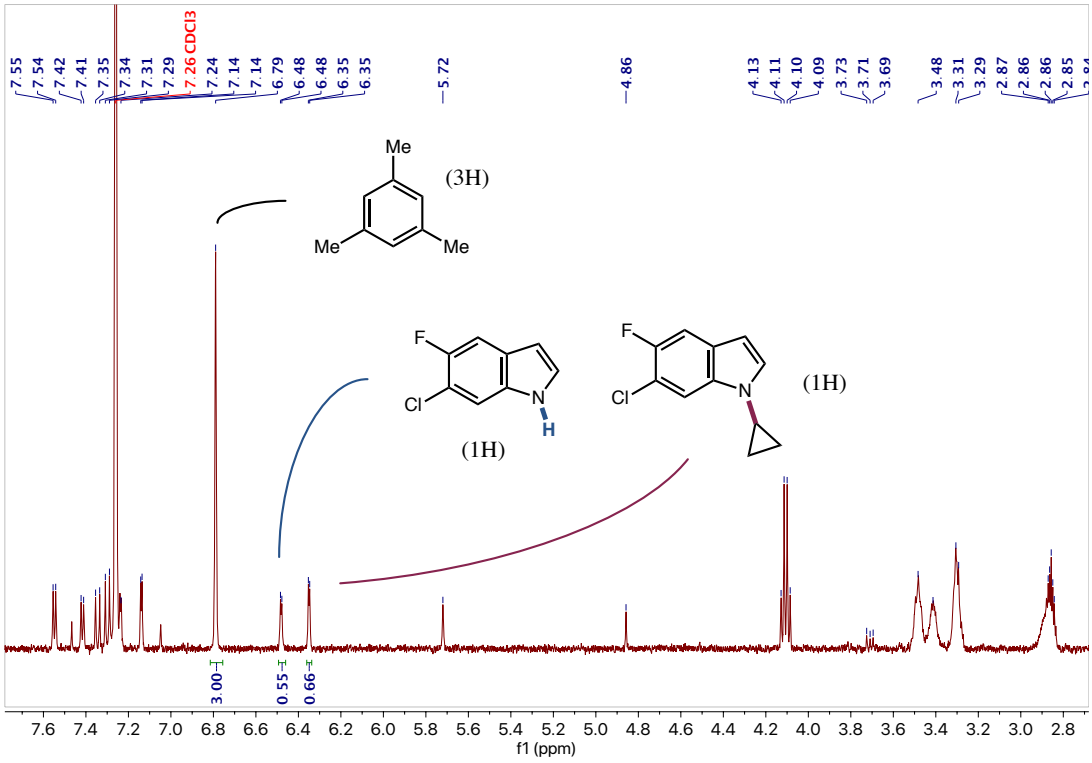


Figure S159: Assignment of **Figure S158** (500 MHz, $CDCl_3$).

[(0.66 mmol **55**/mmol Mes) * 0.180 mmol Mes]/0.250 mmol **55** (theoretical) = *48% assay yield*

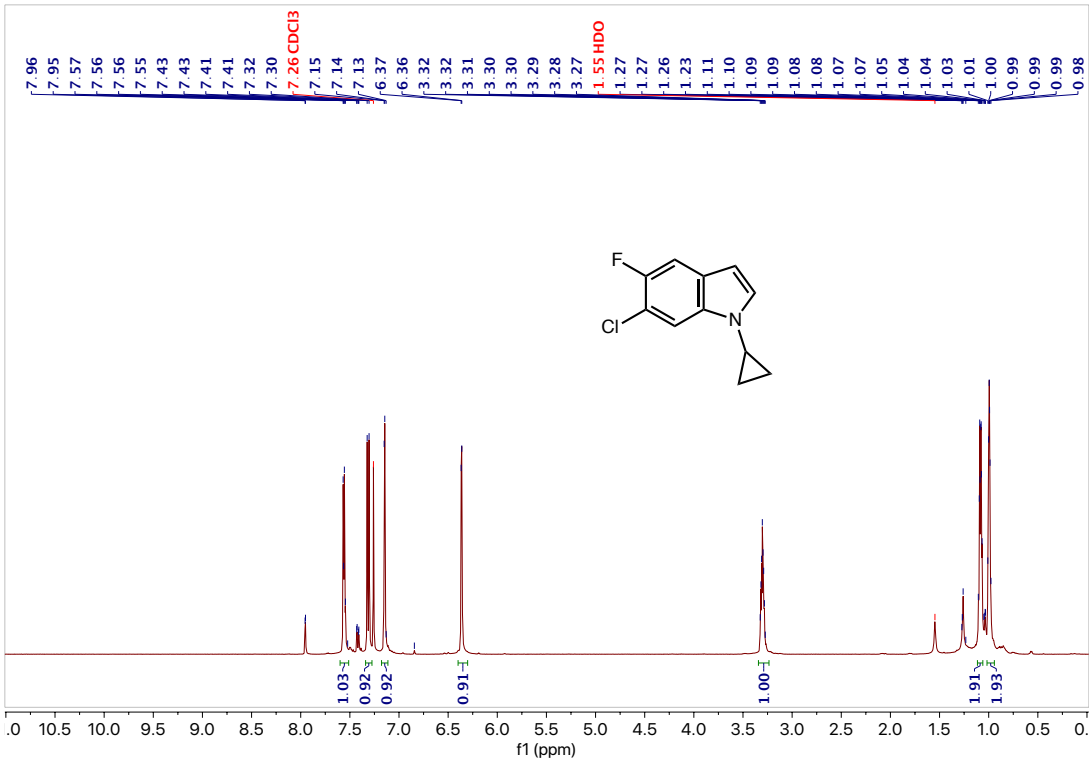


Figure S160: Confirmation of ^{1}H NMR assignments for **55** using semi-pure material (500 MHz, $CDCl_3$).

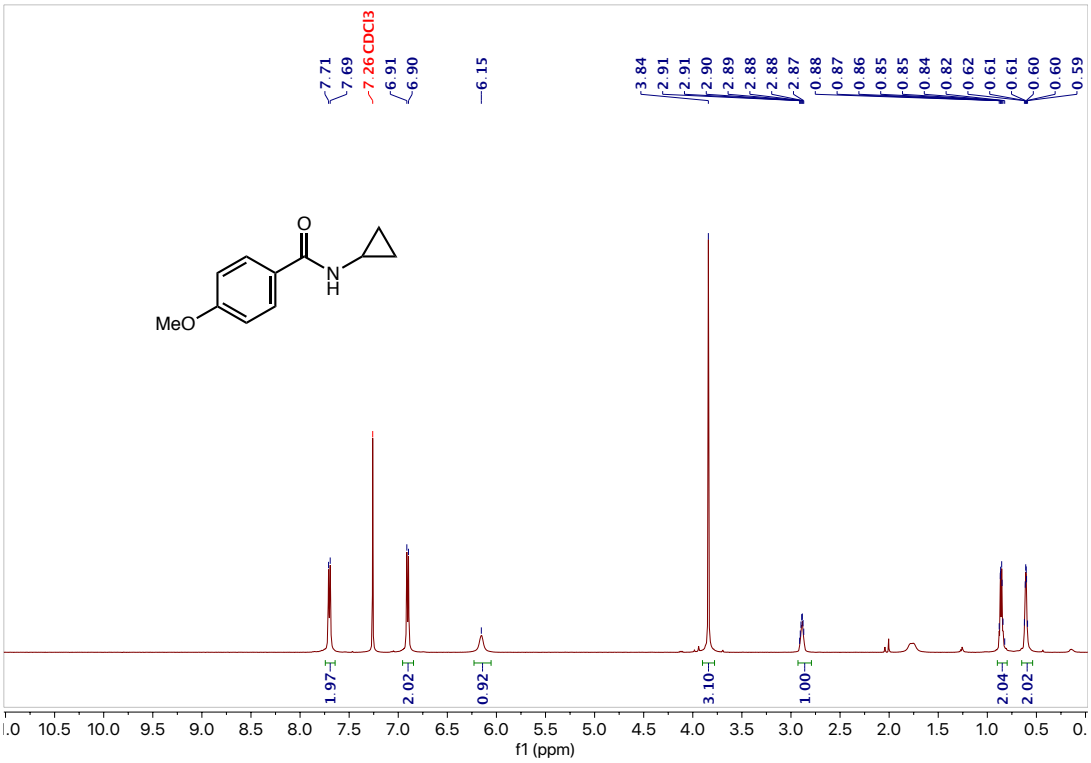


Figure S161: ^{1}H NMR spectrum of **56** (500 MHz, $CDCl_3$).

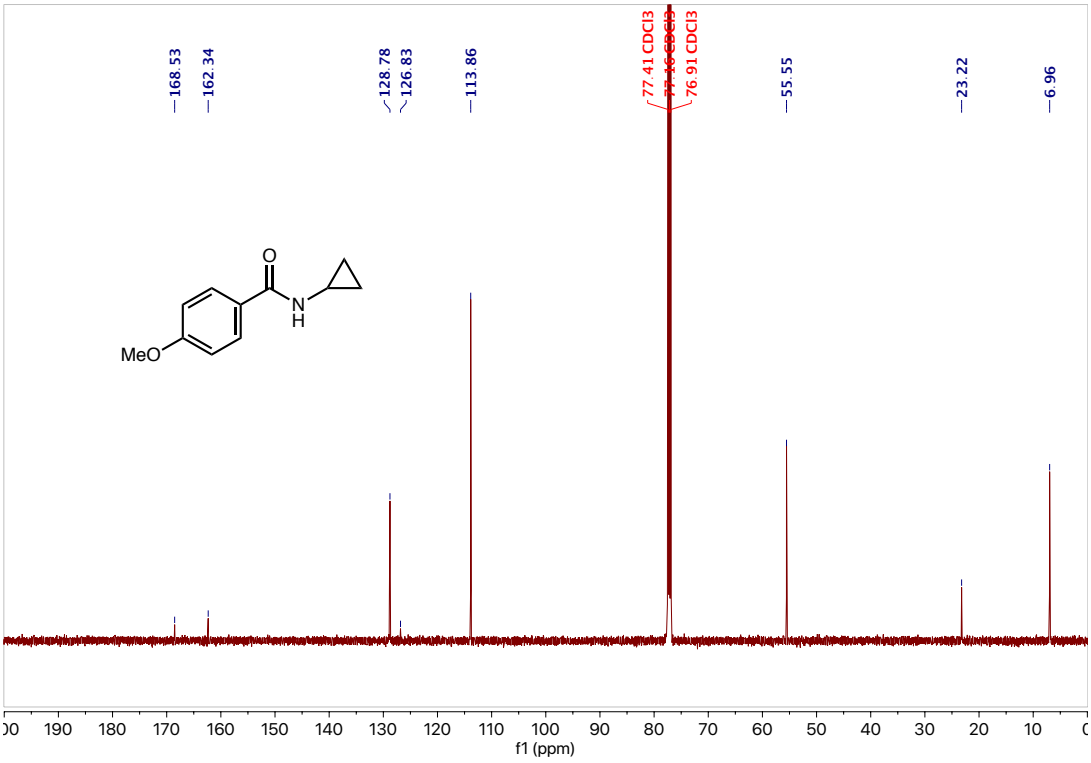


Figure S162: ^{13}C NMR spectrum of **56** (125 MHz, $CDCl_3$).

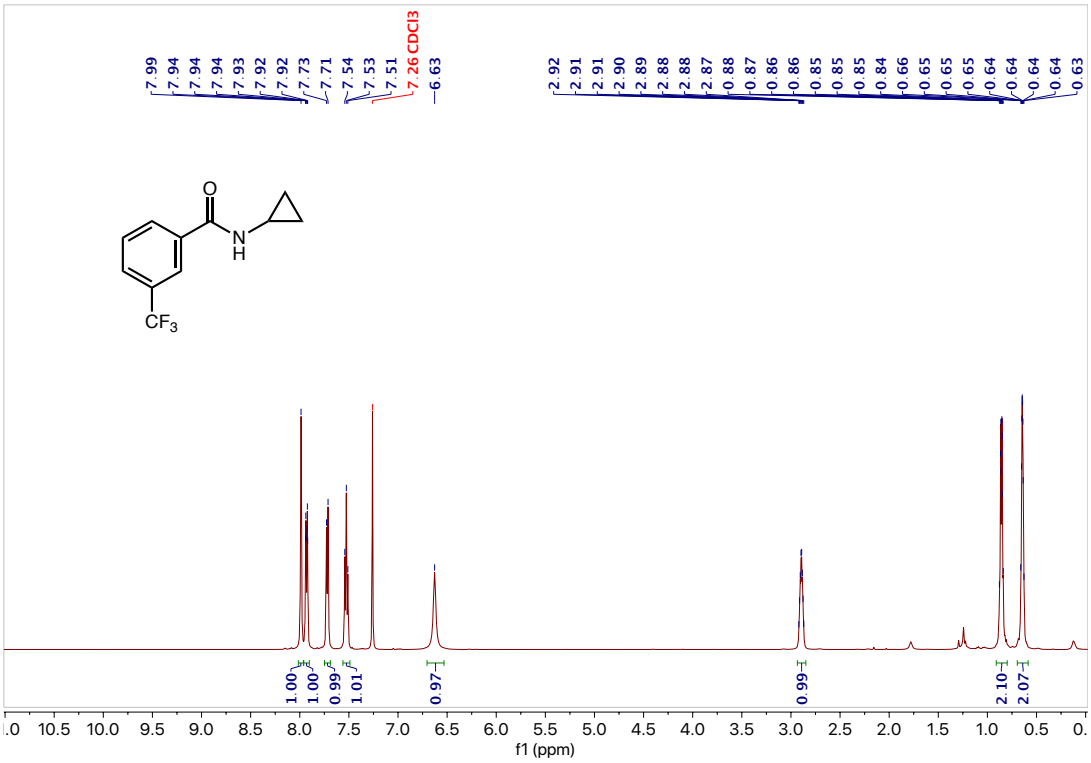


Figure S163: ^{1}H NMR spectrum of **57** (500 MHz, $CDCl_3$).

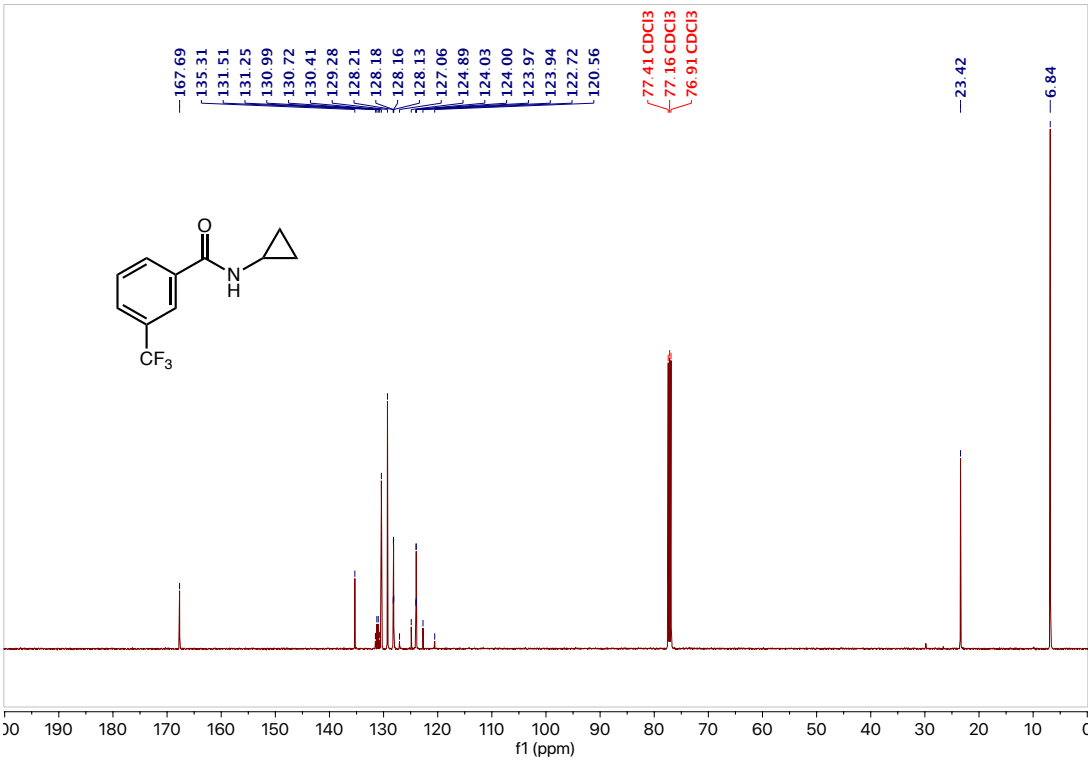


Figure S164: ^{13}C NMR spectrum of **57** (125 MHz, $CDCl_3$).

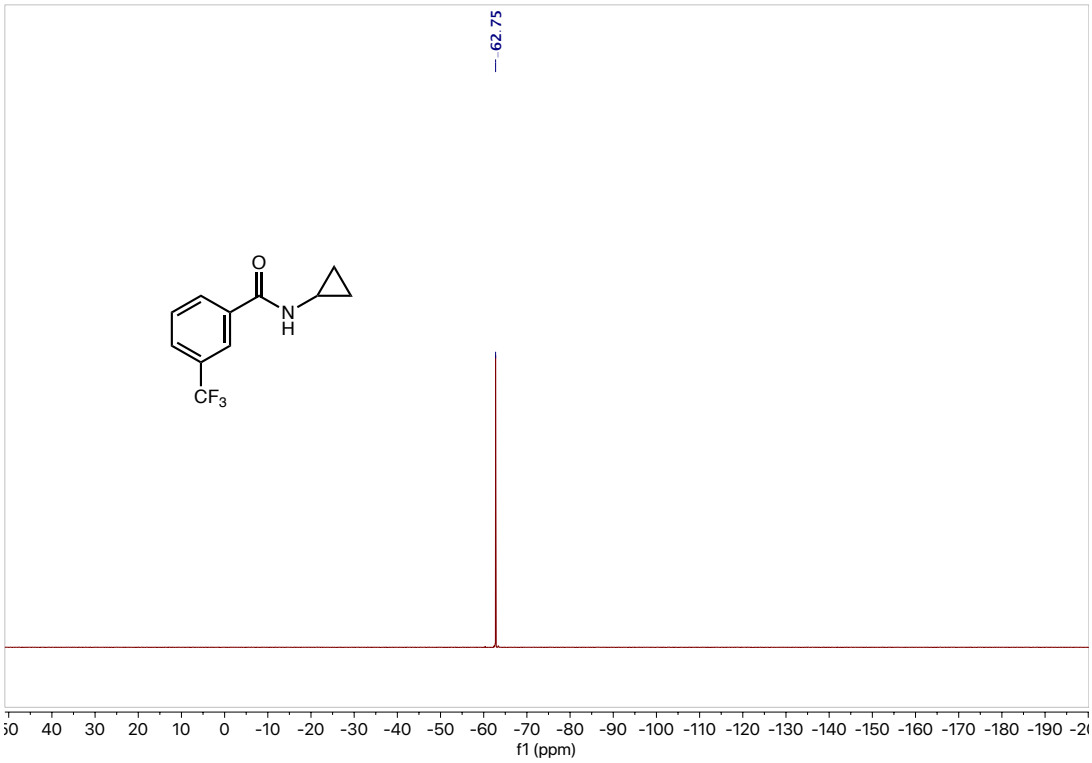


Figure S165: ^{19}F NMR spectrum of **57** (282 MHz, $CDCl_3$).

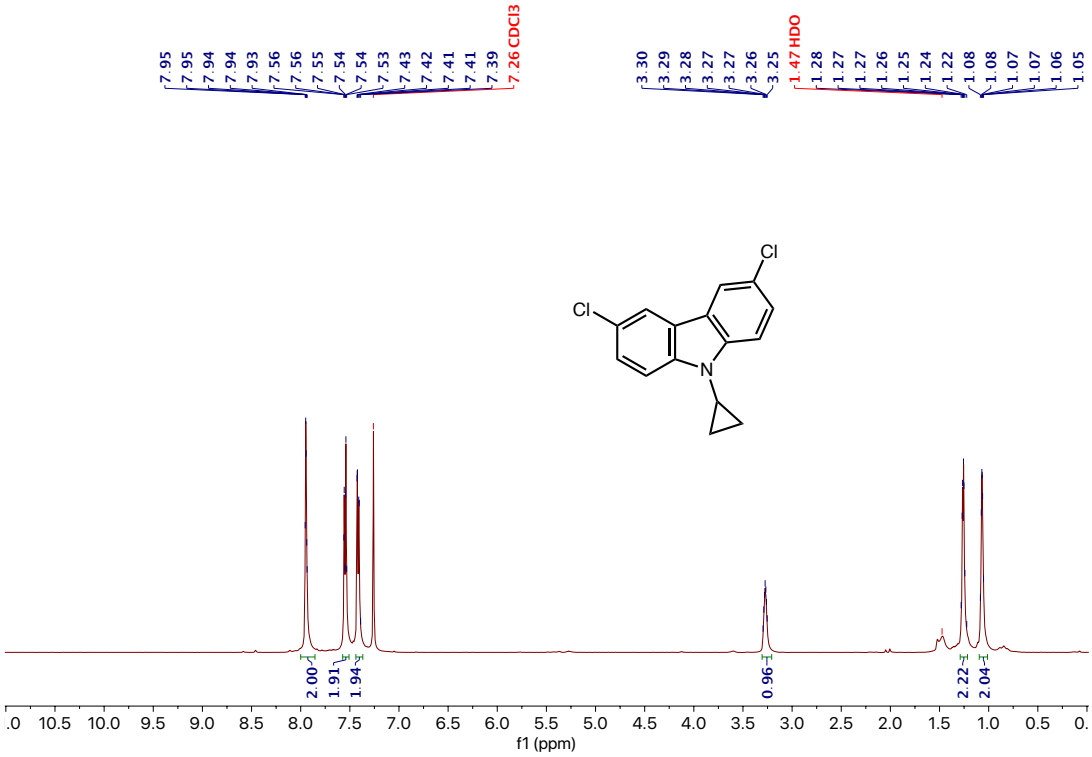


Figure S166: ^{1}H NMR spectrum of **58** (500 MHz, $CDCl_3$).

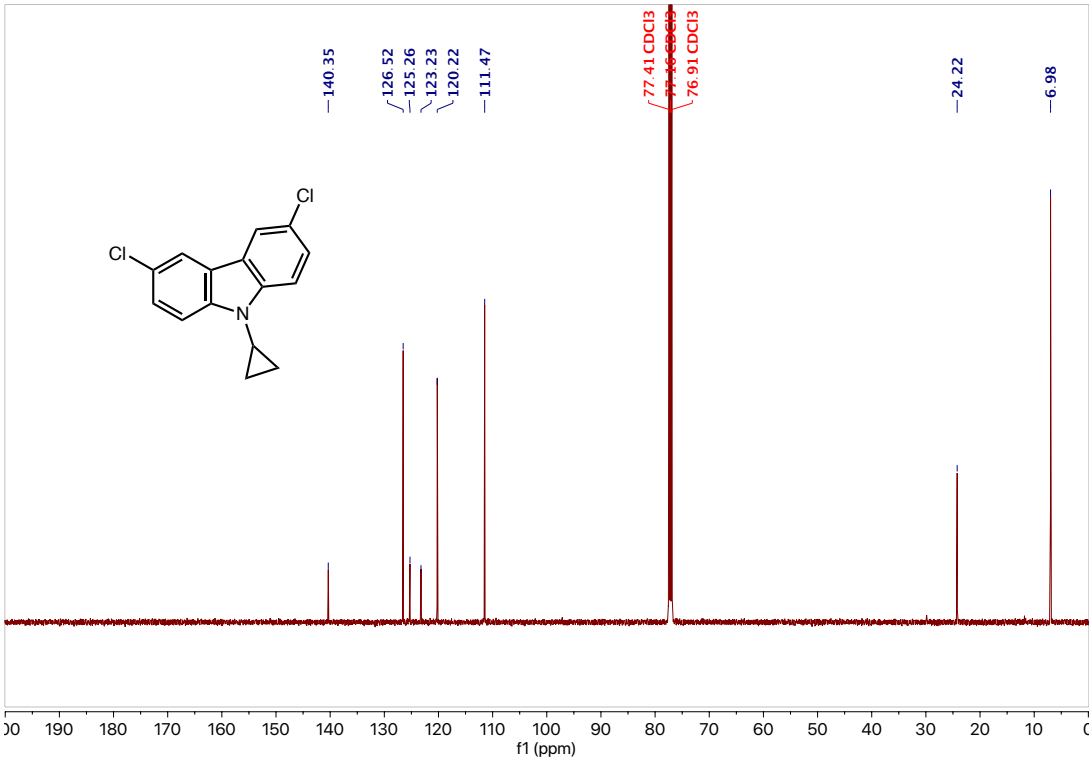


Figure S167: ^{13}C NMR spectrum of **58** (125 MHz, $CDCl_3$).

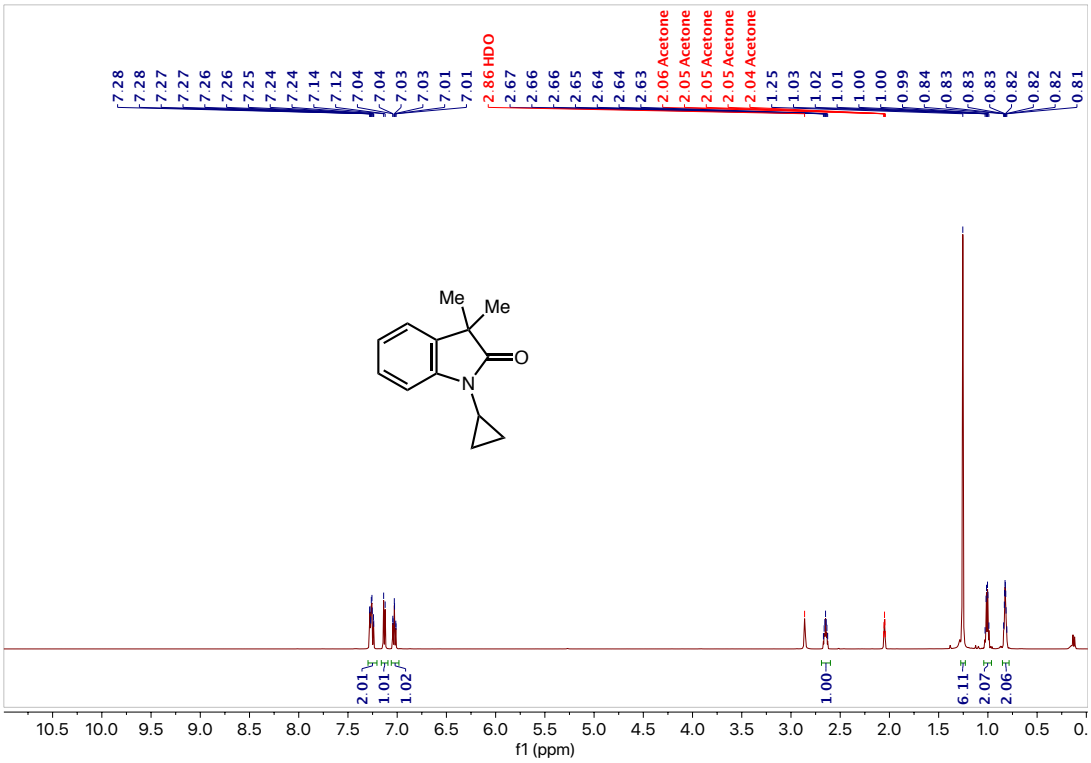


Figure S168: ^{1}H NMR spectrum of **59** (500 MHz, $(CD_3)_2CO$).

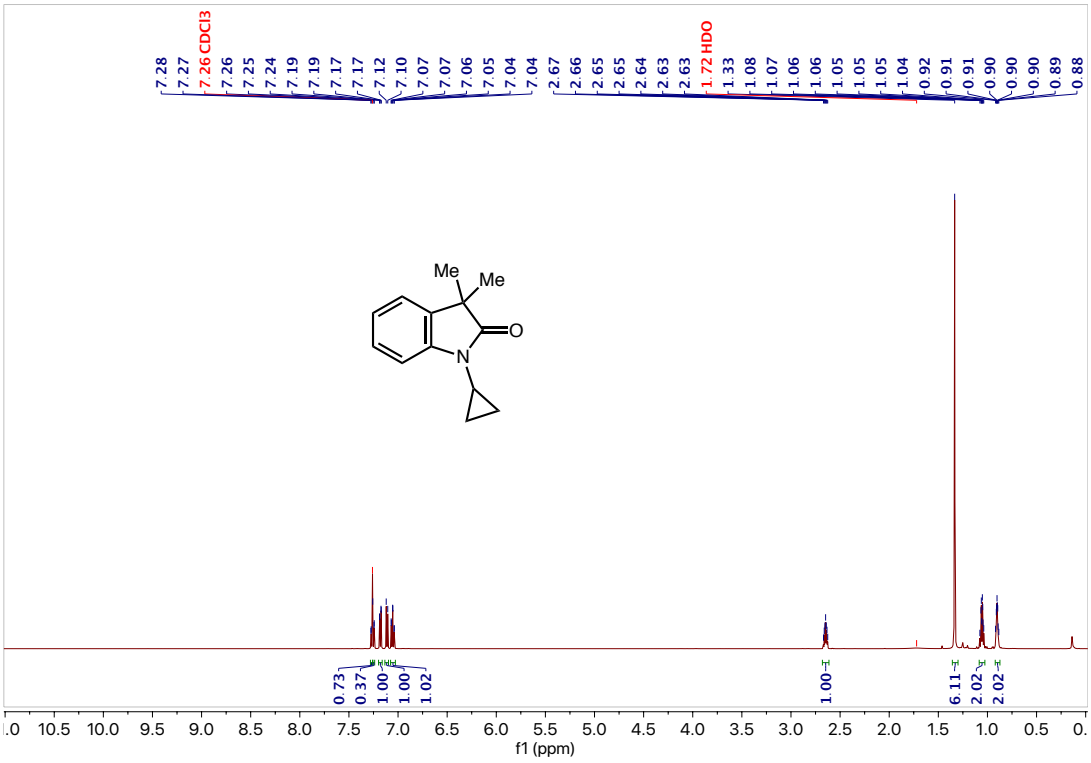


Figure S169: ^{1}H NMR spectrum of **59** (500 MHz, $CDCl_3$).

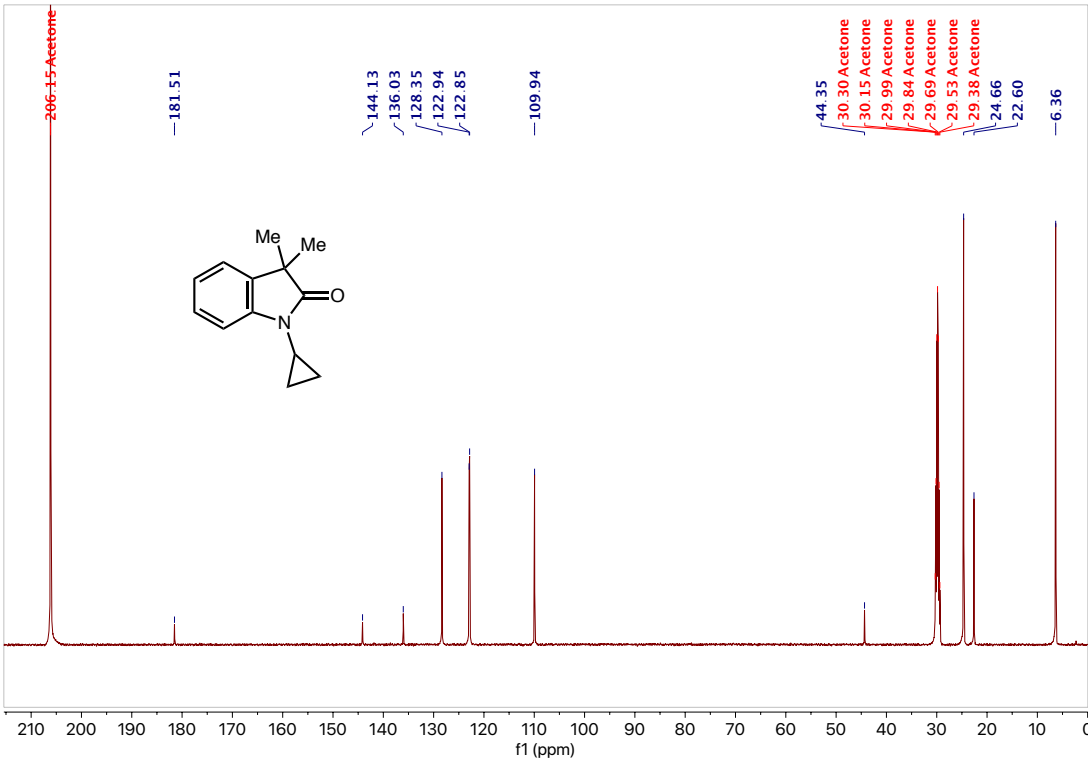


Figure S170: ^{13}C NMR spectrum of **59** (125 MHz, $(CD_3)_2CO$).

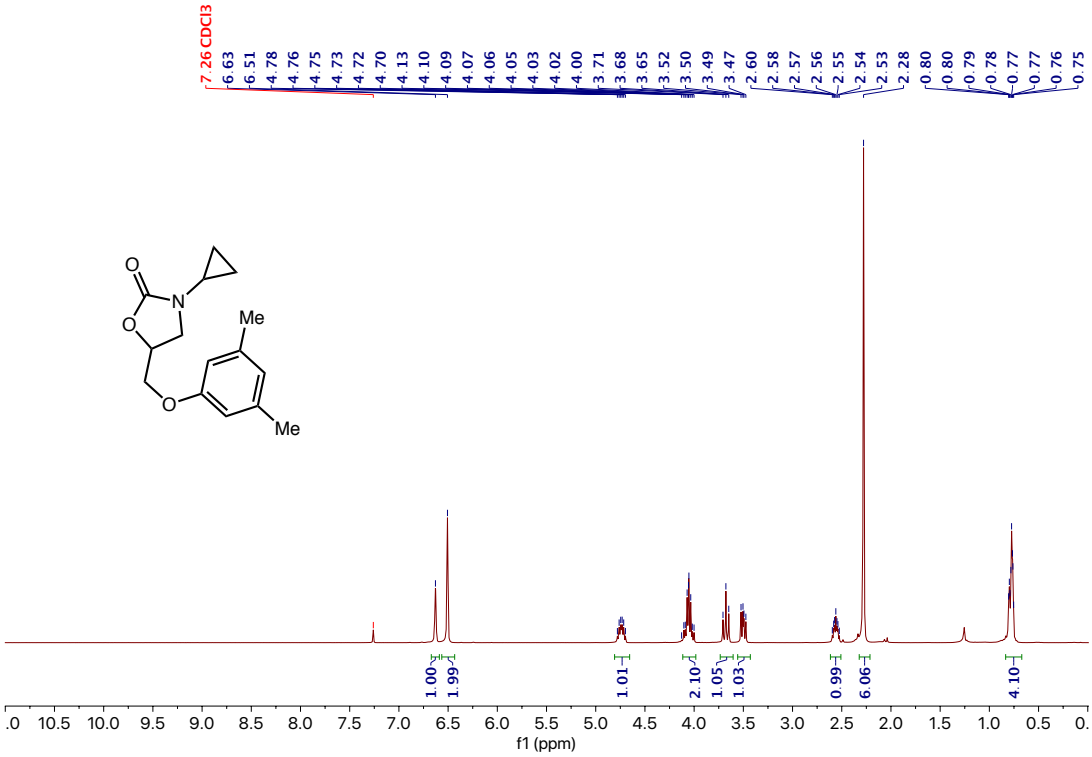


Figure S171: ^{1}H NMR spectrum of **(±)-60** (500 MHz, $CDCl_3$).

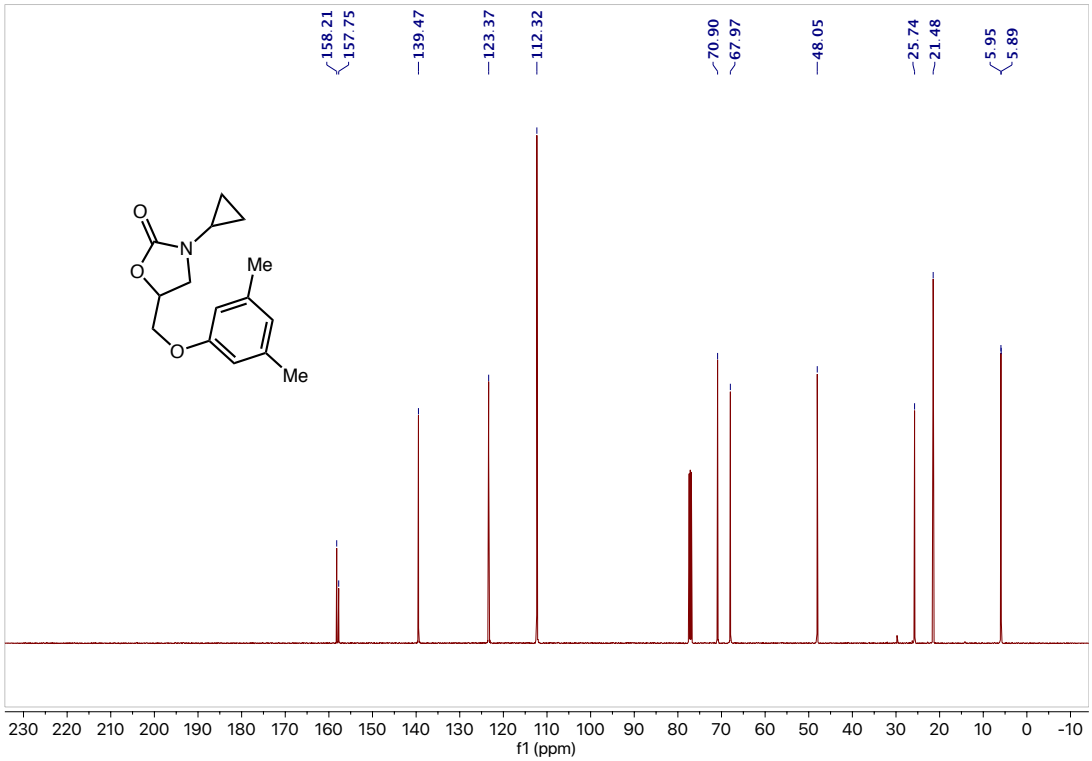


Figure S172: ^{13}C NMR spectrum of **(±)-60** (125 MHz, $CDCl_3$).

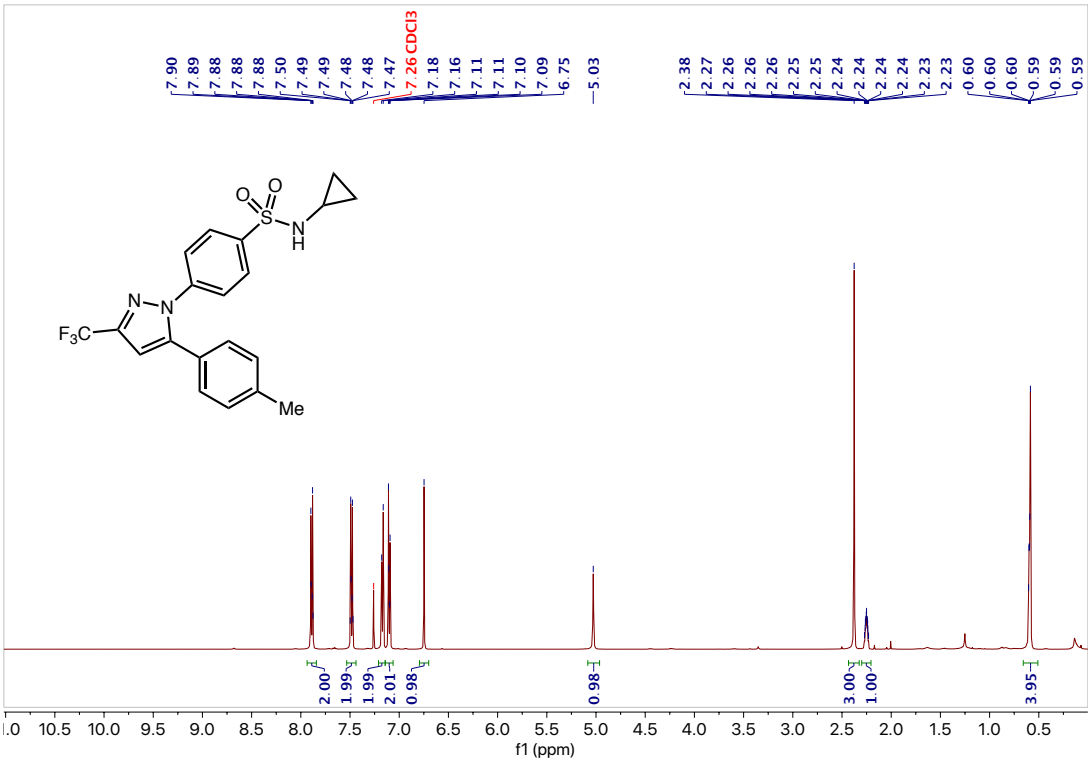


Figure S173: ^{1}H NMR spectrum of **61** (500 MHz, $CDCl_3$).

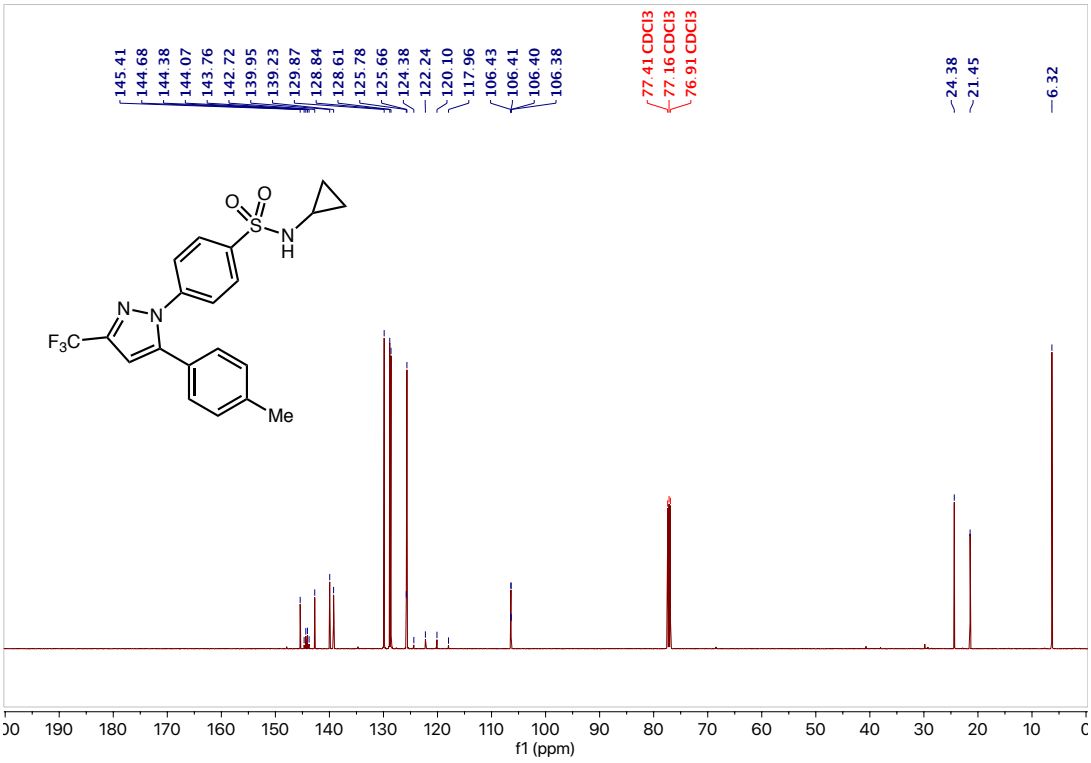


Figure S174: ^{13}C NMR spectrum of **61** (125 MHz, $CDCl_3$).

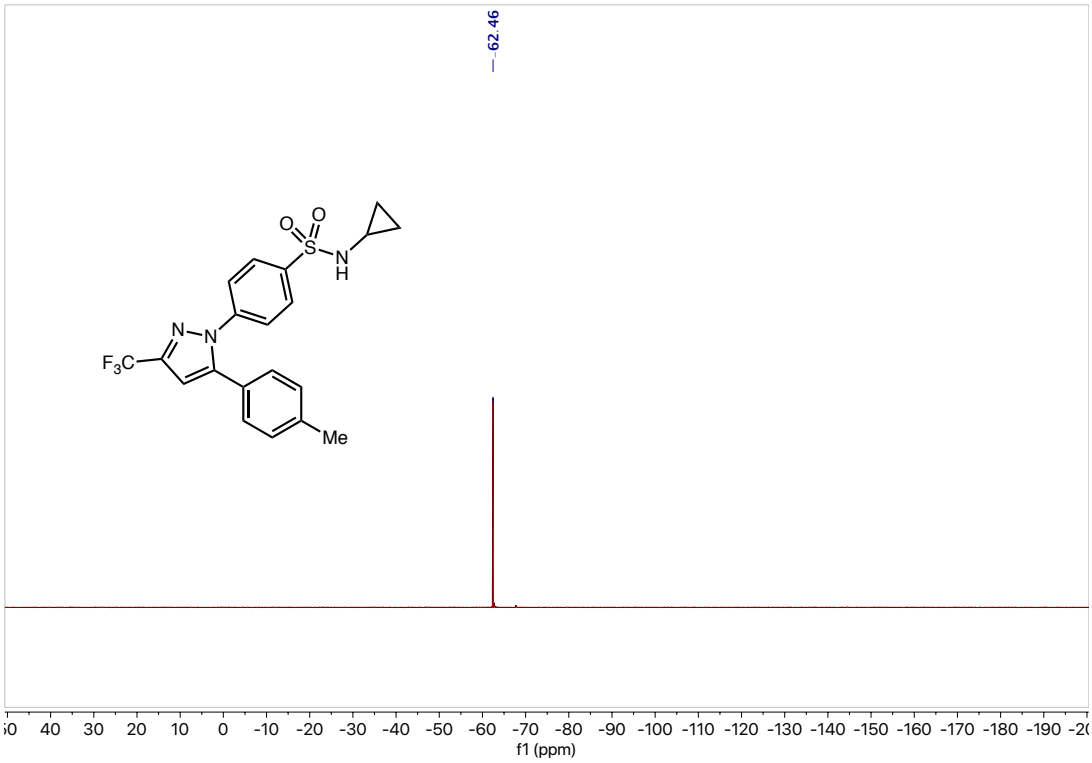


Figure S175: ^{19}F NMR spectrum of **61** (282 MHz, $CDCl_3$).

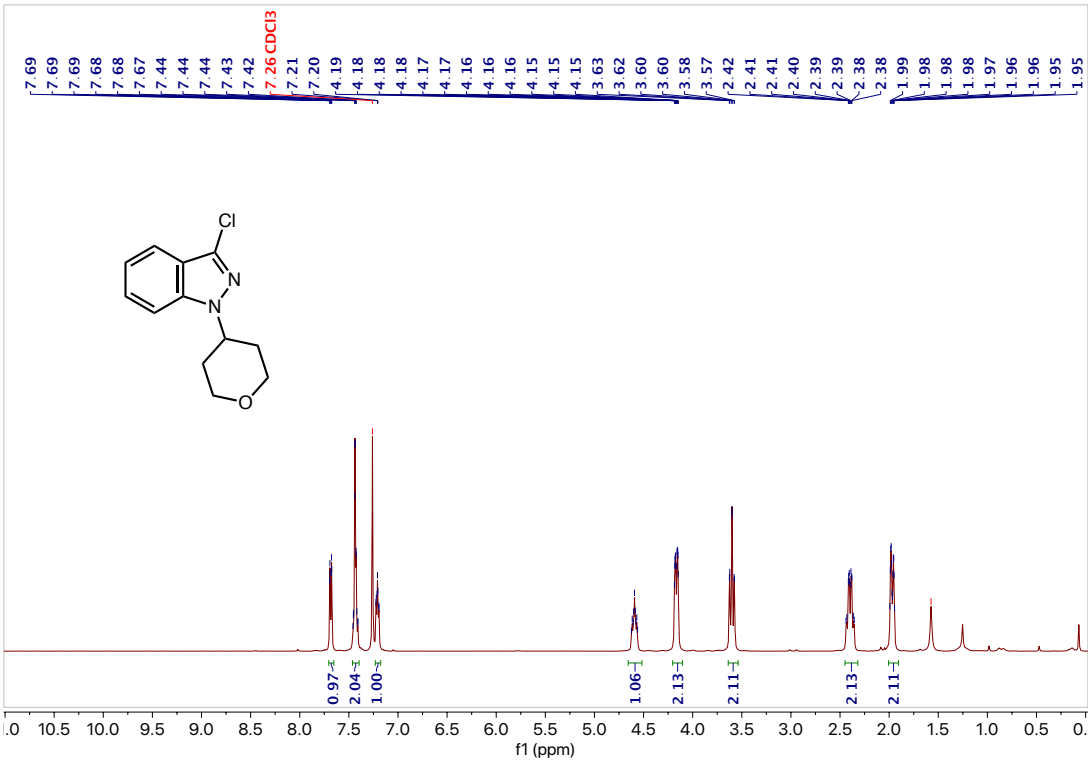


Figure S176: ^{1}H NMR spectrum of **62** (500 MHz, $CDCl_3$).

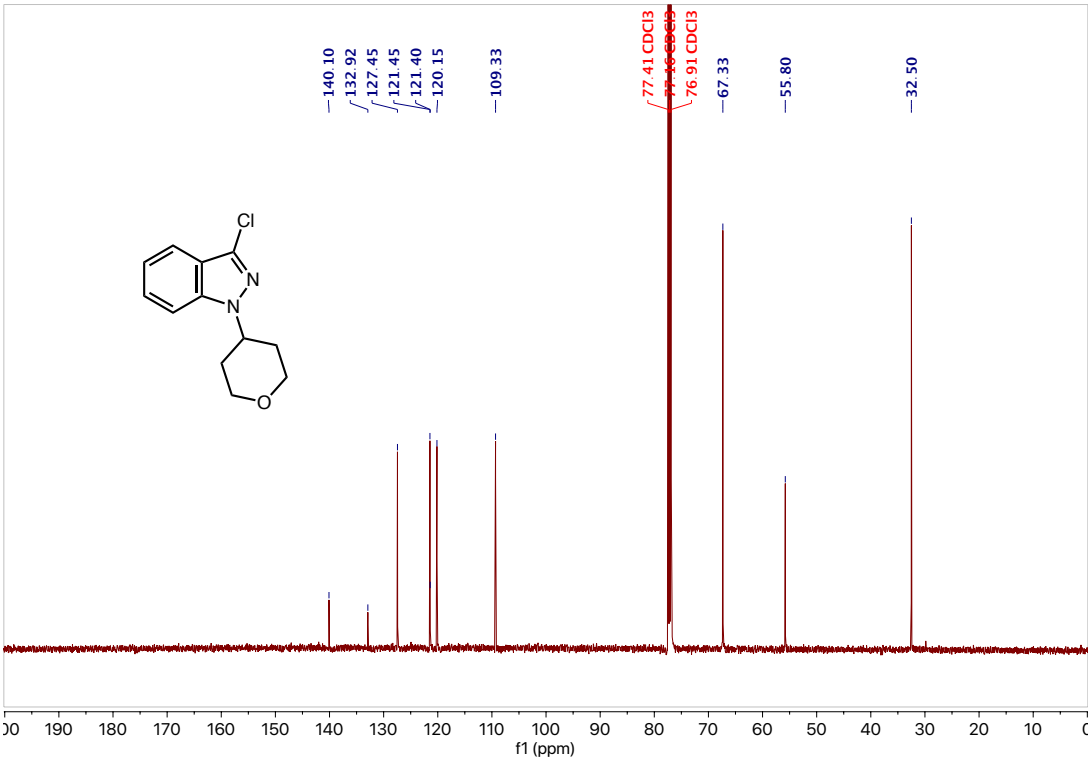


Figure S177: ^{13}C NMR spectrum of **62** (125 MHz, $CDCl_3$).

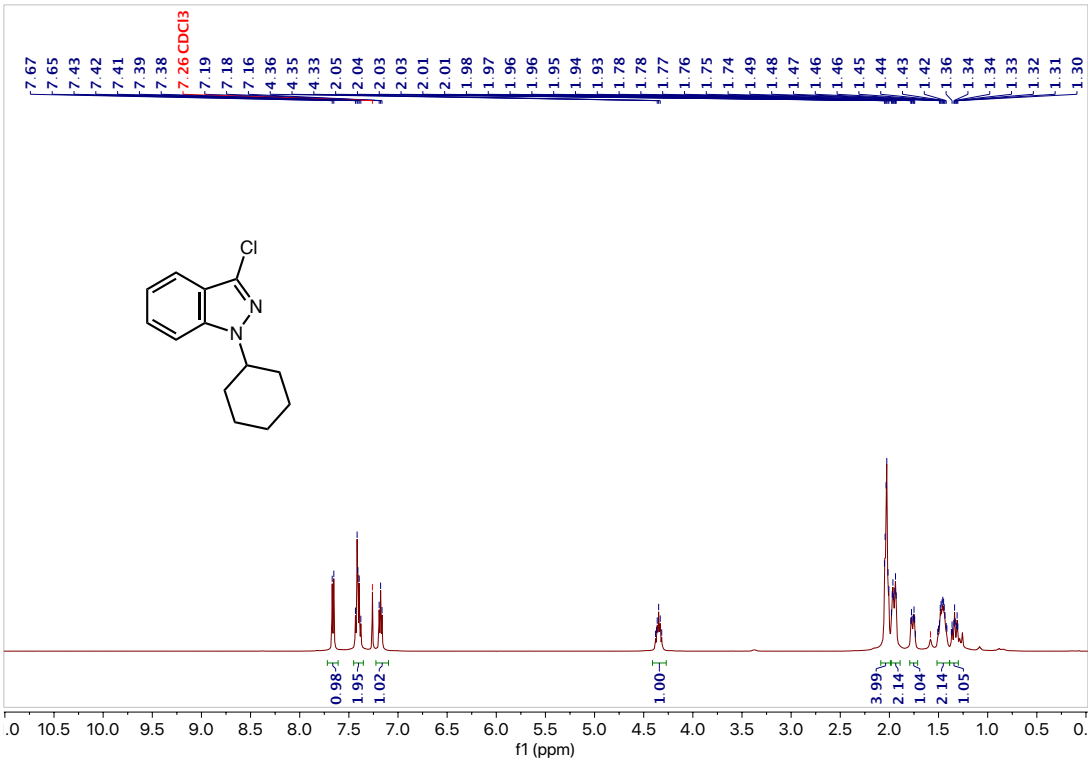


Figure S178: ^{1}H NMR spectrum of **1**, generated from alkyl chloride (500 MHz, $CDCl_3$).

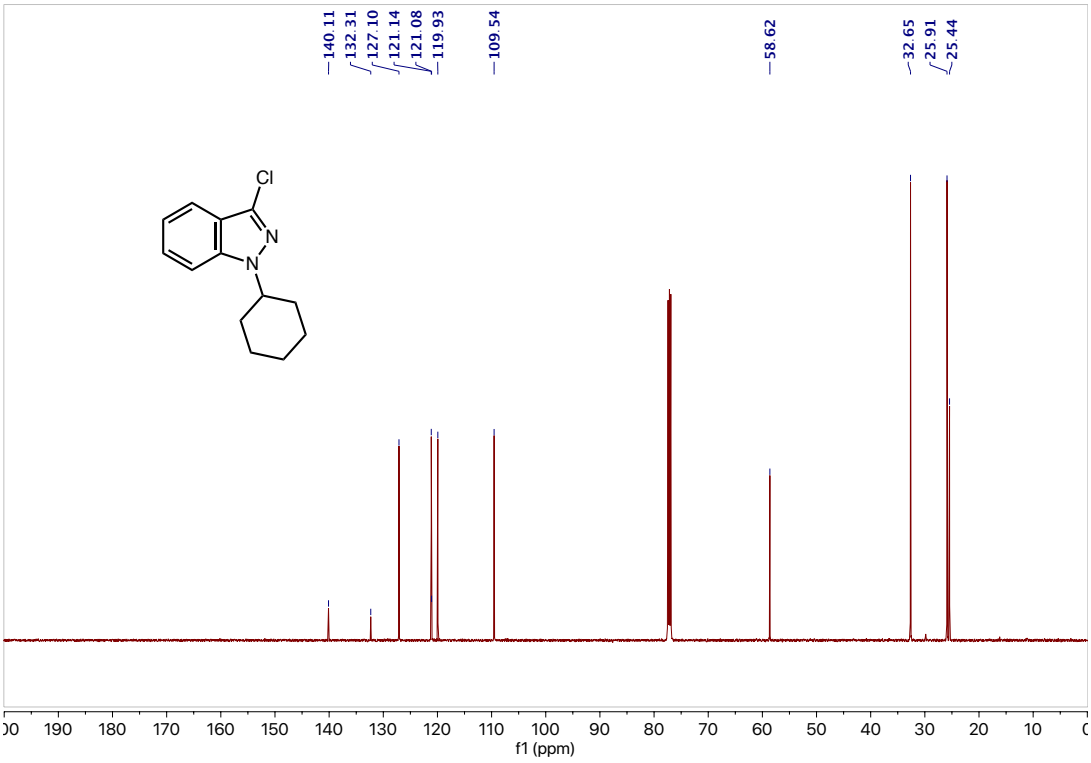


Figure S179: ^{13}C NMR spectrum of **1**, generated from alkyl chloride (125 MHz, $CDCl_3$).

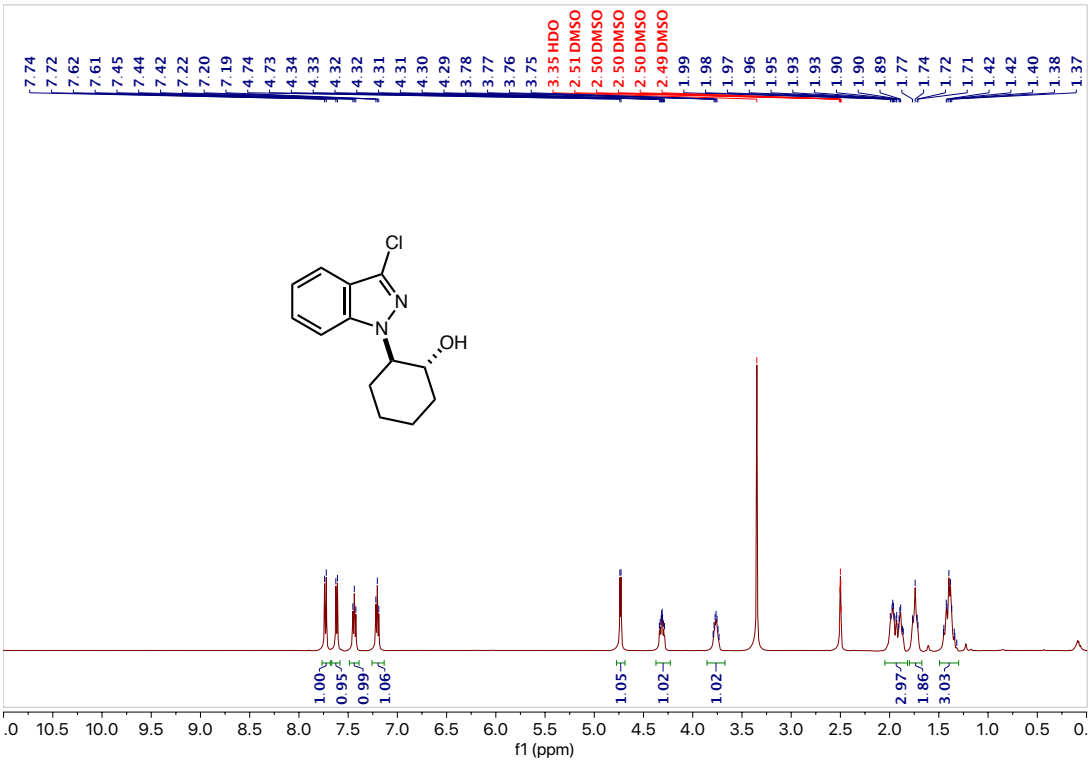


Figure S180: ^{1}H NMR spectrum of **(±)-63** (500 MHz, $(CD_3)_2SO$).

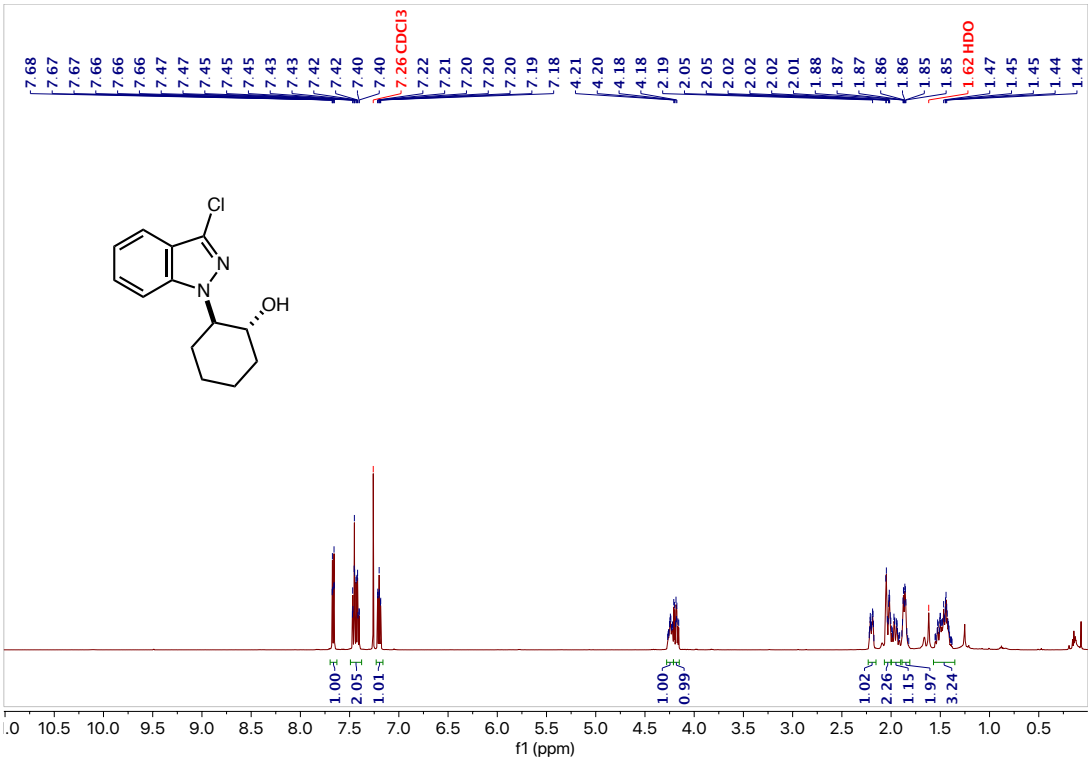


Figure S181: ^{1}H NMR spectrum of **(±)-63** (500 MHz, $CDCl_3$).

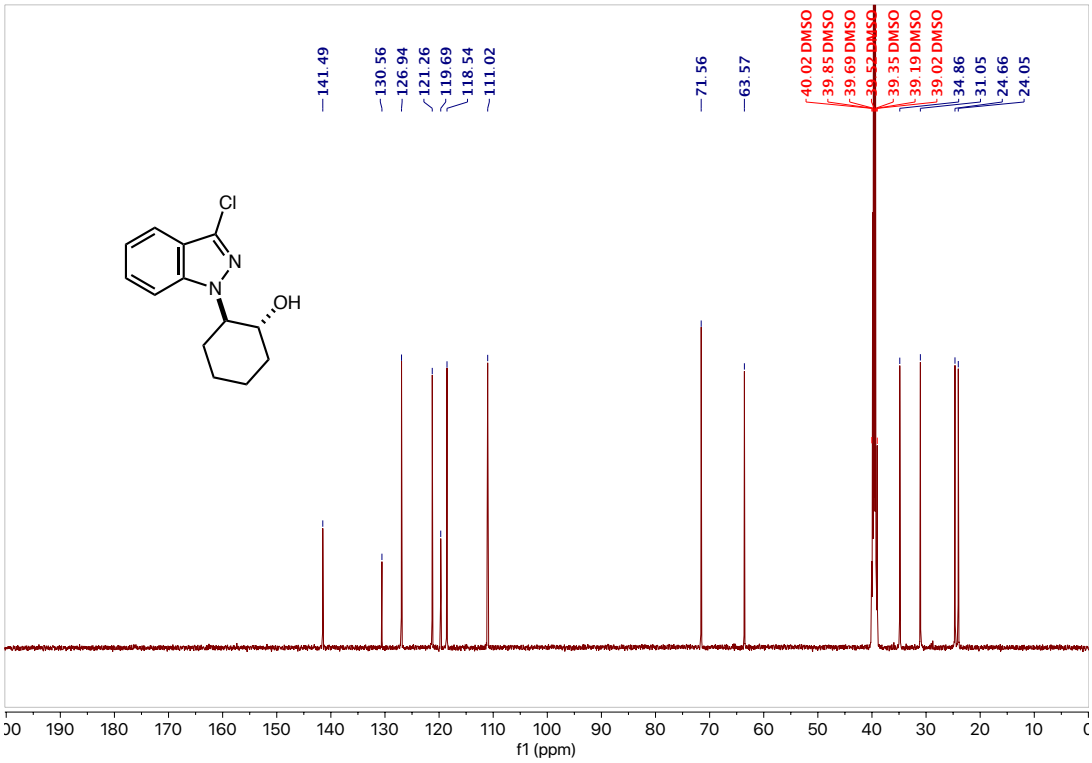


Figure S182: ^{13}C NMR spectrum of **(±)-63** (125 MHz, $(CD_3)_2SO$).

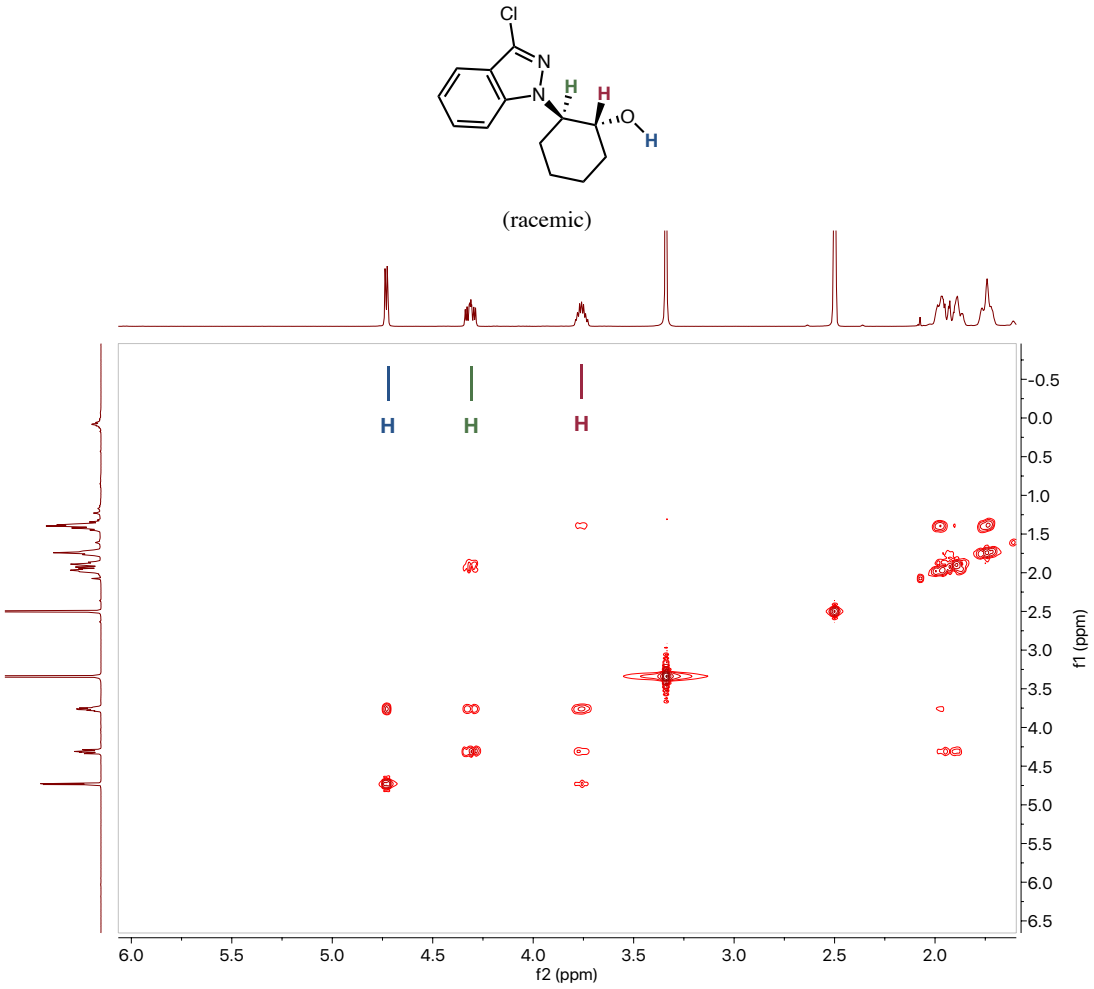


Figure S183: ^{1}H 2D NMR: COSY spectrum of **(±)-63** (500 MHz, $(CD_3)_2SO$).

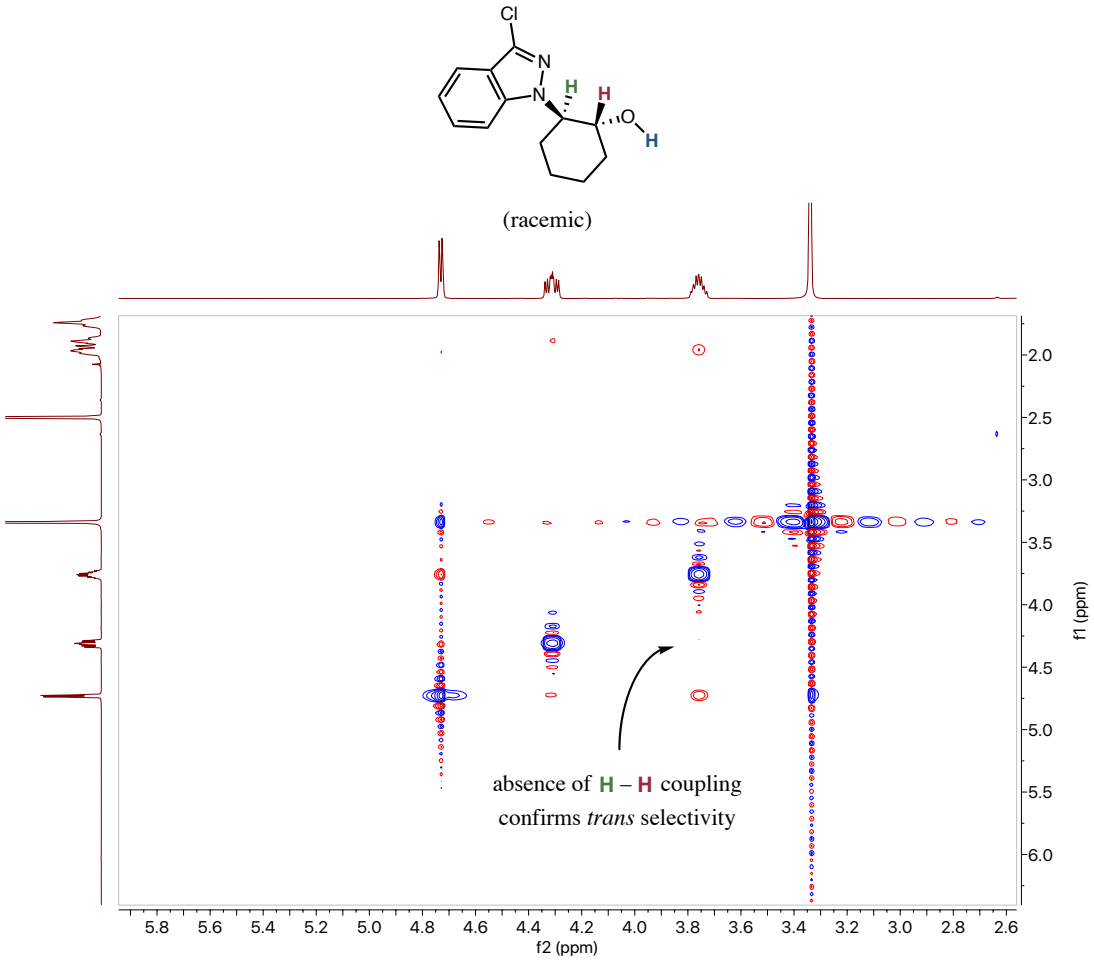


Figure S184: ^{1}H 2D NMR: NOESY spectrum of **(±)-63** (500 MHz, $(CD_3)_2SO$).

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