Supporting Information

ortho-Selective Dearomative [2π + 2σ] Photocycloadditions of Bicyclic Aza-Arenes

Roman Kleinmans,[1,§] Subhabrata Dutta,[1,§] Kristers Ozols,[1] Huiling Shao,[2] Felix Schäfer,[1] Rebecca E. Thielemann,[1] Hok Tsun Chan,[2] Constantin G. Daniliuc,[1] K. N. Houk,[2]* and Frank Glorius[1]*

[1]Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Corrensstraße 36, 48149 Münster, Germany.

[2]Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States.

[§]These authors contributed equally to this work.

*Email: glorius@uni-muenster.de (F.G.) and houk@chem.ucla.edu (K.N.H.).

Table of Contents

1 General Information

Unless otherwise noted, reactions were carried out in cabinet-dry glassware under air. Reactions performed under an argon atmosphere were carried out in oven-dried glassware with oven-dried Teflon-coated magnetic stir bars. Dry solvents for sensitive reactions were either taken from a solvent purification system (HPCL grad, dried over activated alumina columns) or purchased from Acros Organics, Sigma-Aldrich or Carl Roth (stored over activated molecular sieves). Other solvents (*e.g.* for column chromatography or work-up) were purified by distillation. Starting materials which were not synthesized in our laboratory, were obtained from commercial suppliers and used as received, unless otherwise noted. The employed photocatalysts $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$,[1] *fac*-$[Ir(ppy)_3]$,[2] *fac*-$[Ir(dFppy)_3]$,[2] $[Ir(ppy)_2(dtbbpy)](PF_6)$,[3] $[Ru(bpy)_3](PF_6)_2$,[4] $[Ru(bpz)_3](PF_6)_2$,[5] 4CzIPN,[6] and $[Mes_2Acr(t\text{-}Bu)_2](ClO_4)$[7] were prepared following (modified) literature procedures.

Products were purified by column chromatography on Acros Organics silica gel (35–70 mesh) or by preparative thin-layer chromatography (PTLC) using PTLC-plates purchased from Analtech (L × W = 20 × 20 cm, layer thickness 1,000 µm). Suitable solvent mixtures for separation were identified by thin-layer chromatography (TLC) analysis on silica gel 60 F254 aluminum plates from Merck. Spots were visualized under UV light (254 nm) or by staining in an alkaline $KMnO_4$ solution (+ heat).

NMR spectra were recorded on Bruker Avance II 400, Agilent DD2 500 or on Agilent DD2 600 spectrometer. Chemicals shifts (δ) are quoted in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for ^1H and ^{13}C NMR spectra ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; $(CD_3)_2SO$: δ_H = 2.50 ppm, δ_C = 39.52 ppm). The multiplicity of all signals was described with standard abbreviations. Coupling constants (J) are quoted in Hz.

Samples for GC were filtered over a pad of silica and eluted with EtOAc before analysis. GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system (HP-5MS column: 0.25 mm × 30 m, film: 0.25 µm) with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI). The method starts with an injection temperature T_0 (50 °C). After holding this temperature for 3 min, the column is heated by 40 °C/min to temperature T_1 (290 °C) and this temperature is held for an additional time.

All photochemical reactions were performed in 10 mL Schlenk tubes (unless stated otherwise) under an argon atmosphere. The reactions were carried out in a commercial EvoluChem™ PhotoRedOx Duo photobox with irradiation by EvoluChem HCK1021-01-008 blue LEDs (30 W, λ_{max} = 450 nm). The reaction temperature in this set-up was approx. 30 °C. Degassing of reactions (only carried out if stated) was achieved by three freeze-pump-thaw cycles.

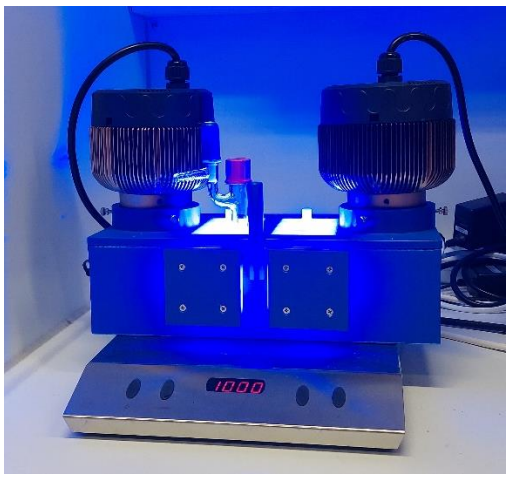


Figure S1. Commercial EvoluChem™ PhotoRedOx Duo photobox with irradiation by EvoluChem HCK1021-01-008 blue LEDs (30 W, λ_{max} = 450 nm).

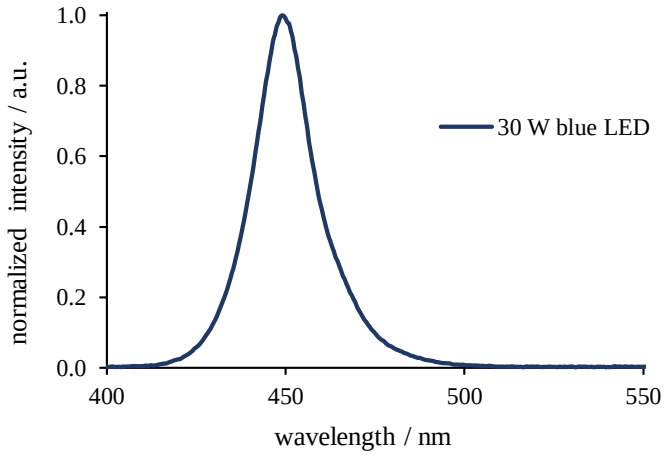
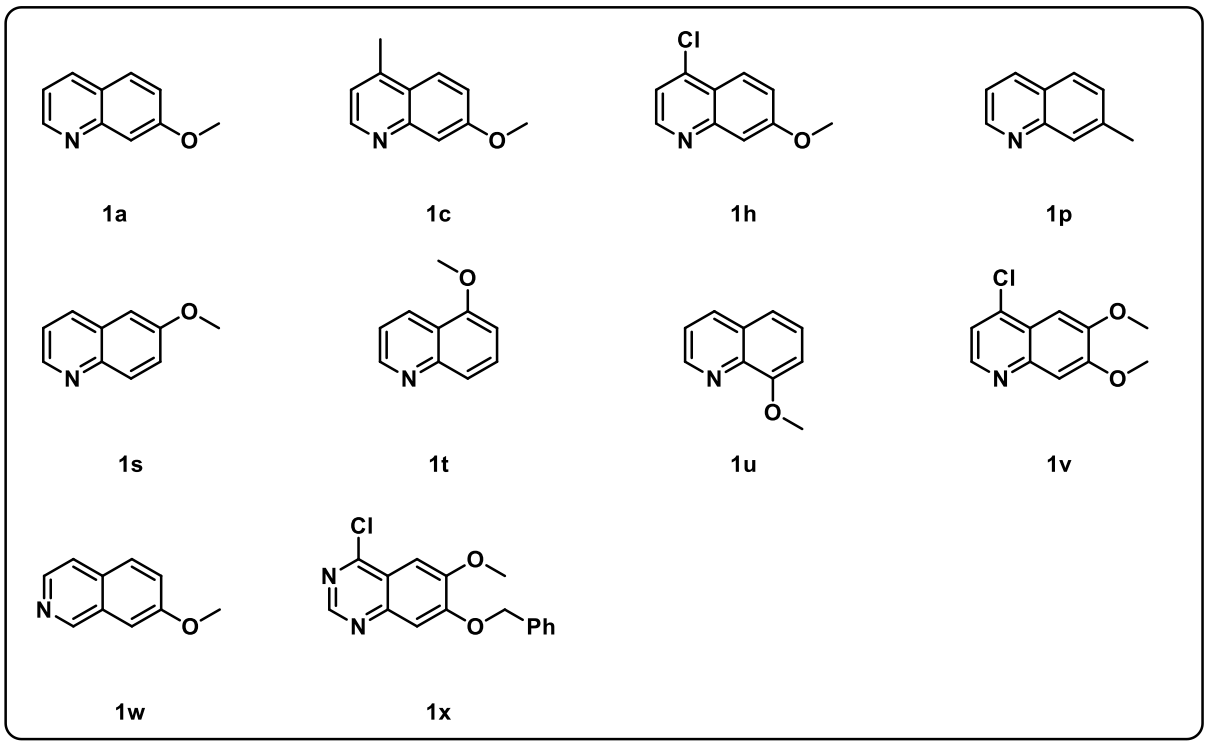


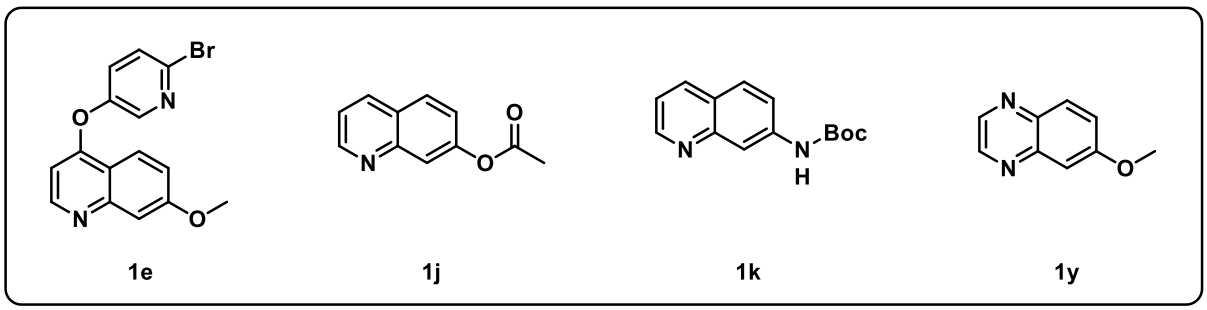
Figure S2. Emission spectrum of blue LED (30 W, λ_{max} = 450 nm).

2 Experimental Procedures and Characterization Data

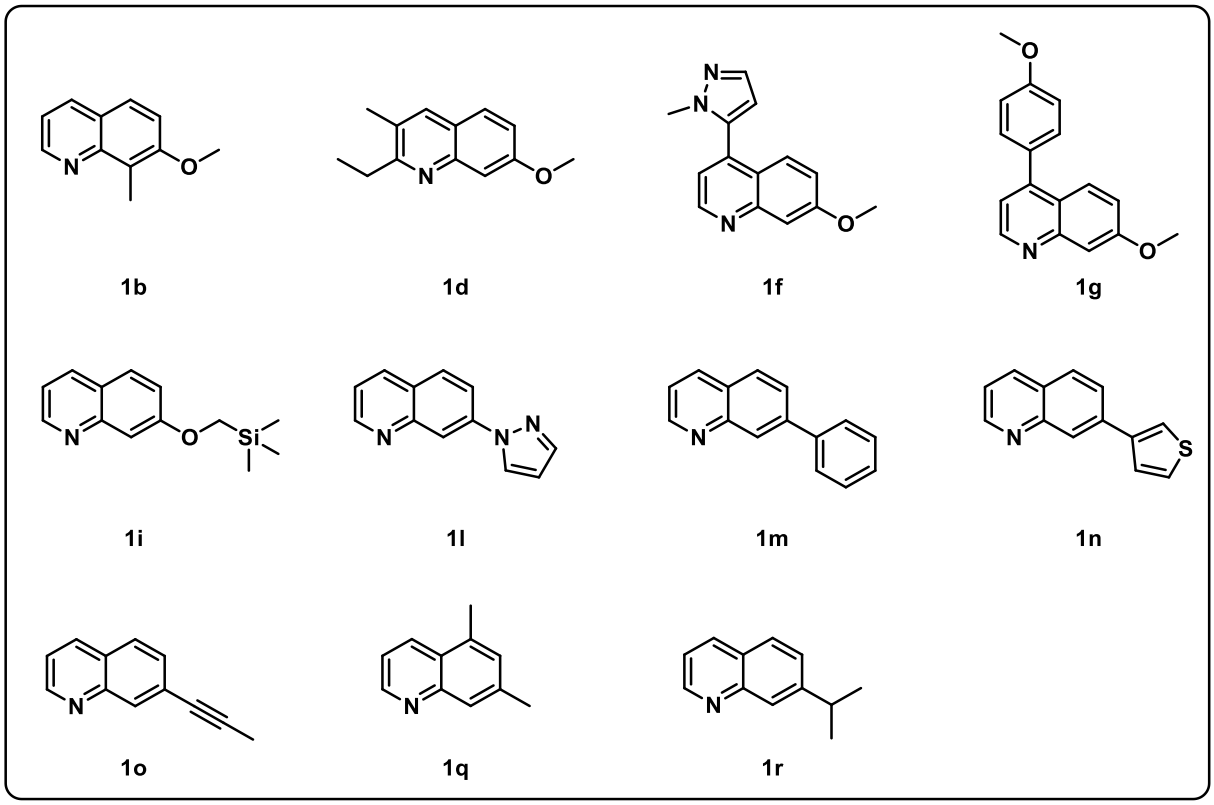
2.1 Starting Material Synthesis



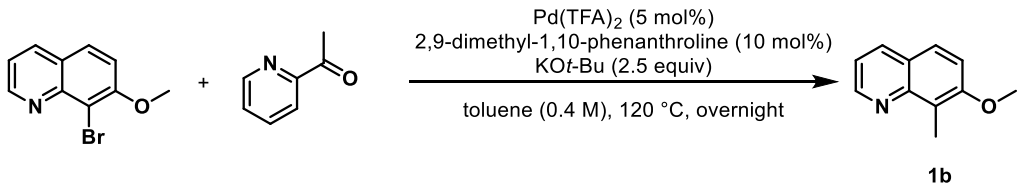
Compounds **1a**, **1c**, **1h**, **1p**, **1s**–**1x** are commercially available and were used as received.



Compounds **1e**, **1j**, **1k**, and **1y** are literature known and were prepared following the respective procedures.[8–11]



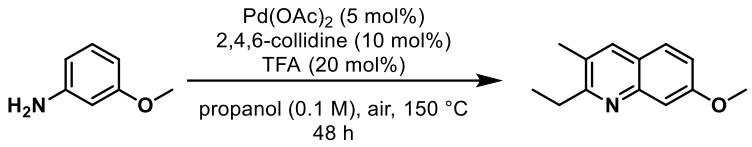
7-Methoxy-8-methylquinoline (1b):



The title compound was prepared according to a modified literature procedure by Wu and co-workers.[12] To an oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar were added 8-bromo-7-methoxyquinoline (357 mg, 1.5 mmol, 1.0 equiv), $Pd(TFA)_2$ (0.075 mmol, 5 mol%), 2,9-dimethyl-1,10-phenanthroline (0.15 mmol, 10 mol%), *t*-BuOK (3.75 mmol, 2.5 equiv), 1-(pyridin-3-yl)ethan-1-one (3.0 mmol, 2.0 equiv), and toluene (4 mL) as the solvent. The resulting mixture was stirred overnight at 120 °C under inert atmosphere. The crude reaction mixture was diluted with EtOAc and water followed by filtration through a pad of Celite®. The filtrate was extracted with EtOAc and the combined organic layers were passed through a pad of $MgSO_4$. The crude material was concentrated and purified by silica gel column chromatography (25% EtOAc in pentane) yielding the product (147 mg, 57%) as yellow solid. The spectral data matched those reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, J = 4.2, 1.8 Hz, 1H), 8.06 (dd, J = 8.2, 1.8 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 7.25 (dd, J = 8.2, 4.2 Hz, 1H), 3.98 (s, 3H), 2.69 (s, 3H).

2-Ethyl-7-methoxy-3-methylquinoline (**1d**):

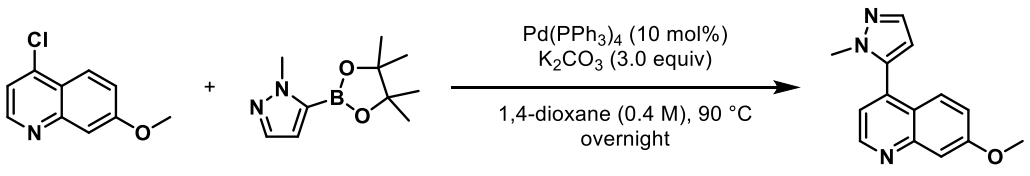


1d

The title compound was prepared according to a modified literature procedure by Jiang and co-workers.[14] To an oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar were added 3-methoxyaniline (616 mg, 5.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (56.2 mg, 5 mol%), 2,4,6-collidine (66 µL, 10 mol%), trifluoroacetic acid (81 µL, 20 mol%) and propanol (40 mL) as the solvent. The resulting mixture was stirred at 150 °C under air for 48 h. The crude reaction mixture was quenched with water (100 mL) and was extracted with EtOAc (3×). The combined org. layers were dried with $MgSO_4$, concentrated under reduced pressure, and purification by silica gel column chromatography (4% EtOAc in pentane) gave the product (333 mg, 33%) as yellow oil. The spectral data matched those reported in the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.58 (d, J = 8.9 Hz, 1H), 7.37 (d, J = 2.5 Hz, 1H), 7.10 (dd, J = 8.9, 2.5 Hz, 1H), 2.97 (q, J = 7.6 Hz, 2H), 2.46 (d, J = 0.9 Hz, 3H), 1.36 (t, J = 7.6 Hz, 3H).

7-Methoxy-4-(1-methyl-1*H*-pyrazol-5-yl)quinoline (**1f**)**:**



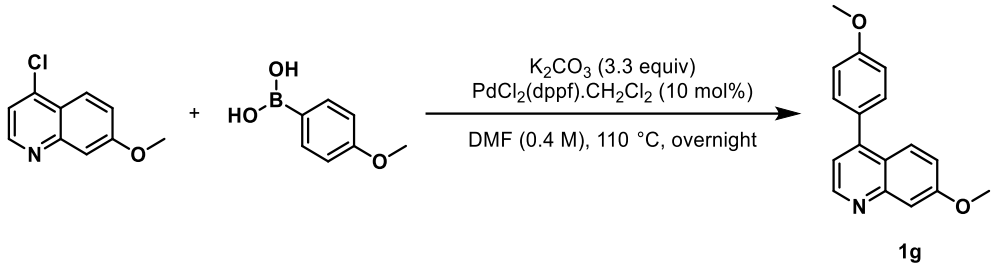
1f

The title compound was prepared according to a modified literature procedure by Chen and co-workers.[16] To an oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar were added 4-chloro-7-methoxyquinoline (387 mg, 2.0 mmol, 1.0 equiv), 1-methyl-5-(4,4,5,5-

tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (832 mg, 8.0 mmol, 4.0 equiv), $Pd(PPh_3)_4$ (230 mg, 10 mol%), K_2CO_3 (414 mg, 6.0 mmol, 3.0 equiv), and 1,4-dioxane (4.0 mL) under argon. The resulting mixture was stirred at 90 °C overnight. The reaction mixture was cooled to room temperature, quenched with dest. water (10 mL), diluted and then extracted with EtOAc (3×). The combined org. layers were dried over $MgSO_4$, concentrated under reduced pressure, and purification by silica gel column chromatography (100% EtOAc) gave the pure product (363 mg, 76%) as pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 4.4 Hz, 1H), 7.64 (d, J = 1.9 Hz, 1H), 7.57 (d, J = 9.2 Hz, 1H), 7.50 (d, J = 2.6 Hz, 1H), 7.24 – 7.16 (m, 2H), 6.43 (d, J = 1.9 Hz, 1H), 3.97 (s, 3H), 3.71 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.1, 150.6, 150.2, 139.1, 139.0, 137.0, 126.6, 122.1, 120.8, 120.3, 108.3, 107.9, 55.8, 37.4; **HRMS** (ESI^+) calc'd for $[M+H]^+$ 240.1131, found 240.1132; **R_f** (80% EtOAc in pentane) = 0.38.

7-Methoxy-4-(4-methoxyphenyl)quinoline (1g):



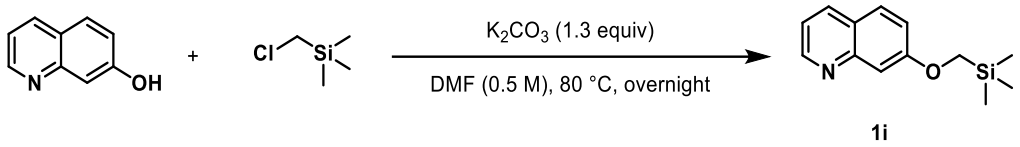
1g

The title compound was prepared according to a modified literature procedure by Maloney and co-workers.[17] To an oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar were added 4-chloro-7-methoxyquinoline (290 mg, 1.5 mmol, 1.0 equiv), (4-methoxyphenyl)boronic acid (296 mg, 1.95 mmol, 1.3 equiv), $PdCl_2(dppf)\cdot CH_2Cl_2$ (123 mg, 10 mol%), K_2CO_3 (684 mg, 4.95 mmol, 3.3 equiv), and DMF (4.0 mL) under argon. The resulting mixture was stirred at 110 °C overnight. The reaction mixture was cooled to room temperature, quenched with water/brine (10 mL), and extracted with EtOAc (3×). The combined org. layers were dried with $MgSO_4$ and concentrated under reduced pressure. Purification by silica gel column chromatography (30% EtOAc in pentane) gave the product (340 mg, 86%) as pale-yellow solid. The spectral data are in accordance with the literature.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 4.5 Hz, 1H), 7.84 (d, J = 9.3 Hz, 1H), 7.49 (d, J = 2.6 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.18 (d, J = 4.5 Hz, 1H), 7.15 (dd, J = 9.3, 2.7 Hz, 1H), 7.07

– 7.02 (m, 2H), 3.96 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 160.0, 150.6, 150.3, 148.3, 130.9, 130.6, 127.2, 122.2, 119.7, 119.5, 114.2, 107.7, 55.6, 55.5.

7-((Trimethylsilyl)methoxy)quinoline (**1i**)**:**

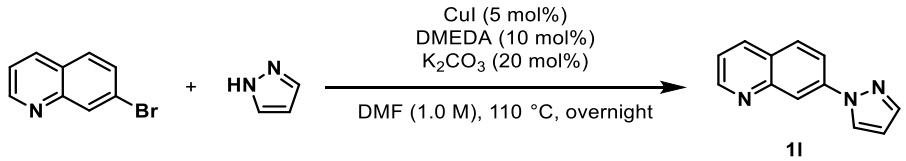


1i

The title compound was prepared according to a modified literature procedure by Yoon and co-workers.[19] To an oven dried Schlenk tube equipped with a Teflon-coated magnetic stir bar were added 7-quinolinol (726 mg, 5.0 mmol, 1.0 equiv) and K_2CO_3 (920 mg, 6.7 mmol, 1.3 equiv). The tube was then evacuated and backfilled with argon three times. Dry DMF (10 mL) was added and while heating up the mixture to 80 °C, (chloromethyl)trimethylsilane (1.0 mL, 7.2 mmol, 1.4 equiv) was added. The reaction mixture was stirred at this temperature overnight and then diluted with dest. H_2O (10 mL). The aq. layer was diluted with brine and then extracted with EtOAc (4×). The combined org. layers were dried with $MgSO_4$, filtered, and the solvents were removed *in vacuo*. Purification by silica gel column chromatography (20% EtOAc in pentane) gave the product (748 mg, 65%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, J = 4.3, 1.8 Hz, 1H), 8.04 (dd, J = 8.1, 1.8 Hz, 1H), 7.65 (d, J = 8.9 Hz, 1H), 7.50 (d, J = 2.5 Hz, 1H), 7.25 – 7.18 (m, 2H), 3.74 (s, 2H), 0.18 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8, 150.5, 150.2, 135.7, 128.6, 123.5, 120.3, 118.8, 107.6, 61.6, −3.0; **HRMS** (ESI^+) calc'd for $[M+H]^+$ 232.1152, found 232.1150; **R_f** (50% EtOAc in pentane) = 0.50.

7-(1*H*-Pyrazol-1-yl)quinoline (**1l**)**:**



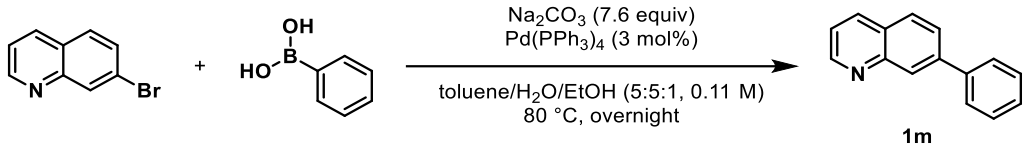
1l

The title compound was prepared according to a modified literature procedure.[20] To an oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar were added 7-bromoquinoline (1.03 g, 5.0 mmol, 1.0 equiv), 1*H*-pyrazole (340 mg, 5.0 mmol, 1.0 equiv),

CuI (47.5 mg, 5 mol%), DMEDA (45 mg, 10 mol%), K_2CO_3 (138 mg, 20 mol%) and DMF (5.0 mL) under argon. The resulting mixture was stirred at 110 °C under overnight. The crude reaction mixture was cooled to room temperature, quenched with water/brine (10 mL) and filtered through a pad of Celite®. The filtrate was extracted with EtOAc (3×), the combined org. layers were dried with $MgSO_4$, and concentrated under reduced pressure. Purification by silica gel column chromatography (30% EtOAc in pentane) gave the product (820 mg, 84%) as pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.3, 1.7 Hz, 1H), 8.26 (d, J = 2.2 Hz, 1H), 8.19 – 8.10 (m, 3H), 7.91 (d, J = 8.9 Hz, 1H), 7.80 (d, J = 1.8 Hz, 1H), 7.39 (dd, J = 8.3, 4.3 Hz, 1H), 6.54 (dd, J = 2.5, 1.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 148.7, 141.9, 140.8, 136.0, 129.5, 127.2, 126.7, 121.1, 119.7, 116.9, 108.5; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 218.0689, found 218.0688; **R_f** (80% EtOAc in pentane) = 0.24.

7-Phenylquinoline (1m):

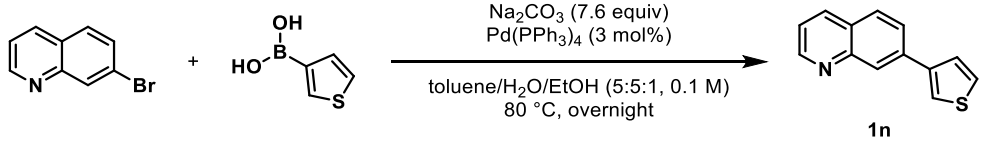


The title compound was prepared following a literature procedure by Bao and co-workers.[21] A Schlenk tube was charged with 7-bromoquinoline (1.040 g, 5.0 mmol, 1.0 equiv), phenylboronic acid (793 mg, 6.5 mmol, 1.3 equiv), and Na_2CO_3 (4.027 g, 38.0 mmol, 7.6 equiv). The tube was evacuated and backfilled with argon three times before $Pd(PPh_3)_4$ (176 mg, 0.15 mmol, 3 mol%) was added. Subsequently, toluene (20 mL), dest. H_2O (20 mL), and ethanol (4 mL) were added, and the reaction mixture was heated to 80 °C and stirred overnight. The mixture was allowed to cool to room temperature and quenched with sat. aq. NH_4Cl. The aq. layer was extracted with EtOAc (2×), and the combined org. layers were dried over MgSO4, filtered and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (10 to 20% EtOAc in pentane) gave the product (880 mg, 86%) as a yellow liquid. The spectral data matched those reported in the literature.[22]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.3, 1.7 Hz, 1H), 8.36 (s, 1H), 8.19 – 8.13 (m, 1H), 7.90 – 7.85 (m, 1H), 7.84 – 7.80 (m, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.51 (dd, J = 6.9, 6.9 Hz, 2H), 7.42 (dd, J = 7.5, 1.5 Hz, 1H), 7.40 – 7.36 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0,

148.6, 142.4, 140.4, 135.9, 129.1, 128.3, 128.0, 127.6, 127.5, 127.2, 126.4, 121.1; **HRMS** (ESI^+) calc'd for $[M+H]^+$ 206.0964, found 206.0963; $\mathbf{R_f}$ (20% EtOAc in pentane) = 0.23.

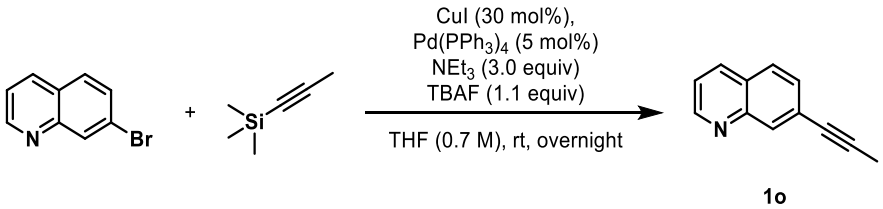
7-(3-Thienyl)quinoline (1n):



The title compound was prepared following a literature procedure by Bao and co-workers.[21] A Schlenk tube was charged with 7-bromoquinoline (1.040 g, 5.0 mmol, 1.0 equiv), 3-thienylboronic acid (833 mg, 6.5 mmol, 1.3 equiv), and Na_2CO_3 (4.027 g, 38.0 mmol, 7.6 equiv). The tube was evacuated and backfilled with argon three times before $Pd(PPh_3)_4$ (176 mg, 0.15 mmol, 3 mol%) was added. Subsequently, toluene (18 mL), dest. H_2O (18 mL), and ethanol (3.8 mL) were added, and the reaction mixture was heated to 80 °C and stirred overnight. The mixture was allowed to cool to room temperature and quenched with sat. aq. NH_4Cl. The aq. layer was extracted with EtOAc (2×), and the combined org. layers were dried over MgSO4, filtered and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (10 to 20% EtOAc in pentane) gave the product (760 mg, 72%) as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.2, 1.8 Hz, 1H), 8.32 (s, 1H), 8.11 (dd, J = 8.3, 1.0 Hz, 1H), 7.80 (s, 1H), 7.80 (s, 1H), 7.64 (dd, J = 3.0, 1.4 Hz, 1H), 7.56 (dd, J = 5.1, 1.4 Hz, 1H), 7.43 (dd, J = 5.1, 3.0 Hz, 1H), 7.34 (dd, J = 8.3, 4.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0, 148.8, 141.6, 136.8, 135.8, 128.3, 127.4, 126.8, 126.4, 126.1, 125.7, 121.7, 120.9; **HRMS** (ESI^+) calc'd for $[M+H]^+$ 212.0529, found 212.0527; $\mathbf{R_f}$ (20% EtOAc in pentane) = 0.19.

7-(Prop-1-yn-1-yl)quinoline (1o):

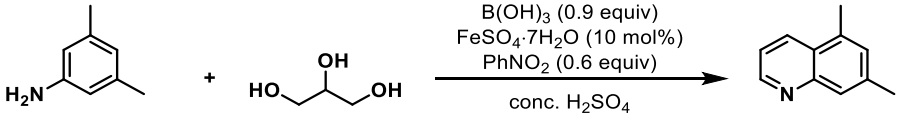


The title compound was prepared according to a modified literature procedure.[23] A Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with 7-bromoquinoline

(1.041 g, 5.0 mmol, 1.0 equiv), CuI (287 mg, 1.5 mmol, 0.30 equiv) and $Pd(PPh_3)_4$ (287 mg, 0.25 mmol, 5 mol%). After evacuating and backfilling the tube with argon three times, dry THF (7 mL), triethylamine (2.1 mL, 15 mmol, 3.0 equiv) and 1-(trimethylsilyl)propyne (0.78 mL, 0.59 g, 5.3 mmol, 1.1 equiv) were added under argon. Subsequently, TBAF (1 M in THF, 5.3 mL, 5.3 mmol, 1.1 equiv) was added dropwise. The reaction mixture was stirred at room temperature overnight before CH_2Cl_2/MeOH (1:1, 38 mL) was added. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (1st column: 10 to 20% EtOAc in pentane, 2nd column: 5% EtOAc in pentane) and the product (456 mg, 55%) was obtained as a brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 – 8.85 (m, 1H), 8.12 (s, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.69 (dd, J = 8.4, 2.2 Hz, 1H), 7.49 (ddd, J = 8.4, 1.6, 1.6 Hz, 1H), 7.35 – 7.29 (m, 1H), 2.13 – 2.06 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 148.1, 135.8, 132.3, 129.6, 127.8, 127.6, 125.4, 121.3, 88.3, 79.7, 4.6; **HRMS** (ESI^+) calc'd for $[M+H]^+$ 168.0808, found 168.0807; **R_f** (20% EtOAc in pentane) = 0.36.

5,7-Dimethylquinoline (1q):



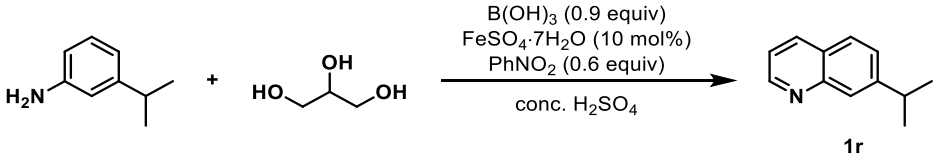
1q

The title compound was prepared following a modified literature procedure.[24] To a mixture of 3,5-dimethylaniline (2.42 g, 20.0 mmol, 1.0 equiv), $FeSO_4·7H_2O$ (556 mg, 2.0 mmol, 10 mol%), and nitrobenzene (1.48 g, 12 mmol, 0.60 equiv) was added boronic acid (1.24 g, 18.5 mmol, 0.9 equiv) and glycerol (3.68 g, 40 mmol, 2.0 equiv). The mixture was cooled to 0 °C and conc. aq. H_2SO_4 (3.05 mL) was added dropwise. The resulting mixture was heated to 125 °C and stirred overnight. After cooling to room temperature, the mixture was poured into ice water and the pH was adjusted to pH = 10 by addition of an aq. ammonia solution. The mixture was extracted with Et_2O (3×), and the combined organic layers were washed with brine, dried with $MgSO_4$, and the solvent was removed *in vacuo*. Purification by silica gel column chromatography afforded the product (1.51 g, 48%) as a brown liquid. The spectral data matched those reported in the literature.[25]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, J = 4.2, 1.7 Hz, 1H), 8.23 (ddd, J = 8.5, 1.7, 0.9 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.32 (dd, J = 8.4, 4.2 Hz, 1H), 7.19 (s, 1H), 2.62 (s, 3H), 2.50 (d, J =

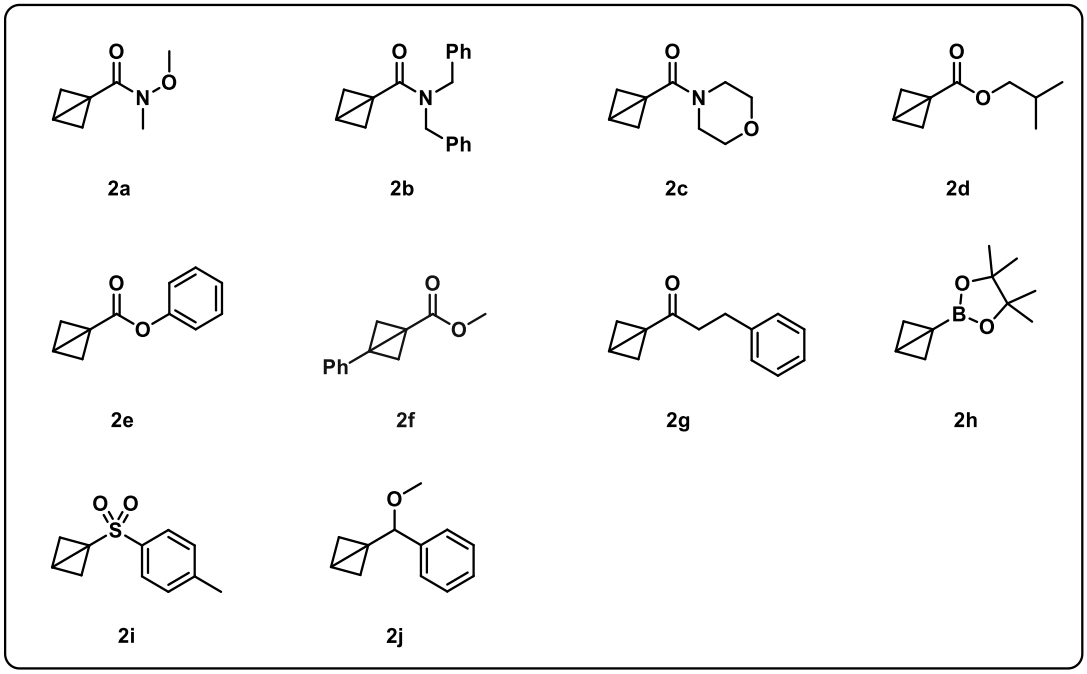
1.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0, 148.9, 139.4, 134.2, 132.3, 129.4, 126.7, 125.8, 112.0, 21.9, 18.6; **HRMS** (ESI^+) calc'd for $[M+H]^+$ 158.09643 found 158.09637.

7-Isopropylquinoline (**1r**)**:**



The title compound was prepared following a modified literature procedure.[24] To a mixture of 3-isopropylaniline (2.70 g, 20.0 mmol, 1.0 equiv), $FeSO_4·7H_2O$ (556 mg, 2.0 mmol, 10 mol%), and nitrobenzene (1.48 g, 12 mmol, 0.60 equiv) was added boronic acid (1.24 g, 18.5 mmol, 0.9 equiv) and glycerol (3.68 g, 40 mmol, 2.0 equiv). The mixture was cooled to 0 °C and conc. aq. H_2SO_4 (3.05 mL) was added dropwise. The resulting mixture was heated to 125 °C overnight. After cooling to room temperature, the mixture was poured into ice water and the pH was adjusted to pH = 10 by addition of an aq. ammonia solution. The mixture was extracted with Et_2O (3×), and the combined organic layers were washed with brine, dried with $MgSO_4$ and the solvent was removed *in vacuo*. Purification by silica gel column chromatography afforded the product (950 mg, 28%) as a brown liquid. The spectral data matched those reported in the literature.[26]

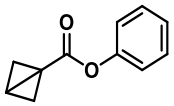
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, J = 4.3, 1.8 Hz, 1H), 8.10 (ddd, J = 8.3, 1.8, 0.8 Hz, 1H), 7.93 (dd, J = 1.7, 0.8 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.45 (dd, J = 8.4, 1.8 Hz, 1H), 7.32 (dd, J = 8.2, 4.2 Hz, 1H), 3.12 (hept, J = 6.9 Hz, 1H), 1.36 (d, J = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7, 150.4, 148.7, 135.8, 127.7, 126.8, 126.7, 125.7, 120.5, 34.4, 23.9; **HRMS** (ESI^+) calc'd for $[M+H]^+$ 172.1121 found 172.1121.



Compounds **2a**–**2i** are literature known compounds. **2a**–**2c** were prepared according to a modified literature procedure by Gryko and co-workers.[27] Ester **2d** has been previously synthesized in our laboratory,[28] and **2e** and was prepared following the same protocol. 1,3-Disubstituted BCB **2f** was prepared following a procedure by Mykhailiuk and coworkers,[29] ketone **2g** was prepared according to a procedure by Procter and coworkers.[30] BCB-Bpin **2h** was prepared following a procedure by Aggarwal and coworkers,[31] and **2i** was synthesized according to a procedure by Baran and co-workers.[32]

Note: In this Supporting Information bicyclo[1.1.0]butanes are generally abbreviated as BCBs.

Phenyl bicyclo[1.1.0]butane-1-carboxylate (**2e**)**:**



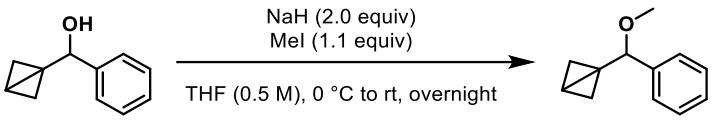
2e

The title compound was prepared following a literature procedure by Glorius and coworkers.[28] The spectral data matched those reported in the literature.[33]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.24 – 7.19 (m, 1H), 7.12 – 7.06 (m, 2H), 2.53 (ddd, J = 3.5, 1.1, 1.1 Hz, 2H), 2.34 (p, J = 3.3 Hz, 1H), 1.31 (ddd, J = 3.0, 1.1, 1.1 Hz, 2H).

Note: For this compound **2e**, following the procedure described by our group led to an unidentified impurity (~5%) that could not be separated *via* silica gel column chromatography.

1-(Methoxy(phenyl)methyl)bicyclo[1.1.0]butane (2j):



S1 **2j**

Alcohol **S1** and the title compound were prepared following a literature procedure by Wipf and co-workers.[34]

In an oven-dried Schlenk flask equipped with a Teflon-coated magnetic stir bar, alcohol **S1** (1.50 g, 9.36 mmol) was dissolved in dry THF (20 mL) under argon. NaH (60 w% dispersion in mineral oil, 749 mg, 18.7 mmol, 2.0 equiv) was added portionwise at 0 °C, and then MeI (1.1 equiv, 1.48 g, 10.3 mmol, 641 µL) was added dropwise and the reaction was allowed to warm up to room temperature overnight. The reaction was quenched with water, and the aq. layer was extracted with Et_2O (3×). The combined org. layers were washed with brine, dried with $MgSO_4$, filtered, and the solvent was removed *in vacuo*. Purification by Kugelrohr distillation gave the product (1.43 g, 88%) as a colorless oil.

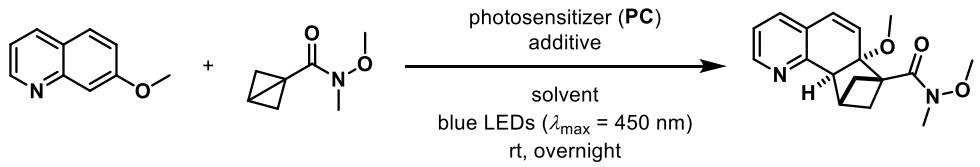
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.29 – 7.23 (m, 3H), 4.57 (s, 1H), 3.36 (s, 3H), 1.65 (dd, J = 6.3, 3.0 Hz, 1H), 1.26 (dd, J = 6.3, 2.9 Hz, 1H), 1.21 (dq, J = 3.0, 1.4 Hz, 1H), 0.85 (t, J = 1.2 Hz, 1H), 0.61 (dp, J = 1.5, 0.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.9, 128.3, 127.7, 126.9, 83.8, 56.9, 34.2, 31.0, 13.8, 0.6; **HRMS** (ESI^+) calc'd for $[M+H]^+$ 175.1117 found 175.1115.

2.2 Optimization Studies

All optimization reactions were performed once and on 0.10 mmol scale.

To an oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar were added photocatalyst (**Ir-F**, for other tested photocatalysts, see section 3.3) and additive. The Schlenk tube was evacuated and backfilled with argon three times. Subsequently, the respective solvent, 7-methoxyquinoline (**1a**), and *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**) were added under positive argon pressure. The reaction mixture was then stirred under irradiation with blue LEDs (30 W, λ_{max} = 450 nm) overnight. The reaction mixture was treated with aq. sat. $NaHCO_3$ and the aq. layer was extracted with EtOAc (3×). The org. layers were combined, and the solvent removed *in vacuo*. CH_2Br_2 (7.0 µL, 0.10 mmol, 1.0 equiv) was added as internal standard, and the yield was determined ^{1}H NMR analysis. The results are compiled in Table S1.

Table S1. Optimization studies with 7-methoxyquinoline (**1a**) as substrate.



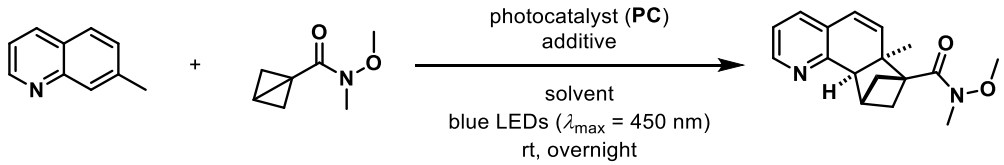
1a **2a** **3a**

entry	solvent (conc.)	equiv **1**	equiv **2**	**PC** (mol%)	additive (equiv)	% yield
1	CH_2Cl_2 (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	---	77
2	HFIP (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	---	81
3	CH_2Cl_2 (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (1.0 equiv)	86
4	CH_2Cl_2 (0.05 M)	1.5	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (1.0 equiv)	76
5	CH_2Cl_2 (0.05 M)	1.0	2.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (1.0 equiv)	60
6	CH_2Cl_2 (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (0.50 equiv)	92 (89)[a]
7	CH_2Cl_2 (0.1 M)	2.0	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (0.50 equiv)	90
8	CH_2Cl_2 (0.05 M)	2.0	1.0	---	$Sc(OTf)_3$ (1.0 equiv)	43
9	CH_2Cl_2 (0.05 M)	2.0	1.0	---	pTsOH·H_2O (1.0 equiv)	15
10[b]	CH_2Cl_2 (0.05 M)	2.0	1.0	---	$Sc(OTf)_3$ (1.0 equiv)	n.d.
11	CH_2Cl_2 (0.05 M)	2.0	1.0	---	---	<5

[a] isolated yield on 0.20 mmol scale. [b] no irradiation (T = 35 °C). **Ir-F**: $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$

During the substrate scope analysis, we realized a decreased yield when less electron-rich 7-methylquinoline was used instead of 7-methoxyquinoline. Thus, re-optimization studies were conducted which are shown in Table S2.

Table S2. Re-optimization of the reaction conditions for 7-methylquinoline (**1p**) as substrate.



1p **2a** **3y**

entry	solvent (conc.)	equiv **1p**	equiv **2a**	**PC** (mol%)	additive (equiv)	% yield **3y**
Equivalents of Sc(OTf)$_3$						
1	CH_2Cl_2 (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (0.50 equiv)	55
2	CH_2Cl_2 (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (1.0 equiv)	70
3	CH_2Cl_2 (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (1.5 equiv)	12
Solvent						
1	MeCN (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (1.0 equiv)	42
2	THF (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (1.0 equiv)	52
3	DMA (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (1.0 equiv)	n.d.
4	HFIP (0.05 M)	2.0	1.0	**Ir-F** (2 mol%)	---	n.d.
Lewis and Brønsted acid						
1	CH_2Cl_2 (0.2 M)	2.0	1.0	**Ir-F** (2 mol%)	$Sc(OTf)_3$ (1.0 equiv)	65
2	CH_2Cl_2 (0.2 M)	2.0	1.0	**Ir-F** (2 mol%)	$In(OTf)_3$ (1.0 equiv)	50
3	CH_2Cl_2 (0.2 M)	2.0	1.0	**Ir-F** (2 mol%)	$BF_3{\cdot}Et_2O$ (1.0 equiv)	50
4	CH_2Cl_2 (0.2 M)	2.0	1.0	**Ir-F** (2 mol%)	$Bi(OTf)_3$ (1.0 equiv)	14
5	CH_2Cl_2 (0.2 M)	2.0	1.0	**Ir-F** (2 mol%)	*p*TsOH·H_2O (1.0 equiv)	58
Control experiments						
1	CH_2Cl_2 (0.2 M)	2.0	1.0	**---**	---	traces
2	CH_2Cl_2 (0.05 M)	2.0	1.0	**---**	$Sc(OTf)_3$ (0.50 equiv)	9

2.3 Substrate Scope

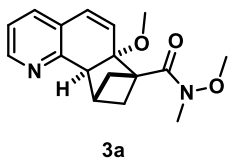
General Procedure

To an oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar were added **Ir-F** (4.4 mg, 4 µmol, 2 mol%), $Sc(OTf)_3$ (49.2 mg, 0.10 mmol, 0.50 equiv), the respective bicyclic aza-arene (if solid, 0.4 mmol, 2.0 equiv), and bicyclo[1.1.0]butane (BCB) derivative (if solid, 0.20 mmol, 1.0 equiv). The Schlenk tube was evacuated and backfilled with argon three times. Subsequently, CH_2Cl_2 (4.0 mL), bicyclic aza-arene (if liquid), and BCB (if liquid) were added under positive argon pressure. The reaction mixture was then stirred under irradiation with blue LEDs (30 W, λ_{max} = 450 nm) for 16 h. The reaction mixture was quenched with aq. sat. $NaHCO_3$, and the aq. layer was extracted with CH_2Cl_2 (3×). The org. layers were combined, and the solvent removed *in vacuo*. CH_2Br_2 (14 µL, 0.20 mmol, 1.0 equiv) was added as internal standard, and crude ^1H NMR was measured. The NMR tube, used pipettes, and the Schlenk tube were carefully rinsed with CH_2Cl_2 into the previously used round bottom flask. After removal of the solvents under reduced pressure, the product was purified by silica gel column chromatography and/or preparative thin-layer chromatography (PTLC).

Note I: If not stated otherwise, all compounds were isolated as single regioisomers and diastereomers. The connectivity of the regioiso- and diastereomers was determined for at least one example of each substrate class (quinolines, isoquinolines, …). Based on the high similarity of the spectral data within one class of product motifs, it was concluded that the same selectivity was obtained.

Note II: For some compounds the ^{13}C NMR carbonyl signal of the Weinreb amide is not detectable with reasonable scans.

***N*,6a-Dimethoxy-*N*-methyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (3a):**



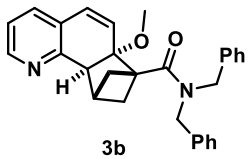
3a

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 7-methoxyquinoline (**1a**, 63.7 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (53.6 mg, 89%) as a colorless solid.

For a scale-up (2.0 mmol scale) experiment, see section: *Sensitivity Assessment*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, J = 4.9, 1.7 Hz, 1H), 7.40 (dd, J = 7.6, 1.7 Hz, 1H), 7.09 (dd, J = 7.6, 4.9 Hz, 1H), 6.64 (d, J = 10.1 Hz, 1H), 5.91 (d, J = 10.0 Hz, 1H), 3.69 (s, 3H), 3.42 – 3.38 (m, 1H), 3.23 (s, 3H), 3.14 (s, 3H), 2.81 – 2.75 (m, 1H), 2.11 (dd, J = 9.2, 7.3 Hz, 1H), 1.99 (dd, J = 7.5, 3.1 Hz, 1H), 1.59 (ddd, J = 7.7, 2.6, 2.6 Hz, 1H), 1.54 (dd, J = 9.2, 7.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.4, 148.0, 134.3, 129.2, 128.4, 127.8, 121.9, 85.6, 61.9, 61.5, 52.3, 50.0, 42.3, 40.1, 38.1, 32.7 – ^{13}C signal of Weinreb amide, expected at ~170 ppm, not observed; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 323.1366, found 323.1363; **R_f** (100% Et_2O) = 0.20; **X-ray** (single-crystal) A colorless plate-like specimen of **3a** (X-ray diffraction quality) was obtained by liquid/liquid diffusion with CH_2Cl_2 and pentane (CCDC 2225189).

***N*,*N*-Dibenzyl-6a-methoxy-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (3b):**



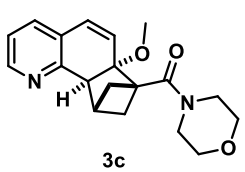
3b

The title compound was prepared from *N*,*N*-dibenzylbicyclo[1.1.0]butane-1-carboxamide (**2b**, 55.5 mg, 0.20 mmol, 1.0 equiv) and 7-methoxyquinoline (**1a**, 63.7 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (50% Et_2O in pentane) gave the product (46.7 mg, 53%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 4.9, 1.7 Hz, 1H), 7.44 (dd, J = 7.6, 1.7 Hz, 1H), 7.38 – 7.26 (m, 6H), 7.25 – 7.17 (m, 4H), 7.13 (dd, J = 7.6, 4.9 Hz, 1H), 6.72 (d, J = 10.0 Hz, 1H), 5.93 (d, J = 10.0 Hz, 1H), 5.16 – 5.02 (m, 2H), 4.37 (d, J = 17.0 Hz, 1H), 4.12 (d, J = 15.0 Hz, 1H), 3.47 – 3.41 (m, 1H), 3.18 (s, 3H), 2.80 – 2.74 (m, 1H), 2.07 – 2.01 (m, 1H), 1.95 (dd, J = 7.0, 3.1 Hz, 1H), 1.71 (ddd, J = 9.3, 3.4, 3.4 Hz, 1H), 1.69 – 1.65 (m, 1H); **^{13}C NMR** (101

MHz, $CDCl_3$) δ 171.9, 157.4, 148.2, 137.7, 137.6, 134.5, 129.9, 128.8, 128.7, 128.0, 127.9, 127.9, 127.3, 127.2, 127.0, 122.0, 85.9, 63.6, 52.4, 50.4, 50.3, 48.0, 42.0, 40.6, 39.3; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 459.2043, found 459.2039; $\mathbf{R_f}$ (50% Et_2O) = 0.11.

(6a-Methoxy-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinolin-7-yl)(morpholino) methanone (**3c**):

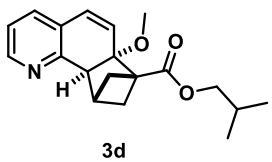


3c

The title compound was prepared from bicyclo[1.1.0]butan-1-yl(morpholino)methanone (**2c**, 33.4 mg, 0.20 mmol, 1.0 equiv) and 7-methoxyquinoline (**1a**, 63.7 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (52.0 mg, 80%) as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 4.9, 1.7 Hz, 1H), 7.42 (dd, J = 7.7, 1.7 Hz, 1H), 7.11 (dd, J = 7.7, 4.8 Hz, 1H), 6.67 (d, J = 10.0 Hz, 1H), 5.81 (d, J = 10.0 Hz, 1H), 4.06 – 3.96 (m, 1H), 3.93 – 3.84 (m, 1H), 3.81 – 3.66 (m, 2H), 3.64 – 3.50 (m, 2H), 3.49 – 3.38 (m, 2H), 3.37 – 3.24 (m, 1H), 3.14 (s, 3H), 2.84 – 2.77 (m, 1H), 2.10 (ddd, J = 6.8, 6.8, 2.9 Hz, 1H), 1.94 (dd, J = 6.7, 3.1 Hz, 1H), 1.64 – 1.52 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 157.2, 148.2, 134.5, 129.9, 127.8, 127.7, 122.0, 85.3, 67.6, 67.3, 63.4, 52.4, 50.5, 46.6, 42.7, 42.1, 40.1, 38.8; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 349.1523, found 349.1528; $\mathbf{R_f}$ (100% EtOAc) = 0.15.

Isobutyl 6a-methoxy-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxylate (**3d**)**:**



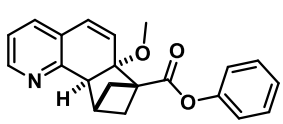
3d

The title compound was prepared from isobutyl bicyclo[1.1.0]butane-1-carboxylate (**2d**, 30.8 mg, 0.20 mmol, 1.0 equiv) and 7-methoxyquinoline (**1a**, 63.7 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (30% Et_2O) gave the product (38.0 mg, 60%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 4.8, 1.7 Hz, 1H), 7.41 (dd, J = 7.6, 1.7 Hz, 1H), 7.11 (dd, J = 7.6, 4.9 Hz, 1H), 6.67 (d, J = 10.1 Hz, 1H), 6.17 (d, J = 10.0 Hz, 1H), 3.92 (d, J = 6.6 Hz, 2H), 3.48 – 3.41 (m, 1H), 3.18 (s, 3H), 2.86 – 2.79 (m, 1H), 2.06 (dd, J = 9.6, 7.1 Hz, 1H), 2.03 – 1.89 (m, 2H), 1.70 (ddd, J = 7.7, 2.7, 2.7 Hz, 1H), 1.47 (dd, J = 9.7, 7.7 Hz, 1H),

0.94 (d, *J* = 1.2 Hz, 3H), 0.93 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.1, 157.3, 148.3, 134.4, 129.7, 128.2, 127.6, 122.0, 84.5, 70.5, 61.8, 52.6, 50.4, 42.6, 39.5, 36.5, 27.9, 19.2, 19.2; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 336.1570, found 336.1569; **R_f** (100% Et_2O) = 0.56.

Phenyl 6a-methoxy-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxylate (**3e**)**:**

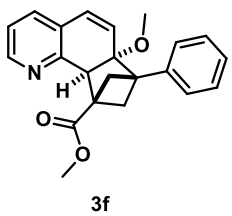


3e

The title compound was prepared from phenyl bicyclo[1.1.0]butane-1-carboxylate (**2e**, 34.8 mg, 0.20 mmol, 1.0 equiv) and 7-methoxyquinoline (**1a**, 63.7 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (30% Et_2O in pentane) gave the product (43.0 mg, 65%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.45 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.25 – 7.19 (m, 1H), 7.17 – 7.10 (m, 3H), 6.72 (d, *J* = 10.1 Hz, 1H), 6.25 (d, *J* = 10.1 Hz, 1H), 3.55 – 3.50 (m, 1H), 3.25 (s, 3H), 2.96 – 2.89 (m, 1H), 2.21 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.13 (dd, *J* = 7.1, 3.1 Hz, 1H), 1.89 (ddd, *J* = 7.7, 2.7, 2.7 Hz, 1H), 1.60 (dd, *J* = 9.5, 7.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 157.2, 150.8, 148.4, 134.5, 130.1, 129.5, 127.8, 127.6, 125. 9, 122.1, 121.0, 84.9, 61.7, 52.7, 50.4, 42.8, 39.7, 36.8; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 356.1257, found 356.1255; **R_f** (100% Et_2O) = 0.63.

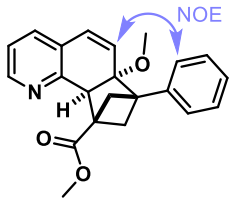
Methyl 6a-methoxy-7-phenyl-6a,7,8,9a-tetrahydro-9*H*-7,9-methanocyclopenta[*h*]quinoline-9-carboxylate (**3f**)**:**



3f

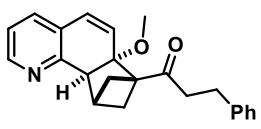
The title compound was prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**2f**, 37.6 mg, 0.20 mmol, 2.0 equiv) and 7-methoxyquinoline (**1a**, 15.9 mg, 0.20 mmol, 1.0 equiv) according to modified the *General Procedure* on 0.10 mmol scale. Purification by silica gel column chromatography (20 to 40% Et_2O in pentane) gave the product (15.7 mg, 45%) as a colorless solid.

Note: In crude GC-MS analysis, traces of another product with the same mass were observed. However, no signals in the crude ^{1}H NMR could be assigned to a specific isomer, and the side product could not be isolated.



^{1}H NMR (599 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.43 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.23 – 7.20 (m, 2H), 7.13 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.65 (d, *J* = 10.0 Hz, 1H), 5.51 (d, *J* = 10.0 Hz, 1H), 3.89 (d, *J* = 2.5 Hz, 1H), 3.76 (s, 3H), 3.14 (s, 3H), 2.80 (dd, *J* = 9.3, 6.6 Hz, 1H), 1.94 – 1.88 (m, 2H), 1.83 (dd, *J* = 7.7, 2.6 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.0, 155.1, 148.3, 138.9, 134.4, 129.9, 128.2, 127.9, 127.8, 127.7, 126.9, 122.4, 84.6, 59.2, 53.5, 53.1, 52.5, 51.7, 42.4, 39.3; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 370.1414, found 370.1417; **R_f** (50% Et_2O in pentane) = 0.38.

1-(6a-Methoxy-6a,8,9,9a-tetrahydro-7H-7,9-methanocyclopenta[h]quinoline-7-yl)-3-phenylpropan-1-one (**3g**)**:**

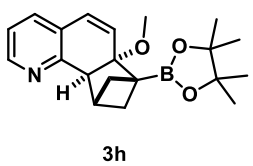


3g

The title compound was prepared from 1-(bicyclo[1.1.0]butan-1-yl)-3-phenylpropan-1-one (**2g**, 37.3 mg, 0.20 mmol, 1.0 equiv) and 7-methoxyquinoline (**1a**, 63.7 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (70% Et_2O in pentane) gave the product (44.3 mg, 64%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.40 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 7.11 (ddd, *J* = 7.7, 4.9, 0.6 Hz, 1H), 6.64 (d, *J* = 10.0 Hz, 1H), 5.67 (d, *J* = 10.0 Hz, 1H), 3.49 – 3.44 (m, 1H), 3.14 (s, 3H), 3.07 – 2.98 (m, 1H), 2.95 – 2.87 (m, 2H), 2.85 – 2.75 (m, 2H), 2.15 (dd, *J* = 9.6, 6.8 Hz, 1H), 1.77 (dd, *J* = 6.8, 3.1 Hz, 1H), 1.52 (ddd, *J* = 8.0, 2.7, 2.7 Hz, 1H), 1.41 (dd, *J* = 9.6, 7.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.5, 157.3, 148.3, 141.7, 134.4, 130.2, 128.6, 128.5, 127.6, 126.0, 122.0, 85.3, 68.5, 52.5, 50.5, 43.0, 42.1, 38.1, 37.1, 29.3 – one carbon signal missing; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 368.1621, found 368.1616; **R_f** (100% EtOAc) = 0.70.

6a-Methoxy-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline (3h):

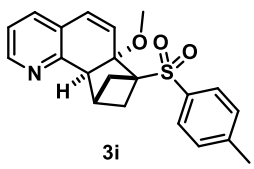


3h

The title compound was prepared from 2-(bicyclo[1.1.0]butan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2h**, 108.1 mg, 0.60 mmol, 3.0 equiv) and 7-methoxyquinoline (**1a**, 31.8 mg, 0.20 mmol, 1.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (50% Et_2O in pentane) and gave the product (30.0 mg, 44%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.07 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.59 (d, *J* = 10.0 Hz, 1H), 6.09 (d, *J* = 10.0 Hz, 1H), 3.43 – 3.38 (m, 1H), 3.18 (s, 3H), 2.94 – 2.88 (m, 1H), 1.76 – 1.66 (m, 2H), 1.52 (ddd, *J* = 7.8, 2.4, 2.4 Hz, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.16 – 1.10 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 158.4, 147.9, 134.0, 130.4, 128.8, 128.1, 121.6, 86.9, 83.4, 52.6, 50.1, 48.4, 38.0, 35.4, 25.0, 24.8; **^{11}B NMR** (128 MHz, $CDCl_3$) *δ* 31.7; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 362.1902, found 362.1899; **R_f** (100% Et_2O) = 0.76.

6a-Methoxy-7-tosyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline (3i):

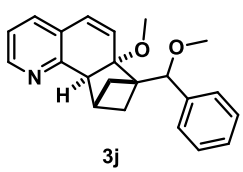


3i

The title compound was prepared from 1-tosylbicyclo[1.1.0]butane (**2i**, 83 mg, 0.40 mmol, 2.0 equiv) and 7-methoxyquinoline (**1a**, 31.8 mg, 0.20 mmol, 1.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (50% Et_2O in pentane) and gave the product (49.6 mg, 67%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.39 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.83 – 7.75 (m, 2H), 7.44 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.72 (d, *J* = 10.2 Hz, 1H), 6.49 (d, *J* = 10.1 Hz, 1H), 3.41 – 3.35 (m, 1H), 3.00 (s, 3H), 2.97 – 2.92 (m, 1H), 2.43 (s, 3H), 2.07 – 1.97 (m, 2H), 1.92 (dd, *J* = 9.5, 6.7 Hz, 1H), 1.59 (dd, *J* = 9.5, 7.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 156.3, 148.4, 144.3, 136.4, 134.6, 130.3, 129.4, 129.2, 127.2, 127.2, 122.3, 83.6, 75.9, 52.1, 51.7, 41.2, 37.3, 37.2, 21.8; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 390.1134, found 390.1138; **R_f** (100% Et_2O) = 0.29.

6a-Methoxy-7-(methoxy(phenyl)methyl)-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline (3j):

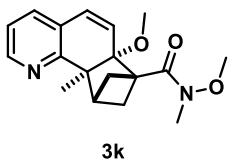


3j

The title compound was prepared from 1-(methoxy(phenyl)methyl)bicyclo[1.1.0]butane (**2j**, 34.8 mg, 0.20 mmol, 1.0 equiv) and 7-methoxyquinoline (**1a**, 63.7 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (40% Et_2O in pentane) and gave the product (31.5 mg, 47%) as a colorless solid. The d.r. was determined to be 1:1 by crude ^1H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$; mixture of diastereomers) δ 8.40 – 8.36 (m, 2H), 7.39 (dd, J = 7.7, 1.7 Hz, 1H), 7.37 – 7.27 (m, 7H), 7.26 – 7.22 (m, 4H), 7.08 (dd, J = 7.9, 4.6 Hz, 1H), 7.04 (dd, J = 7.6, 4.8 Hz, 1H), 6.64 (d, J = 10.1 Hz, 1H), 6.30 (d, J = 10.2 Hz, 1H), 6.16 (d, J = 10.1 Hz, 1H), 5.34 (d, J = 10.1 Hz, 1H), 4.64 (s, 1H), 4.36 (s, 1H), 3.43 – 3.38 (m, 2H), 3.26 (s, 3H), 3.24 (s, 3H), 3.19 (s, 3H), 3.14 (s, 3H), 2.80 – 2.77 (m, 1H), 2.71 – 2.68 (m, 1H), 1.87 (dd, J = 6.9, 3.0 Hz, 1H), 1.81 (dd, J = 9.5, 6.9 Hz, 1H), 1.54 (dd, J = 9.8, 6.9 Hz, 1H), 1.41 (ddd, J = 7.5, 2.7, 2.7 Hz, 1H), 1.34 (ddd, J = 7.8, 2.6, 2.6 Hz, 1H), 1.19 (dd, J = 9.8, 7.7 Hz, 1H), 1.02 (dd, J = 9.5, 7.5 Hz, 1H), 0.75 (dd, J = 6.9, 3.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$; mixture of diastereomers) δ 158.1, 157.9, 148.1, 147.9, 141.4, 141.2, 134.0, 134.0, 130.3, 128.8, 128.7, 128.3, 128.3, 128.2, 128.2, 128.0, 127.7, 127.5, 127.3, 127.2, 121.8, 121.6, 84.4, 83.8, 81.6, 80.8, 65.4, 65.0, 56.8, 56.7, 52.5, 52.4, 51.5, 51.2, 42.9, 42.1, 36.0, 35.5, 34.5, 33.1; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 356.1621, found 356.1620; **R_f** (100% Et_2O) = 0.63.

***N*,6a-Dimethoxy-*N*,9a-dimethyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (3k):**



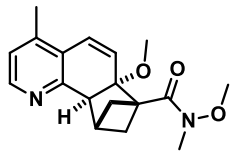
3k

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 7-methoxy-8-methylquinoline (**1b**, 70.0 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (50.7 mg, 80%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, J = 4.8, 1.8 Hz, 1H), 7.33 (dd, J = 7.6, 1.7 Hz, 1H), 7.05 (dd, J = 7.6, 4.8 Hz, 1H), 6.61 (d, J = 10.2 Hz, 1H), 6.00 (d, J = 10.2 Hz, 1H), 3.70 (s, 3H), 3.30 (s, 3H), 3.23 (s, 3H), 2.53 (dd, J = 2.6, 2.6 Hz, 1H), 2.33 – 2.22 (m, 1H), 1.85 (dd, J = 7.9, 2.9 Hz, 1H), 1.62 (s, 3H), 1.49 – 1.40 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.5, 162.5,

147.9, 134.0, 129.8, 128.6, 126.8, 121.4, 86.7, 62.5, 61.4, 54.1, 52.0, 48.1, 39.5, 35.0, 32.7, 20.5; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 337.1523, found 337.1528; $\mathbf{R_f}$ (100% Et_2O) = 0.26.

_N_,6a-Dimethoxy-_N_,4-dimethyl-6a,8,9,9a-tetrahydro-7_H_-7,9-methanocyclopenta[_h_]quinoline-7-carboxamide (3l):

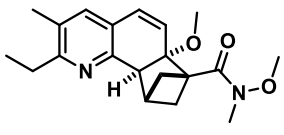


3l

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 7-methoxy-4-methylquinoline (**1c**, 69.3 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (53.0 mg, 84%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 5.0 Hz, 1H), 6.93 (s, 1H), 6.91 (d, J = 4.3 Hz, 1H), 5.94 (d, J = 10.3 Hz, 1H), 3.70 (s, 3H), 3.42 – 3.36 (m, 1H), 3.23 (s, 3H), 3.14 (s, 3H), 2.80 – 2.73 (m, 1H), 2.36 (s, 3H), 2.11 (dd, J = 8.7, 7.5 Hz, 1H), 1.98 (dd, J = 7.4, 3.1 Hz, 1H), 1.60 – 1.56 (m, 1H), 1.54 (dd, J = 8.9, 7.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.9, 147.5, 142.9, 128.1, 126.3, 125.5, 123.8, 85.3, 62.0, 61.5, 52.3, 50.0, 42.6, 40.1, 38.1, 32.7, 18.7 – ^{13}C signal of Weinreb amide, expected at ~170 ppm, not observed; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 337.1523, found 337.1527; $\mathbf{R_f}$ (100% Et_2O) = 0.28.

2-Ethyl-_N_,6a-dimethoxy-_N_,3-dimethyl-6a,8,9,9a-tetrahydro-7_H_-7,9-methanocyclopenta[_h_]quinoline-7-carboxamide (3m):



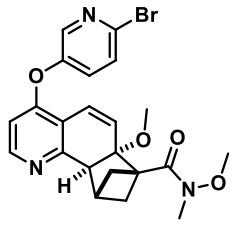
3m

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 2-ethyl-7-methoxy-3-methylquinoline (**1d**, 80.0 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (25.0 mg, 40%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 6.61 (d, J = 10.0 Hz, 1H), 5.83 (d, J = 10.0 Hz, 1H), 3.71 (s, 3H), 3.41 – 3.36 (m, 1H), 3.24 (s, 3H), 3.15 (s, 3H), 2.83 – 2.73 (m, 3H), 2.28 (s, 3H), 2.11 (ddd, J = 7.5, 7.5, 2.1 Hz, 1H), 1.97 (dd, J = 7.3, 3.1 Hz, 1H), 1.61 – 1.51 (m, 2H), 1.24 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4, 154.1, 136.0, 129.3, 128.6, 127.1, 125.3, 85.9, 61.9, 61.5, 52.3, 49.7, 42.4, 40.0, 38.2, 33.0, 28.9, 18.3, 13.5 – ^{13}C signal of

Weinreb amide, expected at ~170 ppm, not observed; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 365.1836, found 365.1837; $\mathbf{R_f}$ (100% Et_2O) = 0.36.

4-((6-Bromopyridin-3-yl)oxy)-*N*,6a-dimethoxy-*N*-methyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (**3n**)**:**

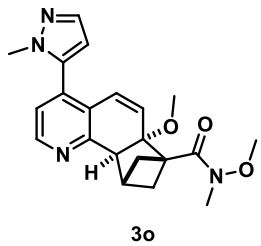


3n

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 4-((6-bromopyridin-3-yl)oxy)-7-methoxyquinoline (**1e**, 132.5 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (60% EtOAc in pentane) gave the product (54.8 mg, 58%) as a colorless solid.

^{1}H NMR (599 MHz, $CDCl_3$) δ 8.26 (d, J = 5.7 Hz, 1H), 8.20 (dd, J = 3.0, 0.6 Hz, 1H), 7.50 (dd, J = 8.6, 0.7 Hz, 1H), 7.26 (dd, J = 11.7, 3.0 Hz, 1H), 7.08 (d, J = 10.3 Hz, 1H), 6.45 (dd, J = 5.6, 0.5 Hz, 1H), 5.99 (d, J = 10.3 Hz, 1H), 3.69 (s, 3H), 3.43 – 3.39 (m, 1H), 3.22 (s, 3H), 3.16 (s, 3H), 2.82 – 2.77 (m, 1H), 2.12 (dd, J = 9.3, 7.2 Hz, 1H), 2.03 – 1.98 (m, 1H), 1.62 (ddd, J = 7.9, 2.6, 2.6 Hz, 1H), 1.57 (dd, J = 9.5, 7.9 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.1, 160.1, 158.8, 151.3, 149.3, 142.8, 137.0, 130.4, 129.2, 128.9, 121.7, 118.7, 109.0, 85.4, 62.1, 61.5, 52.5, 49.9, 42.5, 40.2, 38.1, 32.7; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 494.0686, found 494.0683; $\mathbf{R_f}$ (60% EtOAc in pentane) = 0.11.

***N*,6a-dimethoxy-*N*-methyl-4-(1-methyl-1*H*-pyrazol-5-yl)-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide** (**3o**)**:**



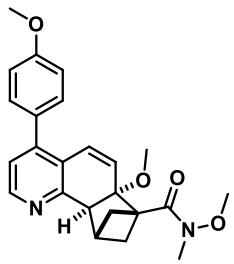
3o

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 7-methoxy-4-(1-methyl-1*H*-pyrazol-5-yl)quinoline (**1f**, 95.7 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% EtOAc) gave the product (60.0 mg, 79%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 5.0 Hz, 1H), 7.55 (d, J = 1.9 Hz, 1H), 7.04 (d, J = 5.0 Hz, 1H), 6.51 (d, J = 10.3 Hz, 1H), 6.30 (d, J = 1.9 Hz, 1H), 5.96 (d, J = 10.3 Hz, 1H), 3.69 (s, 3H), 3.68 (s, 3H), 3.50 – 3.46 (m, 1H), 3.22 (s, 3H), 3.15 (s, 3H), 2.85 – 2.80 (m, 1H), 2.14

(dd, *J* = 9.5, 7.4 Hz, 1H), 2.03 (dd, *J* = 7.6, 3.0 Hz, 1H), 1.63 (ddd, *J* = 7.9, 2.7, 2.7 Hz, 1H), 1.55 (dd, *J* = 9.5, 7.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 158.3, 147.6, 138.9, 138.9, 135.7, 130.2, 126.4, 125.8, 123.1, 107.8, 85.3, 61.9, 61.5, 52.4, 50.1, 42.7, 40.2, 38.0, 37.2, 32.7 – ^{13}C signal of Weinreb amide, expected at ~170 ppm, not observed; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 403.1741, found 403.1749; **R_f** (10% MeOH in EtOAc) = 0.20.

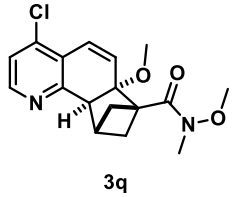
_N_,6a-Dimethoxy-4-(4-methoxyphenyl)-_N_-methyl-6a,8,9,9a-tetrahydro-7_H_-7,9-methanocyclopenta[_h_]quinoline-7-carboxamide (**3p**)**:**


3p

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 7-methoxy-4-(4-methoxyphenyl)quinoline (**1g**, 106.1 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (66.0 mg, 81%) as a pale brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 5.0 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.05 (dd, *J* = 5.0, 0.5 Hz, 1H), 7.01 – 6.96 (m, 2H), 6.86 (d, *J* = 10.3 Hz, 1H), 5.87 (d, *J* = 10.4 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 3.52 – 3.46 (m, 1H), 3.24 (s, 3H), 3.17 (s, 3H), 2.86 – 2.80 (m, 1H), 2.18 – 2.12 (m, 1H), 2.03 (dd, *J* = 7.5, 3.1 Hz, 1H), 1.70 – 1.61 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 159.8, 158.0, 147.5, 146.9, 130.8, 130.3, 128.2, 126.9, 125.0, 123.0, 114.1, 85.4, 62.0, 61.5, 55.5, 52.4, 50.4, 42.8, 40.3, 38.2, 32.7 – ^{13}C signal of Weinreb amide, expected at ~170 ppm, not observed; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 429.1785, found 429.1789; **R_f** (100% EtOAc) = 0.30.

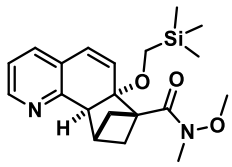
4-Chloro-_N_,6a-dimethoxy-_N_-methyl-6a,8,9,9a-tetrahydro-7_H_-7,9-methanocyclopenta[_h_]quinoline-7-carboxamide (**3q**)**:**


3q

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 4-chloro-7-methoxyquinoline (**1h**, 77.4 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (57.0 mg, 85%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 5.3 Hz, 1H), 7.16 (dd, J = 5.3, 0.6 Hz, 1H), 7.12 (d, J = 10.3 Hz, 1H), 6.06 (d, J = 10.3 Hz, 1H), 3.70 (s, 3H), 3.43 – 3.38 (m, 1H), 3.24 (s, 3H), 3.15 (s, 3H), 2.81 – 2.75 (m, 1H), 2.12 (dd, J = 9.5, 7.5 Hz, 1H), 2.01 (dd, J = 7.5, 3.1 Hz, 1H), 1.62 (ddd, J = 7.9, 2.6, 2.6 Hz, 1H), 1.52 (dd, J = 9.5, 7.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 148.1, 141.4, 130.3, 125.9, 124.7, 123.0, 85.6, 61.9, 61.5, 52.5, 50.1, 42.7, 40.2, 38.1, 32.8 – ^{13}C signal of Weinreb amide, expected at ~170 ppm, not observed; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 357.0978, found 357.0985; **R_f** (100% Et_2O) = 0.43.

_N_-Methoxy-_N_-methyl-6a-((trimethylsilyl)methoxy)-6a,8,9,9a-tetrahydro-7_H_-7,9-methanocyclopenta[_h_]quinoline-7-carboxamide (**3r**)**:**

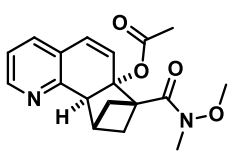


3r

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 7-((trimethylsilyl)methoxy)quinoline (**1i**, 92.5 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (61.1 mg, 82%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, J = 4.9, 1.7 Hz, 1H), 7.39 (dd, J = 7.7, 1.7 Hz, 1H), 7.08 (dd, J = 7.6, 4.9 Hz, 1H), 6.64 (d, J = 10.1 Hz, 1H), 5.88 (d, J = 10.1 Hz, 1H), 3.72 (s, 3H), 3.35 (s, 1H), 3.24 (s, 3H), 2.96 (d, J = 12.5 Hz, 1H), 2.80 – 2.77 (m, 1H), 2.75 (d, J = 12.8 Hz, 1H), 2.15 – 1.91 (m, 2H), 1.61 – 1.50 (m, 2H), −0.04 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.5, 147.9, 134.3, 129.1, 128.0, 121.9, 87.0, 62.2, 61.4, 57.4, 50.2, 42.3, 40.6, 38.1, 32.7, −2.9 – ^{13}C signal of Weinreb amide, expected at ~170 ppm, not observed; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 395.1761, found 395.1758; **R_f** (100% Et_2O) = 0.44.

7-(Methoxy(methyl)carbamoyl)-7,8,9,9a-tetrahydro-6a_H_-7,9-methanocyclopenta[_h_]quinolin-6a-yl acetate (**3s**)**:**

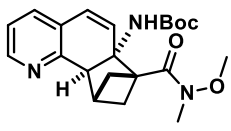


3s

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and quinolin-7-yl acetate (**1j**, 74.9 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (39.5 mg, 60%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 4.9, 1.7 Hz, 1H), 7.43 (dd, J = 7.6, 1.7 Hz, 1H), 7.11 (dd, J = 7.6, 4.9 Hz, 1H), 6.59 (d, J = 10.0 Hz, 1H), 5.98 (d, J = 10.0 Hz, 1H), 3.73 (s, 3H), 3.62 – 3.57 (m, 1H), 3.26 (s, 3H), 2.85 – 2.78 (m, 1H), 2.07 (dd, J = 7.6, 3.0 Hz, 1H), 2.04 – 1.98 (m, 4H), 1.65 (ddd, J = 8.0, 2.8, 2.8 Hz, 1H), 1.56 (dd, J = 9.3, 8.0 Hz, 1H; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 169.9, 156.8, 147.9, 134.4, 128.2, 127.3, 125.2, 121.7, 86.0, 61.3, 53.3, 41.8, 39.0, 37.9, 32.7, 30.1, 21.6.; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 351.1315, found 351.1310; **R_f** (10% EtOAc in Et_2O) = 0.10.

***tert*-Butyl (7-(methoxy(methyl)carbamoyl)-7,8,9,9a-tetrahydro-6a*H*-7,9-methanocyclopenta[*h*]quinolin-6a-yl)carbamate (3t):**

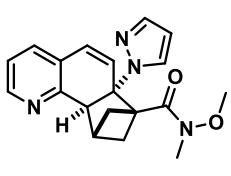


3t

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and *tert*-butyl quinolin-7-ylcarbamate (**1k**, 97.6 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (42.1 mg, 55%) as a slightly yellow solid.

^{1}H NMR (500 MHz, $(CD_3)_2SO$ at 363 K) δ 8.39 – 8.33 (m, 1H), 7.52 (dd, J = 7.6, 1.7 Hz, 1H), 7.17 (dd, J = 7.6, 4.8 Hz, 1H), 6.54 (dd, J = 9.9, 1.0 Hz, 2H), 5.67 (d, J = 9.8 Hz, 1H), 3.65 (d, J = 1.3 Hz, 3H), 3.52 – 3.47 (m, 1H), 3.18 (d, J = 1.3 Hz, 3H), 2.73 – 2.67 (m, 1H), 1.96 (ddd, J = 9.0, 7.1, 1.5 Hz, 1H), 1.88 – 1.80 (m, 2H), 1.48 – 1.41 (m, 1H), 1.18 (s, 9H); **^{13}C NMR** (126 MHz, $(CD_3)_2SO$ at 363 K) δ 170.4, 156.7, 154.0, 147.1, 133.2, 127.9, 126.8, 125.7, 121.0, 78.0, 61.9, 60.9, 59.2, 52.5, 41.7, 37.4, 36.8, 32.1, 27.5; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 408.1894, found 408.1903; **R_f** (100% Et_2O) = 0.10.

***N*-Methoxy-*N*-methyl-6a-(1*H*-pyrazol-1-yl)-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (3u)**



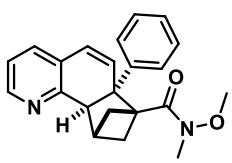
3u

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 7-(1*H*-pyrazol-1-yl)quinoline (**1l**, 78.1 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel

column chromatography (10-20% EtOAc in Et_2O) gave the product (45.7 mg, 68%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 4.9, 1.7 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.48 (d, J = 1.8 Hz, 1H), 7.39 (dd, J = 7.7, 1.7 Hz, 1H), 7.10 (dd, J = 7.6, 4.9 Hz, 1H), 6.49 (d, J = 10.1 Hz, 1H), 6.46 (d, J = 10.1 Hz, 1H), 6.24 (dd, J = 2.1, 2.1 Hz, 1H), 4.39 – 4.33 (m, 1H), 3.49 (s, 3H), 3.14 (s, 3H), 2.95 – 2.89 (m, 1H), 2.10 (dd, J = 7.7, 3.0 Hz, 1H), 2.03 (dd, J = 9.4, 7.7 Hz, 1H), 1.88 (dd, J = 9.4, 7.8 Hz, 1H), 1.82 (ddd, J = 7.9, 2.6, 2.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1, 148.3, 138.9, 134.3, 128.3, 127.7, 127.0, 125.5, 122.2, 106.0, 71.5, 62.0, 60.9, 51.5, 43.2, 41.8, 37.7, 33.4 – ^{13}C signal of Weinreb amide, expected at ~170 ppm, not observed; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 359.1479, found 359.1488; **R_f** (100% EtOAc) = 0.25.

***N*-Methoxy-*N*-methyl-6a-phenyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (3v):**

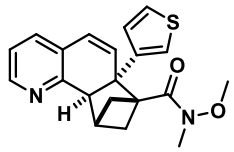


3v

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv), 7-phenylquinoline (**1m**, 82 mg, 0.40 mmol, 2.0 equiv), and CH_2Cl_2 (3.0 mL) according to modified *General Procedure*. BCB **2a** was dissolved in CH_2Cl_2 (1.0 mL) and slowly added *via* syringe pump over 8 h under irradiation (overall reaction time was 18 h). Purification by silica gel column chromatography (100% Et_2O) gave the product (42.1 mg, 61%) as a slightly yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, J = 4.9, 1.7 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.33 (dd, J = 7.6, 1.7 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.18 – 7.13 (m, 1H), 7.10 – 7.03 (m, 1H), 6.36 (d, J = 10.0 Hz, 1H), 6.31 (d, J = 10.0 Hz, 1H), 4.01 – 3.96 (m, 1H), 3.45 (s, 3H), 3.16 (s, 3H), 2.90 – 2.83 (m, 1H), 2.08 – 1.96 (m, 2H), 1.80 (ddd, J = 7.6, 3.0, 1.9 Hz, 1H), 1.76 (dd, J = 9.7, 7.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 156.9, 147.9, 145.4, 134.5, 133.6, 128.5, 128.1, 127.3, 126.5, 122.3, 122.0, 60.9, 60.7, 56.2, 51.5, 44.1, 41.9, 38.0, 33.3; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 369.1574, found 369.1569; **R_f** (100% Et_2O) = 0.27.

***N*-Methoxy-*N*-methyl-6a-(thiophen-3-yl)-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (3w):**

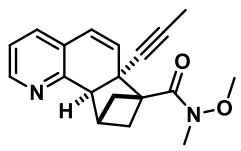


3w

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 56.5 mg, 0.40 mmol, 2.0 equiv) and 7-(thiophen-3-yl)quinoline (**1n**, 42.3 mg, 0.20 mmol, 1.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (5 to 40% EtOAc in pentane) and subsequent PTLC (20% toluene in EtOAc) gave the product (31.8 mg, 45%) as a slight yellow solid.

^{1}H NMR (599 MHz, $CDCl_3$) δ 8.38 (dd, J = 5.0, 1.7 Hz, 1H), 7.40 (dd, J = 7.6, 1.6 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.14 (dd, J = 7.6, 5.0 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.39 (d, J = 10.0 Hz, 1H), 6.35 (d, J = 10.0 Hz, 1H), 4.01 (s, 1H), 3.33 (s, 3H), 3.13 (s, 3H), 2.95 – 2.90 (m, 1H), 2.02 – 1.94 (m, 2H), 1.84 (dd, J = 9.8, 7.7 Hz, 1H), 1.80 (ddd, J = 7.6, 3.0, 1.8 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.3, 156.4, 146.6, 145.3, 134.5, 133.6, 128.5, 127.2, 125.9, 122.6, 122.4, 121.0, 61.3, 60.9, 53.1, 51.0, 44.1, 41.5, 38.1, 33.0; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 375.1135, found 375.1138; **R_f** (33% EtOAc in pentane) = 0.30.

***N*-Methoxy-*N*-methyl-6a-(prop-1-yn-1-yl)-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (3x):**

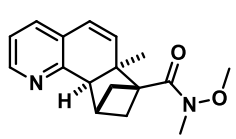


3x

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv), 7-(prop-1-yn-1-yl)quinoline (**1o**, 70.0 mg, 0.40 mmol, 2.0 equiv), and $Sc(OTf)_3$ (98.2 mg, 0.10 mmol, 1.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (40.0 mg, 65%) as a slight yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, J = 4.9, 1.7 Hz, 1H), 7.30 (dd, J = 7.6, 1.7 Hz, 1H), 7.04 (dd, J = 7.6, 4.9 Hz, 1H), 6.31 (d, J = 9.9 Hz, 1H), 5.91 (d, J = 9.8 Hz, 1H), 3.69 (s, 3H), 3.68 – 3.64 (m, 1H), 3.26 (s, 3H), 2.83 – 2.76 (m, 1H), 2.09 – 2.03 (m, 1H), 2.00 (dd, J = 7.5, 3.0 Hz, 1H), 1.81 (s, 3H), 1.74 – 1.64 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.3, 148.0, 133.8, 129.8, 127.5, 123.9, 121.9, 82.8, 81.3, 61.8, 61.4, 54.1, 45.7, 43.3, 39.3, 39.0, 33.5, 4.1 – ^{13}C signal of Weinreb amide, expected at ~170 ppm, not observed; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 331.1417, found 331.1413; **R_f** (100% Et_2O) = 0.18.

***N*-methoxy-*N*,6a-dimethyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (3y):**

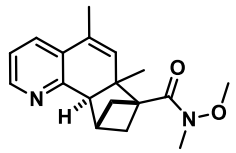


3y

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv), 7-methylquinoline (**1p**, 57.3 mg, 0.40 mmol, 2.0 equiv), and $Sc(OTf)_3$ (98.2 mg, 0.10 mmol, 1.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (39.0 mg, 69%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, J = 4.9, 1.7 Hz, 1H), 7.29 (dd, J = 7.6, 1.7 Hz, 1H), 7.04 (dd, J = 7.6, 4.9 Hz, 1H), 6.26 (d, J = 9.9 Hz, 1H), 5.76 (d, J = 9.9 Hz, 1H), 3.64 (s, 3H), 3.22 (s, 3H), 3.20 – 3.18 (m, 1H), 2.75 – 2.72 (m, 1H), 1.90 (dd, J = 9.5, 7.4 Hz, 1H), 1.84 (dd, J = 7.3, 3.0 Hz, 1H), 1.80 (dd, J = 9.4, 7.4 Hz, 1H), 1.69 (ddd, J = 7.4, 3.0, 1.8 Hz, 1H), 1.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.8, 157.4, 147.7, 134.6, 133.5, 128.3, 123.5, 121.8, 61.1, 60.8, 52.7, 47.8, 43.7, 40.1, 38.1, 32.5, 25.5; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 307.1417, found 307.1414; **R_f** (100% Et_2O) = 0.18; **X-ray** (single-crystal) A colorless prism-like specimen of **3y** (X-ray diffraction quality) was obtained by liquid/liquid diffusion with CH_2Cl_2 and pentane (CCDC 2225190).

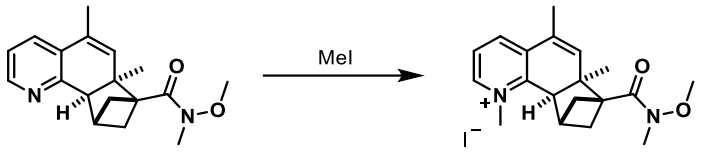
***N*-Methoxy-*N*,5,6a-trimethyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (3z):**



3z

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 5,7-dimethylquinoline (**1q**, 62.8 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (28.8 mg, 48%) as a slight brown oil.

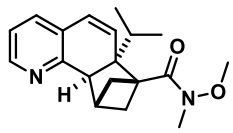
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, J = 4.8, 1.6 Hz, 1H), 7.49 (dd, J = 7.8, 1.7 Hz, 1H), 7.09 (dd, J = 7.8, 4.8 Hz, 1H), 5.60 (d, J = 1.6 Hz, 1H), 3.63 (s, 3H), 3.22 (s, 3H), 3.20 – 3.15 (m, 1H), 2.74 – 2.67 (m, 1H), 2.02 (d, J = 1.5 Hz, 3H), 1.88 (dd, J = 9.4, 7.4 Hz, 1H), 1.82 (dd, J = 7.3, 3.0 Hz, 1H), 1.73 (dd, J = 9.4, 7.4 Hz, 1H), 1.65 (ddd, J = 7.4, 2.9, 1.8 Hz, 1H), 1.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 157.9, 147.3, 132.0, 130.3, 129.8, 127.3, 121.6, 61.1, 60.8, 52.6, 46.8, 43.7, 40.0, 38.2, 32.7, 25.6, 19.4; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 321.1574, found 321.1571; **R_f** (100% Et_2O) = 0.09.



3z **3z**·MeI

MeI-Adduct of cycloaddition product **3z** was formed to enable crystal growing. **X-ray** (single-crystal) A colorless prism-like specimen of **3z**·MeI (X-ray diffraction quality) was obtained by slow evaporation from CH_2Cl_2 (CCDC 2225191).

6a-Isopropyl-*N*-methoxy-*N*-methyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (**3aa**)**:**

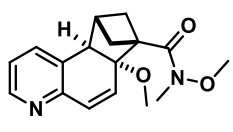


3aa

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 7-isopropylquinoline (**1r**, 68.5 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (50 to 100% Et_2O in pentane) gave the product (30.4 mg, 49%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, J = 4.9, 1.7 Hz, 1H), 7.30 (dd, J = 7.6, 1.7 Hz, 1H), 7.04 (dd, J = 7.6, 4.9 Hz, 1H), 6.47 (d, J = 10.2 Hz, 1H), 6.05 (d, J = 10.2 Hz, 1H), 3.69 (s, 3H), 3.22 – 3.19 (m, 1H), 3.18 (s, 3H), 2.72 – 2.66 (m, 1H), 2.06 (hept, J = 6.7 Hz, 1H), 1.98 – 1.83 (m, 3H), 1.62 (ddd, J = 7.0, 2.9, 1.8 Hz, 1H), 0.87 (d, J = 6.7 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.1, 157.8, 147.5, 133.6, 130.1, 128.7, 126.3, 121.9, 61.0, 59.6, 55.7, 52.3, 43.7, 42.6, 38.0, 35.4, 33.1, 19.8, 17.4; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 335.1730, found 335.1726; **R_f** (100% Et_2O) = 0.15.

***N*,6a-dimethoxy-*N*-methyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*f*]quinoline-7-carboxamide** (**3ab**)**:**

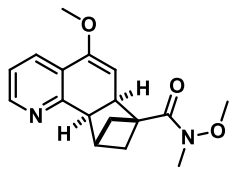


3ab

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 6-methoxyquinoline (**1s**, 63.7 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (23.3 mg, 39%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (ddd, J = 4.8, 1.6, 0.6 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.09 (dd, J = 7.7, 4.8 Hz, 1H), 6.90 (dd, J = 10.2, 0.7 Hz, 1H), 6.10 (d, J = 10.3 Hz, 1H), 3.68 (s, 3H), 3.35 – 3.30 (m, 1H), 3.23 (s, 3H), 3.16 (s, 3H), 2.57 – 2.50 (m, 1H), 2.14 – 2.08 (m, 1H), 1.96 (dd, J = 7.4, 3.1 Hz, 1H), 1.64 (ddd, J = 6.9, 2.3, 2.3 Hz, 1H), 1.60 (dd, J = 9.1, 7.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 151.6, 148.0, 135.6, 133.1, 132.4, 131.5, 122.2, 84.1, 61.5, 61.4, 52.4, 46.8, 42.9, 40.1, 37.7, 32.7; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 323.1366, found 323.1363; **R_f** (100% Et_2O) = 0.27; **X-ray** (single-crystal) A colorless plate-like specimen of **3ab** (X-ray diffraction quality) was obtained by liquid/liquid diffusion with CH_2Cl_2 and pentane (CCDC 2225192).

_N_,5-Dimethoxy-_N_-methyl-6a,8,9,9a-tetrahydro-7_H_-7,9-methanocyclopenta[_h_]quinoline-7-carboxamide (**3ac**)**:**

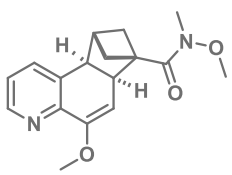


3ac

The title compound was prepared from _N_-methoxy-_N_-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 5-methoxyquinoline (**1t**, 63.6 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (18.0 mg, 30%) as a slightly green oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (dd, J = 4.9, 1.7 Hz, 1H), 7.78 (dd, J = 7.8, 1.7 Hz, 1H), 7.07 (ddd, J = 7.8, 4.9, 0.6 Hz, 1H), 4.78 (d, J = 4.2 Hz, 1H), 3.69 (s, 3H), 3.67 (s, 3H), 3.60 (ddd, J = 10.0, 1.6, 1.6 Hz, 1H), 3.56 (ddd, J = 10.1, 4.2, 1.5 Hz, 1H), 3.24 (s, 3H), 2.83 – 2.80 (m, 1H), 1.92 (dd, J = 6.5, 3.1 Hz, 1H), 1.69 – 1.65 (m, 1H), 1.63 (dd, J = 9.5, 6.6 Hz, 1H), 1.56 (dd, J = 9.5, 7.6 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.6, 158.0, 150.9, 148.2, 129.1, 127.0, 121.4, 95.8, 61.6, 59.3, 55.0, 44.2, 43.3, 41.8, 41.4, 35.1, 32.7; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 323.1366, found 323.1364; **R_f** (100% Et_2O) = 0.11.

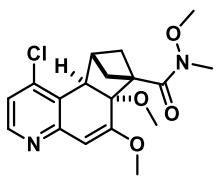
***N*,5-Dimethoxy-*N*-methyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*f*]quinoline-7-carboxamide (S2):**



S2

The reaction was performed with *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 8-methoxyquinoline (**1u**, 63.6 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Crude ^{1}H NMR analysis revealed the formation (14% yield) of an addition product which could be attributed (spectral similarity of the olefinic signal, compare structure **3ac**) to structure **S2**.

1-Chloro-*N*,6,6a-trimethoxy-*N*-methyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*f*]quinoline-7-carboxamide (3ad):



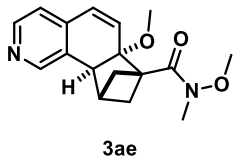
3ad

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 56.5 mg, 0.40 mmol, 2.0 equiv) and 4-chloro-6,7-dimethoxyquinoline (**1v**, 44.7 mg, 0.20 mmol, 1.0 equiv) according to the *General Procedure*. Purification by PTLC (1st: 5% MeOH in CH_2Cl_2; 2nd 10% MeOH in EtOAc) gave the product (56.6 mg, 77%) as a colorless solid.

Note: For this example, an unidentified side-product (product to side-product ratio: 16:1) was observed in the crude reaction mixture by ^{1}H NMR.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 5.5 Hz, 1H), 6.99 (d, J = 5.3 Hz, 1H), 6.03 (s, 1H), 3.70 (s, 3H), 3.55 (s, 3H), 3.50 – 3.46 (m, 1H), 3.17 (s, 3H), 3.15 (s, 3H), 2.89 – 2.83 (m, 1H), 2.24 (dd, J = 8.1, 8.1 Hz, 1H), 1.86 (dd, J = 7.5, 3.1 Hz, 1H), 1.78 (d, J = 8.2 Hz, 1H), 1.65 (dd, J = 9.7, 8.2 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.7, 159.3, 155.6, 148.2, 142.6, 127.0, 121.3, 104.5, 85.7, 60.9, 55.8, 52.6, 49.0, 39.8, 39.7, 38.5, 33.0 – one carbon signal is missing; **HRMS** (ESI$^+$) calc'd for $[M+Na]^+$ 387.1085, found 387.1082; **R_f** (5% MeOH in CH_2Cl_2) = 0.30; **X-ray** (single-crystal) A colorless plate-like specimen of **3ad** (X-ray diffraction quality) was obtained by slow evaporation (CCDC 2225193).

***N*,6a-Dimethoxy-*N*-methyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]isoquinoline-7-carboxamide (3ae):**

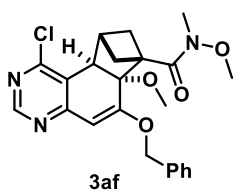


3ae

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 56.5 mg, 0.40 mmol, 2.0 equiv), 7-methoxyisoquinoline (**1w**, 31.8 mg, 0.20 mmol, 1.0 equiv), and CH_2Cl_2 (3.0 mL) according to modified *General Procedure*. BCB **2a** was dissolved in CH_2Cl_2 (1.0 mL) and added slowly *via* syringe pump over 8 h under irradiation (overall reaction time was 18 h). Purification by silica gel column chromatography (50% acetone in pentane) and subsequent PTLC (100% EtOAc) gave the product (33.9 mg, 56%) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.39 (d, J = 5.0 Hz, 1H), 7.01 (d, J = 5.0 Hz, 1H), 6.66 (d, J = 10.1 Hz, 1H), 6.09 (d, J = 10.1 Hz, 1H), 3.68 (s, 3H), 3.34 – 3.31 (m, 1H), 3.22 (s, 3H), 3.13 (s, 3H), 2.58 (s, 1H), 2.10 (dd, J = 9.6, 7.4 Hz, 1H), 1.98 (dd, J = 7.4, 3.1 Hz, 1H), 1.60 (ddd, J = 6.4, 3.3, 1.6 Hz, 1H), 1.50 (ddd, J = 9.1, 7.9, 1.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.1, 149.5, 148.3, 139.1, 132.4, 131.6, 129.1, 121.3, 84.2, 61.6, 61.5, 52.4, 44.4, 43.1, 40.1, 37.6, 32.7; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 323.1366, found 323.1364; **R_f** (100% EtOAc) = 0.15; **X-ray** (single-crystal) A colorless plate-like specimen of **3ae** (X-ray diffraction quality) was obtained by slow evaporation (CCDC 2225194).

6-(Benzyloxy)-1-chloro-*N*,6a-dimethoxy-*N*-methyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*f*]quinazoline-7-carboxamide (3af):



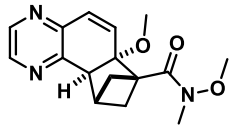
3af

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 56.5 mg, 0.40 mmol, 2.0 equiv) and 7-(benzyloxy)-4-chloro-6-methoxyquinazoline (**1x**, 60.2 mg, 0.20 mmol, 1.0 equiv) according to the *General Procedure*. Note: The extraction during the work-up was performed with CH_2Cl_2. Purification by silica gel column chromatography (33% EtOAc to 60% EtOAc in pentane) and subsequent PTLC (33% EtOAc in pentane) gave the product (58.1 mg, 66%) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.40 – 7.37 (m, 2H), 7.37 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 6.13 (s, 1H), 5.01 (d, J = 11.5 Hz, 1H), 4.91 (d, J = 11.5 Hz, 1H), 3.50 (s, 3H), 3.46 – 3.44 (m, 1H), 3.23 (s, 3H), 2.95 – 2.91 (m, 1H), 2.81 (s, 3H), 2.25 (dd, J = 8.7, 8.7 Hz, 1H), 1.93 (dd, J = 7.5, 3.1 Hz, 1H), 1.80 (ddd, J = 8.3, 2.8, 2.8 Hz, 1H), 1.65 (dd, J = 9.8, 8.4

Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.3, 163.6, 162.5, 158.7, 156.9, 135.5, 128.6, 128.3, 127.6, 124.3, 103.7, 85.9, 70.8, 61.5, 61.1, 52.8, 48.3, 39.8, 39.6, 38.2, 32.3; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 464.1347, found 464.1349; **R_f** (33% EtOAc in pentane) = 0.54; **X-ray** (single-crystal) A colorless plate-like specimen of **3af** (X-ray diffraction quality) was obtained by slow evaporation (CCDC 2225195).

***N*,6a-Dimethoxy-*N*-methyl-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*f*]quinoxaline-7-carboxamide (3ag):**



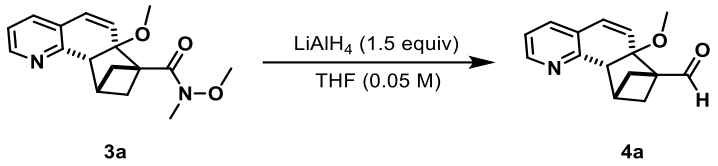
3ag

The title compound was prepared from *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 28.2 mg, 0.20 mmol, 1.0 equiv) and 6-methoxyquinoxaline (**1y**, 64.1 mg, 0.40 mmol, 2.0 equiv) according to the *General Procedure*. Purification by silica gel column chromatography (100% Et_2O) gave the product (23.1 mg, 38%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, J = 2.5, 0.7 Hz, 1H), 8.33 (d, J = 2.6 Hz, 1H), 6.89 (d, J = 10.2 Hz, 1H), 6.24 (d, J = 10.3 Hz, 1H), 3.70 (s, 3H), 3.48 – 3.43 (m, 1H), 3.24 (s, 3H), 3.19 (s, 3H), 2.82 – 2.75 (m, 1H), 2.14 (dd, J = 9.5, 7.5 Hz, 1H), 2.04 (dd, J = 7.5, 3.1 Hz, 1H), 1.67 (ddd, J = 8.0, 2.6, 2.6 Hz, 1H), 1.56 (dd, J = 9.5, 8.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.2, 147.5, 142.7, 142.3, 133.9, 131.2, 85.4, 61.6, 61.6, 52.7, 49.6, 42.2, 40.2, 38.0, 33.1 – ^{13}C signal of Weinreb amide, expected at ~170 ppm, not observed; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 324.1318, found 324.1325; **R_f** (100% Et_2O) = 0.17.

2.4 Product Diversification

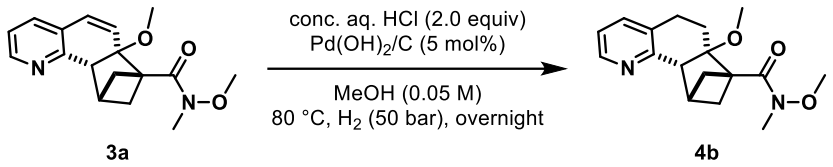
6a-Methoxy-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carbaldehyde (**4a**)**:**



The title compound was prepared following a modified literature procedure.[35] To an oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was added Weinreb amide **3a** (30.0 mg, 0.10 mmol, 1.0 equiv), and the Schlenk tube was evacuated and backfilled with argon three times. Subsequently, the dry THF (2 mL) was added, and the solution was cooled to −78 °C. A solution of $LiAlH_4$ (5.7 mg, 0.15 mmol, 1.5 equiv) in THF (1 mL) was added dropwise at this temperature, and the mixture was stirred for 1.5 h. After warming up to 0 °C, the reaction was quenched by addition of aq. NaOH (1 M, 0.1 mL) and water (0.5 mL). The mixture was stirred at room temperature for 15 min, and then filtered through a pad of silica (eluted with EtOAc). The solvent was removed *in vacuo*, and purification by silica gel column chromatography (70% Et_2O in pentane) gave the product (21.9 mg, 91%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.43 (dd, J = 4.9, 1.7 Hz, 1H), 7.43 (dd, J = 7.6, 1.7 Hz, 1H), 7.13 (dd, J = 7.6, 4.9 Hz, 1H), 6.69 (d, J = 10.0 Hz, 1H), 5.96 (d, J = 9.9 Hz, 1H), 3.56 – 3.50 (m, 1H), 3.22 (s, 3H), 2.93 – 2.87 (m, 1H), 2.11 (dd, J = 9.7, 6.8 Hz, 1H), 1.86 (dd, J = 6.8, 3.1 Hz, 1H), 1.66 (ddd, J = 7.8, 2.6, 2.6 Hz, 1H), 1.35 (dd, J = 9.7, 7.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 157.1, 148.6, 134.6, 130.7, 127.5, 127.4, 122.1, 84.9, 68.5, 52.7, 51.0, 43.3, 36.8, 36.2; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 264.0995, found 264.0994; **R_f** (100% Et_2O) = 0.62.

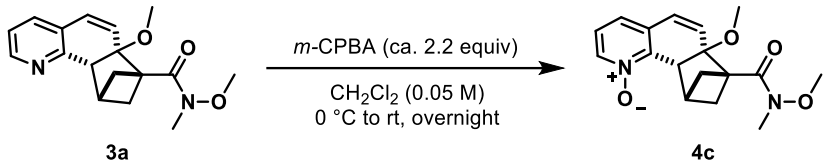
***N*,6a-Dimethoxy-*N*-methyl-5,6,6a,8,9,9a-hexahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (4b):**



The title compound was prepared applying reaction conditions from a modified literature procedure.[36] To a 4 mL screw-cap vial equipped with a Teflon-coated magnetic stir bar were added $Pd(OH)_2$ on activated charcoal (8.8 mg, 5 mol%), **3a** (30.0 mg, 0.10 mmol, 1.0 equiv), MeOH (2.0 ml), and conc. aq. HCl (17 µL, 2.0 equiv). The vial was placed in a 150 mL stainless steel autoclave. The autoclave was pressurized and depressurized (4×) with H_2 gas before a pressure of 50 bar was set. The reaction was stirred at 80 °C overnight. The crude was filtered through a pad of Celite® (eluted with CH_2Cl_2), the solvent was removed *in vacuo*, and purification by silica gel column chromatography (100% Et_2O) gave the product (23.3 mg, 77%) as colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 4.9 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.04 (dd, J = 7.6, 4.8 Hz, 1H), 3.69 (s, 3H), 3.29 (s, 3H), 3.20 (s, 3H), 3.06 – 2.98 (m, 2H), 2.91 – 2.78 (m, 1H), 2.70 (ddd, J = 15.4, 4.0, 4.0 Hz, 1H), 2.43 (ddd, J = 15.6, 3.9, 3.9 Hz, 1H), 2.30 (dd, J = 9.7, 7.1 Hz, 1H), 2.13 (dd, J = 7.1, 3.1 Hz, 1H), 1.96 – 1.85 (m, 1H), 1.81 (ddd, J = 7.9, 3.0, 3.0 Hz, 1H), 1.51 (dd, J = 9.7, 7.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 158.7, 147.5, 135.3, 134.3, 121.2, 87.5, 61.3, 58.7, 53.7, 51.6, 43.6, 39.9, 37.3, 33.0, 26.9, 26.0; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 325.1523, found 325.1526; **R_f** (100% Et_2O) = 0.12.

6a-Methoxy-7-(methoxy(methyl)carbamoyl)-6a,8,9,9a-tetrahydro-7*H*-7,9-methanocyclopenta[*h*]quinoline 1-oxide (**4c**)**:**

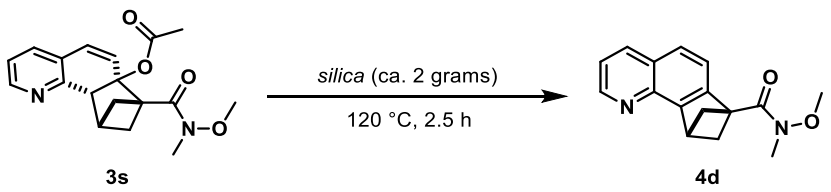


3a **4c**

The title compound was prepared following a modified literature procedure.[37] In a 4 mL screw-cap vial equipped with a Teflon-coated magnetic stir bar **3a** (30.0 mg, 0.10 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.0 mL). The solution was cooled to 0 °C and *m*-CPBA (purity ≤ 77%, 50 mg, ca. 2.2 equiv) was added portionwise. The reaction was allowed to warm up to room temperature and stirred until full conversion (monitored by TLC). The mixture was quenched by addition of aq. NaOH (1 M). The aq. layer was extracted with CH_2Cl_2, and the combined org. layers were again extracted with aq. NaOH (1 M). The aq. layer was once more extracted with CH_2Cl_2, and the combined org. layers were dried over $MgSO_4$. Subsequently, the solvent was removed *in vacuo*, and purification by silica gel column chromatography (5% MeOH in CH_2Cl_2) gave the product (30.1 mg, 95%) as a slight yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 6.4, 1.3 Hz, 1H), 7.13 (dd, J = 7.7, 6.5 Hz, 1H), 7.06 (dd, J = 7.8, 1.3 Hz, 1H), 6.62 (d, J = 10.1 Hz, 1H), 6.06 (d, J = 10.0 Hz, 1H), 3.70 (s, 3H), 3.68 – 3.65 (m, 1H), 3.23 (s, 3H), 3.19 – 3.15 (m, 1H), 3.10 (s, 3H), 2.16 (dd, J = 9.6, 7.6 Hz, 1H), 2.05 (dd, J = 7.7, 3.1 Hz, 1H), 1.64 (ddd, J = 8.1, 2.6, 2.6 Hz, 1H), 1.43 (dd, J = 9.6, 8.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.1, 147.2, 138.6, 131.8, 130.8, 127.5, 124.1, 123.6, 85.4, 61.6, 52.5, 44.0, 40.7, 38.3, 38.2, 32.6, 29.8; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 339.1315, found 339.1319; $\mathbf{R_f}$ (5% MeOH in CH_2Cl_2) = 0.09.

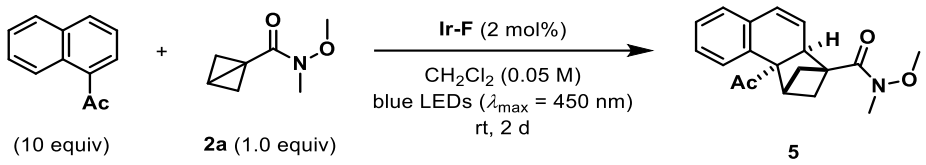
***N*-Methoxy-*N*-methyl-8,9-dihydro-7*H*-7,9-methanocyclopenta[*h*]quinoline-7-carboxamide (4d):**



The title compound was prepared following a modified literature procedure.[38] To a round-bottom flask equipped with a Teflon-coated magnetic stir bar were added **3s** (32.8 mg, 0.10 mmol, 1.0 equiv), silica (ca. 2 g), and CH_2Cl_2 (15 mL). After stirring the thick suspension for ca. 10 min and subsequent removal of the solvent *in vacuo*, the remaining solid was stirred at 120 °C for 2.5 h. The reaction was cooled to room temperature, and purification (the solid was directly used for dry-loading; 50% EtOAc in CH_2Cl_2) gave the product (22.7 mg, 85%) as a slight green solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, J = 4.2, 1.8 Hz, 1H), 8.13 (dd, J = 8.5, 1.8 Hz, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.26 (dd, J = 8.4, 4.2 Hz, 1H), 3.95 (t, J = 2.7 Hz, 1H), 3.60 (s, 3H), 3.36 (s, 3H), 3.24 – 3.20 (m, 2H), 3.06 (dd, J = 3.6, 1.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 154.2, 150.7, 150.1, 141.8, 137.3, 126.7, 124.5, 119.9, 119.2, 69.1, 61.5, 58.9, 38.7, 32.6, 30.3; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 291.1104, found 291.1102; **R_f** (5% MeOH in CH_2Cl_2) = 0.17.

9b-Acetyl-*N*-methoxy-*N*-methyl-1,2,3a,9b-tetrahydro-3*H*-1,3-methanocyclopenta[*a*] naphthalene-3-carboxamide (**5**)**:**



To an oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar was added **Ir-F** (2.2 mg, 0.02 mmol, 2 mol%). The Schlenk tube was evacuated and backfilled with argon three times. Subsequently, CH_2Cl_2 (2 mL), *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 14.1 mg, 0.10 mmol, 1.0 equiv), and 1-acetonaphthone (150 μL, 1.0 mmol, 10.0 equiv) were added. The reaction was stirred and irradiated with blue LEDs (30 W, λ_{max} = 450 nm) for 2 d. After measuring crude GC-MS, the solvent was removed by a stream of argon and then CH_2Br_2 (7.0 μL, 0.10 mmol, 1.0 equiv) was added as internal standard for ^{1}H NMR analysis. Purification by silica gel column chromatography gave the product (10.4 mg. 33%) as a colorless solid.

Note: In crude GC-MS analysis, traces of another product with the same mass were observed. However, no signals in the crude ^{1}H NMR could be assigned to a specific isomer, and the side product could not be isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (ddd, J = 7.3, 7.3, 1.6 Hz, 1H), 7.14 (ddd, J = 7.4, 7.4, 1.8 Hz, 1H), 7.07 (dd, J = 7.2, 1.7 Hz, 1H), 7.04 – 7.01 (m, 1H), 6.53 (ddd, J = 10.1, 1.7, 0.7 Hz, 1H), 5.82 (dd, J = 10.0, 4.4 Hz, 1H), 3.63 (s, 3H), 3.38 – 3.31 (m, 1H), 3.22 (s, 3H), 2.90 – 2.86 (m, 1H), 2.04 (s, 3H), 1.90 (dd, J = 7.2, 2.9 Hz, 1H), 1.77 (ddd, J = 7.7, 3.0, 1.8 Hz, 1H), 1.64 (dd, J = 9.7, 7.7 Hz, 1H), 1.55 (dd, J = 9.6, 7.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.9, 172.4, 133.3, 132.5, 128.8, 128.5, 128.1, 128.0, 126. 8, 125.1, 61.7, 61.5, 58.5, 46.3, 45.4, 40.9, 37.0, 32. 7, 27.6; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 334.1414, found 334.1411; **R_f** (50% Et_2O in pentane) = 0.10; **X-ray** (single-crystal) A colorless plate-like specimen of **5** (X-ray diffraction quality) was obtained by liquid/liquid diffusion with EtOAc and pentane (CCDC 2225196).

2.5 Sensitivity Assessment

In 2019, a reaction condition-based sensitivity assessment was published by our group to improve the reproducibility of chemical transformations.[39]

For the reaction set-up a stock solution was prepared.

stock solution: In an oven-dried Schlenk flask **Ir-F** (22.4 mg, 0.020 mmol, 2.0 mol%) was dissolved in CH_2Cl_2 (18 mL) under argon. Subsequently, *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 141 mg, 1.0 mmol, 1.0 equiv) and 7-methoxyquinoline (**1a**, 318 mg, 2.0 mmol, 2.0 equiv) were added. The Schlenk flask was covered with alumina foil to prevent undesired irradiation.

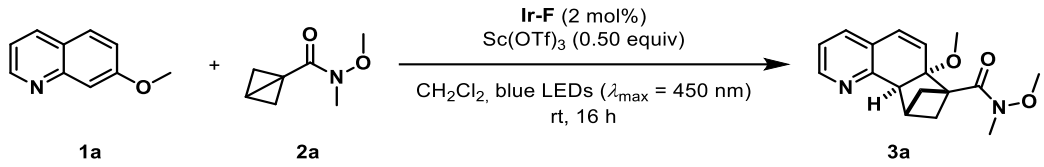
Standard conditions: All reactions were carried out in oven-dried 10 mL Schlenk tubes equipped with a Teflon-coated magnetic stir bar. The Schlenk tubes were charged with $Sc(OTf)_3$ (25 mg, 0.050 mmol, 0.5 equiv), and subsequently evacuated and backfilled with argon three times. Under positive argon pressure, 1.8 mL of the stock solution was added, and the reaction conditions were adjusted as shown in Table S3. The reactions were placed in a photoreaction set-up (all in the same distance to the lamps) stirred and irradiated with blue LEDs (30 W, λ_{max} = 450 nm) for 16 h. The solvent was removed by a stream of argon, and CH_2Br_2 (7.0 µL, 0.10 mmol, 1.0 equiv) was added as internal standard. The residue was dissolved in $CDCl_3$ which was then directly filtered over Celite® into a NMR tube to determine the crude ^{1}H NMR yield.

To entries 3–8 was added CH_2Cl_2 (0.2 mL) to reach the standard concentration (0.05 M). The reactions from entry 9 was performed in a cryo pool (with *i*-PrOH) at 15 °C. The temperature of reaction 10 exceeded the boiling point (at 1 atm), so that an accurate measurement was not possible due to pressure release. Entries 10–11 were performed from another stock solution (this time directly 0.05 M) which is why another control reaction (entry 11) was carried out.

Big scale: To an oven-dried 100 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar were added **Ir-F** (44.8 mg, 0.04 mmol, 2 mol%) and $Sc(OTf)_3$ (492 mg, 1.0 mmol, 0.5 equiv). The Schlenk tube was evacuated and backfilled with argon three times.

Subsequently, CH_2Cl_2 (40 mL), *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 282 mg, 2.0 mmol, 1.0 equiv), and 7-methoxyquinoline (**1a**, 637 mg, 4.0 mmol, 2.0 equiv) were added. The reaction was stirred and irradiated with blue LEDs (30 W, λ_{max} = 450 nm) for 16 h (Figure S4). The reaction mixture was quenched with aq. sat. $NaHCO_3$, and the aq. layer was extracted with CH_2Cl_2 (3×). The org. layers were combined, and the solvent removed *in vacuo*. CH_2Br_2 (140 µL, 2.0 mmol, 1.0 equiv) was added as internal standard, and crude ^1H NMR was measured (84%). The NMR tube, used pipettes, and the Schlenk tube were carefully rinsed with CH_2Cl_2 into the previously used round bottom flask. After removal of the solvents under reduced pressure, purification by silica gel column chromatography (100% Et_2O) gave the product (474 mg, 79%) as a slightly yellow solid.

Table S3. Sensitivity Assessment: reaction conditions and results.



entry	modification	execution	% yield	% deviation
1	high *c*	no additional solvent	98	−2
2	low *c*	+0.4 mL CH_2Cl_2	98	−2
3	high H_2O	+20 µL H_2O	99	−1
4	low O_2	no degassing	>99	0
5	high O_2	+20 mL air	99	−1
6	**control I**	---	>99	
7	high *I*	*d* = 2 cm	99	−1
8	low *I*	*d* = 32 cm	99	−1
9	low *T*	15 °C	>99	0
10	high *T*	> 40 °C	>99	0
11	**control II**		>99	
12	big scale	2.0 mmol scale	84	−9

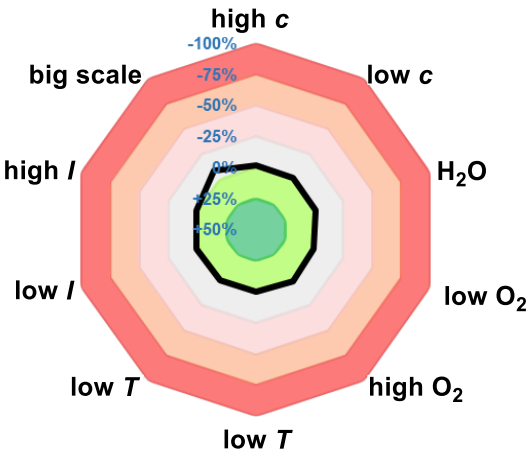


Figure S3. Graphical depiction of the results of the *Sensitivity Assessment*.

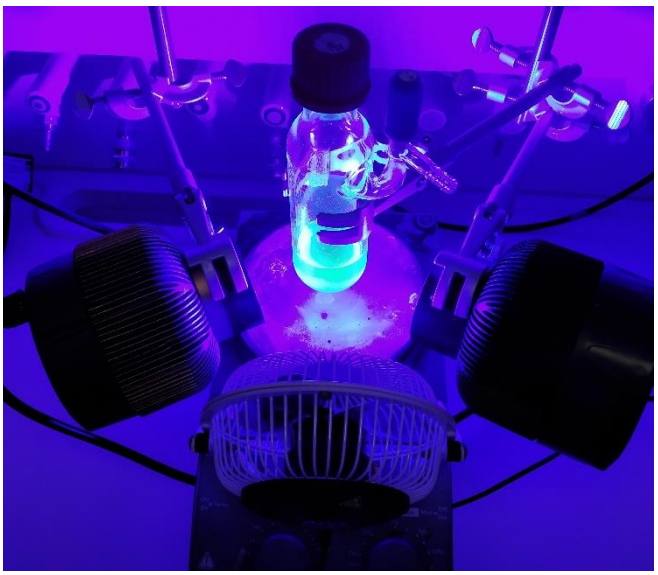


Figure S4. Large-scale reaction set-up.

2.6 Crystal Structures

X-Ray diffraction: Data sets for compounds **3a**, **3y**, **3z**·MeI, **3ab**, **3ad**, **3ae**, **3af** and **5** were collected with a Bruker D8 Venture Photon III Diffractometer. Programs used: data collection: *APEX4* Version 2021.4-0;[1] cell refinement: *SAINT* Version 8.40B;[1] data reduction: *SAINT* Version 8.40B;[1] absorption correction, *SADABS* Version 2016/2;[1] structure solution *SHELXT*-Version 2018-3;[2] structure refinement *SHELXL*- Version 2018-3[3] and graphics, *XP*.[4] *R*-values are given for observed reflections, and *w*R^2 values are given for all reflections.
Exceptions and special features: For compound **3z**·MeI one half dichloromethane molecule is disordered over two positions. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

X-ray crystal structure analysis of 3a (glo10365): A colorless, plate-like specimen of $C_{17}H_{20}N_2O_3$, approximate dimensions 0.031 mm x 0.086 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 583 frames were collected. The total exposure time was 4.37 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 14246 reflections to a maximum θ angle of 25.43° (0.83 Å resolution), of which 2692 were independent (average redundancy 5.292, completeness = 99.6%, R_{int} = 7.88%, R_{sig} = 5.13%) and 2379 (88.37%) were greater than 2σ(F^2). The final cell constants of a = 9.2768(8) Å, b = 6.9828(7) Å, c = 11.3357(12) Å, β = 95.866(3)°, volume = 730.46(12) $Å^3$, are based upon the refinement of the XYZ-centroids of 3799 reflections above 20 σ(I) with 5.983° < 2θ < 50.67°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.861. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9800 and 0.9970. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1$, with Z = 2 for the formula unit, $C_{17}H_{20}N_2O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 202 variables converged at R1 = 4.01%, for the observed data and wR2 = 10.22% for all data. The goodness-of-fit was 1.062. The largest peak in the final difference electron density synthesis was 0.154 $e^-/Å^3$ and the largest hole was -0.185 $e^-/Å^3$ with an RMS deviation

of 0.041 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.366 g/cm^3 and F(000), 320 e^-. CCDC Nr.: 2225189.

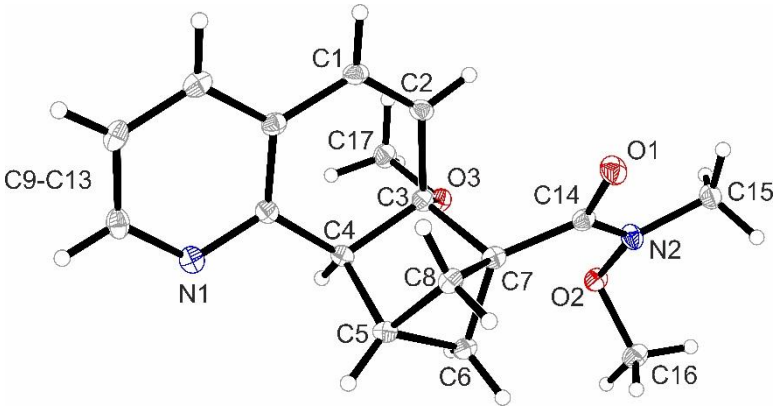


Figure S5. Crystal structure of compound **3a**. Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 3y (glo10364): A colorless, prism-like specimen of $C_{17}H_{20}N_2O_2$, approximate dimensions 0.064 mm x 0.146 mm x 0.170 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 1.54178 Å). A total of 979 frames were collected. The total exposure time was 14.77 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 9742 reflections to a maximum θ angle of 66.63° (0.84 Å resolution), of which 2376 were independent (average redundancy 4.100, completeness = 98.9%, R_{int} = 5.16%, R_{sig} = 4.34%) and 2289 (96.34%) were greater than $2\sigma(F^2)$. The final cell constants of a = 17.3421(4) Å, b = 6.74680(10) Å, c = 12.6147(2) Å, volume = 1475.97(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 7266 reflections above 20 σ(I) with 7.007° < 2θ < 133.1°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.882. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8940 and 0.9580. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Pna*2_1, with Z = 4 for the formula unit, $C_{17}H_{20}N_2O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 193 variables converged at R1 = 5.26%, for the observed data and wR2 = 13.40% for all data. The goodness-of-fit was 1.082. The largest peak in the final difference electron density synthesis was 0.473 $e^-/Å^3$ and the largest hole was -0.241 $e^-/Å^3$ with an RMS deviation of 0.063 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.280 g/cm^3 and F(000), 608 e^-. CCDC Nr.: 2225190.

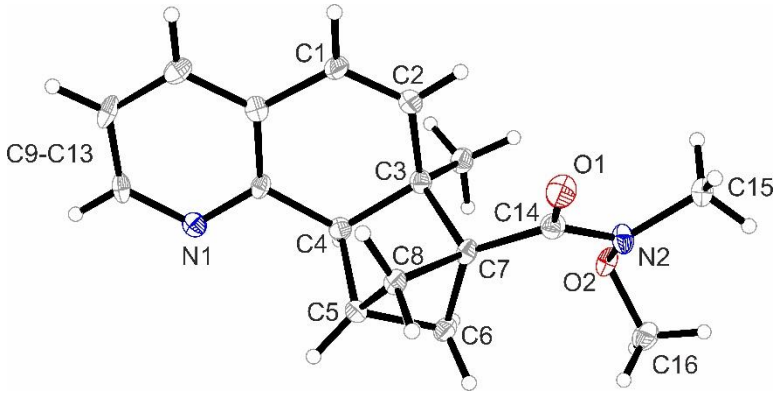


Figure S6. Crystal structure of compound **3y**. Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 3z·MeI **(glo10395):** A colorless, plate-like specimen of $C_{19.50}H_{26}ClIN_2O_2$, approximate dimensions 0.068 mm x 0.095 mm x 0.226 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 600 frames were collected. The total exposure time was 5.00 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 23409 reflections to a maximum θ angle of 26.75° (0.79 Å resolution), of which 4320 were independent (average redundancy 5.419, completeness = 99.4%, R_{int} = 3.01%, R_{sig} = 2.27%) and 4244 (98.24%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.1568(4) Å, b = 9.1031(3) Å, c = 17.3370(5) Å, β = 99.9480(10)°, volume = 2045.19(11) $Å^3$, are based upon the refinement of the XYZ-centroids of 9913 reflections above 20 σ(I) with 4.770° < 2θ < 53.50°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.940. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6980 and 0.8920. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2, with Z = 4 for the formula unit, $C_{19.50}H_{26}ClIN_2O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 246 variables converged at R1 = 1.42%, for the observed data and wR2 = 3.50% for all data. The goodness-of-fit was 1.075. The largest peak in the final difference electron density synthesis was 0.311 $e^-/Å^3$ and the largest hole was -0.179 $e^-/Å^3$ with an RMS deviation of 0.042 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.568 g/cm^3 and F(000), 972 e^-. CCDC Nr.: 2225191.

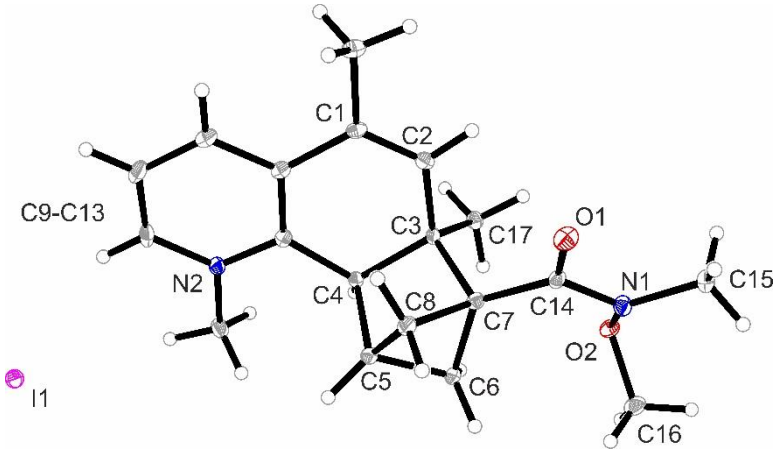


Figure S7. Crystal structure of compound **3z**·MeI. Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 3ab (glo10385): A colorless, plate-like specimen of $C_{17}H_{20}N_2O_3$, approximate dimensions 0.065 mm x 0.121 mm x 0.209 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1123 frames were collected. The total exposure time was 14.61 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 16277 reflections to a maximum θ angle of 66.58° (0.84 Å resolution), of which 2475 were independent (average redundancy 6.577, completeness = 96.6%, R_{int} = 3.52%, R_{sig} = 2.30%) and 2468 (99.72%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.7139(5) Å, b = 6.6239(2) Å, c = 13.1982(4) Å, volume = 1461.19(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 9914 reflections above 20 σ(I) with 17.08° < 2θ < 136.4°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.845. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8560 and 0.9520. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Pna*2_1, with Z = 4 for the formula unit, $C_{17}H_{20}N_2O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 202 variables converged at R1 = 2.36%, for the observed data and wR2 = 6.03% for all data. The goodness-of-fit was 1.036. The largest peak in the final difference electron density synthesis was 0.154 $e^-/Å^3$ and the largest hole was -0.120 $e^-/Å^3$ with an RMS deviation of 0.027 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.365 g/cm^3 and F(000), 640 e^-. CCDC Nr.: 2225192.

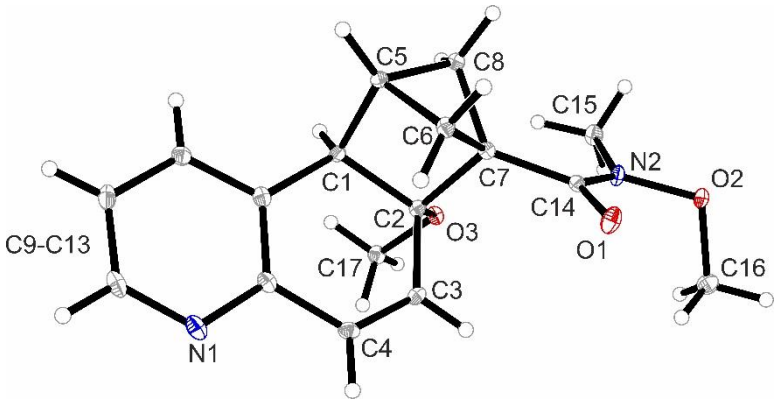


Figure S8. Crystal structure of compound **3ab**. Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 3ad (glo10388): A colorless, plate-like specimen of $C_{18}H_{21}ClN_2O_4$, approximate dimensions 0.040 mm x 0.088 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 592 frames were collected. The total exposure time was 5.76 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 38611 reflections to a maximum θ angle of 26.85° (0.79 Å resolution), of which 3611 were independent (average redundancy 10.693, completeness = 99.4%, R_{int} = 6.68%, R_{sig} = 2.83%) and 3082 (85.35%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.8239(2) Å, b = 12.1414(4) Å, c = 20.5302(7) Å, β = 97.1830(10)°, volume = 1687.61(9) $Å^3$, are based upon the refinement of the XYZ-centroids of 8454 reflections above 20 σ(I) with 5.220° < 2θ < 53.57°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.929. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9700 and 0.9900. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{18}H_{21}ClN_2O_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 230 variables converged at R1 = 3.52%, for the observed data and wR2 = 9.00% for all data. The goodness-of-fit was 1.032. The largest peak in the final difference electron density synthesis was 0.365 $e^-/Å^3$ and the largest hole was -0.240 $e^-/Å^3$ with an RMS deviation of 0.049 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.436 g/cm^3 and F(000), 768 e^-. CCDC Nr.: 2225193.

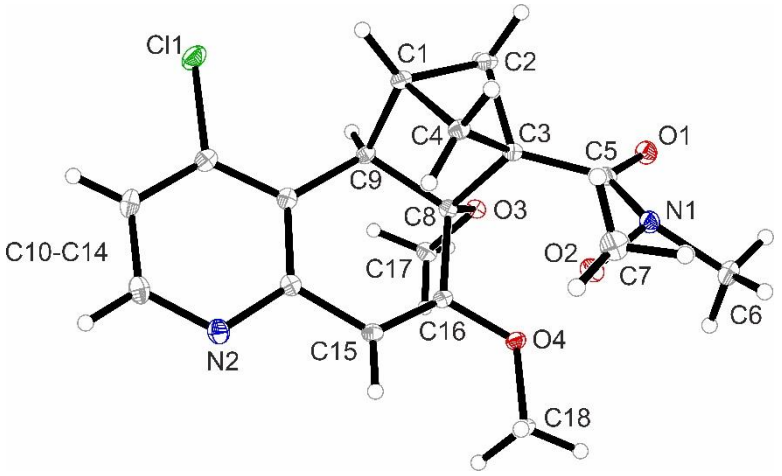


Figure S9. Crystal structure of compound **3ad**. Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 3ae (glo10362): A colorless, prism-like specimen of $C_{17}H_{20}N_2O_3$, approximate dimensions 0.112 mm x 0.176 mm x 0.287 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Mo ImS (MoKα, λ = 0.71073 Å) and a MX mirror monochromator. A total of 1428 frames were collected. The total exposure time was 11.90 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 12138 reflections to a maximum θ angle of 26.73° (0.79 Å resolution), of which 3064 were independent (average redundancy 3.961, completeness = 96.1%, R_{int} = 2.53%, R_{sig} = 2.28%) and 2619 (85.48%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.6786(5) Å, b = 8.7980(5) Å, c = 12.2148(7) Å, α = 80.825(2)°, β = 86.053(3)°, γ = 66.933(2)°, volume = 749.48(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 7117 reflections above 20 σ(I) with 5.085° < 2θ < 53.47°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.942. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9740 and 0.9900. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{17}H_{20}N_2O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 202 variables converged at R1 = 3.90%, for the observed data and wR2 = 10.42% for all data. The goodness-of-fit was 1.049. The largest peak in the final difference electron density synthesis was 0.294 $e^-/Å^3$ and the largest hole was -0.206 $e^-/Å^3$ with an RMS deviation of 0.041 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.331 g/cm^3 and F(000), 320 e^-. CCDC Nr.: 2225194.

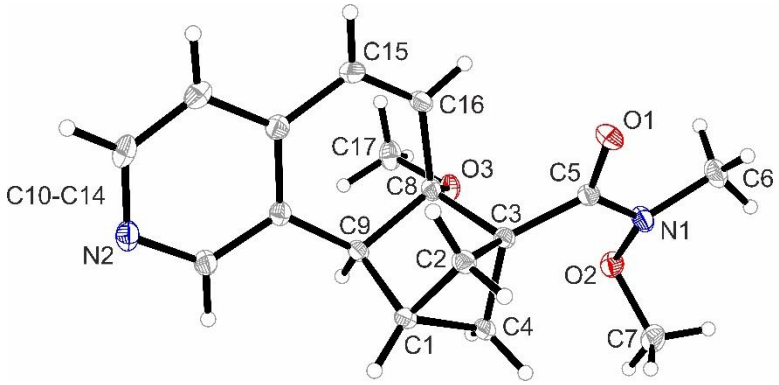


Figure S10. Crystal structure of compound **3ae**. Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 3af (glo10375): A pale yellow, plate-like specimen of $C_{23}H_{24}ClN_3O_4$, approximate dimensions 0.039 mm x 0.092 mm x 0.173 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1992 frames were collected. The total exposure time was 21.95 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 45084 reflections to a maximum θ angle of 66.69° (0.84 Å resolution), of which 3771 were independent (average redundancy 11.955, completeness = 99.8%, R_{int} = 10.07%, R_{sig} = 3.90%) and 2889 (76.61%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.8028(2) Å, b = 19.9487(6) Å, c = 15.8208(5) Å, β = 92.783(2)°, volume = 2144.46(11) $Å^3$, are based upon the refinement of the XYZ-centroids of 9778 reflections above 20 σ(I) with 7.136° < 2θ < 132.7°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.815. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7370 and 0.9300. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{23}H_{24}ClN_3O_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 283 variables converged at R1 = 4.63%, for the observed data and wR2 = 11.96% for all data. The goodness-of-fit was 1.026. The largest peak in the final difference electron density synthesis was 0.233 $e^-/Å^3$ and the largest hole was -0.348 $e^-/Å^3$ with an RMS deviation of 0.059 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.369 g/cm^3 and F(000), 928 e^-. CCDC Nr.: 2225195.

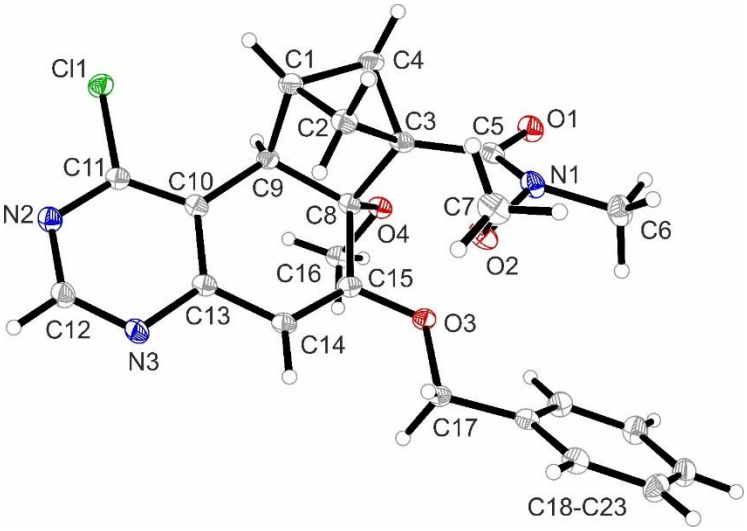


Figure S11. Crystal structure of compound **3af**. Thermal ellipsoids are shown at 30% probability.

X-ray crystal structure analysis of 5 (glo10348): A colorless, plate-like specimen of $C_{19}H_{21}NO_3$, approximate dimensions 0.055 mm x 0.066 mm x 0.145 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a single crystal diffractometer Bruker D8 Venture Photon III system equipped with a micro focus tube Cu ImS (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1646 frames were collected. The total exposure time was 20.75 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 34180 reflections to a maximum θ angle of 68.31° (0.83 Å resolution), of which 2879 were independent (average redundancy 11.872, completeness = 99.5%, R_{int} = 6.65%, R_{sig} = 2.85%) and 2472 (85.86%) were greater than 2σ(F^2). The final cell constants of a = 14.1119(3) Å, b = 8.5669(2) Å, c = 14.8069(3) Å, β = 118.1120(10)°, volume = 1578.90(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 9967 reflections above 20 σ(I) with 7.138° < 2θ < 136.4°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.910. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9040 and 0.9620. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{19}H_{21}NO_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 211 variables converged at R1 = 3.84%, for the observed data and wR2 = 9.54% for all data. The goodness-of-fit was 1.045. The largest peak in the final difference electron density synthesis was 0.411 $e^-/Å^3$ and the largest hole was -0.199 $e^-/Å^3$ with an RMS deviation

of 0.040 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.310 g/cm^3 and F(000), 664 e^-. CCDC Nr.: 2225196.

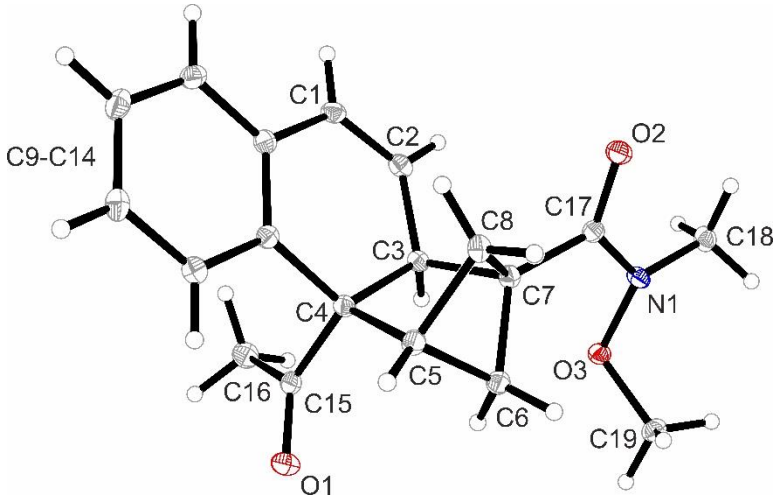


Figure S12. Crystal structure of compound **5**. Thermal ellipsoids are shown at 30% probability.

References X-Ray Part:

1. Bruker AXS (**2021**) *APEX4 Version 2021.4-0, SAINT Version 8.40B* and *SADABS Bruker AXS area detector scaling and absorption correction Version 2016/2*, Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M. SHELXT – Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3–8.
3. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.
4. Bruker AXS (**1998**) *XP – Interactive molecular graphics, Version 5.1*, Bruker AXS Inc., Madison, Wisconsin, USA.

3 Mechanistic Analysis

3.1 UV/Vis Absorption Spectroscopy

UV/Vis absorption spectra were recorded on a Jasco V-730 spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in Starna® fluorescence quartz cuvettes (type: 29-F, chamber volume = 1.400 mL, H × W × D = 48 mm × 12.5 mm × 12.5 mm, path length = 10 mm). All samples containing $Sc(OTf)_3$ were filtered (Whatman filter paper) into the cuvette to prevent undesired scattering.

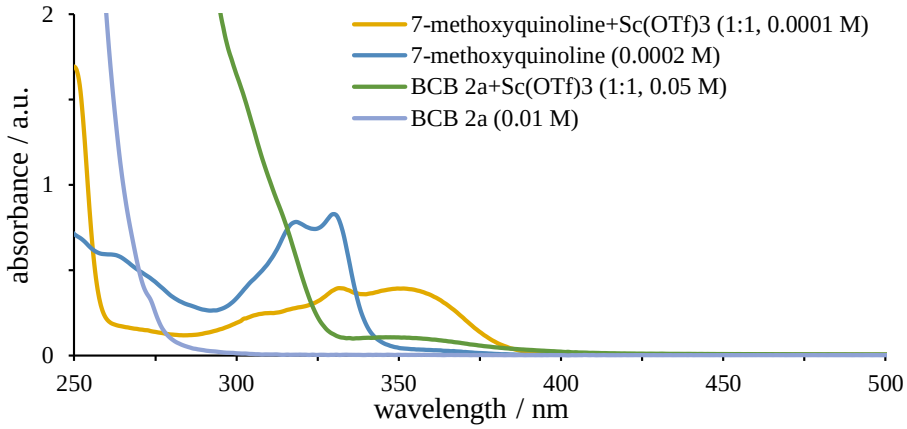


Figure S13. UV/Vis absorption spectra of starting materials **1a** and **2a** in isolation and 1:1 adducts with $Sc(OTf)_3$ in CH_2Cl_2.

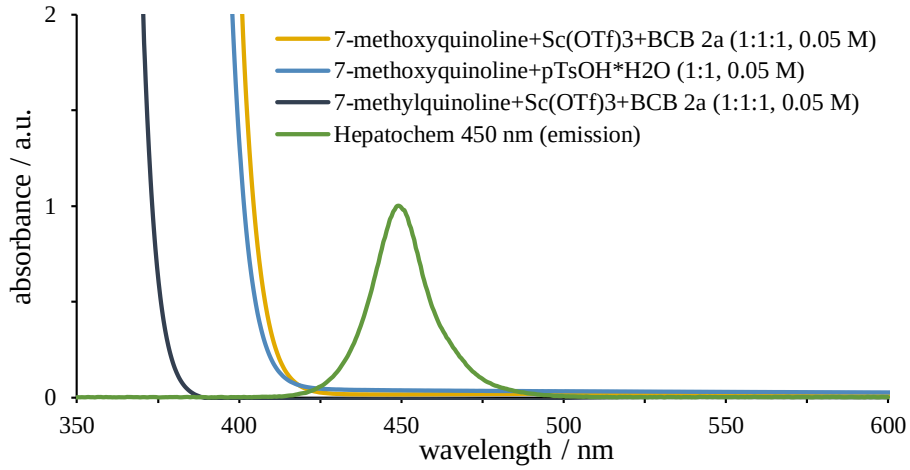


Figure S14. UV/Vis absorption spectra of the reaction mixture with 7-methoxyquinoline (**1a**, orange) or 7-methylquinoline (**1p**, dark blue), 7-methoxyquinoline–Brønsted acid adduct (1:1, light blue), and the emission spectra of HCK1021-01-008 blue LEDs (30 W, λ_{max} = 450 nm, green).

3.2 Stern–Volmer Luminescence Quenching Studies

Stern–Volmer luminescence quenching analysis was carried out, to identify quenchers of the excited photocatalyst. Therefore, the luminescence of the excited photocatalyst Ir[(dF(CF_3)ppy)$_2$dtbbpy](PF_6) (**Ir-F**) is measured in the presence of varying concentrations of potential quenchers.

The quenching studies were carried out on a JASCO FP-8300 spectrofluorometer using Starna® fluorescence quartz cuvettes (type: 29-F, chamber volume = 1.400 mL, H × W × D = 48 mm × 12.5 mm × 12.5 mm, path length = 10 mm). The following parameters were set: data interval = 0.5 nm, scan-speed = 500 nm/min, excitation wavelength λ_{ex} = 405 nm, measured luminescence wavelength λ = 466 nm. All samples were prepared in an argon-filled glovebox with degassed and dry CH_2Cl_2. The quenching studies were performed using a solution of (**Ir-F**, $1 \cdot 10^{-4}$ M). The varying concentrations of the potential quencher were achieved by dilution of the respective stock solutions in the cuvettes. The samples were sealed with PTFE stoppers and removed from the glovebox for the measurement.

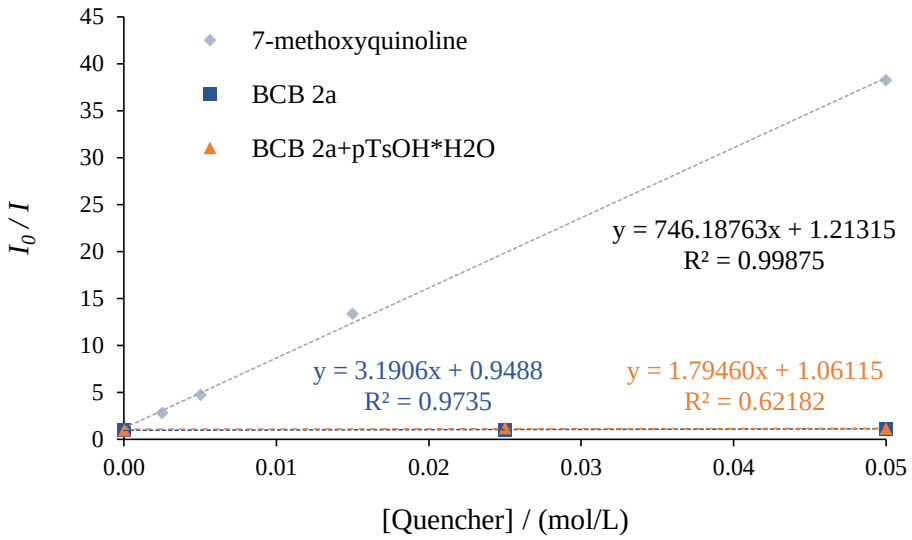


Figure S15. Results of Stern–Volmer luminescence quenching studies.

Note I: For practical reasons *p*-TsOH·H_2O was used as additive because addition of $Sc(OTf)_3$ led to light scattering.

Note II: Addition of *p*-TsOH·H_2O to 7-methoxyquinoline (**1a**) resulted in luminescence overlapping with the luminescence of photocatalyst **Ir-F** (see below, Figure S16). Thus, the effect of acid on the quenching was studied on 7-methylquinoline **1q**.

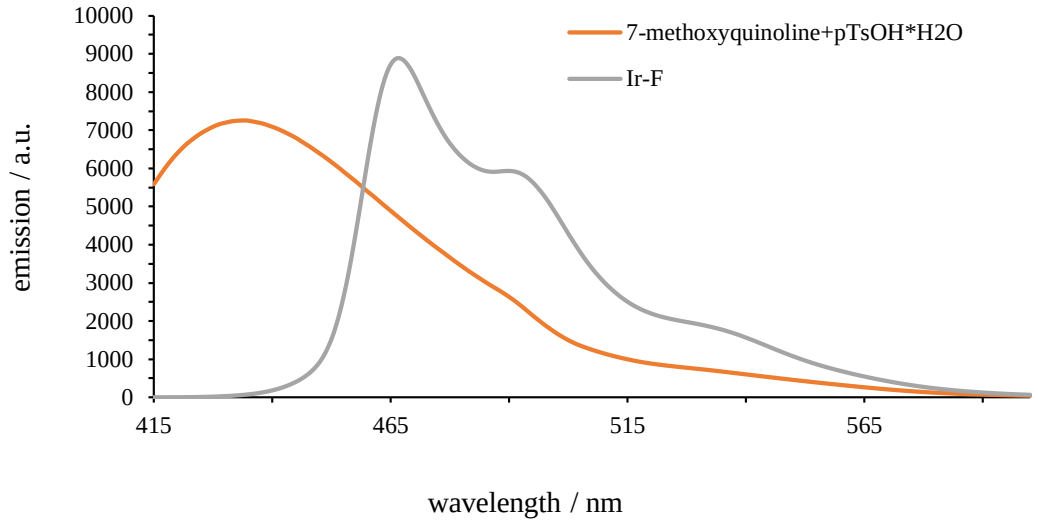


Figure S16. Overlap of the emission spectra of photocatalyst **Ir-F** and protonated 7-methoxyquinoline (**2a**) – excitation wavelength: λ_{ex} = 405 nm.

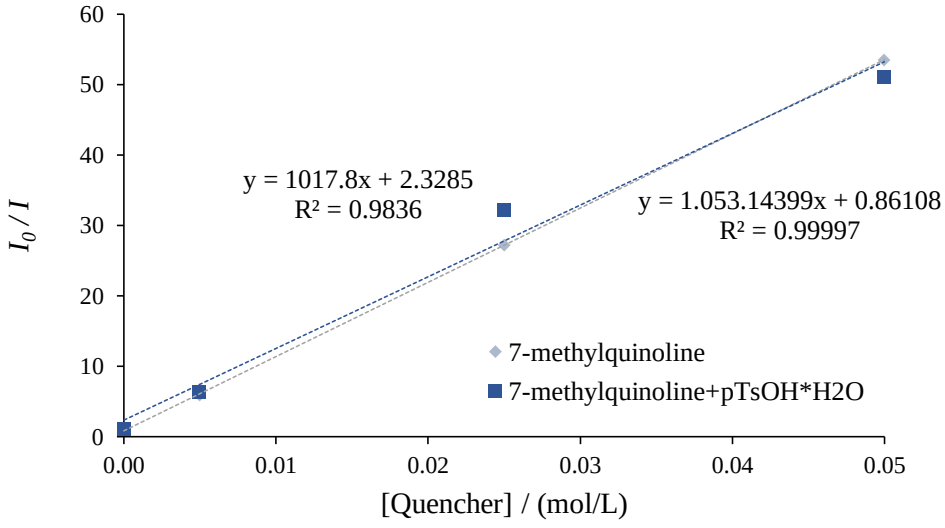
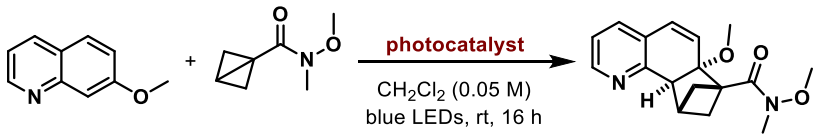


Figure S17. Results of Stern–Volmer luminescence quenching studies for **1q** and protonated **1q**.

3.3 Comparison of Various Photosensitizers

In order to investigate the effect of photocatalysts with different triplet state energies on our developed dearomative [2π+2σ]-photocycloaddition reaction, various catalysts were tested. In these experiments, **no additive** (Lewis or Brønsted acid) was added to avoid undesired direct excitation side-reaction. The reactions were performed following the *General Procedure* on a 0.10 mmol scale. The solvent was removed by a stream of argon, and CH_2Br_2 (7.0 µL, 0.10 mmol, 1.0 equiv) was added as internal standard. The residue was dissolved in $CDCl_3$ to determine the crude ^{1}H NMR yield.

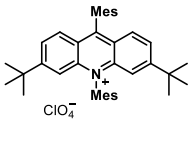
Table S4. Evaluation of various triplet photosensitizers.



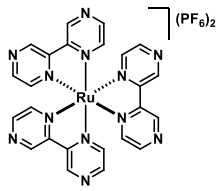
1a (2.0 equiv) **2a** (1.0 equiv) **3a**

entry	PC (2 mol%)	$E_{1/2}$ ($M^*/M^{\bullet-}$) (V)	$E_{1/2}$ ($M^{\bullet+}/M^*$) (V)	E_T (kcal/mol)	**3a** yield (%)
1[a]	$[Mes_2Acr(t\text{-}Bu)_2]ClO_4$	+2.00	---	---	6
2[a]	---	---	---	---	9
3[b]	$[Ru(bpz)_3](PF_6)_2$	+1.45	–0.26	48.4	n.d.
4[b]	$[Ir(ppy)_2(dtbbpy)](PF_6)$	+0.66	–0.96	49.2	8
5[b]	*fac*-$[Ir(ppy)_3]$	+0.31	–1.73	58.1	35
6[b]	**Ir-F**	+1.21	–0.89	61.8	77
7[b]	*fac*-$[Ir(dFppy)_3]$	+0.34	–1.44	63.5	76
8[c]	thioxanthone (**TXT**)	+1.18	–1.11	65.5	69

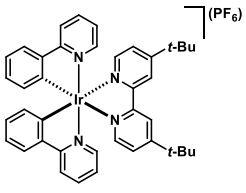
increasing triplet-state energy



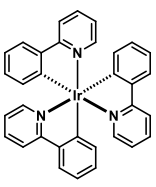
$[Mes_2Acr(t\text{-}Bu)_2](ClO_4)$



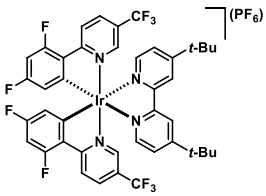
$[Ru(bpy)_3](PF_6)_2$



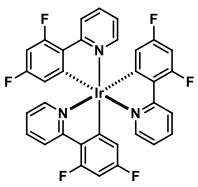
$[Ir(ppy)_2(dtbbpy)](PF_6)$



fac-$[Ir(ppy)_3]$



Ir-F



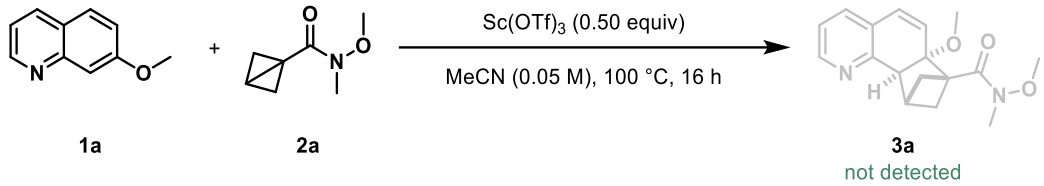
fac-$[Ir(dFppy)_3]$

[a] Irradiated with blue LEDs (λ_{max} = 425 nm) and 5 mol% **PC**. [b] Irradiated with blue LEDs (λ_{max} = 450 nm). [c] Irradiated with blue LEDs (λ_{max} = 405 nm), and 5 mol% **PC**. Triplet energies and redox potentials were taken from the following sources.[7,40–43]

3.4 Heating Control Experiment

To gain insights about possible thermal background reactivity, the reaction was performed in the absence of light and photocatalyst at high temperature.

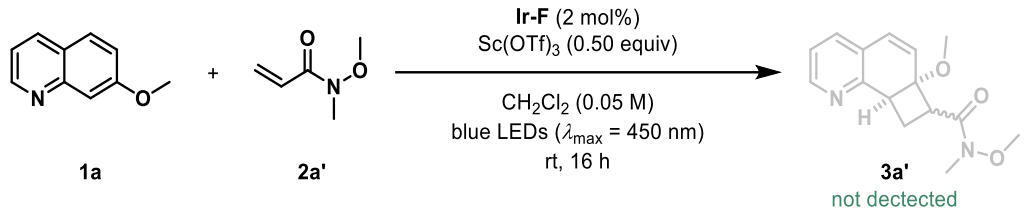
Note: Due to the low boiling point of CH_2Cl_2, MeCN was chosen as solvent for this experiment.



To an oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar $Sc(OTf)_3$ (25 mg, 0.05 mmol, 0.5 equiv) was added. The Schlenk tube was evacuated and backfilled with argon three times. Subsequently, MeCN (2.0 mL), *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 14.1 mg, 0.10 mmol, 1.0 equiv), and 7-methoxyquinoline (**1a**, 31.8 mg, 0.20 mmol, 2.0 equiv) were added. The reaction was stirred in the dark at 100 °C for 16 h. After cooling to room temperature, the solvent was removed by a stream of argon, CH_2Br_2 (7.0 µL, 0.10 mmol, 1.0 equiv) was added as internal standard, and the yield was determined by crude ^1H NMR analysis. No product formation was observed, suggesting a sole photochemical reaction mechanism.

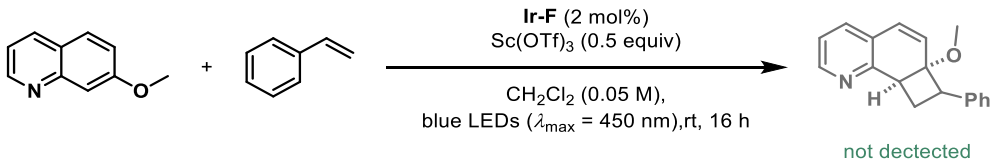
3.5 Olefin Control Experiment

To gain a better understanding of the strain-release reagent's role in this *ortho*-selective dearomative cycloaddition, olefins were tested under our developed standard reaction conditions starting with the corresponding acryl amide **2a'** instead of BCB **2a**.



To an oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar $Sc(OTf)_3$ (25 mg, 0.05 mmol, 0.5 equiv) and **Ir-F** (2.2 mg, 0.002 mmol, 2 mol%) were added. The Schlenk tube was evacuated and backfilled with argon three times. Subsequently, CH_2Cl_2 (2.0 mL), *N*-methoxy-*N*-methylacrylamide (**2a'**, 11.5 mg, 0.10 mmol, 1.0 equiv), and 7-methoxyquinoline (**1a**, 31.8 mg, 0.20 mmol, 2.0 equiv) were added. The reaction was stirred and irradiated with blue LEDs (30 W, λ_{max} = 450 nm) for 16 h. The same reaction was performed in the absence of photocatalyst **Ir-F**. In both cases no product formation was observed by crude GC-MS and ^{1}H NMR analysis.

Furthermore, styrene was tested as olefin coupling partner under our standard conditions.



To an oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar $Sc(OTf)_3$ (25 mg, 0.05 mmol, 0.5 equiv) and **Ir-F** (2.2 mg, 0.002 mmol, 2 mol%) were added. The Schlenk tube was evacuated and backfilled with argon three times. Subsequently, CH_2Cl_2 (2.0 mL), styrene (11 μL, 0.10 mmol, 1.0 equiv), and 7-methoxyquinoline (**1a**, 31.8 mg, 0.20 mmol, 2.0 equiv) were added. The reaction was stirred and irradiated with blue LEDs (30 W, λ_{max} = 450 nm) for 16 h. The reaction mixture was then analyzed by GC-MS and ^{1}H NMR. Purification by PTLC (1st: 50% Et_2O in pentane, 2nd: 100% Et_2O) gave two cycloaddition products as colorless solids.

*Characterization of major product **S3**:*

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (dd, J = 5.1, 1.7 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.25 – 7.11 (m, 4H), 6.65 – 6.56 (m, 2H), 3.99 (t, J = 2.8 Hz, 1H), 3.48 (ddd, J = 10.4, 5.8, 2.3 Hz, 1H), 3.43 – 3.38 (m, 1H), 2.70 (ddd, J = 14.2, 10.3, 2.8 Hz, 1H), 2.60 (dd, J = 18.7 ,2.6 Hz, 1H), 2.29 (dd, J = 18.7, 3.0, 1H), 2.06 (ddd, J = 14.1, 5.8, 2.9 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 209.7, 157.2, 148.6, 144.4, 134.9, 133.9, 128.4, 127.5, 126.8, 122.8, 56.0, 43.9, 43.3, 42.4, 32.2; **HRMS** (ESI^+) calc'd for $[M+H]^+$ 250.1232, found 250.1226; **R_f** (100% Et_2O) = 0.63.

*Characterization of minor product **S4**:*

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, J = 5.0, 1.8 Hz, 1H), 7.14 (dd, J = 7.4, 1.8 Hz, 1H), 7.12 – 7.05 (m, 4H), 6.57 (dd, J = 7.0, 2.6 Hz, 2H), 3.66 (t, J = 2.9 Hz, 1H), 3.35 (s, 3H), 3.31 (ddd, J = 10.3, 5.8, 2.2 Hz, 1H), 3.15 (s, 3H), 3.11 – 3.08 (m, 1H), 2.61 (ddd, J = 13.5, 10.3, 2.9 Hz, 1H), 2.08 (dd, J = 13.3, 2.8 Hz, 1H), 1.78 (dd, J = 13.3, 3.4 Hz, 1H), 1.63 – 1.57 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 147.5, 145.9, 134.4, 133.2, 128.2, 127.7, 126.3, 122.1, 104.2, 49.2, 48.1, 44.7, 43.0, 42.9, 40.3, 29.6; **HRMS** (ESI^+) calc'd for $[M+H]^+$ 318.1470, found 318.1466; **R_f** (100% Et_2O) = 0.58.

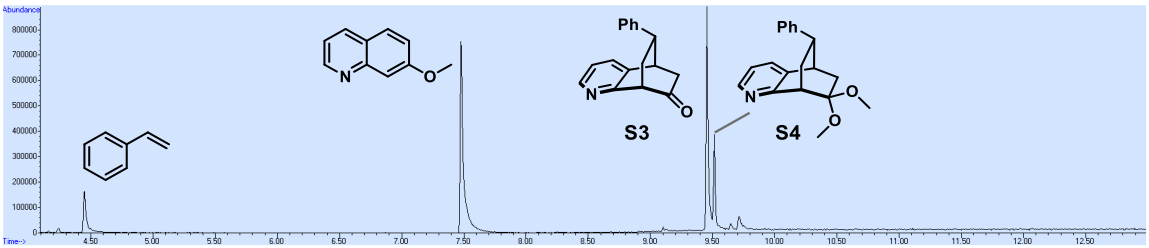


Figure S18. GC-MS chromatogram of the crude reaction mixture of quinoline **1a** and styrene under the standard reaction conditions.

While the *ortho*-[2+2]-adduct was not observed, in this case *para*-[4+2]-addition products were detected (Figure S18). Thus, these results support our hypothesis that the strain-release approach is pivotal to first enable and second conserve the *ortho*-cycloaddition.

3.6 Quantum Yield Analysis

Part I

First, the photon flux of utilized blue LED (3 W, λ_{max} = 455 nm) was determined by standard ferrioxalate actinometry according to a modified literature procedure by Yoon and co-workers.[44]

Determination of the photon flux

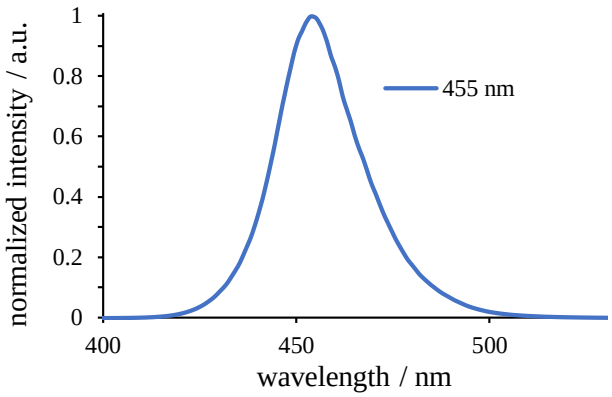


Figure S19. Emission spectrum of the utilized blue LED (3 W, λ_{max} = 455 nm).

Two solutions were prepared and stored in the dark. All following steps were also carried out in a darkened lab to prevent undesired irradiation.

solution 1: Potassium ferrioxalate hydrate (1.474 g, 3.0 mmol) was dissolved in aq. H_2SO_4 (0.05 M, 20 mL) to afford a 0.15 M ferrioxalate solution (attention: light sensitive!).

solution 2: 1,10-Phenanthroline (18 mg, 0.10 mmol), NaOAc (4.50 g) were dissolved in aq. H_2SO_4 (0.5 M, 20 mL).

To determine the photon flux, the reduction of $[Fe(C_2O_4)_3]^{3-}$ to $[Fe(C_2O_4)_2]^{2-}$ by irradiation in a settled time is measured.[45,46] For that, *solution 1* (2 mL) was irradiated for 60 s at λ_{max} = 455 nm (distance: 5 cm) in a standard Schlenk tube. Subsequently, s*olution 2* (350 µL) was added and the mixture was stirred in the dark for 1 h to ensure that all Fe(II)-ions were coordinated by phenanthroline. The absorbance was measured at λ = 510 nm. In addition, the absorbance of a non-irradiated control sample was measured as well. The same procedure was repeated two times. The average absorbance of the three irradiated samples and the control

samples were used to calculate the generated amount of Fe(II) ($n_{Fe(II)}$) according to the Lambert–Beer law (equation 1),

$$n_{Fe(II)} = \frac{V \cdot \Delta A_{510\,\mathrm{nm}}}{l \cdot \varepsilon} \quad (1)$$

where V is the total volume ($2.350 \cdot 10^{-3}$ L). The photon flux (ϕ_q) was calculated using equation 2,

$$\phi_q = \frac{n_{Fe(II)}}{\phi_F \cdot t \cdot f} \quad (2)$$

where ϕ_F is the quantum yield of the ferrioxalate actinometer (0.92 at λ = 468 nm)[47] and t is the irradiation time (60 s). The fraction of light absorbed at λ = 455 nm by the actinometer (f) was calculated by using equation 3,

$$f = 1 - 10^{-A_{455\,\mathrm{nm}}} \quad (3)$$

where $A_{455\,\mathrm{nm}}$ is the absorbance of *solution 1* at λ = 455 nm. In this case, the absorbance ($A_{455\,\mathrm{nm}}$) of *solution 1* was $A_{455\,\mathrm{nm}}$ = 1.384.

Table S5. Results of photon flux measurement with 455 nm blue LED.

	experiment 1	experiment 2	experiment 3	average
A(510nm)	2.639	2.535	2.635	2.603
$A_{control}$(510nm)	0.212	0.120	0.232	0.188
ΔA =	2.415			
ϕ_q =	**$9.661 \cdot 10^{-9}$ mol·s^{-1}**			

Determination of the reaction quantum yield

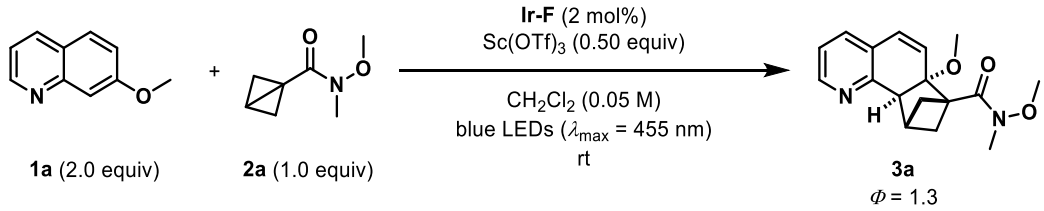
The quantum yield of the reaction can be calculated using equation 4,

$$\phi = \frac{n_{\text{product}}}{\phi_q \cdot t \cdot f_{\text{R}}} \tag{4}$$

where ϕ_q is the photon flux, t is the irradiation time. The fraction of light absorbed (f_{R}) by the reaction was determined by measuring the absorbance of a non-irradiated control reaction (equation 3).

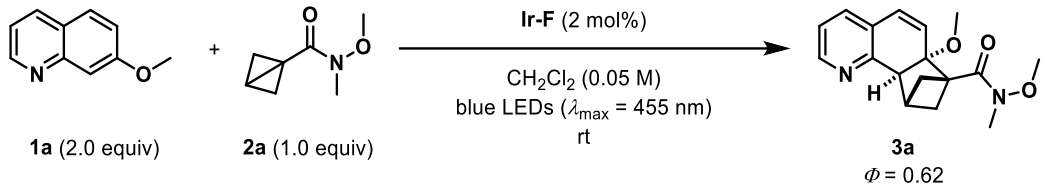
The reactions were performed according to the *General Procedure* on a 0.10 mmol scale. The reaction mixture was stirred under irradiation in the calibrated set-up (3 W, λ = 455 nm) for the indicated time. The solvent was removed by a stream of argon, CH_2Br_2 (7.0 µL, 0.10 mmol, 1.0 equiv) was added as internal standard, and the yield was determined by crude ^{1}H NMR analysis. **Note:** When $Sc(OTf)_3$ was used as additive, the in $CDCl_3$ dissolved residue was filtered over Celite® directly into the NMR tube.

Table S6. Results of the quantum yield measurement with $Sc(OTf)_3$ and **Ir-F**. Fraction of absorbance: f_{R} = 0.533.



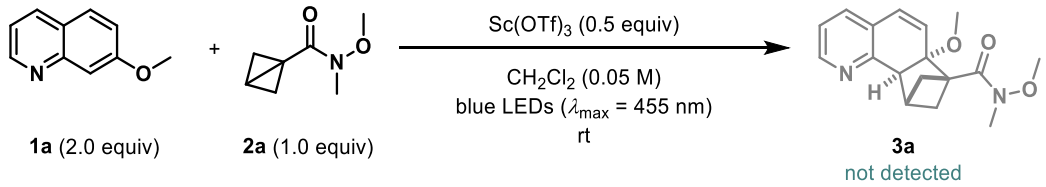
time	yield **3a**	quantum yield
900 s	6%	ϕ = 1.30
1800 s	12%	ϕ = 1.30

Table S7. Results of the quantum yield measurement without $Sc(OTf)_3$. Fraction of absorbance: f_R = 0.695.



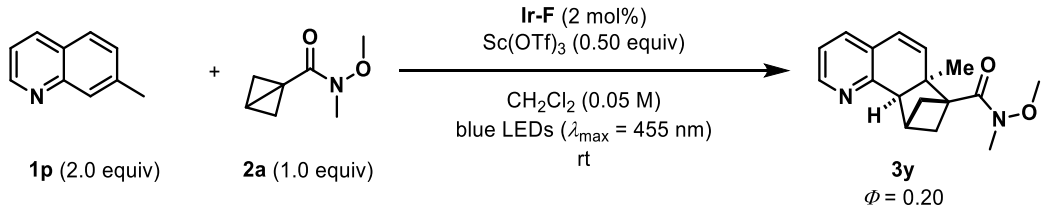
time	yield **3a**	quantum yield
900 s	4%	ϕ = 0.66
1800 s	7%	ϕ = 0.58

Table S8. Result of the quantum yield measurement without **Ir-F**. Fraction of absorbance: f_R = 0.695.



time	yield **3a**	quantum yield
3600 s	not detected	---

Table S9. Results of the quantum yield measurement with $Sc(OTf)_3$ and **Ir-F**. Fraction of absorbance: f_R = 0.522.



time	yield **3a**	quantum yield
1800 s	2%	ϕ = 0.22
3600 s	3%	ϕ = 0.17

Part II

Determination of the photon flux

The photon flux was also determined utilizing a blue LED (3 W, λ_{max} = 415 nm) by standard ferrioxalate actinometry according to a modified literature procedure by Yoon and co-workers.[44]

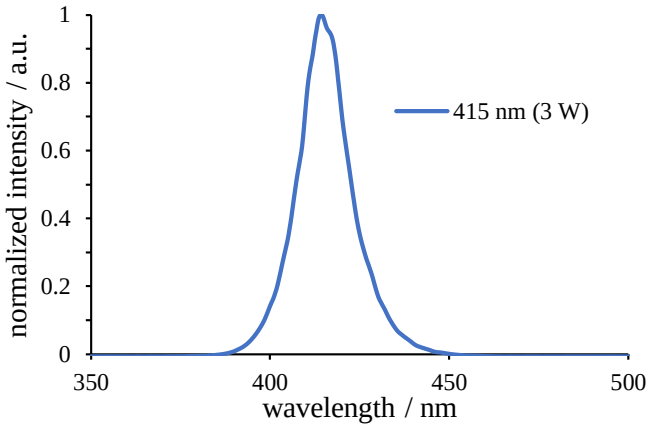


Figure S20. Emission spectrum of the utilized blue LED (3 W, λ_{max} = 415 nm).

Two solutions were prepared and stored in the dark. All following steps were also carried out in a darkened lab to prevent undesired irradiation.

solution 1: Potassium ferrioxalate hydrate (737 mg, 1.50 mmol) was dissolved in aq. H_2SO_4 (0.05 M, 10 mL) to afford a 0.15 M ferrioxalate solution (attention: light sensitive!).

solution 2: 1,10-Phenanthroline (18 mg, 0.10 mmol), NaOAc (4.50 g) were dissolved in aq. H_2SO_4 (0.5 M, 20 mL).

To determine the photon flux, the reduction of $[Fe(C_2O_4)_3]^{3-}$ to $[Fe(C_2O_4)_2]^{2-}$ by irradiation in a settled time is measured.[45,46] For that, *solution 1* (1 mL) was irradiated for 60 s at λ_{max} = 415 nm (distance: 5 cm) in a standard Schlenk tube. Subsequently, s*olution 2* (175 µL) was added and the mixture was stirred in the dark for 1 h to ensure that all Fe(II)-ions were coordinated by phenanthroline. The absorbance was measured at λ = 510 nm. In addition, the absorbance of a non-irradiated control sample was measured as well. The same procedure was repeated two times. The average absorbance of the three irradiated samples and the control samples were used to calculate the generated amount of Fe(II) ($n_{Fe(II)}$) according to the Lambert–Beer law (equation 1), where V is the total volume ($1.175 \cdot 10^{-3}$ L), $\Delta A_{510\,nm}$ is the difference in absorbance of irradiated and non-irradiated control samples (at λ = 510 nm), l is

the path length of the cuvette (1.0 cm), and ε is the molar attenuation coefficient of the ferrioxalate actinometer at λ = 510 nm (11100 L·mol^{-1}·cm^{-1}).[45] The photonflux (ϕ_q) can be calculated using equation 2, where ϕ_F is the quantum yield of the ferrioxalate actinometer (1.12 at λ = 416 nm)[47] and t is the irradiation time (60 s). The fraction of light absorbed at λ = 415 nm by the actinometer (f) was calculated by using equation 3, where $A_{415\,nm}$ is the absorbance of *solution 1* at λ = 415 nm.

In this case, the absorbance ($A_{415\,nm}$) of *solution 1* was > 3, which indicates that > 99.9% of the photons were absorbed (f > 0.999).

Table S10. Results of photonflux measurement.

	experiment 1	experiment 2	experiment 3	average
A(510nm)	2.008	2.106	1.996	2.037
$A_{control}$(510nm)	0.827	0.762	0.771	0.787
ΔA =	1.250			
ϕ_q =	**$1.971 \cdot 10^{-9}$ mol·s^{-1}**			

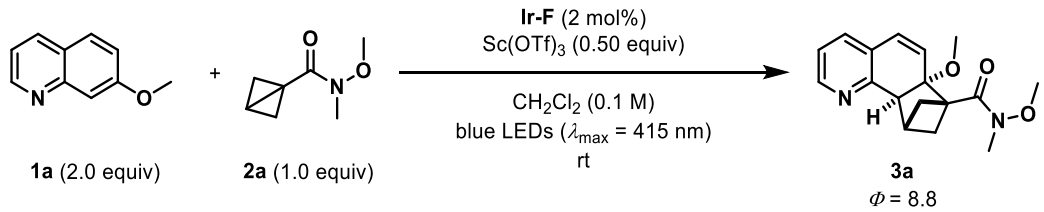
Determination of the reaction quantum yield

Note I: The reactions were performed in higher concentration (0.10 M) compared to the standard reaction conditions.

Note II: For all reactions, the fraction of light absorbed (f_R) was determined to be >0.999.

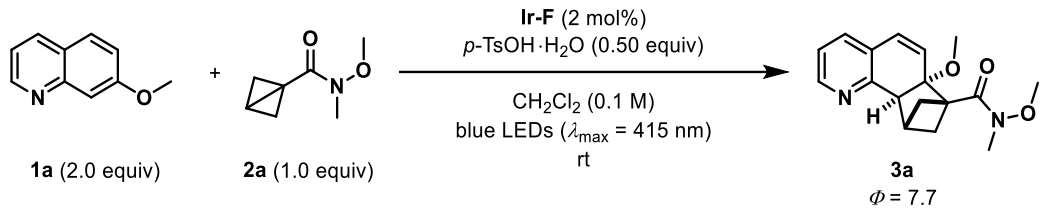
The reactions were performed according to the *General Procedure* on a 0.10 mmol scale. The reaction mixture was stirred under irradiation in the calibrated set-up (3 W, λ = 415 nm) for the indicated time. The solvent was removed by a stream of argon, CH_2Br_2 (7.0 µL, 0.10 mmol, 1.0 equiv) was added as internal standard, and the yield was determined by crude ^{1}H NMR analysis. **Note:** When $Sc(OTf)_3$ was used as additive, the in $CDCl_3$ dissolved residue was filtered over Celite® directly into the NMR tube.

Table S11. Results of the quantum yield measurement with $Sc(OTf)_3$ and **Ir-F**.



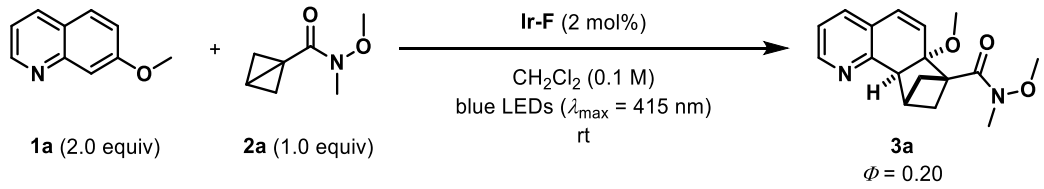
time	yield **3a**	quantum yield
1800 s	32%	ϕ = 9.0
3600 s	60%	ϕ = 8.5

Table S12. Results of the quantum yield measurement with *p*-TsOH·H_2O and **Ir-F**.



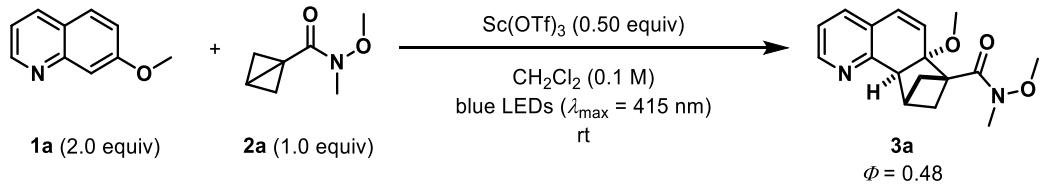
time	yield **3a**	quantum yield
1800 s	27%	ϕ = 7.6
3600 s	55%	ϕ = 7.8

Table 13. Results of the quantum yield measurement without $Sc(OTf)_3$.



time	yield **3a**	quantum yield
3600 s	1.6%	ϕ = 0.23
7200 s	2.3%	ϕ = 0.16

Table S14. Results of the quantum yield measurement without **Ir-F**.



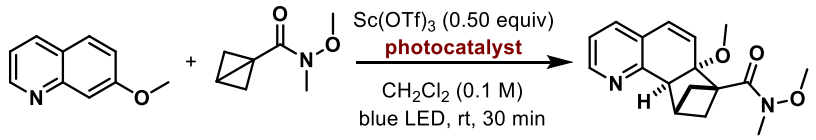
time	yield **3a**	quantum yield
3600 s	3.7%	ϕ = 0.52
7200 s	6.1%	ϕ = 0.43

The results of the quantum yield measurements suggest that an efficient chain reaction is operative when both **Ir-F** as photocatalyst and Lewis or Brønsted acid are present. Based on these results, we were interested if other photocatalyst with different properties induce such a chain reaction as well.

The reactions were performed according to the *General Procedure* on a 0.10 mmol scale in the **quantum yield measurement reaction set-up** for 30 min. The solvent was removed by a stream of argon, and CH_2Br_2 (7.0 µL, 0.10 mmol, 1.0 equiv) was added as internal standard. The residue was dissolved in $CDCl_3$ to determine the yield by crude ^1H NMR analysis.

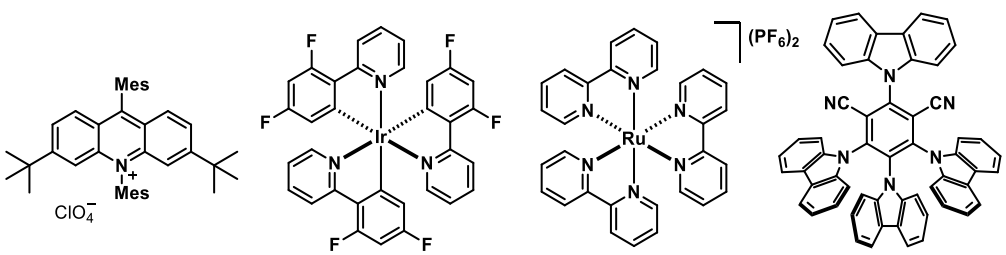
Note: Since the reaction set-up was used several days after the determination of the photon flux, the quantum yield of these transformations should not be reported and only qualitative conclusions should be drawn.

Table S15. Screening other photocatalyst on its ability to induce a chain reaction in the presence of $Sc(OTf)_3$ as Lewis acid.



1a (2.0 equiv) **2a** (1.0 equiv) **3a**

entry	**PC** (2 mol%)	$E_{1/2}$ ($M^*/M^{\bullet-}$) (V)	$E_{1/2}$ ($M^{\bullet+}/M^*$) (V)	E_T (kcal/mol)	**3a** yield (%)	**Chain?!**
1	$[Mes_2Acr(t\text{-}Bu)_2]ClO_4$	+2.00	---	---	1	x
2	$[Ru(bpy)_3](PF_6)_2$	+0.77	–0.81	46.5	<1	x
3	$[Ru(bpz)_3](PF_6)_2$	+1.45	–0.26	48.4	1	x
4	$[Ir(ppy)_2(dtbbpy)](PF_6)$	+0.66	–0.96	49.2	<1	x
5	*fac*-$[Ir(ppy)_3]$	+0.31	–1.73	58.1	<1	x
6	4CzIPN	+1.35	–1.04	~60	17	yes
7	**Ir-F**	+1.21	–0.89	61.8	32	yes
8	*fac*-$[Ir(dFppy)_3]$	+0.34	–1.44	63.5	2	x



$[Mes_2Acr(t\text{-}Bu)_2](ClO_4)$ *fac*-$[Ir(dFppy)_3]$ $[Ru(bpy)_3](PF_6)_2$ 4CzIPN

Triplet energies and redox potentials of the depicted photocatalysts were taken from the following sources.[7,40–43,48]

3.7 Cyclic Voltammetry Measurements

The cyclic voltammograms (CVs) were recorded with a standard three-electrode cell set-up (reference electrode: Ag/AgCl (sat. aq. KCl), working electrode: 3 mm glassy carbon disc electrode, and counter electrode: platinum wire) on CHI600e electrochemical workstation (CH Instruments, Austin, Texas, USA). As electrolyte a 0.10 M solution of *n*-$Bu_4N(PF_6)$ in MeCN was prepared, which was degassed inside the set-up (4 mL of the electrolyte solution was used per measurement) by bubbling argon through it. After measuring a blanc CV, the substance (40 µL of a 0.10 M solution in MeCN) was added, and the CV was recorded. All electrodes and the set-up were cleaned and the procedure was repeated (another blanc measurement was not performed). All measurements were carried out under argon atmosphere, at room temperature, and with a scan rate of 100 mV/s. The redox potentials were converted to the saturated calomel electrode (SCE) scale by subtracting 45 mV (0.045 V).

Note: For practical reasons, *p*-$TsOH{\cdot}H_2O$ was tested as representative acid because $Sc(OTf)_3$ and *p*-$TsOH{\cdot}H_2O$ had a similar effect on the quantum yield.

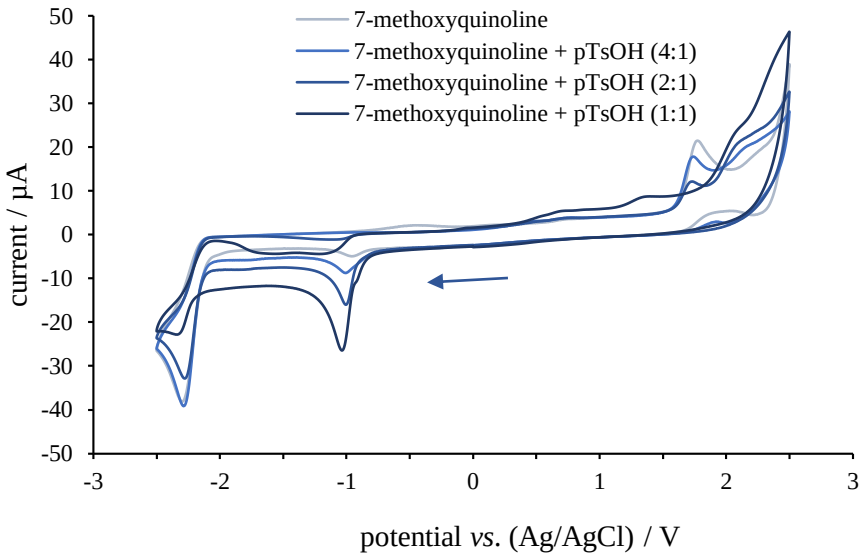


Figure S21. Cyclic voltammograms of 7-methoxyquinoline (**1a**, 1 mM) in MeCN (0.10 M *n*-$Bu_4N(PF_6)$) with increasing ratios of *p*-$TsOH{\cdot}H_2O$.

Discussion: Figure S21 shows irreversible oxidation of **1a** at E_{ox}(**1a**) = 1.78 V *vs.* Ag/AgCl (sat. KCl) and irreversible reduction of protonated **1a** at E_{red}(**1a**+H^+) = −1.00 V *vs.* Ag/AgCl (sat. KCl). The increase in the reduction peak at higher ratios of added acid is associated with suppression of the oxidation peak, supporting that the new reduction peak is due to protonation of **1a**.

E_{ox}(**1a**) = 1.78 V−0.045 V = 1.74 V (*vs*. SCE)

E_{red}(**1a**+H^+) = −1.00 V−0.045 V = −1.05 V (*vs*. SCE)

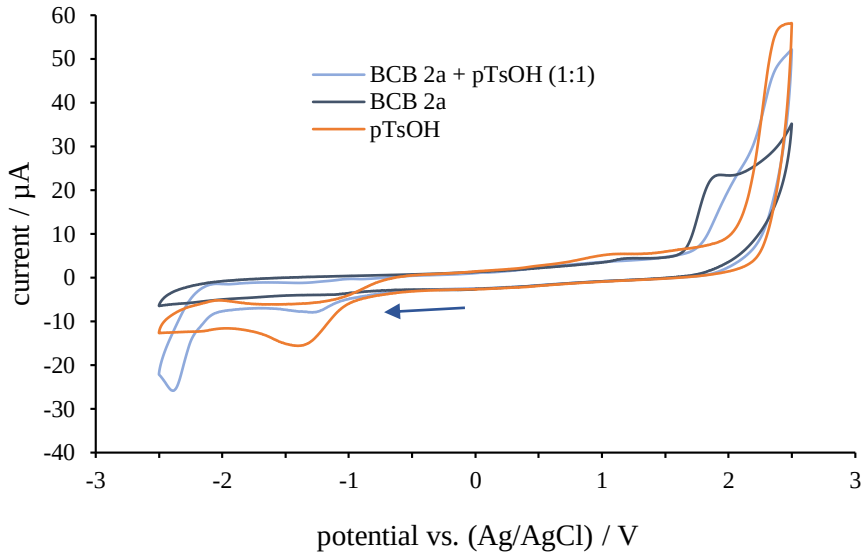


Figure S22. Cyclic voltammograms of BCB **2a** (1 mM), *p*-TsOH·H_2O (1 mM) and their mixture (**2a**:*p*-TsOH·H_2O, 1:1, 1 mM) in MeCN (0.10 M *n*-$Bu_4N(PF_6)$).

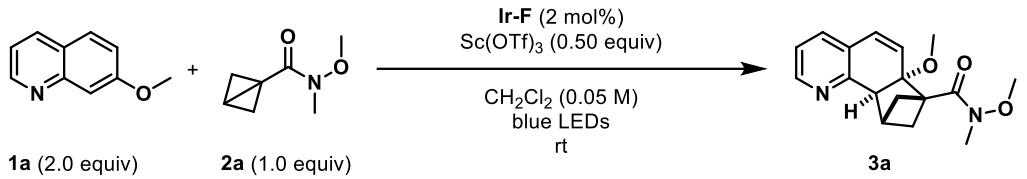
According to this CV measurement, BCB **2a** shows irreversible oxidation at E_{ox}(**1a**) = 1.87 V *vs*. Ag/AgCl (sat. KCl). Addition of acid again suppresses the oxidation peak, however, in this case no new reduction peak is observed that could be ascribed to BCB.

E_{ox}(**2a**) = 1.87 V−0.045 V = 1.83 V (*vs*. SCE)

Discussion: Protonated **1a** shows a new reduction peak at E_{red} = −1.05 V *vs*. SCE while simultaneously suppressing the oxidation peak. However, when various photocatalysts were screened in the presence of $Sc(OTf)_3$ (see Table 10, using the quantum yield measurement set-up) no chain reaction with Φ >> 1 was observed even for more reducing or oxidizing catalysts (only 4CzIPN of the other tested catalyst). Thus, these results do not support a simple redox-initiated chain reaction by **Ir-F**.

3.8 Kinetic Studies – Irradiation Intensity Dependency

In order to test if a two photon process is involved to induce the chain reaction, the dependency of the initial reaction rate was studied with respect to the light intensity.[49]



stock solution: In an oven-dried Schlenk flask **Ir-F** (33 mg, 0.030 mmol, 2.0 mol%) was dissolved in CH_2Cl_2 (30 mL) under argon. Subsequently, *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 212 mg, 1.5 mmol, 1.0 equiv) and quinoline (**1a**, 476 mg, 3.0 mmol, 2.0 equiv) were added. The Schlenk flask was covered with alumina foil to prevent undesired irradiation.

All reactions were carried out in 7 mL screw-cap vials equipped with a Teflon-coated magnetic stir bar. The vials were charged with $Sc(OTf)_3$ (25 mg, 0.050 mmol, 0.5 equiv), and after sealing with a septum cap evacuated and backfilled with argon three times. Under positive argon pressure, 2.0 mL of the stock solution (0.10 mmol scale) was added. The reactions were stirred under irradiation (1 or 2 blue LEDs, λ_{max} = 450 nm, 30 W, distance: 10 cm. See Figure 23) for the indicated time. The solvent was removed by a stream of argon, and CH_2Br_2 (7.0 µL, 0.10 mmol, 1.0 equiv) was added as internal standard. The residue was dissolved in $CDCl_3$, and then directly filtered over Celite® into a NMR tube to determine the crude ^1H NMR yield. Two independent series of measurements were performed for each set-up.

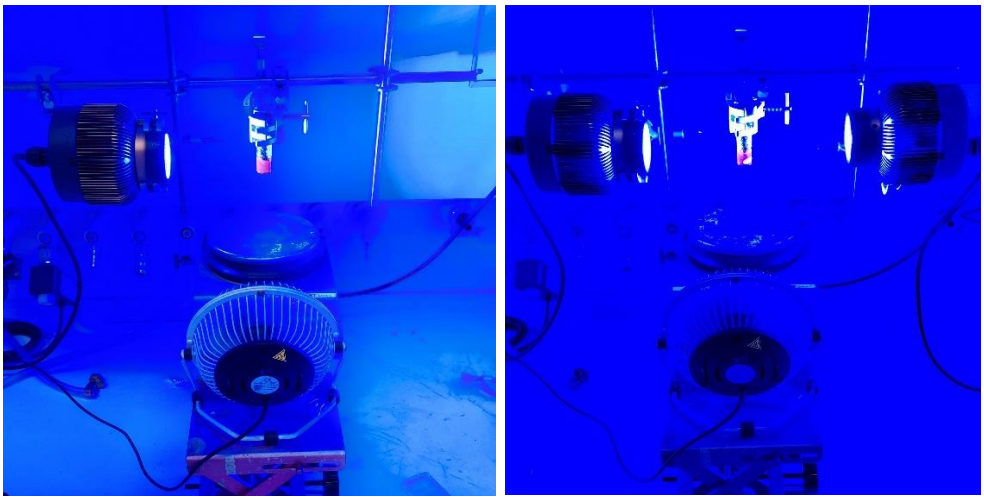


Figure S23. Utilized photoreaction set-up to double the light intensity.

Table S16. Initial reaction rates at different light intensities: λ_{max} = 450 nm – 1st measurement.

entry	light power (#30 W lamps)	reaction time / sec	% yield **3a**
1	1	20	3
2	1	40	6
3	1	60	8
4	2	23	7
5	2	40	11
6	2	60	16
direct excitation control (no **Ir-F**)	2	60	n.d.

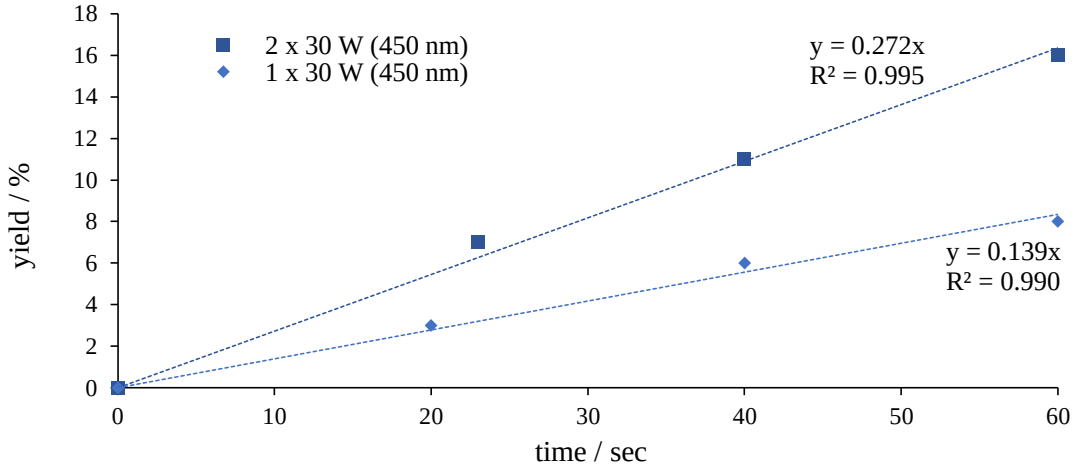


Figure S24. Results of the irradiation intensity dependency study with 450 nm lamps – 1st measurement. Reaction rate increase (high intensity/low intensity): 1.9.

Table S17. Initial reaction rates at different light intensities: λ_{max} = 450 nm – 2nd measurement.

entry	light power (#30 W lamps)	reaction time / sec	% yield **3a**
1	1	10	2
2	1	20	4
3	1	30	6
4	1	40	8
5	1	50	9
6	1	60	11
7	2	10	4
8	2	20	7
9	2	30	10
10	2	40	13
11	2	50	17
12	2	60	19

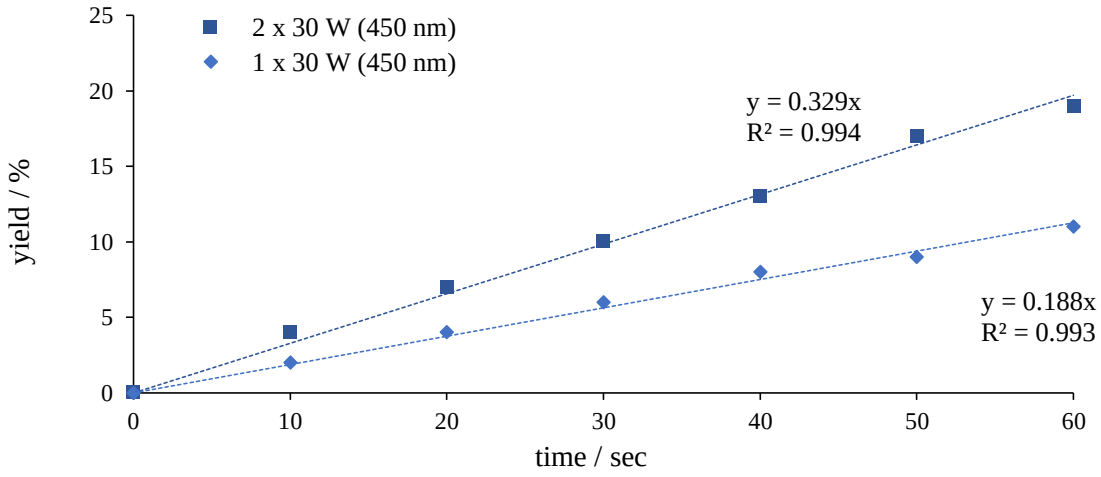


Figure S25. Results of the irradiation intensity dependency study with 450 nm lamps – 2nd measurement. Reaction rate increase (high intensity/low intensity): 1.7.

Given the results from section 3.6, the quantum yield of the reaction appears to be extremely dependent on the irradiation wavelength. Therefore, the dependency on the initial reaction rate was also investigated using blue 415 nm LEDs (distance: 5 cm, external fan cooling). The experiments were performed according to the procedure described above.

Table S18. Initial reaction rates at different light intensities: λ_{max} = 415 nm – 1st measurement.

entry	light power (#3 W lamps)	reaction time / sec	% yield **3a**
1	1	75	2
2	1	150	4
3	1	225	6
4	1	300	8
5	1	375	9
6	1	450	11
7	2	75	5
8	2	150	9
9	2	225	13
10	2	300	16
11	2	375	20
12	2	450	23
direct excitation control (no **Ir-F**)	2	450	2

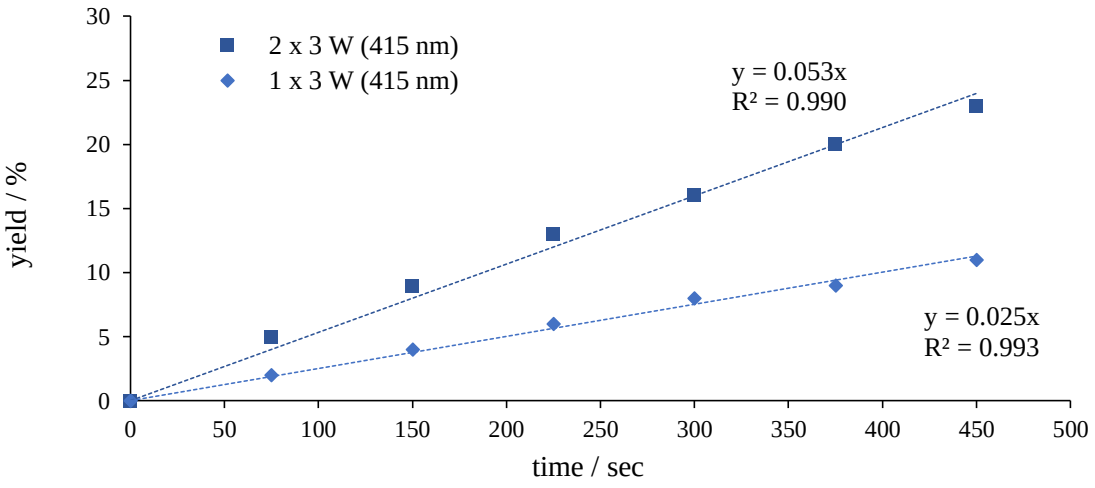


Figure S26. Results of the irradiation intensity dependency study with 415 nm lamps – 1st measurement. Reaction rate increase (high intensity/low intensity): 2.1.

Table S19. Initial reaction rates at different light intensities: λ_{max} = 415 nm – 2nd measurement.

entry	light power (#3 W lamps)	reaction time / sec	% yield **3a**
1	1	75	2
2	1	150	3
3	1	225	5
4	1	300	6
5	1	375	8
6	2	75	3
7	2	150	6
8	2	225	9
9	2	300	12
10	2	375	15

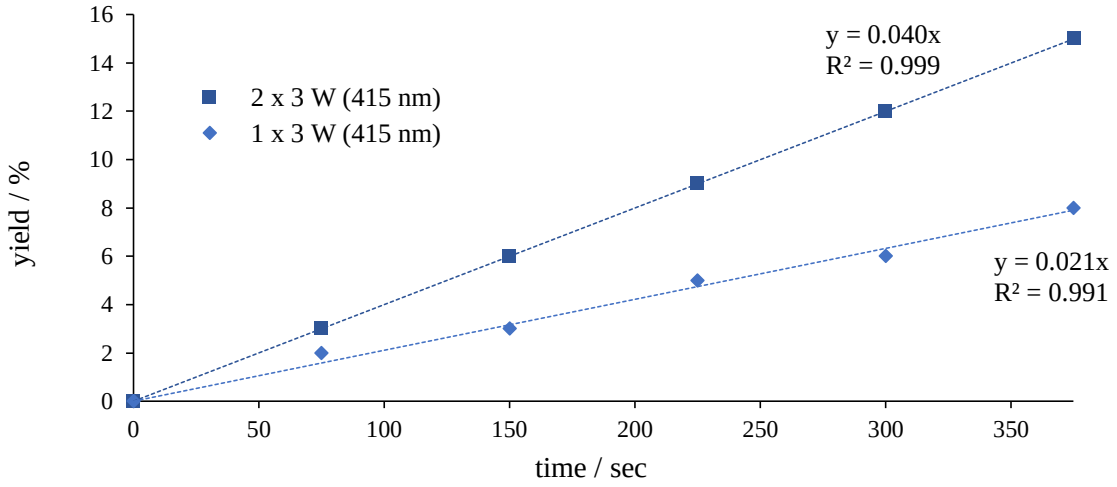


Figure S27. Results of the irradiation intensity dependency study with 415 nm lamps – 1st measurement. Reaction rate increase (high intensity/low intensity): 1.9.

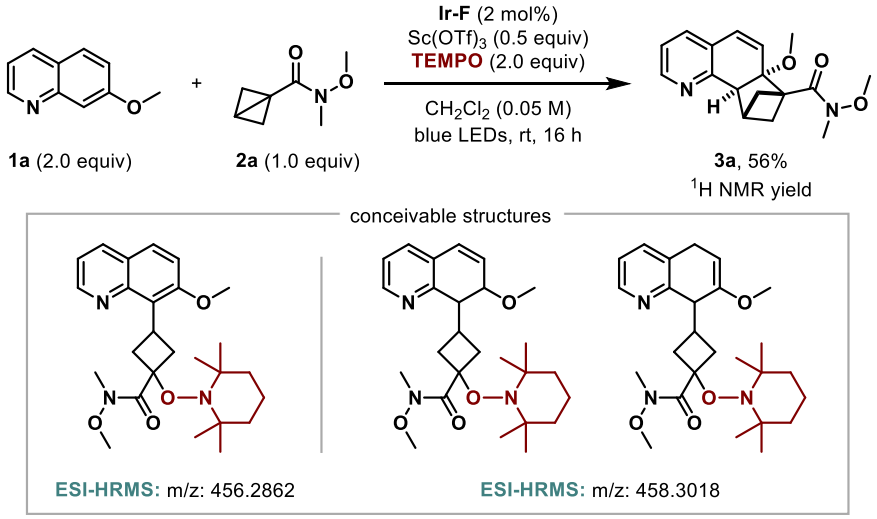
Discussion: In contrast to a one photon process where doubling the light intensity should result in a doubled initial reaction rate, ideally a four-fold increase would be expected in case two photons are required for one single reaction step due to the quadratic dependency. As can be taken from Figure S24–S27 doubling the light intensity of the blue LEDs (λ_{max} = 450 nm, and λ_{max} = 415 nm) causes an initial reaction rate increase by a factor of around two, suggesting that one photon processes are predominant. Notably, since direct excitation as well as EnT pose competitive pathways, the increase in reaction rate compared to a solely biphotonic process (with product yield $\propto P^{2.0}$) is expected to be lower, thus these results do not exclude the existence of a parallel biphotonic process.

3.9 Trapping Experiments

To probe whether radical and/or cationic intermediates are involved in our developed reaction, various trapping experiments were conducted.

TEMPO-trapping experiment

To an oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar were added **Ir-F** (2.2 mg, 2 µmol, 2 mol%), $Sc(OTf)_3$ (25 mg, 0.10 mmol, 0.50 equiv), and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, free radical, 31 mg, 0.20 mmol, 2.0 equiv). The Schlenk tube was evacuated and backfilled with argon three times. Subsequently, CH_2Cl_2 (2.0 mL), 7-methoxyquinoline (**1a**, 31.8 mg, 0.20 mmol, 2.0 equiv), and *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 14.1 mg, 0.10 mmol, 1.0 equiv) were added under positive argon pressure. Then, the reaction mixture was stirred under irradiation with blue LEDs (30 W, λ_{max} = 450 nm) for 16 h. The solvent was removed by a stream of argon, CH_2Br_2 (7.0 µL, 0.10 mmol, 1.0 equiv) was added as internal standard, and the yield was determined by crude ^{1}H NMR analysis. Further, the crude reaction was analyzed by GC-MS and ESI-HRMS.



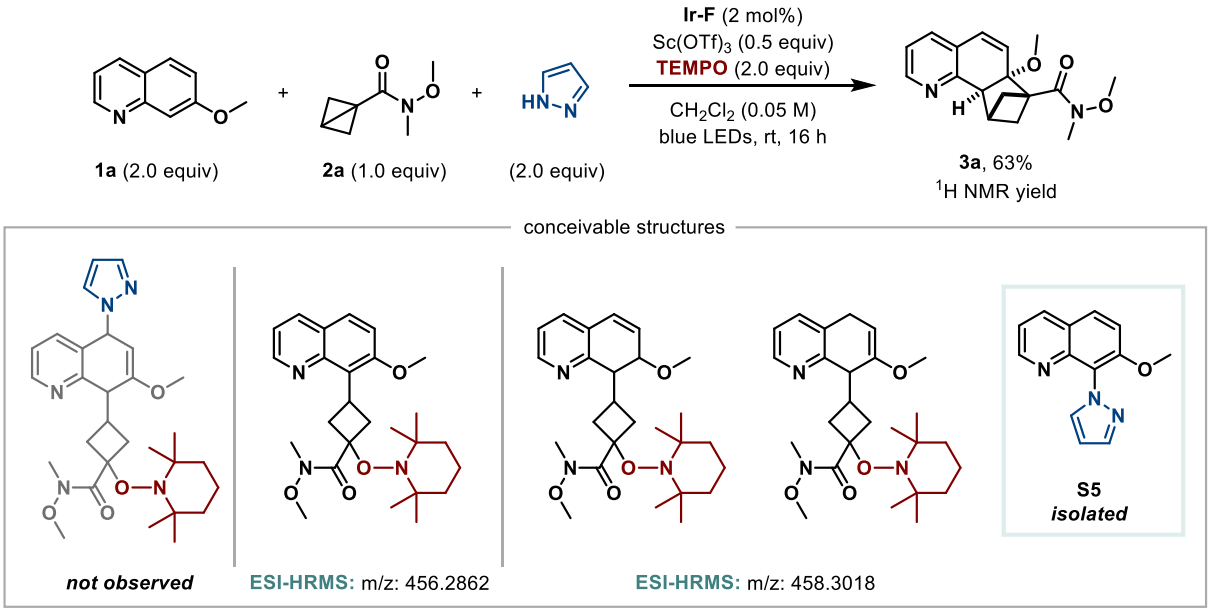
Scheme S1. TEMPO trapping experiment of the standard reaction.

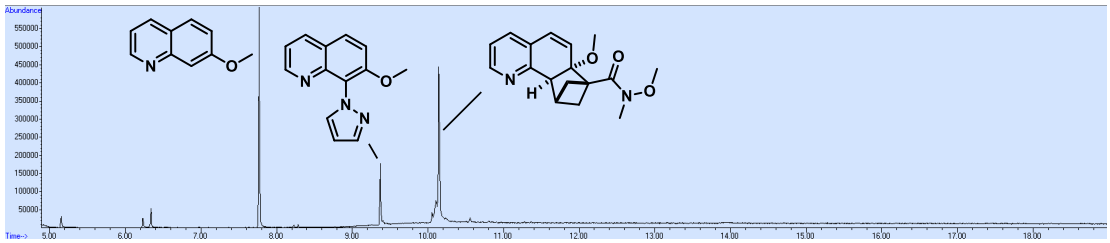
The reaction yield was diminished to 56% of product **3a** and TEMPO adducts were detected by ESI-HRMS (see above), supporting radical intermediates being involved in the reaction.

Nucleophile-trapping experiments

Considering a conceivable biphotonic-initiated chain reaction with radical (cat)ion intermediates, we performed nucleophile-trapping experiments. Following work by Nicewicz and co-workers, pyrazole was chosen as nucleophile.[50]

To an oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar were added **Ir-F** (2.2 mg, 2 µmol, 2 mol%), $Sc(OTf)_3$ (25 mg, 0.10 mmol, 0.50 equiv), pyrazole (13.6 mg, 0.20 mmol, 2.0 equiv), and TEMPO (31 mg, 0.20 mmol, 2.0 equiv). The Schlenk tube was evacuated and backfilled with argon three times. Subsequently, CH_2Cl_2 (2.0 mL), 7-methoxyquinoline (**1a**, 31.8 mg, 0.20 mmol, 2.0 equiv), and *N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (**2a**, 14.1 mg, 0.10 mmol, 1.0 equiv) were added under positive argon pressure. Then, the reaction mixture was stirred under irradiation with blue LEDs (30 W, λ_{max} = 450 nm) for 16 h. The solvent was removed by a stream of argon, CH_2Br_2 (7.0 µL, 0.10 mmol, 1.0 equiv) was added as internal standard, and the yield was determined by crude ^{1}H NMR analysis. Further, the crude reaction was analyzed by GC-MS and ESI-HRMS.





Scheme S2. TEMPO and nucleophile-trapping experiment of the standard reaction.

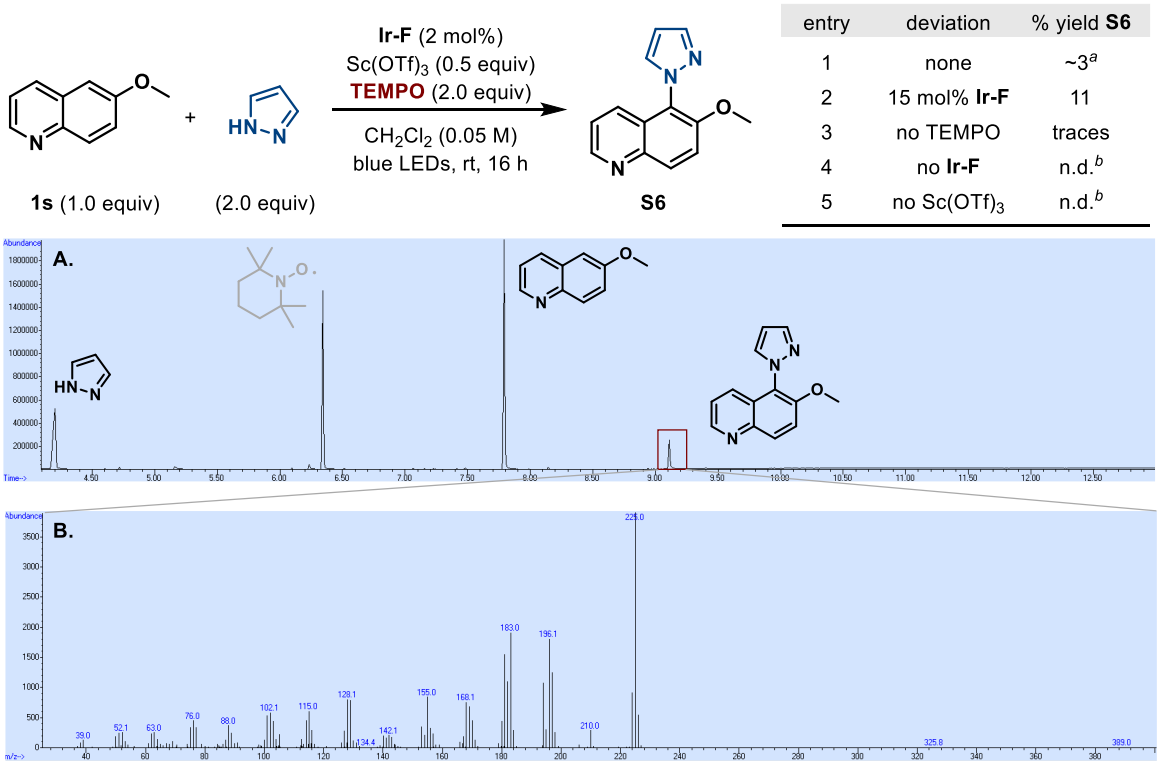
While a nucleophile and TEMPO trapped adduct could not be detected by ESI-HRMS, C–H amination in C8-position (**S5**) of the quinoline **1a** was observed. With the work of Nicewicz and co-workers on such C–H aminations in mind,[50] it is also assumed that the formation of **S5** occurs via a quinoline radical cation. However, considering the redox-potentials, **S5** is unlikely obtained via direct oxidation of **1a** by photo-excited **Ir-F*** with subsequent nucleophilic attack by pyrazole.

*Characterization of **S5**:*

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.3, 1.7 Hz, 1H), 8.15 (dd, J = 8.3, 1.8 Hz, 1H), 7.94 (d, J = 9.2 Hz, 1H), 7.90 (dd, J = 1.9, 0.7 Hz, 1H), 7.71 (dd, J = 2.4, 0.6 Hz, 1H), 7.47 (d, J = 9.2 Hz, 1H), 7.31 (dd, J = 8.2, 4.3 Hz, 1H), 6.58 (t, J = 2.1 Hz, 1H), 3.94 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.0, 152.5, 145.9, 140.7, 135.9, 133.3, 130.1, 123.6, 119.8, 114.4, 106.0, 57.1 – one carbon signal is missing; **HRMS** (ESI^+) calc'd for $[M+Na]^+$ 248.0794, found 248.0794; **R_f** (100% EtOAc) = 0.17.

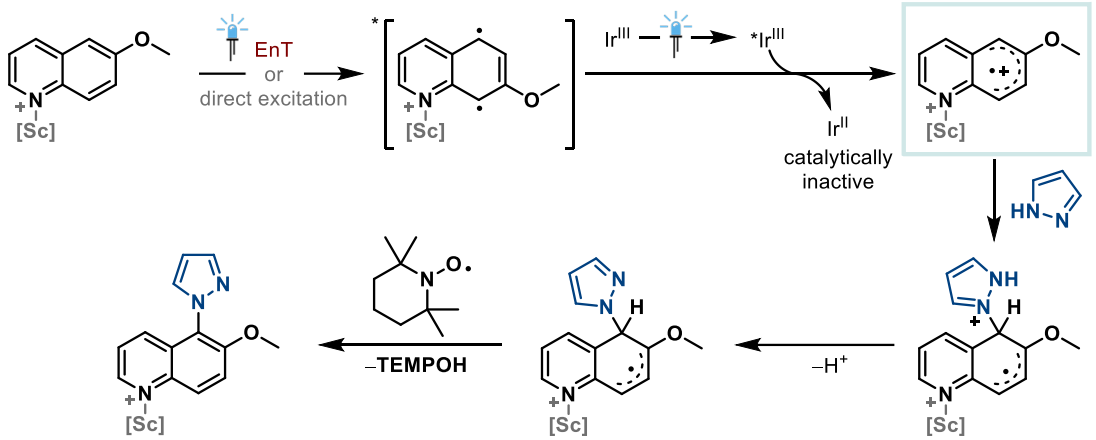
To investigate this observation, further experiments on the C–H amination were conducted using 6-methoxyquinoline (**1s**) substrate (better comparison with the work by Nicewicz and co-workers) in the absence of BCB.

Entry 1: To an oven-dried 10 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar were added 6-methoxyquinoline (**1s**, 31.8 mg, 0.20 mmol, 2.0 equiv), **Ir-F** (2.2 mg, 2 µmol, 2 mol%), $Sc(OTf)_3$ (25 mg, 0.10 mmol, 0.50 equiv), pyrazole (13.6 mg, 0.20 mmol, 2.0 equiv), and TEMPO (31 mg, 0.20 mmol, 2.0 equiv). The Schlenk tube was evacuated and backfilled with argon three times. Subsequently, CH_2Cl_2 (2.0 mL) was added under positive argon pressure, and the reaction mixture was stirred under irradiation with blue LEDs (30 W, λ_{max} = 450 nm) for 16 h. The reaction mixture was quenched with sat. aq. $NaHCO_3$, and the aq. layer was extracted with EtOAc (3×). The org. layers were combined, and the solvent removed *in vacuo*. CH_2Br_2 (7.0 µL, 0.20 mmol, 1.0 equiv) was added as internal standard, and the crude was analyzed by ^{1}H NMR and GC-MS. Reactions for entries 2–5 were carried out accordingly with respect to the indicated deviation from above.



entry	deviation	% yield **S6**
1	none	~3[a]
2	15 mol% **Ir-F**	11
3	no TEMPO	traces
4	no **Ir-F**	n.d.[b]
5	no $Sc(OTf)_3$	n.d.[b]

Scheme S3. C–H amination of **1s** via radical cation intebrmediates. **A.** GC-MS trace of entry 2. **B.** EI-MS spectrum of product **S6**. [a]1,3,5-Trimethoxybenzene was used as internal standard. [b]Not detected by GC-MS analysis.



Scheme S4. Proposed mechanism for C–H amination with **Ir-F** via a quinoline radical cation.[50]

Discussion: As can be taken from entry 1 and 2, the yield of **S6** increases with the "photocatalyst" loading. This is consistent with the proposed mechanism for the C–H amination (see, Scheme S4), since the reduced **Ir-F** (Ir^{II}) cannot participate in another turnover. TEMPO is attributed to undergo HAT after the nucleophilic attack to give the re-aromatized product (entry 3). Without **Ir-F** or $Sc(OTf)_3$ no product formation was obtained (entry 4 and 5). Taken together, these results support our hypothesis that a two photon pathway to generate quinoline radical cation from excited-state quinoline via oxidation by **Ir-F*** is feasible.

3.10 DFT Calculations

Computational Methods

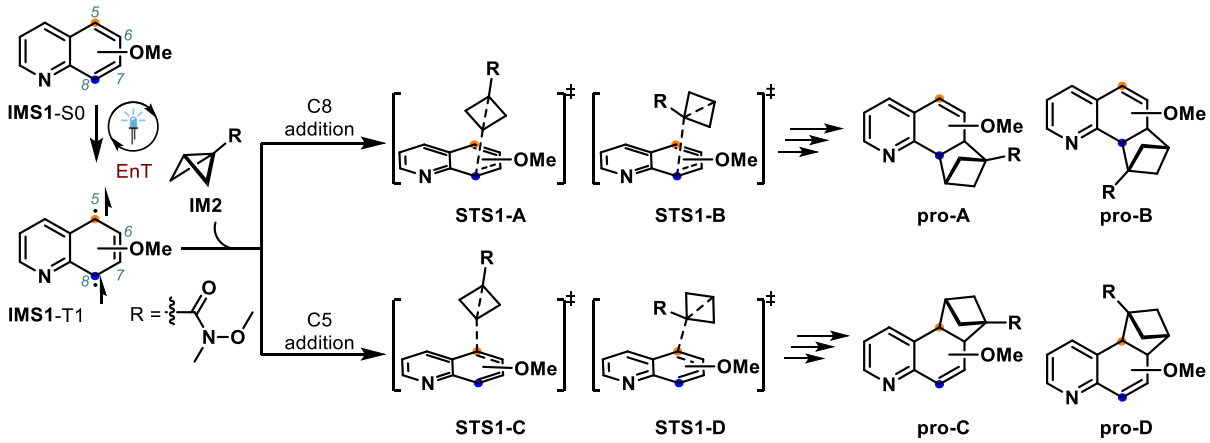
All geometry optimizations were performed in water using the dispersion-corrected M06-2X[51] functional with def2SVP[52] basis set. Single point energies were calculated with the ωb97xd[53] functional and the def2TZVPP basis set. Solvation effects were included by performing single point energy calculations with the SMD[54] solvation model in corresponding solvents. To obtain more accurate Gibbs free energies and enthalpies, we applied the quasiharmonic approximation from Grimme to compute the thermal corrections with a cut-off frequency of 50 cm^{-1}.[55] The quasiharmonic approximations were calculated using GoodVibes.[56] Minimum energy crossing points (MECPs) were located using easymecp (https://github.com/jaimergp/, easymecp repository, DOI: 10.5281/zenodo.4293421), a simplified Python wrapper developed by J. Rodríguez-Guerra and I. Funes-Ardóiz around the original MECP Fortran code from J. Harvey.

All calculations were performed with Gaussian 16[57] on UCLA Hoffman2 and XSEDE[58] supercomputers.

DFT computed regioselectivity of 5-, 6-, 7- and 8-methoxyquinoline

We conducted DFT calculations on regioselectivity of the [2π+2σ] photocyclization of BCB IM2 with 5-, 6-, 7- and 8-OMe quinoline. We identified that the spin density on quinolines C5 and C8 controls the regioselectivity. The C8 addition is favored over C5 addition for 5- and 7-methoxyquinoline. Alternatively, the C5 addition is favored over C8 addition for 6- and 8-methoxyquinoline. The BCB addition on the less substituted carbon is always favored due to formation of the thermodynamically more stable diradical intermediate. Our DFT predicted formation of **3ac**, **3ab**, **3a**, and **S2** from 5-, 6-, 7-, and 8-methoxyquinoline are consistent with the experimental observation.

Table S20. DFT predicted regioselectivity.



	Spin density on C5	Spin density on C8	$\Delta G^{\ddagger}_{TS2\text{-}A}$	$\Delta G^{\ddagger}_{TS2\text{-}B}$	$\Delta G^{\ddagger}_{TS2\text{-}C}$	$\Delta G^{\ddagger}_{TS2\text{-}D}$	DFT predicted product	Experimental observed product (yield)
5-OMe	0.46	0.61	**20.3**	26.1	25.8	31.1	**pro-A**	**pro-A** (**3ac**, 30%)
6-OMe	0.62	0.53	23.5	27.7	**20.4**	23.2	**pro-C**	**pro-C** (**3ab**, 39%)
7-OMe	0.57	0.68	**18.2**	26.1	21.7	27.4	**pro-A**	**pro-A** (**3a**, 89%)
8-OMe	0.57	0.45	26.1	32.8	**22.9**	26.3	**pro-C**	**pro-C** (**S2**, 14%)

***** All $\Delta G^{\ddagger}$ (kcal/mol) are calculated with respect to excited quinoline (**IMS1-T1**) and ground state BCB (**IM2**).

Effects of Lewis and Brønsted acids on triplet EnT enabled [2π+2σ] cycloadditions

As demonstrated in Figure S28, we observed that addition of $Sc(OTf)_3$ can effectively decrease the triplet energy of quinoline (E_T (**IM1**-[**LA**]-S_0) = 52.1 kcal/mol. In comparison, the triplet energy of the native quinoline (**1a**-S_0) is 67.4 kcal/mol.

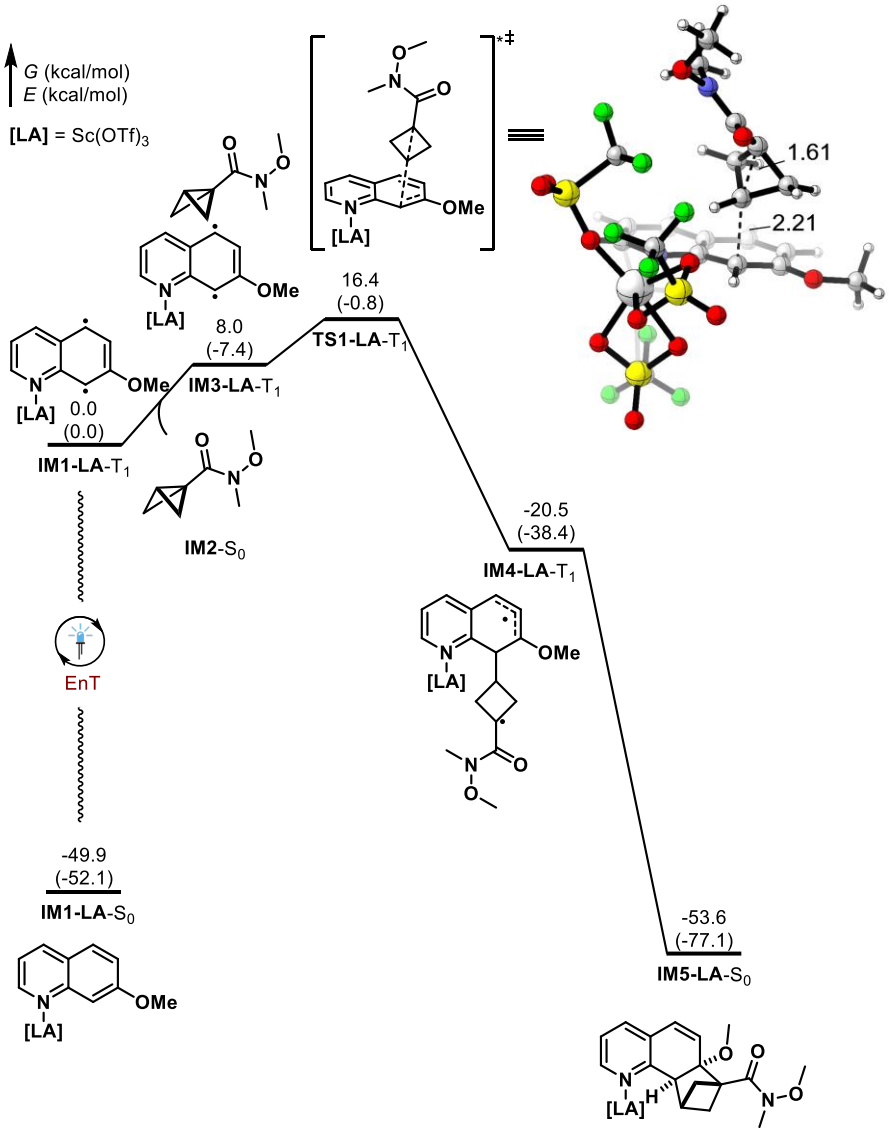


Figure S28. Computed reaction coordinate profile with Lewis acid $Sc(OTf)_3$.

Addition of Brønsted acid leads to protonated quinoline. As demonstrated in Figure S29, we observed that protonation of the quinoline also decreases the triplet energy of quinoline (E_T (**IM1-H**$^+$-S_0) = 59.4 kcal/mol. In comparison, the triplet energy of the native quinoline (**1a**-S_0) is 67.4 kcal/mol. Moreover, the protonation of the quinoline decreases the rate-limiting BCB insertion transition state. Our calculations demonstrate that **TS1-H**$^+$-T_1 has a free energy barrier of 12.3 kcal/mol, with respect to **IM1-H**$^+$-T_1 ($\Delta G^‡$ = 12.3 kcal/mol). In comparison, **TS1-T₁** with neutral quinoline has a free energy barrier of 15.0 kcal/mol.

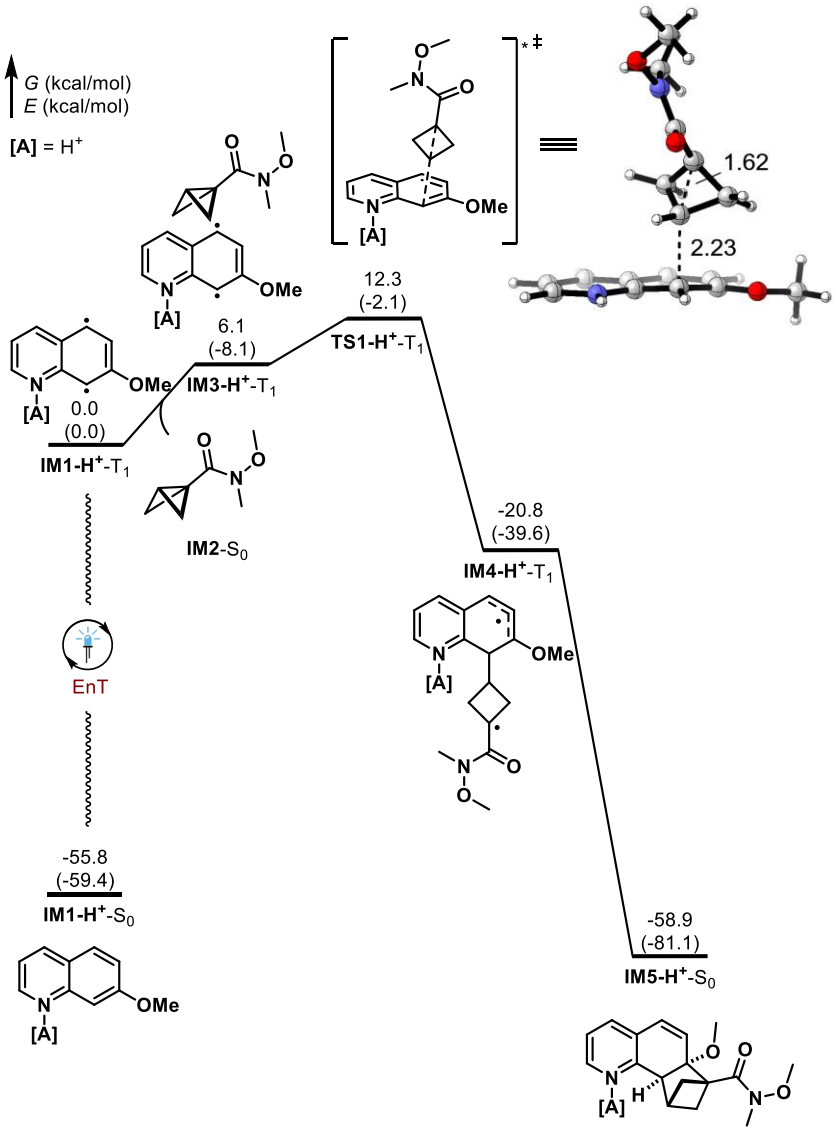
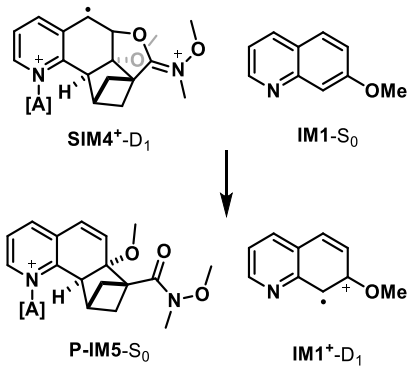


Figure S29. Computed reaction coordinate profile with Brønsted acid.

Preliminary calculations supporting the acid-mediated oxidative chain reaction

As this article focuses on synthetic aspect of the dearomative [2π+2σ]-cycloaddition of bicyclic aza-arenes and under our standard reaction conditions the EnT pathway is predominant, we only present preliminary computational studies on the thermodynamics of the potential chain reaction. Interestingly, the carbonyl group of the electron withdrawing *N*-methoxy-*N*-methylacetamide substitution forms a thermodynamically more stable fused heterocycle **SIM4**$^{+}$-D_1 radical cation. As demonstrated in Figure S30, without acid additive, the oxidation of **IM1**-S_0 by **N-SIM4**$^{+}$-D_1 radical cation is a thermo-neutral process (ΔG = 0.1 kcal/mol). In comparison, addition of Brønsted acid (**[A]** = H^{+}) or Lewis acid (**[A]** = $Sc(OTf)_3$) can both facilitate the oxidation of the ground-state quinoline substrate (ΔG_{H+} = −8.8 kcal/mol, $\Delta G_{Sc(OTf)3}$ = −3.6 kcal/mol).



[A] =	ΔG (kcal/mol)	ΔE (kcal/mol)
none	0.1	1.9
H^{+}	-8.8	-7.0
$Sc(OTf)_3$	-5.2	-3.6

Figure S30. Preliminary calculations supporting the proposed origin of chain reaction.

Effect of acid on spin densities of the oxidized radical cation

To review the nature of the cation diradical intermediates, we calculated the spin densities (red) and Mulliken charges (blue) of the radical cation intermediate. In all three radical cation intermediates, our DFT calculations showed that radical density is high on C8, while the cation charge localizes on C7. Addition of the acids can effectively increase the spin density on C8.

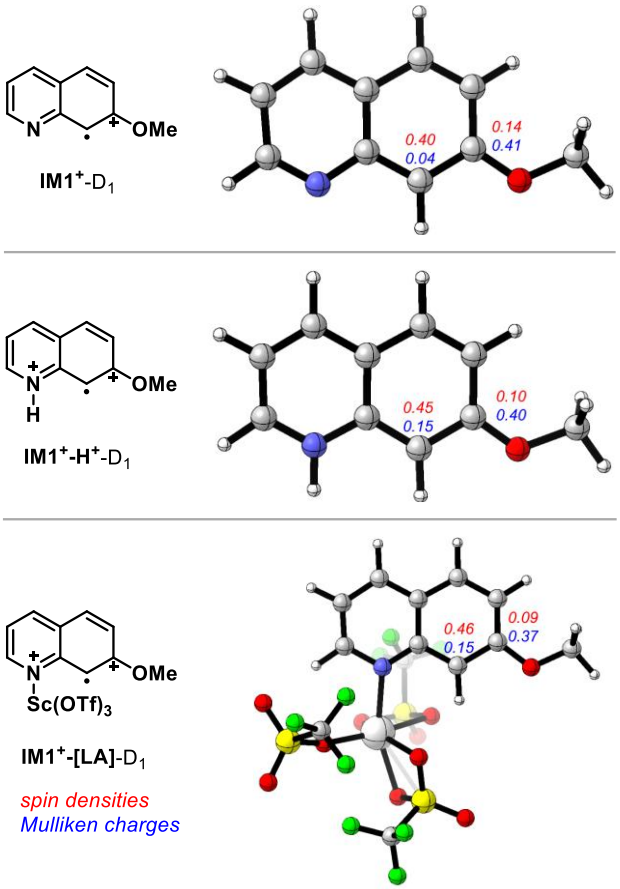


Figure S31. Computed spin densities and Mulliken charges of radical (di)cationic intermediates **IM1**.

Alternatively, reduction of quinoline forms the radical anion **IM1**$^{-}$-D_1. Our preliminary DFT calculations suggest that the spin density localizes on C4 in all three radical anion intermediates, which does not lead to formation of the C8-BCB insertion product.

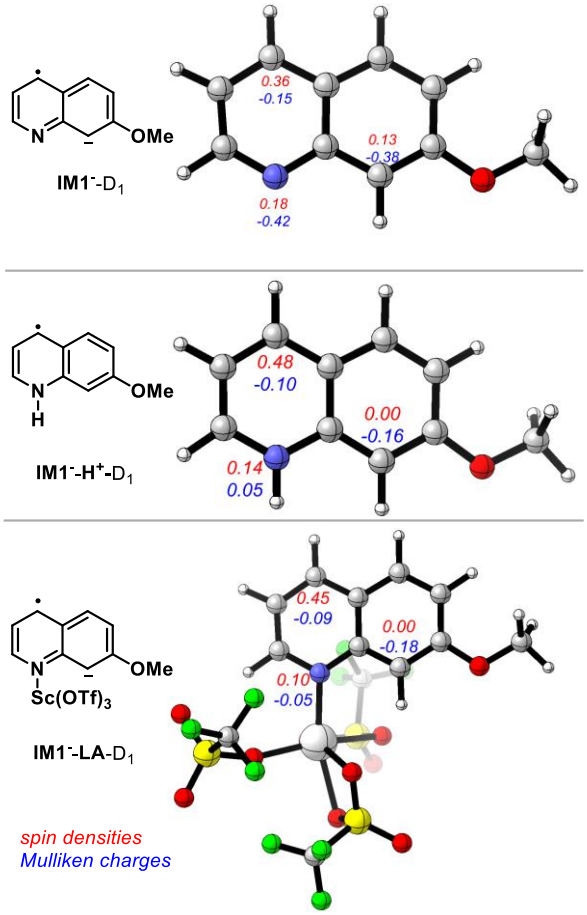


Figure S32. Computed spin density and charge of reduced (radical anion) intermediates **IM1**.

4 References

[1] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, S. Bernhard, *Chem. Mater.* **2005**, *17*, 5712–5719.

[2] A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* **2003**, *125*, 7377–7387.

[3] J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard, G. G. Malliaras, *J. Am. Chem. Soc.* **2004**, *126*, 2763–2767.

[4] G. Kalyuzhny, M. Buda, J. McNeill, P. Barbara, A. J. Bard, *J. Am. Chem. Soc.* **2003**, *125*, 6272–6283.

[5] D. M. Schultz, J. W. Sawicki, T. P. Yoon, *Beilstein J. Org. Chem.* **2015**, *11*, 61–65.

[6] J. Luo, J. Zhang, *ACS Catal.* **2016**, *6*, 873–877.

[7] L. Pitzer, F. Sandfort, F. Strieth-Kalthoff, F. Glorius, *Angew. Chem., Int. Ed.* **2018**, *57*, 16219–16223.

[8] L. Liu, A. Siegmund, N. Xi, P. Kaplan-Lefko, K. Rex, A. Chen, J. Lin, J. Moriguchi, L. Berry, L. Huang, Y. Teffera, Y. Yang, Y. Zhang, S. F. Bellon, M. Lee, R. Shimanovich, A. Bak, C. Dominguez, M. H. Norman, J.-C. Harmange, I. Dussault, T.-S. Kim, *J. Med. Chem.* **2008**, *51*, 3688–3691.

[9] T. MOMOSE, S. UCHIDA, N. YAMAASHI, T. IMANISHI, *Chem. Pharm. Bull.* **1977**, *25*, 1436–1442.

[10] K. H. Chang, Y. H. Liu, J. C. Liu, Y. C. Peng, Y. H. Yang, Z. Bin Li, R. H. Jheng, C. M. Chao, K. M. Liu, P. T. Chou, *Chem. Eur. J.* **2019**, *25*, 14972–14982.

[11] V. Satam, R. Rajule, S. Bendre, P. Bineesh, V. Kanetkar, *J. Heterocycl. Chem.* **2009**, *46*, 221–225.

[12] Q. Wu, S. Han, X. Ren, H. Lu, J. Li, D. Zou, Y. Wu, Y. Wu, *Org. Lett.* **2018**, *20*, 6345–6348.

[13] B. Liu, T. Zhou, B. Li, S. Xu, H. Song, B. Wang, *Angew. Chem., Int. Ed.* **2014**, *53*, 4191–4195.

[14] J. Li, J. Zhang, H. Yang, G. Jiang, *J. Org. Chem.* **2017**, *82*, 3284–3290.

[15] C. S. Cho, B. Ho Oh, S. C. Shim, D. H. Oh, *J. Heterocycl. Chem.* **2000**, *37*, 1315–1320.

[16] G. S. Hassan, D. E. Abdel Rahman, E. A. Abdelmajeed, R. H. Refaey, M. Alaraby Salem, Y. M. Nissan, *Eur. J. Med. Chem.* **2019**, *171*, 332–342.

[17] S.-M. Yang, N. J. Martinez, A. Yasgar, C. Danchik, C. Johansson, Y. Wang, B. Baljinnyam, A. Q. Wang, X. Xu, P. Shah, D. Cheff, X. S. Wang, J. Roth, M. Lal-Nag, J. E. Dunford, U. Oppermann, V. Vasiliou, A. Simeonov, A. Jadhav, D. J. Maloney, *J. Med. Chem.* **2018**, *61*, 4883–4903.

[18] X.-D. An, S. Yu, *Org. Lett.* **2015**, *17*, 2692–2695.

[19] X. Dong, Q. Y. Li, T. P. Yoon, *Org. Lett.* **2021**, *23*, 5703–5708.

[20] N. Shevchuk, K. Liubchak, K. Nazarenko, A. Yurchenko, D. Volochnyuk, O. Grygorenko, A. Tolmachev, *Synthesis* **2012**, *44*, 2041–2048.

[21] X. Yu, J. Tang, X. Jin, Y. Yamamoto, M. Bao, *Asian J. Org. Chem.* **2018**, *7*, 550–553.

[22] N. Gandhamsetty, S. Joung, S.-W. Park, S. Park, S. Chang, *J. Am. Chem. Soc.* **2014**, *136*, 16780–16783.

[23] L. Pfeifer, V. Gouverneur, *Org. Lett.* **2018**, *20*, 1576–1579.

[24] W. Ma, J. Zhang, C. Xu, F. Chen, Y.-M. He, Q.-H. Fan, *Angew. Chem., Int. Ed.* **2016**, *55*, 12891–12894.

[25] X. Yi, C. Xi, *Org. Lett.* **2015**, *17*, 5836–5839.

[26] H. Lee, C. S. Yi, *Organometallics* **2016**, *35*, 1973–1977.

[27] M. Ociepa, A. J. Wierzba, J. Turkowska, D. Gryko, *J. Am. Chem. Soc.* **2020**, *142*, 5355–5361.

[28] T. Pinkert, M. Das, M. L. Schrader, F. Glorius, *J. Am. Chem. Soc.* **2021**, *143*, 7648–7654.

[29] R. M. Bychek, V. Hutskalova, Y. P. Bas, O. A. Zaporozhets, S. Zozulya, V. V. Levterov, P. K. Mykhailiuk, *J. Org. Chem.* **2019**, *84*, 15106–15117.

[30] S. Agasti, F. Beltran, E. Pye, N. Kaltsoyannis, G. E. M. Crisenza, D. J. Procter, *Nat. Chem.* **2023**. https://doi.org/10.1038/s41557-023-01135-y.

[31] L. Guo, A. Noble, V. K. Aggarwal, *Angew. Chem., Int. Ed.* **2021**, *60*, 212–216.

[32] J. M. Lopchuk, K. Fjelbye, Y. Kawamata, L. R. Malins, C.-M. Pan, R. Gianatassio, J. Wang, L. Prieto, J. Bradow, T. A. Brandt, M. R. Collins, J. Elleraas, J. Ewanicki, W. Farrell, O. O. Fadeyi, G. M. Gallego, J. J. Mousseau, R. Oliver, N. W. Sach, J. K. Smith, J. E. Spangler, H. Zhu, J. Zhu, P. S. Baran, *J. Am. Chem. Soc.* **2017**, *139*, 3209–3226.

[33] X. Wu, W. Hao, K.-Y. Ye, B. Jiang, G. Pombar, Z. Song, S. Lin, *J. Am. Chem. Soc.* **2018**, *140*, 14836–14843.

[34] M. A. A. Walczak, P. Wipf, *J. Am. Chem. Soc.* **2008**, *130*, 6924–6925.

[35] H. Wu, Q. Wang, J. Zhu, *Angew. Chem., Int. Ed.* **2018**, *57*, 2721–2725.

[36] T. Wagener, A. Heusler, Z. Nairoukh, K. Bergander, C. G. Daniliuc, F. Glorius, *ACS Catal.* **2020**, *10*, 12052–12057.

[37] J. Ma, S. Chen, P. Bellotti, R. Guo, F. Schäfer, A. Heusler, X. Zhang, C. Daniliuc, M. K. Brown, K. N. Houk, F. Glorius, *Science* **2021**, *371*, 1338–1345.

[38] O. Songis, J. Míšek, M. B. Schmid, A. Kollárovič, I. G. Stará, D. Šaman, I. Císařová, I. Starý, *J. Org. Chem.* **2010**, *75*, 6889–6899.

[39] L. Pitzer, F. Schäfers, F. Glorius, *Angew. Chem., Int. Ed.* **2019**, *58*, 8572–8576.

[40] F. Strieth-Kalthoff, M. J. James, M. Teders, L. Pitzer, F. Glorius, *Chem. Soc. Rev.* **2018**, *47*, 7190–7202.

[41] N. F. Nikitas, P. L. Gkizis, C. G. Kokotos, *Org. Biomol. Chem.* **2021**, *19*, 5237–5253.

[42] M. Teders, C. Henkel, L. Anhäuser, F. Strieth-Kalthoff, A. Gómez-Suárez, R. Kleinmans, A. Kahnt, A. Rentmeister, D. Guldi, F. Glorius, *Nat. Chem.* **2018**, *10*, 981–988.

[43] J. D. Bell, J. A. Murphy, *Chem. Soc. Rev.* **2021**, *50*, 9540–9685.

[44] M. A. Cismesia, T. P. Yoon, *Chem. Sci.* **2015**, *6*, 5426–5434.

[45] C. G. Hatchard, C. A. Parker, *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.* **1956**, *235*, 518–536.

[46] J. Chen, A. S. Dvornikov, P. M. Rentzepis, *J. Phys. Chem. A* **2009**, *113*, 8818–8819.

[47] E. E. Wegner, A. W. Adamson, *J. Am. Chem. Soc.* **1966**, *88*, 394–404.

[48] Y.-F. Song, X. Niu, J. Zhao, S. Shen, X.-L. Yang, *Org. Chem. Front.* **2022**, *9*, 3499–3505.

[49] F. Glaser, C. Kerzig, O. S. Wenger, *Angew. Chem., Int. Ed.* **2020**, *59*, 10266–10284.

[50] N. A. Romero, K. A. Margrey, N. E. Tay, D. A. Nicewicz, *Science* **2015**, *349*, 1326–1330.

[51] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.

[52] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[53] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615.

[54] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

[55] S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955–9964.

[56] G. Luchini, J. V. Alegre-Requena, I. Funes-Ardoiz, R. S. Paton, *F1000Research* **2020**, *9*, 291.

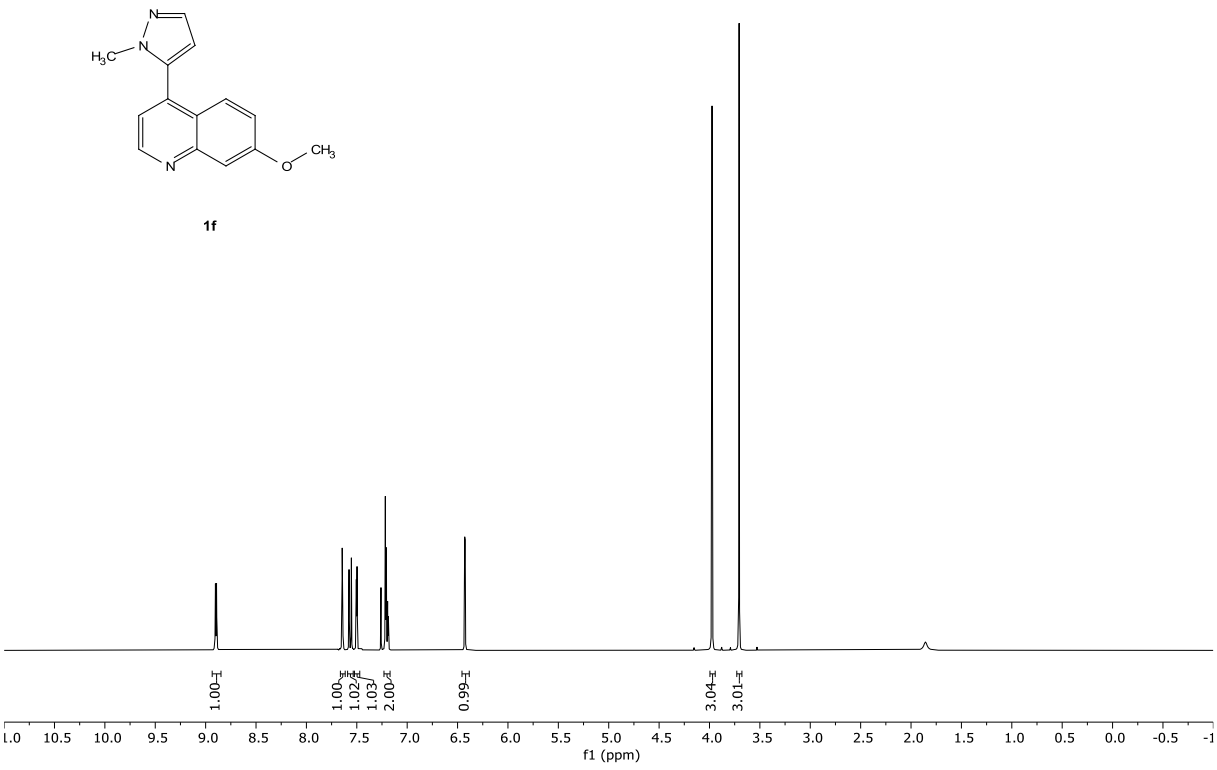
[57] J. Towns, T. Cockerill, M. Dahan, I. Foster, K. Gaither, A. Grimshaw, V. Hazlewood, S. Lathrop, D. Lifka, G. D. Peterson, R. Roskies, J. R. Scott, N. Wilkins-Diehr, *Comput. Sci. Eng.* **2014**, *16*, 62–74.

[58] Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.;

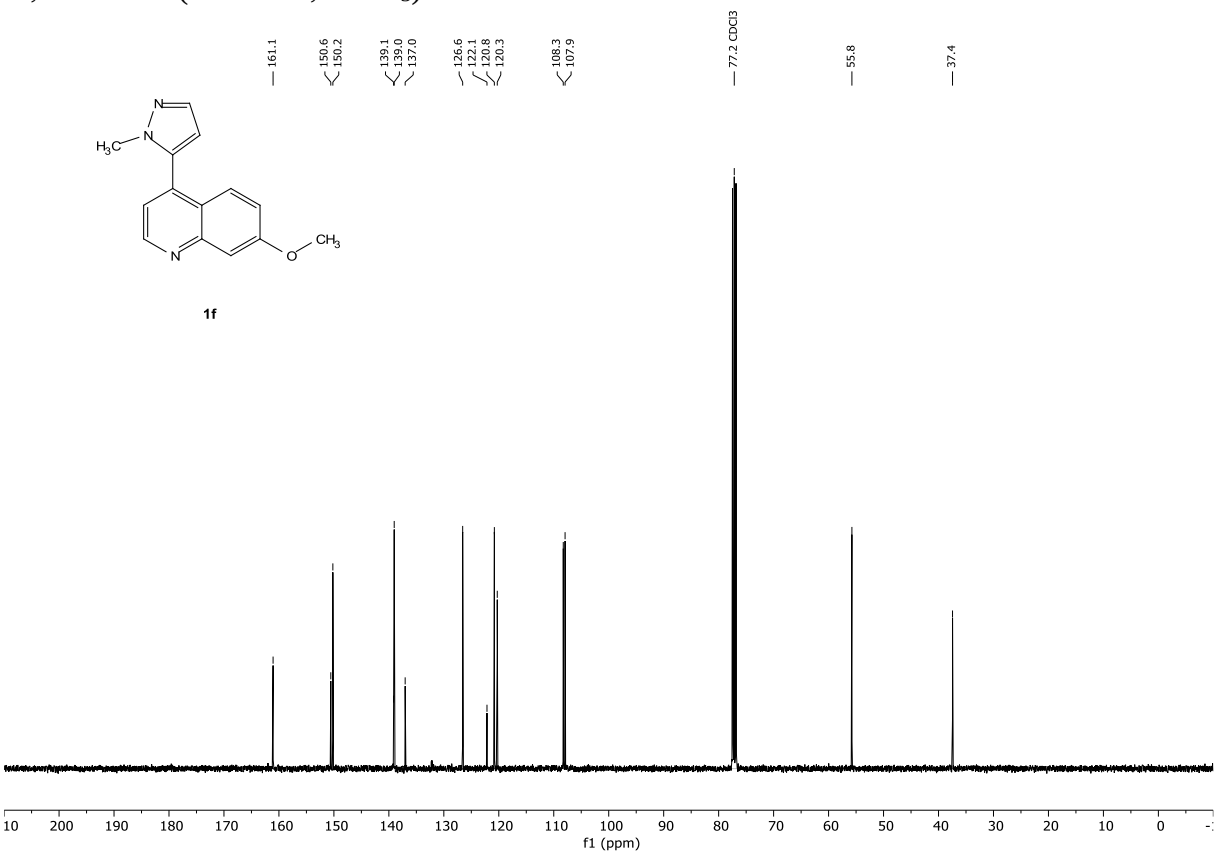
Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

5 Spectra

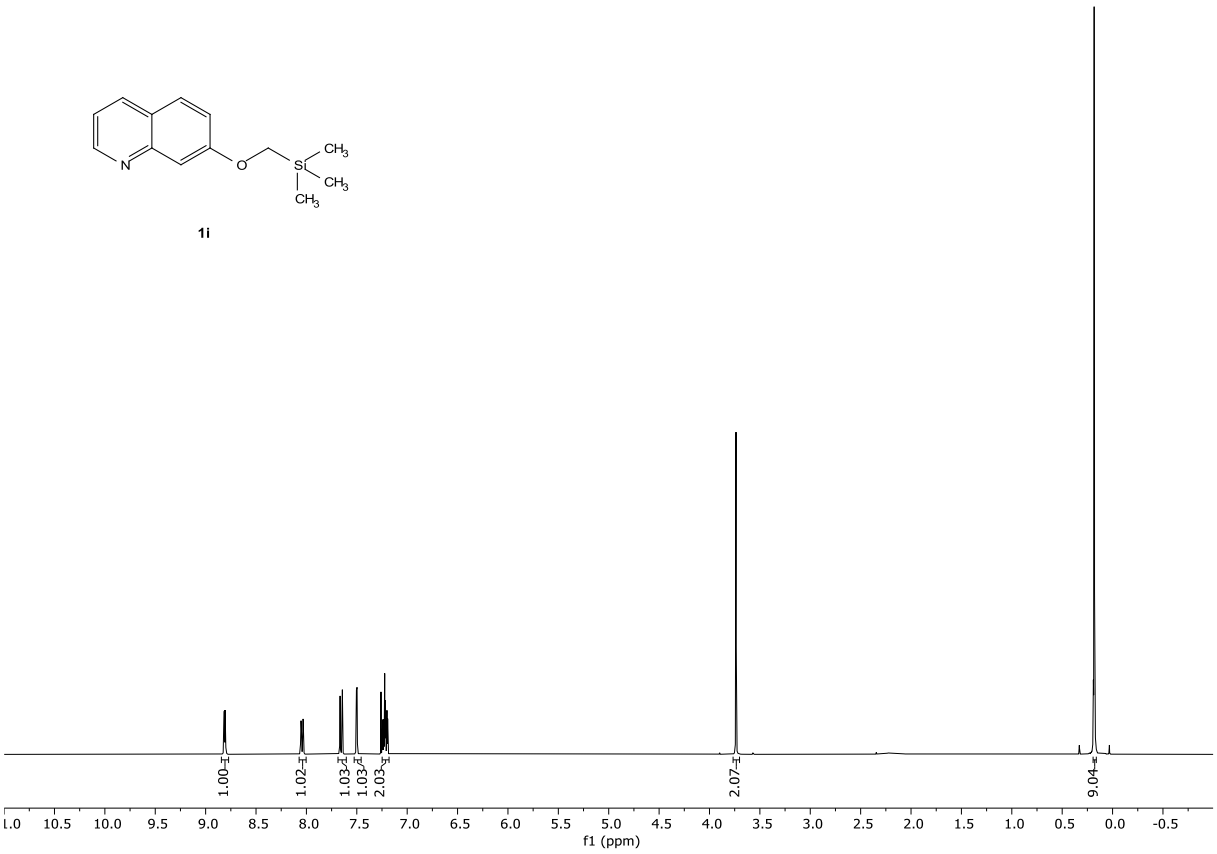
1f, ^{1}H NMR (400 MHz, $CDCl_3$



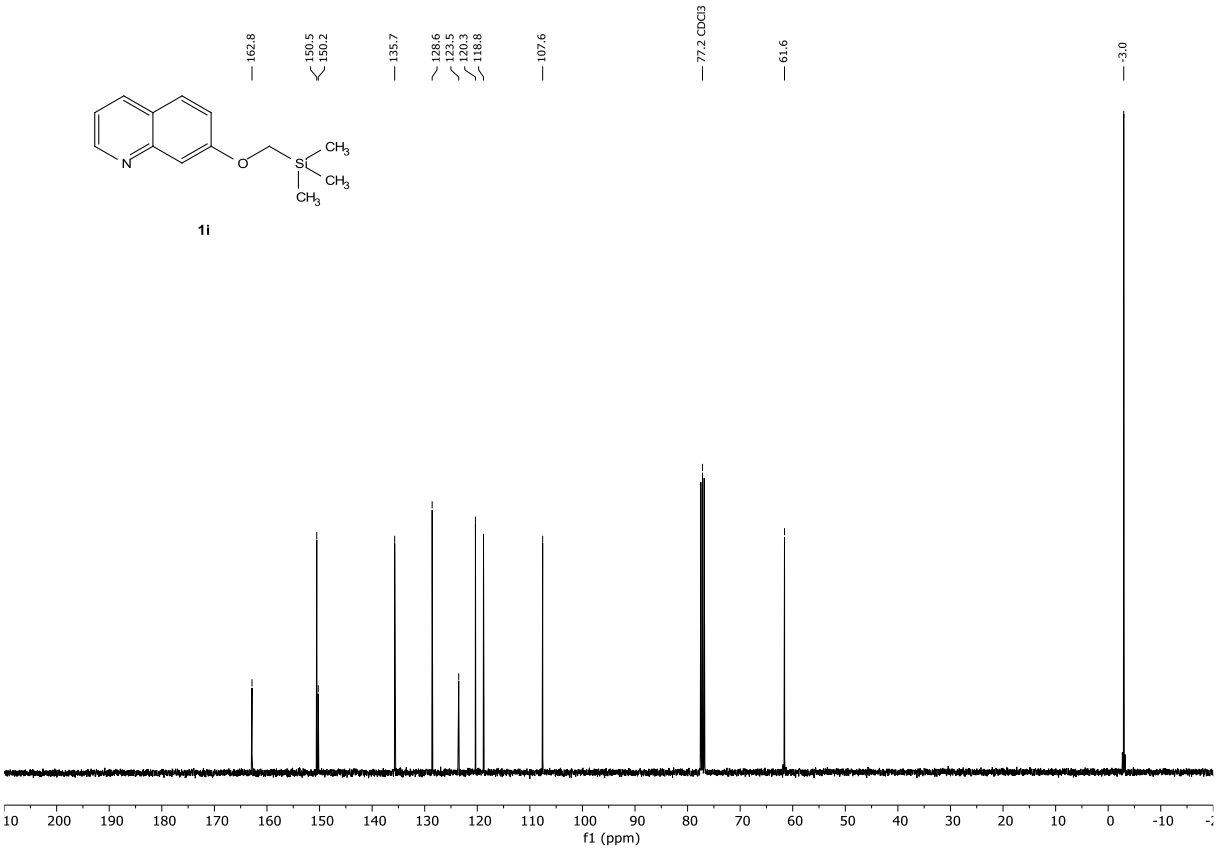
1f, ^{13}C NMR (101 MHz, $CDCl_3$)



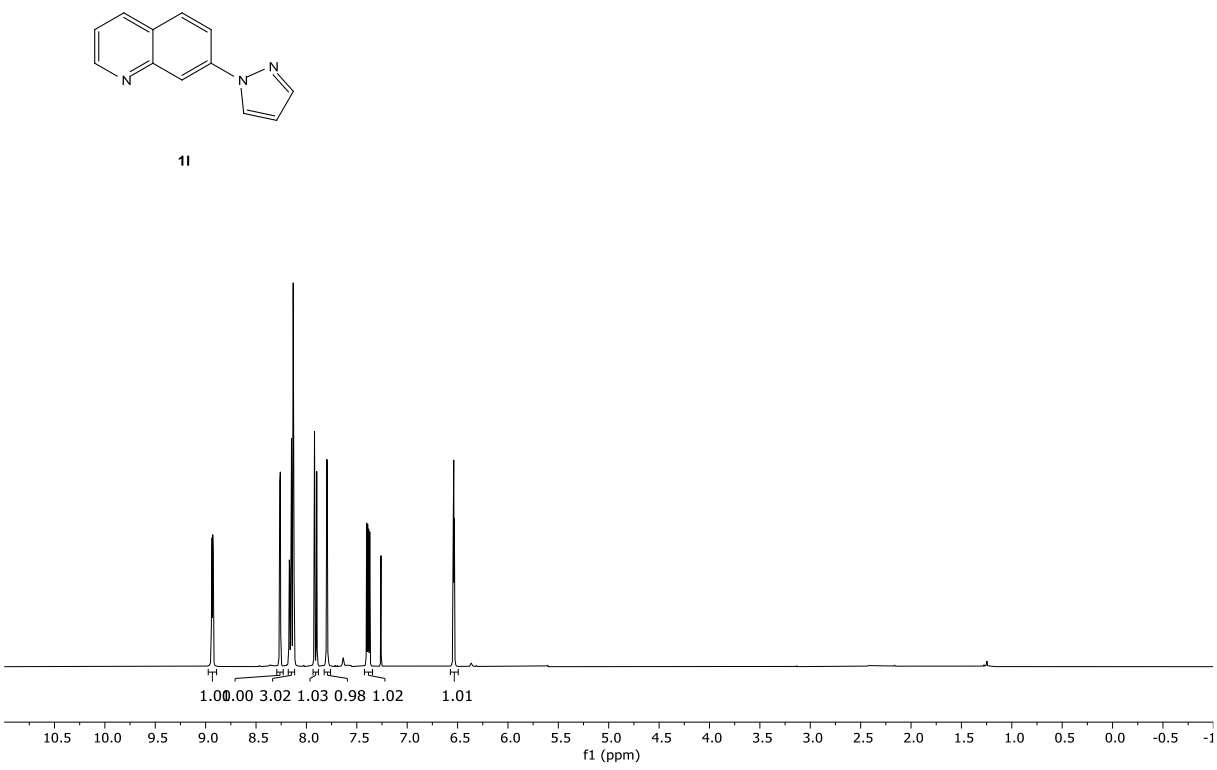
1i, ^{1}H NMR (400 MHz, $CDCl_3$)



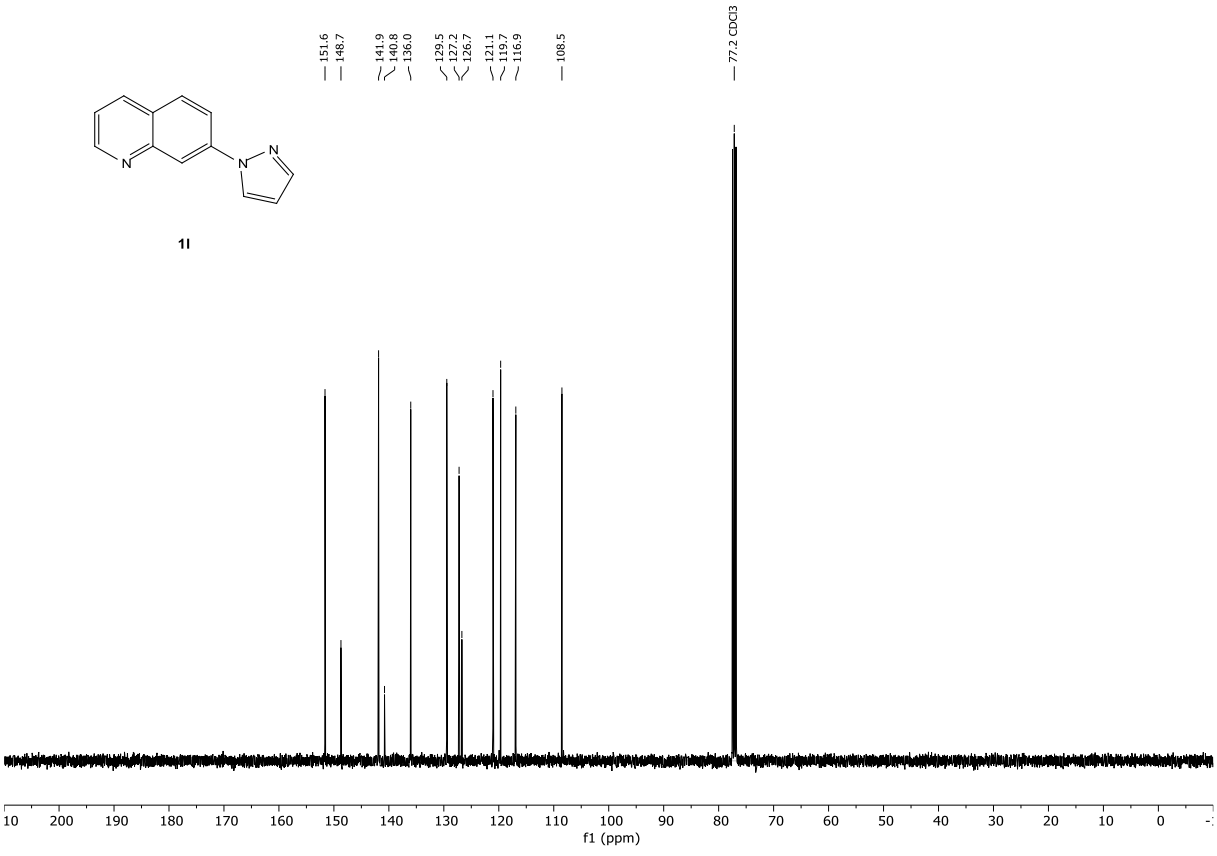
1i, ^{13}C NMR (101 MHz, $CDCl_3$)



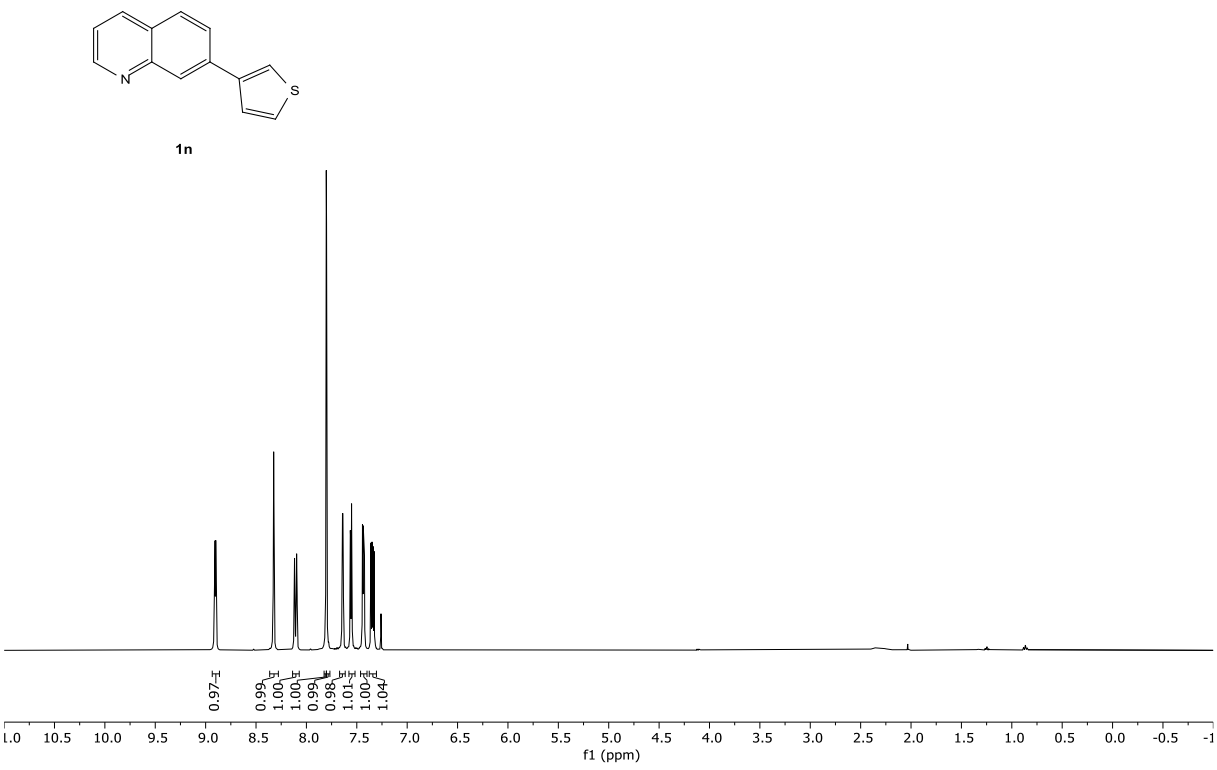
1l, ^{1}H NMR (400 MHz, $CDCl_3$)



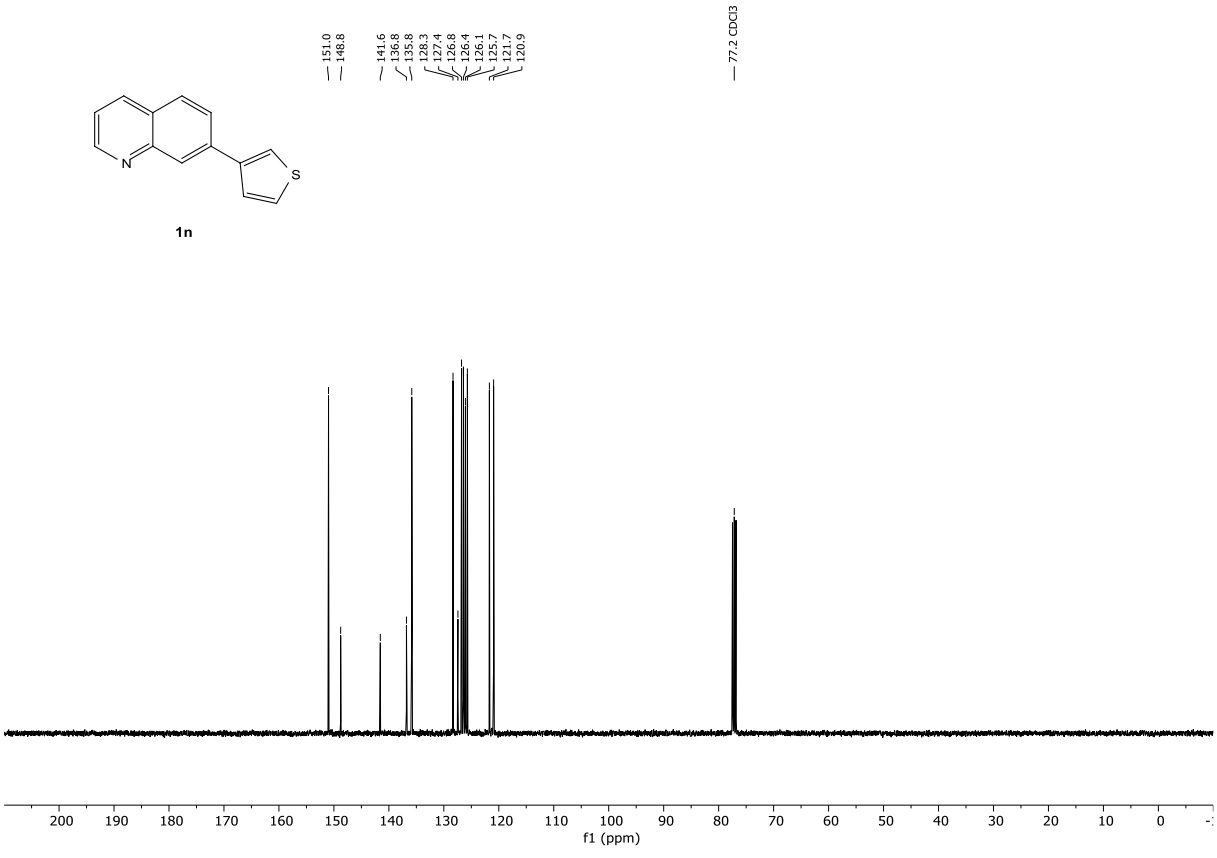
1l, ^{13}C NMR (101 MHz, $CDCl_3$)



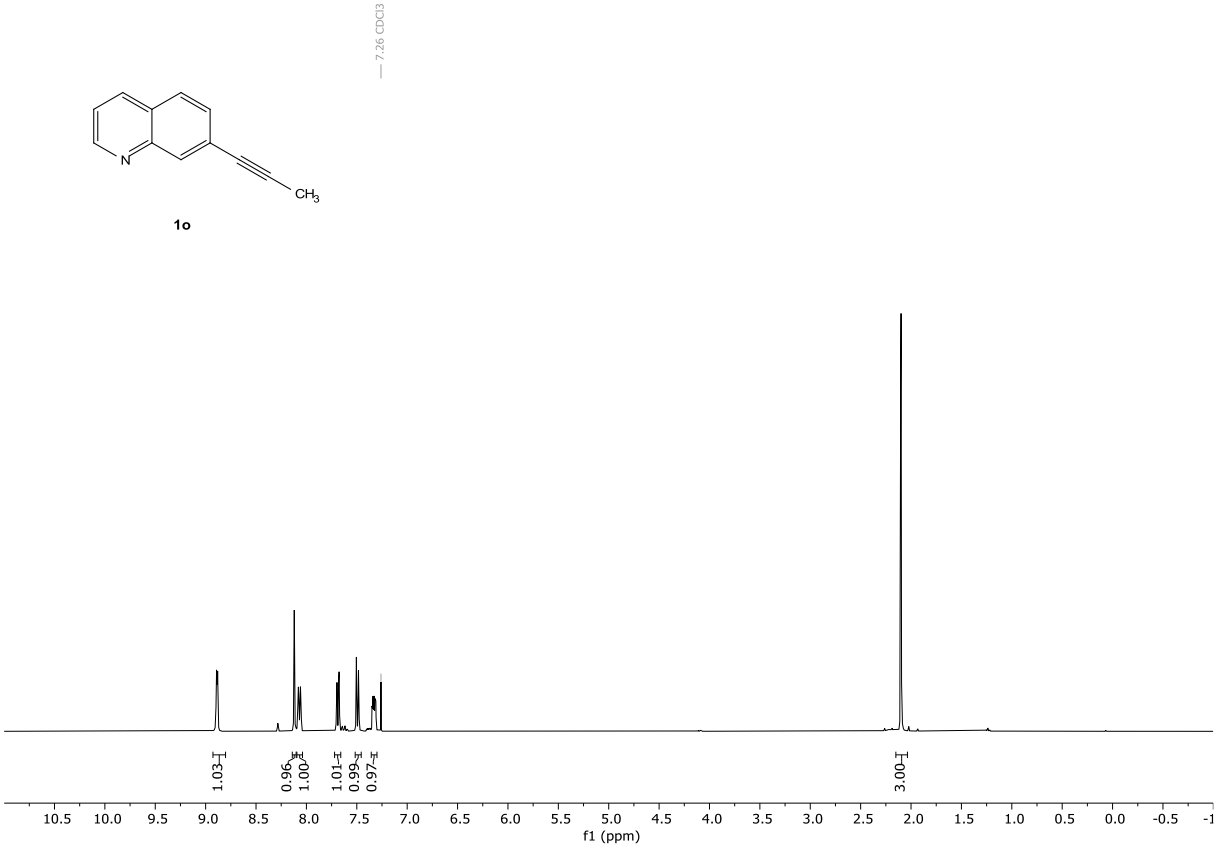
1n, ^{1}H NMR (400 MHz, $CDCl_3$)



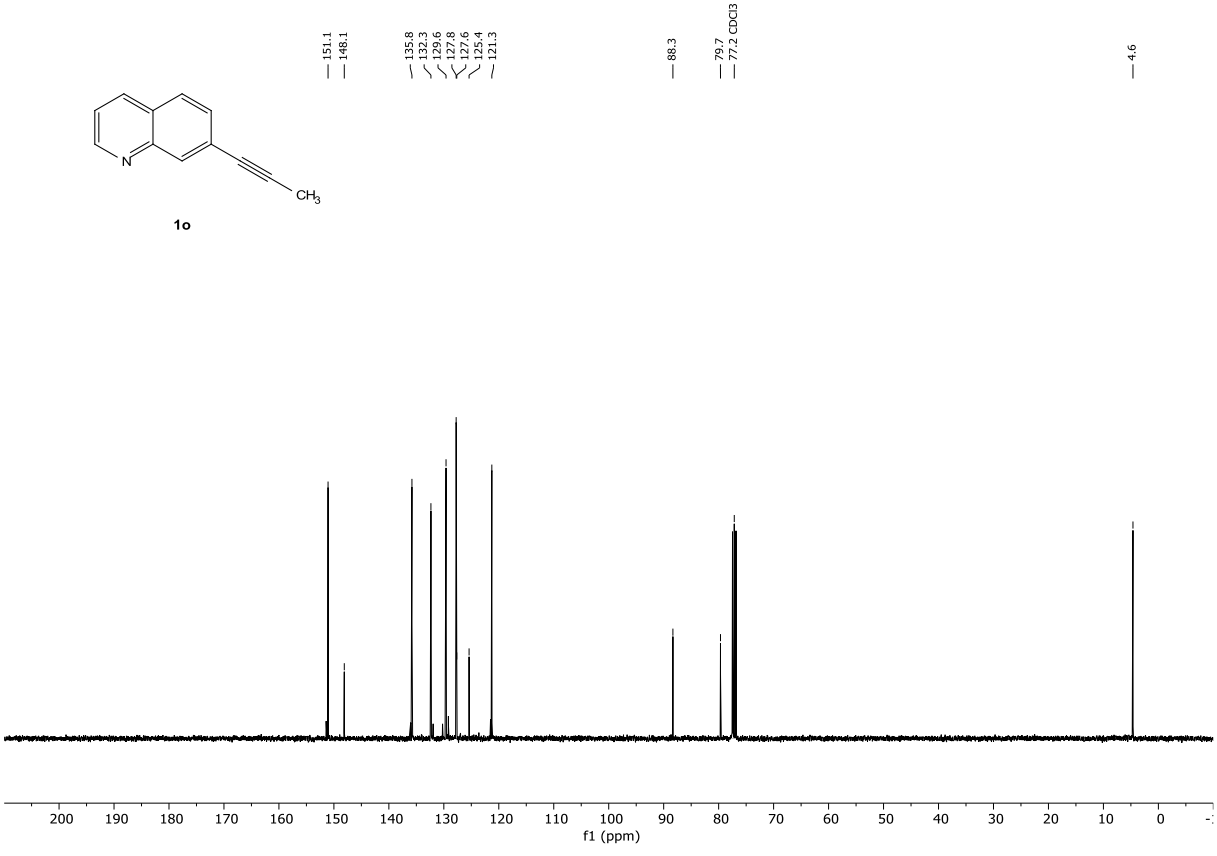
1n, ^{13}C NMR (101 MHz, $CDCl_3$)



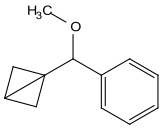
1o, ^{1}H NMR (400 MHz, $CDCl_3$)



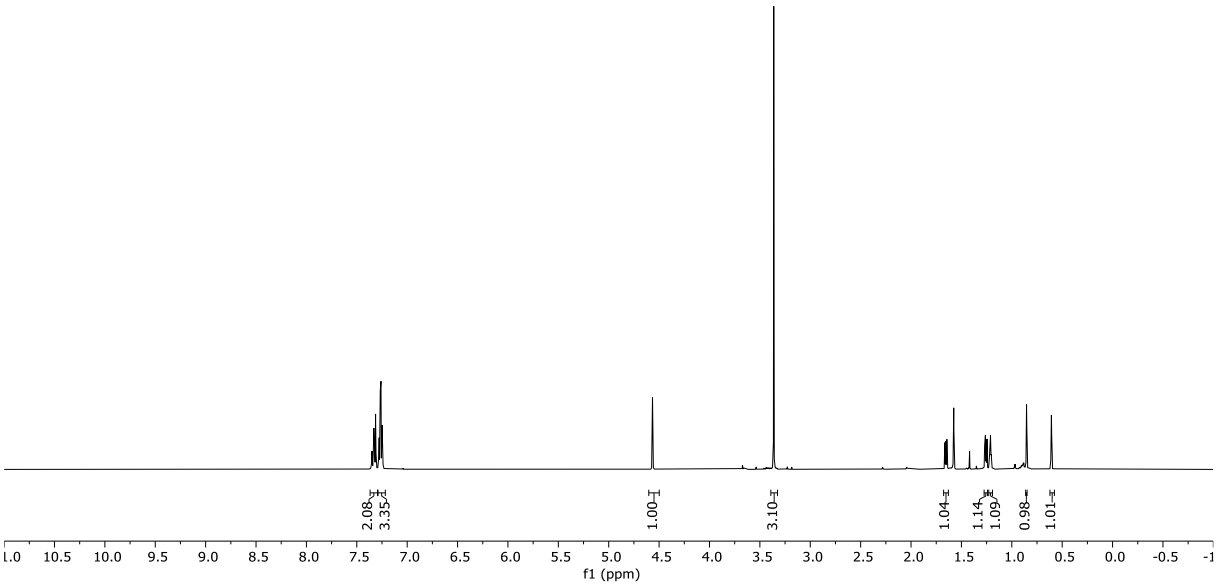
1o, ^{13}C NMR (101 MHz, $CDCl_3$)



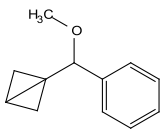
2j, ^{1}H NMR (400 MHz, $CDCl_3$)



2j

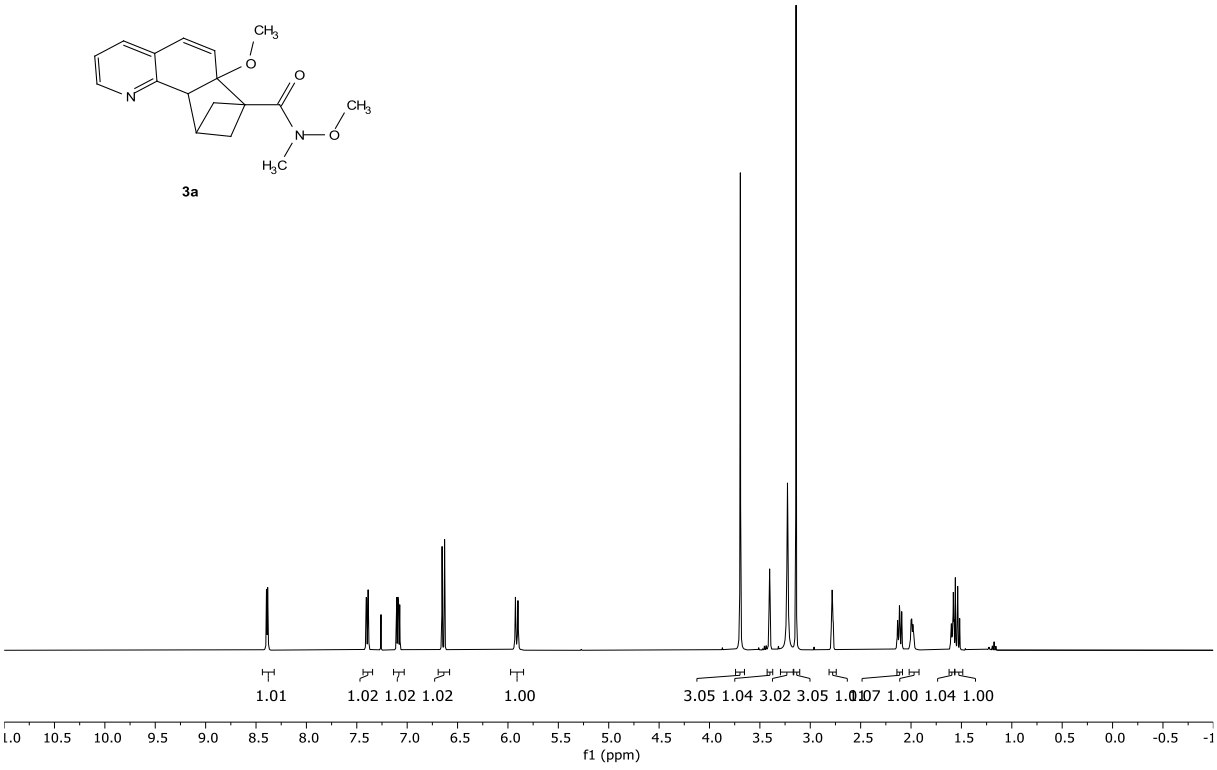


2j, ^{13}C NMR (101 MHz, $CDCl_3$)

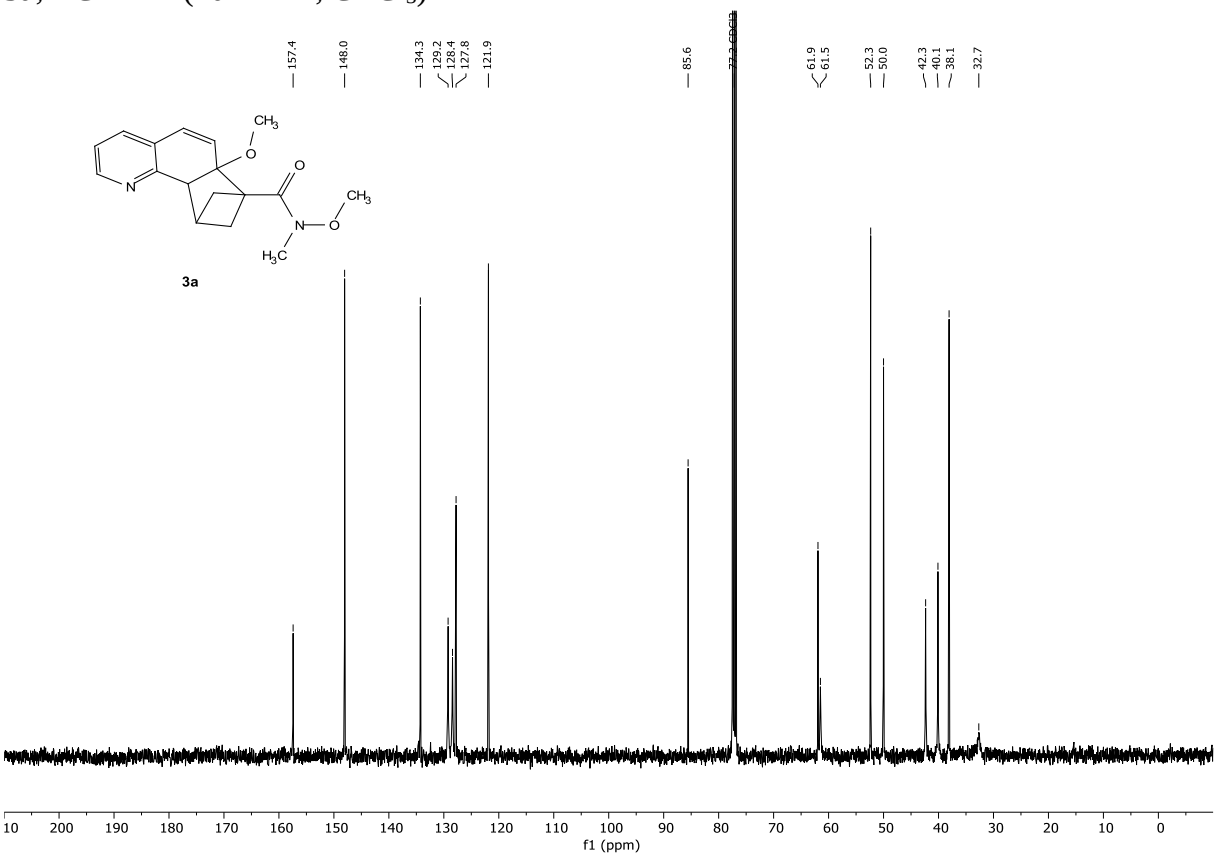


2j

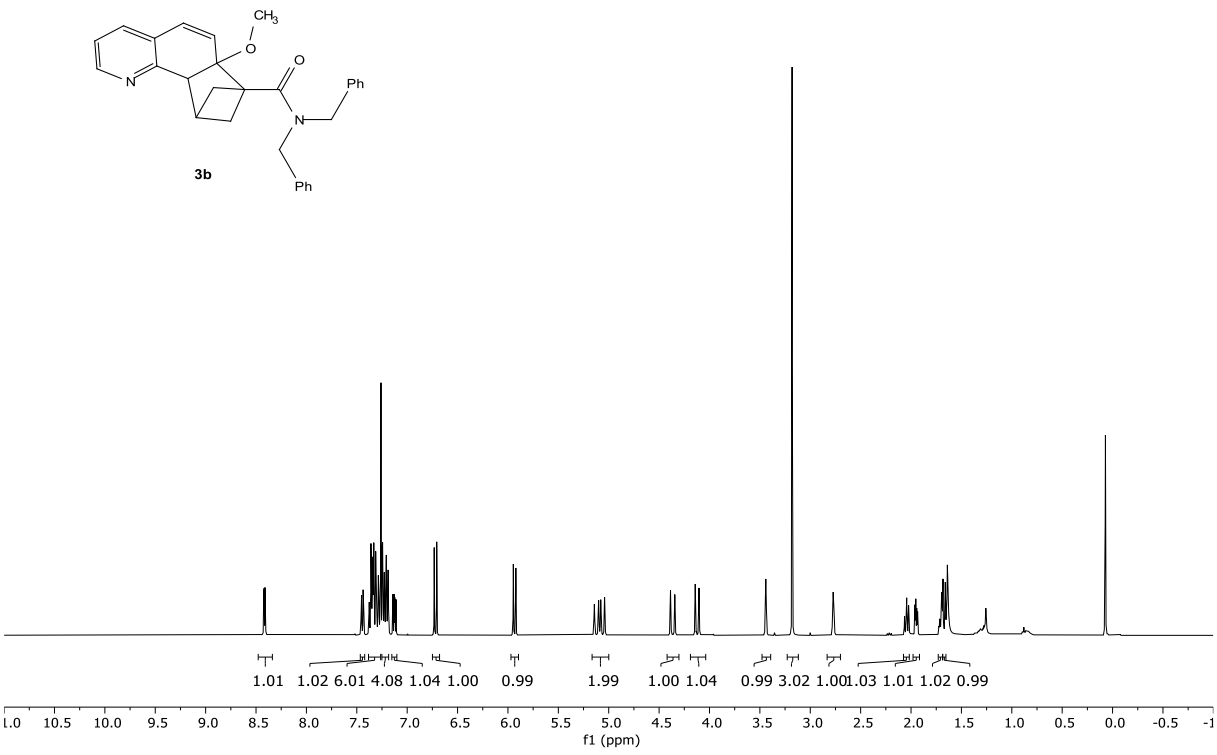
3a, ^{1}H NMR (400 MHz, $CDCl_3$)



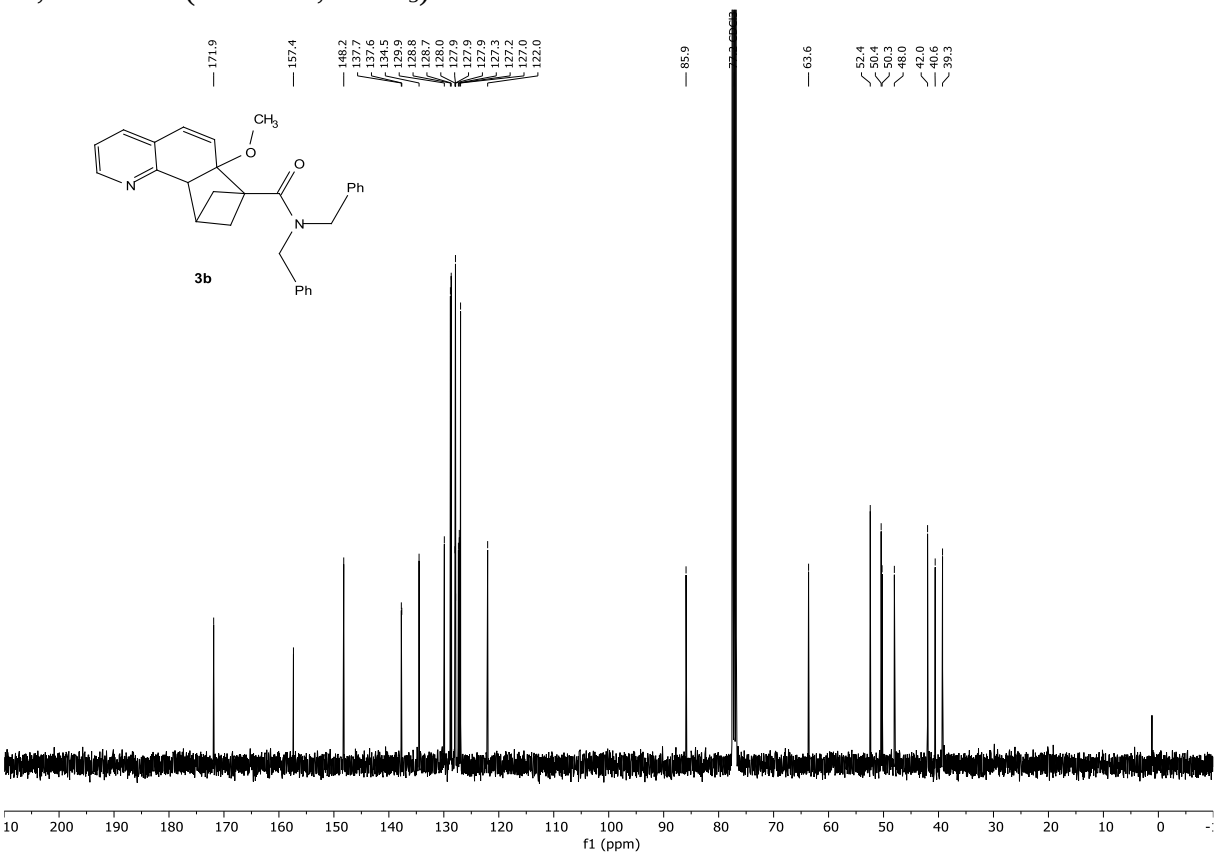
3a, ^{13}C NMR (101 MHz, $CDCl_3$)



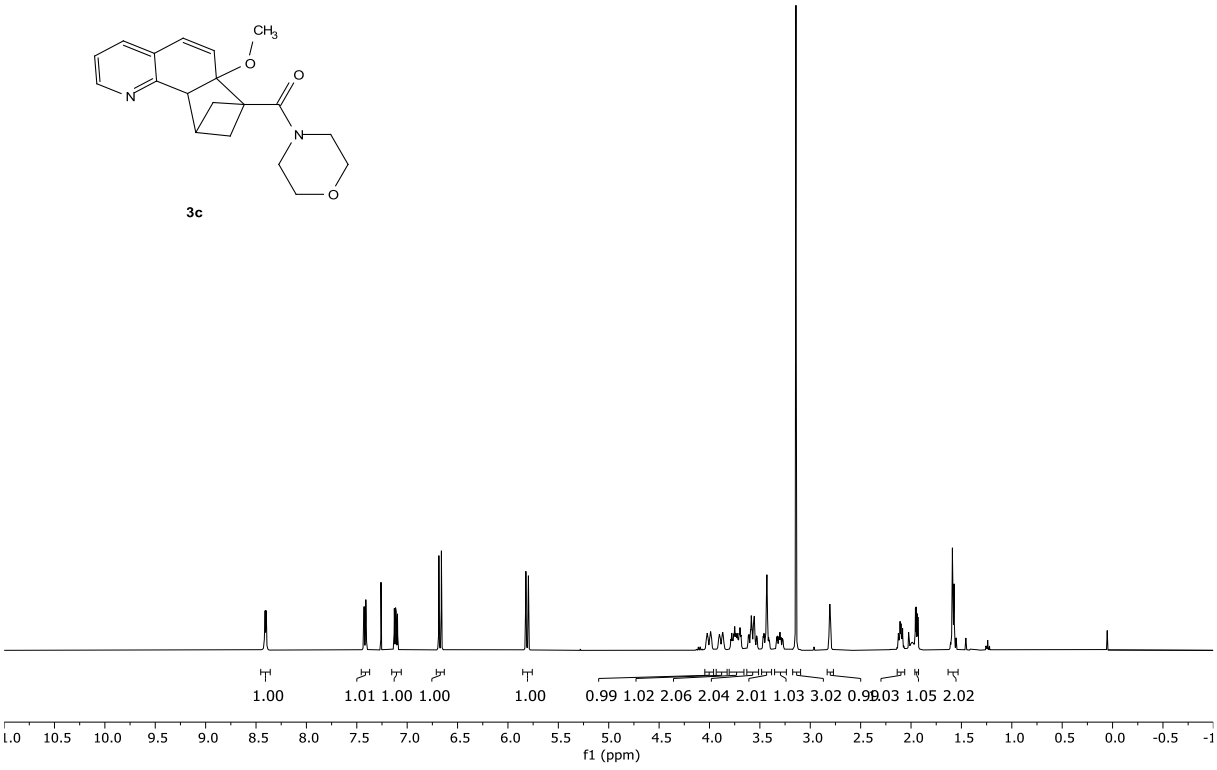
3b, ^{1}H NMR (400 MHz, $CDCl_3$)



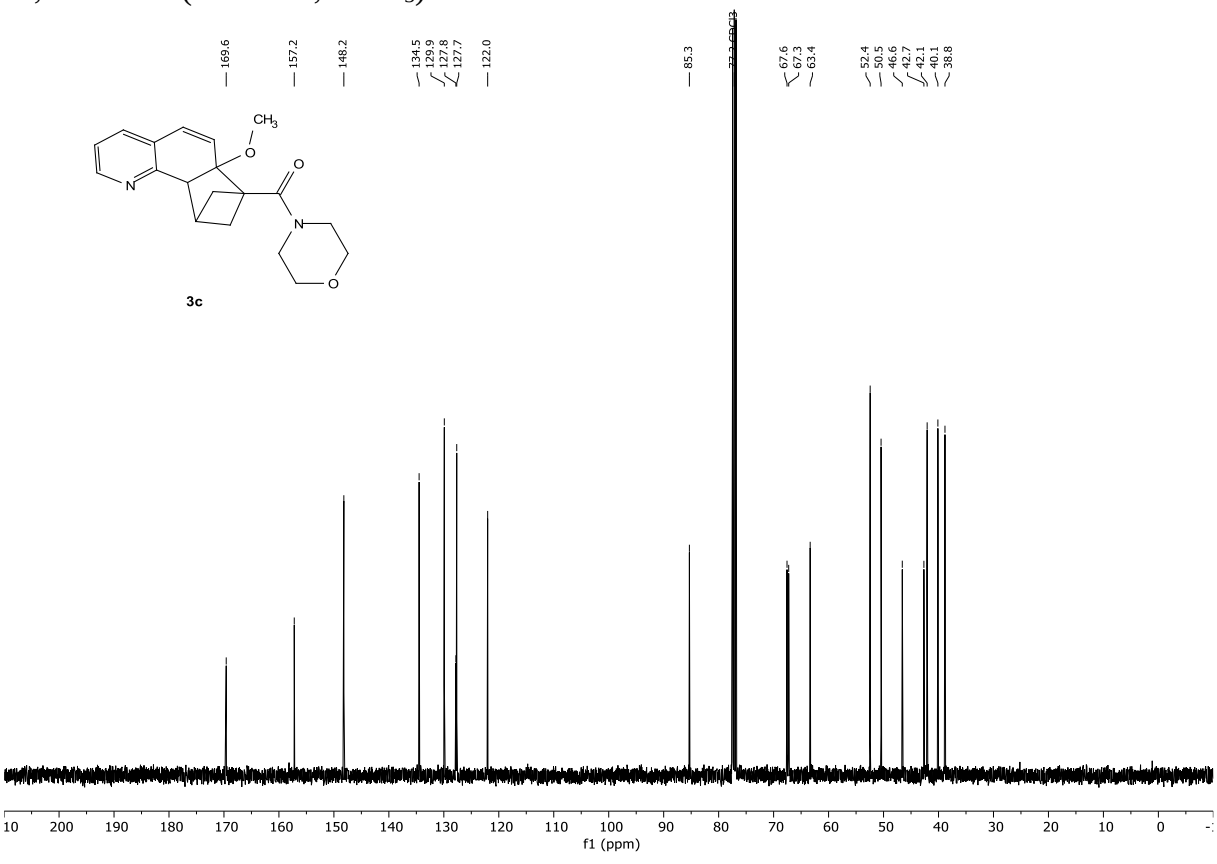
3b, ^{13}C NMR (101 MHz, $CDCl_3$)



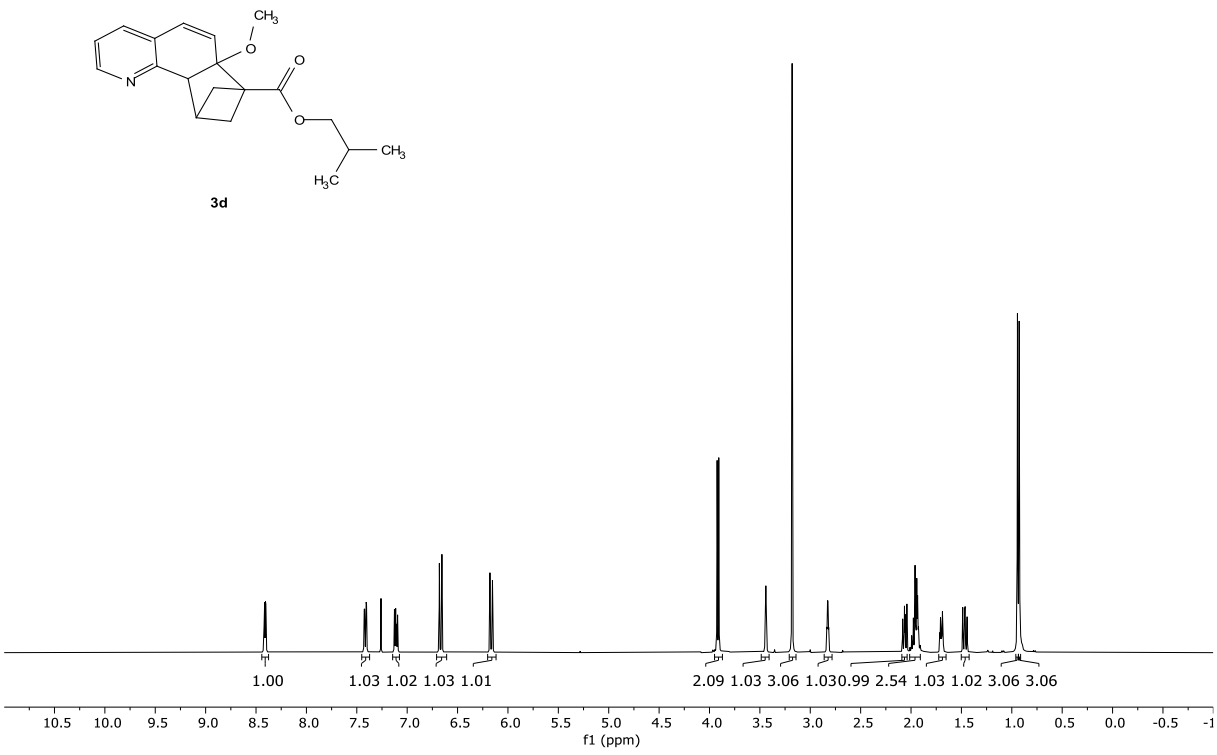
3c, ^{1}H NMR (400 MHz, $CDCl_3$)



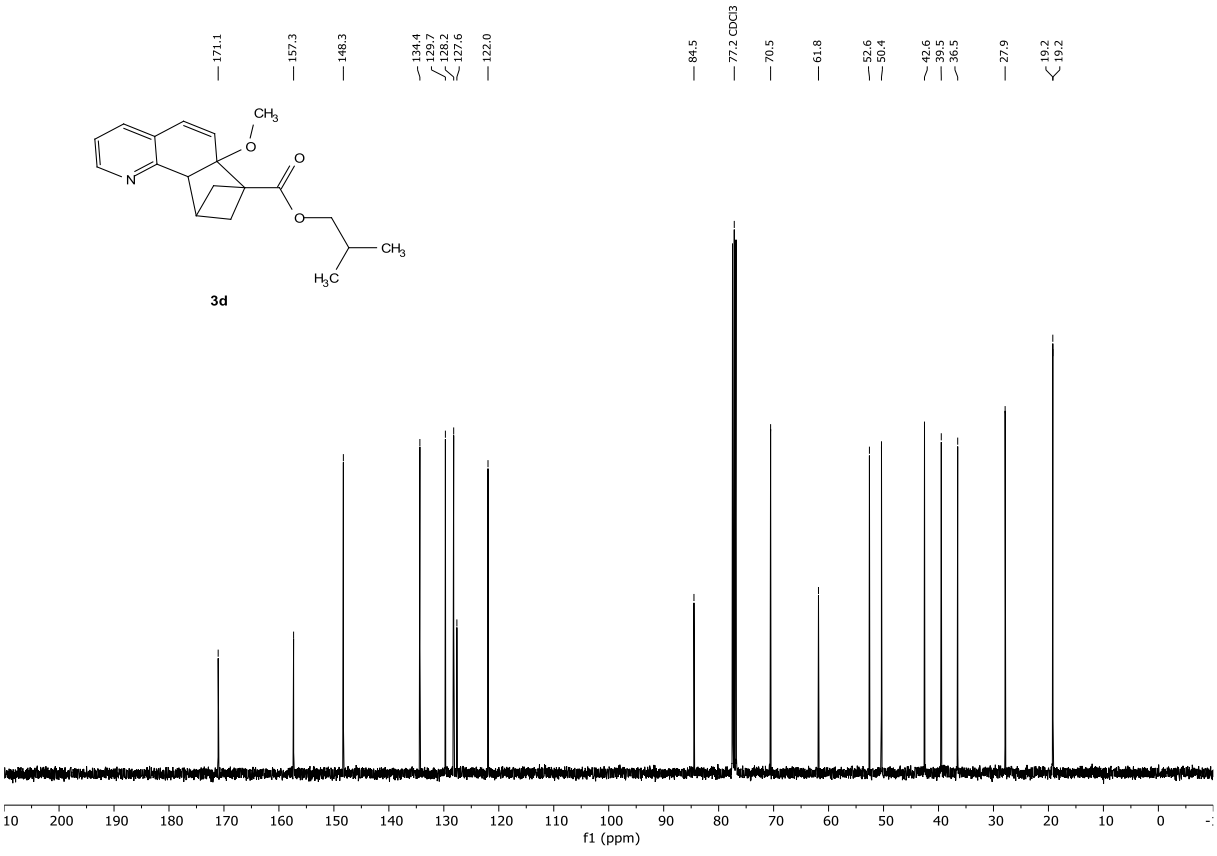
3c, ^{13}C NMR (101 MHz, $CDCl_3$)



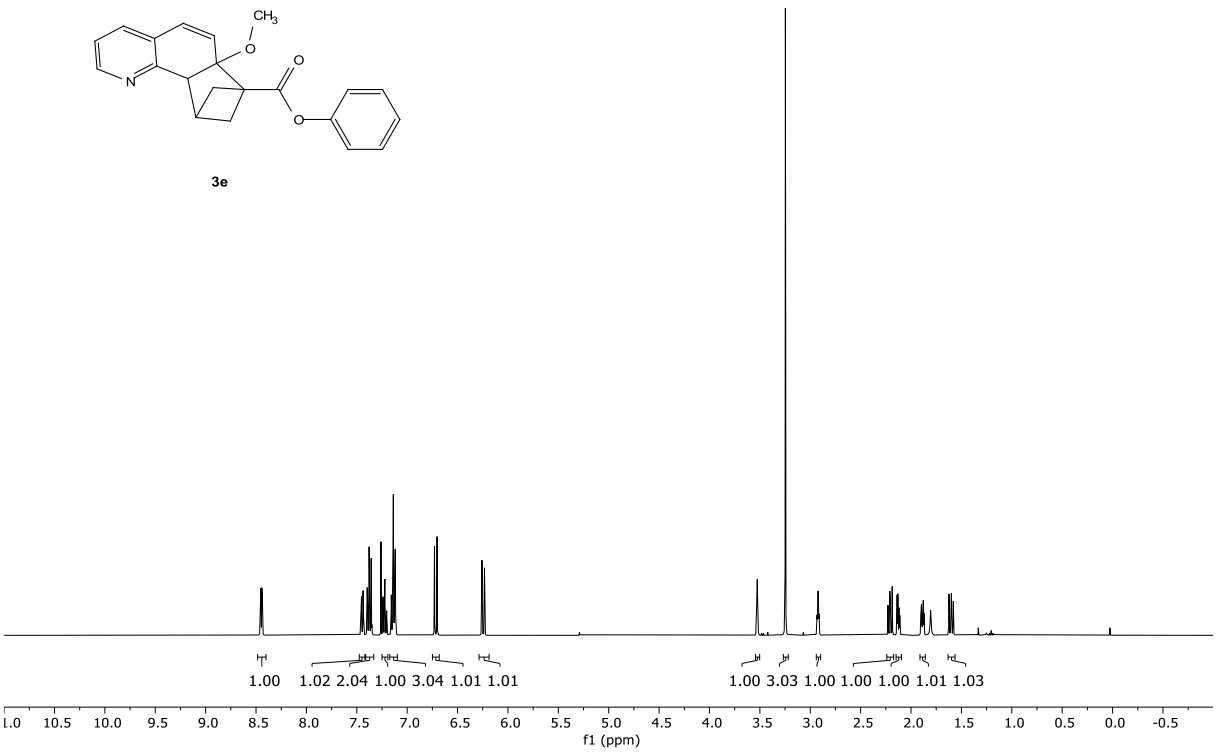
3d, ^{1}H NMR (400 MHz, $CDCl_3$)



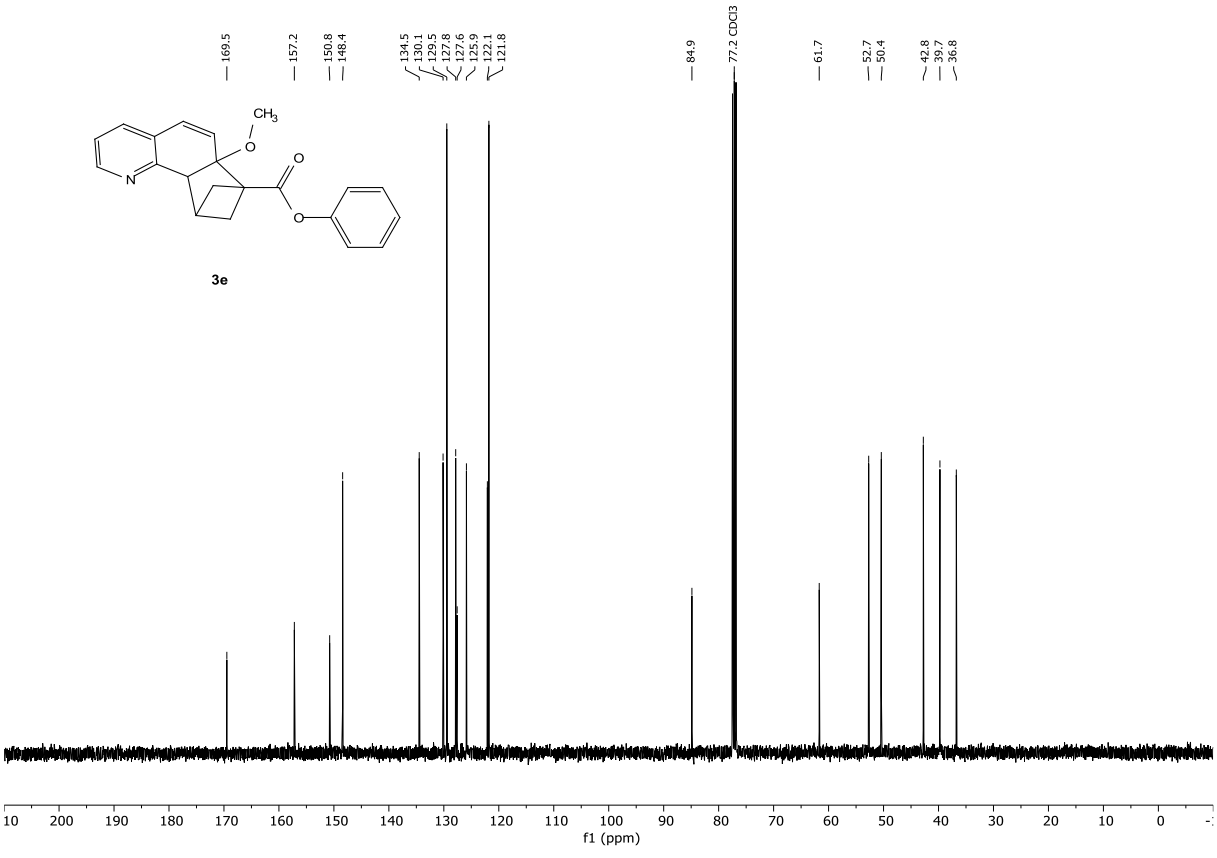
3d, ^{13}C NMR (101 MHz, $CDCl_3$)



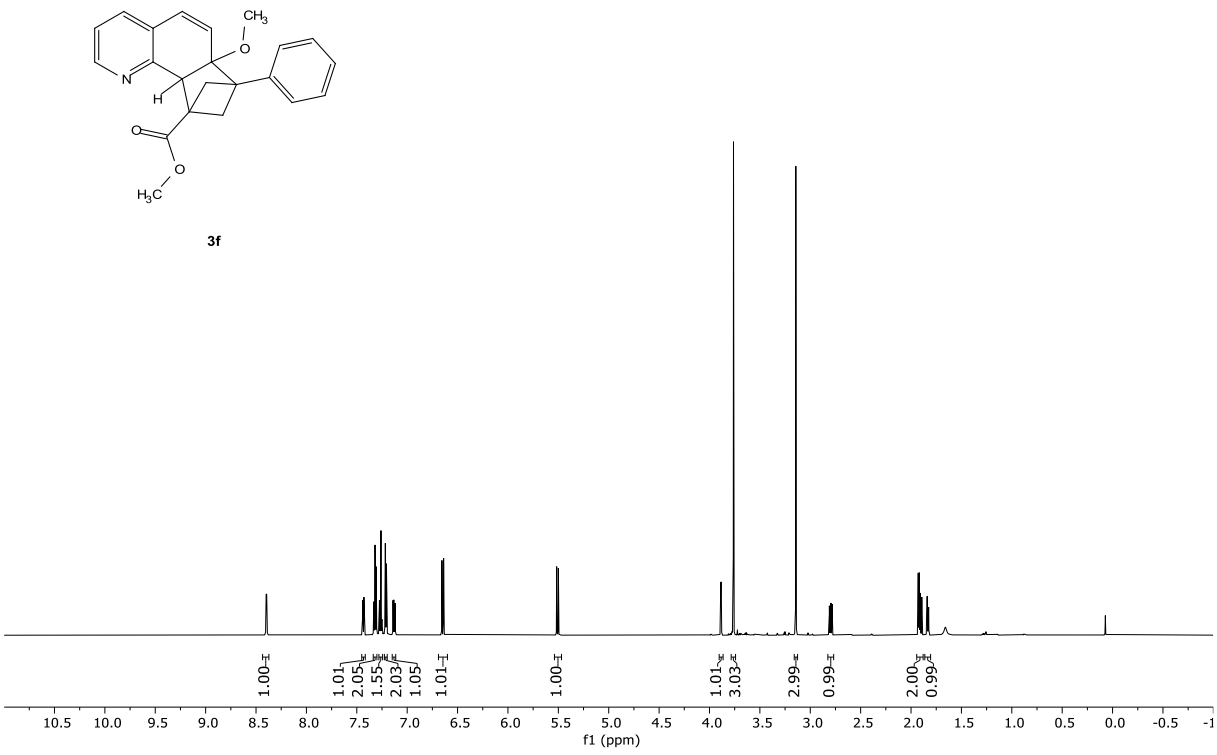
3e, ^{1}H NMR (400 MHz, $CDCl_3$)



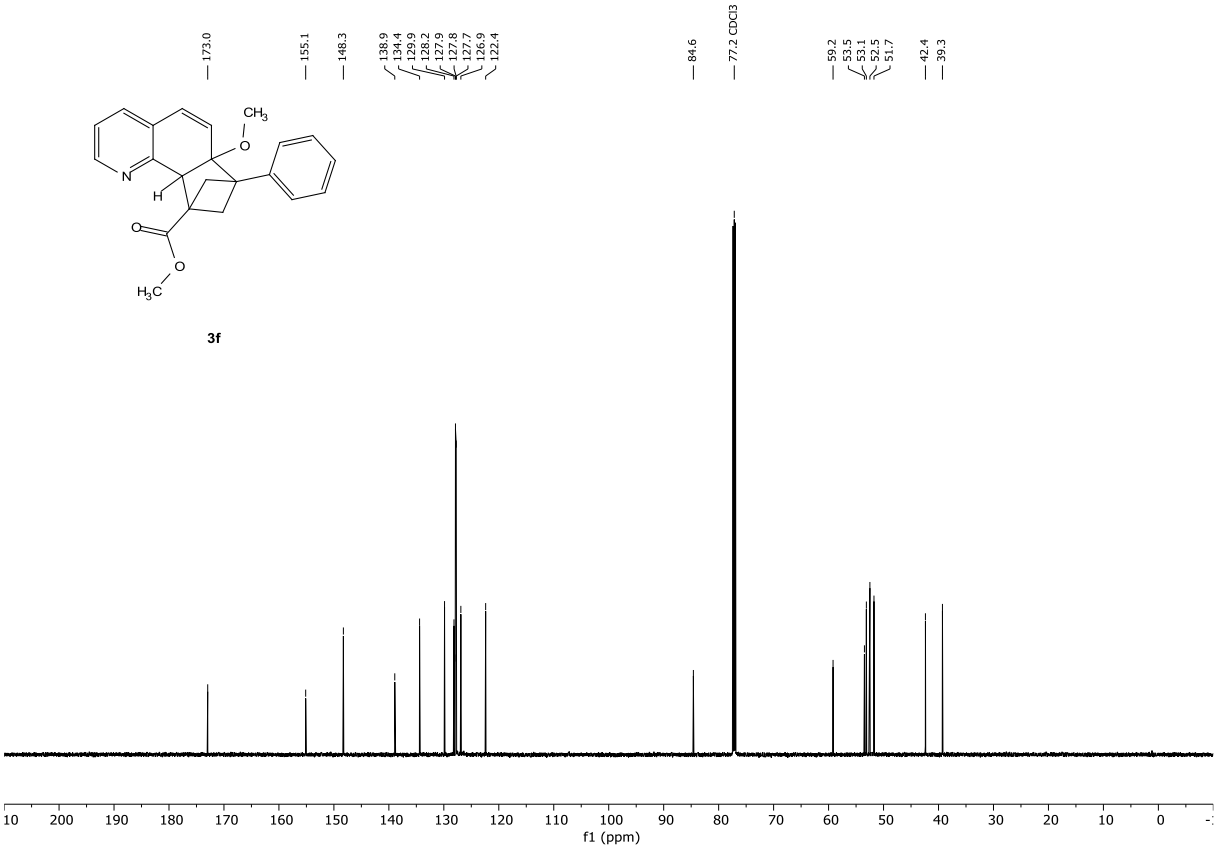
3e, ^{13}C NMR (101 MHz, $CDCl_3$)



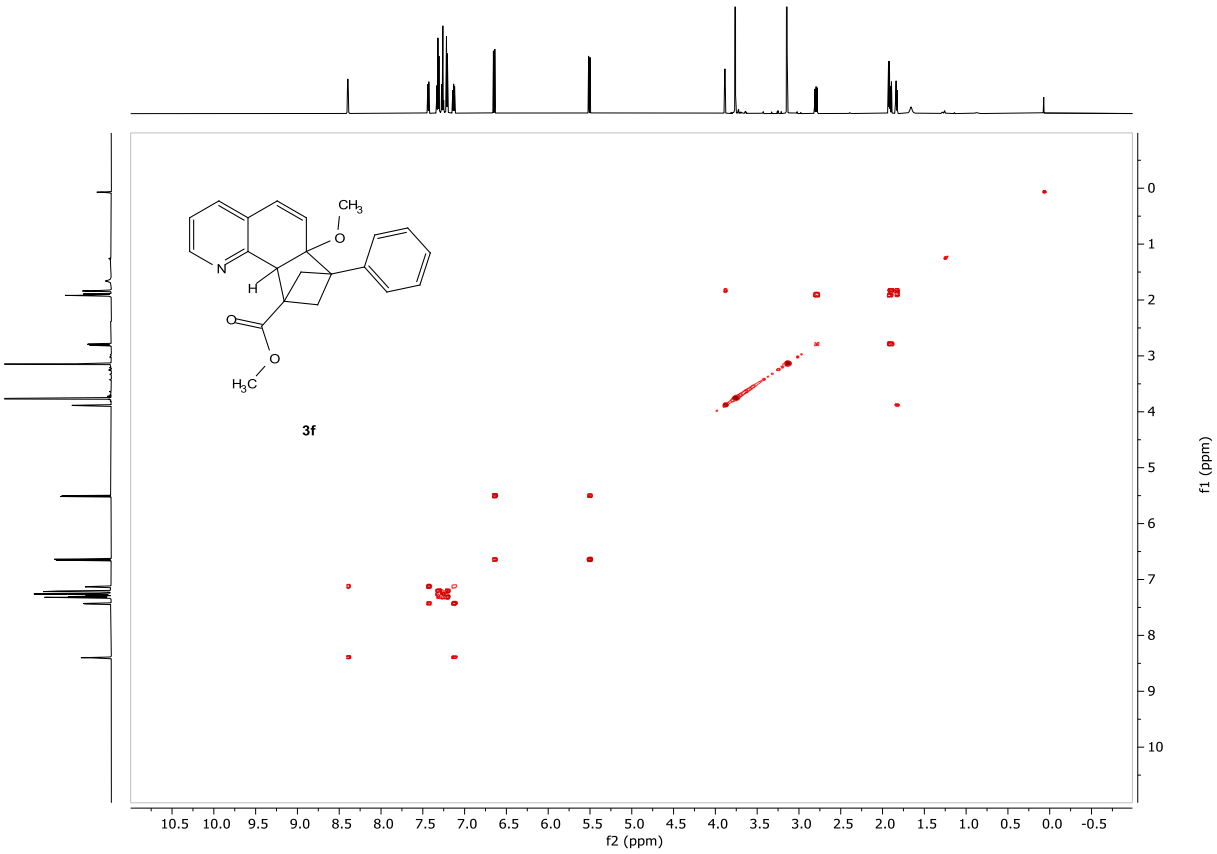
3f, ^{1}H NMR (599 MHz, $CDCl_3$)



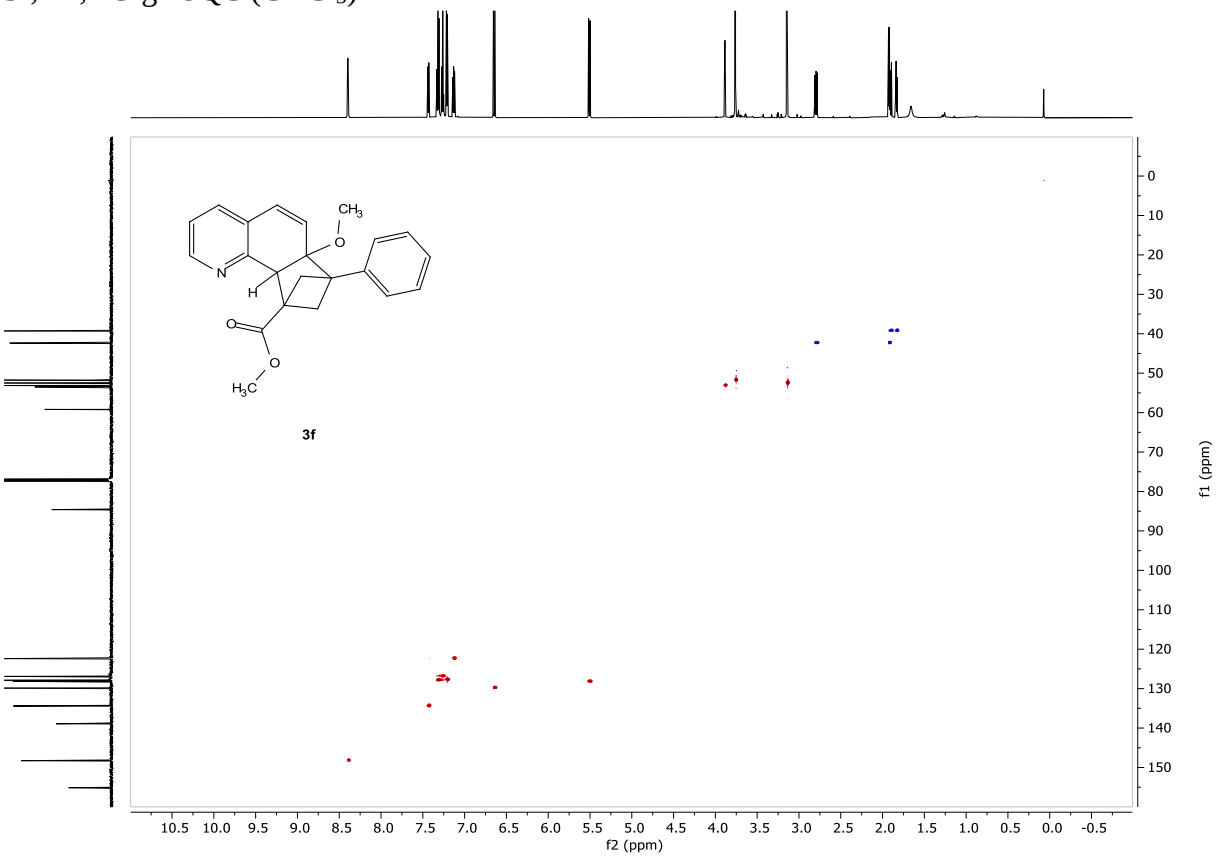
3f, ^{13}C NMR (151 MHz, $CDCl_3$)



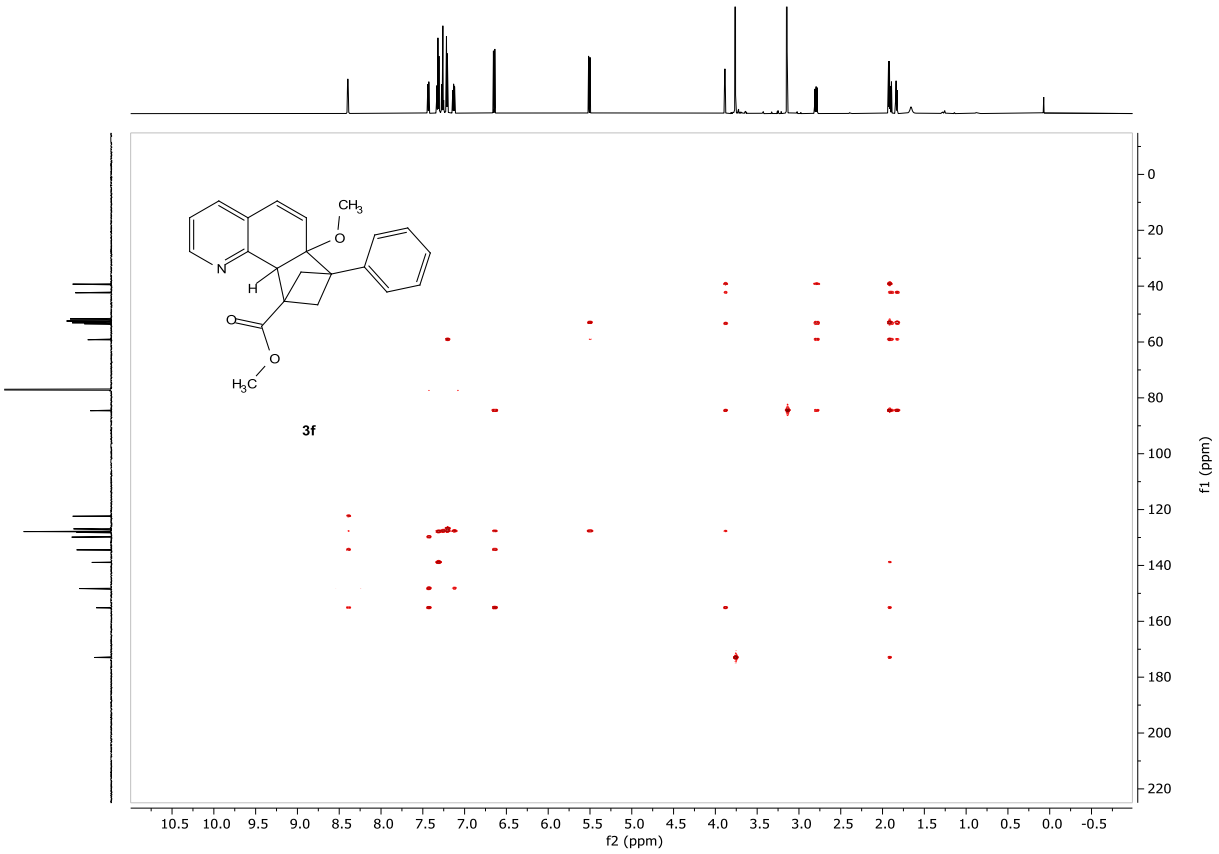
3f, $^{1}H,^{1}H$-gCOSY ($CDCl_3$)



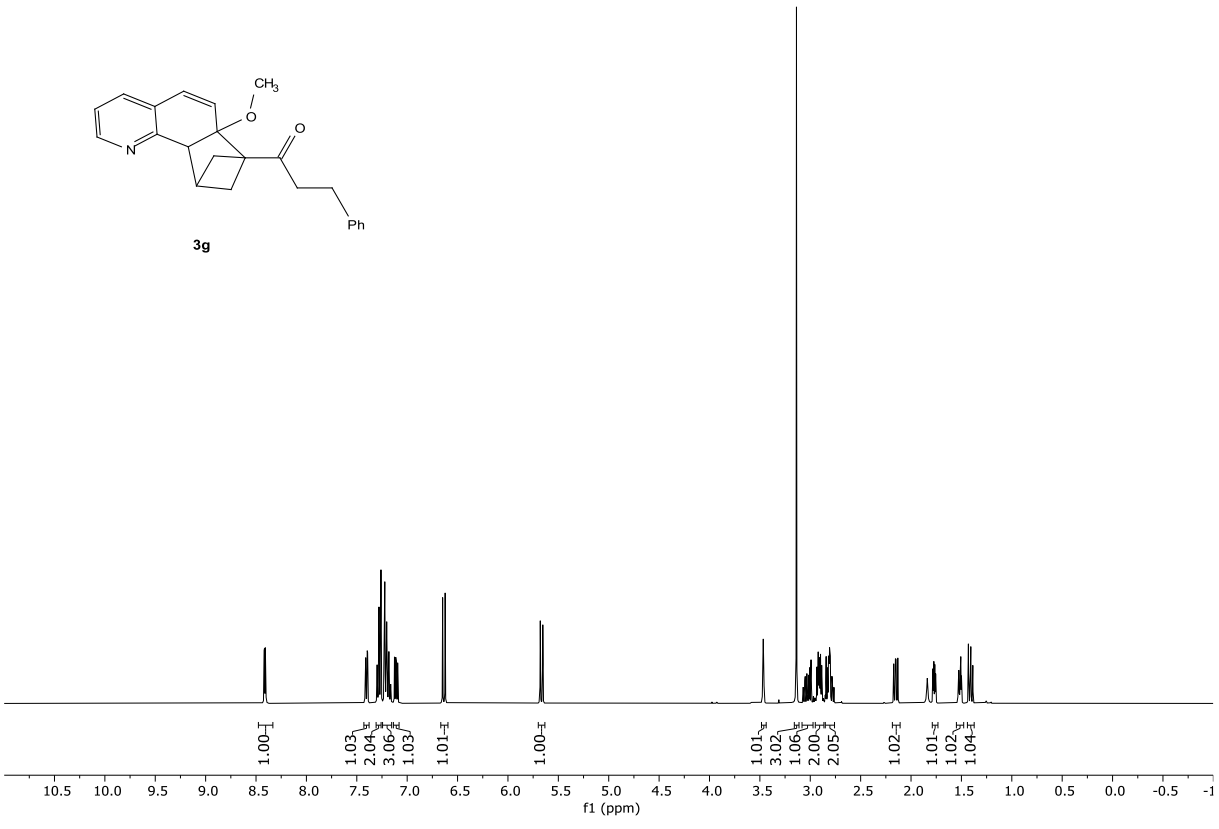
3f, $^{1}H,^{13}C$-gHSQC ($CDCl_3$)



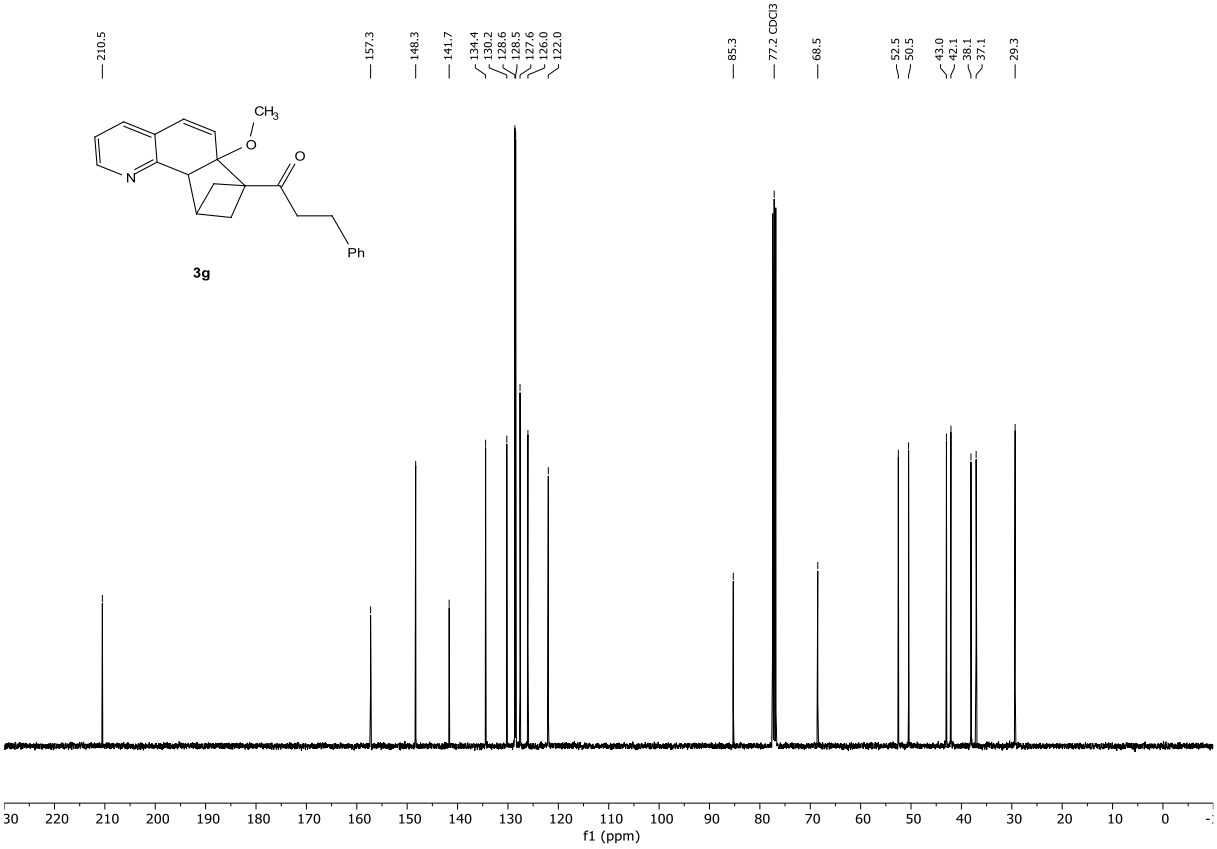
3f, $^{1}H,^{13}C$-gHMBC ($CDCl_3$)



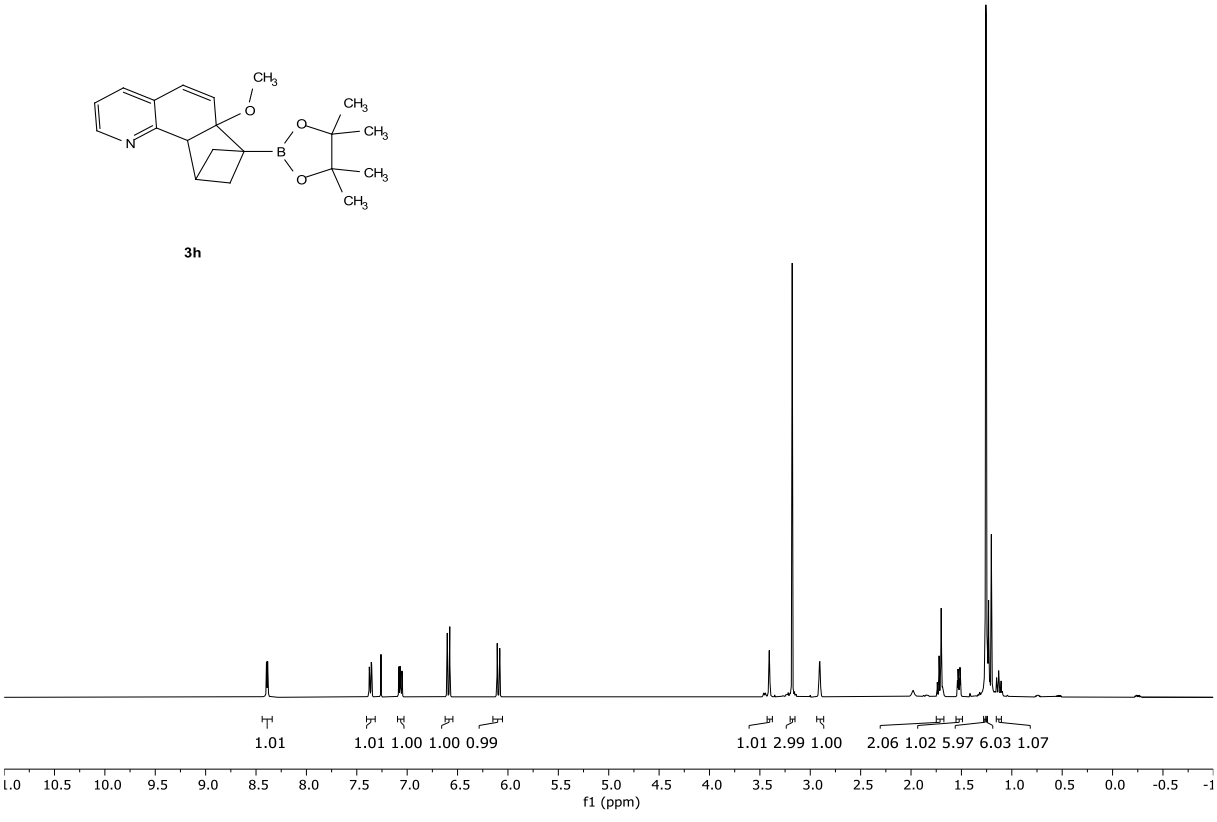
3g, ^{1}H NMR (400 MHz, $CDCl_3$)



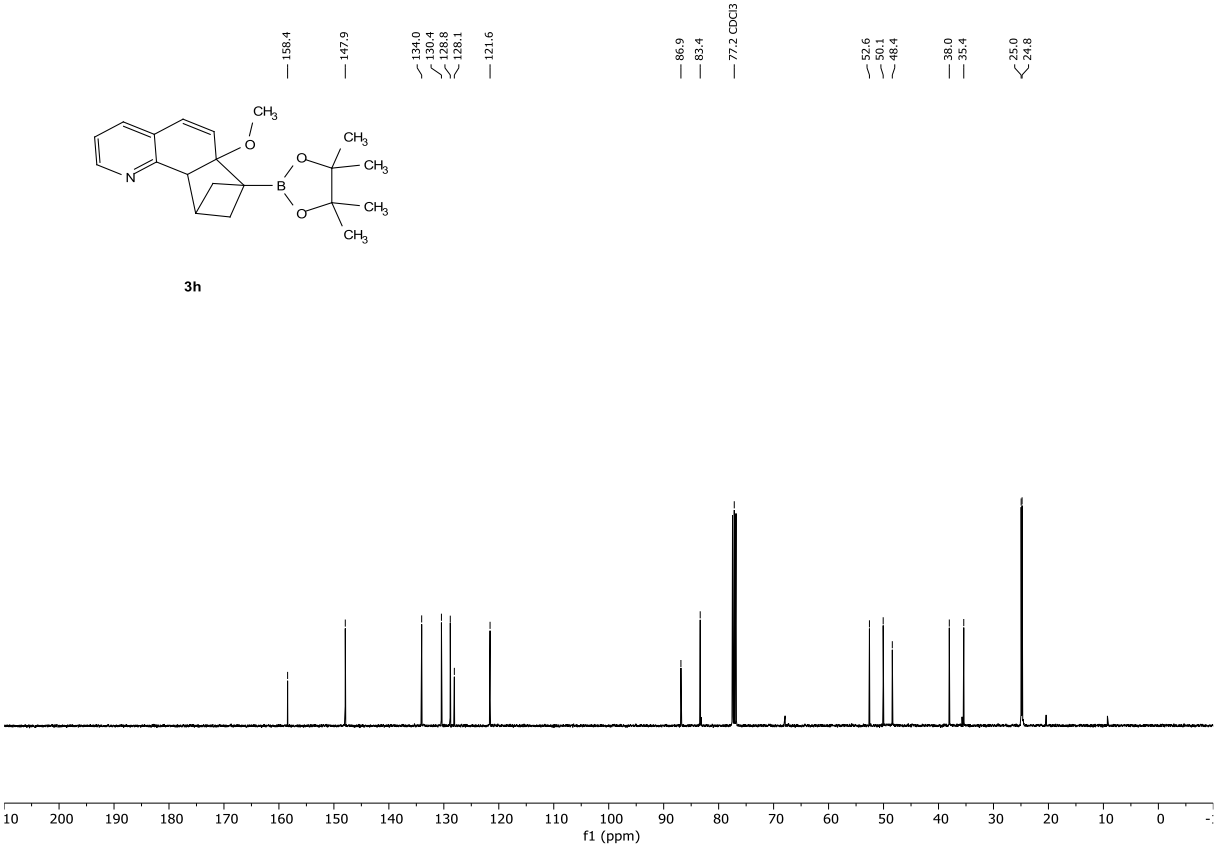
3g, ^{13}C NMR (101 MHz, $CDCl_3$)



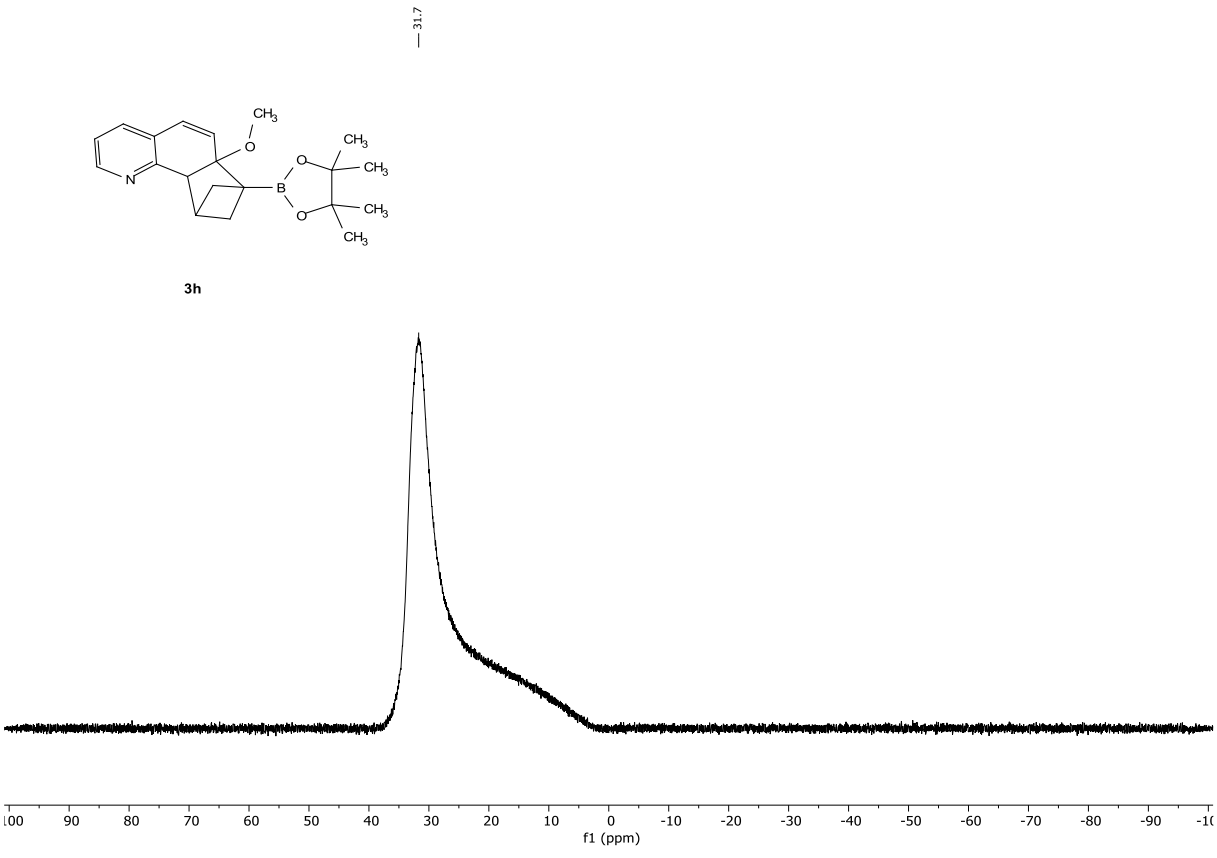
3h, ^{1}H NMR (400 MHz, $CDCl_3$)



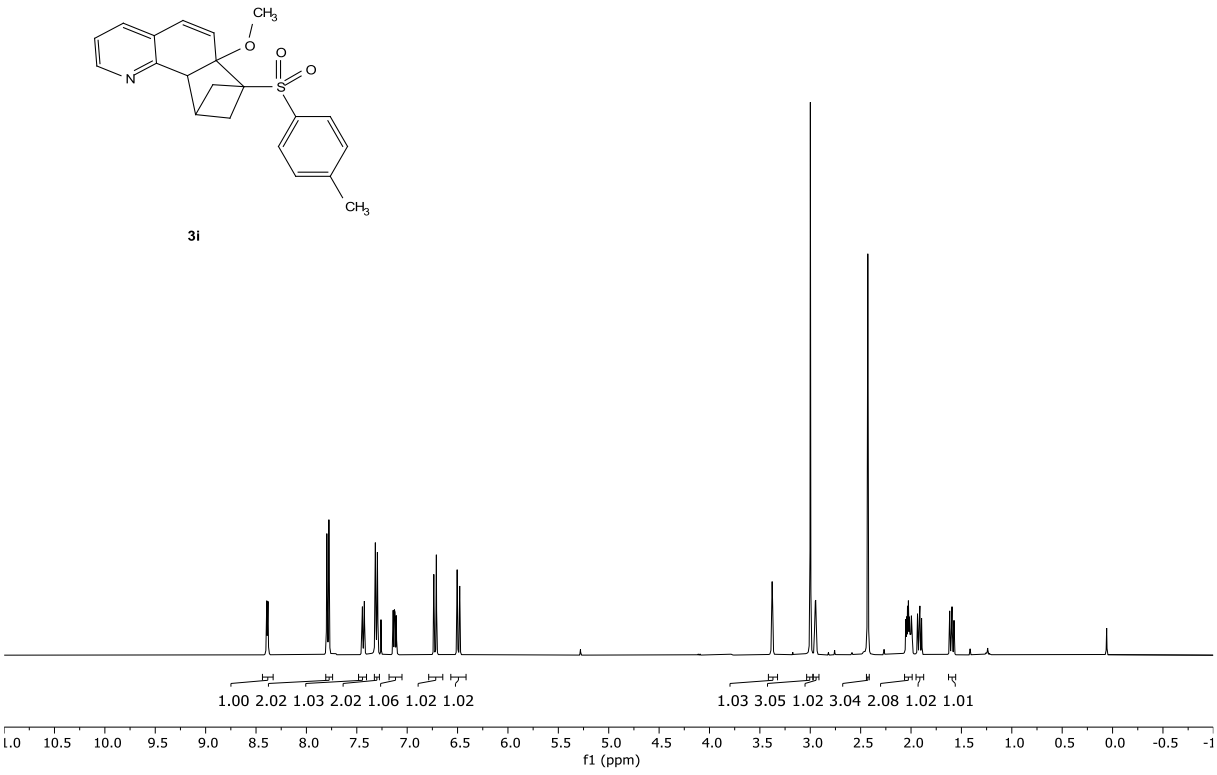
3h, ^{13}C NMR (101 MHz, $CDCl_3$)



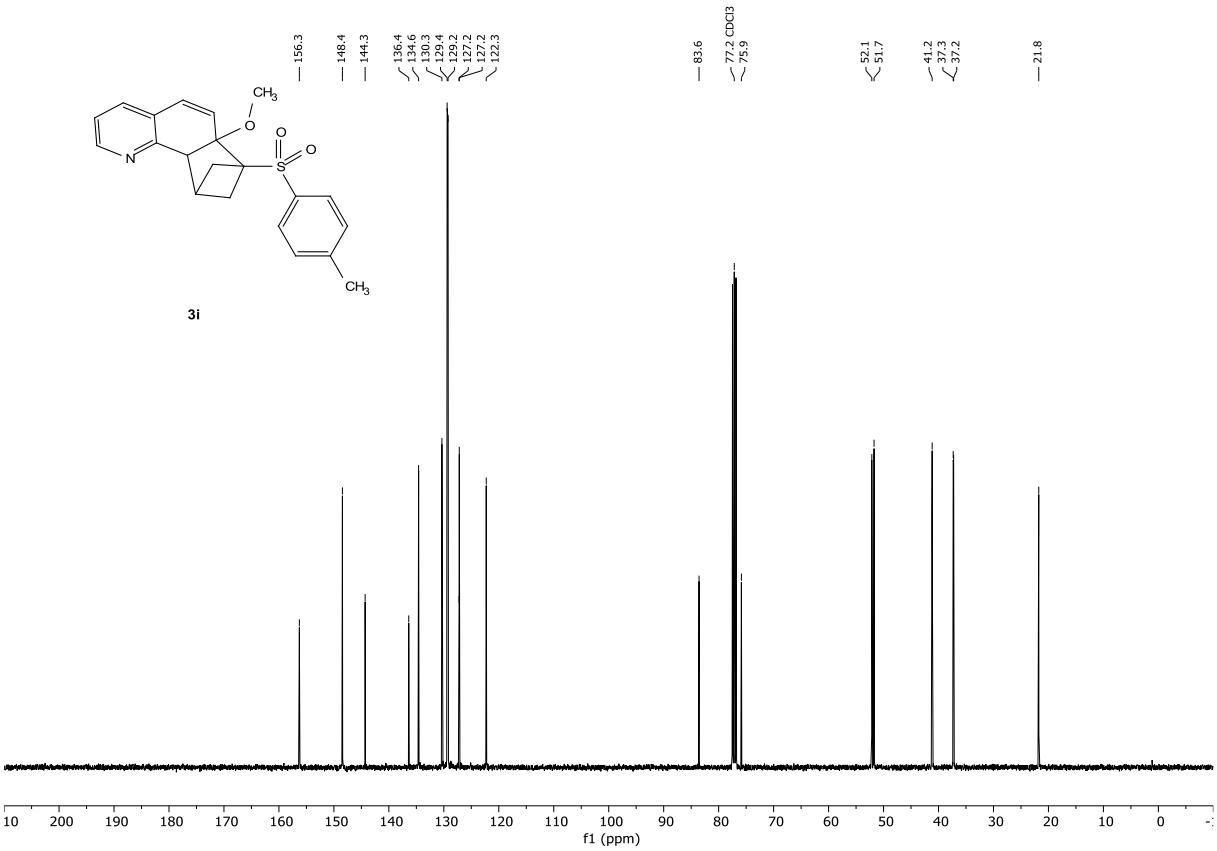
3h, ^{11}B NMR (128 MHz, $CDCl_3$)



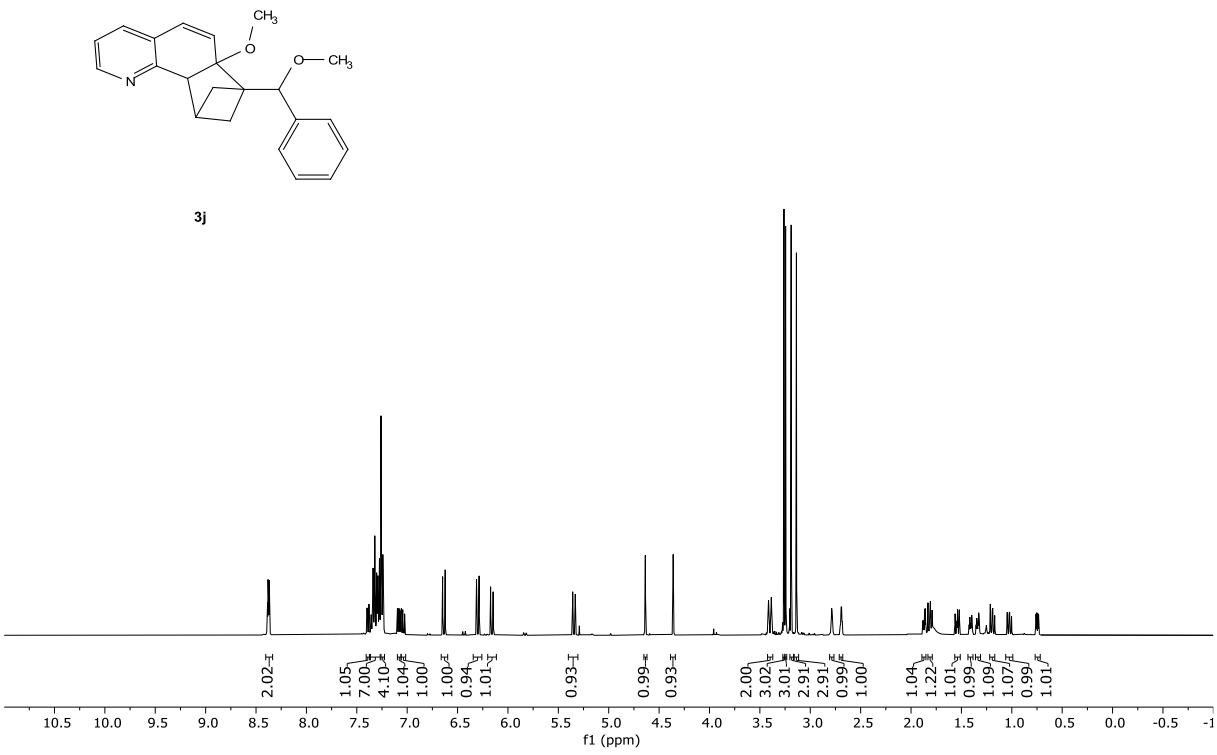
3i, ^{1}H NMR (400 MHz, $CDCl_3$)



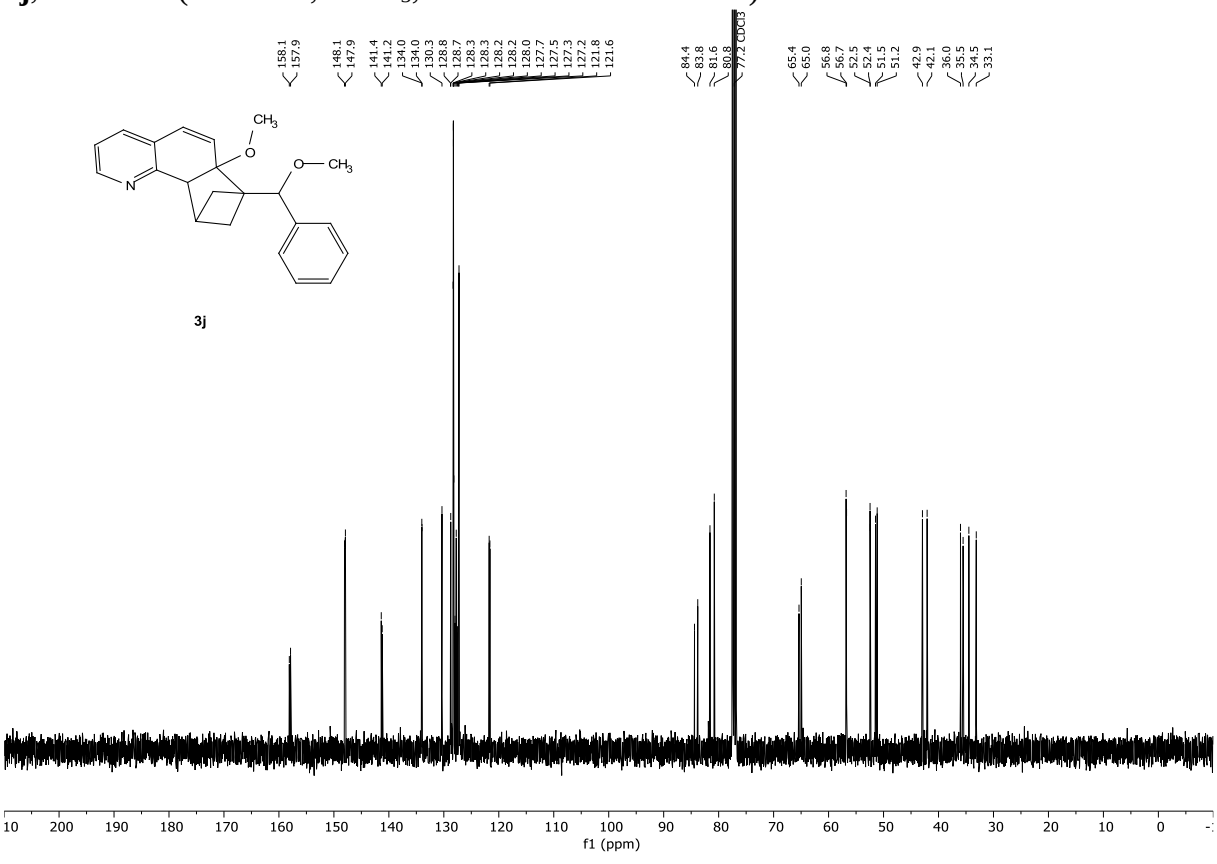
3i, ^{13}C NMR (101 MHz, $CDCl_3$)



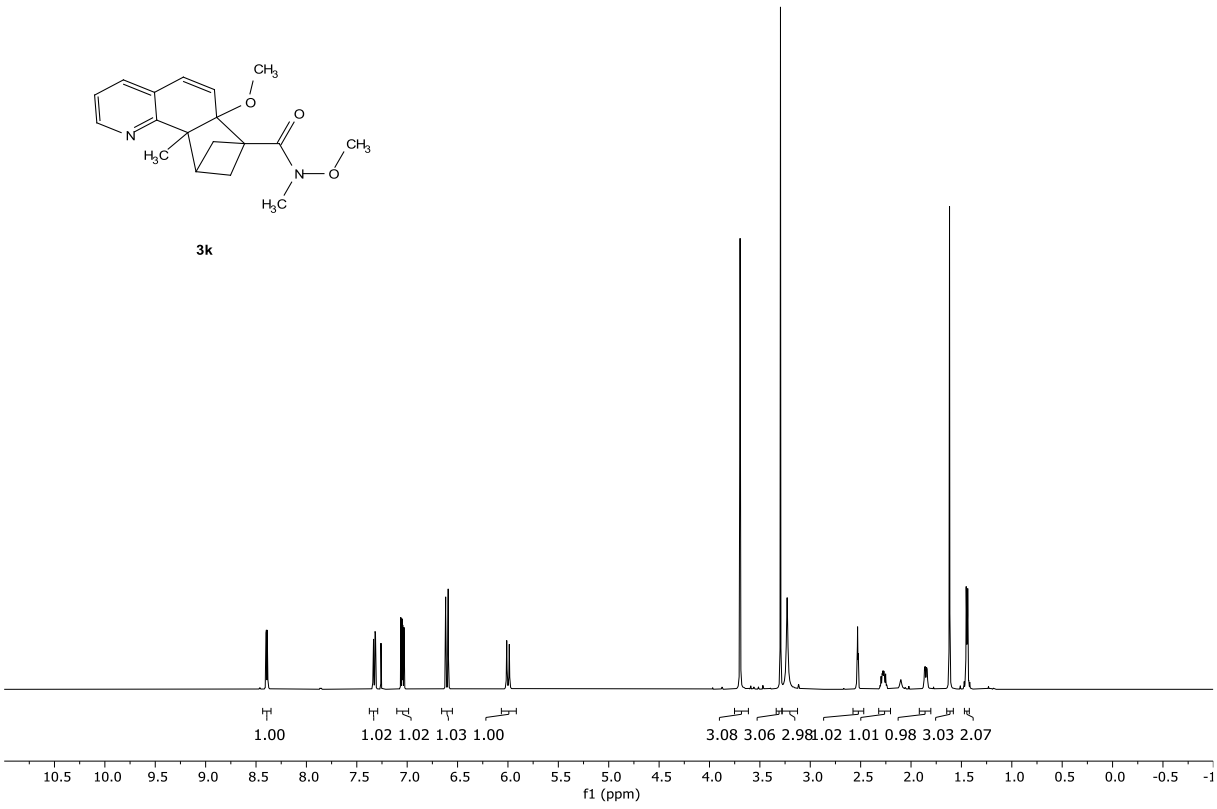
3j, ^{1}H NMR (400 MHz, $CDCl_3$; mixture of diastereomers)



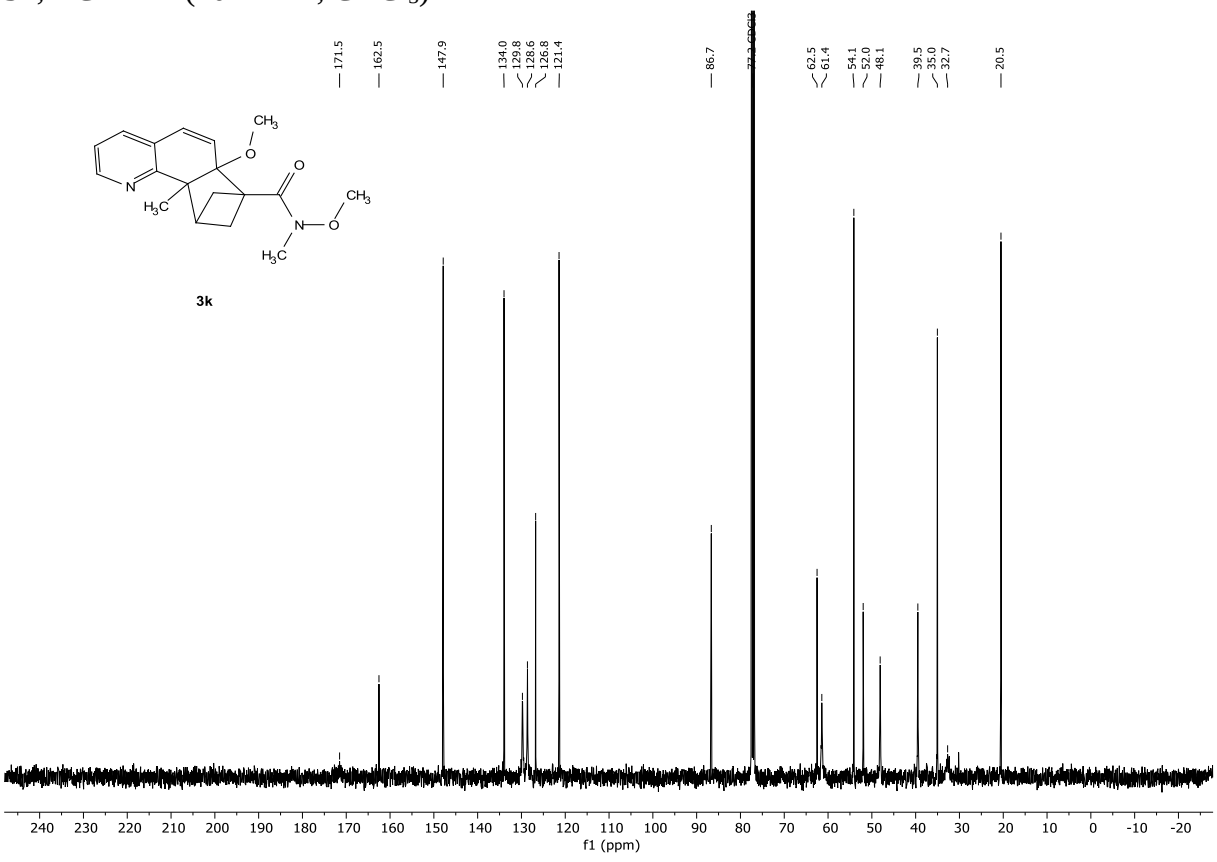
3j, ^{13}C NMR (101 MHz, $CDCl_3$; mixture of diastereomers)



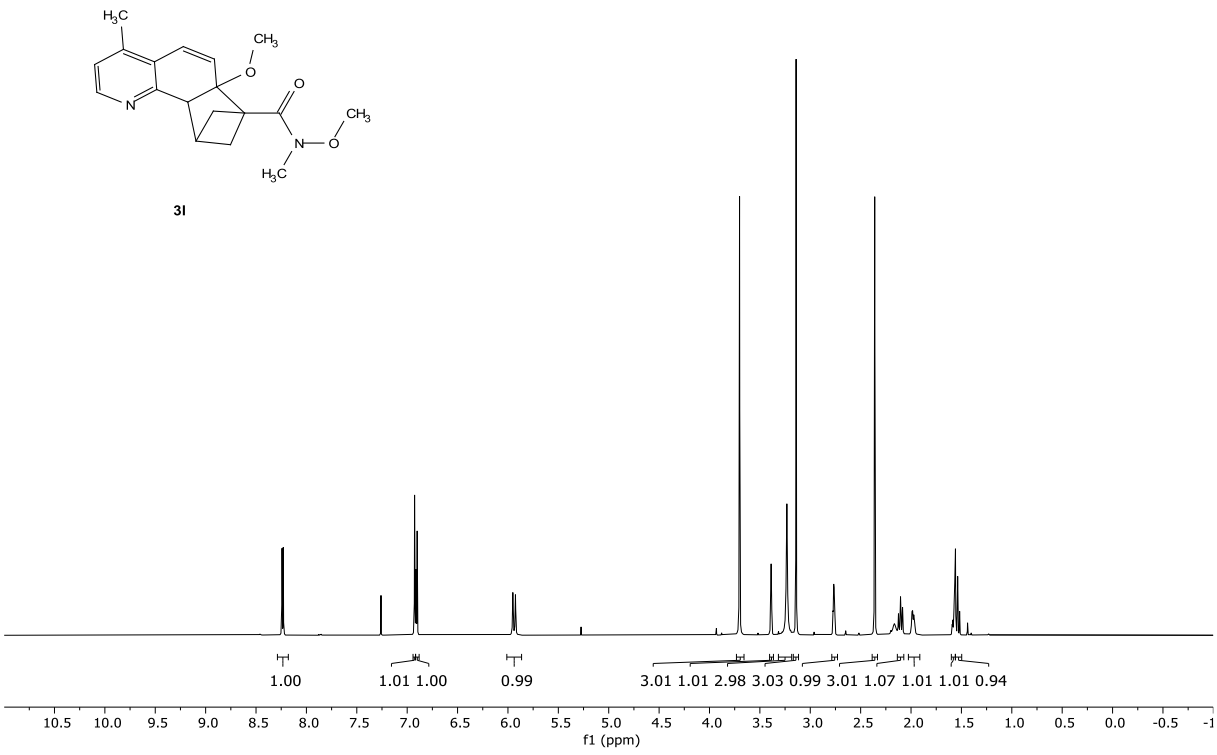
3k, ^{1}H NMR (400 MHz, $CDCl_3$)



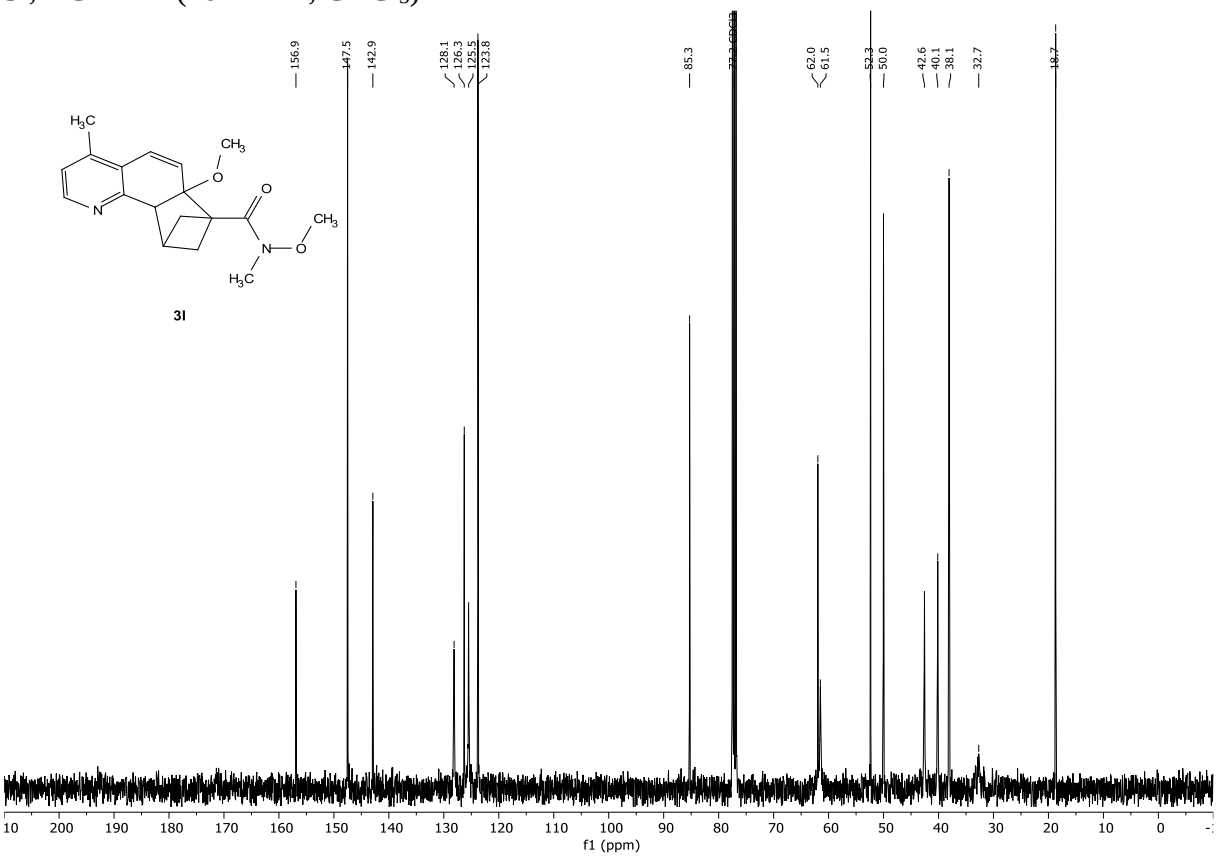
3k, ^{13}C NMR (101 MHz, $CDCl_3$)



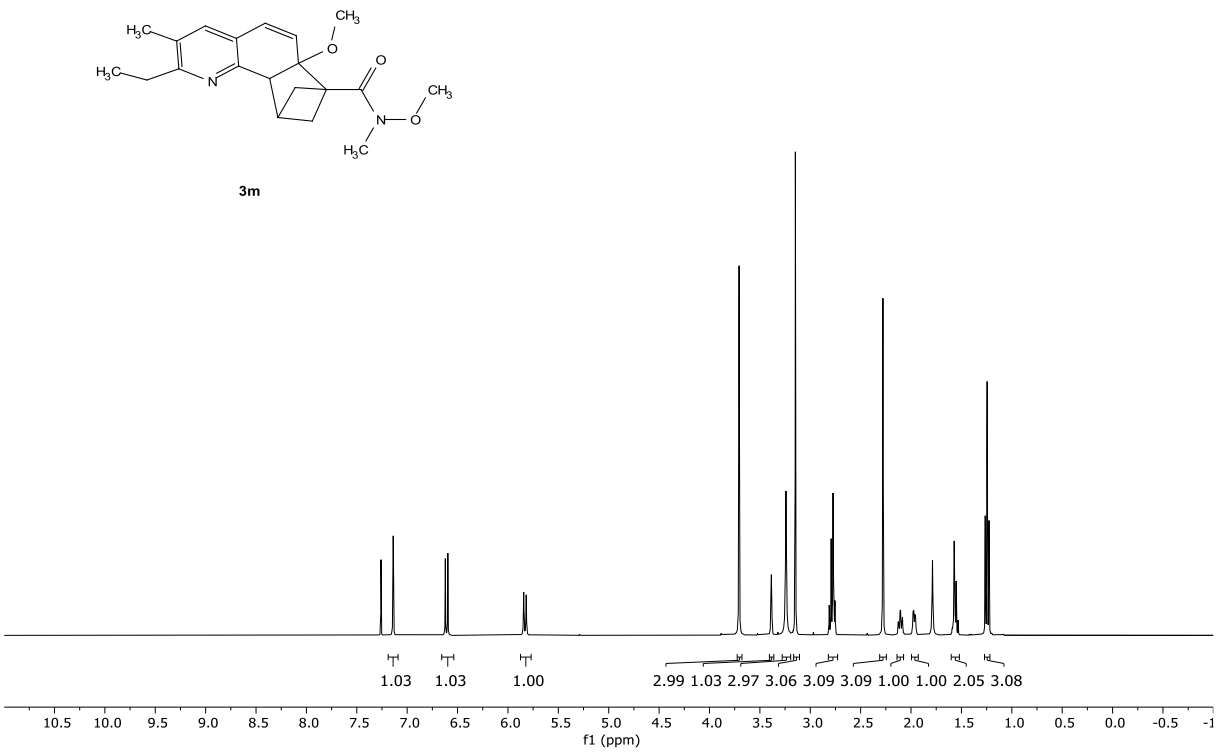
3l, ^{1}H NMR (400 MHz, $CDCl_3$)



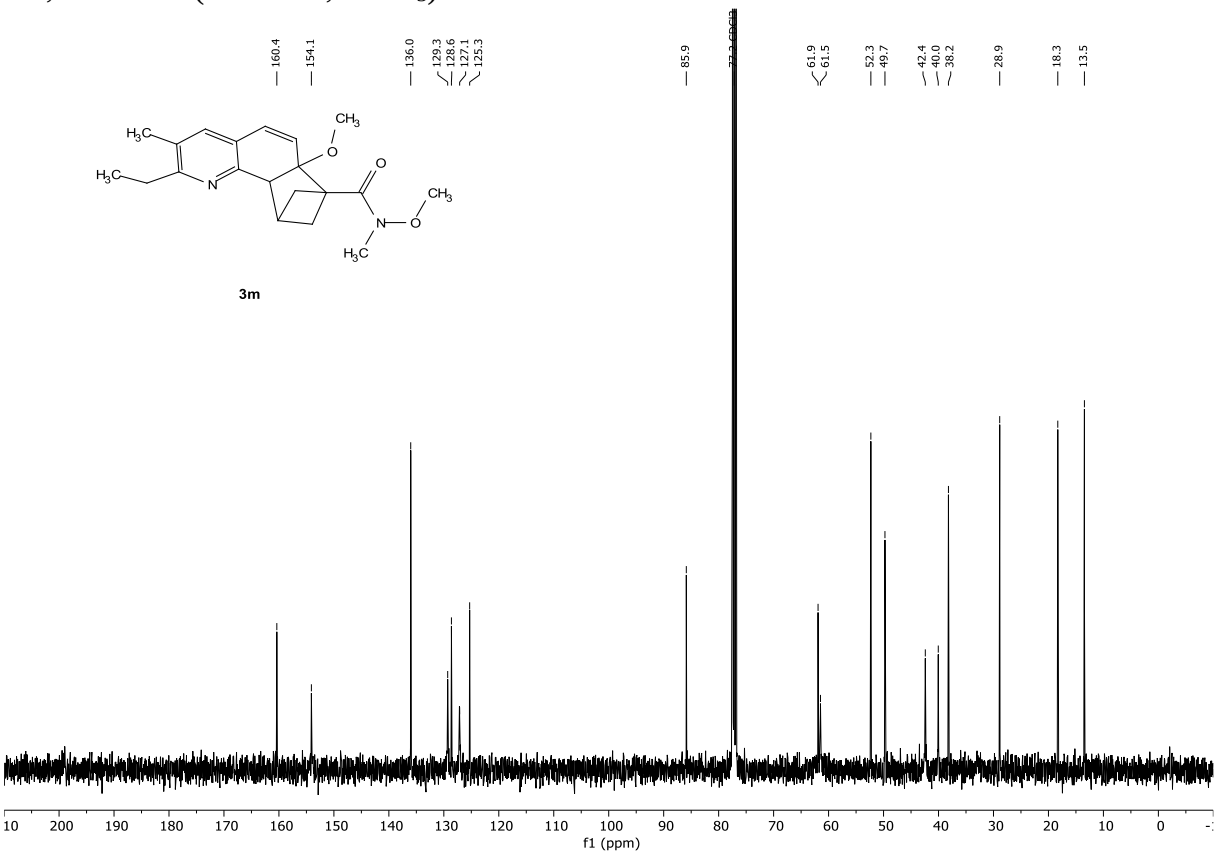
3l, ^{13}C NMR (101 MHz, $CDCl_3$)



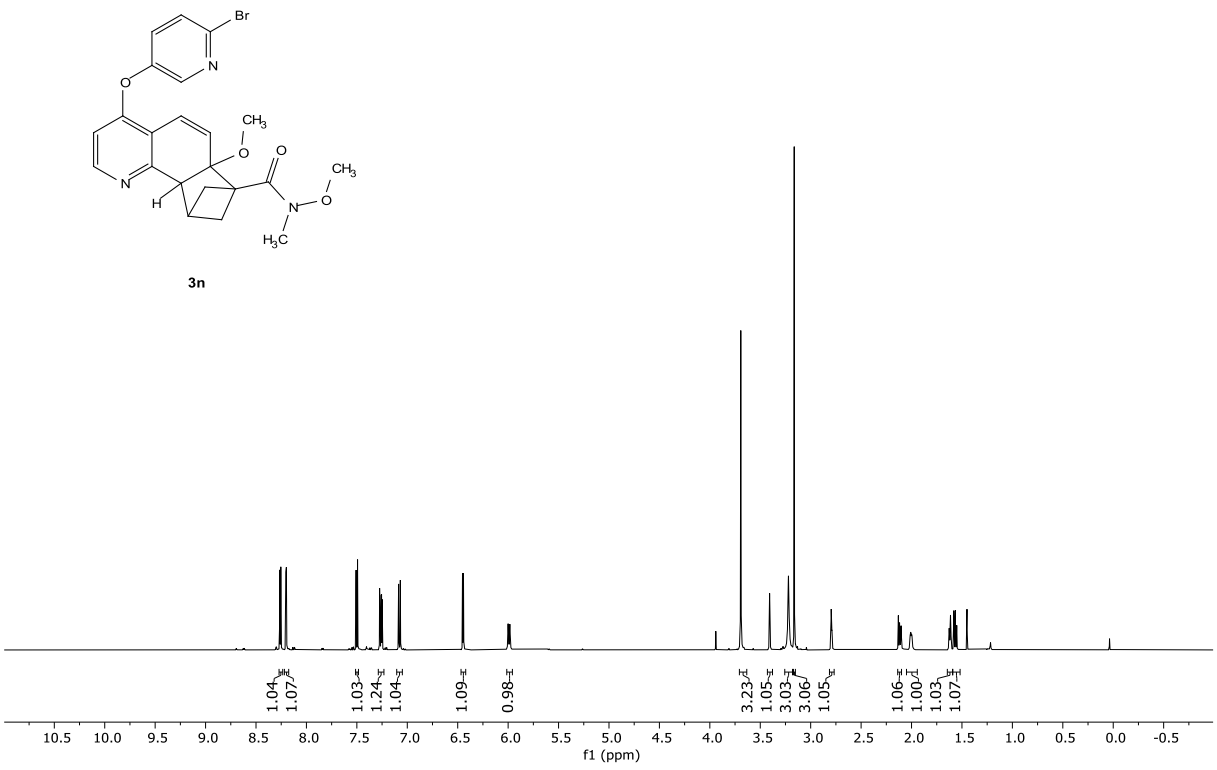
3m, ^{1}H NMR (400 MHz, $CDCl_3$)



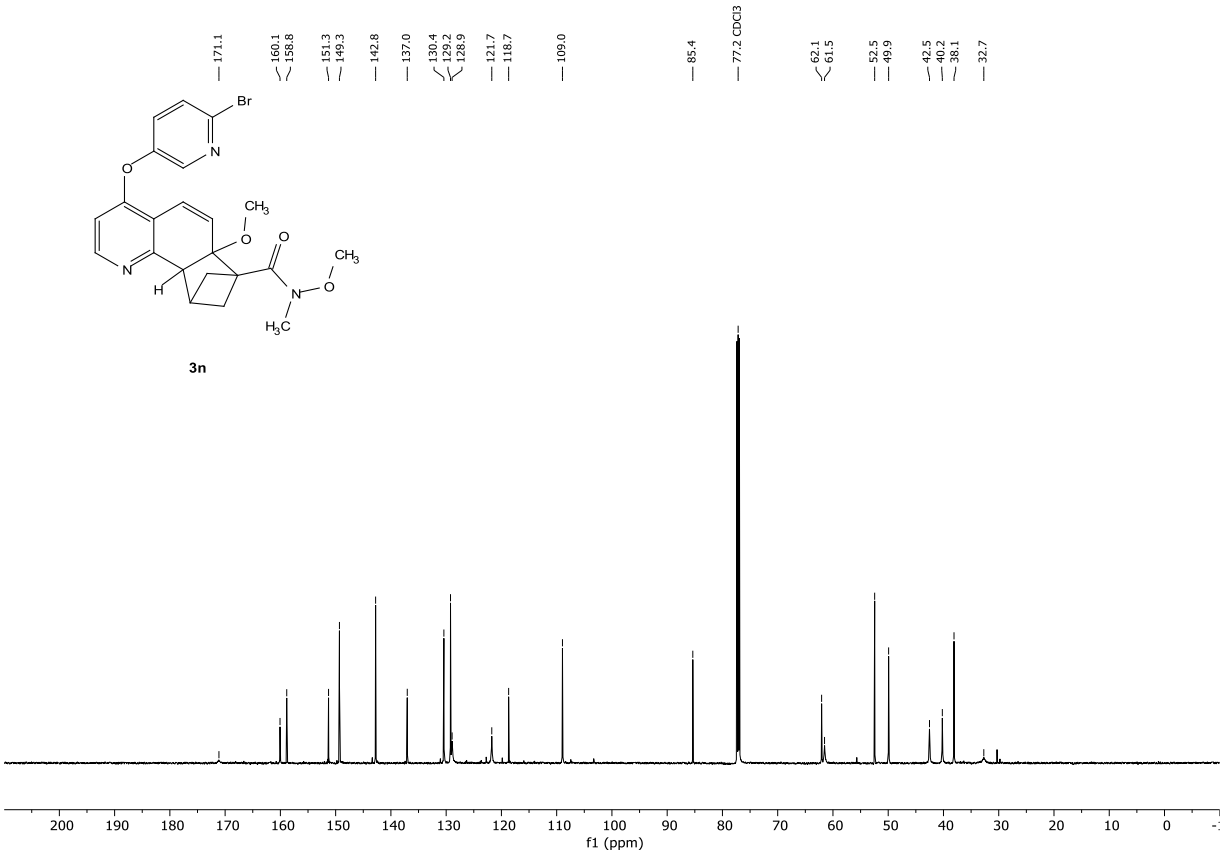
3m, ^{13}C NMR (101 MHz, $CDCl_3$)



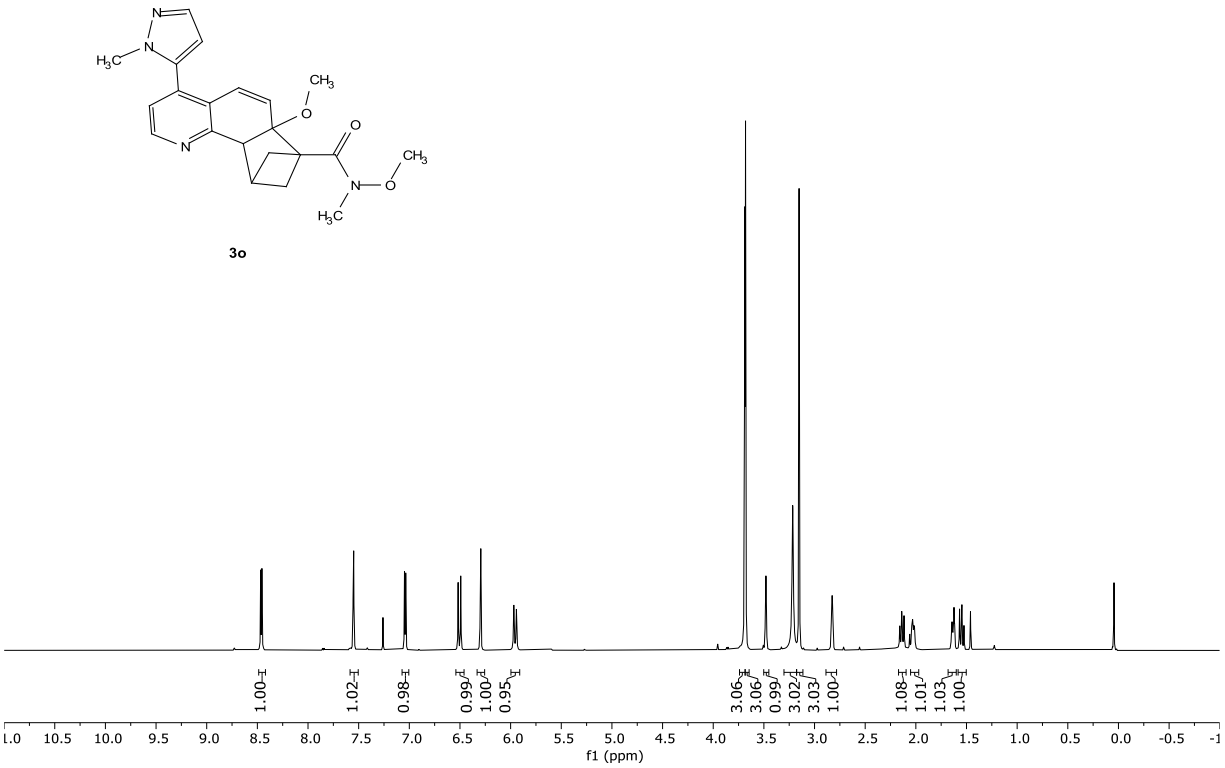
3n, ^{1}H NMR (599 MHz, $CDCl_3$)



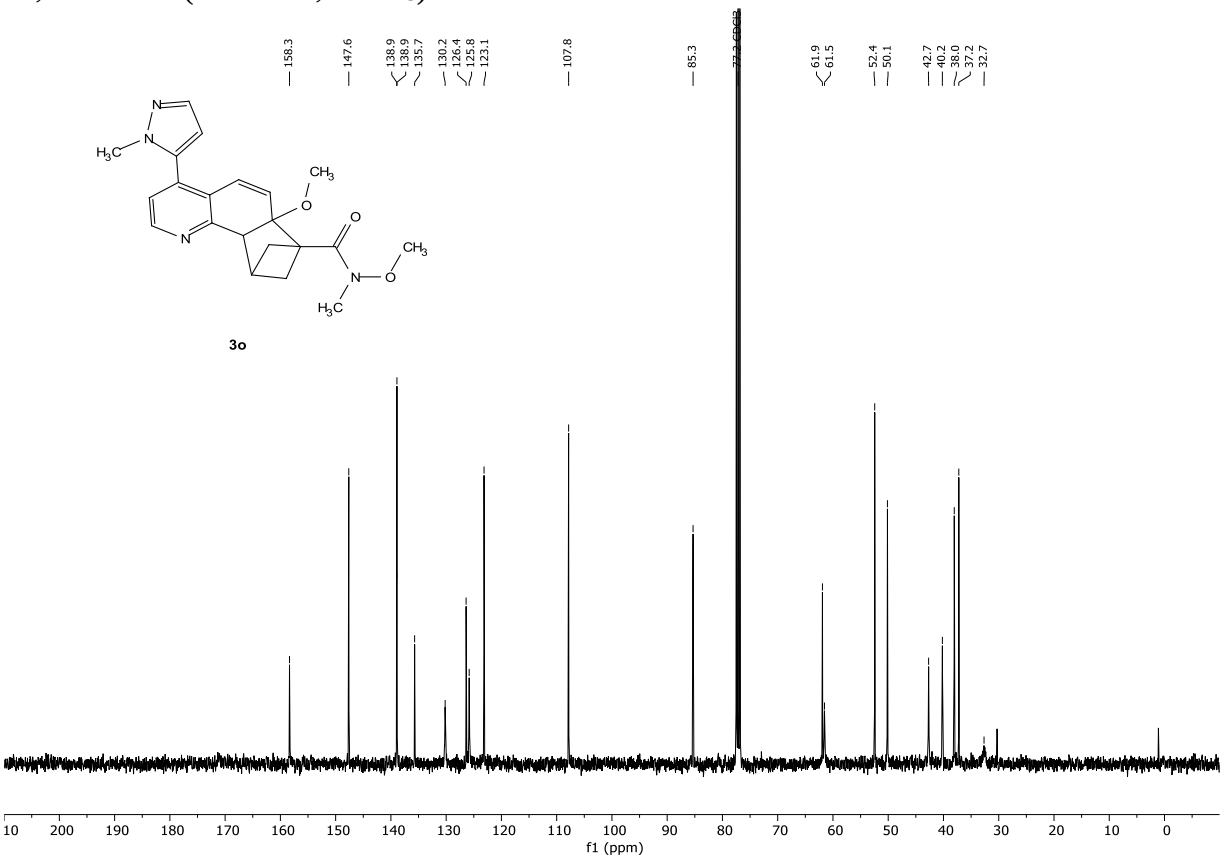
3n, ^{13}C NMR (151 MHz, $CDCl_3$)



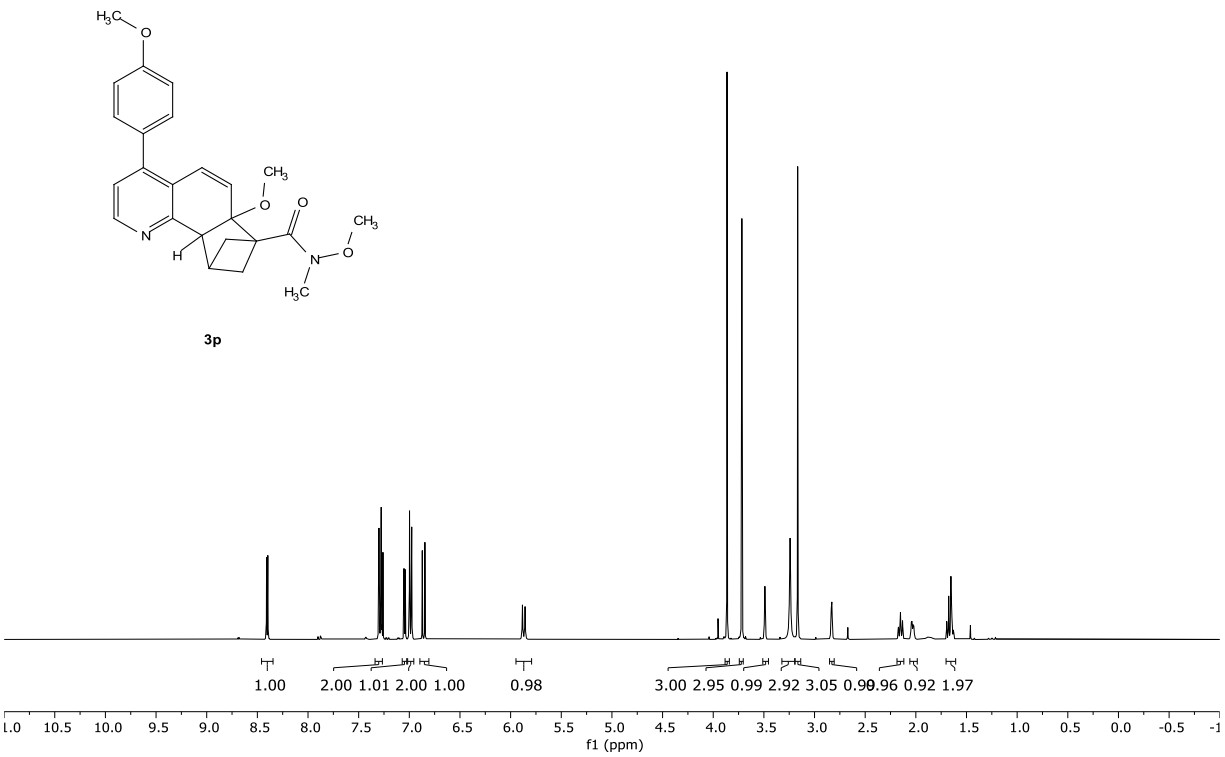
3o, ^{1}H NMR (400 MHz, $CDCl_3$)



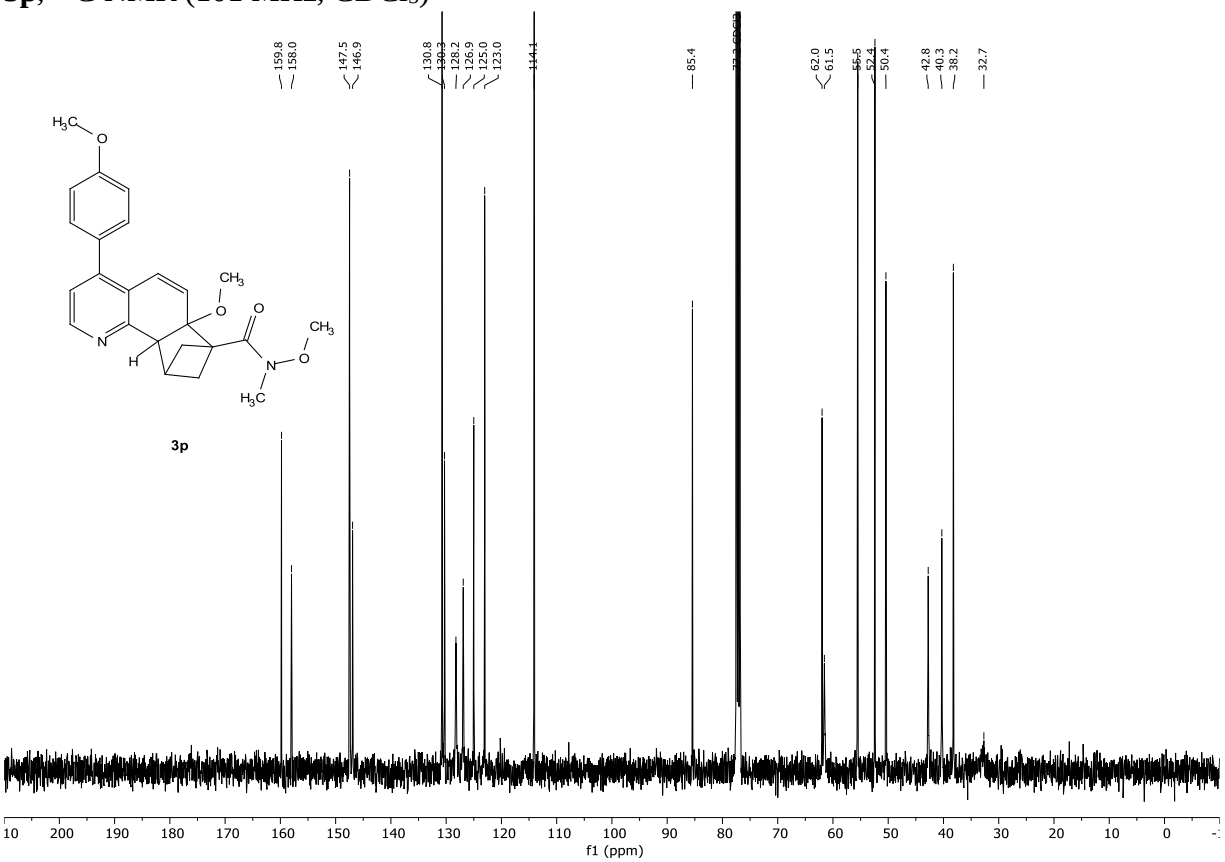
3o, ^{13}C NMR (101 MHz, $CDCl_3$)



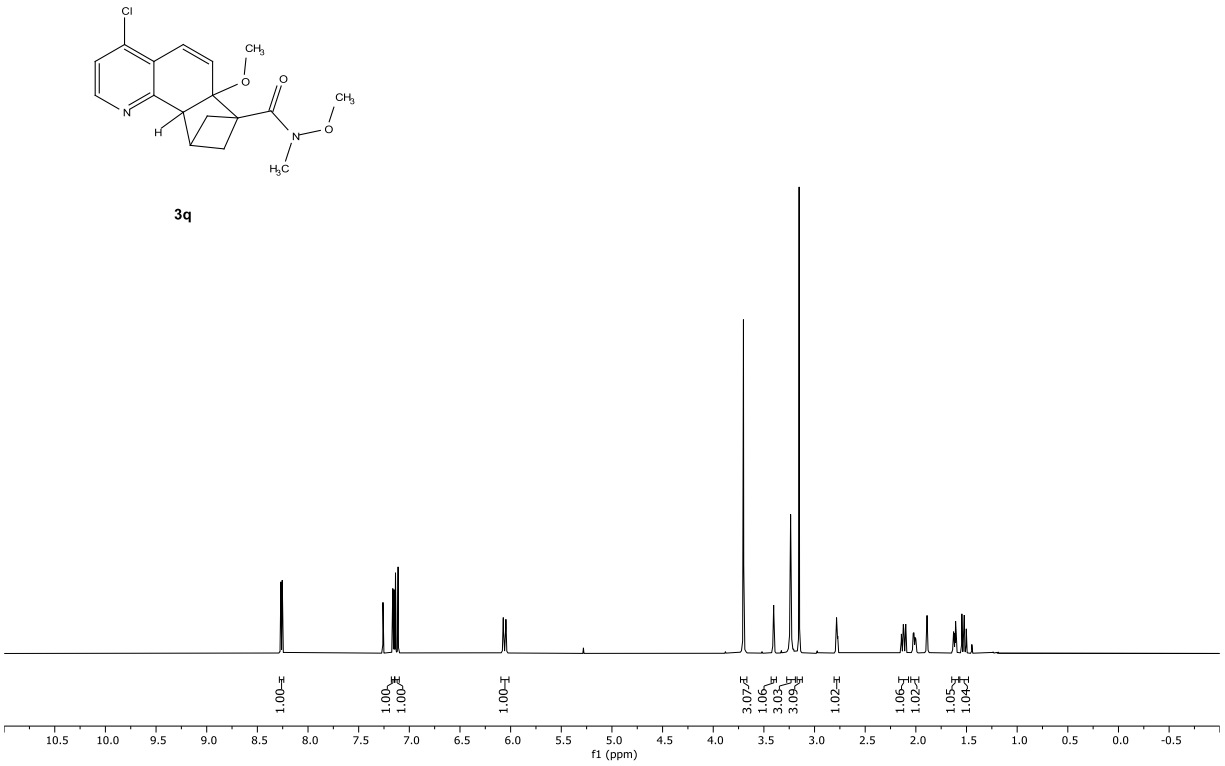
3p, ^{1}H NMR (400 MHz, $CDCl_3$)



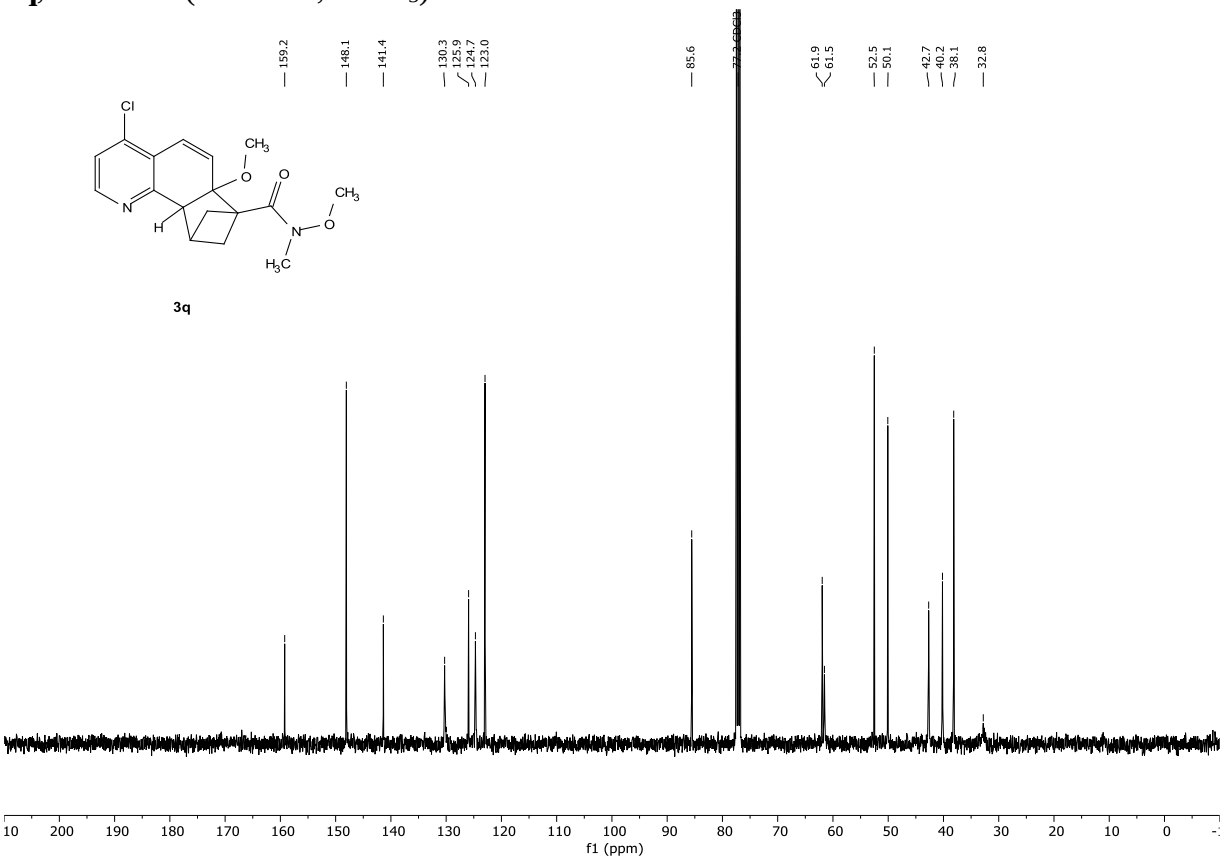
3p, ^{13}C NMR (101 MHz, $CDCl_3$)



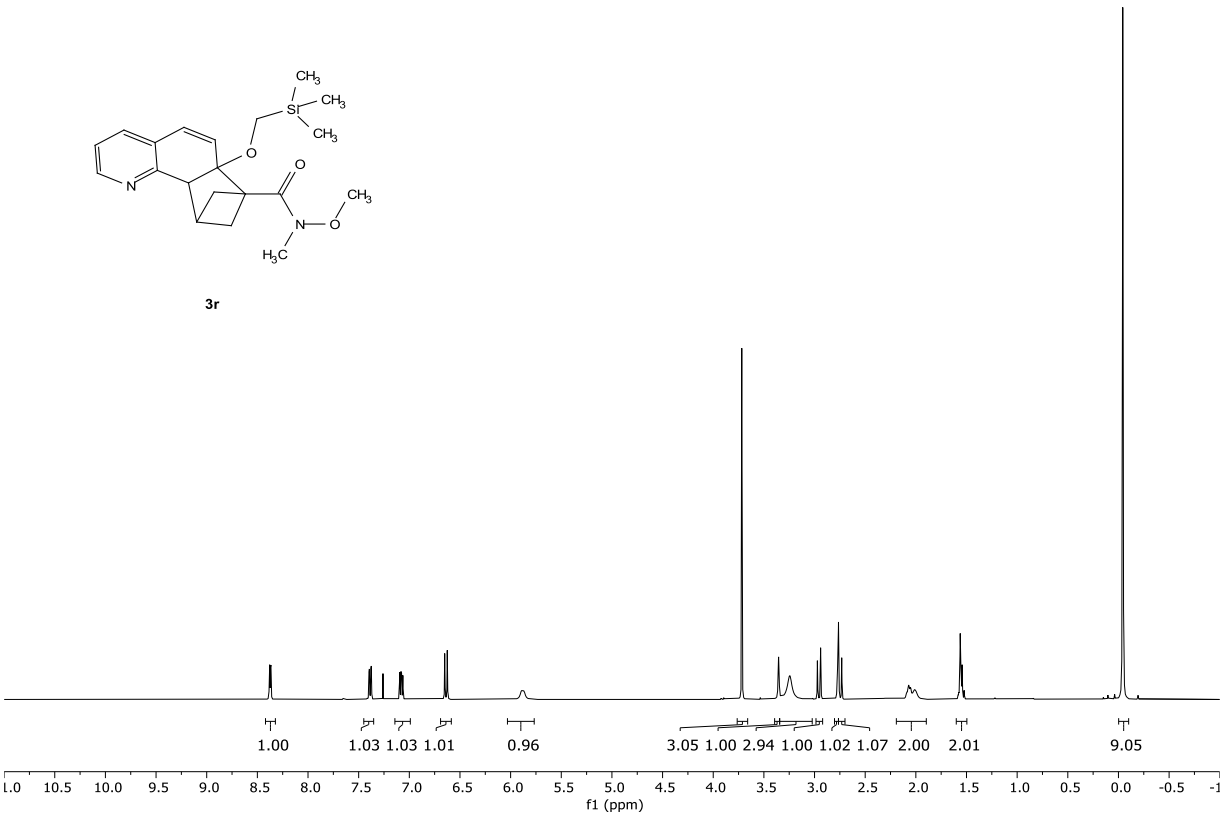
3q, ^{1}H NMR (400 MHz, $CDCl_3$)



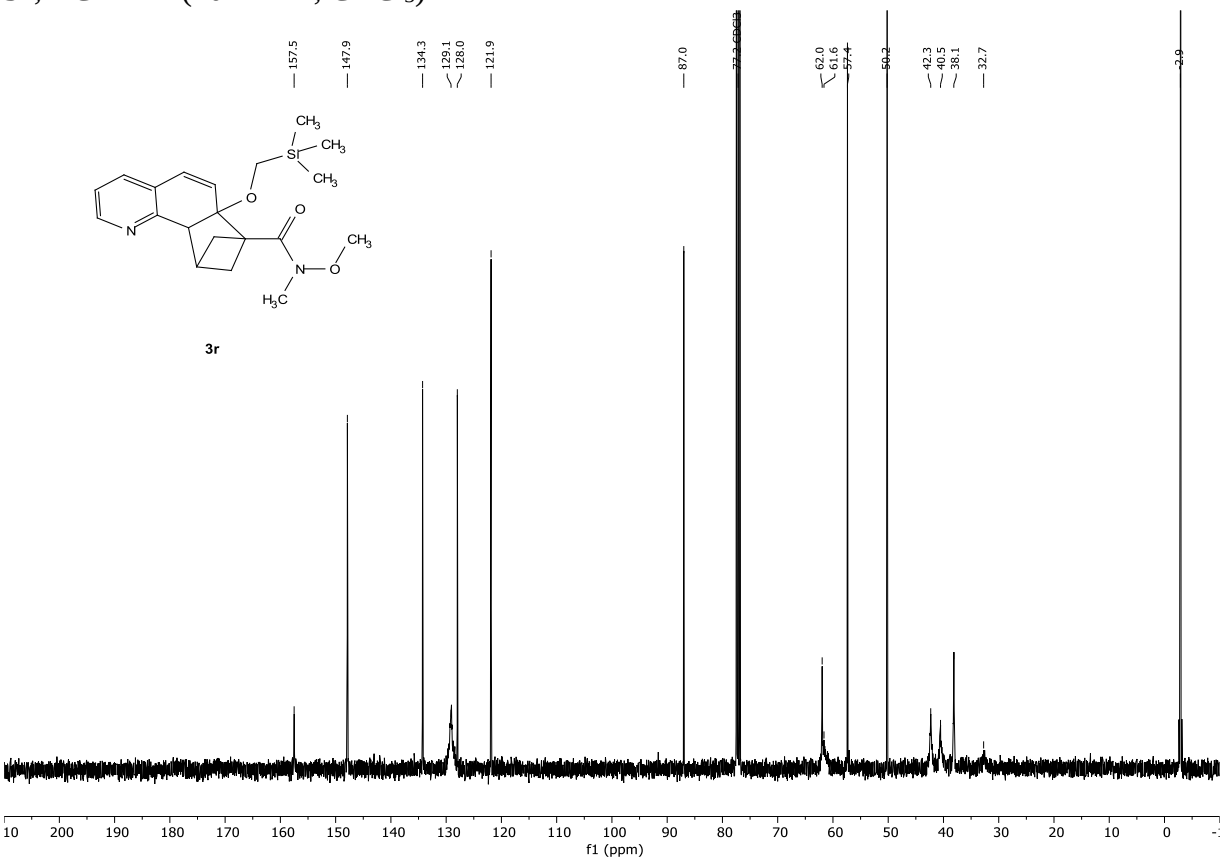
3q, ^{13}C NMR (101 MHz, $CDCl_3$)



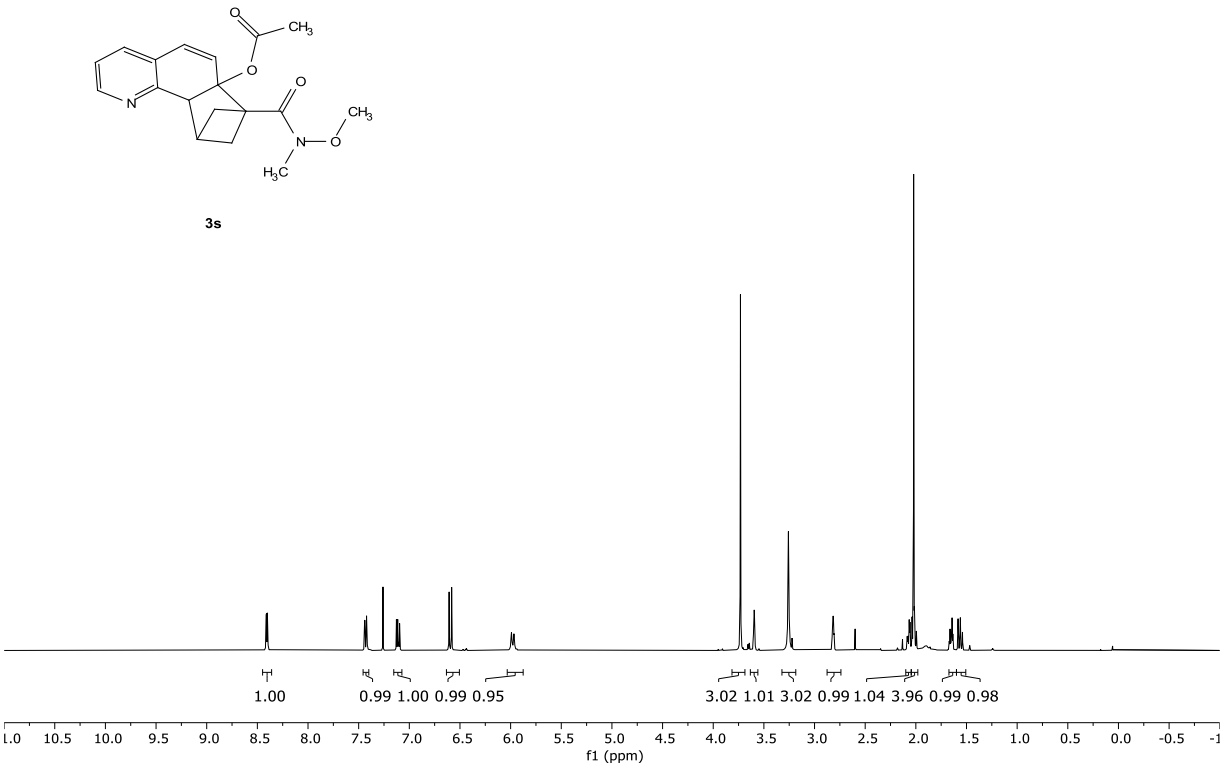
3r, ^{1}H NMR (400 MHz, $CDCl_3$)



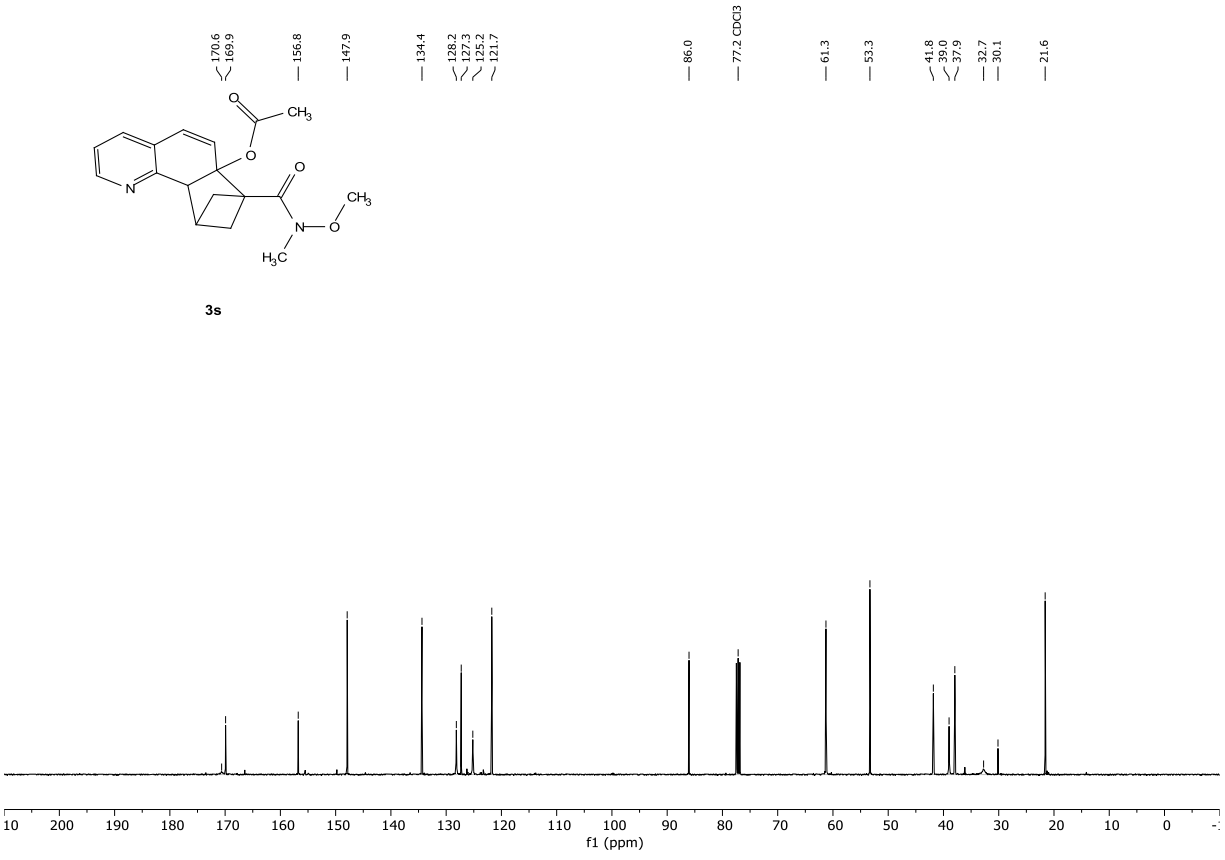
3r, ^{13}C NMR (101 MHz, $CDCl_3$)



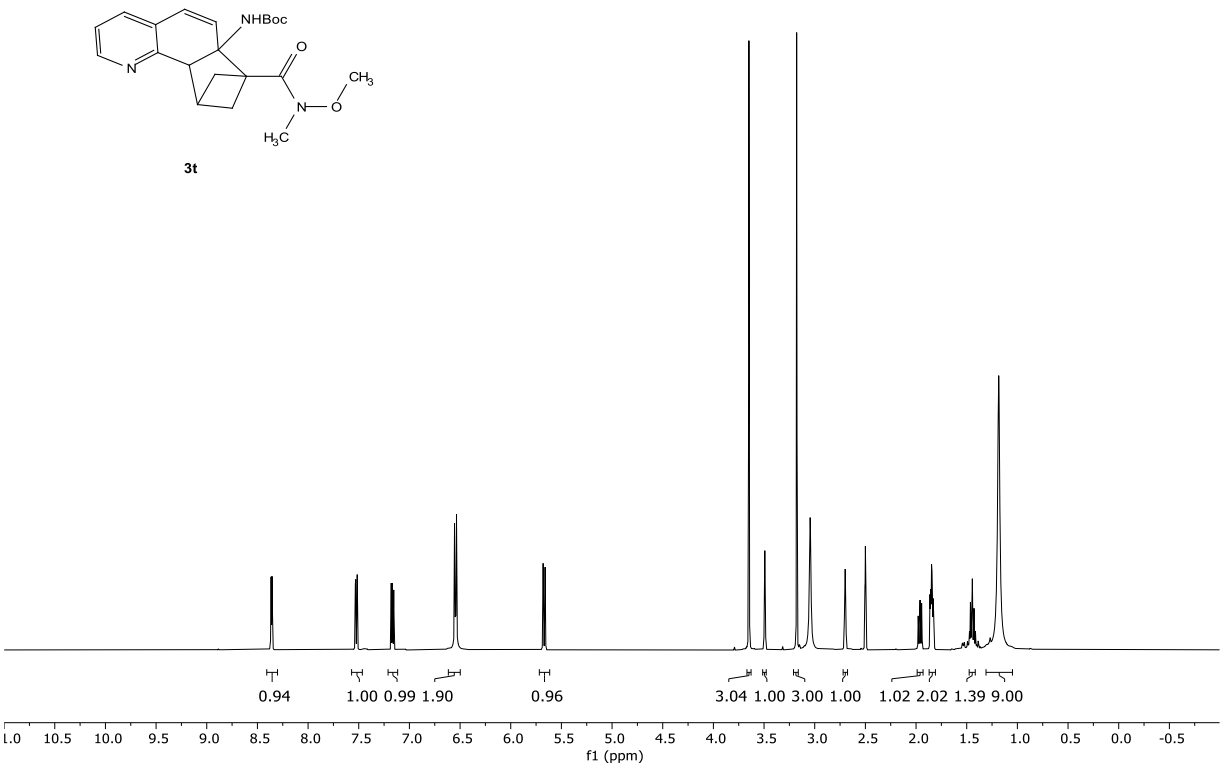
3s, ^{1}H NMR (400 MHz, $CDCl_3$)



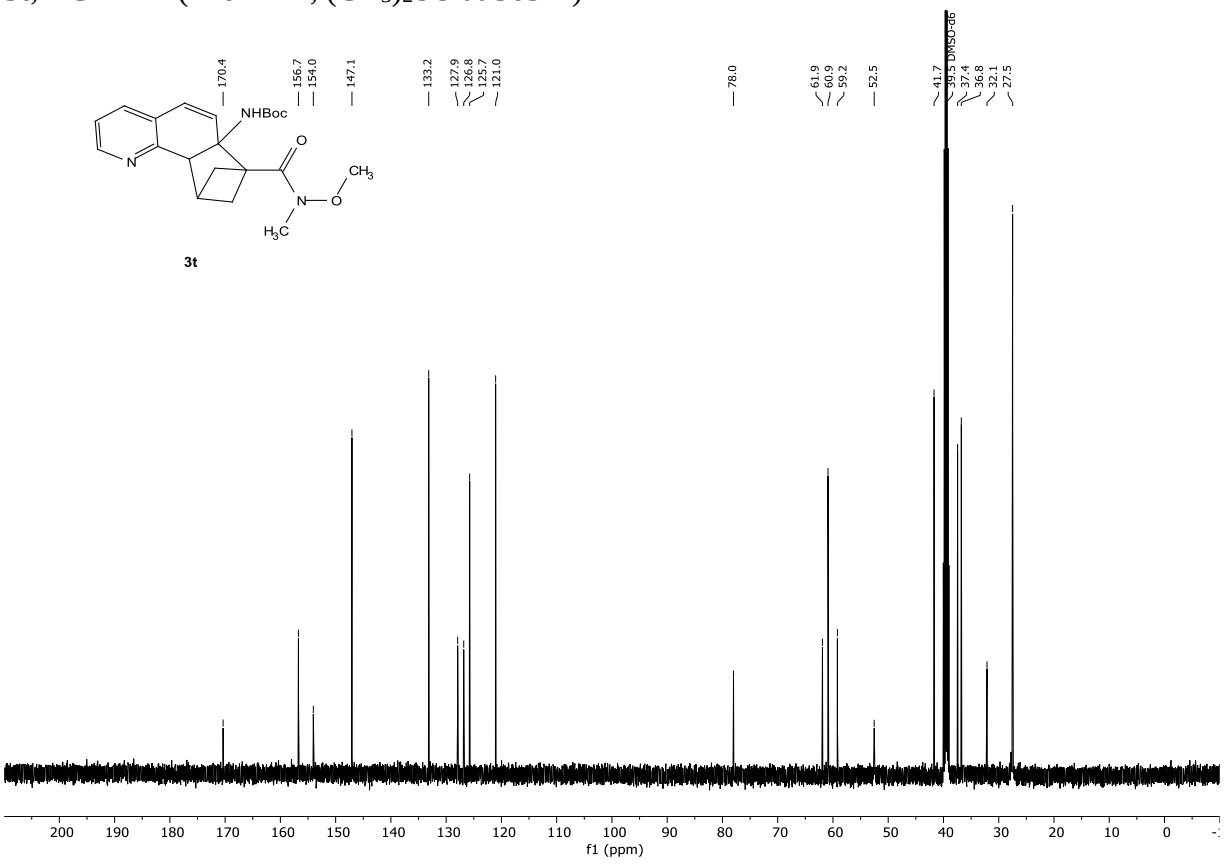
3s, ^{13}C NMR (101 MHz, $CDCl_3$)



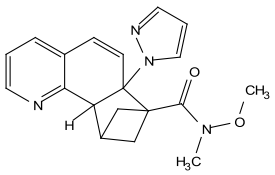
3t, ^{1}H NMR (500 MHz, $(CD_3)_2SO$ at 363 K)



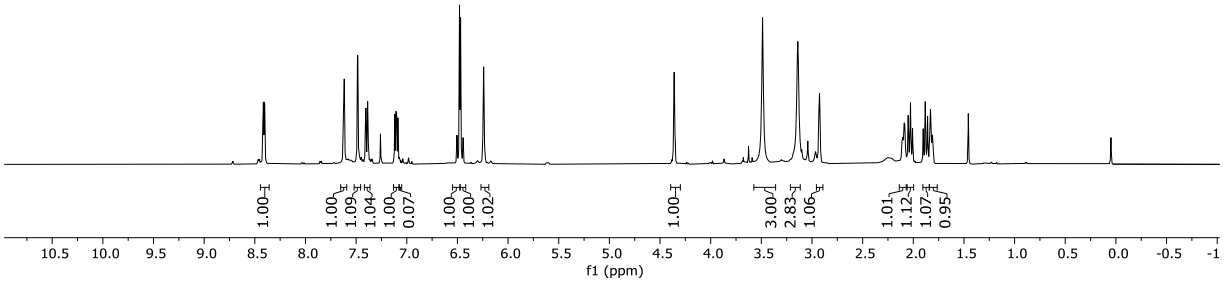
3t, ^{13}C NMR (126 MHz, $(CD_3)_2SO$ at 363 K)



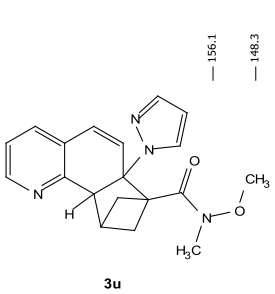
3u, ^{1}H NMR (400 MHz, $CDCl_3$)



3u

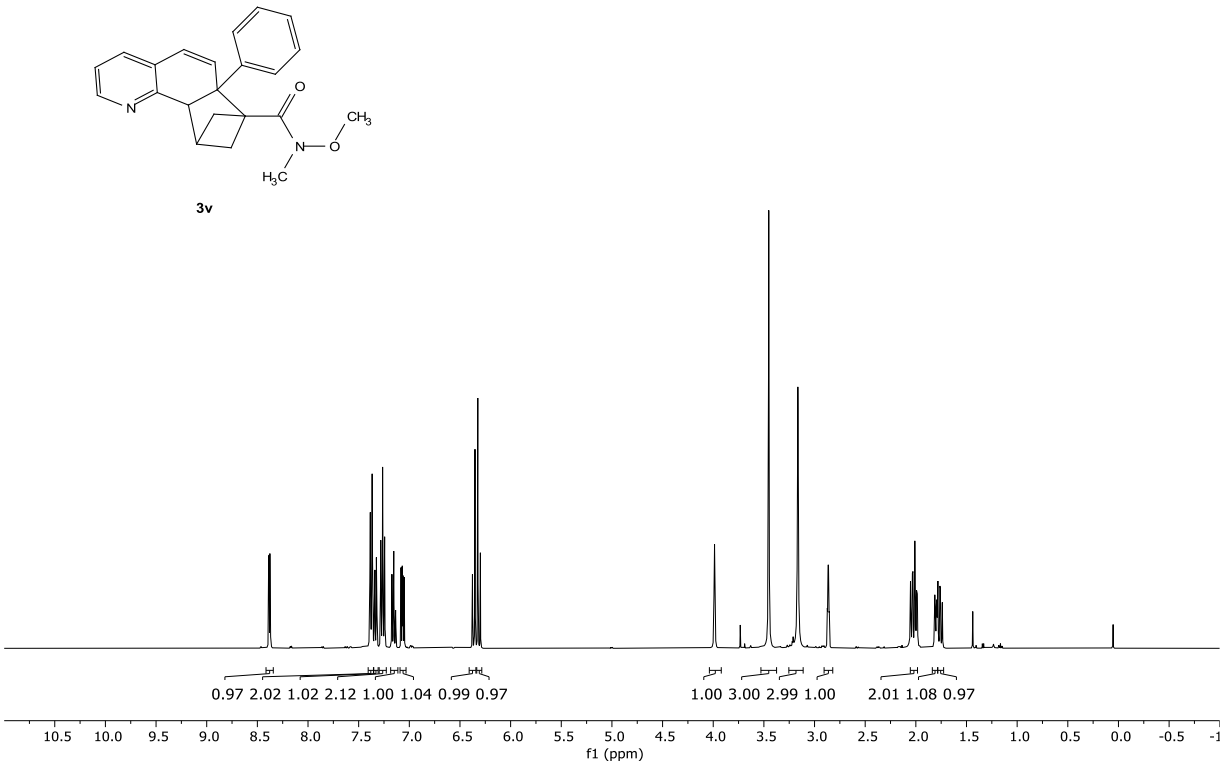


3u, ^{13}C NMR (101 MHz, $CDCl_3$)

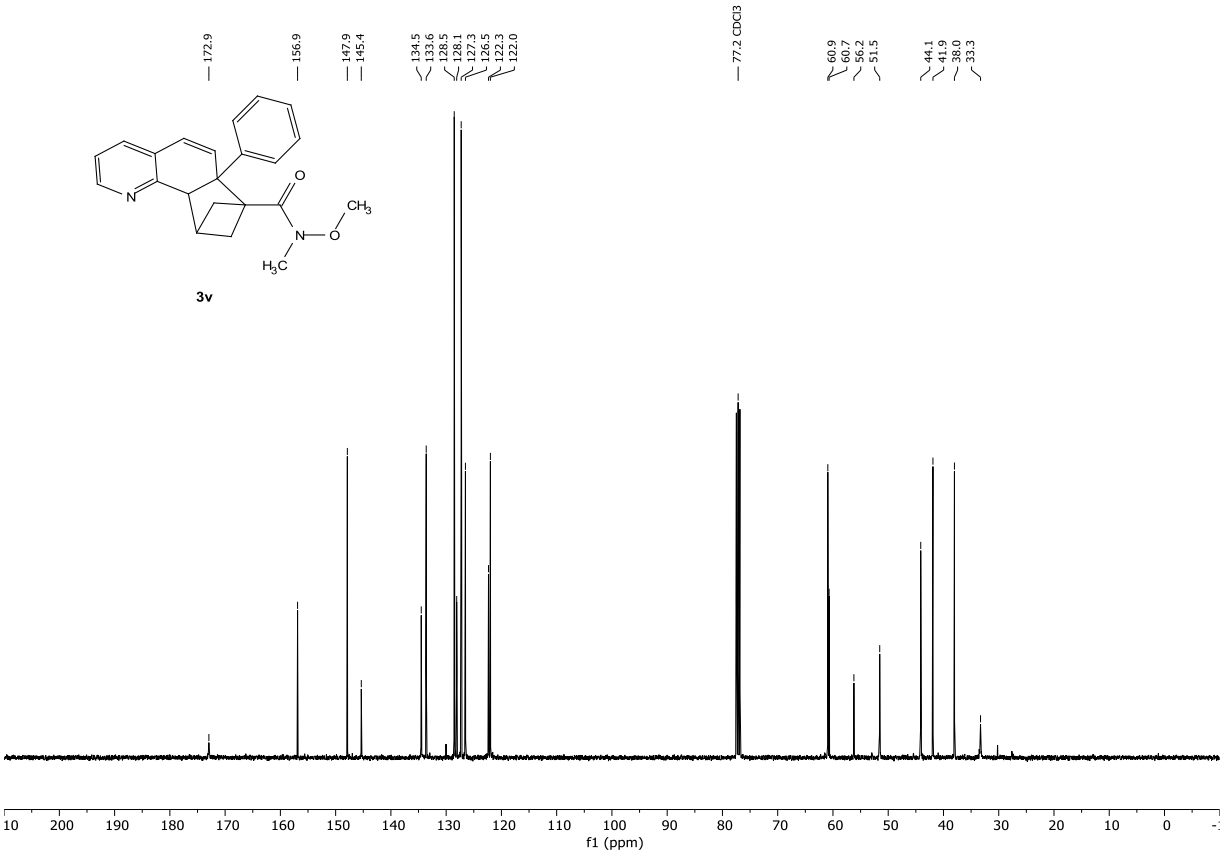


3u

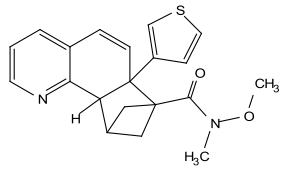
3v, ^{1}H NMR (400 MHz, $CDCl_3$)



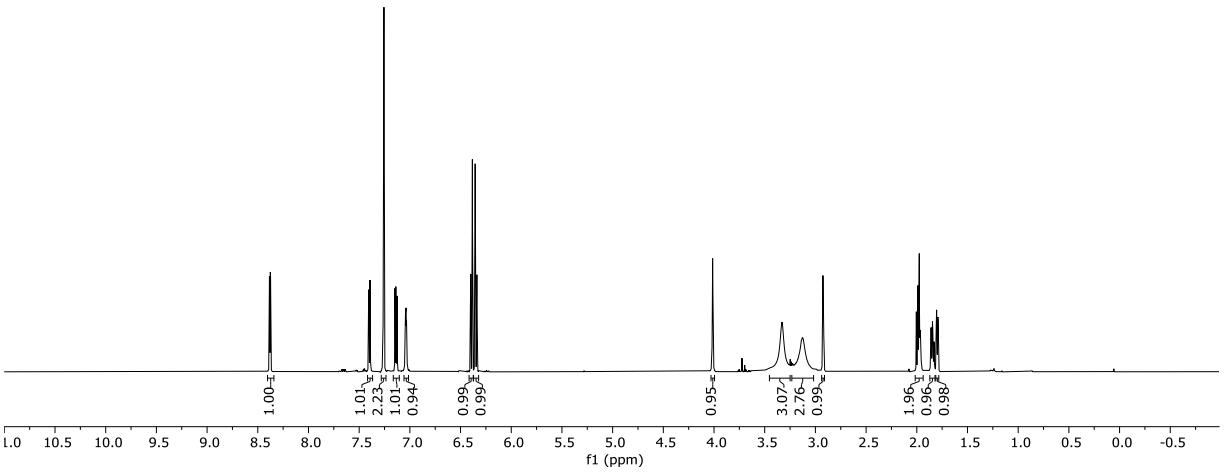
3v, ^{13}C NMR (101 MHz, $CDCl_3$)



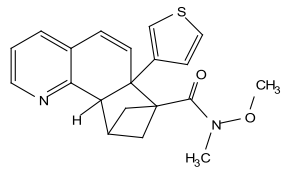
3w, ^{1}H NMR (599 MHz, $CDCl_3$)



3w

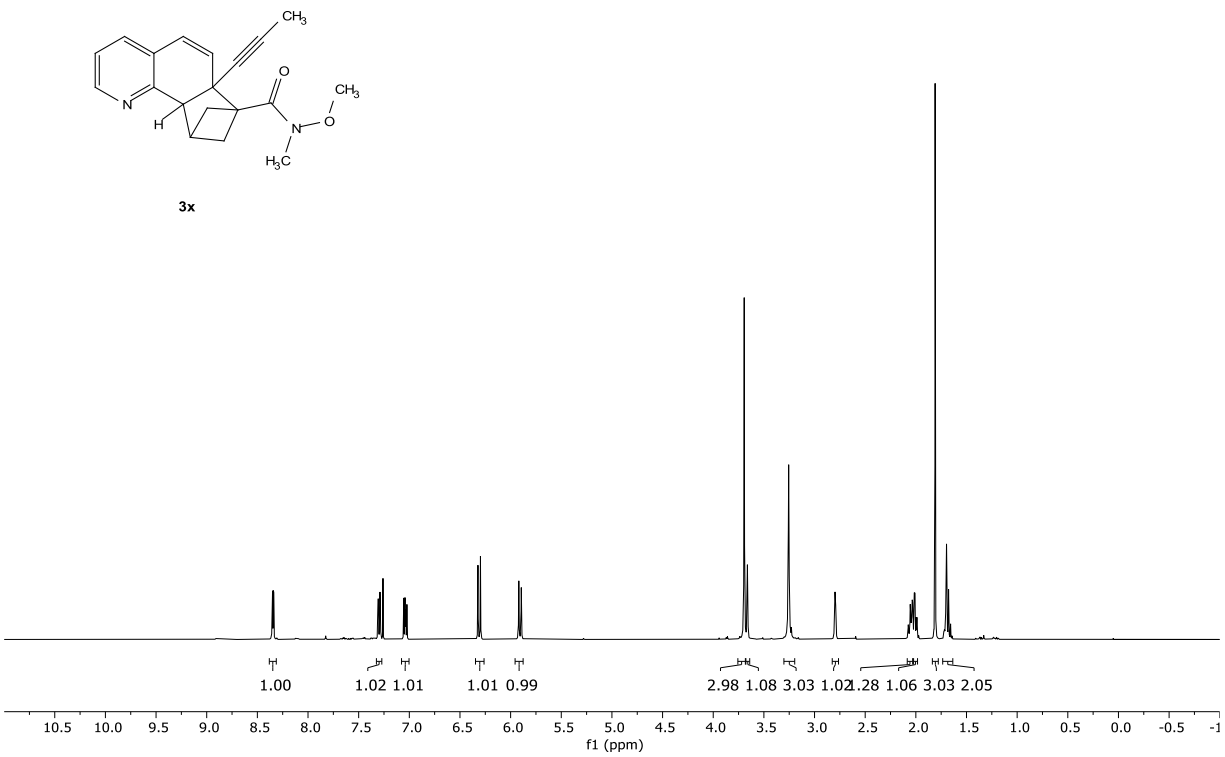


3w, ^{13}C NMR (151 MHz, $CDCl_3$)

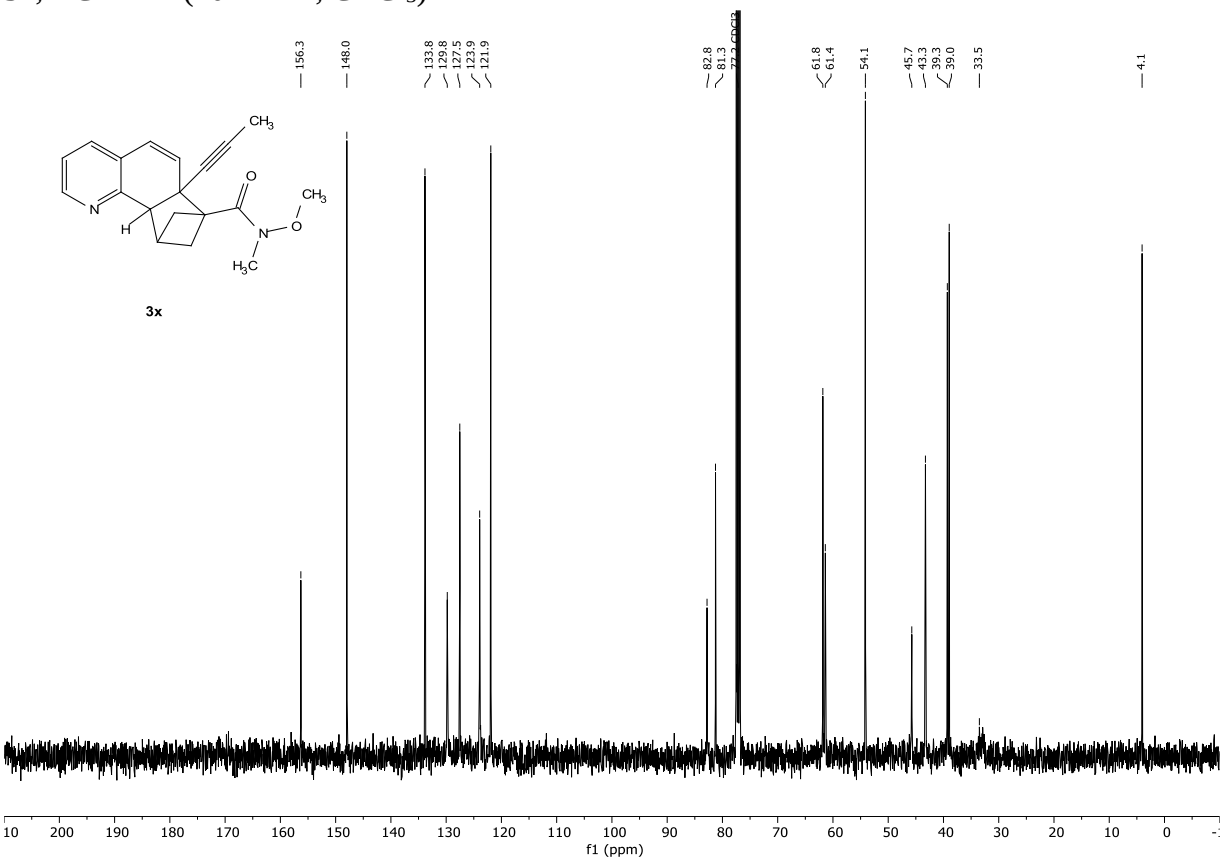


3v

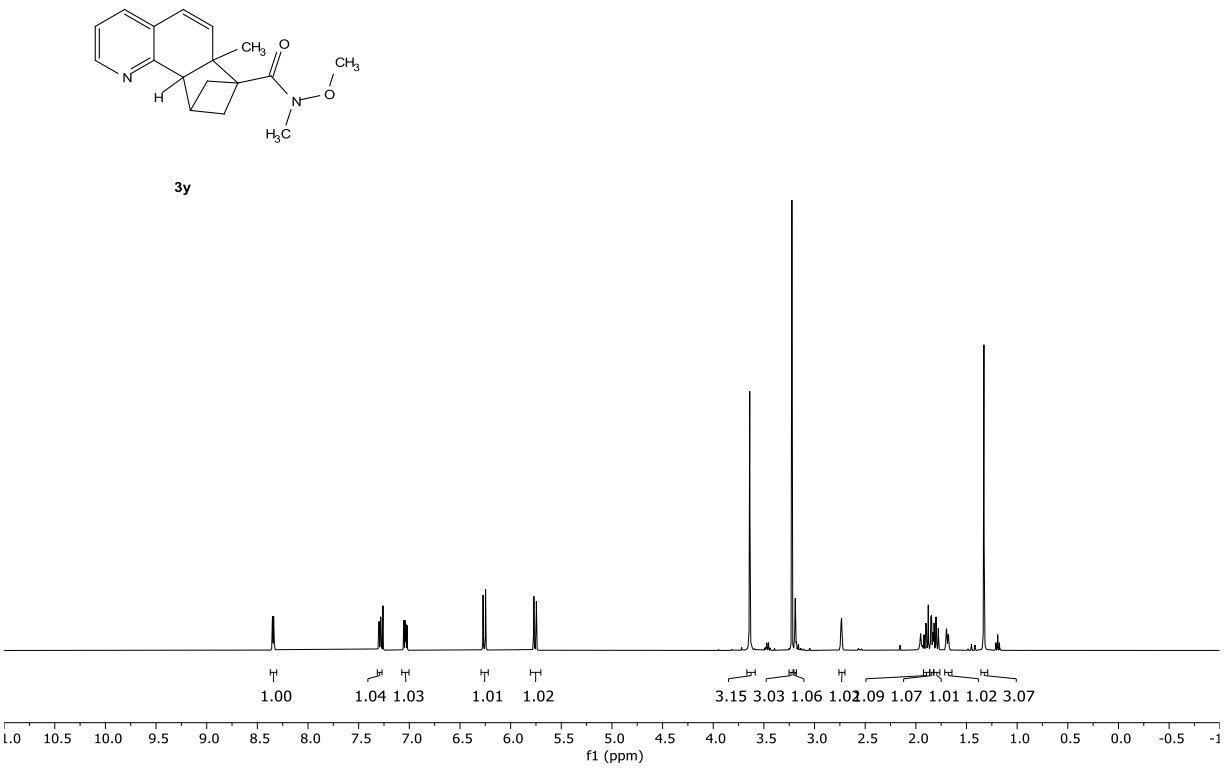
3x, ^{1}H NMR (400 MHz, $CDCl_3$)



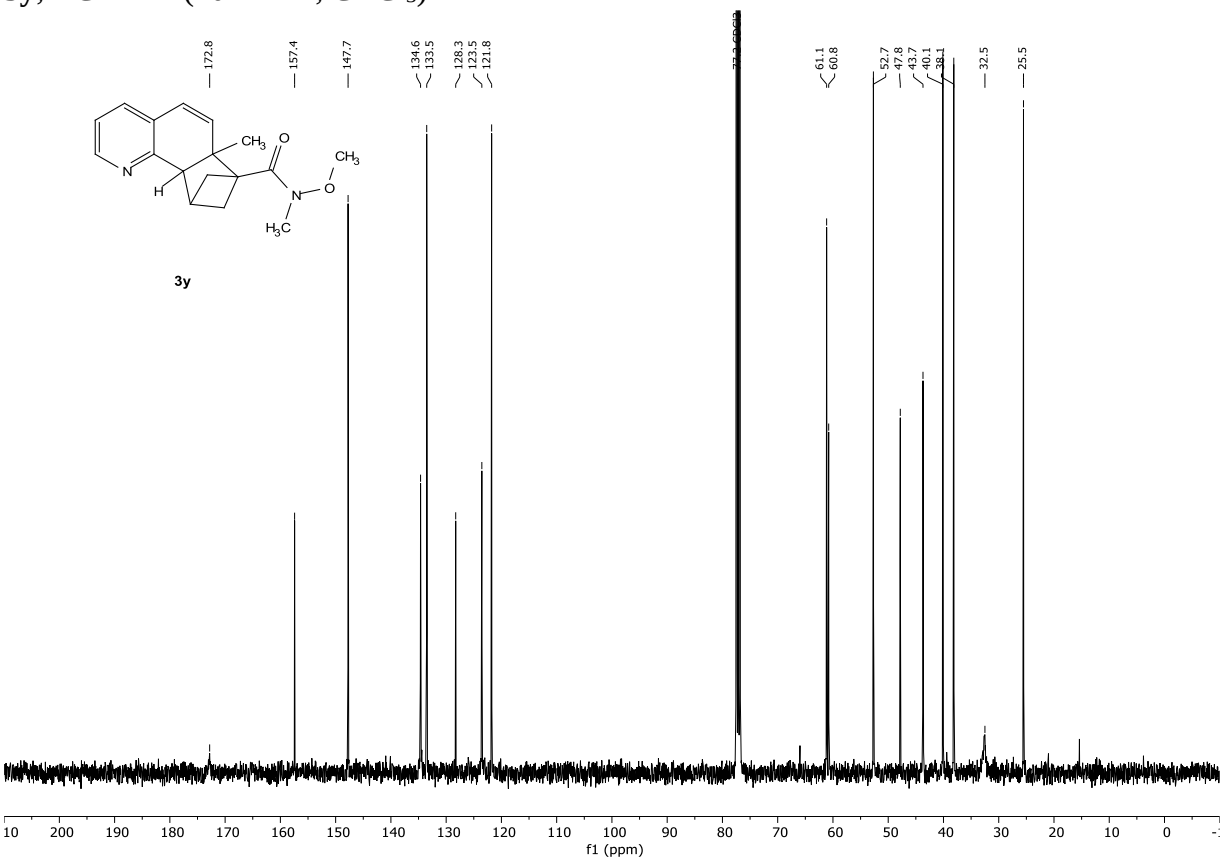
3x, ^{13}C NMR (101 MHz, $CDCl_3$)



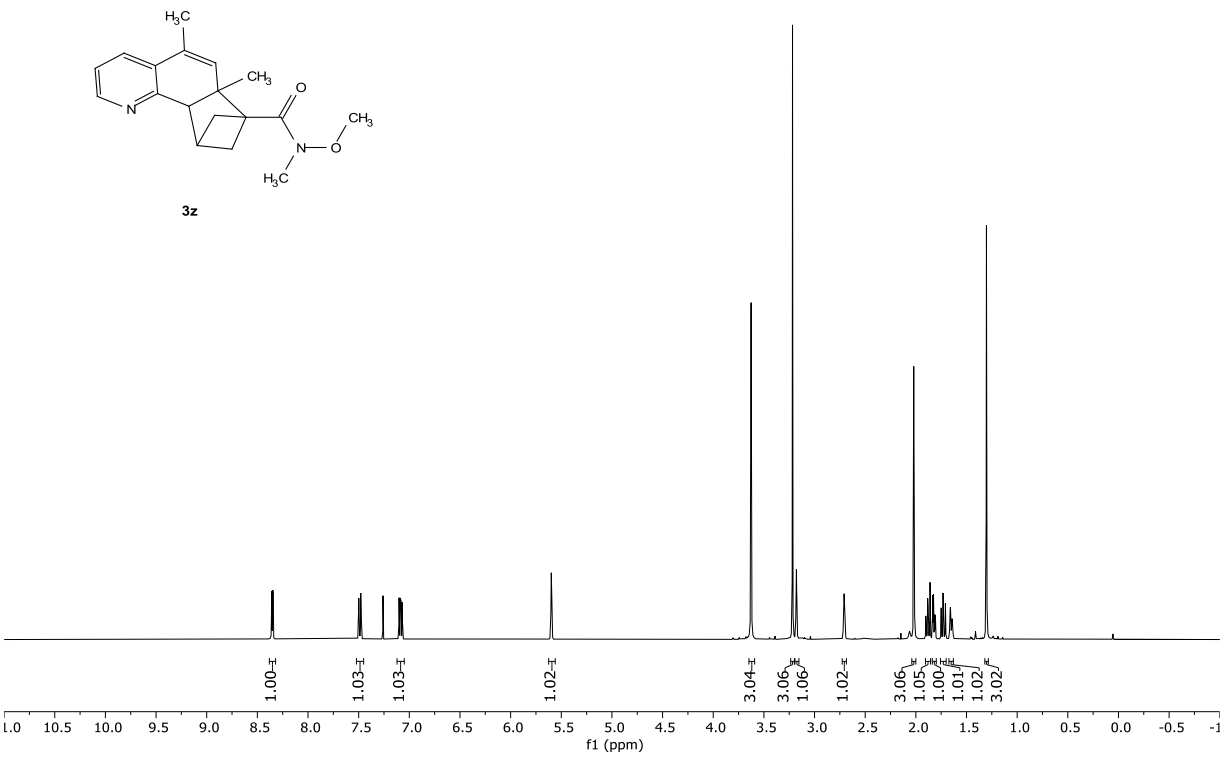
3y, ^{1}H NMR (400 MHz, $CDCl_3$)



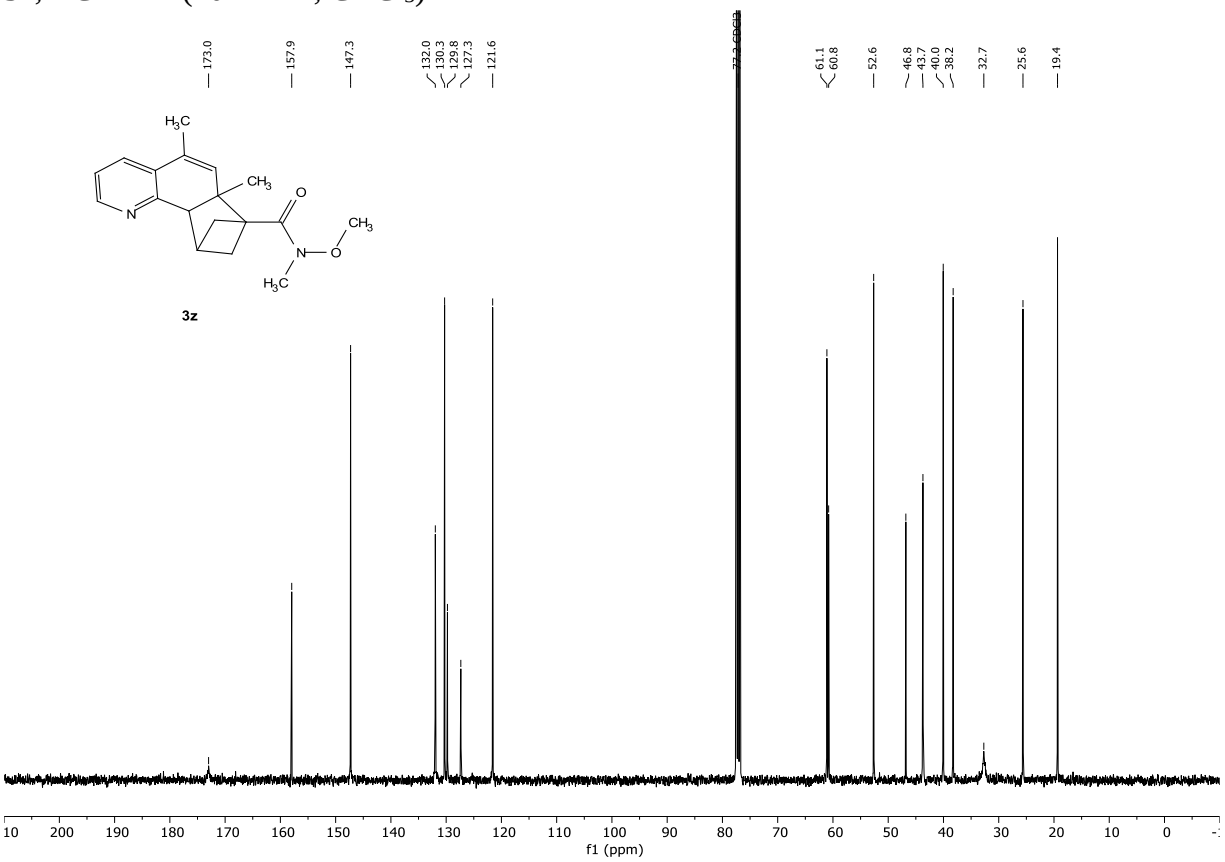
3y, ^{13}C NMR (101 MHz, $CDCl_3$)



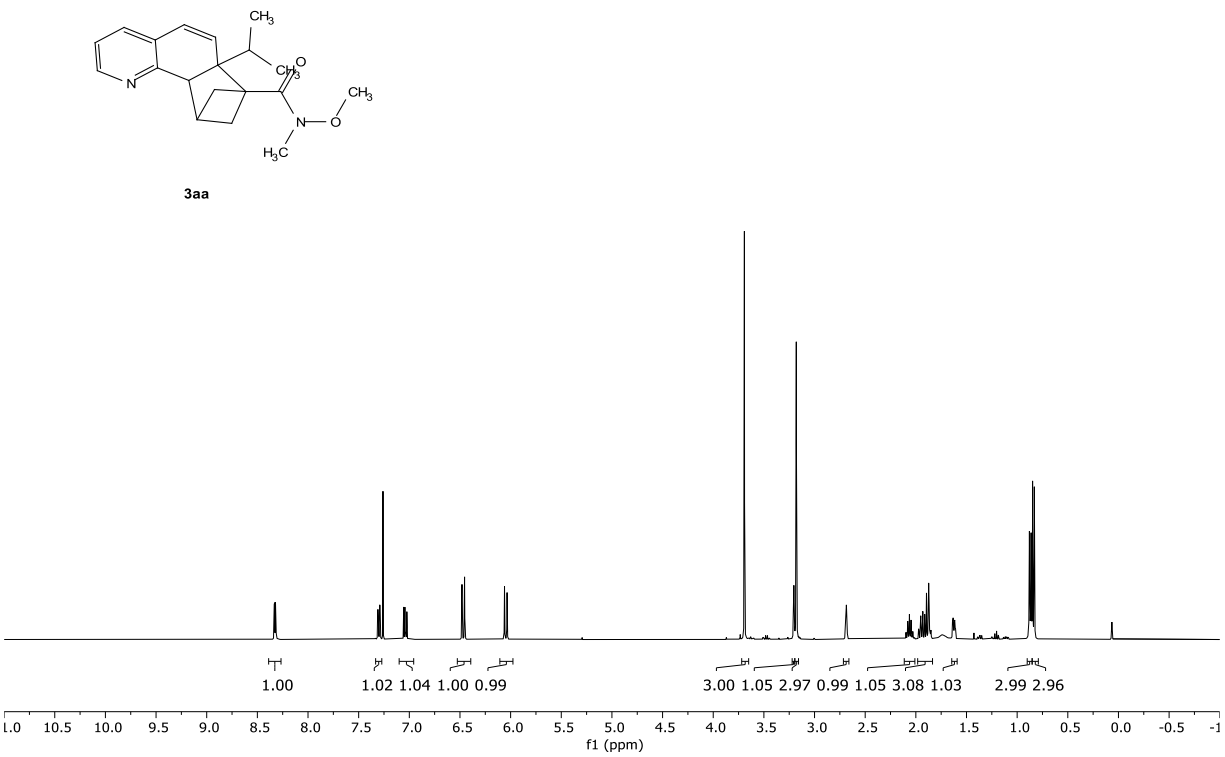
3z, ^{1}H NMR (400 MHz, $CDCl_3$)



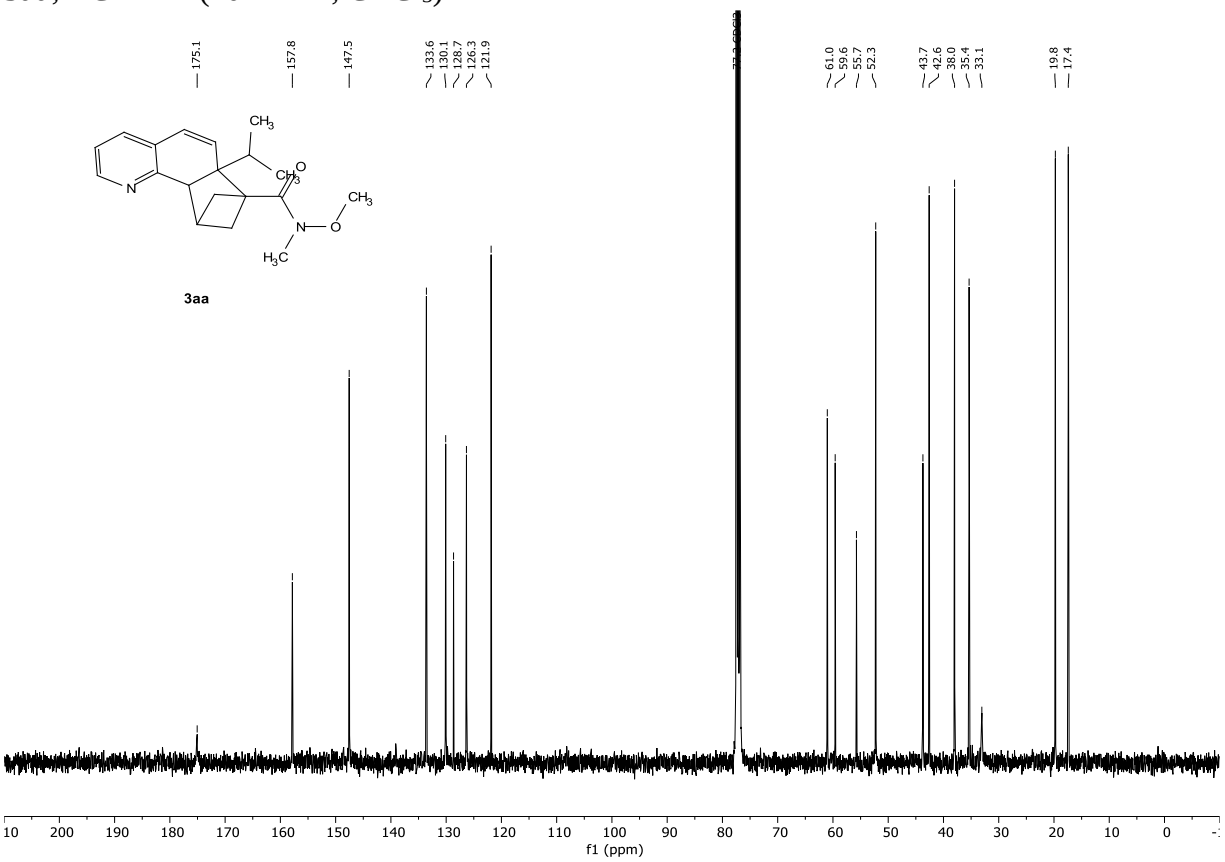
3z, ^{13}C NMR (101 MHz, $CDCl_3$)



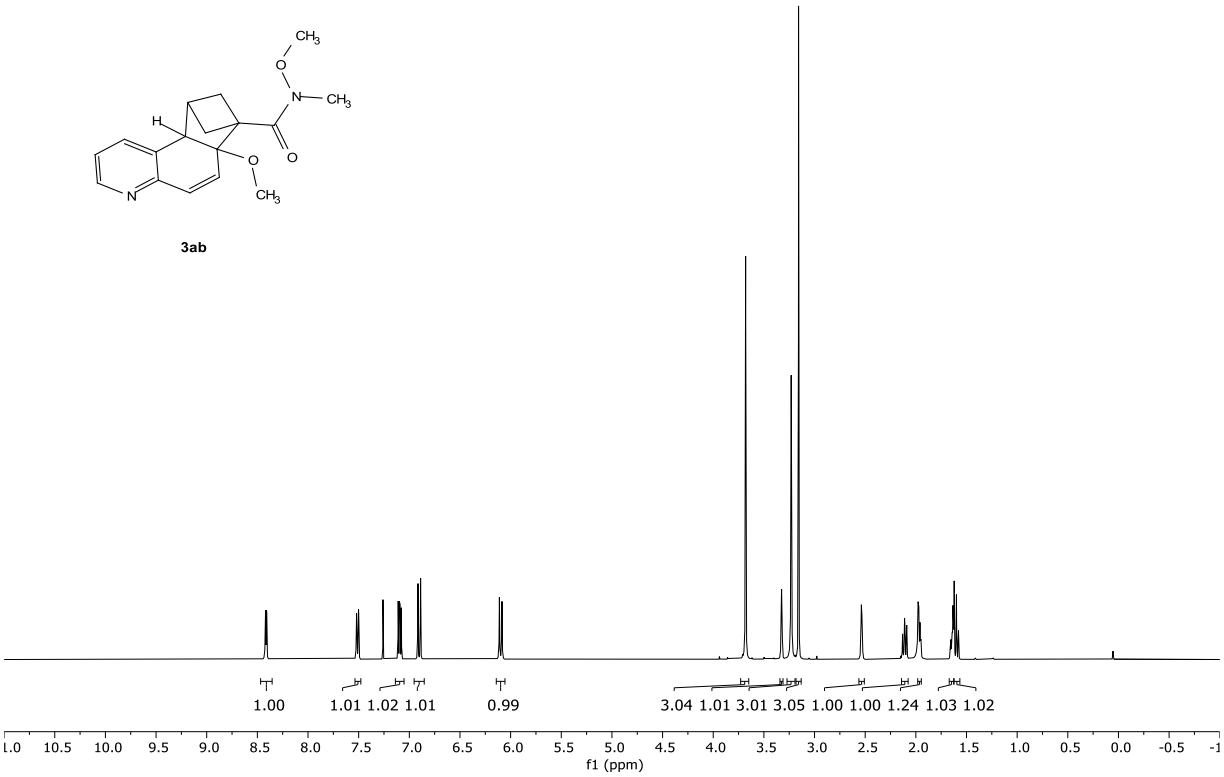
3aa, ^{1}H NMR (400 MHz, $CDCl_3$)



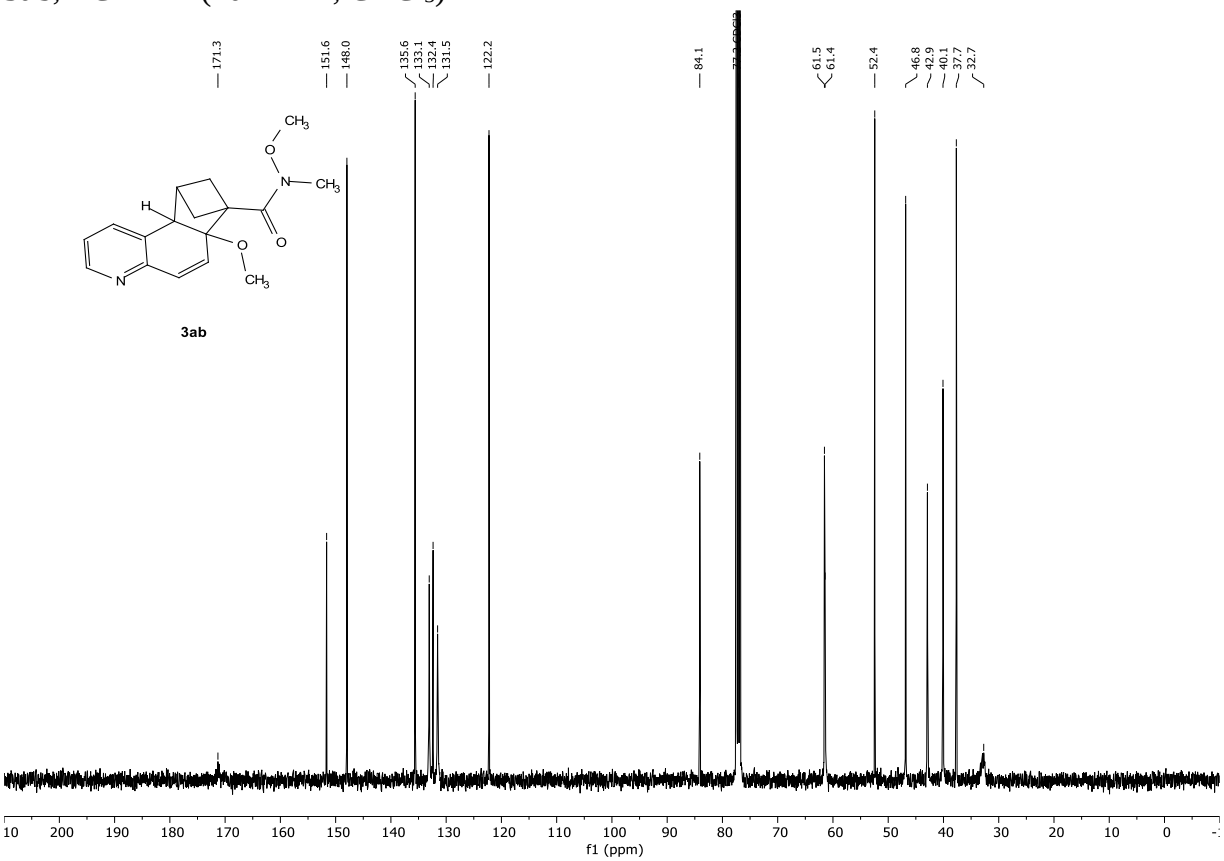
3aa, ^{13}C NMR (101 MHz, $CDCl_3$)



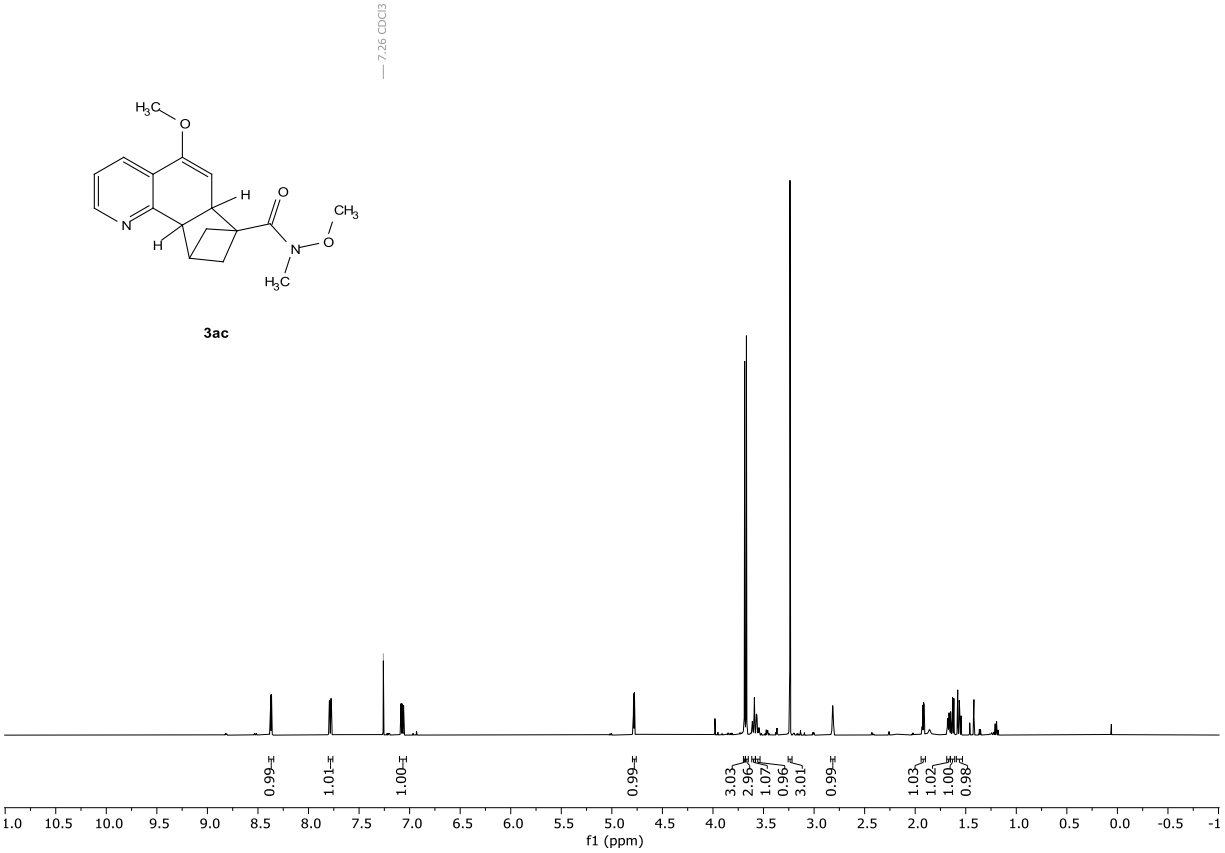
3ab, ^{1}H NMR (400 MHz, $CDCl_3$)



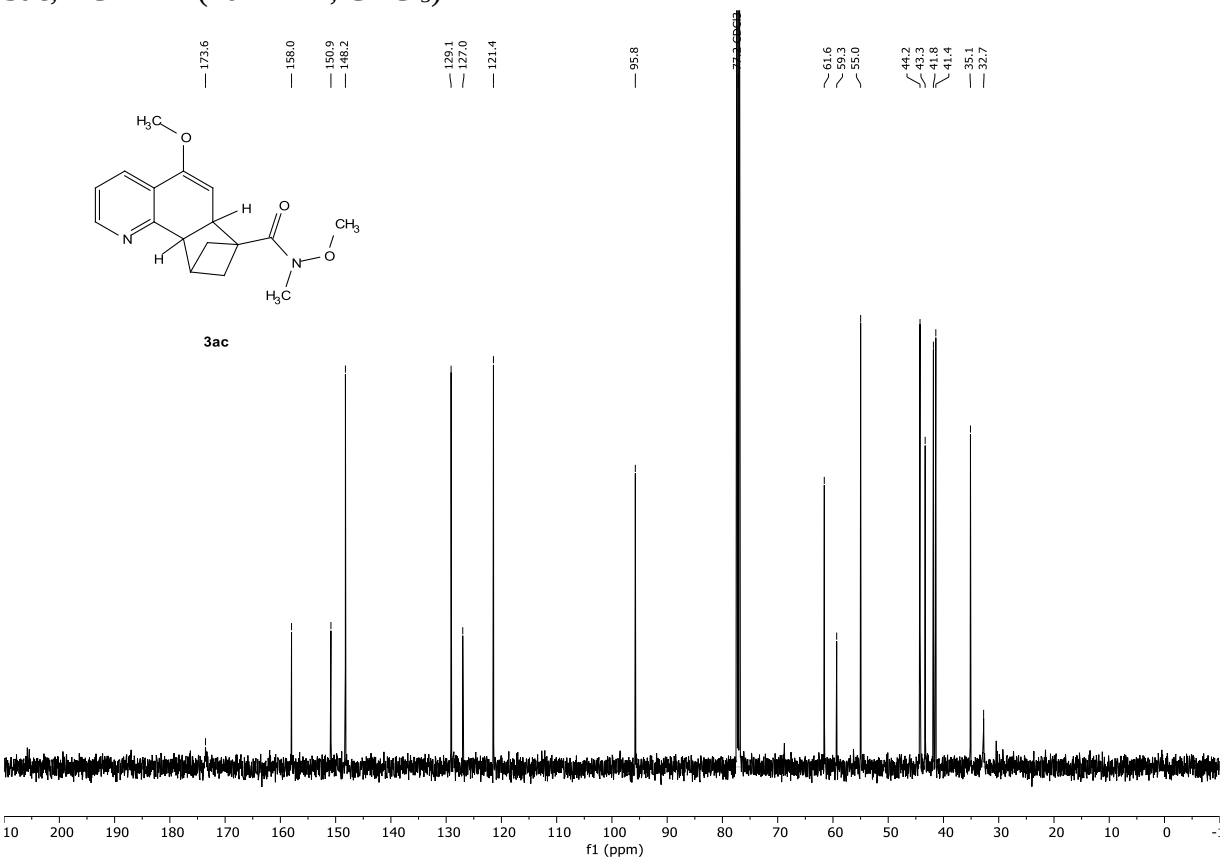
3ab, ^{13}C NMR (101 MHz, $CDCl_3$)



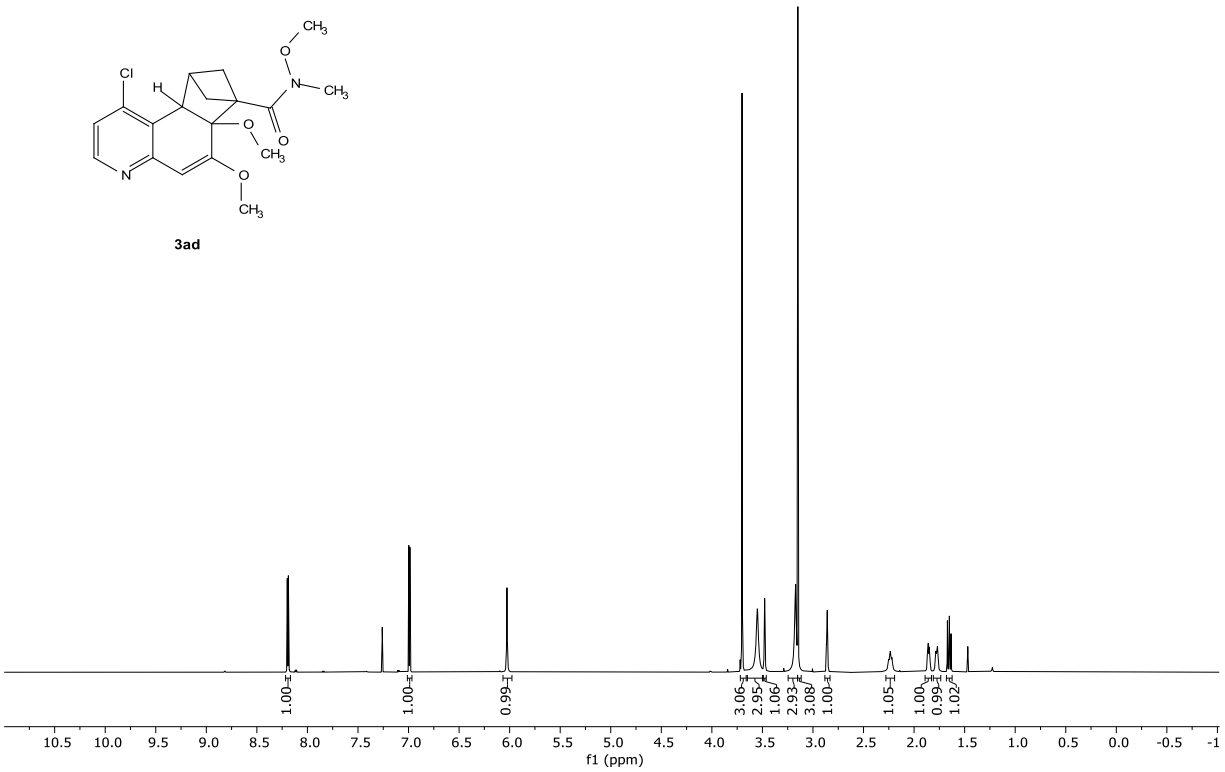
3ac, ^{1}H NMR (400 MHz, $CDCl_3$)



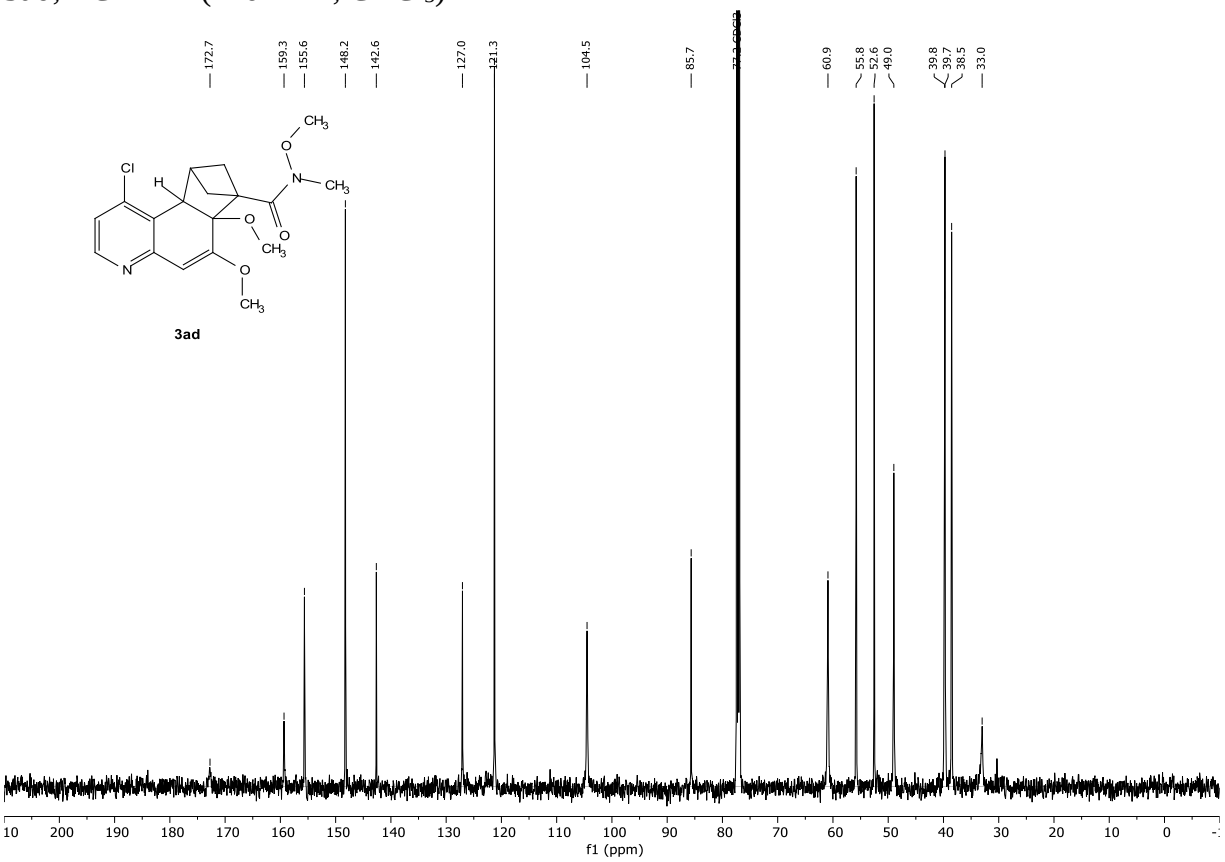
3ac, ^{13}C NMR (101 MHz, $CDCl_3$)



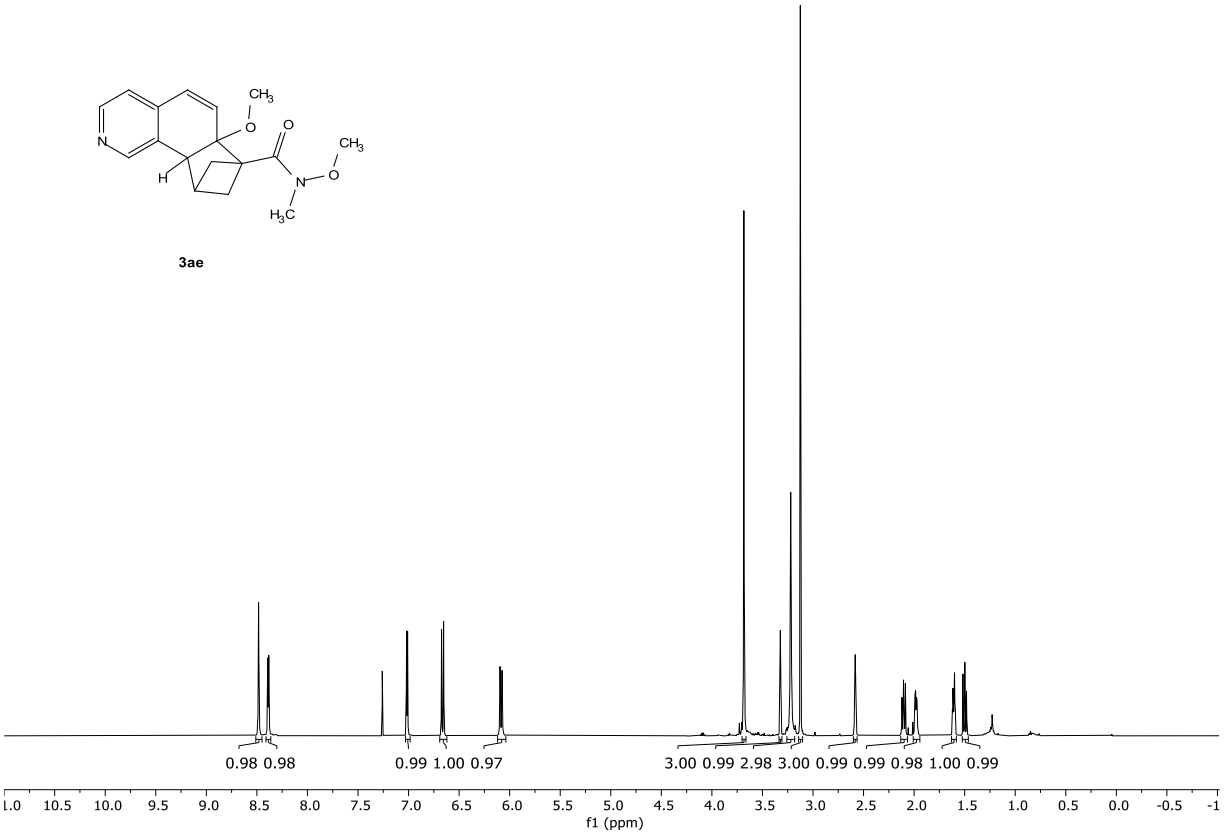
3ad, ^{1}H NMR (500 MHz, $CDCl_3$)



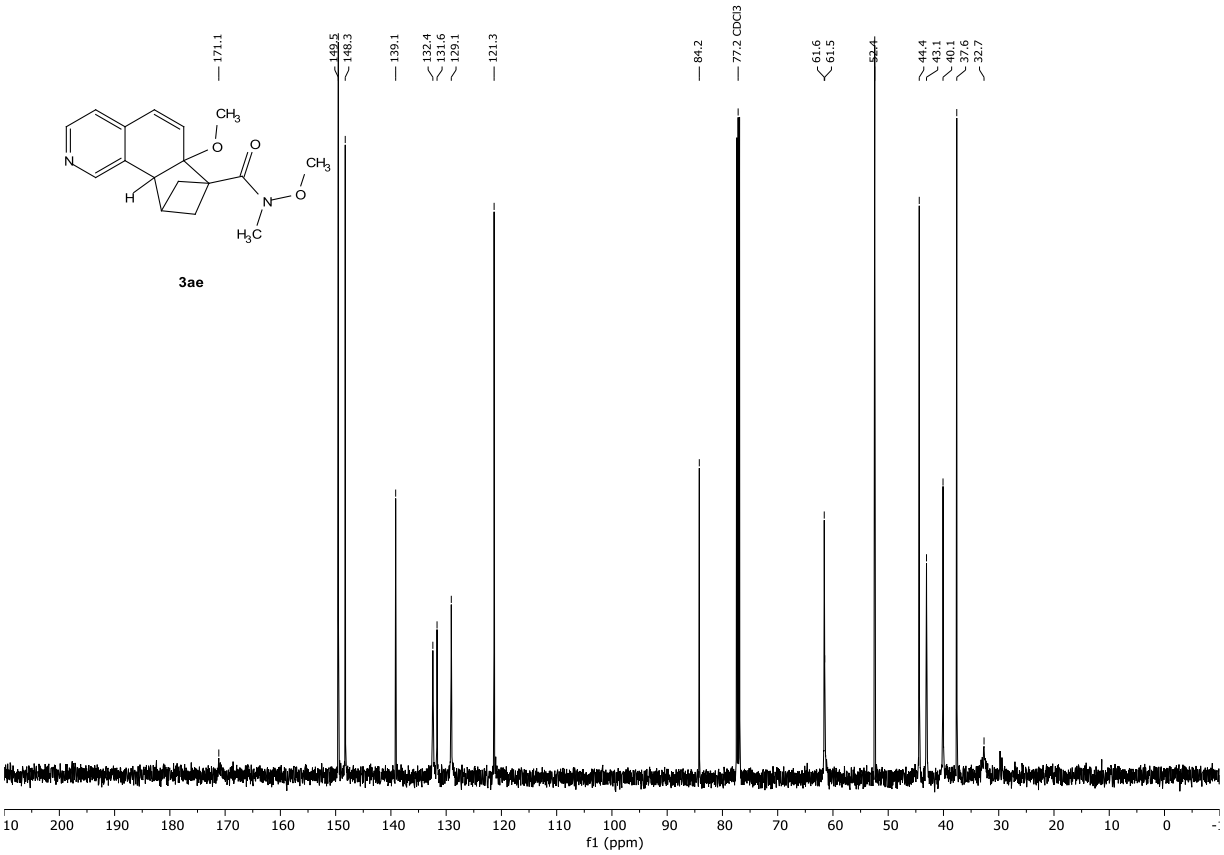
3ad, ^{13}C NMR (126 MHz, $CDCl_3$)



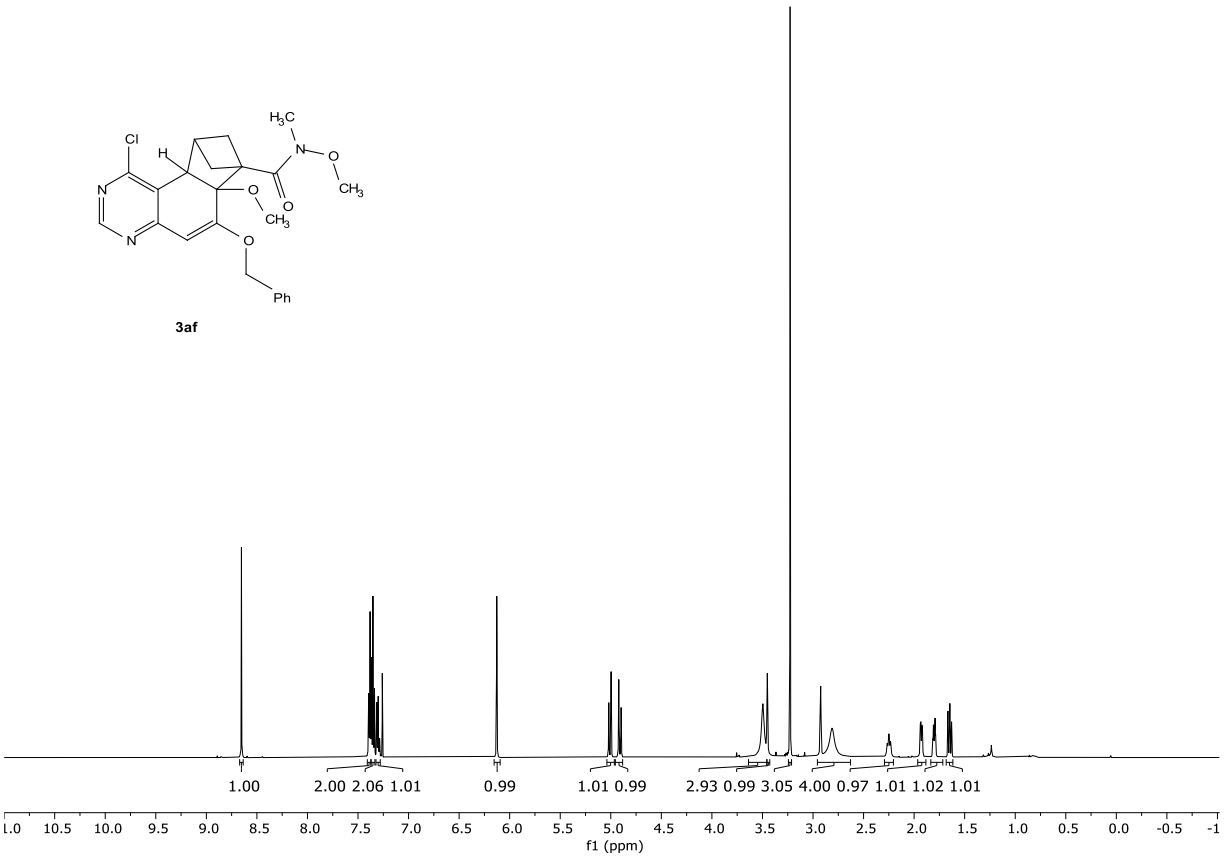
3ae, ^{1}H NMR (500 MHz, $CDCl_3$)



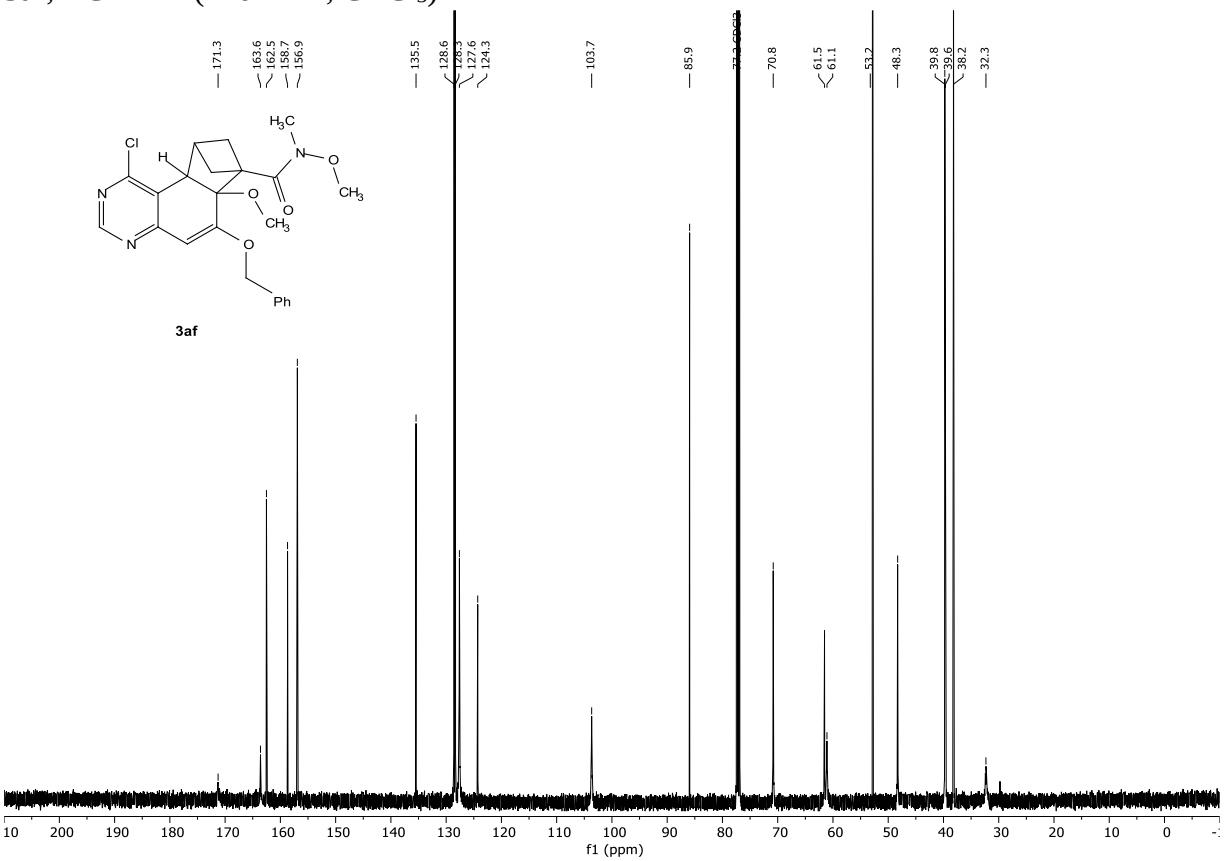
3ae, ^{13}C NMR (126 MHz, $CDCl_3$)



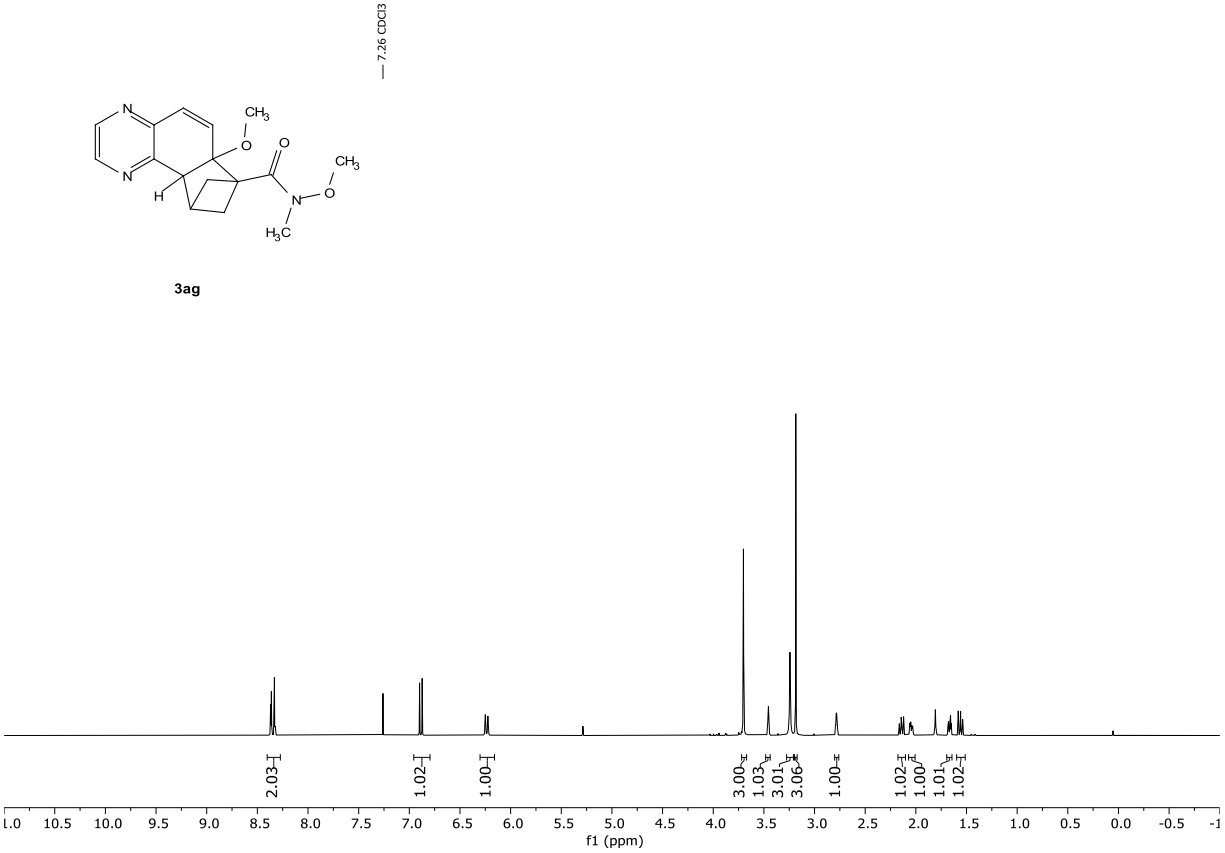
3af, ^{1}H NMR (500 MHz, $CDCl_3$)



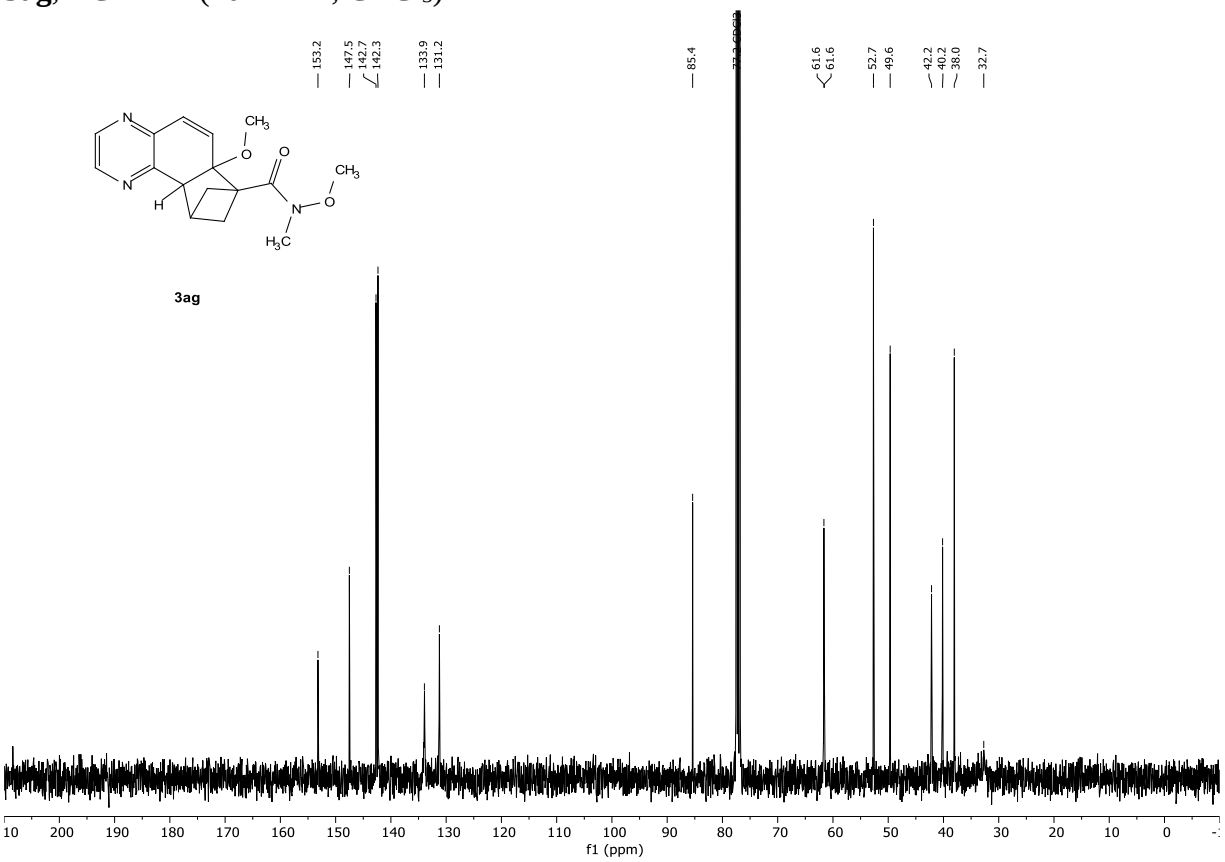
3af, ^{13}C NMR (126 MHz, $CDCl_3$)



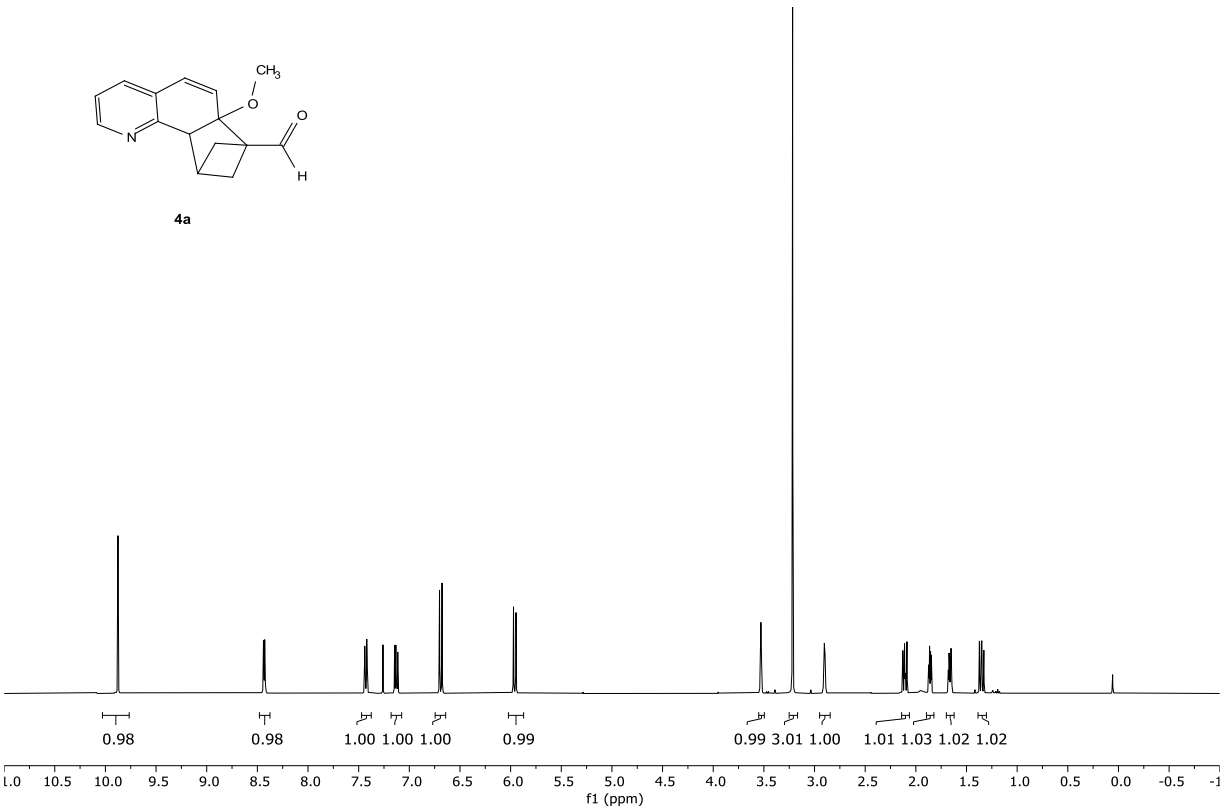
3ag, ^{1}H NMR (400 MHz, $CDCl_3$)



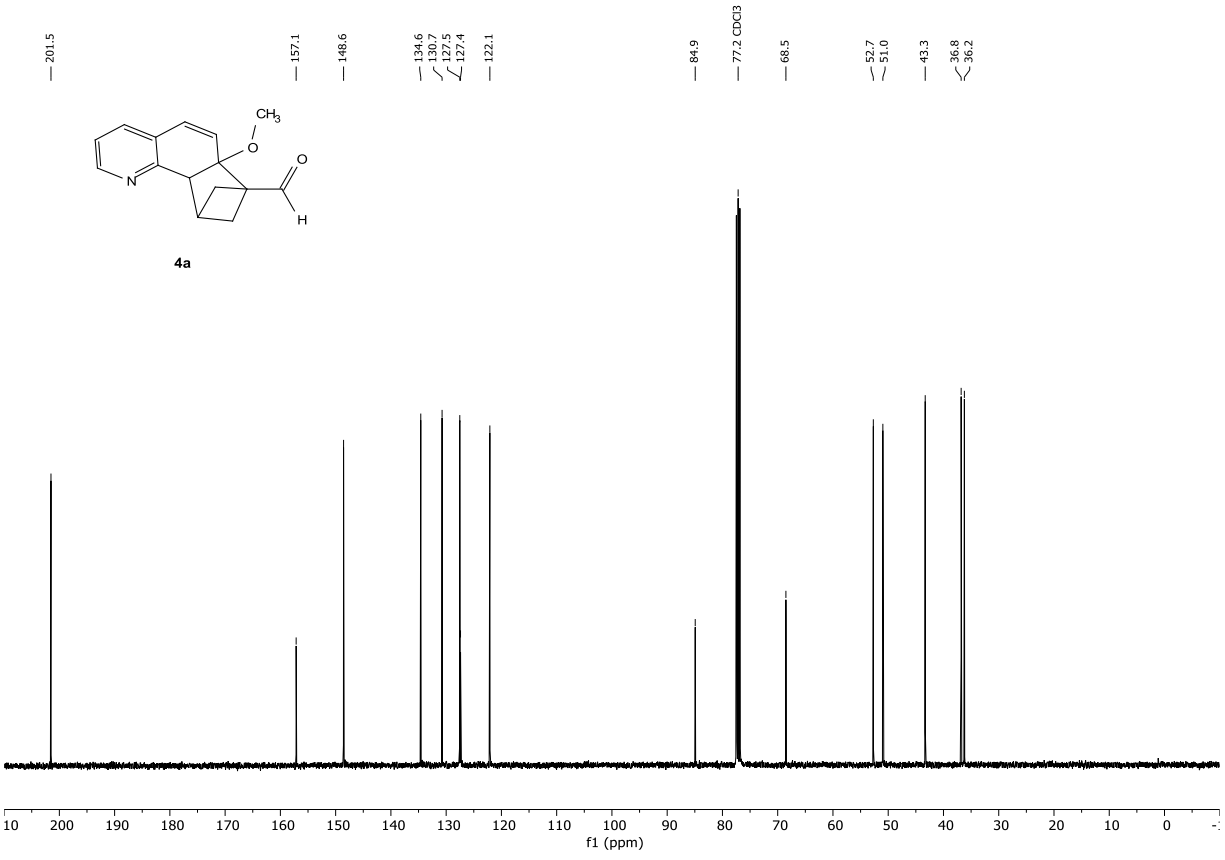
3ag, ^{13}C NMR (101 MHz, $CDCl_3$)



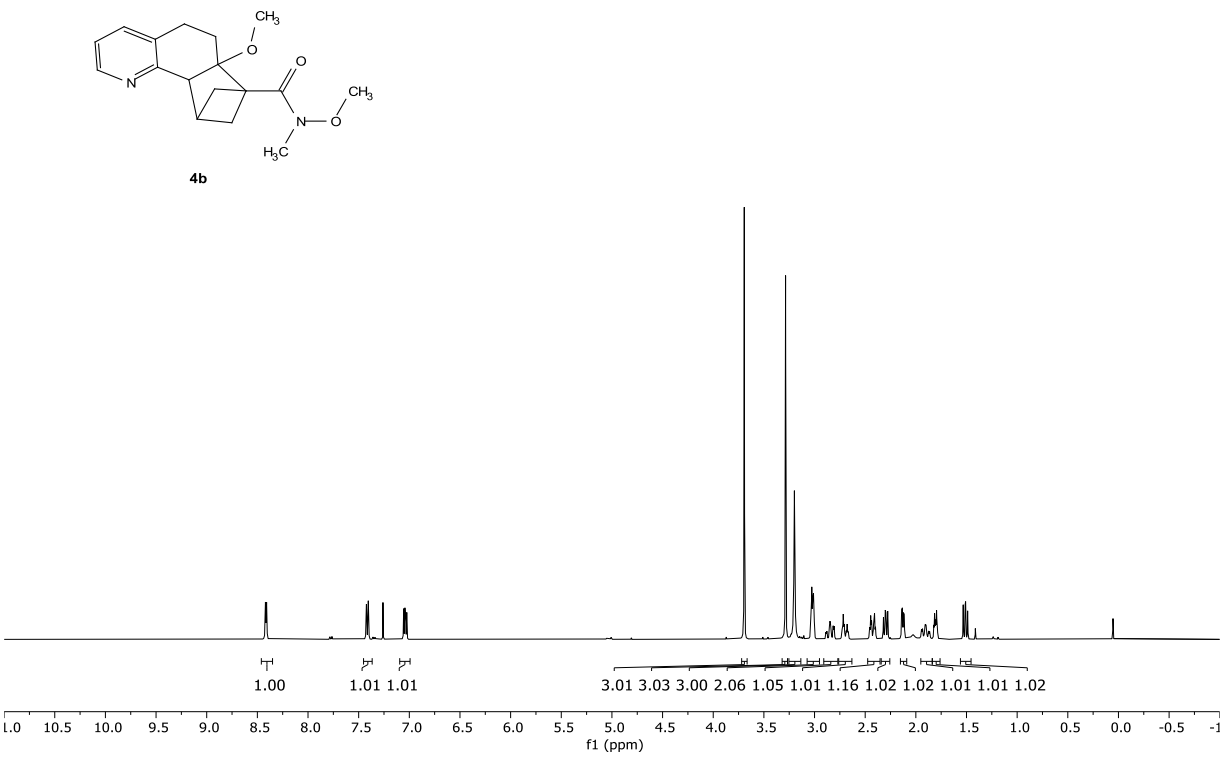
4a, ^{1}H NMR (400 MHz, $CDCl_3$)



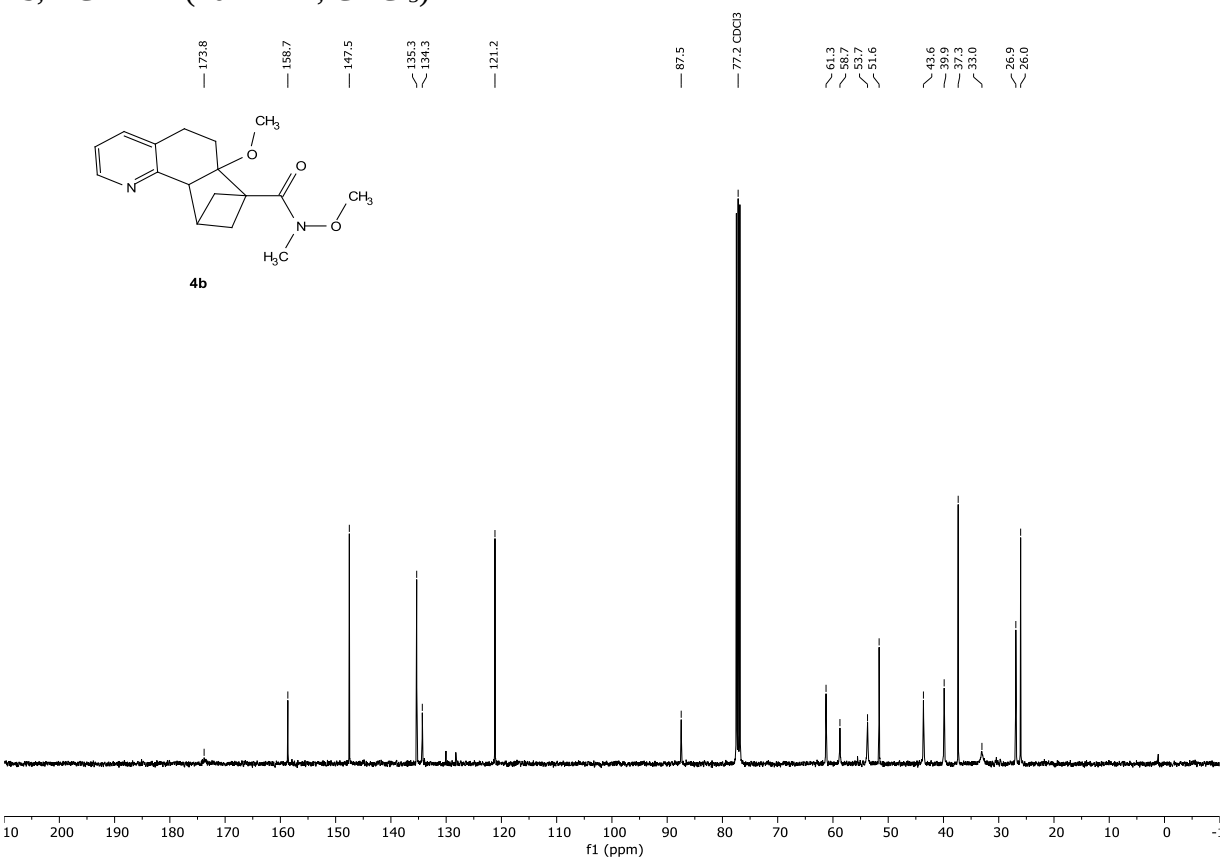
4a, ^{13}C NMR (101 MHz, $CDCl_3$)



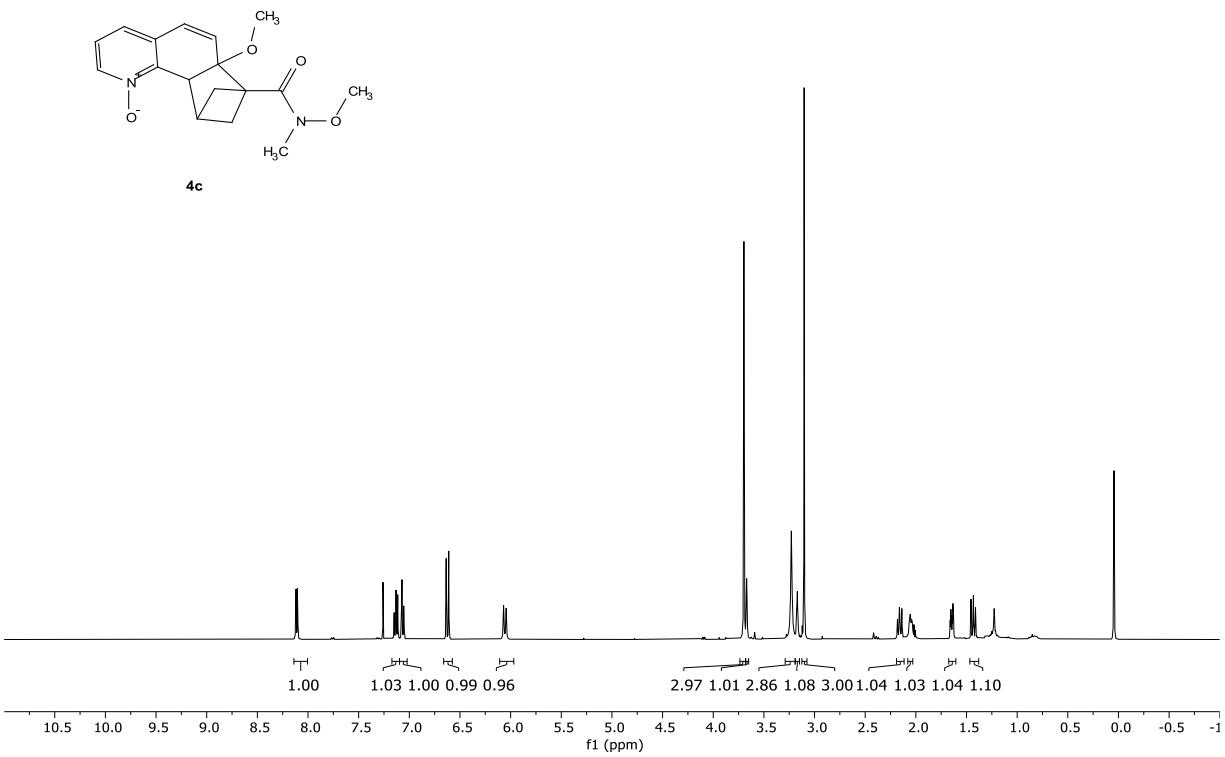
4b, ^{1}H NMR (400 MHz, $CDCl_3$)



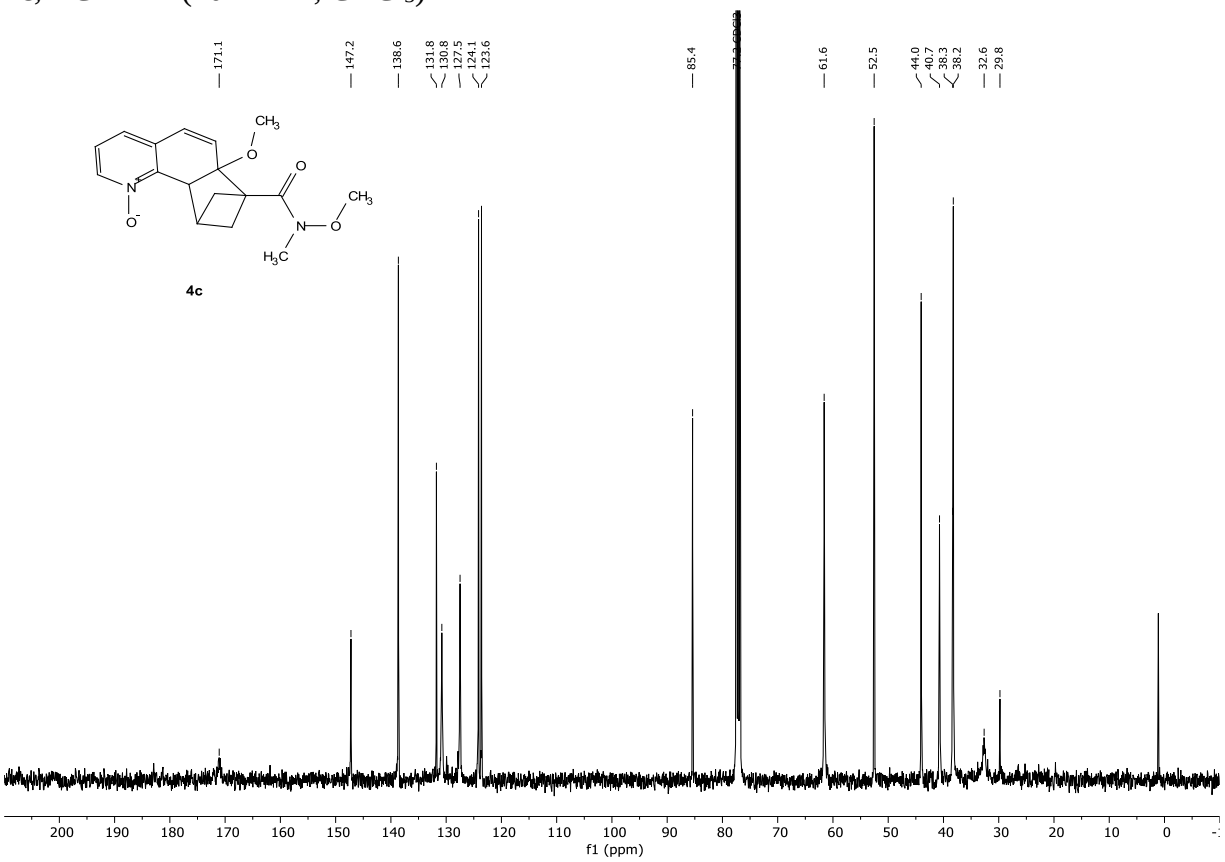
4b, ^{13}C NMR (101 MHz, $CDCl_3$)



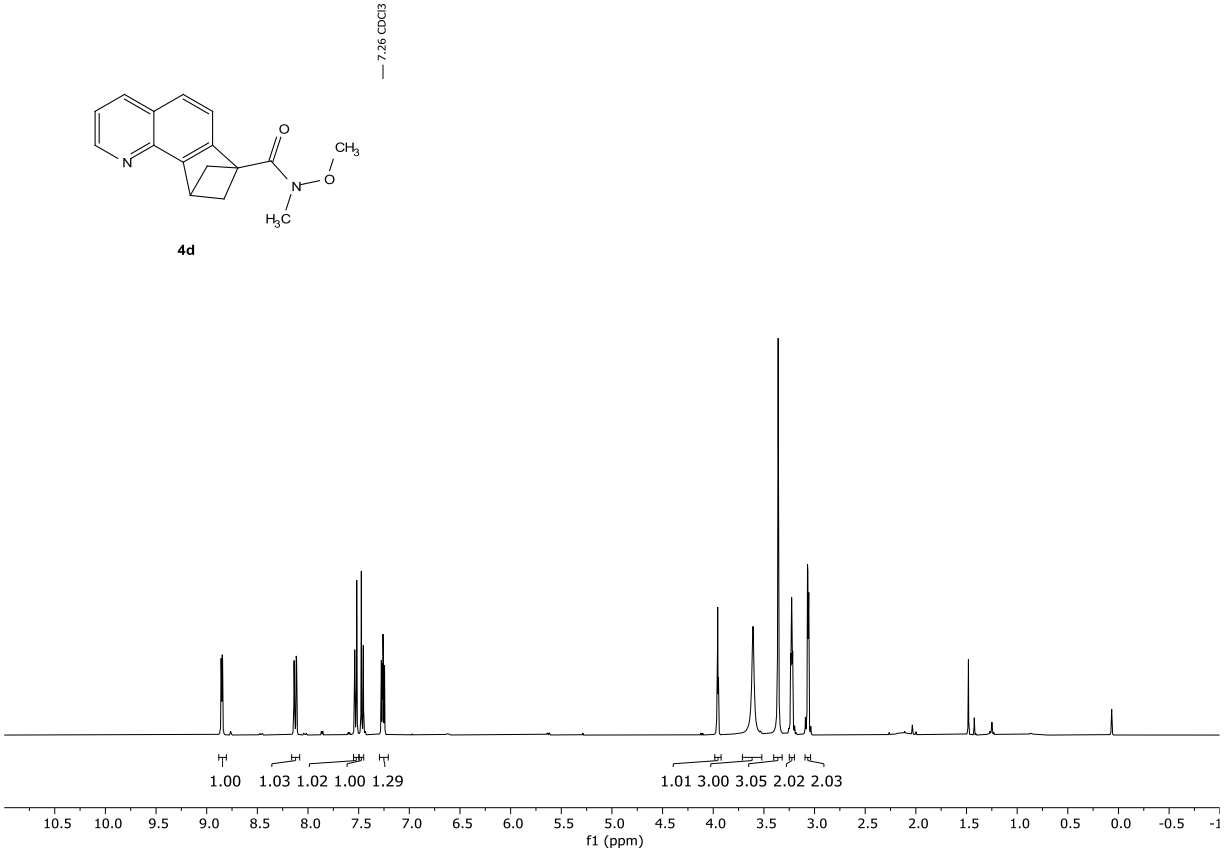
4c, ^{1}H NMR (400 MHz, $CDCl_3$)



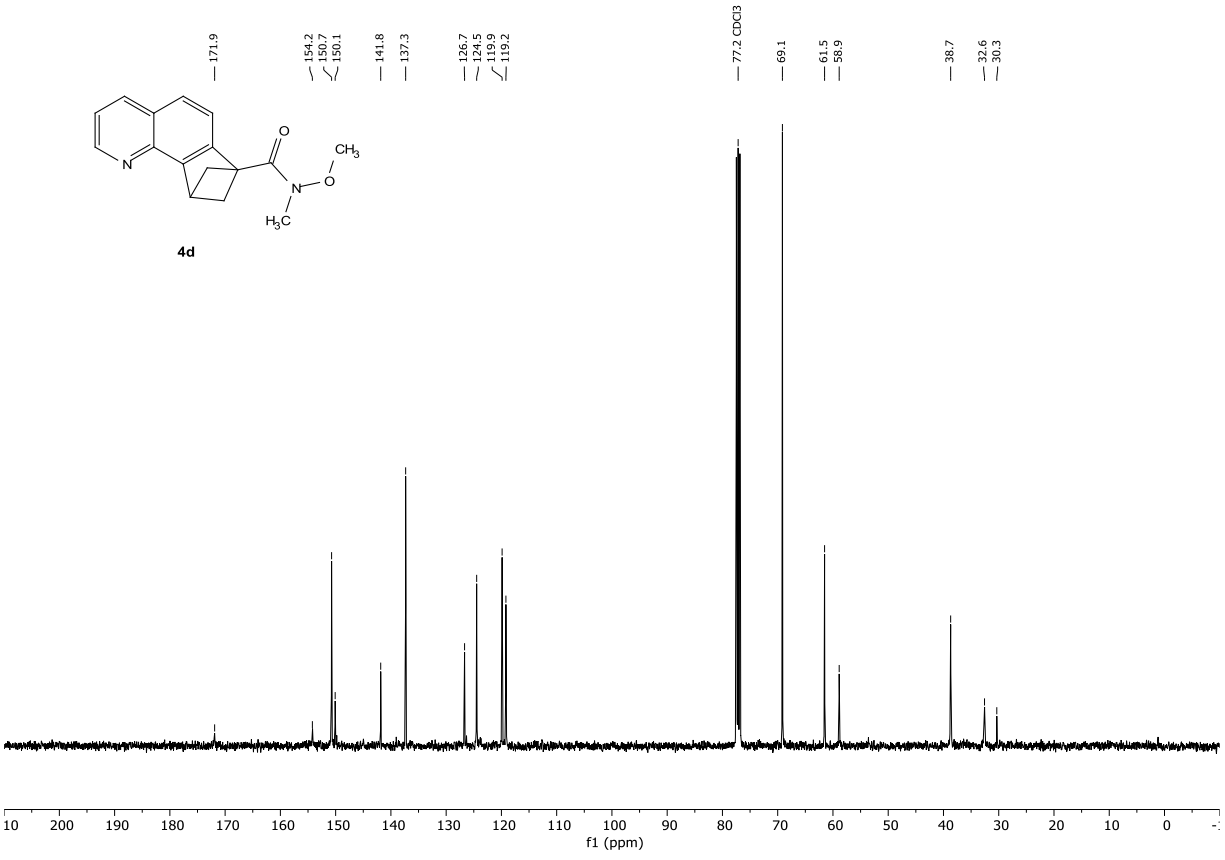
4c, ^{13}C NMR (101 MHz, $CDCl_3$)



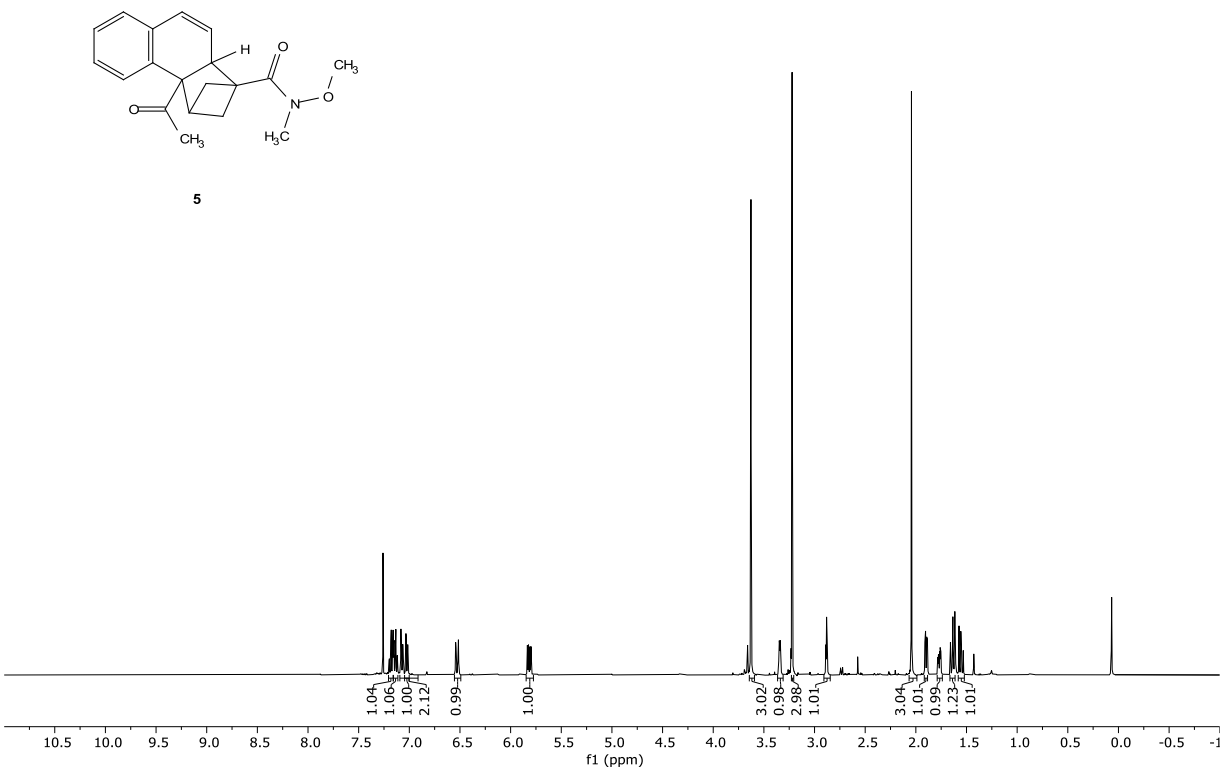
4d, ^{1}H NMR (400 MHz, $CDCl_3$)



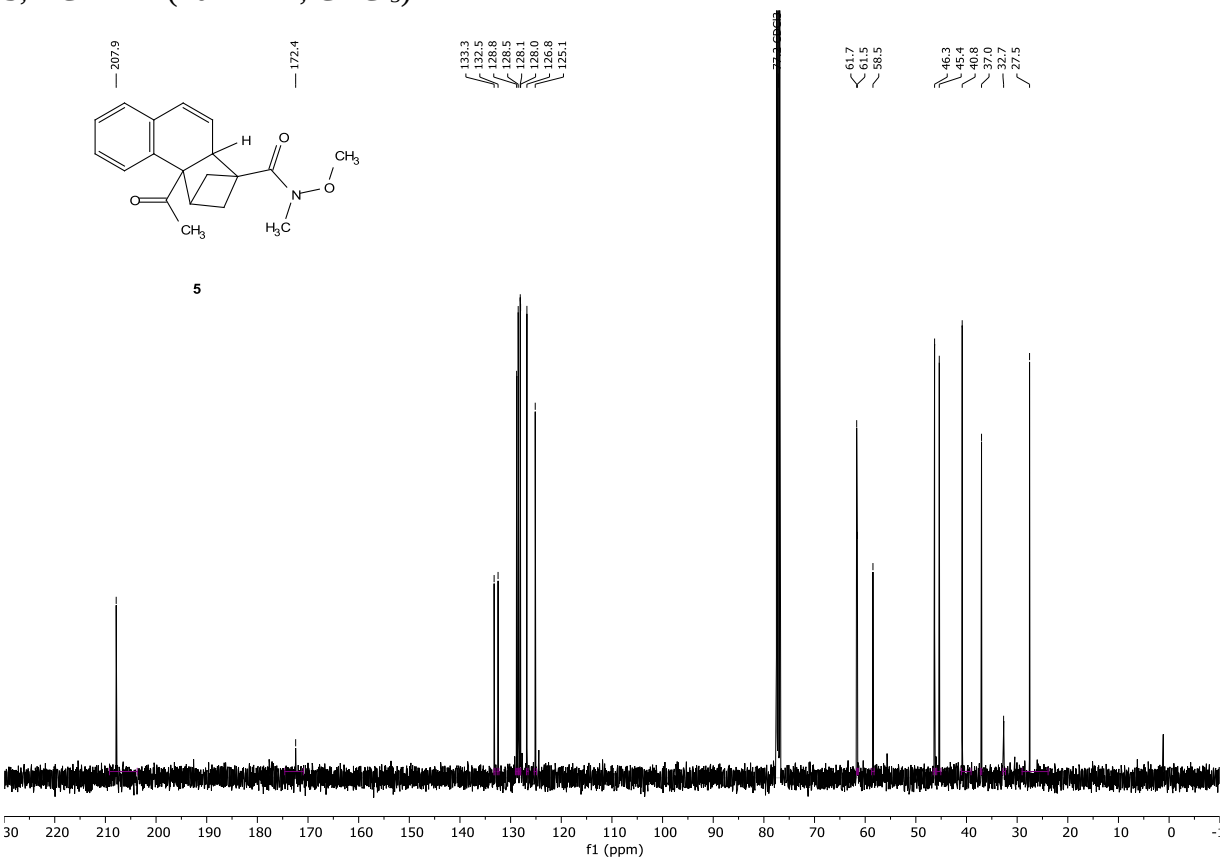
4d, ^{13}C NMR (101 MHz, $CDCl_3$)



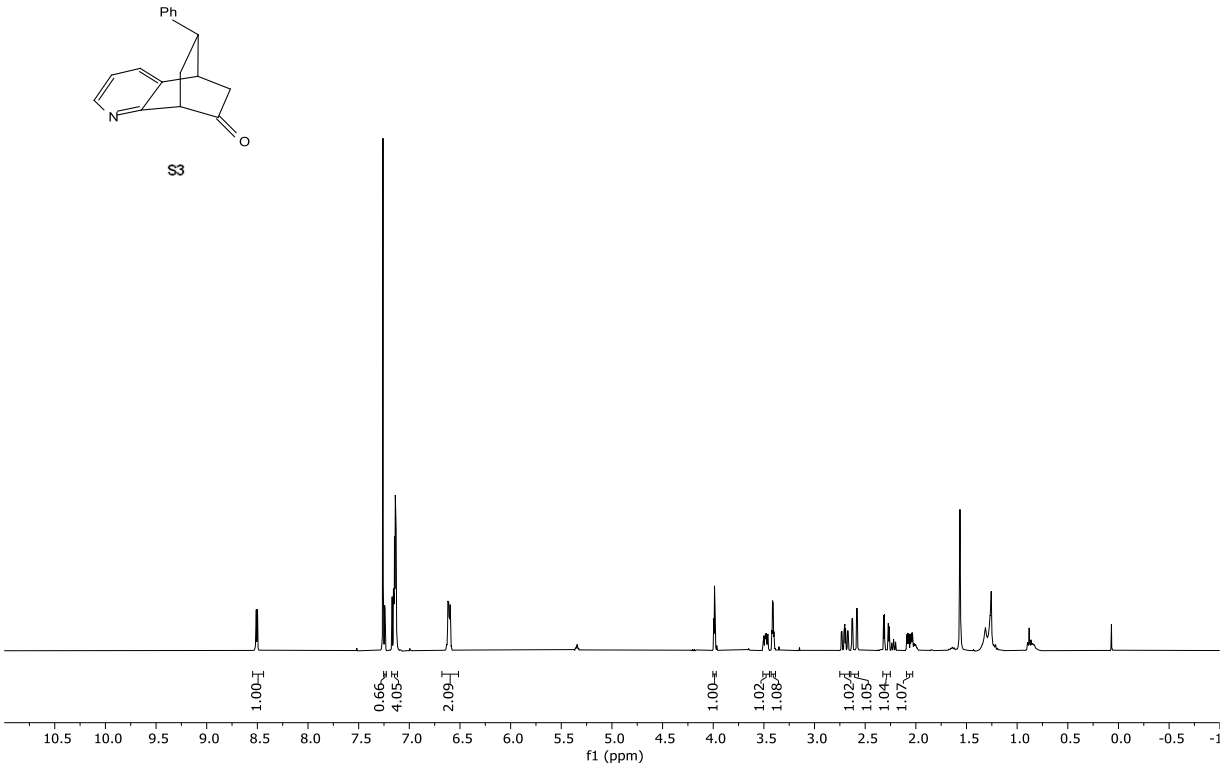
5, ^{1}H NMR (400 MHz, $CDCl_3$)



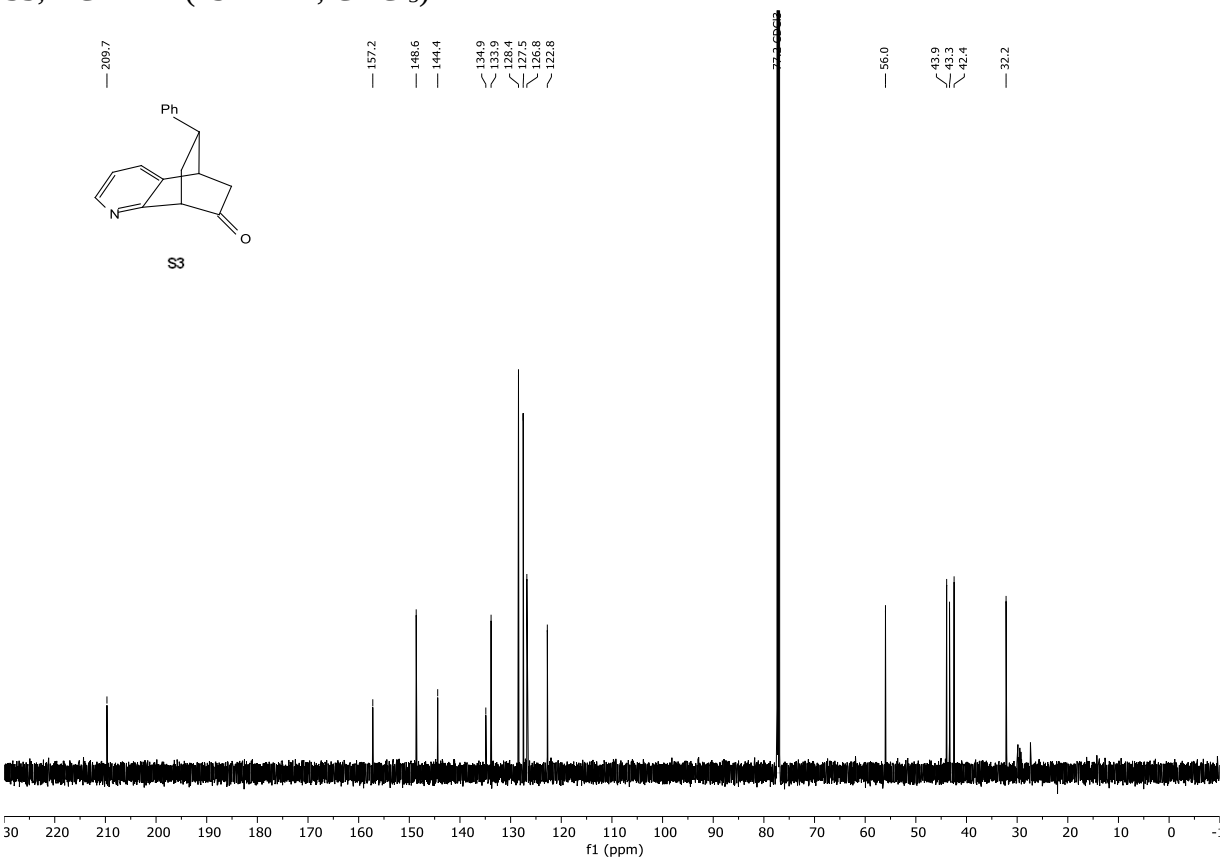
5, ^{13}C NMR (101 MHz, $CDCl_3$)



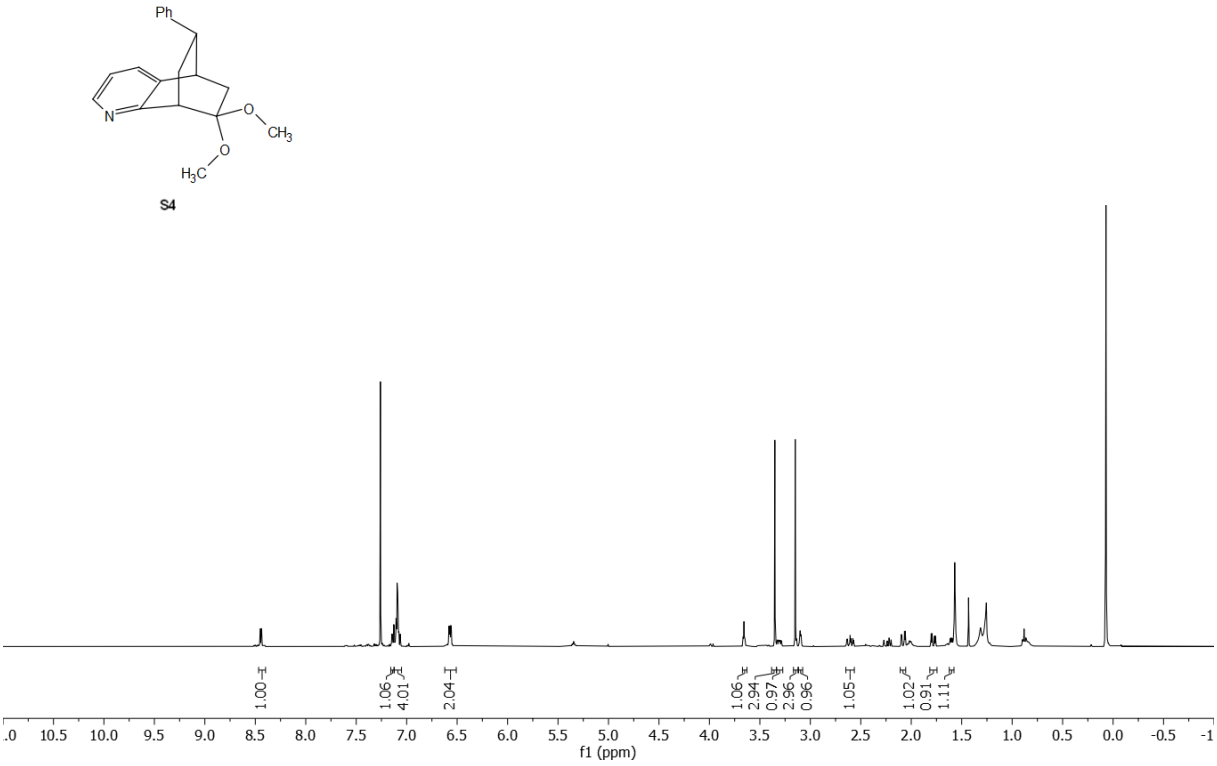
S3, ^{1}H NMR (400 MHz, $CDCl_3$)



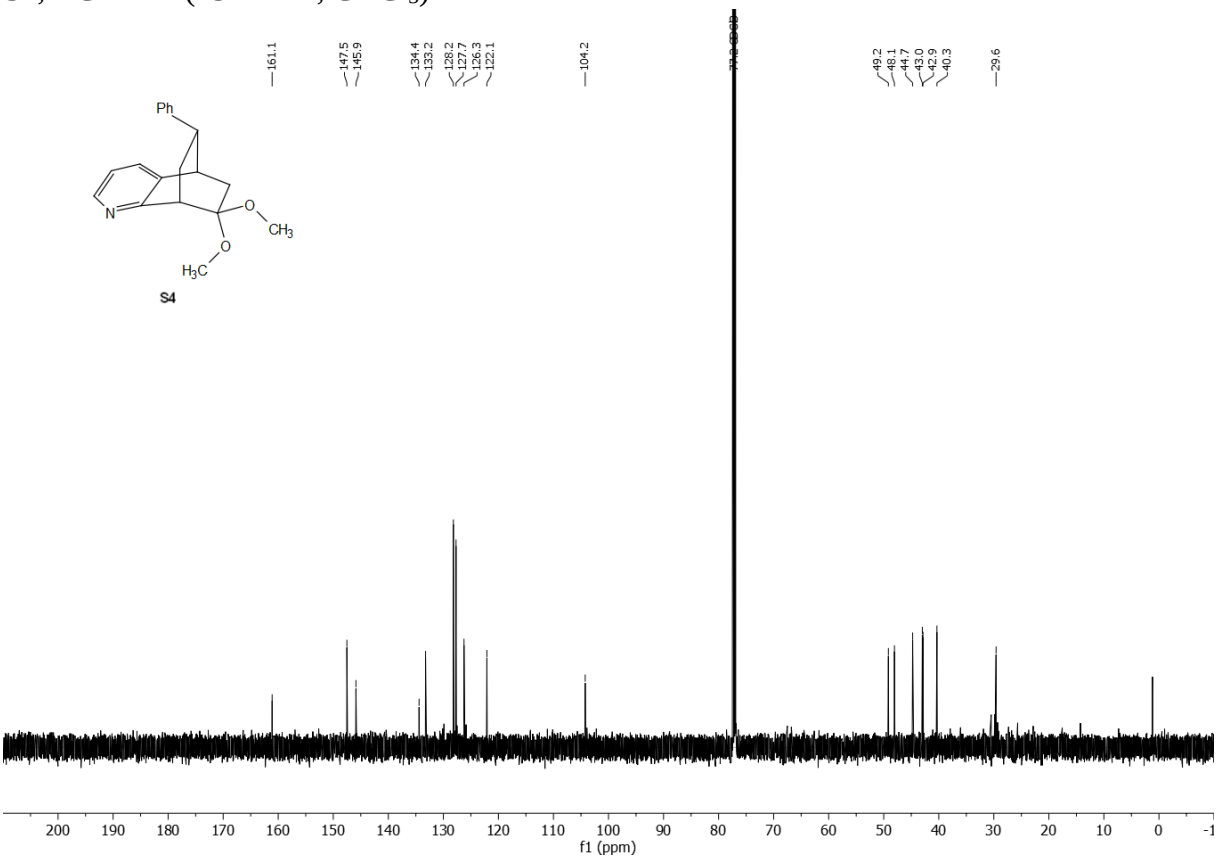
S3, ^{13}C NMR (151 MHz, $CDCl_3$)



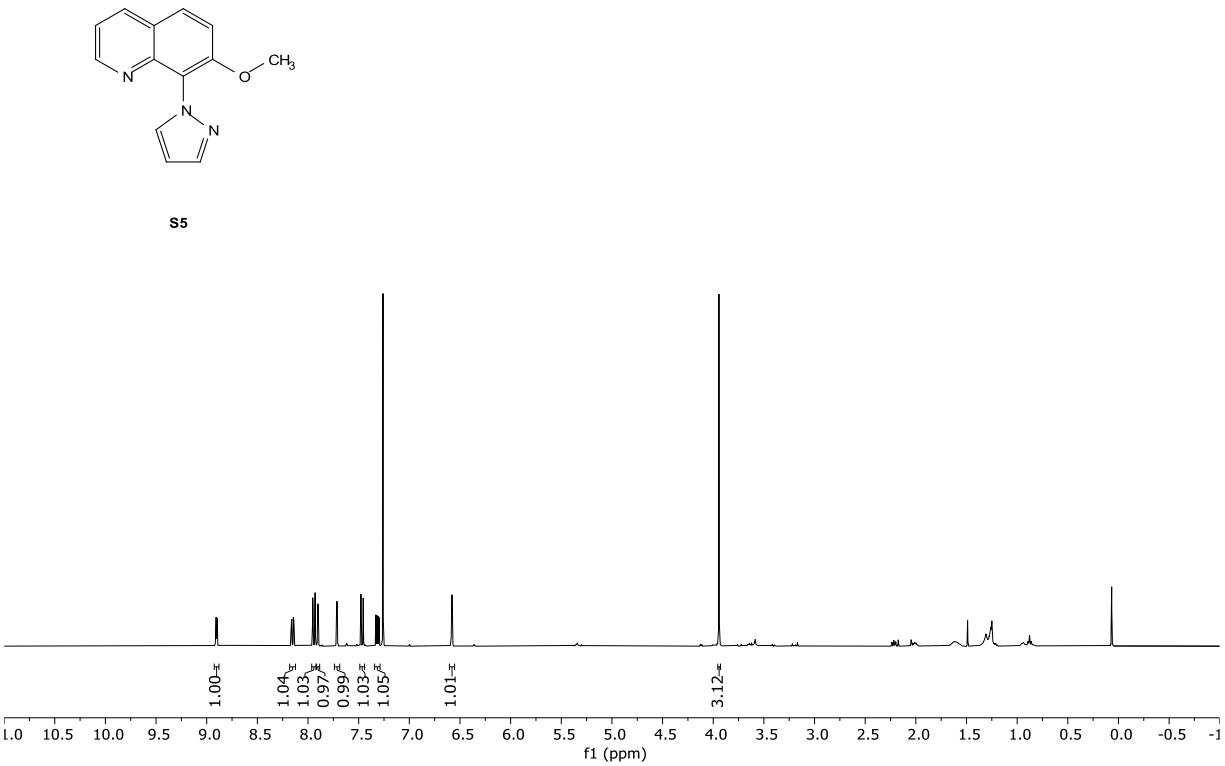
S4, ^{1}H NMR (400 MHz, $CDCl_3$)



S4, ^{13}C NMR (151 MHz, $CDCl_3$)



S5, ^{1}H NMR (400 MHz, $CDCl_3$)



S5, ^{13}C NMR (151 MHz, $CDCl_3$)