Supporting Information

Metal-Free Visible-Light Carbonylation of Alkyl Iodides to Amides *via* Consecutive Photoinduced Electron Transfer

Fatima Akhssas,[1] Guillaume Chu,[1] Meriem El malamy,[1] Naomi Illi,[1] Jasmine Hertzog,[2] Bertrand Vileno,[3] Nolwenn Le Breton,[3] Michael Badawi,[4] Miguel Ponce-Vargas,[4,5] Philipp Gotico,[6,*] Alexandre Vasseur,[4] Zakaria Halime,[7,*] Christophe Werlé,[4,8,*] and Ibrahim Abdellah[1,*]

[1] Université de Lorraine, CNRS, L2CM, F-57000 Metz, France.
E-mail: ibrahim.abdellah@univ-lorraine.fr

[2] Université de Lorraine, LCP-A2MC, F-57000 Metz, France

[3] Institut de Chimie de Strasbourg, CNRS UMR 7177, Université de Strasbourg, F-67000 Strasbourg, France.

[4] Université de Lorraine, CNRS, L2CM, F-54000 Nancy, France.
E-mail: christophe.werle@univ-lorraine.fr

[5] Université de Reims Champagne-Ardenne, Moulin de la Housse, 51687 Reims Cedex 02 BP39, France.

[6] Institute for Integrative Biology of the Cell, CEA, CNRS, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France.
E-mail: philipp.gotico@cea.fr

[7] Université Paris-Saclay, CNRS, Institut de Chimie Moléculaire et des Matériaux d'Orsay, F-91405, Orsay, France.
E-mail: zakaria.halime@universite-paris-saclay.fr

[8] Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34−36, 45470 Mülheim an der Ruhr, Germany.
E-Mail: christophe.werle@cec.mpg.de

1. General information

All reactions were carried out under argon using dry, oxygen-free solvents and standard Schlenk techniques. Unless otherwise noted, reagents were obtained from Sigma-Aldrich, BLDpharm, or Fisher Scientific and used as received. Solvents and liquid reagents were handled with disposable graduated syringes or Hamilton microsyringes. EtOAc, THF, DMF, DMSO, MeCN, and acetone (Fisher Scientific) were supplied in AcroSeal® packaging and used without further purification. The CO surrogates SilaCOgen® ($MePh_2SiCO_2H$) and Sila^{13}COgen® ($MePh_2Si^{13}CO_2H$) were prepared according to literature procedures.[1] Photocatalysts **4CzIPN**,[2] **4DPAIPN**,[2] **[Ru(bpy)$_3$][PF$_6$]$_2$**,[3] **4CzTPN**,[4] and **3CzMAPIN**[5] were synthesized as reported.

Photochemical Setup. Reactions were carried out in a COware® two-chamber reactor under visible-light irradiation. The reaction chamber was externally illuminated using a Kessil® PR160L blue LED (λ = 456 nm, 50 W), positioned 5 cm from the vial (https://www.kessil.com/products/science_PR160L.php). The reactor was fan-cooled to maintain the solution temperature at 25–30°C during irradiation.

Chromatography. Thin-layer chromatography (TLC) was performed on silica gel pre-coated aluminum plates (Merck 60 F_{254}) and visualized under UV light (254 nm) and/or by staining with $KMnO_4$ or phosphomolybdic acid, followed by heating. Crude mixtures were purified by flash column chromatography on silica gel (40–63 μm) or using a BUCHI flash purification system with silica cartridges (12 or 25 g, 40–63 μm).

Gas Chromatography–Mass Spectrometry (GC–MS). Analyses were performed on an Agilent 5977C GC/MSD system coupled with an Agilent 8890 GC equipped with an HP-5MS UI column (30 m × 0.25 mm, 0.25 μm film thickness).

NMR Spectroscopy. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance III 400 spectrometer in $CDCl_3$, with chemical shifts (δ) referenced to residual solvent peaks (δ ^{1}H = 7.26 ppm; δ ^{13}C = 77.16 ppm). Chemical shifts are reported in ppm, coupling constants (*J*) in Hz, and multiplicities as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), or m (multiplet).

High-Resolution Mass Spectrometry (HRMS). HRMS data were acquired on a Waters Xevo G2 ESI/QqTOF system equipped with a Waters Acquity UPLC H-Class PLUS system and API source, or on a Bruker micrOTOF-Q ESI/QqTOF mass spectrometer with an API source.

Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS). Samples were prepared as 1 μg mL^{-1} solutions in methanol (LC–MS grade, VWR Chemicals) and analyzed on a 7 T FTICR mass spectrometer (Solarix 2XR, Bruker Daltonics, Bremen, Germany) equipped with an ESI source, operated in positive-ion mode.

Electron Paramagnetic Resonance (EPR). Room-temperature continuous-wave X-band EPR spectra were recorded on a Bruker Elexsys E580 spectrometer equipped with a high-sensitivity resonator (ER 4119 HS-W1). The g factor was calibrated using a Bruker strong pitch standard (g = 2.0028). Simulations were performed using custom routines based on the EasySpin toolbox under Matlab

(MathWorks).[6] Typical parameters: microwave frequency ~9.8 GHz; power 5.1 mW; modulation amplitude 0.1 G; time constant ~20 ms; conversion time ~50 ms; 1–10 scans accumulated per spectrum (1–10 min total acquisition).

Electrochemistry. Cyclic voltammetry (CV) was conducted using a three-electrode setup comprising a glassy carbon working electrode (3 mm diameter), $Ag/AgNO_3$ (10^{-2} M) reference electrode, and platinum wire counter electrode. Measurements were performed in acetonitrile (MeCN) with 0.1 M tetrabutylammonium hexafluorophosphate ($[Bu_4N]PF_6$) as supporting electrolyte. Sample concentrations were typically 0.5 mM. Solutions were purged with argon, and voltammograms were recorded at a scan rate of 100 mV s^{-1}. Ferrocene was used as internal standard, and all potentials were converted to SCE using Fc^+/Fc = +0.38 V.
Irradiated thin-layer CV experiments were performed by illuminating the electrochemical cell with a SugarCube blue LED source (λ = 463 nm, FWHM ~50 nm) at adjustable intensity (levels 1–10), positioned 3.5 mm from the working electrode. Light intensity measured using a solar meter for the various intensity levels at the proper distance from the working electrode are as follows: 380, 810, 1270, 1730, 2300, 2800, 3340, 3780, 4260, 4710 W m^{-2}.

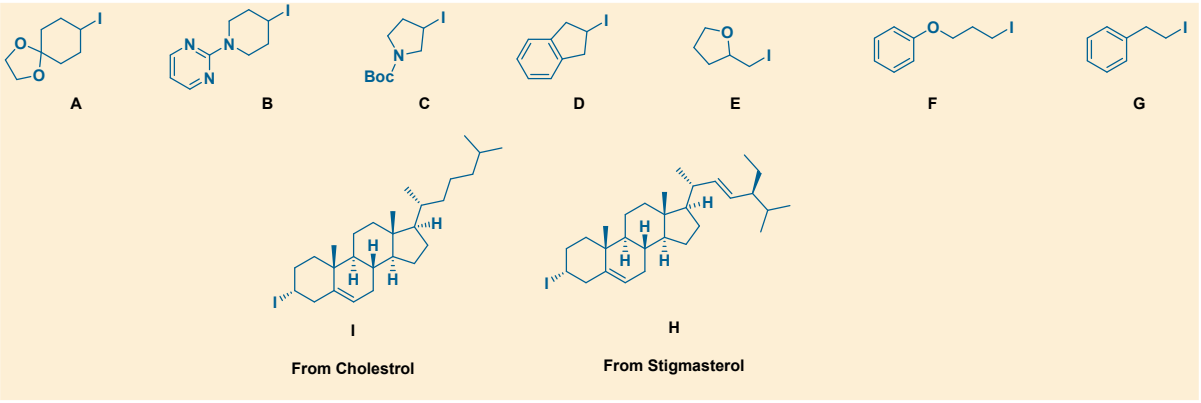
Spectroelectrochemistry (SEC). UV–vis spectroelectrochemical measurements were performed in a quartz cuvette equipped with a Pt honeycomb working electrode, Pt counter electrode, and Pt wire pseudo-reference electrode. Absorption spectra were recorded using an Agilent Cary 50 UV–Vis spectrophotometer. Potentials were applied with an Admiral Instruments potentiostat using chronoamperometry at 100 mV intervals (5 min each).

***In-situ* UV–Vis Spectroscopy.** Time-resolved UV–vis monitoring was carried out in a 1 cm quartz cuvette sealed with a septum. Ar-saturated solutions were stirred and irradiated with a perpendicular blue LED (SugarCube, λ = 463 nm) while spectra were collected using an Agilent Technologies Cary 50 UV–Vis spectrophotometer (Scanning Kinetics mode, CaryWin software).

Laser Flash Photolysis (LFP). Excited state absorption and emission measurements were conducted on an Edinburgh Instruments LP920 flash photolysis spectrometer. Samples were excited with 5 ns pulses (λ = 430 nm) from a Continuum Surelite Q-switched Nd:YAG laser coupled with an optical parametric oscillator (OPO) delivering ~11 mJ per pulse. The probe source was a 450 W pulsed xenon lamp, and detection employed either a water-cooled Andor intensified charge-coupled ICCD camera (spectral mode) or a Hamamatsu photomultiplier tube PMT (kinetic mode). Data analysis was performed using LP920 software for ΔOD calculation, spectral smoothing, and kinetic data extraction.

Disclaimer:
CAUTION: *All experiments were performed in a ventilated fume hood with appropriate PPE (lab coat, nitrile gloves, splash goggles). Amines are corrosive/volatile and iodine-containing substrates are irritants; avoid inhalation/skin contact and segregate iodine-containing waste. Photochemical work requires blue-light eye protection and shielding (≈450–470 nm); SilaCOgen®/Sila^{13}COgen® are silicon formate CO surrogates that can release CO upon activation—ensure effective ventilation and avoid confined spaces.*

2. Preparation of Halide Precursors



Scheme S1. Collection of Halide Starting Materials.

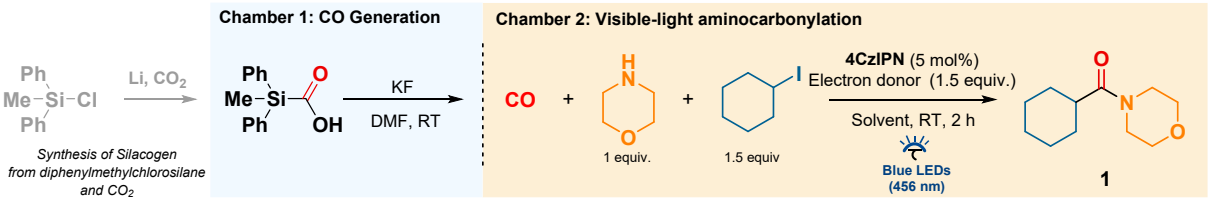
General. Organic halides **A–G** were synthesized according to reported procedures.[7] **Compound I** was prepared from cholesterol following the literature method.[8]

Experimental Procedure for the Preparation of Compound H[9]

In a flame-dried Schlenk tube under argon, stigmasterol (3.20 g, 7.75 mmol), PPh_3 (2.44 g, 9.30 mmol), and imidazole (0.633 g, 9.30 mmol) were dissolved in dry CH_2Cl_2 (70 mL) and cooled to 0 °C. I_2 (2.36 g, 18.6 mmol, 2.4 equiv) was added portion wise, and the reaction mixture was stirred at rt for 16 h. The reaction was quenched with H_2O, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed successively with sat. $Na_2S_2O_3$, brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (silica gel, petroleum ether) to afford **Compound H** as a white solid (3.50 g, 86%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.37–5.28 (m, 1H), 5.15 (dd, *J* = 15.1, 8.6 Hz, 1H), 5.02 (dd, *J* = 15.2, 8.6 Hz, 1H), 4.04 (tt, *J* = 12.5, 4.4 Hz, 1H), 2.99–2.84 (m, 1H), 2.67 (ddd, *J* = 13.7, 4.4, 2.2 Hz, 1H), 2.33–2.12 (m, 2H), 2.08–1.88 (m, 3H), 1.71 (ddt, *J* = 15.0, 13.3, 4.6 Hz, 2H), 1.60–1.36 (m, 8H), 1.31–1.10 (m, 6H), 1.05–1.00 (m, 7H), 0.98–0.89 (m, 1H), 0.87–0.78 (m, 9H), 0.69 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 142.9, 138.4, 129.4, 121.8, 56.9, 56.0, 51.3, 50.5, 46.5, 42.3, 42.0, 40.6, 39.7, 36.7, 36.6, 32.0, 31.8, 31.7, 30.6, 29.0, 25.5, 24.4, 21.3, 21.2, 20.9, 19.3, 19.1, 12.4, 12.1.
HRMS (APCI): Calcd. for $C_{29}H_{48}I^+$ $[M+H]^+$ 523.2801; found 523.2802.

3. General Optimization Procedure



Scheme S2. General Procedure.

Under an argon atmosphere, a COware® two-chamber reactor (20 mL total volume) was charged as follows: **Chamber 2** was sequentially loaded with the photocatalyst (**PC**) (5 mol%), morpholine (0.10 mmol, 1.0 equiv), iodocyclohexane (0.15 mmol, 1.5 equiv), the sacrificial electron donor (0.15 mmol, 1.5 equiv), and ethyl acetate (1.0 mL, 0.10 M). The chamber was sealed with a PTFE-faced silicone septum screw cap.

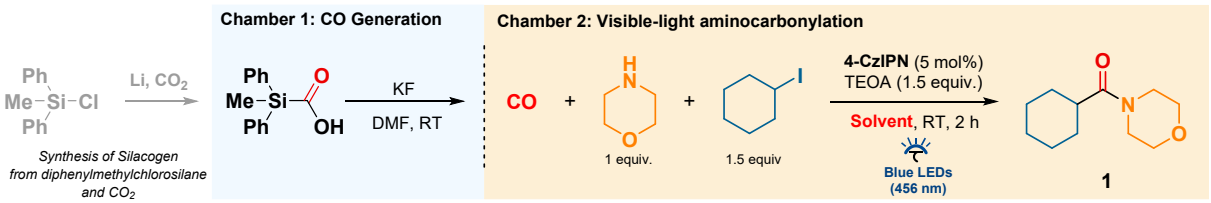
Chamber 1 was charged with SilaCOgen® ($MePh_2SiCO_2H$) (0.60 mmol, 6.0 equiv) and KF (0.66 mmol, 6.6 equiv), sealed under identical conditions, and treated with anhydrous DMF (1.0 mL).

The sealed reactor was positioned ca. 5 cm from a Kessil blue LED light source (λ = 456 nm, 50 W, 50 % intensity) and stirred at ambient temperature for 2 h. After completion, the reaction mixture was diluted with ethyl acetate and analyzed by GC–MS, employing n-hexadecane as an internal standard.

4. Optimization of the Reaction Conditions

a. Solvent Screening

Table S1. Optimization of the Reaction Conditions: **Solvent Screening**.

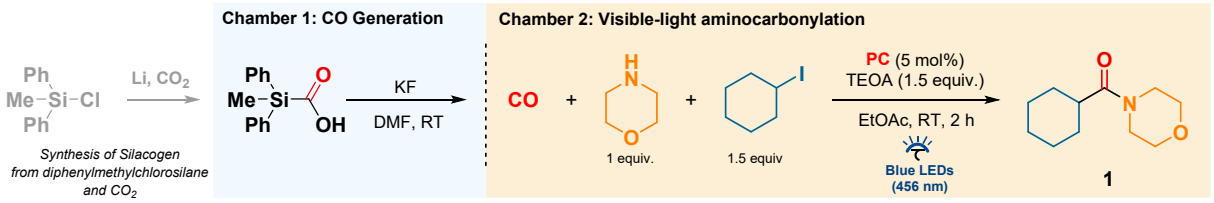


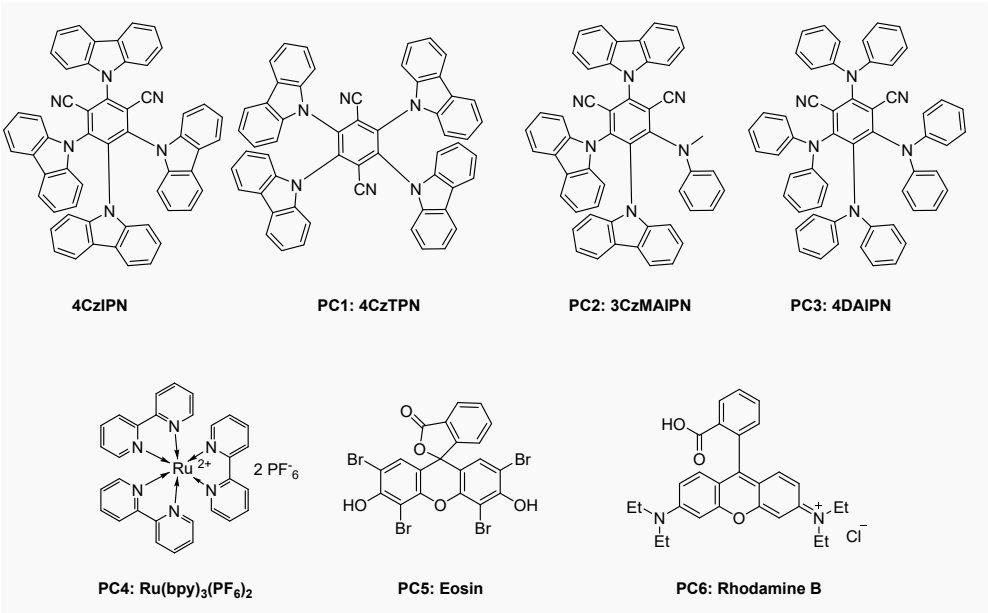
Entry	Solvent	Yield (%)[1]
1	DMSO	40
2	DMF	44
3	CH_3CN	29
4	Acetone	71
5	**EtOAc**	**98**
6	1,4-dioxane	84
7	EtOH	13

Reaction conditions. Chamber 1: SilaCOgen® ($MePh_2SiCO_2H$, 0.60 mmol), KF (0.66 mmol) in DMF (1.0 mL). **Chamber 2**: morpholine (0.10 mmol), iodocyclohexane (0.15 mmol), **4CzIPN** (5 mol%), triethanolamine (TEOA, 0.15 mmol), **solvent** (1.0 mL, 0.10 M). The reaction mixture was stirred under 456 nm Kessil® blue LED irradiation (50% intensity) at RT for 2 h. Yields of amide **1** were determined by GC–MS using *n*-hexadecane as internal standard.

b. Photocatalyst Screening

Table S2. Optimization of the Reaction Conditions: **Photocatalyst Screening**.



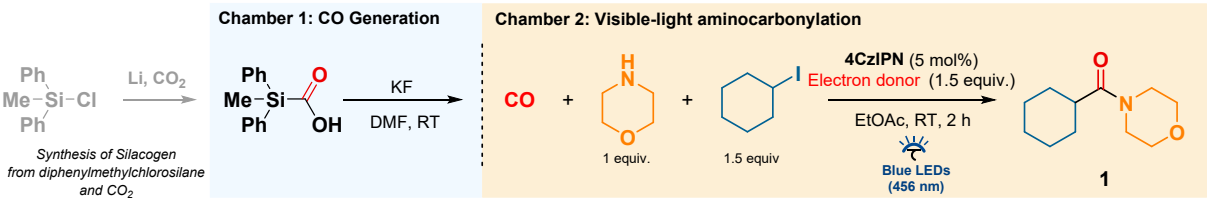


Entry	Photocatalyst (PC)	Yield (%)[1]
1	**4CzIPN**	**98**
2	PC1	81
3	PC2	67
4	PC3	60
5	PC4	0
6	PC5	19
7	PC6	8
8	Without PC	0
9	Without light	0

Reaction conditions. Chamber 1: SilaCOgen® ($MePh_2SiCO_2H$, 0.60 mmol), KF (0.66 mmol) in DMF (1.0 mL). **Chamber 2:** morpholine (0.10 mmol), iodocyclohexane (0.15 mmol), **photocatalyst** (5 mol%), TEOA (0.15 mmol), EtOAc (1.0 mL, 0.10 M). Reactions were stirred under 456 nm Kessil® blue LED irradiation (50% intensity) at RT for 2 h.[1]Yields of amide **1** were determined by GC–MS using *n*-hexadecane as internal standard.

c. Sacrificial Electron Donors Screening

Table S3. Optimization of the Reaction Conditions: **Sacrificial Electron Donors Screening**.

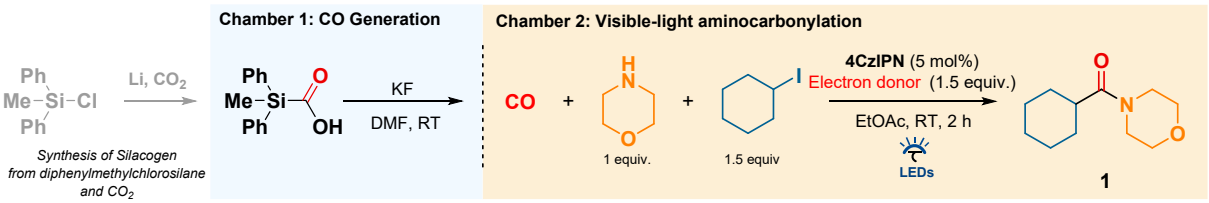


Entry	Sacrificial electron donor	Yield (%)[1]
1	TEA	79
2	$(n\text{-Bu})_3N$	67
3	**$(EtOH)_3N$**	**98**
4	DIPEA	90
5	DABCO	0
6	Quinuclidine	0
7	Without sacrificial agent	37

Reaction conditions. Chamber 1: SilaCOgen® ($MePh_2SiCO_2H$, 0.60 mmol), KF (0.66 mmol) in DMF (1.0 mL). **Chamber 2**: morpholine (0.10 mmol), iodocyclohexane (0.15 mmol), **4CzIPN** (5 mol%), **sacrificial electron donor** (0.15 mmol), EtOAc (1.0 mL, 0.10 M). Reactions were stirred under 456 nm Kessil® blue LED irradiation (50% intensity) at RT for 2 h. [1]Yields of amide **1** were determined by GC–MS using *n*-hexadecane as internal standard.

d. LED wavelength Screening

Table S4. Optimization of the Reaction Conditions: **LED wavelength Screening**.



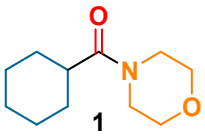
Entry	LED wavelength	Yield (%)[1]
1	390 nm	49
2	427 nm	72
3	**456 nm**	**98**
4	525 nm	0

Reaction conditions. Chamber 1: SilaCOgen® ($MePh_2SiCO_2H$, 0.60 mmol), KF (0.66 mmol) in DMF (1.0 mL). **Chamber 2**: morpholine (0.10 mmol), iodocyclohexane (0.15 mmol), **4CzIPN** (5 mol%), **sacrificial electron donor** (0.15 mmol), EtOAc (1.0 mL, 0.10 M). Reactions were stirred under **Kessil® LED** irradiation (50% intensity) at RT for 2 h. [1]Yields of amide **1** were determined by GC–MS using *n*-hexadecane as internal standard.

5. General Procedure for the Photocatalytic Carbonylation/Amidation of Alkyl Iodides

Under an argon atmosphere, a COware® two-chamber reactor (20 mL total volume) was charged as follows**: Chamber 2** was sequentially loaded with **4CzIPN** (7.8 mg, 5 mol%), the amine (0.20 mmol, 1.0 equiv), the alkyl iodide (0.30 mmol, 1.5 equiv), TEOA (45 mg, 0.30 mmol, 1.5 equiv), and EtOAc (2.0 mL, 0.10 M). The chamber was sealed with a PTFE-faced silicone septum screw cap. **Chamber 1** was charged with SilaCOgen® ($MePh_2SiCO_2H$, 291 mg, 1.20 mmol, 6.0 equiv) and KF (76.6 mg, 1.32 mmol, 6.6 equiv), sealed under the same conditions, and treated with anhydrous DMF (2.0 mL). The reactor was then stirred under 456 nm Kessil® blue LED irradiation (50% intensity) at RT for 2, 4, or 8 h, depending on the substrate. Upon completion, the contents of **Chamber 2** were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the corresponding amide.

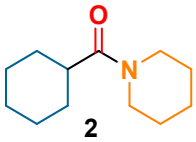
6. Synthesis and Characterization of Amide Products



1

Cyclohexyl(morpholino)methanone (1).
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 2:1, v/v) afforded **1** as a white solid (29.1 mg, 74%).
The spectroscopic data agree with those reported in the literature.[8]

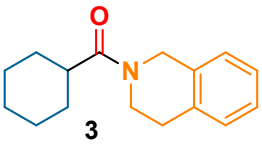
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.69–3.42 (m, 8H), 2.42 (tt, *J* = 11.6, 3.4 Hz, 1H), 1.87–1.75 (m, 2H), 1.75–1.62 (m, 3H), 1.59–1.43 (m, 2H), 1.31–1.20 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 174.9, 67.2, 67.1, 46.1, 42.1, 40.4, 29.5, 26.0, 25.9.
FT-ICR-MS (ESI$^+$): Calcd. for $C_{11}H_{19}NO_2Na^+$ [M + Na]$^+$: 220.1308; found 220.1308.



2

Cyclohexyl(piperidin-1-yl)methanone (2).
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), piperidine (19.8 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 3:7, v/v) afforded **2** as a pale-yellow oil (33.4 mg, 85%).
The spectroscopic data agree with those reported in the literature.[8]

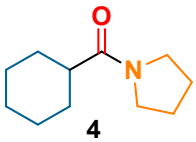
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.60–3.50 (m, 2H), 3.50–3.39 (m, 2H), 2.46 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.85–1.75 (m, 2H), 1.75–1.60 (m, 5H), 1.60–1.45 (m, 6H), 1.34–1.18 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 174.5, 46.6, 42.8, 40.6, 29.6, 27.0, 26.1, 26.1, 25.8, 24.9.
FT-ICR-MS (ESI$^+$): Calcd. for $C_{12}H_{21}NONa^+$ [M + Na]$^+$: 218.1515; found 218.1515.



3

Cyclohexyl(3,4-dihydroisoquinolin-2(1*H*)-yl)methanone (3).
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), 1,2,3,4-tetrahydroisoquinoline (25 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:2, v/v) afforded **3** as a pale-yellow oil (36.5 mg, 75%). *Note: The product was obtained as a mixture of rotamers.*
The spectroscopic data agree with those reported in the literature.[8]

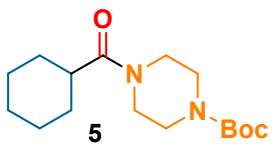
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.23–7.08 (m, 4H), 4.72 (s, 1H), 4.66 (s, 1H), 3.82 (t, *J* = 6.0 Hz, 1H), 3.72 (t, *J* = 5.9 Hz, 1H), 2.90 (t, *J* = 5.9 Hz, 1H), 2.83 (t, *J* = 6.0 Hz, 1H), 2.60–2.50 (m, 1H), 1.87–1.65 (m, 5H), 1.64–1.46 (m, 2H), 1.39–1.16 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 175.2, 175.0, 135.4, 134.2, 133.9, 133.0, 129.1, 128.4, 127.0, 126.8, 126.6, 126.5, 126.4, 126.1, 47.4, 44.4, 43.1, 41.2, 41.0, 39.9, 30.0, 29.5, 29.4, 28.6, 26.0, 26.0.
HRMS (ESI$^+$): Calcd. for $C_{16}H_{22}NO^+$ [M + H]$^+$: 244.1701; found 244.1700.



4

Cyclohexyl(pyrrolidin-1-yl)methanone (4).
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), pyrrolidine (17 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 7:3, v/v) afforded **4** as a pale-yellow oil (22.1 mg, 61%).
The spectroscopic data agree with those reported in the literature.[8]

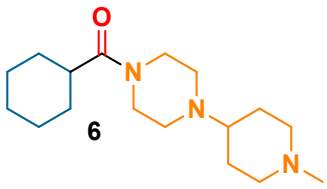
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.45 (q, *J* = 6.4 Hz, 4H), 2.32 (tt, *J* = 11.5, 3.3 Hz, 1H), 1.97–1.90 (m, 2H), 1.87–1.65 (m, 7H), 1.57–1.47 (m, 2H), 1.32–1.18 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 174.9, 46.4, 45.8, 43.1, 29.0, 26.3, 26.0, 26.0, 24.4.
HRMS (ESI$^+$): Calcd. for $C_{11}H_{20}NO^+$ [M + H]$^+$: 182.1545; found 182.1538.



5

***tert*-butyl-4-(cyclohexanecarbonyl)piperazine-1-carboxylate (5).**
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), *tert*-butyl piperazine-1-carboxylate (37.3 mg, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:1, v/v) afforded **5** as a white solid (35.5 mg, 59%).
The spectroscopic data agree with those reported in the literature.[8]

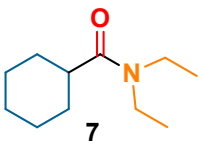
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.62–3.32 (m, 8H), 2.45 (tt, *J* = 11.5, 3.2 Hz, 1H), 1.85–1.76 (m, 2H), 1.74–1.64 (m, 3H), 1.59–1.49 (m, 2H), 1.47 (s, 9H), 1.33–1.21 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 175.0, 154.8, 80.4, 45.4, 41.5, 40.7, 29.5, 28.5, 26.0.
FT-ICR-MS (ESI$^+$): Calcd. for $C_{16}H_{28}N_2O_3Na^+$ [M + Na]$^+$: 319.1992; found 319.1992.



6

(4-(1-methylpiperidin-4-yl)piperazin-1-yl)cyclohexanecarboxamide (6).
Prepared according to the general procedure using iodocyclohexane (37.5 µL, 0.30 mmol), (1-methyl-4-piperidinyl)piperazine (36.6 mg, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/MeOH/Et_3N = 65:30:5, v/v/v), followed by trituration with EtOAc/n-heptane and filtration, afforded **6** as a pale-yellow oil (29.9 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.64–3.56 (m, 2H), 3.53–3.44 (m, 2H), 3.04 (d, *J* = 11.8 Hz, 2H), 2.67–2.20 (m, 12H), 1.88–1.61 (m, 9H), 1.57–1.43 (m, 2H), 1.32–1.18 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 174.6, 61.4, 55.3, 49.6, 49.3, 46.0, 45.8, 42.0, 40.5, 29.5, 27.9, 26.0.
HRMS (ESI$^+$): Calcd. for $C_{17}H_{32}N_3O^+$ [M + H]$^+$: 294.2542; found 294.2543.



7

***N,N*-diethylcyclohexanecarboxamide (7).**

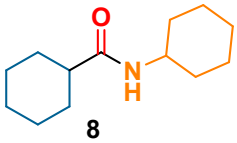
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), diethylamine (21 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:2, v/v) afforded **7** as a colorless oil (20.9 mg, 57%).

The spectroscopic data agree with those reported in the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.37–3.25 (m, 4H), 2.38 (tt, *J* = 11.5, 3.2 Hz, 1H), 1.83–1.72 (m, 2H), 1.71–1.61 (m, 3H), 1.60–1.47 (m, 2H), 1.29–1.21 (m, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 175.6, 41.8, 40.9, 40.2, 29.8, 26.0, 26.0, 15.1, 13.3.

HRMS (ESI$^+$): Calcd. for $C_{11}H_{22}NO^+$ [M + H]$^+$: 184.1701; found 184.1706.



8

***N*-cyclohexylohexanecarboxamide (8)**:

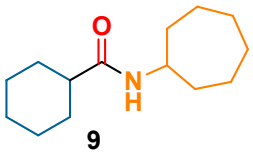
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), cyclohexylamine (23 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:5, v/v) afforded **8** as a white solid (30.1 mg, 72%).

The spectroscopic data agree with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.29 (br s, 1H), 3.79–3.68 (m, 1H), 2.04–1.97 (m, 1H), 1.92–1.54 (m, 10H), 1.48–1.01 (m, 10H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 175.2, 47.8, 45.8, 33.4, 29.9, 25.9, 25.7, 25.0.

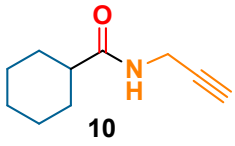
FT-ICR-MS (ESI$^+$): Calcd. for $C_{13}H_{23}NONa^+$ [M + Na]$^+$: 232.1672; found 232.1672.



9

***N*-cycloheptylcyclohexanecarboxamide (9)**:
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), cycloheptylamine (25.5 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:2, v/v) afforded **9** as a white solid (30.9 mg, 69%).
The spectroscopic data agree with those reported in the literature.[8]

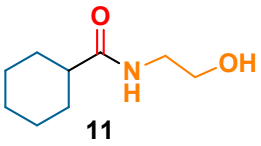
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.35 (brs, 1H), 3.97–3.89 (m, 1H), 1.99 (tt, *J* = 11.5, 3.2 Hz, 1H), 1.94–1.72 (m, 6H), 1.70–1.35 (m, 13H), 1.32–1.14 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 174.9, 50.1, 45.8, 35.4, 29.9, 28.2, 25.9, 24.3.
HRMS (ESI$^+$): Calcd. for $C_{14}H_{26}NO^+$ [M + H]$^+$: 224.2014; found 224.2010.



10

***N*-(prop-2-yn-1-yl)cyclohexanecarboxamide (10):**
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), propargylamine (13 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 2:1, v/v) afforded **10** as a white solid (13.4 mg, 40%).
The spectroscopic data agree with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.63 (s, 1H), 4.11–3.99 (m, 2H), 2.22 (t, *J* = 2.5 Hz, 1H), 2.09 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.90–1.74 (m, 4H), 1.69–1.61 (m, 1H), 1.49–1.36 (m, 2H), 1.32–1.15 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 175.7, 79.9, 71.6, 45.4, 29.7, 29.3, 25.8.
HRMS (ESI$^+$): Calcd. for $C_{10}H_{16}NO^+$ [M + H]$^+$: 166.1232; found 166.1230.



11

***N*-(2-hydroxyethyl)cyclohexanecarboxamide (11).**

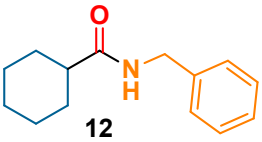
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), 2-aminoethan-1-ol (12 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:2, v/v) afforded **11** as a white solid (25.2 mg, 73%).

The spectroscopic data agree with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.03 (brs, 1H), 3.73–3.69 (m, 2H), 3.43–3.36 (m, 2H), 2.97 (brs, 1H), 2.11 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.90–1.76 (m, 4H), 1.69–1.65 (m, 1H), 1.49–1.36 (m, 2H), 1.33–1.15 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 177.7, 62.8, 45.6, 42.5, 29.8, 25.8.

FT-ICR-MS (ESI$^+$): Calcd. for $C_9H_{17}NO_2Na^+$ [M + Na]$^+$: 194.1151; found 194.1151.



12

***N*-benzylcyclohexanecarboxamide (12).**

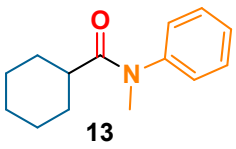
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), benzylamine (22 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:1, v/v) afforded **12** as a white solid (37.0 mg, 85%).

The spectroscopic data agree with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.35–7.29 (m, 2H), 7.29–7.22 (m, 3H), 5.72 (brs, 1H), 4.43 (s, 1H), 4.42 (s, 1H), 2.10 (tt, *J* = 11.8, 3.5 Hz, 1H), 1.93–1.83 (m, 2H), 1.83–1.72 (m, 2H), 1.70–1.59 (m, 1H), 1.52–1.36 (m, 2H), 1.31–1.15 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 176.0, 138.7, 128.8, 127.9, 127.6, 45.7, 43.5, 29.9, 25.9.

HRMS (ESI$^+$): Calcd. for $C_{14}H_{20}NO^+$ [M + H]$^+$: 218.1545; found 218.1540.



13

***N*-methyl-*N*-phenylcyclohexanecarboxamide (13).**

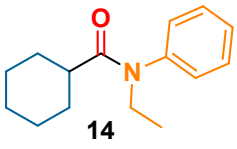
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), *N*-methylaniline (22 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 8 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:2, v/v) afforded **13** as a pale-yellow oil (31.7 mg, 75%).

The spectroscopic data agree with those reported in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.43–7.37 (m, 2H), 7.36–7.29 (m, 1H), 7.19–7.13 (m, 2H), 3.23 (s, 3H), 2.26–2.10 (m, 1H), 1.69–1.45 (m, 7H), 1.30–1.09 (m, 1H), 1.03–0.82 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 176.6, 144.4, 129.8, 127.8, 127.3, 41.5, 37.5, 29.5, 25.7, 25.6.

FT-ICR-MS (ESI$^+$): Calcd. for $C_{14}H_{19}NONa^+$ $[M + Na]^+$: 240.1359; found 240.1359.



14

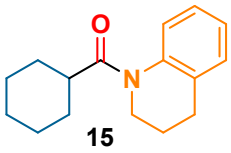
***N*-ethyl-N-phenylcyclohexanecarboxamide (14).**

Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), *N*-ethylaniline (25.2 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 8 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:2, v/v) afforded **14** as a pale-yellow oil (23.3 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.45–7.38 (m, 2H), 7.38–7.31 (m, 1H), 7.15–7.11 (m, 2H), 3.71 (q, *J* = 7.1 Hz, 2H), 2.07 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.68–1.57 (m, 4H), 1.56–1.43 (m, 3H), 1.23–1.10 (m, 1H), 1.08 (t, *J* = 7.1 Hz, 3H), 1.00–0.84 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 175.9, 142.7, 129.6, 128.5, 127.9, 44.0, 41.8, 29.6, 25.8, 25.7, 13.2.

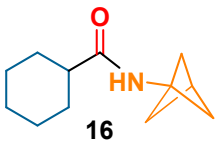
FT-ICR-MS (ESI$^+$): Calcd. for $C_{15}H_{21}NONa^+$ $[M + Na]^+$: 254.1515; found 254.1515.



15

Cyclohexyl(3,4-dihydroquinolin-1(2H)-yl)methanone (15).
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), 1,2,3,4-tetrahydroquinoline (37.5 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 8 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:5, v/v) afforded **15** as a pale-yellow oil (20.6 mg, 42%).
The spectroscopic data agree with those reported in the literature.[8]

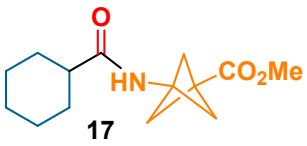
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.23–7.07 (m, 4H), 3.76 (t, *J* = 6.8 Hz, 2H), 2.86–2.76 (m, 1H), 2.70 (t, *J* = 6.8 Hz, 2H), 1.95 (quint, *J* = 6.8 Hz, 2H), 1.79–1.66 (m, 4H), 1.66–1.52 (m, 3H), 1.32–1.05 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 176.6, 139.6, 128.6, 126.2, 125.3, 124.5, 42.8, 41.5, 30.0, 26.8, 25.8, 25.8, 24.5.
FT-ICR-MS (ESI$^+$): Calcd. for $C_{16}H_{21}NONa^+$ [M + Na]$^+$: 266.1515; found 266.1516.



16

***N*-(bicyclo[1.1.1]pentan-1-yl)cyclohexanecarboxamide(16).**
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), bicyclo[1.1.1]pentan-1-amine hydrochloride (24 mg, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), triethanolamine (45 mg, 0.30 mmol), and K_2CO_3 (28.0 mg, 0.20 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, CH_2Cl_2) afforded **16** as a white solid (27.9 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.79 (s, 1H), 2.42 (s, 1H), 2.07 (s, 5H), 1.96 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.88–1.72 (m, 4H), 1.69–1.60 (m, 1H), 1.45–1.32 (m, 2H), 1.29–1.13 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 176.4, 52.8, 48.9, 45.6, 29.8, 29.7, 25.9, 24.8.
FT-ICR-MS (ESI$^+$): Calcd. for $C_{12}H_{19}NONa^+$ [M + Na]$^+$: 216.1359; found 216.1359.

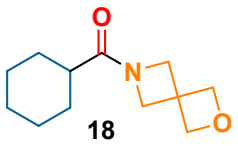


17

Methyl 3-(cyclohexanecarboxamido)bicyclo[1.1.1]pentane-1-carboxylate (17).

Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), methyl 3-aminobicyclo[1.1.1]pentane-1-carboxylate hydrochloride (36 mg, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), triethanolamine (45 mg, 0.30 mmol), and K_2CO_3 (28.0 mg, 0.20 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:4, v/v) afforded **17** as a white solid (25.2 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.88 (s, 1H), 3.68 (s, 3H), 3.35 (s, 6H), 2.00 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.88–1.71 (m, 4H), 1.69–1.59 (m, 1H), 1.46–1.30 (m, 2H), 1.29–1.12 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 176.7, 170.2, 54.5, 51.9, 45.8, 45.6, 36.0, 29.7, 25.8.
FT-ICR-MS (ESI$^+$): Calcd. for $C_{14}H_{21}NO_3Na$ $[M + Na]^+$: 274.1414; found 274.1414.

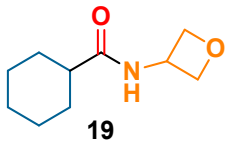


18

Cyclohexyl(2-oxa-6-azaspiro[3.3]heptan-6-yl)methanone (18).

Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), 2-oxa-6-azaspiro[3.3]heptane (18 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc, then EtOAc/MeOH = 99:1) afforded **18** as a white solid (30.9 mg, 74%).

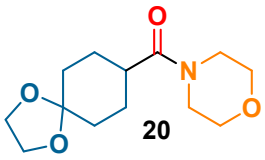
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 4.78 (q, *J* = 6.8 Hz, 4H), 4.30 (s, 2H), 4.12 (s, 2H), 2.11 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.84–1.72 (m, 2H), 1.70–1.61 (m, 3H), 1.51–1.39 (m, 2H), 1.29–1.16 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 176.3, 81.0, 59.9, 57.3, 40.2, 37.8, 28.8, 25.8, 25.8.
HRMS (ESI$^+$): Calcd. for $C_{12}H_{20}NO_2^+$ $[M + H]^+$: 210.1494; found 210.1501.



19

***N*-(oxetan-3-yl)cyclohexanecarboxamide (19):**
Prepared according to the general procedure using iodocyclohexane (39 µL, 0.30 mmol), 3-oxetamine (14 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc) afforded **19** as a white solid (27.0 mg, 74%).
The spectroscopic data agree with those reported in the literature.[12]

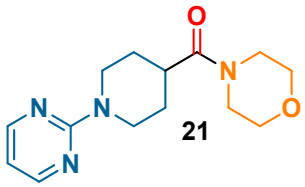
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.98 (s, 1H), 5.11–4.99 (m, 1H), 4.92 (t, *J* = 7.0 Hz, 2H), 4.46 (t, *J* = 6.7 Hz, 2H), 2.09 (tt, *J* = 11.5, 3.2 Hz, 1H), 1.87–1.77 (m, 4H), 1.69–1.62 (m, 1H), 1.47–1.37 (m, 2H), 1.32–1.14 (m, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 175.8, 78.9, 45.4, 44.7, 29.7, 25.8.
FT-ICR-MS (ESI$^+$): Calcd. for $C_{10}H_{17}NO_2Na^+$ [M + Na]$^+$: 206.1151; found 206.1151.



20

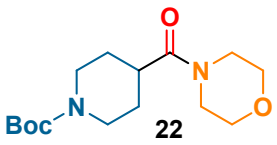
Morpholino(1,4-dioxaspiro[4.5]decan-8-yl)methanone (20).
Prepared according to the general procedure using 8-iodo-1,4-dioxaspiro[4.5]decane (80 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 2:1, v/v) afforded **20** as a white solid (26.0 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.94 (s, 4H), 3.70–3.45 (m, 8H), 2.45 (tt, *J* = 11.5, 3.2 Hz, 1H), 1.95–1.80 (m, 4H), 1.76–1.67 (m, 2H), 1.59–1.48 (m, 2H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 173.9, 108.0, 67.2, 67.0, 64.5, 46.1, 42.1, 39.0, 34.3, 26.9.
FT-ICR-MS (ESI$^+$): Calcd. for $C_{13}H_{21}NO_4Na$ [M + Na]$^+$: 278.1363; found 278.1363.



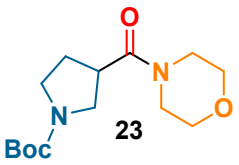
Morpholino(1-(pyrimidin-2-yl)piperidin-4-yl)methanone (21). Prepared according to the general procedure using 2-(4-Iodopiperidin-1-yl)pyrimidine (87 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:1, v/v) afforded **21** as a pale-yellow oil (25.8 mg, 47%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.29 (d, *J* = 4.7 Hz, 2H), 6.46 (t, *J* = 4.7 Hz, 1H), 4.92–4.71 (m, 2H), 3.79–3.52 (m, 8H), 3.01–2.87 (m, 2H), 2.81–2.68 (m, 1H), 1.88–1.72 (m, 4H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 173.4, 161.7, 157.9, 109.9, 67.1, 67.0, 46.1, 43.5, 42.2, 38.8, 28.4.
FT-ICR-MS (ESI$^+$): Calcd. for $C_{14}H_{20}N_4O_2Na^+$ [M + Na]$^+$: 299.1478; found 299.1479.



***tert*-butyl-4-(morpholine-4-carbonyl)piperidine-1-carboxylate (22).** Prepared according to the general procedure using *tert*-butyl 4-iodopiperidine-1-carboxylate (93 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc) afforded **22** as a pale-yellow solid (46.4 mg, 78%).
The spectroscopic data agree with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 4.14 (brs, 2H), 3.74–3.43 (m, 8H), 2.83–2.65 (m, 2H), 2.63–2.52 (m, 1H), 1.81–1.58 (m, 4H), 1.45 (s, 9H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 173.2, 154.8, 79.7, 67.1, 66.9, 46.1, 43.3, 42.2 (br), 38.4, 28.5.
FT-ICR-MS (ESI$^+$): Calcd. for $C_{15}H_{26}N_2O_4Na^+$ [M + Na]$^+$: 321.1785; found 321.1785.



23

***tert*-butyl-3-(morpholine-4-carbonyl)pyrrolidine-1-carboxylate (23).**

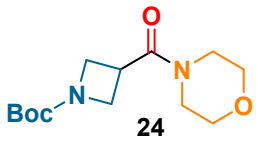
Prepared according to the general procedure using *tert*-butyl 3-iodopyrrolidine-1-carboxylate (89 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/cyclohexane = 1:1, v/v) afforded **23** as a pale-yellow solid (25.5 mg, 45%).

The spectroscopic data agree with those reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.77–3.27 (m, 10H), 3.25–3.07 (m, 1H), 2.34–1.92 (m, 2H), 1.67–1.55 (m, 2H), 1.45 (s, 9H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 170.9, 154.5, 79.5, 67.0, 66.8, 48.6, 46.2, 42.5, 28.8, 28.6.

HRMS (ESI$^+$): Calcd. for $C_{14}H_{24}N_2O_4Na^+$ [M + Na]$^+$: 307.1634; found 307.1622.



24

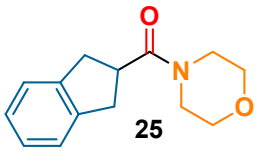
***tert*-butyl 3-(morpholine-4-carbonyl)azetidine-1-carboxylate (24).**

Prepared according to the general procedure using *tert*-butyl 3-iodoazetidine-1-carboxylate (84.9 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:1, v/v) afforded **24** as a pale-yellow oil (31.2 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 4.17 (t, *J* = 7.2 Hz, 2H), 4.05 (t, *J* = 8.6 Hz, 2H), 3.70–3.60 (m, 6H), 3.48–3.38 (m, 1H), 3.26 (t, *J* = 4.9 Hz, 2H), 1.43 (s, 9H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 169.9, 156.3, 79.9, 66.9, 66.6, 51.3, 45.6, 42.3, 31.0, 28.4.

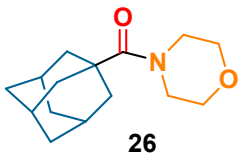
FT-ICR-MS (ESI$^+$): Calcd. for $C_{13}H_{22}N_2O_4Na^+$ [M + Na]$^+$: 293.1472; found 293.1472.



25

(2,3-dihydro-1H-inden-2-yl)(morpholino)methanone (25).
Prepared according to the general procedure using 2-iodo-2,3-dihydro-1H-indene (73.2 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc) afforded **25** as a white solid (28.9 mg, 62%).

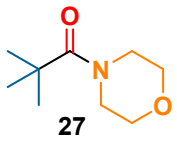
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.23–7.12 (m, 4H), 3.75–3.63 (m, 6H), 3.62–3.55 (m, 2H), 3.50 (quin, *J* = 8.7 Hz, 1H), 3.39–3.29 (m, 2H), 3.16–3.06 (m, 2H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 173.2, 141.7, 126.7, 124.4, 67.2, 67.0, 46.3, 42.5, 41.5, 36.7.
HRMS (ESI$^+$): Calcd. for $C_{14}H_{18}NO_2^+$ [M + H]$^+$: 232.1338; found 232.1338.



26

Adamantan-1-yl(morpholino)methanone (26).
Prepared according to the general procedure using 1-iodoadamantane (78.6 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/cyclohexane = 1:1, v/v) afforded **26** as a pale-yellow solid (29.0 mg, 58%).
The spectroscopic data agree with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 3.72–3.62 (m, 8H), 2.07–2.01 (m, 3H), 2.00–1.96 (m, 6H), 1.77–1.66 (m, 6H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 176.0, 67.2, 46.1, 41.8, 39.1, 36.8, 28.6.
HRMS (ESI$^+$): Calcd. for $C_{15}H_{24}NO_2^+$ [M + H]$^+$: 250.1807; found 250.1807.



27

2,2-dimethyl-1-morpholinopropan-1-one (27).

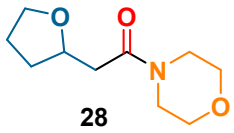
Prepared according to the general procedure using 2-iodo-2-methylpropane (35.7 µL, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:1, v/v) afforded **27** as a pale-yellow solid (17.8 mg, 52%).

The spectroscopic data agree with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.67–3.61 (m, 8H), 1.27 (s, 9H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ 176.6, 67.0, 45.9, 38.7, 28.4.

FT-ICR-MS (ESI$^+$): Calcd. for $C_9H_{17}NO_2Na^+$ [M + Na]$^+$: 194.1151; found 194.1152.



28

1-morpholino-2-(tetrahydrofuran-2-yl)ethan-1-one (28).

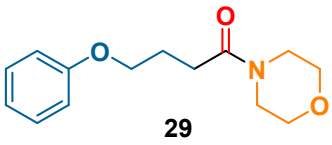
Prepared according to the general procedure using 2-(iodomethyl)tetrahydrofuran (63.6 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, acetone/petroleum ether = 1:1, v/v) afforded **28** as a pale-yellow oil (14.9 mg, 37%).

The spectroscopic data agree with those reported in the literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 4.25 (dq, *J* = 7.8, 6.4 Hz, 1H), 3.85 (dt, *J* = 8.4, 6.7 Hz, 1H), 3.77–3.40 (m, 9H), 2.68 (dd, *J* = 14.9, 6.5 Hz, 1H), 2.45 (dd, *J* = 14.9, 6.0 Hz, 1H), 2.21–2.05 (m, 1H), 1.95–1.81 (m, 2H), 1.63–1.49 (m, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ 169.6, 76.2, 68.1, 67.0, 66.9, 46.5, 42.0, 39.2, 31.7, 25.8.

FT-ICR-MS (ESI$^+$): Calcd. for $C_{10}H_{17}NO_3Na^+$ [M + Na]$^+$: 222.1101; found 222.1101.



29

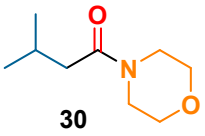
1-morpholino-4-phenoxybutan-1-one **(29).**

Prepared according to the general procedure using (3-iodopropoxy)benzene (78.6 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, acetone/petroleum ether = 1:2, v/v) afforded **29** as a pale-yellow oil (34.1 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.34–7.19 (m, 2H), 6.98–6.84 (m, 3H), 4.04 (t, *J* = 5.8 Hz, 2H), 3.71–3.56 (m, 6H), 3.50–3.45 (m, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.15 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 171.2, 158.9, 129.6, 120.9, 114.6, 67.1, 66.9, 66.7, 46.0, 42.1, 29.4, 25.0.

HRMS (ESI$^+$): Calcd. for $C_{14}H_{20}NO_3^+$ [M + H]$^+$: 250.1443; found 250.1440.



30

3-methyl-1-morpholinobutan-1-one (30).

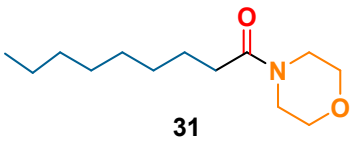
Prepared according to the general procedure using 1-iodo-2-methylpropane (34.5 µL, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:1, v/v) afforded **30** as a pale-yellow oil (15.3 mg, 45%).

The spectroscopic data agree with those reported in the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.70–3.60 (m, 6H), 3.49–3.44 (m, 2H), 2.21–2.17 (m, 2H), 2.16–2.06 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 171.3, 67.2, 66.9, 46.4, 42.0, 42.0, 25.9, 22.9.

HRMS (ESI$^+$): Calcd. for $C_9H_{17}NO_2^+$ [M + H]$^+$: 172.1338; found 172.1339.



31

1-morpholinononan-1-one (31).

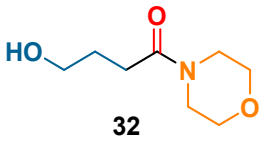
Prepared according to the general procedure using 1-iodooctane (54.0 µL, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 6:4, v/v) afforded **31** as a pale-yellow oil (29.0 mg, 64%).

The spectroscopic data agree with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.69–3.54 (m, 6H), 3.48–3.41 (m, 2H), 2.34–2.25 (m, 2H), 1.70–1.55 (m, 2H), 1.36–1.17 (m, 10H), 0.91–0.77 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 172.1, 67.1, 66.9, 46.2, 42.0, 33.3, 32.0, 29.6, 29.5, 29.3, 25.4, 22.8, 14.2.

HRMS (ESI$^+$): Calcd. for $C_{13}H_{26}NO_2^+$ [M + H]$^+$: 228.1964; found 228.1962.



32

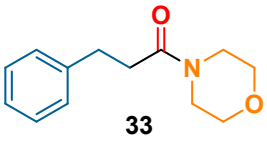
4-hydroxy-1-morpholinobutan-1-one (32).

Prepared according to the general procedure using 3-iodo-1-propanol (28.7 µL, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, acetone/petroleum ether = 4:6, v/v) afforded **32** as a pale-yellow oil (27.6 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 3.71–3.55 (m, 8H), 3.51–3.40 (m, 2H), 2.46 (t, *J* = 6.9 Hz, 2H), 1.91–1.85 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 172.3, 66.9, 66.7, 62.4, 46.1, 42.1, 30.4, 27.7.

FT-ICR-MS (ESI$^+$): Calcd. for $C_8H_{15}NO_3Na^+$ [M + Na]$^+$: 196.0944; found 196.0944.



33

1-morpholino-3-phenylpropan-1-one (33).

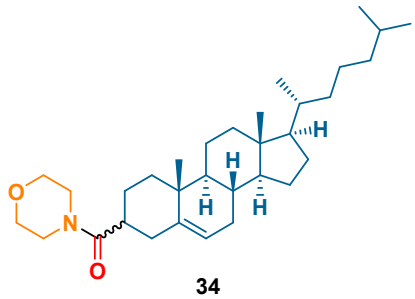
Prepared according to the general procedure using (2-iodoethyl)benzene (69.6 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 4 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 7:3, v/v) afforded **33** as a pale-yellow oil (32.9 mg, 75%).

The spectroscopic data agree with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.36–7.29 (m, 2H), 7.28–7.21 (m, 3H), 3.72–3.61 (m, 4H), 3.61–3.49 (m, 2H), 3.45–3.36 (m, 2H), 3.07–2.96 (m, 2H), 2.70–2.60 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 171.0, 141.2, 128.7, 128.6, 126.4, 67.0, 66.6, 46.1, 42.1, 34.9, 31.6.

FT-ICR-MS (ESI$^+$): Calcd. for $C_{13}H_{17}NO_2Na^+$ [M + Na]$^+$: 242.1151; found 242.1153.



34

((8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)(morpholino)methanone (34).

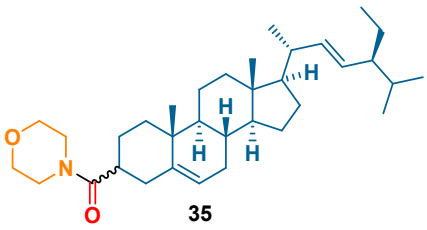
Prepared according to the general procedure using **compound I** (148.96 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (15.6 mg, 0.020 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 8 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 4:6, v/v) afforded **34** as a diastereomeric mixture (55.1 mg, 57%).

The spectroscopic data agree with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.40–5.19 (m, 2H), 3.78–3.31 (m, 16H), 2.90–2.77 (m, 1H), 2.66–2.50 (m, 2H), 2.50–2.34 (m, 1H), 2.22–2.08 (m, 1H), 2.07–1.86 (m, 6H), 1.86–0.94 (m, 53H), 0.94–0.88 (m, 6H), 0.88–0.83 (m, 12H), 0.75–0.54 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 174.2, 174.1, 141.9, 139.9, 121.2, 121.0, 67.2, 67.0, 57.0, 56.3, 50.6, 49.5, 46.0, 42.4, 42.1, 41.8, 39.9, 39.6, 39.1, 37.2, 36.9, 36.3, 36.1, 35.9, 35.6, 35.0, 33.8, 32.0, 31.9, 28.4, 28.3, 28.1, 25.6, 24.4, 24.0, 23.9, 22.9, 22.7, 21.0, 20.8, 19.6, 18.8, 12.0.

HRMS (APCI): Calcd. for $C_{32}H_{54}NO_2^+$ [M + H]$^+$: 484.4155; found 484.4158.



35

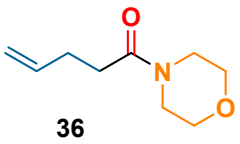
((8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*S*, *E*)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)(morpholino)methanone (35).

Prepared according to the general procedure using **compound H** (156.77 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (15.6 mg, 0.020 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 8 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether = 4:6, v/v) afforded **35** as a diastereomeric mixture (68.3 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.40–5.26 (m, 2H), 5.22–5.08 (m, 2H), 5.08–4.92 (m, 2H), 3.79–3.33 (m, 16H), 2.91–2.75 (m, 1H), 2.62–2.50 (m, 2H), 2.50–2.36 (m, 1H), 2.09–1.40 (m, 33H), 1.27–0.96 (m, 27H), 0.90–0.75 (m, 18H), 0.74–0.62 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 174.2, 174.1, 141.8, 139.9, 138.5, 138.4, 129.4, 129.3, 121.1, 120.9, 67.1, 67.0, 57.1, 56.9, 56.1, 55.9, 51.3, 51.3, 50.6, 49.5, 46.4, 46.0, 42.3, 42.1, 41.8, 41.0, 40.6, 40.6, 39.8, 39.8, 39.1, 37.3, 36.9, 36.1, 35.6, 35.0, 33.9, 32.0, 32.0, 32.0, 31.9, 31.9, 29.1, 29.0, 25.7, 25.5, 24.5, 23.9, 21.3, 21.3, 21.2, 21.0, 20.8, 19.6, 19.6, 19.1, 12.3, 12.1.

FT-ICR-MS (ESI$^+$): Calcd. for $C_{34}H_{55}NO_2Na^+$ [M + Na]$^+$: 532.4125; found 532.4124.



36

1-morpholinopent-4-en-1-one (36).

Prepared according to the general procedure using (iodomethyl)cyclopropane (54.6 mg, 0.30 mmol), morpholine (17.6 µL, 0.20 mmol), **4CzIPN** (7.8 mg, 0.010 mmol, 5 mol%), and triethanolamine (45 mg, 0.30 mmol). The reaction mixture was stirred for 2 h under irradiation with blue LEDs. Purification by flash column chromatography (SiO_2, EtOAc) afforded **36** as a pale-yellow oil (15.1 mg, 45%).

The spectroscopic data agree with those reported in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.97–5.78 (m, 1H), 5.18–4.94 (m, 2H), 3.74–3.56 (m, 6H), 3.56–3.40 (m, 2H), 2.51–2.30 (m, 4H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ 171.0, 137.5, 115.5, 67.1, 66.8, 46.1, 42.1, 32.5, 29.3.

HRMS (ESI$^+$): Calcd. for $C_9H_{16}NO_2^+$ [M + H]$^+$: 170.1181; found 170.1179.

7. General Procedure for Carbon-13 Isotopic Labeling of Compound 35

Under an argon atmosphere, a COware® two-chamber reactor (20 mL total volume) was charged as follows: **Chamber 2** was sequentially loaded with **4CzIPN** (15.6 mg, 5 mol%), morpholine (17.6 µL, 0.20 mmol, 1.0 equiv), compound **H** (0.30 mmol, 1.5 equiv), TEOA (45 mg, 0.30 mmol, 1.5 equiv), and EtOAc (2.0 mL, 0.10 M), then sealed with a PTFE-faced silicone septum screw cap.

Chamber 1 was charged with Sila^{13}COgen® ($MePh_2Si^{13}CO_2H$, 291 mg, 1.20 mmol, 6.0 equiv) and KF (76.6 mg, 1.32 mmol, 6.6 equiv), sealed under identical conditions, and treated with anhydrous DMF (2.0 mL).

The reactor was stirred under 456 nm Kessil® blue LED irradiation (50% intensity) at RT for 8 h. The contents of **Chamber 2** were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether, 4:6 v/v) afforded amide **35 (^{13}CO)** as a diastereomeric mixture (65.25 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.40–5.23 (m, 2H), 5.22–5.09 (m, 2H), 5.07–4.92 (m, 2H), 3.84–3.28 (m, 16H), 2.92–2.75 (m, 1H), 2.56 (tt, *J* = 12.1, 2.2 Hz, 2H), 2.50–2.34 (m, 1H), 2.19–1.34 (m, 33H), 1.29–0.90 (m, 28H), 0.90–0.73 (m, 18H), 0.75–0.60 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ **174.2 (^{13}CO)**, **174.1 (^{13}CO)**, 141.9, 141.8, 139.9, 138.5, 138.4, 129.4, 129.3, 121.1, 120.9, 67.1, 67.0, 57.0, 56.9, 56.1, 55.9, 51.3, 51.3, 50.6, 49.6, 46.0, 42.3, 42.1, 42.0, 41.5, 40.6, 40.6, 39.8, 39.8, 39.1, 39.0, 37.3, 36.9, 36.4, 35.9, 35.6, 35.0, 33.9, 32.0, 32.0, 32.0, 31.9, 31.8, 29.0, 29.0, 25.6, 25.5, 24.4, 23.9, 21.3, 21.3, 21.2, 21.0, 20.8, 19.6, 19.6, 19.1, 12.4, 12.1, 12.1.

FT-ICR-MS (ESI$^+$): Calcd. for $^{13}C_1C_{33}H_{55}NO_2Na^+$ $[M + Na]^+$: 533.4159; found 533.4158.

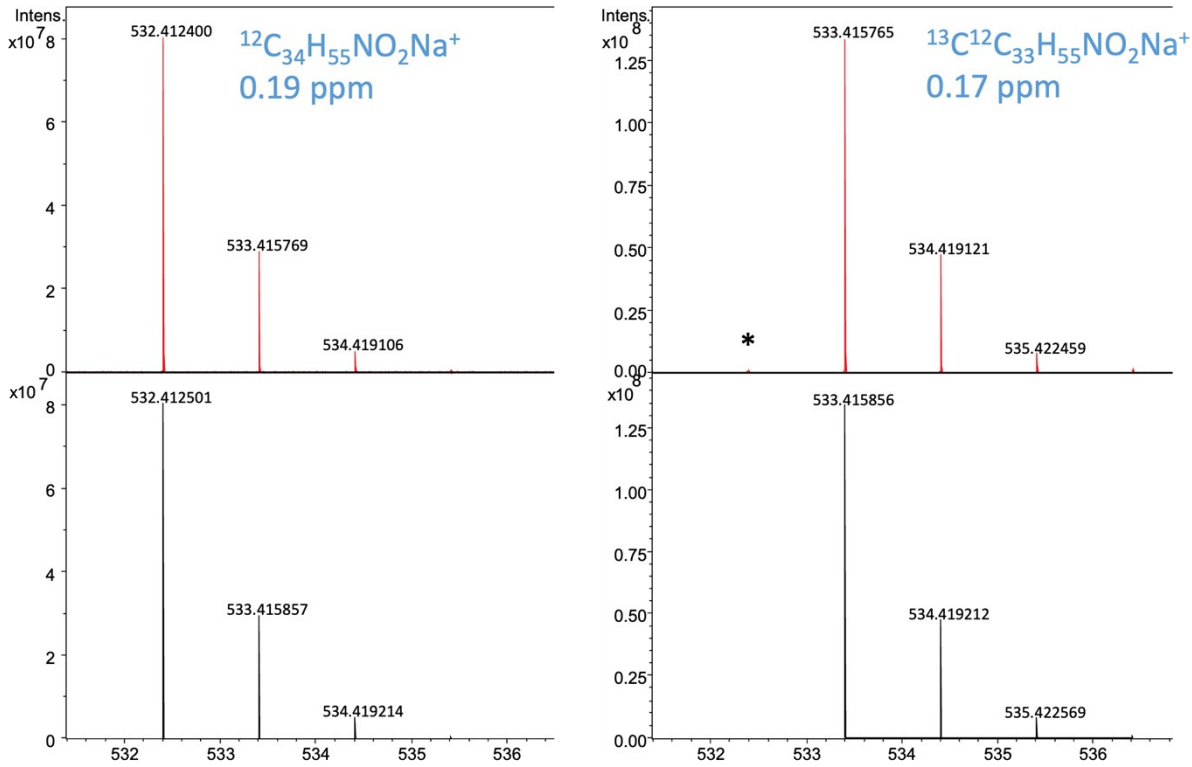


Figure S1. Experimental (top, red) and **simulated** (bottom, black) isotopic distributions for $[^{12}C_{34}H_{55}NO_2Na]^+$ — 35 (^{12}CO) — (left) and $[^{13}C_1{}^{12}C_{33}H_{55}NO_2Na]^+$ — 35 (^{13}CO) — (right) detected by ESI(+) FT-ICR MS. (*) The $[^{12}C_{34}H_{55}NO_2Na]^+$ ion is observed at 0.7% relative intensity compared to the $[^{13}C_1{}^{12}C_{33}H_{55}NO_2Na]^+$ isotopologue (100% intensity).

8. Gram-Scale Preparation of Amide 35

Under an argon atmosphere, a COware® two-chamber reactor (400 mL total volume) was charged as follows: **Chamber 2** was sequentially loaded with **4CzIPN** (15.6 mg, 5 mol%), morpholine (0.262 mL, 3.0 mmol), compound **H** (2.35 g, 4.50 mmol), TEOA (0.671 g, 4.50 mmol), and EtOAc (30.0 mL, 0.10 M), then sealed with a PTFE-faced silicone septum screw cap.

Chamber 1 was charged with SilaCOgen® ($MePh_2SiCO_2H$) (4.36 g, 18.0 mmol) and KF (1.15 g, 19.8 mmol), sealed under identical conditions, and treated with anhydrous DMF (30.0 mL). The reactor was stirred under 456 nm Kessil® blue LED irradiation (100% intensity) at RT for 8 h.

The contents of **Chamber 2** were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, EtOAc/petroleum ether, 4:6 v/v) yielded amide **35** as a diastereomeric mixture (1.04 g, 68%).

9. EPR Analysis

Sample preparation: 4CzIPN (5.0×10^{-3} M) and morpholine (1.0×10^{-1} M) or TEOA (1.5×10^{-1} M) were dissolved in EtOAc (1.0 mL). Solutions were degassed by N_2 bubbling for 5 min and immediately transferred into 50 µL Hirschmann glass capillaries, which were sealed at both ends before introduction into the EPR cavity.

EPR measurement conditions: Continuous-wave X-band EPR spectra were recorded under *in situ* illumination using an Aura Light Engine (Lumencor, λ = 475 nm, maximum output ~500 mW).

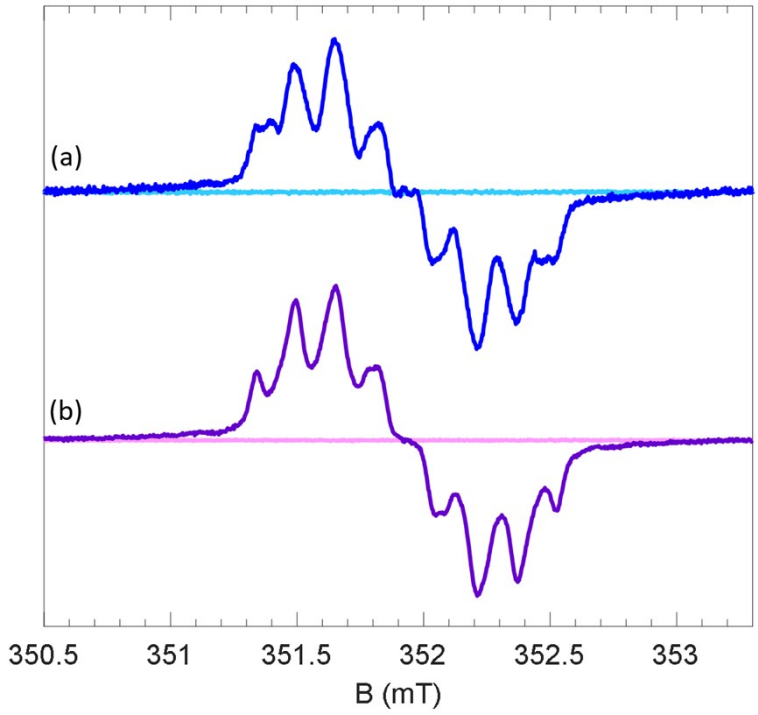


Figure S2. Continuous-wave EPR analysis under catalytic conditions. (a) EPR spectra of a solution of **4CzIPN** and morpholine recorded in the dark (light blue) and under *in situ* 475 nm illumination (dark blue). (b) EPR spectra of **4CzIPN** in the presence of morpholine and TEOA recorded in the dark (light purple) and under illumination (dark purple). Subtle alterations are observed when comparing the spectra collected in the presence of morpholine only *vs.* morpholine + TEOA. In particular, additional peripheral features in the 351.0–352.5 G region appear under illumination in the morpholine-only system, consistent with the formation of trace morpholine-derived radical species.

10. DFT Calculations

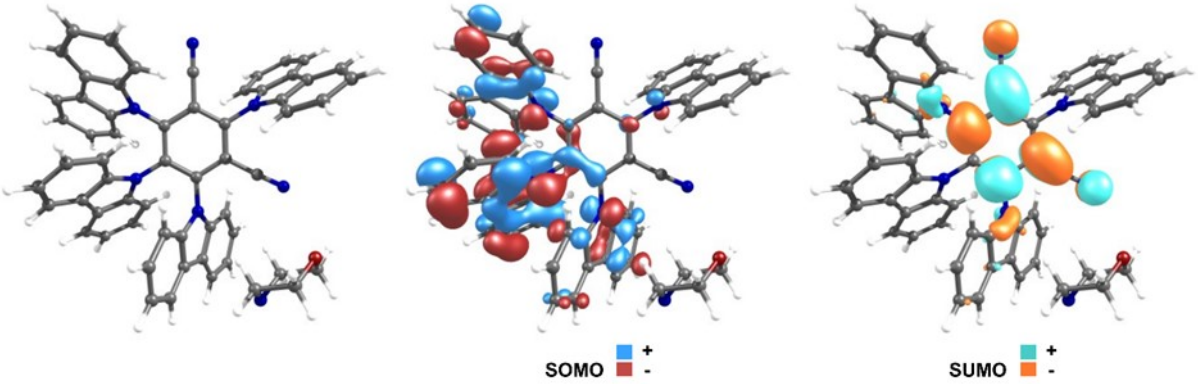


Figure S3. Optimized structure of the carbazole-cyano-functionalized benzene and morpholine radicals, and the corresponding SOMO and SUMO distributions.

The geometry optimization of the system comprising the carbazole-cyano-functionalized benzene and morpholine radicals was performed at the UM06-2X/6-311+G(d,p) level of theory using Gaussian 16 software.[16,17] The singly occupied molecular orbital (SOMO) is distributed along the carbazole moieties, while the singly unoccupied molecular orbital (SUMO) is primarily distributed along the phenyl core and the cyanide groups. Remarkably, the carbazole situated between the cyanide groups has a negligible contribution to the SOMO-SUMO interaction. This suggests that this carbazole moiety may not significantly influence the electronic properties associated with the frontier orbitals. The same occurs with the morpholine molecule. The energies associated with the frontier orbitals are -7.39 eV for the SOMO and -2.02 eV for the LUMO. The energy difference between the SOMO and LUMO (5.37 eV) indicates a relatively large band gap, which may suggest the system's stability and its potential as a semiconductor or optoelectronic material.

For the mechanistic study, the transition states and reaction pathways were optimized using the QST3 method implemented in Gaussian 16.[16] This method was employed to accurately determine the activation barriers and the geometries of the transition states (TS1, TS2, TS3, and TS4) along the reaction coordinate. The QST3 method provides a reliable way to obtain second-order saddle points on the potential energy surface, ensuring the identification of the correct mechanistic steps in the reaction.

Table S5. Calculated energy difference (ΔE) for the formation of the reduced form of 4CzIPN, 4DPAIPN, and Eosin-Y (M06-2X/6-311G(d,p).

PC	ΔE (kcal mol^{-1})
4-CzIPN → 4-CzIPN$^{\cdot-}$	-73.9
4-DPAIPN → 4-DPAIPN$^{\cdot-}$	-66.9
Eosin-Y → Eosin Y$^{\cdot-}$	-54.9

Optimized geometries

1a

C	-0.069933000	-0.006180000	-3.000016000
C	0.253557000	1.289449000	-2.252530000
C	-0.318949000	1.258508000	-0.826377000

C	0.071767000	0.006620000	-0.109701000
C	-0.091519000	-1.294731000	-0.826089000
C	0.477149000	-1.224361000	-2.252413000
H	0.340669000	0.030228000	-4.012626000
H	-1.158528000	-0.102999000	-3.099066000
H	-0.140898000	2.153297000	-2.794032000
H	1.341663000	1.408883000	-2.198669000
H	-0.007694000	2.142850000	-0.265290000
H	-1.418957000	1.309752000	-0.902257000
H	0.187466000	0.016966000	0.967722000
H	0.371545000	-2.109942000	-0.265026000
H	-1.165065000	-1.539994000	-0.901704000
H	0.241145000	-2.144259000	-2.793837000
H	1.569269000	-1.149882000	-2.198859000

TS1

C	-2.140260000	0.273810000	-0.483833000
C	-1.778033000	-1.108282000	0.066571000
C	-0.263499000	-1.368975000	-0.065639000
C	0.489086000	-0.251672000	0.590827000
C	0.178201000	1.120239000	0.074309000
C	-1.337267000	1.379499000	0.206619000
H	-3.211051000	0.457199000	-0.362687000
H	-1.931300000	0.297413000	-1.560200000
H	-2.334278000	-1.889436000	-0.458322000
H	-2.060438000	-1.163627000	1.123917000
H	0.004456000	-2.334295000	0.368707000
H	-0.010401000	-1.403416000	-1.132891000
H	0.661186000	-0.344132000	1.661011000
H	0.749623000	1.884762000	0.605034000
H	0.448273000	1.182480000	-0.987546000
H	-1.581171000	2.356240000	-0.219686000
H	-1.603949000	1.413463000	1.268764000
C	2.557895000	-0.599865000	0.000856000
O	3.079039000	0.359353000	-0.330544000

1b

C	-0.001769000	0.002647000	-2.969867000
C	0.224541000	1.283507000	-2.163768000
C	-0.470715000	1.213929000	-0.802347000
C	-0.004053000	-0.029395000	-0.030331000
C	-0.228772000	-1.317833000	-0.829229000
C	0.466544000	-1.227655000	-2.189755000
H	0.520254000	0.063774000	-3.927990000
H	-1.070765000	-0.098014000	-3.192592000
H	-0.139573000	2.152575000	-2.716915000
H	1.300201000	1.428574000	-2.008731000
H	-0.269448000	2.112451000	-0.214517000
H	-1.555417000	1.153713000	-0.948426000
H	1.062556000	0.091088000	0.200052000
H	0.135168000	-2.176973000	-0.261129000
H	-1.306241000	-1.456213000	-0.973594000
H	0.274634000	-2.138779000	-2.761994000
H	1.550636000	-1.168264000	-2.037068000
C	-0.690052000	-0.073519000	1.324357000
O	-1.310176000	-0.949116000	1.810584000

TS2

C	5.208580000	1.320281000	0.495023000
C	5.092072000	-0.186202000	0.737197000
C	3.611483000	-0.620607000	0.786656000
C	2.928301000	-0.175556000	-0.475141000
C	2.996794000	1.302585000	-0.734102000

C	4.477321000	1.736661000	-0.783089000
H	6.260873000	1.610709000	0.436902000
H	4.774994000	1.856079000	1.347973000
H	5.586135000	-0.467012000	1.671211000
H	5.597385000	-0.725399000	-0.071818000
H	3.532622000	-1.701561000	0.920723000
H	3.136215000	-0.141466000	1.651076000
H	3.102668000	-0.807701000	-1.344768000
H	2.487959000	1.566728000	-1.663609000
H	2.501685000	1.841881000	0.082399000
H	4.535873000	2.818933000	-0.926669000
H	4.960061000	1.268206000	-1.648030000
I	0.439877000	-0.754544000	-0.187102000
C	-5.073923000	1.678962000	0.386836000
C	-3.629951000	2.135060000	0.602723000
C	-2.709229000	0.952138000	0.912113000
C	-2.803836000	-0.095256000	-0.214216000
C	-4.248148000	-0.566505000	-0.416284000
C	-5.155976000	0.627231000	-0.720736000
H	-5.706287000	2.535925000	0.142396000
H	-5.459625000	1.250726000	1.319591000
H	-3.575017000	2.858614000	1.419498000
H	-3.269220000	2.641123000	-0.300232000
H	-1.677115000	1.288790000	1.027751000
H	-3.013713000	0.483097000	1.854734000
H	-2.411315000	0.350762000	-1.134235000
H	-4.290653000	-1.303196000	-1.221950000
H	-4.586355000	-1.064019000	0.498829000
H	-6.184936000	0.280820000	-0.844021000
H	-4.853674000	1.078066000	-1.673169000
C	-1.901531000	-1.259249000	0.124348000
O	-2.189225000	-2.328318000	0.520484000

1c

C	0.064614000	-0.038736000	-2.985045000
C	0.158170000	1.278182000	-2.213250000
C	-0.618183000	1.213084000	-0.895690000
C	-0.110687000	0.028850000	-0.048769000
C	-0.231069000	-1.293032000	-0.815664000
C	0.549772000	-1.209387000	-2.128952000
H	0.648646000	0.023608000	-3.906323000
H	-0.977917000	-0.212851000	-3.276126000
H	-0.227247000	2.104001000	-2.815560000
H	1.209369000	1.500725000	-1.997174000
H	-0.510210000	2.147690000	-0.342420000
H	-1.684770000	1.066754000	-1.099766000
H	0.931234000	0.218239000	0.227100000
H	0.134087000	-2.116353000	-0.197610000
H	-1.288165000	-1.484972000	-1.025703000
H	0.445664000	-2.150997000	-2.672937000
H	1.616060000	-1.082735000	-1.908719000
C	-0.901188000	-0.047262000	1.233053000
O	-1.755620000	-0.788866000	1.539624000
I	-0.325778000	1.557665000	2.715837000

TS3

C	-3.519499000	-2.567632000	0.043802000
C	-3.692146000	-1.080284000	-0.262814000
C	-2.621274000	-0.231474000	0.428745000
C	-1.222750000	-0.713982000	0.003349000
C	-1.045748000	-2.196683000	0.368182000
C	-2.114869000	-3.038485000	-0.332148000
H	-4.270998000	-3.153261000	-0.490951000

H	-3.680900000	-2.736952000	1.114747000
H	-4.679090000	-0.735159000	0.053501000
H	-3.628601000	-0.920730000	-1.345387000
H	-2.751163000	0.820352000	0.175953000
H	-2.712247000	-0.329819000	1.516251000
H	-1.089088000	-0.557452000	-1.069122000
H	-0.049850000	-2.537704000	0.092221000
H	-1.140300000	-2.303860000	1.453779000
H	-1.976300000	-4.088645000	-0.064990000
H	-1.979506000	-2.962521000	-1.417366000
C	-0.163884000	0.080872000	0.723554000
O	0.292025000	0.048051000	1.791198000
I	-0.302171000	2.448961000	-0.174398000
C	2.729118000	0.303590000	0.034475000
N	1.573674000	-0.276226000	-0.668539000
C	1.950512000	-1.518443000	-1.369726000
C	2.645335000	-2.484139000	-0.421576000
O	3.768184000	-1.874178000	0.190409000
C	3.357171000	-0.740743000	0.940325000
H	2.389060000	1.157139000	0.624779000
H	3.479303000	0.656067000	-0.683788000
H	1.054573000	-1.977492000	-1.794496000
H	2.636990000	-1.286608000	-2.193929000
H	3.008397000	-3.349872000	-0.974771000
H	1.958291000	-2.829852000	0.360991000
H	4.245783000	-0.335253000	1.422750000
H	2.641896000	-1.052273000	1.712068000
H	1.249648000	0.395998000	-1.359240000

1d

C	0.430161000	-0.263673000	-2.899658000
C	0.413015000	1.013556000	-2.059167000
C	-0.305203000	0.791001000	-0.728399000
C	0.361090000	-0.362227000	0.049086000
C	0.356588000	-1.657476000	-0.794647000
C	1.067538000	-1.419212000	-2.127411000
H	0.971391000	-0.093213000	-3.832966000
H	-0.597971000	-0.532823000	-3.167848000
H	-0.081117000	1.822489000	-2.601679000
H	1.441397000	1.338998000	-1.865493000
H	-0.292040000	1.701744000	-0.125247000
H	-1.351834000	0.525973000	-0.907142000
H	1.394425000	-0.084712000	0.280569000
H	0.835905000	-2.476597000	-0.251911000
H	-0.684900000	-1.946305000	-0.969779000
H	1.036534000	-2.338036000	-2.716921000
H	2.123244000	-1.195366000	-1.936752000
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H	-1.663582000	-2.323985000	3.366441000

H	0.954657000	0.294081000	2.592574000

TS4

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C	-2.044000000	1.428673000	0.970466000
C	-1.613695000	0.216272000	0.135594000
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1e

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11. Laser Flash Photolysis

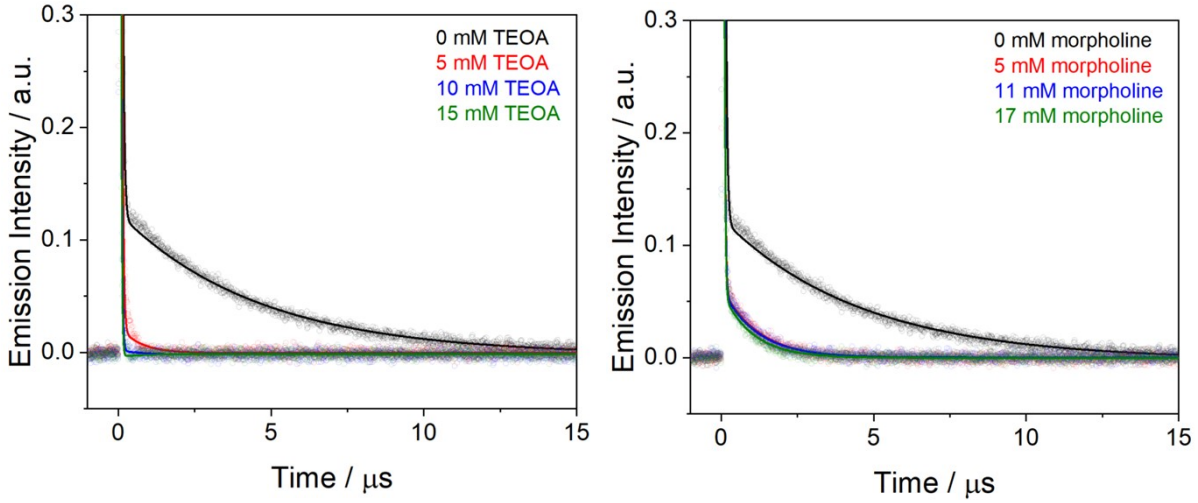

Figure S4. Kinetic fitting of the emission kinetics at 514 nm of **4CzIPN** (30 μM) in Ar-saturated EtOAc, upon incremental addition of triethanolamine (left) or morpholine (right) under λexc = 430 nm (E = 11 mJ). Fitting results are summarized in Table S4.

Table S4. Summary of kinetic parameters for **4CzIPN** (30 μM) in Ar-saturated EtOAc, monitored at 514 nm under λexc = 430 nm (E = 11 mJ). Extracted lifetimes correspond to prompt fluorescence (PF) and thermally activated delayed fluorescence (TADF) components obtained by biexponential fitting.

[TEOA] / mM	τ_{PF} / ns	τ_{TADF} / ns
0	42	4540
5	35	672
10	28	289
15	23	209
[morpholine] / mM	**τ_{PF} / ns**	**τ_{TADF} / ns**
0	42	4540
5	33	1650
11	29	1142
17	27	991

12. Spectroelectrochemistry

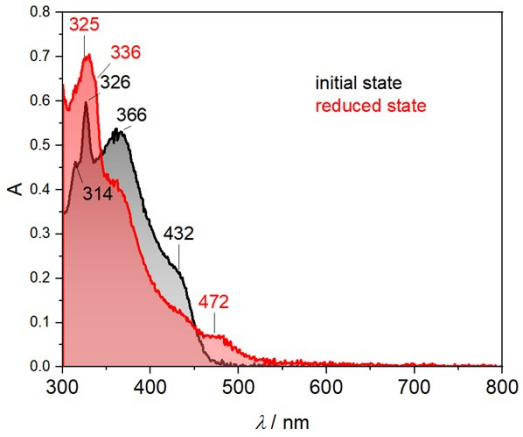

Figure S5. Spectroelectrochemical generation of **4CzIPN**$^{\bullet-}$ in Ar-saturated ethyl acetate under applied potential, showing characteristic absorption features of the radical anion species.

13. Electrochemistry

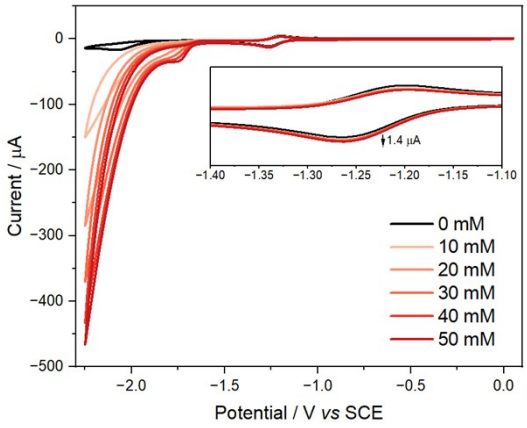

Figure S6. Cyclic voltammograms of 4CzIPN (0.5 mM) in Ar-saturated MeCN with 0.1 M NBu_4PF_6, recorded in the absence of iodocyclohexane (black trace) and upon incremental addition of iodocyclohexane, showing progressive changes in the reductive wave.

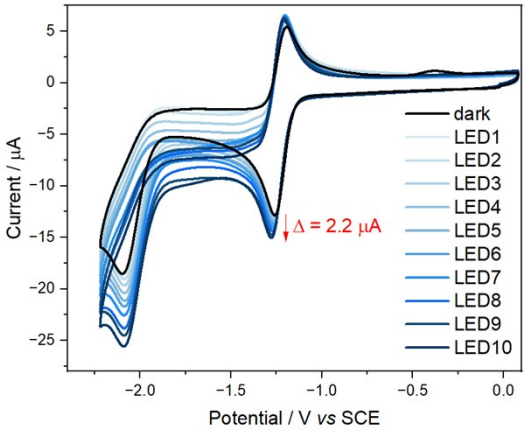

Figure S7. Cyclic voltammograms of 4CzIPN (0.5 mM) in Ar-saturated MeCN with 0.1 M NBu_4PF_6 under increasing blue LED irradiation intensity, highlighting the emergence of minimal light-induced current at the first reduction wave. This current enhancement may come from solvent-mediated reduction and needs to be compared relative to the pronounced effects in presence of relevant substrates (Figure S7).

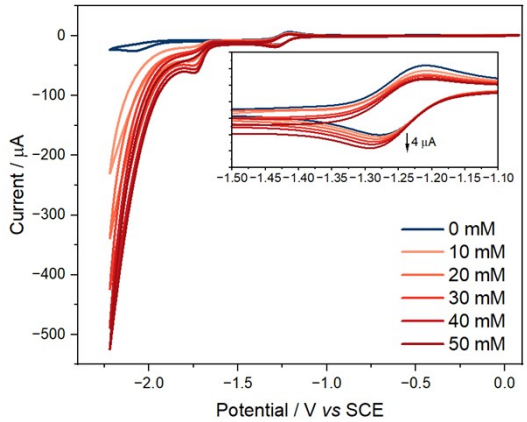

Figure S8. Cyclic voltammograms of 4CzIPN (0.5 mM) in Ar-saturated MeCN with 0.1 M NBu_4PF_6 recorded under blue LED irradiation (intensity level 10), with incremental addition of iodocyclohexane, illustrating photocurrent enhancement in the presence of substrate.

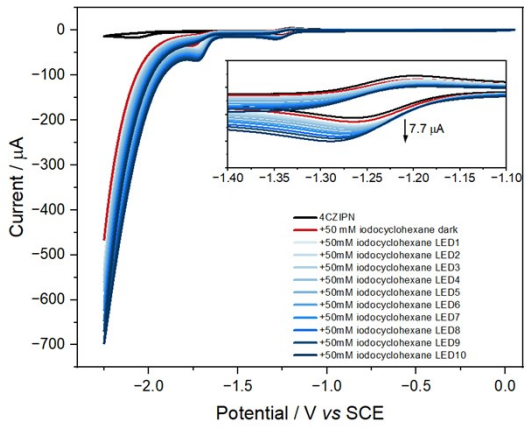

Figure S9. Cyclic voltammograms of 4CzIPN (0.5 mM) in Ar-saturated MeCN with 0.1 M NBu_4PF_6, showing the dark trace (black), the effect of 50 mM iodocyclohexane (red), and the corresponding light-activated response under blue LED irradiation, indicating the photocatalytic reduction onset and current enhancement.

14. *In situ* UV-Vis Spectroscopy

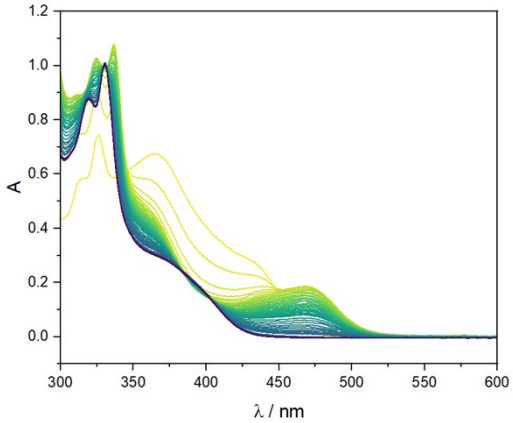

Figure S10. ***In situ*** **UV-Vis monitoring** of Ar-saturated MeCN containing **4CzIPN** (45 µM) and TEOA (45 mM) under 463 nm irradiation (color progression yellow → blue, 0 → 60 min).

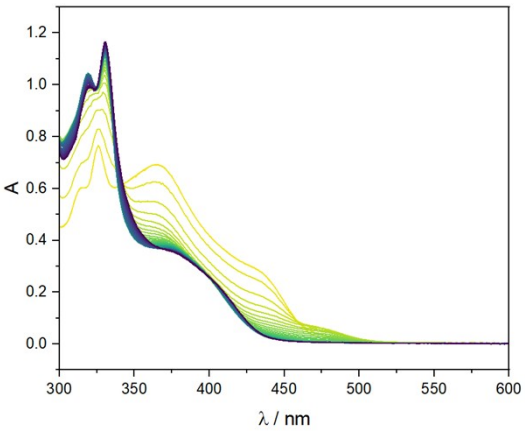

Figure S11. ***In situ*** **UV-Vis monitoring** of Ar-saturated MeCN containing **4CzIPN** (45 µM) and morpholine (45 mM) under 463 nm irradiation (yellow → blue, 0 → 60 min).

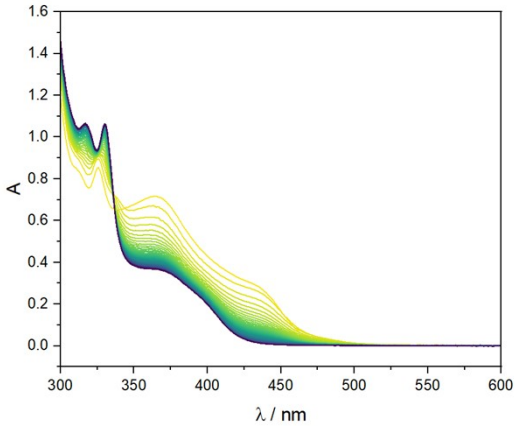

Figure S12. ***In situ*** **UV-Vis monitoring** of Ar-saturated MeCN containing **4CzIPN** (45 µM), TEOA (45 mM), and iodocyclohexane (45 mM) under 463 nm irradiation (yellow → blue, 0 → 60 min).

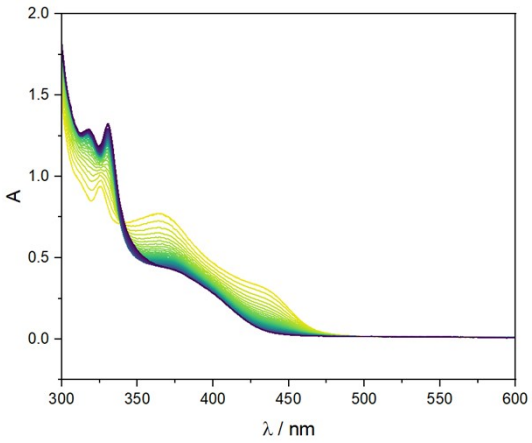

Figure S13. ***In situ*** **UV-Vis monitoring** of Ar-saturated MeCN containing **4CzIPN** (45 µM), TEOA (45 mM), morpholine (45 mM), and iodocyclohexane (45 mM) under 463 nm irradiation (yellow → blue, 0 → 60 min).

15. NMR spectra

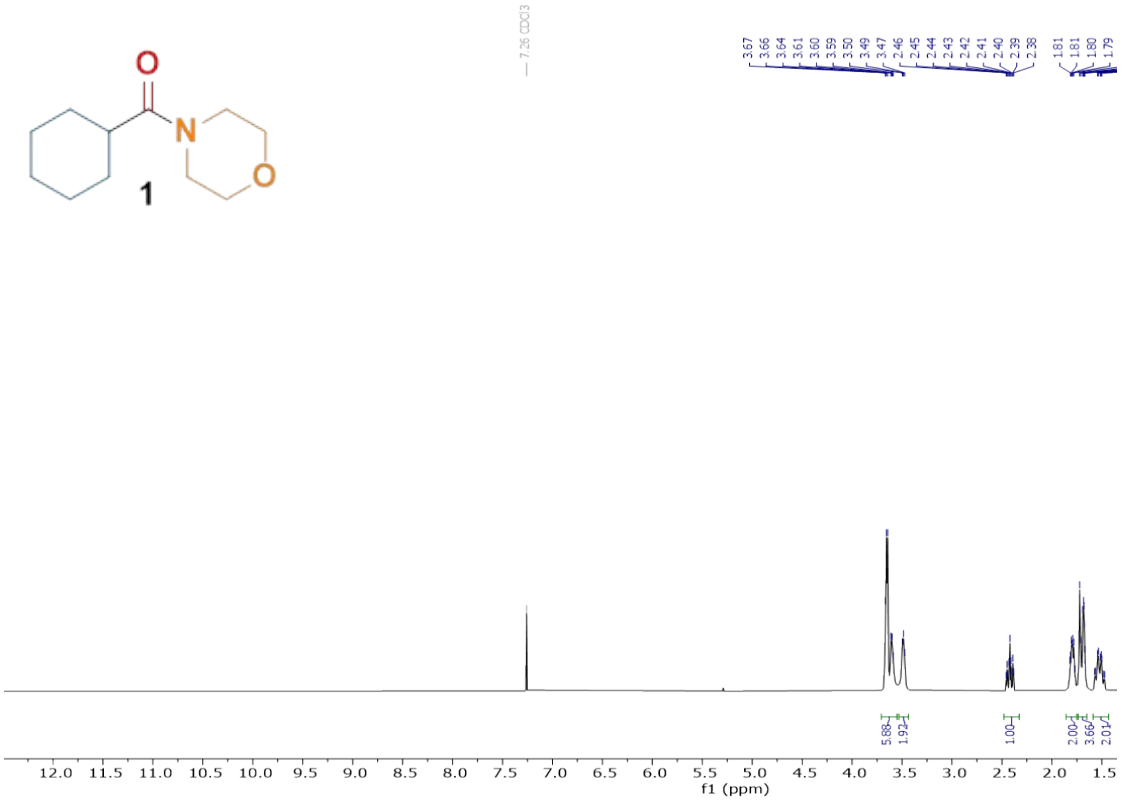

Figure S14 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **1**.

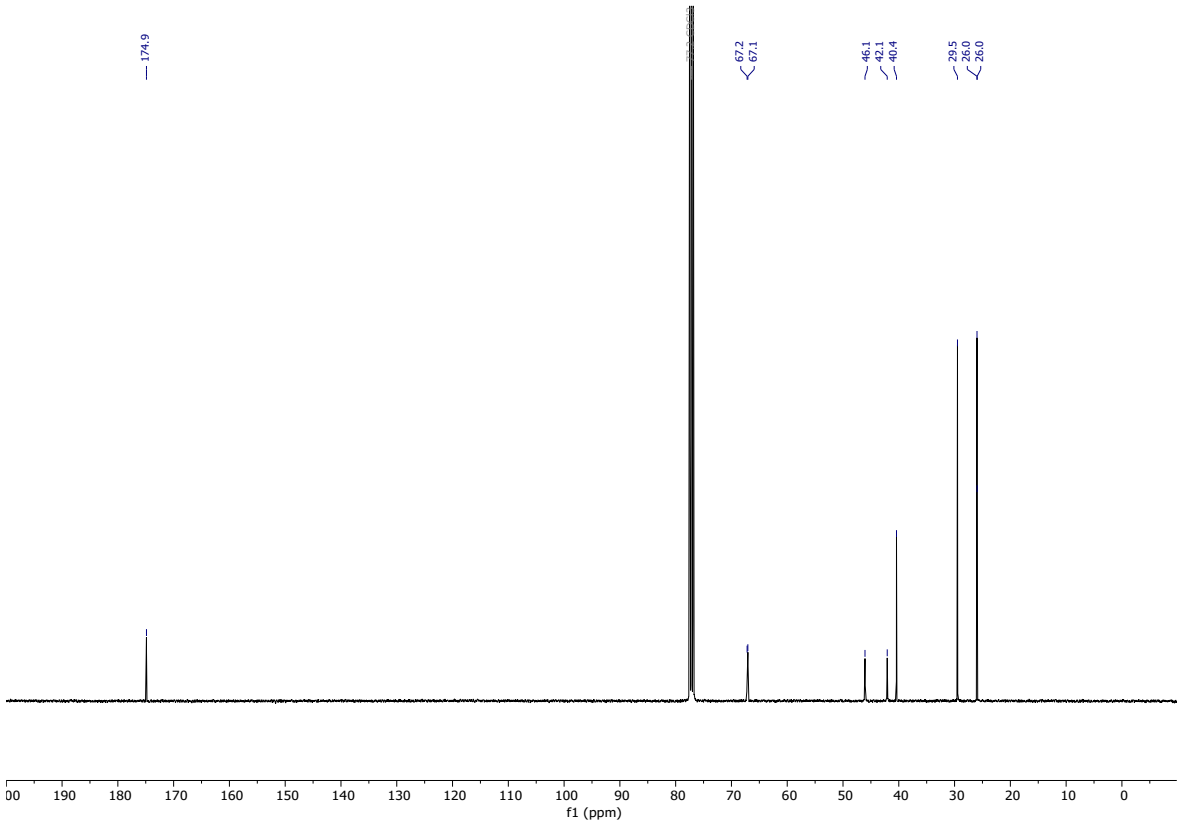

Figure S15 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **1**.

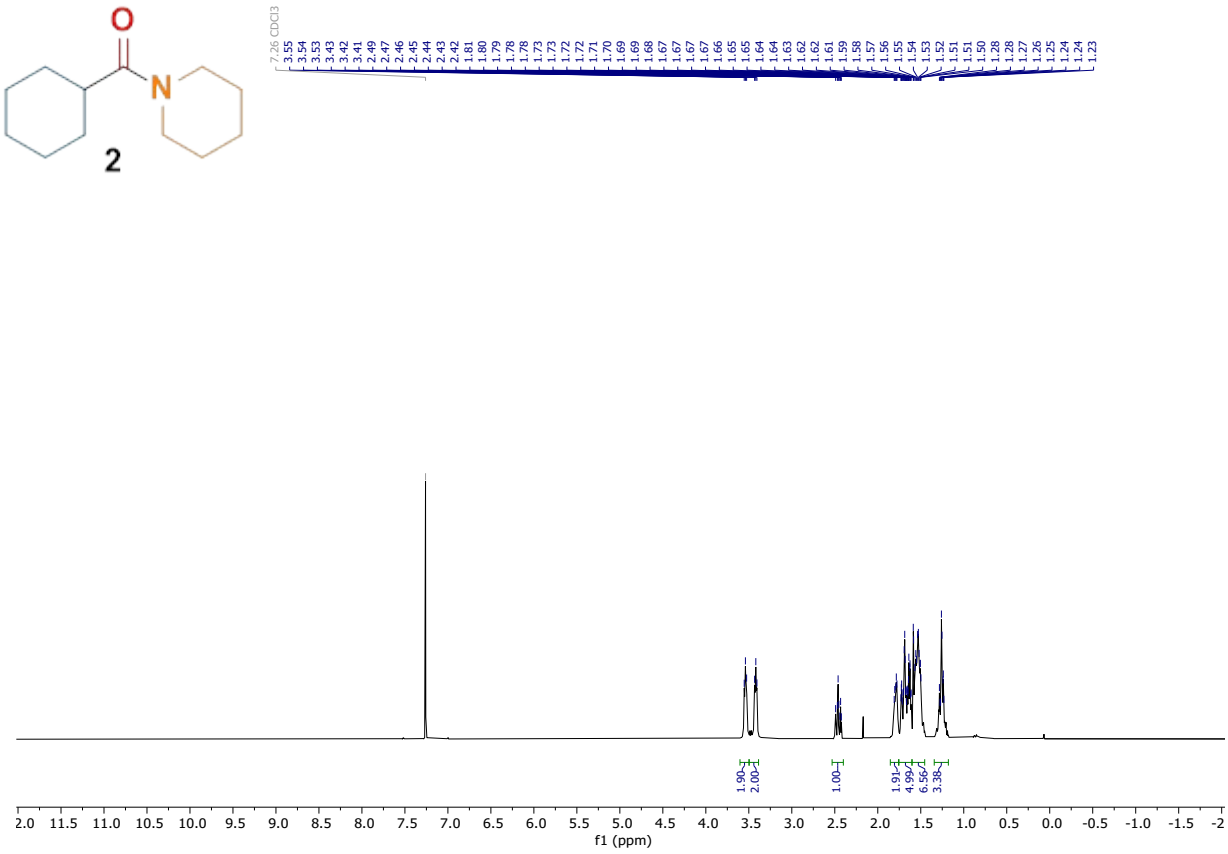

Figure S16 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **2**.

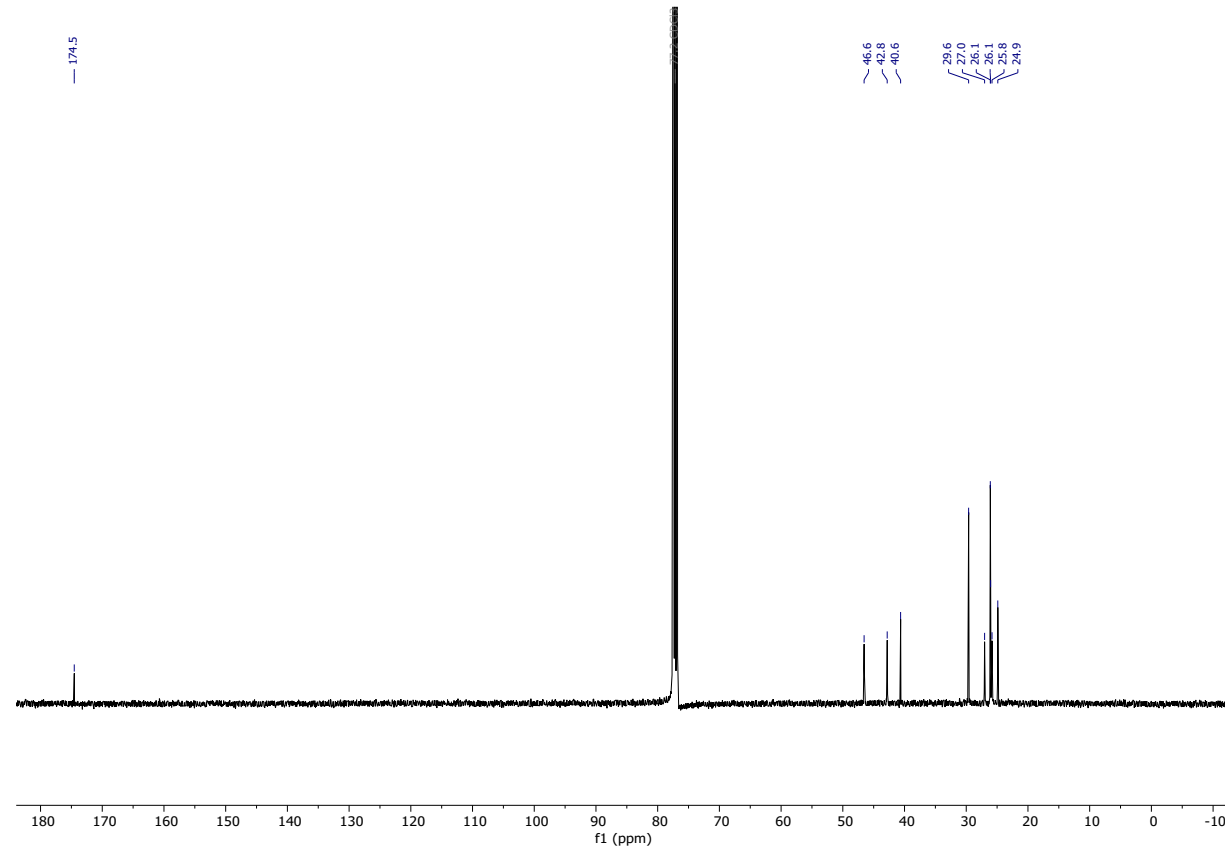

Figure S17 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **2**.

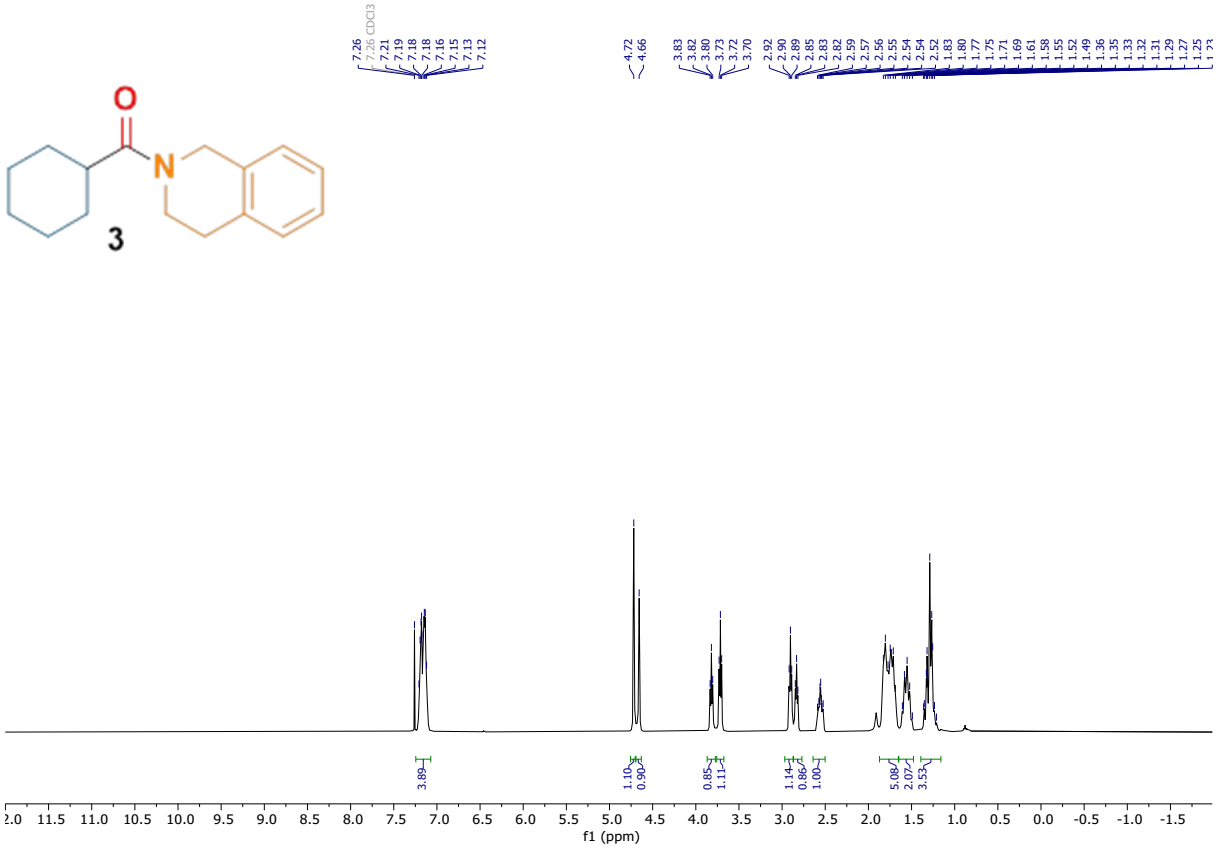

Figure S18 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **3**.

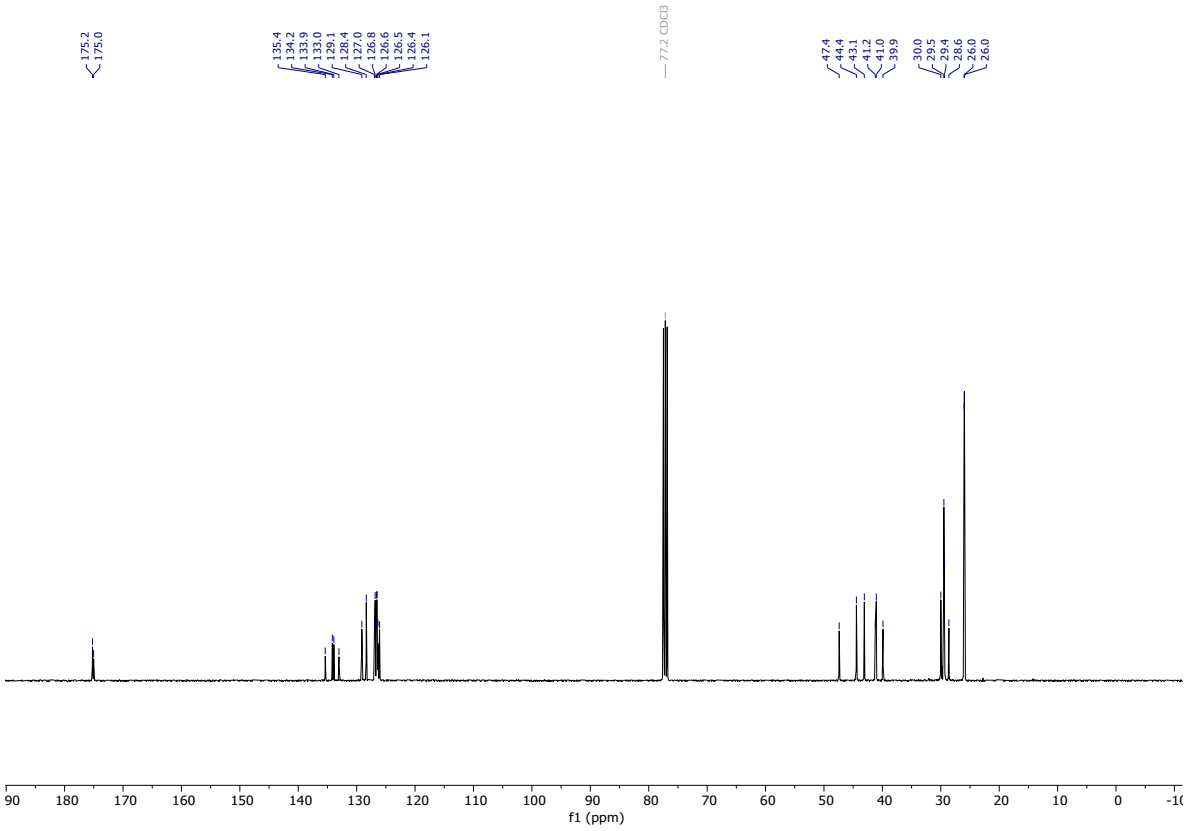

Figure S19 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **3**.

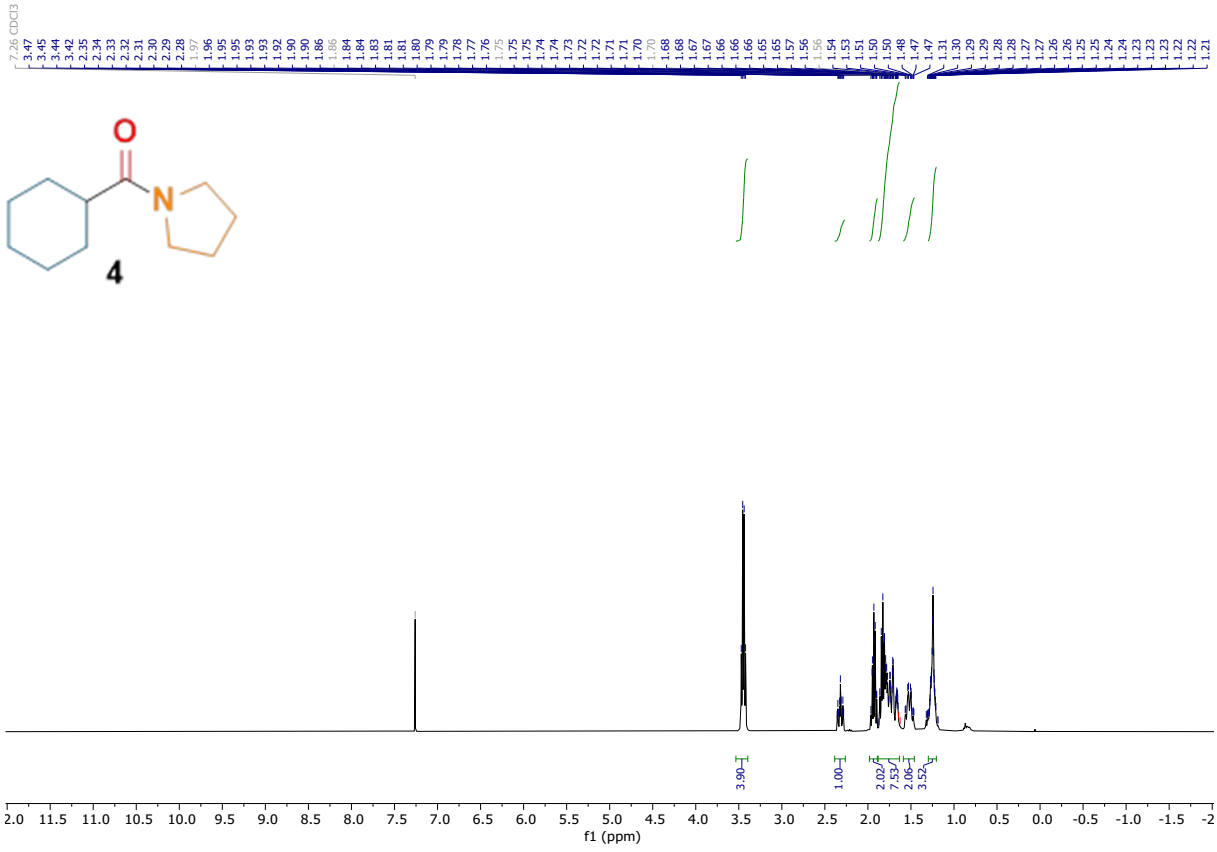

Figure S20 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **4**.

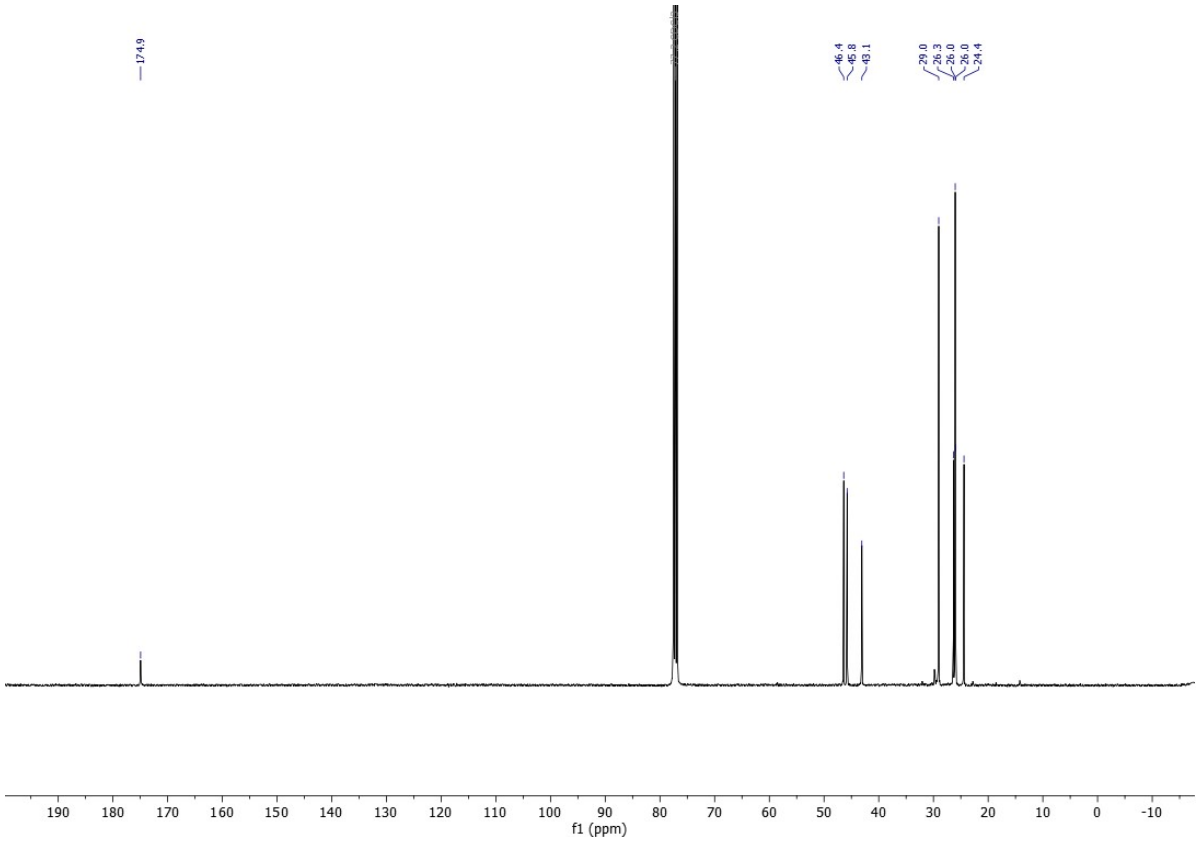

Figure S21 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **4**.

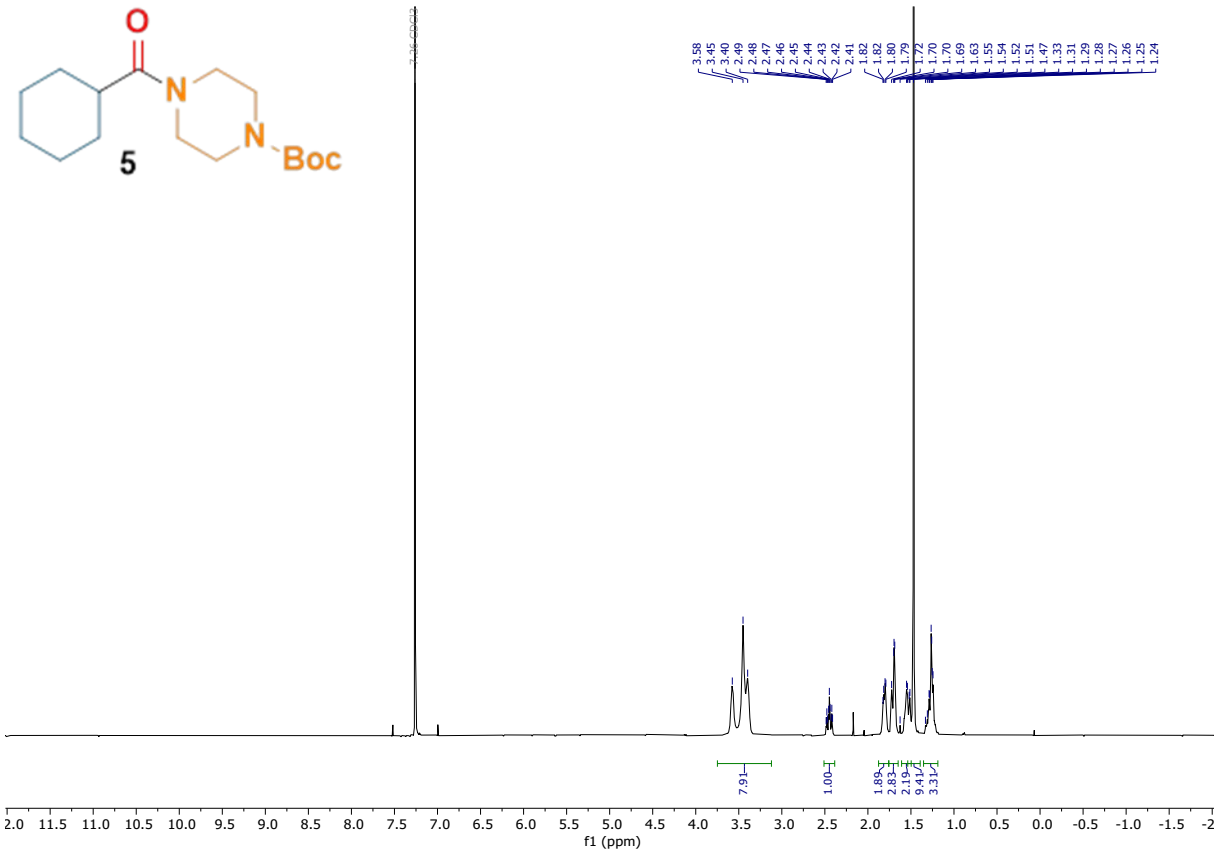

Figure S22 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **5**.

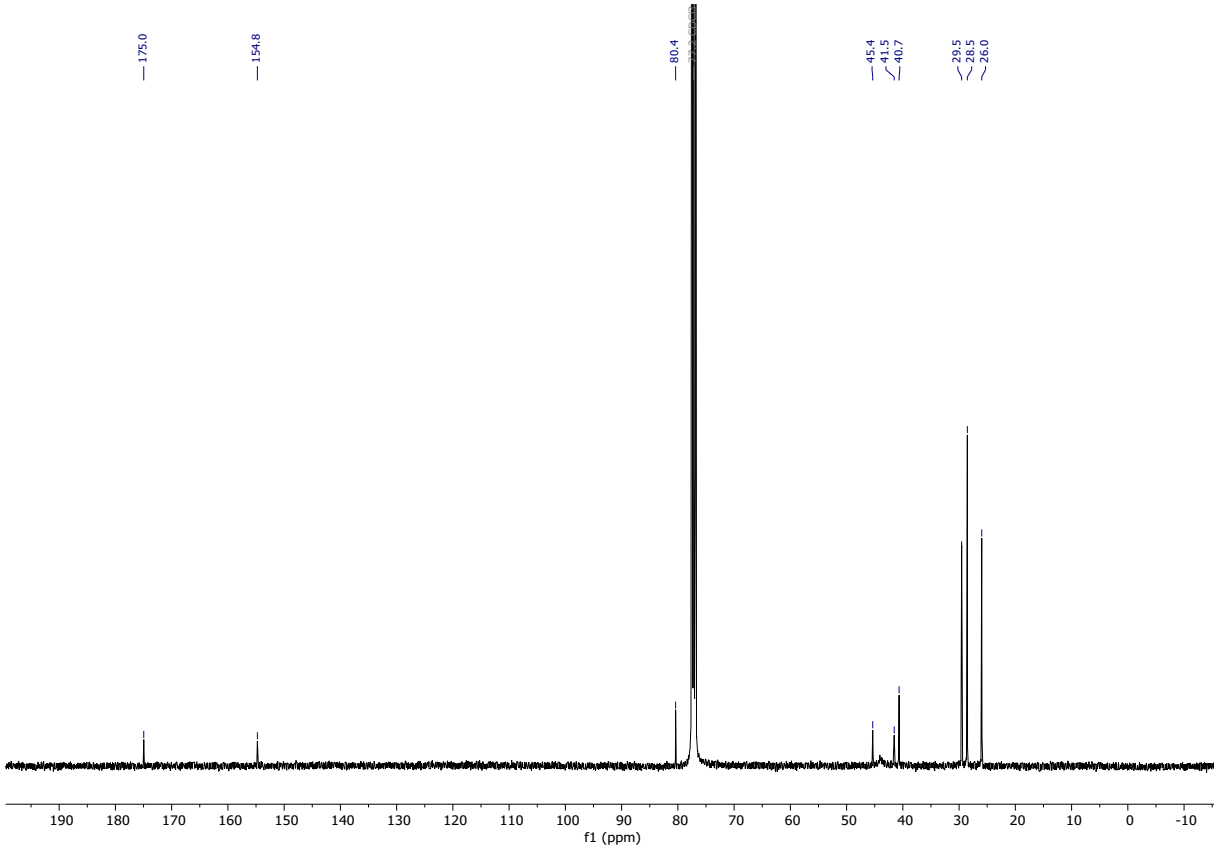

Figure S23 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **5**.

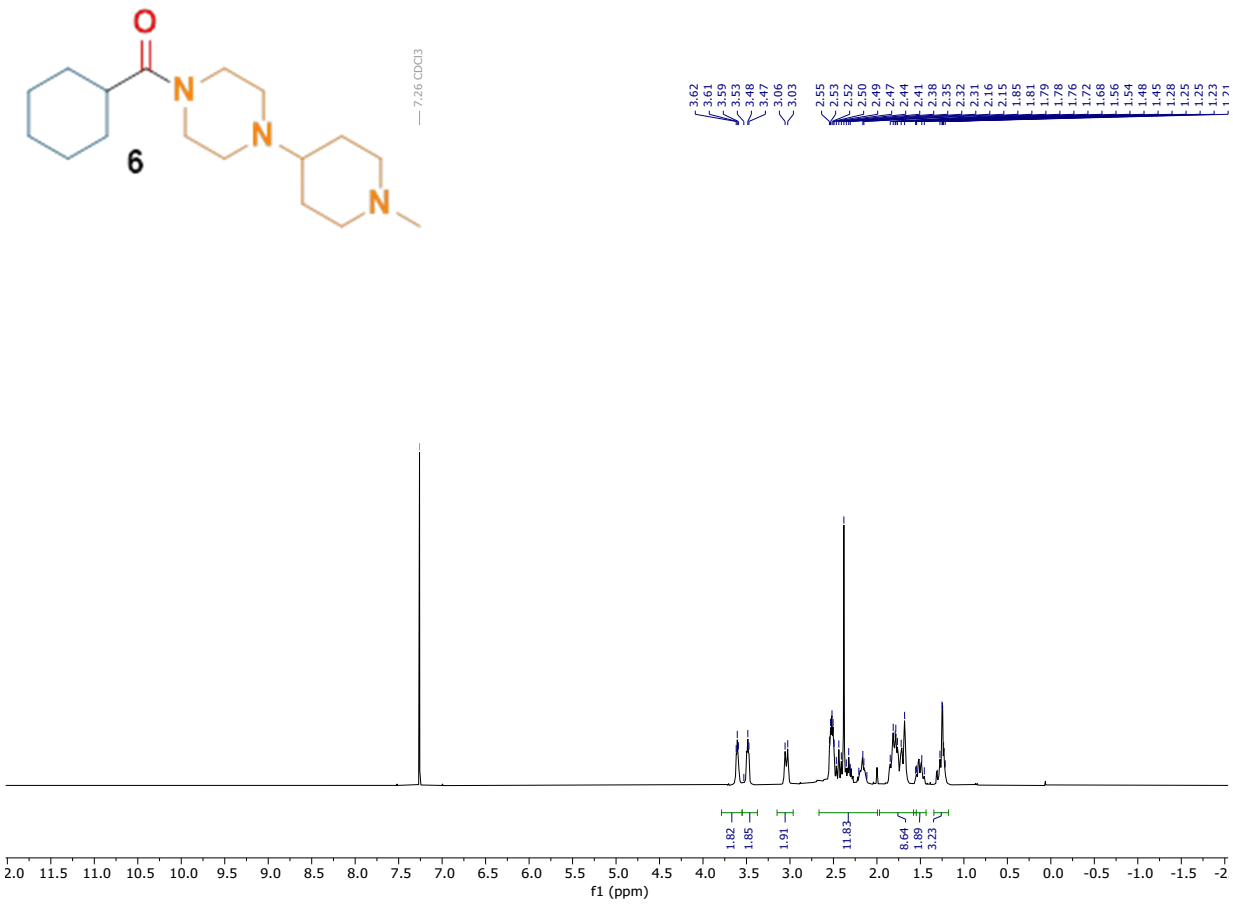

Figure S24 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **6**.

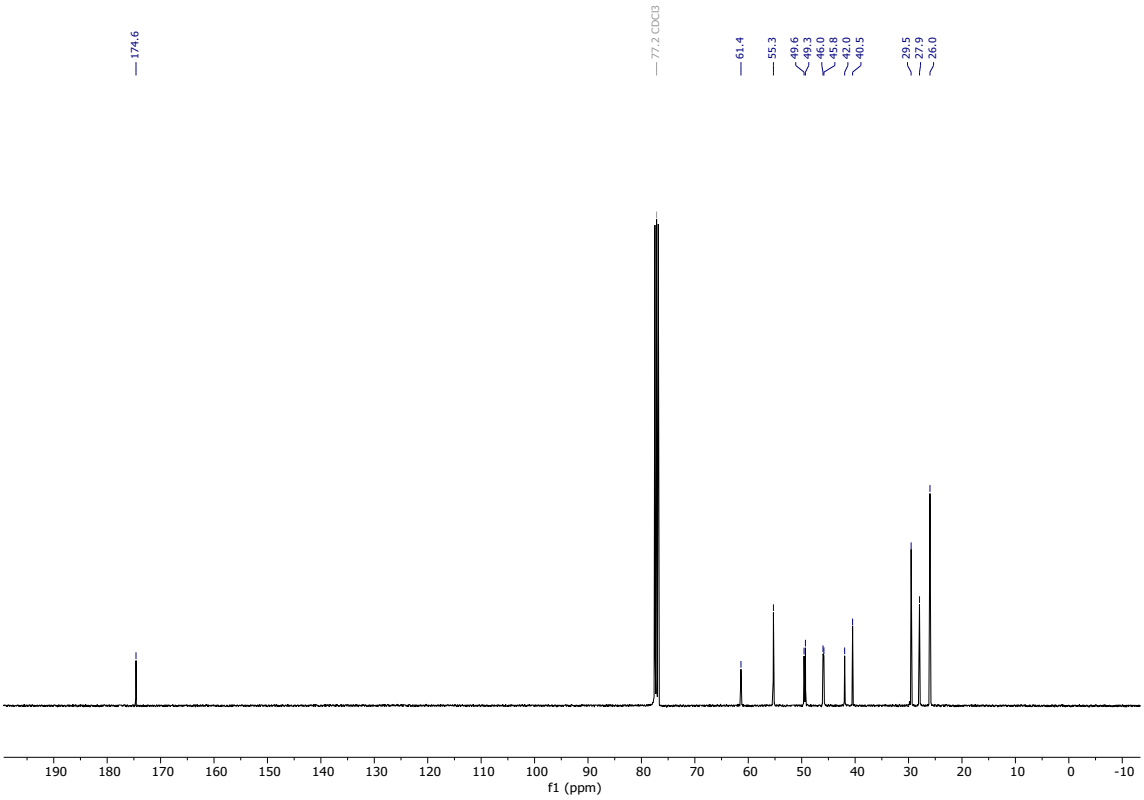

Figure S25 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **6**.

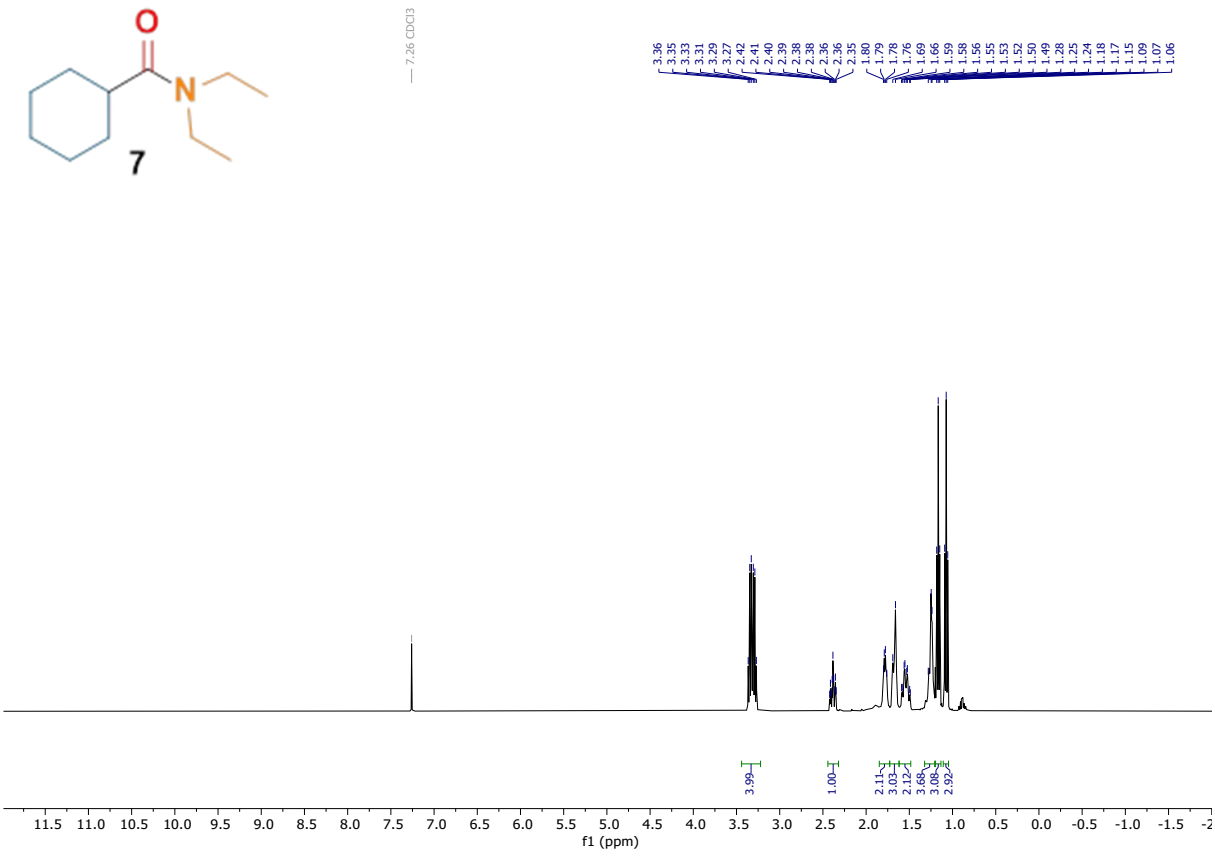

Figure S26 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **7**.

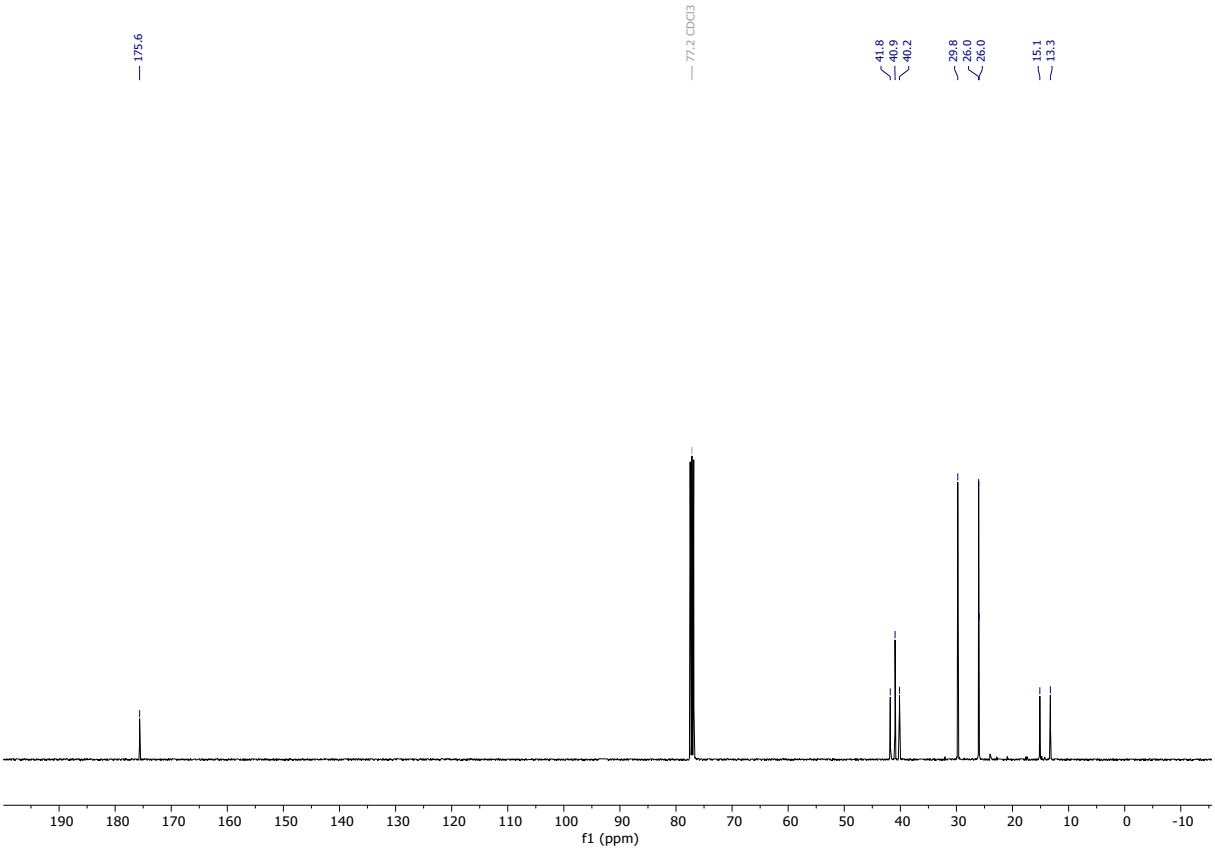

Figure S27 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **7**.

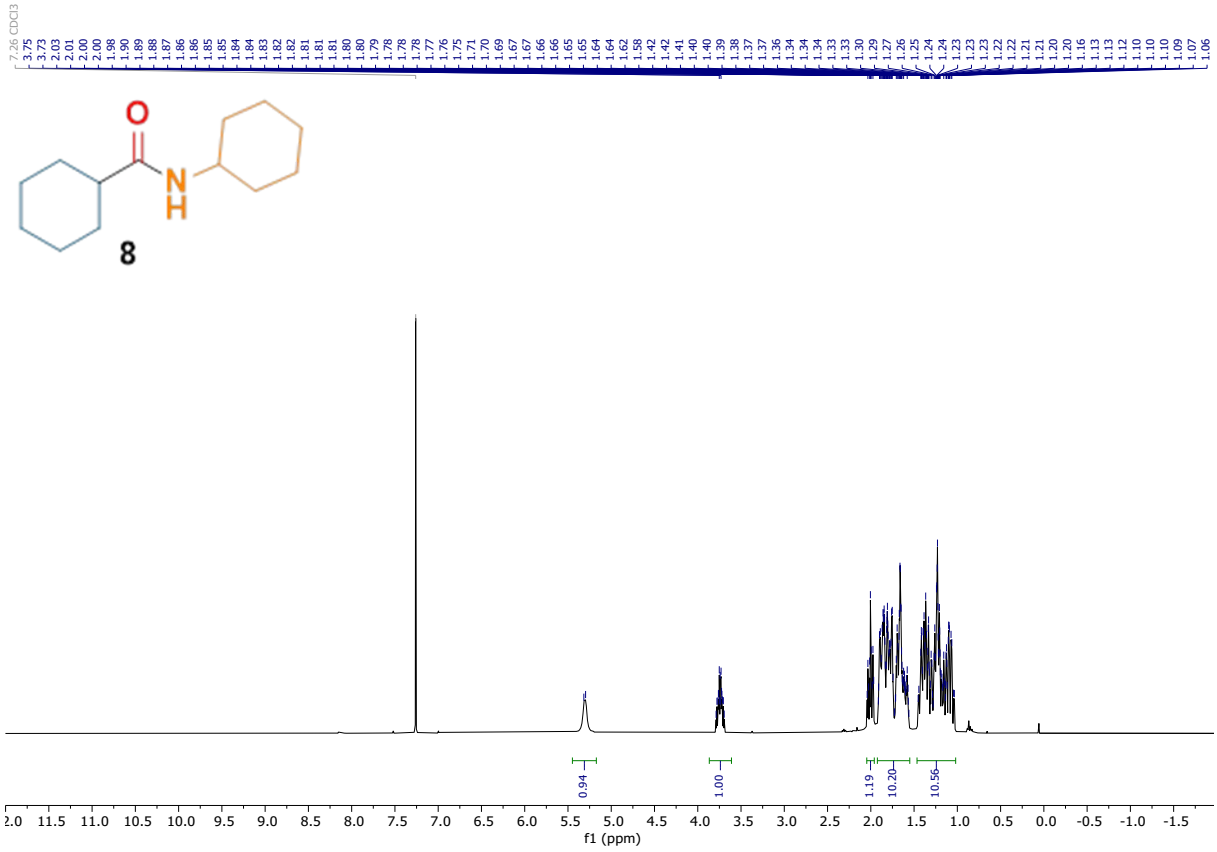

Figure S28 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **8**.

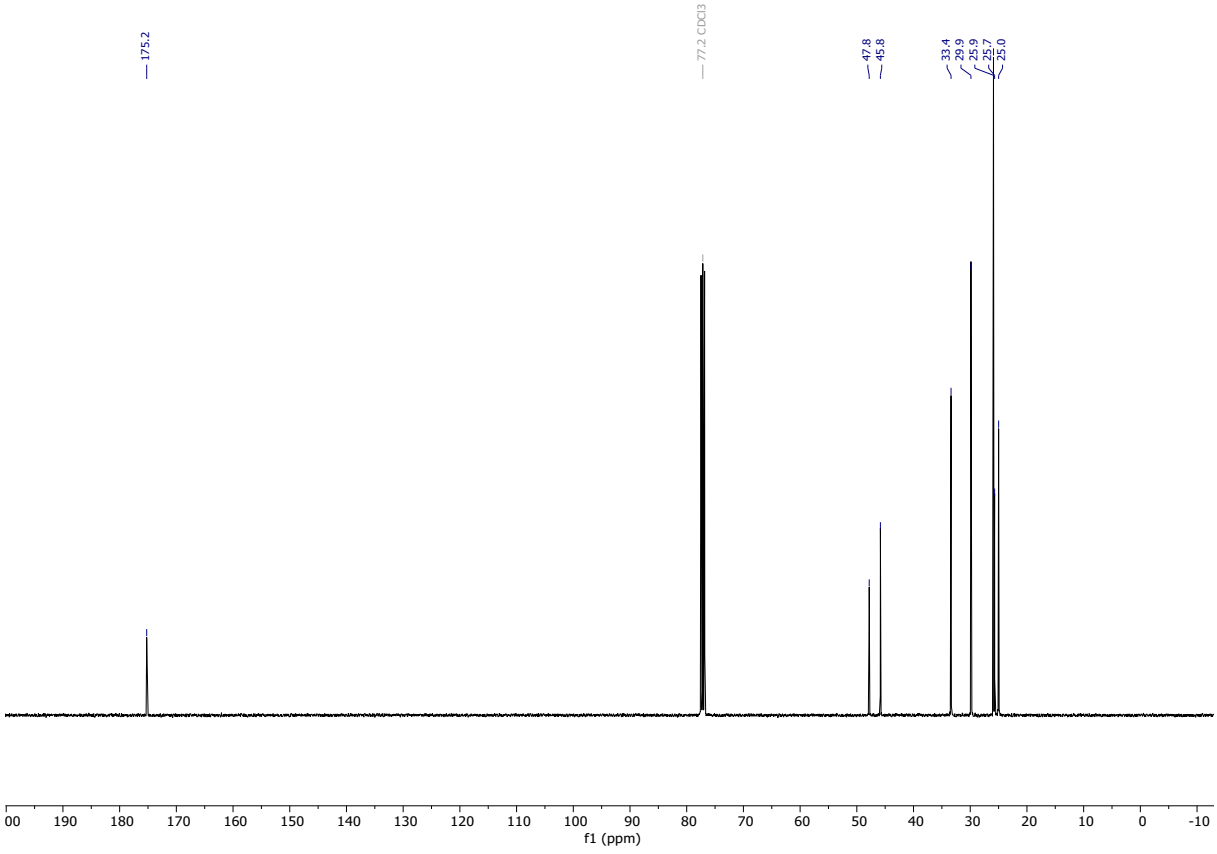

Figure S29 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **8**.

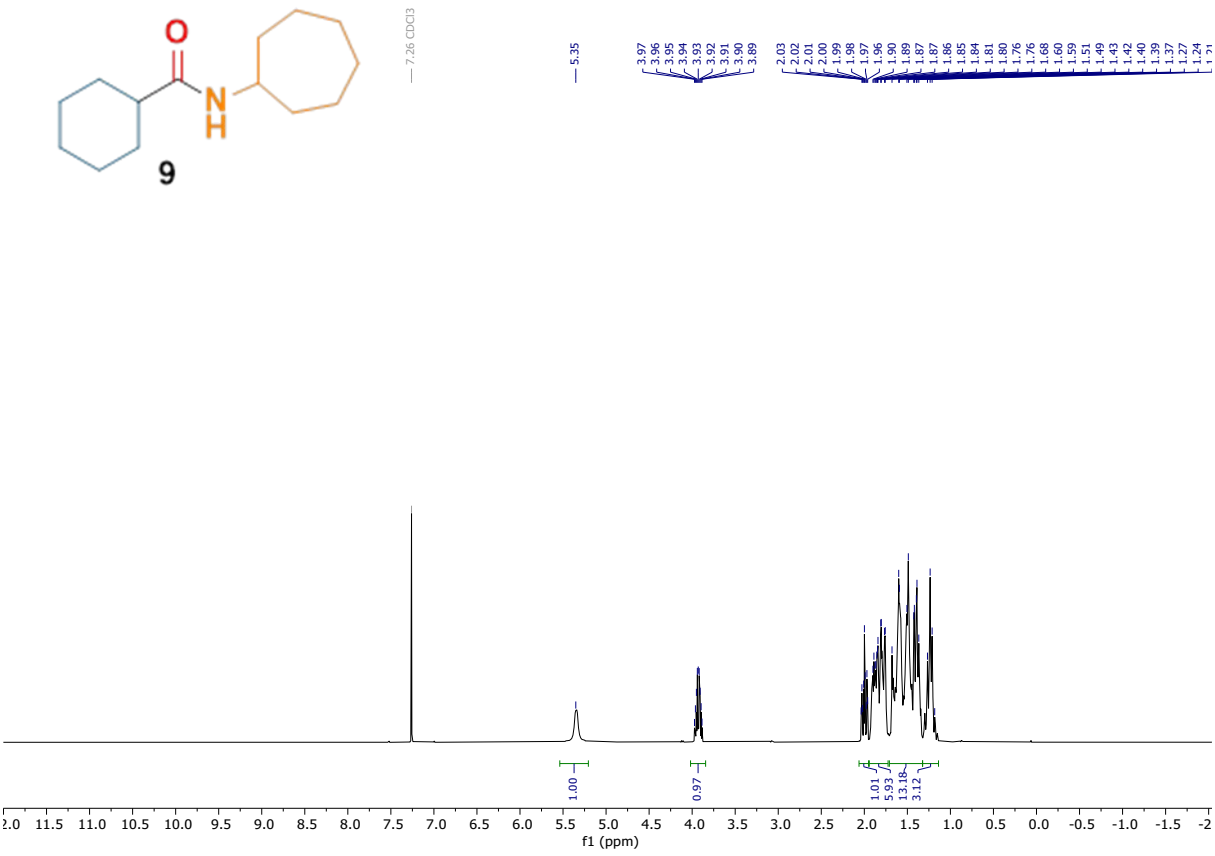

Figure S30 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **9**.

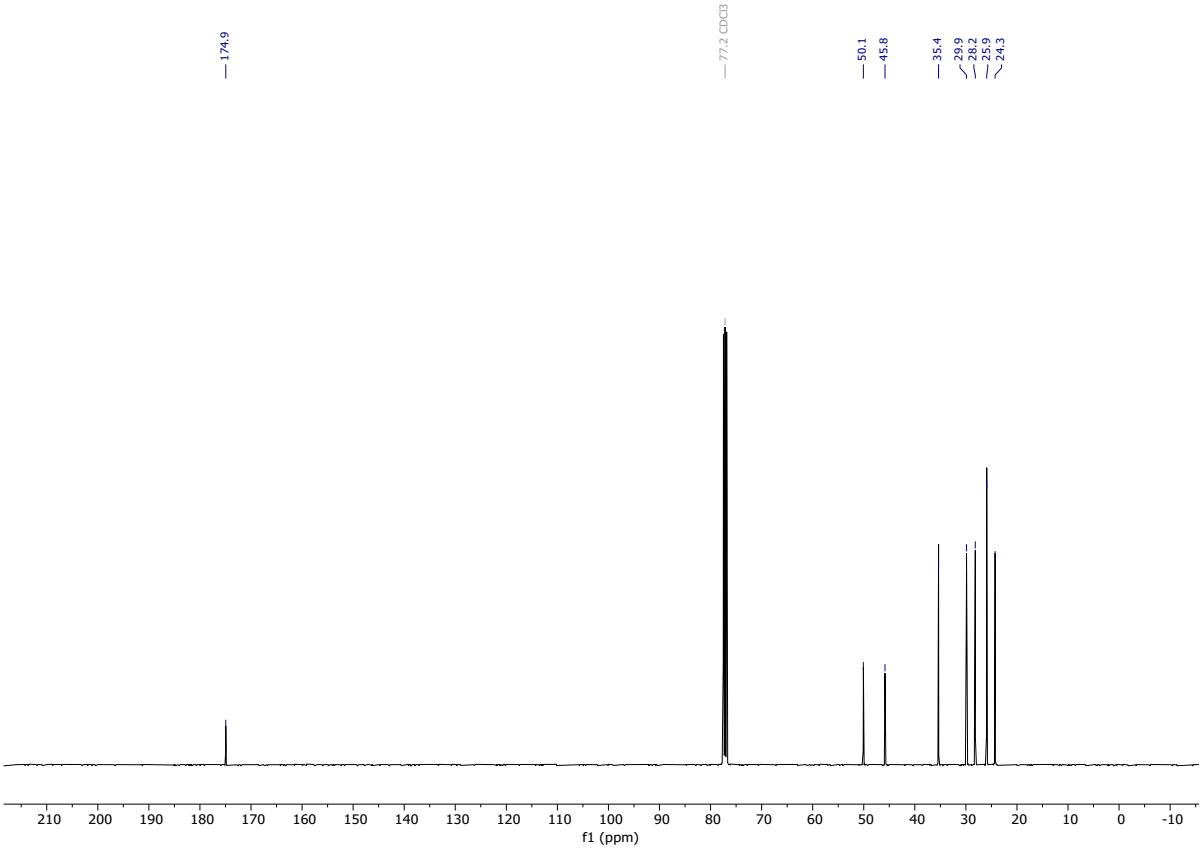

Figure S31 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **9**.

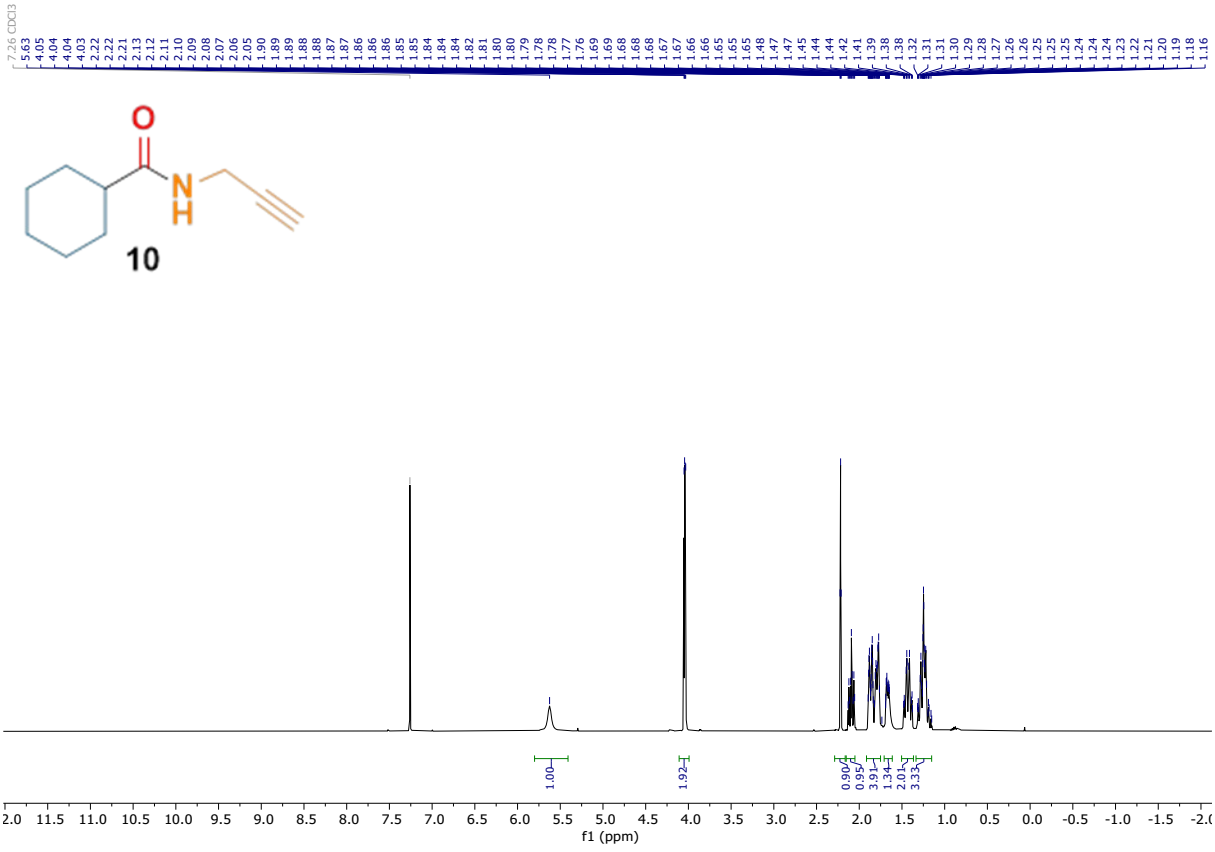

Figure S32 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **10**.

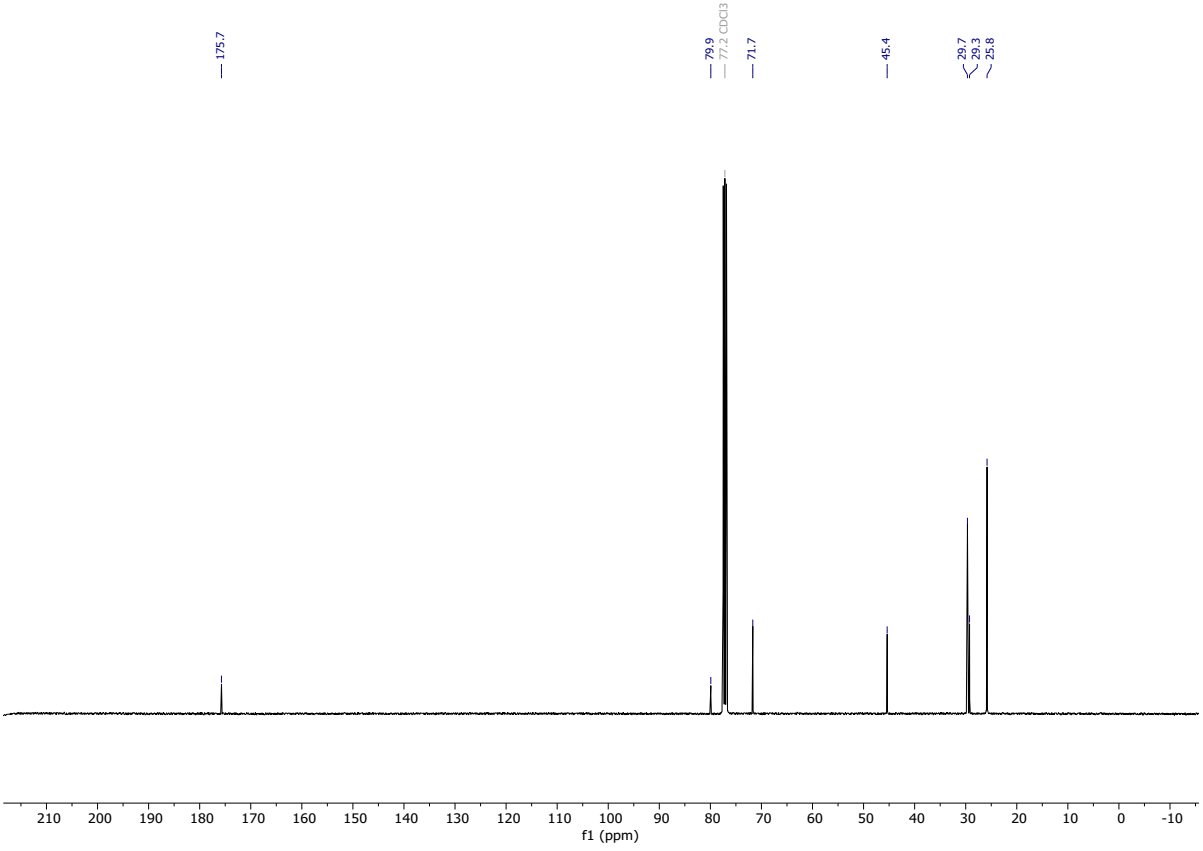

Figure S33 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **10**.

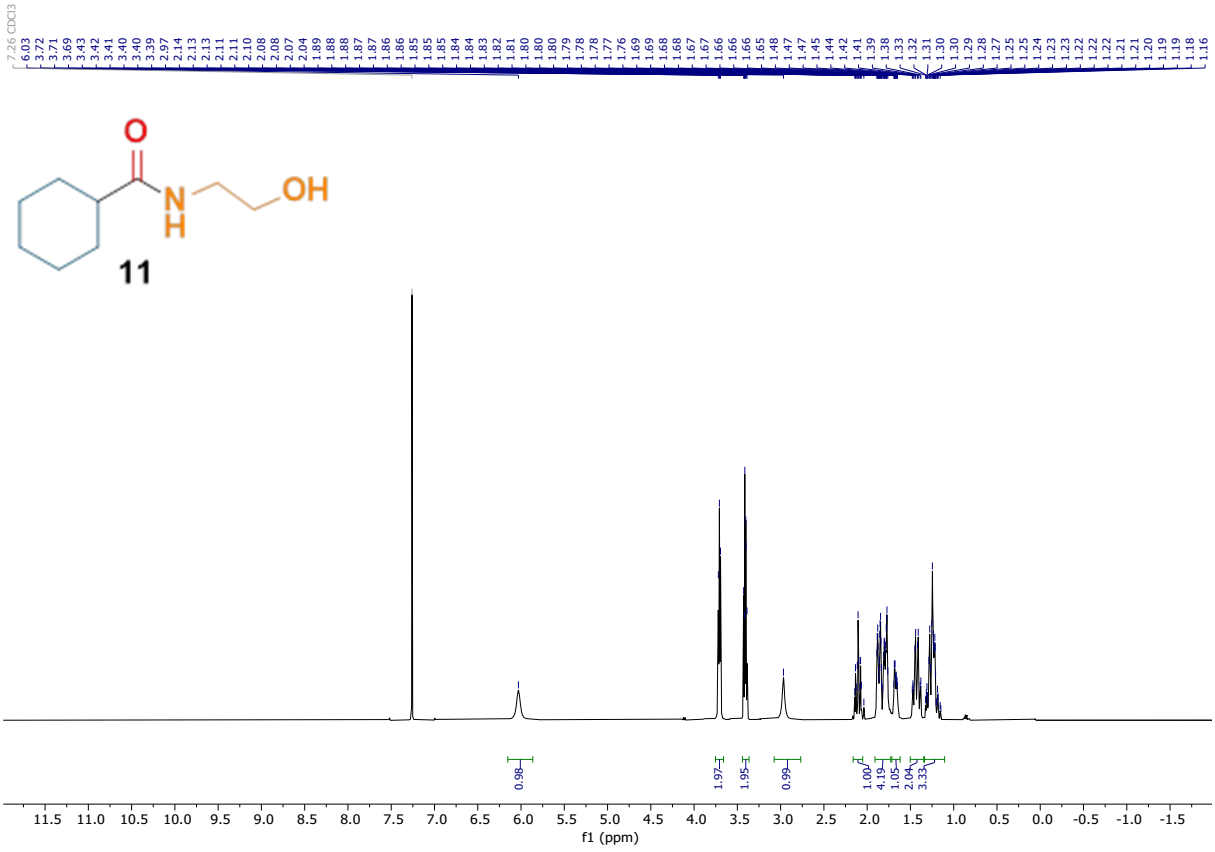

Figure S34 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **11**.

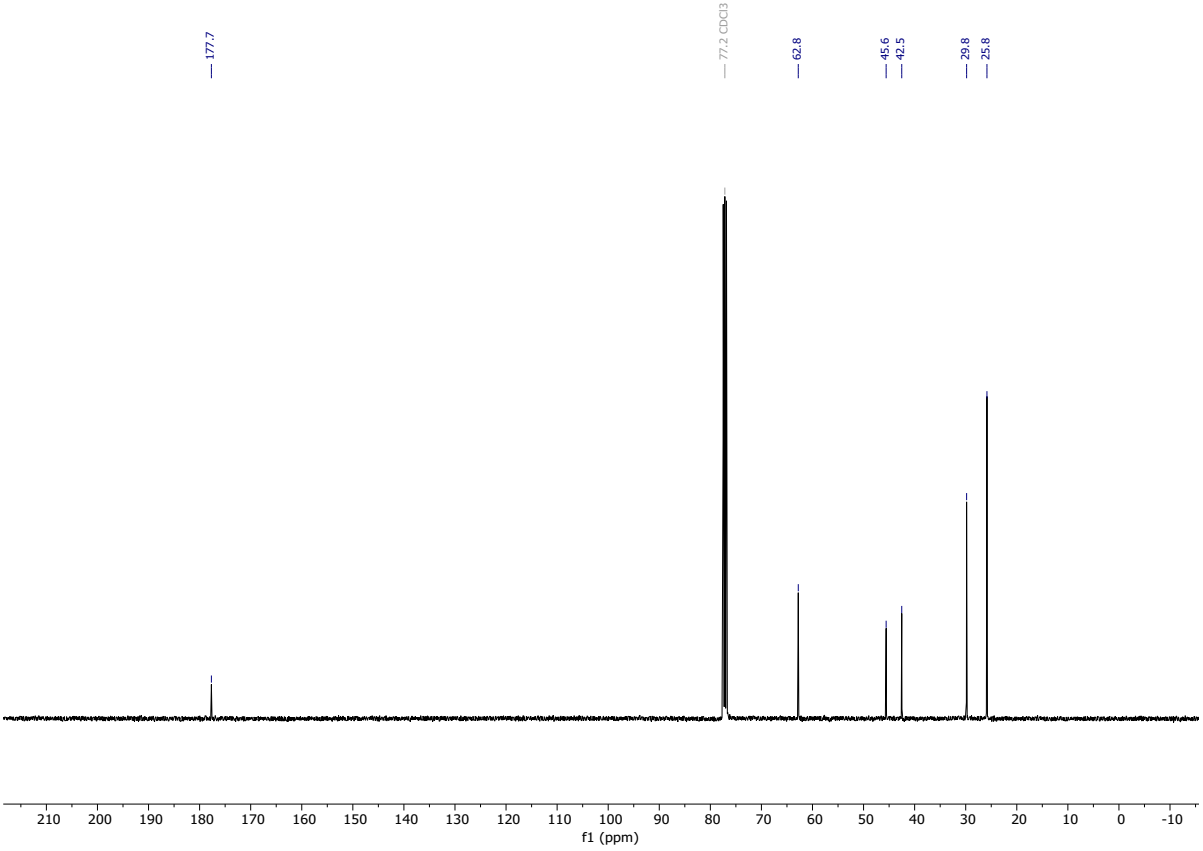

Figure S35 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **11**.

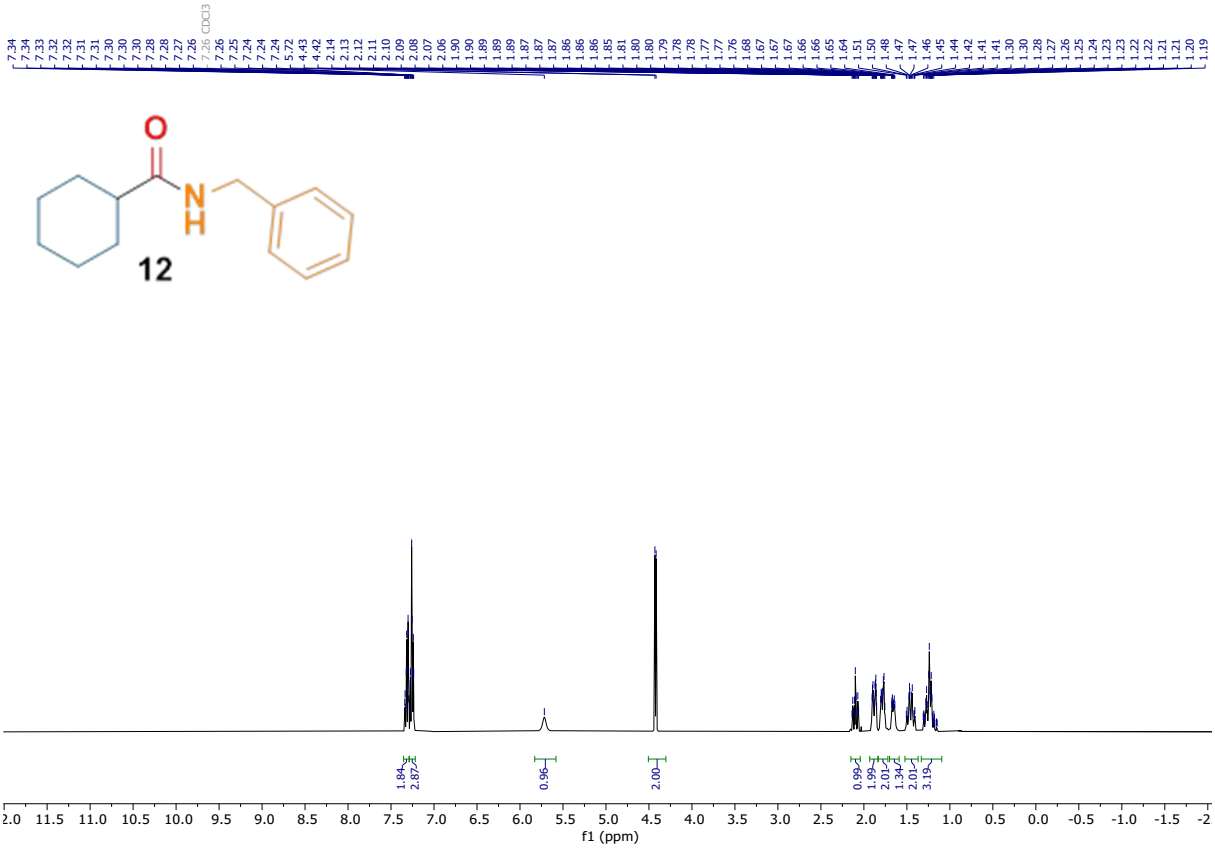

Figure S36 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **12**.

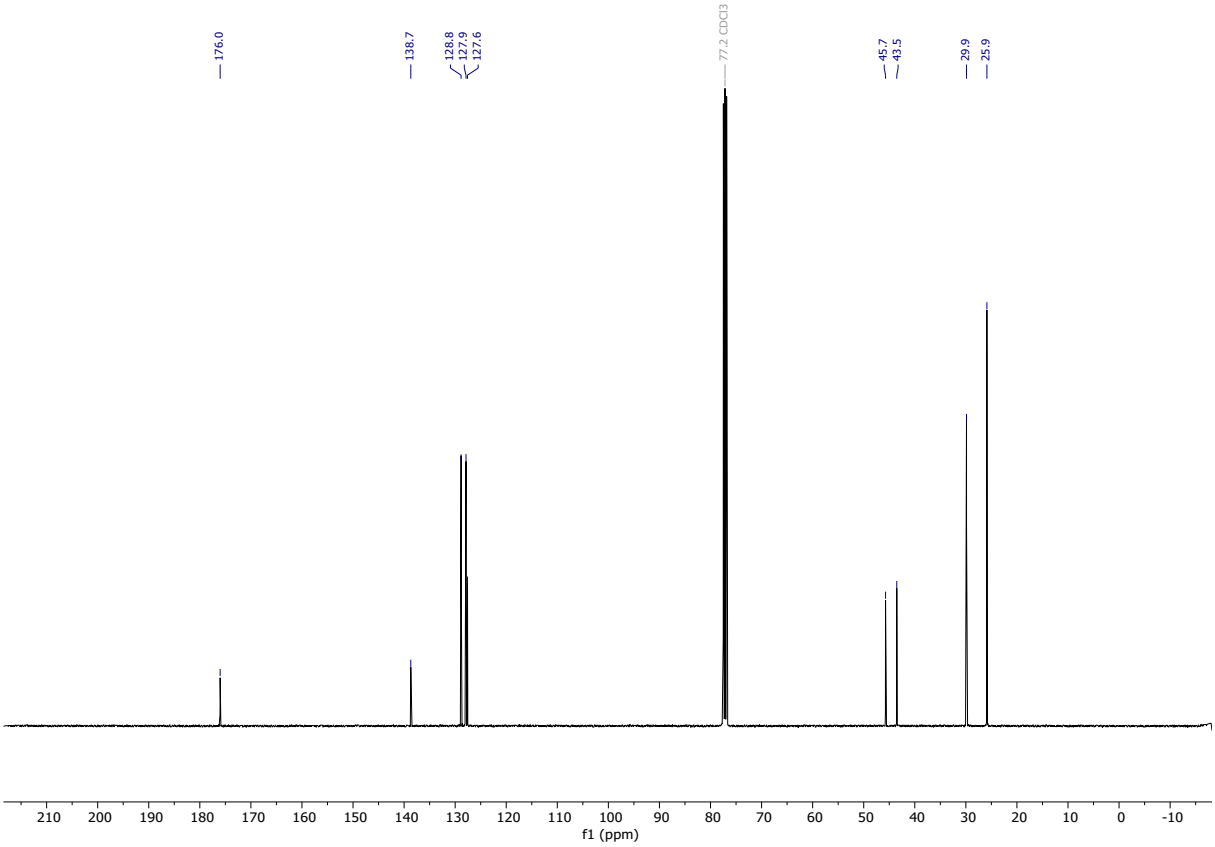

Figure S37 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **12**.

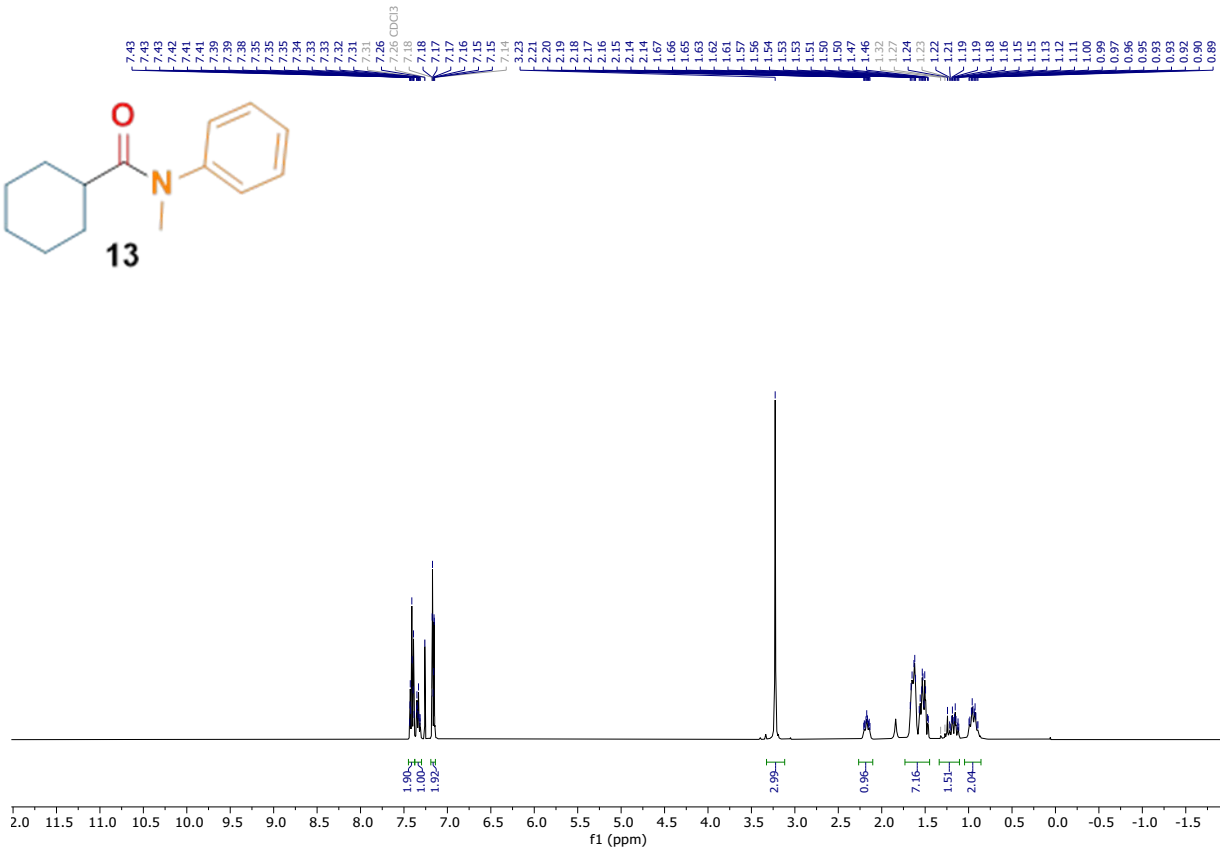

Figure S38 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **13**.

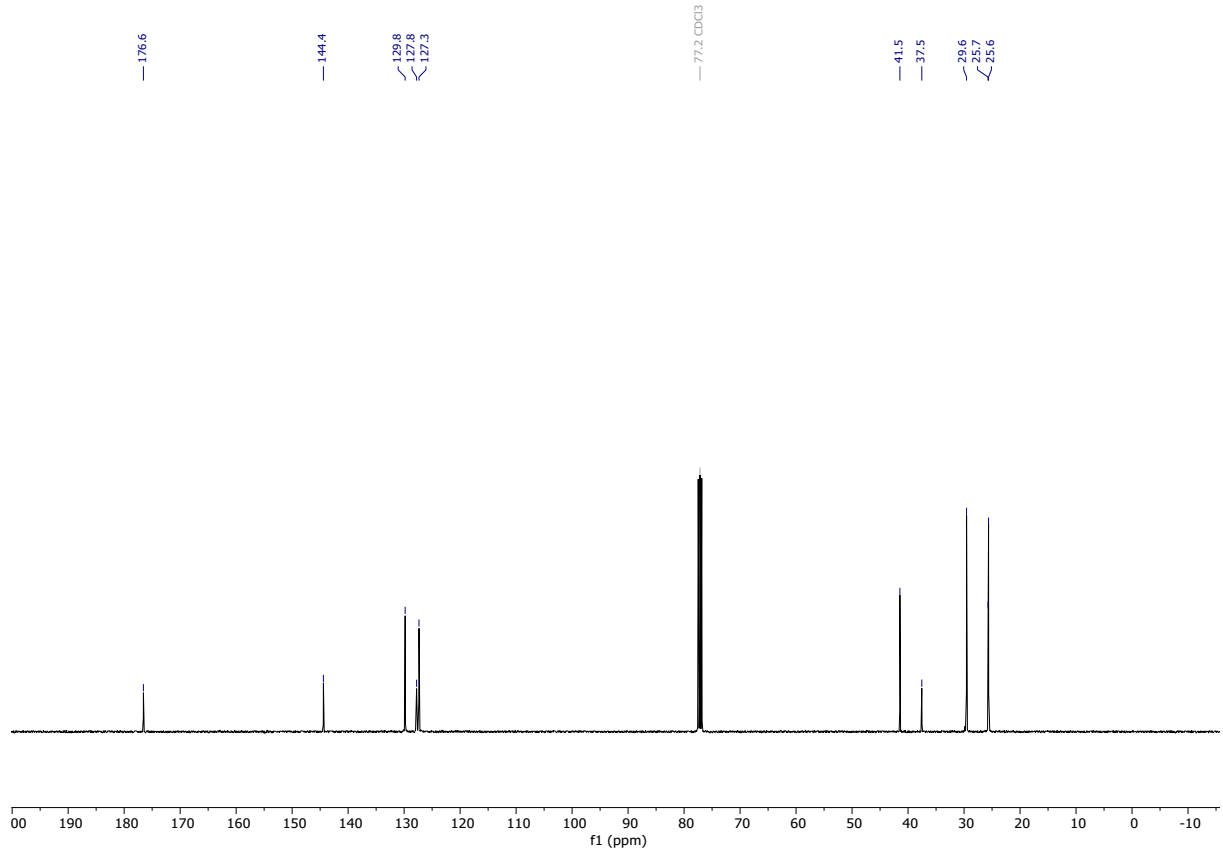

Figure S39 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **13**.

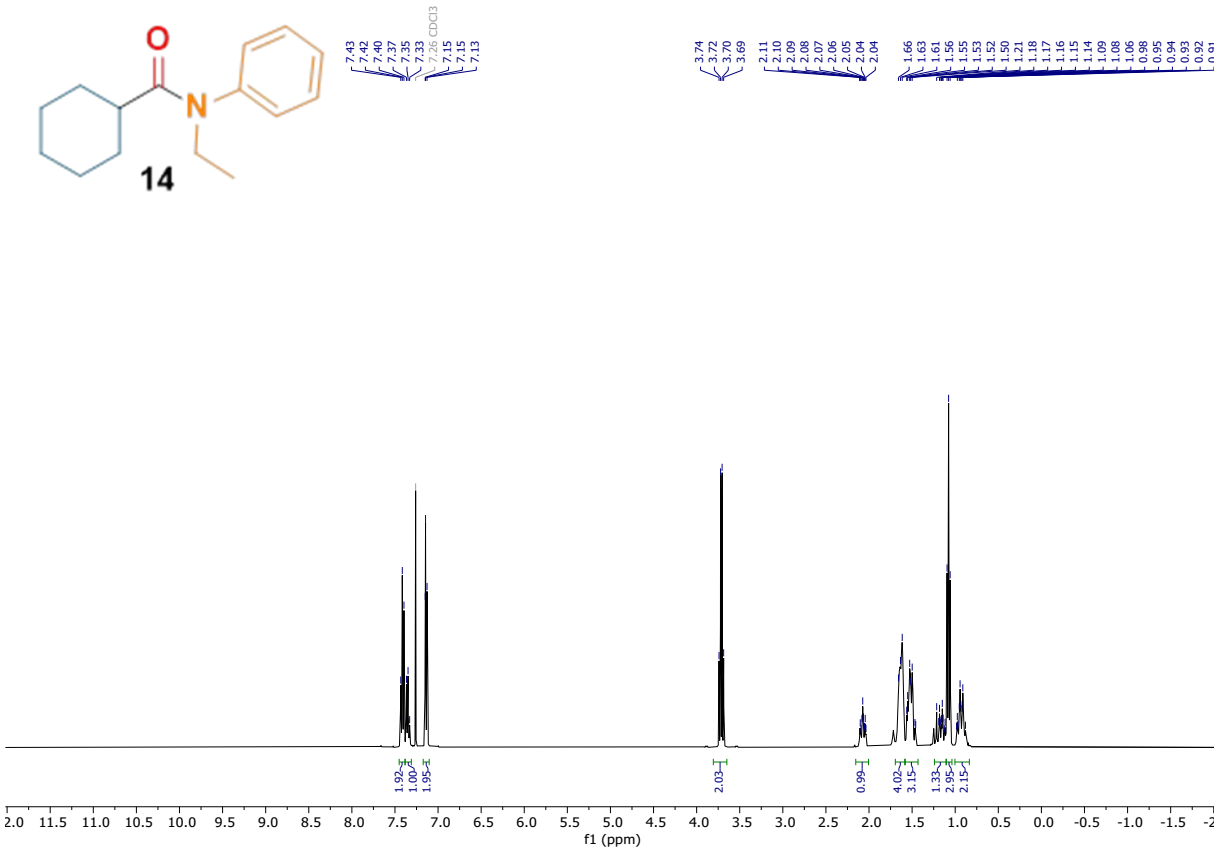

Figure S40 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **14**.

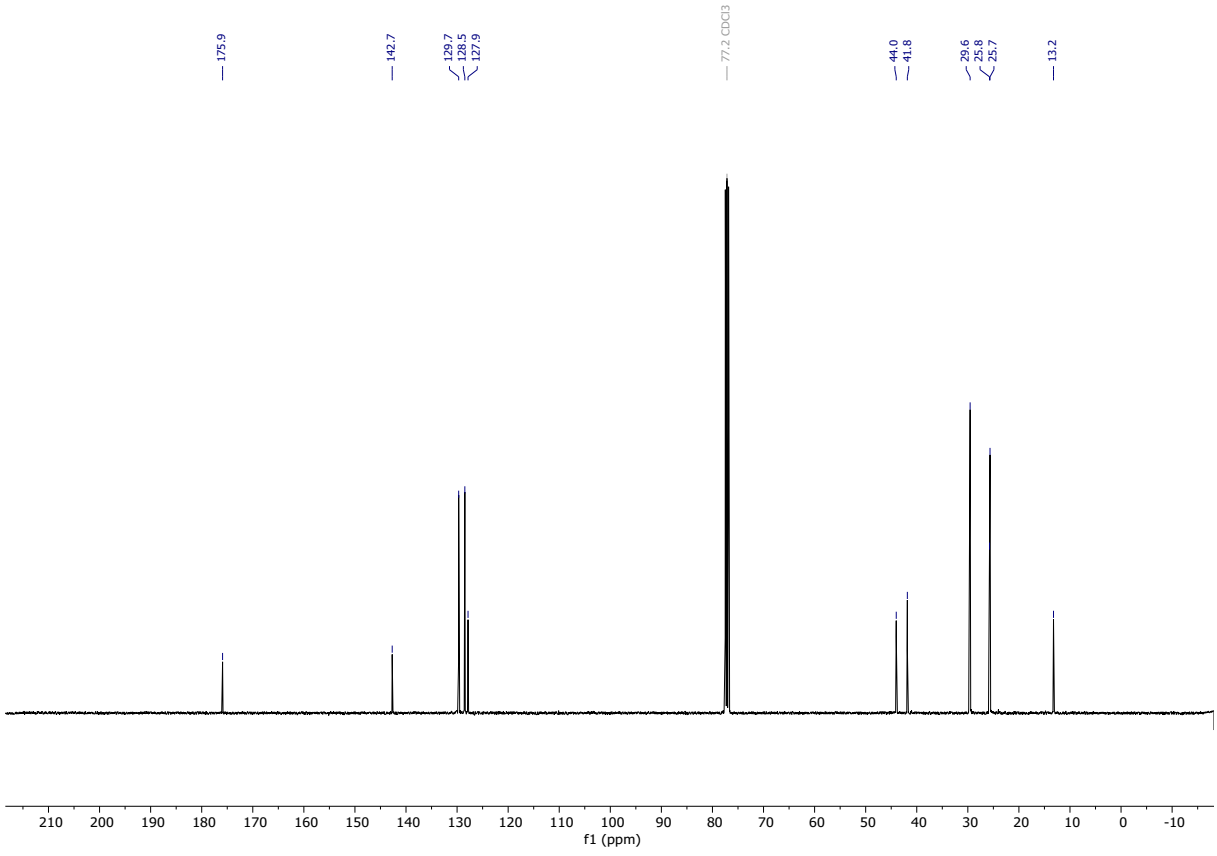

Figure S41 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **14**.

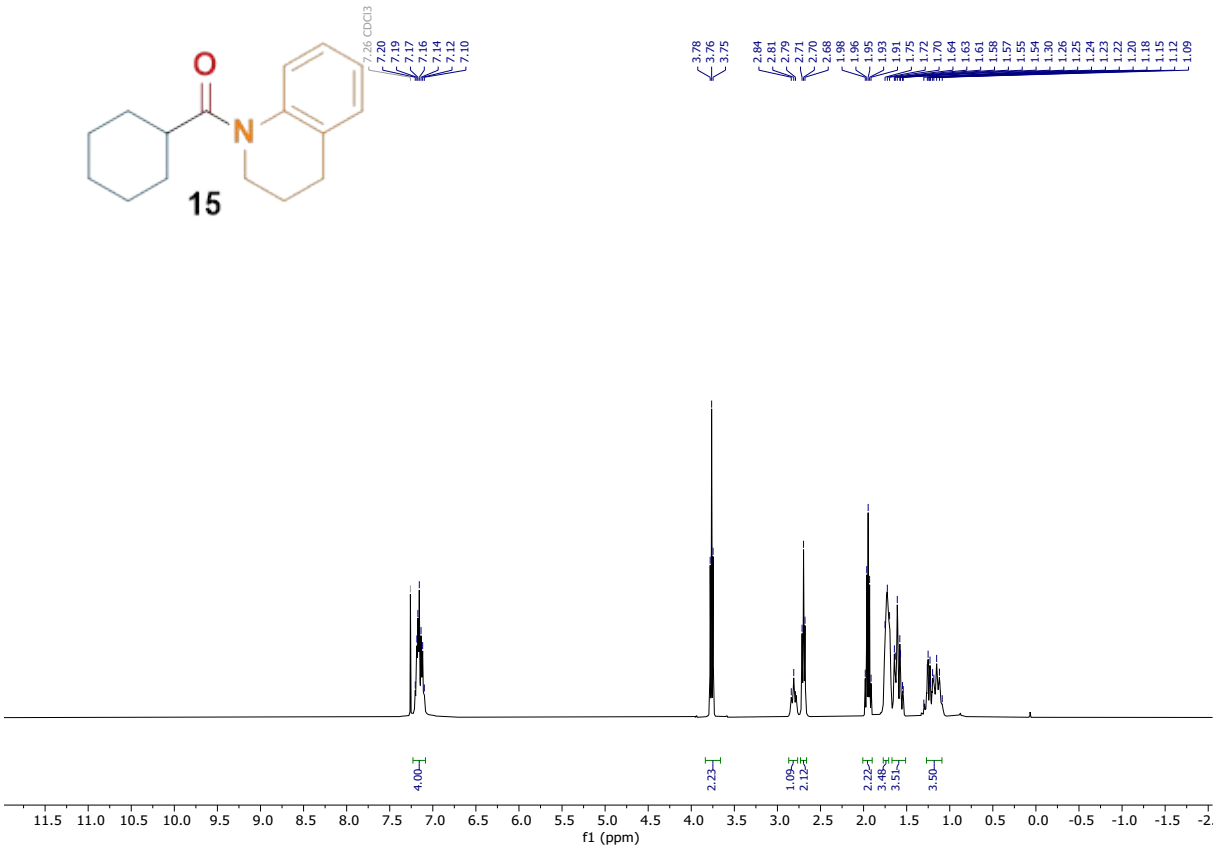

Figure S42 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **15**.

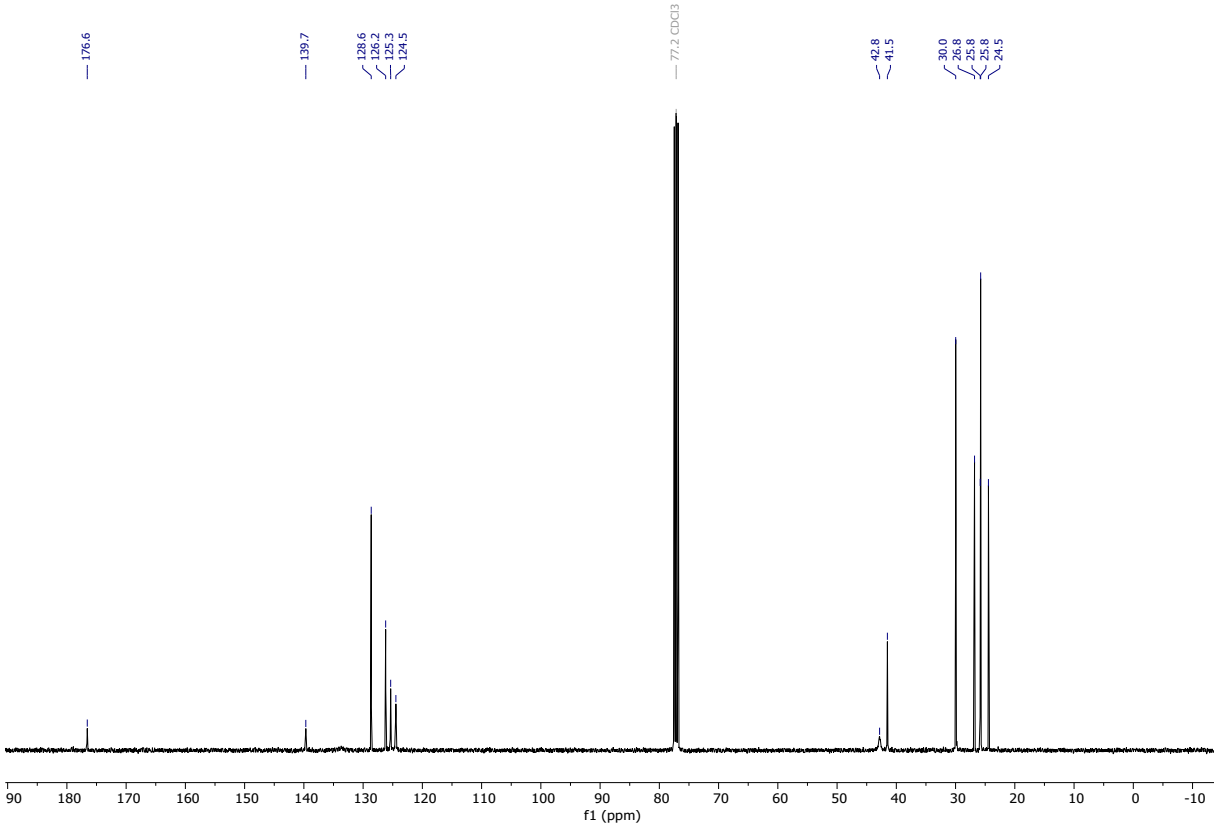

Figure S43 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **15**.

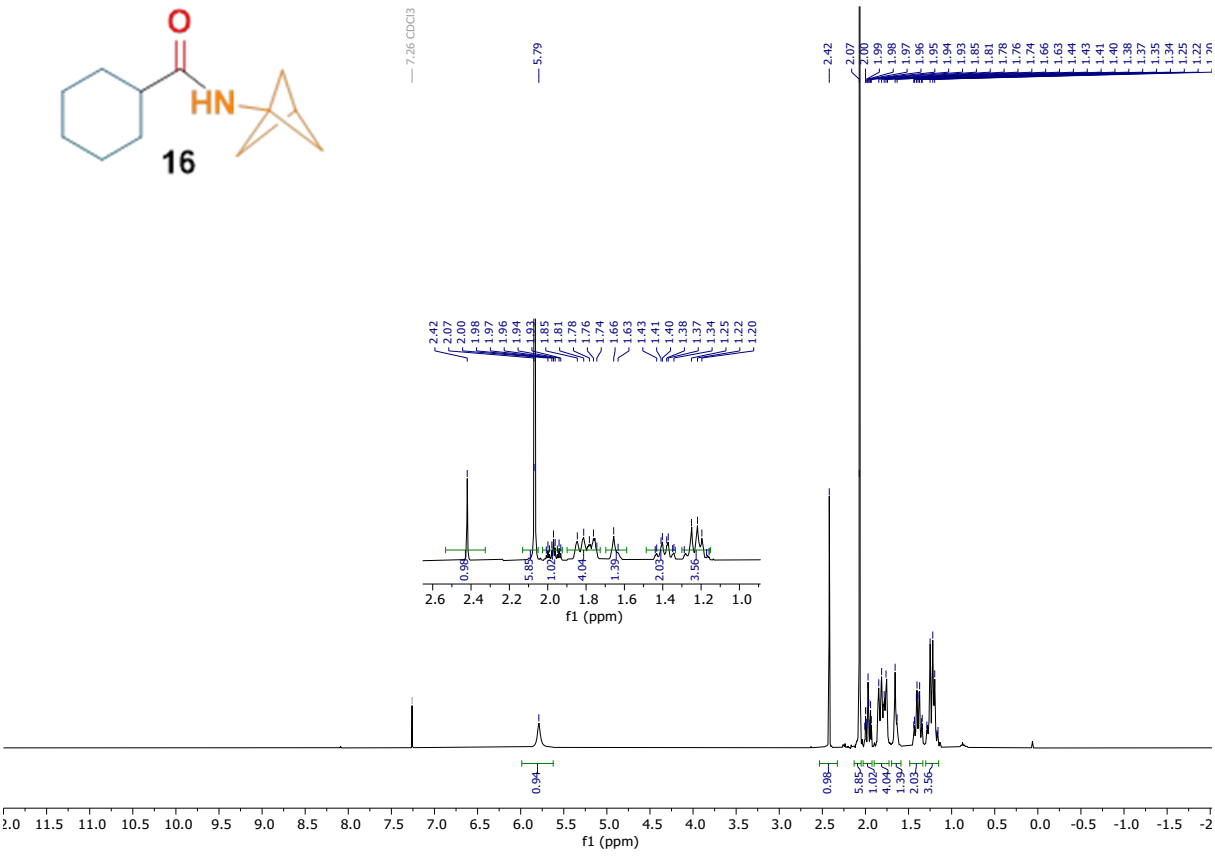

Figure S44 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **16**.

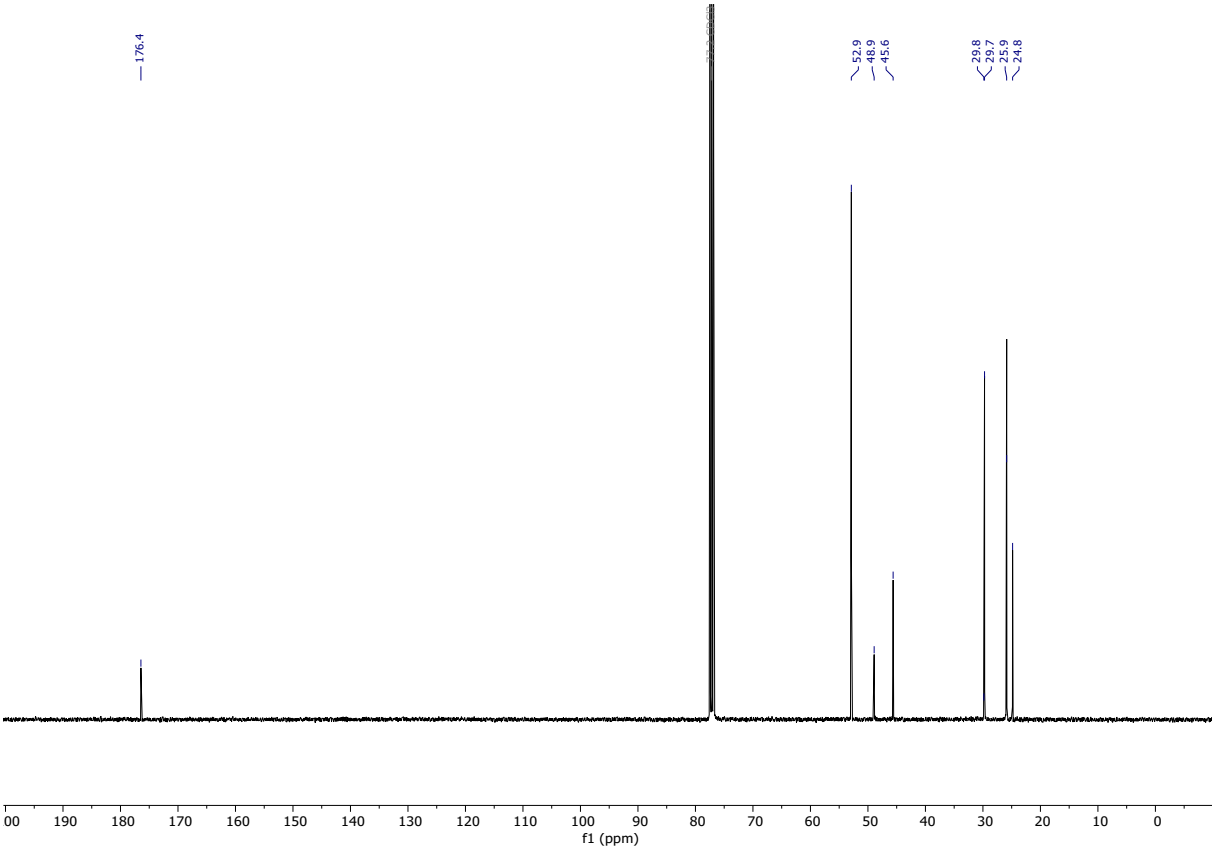

Figure S45 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **16**.

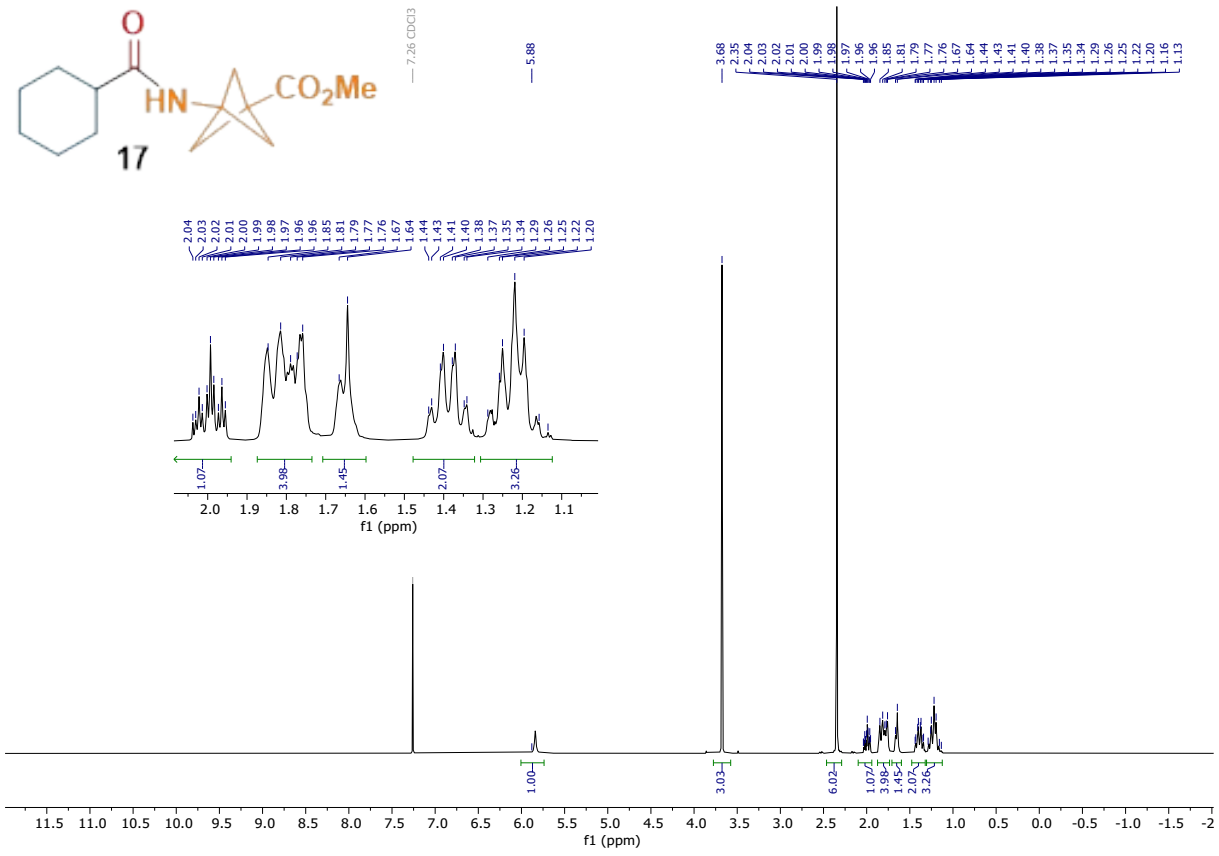

Figure S46 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **17**.

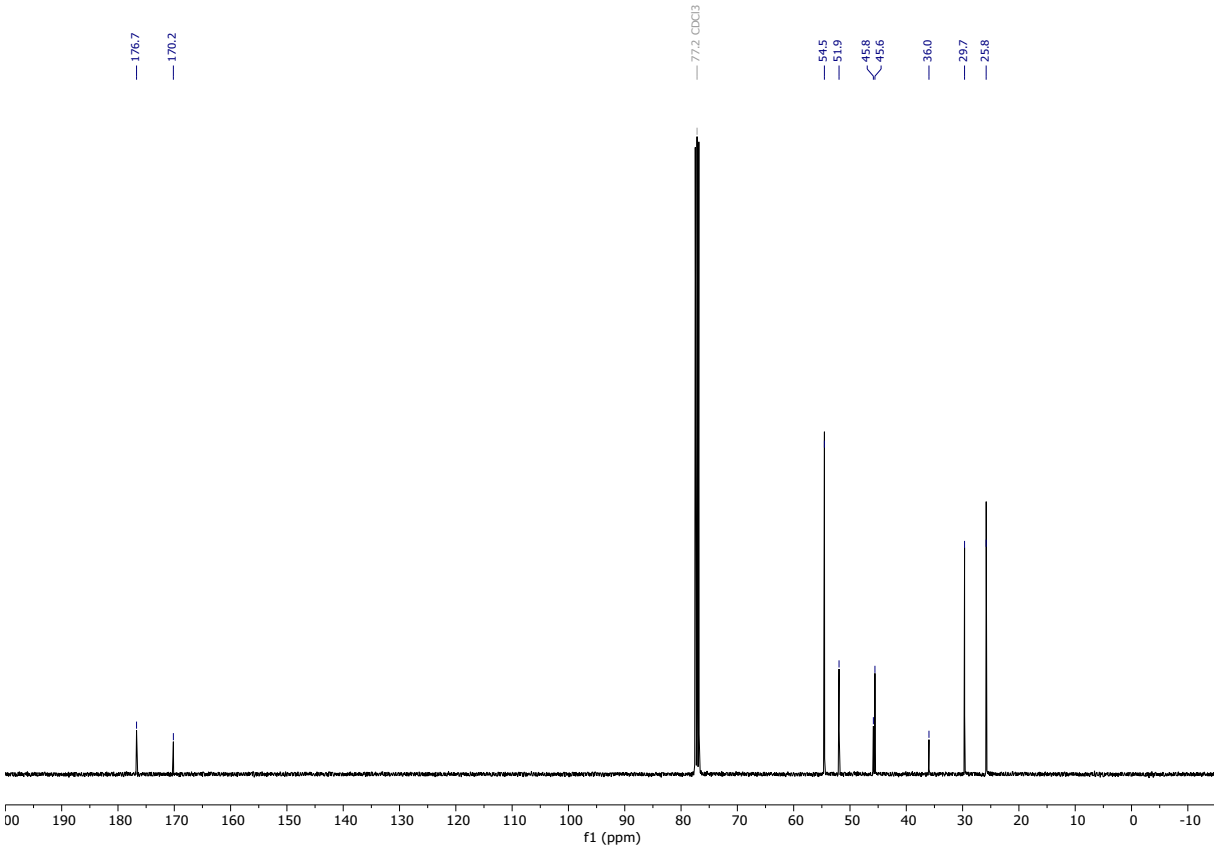

Figure S47 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **17**.

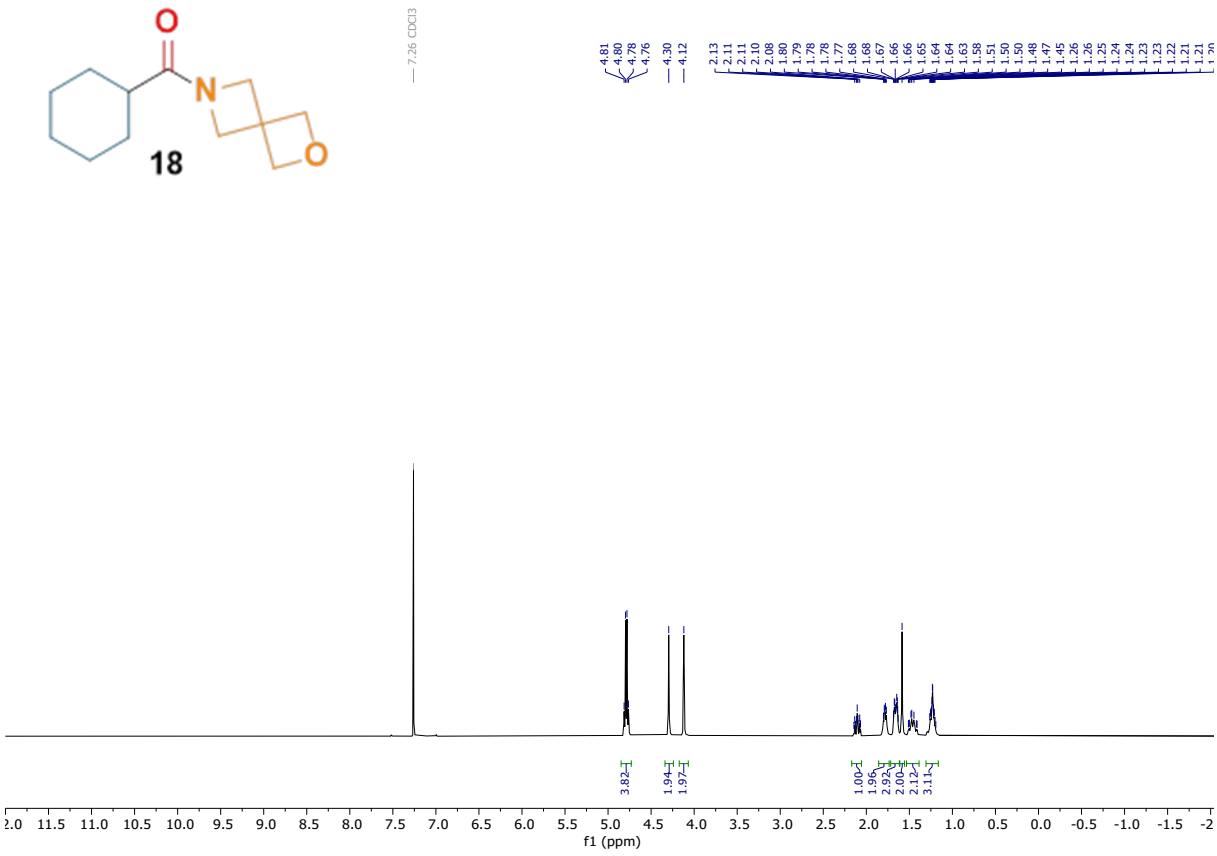

Figure S48 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **18**.

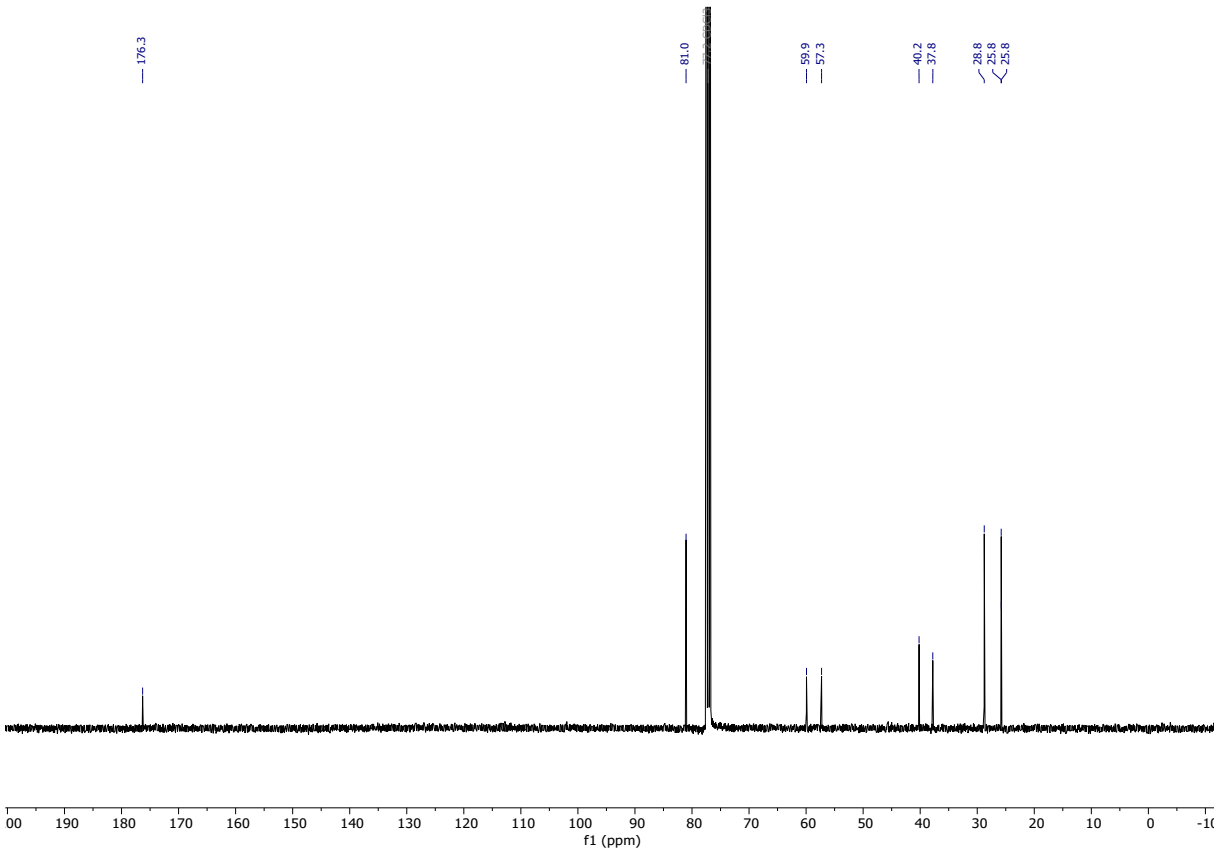

Figure S49 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **18**.

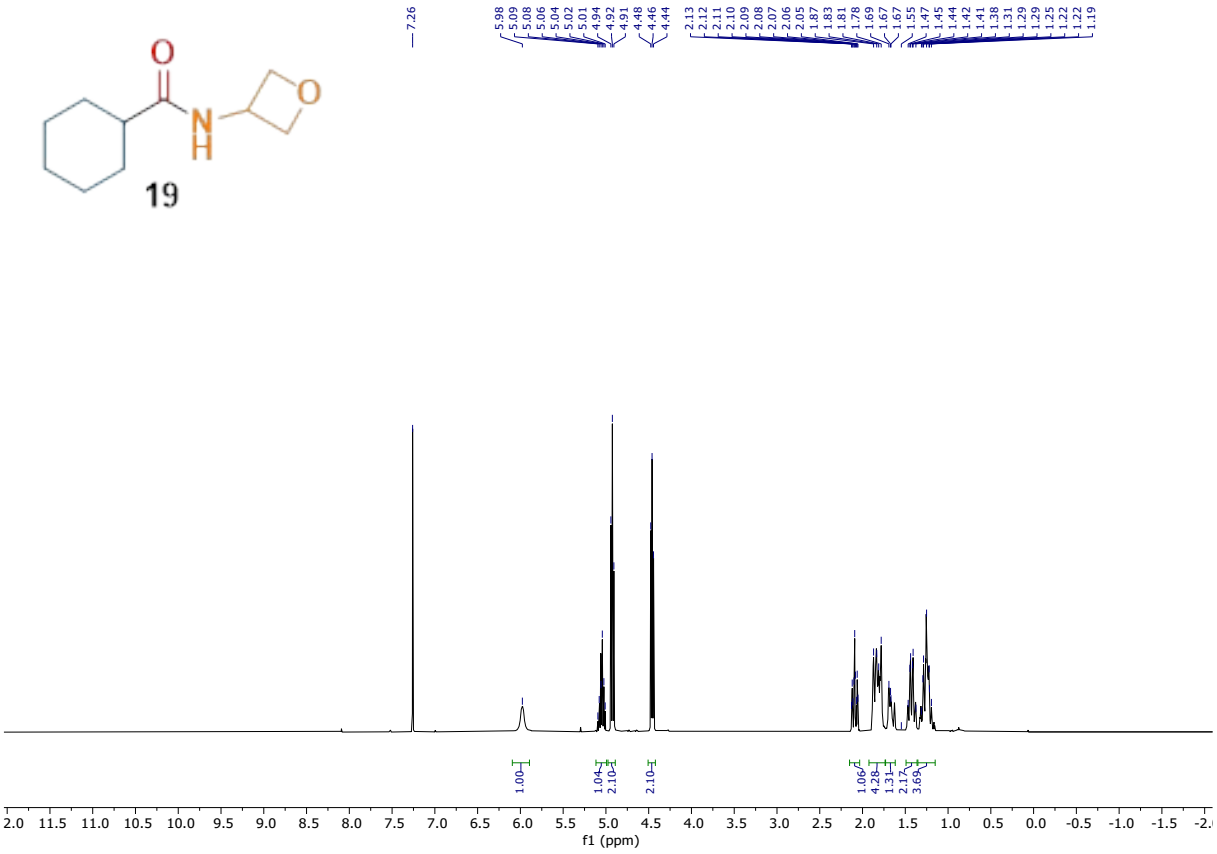

Figure S50 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **19**.

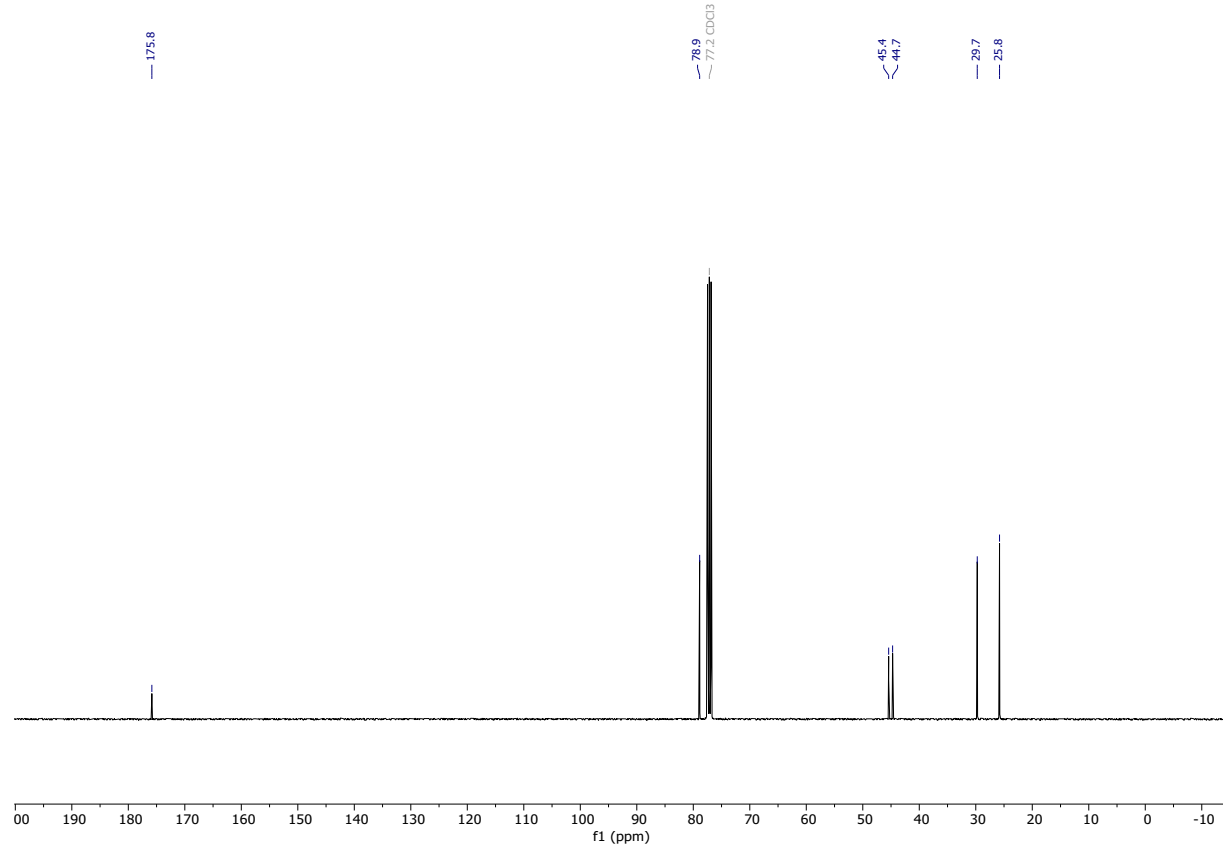

Figure S51 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **19**.

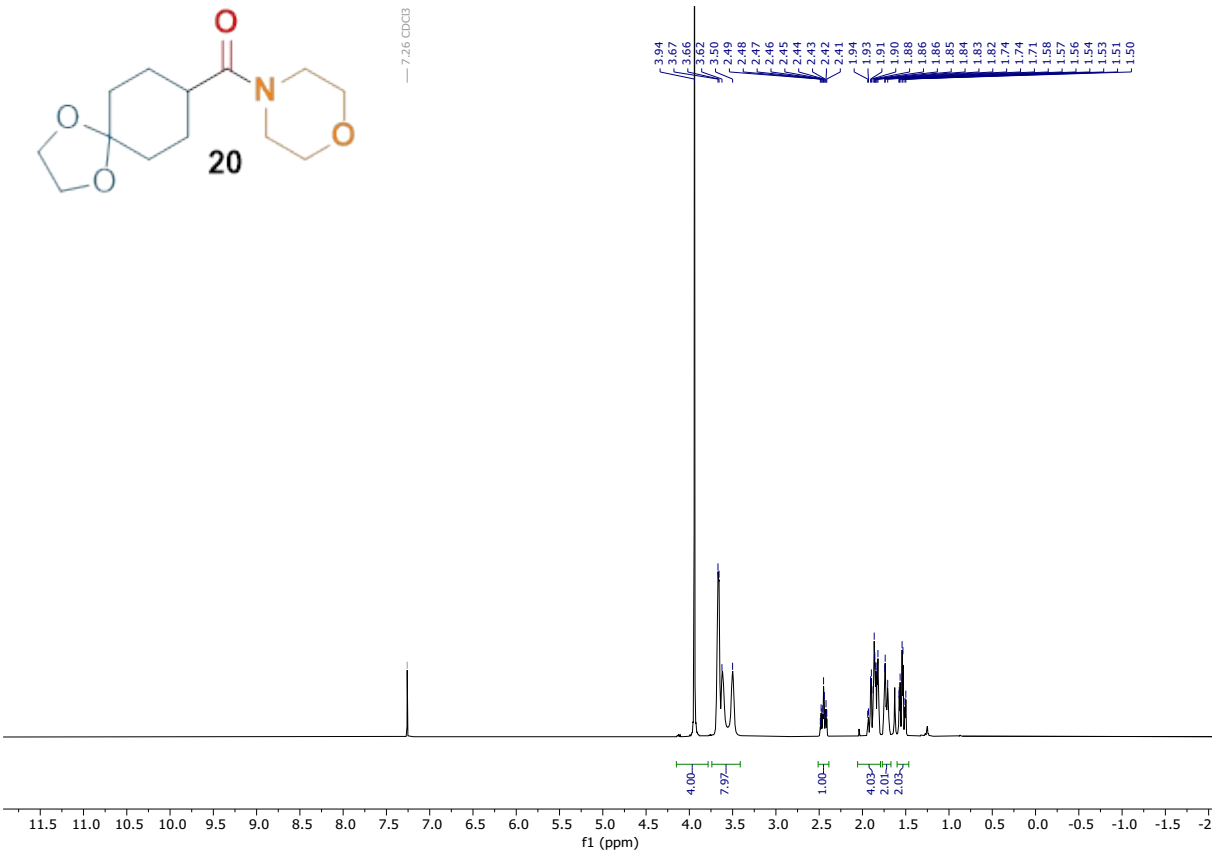

Figure S52 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **20**.

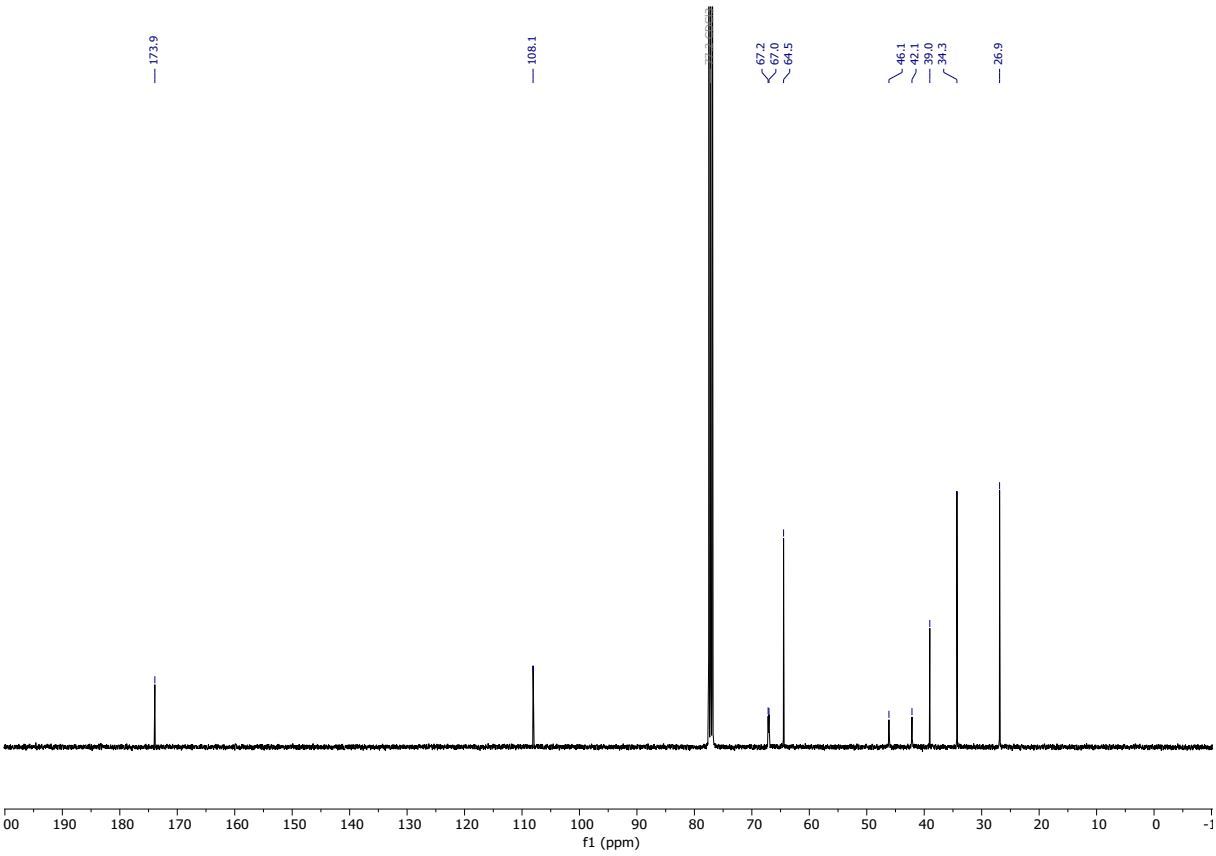

Figure S53 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **20**.

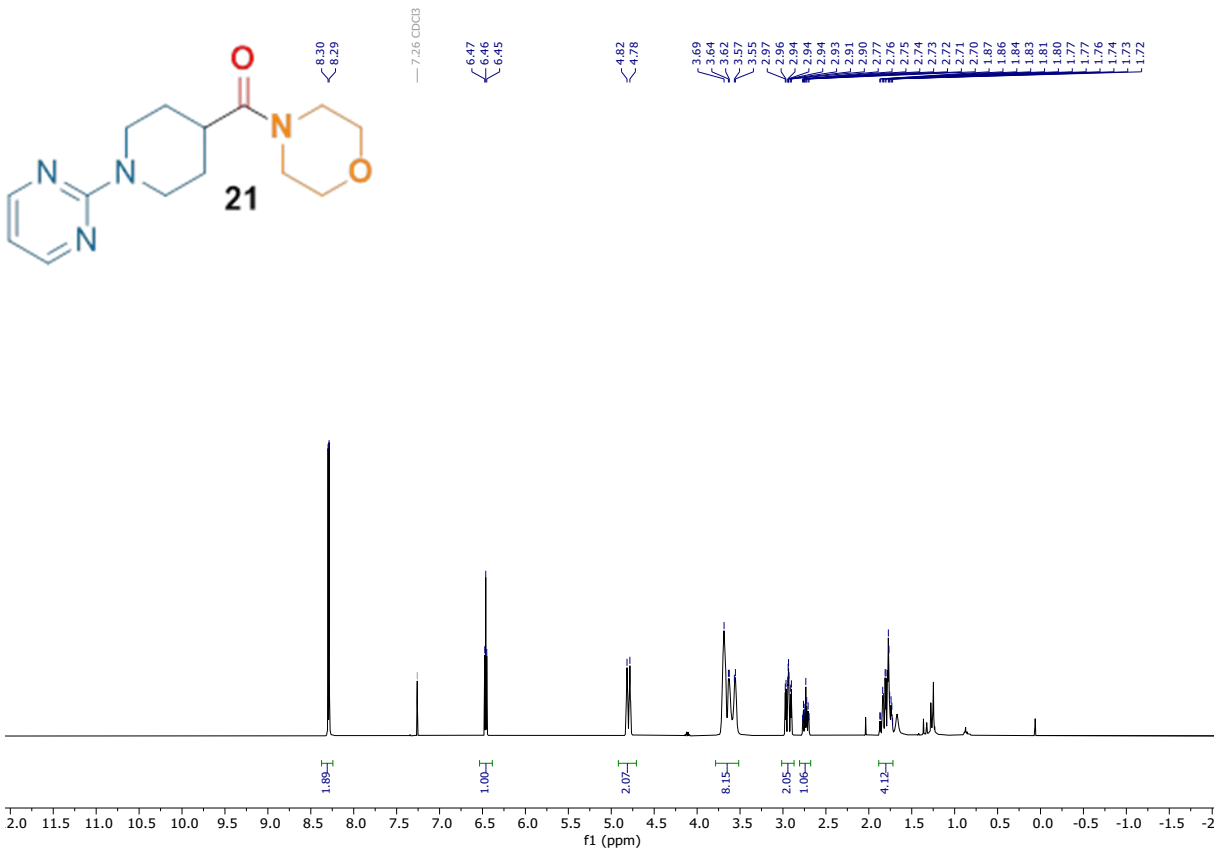

Figure S54 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **21**.

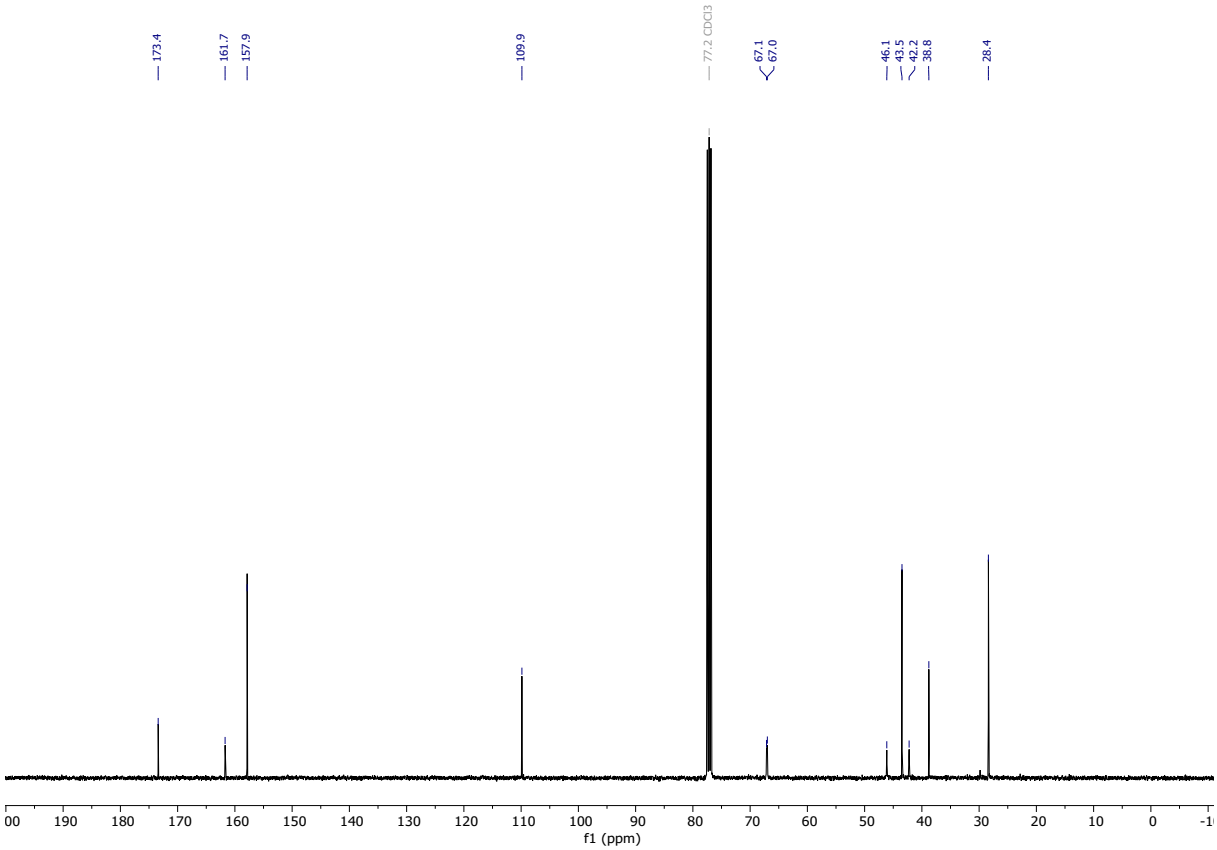

Figure S55 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **21**.

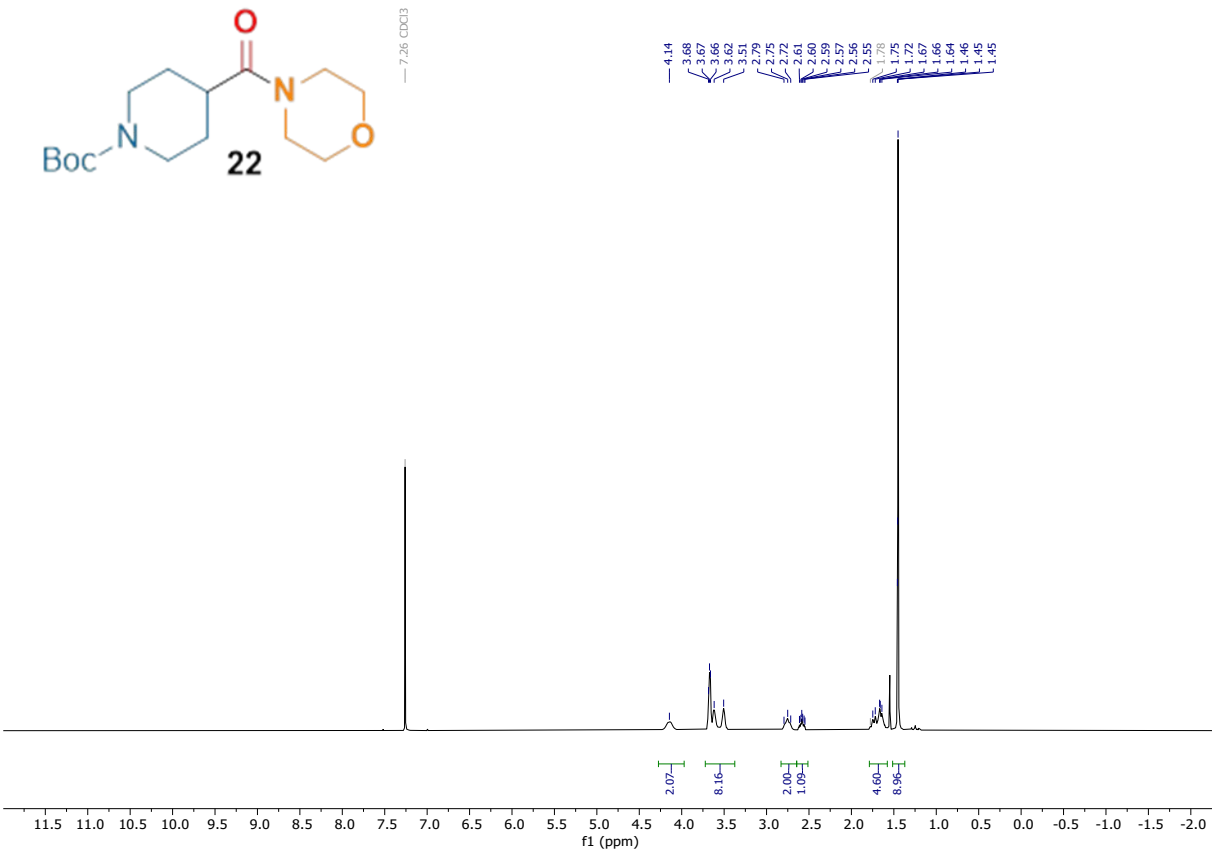

Figure S56 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **22**.

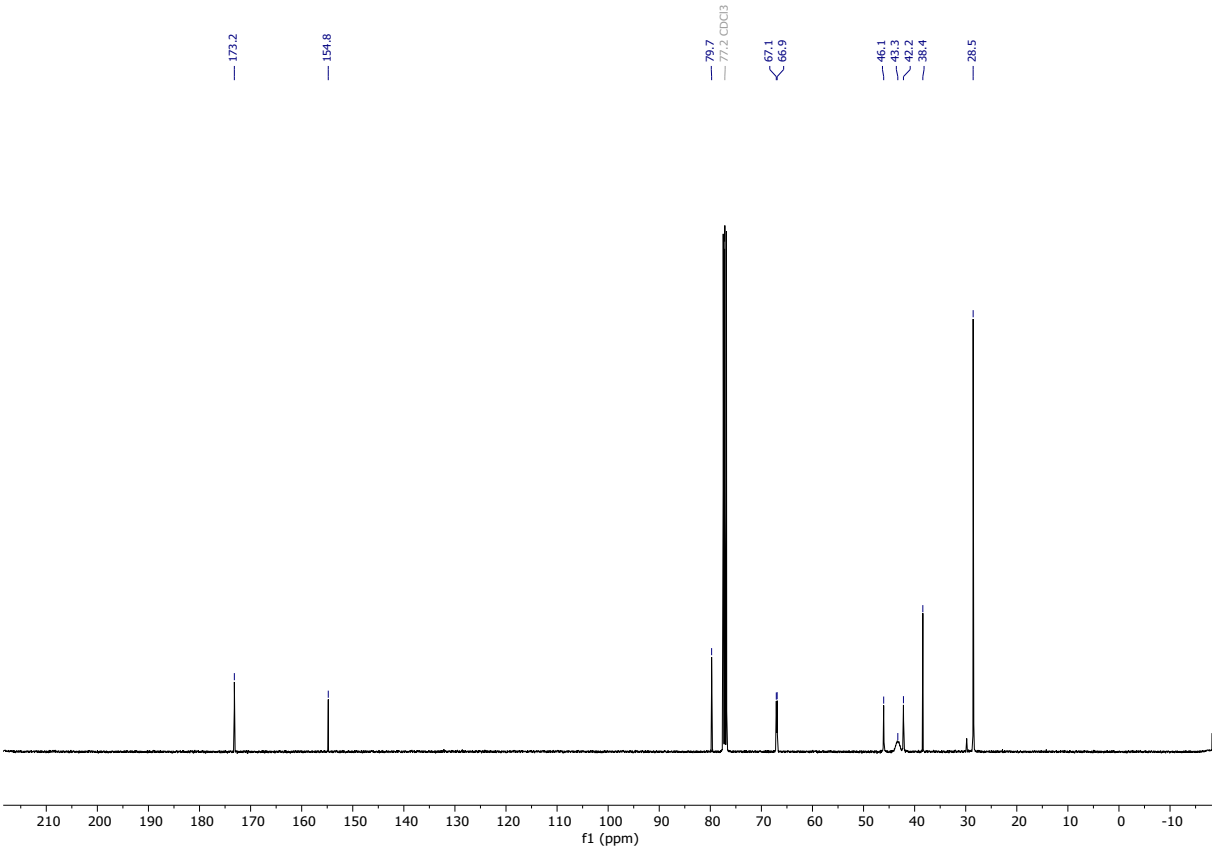

Figure S57 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **22**.

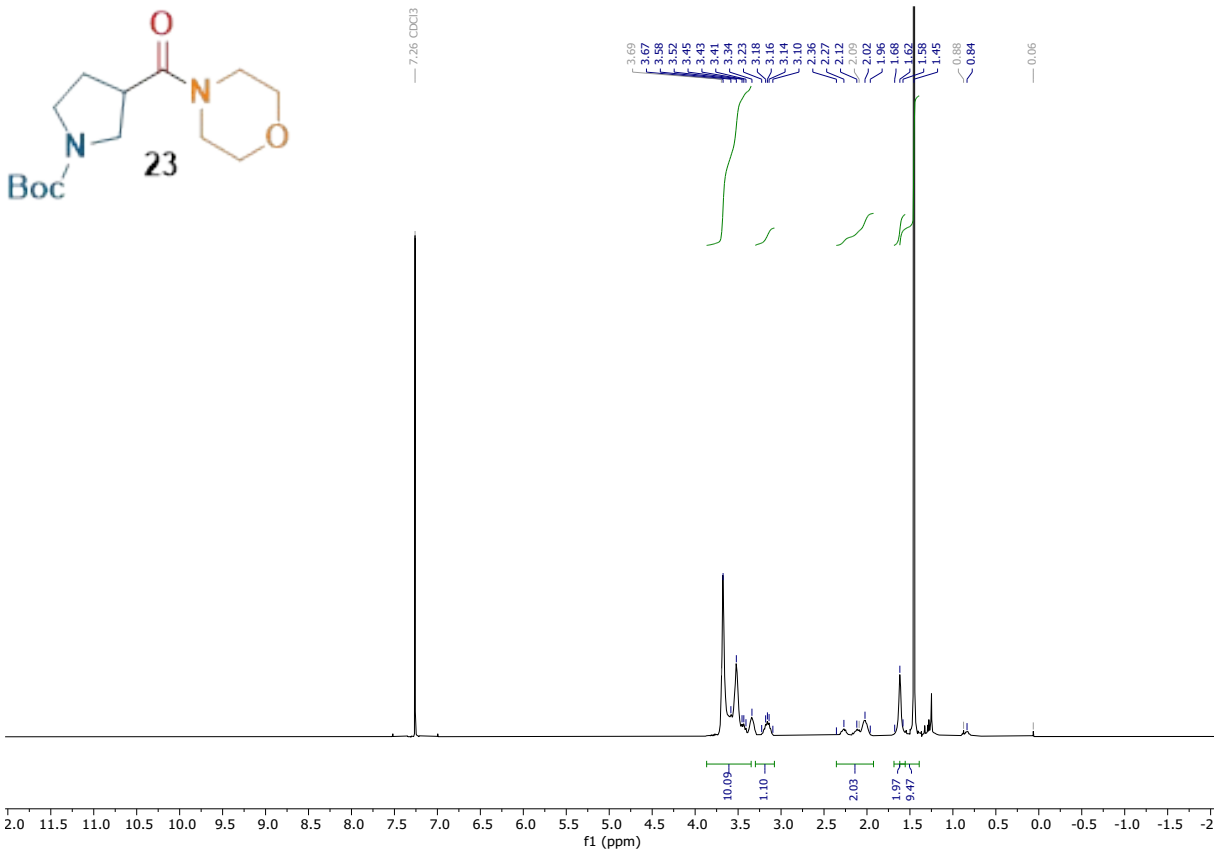

Figure S58 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **23**.

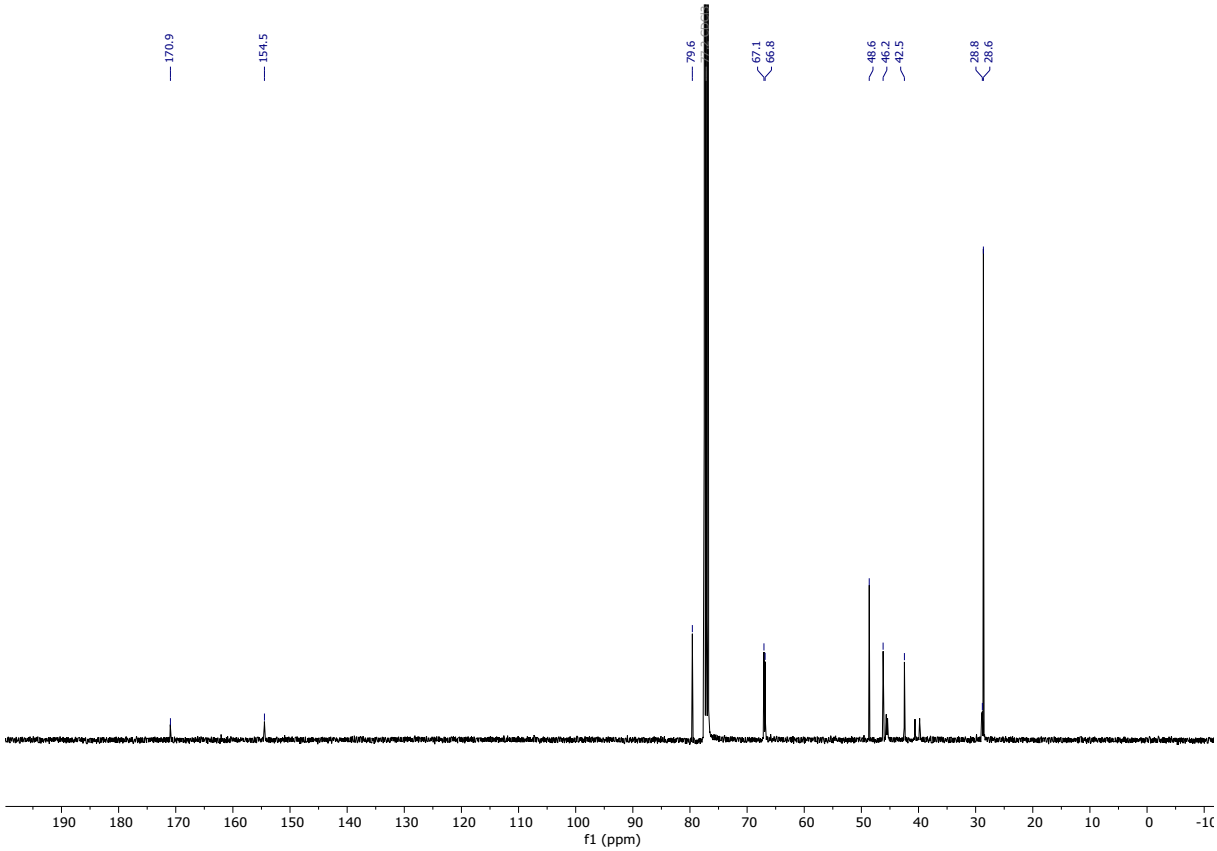

Figure S59 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **23**.

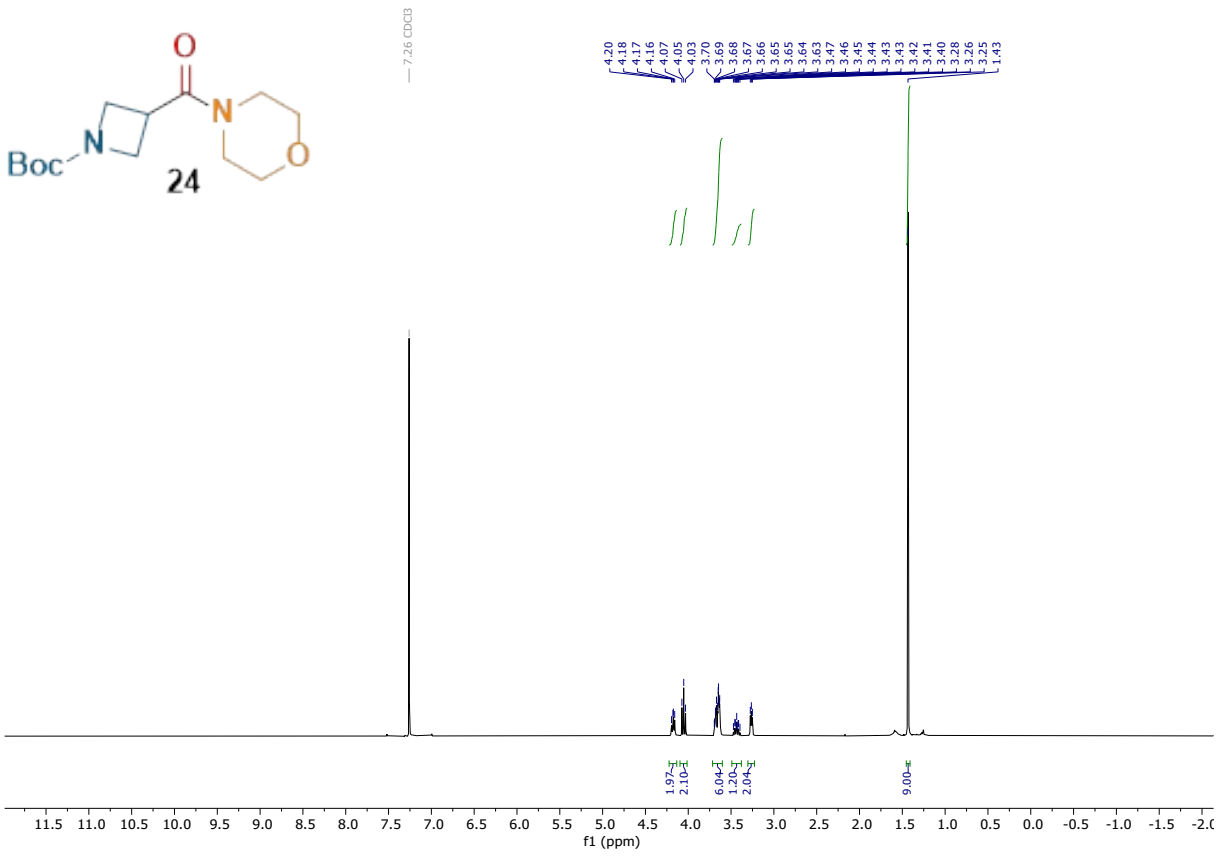

Figure S60 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **24**.

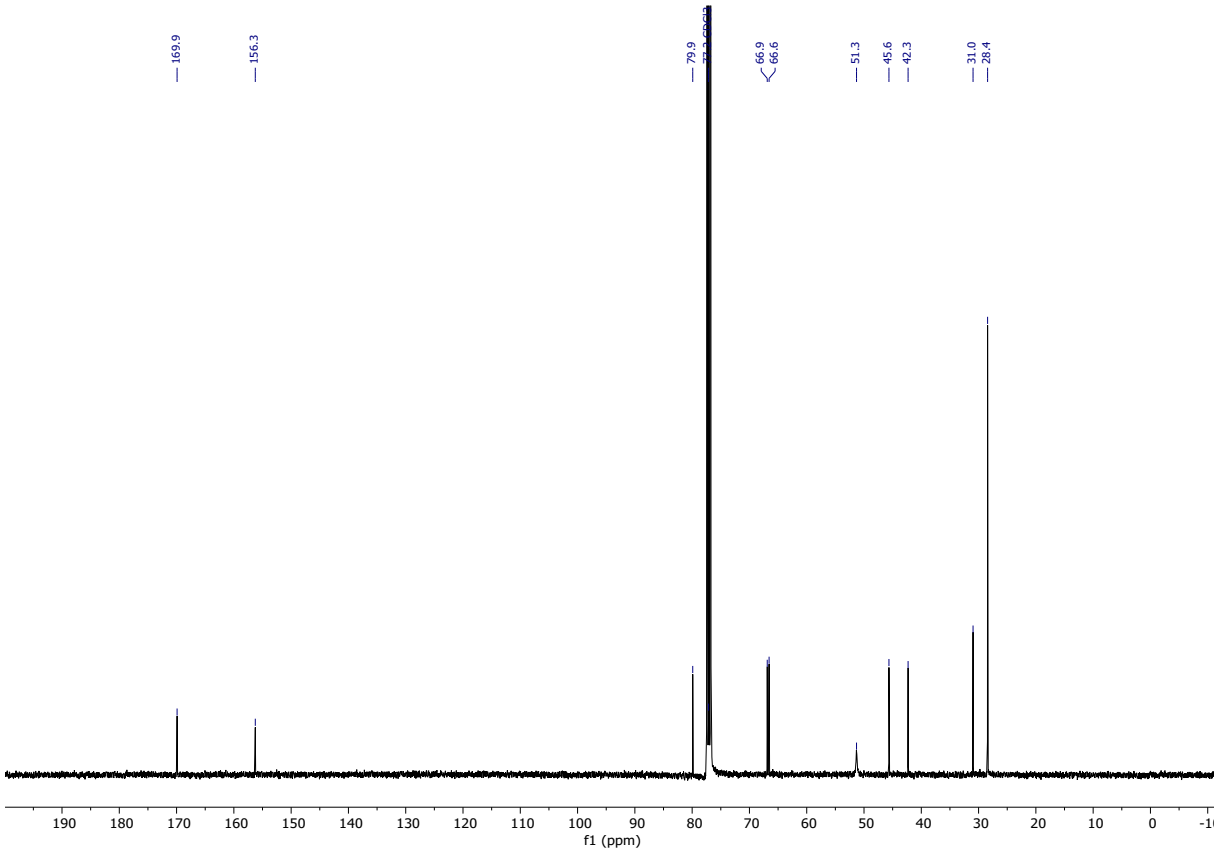

Figure S61 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **24**.

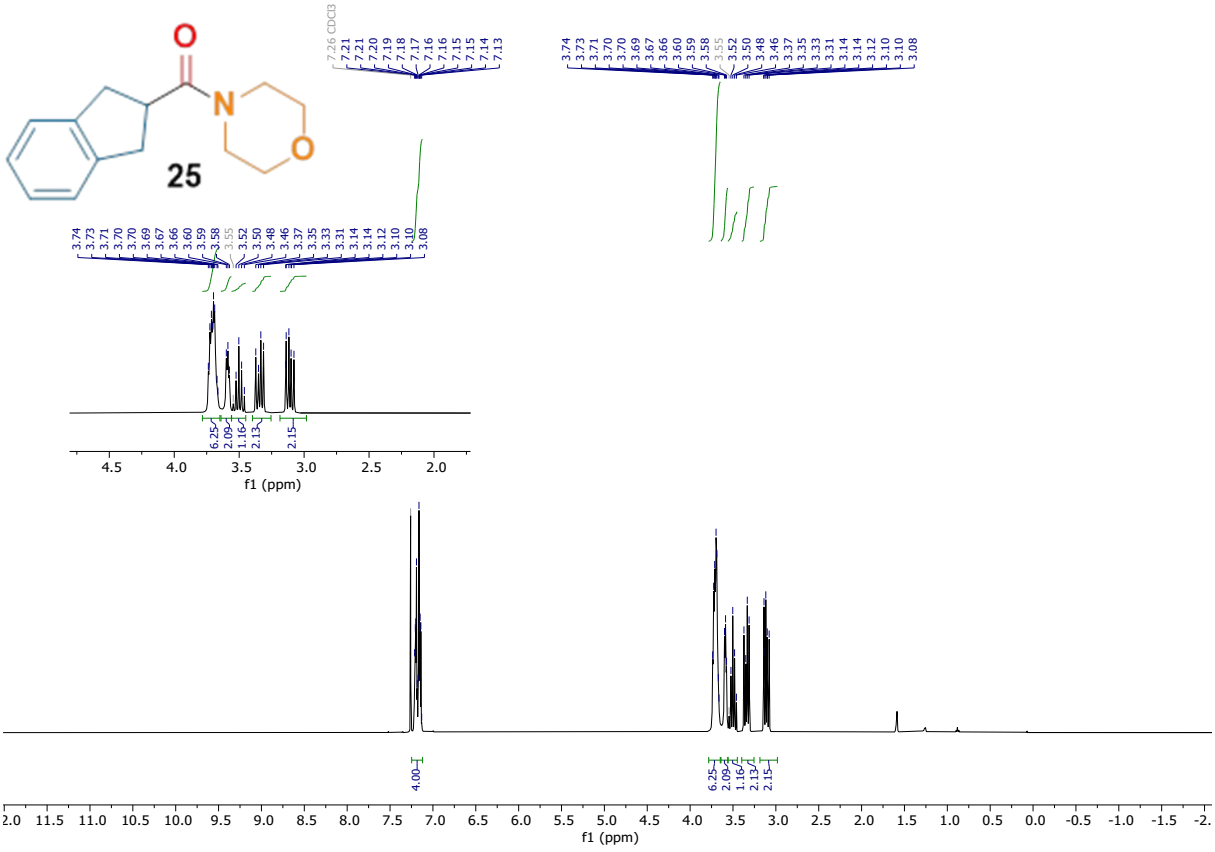

Figure S62 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **25**.

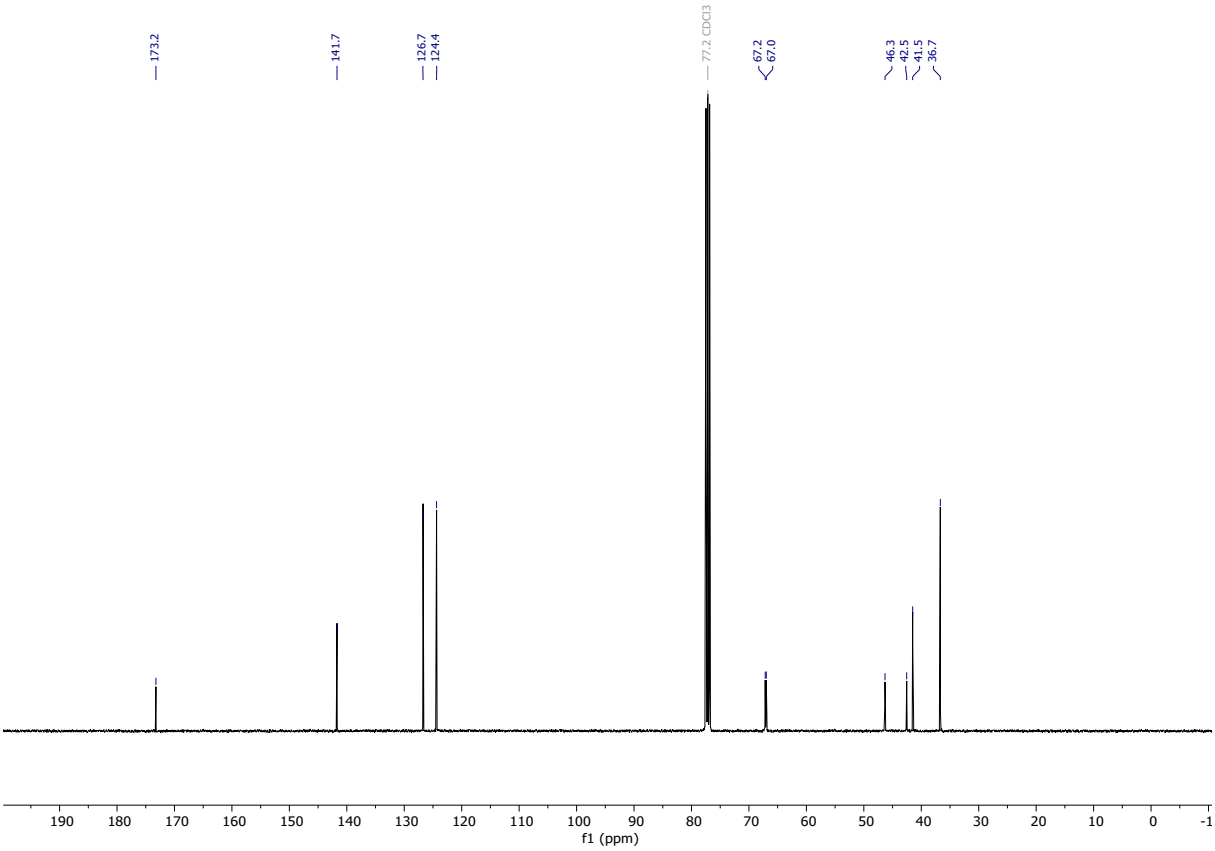

Figure S63 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **25**.

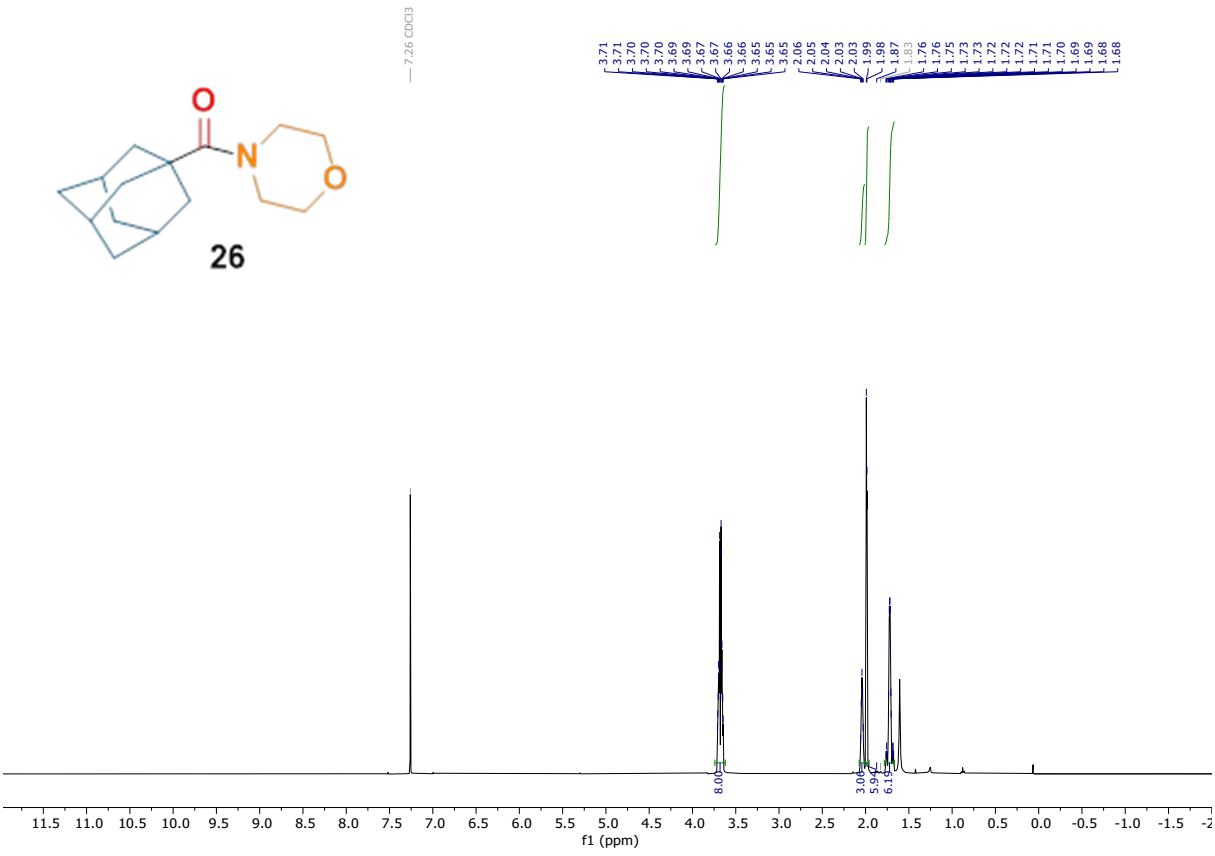

Figure S64 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **26**.

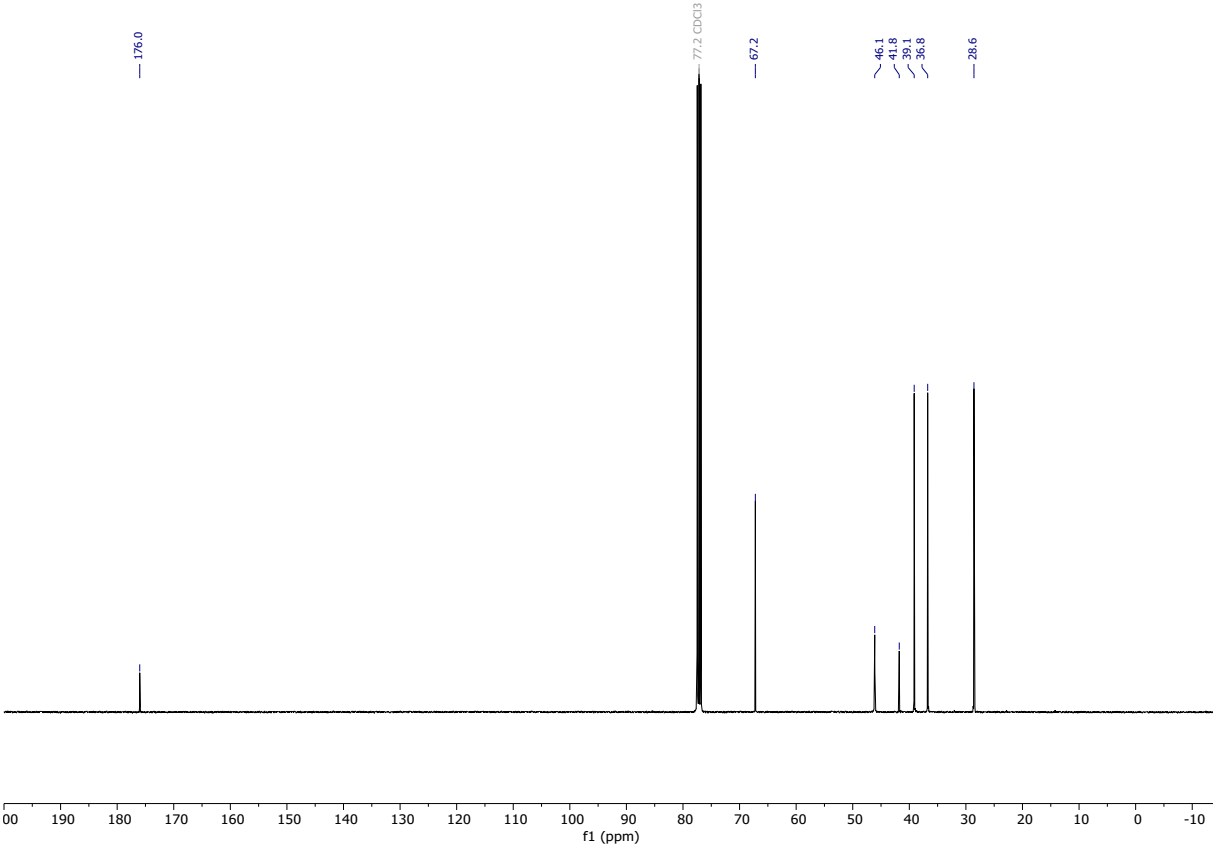

Figure S65 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **26**.

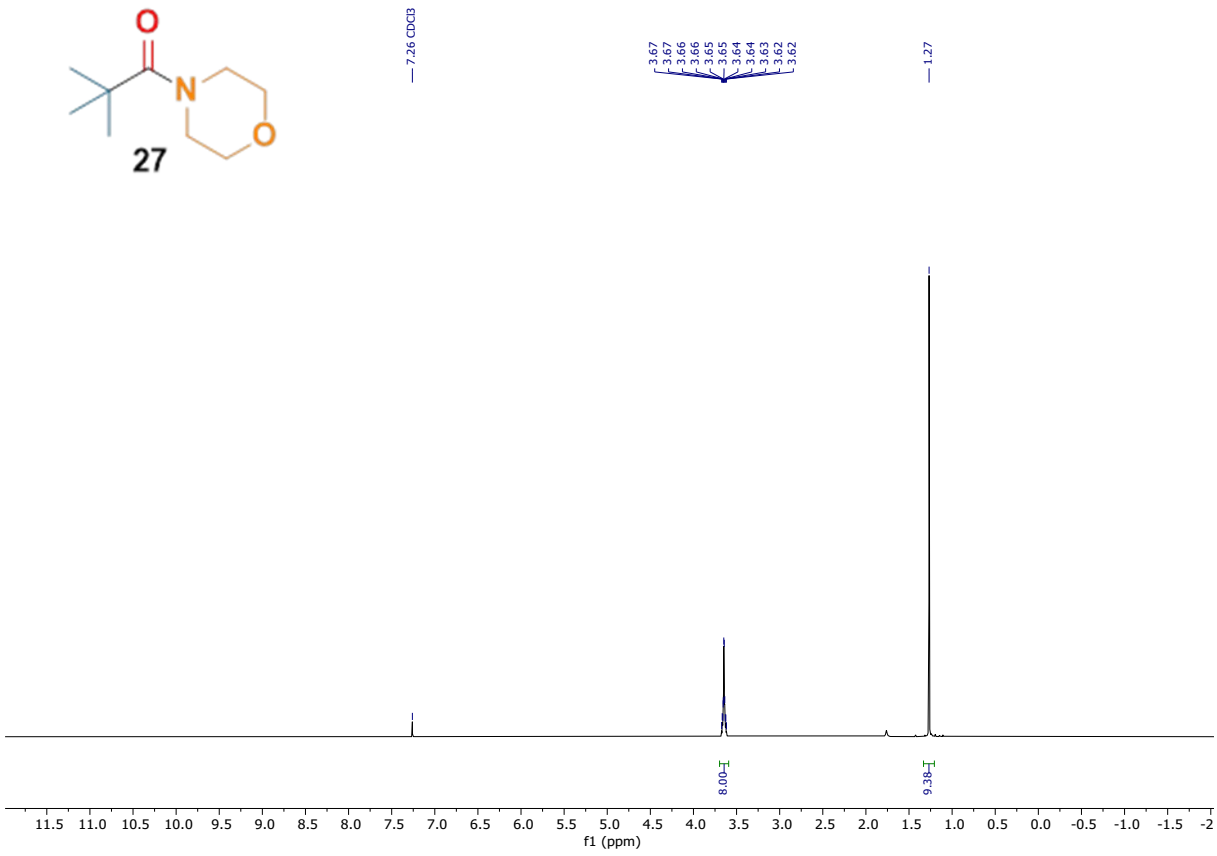

Figure S66 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **27**.

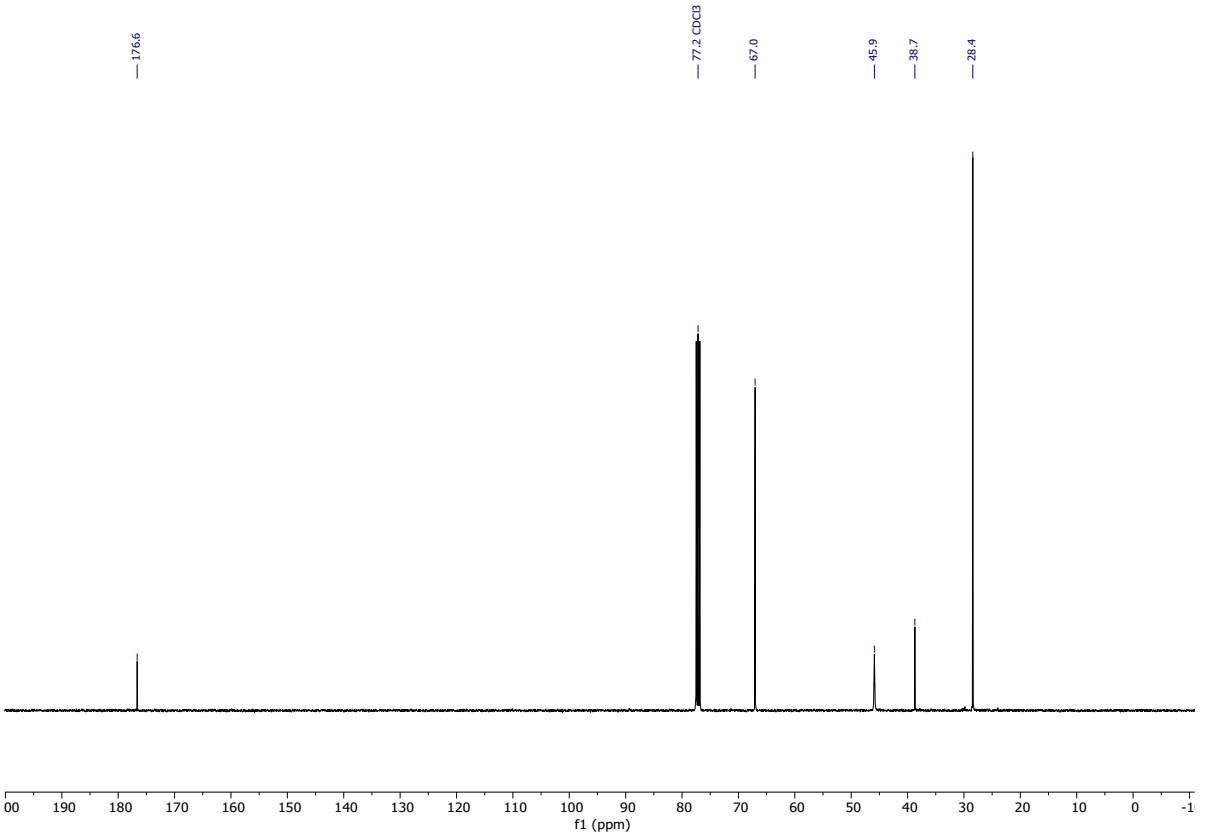

Figure S67 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **27**.

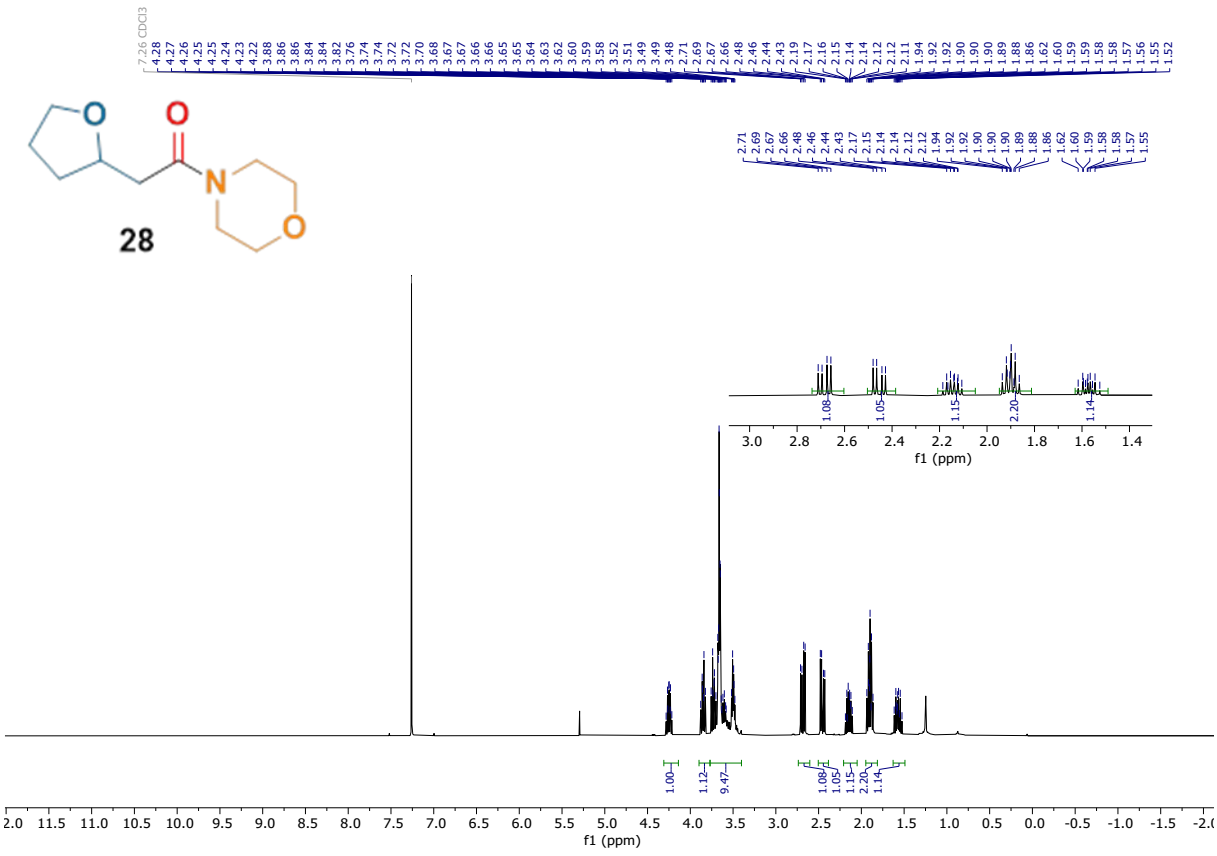

Figure S68 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **28**.

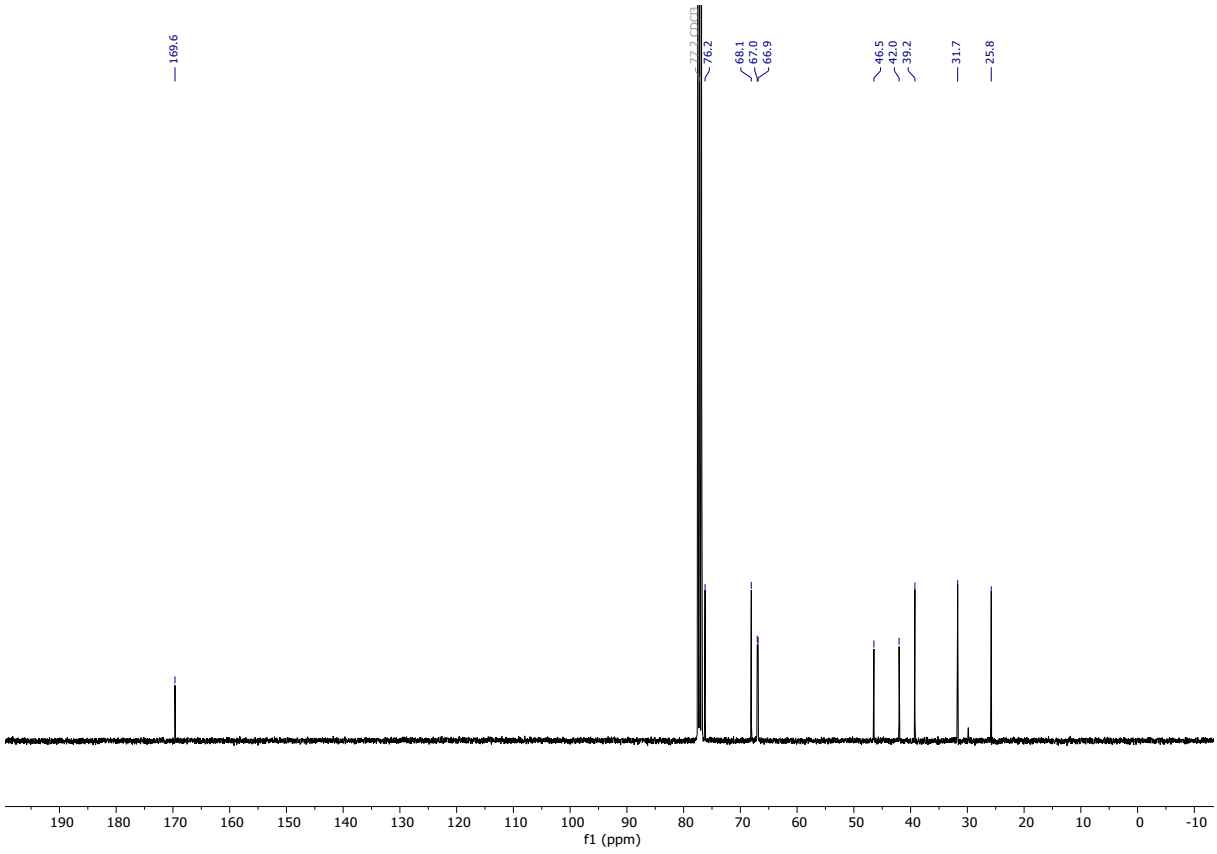

Figure S69 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **28**.

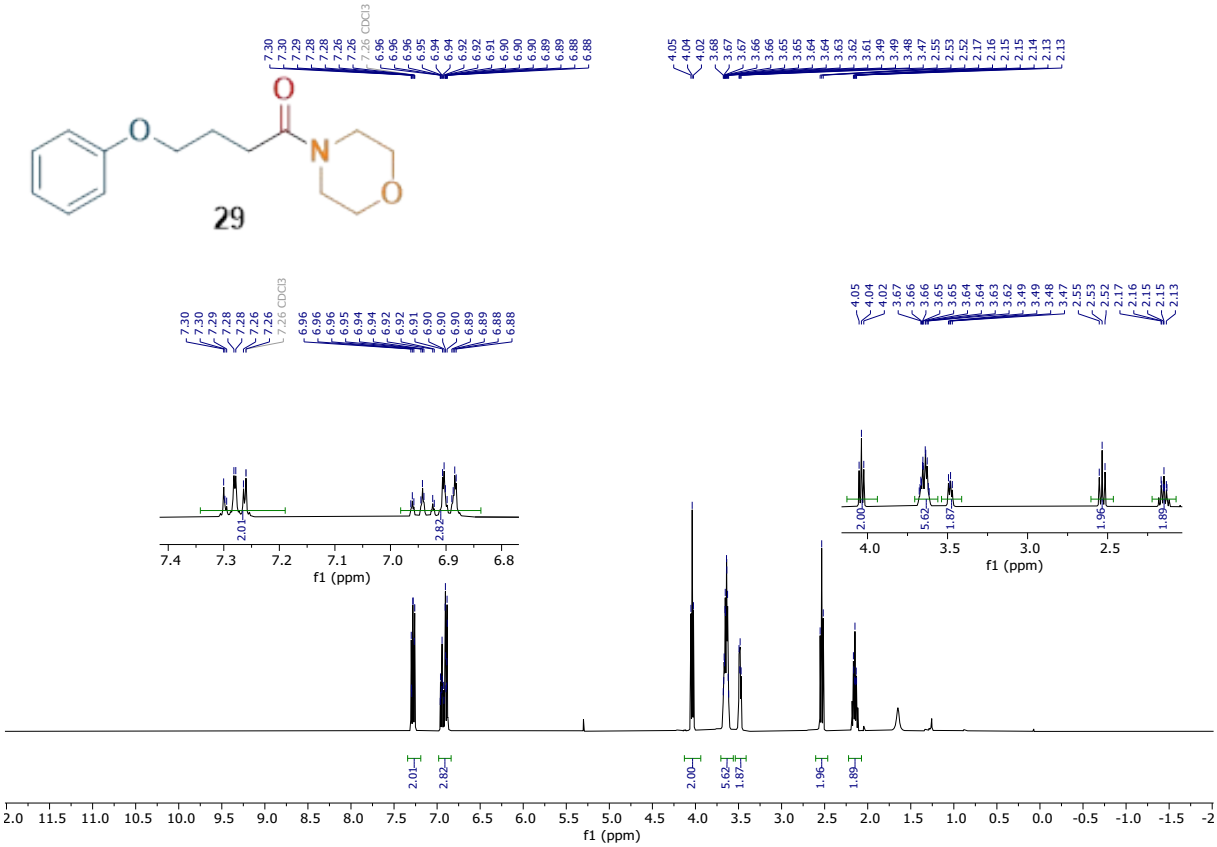

Figure S70 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **29**.

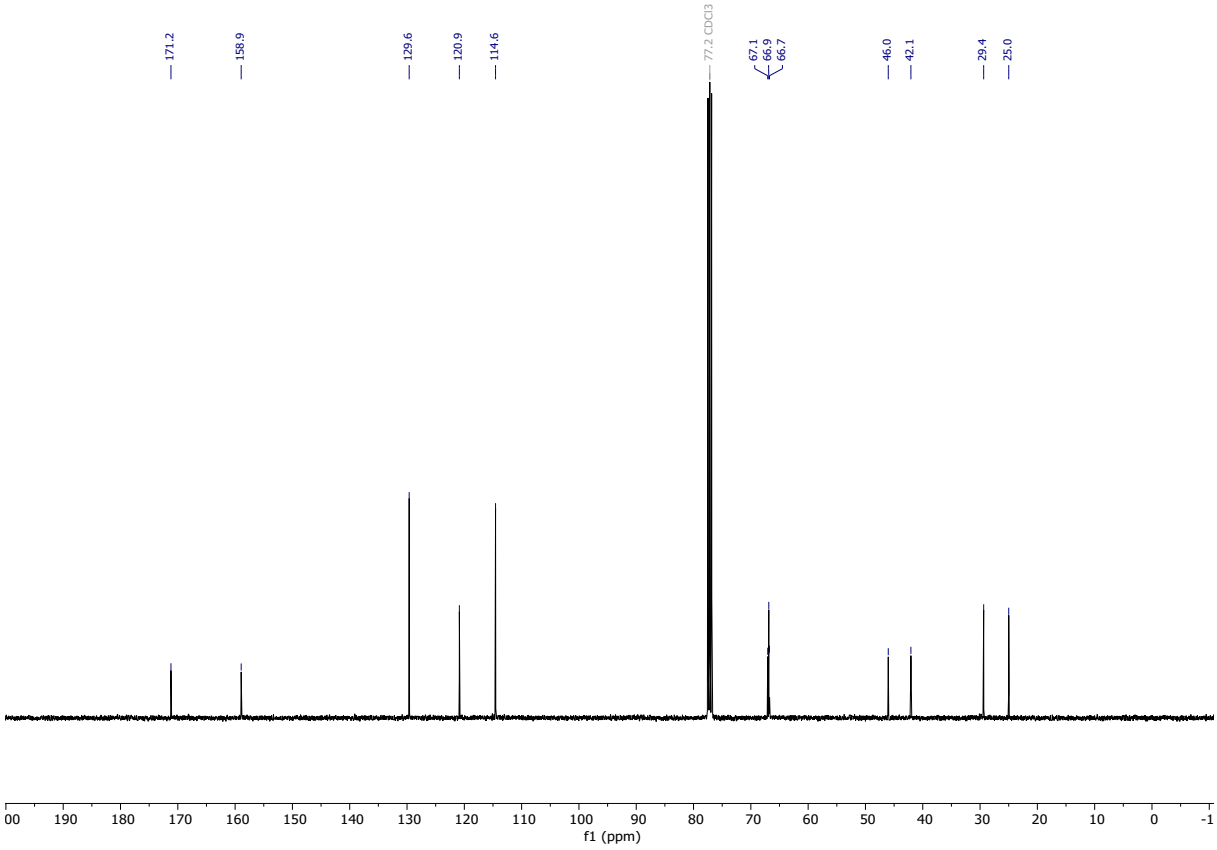

Figure S71 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **29**.

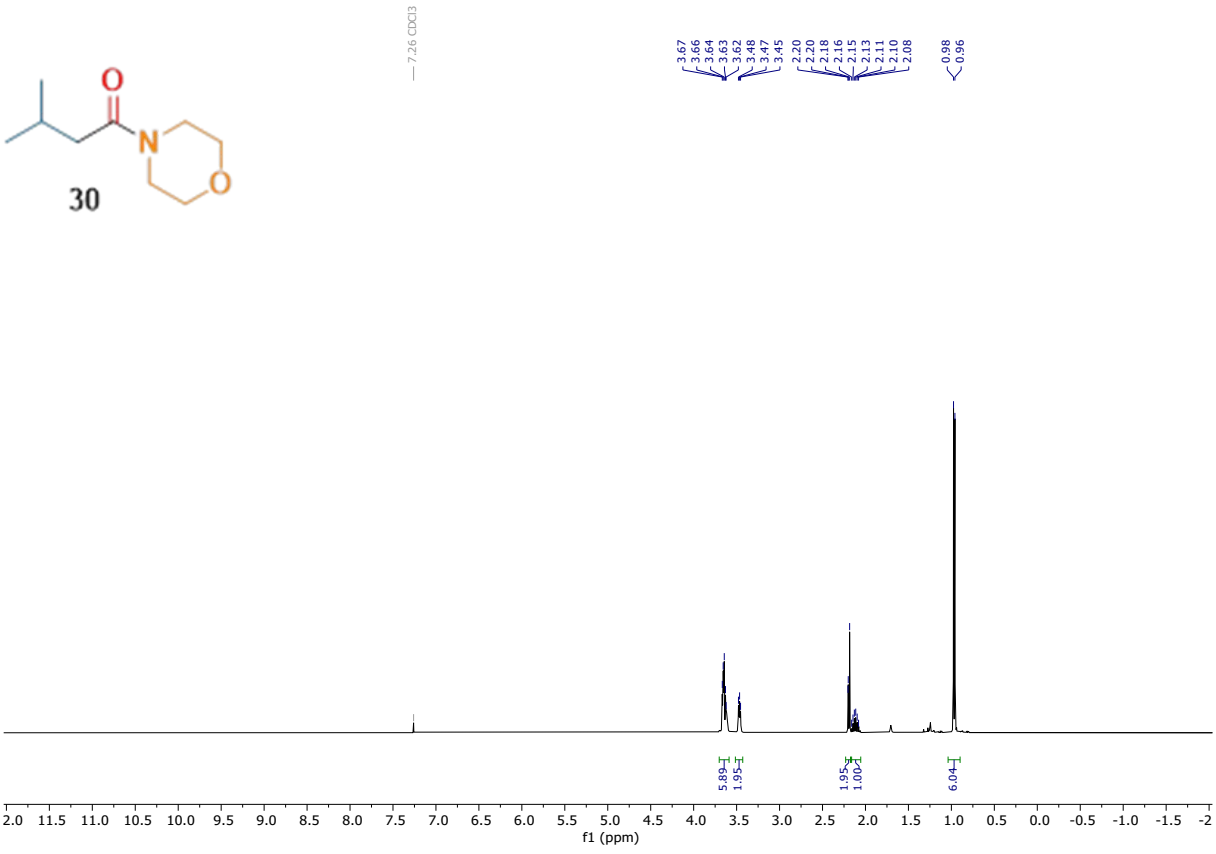

Figure S72 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **30**.

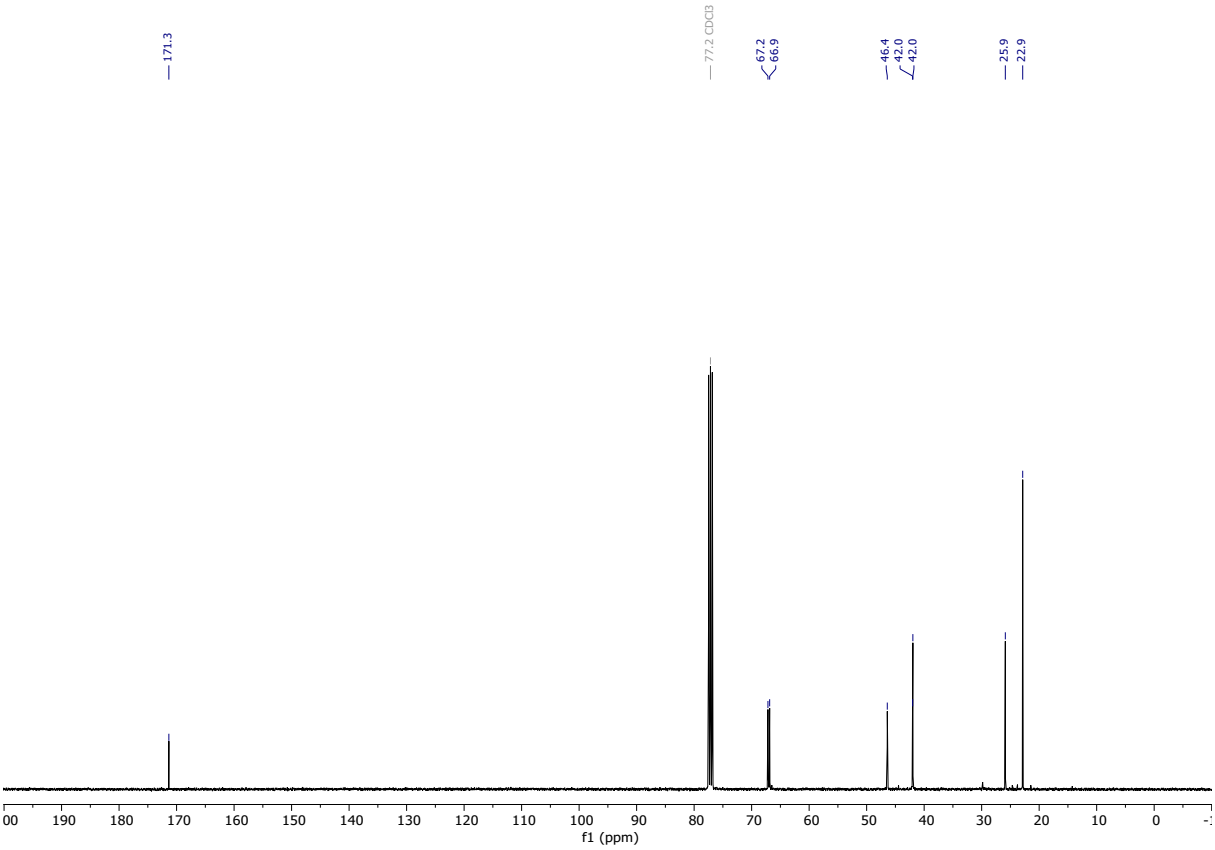

Figure S73 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **30**.

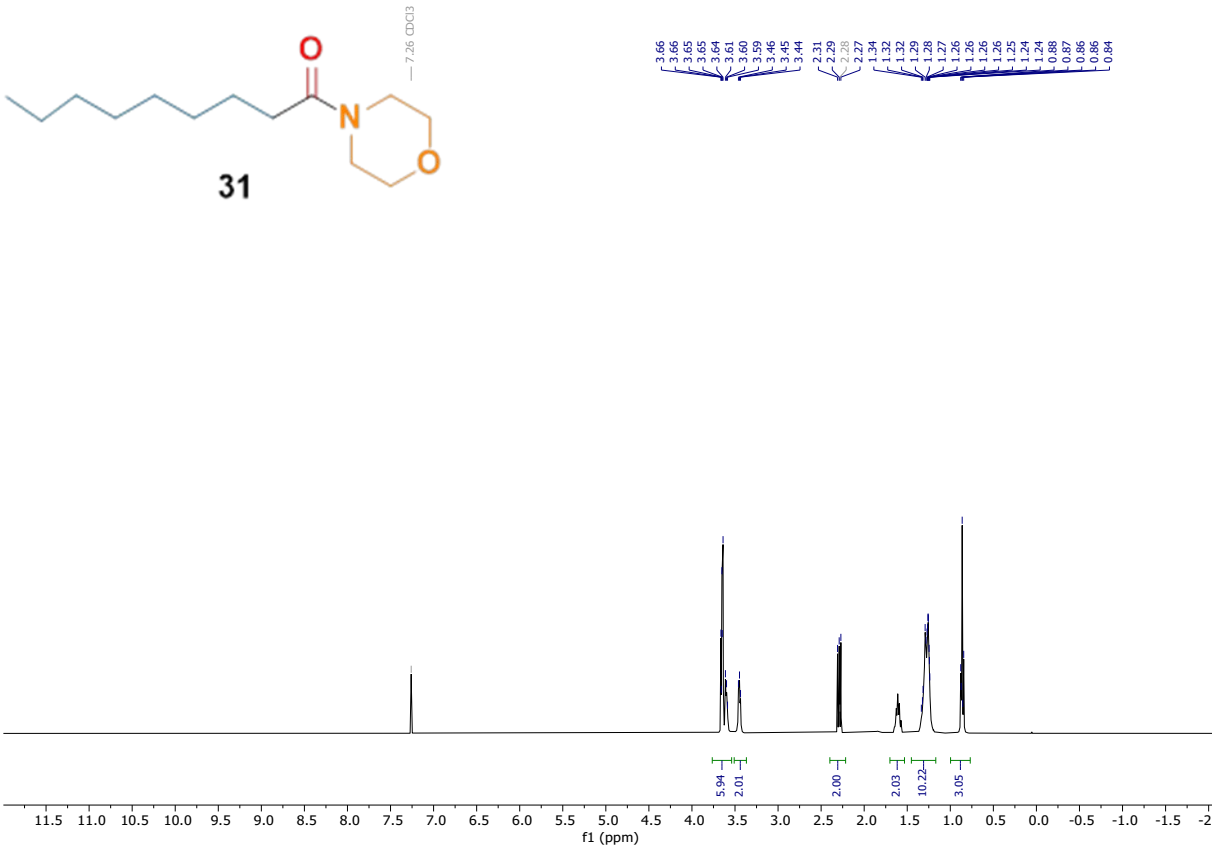

Figure S74 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **31**.

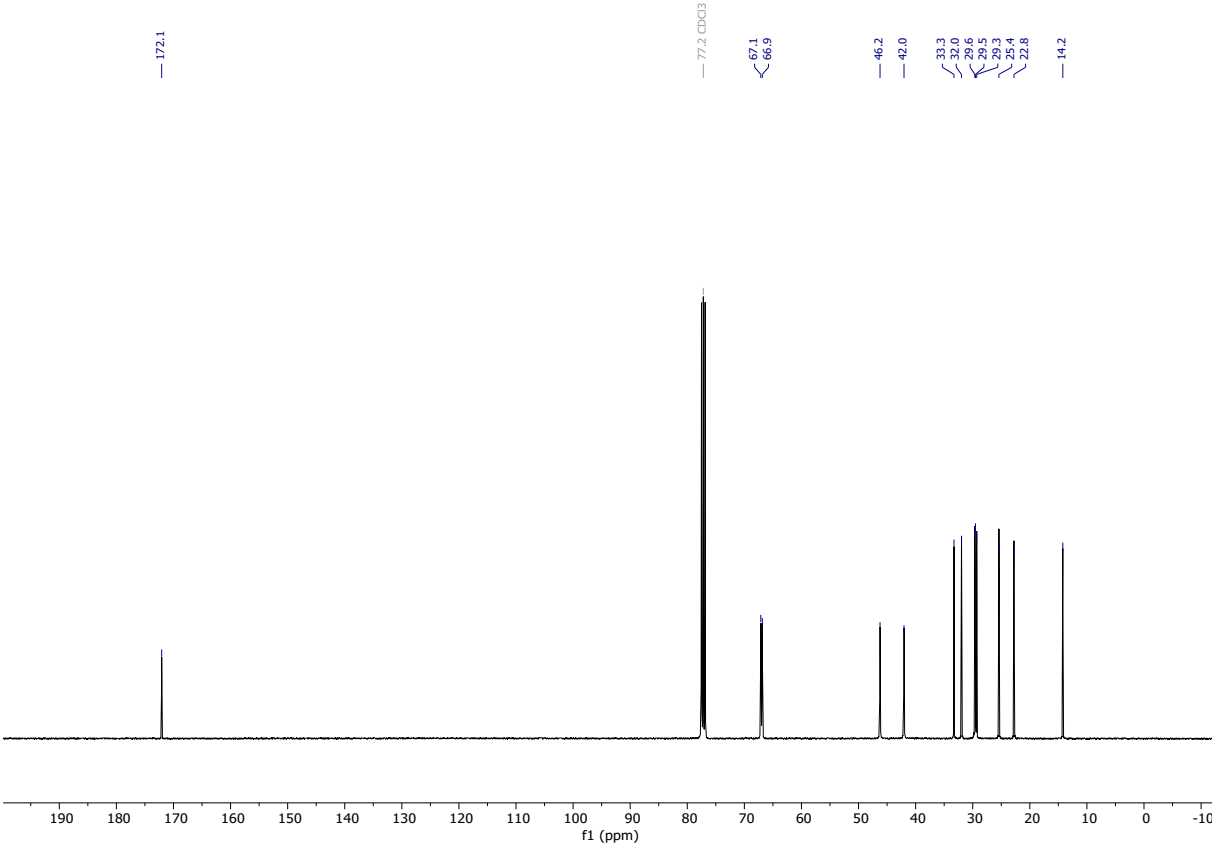

Figure S75 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **31**.

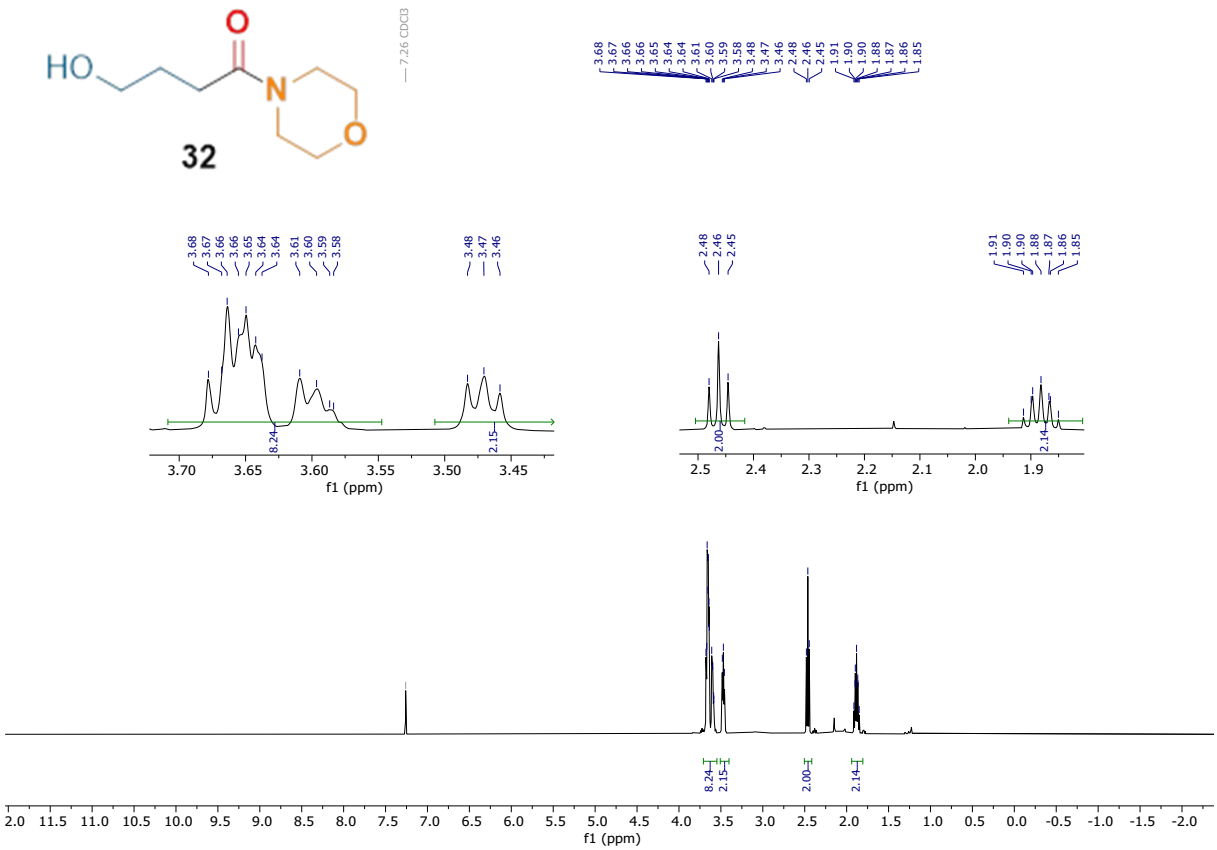

Figure S76 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **32**.

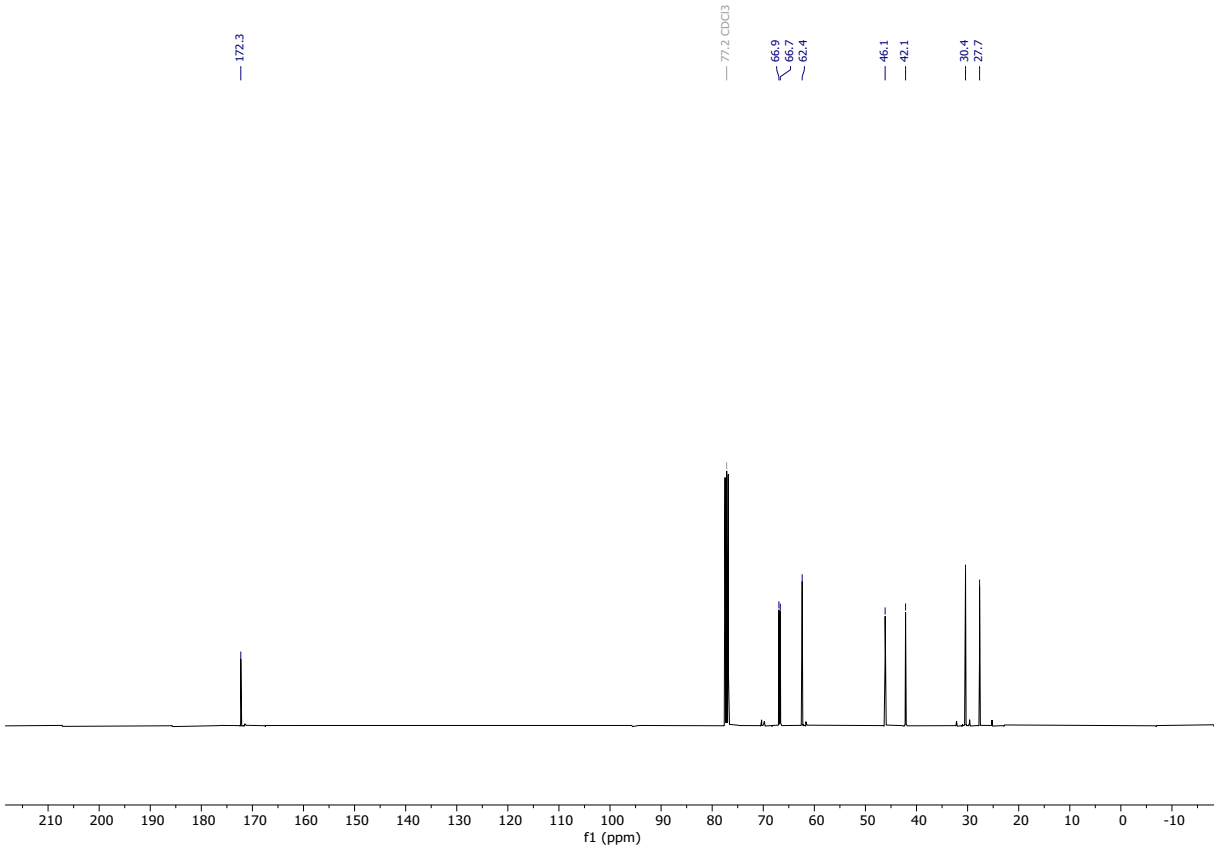

Figure S77 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **32**.

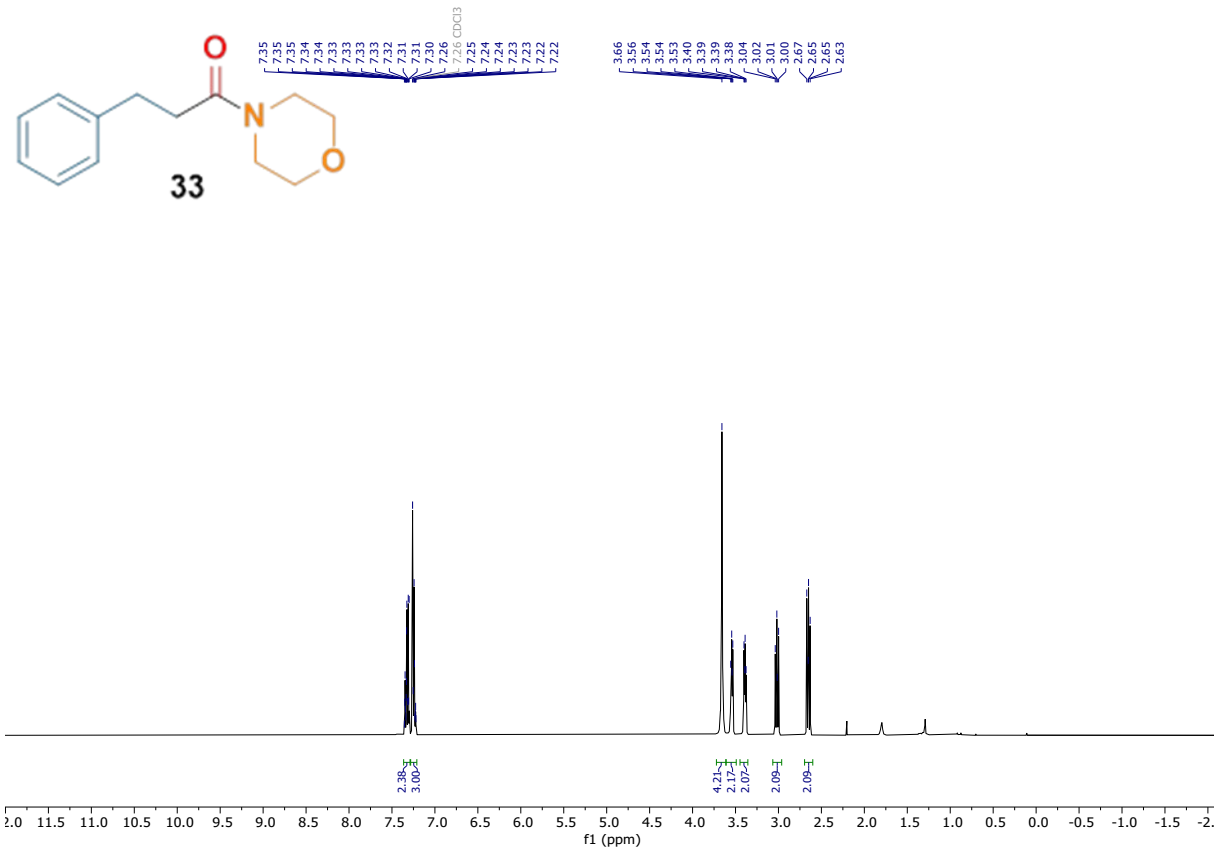

Figure S78 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **33**.

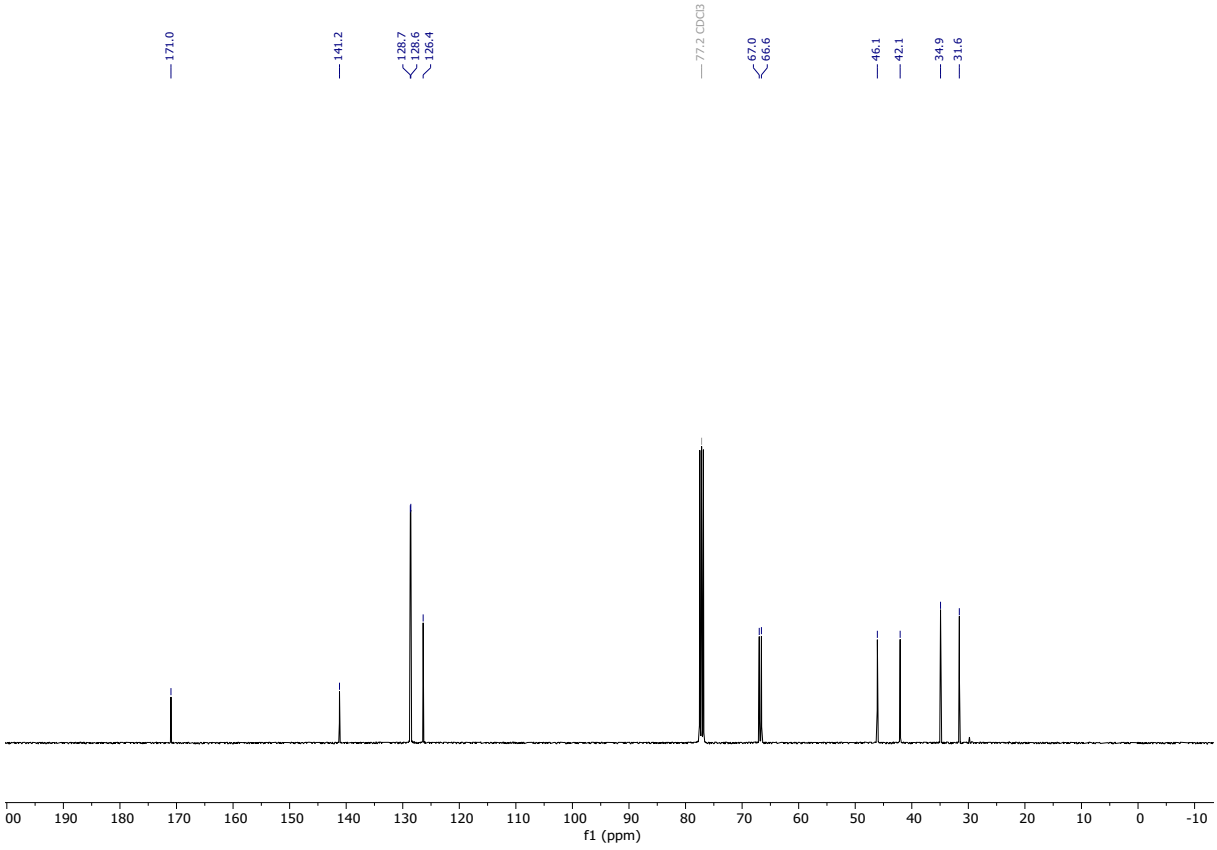

Figure S79 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **33**.

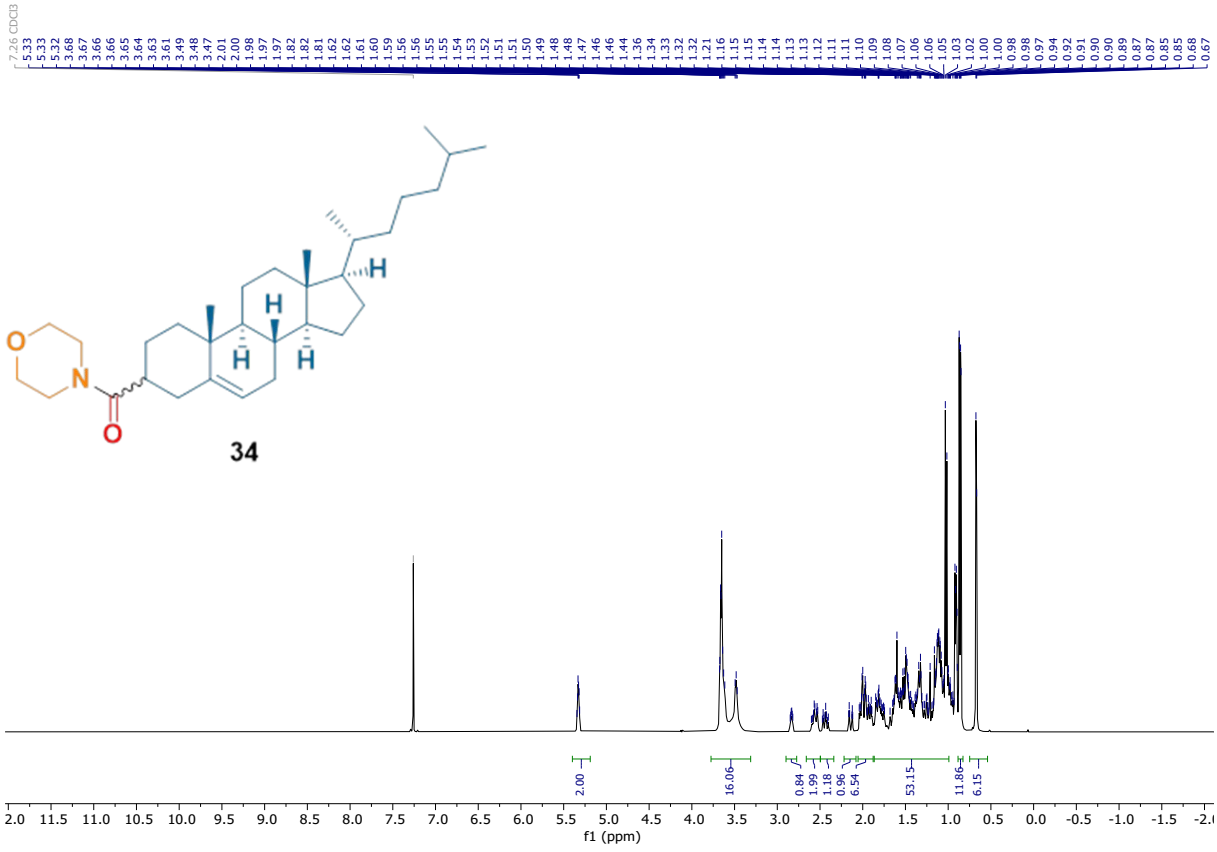

Figure S80 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **34**.

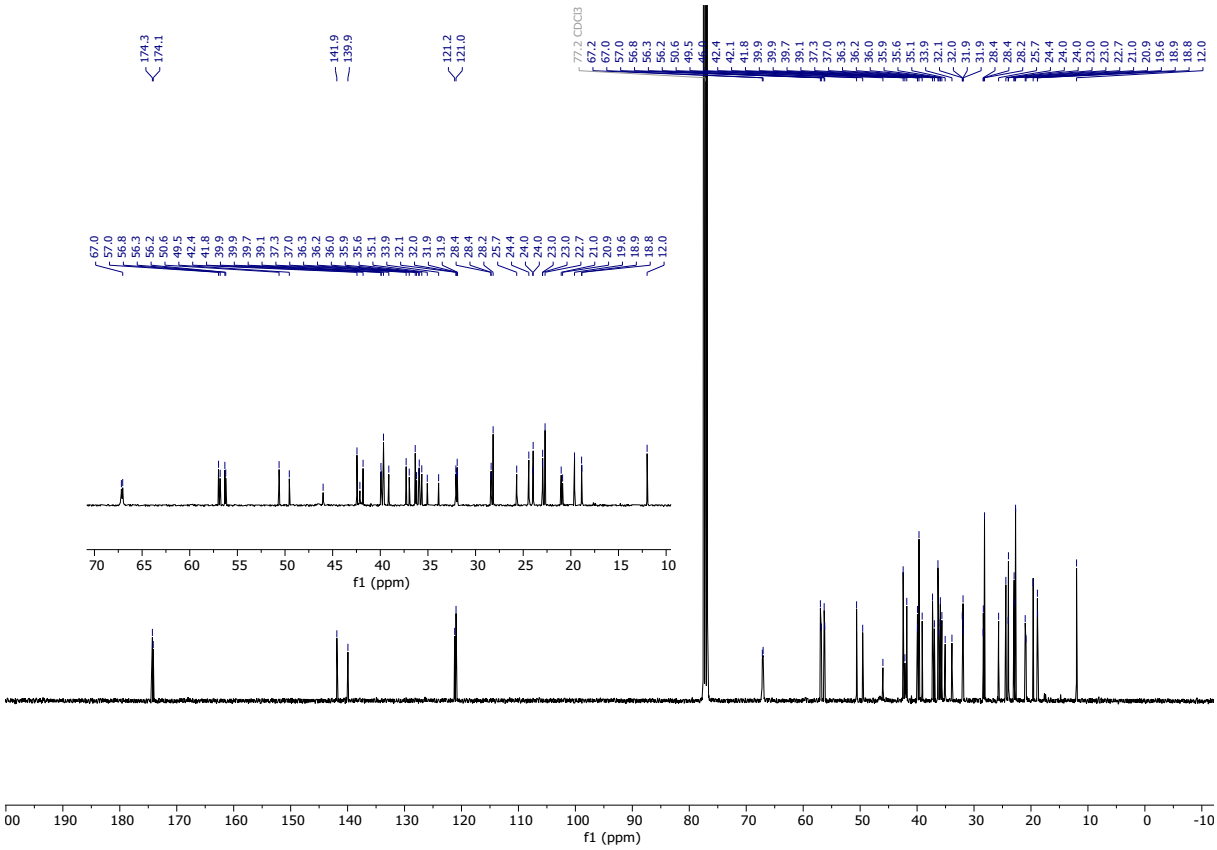

Figure S81 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **34**.

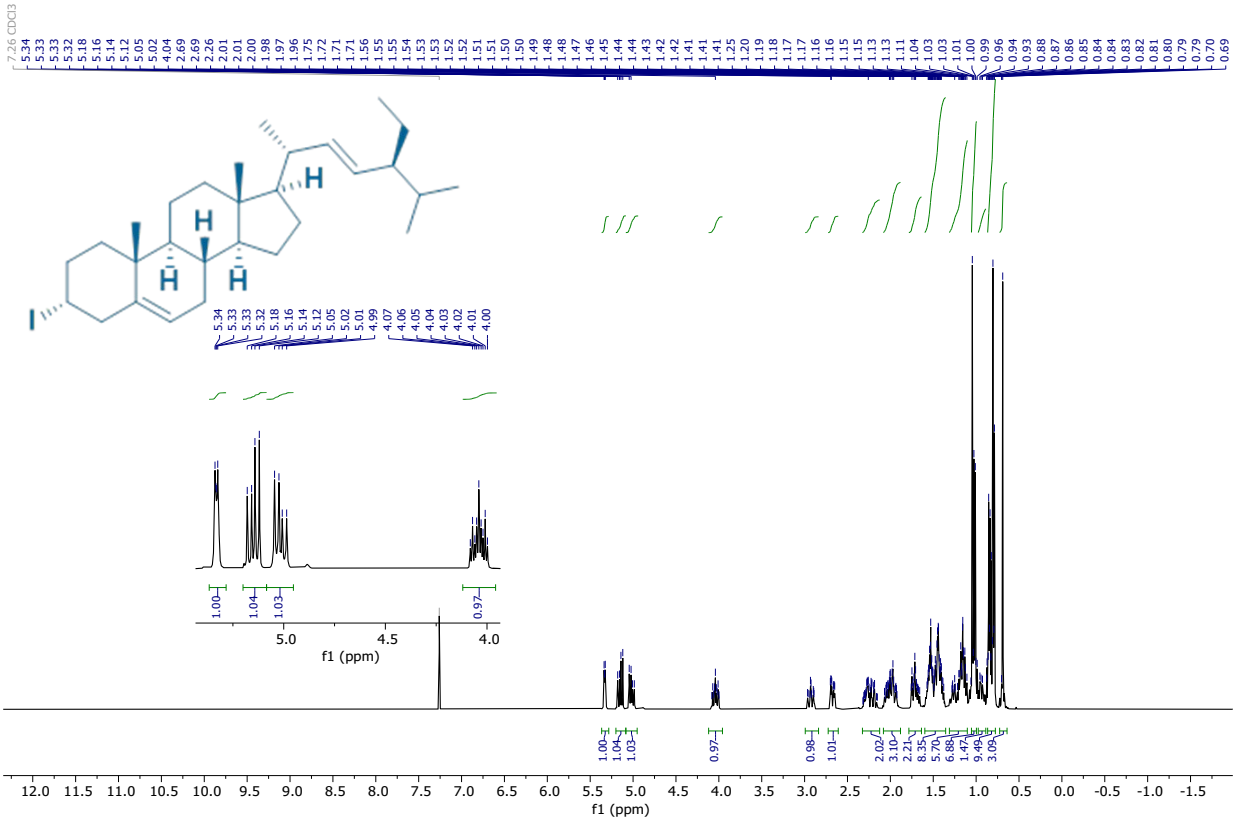

Figure S82 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **H**.

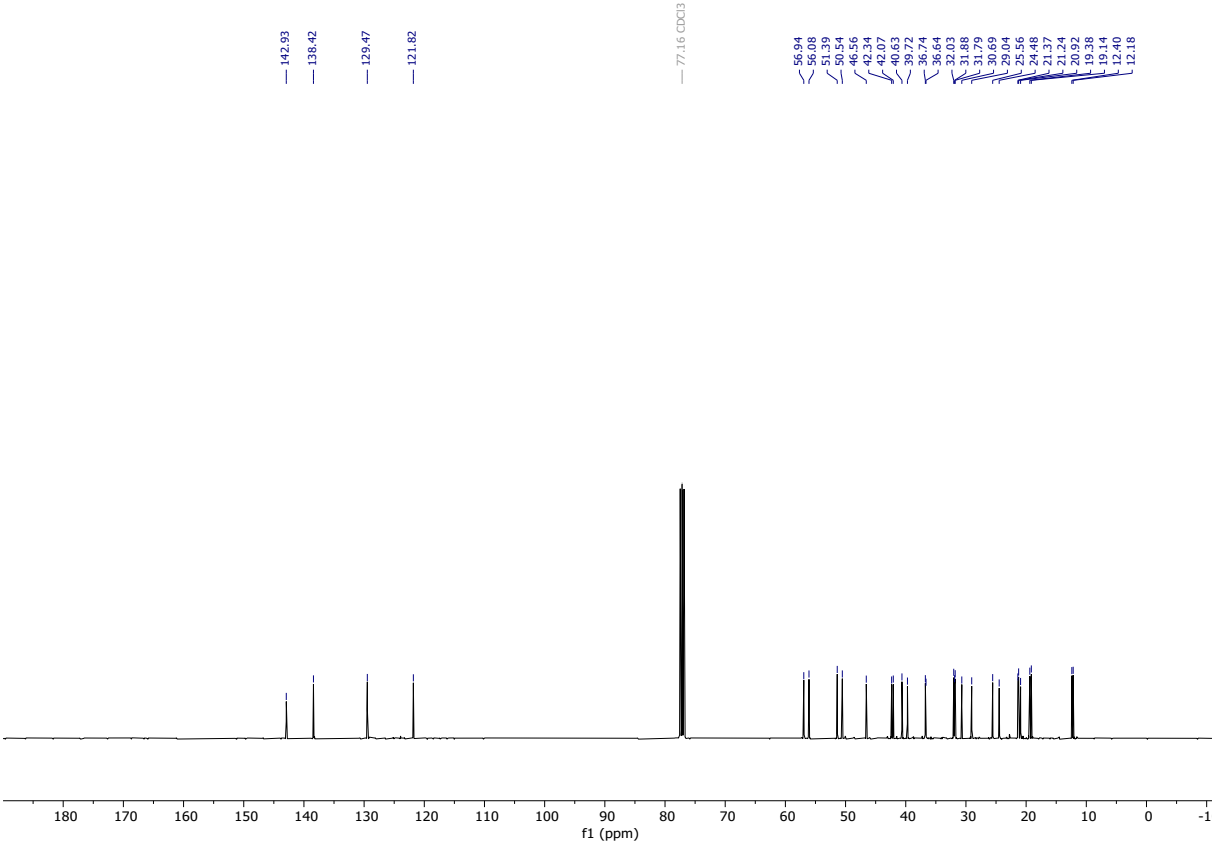

Figure S83 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **H**.

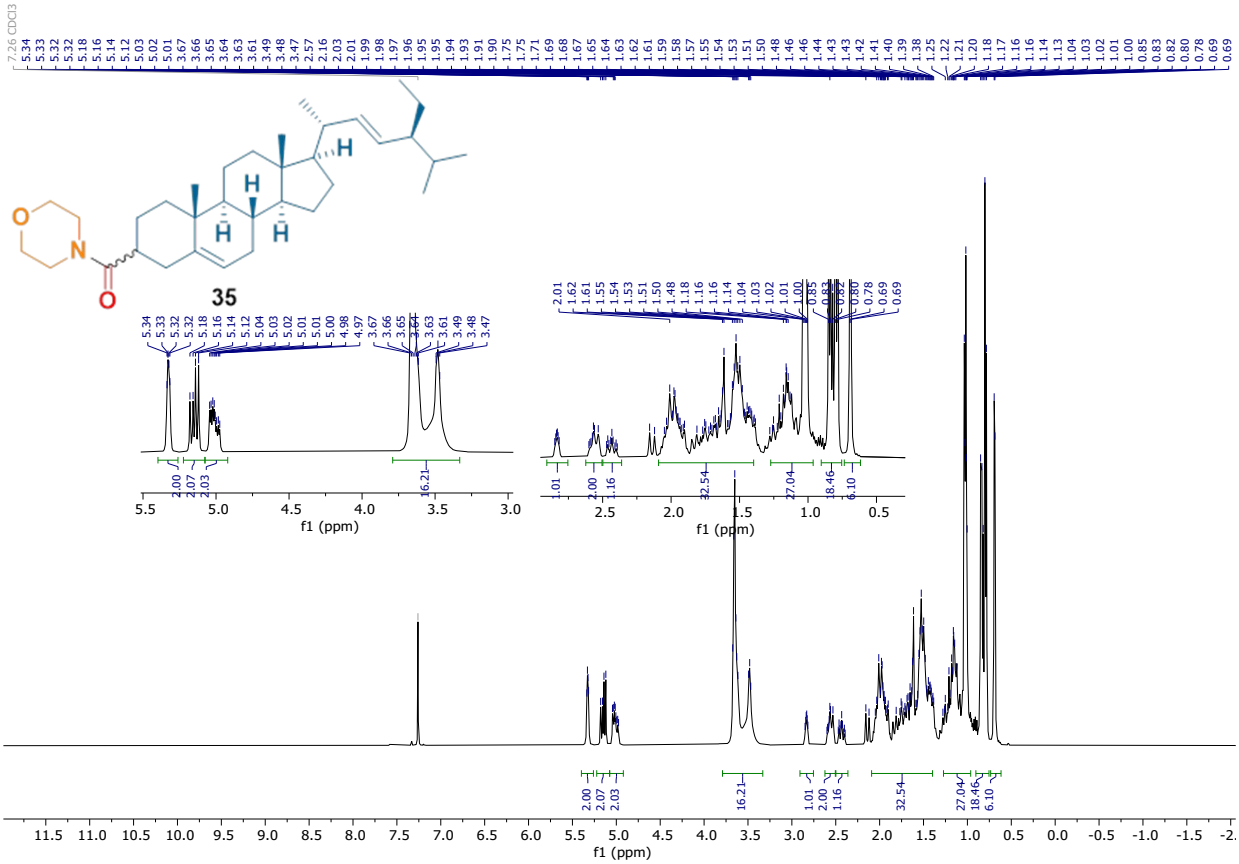

Figure S84 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **35**.

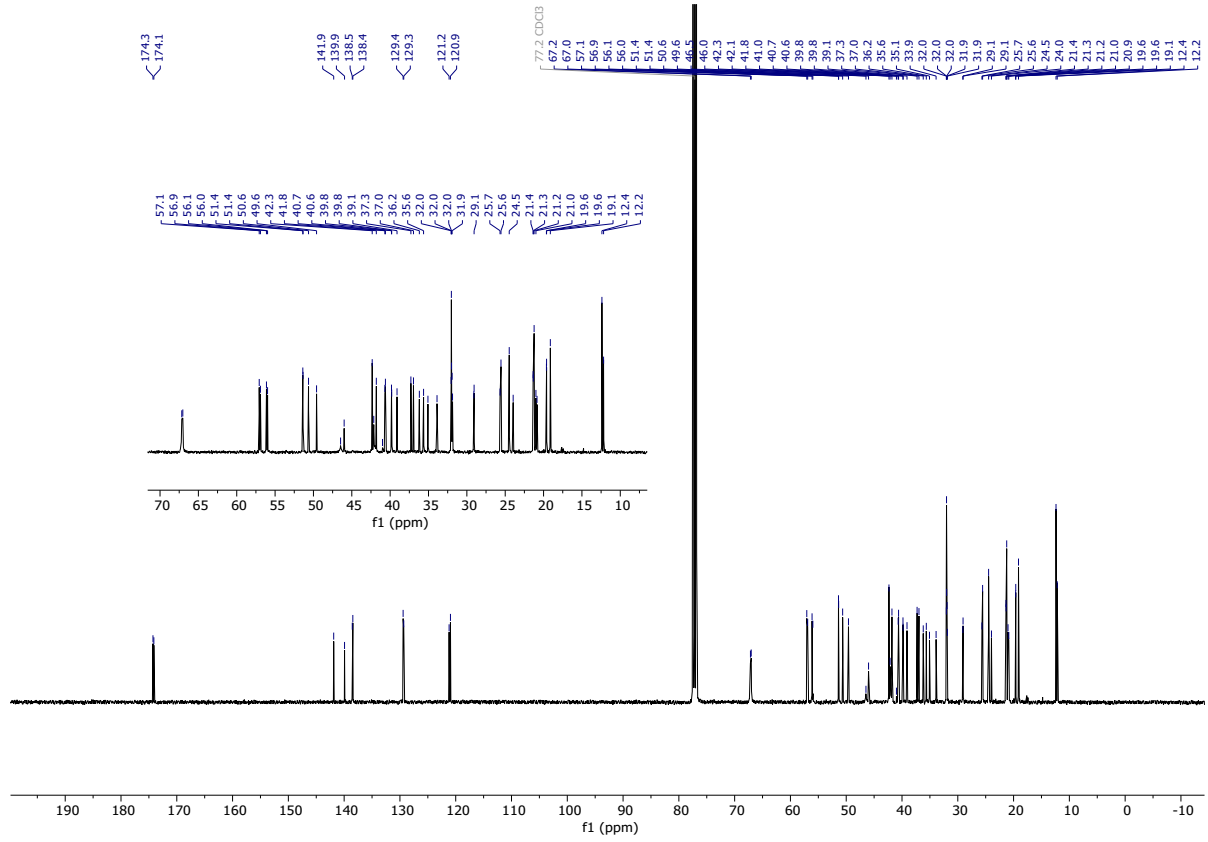

Figure S85 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **35**.

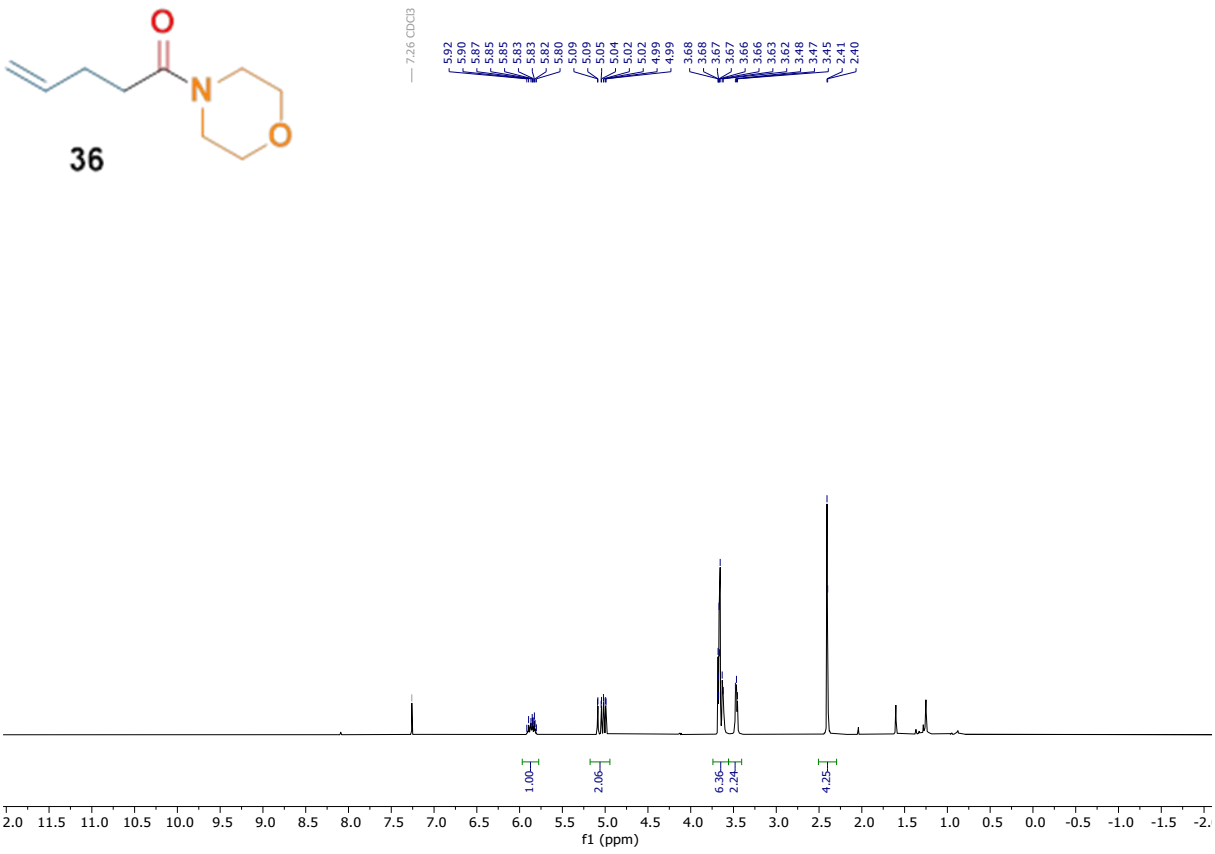

Figure S86 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **36**.

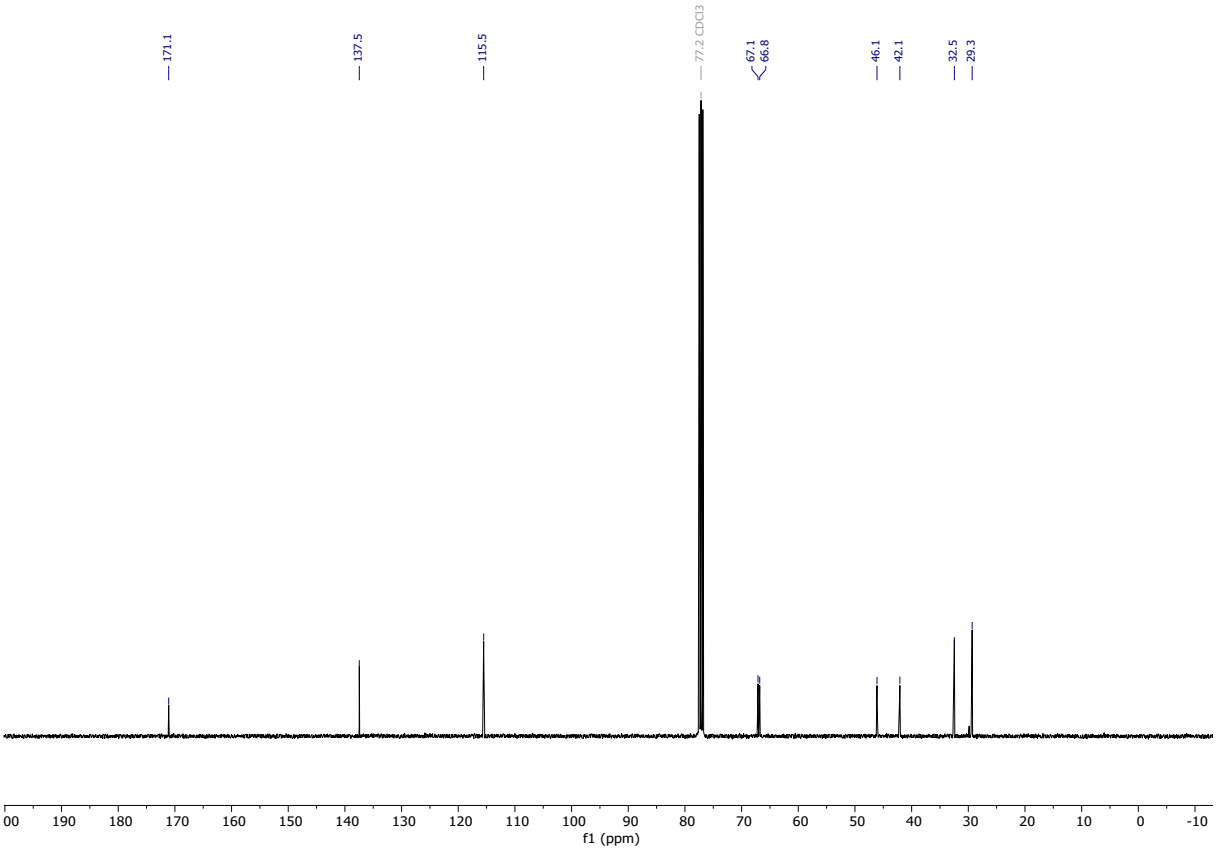

Figure S87 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **36**.

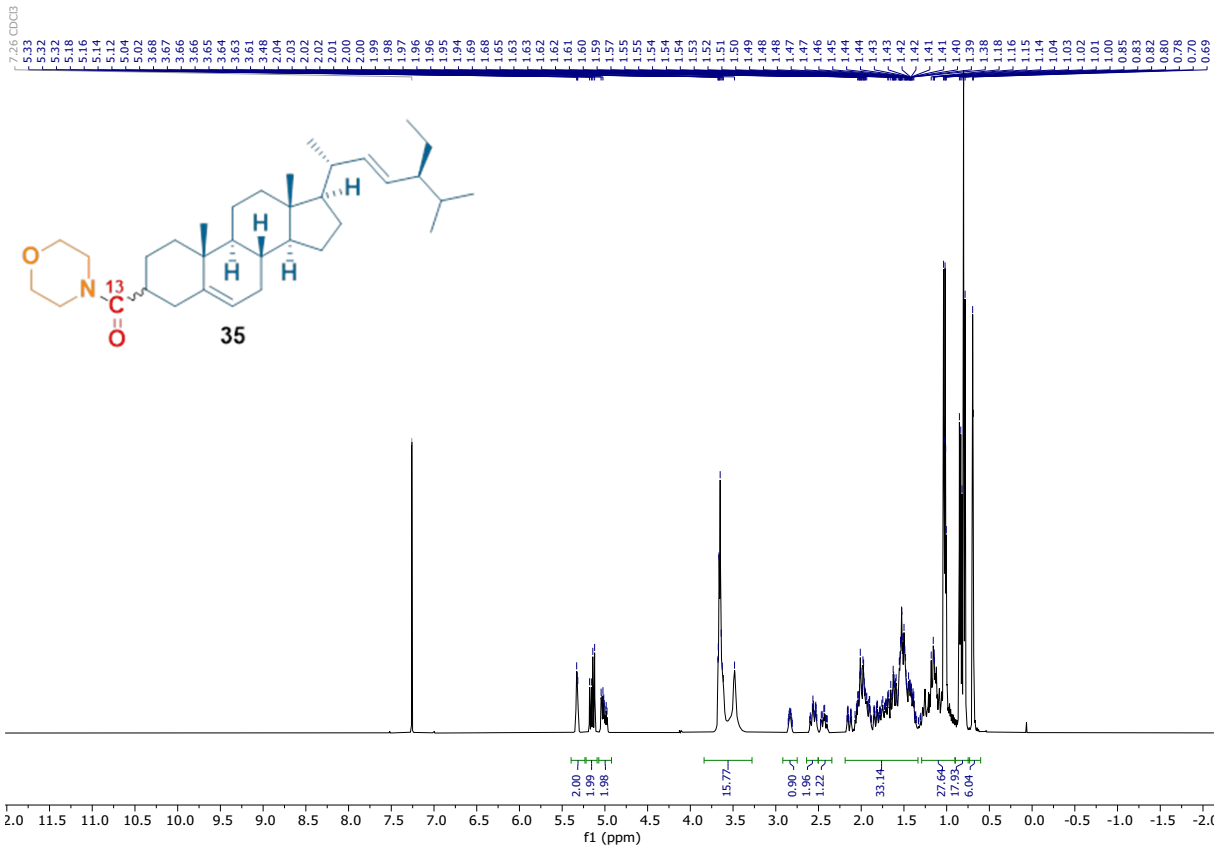

Figure S88 – ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **35** using ^{13}CO.

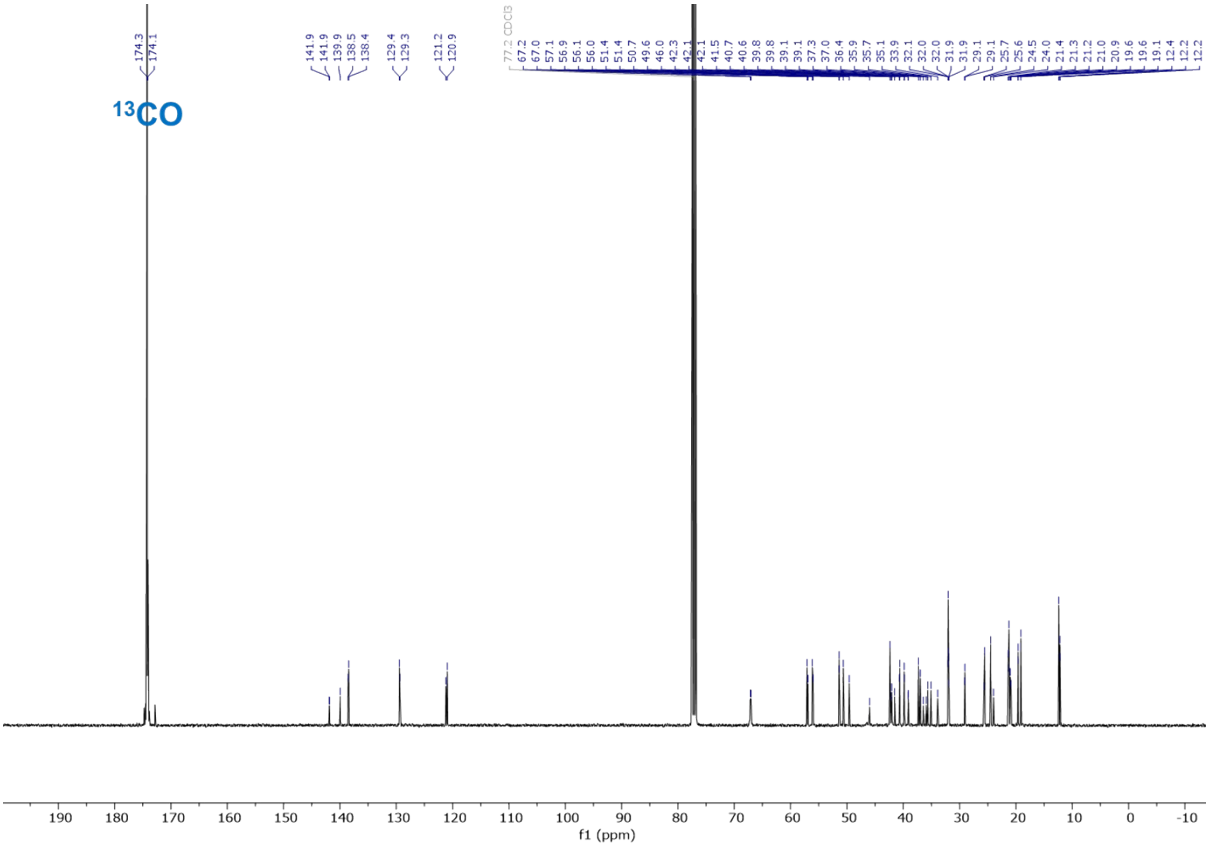

Figure S89 – ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **35** using ^{13}CO.

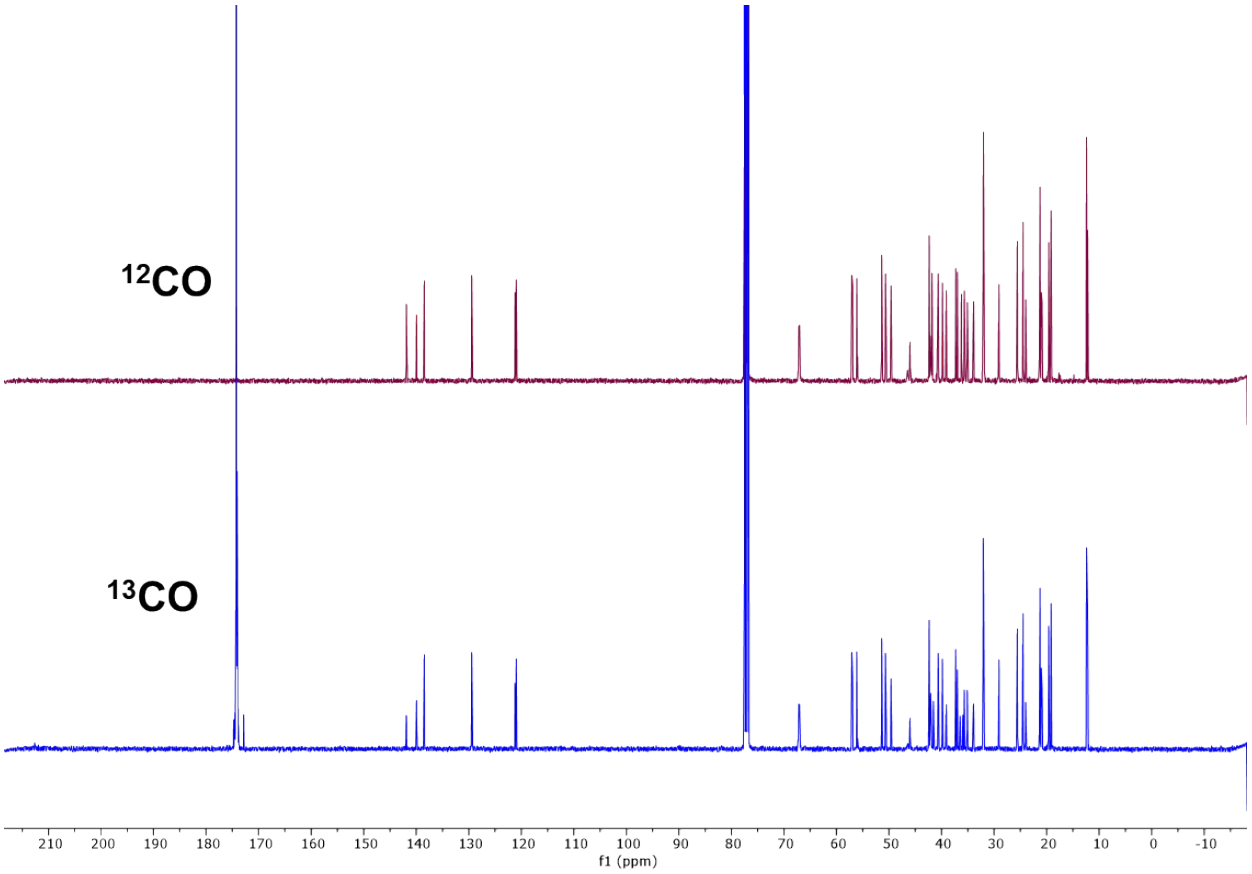

Figure S90 – ^{13}C and ^{12}C NMR (101 MHz, $CDCl_3$, 298 K) spectra of **35**.

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