

Supporting Information

A General Organocatalytic System for Electron Donor–Acceptor Complex Photoactivation and its Use in Radical Processes

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A. General Information

The NMR spectra were recorded at 400 MHz and 500 MHz for ^1H and 100 or 125 MHz for ^{13}C . The chemical shift (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvents (CHCl_3 @ 7.26 ppm ^1H NMR and 77.16 ppm ^{13}C NMR, and tetramethylsilane @ 0 ppm). Coupling constants are given in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; m, multiplet; bs, broad signal; app, apparent.

High resolution mass spectra (HRMS) were obtained from the ICIQ HRMS unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) with electrospray ionization. (ESI).

UV-vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with photomultiplier detector, double beam optics and D₂ and W light sources or an Agilent Cary60 spectrophotometer.

Emission spectra of light sources were recorded on Ocean Optics USB4000 fiber optic spectrometer.

Isolated yields refer to materials of >95% purity as determined by ^1H NMR.

The authors are indebted to the team of the Research Support Area at ICIQ, particularly to the NMR and the High-Resolution Mass Spectrometry Units. Grace Fox is thanked for proofreading the manuscript.

General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware. Synthesis grade solvents were used as purchased, anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using forced-flow chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) were employed, using UV light as the visualizing agent and an acidic mixture of vanillin or basic aqueous potassium permanganate (KMnO_4) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

Determination of Enantiomeric Purity. HPLC analysis on chiral stationary phase was performed on an Agilent 1200-series instrument, employing Daicel Chiralpak IC column.

Materials. Most of the starting materials used in this study are commercial and were purchased at the highest purity available from Sigma-Aldrich, Fluka, Alfa Aesar, Fluorochem, and used as received, without further purifications.

B: Substrate Syntheses

The following substrates were synthesized according to reported procedures (Figure S1).¹⁻¹⁴

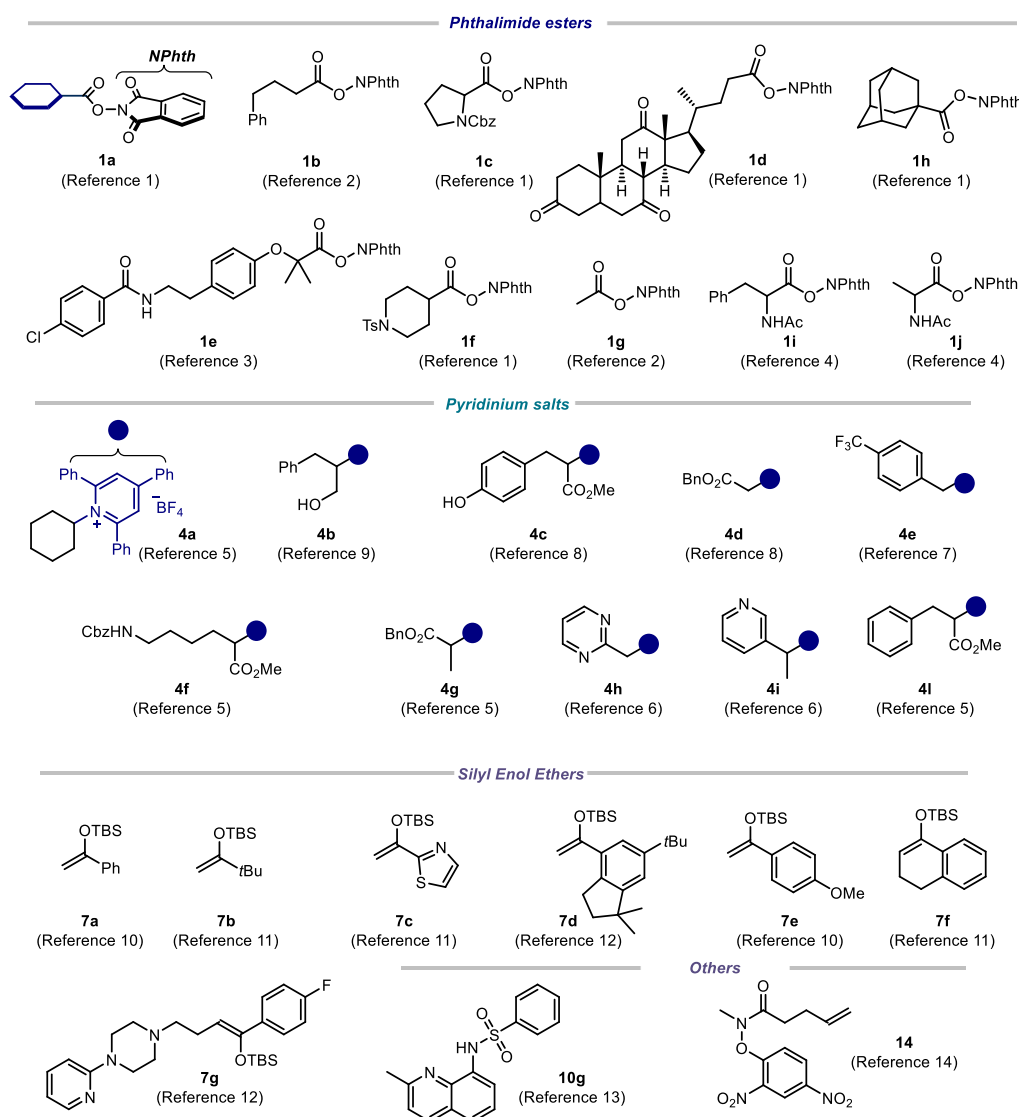


Figure S1: Starting materials synthesized according to known procedures.

C. Experimental Procedures

C1. Experimental Setup

- **Set-up 1** 3D printed reactor with LED strip

For reactions performed using a blue LED strip as the light source, a 3D-printed photoreactor was used, consisting of a 9 cm diameter crystallizing dish with a 3D printed support of 6 positions, and a hole of 22 mm in the middle to allow ventilation (Figure S2, left). A commercial 1-meter LED strip was wrapped around the crystallizing dish, while a fan was used to cool down the reactor (the reaction temperature was measured to be between 35-40 °C). Each of the positions could be used to fit a standard 16 mm diameter vial with a Teflon screw cap. Experiments at 465 nm were conducted using a 1m strip, 14.4W “LEDXON MODULAR 9009083 LED, SINGLE

5050” purchased from Farnell, catalog number 9009083. The emission spectrum of these LEDs is shown in Figure S2, right panel.

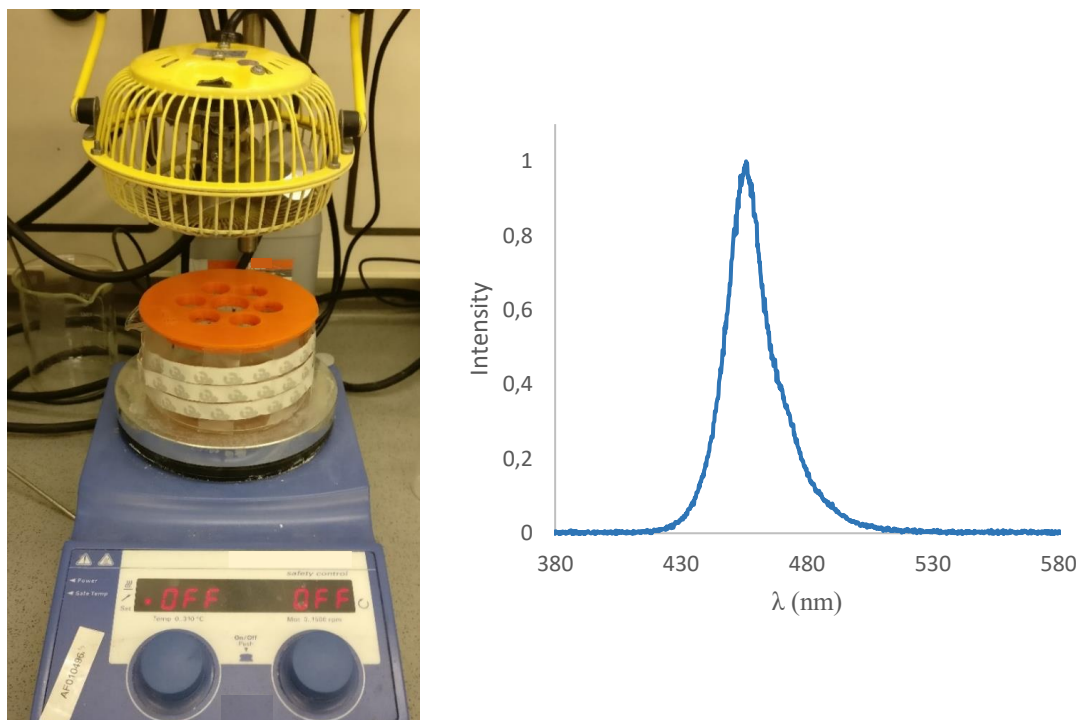


Figure S2: Blue LEDs photoreactor used for reactions where temperature control was not needed (*left*). Emission spectrum of the 465 nm LED strip used in this reactor (*right*).

- **Set-up 2** Kessil Lamp setup

For reactions performed with a Kessil lamp, the irradiation set-up consisted of a 50 W Kessil blue LED lamp (PR160L-456, 100% intensity, 2-3 cm away – Figure S3).

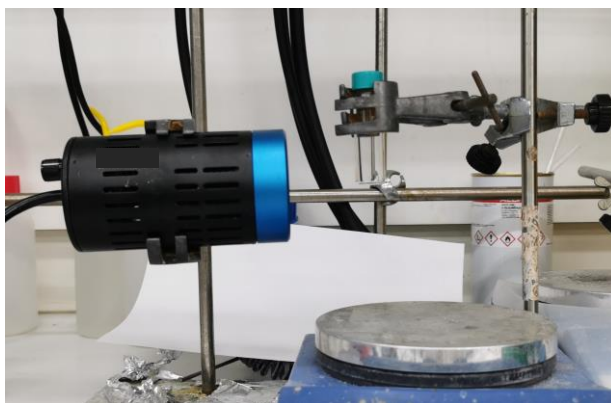


Figure S3: Kessil lamp set-up.

- **Set-up 3** Temperature-controlled 4-position reactor with LED strip

For reactions where temperature control was employed, the photoreactor consisted of a 12.5 cm diameter jar fitted with 4 standard B29 size quickfit-glass joints arranged around a central B29size

joint. A commercial 1-meter LED strip was wrapped around the jar, followed by a layer of aluminium foil and cotton for insulation (Figure S4).

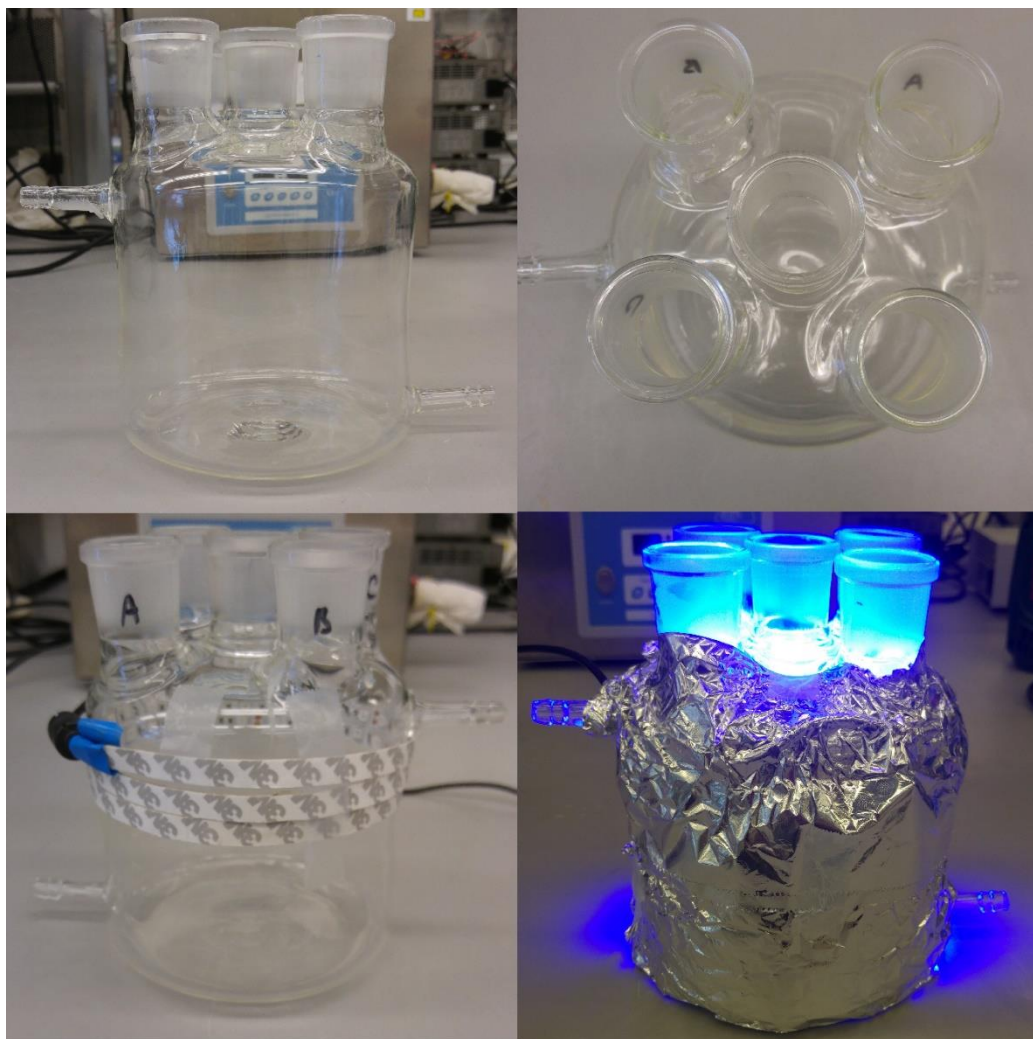


Figure S4: Photoreactor used for temperature-controlled reactions - pictures taken at different stages of the set-up assembly.

Each of the joints could be used to fit a standard 16 mm or 25 mm diameter Schlenk tube with a Teflon adaptor (Figure S5).



Figure S5: Teflon adaptors to use Schlenk tubes in the photoreactor.

An inlet/outlet system provided circulation of liquid (ethylene glycol/water mixture) from a Huber Minichiller 300 inside the jar. This setup allowed the performance of reactions at temperatures ranging from $-20\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$ with accurate control of the reaction temperature ($\pm 1^{\circ}\text{C}$, Figure S6).

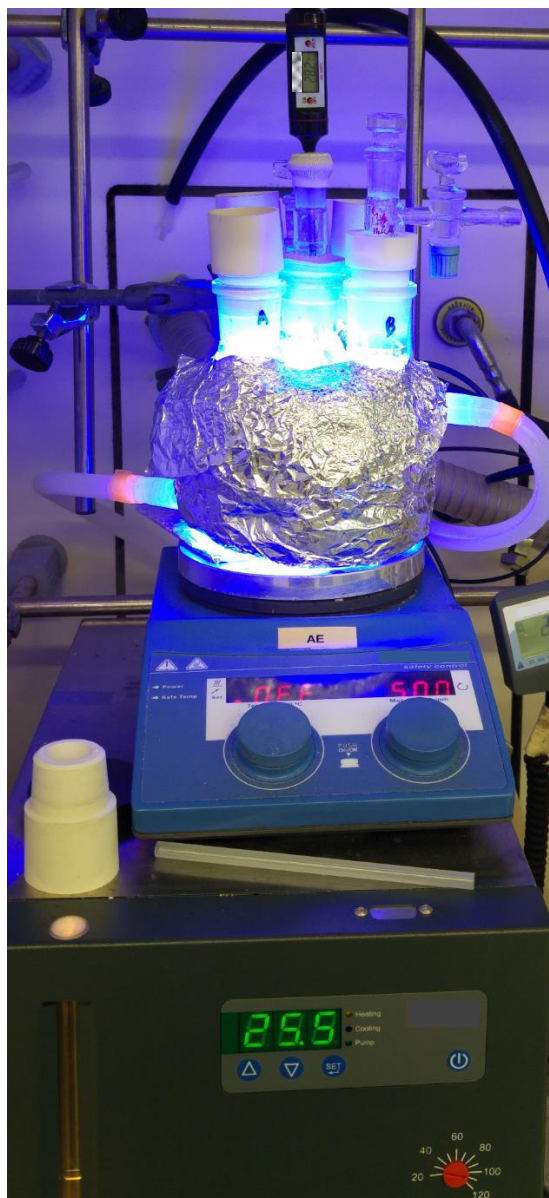


Figure S6: Fully assembled temperature-controlled photoreactor in operation.

In order to maintain consistent illumination between different experiments, only the four external positions were used to perform reactions. The central position was used to monitor the temperature using a thermometer inside another inserted Schlenk tube identical to those used to perform reactions, ensuring that the reaction mixtures were at the desired temperature.

Set-up 4 *Temperature controlled one-position reactor with LED strip*

Our photoreactor for the enantioselective version of the Minisci reaction consisted of a consisted of a 4 cm diameter jar fitted with a standard 29 sized ground glass joint. A commercial 1 meter LED strip was wrapped around the jar, followed by a layer of aluminium foil and cotton for insulation. An inlet and an outlet allow the circulation of liquid from a Huber Minichiller 300 inside the jar. This setup allows to perform reactions at temperatures ranging from -20 °C to 80 °C with accurate control of the reaction temperature (± 1 °C). An inlet and an outlet allow the circulation of liquid from a Huber Minichiller 300 inside the jar. This setup allows to perform reactions at temperatures ranging from -20 °C to 80 °C with accurate control of the reaction temperature (± 1 °C, Figure S5).

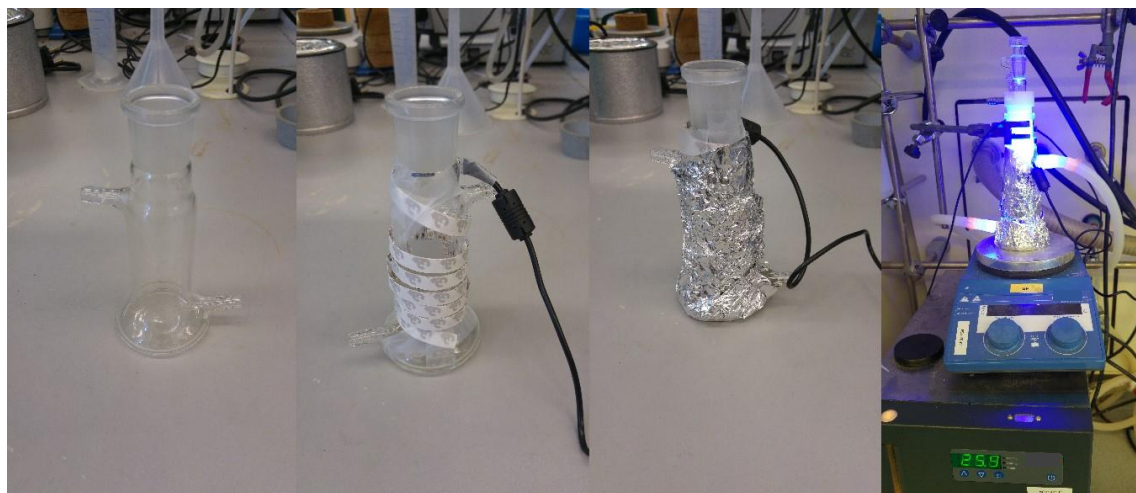
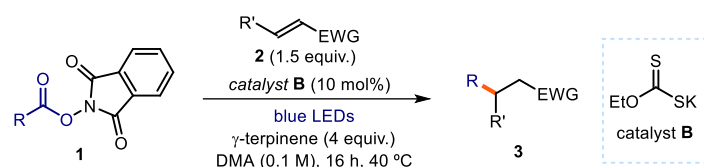


Figure S7: Fully assembled controlled temperature photoreactor in operation for enantioselective Minisci reaction.

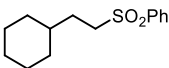
C2. Giese Addition

C2.1 General Procedure A



Reactions performed using *set-up 1* in Figure S2. In an oven dried vial with a Teflon septum screw cap, potassium ethyl xanthogenate **B** (3.2 mg, 0.02 mmol, 0.1 equiv.), *N*-hydroxyphthalimide ester **1** (0.2 mmol, 1 equiv.) and the electron-poor olefin **2** (0.3 mmol, 1.5 equiv., *if solid*), were dissolved in DMA (2 mL, synthesis grade solvent). Then, γ -terpinene (128 μ L, 0.8 mmol, 4 equiv.) was added. The resulting orange mixture was degassed with argon sparging for 60 seconds. If the electron-poor olefin **2** was *liquid*, it was added via syringe after the argon sparging. The vial was then placed in the 3D printed support photoreactor (Figure S2) and irradiated under stirring for 16 hours, unless otherwise specified. The mixture was transferred to an extraction funnel, NaOH 1M solution was added, and the organic layer was extracted with DCM. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous MgSO_4 , filtered, and concentrated to dryness. The crude residue was purified by column chromatography to afford the corresponding product **3** in the stated yield with >95% purity according to ^1H NMR analysis.

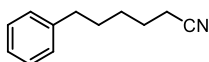
C2.2 Characterization of Products with General Procedure A

 **2-cyclohexylethyl)sulfonyl)benzene (3a):** Synthesized according to General Procedure A using 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (54.5 mg, 0.2 mmol, 1 equiv.) and phenyl vinyl sulfone **2a** (50.4 mg, 0.3 mmol, 1.5 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford **3a** (43.5 mg, 86% yield) as a white solid.

^1H NMR (500 MHz, CDCl_3) δ 7.94 – 7.85 (m, 2H), 7.69 – 7.61 (m, 1H), 7.61 – 7.52 (m, 2H), 3.13 – 3.05 (m, 2H), 1.71 – 1.54 (m, 7H), 1.28 (ddt, J = 14.6, 7.5, 3.8 Hz, 1H), 1.23 – 1.06 (m, 3H), 0.92 – 0.76 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 139.4, 133.7, 129.4, 128.2, 54.5, 36.8, 32.9, 29.7, 26.4, 26.1.

Matching reported literature data.¹⁵

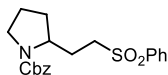


6-phenylhexanenitrile (3b): Synthesized according to General Procedure A using 5 equiv. of γ -terpinene, 1,3-dioxoisindolin-2-yl 4-phenylbutanoate **1b** (62 mg, 0.2 mmol, 1 equiv.) and acrylonitrile **2b** (26.3 μ L, 0.4 mmol, 2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford **3b** (21 mg, 61% yield) as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 2.64 (t, J = 7.6 Hz, 2H), 2.33 (t, J = 7.1 Hz, 2H), 1.75 – 1.62 (m, 4H), 1.54 – 1.42 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 142.1, 128.5, 128.5, 126.0, 119.9, 35.7, 30.7, 28.4, 25.4, 17.2.

Matching reported literature data.¹⁶

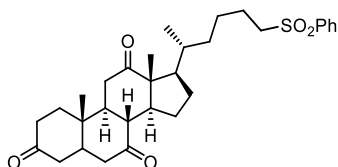


Benzyl 2-(2-(phenylsulfonyl)ethyl)pyrrolidine-1-carboxylate (3h): Synthesized according to General Procedure A using 1-benzyl 2-(1,3-dioxoisindolin-2-yl) pyrrolidine-1,2-dicarboxylate **1c** (54.5 mg, 0.2 mmol, 1 equiv.) and phenyl vinyl sulfone **2a** (50.4 mg, 0.3 mmol, 1.5 equiv.). The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **3h** (56 mg, 75% yield) as a white solid.

^1H NMR (400 MHz, CDCl_3) mixture of rotamers: δ 7.96 – 7.77 (m, 2H), 7.68 – 7.60 (m, 1H), 7.54 (d, J = 7.5 Hz, 2H), 7.40 – 7.20 (m, 5H), 5.05 (d, J = 7.6 Hz, 2H), 3.94 (d, J = 9.9 Hz, 1H), 3.58 – 3.28 (m, 2H), 3.27 – 2.91 (m, 2H), 2.23 – 1.74 (m, 5H), 1.63 (ddd, J = 11.3, 5.5, 3.0 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) mixture of rotamers: δ 155.5, 139.3, 136.9, 133.8, 129.4, 128.6, 128.1, 127.9, 67.2, 66.9, 56.5, 55.9, 54.0, 53.7, 46.9, 46.5, 31.2, 30.7, 27.9, 23.8, 23.1.

Matching reported literature data.¹⁷



(5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-(6-(phenylsulfonyl)hexan-2-yl)dodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (3k):

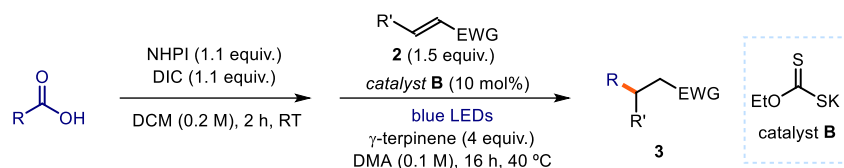
Synthesized according to General Procedure A using 1,3-dioxoisindolin-2-yl 4-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate **1d** (54.5 mg, 0.2 mmol, 1 equiv.) and phenyl vinyl sulfone **2a** (50.4 mg, 0.3 mmol, 1.5 equiv.). The crude mixture was purified by flash column chromatography on silica gel (50% AcOEt in hexanes as eluent) to afford **3k** (48.0 mg, 46% yield) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 7.95 – 7.85 (m, 2H), 7.70 – 7.61 (m, 1H), 7.61 – 7.53 (m, 2H), 3.16 – 3.00 (m, 2H), 2.95 – 2.78 (m, 3H), 2.38 – 2.17 (m, 6H), 2.16 – 2.06 (m, 2H), 2.02 – 1.90 (m, 4H), 1.88 – 1.52 (m, 5H), 1.47 – 1.30 (m, 1H), 1.39 (s, 3H), 1.32 – 1.12 (m, 5H), 1.04 (s, 3H), 0.78 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 212.1, 209.1, 208.9, 139.4, 133.8, 129.4, 128.2, 57.0, 56.5, 51.9, 49.1, 47.0, 45.8, 45.7, 45.1, 42.9, 38.8, 36.6, 36.2, 35.9, 35.4, 34.9, 28.0, 25.4, 25.3, 23.1, 22.0, 19.0, 12.0.

Matching reported literature data.¹⁵

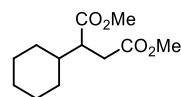
C2.3 General Procedure B (*one-pot telescoped from carboxylic acids*)



Reactions performed using *set-up 1* in Figure S2. In an oven dried vial with a Teflon septum screw cap, carboxylic acid (0.2 mmol, 1 equiv.) and *N*-hydroxyphthalimide (NHPI, 35.8 mg, 0.22 mmol, 1.1 equiv.) were dissolved in CH₂Cl₂ (1 mL, HPLC grade) and *N,N'*-diisopropylcarbodiimide (DIC, 34 μ L, 0.22 mmol, 1.1 equiv.) was added via syringe. The reaction was stirred at ambient temperature until complete consumption of the carboxylic acid was observed by TLC (usually 1-2 hours). The crude reaction mixture was concentrated under vacuum to obtain the crude phthalimide ester, which was used without further purification in the next step.

In the same vial containing the crude phthalimide ester, xanthogenate **B** (3.2 mg, 0.02 mmol, 0.1 equiv.) and the electron-poor olefin **2** (0.3 mmol, 1.5 equiv., *if solid*) were dissolved in DMA (2 mL, synthesis grade). Next, γ -terpinene (128 μ L, 0.8 mmol, 4 equiv.) was added and the resulting orange mixture was degassed with argon sparging for 60 seconds. If the electron-poor olefin **2** was *liquid*, it was added via syringe after the argon sparging. The vial was then placed in the 3D printed support photoreactor (Figure S2) and irradiated under stirring for 16 hours, if not otherwise specified. The mixture was transferred to an extraction funnel, NaOH 1M solution was added and the organic layer was extracted with CH₂Cl₂. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated to dryness. The crude residue was purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C2.4 Characterization of Products with General Procedure B

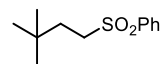


dimethyl 2-cyclohexylsuccinate (3c): Synthesized according to General Procedure B using 2 equiv. of γ -terpinene, 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (54.5 mg, 0.2 mmol, 1 equiv.) and dimethyl fumarate **2c** (43 mg, 0.3 mmol, 1.5 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford **3c** (44 mg, 95% yield) as a yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 3.69 (s, 3H), 3.66 (s, 3H), 2.78 – 2.66 (m, 2H), 2.45 (dt, *J* = 13.1, 8.9 Hz, 1H), 1.78 – 1.69 (m, 2H), 1.69 – 1.52 (m, 4H), 1.31 – 1.15 (m, 2H), 1.15 – 1.07 (m, 1H), 1.06 – 0.92 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 175.1, 173.1, 51.9, 51.7, 47.2, 40.1, 33.4, 30.8, 30.3, 26.4, 26.3.

Matching reported literature data.¹⁵

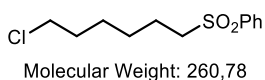


((3,3-dimethylbutyl)sulfonyl)benzene (3d): Synthesized according to General Procedure B using pivalic acid (20.4 mg, 0.2 mmol, 1 equiv.) and phenyl vinyl sulfone **2a** (50.4 mg, 0.3 mmol, 1.5 equiv.). The crude mixture was purified by flash column chromatography on silica gel (7% AcOEt in hexanes as eluent) to afford **3d** (33.0 mg, 73% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.85 (m, 2H), 7.71 – 7.62 (m, 1H), 7.65 – 7.53 (m, 2H), 3.10 – 3.01 (m, 2H), 1.64 – 1.55 (m, 2H), 0.86 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 142.1, 128.5, 128.5, 126.0, 119.9, 35.7, 30.7, 28.4, 25.4, 17.2.

Matching reported literature data.¹⁵



((7-chloroheptyl)sulfonyl)benzene (3e): Synthesized according to General Procedure B using 5-Chlorovaleric acid (27.3 mg, 0.2 mmol, 1.0 equiv.) and (vinylsulfonyl)benzene (50.5 mg, 0.3 mmol, 1.5 equiv.).

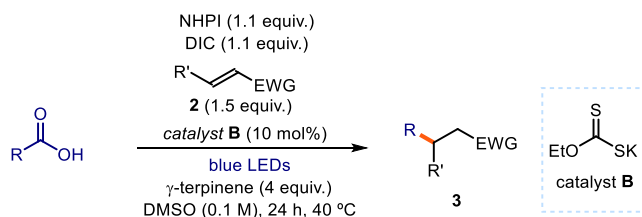
The crude mixture was purified by flash column chromatography on silica gel (20% DCM in hexanes) to afford **3e** (29.1 mg, 56% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.88 (m, 2H), 7.69 – 7.64 (m, 1H), 7.61 – 7.55 (m, 2H), 3.50 (t, *J* = 6.5 Hz, 2H), 3.12 – 3.05 (m, 2H), 1.77 – 1.71 (m, 4H), 1.44 – 1.39 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 139.3, 133.8, 129.4, 128.2, 56.3, 44.9, 32.2, 29.8, 27.7, 26.4, 22.7.

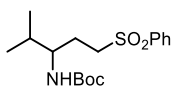
Matching reported literature data.¹⁸

C2.5 General Procedure C (*one-pot domino from carboxylic acids*)



Reactions performed using *set-up 1* in Figure S2. In an oven dried vial with a Teflon septum screw cap, carboxylic acid (0.2 mmol, 1 equiv.), *N*-hydroxyphthalimide (NHPI, 35.8 mg, 0.22 mmol, 1.1 equiv.), xanthogenate catalyst **B** (3.2 mg, 0.02 mmol, 0.1 equiv.), and the electron-poor olefin **2** (0.3 mmol, 1.5 equiv., *if solid*) were dissolved in DMSO (2 mL) and *N,N'*-diisopropylcarbodiimide (DIC, 34 μL, 0.22 mmol, 1.1 equiv.) was added via syringe. Next, γ -terpinene (128 μL, 0.8 mmol, 4 equiv.) was added and the resulting orange mixture was degassed with argon sparging for 60 seconds. If the electron-poor olefin **2** were *liquid*, it was added via syringe after the argon sparging. The vial was then placed in the 3D printed support photoreactor (Figure S2) and irradiated under stirring for 24 hours, unless otherwise specified. The mixture was transferred to an extraction funnel, NaOH 1M solution was added and the organic layer was extracted with CH₂Cl₂. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated to dryness. The crude residue was purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C2.6 Characterization of Products with General Procedure C

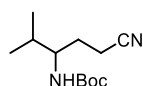


tert-butyl (4-methyl-1-(phenylsulfonyl)pentan-3-yl)carbamate (3f): Synthesized according to General Procedure C using NMP as solvent, L-valine (43.5 mg, 0.2 mmol, 1 equiv.) and phenyl vinyl sulfone **2a** (50.4 mg, 0.3 mmol, 1.5 equiv.). The crude mixture was purified by flash column chromatography on silica gel (25% AcOEt in hexanes as eluent) to afford **3f** (63 mg, 92% yield) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 7.93 – 7.88 (m, 2H), 7.69 – 7.63 (m, 1H), 7.57 (dd, *J* = 8.4, 7.1 Hz, 2H), 4.32 (d, *J* = 10.1 Hz, 1H), 3.42 (td, *J* = 10.4, 4.8 Hz, 1H), 3.15 (ddd, *J* = 9.1, 6.1, 1.7 Hz, 2H), 1.93 (tdd, *J* = 12.1, 7.4, 3.4 Hz, 1H), 1.82 – 1.61 (m, 2H), 1.40 (s, 9H), 0.87 (dd, *J* = 10.0, 6.8 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 156.1, 139.4, 133.9, 129.5, 128.1, 79.7, 54.7, 54.1, 32.8, 28.5, 25.9, 19.2, 17.8.

Matching reported literature data.¹⁹

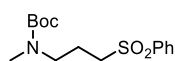


tert-butyl (1-cyano-4-methylpentan-3-yl)carbamate (3g): Synthesized according to General Procedure C using 5 equiv. of γ -terpinene, L-valine (43.5 mg, 0.2 mmol, 1 equiv.) and acrylonitrile **2b** (26.3 μ L, 0.4 mmol, 2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **3g** (27 mg, 60% yield) as a yellow oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.34 (d, J = 9.9 Hz, 1H), 3.45 (tdd, J = 10.4, 5.5, 3.4 Hz, 1H), 2.49 – 2.30 (m, 2H), 1.90 (td, J = 11.7, 9.8, 5.5 Hz, 1H), 1.72 (dt, J = 13.0, 6.5 Hz, 1H), 1.62 (td, J = 15.0, 14.5, 9.7 Hz, 1H), 1.44 (s, 9H), 0.91 (dd, J = 10.4, 6.8 Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.1, 119.9, 79.7, 55.4, 32.5, 29.4, 28.5, 19.2, 17.9, 14.7.

Matching reported literature data.¹⁹

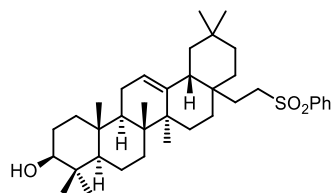


tert-butyl methyl(3-(phenylsulfonyl)propyl)carbamate (3i): Synthesized according to General Procedure C using *N*-(tert-butoxycarbonyl)-*N*-methylglycine (38 mg, 0.2 mmol, 1 equiv.) and phenyl vinyl sulfone **2a** (50.4 mg, 0.3 mmol, 1.5 equiv.). The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **3i** (47 mg, 75% yield) as a yellow oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) mixture of rotamers: δ 7.94 – 7.86 (m, 2H), 7.70 – 7.62 (m, 1H), 7.57 (dd, J = 8.3, 6.8 Hz, 2H), 3.29 (t, J = 6.8 Hz, 2H), 3.11 – 2.99 (m, 2H), 2.79 (s, 3H), 1.99 – 1.87 (m, 2H), 1.40 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) mixture of rotamers: δ 155.9, 139.2, 133.9, 129.5, 128.1, 79.9, 53.9, 47.4, 34.3, 28.5, 21.0.

HRMS: calculated for $\text{C}_{15}\text{H}_{23}\text{NNaO}_4\text{S}$ ($\text{M}+\text{Na}^+$): 336.1240, found 336.1236 (+1.2 ppm).

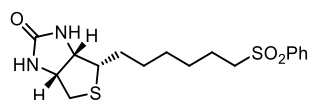


(3S,4aR,6aR,6bS,12aR,14aR,14bR)-4,4,6a,6b,11,11,14b-heptamethyl-8a-(2-(phenylsulfonyl)ethyl)-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydricen-3-ol (3j): Synthesized according to General Procedure C using NMP as solvent, oleanolic acid (91 mg, 0.2 mmol, 1 equiv) and phenyl vinyl sulfone **2a** (50.4 mg, 0.3 mmol, 1.5 equiv.). The crude mixture was purified by flash column chromatography on silica gel (40% AcOEt in hexanes as eluent) to afford **3j** (84 mg, 72% yield) as light-yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90 – 7.84 (m, 2H), 7.67 – 7.59 (m, 1H), 7.58 – 7.50 (m, 2H), 5.15 (t, J = 3.6 Hz, 1H), 3.19 (dd, J = 10.7, 4.8 Hz, 1H), 3.01 (dtd, J = 37.9, 13.5, 4.3 Hz, 2H), 2.01 – 1.76 (m, 7H), 1.66 (t, J = 13.5 Hz, 1H), 1.62 – 1.36 (m, 7H), 1.37 – 1.26 (m, 3H), 1.23 – 1.11 (m, 4H), 1.09 (s, 3H), 1.02 (dd, J = 13.7, 2.1 Hz, 1H), 0.97 (s, 3H), 0.94 – 0.90 (m, 1H), 0.88 (s, 3H), 0.85 (s, 3H), 0.82 (s, 3H), 0.77 (s, 3H), 0.68 (dd, J = 11.5, 1.9 Hz, 1H), 0.60 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.6, 139.3, 133.6, 129.4, 128.1, 123.1, 79.0, 55.2, 51.6, 47.6, 46.9, 46.5, 41.6, 39.7, 38.9, 38.7, 37.0, 34.7, 34.3, 33.2, 32.9, 32.5, 31.9, 31.0, 29.8, 28.2, 27.3, 26.1, 25.5, 23.6, 23.3, 18.4, 16.5, 15.7, 15.6.

Matching reported literature data.¹⁵



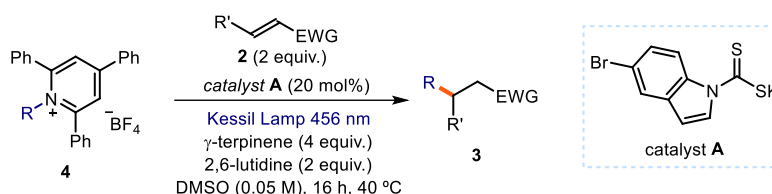
(3aS,4S,6aR)-4-(6-(phenylsulfonyl)hexyl)tetrahydro-1H-thieno[3,4-d]imidazol-2(3H)-one (3l): Synthesized according to General Procedure C using 4 mL of DMSO, biotin (49 mg, 0.2 mmol, 1 equiv.) and phenyl vinyl sulfone **2a** (50.4 mg, 0.3 mmol, 1.5 equiv.). The crude mixture was purified by flash column chromatography on silica gel (2-5% MeOH in DCM as eluent) to afford **3l** (48 mg, 65% yield) as a yellow oil.

¹H NMR (500 MHz, Methanol-*d*₄) δ 7.99 – 7.89 (m, 2H), 7.77 – 7.70 (m, 1H), 7.72 – 7.58 (m, 2H), 4.53 – 4.46 (m, 1H), 4.29 (ddd, *J* = 12.2, 7.9, 4.5 Hz, 1H), 3.24 – 3.19 (m, 2H), 3.19 – 3.14 (m, 1H), 2.92 (dt, *J* = 12.7, 5.1 Hz, 1H), 2.70 (dd, *J* = 12.7, 4.4 Hz, 1H), 1.66 (tdd, *J* = 15.3, 8.3, 4.4 Hz, 3H), 1.53 (ddd, *J* = 16.8, 8.8, 5.5 Hz, 1H), 1.45 – 1.27 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 164.5, 139.2, 133.8, 129.4, 128.1, 62.4, 60.8, 56.1, 55.8, 40.6, 31.4, 31.0, 28.8, 28.7, 28.4, 27.9, 22.7, 22.5, 14.1.

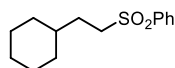
HRMS: calculated for C₁₇H₂₄N₂NaO₃S₂ (M+Na⁺): 391.1120, found 391.1121 (–0.3 ppm).

C2.7 General Procedure D (using pyridinium salts)



Reactions performed using *set-up 2* in Figure S3. In an oven dried vial, with a Teflon septum screw cap, dithiocarbamate **A** (12.4 mg, 0.04 mmol, 0.2 equiv.), pyridinium salt **4** (0.2 mmol, 1 equiv.) and the electron-poor olefin **2** (0.4 mmol, 2 equiv.), were dissolved in DMSO (4 mL). Then, γ-terpinene (128 μL, 0.8 mmol, 4 equiv.) and 2,6-lutidine (46 μL, 0.4 mmol, 2 equiv.) were added. The resulting orange mixture was degassed with argon sparging for 60 seconds. The vial was then placed at 2-3 cm of a 50 W Kessil blue LED lamp and irradiated under stirring for 16 hours (see Figure S3). The mixture was transferred to an extraction funnel, NaHCO₃ sat. solution was added and the organic layer was extracted with EtOAc. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated to dryness. The crude residue was purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C2.8 Characterization of Products with General Procedure D

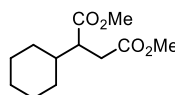


((2-cyclohexylethyl)sulfonyl)benzene (3a): Synthesized according to General Procedure D using 1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4a** (95 mg, 0.2 mmol, 1 equiv.) and phenyl vinyl sulfone **2a** (67 mg, 0.4 mmol, 2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **3a** (34 mg, 67% yield) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 7.94 – 7.85 (m, 2H), 7.69 – 7.61 (m, 1H), 7.61 – 7.52 (m, 2H), 3.13 – 3.05 (m, 2H), 1.71 – 1.54 (m, 7H), 1.28 (ddt, *J* = 14.6, 7.5, 3.8 Hz, 1H), 1.23 – 1.06 (m, 3H), 0.92 – 0.76 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 139.4, 133.7, 129.4, 128.2, 54.5, 36.8, 32.9, 29.7, 26.4, 26.1.

Matching reported literature data.¹⁵

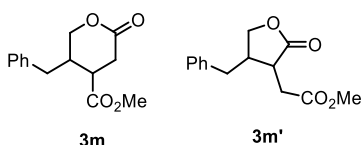


dimethyl 2-cyclohexylsuccinate (3c): Synthesized according to General Procedure D using 2 equiv. of γ-terpinene, 1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4a** (95 mg, 0.2 mmol, 1 equiv.) and dimethyl fumarate **2c** (57 mg, 0.4 mmol, 2 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford **3c** (41 mg, 90% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 3.69 (s, 3H), 3.66 (s, 3H), 2.78 – 2.66 (m, 2H), 2.45 (dt, *J* = 13.1, 8.9 Hz, 1H), 1.78 – 1.69 (m, 2H), 1.69 – 1.52 (m, 4H), 1.31 – 1.15 (m, 2H), 1.15 – 1.07 (m, 1H), 1.06 – 0.92 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 175.1, 173.1, 51.9, 51.7, 47.2, 40.1, 33.4, 30.8, 30.3, 26.4, 26.3.

Matching reported literature data.¹⁵



methyl 5-benzyl-2-oxotetrahydro-2H-pyran-4-carboxylate (3m): Synthesized according to General Procedure D using 2 equiv. of γ -terpinene, 1-(1-hydroxy-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4b** (106 mg, 0.2 mmol, 1 equiv.) and dimethyl fumarate **2c** (57 mg, 0.4 mmol, 2 equiv.).

The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford an unseparable mixture of regioisomers **3m/3m'** (3.8:1) (27 mg, 54% yield) as a yellow oil. Corrected yield for **3m** (42% yield)

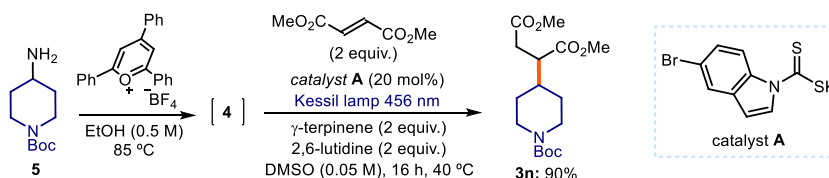
Products formed upon intramolecular esterification promoted by the acidic conditions delivered by the silica used for purification.

$^1\text{H NMR}$ (400 MHz, CDCl_3) mixture of regioisomers δ 7.35 – 7.28 (m, 2.5H), 7.28 – 7.21 (m, 1.25H), 7.19 – 7.10 (m, 2.5H), 4.35 – 4.28 (m, 1H), 4.14 – 4.06 (m, 0.5H), 3.96 – 3.88 (m, 1H), 3.74 (s, 0.75H), 3.69 (s, 3H), 3.31 – 3.23 (m, 0.25H), 3.05 – 2.85 (m, 1.5H), 2.85 – 2.66 (m, 3.25H), 2.63 (d, J = 10.2 Hz, 0.25H), 2.61 – 2.55 (m, 2H), 2.34 (dd, J = 13.7, 11.9 Hz, 0.25H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) mixture of regioisomers: δ 177.8, 171.6, 137.8, 129.1, 129.0, 129.0, 128.7, 127.1, 126.9, 71.4, 70.1, 52.3, 52.2, 42.4, 42.0, 40.8, 39.7, 38.4, 33.6, 33.3, 30.2, 29.8.

HRMS: calculated for $\text{C}_{14}\text{H}_{16}\text{NaO}_4$ ($\text{M}+\text{Na}^+$): 271.0941, found 271.0939 (+0.7 ppm).

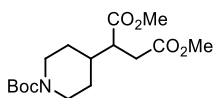
C2.9 General Procedure E (telescoped reaction from amine 5)



Reactions performed using *set-up 2* in Figure S3. In an oven dried vial, with a Teflon septum screw cap, primary amine (0.22 mmol, 1.1 equiv.) and 2,4,6-triphenylpyrylium tetrafluoroborate (79.2 mg, 0.2 mmol, 1 equiv.) were dissolved in ethanol (0.4 mL, HPLC grade). The reaction was stirred at 80 °C for 4 hours. In the same vial without evaporating the solvent, dithiocarbamate **A** (12.4 mg, 0.04 mmol, 0.2 equiv.), electron-poor olefin **2** (0.4 mmol, 2 equiv.), DMSO (4 mL), γ -terpinene (64 μL , 0.4 mmol, 2 equiv.) and 2,6-lutidine (46 μL , 0.4 mmol, 2 equiv.) were added sequentially. The resulting orange mixture was degassed with argon sparging for 60 seconds. The vial was then placed at 2-3 cm of a 50 W Kessil blue LED lamp and irradiated under stirring for 16 hours (see Figure S3). The mixture was transferred to an extraction funnel, saturated aqueous NaHCO_3 was added, and the organic layer extracted with EtOAc. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous MgSO_4 , filtered, and concentrated to dryness. The crude residue was purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to $^1\text{H NMR}$ analysis.

A control experiment without catalyst **A** delivered no conversion of the pyridinium salt upon irradiation.

C2.10 Characterization of Products with General Procedure E



dimethyl 2-(1-(tert-butoxycarbonyl)piperidin-4-yl)succinate (3n): Synthesized according to General Procedure E using 2 equiv. of γ -terpinene, tert-butyl 4-aminopiperidine-1-carboxylate (40 mg, 0.2 mmol, 1 equiv.) and dimethyl fumarate **2c** (57 mg, 0.4 mmol, 2 equiv.).

The crude mixture was purified by flash column chromatography on silica gel (0-40% AcOEt in hexanes as eluent) to afford **3n** (59 mg, 90% yield) as a yellow oil.

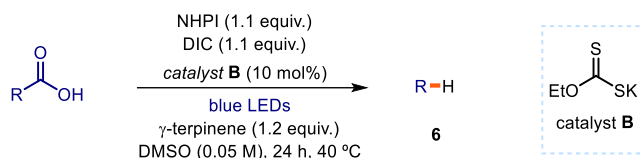
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.12 (d, J = 13.3 Hz, 2H), 3.70 (s, 3H), 3.66 (s, 3H), 2.81 – 2.68 (m, 2H), 2.63 (tt, J = 13.0, 3.0 Hz, 2H), 2.52 – 2.41 (m, 1H), 1.73 (tdd, J = 12.3, 6.1, 3.6 Hz, 1H), 1.57 (ddt, J = 23.3, 13.0, 3.0 Hz, 2H), 1.44 (s, 9H), 1.34 – 1.15 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 174.7, 172.9, 155.1, 79.9, 52.2, 46.6, 44.2, 38.7, 33.6, 33.6, 29.9, 29.7, 28.8, 28.8.

HRMS: calculated for C₁₆H₂₇NNaO₆ (M+Na⁺): 352.1731, found 352.1726. (+1.4 ppm)

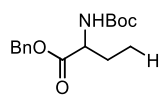
C3. Reduction

C3.1 General Procedure F (*Barton decarboxylation*)



Reactions performed using *set-up 1* in Figure S2. In an oven dried vial, with a Teflon septum screw cap, carboxylic acid (0.2 mmol, 1 equiv.), *N*-hydroxyphthalimide (NHPI, 35.8 mg, 0.22 mmol, 1.1 equiv.) and xanthogenate **B** (3.2 mg, 0.02 mmol, 0.1 equiv.) were dissolved in DMSO (4 mL) and *N,N'*-diisopropylcarbodiimide (DIC, 34 μL, 0.22 mmol, 1.1 equiv.) was added via syringe. Then, γ-terpinene (38 μL, 0.24 mmol, 1.2 equiv.) was added. The resulting orange mixture was degassed with argon sparging for 60 seconds. The vial was then placed in the 3D printed support photoreactor (Figure S2) and irradiated under stirring for 24 hours, unless otherwise specified. The mixture was transferred to an extraction funnel, NaOH 1M solution was added and the organic layer was extracted with CH₂Cl₂. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated to dryness. The crude residue was purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

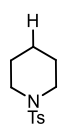
C3.2 Characterization of Products with General Procedure F

 **benzyl (S)-2-((tert-butoxycarbonyl)amino)butanoate (6a):** Synthesized according to General Procedure F using (*S*)-5-(benzyloxy)-4-((tert-butoxycarbonyl)amino)-5-oxopentanoic acid (67 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (25% AcOEt in hexanes as eluent) to afford **6a** (38 mg, 65% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.28 (m, 5H), 5.24 – 5.10 (m, 2H), 5.04 (d, *J* = 8.3 Hz, 1H), 4.30 (t, *J* = 7.1 Hz, 1H), 1.93 – 1.80 (m, 1H), 1.69 (dt, *J* = 14.2, 7.2 Hz, 1H), 1.44 (s, 9H), 0.90 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 172.8, 155.5, 135.6, 128.7, 128.5, 128.4, 79.9, 67.1, 54.8, 28.5, 26.1, 9.7.

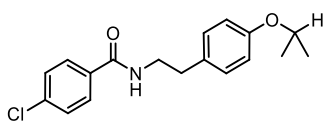
Matching reported literature data.¹

 **1-tosylpiperidine (6b):** Synthesized according to General Procedure F using 1-tosylpiperidine-4-carboxylic acid (57 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **6b** (37 mg, 77% yield) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 7.66 – 7.60 (m, 2H), 7.34 – 7.28 (m, 2H), 2.99 – 2.93 (m, 4H), 2.42 (s, 3H), 1.63 (p, *J* = 5.9 Hz, 4H), 1.40 (tt, *J* = 8.2, 4.7 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 143.4, 133.5, 129.7, 127.8, 47.1, 25.3, 23.7, 21.6.

Matching reported literature data.¹



4-chloro-N-(4-isopropoxyphenethyl)benzamide

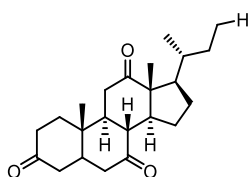
(6c):

Synthesized according to General Procedure F using Bezafibrate (72 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (25% AcOEt in hexanes as eluent) to afford **6c** (32 mg, 50% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) mixture of rotamers: δ 7.65 – 7.59 (m, 2H), 7.37 (dd, *J* = 8.6, 2.0 Hz, 2H), 7.15 – 7.04 (m, 2H), 6.89 – 6.79 (m, 2H), 6.13 (s, 1H), 4.52 (p, *J* = 6.1 Hz, 1H), 3.67 (qd, *J* = 6.7, 6.3, 3.7 Hz, 2H), 2.85 (t, *J* = 6.9 Hz, 2H), 1.33 (d, *J* = 6.1 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) mixture of rotamers: δ 166.6, 156.8, 137.8, 133.1, 130.6, 130.0, 129.9, 129.0, 128.4, 116.3, 115.8, 70.1, 41.5, 34.8, 22.2.

HRMS: calculated for C₁₆H₁₈ClN₄NaO (*M*+Na⁺): 340.1061, found 340.1075 (+4.1 ppm).

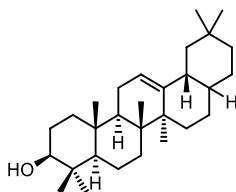


(5S,8R,9S,10S,13R,14S,17R)-17-(sec-butyl)-10,13-dimethyldodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (6d): Synthesized according to General Procedure F using dehydrocholic acid (81 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (30% AcOEt in hexanes as eluent) to afford **6d** (37 mg, 51% yield) as a light-yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 2.96 – 2.80 (m, 3H), 2.39 – 2.17 (m, 6H), 2.13 (dd, *J* = 12.5, 4.8 Hz, 2H), 2.09 – 1.90 (m, 4H), 1.85 (td, *J* = 11.2, 7.0 Hz, 1H), 1.68 – 1.56 (m, 2H), 1.52 – 1.44 (m, 1H), 1.40 (s, 3H), 1.35 – 1.20 (m, 3H), 1.20 – 1.10 (m, 1H), 1.07 (s, 3H), 0.85 (dd, *J* = 15.9, 6.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 212.2, 209.2, 208.9, 57.0, 52.0, 49.2, 47.0, 45.7, 45.6, 45.1, 42.9, 38.8, 37.6, 36.6, 36.2, 35.4, 28.0, 27.8, 25.4, 22.1, 18.6, 12.0, 11.0.

Matching reported literature data.¹

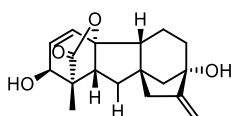


(3S,4aR,6aR,6bS,12aR,14aR,14bR)-4,4,6a,6b,11,11,14b-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydricen-3-ol (6e): Synthesized according to General Procedure F using oleanolic acid (91 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **6e** (74 mg, 90% yield) as white solid.

¹H NMR (400 MHz, CDCl₃) δ 5.19 (t, *J* = 3.7 Hz, 1H), 3.22 (ddz, *J* = 11.0, 5.0 Hz, 1H), 2.34 (dt, *J* = 13.7, 4.8 Hz, 1H), 1.91 – 1.83 (m, 2H), 1.83 – 1.75 (m, 1H), 1.74 – 1.65 (m, 2H), 1.65 – 1.58 (m, 4H), 1.5 – 1.54 (m, 2H), 1.50 – 1.31 (m, 6H), 1.29 – 1.17 (m, 4H), 1.11 (d, *J* = 0.9 Hz, 3H), 1.08 – 1.04 (m, 1H), 1.02 – 0.96 (m, 4H), 0.93 (s, 3H), 0.89 (s, 3H), 0.87 (s, 6H), 0.79 (s, 3H), 0.77 – 0.70 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 146.1, 121.2, 79.2, 55.4, 47.9, 45.1, 42.6, 41.1, 39.3, 38.9, 38.6, 37.3, 35.9, 33.8, 33.8, 33.2, 31.3, 31.2, 29.9, 28.3, 28.1, 27.4, 25.2, 24.0, 23.5, 22.4, 18.6, 17.6, 15.8, 15.5.

Matching reported literature data.¹



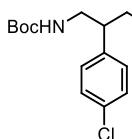
(1S,2S,4aR,4bR,7S,9aR,10aR)-2,7-dihydroxy-1-methyl-8-methylene-1,2,4b,5,6,7,8,9,10,10a-decahydro-4a,1-(epoxymethano)-7,9a-methanobenzo[a]azulen-13-one (6f): Synthesized according to General Procedure F using gibberellic acid (69 mg, 0.2 mmol, 1 equiv.). The crude

mixture was purified by flash column chromatography on silica gel (40% AcOEt in hexanes as eluent) to afford **6f** (36 mg, 60% yield) as a white solid.

¹H NMR (400 MHz, Acetone-*d*₆) δ 6.34 (dd, *J* = 9.3, 0.9 Hz, 1H), 5.85 (dd, *J* = 9.3, 3.7 Hz, 1H), 5.16 (td, *J* = 2.5, 1.1 Hz, 1H), 4.81 (tt, *J* = 2.1, 1.0 Hz, 1H), 4.56 – 4.50 (m, 1H), 4.01 (dd, *J* = 6.4, 3.6 Hz, 1H), 3.71 (s, 1H), 2.85 – 2.74 (m, 1H), 2.40 (q, *J* = 2.0 Hz, 2H), 2.03 – 2.00 (m, 1H), 1.91 (dd, *J* = 13.6, 8.2 Hz, 1H), 1.87 – 1.80 (m, 2H), 1.79 – 1.65 (m, 3H), 1.61 (dd, *J* = 13.6, 11.0 Hz, 1H), 1.53 – 1.47 (m, 1H), 1.21 (s, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 179.6, 160.6, 134.0, 133.3, 105.7, 92.8, 78.9, 70.2, 54.5, 52.3, 50.2, 48.2, 45.9, 40.1, 36.4, 30.2, 17.6, 15.2.

HRMS: calculated for C₁₈H₂₂NaO₄ (M+Na⁺): 325.1410, found 325.1400 (–3.3 ppm).



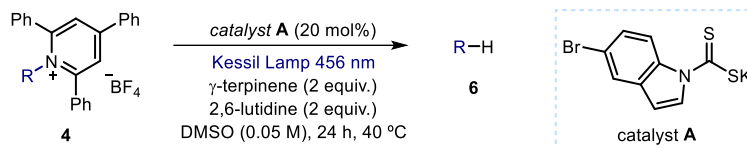
tert-butyl (2-(4-chlorophenyl)propyl)carbamate (6g): Synthesized according to General Procedure F using 4-((*tert*-butoxycarbonyl)amino)-3-(4-chlorophenyl)butanoic acid (63 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **6g** (40 mg, 74% yield) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.20 (m, 2H), 7.17 – 7.07 (m, 2H), 4.41 (s, 1H), 3.35 (s, 1H), 3.15 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.91 (q, *J* = 7.1 Hz, 1H), 1.41 (s, 9H), 1.24 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 156.0, 142.9, 132.4, 129.8, 128.8, 128.8, 128.6, 47.4, 39.8, 28.5, 28.5, 19.2, 1.2.

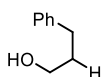
Matching reported literature data.²⁰

C3.3 General Procedure G (*deaminative reduction*)



Reactions performed using *set-up 2* in Figure S3. In an oven dried vial, with a Teflon septum screw cap, dithiocarbamate **A** (12.4 mg, 0.04 mmol, 0.2 equiv.) and pyridinium salt **4** (0.2 mmol, 1 equiv.) were dissolved in DMSO (4 mL). Then, γ-terpinene (64 μL, 0.4 mmol, 2 equiv.) and 2,6-lutidine (46 μL, 0.4 mmol, 2 equiv.) were added. The resulting orange mixture was degassed with argon sparging for 60 seconds. The vial was then placed at 2-3 cm of a 50 W Kessil blue LED lamp and irradiated under stirring for 16 hours (see Figure S3). The mixture was transferred to an extraction funnel, NaHCO₃ sat. solution was added and the organic layer was extracted with EtOAc. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated to dryness. The crude residue was purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C3.4 Characterization of Products

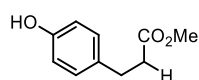


3-phenylpropan-1-ol (6h): Synthesized according to General Procedure G using 1-(1-hydroxy-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4b** (106 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in pentane as eluent) to afford **6h** (21 mg, 77% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.72 (dd, *J* = 8.7, 6.8 Hz, 2H), 1.96 – 1.85 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 141.9, 128.6, 128.5, 126.0, 62.4, 34.4, 32.2.

Matching reported literature data.²¹



methyl 3-(4-hydroxyphenyl)propanoate (6i): Synthesized according to General Procedure G using 1-(3-(4-hydroxyphenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (115 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (0-40% AcOEt in hexanes as eluent) to afford **6i** (28 mg, 78% yield) as a colorless oil.

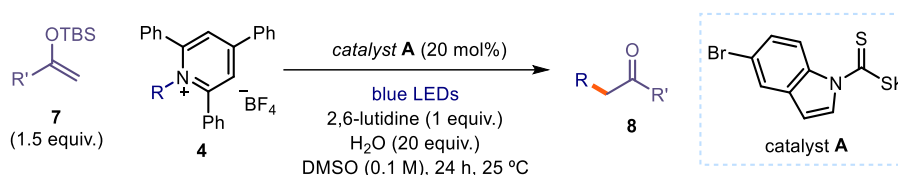
¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, *J* = 8.4 Hz, 2H), 6.79 – 6.71 (m, 2H), 5.74 (s, 1H), 3.67 (s, 3H), 2.88 (t, *J* = 7.7 Hz, 2H), 2.61 (dd, *J* = 9.0, 6.5 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 174.1, 154.4, 132.4, 129.5, 115.5, 51.9, 36.2, 30.2.

Matching reported literature data.²²

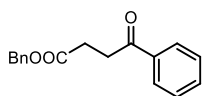
C4. α-Alkylation of Silyl Enol Ethers

C4.1 General Procedure H



Reactions performed using *set-up 3* in Figure S6. In an oven dried vial with a Teflon septum screw cap, silyl enol ether **7** (0.3 mmol, 1.5 equiv.) was dissolved in DMSO (2 mL), followed by addition of 2,6-lutidine (23 μL, 0.2 mmol, 1.0 equiv.), pyridinium salt **4** (0.2 mmol, 1.0 equiv.), catalyst **A** (12.4 mg, 0.04 mmol, 0.2 equiv.) and water (4.0 mmol, 20 equiv.). The resulting orange mixture was degassed by bubbling argon for 60 seconds. The vial was then placed in the irradiation setup (see Figure S6), maintained at a temperature of 25 °C (25-26 °C measured in the central well), and the reaction was stirred for 24 hours under continuous irradiation from a blue LED strip, unless otherwise stated. The crude mixture was diluted with EtOAc and brine was added. The layers were separated, and the aqueous layer extracted with EtOAc (×3). The combined organic fractions were dried over anhydrous MgSO₄, filtered, and concentrated to dryness. The crude residue was purified by column chromatography on silica gel to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C4.2 Characterization of Products with General Procedure H

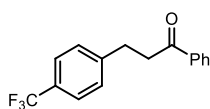


Benzyl 4-oxo-4-phenylbutanoate (8a): Prepared according to General Procedure H using *set-up 2* (75% intensity). 2,6-lutidine (46 μL, 0.4 mmol, 2 equiv.), *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (70 mg, 0.4 mmol, 2 equiv.) and 1-(2-(benzyloxy)-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4d** (109 mg, 0.2 mmol, 1 equiv.). Flash column chromatography (hexanes/EtOAc 95:5) to afford product **8a** as an off-white oil (43 mg, 80% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.03 – 7.94 (m, 2H), 7.56 (m, 1H), 7.46 (m, 2H), 7.40 – 7.23 (m, 5H), 5.15 (s, 3H), 3.34 (t, *J* = 6.6 Hz, 2H), 2.83 (t, *J* = 6.6 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 198.2, 172.9, 136.7, 136.0, 133.4, 128.8, 128.7, 128.4, 128.2, 66.7, 33.5, 28.43.

Matching reported literature data.²³



1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (8b): Prepared according to General Procedure H using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (70 mg, 0.3 mmol,) and 2,4,6-triphenyl-1-(4-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate **4e** (111 mg, 0.2

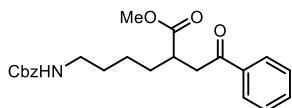
mmol). Time of irradiation: 24 hours at 25 °C. Flash column chromatography (Toluene) to afford product **8b** as a white solid (35 mg, 55% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.97 – 7.90 (m, 2H), 7.59 – 7.50 (m, 3H), 7.48 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 3.33 (t, *J* = 7.5 Hz, 2H), 3.15 (t, *J* = 7.5 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 198.2, 145.5, 136.8, 136.8, 133.4, 129.1, 128.8, 128.7, 128.1, 125.4 (q, *J* = 3.9 Hz), 124.5 (q, *J* = 270 Hz), 39.9, 29.9.

¹⁹F NMR (376 MHz, CDCl₃) δ –62.49.

Matching reported literature data.²⁴

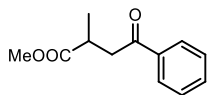


Methyl 6-(((benzyloxy)carbonyl)amino)-2-(2-oxo-2-phenylethyl)hexanoate (8c): Prepared according to General Procedure H using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (70 mg, 0.3 mmol) and (±)-1-(6-(((benzyloxy)carbonyl)amino)-1-methoxy-1-oxohexan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4f** (135 mg, 0.2 mmol). Flash column chromatography (hexanes/EtOAc 7:3 to 1:1) to afford product **3e** as a yellowish oil (53 mg, 67% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.93 (m, 2H), 7.60 – 7.54 (m, 1H), 7.49 – 7.44 (m, 2H), 7.36 – 7.30 (m, 5H), 5.09 (s, 2H), 4.76 (s, 1H), 3.69 (s, 3H), 3.56 – 3.34 (m, 1H), 3.20 (q, *J* = 6.7 Hz, 2H), 3.15 – 2.99 (m, 2H), 1.77 – 1.50 (m, 5H), 1.39 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 198.2, 176.1, 156.5, 136.8, 136.7, 133.4, 128.8, 128.7, 128.3, 128.2, 66.8, 52.0, 40.9, 40.6, 40.3, 31.9, 29.9, 24.5.

HRMS: calculated for C₂₃H₂₇NNaO₅ (M+Na⁺): 420.1781, found 420.1771 (+2.3 ppm).

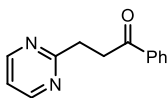


Benzyl 2-methyl-4-oxo-4-phenylbutanoate (8d): Prepared according to General Procedure H using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (70 mg, 0.3 mmol) and (±)-1-(1-(benzyloxy)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4g** (111 mg, 0.2 mmol). Time of irradiation: 24 hours at 25 °C. Flash column chromatography (hexanes/EtOAc 98:2 to 90:10) to afford product **8d** as a yellowish oil (39 mg, 69% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.07 – 7.88 (m, 2H), 7.72 – 7.53 (m, 1H), 7.53 – 7.42 (m, 2H), 7.35 (m, 5H), 5.22 – 5.09 (dd, *J* = 16.5 Hz, 12.4 Hz, 2H), 3.52 (dd, *J* = 17.5 Hz, 7.8 Hz, 1H), 3.22 (m, 1H), 3.06 (dd, *J* = 17.5 Hz, 5.5 Hz, 1H), 1.32 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 198.1, 175.9, 136.8, 136.2, 133.3, 128.7, 128., 128.2, 128.2, 128.2, 66.5, 42.0, 35.2, 17.4.

Matching reported literature data.²³

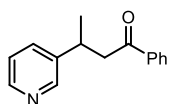


1-phenyl-3-(pyrimidin-2-yl)propan-1-one (8e): Prepared according to General Procedure H at 40 °C using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (70 mg, 0.3 mmol) and 2,4,6-triphenyl-1-(pyrimidin-2-ylmethyl)pyridin-1-ium tetrafluoroborate **4h** (98 mg, 0.2 mmol). Flash column chromatography (hexanes/EtOAc 7:3) to afford product **8e** as a yellowish oil (32 mg, 75% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.66 (d, *J* = 4.9 Hz, 2H), 8.25 – 7.88 (m, 2H), 7.61 – 7.52 (m, 1H), 7.51 – 7.39 (m, 2H), 7.13 (t, *J* = 4.9 Hz, 1H), 3.66 – 3.55 (m, 2H), 3.46 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 199.0, 170., 157.1, 137.1, 133.2, 128.7, 128.3, 118.8, 36.2, 33.1.

HRMS: calculated for C₁₃H₁₃N₂O (M+H⁺): 213.1022, found 213.1020 (+1.0 ppm).

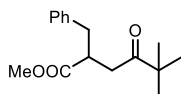


1-phenyl-3-(pyridin-3-yl)butan-1-one (8f): Prepared according to General Procedure H at 60 °C using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (70 mg, 0.3 mmol) and (\pm)-2,4,6-triphenyl-1-(1-(pyridin-3-yl)ethyl)pyridin-1-ium tetrafluoroborate **4i** (100 mg, 0.2 mmol). Flash column chromatography (hexanes/EtOAc 8:2) to afford product **8f** as a yellowish oil (20 mg, 44% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.52 (d, J = 4.9, 1H), 8.04 – 7.91 (m, 2H), 7.64 (td, J = 7.7 Hz, 1.9 Hz, 1H), 7.58 – 7.49 (m, 1H), 7.48 – 7.37 (m, 2H), 7.30 (d, J = 7.8 Hz, 1H), 7.13 (m, 1H), 3.82 – 3.60 (m, 2H), 3.25 (dd, J = 16.4 Hz, 5.6 Hz, 1H), 1.40 (d, J = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 199.3, 164.9, 148.7, 137.3, 133.1, 128.6, 128.3, 123.0, 121.7, 45.0, 37.2, 21.2.

HRMS: calculated for C₁₅H₁₆NO ($M+H^+$): 226.1226, found 226.1222 (+1.8 ppm).

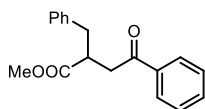


Methyl 2-benzyl-5,5-dimethyl-4-oxohexanoate (8g): Prepared according to General Procedure H with *set-up* **2** (75% intensity) and solvent system DMSO/DCE (1:1). 2,6-Lutidine (47 μ L, 0.4 mmol, 2.0 equiv.), methyl 2-benzyl-5,5-dimethyl-4-oxohexanoate **7b** (119 mg, 0.5 mmol) and (\pm)-1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4i** (111 mg, 0.2 mmol). Flash column chromatography (Hexanes/EtOAc from 98:2 to 96:4) to afford product **8g** as a yellow oil (33 mg, 63% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.17 – 7.10 (m, 2H), 3.63 (s, 3H), 3.21 – 3.09 (m, 1H), 3.01 (dd, J = 13.6 Hz, 6.6 Hz, 1H), 2.93 (dd, J = 18.1, 8.9 Hz, 1H), 2.73 (dd, J = 13.6 Hz, 8.3 Hz, 1H), 2.52 (dd, J = 18.1 Hz, 4.6 Hz, 1H), 1.10 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 214.2, 175.6, 138.8, 129.1, 128.6, 126.7, 51.9, 44.1, 42.1, 37.93, 37.9, 26.5.

HRMS: calculated for C₁₈H₂₁O₃ ($M+H^+$): 285.1485, found 285.1475 (+3.5 ppm).

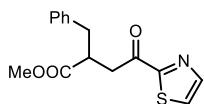


Methyl 2-benzyl-4-oxo-4-phenylbutanoate (8h): Prepared according to General Procedure H using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (70 mg, 0.3 mmol) and (\pm)-1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4i** (111 mg, 0.2 mmol). Flash column chromatography (hexanes/EtOAc 92:8) to afford product **3a** as a yellowish oil (50 mg, 89% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.87 (m, 2H), 7.59 – 7.50 (m, 1H), 7.43 (dd, J = 8.4 Hz, 7.0 Hz, 2H), 7.34 – 7.16 (m, 5H), 3.67 (s, 3H), 3.47 – 3.32 (m, 2H), 3.12 (dd, J = 13.6 Hz, 6.0 Hz, 1H), 3.05 – 2.99 (m, 1H), 2.85 (dd, J = 13.6, 8.1 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 198.2, 175.4, 133.4, 129.2, 128.7, 128.7, 128.2, 126.8, 52.1, 42.4, 39.5, 38.0.

HRMS: calculated for C₁₈H₁₈NaO₃ ($M+Na^+$): 305.1148, found 305.1142 (+2.0 ppm).

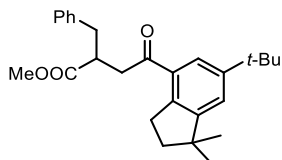


Methyl 2-benzyl-4-oxo-4-(thiazol-2-yl)butanoate (8i): Prepared according to General Procedure H using 2-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)thiazole **7c** (73 mg, 0.3 mmol) and (\pm)-1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4i** (111 mg, 0.2 mmol). Flash column chromatography (Hexanes/Acetone 95:5) to afford product **8i** as a yellowish solid (46 mg, 79% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.98 (d, *J* = 3.0 Hz, 1H), 7.65 (d, *J* = 3.0 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.23 – 7.18 (m, 3H), 3.76 – 3.58 (m, 4H), 3.40 – 3.30 (m, 1H), 3.26 – 3.10 (m, 2H), 2.84 (dd, *J* = 13.6, 8.6 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 192.0 (C), 174.9 (C), 166.7 (C), 144.9 (CH), 138.5 (C), 129.2 (CH), 128.7 (CH), 126.8 (CH), 126.4 (CH), 52.1 (CH₃), 42.3 (CH), 39.5 (CH₂), 38.0 (CH₂).

HRMS: calculated for C₁₅H₁₅NNaO₃S (M+Na⁺): 312.0665, found 312.0665 (+0.0 ppm).

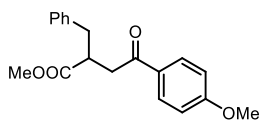


Methyl 2-benzyl-4-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)-4-oxobutanoate (8j): Prepared according to General Procedure H using tert-butyl((1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)vinyl)oxy)dimethylsilane **7d** (108 mg, 0.3 mmol) and (±)-1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4l** (111 mg, 0.2 mmol). Flash column chromatography (Hexanes/EtOAc 98:2) to afford product **8j** as a yellowish oil (74 mg, 91% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 1.8 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.24 – 7.17 (m, 3H), 3.66 (s, 3H), 3.47 – 3.22 (m, 2H), 3.14 – 3.07 (m, 3H), 3.05 – 2.97 (m, 1H), 2.84 (dd, *J* = 13.5, 7.9 Hz, 1H), 1.94 – 1.87 (m, 2H), 1.33 (s, 9H), 1.24 (d, *J* = 2.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 200.2, 175.6, 154.5, 150.1, 141.2, 138.9, 133.3, 129.2, 128.6, 126.7, 124.0, 123.5, 52.0, 43.6, 42.6, 41.6, 41.5, 38.1, 34.9, 31.6, 30.88, 28.9.

HRMS: calculated for C₂₇H₃₄NaO₃ (M+Na⁺): 429.2400, found 429.2409 (+2.1 ppm).

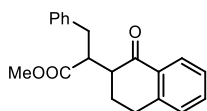


Methyl 2-benzyl-4-(4-methoxyphenyl)-4-oxobutanoate (8k): Prepared according to General Procedure H using tert-butyl((1-(4-methoxyphenyl)vinyl)oxy)dimethylsilane **7e** (80 mg, 0.3 mmol) and (±)-1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4l** (111 mg, 0.2 mmol). Flash column chromatography (Hexanes/EtOAc 93:7) to afford product **8k** as an off-white solid (52 mg, 83% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 9.0 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 6.90 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H), 3.66 (s, 3H), 3.44 – 3.26 (m, 2H), 3.10 (dd, *J* = 13.6, 5.9 Hz, 1H), 2.97 (d, *J* = 12.9 Hz, 1H), 2.84 (dd, *J* = 13.6, 7.9 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 196.7, 175.6, 163.7, 138.7, 130.4, 129.9, 129.2, 128.7, 126.8, 113.8, 55.6, 52.0, 42.4, 39.2, 38.0.

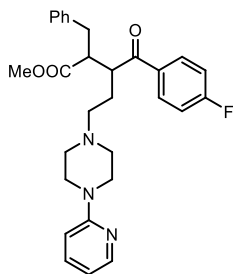
HRMS: calculated for C₂₇H₃₄NaO₃ (M+Na⁺): 429.2400, found 429.2409 (−2.1 ppm).



Methyl 2-benzyl-4-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)-4-oxobutanoate (8l): Prepared according to General Procedure H using tert-butyl((3,4-dihydronaphthalen-1-yl)oxy)dimethylsilane **7f** (104 mg, 0.4 mmol) and (±)-1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4l** (111 mg, 0.2 mmol). Flash column chromatography (Hexanes/EtOAc from 95:5 to 85:15) to afford product **3m** as an off-green solid (50 mg, 81% yield, 1:1 dr).

¹H NMR (300 MHz, CDCl₃) (1:1 mixture of diastereoisomers) δ 8.02 (ddd, *J* = 9.7, 7.8, 1.5 Hz, 1H), 7.54 – 7.39 (m, 1H), 7.35 – 7.26 (m, 3H), 7.26 – 7.14 (m, 4H), 3.66 – 3.60 (m, 0.4 H), 3.59 (s, 1.1 H), 3.57 (s, 1.8 H), 3.47 – 3.38 (m, 0.6 H), 3.26 – 3.17 (m, 0.5H), 3.05 – 2.75 (m, 4H), 2.66 – 2.58 (m, 0.7H), 2.19 – 2.32 (m, 1H), 1.94 – 1.87 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) (1:1 mixture of diastereoisomers) δ 197.8, 175.3, 174.3, 143.9, 143.7, 139.9, 139.3, 133.7, 133.5, 132.6, 129.2, 129.0, 128.8, 128.8, 128.7, 128.5, 127.7, 127.7, 126.9, 126.8, 126.6, 126.5, 51.80, 50.3, 48.7, 47.3, 46.1, 35.4, 34.7, 29.6, 29.2, 26.1, 25.4.
HRMS: calculated for C₂₀H₂₀NaO₃ (M+Na⁺): 331.1305, found 331.1289 (+4.8 ppm).



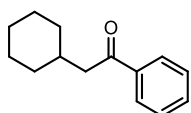
Methyl 2-benzyl-3-(4-fluorobenzoyl)-5-(4-(pyridin-2-yl)piperazin-1-yl)pentanoate (8m): Prepared according to General Procedure H using (Z)-1-(4-((tert-butyldimethylsilyl)oxy)-4-(4-fluorophenyl)but-3-en-1-yl)-4-(pyridin-2-yl)piperazine **7g** (133 mg, 0.3 mmol) and (±)-1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate **4l** (111 mg, 0.2 mmol), no water is added into the reaction mixture. Flash column chromatography (Hexanes/Acetone from 7:3 to 1:1) to afford product **8m** as an off-white solid (49 mg, 50% yield, 1.2:1 dr).

¹H NMR (500 MHz, CDCl₃) δ 8.14 (m, 1H), 8.05 – 7.97 (m, 2H), 7.47 – 7.39 (m, 1H), 7.25 – 7.14 (m, 4H), 7.13 – 7.04 (m, 5H), 6.62 – 6.51 (m, 2H), 3.95 – 3.82 (m, 1H), 3.49 (s, 1H), 3.44 (s, 2H), 3.28 (t, *J* = 44.1 Hz, 4H), 3.12 – 3.04 (m, 1H), 2.80 – 2.61 (m, 1H), 2.34 (d, *J* = 37.0 Hz, 6H), 2.13 (ddd, *J* = 13.9, 10.4, 6.4 Hz, 1H), 1.99 (s, 1H), 1.70 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) 1:1 mixture of diastereoisomer δ 200.5, 200.1, 174.5, 174.4, 159.5, 148.1, 148.1, 138.8, 138.6, 137.6, 137.6, 135.1, 134.0, 131.2, 131.2, 131.1, 131.0, 129.0, 128.9, 128.6, 128.5, 126.7, 126.7, 115.9, 115.9, 115.8, 115.7, 113.5, 113.4, 107.2, 107.1, 56.1, 55.9, 52.8, 52.6, 51.8, 51.6, 51.4, 49.2, 45.9, 45.6, 44.9, 44.8, 37.2, 34.9.

¹⁹F NMR (376 MHz, CDCl₃) 1:1 mixture of diastereoisomer δ –105.4 (s, 1F), –105.6 (s, 1F).

HRMS: calculated for C₂₉H₃₃FN₃O₃ (M+H⁺): 490.2500, found 490.2500 (0.0 ppm).

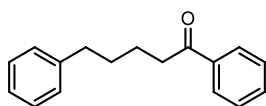


Methyl 2-benzyl-5,5-dimethyl-4-oxohexanoate (8n): Prepared according to General Procedure H with *set-up 1* and no 2,6-Lutidine. *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (70 mg, 0.3 mmol) and 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (54.5 mg, 0.2 mmol, 1 equiv.). Flash column chromatography (Hexanes/EtOAc from 100:0 to 98:2) to afford product **8n** as a yellow oil (17 mg, 42% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.92 (m, 2H), 7.58 – 7.51 (m, 1H), 7.49 – 7.42 (m, 2H), 2.82 (d, *J* = 6.8 Hz, 2H), 2.04 – 1.93 (m, 1H), 1.80 – 1.73 (m, 2H), 1.73 – 1.61 (m, 2H), 1.34 – 1.23 (m, 3H), 1.22 – 1.14 (m, 1H), 1.07 – 0.96 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 200.5, 137.6, 133.0, 128.7, 128.3, 46.4, 34.7, 33.6, 26.4, 26.3.

Matching reported literature data.²⁵



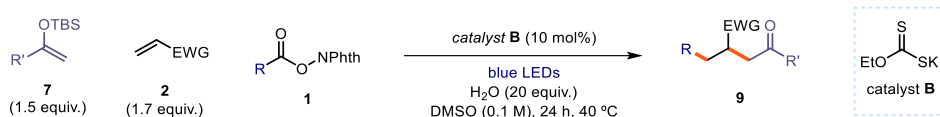
Methyl 2-benzyl-5,5-dimethyl-4-oxohexanoate (8o): Prepared according to General Procedure H with *set-up 1* and no 2,6-Lutidine. *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (70 mg, 0.3 mmol) and 1,3-dioxoisindolin-2-yl 4-phenylbutanoate **1b** (62 mg, 0.2 mmol, 1 equiv.). Flash column chromatography (Hexanes/EtOAc from 100:0 to 98:2) to afford product **8o** as a yellow oil (18 mg, 38% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.92 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.42 (m, 2H), 7.31 – 7.21 (m, 2H), 7.19 (dt, *J* = 8.0, 1.8 Hz, 3H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.76 (m, 2H), 1.76 – 1.68 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 200.4, 142.4, 137.2, 133.1, 128.7, 128.5, 128.5, 128.2, 125.9, 38.5, 35.9, 31.2, 29.8, 24.1.

Matching reported literature data.²⁶

C4.3 General Procedure I (three-component reaction)



Reactions performed using *set-up 1* in Figure S2. In an oven dried vial, with a Teflon septum screw cap, silyl enol ether **7** (0.3 mmol, 1.5 equiv.) was dissolved in DMSO (2 mL), then phthalimide ester **1** (0.2 mmol, 1.0 equiv.) was added, followed by catalyst **B** (3.2 mg, 0.02 mmol, 0.1 equiv.), electron-poor olefin **2** (0.34 mmol, 1.7 equiv.) and water (4.0 mmol, 20 equiv.). The resulting orange mixture was degassed by bubbling argon for 60 seconds. The vial was then placed in the 3D printed support photoreactor (Figure S2) and irradiated under stirring for 24 hours, unless otherwise specified. The crude mixture was diluted with EtOAc and brine was added. The combined organic fractions were dried over anhydrous MgSO₄ and concentrated to dryness. The crude residue was purified by column chromatography on silica gel to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C4.4 Characterization of Products

2-(cyclohexylmethyl)-4-oxo-4-phenylbutanenitrile (9a): Prepared according to General Procedure I using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (63 mg, 0.24 mmol), 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (55 mg, 0.2 mmol), and acrylonitrile **2b** (22 μL 0.34 mmol). Flash column chromatography (hexanes/EtOAc 94:6) to afford product **9a** as an off-white solid (31 mg, 61% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.04 – 7.86 (m, 2H), 7.72 – 7.59 (m, 1H), 7.52 – 7.45 (m, 2H), 3.52 – 3.30 (m, 2H), 3.30 – 3.13 (m, 1H), 1.89 (d, *J* = 12.9 Hz, 1H), 1.83 – 1.57 (m, 6H), 1.49 – 1.40 (m, 1H), 1.24 – 1.08 (m, 2H), 1.06 – 0.83 (m, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 195.5, 136.1, 134.0, 129.0, 128.2, 122.3, 41.5, 39.9, 35.7, 33.8, 32.2, 26.5, 26.2, 26.0, 24.0.

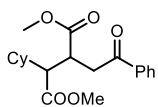
HRMS: calculated for C₁₇H₂₁NNaO (M+Na⁺): 278.1515, found 278.1511 (+1.4 ppm).

4-chloro-N-(4-((4-cyano-2-methyl-6-oxo-6-phenylhexan-2-yl)oxy)phenethyl)benzamide (9b): Prepared according to General Procedure I using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (63 mg, 0.24 mmol), 1,3-dioxoisindolin-2-yl 2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanoate **1e** (101 mg, 0.2 mmol), and acrylonitrile **2b** (22 μL, 0.34 mmol). Flash column chromatography (hexanes/EtOAc from 7:3 to 1:1) to afford product **9b** as a yellowish fluffy solid (51 mg, 52% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.05 – 7.86 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 3H), 7.57 – 7.46 (m, 2H), 7.42 – 7.38 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.09 (s, 1H), 3.74 – 3.61 (m, 3H), 3.57 – 3.37 (m, 2H), 2.90 (t, *J* = 6.9 Hz, 2H), 2.23 (dd, *J* = 14.2, 9.2 Hz, 1H), 1.99 (dd, *J* = 14.2, 3.8 Hz, 1H), 1.44 (s, 3H), 1.40 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 195.8, 166.5, 153.4, 136.1, 134.2, 134.0, 133.5, 129.6, 129.0, 128.4, 128.2, 124.3, 79.2, 44.8, 42.3, 35.0, 27.1, 26.2, 21.9.

HRMS: calculated for C₂₉H₂₉ClN₂NaO₃ (M+Na⁺): 511.1759, found 511.1759 (+0.0 ppm).



Dimethyl 2-cyclohexyl-3-(2-oxo-2-phenylethyl)succinate (9c): Prepared according to General Procedure I using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (63 mg, 0.24 mmol), 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (55 mg, 0.2 mmol), and dimethylfumarate **2c** (43 mg, 0.3 mmol). Flash column chromatography (hexanes/EtOAc 88:12) to afford the two separable diastereoisomeric products **9c** (major diastereoisomer) and **9c'** (minor diastereoisomer) as off-white solids (d.r. 1:2.5, 50 mg, 72% yield).

Spectroscopic data for 9c:

¹H NMR (300 MHz, CDCl₃) δ 8.05 – 7.86 (m, 2H), 7.63 – 7.52 (m, 1H), 7.52 – 7.45 (m, 2H), 3.69 (s, 3H), 3.67 (s, 3H), 3.67 – 3.59 (m, 1H), 3.46 – 2.94 (m, 2H), 2.71 (dd, *J* = 8.7, 5.6 Hz, 1H), 1.81 – 1.59 (m, 6H), 1.22 – 1.17 (m, 2H), 1.09 – 0.77 (m, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 198.3, 174.7, 173.8, 136.7, 133.4, 128.7, 128.3, 52.6, 52.3, 51.7, 39.8, 37.4, 36.6, 31.1, 30.4, 26.3, 26.3, 26.2.

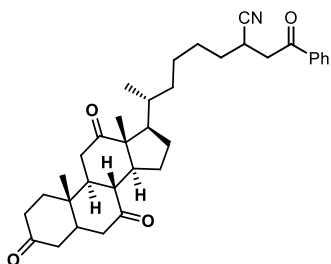
HRMS: calculated for C₂₀H₂₆NaO₅ (M+Na⁺): 369.1677, found 369.1672 (+1.4 ppm).

Spectroscopic data for 9c':

¹H NMR (300 MHz, CDCl₃) δ 8.01 – 7.94 (m, 2H), 7.61 – 7.54 (m, 1H), 7.50 – 7.42 (m, 2H), 3.68 (s, 3H), 3.68 (s, 3H), 3.58 – 3.47 (m, 2H), 3.24 – 3.10 (m, 1H), 2.66 – 2.55 (m, 1H), 1.96 (m, 1H), 1.80 – 1.64 (m, 6H), 1.07 – 0.85 (m, 5H).

¹³C NMR (75 MHz, CDCl₃) δ 197.9, 174.2, 173.9, 136.8, 133.4, 128.8, 128.2, 53.4, 52.2, 51.7, 39.3, 38.1, 37.4, 31.1, 30.9, 26.4, 26.4.

HRMS: calculated for C₂₀H₂₆NaO₅ (M+Na⁺): 369.1677, found 369.1672 (+1.4 ppm).

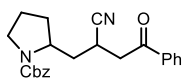


6-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(2-oxo-2-phenylethyl)heptanenitrile (9d): Prepared according to General Procedure I using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (63 mg, 0.24 mmol), 1,3-dioxoisindolin-2-yl 4-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate **1d** (110 mg, 0.2 mmol), and acrylonitrile **2b** (22 μL, 0.340 mmol). Flash column chromatography (hexanes/EtOAc 1:1) to afford product **9d** as a white solid (64 mg, 60% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.03 – 7.89 (m, 2H), 7.72 – 7.57 (m, 1H), 7.53 – 7.45 (m, 2H), 3.63 – 3.15 (m, 3H), 2.99 – 2.75 (m, 3H), 2.39 – 1.80 (m, 14H), 1.77 – 1.43 (m, 6H), 1.40 (s, 3H), 1.35 – 1.16 (m, 3H), 1.07 (s, 3H), 0.86 (dd, *J* = 6.4, 2.0 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 212.0, 209.1, 208.8, 195.3, 135.9, 133.9, 128.9, 128.1, 121.9, 56.9, 51.8, 49.0, 46.9, 45.8, 45.6, 45.0, 42.8, 40.9, 40.8, 38.7, 36.5, 36.0, 36.0, 35.3, 34.8, 32.4, 29.7, 27.9, 26.4, 26.3, 25.2, 24.5, 24.4, 21.9, 19.0, 18.9, 11.9.

HRMS: calculated for C₃₄H₄₃NNaO₄ (M+Na⁺): 552.3081, found 552.3084 (−0.5 ppm).

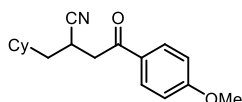


Benzyl 2-(2-cyano-4-oxo-4-phenylbutyl)pyrrolidine-1-carboxylate (9e): Prepared according to General Procedure I using *tert*-butyldimethyl((1-phenylvinyl)oxy)silane **7a** (63 mg, 0.240 mmol), 1-benzyl 2-(1,3-dioxoisindolin-2-yl)pyrrolidine-1,2-dicarboxylate **1c** (55 mg, 0.2 mmol), and acrylonitrile **2b** (22 μL, 0.34 mmol). Flash column chromatography (hexanes/acetone 7:3) to afford product **9e** as a reddish oil (47 mg, 62% yield, 1:1 dr).

^1H NMR (400 MHz, CDCl_3) (1:1 mixture of diastereoisomers) δ 8.01 – 7.79 (m, 2H), 7.68 – 7.59 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.46 – 7.30 (m, 5H), 5.26 – 5.10 (m, 2H), 4.24 – 3.96 (m, 1H), 3.57 – 3.19 (m, 5H), 2.15 – 2.04 (m, 1H), 2.02 – 1.65 (m, 5H).

^{13}C NMR (101 MHz, CDCl_3) (1:1 mixture of diastereoisomers) δ 195.3, 194.8, 155.3, 136.8, 136.8, 133.8, 128.8, 128.5, 128.1, 127.8, 123.7, 122.0, 121.1, 66.9, 66.8, 56.2, 55.6, 55.3, 46.4, 41.0, 40.7, 36.9, 36.5, 36.0, 32.5, 30.6, 30.3, 29.7, 24.3, 23.9, 23.4, 23.0.

HRMS: calculated for $\text{C}_{23}\text{H}_{24}\text{N}_2\text{NaO}_3$ ($\text{M}+\text{Na}^+$): 399.1679, found 399.1682 (–0.75 ppm).



2-(cyclohexylmethyl)-4-(4-methoxyphenyl)-4-oxobutanenitrile (9f):

Prepared according to General Procedure I using tert-butyl((1-(4-methoxyphenyl)vinyl)oxy)dimethylsilane **7e** (65 mg, 0.24 mmol), 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (55 mg, 0.2 mmol), and acrylonitrile (22 μL , 0.34 mmol). Flash column chromatography (hexanes/acetone 88:12) to afford product **9f** as an off-white solid (31 mg, 61% yield).

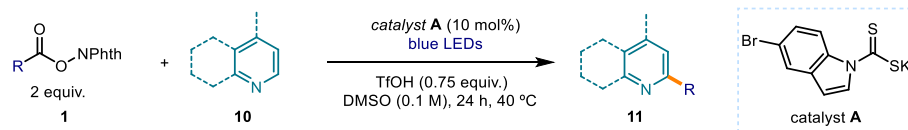
^1H NMR (300 MHz, CDCl_3) δ 7.93 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), 3.42 – 3.29 (m, 2H), 3.21 – 3.10 (m, 1H), 1.88 (d, J = 12.8 Hz, 1H), 1.77 – 1.58 (m, 7H), 1.23 – 1.10 (m, 2H), 1.00 – 0.79 (m, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 193.9, 164.2, 130.5, 129.2, 122.4, 114.1, 55.7, 41.1, 39.9, 35.7, 33.8, 32.2, 26.5, 26.2, 26.0, 24.0.

HRMS: calculated for $\text{C}_{18}\text{H}_{23}\text{NNaO}_2$ ($\text{M}+\text{Na}^+$): 308.1630, found 308.1621 (+2.9 ppm).

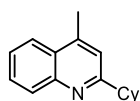
C5. Minisci Reaction

C5.1 General Procedure J



Reactions performed using *set-up 1* in Figure S2. In an oven dried vial, with a Teflon septum screw cap, heteroarene **10** (0.2 mmol, 1.0 equiv.) and trifluoromethanesulfonic acid (13.3 μ L, 0.15 mmol, 0.75 equiv.) were dissolved in DMSO (2 ml). Then, phthalimide ester **1** (0.4 mmol, 2 equiv.) and catalyst **A** (6.2 mg, 0.02 mmol, 0.1 equiv.) were added. The resulting yellow mixture was degassed with argon sparging for 60 seconds. The vial was placed in the 3D printed photoreactor and irradiated under stirring for 24 hours, unless otherwise specified (Figure S2). The mixture was transferred to an extraction funnel, NaHCO₃ sat. solution was added and the organic layer was extracted with EtOAc. The organic layer was washed with brine twice. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated to dryness. The crude residue was purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C5.2 Characterization of Products with General Procedure J



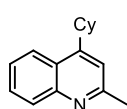
2-Cyclohexyl-4-methylquinoline (11a): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (109 mg, 0.4 mmol, 2 equiv.) and 4-methylquinoline **10a** (26.4 μ L, 0.2 mmol, 1.0 equiv.).

The crude mixture was purified by flash column chromatography on silica gel (10% EtOAc in hexane as eluent) to afford **11a** (39.6 mg, 88% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.28 (s, 1H), 7.98 – 7.96 (m, 1H), 7.74 – 7.70 (m, 1H), 7.57 – 7.53 (m, 1H), 7.23 (s, 1H), 3.15 – 3.10 (m, 1H), 2.73 (s, 3H), 2.06 – 2.01 (m, 2H), 1.89 (dt, J = 13.0, 3.3 Hz, 2H), 1.83 – 1.76 (m, 1H), 1.63 (qd, J = 12.3, 3.0 Hz, 2H), 1.49 (qt, J = 12.8, 3.0 Hz, 2H), 1.38 – 1.30 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 166.0, 130.2, 128.1, 127.1, 126.3, 123.8, 120.3, 46.5, 32.9, 26.5, 26.1, 19.3.

Matching reported literature data.²⁷



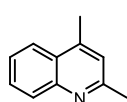
4-Cyclohexyl-2-methylquinoline (11b): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (109 mg, 0.4 mmol, 2 equiv.) and 2-methylquinoline **10b** (27.1 μ L, 0.2 mmol, 1.0 equiv.).

The crude mixture was purified by flash column chromatography on silica gel (10% EtOAc in hexane as eluent) to afford **11b** (42.3 mg, 94% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.05 (t, J = 9.8 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.51 – 7.47 (m, 1H), 7.17 (s, 1H), 3.32 – 3.27 (ddd, J = 11.4, 8.3, 3.4 Hz, 1H), 2.73 (s, 3H), 2.05 – 1.90 (m, 4H), 1.88 – 1.83 (m, 1H), 1.61 – 1.48 (m, 4H), 1.40 – 1.31 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 158.8, 153.8, 147.9, 129.4, 129.1, 125.5, 125.3, 123.0, 118.5, 39.0, 33.7, 27.1, 26.5, 25.5.

Matching reported literature data.²⁷

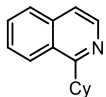


2,4-Dimethylquinoline (11c): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl acetate **1g** (82.1 mg, 0.4 mmol, 2 equiv.) and 2-methylquinoline **10b** (27.1 μ L, 0.2 mmol, 1.0 equiv.) in NMP (2 ml) for 48 hours.

The crude mixture was purified by flash column chromatography on silica gel (20% CH₂Cl₂ in MeOH as eluent) to afford **11c** (28.3 mg, 90% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.09 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.72 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 6.98 (s, 1H), 2.86 (s, 3H), 2.73 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.2, 148.6, 129.9, 129.7, 126.4, 124.1, 123.4, 122.1, 29.8, 25.6. Matching reported literature data.²⁸

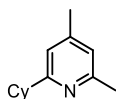


1-Cyclohexylisoquinoline (11d): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (109 mg, 0.4 mmol, 2 equiv.) and isoquinoline **10c** (25.8 mg, 0.2 mmol, 1.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (10% EtOAc in hexane as eluent) to afford **11d** (40.9 mg, 97% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 5.8 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.63 – 7.59 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.53 (d, *J* = 5.8 Hz, 1H), 3.58 (tt, *J* = 11.6, 3.2 Hz, 1H), 2.05 – 1.78 (m, 7H), 1.61 – 1.37 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.7, 141.1, 136.8, 130.3, 127.8, 127.3, 126.4, 125.1, 119.4, 41.6, 32.7, 27.0, 26.3.

Matching reported literature data.²⁷

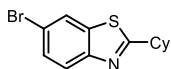


2-Cyclohexyl-4,6-dimethylpyridine (11e): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl acetate **1a** (109 mg, 0.4 mmol, 2 equiv.) and 2,4-dimethylpyridine **10d** (23.1 μL, 0.2 mmol, 1.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (10% EtOAc in hexane as eluent) to afford **11e** (31.3 mg, 83% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.80 (s, 2H), 2.71 (dd, *J* = 8.5, 4.8 Hz, 1H), 2.50 (s, 3H), 2.29 (s, 3H), 1.95 (dd, *J* = 13.4, 3.0 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.78 – 1.70 (m, 1H), 1.51 – 1.36 (m, 4H), 1.33 – 1.25 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 165.8, 157.0, 122.0, 118.6, 44.1, 33.3, 26.7, 26.3, 23.1, 21.2.

Matching reported literature data.²⁷

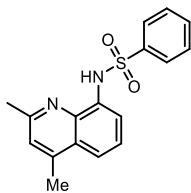


6-Bromo-2-cyclohexylbenzo[d]thiazole (11f): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (109 mg, 0.4 mmol, 2 equiv.) and 6-bromo-1,3-benzothiazole **10e** (42.8 mg, 0.2 mmol, 1.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexane as eluent) to afford **11f** (49.1 mg, 83% yield) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, *J* = 2.0 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.53 (dd, *J* = 8.7, 2.0 Hz, 1H), 3.07 (tt, *J* = 11.6, 3.6 Hz, 1H), 2.22 – 2.15 (m, 2H), 1.88 (dp, *J* = 10.6, 3.5 Hz, 2H), 1.76 (dtt, *J* = 13.1, 3.4, 1.5 Hz, 1H), 1.69 – 1.57 (m, 2H), 1.50 – 1.37 (m, 2H), 1.32 (tt, *J* = 12.5, 3.5 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 178.3, 152.1, 136.4, 129.4, 124.2, 123.8, 118.2, 43.5, 33.5, 26.1, 25.9.

Matching reported literature data.²⁸

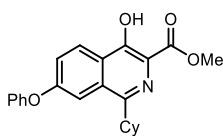


N-(2,4-Dimethylquinolin-8-yl) benzenesulfonamide (11g): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl acetate **1g** (82.1 mg, 0.4 mmol, 2.0 equiv.) and 2-((4-((7-chloro-2-methylquinolin-4-yl) amino) pentyl) (ethyl) amino) ethan-1-ol **10f** (59.7 mg, 0.2 mmol, 1.0 equiv.) in NMP (2 ml, 0.1 M) for 48 hours. The crude mixture was purified by flash column chromatography on silica gel (20% CH₂Cl₂ in MeOH as eluent) to afford **11g** (37.5 mg, 60% yield) as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 9.48 (s, 1H), 8.01 – 7.91 (m, 2H), 7.80 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.53 – 7.36 (m, 5H), 6.98 (s, 1H), 2.82 (s, 3H), 2.70 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 176.0, 158.0, 139.6, 138.2, 134.0, 133.0, 129.1, 127.4, 126.7, 124.2, 116.7, 115.4, 29.1, 25.3.

HRMS: calculated for C₁₇H₁₆N₂NaO₂S (M+Na⁺): 335.3762, found: 335.3768.



Methyl 1-cyclohexyl-4-hydroxy-7-phenoxyisoquinoline-3-carboxylate

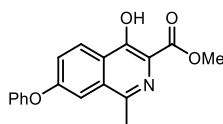
(11h): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (109 mg, 0.4 mmol, 2.0 equiv.) and Roxadustat analogue **10g** (59.1 mg, 0.2 mmol, 1.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel

(50% EtOAc in hexane as eluent) to afford **11h** (67.1 mg, 89% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 9.1 Hz, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.27 – 7.21 (m, 1H), 7.17 – 7.10 (m, 2H), 4.08 (s, 3H), 3.18 (tt, *J* = 11.6, 3.3 Hz, 1H), 1.99 – 1.85 (m, 4H), 1.86 – 1.71 (m, 3H), 1.51 – 1.31 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.8, 159.0, 156.1, 155.4, 155.4, 131.4, 130.3, 126.2, 124.6, 124.2, 121.9, 119.8, 119.0, 111.4, 53.0, 41.9, 32.2, 26.8, 26.2.

HRMS: calculated for C₂₃H₂₄NO₄ (M+H⁺): 378.1700, found: 378.1702.



Methyl 4-hydroxy-1-methyl-7-phenoxyisoquinoline-3-carboxylate

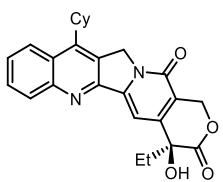
(11i): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl acetate **1g** (82.1 mg, 0.4 mmol, 2.0 equiv.) and Roxadustat analogue **10g** (59.1 mg, 0.2 mmol, 1.0 equiv.) in NMP (2 ml) for 48 hours. The crude mixture was purified by flash column chromatography on silica gel (50% EtOAc in hexane as

eluent) to afford **11i** (57.5 mg, 93% yield) as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 11.83 (s, 1H), 8.44 (d, *J* = 9.1 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.38 (m, 1H), 7.29 (tt, *J* = 6.4, 1.2 Hz, 1H), 7.16 – 7.09 (m, 2H), 4.04 (s, 3H), 2.71 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 175.4, 160.1, 156.4, 155.2, 147.5, 130.7, 130.5, 126.7, 125.4, 124.2, 122.4, 120.4, 119.1, 108.6, 53.0, 30.0.

Matching reported literature data.²⁹



(S)-11-Cyclohexyl-4-ethyl-4-hydroxy-1,12-dihydro-14H-pyrano [3',4':6,7] indolizino [1,2-b] quinoline-3,14(4H)-dione (11j)

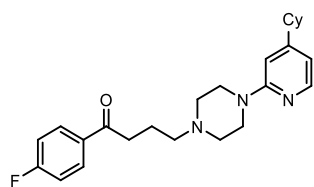
Synthesized according to General Procedure using J 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (109 mg, 0.4 mmol, 2 equiv.) and Camptothecin **10h** (69.7 mg, 0.2 mmol, 1.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% CH₂Cl₂ in MeOH as eluent)

to afford **11j** (41.3 mg, 48% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.27 – 8.15 (d, *J* = 8.4 Hz, 2H), δ 7.76 (t, *J* = 7.5 Hz, 1H), 7.66 – 7.61 (m, 2H), 5.74 (d, *J* = 16.3 Hz, 1H), 5.39 (s, 2H), 5.29 (d, *J* = 16.3 Hz, 1H), 3.95 (s, 1H), 3.61 (s, 1H), 2.06 – 1.82 (m, 8H), 1.66 – 1.53 (m, 3H), 1.46 (t, *J* = 12.7 Hz, 1H), 1.03 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 174.1, 157.7, 150.4, 148.8, 130.9, 130.0, 127.8, 127.1, 118.5, 97.9, 72.9, 66.5, 50.8, 31.9, 31.8, 29.8, 27.1, 26.1, 8.0.

Matching reported literature data.³⁰



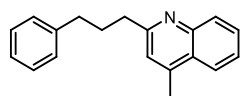
4-(4-(4-Cyclohexylpyridin-2-yl)piperazin-1-yl)-1-(4-fluorophenyl) butan-1-one (11k): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate **1a** (109 mg, 0.4 mmol, 2.0 equiv.) and Azaperone **10i** (65.5 mg, 0.2 mmol, 1.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (50% EtOAc in hexane as eluent) to afford **11k** (21.3 mg, 26% yield) as a white solid.

¹H NMR (400 MHz, Acetone-*d*₆) δ 8.15 – 8.07 (m, 2H), 7.46 (dd, *J* = 8.4, 7.3 Hz, 1H), 7.30 – 7.24 (m, 2H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 7.4 Hz, 1H), 3.65 – 3.53 (m, 4H), 3.19 (t, *J* = 6.9 Hz, 2H), 3.00 – 2.90 (m, 5H), 2.52 (tt, *J* = 11.8, 3.4 Hz, 1H), 2.15 – 2.07 (m, 2H), 1.83 – 1.28 (m, 10H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 198.7, 165.1, 159.5, 138.7, 131.8, 131.7, 116.4, 116.2, 111.1, 105.1, 58.1, 53.5, 47.1, 45.1, 36.4, 33.5, 30.6, 27.3, 26.9.

¹⁹F NMR (376 MHz, Acetone-*d*₆) δ –108.12.

HRMS: calculated for C₂₅H₃₃FN₃O (M+H⁺): 410.2602, found 410.2595 (–1.7 ppm).

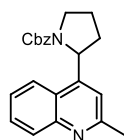


4-Methyl-2-(3-phenylpropyl)quinoline (11l): Synthesized according to General Procedure J using 1,3-dioxoisindolin-2-yl 4-phenylbutanoate **1b** (123 mg, 0.4 mmol, 2.0 equiv.) and 4-methylquinoline **10a** (26.4 μL, 0.2 mmol, 1.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (10% EtOAc in hexane as eluent) to afford **11l** (46.0 mg, 88% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.03 (m, 1H), 7.95 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.26 – 7.15 (m, 3H), 7.13 (d, *J* = 1.1 Hz, 1H), 3.03 – 2.95 (m, 2H), 2.79 – 2.71 (m, 2H), 2.67 (d, *J* = 1.0 Hz, 3H), 2.21 – 2.10 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 162.3, 147.7, 144.6, 142.3, 129.4, 129.3, 128.6, 128.4, 126.9, 125.9, 125.7, 123.7, 122.2, 38.8, 35.9, 31.7, 18.8.

HRMS: calculated for C₁₉H₂₀N (M+H⁺): 262.1586, found 262.1590 (+1.5 ppm).

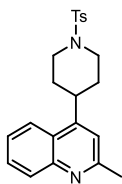


Benzyl 2-(2-methylquinolin-4-yl)pyrrolidine-1-carboxylate (11m): Synthesized according to General Procedure J using 1-benzyl 2-(1,3-dioxoisindolin-2-yl)pyrrolidine-1,2-dicarboxylate **1c** (157 mg, 0.4 mmol, 2 equiv.) and 2-methylquinoline **10b** (27.1 μL, 0.2 mmol, 1.0 equiv.). The crude mixture was purified by flash column chromatography on silica gel (30% EtOAc in hexane as eluent) to afford **11m** (57.3 mg, 83% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) mixture of rotamers: δ 8.08 (t, *J* = 9.5 Hz, 1H), 7.92 (dd, *J* = 8.8, 4.0 Hz, 1H), 7.67 (dt, *J* = 12.4, 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44 – 7.28 (m, 2H), 7.11 (dt, *J* = 14.7, 7.2 Hz, 2H), 6.98 (d, *J* = 3.3 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 5.76 – 5.61 (m, 1H), 5.18 (s, 1H), 5.10 – 4.83 (m, 1H), 3.82 (td, *J* = 9.5, 8.2, 3.1 Hz, 1H), 3.77 – 3.62 (m, 1H), 2.67 (d, *J* = 26.7 Hz, 3H), 2.59 – 2.40 (m, 1H), 2.00 – 1.79 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) mixture of rotamers: δ 158.8, 158.6, 154.9, 149.3, 148.6, 148.0, 136.9, 136.5, 129.5, 129.3, 128.6, 128.3, 128.2, 128.1, 127.8, 127.4, 125.8, 124.1, 124.0, 123.0, 122.8, 117.6, 117.3, 67.2, 66.7, 58.1, 57.5, 47.6, 47.3, 34.2, 33.2, 25.5, 23.7, 23.0.

HRMS: calculated for C₂₂H₂₃N₂O₂ (M+H⁺): 347.1754, found 347.1760 (–1.7 ppm).

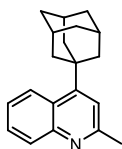


2-Methyl-4-(1-tosylpiperidin-4-yl)quinoline (11n): Synthesized according to General Procedure J using 1,3-dioxisoindolin-2-yl 1-tosylpiperidine-4-carboxylate **1f** (171 mg, 0.4 mmol, 2.0 equiv.) and 2-methylquinoline **10b** (27.1 μ L, 0.2 mmol, 1.0 equiv.) using *set-up 4* at 60 °C (Figure S7). The crude mixture was purified by flash column chromatography on silica gel (30% EtOAc in hexane as eluent) to afford **11n** (56.2 mg, 74% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, J = 8.5, 1.3 Hz, 1H), 7.85 (dd, J = 8.5, 1.4 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.63 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.43 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.36 (d, J = 2.0 Hz, 2H), 7.12 (s, 1H), 4.08 – 3.96 (m, 2H), 3.20 (tt, J = 11.5, 3.8 Hz, 1H), 2.71 (s, 3H), 2.47 (m, 5H), 2.07 – 1.85 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 159.0, 150.3, 148.2, 143.8, 133.1, 129.9, 129.8, 129.2, 127.9, 125.8, 124.8, 122.2, 118.6, 47.0, 36.4, 31.8, 25.5, 21.7.

HRMS: calculated for C₂₂H₂₅N₂O₂S (M+H⁺): 381.1627, found 381.1631 (+1.1 ppm).

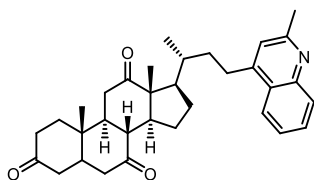


4-((3S)-Adamantan-1-yl)-2-methylquinoline (11o): Synthesized according to General Procedure J using 1,3-dioxisoindolin-2-yl (3r,5r,7r)-adamantane-1-carboxylate **1h** (130 mg, 0.4 mmol, 2 equiv.) and 2-methylquinoline **10b** (27.1 μ L, 0.2 mmol, 1.0 equiv.) using *set-up 4* at 60 °C (Figure S7). The crude mixture was purified by flash column chromatography on silica gel (10% EtOAc in hexane as eluent) to afford **11n** (38.2 mg, 69% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, J = 8.8 Hz, 1H), 8.35 (s, 1H), 7.69 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.52 (ddd, J = 8.5, 6.8, 1.5 Hz, 1H), 7.28 (s, 1H), 2.85 (s, 3H), 2.29 – 2.28 (m, 6H), 2.23 – 2.22 (m, 3H), 1.89 (t, J = 3.1 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 159.5, 130.1, 126.3, 125.4, 125.3, 119.7, 42.3, 39.3, 36.9, 29.1.

HRMS: calculated for C₂₀H₂₄N (M+H⁺): 278.1897, found 278.1903 (+2.2 ppm).



(8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-4-(2-methylquinolin-4-yl)butan-2-yl)dodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (11p): Synthesized according to General Procedure J using Dehydrocholic acid phthalimide ester **1d** (219 mg, 0.4 mmol, 2.0 equiv.) and 2-methylquinoline **10b** (27.1 μ L, 0.2 mmol, 1.0 equiv.). The crude

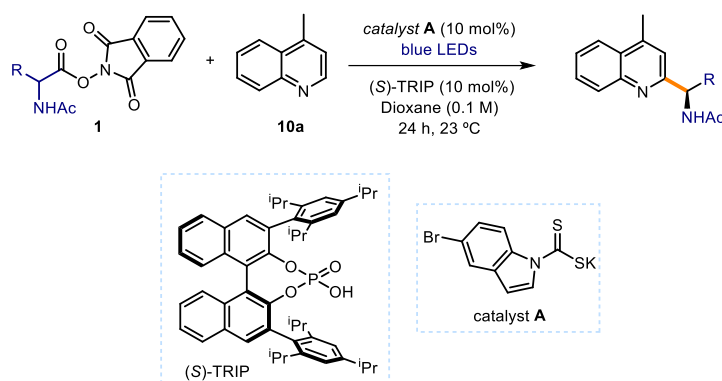
mixture was purified by flash column chromatography on silica gel (30% EtOAc in hexane as eluent) to afford **11p** (70.0 mg, 61% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 8.4 Hz, 1H), 7.96 (dd, J = 8.5, 1.4 Hz, 1H), 7.67 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.51 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.14 (s, 1H), 3.15 (ddd, J = 13.7, 11.7, 5.0 Hz, 1H), 2.96 – 2.85 (m, 4H), 2.74 (s, 3H), 2.41 – 1.22 (m, 19H), 1.39 (s, 3H), 1.08 (s, 3H), 1.05 (d, J = 6.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 212.1, 209.1, 208.8, 158.4, 150.6, 146.9, 129.7, 128.6, 126.0, 125.9, 123.4, 121.8, 57.0, 51.9, 49.1, 46.9, 45.7, 45.6, 45.1, 42.9, 38.7, 36.6, 36.5, 36.3, 36.1, 35.4, 29.5, 27.9, 25.2, 24.8, 22.0, 19.2, 12.0.

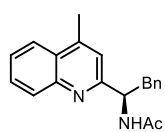
HRMS: calculated for C₃₃H₄₂NO₃ (M+H⁺): 500.3157, found: 500.3159 (+0.4 ppm).

C5.3 General Procedure K (enantioselective variant)



Reactions performed using [set-up 4](#) in Figure S7. In an oven dried vial, with a Teflon septum screw cap, 4-methylquinoline (26.4 μL , 0.2 mmol, 1.0 equiv.) and chiral phosphoric acid (*S*)-TRIP (7.5 mg, 0.01 mmol, 5 mol%) were dissolved in dioxane (2 ml). Then, phthalimide ester **1** (0.4 mmol, 2 equiv.) and catalyst **A** (6.2 mg, 0.02 mmol, 0.1 equiv.) were added. The resulting yellow mixture was degassed with argon sparging for 60 seconds. The vial was placed in the one-position photoreactor with temperature control (Figure S7) and irradiated under stirring for 24 hours, unless otherwise specified. The solvent was evaporated, and the residue purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ^1H NMR analysis.

C5.4 Characterization of Products

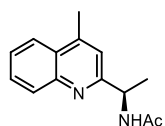


(*R*)-*N*-(1-(4-methylquinolin-2-yl)-2-phenylethyl) acetamide (11q**):** Synthesized according to General Procedure K using 1,3-dioxoisindolin-2-yl acetylphenylalaninate **1i** (140 mg, 0.4 mmol) and 4-methylquinoline **10a** (26.4 μL , 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (40% EtOAc in hexane as eluent) to afford **11q** (60.0 mg, 97% yield) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 8.05 (dt, J = 8.5, 0.9 Hz, 1H), 7.96 (ddd, J = 8.3, 1.5, 0.6 Hz, 1H), 7.70 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.27 (s, 1H), 7.18 – 7.13 (m, 3H), 6.99 – 6.92 (m, 2H), 6.82 (d, J = 1.2 Hz, 1H), 5.39 (td, J = 7.7, 5.4 Hz, 1H), 3.35 (dd, J = 13.3, 5.4 Hz, 1H), 3.17 (dd, J = 13.3, 7.9 Hz, 1H), 2.59 (d, J = 0.9 Hz, 3H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.6, 158.9, 147.1, 144.9, 137.3, 129.8, 129.5, 129.4, 128.2, 127.6, 126.6, 126.3, 124.00, 121.7, 55.6, 42.3, 23.7, 18.9.

Matching reported literature data.⁴



(*R*)-*N*-(1-(4-methylquinolin-2-yl) ethyl) acetamide (11r**):** Synthesized according to General Procedure K using 1,3-dioxoisindolin-2-yl acetylalaninate **1j** (110 mg, 0.4 mmol) and 4-methylquinoline **10a** (26.4 μL , 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (40% AcOEt in hexane as eluent) to afford **11r** (38.3 mg, 84% yield) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 8.08 (dt, J = 8.1, 1.0 Hz, 1H), 7.98 (ddd, J = 8.3, 1.5, 0.7 Hz, 1H), 7.71 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.56 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.51 (s, 1H), 7.17 (d, J = 1.1 Hz, 1H), 5.21 (p, J = 6.8 Hz, 1H), 2.70 (d, J = 1.0 Hz, 3H), 2.11 (s, 3H), 1.54 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.6, 160.7, 146.9, 145.8, 129.6, 129.3, 127.6, 126.4, 123.9, 120.5, 50.1, 23.74, 22.8, 19.0.

Matching reported literature data.⁴

C6 Trifluoromethylation

C6.1 Procedure



Reactions performed using *set-up 3* in Figure S6. In an oven dried vial with a Teflon septum screw cap, silyl enol ether **7a** (117 mg, 0.5 mmol, 2.5 equiv.) was dissolved in MeCN (2 mL), then the Togni reagent **12** (105 mg (60% Wt) 0.2 mmol, 1.0 equiv.), catalyst **A** (6.2 mg, 0.02 mmol, 0.1 equiv.). The resulting orange mixture was degassed bubbling argon for 60 seconds. The vial was then placed in the irradiation setup (see Figure S6), maintained at a temperature of 25 °C (25-26 °C measured in the central well), and the reaction, unless otherwise stated, was stirred for 24 hours under continuous irradiation from a blue LED strip. The crude mixture was diluted with AcOEt and brine was added. The combined organic fractions were dried over anhydrous MgSO₄, filtered, and concentrated to dryness. The crude mixture was purified by flash column chromatography on silica gel (Hexane/AcOEt) to afford **13** (22 mg, 58% yield) as a yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 8.01 – 7.91 (m, 2H), 7.69 – 7.61 (m, 1H), 7.60 – 7.46 (m, 3H), 3.82 (q, *J* = 10.0 Hz, 2H).

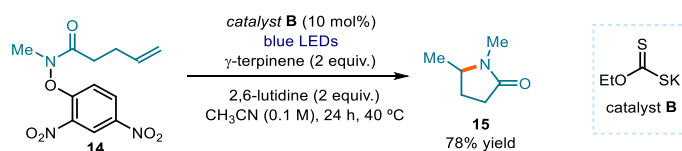
¹⁹F NMR (376 MHz, CDCl₃) δ –62.11.

¹³C NMR (126 MHz, CDCl₃) δ 135.7, 134.2, 128.9, 128.4, 124.7, 42.2.

Matching reported literature data.³¹

C7 Amidyl Radical Cyclization

C7.1 Procedure



Reactions performed using *set-up 1* in Figure S2. In an oven dried vial, with a Teflon septum screw cap, **14** (29 mg, 0.1 mmol, 1 equiv.) and catalyst **B** (1.6 mg, 0.01 mmol, 0.1 equiv.) were dissolved in CH₃CN (1 mL), then 2,6-lutidine (23 μL, 0.2 mmol, 2.0 equiv.) was added, followed by γ-terpinene (32 μL, 0.2 mmol, 2 equiv.). The resulting orange mixture was degassed with argon sparging for 60 seconds. The vial was then placed in the 3D printed support photoreactor (Figure S2) and irradiated under stirring for 16 hours. The crude mixture was concentrated to dryness. Trichloroethylene was added as internal standard (9 μL, 0.1 mmol, 1.0 equiv) and NMR yield was determined by ¹H NMR in CDCl₃ matching reported literature data.¹⁴

C8 Large-scale Reactions

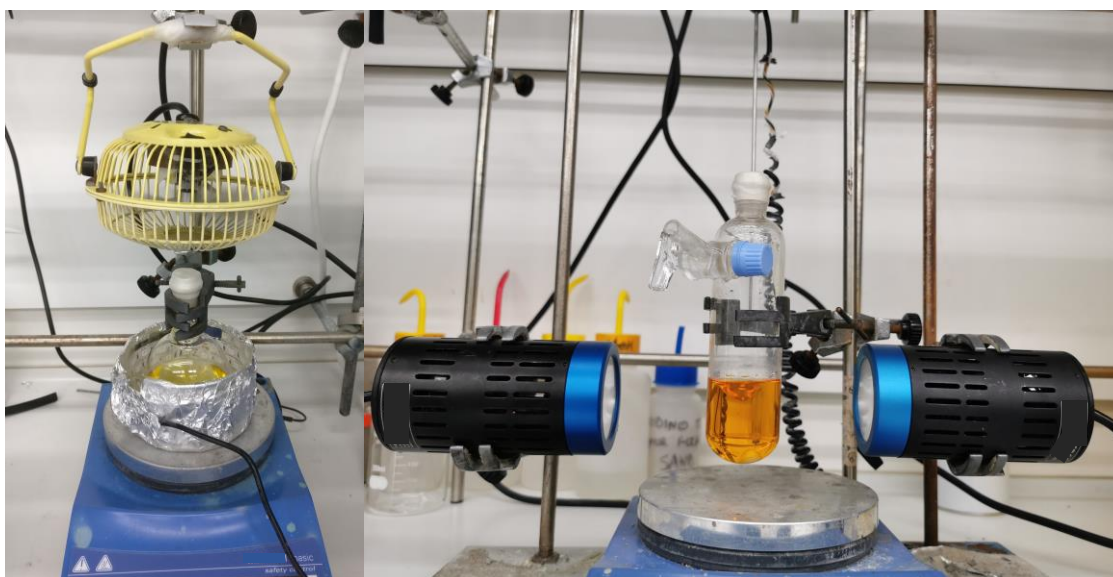
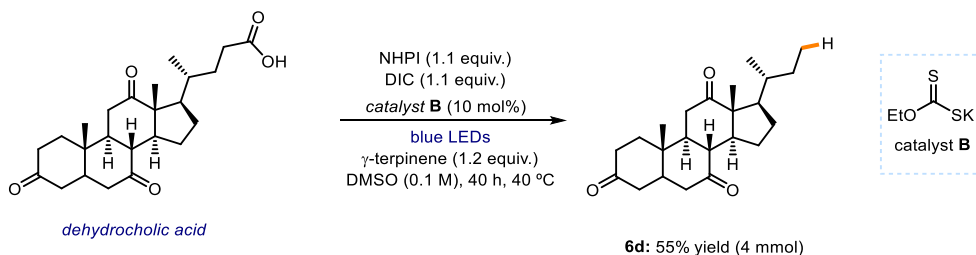


Figure S8: Experimental setup used for the large scale set up. (Left) Barton decarboxylation. (Right) Minisci reaction.

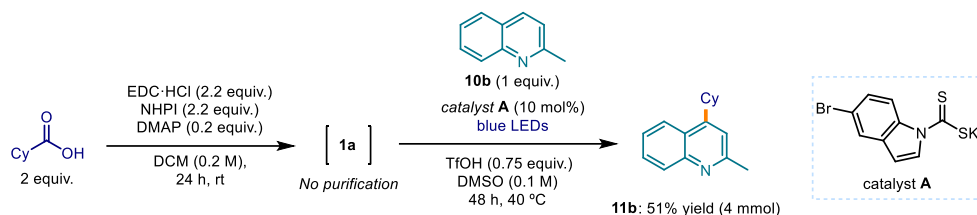
C8.1 Barton decarboxylation



Using set-up in Figure S8. In a 100 mL round bottom flask with a Teflon cap, dehydrocholic acid (1.62 g, 4 mmol, 1 equiv.), *N*-hydroxyphthalimide (NHPI, 716 mg, 4.4 mmol, 1.1 equiv.), and xanthogenate catalyst **A** (64 mg, 0.4 mmol, 0.1 equiv.) were dissolved in DMSO (40 mL), and *N,N'*-diisopropylcarbodiimide (DIC, 760 μL , 4.4 mmol, 1.1 equiv.) was added via syringe. Then, γ -terpinene (760 μL , 4.8 mmol, 1.2 equiv.) was added. The resulting orange mixture was degassed with nitrogen sparging for 5 min. The round bottom flask was then irradiated for 40 hours with a 1-meter 14W blue LED strip and cooled with a fan to keep the temperature between 30 and 35 $^\circ\text{C}$ (see

Figure S8, left). The mixture was transferred to an extraction funnel, NaOH 1M solution was added and the organic layer was extracted with CH_2Cl_2 . The organic layer was dried over anhydrous MgSO_4 , filtered, and concentrated to dryness. The crude residue was purified by chromatography on silica gel (10% AcOEt in hexanes) to afford 800 mg of product **6d** (2.2 mmol, 55% yield) as an off white solid. NMR analysis was consistent with product synthesized in the small scale process.

C8.2 Minisci reaction



Using set-up in Figure S8. In a 100 mL round bottom flask, cyclohexanecarboxylic acid (1.03 g, 8 mmol, 2 equiv.), EDC·HCl (1.69 g, 8.8 mmol, 2.2 equiv.), DMAP (97.7 mg, 0.8 mmol, 0.2 equiv.), and *N*-hydroxyphthalimide (1.44 g, 8.8 mmol, 2.2 equiv.) were dissolved in CH₂Cl₂ (20 mL). The reaction was stirred at ambient temperature for 24 hours. The mixture was transferred to an extraction funnel, NaHCO₃ sat. solution was added and the organic layer was extracted with CH₂Cl₂. The organic phase was concentrated to dryness under vacuum to obtain the crude phthalimide ester, which was used without further purification in the next step.

In a 100 mL Schlenk flask with a Teflon septum, the crude phthalimide ester was dissolved in DMSO (40 mL). Then, 2-methylquinoline (540 μL, 4.00 mmol, 1.0 equiv.), trifluoromethanesulfonic acid (265 μL, 3.00 mmol, 0.75 equiv.) and catalyst **A** (124 mg, 0.40 mmol, 0.1 equiv.) were added. The resulting orange mixture was degassed with nitrogen sparging for 5 minutes. The Schlenk flask was irradiated with stirring for 48 hours using two 50 W Kessil blue LED lamp (one PR160L-456 and one PR160L-427, 100% intensity, 4-5 cm away) (see

Figure S8, right). The mixture was transferred to an extraction funnel, NaHCO₃ sat. solution was added and the organic layer was extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated to dryness. The crude residue was purified by chromatography on silica gel (10% AcOEt in hexanes) to afford 459 mg of product **11b** (2.04 mmol, 51% yield) as a yellowish oil. NMR analysis was consistent with product synthesized in the small scale process.

C9. Unsuccessful Substrates

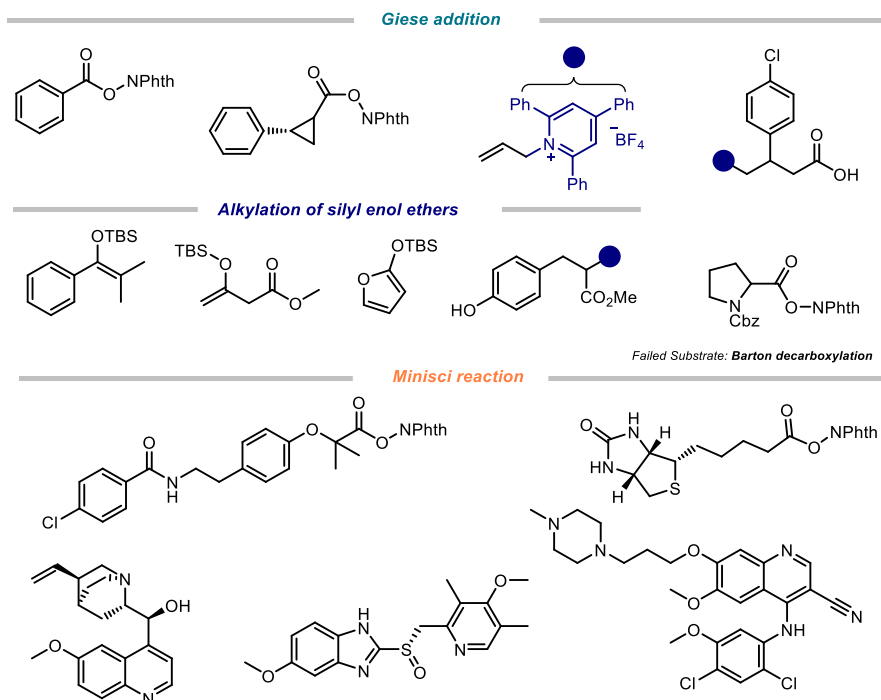


Figure S9: Unsuccessful substrates that offered poor yields (ranging from 0 to <20%)

D. Mechanistic Studies

D1. Control reactions

D1.1 Experiments with green light

For the reactions performed under green light irradiation, an EvoluChem™ P303-30-1 LEDs (18 W, $\lambda_{\text{max}} = 520$ nm) was used. The reaction temperature was measured to be between 25 °C and 30 °C using the setup depicted in Figure S10).

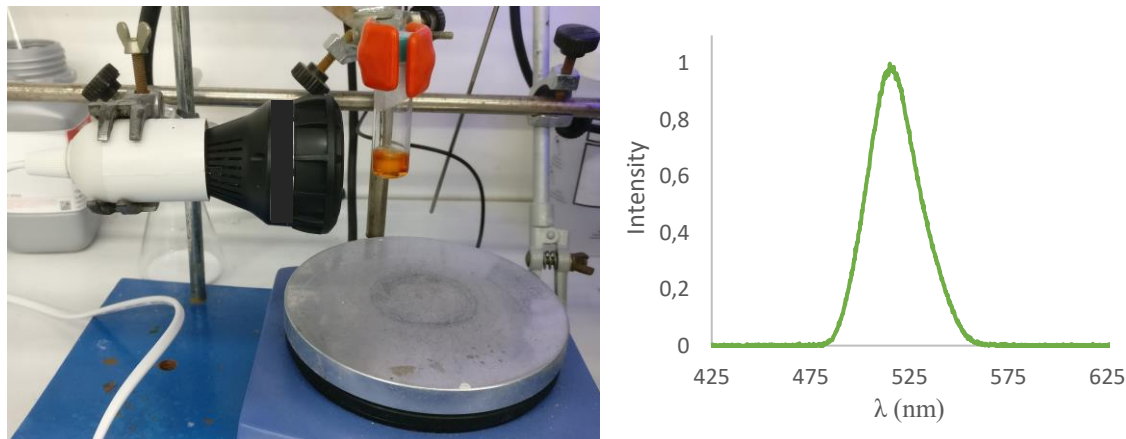


Figure S10: Reaction set-up for green light irradiation.

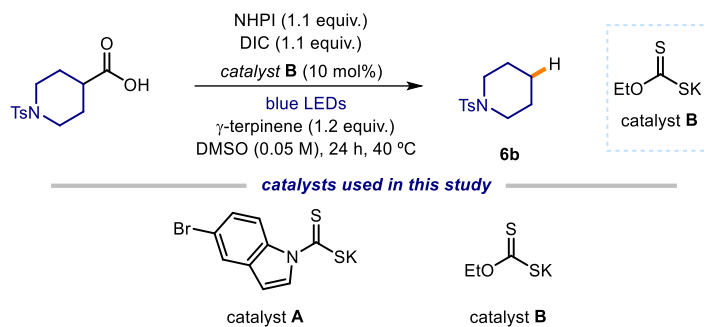
D1.2 Optimization studies.

Table S1. Giese addition with pyridinium salts as radical precursors

$ \begin{array}{c} \text{Ph} \\ \\ \text{Cy}^+ - \text{N} - \text{C}_6\text{H}_4 - \text{Ph} \\ \\ \text{BF}_4^- \end{array} + \text{CH}_2=\text{CH}-\text{SO}_2\text{Ph} \xrightarrow[\text{DMSO [0.05 M], 40 °C, 16 h}]{\text{catalyst (20 mol\%), Kessil lamp 456 nm, 2,6-lutidine (2 equiv.), } \gamma\text{-terpinene (4 equiv.)}} \begin{array}{c} \text{Cy} \\ \\ \text{CH}_2-\text{CH}-\text{SO}_2\text{Ph} \end{array} $			
<i>catalysts used in this study</i>			
 catalyst A		 catalyst B	
entry	catalyst	deviation	yield (%) ^a
1	A	none	83 (67) ^b
2	B	none	70
3	A	Green light	24
4	B	Green light	20
5	A	under air	0
6	A	no light	0

Reactions performed using [set-up 2](#) in Figure S3. All reactions performed under inert atmosphere on a 0.1 mmol scale.

^a Yield determined by ¹H NMR analysis of the crude mixture using trimethoxybenzene as the internal standard. ^b Yield of the isolated product on a 0.2 mmol scale.

Table S2. Barton decarboxylation

entry	catalyst	deviation	yield (%) ^a
1	B	none	80 (77) ^b
2	B	isolated RAE	80
3	A	none	traces
4	B	under air	0
5	B	no light	0
6	none	none	0

Reactions performed using *set-up 1* in Figure S2.

Table S3. Deamination with pyridinium salts as radical precursors

entry	catalyst	deviation	yield (%) ^a
1	A	none	95 (78) ^b
2	A	under air	0
3	A	no light	0
4	none	none	0

Reactions performed using *set-up 2* in Figure S3.

Table S4. α -alkylation of silyl enol ethers

catalysts used in this study

catalyst A

catalyst B

entry	catalyst	Base	deviation	yield (%) ^a
1	A	-	none	16
2	A	Lutidine (1 equiv.)	none	95 (89%) ^b
3	B	Lutidine (1 equiv.)	none	80
4	B	Lutidine (1 equiv.)	Green light	45
5	A	Lutidine (1 equiv.)	cat. 10 mol%	62
6	A	Lutidine (1 equiv.)	under air	0
7	A	Lutidine (1 equiv.)	no light	0
8	none	Lutidine (1 equiv.)	none	0

Reactions performed using *set-up 3* in Figure S6.

Table S5. Minisci reaction

catalysts used in this study

catalyst A

catalyst B

catalyst C

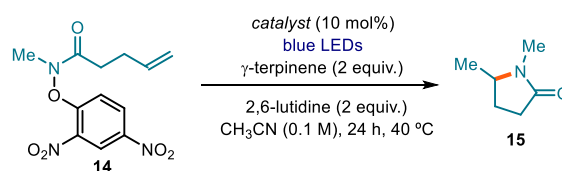
entry	catalyst	Solvents	deviation	yield (%) ^a
1	A	DMSO	TFA	82
2	B	DMSO	TFA	0
3	C	DMSO	TFA	0
4	A	DMA	TFA	41
5	A	NMP	TFA	57
6	A	DMSO	none	97(95) ^b
7	A	DMSO	Cat. 5 mol%	64
8	A	DMSO	Green light	8
9	A	DMSO	No acid	0
10	A	DMSO	no light	0
11	A	DMSO	under air	0
12	none	DMSO	none	0

Reactions performed using *set-up 2* in Figure S3.

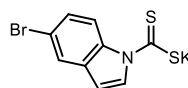
Table S6. Trifluoromethylation of silyl enol ethers.

entry	catalyst	Base	deviation	yield (%) ^a
1	A	-	Acetone	21
2	A	-	none	63(58%) ^b
3	A	Lutidine (1 equiv.)	none	62
4	B	-	none	22
5	C	-	none	27
6	-	-	No catalyst	0

Reactions performed using *set-up 3* in Figure S6.

Table S7 Minisci reaction

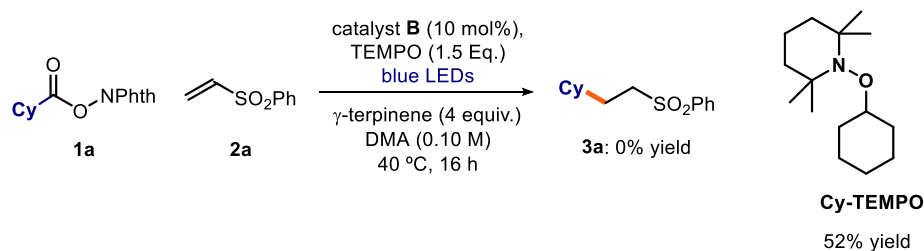
catalysts used in this study

catalyst **A**catalyst **B**

entry	catalyst	deviation	yield (%) ^a
1	A	None	86
2	B	None	78
3	A	No base	60
4	B	No base	50
5	A	Under air	0
6	A	No light	0
7	none	None	0

Reactions performed using *set-up 1* in Figure S2.

D1.3 TEMPO Trapping Experiment.



Reactions performed using *set-up 1* in Figure S2. In an oven dried vial with a Teflon septum screw cap, potassium ethyl xanthogenate **B** (1.6 mg, 0.01 mmol, 0.1 equiv.), phthalimide ester **1a** (0.1 mmol, 27.3 mg, 1 equiv.), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 0.15 mmol, 23.5

mg, 1.5 equiv.) and **2a** (0.15 mmol, 25.2 mg, 1.5 equiv.) were dissolved in DMA (1 mL). Then, γ -terpinene (64 μ L, 0.4 mmol, 4 equiv.) was added. The resulting orange mixture was degassed by argon sparging for 60 seconds. The vial was then placed in the 3D printed support photoreactor (Figure S2) and irradiated under stirring for 16 hours. The mixture was transferred to an extraction funnel, brine was added and the organic layer was extracted with EtOAc. The organic layer was dried over anhydrous MgSO_4 , filtered, and concentrated to dryness. The crude residue was then purified by column chromatography (2% EtOAc in hexanes) to afford the corresponding Cy-TEMPO adduct in 52% yield. No product corresponding with giese addition was detected in the crude NMR or during the purification.

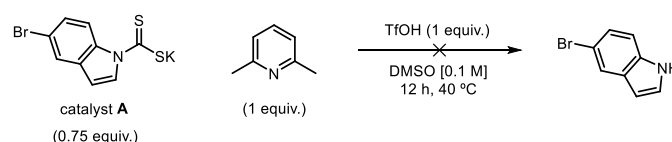
^1H NMR (500 MHz, CDCl_3) δ 3.68 – 3.64 (m, 1H), 2.07 (brs, 2H), 1.76 (brs, 2H), 1.57 – 1.54 (m, 2H), 1.48 – 1.45 (m, 4H), 1.31 – 1.06 (m, 19H).

^{13}C NMR (126 MHz, CDCl_3) δ 81.7, 59.6, 40.3, 32.9, 26.0, 25.1, 17.3.

Characterization data matching data reported in the literature.³²

D1.4 Catalysts' stability experiments

- Catalyst A:



In an oven dried vial with a Teflon septum screw cap, 2,6-lutidine (0.1 mmol, 12 μ L) was added followed by triflic acid (0.1 mmol, 8.9 μ L). The resulting pyridinium salt was then dissolved in 1 mL of d^6 -DMSO, followed by the addition of catalyst A (23.3 mg, 0.075 mmol). The mixture was stirred overnight and the crude mixture was analyzed by ^1H NMR. Catalyst A showed no degradation to the corresponding indole (see Fig. S11).

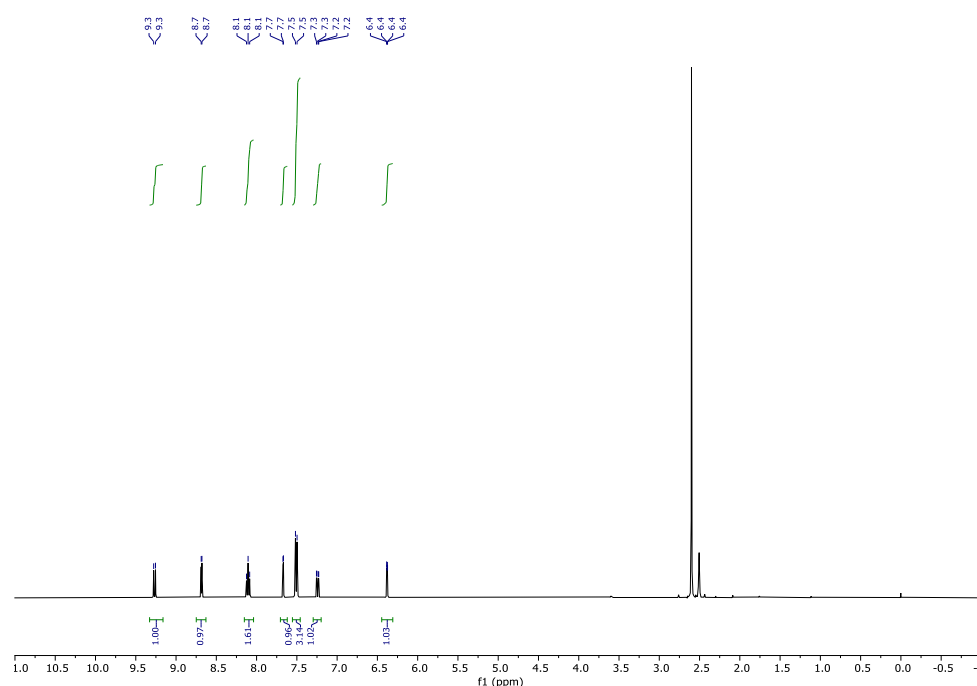
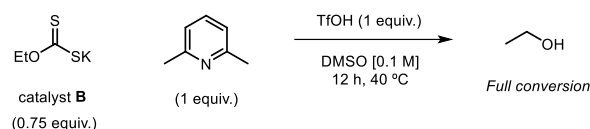


Figure S11. ^1H NMR analysis to evaluate catalyst A stability

- **Catalyst B:**



In an oven dried vial with a Teflon septum screw cap, 2,6-lutidine (0.1 mmol, 12 μ L) was added followed by triflic acid (0.1 mmol, 8.9 μ L). The resulting pyridinium salt was then dissolved in 1 mL of d⁶-DMSO, followed by the addition of catalyst **B** (12 mg, 0.075 mmol). The mixture was left stirring overnight and the crude mixture is analyzed by ¹H NMR. Catalyst **B** showed complete degradation to ethanol (see Fig. S12).

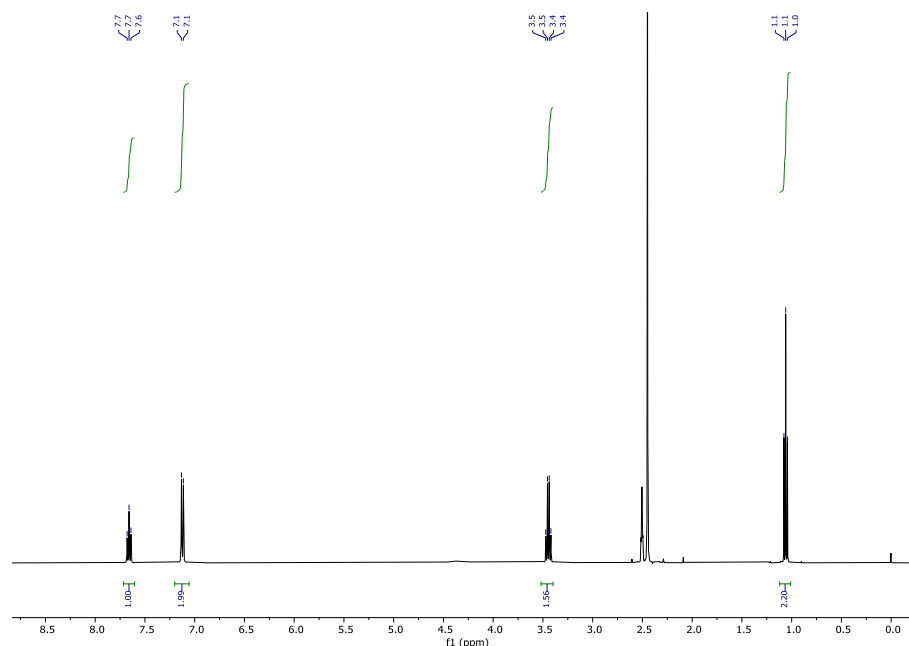


Figure S12. ¹H NMR analysis to evaluate catalyst **B** stability

D2. UV-Vis measurements

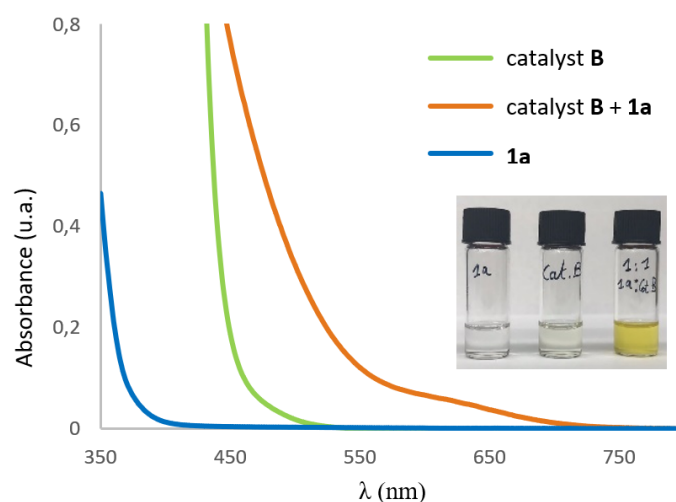


Figure S13: Optical absorption spectra, recorded in DMA in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV-vis spectrophotometer, and visual appearance of the separate reaction components and of the colored EDA complex between catalyst **B** and **1a**. [**1a**] = 0.10 M, [catalyst **B**] = 0.01 M.

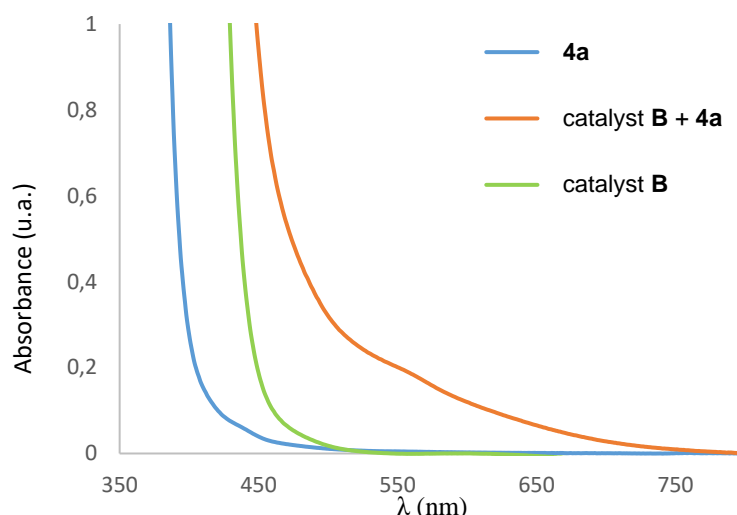


Figure S14: Optical absorption spectra, recorded in DMA in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV-vis spectrophotometer of the separate reaction components and of the colored EDA complex between catalyst **B** and **4a**. [**4a**] = 0.10 M, [catalyst **B**] = 0.01 M.

D3. Transient Absorption Spectroscopy (TAS).

Studies with microsecond transient absorption spectroscopy (TAS) were performed using an excitation source of NdYAG (neodymium-doped yttrium aluminium garnet) Opolette laser with an optical parametric oscillator (OPO) system that allows variable wavelength excitation from 400 -1800 nm, pulse width of 6 ns, up to 2 mJ of energy from OPO output with fiber optic coupled, and high energy output from direct NdYAG harmonics 355 (20 mJ, 5 ns) and 532 (45mJ, 6 ns). The system is completed with 150 W tungsten lamp as probe; 2 monochromators Minuteman MM151; Si amplified photodetector module for VIS; DSPDAU high speed data rate recorder and interface software from RAMDSP. Laser intensity for the chosen wavelength was 355 nm – 1.30 mJ.

We selected a logarithmic time scale suitable for clearly showing the decay of the transient species in the samples. The characteristics of the detected transient species match literature data.³³

In a typical transient absorption spectroscopy experiment, solutions in DMA of a mixture of **1a** and catalyst **B** was prepared under an argon atmosphere and transferred into a screw-top 3.0 mL quartz cuvette for measurement. Upon irradiation with the appropriated wavelength, the decay of absorption at 620 nm of the transient xanthyl radical **IIa** was recorded.

Irradiation at 420 nm and 460 nm of the sample also provided signal absorbing at 620 nm, but in a much lower intensity and higher noise.

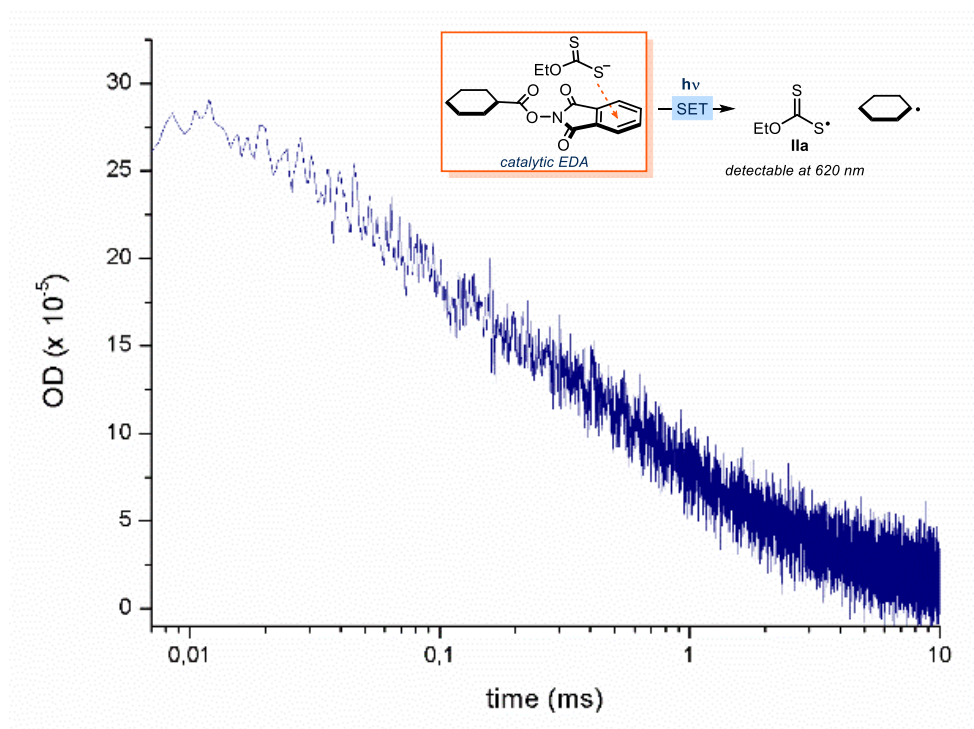


Figure S15: Absorption at 620 nm of the transient xanthyl radical IIa (blue line) generated upon 355 nm laser excitation of a 1:1 mixture of **1a** and catalyst **B** 30 mM in DMA. Note logarithmic scale for time. ΔOD : optical density variation.

D4. Cyclic Voltammetry Measurements

For all cyclic voltammetry (CV) measurements, a glassy carbon disk electrode (diameter 3 mm) was used as the working electrode. A silver wire coated with AgCl immersed in a 3.5 M aqueous solution of KCl and separated from the analyte by a fritted glass disk was employed as the reference electrode. A Pt wire counter-electrode completed the electrochemical setup. The scan rate used in each CV experiment is indicated case by case.

Potentials are quoted with the following notation: E_p^C refers to the cathodic peak potential, E_p^A refers to the anodic peak potential, while the E^{red} value describes the electrochemical properties of the referred compound.

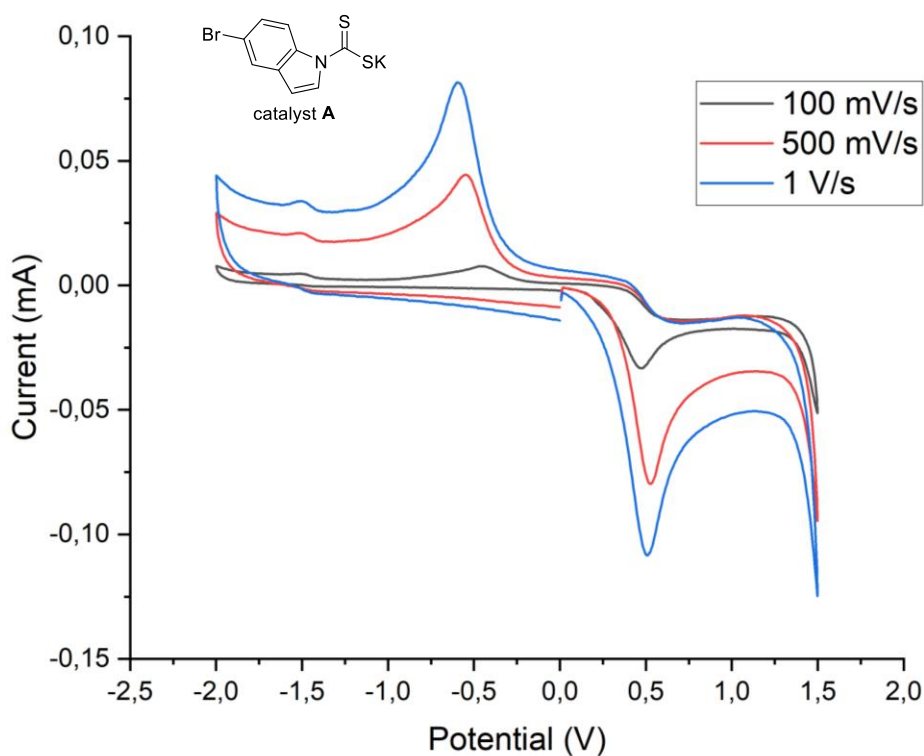


Figure S16: Cyclic voltammogram for catalyst **A** [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Measurement started by oxidation from 0 to +1.5 V, followed by reduction from +1.5 V to -2.0 V, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Two irreversible peaks observed increasing with sweep rate.

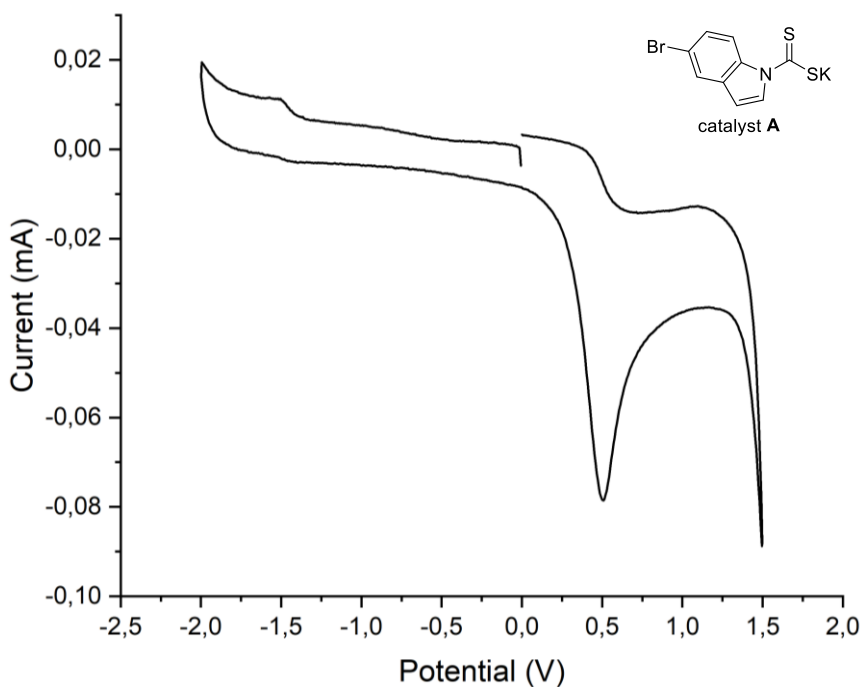


Figure S17: Cyclic voltammogram for catalyst **A** [0.02M] in [0.1 M] TBAPF₆ in CH₃CN. Measurement started by reduction from 0 to -2.0 V, followed by oxidation from -2.0 V to +1.5 V, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Only one irreversible peak observed. Sweep rate: 500 mV/s.

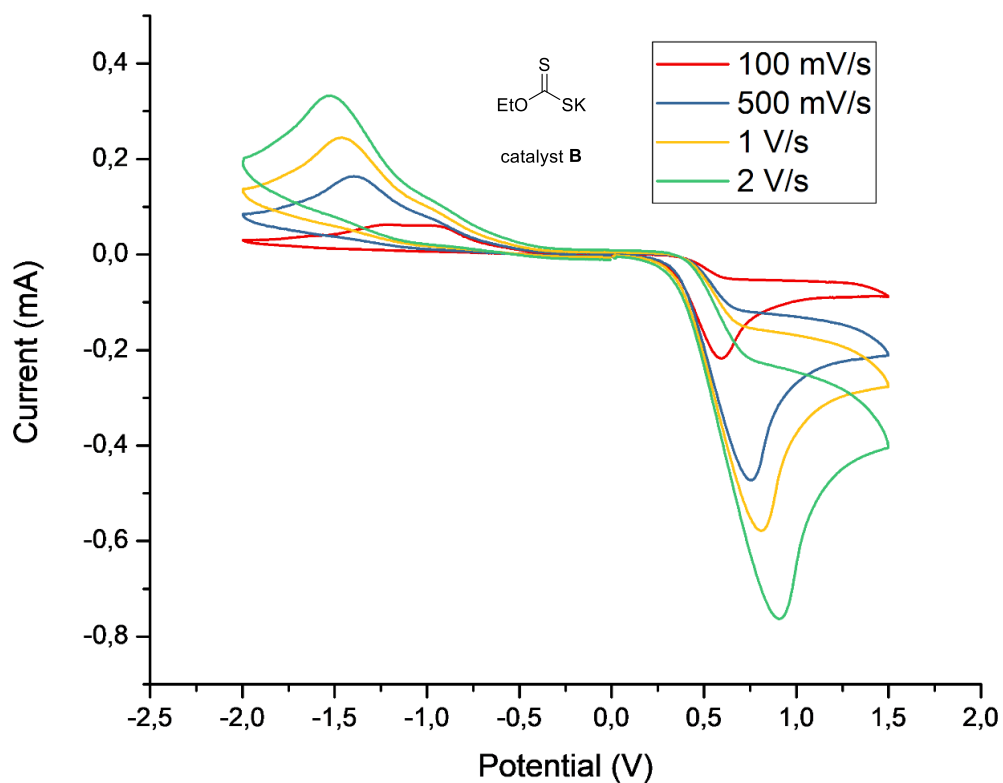


Figure S18: Cyclic voltammogram for catalyst **B** [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Measurement started by oxidation from 0 to +1.5 V, followed by reduction from +1.5 V to -2.0 V, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Two irreversible peaks observed increasing with sweep rate.

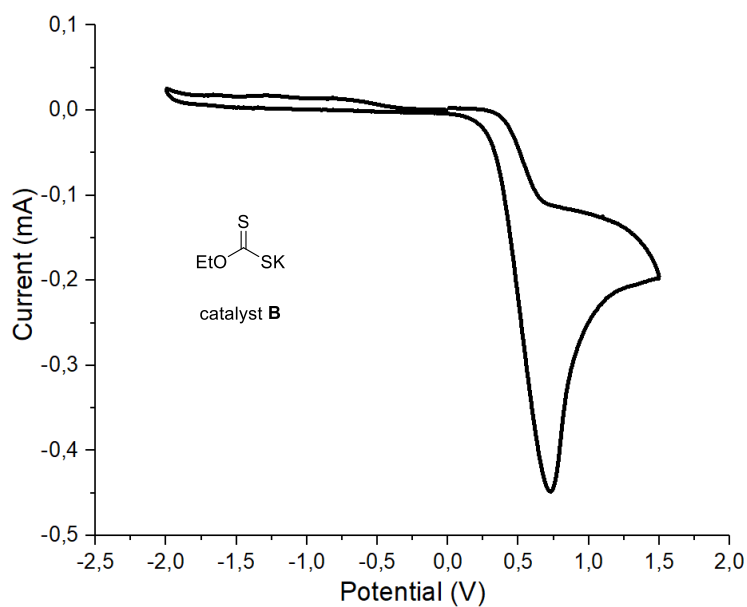


Figure S19: Cyclic voltammogram for catalyst **B** [0.02M] in [0.1 M] TBAPF₆ in CH₃CN. Measurement started by reduction from 0 to -2.0 V, followed by oxidation from -2.0 V to +1.5 V, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Only one irreversible peak observed. Sweep rate: 500 mV/s.

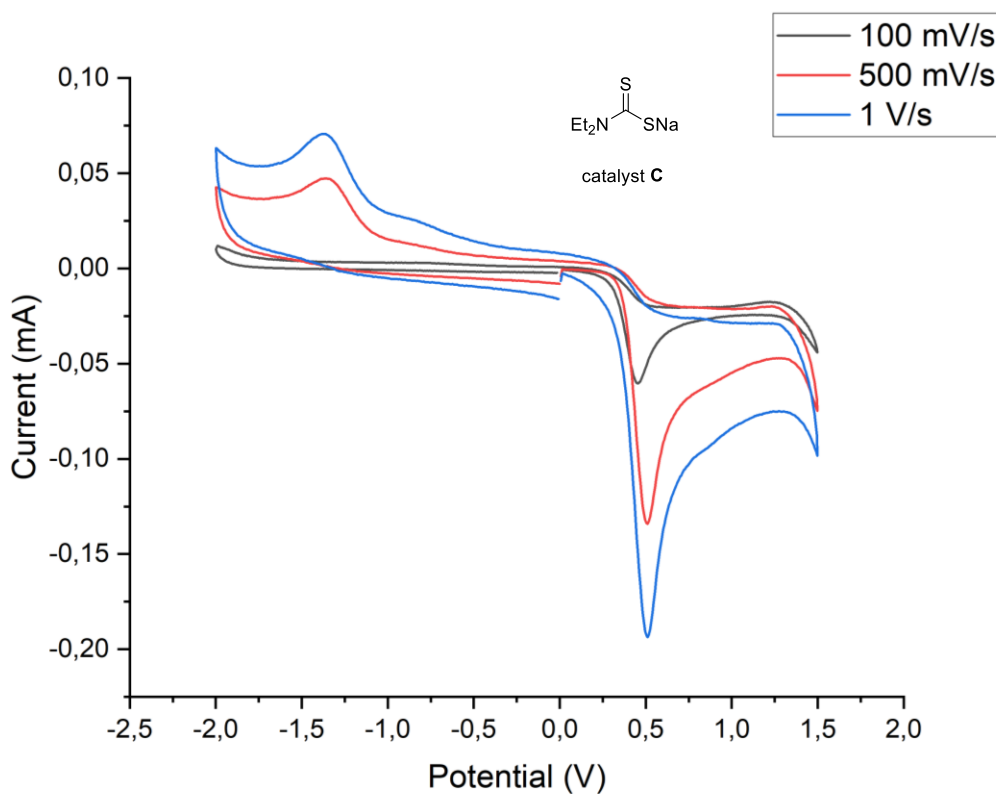


Figure S20: Cyclic voltammogram for catalyst **C** [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Measurement started by oxidation from 0 to +1.5 V, followed by reduction from +1.5 V to -2.0 V, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Two irreversible peaks observed increasing with sweep rate.

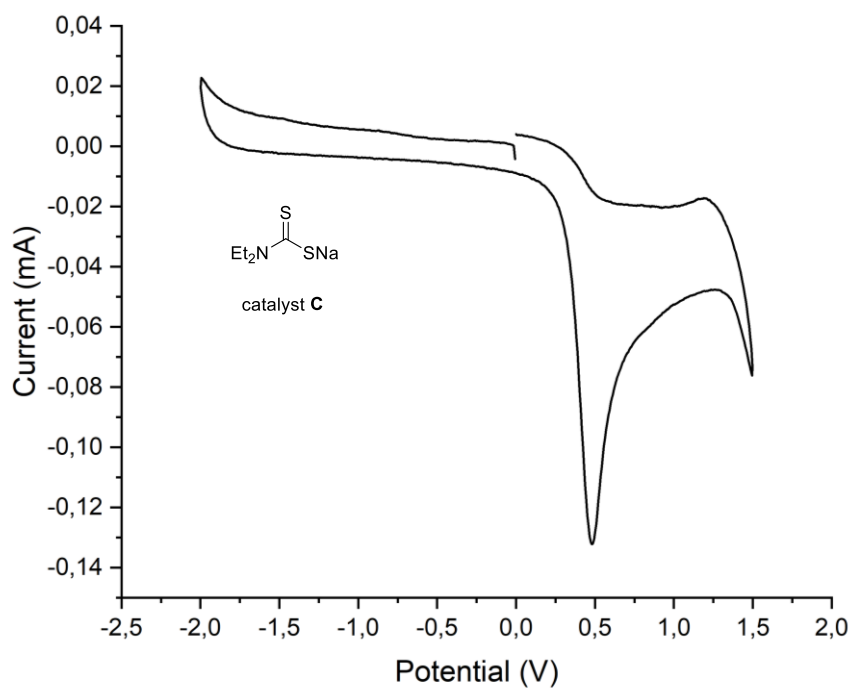


Figure S21: Cyclic voltammogram for catalyst **C** [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Measurement started by reduction from 0 to -2.0 V, followed by oxidation from -2.0 V to +1.5 V, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Only one irreversible peak observed. Sweep rate: 500 mV/s.

D5. Quantum Yield Determination

D5.1 Giese addition

A ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in the Handbook of Photochemistry.³⁴ The ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The following solutions were prepared and stored in a dark laboratory (red light):

1. Potassium ferrioxalate solution: 294.8 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 139 μ L of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water (HPLC grade).
2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask).
3. Buffer solution: 2.47 g of NaOAc and 0.5 mL of sulfuric acid (96%) were added to a 50 mL volumetric flask and filled to the mark with water (HPLC grade).

The actinometry measurements were done as follows:

1. 1 mL of the actinometer solution was added to a Schlenk tube (diameter = 12 mm). The Schlenk tube was placed in one of the positions of the 3D printed reactor (Figure S2). The solution was irradiated at 460 nm. This procedure was repeated 4 times, quenching the solutions after different time intervals: 1 sec, 2 sec, 4 sec, and 8 sec.
2. Then 1 mL of the model reaction following general procedure A with **1a** (0.10 mmol) and **2a** as substrates was placed in a Schlenk tube, degassed via argon bubbling, placed in the irradiation set up and irradiated for 15 minutes. This procedure was performed a total of four times with different irradiation times (30 min, 45 min, 60 min).
3. After irradiation, the actinometer solutions were removed and placed in a 10 mL volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. These flasks were filled to the mark with water (HPLC grade).
4. The UV-Vis spectra of the complexed actinometer samples were recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm.

The moles of Fe^{2+} formed for each sample is determined using Beers' Law (Eq. 1):

$$\text{Mols of Fe(II)} = V_1 \times V_3 \times \Delta A(510 \text{ nm}) / 10^3 \times V_2 \times l \times \epsilon(510 \text{ nm}) \text{ (Eq. 1)}$$

where V_1 is the irradiated volume (1 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), $\Delta A(510 \text{ nm})$ is the optical difference in absorbance between the irradiated solution and the one stored in the dark, $\epsilon(510 \text{ nm})$ is the extinction coefficient the complex Fe(phen)_3^{2+} at 510 nm (11100 L mol⁻¹ cm⁻¹). The moles of Fe^{2+} formed (x) are plotted as a function of time (t). The slope of this line was correlated to the moles of incident photons by unit of time (q_0 n,p) by the use of the following Equation 2:

$$\Phi(\lambda) = dx/dt \cdot q_{n,p} / [1 - 10^{-A(\lambda)}] \text{ (Eq. 2)}$$

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe^{2+} at 458 nm is 1.1,³⁵ $[1 - 10^{-A(\lambda)}]$ is the ratio of absorbed photons by the solution, and $A(\lambda)$ is the absorbance of the actinometer at the wavelength used to carry out the experiments (460 nm). The absorbance at 460 nm $A(460)$ was measured using a Shimadzu

2401PC UV-Vis spectrophotometer in a 10 mm path quartz cuvette, obtaining an absorbance of 0.183. $q_{n,p}^0$, which is the photon flux, was determined to be 5.3×10^{-7} .

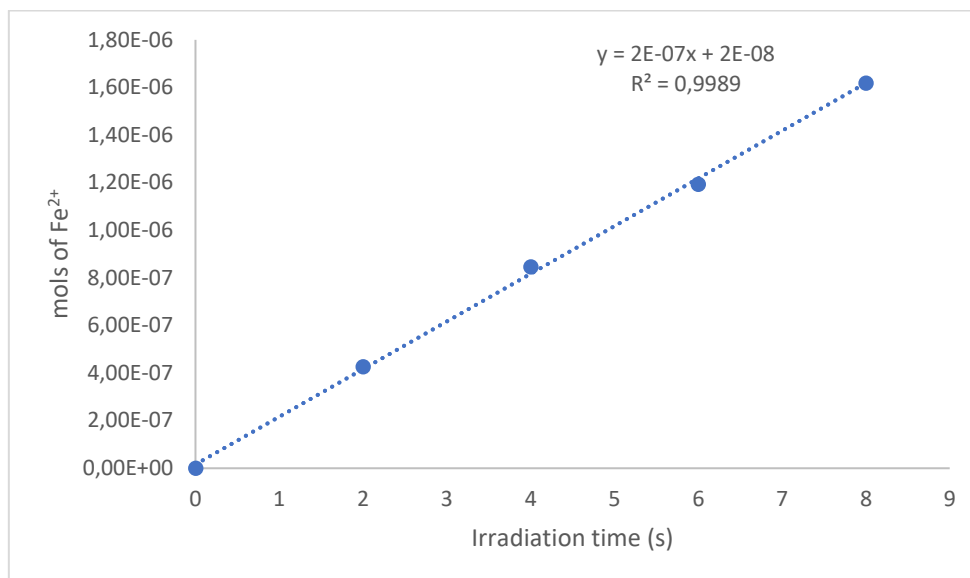


Figure S22: Plot of mols of Fe²⁺ formed vs irradiation time. Slope of the line correlates to the moles of incident photons by unit of time.

The moles of product **3a** formed for the model reaction were determined by GC measurement (FID detector) using 1,3,5-trimethoxybenzene as internal standard. The moles of product per unit of time are related to the number of photons absorbed.

The photons absorbed are correlated to the number of incident photons by the use of Equation 1. According to this, if we plot the moles of product (y) versus the moles of incident photons ($q_{n,p}^0 \cdot dt$), the slope is equal to: $\Phi \cdot (1 - 10^{-A(460 \text{ nm})})$, where Φ is the quantum yield to be determined and $A(460 \text{ nm})$ is the absorption of the reaction under study. $A(460 \text{ nm})$ was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 10 mm path quartz. An absorbance of 0.049 was determined for the model reaction mixture (1:4 dilution). The quantum yield (Φ)_{cat.} of the photochemical transformation was measured to be 0.01.

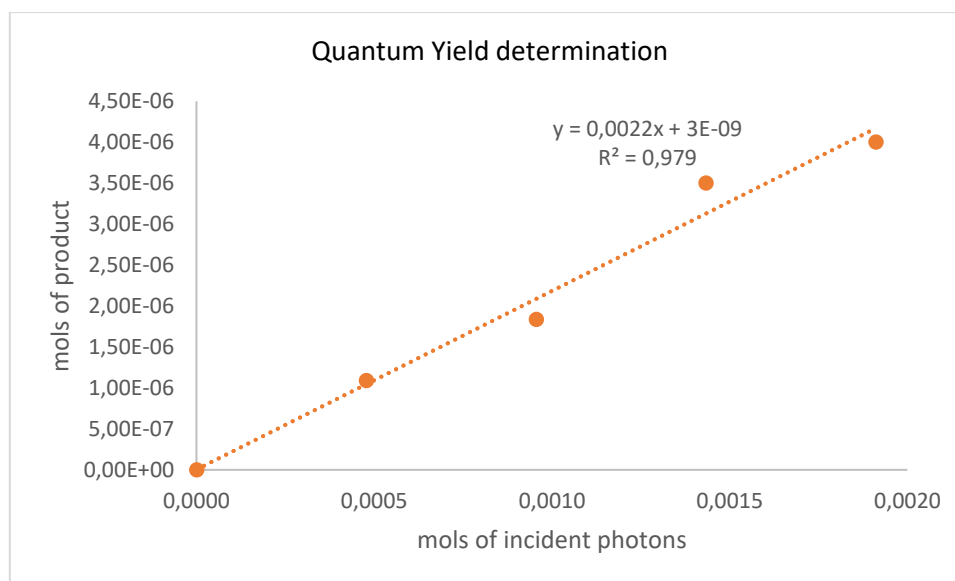


Figure S23: Plot of mols of incident photons vs mols of product formed. Slope of the line correlates to quantum yield of the photochemical transformation.

D5.2 Barton decarboxylation

A ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in the Handbook of Photochemistry.³⁴ The ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The following solutions were prepared and stored in a dark laboratory (red light):

1. Potassium ferrioxalate solution: 294.8 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 139 μ L of sulfuric acid (96%) were added to a 50 mL volumetric flask and filled to the mark with water (HPLC grade).
2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask).
3. Buffer solution: 2.47 g of NaOAc and 0.5 mL of sulfuric acid (96%) were added to a 50 mL volumetric flask and filled to the mark with water (HPLC grade).

The actinometry measurements were done as follows:

1. 1 mL of the actinometer solution was added to a Schlenk tube (diameter = 12 mm). The Schlenk tube was placed in one of the positions of the 3D printed reactor (Figure S2). The solution was irradiated at 460 nm. This procedure was repeated 4 times, quenching the solutions after different time intervals: 1 sec, 2 sec, 4 sec, and 8 sec.
2. Then 1 mL of the model reaction following general procedure F starting from isolated **1a** (0.10 mmol) as substrate was placed in a Schlenk tube, degassed via argon bubbling, placed in the irradiation set up and irradiated for 15 minutes. This procedure was performed a total of four times with different irradiation times (30 min, 60 min, 120 min).
3. After irradiation, the actinometer solutions were removed and placed in a 10 mL volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. These flasks were filled to the mark with water (HPLC grade).
4. The UV-Vis spectra of the complexed actinometer samples were recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm.

The moles of Fe^{2+} formed for each sample is determined using Beers' Law (Eq. 1) :

$$\text{Mols of Fe(II)} = V_1 \times V_3 \times \Delta A(510 \text{ nm}) / 10^3 \times V_2 \times l \times \epsilon(510 \text{ nm}) \text{ (Eq. 1)}$$

where V_1 is the irradiated volume (1 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), $\Delta A(510 \text{ nm})$ is the optical difference in absorbance between the irradiated solution and the one stored in the dark, $\epsilon(510 \text{ nm})$ is the extinction coefficient the complex Fe(phen)_3^{2+} at 510 nm (11100 L mol⁻¹ cm⁻¹). The moles of Fe^{2+} formed (x) are plotted as a function of time (t). The slope of this line was correlated to the moles of incident photons by unit of time (q_0 n,p) by the use of the following Equation 2:

$$\Phi(\lambda) = dx/dt \cdot q_{n,p} / [1 - 10^{-A(\lambda)}] \text{ (Eq. 2)}$$

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe^{2+} at 458 nm is 1.1,³⁵ $[1 - 10^{-A(\lambda)}]$ is the ratio of absorbed photons by the solution, and $A(\lambda)$ is the absorbance of the actinometer at the wavelength used to carry out the experiments (460 nm). The absorbance at 460 nm $A(460)$ was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in a 10 mm path quartz cuvette, obtaining an absorbance of 0.183. $q_{n,p}^0$, which is the photon flux, was determined to be 5.2×10^{-7} .

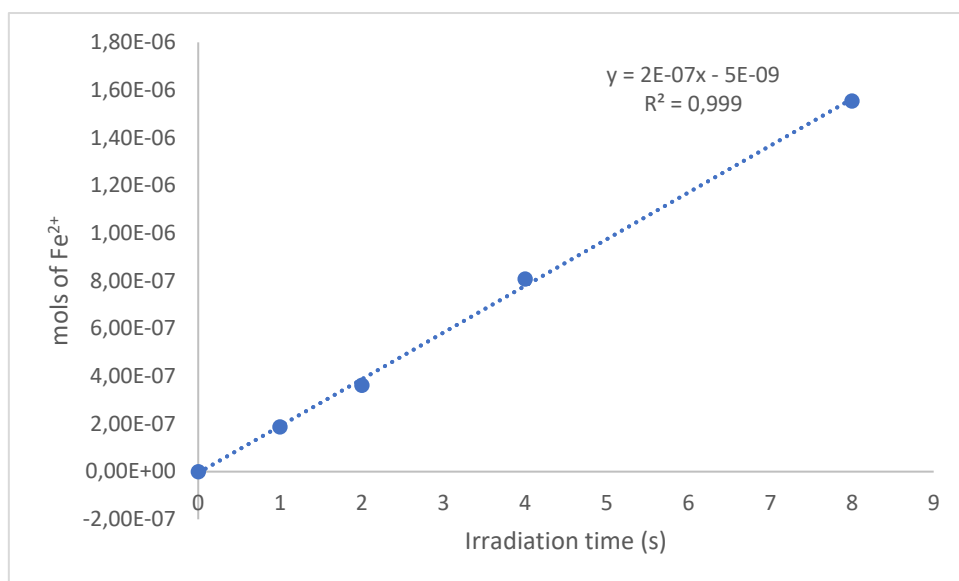


Figure S24: Plot of mols of Fe²⁺ formed vs irradiation time. Slope of the line correlates to the moles of incident photons by unit of time.

The moles of product **6b** formed for the model reaction were determined by GC measurement (FID detector) using 1,3,5-trimethoxybenzene as internal standard. The moles of product per unit of time are related to the number of photons absorbed.

The photons absorbed are correlated to the number of incident photons by the use of Equation 1. According to this, if we plot the moles of product (y) versus the moles of incident photons ($q_0 n_p \cdot dt$), the slope is equal to: $\Phi \cdot (1 - 10^{-A(460 \text{ nm})})$, where Φ is the quantum yield to be determined and $A(460 \text{ nm})$ is the absorption of the reaction under study. $A(460 \text{ nm})$ was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 10 mm path quartz. An absorbance of 0.052 was determined for the model reaction mixture. The quantum yield (Φ)_{cat.} of the photochemical transformation was measured to be 0.01.

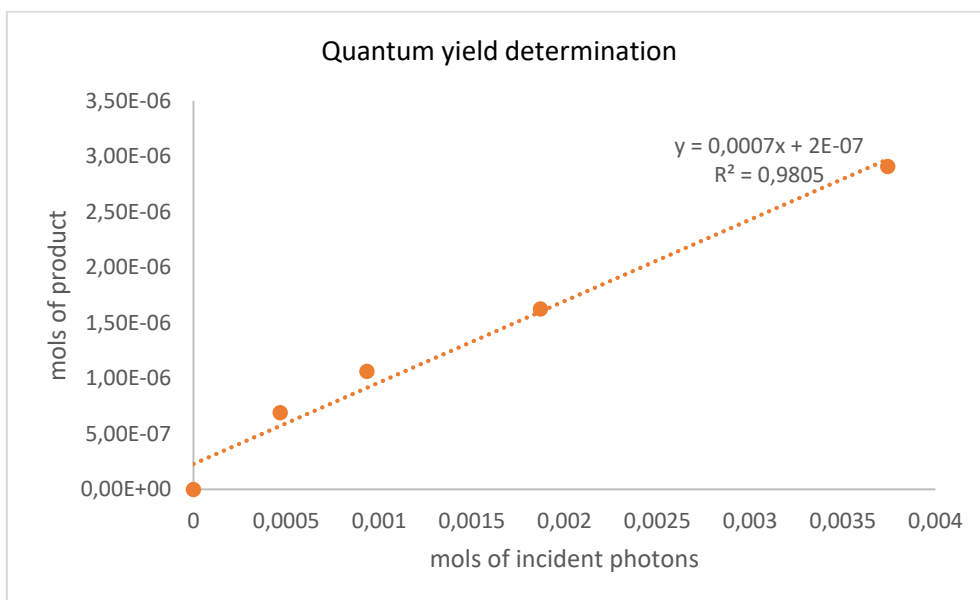


Figure S25: Plot of mols of incident photons vs mols of product formed. Slope of the line correlates to quantum yield of the photochemical transformation.

D5.3 Alkylation enol ethers

A ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in the Handbook of Photochemistry.³⁴ The ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The following solutions were prepared and stored in a dark laboratory (red light):

1. Potassium ferrioxalate solution: 294.8 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 139 μ L of sulfuric acid (96%) were added to a 50 mL volumetric flask and filled to the mark with water (HPLC grade).
2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask).
3. Buffer solution: 2.47 g of NaOAc and 0.5 mL of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water (HPLC grade).

The actinometry measurements were done as follows:

1. 1 mL of the actinometer solution was added to a Schlenk tube (diameter = 12 mm). The Schlenk tube was placed in a single HP LED 1.5 cm away from the light source (irradiance 10 mW/cm²).¹² The solution was irradiated at 460 nm. This procedure was repeated 4 times, quenching the solutions after different time intervals: 5 sec, 10 sec, 20 sec, and 40 sec.
2. Then 1 mL of the model reaction following general procedure H with **7a** (0.10 mmol) and **4l** as substrates was placed in a Schlenk tube, degassed via argon bubbling, placed in the irradiation set up and irradiated for 15 minutes. This procedure was performed a total of four times with different irradiation times (30 min, 50 min, 70 min).
3. After irradiation, the actinometer solutions were removed and placed in a 10 mL volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. These flasks were filled to the mark with water (HPLC grade).
4. The UV-Vis spectra of the complexed actinometer samples were recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm.

The moles of Fe²⁺ formed for each sample is determined using Beers' Law (Eq. 1):

$$\text{Mols of Fe(II)} = V_1 \times V_3 \times \Delta A(510 \text{ nm}) / 10^3 \times V_2 \times l \times \epsilon(510 \text{ nm}) \text{ (Eq. 1)}$$

where V_1 is the irradiated volume (1 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), $\Delta A(510 \text{ nm})$ is the optical difference in absorbance between the irradiated solution and the one stored in the dark, $\epsilon(510 \text{ nm})$ is the extinction coefficient the complex Fe(phen)₃²⁺ at 510 nm (11100 L mol⁻¹ cm⁻¹). The moles of Fe²⁺ formed (x) are plotted as a function of time (t). The slope of this line was correlated to the moles of incident photons by unit of time (q_0 n.p) by the use of the following Equation 2:

$$\Phi(\lambda) = dx/dt \ q_{n,p}^0 [1 - 10^{-A(\lambda)}] \text{ (Eq. 2)}$$

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe²⁺ at 458 nm is 1.1,³⁵ $[1 - 10^{-A(\lambda)}]$ is the ratio of absorbed photons by the solution, and $A(\lambda)$ is the absorbance of the actinometer at the wavelength used to carry out the experiments (460 nm). The absorbance at 460 nm $A(460)$ was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in a 10 mm path quartz cuvette, obtaining an absorbance of 0.148. $q_{n,p}^0$, which is the photon flux, was determined to be 1.18×10^{-7} .

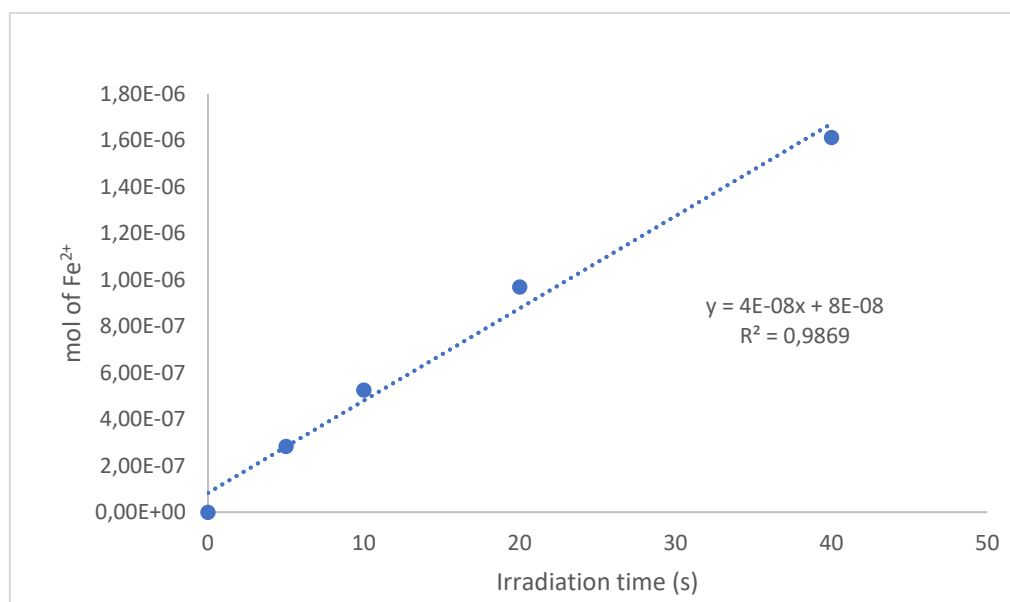


Figure S26: Plot of moles of Fe²⁺ formed vs irradiation time. Slope of the line correlates to the moles of incident photons by unit of time.

The moles of product **8h** formed for the model reaction were determined by GC measurement (FID detector) using 1,3,5-trimethoxybenzene as internal standard. The moles of product per unit of time are related to the number of photons absorbed.

The photons absorbed are correlated to the number of incident photons by the use of Equation 1. According to this, if we plot the moles of product (y) versus the moles of incident photons (q₀ n_p·dt), the slope is equal to: $\Phi \cdot (1 - 10^{-A(460 \text{ nm})})$, where Φ is the quantum yield to be determined and A(460 nm) is the absorption of the reaction under study. A(460 nm) was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 10 mm path quartz. An absorbance of 0.018 was determined for the model reaction mixture (1:100 dilution). The quantum yield (Φ)_{cat.} of the photochemical transformation was measured to be 0.02.

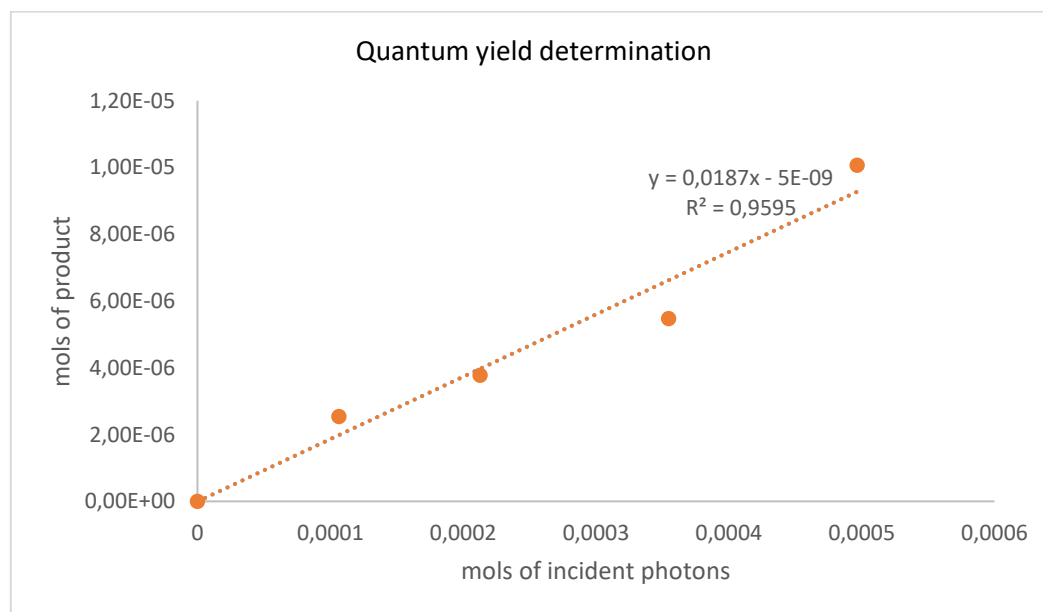


Figure S27: Plot of moles of incident photons vs moles of product formed. Slope of the line correlates to quantum yield of the photochemical transformation.

D5.4 Minisci reaction

A ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in the Handbook of Photochemistry.³⁴ The ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The following solutions were prepared and stored in a dark laboratory (red light):

1. Potassium ferrioxalate solution: 294.8 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 139 μ L of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water (HPLC grade).
2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask).
3. Buffer solution: 2.47 g of NaOAc and 0.5 mL of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water (HPLC grade).

The actinometry measurements were done as follows:

1. 1 mL of the actinometer solution was added to a Schlenk tube (diameter = 12 mm). The Schlenk tube was placed in one of the position of the 3D printed reactor (Figure S2). The solution was irradiated at 460 nm. This procedure was repeated 4 times, quenching the solutions after different time intervals: 1 sec, 2 sec, 4 sec, and 8 sec.
2. Then 1 mL of the model reaction following general procedure J with **1a** (0.10 mmol) and 2-methylquinoline as substrates was placed in a Schlenk tube, degassed via argon bubbling, placed in the irradiation set up and irradiated for 60 minutes. This procedure was performed a total of four times with different irradiation times (90 min, 120 min, 150 min).
3. After irradiation, the actinometer solutions were removed and placed in a 10 mL volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. These flasks were filled to the mark with water (HPLC grade).
4. The UV-Vis spectra of the complexed actinometer samples were recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm.

The moles of Fe^{2+} formed for each sample is determined using Beers' Law (Eq. 1) :

$$\text{Mols of Fe(II)} = V_1 \times V_3 \times \Delta A(510 \text{ nm}) / 10^3 \times V_2 \times l \times \epsilon(510 \text{ nm}) \text{ (Eq. 1)}$$

where V_1 is the irradiated volume (1 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), $\Delta A(510 \text{ nm})$ is the optical difference in absorbance between the irradiated solution and the one stored in the dark, $\epsilon(510 \text{ nm})$ is the extinction coefficient the complex Fe(phen)_3^{2+} at 510 nm (11100 L mol⁻¹ cm⁻¹). The moles of Fe^{2+} formed (x) are plotted as a function of time (t). The slope of this line was correlated to the moles of incident photons by unit of time (q_0 n,p) by the use of the following Equation 2:

$$\Phi(\lambda) = dx/dt \cdot q_{n,p} / [1 - 10^{-A(\lambda)}] \text{ (Eq. 2)}$$

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe^{2+} at 458 nm is 1.1,³⁵ $[1 - 10^{-A(\lambda)}]$ is the ratio of absorbed photons by the solution, and $A(\lambda)$ is the absorbance of the actinometer at the wavelength used to carry out the experiments (460 nm). The absorbance at 460 nm $A(460)$ was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in a 10 mm path quartz cuvette, obtaining an absorbance of 0.183. $q_{n,p}^0$, which is the photon flux, was determined to be 4.68×10^{-7} .

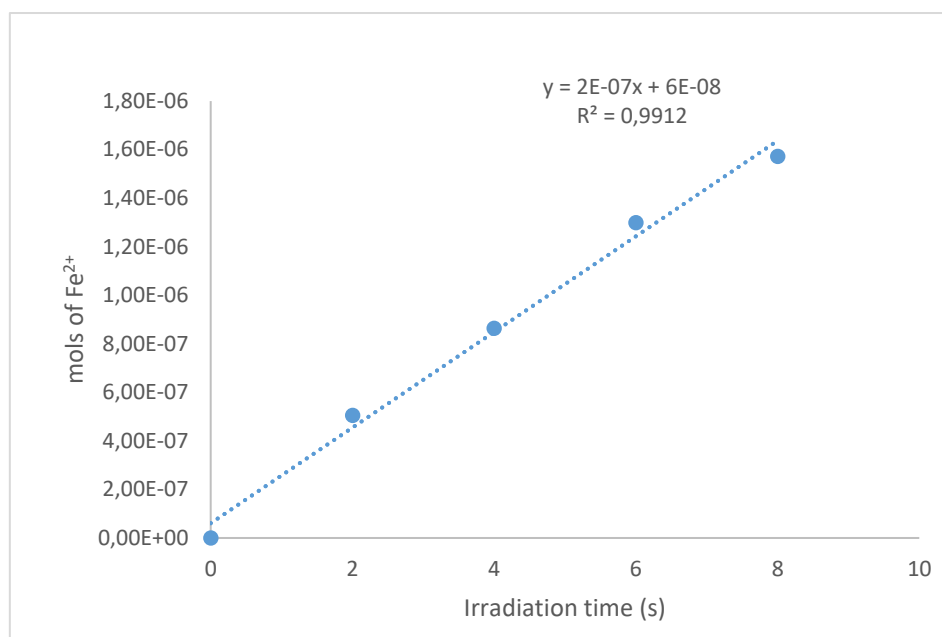


Figure S28: Plot of mols of Fe²⁺ formed vs irradiation time. Slope of the line correlates to the moles of incident photons by unit of time.

The moles of product **11b** formed for the model reaction were determined by GC measurement (FID detector) using 1,3,5-trimethoxybenzene as internal standard. The moles of product per unit of time are related to the number of photons absorbed.

The photons absorbed are correlated to the number of incident photons by the use of Equation 1. According to this, if we plot the moles of product (y) versus the moles of incident photons ($q_0 n_p \cdot dt$), the slope is equal to: $\Phi \cdot (1 - 10^{-A(460 \text{ nm})})$, where Φ is the quantum yield to be determined and $A(460 \text{ nm})$ is the absorption of the reaction under study. $A(460 \text{ nm})$ was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 10 mm path quartz. An absorbance of 0.174 was determined for the model reaction mixture (1:10 dilution). The quantum yield (Φ)_{cat.} of the photochemical transformation was measured to be 0.0003.

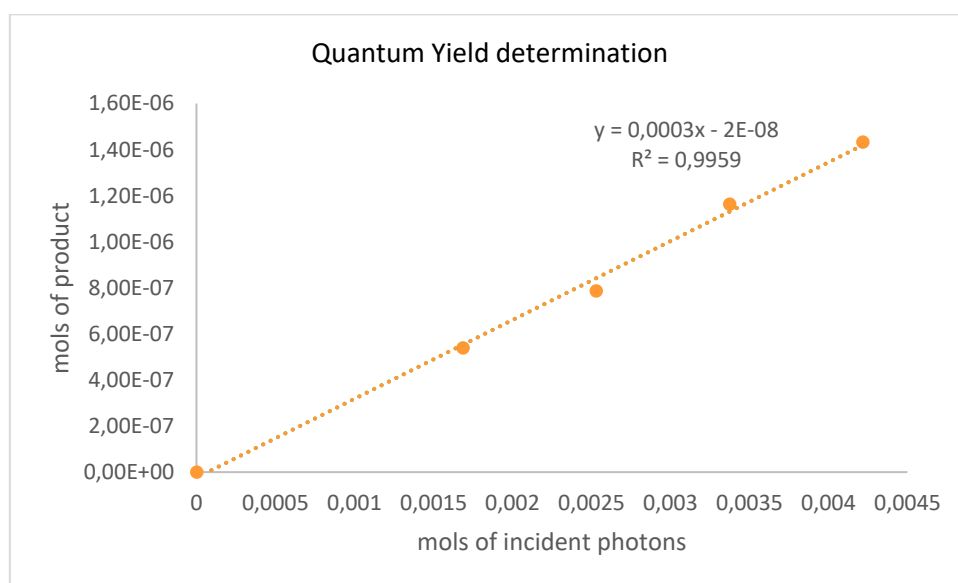


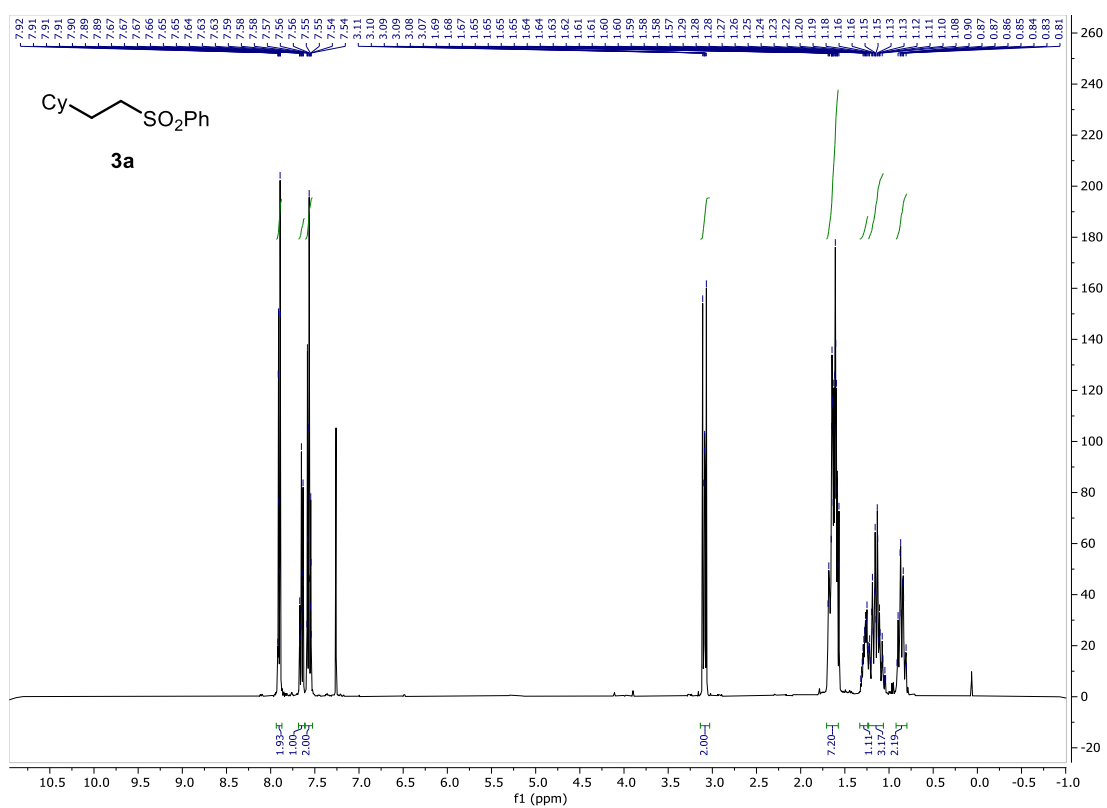
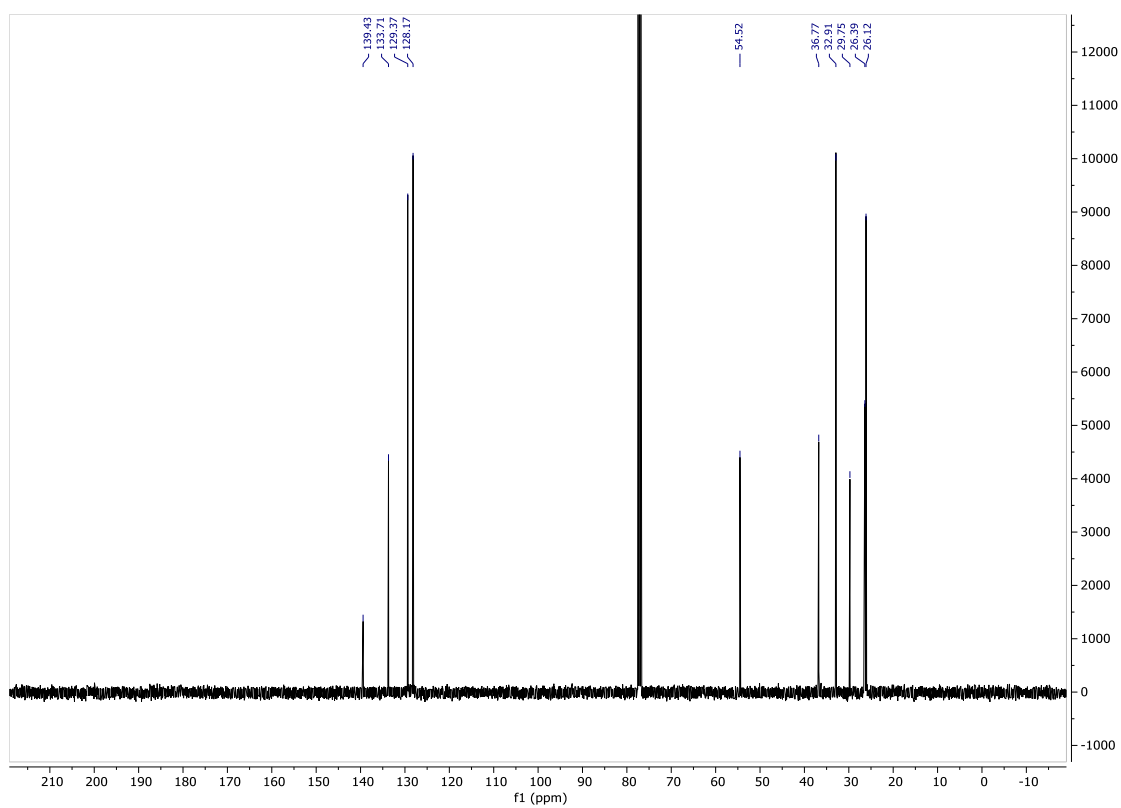
Figure S29: Plot of mols of incident photons vs mols of product formed. Slope of the line correlates to quantum yield of the photochemical transformation.

E. References

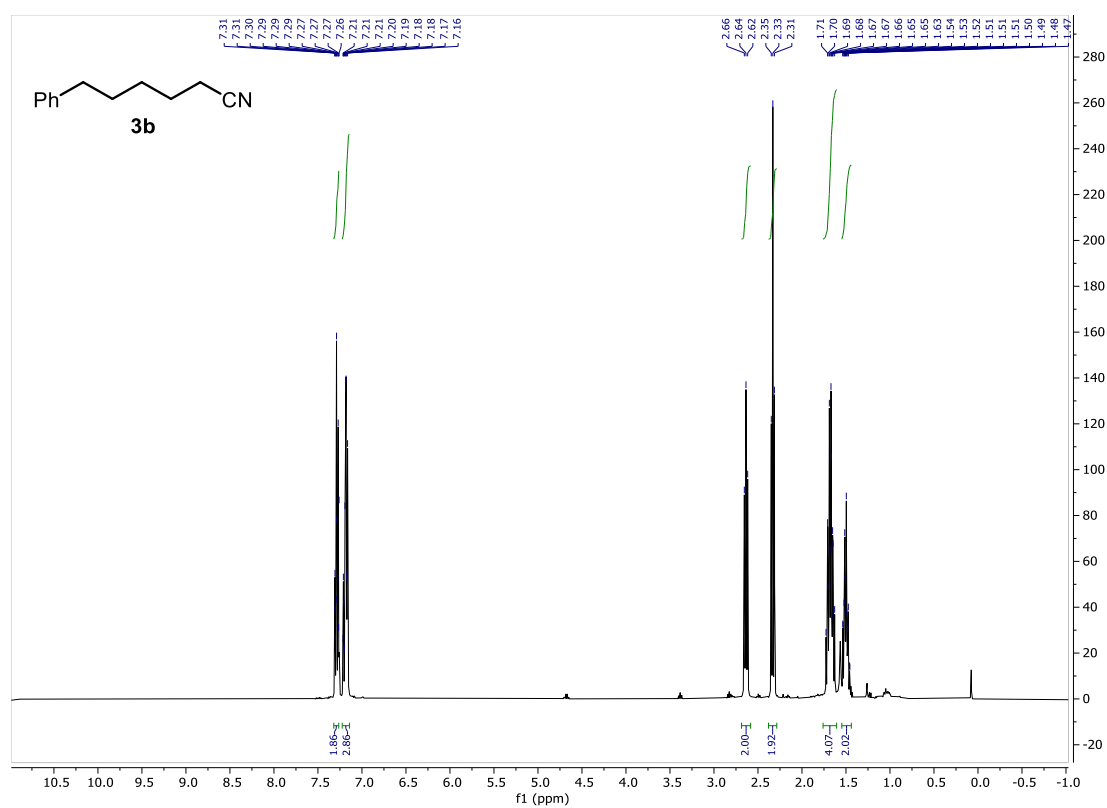
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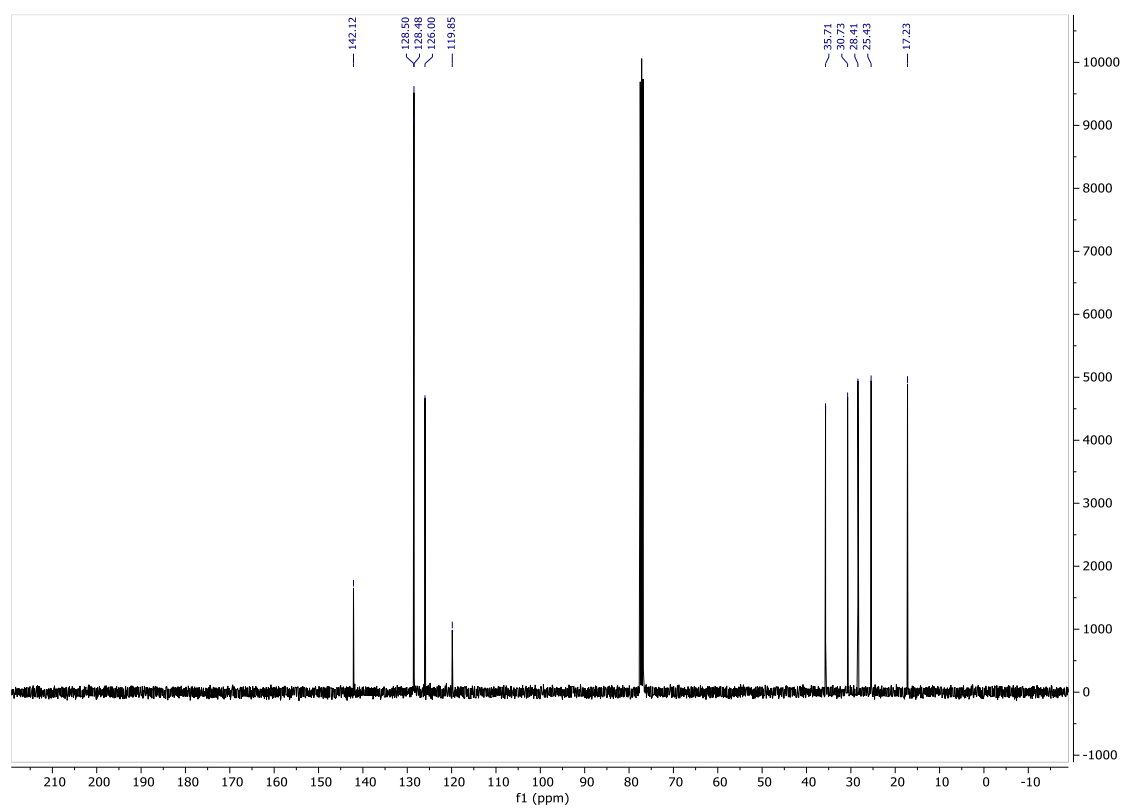
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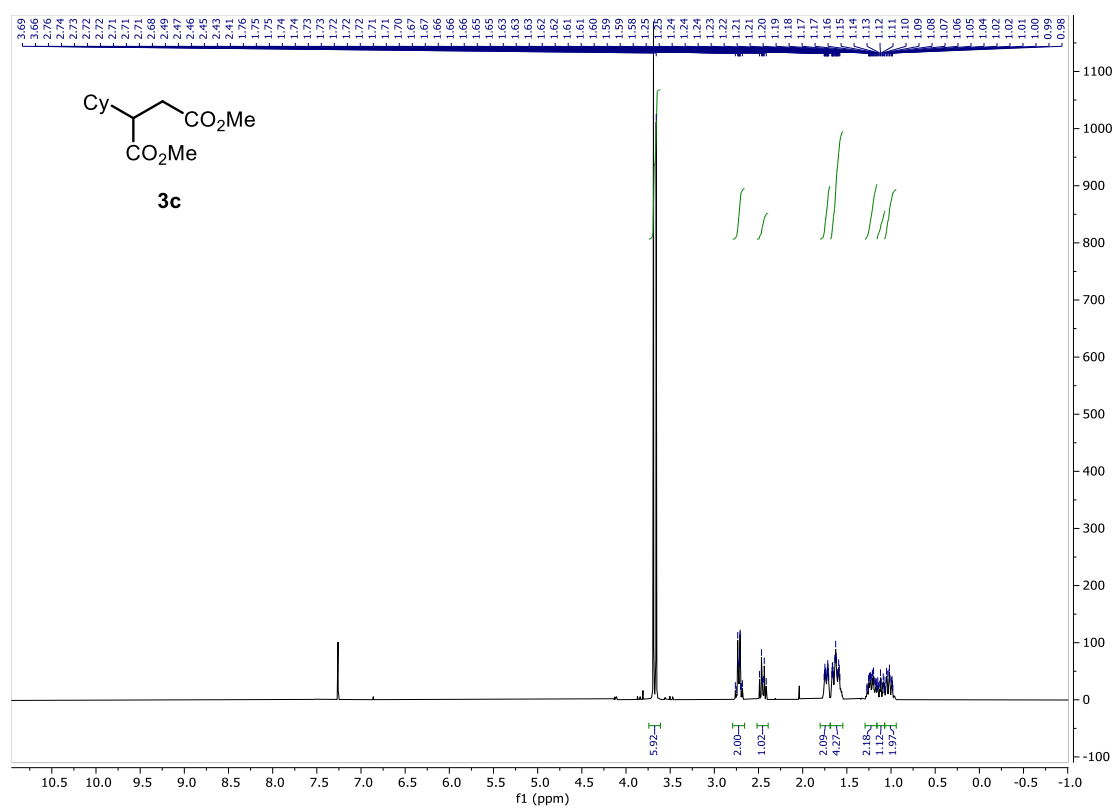
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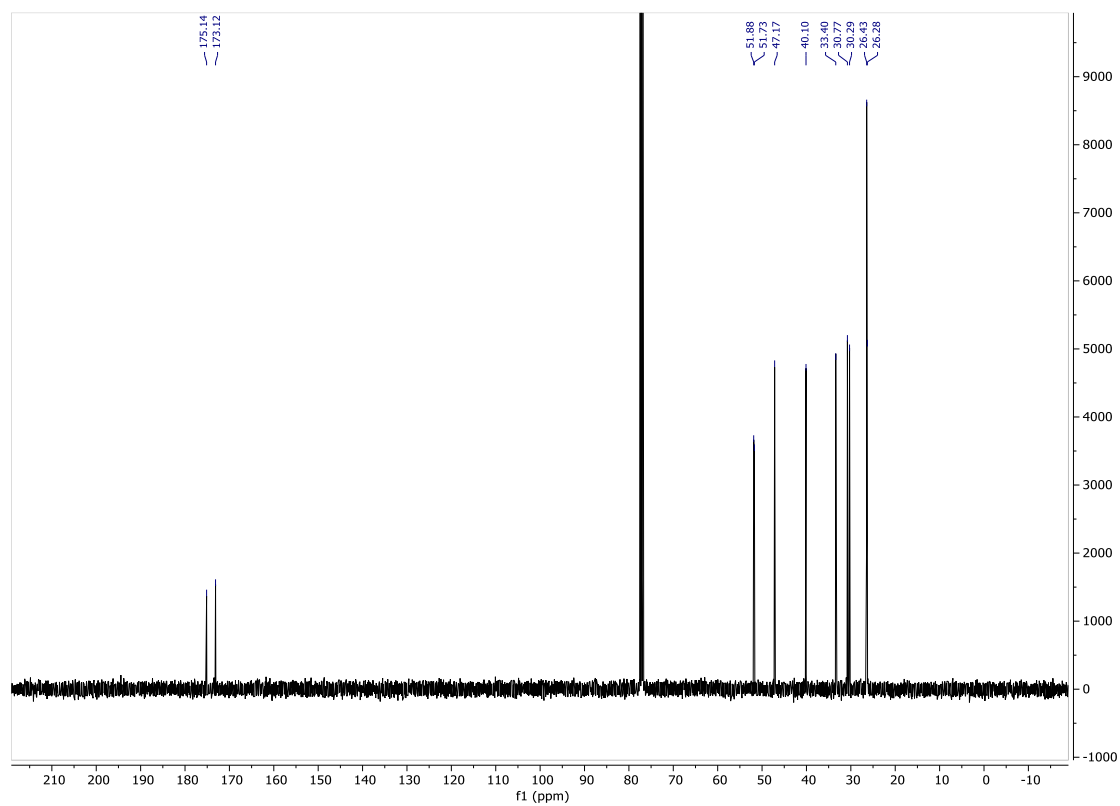
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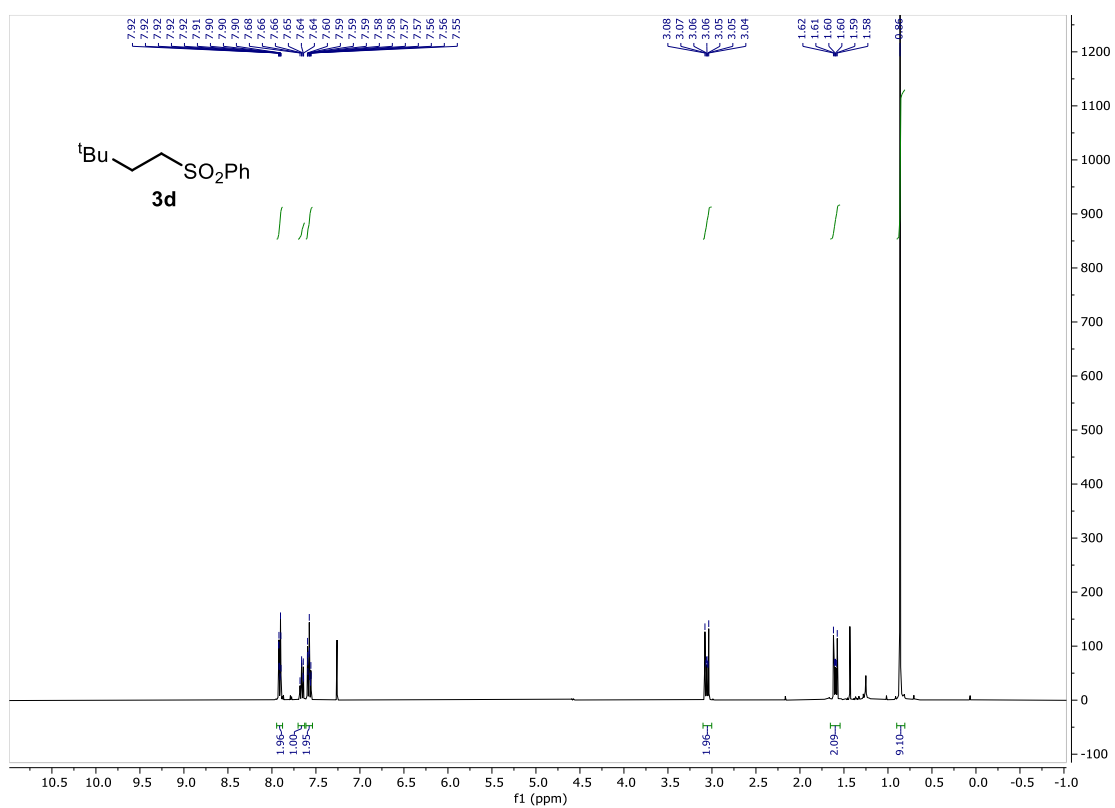
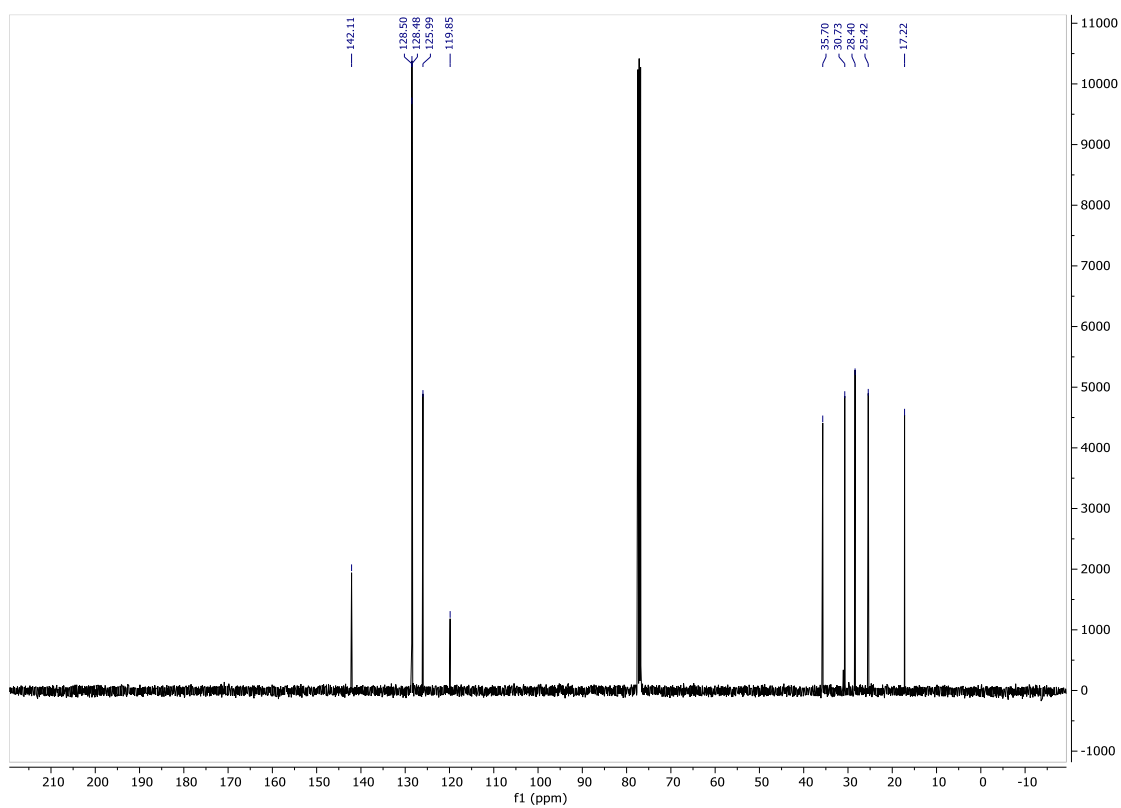


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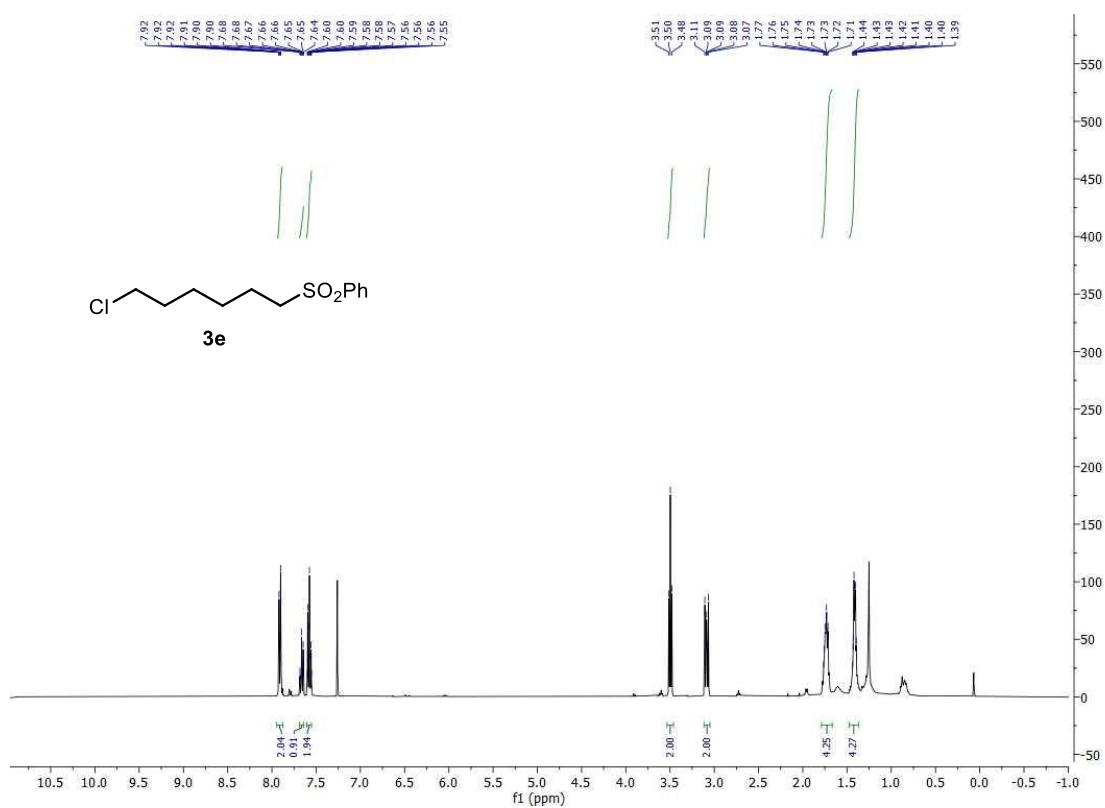


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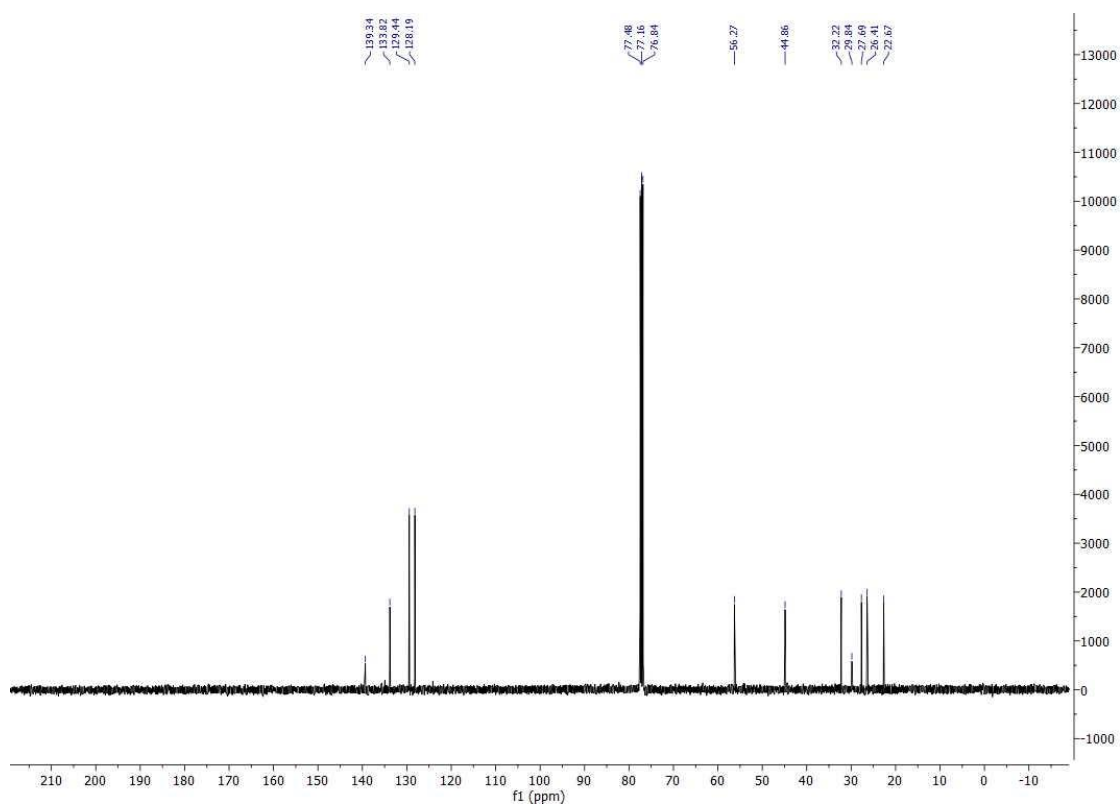


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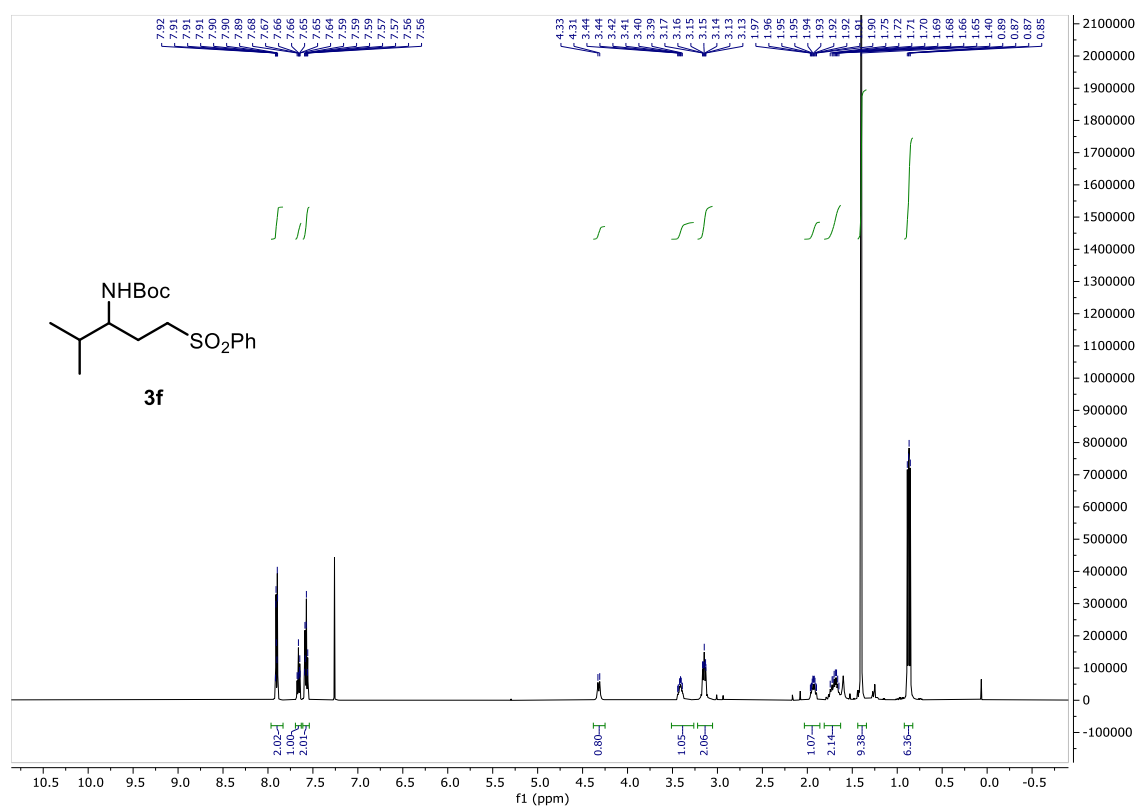
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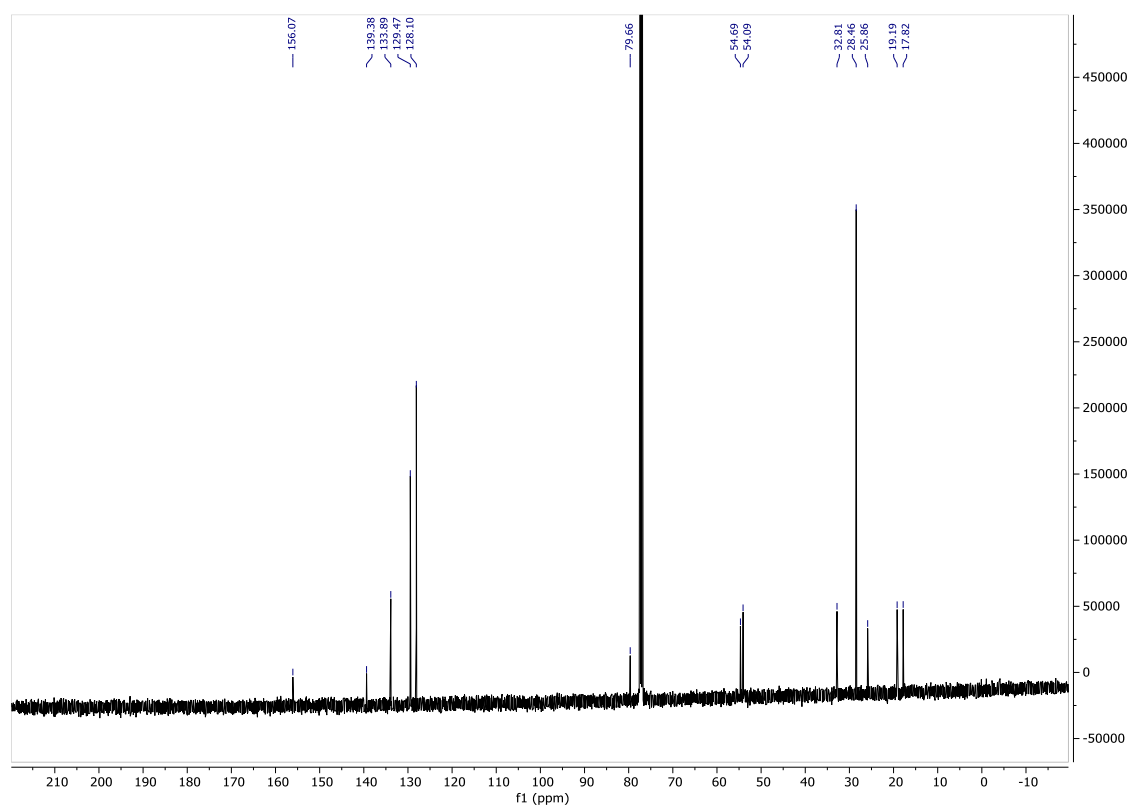
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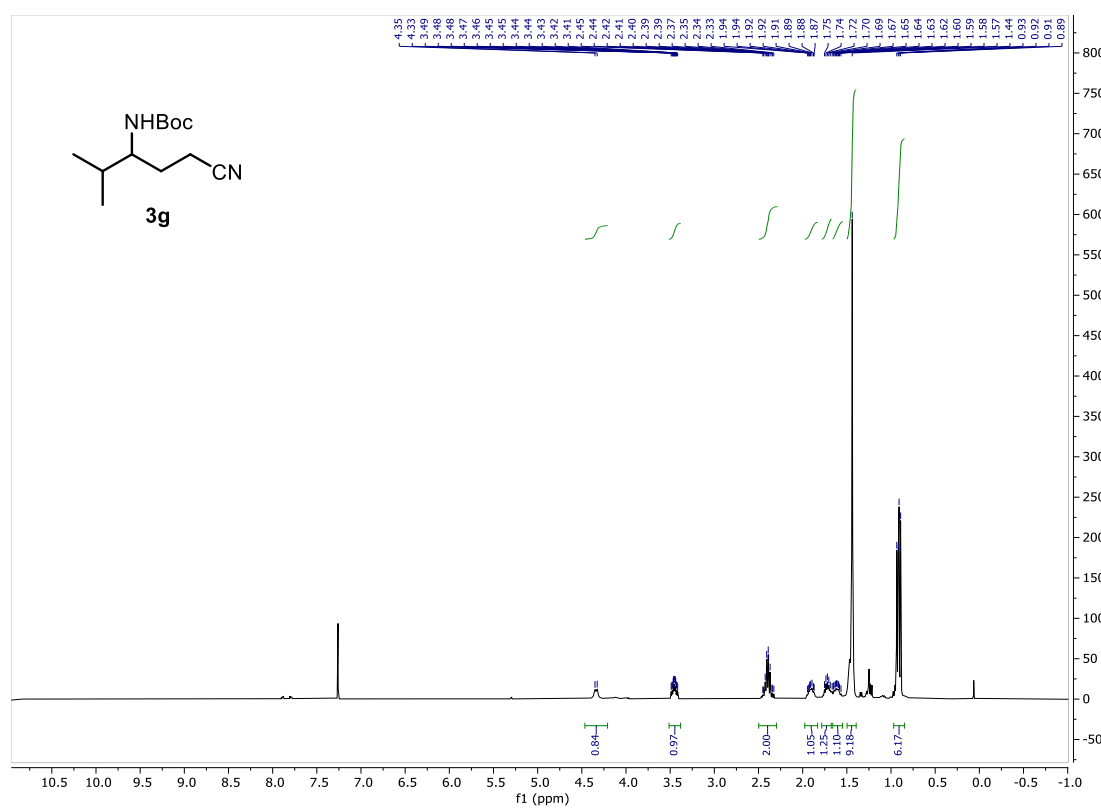
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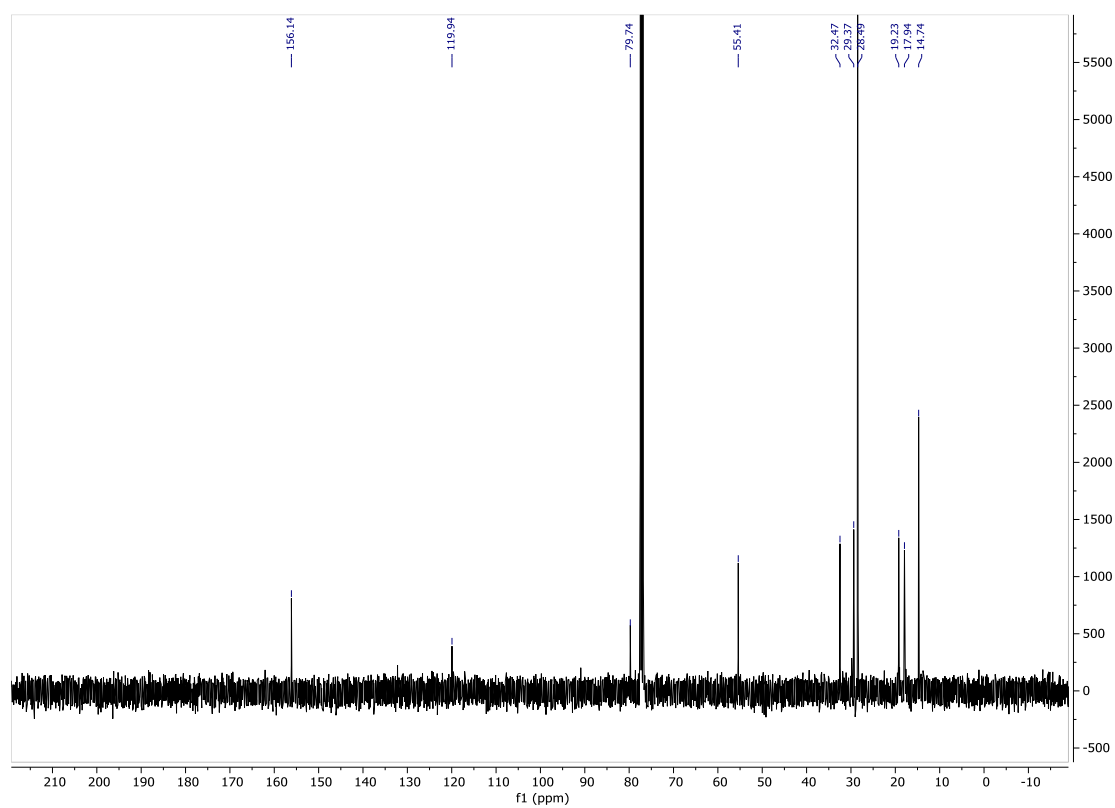
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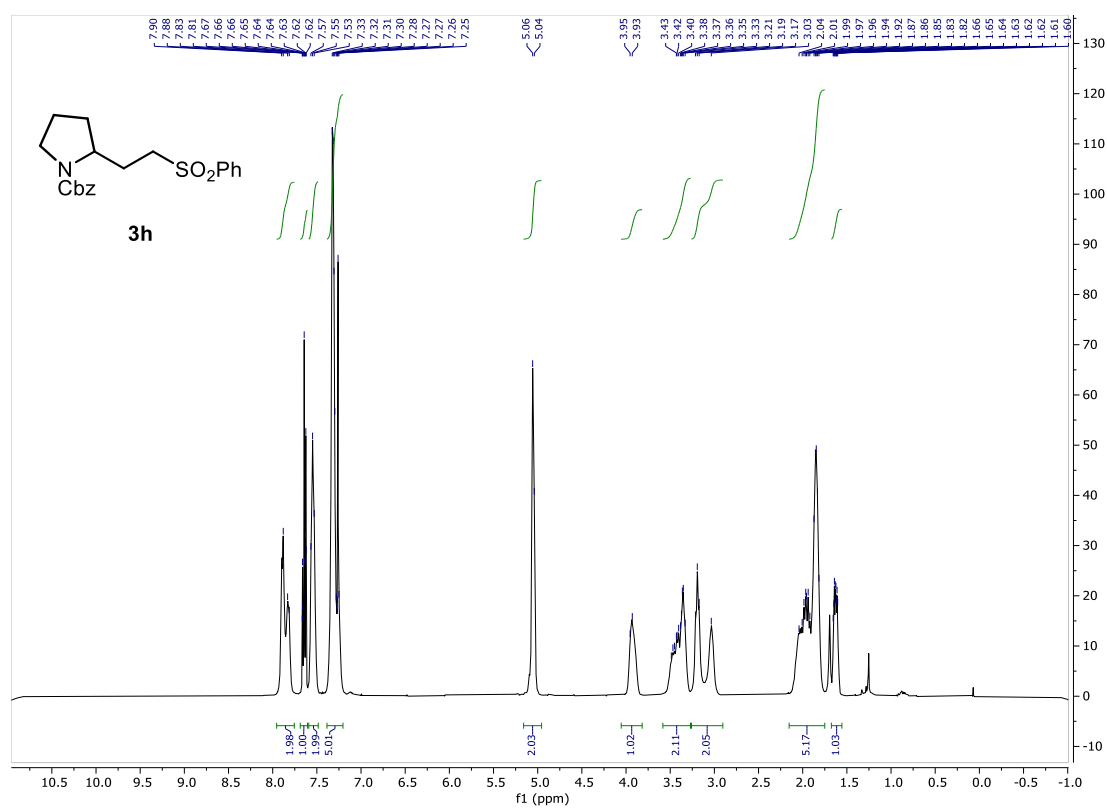
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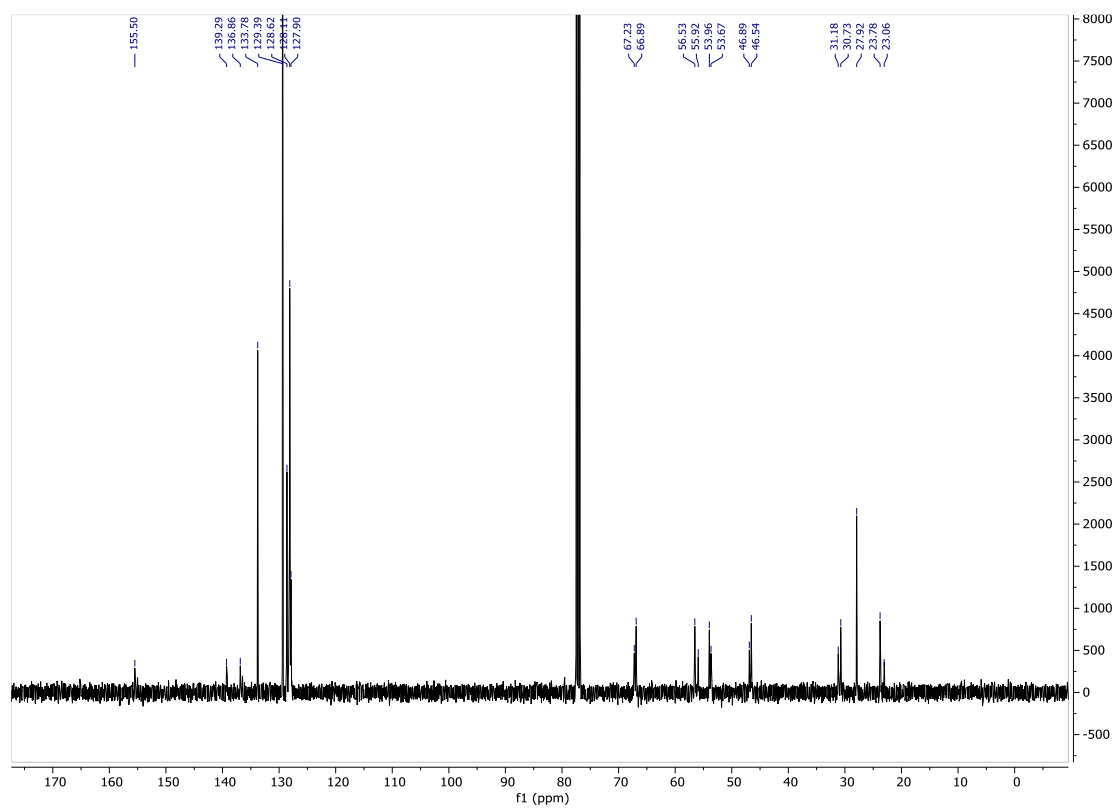
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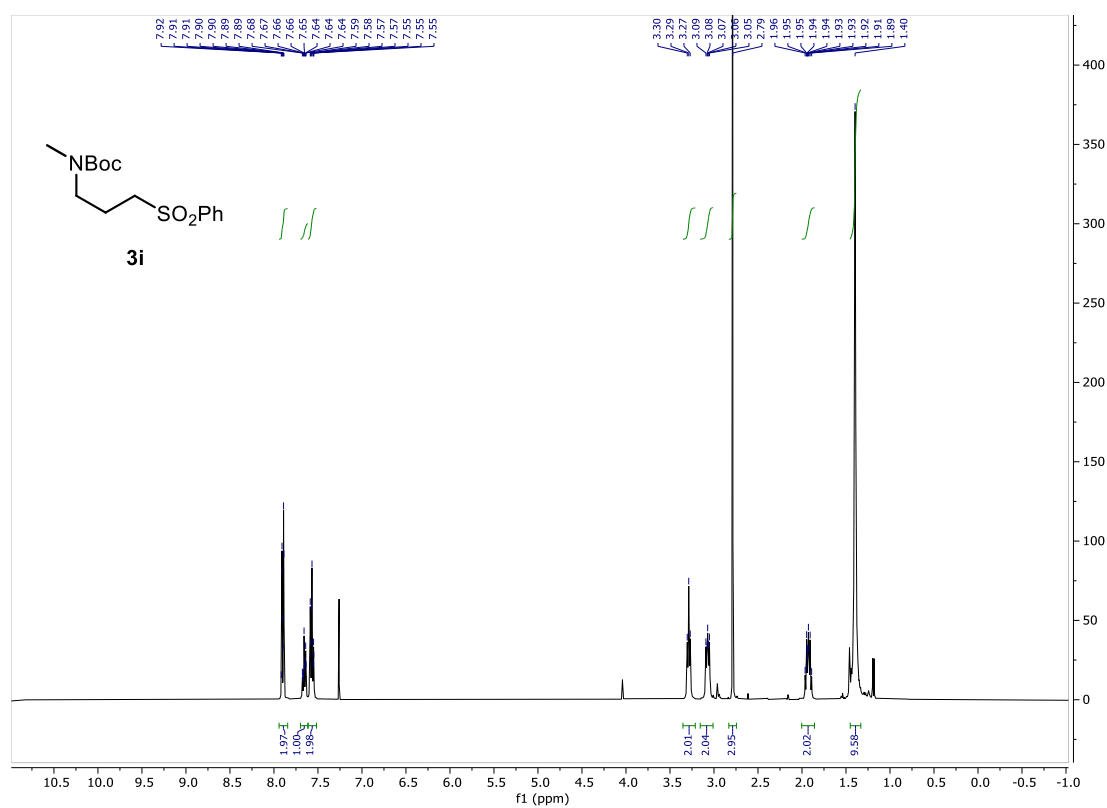
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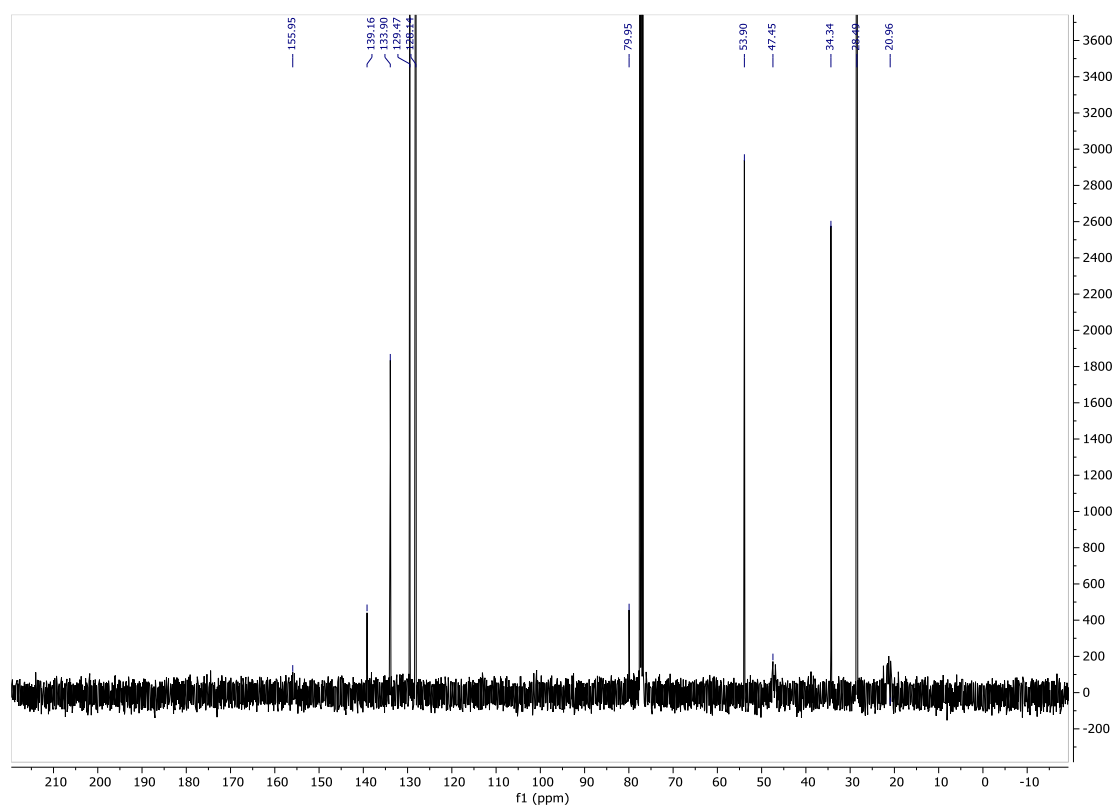
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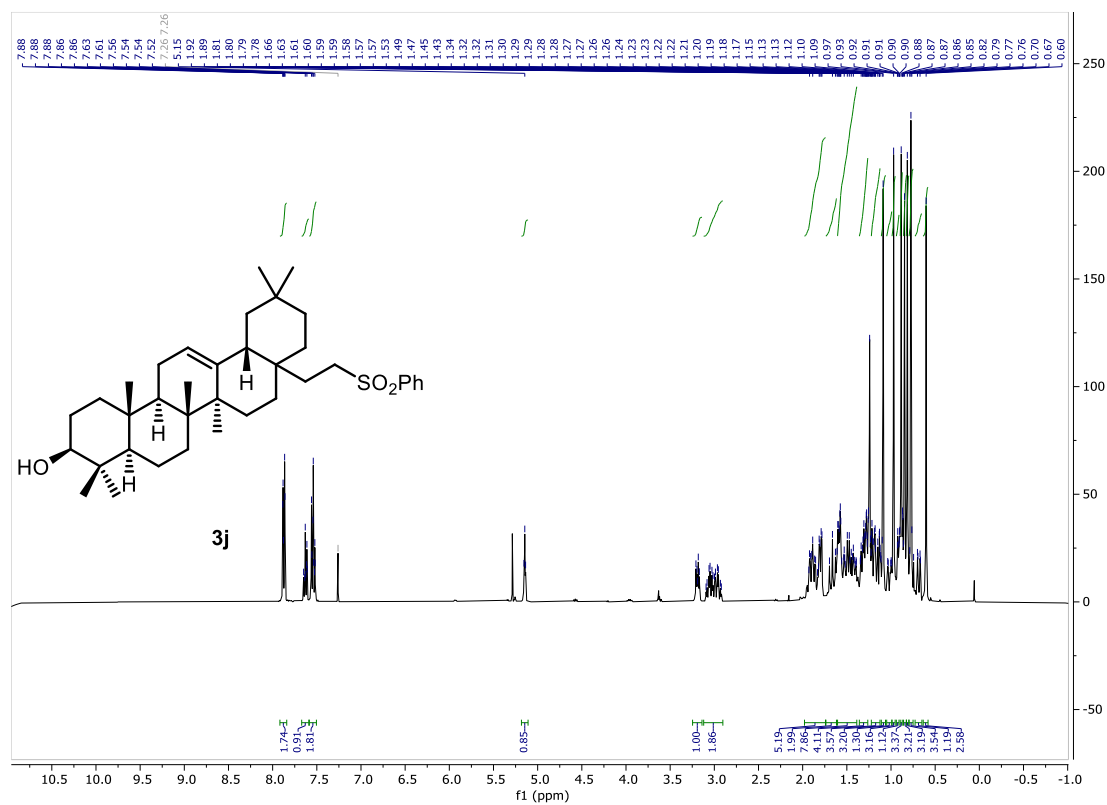
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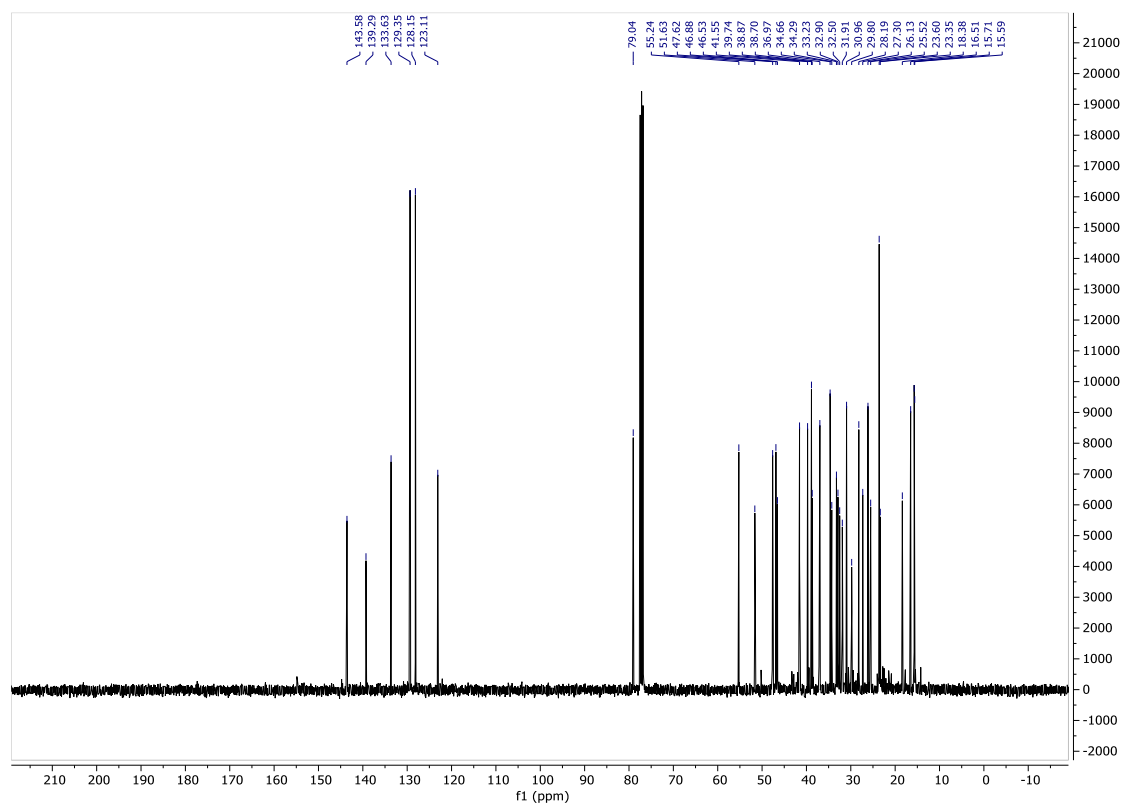
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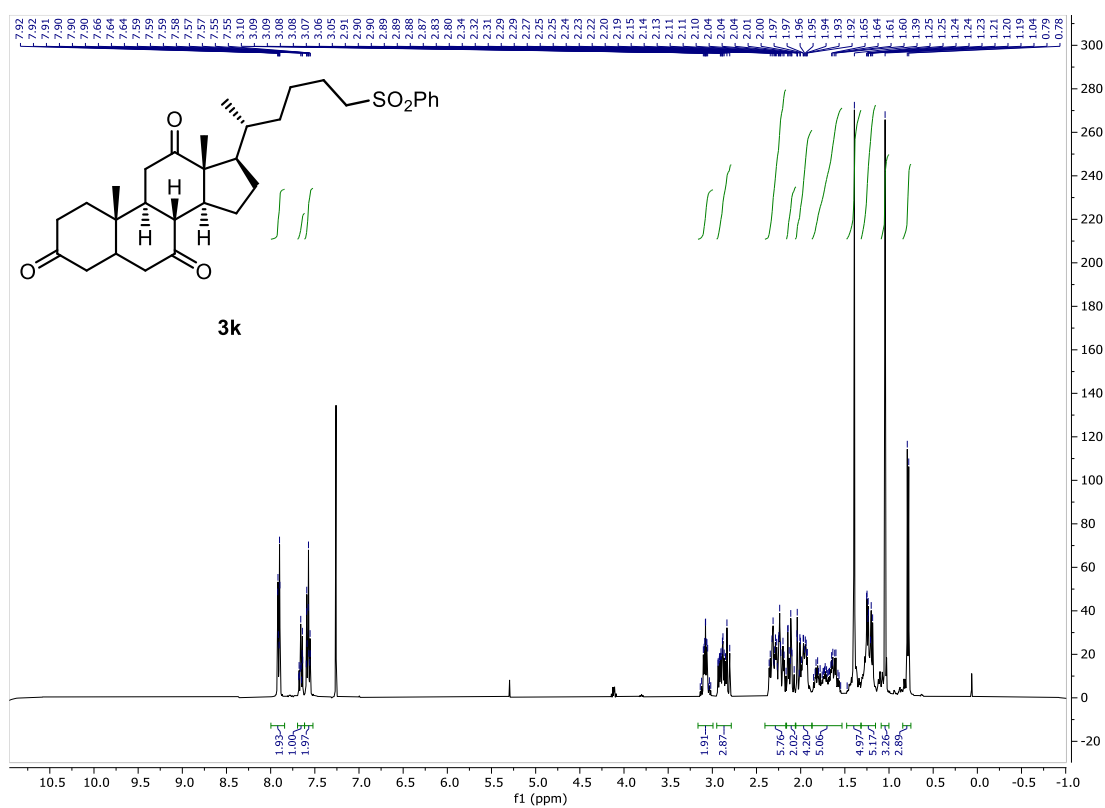
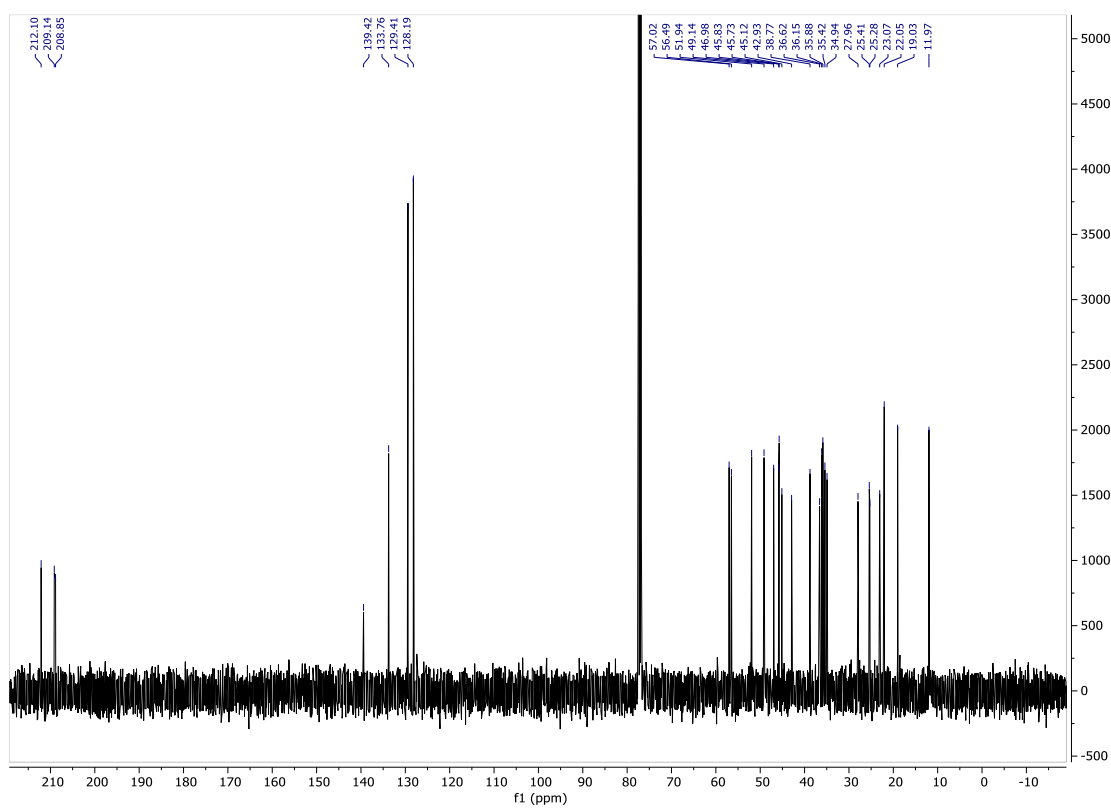


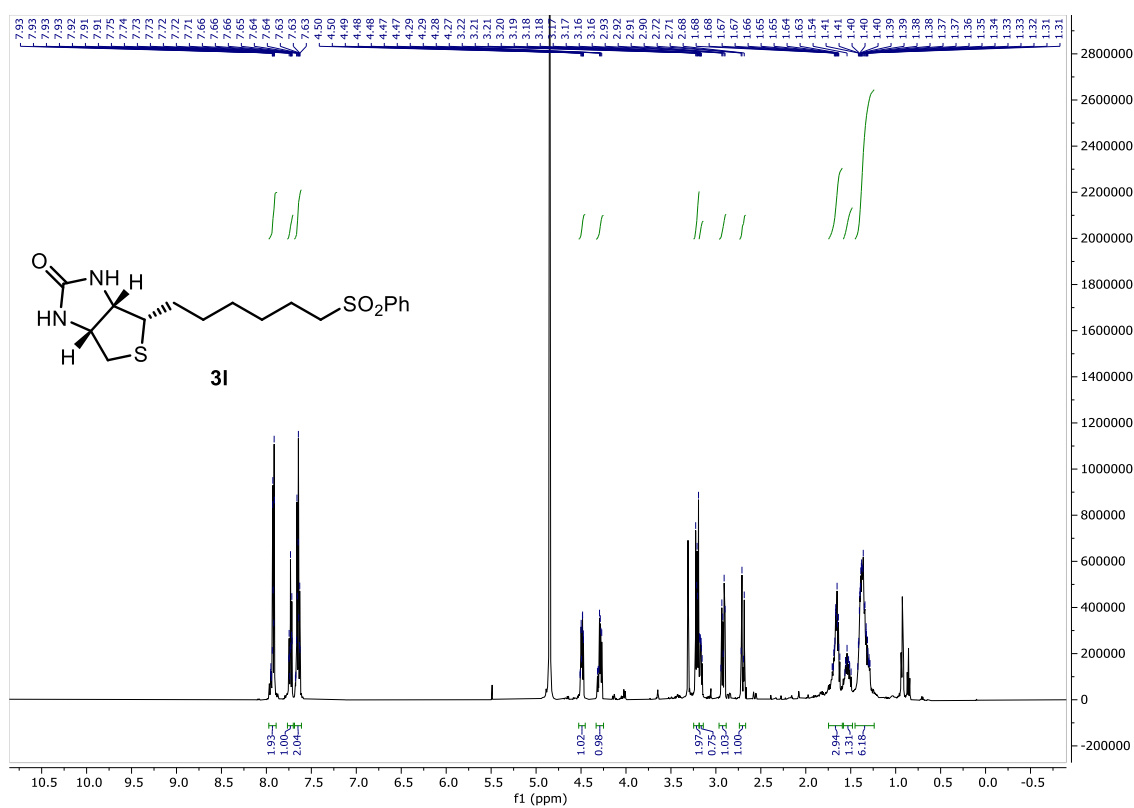
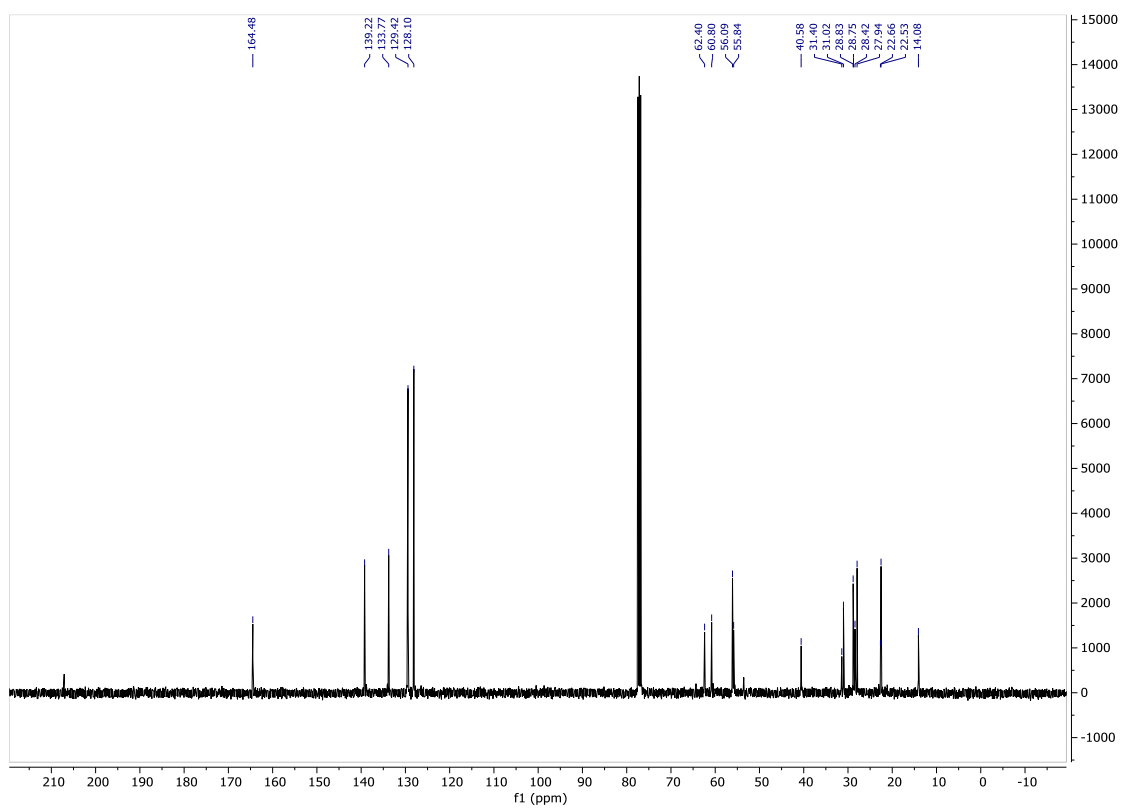
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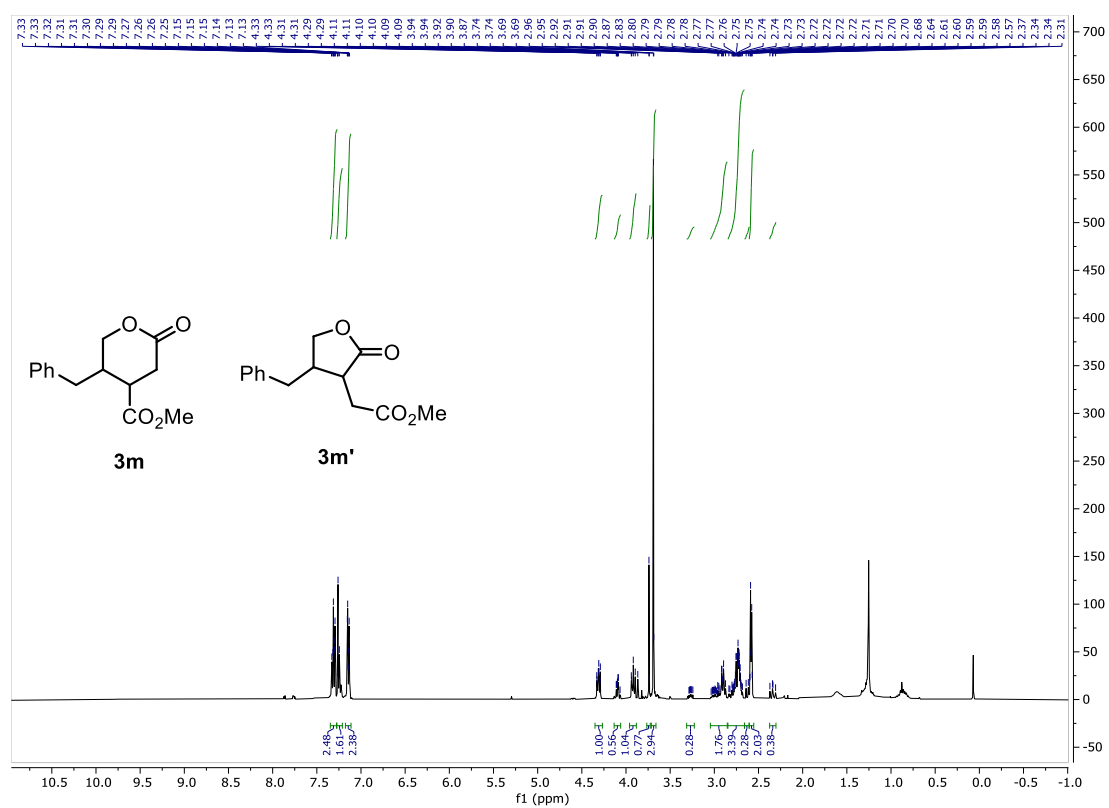
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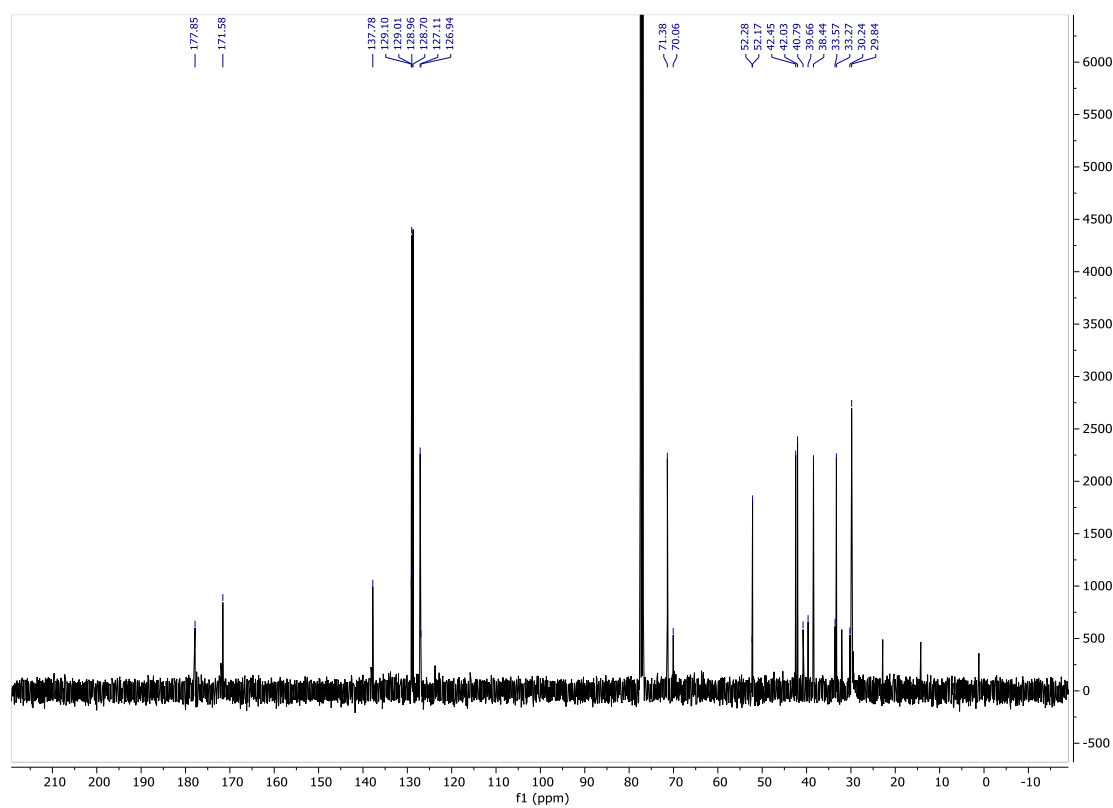
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¹H NMR (500 MHz, Methanol-*d*₄) ^{13}C NMR (101 MHz, CDCl_3)

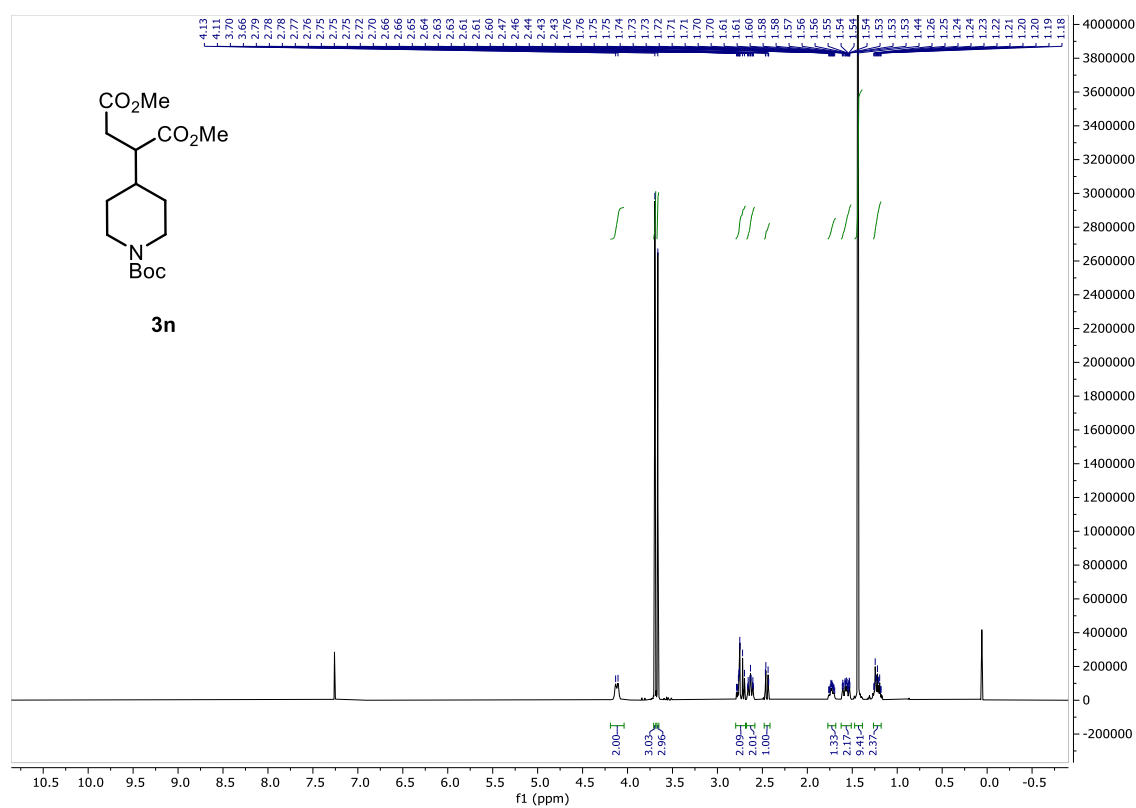
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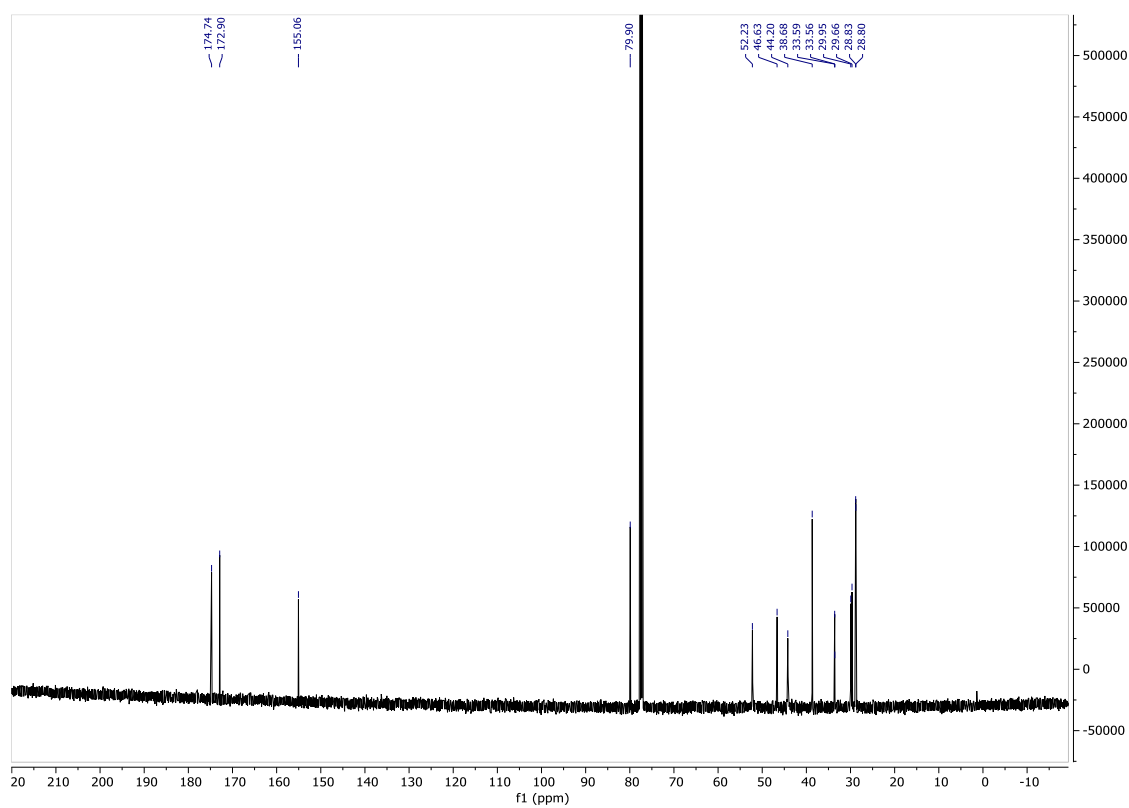
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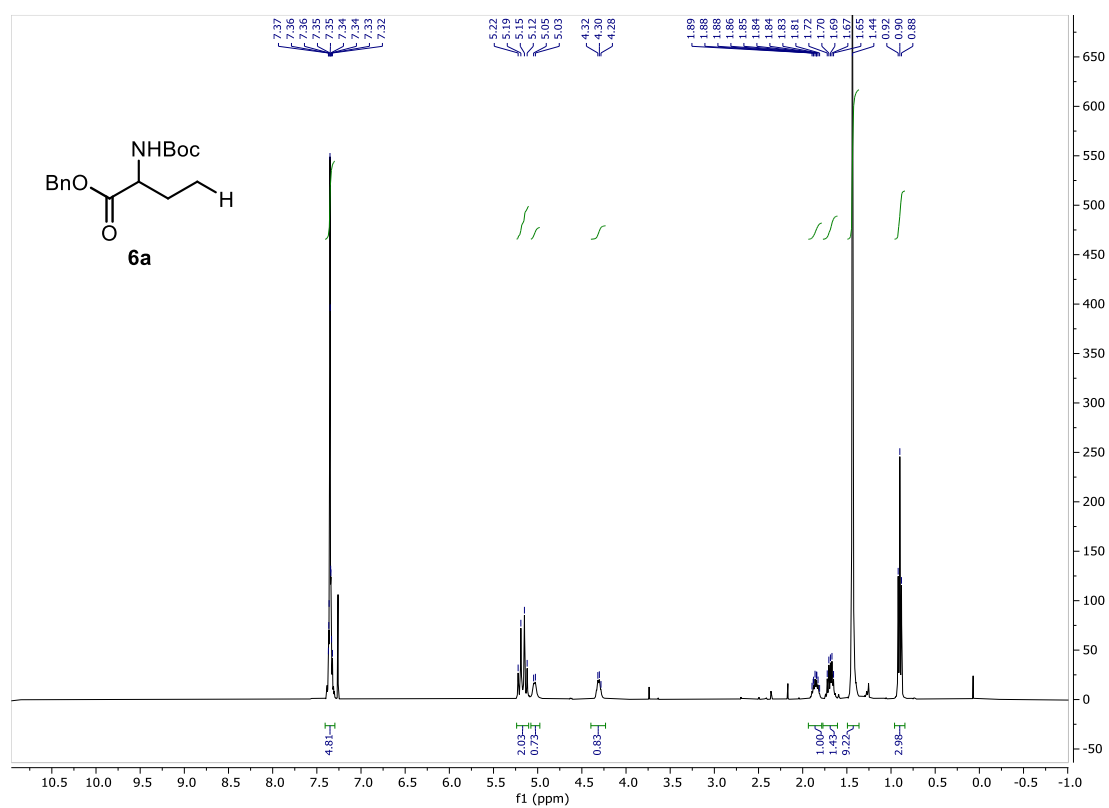
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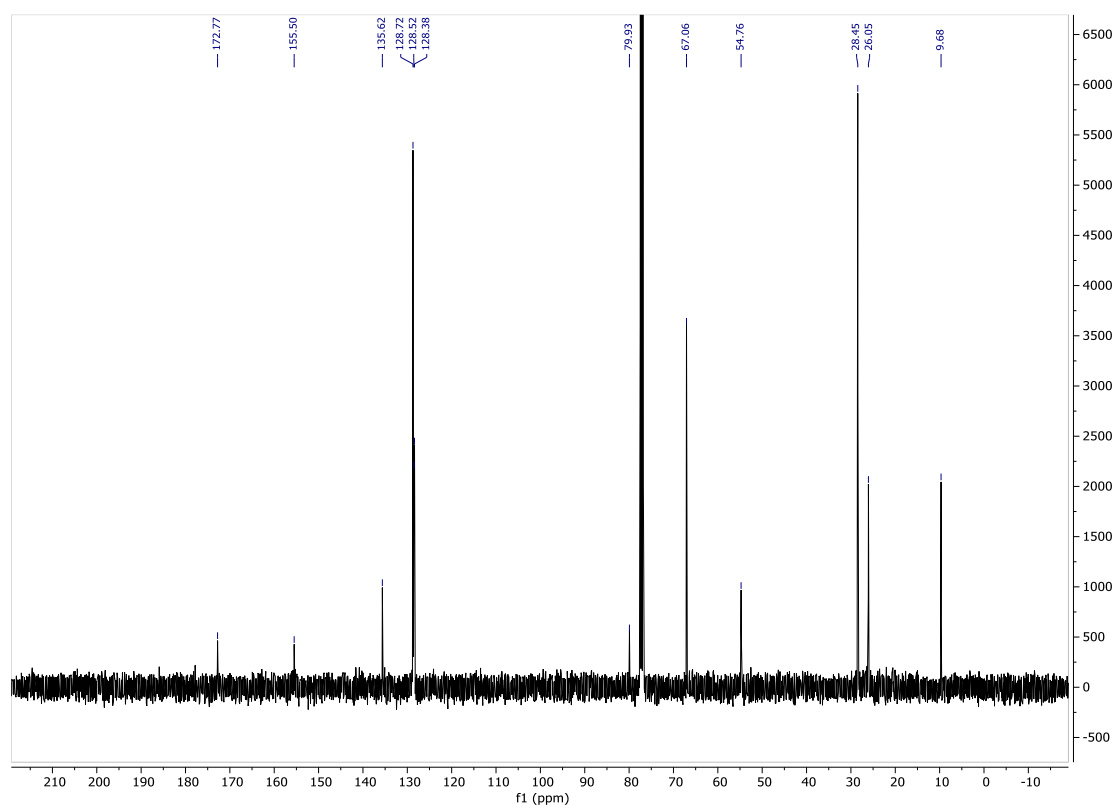
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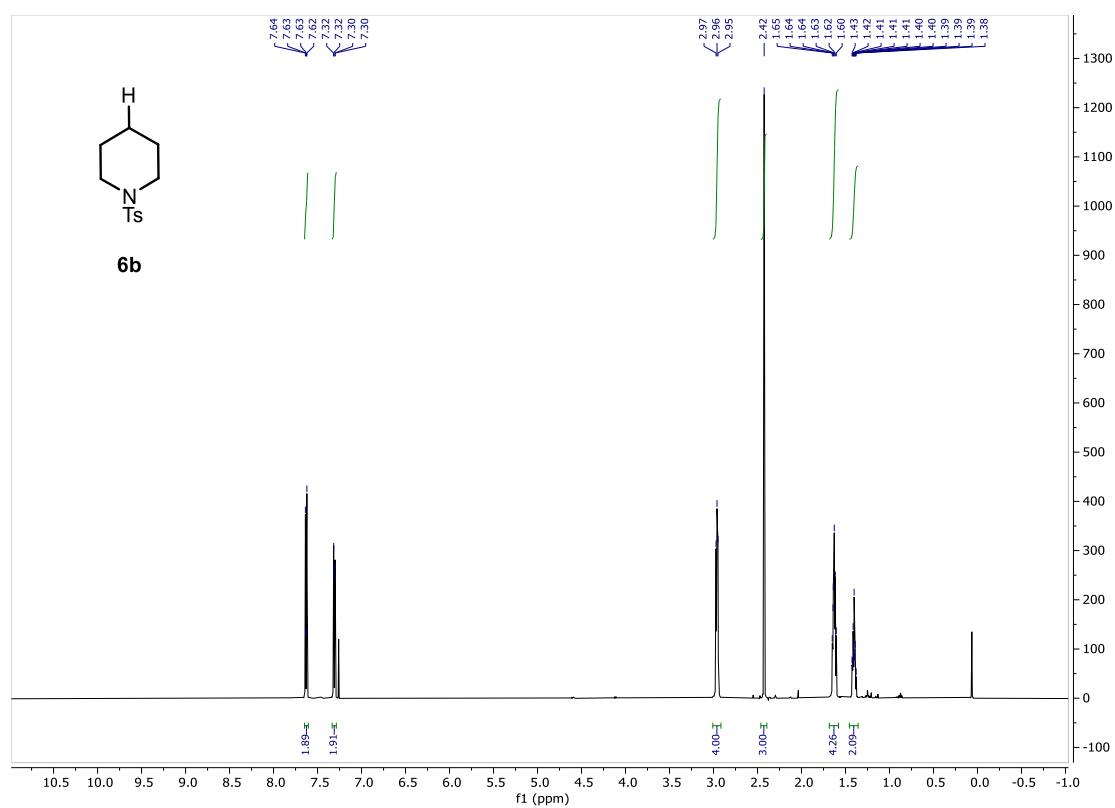
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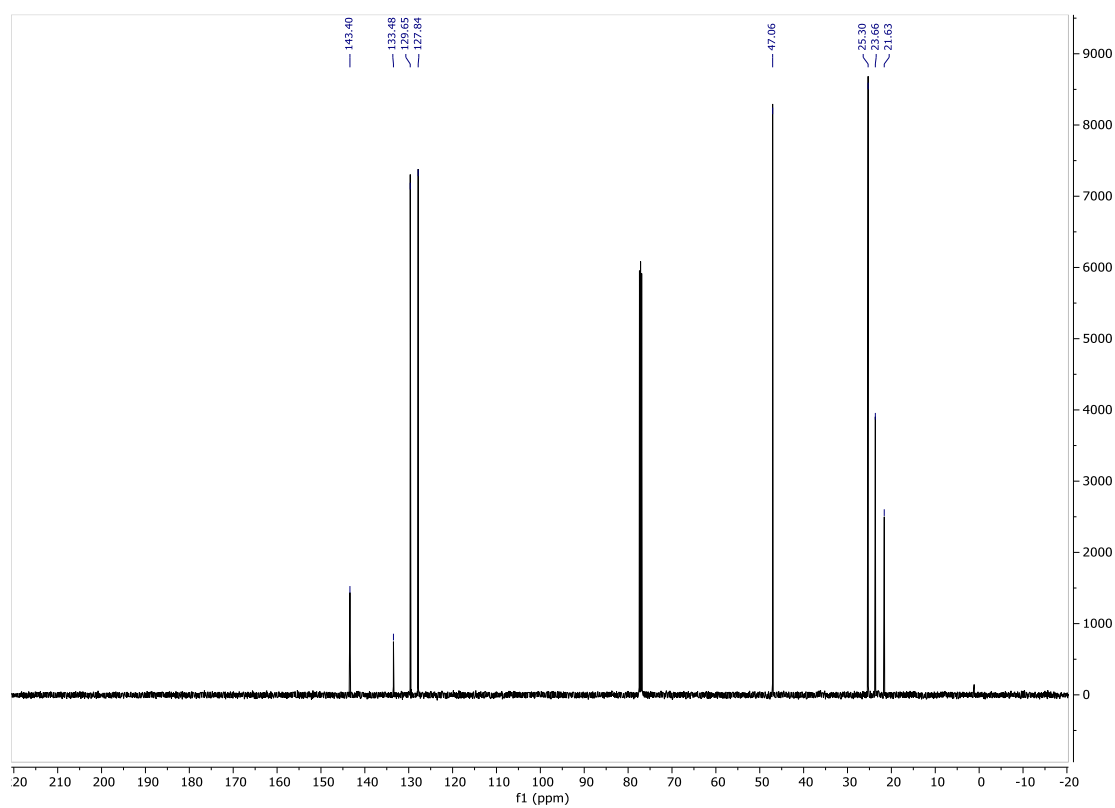
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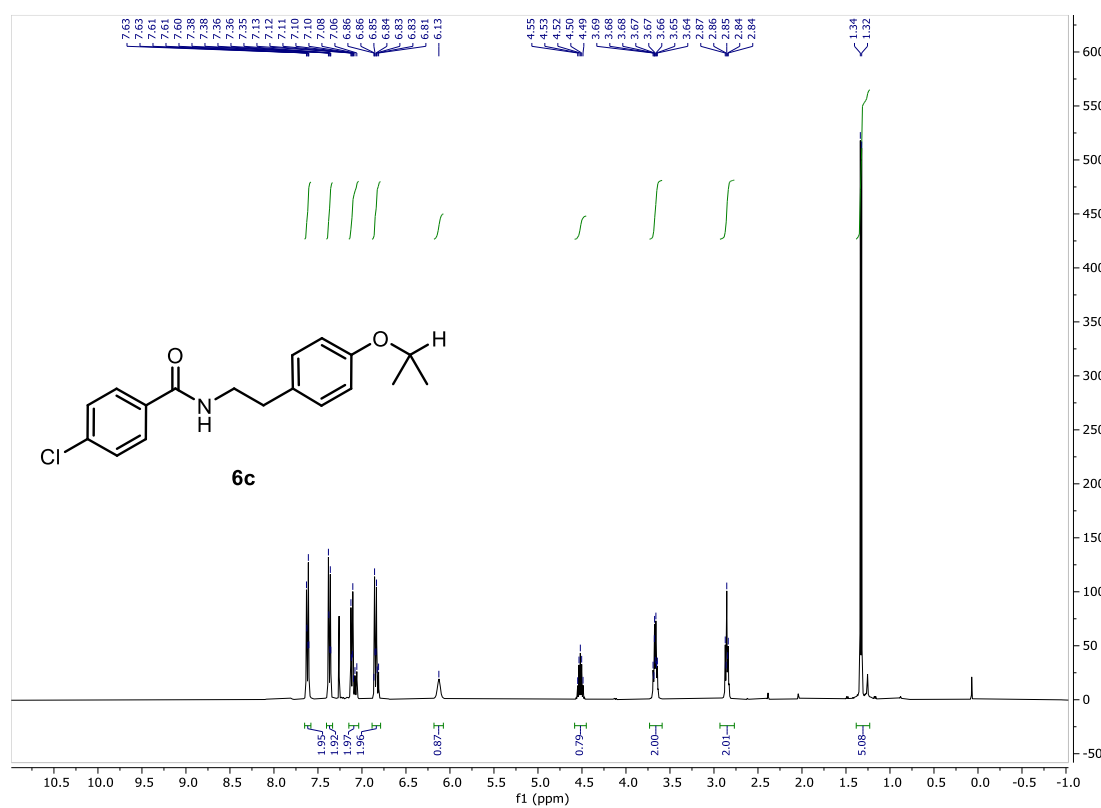
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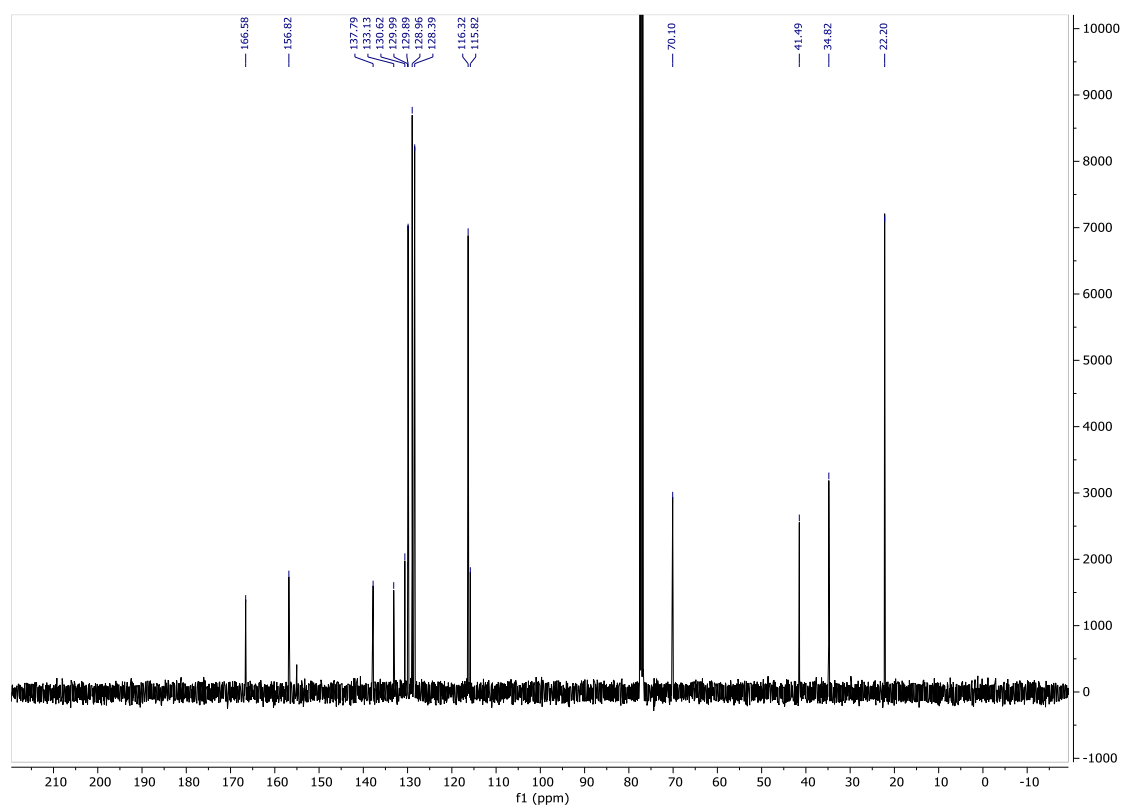
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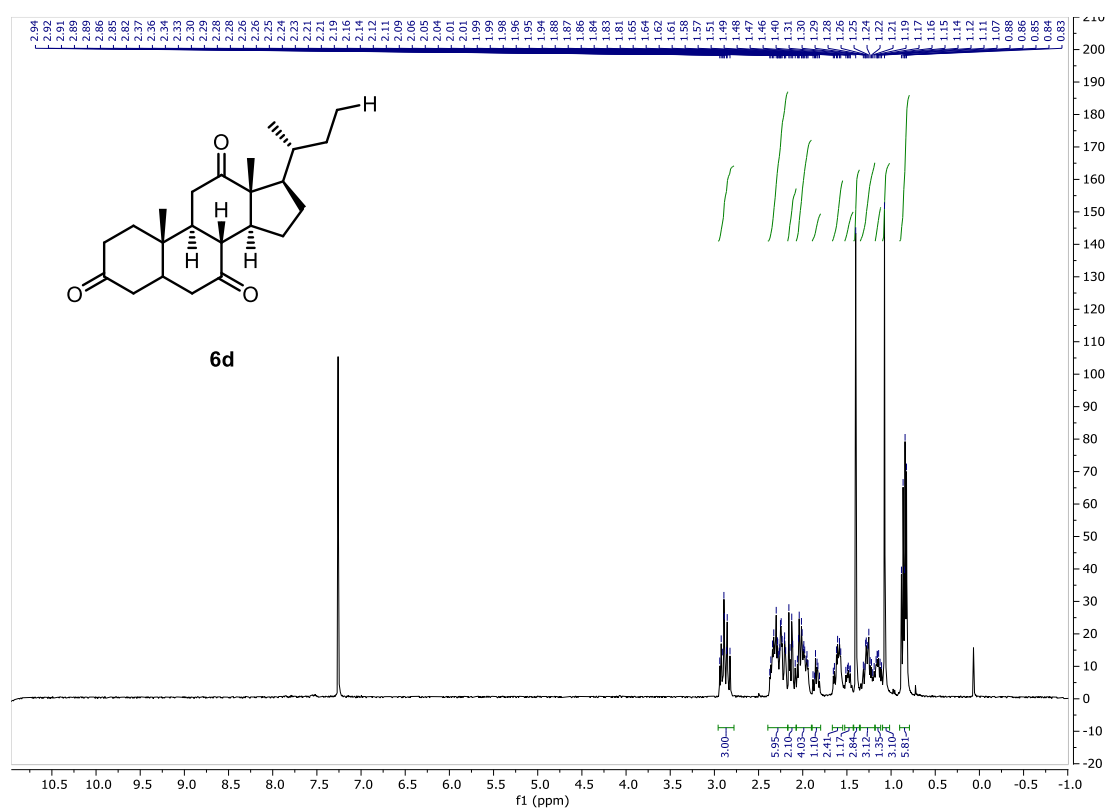
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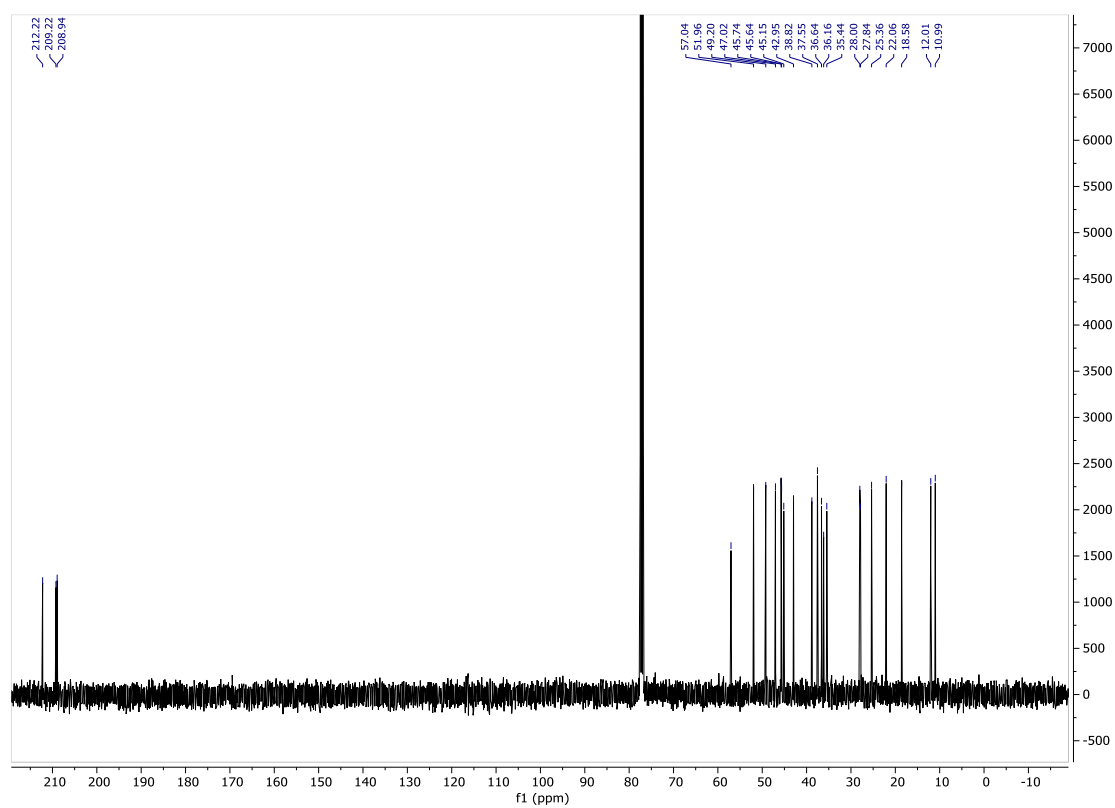
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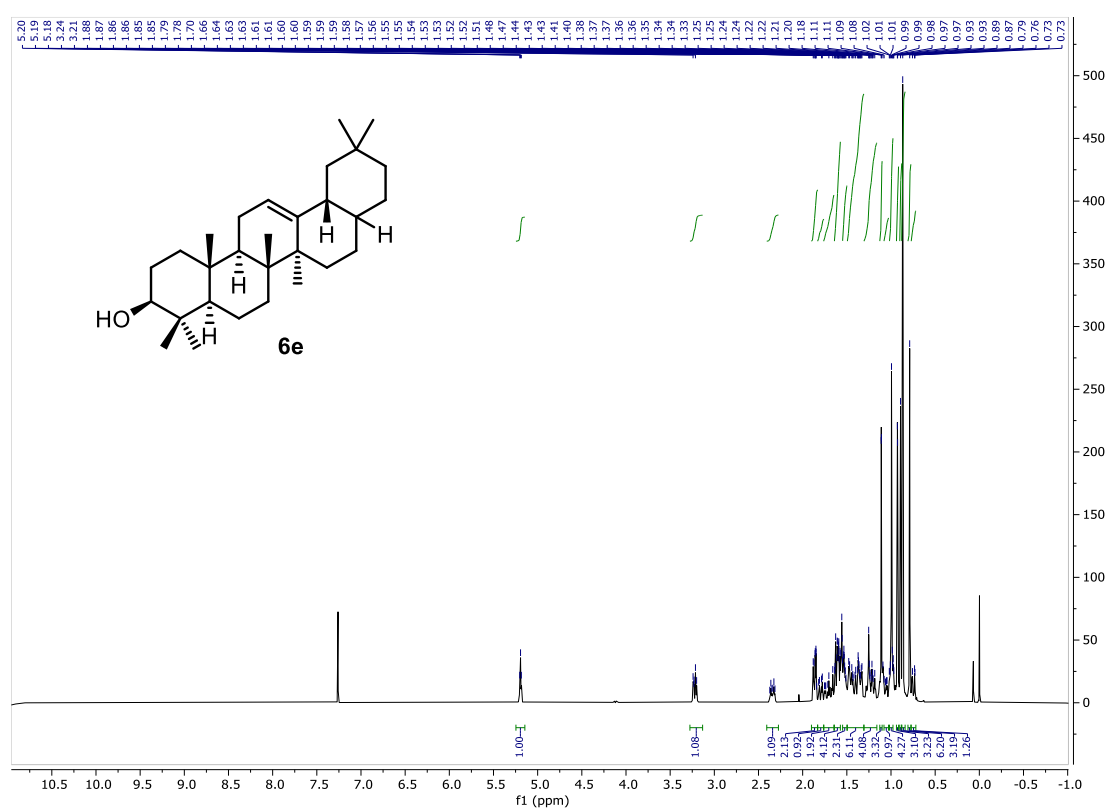
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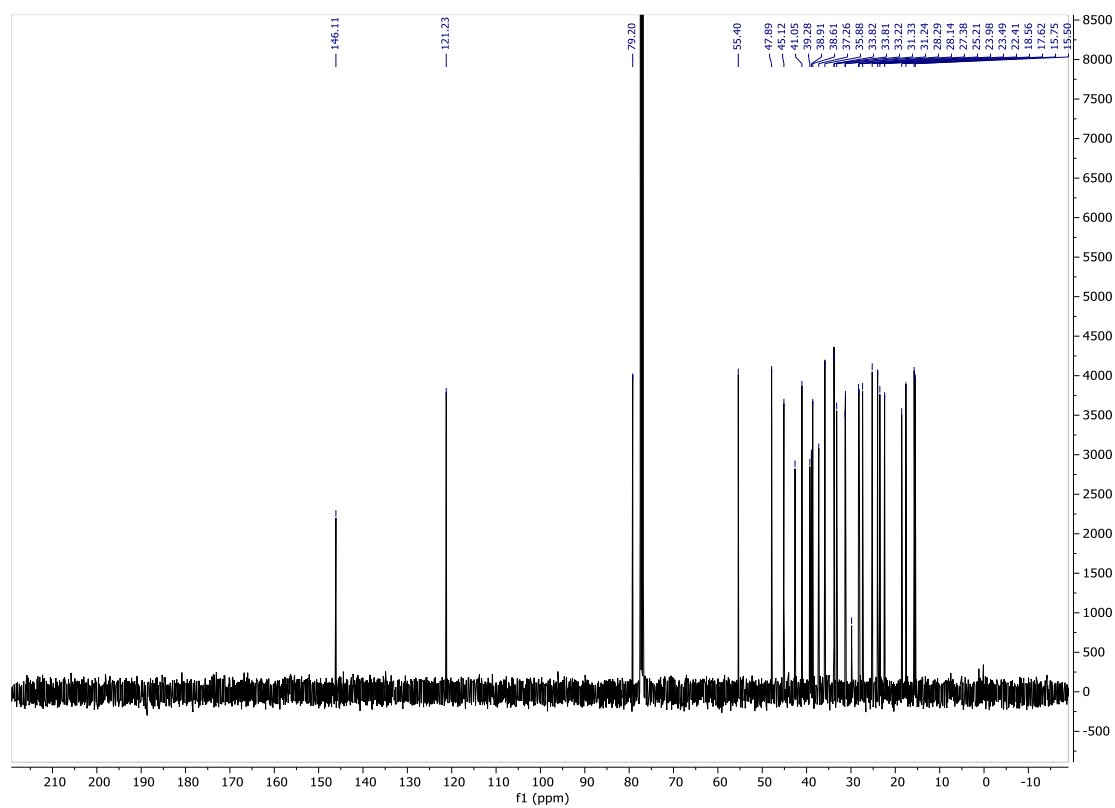
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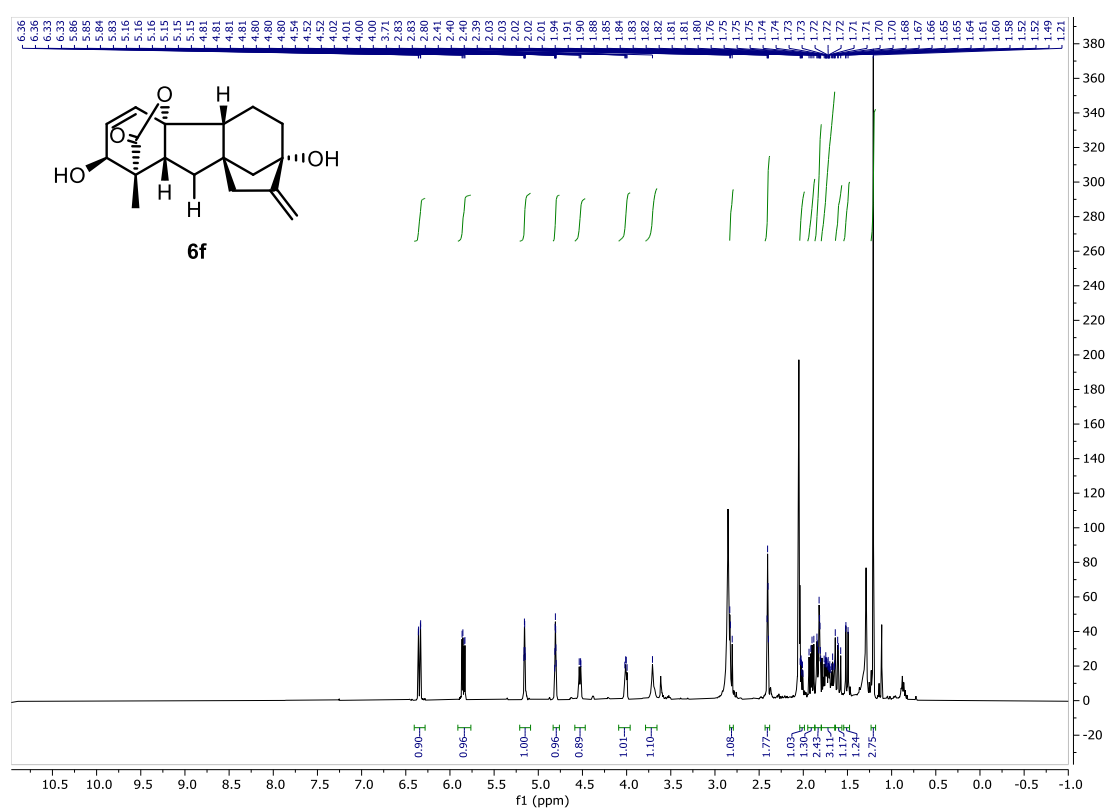
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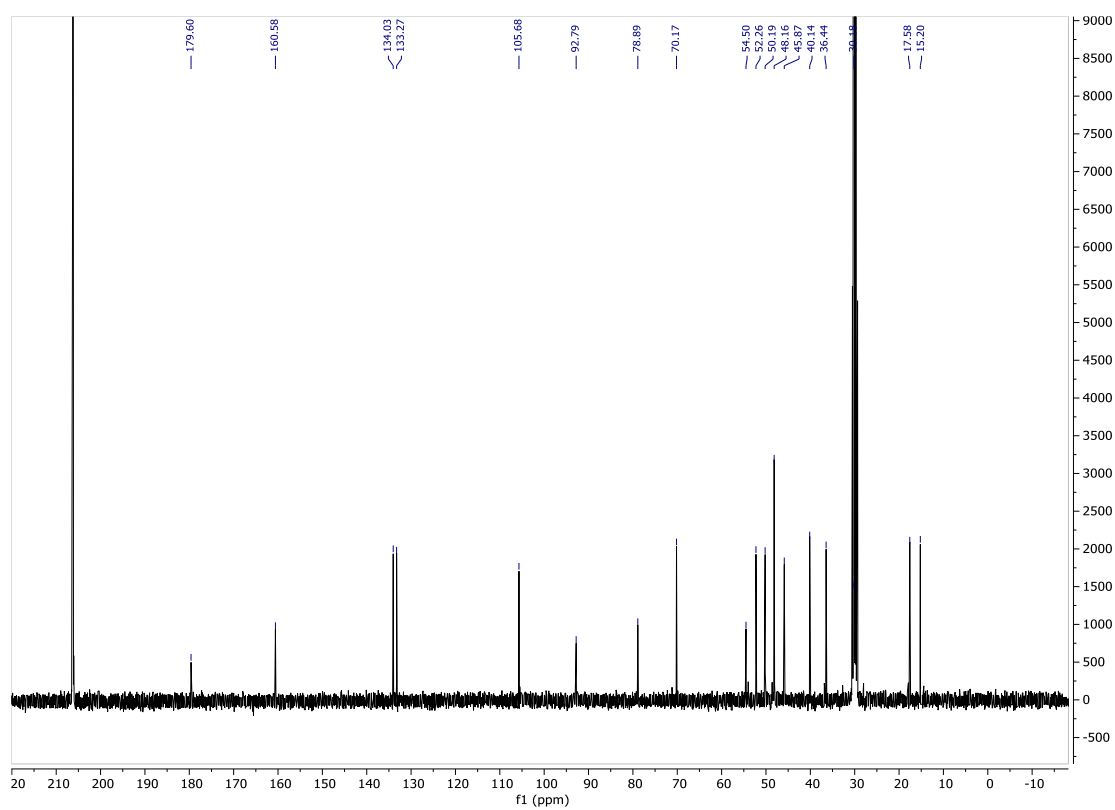
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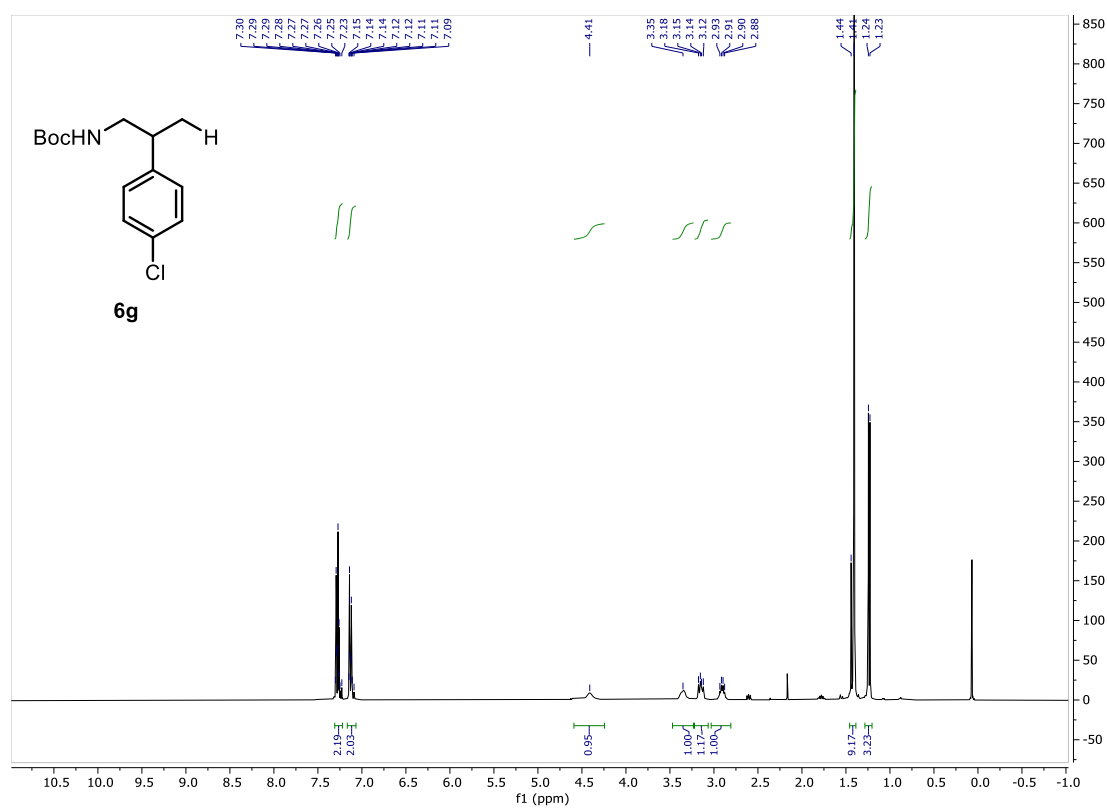
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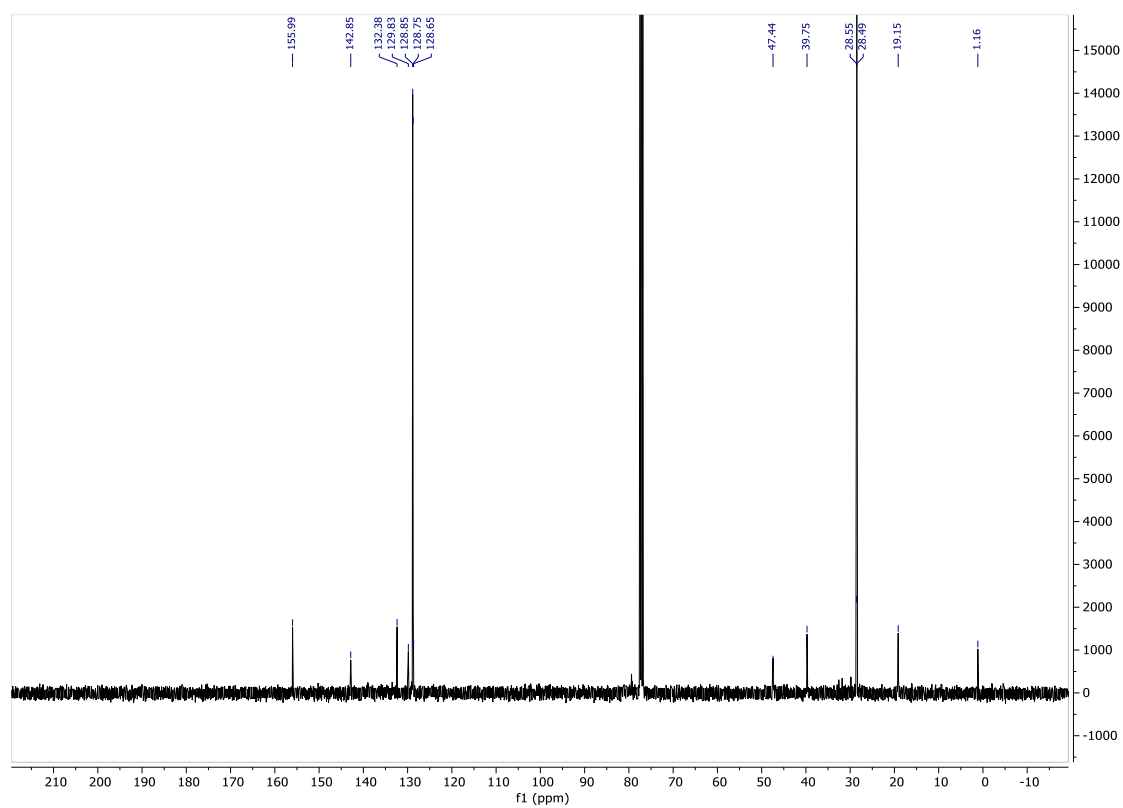
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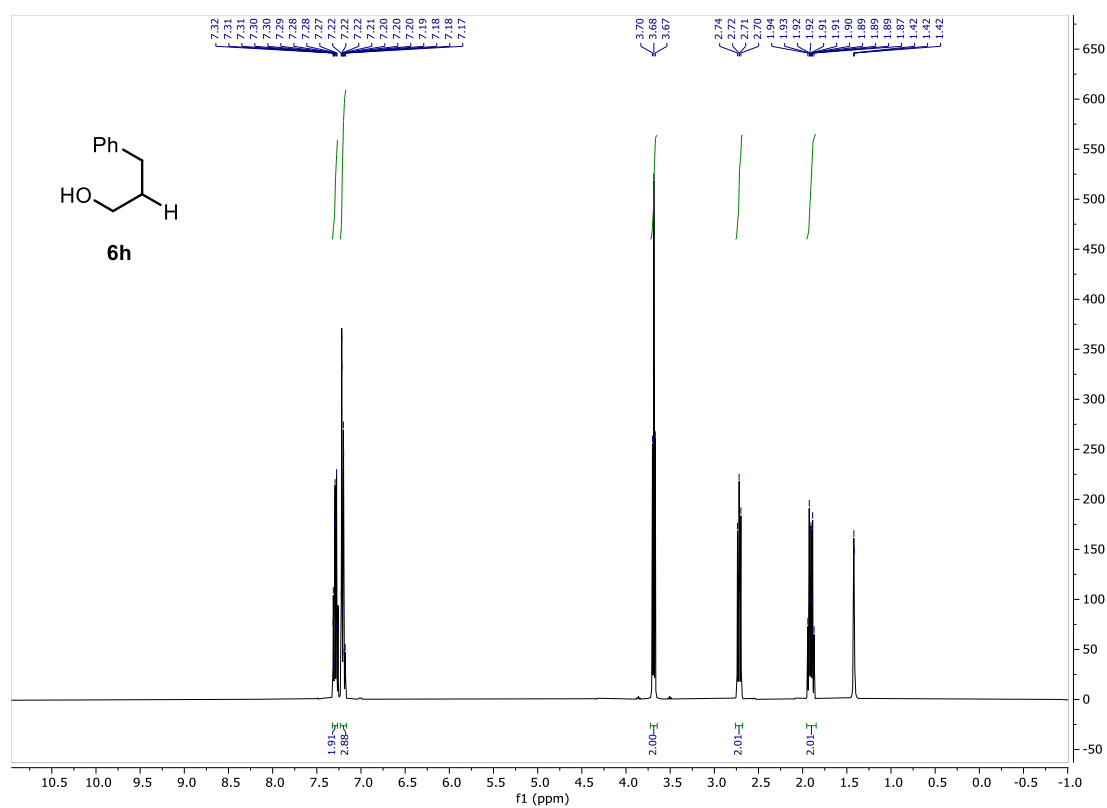
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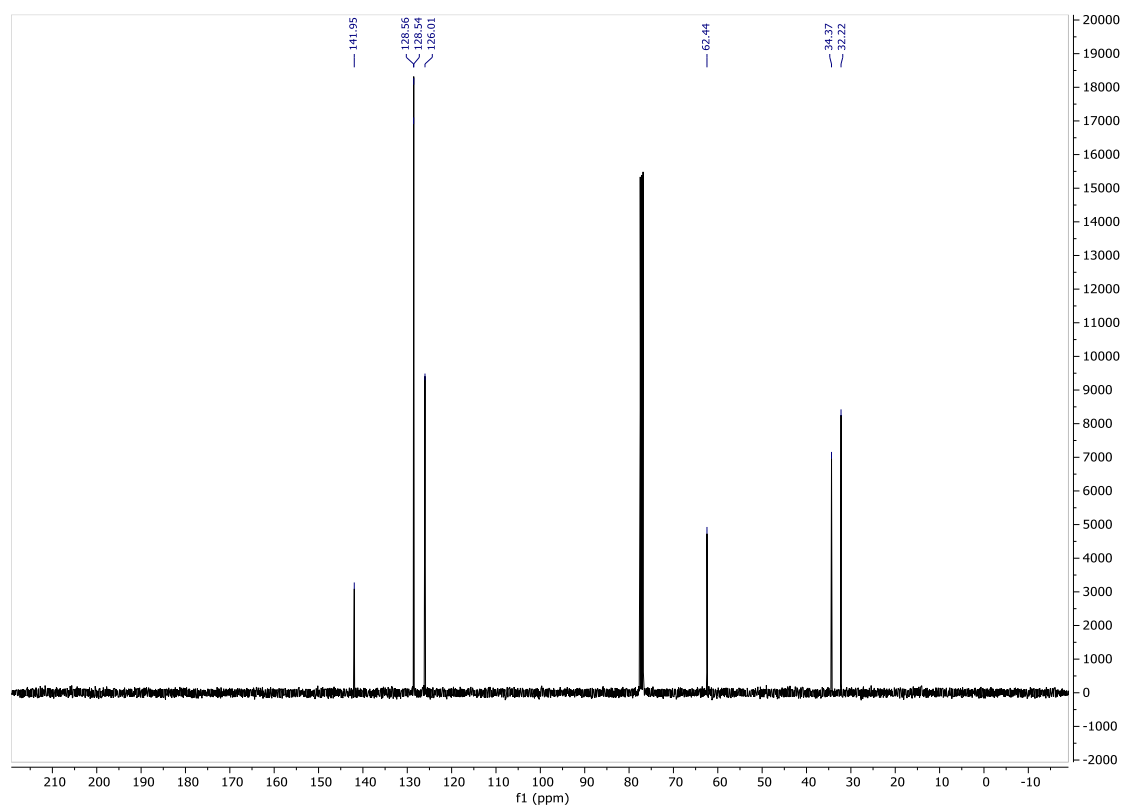
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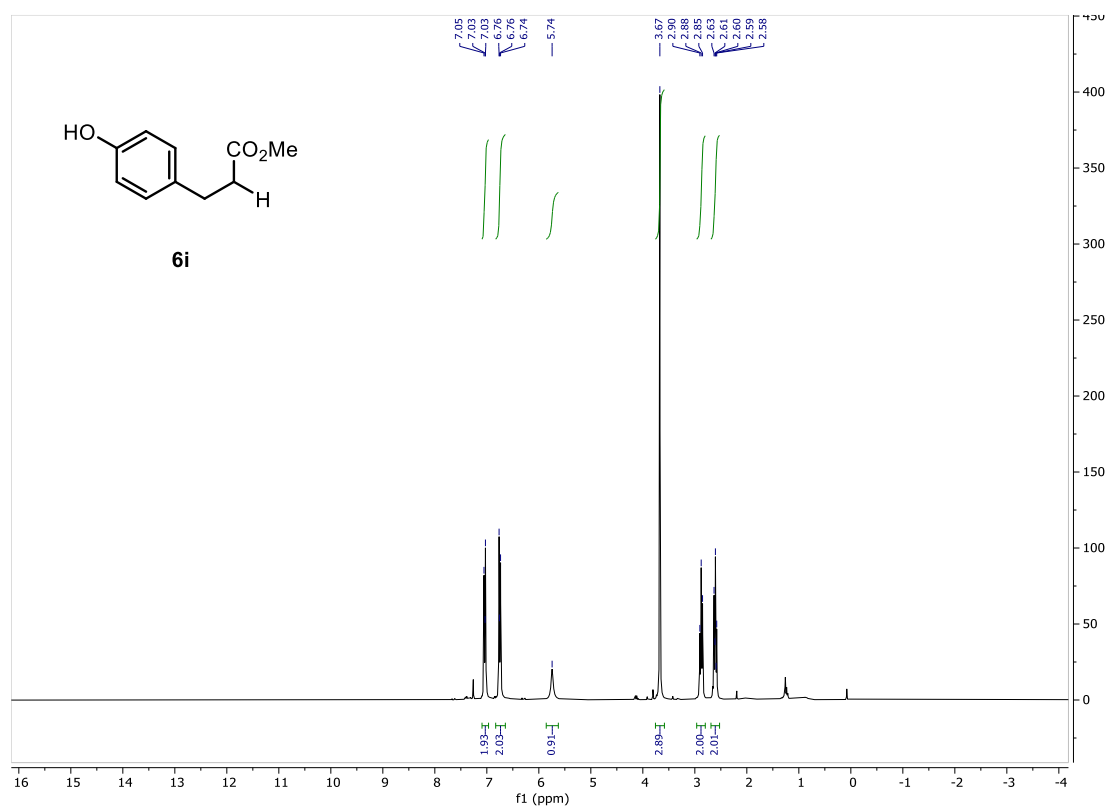
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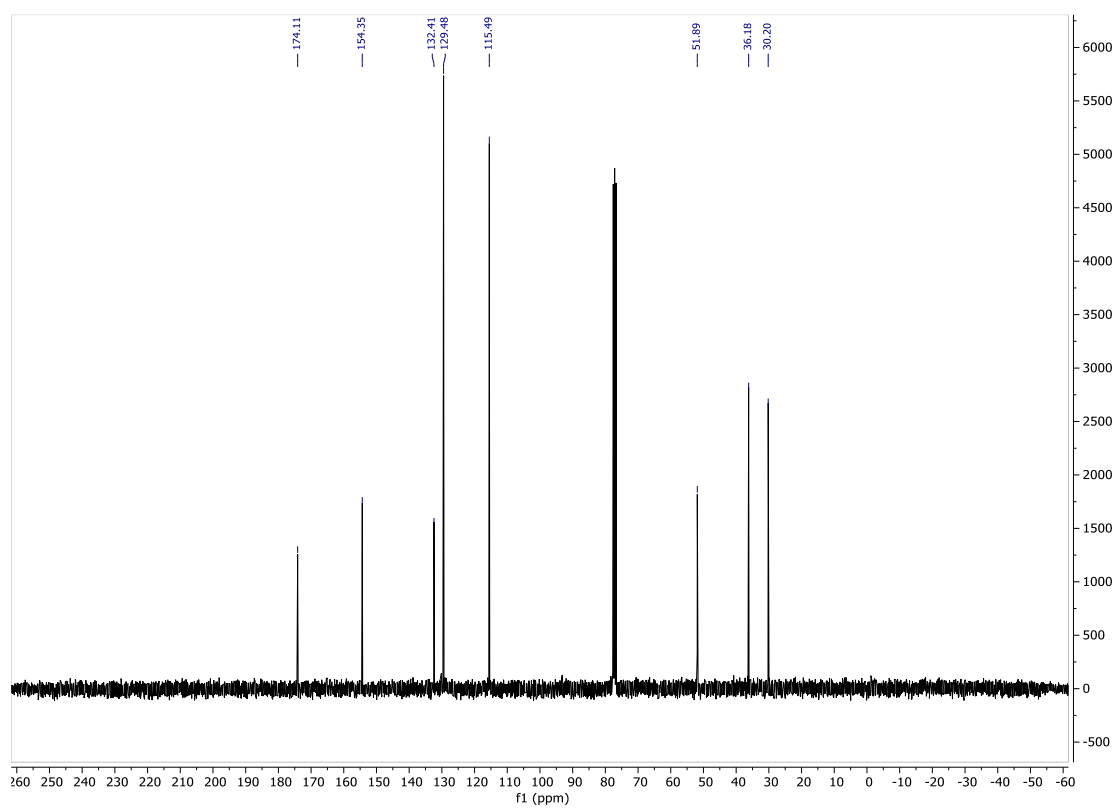
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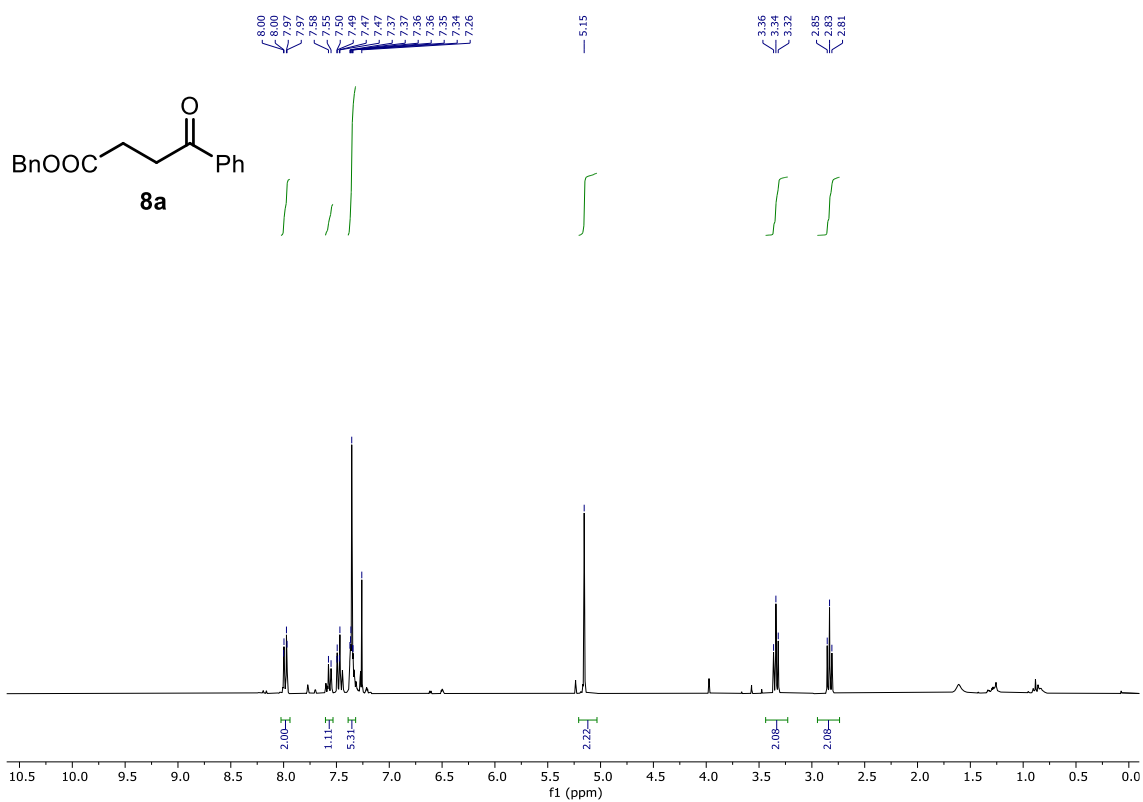
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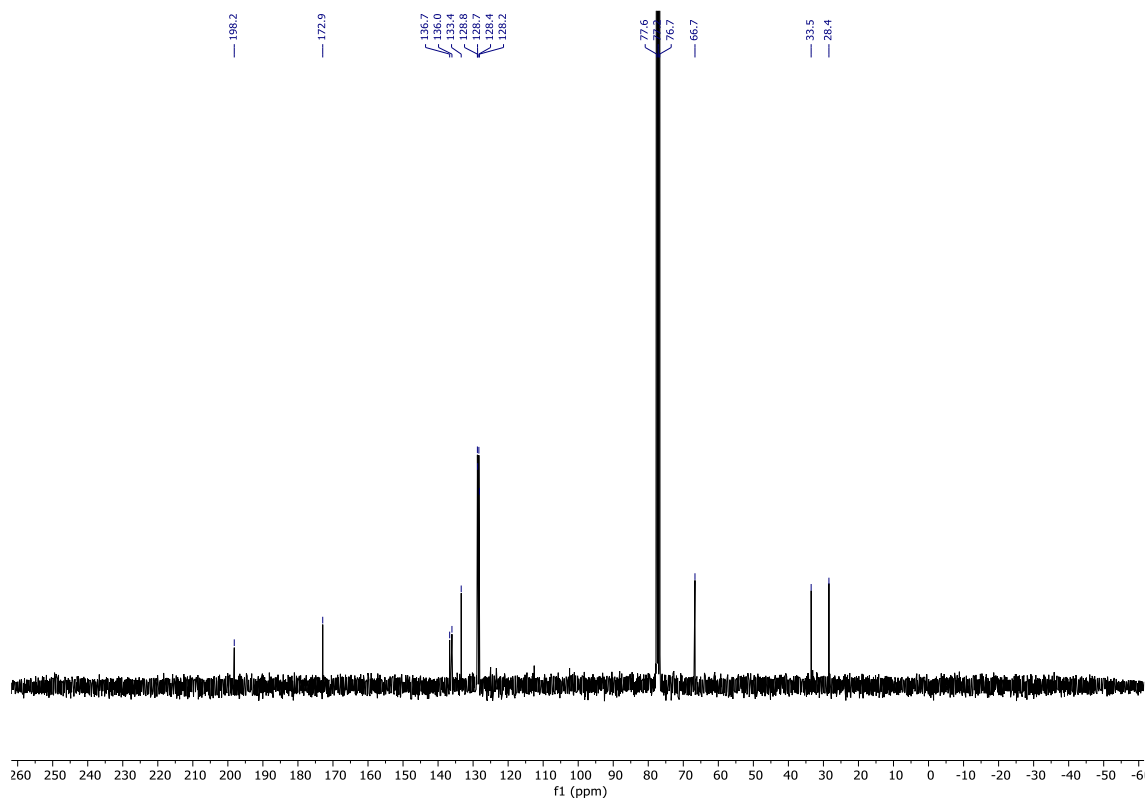
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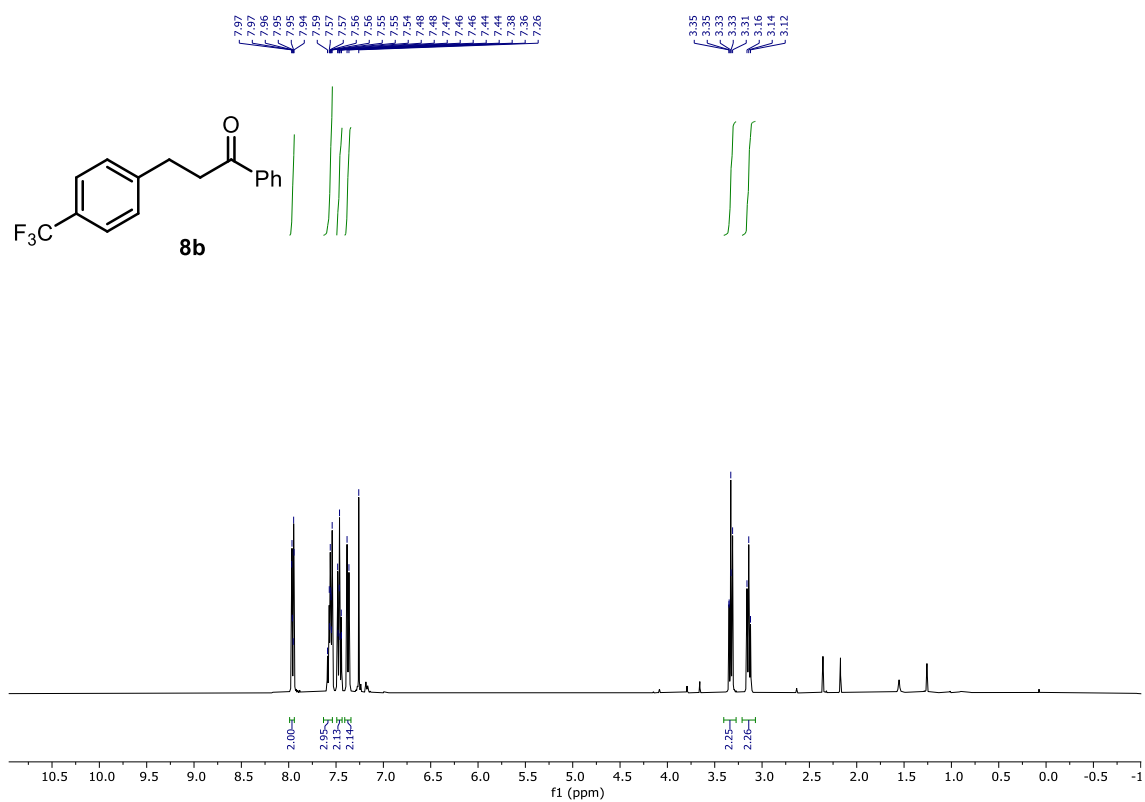
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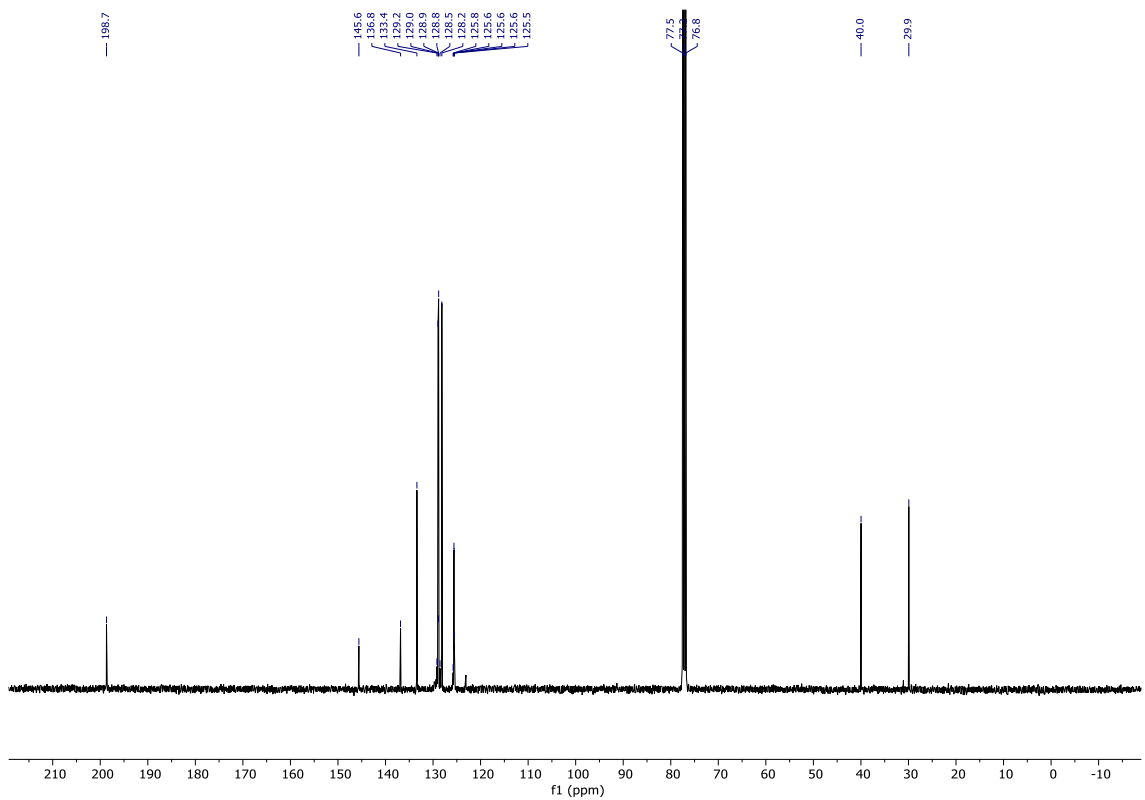
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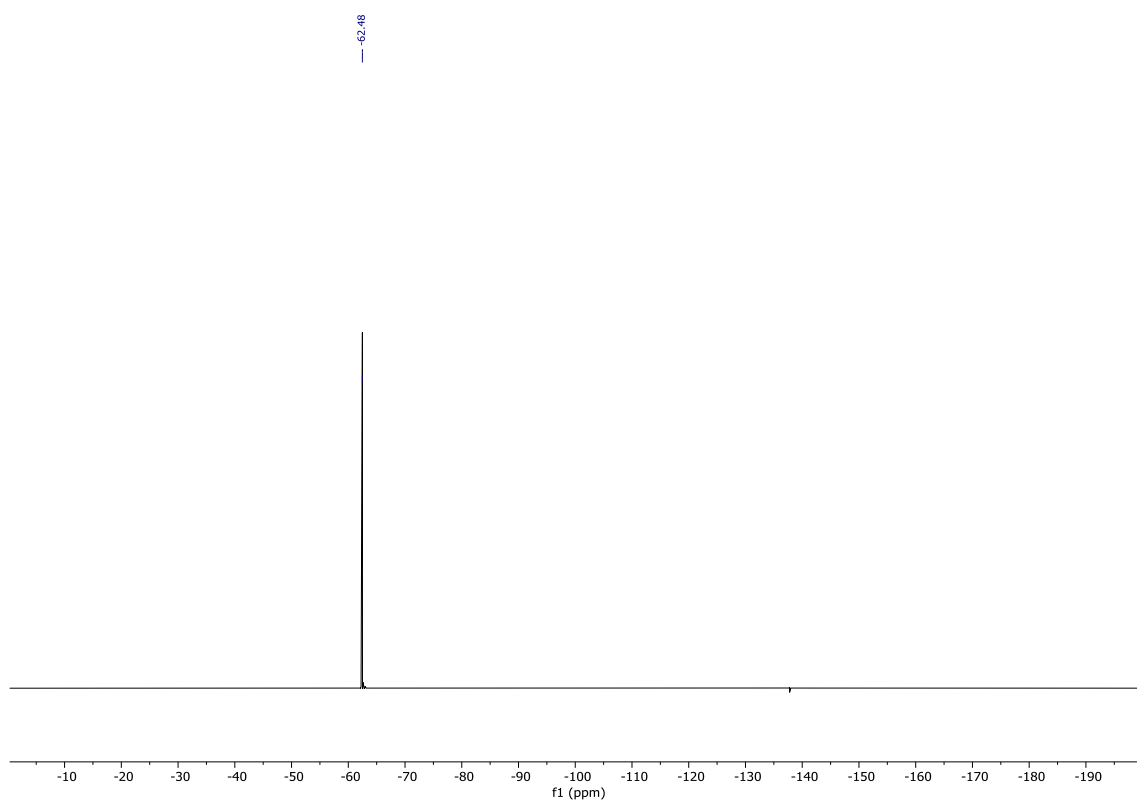
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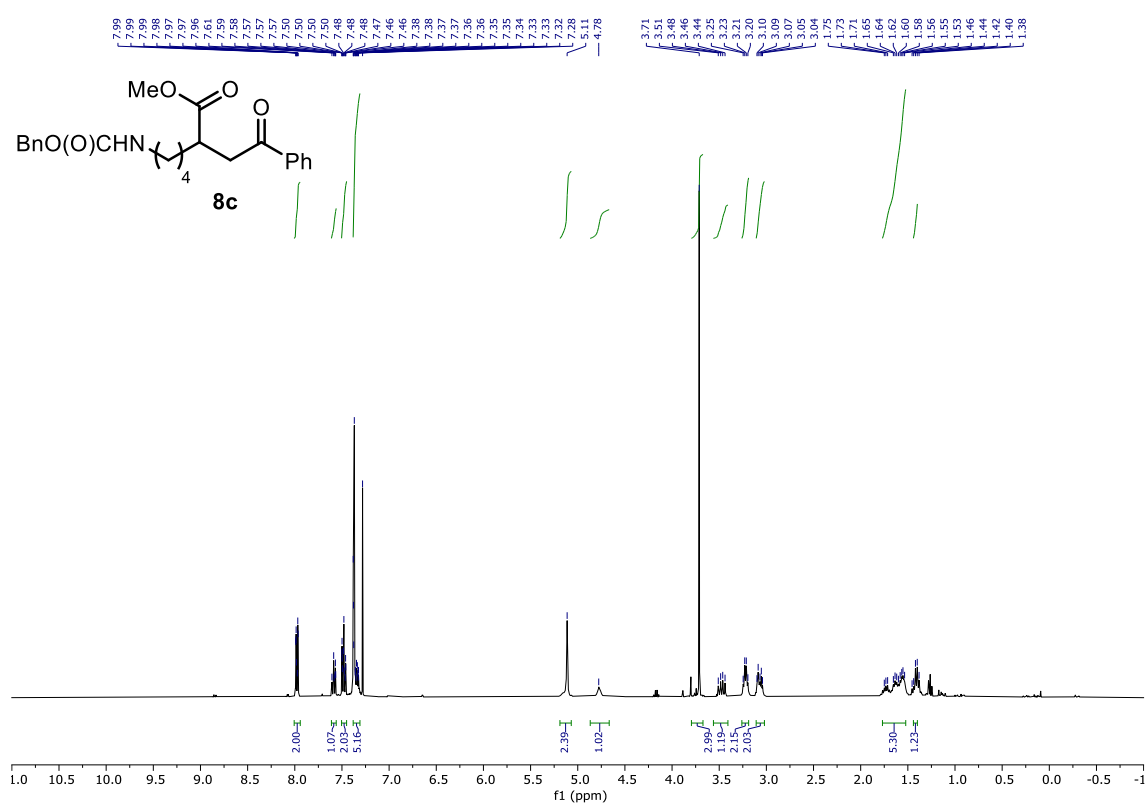
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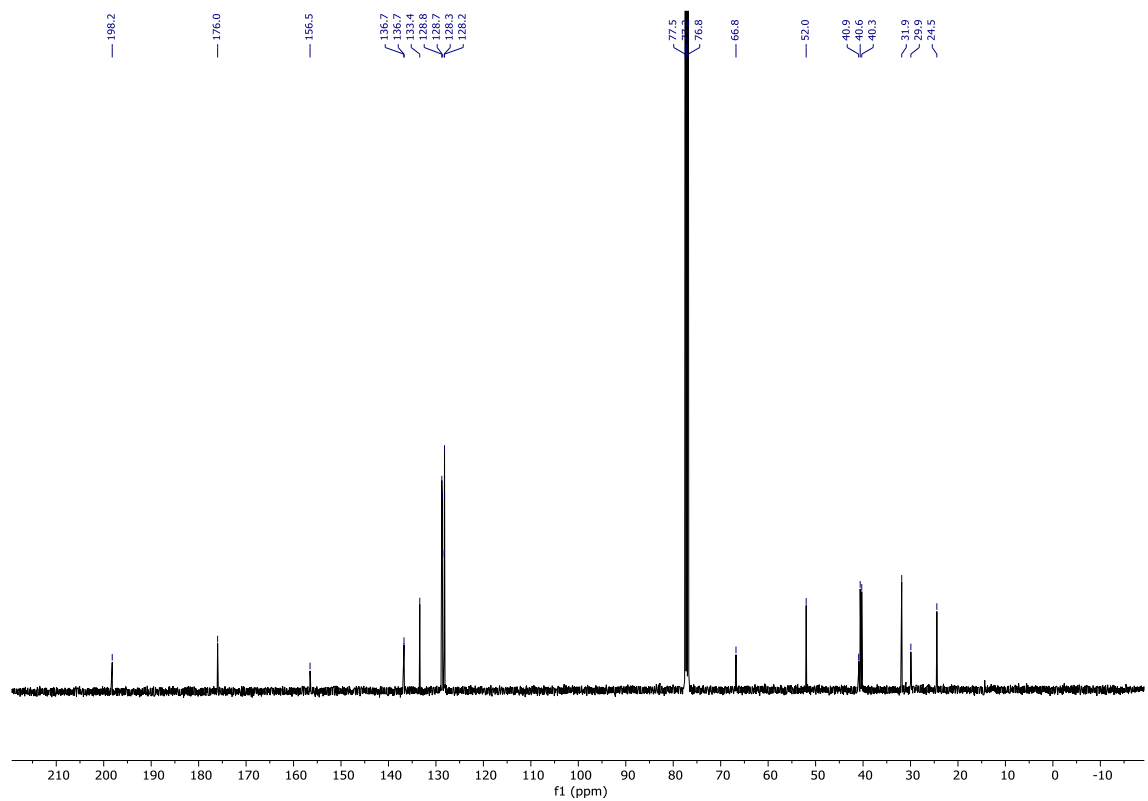
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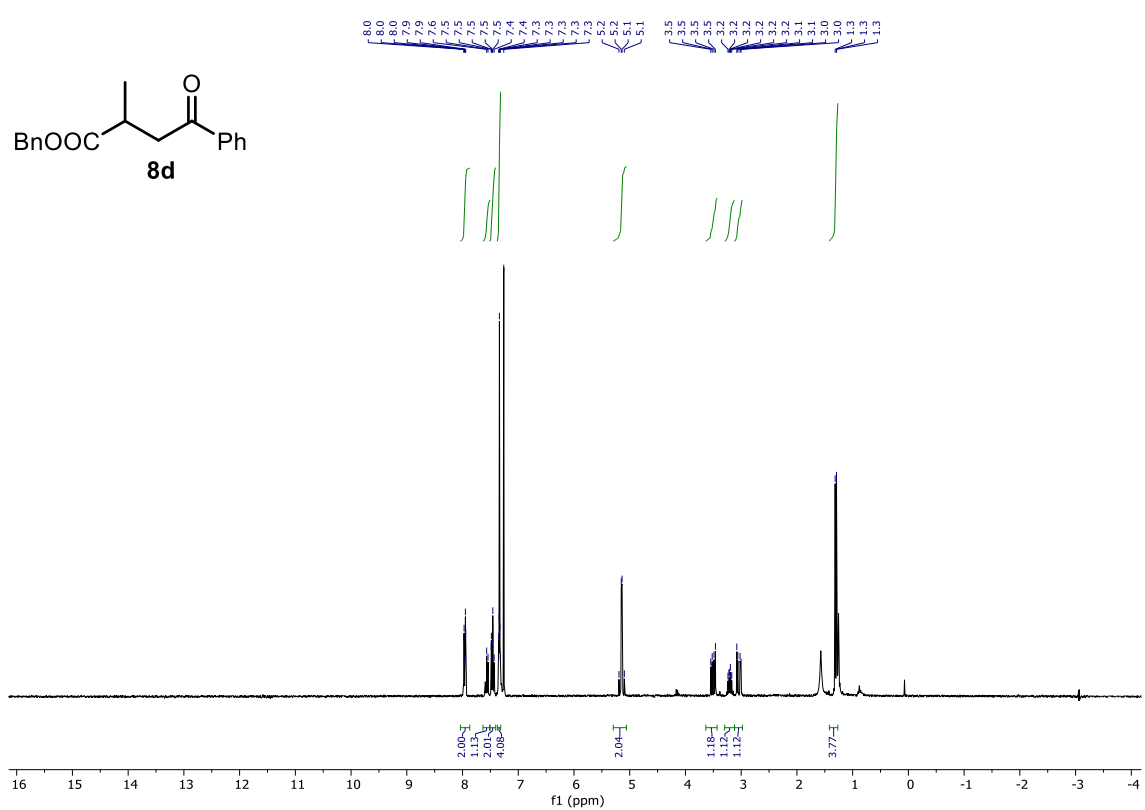
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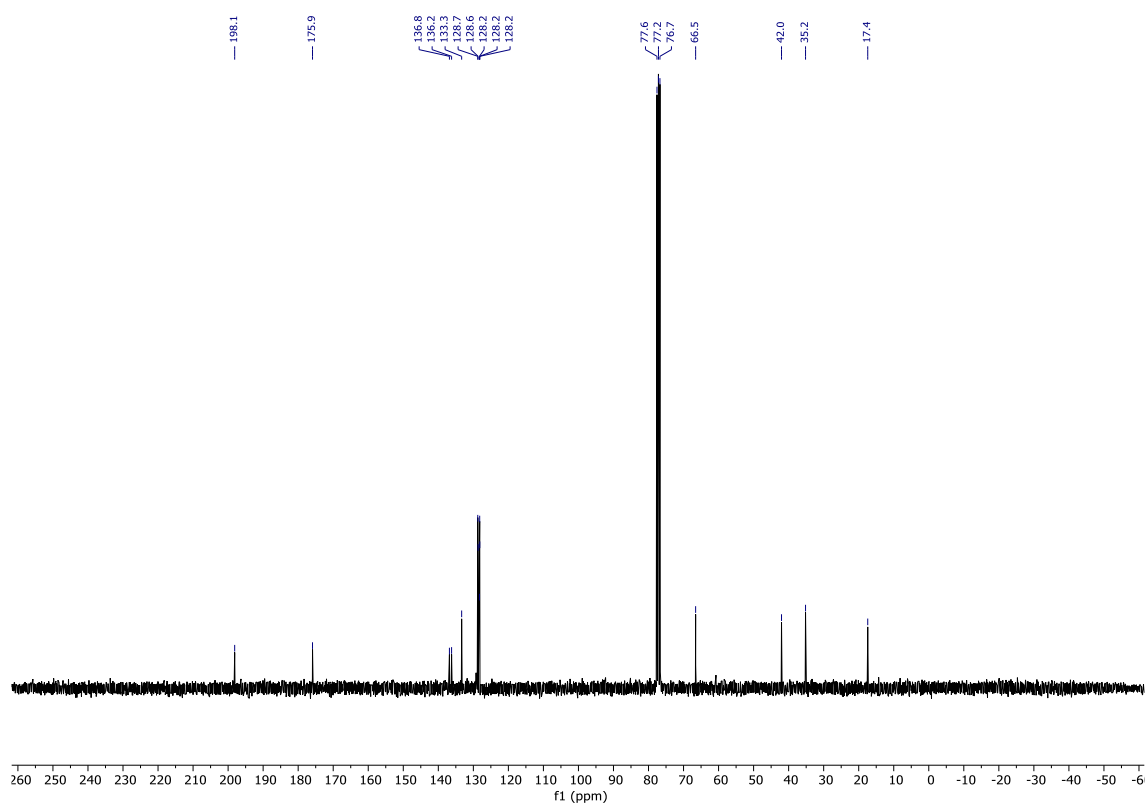
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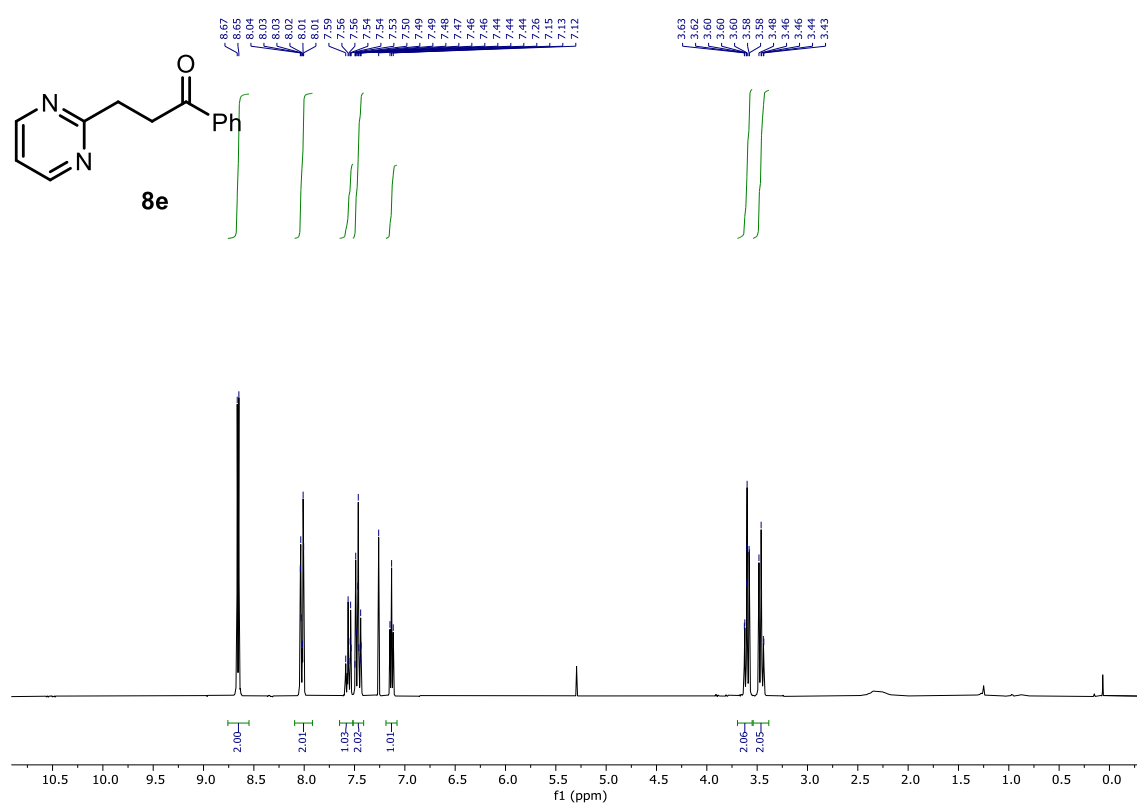
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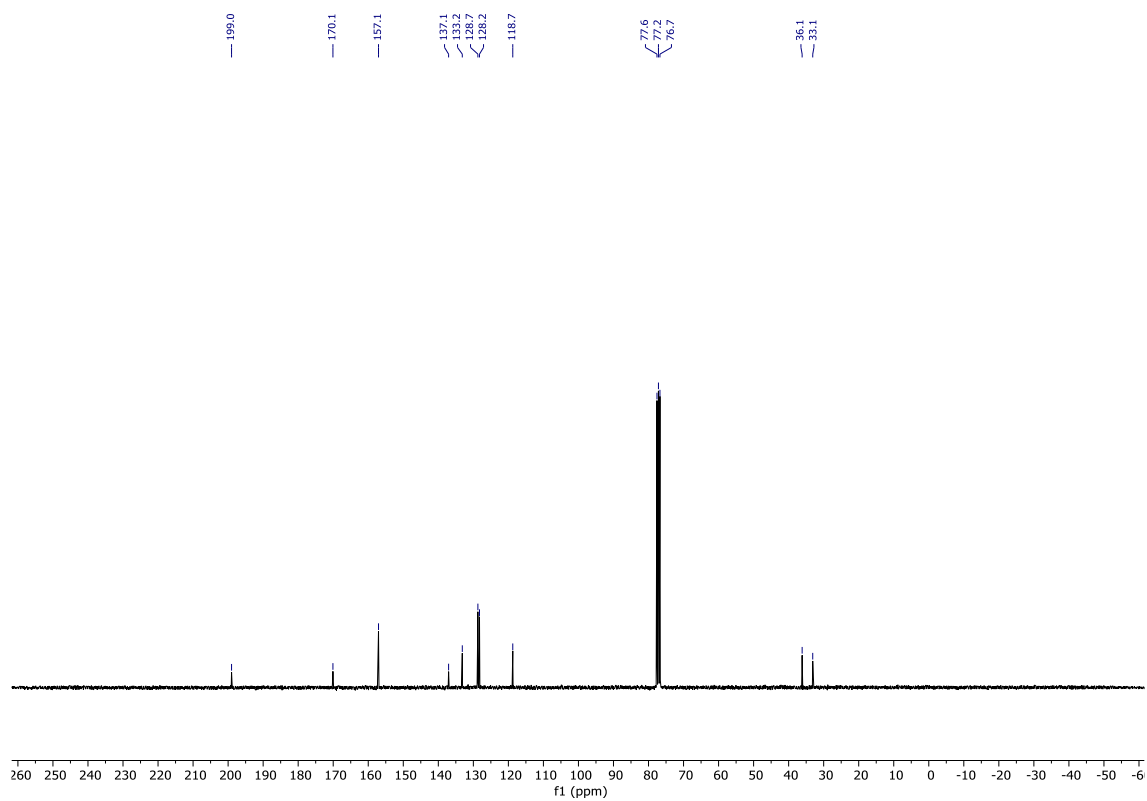
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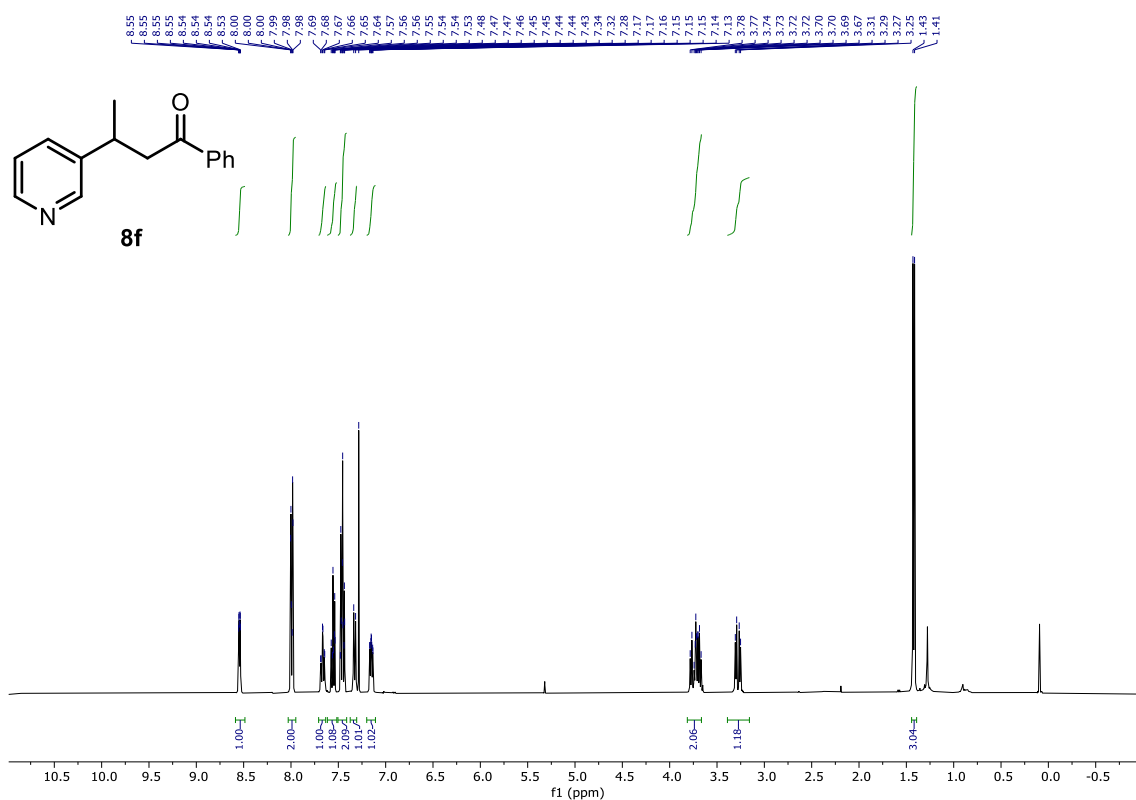
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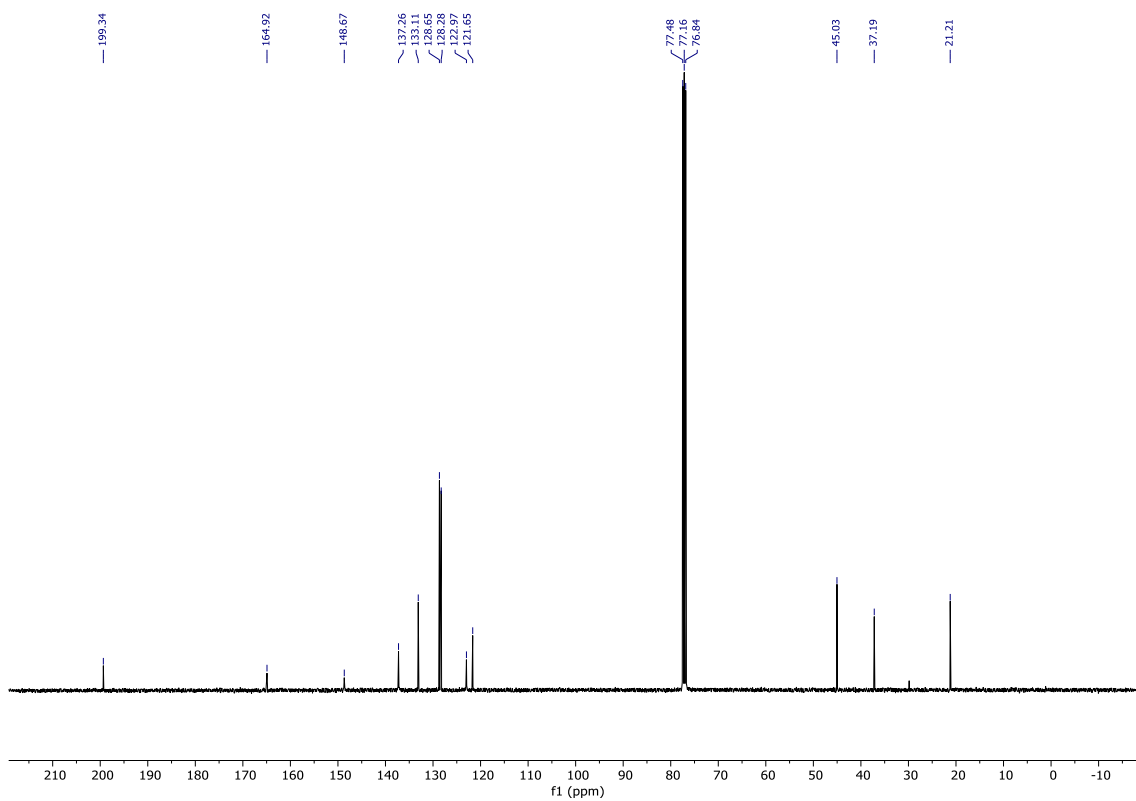
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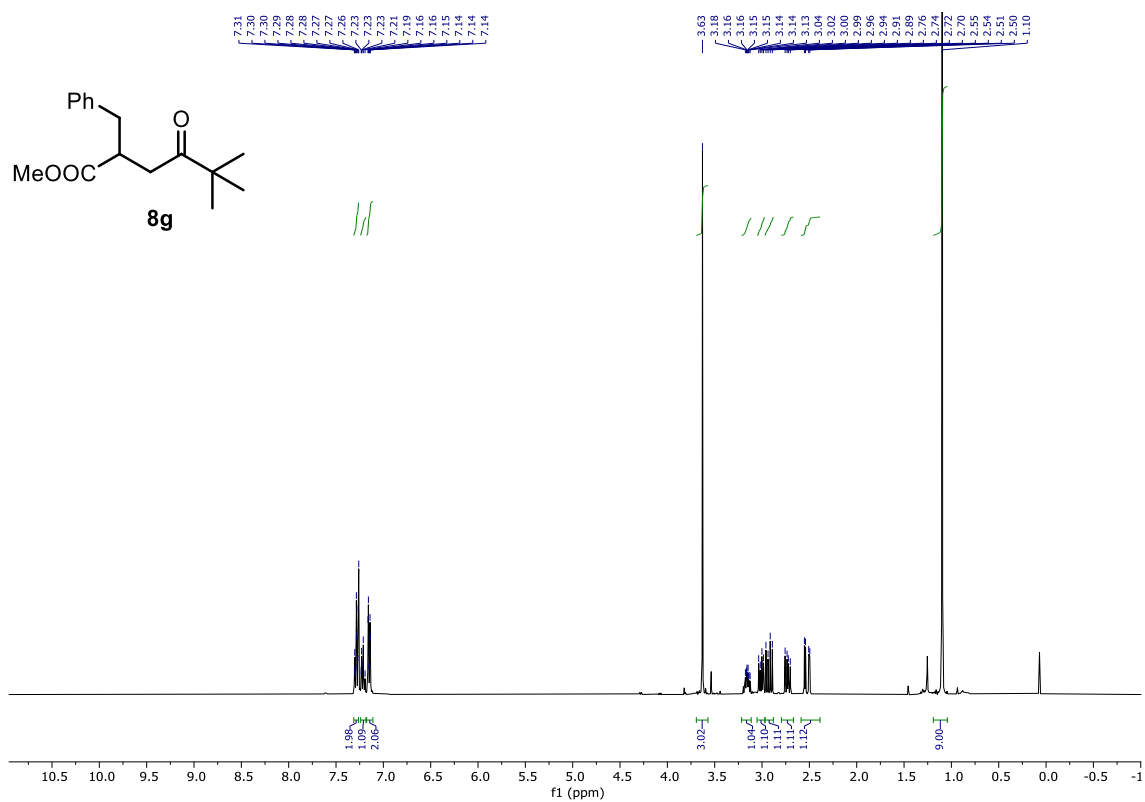
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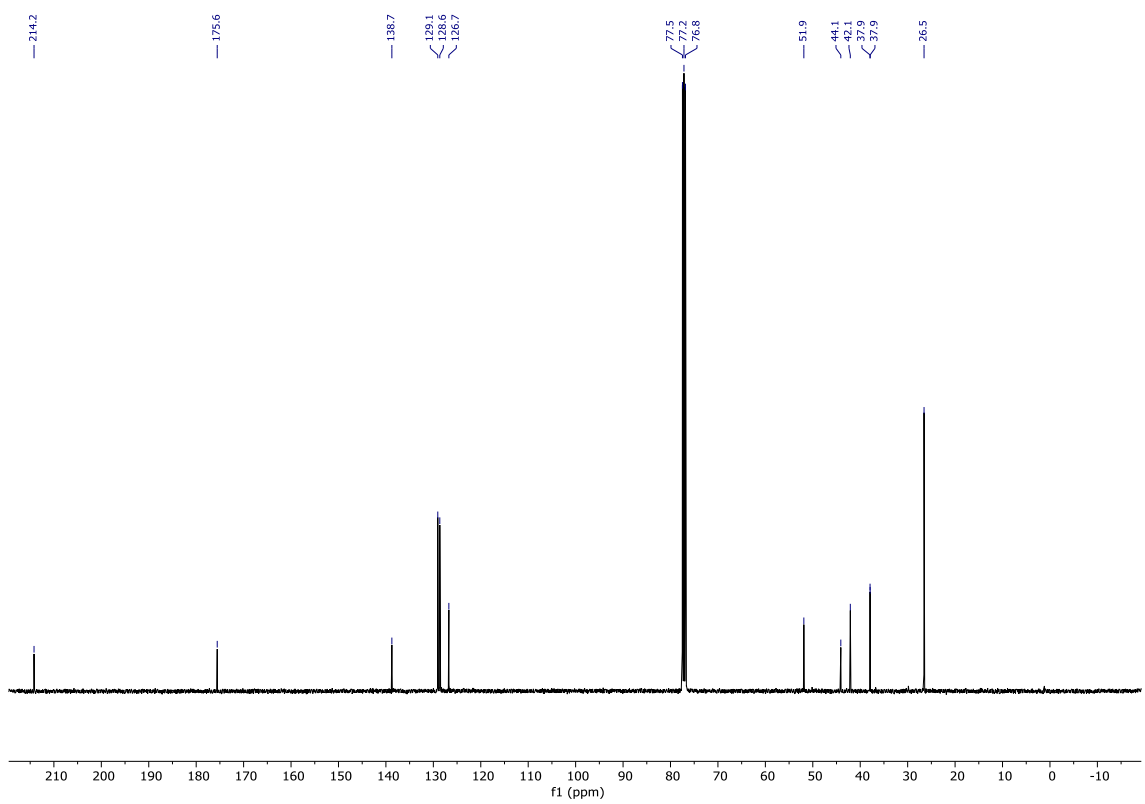
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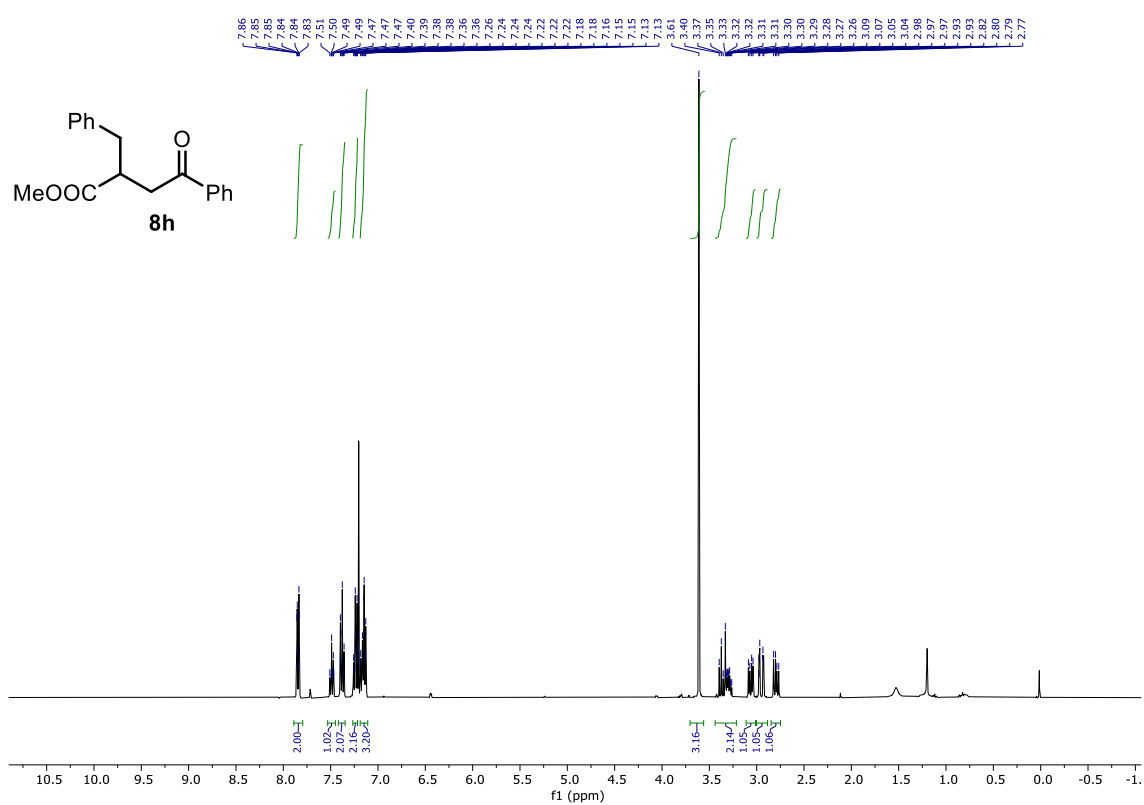
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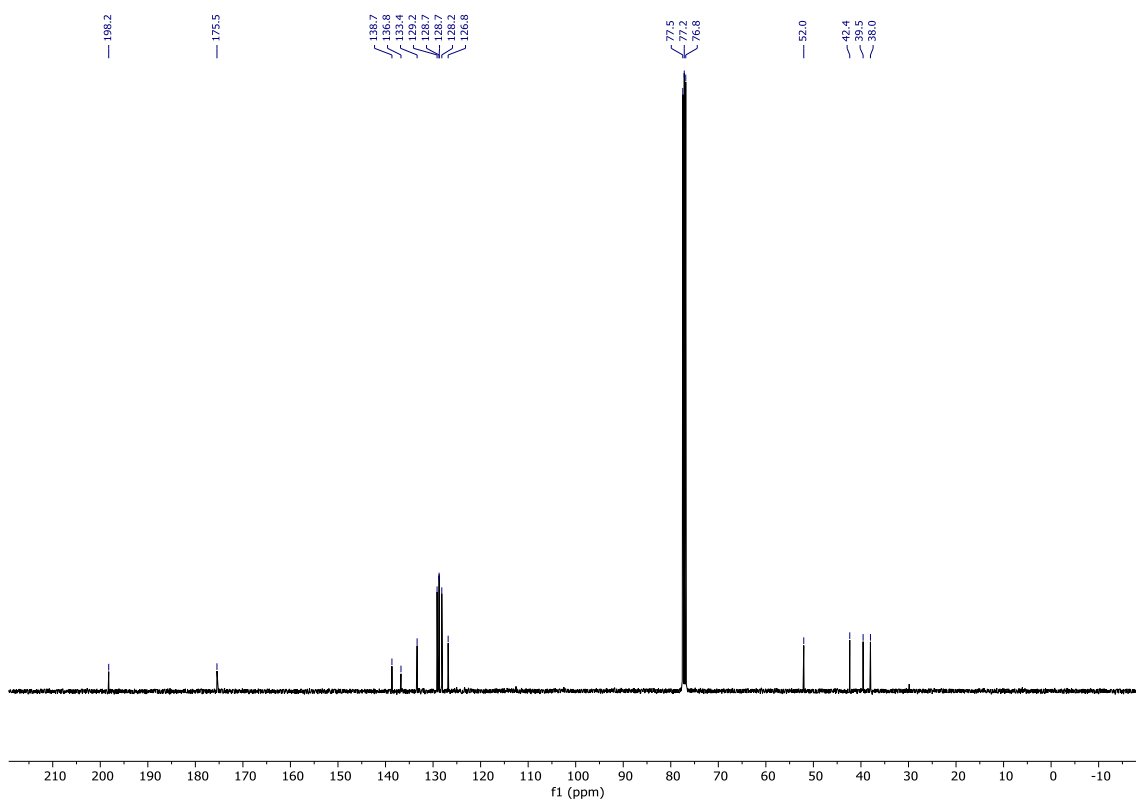
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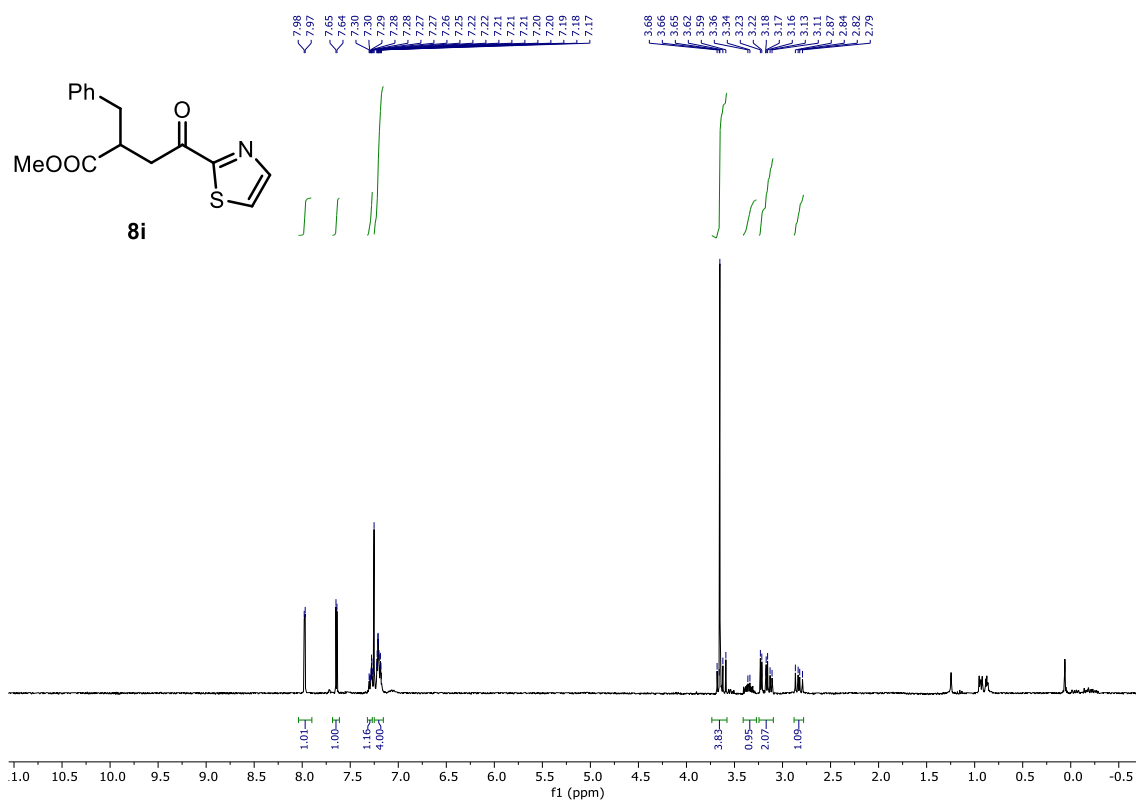
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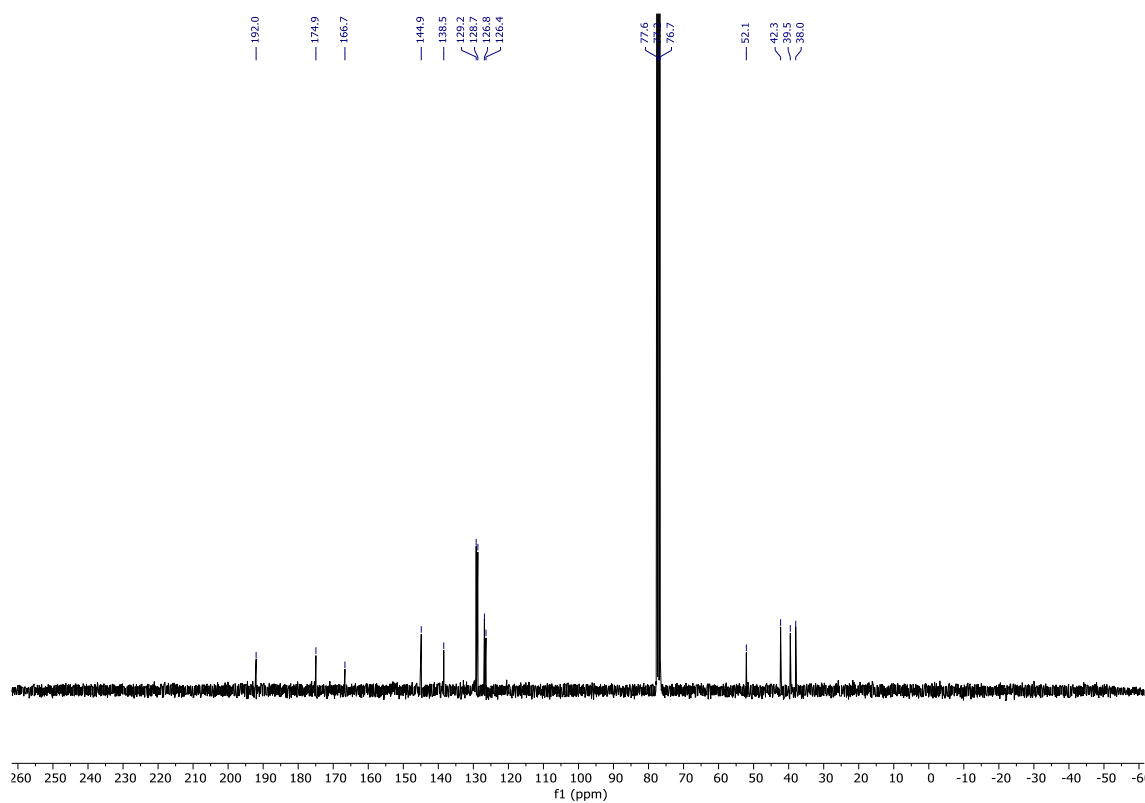
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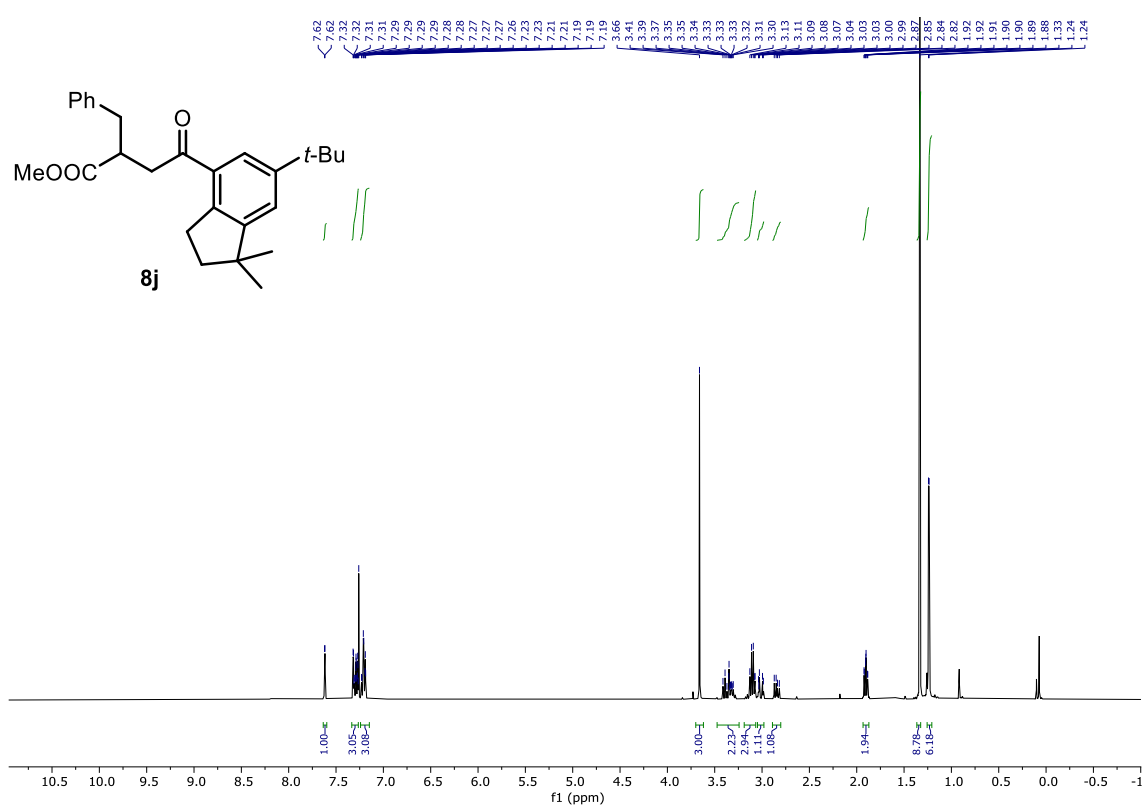
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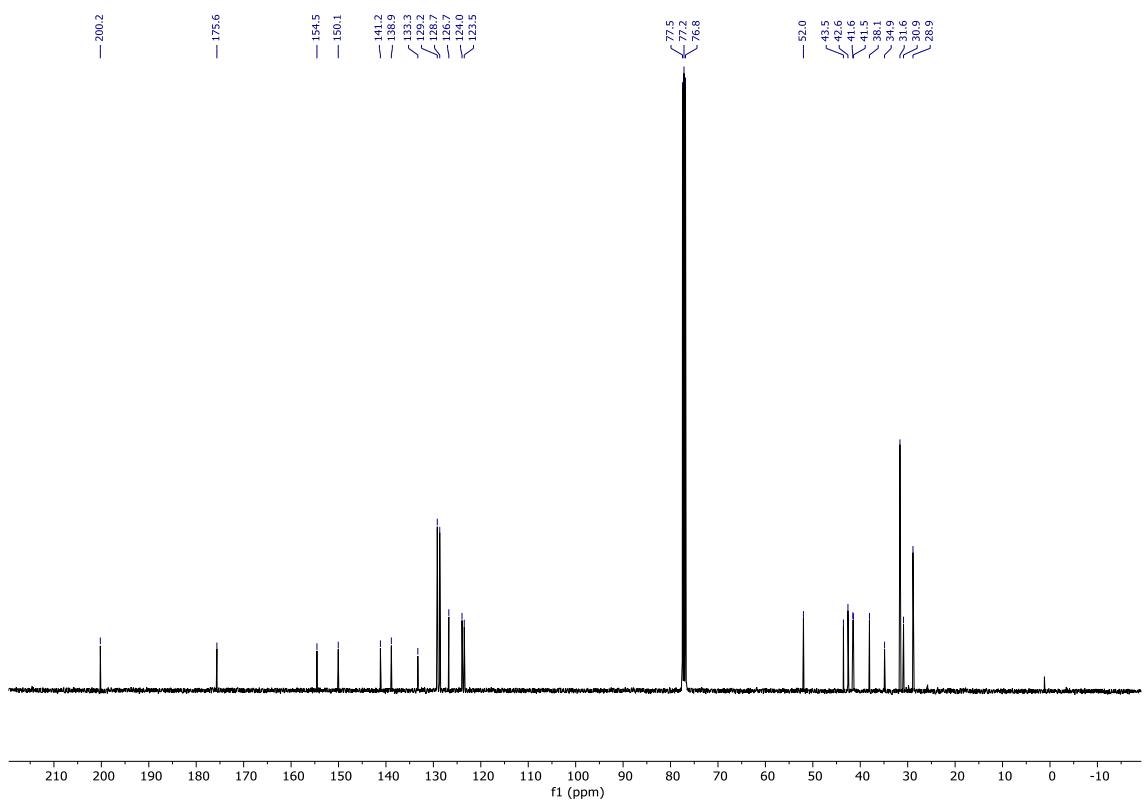
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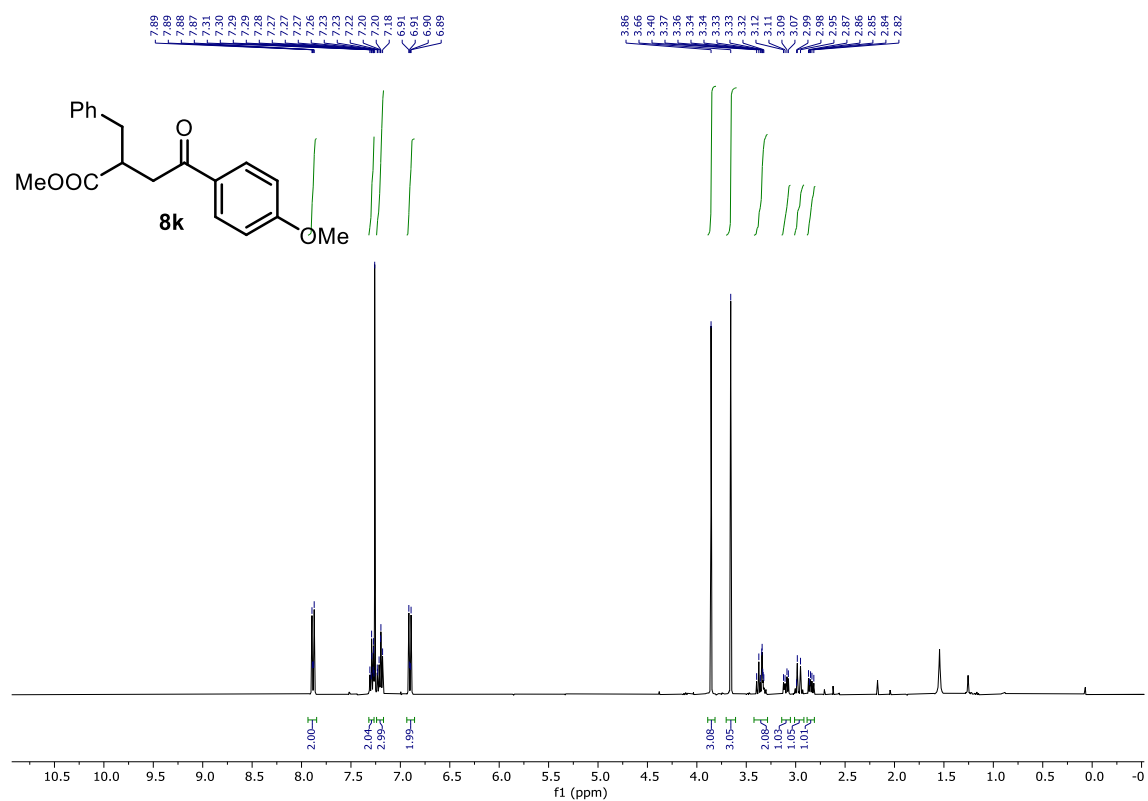
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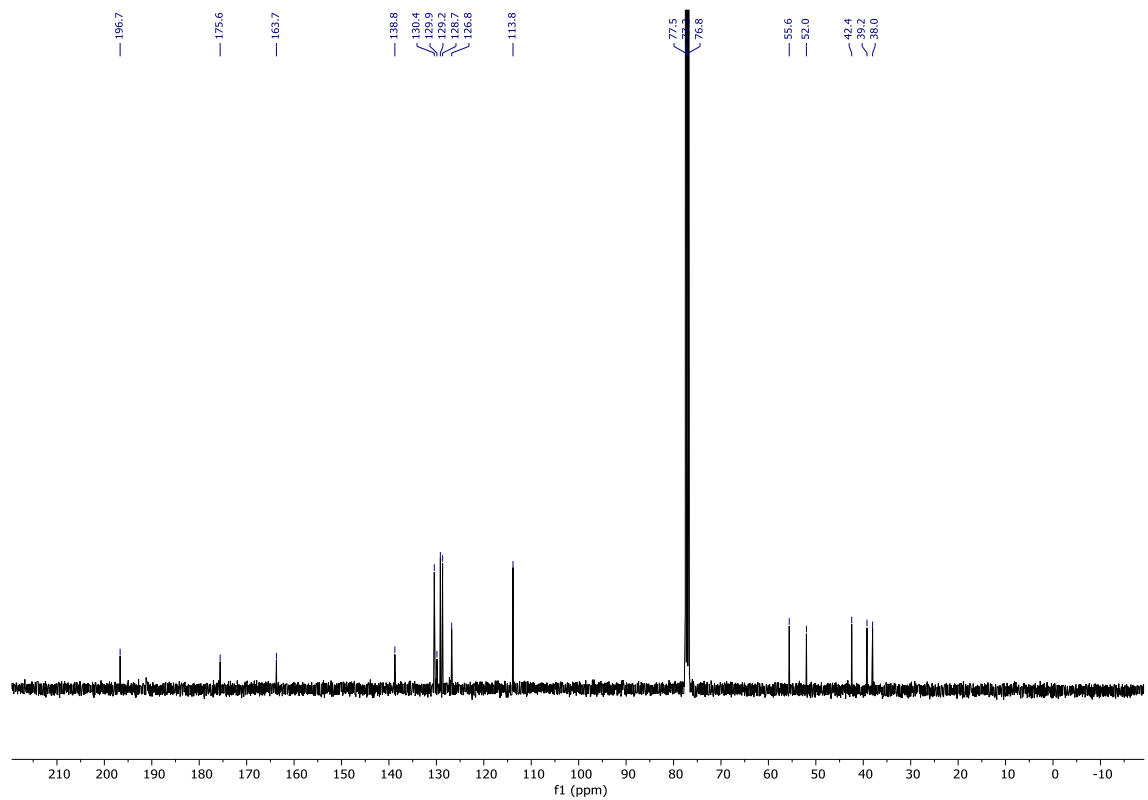
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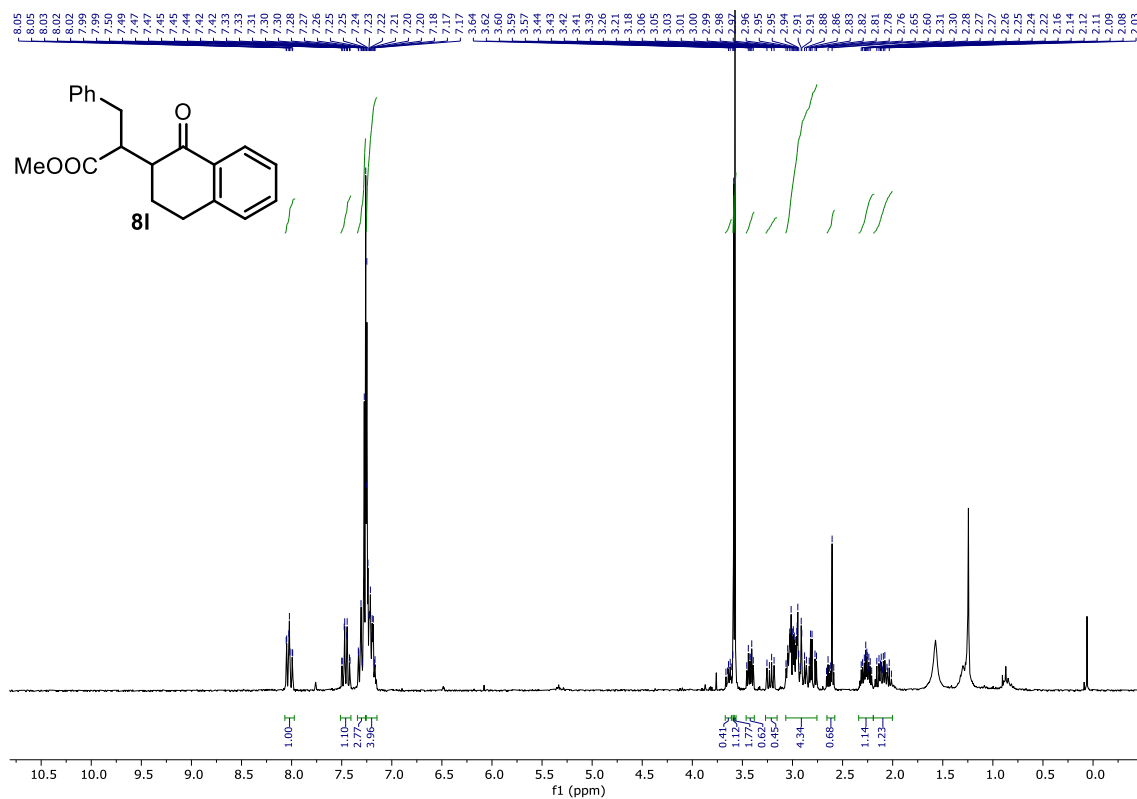
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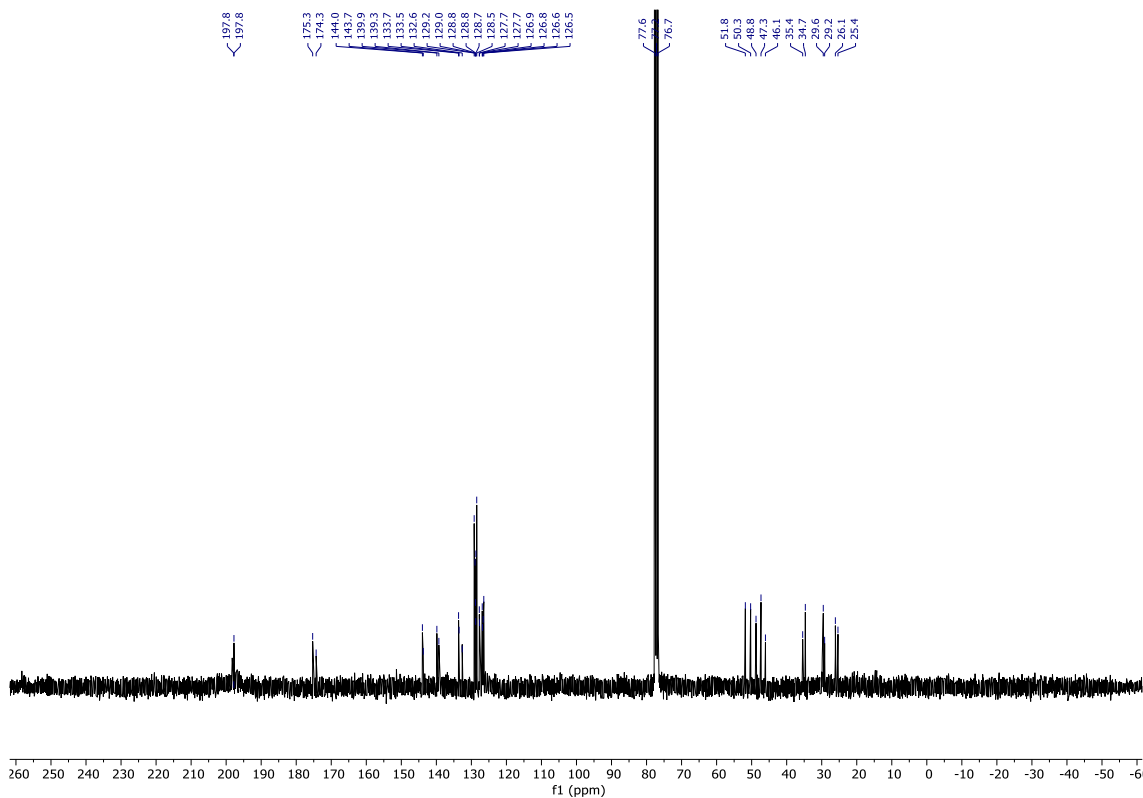
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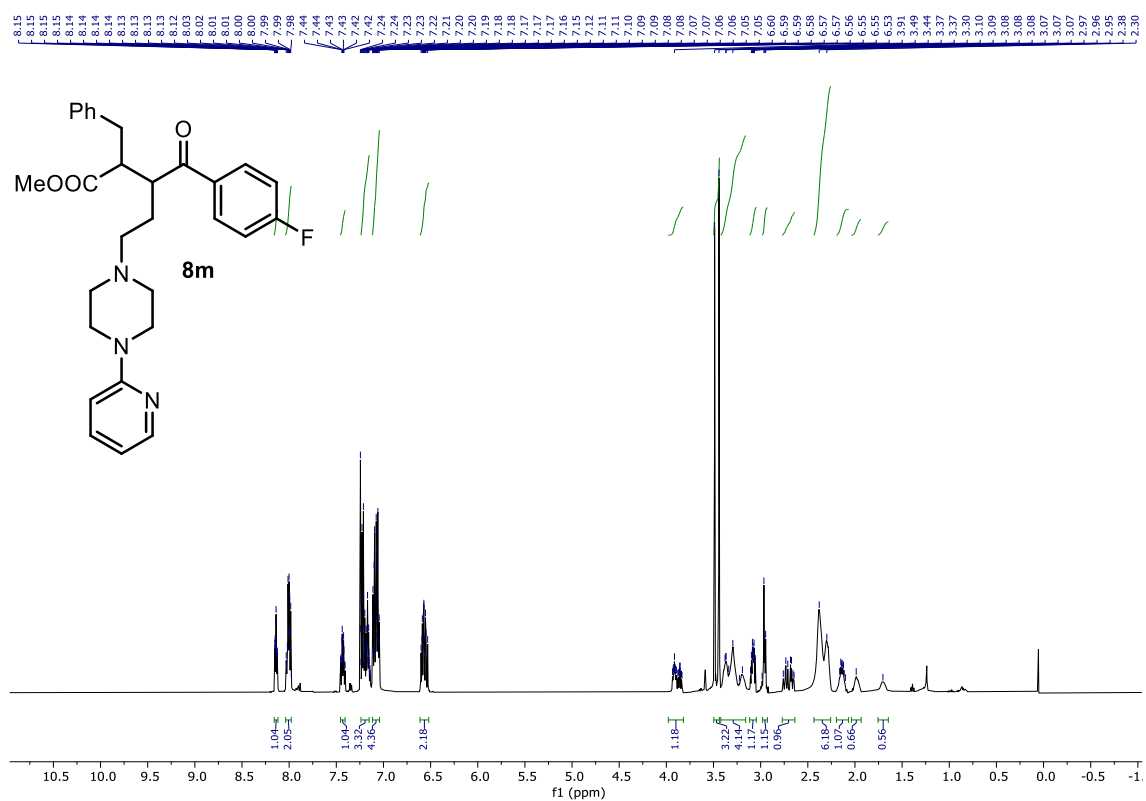
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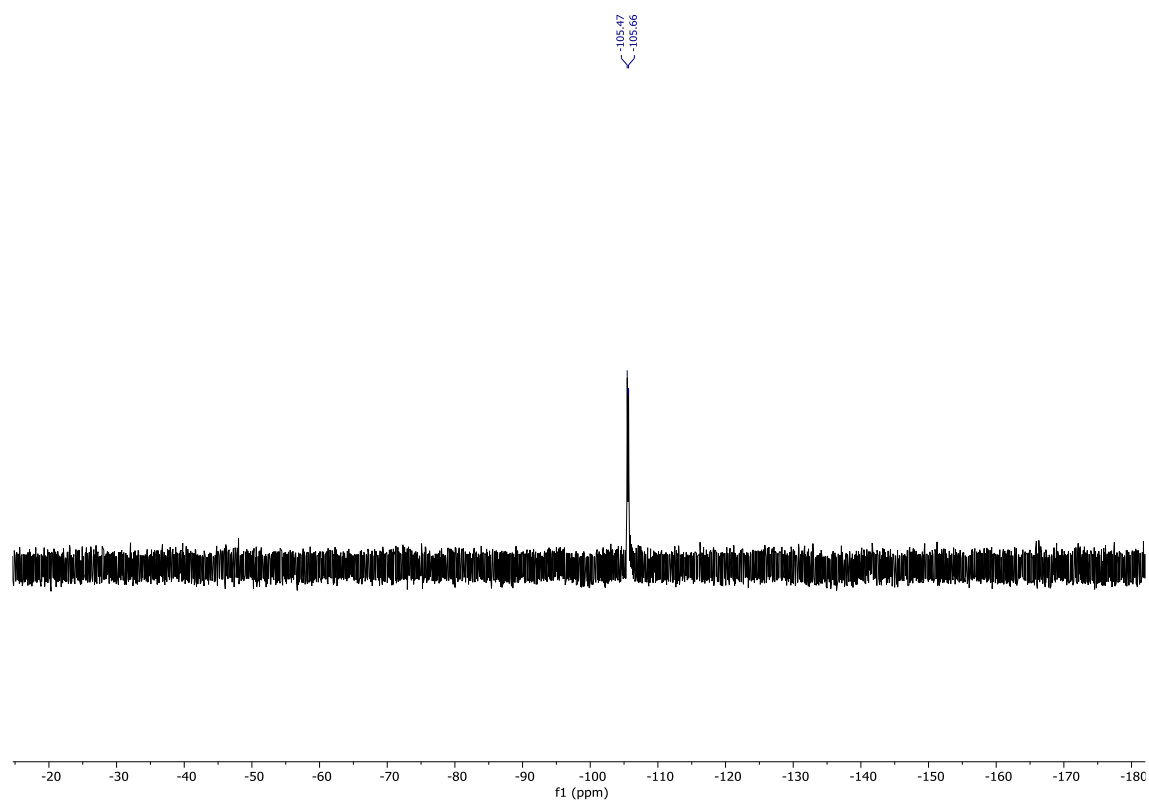
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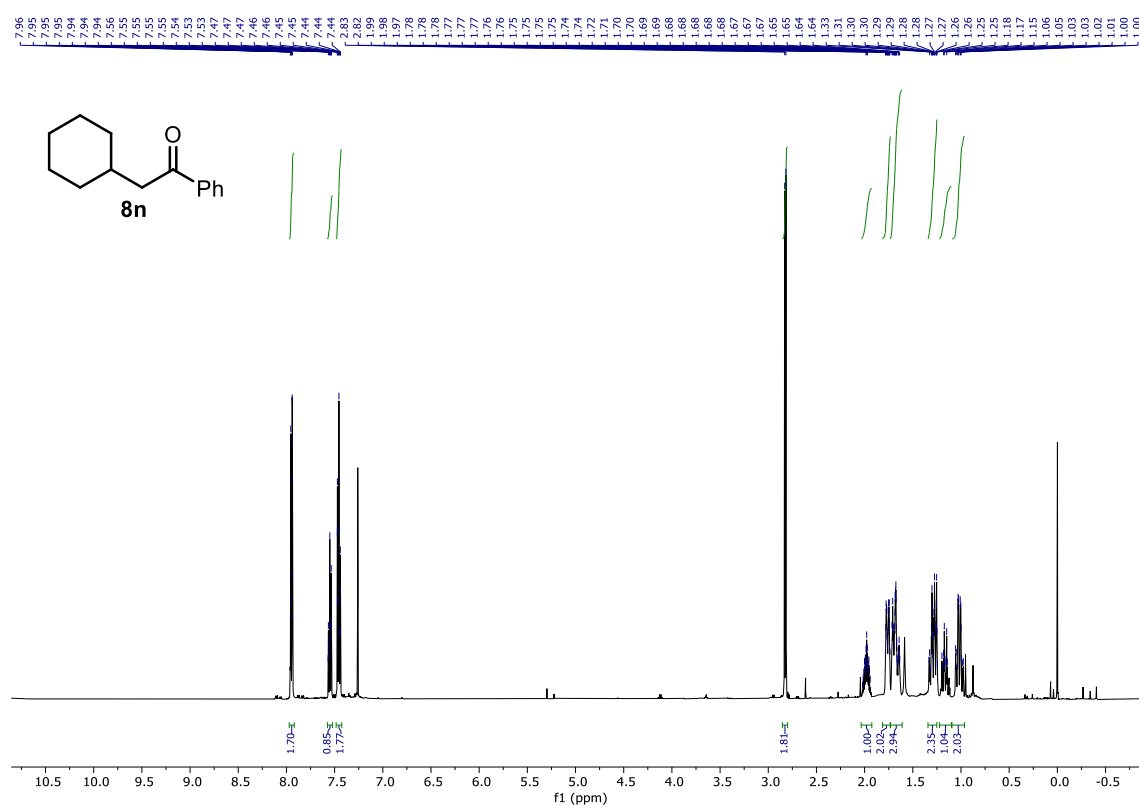
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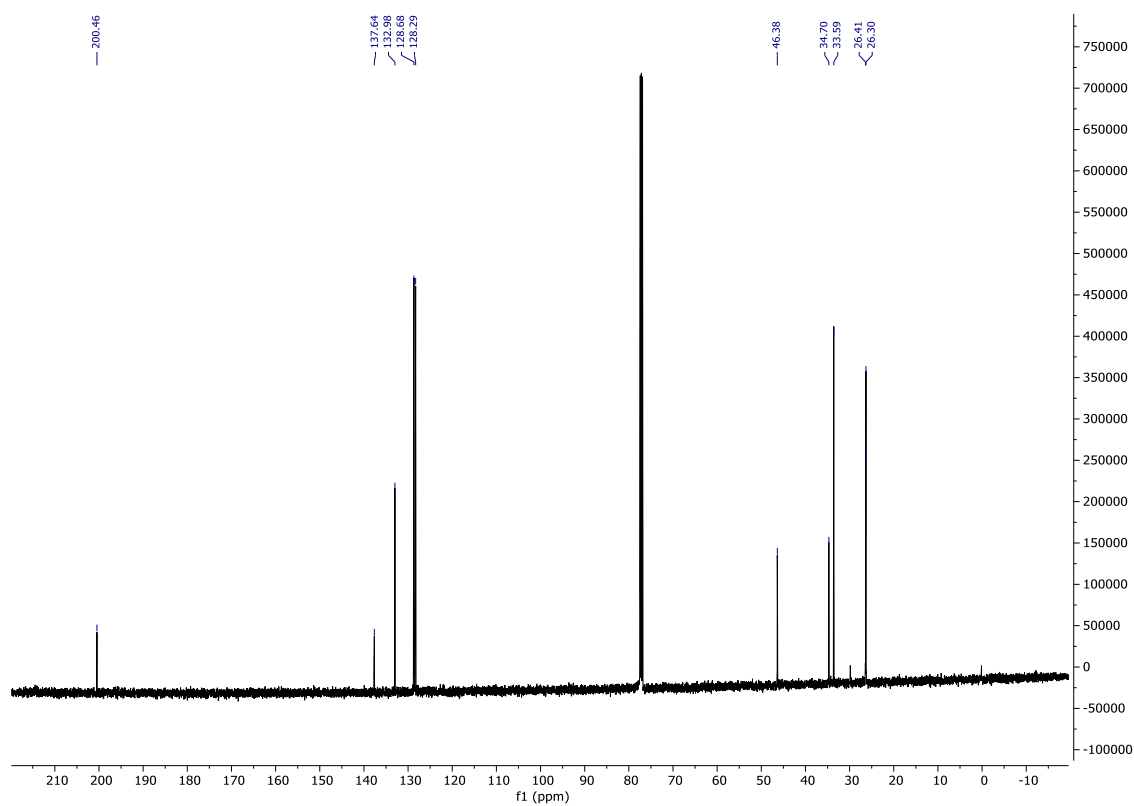
^{19}F NMR (376 MHz, CDCl_3)



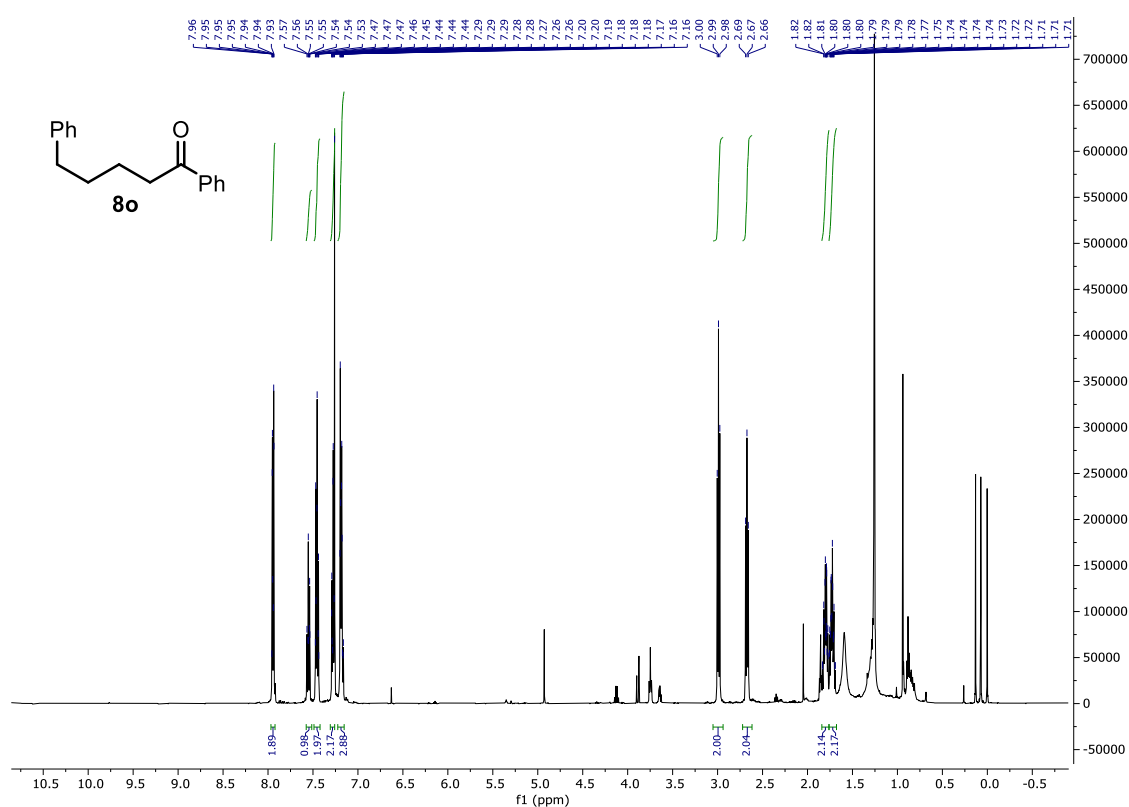
¹H NMR (400 MHz, CDCl₃)



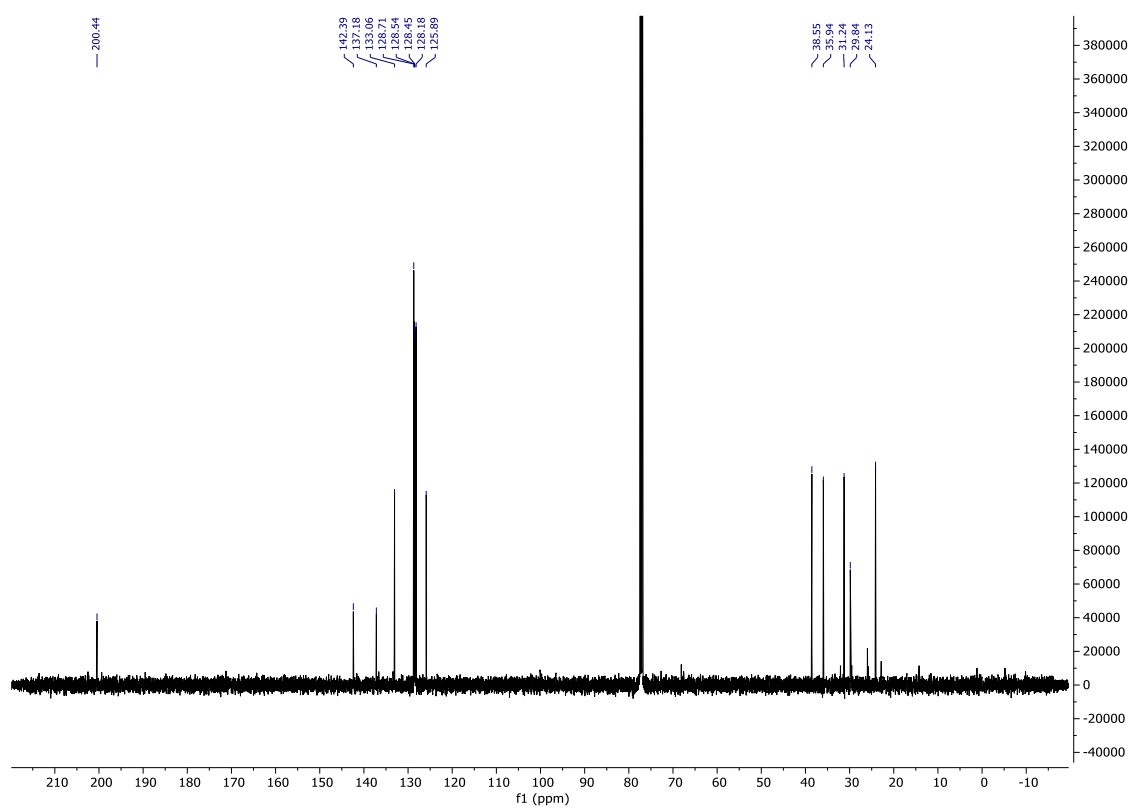
¹³C NMR (101 MHz, CDCl₃)



^1H NMR (400 MHz, CDCl_3)

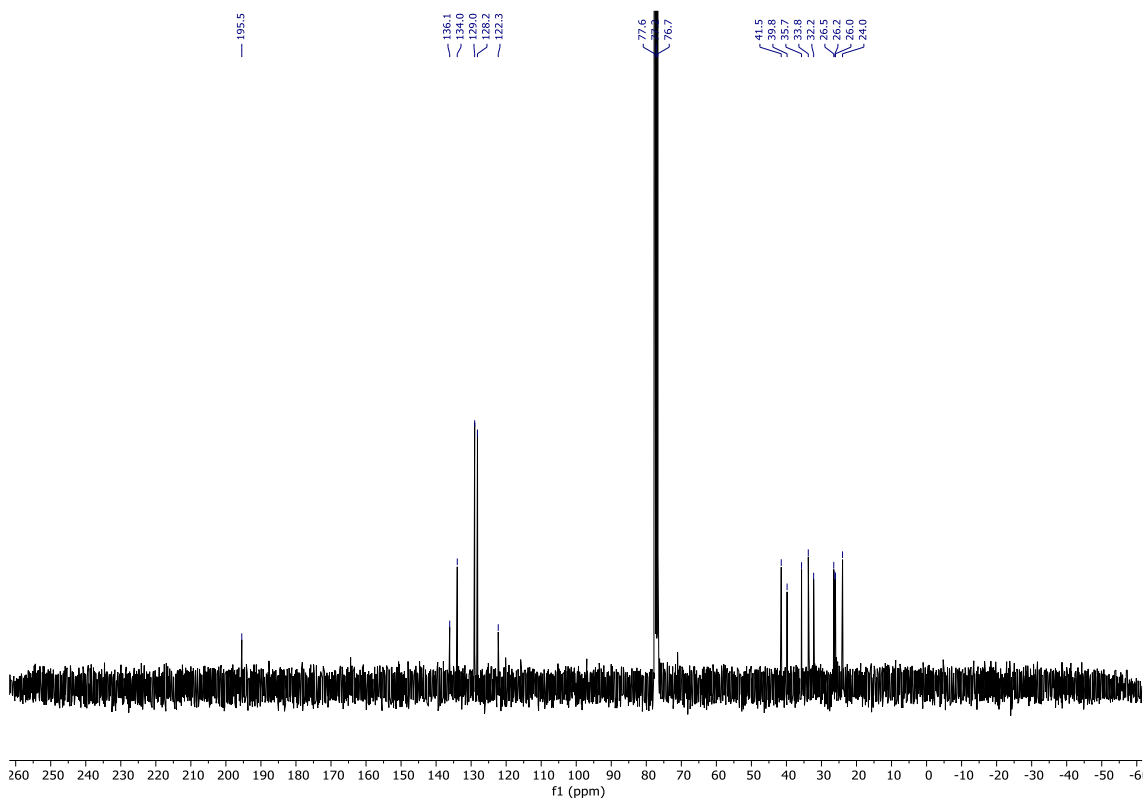


^{13}C NMR (101 MHz, CDCl_3)

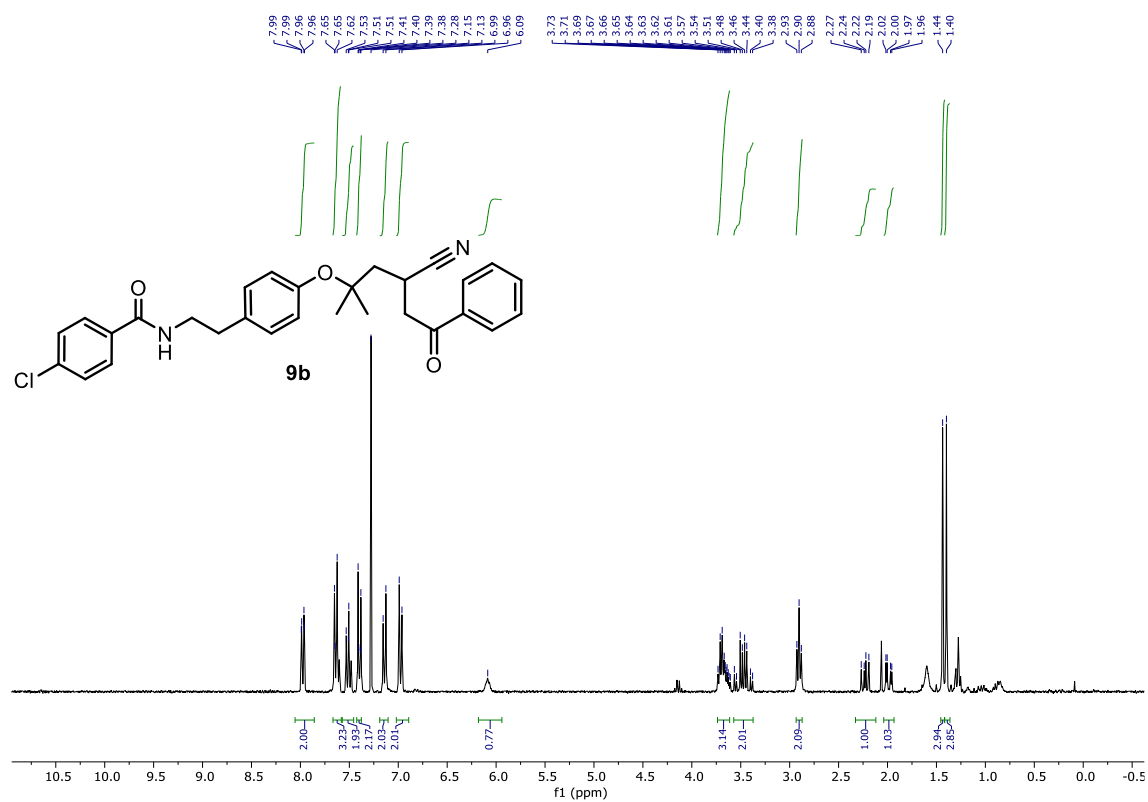


CC(C#N)CC(=O)c1ccccc1

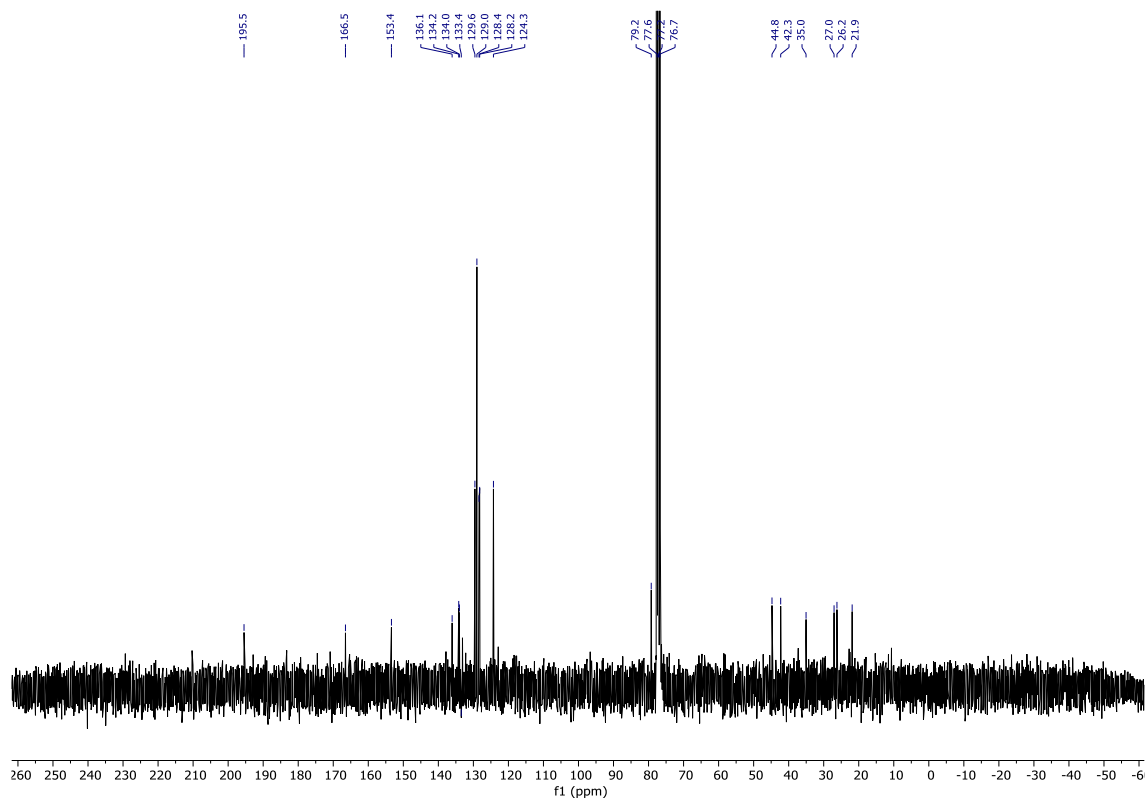
9a



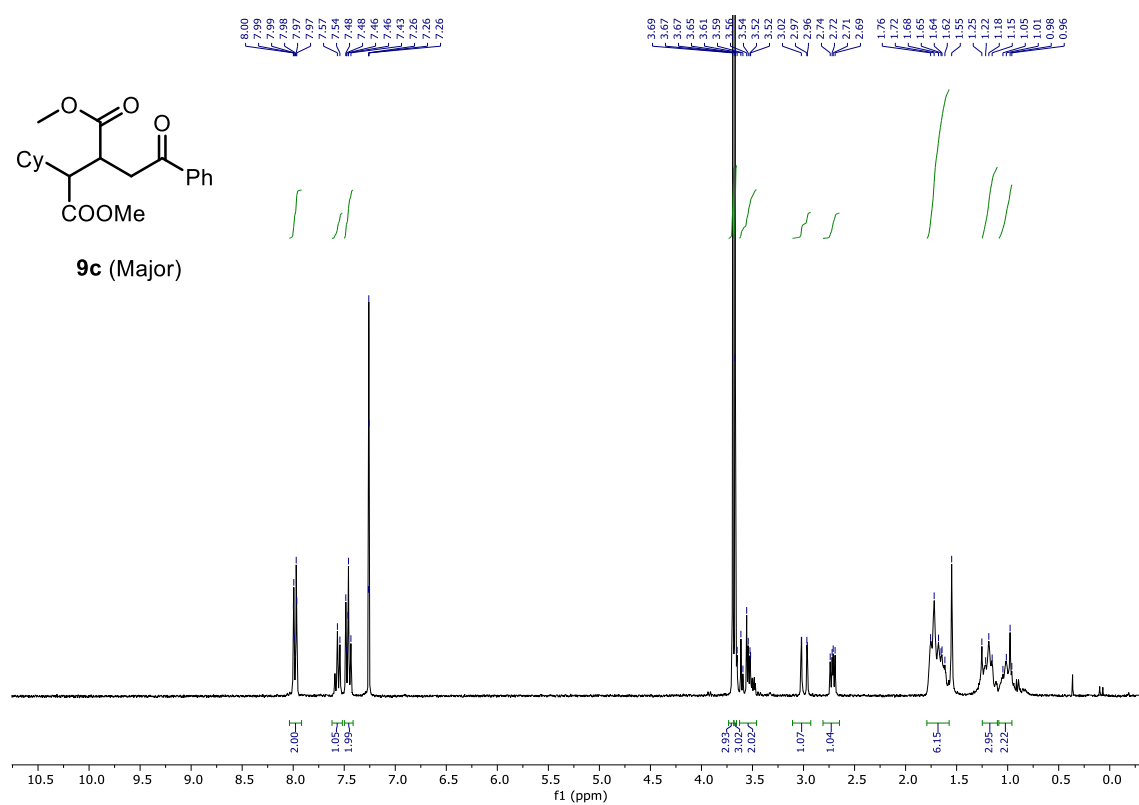
^1H NMR (300 MHz, CDCl_3)



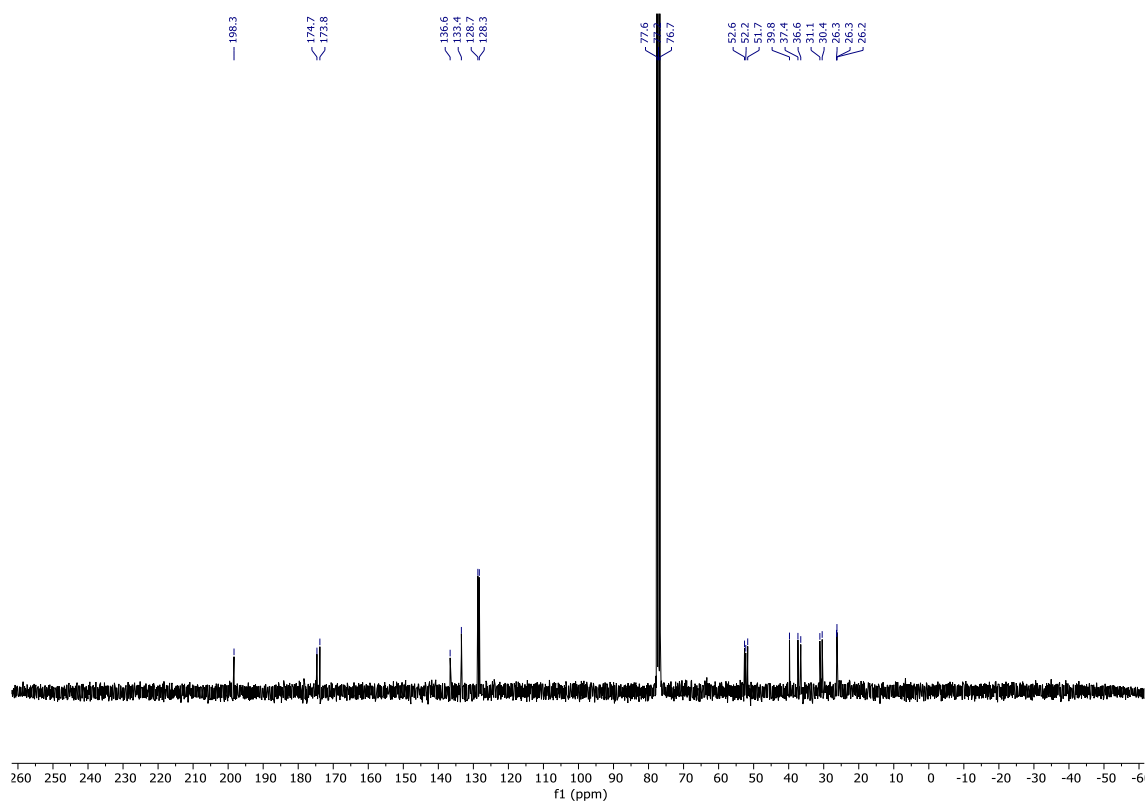
^{13}C NMR (75 MHz, CDCl_3)



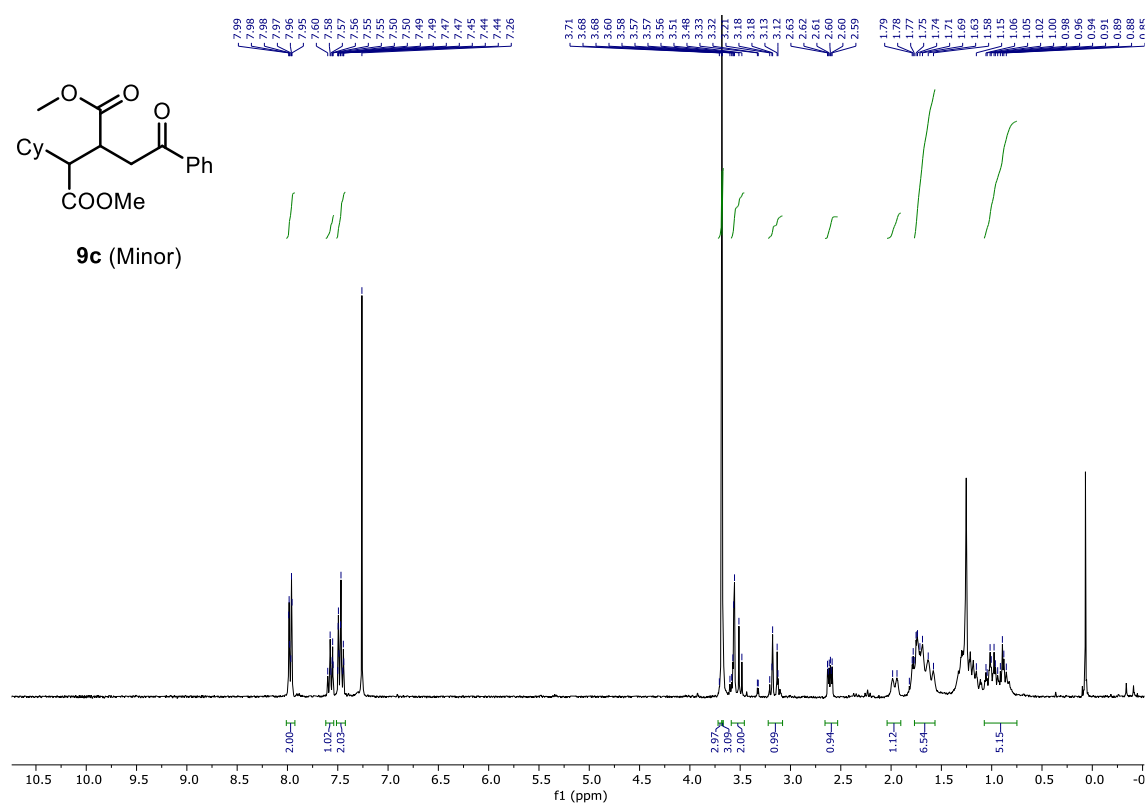
^1H NMR (300 MHz, CDCl_3)



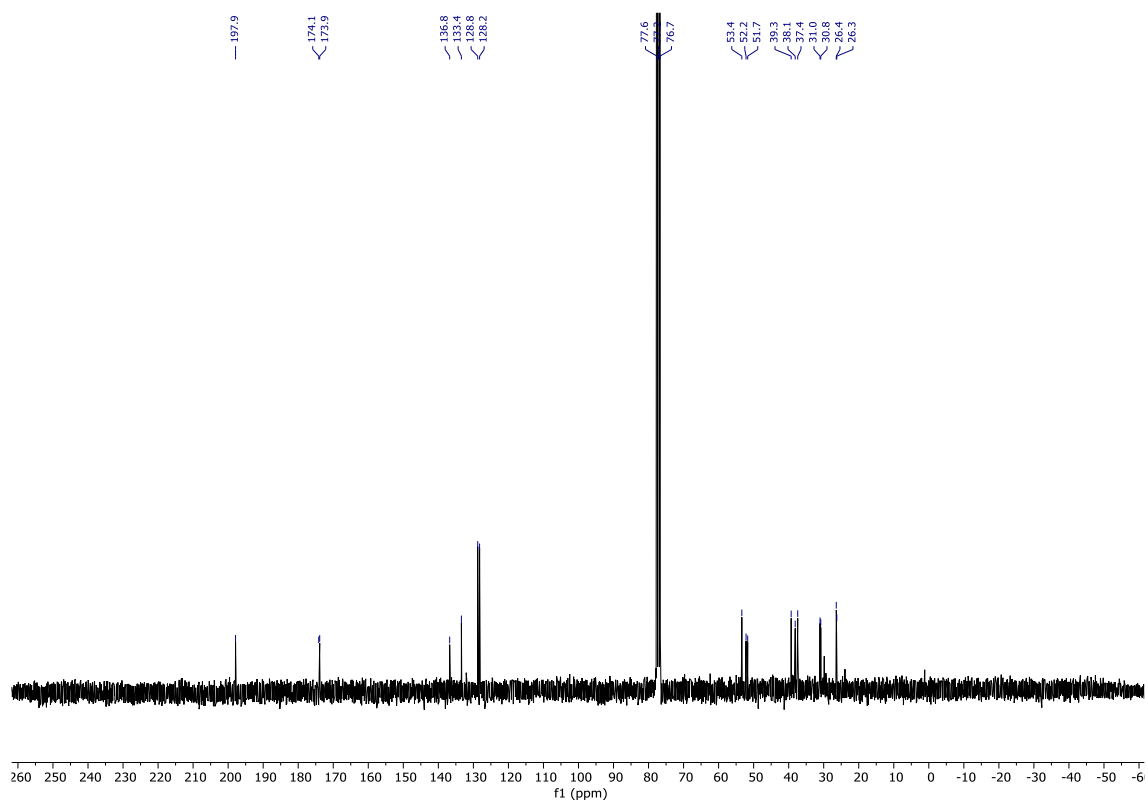
^{13}C NMR (75 MHz, CDCl_3)



¹H NMR (300 MHz, CDCl₃)

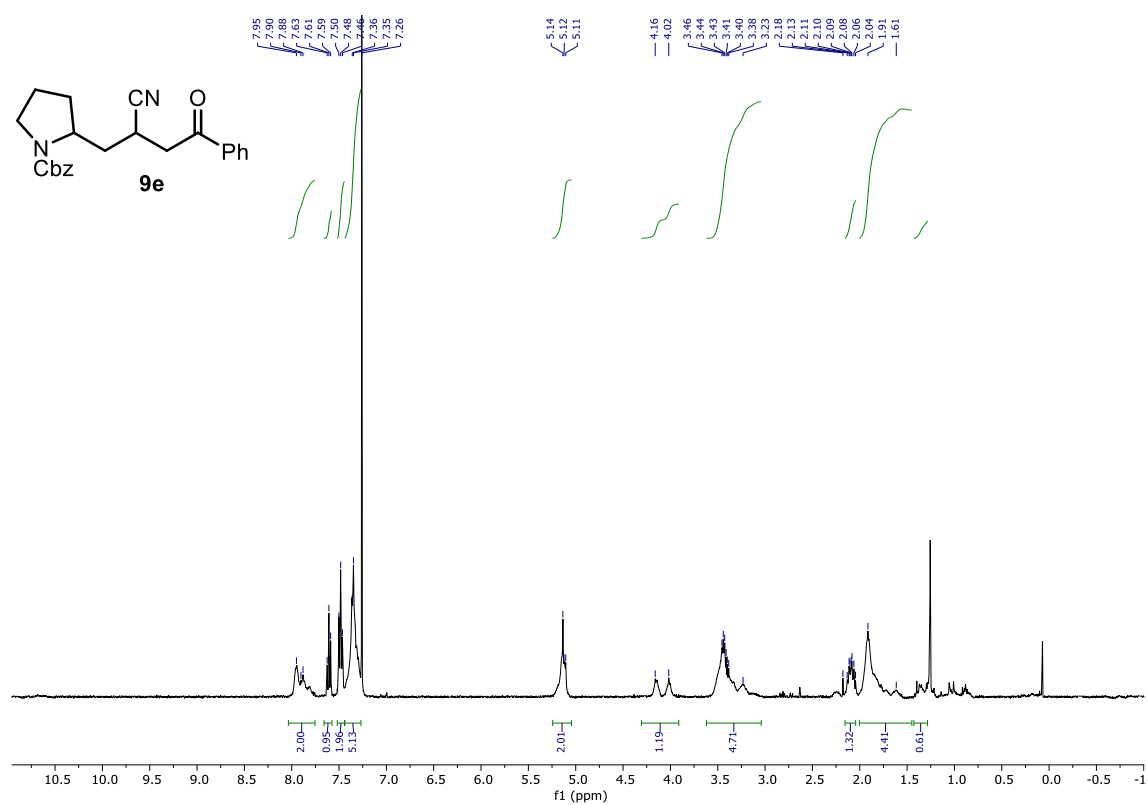


¹³C NMR (75 MHz, CDCl₃)

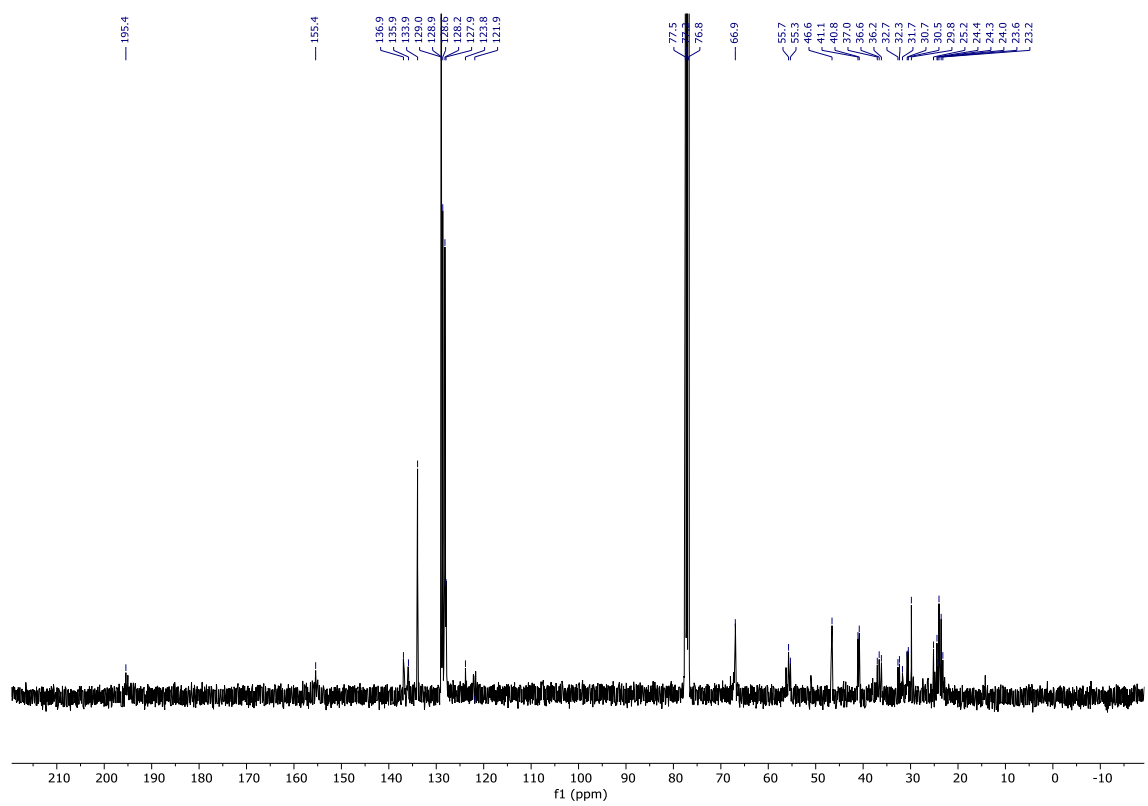


¹H NMR (300 MHz, CDCl₃)

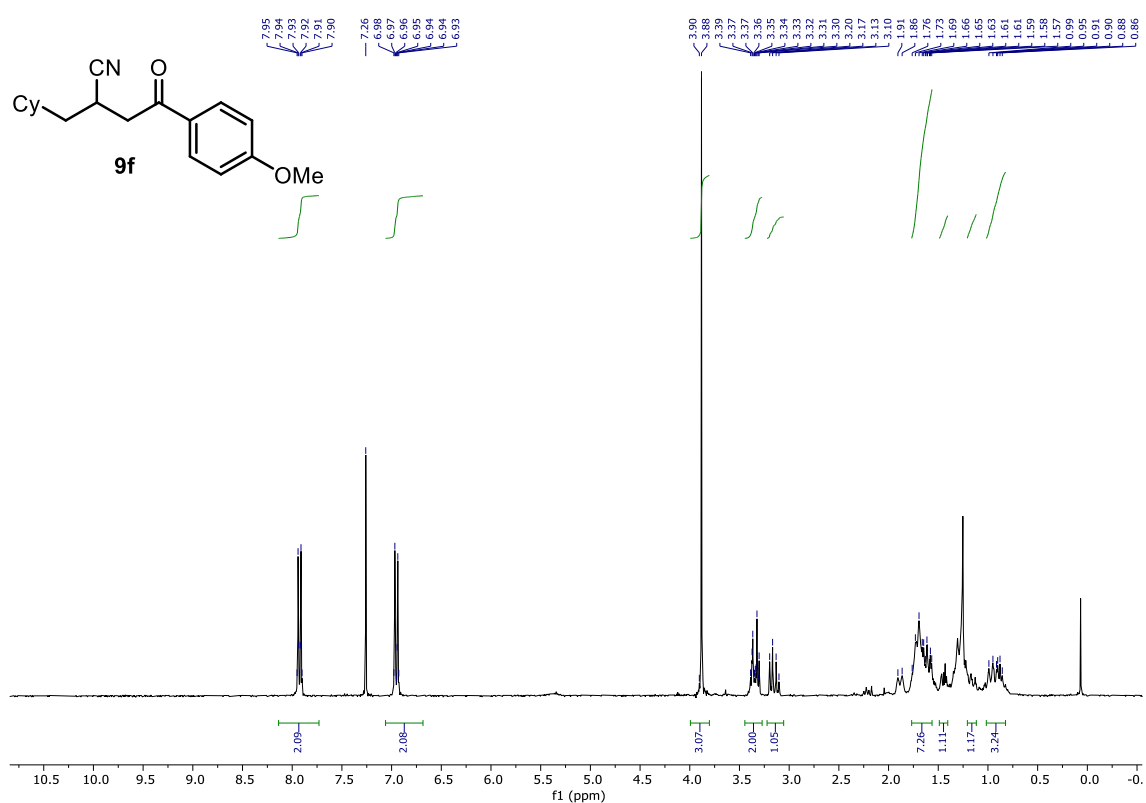
^1H NMR (400 MHz, CDCl_3)



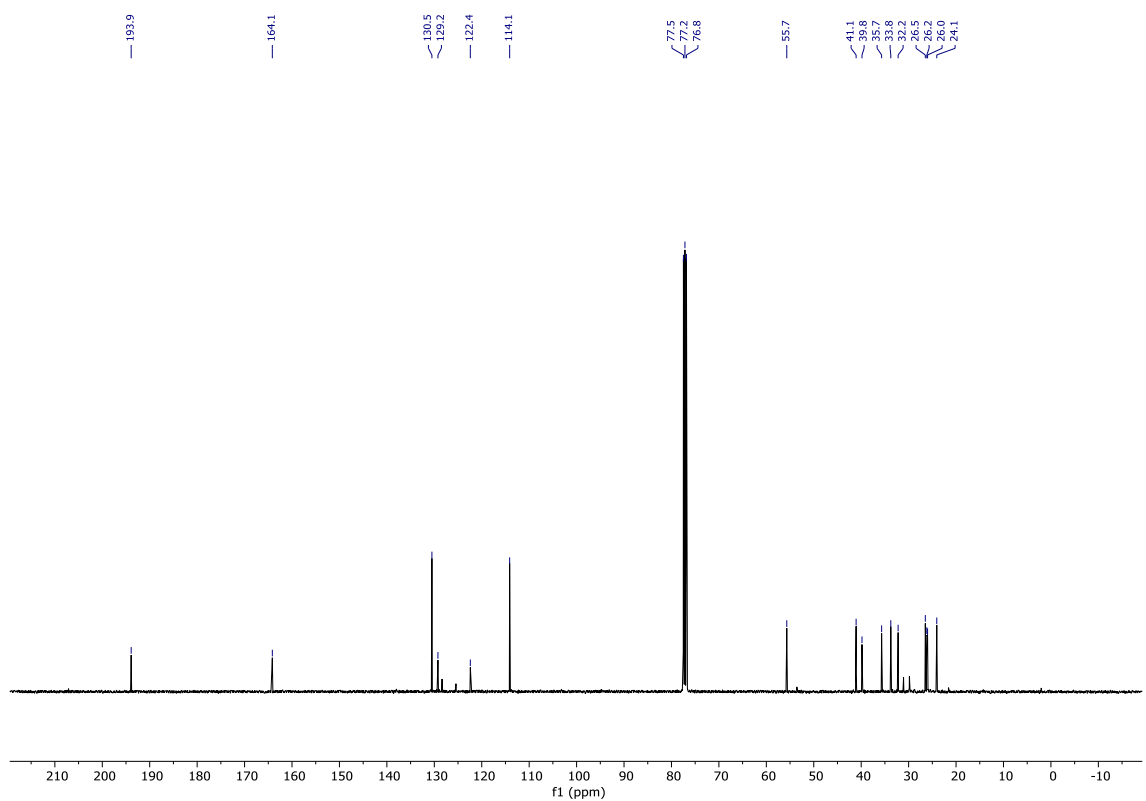
^{13}C NMR (101 MHz, CDCl_3)



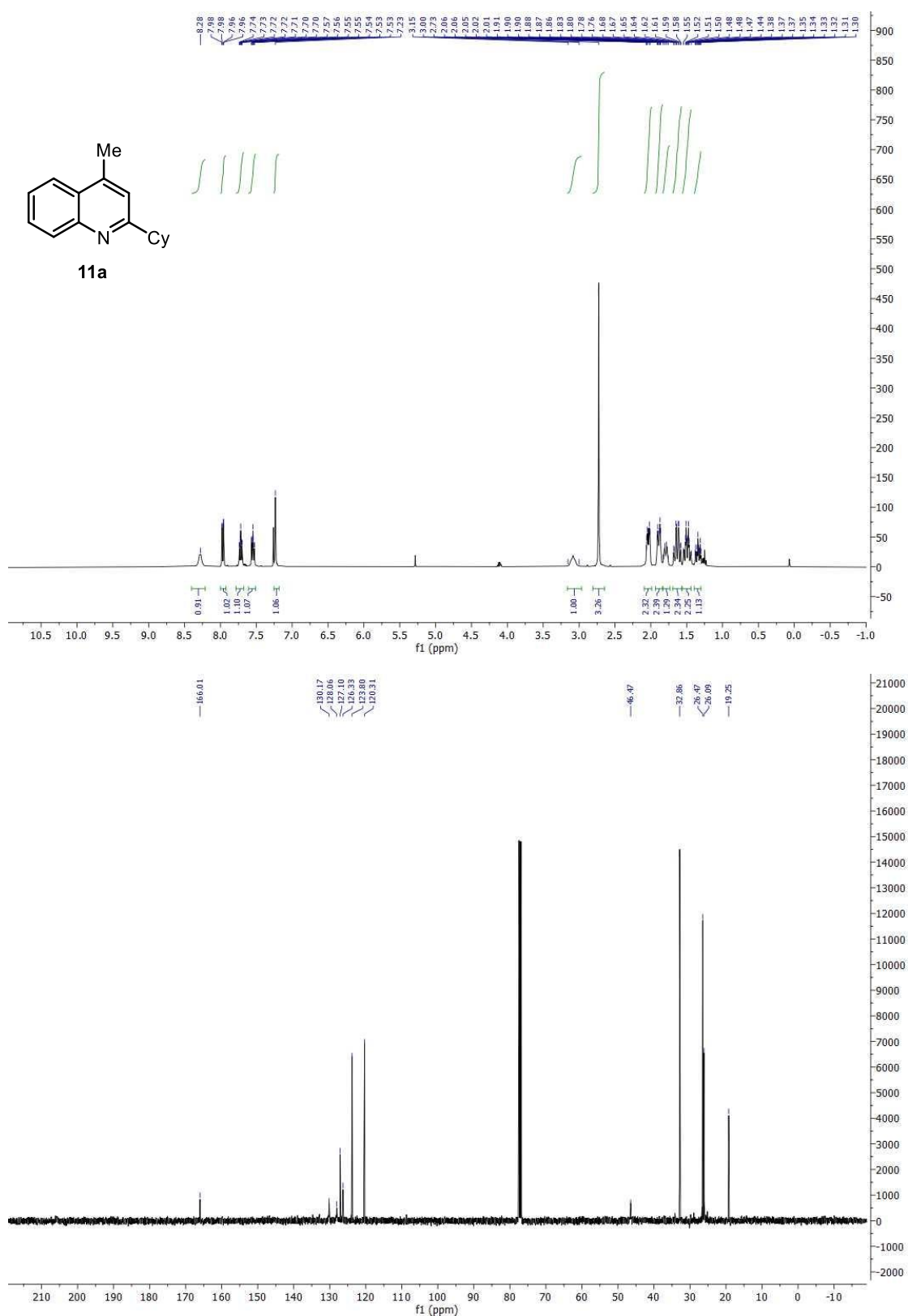
^1H NMR (300 MHz, CDCl_3)



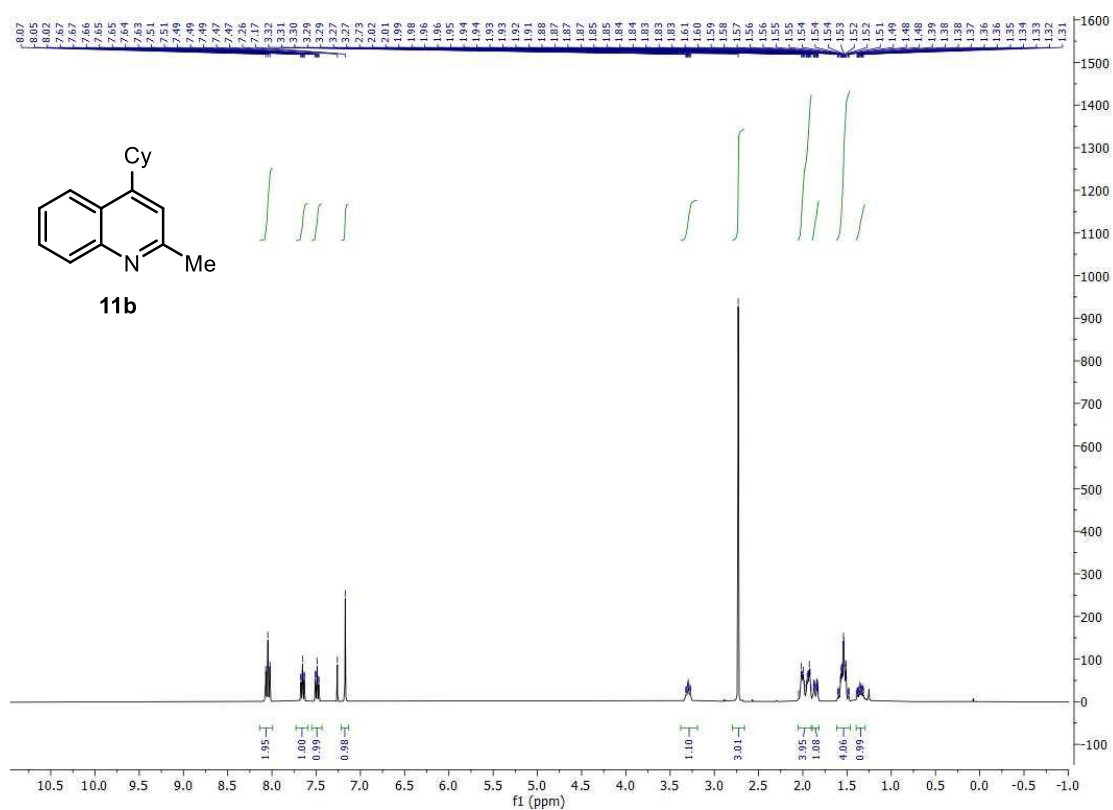
^{13}C NMR (75 MHz, CDCl_3)



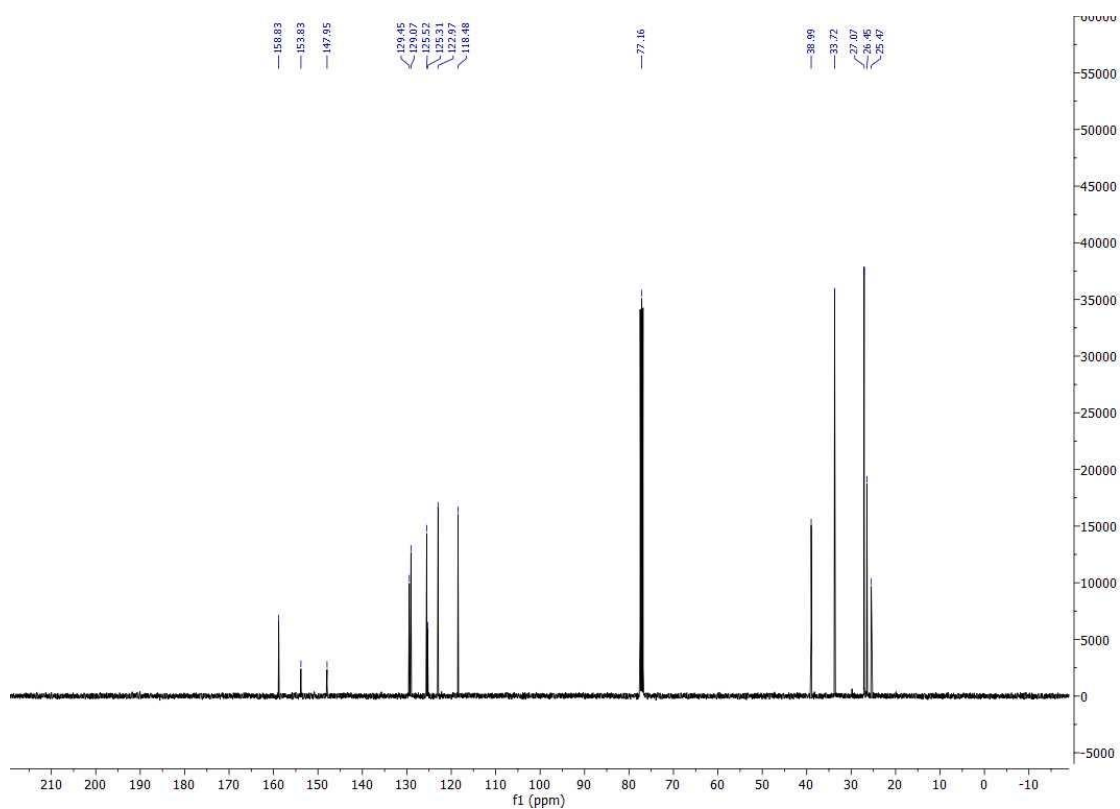
^1H NMR (400 MHz, CDCl_3)



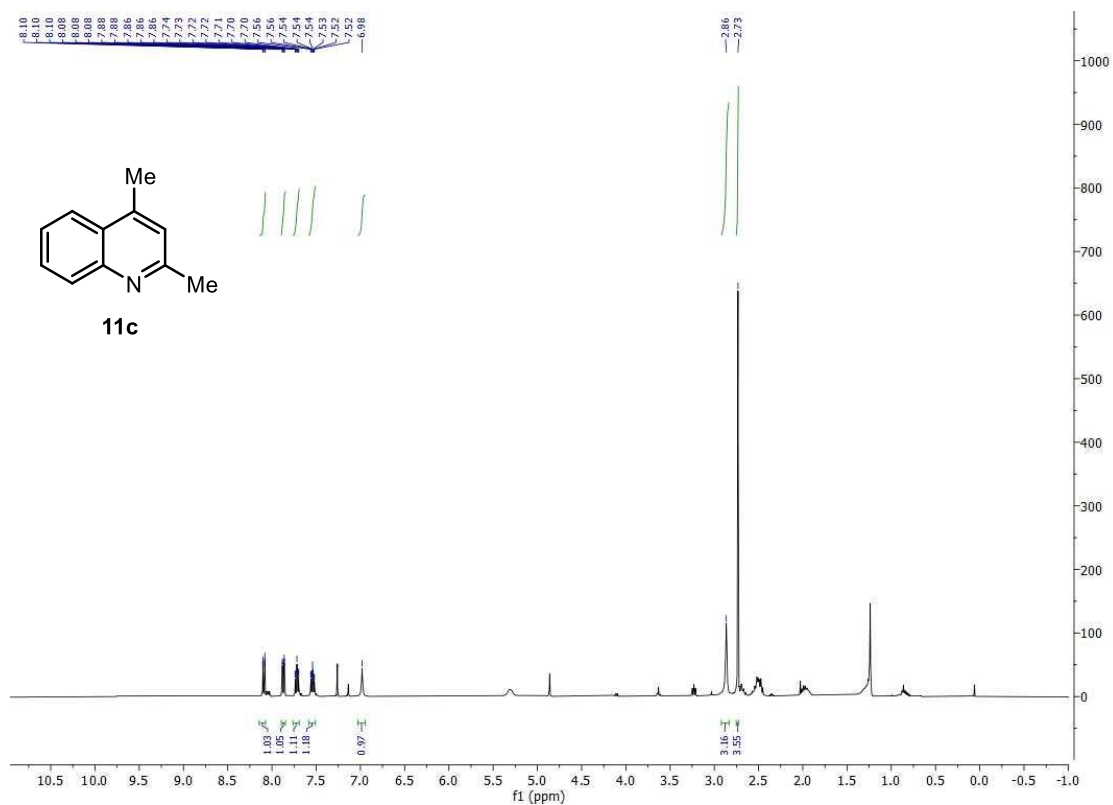
^1H NMR (400 MHz, CDCl_3)



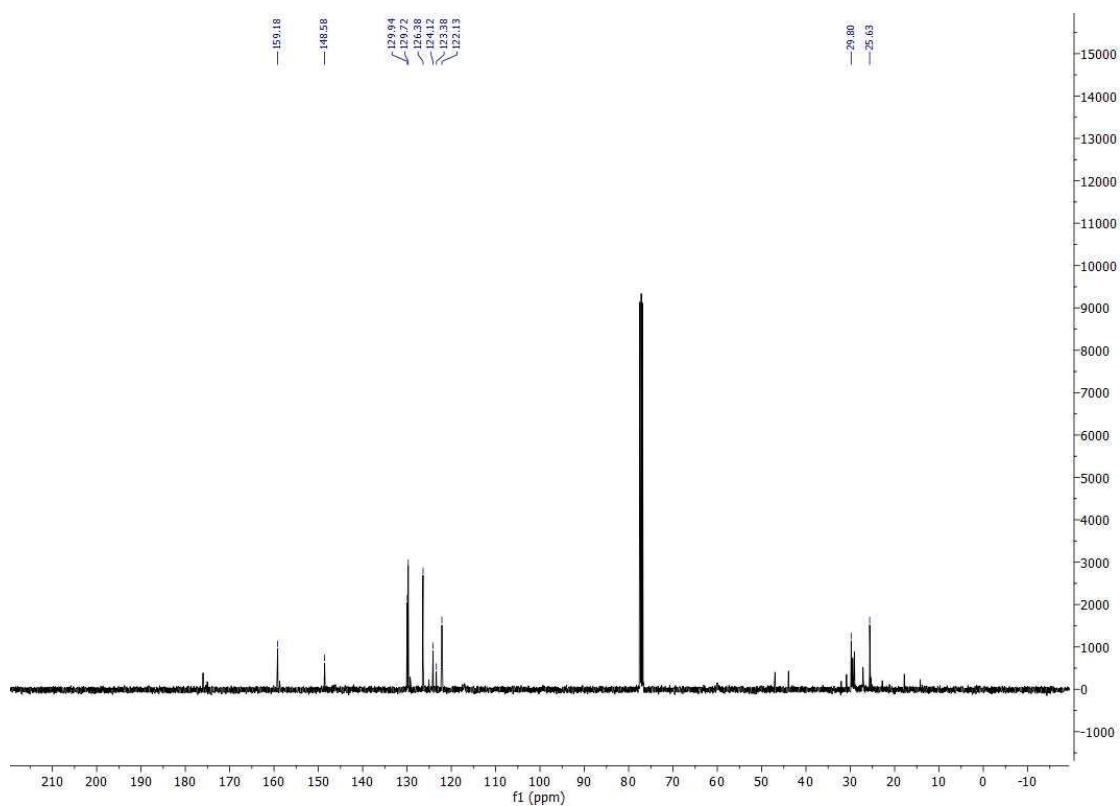
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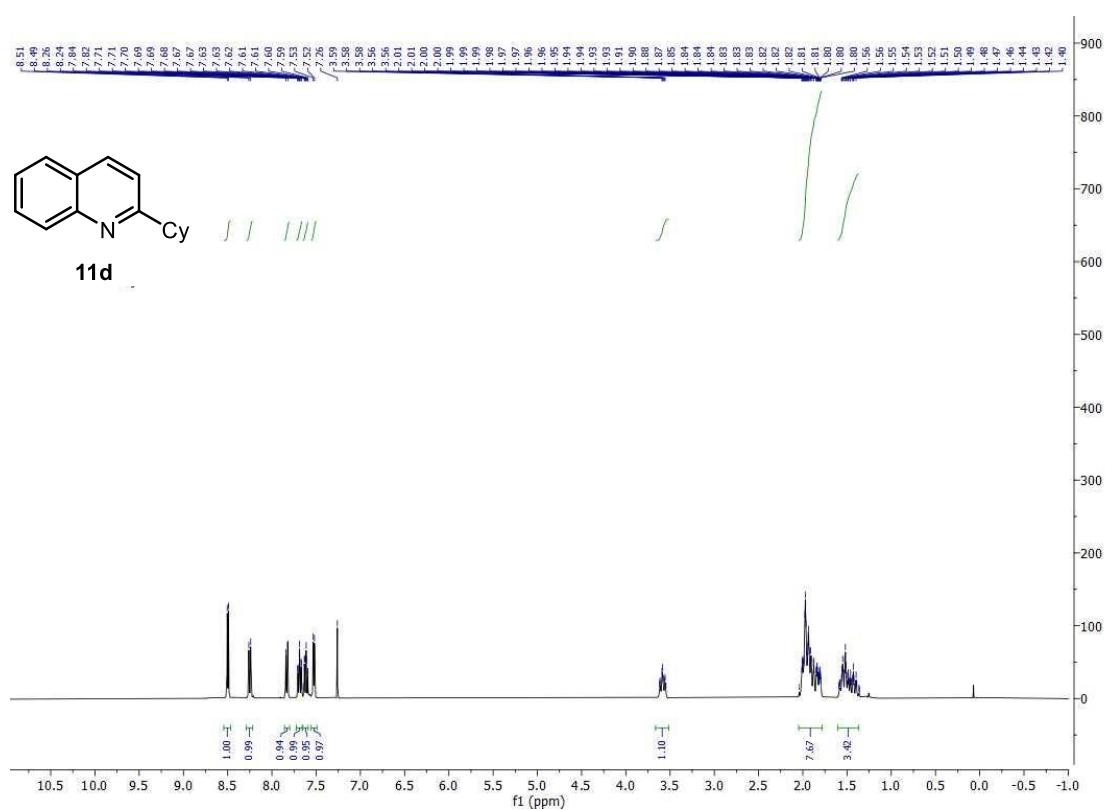
^1H NMR (400 MHz, CDCl_3)



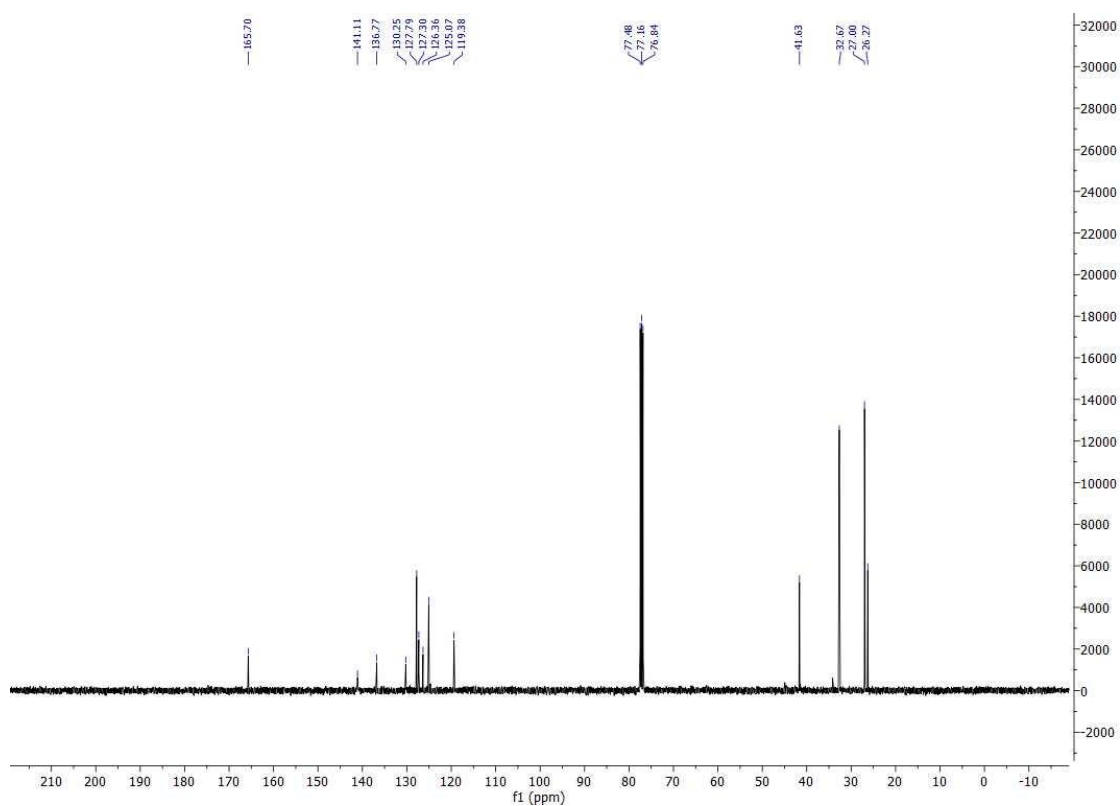
^{13}C NMR (101 MHz, CDCl_3)



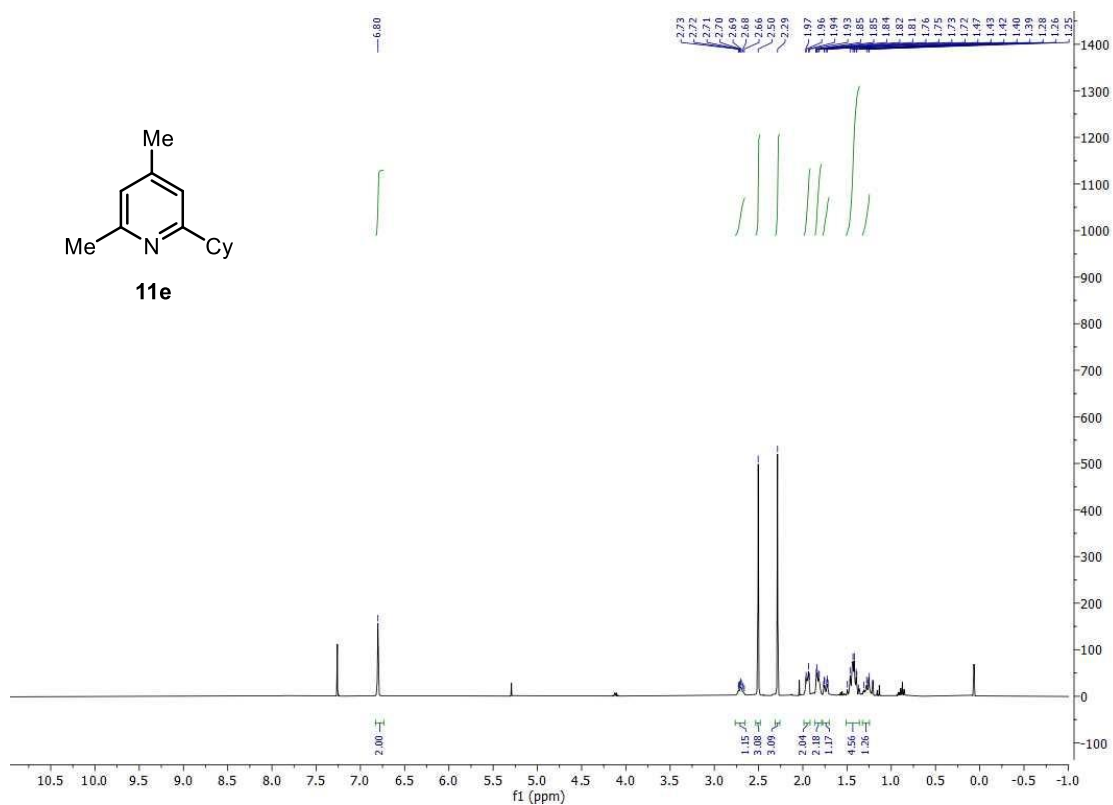
^1H NMR (400 MHz, CDCl_3)



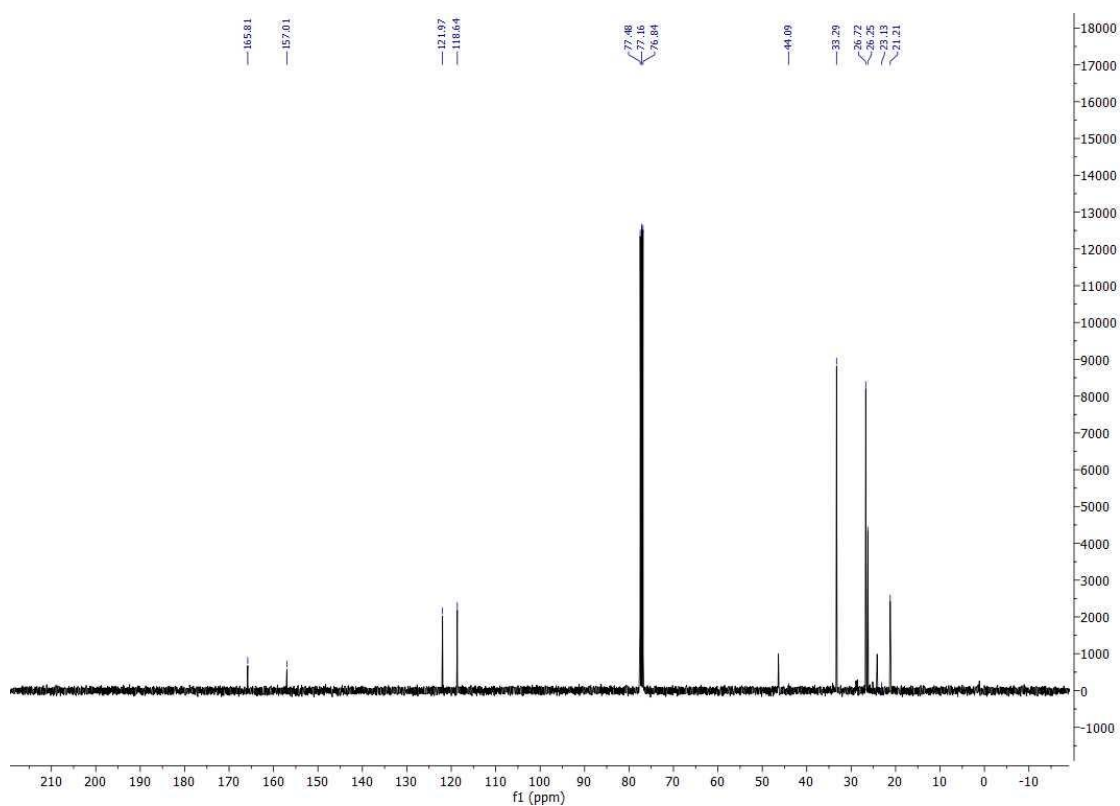
^{13}C NMR (101 MHz, CDCl_3)



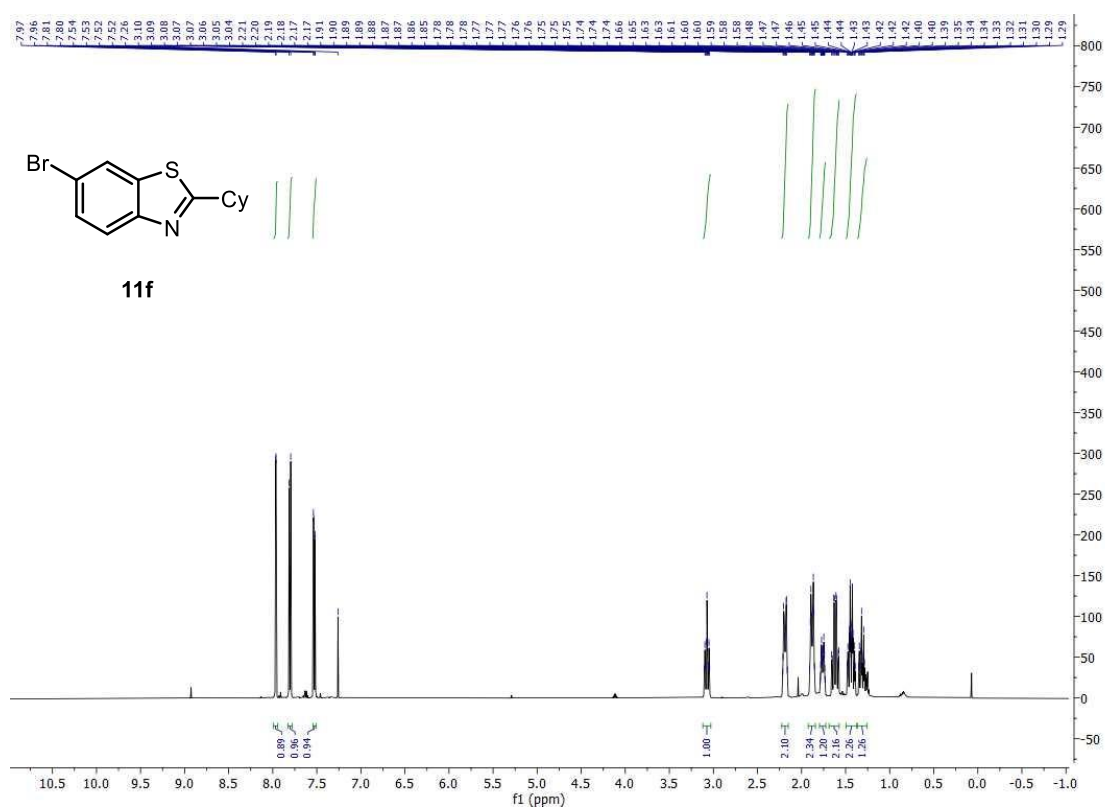
^1H NMR (400 MHz, CDCl_3)



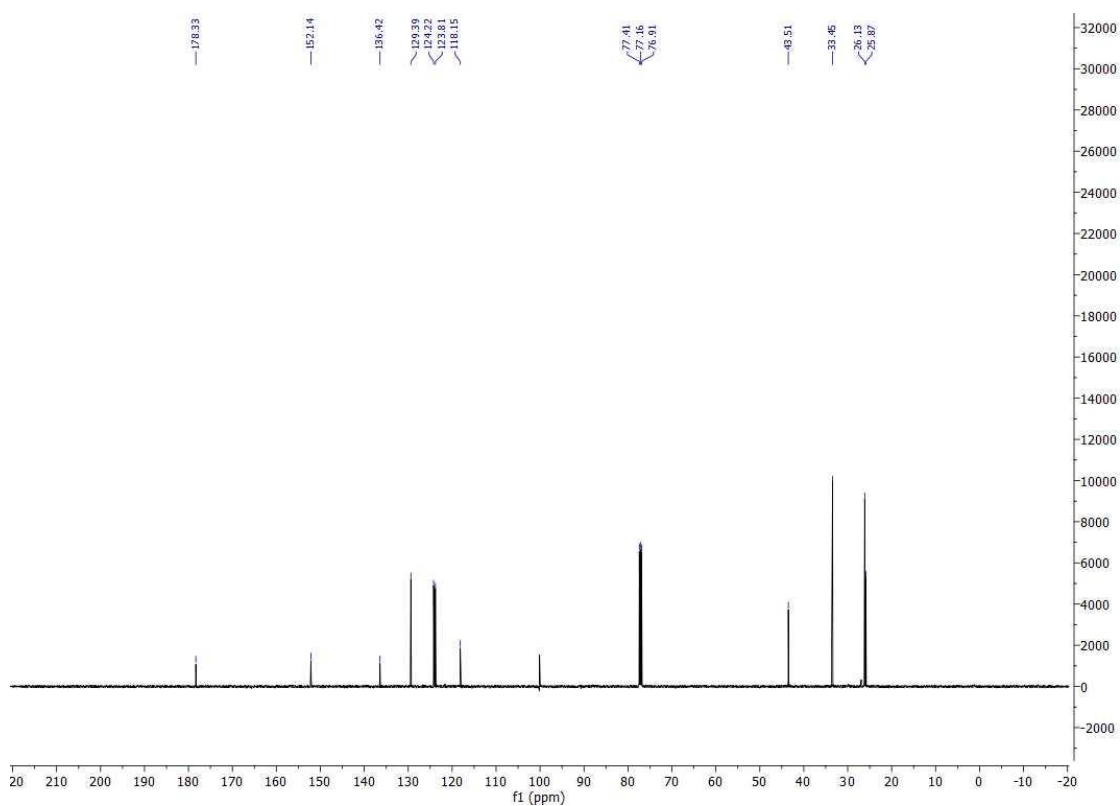
^{13}C NMR (101 MHz, CDCl_3)



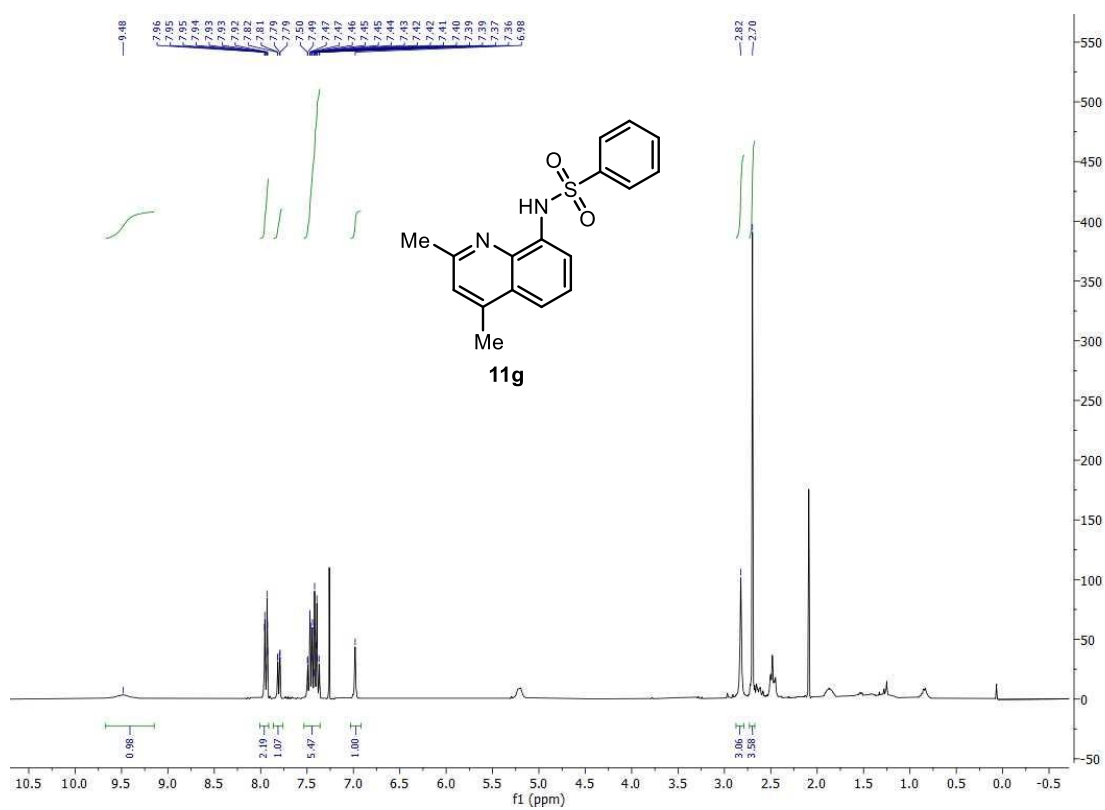
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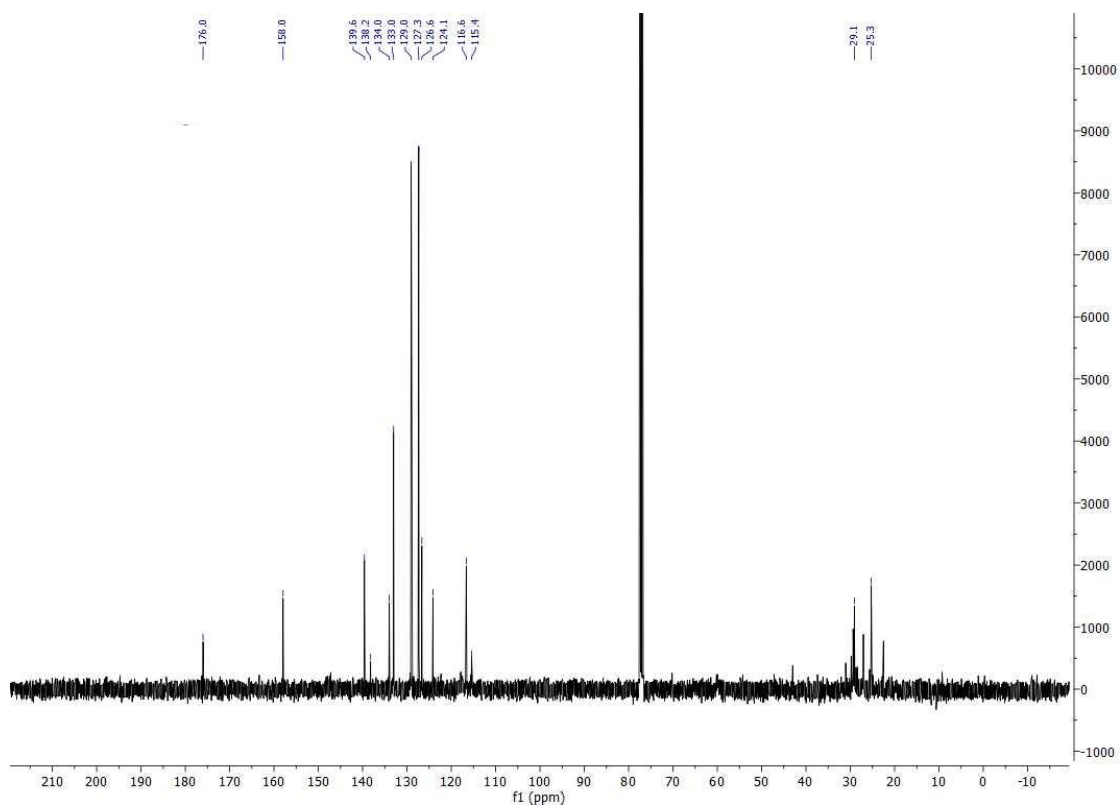
^{13}C NMR (101 MHz, CDCl_3)



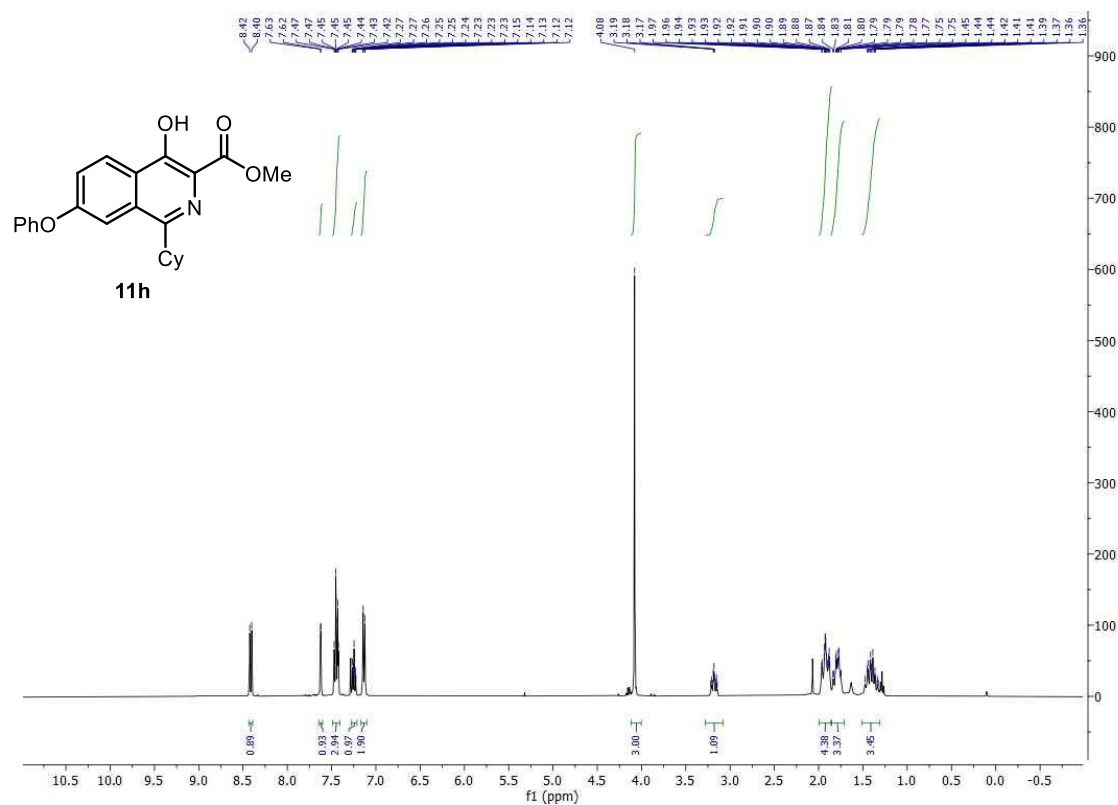
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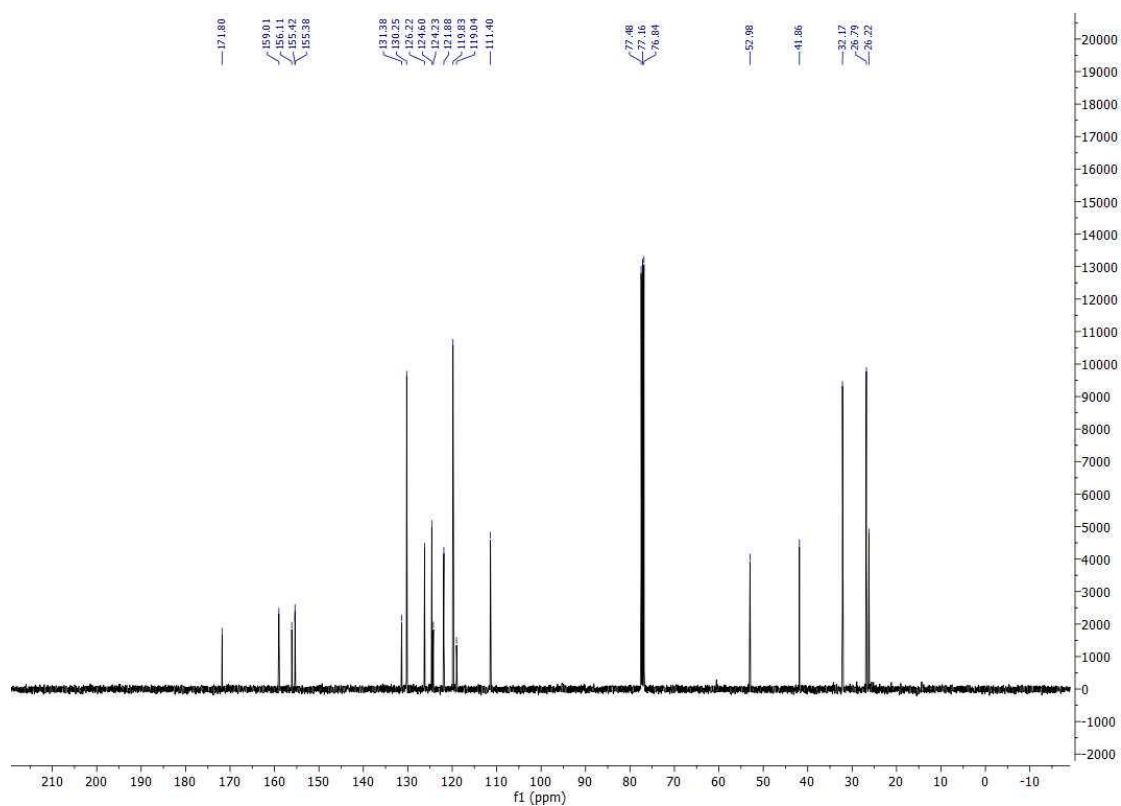
^{13}C NMR (101 MHz, CDCl_3)



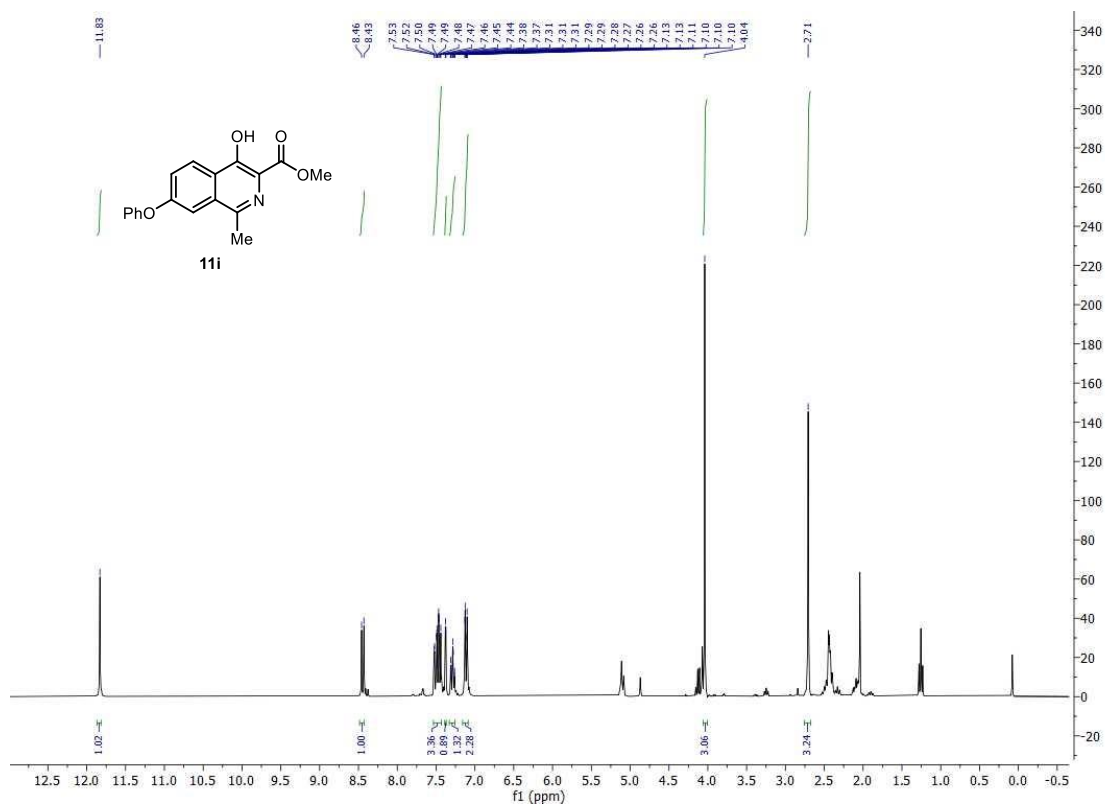
^1H NMR (400 MHz, CDCl_3)



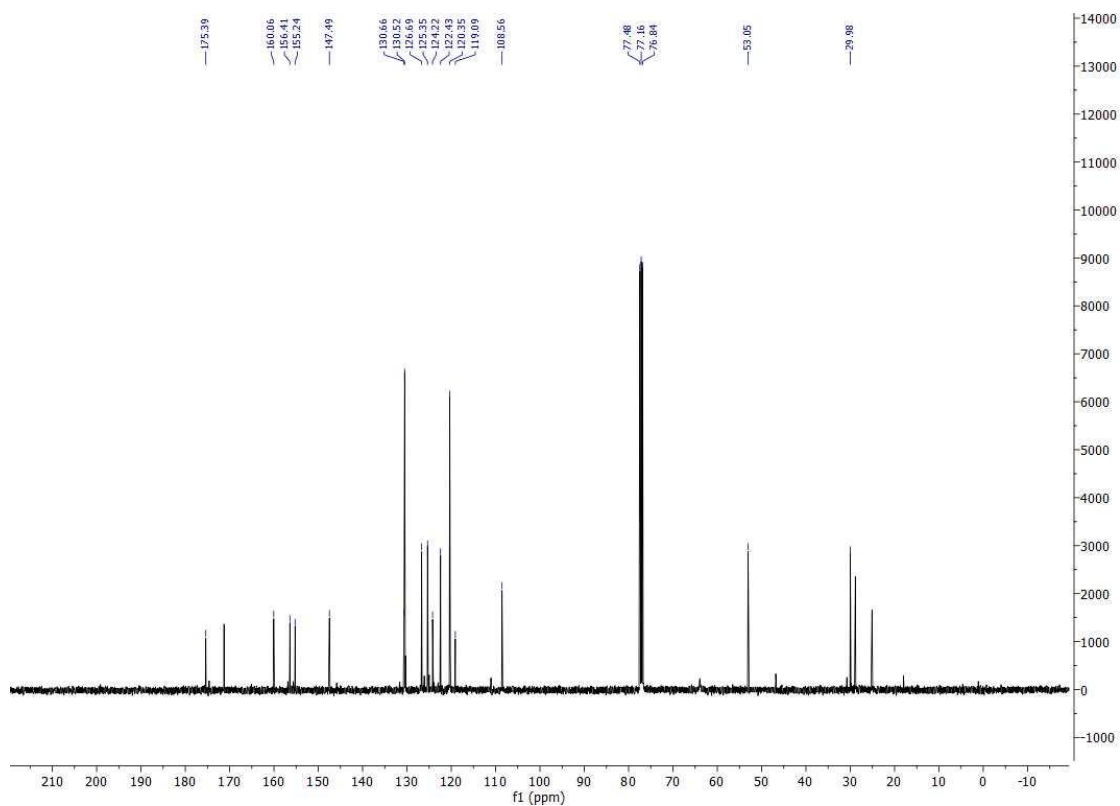
^{13}C NMR (101 MHz, CDCl_3)



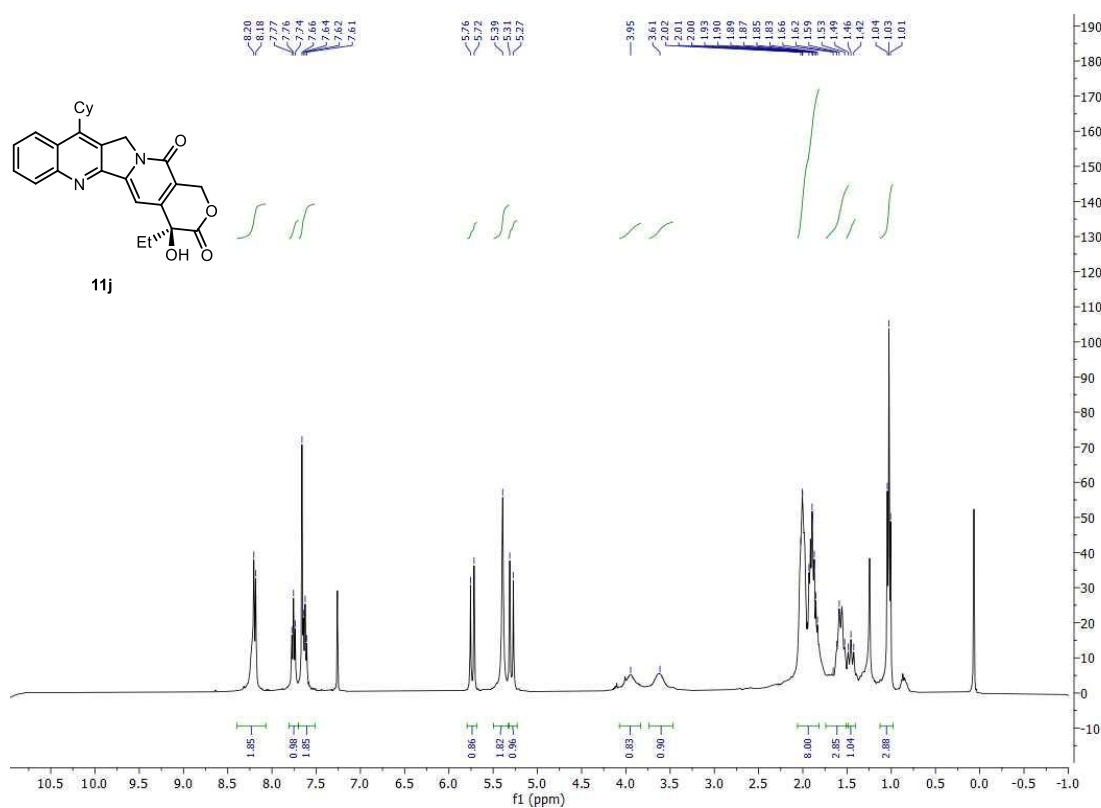
^1H NMR (400 MHz, CDCl_3)



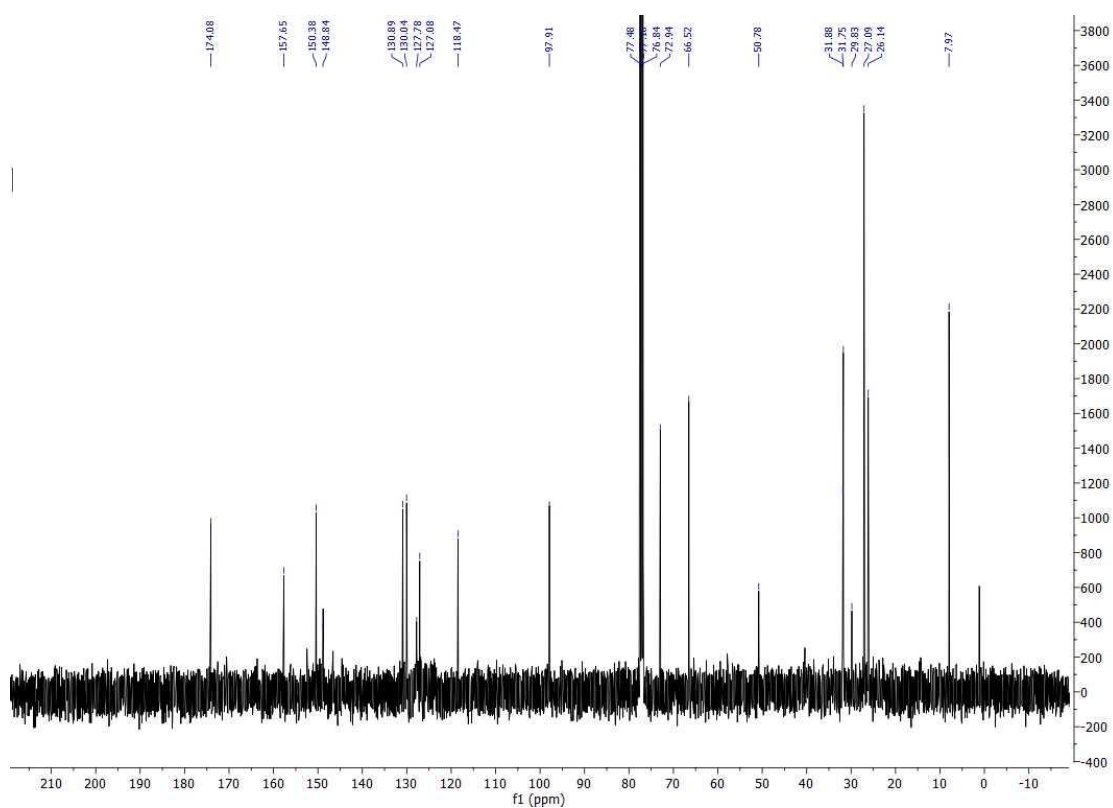
^{13}C NMR (101 MHz, CDCl_3)



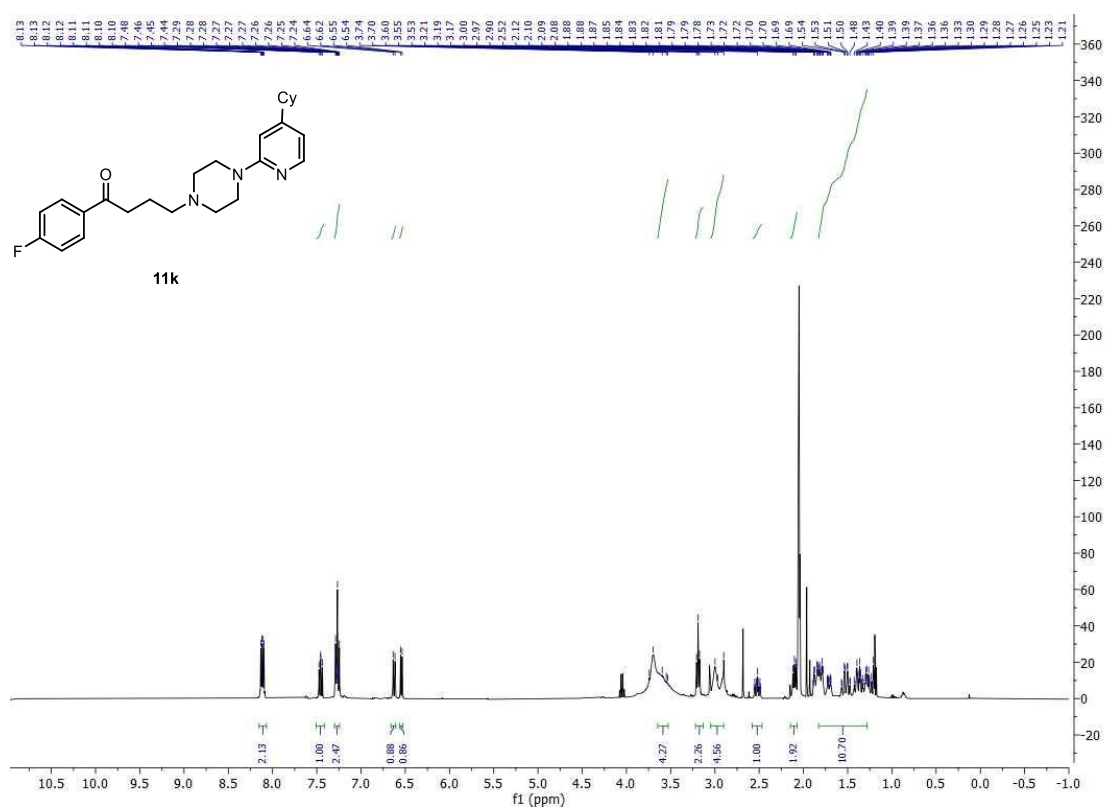
^1H NMR (400 MHz, CDCl_3)



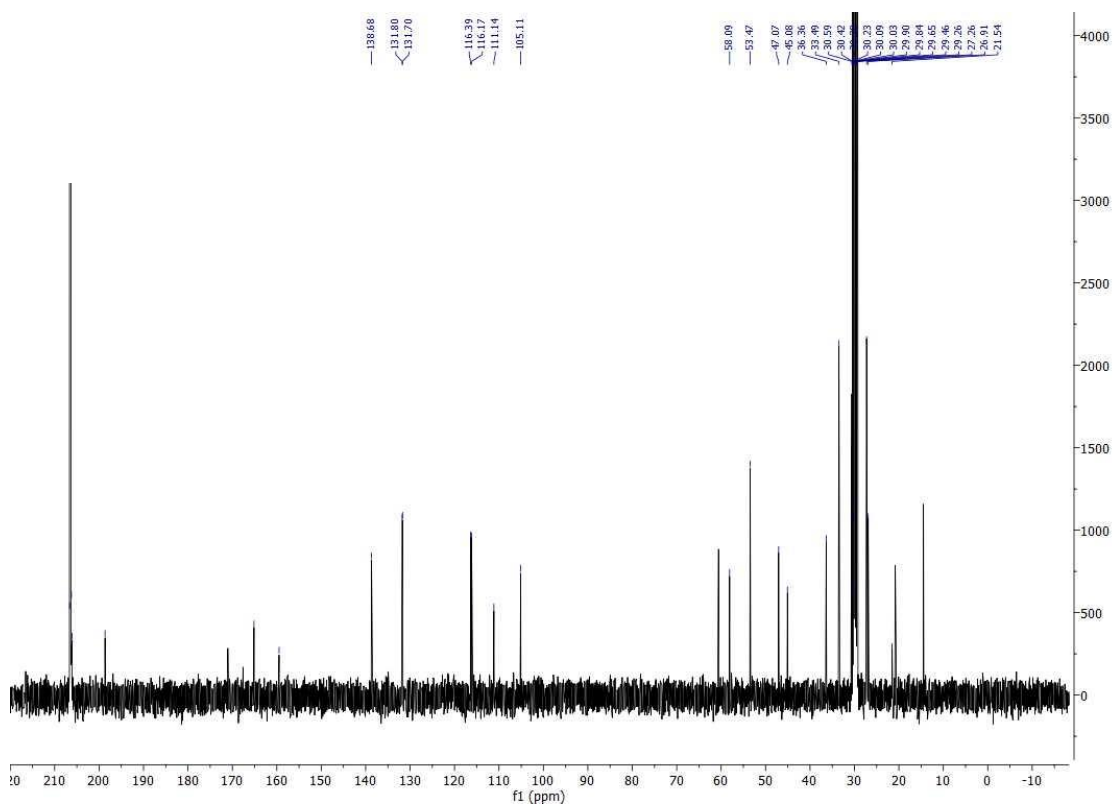
^{13}C NMR (101 MHz, CDCl_3)



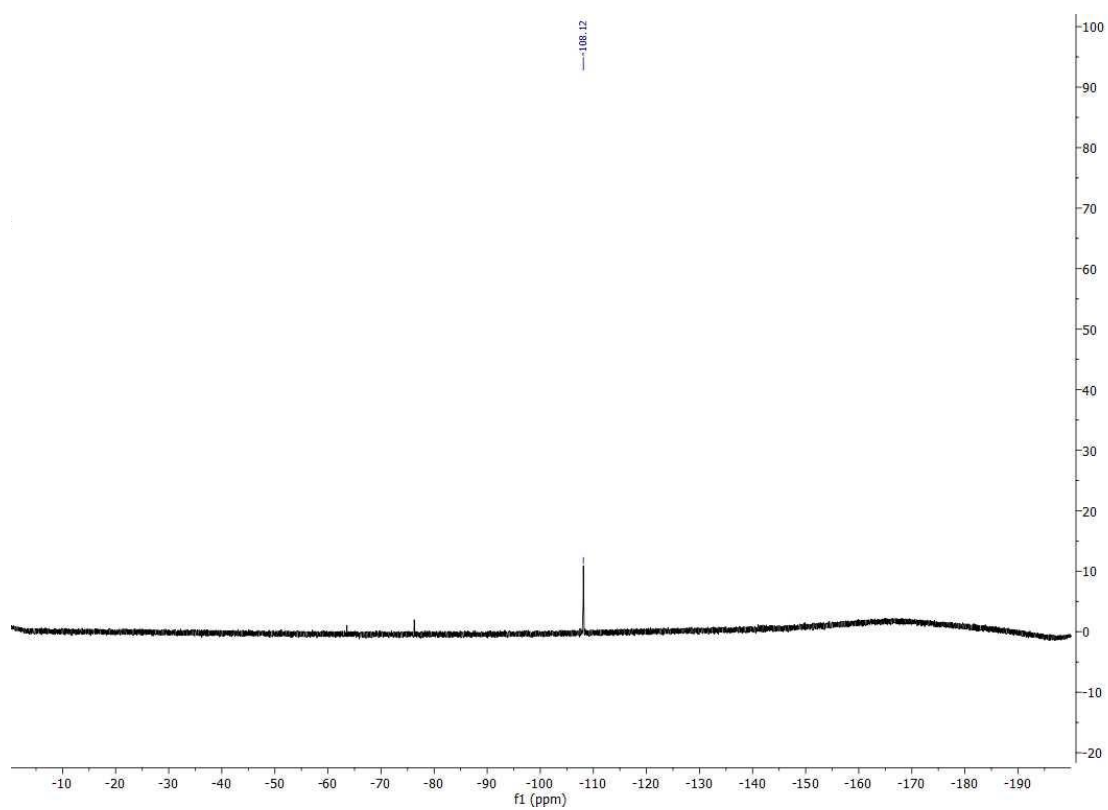
¹H NMR (400 MHz, Acetone-*d*₆)



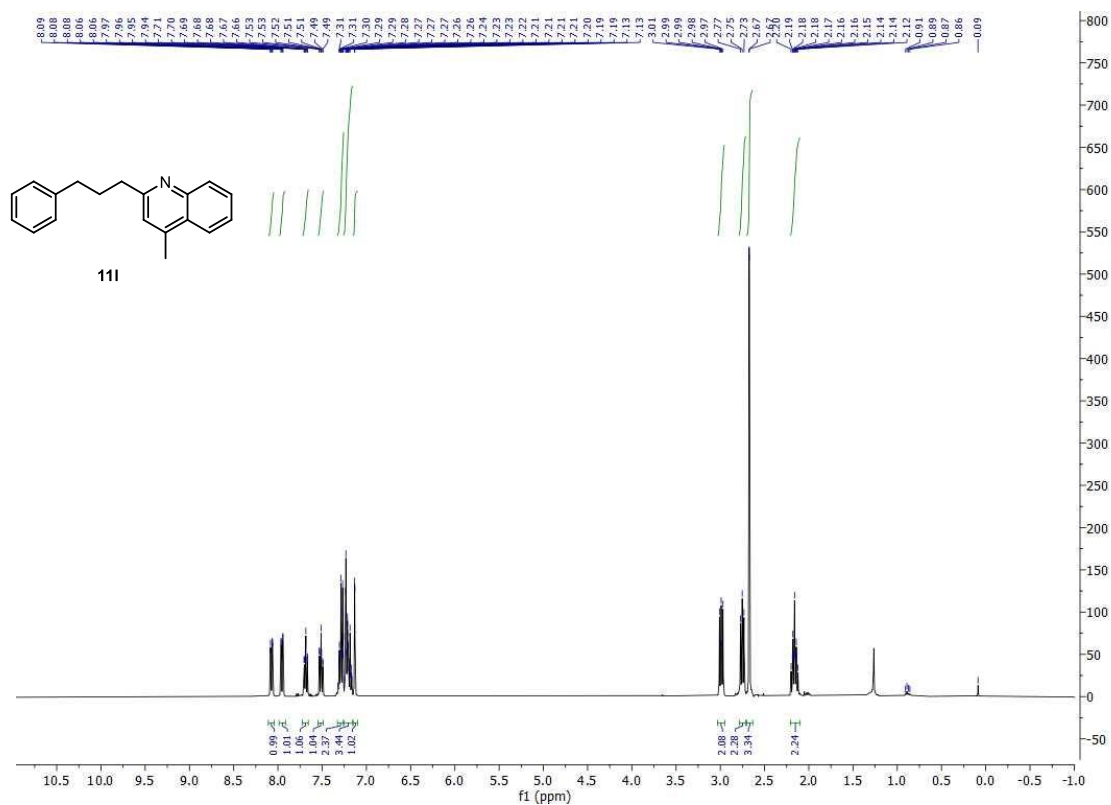
¹³C NMR (101 MHz, Acetone-*d*₆)



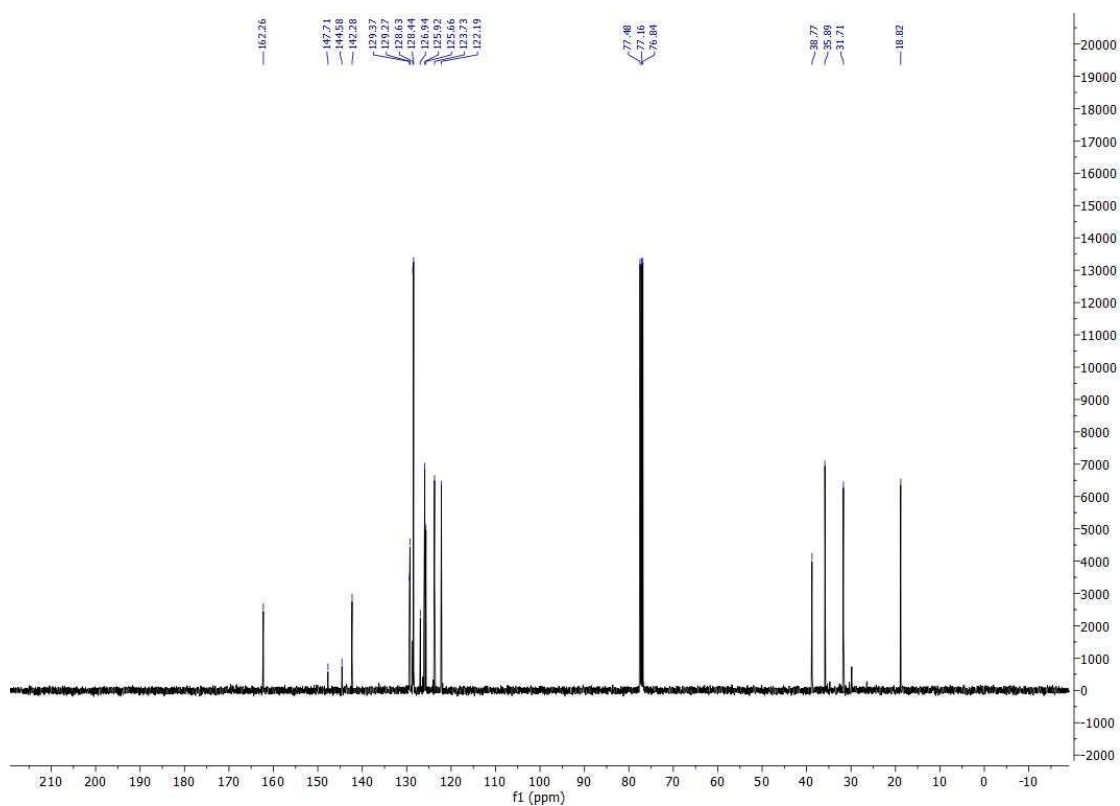
^{19}F NMR (376 MHz, Acetone- d_6)



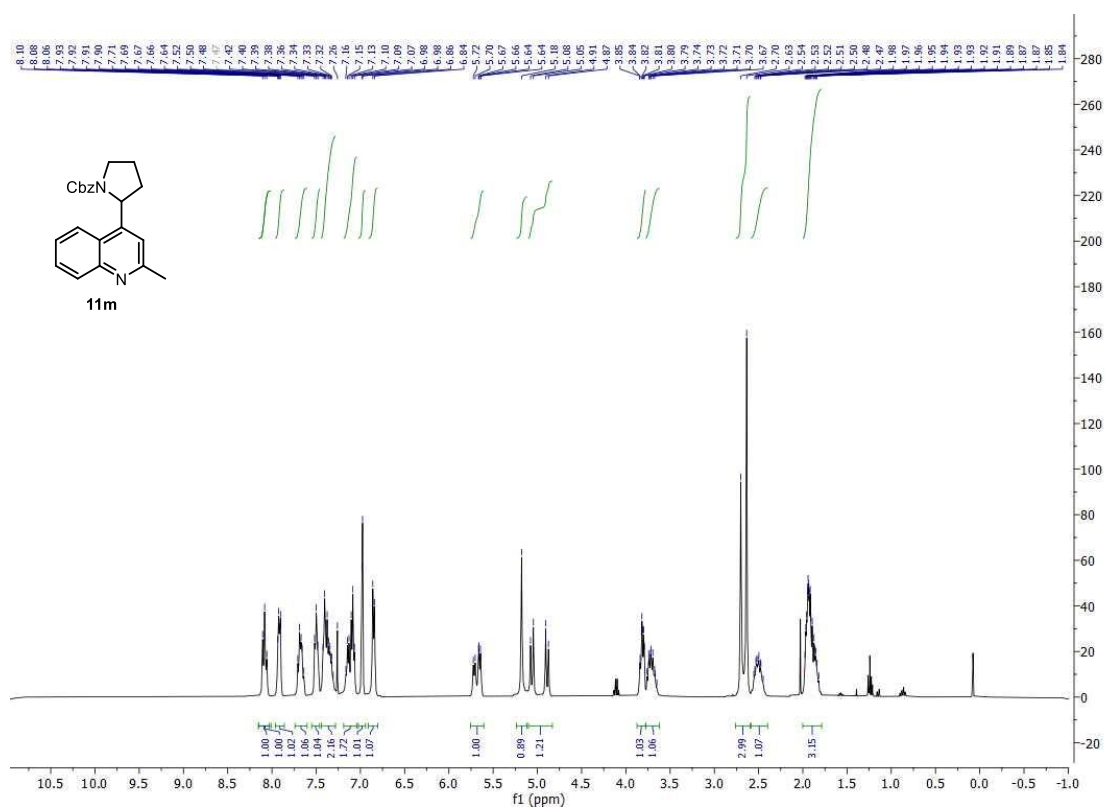
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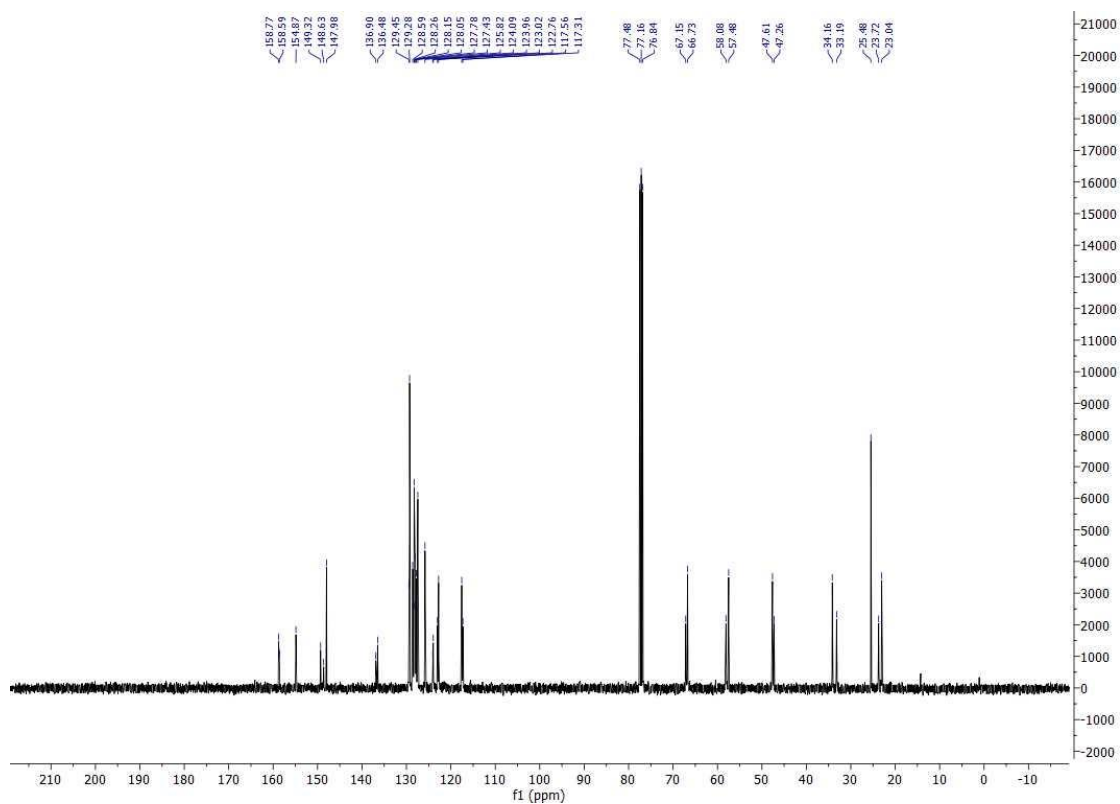
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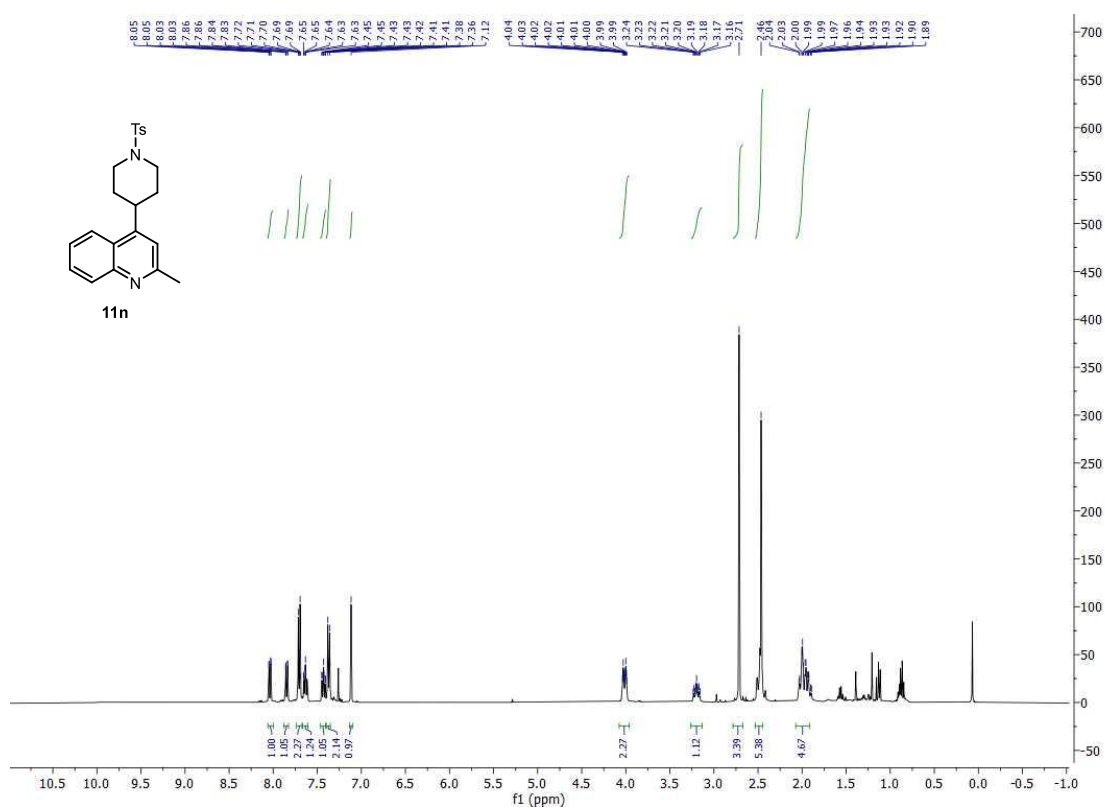
^1H NMR (400 MHz, CDCl_3)



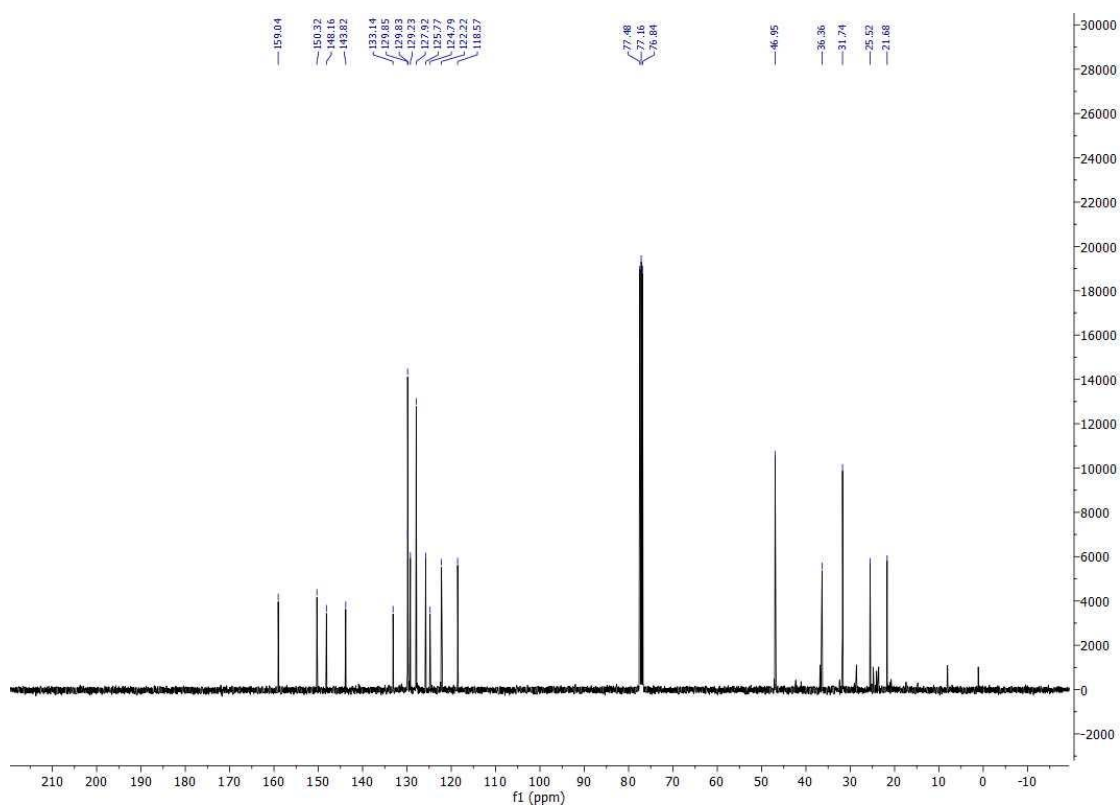
^{13}C NMR (101 MHz, CDCl_3)



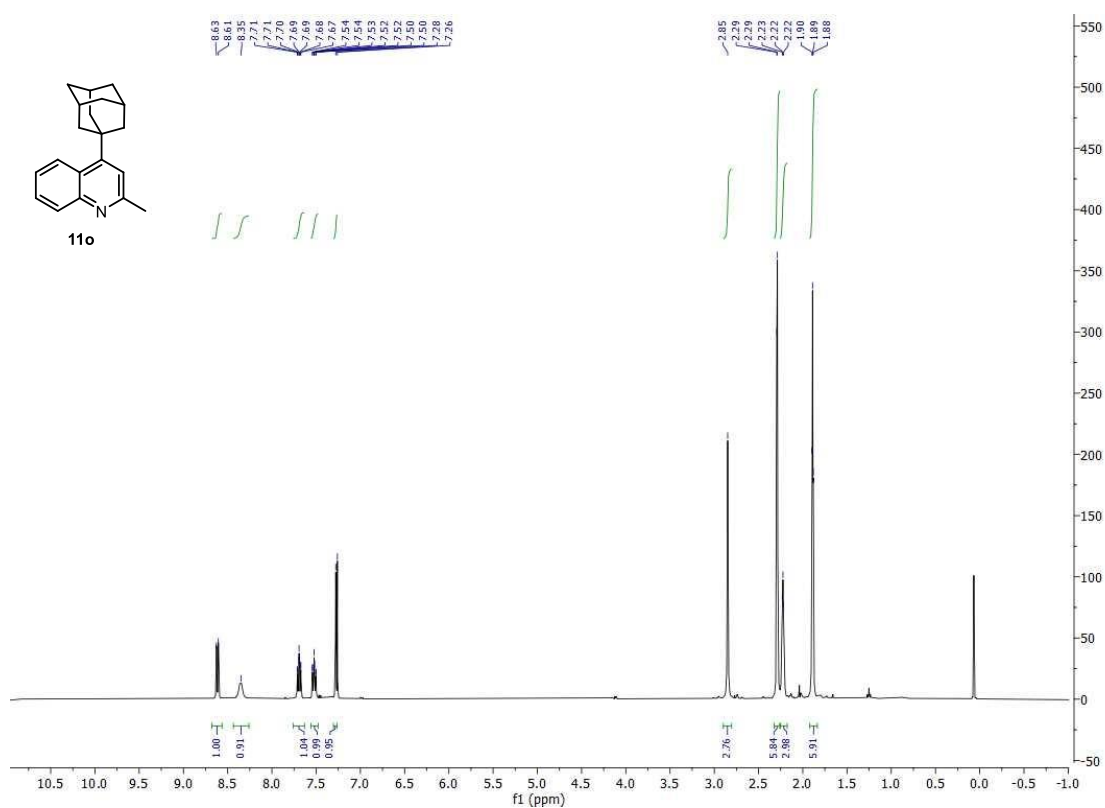
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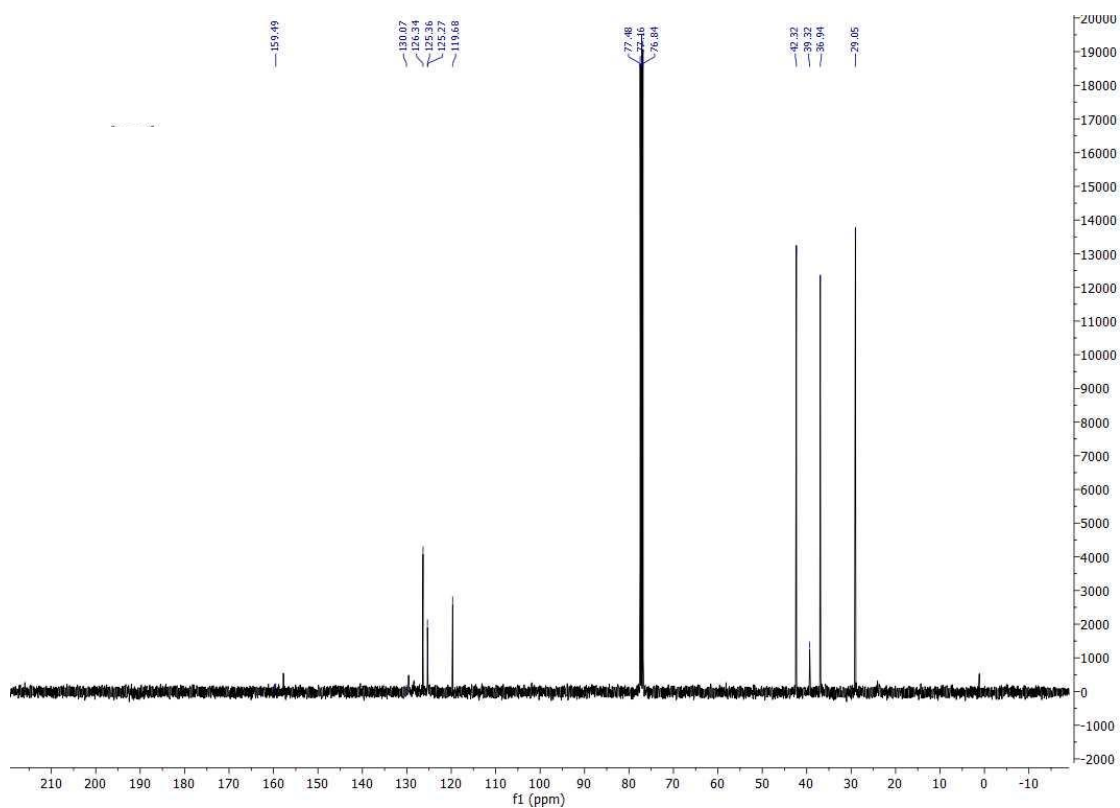
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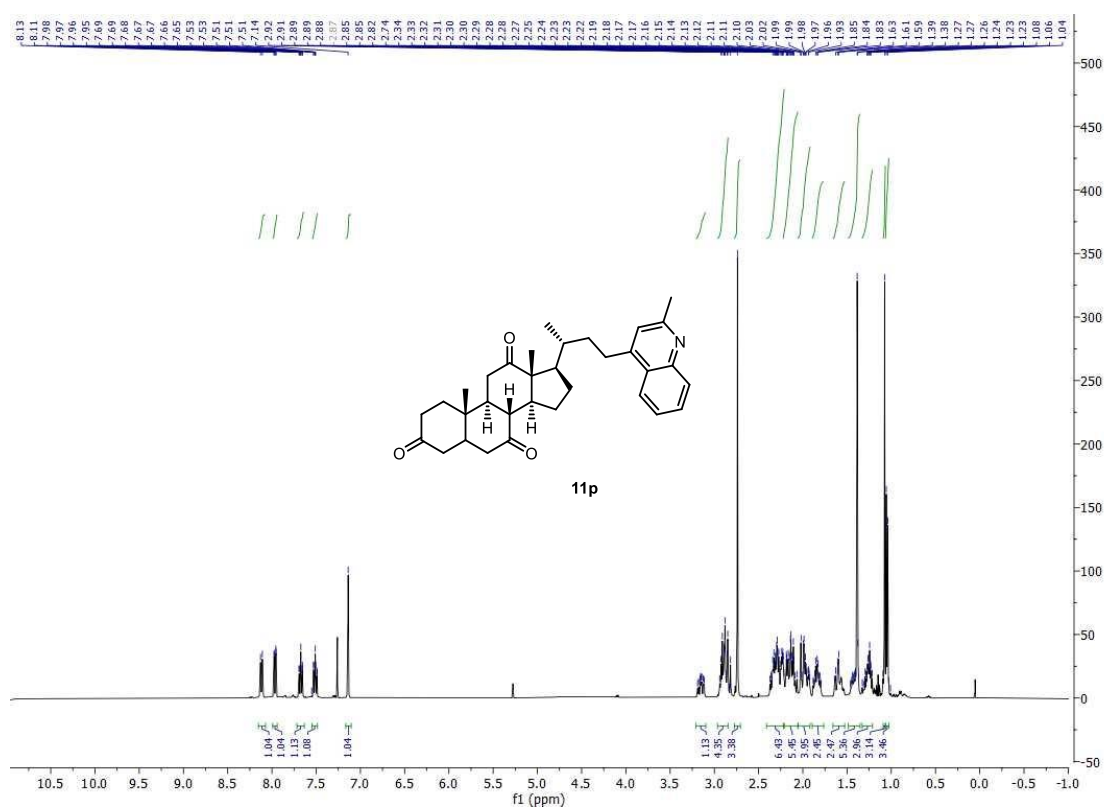
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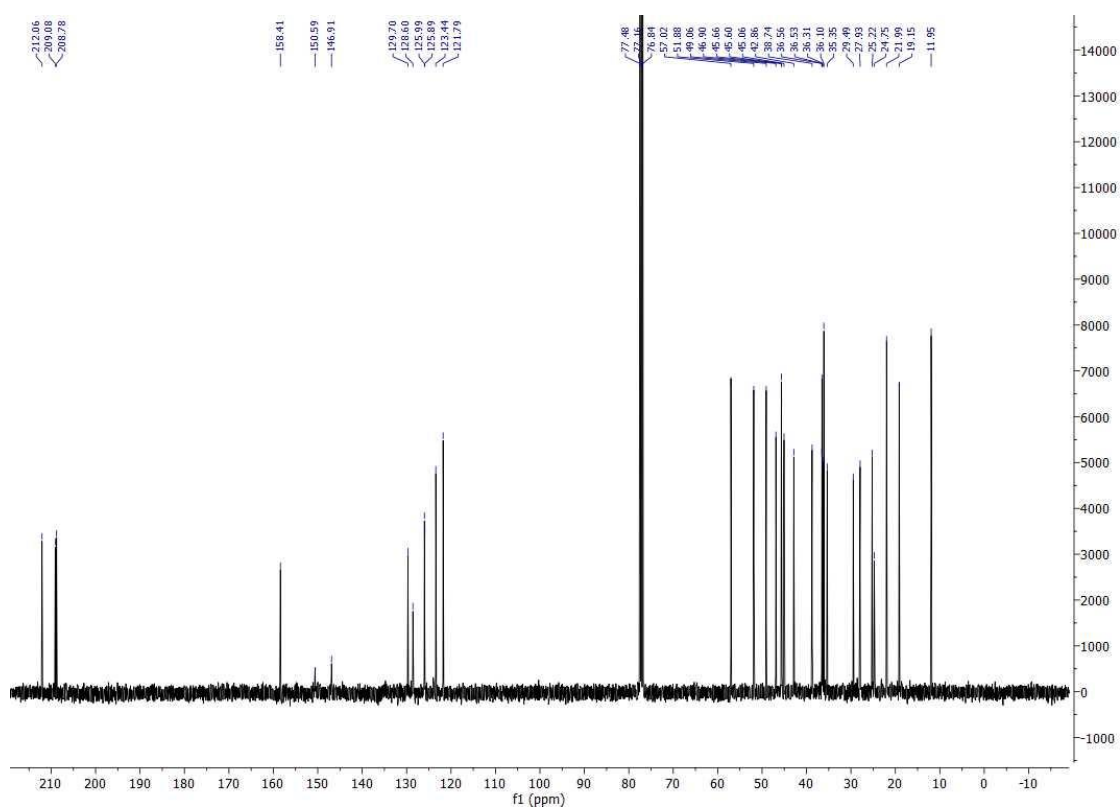
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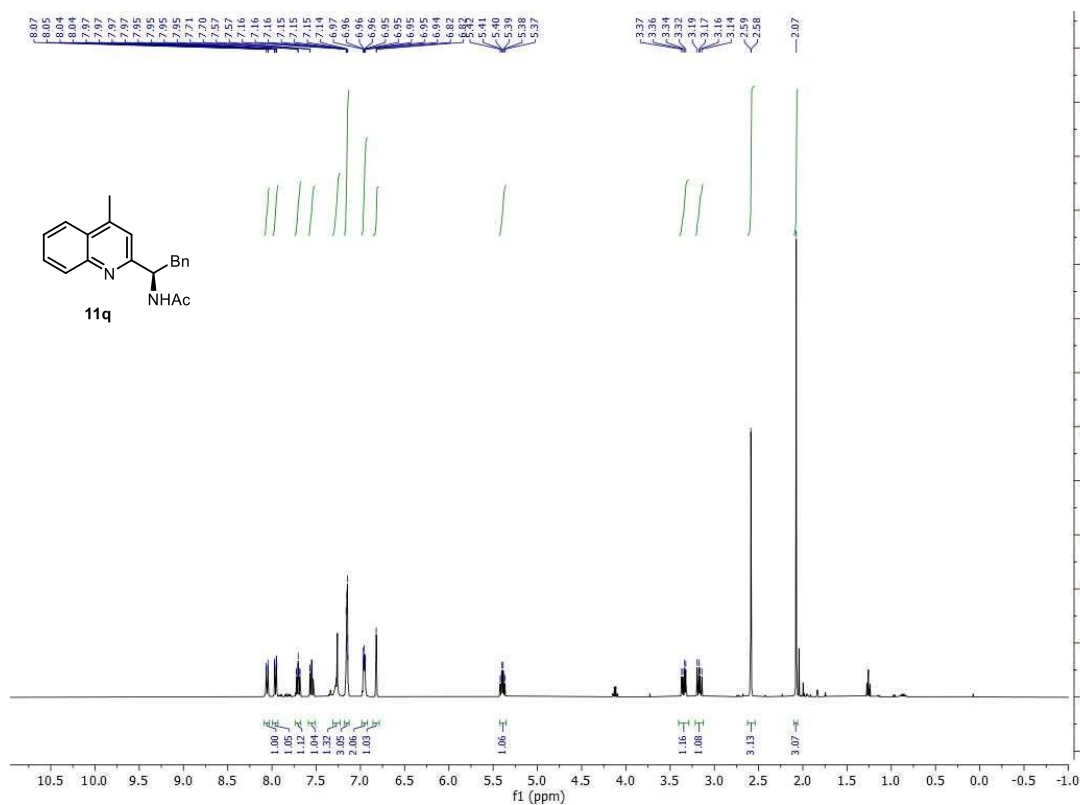
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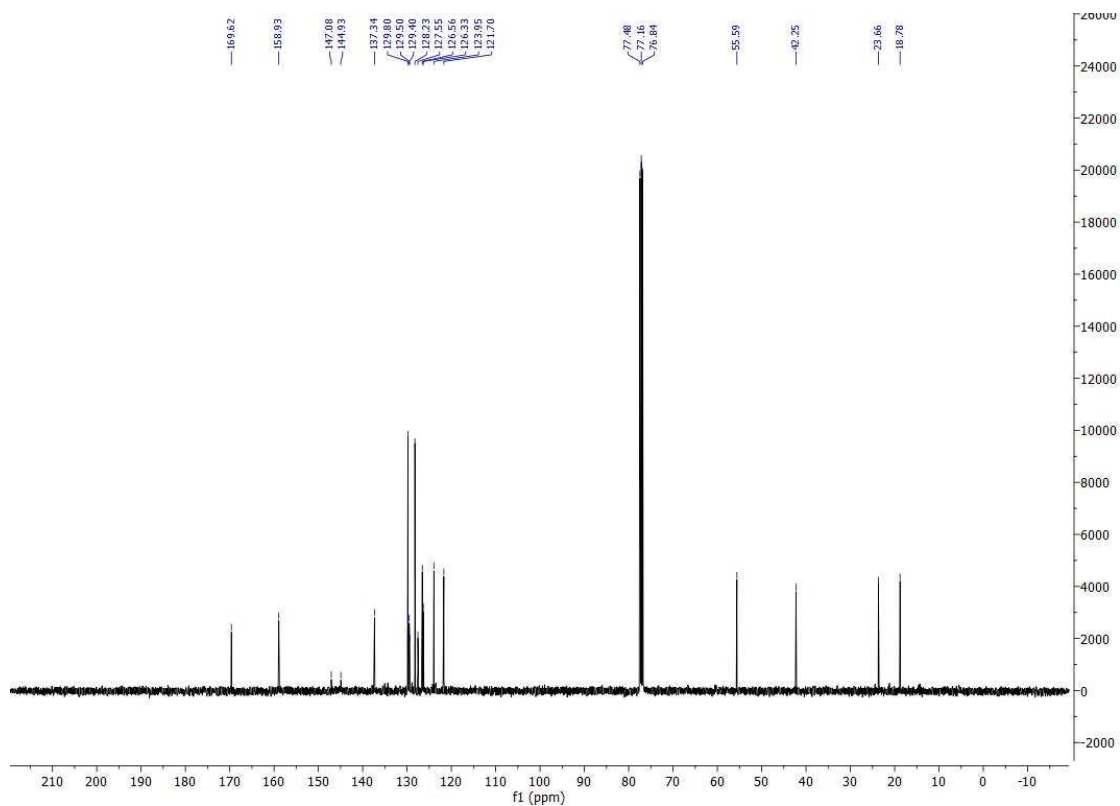
¹³C NMR (101 MHz, CDCl₃)



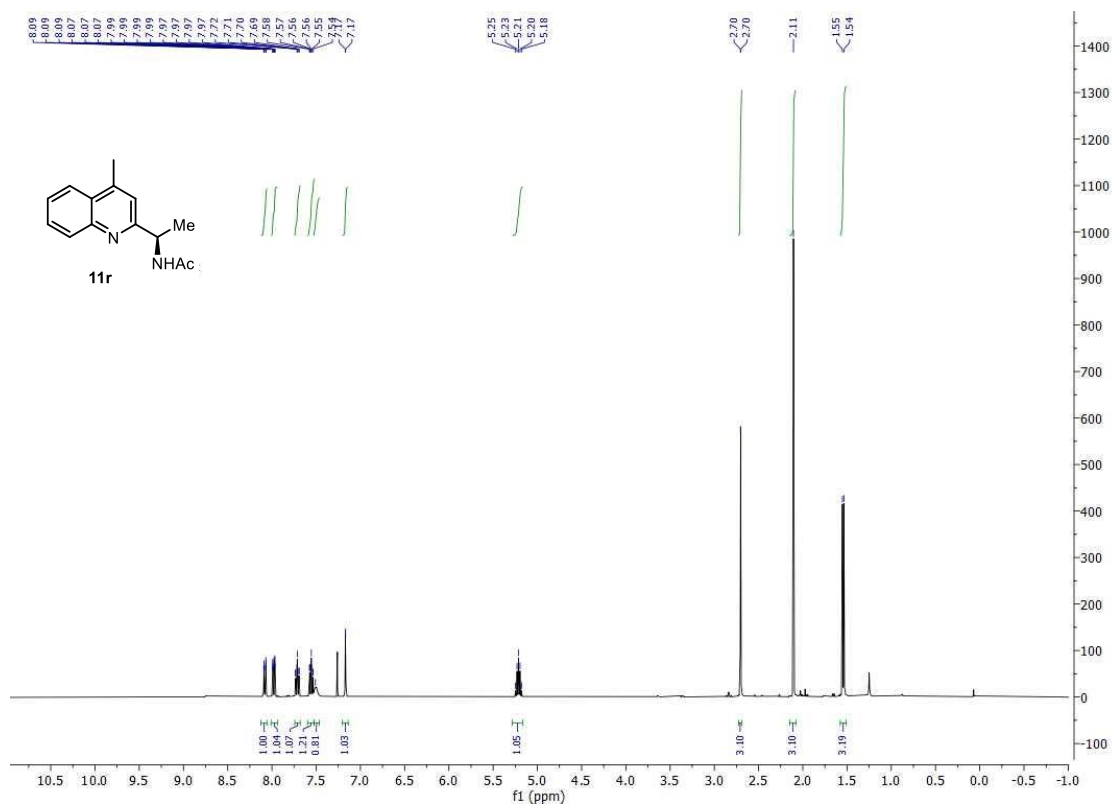
¹H NMR (400 MHz, CDCl₃)



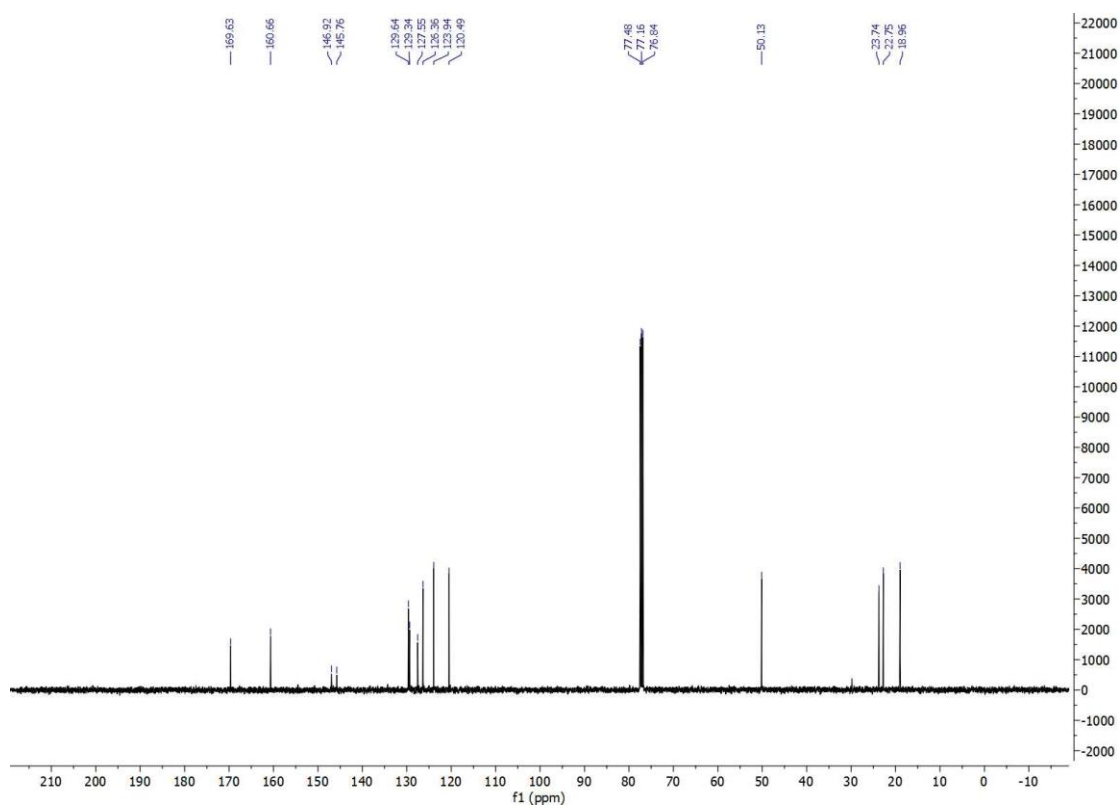
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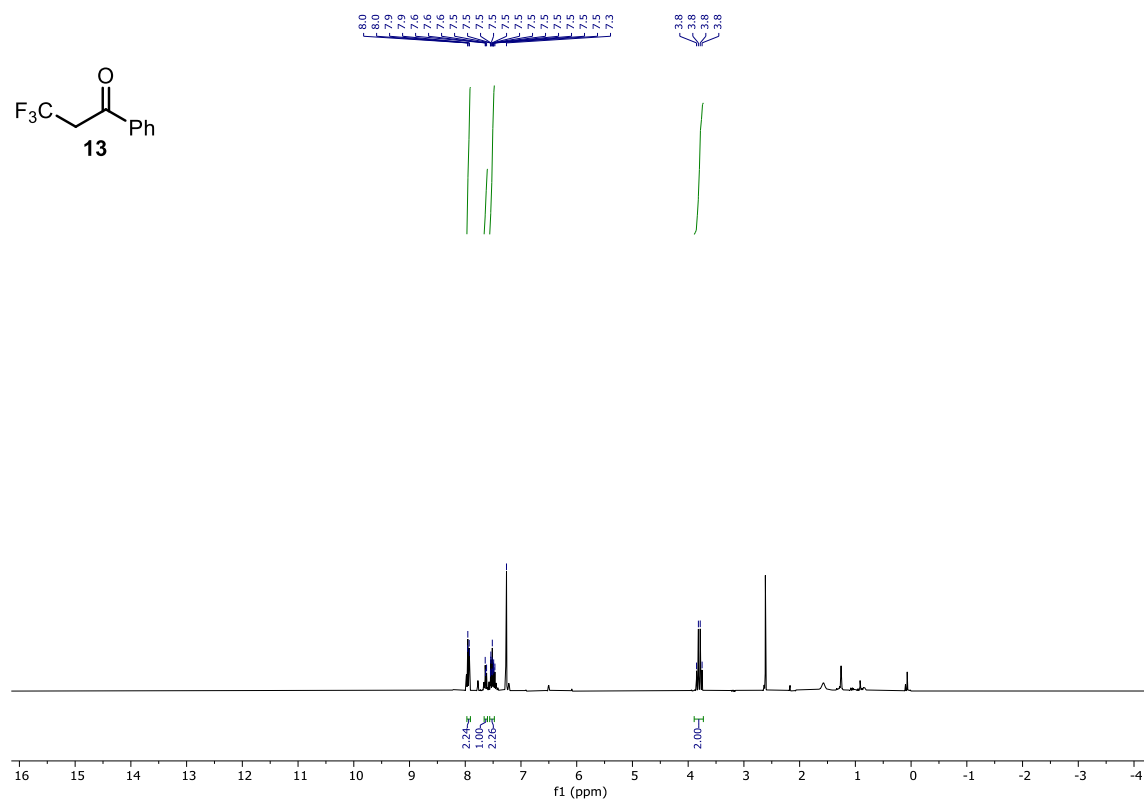
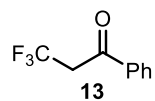
¹H NMR (400 MHz, CDCl₃)



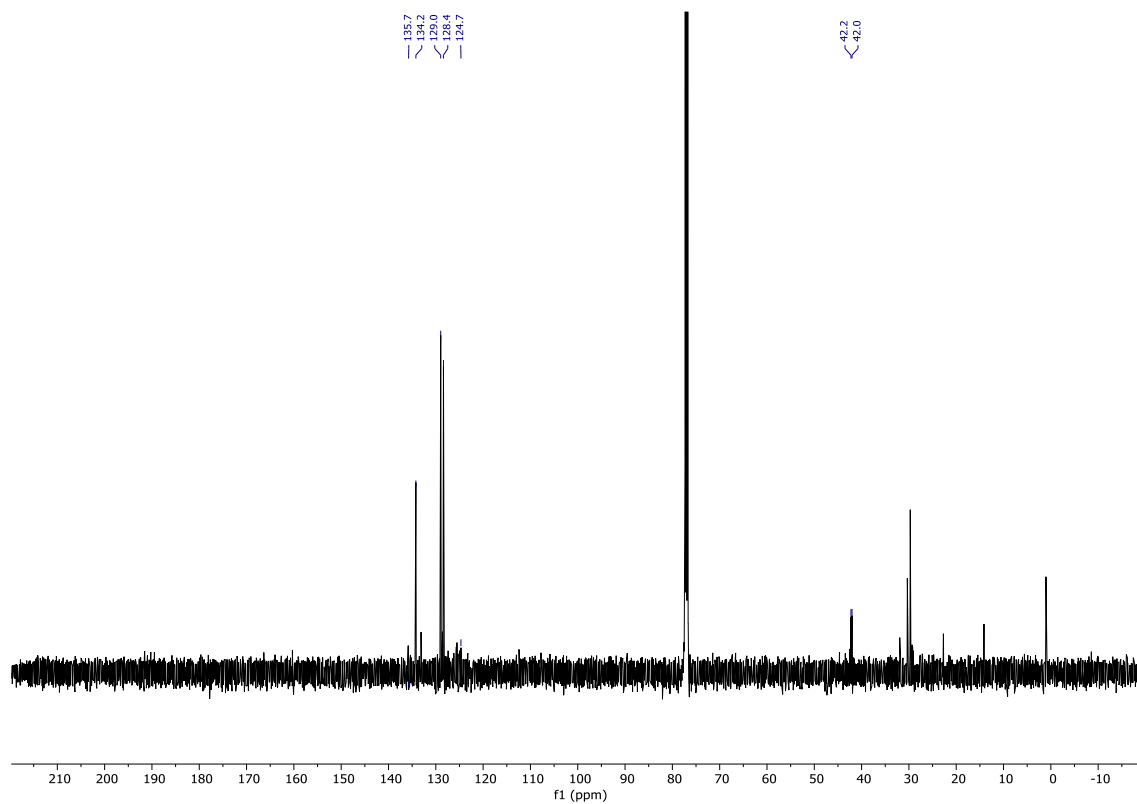
¹³C NMR (101 MHz, CDCl₃)



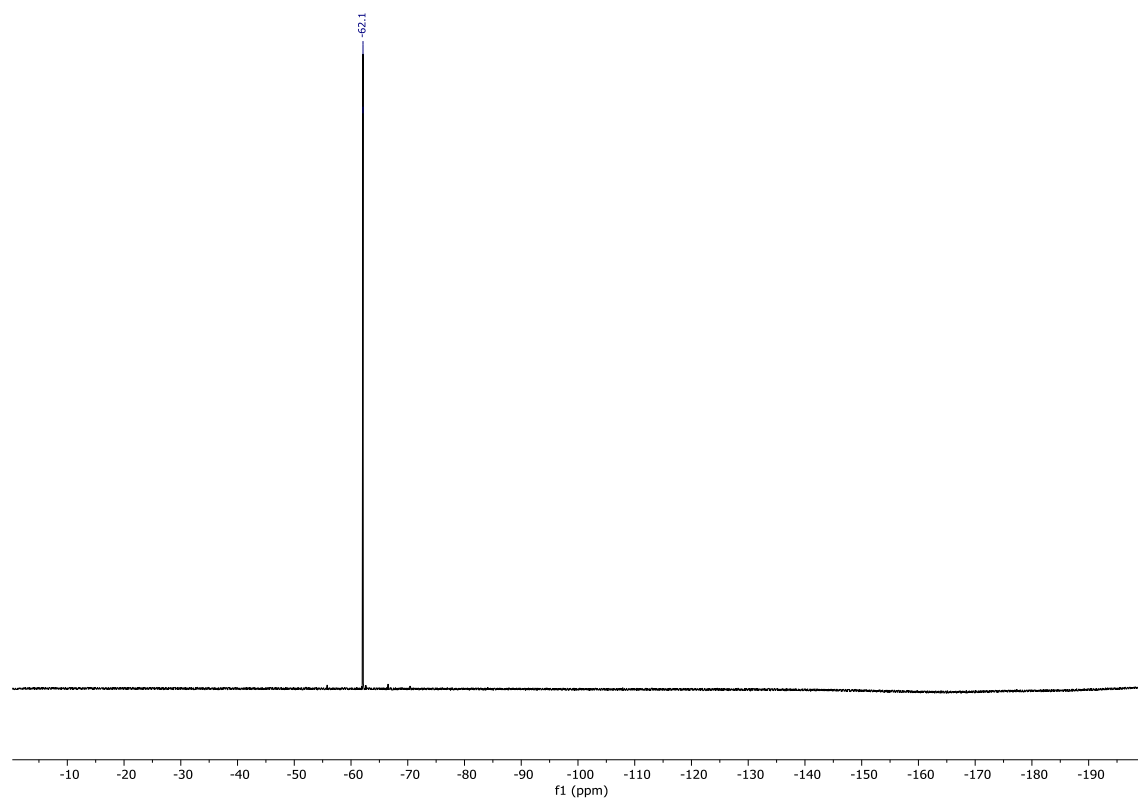
^1H NMR (300 MHz, CDCl_3)



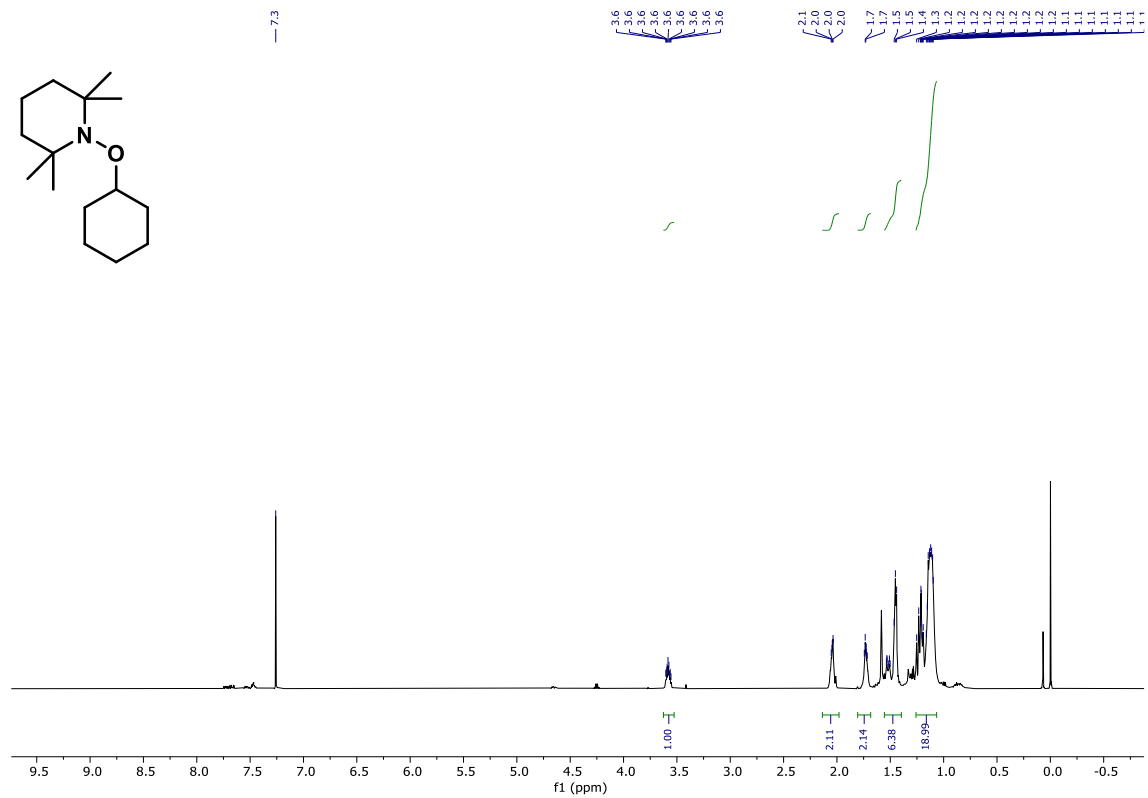
^{13}C NMR (126 MHz, CDCl_3)



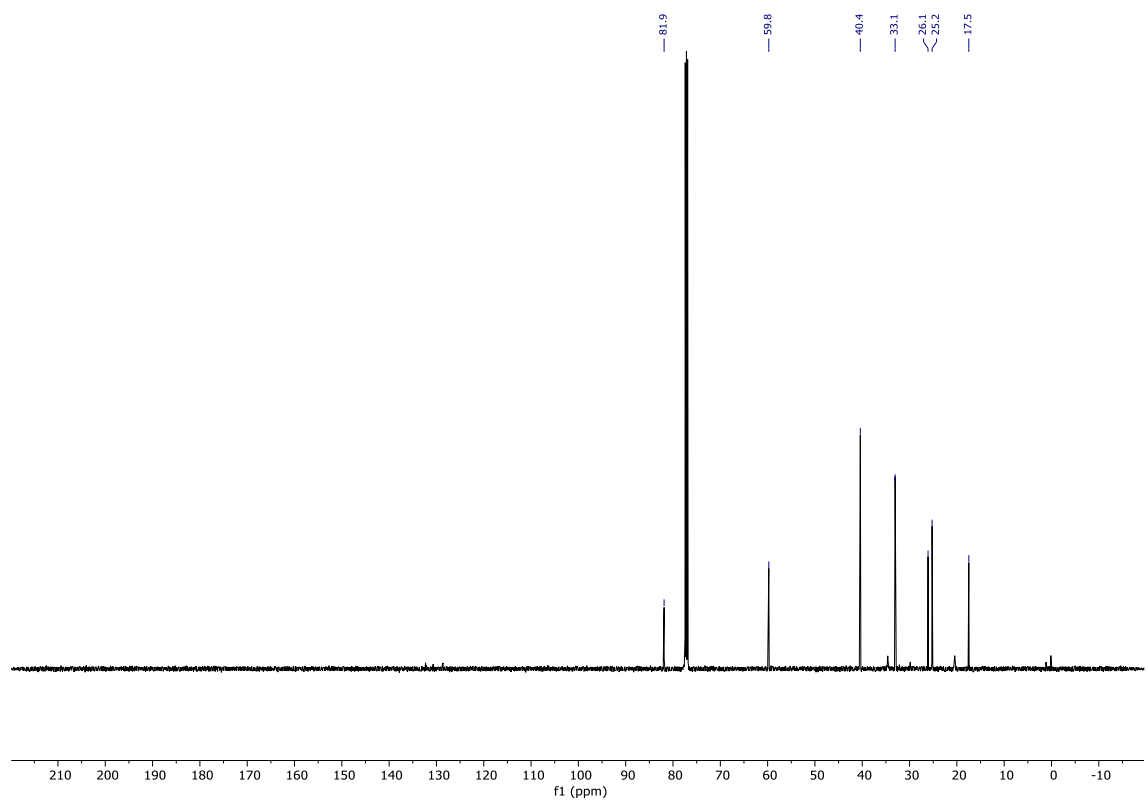
^{19}F NMR (376 MHz, CDCl_3)



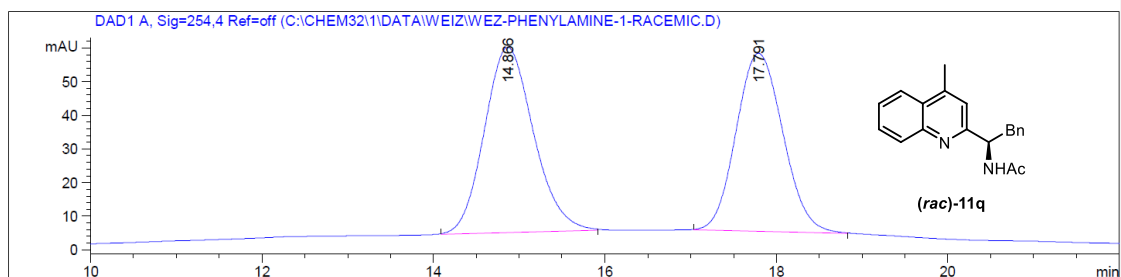
^1H NMR (500 MHz, CDCl_3)



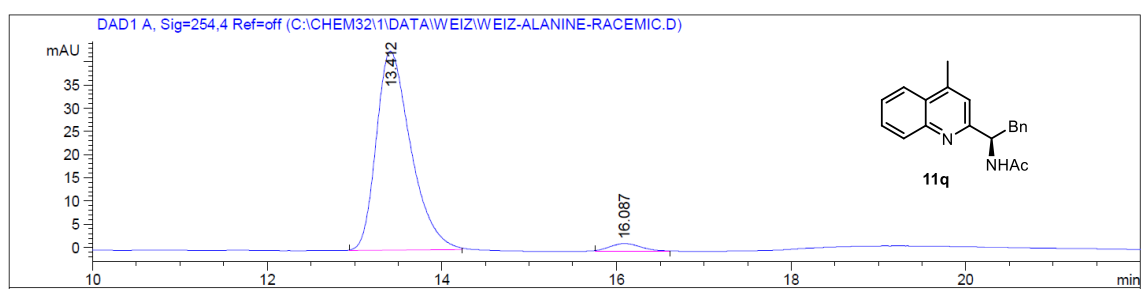
^{13}C NMR (126 MHz, CDCl_3)



Conditions: HPLC analysis on a Daicel Chiralpak IC-3 column: 30:70 *i*PrOH:nhexane 1.0mL/min, 20 °C; λ = 254 nm.

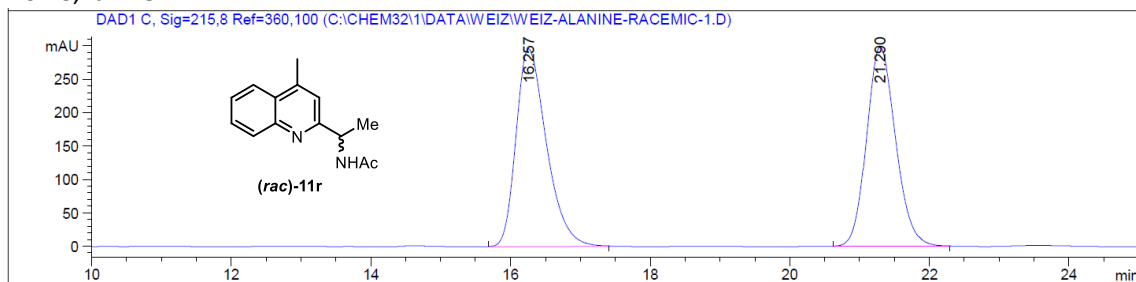


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.866	BB	0.6192	2198.58643	55.14148	52.2400
2	17.791	BB	0.5985	2010.03992	52.99304	47.7600

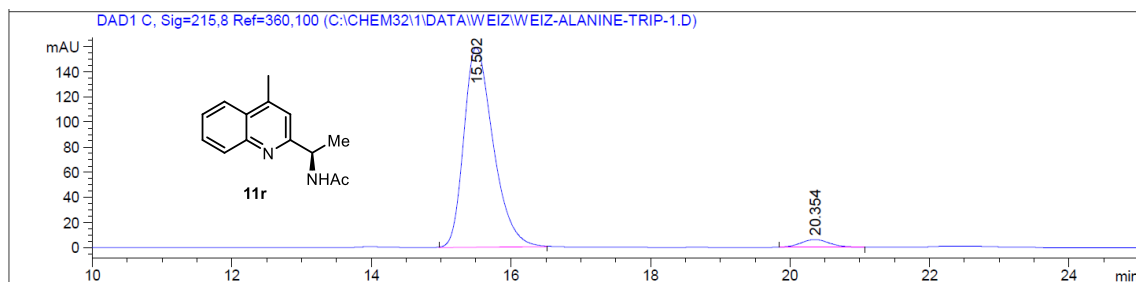


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.412	BB	0.4182	1175.41663	42.82244	96.8523
2	16.087	BB	0.3223	38.20099	1.59021	3.1477

Conditions: HPLC analysis on a Daicel Chiralpak IC-3 column: 30:70 ⁱPrOH:hexane 1.0mL/min, 20° C; λ = 254 nm.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.257	BB	0.4601	8918.09570	295.53592	50.7632
2	21.290	BB	0.4483	8649.93359	298.29034	49.2368



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.502	BB	0.4434	4614.16309	158.62767	96.3061
2	20.354	BB	0.4355	176.97900	6.19149	3.6939