Supporting Information

Tetrachlorophthalimides as Organocatalytic Acceptors for Electron Donor–Acceptor Complex Photoactivation

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A. General Information

The NMR spectra were recorded at 400 MHz and 500 MHz for ^{1}H and 100 or 125 MHz for ^{13}C. The chemical shift (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm ^{1}H NMR 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 D_2 and W light sources or an Agilent Cary60 spectrophotometer.
Isolated yields refer to materials of >95% purity as determined by ^{1}H NMR analysis.

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.

Determination of *E/Z* Ratio. The *E/Z* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture through integration of diagnostic signals.

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 GF_{254}, 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.

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. Synthesis of Substrate and Catalysts

B1. Substrate Synthesis

The following substrates were synthesized according to reported procedures (Figure S1).[1-7]

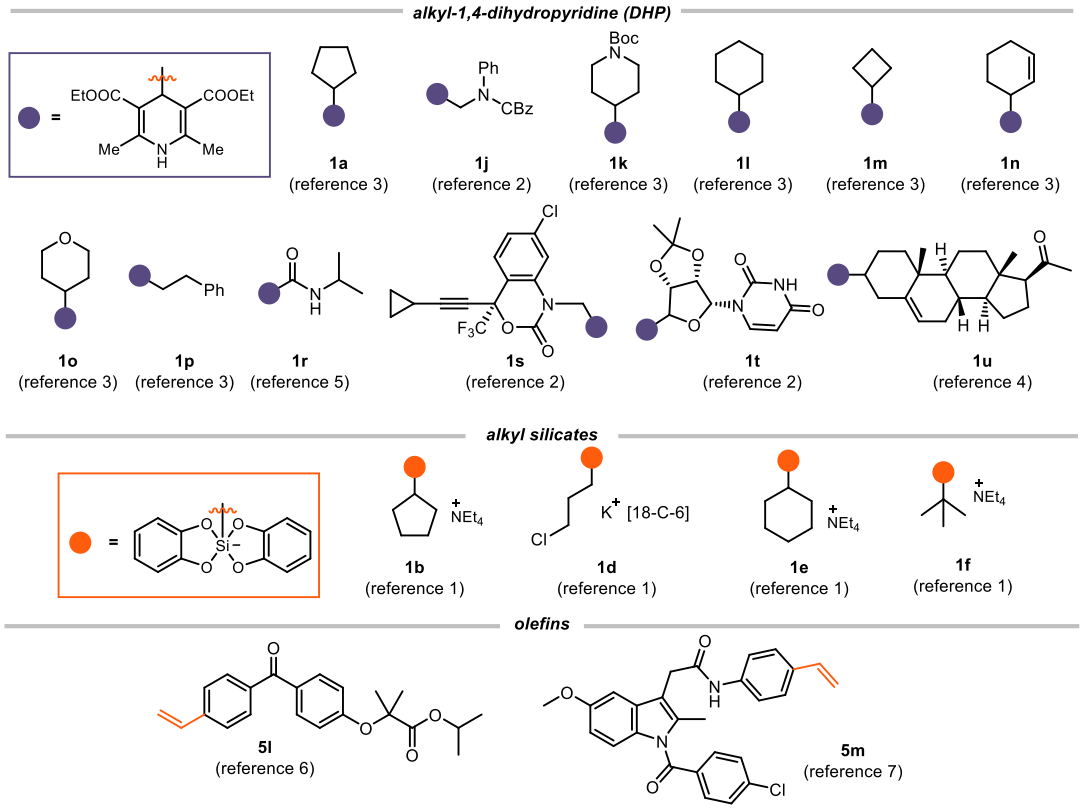


Figure S1: Starting materials synthesized according to known procedures.

B2. Catalysts Synthesis

B2.1 General Procedure

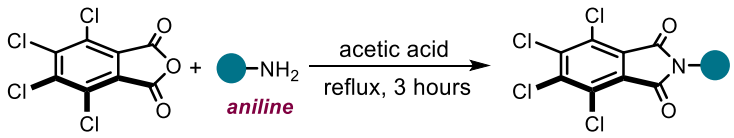
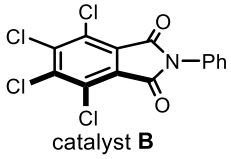


Figure S2: Catalysts synthesized according to known procedures.[8]

An oven dried flask was charged with 4,5,6,7-tetrachlorophthalic anhydride (5.72 g, 20.0 mmol, 1.0 equiv.), the corresponding aniline (24.0 mmol, 1.2 equiv.) and anhydrous acetic acid (40 mL). The flask was equipped with a condenser and placed in an oil-bath preheated to 120 ºC. After 3 hours stirring, the solution was concentrated. The solid which precipitated on cooling was collected by filtration and washed first with 10 % aqueous sodium carbonate (100 mL x 3), water (100 mL x 3) and methanol (10 mL x 3). The resulting white solid was dried under reduced pressure to afford the final catalyst **B** and **C**.

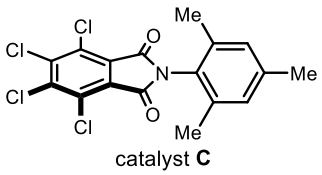
B2.2 Characterization



catalyst **B**

4,5,6,7-tetrachloro-2-phenylisoindoline-1,3-dione (catalyst **B**): Synthesized according to General Procedure using aniline (2.2 mL, 24.0 mmol, 1.2 equiv.). Catalyst **B** was obtained as a white solid (5.8 g, 81% yield). Melting point: 273 - 274 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.47 – 7.38 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 139.6, 129.9, 129.3, 128.3, 127.9, 126.4, 125.6.
Matching reported literature data.[8]



catalyst **C**

4,5,6,7-tetrachloro-2-mesitylisoindoline-1,3-dione (catalyst **C**): Synthesized according to General Procedure using 2,4,6-trimethylaniline (3.4 mL, 24.0 mmol, 1.2 equiv.). Catalyst **C** was obtained as a white solid (2.6 g, 77% yield). Melting point: 210 - 211 ºC.

^{1}H NMR (400 MHz, CDCl3) δ 7.00 (q, *J* = 0.7 Hz, 2H), 2.34 (s, 3H), 2.10 (s, 6H).
^{13}C NMR (101 MHz, CDCl3) δ 162.6, 140.6, 140.0, 136.3, 130.2, 129.6, 127.6, 126.4, 21.3, 18.1. Matching reported literature data.[8]

C. Experimental Procedures

C1. Experimental Setup

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

For reactions (details in Section C2 and C3) 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 10 positions (Figure S3, 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 within the reaction vessel was measured to be between 35-40 ºC). 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 S3, right panel.

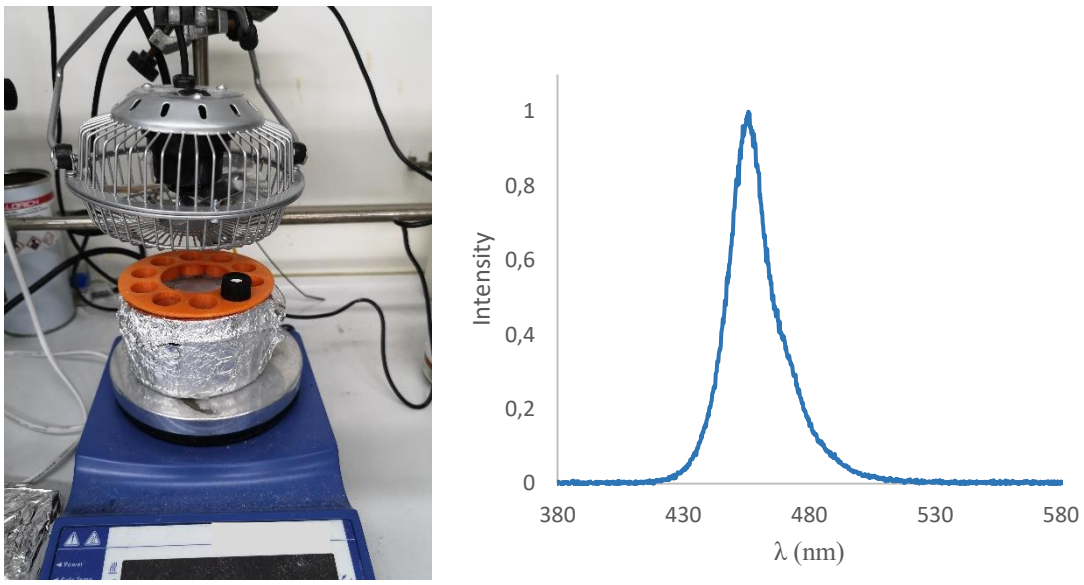


Figure S3: *Left panel*: Blue LEDs photoreactor used for reactions. R*ight panel:* Emission spectrum of the 465 nm LED strip used in this reactor.

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

For reactions (details in Section C2 and C3) 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 S4) and a fan which was used to cool down the reactor (the reaction temperature within the reaction vessel was measured to be between 35-40 ºC).

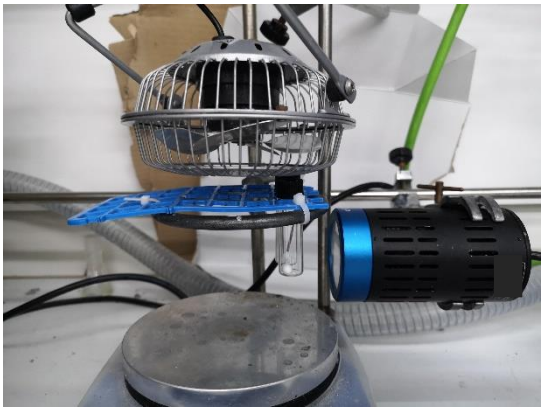


Figure S4: Kessil lamp set-up.

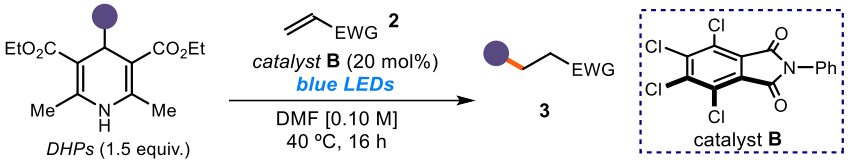
- ***Set-up 3*** *456nm EvoluChem™ setup*

For reactions (details in Section C2 and C3) performed using an EvoluChem™ P303-30-1 LEDs (18 W, λmax= 456 nm, 2-3 cm away), a fan was used to cool down the reactor (the reaction temperature within the reaction vessel was measured to be between 35-40 ºC, setup depicted in Figure S5).

Figure S5: 456nm EvoluChem™ setup.

C2. Experimental Procedure for the Giese Addition

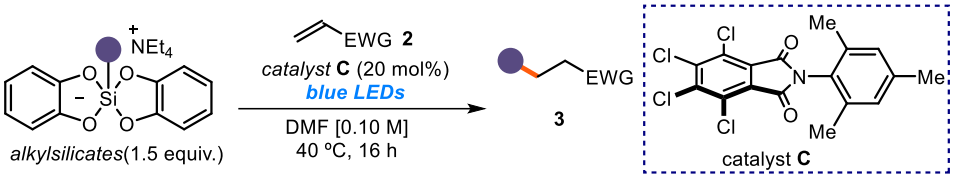
C2.1 General Procedure A



Reactions with alkyl-1,4-dihydropyridines (DHPs) as radical precursors: *performed using **set-up 2** in Figure S4*.

In an oven dried vial with a Teflon septum screw cap, the acceptor catalyst **B** (14.5 mg, 0.04 mmol, 0.2 equiv.), alkyl-1,4-dihydropyridine **1** (0.3 mmol, 1.5 equiv.) and the electron-poor olefin **2** (0.2 mmol, 1.5 equiv., *if solid*) were dissolved in DMF (2 mL, synthesis grade solvent). The resulting 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 photoreactor (Figure S4) and irradiated under stirring for 16 hours, unless otherwise specified. Then the solvent was evaporated and the crude mixture purified by flash column chromatography on silica gel to furnish the target product **3**.

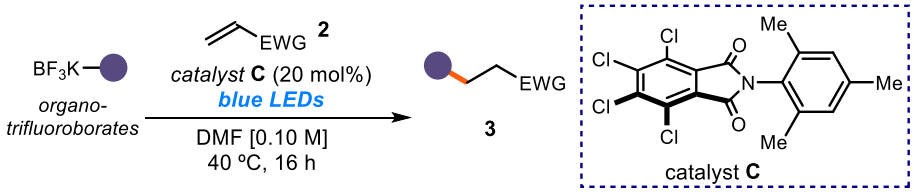
C2.2 General Procedure B



Reactions with alkylsilicates as radical precursors: *performed using **set-up 1** in Figure S3*.

In an oven dried vial with a Teflon septum screw cap, acceptor catalyst **C** (16.0 mg, 0.04 mmol, 0.2 equiv.), alkylsilicates **1** (0.3 mmol, 1.5 equiv.) and the electron-poor olefin **2** (0.2 mmol, 1.0 equiv., *if solid*), were dissolved in DMF (2 mL, synthesis grade solvent). The resulting 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 S3) and irradiated under stirring for 16 hours, unless otherwise specified. Then the solvent was evaporated and the crude mixture purified by flash column chromatography on silica gel to furnish the target product **3**.

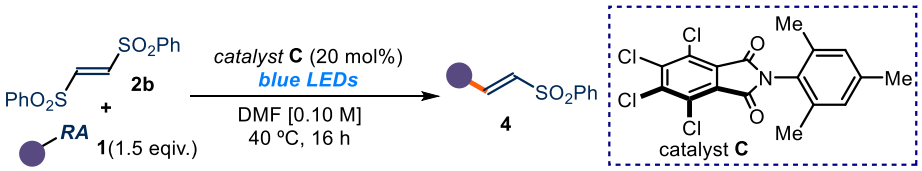
C2.3 General Procedure C



Reactions with organotrifluoroborates as precursors: *performed using **set-up 1** in Figure S3*.

In an oven dried vial with a Teflon septum screw cap, acceptor catalyst **C** (16.0 mg, 0.04 mmol, 0.2 equiv.), organotrifluoroborates **1** (0.3 mmol, 1.5 equiv.) and the electron-poor olefin **2** (0.2 mmol, 1.0 equiv., *if solid*), were dissolved in DMF (2 mL, synthesis grade solvent). The resulting 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 S3) and irradiated under stirring for 16 hours, unless otherwise specified. Then the solvent was evaporated and the crude mixture purified by flash column chromatography on silica gel to furnish the target product **3**.

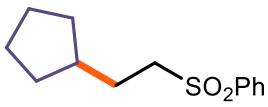
C2.4 General Procedure D



*Reactions performed using **set-up 1** in Figure S3*. In an oven dried vial with a Teflon septum screw cap, acceptor catalyst **C** (16.0 mg, 0.04 mmol, 0.2 equiv.), radical precursors **1** (0.3 mmol,

1.5 equiv.) and (*E*)-1,2-Bis(phenylsulfonyl)ethene **2b** (61.7 mg, 0.2 mmol, 1.0 equiv), were dissolved in DMF (2 mL, synthesis grade solvent). The resulting mixture was degassed with argon sparging for 60 seconds. The vial was then placed in the 3D printed support photoreactor (Figure S3) and irradiated under stirring for 16 hours, unless otherwise specified. Then the solvent was evaporated and the crude mixture purified by flash column chromatography on silica gel to furnish the product **4**.

C2.5 Characterization of Products

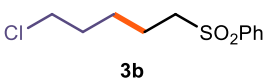


3a

((2-Cyclopentylethyl)sulfonyl)benzene (3a): Synthesized according to General Procedure A, B or C using DHP **1a** (96.5 mg, 0.3 mmol, 1.5 equiv.), silicate **1b** (137.5 mg, 0.3 mmol, 1.5 equiv.) or trifluoroborate **1c** (53.0 mg, 0.3 mmol, 1.5 equiv.), respectively, and phenyl vinyl sulfone **2a** (33.5 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 **3a** as a yellow oil (obtained in 87% yield (41.5 mg) from **1a**, obtained in 70% yield (33.5 mg) from **1b,** 63% yield (30.0 mg) from **1c**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.84 (m, 2H), 7.70 – 7.62 (m, 1H), 7.61 – 7.51 (m, 2H), 3.14 – 3.03 (m, 2H), 1.74 – 1.66 (m, 4H), 1.64 – 1.43 (m, 4H), 1.12 – 0.98 (m, 2H).

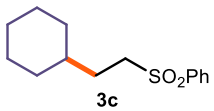
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 133.7, 129.4, 128.2, 55.9, 38.9, 32.4, 28.7, 25.2.
Matching reported literature data.[9]



3b

((5-Chloropentyl)sulfonyl)benzene (3b): Synthesized according to General Procedure B using silicate **1d** (187.5 mg, 0.3 mmol, 1.5 equiv.) and phenyl vinyl sulfone **2a** (33.5 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 **3b** (30.0 mg, 61% yield) as a white solid.

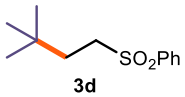
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.87 (m, 2H), 7.72 – 7.63 (m, 1H), 7.62 – 7.52 (m, 2H), 3.49 (t, *J* = 6.5 Hz, 2H), 3.18 – 3.02 (m, 2H), 1.82 – 1.68 (m, 4H), 1.65 – 1.48 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 133.9, 129.5, 128.2, 56.2, 44.5, 32.0, 25.7, 22.2.
Matching reported literature data.[10]



3c

((2-Cyclohexylethyl)sulfonyl)benzene (3c): Synthesized according to General Procedure B using silicate **1e** (137.0 mg, 0.3 mmol, 1.5 equiv.) and phenyl vinyl sulfone **2a** (33.5 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 **3c** (28.5 mg, 56% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 - 7.87 (m, 2H), 7.69 - 7.61 (m, 1H), 7.60 - 7.52 (m, 2H), 3.13 - 3.05 (m, 2H), 1.70 - 1.58 (m, 7H), 1.30 - 1.24 (m, 1H), 1.20 - 1.06 (m, 3H), 0.90 - 0.80 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.3, 133.6, 129.2, 128.0, 54.4, 36.6, 32.8, 29.6, 26.3, 26.0. Matching reported literature data.[11]



((3,3-Dimethylbutyl)sulfonyl)benzene (3d): Synthesized according to General Procedure B using silicate **1f** (129.5 mg, 0.3 mmol, 1.5 equiv.) or tertbutyl trifluoroborate (49.0 mg, 0.3 mmol, 1.5 equiv.) and phenyl vinyl sulfone **2a** (33.5 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (7% AcOEt in hexanes as eluent) to afford **3d** as a colorless oil (obtained 76% yield (34.5mg) from **1f**, 84% yield (38.0 mg) from **1g**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 - 7.87 (m, 2H), 7.68 - 7.62 (m, 1H), 7.60 - 7.53 (m, 2H), 3.08 - 3.02 (m, 2H), 1.62 - 1.55 (m, 2H), 0.85 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 133.6, 129.2, 128.0, 52.9, 35.6, 30.0, 28.9.
Matching reported literature data.[11]

5 mmol scale-up reaction: in a 100 mL Schlenk tube with a Teflon septum, *tert*-butyl trifluoroborate (1.23 g, 6.0 mmol, 1.5 equiv.), phenyl vinyl sulfone **2a** (0.84 g, 5.0 mmol, 1.0 equiv.) and catalyst **C** (0.40 g, 1.0 mmol, 0.2 equiv.) were sequentially added. Then the tube was evacuated and backfilled with argon three times followed by the addition of DMF (25 mL) via syringe. The round Schlenk flask was irradiated for 36 hours with two 50 W Kessil blue LED lamp (one PR160L-456 and one PR160L-427, 100% intensity, 4-5 cm away, see **Error! Reference source not found.**8 for the set-up). The mixture was transferred to an extraction funnel, brine (25 mL) was added and the organic layer was extracted with DCM (50×3 mL). The organic layer was dried ($MgSO_4$) and concentrated to dryness. The product was then purified by chromatography on silica gel (7% AcOEt in hexanes) to afford 590 mg of product **3d** (2.6 mmol, 52% yield) as a colorless oil. NMR analysis was consistent with the product synthesized in the small scale process.

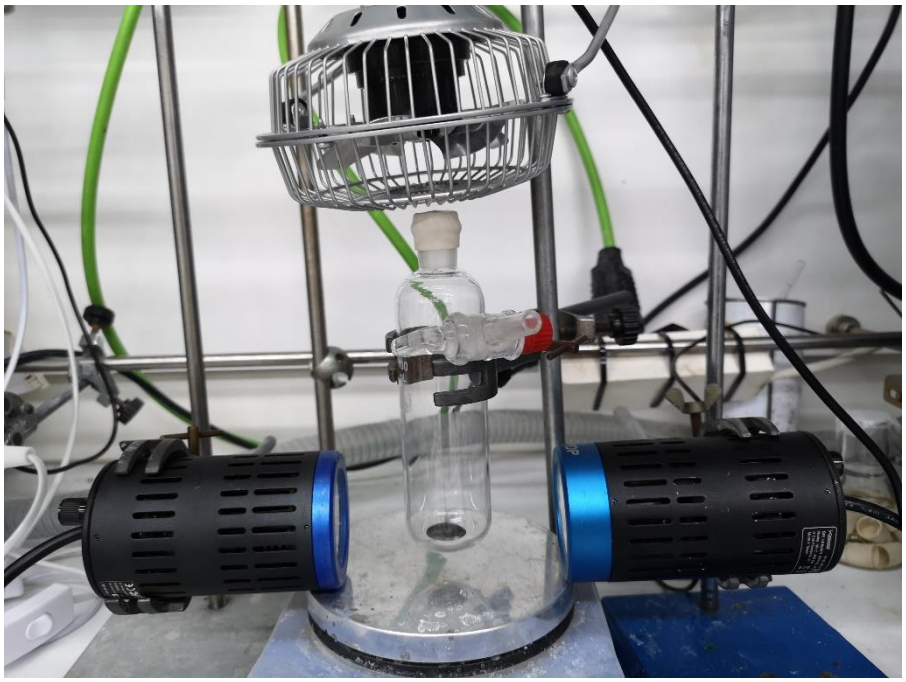
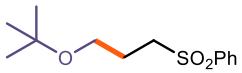


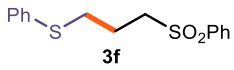
Figure S6: Experimental setup used for the 5 mmol reaction.



3e

((3-(*tert*-Butoxy)propyl)sulfonyl)benzene (3e): Synthesized according to General Procedure C using 2-methoxy-2-methylpropyl trifluoroborate (58.0 mg, 0.3 mmol, 1.5 equiv.) and phenyl vinyl sulfone **2a** (33.5 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 **3e** (41.0 mg, 80% yield) as a colorless oil.

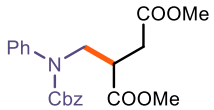
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.67 – 7.61 (m, 1H), 7.60 – 7.53 (m, 2H), 3.38 (t, *J* = 5.9 Hz, 2H), 3.22 – 3.15 (m, 2H), 1.95 – 1.86 (m, 2H), 1.11 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.38, 133.7, 129.4, 128.2, 73.1, 59.4, 53.9, 27.6, 24.2.
Matching reported literature data.[11]



3f

Phenyl-(3-(phenylsulfonyl)propyl)sulfane (3f): Synthesized according to General Procedure C using (phenylthio)methyl trifluoroborate (69.0 mg, 0.3 mmol, 1.5 equiv.) and phenyl vinyl sulfone **2a** (33.5 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 **3f** (28.0 mg, 48% yield) as a yellow oil.

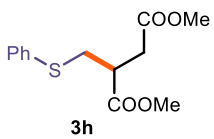
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.69 – 7.62 (m, 1H), 7.55 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.29 – 7.26 (m, 5H), 3.29 – 3.22 (m, 2H), 2.98 (t, *J* = 6.9 Hz, 2H), 2.05 – 1.97 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 134.7, 133.8, 130.4, 129.4, 129.1, 128.0, 126.8, 54.7, 32.7, 22.4.
Matching reported literature data.[12]



3g

Dimethyl-2-((((benzyloxy)carbonyl)(phenyl)amino)methyl)succinate (3g): Synthesized according to General Procedure A using DHP **1j** (148.0 mg, 0.3 mmol, 1.5 equiv.) and dimethyl fumarate (28.5 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 **3g** (33.0 mg, 43% yield) as a colorless oil.

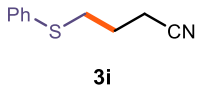
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.34 (m, 2H), 7.33 - 7.17 (m, 8H), 5.18 - 5.06 (m, 2H), 4.10 (dd, *J* = 16, 8 Hz, 1H), 3.90 (d, *J* = 12, 8 Hz, 1H), 3.60 (s, 3H), 3.49 (s, 3H), 3.14 - 3.04 (m, 1H),), 2.75 (dd, *J* = 2.0, 1.2 Hz, 1H), 2.50 (d, *J* = 16, 8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 171.8, 155.5, 141.1, 136.4, 129.1, 128.4, 127.9, 127.5, 127.1, 67.5, 52.0, 51.8, 51.3, 40.5, 33.3.
HRMS: calculated for $C_{21}H_{23}NNaO_6$ ($M+Na^+$): 408.1417, found 408.1409.



3h

Dimethyl-2-((phenylthio)methyl)succinate (3h): Synthesized according to General Procedure C using (phenylthio)methyl trifluoroborate (69.0 mg, 0.3 mmol, 1.5 equiv.) and dimethyl fumarate (28.5 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford **3h** (44.5 mg, 83% yield) as a colorless oil.

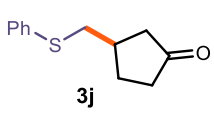
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 3.66 (s, 6H), 3.38 – 3.27 (m, 1H), 3.14 – 3.01 (m, 2H), 2.89 – 2.68 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 172.1, 135.1, 130.4, 129.2, 126.9, 52.3, 52.0, 41.3, 35.6, 34.6. Matching reported literature data.[13]



3i

4-(Phenylthio)butanenitrile (3i): Synthesized according to General Procedure C using (phenylthio)methyl trifluoroborate (69.0 mg, 0.3 mmol, 1.5 equiv.) and acrylonitrile (10.5 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (7% AcOEt in hexanes as eluent) to afford **3i** (19.0 mg, 53% yield) as a colorless oil.

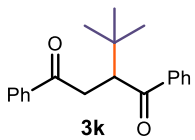
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.33 (ddd, *J* = 7.8, 6.8, 1.2 Hz, 2H), 7.28 – 7.23 (m, 1H), 3.06 (t, *J* = 6.9 Hz, 2H), 2.54 (t, *J* = 7.1 Hz, 2H), 1.98 (p, *J* = 7.0 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9, 130.3, 129.3, 127.0, 119.2, 32.8, 25.0, 16.1.
Matching reported literature data.[14]



3j

3-((Phenylthio)methyl)cyclopentan-1-one (3j): Synthesized according to General Procedure C using (phenylthio)methyl trifluoroborate (69.0 mg, 0.3 mmol, 1.5 equiv.) and cyclopent-2-en-1-one (16.5 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford **3j** (20.0 mg, 49% yield) as a colorless oil

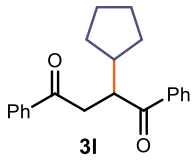
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.18 (m, 1H), 3.03 (dd, *J* = 6.7, 2.8 Hz, 2H), 2.53 – 2.43 (m, 2H), 2.39 – 2.19 (m, 3H), 2.06 – 1.94 (m, 1H), 1.76 – 1.64 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 218.1, 136.1, 129.7, 129.0, 126.4, 44.5, 39.3, 38.3, 36.8, 28.8.
Matching reported literature data.[15]



3k

2-(*tert*-Butyl)-1,4-diphenylbutane-1,4-dione (3k): Synthesized according to General Procedure B using silicate **1f** (129.5 mg, 0.3 mmol, 1.5 equiv.) and (*E*)-1,4-diphenylbut-2-ene-1,4-dione (47.5 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford **3k** (36.0 mg, 61% yield) as a white solid.

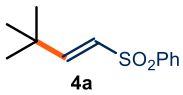
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 - 8.09 (m, 2H), 7.99 - 7.93 (m, 2H), 7.57 - 7.51 (m, 2H), 7.51 – 7.40 (m, 4H), 4.06 (dd, *J* = 12, 4 Hz, 1H), 3.89 (dd, *J* = 16, 12 Hz, 1H), 3.24 (dd, *J* = 16, 4 Hz, 1H), 0.99 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 199.4, 140.0, 136.7, 133.2, 132.4, 128.6, 128.5, 128.5, 128.1, 49.4, 38.8, 33.5, 28.6.
HRMS: calculated for $C_{20}H_{23}O_2$ ($M+H^+$): 295.1693, found 295.1695.



3l

2-Cyclopentyl-1,4-diphenylbutane-1,4-dione (3l): Synthesized according to General Procedure A using DHP **1a** (96.5 mg, 0.3 mmol, 1.5 equiv.) and (*E*)-1,4-diphenylbut-2-ene-1,4-dione (47.5 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford **3l** (38.5 mg, 63% yield) as a yellow oil.

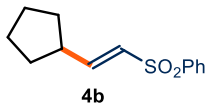
^{1}H NMR (400 MHz, CDCl3) δ 8.13 - 8.09 (m, 2H), 7.99 - 7.93 (m, 2H), 7.60 - 7.52 (m, 2H), 7.51 - 7.42 (m, 4H), 4.09 - 4.01 (m, 1H), 3.82 (dd, *J* = 20, 12 Hz, 1H), 3.24 (dd, *J* = 16, 4 Hz, 1H), 2.14 - 2.01 (m, 1H), 1.86 - 1.78 (m, 1H), 1.66 - 1.53 (m, 4H), 1.51 - 1.39 (m, 1H), 1.29 - 1.24 (m, 1 H), 1.19 -1.10 (m, 1H).
^{13}C NMR (101 MHz, CDCl3) δ 204.2, 198.9, 138.2, 136.6, 133.2, 132.7, 129.2, 128.6, 128.5, 128.1, 45.5, 43.2, 40.7, 31.2, 30.6, 25.1, 24.5.
HRMS: calculated for $C_{21}H_{23}O_2$ ($M+H^+$): 307.1693, found 307.1688.



4a

(*E*)-((3,3-Dimethylbut-1-en-1-yl)sulfonyl)benzene (4a): Synthesized according to General Procedure D using silicate **1f** (129.5 mg, 0.3 mmol, 1.5 equiv.) and (*E*)-1,2-bis(phenylsulfonyl)ethene **2b** (61.5 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford **4a** (28.5 mg, 63% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 - 7.84 (m, 2H), 7.63- 7.57 (m, 1H), 7.55 - 7.49 (m, 2H), 6.98 (d, *J* = 16 Hz, 1H), 6.19 (d, *J* = 16 Hz, 1H), 1.07 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 140.8, 133.2, 129.3, 127.5, 126.5, 34.1, 28.3.
Matching reported literature data.[16]



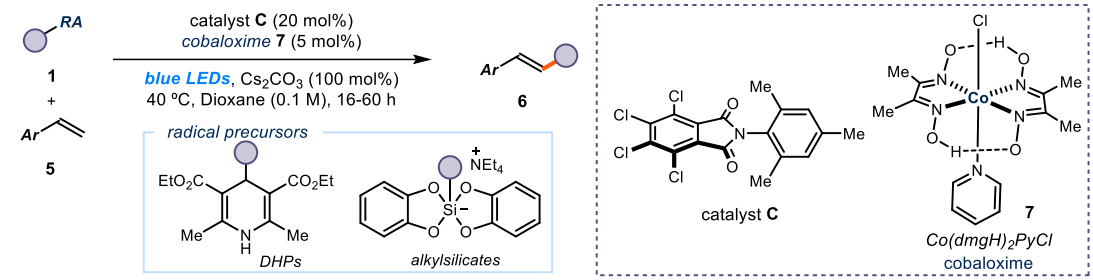
4b

(*E*)-((2-Cyclopentylvinyl)sulfonyl)benzene (4b): Synthesized according to General Procedure D using DHP **1a** (96.5 mg, 0.3 mmol, 1.5 equiv.) and (*E*)-1,2-bis(phenylsulfonyl)ethene **2b** (61.5 mg, 0.2 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford **4b** (33.0 mg, 70% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 - 7.84 (m, 2H), 7.63- 7.57 (m, 1H), 7.55 - 7.49 (m, 2H), 6.97 (d, *J* = 12, 8 Hz, 1H), 6.27 (dd, *J* = 20, 1.2 Hz, 1H), 2.67-2.54 (m, 1H), 1.89-1.77 (m, 2H), 1.71-1.65 (m, 2H), 1.63-1.54 (m, 2H), 1.46-1.35 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 140.9, 133.2, 129.2, 128.5, 127.5, 42.1, 32.1, 25.2.
HRMS: calculated for $C_{13}H_{17}O_2S$ ($M+H^+$): 237.0944, found 237.0935.

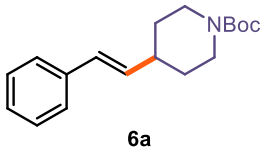
C3. Experimental Procedure for Heck-type reaction

C3.1 General Procedure E



*Reactions performed using **set-up 3** in Figure S5*. To an oven dried vial with a Teflon septum screw cap, the acceptor catalyst **C** (16.0 mg, 0.04 mmol, 0.2 equiv.), the radical precursor **1** (0.2 mmol, 1.0 equiv.), cesium carbonate (32.5 mg, 0.1 mmol, 1.0 equiv), the styrene derivative **5** (1.0 mmol, 1.0 equiv., *if solid*) and $Co(dmgH)_2PyCl$ (2.0 mg, 0.01 mmol, 5 mol%) were sequentially added. Then the vial was evacuated and backfilled with argon three times followed by the addition of dioxane (2 mL) via syringe. If the styrene derivative **5** was *liquid*, it was added via syringe afterwards. The vial was then placed in the photoreactor (Figure S5) and irradiated under stirring for 16-60 hours. The solvent was evaporated and the crude mixture purified by flash column chromatography on silica gel to furnish product **6**.

C3.2 Characterization of Products.

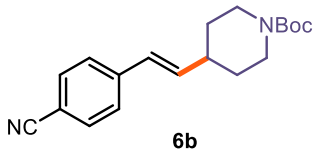


6a

***tert*-Butyl-(*E*)-4-styrylpiperidine-1-carboxylate (6a):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and styrene (104.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 14:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **6a** (49.5 mg, 86% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.30 (dd, *J* = 10.2, 4.9 Hz, 2H), 7.23 – 7.16 (m, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 16.0, 6.9 Hz, 1H), 4.12 (s, 2H), 2.78 (t, *J* = 12.2 Hz, 2H), 2.35 – 2.21 (m, 1H), 1.76 (d, *J* = 12.8 Hz, 2H), 1.47 (s, 9H), 1.45 – 1.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 137.6, 134.5, 128.7, 128.6, 127.2, 126.2, 79.5, 43.8, 39.5, 32.0, 28.6.

Matching reported literature data.[17]

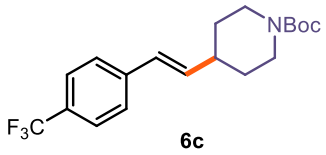


6b

***tert*-Butyl-(*E*)-4-(4-cyanostyryl)piperidine-1-carboxylate (6a):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and 4-vinylbenzonitrile (129.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of >20:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **6b** (52.0 mg, 83% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 6.41 (d, *J* = 16.1 Hz, 1H), 6.30 (dd, *J* = 16.0, 6.6 Hz, 1H), 4.16 (s, 2H), 2.80 (t, *J* = 12.1 Hz, 2H), 2.41 – 2.28 (m, 1H), 1.78 (d, *J* = 12.4 Hz, 2H), 1.48 (s, 9H), 1.40 (ddd, *J* = 16.4, 12.7, 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 142.1, 138.6, 132.5, 127.3, 126.7, 119.2, 110.4, 79.6, 43.7, 39.6, 31.6, 28.6. Matching reported literature data.[17]



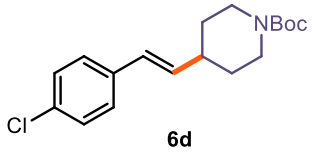
6c

***tert*-Butyl-(*E*)-4-(4-(trifluoromethyl)styryl)piperidine-1-carboxylate (6c):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and 1-(trifluoromethyl)-4-vinylbenzene (172.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 13:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **6c** (63.5 mg, 89% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.25 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.14 (s, 2H), 2.79 (t, *J* = 11.3 Hz, 2H), 2.37 – 2.27 (m, 1H), 1.77 (d, *J* = 12.6 Hz, 2H), 1.47 (s, 9H), 1.38 (ddd, *J* = 17.5, 11.6, 7.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 141.1, 137.3, 129.1 (q, J = 31.5 Hz), 127.5, 126.3, 125.6(q, J = 31.5 Hz), 124.9(q, J = 31.5 Hz) 79.6, 43.9, 39.6, 31.8, 28.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -150.78 (s). Matching reported literature data.[17]

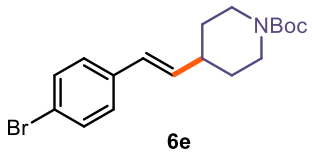


6d

***tert*-Butyl-(*E*)-4-(4-chlorostyryl)piperidine-1-carboxylate (6d):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and 1-chloro-4-vinylbenzene (138.5 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 7:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **6d** (48.5 mg, 75% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.26 (m, 4H), 6.33 (dd, *J* = 16.0, 1.3 Hz, 1H), 6.12 (dd, *J* = 16.0, 6.9 Hz, 1H), 4.13 (s, 2H), 2.77 (t, *J* = 13.1 Hz, 2H), 2.34 – 2.21 (m, 1H), 1.75 (d, *J* = 13.2 Hz, 2H), 1.47 (s, 9H), 1.35 (dd, *J* = 12.4, 4.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 136.2, 135.2, 132.8, 128.8, 127.5, 127.4, 79.6, 43.4, 39.5, 31.9, 28.6. Matching reported literature data.[17]



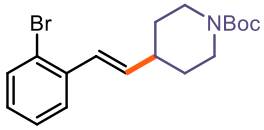
6e

***tert*-Butyl-(*E*)-4-(4-bromostyryl)piperidine-1-carboxylate (6e):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and 1-bromo-4-vinylbenzene (183.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 7:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **6e** (56.5 mg, 77% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.23 – 7.15 (m, 2H), 6.31 (d, J = 15.6 Hz, 1H), 6.13 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.13 (s, 2H), 2.77 (t, *J* = 12.7 Hz, 2H), 2.26 (dtd, *J* = 14.8, 6.8, 3.4 Hz, 1H), 1.74 (d, *J* = 13.1 Hz, 2H), 1.46 (s, 9H), 1.44 – 1.30 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 136.6, 135.3, 131.7, 127.7, 127.5, 120.9, 79,5, 39.51, 31.8, 28.6.

Matching reported literature data.[17]



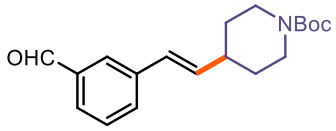
6f

***tert*-Butyl-(*E*)-4-(2-bromostyryl)piperidine-1-carboxylate (6f):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and 1-bromo-2-vinylbenzene (183.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 20:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **6f** (42.5 mg, 58% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.48 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.07 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 6.72 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.9, 6.9 Hz, 1H), 4.14 (s, 2H), 2.80 (t, *J* = 12.4 Hz, 2H), 2.40 – 2.30 (m, 1H), 1.79 (d, *J* = 12.5 Hz, 2H), 1.47 (s, 9H), 1.46 – 1.34 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 137.5, 137.4, 133.0, 128.6, 127.7, 127.6, 126.9, 123.6, 79.5, 39.6, 31.8, 28.6.

Matching reported literature data.[17]



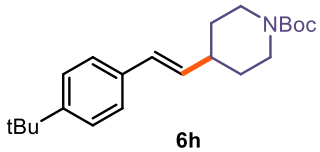
6g

***tert*-Butyl-(*E*)-4-(3-formylstyryl)piperidine-1-carboxylate (6g):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and 3-vinylbenzaldehyde (132.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 6:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **6g** (42.5 mg, 58% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.85 (t, *J* = 1.8 Hz, 1H), 7.71 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.59 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.26 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.14 (s, 2H), 2.79 (t, *J* = 12.8 Hz, 2H), 2.32 (dtd, *J* = 11.2, 7.3, 3.5 Hz, 1H), 1.77 (d, *J* = 13.2 Hz, 2H), 1.47 (s, 9H), 1.45 – 1.35 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 155.0, 138.7, 136.8, 136.6, 132.2, 129.4, 128.7, 127.4, 126.9, 79,6, 43,7, 39.6, 31.8, 28.6.

HRMS: calculated for $C_{19}H_{25}NNaO_3$ ($M+Na^+$): 338.1727, found 338.1729.



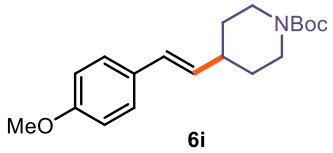
6h

***tert*-Butyl-(*E*)-4-(4-(tert-butyl)styryl)piperidine-1-carboxylate (6h):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and 1-(tert-butyl)-4-vinylbenzene (160.5 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of >20:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **6h** (50.0 mg, 73% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.31 – 7.27 (m, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.10 (dd, *J* = 16.0, 6.9 Hz, 1H), 4.12 (s, 2H), 2.78 (t, *J* = 10.6 Hz, 2H), 2.42 – 2.30(m, 1H), 1.75 (d, *J* = 12.5 Hz, 2H), 1.46 (d, *J* = 13.0 Hz, 9H), 1.45 – 1.34 (m, 2H), 1.31 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 150.3, 134.9, 133.8, 128.3, 125.9, 125.6, 79.5, 43.9, 39.5, 34.7, 32.0, 31.5, 28.6.

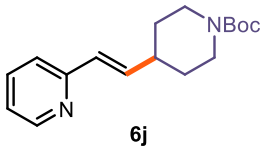
Matching reported literature data.[18]



6i

***tert*-Butyl-(*E*)-4-(4-methoxystyryl)piperidine-1-carboxylate (6i):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and 1-methoxy-4-vinylbenzene (134.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of >20:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **6i** (37.0 mg, 58% yield) as a white solid.

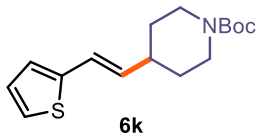
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 6.90 – 6.84 (m, 2H), 6.35 (d, *J* = 15.7 Hz, 1H), 6.02 (dd, *J* = 16.0, 6.9 Hz, 1H), 4.14 (s, 2H), 3.82 (s, 3H), 2.80 (t, *J* = 12.7 Hz, 2H), 2.28 (dtd, *J* = 14.8, 7.0, 3.2 Hz, 1H), 1.77 (d, *J* = 13.1 Hz, 2H), 1.49 (s, 9H), 1.39 (qd, *J* = 12.2, 4.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 155.0, 132.4, 130.5, 127.9, 127.3, 114.1, 79.5, 55.4, 43.9, 39.5, 32.1, 28.6.
Matching reported literature data.[17]



6j

***tert*-Butyl-(*E*)-4-(2-(pyridin-2-yl)vinyl)piperidine-1-carboxylate (6j):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and 2-vinylpyridine (105.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 10:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **6j** (40.5 mg, 70% yield) as a white solid.

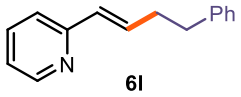
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.9 Hz, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.23 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.09 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 6.68 (dd, *J* = 15.8, 6.8 Hz, 1H), 6.47 (dd, *J* = 15.8, 1.4 Hz, 1H), 4.13 (s, 2H), 2.78 (t, *J* = 12.7 Hz, 2H), 2.33 (dtdd, *J* = 10.8, 6.4, 4.0, 2.0 Hz, 1H), 1.79 (d, *J* = 15.8 Hz, 2H), 1.46 (s, 9H), 1.44 – 1.32 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 155.0, 149.6, 139.0, 136.6, 128.7, 122.0, 121.5, 79,5, 43.8, 39.3, 31.6, 28.6.
Matching reported literature data.[18]



6k

***tert*-Butyl-(*E*)-4-(2-(thiophen-2-yl)vinyl)piperidine-1-carboxylate (6k):** Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and 2-vinylthiophene (110.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of >20:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **6k** (28.8 mg, 49% yield) as a white solid.

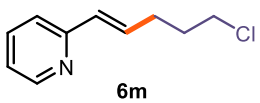
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 5.0 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.89 (d, *J* = 3.3 Hz, 1H), 6.55 – 6.46 (m, 1H), 6.00 (dd, *J* = 15.8, 6.8 Hz, 1H), 4.12 (s, 2H), 2.77 (t, *J* = 12.6 Hz, 2H), 2.24 (dtt, *J* = 10.9, 7.0, 3.6 Hz, 1H), 1.74 (d, *J* = 13.1 Hz, 2H), 1.46 (s, 9H), 1.36 (qd, *J* = 12.6, 4.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 142.9, 134.3, 127.4, 124.9, 123.6, 122.0, 79.5, 43.8, 39.3, 31.8, 28.6.
Matching reported literature data.[18]



6l

(*E*)-2-(4-Phenylbut-1-en-1-yl)pyridine (6l): Synthesized according to General Procedure E using DHP **1p** (71.5 mg, 0.2 mmol, 1.0 equiv.) and 2-vinylpyridine (105.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 10:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **6l** (22.0 mg, 53% yield) as a colorless oil.

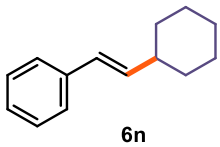
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.0 Hz, 1H), 7.72 (dt, *J* = 8.6, 4.1 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.21 (dt, *J* = 14.3, 4.3 Hz, 4H), 6.94 – 6.84 (m, 1H), 6.62 (d, *J* = 15.7 Hz, 1H), 2.92 – 2.77 (m, 2H), 2.69 – 2.56 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 141.5, 138.3, 135.0, 130.5, 128.6, 126.2, 122.2, 121.6, 35.4, 34.9.
Matching reported literature data.[19]



6m

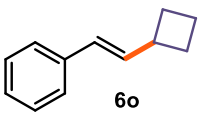
(*E*)-2-(5-Chloropent-1-en-1-yl)pyridine (6m): Synthesized according to General Procedure E using silicate **1d** (125.0 mg, 0.2 mmol, 1.0 equiv.) and 2-vinylpyridine (105.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 13:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **6m** (20.5 mg, 57% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 3.9 Hz, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.23 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.11 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.72 (dt, *J* = 15.7, 7.1 Hz, 1H), 6.54 (dt, *J* = 15.6, 1.5 Hz, 1H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.44 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.02 – 1.95 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 149.4, 136.8, 134.0, 131.0, 122.0, 121.5, 44.5, 31.8, 30.0.
Matching reported literature data.[19]


6n

(*E*)-(2-Cyclohexylvinyl)benzene (6n): Synthesized according to General Procedure E using DHP **1l** (67.0 mg, 0.2 mmol, 1.0 equiv.) and styrene (104.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 9:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (2% AcOEt in hexanes as eluent) to afford **6n** (27.0 mg, 73% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.20 – 7.14 (m, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.13 (dtd, *J* = 11.3, 7.4, 3.8 Hz, 1H), 1.85 – 1.74 (m, 4H), 1.71 – 1.65 (m, 1H), 1.38 – 1.28 (m, 3H), 0.87 (dd, *J* = 15.7, 9.0 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 137.0, 128.6, 127.4, 126.9, 126.1, 41.3, 33.1, 26.3, 26.2.
Matching reported literature data.[20]



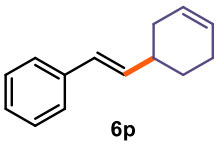
6o

(*E*)-(2-Cyclobutylvinyl)benzene (6n): Synthesized according to General Procedure E using DHP **1m** (61.5 mg, 0.2 mmol, 1.0 equiv.) and styrene (104.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 10:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (2% AcOEt in hexanes as eluent) to afford **6o** (20.0 mg, 64% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.29 (ddd, *J* = 7.8, 6.8, 1.2 Hz, 2H), 7.23 – 7.15 (m, 1H), 6.40 – 6.25 (m, 2H), 3.17 – 3.05 (m, 1H), 2.24 – 2.12 (m, 2H), 2.03 – 1.78 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 135.4, 128.6, 127.7, 127.0, 126.1, 38.9, 28.9, 18.7.

Matching reported literature data.[20]



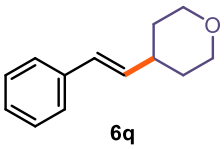
6p

(*E*)-(2-(Cyclohex-3-en-1-yl)vinyl)benzene (6p): Synthesized according to General Procedure E using DHP **1n** (66.5 mg, 0.2 mmol, 1.0 equiv.) and styrene (104.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of >20:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (2% AcOEt in hexanes as eluent) to afford **6p** (21.0 mg, 57% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 7.2 Hz, 1H), 5.71 (d, *J* = 2.2 Hz, 2H), 2.50 – 2.39 (m, 1H), 2.26 – 2.09 (m, 3H), 2.01 – 1.91 (m, 1H), 1.90 – 1.82 (m, 1H), 1.61 – 1.49 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 135.9, 128.6, 128.1, 127.2, 127.0, 126.2, 126.1, 37.3, 31.5, 28.9, 25.0.

Matching reported literature data.[21]



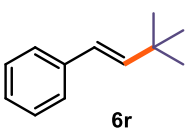
6q

(*E*)-4-Styryltetrahydro-2H-pyran (6q): Synthesized according to General Procedure E using DHP **1n** (67.5 mg, 0.2 mmol, 1.0 equiv.) and styrene (104.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of >20:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (2% AcOEt in hexanes as eluent) to afford **6q** (28.5 mg, 75% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 6.16 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.01 (ddd, *J* = 11.8, 4.6, 2.0 Hz, 2H), 3.47 (td, *J* = 11.6, 2.2 Hz, 2H), 2.38 (ddd, *J* = 20.3, 11.8, 6.3 Hz, 1H), 1.81 – 1.66 (m, 2H), 1.64 – 1.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 134.8, 128.7, 128.4, 127.2, 126.2, 67.9, 38.5, 32.8.

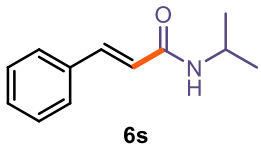
Matching reported literature data.[20]



6r

(*E*)-(3,3-Dimethylbut-1-en-1-yl)benzene (6r): Synthesized according to General Procedure E using silicate **1f** (86.5 mg, 0.2 mmol, 1.0 equiv.) and styrene (104.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of >20:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (2% AcOEt in hexanes as eluent) to afford **6r** (22.0 mg, 68% yield) as a colorless oil.

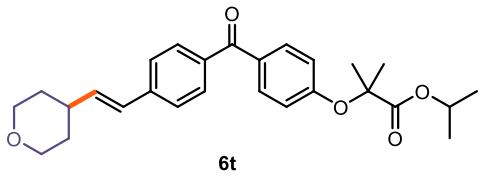
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.33 – 7.26 (m, 2H), 7.21 – 7.15 (m, 1H), 6.34 – 6.21 (m, 2H), 1.12 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 138.2, 128.6, 126.9, 126.2, 124.7, 33.5, 29.8.
Matching reported literature data.[20]



6s

(*E*)-*N*-Isopropyl-4-phenylbut-3-enamide (6s): Synthesized according to General Procedure E using DHP **1r** (67.5 mg, 0.2 mmol, 1.0 equiv.) and styrene (104.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 11:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **6s** (27.0 mg, 67% yield) as a white solid.

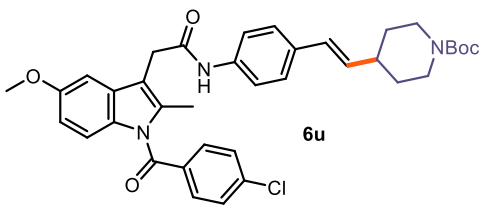
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 15.6 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.41 – 7.35 (m, 3H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.48 (s, 1H), 4.31 – 4.20 (m, 1H), 1.25 (d, *J* = 6.5 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 140.9, 135.1, 129.7, 128.9, 127.9, 121.2, 41.7, 23.0.
Matching reported literature data.[22]



6t

(*E*)-2-Methyl-2-(4-(4-(2-(tetrahydro-2H-pyran-4-yl)vinyl)benzoyl)phenoxy) propanoate (6t): Synthesized according to General Procedure E using DHP **1n** (67.5 mg, 0.2 mmol, 1.0 equiv.) and styrene derivative **5l** (211.5 mg, 0.6mmol, 3.0 equiv.). An *E*/*Z* ratio of 15:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **6t** (63.5 mg, 73% yield) as a white solid.

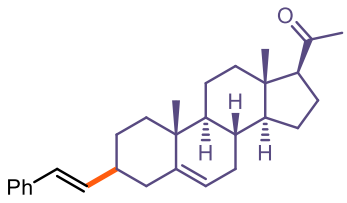
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 4H), 7.45 – 7.42 (m, 2H), 6.88 – 6.84 (m, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 16.0, 6.7 Hz, 1H), 5.09 (p, *J* = 6.3 Hz, 1H), 4.07 – 3.99 (m, 2H), 3.48 (td, *J* = 11.7, 2.1 Hz, 2H), 2.43 (ddt, *J* = 11.1, 7.0, 4.1 Hz, 1H), 1.77 – 1.69 (m, 2H), 1.66 (s, 6H), 1.62 (dd, *J* = 11.9, 4.5 Hz, 2H), 1.20 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 173.4, 159.6, 141.5, 137.4, 136.7, 132.1, 131.0, 130.5, 127.7, 125.9, 117.3, 79.5, 69.5, 67.8, 38.7, 32.6, 29.8, 21.7.
HRMS: calculated for $C_{27}H_{33}O_5$ ($M+H^+$): 437.2323, found 437.2307.



6u

tert-Butyl-(E)-4-(4-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl) acetamido)styryl)piperidine-1-carboxylate (6t): Synthesized according to General Procedure E using DHP **1k** (87.5 mg, 0.2 mmol, 1.0 equiv.) and styrene derivative **5m** (275.5 mg, 0.6mmol, 3.0 equiv.). An *E*/*Z* ratio of >20:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (30% AcOEt in hexanes as eluent) to afford **6u** (70.5 mg, 55% yield) as a white solid.

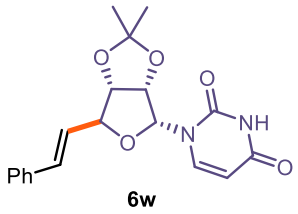
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 2H), 7.54 – 7.47 (m, 2H), 7.38 – 7.32 (m, 2H), 7.29 (s, 1H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.72 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.31 (d, *J* = 11.7 Hz, 1H), 5.41 (dd, *J* = 11.6, 10.0 Hz, 1H), 4.11 – 4.02 (m, 2H), 3.81 (s, 5H), 2.77 – 2.59 (m, 3H), 2.46 (s, 3H), 1.63 (d, *J* = 13.4 Hz, 2H), 1.45 (s, 9H), 1.40 – 1.32 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 168.1, 156.4, 154.8, 139.8, 136.7, 136.5, 136.0, 134.0, 133.5, 131.3, 131.0, 130.1, 129.3, 129.1, 127.6, 120.0, 115.2, 112.5, 112.3, 100.7, 79.4, 55.8, 43.4, 35.1, 33.3, 32.0, 28.5, 13.3.
HRMS: calculated for $C_{37}H_{40}ClN_3NaO_5$ ($M+Na^+$): 664.2549, found 664.2560.



6v

1-((3S,8S,9S,10R,13S,14S,17S)-10,13-Dimethyl-3-((E)-styryl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one (6v): Synthesized according to General Procedure E using DHP **1u** (110.5 mg, 0.2 mmol, 1.0 equiv.) and styrene (104.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 8:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **6v** (dr = 1.6:1, 56.5 mg, 70% yield) as a white solid.

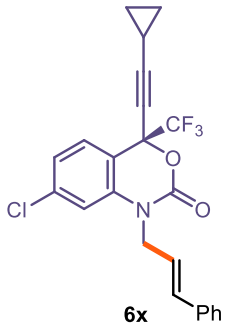
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 4.37H), 7.22 – 7.16 (m, 1.05H), 6.46 – 6.37 (m, 0.78H), 6.36 – 6.29 (m, 0.86H), 5.34 (dq, *J* = 5.2, 2.7, 2.0 Hz, 1.00H), 2.68 – 2.60 (m, 1.27H), 2.54 (td, *J* = 9.0, 6.5 Hz, 1.24H), 2.13 (s, 1.85H), 2.12 (s, 2.20H), 2.24 – 1.87 (m, 10.69H), 1.75 – 1.13 (m, 16.03H), 1.05 (s, 2.34H), 1.02 (s, 1,26H), 0.64 (s, 1.06H), 0.64 (s, 1.89H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 209.8, 142.6, 140.5, 138.3, 138.0, 136.0, 134.2, 129.4, 128.6, 128.6, 127.9, 127.0, 126.9, 126.1, 126.1, 121.3, 119.9, 63.9, 57.2, 57.2, 50.5, 50.3, 44.2, 43.1, 39.4, 39.2, 39.1, 37.9, 37.6, 37.2, 37.1, 34.5, 32.0, 32.0, 31.97, 31.93, 31.7, 29.0, 28.1, 24.7, 24.6, 23.0, 21.1, 20.92, 19.6, 19.6, 13.4, 13.4.
HRMS: calculated for $C_{29}H_{39}O$ ($M+H^+$): 403.2995, found 403.3004.



6w

1-((3aS,4R,6S,6aS)-2,2-Dimethyl-6-((E)-styryl)tetrahydrofuro[3,4-d][1,3]dioxol-4-yl)pyrimidine-2,4(1H,3H)-dione (6w): Synthesized according to General Procedure E using DHP **1t** (101.0 mg, 0.2 mmol, 1.0 equiv.) and styrene (104.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of 7:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (25% AcOEt in hexanes as eluent) to afford **6w** (diastereomers, dr = 5:1 , 57.5 mg, 81% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.48 – 7.26 (m, 7H), 6.68 (d, *J* = 16.1 Hz, 1H), 6.31 (dd, *J* = 15.9, 7.8 Hz, 1H), 5.74 (dd, *J* = 8.1, 2.0 Hz, 1H), 5.66 (d, *J* = 1.8 Hz, 1H), 5.08 (dd, *J* = 6.4, 1.9 Hz, 1H), 4.86 (dd, *J* = 6.4, 4.3 Hz, 1H), 4.71 (ddd, *J* = 7.7, 4.3, 1.1 Hz, 1H), 1.61 (s, 3H), 1.37 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 150.1, 142.6, 136.1, 134.1, 128.7, 128.7, 128.4, 127.0, 126.9, 125.9, 114.8, 102.7, 94.9, 89.1, 85.0, 84.6, 27.3, 25.5.
HRMS: calculated for $C_{19}H_{20}N_2NaO_5$ ($M+Na^+$): 379.1264, found 379.1258.



6x

(*S*)-7-Chloro-1-cinnamyl-4-(cyclopropylethynyl)-4-(trifluoromethyl)-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (6x): Synthesized according to General Procedure E using DHP **1s** (116.0 mg, 0.2 mmol, 1.0 equiv.) and styrene (104.0 mg, 1.0 mmol, 5.0 equiv.). An *E*/*Z* ratio of >20:1 was determined by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **6x** (54.5 mg, 63% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 1H), 7.42 – 7.27 (m, 5H), 7.25 – 7.22(m, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.58 (dt, *J* = 16.1, 1.7 Hz, 1H), 6.18 (dt, *J* = 16.1, 5.6 Hz, 1H), 4.79 – 4.59 (m, 2H), 1.40 (tt, *J* = 8.3, 5.1 Hz, 1H), 0.99 – 0.78 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 136.0, 135.4, 133.4, 131.6, 129.1, 128.8, 128.3, 126.6, 122.1, 117.8, 115.8, 95.8, 66.4, 46.9, 8.94, 8.91, -0.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.20.

HRMS: calculated for $C_{23}H_{17}ClF_3NNaO_2$ ($M+Na^+$): 454.0792, found 454.0800.

C4. Unsuccessful Substrates

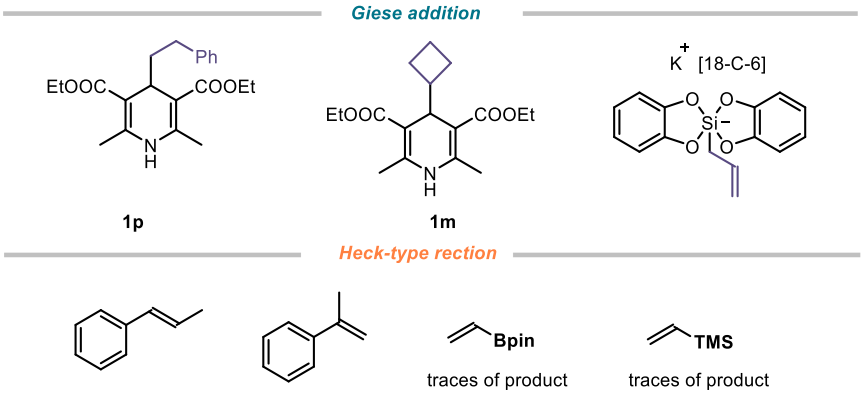


Figure S7: Unsuccessful substrates that offered poor yields (ranging from 0 to <20%)

D. Mechanistic Studies

D1. Control reactions *with green light*

For the reactions performed under green light irradiation, an EvoluChem™ P303-30-1 LEDs (18 W, λ_{max}= 520 nm, 2-3 cm away) was used. The reaction temperature was controlled by a fan (T internal to the vial was measured to be between 35 °C and 40 °C - the setup is depicted in Figure S8).

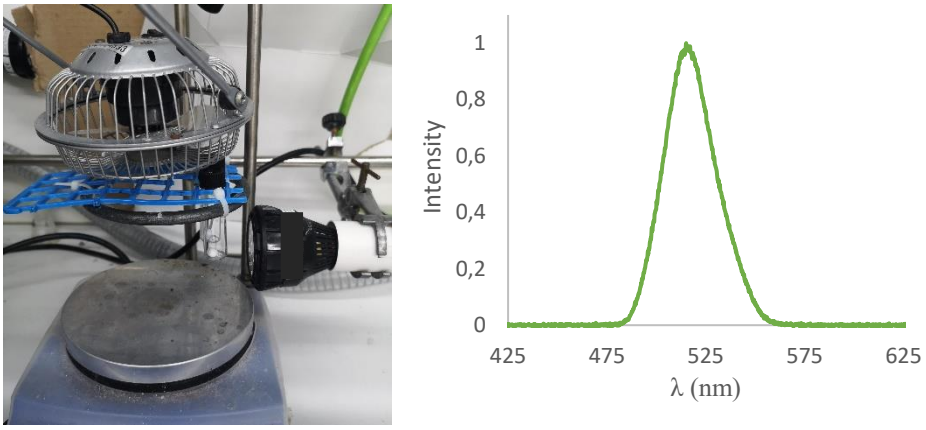


Figure S8: Reaction set-up for green light irradiation.

D2. UV-Vis measurements

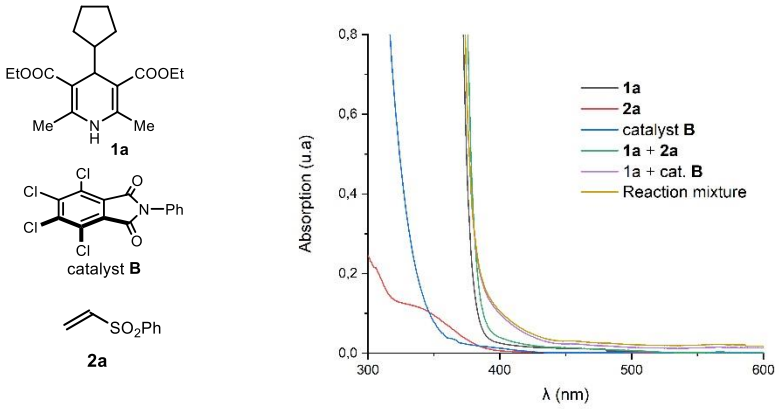


Figure S9: Optical absorption spectra, recorded in DMF in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−vis spectrophotometer, and visual appearance of the separate reaction components and of the colored EDA complex between catalyst **B** and **1a**. [**1a**] = 0.15 M, [**2a**] = 0.10 M [catalyst **B**] = 0.02 M.

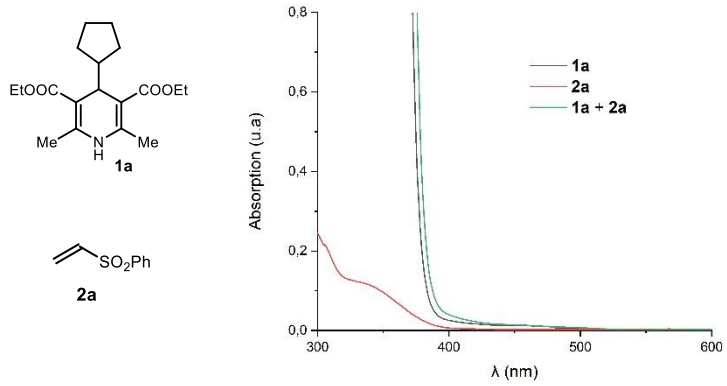


Figure S10: Optical absorption spectra, recorded in DMF in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−vis spectrophotometer, and visual appearance of the substrates **1a**, **2a** and of their mixture. [**1a**] = 0.15 M, [**2a**] = 0.10 M – *no EDA complex formed upon mixing substrates **1a** and **2a***.

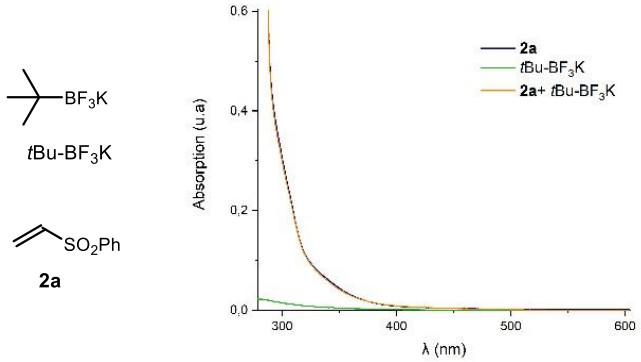


Figure S11: Optical absorption spectra, recorded in DMF in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−vis spectrophotometer, and visual appearance of the substrates *t*Bu-BF_3K, **2b** and of their mixture. [*t*Bu-BF_3K] = 0.15 M, [**2b**] = 0.10 M - *no EDA complex formed upon mixing the two substrates*.

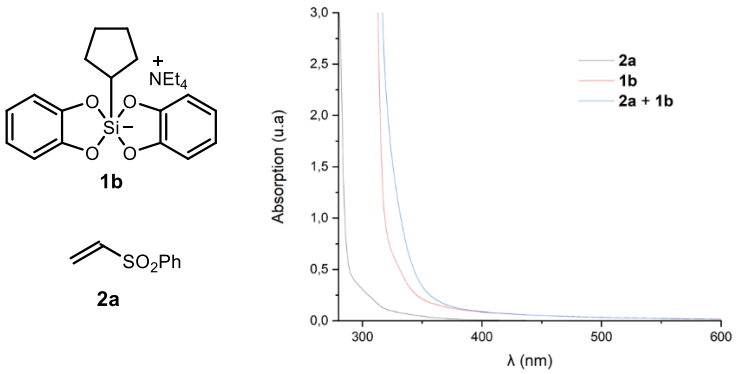


Figure S12: Optical absorption spectra, recorded in DMF in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−vis spectrophotometer, and visual appearance of the substrates **2a**, **1b** and of their mixture. [**1b**] = 0.15 M, [**2a**] = 0.10 M - *no EDA complex formed upon mixing substrates **1b** and **2a***.

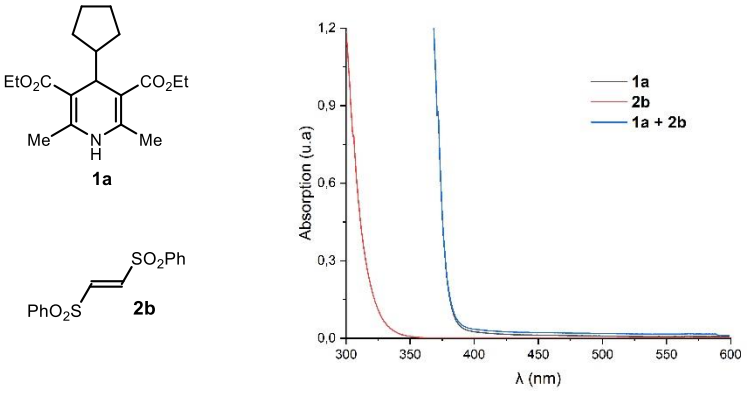


Figure 13: Optical absorption spectra, recorded in DMF in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−visspectrophotometer, and visual appearance of the substrates **1a**, **2b** and of their mixture. [**1a**] = 0.15 M, [**2b**] = 0.10 M - *no EDA complex formed upon mixing substrates **1a** and **2b***.

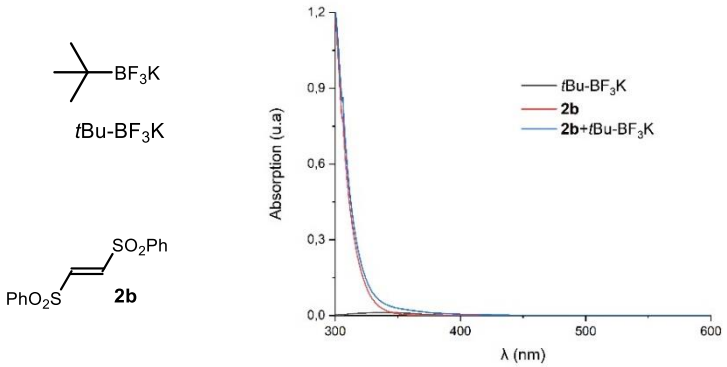


Figure 14: Optical absorption spectra, recorded in DMF in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−visspectrophotometer, and visual appearance of the substrates *t*Bu-BF_3K, **2b** and of their mixture. [*t*Bu-BF_3K] = 0.15 M, [**2b**] = 0.10 M - *no EDA complex formed upon mixing the two substrates*.

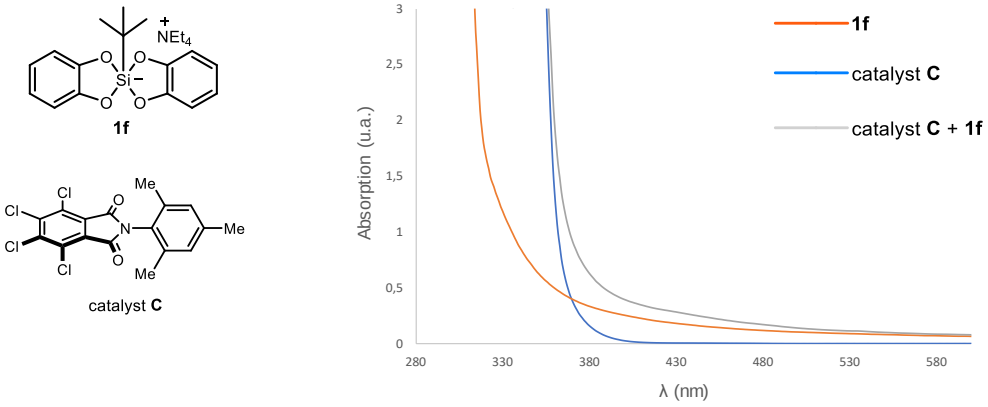


Figure S15: Optical absorption spectra, recorded in DMF in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−vis spectrophotometer, and visual appearance of the separate reaction components and of the colored EDA complex between catalyst **C** and silicate **1b**. [**1b**] = 0.15 M, [catalyst **C**] = 0.02 M.

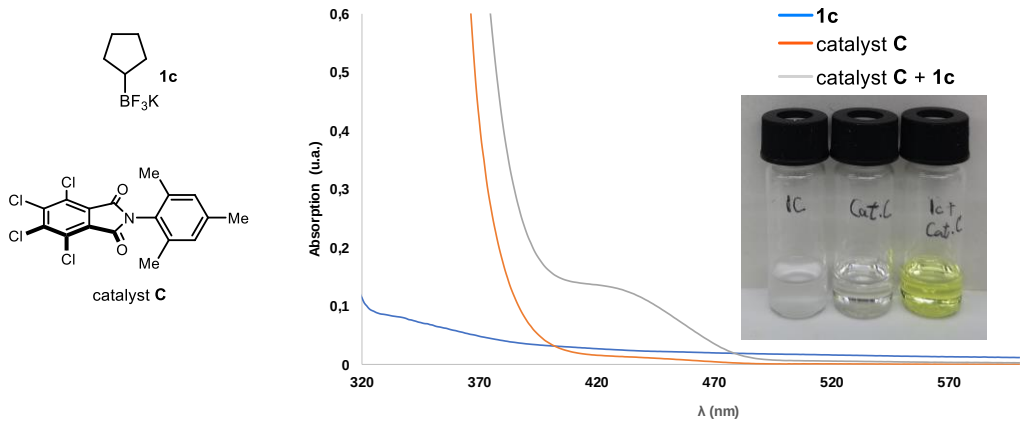


Figure S16: Optical absorption spectra, recorded in DMF in 1 mm path quartz cuvettes using a Shimadzu 2401PC UV−vis spectrophotometer, and visual appearance of the separate reaction components and of the colored EDA complex between catalyst **C** and trifluoroborate salt **1c**. [**1c**] = 0.15 M, [catalyst **C**] = 0.02 M.

D3. 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.

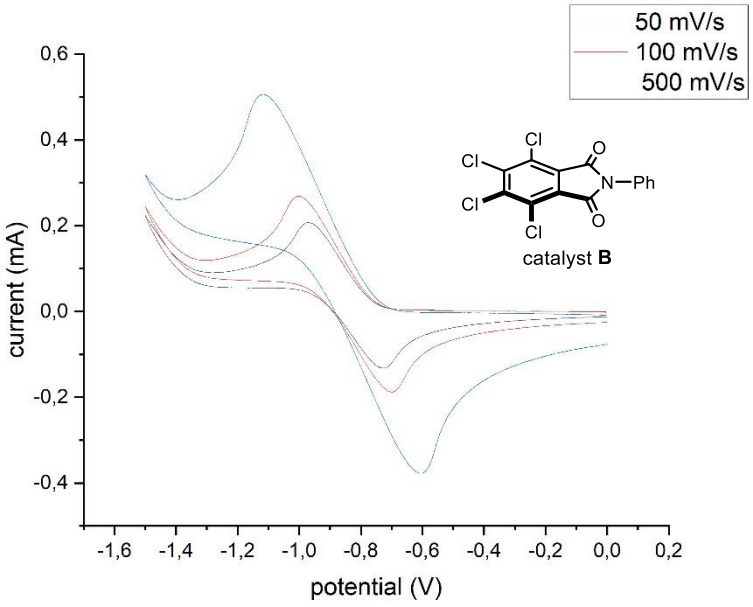


Figure S17: Cyclic voltammogram for catalyst **B** [0.02 M] in [0.1 M] $TBAPF_6$ in DMF. Measurement started by reduction from 0 to -2.0 V, followed by oxidation from -2.0 V to 0, and finishing at 0 V. Glassy carbon electrode

working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Two irreversible peaks observed increasing with sweep rate.

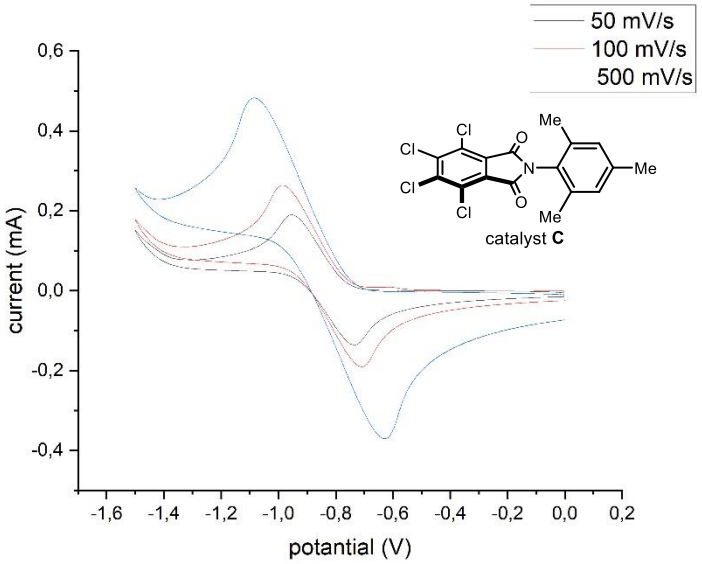


Figure S18: Cyclic voltammogram for catalyst **C** [0.02 M] in [0.1 M] $TBAPF_6$ in DMF. Measurement started by reduction from 0 to -2.0 V, followed by oxidation from -2.0 V to 0, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Two irreversible peaks observed increasing with sweep rate.

D4. Quantum Yield Determination

D4.1 Experimental Setup

The experiments for the quantum yield determination were conducted under illumination by a 460 nm high-power single LED (setup depicted in Figure S19), using an aluminum block on a 3D-printed holder, fitted with a 460 nm high-power single LED. The irradiance was fixed at 60±2 mW/cm^2, as controlled by an external power supply and measured using a photodiode light detector at the start of each reaction. This setup secured a reliable irradiation while keeping a distance of 1 cm between the reaction vessel and the light source.

Figure S19: high-power single LED setup

D4.2 General Procedure F for quantum yield determinations.

A ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in the Handbook of Photochemistry.[23] 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 µL 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 16 mm diameter vial. The vial was placed into an aluminum block on a 3D-printed holder, fitted with a 460 nm high-power single LED (Figure S19). The solution was irradiated at 460 nm. This procedure was repeated 4 times, quenching the solutions after different time intervals.
2. Then 1 mL of the model reaction following General Procedure A, B or E was placed in the irradiation set up and irradiated for different irradiation times.
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):

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

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), ΔA(510 nm) is the optical difference in absorbance between the irradiated solution and the one stored in the dark, ε(510 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 (q0 n,p) by the use of the following Equation 2:

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

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe^{2+} at 458 nm is 1.1,[24] $[1\text{-}10^{-A(\lambda)}]$ is the ratio of absorbed photons by the solution, and A (λ) 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.

The moles of product 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: $\Phi\cdot(1\text{-}10^{-A(460\ nm)})$, 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.

*D4.3 Quantum Yield of the Giese addition to vinylsulfone **2a** using DHP **1a** catalyzed by **B***

The quantum yield has been determined following general procedure F. The actinometer solution was irradiated for 3 sec, 6 sec, 9 sec, and 12 sec. The model reaction was prepared according to General Procedure A and each reaction mixture was irradiated for 52min, 60 min, 90 min, 140 min. The absorbance at 460 nm of the non-complexed actinometer solution was measured to be 0.186. An absorbance of 0.064 was determined for the model reaction mixture (1:4 dilution). Plot of mols of Fe^{2+} formed vs irradiation time and plot of mols of incident photons vs mols of product formed were depicted as figure S20 and figure S21, respectively.

The quantum yield $(\Phi)_{cat.}$ of the photochemical transformation was measured to be **0.04**.

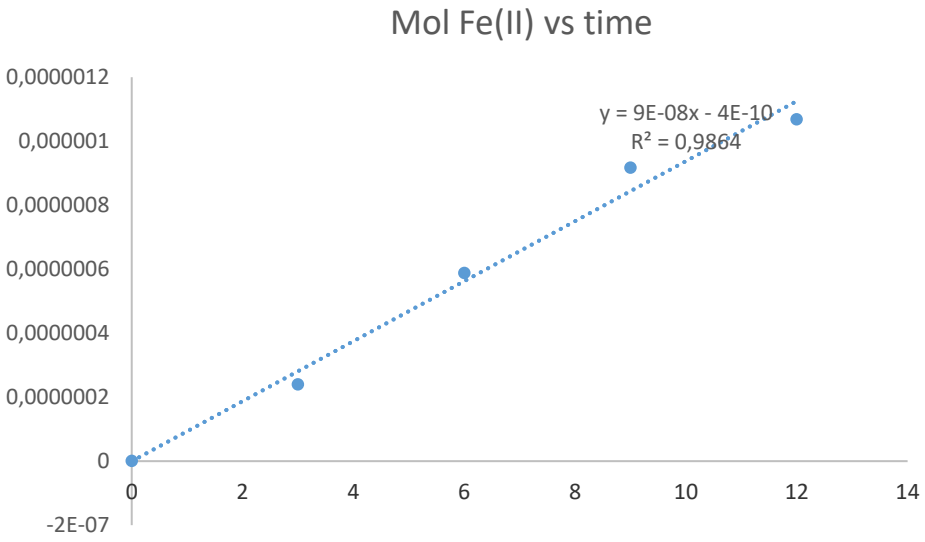


Figure S20: Plot of moles of Fe^{2+} formed vs irradiation time. Slope of the line correlates to the moles of incident photons by unit of time.

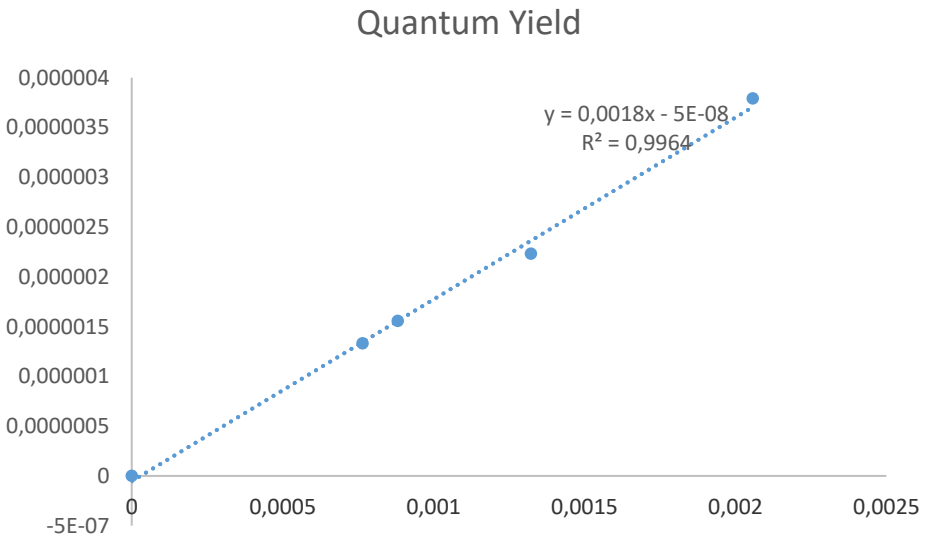


Figure S21: Plot of moles of incident photons vs moles of product formed. Slope of the line correlates to quantum yield of the photochemical transformation.

*D4.4 Quantum yield of the Giese addition to vinylsulfone **2a** using silicate **1f** catalyzed by **C***

The quantum yield has been determined following general procedure F. The actinometer solution was irradiated for 3 sec, 6 sec, 9 sec, and 12 sec. The model reaction was prepared according to General Procedure B and each reaction mixture was irradiated for 15min, 30 min, 45 min, 63 min. The absorbance at 460 nm of the non-complexed actinometer solution was measured to be 0.144. An absorbance of 0.09 was determined for the model reaction mixture (1:4 dilution). Plot of mols of Fe^{2+} formed vs irradiation time and plot of mols of incident photons vs mols of product formed were depicted as figure S22 and figure S23, respectively.

The quantum yield $(\Phi)_{cat.}$ of the photochemical transformation was measured to be **0.03**.

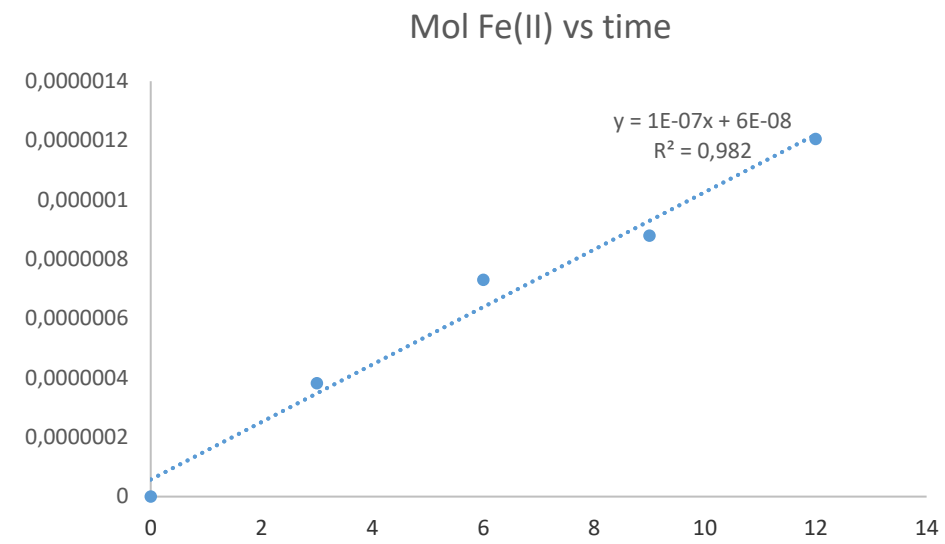


Figure S22: Plot of mols of Fe^{2+} formed vs irradiation time. Slope of the line correlates to the moles of incident photons by unit of time.

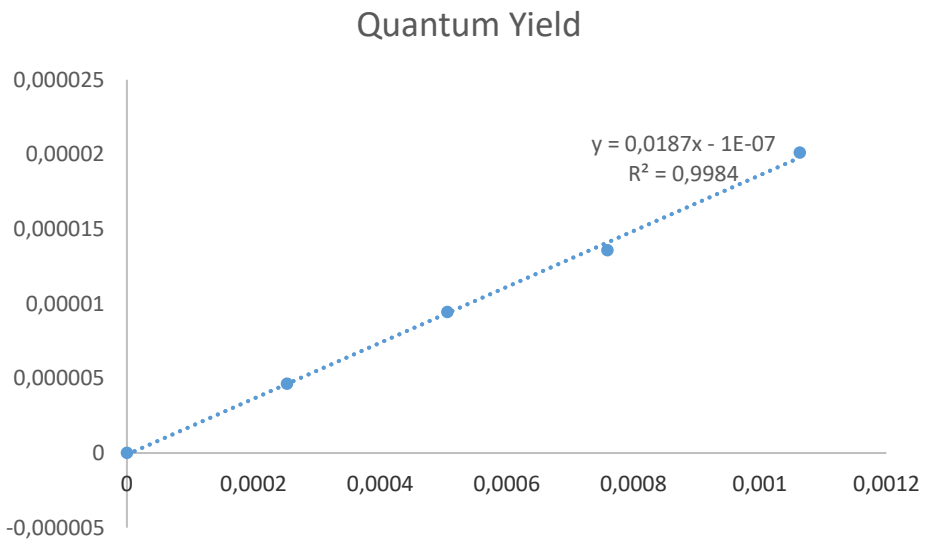


Figure S23: Plot of mols of incident photons vs mols of product formed. Slope of the line correlates to quantum yield of the photochemical transformation.

*D4.5 Quantum yield of the Heck-type reaction using styrene and DHP **1k** catalyzed by **C***

The quantum yield has been determined following general procedure F. The actinometer solution was irradiated for 1 sec, 3 sec, 6 sec, and 9 sec. The model reaction was prepared with 0.9 mL dioxane and 0.1 mL water instead of 1mL dioxane according to General Procedure E and each reaction mixture was irradiated for 90 min, 150 min, 210 min, 270 min. The absorbance at 460 nm of the non-complexed actinometer solution was measured to be 0.139. An absorbance of 0.037 was determined for the model reaction mixture (1:4 dilution). Plot of mols of Fe^{2+} formed vs irradiation time and plot of mols of incident photons vs mols of product formed were depicted as Figure S24 and Figure S25, respectively.

The quantum yield $(\Phi)_{cat.}$ of the photochemical transformation was measured to be **0.01**.

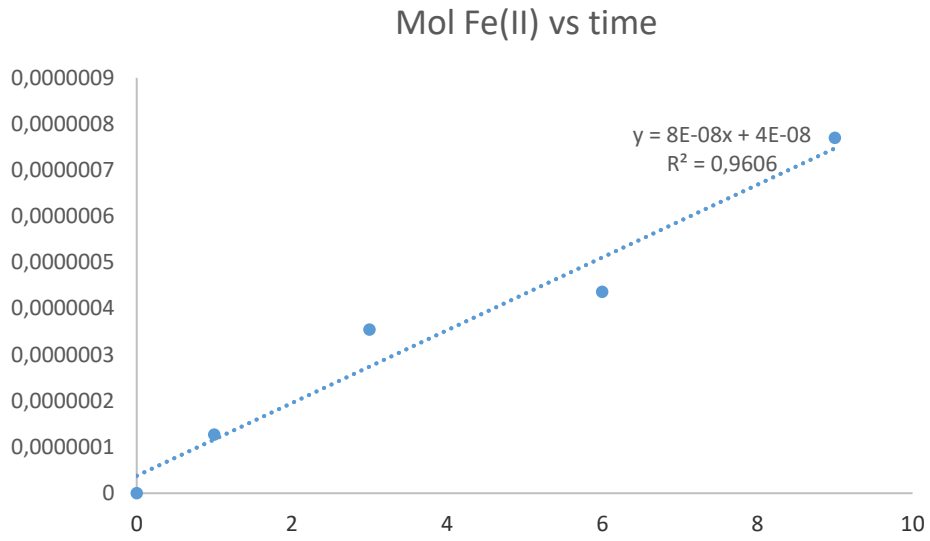


Figure S24: Plot of mols of Fe^{2+} formed vs irradiation time. Slope of the line correlates to the moles of incident photons by unit of time.

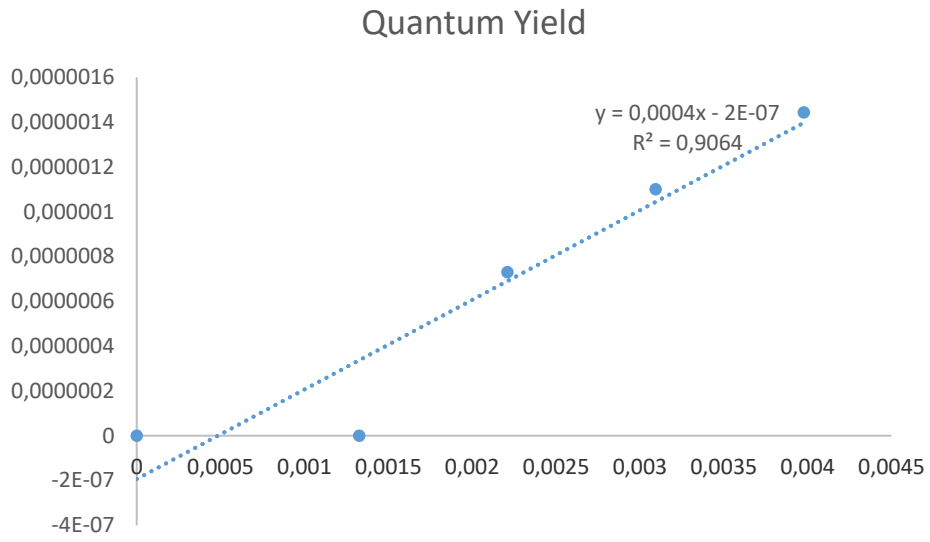


Figure S25: Plot of mols of incident photons vs mols of product formed. Slope of the line correlates to quantum yield of the photochemical transformation.

E. References

(1) Corcé, V.; Chamoreau, L.-M.; Derat, E.; Goddard, J.-P.; Ollivier, C.; Fensterbank, L., Silicates as Latent Alkyl Radical Precursors: Visible-Light Photocatalytic Oxidation of Hypervalent Bis-Catecholato Silicon Compounds. *Angew. Chem., Int. Ed.* **2015**, *54*, 11414–11418.

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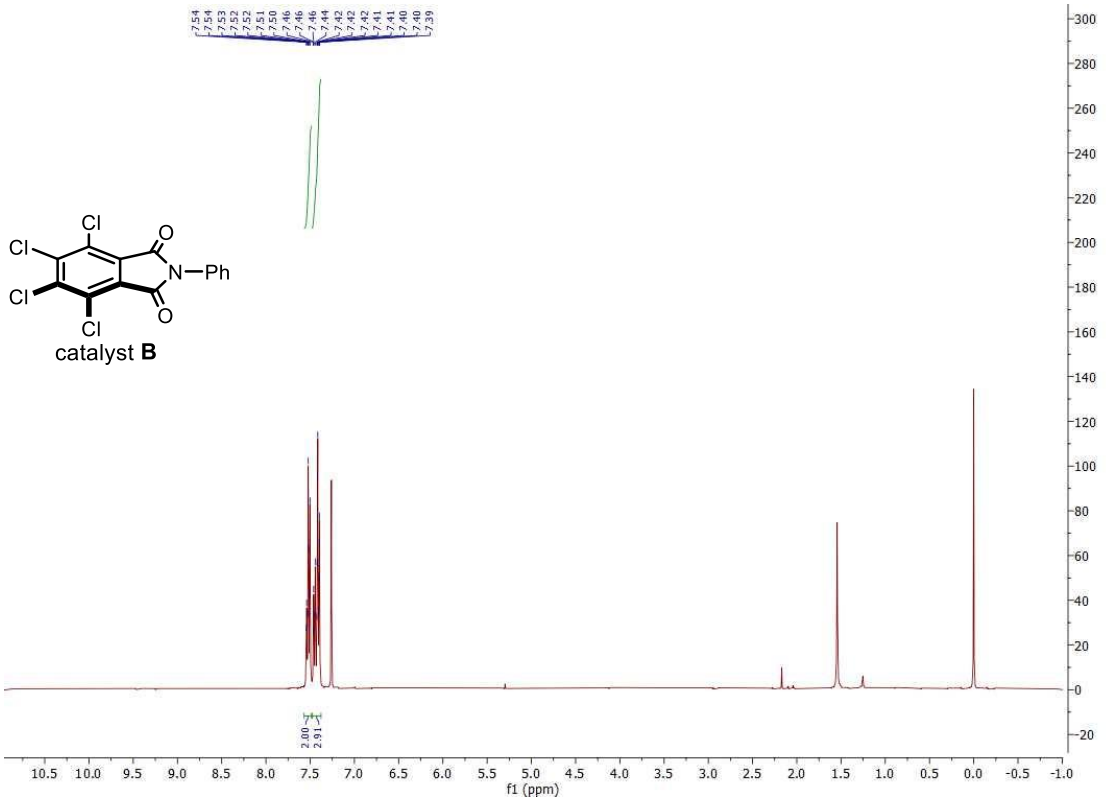
F. NMR spectra

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



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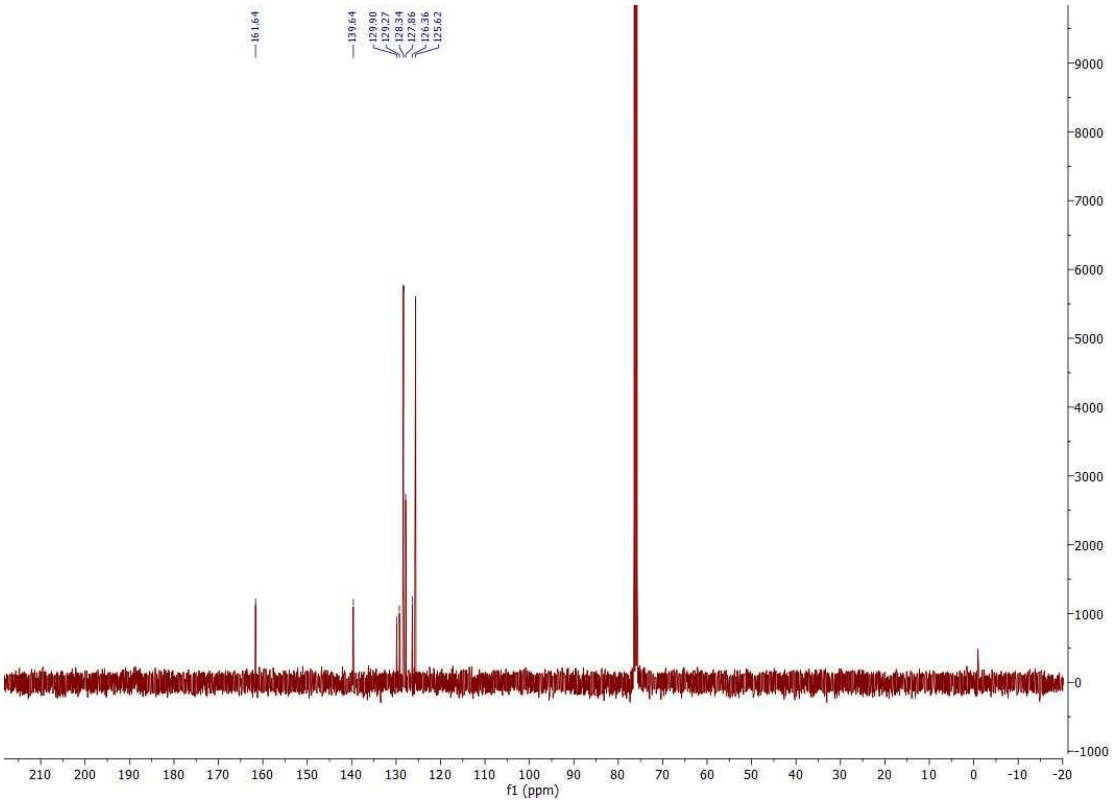

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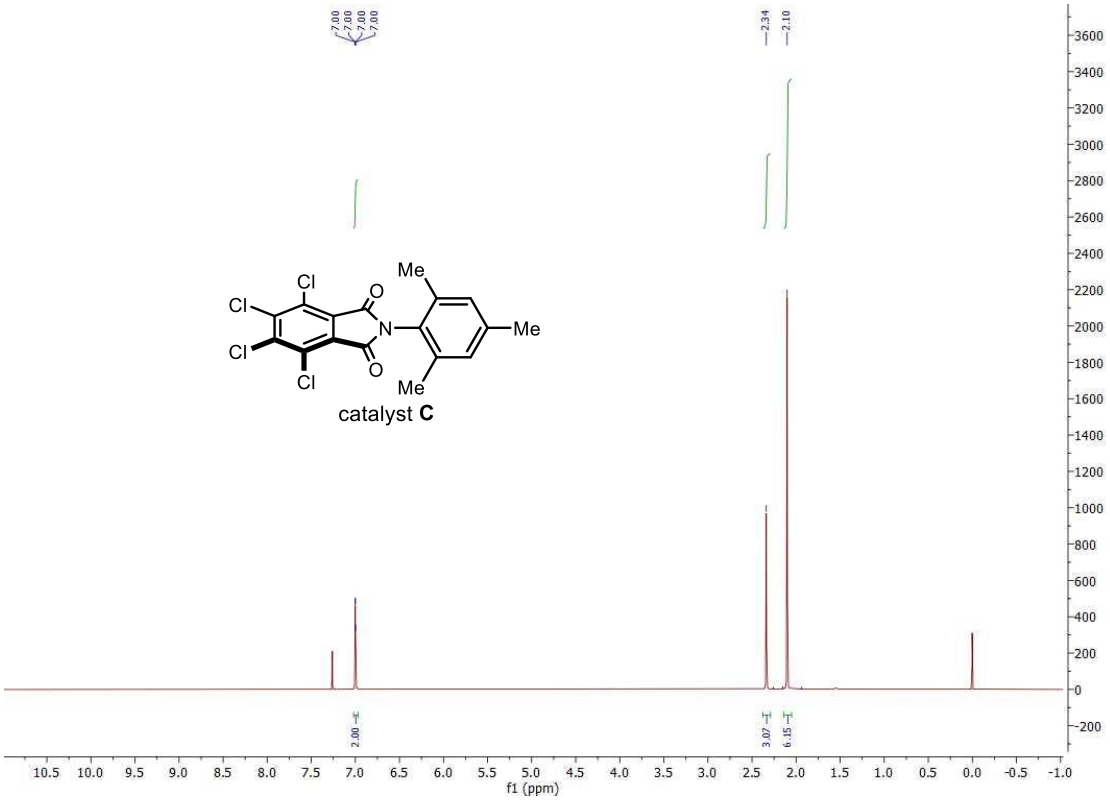

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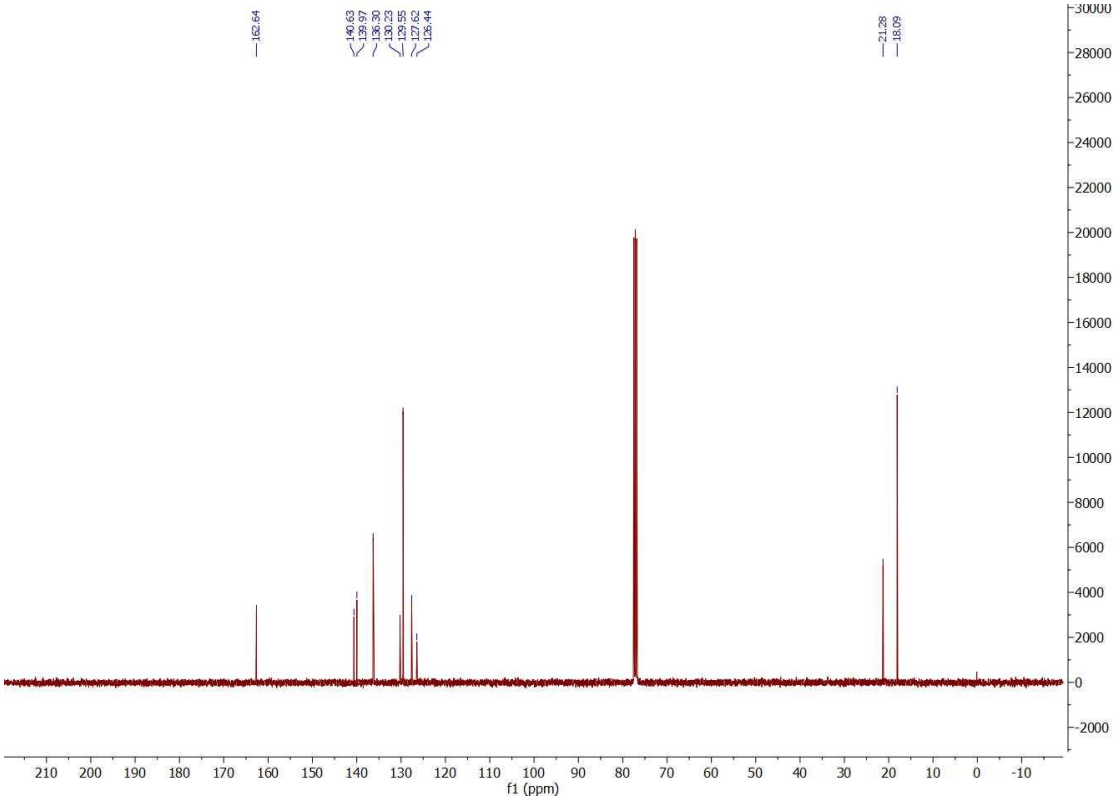

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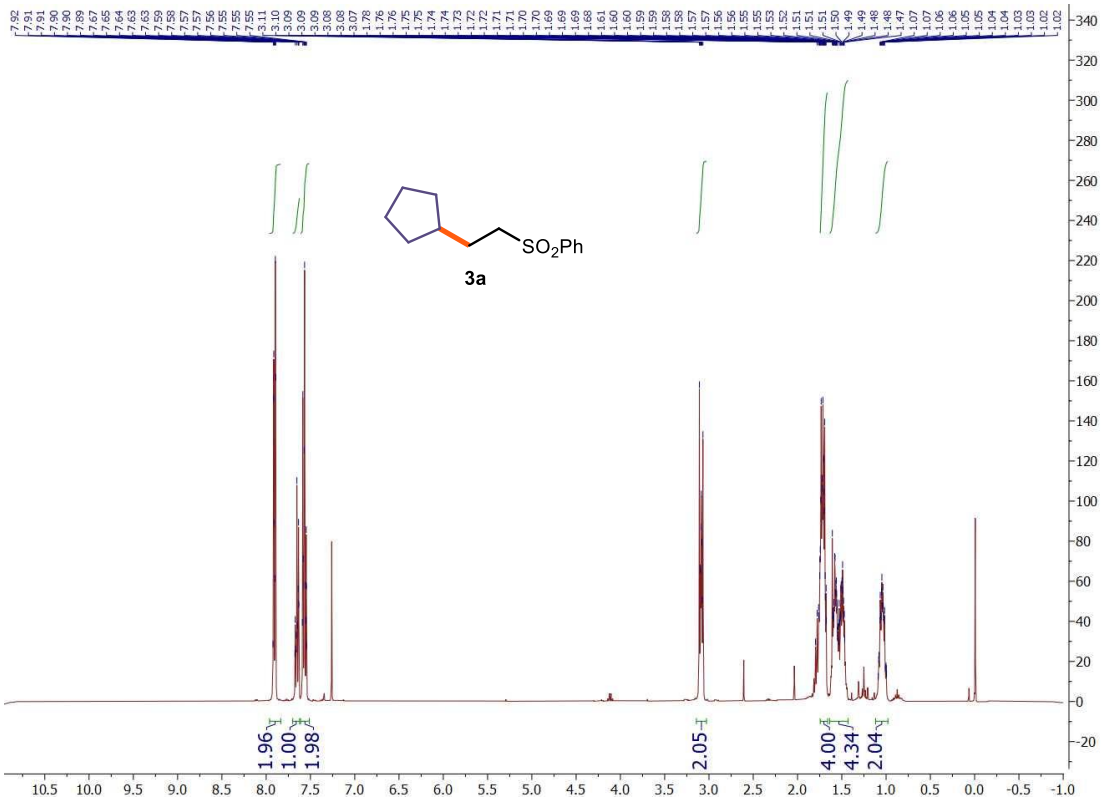

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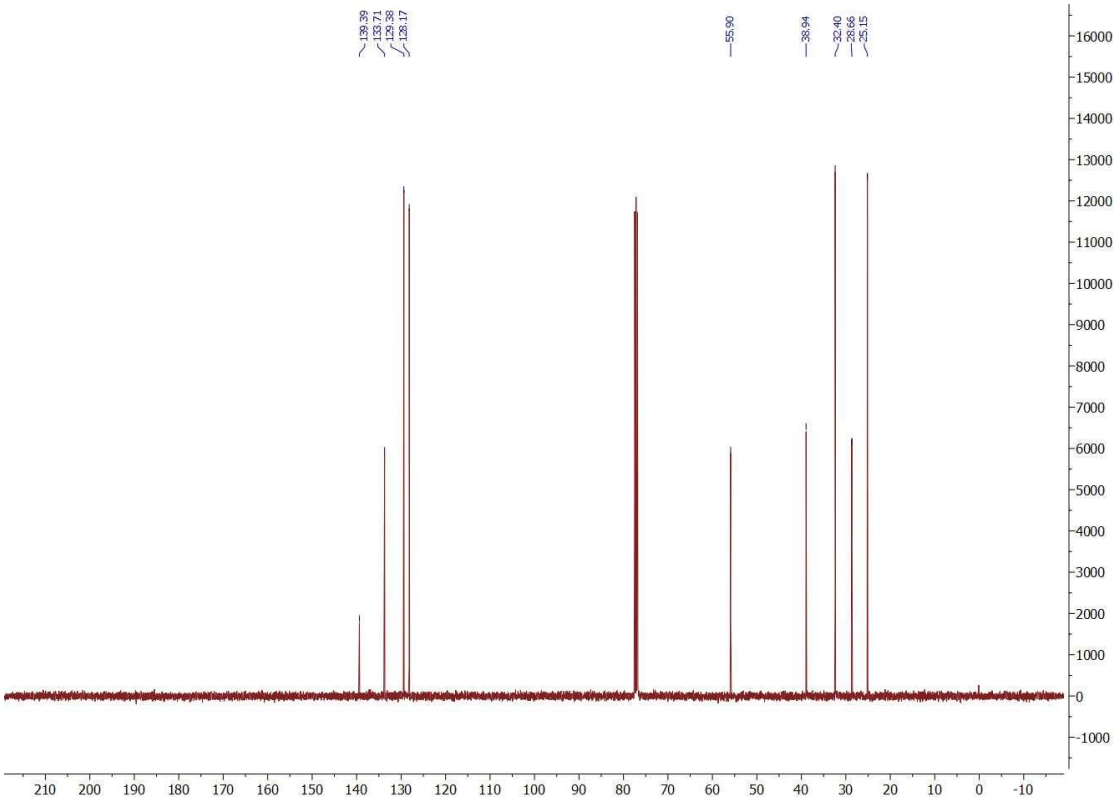

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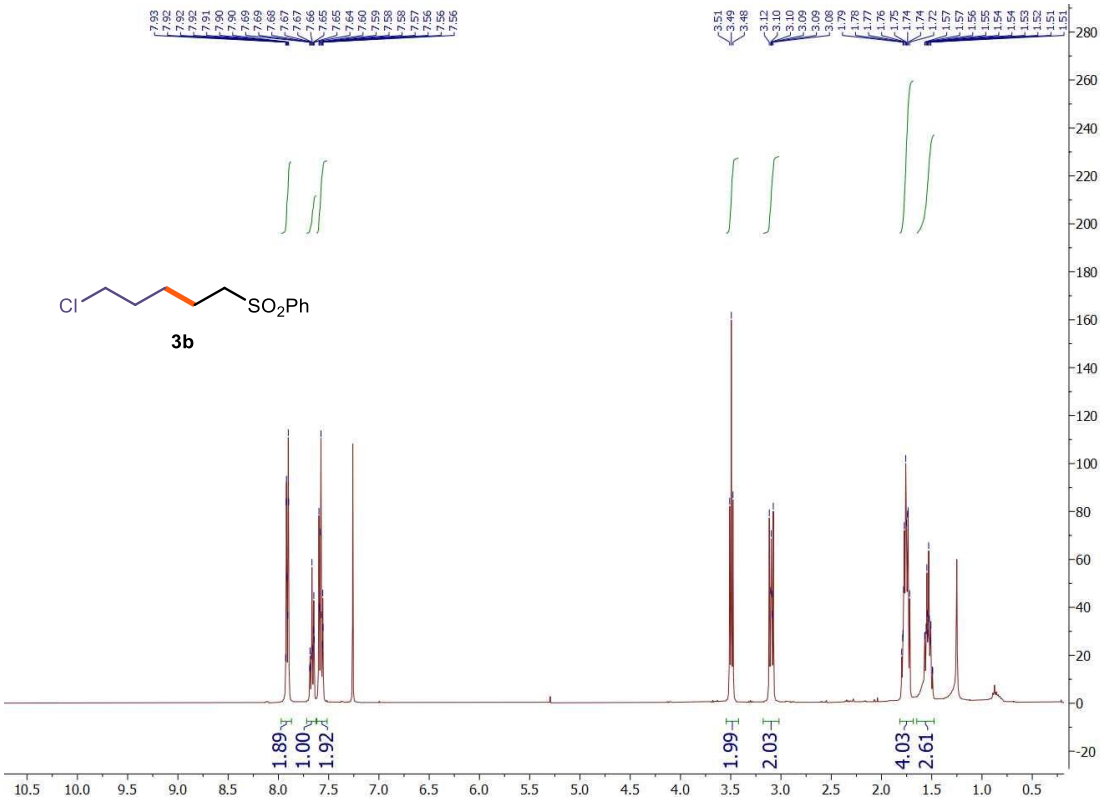

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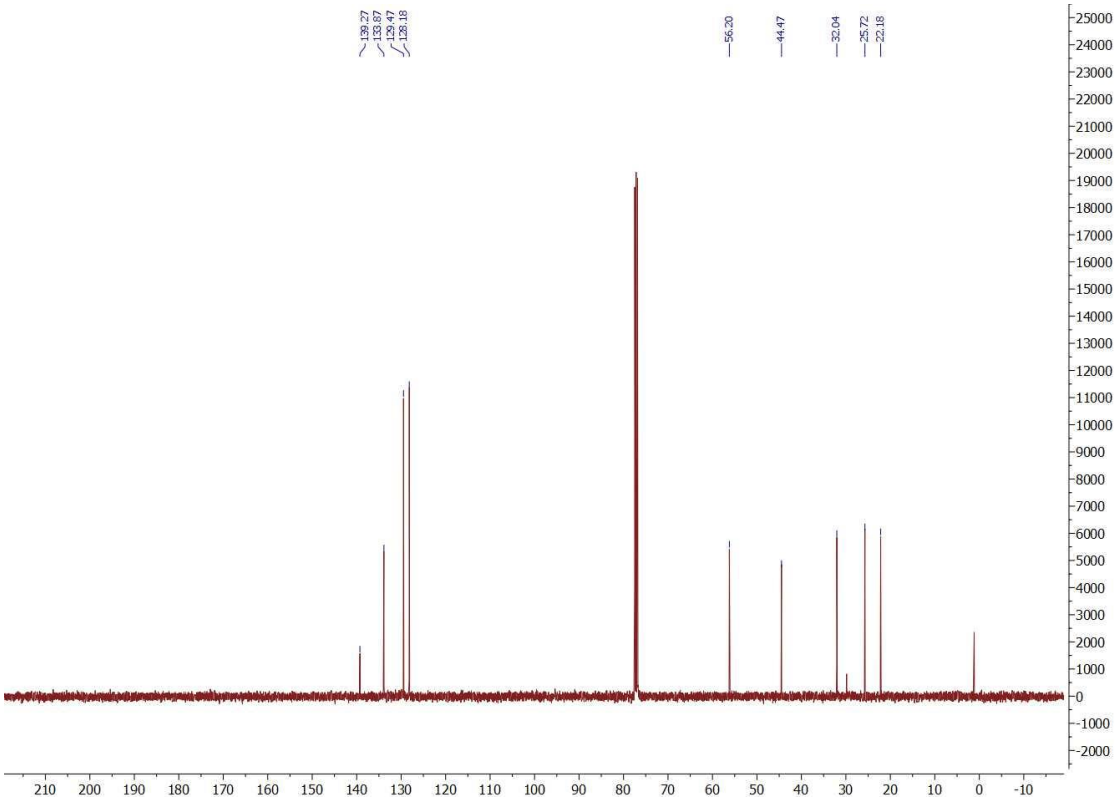

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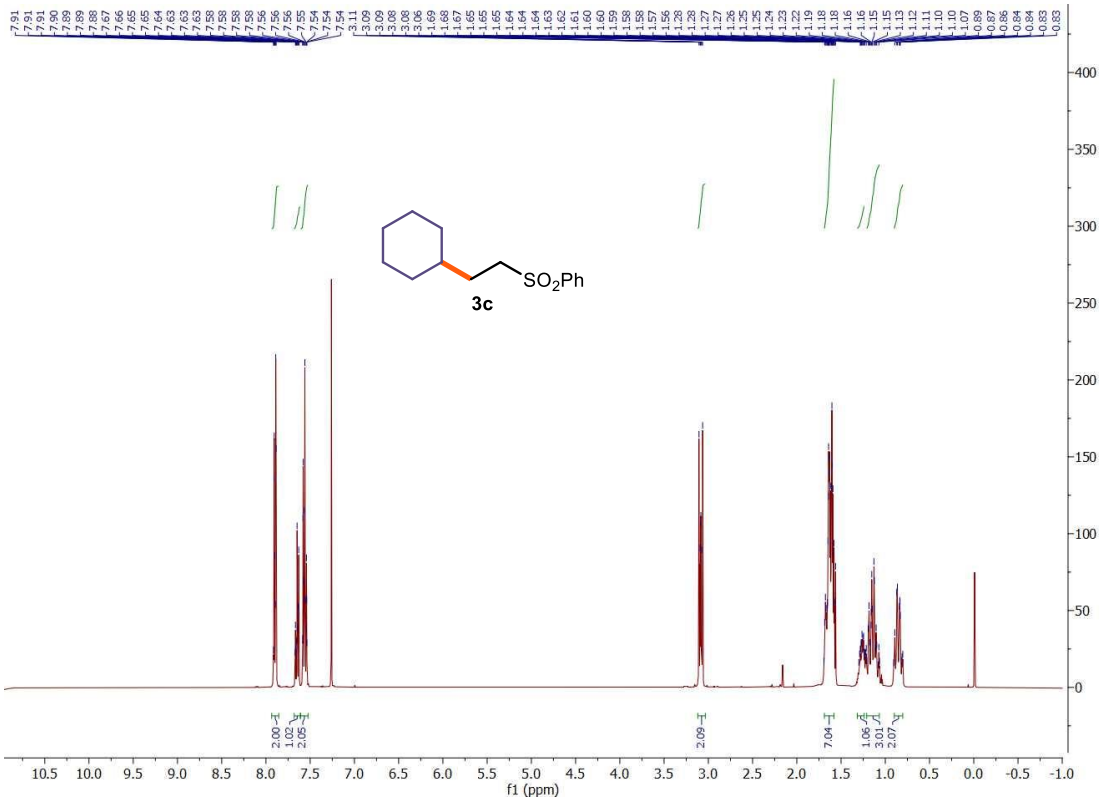

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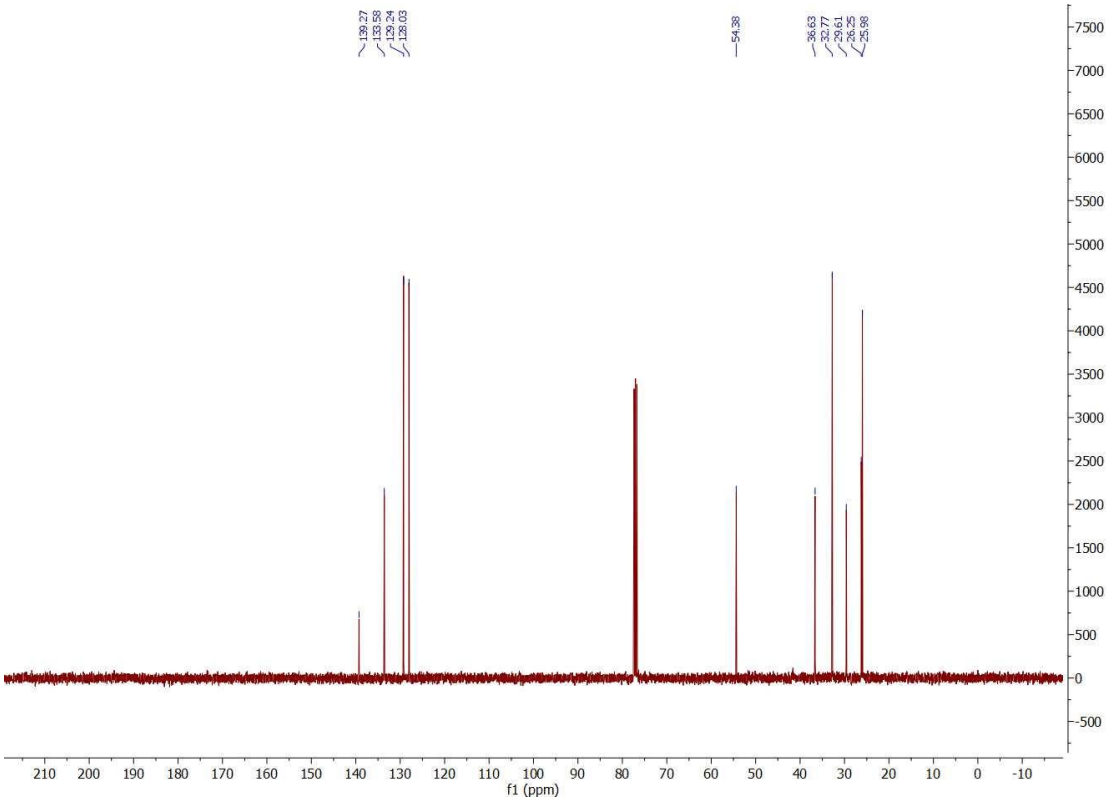

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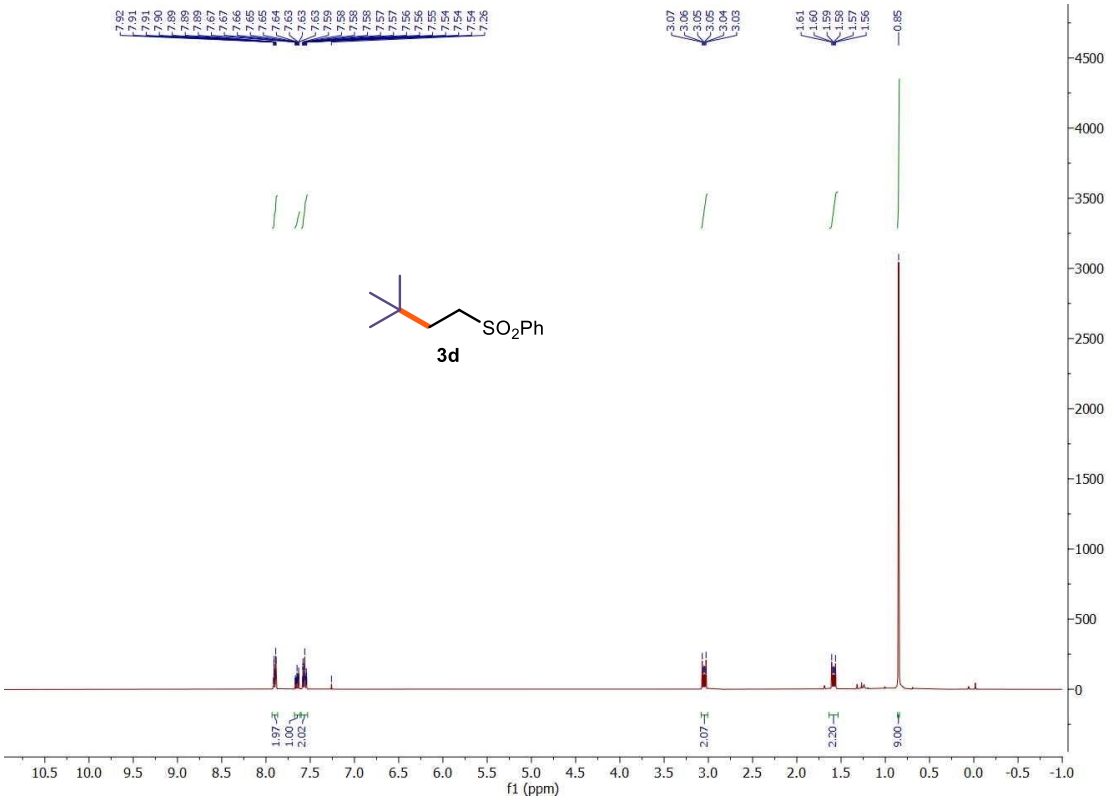

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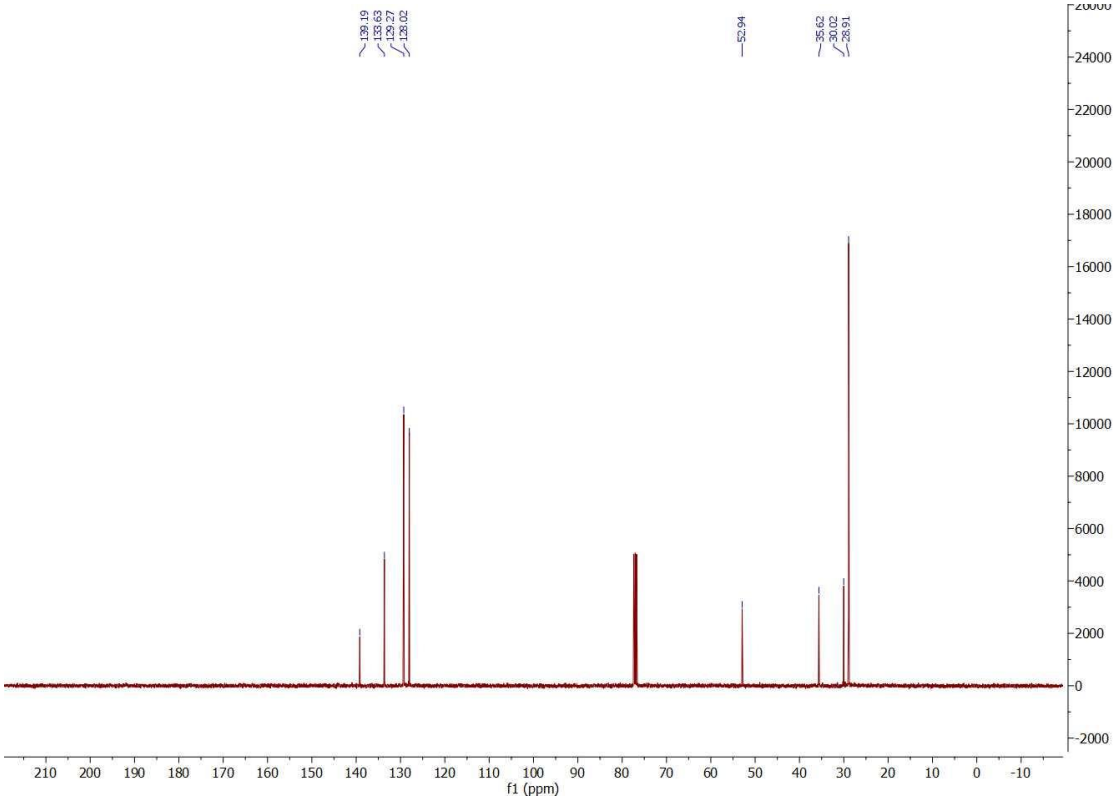

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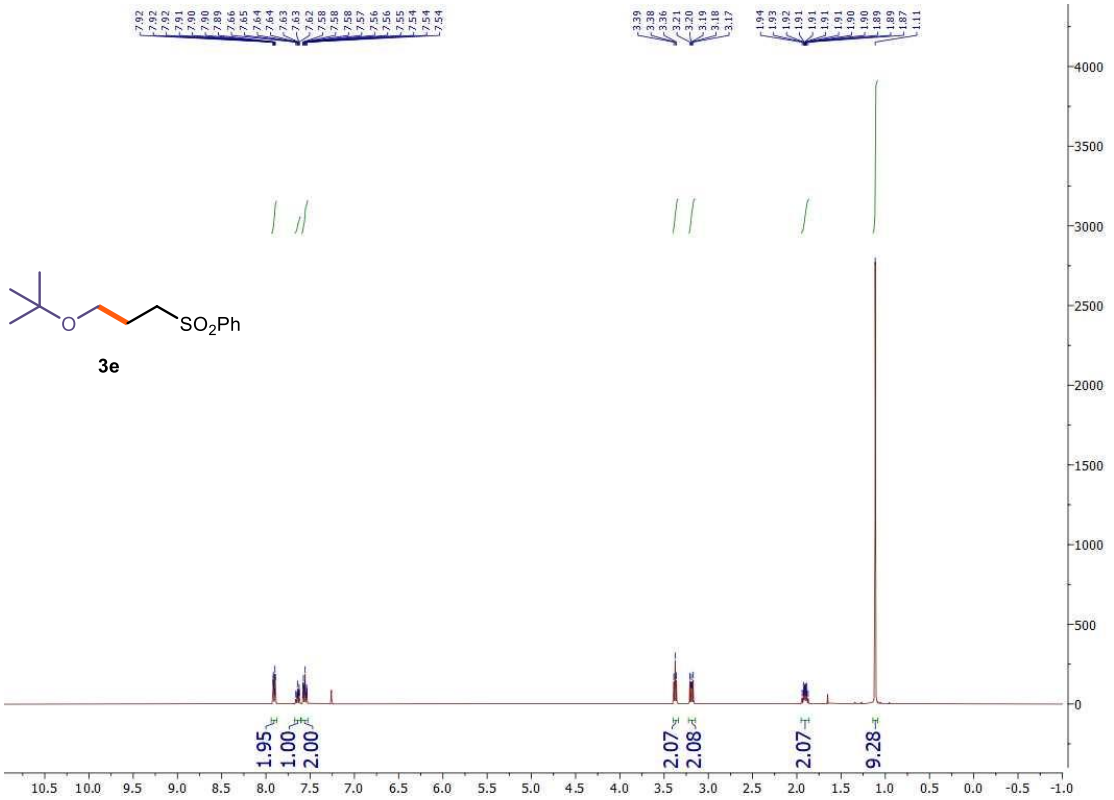

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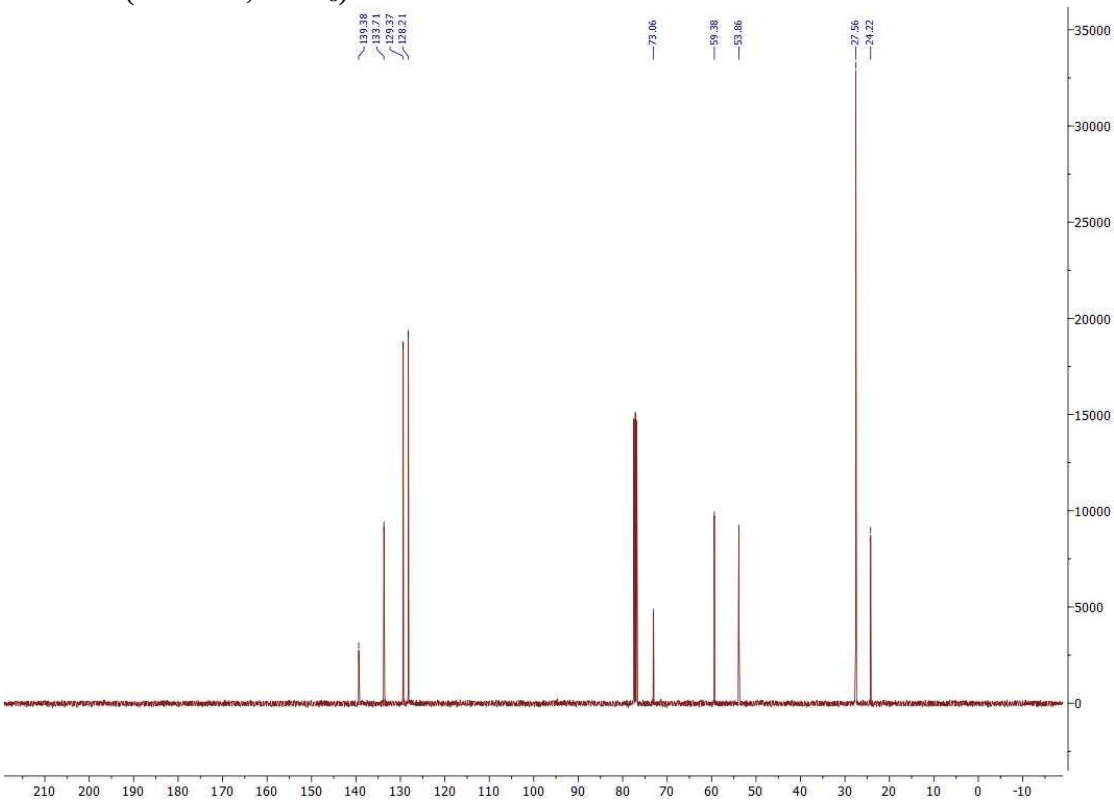

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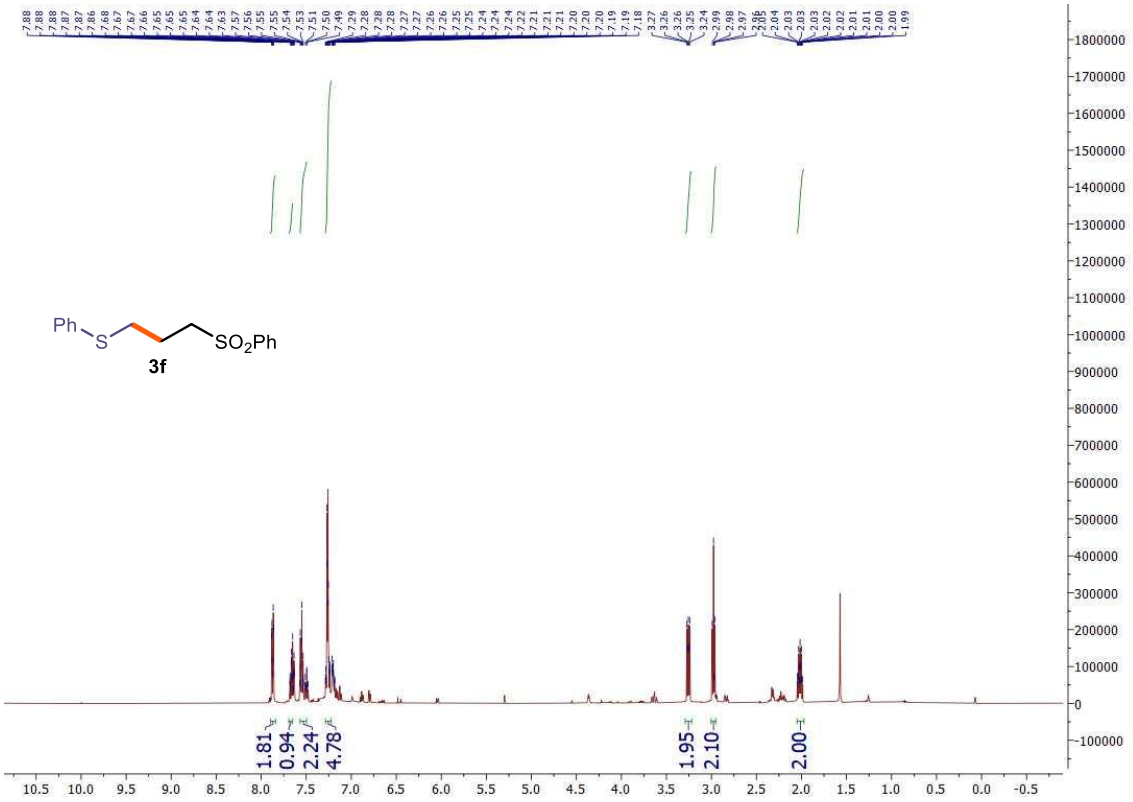

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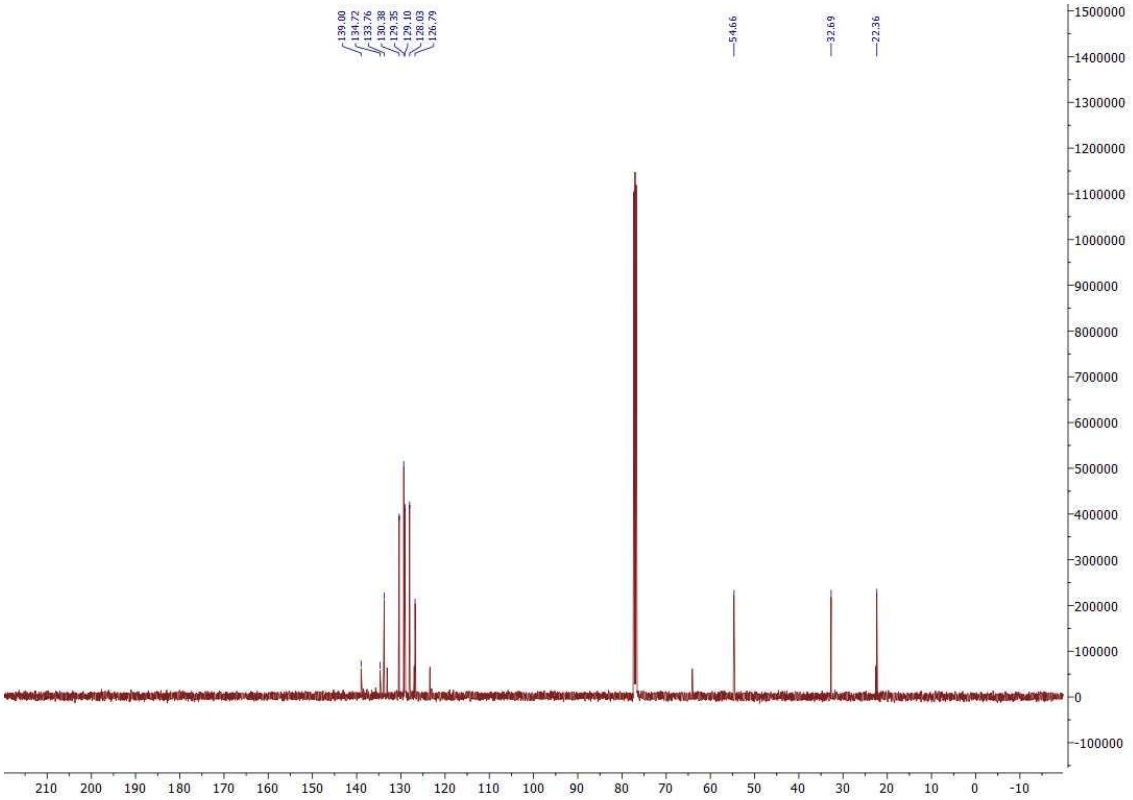

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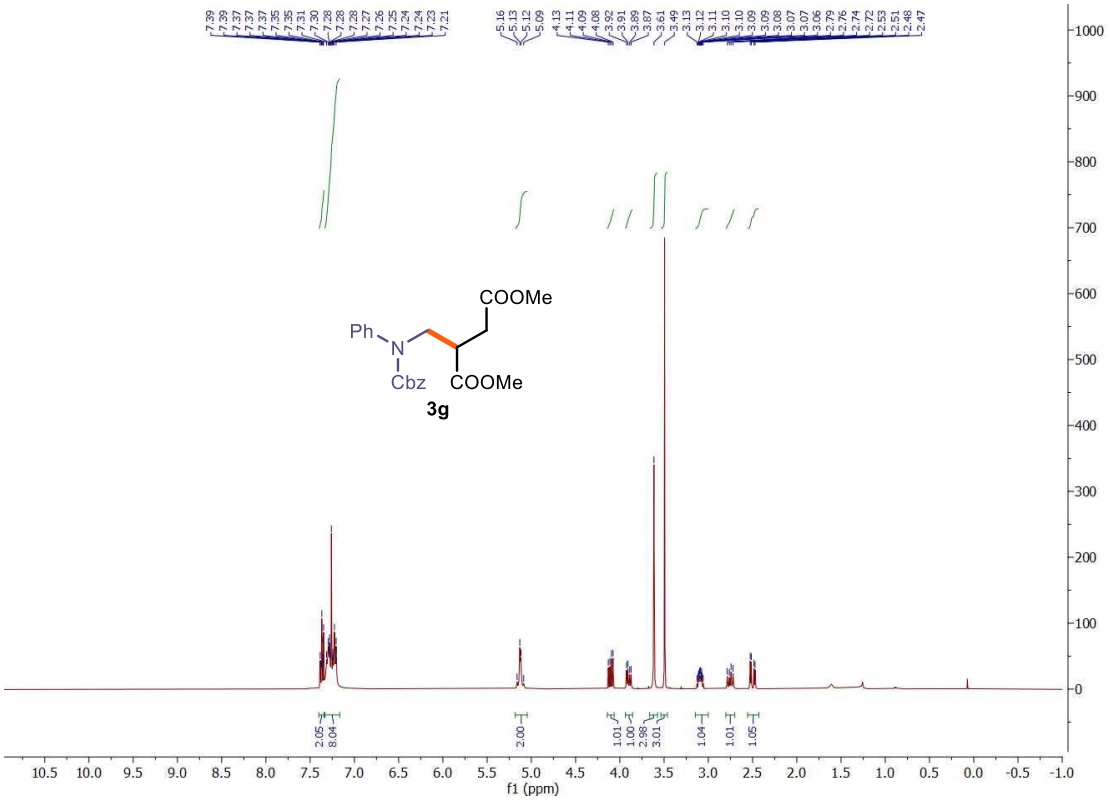

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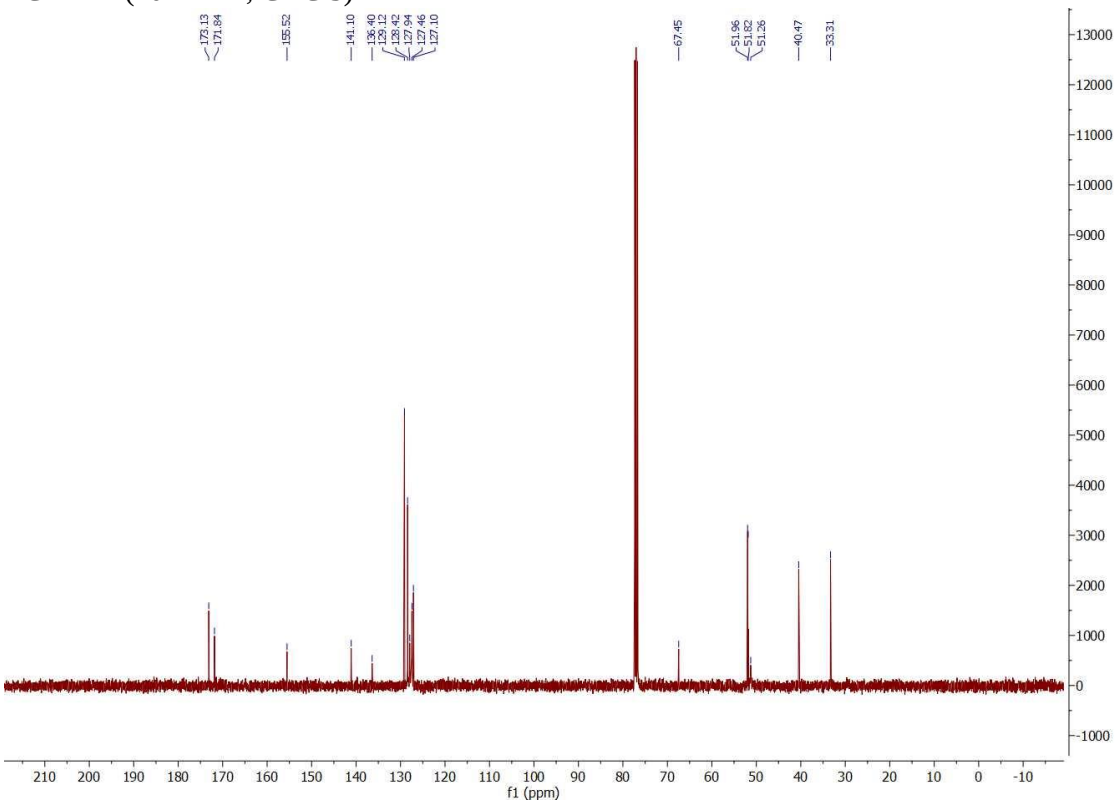

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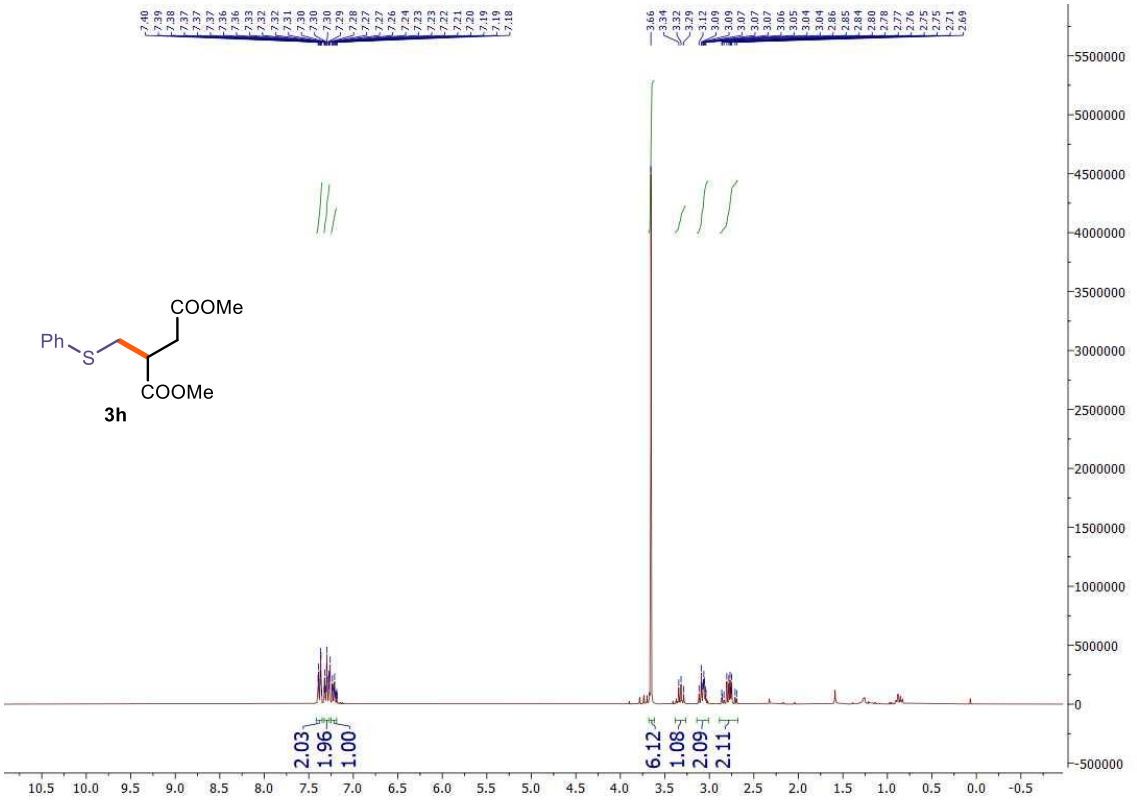

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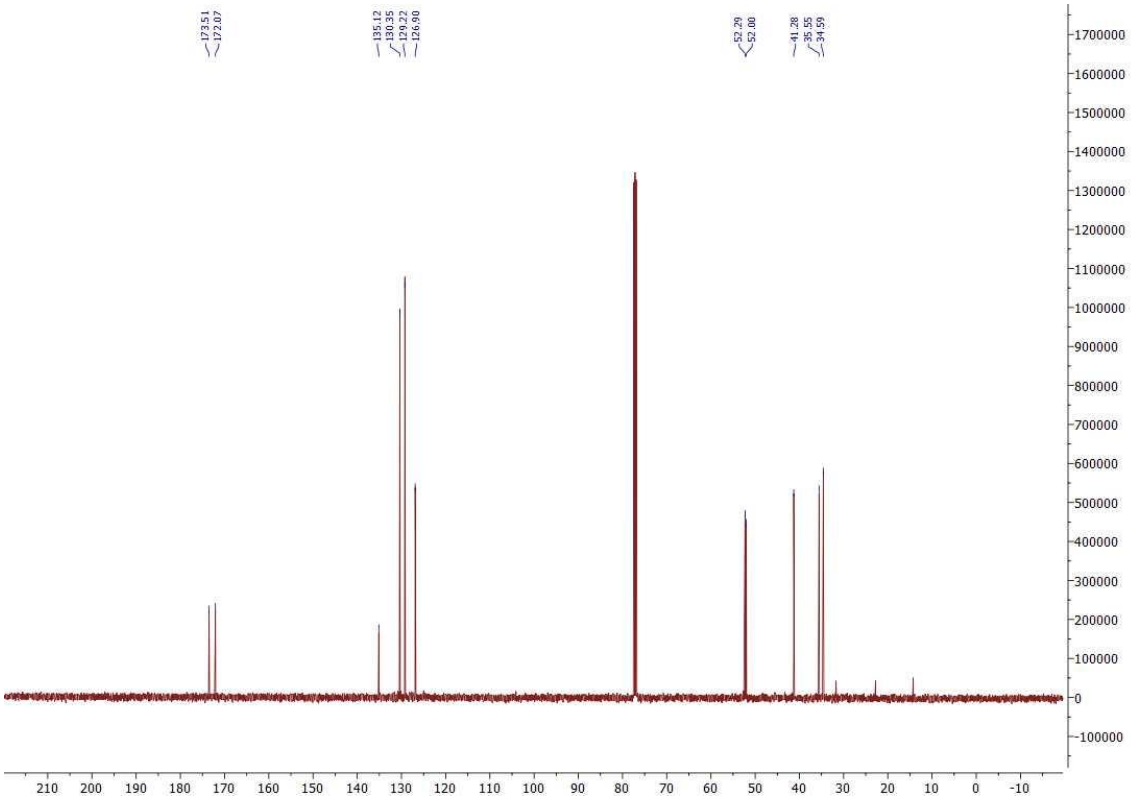

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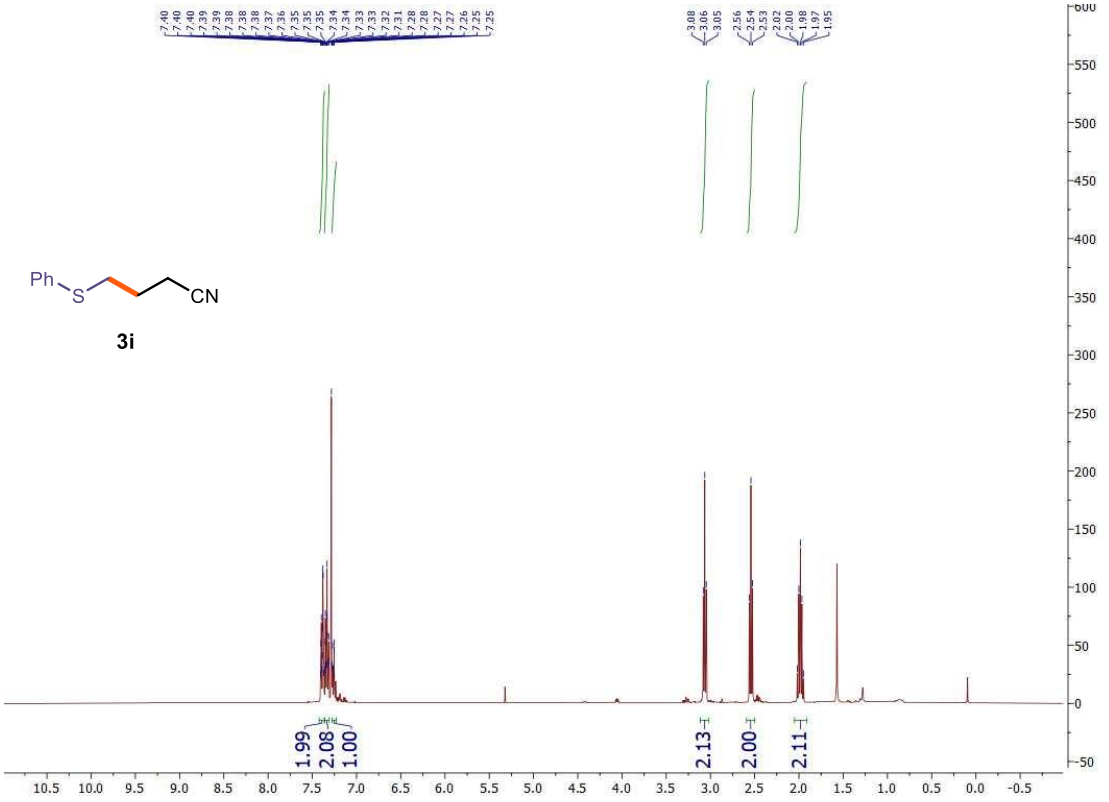

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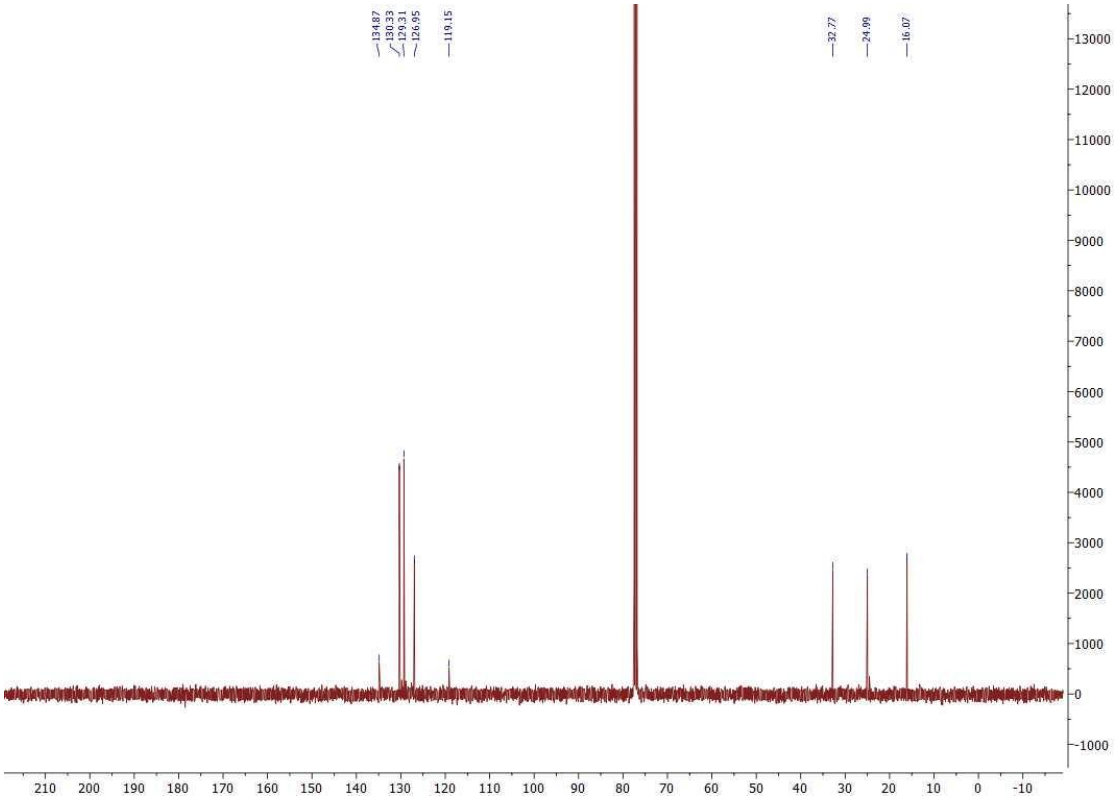

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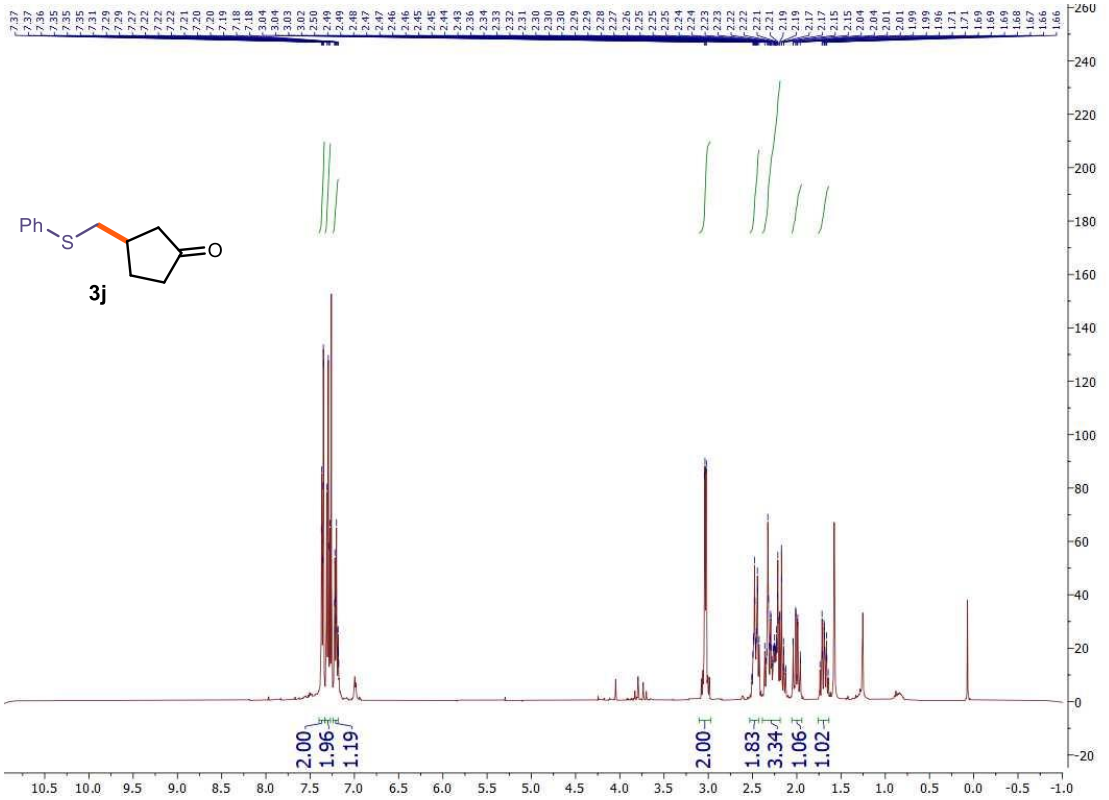

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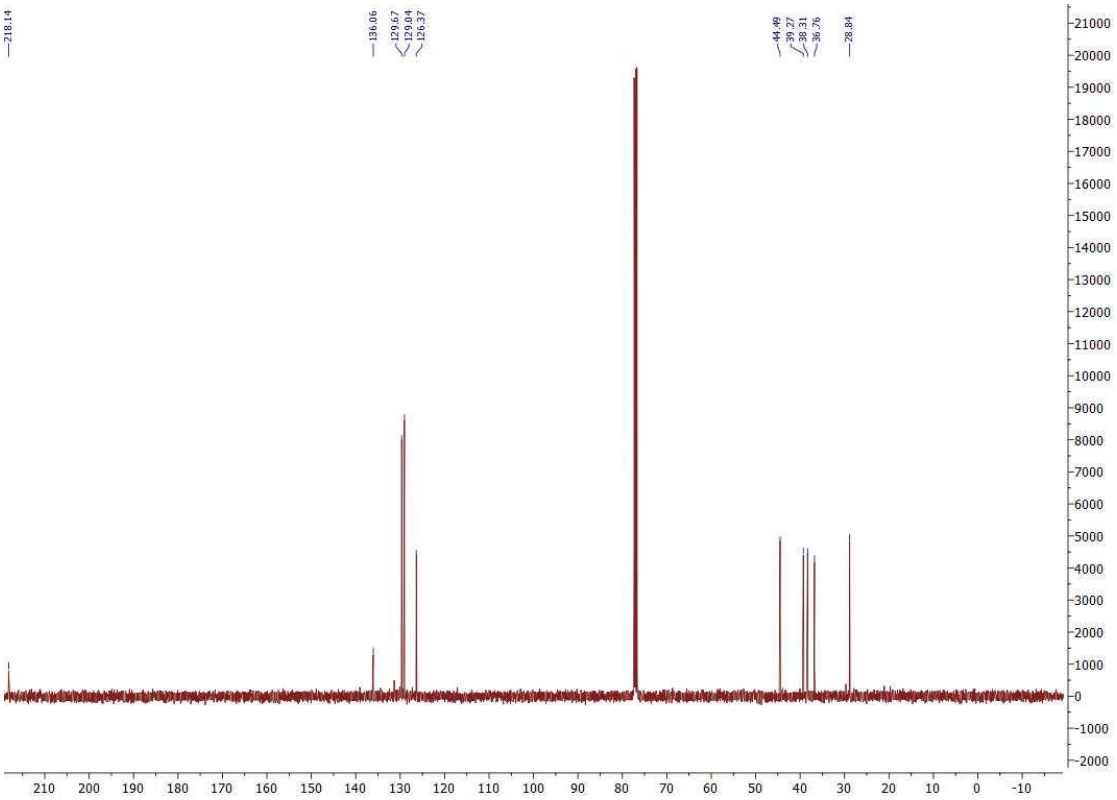

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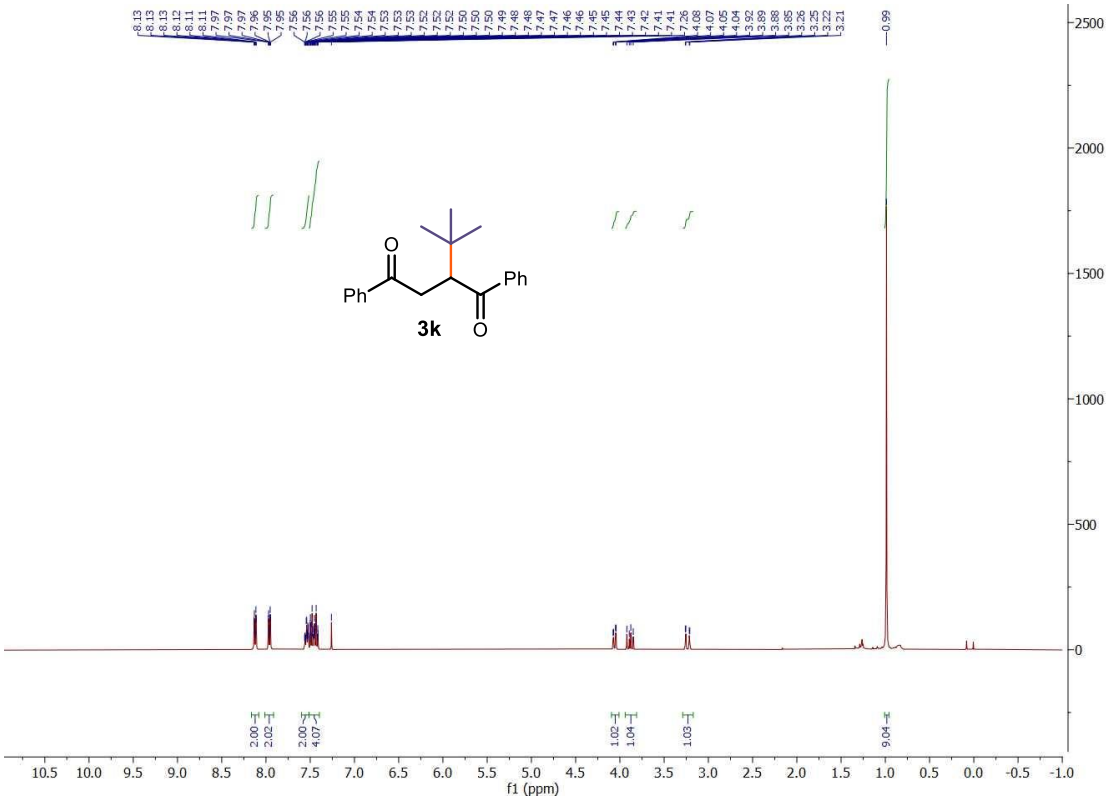

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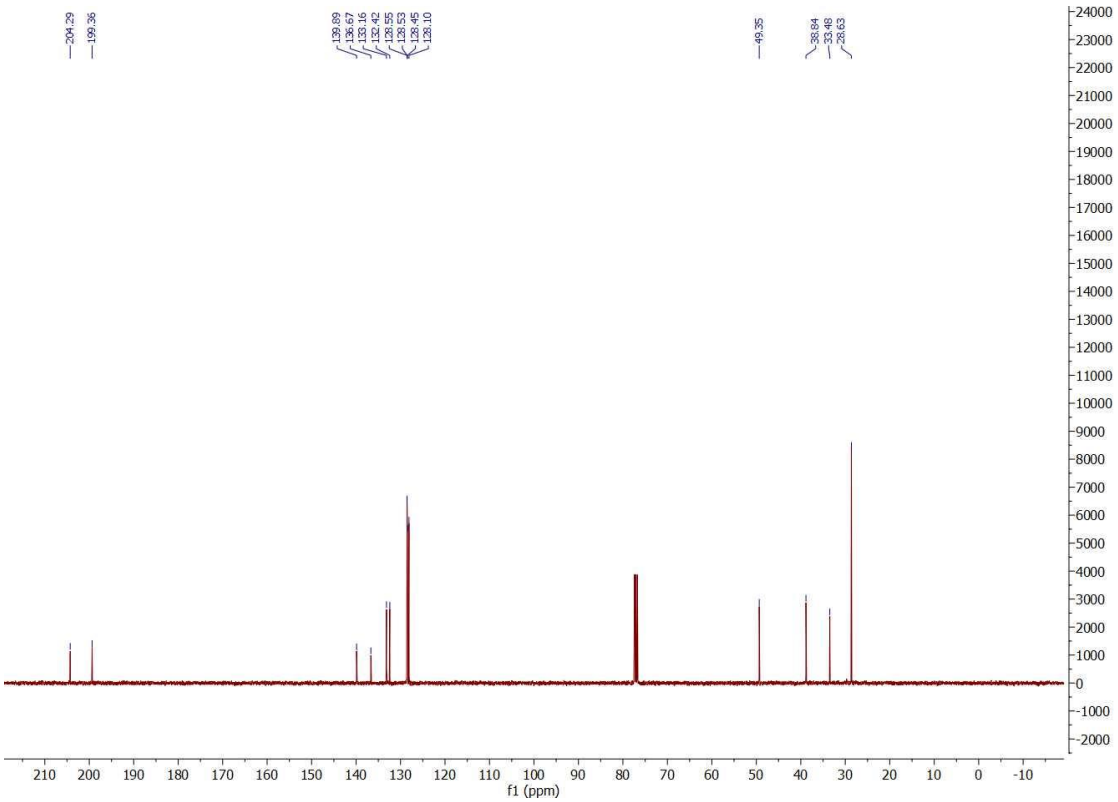

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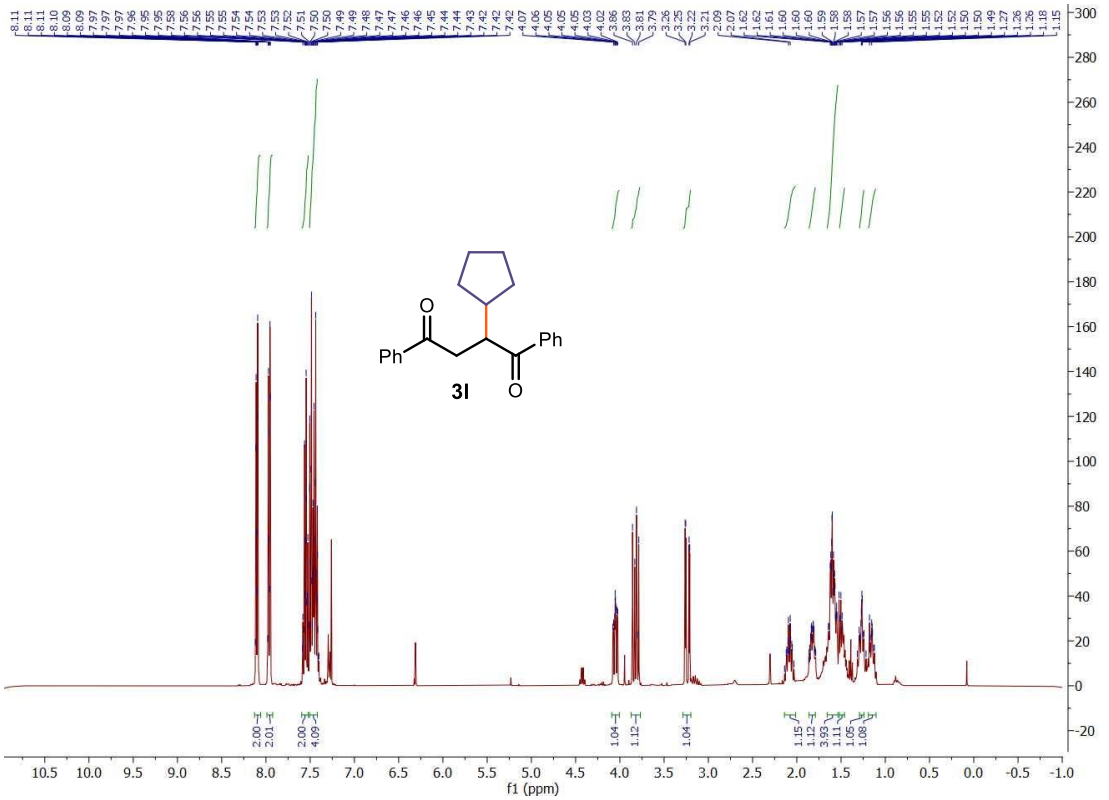

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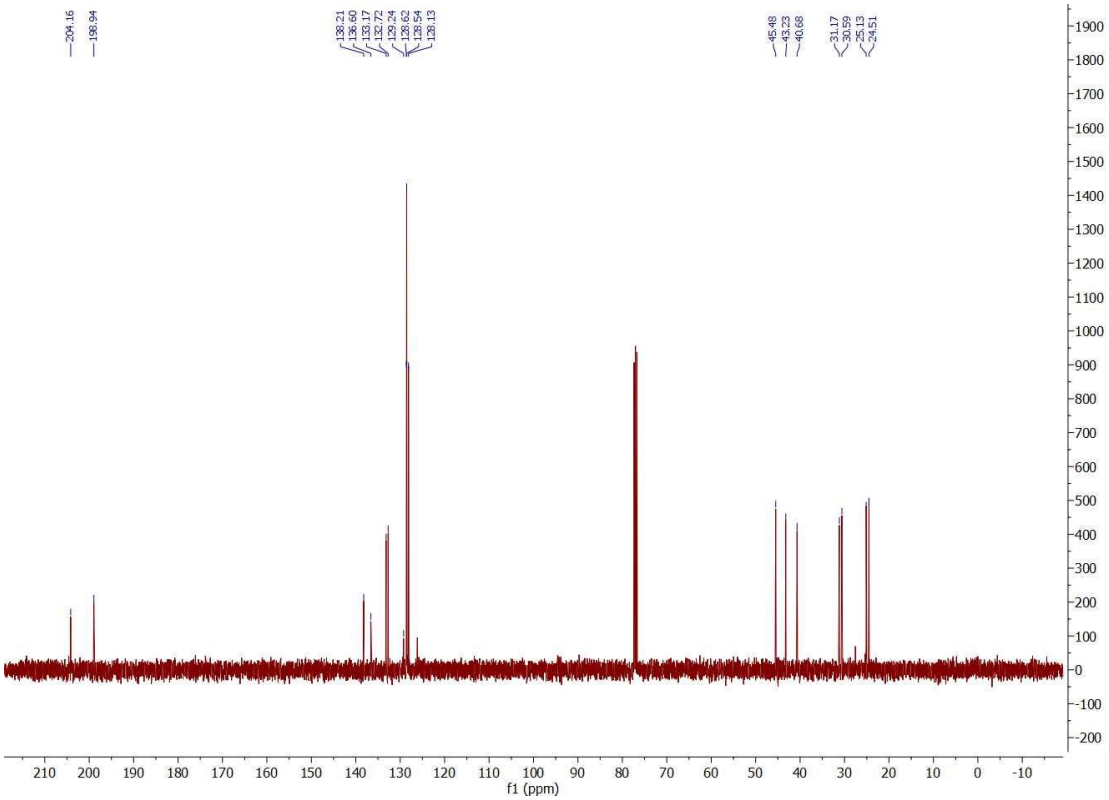

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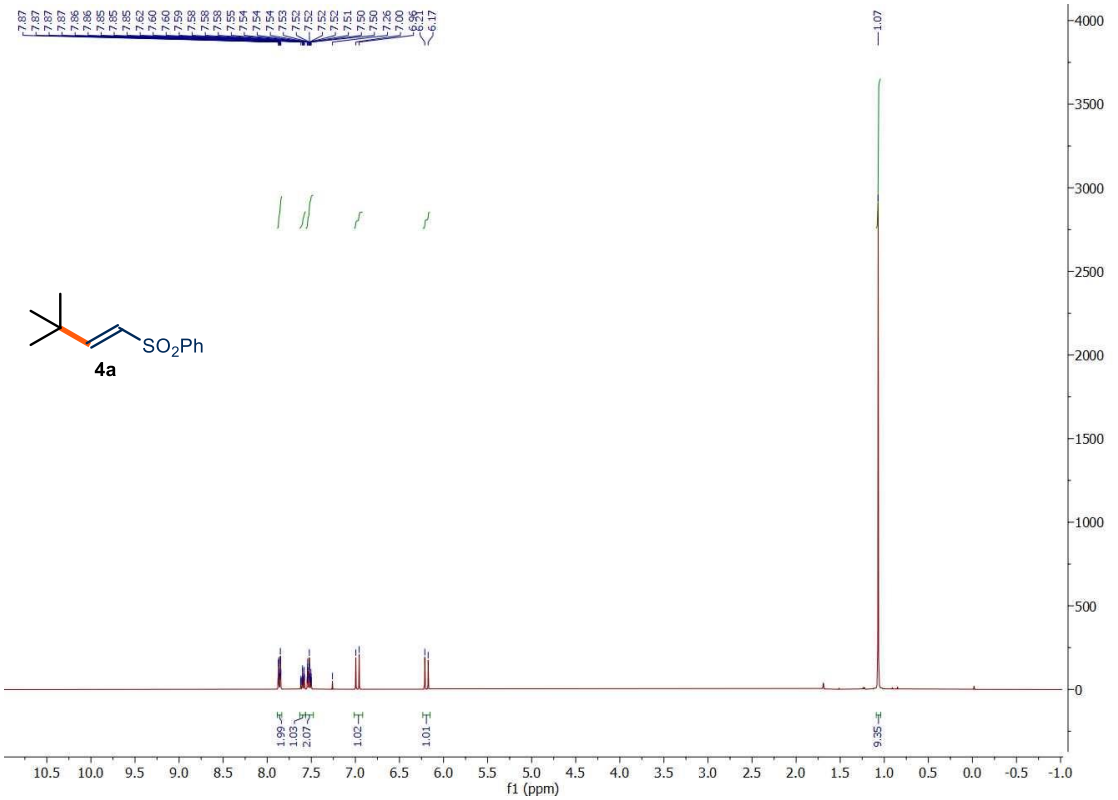

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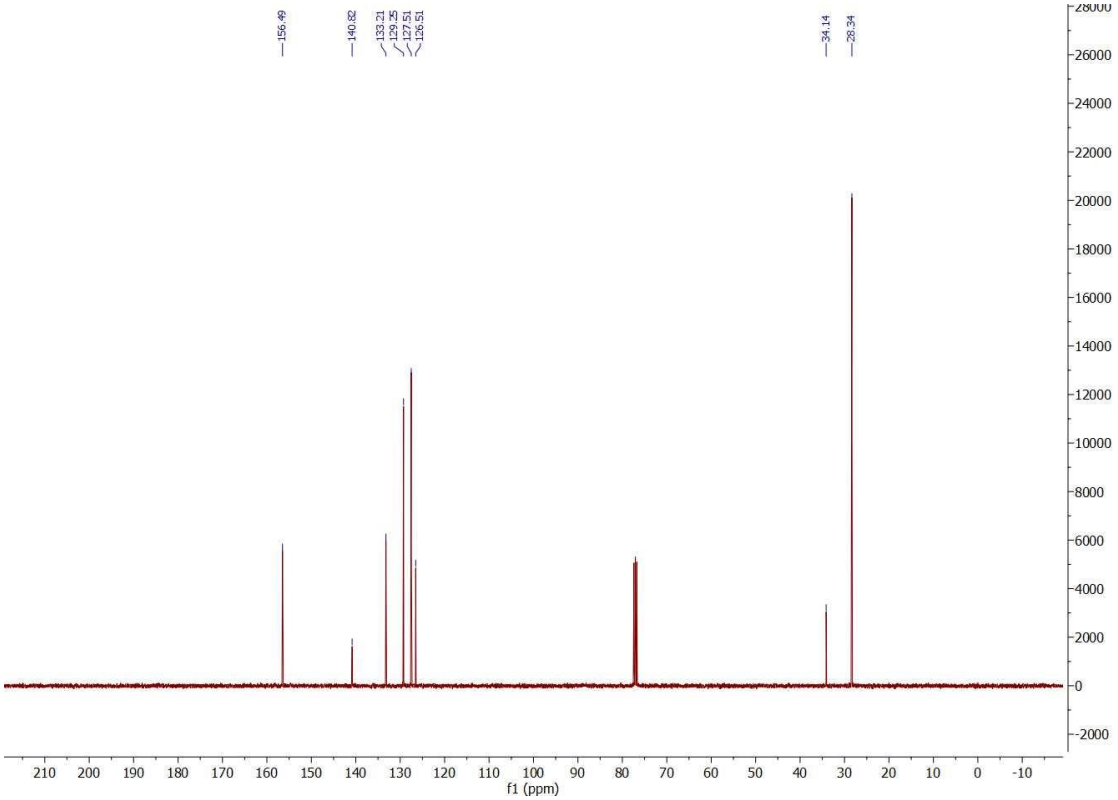

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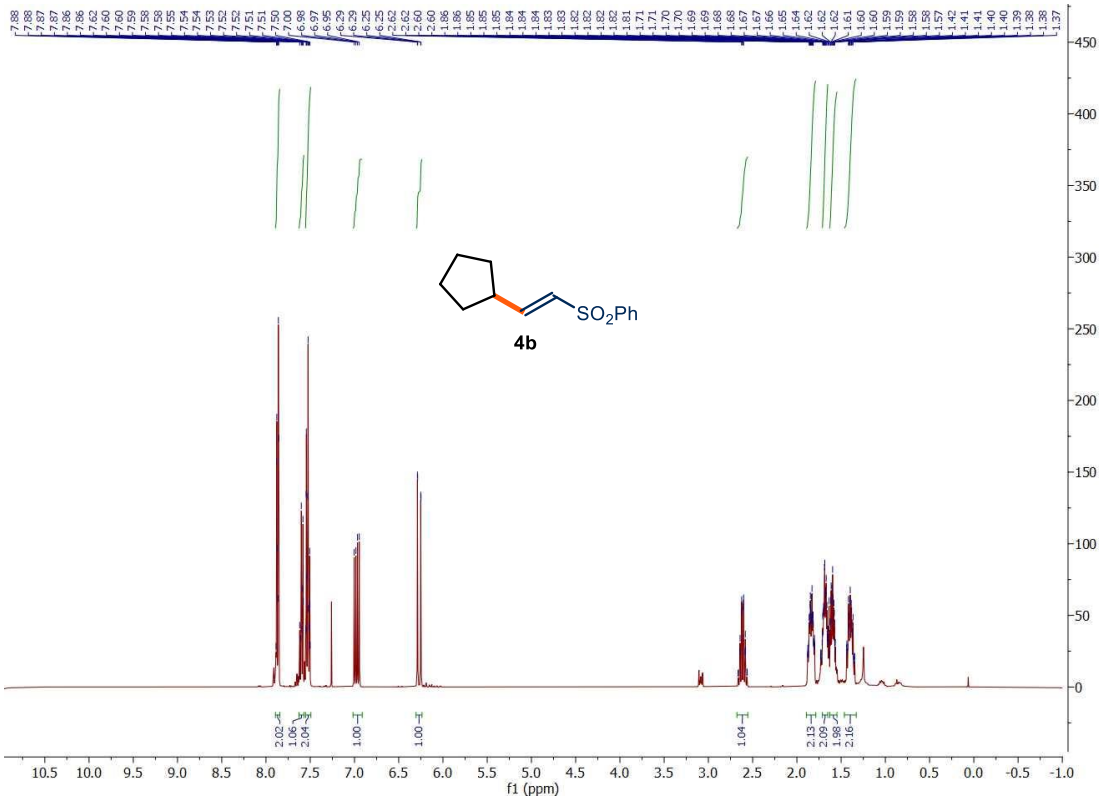

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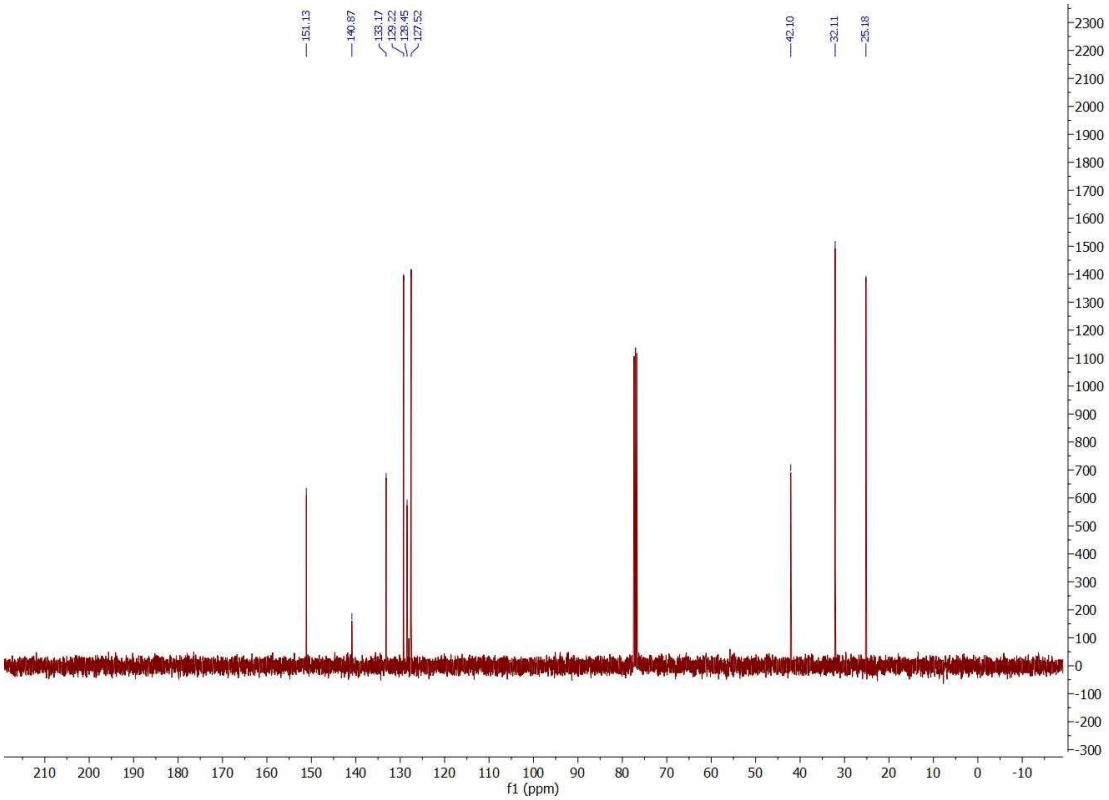

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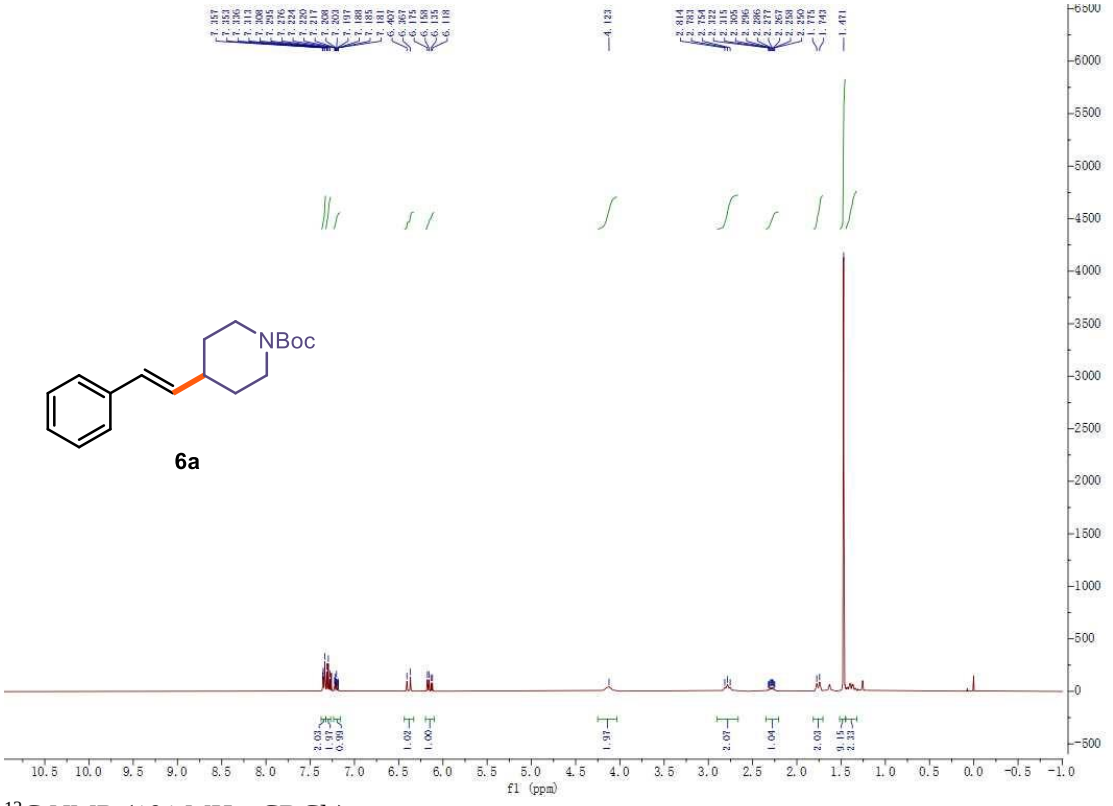

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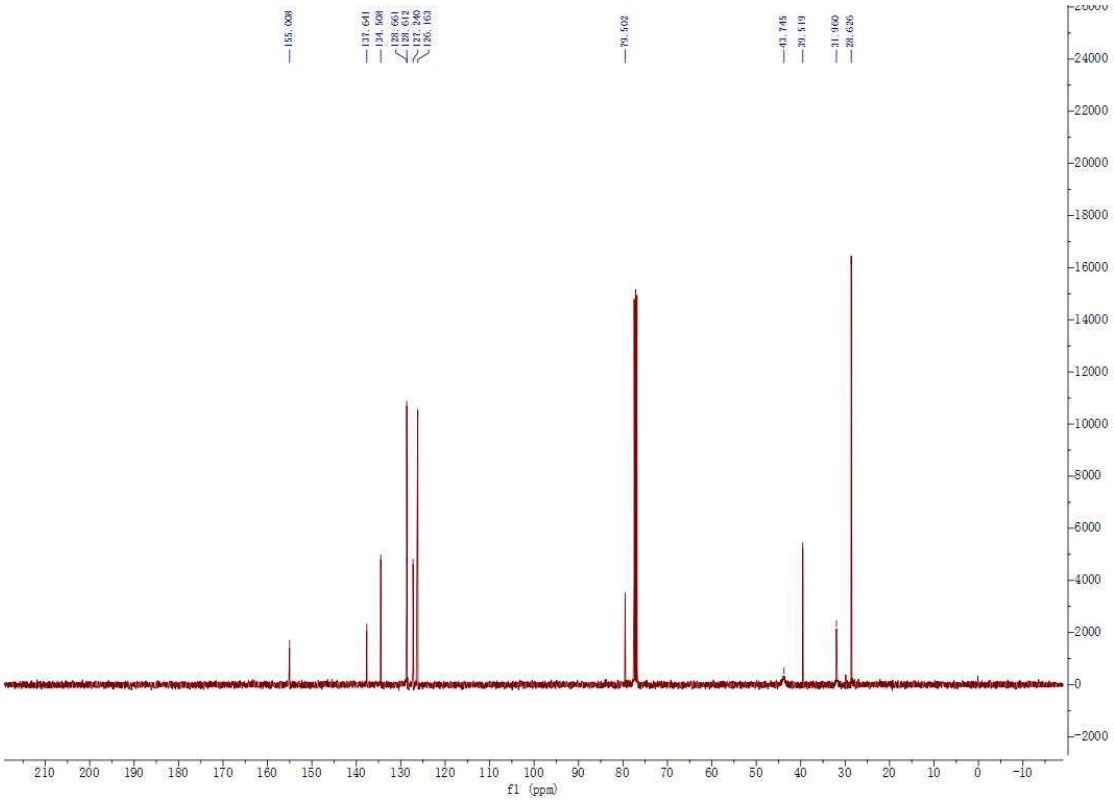

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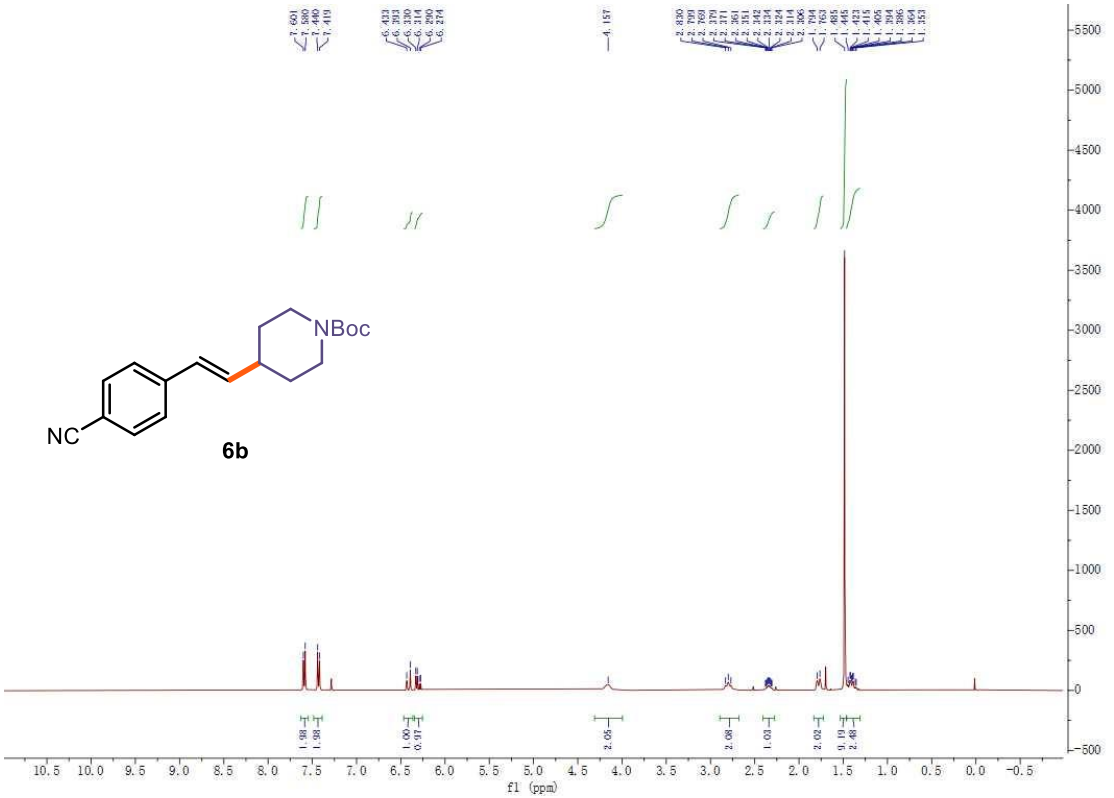

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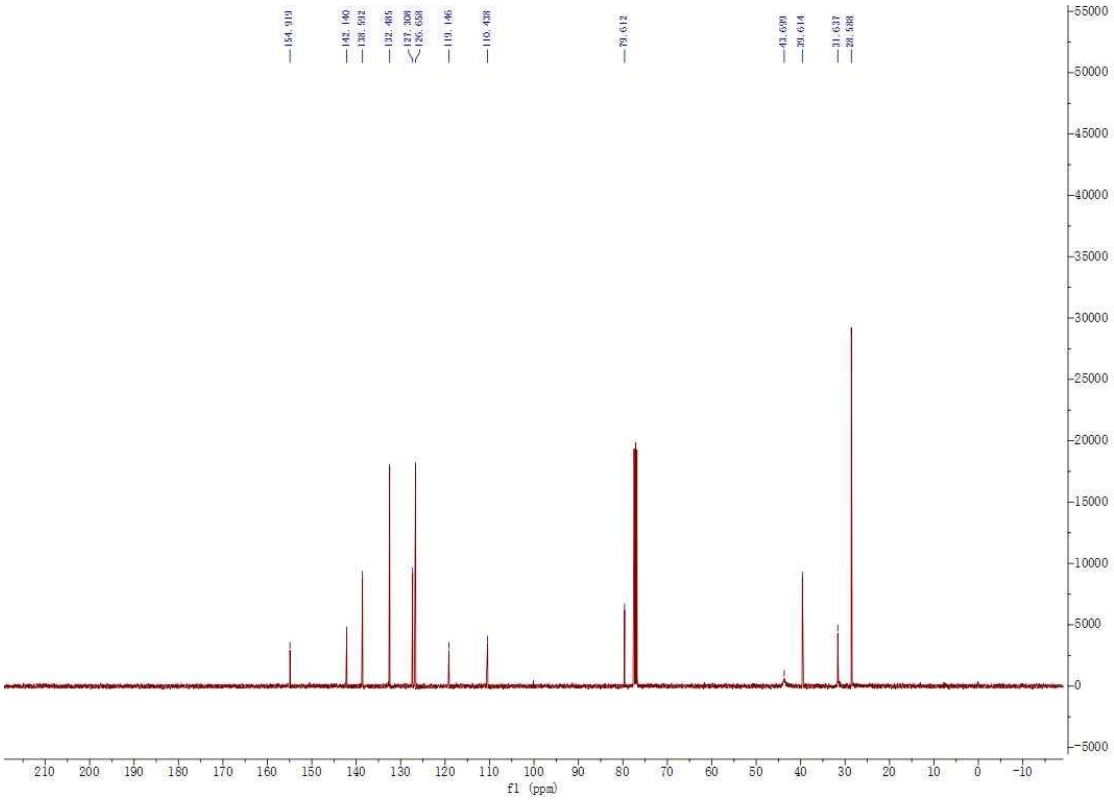

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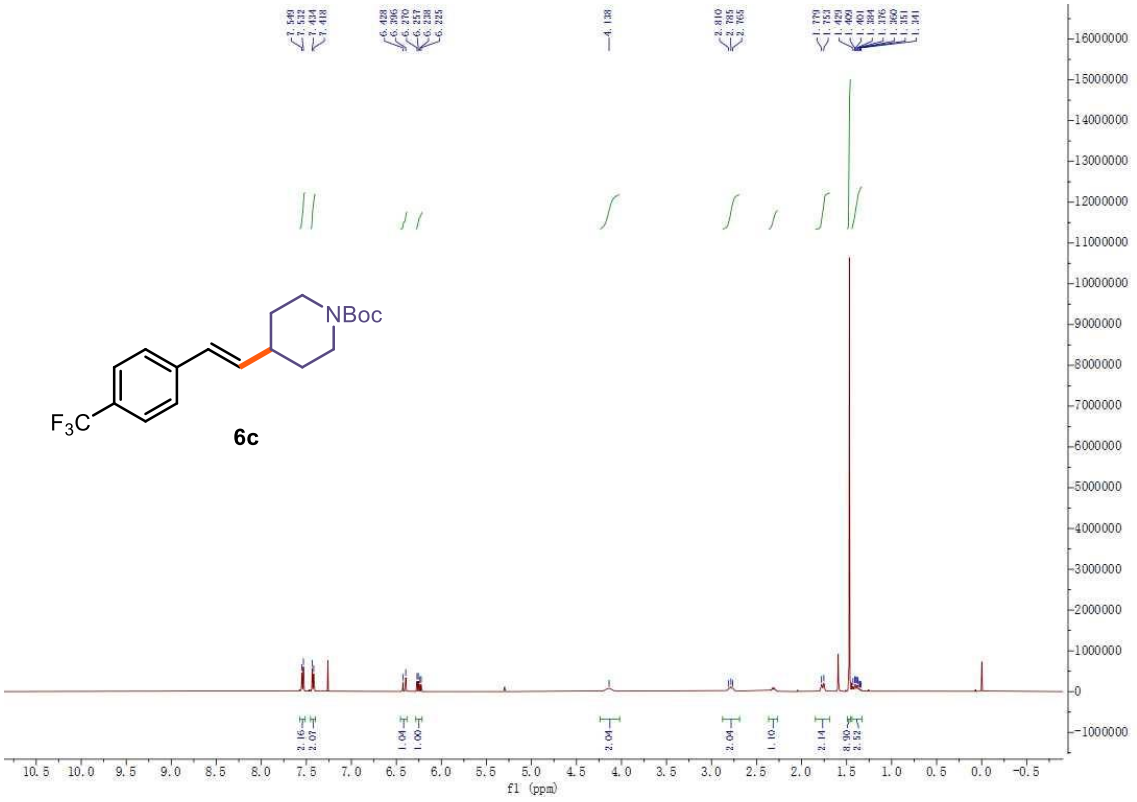

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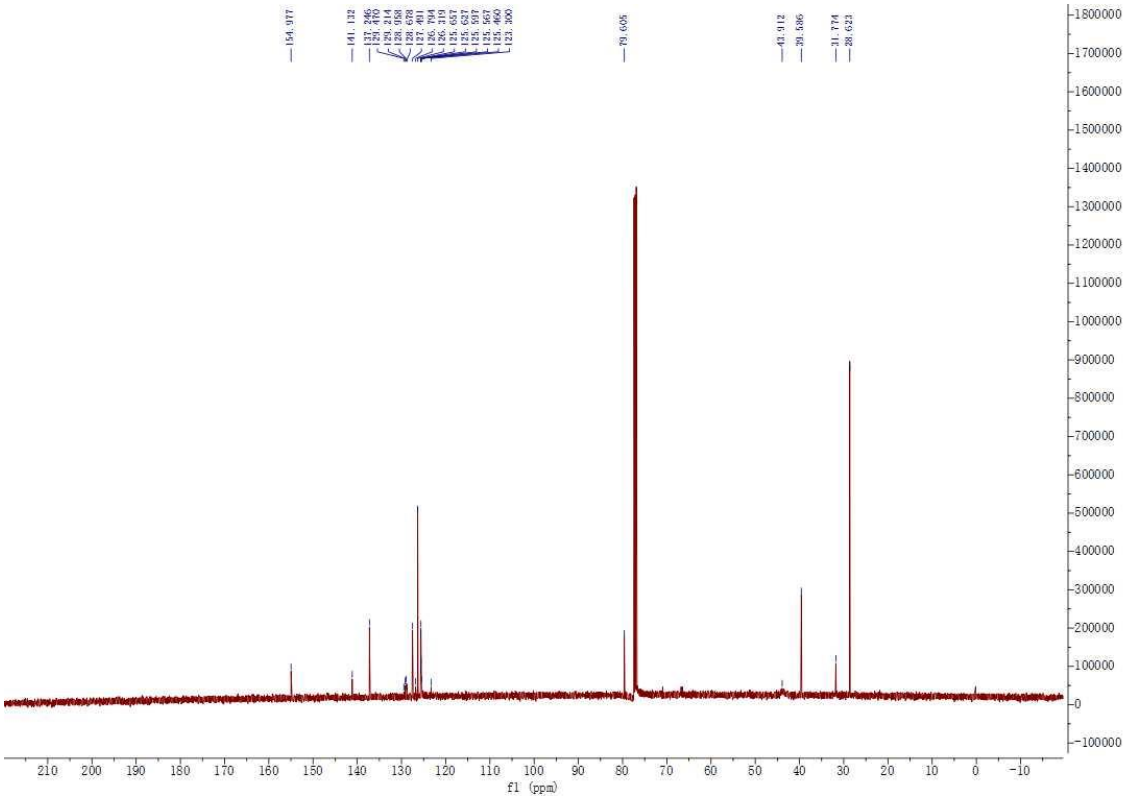

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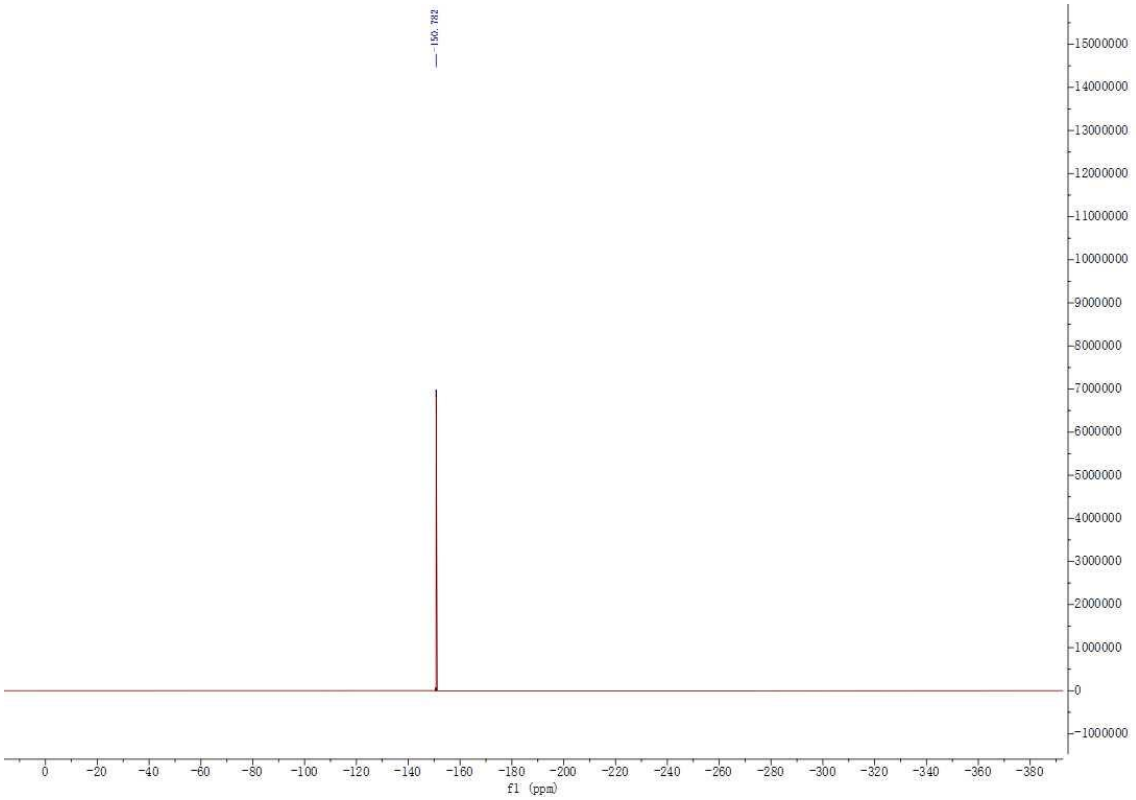

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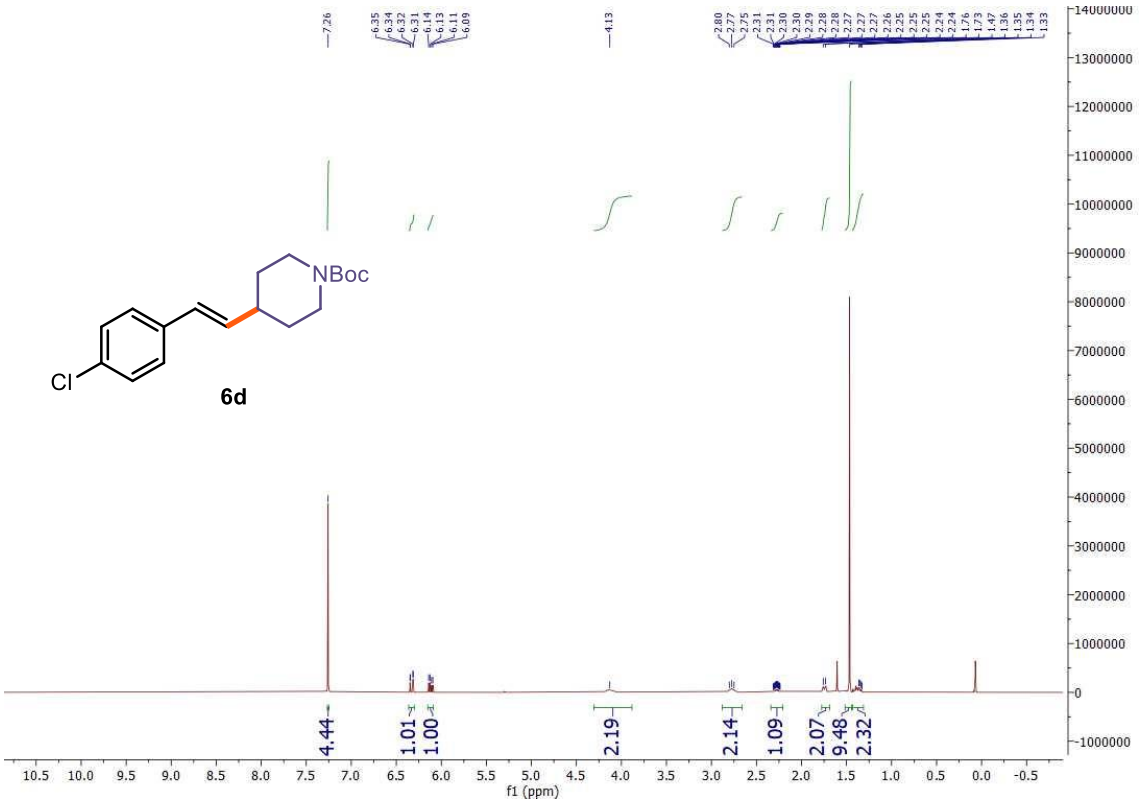

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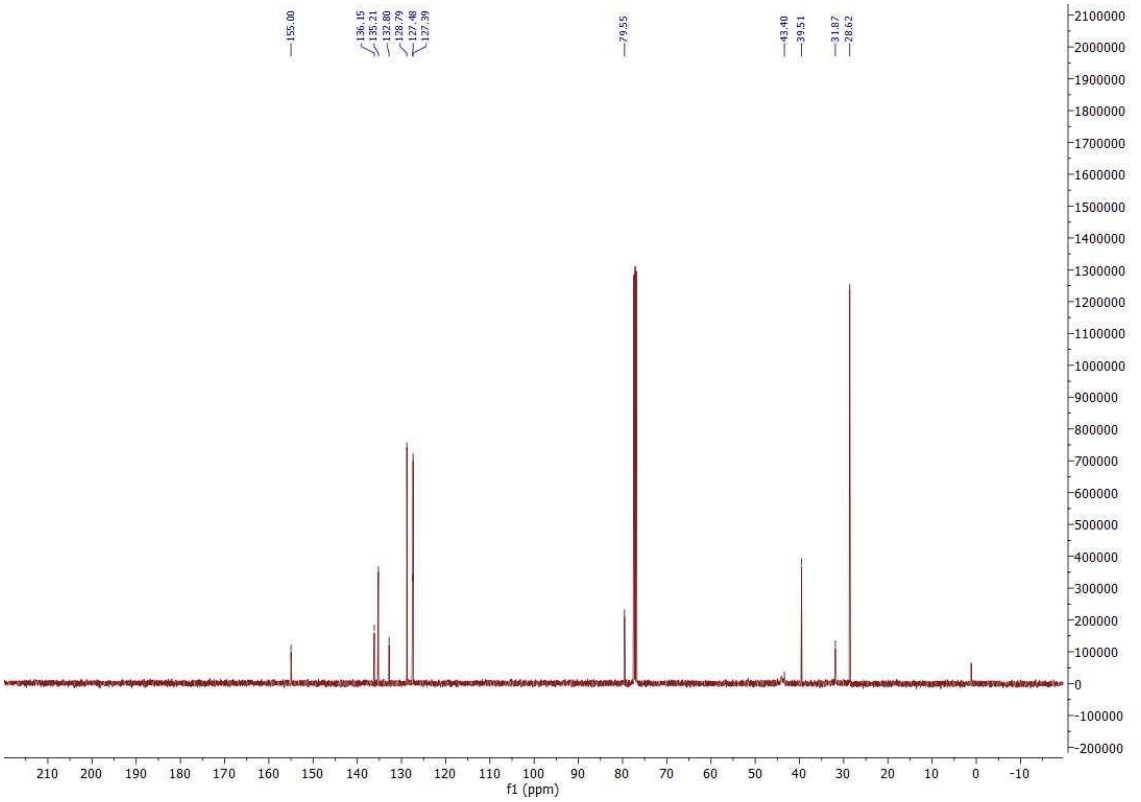

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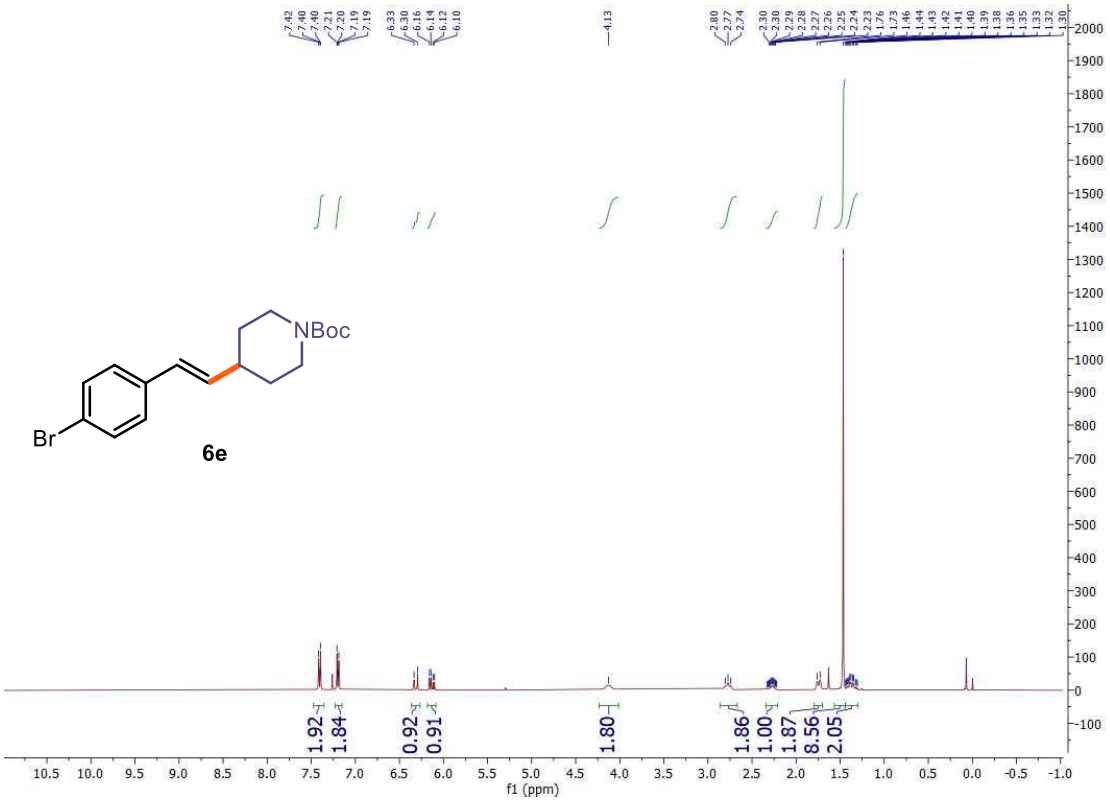
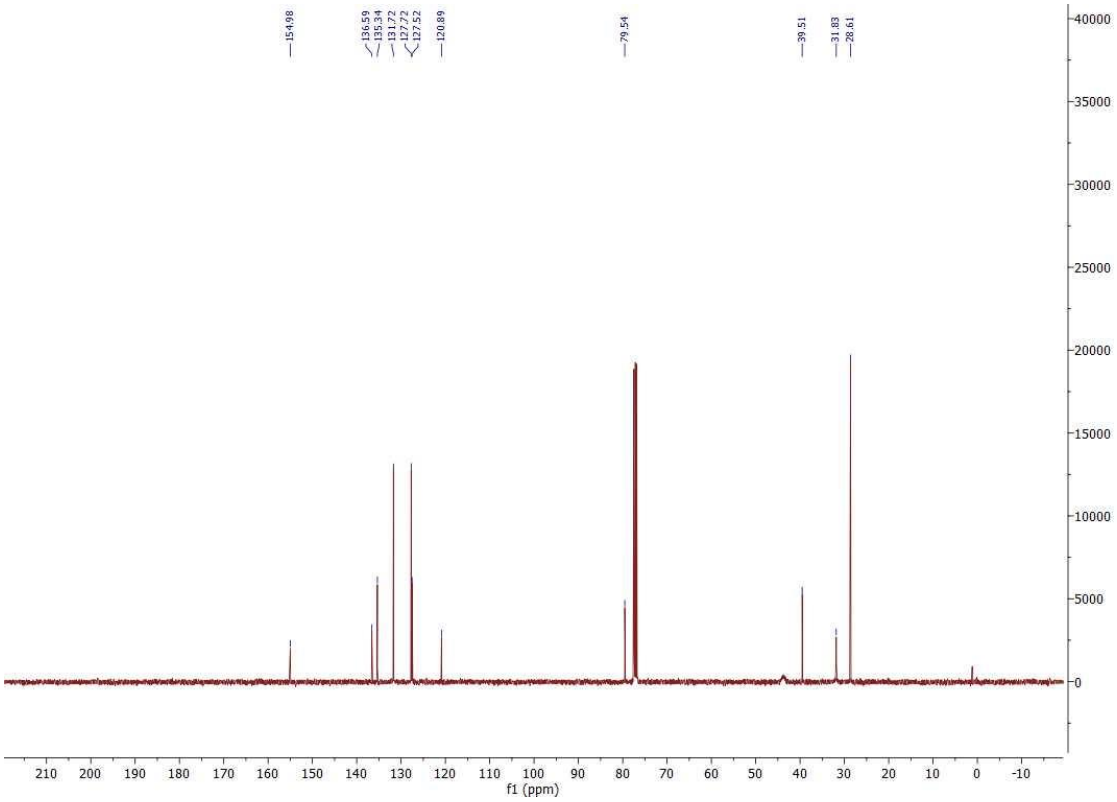
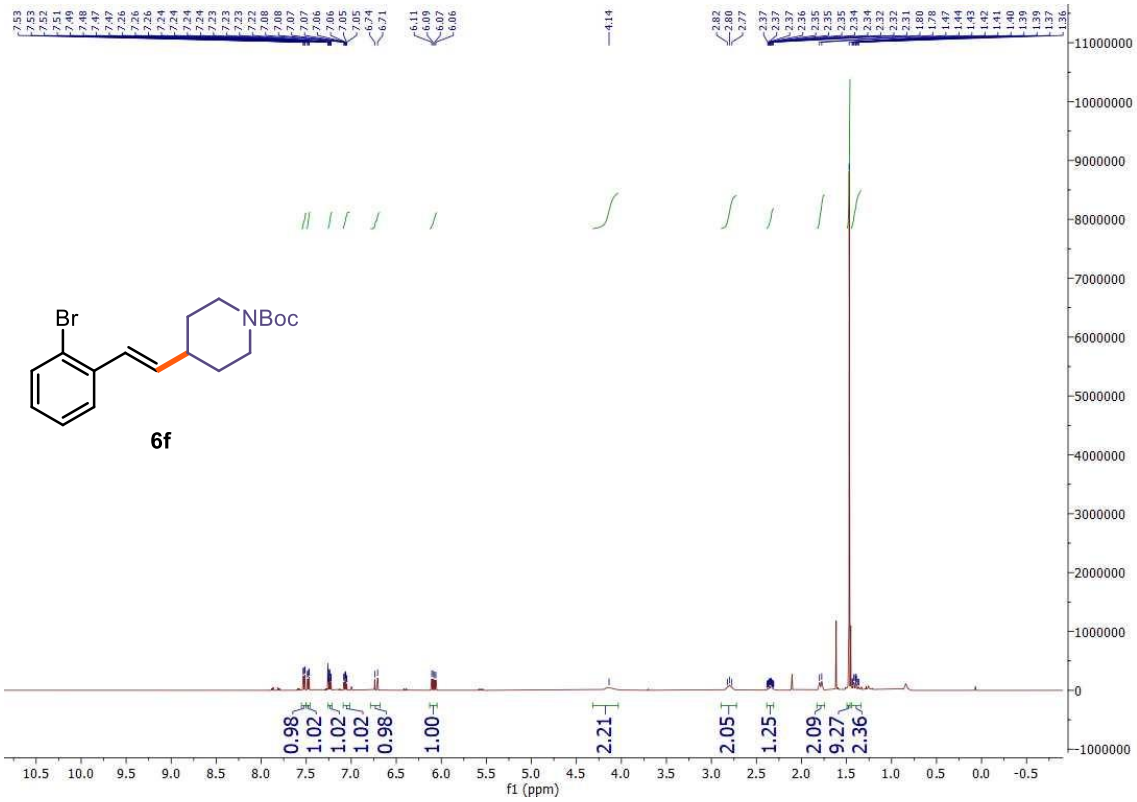


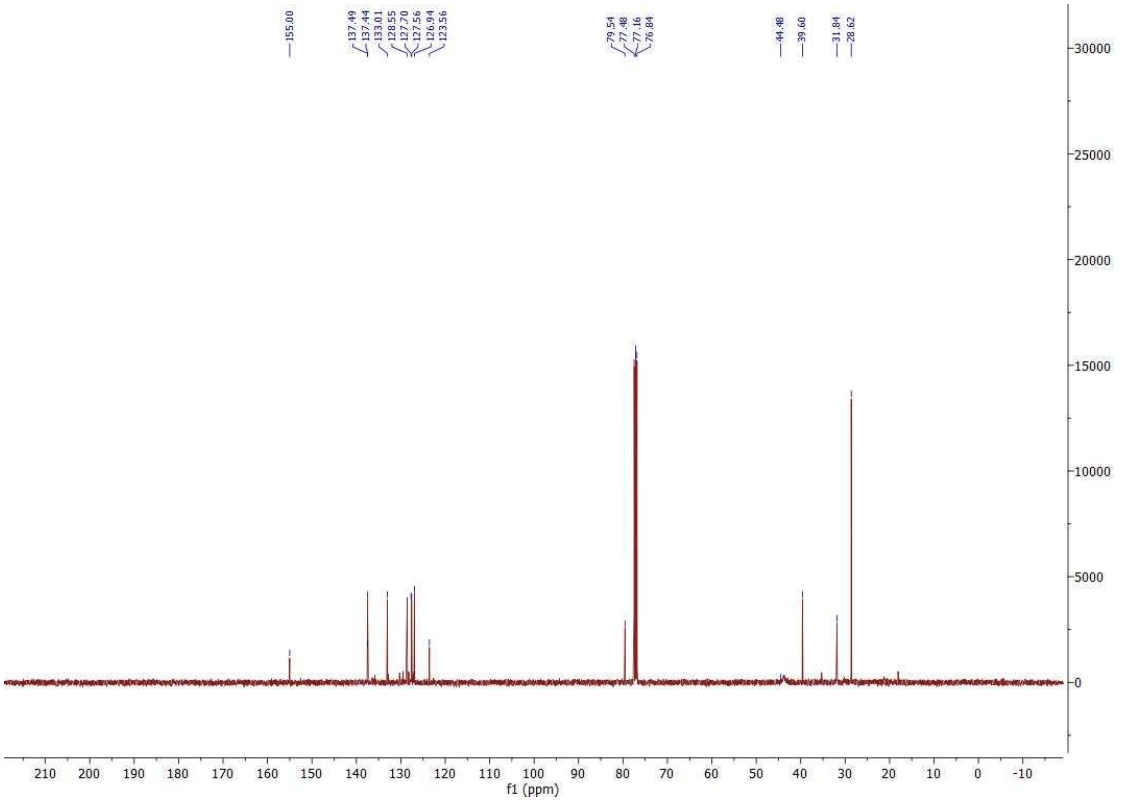
^{13}C NMR (101 MHz, $CDCl_3$)



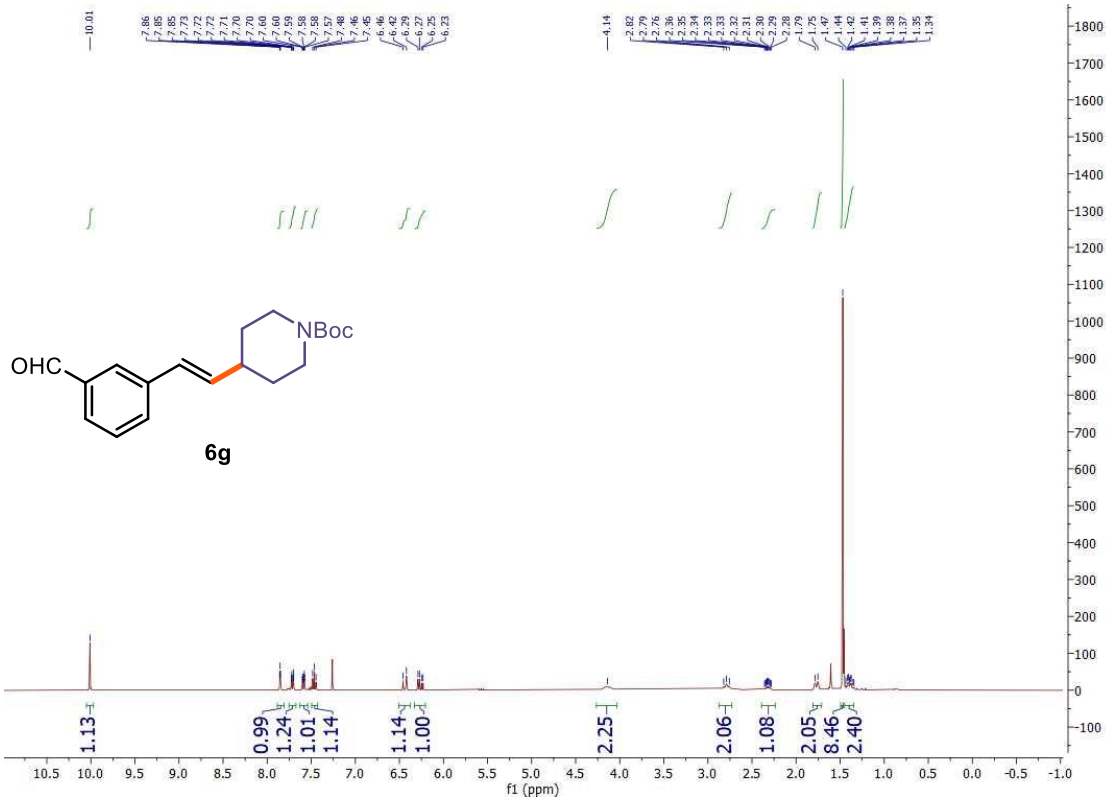
^{1}H NMR (500 MHz, $CDCl_3$)



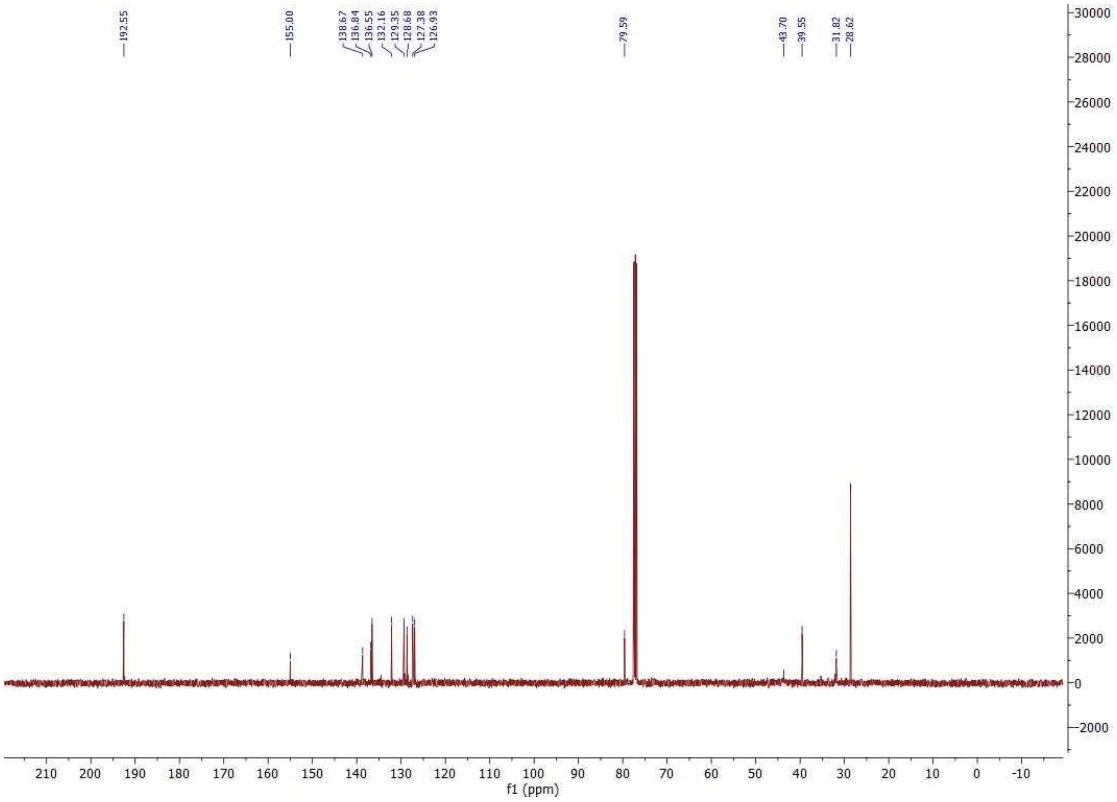
^{13}C NMR (101 MHz, $CDCl_3$)



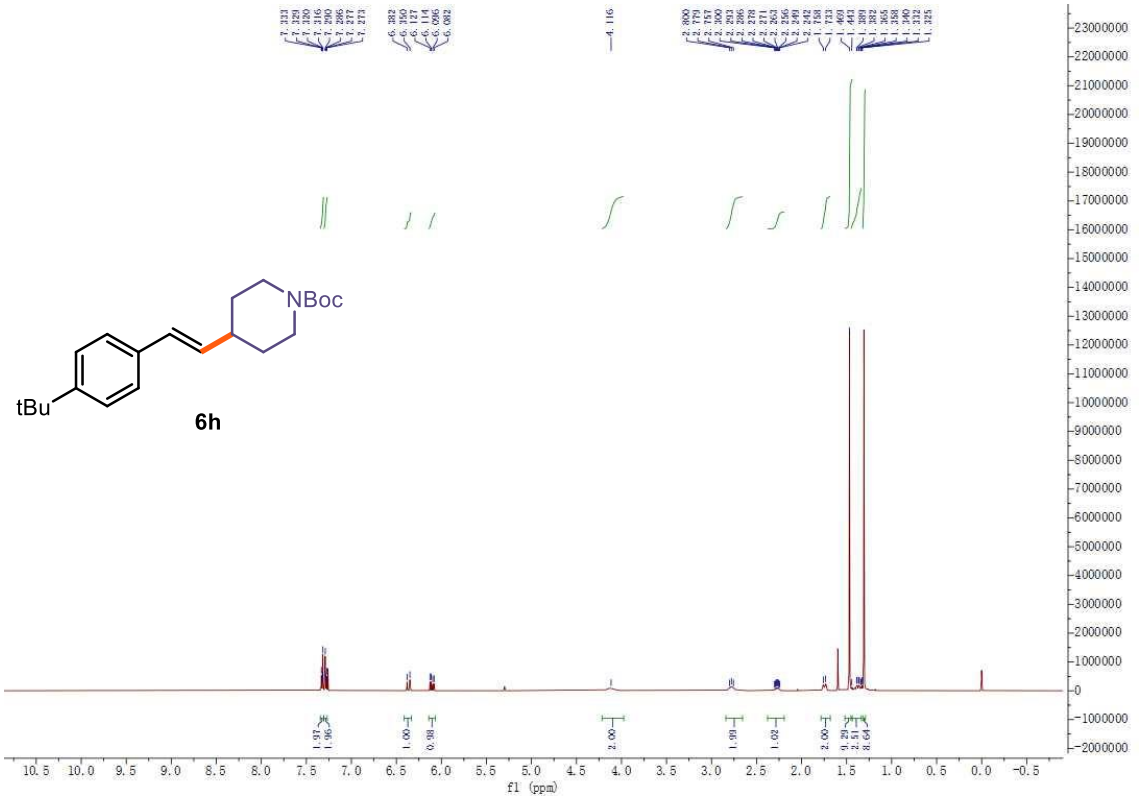
^{1}H NMR (400 MHz, $CDCl_3$)



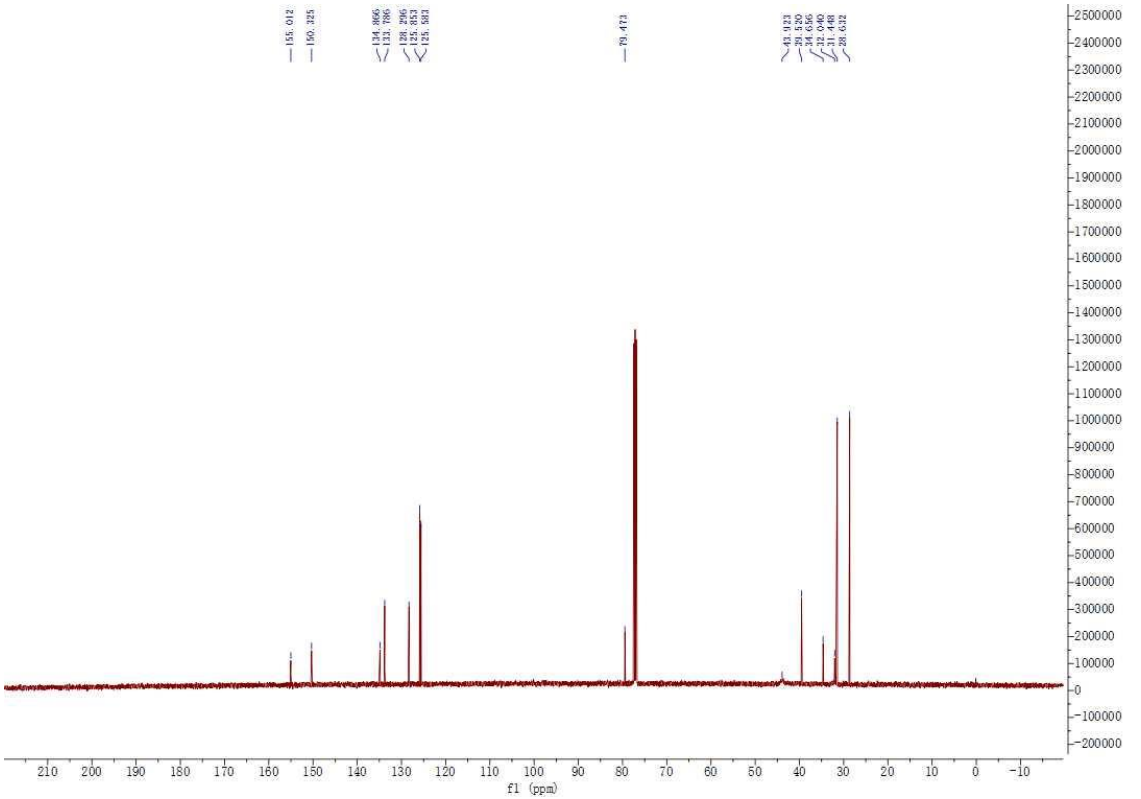
^{13}C NMR (101 MHz, $CDCl_3$)



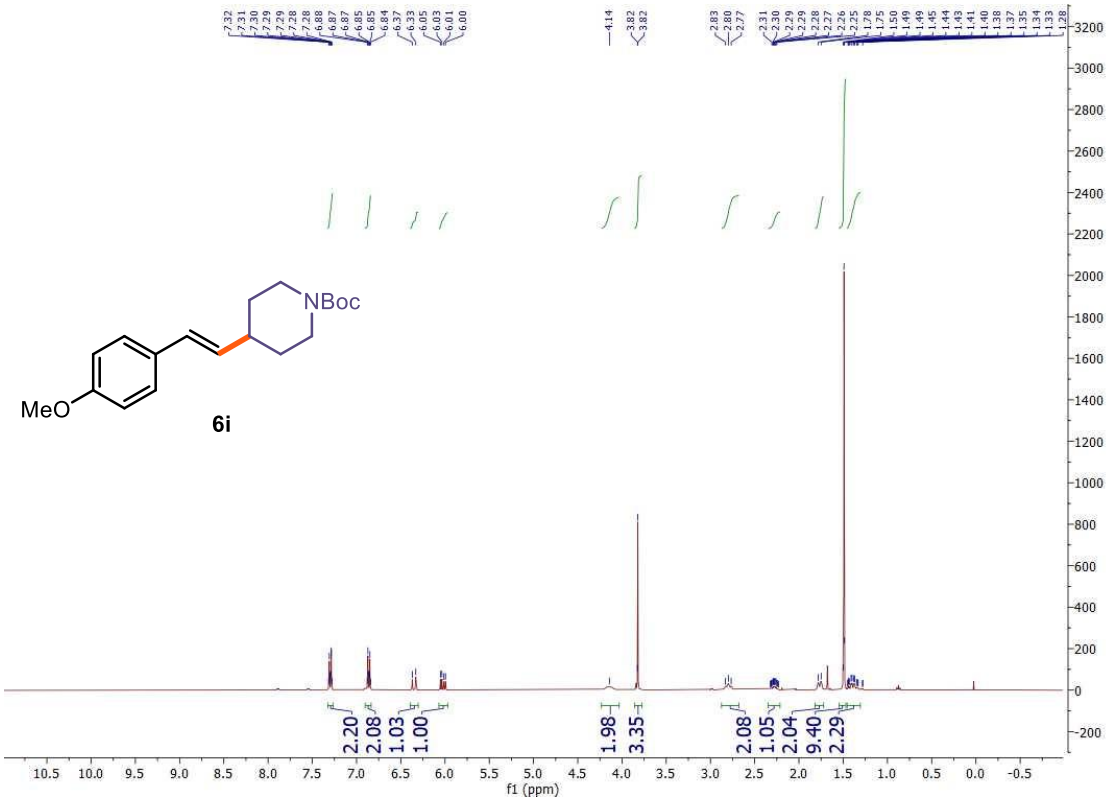
^{1}H NMR (500 MHz, $CDCl_3$)



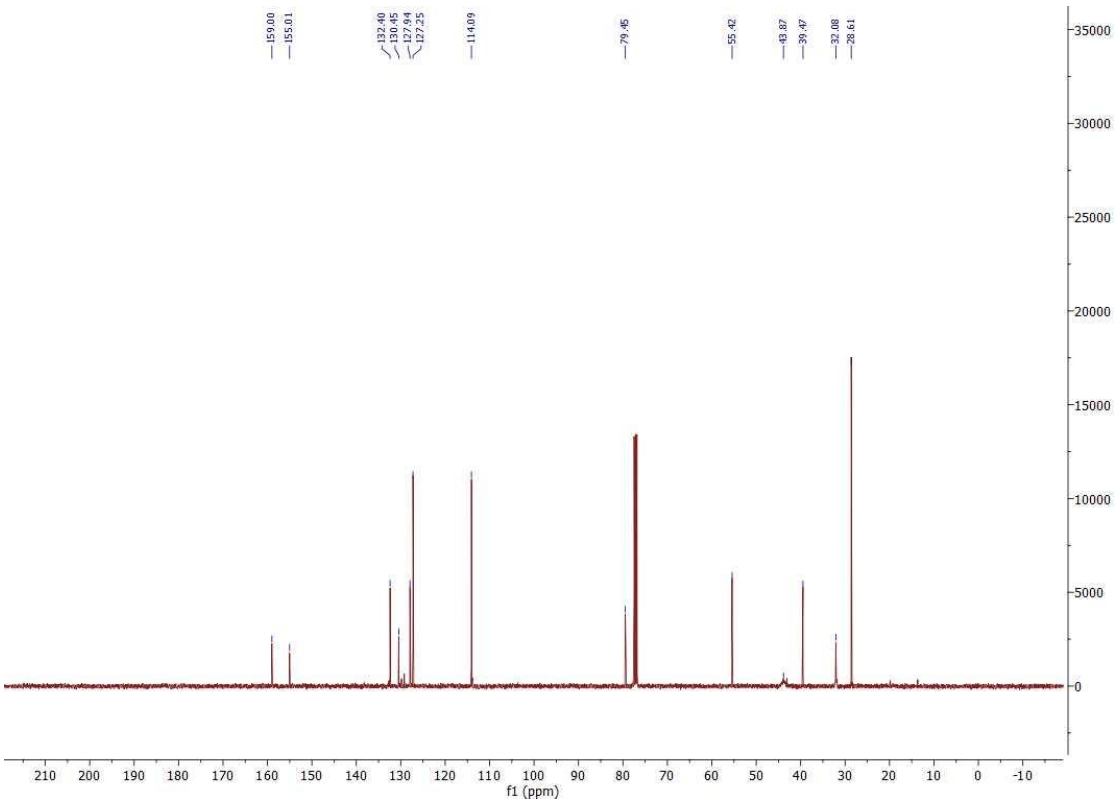
^{13}C NMR (126 MHz, $CDCl_3$)



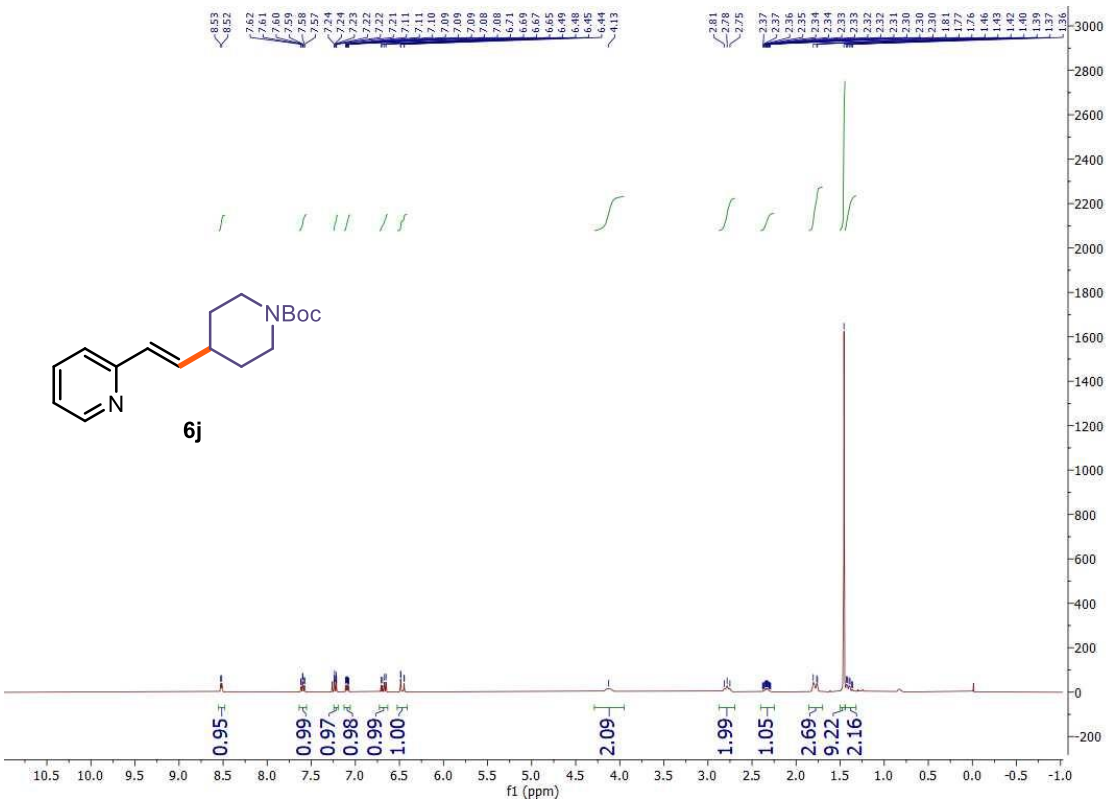
^{1}H NMR (400 MHz, $CDCl_3$)



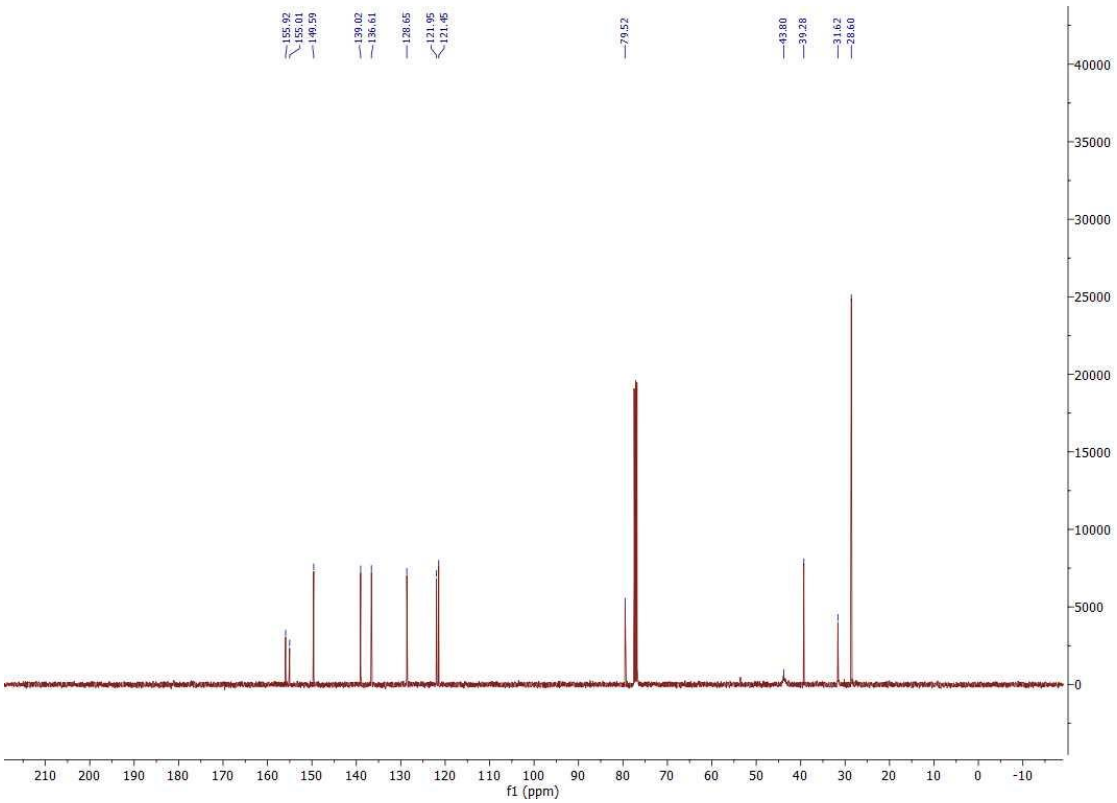
^{13}C NMR (101 MHz, $CDCl_3$)



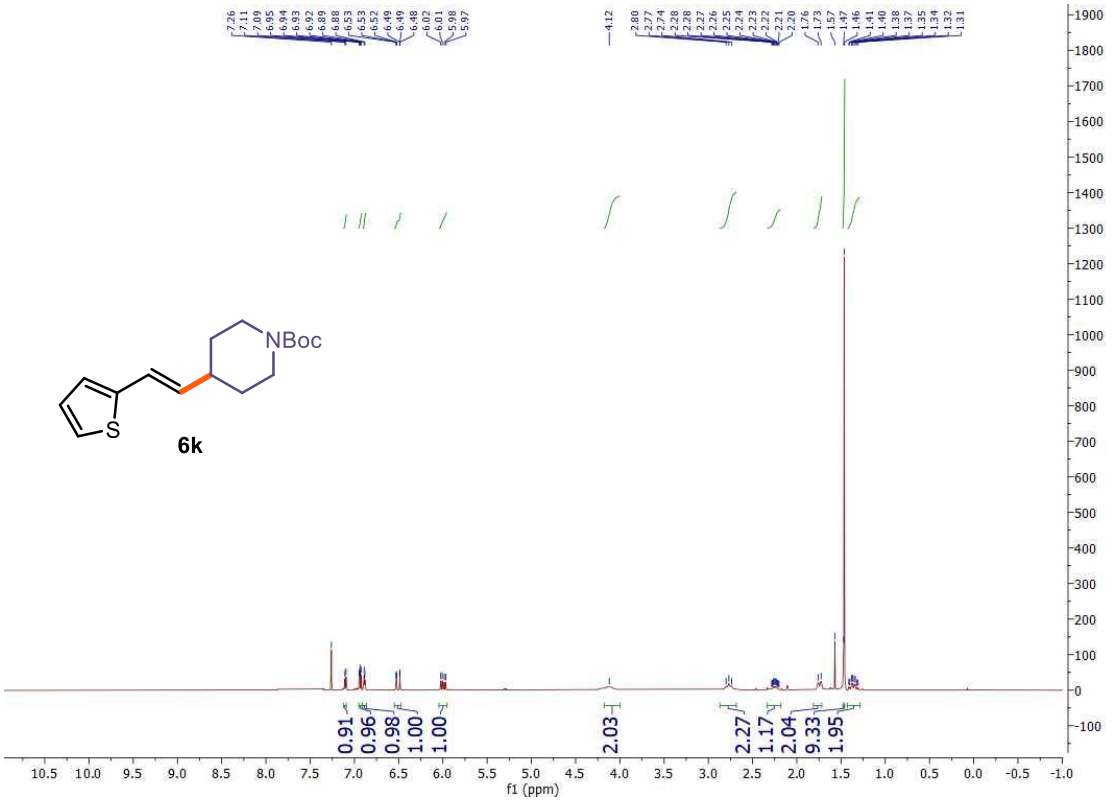
^{1}H NMR (400 MHz, $CDCl_3$)



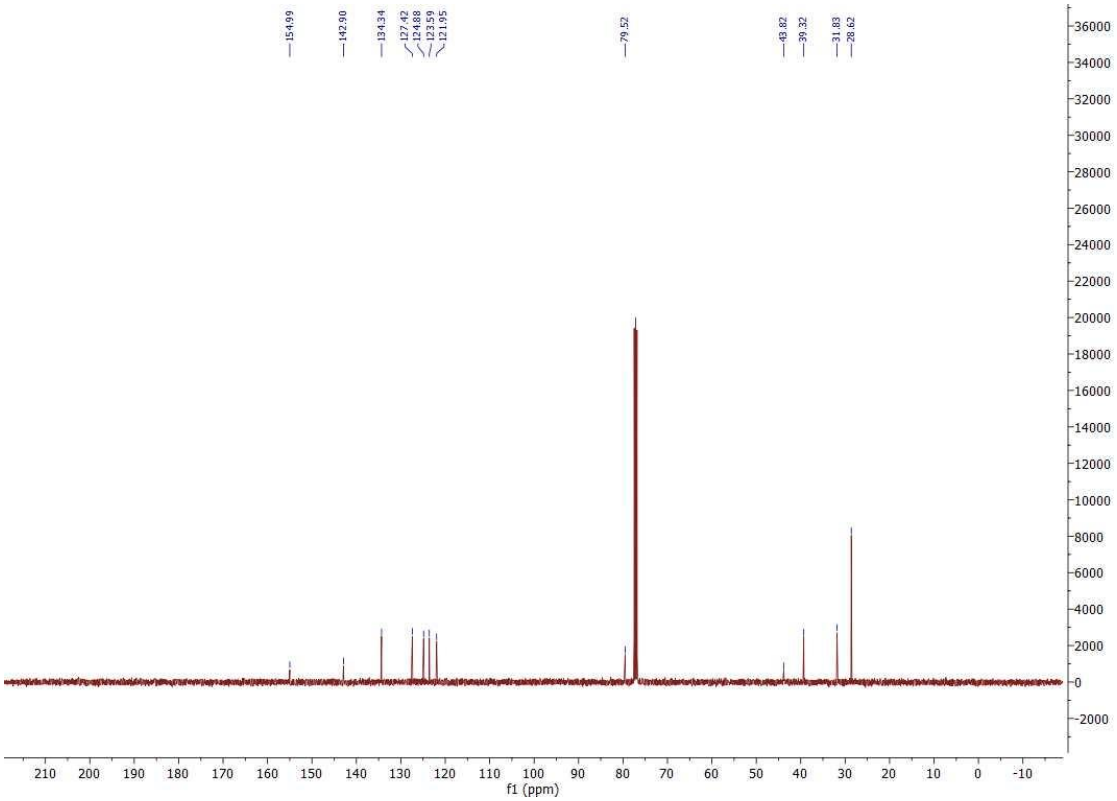
^{13}C NMR (101 MHz, $CDCl_3$)



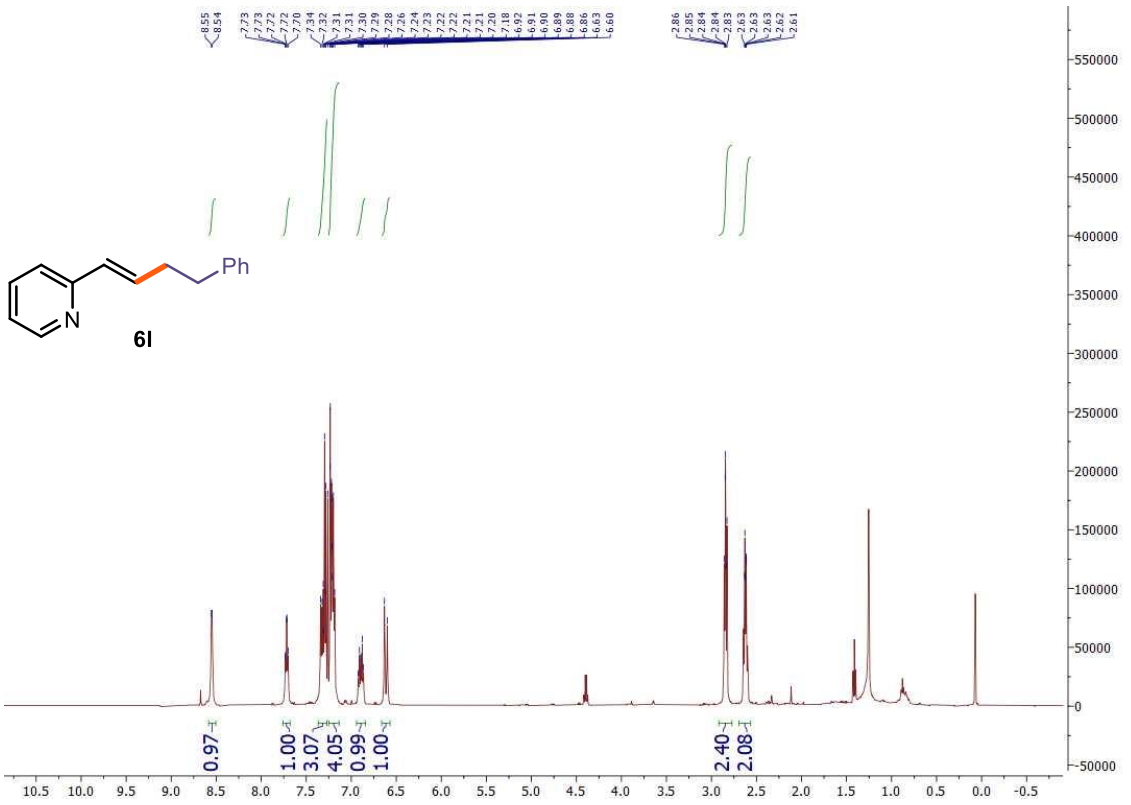
^{1}H NMR (400 MHz, $CDCl_3$)



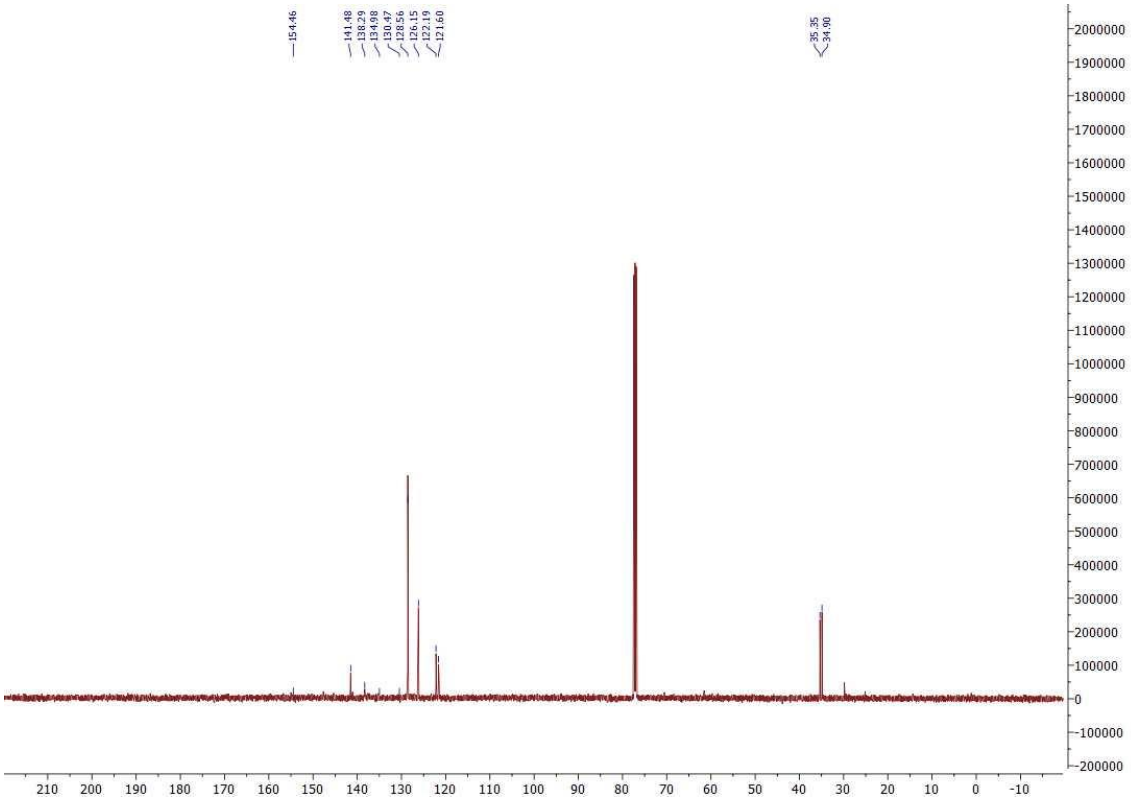
^{13}C NMR (101 MHz, $CDCl_3$)



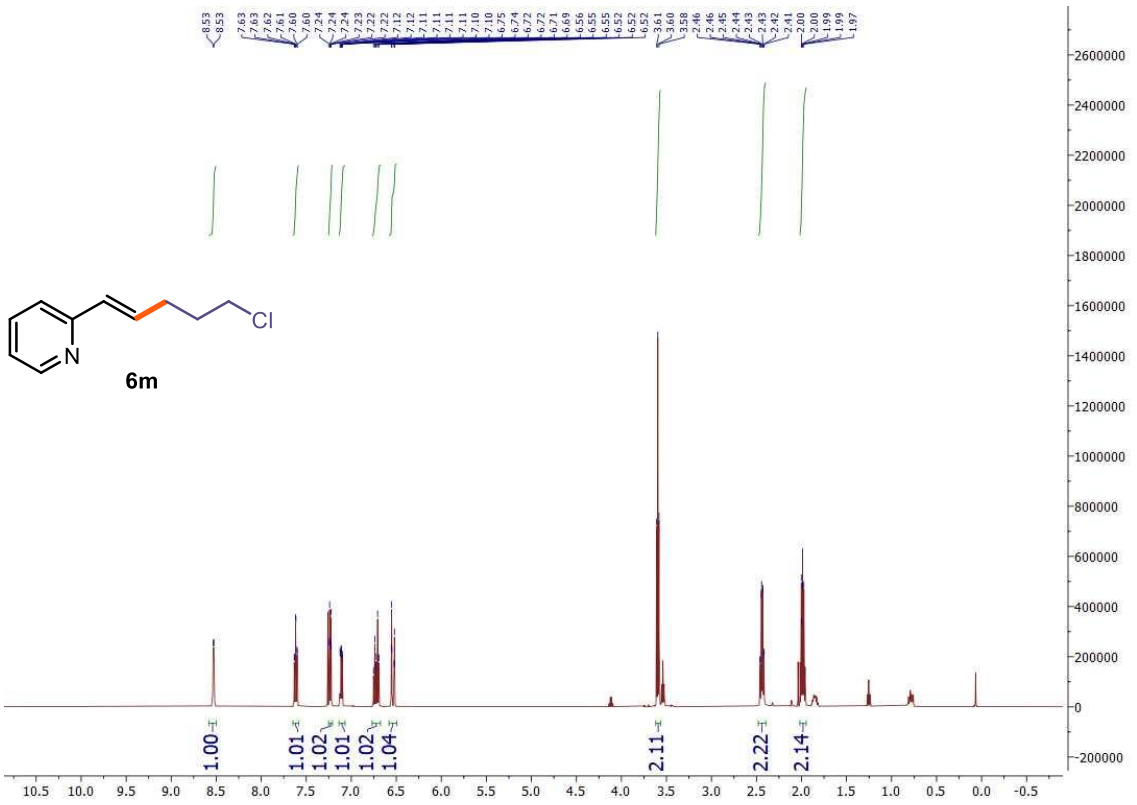
^{1}H NMR (500 MHz, $CDCl_3$)



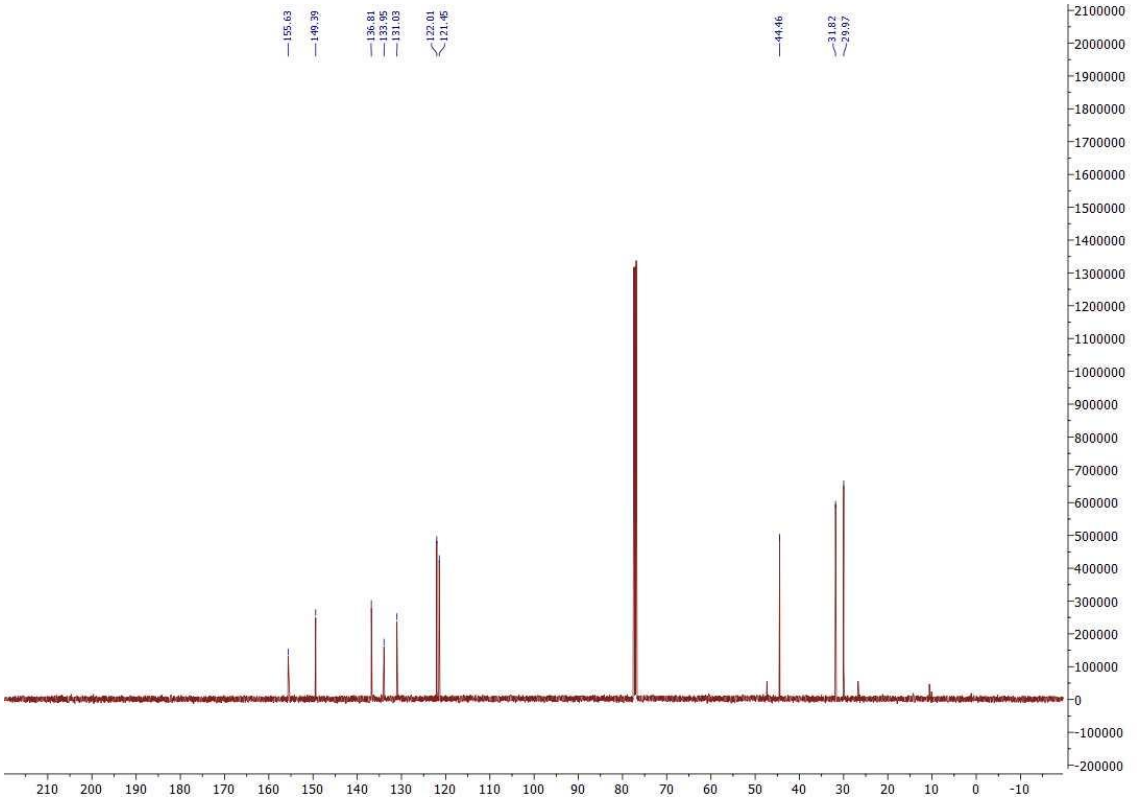
^{13}C NMR (126 MHz, $CDCl_3$)



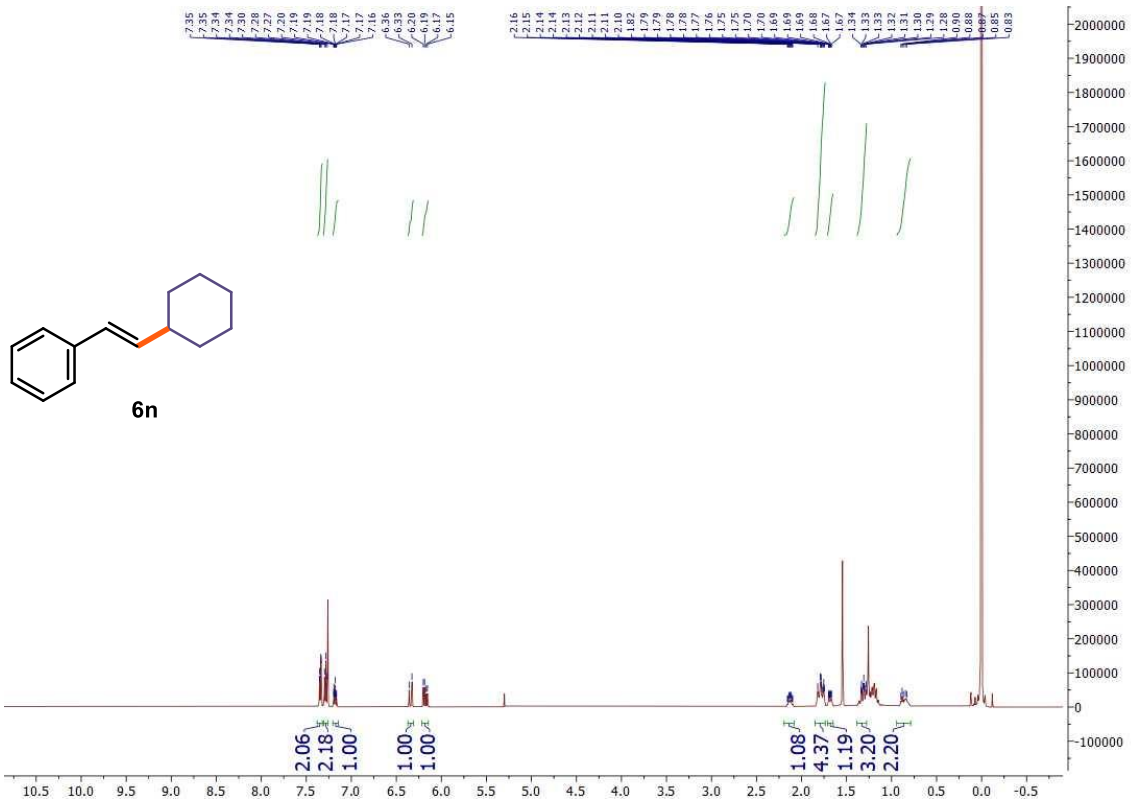
^{1}H NMR (500 MHz, $CDCl_3$)



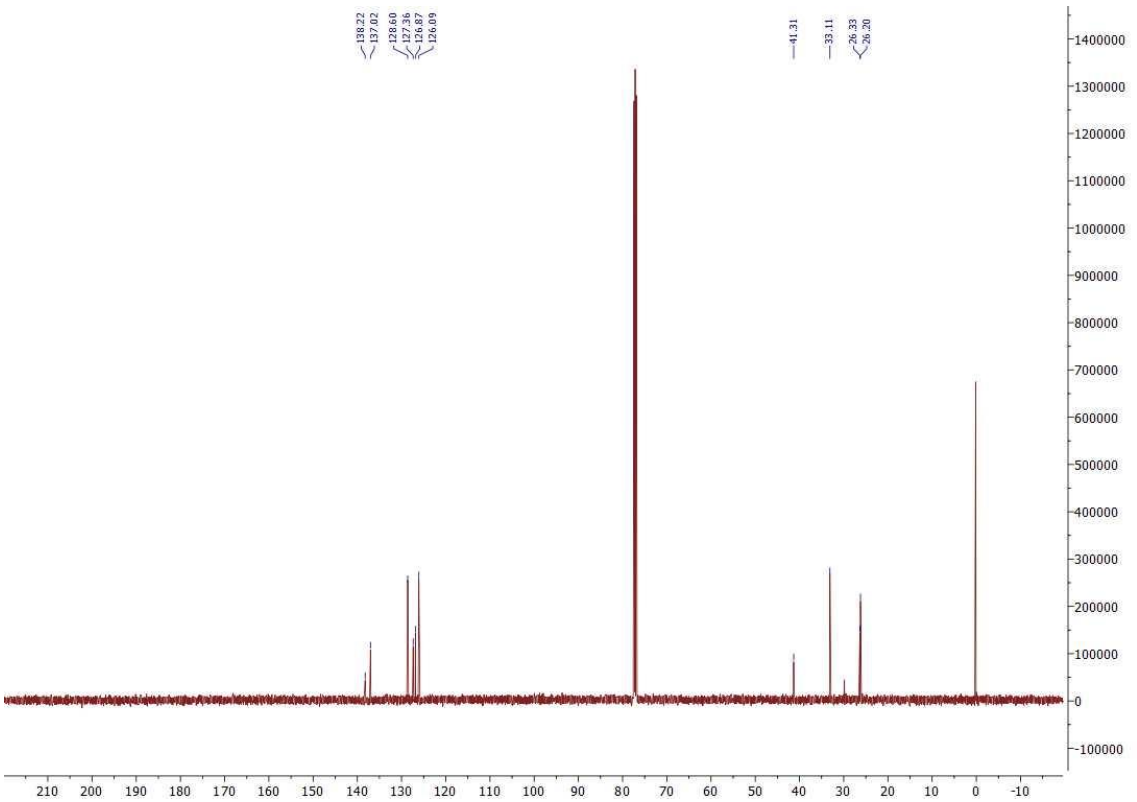
^{13}C NMR (126 MHz, $CDCl_3$)



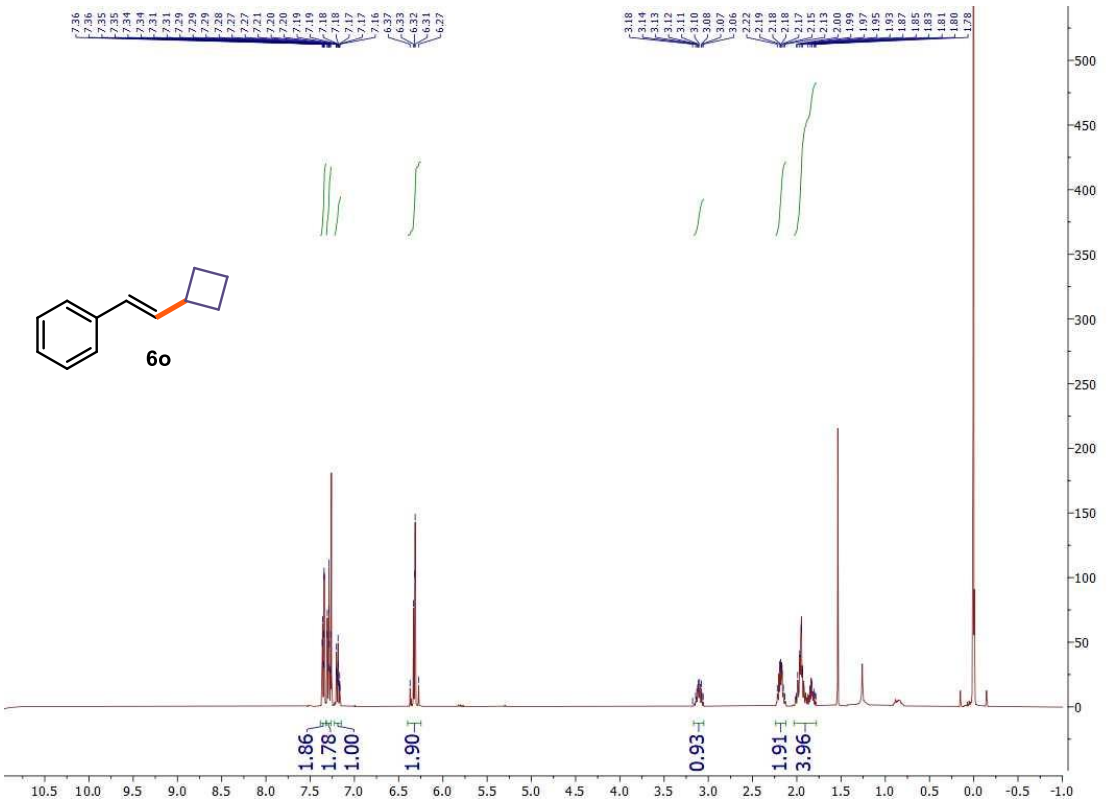
^{1}H NMR (500 MHz, $CDCl_3$)



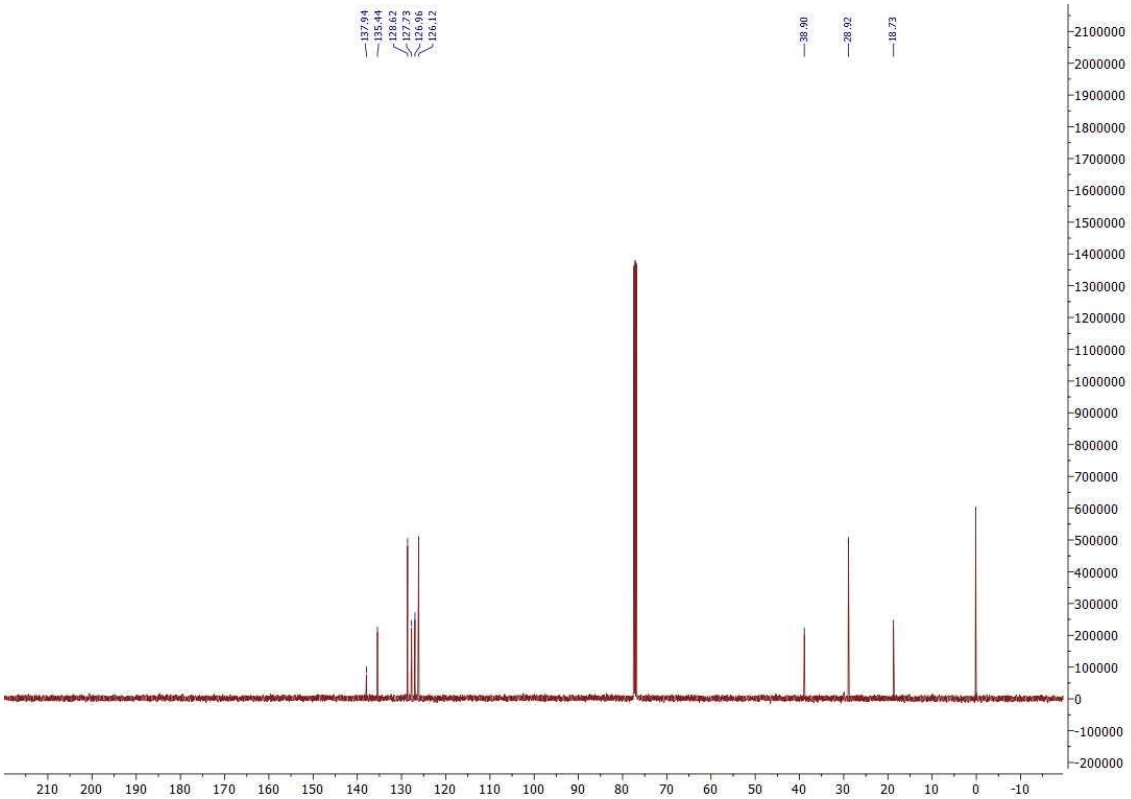
^{13}C NMR (126 MHz, $CDCl_3$)



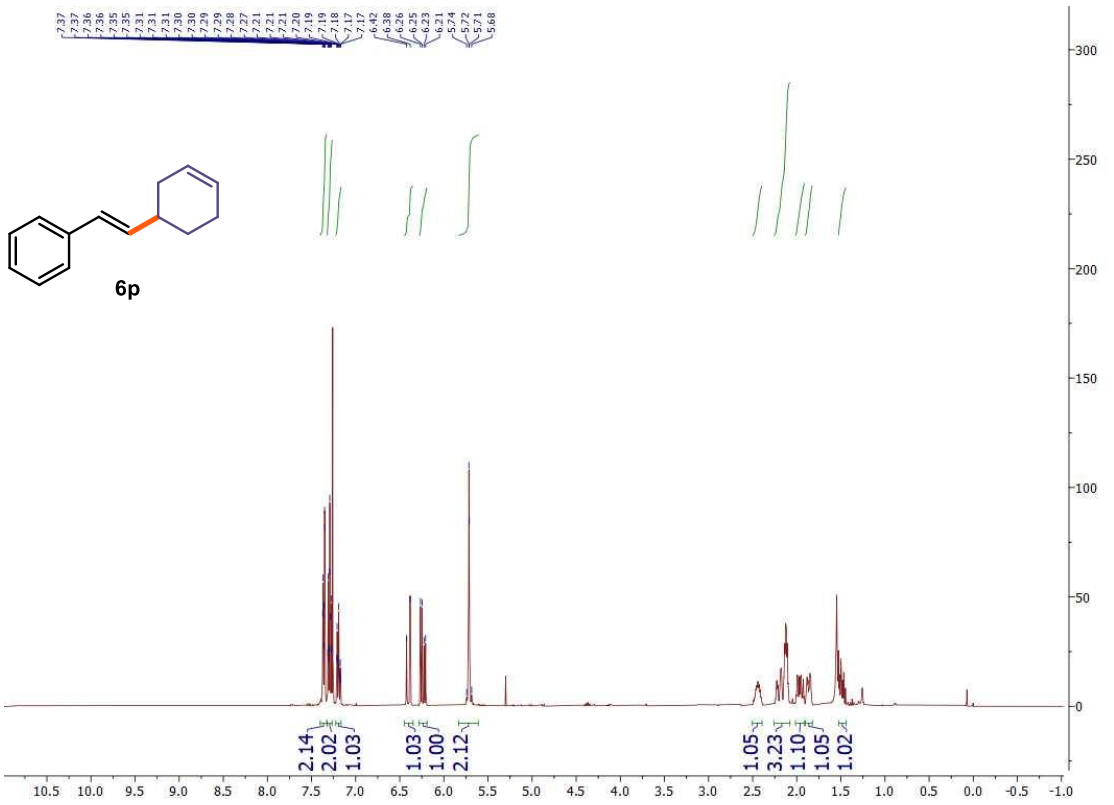
^{1}H NMR (400 MHz, $CDCl_3$)



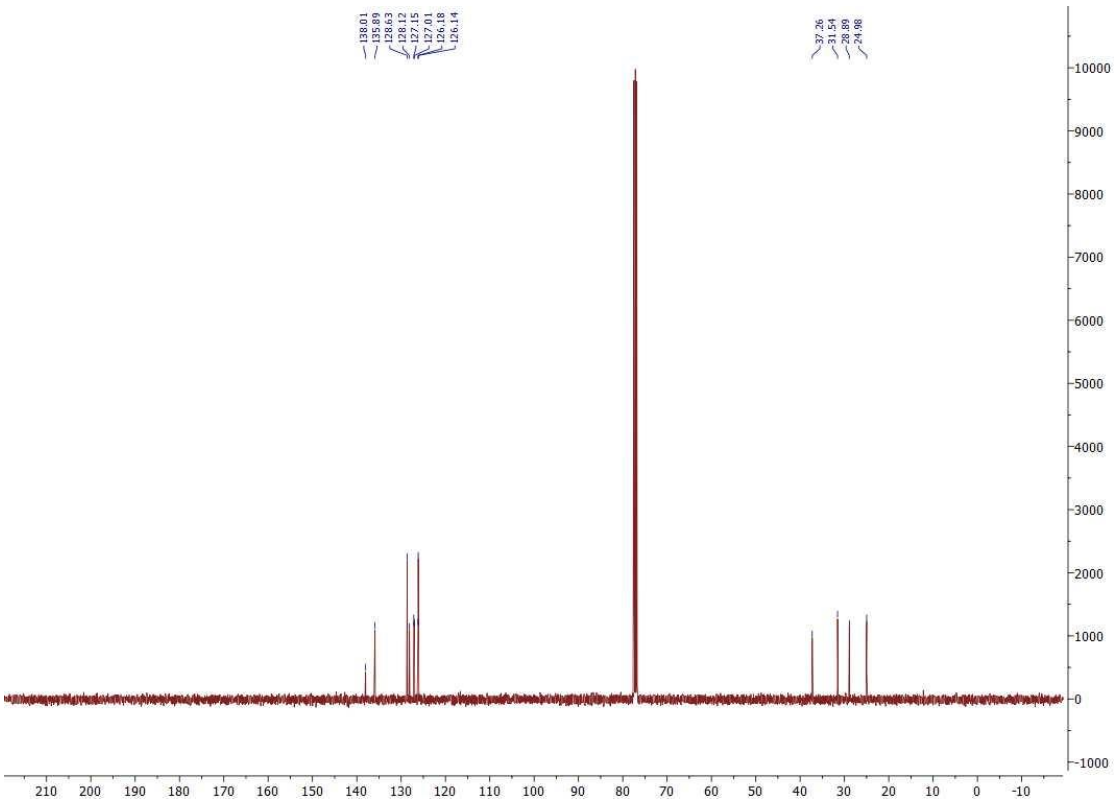
^{13}C NMR (126 MHz, $CDCl_3$)



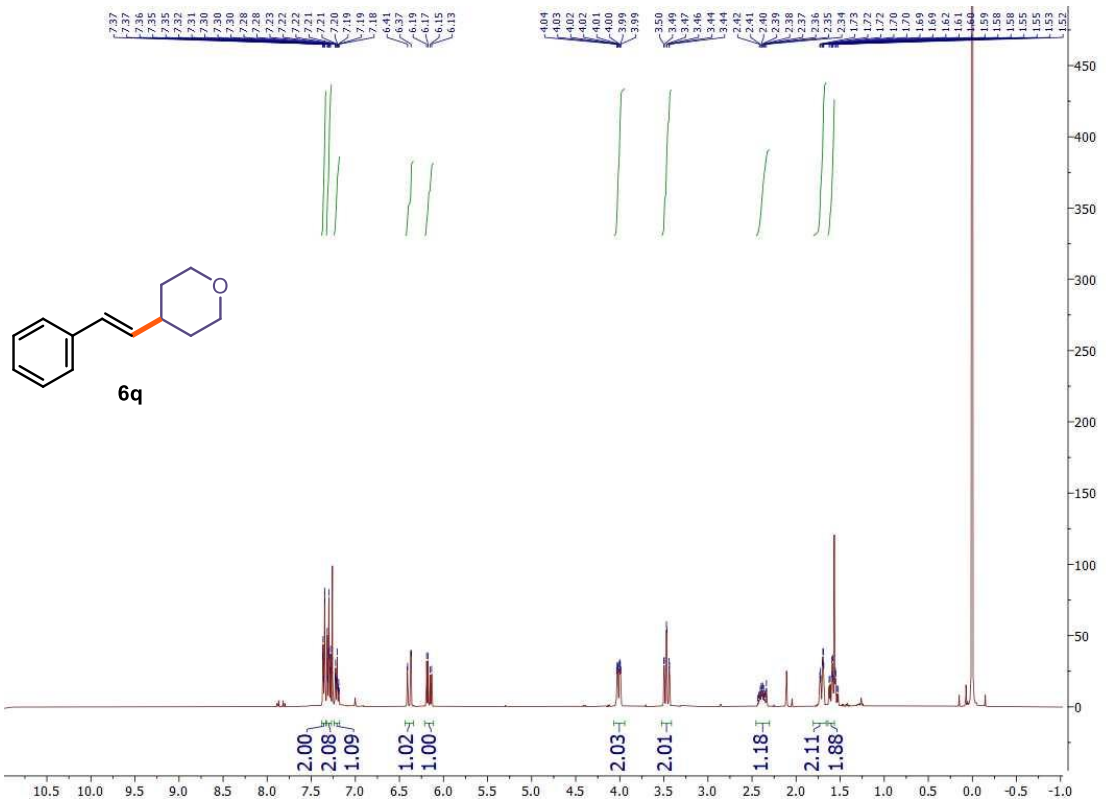
^{1}H NMR (400 MHz, $CDCl_3$)



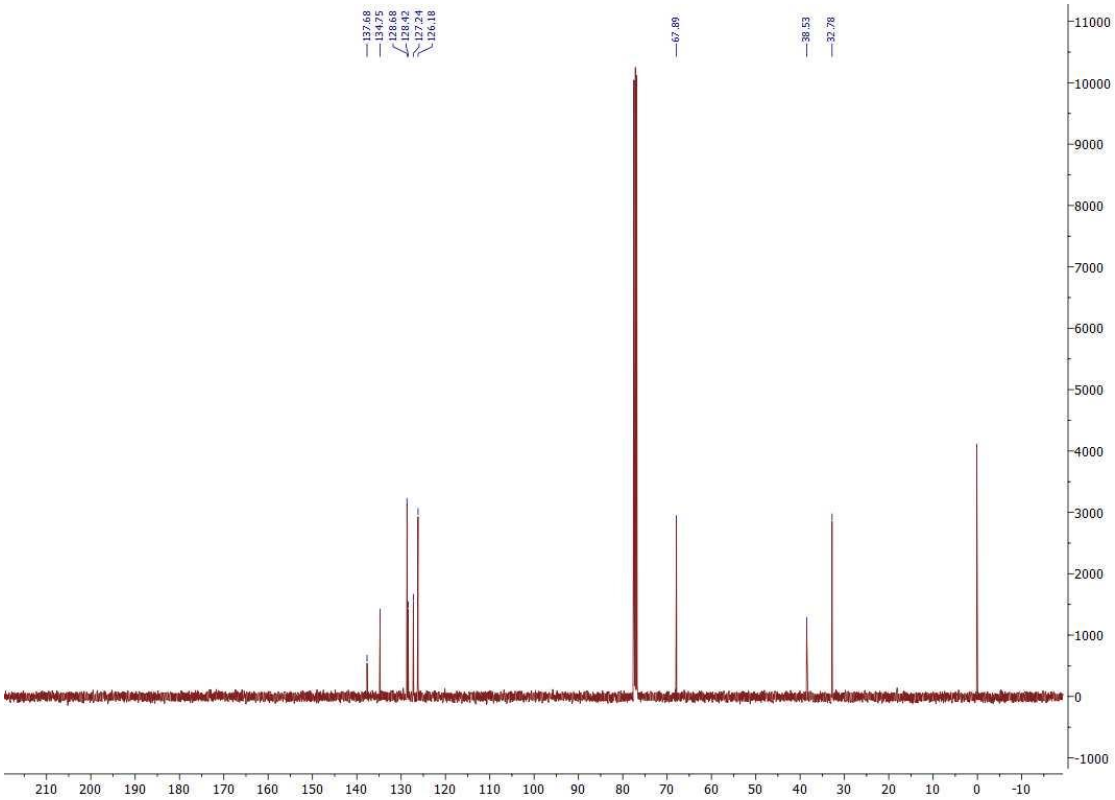
^{13}C NMR (101 MHz, $CDCl_3$)



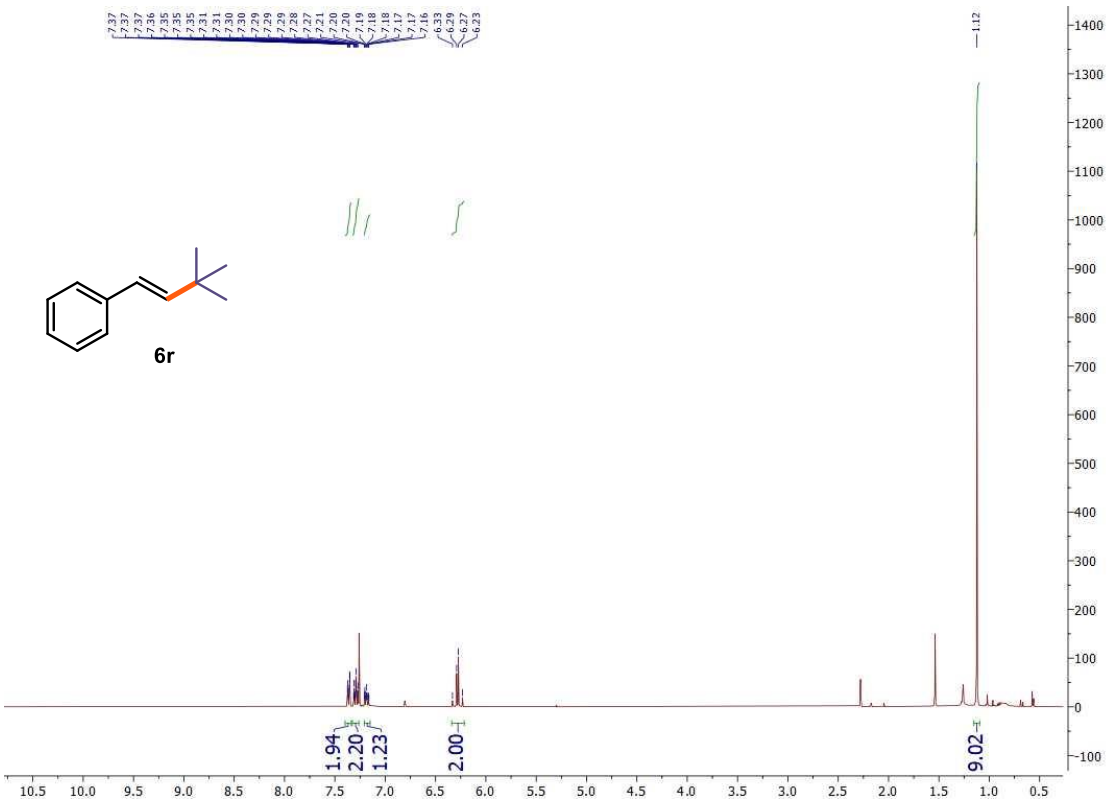
^{1}H NMR (400 MHz, $CDCl_3$)



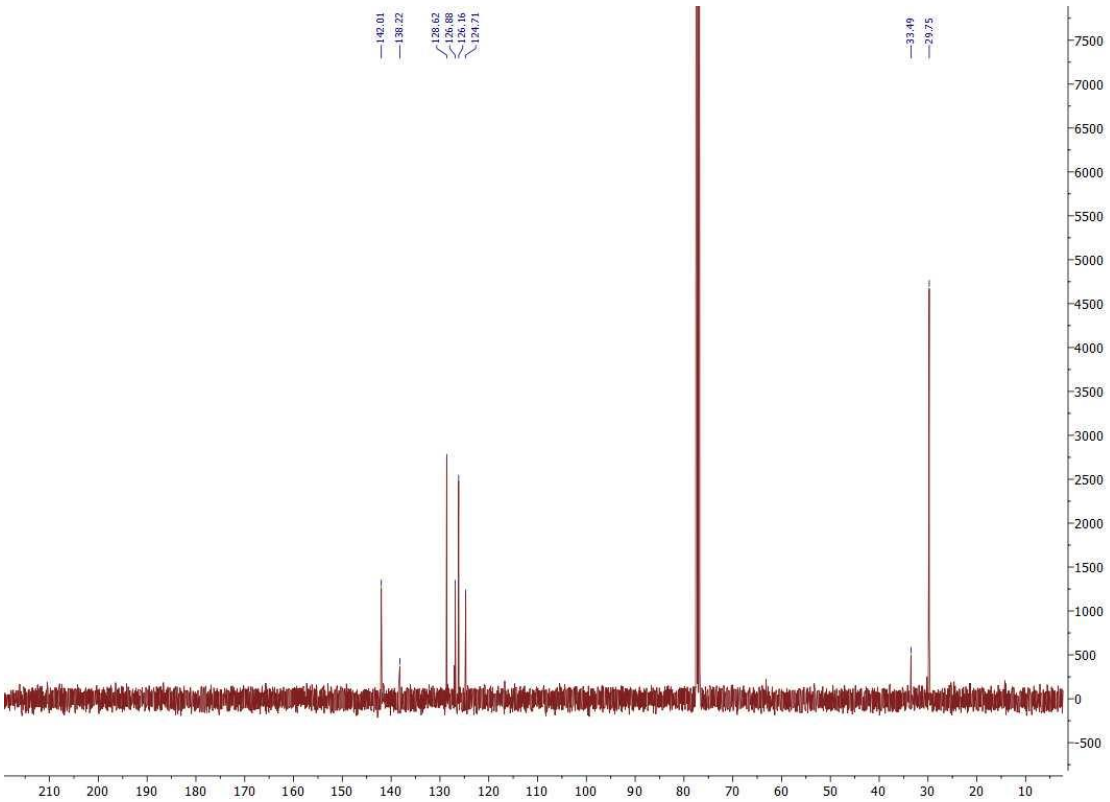
^{13}C NMR (101 MHz, $CDCl_3$)



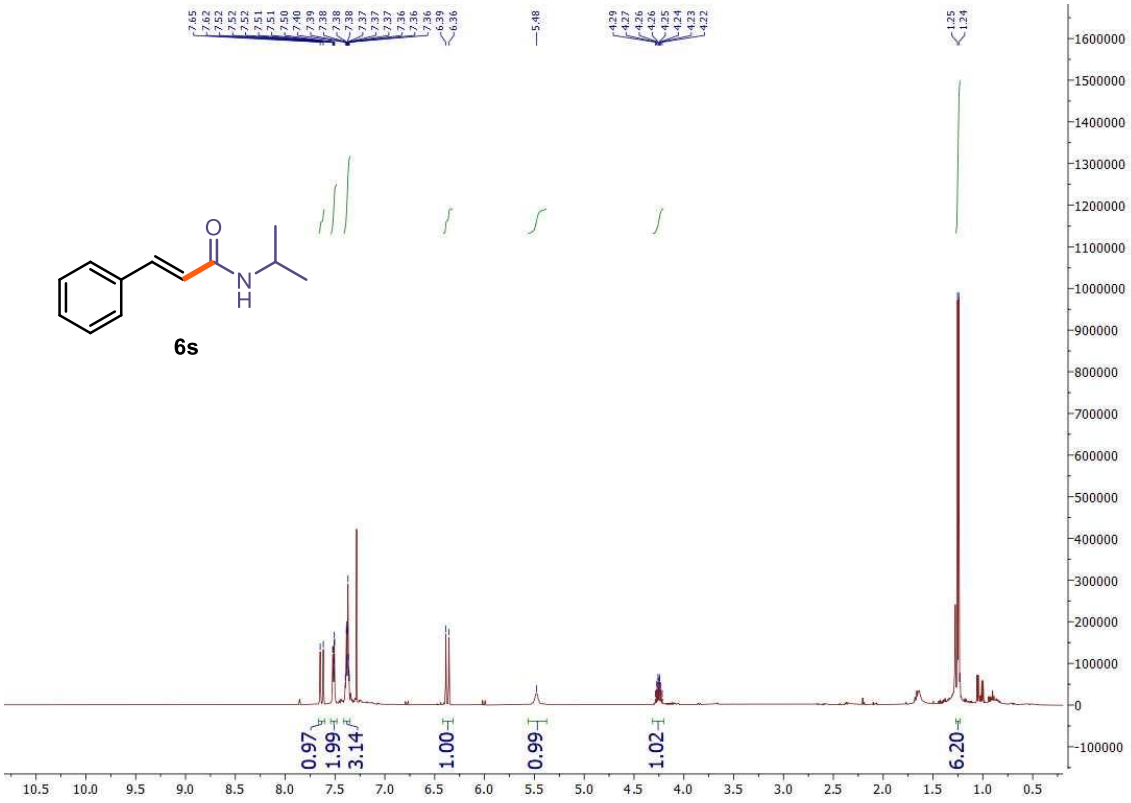
^{1}H NMR (400 MHz, $CDCl_3$)



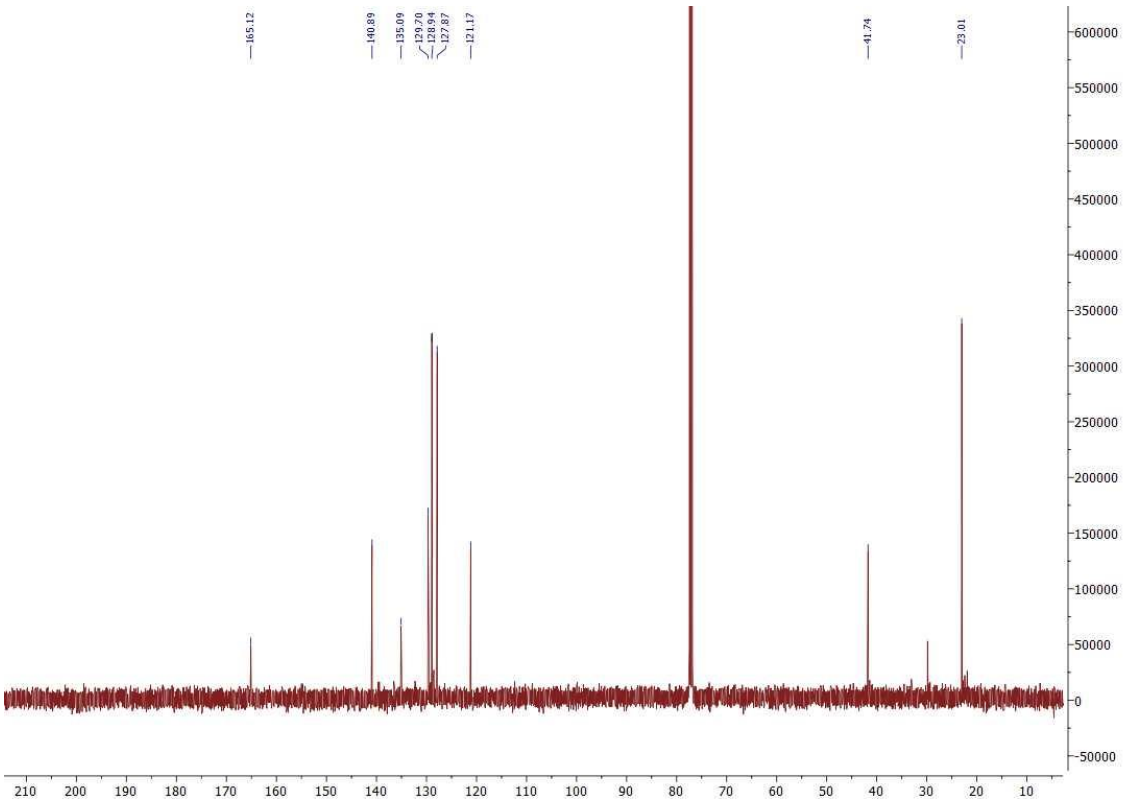
^{13}C NMR (101 MHz, $CDCl_3$)



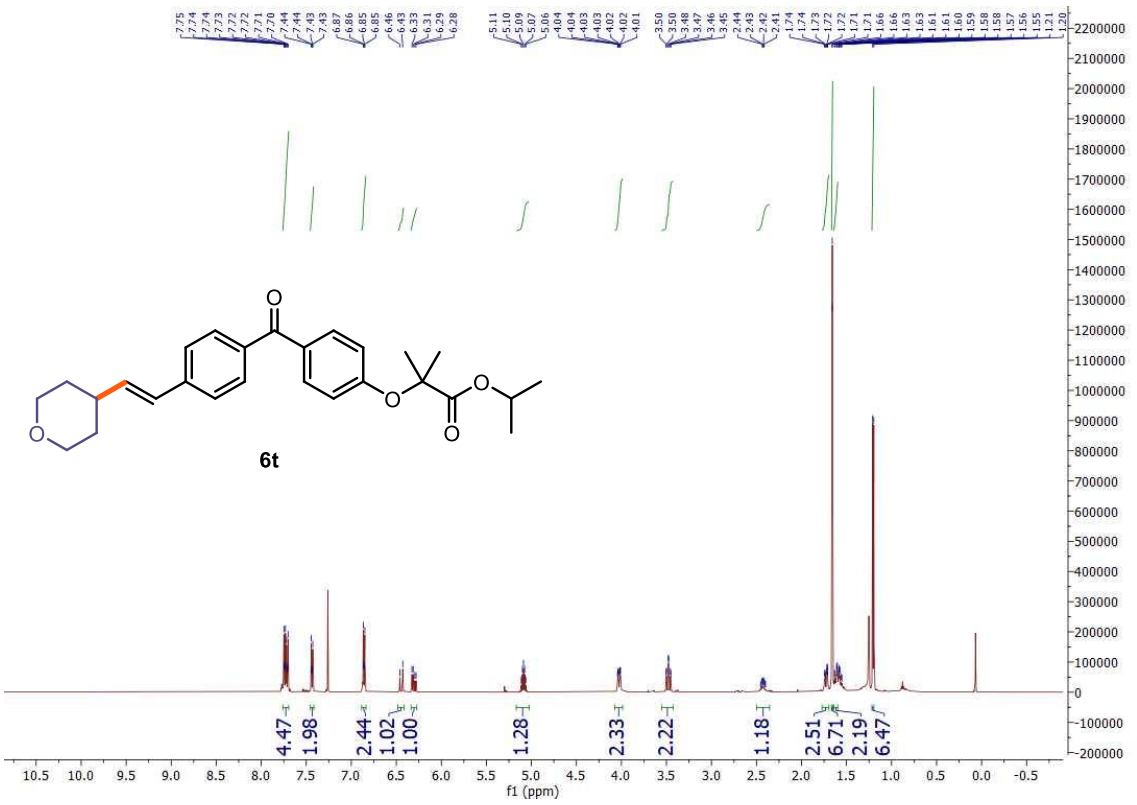
^{1}H NMR (500 MHz, $CDCl_3$)



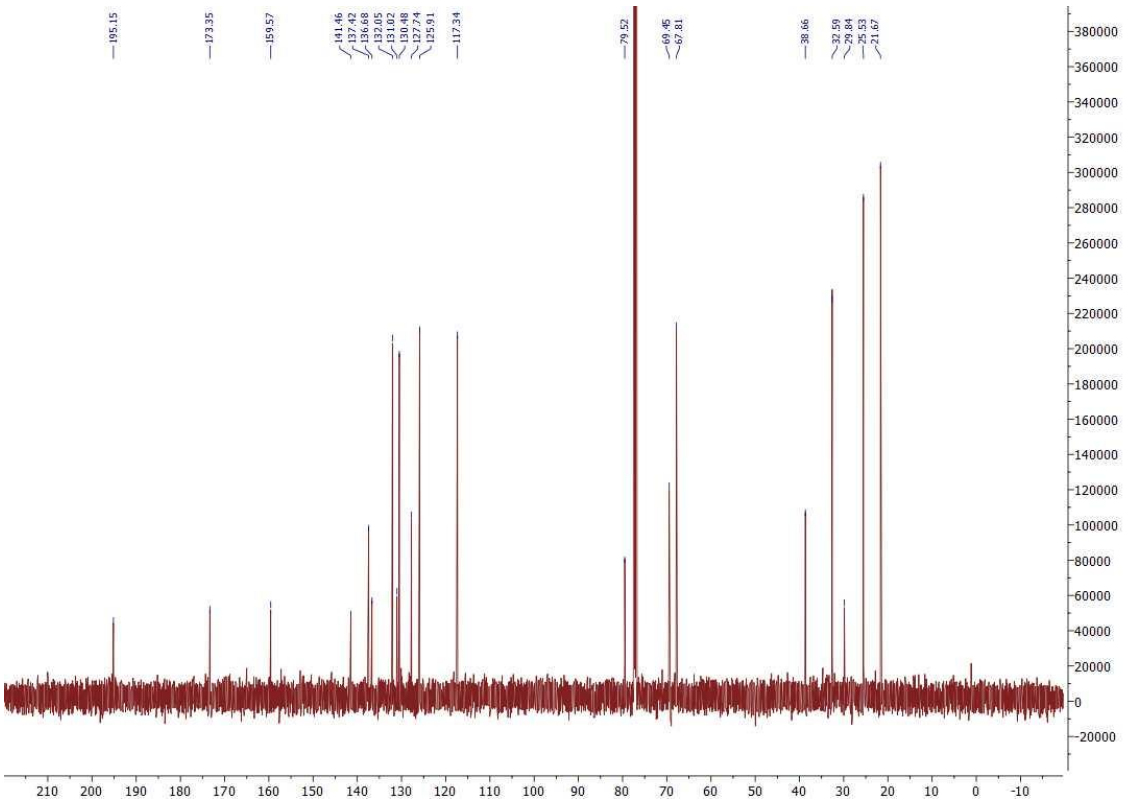
^{13}C NMR (126 MHz, $CDCl_3$)



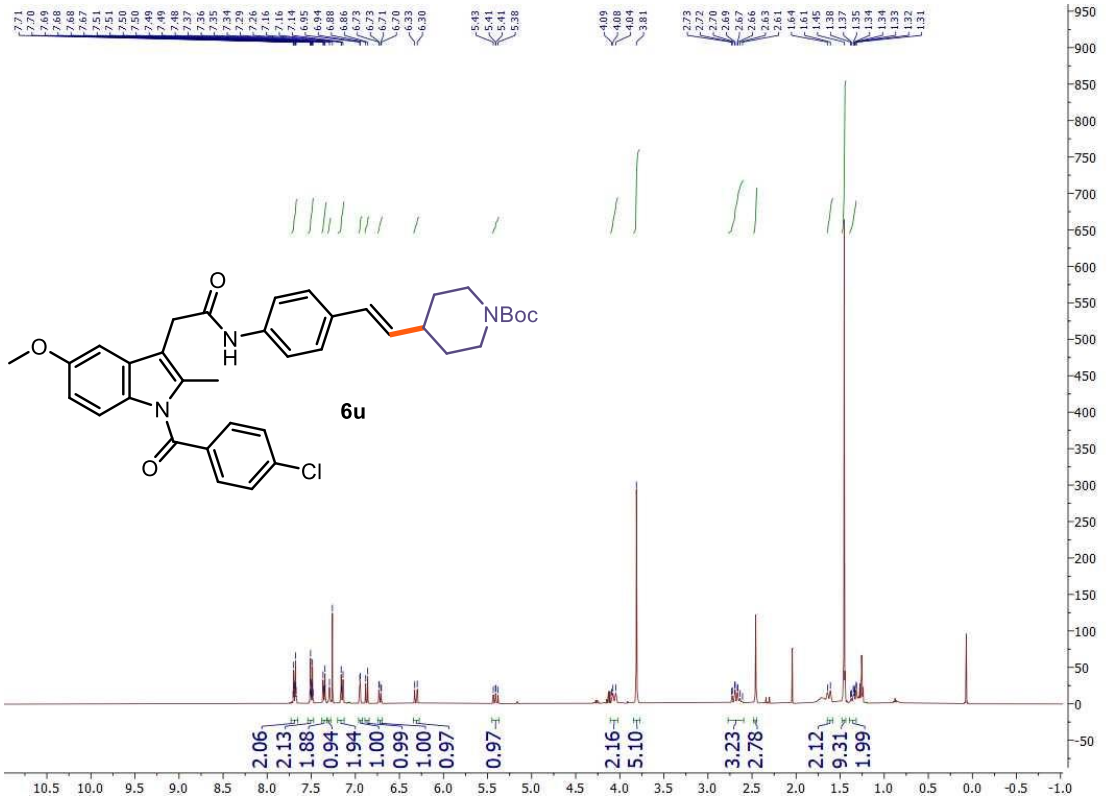
^{1}H NMR (500 MHz, $CDCl_3$)



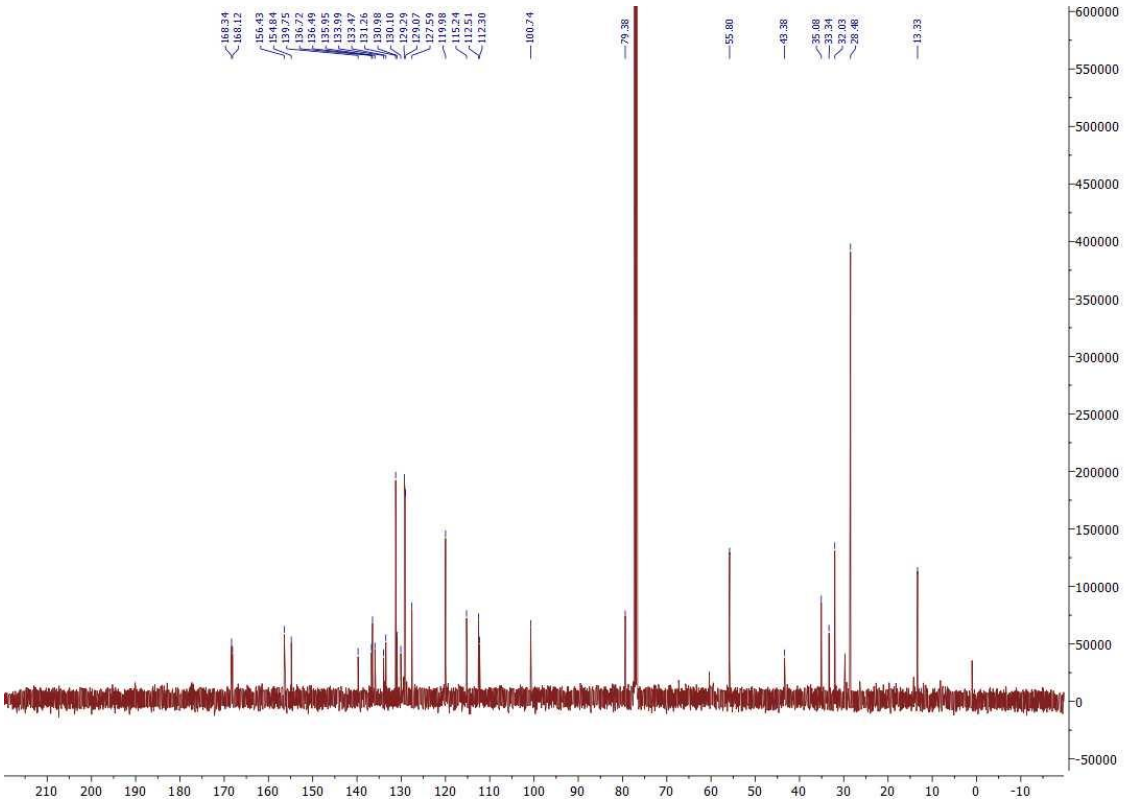
^{13}C NMR (126 MHz, $CDCl_3$)



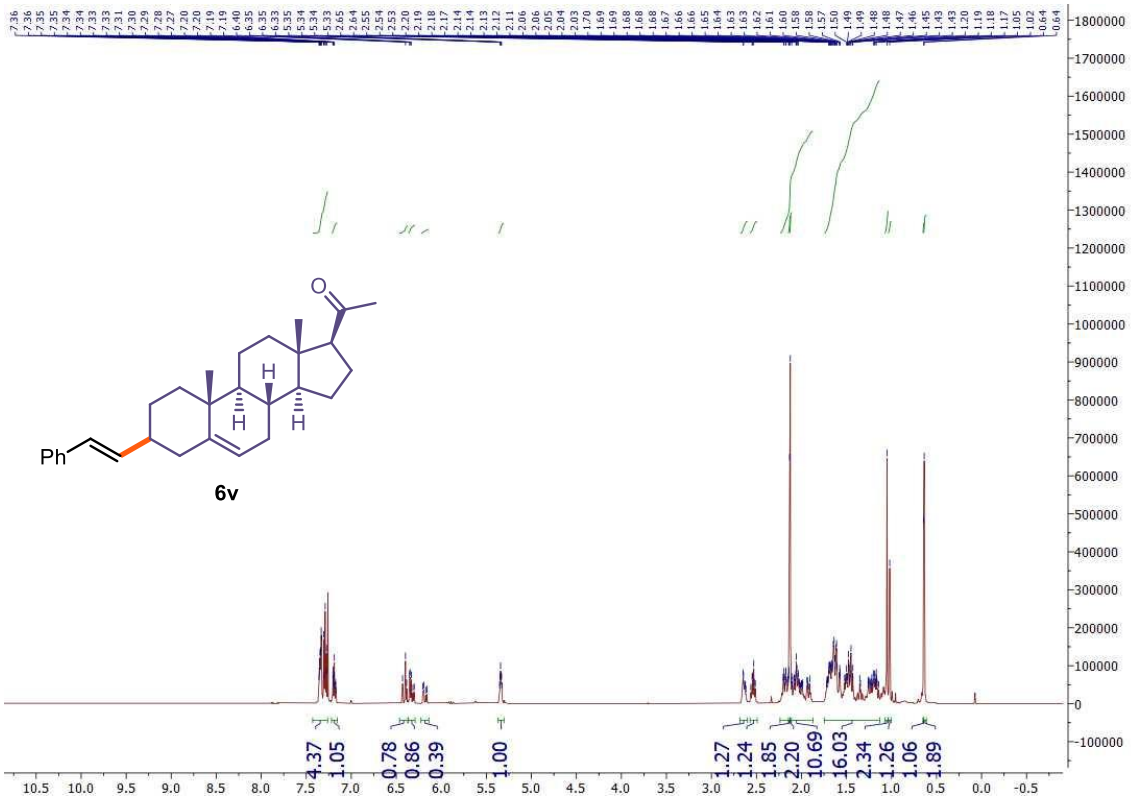
^{1}H NMR (400 MHz, $CDCl_3$)



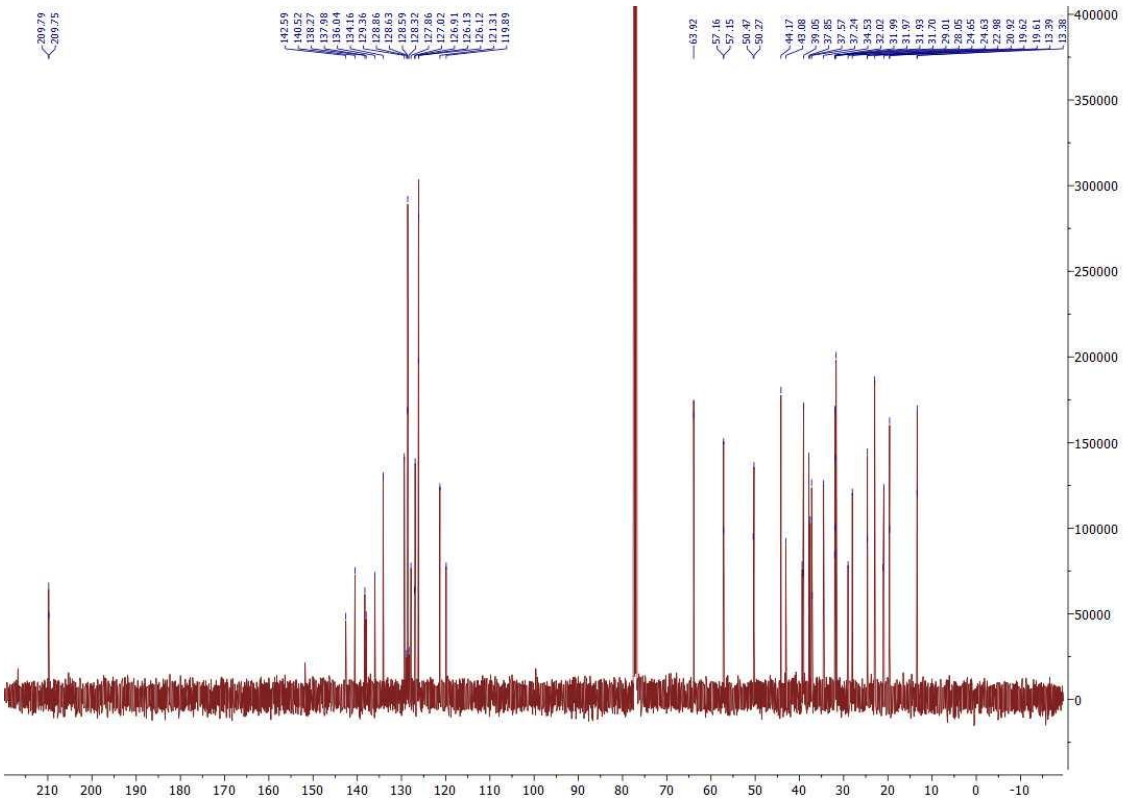
^{13}C NMR (126 MHz, $CDCl_3$)



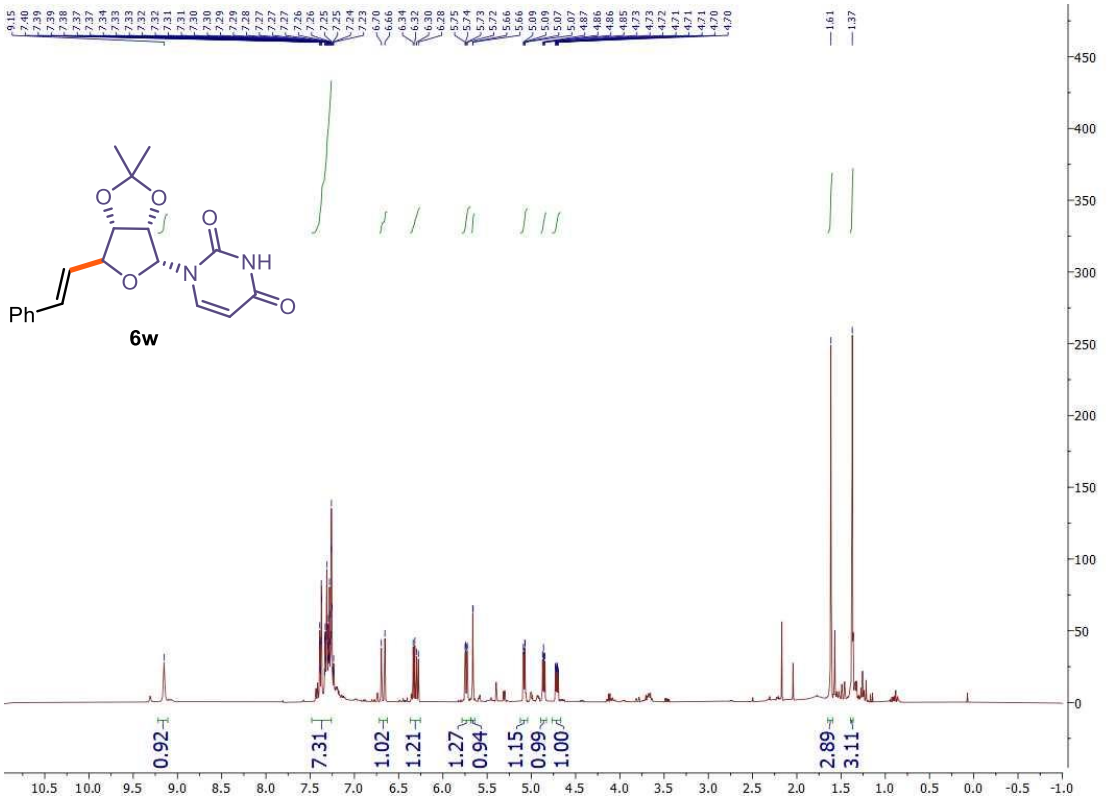
^{1}H NMR (500 MHz, $CDCl_3$)



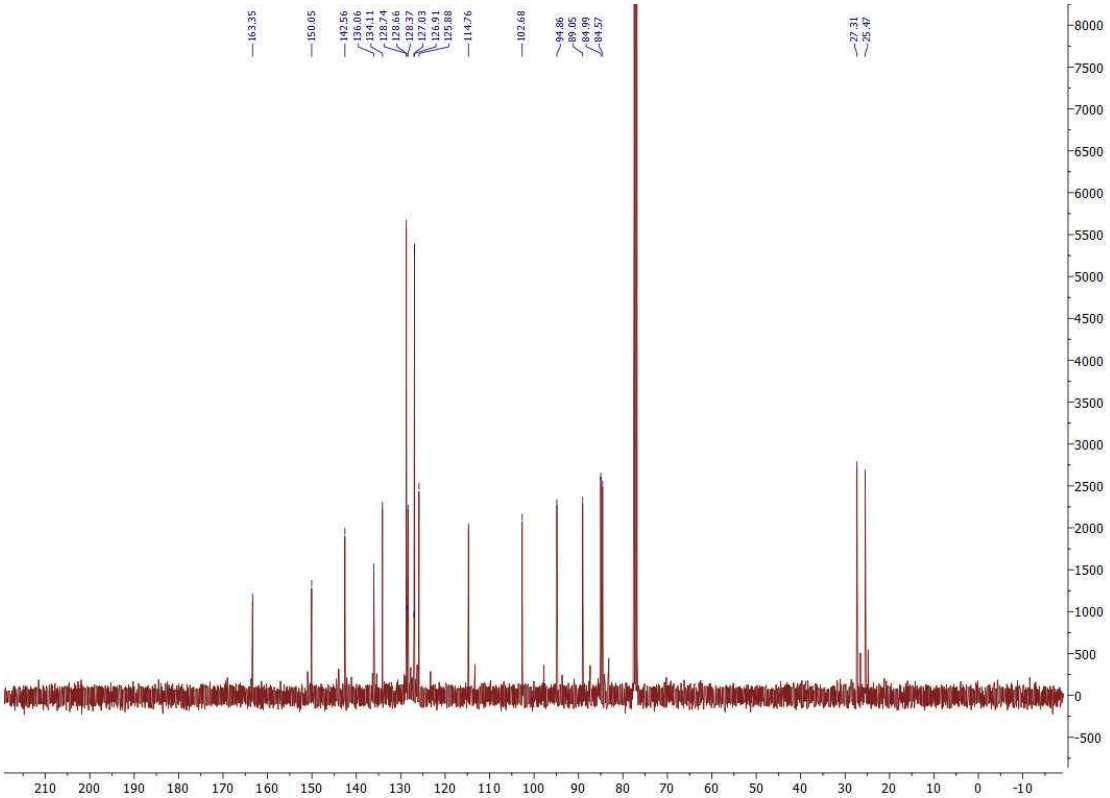
^{13}C NMR (126 MHz, $CDCl_3$)



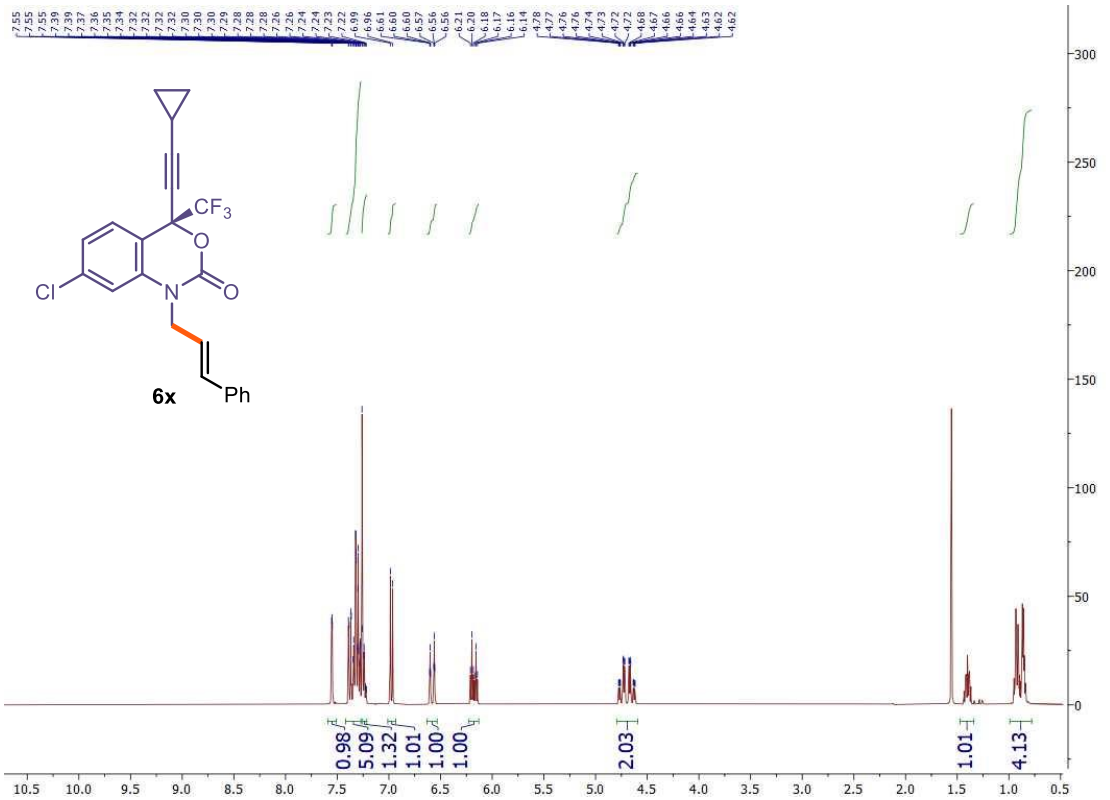
^{1}H NMR (400 MHz, $CDCl_3$)



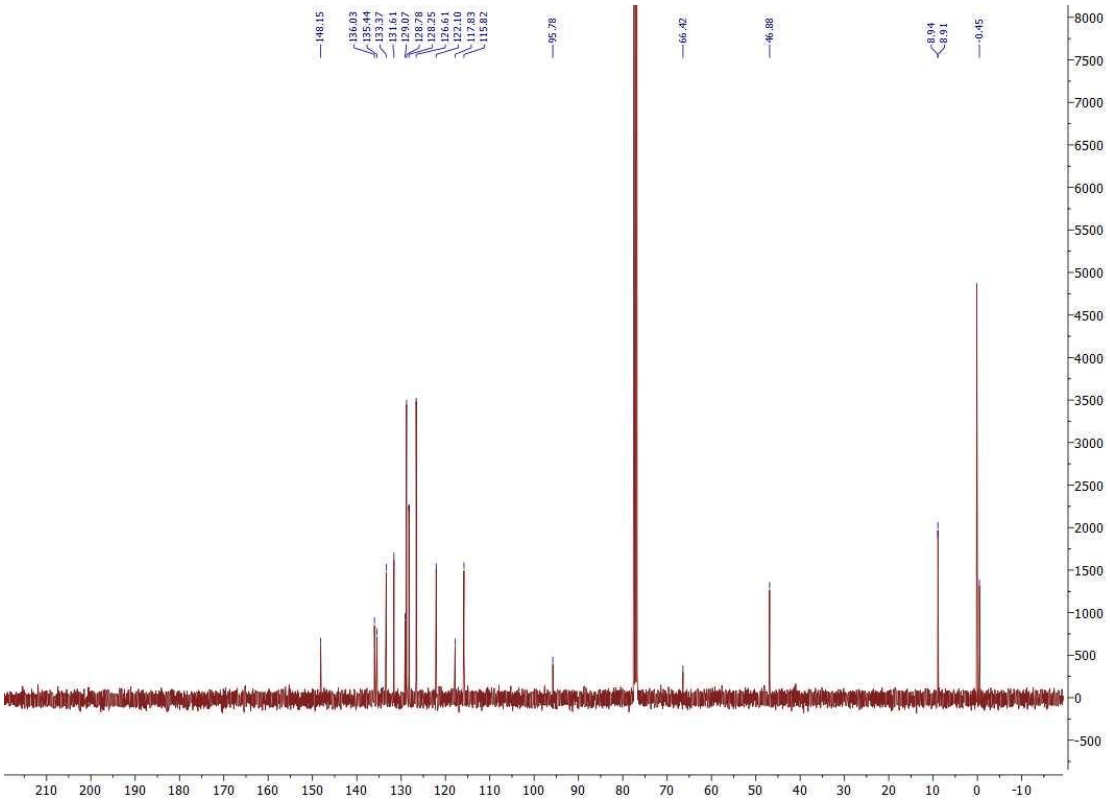
^{13}C NMR (101 MHz, $CDCl_3$)



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



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



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