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Supporting Information

A Redox Active Nickel Complex that Acts as an Electron Mediator in Photochemical Giese Reactions

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A. General Information

NMR spectra were recorded at 400 MHz and 500 MHz for ^1H and 100 or 125 MHz for ^{13}C. Chemical shifts (δ) are given in ppm relative to residual signals of the solvents ($CHCl_3$ at 7.26 ppm for ^1H NMR and $CDCl_3$ at 77.0 ppm for ^{13}C NMR). Coupling constants are given in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; p, pentet; sept, septet; m, multiplet; br, broad signal. NMR yields were determined by adding trichloroethylene (δ = 6.44 ppm) as an internal standard to the crude reaction mixtures and by integration of diagnostic signals. High-resolution mass spectra (HRMS) were obtained by the ICIQ High Resolution Mass Spectrometry Unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) apparatus with electrospray (ESI) or atmospheric pressure chemical ionization (APCI). Cyclic voltammetry (CV) studies were carried out on a Princeton Applied Research PARSTAT 2273 potentiostat. UV-Vis spectroscopy was performed on an Agilent Cary 60 UV-Vis spectrophotometer.

General Procedures

Chromatographic purification of products was accomplished using flash column chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used, employing UV light as the visualizing agent and either phosphomolybdic acid in EtOH or basic aqueous potassium permanganate ($KMnO_4$) and heat as developing agents. All reactions were set up under argon atmosphere in oven-dried glassware using standard Schlenk techniques, unless otherwise stated.

Materials

All reagents and solvents were obtained from commercial sources and used as received without further purification. $Ni(bpy)_3(BF_4)_2$ was prepared according to a literature procedure.[1]

B. Experimental Procedures

B1. Synthesis of Dihydropyridines

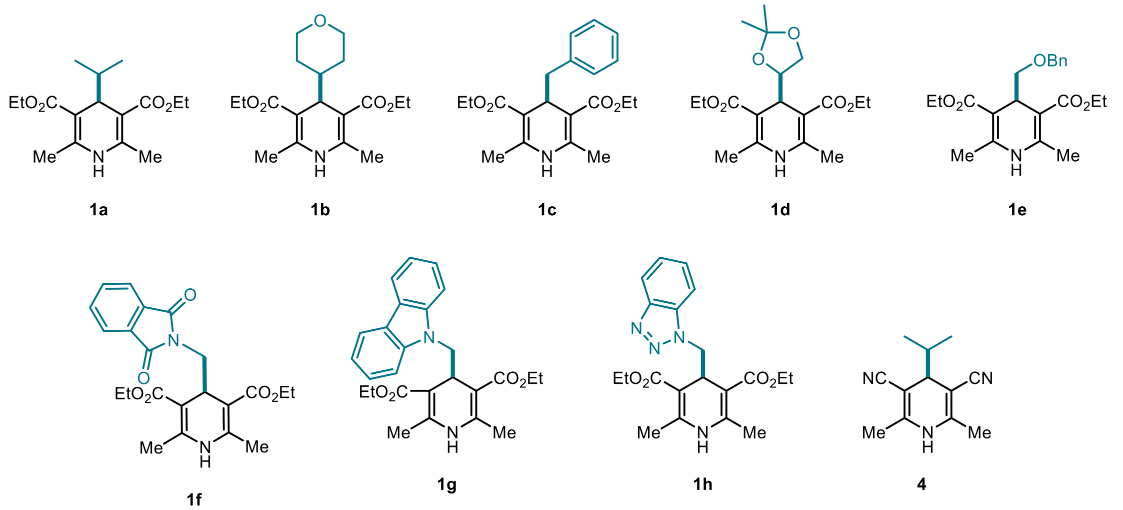
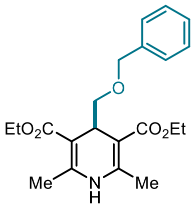

1a **1b** **1c** **1d** **1e** **1f** **1g** **1h** **4**

Figure S1. Dihydropyridines (**1a**-**h**, **4**) used in this study.

Compounds **1a-d** and **4** were prepared according to literature procedures.[2]

Preparation of **1e-h** - in accordance with the reported procedure,[2a] a solution of ethyl-3-aminocrotonate (1.0 equiv) in ethylene glycol (2.5 M) was added to a flask under nitrogen. Next, ethyl acetoacetate (1.0 equiv) was added followed by the appropriate aldehyde (1.0 equiv.) and tetrabutylammonium hydrogen sulfate (12 mol%). This solution was heated at 100 °C for 4 hours, then cooled and diluted with ethyl acetate. The solution was added to brine and separated using ethyl acetate. The organic layers were combined, dried (Na_2SO_4) and concentrated in vacuo. The crude material was purified by flash column chromatography to furnish the desired 4-alkyl-1,4-dihydropyridine.



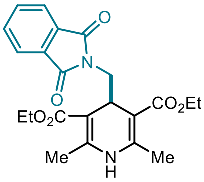
Diethyl 4-((benzyloxy)methyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1e):

Prepared according to the procedure described above using 2-(benzyloxy)acetaldehyde (2.00 g, 13.3 mmol). The crude material was purified by flash column chromatography (hexane/EtOAc 1:1) to afford **1e** (1.90 g, 38%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.18 (m, 5H), 5.54 (br, 1H), 4.52 (s, 2H), 4.27 (t, J = 5.6 Hz, 1H), 4.18 (qd, J = 7.1, 2.0 Hz, 4H), 3.37 (d, J = 5.6 Hz, 2H), 2.31 (s, 6H), 1.28 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 145.3, 139.1, 128.1, 127.1, 127.1, 100.7, 73.2, 72.4, 59.7, 34.1, 19.5, 14.4.

HRMS (ESI) calculated for $C_{21}H_{27}NNaO_5$ $[M+Na]^+$: 396.1781, found: 396.1771.



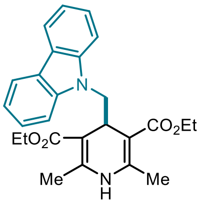
Diethyl 4-((1,3-dioxoisoindolin-2-yl)methyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1f):

Prepared according to the procedure described above using 2-(1,3-dioxoisoindolin-2-yl)acetaldehyde (0.90 g, 4.76 mmol). The crude material was purified by flash column chromatography (hexane/EtOAc 1:1) to afford **1f** (0.29 g, 15%) as a pale yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 – 7.76 (m, 2H), 7.70 – 7.65 (m, 2H), 5.82 (br, 1H), 4.37 (t, *J* = 6.5 Hz, 1H), 4.09 – 3.90 (m, 4H), 3.62 (d, *J* = 6.5 Hz, 2H), 2.29 (s, 6H), 1.21 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 168.5, 167.2, 146.6, 133.6, 132.2, 122.9, 100.4, 59.8, 41.0, 33.1, 19.4, 14.2.

HRMS (ESI) calculated for $C_{22}H_{23}N_2O_6$ [M–H]$^-$: 411.1562, found: 411.1569.



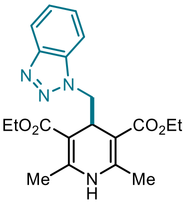
Diethyl 4-((9*H*-carbazol-9-yl)methyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1g):

Prepared according to the procedure described above using 2-(9*H*-carbazol-9-yl)acetaldehyde (2.34 g, 11.8 mmol).[3] The crude material was purified by flash column chromatography (hexane/EtOAc 7:3) to afford **1g** (0.73 g, 15%) as a pale yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.39 (d, *J* = 3.7 Hz, 4H), 7.15 (dt, *J* = 7.9, 4.0 Hz, 2H), 5.45 (s, 1H), 4.53 (t, *J* = 5.6 Hz, 1H), 4.28 (d, *J* = 5.6 Hz, 2H), 4.01 (dq, *J* = 10.8, 7.1 Hz, 2H), 3.83 (dq, *J* = 10.8, 7.1 Hz, 2H), 2.01 (s, 6H), 1.08 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.1, 146.7, 141.3, 125.1, 122.5, 119.8, 118.5, 109.2, 100.6, 59.8, 46.5, 34.3, 19.2, 14.0.

HRMS (ESI) calculated for $C_{26}H_{27}N_2O_4$ [M–H]$^-$: 431.1976, found: 431.1975.



Diethyl 4-((1*H*-benzo[d][1,2,3]triazol-1-yl)methyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1h):

Prepared according to the procedure described above using 2-(1*H*-benzo[d][1,2,3]triazol-1-yl)acetaldehyde (2.00 g, 12.4 mmol).[4] The crude material was purified by flash column chromatography (hexane/EtOAc 6:4) to afford **1h** (1.9 g, 40%) as a pale yellow solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.94 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.50 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.42 (ddd, *J* = 8.3, 6.8, 1.0 Hz, 1H), 7.29 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 5.78 (s, 1H), 4.60 (d, *J* = 4.6 Hz, 2H), 4.47 (t, *J* = 4.5 Hz, 1H), 4.25 – 3.91 (m, 4H), 2.04 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 167.0, 147.4, 145.4, 134.1, 126.7, 123.4, 119.4, 109.9, 98.9, 60.0, 52.2, 35.3, 19.2, 14.3.

HRMS (ESI) calculated for $C_{20}H_{24}N_4NaO_4$ [M+Na]$^+$: 407.1690, found: 407.1676.

B2. Reaction Setup

The photochemical reaction setup is shown in Figure S2. The reactions were performed in a 15 mL Schlenk tube. After addition of the reagents and the solvent, the reaction mixture was degassed using three freeze-pump-thaw cycles. Subsequently, the flask was backfilled with argon, sealed with Parafilm and placed into a 3D-printed plastic support mounted on an aluminum block fitted with a 405 nm high-power single LED (λ_{max} = 405 nm). The irradiance was fixed at 50±3 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.

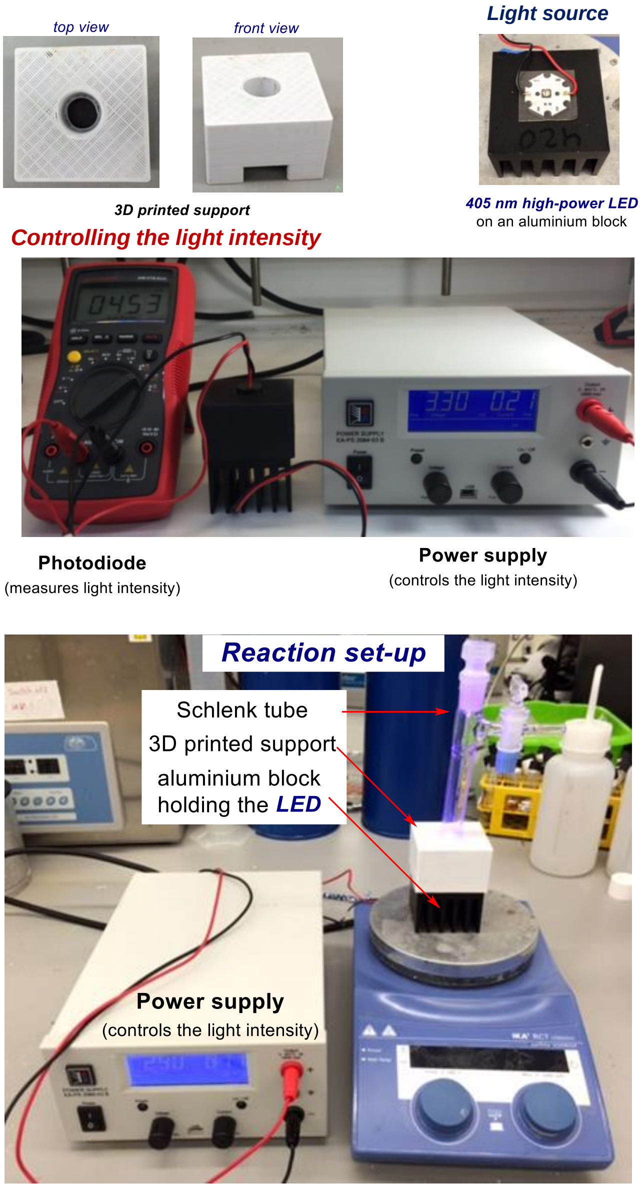


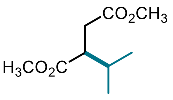
Figure S2. Experimental set-up and illumination system.

B3. Experimental Procedure for the Giese Reaction

In a Schlenk tube, $Ni(bpy)_3(BF_4)_2$ (0.01 mmol, 0.1 equiv.), the acceptor **2** (0.1 mmol, 1.0 equiv.), and dihydropyridine **1** (0.15 mmol, 1.5 equiv.) were added. Subsequently, CH_3CN (0.2 mL) was added (in the case of dihydropyridines **1b**, **1d**, **1e** and **1f**, CH_3CN (0.2 mL) and CH_2Cl_2 (0.2 mL) were added). The resulting solution was degassed by three freeze-pump-thaw cycles and conditioned under Ar atmosphere. The reaction mixture was stirred under irradiation at ambient temperature for 16 hours. The mixture was filtered over a plug of silica and concentrated in vacuo. The residue was purified by flash chromatography (silica gel) to afford the corresponding product **3**.

When the diethyl 2,6-dimethylpyridine-3,5-dicarboxylate byproduct had a R_f similar to that of products **3**, the pyridine was removed by dissolving the crude product in Et_2O (10 mL) and washing the organic layer with 1 M HCl_{aq} (3 x 10 mL) prior to purification by column chromatography.

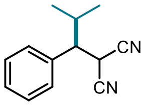
B4. Characterization of Products 3



Dimethyl 2-isopropylsuccinate (3a) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), dimethyl fumarate (14.4 mg, 0.1 mmol), dihydropyridine **1a** (44 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 19:1) to give the product **3a** (13.9 mg, 74% yield, average of two runs) as a colorless oil. The spectroscopic characterization matched with data reported in the literature.[5]

<u>^{1}H NMR</u> (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.66 (s, 3H), 2.79 – 2.66 (m, 2H), 2.48 – 2.35 (m, 1H), 1.98 (pd, *J* = 6.9, 4.8 Hz, 1H), 0.92 (dd, *J* = 6.9, 5.6 Hz, 6H).

<u>^{13}C NMR</u> (101 MHz, $CDCl_3$) δ 174.9, 172.9, 51.7, 51.6, 47.4, 32.9, 30.1, 20.0, 19.6.

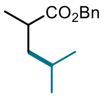


2-(2-Methyl-1-phenylpropyl)malononitrile (3b) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), 2-benzylidenemalononitrile (15.4 mg, 0.1 mmol) and dihydropyridine **1a** (44 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 9:1) to give the product **3a** (16.7 mg, 87% yield, average of two runs) as a colorless oil.

<u>^{1}H NMR</u> (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 5H), 4.16 (d, *J* = 5.7 Hz, 1H), 2.84 (dd, *J* = 9.7, 5.6 Hz, 1H), 2.39 (dsept, *J* = 9.6, 6.6 Hz, 1H), 1.14 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H).

<u>^{13}C NMR</u> (101 MHz, $CDCl_3$) δ 136.6, 129.1, 128.8, 128.2, 112.1, 111.8, 53.4, 30.2, 27.7, 20.9, 20.3.

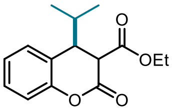
<u>HRMS</u> (APCI) calculated for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1230, found: 199.1229.



Benzyl 2,4-dimethylpentanoate (3c) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), benzyl methacrylate (17.6 mg, 0.1 mmol) and dihydropyridine **1a** (44 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 97:3) to give the product **3c** (18 mg, 82% yield, average of two runs) as a colorless oil. The spectroscopic characterization matched with data reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 5.11 (s, 2H), 2.64 – 2.51 (m, 1H), 1.67 – 1.51 (m, 2H), 1.30 – 1.18 (m, 1H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 136.3, 128.5, 128.1, 128.0, 66.0, 43.0, 37.6, 25.9, 22.5, 22.4, 17.5.



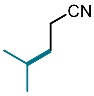
***Trans*-ethyl 4-isopropyl-2-oxochromane-3-carboxylate (3d)**

Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), ethyl 2-oxo-2*H*-chromene-3-carboxylate (21.8 mg, 0.1 mmol) and dihydropyridine **1a** (44 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 9:1) to give the product **3d** (22.5 mg, 86% yield, average of two runs) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.16 – 7.06 (m, 3H), 4.06 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.98 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.90 (d, *J* = 1.7 Hz, 1H), 3.08 (dd, *J* = 8.1, 1.8 Hz, 1H), 1.79 (dsept, *J* = 8.1, 6.7 Hz, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.99 (t, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H).

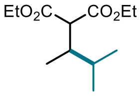
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 165.0, 151.0, 129.8, 128.8, 124.3, 123.1, 116.9, 62.1, 50.1, 46.9, 32.0, 20.1, 19.7, 13.7.

HRMS (ESI) calculated for $C_{15}H_{18}NaO_4$ $[M+Na]^+$: 285.1097, found: 285.1085.



4-Methylpentanenitrile (3e) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), acrylonitrile (5.3 mg, 0.1 mmol) and dihydropyridine **1a** (44 mg, 0.15 mmol) and CH_3CN (200 µL). The yield of **3e** (average of two runs) was determined by ^{1}H NMR using 1,1,2-trichloroethene as internal standard (volatility of the compound prevented us to obtain accurate isolated yields). The spectroscopic characterization matched with data reported in the literature.[7]

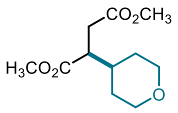
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (t, *J* = 7.4 Hz, 2H), 1.77 – 1.62 (m, 1H), 1.52 (q, *J* = 7.2 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H).



Diethyl 2-(3-methylbutan-2-yl)malonate (3f) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), diethyl 2-ethylidenemalonate (18.6 mg, 0.1 mmol) and dihydropyridine **1a** (44 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc: 19:1) to give the product **3f** (16 mg, 70% yield, average of two runs) as a colorless oil. The spectroscopic characterization matched with data reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (q, *J* = 7.1 Hz, 4H), 3.33 (d, *J* = 9.4 Hz, 1H), 2.20 (dqd, *J* = 9.4, 6.9, 4.4 Hz, 1H), 1.67 (hd, *J* = 6.8, 4.3 Hz, 1H), 1.26 (td, *J* = 7.1, 2.7 Hz, 6H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 169.0, 61.2, 61.1, 56.5, 38.9, 29.6, 21.3, 16.6, 14.1, 14.1, 11.7.

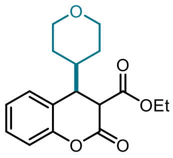


Dimethyl 2-(tetrahydro-2H-pyran-4-yl)succinate (3g) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), dimethyl fumarate (14.4 mg, 0.1 mmol) and dihydropyridine **1b** (50.6 mg, 0.15 mmol), CH_2Cl_2 (200 µL) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 7:3) to give the product **3g** (16.5 mg, 72% yield, average of two runs) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 – 3.92 (m, 2H), 3.71 (s, 3H), 3.67 (s, 3H), 3.40 – 3.29 (m, 2H), 2.80 – 2.66 (m, 2H), 2.54 – 2.40 (m, 1H), 1.92 – 1.74 (m, 1H), 1.60 – 1.33 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 172.9, 68.2, 68.2, 52.2, 52.1, 46.9, 37.6, 33.5, 30.8, 30.5.

HRMS (ESI) calculated for $C_{11}H_{18}NaO_5$ $[M+Na]^+$: 253.1046, found: 253.1049.



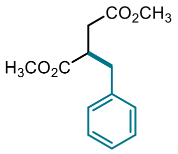
Ethyl 2-oxo-4-(tetrahydro-2*H*-pyran-4-yl)chromane-3-carboxylate (3h)

Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), ethyl 2-oxo-2*H*-chromene-3-carboxylate (21.8 mg, 0.1 mmol) and dihydropyridine **1b** (50.6 mg, 0.15 mmol), CH_2Cl_2 (200 µL) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 7:3) to give the product **3h** (21.5 mg, 71% yield, average of two runs) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (ddd, J = 8.0, 6.5, 2.7 Hz, 1H), 7.15 – 7.07 (m, 3H), 4.13 – 3.88 (m, 5H), 3.31 (td, J = 11.8, 2.3 Hz, 1H), 3.27 – 3.17 (m, 1H), 3.11 (dd, J = 8.9, 1.9 Hz, 1H), 1.78 – 1.71 (m, 1H), 1.64 – 1.54 (m, 1H) 1.51 – 1.34 (m, 3H), 0.98 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 164.7, 150.9, 129.8, 129.1, 124.4, 122.2, 117.1, 67.5, 67.5, 62.2, 49.5, 45.6, 38.2, 30.6, 30.1, 13.7.

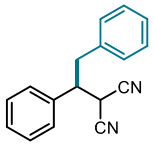
HRMS (ESI) calculated for $C_{17}H_{20}NaO_5$ $[M+Na]^+$: 327.1203, found 327.1205.



Dimethyl 2-benzylsuccinate (3i) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), dimethyl fumarate (14.4 mg, 0.1 mmol) and dihydropyridine **1c** (51.5 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 9:1) to give the product **3i** (11 mg, 47% yield, average of two runs) as a colorless oil. The spectroscopic characterization matched with data reported in the literature.[9]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.17 – 7.13 (m, 2H), 3.67 (s, 3H), 3.64 (s, 3H), 3.18 – 3.10 (m, 1H), 3.05 (dd, J = 13.6, 6.4 Hz, 1H), 2.76 (dd, J = 13.6, 8.3 Hz, 1H), 2.68 (dd, J = 16.8, 9.1 Hz, 1H), 2.41 (dd, J = 16.8, 5.0 Hz, 1H).

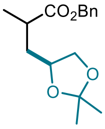
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 172.2, 138.1, 129.0, 128.5, 126.7, 51.9, 51.7, 43.0, 37.7, 34.9.



2-(1,2-Diphenylethyl)malononitrile (3j) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), 2-benzylidenemalononitrile (15.4 mg, 0.1 mmol) and dihydropyridine **1c** (51.5 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 9:1) to give the product **3j** (20.2 mg, 82% yield, average of two runs) as a colorless film. The spectroscopic characterization matched with data reported in the literature.[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 5H), 7.36 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 7.21 – 7.17 (m, 2H), 3.86 (d, *J* = 5.1 Hz, 1H), 3.47 (ddd, *J* = 8.5, 7.1, 5.1 Hz, 1H), 3.33 – 3.21 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 136.4, 129.2, 129.1, 129.0, 128.9, 128.0, 127.6, 112.0, 111.4, 48.3, 38.5, 28.5.



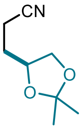
Benzyl 3-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-methylpropanoate (3k)

Prepared according to the general procedure using Ni(bpy)$_3$(BF)$_2$ (7.0 mg, 0.01 mmol), benzyl methacrylate (17.6 mg, 0.1 mmol) and dihydropyridine **1d** (53.0 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 9:1) to give the product **3k**, 1:1 mixture of diastereoisomers (16 mg, 58% yield, average of two runs) as a colorless oil.

<u>^{1}H NMR</u> (500 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 5H), 5.13 (s, 2H, diastereoisomer A), 5.12 (d, *J* = 2.8 Hz, 2H, diastereoisomer B), 4.14 – 4.05 (m, 1H), 4.03 (dd, *J* = 7.9, 5.9 Hz, 1H, diastereoisomer B), 3.98 (dd, *J* = 7.9, 6.0 Hz, 1H, diastereoisomer A), 3.51 (dd, *J* = 7.9, 7.0 Hz, 1H, diastereoisomer B), 3.46 (dd, *J* = 7.9, 7.2 Hz, 1H, diastereoisomer A), 2.72 (dqd, *J* = 9.3, 7.1, 4.8 Hz, 1H, diastereoisomer A), 2.65 (h, *J* = 7.0 Hz, 1H, diastereoisomer B), 2.05 (ddd, *J* = 13.8, 8.1, 7.0 Hz, 1H, diastereoisomer B), 1.94 (ddd, *J* = 13.7, 9.3, 4.3 Hz, 1H, diastereoisomer A), 1.70 – 1.56 (m, 1H), 1.38 (s, 3H), 1.31 (s, 3H, diastereoisomer B), 1.30 (s, 3H, diastereoisomer A), 1.23 (d, *J* = 7.1, 3H, diastereoisomer B), 1.23 (d, *J* = 7.0, 3H, diastereoisomer A).

<u>^{13}C NMR</u> (126 MHz, $CDCl_3$) δ 176.1 (diastereoisomer B), 176.0 (diastereoisomer A), 136.0, 128.5, 128.1, 128.1 (diastereoisomer B), 128.0 (diastereoisomer A), 108.9 (diastereoisomer B), 108.9 (diastereoisomer A), 74.2 (diastereoisomer A), 73.6 (diastereoisomer B), 69.4 (diastereoisomer A), 69.4 (diastereoisomer B), 66.2 (diastereoisomer B), 66.2 (diastereoisomer A), 37.6 (diastereoisomer A), 37.3 (diastereoisomer B), 36.7 (diastereoisomer A), 36.6 (diastereoisomer B), 26.9 (diastereoisomer A), 26.9 (diastereoisomer B), 25.7 (diastereoisomer A), 25.6 (diastereoisomer B), 18.1 (diastereoisomer A), 16.9 (diastereoisomer B).

<u>HRMS</u> (ESI) calculated for $C_{16}H_{22}NaO_4$ $[M+Na]^+$: 301.1410, found: 301.1411.



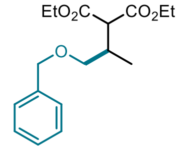
3-(2,2-Dimethyl-1,3-dioxolan-4-yl)propanenitrile (3l)

Prepared according to the general procedure using Ni(bpy)$_3$(BF)$_2$ (7.0 mg, 0.01 mmol), acrylonitrile (5.3 mg, 0.1 mmol) and dihydropyridine **1d** (53.0 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 8:2) to give the product **3l**, (7.9 mg, 51% yield, average of two runs) as a colorless oil.

<u>^{1}H NMR</u> (500 MHz, $CDCl_3$) δ 4.19 (dtd, *J* = 8.4, 6.2, 3.9 Hz, 1H), 4.10 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.60 (dd, *J* = 8.2, 6.3 Hz, 1H), 2.56 – 2.41 (m, 2H), 1.97 – 1.79 (m, 2H), 1.41 (d, *J* = 0.7 Hz, 3H), 1.35 (d, *J* = 0.7 Hz, 3H).

<u>^{13}C NMR</u> (101 MHz, $CDCl_3$) δ 119.3, 109.5, 73.8, 68.6, 29.8, 26.9, 25.4, 13.8.

<u>HRMS</u> (APCI) calculated for $C_8H_{14}NO_2$ $[M+H]^+$: 156.1019, found: 156.1013.



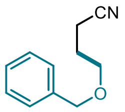
Diethyl 2-(1-(benzyloxy)propan-2-yl)malonate (3m)

Prepared according to the general procedure using Ni(bpy)$_3$(BF)$_2$ (7.0 mg, 0.01 mmol), diethyl 2-ethylidenemalonate (18.6 mg, 0.1 mmol) and dihydropyridine **1e** (56.0 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 24:1) to give the product **3m**, (12 mg, 39% yield, average of two runs) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 4.47 (s, 2H), 4.21 – 4.09 (m, 4H), 3.51 (d, J = 7.6 Hz, 1H), 3.44 (d, J = 6.3 Hz, 2H), 2.59 (tt, J = 7.4, 6.2 Hz, 1H), 1.24 (dt, J = 10.2, 7.1 Hz, 6H), 1.04 (d, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 168.7, 138.4, 128.3, 127.6, 127.5, 73.0, 72.9, 61.2, 61.1, 54.3, 33.9, 14.7, 14.1, 14.0.

HRMS (ESI) calculated for $C_{17}H_{24}NaO_5$ $[M+Na]^+$: 331.1516, found: 331.1514.

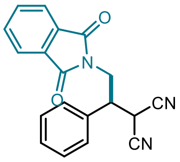


4-(Benzyloxy)butanenitrile (3n) - Prepared according to the general procedure using Ni(bpy)$_3$(BF)$_2$ (7.0 mg, 0.01 mmol), acrylonitrile (5.3 mg, 0.1 mmol) and dihydropyridine **1e** (56.0 mg, 0.15 mmol) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 9:1) to give the product **3n**, (10.5 mg, 60% yield, average of two runs) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 4.52 (s, 2H), 3.59 (t, J = 5.8 Hz, 2H), 2.49 (t, J = 7.1 Hz, 2H), 1.95 (tt, J = 7.2, 5.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 128.5, 127.8, 127.7, 119.5, 73.2, 67.6, 25.8, 14.2.

HRMS (ESI) calculated for $C_{11}H_{13}NNaO$ $[M+Na]^+$: 198.0889, found: 198.0888.



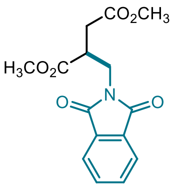
2-(2-(1,3-Dioxoisoindolin-2-yl)-1-phenylethyl)malononitrile (3o)

Prepared according to the general procedure using Ni(bpy)$_3$(BF)$_2$ (7.0 mg, 0.01 mmol), 2-benzylidenemalononitrile (15.4 mg, 0.1 mmol) and dihydropyridine **1f** (56.0 mg, 0.15 mmol), CH_2Cl_2 (200 µL) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 3:1) to give the product **3o**, (28 mg, 89% yield, average of two runs) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.79 (m, 2H), 7.80 – 7.65 (m, 2H), 7.47 – 7.33 (m, 5H), 4.25 (d, J = 7.5 Hz, 2H), 4.12 (d, J = 6.2 Hz, 1H), 4.00 – 3.79 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 134.5, 133.8, 131.5, 129.5, 129.4, 128.0, 123.7, 111.4, 111.0, 44.8, 39.7, 27.9.

HRMS (ESI) calculated for $C_{19}H_{13}N_3NaO_2$ $[M+Na]^+$: 338.0900, found: 338.0906.



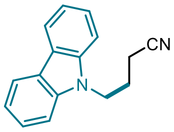
Dimethyl 2-((1,3-dioxoisoindolin-2-yl)methyl)succinate (3p)

Prepared according to the general procedure using Ni(bpy)$_3$(BF)$_2$ (7.0 mg, 0.01 mmol), dimethyl fumarate (14.4 mg, 0.1 mmol) and dihydropyridine **1f** (61.9 mg, 0.15 mmol), CH_2Cl_2 (200 µL) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 7:3) to give the product **3p**, (16 mg, 52% yield, average of two runs) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.76 – 7.70 (m, 2H), 4.04 (dd, *J* = 14.0, 6.7 Hz, 1H), 3.93 (dd, *J* = 14.0, 6.4 Hz, 1H), 3.71 (d, *J* = 0.6 Hz, 3H), 3.65 (d, *J* = 0.5 Hz, 3H), 3.33 – 3.24 (m, 1H), 2.78 (dd, *J* = 17.2, 8.7 Hz, 1H), 2.58 (dd, *J* = 17.2, 5.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 171.6, 168.0, 134.2, 131.9, 123.5, 52.4, 51.9, 40.5, 38.7, 33.4.

HRMS (ESI) calculated for $C_{15}H_{15}NNaO_6$ $[M+Na]^+$:328.0792, found: 328.0784.

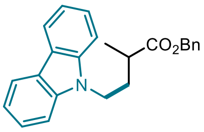


4-(9*H*-Carbazol-9-yl)butanenitrile (3q) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), acrylonitrile (5.3 mg, 0.1 mmol) and dihydropyridine **1g** (56.0 mg, 0.15 mmol), CH_2Cl_2 (200 µL) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 8:2) to give the product **3q**, (14 mg, 60% yield, average of two runs) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.50 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.44 (dt, *J* = 8.3, 1.0 Hz, 2H), 7.27 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 2H), 4.52 – 4.47 (m, 2H), 2.35 – 2.21 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 126.0, 123.0, 120.5, 119.4, 119.1, 108.3, 41.0, 25.0, 15.0.

HRMS (ESI) calculated for $C_{16}H_{14}N_2Na$ $[M+Na]^+$: 257.1049, found: 257.1047.

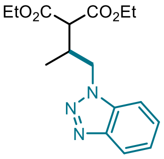


Benzyl 4-(9*H*-carbazol-9-yl)-2-methylbutanoate (3r) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), benzyl methacrylate (17.6 mg, 0.1 mmol) and dihydropyridine **1g** (56.0 mg, 0.15 mmol), CH_2Cl_2 (200 µL) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 19:1) to give the product **3r**, (19 mg, 53% yield, average of two runs) as a colorless film.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.32 – 7.21 (m, 7H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.10 (ddd, *J* = 8.0, 7.2, 0.9 Hz, 2H), 5.04 (s, 2H), 4.20 (dd, *J* = 8.3, 6.8 Hz, 2H), 2.46 (dqd, *J* = 9.1, 7.1, 4.7 Hz, 1H), 2.18 – 2.09 (m, 1H), 1.90 – 1.81 (m, 1H), 1.13 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 140.2, 135.8, 128.6, 128.4, 128.4, 125.7, 122.9, 120.3, 118.9, 108.5, 66.5, 40.8, 37.2, 32.3, 17.7.

HRMS (ESI) calculated for $C_{24}H_{23}NNaO_2$ $[M+Na]^+$: 380.1621, found: 380.1626.



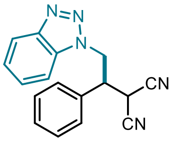
Diethyl 2-(1-(1*H*-benzo[d][1,2,3]triazol-1-yl)propan-2-yl)malonate (3s)

Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), diethyl 2-ethylidenemalonate (18.6 mg, 0.1 mmol) and dihydropyridine **1h** (56.0 mg, 0.15 mmol), CH_2Cl_2 (200 µL) and CH_3CN (200 µL). The crude material was purified by flash column chromatography (hexane/EtOAc 17:3) to give the product **3s**, (25 mg, 78% yield, average of two runs) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.54 – 7.44 (m, 1H), 7.41 – 7.34 (m, 1H), 4.82 (dd, *J* = 14.1, 4.8 Hz, 1H), 4.65 (dd, *J* = 14.0, 8.9 Hz, 1H), 4.32 – 4.17 (m, 4H), 3.39 (d, *J* = 6.9 Hz, 1H), 2.97 (dtd, *J* = 8.9, 6.9, 4.8 Hz, 1H), 1.29 (q, *J* = 7.2 Hz, 6H), 1.03 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 168.1, 145.9, 133.3, 127.4, 123.9, 120.0, 109.8, 61.7, 54.6, 51.3, 33.8, 15.5, 14.1, 14.0.

HRMS (ESI) calculated for $C_{16}H_{21}N_3NaO_4$ $[M+Na]^+$: 342.1424, found: 342.1420.



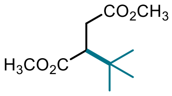
2-(2-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-1-phenylethyl)malononitrile (3t)

Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), 2-benzylidenemalononitrile (15.4 mg, 0.1 mmol) and dihydropyridine **1h** (56.0 mg, 0.15 mmol), CH_2Cl_2 (200 µL) and CH_3CN (200 µL). The crude material was purified by flash column chromatography ($CHCl_3$:hexane/EtOAc 10:7:3) to give the product **3t**, (26.5 mg, 92% yield, average of two runs) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.49 (ddd, *J* = 8.2, 6.9, 1.0 Hz, 1H), 7.44 – 7.31 (m, 7H), 5.17 (dd, *J* = 14.7, 8.8 Hz, 1H), 5.05 (dd, *J* = 14.7, 4.9 Hz, 1H), 4.36 (d, *J* = 6.0 Hz, 1H), 4.10 (ddd, *J* = 8.8, 5.9, 4.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 133.4, 133.4, 130.0, 129.8, 128.5, 127.9, 124.7, 120.5, 111.4, 111.1, 108.7, 49.0, 46.4, 27.4.

HRMS (ESI) calculated for $C_{17}H_{12}N_5$ $[M-H]^-$: 286.1098, found: 286.1100.



Dimethyl 2-*tert*-butylsuccinate (5) - Prepared according to the general procedure using $Ni(bpy)_3(BF)_2$ (7.0 mg, 0.01 mmol), dimethyl fumarate (14.4 mg, 0.1 mmol), dihydropyridine **4** (32 mg, 0.15 mmol), CH_2Cl_2 (200 µL) and CH_3CN (200 µL). A single high-power LED emitting at 365 nm (irradiance: 100 mW cm^{-2}) was employed as the light source. The crude material was purified by flash column chromatography (hexane/EtOAc 9:1) to give the product **5** (16.1 mg, 80% yield) as a colorless liquid. The spectroscopic characterization matched with data reported in the literature.[11]

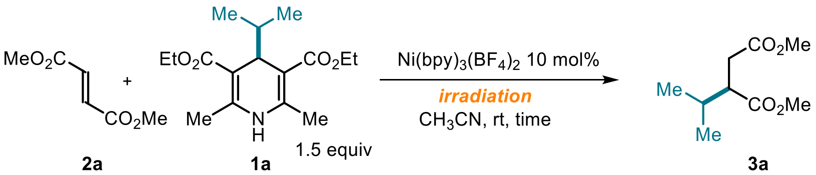
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.65 (s, 3H), 2.79 (dd, *J* = 16.5, 11.8 Hz, 1H), 2.64 (dd, *J* = 11.8, 3.0 Hz, 1H), 2.47 (dd, *J* = 16.5, 3.0 Hz, 1H), 0.96 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 173.3, 51.9, 51.5, 51.4, 32.8, 27.9.

B5. Scale-Up Experiments

We conducted further experimentations to scale up the model reaction, using 4-isopropyl-DHP **1a** as the radical precursor and dimethyl fumarate **2a** as the acceptor. The reaction could be successfully performed on a 0.5 mol scale without losing efficiency (see entry 2 in Table S1).

Table S1. Scale-up experiments.



Entry	Scale	Irradiation	Time	NMR yield (%)
1	0.1	single LED (405 nm) *50 mW cm^{-2}*	16 h	85 (74)[a]
2	0.5	single LED (405 nm) *100 mW cm^{-2}*	48 h	86
3	**2.0**	**Kessil PR-160 (390 nm)**	**16 h**	**91 (78)[a]**

[a] Yield of isolated product **3a**.

For the experiment on 0.5 mmol, we employed the same photochemical setup adopted in the optimization on a 0.1 mmol scale (irradiation by a single high-power LED, as described in section B2). To secure a high chemical yield, the light intensity was increased from 50 to 100 mW cm^{-2} while the reaction time was extended from 16 to 48 hours.

To further increase the synthetic utility of the process, we performed the model reaction on a larger scale (2 mmol) using a commercially available Kessil lamp (λ_{max} = 390 nm). This simple experimental setup (detailed in Figure S3) secured a high chemical yield without the need to extend the reaction time (entry 3 in Table S1). Product **3a** was obtained in 78% yield (294 mg) after purification by bulb-to-bulb distillation.

Experimental Procedure for the Giese Reaction on a 2.0 mmol scale

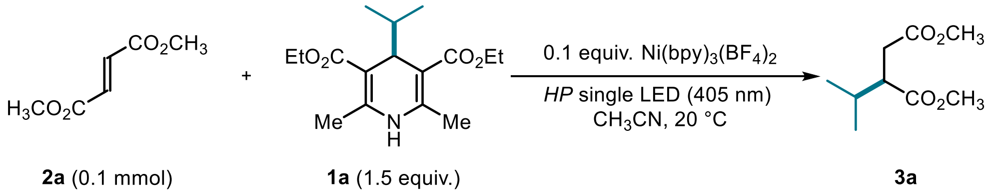
A Schlenk tube (1.3 cm internal diameter) equipped with a stirring bar was charged with $Ni(bpy)_3(BF_4)_2$ (140 mg, 0.2 mmol, 0.10 equiv.), dimethyl fumarate **2a** (288 mg, 2.0 mmol), and dihydropyridine **1a** (886 mg, 3.0 mmol, 1.5 equiv.) dissolved in CH_3CN (4 mL). The resulting solution was degassed by three freeze-pump-thaw cycles and conditioned under Ar atmosphere. The reaction vessel was fixed at approx. 1 cm distance from a commercially available Kessil PR160-390 lamp (λ_{max} = 390 nm). Overheating of the reaction mixture was prevented by an efficient cooling fan (see Figure S3 for a picture of the experimental setup). Irradiance (measured by the use of a calibrated photodiode) was approximately 400 mW cm^{-2} at 1 cm distance from the light source.

The reaction was stirred under irradiation for 16 hours. The mixture was diluted with EtOAc (40 mL), filtered over a plug of silica gel and concentrated in vacuo. The residue was purified by bulb-to-bulb distillation at reduced pressure (10 mbar) with the aid of a Kugelrhor apparatus (air bath temperature: 150 ºC) to afford product **3a** in the form of a colorless liquid (294 mg, 78%).

Figure S3. Experimental setup for 2 mmol scale reactions.

C. Mechanistic Experiments

C1. Quantum yield determination



The number of photons emitted per second was determined using azobenzene as actinometer. Using the reaction setup depicted in Figure S2, a Schlenk tube was filled with a solution of *trans*-azobenzene in CD_3OD and irradiated with a 405 nm light. The *trans-cis* isomerization was followed in time using ^{1}H-NMR and knowing the quantum yield of this process ($\Phi = 0.2$),[12] the number of photons emitted per time unit was determined (2.5×10^{-7} mol s^{-1}).

The amount of product **3a** formed was determined by GC measurement (FID detector) using 1,3,5-trimethoxybenzene as the internal standard. An independent reaction was performed for each point, using irradiation times short enough to obtain yields of **3a** under 10%. The moles of the formed product are plotted against the number of incident photons (Figure S4). The slope gives the overall quantum yield (Φ) of the process and was found to be $\Phi = 0.014$.

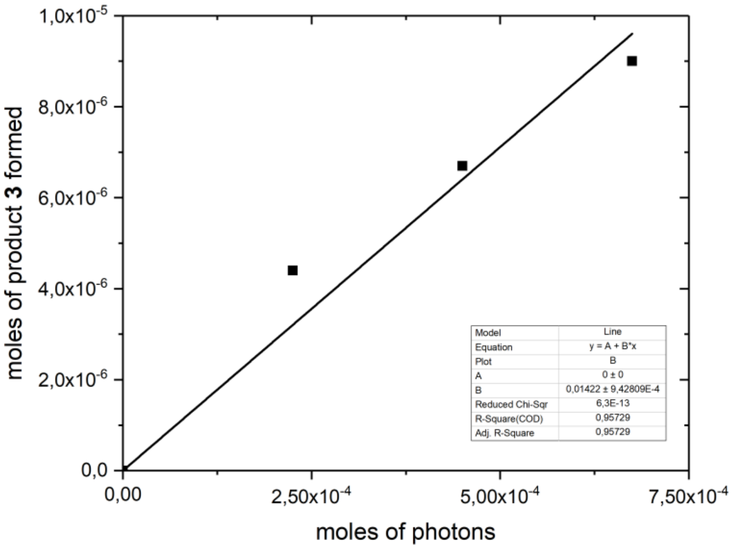


Figure S4. Plot of the formation of product **3a** against the number of photons absorbed.

C2. UV-Vis Spectra

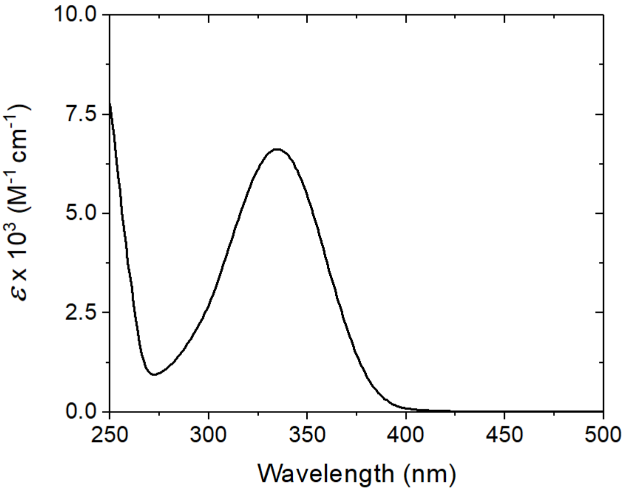


Figure S5. UV-Vis spectrum of **1a** (1.5×10^{-4} M) in acetonitrile.

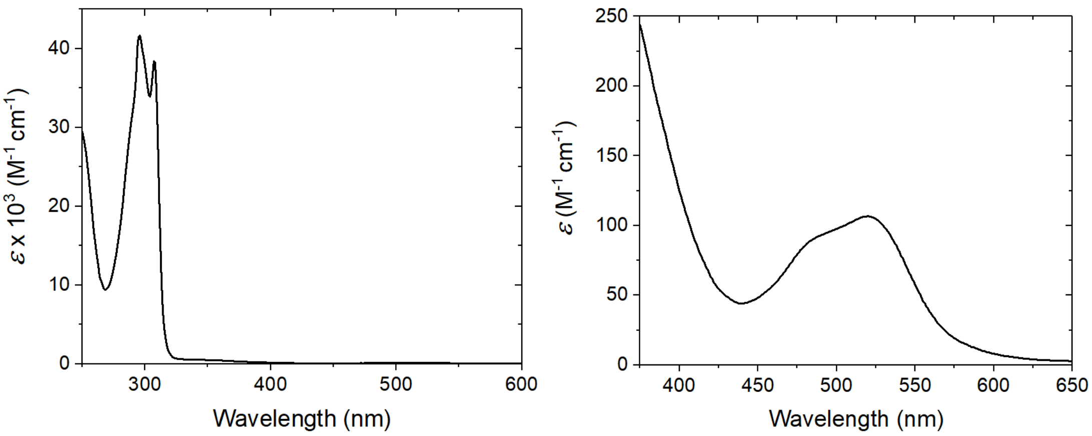


Figure S6. UV-Vis spectra of Ni(bpy)$_3$(BF$_4$)$_2$ (2.0 10^{-5} M (left) and 5.8 10^{-3} M (right)) in acetonitrile.

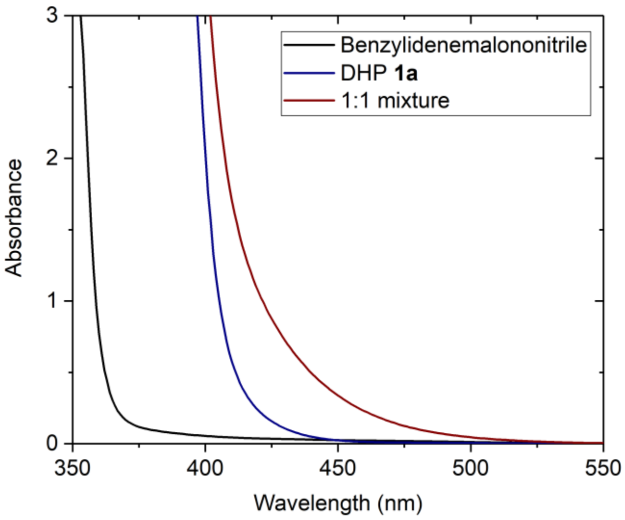


Figure S7. UV-Vis spectra of benzylidenemalononitrile (0.5 M, black), DHP **1a** (0.5 M, blue) and a 1:1 mixture in acetonitrile (0.5 M in each of the two, red). Spectra recorded in an 1 mm quartz cuvette.

C3. Cyclic Voltammograms and Estimation of Excited State Redox Potentials

For the cyclic voltammetry (CV) measurements, a glassy carbon disk electrode (diameter: 3 mm) was used as a working electrode. A silver wire coated with AgCl immersed in a 3 M aqueous solution of NaCl 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. For comparison, all the potentials in the main text are quoted with respect to the saturated calomel electrode (SCE, +0.040 V vs. Ag/AgCl, 3 M Cl^-).[13] A scan rate of 500 mV/s was used for all CV experiments.

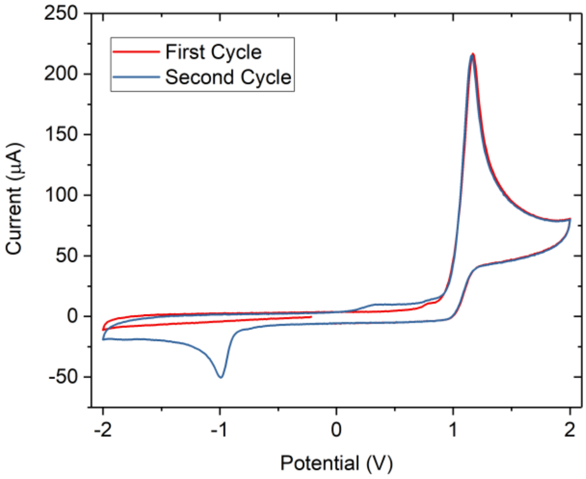


Figure S8. CV of compound **1a** (0.01 M in acetonitrile with $TBAPF_6$ 0.1 M as the supporting electrolyte).

Using the data collected from the cyclic voltammetry studies and from the absorption spectra of the *i*Pr-DHP **1a**, we could estimate the redox potential of photoexcited **1a*** employing the Rehm-Weller equation:

$$E\,(\mathbf{1a}^{+\bullet}/\mathbf{1a^*}) = E\,(\mathbf{1a}^{+\bullet}/\mathbf{1a}) - E_{00}\,(\mathbf{1a^*}/\mathbf{1a})$$

Since the electrochemical oxidation of **1a** is irreversible, its anodic half peak potential ($E_{p/2}$ = +1.04 V vs. SCE) was used for $E\,(\mathbf{1a}^{+\bullet}/\mathbf{1a})$. $E_{00}\,(\mathbf{1a^*}/\mathbf{1a})$, which is the excited state energy of the *i*Pr-DHP **1a**, was estimated spectroscopically from the position (λ = 420 nm) of the long wavelength tail of the absorption spectrum recorded in acetonitrile, the solvent used for the electrochemical analysis, which translates into $E_{00}\,(\mathbf{1a^*}/\mathbf{1a})$ = 2.95 eV. Using these data, the following value was obtained:

$$E\,(\mathbf{1a}^{+\bullet}/\mathbf{1a^*}) = 1.04 - 2.95 = -1.9 \text{ V vs. SCE.}$$

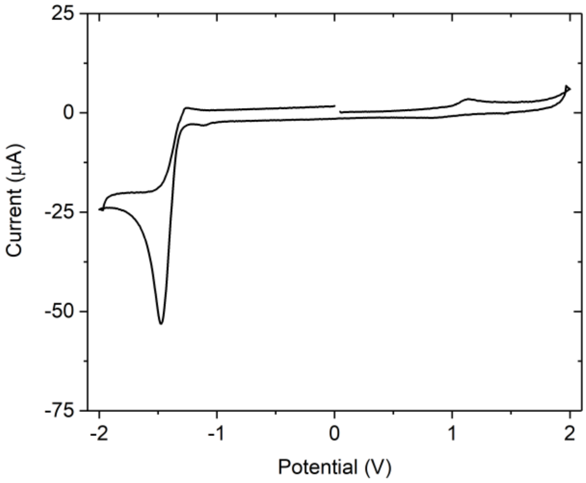
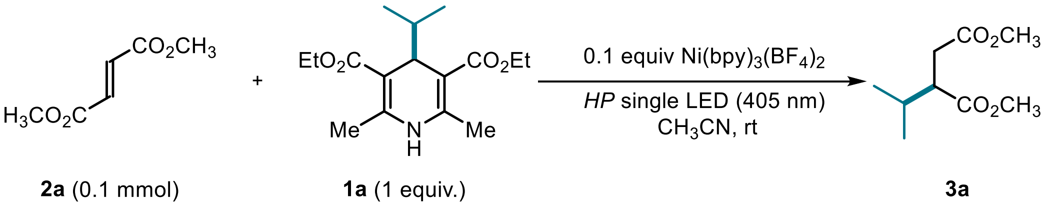


Figure S9. CV of compound **2a** (0.01 M in acetonitrile with $TBAPF_6$ 0.1 M as the supporting electrolyte).

C4. Recovery of the Mediator

The model reaction was performed using 1.0 equiv of **1a**. After irradiation for 16 h, Et_2O (5 mL) was added to the reaction mixture, causing precipitation. After 1 h stirring, the suspension was filtered over a piece of cotton. The residue was dissolved in acetonitrile and analyzed with UV-Vis and IR spectroscopy and compared to the spectra of $Ni(bpy)_3(BF_4)_2$.



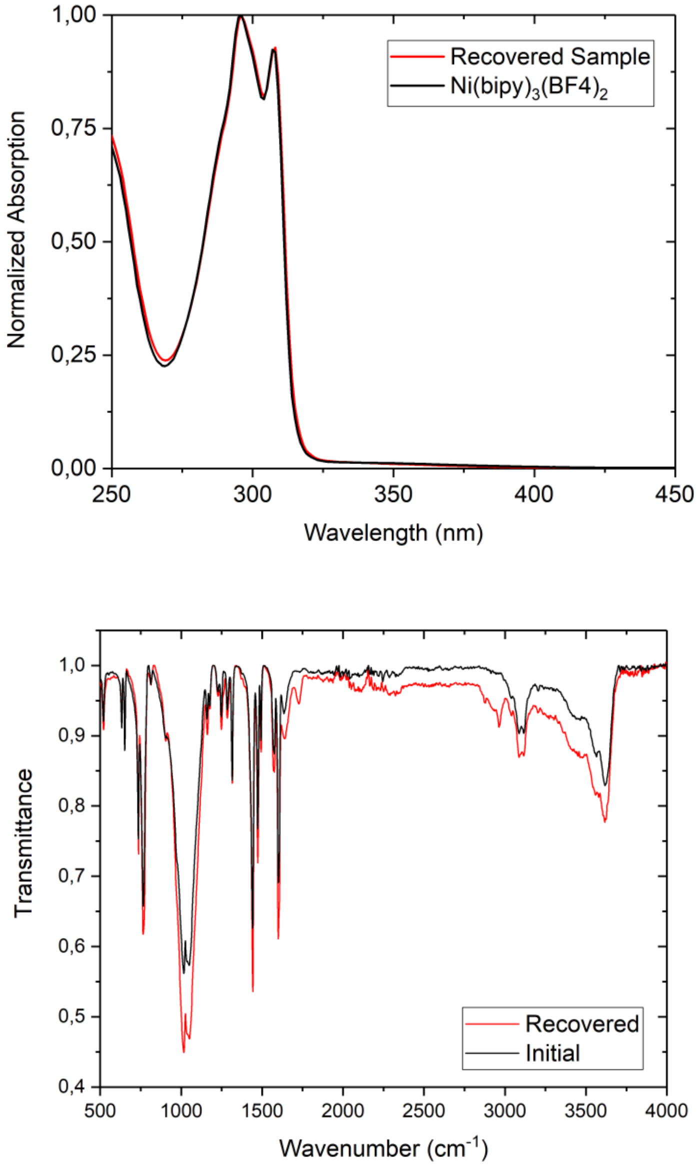


Figure S10. UV-vis spectra (top) and IR spectra (bottom) of the recovered mediator and an authentic sample of $Ni(bpy)_3(BF_4)_2$.

C5. *In Situ* Monitoring of Magnetic Susceptibility

The Evans NMR method[16] was employed to monitor the magnetic susceptibility of the reaction mixture while the transformation was ongoing. The model reaction of **1a** with dimethyl fumarate (Table 1 in the main text) was studied.

An NMR tube (5 mm diameter) equipped with a rubber septum and a coaxial insert containing a mixture of CH_3CN and CD_3CN (20:80 ratio), was charged with $Ni(bpy)_3(BF_4)_2$ (10 mg, 0.014 mmol), dimethyl fumarate (30.8 mg, 0.214 mmol, 15 equiv.) and dihydropyridine **1a** (42.1 mg, 0.143 mmol, 10 equiv.) and conditioned under argon. The same degassed mixture of CH_3CN and CD_3CN was added by syringe to yield a homogeneous solution (total volume: 0.50 mL).

The solution was irradiated with a single high-power LED (λ_{max} = 405 nm, irradiance 50 mW/cm^2), keeping the light source approximately centered with respect to the liquid column. ^{1}H NMR spectra were recorded before irradiating and after 1, 3 and 6 hours of irradiation. The magnetic susceptibility (χ_M) of the solution (at 25 ºC) was deduced from the chemical shift difference between the signal of CH_3CN in the coaxial insert and that in the solution sorrounding the insert. The effective magnetic moment (μ_{eff}) was deduced from χ_M.[†] Results are reported in Table S2. The initial value is in agreement with that expected for two unpaired electrons within the spin-only approximation (2.83). After irradiation for the indicated time, μ_{eff} decreased only slightly, compatibly with the fact that most $Ni(bpy)_3^{2+}$ was almost unchanged.

Table S2. *In situ* determination of the apparent magnetic moment for the reaction reported in Scheme 1. See the above for detailed experimental conditions.

Irradiation time (h)	μ_{eff}
0	2.81
1	2.77
3	2.69
6	2.68

After irradiating for 6 h, workup and NMR analysis (with trichloroethylene as an internal standard) demonstrated that compound **2a** was formed in 55% yield.

[†] Neglecting diamagnetic contributions, the (molar) magnetic susceptibility χ_M was calculated from the chemical shift difference (Δf, in Hz) with the following formula: $\chi_M = 3|\Delta f|(4\pi f c)^{-1}$, in which f is the frequency at which the spectrometer operated (in Hz) and c is the concentration (in mol cm^{-3}). The molar susceptibility χ_M was then related to the magnetic moment μ_{eff} through the Curie law: $\mu_{eff} = (3k T \chi_M)^{1/2}(N \mu_B^2)^{-1/2}$, in which k is the Boltzmann constant, T the temperature, N the Avogadro number and μ_B the Bohr magneton.

C6. Additional Mechanistic Discussion

The following experiments were conducted to support the proposed mechanism, in which the nickel complex acts as an electron mediator in its ground state. The results are not congruent with the $[Ni(bpy)_3]^{2+}$ complex acting as a photoredox/energy transfer catalyst in its excited state.

a. *Dependence of the reactivity on the wavelength and the nature of the substrate.* In consonance with the notion that the reaction is promoted by direct excitation of alkyl-DHP **1** and not of $Ni(bpy)_3^{2+}$, we found that the optimal irradiation wavelength changes according to the nature of the substrate. Dihydropyridine **4** (Meyer nitrile) absorbs at significantly shorter wavelength (λ_{max} = 323 nm) than esters **1** (λ_{max} = 335 nm for **1a**). Absorption spectra of **4** and **1a** are compared in Figure S11.

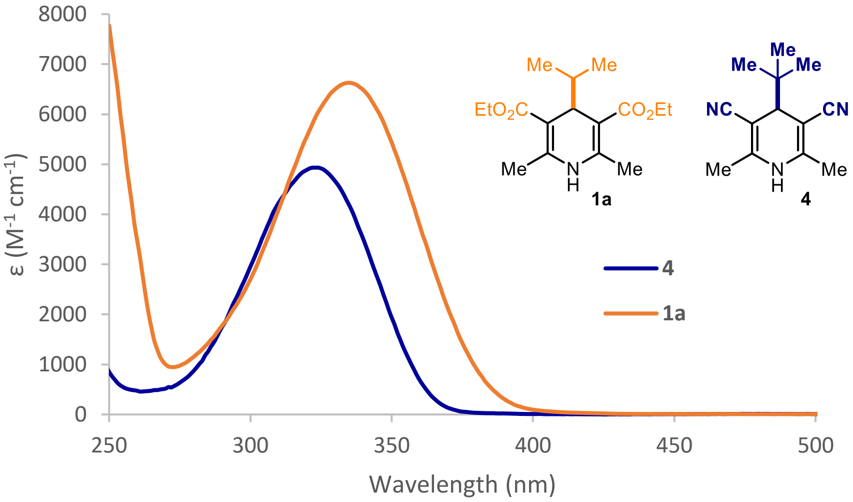
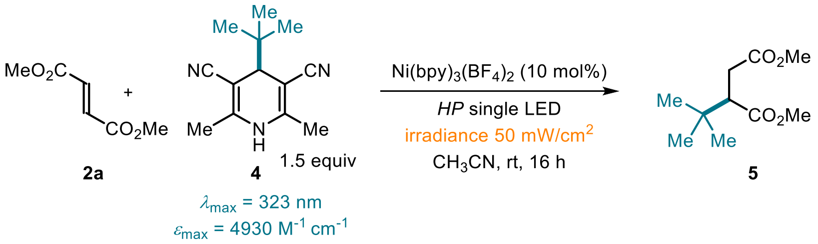


Figure S11. UV-Vis absorption spectra of compounds **4** and **1a** (in MeCN, $5 \cdot 10^{-5}$ M).

Assuming that the excitation of the nickel (II) complex is responsible of the Giese addition reaction, the optimal irradiation wavelength should remain constant, irrespective of the radical precursor substrate used. However, we found that to achieve a satisfactory reactivity with the Meyer nitrile **4**, a shorter light wavelength is necessary (365 nm vs 405 nm, the usual wavelength applied with substrates **1**). Specifically, irradiation at 365 nm gave satisfactory reactivity (see Table S3, entry 1), a 380 nm illumination lowered the reactivity (entry 2) while the process was completely inhibited when shining light at 405 or 420 nm (entries 3-4). Complete conversion of **2a** and an improved yield was obtained by using a 365 nm LED and higher irradiance (100 mW cm^{-2}, see Scheme 4 in the main text). These results indicate that the reaction is triggered by the direct photoexcitation of the dihydropyridine derivative, and exclude that the excited-state of the nickel (II) complex can play a role in the present system.

Table S3 – Reactivity/wavelength correlation studies for substrate **4**. NMR yields reported.

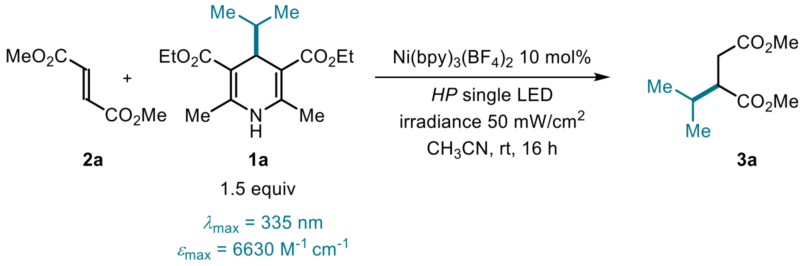


Entry	**Wavelength** (nm)	***ε*** **of 4** (M^{-1} cm^{-1})	Leftover **4** (equiv.)	Leftover **2a (%)**	Yield of **5** (%)
1	**365**	**319**	**0.41**	**5**	**66**
2	380	33	0.83	26	37
3	405	5	1.5	≈ 100	0
4	405	5	1.5	≈ 100	0[a]
5	420	3	1.5	≈ 100	0

[a] Reaction performed at 60 °C.

b. We studied in detail the dependence of the reactivity of the model reaction on the irradiation wavelength. The reaction was performed using LEDs emitting at different wavelengths, while keeping the irradiance constant (see Table S4). The molar absorption coefficients (*ε*) of DHP **1a** and of $[Ni(bpy)_3]^{2+}$ are also reported for comparison.

Table S4. Influence of the irradiation wavelength on the reaction of **1a**. NMR yields reported.



Entry	**Wavelength** (nm)	**ε of 1a** (M^{-1} cm^{-1})	**ε of** $[Ni(bpy)_3]^{2+}$ (M^{-1} cm^{-1})	Leftover **1a** (equiv.)	Leftover **2a** (%)	Yield **3a** (%)
1	390	301	215	0.35	0	82
2	405	64	140	0.33	0	85
3	420	26	95	0.75	2	69
4	460	7	76	≈ 1.5	91	0
5	530	8	113	≈ 1.5	≈ 100	0

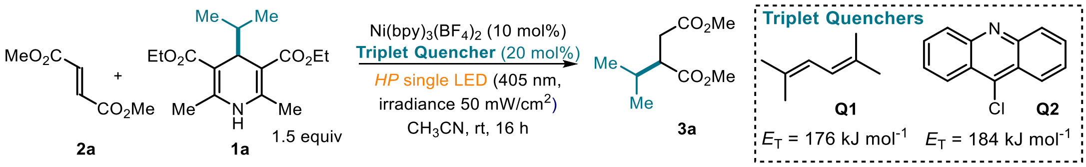
The results show a positive correlation between the observed reactivity and absorption of light by **1a**. The reactivity is high at 390 nm and at 405 nm, where **1a** absorbs significantly, it decreases at 420 nm, where **1a** absorbs poorly, and is completely lost at 460 nm and 530 nm, where **1a** does not significantly absorb. Importantly, no correlation is found between absorption of light by $[Ni(bpy)_3]^{2+}$ and yield of **3a**, which is incongruent with the photoexcitation of the nickel complex being involved in the reaction.

c. The excited state reduction potential of $[Ni(bpy)_3]^{2+}$ $E(Ni^{II}*/Ni^{I})$ can be estimated from electrochemical and spectral data applying the Rehm-Weller approximation, according to the following equation:

$$E(Ni^{II}*/Ni^{I}) \approx E(Ni^{II}/Ni^{I}) + E_{00}(Ni^{II*}/Ni^{II})$$

Using $E(\mathrm{Ni^{II}/Ni^{I}})$ = –1.35 V (vs. SCE, electrochemical measurement, see Ref. 19 in the main text) and estimating $E_{00}(\mathrm{Ni^{II*}/Ni^{II}})$ as the position of the long wavelength tail of the absorption spectrum of $[\mathrm{Ni(bpy)_3}]^{2+}$ (575 nm, see Figure S6), which translates to 2.16 eV, we obtain $E(\mathrm{Ni^{II}*/Ni^{I}}) \approx +0.81$ V vs. SCE. This value is not compatible with the photoinduced oxidation of dihydropyridine **1a**, since $E(\mathbf{1a}^{\bullet+}/\mathbf{1a})$ = +1.04 V vs. SCE (this value would imply an endergonic SET oxidation of **1a**).

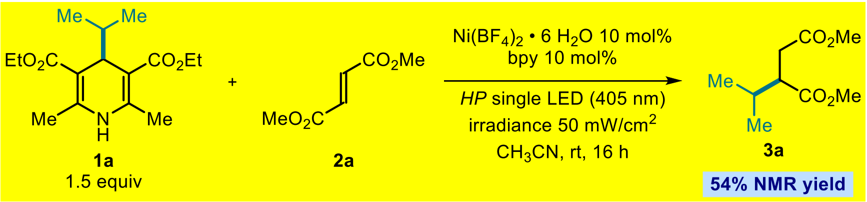
Table S5. Triplet quenching experiments. NMR yields reported.



Entry	Triplet quencher	Yield of **3a** (%)
1	none	85
2	2,5-dimethyl-2,4-hexadiene (**Q1**)	72
3	9-chloroacridine (**Q2**)	86

The results in Table S5 indicate that the presence of triplet quenchers (2,5-dimethyl-2,4-hexadiene and 9-chloroacridine) having comparatively low triplet state energies (E_T = 176 kJ mol^{-1} and E_T = 184 kJ mol^{-1})[17] do not significantly affect the reactivity of the model reaction. Therefore, the mechanistic possibility for the nickel (II) complex to act as an energy transfer mediator from its excited state is not operative in this system.

The possible role of coordinatively unsaturated nickel(II) complexes has also been examined. The model reaction of DHP **1a** with dimethyl fumarate (**2a**) was performed in the presence of a 1:1 mixture of $\mathrm{Ni(BF_4)_2 \cdot 6\,H_2O}$ and bpy instead of $\mathrm{Ni(bpy)_3BF_4}$ (Scheme S1). The Giese addition product (**3a**) was obtained in 54% NMR yield and conversion was not complete (0.49 equivalents of **1a** and 0.31 of **2a** remained after 16 hours). Therefore, the transformation was less efficient than in the presence of $\mathrm{Ni(bpy)_3(BF_4)_2}$ (85% yield and complete conversion, Table 1, entry 4 in the main text), but more efficient than in the absence of any catalyst (32% yield, Table 1, entry 1).



Scheme S1. Control experiment performed with a 1:1 Ni(II)/bpy ratio.

The formation constants reported in the literature[18] indicate that, upon mixing Ni(II) and bpy in a 1:1 ratio (0.5 M each), $[\mathrm{Ni(bpy)}]^{2+}$, $[\mathrm{Ni(bpy)_2}]^{2+}$ and $[\mathrm{Ni(bpy)_3}]^{2+}$ are all present in non-negligible concentration at equilibrium. The slight catalytic activity of the 1:1 mixture of $\mathrm{Ni(BF_4)_2 \cdot 6\,H_2O}$ and bpy observed in the model reaction (Scheme S1) may be simply explained by the formation of a small amount of $[\mathrm{Ni(bpy)_3}]^{2+}$ at equilibrium. Finally, as discussed in the main manuscript, since added bpy (up to 10 equiv.) does not reduce the efficiency of the model reaction and $\mathrm{Ni(bpy)_3(BF_4)_2}$ could be recover and reused, it is highly unlikely that coordinatively unsaturated Ni(II) complexes are the main active species in this transformation.

D. Theoretical Estimation of the Reduction Potentials of Radicals

D1. Computational Details

All DFT calculations were performed with the Gaussian09 suite of programs (Rev. A.01).[19] The structures of all the studied species were fully optimized without any symmetry constraint using the B3LYP functional[20] in conjunction with the split-valence 6-31+G(d) basis set (unrestricted spin mode). All stationary points were characterized as minima by harmonic frequency calculations. Computed harmonic frequencies were used to calculate the thermal contribution to Gibbs free energy with the usual approximations. Temperature and pressure were fixed at 298 K and 1 atm, respectively. To obtain more accurate electronic energies, single-point calculations were performed with the same functional and the larger 6-311++G(2d,2p) basis set. Bulk solvent effects were accounted for by the Polarizable Continuum Model in its Integral Equation Formalism variant (IEF-PCM), as implemented in Gaussian09.[21] The default parameters for dimethyl sulfoxide were used.

D2. Validation of the Computational Method and Results

A number of DFT-based computational approaches for the estimation of redox potentials have been proposed.[22] The B3LYP/6-311++G(2df,2p)//B3LYP/6-31+G(d) model chemistry was suitable to predict redox potentials in acetonitrile with a mean unsigned error of 0.17 V over a large benchmark set of 270 organic molecules.[22a] However, organic anionic species are a known pitfall for quantum chemical methods,[23] thus validation of our theoretical protocol by comparison with experimental data was desirable.

A small benchmark set of 10 experimental reduction potentials of radicals α to electron withdrawing groups to the corresponding enolate anions was extracted from the literature (Figure S12).[24] The purpose of this benchmark was twofold: 1) to validate the theoretical approach; 2) to obtain by data fitting a value for the absolute redox potential of the chosen reference electrode (SCE), also including a correction for systematic errors.[22j]

The geometries of radicals **T1-T10** and of the corresponding anions were optimized (including implicit solvation),[25] and the associated absolute reduction potentials were calculated directly from computed ΔG at 298 K. Absolute potentials were reported as a function of the corresponding experimental redox potentials (Figure S13). Least-square linear regression revealed a satisfactory correlation ($R^2 = 0.982$), with a slope close to 1 (slope = 1.053), implying that the chosen method can predict reliably relative redox potentials and no scaling of the computed values is necessary. The absolute potential of the reference electrode was assumed +4.46 V, *i.e.* the intercept of the fitting line. This value is in good agreement with the estimation (+4.525 V) based on the reported absolute potential of the normal hydrogen electrode (SHE).[26] With respect to this fitted reference, the proposed method was capable of reproducing the experimental electrode potentials for the oxidation of **T1-T10** with a mean unsigned error lower than 0.07 V (calculated values reported in in Figure S12).

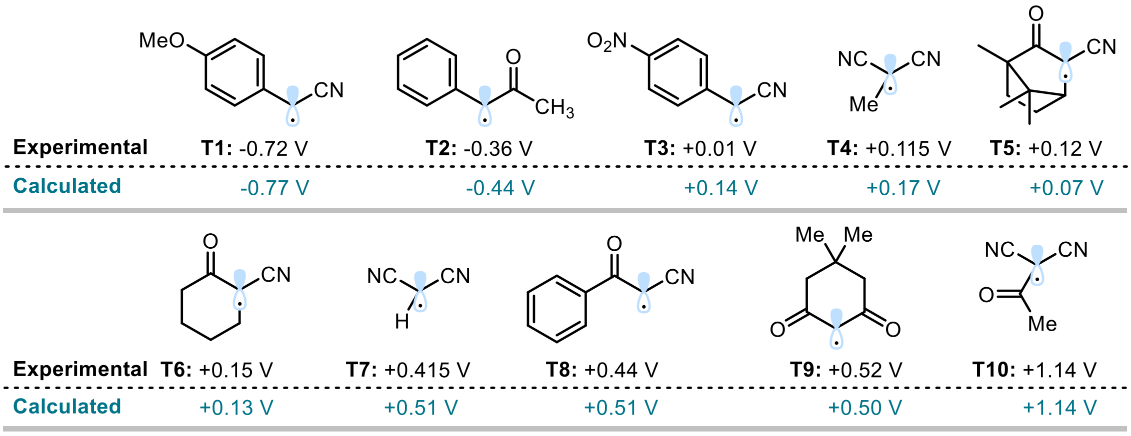


Figure S12. Benchmark set for the validation of the theoretical method for the prediction of reduction potentials.[24] Experimental (black) and calculated potentials (green) are reported vs. SCE.

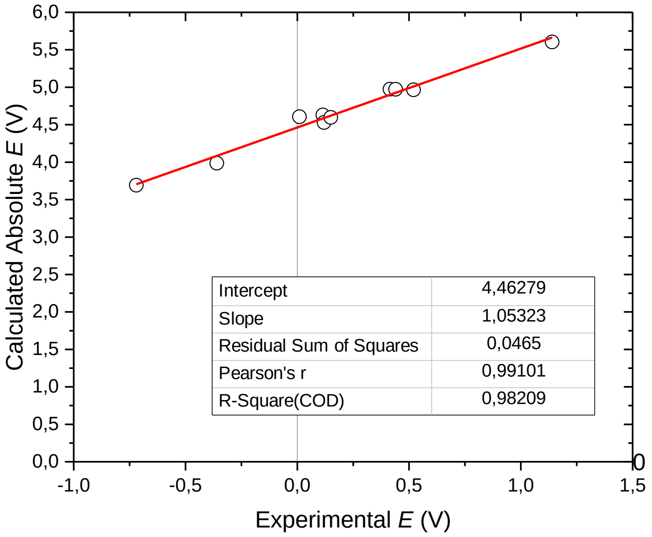


Figure S13. Linear correlation between experimental reduction potentials of benchmark species (Figure S12) and calculated absolute potentials.

With this validated protocol in hand, we computed the reduction potentials *E*(**A**/**B**) of intermediates **A_a**, **A_b**, and **A_l** (corresponding to the products **3a**, **3b** and **3l**, Figure S14). The values obtained cover a range of almost 1 V (–0.74 V to +0.21 V), but they are all compatible with the proposed reduction of intermediates **A** by Ni(I) (see the main text).

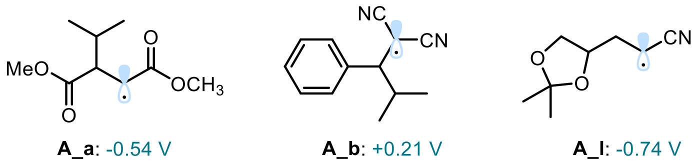


Figure S14. Calculated reduction potentials of intermediates **Aa**, **Ab**, **Ai**, **Al**.

The same computational protocol was employed to to calculate the reduction potential of the isopropyl radical (E_{calc} ($i\mathrm{Pr}^{\bullet}/i\mathrm{Pr}^{-}$) = –2.26 V). As a further confirmation of the reliability of the adopted approach, the known reduction potential of the benzyl radical was also computed. The value found (E_{calc} ($\mathrm{Bn}^{\bullet}/\mathrm{Bn}^{-}$) = –1.42 V) is in agreement with the experimental measurement reported in the literature ($E_{1/2}$ ($\mathrm{Bn}^{\bullet}/\mathrm{Bn}^{-}$) = –1.45 V).[27]

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F. Absolute Energies and Cartesian Coordinates

Here follow the computed absolute energies (Table S6) and the cartesian geometries (in Å) of all the species studied by DFT calculations.

Table S6. Absolute electronic energies and thermal corrections to Gibbs free energy of all the species studied by DFT calculations (in Hartree per particle).

Chemical species	**Electronic energy (U)B3LYP/6-31+G(d)**	**Electronic energy (U)B3LYP/ 6-311++G(2d,2p)**	**Thermal correction to *G* – (U)B3LYP/ 6-31+G(d)**
T1 radical	–477.722858529	–477.849413290	0.110880
T1 anion	–477.855881141	–477.983758468	0.109574
T2 radical	–423.595207434	–423.708233100	0.117037
T2 anion	–423.741749115	–423.856271960	0.118580
T3 radical	–567.704477604	–567.855056484	0.079452
T3 anion	–567.873676795	–568.025125070	0.080268
T4 radical	–263.677898899	–263.747677959	0.027936
T4 anion	–263.847448054	–263.918350864	0.028497
T5 radical	–557.549673644	–557.698396173	0.189038
T5 anion	–557.715990297	–557.865254951	0.189423
T6 radical	–401.515749629	–401.623827612	0.102593
T6 anion	–401.685221881	–401.794000844	0.103798
T7 radical	–224.353863491	–224.412242976	0.003122
T7 anion	–224.535729939	–224.595861049	0.003944
T8 radical	–476.512854078	–476.635926574	0.087430
T8 anion	–476.695715401	–476.820049330	0.088808
T9 radical	–461.914347075	–462.042395843	0.138841
T9 anion	–462.097794585	–462.226682195	0.140669
T10 radical	–377.005784528	–377.106858204	0.034525
T10 anion	–377.213681964	–377.315637918	0.037369
A_a	–652.897073948	–653.087498887	0.186991
B_a	–653.040296042	–653.231704609	0.186991
A_b	–612.678166953	–612.837345575	0.182213
B_b	–612.848846613	–613.009135475	0.182411
A_l	–517.238545900	–517.383703572	0.150387
B_l	–517.374261227	–517.520907619	0.150622
Bn$^{\bullet}$	–270.929998231	–271.000735368	0.084989
Bn^{-}	–271.036391497	–271.110291780	0.082703
***i*–Pr$^{\bullet}$**	–118.484299304	–118.521614970	0.060983
***i*–Pr^{-}**	–118.563833328	–118.603256969	0.061779

T1 radical

C	-0.854515001882	1.287772999299	-1.217981997468
H	-0.238478999765	0.769265998232	-1.947376001188
C	-1.146610999495	2.631148002598	-1.490601998343
N	-1.383603001779	3.755362000082	-1.730986000075
C	-1.312683000373	0.592709001854	-0.065256000250
C	-0.959574997902	-0.771794999613	0.119913999736
C	-2.125346001257	1.203383998573	0.935764997492
C	-1.384055998636	-1.492051001959	1.227761001779
H	-0.341061999823	-1.263083998503	-0.626385998162
C	-2.550234997619	0.491929000093	2.038659000877
H	-2.414532000482	2.245057998707	0.828703002381
C	-2.186412998211	-0.864222001051	2.199856999200
H	-1.092092999131	-2.530662997552	1.330163999035
H	-3.168792999045	0.958724001574	2.799372997992
O	-2.656392999304	-1.469468999595	3.316487998412
C	-2.334052000046	-2.846631999413	3.554939000469
H	-2.819118001964	-3.099642000005	4.497671002211
H	-2.726607999082	-3.482574001319	2.754263001090
H	-1.251272001192	-2.982850002393	3.647507001173

T1 anion

C	-0.839116998175	1.312978000792	-1.253884998871
H	-0.221926000123	0.786044000848	-1.977829001228
C	-1.131481997730	2.639321001707	-1.512257998801
N	-1.387871001178	3.780614997947	-1.727013001094
C	-1.304210000121	0.600134998540	-0.085876999940
C	-0.969576997489	-0.762390001878	0.123711999814
C	-2.116078002210	1.192015001962	0.923920000690
C	-1.401541998023	-1.484775000553	1.242137000252
H	-0.351146000181	-1.271545002307	-0.614024000519
C	-2.549084000148	0.479161999849	2.038632002256
H	-2.409773998863	2.235158998172	0.825372001190
C	-2.198821002520	-0.867697001944	2.213902997474
H	-1.106977002432	-2.525240000102	1.337704001659
H	-3.168094998431	0.963505001235	2.791049998312
O	-2.681298999799	-1.486469002633	3.356632000593
C	-2.336093999642	-2.850153001682	3.568321997909
H	-2.807293997622	-3.137870999829	4.510169998541
H	-2.716344998712	-3.490287002555	2.761023001800
H	-1.248709000175	-2.980130999935	3.650783999830

T2 radical

C	-2.285553231676	0.259424837001	-0.000045781904
C	-0.908733731368	0.375034803545	0.000609158639
C	-0.275555125125	1.647259269917	0.000215668498
C	-1.107620079743	2.798210141660	-0.000863792764
C	-2.484642831726	2.669021855722	-0.001513528373
C	-3.083288757352	1.406288357743	-0.001116585564
H	-2.744578910003	-0.719389088367	0.000271818153
H	-0.292586531126	-0.514097406018	0.001435966399
H	-0.646438337673	3.771674263252	-0.001160455863
H	-3.103843053196	3.555584533162	-0.002336809442
H	-4.160706693511	1.317162808242	-0.001630049914
C	1.144831731091	1.686356078028	0.000931033571
H	1.646276884180	0.726753467659	0.001763792458
C	2.019318007828	2.844580506378	0.000702723525
O	1.609549583439	4.011424257770	-0.000256939074
C	3.506351573750	2.551753281115	0.001683638250
H	3.778979829789	1.963430179343	0.879761363866
H	3.779883489833	1.961926136005	-0.875099571955
H	4.067250982164	3.482145013231	0.001187409843

T2 anion

C	-2.312888097349	0.273943513291	-0.127462711558
C	-0.930232433901	0.379295501886	-0.132707642994
C	-0.266728265662	1.628401373325	-0.020081611319
C	-1.102618757152	2.768168952615	0.098910705497
C	-2.488606723567	2.653825045189	0.103913751619
C	-3.114471275799	1.412408054031	-0.008384251466
H	-2.772476693223	-0.702879510891	-0.217107733687
H	-0.331864811565	-0.519552052498	-0.226796894821
H	-0.631393326915	3.734761073142	0.184387724198
H	-3.090554265174	3.550109713388	0.197170288602
H	-4.193067477931	1.332046822127	-0.003901708285
C	1.176414058796	1.672102838084	-0.032535538473
H	1.668904448701	0.711952100671	-0.128456848734
C	2.003452518392	2.789816883121	0.062103110053
O	1.630260187647	4.007212504617	0.178025544625
C	3.513158157930	2.552342096595	0.024849987087
H	3.968678550552	2.946990038972	0.936454906986
H	3.782668914614	1.500808408502	-0.071901435153
H	3.950261294530	3.102789646586	-0.811940642244

T3 radical

C	2.754359623557	0.772252716732	-0.000315171196
H	3.090586005223	1.799642361302	-0.001071708908
C	3.752142560029	-0.210021415851	-0.000664435120
N	4.592358521681	-1.009912450692	-0.000880598416
C	1.368567193412	0.484966439873	0.000421736701
C	0.440358346915	1.558218367602	0.001088837993
C	0.870007987607	-0.843427585756	0.000497508710
C	-0.915500315042	1.318501504869	0.001121958025
H	0.805242989192	2.575012598555	0.001615963841
C	-0.484810472828	-1.085436076850	0.000515615625
H	1.559860198101	-1.674606153204	-0.000273188689
C	-1.366576270000	-0.002373702502	0.000679369168
H	-1.624833401288	2.129854866247	0.001599613286
H	-0.870135831529	-2.091887539261	0.000120847936
N	-2.803395596753	-0.260156963194	-0.000343859201
O	-3.183021399410	-1.430207310449	0.000993040096
O	-3.566322644705	0.704755840978	-0.002679645543

T3 anion

C	2.761969742160	0.774405012733	-0.000408988800
H	3.099992087771	1.801111986954	-0.001092132582
C	3.754616765111	-0.208858344144	-0.000810637311
N	4.592446724938	-1.019165225312	-0.001306170887
C	1.395170969020	0.493165806823	0.000440616764
C	0.432622155546	1.558946705945	0.000754809480
C	0.864593515202	-0.841126617418	0.001269535896
C	-0.911589727221	1.319534501114	0.000806157561
H	0.791427114212	2.579634945597	0.000927807670
C	-0.480158641620	-1.080738946485	0.001513959843
H	1.550543318955	-1.677072018452	0.001733471540
C	-1.400769076500	-0.007717821300	0.000859212513
H	-1.614984021700	2.137424661547	0.000808333564
H	-0.856272949736	-2.091755239667	0.002104763590
N	-2.775478482689	-0.256205693817	-0.000460810356
O	-3.192200279724	-1.443067396139	-0.000618735699
O	-3.581326903526	0.709641183801	-0.001713935651

T4 radical

C	-0.413948974080	-0.457711268288	0.022151075001
C	0.318278552396	0.744165667992	0.026865224286
N	0.903024713636	1.758225211675	0.037064278670
C	0.309739362130	-1.663812737351	-0.025538316246

N	0.887230509661	-2.681503764920	-0.059357112678
C	-1.917948276698	-0.452351611762	0.011586000860
H	-2.302191584426	0.433652765731	0.522873097749
H	-2.281428279460	-0.432277544764	-1.025834429796
H	-2.308296469044	-1.353881774442	0.490190199987

T4 anion

C	-0.388474195400	-0.458548577977	0.037146192656
C	0.327051021439	0.737452600008	0.021440115684
N	0.905970076937	1.768489302149	0.017125380624
C	0.317792822753	-1.658935348062	-0.012635190774
N	0.890053045640	-2.693232781953	-0.045799675675
C	-1.912637962243	-0.450771935772	-0.004290165749
H	-2.311937271740	0.407300223882	0.549566718652
H	-2.318362213317	-0.400629663116	-1.026618231202
H	-2.314995762545	-1.356618880052	0.464064877306

T5 radical

C	0.919938000405	0.282700000123	-1.691600001911
C	0.896075997750	0.706399999857	-0.179164000068
C	-0.308668000008	-1.252075001147	-0.241370999777
C	0.129469999775	-1.058404001084	-1.734228999096
H	0.476937000190	1.054871002369	-2.328884997362
H	1.957135997454	0.156408000004	-2.016788001011
H	-0.730956997399	-1.024831998827	-2.408266002572
H	0.754711000277	-1.901022998774	-2.043615999586
C	0.926564997715	-0.690106998737	0.552060000571
H	-0.638616997986	-2.261580001264	0.011032999987
C	0.679308000064	-0.605767999965	2.069898998553
H	0.562626997372	-1.612304998581	2.488870999957
H	1.531344002520	-0.134614000184	2.572762997449
H	-0.217953000084	-0.034649000011	2.334771998556
C	2.213398998517	-1.499458001183	0.327978000206
H	3.044458998519	-1.041799002374	0.876993999903
H	2.083379999613	-2.517084998310	0.715926999398
H	2.513322998157	-1.578373002360	-0.719213999504
C	1.910158999859	1.769391999090	0.207193999800
H	2.929667999852	1.419304000366	0.012240000018
H	1.751430999658	2.683933000522	-0.375102000054
H	1.834364001045	2.032908998371	1.267956000768
C	-0.565646000973	1.108251001854	0.048031999992
C	-1.319076000814	-0.168543000204	0.001221000001
O	-1.034425997494	2.230435001480	0.203959999966
C	-2.704342000180	-0.283163000018	0.078391999995
N	-3.871999001690	-0.370523000034	0.155225000012

T5 anion

C	0.913010001807	0.271549999796	-1.681682998767
C	0.871023002411	0.701944999816	-0.170741000183
C	-0.320704999763	-1.228271001606	-0.233808999786
C	0.141322999853	-1.084925997647	-1.715565998471
H	0.454750000037	1.037934998023	-2.317433999451
H	1.950861998384	0.157741000038	-2.018155998180
H	-0.716753997539	-1.066444002085	-2.395299001918
H	0.790426000893	-1.911938998527	-2.030084001718
C	0.921119002224	-0.692500001575	0.554458998987
H	-0.656803998421	-2.233481998556	0.044150000018
C	0.708780000811	-0.622905001691	2.077976999770
H	0.619795000777	-1.635777997778	2.493565997738
H	1.567429998693	-0.145685000175	2.567720002152
H	-0.191488999757	-0.068253999749	2.355689997895
C	2.215469002171	-1.494774999850	0.318616000235
H	3.049992001327	-1.048640999092	0.874456002509
H	2.091216997653	-2.521944998836	0.687657998366

H	2.516939998463	-1.556131001644	-0.729628000590
C	1.892397997661	1.759663002026	0.211465999779
H	2.914273001872	1.413708999156	0.010922999974
H	1.731388000125	2.680045998129	-0.362615999787
H	1.825501002482	2.021867001525	1.274440998666
C	-0.614137001020	1.105921997707	0.052542000014
C	-1.333769997746	-0.110599000227	0.017163999976
O	-1.014362000208	2.297090998774	0.173980000212
C	-2.714873002347	-0.247283999976	0.045582999992
N	-3.890190997557	-0.367606000103	0.080906000261

T6 radical

C	1.598024998145	1.364379999372	-0.335321000209
C	0.128330999810	1.550188997771	0.070514999862
C	-0.660676998785	0.270363999899	0.022871000008
C	-0.041043000015	-1.064498000527	-0.008455000025
C	1.469225001276	-1.145903997577	-0.110383999761
C	2.202617002308	0.127600000235	0.337216000197
H	0.076481999950	1.929029998878	1.106034998208
H	-0.367011000129	2.312432999658	-0.543819002191
H	1.668782002387	1.263224997770	-1.426557998583
H	2.154267001528	2.267098001898	-0.060677000230
H	1.793256002035	-2.029251997560	0.450356999985
H	1.694823998179	-1.349022001462	-1.168662999134
H	2.138389002342	0.230902999862	1.429204001045
H	3.265952998478	0.036935999977	0.089668000062
O	-0.747984999203	-2.079657999966	0.024244000018
C	-2.068982998097	0.329863999948	0.064890999741
N	-3.235846000956	0.414505999768	0.094115000002

T6 anion

C	1.583633997499	1.368404000452	-0.341733999844
C	0.127601999996	1.543992999422	0.107780000210
C	-0.661253997738	0.237332999843	0.026292999994
C	-0.072990999912	-1.042243998072	-0.042864000021
C	1.455987998535	-1.135344001791	-0.093401999860
C	2.203760998765	0.137444000207	0.326024999749
H	0.124229000126	1.938148997499	1.138961002097
H	-0.356197999957	2.316309000456	-0.506960999972
H	1.622324000631	1.245813998669	-1.434594999150
H	2.156965000942	2.273248999018	-0.099983000029
H	1.755511998415	-1.990163000105	0.526571000254
H	1.728061999658	-1.401540997878	-1.126993998198
H	2.150423000075	0.255910999792	1.418725001123
H	3.268221999221	0.047829999981	0.071197999889
O	-0.721325998661	-2.138810999998	-0.095898000163
C	-2.062060000223	0.326682999857	0.064763000241
N	-3.234287002565	0.445177999796	0.097355000176

T7 radical

C	-0.364311180874	-0.478139036274	0.000001021128
H	-1.451219196409	-0.487985442415	-0.000000651452
C	0.307724447411	0.749626517487	0.000000225111
N	0.848589471296	1.788139583401	-0.000000411163
C	0.330040121765	-1.693312631029	0.000000230041
N	0.889242938835	-2.722141791067	-0.000000413664

T7 anion

C	-0.365610705687	-0.478149105987	-0.000000072834
H	-1.451010097327	-0.487928351603	0.000000047273
C	0.302768666868	0.744610383226	-0.000000017770
N	0.854102148408	1.788352333806	0.000000030227
C	0.325069001434	-1.688371856893	-0.000000015952

N	0.894747588328	-2.722326198741	0.000000029057

T8 radical

C	-2.626599999663	0.213463999878	-1.240344999844
N	-3.280954997713	0.148987999954	-2.210512998315
C	-1.825484000019	0.290854999799	-0.096723000132
H	-0.756476002063	0.376396999873	-0.250618000015
C	-2.446389997762	0.263169999793	1.236682998309
O	-3.680557001865	0.182704999942	1.318333999115
C	-1.582766998852	0.338195000259	2.447813997755
C	-2.218905997557	0.371447000062	3.703864998317
C	-0.176473000080	0.373325000233	2.393410998182
C	-1.469197997363	0.440292999880	4.874754997399
H	-3.302727999252	0.344157999766	3.743904001156
C	0.572752999053	0.440013000048	3.569424999008
H	0.352566000123	0.344738000212	1.447272000109
C	-0.069834999741	0.474676000077	4.810245999043
H	-1.971231997682	0.467585000082	5.837730985471
H	1.657161001006	0.464672000201	3.514339000995
H	0.515712999911	0.528294999803	5.723944021181

T8 anion

C	-2.615489998253	0.351376999791	-1.233433998418
N	-3.217215999821	0.257180000076	-2.241245001747
C	-1.888466999475	0.468115000161	-0.042091000022
H	-0.890958002168	0.886334998946	-0.113388000129
C	-2.447954002169	0.098082000230	1.198986001501
O	-3.631598997639	-0.332130000256	1.356954997539
C	-1.580183000084	0.245921999973	2.432161999571
C	-2.205858001040	0.425065000172	3.677536998119
C	-0.175675999936	0.190944999765	2.394864002378
C	-1.455204001334	0.565718000824	4.847250001254
H	-3.290582001163	0.454886999783	3.713879999788
C	0.578583002570	0.320124000231	3.564922997447
H	0.336613000122	0.023556000007	1.451804000726
C	-0.057631999740	0.513250999773	4.795974999912
H	-1.960072999755	0.714585000705	5.798892976765
H	1.663343997471	0.263808999793	3.514934002557
H	0.528944000194	0.616155002430	5.705518017860

T9 radical

C	-0.437758999891	1.258890999389	-0.470562999858
C	-1.193479002461	-0.000111000000	0.021689999988
C	-0.437524000230	-1.259023002644	-0.470434000213
C	1.038517997845	-1.277986999265	-0.123869999957
C	1.727055001889	0.000160000000	0.005928999978
H	-0.894809999488	-2.175524002371	-0.082044000081
H	-0.500956999814	1.315351000732	-1.568704998260
H	-0.895211999538	2.175344997596	-0.082259000018
H	-0.500697000234	-1.315602000065	-1.568571000007
O	1.668960001725	-2.334440998212	0.028125999993
C	-2.613190998454	-0.000269000000	-0.571739000270
H	-3.170305001208	-0.886682001609	-0.245029000204
H	-3.170475999531	0.886059001281	-0.245090000048
H	-2.587360001491	-0.000304000000	-1.668125002424
C	-1.290389997558	-0.000045000000	1.561952998709
H	-1.830985998334	0.886981002607	1.912684000660
H	-1.830830002185	-0.887132998177	1.912766001961
H	-0.306165999894	0.000064000000	2.047338999378
C	1.038282000685	1.278164998603	-0.124017000094
O	1.668528997472	2.334752000949	0.027864000018
H	2.790332000092	0.000270000000	0.229805000017

T9 anion

C	-0.422743000215	1.250885998169	-0.444652999912
C	-1.193649000639	-0.000108000000	0.028500999993
C	-0.422509999785	-1.251006999829	-0.444526000028
C	1.076348998198	-1.246609997610	-0.133414999990
C	1.731373998096	0.000161000000	-0.010408999991
H	-0.857880997563	-2.160893998838	-0.011740999986
H	-0.526669999785	1.347097997800	-1.537493999495
H	-0.858285998047	2.160740997832	-0.011973999992
H	-0.526435000124	-1.347358998583	-1.537355000517
O	1.663706002308	-2.365506002277	-0.031649000011
C	-2.605955997698	-0.000275000000	-0.584996000617
H	-3.171654000915	-0.887154001220	-0.269917000206
H	-3.171812002646	0.886547998065	-0.270045000235
H	-2.562327998611	-0.000351000000	-1.681573998846
C	-1.325098000405	-0.000045000000	1.566396002303
H	-1.875004001024	0.886700999071	1.907661997824
H	-1.874886999943	-0.886834002470	1.907740998689
H	-0.346670999887	0.000042000000	2.059244999728
C	1.076113001038	1.246797998397	-0.133523999911
O	1.663255000448	2.365812999142	-0.031834999979
H	2.802324002322	0.000271000000	0.193270999773

T10 radical

C	-0.393067000066	-0.449121000250	-0.000008000000
C	0.356349999760	0.741085999515	0.000013000000
N	0.957765000178	1.744676999818	0.000013000000
C	0.293195999864	-1.679777997859	0.000018000000
N	0.854067000458	-2.704977002247	0.000038000000
C	-1.899455999224	-0.454762000189	-0.000022000000
O	-2.465503000102	-1.538723997831	-0.000010000000
C	-2.607558002320	0.870492999686	-0.000006000000
H	-2.327357998317	1.456103999471	0.883953997847
H	-2.327348002160	1.456142999831	-0.883935000385
H	-3.685329000222	0.701321999488	-0.000014000000

T10 anion

C	-0.419646999742	-0.457439000264	0.000132000000
C	0.323573000002	0.741388000948	0.000310000000
N	0.937038002060	1.741424999492	-0.000773000000
C	0.293016999852	-1.676894998092	0.000099000000
N	0.878733998066	-2.692113000645	0.000124000000
C	-1.863011998794	-0.471185000040	0.000001000000
O	-2.518130001586	-1.533827002527	-0.000363000000
C	-2.583521000763	0.869205998380	0.000109000000
H	-2.315069000670	1.462131999932	0.882826998562
H	-2.314878999593	1.462369997382	-0.882392999166
H	-3.662345997953	0.697400002606	-0.000033000000

A_a

C	-0.503962655449	0.352719982224	-0.083295810044
H	-0.366562693369	0.268747022736	-1.164991318947
C	0.804509052155	0.112962191867	0.594445983707
H	0.857527343142	0.134496778965	1.678887419076
C	2.017510068604	-0.170645509097	-0.147759650005
O	2.099902176799	-0.241215718017	-1.374268225859
O	3.078472890205	-0.354954847862	0.675691137345
C	-1.466947480780	-0.752363009252	0.367780926508
O	-1.881359705055	-0.882727349202	1.506466096044
O	-1.790405657794	-1.571925946467	-0.643055672911
C	-2.678799674676	-2.672582218190	-0.331273495194
H	-2.220947288056	-3.321385263597	0.418725537648
H	-3.633700169831	-2.291256867675	0.037037430918
H	-2.813404602646	-3.205307962139	-1.271667088781

C	-1.108588892085	1.759112811190	0.249938751325
H	-1.267819065581	1.791986849877	1.335680438597
C	-2.461864356448	1.952016795348	-0.450616898492
H	-2.874876568333	2.937322971516	-0.205327798694
H	-2.351711061546	1.896231172148	-1.541259947309
H	-3.199046340524	1.200856203716	-0.144112180734
C	-0.129856546263	2.876874545677	-0.137594477038
H	-0.561631398080	3.855211844308	0.103279070762
H	0.822970510349	2.791204835563	0.397460212318
H	0.083029494734	2.859980489208	-1.214288202966
C	4.340066207094	-0.647270886884	0.041744978347
H	4.637763831216	0.178428440573	-0.609829535585
H	5.051846198170	-0.766151255891	0.858122117158
H	4.266932096498	-1.568946895745	-0.541382178188

B_a

C	-0.546744002753	0.477381360876	-0.080822904093
H	-0.412192327473	0.422805215579	-1.167283936870
C	0.778720489912	0.154387740595	0.572240284548
H	0.832542997962	0.180622660639	1.657956814735
C	1.903002936467	-0.199942088128	-0.151828576642
O	2.061106941487	-0.306790486151	-1.404667175739
O	3.028852790039	-0.462312780035	0.679939954070
C	-1.484059738179	-0.649770185548	0.316913881106
O	-2.059717872482	-0.758771874425	1.394318877295
O	-1.588837640413	-1.599444320212	-0.647364905798
C	-2.343087266957	-2.781527290398	-0.315420458355
H	-1.887582204599	-3.299298862148	0.533308706728
H	-3.377416927740	-2.522745903249	-0.074131748279
H	-2.306739105811	-3.408848143600	-1.206491295391
C	-1.151639421251	1.867196636907	0.269340652141
H	-1.277573479028	1.906991159876	1.361214122637
C	-2.530635633798	2.069693397332	-0.382092800345
H	-2.947372237211	3.050246339769	-0.119216854802
H	-2.453506864997	2.025247676580	-1.477487277872
H	-3.252601677585	1.308346350815	-0.064207525571
C	-0.200684626412	2.998575243994	-0.144474170224
H	-0.603932480024	3.973886225795	0.156537162635
H	0.785673206378	2.875782911306	0.314432947537
H	-0.065736524906	3.015819880364	-1.235226919594
C	4.220997689131	-0.872118288105	0.019581771272
H	4.579989099682	-0.114273586126	-0.686833323312
H	4.964837267543	-1.013824017491	0.808944139258
H	4.083382324939	-1.815895779967	-0.522641834609

A_b

C	1.387110949245	-0.806763299437	-0.098863949516
C	1.698293088163	-1.118147488797	1.238998799485
N	1.959469462565	-1.355526732378	2.354907784021
C	1.836748542340	-1.696356267829	-1.089952101607
N	2.202346449877	-2.413246279786	-1.940917287522
C	0.541049320432	0.409225716649	-0.471477523380
H	0.666810808229	0.545500007679	-1.551206256286
C	1.023788583082	1.714189306920	0.225761234697
H	0.938324082597	1.577158810546	1.312421814378
C	0.137061277554	2.901034543894	-0.180760136115
H	-0.910344245160	2.748904245753	0.097896669142
H	0.487913754779	3.814339048692	0.313222240355
H	0.181016491780	3.068058275273	-1.264874014495
C	2.495498346524	2.005937423436	-0.109954251774
H	3.165637594727	1.199519031119	0.209037109730
H	2.628445071252	2.147769308668	-1.190319396475
H	2.821862886479	2.923771595180	0.391573817032
C	-0.926516869048	0.039031077846	-0.222297223756
C	-1.754616196653	-0.269990750576	-1.312342728845
C	-1.463757330686	-0.022272240547	1.074388550102

C	-3.094702300100	-0.615318129842	-1.115795777656
H	-1.351623500120	-0.231626011507	-2.321731590440
C	-2.802534868856	-0.367880191157	1.271828318493
H	-0.845350187099	0.209513878286	1.937301858873
C	-3.622449349074	-0.666406945475	0.177881743365
H	-3.723266693283	-0.842785937224	-1.972661453492
H	-3.204572892662	-0.403538745498	2.280829938790
H	-4.663472392448	-0.936423987161	0.333550698713

B_b

C	1.455917469797	-0.841104164429	-0.051709143828
C	1.797072475690	-1.095916653720	1.275193192317
N	2.085865031660	-1.285421626832	2.405440778373
C	1.876313201313	-1.743364354585	-1.026157042682
N	2.224849721256	-2.487069029851	-1.876715968670
C	0.563650801809	0.351038422159	-0.445673370518
H	0.696008663431	0.479589418397	-1.528686972005
C	1.008783197113	1.692380522418	0.211079435299
H	0.928775524377	1.579078215658	1.302513108734
C	0.100506176369	2.859879453404	-0.211246886019
H	-0.943834034446	2.695529014155	0.073676301331
H	0.433826000357	3.793815355166	0.258085286282
H	0.133376094352	3.004403681146	-1.300120100603
C	2.471611350830	2.023150864809	-0.123768440797
H	3.154432891764	1.235964306867	0.209975962704
H	2.602622922132	2.146068781833	-1.208008245361
H	2.772213073013	2.962652271444	0.356524592784
C	-0.915378075107	0.032818770308	-0.219381301230
C	-1.772227875627	-0.172170423184	-1.311634869660
C	-1.455427811542	-0.093205630665	1.073207976916
C	-3.121410307743	-0.498234962525	-1.127199567668
H	-1.378644590167	-0.076061922148	-2.321958803258
C	-2.801635981990	-0.414197173537	1.264212024391
H	-0.818689006347	0.058550927076	1.941156121072
C	-3.642974407878	-0.620438564931	0.163518747835
H	-3.761879182538	-0.653923141822	-1.992348628979
H	-3.195467377476	-0.504152862905	2.274056676899
H	-4.690086047795	-0.871990211345	0.312416010302

A_l

C	-1.426959215451	1.033647646613	0.355612849029
H	-1.551240372341	0.482782685344	1.293298059157
H	-1.277966504232	2.093090650104	0.618356739458
C	-2.649085866403	0.922700368935	-0.503987626792
C	-3.846393206671	0.385311660949	-0.049327549044
N	-4.860211763053	-0.071720752357	0.336828610730
H	-2.630817213925	1.307254520647	-1.521155848975
C	-0.162081017281	0.558162392764	-0.369803260821
C	-0.043105821517	-0.949265244727	-0.591065774327
H	-0.058716557425	1.092996627425	-1.325401827499
C	1.979262304157	-0.180311867455	0.236062896754
H	-0.470652183151	-1.295485556027	-1.534521447069
H	-0.488261706786	-1.511486257344	0.242674292862
O	0.973555695708	0.832469960924	0.460064891875
O	1.371421538232	-1.142018090581	-0.644026702505
C	2.328124691424	-0.816226871798	1.579174557661
H	3.106489076825	-1.575194330119	1.447456841708
H	2.698237904036	-0.054590559555	2.273663672862
H	1.443247422226	-1.287900081206	2.018123416739
C	3.184833191045	0.420814591681	-0.476120907333
H	3.673791709383	1.159964982149	0.166749528684
H	3.910511084861	-0.362983876374	-0.718187787311
H	2.868966807228	0.908564436995	-1.403568402766

B_l

C	-1.433395740717	1.229047193444	0.371136500044
H	-1.587290998310	0.741344264452	1.345849033752
H	-1.187014721850	2.278753315129	0.589106241707
C	-2.686236445409	1.156493897167	-0.478558364761
C	-3.515422792961	0.060354586316	-0.472274918820
N	-4.250972693981	-0.882896177899	-0.440465215311
H	-2.796921013062	1.867957514357	-1.295580141161
C	-0.191839552669	0.601007415961	-0.272225924195
C	-0.184285815251	-0.919467688869	-0.389220143173
H	-0.018190768705	1.054538070528	-1.260388539139
C	1.926401491015	-0.218101576640	0.302796374587
H	-0.645790661812	-1.299838715914	-1.302640963239
H	-0.662758602003	-1.385607323957	0.484667409770
O	0.972088398436	0.819962238461	0.560464176035
O	1.213812006980	-1.238363146530	-0.428319605108
C	2.415921524580	-0.766874138417	1.640637236289
H	3.152304006562	-1.561580484413	1.479596975108
H	2.886570093451	0.028547244472	2.228958792864
H	1.573904190793	-1.173331199381	2.210148326426
C	3.061392028889	0.294663334178	-0.581285791038
H	3.639934152520	1.058726709222	-0.050862817488
H	3.735152293852	-0.526026399647	-0.851031380692
H	2.655589607758	0.731268111263	-1.499608033505

Bn$^{\bullet}$

C	-1.210245733601	0.001128569951	0.000132004830
C	0.178686626133	-0.005300639350	0.000673439774
C	0.922772913839	1.215390786014	0.000207175636
C	0.178788908679	2.436146719827	-0.000840601441
C	-1.210142189497	2.429833148885	-0.001373106629
C	-1.917795138106	1.215509660383	-0.000892190392
H	-1.753140919389	-0.940911256429	0.000508038966
H	0.719257122155	-0.949055113749	0.001473911924
H	0.719441037694	3.379854725429	-0.001216481108
H	-1.752960649881	3.371916945589	-0.002168923882
H	-3.004302211417	1.215556931783	-0.001307573202
C	2.332486418690	1.215333105699	0.000755295254
H	2.893365062191	2.145160951873	0.000483908952
H	2.893292691916	0.285462086602	0.001604621314

Bn^{-}

C	-1.217679742030	0.012341611302	0.000140492063
C	0.171411422197	0.001637179127	0.000425913523
C	0.962340636748	1.215387441615	-0.000280262069
C	0.171513499422	2.429207095205	-0.001099822077
C	-1.217576547183	2.418620714643	-0.001371037927
C	-1.954444432834	1.215511279665	-0.000789034963
H	-1.747995750557	-0.941112343768	0.000647326673
H	0.695550528262	-0.955015252525	0.001189963848
H	0.695737259024	3.385813297840	-0.001507459690
H	-1.747813951727	3.372118281642	-0.002041435244
H	-3.041510624200	1.215558879155	-0.000991074266
C	2.363310287285	1.215333153325	0.000308462440
H	2.928365747660	2.145893190252	0.001132085657
H	2.928295605221	0.284732086114	0.002275402036

iPr$^{\bullet}$

C	-3.622525804597	-0.319094823587	0.003227827490
H	-3.425440547893	-1.394691635012	-0.118081585536
H	-3.403754590713	0.177903606321	-0.948945039598
H	-4.712103206406	-0.226485491496	0.172361105841
C	-2.832350189192	0.259421692630	1.131854850699
C	-2.793460998467	-0.412614737888	2.466024694744

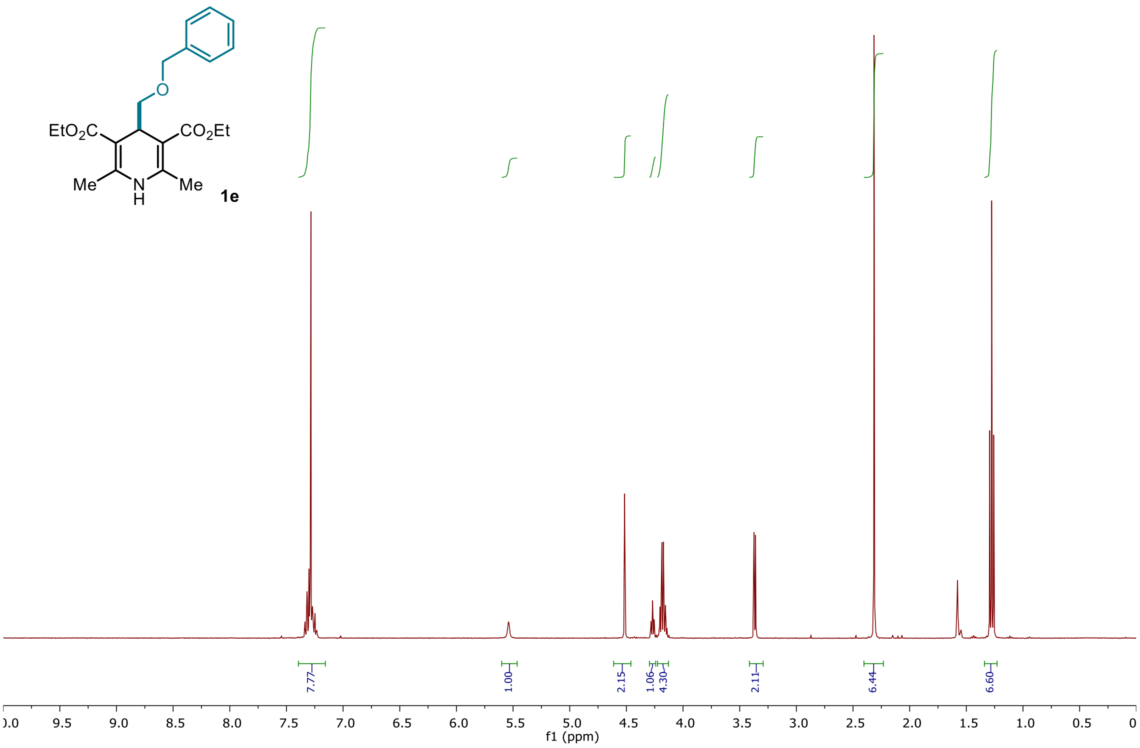
H	-2.595314550956	-1.490464004802	2.369693974207
H	-2.027681738279	0.018587859420	3.121176252663
H	-3.759110405672	-0.326775105267	2.999450042713
H	-2.496660382632	1.292176886114	1.058242310988

iPr$^-$

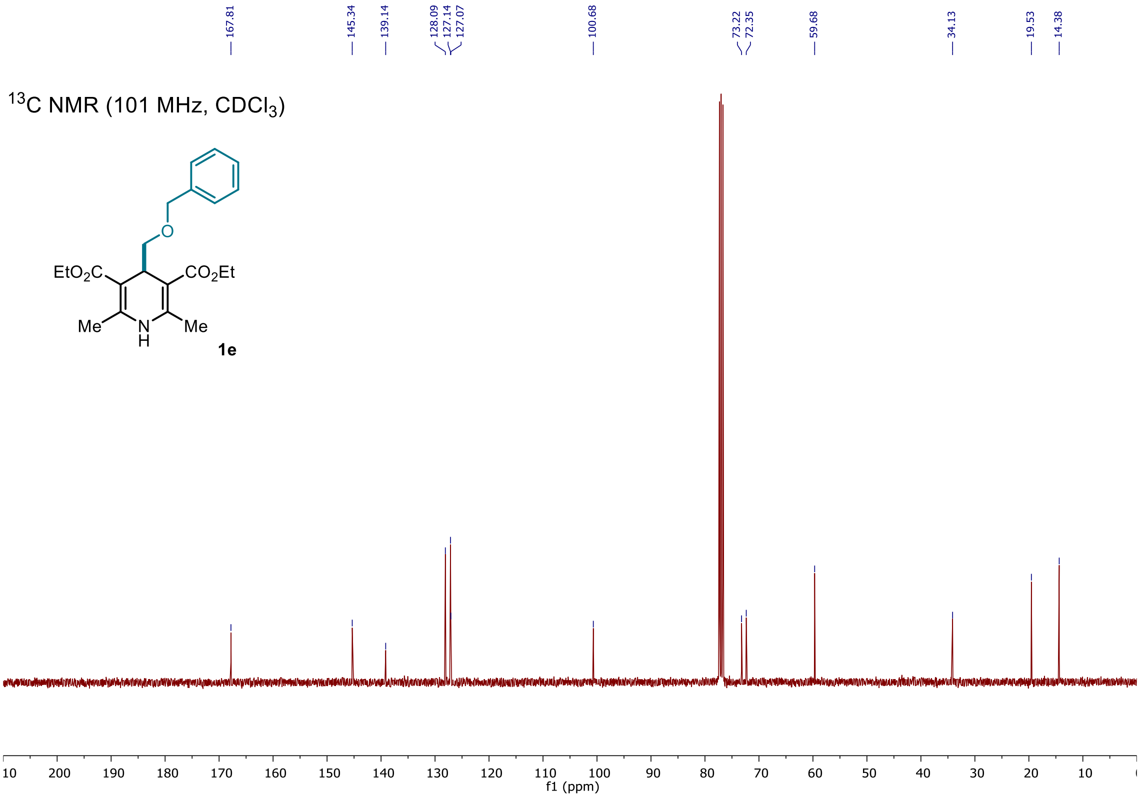
C	-3.573851195933	-0.301488185555	0.039302449814
H	-3.457540474409	-1.375654876525	-0.184618262895
H	-3.525673003117	0.220581053914	-0.929141979594
H	-4.632652651436	-0.194613125997	0.400814171863
C	-2.521529155510	0.199976299435	1.029461262214
C	-2.769751017841	-0.428648789845	2.401872938630
H	-2.570079423405	-1.513860453224	2.406372913442
H	-2.129377252065	0.004584493266	3.186119197498
H	-3.827053531274	-0.326991414918	2.768883939817
H	-2.660894715110	1.294079251720	1.135937796829

G. NMR Spectra

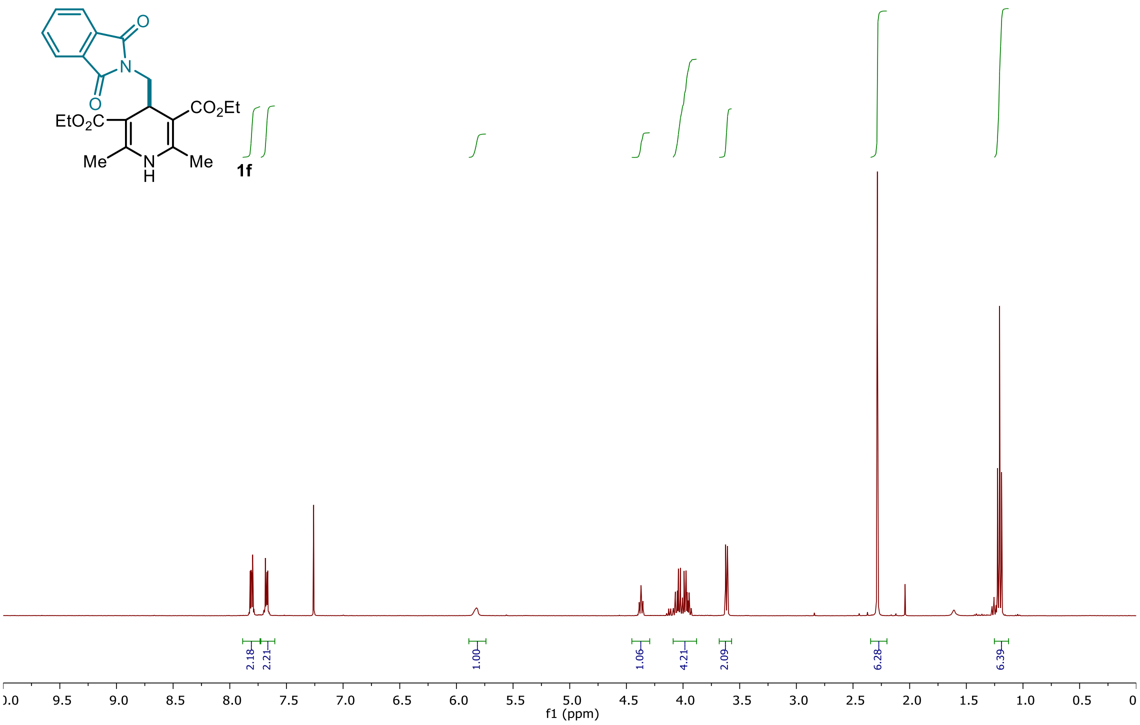
^{1}H NMR (400 MHz, CDCl$_3$)



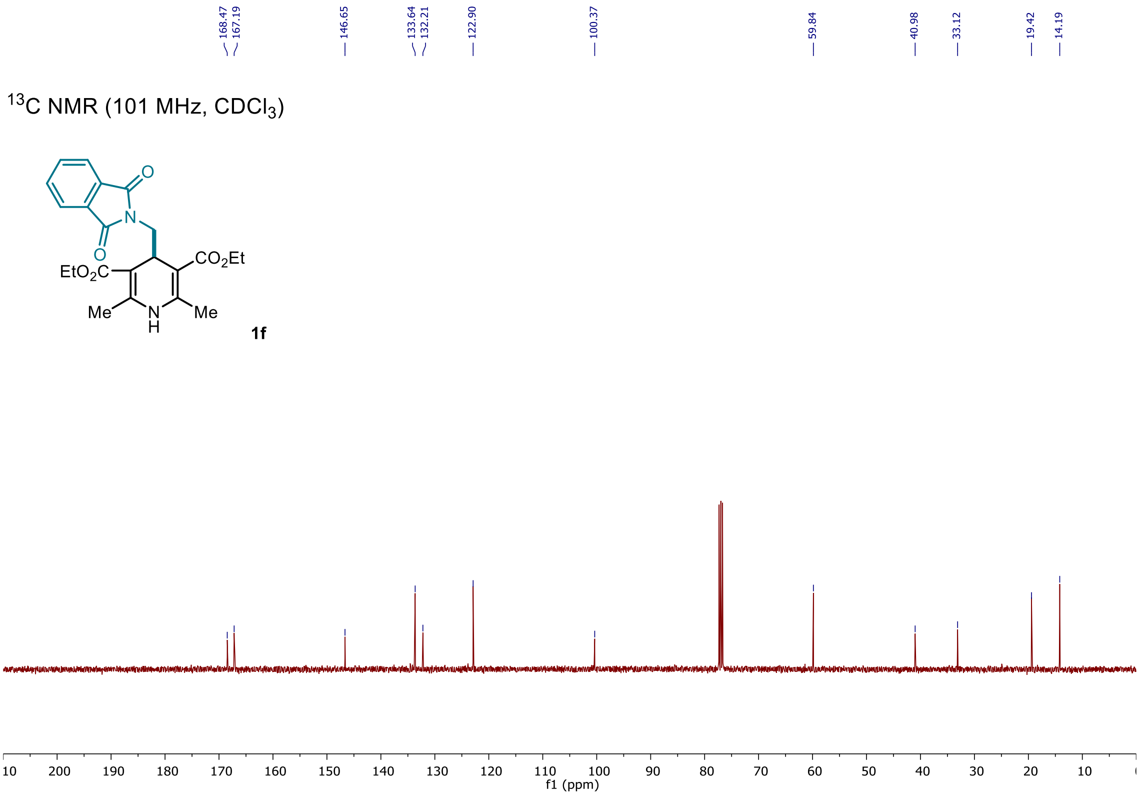
^{13}C NMR (101 MHz, CDCl$_3$)



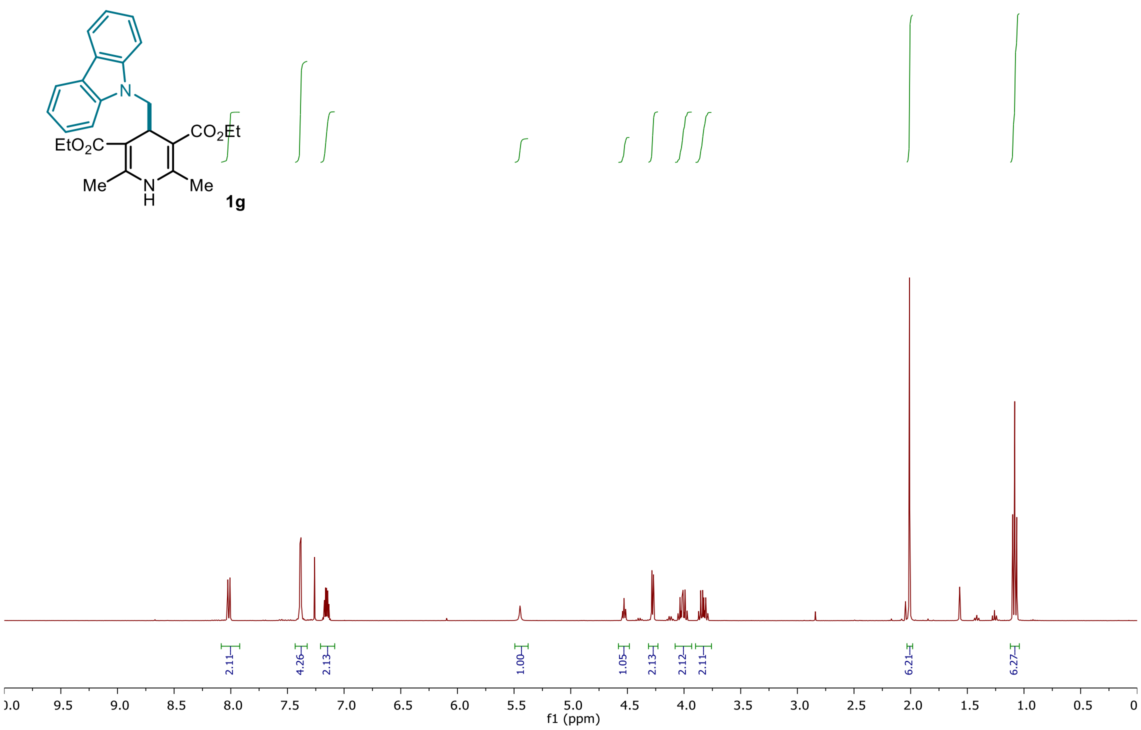
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (101 MHz, CDCl$_3$)

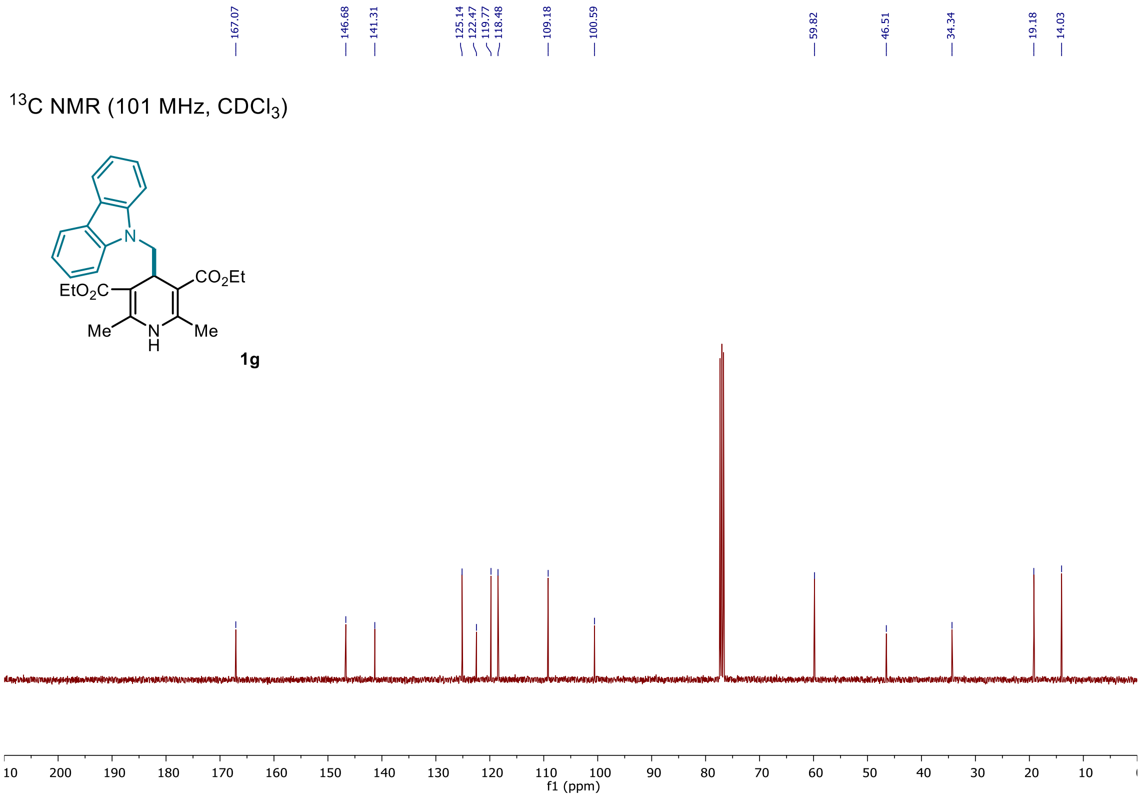


^{1}H NMR (400 MHz, $CDCl_3$)



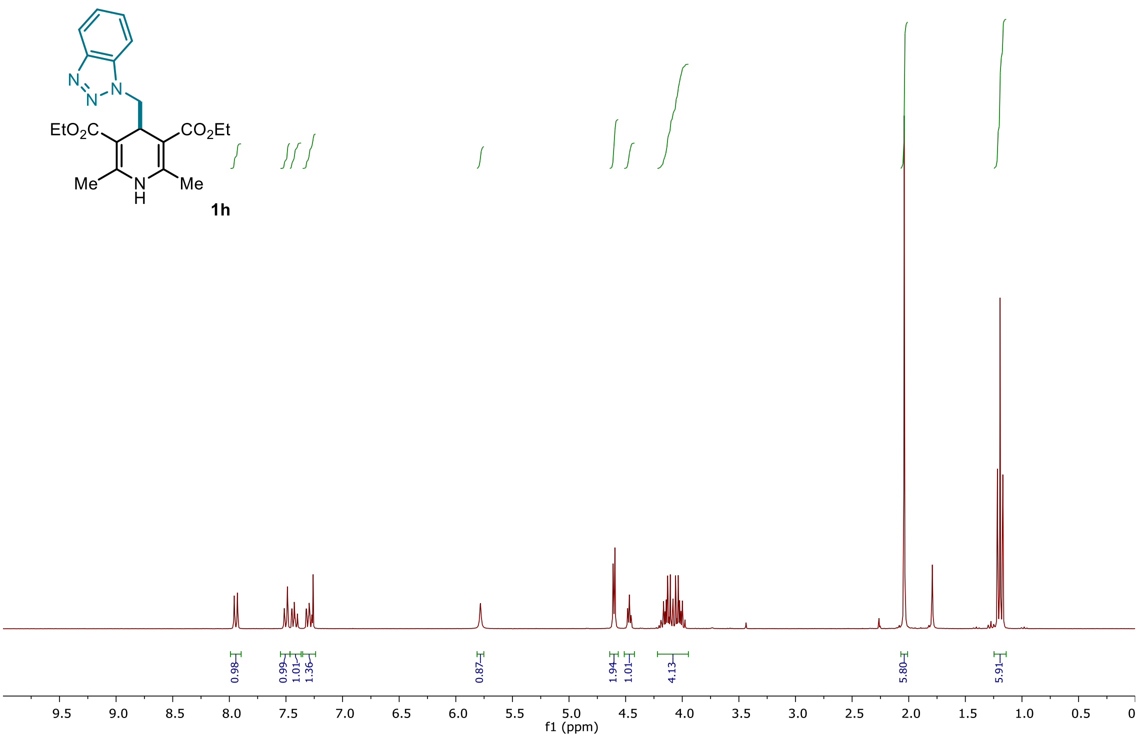
1g

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

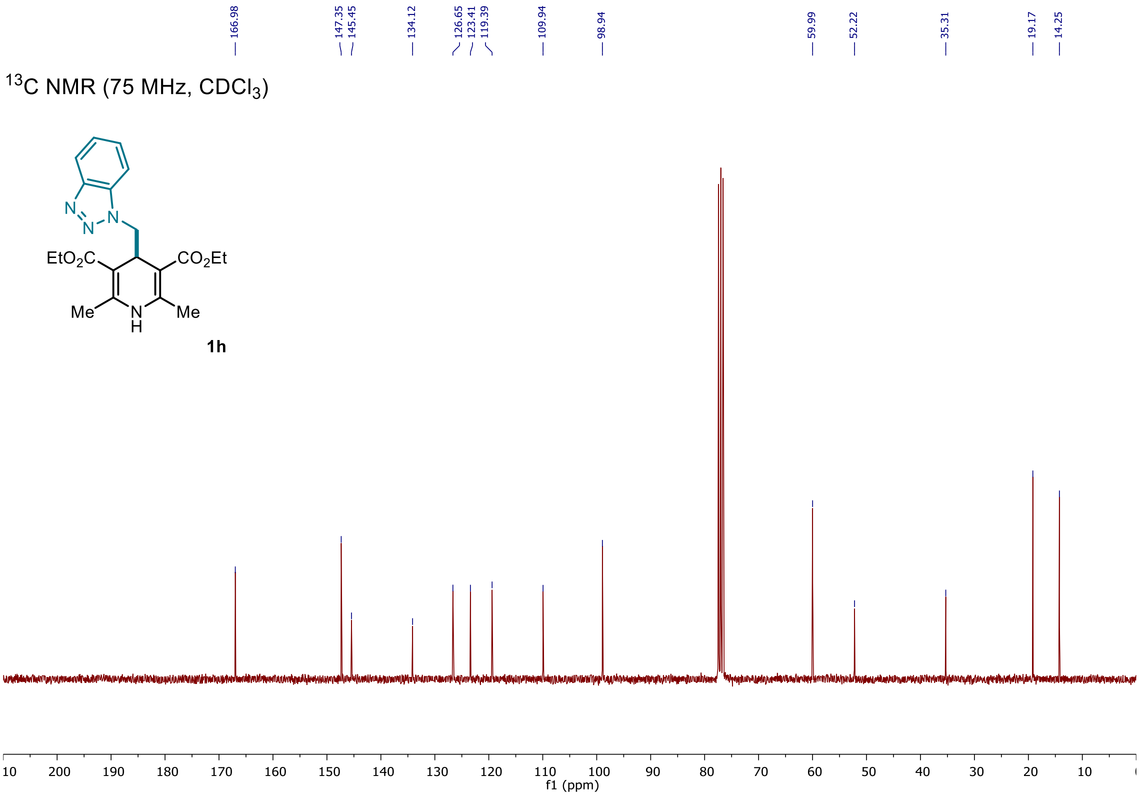


1g

^{1}H NMR (300 MHz, $CDCl_3$)

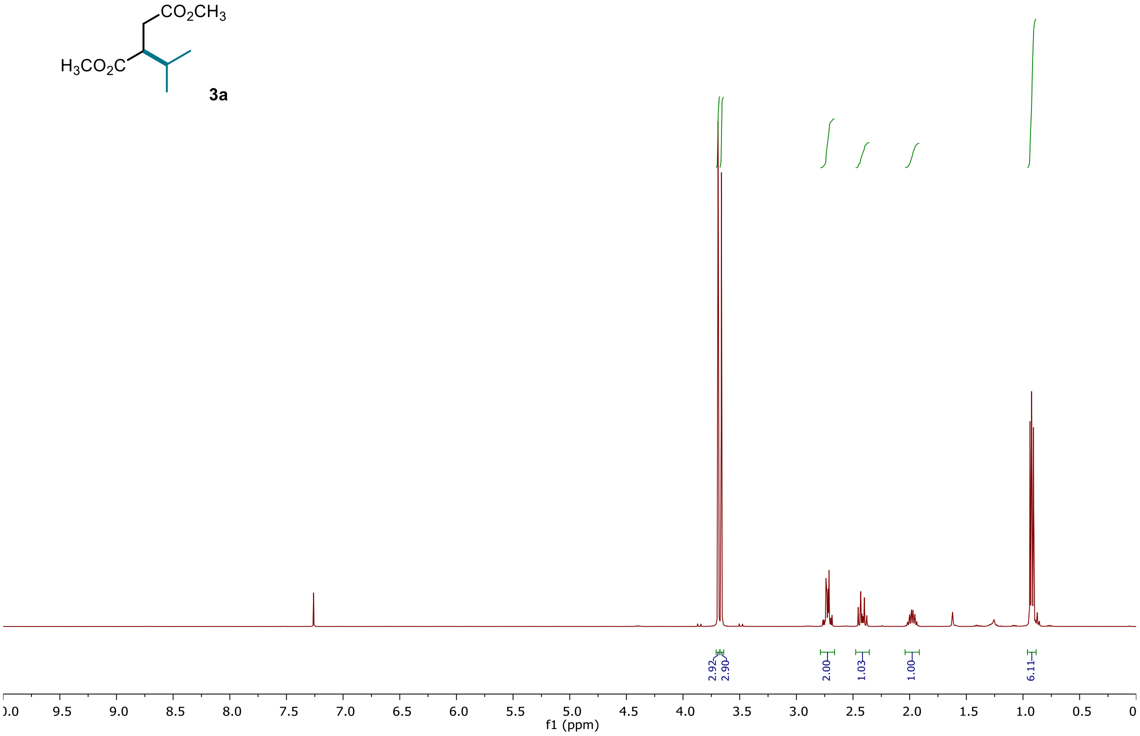


^{13}C NMR (75 MHz, $CDCl_3$)

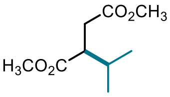


^{1}H NMR (400 MHz, CDCl$_3$)

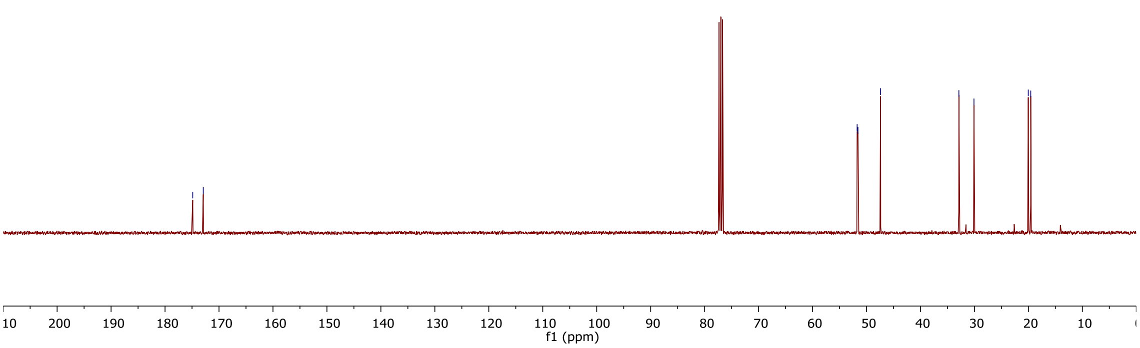
3a



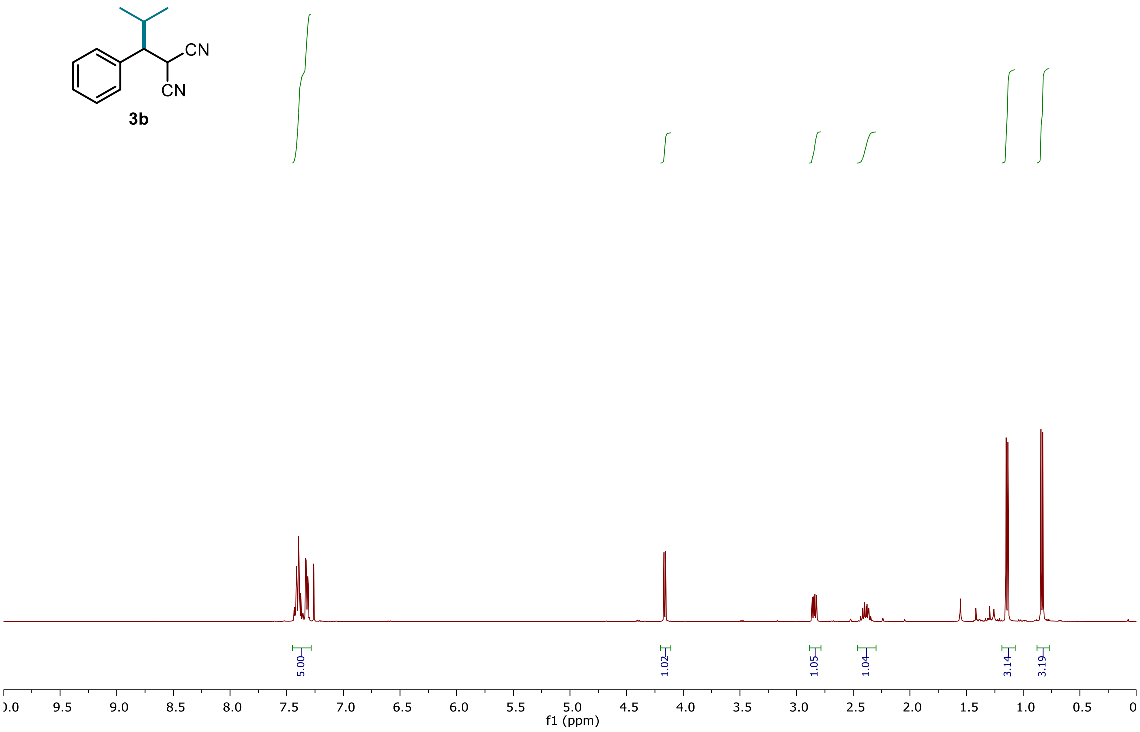
^{13}C NMR (101 MHz, CDCl$_3$)



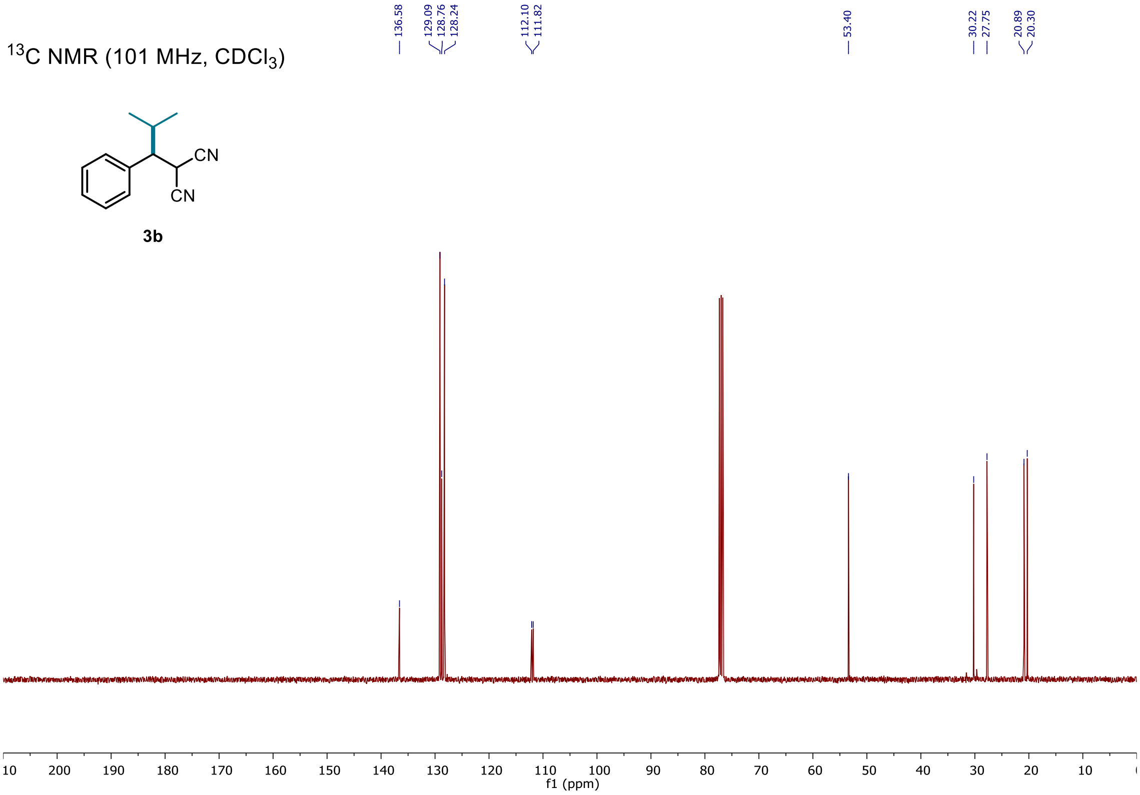
3a



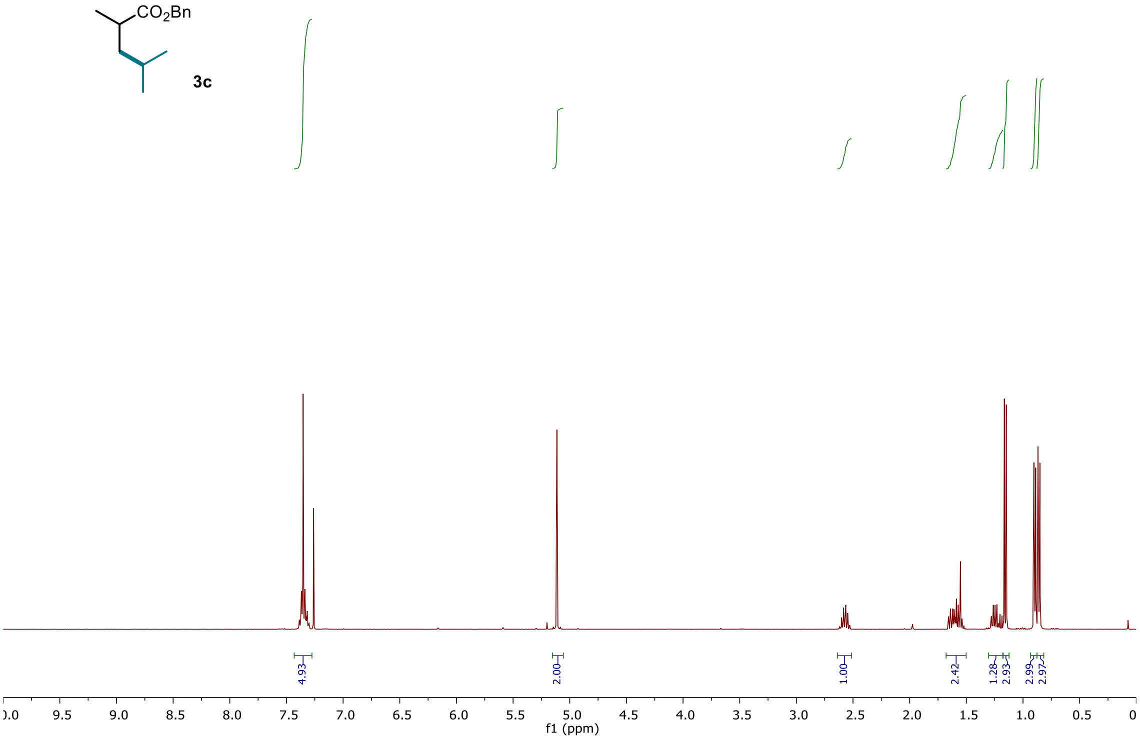
^{1}H NMR (400 MHz, $CDCl_3$)



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

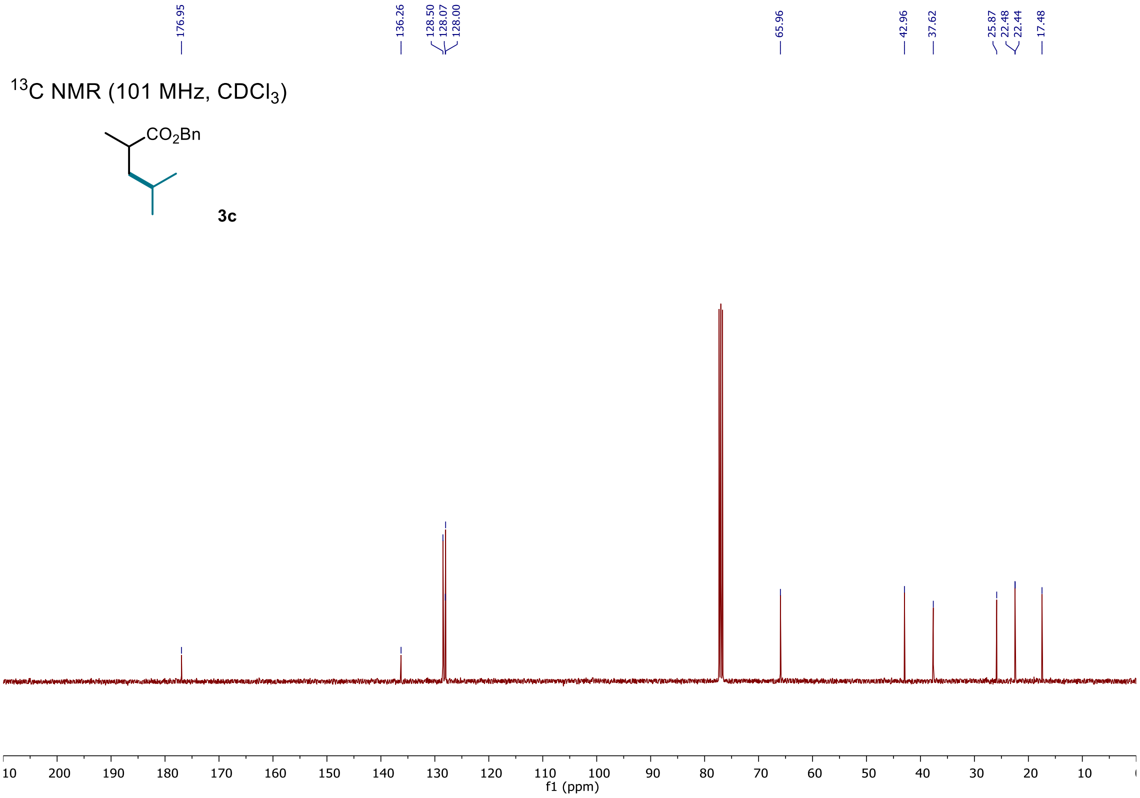


^{1}H NMR (400 MHz, $CDCl_3$)



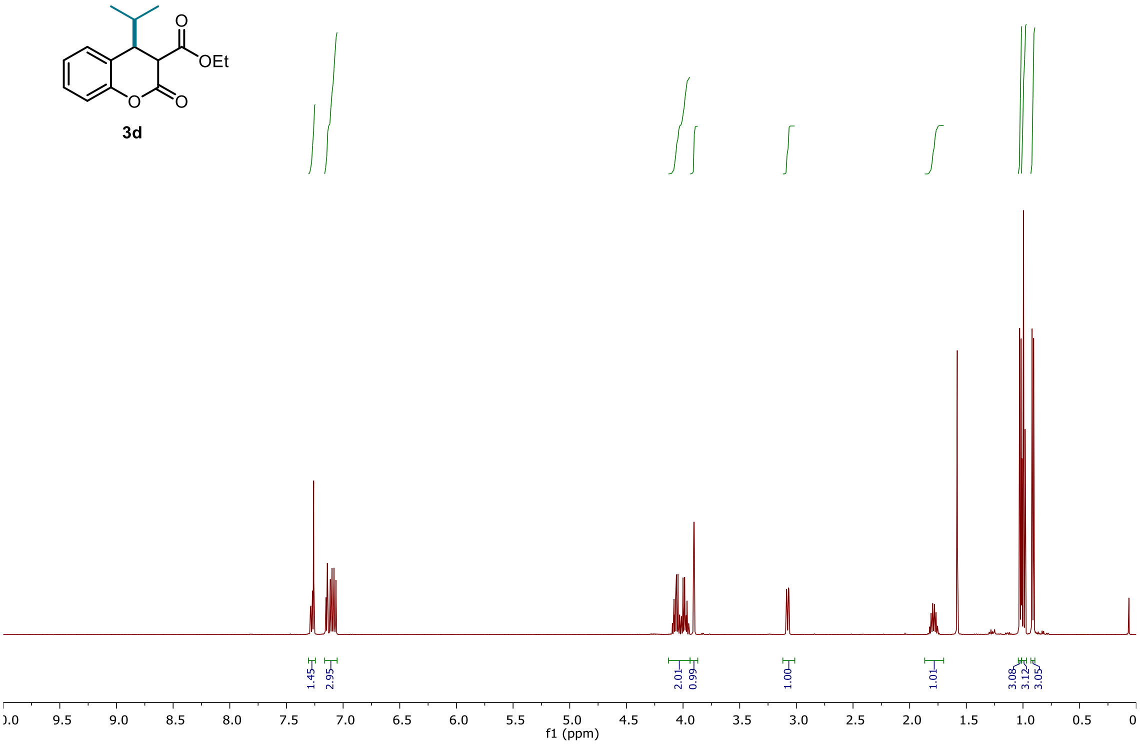
3c

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

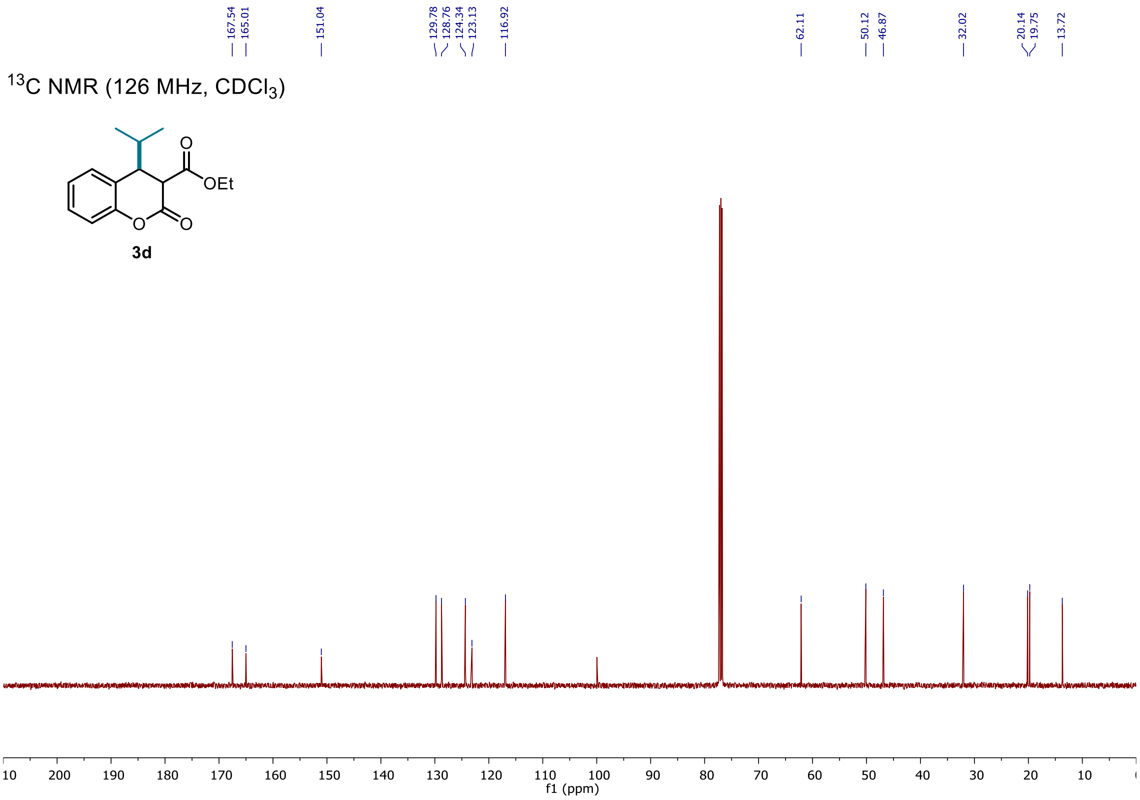


3c

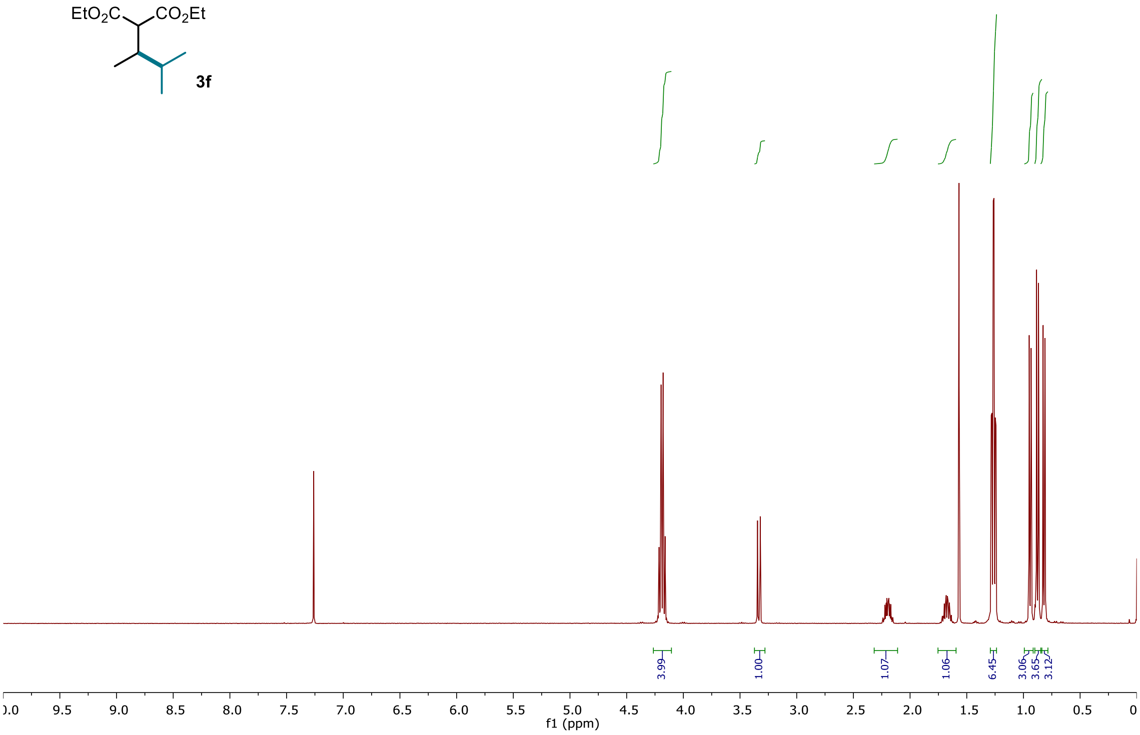
^{1}H NMR (500 MHz, CDCl$_3$)



^{13}C NMR (126 MHz, CDCl$_3$)

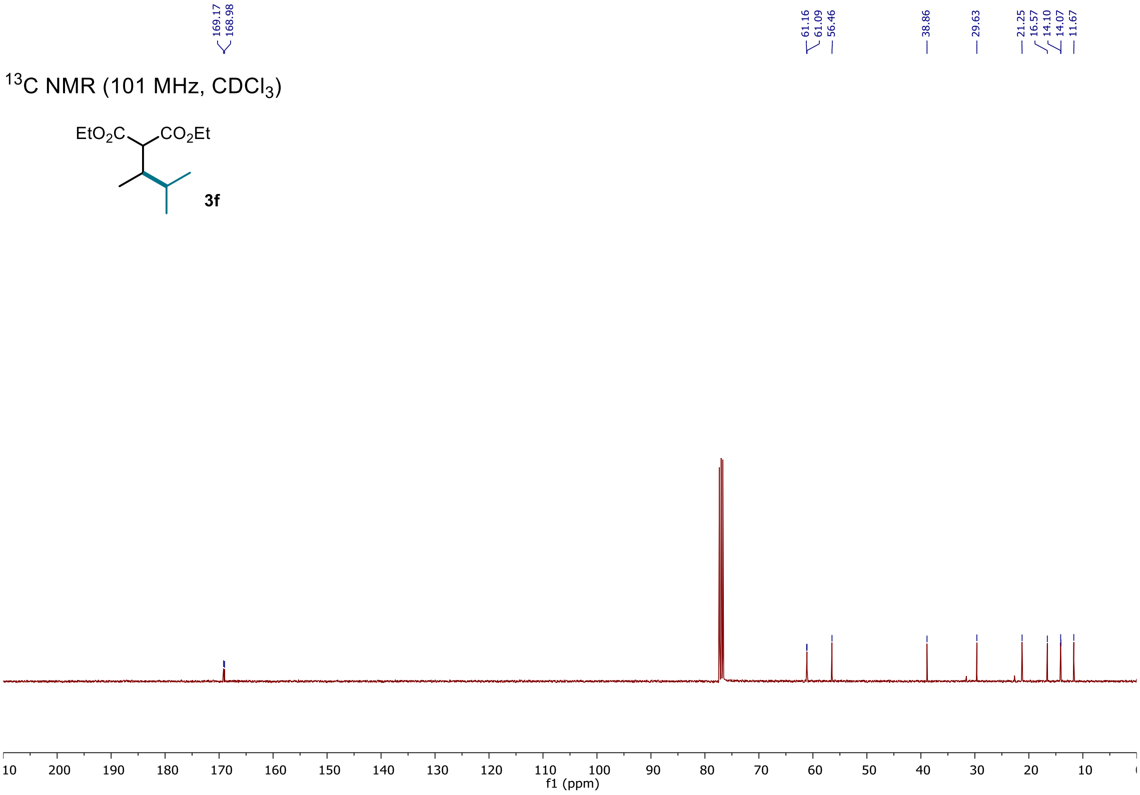


^{1}H NMR (400 MHz, CDCl$_3$)



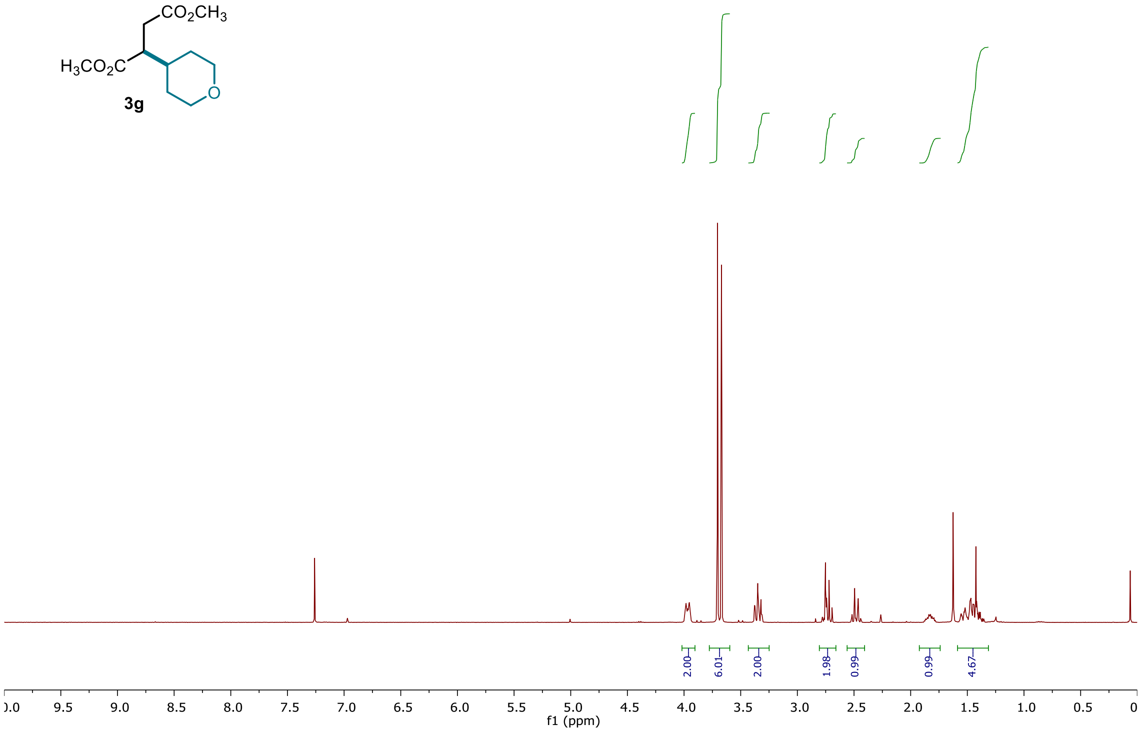
3f

^{13}C NMR (101 MHz, CDCl$_3$)

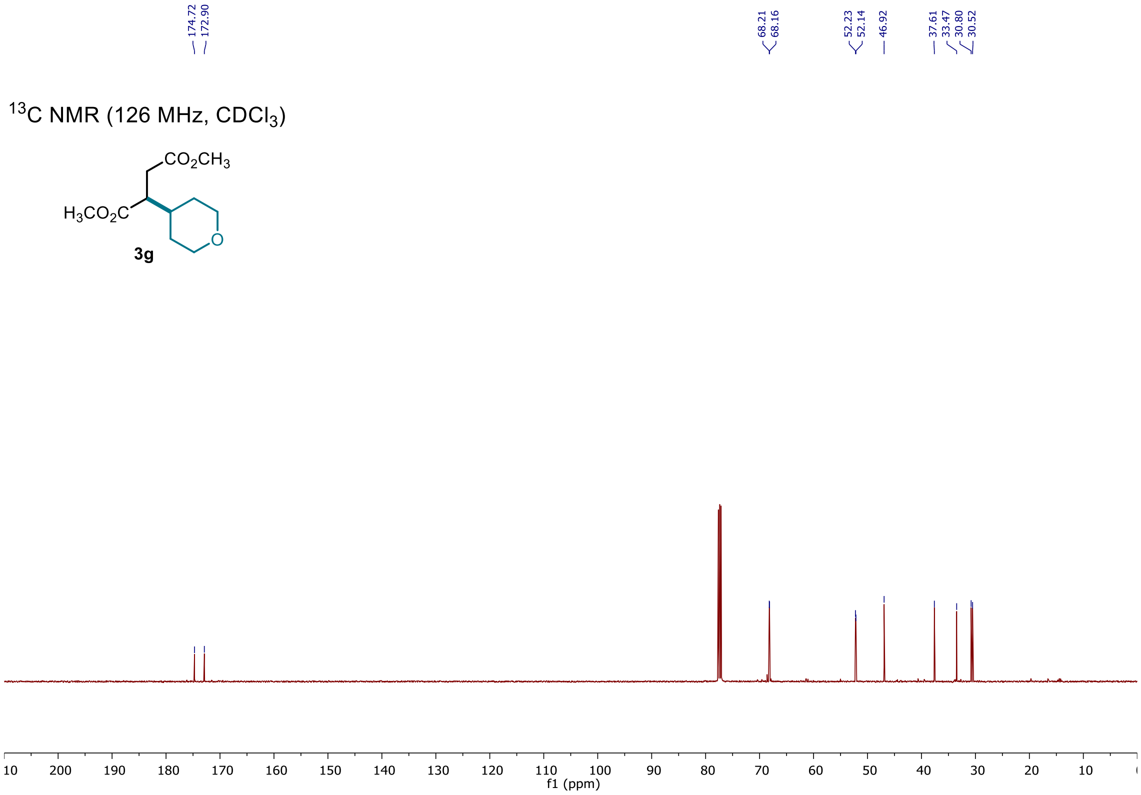


3f

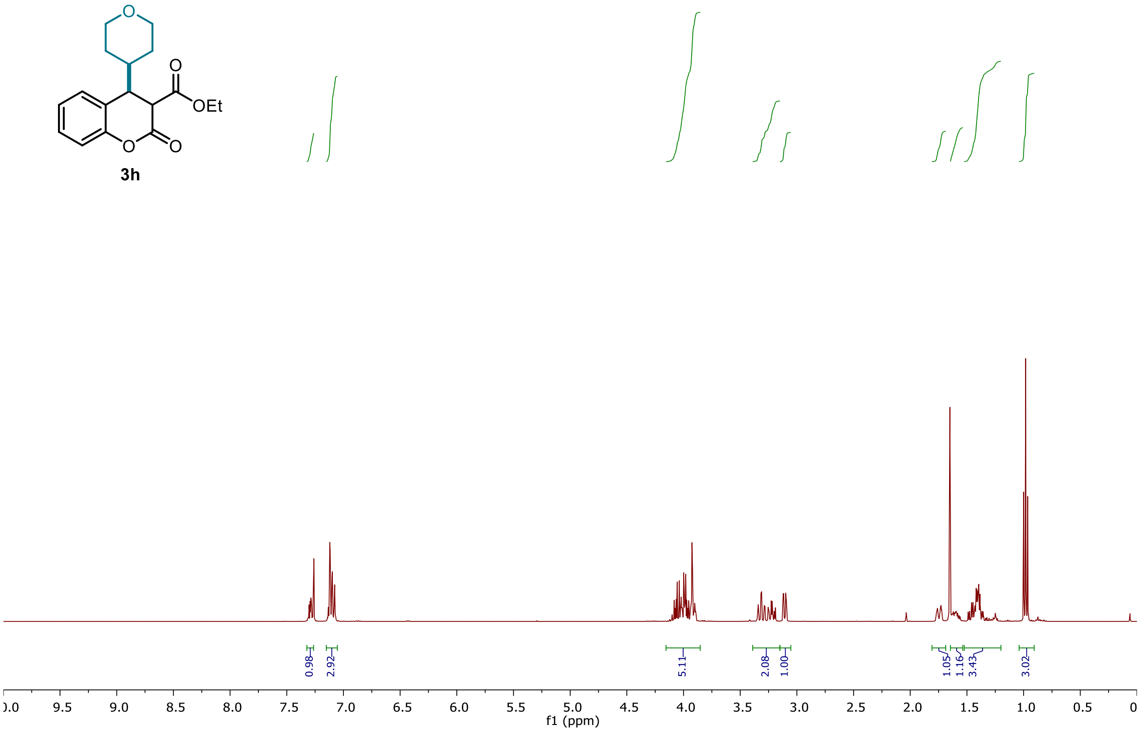
^{1}H NMR (400 MHz, CDCl$_3$)



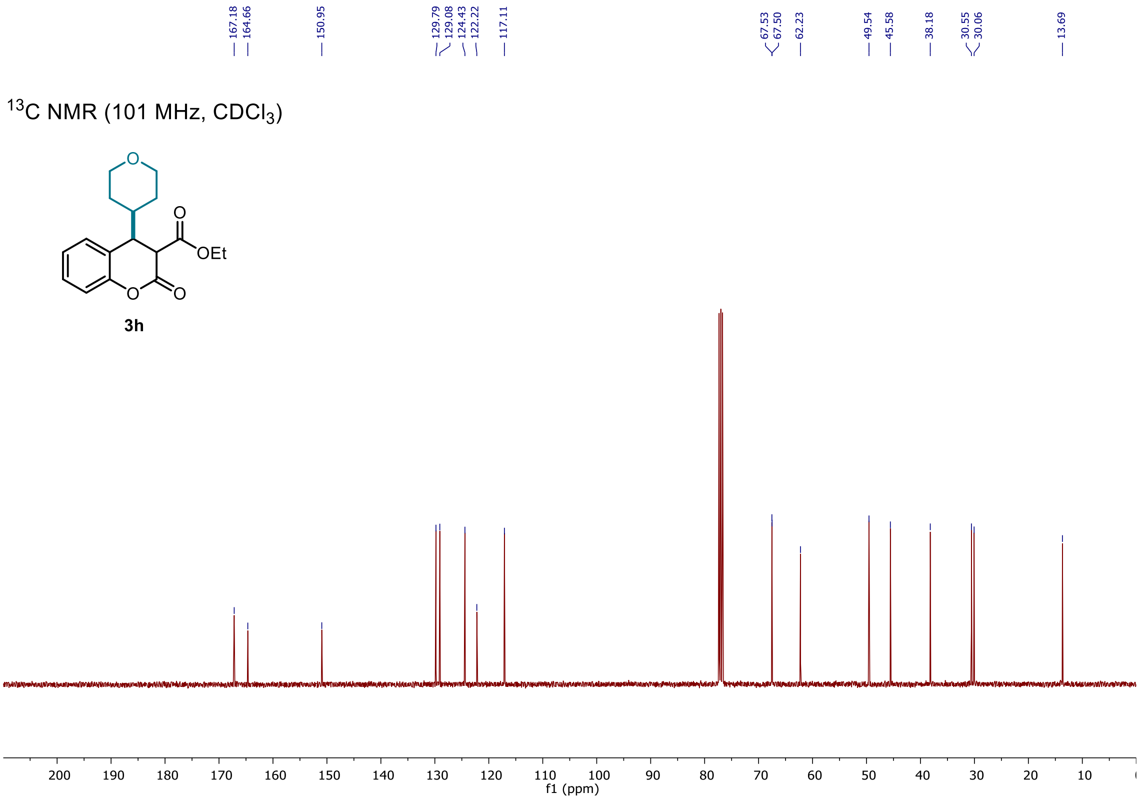
^{13}C NMR (126 MHz, CDCl$_3$)



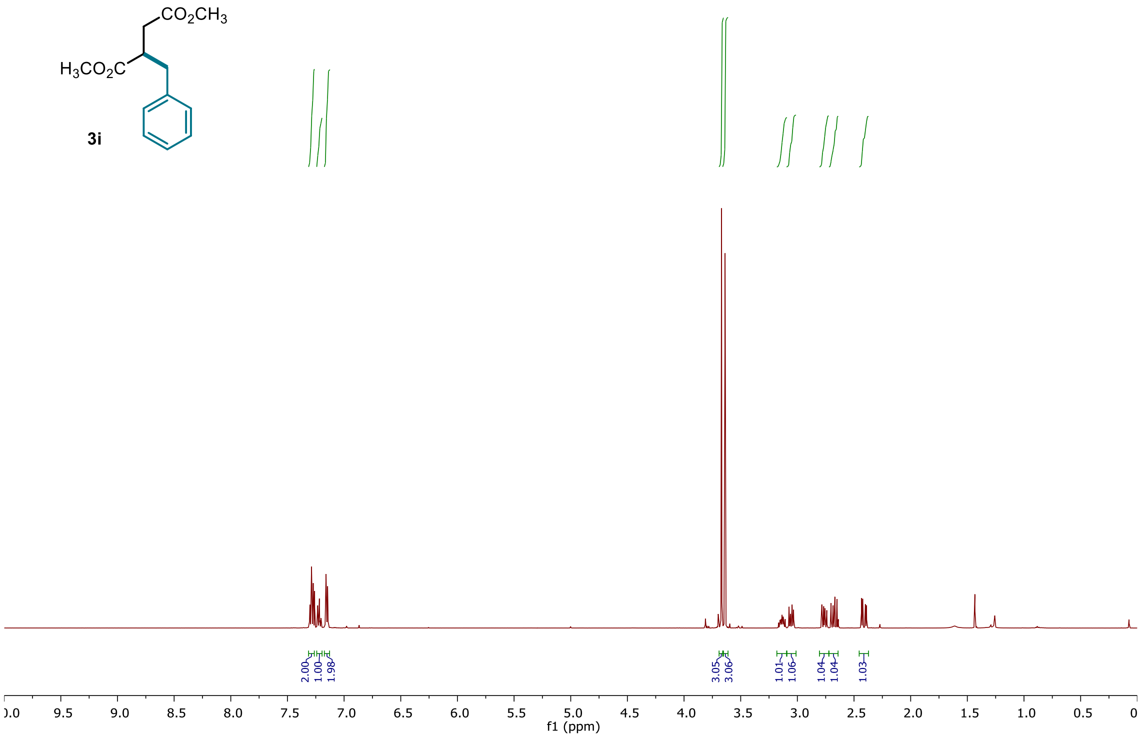
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (101 MHz, CDCl$_3$)

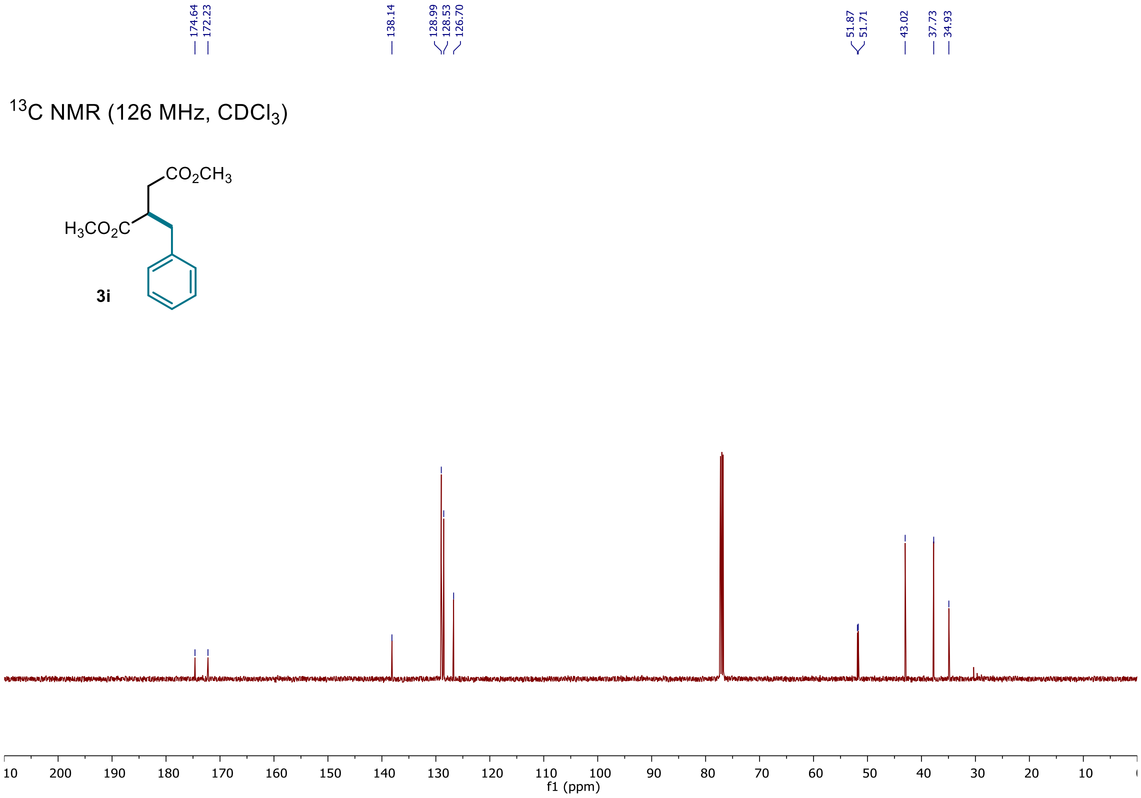


^{1}H NMR (500 MHz, $CDCl_3$)



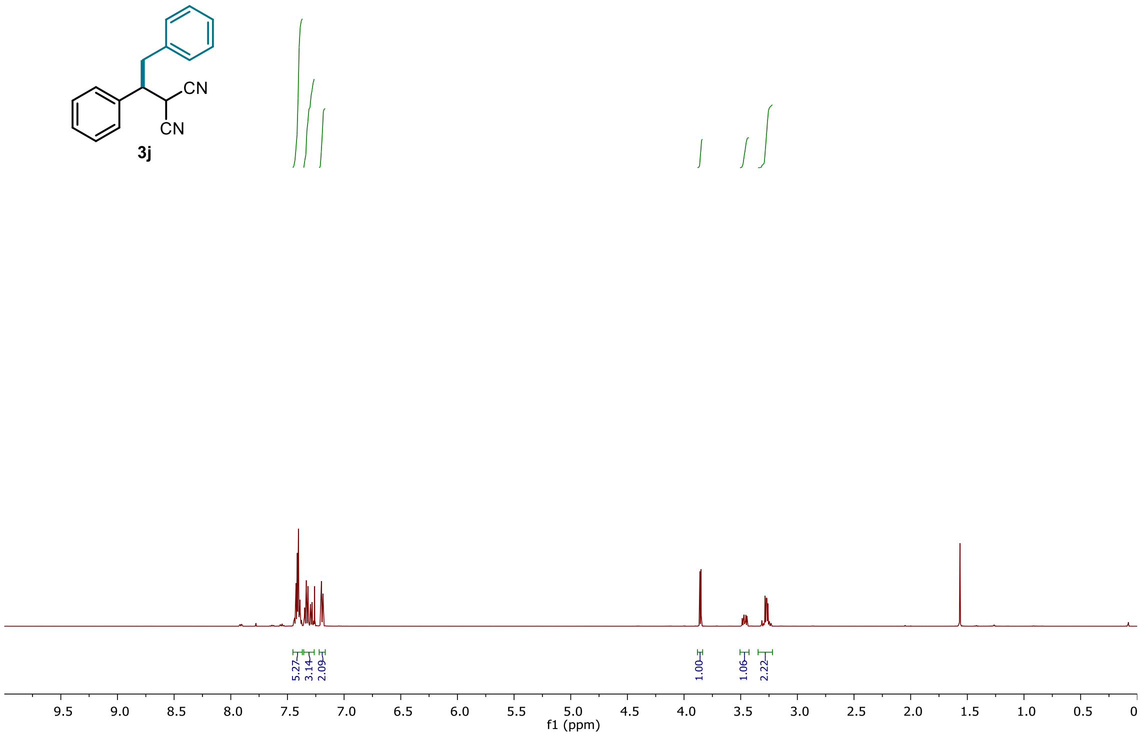
3i

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

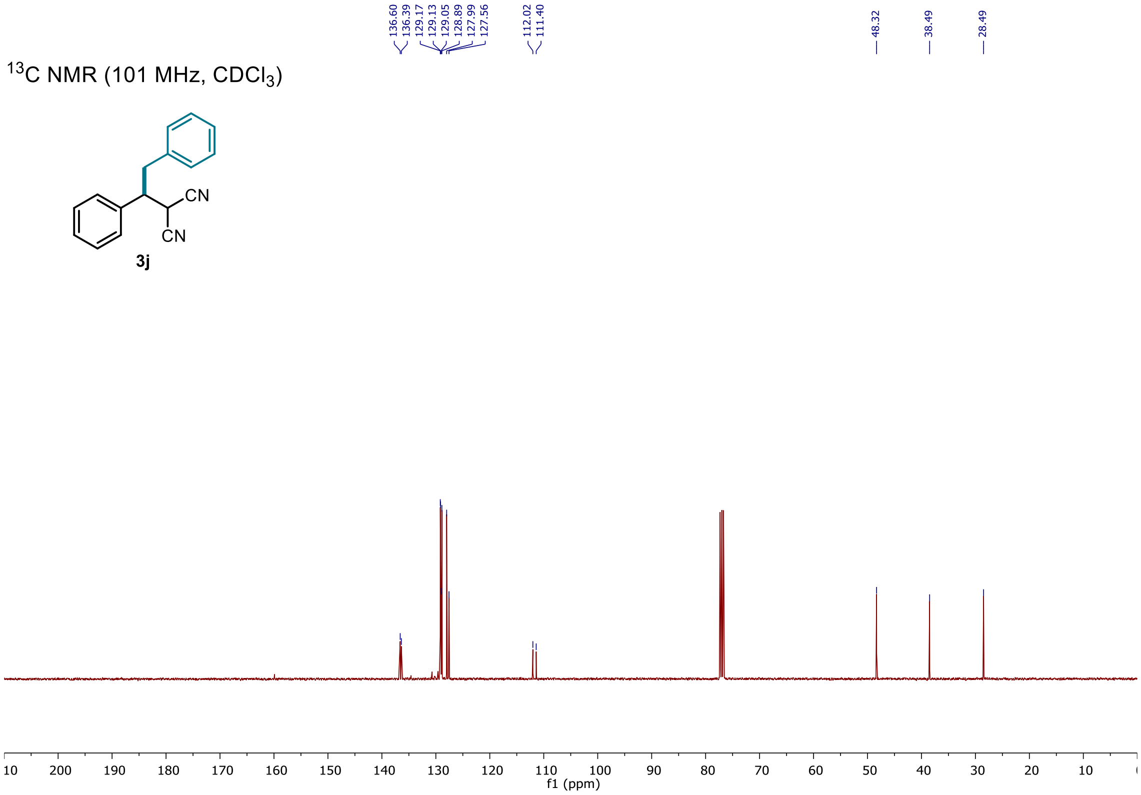


3i

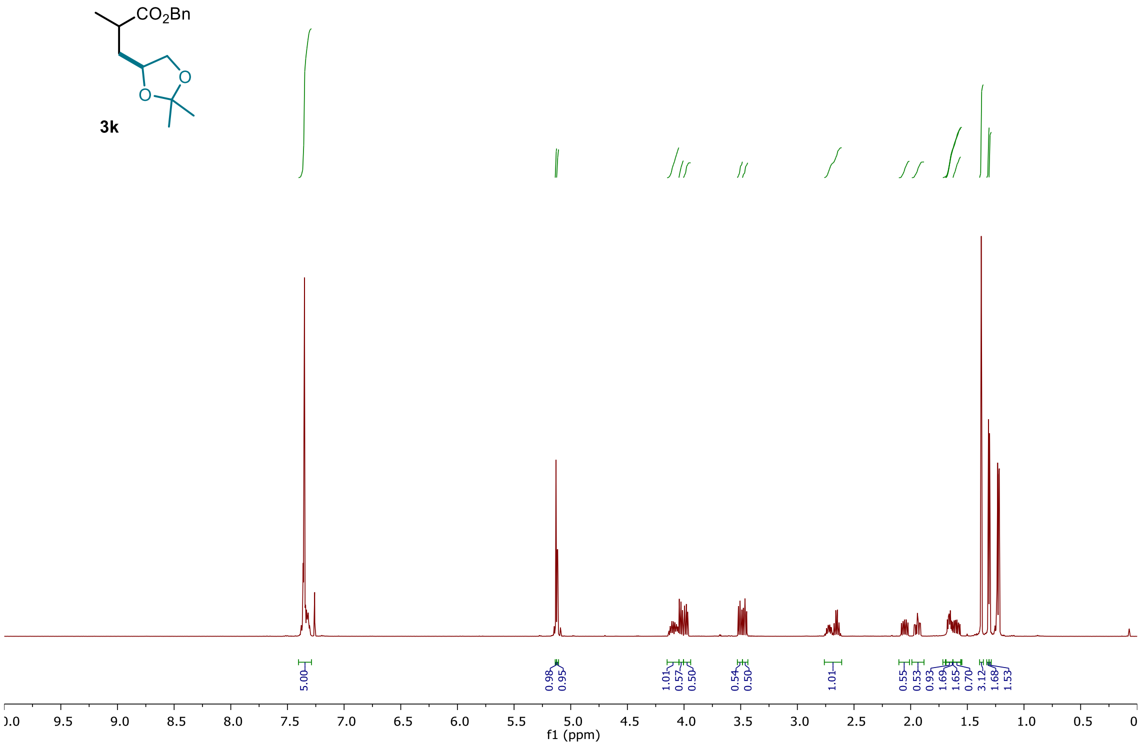
^{1}H NMR (500 MHz, CDCl$_3$)



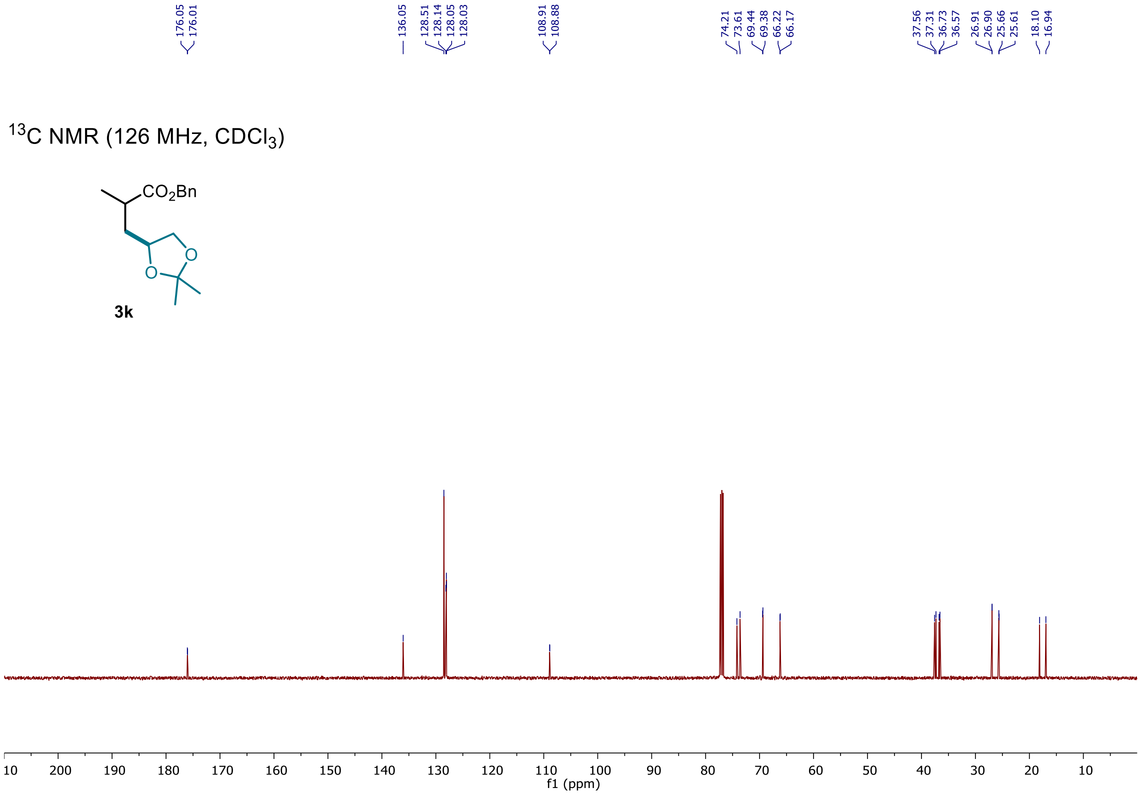
^{13}C NMR (101 MHz, CDCl$_3$)



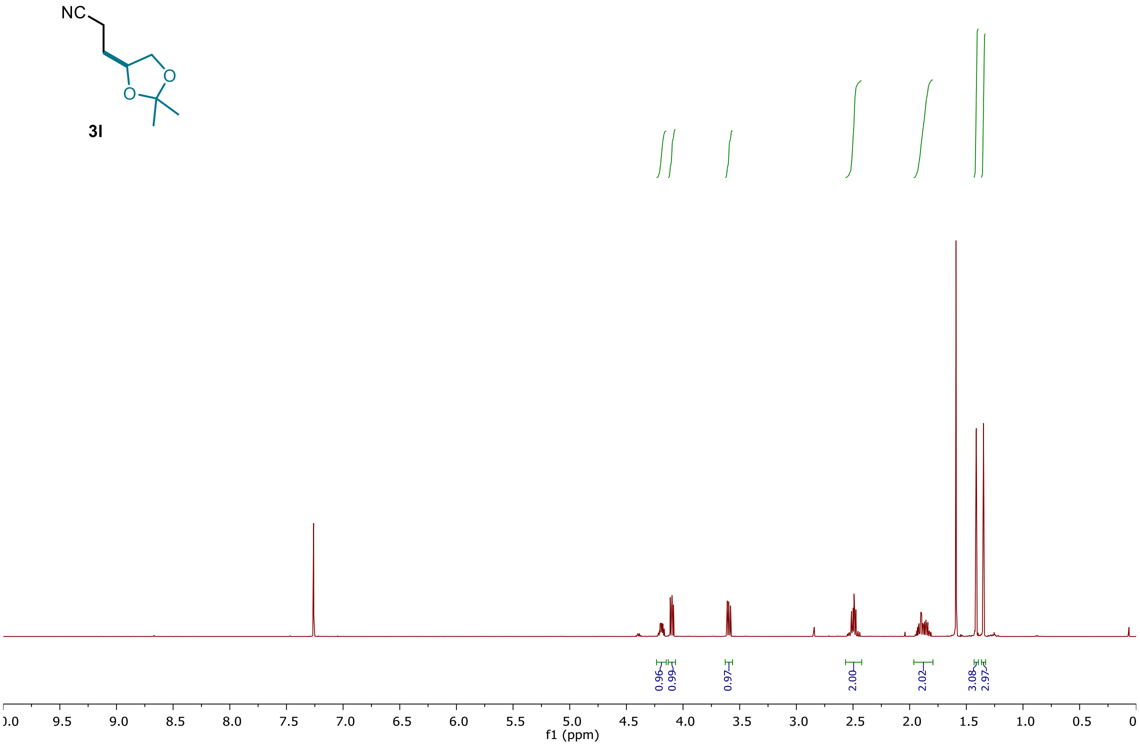
^{1}H NMR (500 MHz, CDCl$_3$)



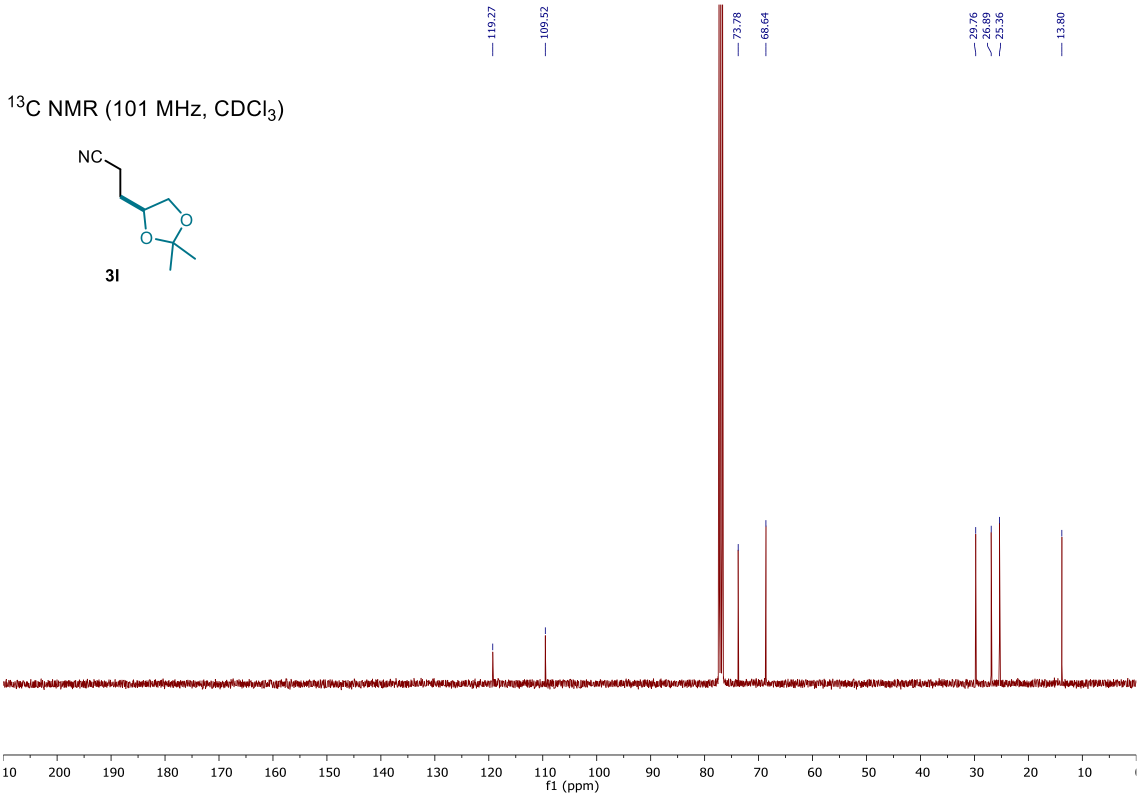
^{13}C NMR (126 MHz, CDCl$_3$)



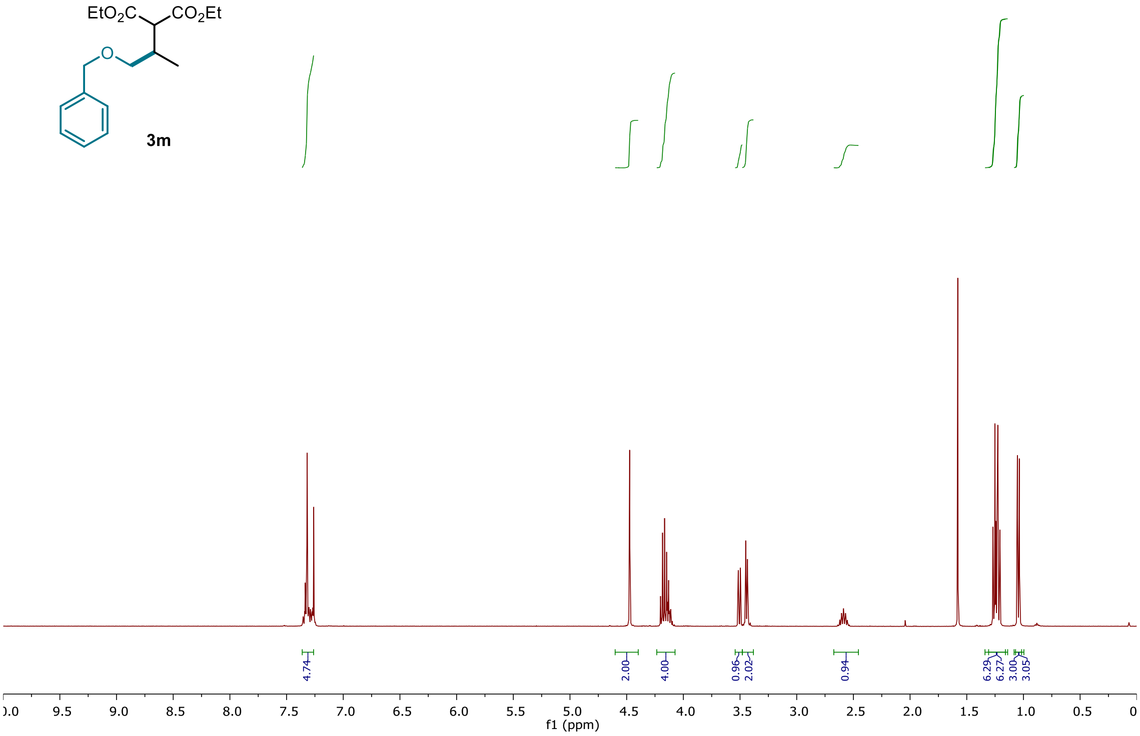
^{1}H NMR (500 MHz, CDCl$_3$)



^{13}C NMR (101 MHz, CDCl$_3$)

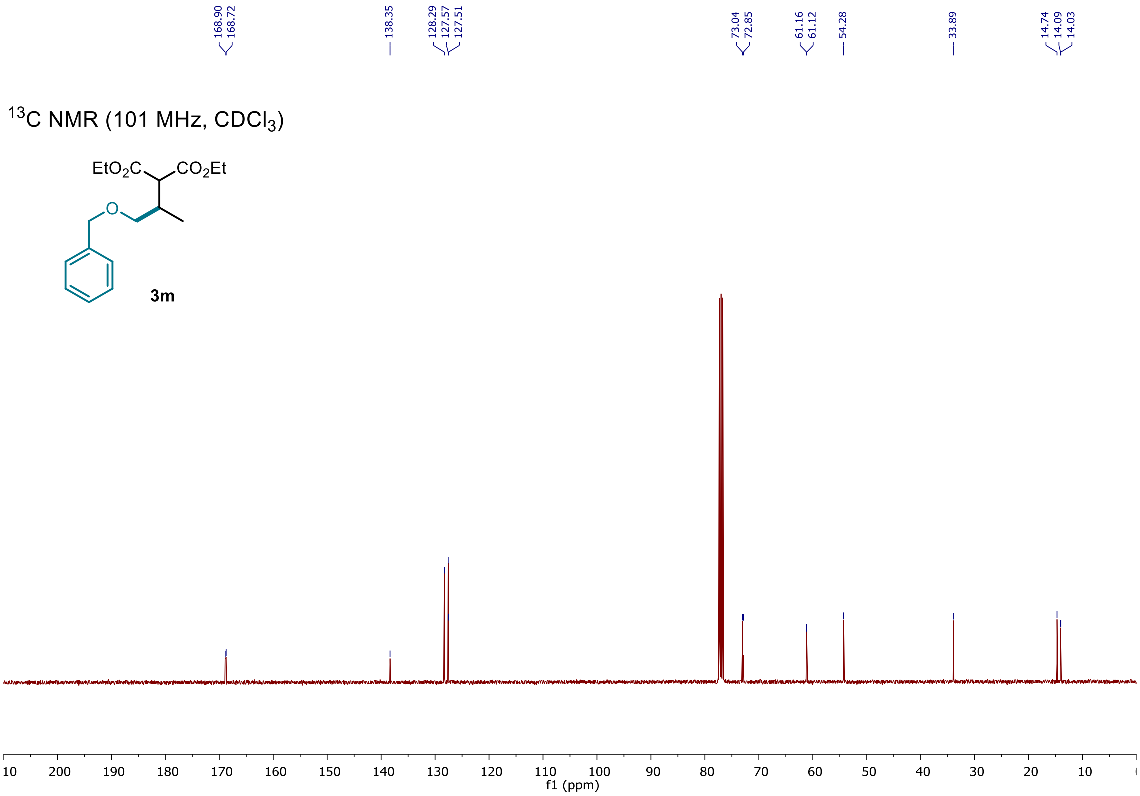


^{1}H NMR (400 MHz, $CDCl_3$)



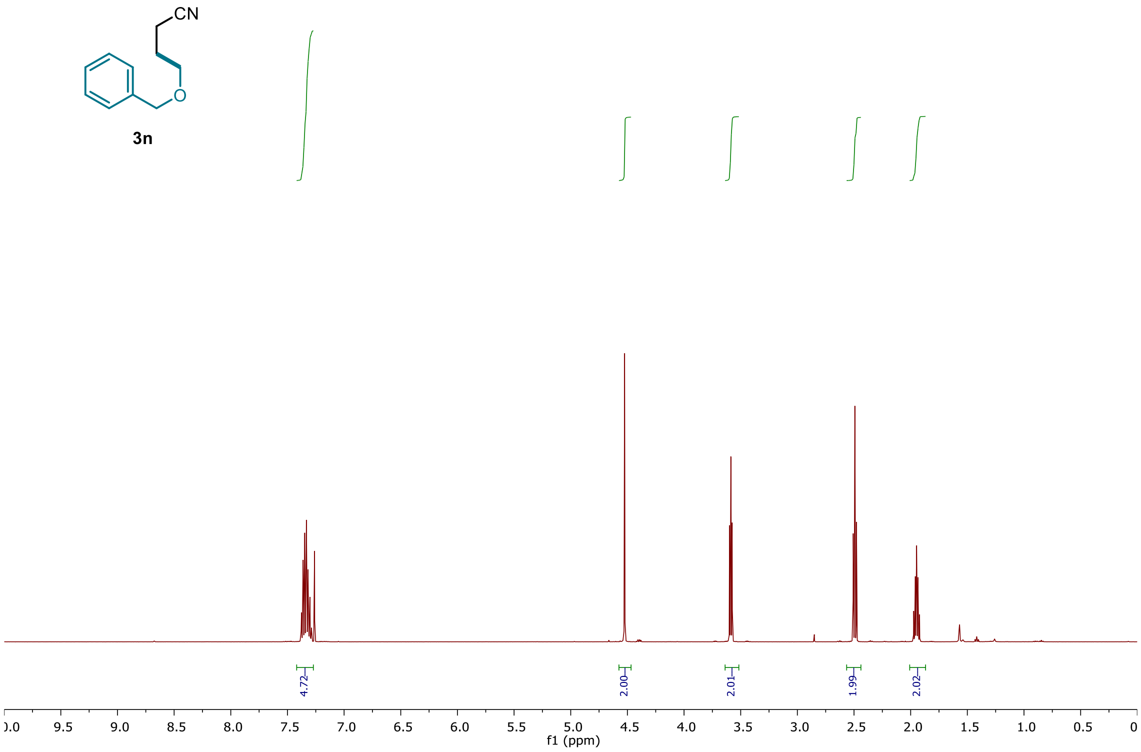
3m

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



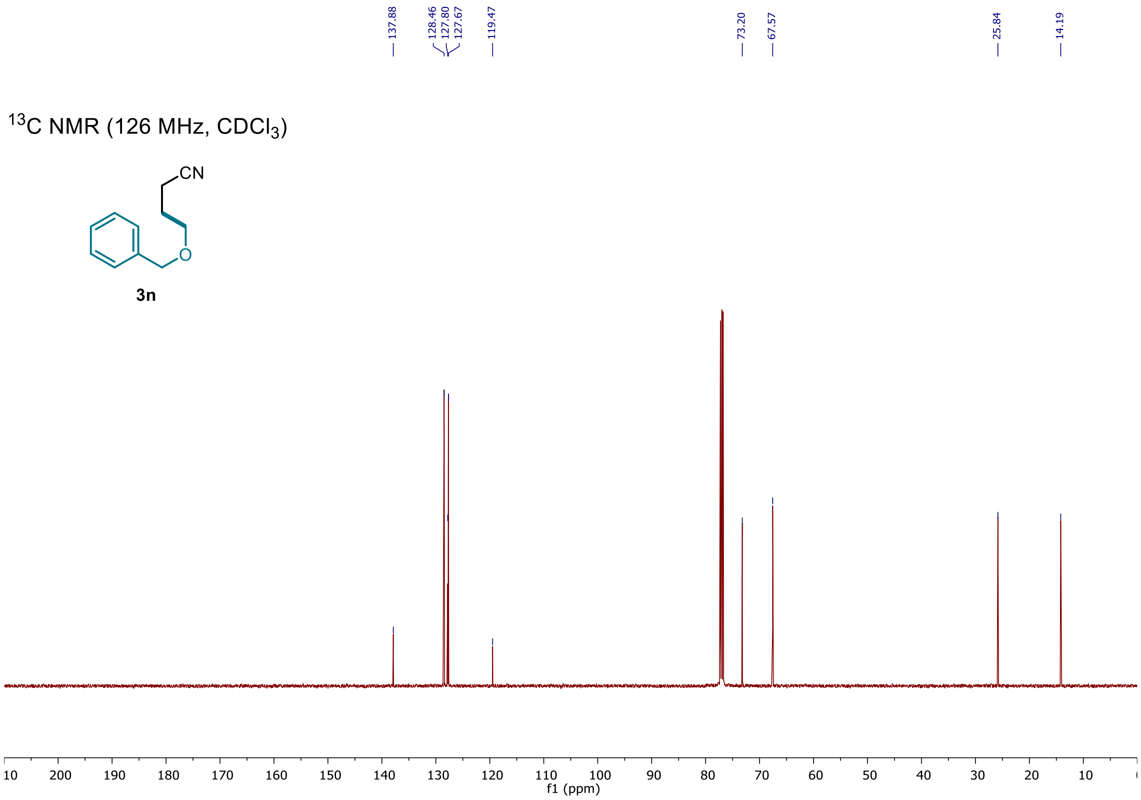
3m

1H NMR (500 MHz, $CDCl_3$)



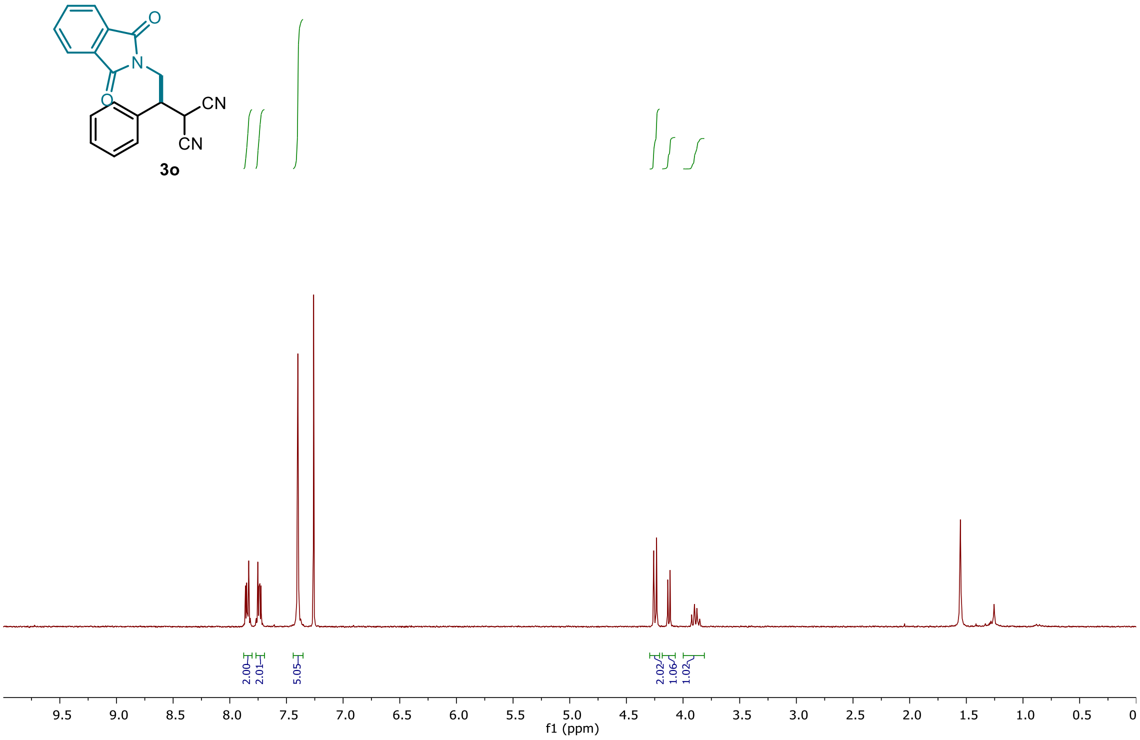
3n

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

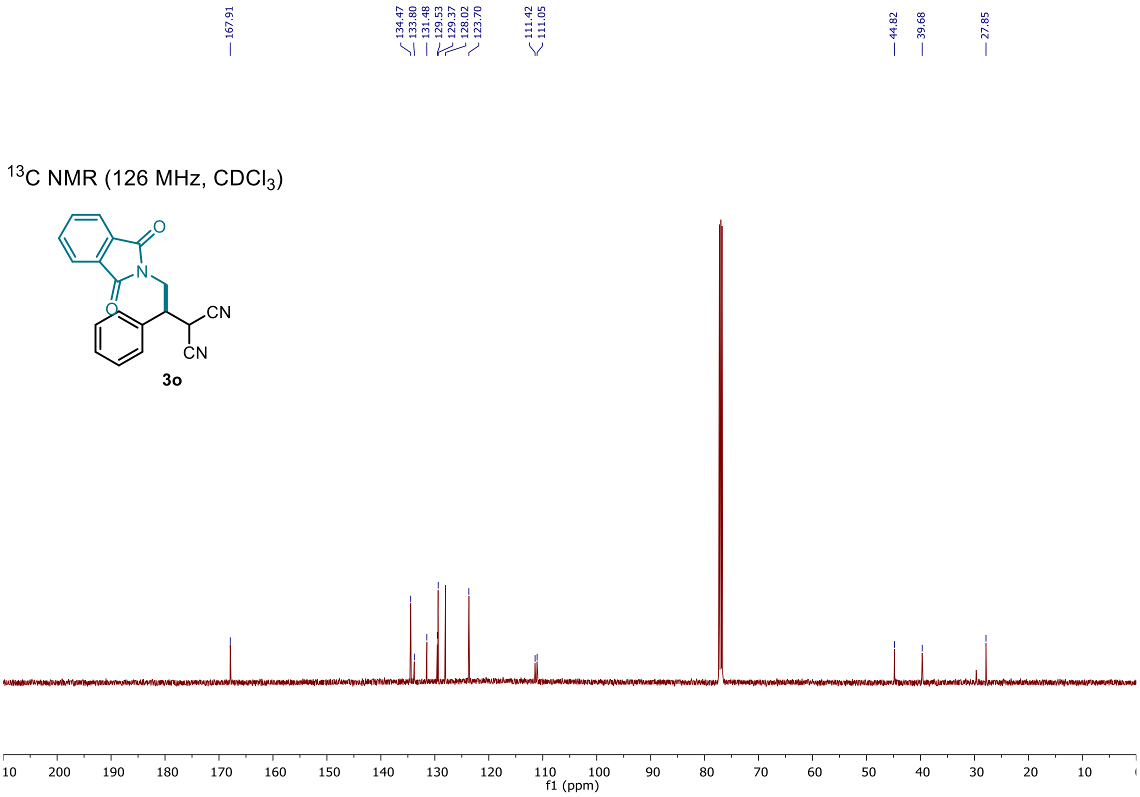


3n

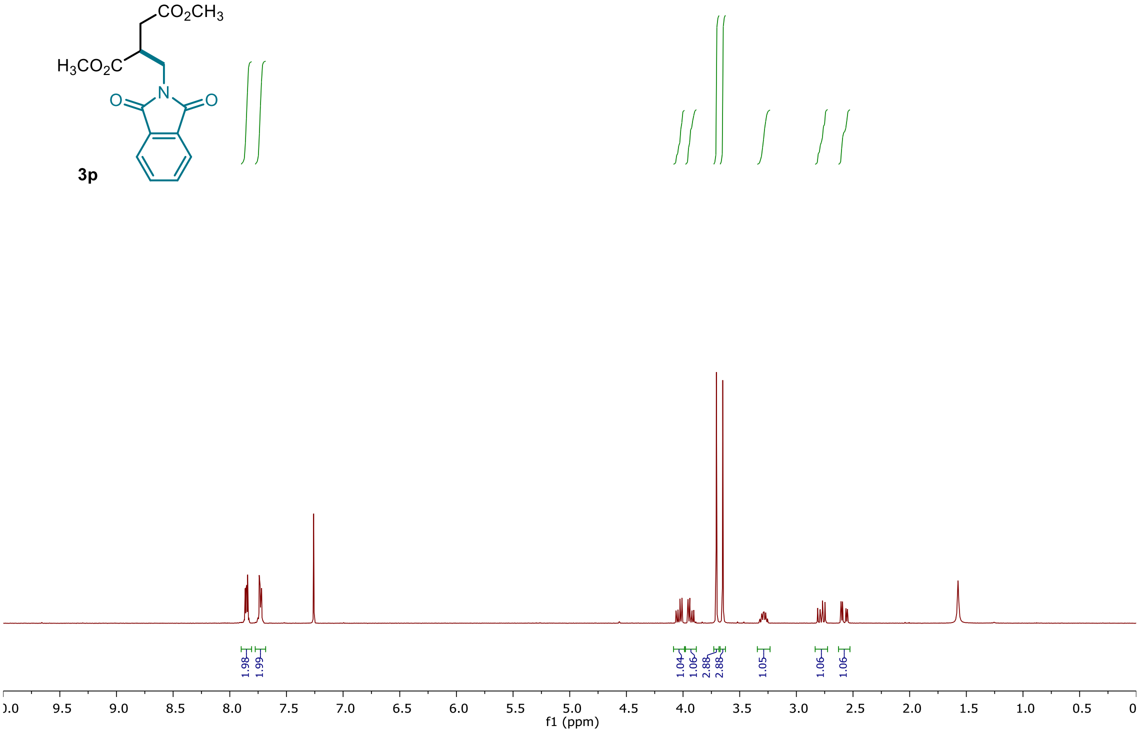
^{1}H NMR (300 MHz, $CDCl_3$)



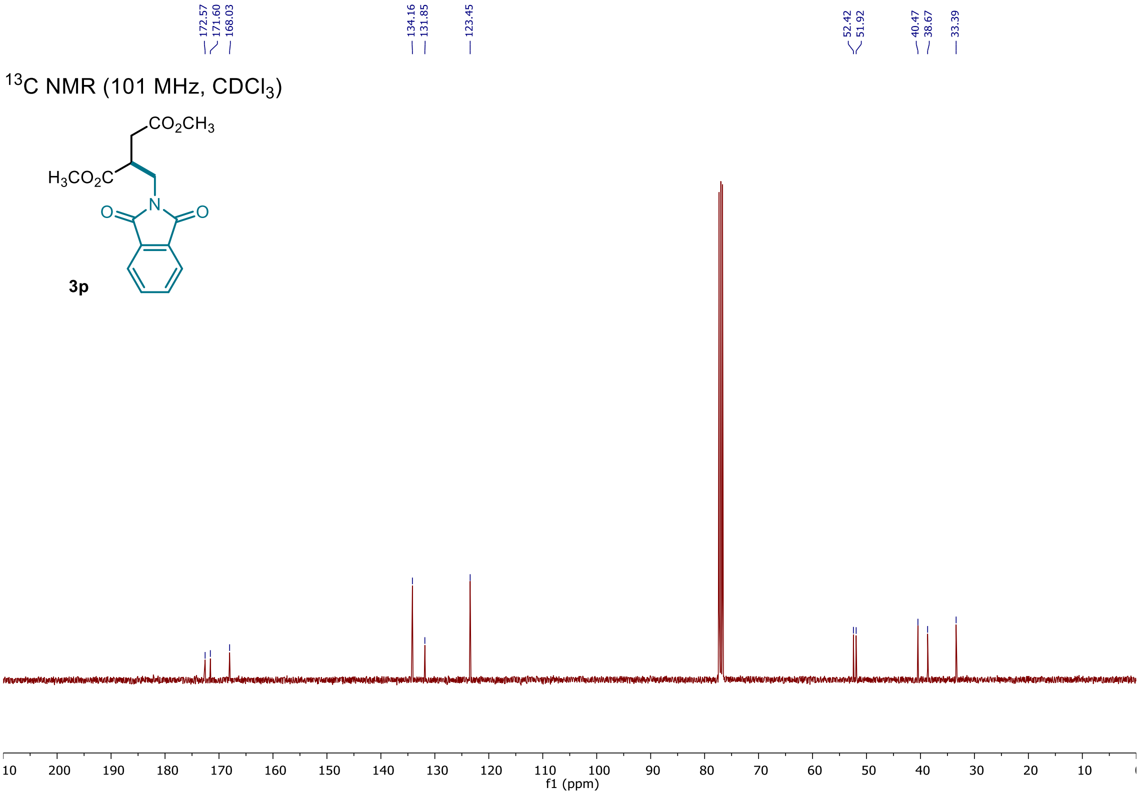
^{13}C NMR (126 MHz, $CDCl_3$)



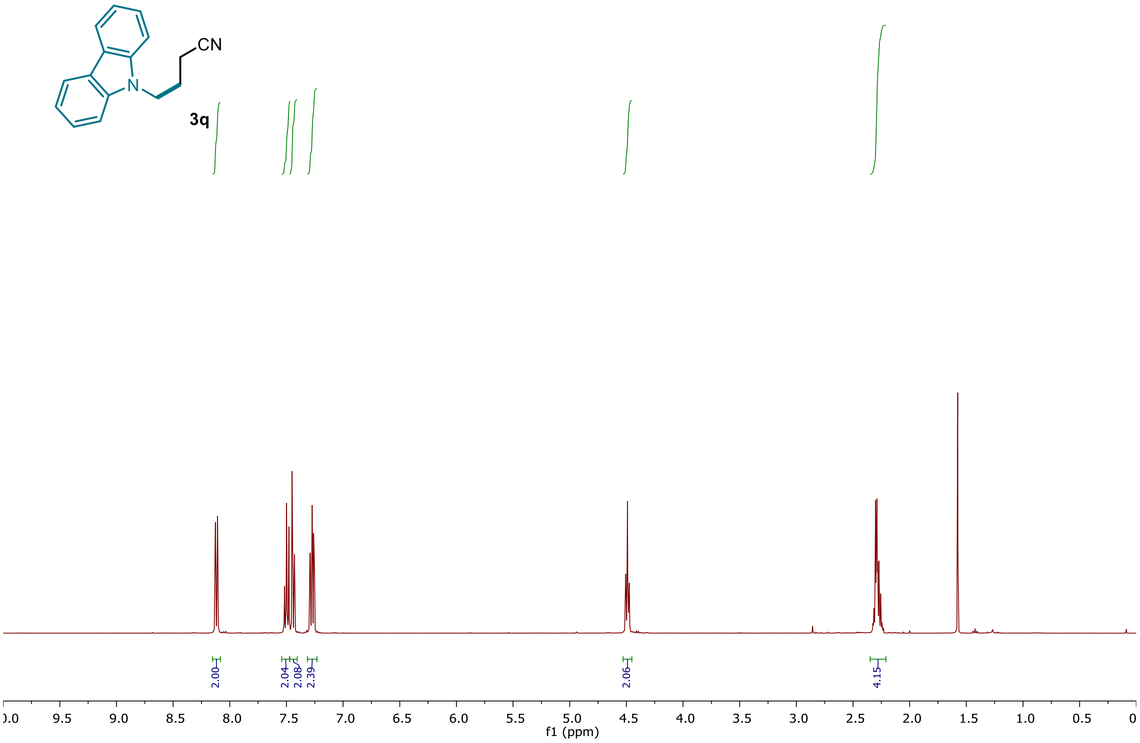
^{1}H NMR (400 MHz, CDCl$_3$)



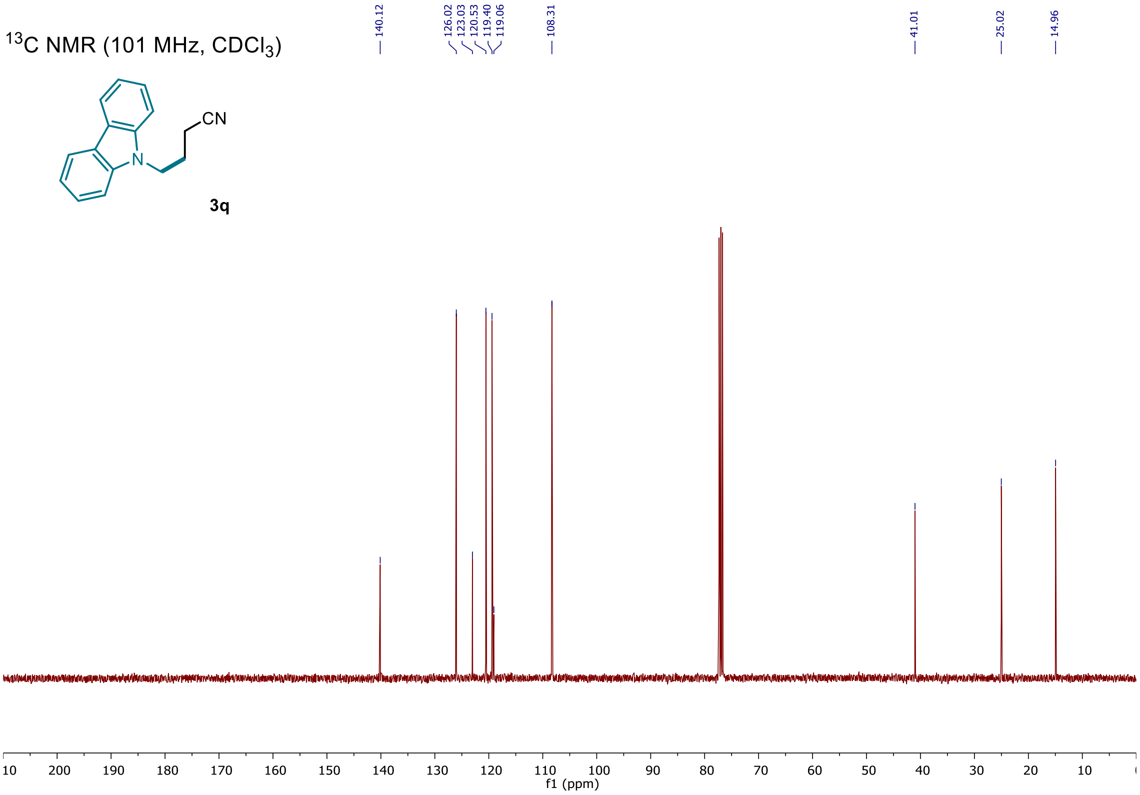
^{13}C NMR (101 MHz, CDCl$_3$)



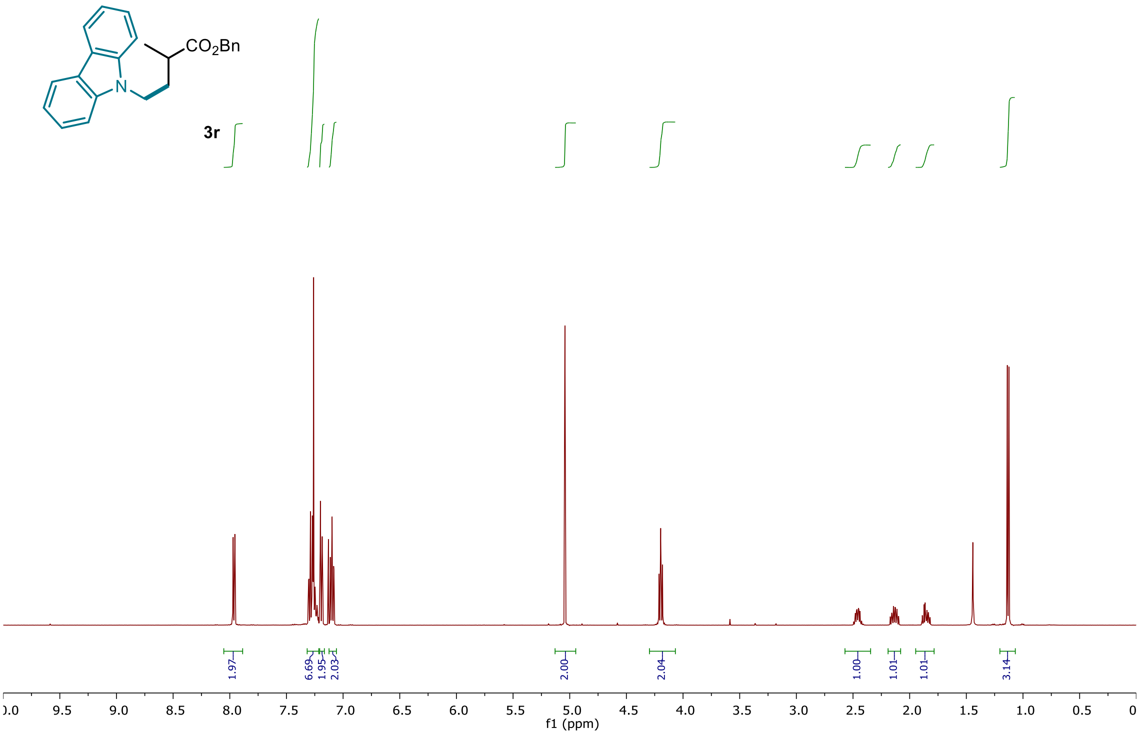
^{1}H NMR (400 MHz, $CDCl_3$)



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

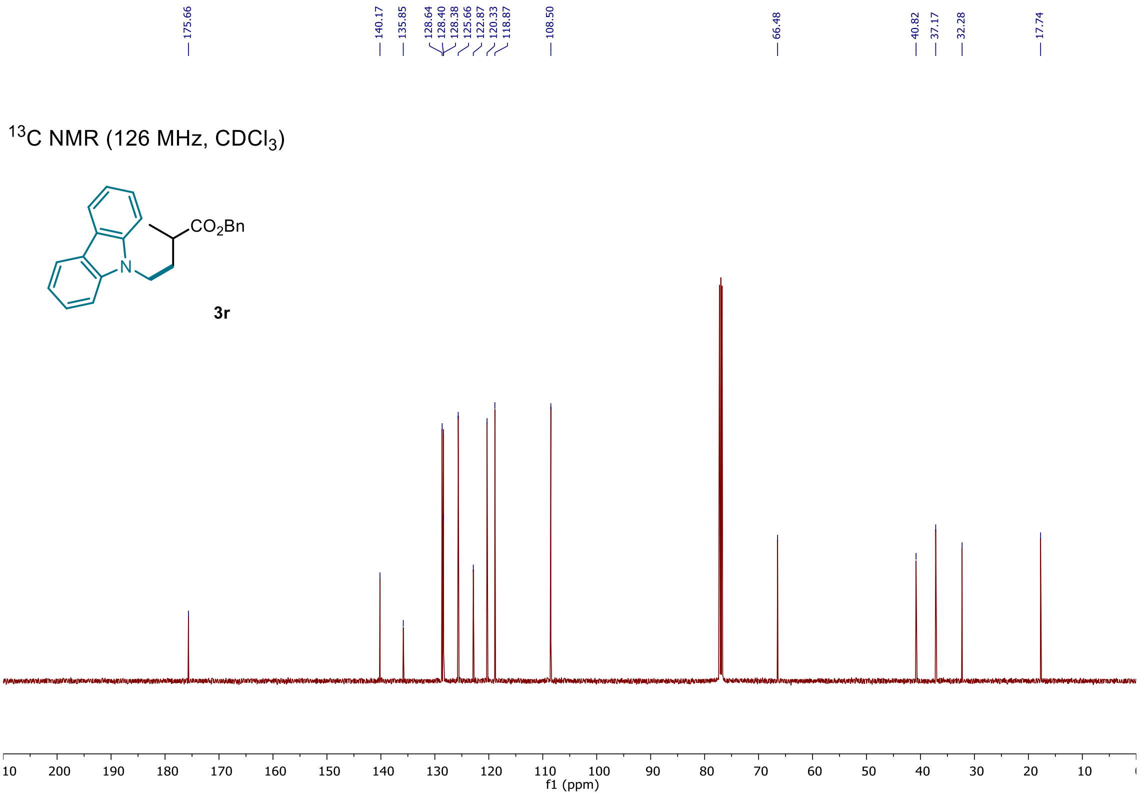


^{1}H NMR (500 MHz, CDCl$_3$)



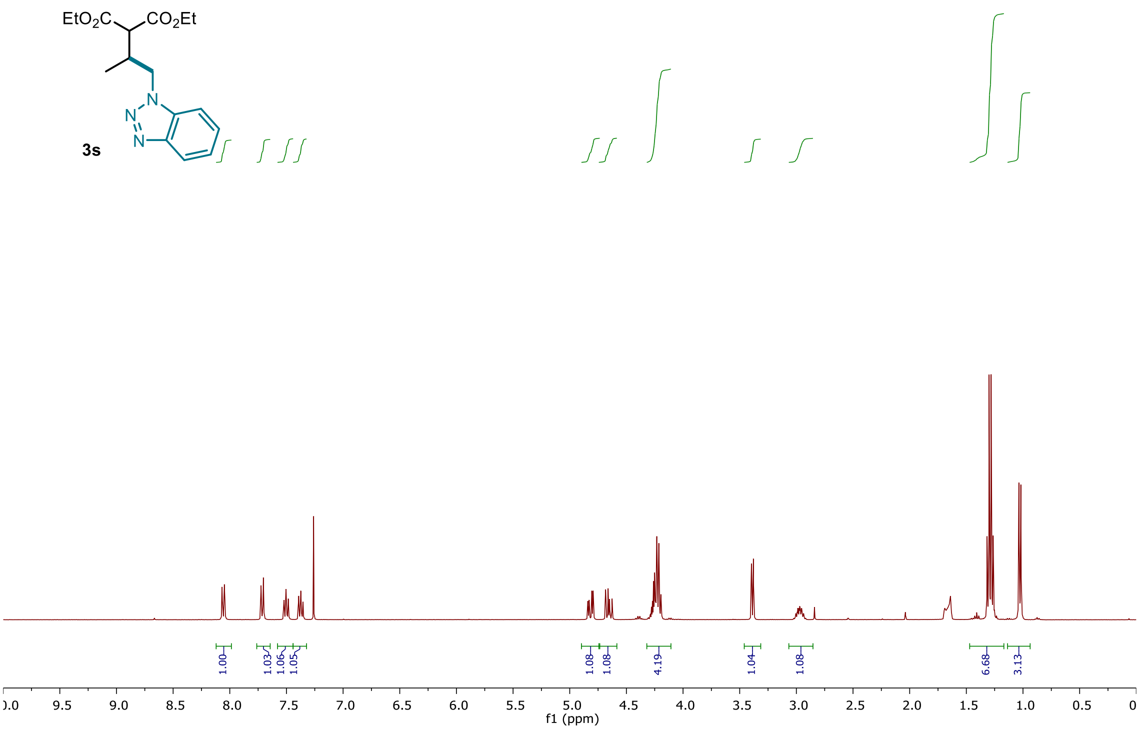
3r

^{13}C NMR (126 MHz, CDCl$_3$)

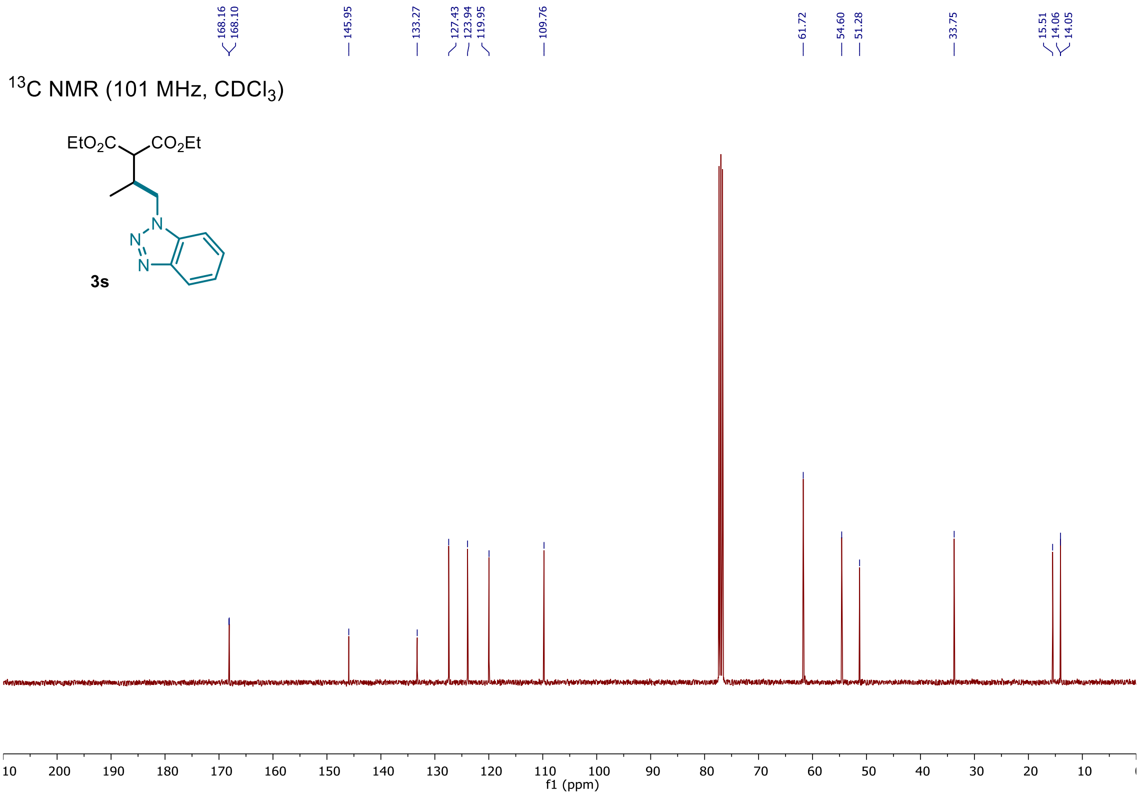


3r

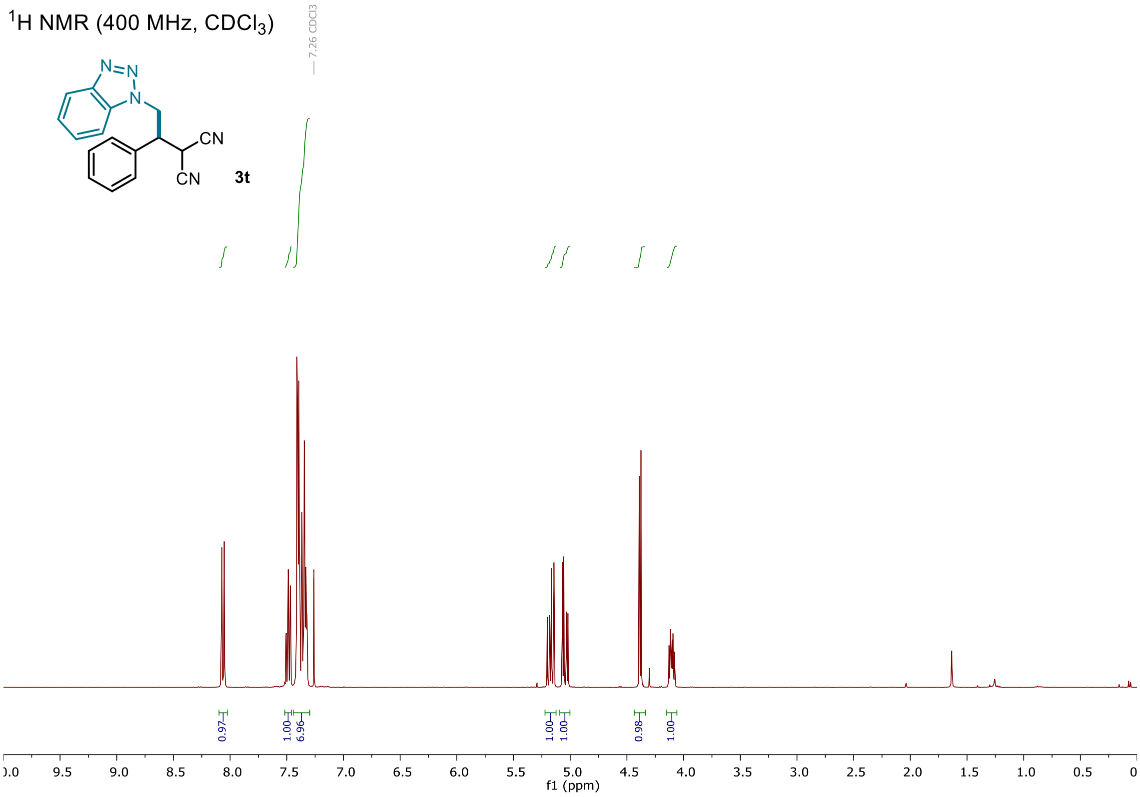
^{1}H NMR (400 MHz, $CDCl_3$)



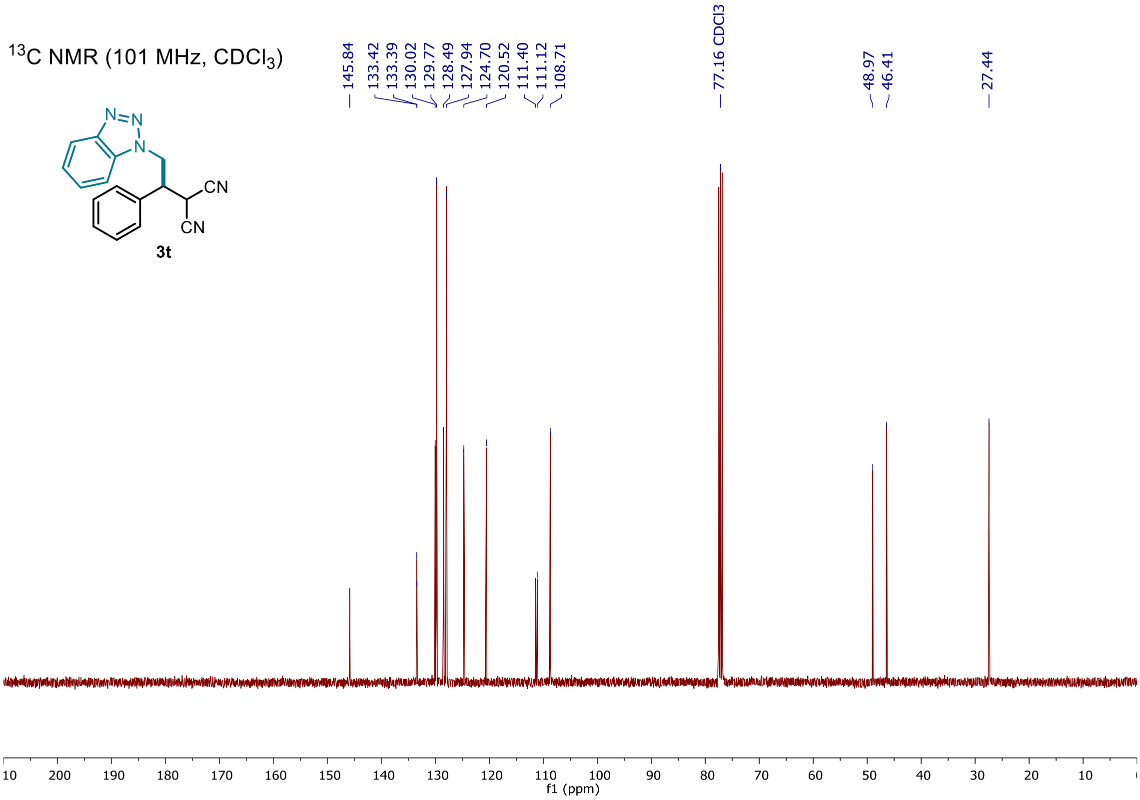
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (101 MHz, CDCl$_3$)



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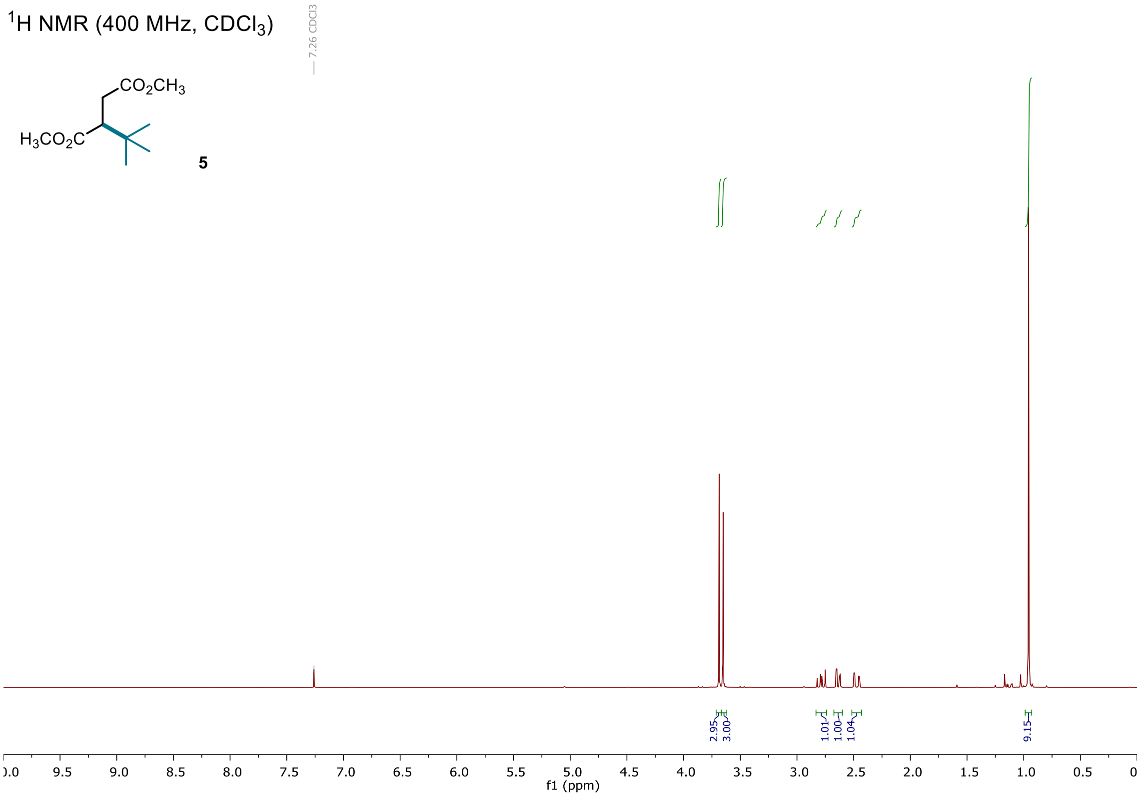
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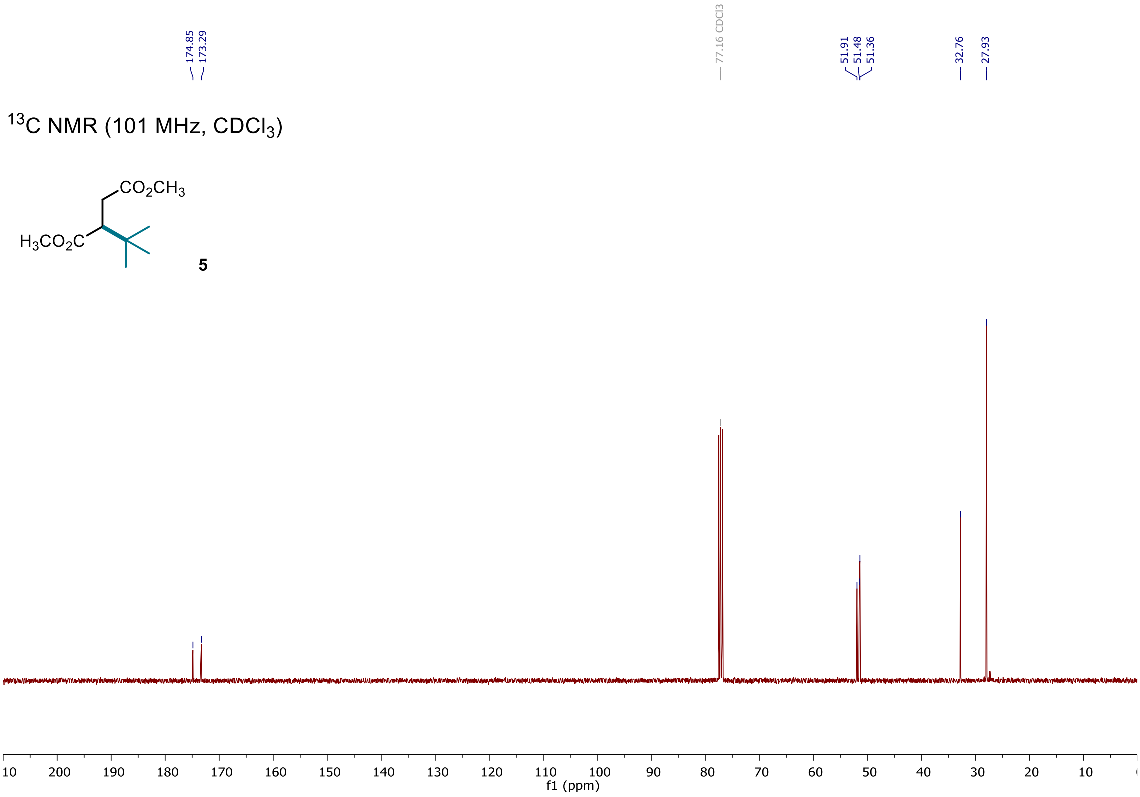
^{13}C NMR (101 MHz, $CDCl_3$)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