

Supporting Information

Radical-Based C–C Bond-Forming Processes Enabled by the Photoexcitation of 4-Alkyl-1,4-dihydropyridines

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L.B. Conceptualization: Lead; Investigation: Supporting; Methodology: Supporting; Supervision: Supporting

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A. General Information

The NMR spectra were recorded at 300 MHz and 400 MHz for ^1H , 75 or 100 MHz for ^{13}C and 286 or 376 MHz for ^{19}F . The chemical shift (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvents (CHCl_3 @ 7.26 ppm ^1H NMR and 77.16 ppm ^{13}C NMR, and tetramethylsilane @ 0 ppm). Coupling constants are given in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; p, pentet; sept, septet; m, multiplet; br, broad signal. NMR yields were determined by adding trichloroethylene ($\text{Cl}_2=\text{CH}$, $\delta = 6.44$ ppm) as an internal standard to the crude reaction mixtures and by integration of diagnostic signals.

High-resolution mass spectra (HRMS) were obtained from the ICIQ High Resolution Mass Spectrometry Unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) with electrospray ionization.

UV-vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with photomultiplier detector, double beam optics and D_2 and W light sources. The emission spectra were recorded in a Fluorolog Horiba Jobin Yvon spectrofluorimeter equipped with a photomultiplier detector, a double monochromator, and a 350W xenon light source.

Cyclic voltammetry studies were carried out on a Princeton Applied Research PARSTAT 2273 potentiostat offering compliance voltage up to ± 100 V (available at the counter electrode), ± 10 V scan range and ± 2 A current range.

Continuous wave (CW) EPR spectra were obtained on a Bruker EMX Micro X-band bridge of 9.1 - 9.9 GHz, using a Bruker ER 1164 HS resonator and equipped with an ESR900 cryostat.

The authors are indebted to the team of the Research Support Area at ICIQ. Grace Fox is thanked for proofreading the manuscript.

General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques, unless otherwise stated. Synthesis grade solvents were used as purchased. Anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) were employed, using UV light as the visualizing agent and ethanol solution of phosphomolybdic acid or basic aqueous potassium permanganate (KMnO_4) stain solutions and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator (*in vacuo* at 40 °C, ~5 mbar).

Materials. Commercial grade reagents and solvents were purchased from Sigma-Aldrich, Fluka, Alfa Aesar, Fluorochem, SynQuest at the highest commercial quality and used without further purification, unless otherwise stated. Nickel(II) chloride ethylene glycol dimethyl ether complex (NiCl_2DME) is commercially available and was used as purchased (from Sigma Aldrich). Other starting materials, including all the aryl bromides **4** and acyl chlorides **6**, were purchased from commercial source and used as received. All of the 4-alkyl-1,4-dihydropyridine (Hantzsch esters) derivatives **1** were prepared according to a literature procedure.¹

B. Photophysical Behavior of Bn-DHP 1a

B.1. UV-vis absorption spectra of diethyl 4-benzyl-1,4-dihydropyridine-3,5-dicarboxylate 1a.

Solutions at different concentrations of **1a**, obtained by opportunely diluting an original stock solution ($[1a] = 15 \text{ mM}$ in CH_3CN) with dry acetonitrile, were introduced to a 1 cm path length quartz cuvette equipped with a Teflon[®] septum. The solution were analyzed using a Shimadzu 2401PC UV-Vis spectrophotometer. The absorption spectra (Figure S1) show a typical Lambert-Beer linear correlation with the concentrations (Figure S2).

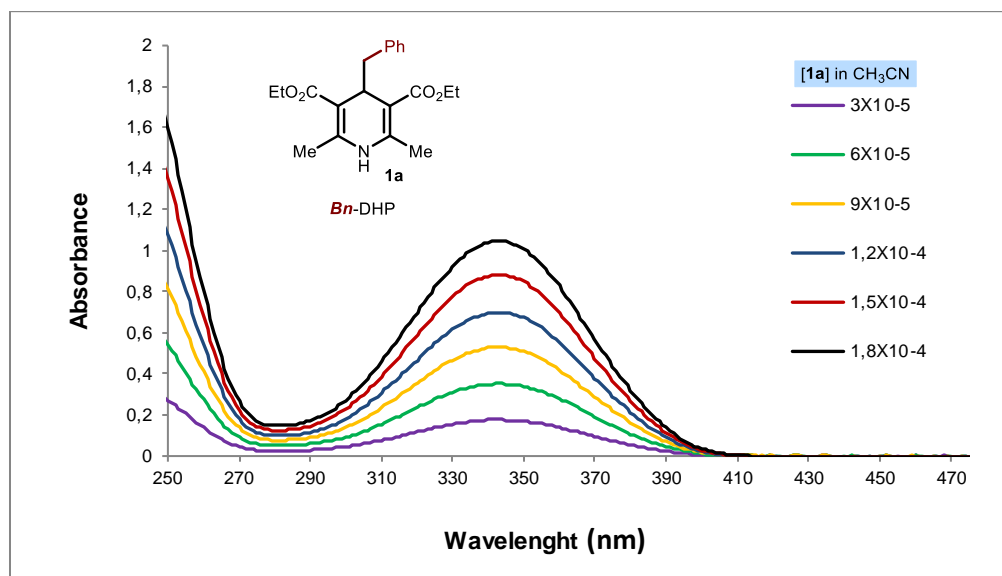


Figure S1. Absorption spectra of diethyl 4-benzyl-1,4-dihydropyridine-3,5-dicarboxylate **1a** at different concentrations in CH_3CN ; $\lambda_{\text{max}} = 343 \text{ nm}$. The tail wavelength of absorption was considered at 420 nm.

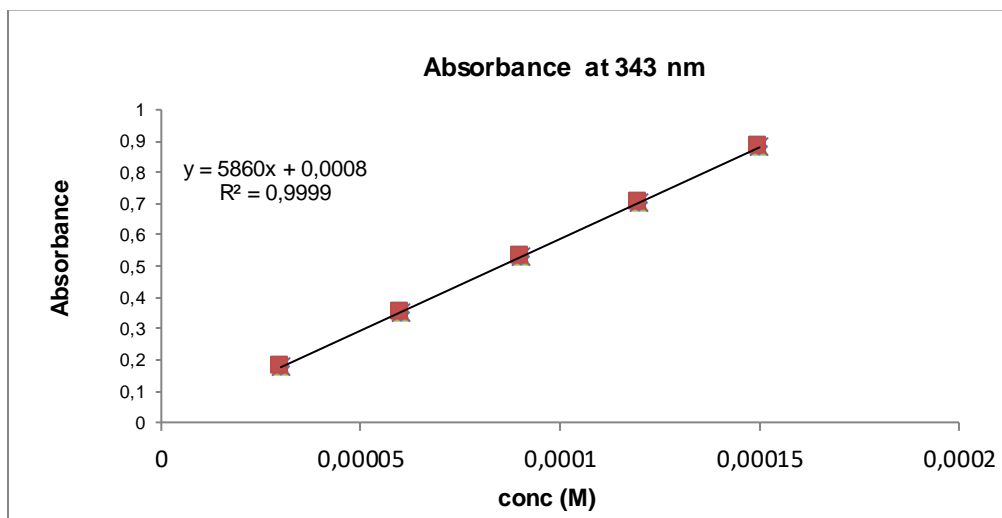


Figure S2. Lambert-Beer linear correlation between absorbance and concentration at 343 nm for **1a**. The slope of the line is the molar extinction coefficient ϵ at 343 nm ($\text{M}^{-1}\text{cm}^{-1}$).

B.2. Cyclic voltammetry study of die thyl 4-benzyl-1,4-dihydropyridine -3,5-dicarboxylate **1a**

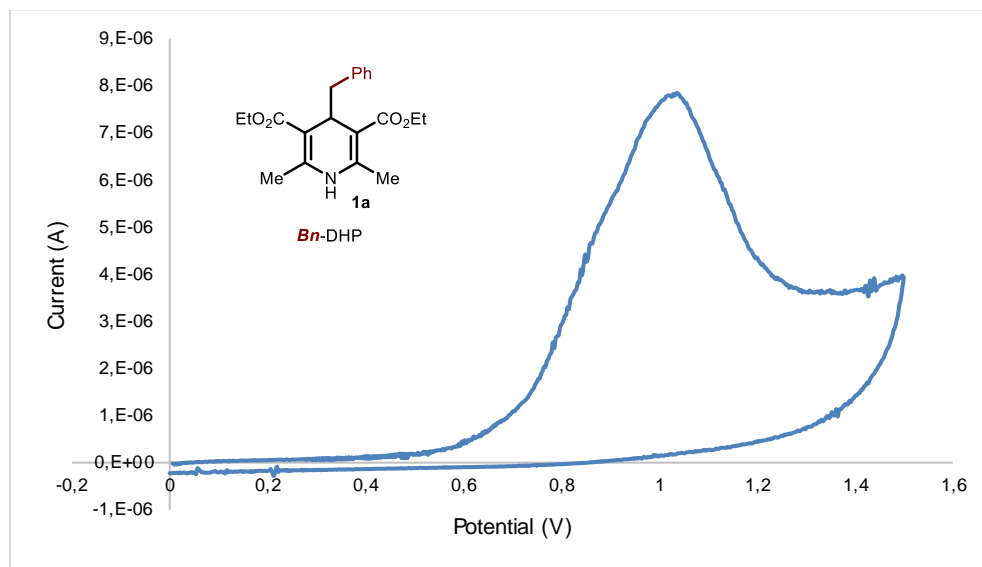


Figure S3. Cyclic voltammogram of **1a** [0.01 M] in [0.1 M] TBAPF₆ in CH₃CN. Sweep rate: 20 mV/s. Pt electrode working electrode, Ag/AgCl (NaCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible oxidation. $E_p^A = E_{ox}(\mathbf{1a}^+/\mathbf{1a}) = +1.00$ V; E_p^A is the anodic peak potential, while E_{ox} value describes the electrochemical properties of **1a**.

B.3. Evaluation of the Excited State Potential of Bn-DHP **1a**

Using the data collected from the cyclic voltammetry studies (Section B.2.) and from the absorption spectra (Section B.1.) of the DHP **1a**, we could estimate the redox potential of the excited compound (**1a***) employing the following Equation 1:²

$$E(\mathbf{1a}^+/\mathbf{1a}^*) = E(\mathbf{1a}^+/\mathbf{1a}) - E_{0,0}(\mathbf{1a}^*/\mathbf{1a}) \quad [\text{Eq. 1}]$$

Since the electrochemical oxidation of the DHP **1a** is irreversible (Figure S3), the irreversible peak potential E_p^{Anode} was used for $E(\mathbf{1a}^+/\mathbf{1a})$. $E_{0,0}(\mathbf{1a}^*/\mathbf{1a})$, which is the excited state energy of the Bn-DHP **1a**, was estimated spectroscopically from the position of the long wavelength tail of the absorption spectrum recorded in acetonitrile (420 nm, Figures S1), the solvent used for the electrochemical analysis.

For the DHP **1a**, the E_p^{Anode} , which provides the $E(\mathbf{1a}^+/\mathbf{1a})$, is 1.00 V (Figures S3), while the position of the long wavelength tail of the absorption spectrum corresponds to 420 nm (Figures S1), which translates into an $E_{0,0}(\mathbf{1a}^*/\mathbf{1a}^+)$ of 2.952 eV.

$$E(\mathbf{1a}^*/\mathbf{1a}^-) = 1.00 - 2.95 = -1.95 \text{ V (vs Ag/AgCl)}$$

B.4. Fluorescence Studies of Benzyl- and isopropyl-DHP Derivatives

The emission spectra were recorded in a Fluorolog Horiba Jobin Yvon spectrofluorimeter equipped with a photomultiplier detector, a double monochromator, and a 350W xenon light source. 2 mL of acetonitrile, thoroughly degassed by freeze pump thaw, were placed in a 10x10 mm light path quartz fluorescence cuvette equipped with Silicone/PTFE 3.2 mm septum under an argon atmosphere. Then, 25 μ L of a 15 mM solution of benzyl-DHP **1a** in acetonitrile was added to afford a final concentration of **1a** of 150 μ M. The excitation wavelength was fixed at 405 nm (incident light slit regulated to 4 mm), while the emission light was acquired from 415 nm to 600 nm (emission light slit regulated to 8 mm). A solvent blank was subtracted from the measurement (Figure S4).

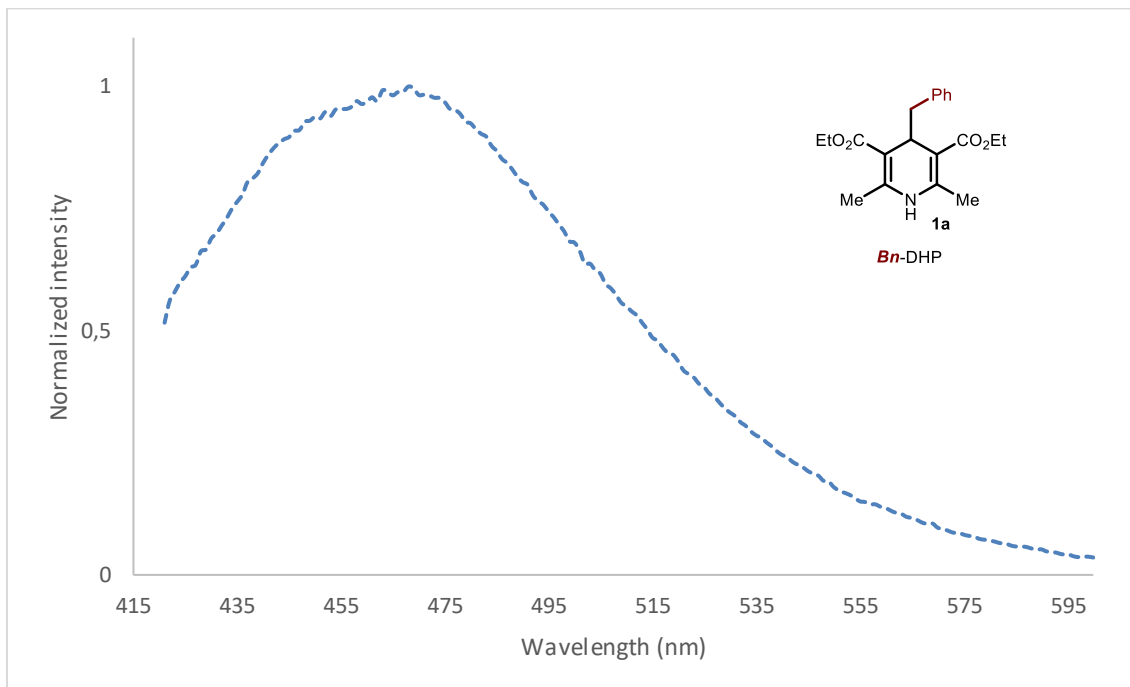


Figure S4. Emission spectrum of Bn-DHP **1a** (excitation wavelength at 405 nm).

The same procedure was repeated to study the photophysical behavior of the isopropyl-DHP derivative (Figure S5). 25 μ L of a 15 mM solution of *i*Pr-DHP in acetonitrile was added to afford a final concentration of 150 μ M. The excitation wavelength was fixed at 390 nm (incident light slit regulated to 4 mm), while the emission light was acquired from 410 nm to 600 nm (emission light slit regulated to 8 mm). A solvent blank was subtracted from the measurement.

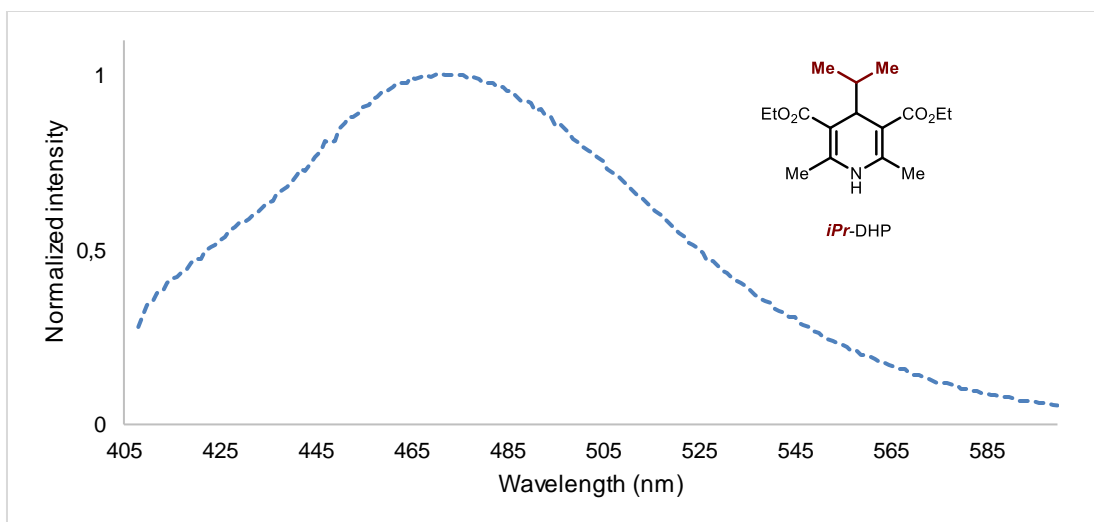


Figure S5. Emission spectrum of *iPr*-DHP (excitation wavelength at 390 nm).

After multiple excitation of solutions of both benzyl- and isopropyl-DHP derivatives (when the DHP substrate was *alone* in the cell), we could observe an increase in the emission intensity. The phenomenon is shown in Figure S6 for the isopropyl-DHP derivative, and an identical behaviour was observed with Bn-DHP **1a**. This phenomenon is likely ascribable to the formation of a strongly emitting compound, which is generated upon photo-degradation of **1**. This emission behavior frustrated any attempt to perform reliable Stern-Volmer quenching studies using different electron acceptors.

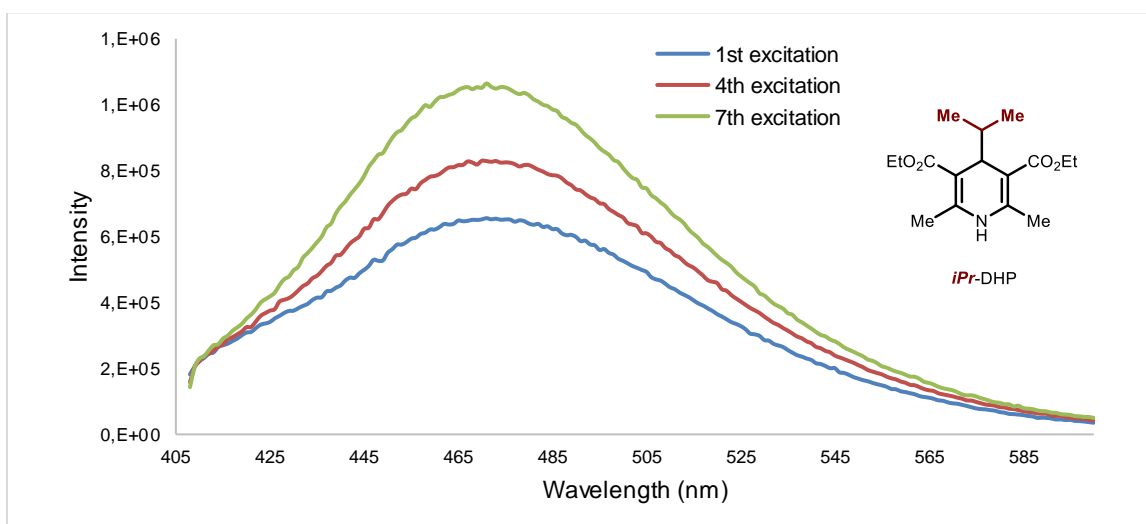


Figure S6. Fluorescence of *iPr*-DHP after several laser-pulse excitations (excitation wavelength at 390 nm).

B.5. Fluorescence Decay of 4-Benzyl-1,4-dihydropyridine-3,5-dicarboxylate **1a**

Lifetime measurements were carried out on an Edinburgh Instruments LifeSpec-II based on the time-correlated single photon counting (TCSPC) technique, equipped with a PMT detector, double subtractive monochromator and picosecond pulsed 405 nm diode laser.

A 600 μM solution of **1a** was introduced into a 1 cm path length quartz cuvette equipped with a Teflon[®] septum and the decay was recorded. The reconvolution fitting from the fluorescence decay trace (Figure

S7) shows a double exponential decay, affording the following values: $\tau_0 = 0.28$ ns (below the limit of the detector) and $\tau_1 = 4.1$ ns.

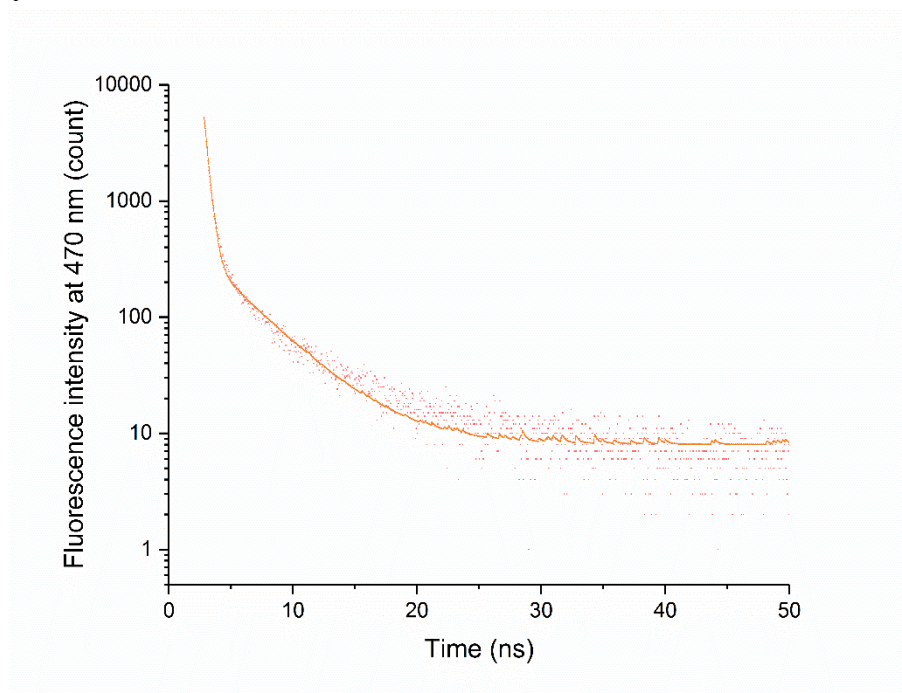


Figure S7. Fluorescence decay trace of 600 μ M of **1a** in CH_3CN after nanosecond photoexcitation of 405 nm laser.

B.6. EPR Experiment

Continuous wave (CW) EPR spectra were obtained on a Bruker EMX Micro X-band spectrometer operating at 9.374 GHz using a Bruker ER 1164 HS resonator and equipped with an ESR900 cryostat. The spectral data was collected at 77 K with the following spectrometer settings: microwave power = 0.5 mW; center field = 3348 G, sweep width = 1000 G, sweep time = 30 s, modulation frequency = 100 KHz, modulation amplitude = 10 G, power attenuation = 25 dB, time constant = 0.01 ms.

The samples were prepared as follow: 4-benzyl-1,4-dihydropyridine-3,5-dicarboxylate **1a** (70 mg, 0.2 mmol) was dissolved in CH_3CN (1 mL, [**1a**] = 200 mM). This solution was transferred into EPR Low Pressure/Vacuum Tube (more information [\[here\]](#)). The reaction mixture was degassed *via* a freeze pump thaw procedure, and kept frozen with liquid nitrogen under vacuum in the EPR tube. The tube was then inserted inside the EPR cavity for the EPR measurements.

Before acquiring the spectra, a 405 nm high power LED purchased from LEDENGIN (which is the same light source used in the synthetic experiments, see Figure S10 for further details) was used to irradiate the samples. The LED was connected to the EPR cavity using an optical fiber supplied with the equipment from Bruker (Figure S8).

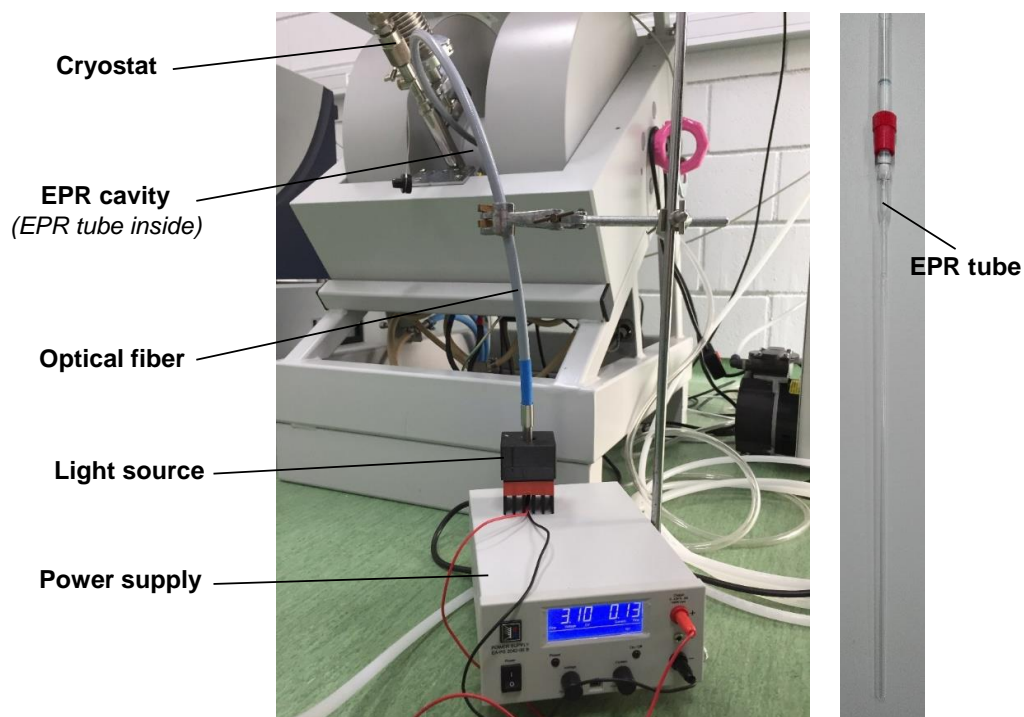


Figure S8. EPR experiment setup

EPR spectra were recorded after 0, 10, 30, and 60 minutes of irradiation (Figure S9). All the spectra, except after 0 minute, showed an isotropic X-band absorption and afforded a g -values of 2.0035, which is consistent with literature data for the characterization of benzyl radicals.³

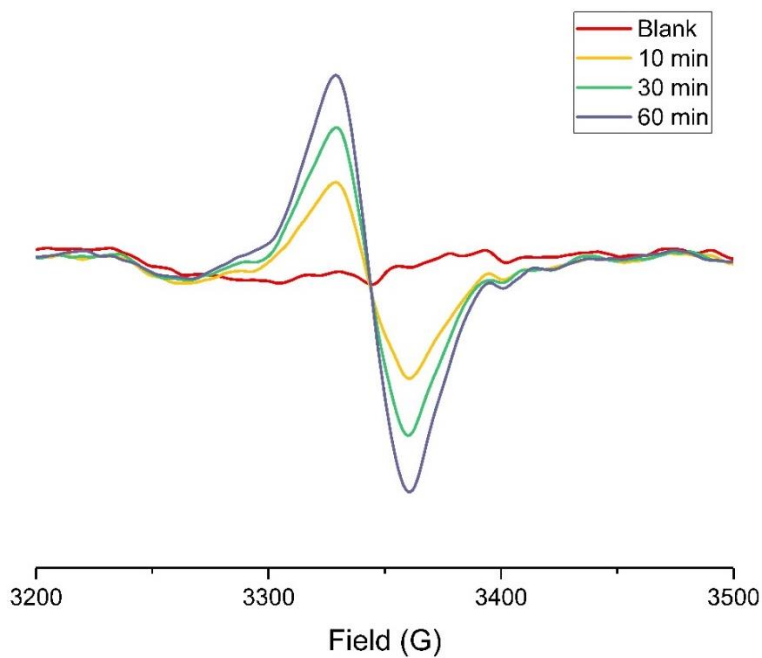


Figure S9. EPR experiment of **1a** at different time intervals.

C. Experimental Procedures

C.1. Light illumination system and reaction set-up

The reaction setup is detailed in Figure S10. The reactions were performed in a 15 mL Schlenk tube that, after addition of reagents and CH₃CN, was placed under an atmosphere of argon, cooled to -78 °C, and degassed via vacuum evacuation (5 min), backfilled with argon, and warmed to room temperature. The freeze-pump-thaw cycle was repeated three times, and then the Schlenk tube was sealed with Parafilm and placed into a 3D-printed plastic support mounted on an aluminium block fitted with a 405 nm high-power single LED ($\lambda = 405$ nm). The irradiance was fixed at 50 ± 3 mW/cm², 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.

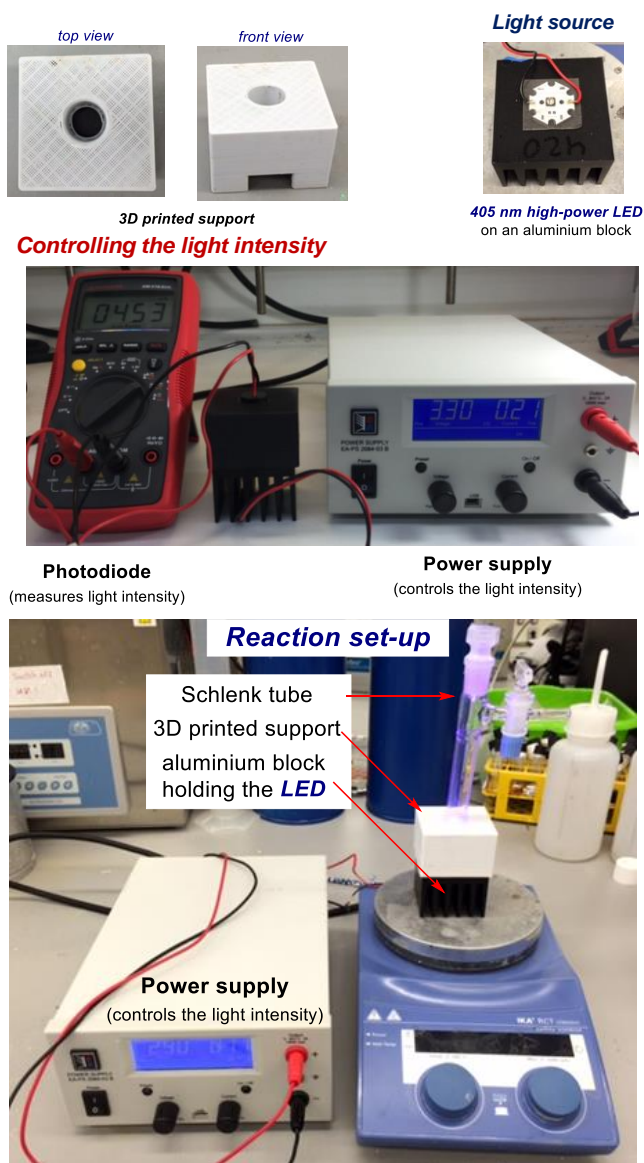
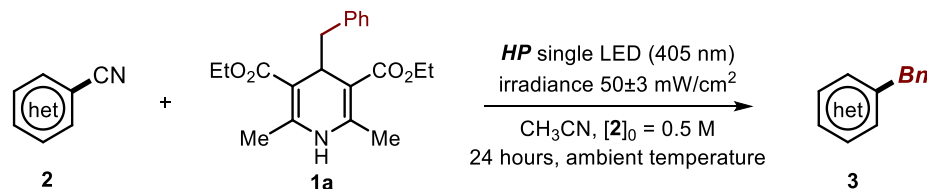


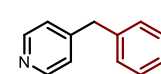
Figure S10. Detailed set-up and illumination system. The light sources for illuminating the reaction vessel consisted in a 405 nm high-power single LED (OCU-440 UE400-X-T) purchased from OSA OPTO (more information [\[here\]](#)) or a 405 nm high-power single LED (LZ1-00UA0) purchased from LEDENGIN (more information [\[here\]](#)). Both light sources provided comparable yields under our reaction conditions.

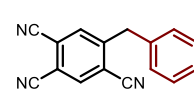
C.2. Benzylation of Cyanoarenes



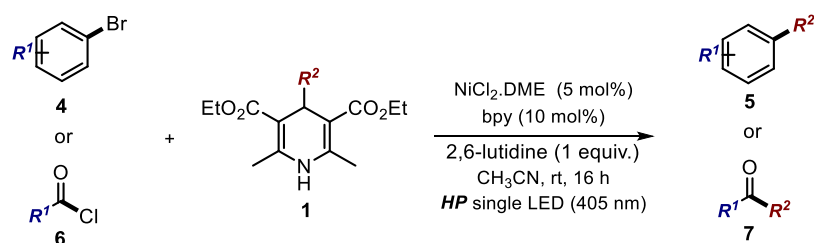
General Procedure A (0.1 mmol scale reaction). In a Schlenk tube, the selected cyanoarenes **2** (0.1 mmol, 1 equiv.) and Bn-DHP **1a** (0.15 mmol, 1.5 equiv.) were dissolved in MeCN (200 μ L). The reaction mixture was degassed *via* a freeze pump thaw procedure, and then placed on a 405 nm high-power single LED ($\lambda = 405$ nm, irradiance = 50 ± 3 mW/cm², as controlled by an external power supply; the set-up is detailed in Figure S10). The reaction was stirred under irradiation at ambient temperature over 24 hours. Then the mixture was concentrated in vacuo and the residue was purified by flash chromatography (silica gel, appropriate mixture of hexane/ethyl acetate) to afford the corresponding product **3**.

Characterization of adducts **3**

 **4-Benzylpyridine (3a)**. Prepared according to the general procedure A, using 4-cyanopyridine **2a** (0.1 mmol, 10 mg, 1 equiv.) and Bn-DHP **1a** (0.15 mmol, 52 mg, 1.5 equiv.); time of irradiation: 24 hours. 44% yield, as determined by ¹H NMR analysis of the crude mixture. Data for **3b** from crude analysis: ¹H NMR (300 MHz, Chloroform-*d*) δ (selected signals) δ 8.53 (d, *J* = 6.1 Hz, 2H), 4.00 (s, 2H). The spectroscopic characterization matched with data reported in the literature.⁴

 **5-Benzylbenzene-1,2,4-tricarbonitrile (3b)**. Prepared according to the general procedure A, using tetracyanobenzene **2b** (0.1 mmol, 18 mg, 1 equiv.) and **1a** (0.15 mmol, 52 mg, 1.5 equiv.); time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a white solid (scale 0.1 mmol : 21 mg, 86% yield). The spectroscopic characterization matched with data reported in the literature.⁵ ¹H NMR (300 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.67 (s, 1H), 7.56 – 7.32 (m, 3H), 7.28 – 7.02 (m, 2H), 4.32 (s, 2H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 151.3, 137.1, 135.6, 135.0, 129.6, 129.2, 128.1, 119.6, 117.8, 114.8, 113.7, 40.4.

C3. Nickel-catalyzed C(sp²)-C(sp³) cross-coupling enabled by the photochemical activity of 1



General Procedure B (0.1 mmol scale reaction). In a Schlenk tube, the aryl bromide **4** or the acyl chloride **6** (0.1 mmol, 1 equiv.), the selected 4-alkyl-1,4-dihydropyridines **1** (0.15 mmol, 1.5 equiv.), and lutidine (11 μ L, 0.1 mmol, 1 equiv.) were successively added to a suspension of NiCl₂·DME (1 mg, 5 mol%) and bipyridine (1.5 mg, 10 mol%) in MeCN (200 μ L). The reaction mixture was degassed *via* a freeze pump thaw procedure, and then placed on a 405 nm high-power single LED ($\lambda = 405$ nm, irradiance = 50 ± 3 mW/cm², as controlled by an external power supply; the set-up is detailed in Figure S10). This set-up secured a reliable irradiation while keeping a constant distance of 1 cm between the reaction vessel and the light source. The reaction was stirred under light irradiation at ambient temperature for the appropriate time (generally 16 hours). Then the reaction mixture was concentrated in vacuo and the residue was purified by flash chromatography (silica gel, appropriate mixture of hexane/ethyl acetate) to afford the corresponding product **5** or **7**. Results on a 0.1 mmol scale are average of two runs.

General Procedure C (0.5 mmol reaction scale). In a 100 mL Schlenk tube (this reaction vessel secures a good ratio between the surface area and volume solvent, thus allowing efficient irradiation of the reaction mixture), the aryl bromide **4** or the acyl chloride **6** (0.5 mmol, 1 equiv.), the selected 4-alkyl-1,4-dihydropyridines **1** (0.75 mmol, 1.5 equiv.), and lutidine (58 μ L, 0.5 mmol, 1 equiv.) were successively added to a suspension of NiCl₂·DME (5.5 mg, 5 mol%) and bipyridine (7.5 mg, 10 mol%) in MeCN (1 mL). The reaction mixture was degassed *via* a freeze pump thaw procedure, and then placed above a 405 nm high-power single LED ($\lambda = 405$ nm, irradiance = 50 ± 3 mW/cm², as controlled by an external power supply; the set-up is detailed in Figure S11). This set-up secured a reliable irradiation while keeping a constant distance of 1 cm (using a spacer of 1 cm) between the reaction vessel and the light source.

The reaction was stirred under light irradiation at ambient temperature for the appropriate time (generally 24 hours). Then the reaction mixture was concentrated in vacuo and the residue purified by flash chromatography (silica gel, appropriate mixture of hexane/ethyl acetate) to afford the corresponding products **5** or **7**.

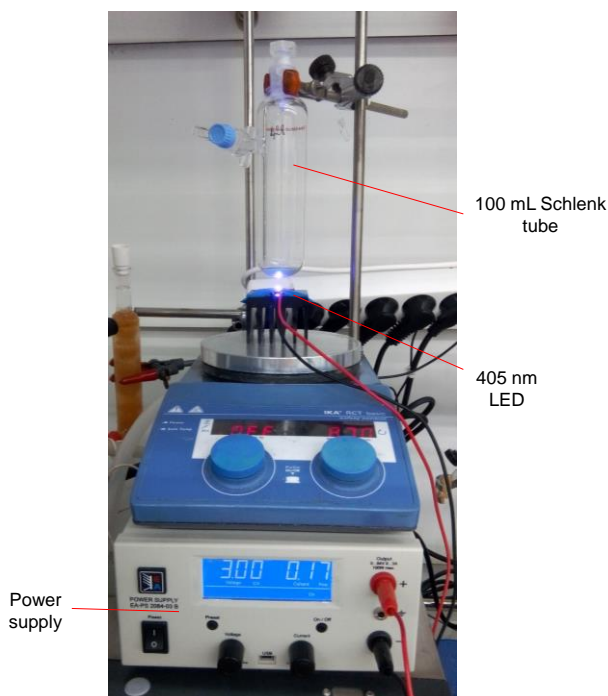
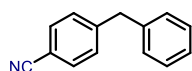


Figure S11. Set-up for 0.5 mmol scale reactions.

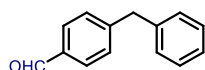
Characterization of products 5



4-Benzylbenzonitrile (5a). Prepared according to the general procedure B, using 4-bromobenzonitrile (0.1 mmol, 18 mg, 1 equiv.) and **1a** (0.15 mmol, 52 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (17 mg, 91% yield, average of two runs).

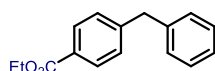
0.5 mmol scale: Prepared according to the general procedure C, using 4-bromobenzonitrile (0.5 mmol, 90 mg, 1 equiv.) and **1a** (0.75 mmol, 260 mg, 1.5 equiv.); time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (82 mg, 89% yield). The spectroscopic characterization matched with data reported in the literature.⁶

¹H NMR (300 MHz, Chloroform-*d*) δ 7.65 – 7.46 (m, 2H), 7.37 – 7.21 (m, 5H), 7.20 – 7.11 (m, 2H), 4.02 (s, 2H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 146.9, 139.4, 132.4, 129.8, 129.1, 128.9, 126.8, 119.1, 110.2, 42.1.



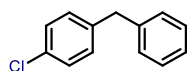
4-Benzylbenzaldehyde (5b). Prepared according to general procedure C, using 4-bromobenzaldehyde (0.5 mmol, 90 mg, 1 equiv.) and **1a** (0.75 mmol, 260 mg, 1.5 equiv.); time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (85 mg, 87% yield). The spectroscopic characterization matched with data reported in the literature.⁷

¹H NMR (300 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.26 (m, 4H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.20 – 7.14 (m, 2H), 4.05 (s, 2H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 192.1, 148.5, 139.9, 134.8, 130.2, 129.7, 129.1, 128.8, 126.7, 42.2.



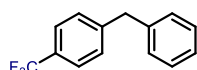
Ethyl 4-benzylbenzoate (5c). Prepared according to the general procedure B, using ethyl 4-bromobenzoate (0.1 mmol, 23 mg, 1 equiv.) and **1a** (0.15 mmol, 52 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (89% NMR yield, the product was isolated with about 10% of ethyl benzoate). The spectroscopic characterization matched with data reported in the literature.⁸

¹H NMR (300 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.01 (m, 7H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 166.7, 146.5, 140.3, 129.9, 129.1, 129.0, 128.7, 128.6, 126.5, 60.9, 42.0, 14.5.



1-Benzyl-4-chlorobenzene (5d). Prepared according to the general procedure C, using 1-bromo-4-chlorobenzene (0.5 mmol, 95 mg, 1 equiv.) and **1a** (0.75 mmol, 260 mg, 1.5 equiv.); time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (67 mg, 67% yield). The spectroscopic characterization matched with data reported in the literature.⁹

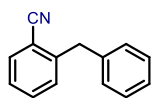
¹H NMR (300 MHz, Chloroform-*d*) δ 7.72 – 6.88 (m, 9H), 4.00 (s, 2H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 140.7, 139.7, 132.0, 130.4, 129.0, 128.7, 128.5, 126.4, 41.4.



1-Benzyl-4-(trifluoromethyl)benzene (5e). Prepared according to the general procedure C, using 1-bromo-4-(trifluoromethyl)benzene (0.5 mmol, 115 mg, 1 equiv.) and **1a** (0.75 mmol, 260 mg, 1.5 equiv.); time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (90 mg, 76% yield). The spectroscopic characterization matched with data reported in the literature.¹⁰

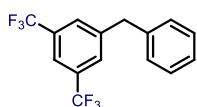
¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.35 – 7.29 (m, 1H), 7.28 – 7.25 (m, 1H), 4.11 (s, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 145.4 (d, *J* = 1.5 Hz), 140.1,

129.3, 129.1, 128.8, 126.6, 125.5 (q, $^2J_{C-F} = 3.8$ Hz), 124.7 (q, $^1J_{C-F} = 271.8$ Hz), 41.9. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -62.4.



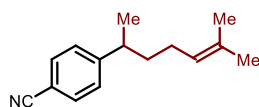
1-Benzyl-3,5-bis(trifluoromethyl)benzene (5f). Prepared according to the general procedure C, using 2-bromobenzonitrile (0.5 mmol, 90 mg, 1 equiv.) and **1a** (0.75 mmol, 260 mg, 1.5 equiv.); time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (70 mg, 75% yield). The spectroscopic characterization matched with data reported in the literature.¹¹

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 7.65 (d, $J = 7.6$ Hz, 1H), 7.52 (td, $J = 7.7, 1.5$ Hz, 1H), 7.42 – 7.16 (m, 7H), 4.24 (s, 2H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 145.0, 138.8, 133.0, 132.9, 130.1, 129.0, 128.8, 126.9, 126.8, 118.2, 112.6, 40.2.



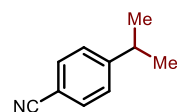
1-Benzyl-3,5-bis(trifluoromethyl)benzene (5g). Prepared according to the general procedure C, using 1-bromo-3,5-bis(trifluoromethyl)benzene (0.5 mmol, 145 mg, 1 equiv.) and **1a** (0.75 mmol, 260 mg, 1.5 equiv.); time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (126 mg, 83% yield). The spectroscopic characterization matched with data reported in the literature.¹²

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.67 (d, $J = 1.7$ Hz, 2H), 7.42 – 7.35 (m, 2H), 7.35 – 7.26 (m, 1H), 7.25 – 7.19 (m, 2H), 4.14 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 143.7, 138.9, 131.9 (q, $^2J_{C-F} = 33.1$ Hz), 129.2-129.0 (m), 129.1, 129.1, 129.0, 127.1, 123.5 (d, $^1J_{C-F} = 272.6$ Hz), 120.5 (p, $^3J_{C-F} = 3.9$ Hz), 41.7. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -62.6.



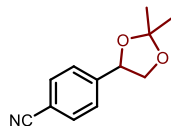
4-(6-Methylhept-5-en-2-yl)benzonitrile (5h). Prepared according to the general procedure C, using 4-bromobenzonitrile (0.5 mmol, 90 mg, 1 equiv.) and diethyl 2,6-dimethyl-4-(6-methylhept-5-en-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (0.75 mmol, 275 mg, 1.5 equiv.); time of irradiation: 72 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a (55 mg, 52% yield).

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 7.58 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 5.05 (tt, $J = 7.1, 1.4$ Hz, 1H), 2.76 (q, $J = 7.1$ Hz, 1H), 2.21 – 1.70 (m, 2H), 1.66 (d, $J = 1.4$ Hz, 3H), 1.65 – 1.52 (m, 2H), 1.50 (d, $J = 1.3$ Hz, 3H), 1.24 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 153.5, 132.3, 132.1, 128.0, 124.0, 119.3, 109.8, 39.8, 38.1, 26.1, 25.8, 22.1, 17.8. **HRMS (ESI):** Calcd for $\text{C}_{15}\text{H}_{19}\text{NNa}$ [$\text{M}+\text{Na}^+$, 100 %]: 236.1410, found 236.1405.



4-isopropylbenzonitrile (5i). Prepared according to the general procedure B, using 4-bromobenzonitrile (0.1 mmol, 18 mg, 1 equiv.) and diethyl 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.15 mmol, 44 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (5 mg, 35% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹

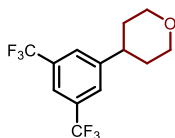
$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 7.57 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 2.96 (p, $J = 6.9$ Hz, 1H), 1.26 (d, $J = 6.9$ Hz, 6H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 154.5, 132.4, 127.4, 119.3, 109.7, 34.5, 23.7.



4-(2,2-dimethyl-1,3-dioxolan-4-yl)benzonitrile (5j). Prepared according to the general procedure B, using 4-bromobenzonitrile (0.1 mmol, 18 mg, 1 equiv.) and diethyl 4-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.15 mmol, 53 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by

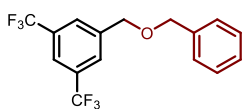
flash column chromatography (gradient from pure toluene to toluene/ethyl acetate 8:2) to afford the product as a colorless oil (15 mg, 77% yield, average of two runs).

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 7.65 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 5.11 (t, J = 7.0 Hz, 1H), 4.35 (dd, J = 8.3, 6.4 Hz, 1H), 3.66 (t, J = 7.9 Hz, 1H), 1.54 (s, 3H), 1.48 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 145.3, 132.5, 126.8, 118.8, 111.9, 110.5, 77.2, 71.4, 26.5, 25.9. **HRMS (ESI):** Calcd for $\text{C}_{11}\text{H}_{10}\text{NO}_2$ [M-Me, 100 %]: 188.0717, found 188.0712.



4-(3,5-bis(trifluoromethyl)phenyl)tetrahydro-2H-pyran (5k). Prepared according to the general procedure B, using 1-bromo-3,5-bis(trifluoromethyl)benzene (0.1 mmol, 29 mg, 1 equiv.) and diethyl diethyl 2,6-dimethyl-4-(tetrahydro-2H-pyran-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate (0.15 mmol, 51 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a white solid (scale 0.1 mmol: 17 mg, 57% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹²

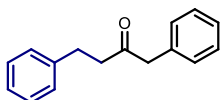
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.67 (s, 2H), 4.26 – 3.88 (m, 2H), 3.65 – 3.37 (m, 2H), 3.10 – 2.77 (m, 1H), 1.92 – 1.78 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 148.3, 132.0 (q, $^2J_{\text{C-F}}$ = 33.1 Hz), 127.4 – 126.9 (m), 123.5 (q, $^1J_{\text{C-F}}$ = 272.7 Hz), 120.6 (dt, J = 7.8, 3.8 Hz), 68.1, 41.5, 33.7. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -63.0.



1-((Benzyloxy)methyl)-3,5-bis(trifluoromethyl)benzene (5l). Prepared according to general procedure C, using 1-bromo-3,5-bis(trifluoromethyl)benzene (0.5 mmol, 145 mg, 1 equiv.) and diethyl 2,6-dimethyl-4-(phenoxy)methyl-1,4-dihydropyridine-3,5-dicarboxylate (0.75 mmol, 300 mg, 1.5 equiv.); time of irradiation: 72 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (83 mg, 50% yield).

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 7.86 (s, 3H), 7.63 – 7.05 (m, 5H), 4.68 (s, 4H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 141.2, 137.5, 131.8 (q, J = 33.3 Hz), 128.8, 128.2, 128.1, 127.5, 121.7 – 121.4 (m), 73.2, 70.6. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -63.0. **HRMS (ESI):** Calcd for $\text{C}_9\text{H}_5\text{F}_6$ [M-OCH₂Ph, 100 %]: 227.0295, found 227.0286.

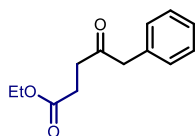
Characterization of ketones 7



1,4-Diphenylbutan-2-one (7a). Prepared according to the general procedure B, using ethyl 4-chloro-4-oxobutanoate (0.1 mmol, 17 mg, 1 equiv.) and **1a** (0.15 mmol, 52 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colourless oil (16 mg, 71% yield, average of two runs).

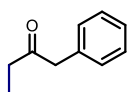
0.5 mmol scale: Prepared according to the general procedure C, using ethyl 4-chloro-4-oxobutanoate (0.5 mmol, 85 mg, 1 equiv.) and **1a** (0.75 mmol, 260 mg, 1.5 equiv.); time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colourless liquid (63 mg, 56% yield). The spectroscopic characterization matched with data reported in the literature.¹³

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 7.25 – 6.92 (m, 10H), 3.57 (s, 2H), 2.78 (dd, J = 8.2, 5.7 Hz, 2H), 2.67 (ddd, J = 8.2, 6.5, 1.8 Hz, 2H). $^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 207.5, 141.0, 134.2, 129.5, 128.8, 128.6, 128.4, 127.1, 126.2, 50.5, 43.6, 29.9.



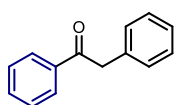
Ethyl 4-oxo-5-phenylpentanoate (7b). Prepared according to the general procedure B, using ethyl 4-chloro-4-oxobutanoate (0.1 mmol, 17 mg, 1 equiv.) and **1a** (0.15 mmol, 52 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colourless oil (12 mg, 55% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹⁴

¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 2H), 7.32 – 7.26 (m, 1H), 7.26 – 7.21 (m, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.76 (s, 2H), 2.78 (t, $J = 6.6$ Hz, 2H), 2.57 (dd, $J = 7.0, 6.2$ Hz, 2H), 1.25 (t, $J = 7.1$ Hz, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 206.6, 172.8, 134.2, 129.6, 128.9, 127.2, 60.8, 50.2, 36.6, 28.2, 14.3.



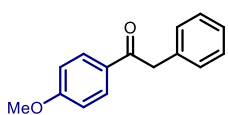
1-Phenylbutan-2-one (7c). Prepared according to the general procedure B, using propionyl chloride (0.1 mmol, 9 mg, 1 equiv.) and **1a** (0.15 mmol, 52 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colourless oil (9 mg, 62% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹⁵

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.18 (m, 2H), 3.69 (s, 2H), 2.47 (q, $J = 7.3$ Hz, 2H), 1.03 (t, $J = 7.3$ Hz, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 209.1, 134.6, 129.5, 128.8, 127.1, 50.0, 35.4, 7.9.



1,2-Diphenylethan-1-one (7d). Prepared according to the general procedure B, using benzoyl chloride (0.1 mmol, 14, mg, 1 equiv.) and **1a** (0.15 mmol, 52 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a white solid (9 mg, 46% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹⁶

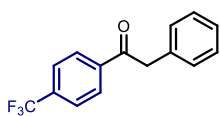
¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.02 (m, 2H), 7.61 – 7.56 (m, 1H), 7.51 – 7.46 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.25 (m, 3H), 4.32 (s, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 197.7, 136.7, 134.7, 133.3, 129.6, 128.8, 128.8, 128.7, 127.0, 45.6.



1-(4-Methoxyphenyl)-2-phenylethan-1-one (7e). Prepared according to the general procedure B, using 4-methoxybenzoyl chloride (0.1 mmol, 17 mg, 1 equiv.) and **1a** (0.15 mmol, 52 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a white solid (16 mg, 71% yield, average of two runs).

0.5 mmol scale: Prepared according to general procedure C using 4-methoxybenzoyl chloride (0.5 mmol, 85, mg, 1 equiv.) and **1a** (0.15 mmol, 260 mg, 1.5 equiv.); time of irradiation: 24 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a white solid (70 mg, 62% yield). The spectroscopic characterization matched with data reported in the literature.¹⁷

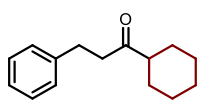
¹H NMR (300 MHz, Chloroform-*d*) δ 8.09 – 7.79 (m, 2H), 7.31 (dtt, $J = 8.0, 6.0, 2.9$ Hz, 5H), 7.02 – 6.75 (m, 2H), 4.25 (s, 2H), 3.87 (s, 3H). **¹³C NMR** (75 MHz, Chloroform-*d*) δ 196.3, 163.6, 135.1, 131.0, 129.7, 129.5, 128.7, 126.9, 113.9, 55.6, 45.4.



2-Phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (7f). Prepared according to the general procedure B, using 4-(trifluoromethyl)benzoyl chloride (21 mg, 1 equiv.) and **1a** (0.15 mmol, 52 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a white solid (12 mg, 46% yield, average of two runs).

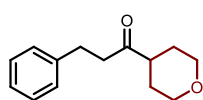
The spectroscopic characterization matched with data reported in the literature.¹⁶

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.10 (dp, $J = 7.7, 0.9$ Hz, 2H), 7.75 – 7.69 (m, 2H), 7.38 – 7.31 (m, 2H), 7.30 – 7.25 (m, 3H), 4.31 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 196.8, 139.4, 134.6 (d, $^2J_{\text{C-F}} = 32.9$ Hz), 133.9, 129.5, 129.1, 129.0, 127.3, 125.9 (q, $^3J_{\text{C-F}} = 3.7$ Hz), 123.7 (d, $^1J_{\text{C-F}} = 272.7$ Hz), 46.0. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -62.9.



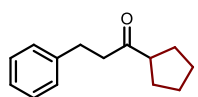
1-Cyclohexyl-3-phenylpropan-1-one (7g). Prepared according to general procedure B, using 3-phenylpropanoyl chloride (0.1 mmol, 17 mg, 1 equiv.) and diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.15 mmol, 50 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (12 mg, 56% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹⁷

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.22 – 7.16 (m, 3H), 2.86 – 2.90 (m, 2H), 2.79 – 2.70 (m, 2H), 2.31 (tt, $J = 11.3, 3.4$ Hz, 1H), 1.84 – 1.73 (m, 4H), 1.64 – 1.67 (m, 1H), 1.41 – 1.14 (m, 5H). $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 213.3, 141.6, 128.6, 128.5, 126.1, 51.1, 42.4, 29.9, 28.6, 26.0, 25.8.



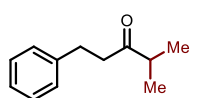
3-Phenyl-1-(tetrahydro-2H-pyran-4-yl)propan-1-one (7h). Prepared according to the general procedure B, using 3-phenylpropanoyl chloride (0.1 mmol, 17 mg, 1 equiv.) and diethyl diethyl 2,6-dimethyl-4-(tetrahydro-2H-pyran-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate (0.15 mmol, 51 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colorless oil (10 mg, 46% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹⁷

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 3.97 (ddd, $J = 11.4, 4.2, 2.6$ Hz, 2H), 3.39 (td, $J = 11.4, 2.9$ Hz, 2H), 2.92 – 2.88 (m, 2H), 2.83 – 2.72 (m, 2H), 2.53 – 2.47 (m, 1H), 1.80 – 1.57 (m, 4H). $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 211.1, 141.3, 128.6, 128.5, 126.3, 67.4, 47.9, 42.1, 29.8, 28.2.



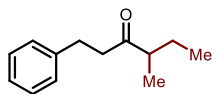
1-Cyclopentyl-3-phenylpropan-1-one (7i). Prepared according to the general procedure B, using 3-phenylpropanoyl chloride (0.1 mmol, 17 mg, 1 equiv.) and diethyl 4-cyclopentyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.15 mmol, 48 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colourless liquid (12 mg, 59% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹⁸

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.16 (m, 3H), 2.92 – 2.89 (m, 2H), 2.84 (ddd, $J = 16.0, 8.6, 7.3$ Hz, 1H), 2.80 – 2.74 (m, 2H), 1.82 – 1.51 (m, 8H). $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 212.4, 141.5, 128.6, 128.5, 126.1, 51.7, 43.5, 30.0, 28.9, 26.1.



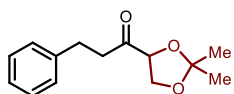
4-Methyl-1-phenylpentan-3-one (7j). Prepared according to the general procedure B, using 3-phenylpropanoyl chloride (0.1 mmol, 17 mg, 1 equiv.) and diethyl 4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.15 mmol, 44 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colourless oil (10 mg, 57% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹⁸

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 2.93 – 2.85 (m, 2H), 2.79 – 2.75 (m, 2H), 2.57 (sept, $J = 6.9$ Hz, 1H), 1.07 (d, $J = 6.9$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 213.9, 141.5, 128.6, 128.5, 126.2, 42.1, 41.2, 30.0, 18.3.



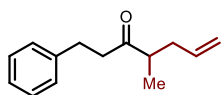
4-Methyl-1-phenylhexan-3-one (7k). Prepared according to the general procedure B, using 3-phenylpropanoyl chloride (0.1 mmol, 17 mg, 1 equiv.) and diethyl 4-(sec-butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.15 mmol, 46 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colourless oil (10 mg, 53% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹⁸

¹H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.16 (m, 3H), 2.92 – 2.86 (m, 2H), 2.78 – 2.72 (m, 2H), 2.43 (h, *J* = 6.8 Hz, 1H), 1.71 – 1.61 (m, 1H), 1.42 – 1.31 (m, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 213.9, 141.5, 128.6, 128.5, 126.2, 48.2, 42.9, 29.9, 26.0, 15.9, 11.8.



1-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-phenylpropan-1-one (7l). Prepared according to the general procedure B, using 3-phenylpropanoyl chloride (0.1 mmol, 17 mg, 1 equiv.) and diethyl 4-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.15 mmol, 53 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colourless oil (12 mg, 51% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.¹⁹

¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.21 – 7.18 (m, 3H), 4.42 (dd, *J* = 7.8, 5.6 Hz, 1H), 4.17 (dd, *J* = 8.7, 7.8 Hz, 1H), 3.92 (dd, *J* = 8.7, 5.6 Hz, 1H), 2.98 – 2.88 (m, 4H), 1.45 (s, 3H), 1.38 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 210.1, 141.1, 128.6, 128.5, 126.3, 111.1, 80.4, 66.6, 40.4, 29.1, 26.2, 25.1.

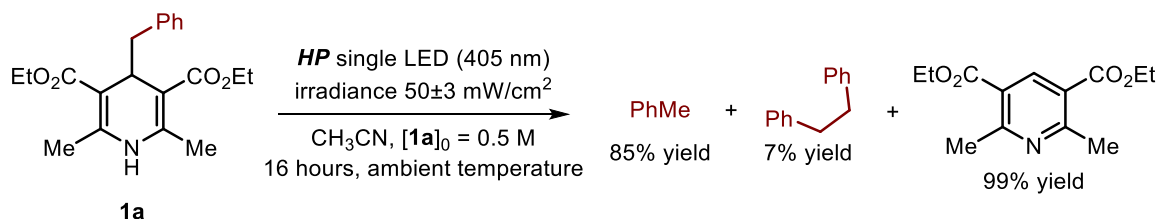


4-Methyl-1-phenylhept-6-en-3-one (7m). Prepared according to the general procedure B, using 3-phenylpropanoyl chloride (0.1 mmol, 17 mg, 1 equiv.) and diethyl 4-(hex-5-en-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.15 mmol, 50 mg, 1.5 equiv.); time of irradiation: 16 hours. The crude mixture was purified by flash column chromatography (gradient from pure hexane to hexane/ethyl acetate 9:1) to afford the product as a colourless oil (12 mg, 56% yield, average of two runs). The spectroscopic characterization matched with data reported in the literature.²⁰

¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 2H), 7.23 – 7.14 (m, 3H), 5.77 – 5.60 (m, 1H), 5.08 – 4.95 (m, 2H), 2.91 – 2.87 (m, 2H), 2.78 – 2.73 (m, 2H), 2.57 (h, *J* = 6.9 Hz, 1H), 2.42 – 2.32 (m, 1H), 2.14 – 2.03 (m, 1H), 1.05 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 213.0, 141.4, 135.8, 128.6, 128.5, 126.2, 117.0, 46.3, 43.1, 37.2, 29.8, 16.1.

D. Mechanistic Experiments

D.1. Irradiation of **1a**



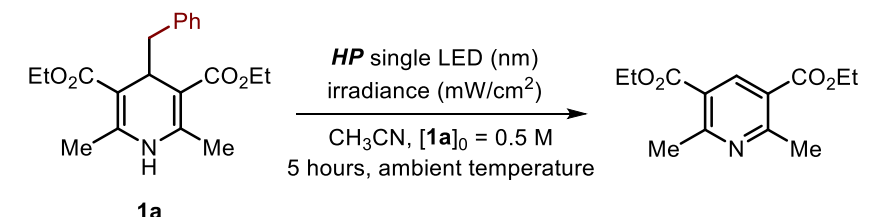
In a Schlenk tube, diethyl 4-benzyl-1,4-dihydropyridine-3,5-dicarboxylate **1a** (0.1 mmol, 1 equiv.) was dissolved in CH₃CN (200 μL). The reaction mixture was degassed *via* a freeze pump thaw procedure, and then placed above a 405 nm high-power single LED ($\lambda = 405$ nm, irradiance = 50 mW/cm², as controlled by an external power supply). The reaction was stirred under visible light irradiation at ambient temperature for 16 hours. Then, the reaction mixture was analyzed by NMR, and GC-MS spectroscopic analysis, confirming the formation toluene, 1,2-diphenylthane, and the corresponding pyridine. Yields were determined by ¹H NMR analysis of the crude mixture using trichloroethylene as the internal standard.

D.2. Studies on the effect of the light irradiance

The photodegradation of **1a**, discussed in Section D1, was used as the test reaction to evaluate the effect of the light intensity, which can directly influence the photochemistry of Bn-DHP **1a**.

A solution of **1a** was irradiated with a high power LED emitting at 405 nm, while the power supplier was used to modulate the irradiance. We measured the formation of the pyridine, formed from the photochemical activity of **1a**, to calculate the reactivity.

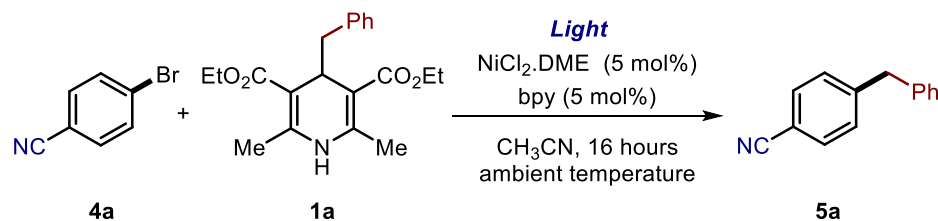
Table S1. Effect of the light intensity on the photodegradation of **1a**



Reaction scheme showing the irradiation of **1a** (diethyl 4-benzyl-1,4-dihydropyridine-3,5-dicarboxylate) under HP single LED (nm) irradiance (mW/cm²) in CH₃CN, [1a]₀ = 0.5 M, for 5 hours at ambient temperature. The product is the corresponding pyridine.

entry	wavelength (nm)	irradiance (mW/cm ²)	yield (%)
1	405	10	30
2	405	30	53
3	405	40	66
4	405	50	88

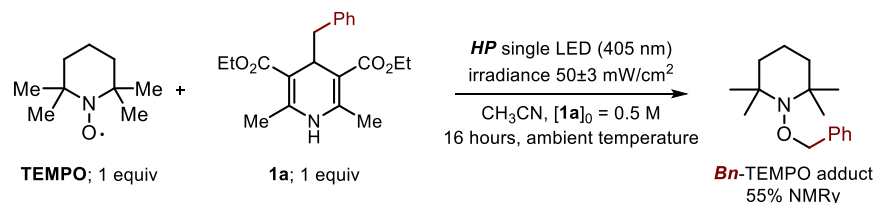
Reaction conditions: DHP **1a** (34 mg, 0.1 mmol) was dissolved in MeCN (200 μL) and irradiated with a HP single LED for 5 hours. Yields determined by ¹H NMR spectroscopy analysis using trichloroethylene as the internal standard; incomplete reaction returned unreacted **1a**.

Table S2. Effect of the light intensity on the nickel-catalyzed coupling

entry	Light	wavelength (nm)	irradiance (mW/cm ²)	yield (%)
1	Single HP LED	420	50	35
2	Single HP LED	405	50	82
3	Single HP LED	405	24	26
4	7.2 W LED Strips	405	n.d.	35
5	23W CFL	$\lambda_{\text{max}} = 365$	n.d.	traces

Reaction conditions: 4-bromobenzene **4a** (0.1 mmol) and DHP **1a** (0.1 mmol) were successively added to a suspension of NiCl₂·DME (1 mg, 5 mol%) and bipyridine (10 mol%) in MeCN (200 μ L) and irradiated for 16 hours. Yields determined by ¹H NMR spectroscopy analysis using trichloroethylene as the internal standard

D.3. Radical trapping experiment

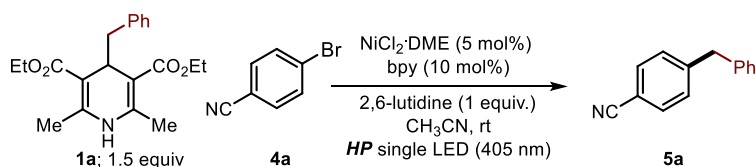


In a Schlenk tube, **1a** (0.1 mmol, 1 equiv) and TEMPO (0.1 mmol, 1 equiv) were dissolved in CH₃CN (200 μ L). The reaction mixture was degassed *via* a freeze pump thaw procedure, and then placed above a 405 nm high-power single LED ($\lambda = 405$ nm, irradiance = 50 mW/cm², as controlled by an external power supply). The reaction was stirred under light irradiation at ambient temperature for 16 hours. Then, the reaction mixture was analyzed by NMR and GC-MS spectroscopic analysis, confirming the formation of the Bn-TEMPO adduct. The ¹H NMR yield was determined using trichloroethylene as the internal standard. Diagnostic signals: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 5H), 4.83 (s, 2H), 1.87 – 1.47 (m, 6H), 1.26 (s, 6H), 1.15 (s, 6H). The spectroscopic characterization of the Bn-TEMPO adduct matched with data reported in the literature.²¹

A control experiment performed in the absence of light did not lead to the formation of the Bn-TEMPO adduct while returning the unreacted starting substrates.

D.4. Quantum Yield Measurement

The photochemical nickel-catalyzed cross-coupling process between Bn-DHP **1a** and was selected as the model for measuring the quantum yield.



Determination of the quantum yield²² was achieved running the reactions using an Osa-Optoelectronic 405nm high power LED. The reactions were carried out in an argon purged flat bottom vial keeping the distance between the light source and vessel at 1 cm with a 3D printed spacer. Specifications from the supplier allowed the determination of the photon flux.¹

The radiant intensity $I_{e,\Omega}$ (mW/sr) for the 405 nm LED with an inlet current of 350 mA corresponds to:

$$I_{e,\Omega} = 110 \text{ mW/sr}$$

Since we kept constant the distance between the light source and the vessel of 1 cm, the irradiance E_e (mW/cm²) was calculated:

$$E_e = I_{e,\Omega} * 1 \text{ sr/cm}^2 = 110 \text{ mW/cm}^2$$

The bottom surface area of the vial was measured as $A = 1,5386 \text{ cm}^2$, which means that the power received by the reaction mixture is: $P = 110 \text{ mW/cm}^2 * 1,5386 \text{ cm}^2 = 169.246 \text{ mW}$

Since W corresponds to J/s and knowing that at 405 nm the energy of the photons is $E_{p,405} = 295370 \text{ J/mol}$. Then, we could calculate the photon flux:

$$\text{photon flux} = P/E_{p,405} = 5.73 \times 10^{-7} \text{ ens/s}$$

Procedure for the quantum yield determination: the samples were prepared within a glovebox. In a glass vial, the 4-bromobenzonitrile (0.1 mmol, 18 mg, 1 equiv.), **1a** (0.15 mmol, 52mg, 1.5 equiv.), and lutidine (11 μL , 0.1 mmol, 1 equiv.) were successively added to a suspension of $\text{NiCl}_2 \cdot \text{DME}$ (1 mg, 5 mol%) and bipyridine (1.5 mg, 10 mol%) in degassed CH_3CN (200 μL). Then, the vial was placed (out of the glovebox) on the LED, keeping the distance between the light source and vessel at 1 cm with a 3D printed spacer. After the appropriate time, the reaction was stopped, and 50 μL of a 1M solution of 4-methylbenzonitrile was added to the reaction mixture as the internal standard. An aliquot was taken and diluted with CH_3CN before being submitting to GC measurements.

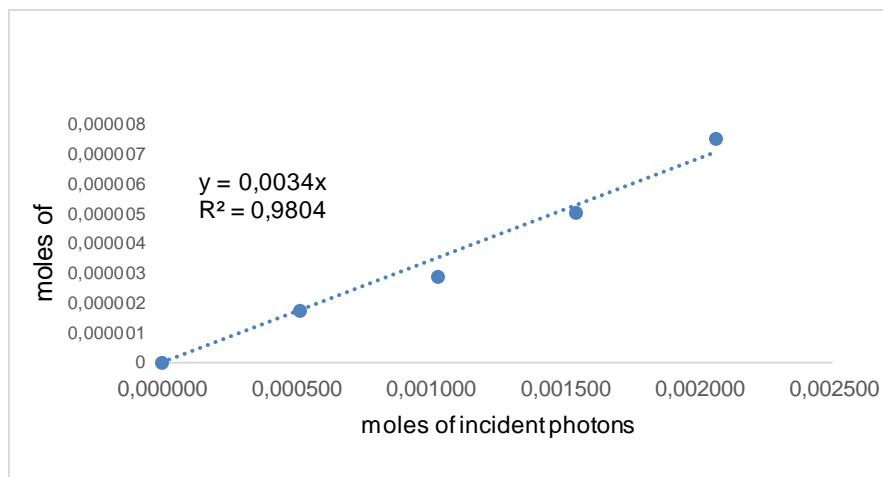
Absorbance of the reaction mixture: in a 1 cm path length quartz cuvette equipped with a Teflon[®] septum, 4-bromobenzonitrile (1 mmol, 180 mg, 1 equiv.), **1a** (1.5 mmol, 520 mg, 1.5 equiv.), and lutidine (110 μL , 1 mmol, 1 equiv.) were successively added to a suspension of $\text{NiCl}_2 \cdot \text{DME}$ (10 mg, 5 mol%) and bipyridine (15 mg, 10 mol%) in degassed CH_3CN (2 mL).

The absorbance of the reaction mixture at 405 nm, measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 10 mm path quartz, was: $A(405 \text{ nm}) > 3$. Since the transmittance of photons is sufficiently small, it can be assumed that all of the photons which pass through the cell are absorbed.

¹ The supplier provides the radiant intensity value when regulating the inlet current at 350 mA with a power supply. The emission from the HP LED is symmetric, with a maximum centered at 405 nm and an emission band of 30 nm; as an approximation, we considered the LED emission at 405 nm as monochromatic.

The moles of product **5a** formed for the model reaction were determined by GC measurement (FID detector) using 4-methylbenzonitrile as the internal standard. An independent reaction was performed for every single point.

The moles of product per unit of time are related to the number of incident photons. According to this, if the moles of product are plotted versus the moles of incident photons, the slope gives the overall quantum yield (Φ) of the process under study.

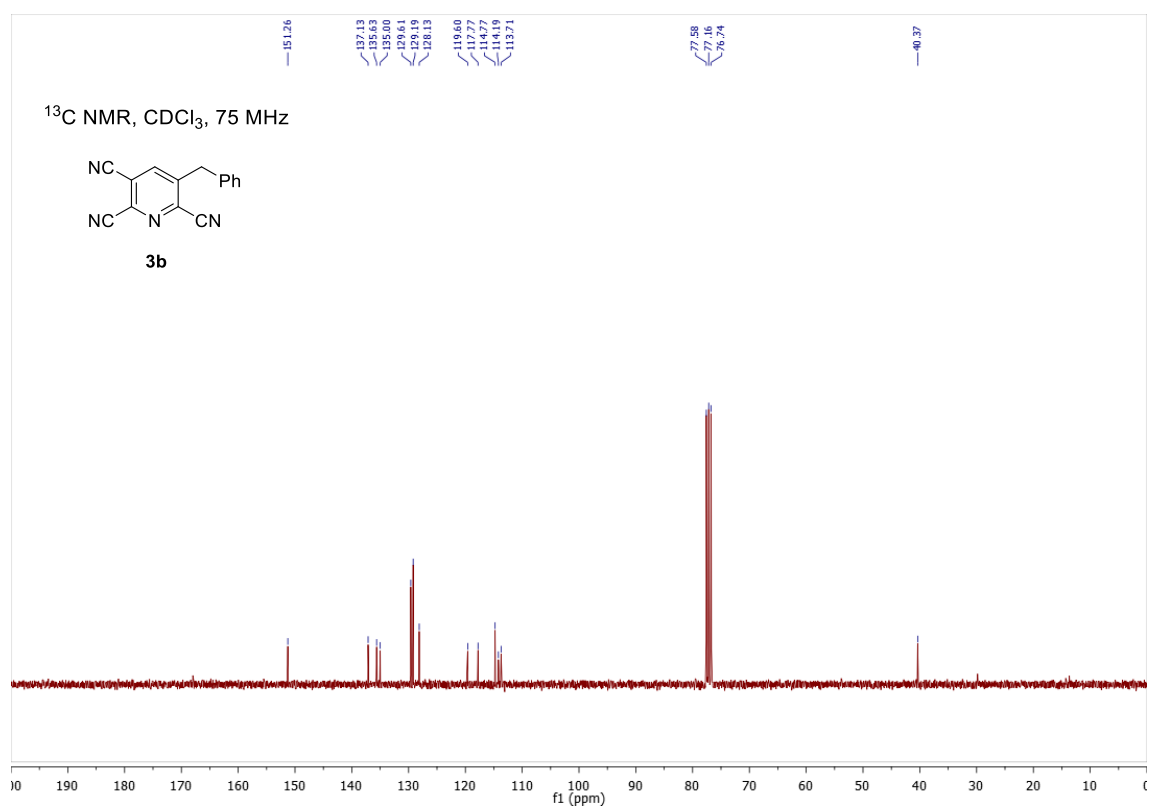
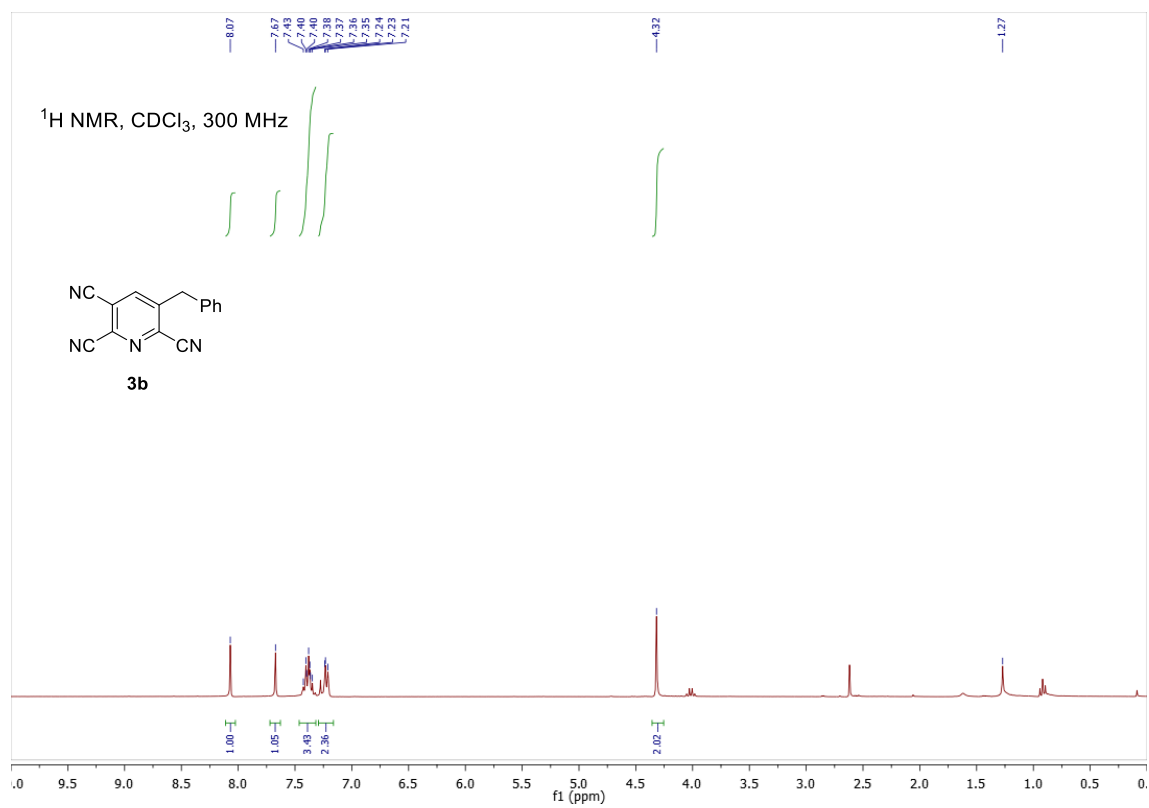


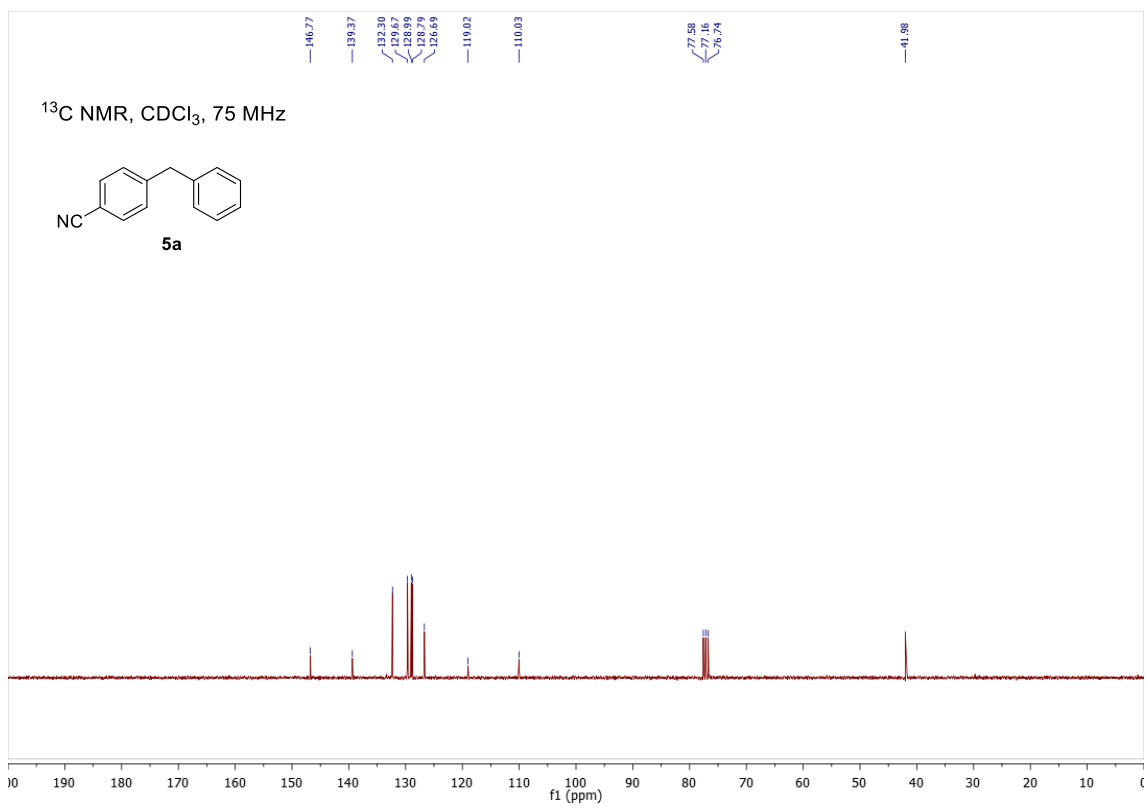
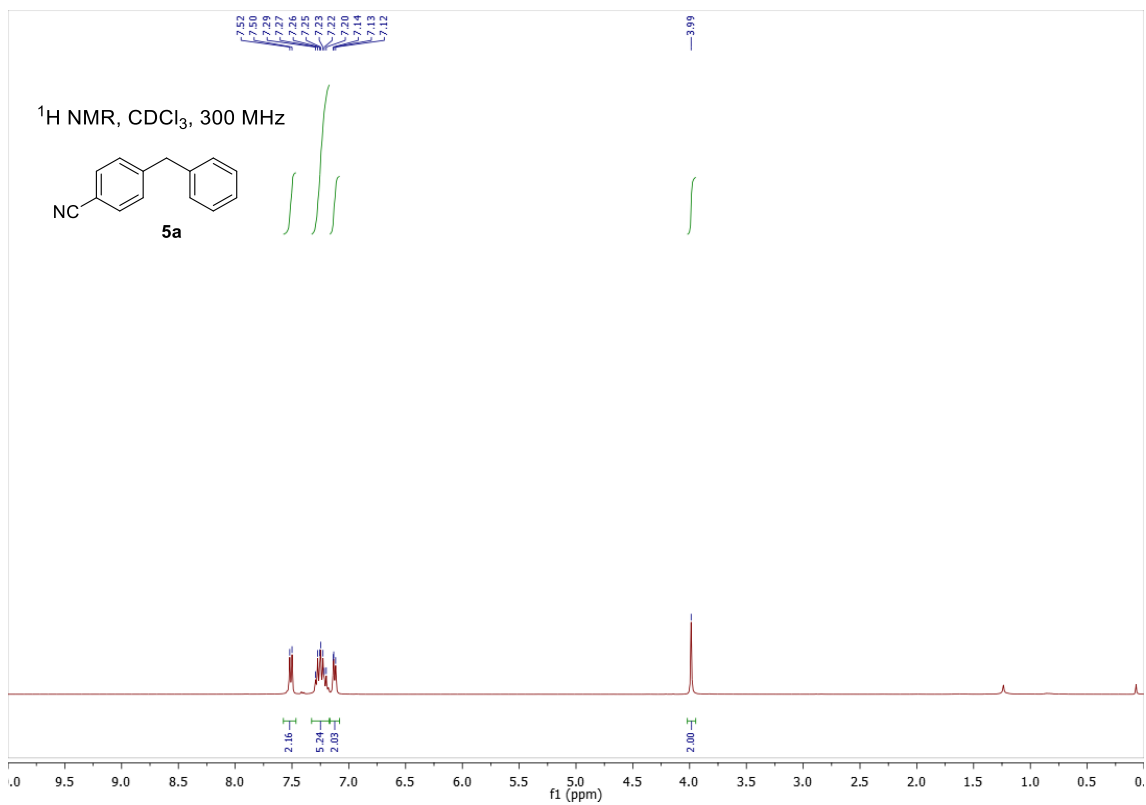
The quantum yield (Φ) of the photochemical benzylation of the 4-bromobenzonitrile **4a** with Bn-DHP **1a** was found to be **0.0034** (average of three independent series of experiments).

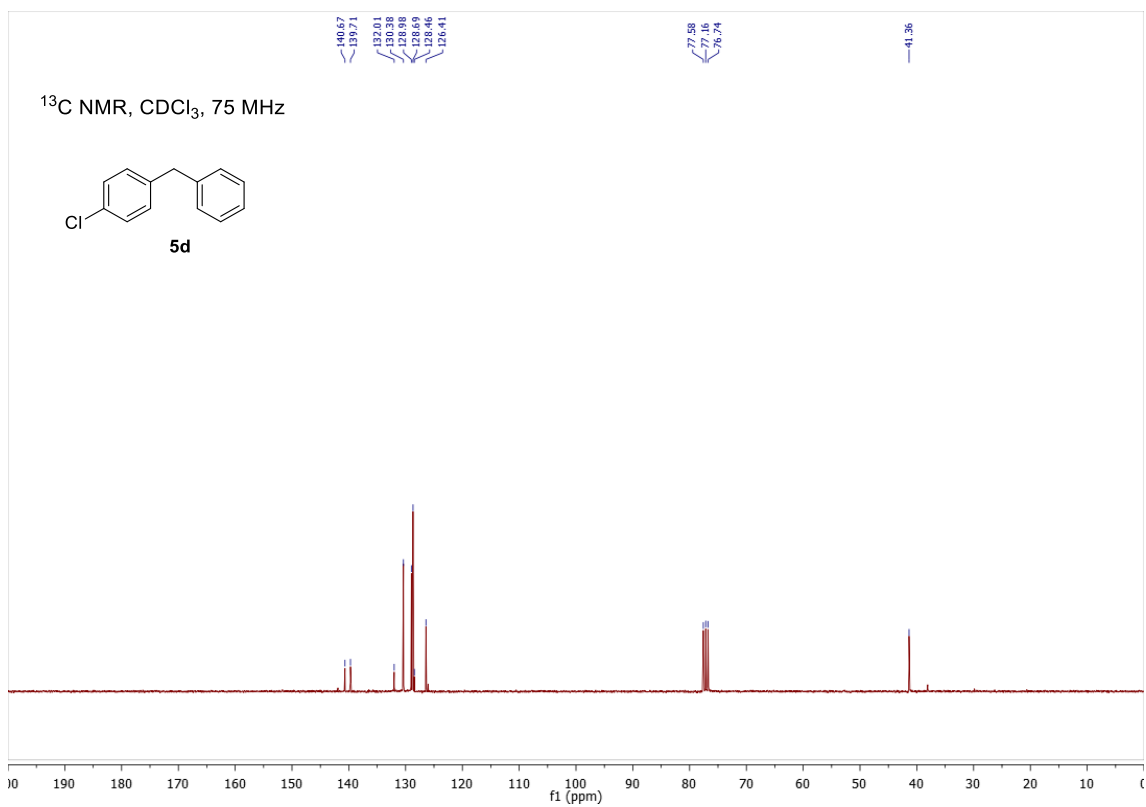
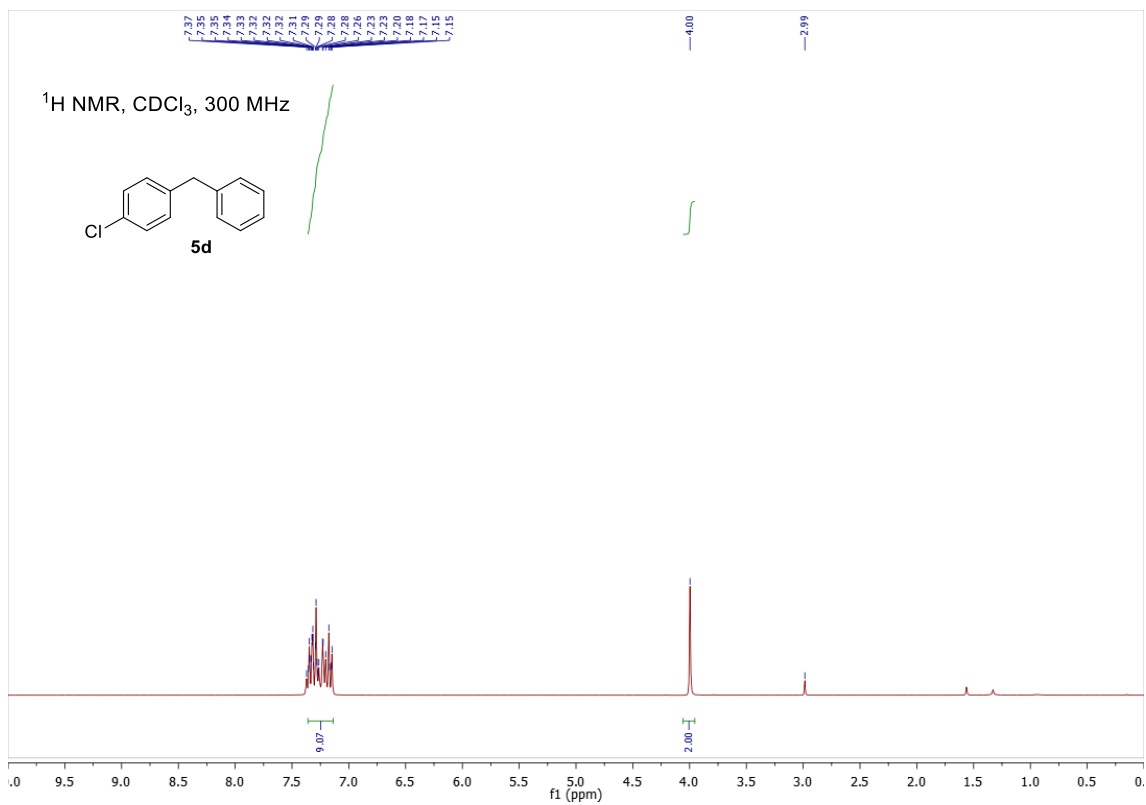
E. References

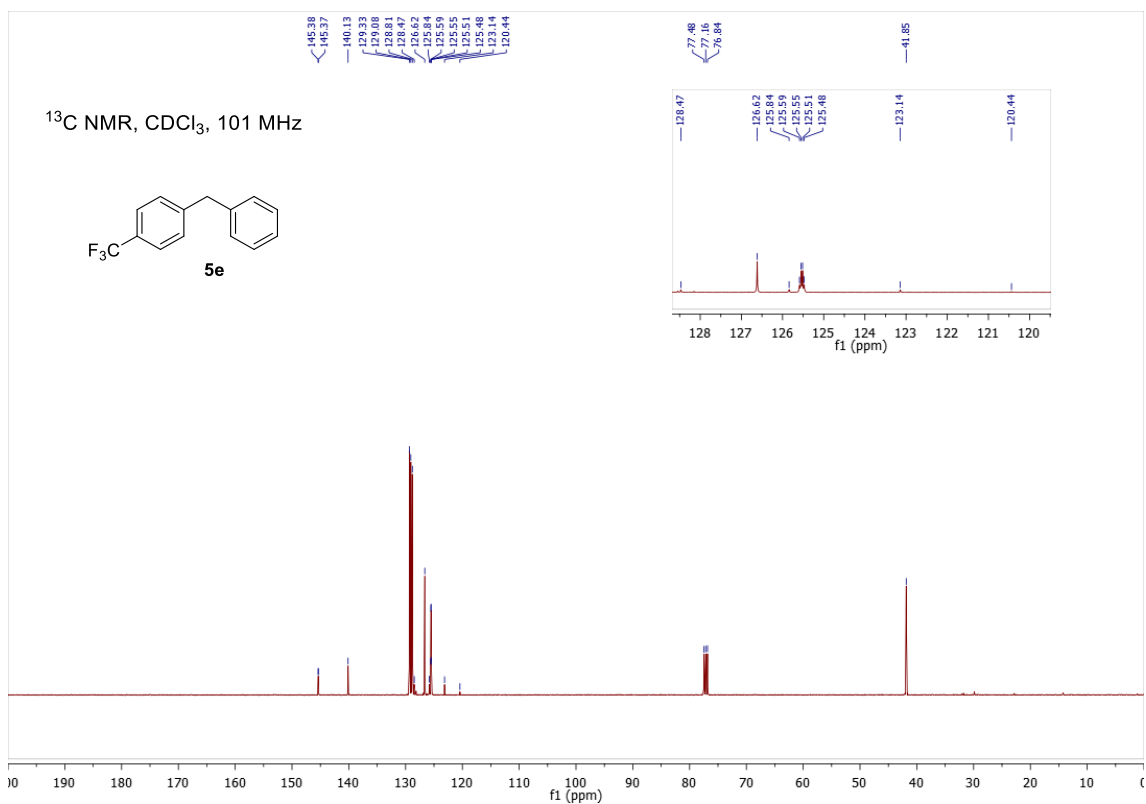
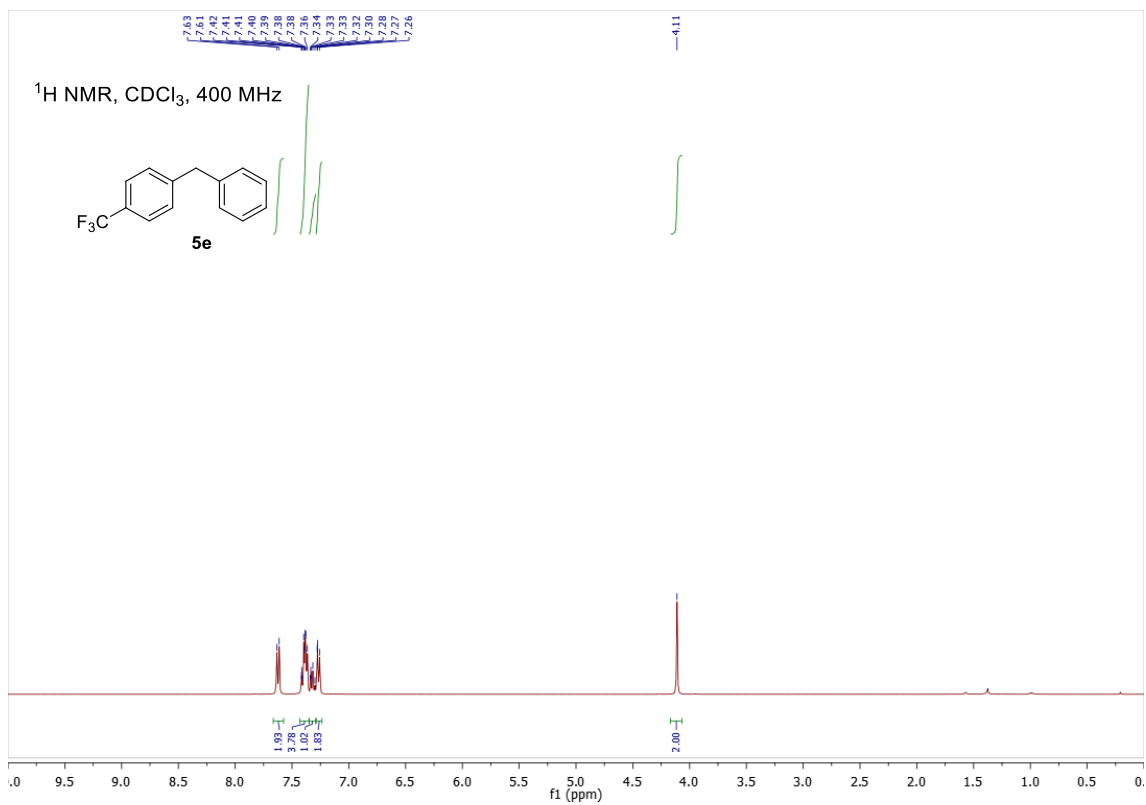
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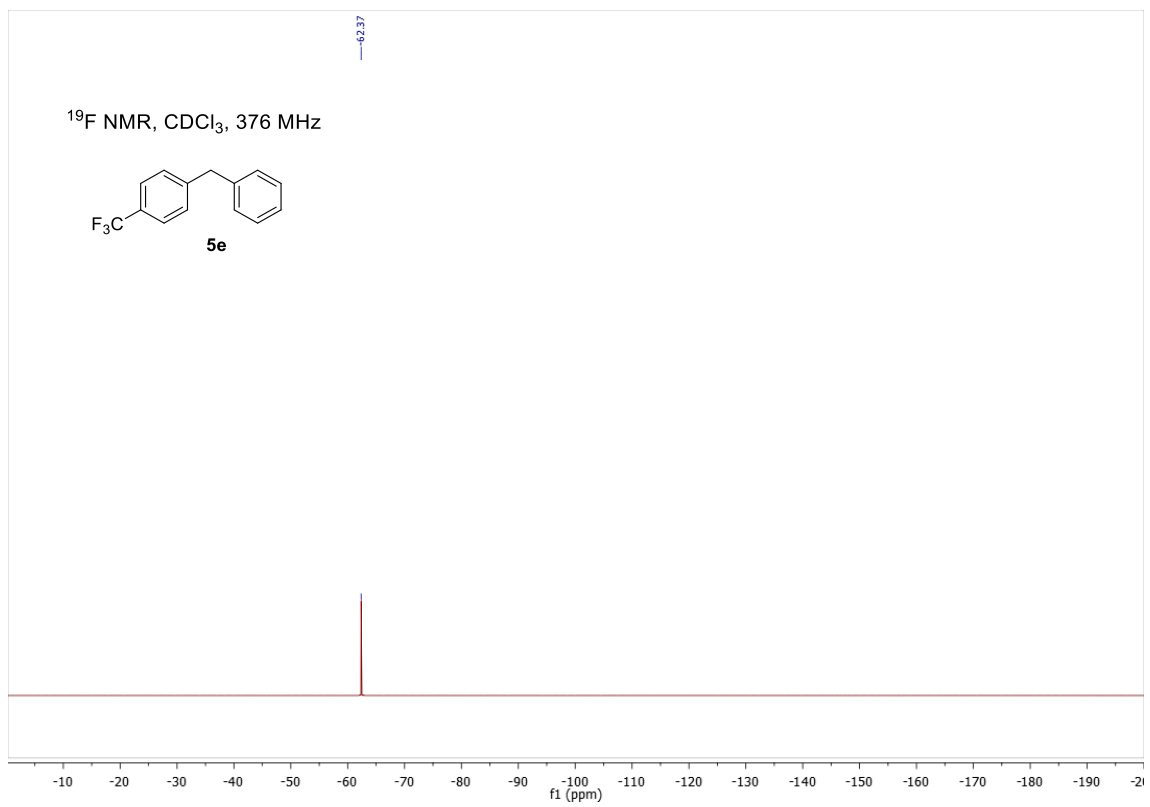
F. NMR spectral data

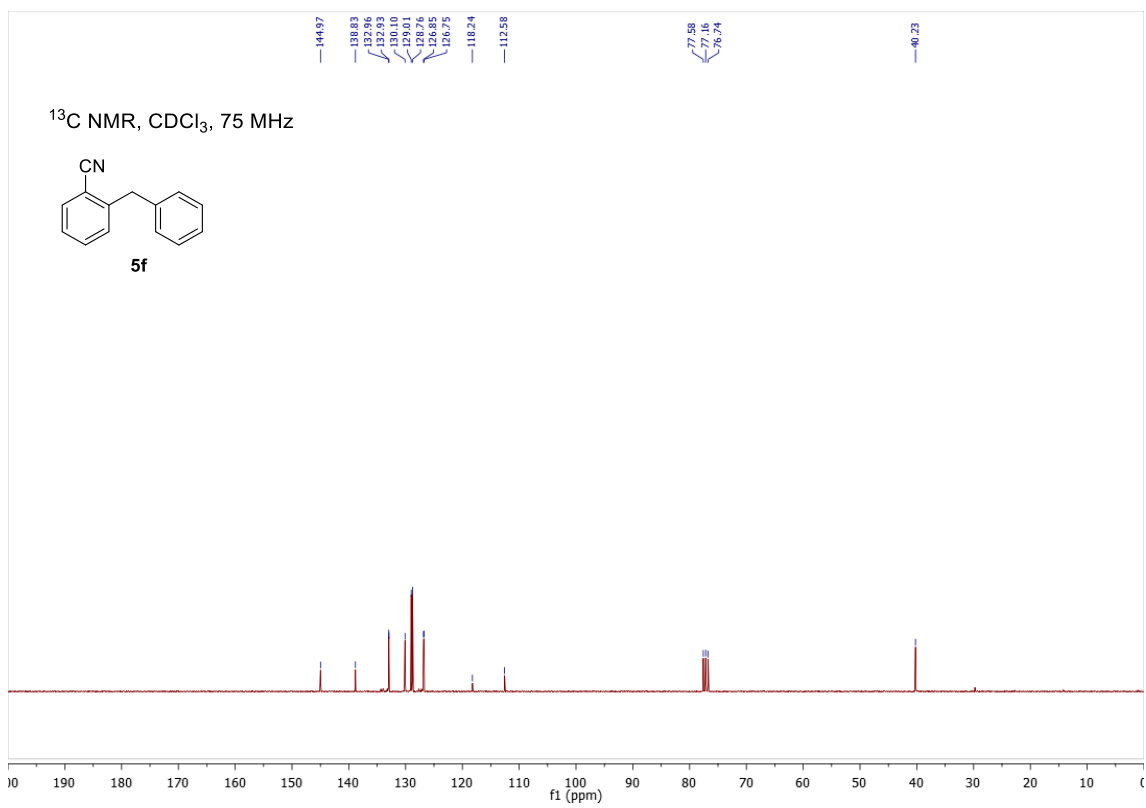
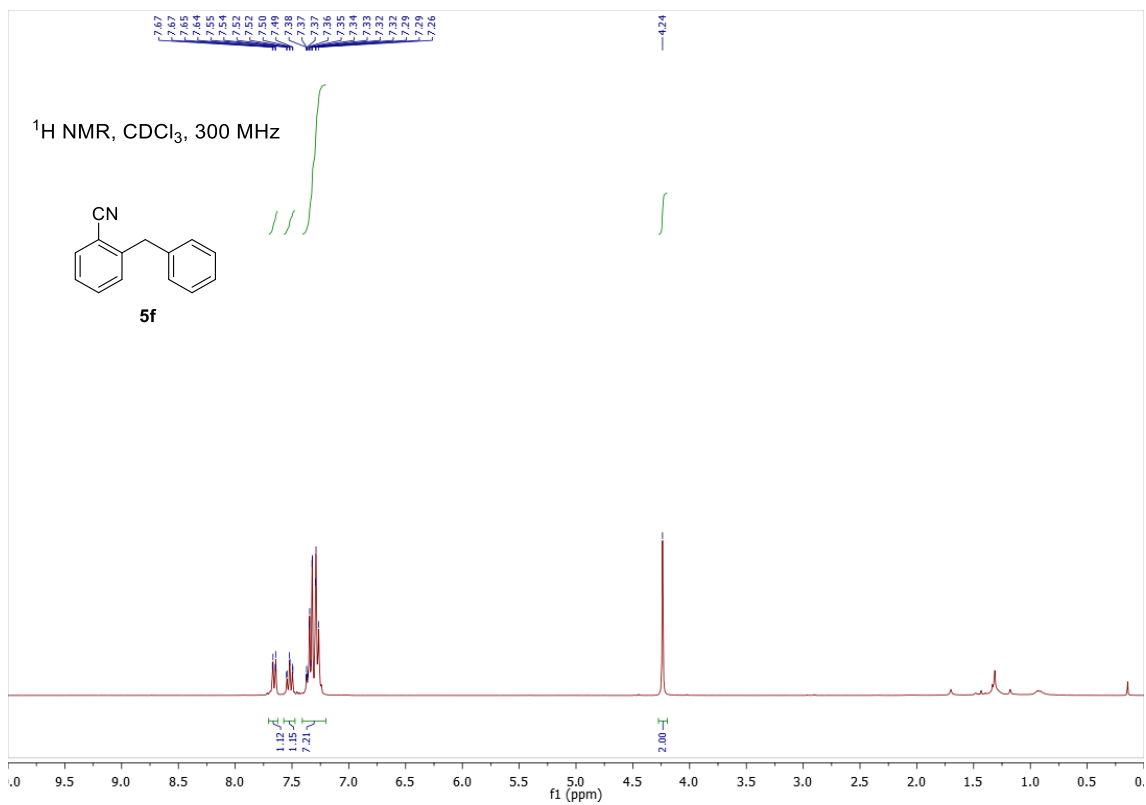


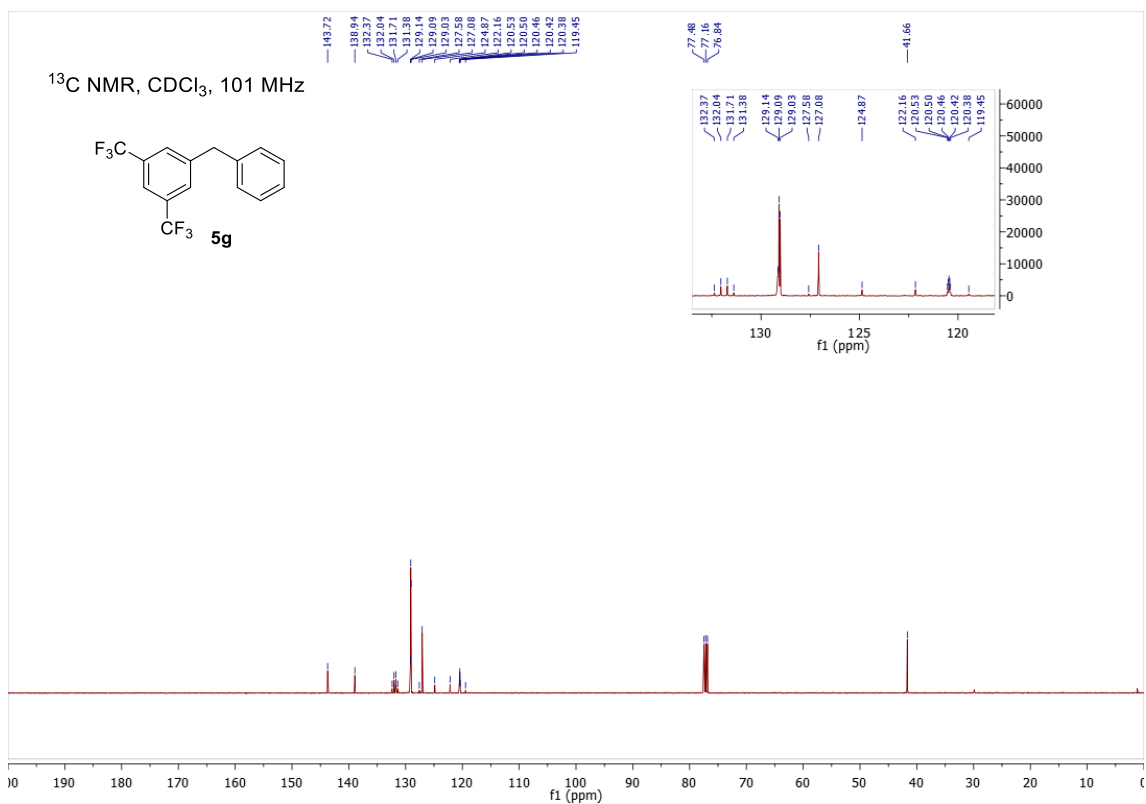
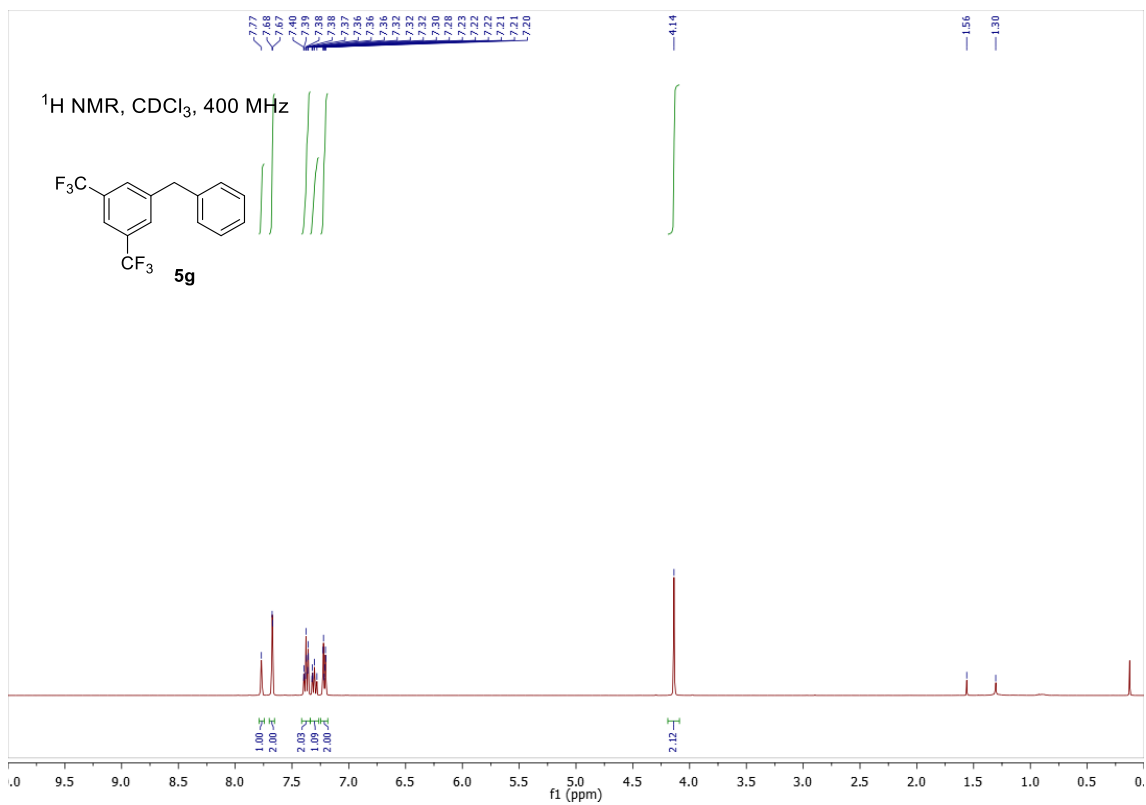




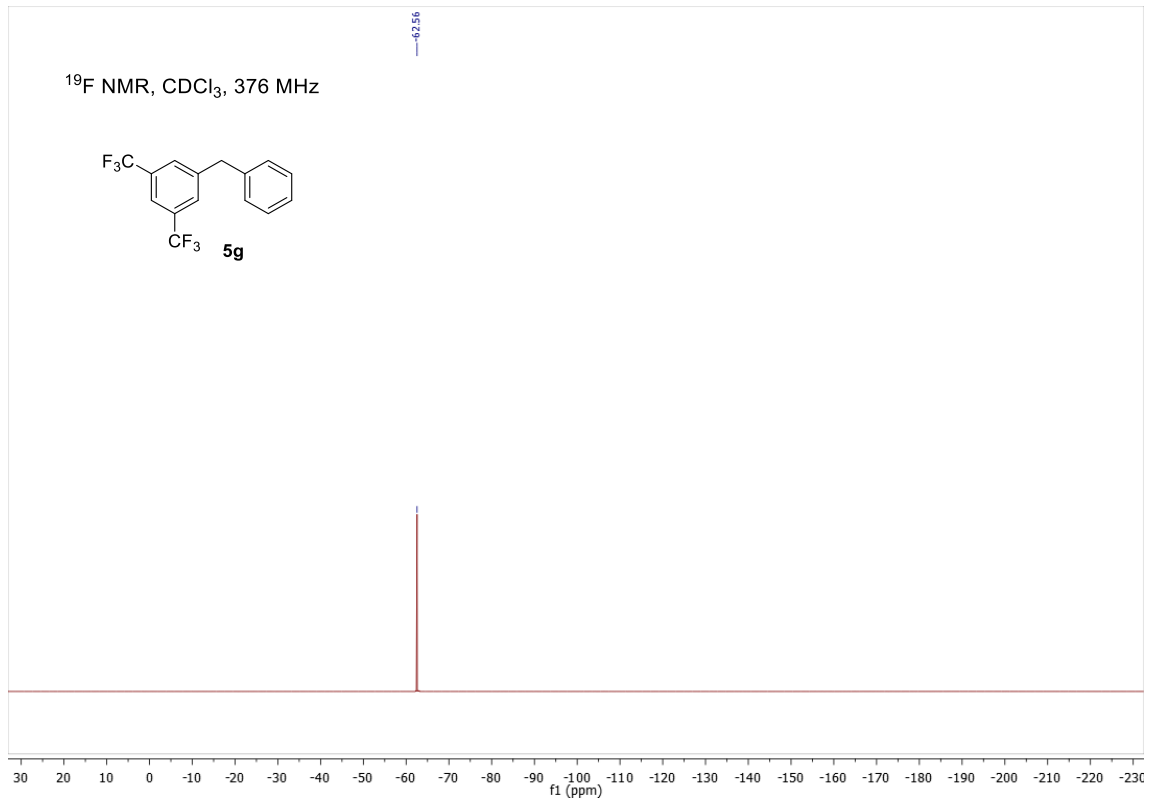
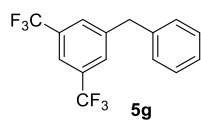


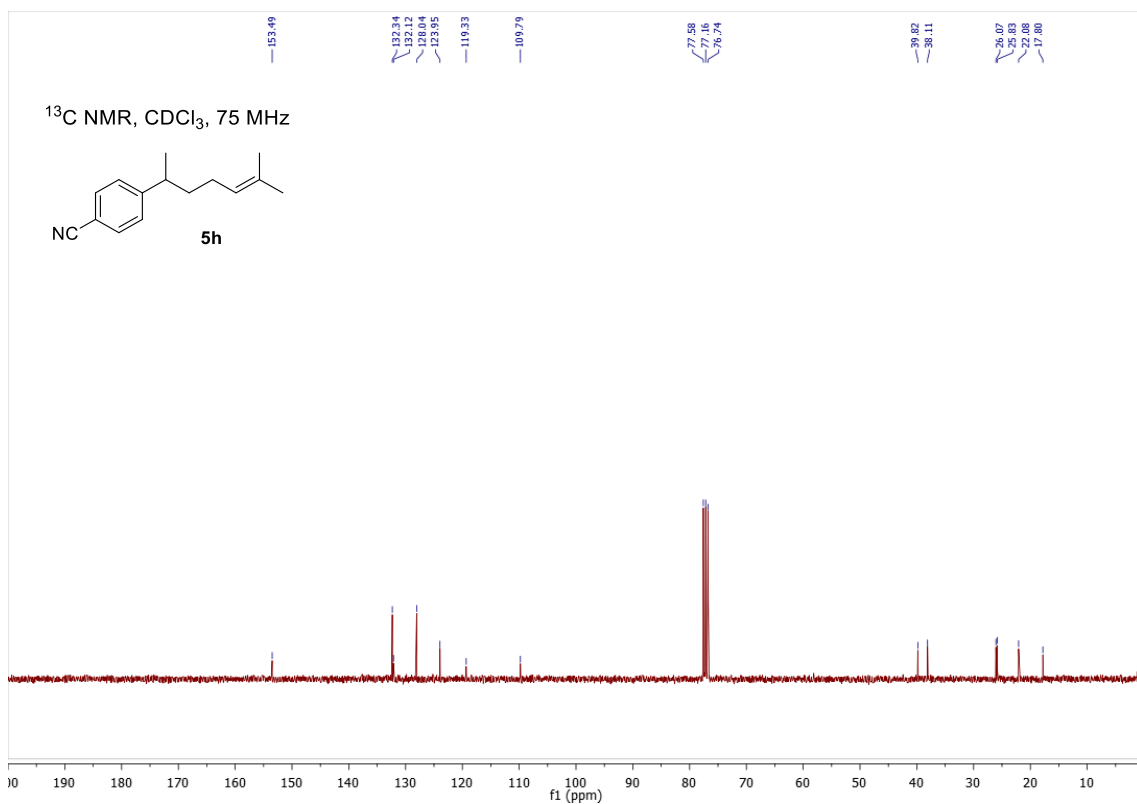
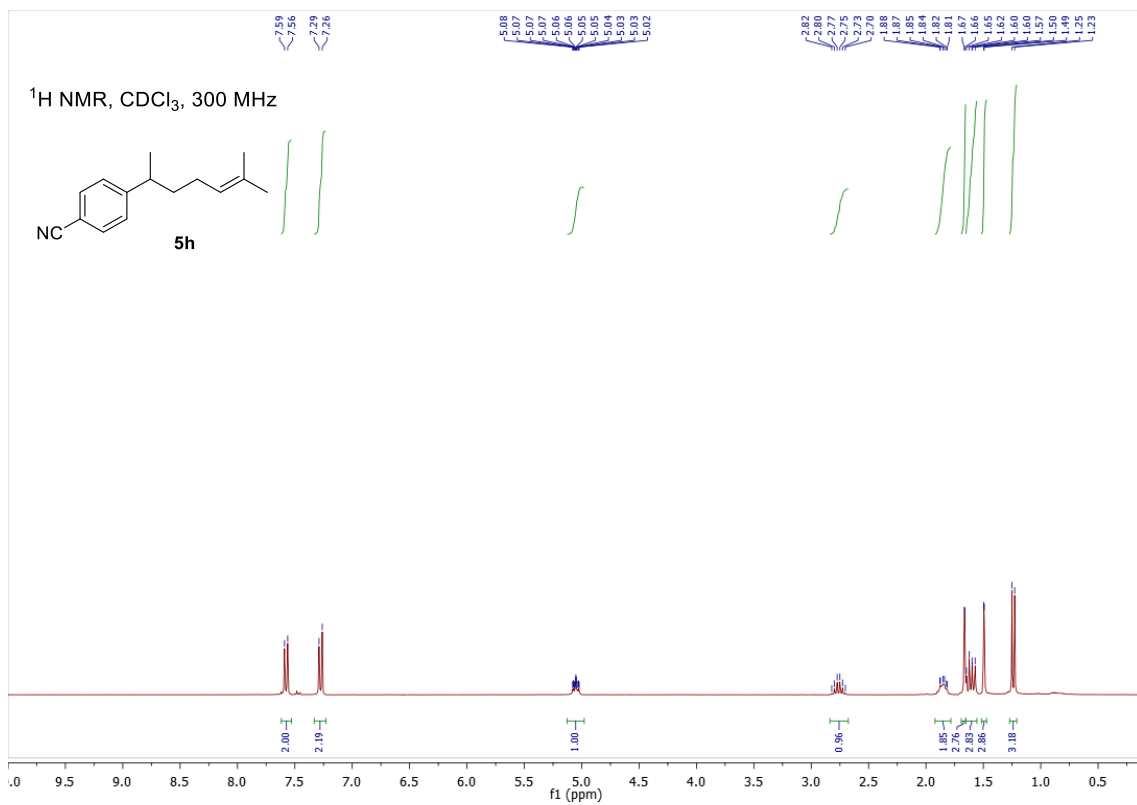


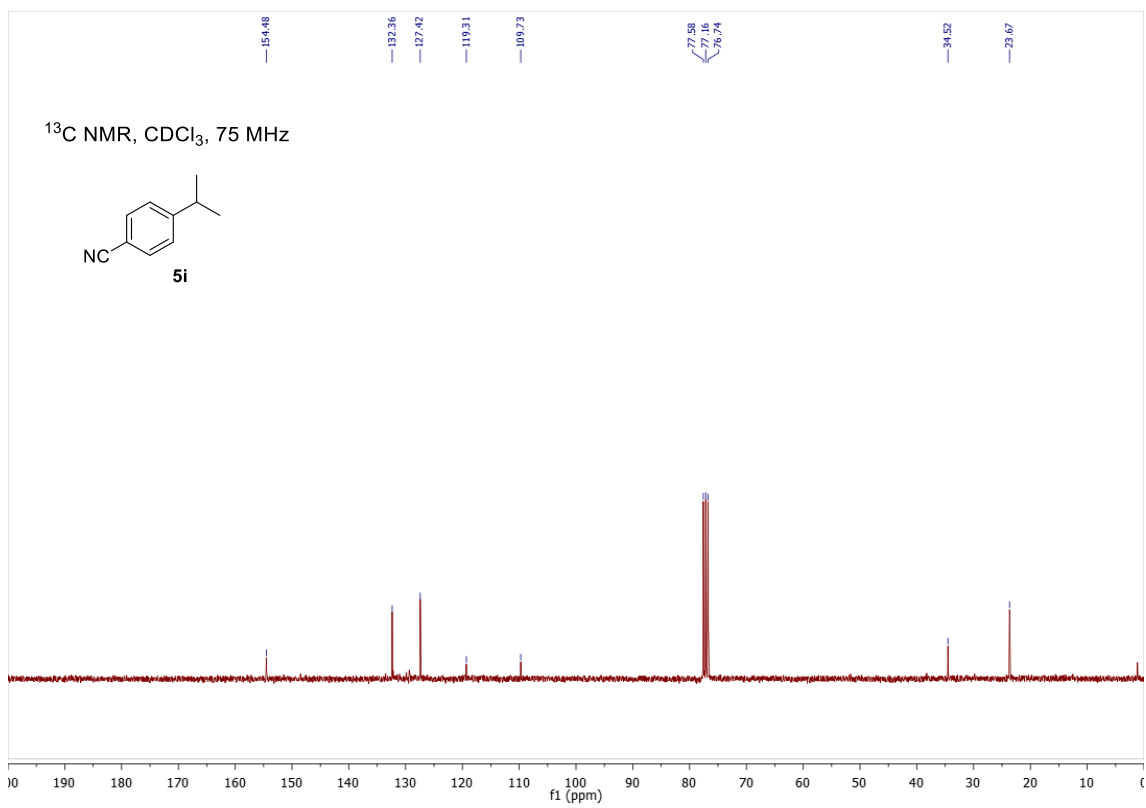
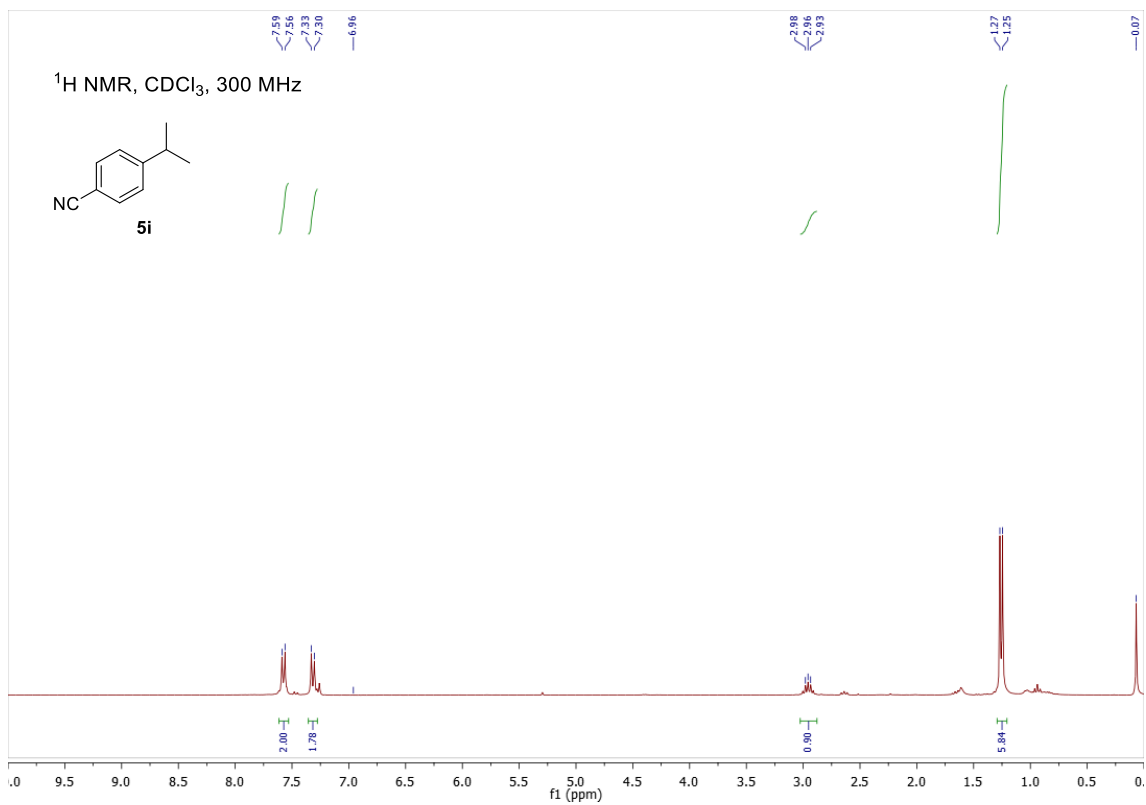


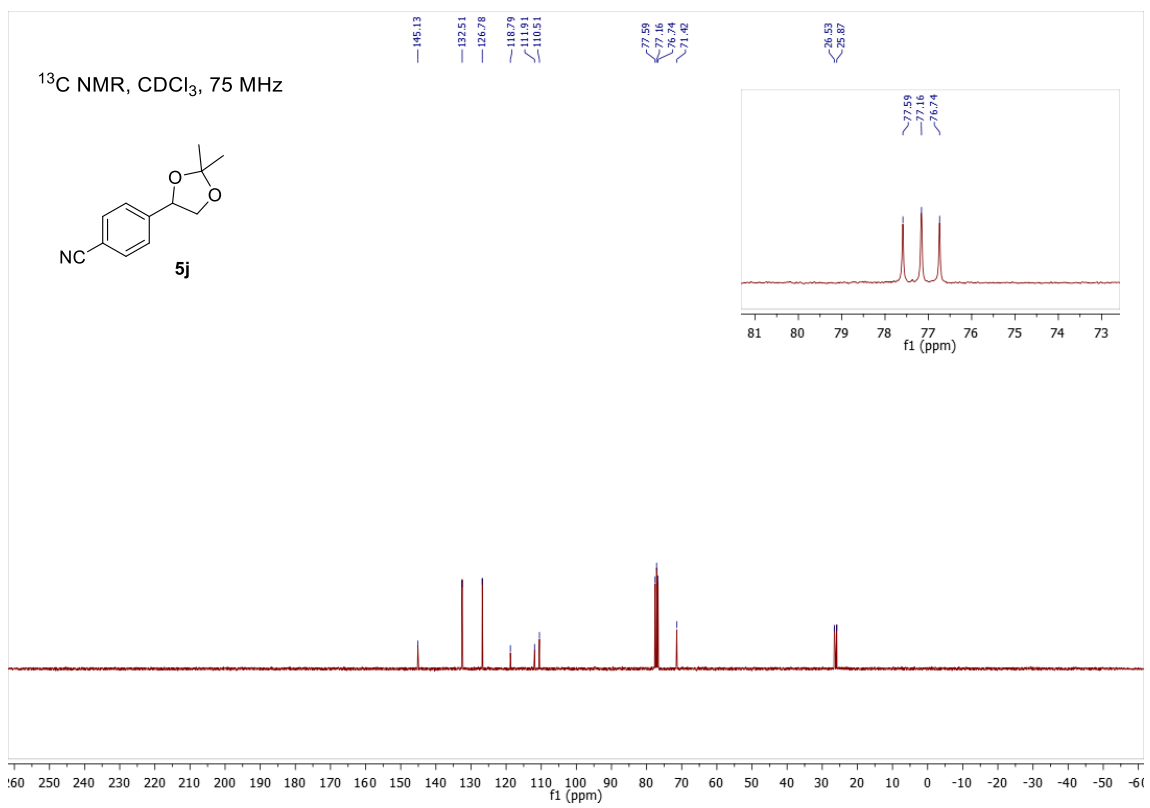
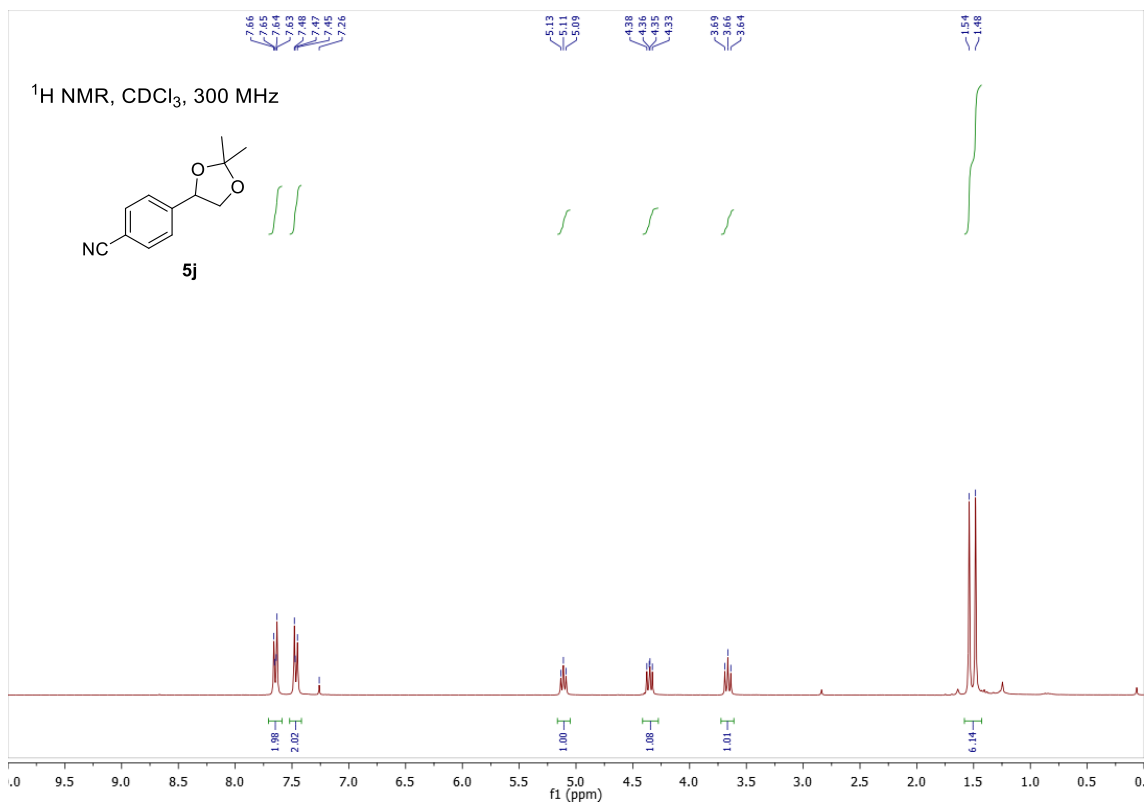


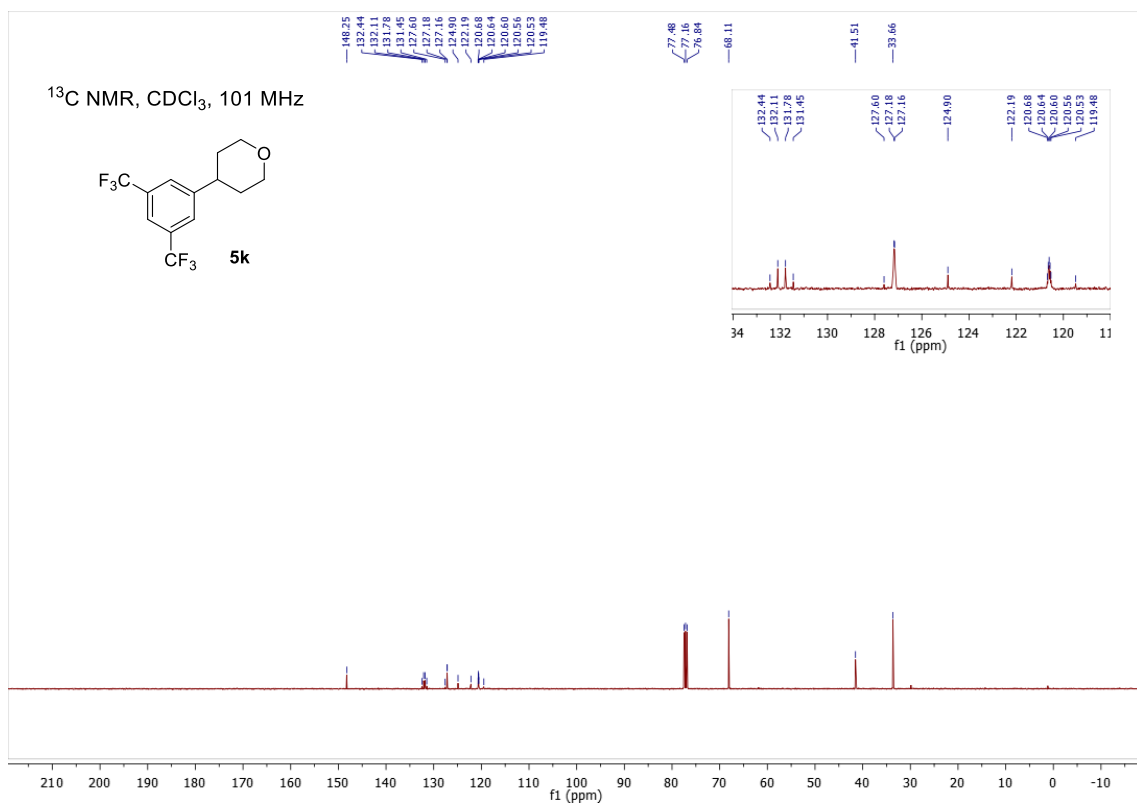
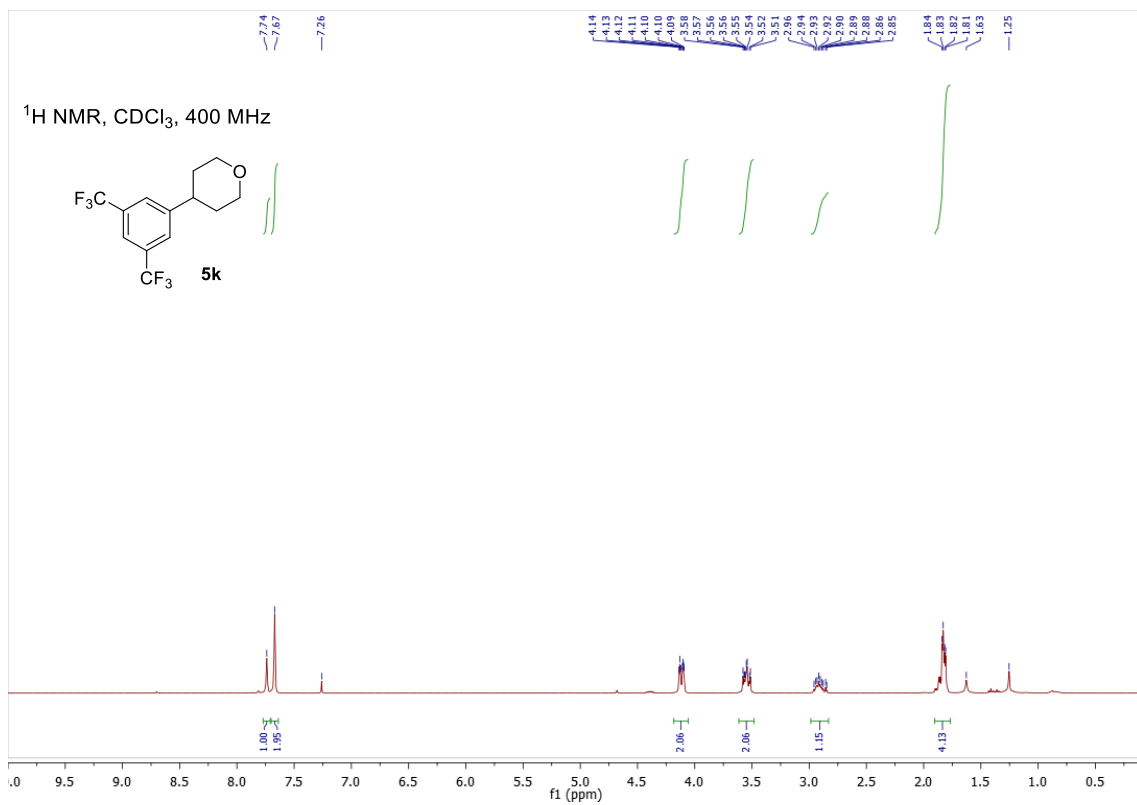
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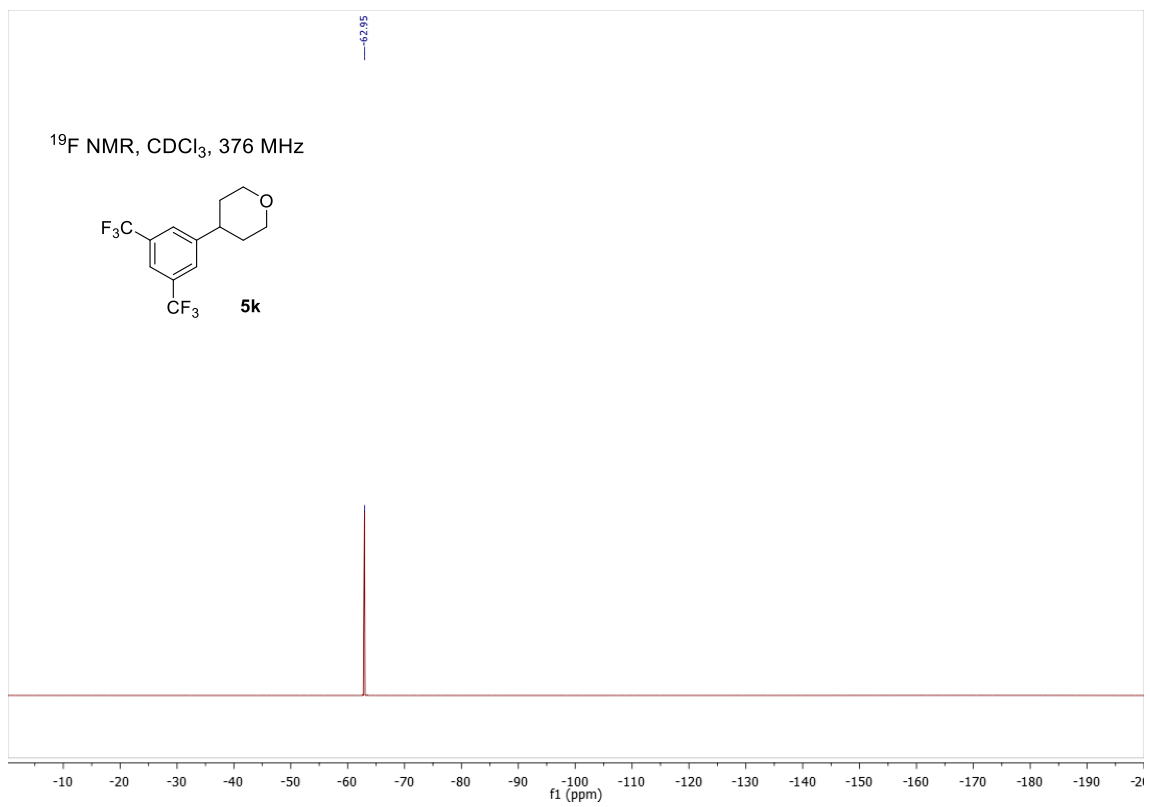


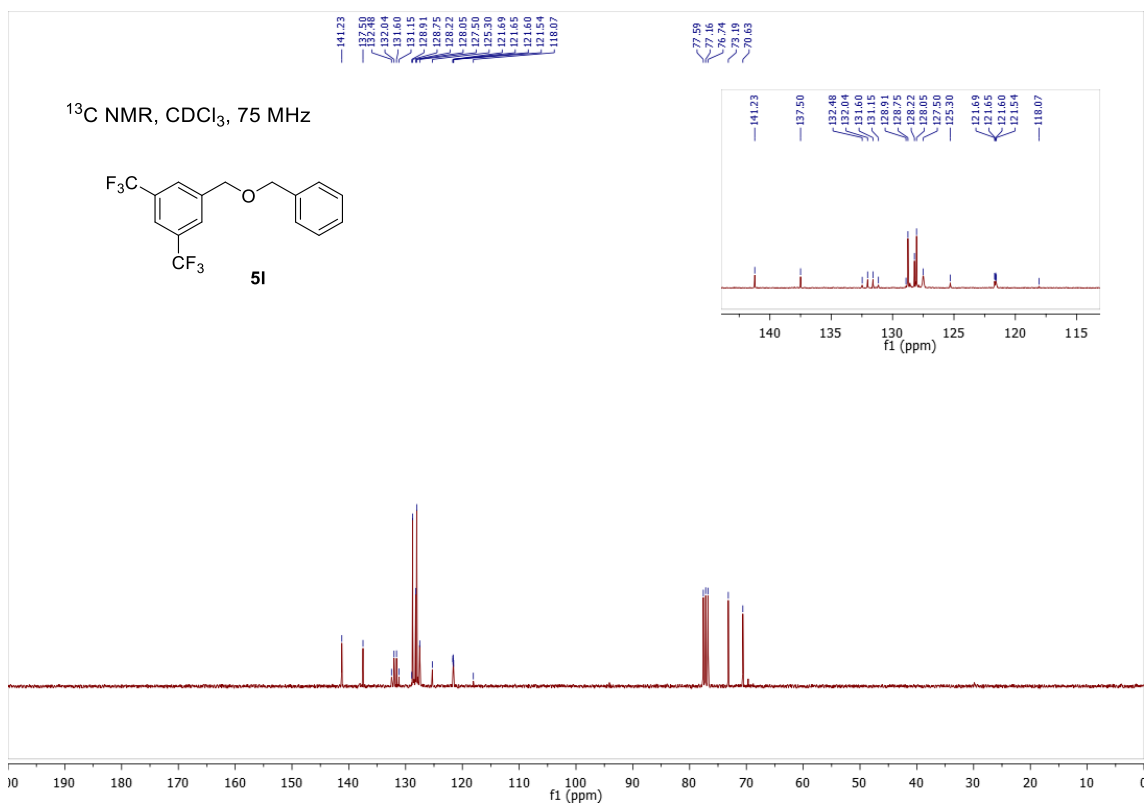
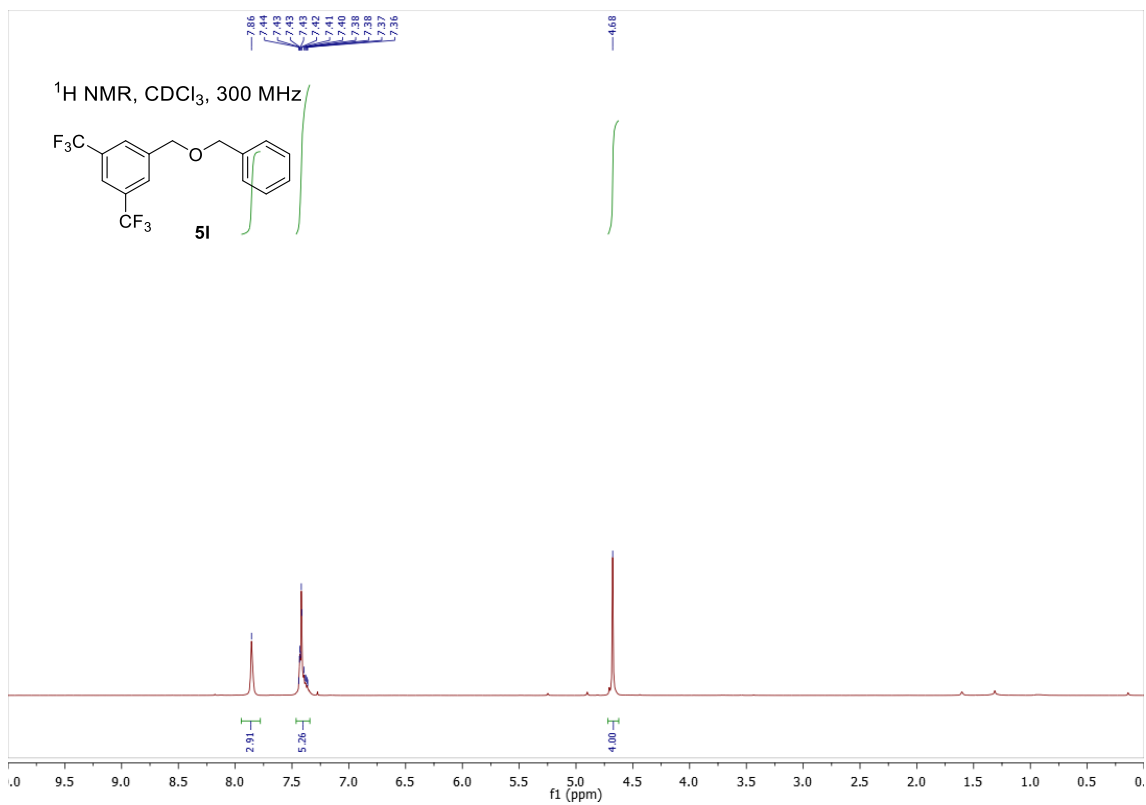


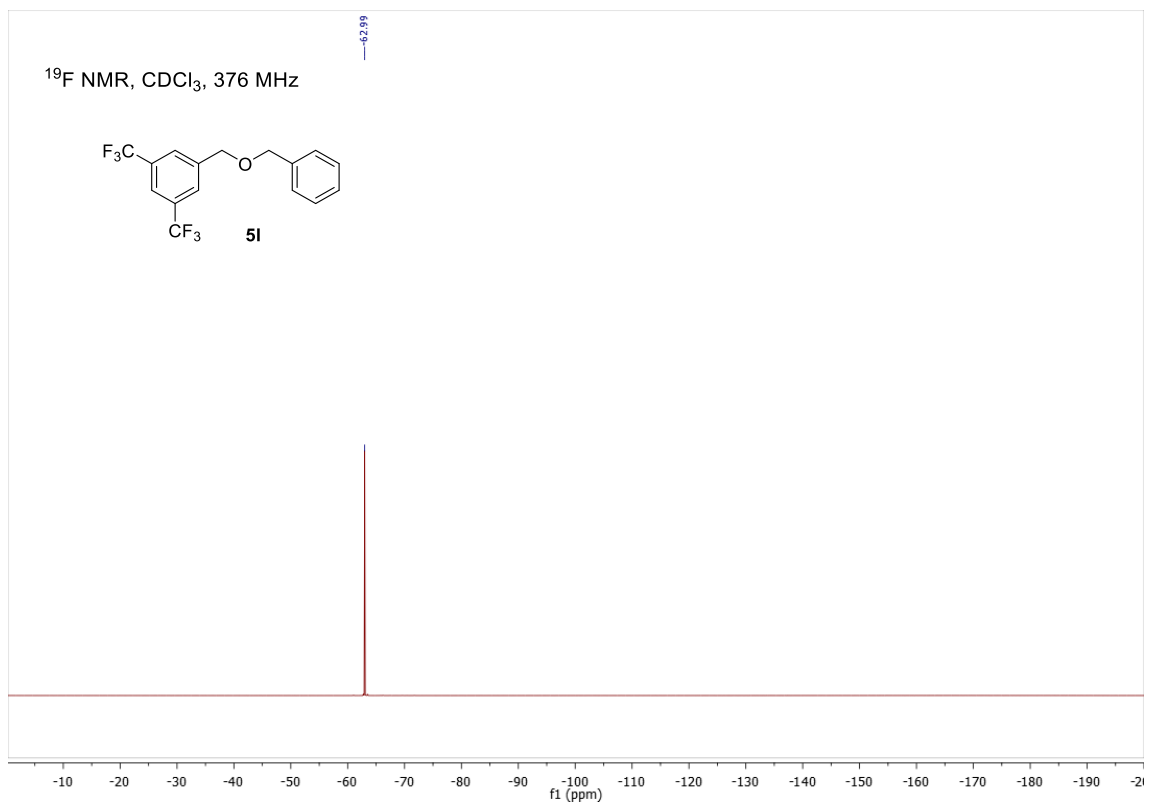


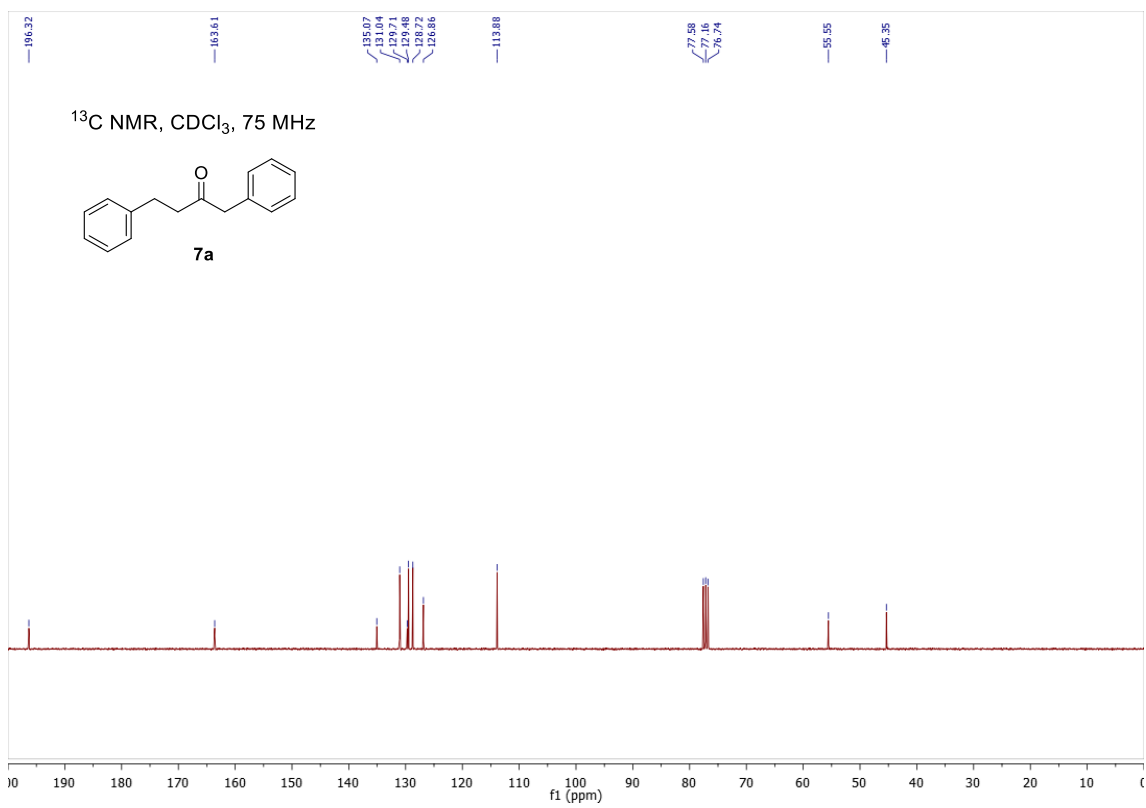
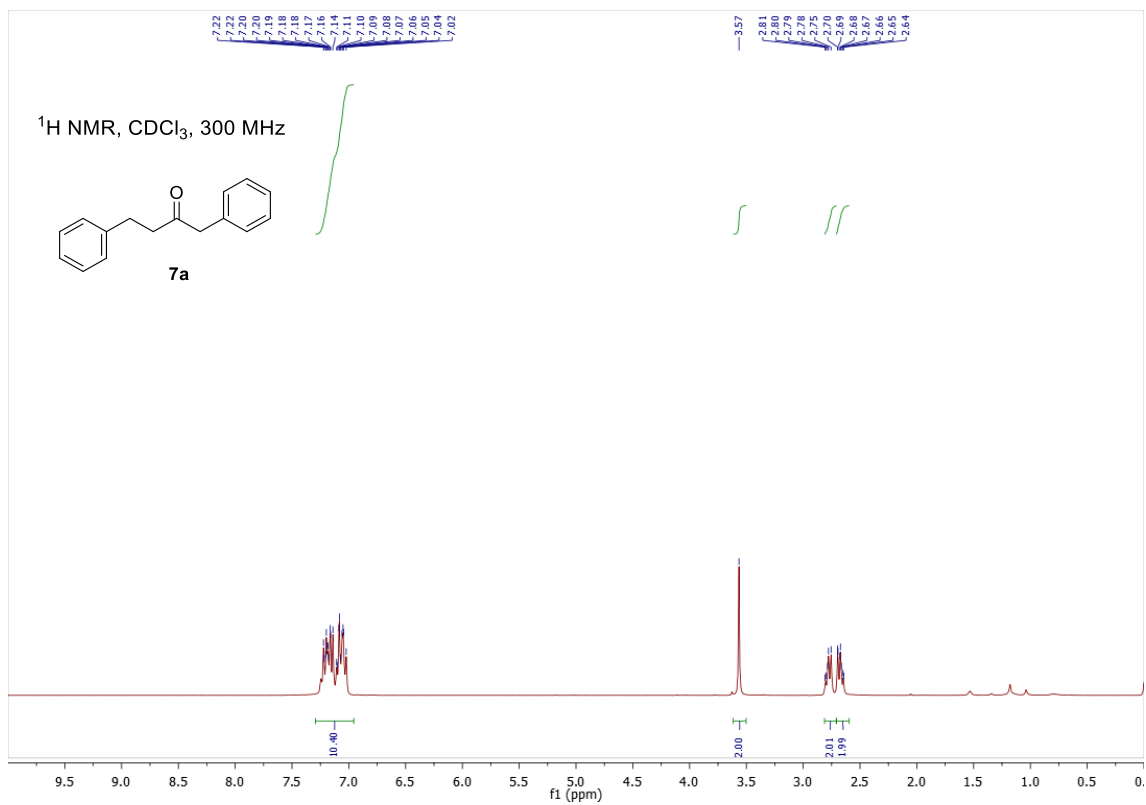




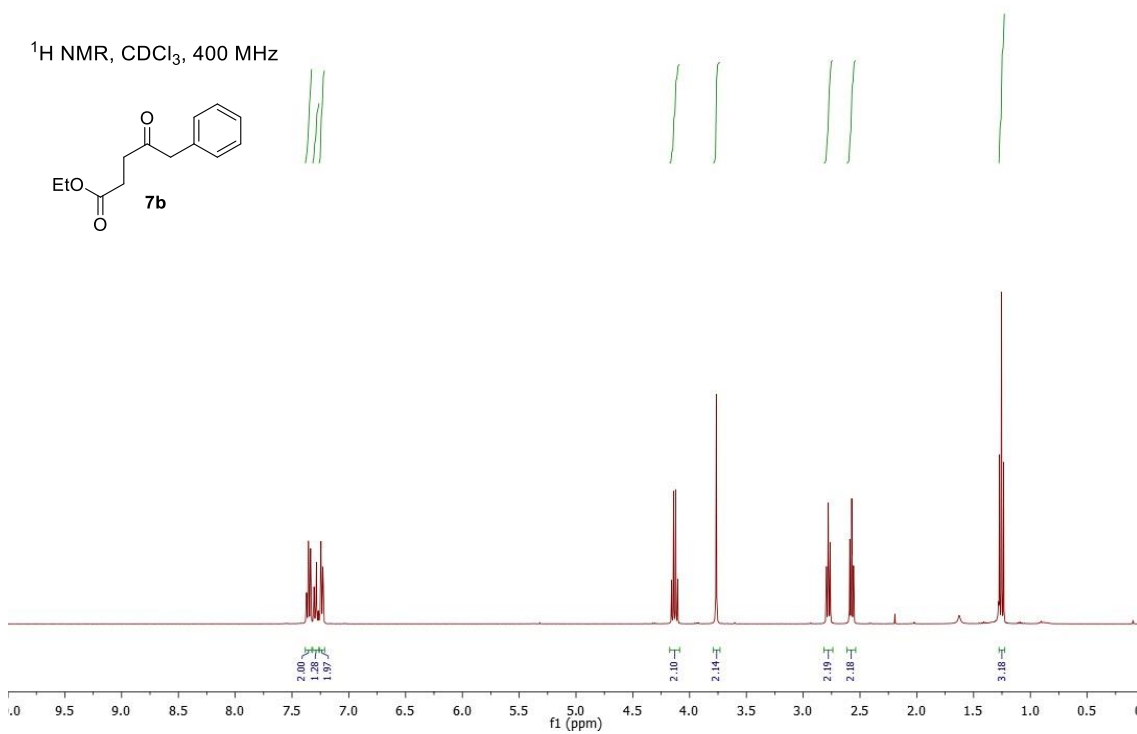
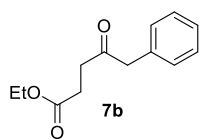




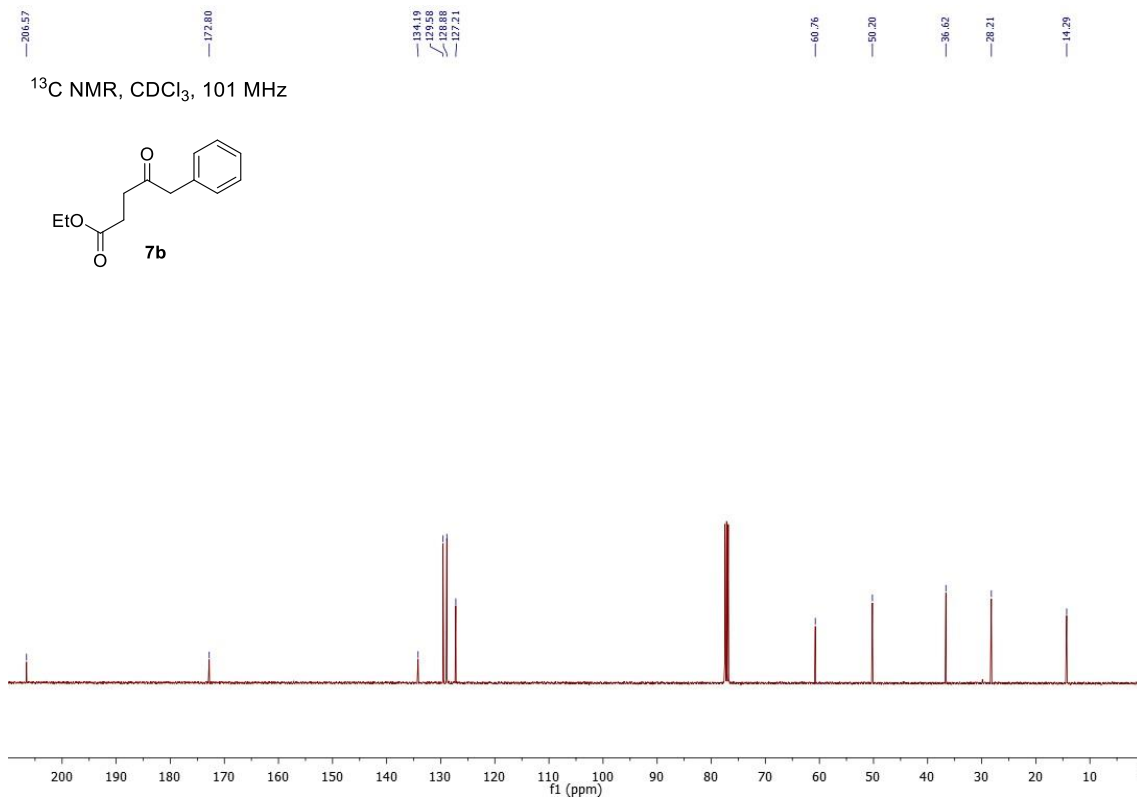
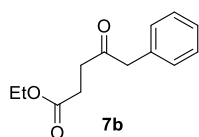


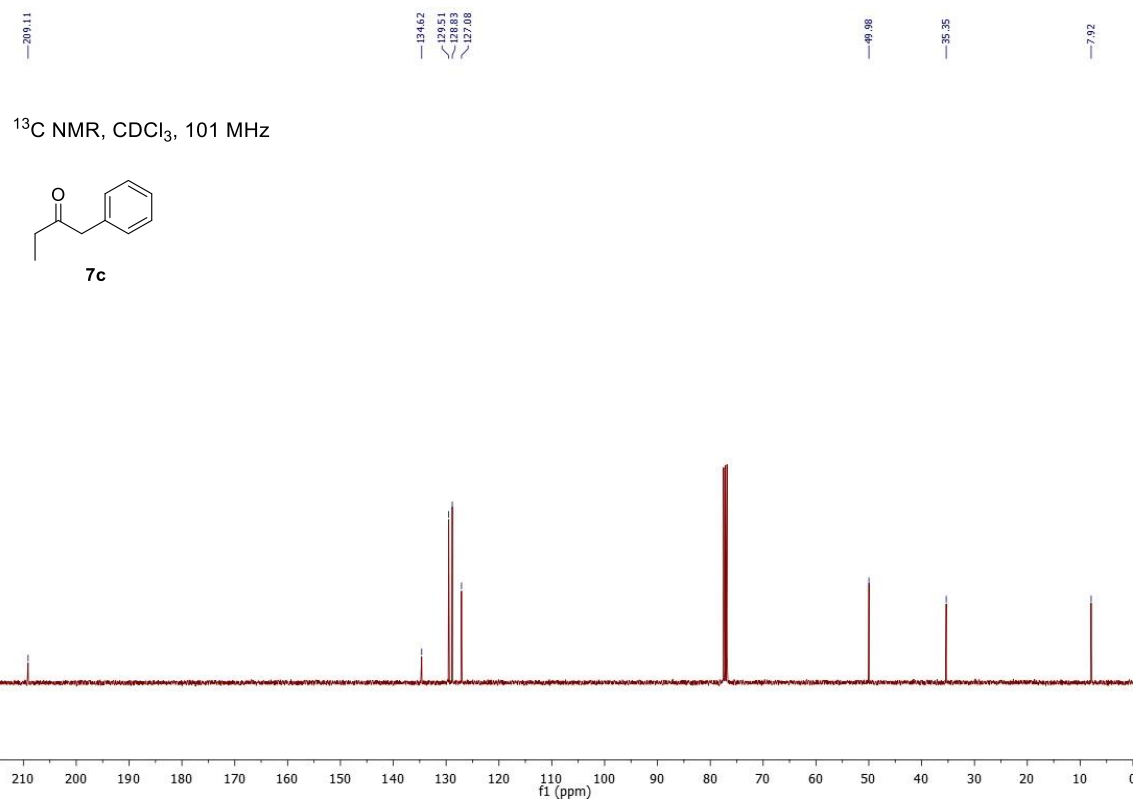
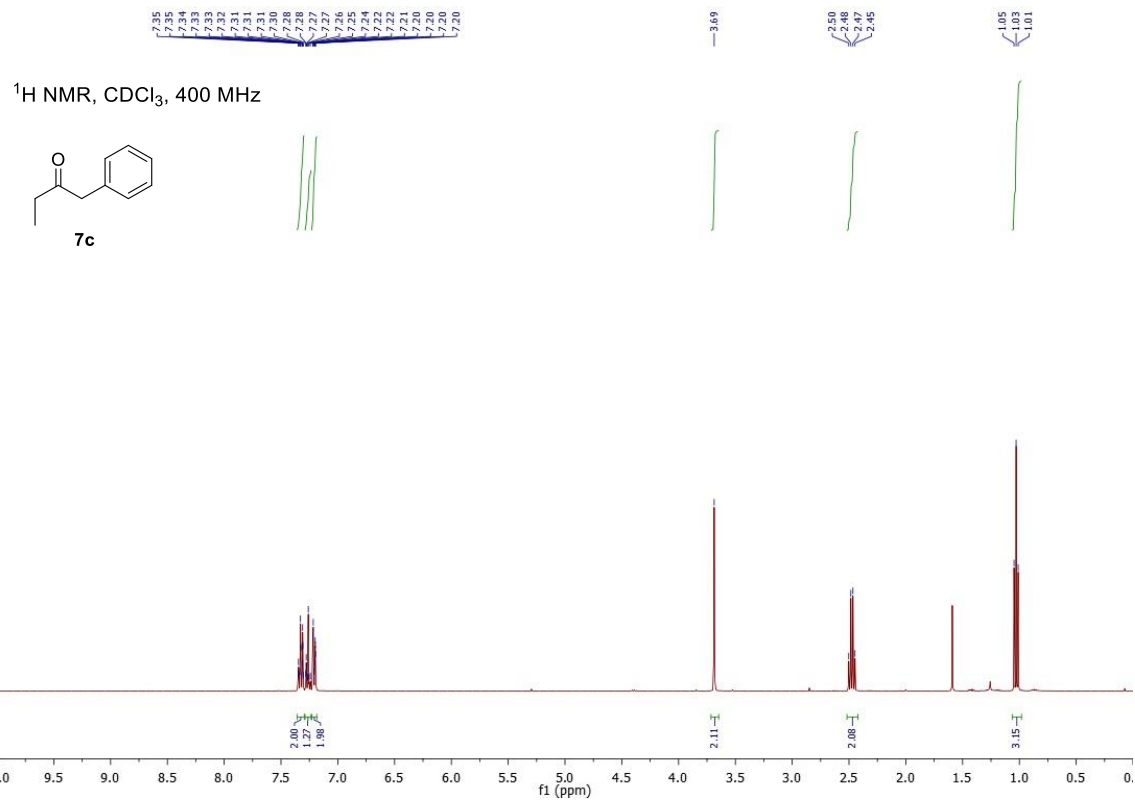


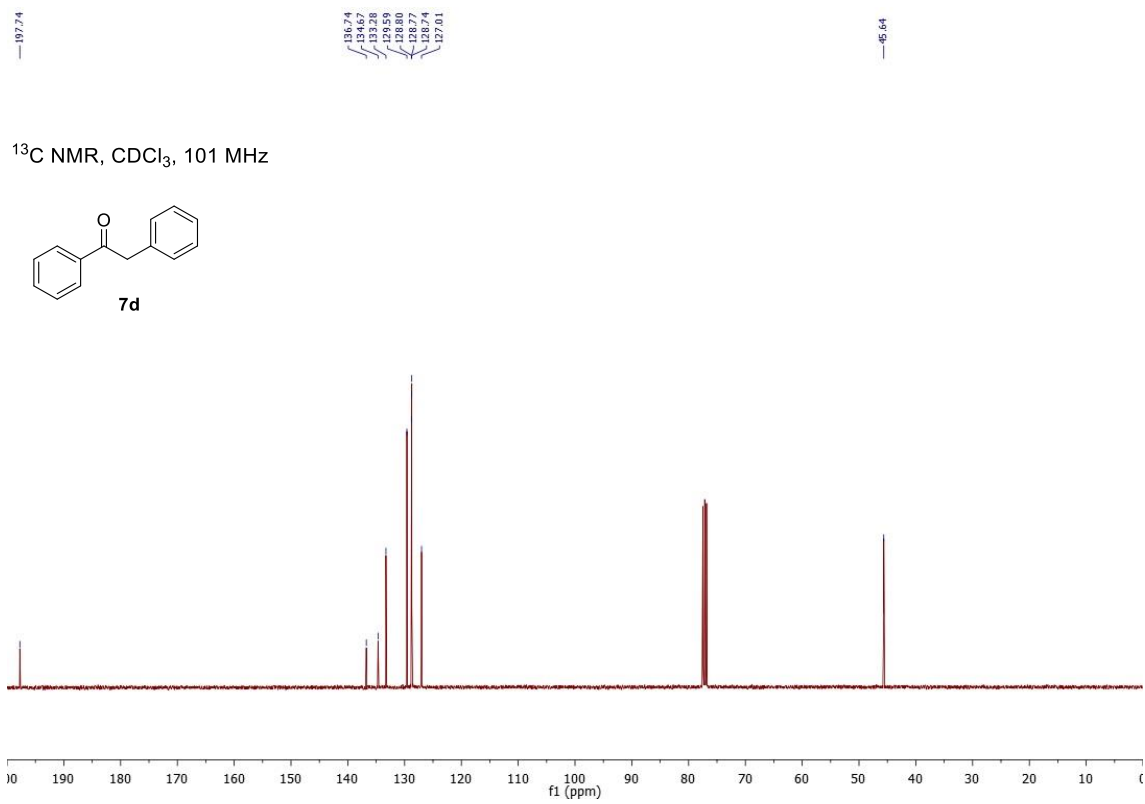
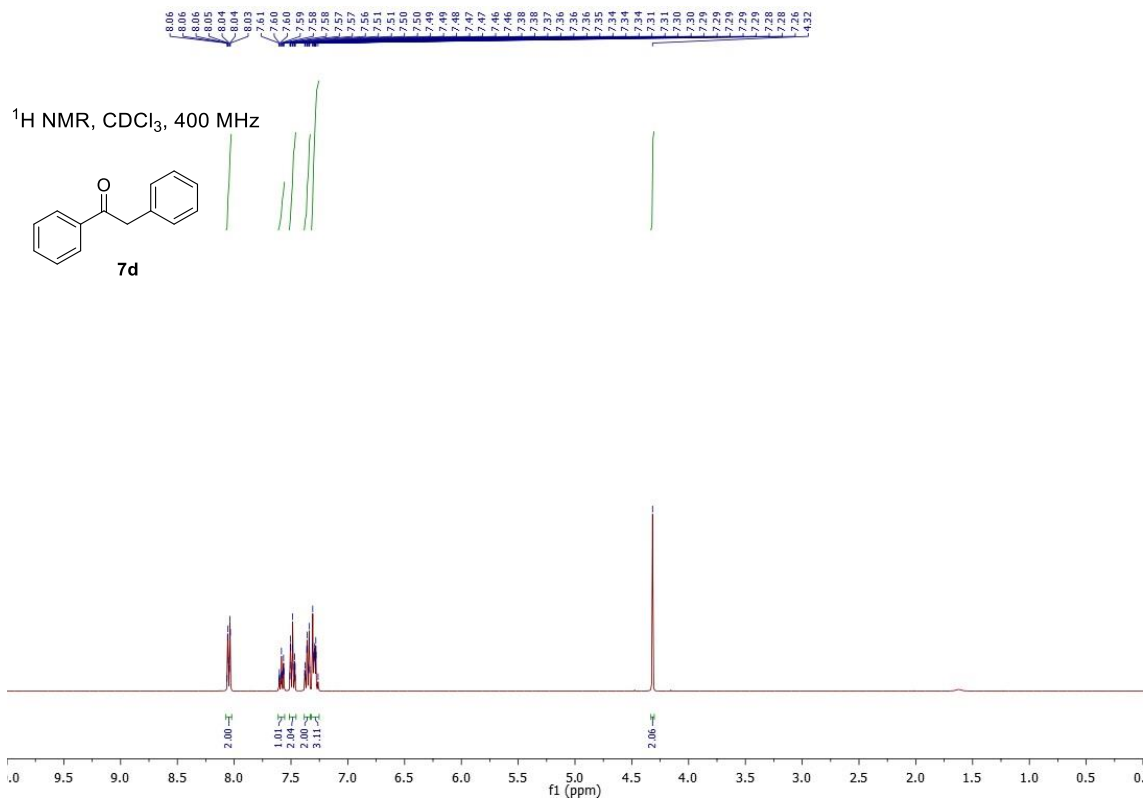
¹H NMR, CDCl₃, 400 MHz

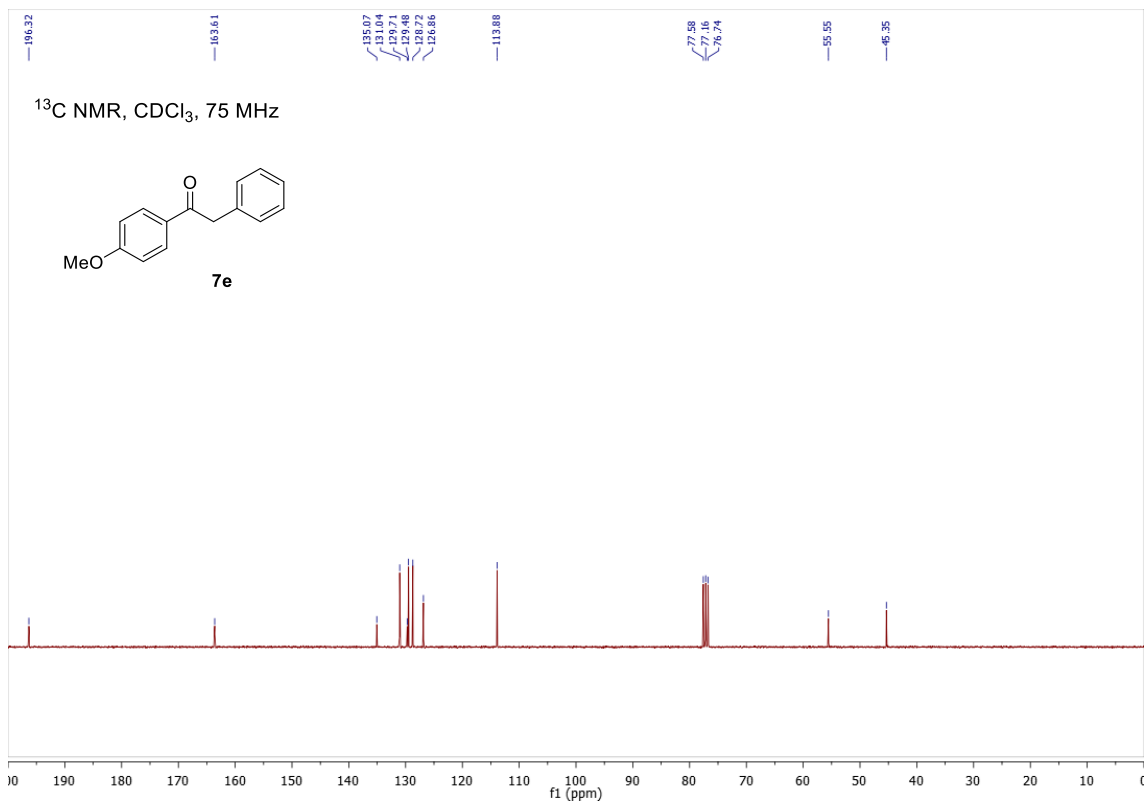
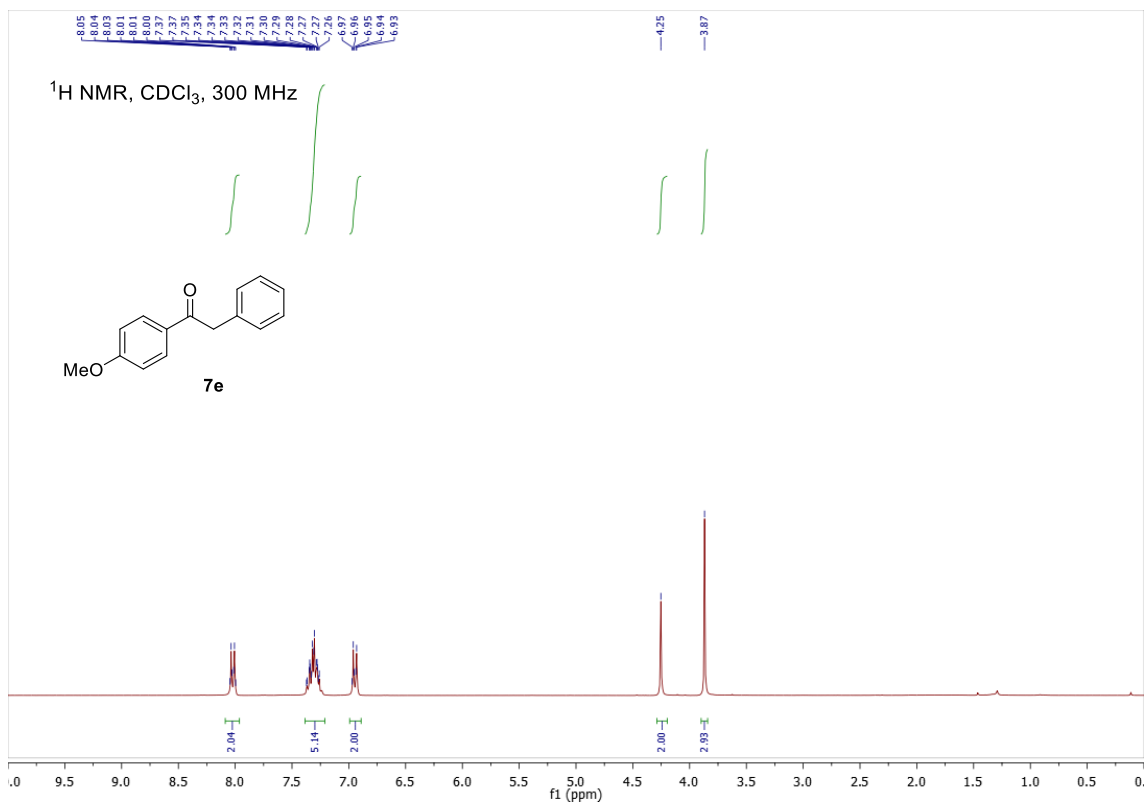


¹³C NMR, CDCl₃, 101 MHz

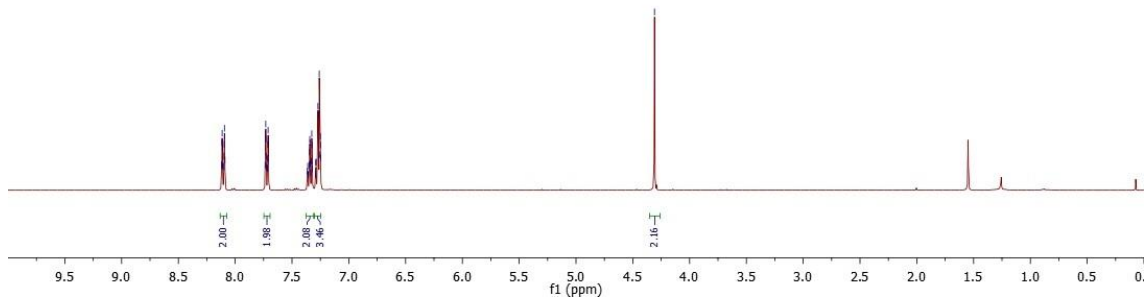
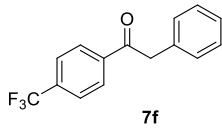




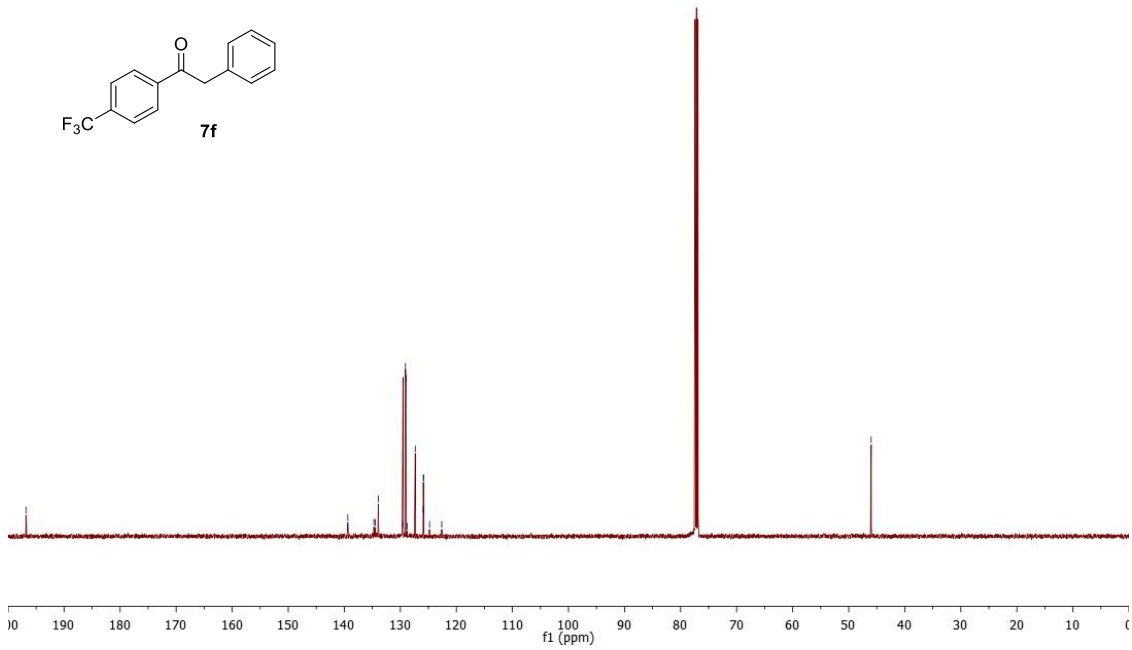
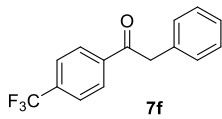




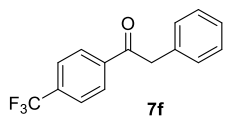
¹H NMR, CDCl₃, 400 MHz



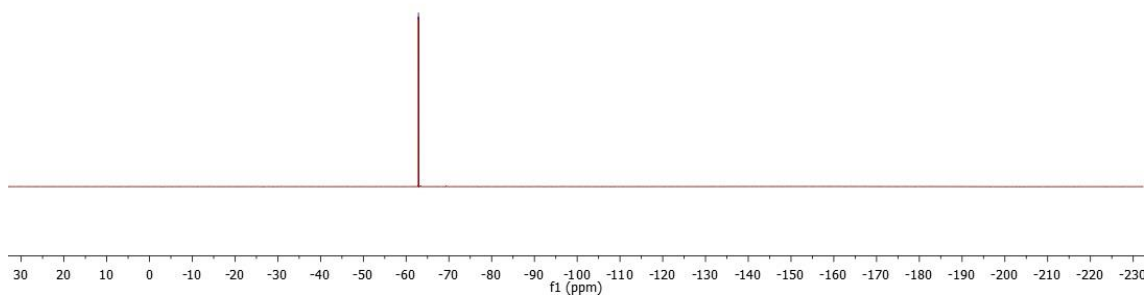
¹³C NMR, CDCl₃, 126 MHz



^{19}F NMR, CDCl_3 , 376 MHz

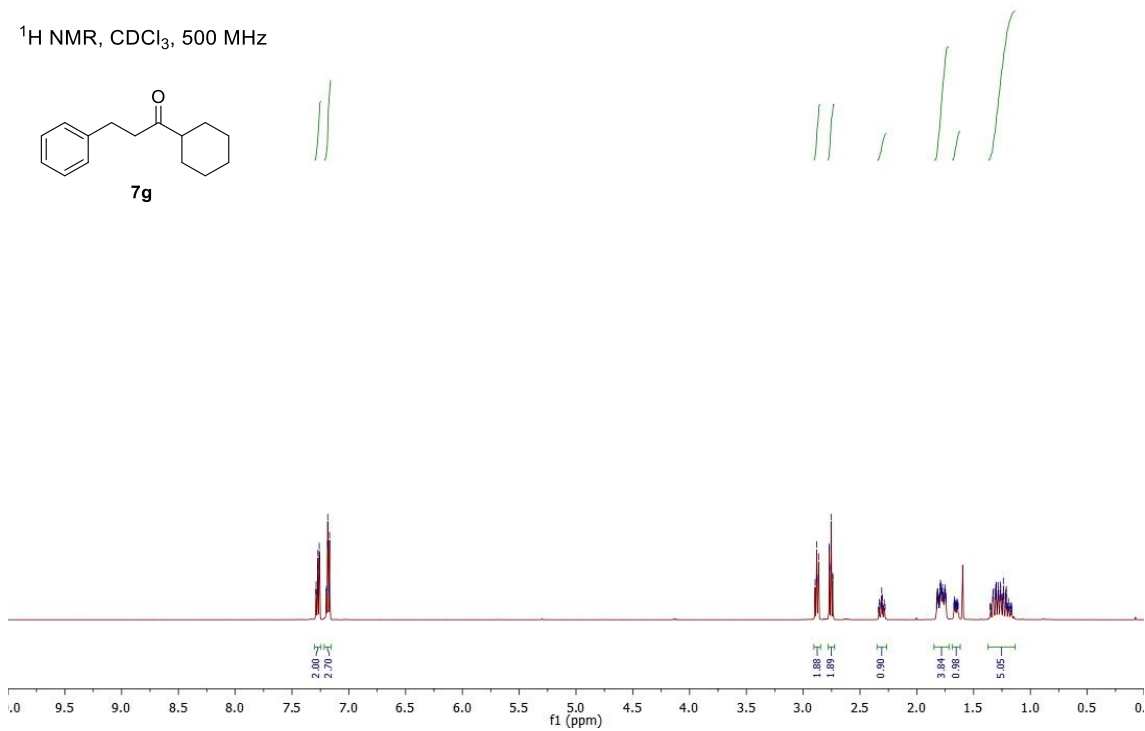
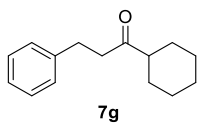


-62.88



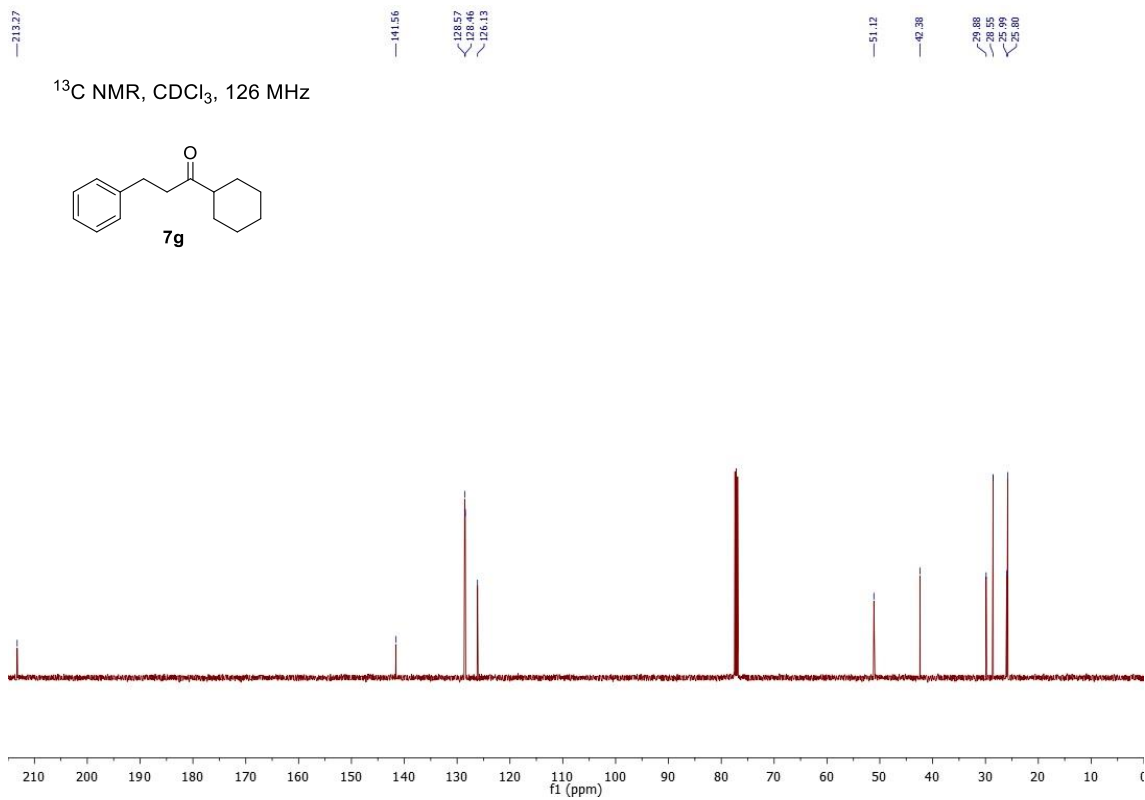
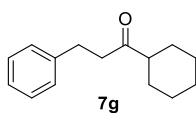
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$^1\text{H NMR}$, CDCl_3 , 500 MHz



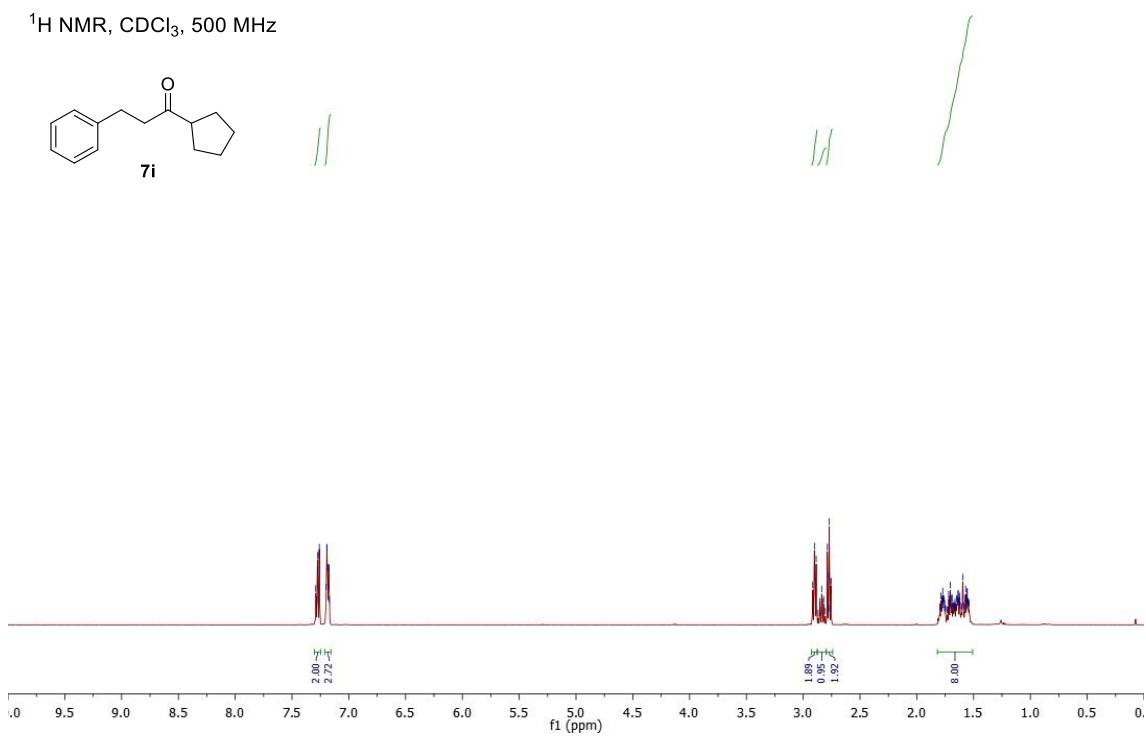
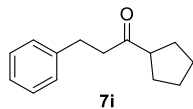
213.27

$^{13}\text{C NMR}$, CDCl_3 , 126 MHz



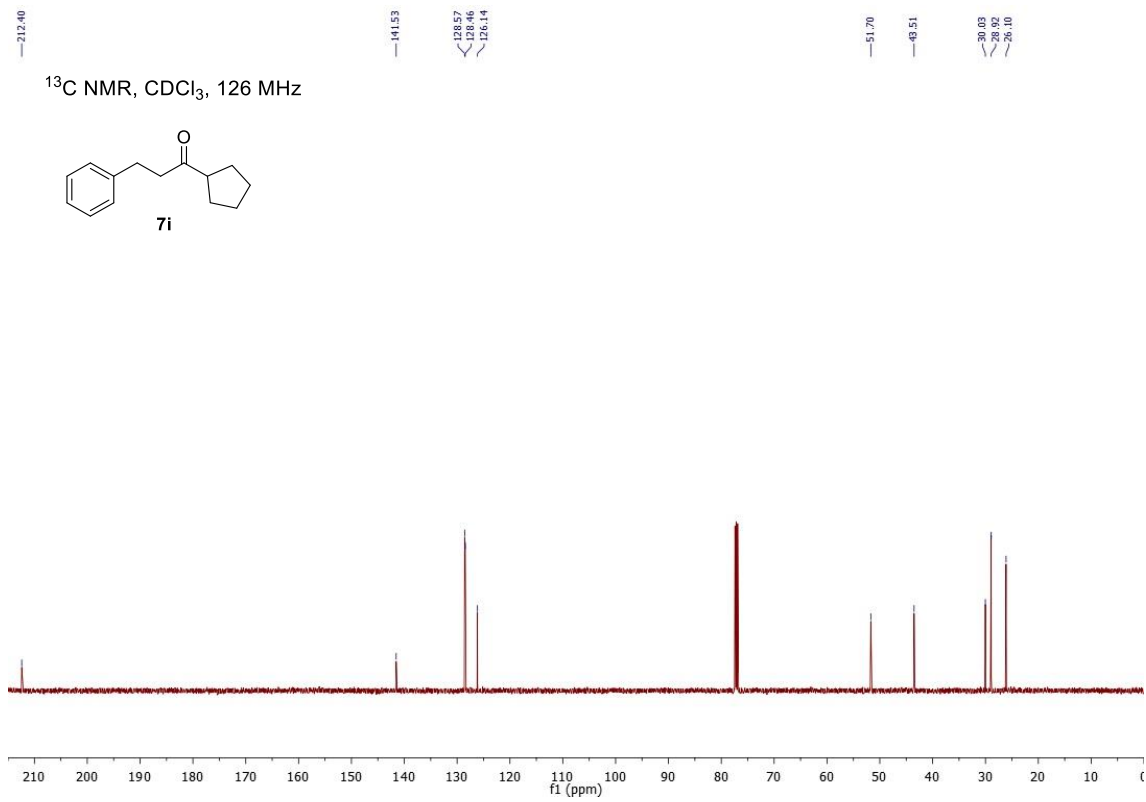
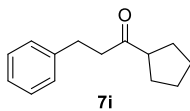
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¹H NMR, CDCl₃, 500 MHz

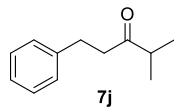


212.40

¹³C NMR, CDCl₃, 126 MHz



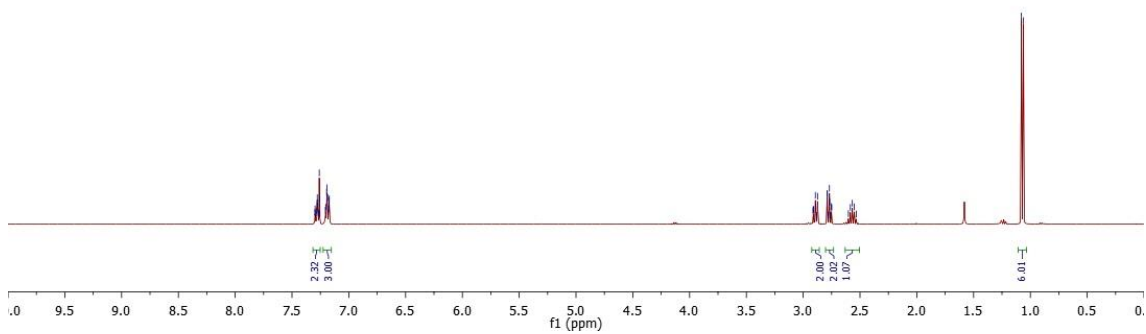
¹H NMR, CDCl₃, 400 MHz



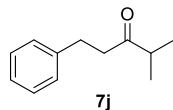
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¹³C NMR, CDCl₃, 101 MHz



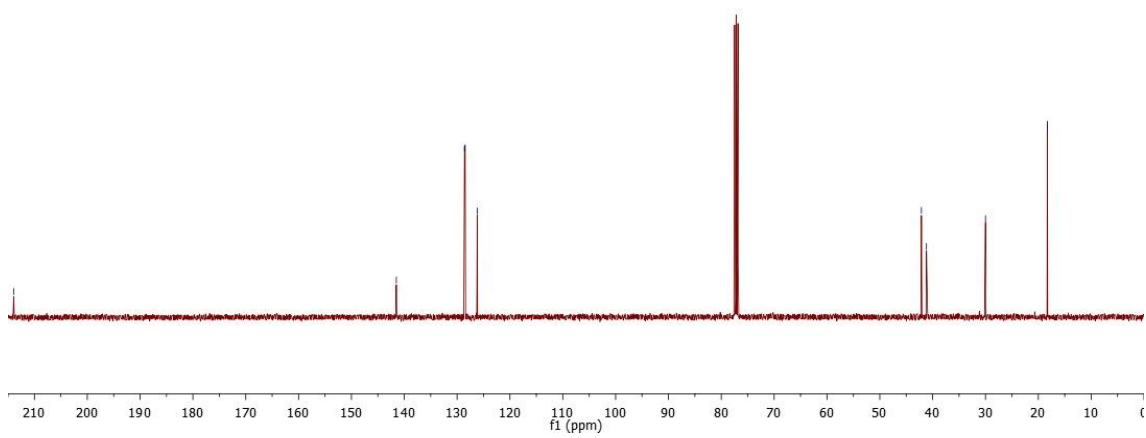
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41.17

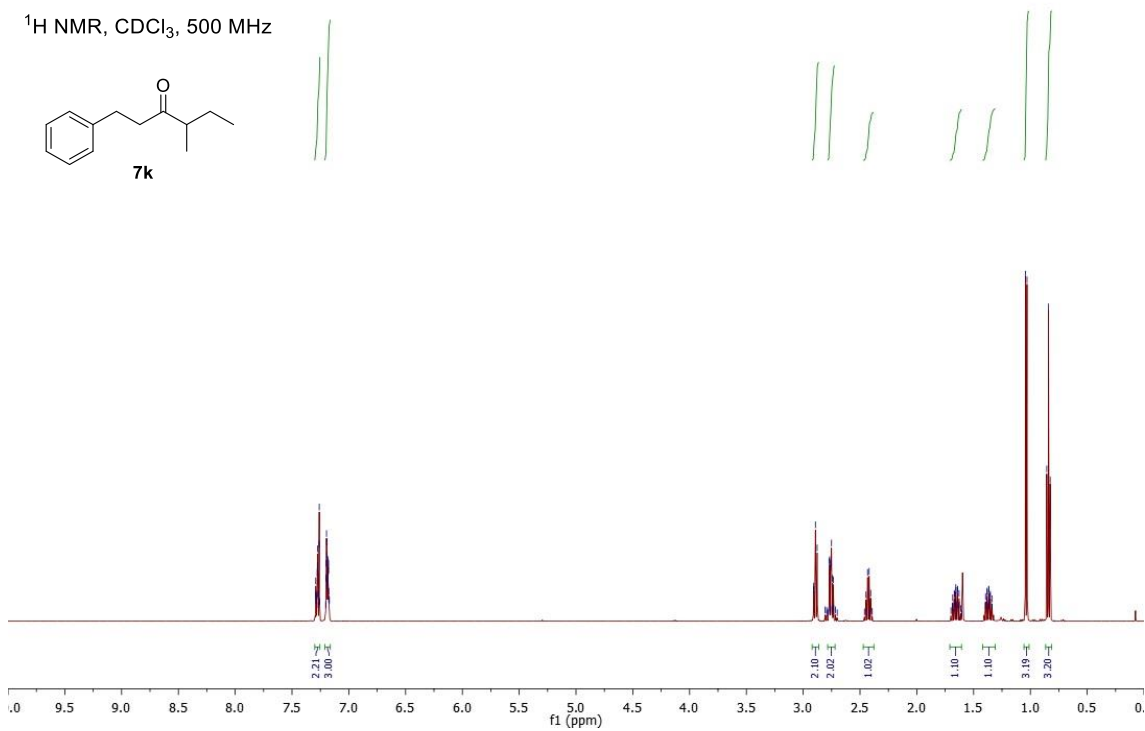
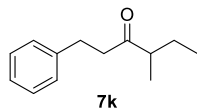
30.00

18.28

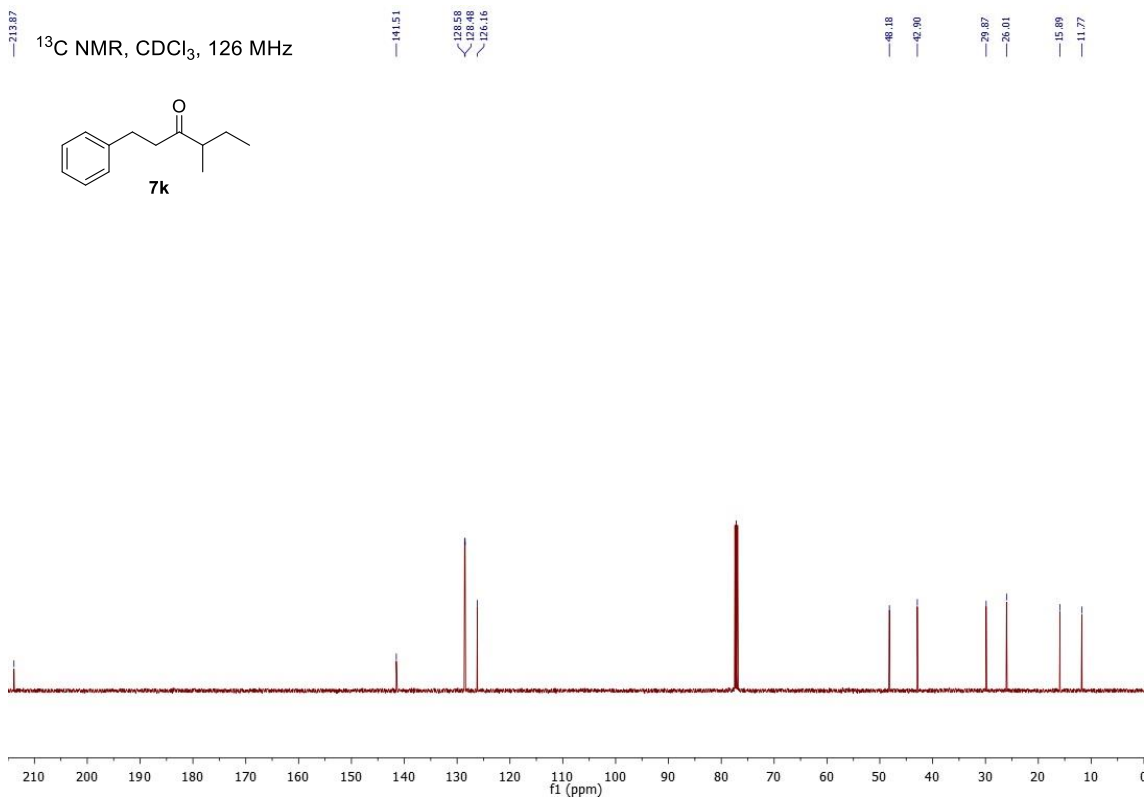
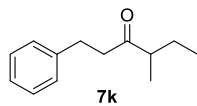


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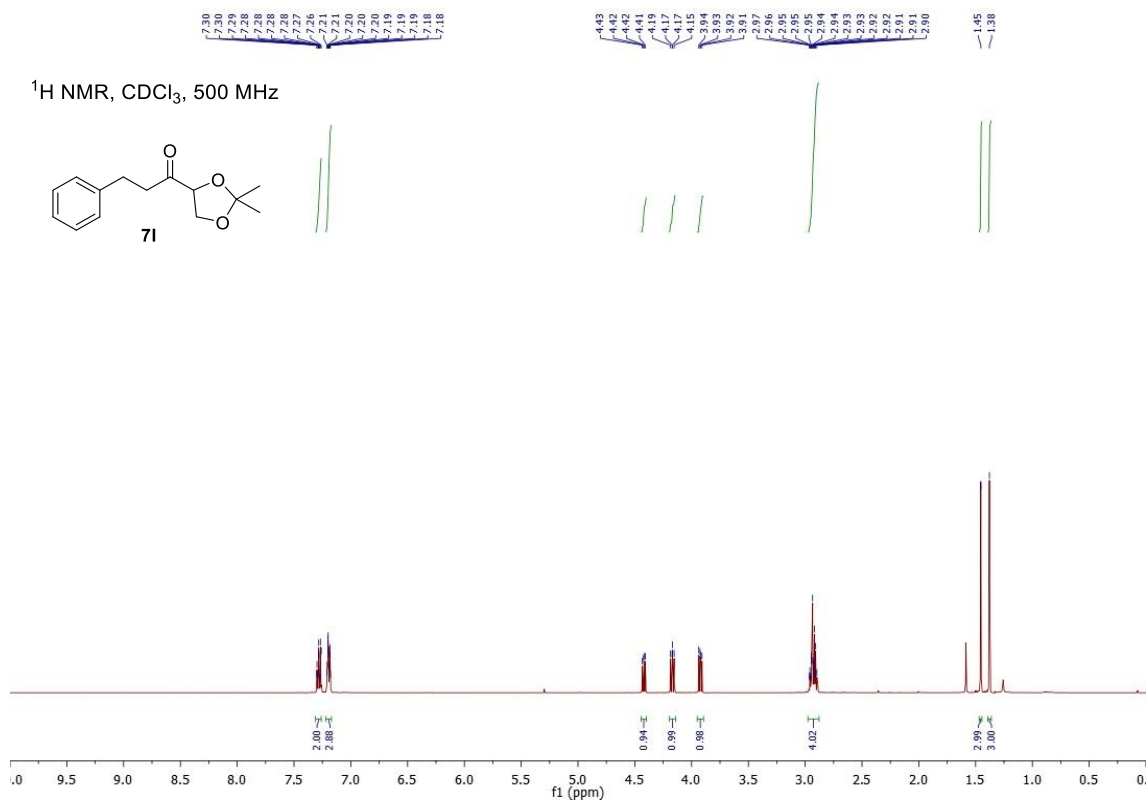
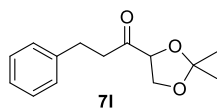
¹H NMR, CDCl₃, 500 MHz



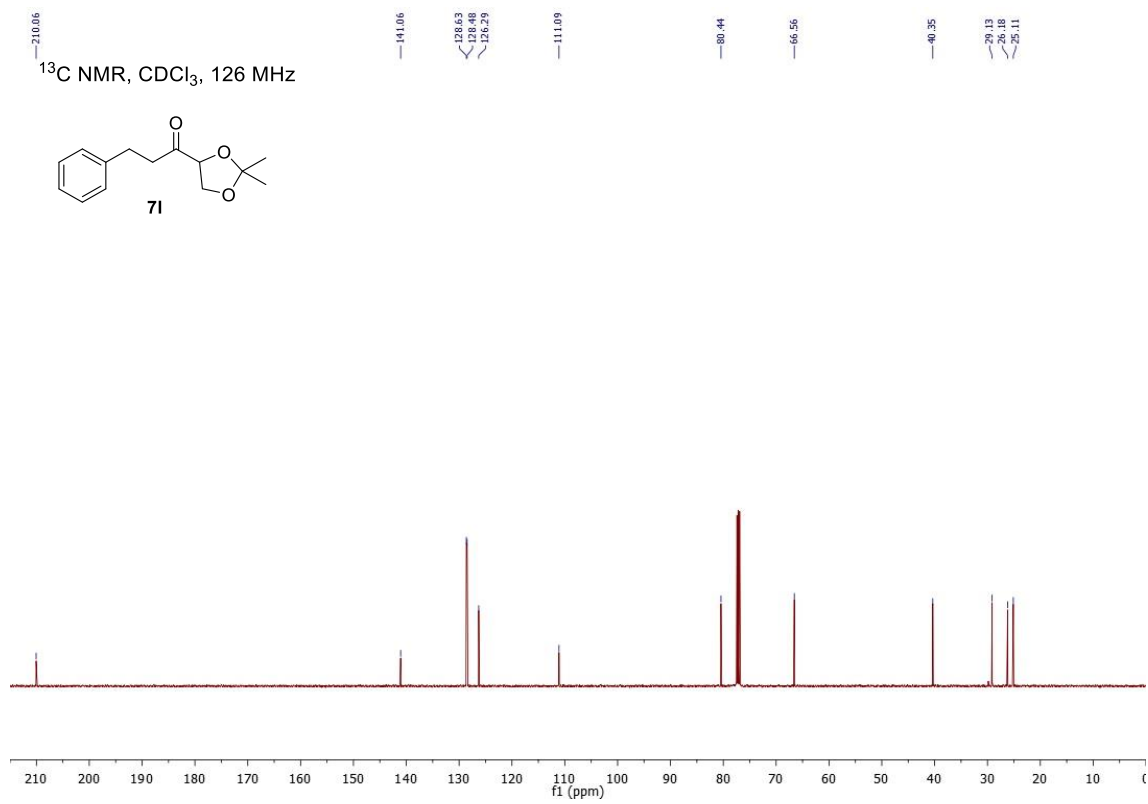
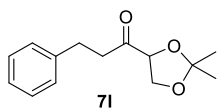
¹³C NMR, CDCl₃, 126 MHz



¹H NMR, CDCl₃, 500 MHz

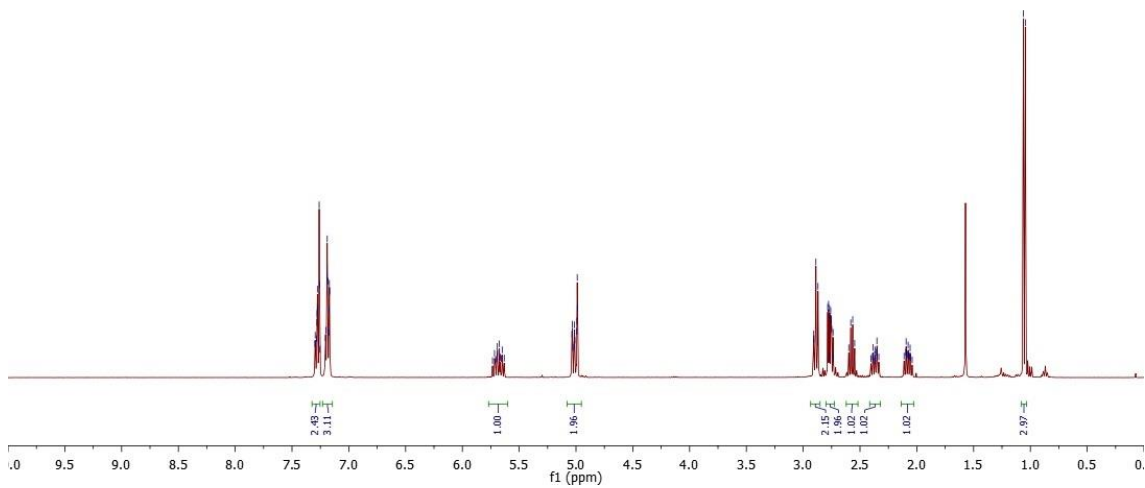
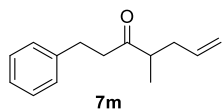


¹³C NMR, CDCl₃, 126 MHz



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¹H NMR, CDCl₃, 400 MHz



—213.01

—141.42
—135.76
—128.60
—128.49
—126.20
—116.96

—46.27
—43.11
—37.17
—29.80
—16.07

¹³C NMR, CDCl₃, 101 MHz

