Supporting Information

Photocatalyst-Free Hydroacylation of Electron-Poor Alkenes and Enones Under Visible-Light Irradiation

Ádám Márk Pálvölgyi[a], Florian Ehrschwendtner[a], Michael Schnürch[a] and Katharina Bica-Schröder*[a]

[a] Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9/163, 1060 Wien, Austria

e-mail: katharina.schroeder@tuwien.ac.at

1. General remarks

All purchased chemicals from commercial suppliers were used without further purification, unless noted otherwise. Dry solvents were obtained as follows:

- Dichloromethane (DCM), toluene, and tetrahydrofuran (THF) were pre-distilled and desiccated on aluminium oxide columns (PURESOLV, Innovative Technology).
- Acetonitrile (ACN) was purchased as water-free solvent from commercial providers (*VWR*, *Acros*)
- All other solvents were technical grade, unless noted otherwise.

Column chromatography was performed on standard manual glass columns using Merck (40-63 µm) silica gel with pre-distilled solvents (PE: petrolether, EtOAc: ethyl acetate). For TLC analysis, precoated aluminium-backed plates were purchased from Merck (silica gel 60 F_{254}). UV active compounds were detected at 254 nm. Non-UV active compounds have been detected using either vanillin staining (5% vanillin in EtOH + H_2SO_4) or by Henessian's staining solutions.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance UltraShield 400 MHz spectrometer and chemical shifts are reported in ppm using TMS (tetramethylsilane) as internal standard. Coupling constants (*J*) are given in Hz.

GC-MS measurements have been performed on a Thermo Scientific DSQ II on BGB5 column (30 m), equipped with a quadrupole MS detector DSQ II.

HR-MS analysis was performed using HTC PAL system autosampler, an Agilent 1100/1200 HPLC with binary pumps and column, column thermostat and Agilent 6230 AJS ESI-TOF mass spectrometer.

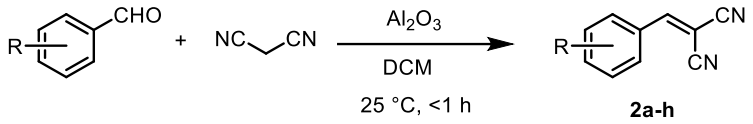
Infrared spectra were recorded on a Perkin-Elmer Spectrum 65 FT IR spectrometer equipped with a specac MK II Golden Gate Single Reflection ATR unit.

UV-VIS spectra have been recorded in 1 cm path length quartz cuvettes on a Shimadzu UV/VIS 1800 spectrometer.

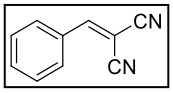
Fluorescence measurements were carried out on a PerkinElmer LS 55 luminescence spectrometer.

2. Substrate synthesis

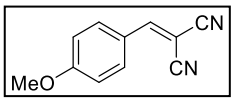
2.1. Synthesis of benzylidene malononitrile derivatives



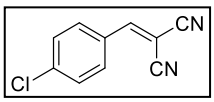
Benzylidene malononitrile derivatives **2a**-**h** were on a 5.0 – 10.0 mmol scales. To the solution of the corresponding benzaldehyde (1.0 equiv.) in DCM (0.25 M), malononitrile (1.0 equiv.) was added, followed by the addition of Al_2O_3 (3.0 equiv.). The reaction mixture was stirred at room temperature until full conversion (*judged by TLC, general reaction times were less than 1 hour*). The reaction mixture was filtered through a plug of celite, and it was washed with DCM (2×). The filtrate was concentrated *in vacuo*, and – if necessary – the crude products were recrystallized from EtOH.



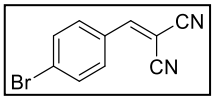
2-Benzylidenemalononitrile, (**2a**). Prepared according to the general procedure from benzaldehyde (1.05 mL, 1.06 g, 10.0 mmol), affording **2a** as a white solid (1.42 g, 91% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.84 (d, *J* = 7.4 Hz, 2H), 7.71 (s, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H).



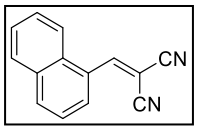
2-(4-Methoxybenzylidene)malononitrile, (**2b**). Prepared according to the general procedure from *p*-anisaldehyde (1.36 g, 10.0 mmol), affording **2b** as a white solid (1.73 g, 94% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.84 (d, *J* = 8.8 Hz, 2H), 7.58 (s, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H).



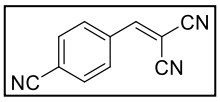
2-(4-Chlorobenzylidene)malononitrile, (**2c**). Prepared according to the general procedure from 4-chlorobenzaldehyde (1.40 g, 10.0 mmol), affording **2c** as a white solid (1.75 g, 93% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.70 (d, *J* = 8.5 Hz, 2H), 7.67 – 7.59 (m, 3H).



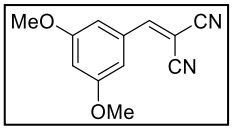
2-(4-Bromobenzylidene)malononitrile, (**2d**). Prepared according to the general procedure from 4-bromobenzaldehyde (0.93 g, 5.0 mmol), affording **2d** as a white solid (1.11 g, 95% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.76 (d, *J* = 8.5 Hz, 2H), 7.62 – 7.55 (m, 3H).



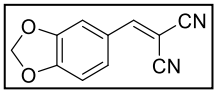
2-(Naphthalen-1-ylmethylene)malononitrile, (**2e**). Prepared according to the general procedure from 1-naphthaldehyde (0.68 mL, 0.78 g, 5.0 mmol), affording **2e** as a light-yellow solid (0.84 g, 82% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.58 (s, 1H), 8.20 (d, *J* = 7.4 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 9.5 Hz, 2H), 7.66 – 7.48 (m, 3H).



2-(4-Cyanobenzylidene)malononitrile, (**2f**). Prepared according to the general procedure from 4-cyanobenzaldehyde (1.31 g, 10.0 mmol), affording **2f** as a white solid (1.61 g, 90% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.93 (d, *J* = 8.3 Hz, 2H), 7.77 (m, *J* = 8.7 Hz, 3H).

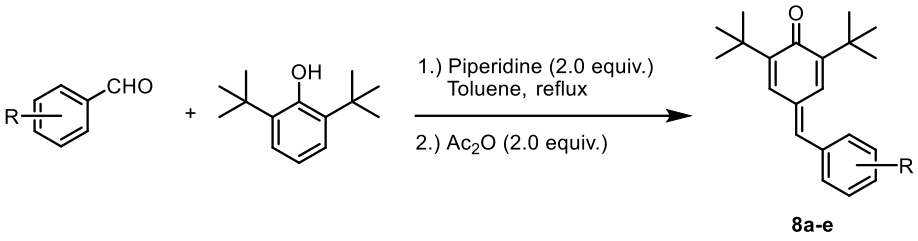


2-(3,5-Dimethoxybenzylidene)malononitrile, (**2g**). Prepared according to the general procedure from 3,5-dimethoxybenzaldehyde (0.83 g, 5.0 mmol), affording **2g** as a yellow solid (0.87 g, 81% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.61 (s, 1H), 6.96 (s, 2H), 6.62 (d, *J* = 2.2 Hz, 1H), 3.77 (s, 6H).



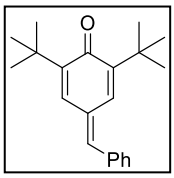
2-(Benzo[d][1,3]dioxol-5-ylmethylene)malononitrile, (**2h**). Prepared according to the general procedure from piperonal (1.125 g, 7.5 mmol), affording **2h** as a white solid (1.38 g, 93% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.53 (d, *J* = 4.1 Hz, 2H), 7.25 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.06 (s, 2H).

2.2. Synthesis of *para*-quinone methide substrates

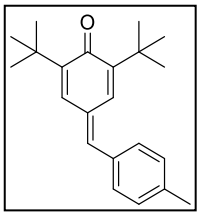


8a-e

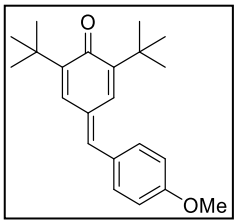
Substrates **8a-e** were prepared according to modified literature procedure on a 6.25 – 12.5 mmol scale.[1] To a three-necked flask equipped with a Dean-Start apparatus, 2,6-di-*tert*butylphenol (1.0 equiv.) and the corresponding aldehyde (1.0 equiv.) were dissolved in toluene (0.25 M). Piperidine (2.0 equiv.) was added within a period of 1 hour (*via syringe pump*) and the reaction mixture was refluxed for 2-3 hours. Then – just below reflux temperature –, acetic anhydride (2.0 equiv.) was added and the reaction mixture was stirred for another 15 minutes. Then the mixture was poured onto ice-water and it was extracted with EtOAc (3×). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude products were purified by column chromatography (PE/DCM mixtures as eluent).



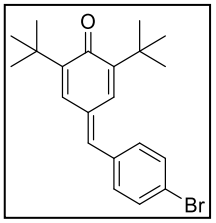
4-Benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one, (**8a**). Prepared according to the general procedure from benzaldehyde (1.32 mL, 1.33 g, 12.5 mmol), using 2.50 mL piperidine and 1.18 mL acetic anhydride. After the general work-up procedure, column chromatography (silica gel, PE/DCM 5/1) afforded **8a** as a bright yellow solid (2.39 g, 65% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.46 (d, *J* = 2.4 Hz, 1H), 7.39 (d, *J* = 4.5 Hz, 5H), 7.12 (s, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 1.27 (s, 9H), 1.23 (s, 9H).



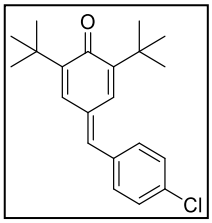
2,6-di-*tert*-Butyl-4-(4-methylbenzylidene)cyclohexa-2,5-dien-1-one, (**8b**). Prepared according to the general procedure from 4-methylbenzaldehyde (0.74 mL, 0.75 g, 6.25 mmol), using 1.25 mL piperidine and 0.59 mL acetic anhydride. After the general work-up procedure, column chromatography (silica gel, PE/DCM 6/1) afforded **8b** as a bright yellow solid (1.12 g, 58% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.48 (d, *J* = 2.1 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 1H), 6.94 (d, *J* = 2.2 Hz, 1H), 2.34 (s, 3H), 1.26 (s, 9H), 1.23 (s, 9H).



2,6-di-*tert*-Butyl-4-(4-methoxybenzylidene)cyclohexa-2,5-dien-1-one (**8c**). Prepared according to the general procedure from *p*-anisaldehyde (0.76 mL, 0.85 g, 6.25 mmol), using 1.25 mL piperidine and 0.59 mL acetic anhydride. After the general work-up procedure, column chromatography (silica gel, PE/DCM 5/1 to 3/1) afforded **8c** as a bright yellow solid (1.43 g, 71% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.49 (d, *J* = 2.3 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.06 (s, 1H), 6.95 – 6.89 (m, 3H), 3.80 (s, 3H), 1.26 (s, 9H), 1.25 (s, 9H).



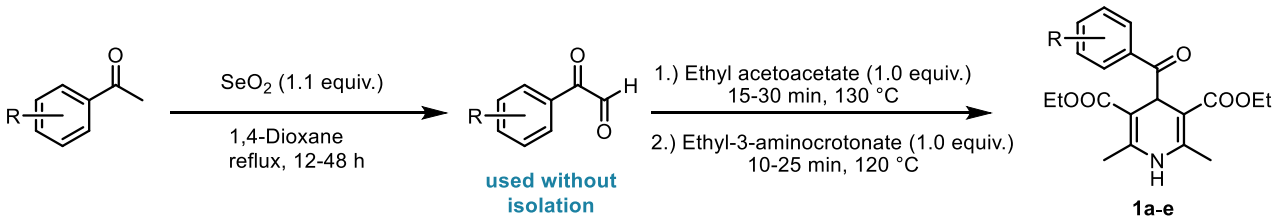
2,6-di-*tert*-Butyl-4-(4-bromobenzylidene)cyclohexa-2,5-dien-1-one (**8d**). Prepared according to the general procedure from 4-bromobenzaldehyde (1.15 g, 6.25 mmol), using 1.25 mL piperidine and 0.59 mL acetic anhydride. After the general work-up procedure, column chromatography (silica gel, PE/DCM 6/1) afforded **8d** as a bright yellow solid (1.03 g, 44% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.51 (d, *J* = 8.4 Hz, 2H), 7.36 (s, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.01 (s, 1H), 6.92 (s, 1H), 1.25 (s, 9H), 1.22 (s, 9H).



2,6-di-*tert*-Butyl-4-(4-chlorobenzylidene)cyclohexa-2,5-dien-1-one (**8e**). Prepared according to the general procedure from 4-chlorobenzaldehyde (0.88 g, 6.25 mmol), using 1.25 mL piperidine and 0.59 mL acetic anhydride. After the general work-up procedure, column chromatography (silica gel, PE/DCM 6/1) afforded **8e** as a bright yellow solid (0.99 g, 48% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.38 – 7.34 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.04 (s, 1H), 6.92 (d, *J* = 2.2 Hz, 1H), 1.26 (s, 9H), 1.23 (s, 9H).

3. Hantzsch ester synthesis

3.1. Synthesis of Hantzsch esters 1a-e



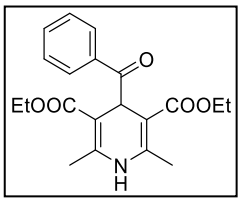
The Hantzsch ester **1a**-**e** were prepared according to modified literature procedure.[2] For the synthesis of **1a**, phenylglyoxal monohydrate was purchase from Sigma-Aldrich. All other glyoxals were prepared *via* Riley oxidation, followed by the one-pot Hantzsch ester synthesis step.

General procedure for the Riley oxidation:

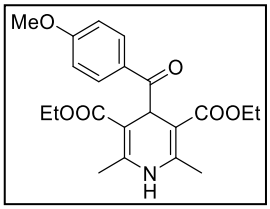
To a one-neck round-bottom flask SeO_2 (1.1 equiv.) was added, followed by the addition of 1,4-dioxane/water (10:1 mixture, 5 × volume) and the acetophenone-derivative (1.0 equiv.). The reaction mixture was refluxed under argon atmosphere for 12-48 h until full conversion (*TLC control, selenium precipitation*). The reaction mixture was cooled to room temperature, the suspension was filtered through a plug of celite and the solvent was removed *in vacuo*. The residue was dried under high vacuum and used directly for the second step without further purification.

General procedure for the Hantzsch ester synthesis

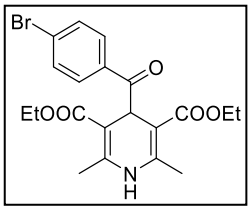
The corresponding glyoxal (1.0 equiv.) and ethyl acetoacetate (1.0 equiv.) were added to a one-neck round-bottom flask, and it was heated to 130 ˚C for 15-30 minutes. As the Knoevenagel-condensation was finished (*TLC control*), the reaction mixture was cooled to 80 ˚C. Ethyl-3-aminocrotonate (1.0 equiv.) was added in smaller portions (*strongly exothermic reaction!*), and the reaction mixture was stirred at 120 ˚C for another 10-25 minutes. Then, the mixture was cooled to room temperature, and the small amount of remaining water was removed by co-evaporation with toluene *in vacuo*. The crude product was dissolved in hot cyclohexane/ethyl acetate mixture (4:1, 6-7 × crude mass). After being stirred for 15 minutes, it was cooled to room temperature, and then to 0 ˚C (*with stirring*). The yellow precipitate was filtered off, washed with cold cyclohexane/ethyl acetate mixture (4:1), and dried under high vacuum. In case of **1c**-**e**, the crude products were purified by column chromatography (silica gel, PE/EE 7/1 to 3/1), followed by recrystallization from cyclohexane/ethyl acetate mixture (4:1).



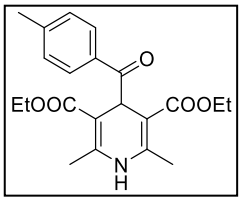
Diethyl 4-benzoyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, (**1a**).[2] Prepared according to the general procedure from phenylglyoxal (3.04 g, 20.0 mmol), using 2.60 mL (20.0 mmol) ethyl acetoacetate and 2.58 g (20.0 mmol) ethyl-3-aminocrotonate. After the general work-up procedure, crystallization afforded **1a** as a yellow solid (4.02 g, 56% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.08 (d, *J* = 7.1 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.23 (s, 1H), 5.67 (s, 1H), 4.01 – 3.81 (m, 4H), 2.20 (s, 6H), 0.96 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 204.64, 167.01, 147.23, 136.99, 132.83, 129.65, 127.98, 99.49, 59.84, 41.80, 19.12, 14.09.



Diethyl 4-(4-methoxybenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, (**1b**). 2-(4-Methoxyphenyl)-2-oxoacetaldehyde was prepared *via* Riley oxidation on a 10.0 mmol scale. The crude glyoxal was reacted with 1.30 mL (10.0 mmol) ethyl acetoacetate and 1.29 g (10.0 mmol) ethyl-3-aminocrotonate as stated above. After the general work-up procedure, crystallization afforded **1b** as an olive green solid (0.55 g, 14% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.10 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 1H), 5.62 (s, 1H), 3.96 (d, *J* = 3.6 Hz, 4H), 3.80 (s, 3H), 2.22 (s, 6H), 1.01 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 202.42, 167.09, 163.50, 146.93, 132.16, 129.61, 113.18, 99.83, 59.84, 55.44, 41.16, 19.39, 14.21.

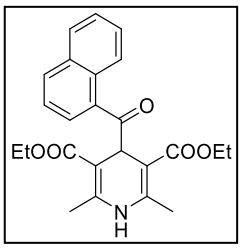


Diethyl 4-(4-bromobenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, (**1c**). 2-(4-Bromophenyl)-2-oxoacetaldehyde was prepared *via* Riley oxidation on a 20.0 mmol scale. The crude glyoxal was reacted with 2.60 mL (20.0 mmol) ethyl acetoacetate and 2.58 g (20.0 mmol) ethyl-3-aminocrotonate as stated above. After the general work-up procedure, column chromatography and subsequent crystallization afforded **1c** as a bright yellow solid (1.48 g, 17% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.98 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.03 (s, 1H), 5.59 (s, 1H), 4.04 – 3.85 (m, 4H), 2.19 (s, 6H), 0.99 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 203.79, 166.93, 147.14, 135.72, 131.22, 128.06, 99.59, 59.97, 41.75, 19.25, 14.17. **IR ATR (ν_{max}/cm^{-1})** 3296, 3241, 3107, 2995, 1670, 1656, 1200, 1106, 699. **HRMS (ESI)** Cald for $C_{20}H_{21}BrNO_5$ $[M - H]^-$ 434.0604, Found 434.0601.



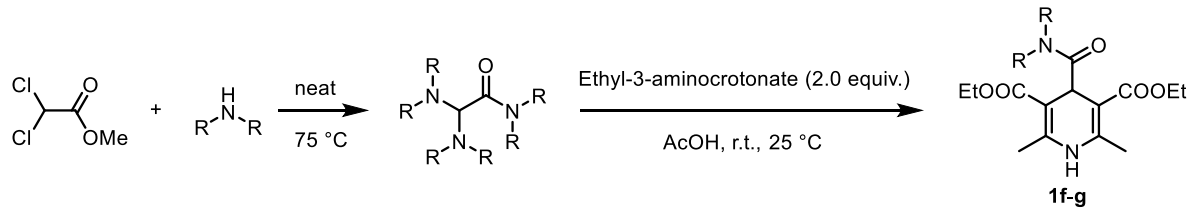
Diethyl 4-(4-metylbenzoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, (**1d**).[2] 2-Oxo-2-(*p*-tolyl)acetaldehyde was prepared *via* Riley oxidation on a 25.0 mmol scale. The crude glyoxal was reacted with 3.25 mL (25.0 mmol) ethyl acetoacetate and 3.23 g (25.0 mmol) ethyl-3-aminocrotonate as stated above. After the general work-up procedure, the crude product was purified by column

chromatography (silica gel, PE/EE 7/1 to 3/1). Subsequent crystallization afforded **1e** as a bright yellow solid (4.91 g, 53% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.00 (d, *J* = 8.3 Hz, 2H), 7.31 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.65 (s, 1H), 3.98 – 3.83 (m, 4H), 2.33 (s, 3H), 2.19 (s, 6H), 0.99 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 204.07, 167.07, 147.22, 143.65, 134.24, 129.89, 128.69, 99.49, 59.80, 41.53, 21.65, 19.09, 14.13.

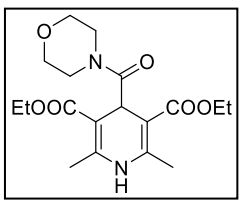


Diethyl 4-(1-naphtoyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, (**1e**).[2] 2-(2-(Naphthalen-1-yl)-2-oxoacetaldehyde was prepared *via* Riley oxidation on a 3.0 mmol scale. The crude glyoxal was reacted with 0.39 mL ethyl acetoacetate (3.0 mmol) and 0.39 g (3.0 mmol) ethyl-3-aminocrotonate as stated above. After the general work-up procedure, crystallization afforded **1e** as a bright yellow solid (0.50 g, 41% yield).**^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.02 (d, *J* = 9.7 Hz, 1H), 7.91 – 7.70 (m, 3H), 7.49 – 7.34 (m, 3H), 5.98 (s, 1H), 5.57 (s, 1H), 3.90 – 3.78 (m, 2H), 3.74 – 3.64 (m, 2H), 2.31 (s, 6H), 0.88 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 203.41, 166.82, 146.51, 137.44, 133.40, 130.72, 130.49, 128.11, 127.07, 126.55, 126.11, 124.38, 98.49, 77.23, 59.89, 46.89, 19.59, 13.92.

3.2. Synthesis of Hantzsch esters 1f-g

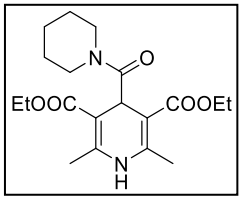


The Hantzsch ester **1f**-**g** were prepared according to literature procedure.[3] A mixture of methyl dichloroacetate (2.16 g, 15.0 mmol, 1.0 equiv.) and the corresponding amine (75.0 mmol, 5.0 equiv.) was heated to 75 ˚C for 30 minutes, upon which the reaction mixture solidified. This was dissolved in glacial acetic acid (30 mL) and ethyl-3-aminocrotonate (3.87 g, 30.0 mmol, 2.0 equiv.) was added. The mixture was stirred at room temperature for 16 hours, upon which a suspension formed. The mixture was diluted with H_2O, the precipitate was filtered off, washed with H_2O (2×) and dried under reduced pressure, yielding **1f**-**g**.



Diethyl 2,6-dimethyl-4-(morpholine-4-carbonyl)-1,4-dihydropyridine-3,5-dicarboxylate, (**1f**).[3] Prepared according to the general procedure on 15.0 mmol scale, using morpholine (6.45 mL, 75.0 mmol, 5.0 equiv.), affording **1f** as a pale white solid (3.08 g, 56% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.82 (s, 1H), 4.96 (s, 1H), 4.23 – 4.01 (m, 4H), 3.87 (s, 2H), 3.70 (s, 2H), 3.56 (d, *J* = 19.8 Hz, 4H), 2.15 (s, 6H), 1.21 (t, *J* = 7.1

Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 174.45, 167.52, 147.70, 98.78, 67.33, 66.92, 59.93, 42.68, 36.39, 19.42, 14.61.



Diethyl 2,6-dimethyl-4-(morpholine-4-carbonyl)-1,4-dihydropyridine-3,5-dicarboxylate, (**1g**).[3] Prepared according to the general procedure on 15.0 mmol scale, using piperidine (6.48 mL, 75.0 mmol, 5.0 equiv.), affording **1f** as a pale white solid (2.90 g, 53% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.26 (s, 1H), 5.05 (s, 1H), 4.24 – 3.96 (m, 4H), 3.76 (s, 2H), 3.47 (s, 2H), 2.13 (s, 6H), 1.57 (s, 4H), 1.44 (s, 2H), 1.21 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 173.94, 167.63, 147.97, 98.59, 59.72, 47.78, 43.44, 36.21, 26.79, 25.77, 24.66, 19.23, 14.57.

4. Catalyst-free hydroacylation of electron-poor alkenes and enones

4.1. General considerations

All reactions were carried out in 8 mL Schlenk-tubes by using standard Schlenk technique. The tubes were charged with the substrate (*if solid*) and with the Hantzsch ester. The tubes were evacuated and back-filled with argon three times, followed by the addition of the solvent and the substrate (*if liquid*) under argon counterflow. The tubes were sealed and placed into a custom-made photoreactor equipped with a blue LED strip (λ_{max} = 460 nm). The reaction mixtures were stirred at room temperature for 16 hours. The solvent was the removed by rotary evaporator, and the crude products were purified by column chromatography.

4.2. Reactor setup

All photoreactions were performed in a custom-made photoreactor (Figure S1). 3.6 m of a flexible blue LED strip (34.5 W, a total of 48 W, 12 V, 4.0 A, 120 LEDs/m, λ_{max} = 460 nm) was coiled into a 3D-printed cylindric case (*diameter x height 10 cm x 14 cm, ABS polymer*). A cylindric lid was used, providing a uniform irradiation environment for the Schenk tubes with a distance of 2 cm from the light source. A computer fan (40 × 10 mm, 6800 rpm) was integrated into the reactor lid, maintaining the temperature not higher than 28 ˚C.

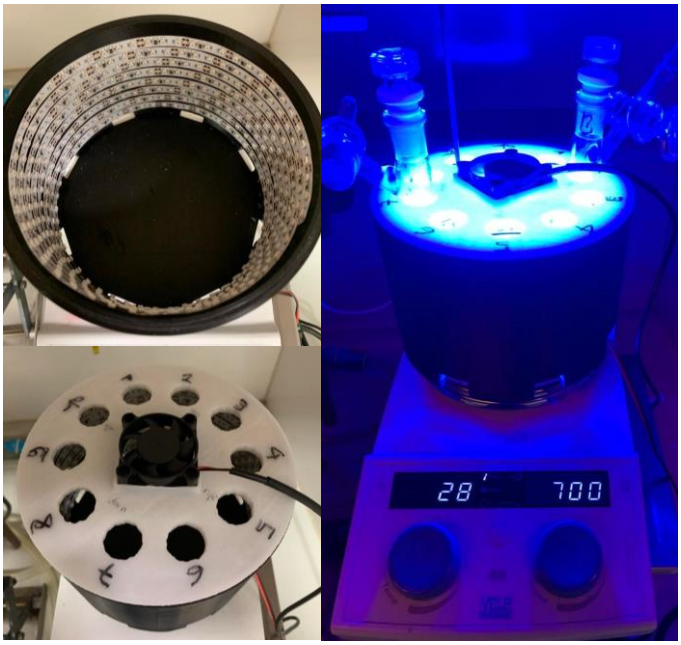
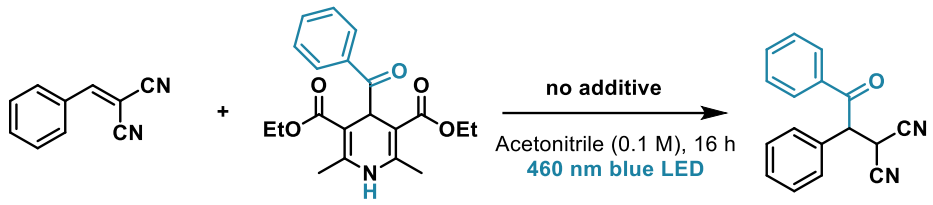
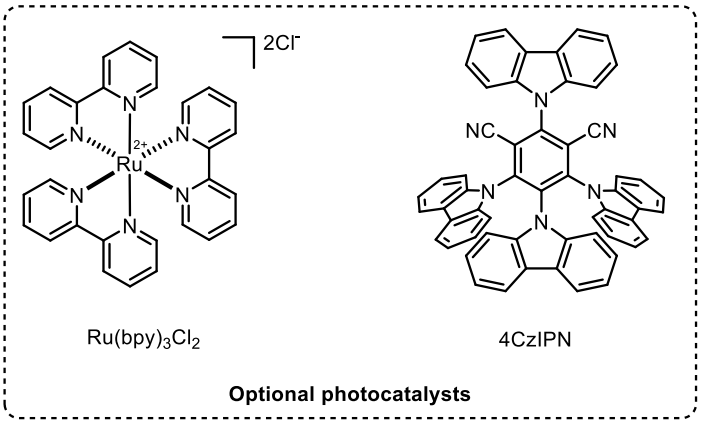


Figure S1.: Photoreactor setup. The picture in the right side was captured from behind the fume hood window, which was covered with an orange UV-protective foil (cut-off at 525 nm).

4.3. Parameter optimization for the hydroacylation of 2a



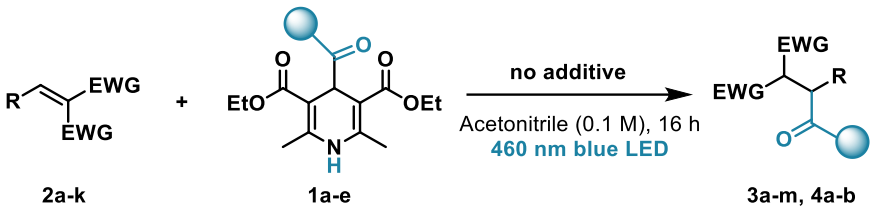
2a (1.0 equiv.) **1a** (1.2 equiv.) **3a**



entry	Alterations from standard reaction conditions	Conversion [%][b]
1[a]	**no change**	**98 (93)**
2	3 hours reaction time	98
3	1.1 equiv. of 1a	90
4	performed in dark	0
5	0.1 M toluene instead of ACN	90
6	0.1 M DCM instead of ACN	89
7	no inert atmosphere	65
8	2 mol% $Ru(bpy)_3Cl_2$ as additive	98
9	2 mol% 4CzIPN as additive	97

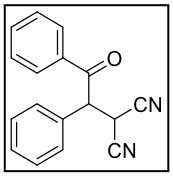
[a] Performed with 0.20 mmol benzylidene malononitrile (**2a**), 0.24 mmol (1.2 equiv.) **1a** in 2.0 mL acetonitrile under blue light irradiation (λ_{max} = 460 nm) for 16 hours. [b] Determined by GC-MS analysis.

4.4. General procedure and analytical data for the hydroacylation of Michael-acceptors

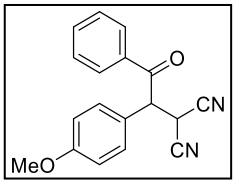


2a-k **1a-e** **3a-m, 4a-b**

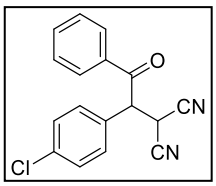
Into an 8 mL Schlenk tube, Hantzsch ester **1a**-**e** (0.24 mmol, 1.2 equiv.) and substrate **2a**-**k** (0.2 mmol, 1.0 equiv.) were added. The Schlenk tube was evacuated and back-filled with argon, and acetonitrile (2.0 mL) was added *via* syringe under argon counterflow. The tubes were sealed and placed into a custom made photoreactor. The reaction mixtures were stirred under blue light irradiation (λ_{max} = 460 nm) for 16 hours. Two parallel runs were merged, the solvent was removed *in vacuo* and the crude products were purified by column chromatography (PE/EE mixtures as mobile phase). *In case the Hantzsch ester residue results in product contamination after column chromatography, it can be easily removed by means of short-path Pasteur-column, eluting with dichloromethane (ca. 25 mL for 0.4 mmol scale).*



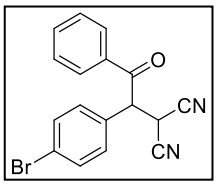
2-(2-Oxo-1,2-diphenylethyl)malononitrile, (**3a**).[4] Purified by column chromato-graphy (silica gel, PE/EE 10/1). Light yellow oil (97 mg, 93% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.90 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.46 – 7.31 (m, 7H), 5.13 (d, *J* = 8.3 Hz, 1H), 4.55 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 193.10, 134.44, 133.88, 132.08, 130.08, 129.90, 129.28, 128.97, 128.64, 112.17, 111.61, 54.78, 26.85.



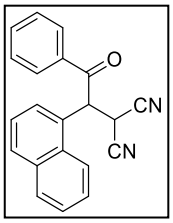
2-(1-(4-Methoxyphenyl)-2-oxo-2-phenylethyl)malononitrile, (**3b**).[4] Purified by column chromatography (silica gel, PE/EE 9/1 to 7/1). Light yellow solid (103 mg, 89% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.82 (d, *J* = 9.5 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.00 (d, *J* = 8.3 Hz, 1H), 4.42 (d, *J* = 8.3 Hz, 1H), 3.70 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 193.21, 160.62, 134.33, 133.93, 129.90, 129.25, 128.94, 123.80, 115.47, 112.23, 111.72, 55.34, 54.19, 26.94.



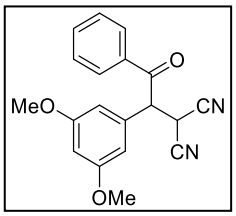
2-(1-(4-Chlorophenyl)-2-oxo-2-phenylethyl)malononitrile, (**3c**).[4] Purified by column chromatography (silica gel, gradient elution, PE/EE 9/1 to 7/1). Light yellow oil (100 mg, 85% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.80 (d, *J* = 9.7 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.39 – 7.30 (m, 4H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.02 (d, *J* = 8.2 Hz, 1H), 4.45 (d, *J* = 8.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 191.66, 135.27, 133.65, 132.57, 129.42, 129.36, 128.92, 128.20, 128.05, 110.82, 110.29, 53.01.



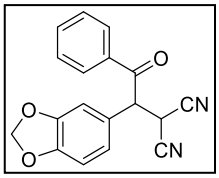
2-(1-(4-Bromophenyl)-2-oxo-2-phenylethyl)malononitrile, (**3d**).[4] Purified by column chromatography (silica gel, gradient elution, PE/EE 9/1 to 7/1). Light yellow oil (120 mg, 88% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.79 (d, *J* = 8.6 Hz, 2H), 7.47 (s, 3H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 12.9 Hz, 2H), 5.02 (d, *J* = 8.1 Hz, 1H), 4.45 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 192.79, 134.70, 133.60, 133.34, 131.03, 130.26, 129.10, 124.47, 111.97, 111.45, 54.01, 26.64.



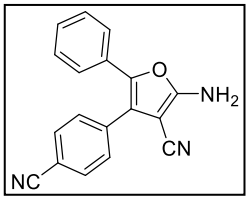
2-(1-(Naphthalen-1-yl)-2-oxo-2-phenylethyl)malononitrile, (**3e**).[4] Purified by column chromatography (silica gel, PE/EE 10/1 to 8/1). Light yellow oil (103 mg, 83% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.23 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.72 (dd, *J* = 14.4, 8.4 Hz, 3H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.41 (s, 1H), 7.35 – 7.29 (m, 1H), 7.28 – 7.18 (m, 3H), 5.87 (d, *J* = 7.5 Hz, 1H), 4.54 (d, *J* = 7.6 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 192.31, 133.55, 133.31, 132.73, 129.72, 129.43, 128.91, 127.90, 127.12, 125.83, 124.61, 120.37, 111.04, 110.62, 25.20.



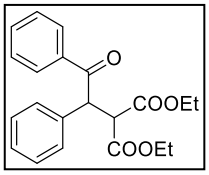
2-(1-(3,5-Dimethoxyphenyl)-2-oxo-2-phenylethyl)malononitrile, (**3f**). Purified by column chromatography (silica gel, gradient elution, PE/EE 9/1 to 7/1). Light yellow amorphous solid (110 mg, 86% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.85 (d, *J* = 9.6 Hz, 2H), 7.57 – 7.44 (m, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 6.43 – 6.31 (m, 3H), 4.93 (d, *J* = 8.6 Hz, 1H), 4.46 (d, *J* = 8.6 Hz, 1H), 3.69 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 191.78, 160.80, 133.43, 132.88, 128.15, 111.11, 110.55, 105.71, 100.17, 54.48, 53.85, 25.66. **IR ATR (ν_{max}/cm^{-1})** 3046, 2912, 1680, 1594, 1451, 1289, 1068, 712, 686. **HRMS (ESI)** Cald for $C_{19}H_{17}N_2O_3$ $[M + H]^+$ 321.1239, Found 322.1247.



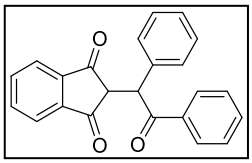
2-(1-(Benzo[d][1,3]dioxol-5-yl)-2-oxo-2-phenylethyl)malononitrile, (**3g**). *The initially turbid solution became homogeneous overnight.* Purified by column chromatography (silica gel, gradient elution, PE/EE 9/1 to 7/1). Light yellow oil (102 mg, 84% yield). **^{1}H NMR (400 MHz, acetone-d_6) δ** 7.93 (d, *J* = 9.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 7.2 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 1H), 5.89 (d, *J* = 11.3 Hz, 2H), 5.59 (d, *J* = 7.3 Hz, 1H), 5.08 – 5.01 (m, 1H). **^{13}C NMR (101 MHz, acetone-d_6) δ** 192.94, 145.97, 132.66, 131.48, 129.98, 129.79, 129.71, 129.41, 128.84, 112.50, 112.03, 54.58, 26.93, 21.58. **IR ATR (ν_{max}/cm^{-1})** 3072, 2915, 1681, 1504, 1247, 1036, 711, 693. **HRMS (ESI)** Cald for $C_{18}H_{13}N_2O_3$ $[M + H]^+$ 305.0926, Found 305.0930.



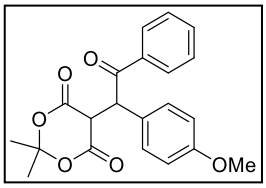
2-Amino-4-(4-cyanophenyl)-5-phenylfuran-3-carbonitrile, (**4a**). Purified by column chromatography (silica gel, gradient elution, PE/EE 7/1 to 5/1). Light yellow solid (88 mg, 77% yield). **^{1}H NMR (400 MHz, acetone-d$_6$) δ** 7.71 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.20 – 7.09 (m, 5H), 6.88 (s, 2H). **^{13}C NMR (101 MHz acetone-d$_6$) δ** 163.54, 139.08, 136.56, 132.70, 129.99, 129.24, 128.68, 127.73, 125.36, 120.27, 118.26, 114.18, 111.76, 70.40. **IR ATR (ν$_{max}$/cm^{-1})** 3465, 3331, 3193, 2918, 2234, 2198, 1597, 1450, 1204, 1065, 698. **HRMS (ESI)** Cald for $C_{18}H_{11}N_3ONa$ $[M + Na]^+$ 308.0800, Found 308.0793.



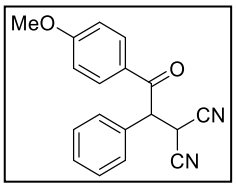
Diethyl 2-(2-oxo-1,2-diphenylethyl)malonate, (**3h**).[5] Purified by column chromatography (silica gel, PE/EE gradient from 14/1 to 11/1). Colorless liquid (120 mg, 85% yield). **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.92 (d, *J* = 9.7 Hz, 2H), 7.46 – 7.11 (m, 8H), 5.25 (d, *J* = 11.4 Hz, 1H), 4.37 (d, *J* = 11.4 Hz, 1H), 4.10 (qq, *J* = 7.0, 3.6 Hz, 2H), 3.86 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 197.35, 168.18, 135.93, 134.54, 133.14, 129.02, 128.98, 128.91, 128.55, 128.01, 61.90, 61.39, 55.99, 52.94, 13.96.



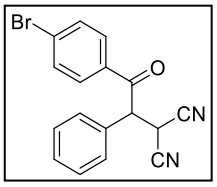
2-(2-Oxo-1,2-diphenylethyl)-1*H*-indene-1,3(2*H*)-dione, (**3i**). *The initially turbid solution became homogeneous overnight.* Purified by crystallization from diethyl ether. White solid (102.5 mg, 75% yield). **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.94 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.82 – 7.67 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.18 (m, 7H), 5.50 (d, *J* = 3.4 Hz, 1H), 3.33 (d, *J* = 3.5 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 199.17, 198.19, 197.54, 143.03, 141.06, 136.60, 135.60, 134.88, 134.77, 133.33, 129.77, 129.44, 128.88, 128.48, 127.70, 55.70, 55.52. **IR ATR (ν$_{max}$/cm^{-1})** 3059, 2899, 1704, 1671, 1278, 1227, 693. **HRMS (ESI)** Cald for $C_{23}H_{17}O_3$ $[M + H]^+$ 341.1178, Found 341.1183.



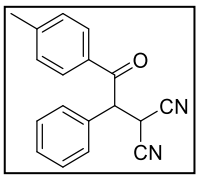
5-(1-(4-Methoxyphenyl)-2-oxo-2-phenylethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione, (**3j**). Purified by crystallization from diethyl ether. White solid (115.5 mg, 78% yield). **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.76 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.15 (m, 4H), 6.74 (d, *J* = 8.7 Hz, 2H), 5.48 (d, *J* = 4.5 Hz, 1H), 4.08 (d, *J* = 4.5 Hz, 1H), 3.68 (s, 3H), 1.74 (m, 6H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 197.01, 164.71, 164.42, 159.05, 135.05, 133.26, 131.55, 129.33, 128.47, 127.94, 114.08, 105.09, 55.18, 53.11, 49.45, 28.42, 26.98. **IR ATR (ν$_{max}$/cm^{-1})** 3004, 2876, 1732, 1686, 1254, 1229, 689. **HRMS (ESI)** Cald for $C_{21}H_{21}O_6$ $[M + H]^+$ 369.1338, Found 369.1347.



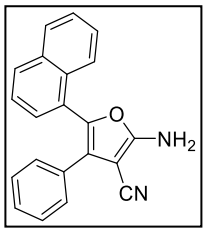
2-(2-Oxo-1,2-diphenylethyl)malononitrile, (**3k**).[4] Purified by column chromatography (silica gel, gradient elution, PE/EE 10/1 to 8/1). Light yellow oil (93 mg, 80% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.81 (d, *J* = 9.0 Hz, 2H), 7.31 (dd, *J* = 23.3, 5.8 Hz, 5H), 6.80 (d, *J* = 9.0 Hz, 2H), 4.97 (d, *J* = 8.5 Hz, 1H), 4.47 (d, *J* = 8.5 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 191.28, 164.46, 132.57, 131.73, 130.00, 129.77, 128.52, 114.20, 112.24, 111.67, 55.59, 54.59, 26.85.



2-(2-Oxo-1,2-diphenylethyl)malononitrile, (**3l**).[4] Purified by column chromatography (silica gel, gradient elution, PE/EE 10/1 to 8/1). Pale white solid (114 mg, 84% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.67 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.34 (s, 3H), 7.26 (d, *J* = 7.8 Hz, 2H), 4.97 (d, *J* = 8.3 Hz, 1H), 4.44 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 191.10, 131.50, 131.34, 130.68, 129.60, 129.18, 129.07, 128.94, 127.53, 110.92, 110.31, 53.83, 25.74.



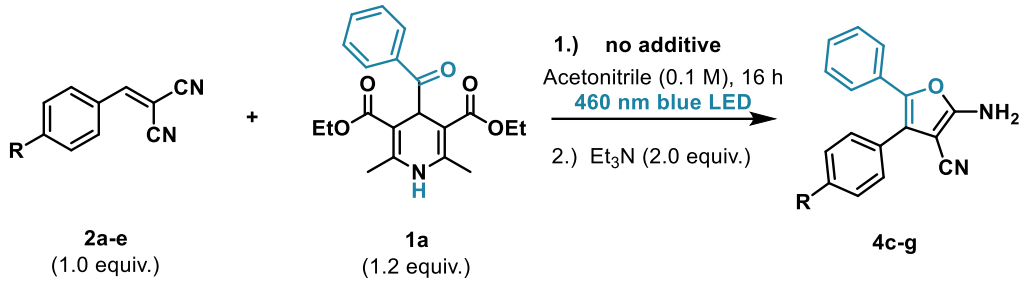
2-(2-Oxo-1,2-diphenylethyl)malononitrile, (**3m**).[4] Purified by column chromatography (silica gel, gradient elution, PE/EE 10/1 to 8/1). Light yellow oil (94 mg, 86% yield). **^{1}H NMR (400 MHz, CD_2Cl_2) δ** 7.75 – 7.68 (m, 2H), 7.40 – 7.24 (m, 5H), 7.12 (d, *J* = 9.0 Hz, 2H), 5.06 (d, *J* = 8.0 Hz, 1H), 4.47 (d, *J* = 8.0 Hz, 1H), 2.25 (s, 3H). **^{13}C NMR (101 MHz, CD_2Cl_2) δ** 192.94, 145.97, 132.66, 131.48, 129.98, 129.79, 129.71, 129.41, 128.84, 112.50, 112.03, 54.58, 26.93, 21.58.



2-Amino-5-(naphthalen-1-yl)-4-phenylfuran-3-carbonitrile, (**4b**). Purified by column chromatography (silica gel, gradient elution, PE/EE 7/1 to 5/1). Light brown solid (100.5 mg, 81% yield). **^{1}H NMR (400 MHz, acetone-d_6) δ** 7.92 (dd, *J* = 20.3, 8.4 Hz, 3H), 7.55 – 7.41 (m, 4H), 7.33 – 7.17 (m, 5H), 6.90 (s, 2H). **^{13}C NMR (101 MHz, acetone-d_6) δ** 164.23, 138.03, 134.00, 131.86, 131.34, 129.45, 129.29, 128.47, 128.42, 128.20, 127.63, 126.56, 126.18, 125.65, 125.31, 123.51, 69.20. **IR ATR (ν_{max}/cm^{-1})** 3454, 3323, 2210, 1450, 1204, 1072, 780, 698. **HRMS (ESI)** Cald for $C_{21}H_{14}N_2ONa$ $[M + Na]^+$ 333.1004, Found 333.1010.

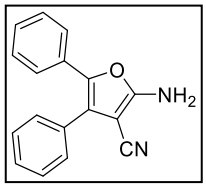
4.5. General procedure and analytical data for the one-pot derivatization of hydroacylation products

4.5.1. One-pot synthesis of tetrasubstituted furan derivatives

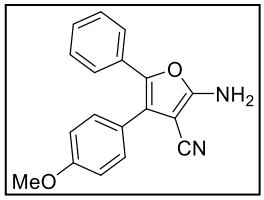


2a-e (1.0 equiv.) **1a** (1.2 equiv.) **4c-g**

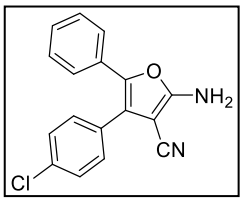
Into an 8 mL Schlenk tube, Hantzsch ester **1a** (85.8 mg, 0.24 mmol, 1.2 equiv.) and substrate **2a**-**e** (0.2 mmol, 1.0 equiv.) were added. The Schlenk tube was evacuated and back-filled with argon, and acetonitrile (2.0 mL) was added *via* syringe under argon counterflow. The tubes were sealed and placed into a custom made photoreactor. The reaction mixtures were stirred under blue light irradiation (λ_{max} = 460 nm) for 16 hours. The tubes were removed from the photoreactor, Et_3N (55.8 µL, 0.4 mmol, 2.0 equiv.) was added and the reaction mixtures were stirred at 25˚ C for another 3 hours *(TLC indicated full conversions*). Two parallel runs were merged, the solvent was removed *in vacuo* and the crude products were purified by column chromatography (PE/EE mixtures as mobile phase).



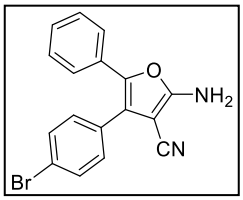
2-Amino-4,5-diphenylfuran-3-carbonitrile, (**4c**).[6] Purified by column chromatography (silica gel, gradient elution, PE/EE 7/1 to 5/1). Light yellow solid (87.5 mg, 84% yield). **^{1}H NMR (400 MHz, DMSO-d_6) δ** 7.72 (s, 2H), 7.54 – 7.37 (m, 5H), 7.35 – 7.15 (m, 5H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 164.01, 137.11, 131.69, 129.88, 129.46, 129.34, 129.09, 128.83, 127.40, 124.72, 122.29, 116.00, 69.69.



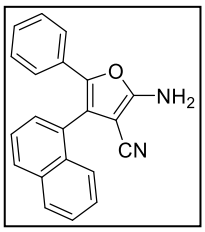
2-Amino-4-(4-methoxyphenyl)-5-phenylfuran-3-carbonitrile, (**4d**).[6] Purified by column chromatography (silica gel, gradient elution, PE/EE 7/1 to 5/1). Light yellow solid (90.6 mg, 78% yield). **^{1}H NMR (400 MHz, DMSO-d_6) δ** 9.48 (s, 1H), 7.91 (d, *J* = 9.0 Hz, 2H), 7.57 (s, 1H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.24 (m, 3H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 168.83, 165.40, 162.71, 140.32, 131.55, 128.99, 128.75, 125.79, 115.17, 114.91, 102.32, 89.79, 55.99.



2-Amino-4-(4-chlorophenyl)-5-phenylfuran-3-carbonitrile, (**4e**).[6] Purified by column chromatography (silica gel, gradient elution, PE/EE 7/1 to 5/1). Light yellow solid (89.7 mg, 76% yield). **^{1}H NMR (400 MHz, DMSO-d_6) δ** 7.76 (s, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.22 (dd, *J* = 10.8, 6.7 Hz, 3H).**^{13}C NMR (101 MHz, DMSO-d_6) δ** 164.05, 137.39, 133.52, 131.21, 130.57, 129.62, 129.21, 127.64, 124.90, 120.98, 115.85, 115.85, 69.38.

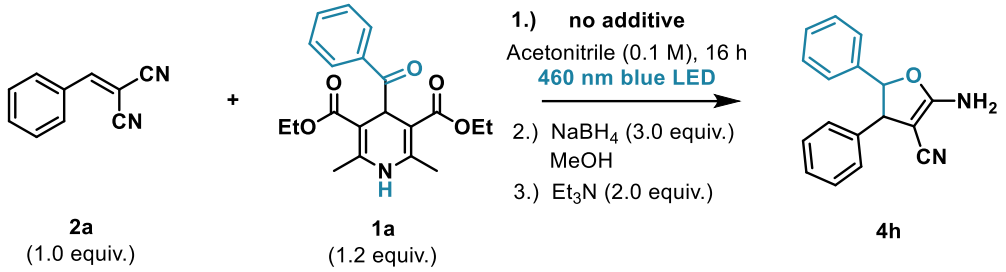


2-Amino-4-(4-bromophenyl)-5-phenylfuran-3-carbonitrile, (**4f**). Purified by column chromatography (silica gel, gradient elution, PE/EE 7/1 to 5/1). W Light yellow solid (104.4 mg, 77% yield). **^{1}H NMR (400 MHz, acetone-d_6) δ** 7.52 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.07 (m, 7H), 6.82 (s, 2H). **^{13}C NMR (101 MHz, acetone-d_6) δ** 163.27, 138.34, 132.06, 131.06, 130.92, 129.60, 128.58, 124.95, 121.86, 120.75, 114.25. **IR ATR (ν_{max}/cm^{-1})** 3446, 3308, 3203, 2224, 1655, 1067, 695.



2-Amino-4-(naphthalen-1-yl)-5-phenylfuran-3-carbonitrile, (**4g**). Purified by column chromatography (silica gel, gradient elution, PE/EE 7/1 to 5/1). Light yellow oil (98.0 mg, 79% yield). **^{1}H NMR (400 MHz, acetone-d_6) δ** 77.94 – 7.84 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.39 (m, 3H), 7.34 (t, *J* = 8.3 Hz, 1H), 7.01 – 6.93 (m, 5H), 6.88 (s, 2H). **^{13}C NMR (101 MHz, acetone-d_6) δ** 162.96, 134.06, 131.68, 129.82, 129.38, 129.05, 128.54, 128.36, 128.01, 126.71, 126.61, 126.32, 125.78, 125.31, 123.67, 120.25, 114.15, 73.02. **IR ATR (ν_{max}/cm^{-1})** 3451, 3321, 3200, 2211, 1452, 1201, 1080, 780, 698. **HRMS (ESI)** Cald for $C_{21}H_{14}N_2ONa$ $[M + Na]^+$ 333.1004, Found 333.1006.

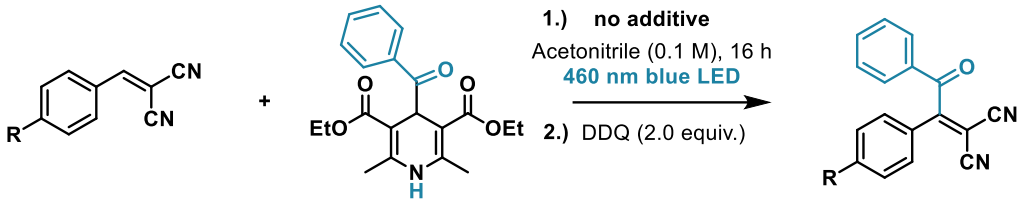
4.5.2. One-pot synthesis of dihydrofuran 4h



2a (1.0 equiv.) + **1a** (1.2 equiv.) → **4h**

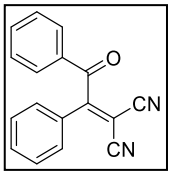
Into an 8 mL Schlenk tube, Hantzsch ester **1a** (85.8 mg, 0.24 mmol, 1.2 equiv.) and benzylidene malononitrile (**2a**, 30.8 mg, 0.2 mmol, 1.0 equiv.) were added. The Schlenk tube was evacuated and back-filled with argon, and acetonitrile (2.0 mL) was added *via* syringe under argon counterflow. The tubes were sealed and placed into a custom made photoreactor. The reaction mixtures were stirred under blue light irradiation (λ_{max} = 460 nm) for 16 hours. The tube was removed from the photoreactor, two parallel runs were merged and the solvent was removed *in vacuo*. Anhydrous MeOH (2.0 mL) and $NaBH_4$ (22.8 mg, 0.6 mmol, 3.0 equiv.) were added. The reaction mixture was stirred for 4 hours (*TLC indicated full conversion*), after which Et_3N (55.8 µL, 0.4 mmol, 2.0 equiv.) was added and the mixture was stirred for another 3 hours. Two parallel runs were merged, the remaining the $NaBH_4$ was hydrolyzed with H_2O (1.0 mL), and the MeOH was removed *in vacuo*. Water (3.0 mL) and DCM (5.0 mL) were added and the aqueous phase was washed with DCM (3 × 3.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, gradient elution, PE/EE 7/1 to 3/1), affording **4h** as a white solid (83 mg, 79% yield). **^{1}H NMR (400 MHz, acetone-d_6) δ** 7.11 – 6.97 (m, 8H), 6.94 (d, *J* = 9.5 Hz, 2H), 6.65 (s, 2H), 6.03 (d, *J* = 8.8 Hz, 1H), 4.60 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR (101 MHz, acetone-d_6) δ** 168.39, 138.99, 136.46, 128.72, 127.66, 127.49, 127.30, 126.67, 126.34, 118.20, 87.53, 55.66, 52.79. **IR ATR (ν_{max}/cm^{-1})** 3450, 3310, 2911, 2200, 1433, 1234, 695.

4.5.3. One-pot synthesis of formal alkenylation products 5a-f

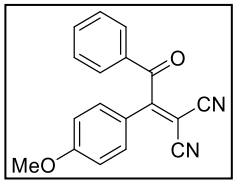


2a-f (1.0 equiv.) **1a** (1.2 equiv.) **5a-f**

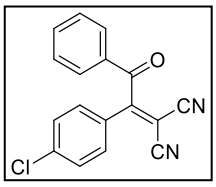
Into an 8 mL Schlenk tube, Hantzsch ester **1a** (85.7 mg, 0.24 mmol, 1.2 equiv.) and substrate **2a**-**e** (0.2 mmol, 1.0 equiv.) were added. The Schlenk tube was evacuated and back-filled with argon, and acetonitrile (2.0 mL) was added *via* syringe under argon counterflow. The tubes were sealed and placed into a custom made photoreactor. The reaction mixtures were stirred under blue light irradiation (λ_{max} = 460 nm) for 16 hours. The tubes were removed from the photoreactor, DDQ (90.8 mg, 0.4 mmol, 2.0 equiv.) was added and the reaction mixtures were stirred at 25˚ C for another 3 hours *(TLC indicated full conversions*). Two parallel runs were merged, the solvent was removed *in vacuo* and the crude products were purified by column chromatography (PE/acetone mixtures as mobile phase) providing the pure products. *In case the Hantzsch ester residue results in product contamination after column chromatography, it can be easily removed by means of short-path Pasteur-column, eluting with dichloromethane (ca. 25 mL for 0.4 mmol scale).*



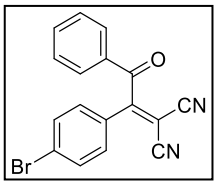
2-(2-Oxo-1,2-diphenylethylidene)malononitrile, (**5a**).[4] Purified by column chromatography (silica gel, PE/acetone 9/1). White solid (88 mg, 85% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.82 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.65 – 7.57 (m, 1H), 7.56 – 7.50 (m, 1H), 7.49 – 7.41 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 190.88, 171.40, 135.79, 133.90, 133.26, 130.02, 129.83, 129.51, 128.61, 111.90, 111.37, 83.91.



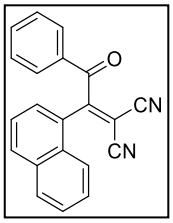
2-(1-(4-Methoxyphenyl)-2-oxo-2-phenylethylidene)malononitrile, (**5b**).[4] Purified by column chromatography (silica gel, PE/acetone 9/1). White solid (95 mg, 82% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.82 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 191.69, 169.91, 164.44, 135.64, 133.58, 131.52, 130.00, 129.45, 122.76, 115.35, 112.81, 112.06, 55.80.



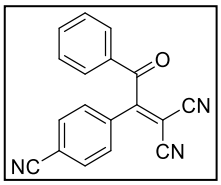
2-(1-(4-Chlorophenyl)-2-oxo-2-phenylethyl)malononitrile, (**5c**).[4] Purified by column chromatography (silica gel, PE/acetone 9/1). White solid (100.8 mg, 86% yield). **^{1}H NMR (400 MHz, CD_2Cl_2) δ** 7.80 (d, *J* = 9.7 Hz, 2H), 7.66 – 7.59 (m, 3H), 7.46 (dd, *J* = 20.6, 8.6 Hz, 4H). **^{13}C NMR (101 MHz, CD_2Cl_2) δ** 190.83, 170.09, 140.51, 136.10, 133.18, 130.28, 130.10, 129.67, 128.95, 111.87, 111.47, 84.64.



2-(1-(4-Bromophenyl)-2-oxo-2-phenylethyl)malononitrile, (**5d**).[4] Purified by column chromatography (silica gel, PE/acetone 9/1). White solid (106.5 mg, 79% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.80 (d, *J* = 1.1 Hz, 2H), 7.65 – 7.52 (m, 5H), 7.45 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 189.54, 139.61, 134.96, 132.03, 129.23, 128.97, 128.86, 128.56, 127.67, 110.10, 83.21.

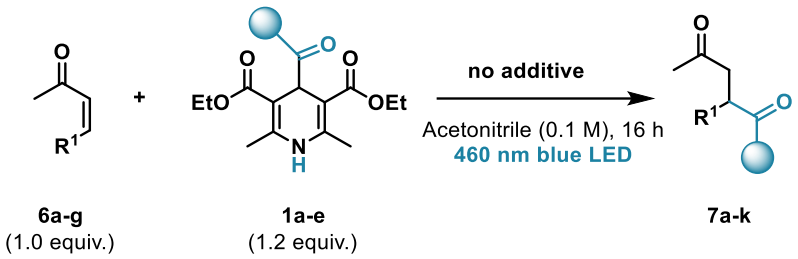


2-(1-(Naphthalen-1-yl)-2-oxo-2-phenylethylidene)malononitrile, (**5e**). Purified by column chromatography (silica gel, PE/acetone 9/1). Pale yellow solid (93.7 mg, 76% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.93 (dd, *J* = 12.5, 8.4 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 3H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (dt, *J* = 15.2, 7.6 Hz, 3H), 7.33 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 190.43, 172.52, 135.52, 133.93, 133.35, 129.79, 129.40, 129.32, 128.92, 128.54, 127.93, 127.41, 125.11, 124.41, 111.37, 111.12, 90.39. **IR ATR (ν_{max}/cm^{-1})** 3057, 2235, 1661, 1256, 801, 678. **HRMS (ESI)** Cald for $C_{21}H_{13}N_2O$ $[M + H]^+$ 309.1028, Found 309.1022.

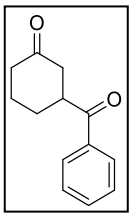


2-(1-(4-Cyanophenyl)-2-oxo-2-phenylethylidene)malononitrile, (**5f**). Purified by column chromatography (silica gel, PE/acetone 9/1). White solid (80.6 mg, 71% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.78 (dd, *J* = 17.4, 6.4 Hz, 6H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 189.75, 169.19, 136.35, 134.21, 133.34, 132.74, 130.02, 129.77, 128.90, 117.15, 116.91, 110.54, 87.23. **IR ATR (ν_{max}/cm^{-1})** 3104, 3065, 2240, 2231, 1672, 1229, 836, 690. **HRMS (ESI)** Cald for $C_{18}H_{10}N_3O$ $[M + H]^+$ 284.0824, Found 284.0421.

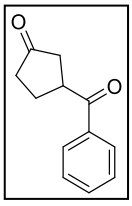
4.6. General procedure and analytical data for the hydroacylation of enones



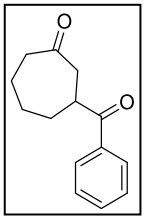
Into an 8 mL Schlenk tube, Hantzsch ester **1a**-**e** (0.24 mmol, 1.2 equiv.) was added. The Schlenk tube was evacuated and back-filled with argon. Acetonitrile (2.0 mL) and substrate **6a**-**g** (0.2 mmol, 1.0 equiv.) were added under argon counterflow. The tubes were sealed and placed into a custom made photoreactor. The reaction mixtures were stirred under blue light irradiation (λ_{max} = 460 nm) for 16 hours. Two parallel runs were merged, the solvent was removed *in vacuo* and the crude products were purified by column chromatography (PE/acetone mixtures as mobile phase) providing the pure products.



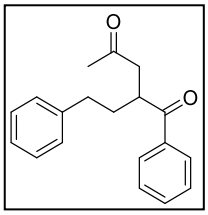
3-Benzoylcyclohexan-1-one, (**7a**).[7] Purified by column chromatography (silica gel, gradient elution, PE/acetone 12/1 to 8/1). Colorless oil (66.3 mg, 82% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.87 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.48 (m, 1H), 7.46 – 7.38 (m, 2H), 3.84 – 3.69 (m, 1H), 2.71 – 2.60 (m, 1H), 2.47 – 2.29 (m, 3H), 2.11 – 1.99 (m, 2H), 1.86 – 1.72 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 210.25, 200.42, 135.36, 133.51, 128.88, 128.40, 45.19, 43.17, 41.02, 28.42, 24.83.



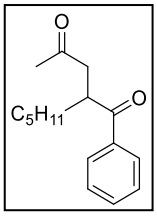
3-Benzoylcyclopentan-1-one, (**7b**).[7] Purified by column chromatography (silica gel, gradient elution, PE/acetone 12/1 to 8/1). Colorless oil (62.6 mg, 85% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.93 (d, *J* = 7.1 Hz, 2H), 7.60 – 7.50 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 4.06 (p, *J* = 7.5 Hz, 1H), 2.63 (dd, *J* = 19.1, 7.5 Hz, 1H), 2.43 – 2.17 (m, 4H), 2.09 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 216.88, 200.24, 135.61, 133.57, 128.89, 128.47, 43.04, 40.98, 37.34, 26.99.



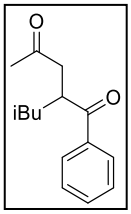
3-Benzoylcycloheptan-1-one, (**7c**).[7] Purified by column chromatography (silica gel, gradient elution, PE/acetone gradient from 12/1 to 8/1). Colorless oil (72.7 mg, 84% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.92 – 7.81 (m, 2H), 7.55 – 7.48 (m, 1H), 7.46 – 7.37 (m, 2H), 3.53 (t, *J* = 10.5 Hz, 1H), 2.87 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.62 – 2.42 (m, 3H), 2.07 (d, *J* = 12.7 Hz, 1H), 2.00 – 1.83 (m, 2H), 1.77 – 1.61 (m, 2H), 1.53 – 1.40 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 212.93, 201.41, 135.30, 133.33, 128.84, 128.39, 45.36, 44.00, 43.22, 33.81, 28.19, 23.85.



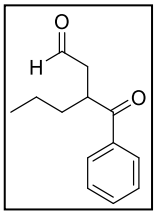
2-Phenethyl-1-phenylpentane-1,4-dione, (**7d**).[8] Purified by column chromatography (silica gel, gradient elution, PE/acetone 15/1 to 12/1). Colorless oil (88.6 mg, 79% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.86 – 7.80 (m, 2H), 7.51 – 7.45 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.09 (m, 1H), 7.02 (d, *J* = 8.3 Hz, 2H), 3.89 (d, *J* = 9.3 Hz, 1H), 3.12 (dd, *J* = 18.0, 9.1 Hz, 1H), 2.65 – 2.43 (m, 3H), 2.10 (s, 3H), 2.02 – 1.87 (m, 1H), 1.78 – 1.64 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 207.04, 202.96, 141.08, 136.57, 133.02, 128.63, 126.17, 45.08, 40.70, 33.80, 33.35, 30.10.



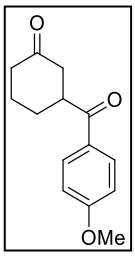
2-Pentyl-1-phenylpentane-1,4-dione, (**7e**).[8] Purified by column chromatography (silica gel, gradient elution, PE/acetone 15/1 to 12/1). Colorless oil (75.9 mg, 77% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.91 (d, *J* = 7.1 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.39 (t, *J* = 7.9 Hz, 2H), 3.89 – 3.80 (m, 1H), 3.08 (dd, *J* = 18.0, 9.3 Hz, 1H), 2.53 (dd, *J* = 18.0, 4.2 Hz, 1H), 2.09 (s, 3H), 1.64 – 1.54 (m, 1H), 1.41 – 1.30 (m, 1H), 1.23 – 1.12 (m, 6H), 0.80 – 0.72 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 207.39, 203.36, 136.80, 132.89, 128.60, 128.41, 45.11, 41.28, 32.27, 31.76, 30.10, 26.83, 22.40, 13.95.



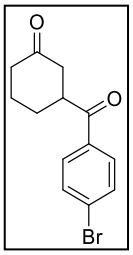
2-Isopropyl-1-phenylpentane-1,4-dione, (**7f**). Purified by column chromatography (silica gel, PE/EE gradient from 16/1 to 13/1). Colorless oil (74.3 mg, 80% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.92 (d, *J* = 9.7 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.44 – 7.36 (m, 2H), 3.99 – 3.88 (m, 1H), 3.05 (dd, *J* = 18.0, 9.4 Hz, 1H), 2.53 (dd, *J* = 18.0, 4.1 Hz, 1H), 2.09 (s, 3H), 1.55 – 1.42 (m, 2H), 1.26 – 1.16 (m, 1H), 0.86 (d, *J* = 6.3 Hz, 3H), 0.81 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 207.35, 203.66, 136.74, 132.90, 128.62, 128.44, 41.44, 39.43, 30.09, 25.99, 23.12, 22.06. **IR ATR (ν_{max}/cm^{-1})** 3041, 3010, 1702, 1681, 1224, 692. **HRMS (ESI)** Cald for $C_{15}H_{20}O_2Na$ $[M + Na]^+$ 255.1361, Found 255.1355.



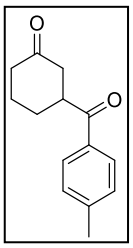
3-Benzoylhexanal, (**7g**).[9] Purified by column chromatography (silica gel, gradient elution, PE/acetone 16/1 to 13/1). Colorless oil (67.7 mg, 83% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 9.80 (s, 1H), 8.04 – 7.94 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.05 – 3.89 (m, 1H), 3.17 (dd, *J* = 18.5, 9.0 Hz, 1H), 2.66 (dd, *J* = 18.5, 4.8 Hz, 1H), 1.74 – 1.65 (m, 1H), 1.51 – 1.41 (m, 1H), 1.36 – 1.27 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 201.53, 199.71, 132.09, 127.67, 127.38, 44.36, 38.88, 33.48, 19.34, 13.01.



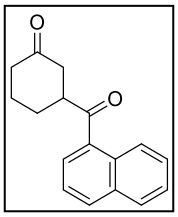
3-(4-Methoxybenzoyl)cyclohexan-1-one, (**7h**).[10] Purified by column chromatography (silica gel, gradient elution, PE/acetone 10/1 to 7/1). Colorless oil (70.6 mg, 76% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.86 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H), 3.76 – 3.64 (m, 1H), 2.65 (dd, *J* = 15.3, 10.9 Hz, 1H), 2.39 (s, 3H), 2.10 – 1.95 (m, 2H), 1.86 – 1.70 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 210.53, 198.87, 163.83, 130.73, 128.27, 114.04, 55.54, 44.88, 43.36, 41.04, 28.58, 24.91.



3-(4-Bromobenzoyl)cyclohexan-1-one, (**7i**).[7] Purified by column chromatography (silica gel, gradient elution, PE/acetone 10/1 to 7/1). White solid (90.0 mg, 80% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.74 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 3.70 (d, *J* = 10.2 Hz, 1H), 2.63 (dd, *J* = 15.5, 10.8 Hz, 1H), 2.45 – 2.25 (m, 3H), 2.03 (d, *J* = 9.4 Hz, 2H), 1.88 – 1.73 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 209.86, 199.41, 134.04, 132.23, 129.91, 128.77, 45.15, 43.04, 40.96, 28.33, 24.75.

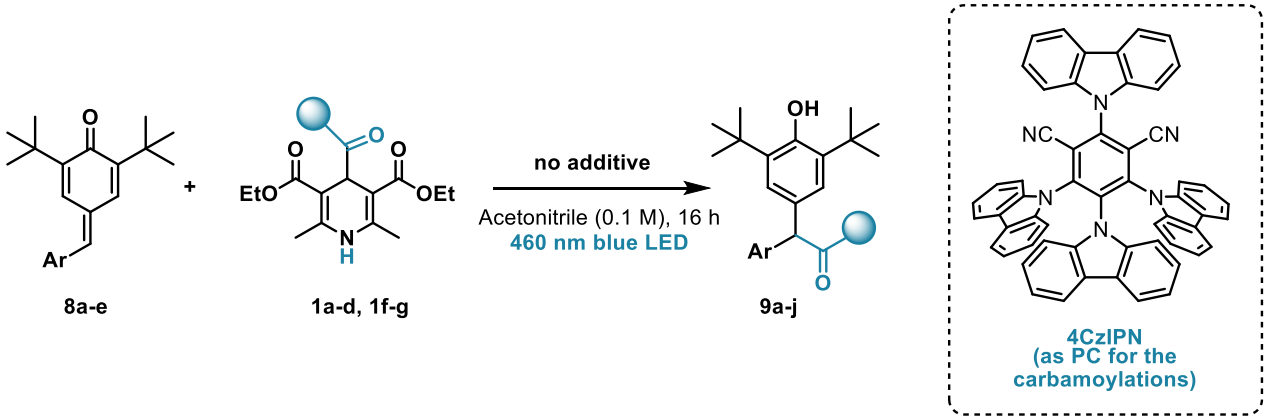


3-(4-Methylbenzoyl)cyclohexan-1-one, (**7j**).[7] Purified by column chromatography (silica gel, gradient elution, PE/acetone 10/1 to 7/1). Light yellow oil (68.0 mg, 79% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.77 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.73 (d, *J* = 6.1 Hz, 1H), 2.64 (dd, *J* = 14.9, 11.2 Hz, 1H), 2.35 (s, 6H), 2.03 (d, *J* = 9.0 Hz, 2H), 1.86 – 1.66 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 210.42, 200.02, 144.43, 132.82, 129.56, 128.53, 45.08, 43.25, 41.03, 28.50, 24.87, 21.67.

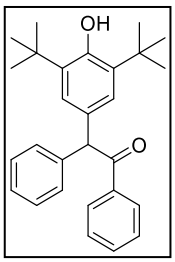


3-Benzoylcyclohexan-1-one, (**7k**). Purified by column chromatography (silica gel, gradient elution, PE/acetone 10/1 to 7/1). Light yellow oil (74.6 mg, 74% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.31 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.56 – 7.39 (m, 3H), 3.72 (dd, *J* = 14.6, 6.6 Hz, 1H), 2.73 (dd, *J* = 14.7, 11.0 Hz, 1H), 2.51 (dd, *J* = 14.6, 4.4 Hz, 1H), 2.39 – 2.32 (m, 2H), 2.09 – 1.99 (m, 2H), 1.85 – 1.65 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 210.26, 204.54, 135.28, 134.00, 132.70, 130.47, 128.55, 128.03, 126.72, 125.45, 124.41, 49.07, 41.07, 28.13, 24.94. **IR ATR (ν_{max}/cm^{-1})** 3049, 2960, 1709, 1675, 1507, 1224, 778, 729. **HRMS (ESI)** Cald for $C_{17}H_{16}O_2Na$ $[M + Na]^+$ 275.1048, Found 275.1043.

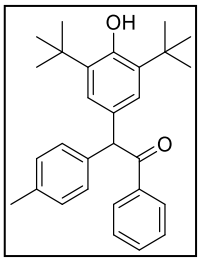
4.7. General procedure and analytical data for the hydroacylation of *para*-quinone methides



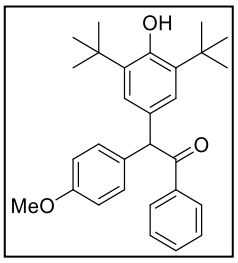
Into an 8 mL Schlenk tube, Hantzsch ester **1a-d** or **1f-g** (85.0 mg, 0.24 mmol, 1.2 equiv.) and substrate **8a**-**e** (0.2 mmol, 1.0 equiv.) were added. The Schlenk tube was evacuated and back-filled with argon and a 1/1 mixture of acetonitrile and DCM (2.0 mL) was added *via* syringe under argon counterflow. The tubes were sealed and placed into a custom made photoreactor. The reaction mixtures were stirred under blue light irradiation (λ_{max} = 460 nm) for 16 hours. The solvent was removed *in vacuo* and the crude products were purified by column chromatography (PE/EE mixtures as mobile phase).



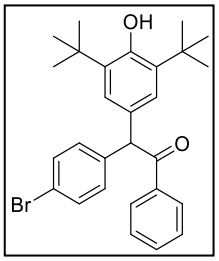
2-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-1,2-diphenylethan-1-one, (**9a**).[11] Purified by column chromatography (silica gel, gradient elution, PE/EE 40/1 to 20/1). Light yellow solid (68.9 mg, 86% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.92 (d, *J* = 8.6 Hz, 2H), 7.43 – 7.36 (m, 1H), 7.34 – 7.28 (m, 2H), 7.22 (d, *J* = 4.4 Hz, 4H), 7.17 – 7.11 (m, 1H), 6.99 (s, 2H), 5.86 (s, 1H), 5.04 (s, 1H), 1.30 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 198.85, 152.92, 139.79, 137.30, 132.82, 129.51, 129.11, 128.96, 128.68, 128.58, 126.96, 125.89, 59.33, 34.41, 30.34.



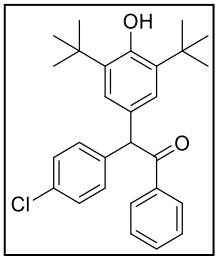
2-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-1-phenyl-2-(p-tolyl)ethan-1-one, (**9b**).[11] Purified by column chromatography (silica gel, gradient elution, PE/EE 40/1 to 20/1). Light yellow oil (65.5 mg, 79% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.92 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.99 (s, 2H), 5.82 (s, 1H), 5.03 (s, 1H), 2.22 (s, 3H), 1.31 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** 197.91, 151.78, 136.27, 135.69, 135.46, 134.74, 131.66, 128.60, 128.32, 127.85, 127.46, 124.76, 57.92, 33.33, 29.27, 20.02.



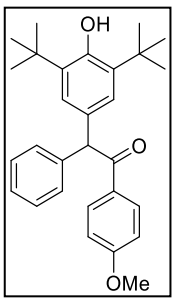
2-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)-1-phenylethan-1-one, (**9c**).[11] Purified by column chromatography (silica gel, gradient elution, PE/EE 40/1 to 20/1). Light yellow solid (70.6 mg, 82% yield). **^{1}H NMR (400 MHz, CD_2Cl_2) δ** 7.90 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.97 (s, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 5.81 (s, 1H), 5.08 (s, 1H), 3.67 (s, 3H), 1.30 (s, 18H). **^{13}C NMR (101 MHz, CD_2Cl_2) δ** 198.75, 158.65, 152.81, 137.22, 136.05, 132.74, 131.87, 129.99, 128.75, 128.51, 125.73, 113.96, 58.39, 55.18, 34.27, 29.99.



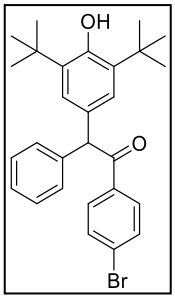
2-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)-1-phenylethan-1-one, (**9d**). Purified by column chromatography (silica gel, gradient elution, PE/EE 40/1 to 20/1). White solid (77.0 mg, 80% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.90 (d, *J* = 8.6 Hz, 2H), 7.44 (t, *J* = 6.7 Hz, 1H), 7.35 (dd, *J* = 8.2, 4.5 Hz, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.97 (s, 2H), 5.81 (s, 1H), 5.07 (s, 1H), 1.31 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 198.41, 153.06, 138.96, 137.01, 136.14, 133.01, 131.67, 128.90, 128.63, 125.68, 121.00, 58.61, 34.41, 30.29. **IR ATR (ν_{max}/cm^{-1})** 3628, 2956, 2915, 1682, 1434, 1234, 687. **HRMS (ESI)** Cald for $C_{28}H_{32}BrO_2$ $[M + H]^+$ 479.1586, Found 479.1580.



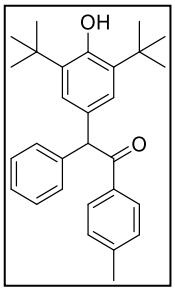
2-(4-Chlorophenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-phenylethan-1-one, (**9e**).[11] Purified by column chromatography (silica gel, gradient elution, PE/EE 40/1 to 20/1). Light yellow oil (66.0 mg, 76% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.90 (d, *J* = 8.6 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 (s, 2H), 7.22 – 7.18 (m, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.96 (s, 2H), 5.83 (s, 1H), 5.07 (s, 1H), 1.30 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 197.36, 152.01, 137.89, 135.92, 135.06, 130.62, 129.77, 127.85, 127.58, 124.62, 119.95, 57.55, 33.35, 29.23.



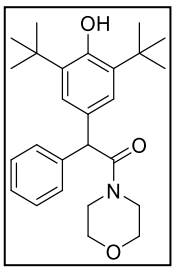
2-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-2-phenylethan-1-one, (**9f**). Purified by column chromatography (silica gel, gradient elution, PE/EE 50/1 to 20/1). Light yellow solid (68.8 mg, 73% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.92 (d, *J* = 9.0 Hz, 2H), 7.22 (d, *J* = 4.4 Hz, 4H), 7.13 (d, *J* = 4.2 Hz, 1H), 6.99 (s, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 5.82 (s, 1H), 5.03 (s, 1H), 3.72 (s, 3H), 1.30 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 197.35, 163.28, 152.83, 140.11, 135.80, 131.27, 130.20, 129.81, 129.09, 128.62, 126.85, 125.88, 113.75, 58.96, 55.45, 34.40, 30.35. **IR ATR (ν_{max}/cm^{-1})** 3622, 2951, 2907, 1678, 1430, 1241, 690. **HRMS (ESI)** Cald for $C_{29}H_{35}O_3$ $[M + H]^+$ 431.2586, Found 431.2579.



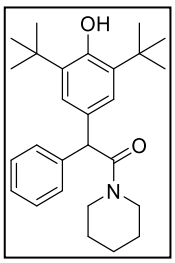
2-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-1,2-diphenylethan-1-one, (**9g**). Purified by column chromatography (silica gel, gradient elution, PE/EE 50/1 to 20/1). White solid (74.9 mg, 78% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.78 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.27 – 7.15 (m, 5H), 6.96 (s, 2H), 5.78 (s, 1H), 5.06 (s, 1H), 1.31 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 196.75, 151.95, 138.34, 134.95, 134.84, 130.82, 129.43, 128.00, 127.67, 126.91, 126.04, 124.74, 75.67, 58.38, 33.35, 29.25. **IR ATR (ν_{max}/cm^{-1})** 3622, 2952, 2917, 1680, 1434, 1236, 687. **HRMS (ESI)** Cald for $C_{28}H_{32}BrO_2$ $[M + H]^+$ 479.1586, Found 479.1582.



2-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-2-phenyl-1-(*p*-tolyl)ethan-1-one, (**9h**). Purified by column chromatography (silica gel, gradient elution, PE/EE 80/1 to 30/1). White solid (58.0 mg, 70% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.84 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 4.4 Hz, 4H), 7.10 (s, 3H), 6.99 (s, 2H), 5.85 (s, 1H), 5.03 (s, 1H), 2.27 (s, 3H), 1.30 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 198.42, 152.86, 143.61, 139.96, 135.81, 134.75, 129.67, 129.27, 129.10, 128.63, 125.89, 59.16, 34.40, 30.34, 21.64. **IR ATR (ν_{max}/cm^{-1})** 3610, 2966, 2861, 1683, 1433, 1234, 720, 695. **HRMS (ESI)** Cald for $C_{29}H_{35}O_2$ $[M + H]^+$ 415.2637, Found 415.2629.



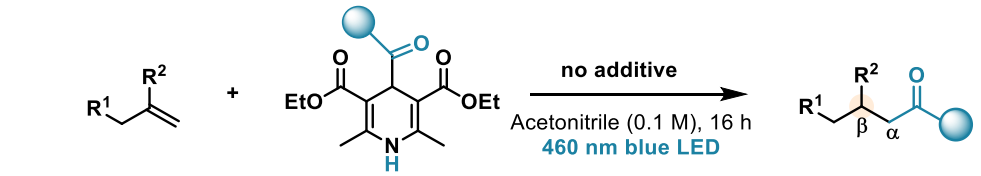
2-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-1-morpholino-2-phenylethan-1-one, (**9i**). The reaction was carried out in the presence of 2 mol% 4CzIPN as additional photocatalyst. Purified by column chromatography (silica gel, gradient elution, PE/EE 12/1 to 4/1). Pale white solid (50.8 mg, 62% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.27 – 7.20 (m, 2H), 7.16 (d, *J* = 7.7 Hz, 3H), 6.93 (s, 2H), 5.06 (s, 1H), 4.98 (m, 1H), 3.64 (m, 1H), 3.55 (m, 3H), 3.37 (m, 2H), 3.24 (m, 2H), 1.32 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 170.98, 152.81, 140.00, 135.86, 129.68, 128.95, 128.50, 126.86, 125.63, 66.37, 54.80, 46.57, 42.62, 34.39, 30.35. **IR ATR (ν_{max}/cm^{-1})** 3648, 3520, 2941, 2861, 1629, 1435, 1113, 700. **HRMS (ESI)** Cald for $C_{26}H_{36}NO_3$ $[M + H]^+$ 410.2695, Found 410.2690.



2-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-1-morpholino-2-phenylethan-1-one, (**9j**). The reaction was carried out in the presence of 2 mol% 4CzIPN as additional photocatalyst. Purified by column chromatography (silica gel, gradient elution, PE/EE 12/1 to 8/1). Light yellow solid (46.5 mg, 57% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.25 – 7.17 (m, 4H), 7.13 (s, 1H), 6.95 (s, 2H), 5.03 (s, 2H), 3.61 (s, 1H), 3.48 – 3.19 (m, 3H), 1.44 (s, 4H), 1.32

(s, 18H), 1.08 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 169.43, 151.57, 139.48, 134.57, 129.21, 127.29, 125.54, 124.73, 53.79, 46.14, 42.32, 33.32, 29.31, 24.86, 24.58, 23.52. **IR ATR (ν_{max}/cm^{-1})** 3625, 3529, 2941, 2854, 1629, 1434, 1112, 699. **HRMS (ESI)** Cald for $C_{27}H_{38}NO_2$ $[M + H]^+$ 408.2903, Found 408.2907.

4.8. General procedure and analytical data for extending the photocatalyst– and additive-free hydroacylation towards unactivated alkenes

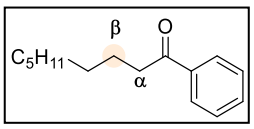


10a $R^1 = C_5H_{11}$, R^2 = H
10b $R^1 = C_4H_{19}$, R^2 = Me
12 $R^1 = CH(COOEt)_2$, R^2 = H
(1.0 equiv.)

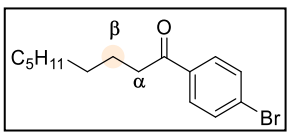
1a, 1c-d
(1.2 equiv.)

11a-d, 13

Into an 8 mL Schlenk tube, Hantzsch ester **1a** or **1c-d** (0.24 mmol, 1.2 equiv.) was added. The Schlenk tube was evacuated and back-filled with argon. Acetonitrile (2.0 mL) and substrate **10a**-**b** or **12** (0.2 mmol, 1.0 equiv.) were added under argon counterflow. The tubes were sealed and placed into a custom made photoreactor. The reaction mixtures were stirred under blue light irradiation (λ_{max} = 460 nm) for 16 hours. Two parallel runs were merged, the solvent was removed *in vacuo* and the crude products were purified by column chromatography (PE/EE mixtures as mobile phase) providing the pure products.

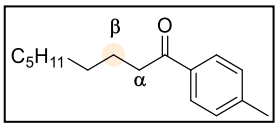


1-Phenylnonan-1-one, (**11a**).[12] Prepared from *n*-octene (**10a**). Purified by column chromatography (silica gel, PE/EE 60/1). Colorless oil (41.8 mg, 48% yield). The ratio of α and β regioisomers was >99/1, the orange circle represents the formation of the minor regioisomer. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.89 (d, *J* = 8.3 Hz, 2H), 7.48 (t, *J* = 6.7 Hz, 1H), 7.42 – 7.36 (m, 2H), 2.92 – 2.86 (m, 2H), 1.72 – 1.62 (m, 2H), 1.20 (s, 10H), 0.82 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 200.65, 137.13, 132.86, 128.55, 128.07, 38.66, 31.85, 29.46, 29.41, 29.19, 24.41, 22.67, 14.11.

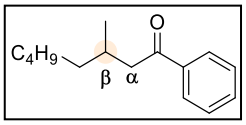


1-(4-Bromophenyl)nonan-1-one, (**11b**).[13] Prepared from *n*-octene (**10a**). Purified by column chromatography (silica gel, PE/EE 60/1). White solid (53.5 mg, 45% yield). The ratio of α and β regioisomers was 95/5, the orange circle represents the formation of the minor regioisomer. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.75 (d, *J* = 8.7 Hz, 2H),

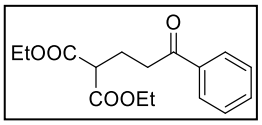
7.53 (d, *J* = 8.7 Hz, 2H), 2.90 – 2.74 (m, 2H), 1.66 (q, *J* = 7.7 Hz, 2H), 1.21 (s, 10H), 0.80 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 199.53, 135.81, 131.87, 129.62, 127.99, 38.61, 31.84, 29.43, 29.34, 29.16, 24.30, 22.66, 14.11.



1-(4-Methylphenyl)nonan-1-one, (**11c**).[12] Prepared from *n*-octene (**10a**). Purified by column chromatography (silica gel, PE/EE 60/1). White solid (40.2 mg, 43% yield). The ratio of α and β regioisomers was >99/1, the orange circle represents the formation of the minor regioisomer. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.78 (d, *J* = 10.3 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 3H), 2.90 – 2.81 (m, 2H), 2.34 (s, 3H), 1.69 – 1.61 (m, 2H), 1.20 (s, 10H), 0.82 (d, *J* = 6.9 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 200.35, 143.58, 134.66, 129.22, 128.21, 38.56, 31.86, 29.47, 29.43, 29.19, 24.54, 22.67, 21.62, 14.11.

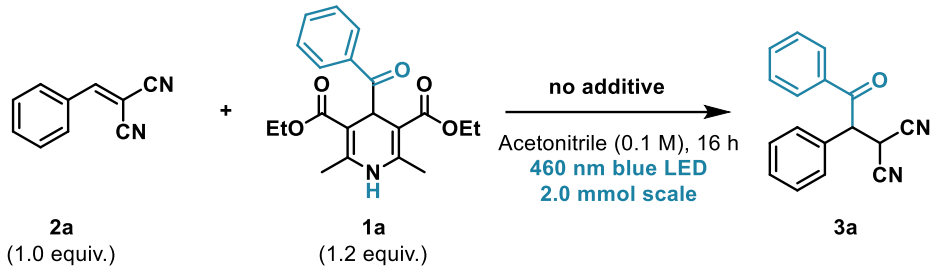


3-Methyl-1-phenyloctan-1-one, (**11d**).[14] Prepared from 2-methyl-1-heptene (**10b**). Purified by column chromatography (silica gel, PE/EE 60/1), resulting in inseparable isomeric mixture. Colorless oil (34.9 mg, 40% yield). The ratio of α and β regioisomers was 9/1, the orange circle represents the formation of the minor regioisomer. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.93 – 7.85 (m, 2H), 7.51 – 7.45 (m, 1H), 7.41 – 7.36 (m, 2H), 3.59 (d, *J* = 18.7 Hz, 1H), 2.88 (dd, *J* = 15.7, 5.7 Hz, 1H), 2.68 (dd, *J* = 15.8, 8.0 Hz, 1H), 1.23 (s, 10H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.83 – 0.78 (m, 3H), for the major α regioisomer. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 200.55, 143.89, 133.06, 128.56, 128.11, 46.04, 37.14, 32.02, 29.84, 26.71, 22.66, 20.04, 14.09, for the major α regioisomer.



Diethyl 2-(3-oxo-3-phenylpropyl)malonate, (**13**).[12] Prepared from diethyl-2-allylmalonate (**12**). Purified by column chromatography (silica gel, PE/EE 60/1). Colorless oil. (37.4 mg, 32% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.88 (d, *J* = 7.0 Hz, 2H), 7.53 – 7.46 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 4H), 3.32 (t, *J* = 7.5 Hz, 1H), 2.95 (t, *J* = 7.3 Hz, 2H), 1.97 – 1.89 (m, 2H), 1.73 (dd, *J* = 15.3, 7.7 Hz, 2H), 1.21 (d, *J* = 7.1 Hz, 6H).**^{13}C NMR (101 MHz, $CDCl_3$) δ** 199.40, 169.33, 136.86, 133.07, 128.62, 127.78, 61.43, 51.97, 38.05, 28.34, 21.91, 14.09.

5. Scale-up experiment for the hydroacylation of 2a



2a (1.0 equiv.) **1a** (1.2 equiv.) **3a**

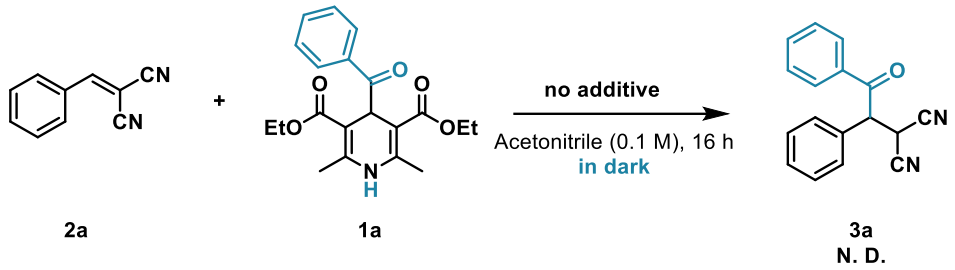
A 25 mL round-bottom microwave vial (Biotage) was used to maximize the light penetration area. Hantzsch ester **1a** (850.0 mg, 2.4 mmol, 1.2 equiv.) and substrate **2a** (308.3 mg, 2.0 mmol, 1.0 equiv.) were added, the vial was sealed and it was evacuated and back-filled with argon *via* a needle (5×). Then, acetonitrile (20.0 mL) was added *via* syringe. The vial was placed into a custom made photoreactor and the reaction mixture was stirred under blue light irradiation (λ_{max} = 460 nm) for 16 hours. The solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica gel, PE/EE 10/1), providing **3a** as a light yellow oil (442 mg, 85% yield).

The scale-up reaction was carried out the same custom-made photoreactor. Nevertheless, a custom-made lid needed to be used as a result of the different vial configuration. A simple white plastic lid was used to maximize light reflectance and intensity. In this case, the reactor was cooled with an external fan and by compressed air. The reactor temperature was 30 °C. The reaction setup is illustrated on Figure S2.

Figure S2. Scale-up experiment for the hydroacylation of **2a**: microwave vial (left), and the reaction setup (middle and right).

6. Mechanistic Considerations

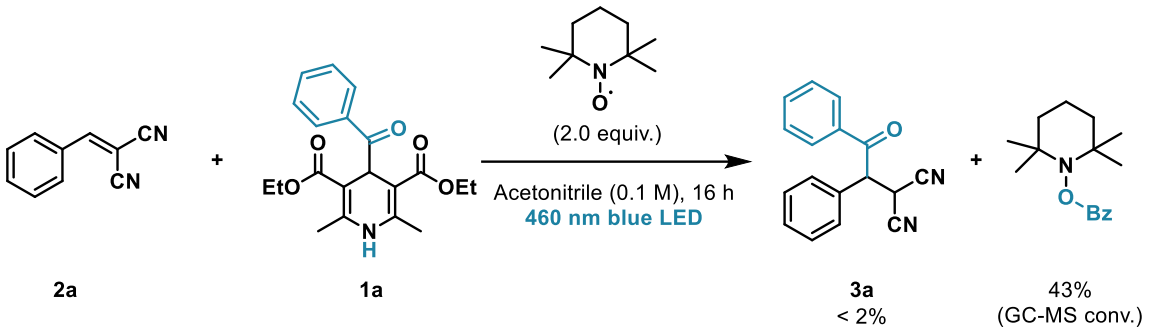
6.1. Control experiment without light irradiation



2a 1a 3a
N. D.

Into an 8 mL Schlenk tube being carefully wrapped into aluminum foil, Hantzsch ester **1a** (85.8 mg, 0.24 mmol, 1.2 equiv.) and substrate **2a** (30.83 mg, 0.2 mmol, 1.0 equiv.) were added, and they were dissolved in 2.0 mL acetonitrile under argon counterflow. After 16 hours reaction time, no product formation could be observed.

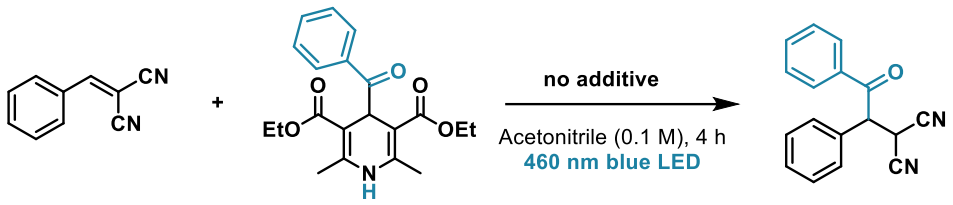
6.2. Control experiment in the presence of a radical scavenger



2a 1a 3a
< 2% 43%
(GC-MS conv.)

Into an 8 mL Schlenk tube, Hantzsch ester **1a** (85.8 mg, 0.24 mmol, 1.2 equiv.), substrate **2a** (30.83 mg, 0.2 mmol, 1.0 equiv.) and TEMPO as radical scavenger (62.4 mg, 0.4 mmol, 2.0 equiv.) were added, and they were dissolved in 2.0 mL acetonitrile under argon counterflow. The product formation was almost completely inhibited as only 2% product could be obtained after 16 hours of irradiation time at 460 nm; meanwhile, the corresponding TEMPO-Bz adduct could be detected *via* GC-MS.

6.3. Light on-off kinetic experiment



2a **1a** **3a**

Into an 8 mL Schlenk tube, Hantzsch ester **1a** (85.8 mg, 0.24 mmol, 1.2 equiv.) and substrate **2a** (30.83 mg, 0.2 mmol, 1.0 equiv.) were added, followed by the addition of 2.0 mL acetonitrile under argon counterflow. The reaction was irradiated for 15 minutes intervals (light on, yellow), followed by another 15 minutes dark periods (light off, grey) for a total of 240 minutes (Figure S3). In every 15 minutes, a sample was taken, and the conversions have been determined by GC-MS analysis (*brown glass vials have been used*). As the reaction basically did not proceed in the light-off periods, it can be basically excluded, that long-living radicals would contribute in the product formation.

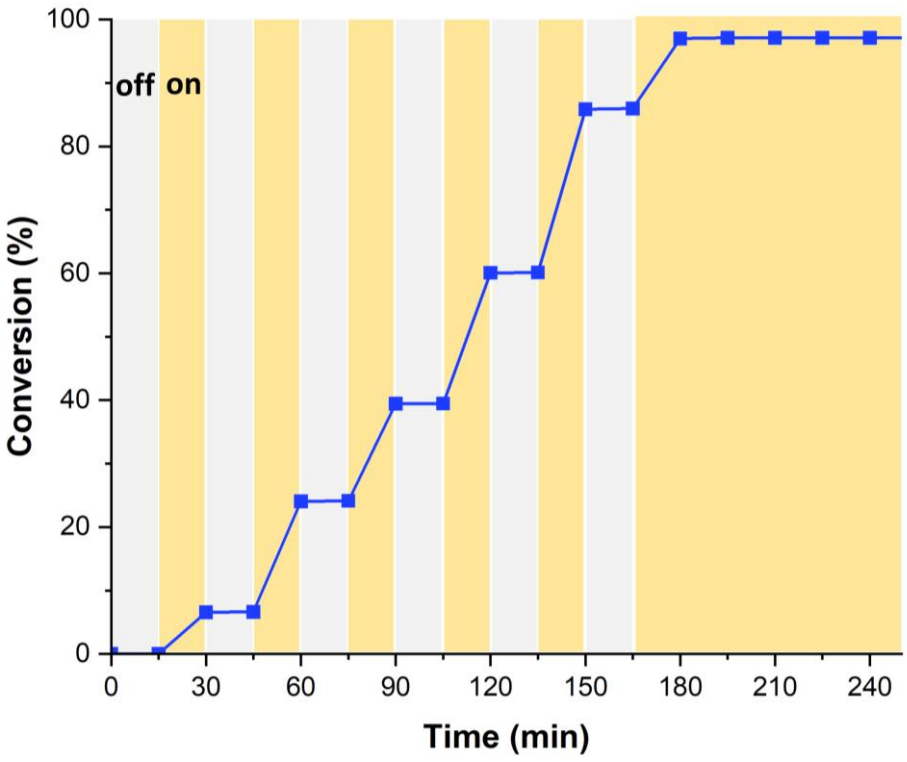


Figure S3. Light on-off kinetic experiment for the hydroacylation of **2a**.

6.4. UV-VIS measurements

In order to investigate, if there is an electron donor-acceptor (EDA) complex-formation between the Hantzsch esters and the substrate, UV-VIS measurements for **1a**, **2a** and **1a + 2a** mixtures have been carried out, respectively. The absorption spectra of the mixture showed no bathochromic shift as it was basically identical with the absorption spectra of **1a** (Figure S4). This strongly indicates, that there is no significant EDA complex-formation and therefore the reaction most likely proceeds *via* direct photoexcitation of the Hantzsch esters.

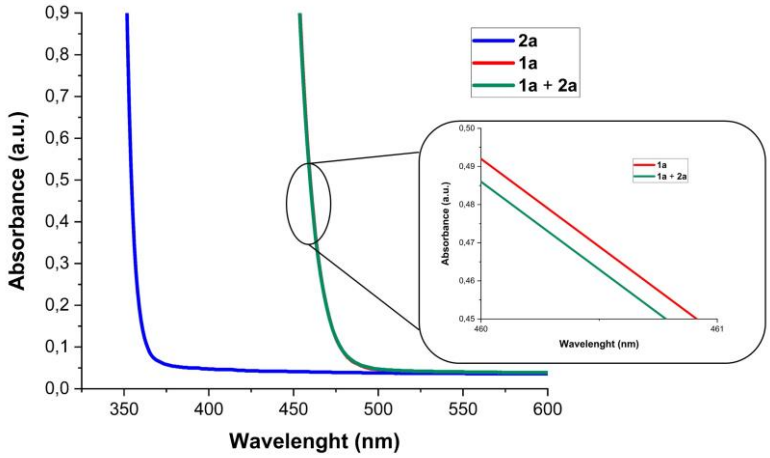


Figure S4. UV-VIS absorption spectra of benzylidene malononitrile (**2a**), Hantzsch ester **1a** and their equimolar mixture. The spectra were as 0.05 M solutions in acetonitrile in 1 cm path length quartz cuvettes (quartz SUPRASIL, Hellma Analytics).

6.5. Fluorescence quenching experiment

Fluorescence measurements were carried out on a PerkinElmer LS 55 luminescence spectrometer using quartz cuvettes (1 cm path length, quartz SUPRASIL, Hellma Analytics) in acetonitrile.

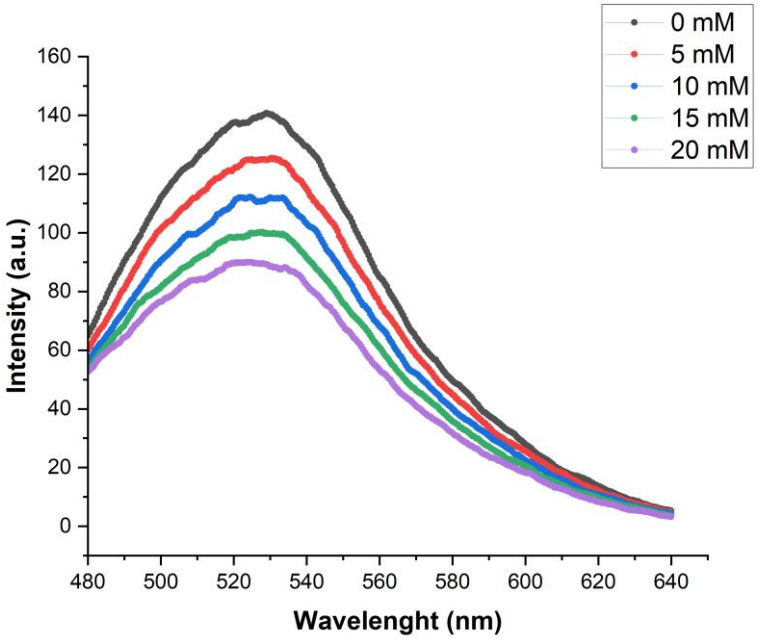


Figure S5. Emission spectra of Hantzsch ester **1a** (top line, grey, 0.15 M) recorded in an increasing concentration of benzylidene malononitrile (**2a**) at an excitation wavelength of λ_{max} = 365 nm.

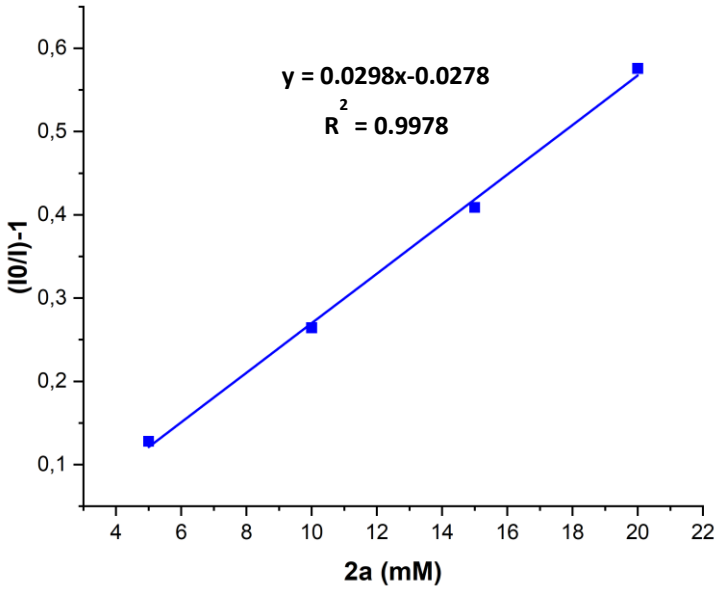
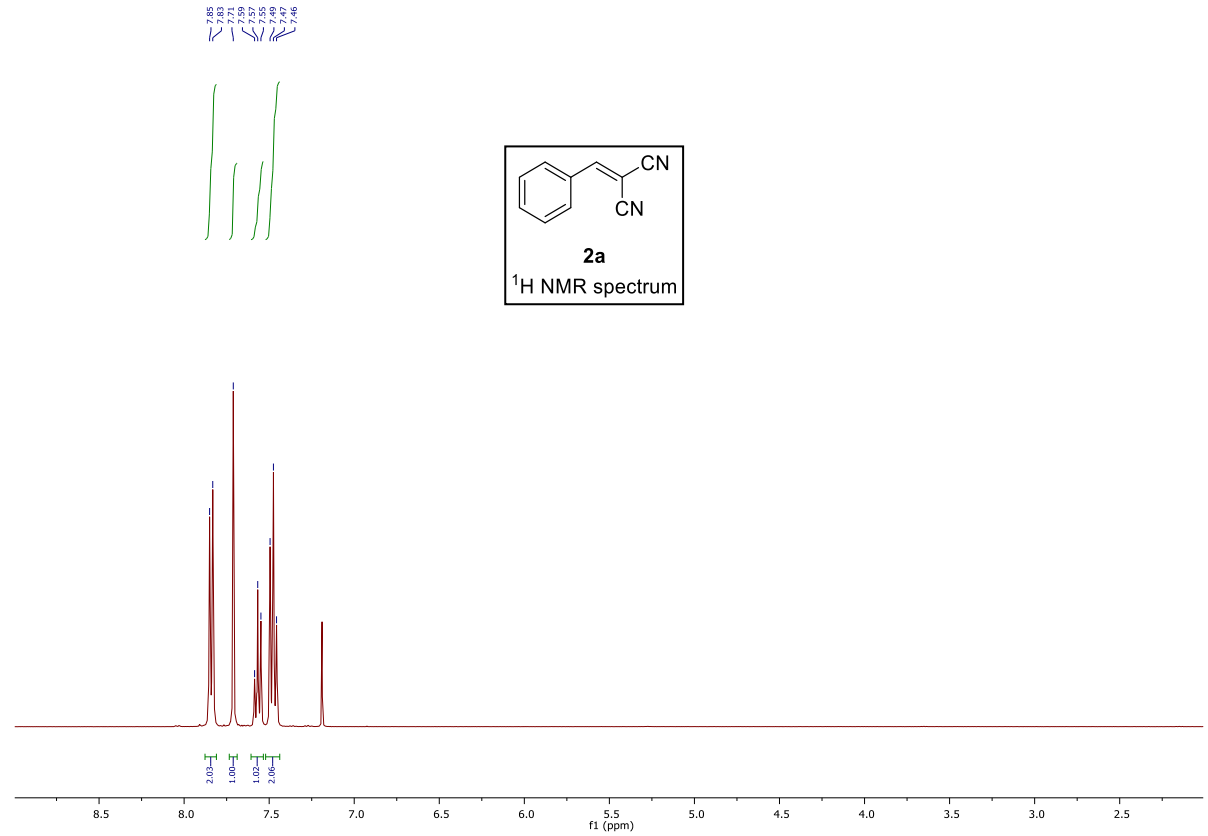
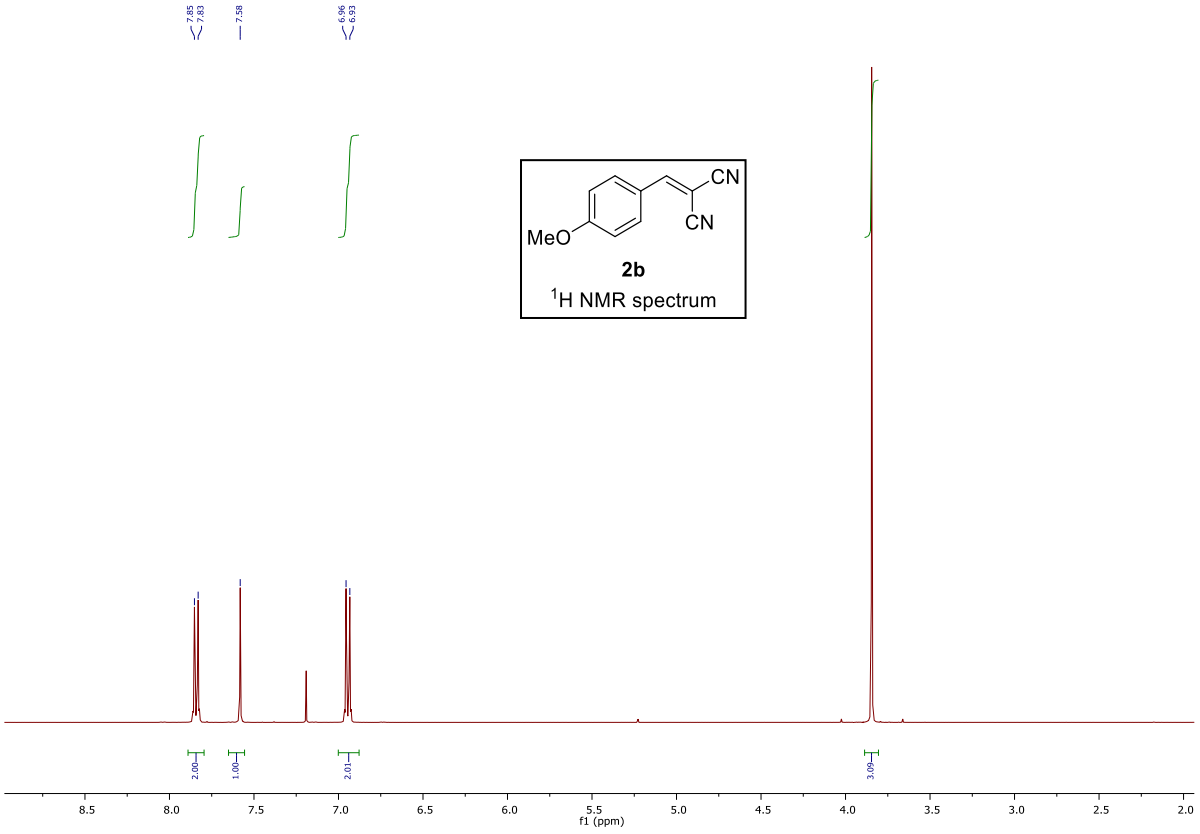
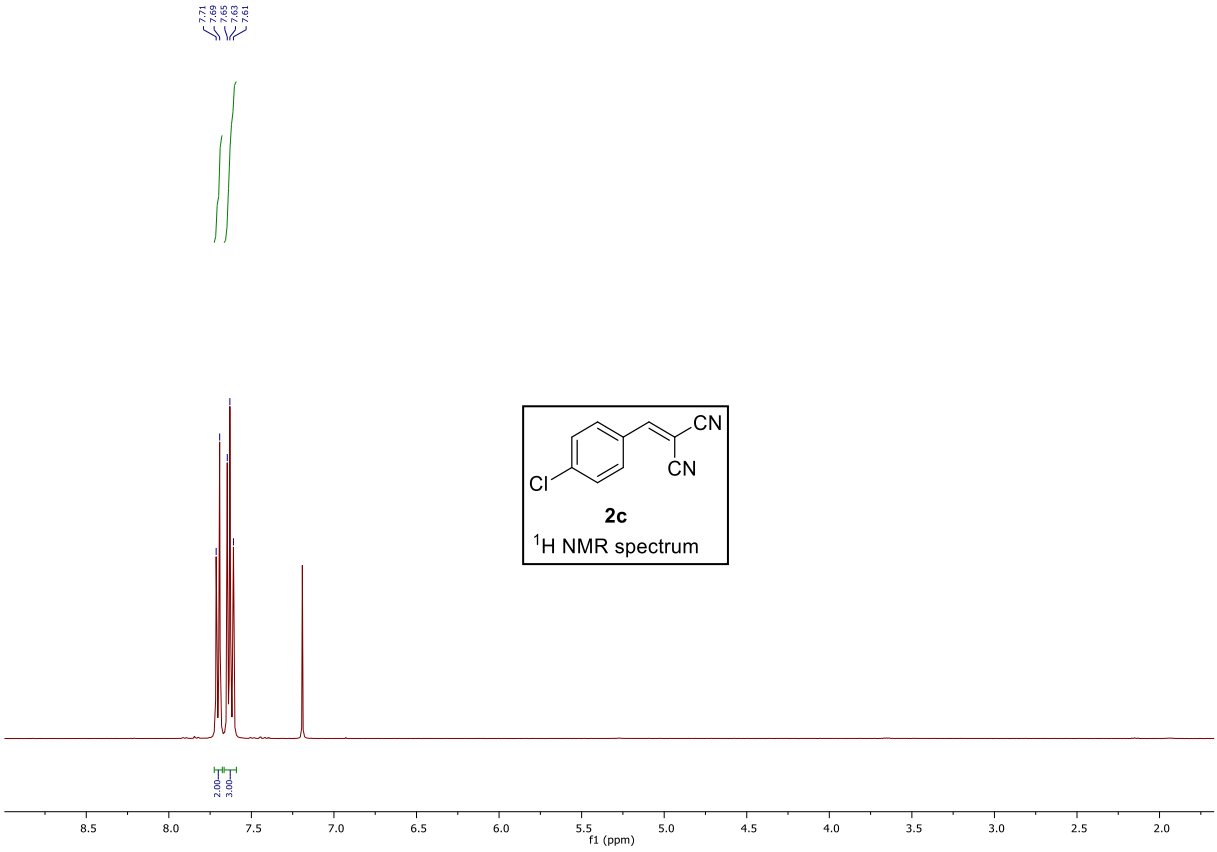


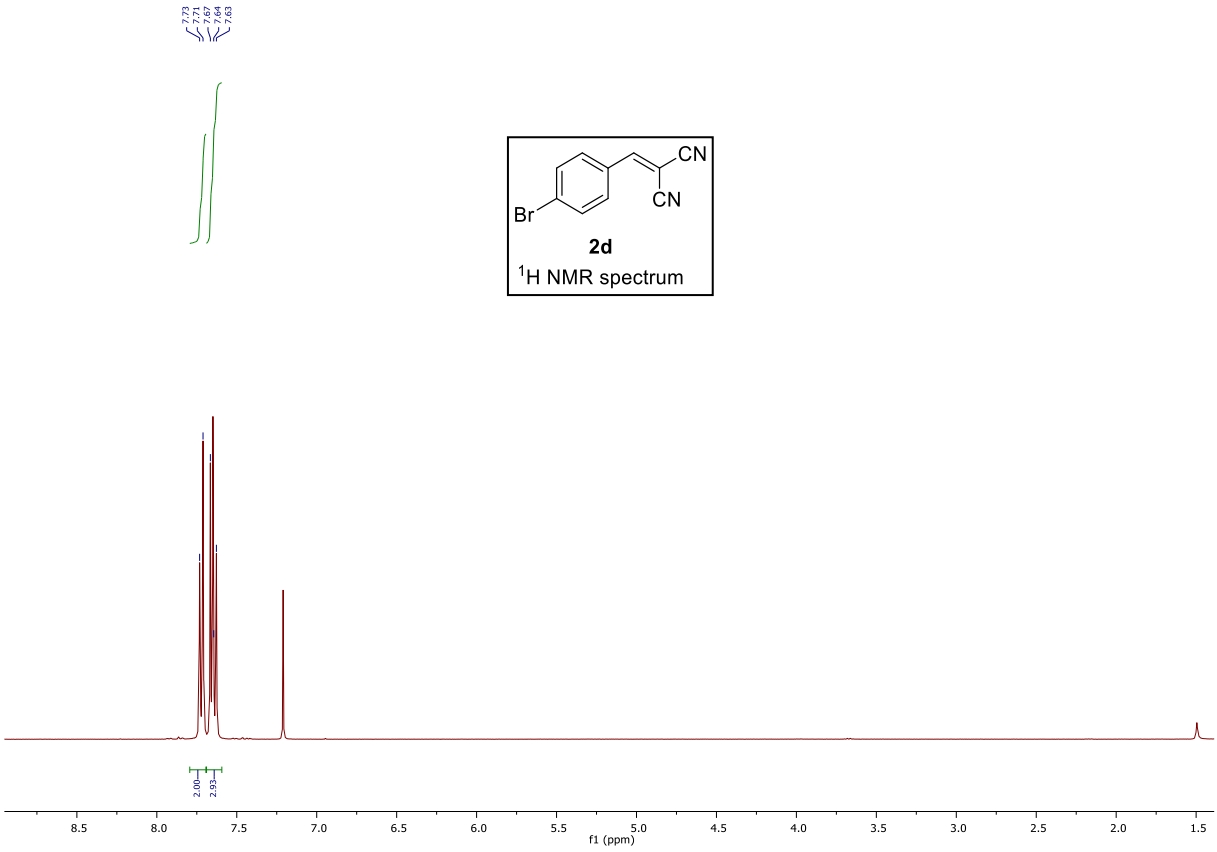
Figure S6. Stern-Volmer plot of data derived from Figure S4.

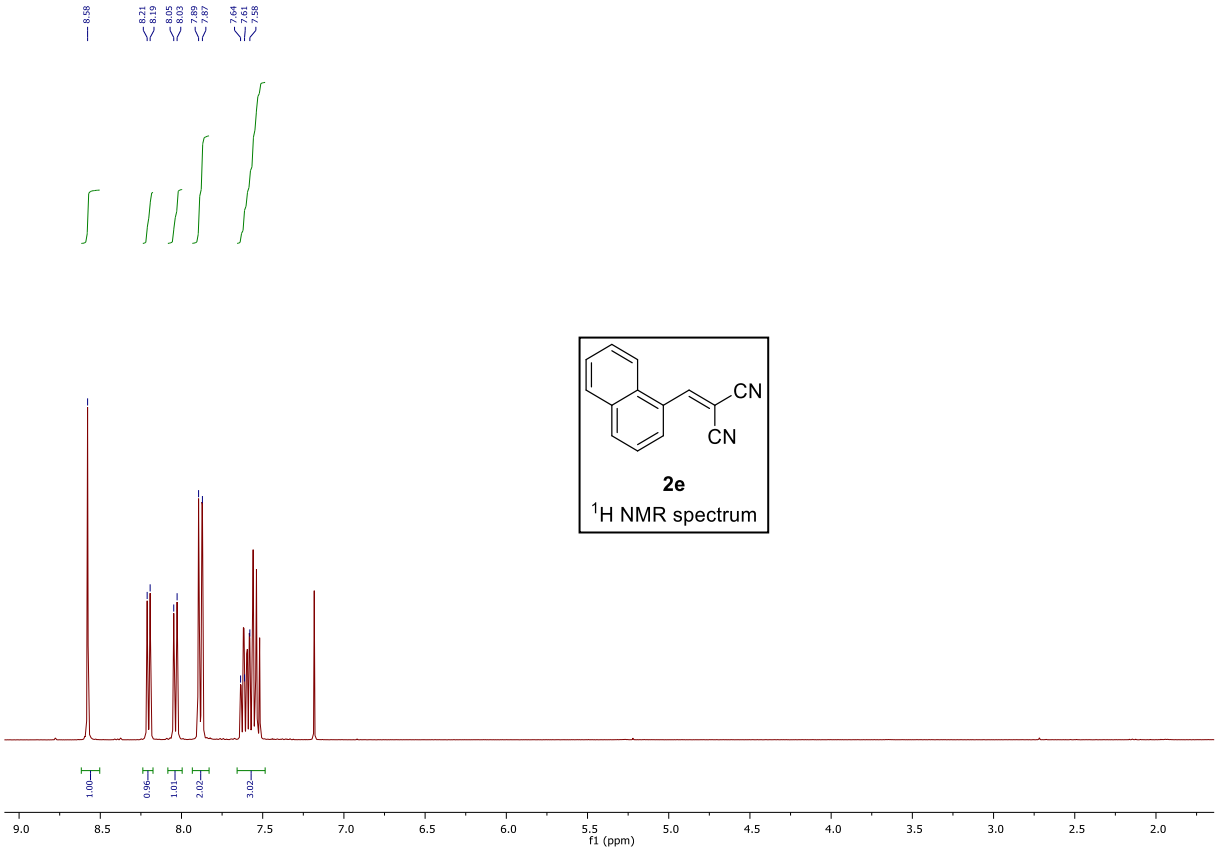
7. NMR spectra of substrates

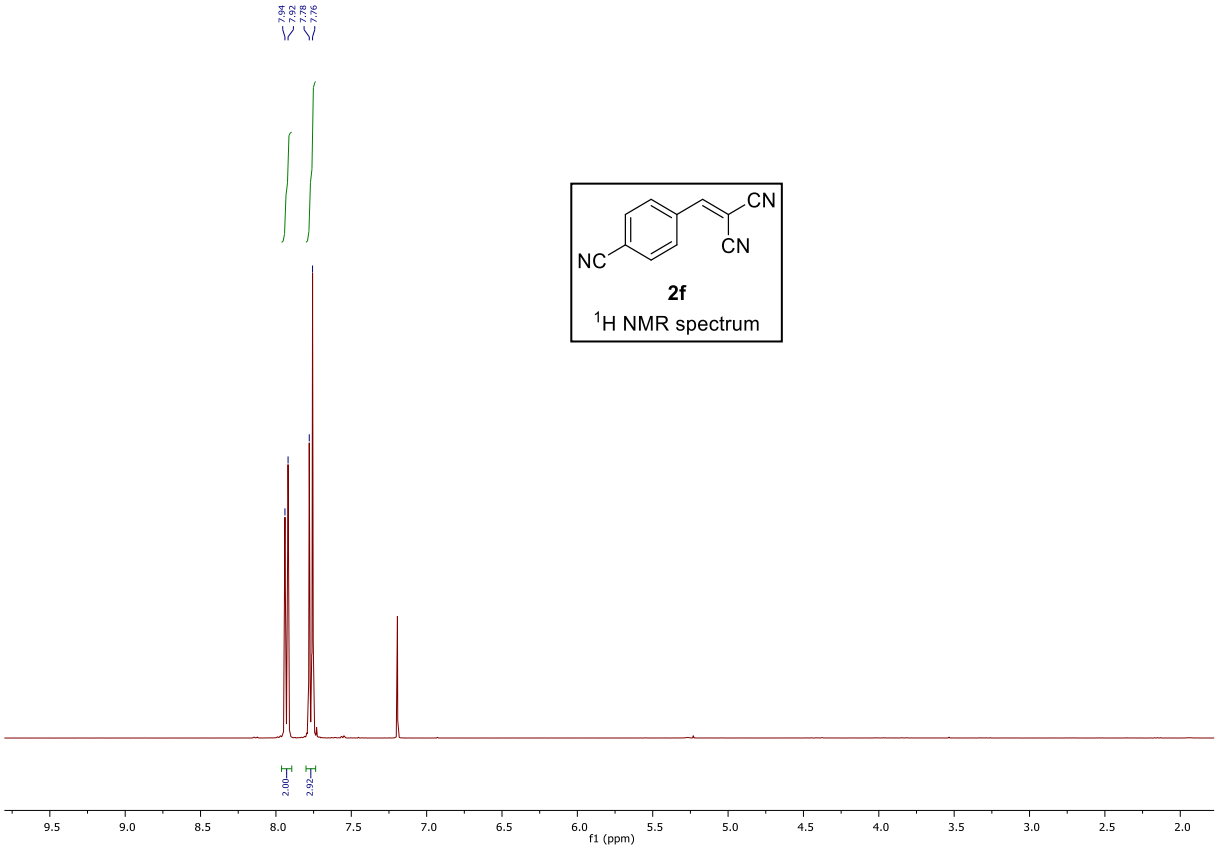


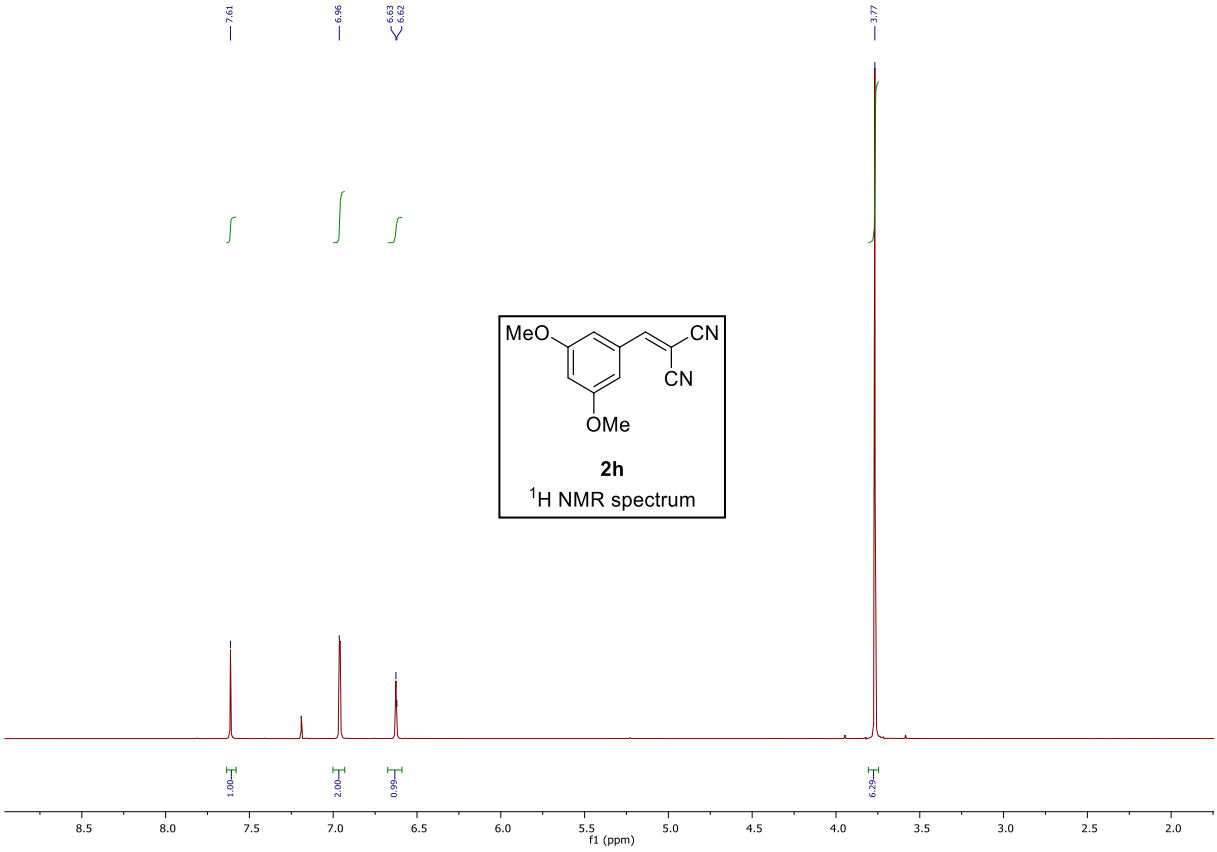


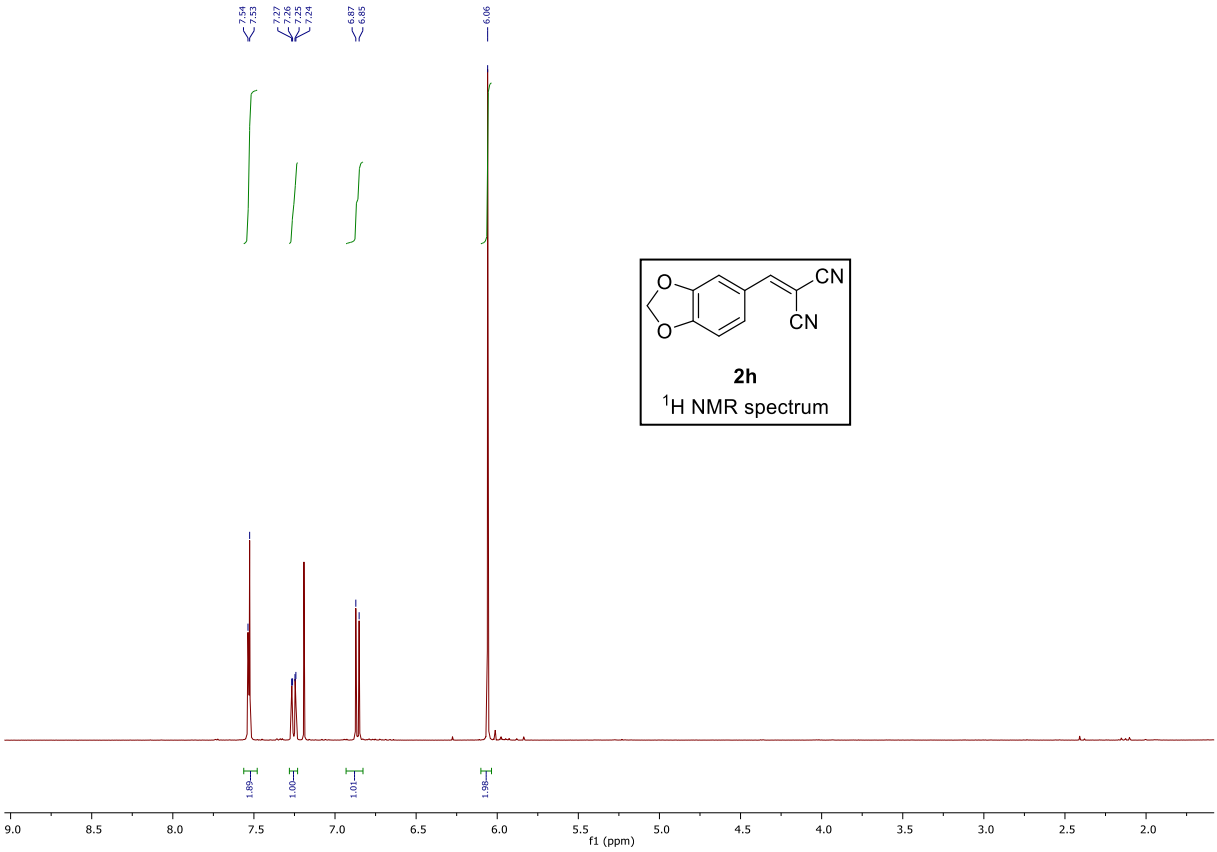

7.71
7.69
7.65
7.63
7.61
CN
CN
Cl
2c
1H NMR spectrum
2.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

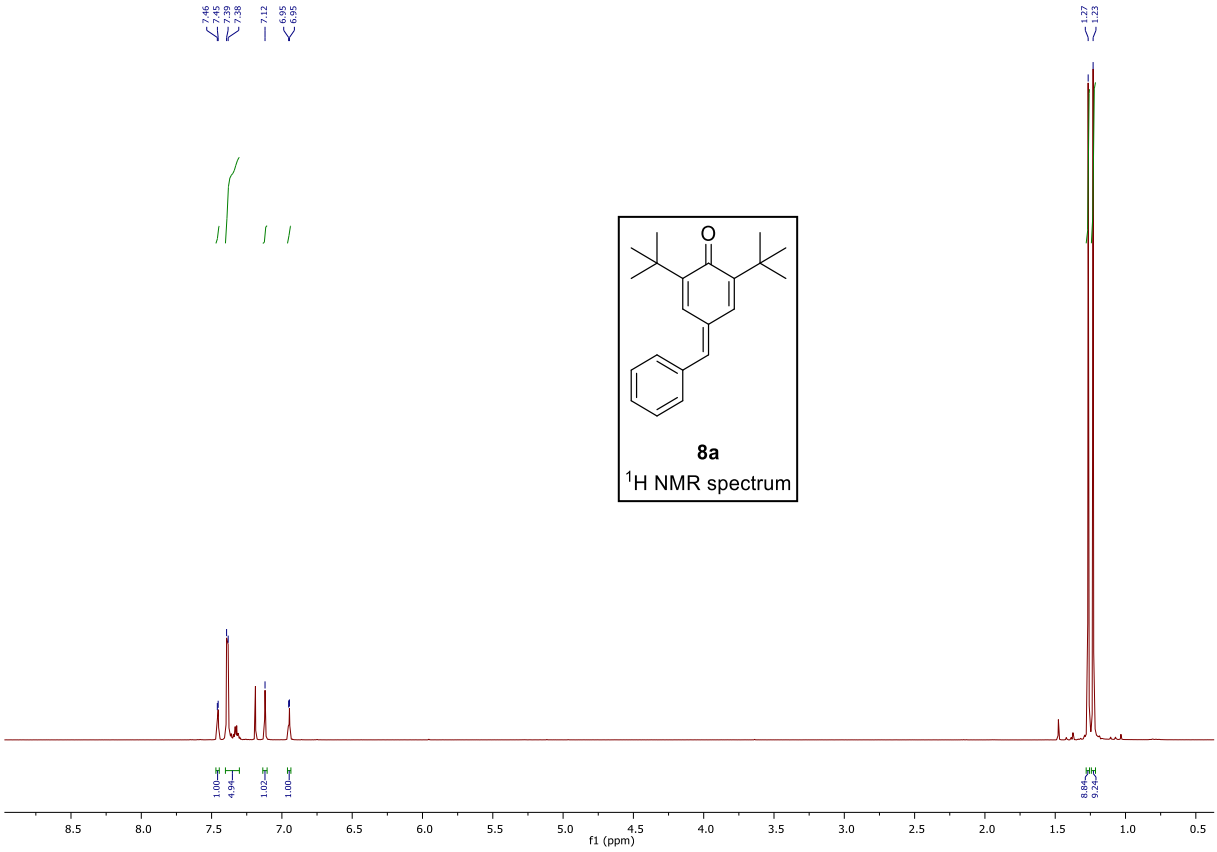

7.73
7.71
7.68
7.64
7.63
CN
CN
Br
2d
1H NMR spectrum
2.00
2.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

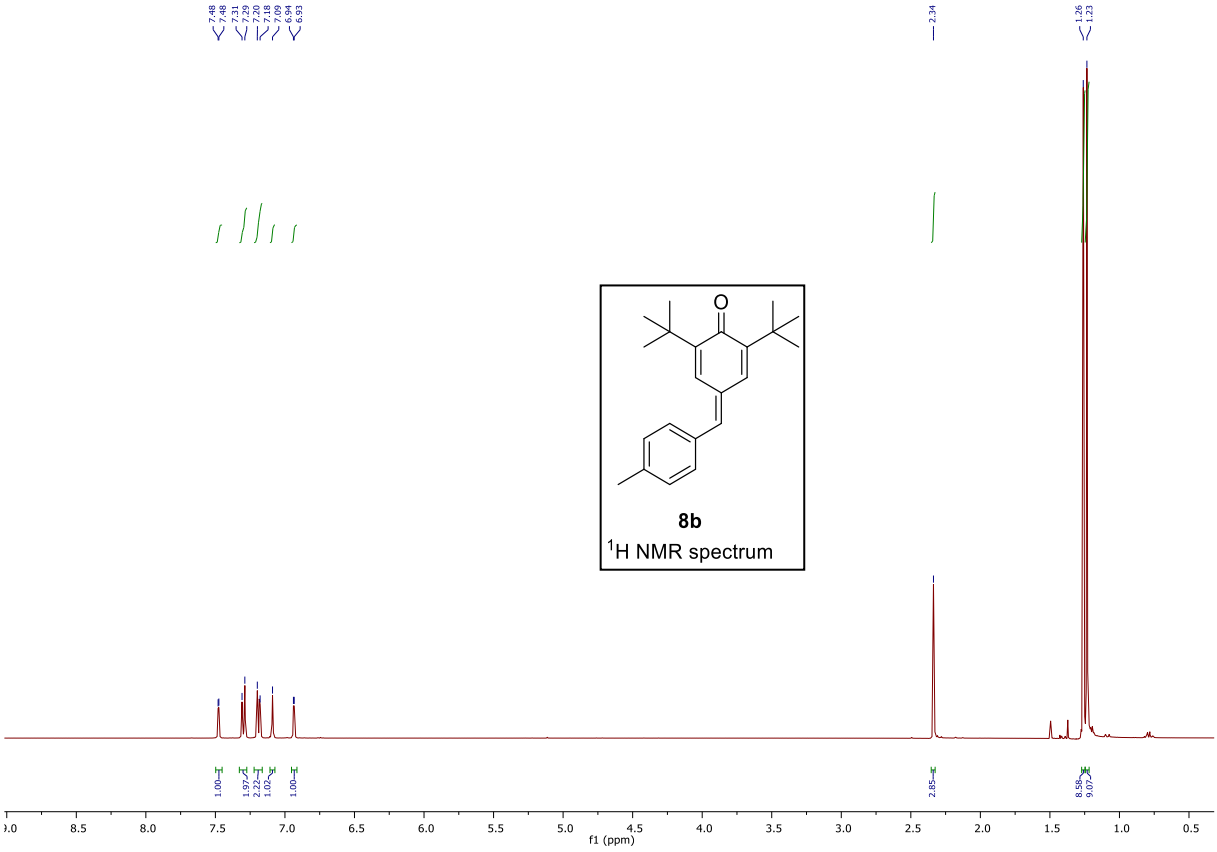

8.58
8.21
8.19
8.05
8.03
7.89
7.87
7.64
7.61
7.58
CN
CN
2e
^{1}H NMR spectrum
1.00
0.96
1.01
2.02
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

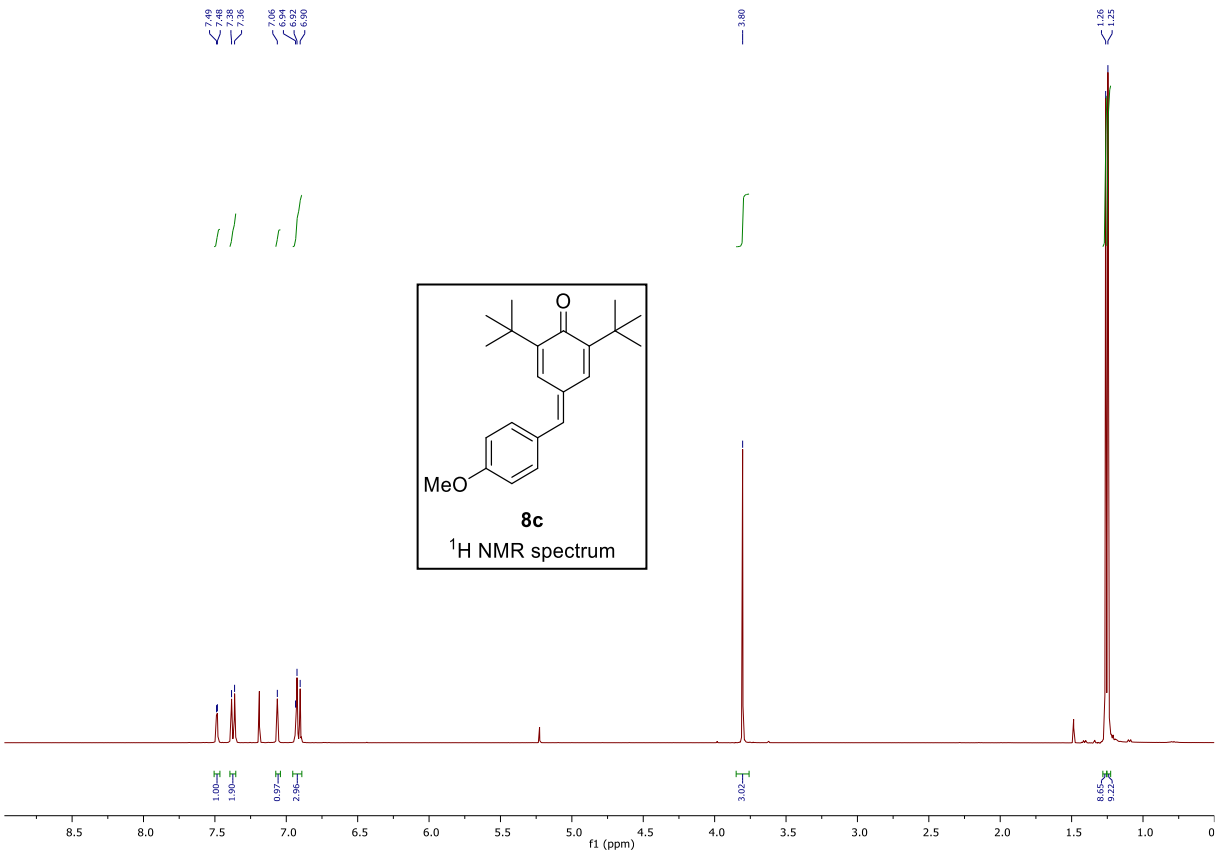

7.94
7.92
7.78
7.76
CN
CN
NC
2f
^{1}H NMR spectrum
2.00
2.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


7.61
6.96
6.63
6.62
3.77
MeO
CN
CN
OMe
2h
1H NMR spectrum
1.00
2.00
0.99
6.29
f1 (ppm)


7.54
7.53
7.27
7.26
7.25
7.24
6.87
6.85
6.06
O
O
CN
CN
2h
1H NMR spectrum
1.89
1.00
1.01
1.98
f1 (ppm)

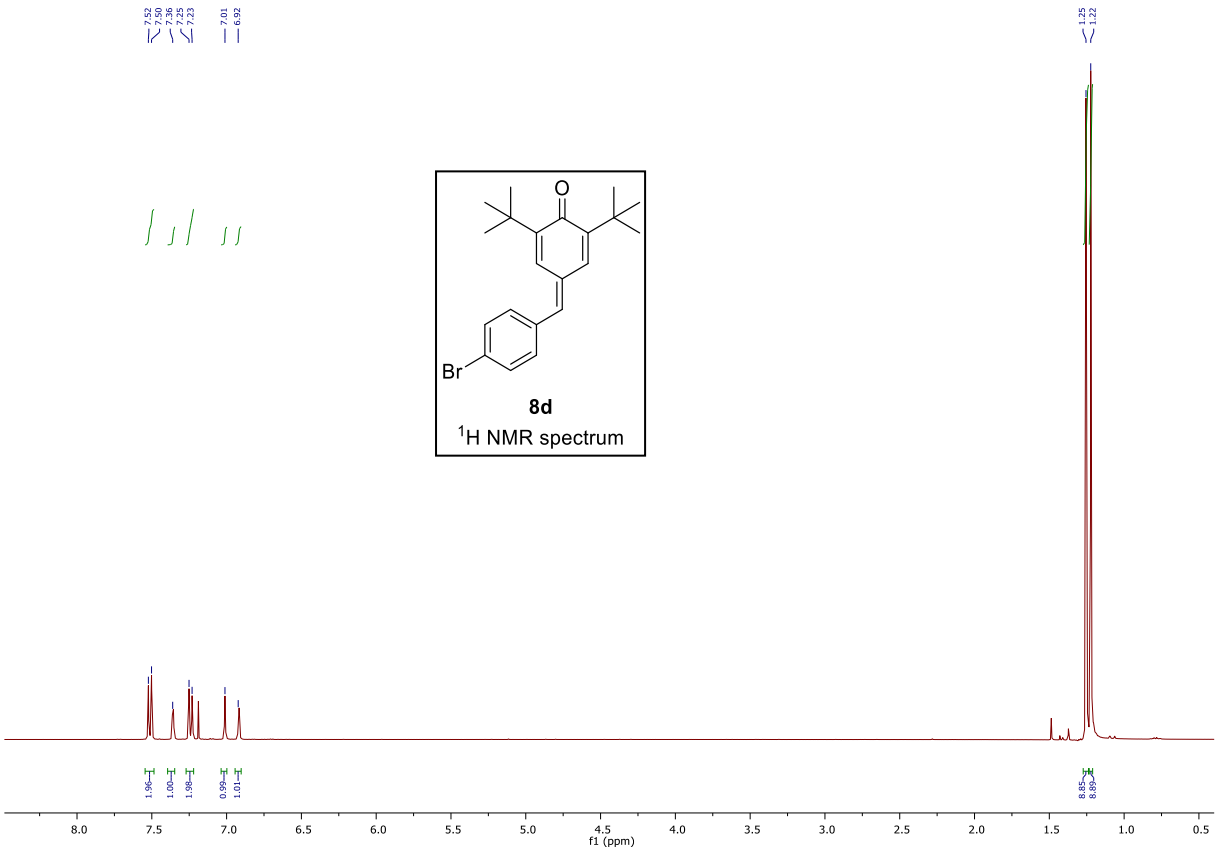

O
8a
1H NMR spectrum
f1 (ppm)


O
8b
1H NMR spectrum
f1 (ppm)



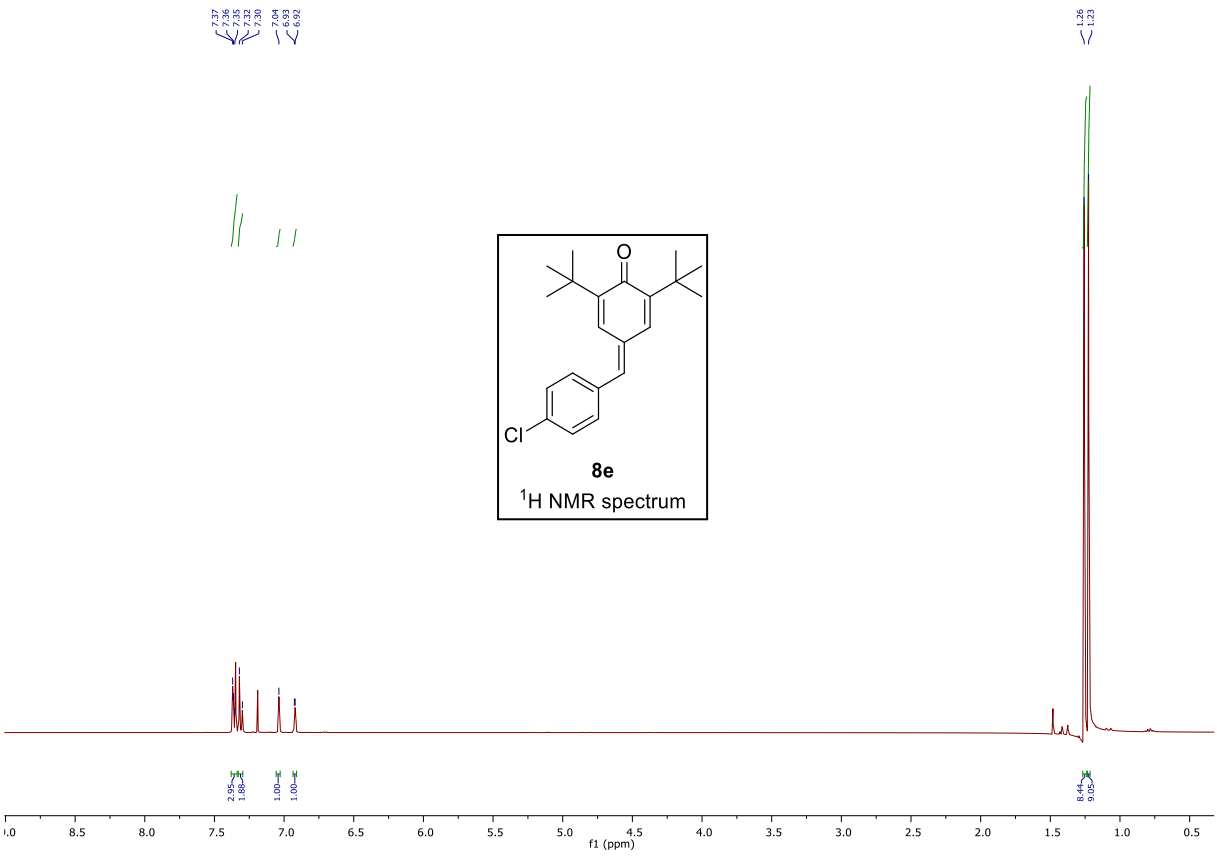
8c

^{1}H NMR spectrum

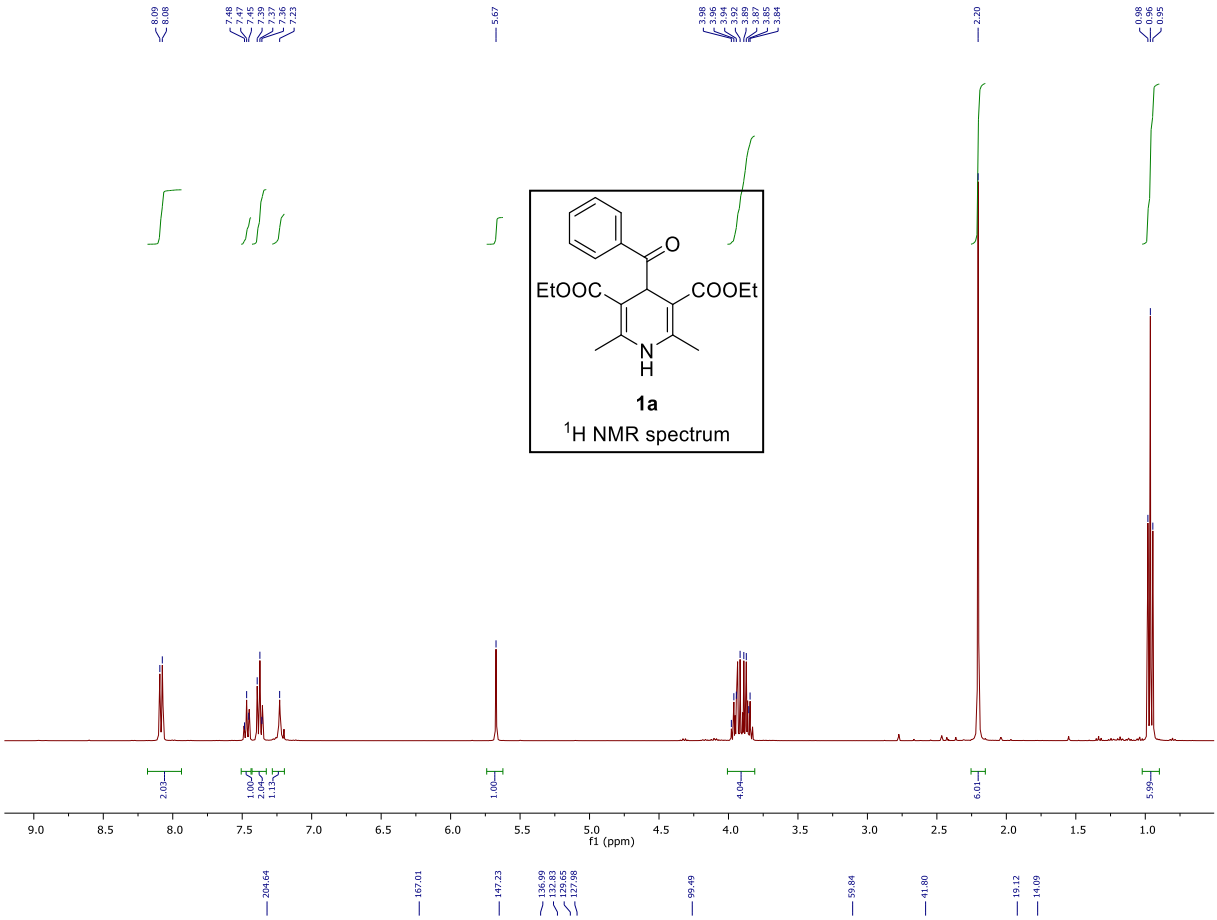


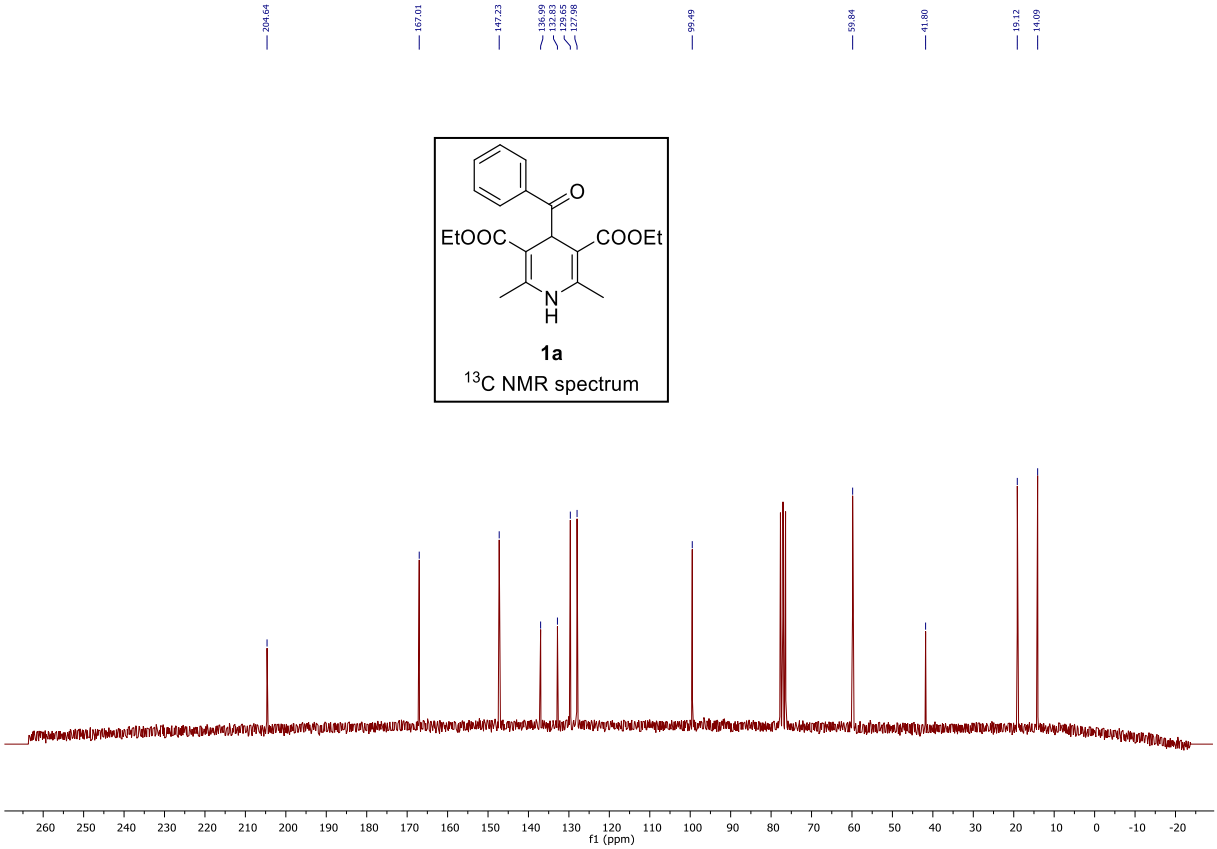
8d

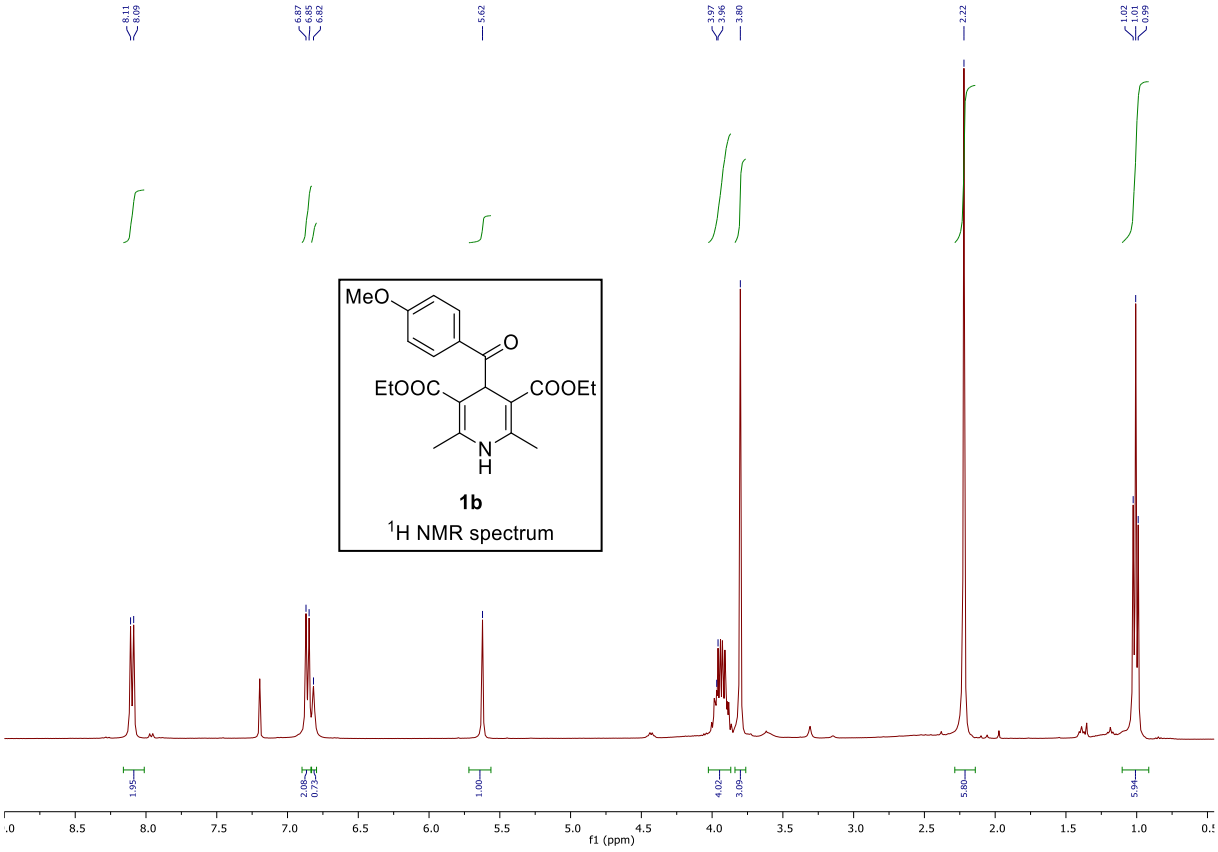
^{1}H NMR spectrum

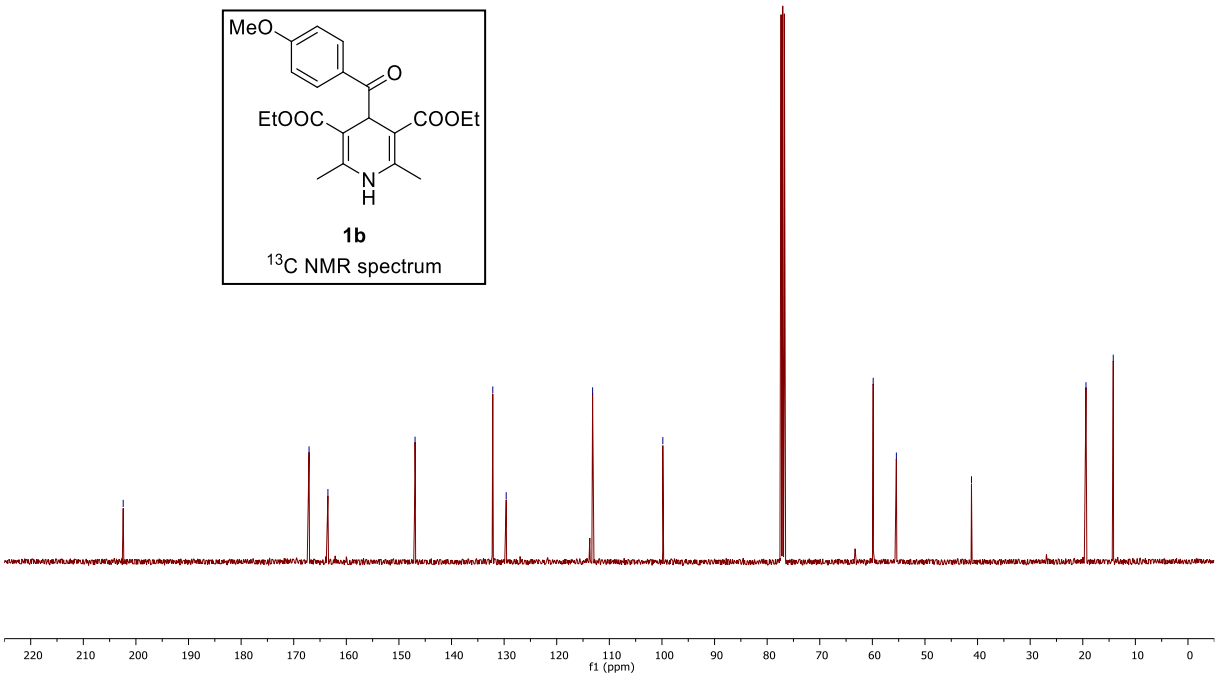

7.37
7.36
7.35
7.32
7.30
7.04
6.93
6.92
1.26
1.23
O
Cl
8e
1H NMR spectrum
2.95
1.88
1.00
1.00
8.44
9.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

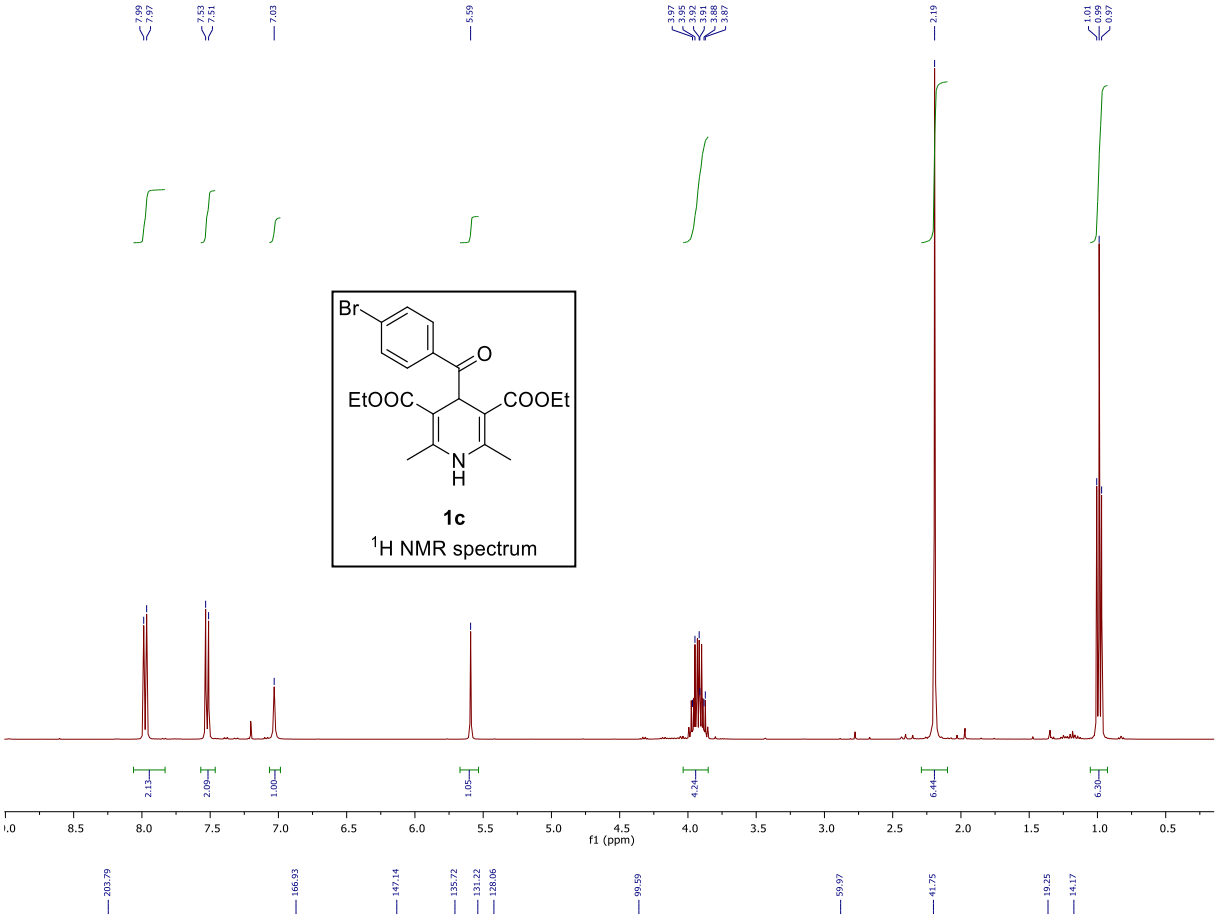
8. NMR spectra of the Hantzsch esters

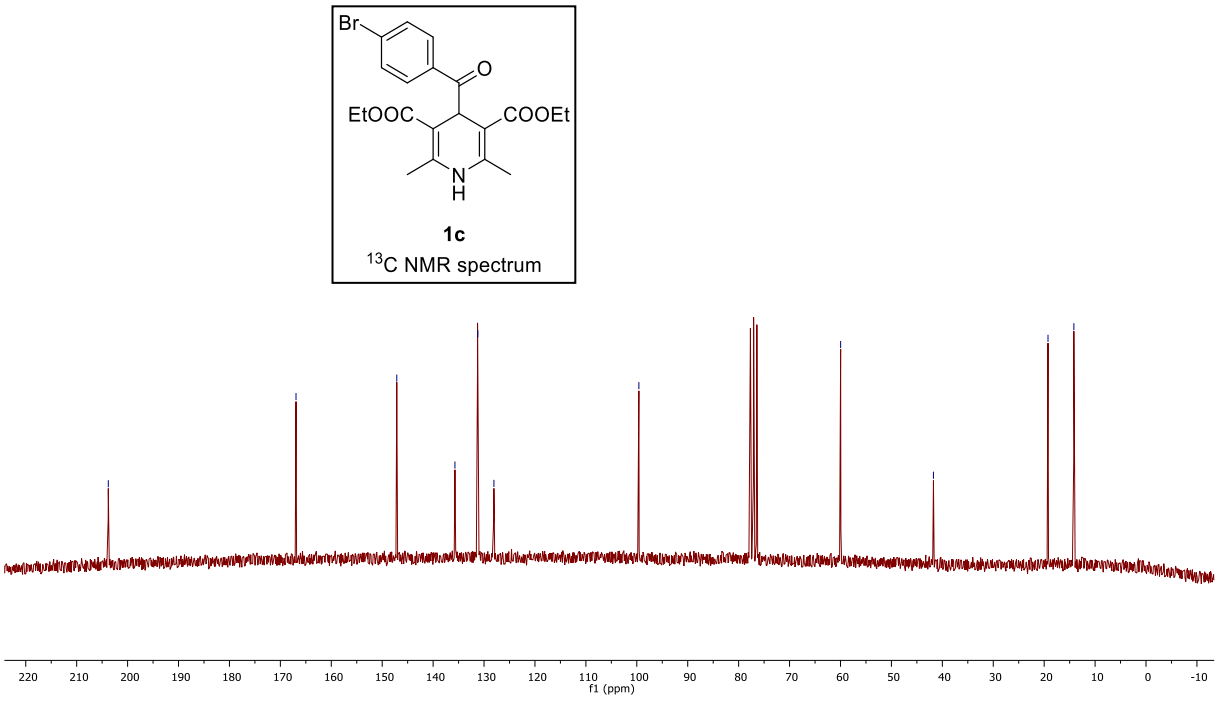


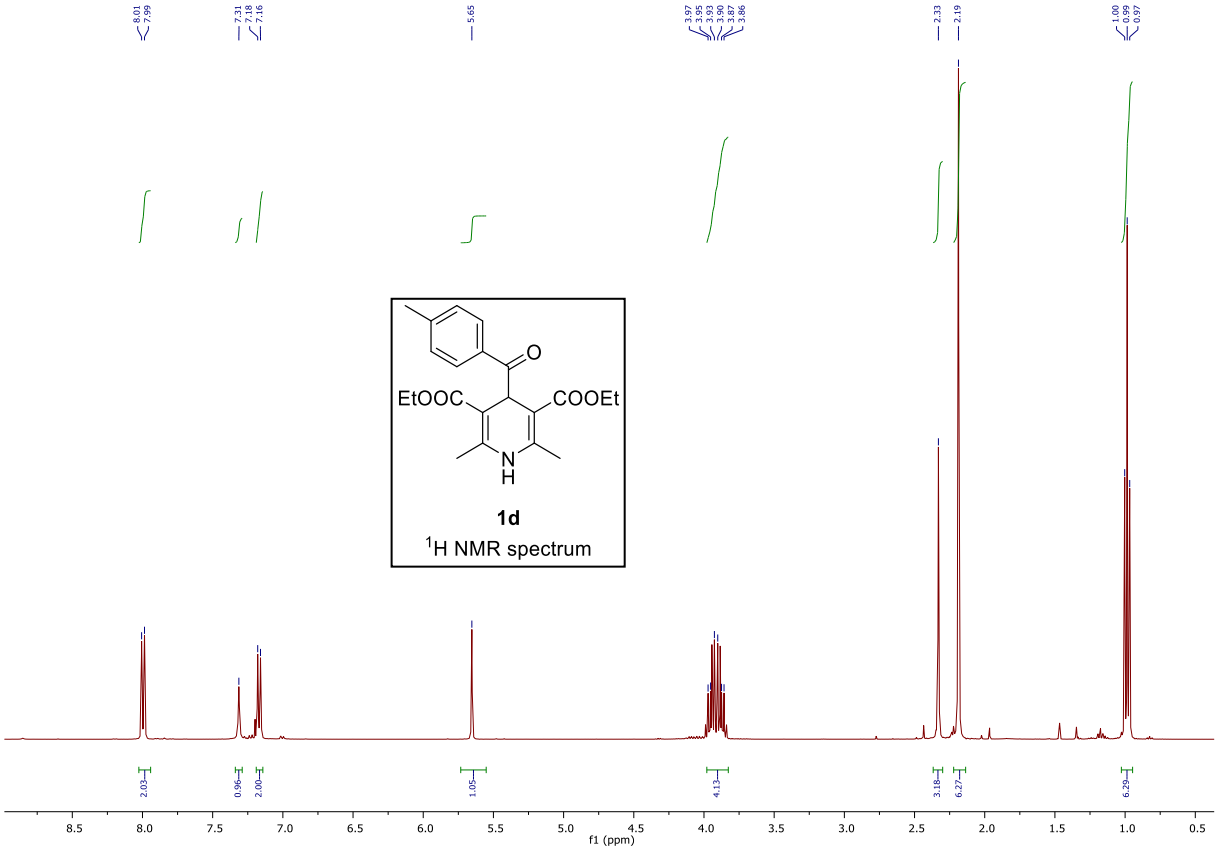


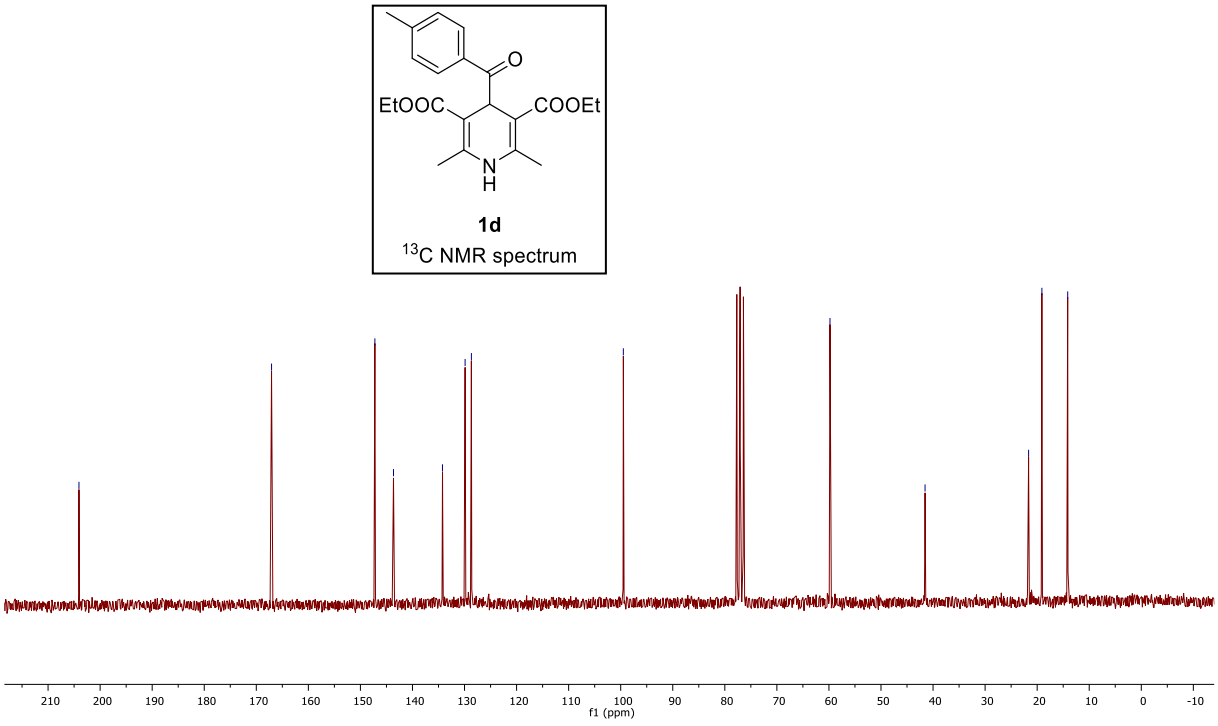

MeO
O
EtOOC
COOEt
N
H
1b
1H NMR spectrum
f1 (ppm)

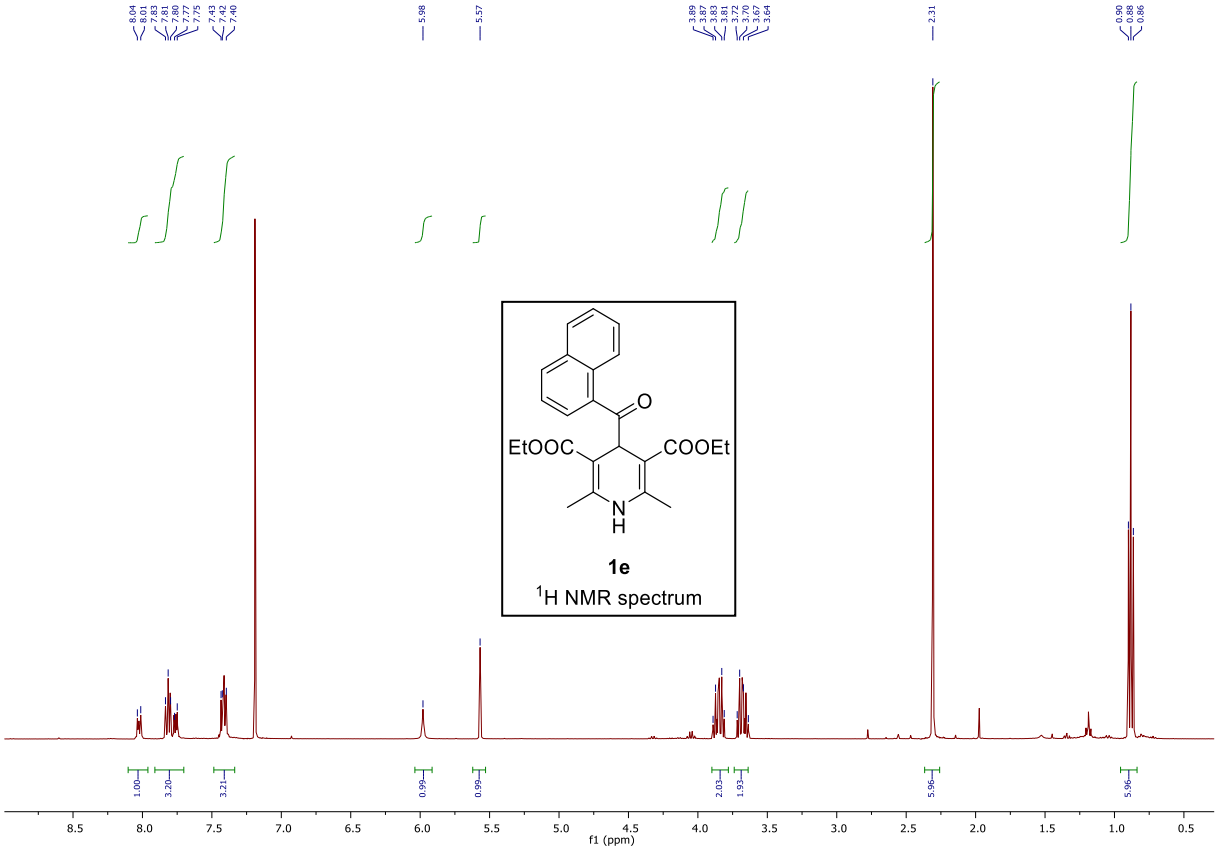

MeO
O
EtOOC
COOEt
N
H
1b
13C NMR spectrum
f1 (ppm)

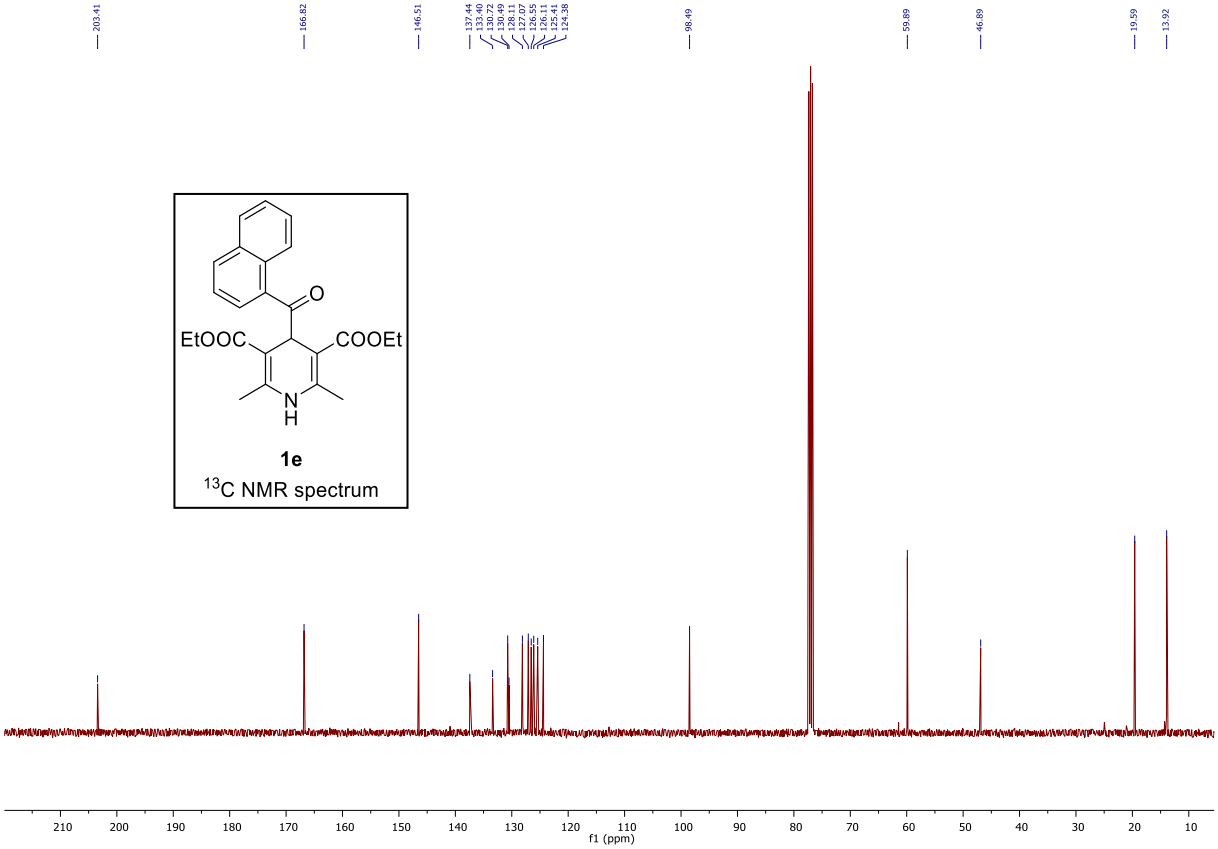

Br
O
EtOOC
COOEt
N
H
1c
1H NMR spectrum
f1 (ppm)

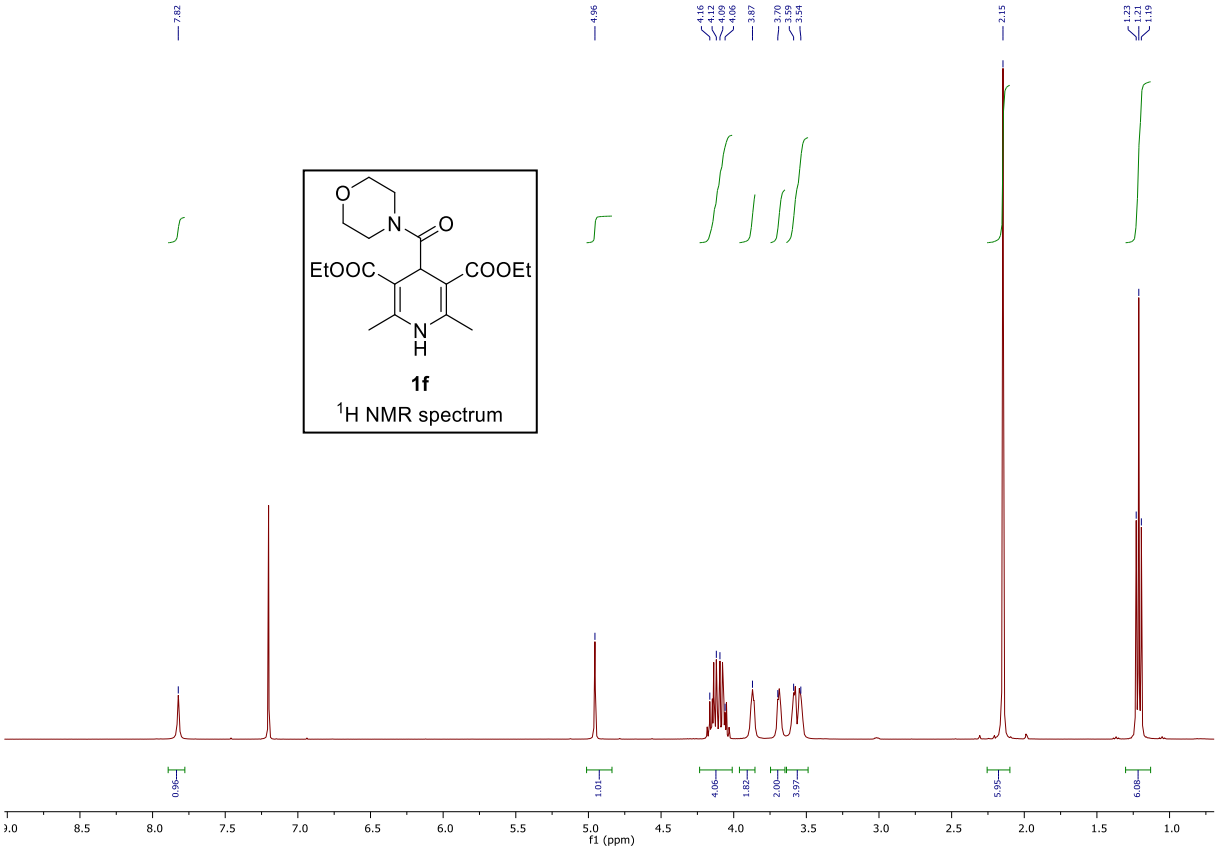

Br
O
EtOOC
COOEt
N
H
1c
13C NMR spectrum
f1 (ppm)

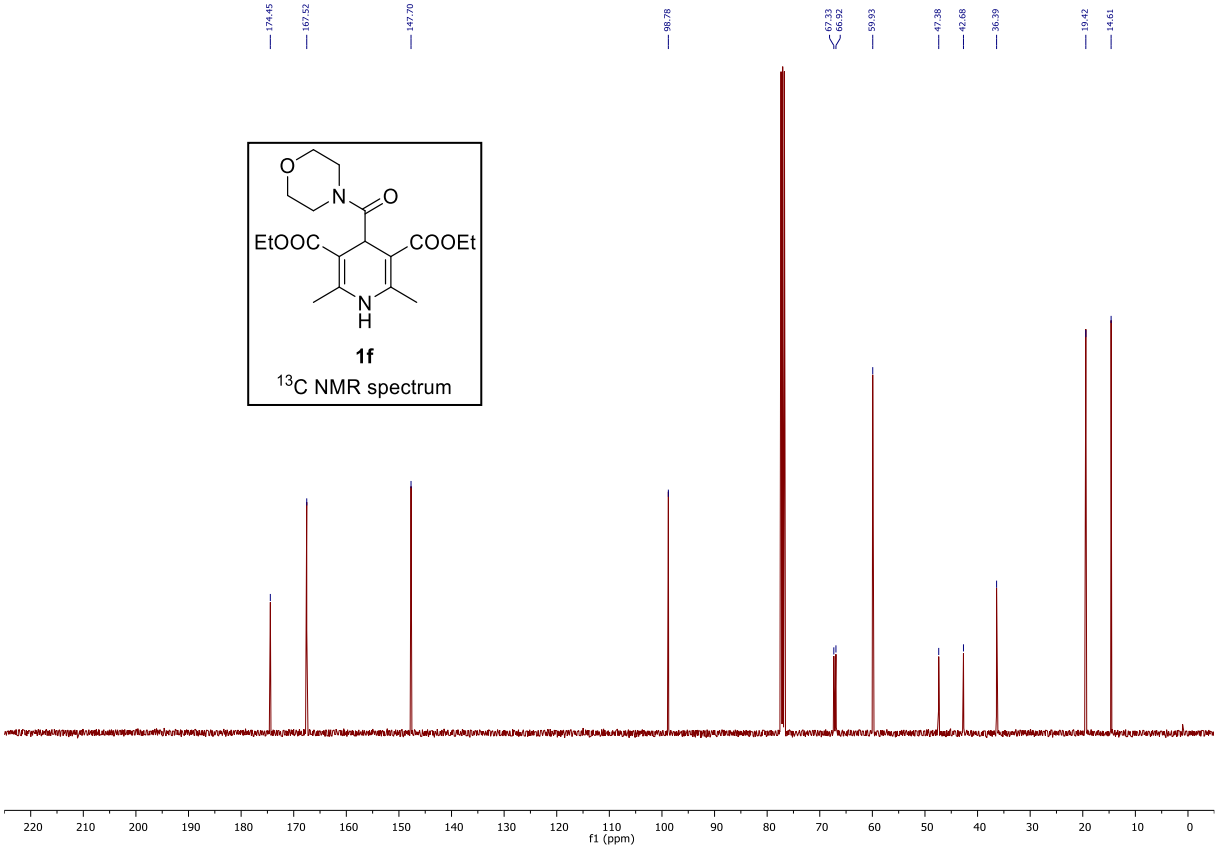

EtOOC
COOEt
O
N
H
1d
1H NMR spectrum
f1 (ppm)

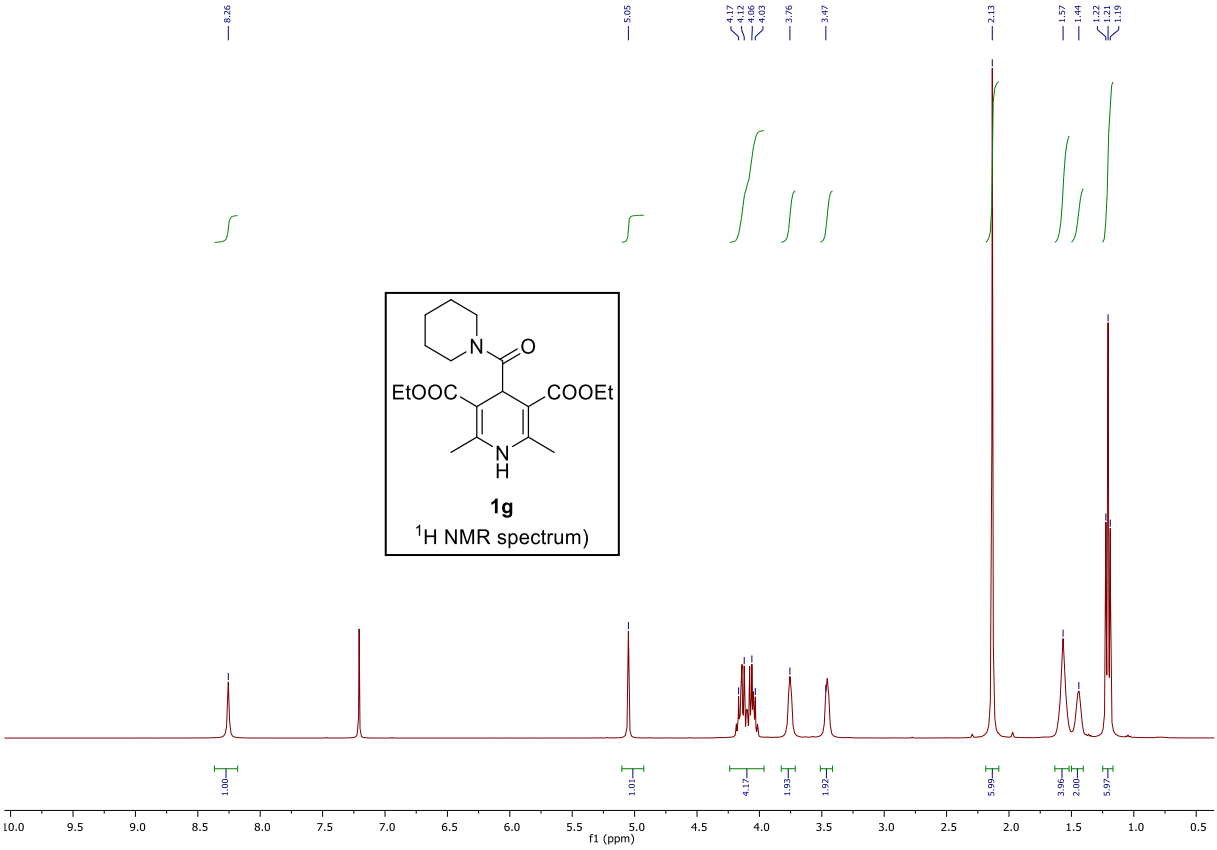

EtOOC
COOEt
O
N
H
1d
13C NMR spectrum
f1 (ppm)

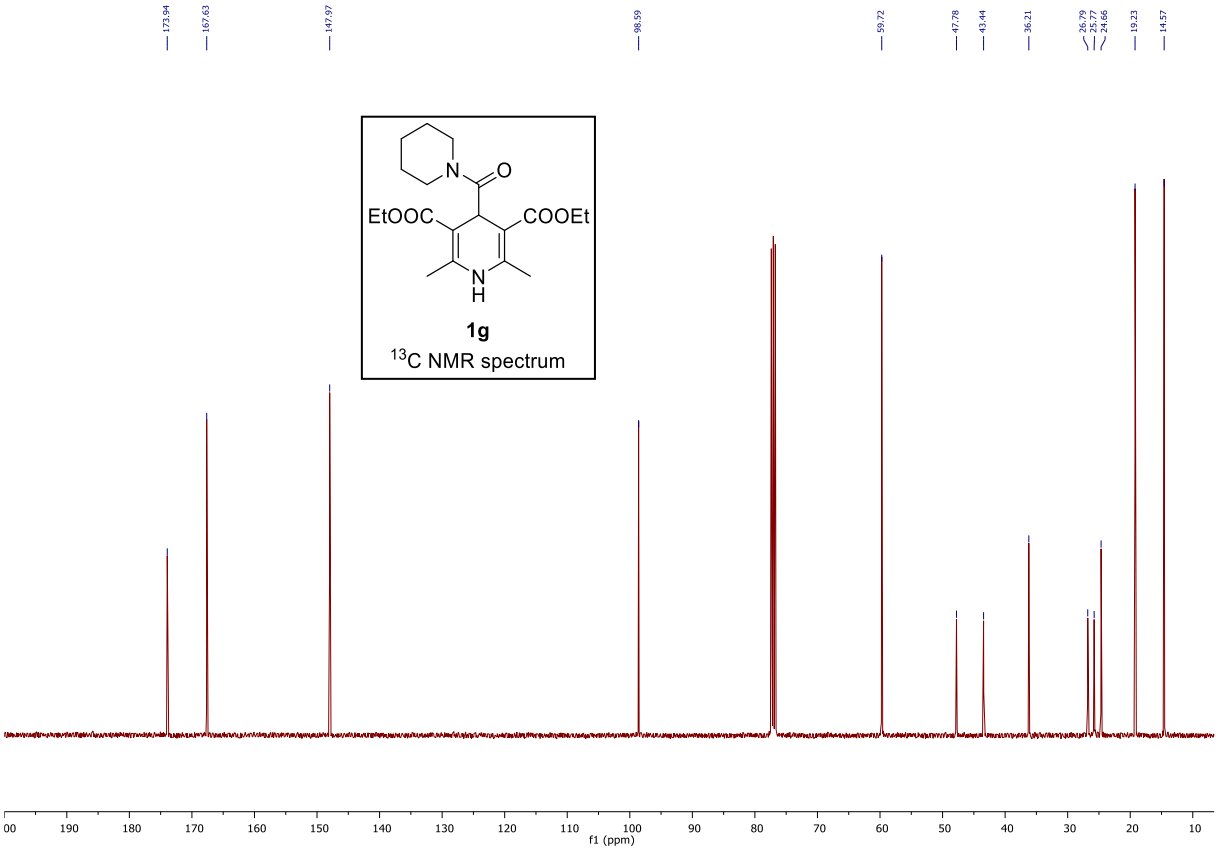

8.04
8.01
7.83
7.81
7.80
7.77
7.75
7.43
7.42
7.40
5.98
5.57
3.89
3.87
3.83
3.81
3.72
3.70
3.67
3.64
2.31
0.90
0.88
0.86
1.00
3.20
3.21
0.99
0.99
2.03
1.93
5.96
5.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
O
EtOOC
COOEt
N
H
1e
1H NMR spectrum


203.41
166.82
146.51
137.44
133.40
130.72
130.49
128.11
127.07
126.55
126.11
125.41
124.38
98.49
59.89
46.89
19.59
13.92
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
O
EtOOC
COOEt
N
H
1e
13C NMR spectrum


7.82
4.96
4.16
4.13
4.09
4.06
3.87
3.70
3.59
3.54
2.15
1.23
1.21
1.19
O
N
O
EtOOC
COOEt
N
H
1f
1H NMR spectrum
0.96
1.01
4.06
1.82
2.00
3.97
5.95
6.08
f1 (ppm)

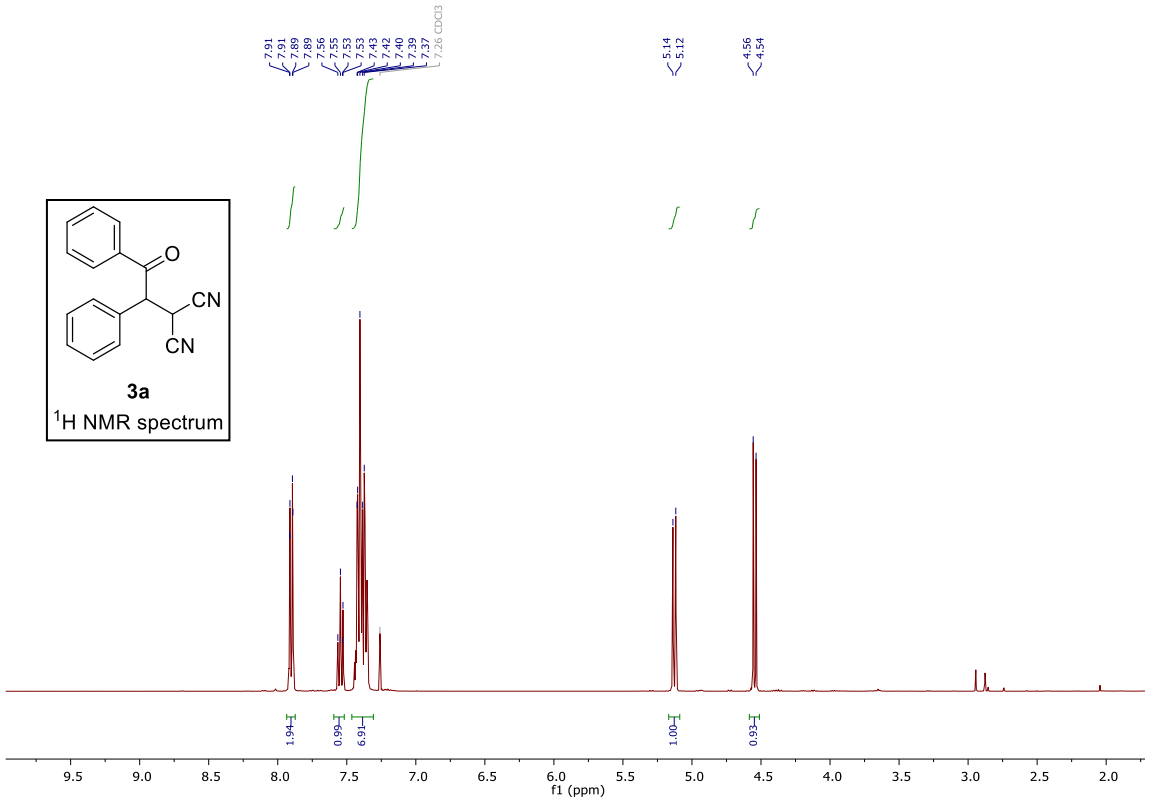

174.45
167.52
147.70
98.78
67.33
66.92
59.93
47.38
42.68
36.39
19.42
14.61
O
N
O
EtOOC
COOEt
N
H
1f
13C NMR spectrum
f1 (ppm)

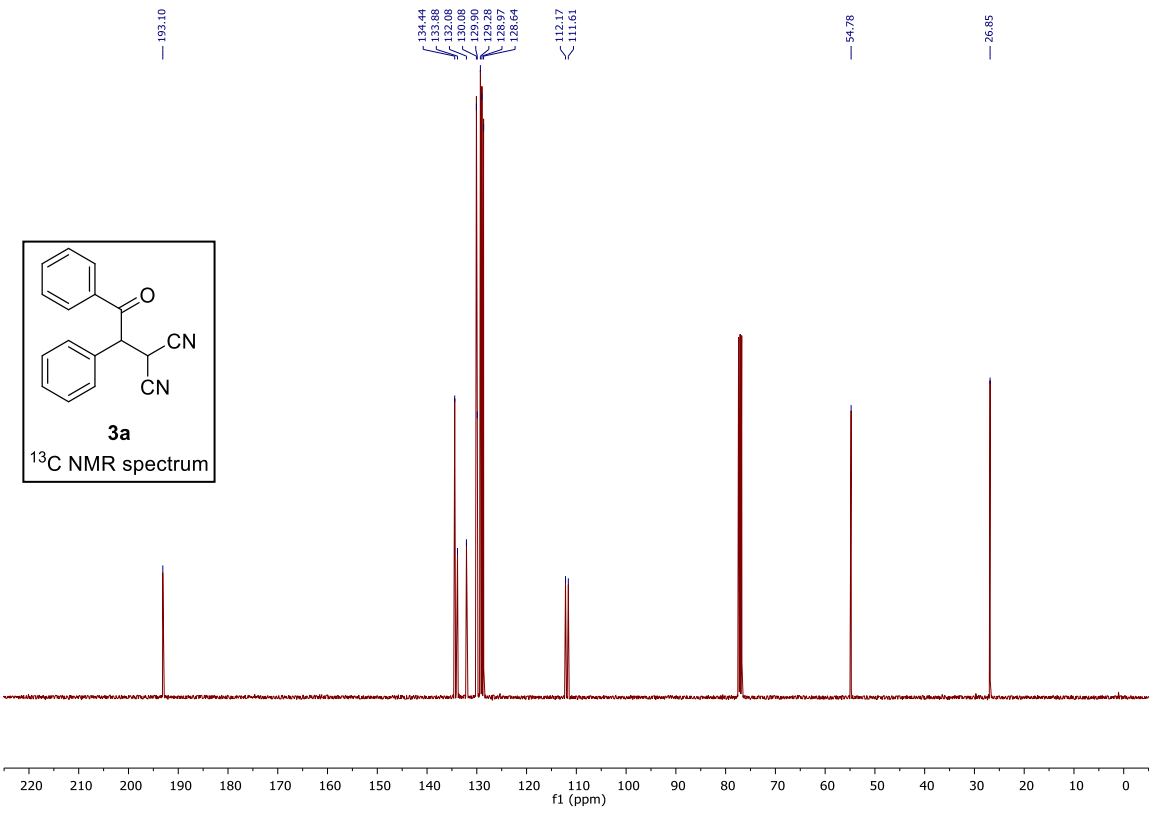

8.26
5.05
4.17
4.12
4.06
4.03
3.76
3.47
2.13
1.57
1.44
1.22
1.21
1.19
EtOOC
COOEt
N
O
H
1g
1H NMR spectrum)
1.00
1.01
4.17
1.93
1.92
5.99
3.96
2.00
5.97
f1 (ppm)

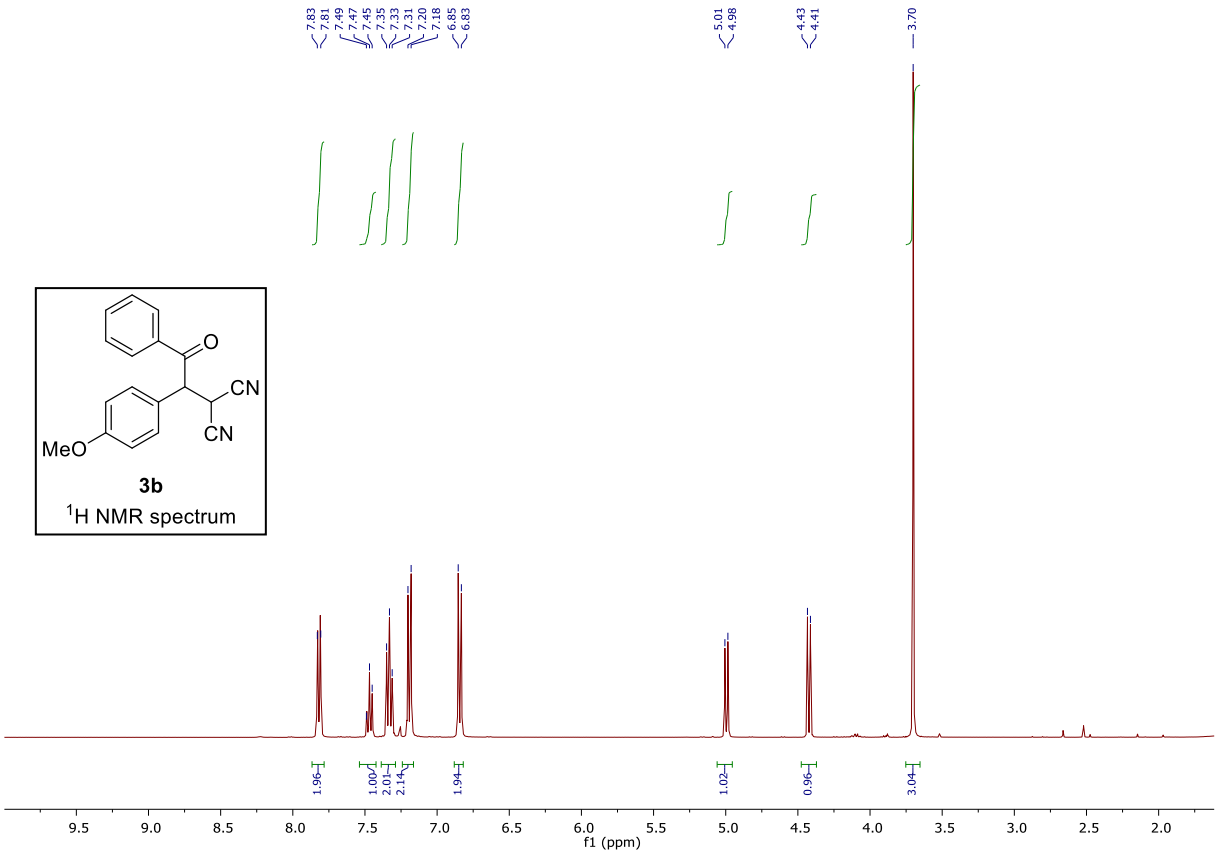

173.94
167.63
147.97
98.59
59.72
47.78
43.44
36.21
26.79
25.77
24.66
19.23
14.57
EtOOC
COOEt
N
O
H
1g
13C NMR spectrum
f1 (ppm)

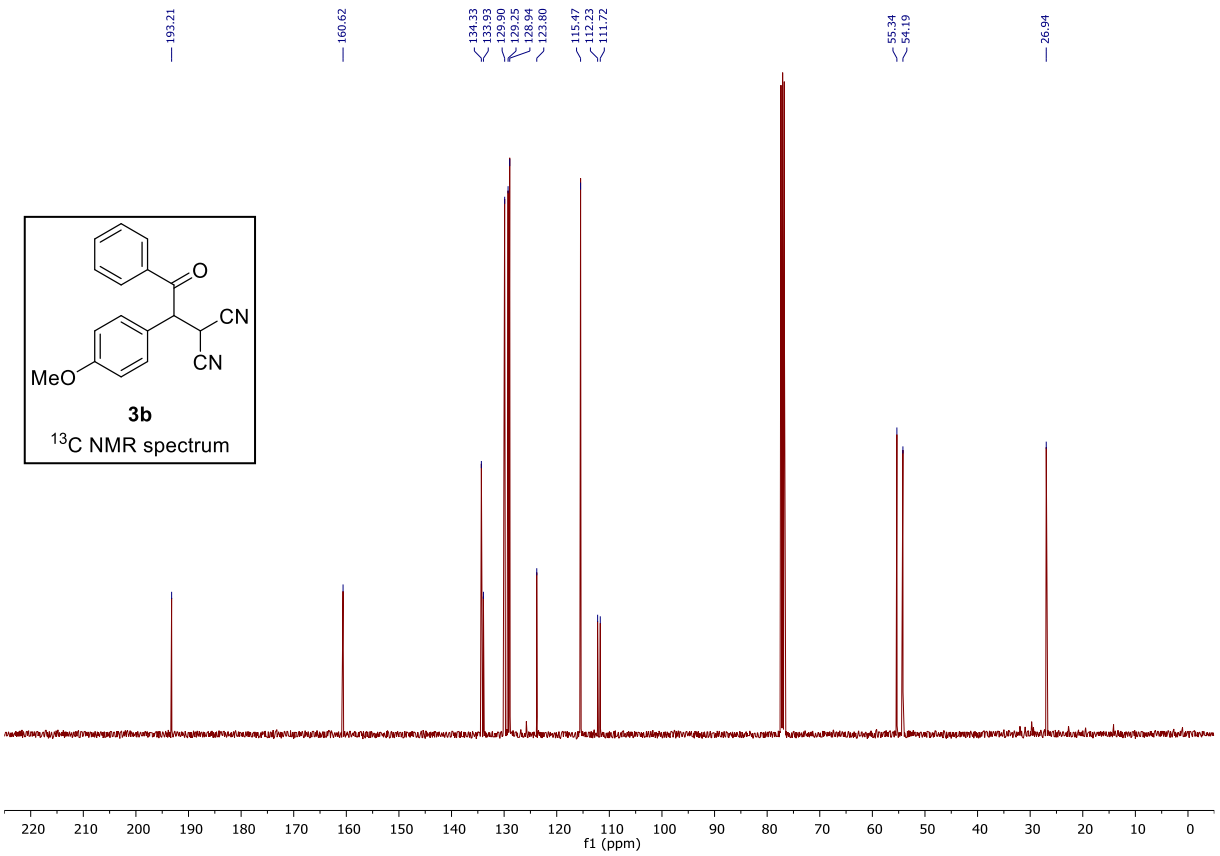
9. NMR spectra of hydroacylation products

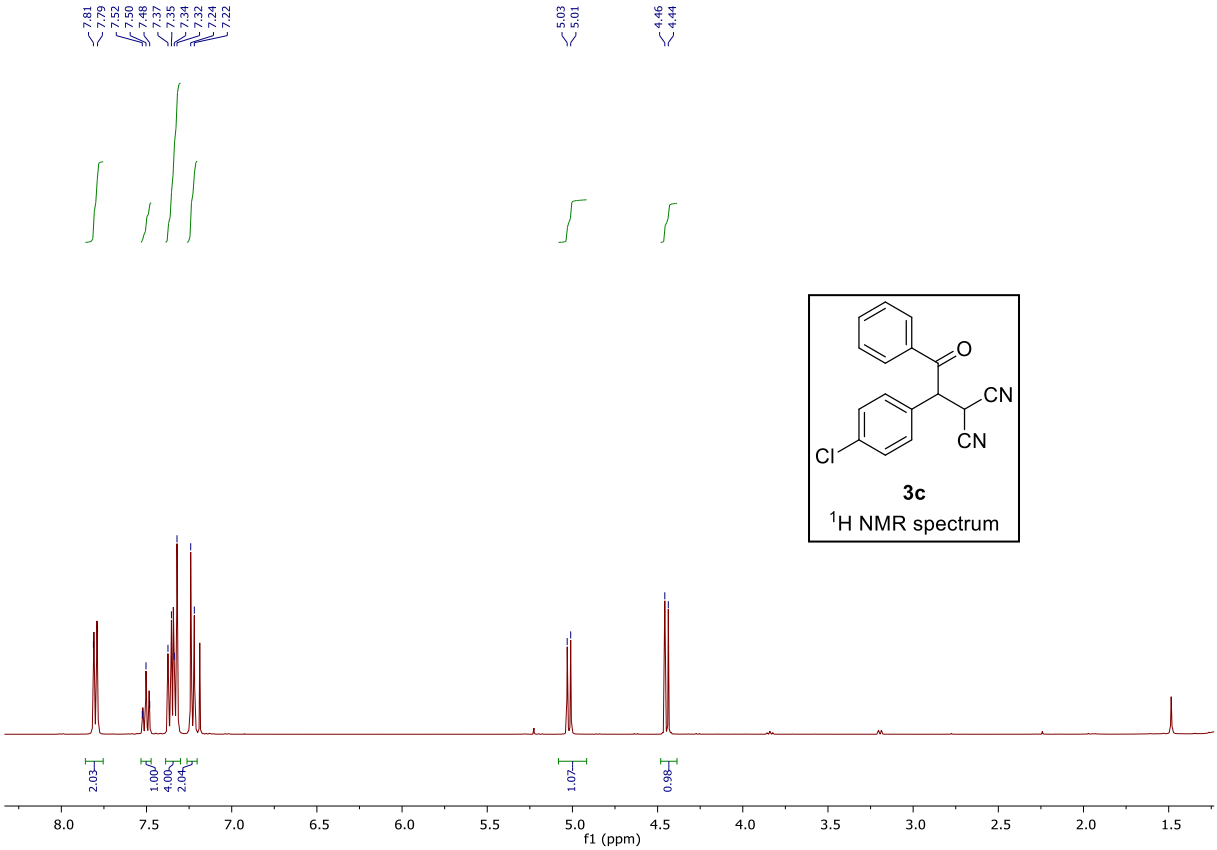
9.1. NMR spectra for the hydroacylation and one-pot derivatization of Michael-acceptors

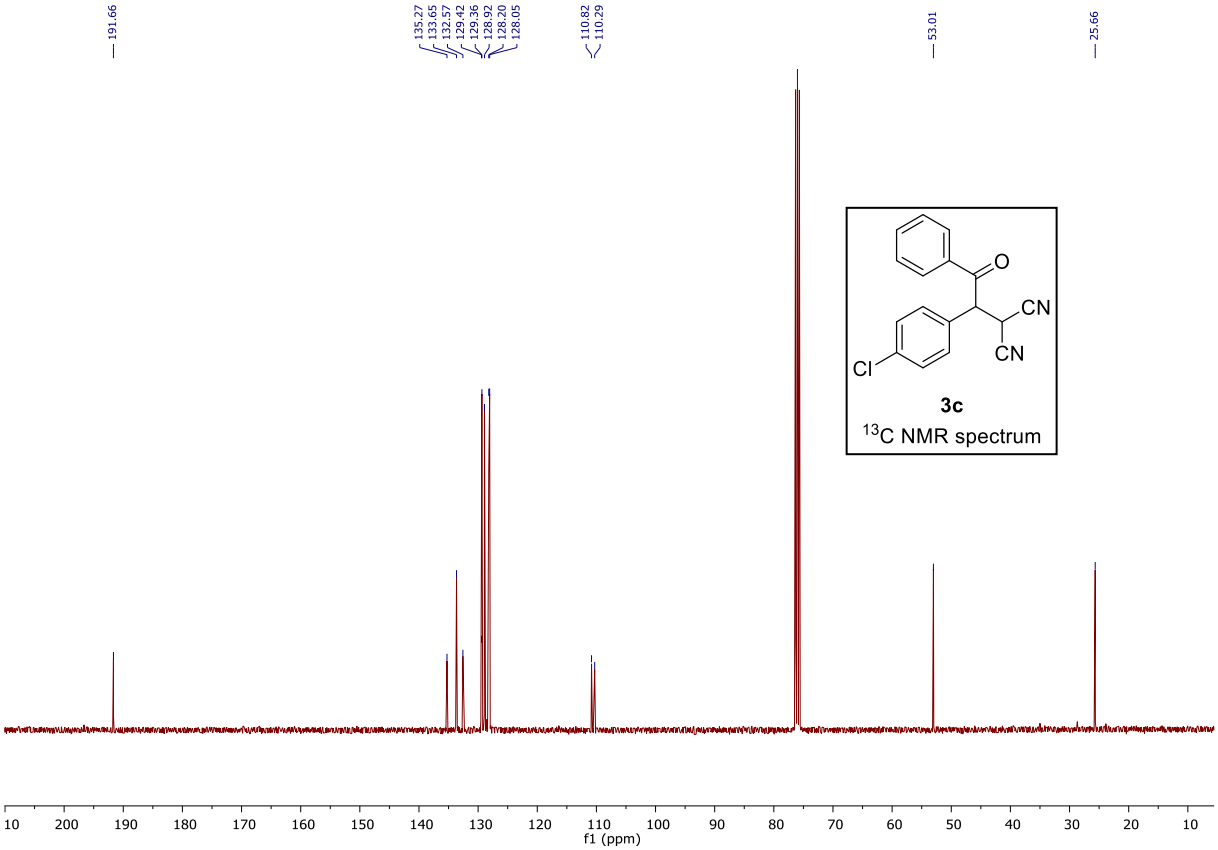


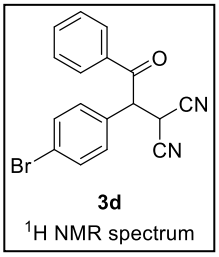



7.83
7.81
7.49
7.47
7.45
7.35
7.33
7.31
7.20
7.18
6.85
6.83
5.01
4.98
4.43
4.41
3.70
O
CN
CN
MeO
3b
1H NMR spectrum
1.96
1.00
2.01
2.14
1.94
1.02
0.96
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


193.21
160.62
134.33
133.93
129.90
129.25
128.94
123.80
115.47
112.23
111.72
55.34
54.19
26.94
O
CN
CN
MeO
3b
13C NMR spectrum
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

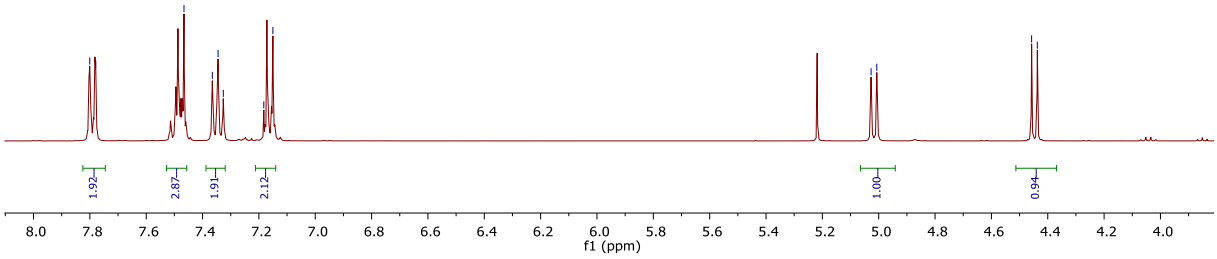

7.81
7.79
7.52
7.50
7.48
7.37
7.35
7.34
7.32
7.24
7.22
5.03
5.01
4.46
4.44
O
CN
CN
Cl
3c
1H NMR spectrum
2.03
1.00
4.00
2.04
1.07
0.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

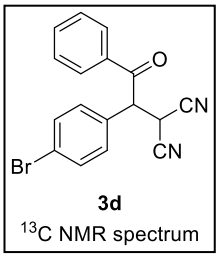

191.66
135.27
133.65
132.57
129.42
129.36
128.92
128.20
128.05
110.82
110.29
53.01
25.66
O
CN
CN
Cl
3c
13C NMR spectrum
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



3d

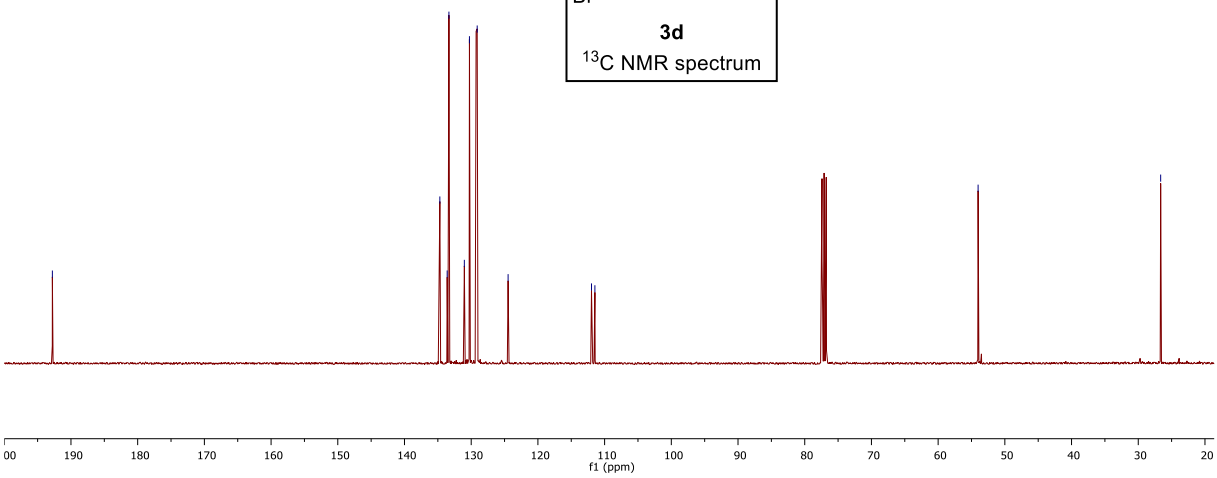
^{1}H NMR spectrum

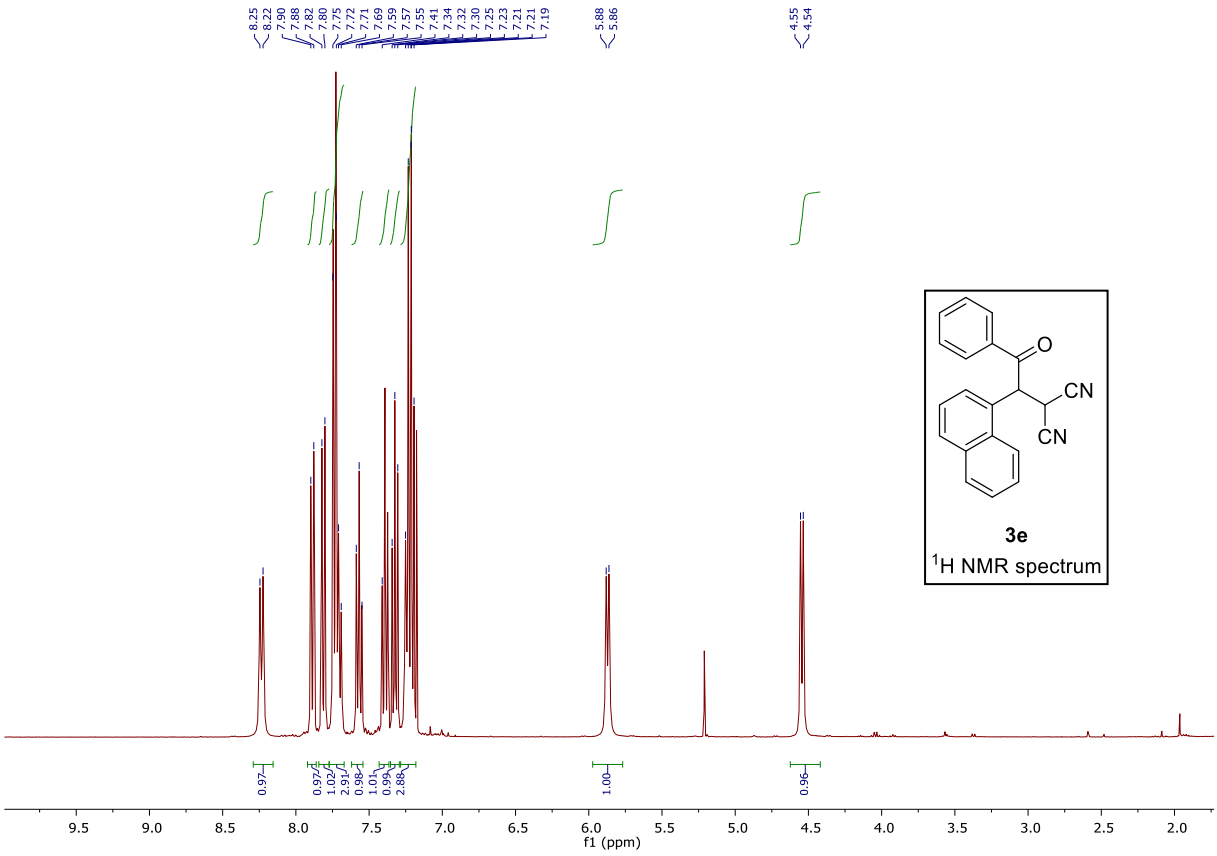


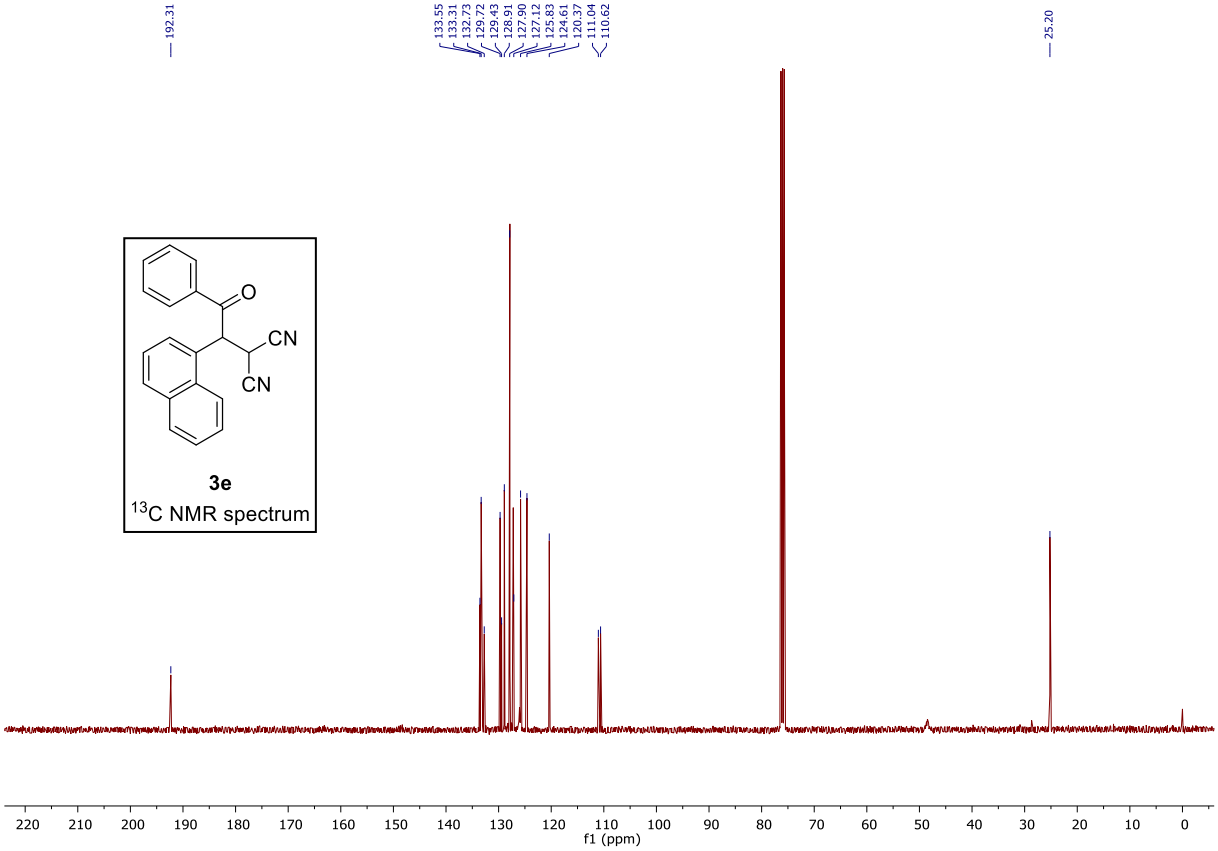


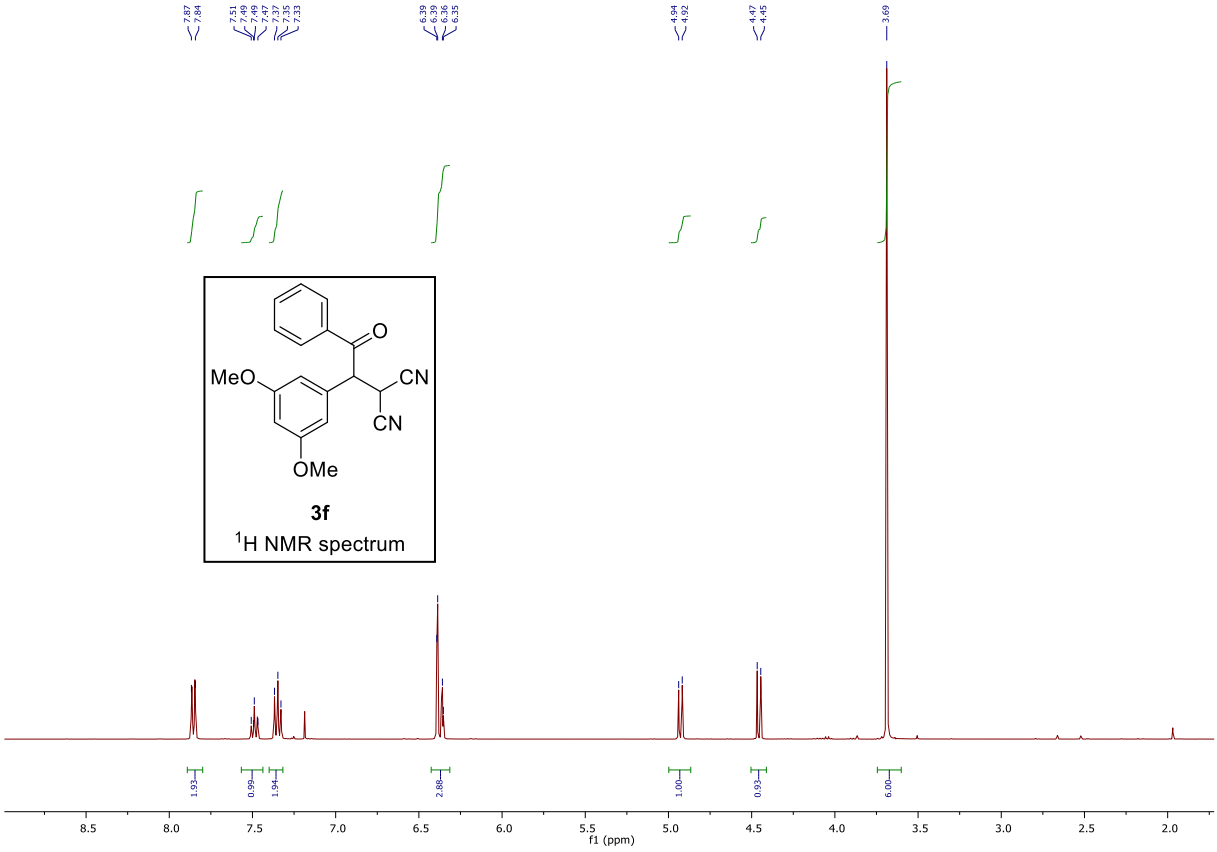
3d

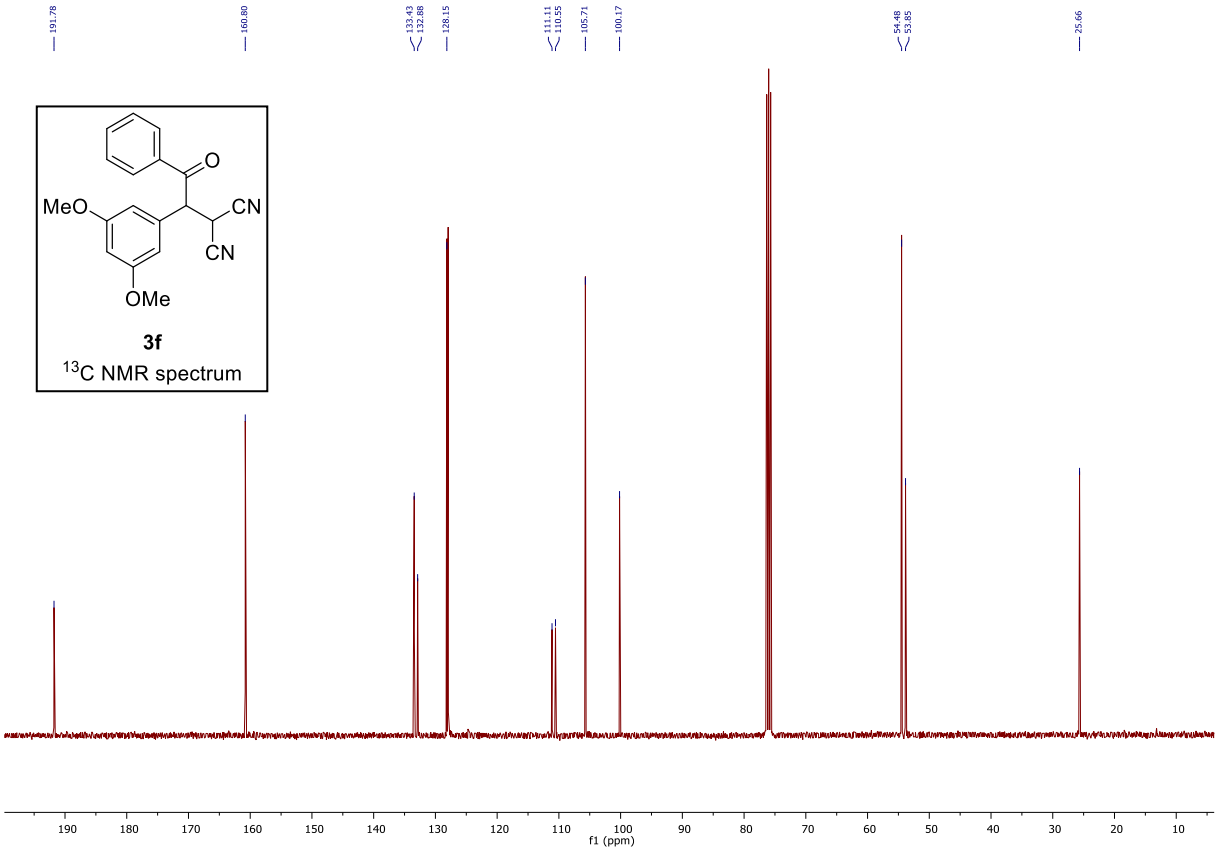
^{13}C NMR spectrum

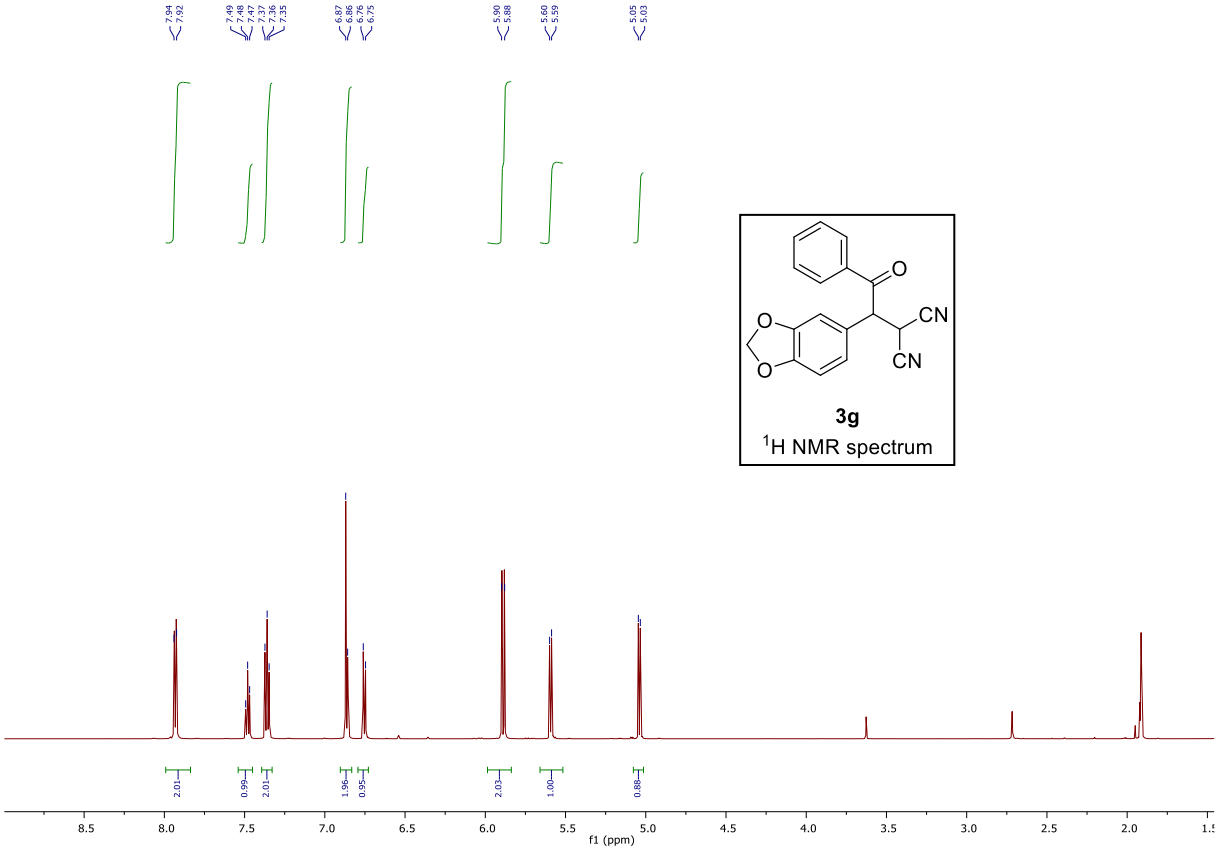


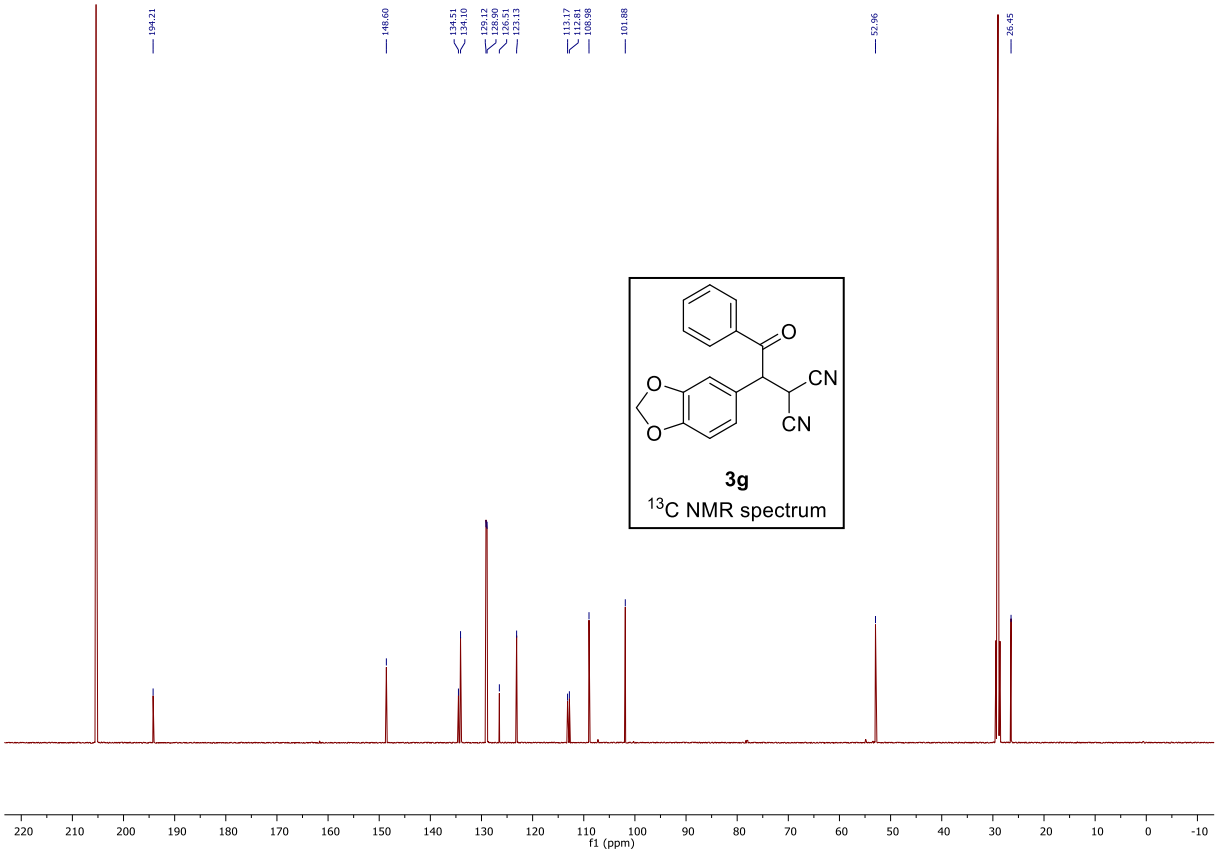

8.25
8.22
7.90
7.88
7.82
7.80
7.75
7.72
7.71
7.69
7.59
7.57
7.55
7.41
7.34
7.32
7.30
7.25
7.23
7.21
7.21
7.19
5.88
5.86
4.55
4.54
0.97
0.97
1.02
2.91
0.98
1.01
0.99
2.88
1.00
0.96
O
CN
CN
3e
1H NMR spectrum
f1 (ppm)

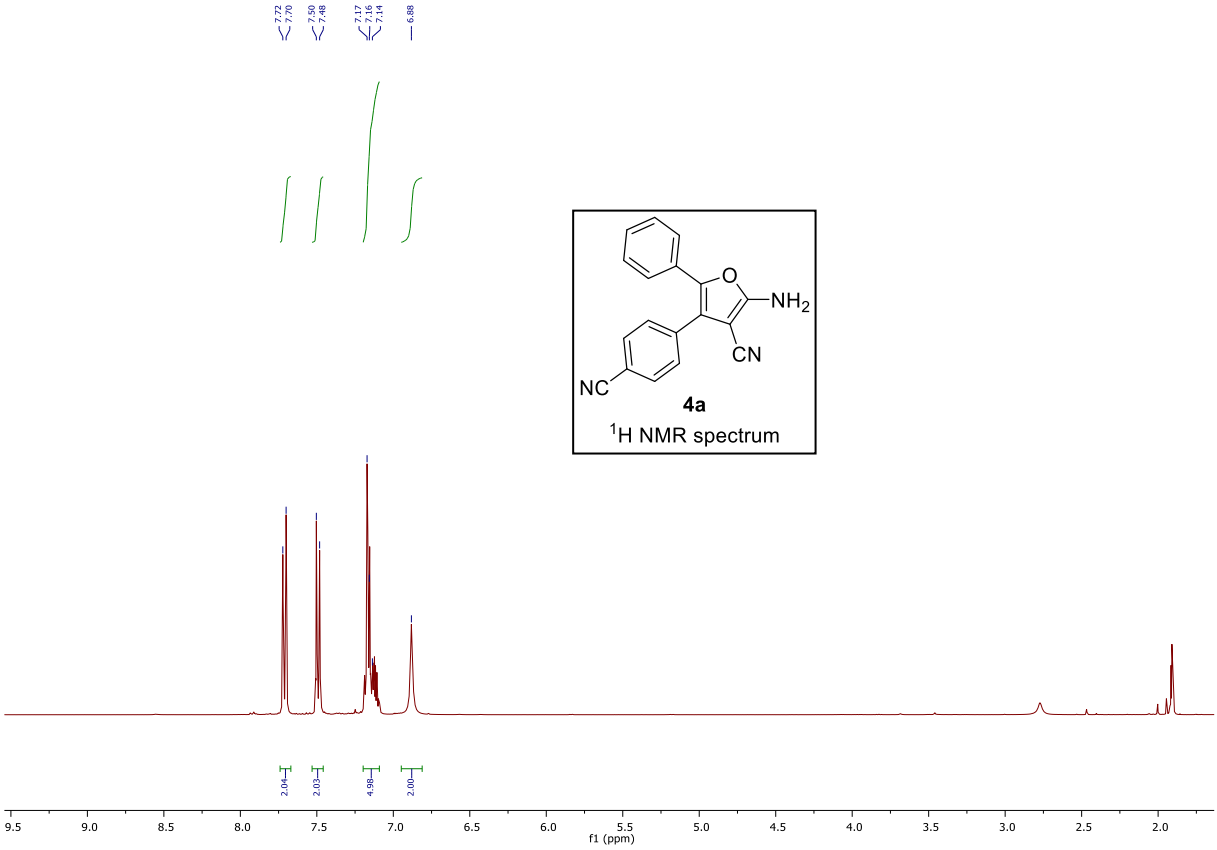

192.31
133.55
133.31
132.73
129.72
129.43
128.91
127.90
127.12
125.83
124.61
120.37
111.04
110.62
25.20
O
CN
CN
3e
13C NMR spectrum
f1 (ppm)

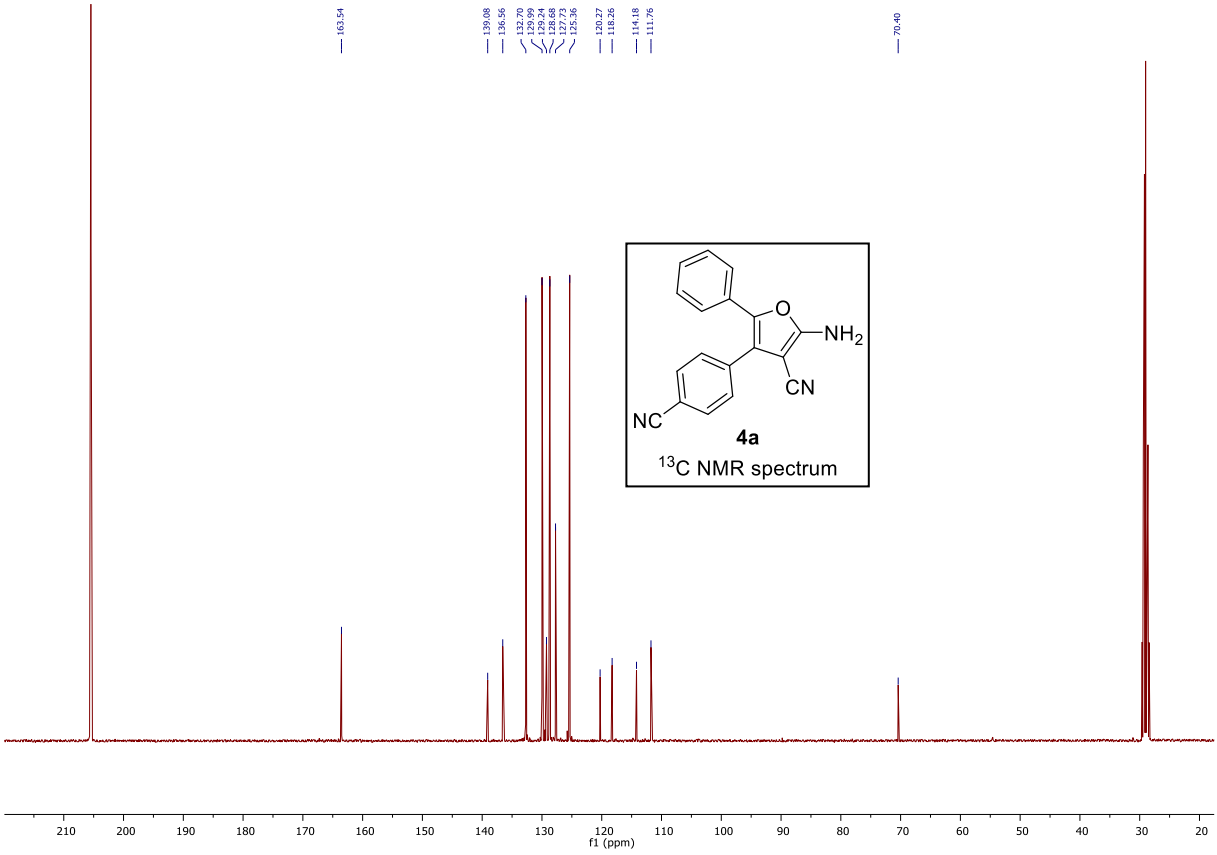

7.87
7.84
7.51
7.49
7.49
7.47
7.37
7.35
7.33
6.39
6.39
6.36
6.35
4.94
4.92
4.47
4.45
3.69
O
MeO
CN
CN
OMe
3f
1H NMR spectrum
1.93
0.99
1.94
2.88
1.00
0.93
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

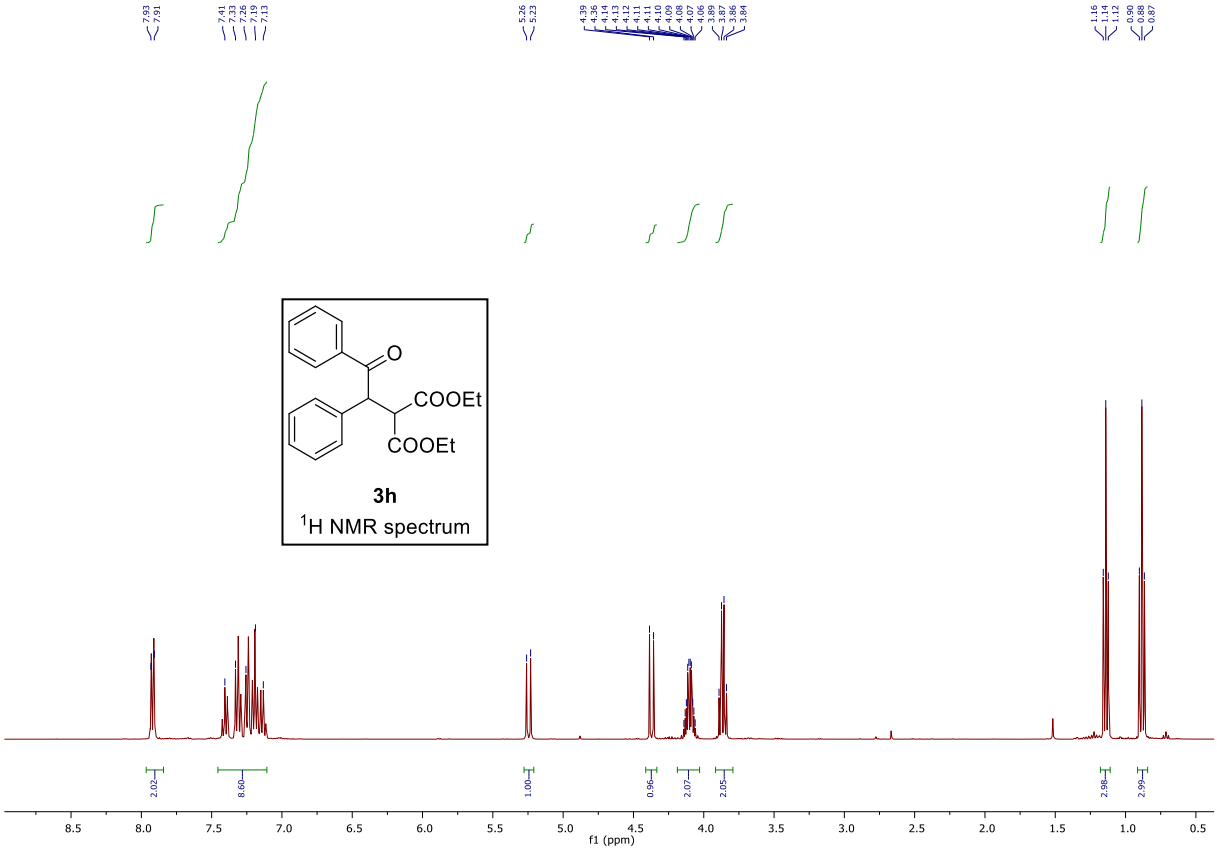

191.78
160.80
133.43
132.88
128.15
111.11
110.55
105.71
100.17
54.48
53.85
25.66
O
MeO
CN
CN
OMe
3f
13C NMR spectrum
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

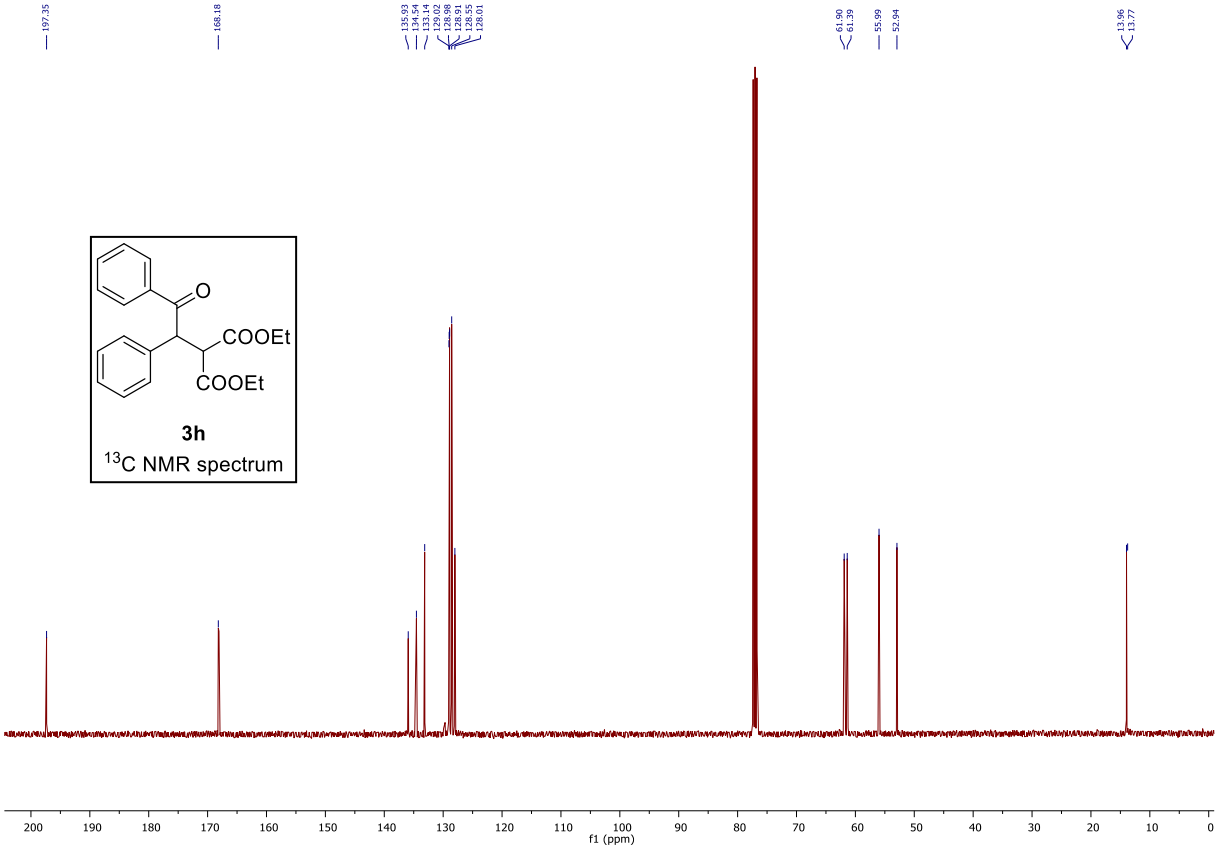

7.94
7.92
7.49
7.48
7.47
7.37
7.36
7.35
6.87
6.86
6.85
6.75
5.90
5.88
5.60
5.59
5.05
5.03
O
O
O
CN
CN
3g
1H NMR spectrum
2.01
0.99
2.01
1.96
0.95
2.03
1.00
0.88
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

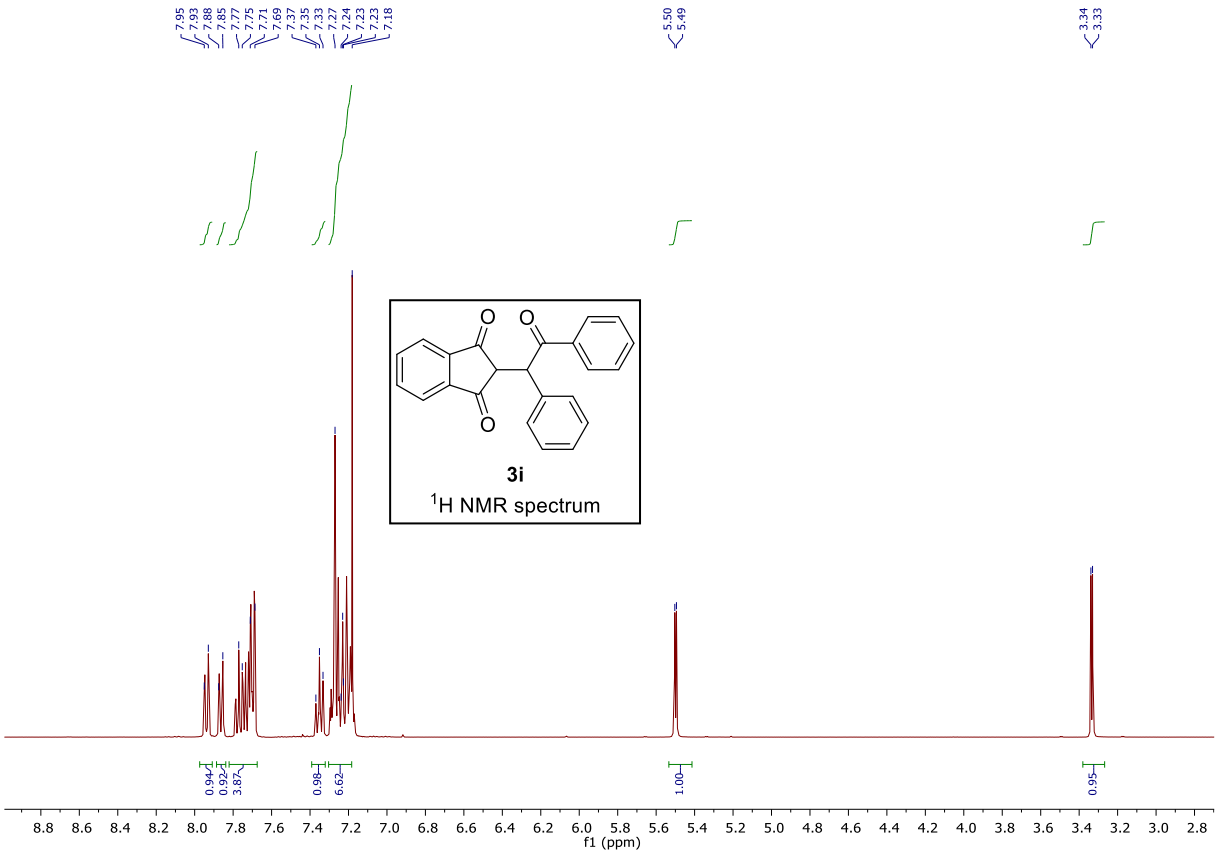

194.21
148.60
134.51
134.10
129.12
128.90
126.51
123.13
113.17
112.81
108.98
101.88
52.96
26.45
O
O
O
CN
CN
3g
13C NMR spectrum
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

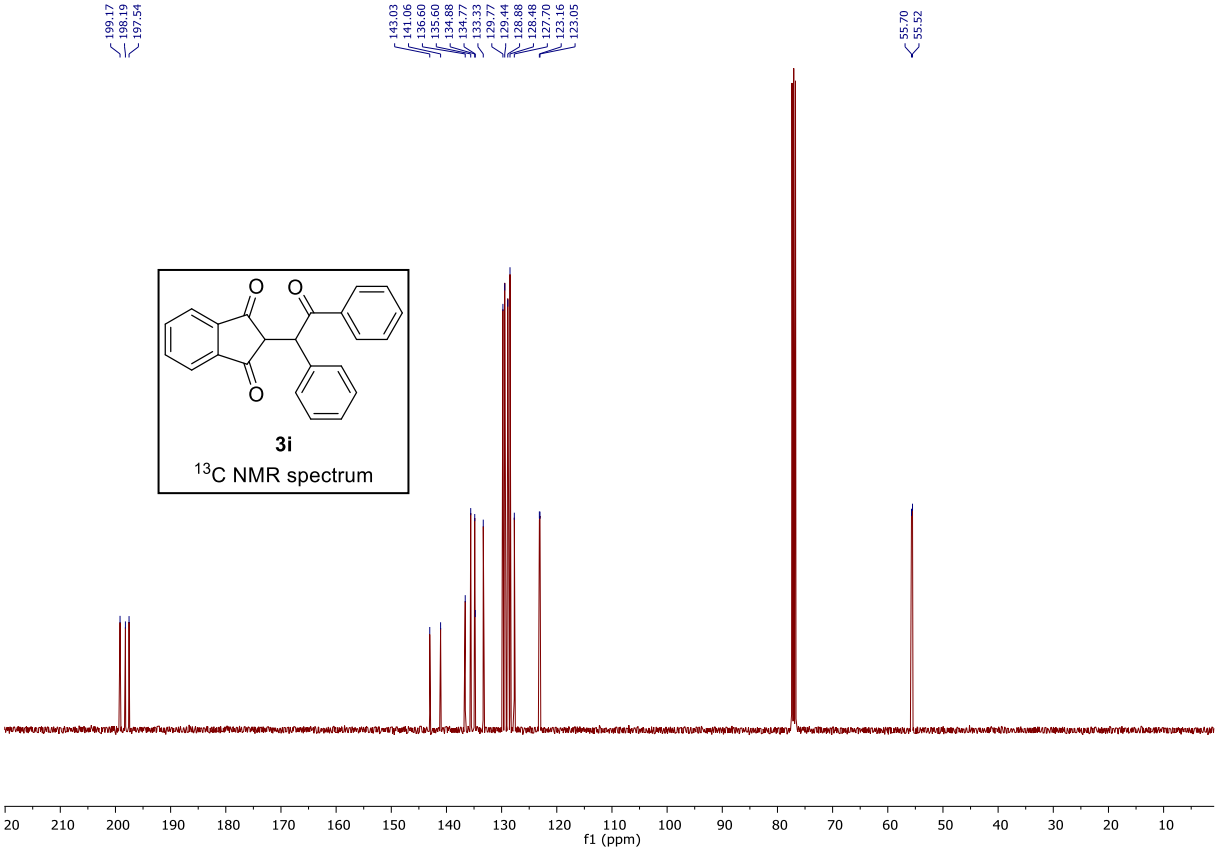

7.72
7.70
7.50
7.48
7.17
7.16
7.14
6.88
O
NH2
CN
NC
4a
1H NMR spectrum
2.04
2.03
4.98
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

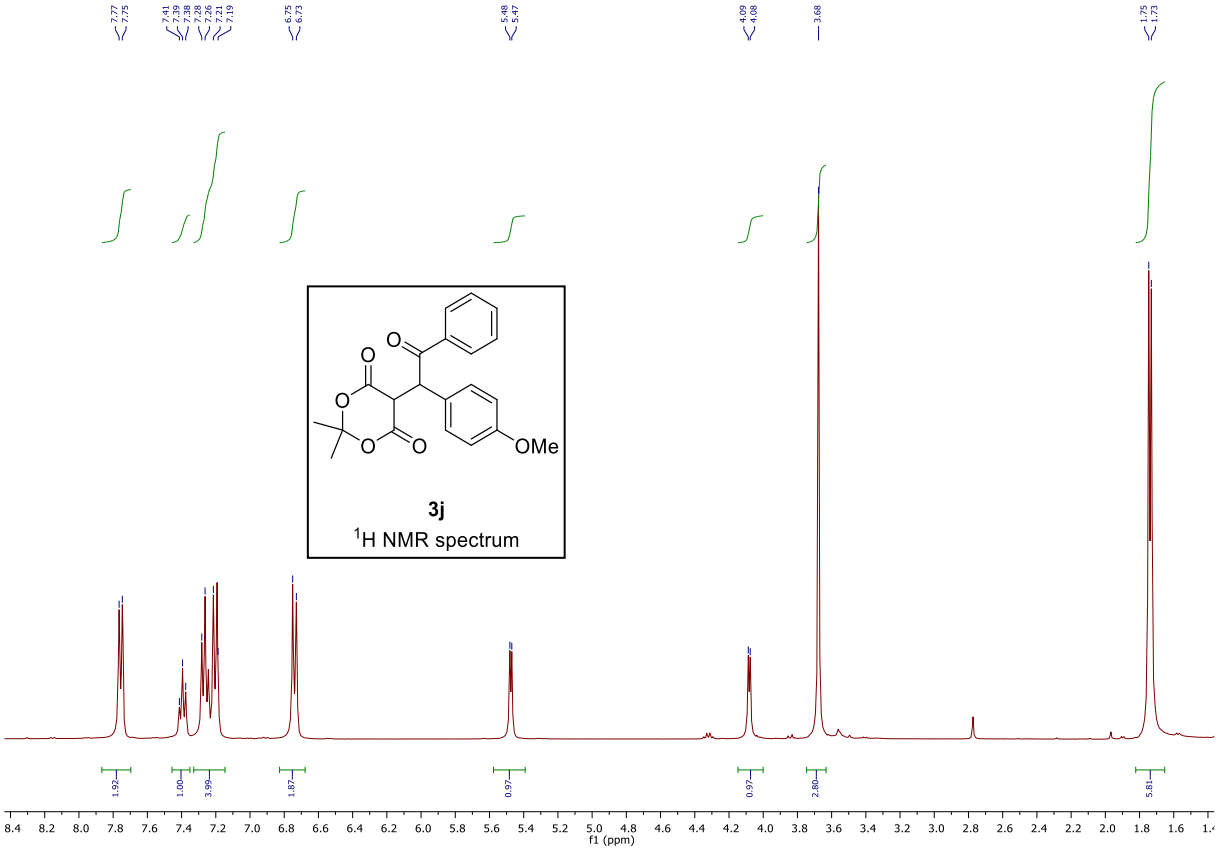

163.54
139.08
136.56
132.70
129.99
129.24
128.68
127.73
125.36
120.27
118.26
114.18
111.76
70.40
O
NH2
CN
NC
4a
13C NMR spectrum
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

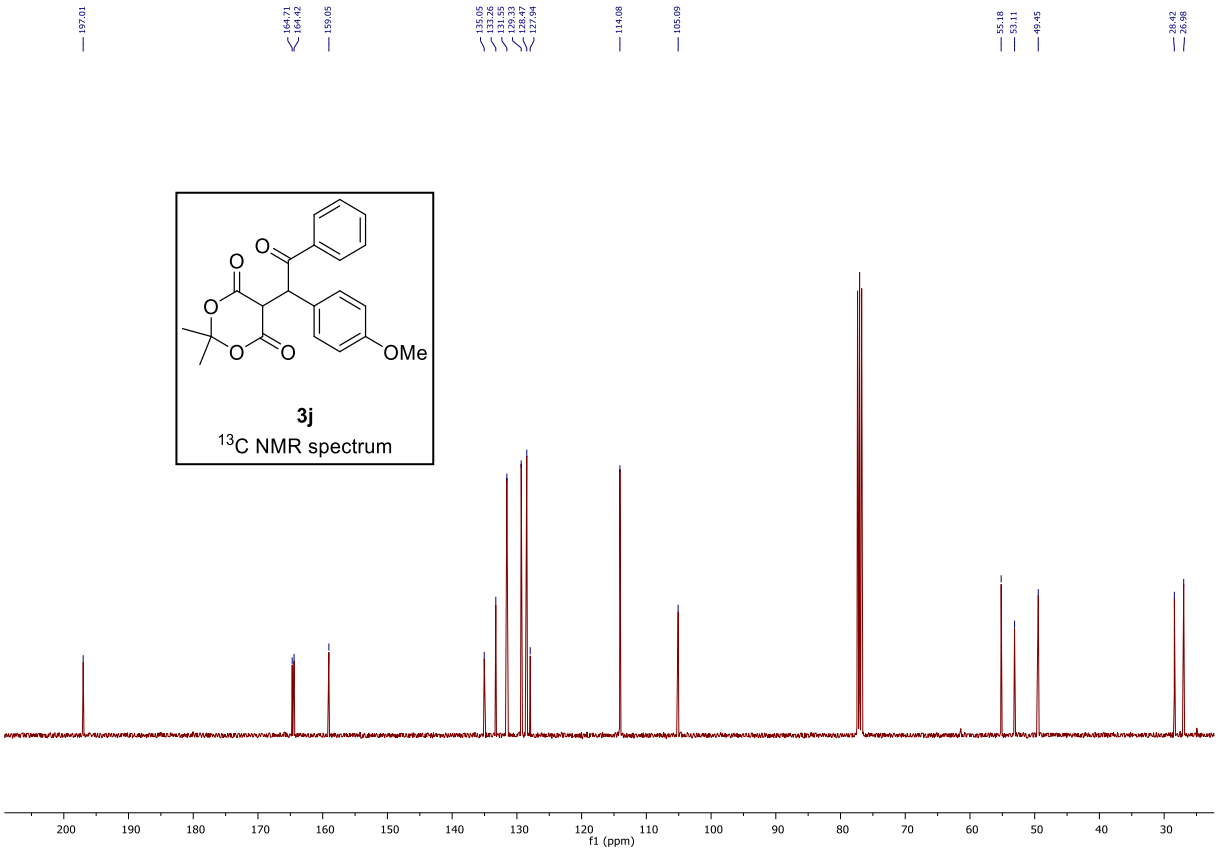

O
COOEt
COOEt
3h
1H NMR spectrum
f1 (ppm)

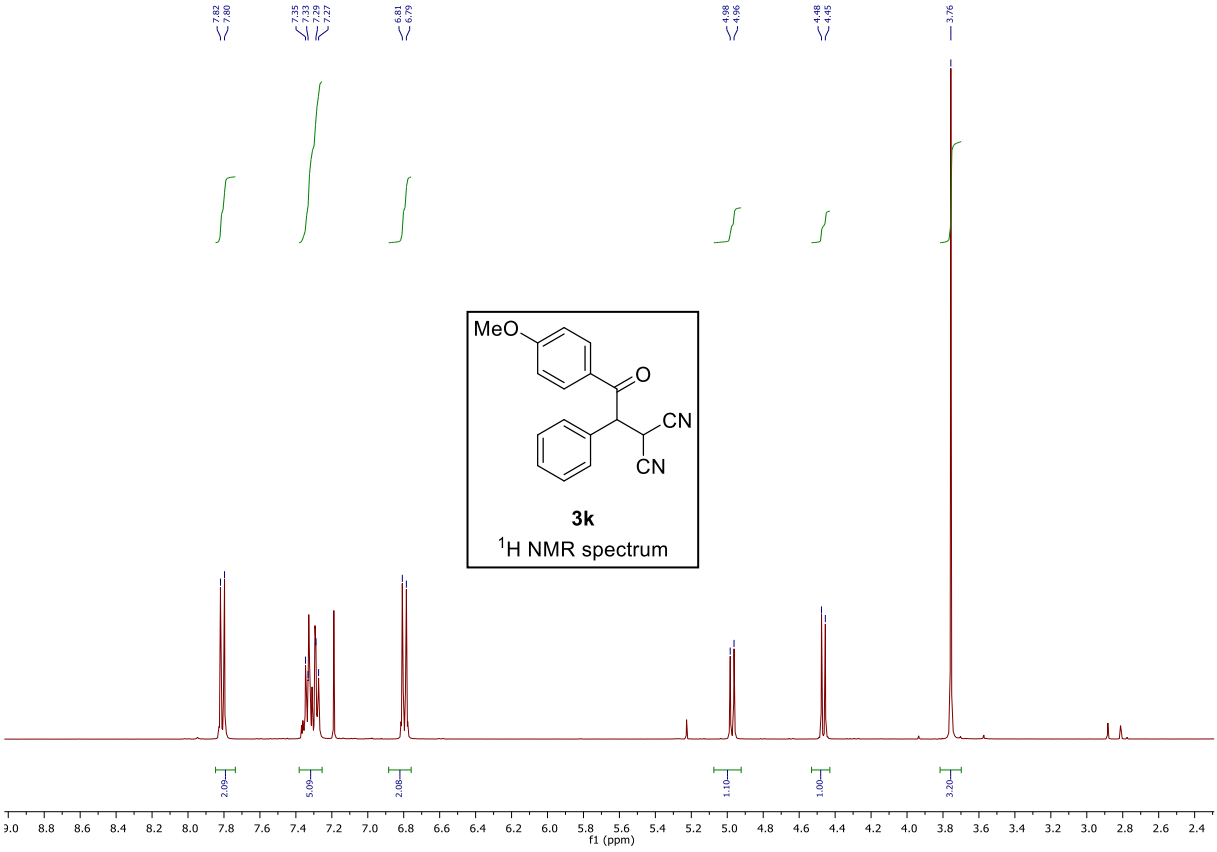

O
COOEt
COOEt
3h
13C NMR spectrum
f1 (ppm)

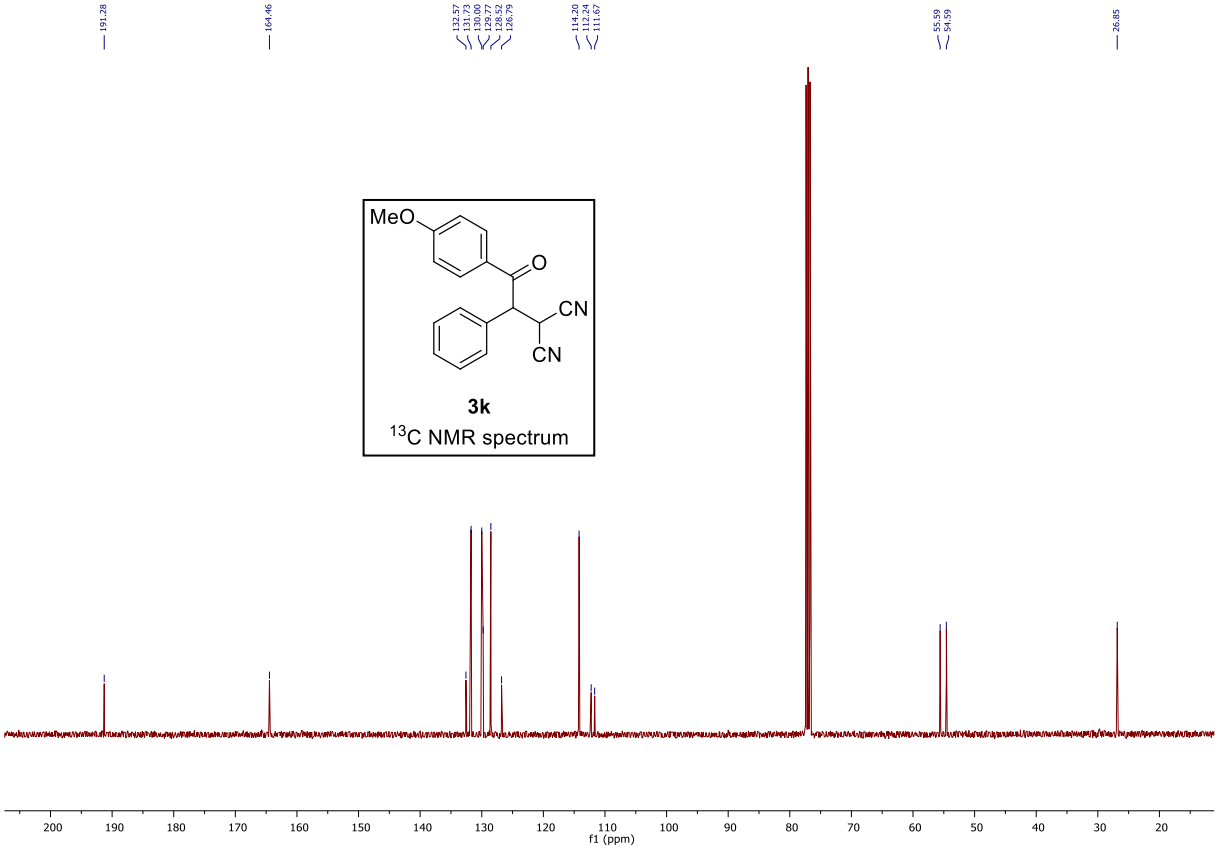

7.95
7.93
7.88
7.85
7.77
7.75
7.71
7.69
7.37
7.35
7.33
7.27
7.24
7.23
7.23
7.18
5.50
5.49
3.34
3.33
O
O
O
3i
1H NMR spectrum
0.94
0.92
3.87
0.98
6.62
1.00
0.95
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8
f1 (ppm)

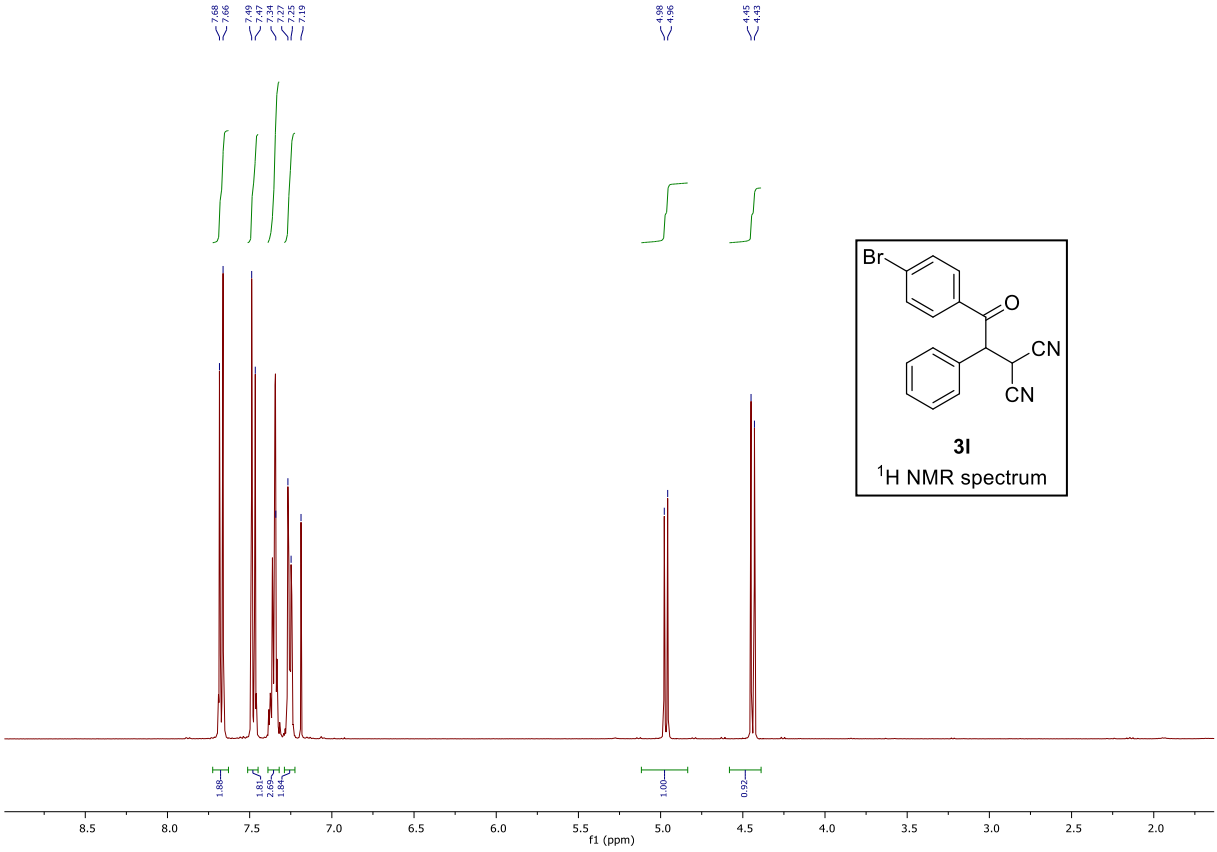

199.17
198.19
197.54
143.03
141.06
136.60
135.60
134.88
134.77
133.33
129.77
129.44
128.88
128.48
127.70
123.16
123.05
55.70
55.52
O
O
O
3i
13C NMR spectrum
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

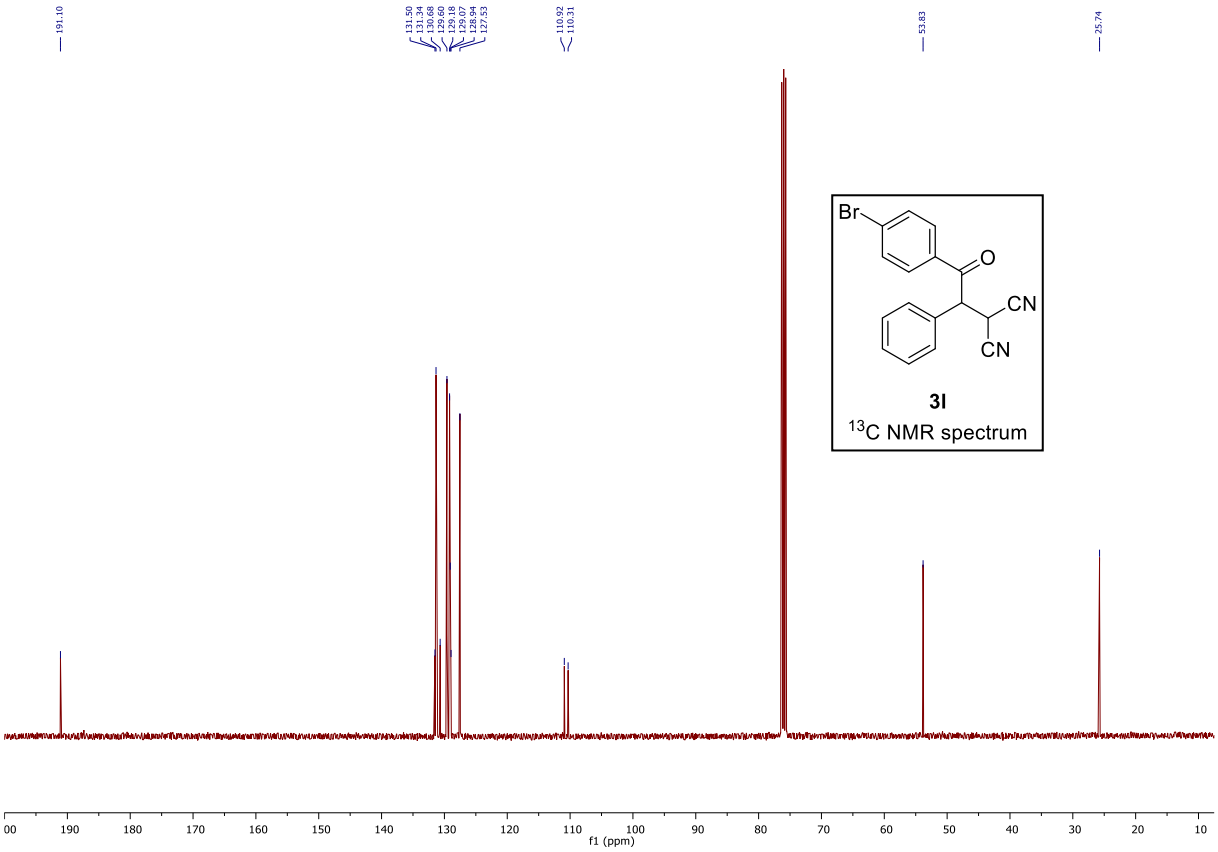

7.77
7.75
7.41
7.39
7.38
7.28
7.26
7.21
7.19
6.75
6.73
5.48
5.47
4.09
4.08
3.68
1.75
1.73
O
O
O
O
O
OMe
3j
1H NMR spectrum
1.92
1.00
3.99
1.87
0.97
0.97
2.80
5.81
f1 (ppm)

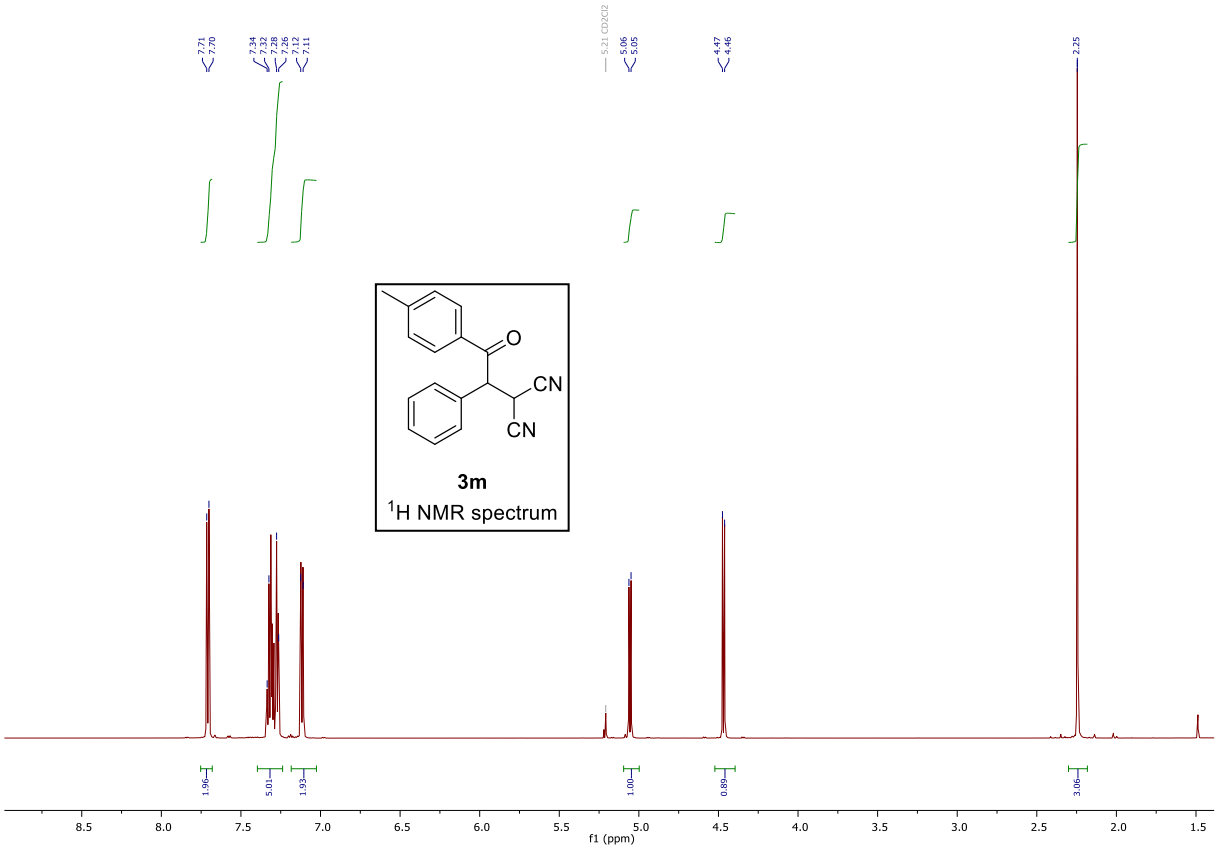

197.01
164.71
164.42
159.05
135.05
133.26
131.55
129.33
128.47
127.94
114.08
105.09
55.18
53.11
49.45
28.42
26.98
O
O
O
O
O
OMe
3j
13C NMR spectrum
f1 (ppm)

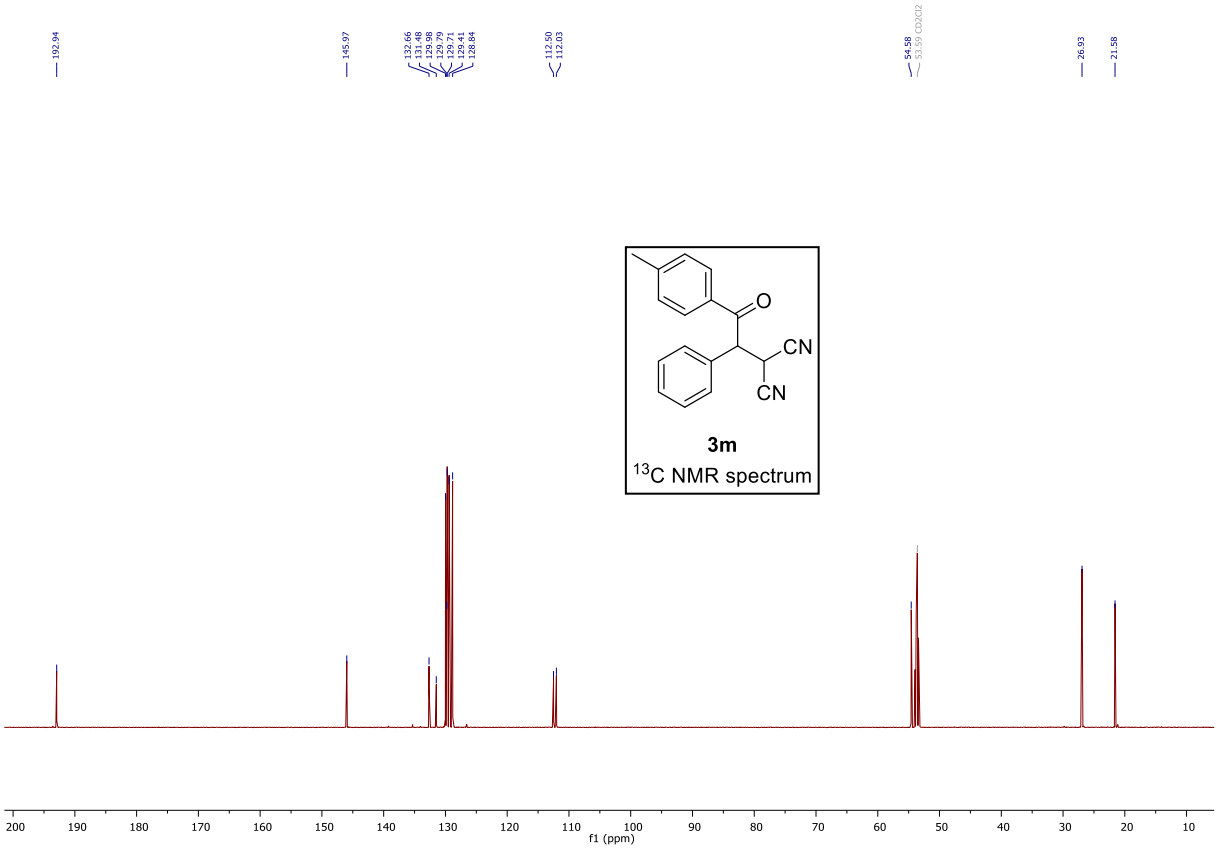

MeO
O
CN
CN
3k
1H NMR spectrum
f1 (ppm)

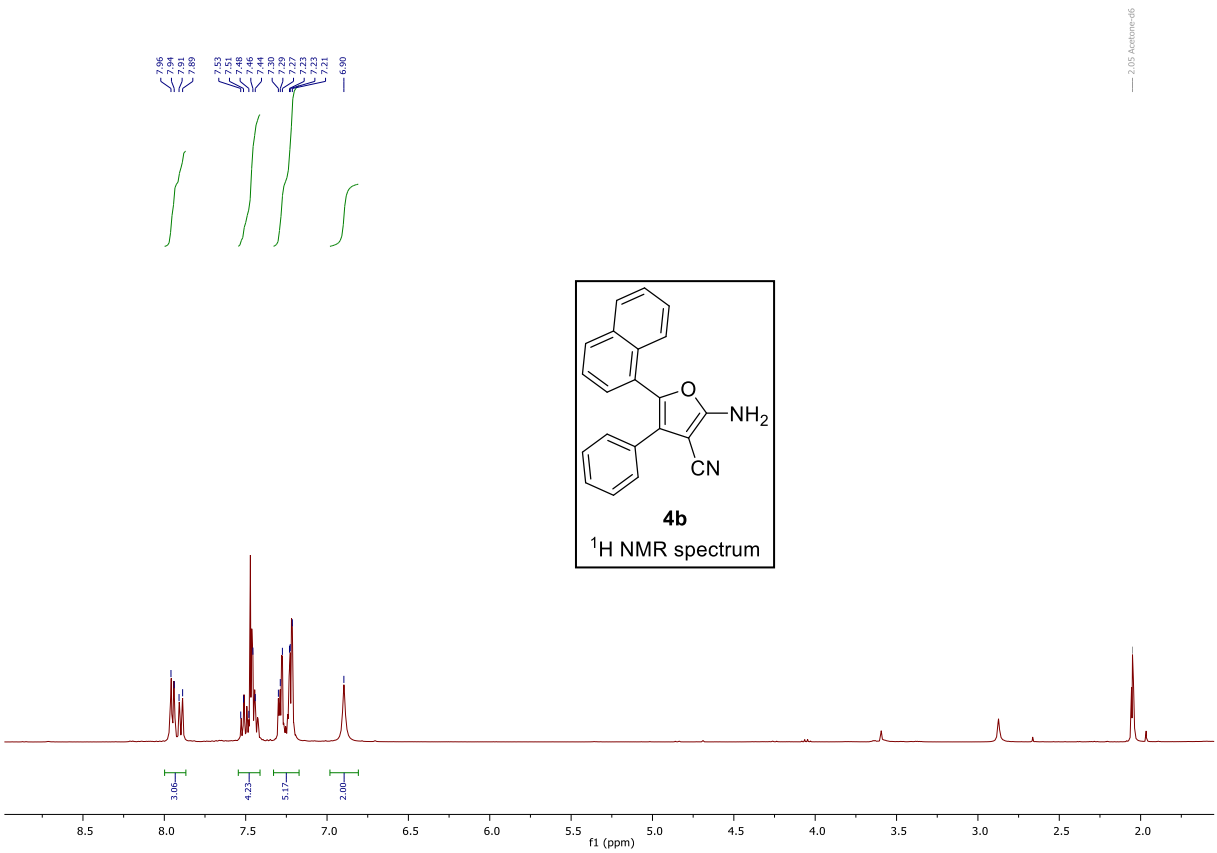

MeO
O
CN
CN
3k
13C NMR spectrum
f1 (ppm)

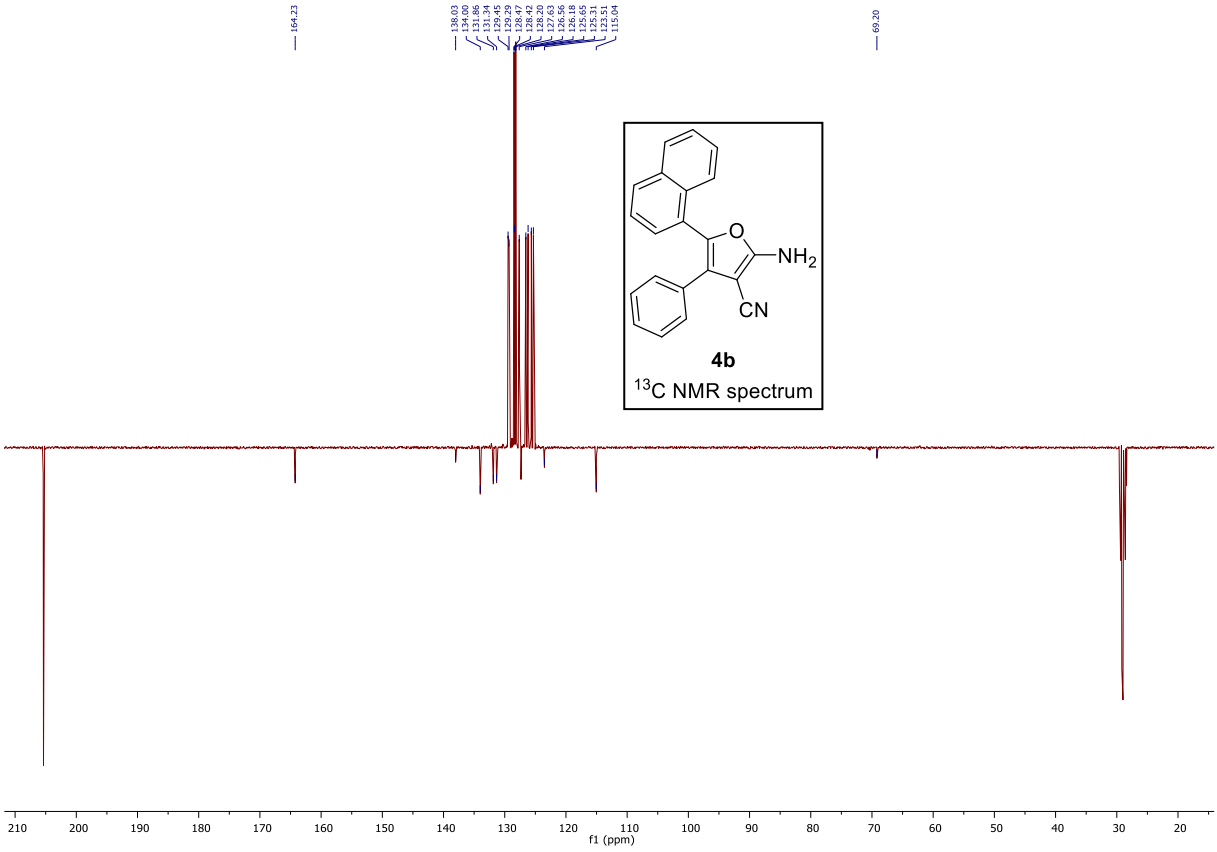

7.68
7.66
7.49
7.47
7.34
7.27
7.25
7.19
4.98
4.96
4.45
4.43
1.88
1.81
2.69
1.84
1.00
0.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)
Br
O
CN
CN
3l
^{1}H NMR spectrum

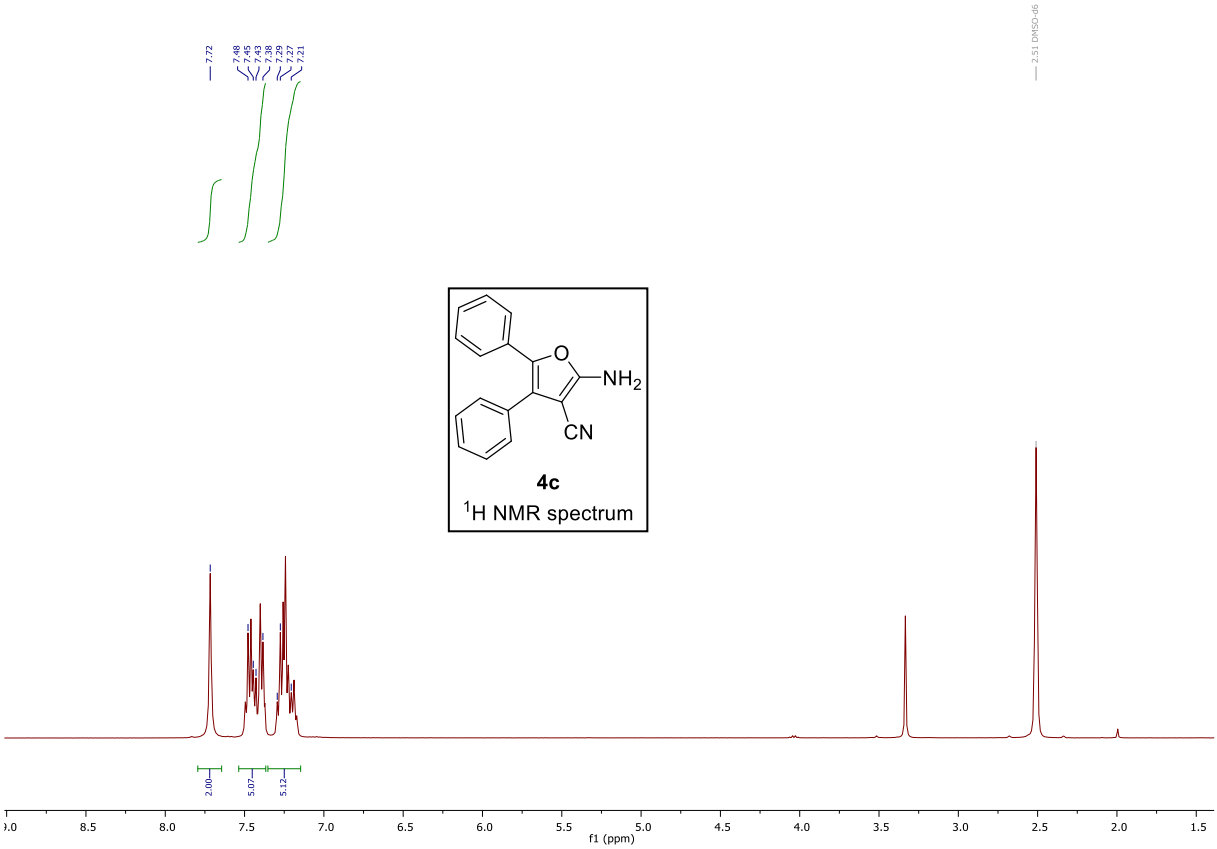

191.10
131.50
131.34
130.68
129.60
129.18
129.07
128.94
127.53
110.92
110.31
53.83
25.74
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
Br
O
CN
CN
3l
^{13}C NMR spectrum

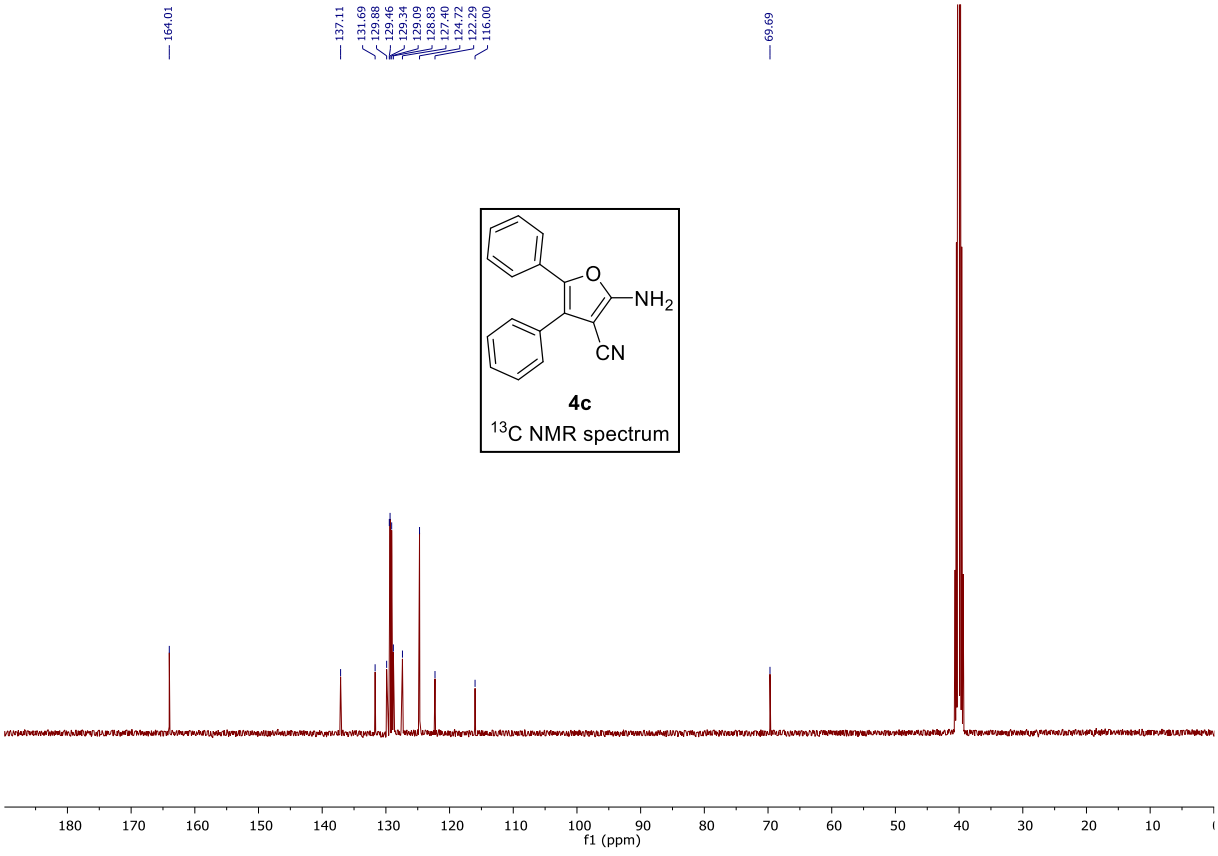

7.71
7.70
7.34
7.33
7.28
7.26
7.12
7.11
5.21 CD2Cl2
5.06
5.05
4.47
4.46
2.25
O
CN
CN
3m
1H NMR spectrum
1.96
5.01
1.93
1.00
0.89
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

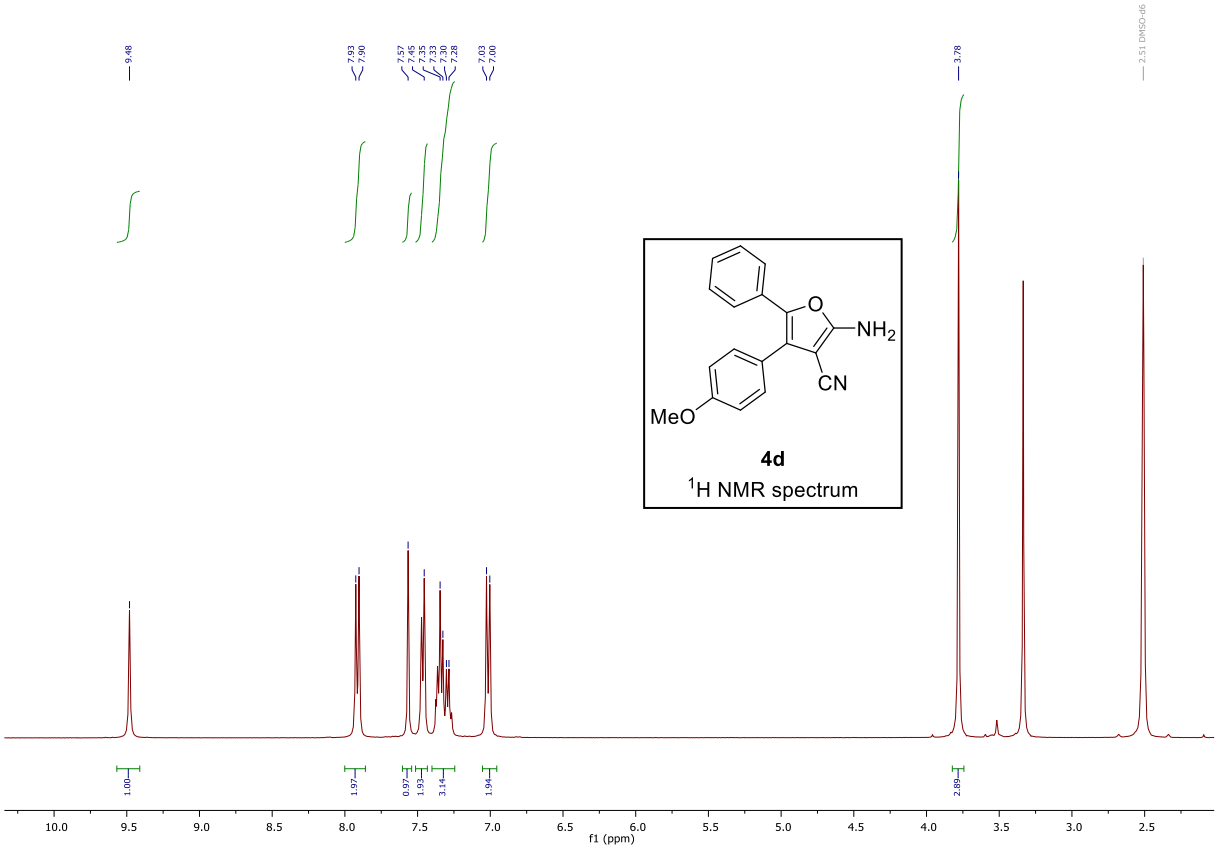

192.94
145.97
132.66
131.48
129.98
129.79
129.71
128.41
128.04
112.50
112.03
54.58
53.59 CD2Cl2
26.93
21.58
O
CN
CN
3m
13C NMR spectrum
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

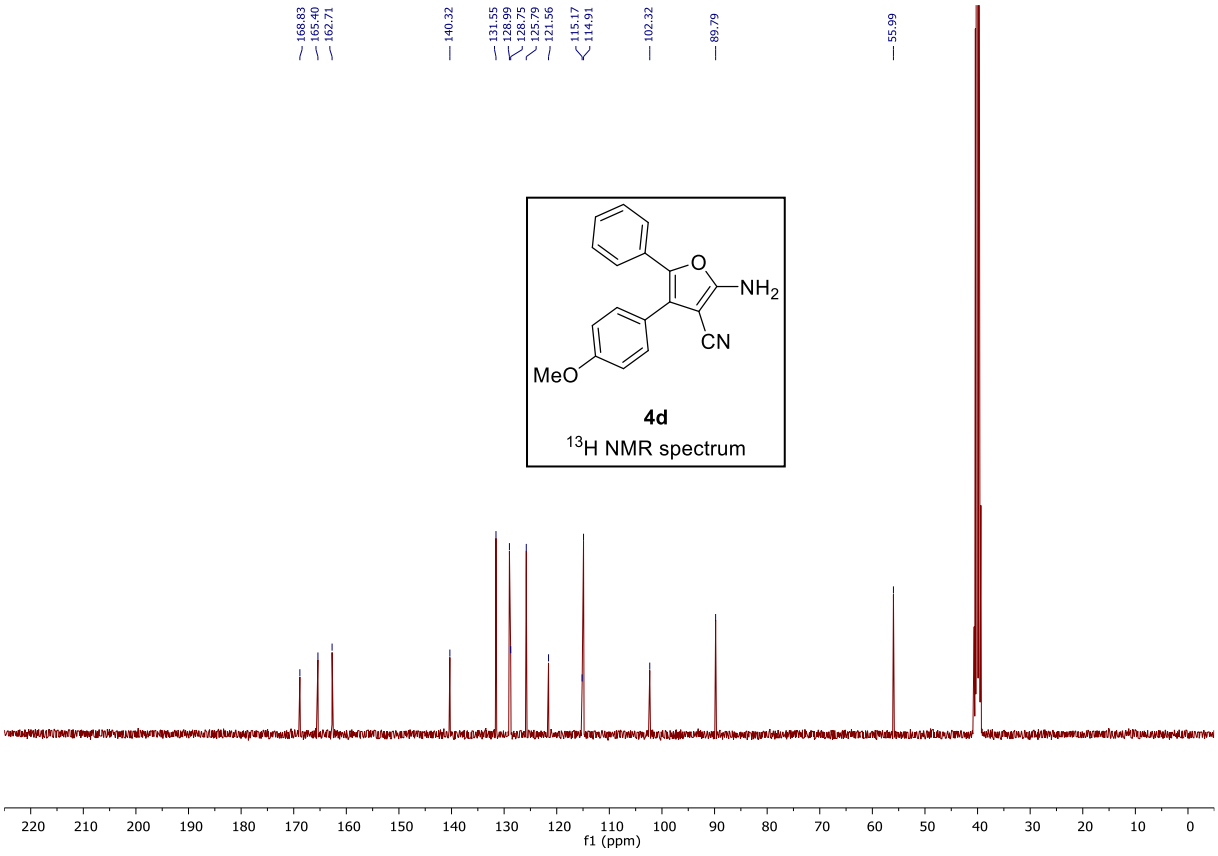

7.96
7.94
7.91
7.89
7.53
7.51
7.48
7.46
7.44
7.30
7.29
7.27
7.23
7.21
6.90
2.05 Acetone-d6
O
NH2
CN
4b
1H NMR spectrum
3.06
4.23
5.17
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

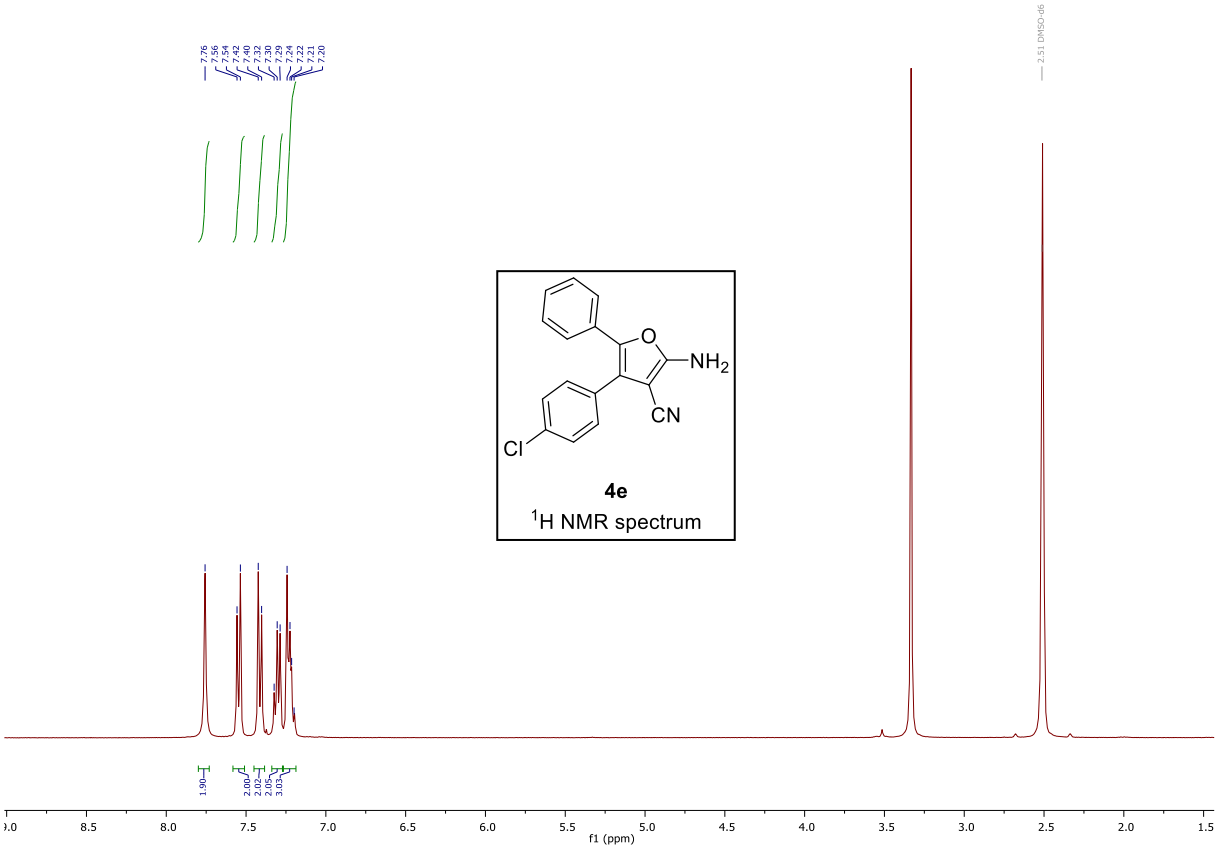

164.23
138.03
134.00
131.86
131.34
129.45
129.29
128.47
128.43
128.20
127.63
126.56
126.18
125.65
125.31
123.51
115.04
69.20
O
NH2
CN
4b
13C NMR spectrum
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

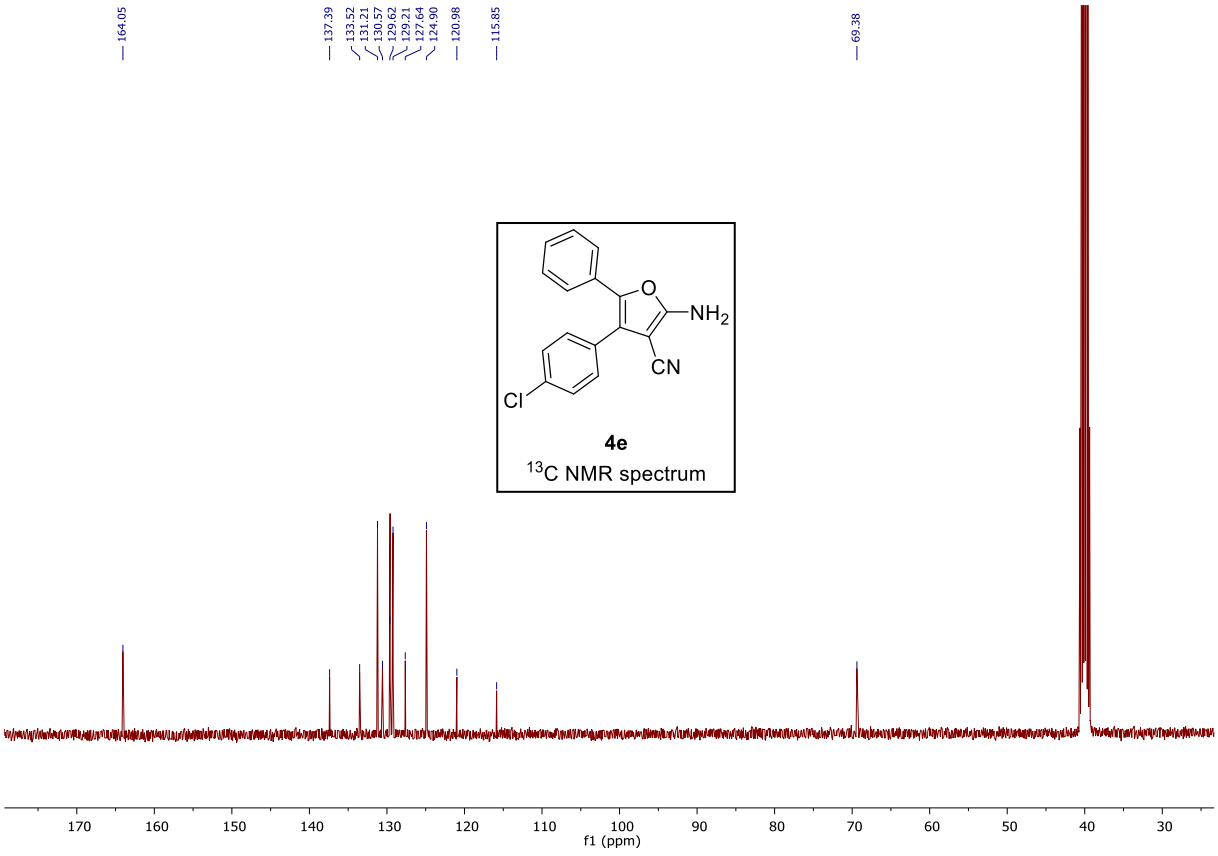

7.72
7.48
7.45
7.43
7.38
7.29
7.27
7.21
2.51 DMSO-d6
O
NH2
CN
4c
1H NMR spectrum
2.00
5.07
5.12
f1 (ppm)

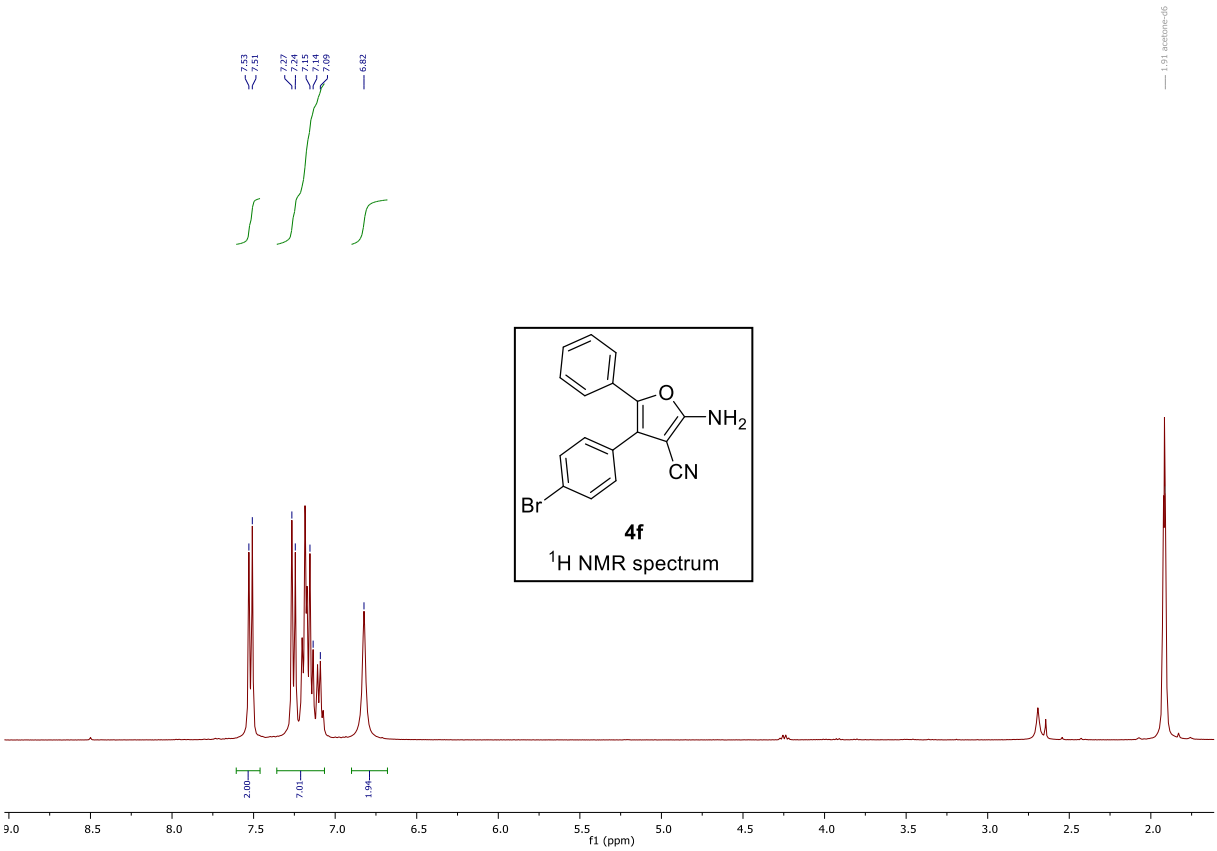

164.01
137.11
131.69
129.88
129.46
129.34
128.89
128.83
127.40
124.72
122.29
116.00
69.69
O
NH2
CN
4c
13C NMR spectrum
f1 (ppm)

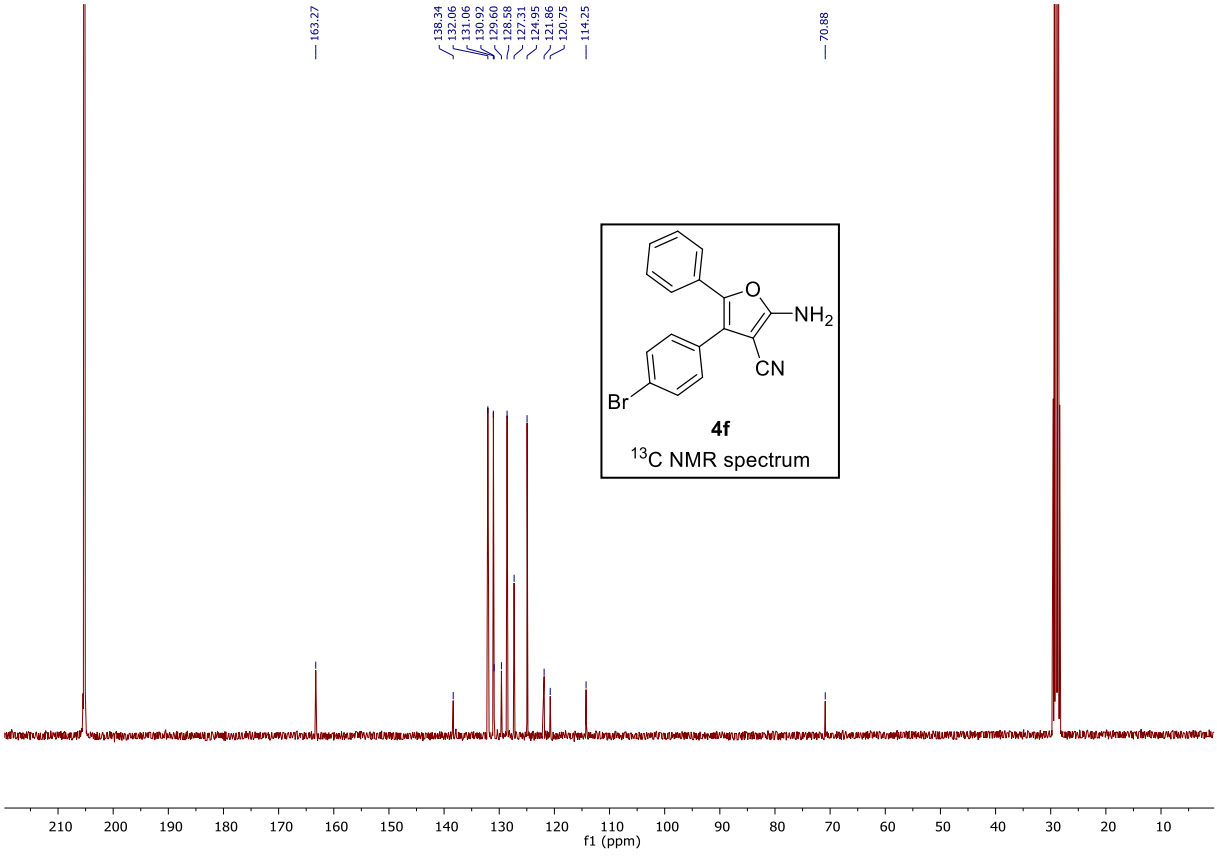

9.48
7.93
7.90
7.57
7.45
7.35
7.33
7.30
7.28
7.03
7.00
3.78
2.51 DMSO-d6
1.00
1.97
0.97
1.93
3.14
1.94
2.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)
O
NH2
CN
MeO
4d
1H NMR spectrum

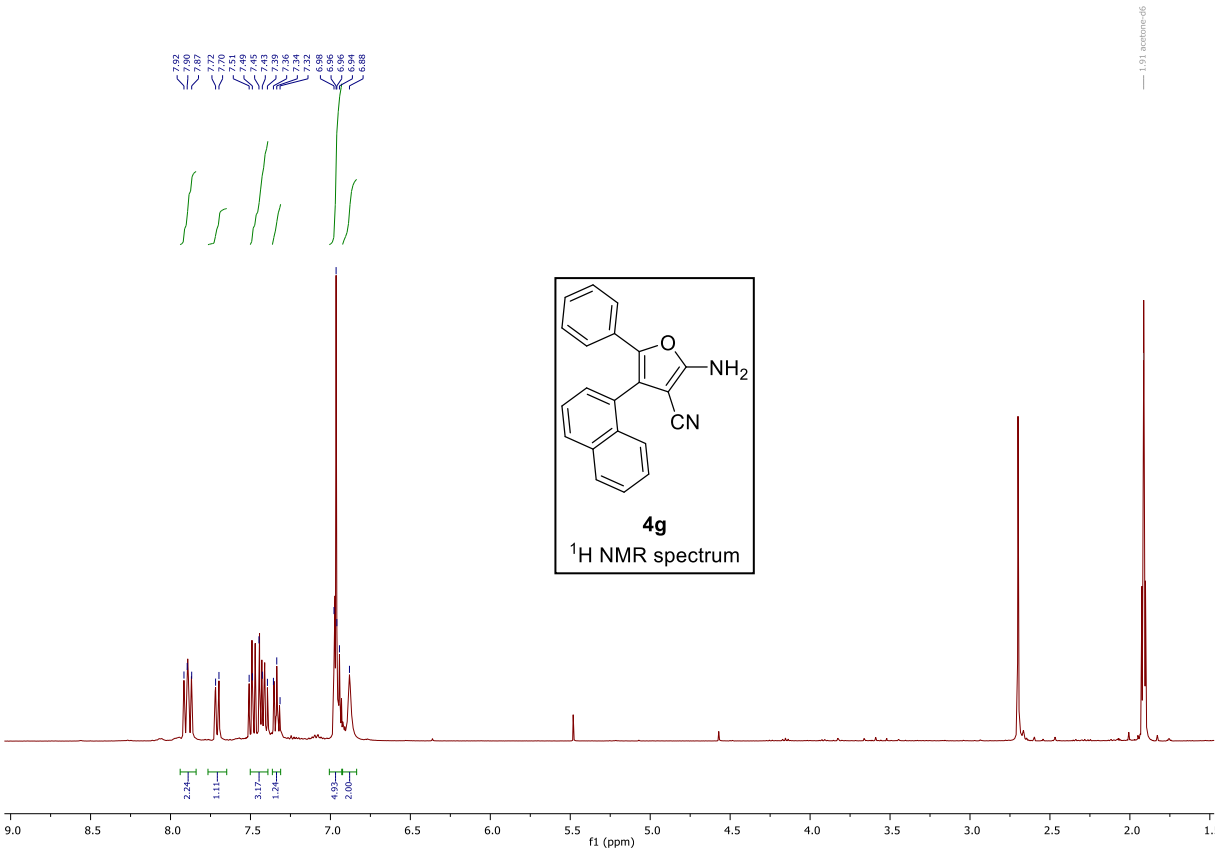

168.83
165.40
162.71
140.32
131.55
128.99
128.75
125.79
121.56
115.17
114.91
102.32
89.79
55.99
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
NH2
CN
MeO
4d
13H NMR spectrum

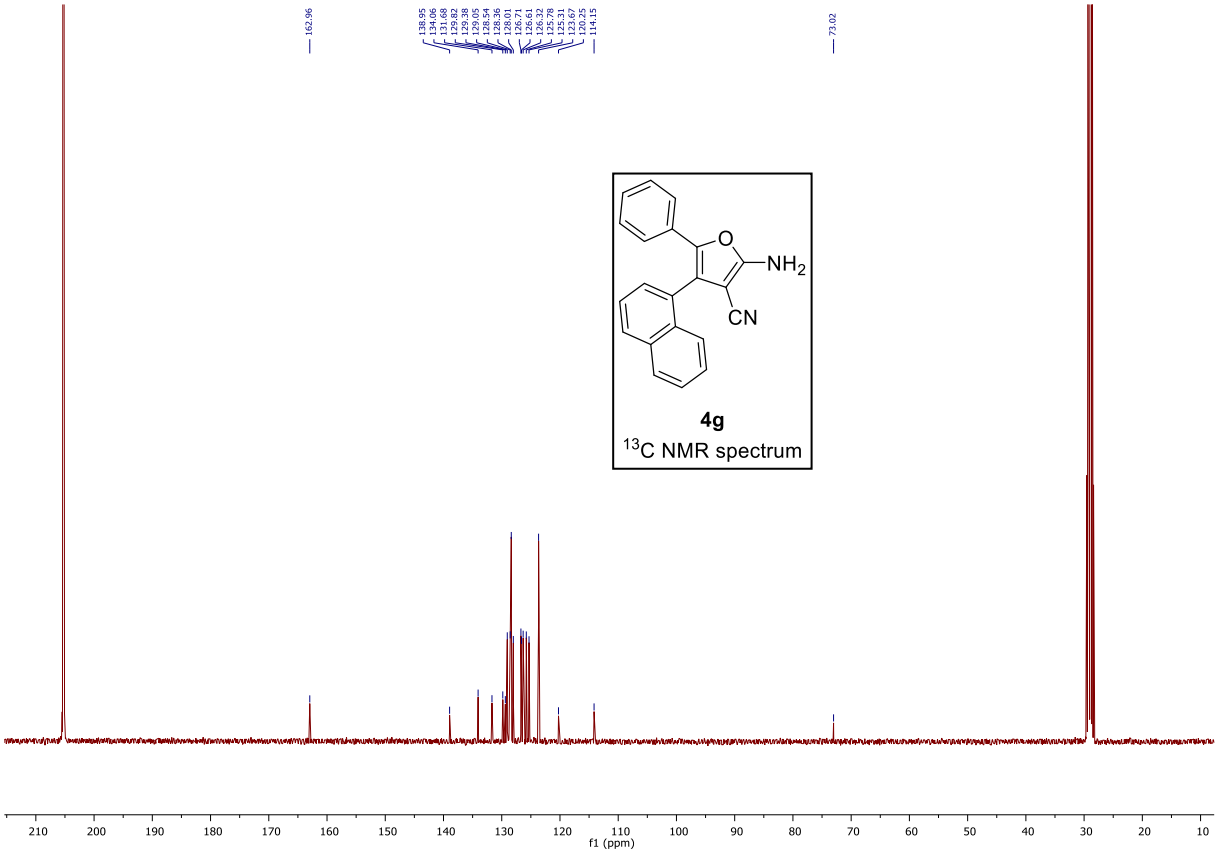

7.76
7.56
7.54
7.42
7.40
7.32
7.30
7.29
7.24
7.22
7.21
7.20
2.51 DMSO-d6
O
NH2
CN
Cl
4e
1H NMR spectrum
1.90
2.00
2.02
2.05
3.03
f1 (ppm)

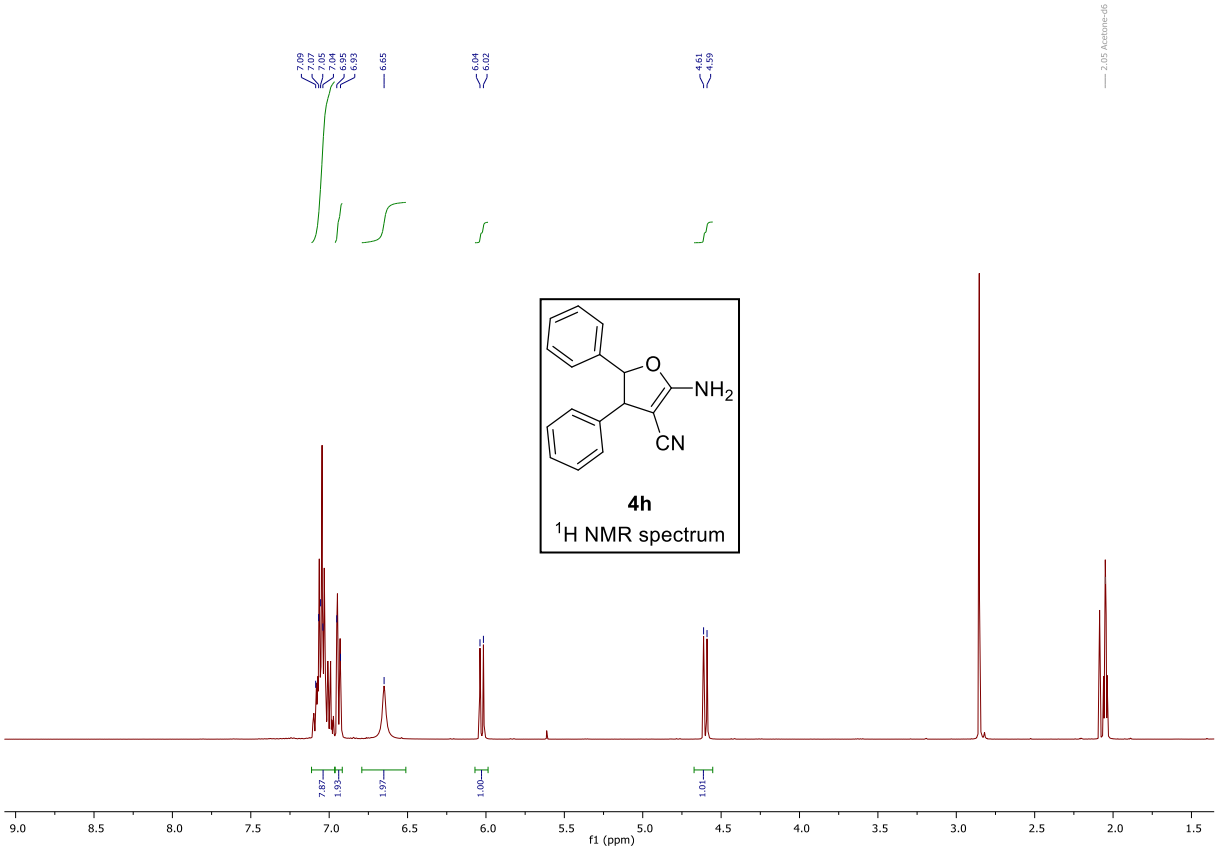

164.05
137.39
133.52
131.21
130.57
129.62
129.21
127.64
124.90
120.98
115.85
69.38
O
NH2
CN
Cl
4e
13C NMR spectrum
f1 (ppm)

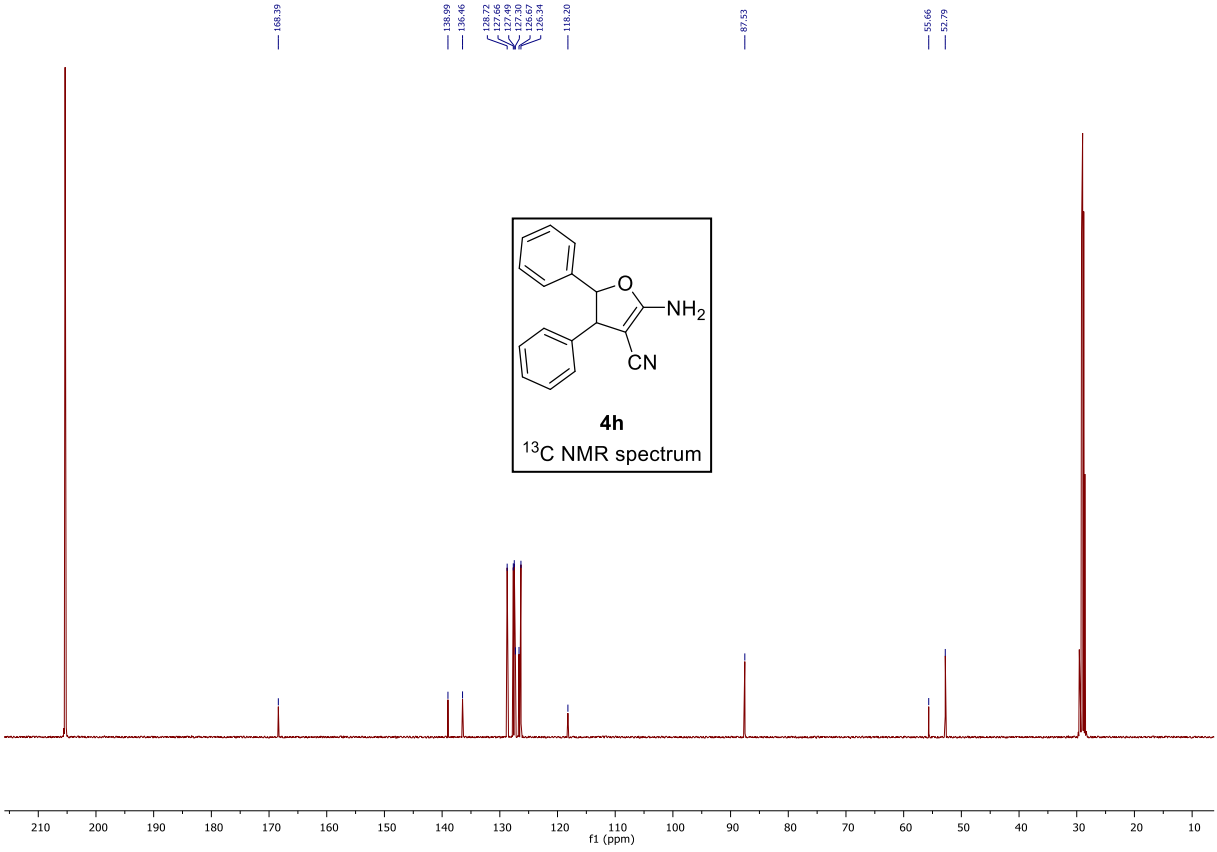

7.53
7.51
7.27
7.24
7.15
7.14
7.09
6.82
1.91 acetone-d6
O
NH2
CN
Br
4f
1H NMR spectrum
2.00
7.01
1.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

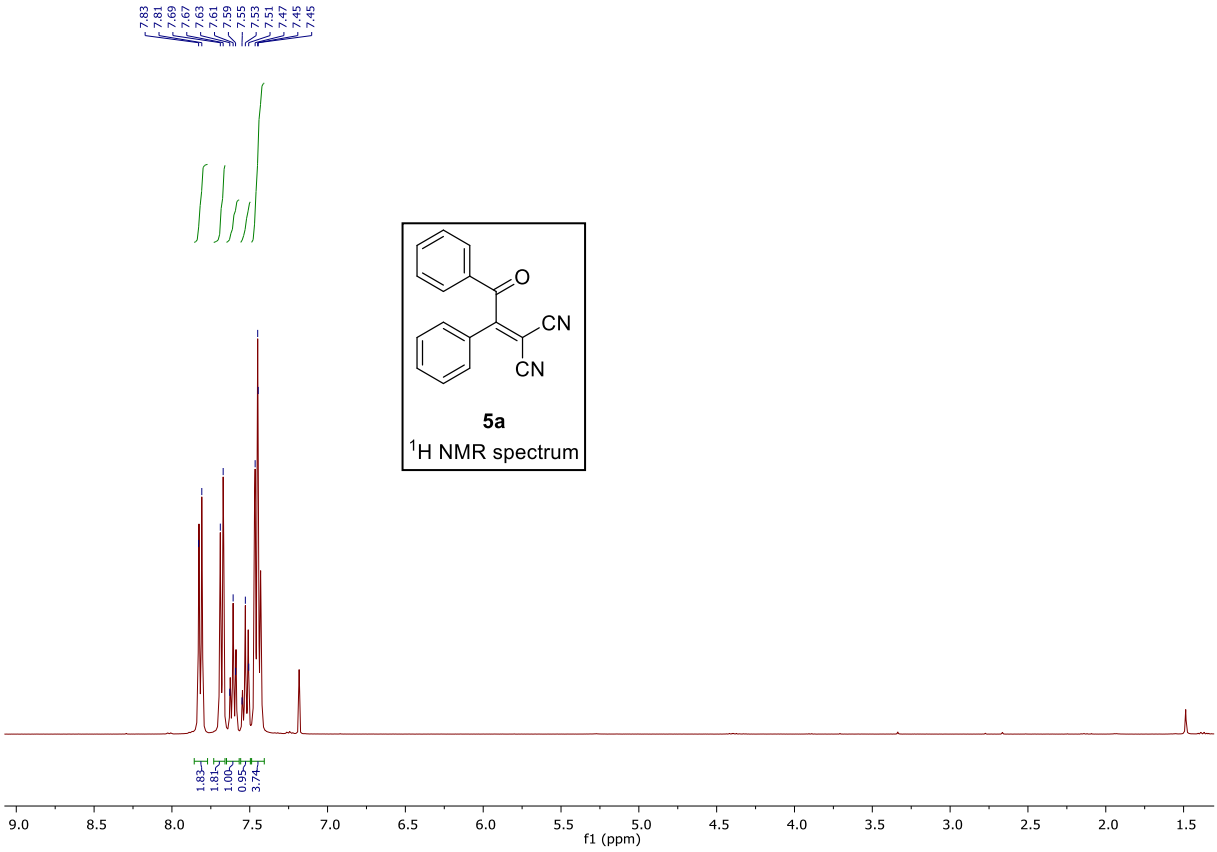

163.27
138.34
132.06
131.06
130.92
129.60
128.58
127.31
124.95
121.86
120.75
114.25
70.88
O
NH2
CN
Br
4f
13C NMR spectrum
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

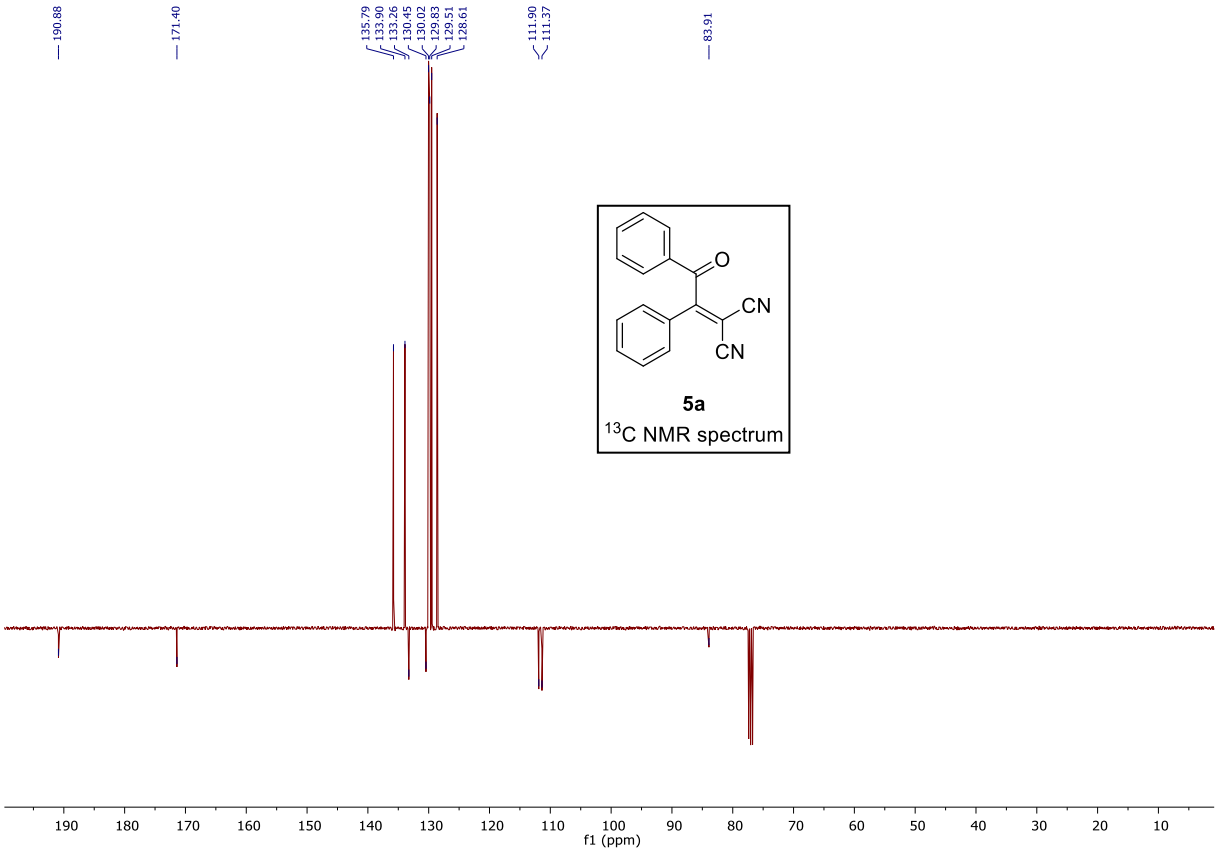

7.92
7.90
7.87
7.72
7.70
7.51
7.49
7.45
7.43
7.39
7.36
7.34
7.32
6.98
6.96
6.96
6.94
6.88
1.91 acetone-d6
O
NH2
CN
4g
1H NMR spectrum
2.24
1.11
3.17
1.24
4.93
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

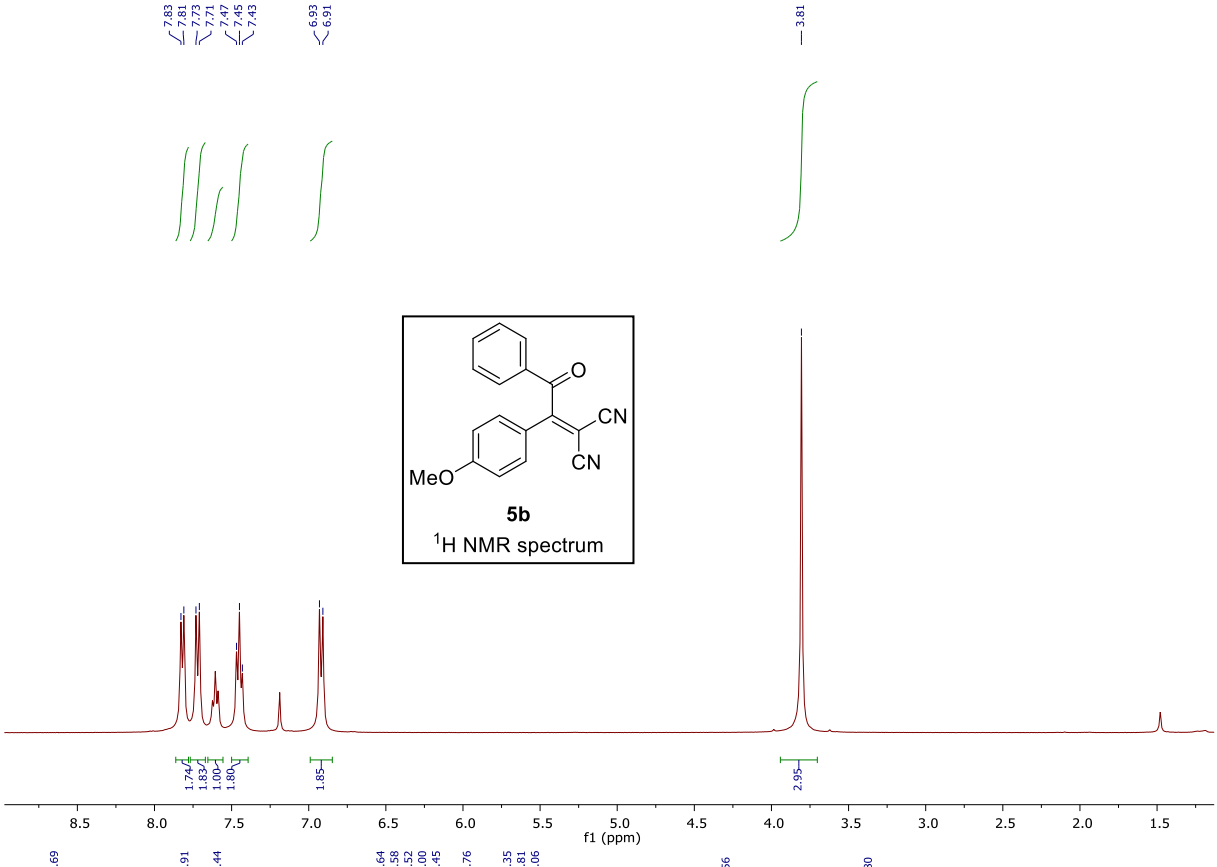

162.96
138.95
134.06
131.68
129.82
129.38
129.05
128.54
128.36
128.01
126.71
126.61
126.32
125.78
125.31
123.67
120.35
114.15
73.02
O
NH2
CN
4g
13C NMR spectrum
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

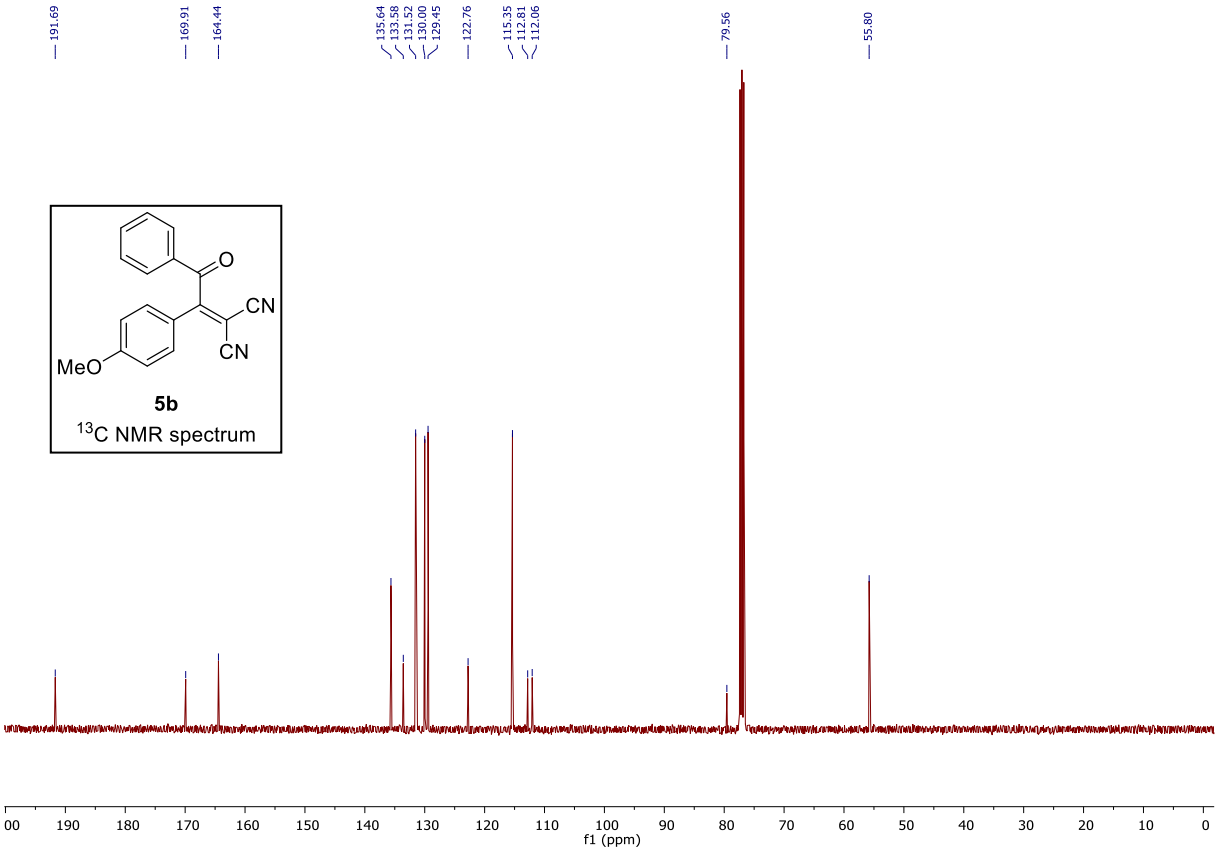

7.09
7.07
7.05
7.04
6.95
6.93
6.65
6.04
6.02
4.61
4.59
2.05 Acetone-d6
O
NH2
CN
4h
1H NMR spectrum
7.87
1.93
1.97
1.00
1.01
f1 (ppm)

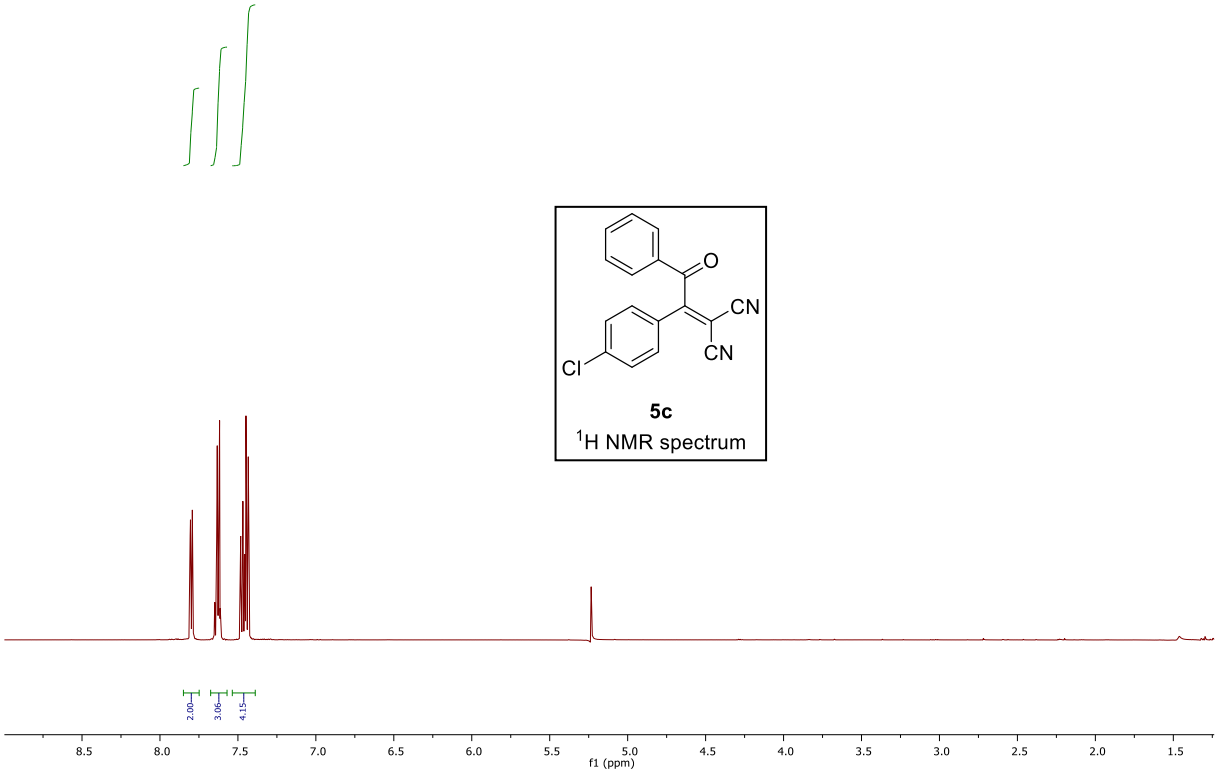

168.39
138.99
136.46
128.72
127.66
127.49
127.30
126.67
126.34
118.20
87.53
55.66
52.79
O
NH2
CN
4h
13C NMR spectrum
f1 (ppm)

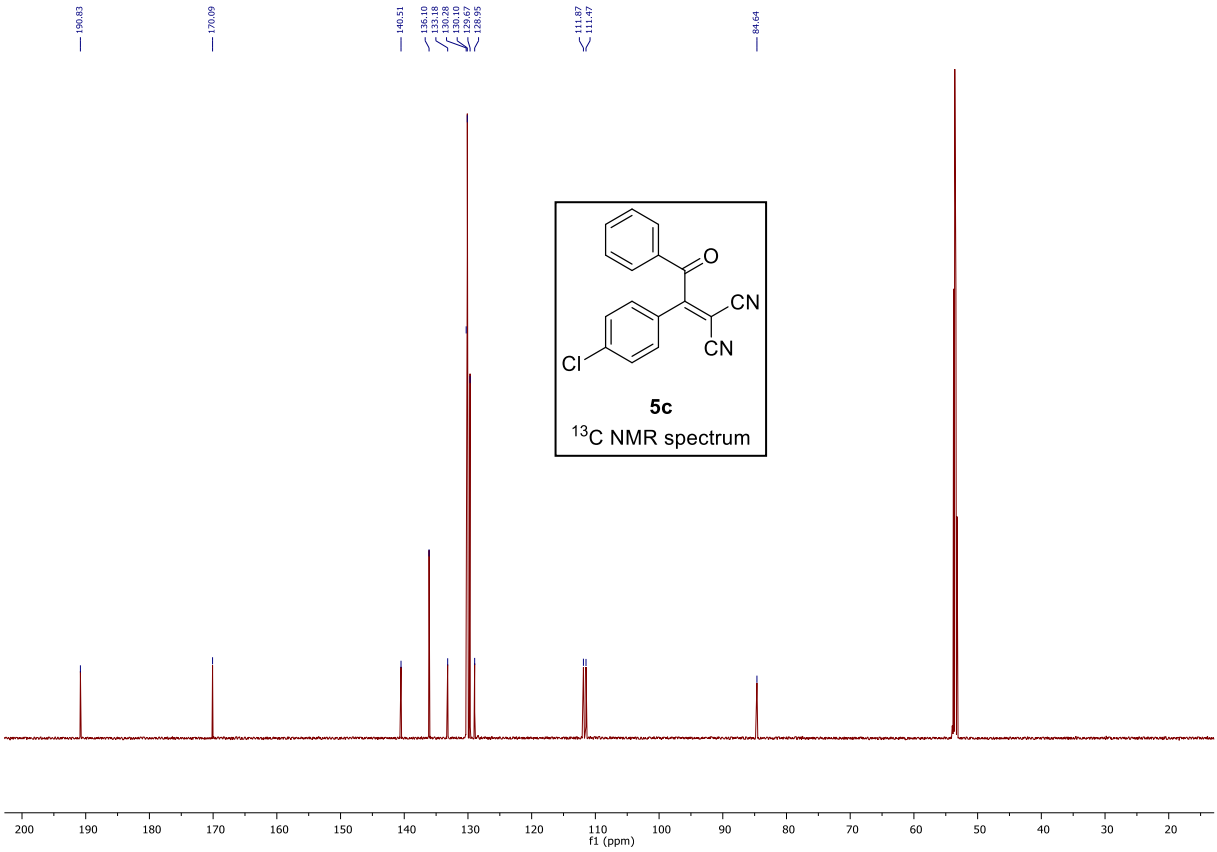

7.83
7.81
7.69
7.67
7.63
7.61
7.59
7.55
7.53
7.51
7.47
7.45
7.45
O
CN
CN
5a
1H NMR spectrum
1.83
1.81
1.00
0.95
3.74
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

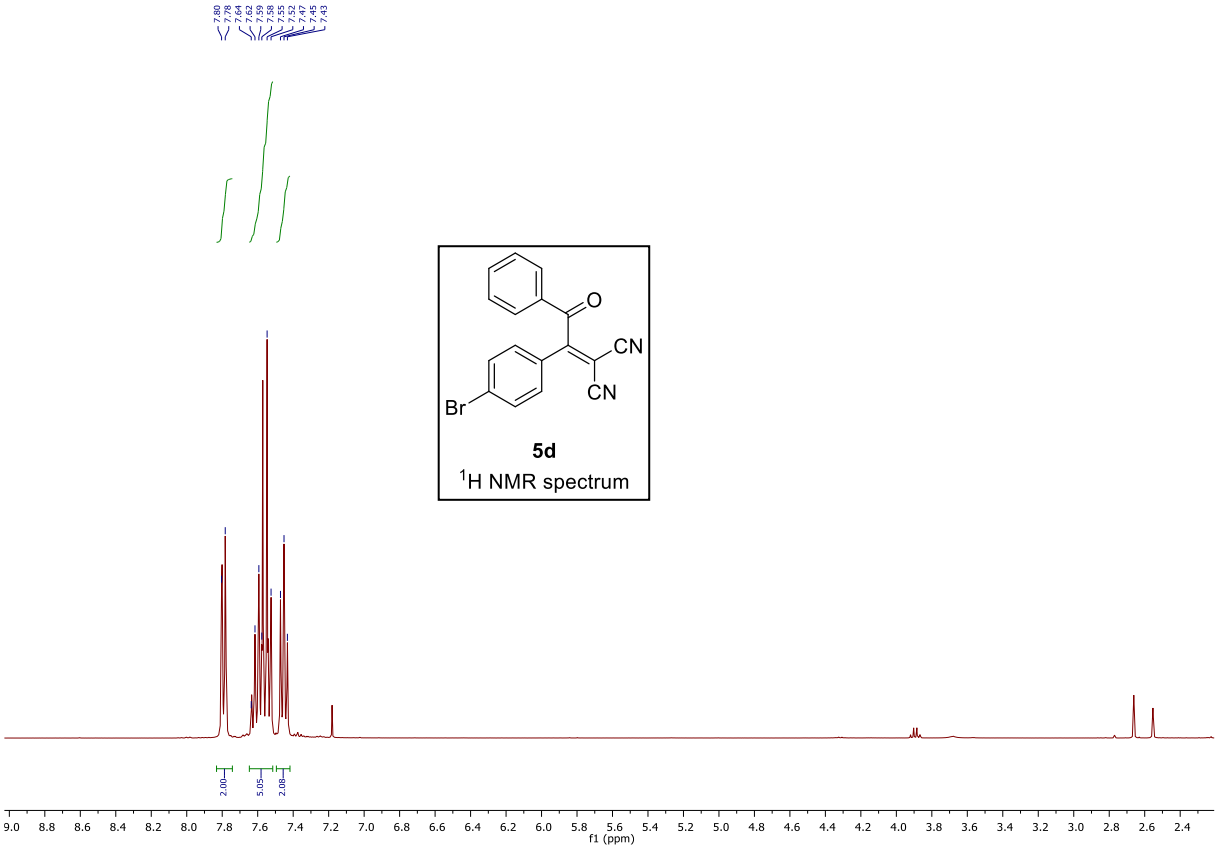

190.88
171.40
135.79
133.90
133.26
130.45
130.02
129.83
129.51
128.61
111.90
111.37
83.91
O
CN
CN
5a
13C NMR spectrum
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

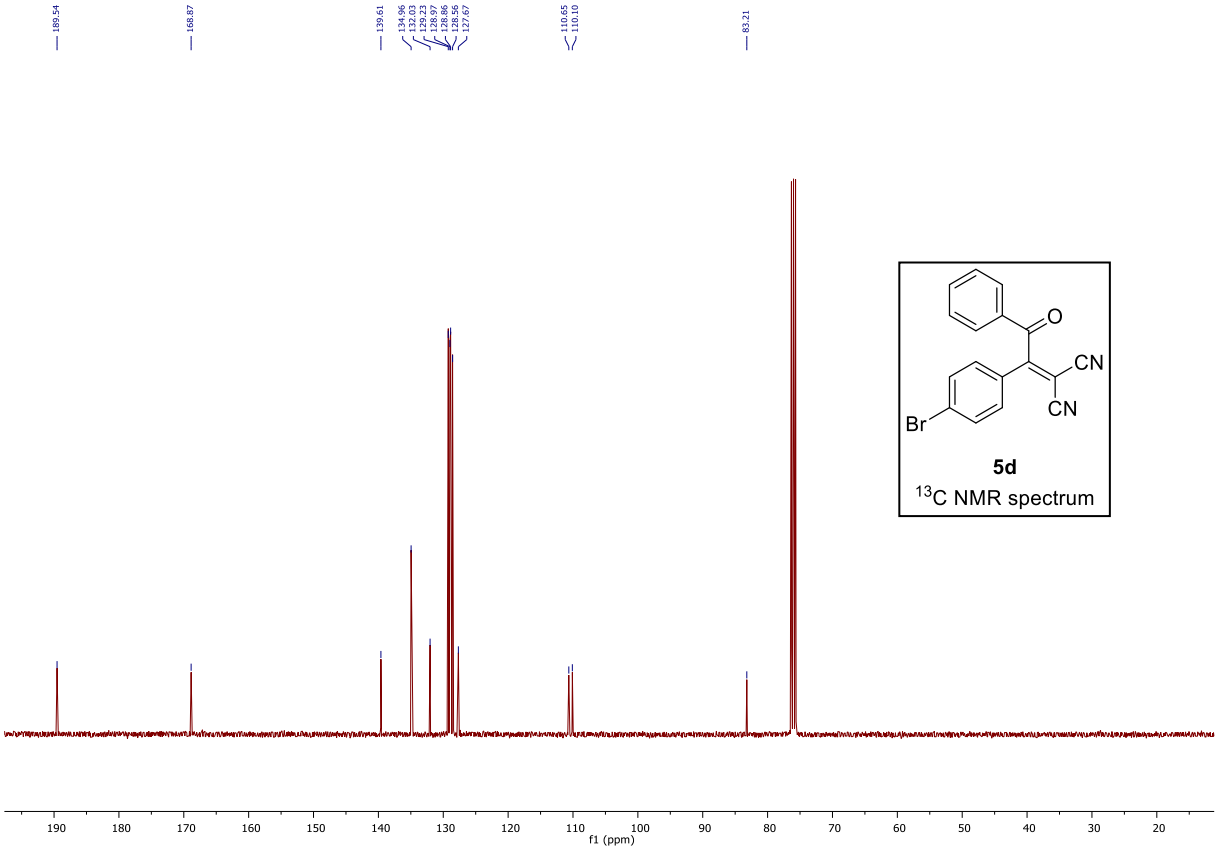

7.83
7.81
7.73
7.71
7.47
7.45
7.43
6.93
6.91
3.81
O
CN
CN
MeO
5b
1H NMR spectrum
1.74
1.83
1.00
1.80
1.85
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

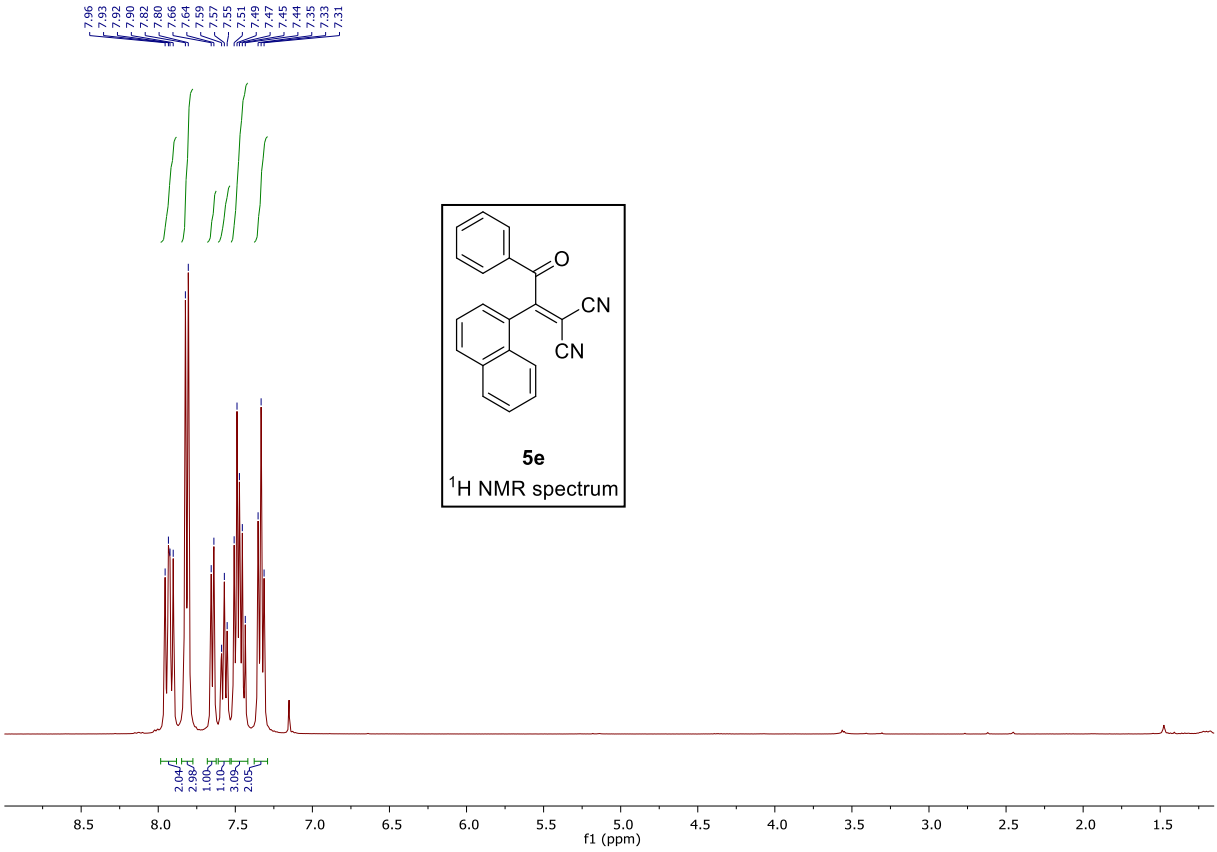

191.69
169.91
164.44
135.64
133.58
131.52
130.00
129.45
122.76
115.35
112.81
112.06
79.56
55.80
O
CN
CN
MeO
5b
13C NMR spectrum
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

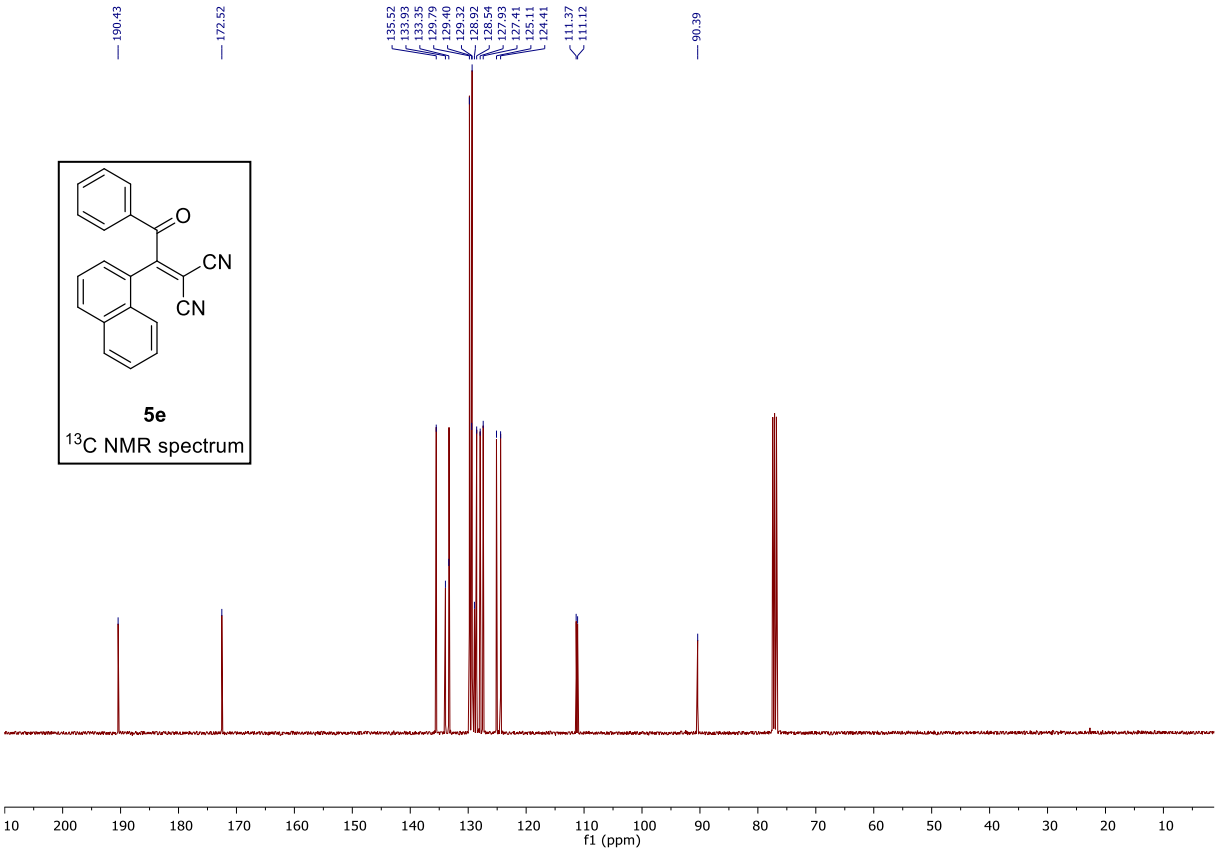

O
CN
CN
Cl
5c
1H NMR spectrum
2.00
3.06
4.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

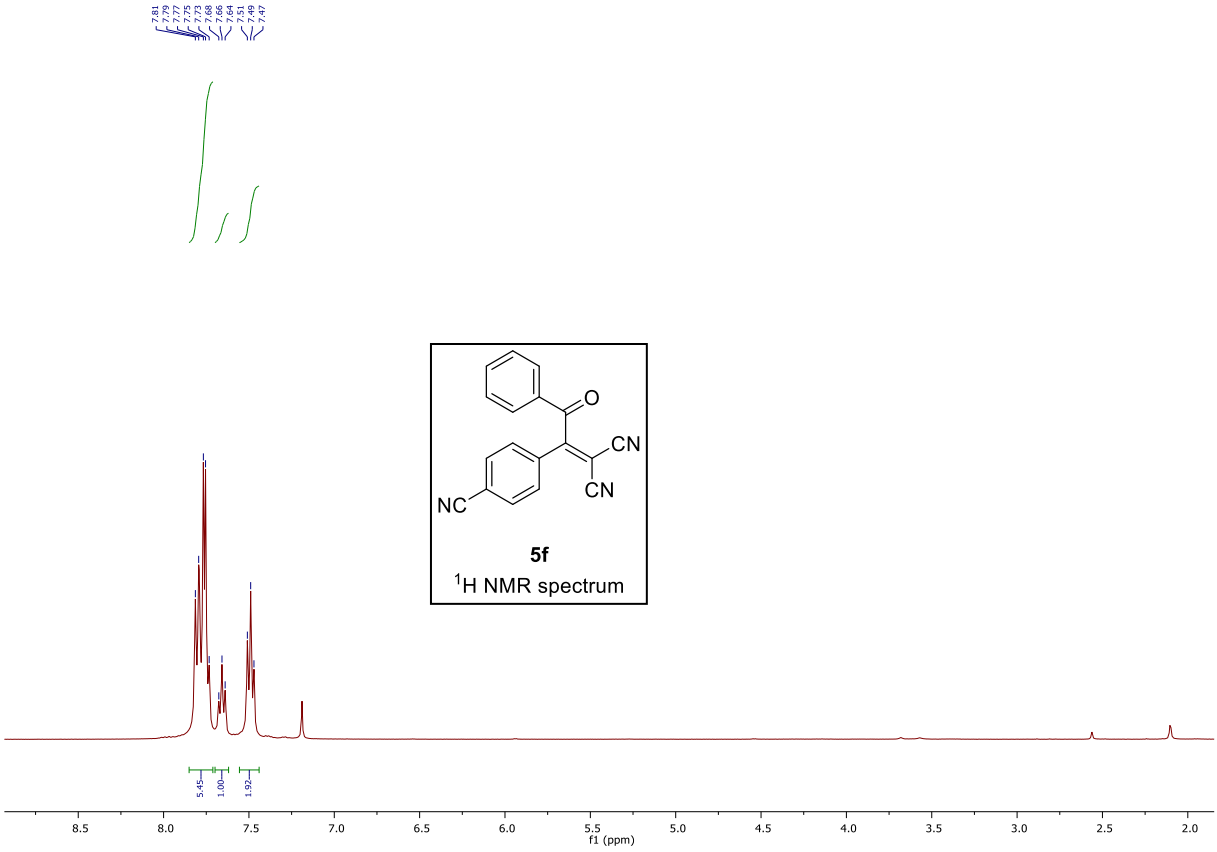

190.83
170.09
140.51
136.10
133.18
130.98
130.10
129.67
128.95
111.87
111.47
84.64
O
CN
CN
Cl
5c
13C NMR spectrum
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

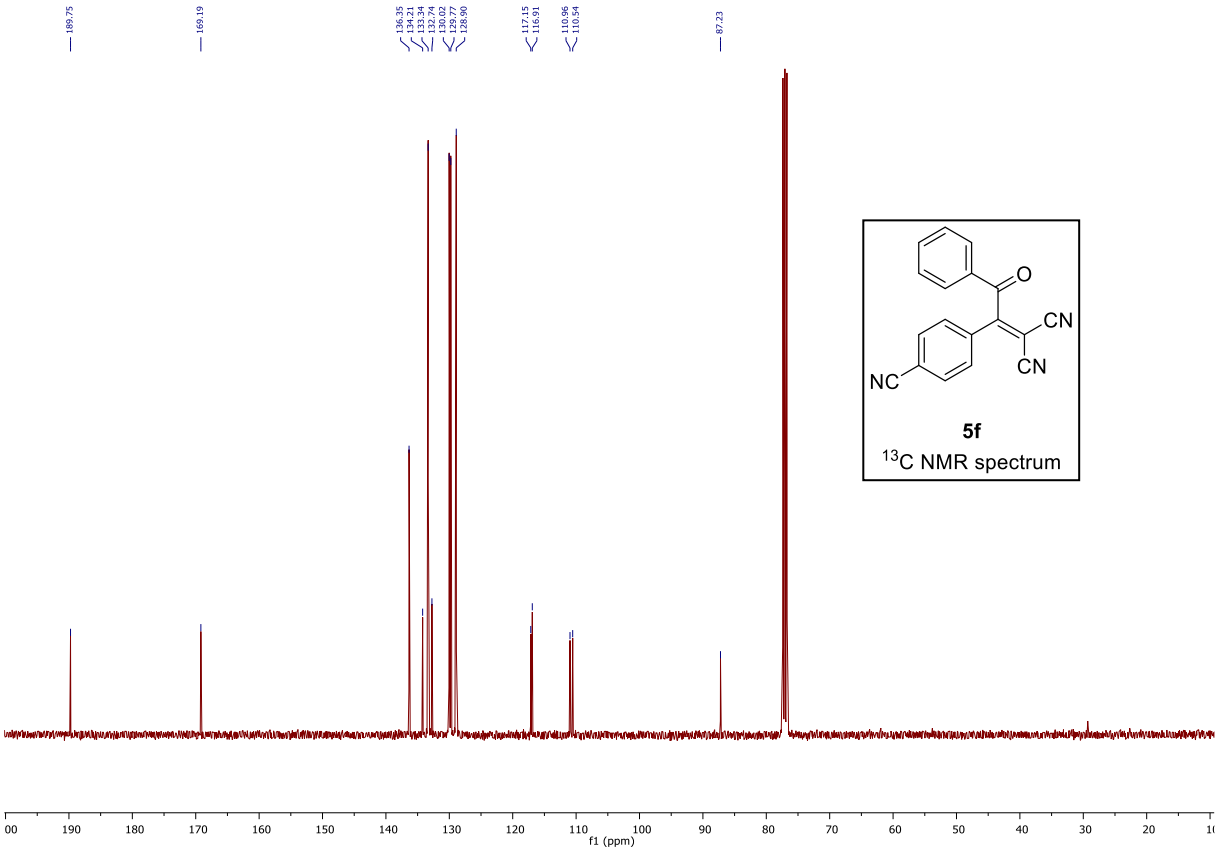

7.80
7.78
7.64
7.62
7.59
7.58
7.55
7.52
7.47
7.45
7.43
O
CN
CN
Br
5d
1H NMR spectrum
2.00
5.05
2.08
f1 (ppm)


189.54
168.87
139.61
134.96
132.03
129.23
128.97
128.86
128.56
127.67
110.65
110.10
83.21
O
CN
CN
Br
5d
13C NMR spectrum
f1 (ppm)

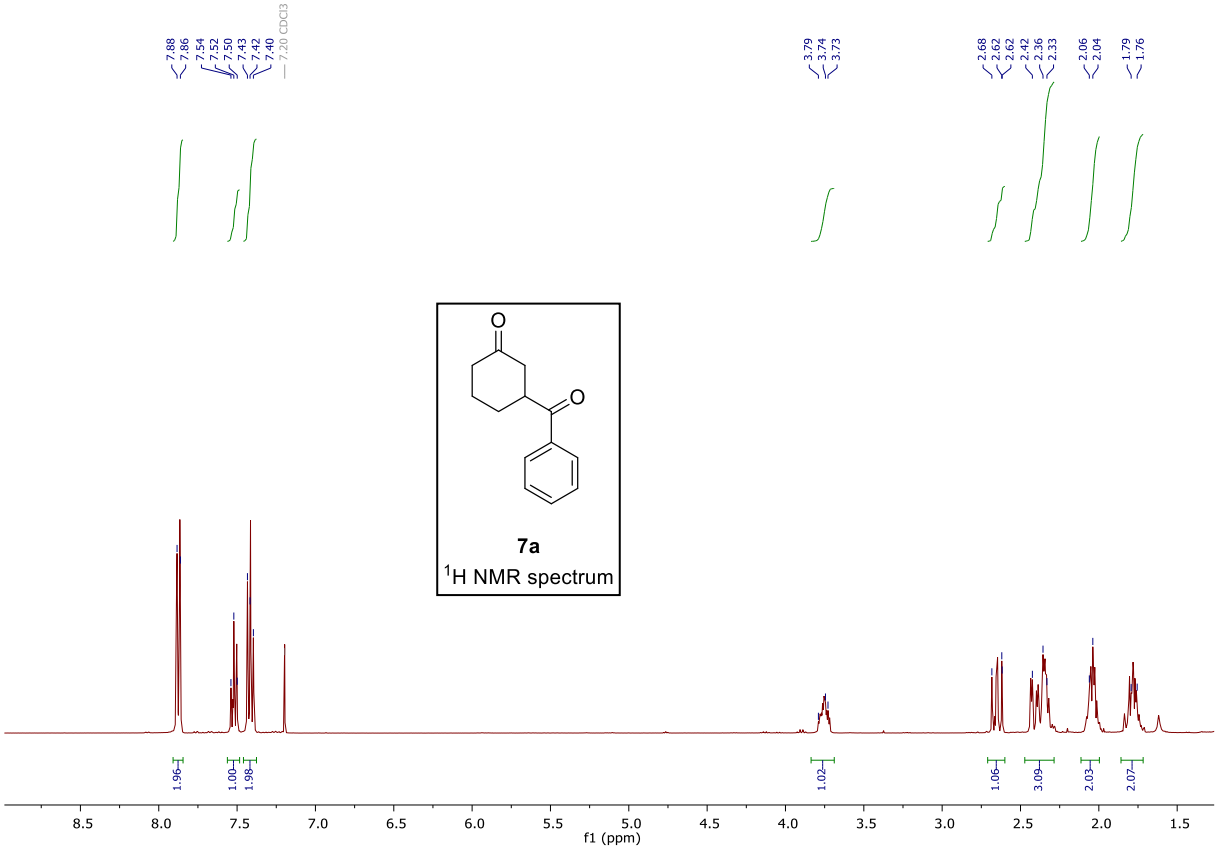

7.96
7.93
7.92
7.90
7.82
7.80
7.66
7.64
7.59
7.57
7.55
7.51
7.49
7.47
7.45
7.44
7.35
7.33
7.31
O
CN
CN
5e
1H NMR spectrum
2.04
2.08
1.00
1.03
3.09
2.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

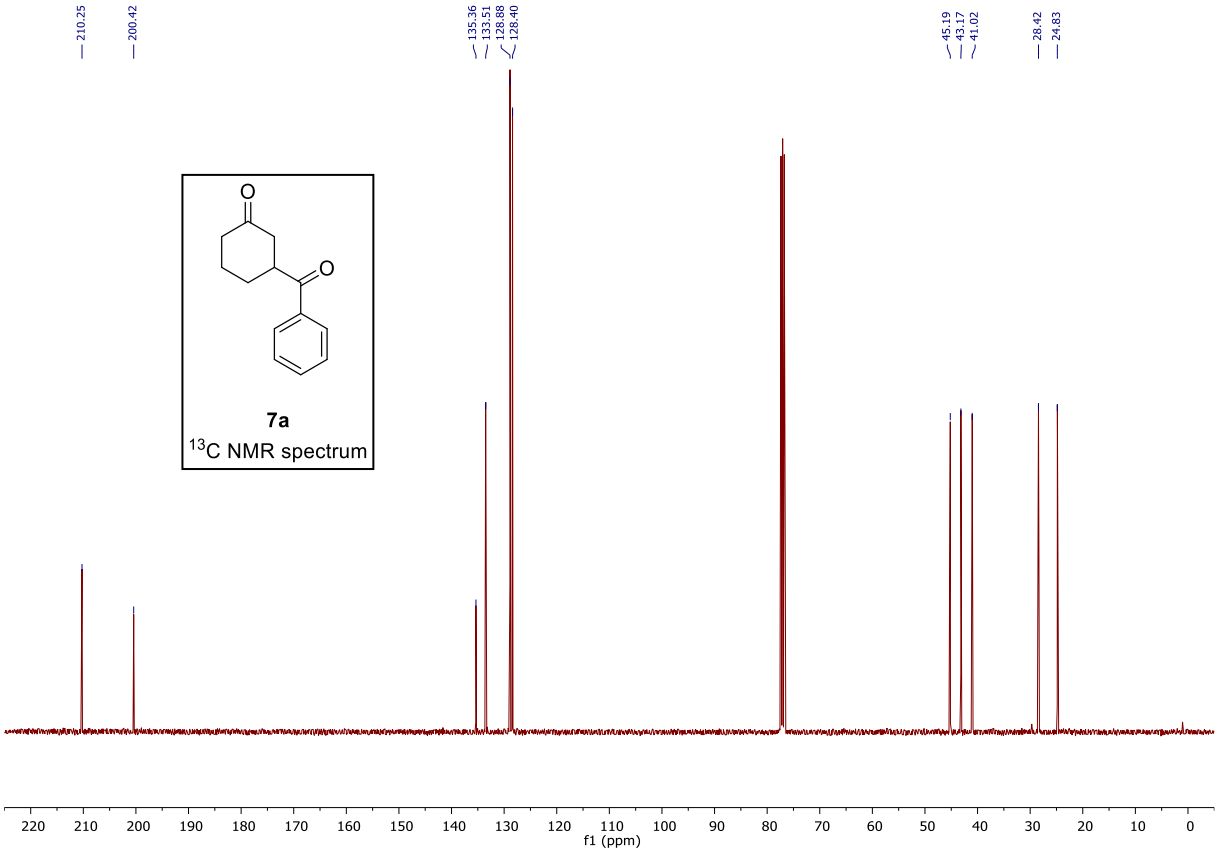

190.43
172.52
135.52
133.93
133.35
129.79
129.40
129.32
128.92
128.54
127.93
127.41
125.11
124.41
111.37
111.12
90.39
O
CN
CN
5e
13C NMR spectrum
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

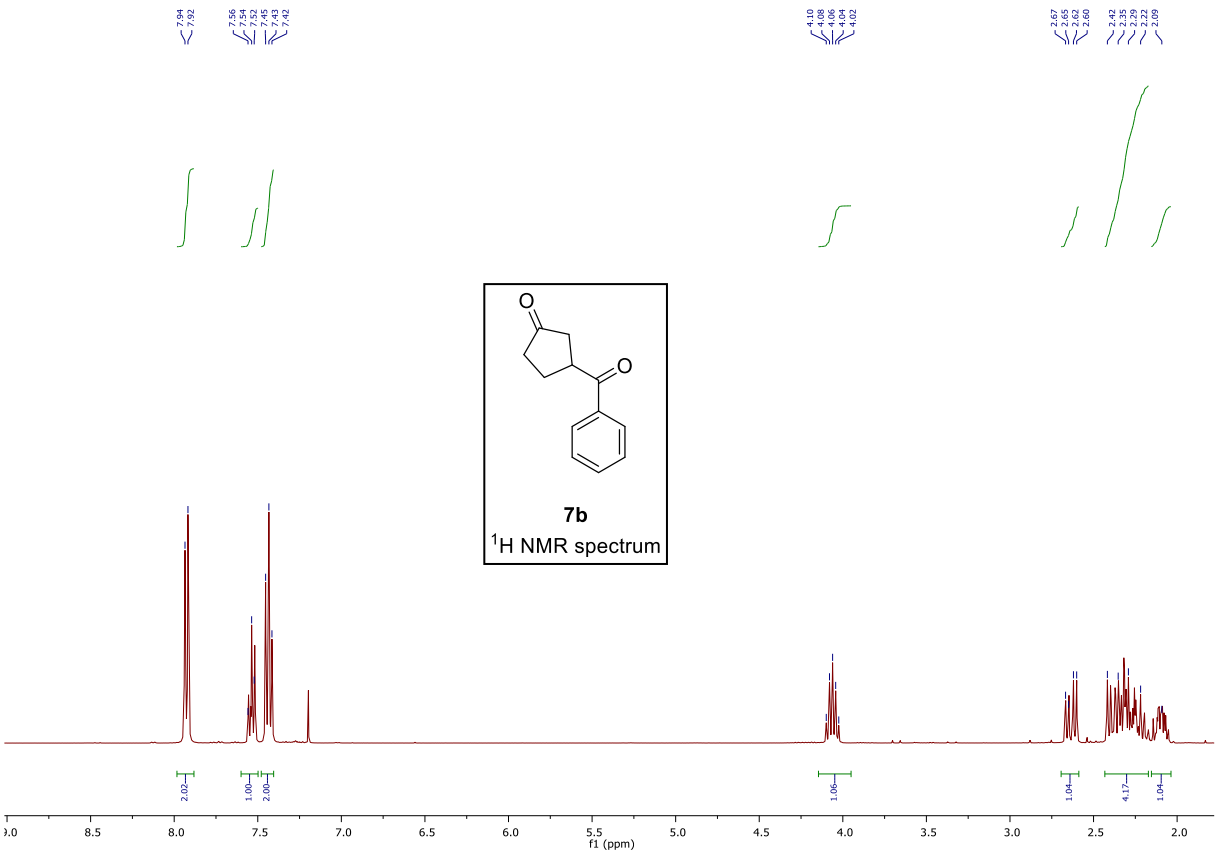

7.81
7.79
7.77
7.75
7.73
7.68
7.66
7.64
7.51
7.49
7.47
O
CN
CN
NC
5f
1H NMR spectrum
5.45
1.00
1.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

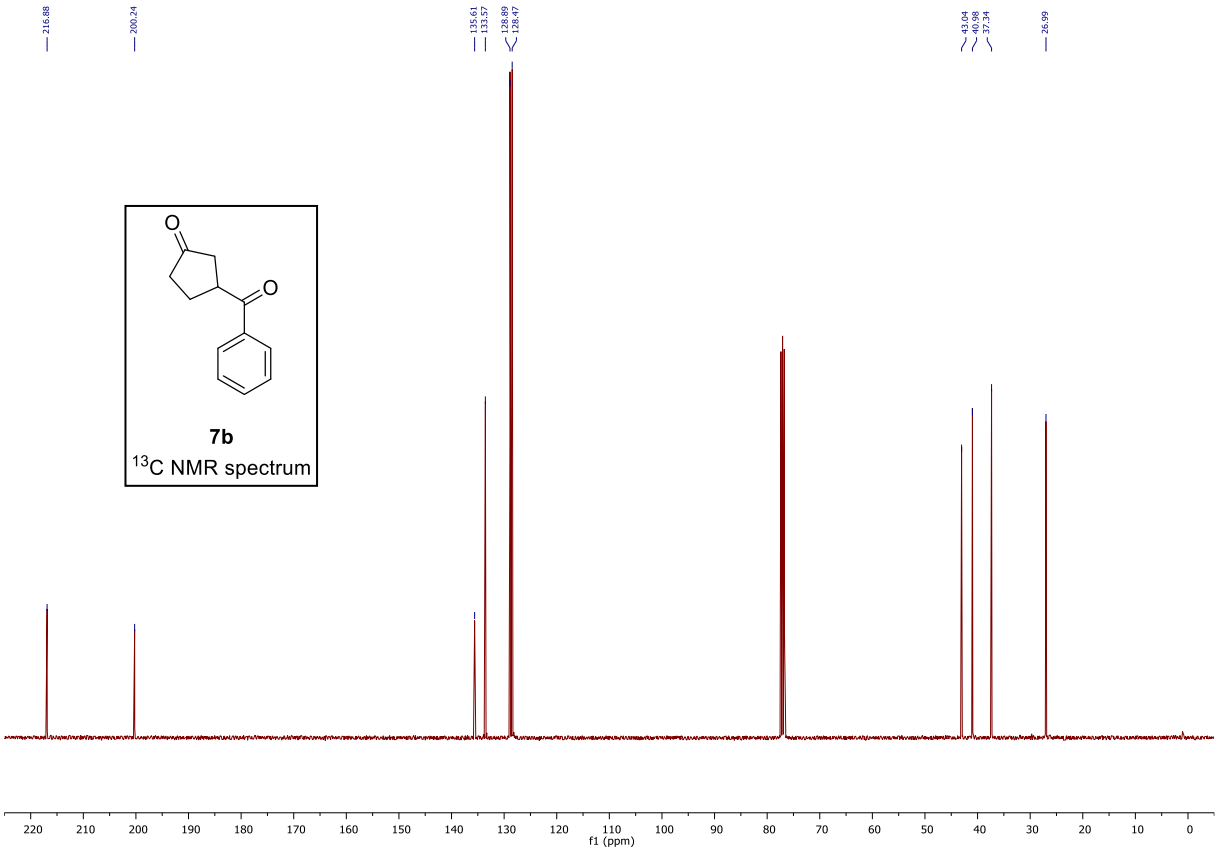

189.75
169.19
136.35
134.21
133.34
132.74
130.02
129.77
128.90
117.15
116.91
110.96
110.54
87.23
O
CN
CN
NC
5f
13C NMR spectrum
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

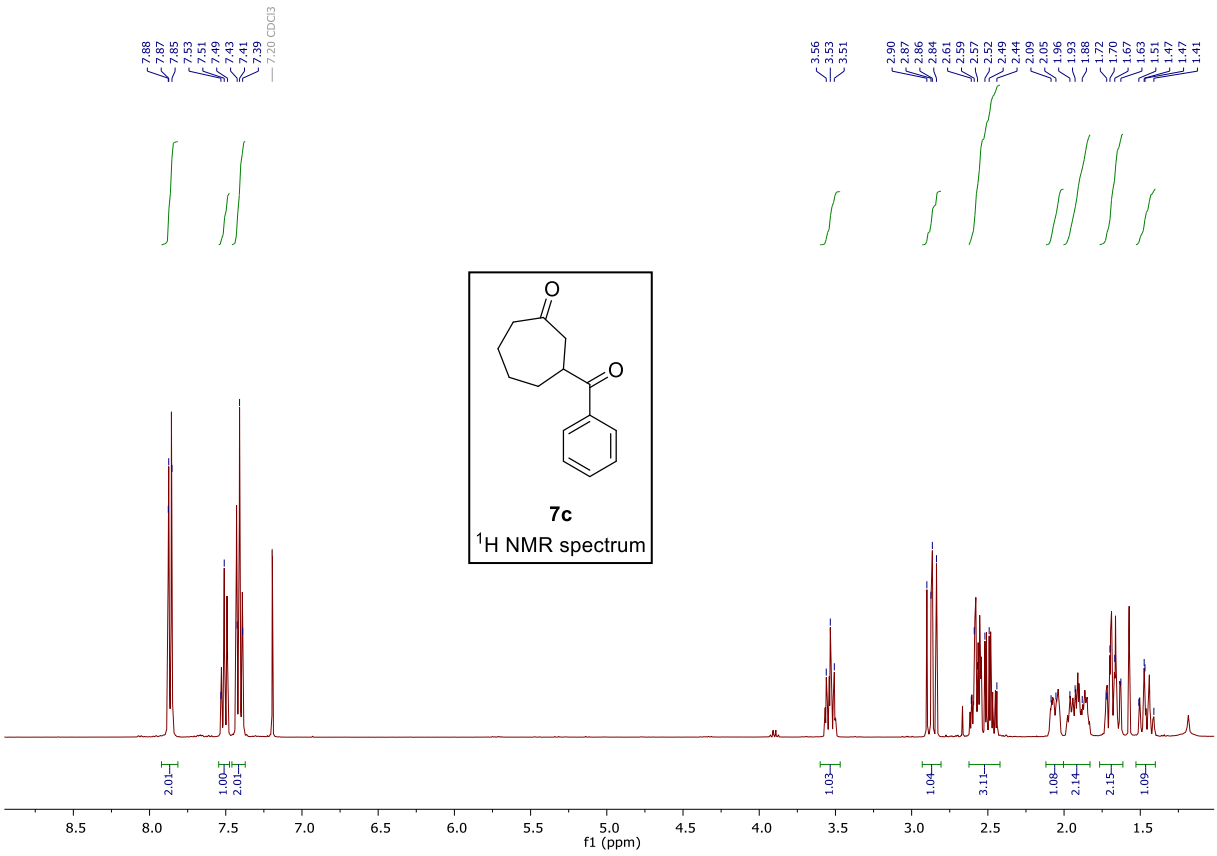
9.2. NMR spectra for the hydroacylation of enones

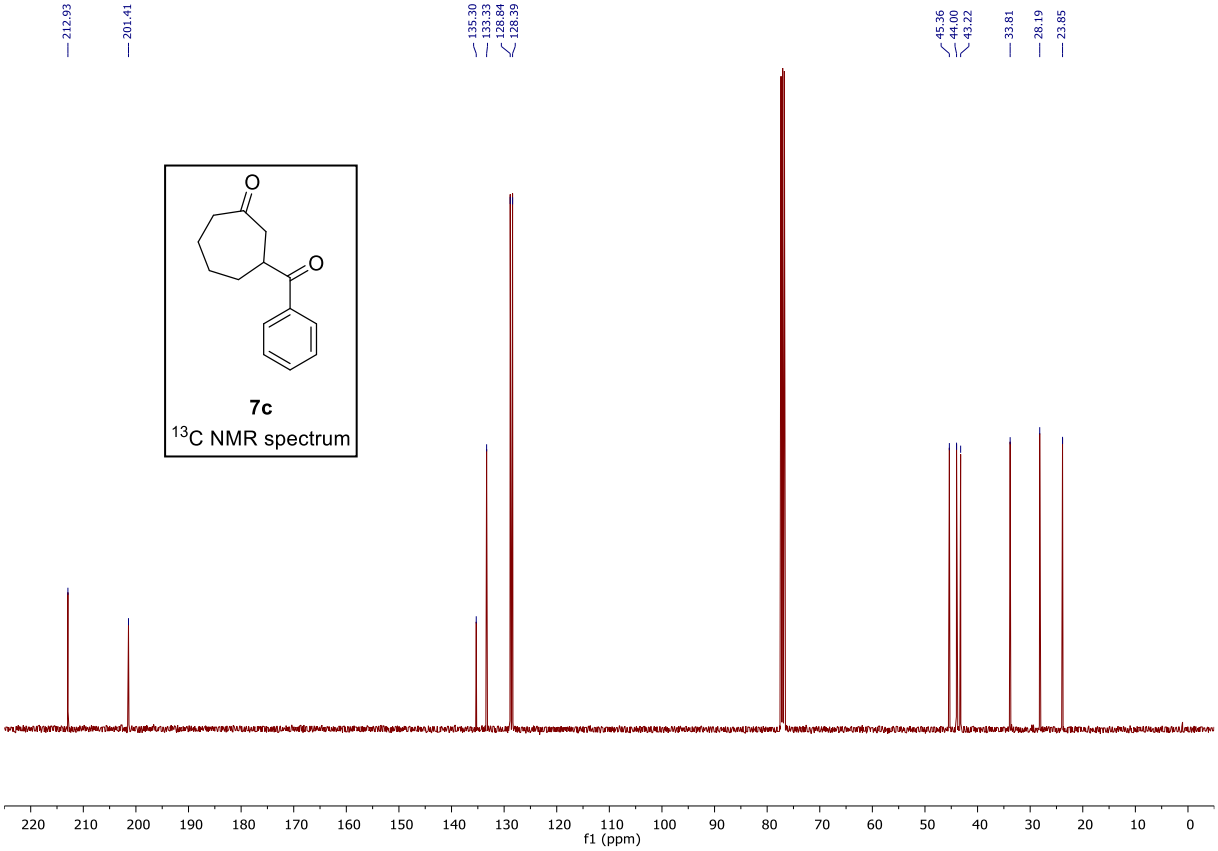


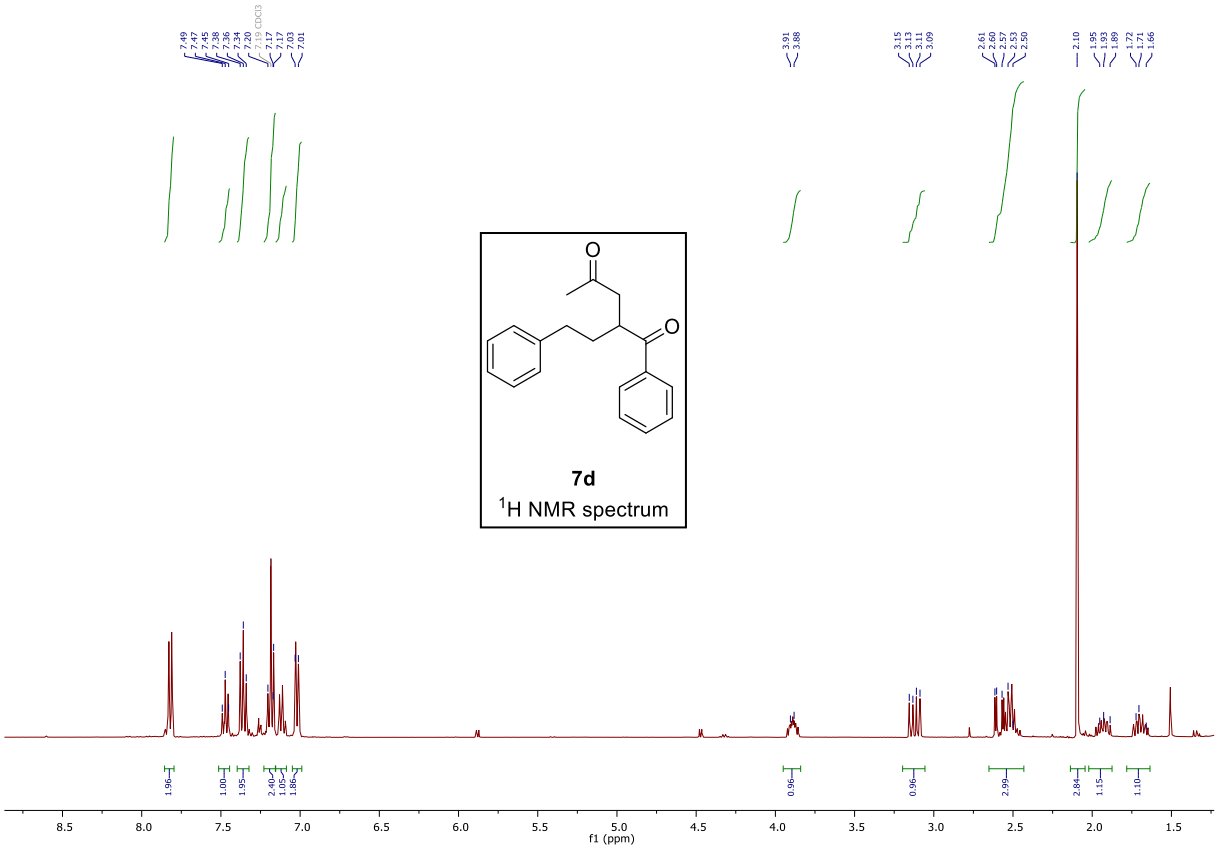


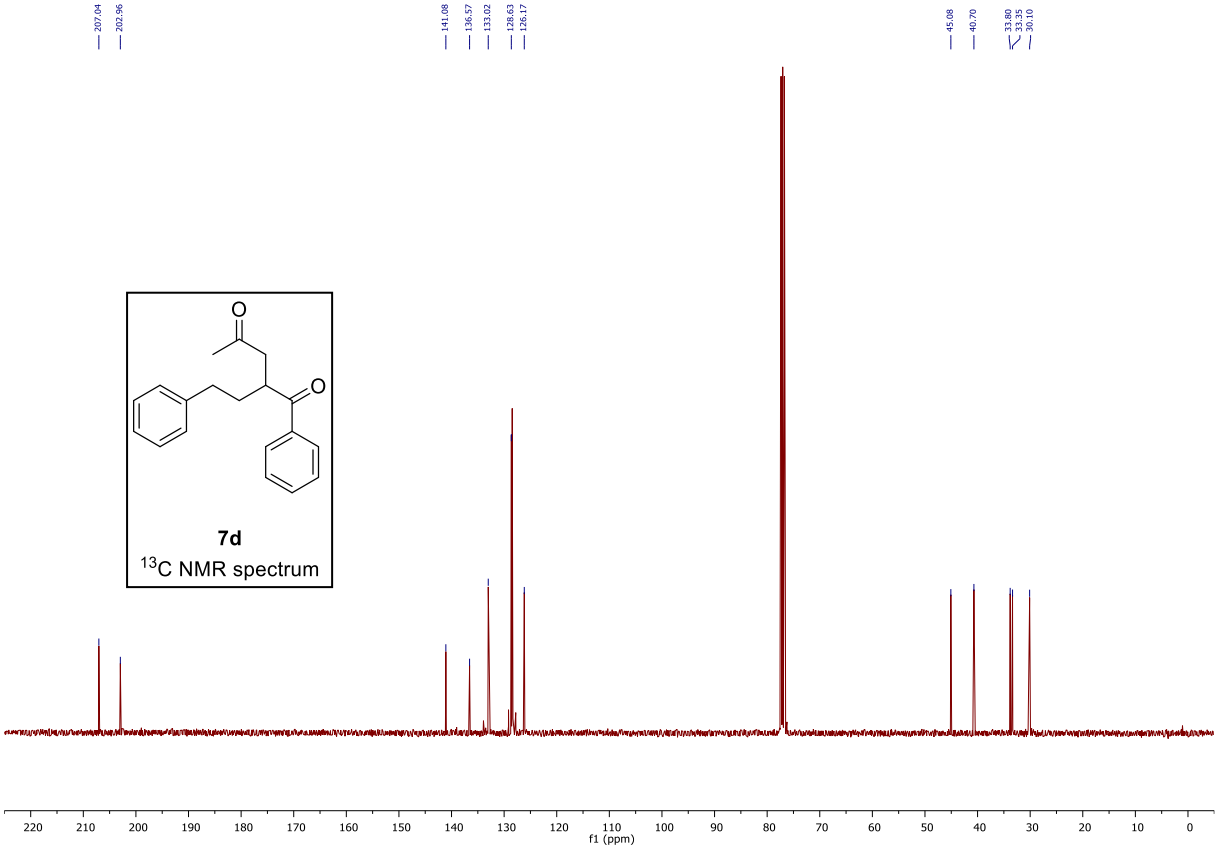

7.94
7.92
7.56
7.54
7.52
7.45
7.43
7.42
4.10
4.08
4.06
4.04
4.02
2.67
2.65
2.63
2.60
2.42
2.35
2.29
2.22
2.09
O
O
7b
1H NMR spectrum
2.02
1.00
2.00
1.06
1.04
4.17
1.04
f1 (ppm)

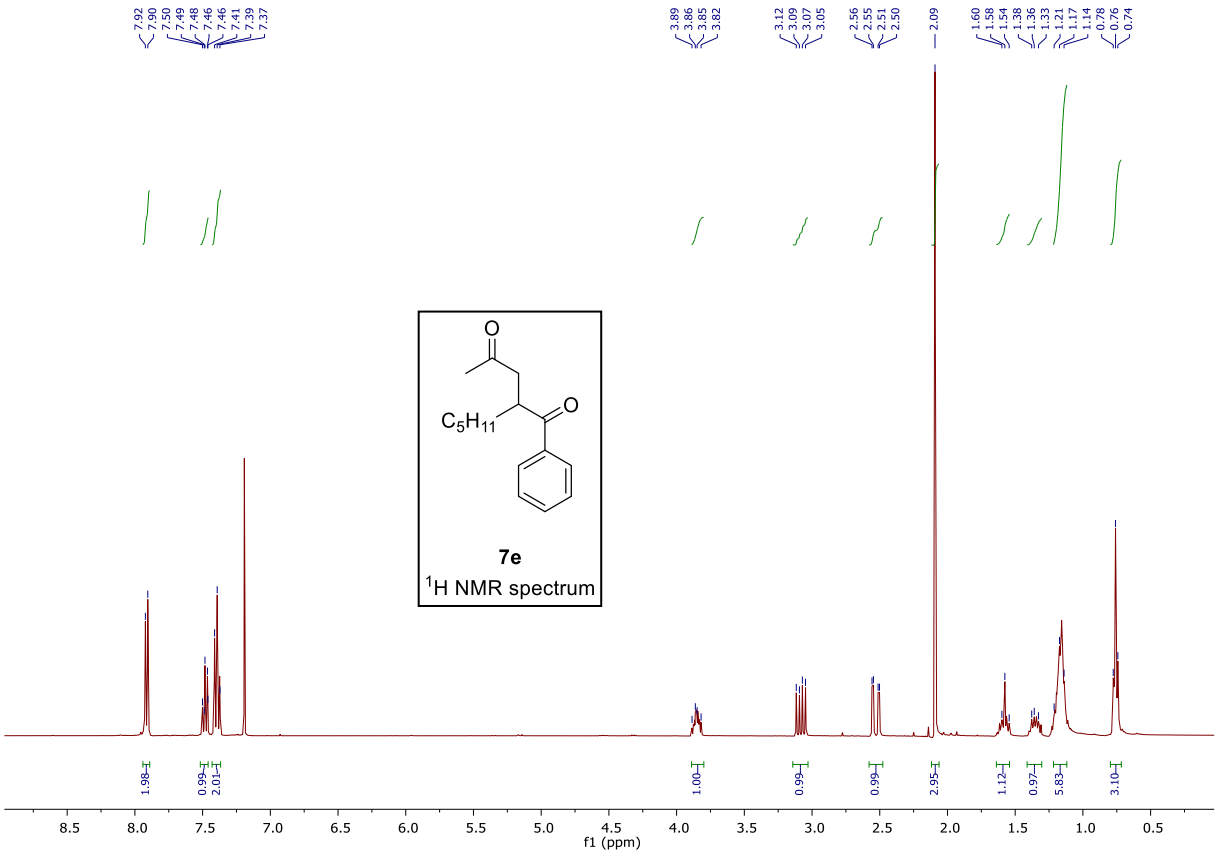

216.88
200.24
135.61
133.57
128.89
128.47
43.04
40.88
37.34
26.99
O
O
7b
13C NMR spectrum
f1 (ppm)

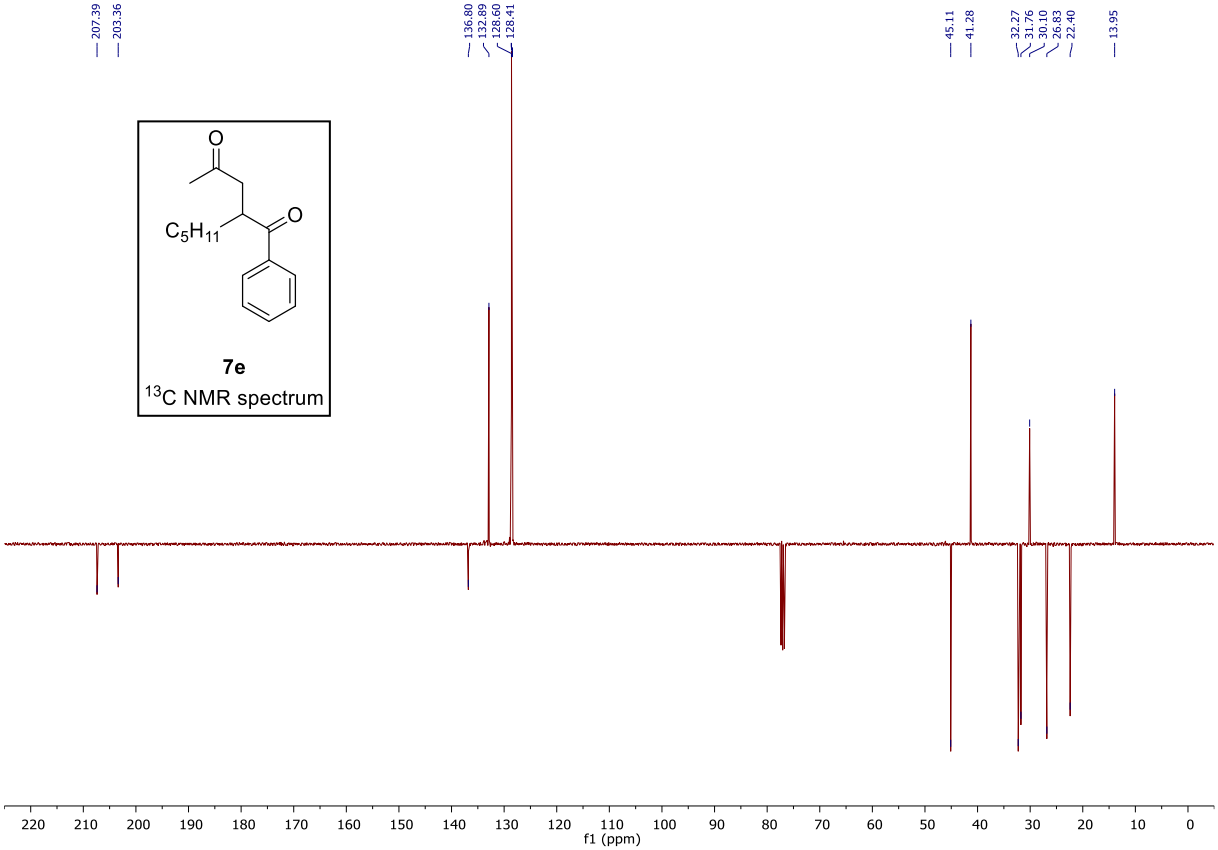

7.88
7.87
7.85
7.53
7.51
7.49
7.43
7.41
7.39
7.20 CDCl3
3.56
3.53
3.51
2.90
2.87
2.86
2.84
2.61
2.59
2.57
2.52
2.49
2.44
2.09
2.05
1.96
1.93
1.88
1.72
1.70
1.67
1.63
1.51
1.47
1.47
1.41
O
O
7c
1H NMR spectrum
2.01
1.00
2.01
1.03
1.04
3.11
1.08
2.14
2.15
1.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

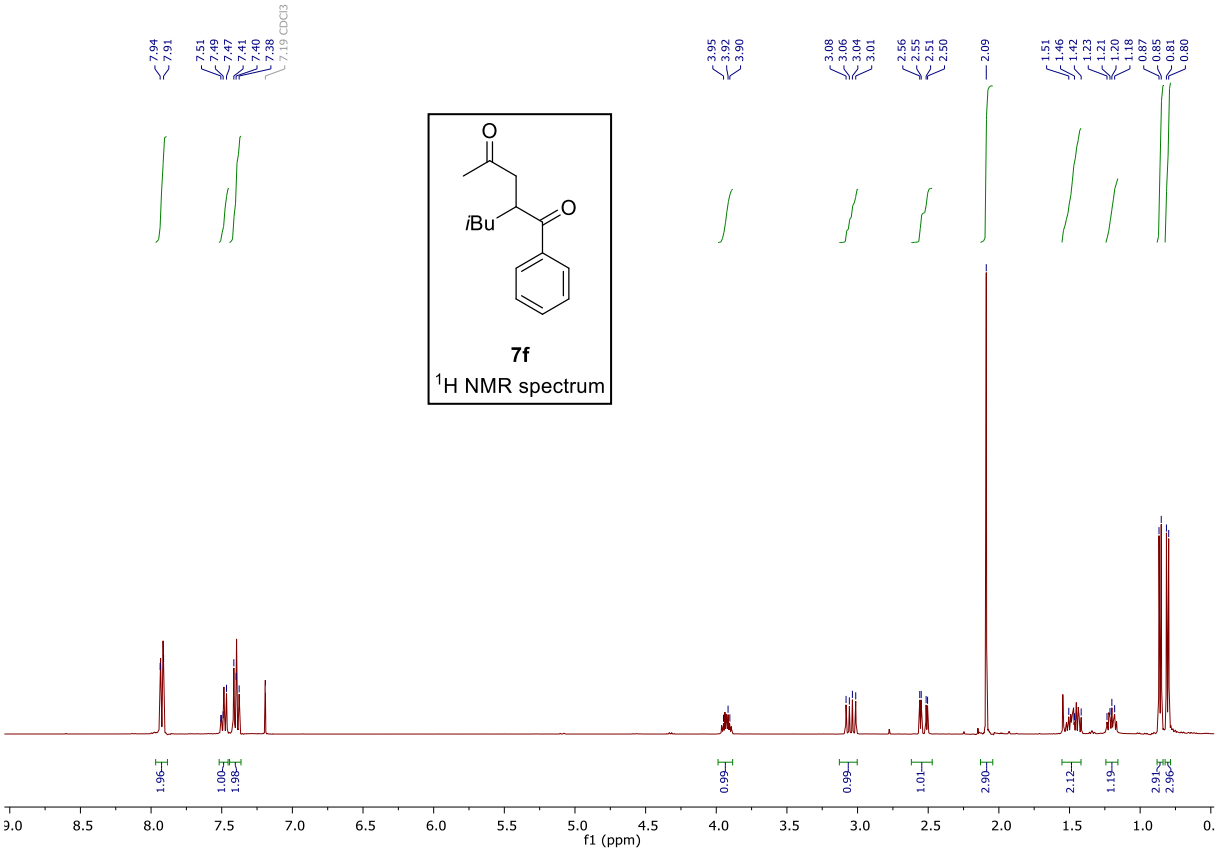

212.93
201.41
135.30
133.33
128.84
128.39
45.36
44.00
43.22
33.81
28.19
23.85
O
O
7c
13C NMR spectrum
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

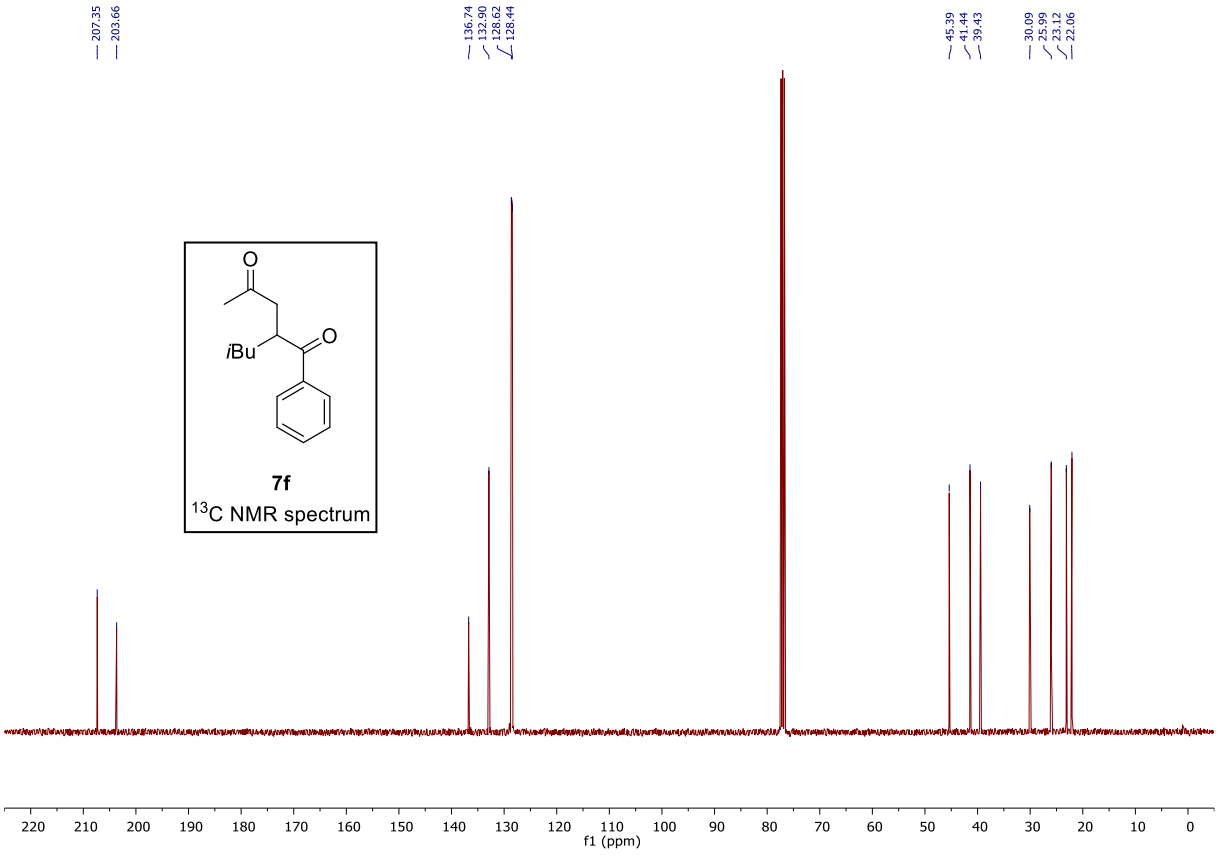

7.49
7.47
7.45
7.38
7.36
7.34
7.30
7.26 CDCl3
7.17
7.17
7.03
7.01
3.91
3.88
3.15
3.13
3.11
3.09
2.61
2.60
2.57
2.53
2.50
2.10
1.95
1.93
1.89
1.72
1.71
1.66
O
O
7d
1H NMR spectrum
1.96
1.00
1.95
2.40
1.05
1.86
0.96
0.96
2.99
2.84
1.15
1.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

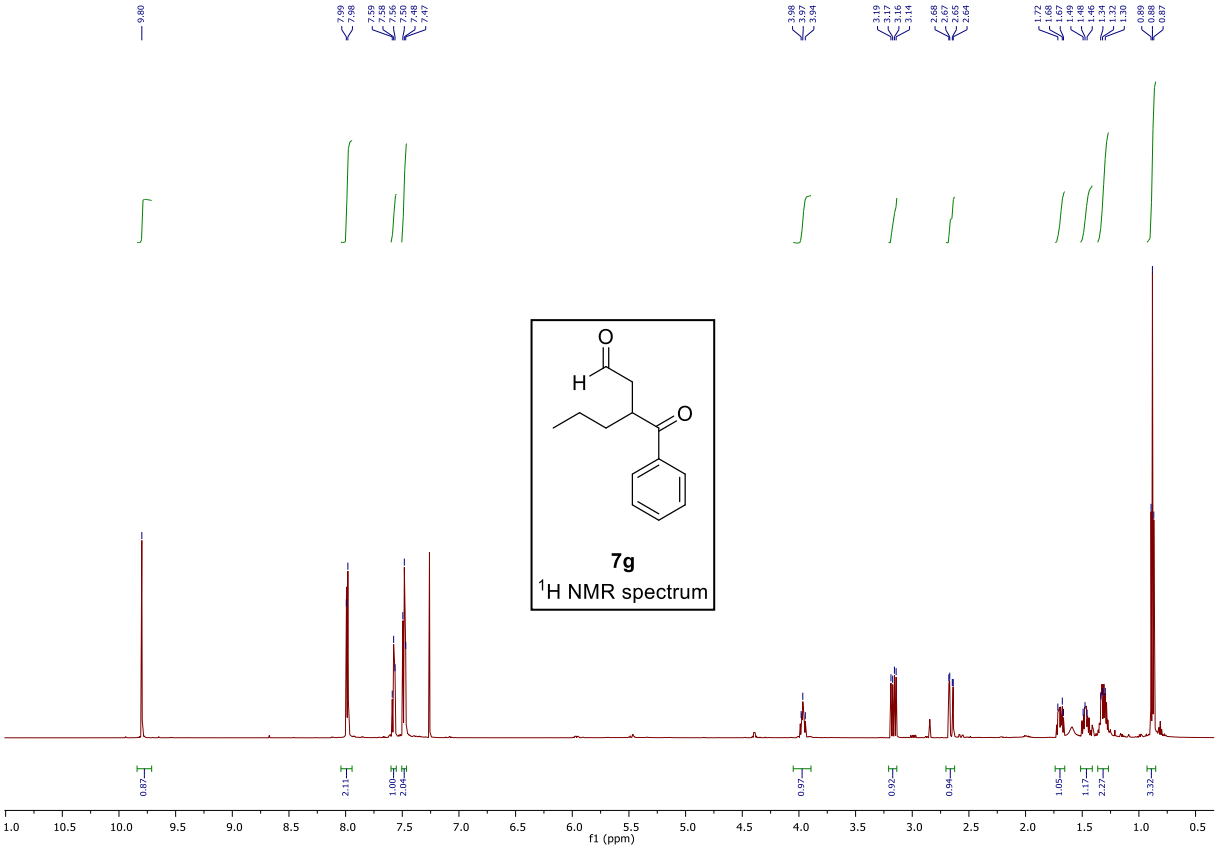

207.04
202.96
141.08
136.57
133.02
128.63
126.17
45.08
40.70
33.80
33.35
30.10
O
O
7d
13C NMR spectrum
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

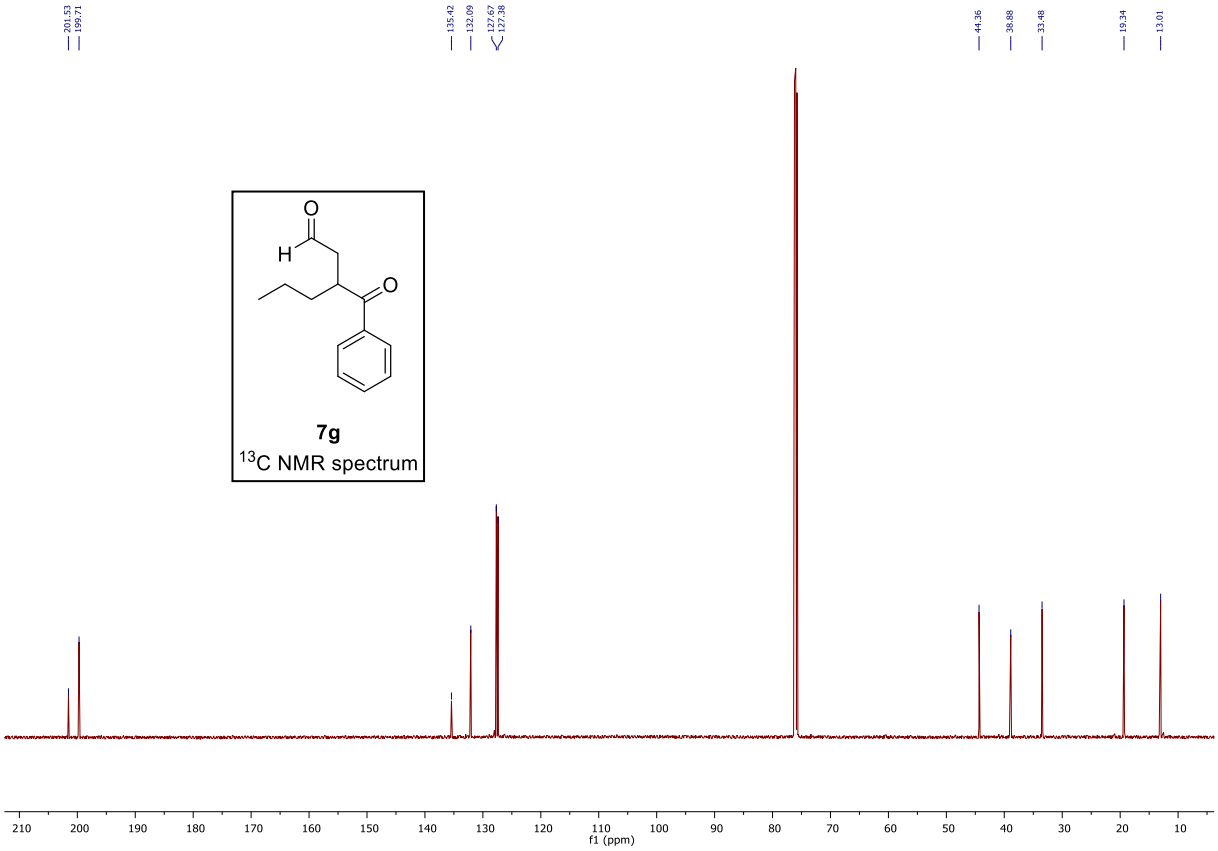

7.92
7.90
7.50
7.49
7.48
7.46
7.46
7.41
7.39
7.37
3.89
3.86
3.85
3.82
3.12
3.09
3.07
3.05
2.56
2.55
2.51
2.50
2.09
1.60
1.58
1.54
1.38
1.36
1.33
1.21
1.17
1.14
0.78
0.76
0.74
O
O
C5H11
7e
1H NMR spectrum
1.98
0.99
2.01
1.00
0.99
0.99
2.95
1.12
0.97
5.83
3.10
f1 (ppm)

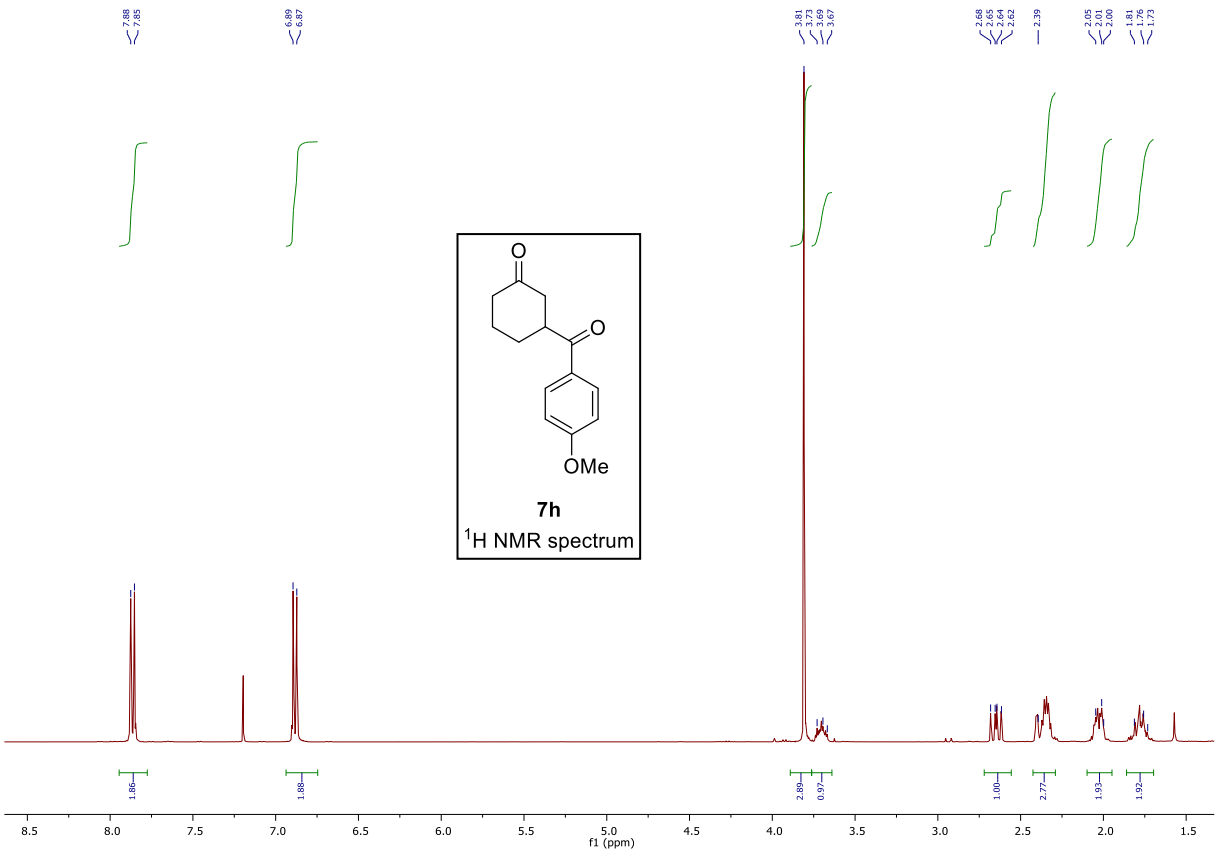

207.39
203.36
136.80
132.89
128.60
128.41
45.11
41.28
32.27
31.76
30.10
26.83
22.40
13.95
O
O
C5H11
7e
13C NMR spectrum
f1 (ppm)

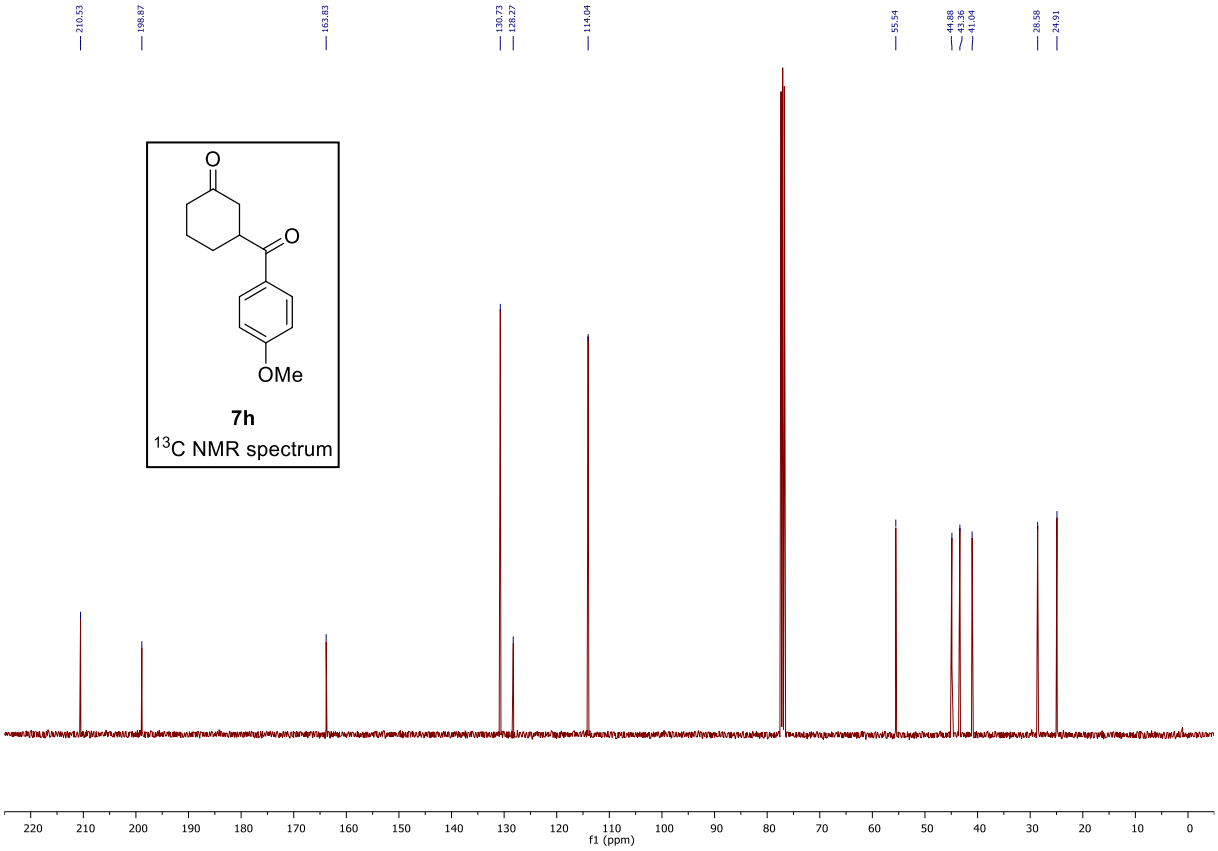

7.94
7.91
7.51
7.49
7.47
7.41
7.40
7.38
7.19 CDCl3
3.95
3.92
3.90
3.08
3.06
3.04
3.01
2.56
2.55
2.51
2.50
2.09
1.51
1.46
1.42
1.23
1.21
1.20
1.18
0.87
0.85
0.81
0.80
O
iBu
O
7f
1H NMR spectrum
1.96
1.00
1.98
0.99
0.99
1.01
2.90
2.12
1.19
2.91
2.96
f1 (ppm)

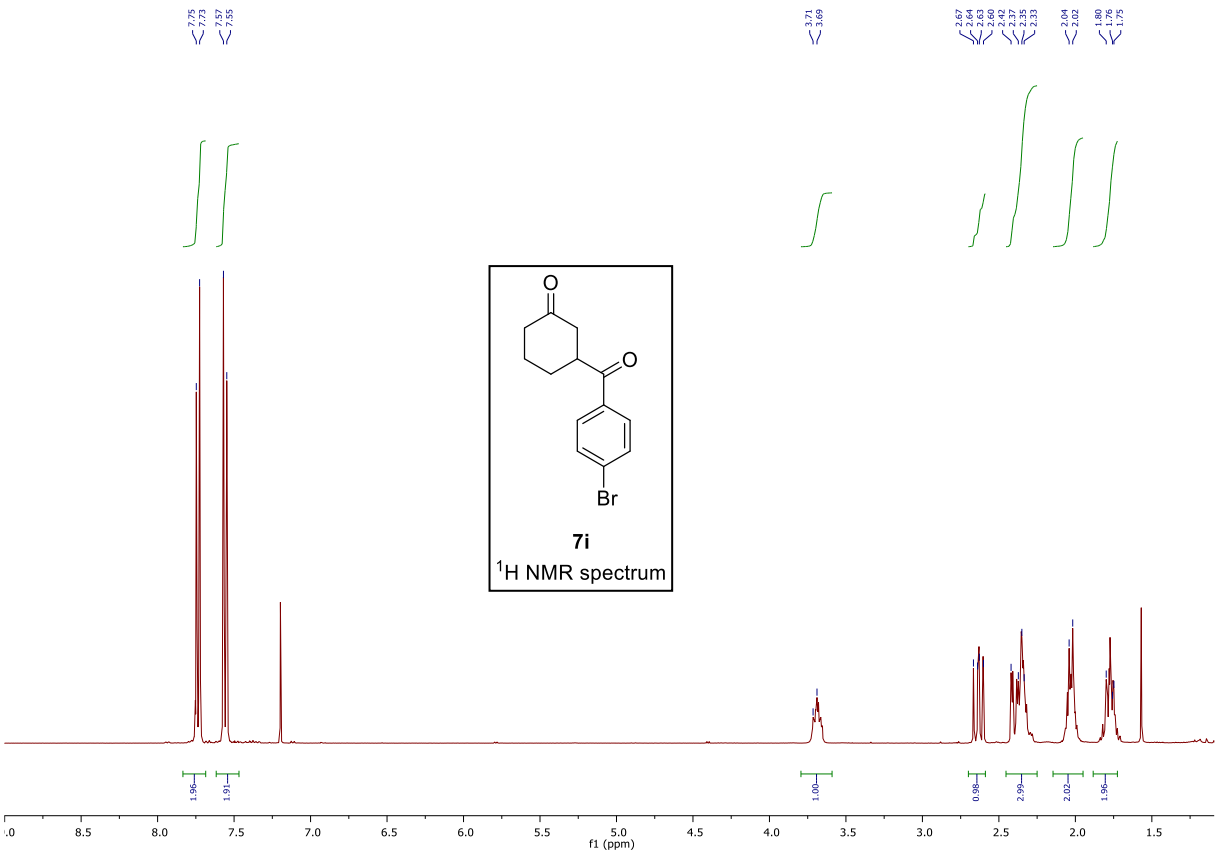

207.35
203.66
136.74
132.90
128.62
128.44
45.39
41.44
39.43
30.09
25.99
23.12
22.06
O
iBu
O
7f
13C NMR spectrum
f1 (ppm)

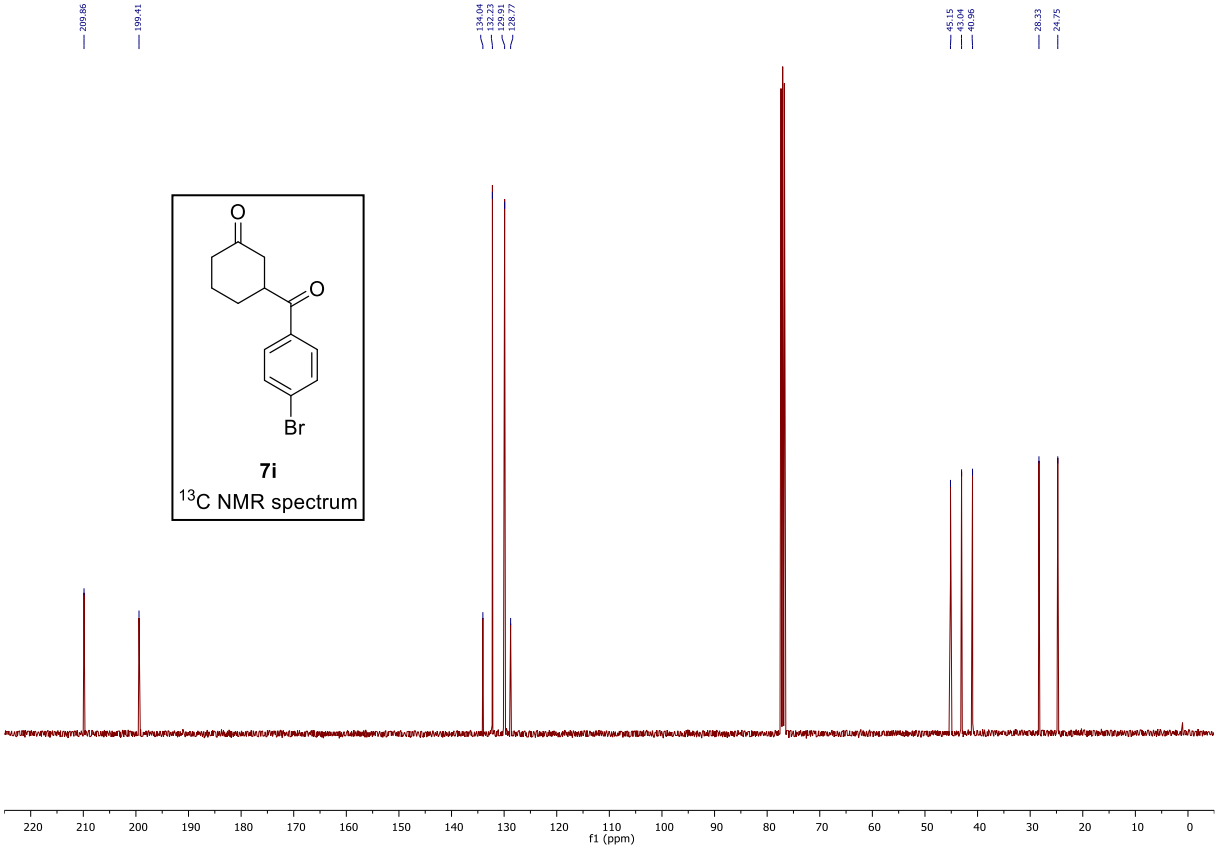

9.80
7.99
7.98
7.59
7.58
7.56
7.55
7.48
7.47
3.98
3.97
3.94
3.19
3.17
3.16
3.14
2.68
2.67
2.65
2.64
1.72
1.68
1.67
1.49
1.48
1.46
1.34
1.32
1.30
0.89
0.88
0.87
O
H
O
7g
1H NMR spectrum
0.87
2.11
1.00
2.04
0.97
0.92
0.94
1.05
1.17
2.27
3.32
f1 (ppm)

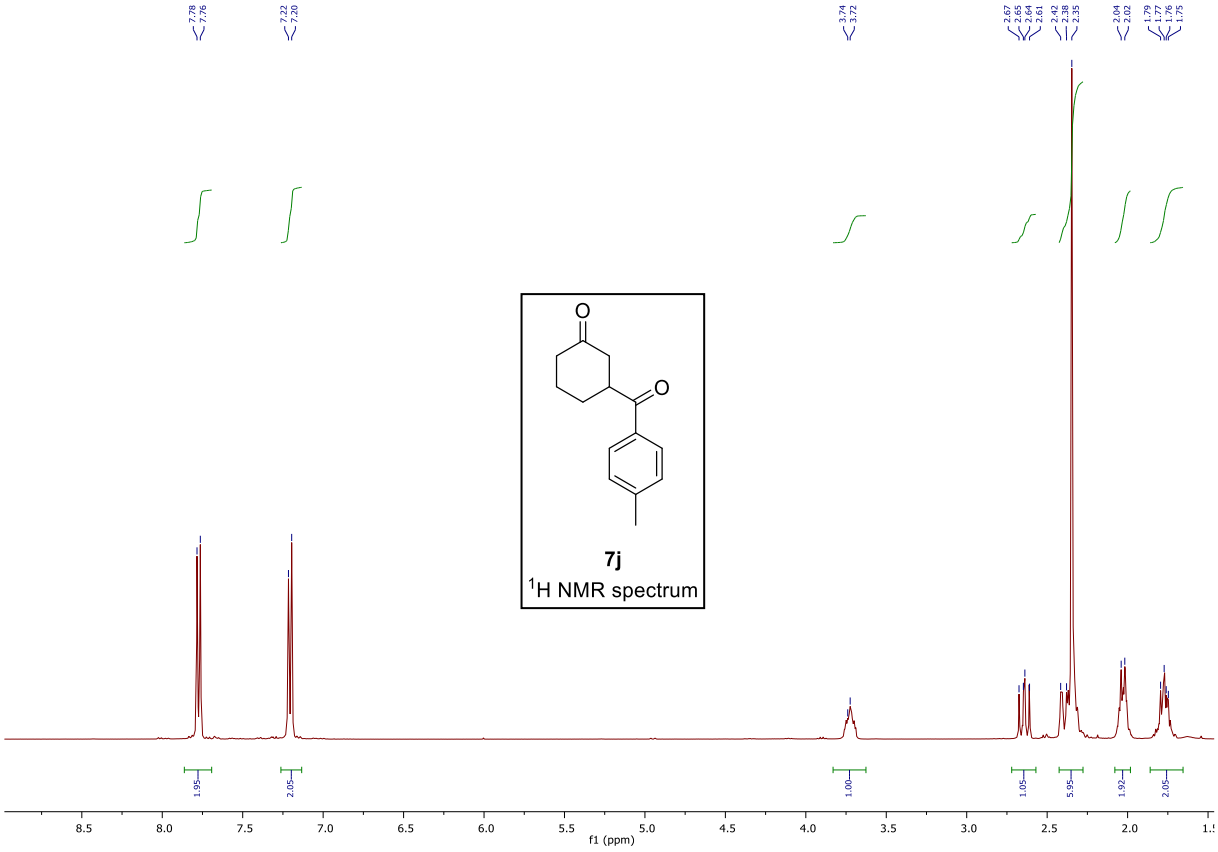

201.53
199.71
135.42
132.09
127.67
127.38
44.36
38.88
33.48
19.34
13.01
O
H
O
7g
13C NMR spectrum
f1 (ppm)

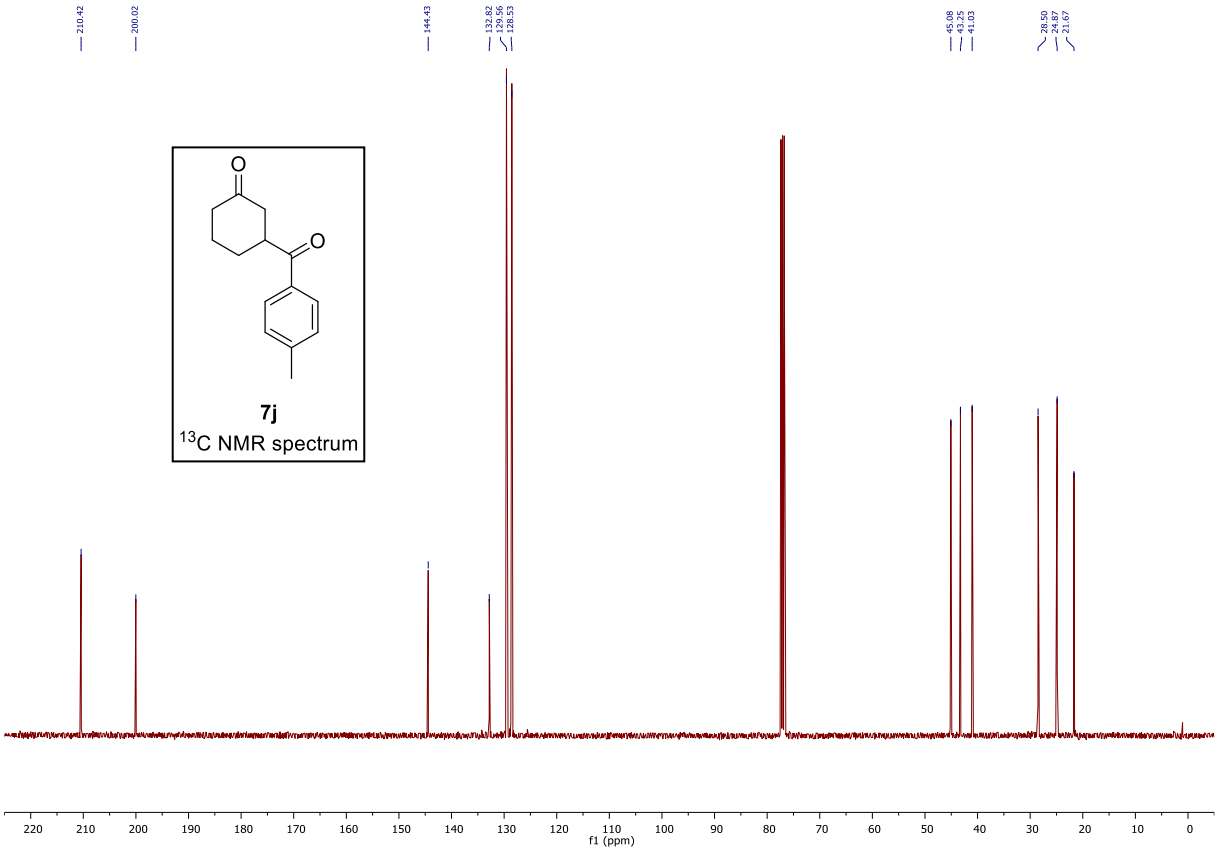

7.88
7.85
6.89
6.87
3.81
3.73
3.69
3.67
2.68
2.65
2.64
2.62
2.39
2.05
2.01
2.00
1.81
1.76
1.73
O
O
OMe
7h
1H NMR spectrum
1.86
1.88
2.89
0.97
1.00
2.77
1.93
1.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

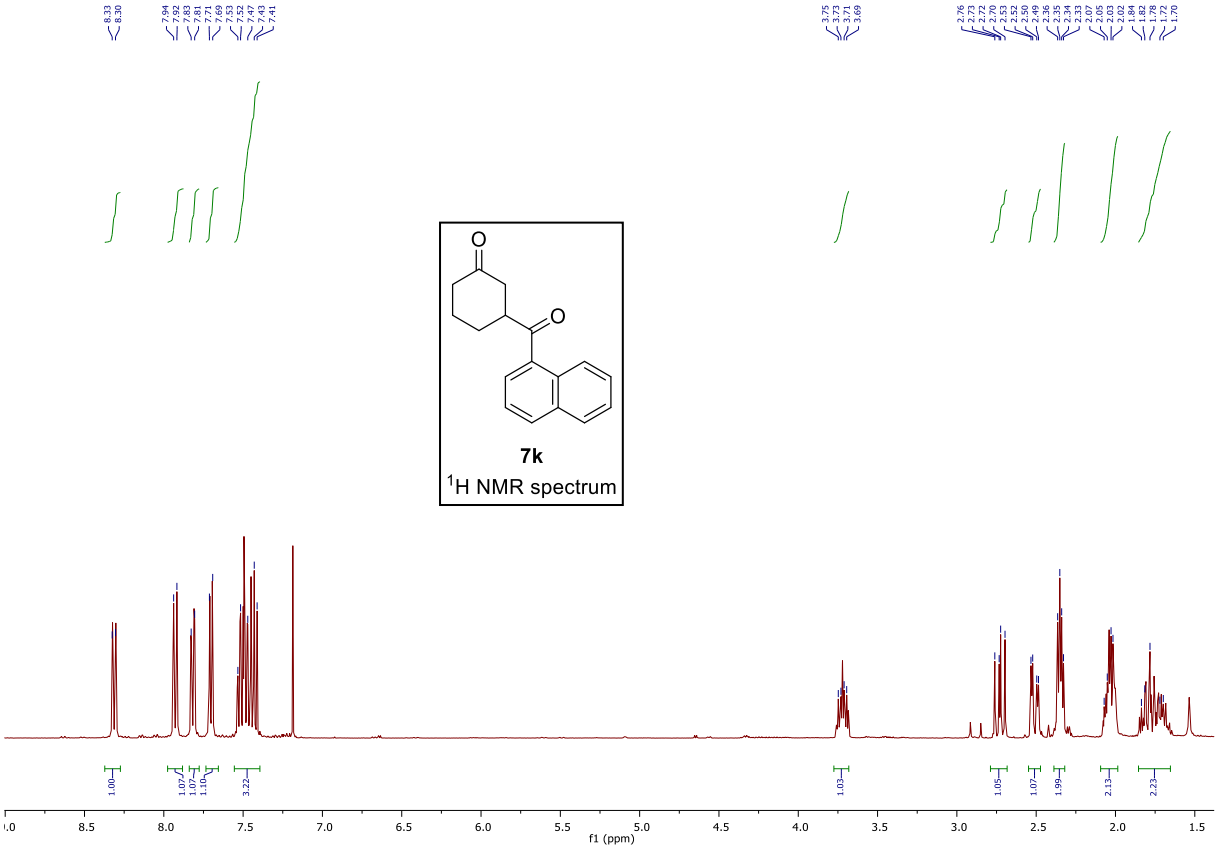

210.53
198.87
163.83
130.73
128.27
114.04
55.54
44.88
43.36
41.04
28.58
24.91
O
O
OMe
7h
13C NMR spectrum
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

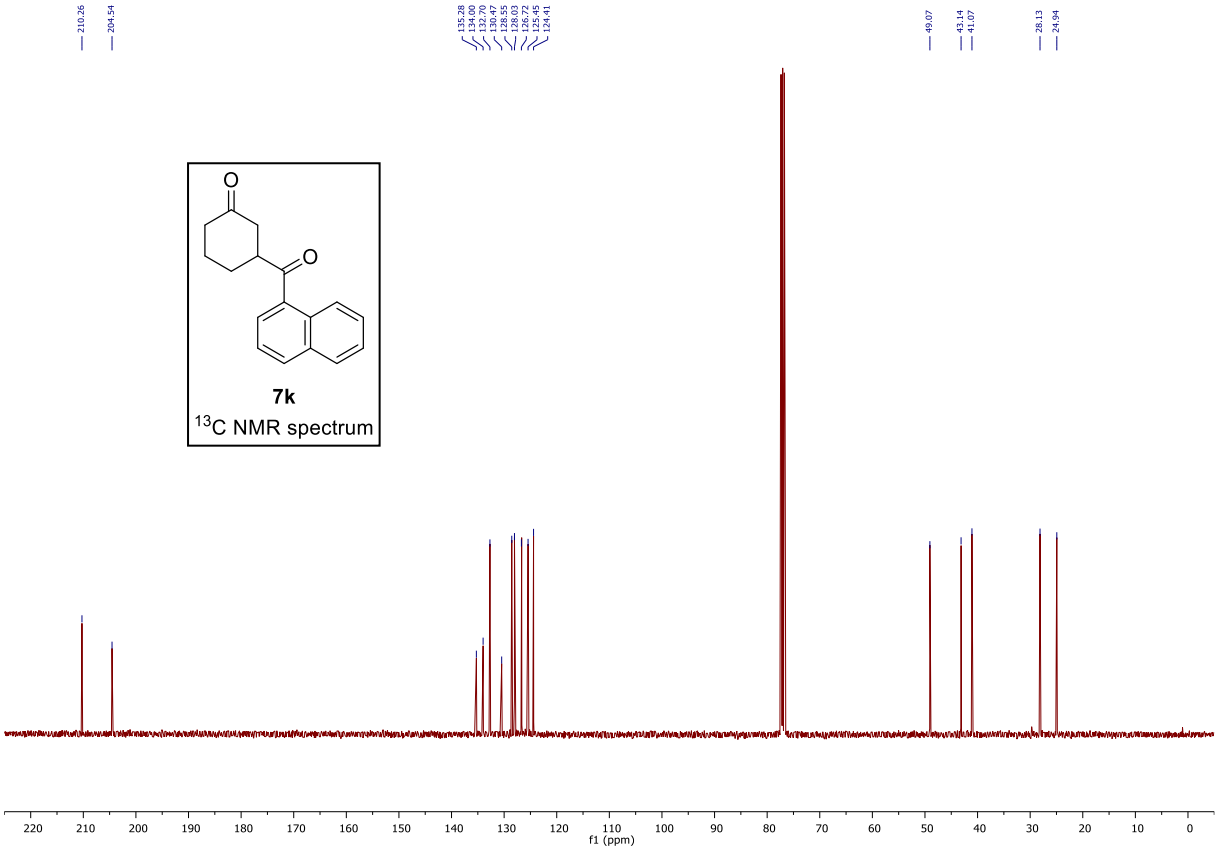

7.75
7.73
7.57
7.55
3.71
3.69
2.67
2.64
2.63
2.60
2.40
2.37
2.35
2.33
2.04
2.02
1.80
1.76
1.75
O
O
Br
7i
1H NMR spectrum
1.96
1.91
1.00
0.98
2.99
2.02
1.96
f1 (ppm)


209.86
199.41
134.04
132.23
129.31
128.77
45.15
43.04
40.96
28.33
24.75
O
O
Br
7i
13C NMR spectrum
f1 (ppm)

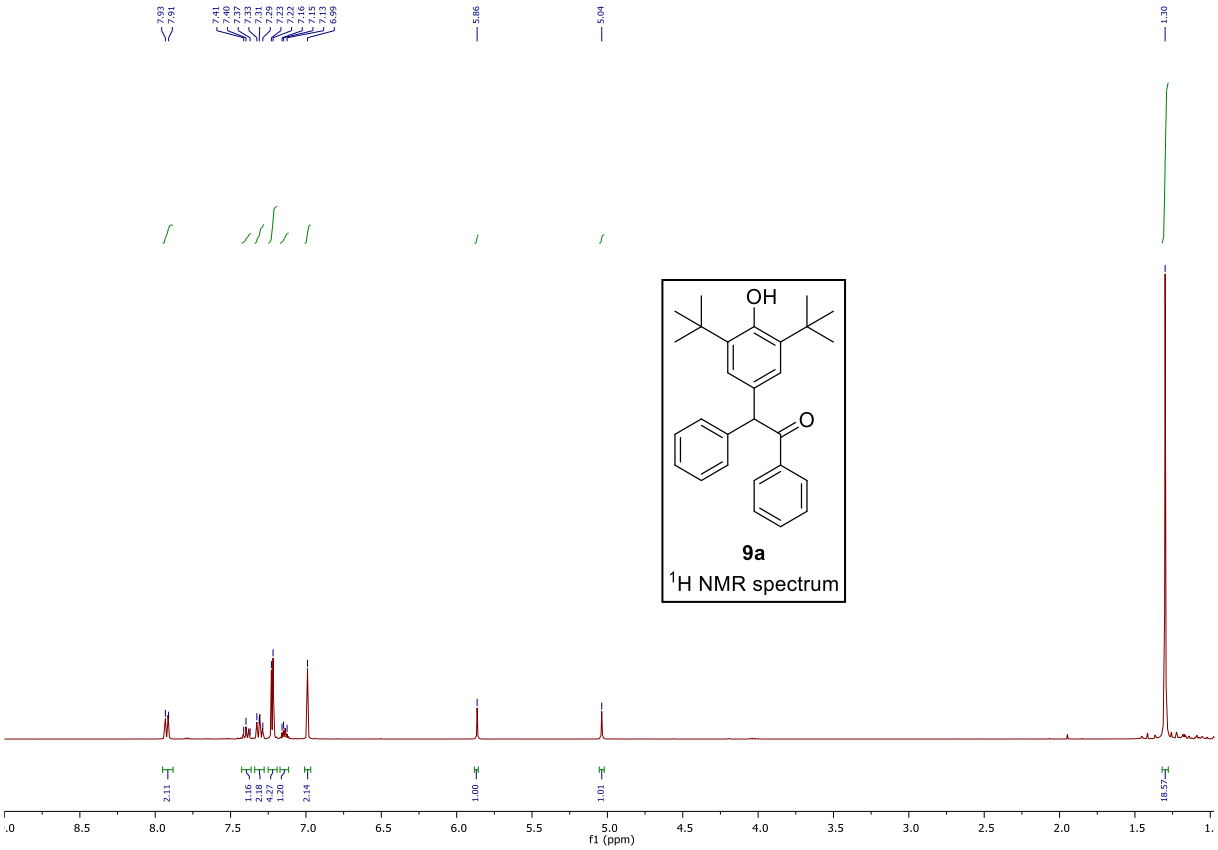

7.78
7.76
7.22
7.20
3.74
3.72
2.67
2.65
2.64
2.61
2.42
2.38
2.35
2.04
2.02
1.79
1.77
1.76
1.75
O
O
7j
1H NMR spectrum
1.95
2.05
1.00
1.05
5.95
1.92
2.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

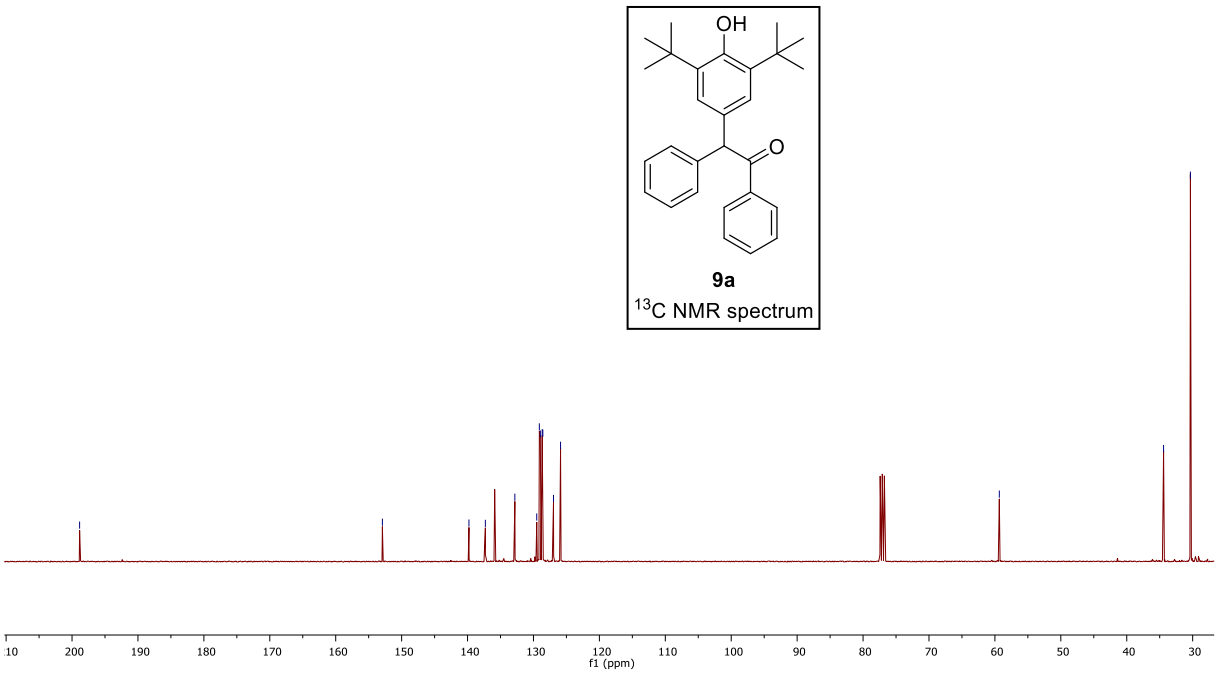

210.42
200.02
144.43
132.82
128.96
128.53
45.08
43.25
41.03
28.50
24.87
21.67
O
O
7j
13C NMR spectrum
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

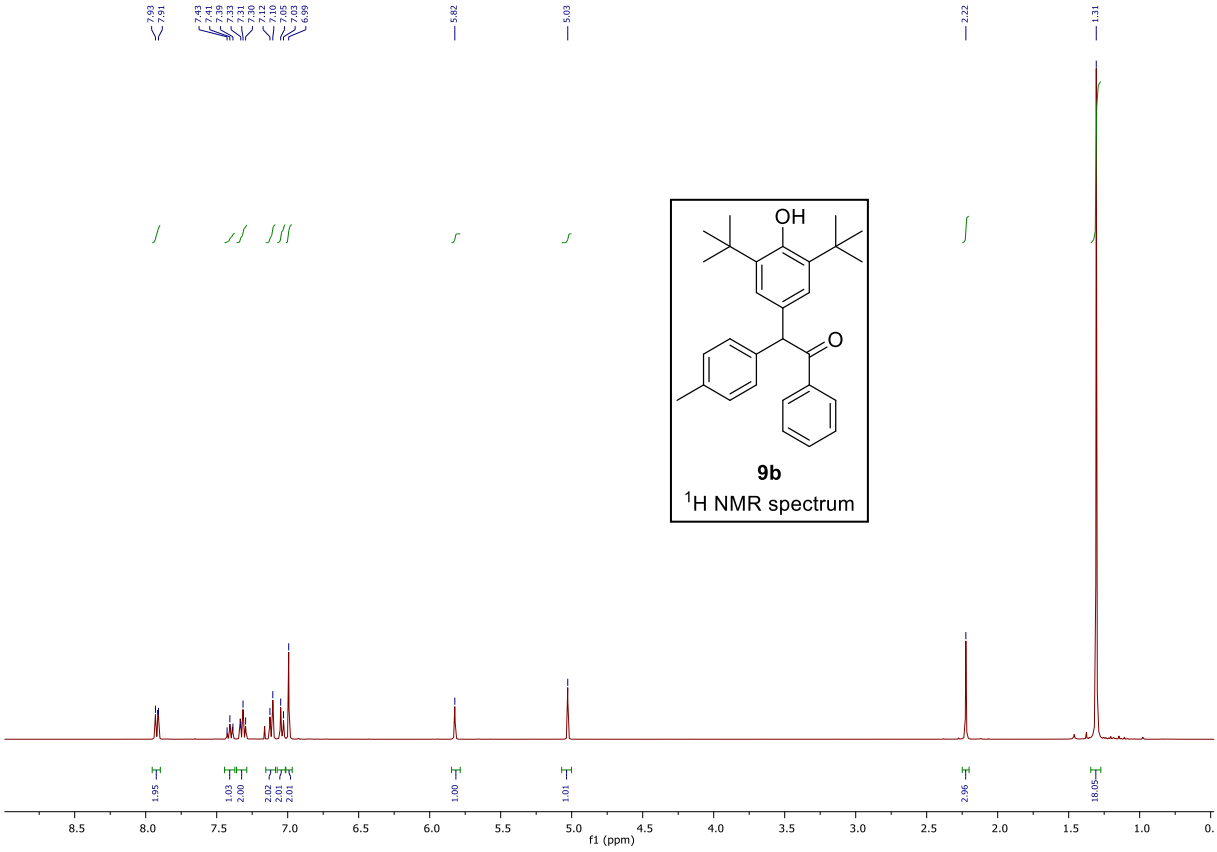

8.33
8.30
7.94
7.92
7.83
7.81
7.71
7.69
7.53
7.52
7.47
7.45
7.41
3.75
3.73
3.71
3.69
2.76
2.73
2.72
2.70
2.53
2.52
2.50
2.49
2.36
2.35
2.34
2.33
2.07
2.05
2.03
2.02
1.84
1.82
1.78
1.72
1.70
O
O
7k
1H NMR spectrum
1.00
1.07
1.07
1.10
3.22
1.03
1.05
1.07
1.99
2.13
2.23
f1 (ppm)

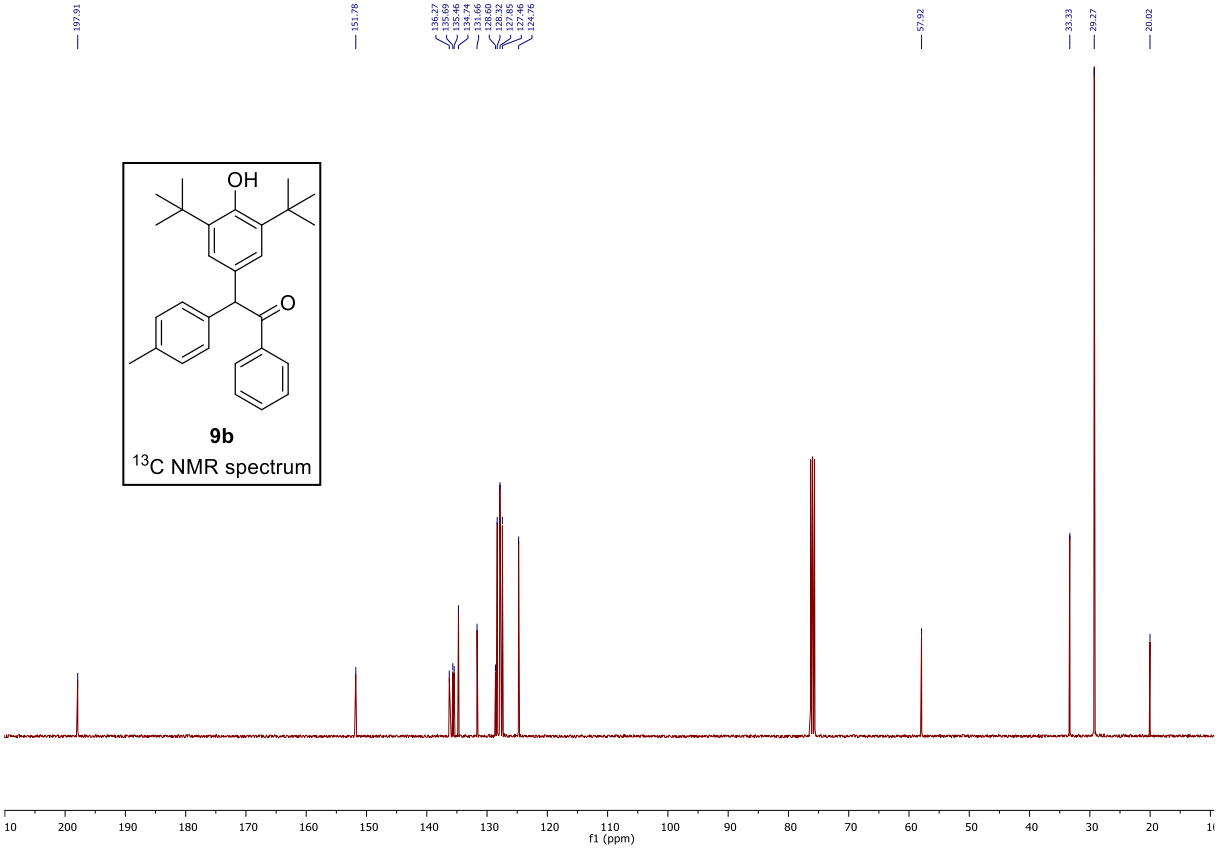

210.26
204.54
135.28
134.60
132.70
130.47
128.55
128.03
126.72
125.45
124.41
49.07
43.14
41.07
28.13
24.94
O
O
7k
13C NMR spectrum
f1 (ppm)

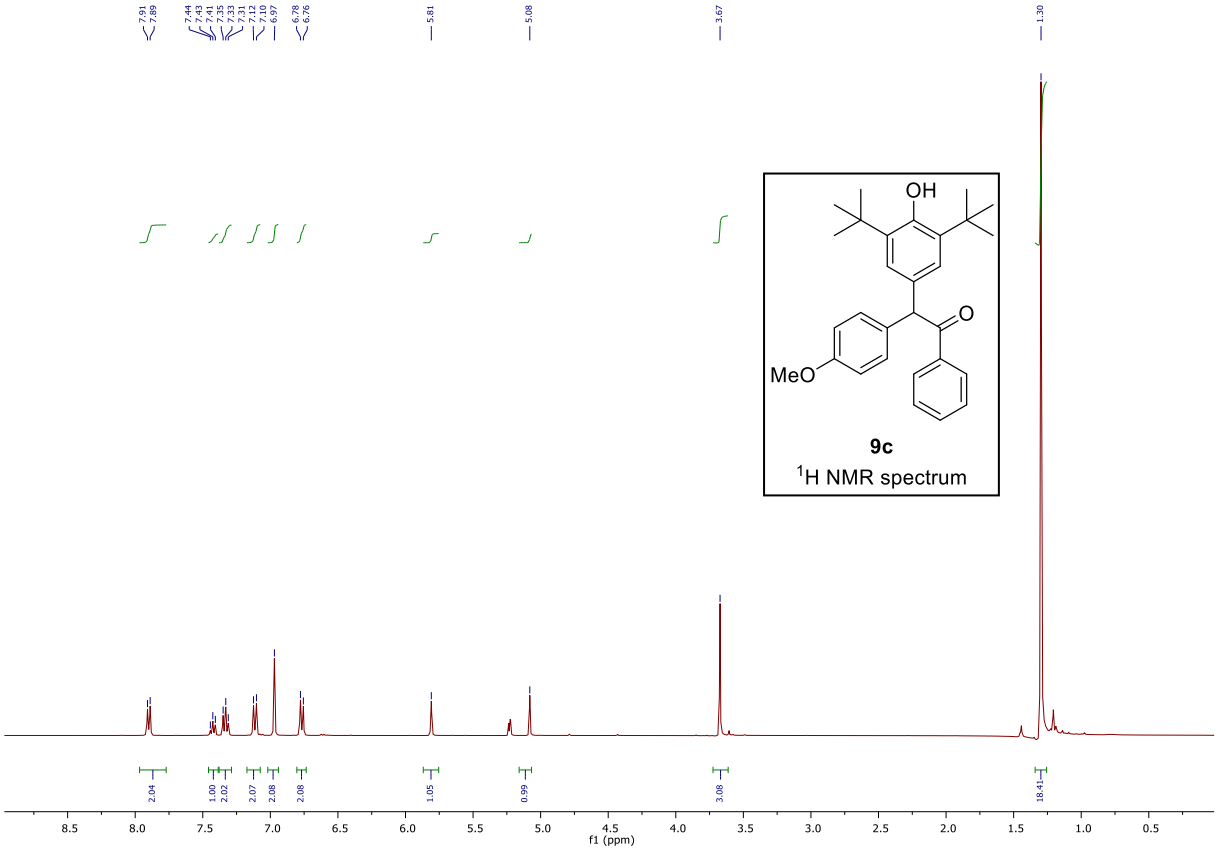
9.3. NMR spectra for the hydroacylation of *para*-quinone methides

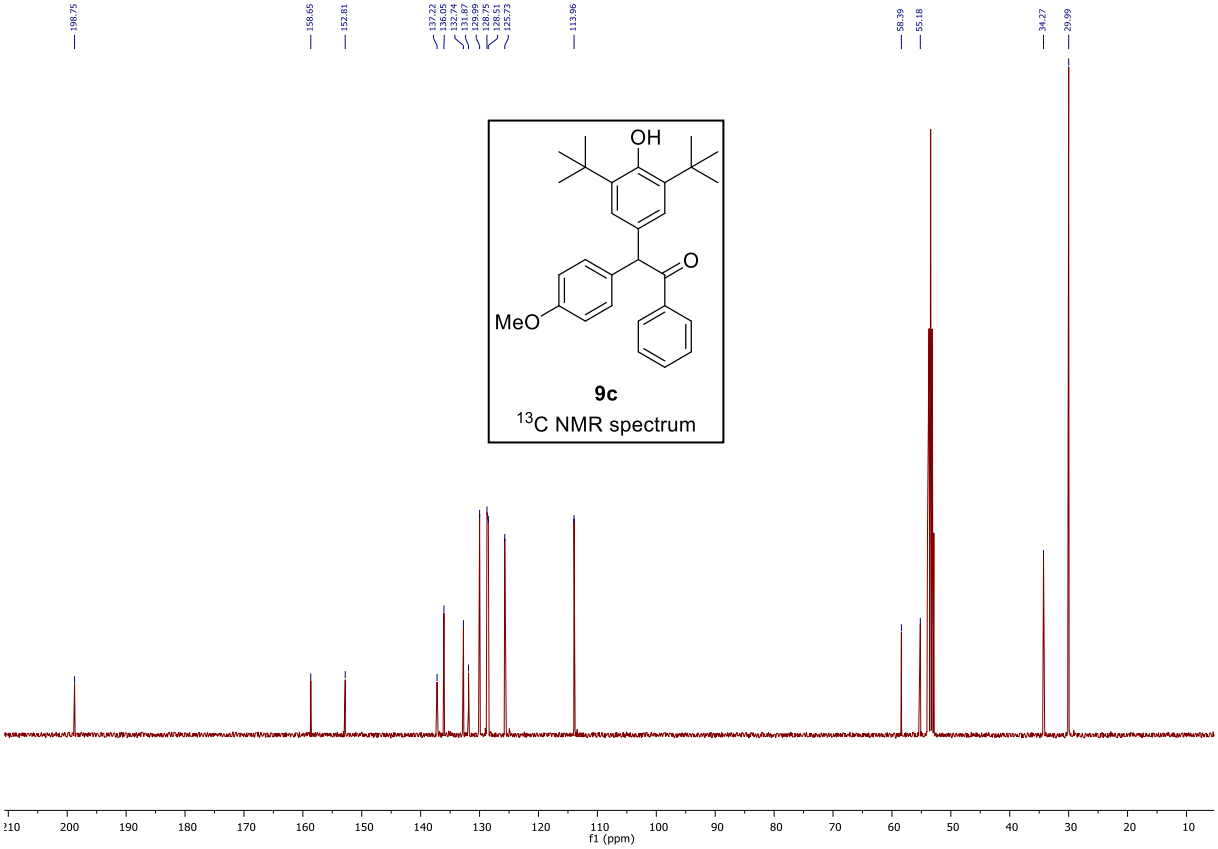


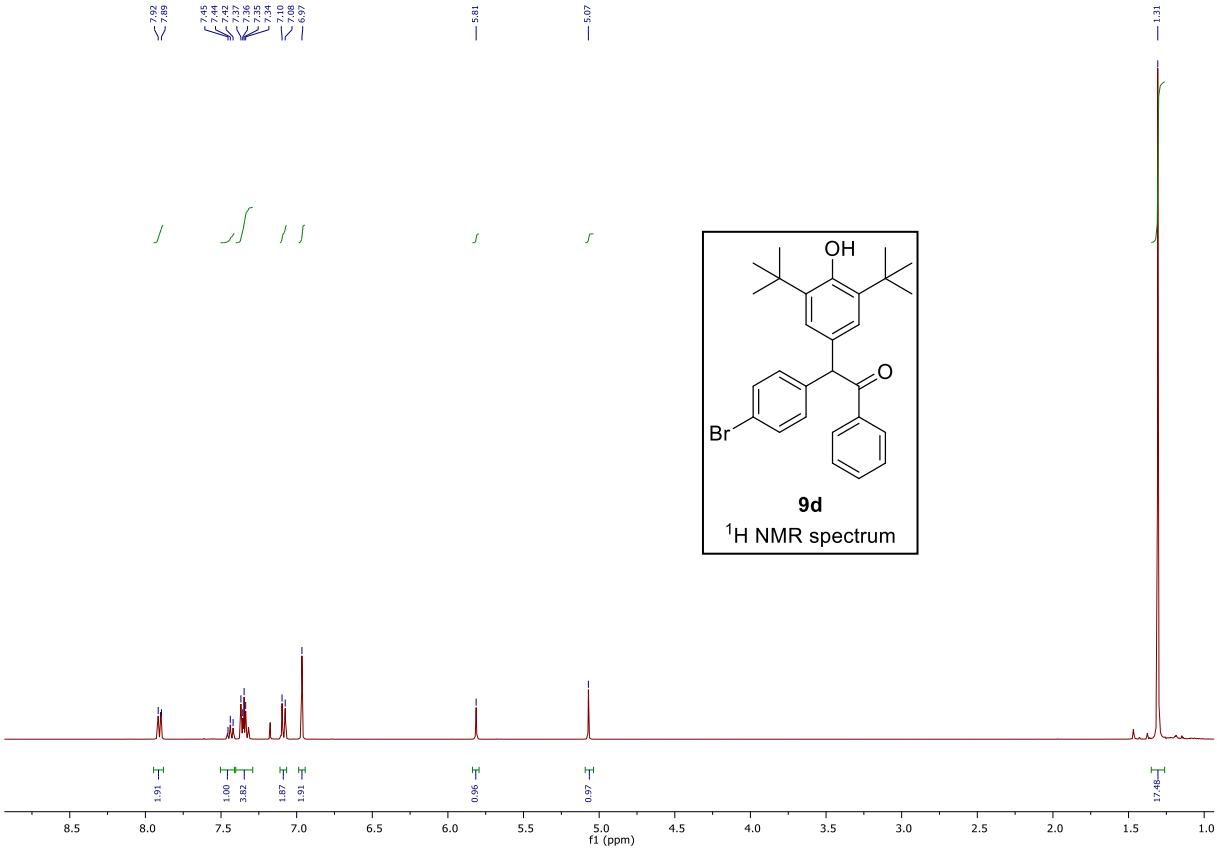


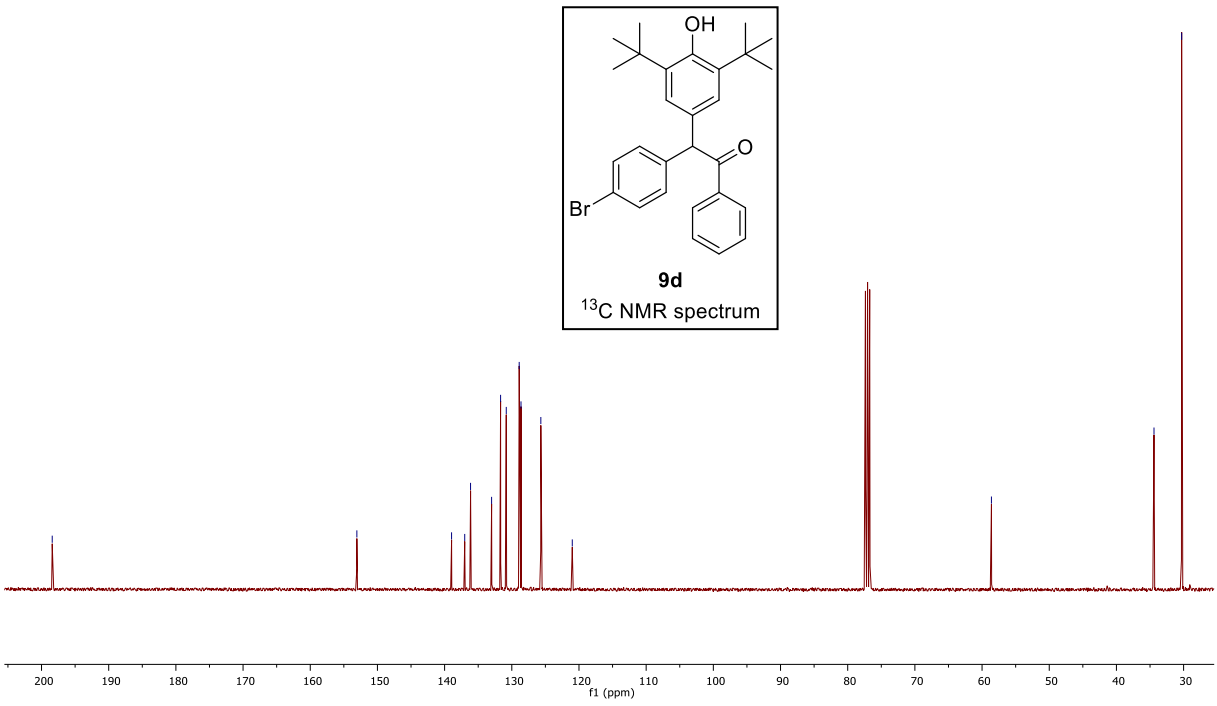

OH
O
9b
1H NMR spectrum
f1 (ppm)

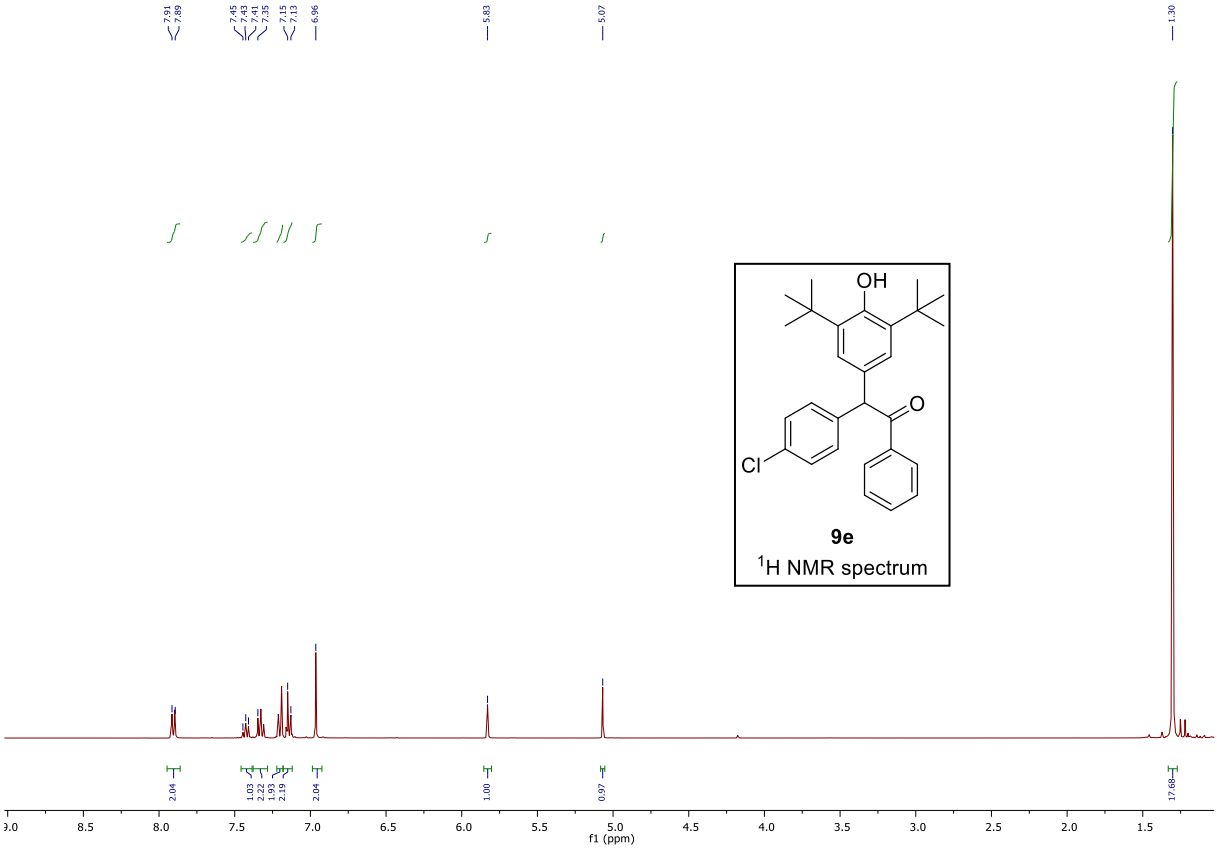

OH
O
9b
13C NMR spectrum
f1 (ppm)

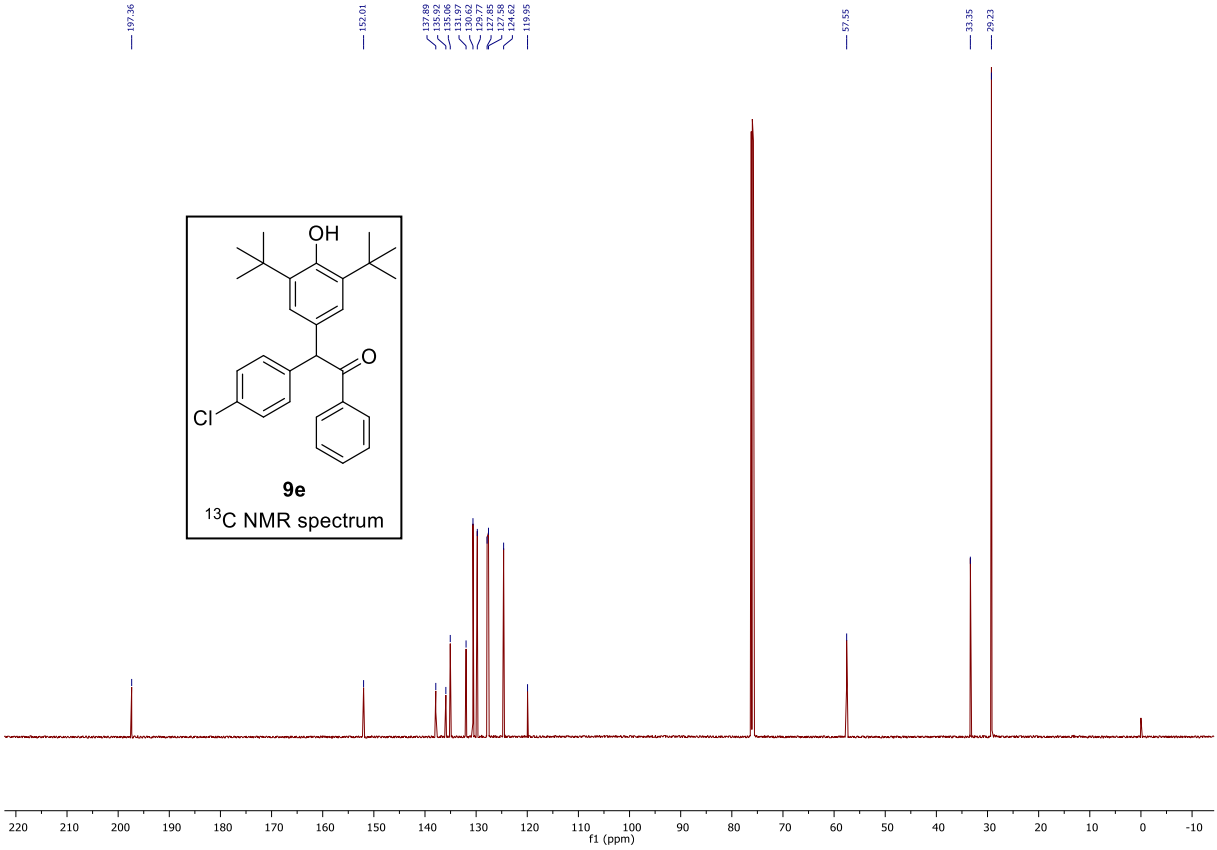

OH
O
MeO
9c
1H NMR spectrum
f1 (ppm)

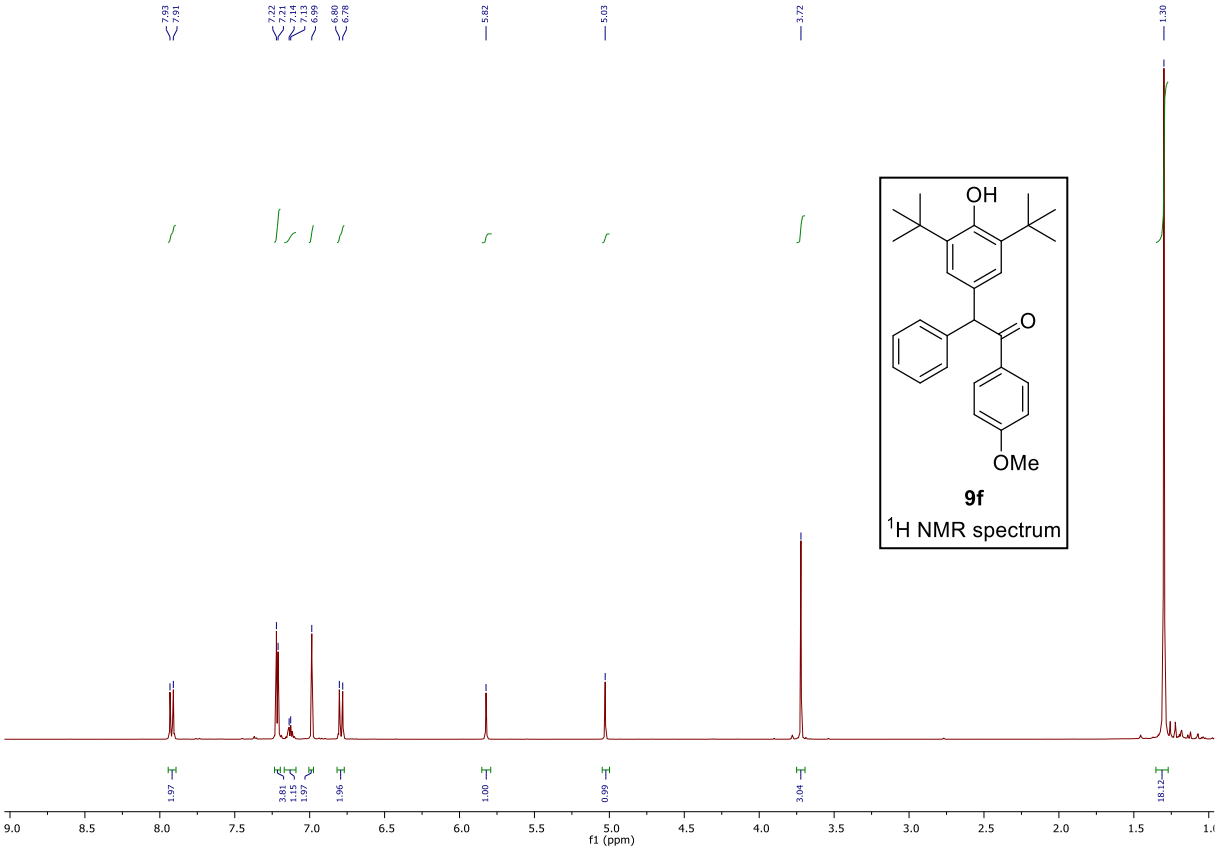

OH
O
MeO
9c
13C NMR spectrum
f1 (ppm)

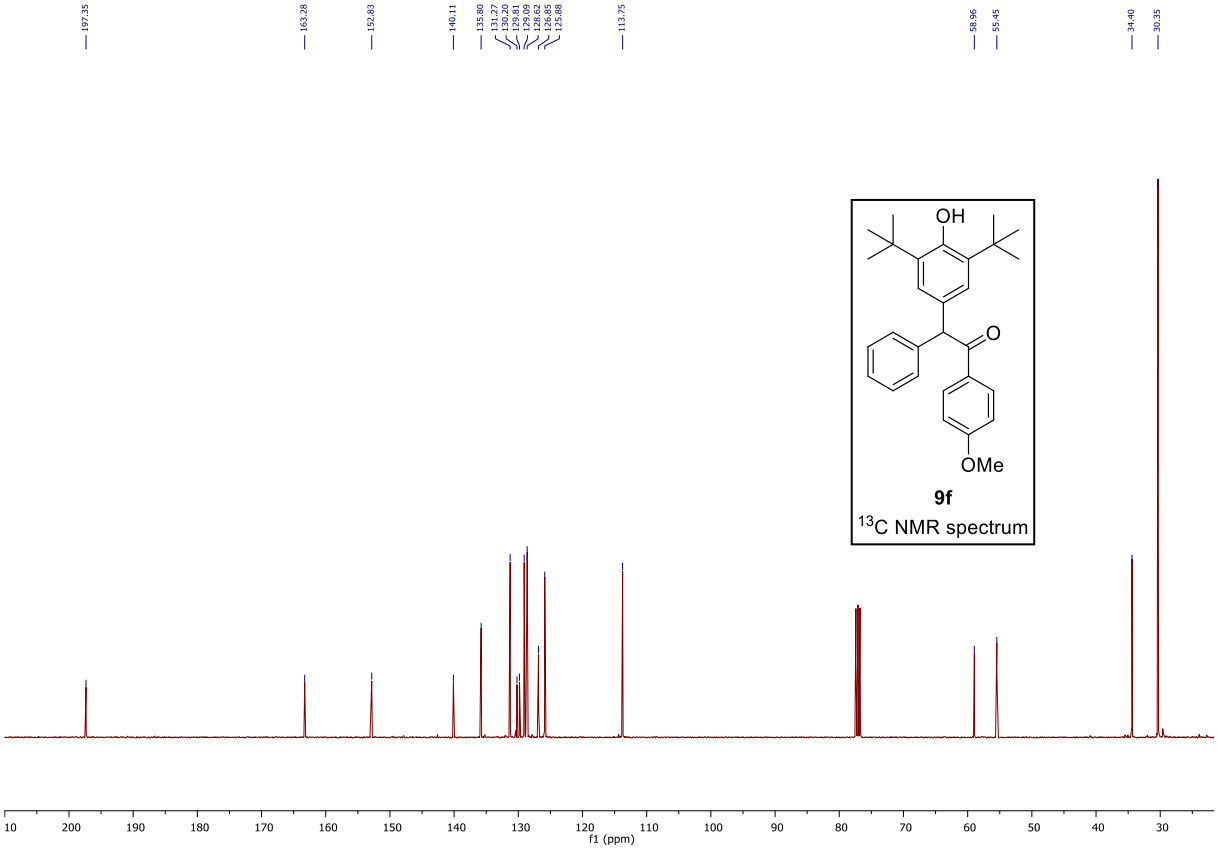

OH
O
Br
9d
1H NMR spectrum
f1 (ppm)

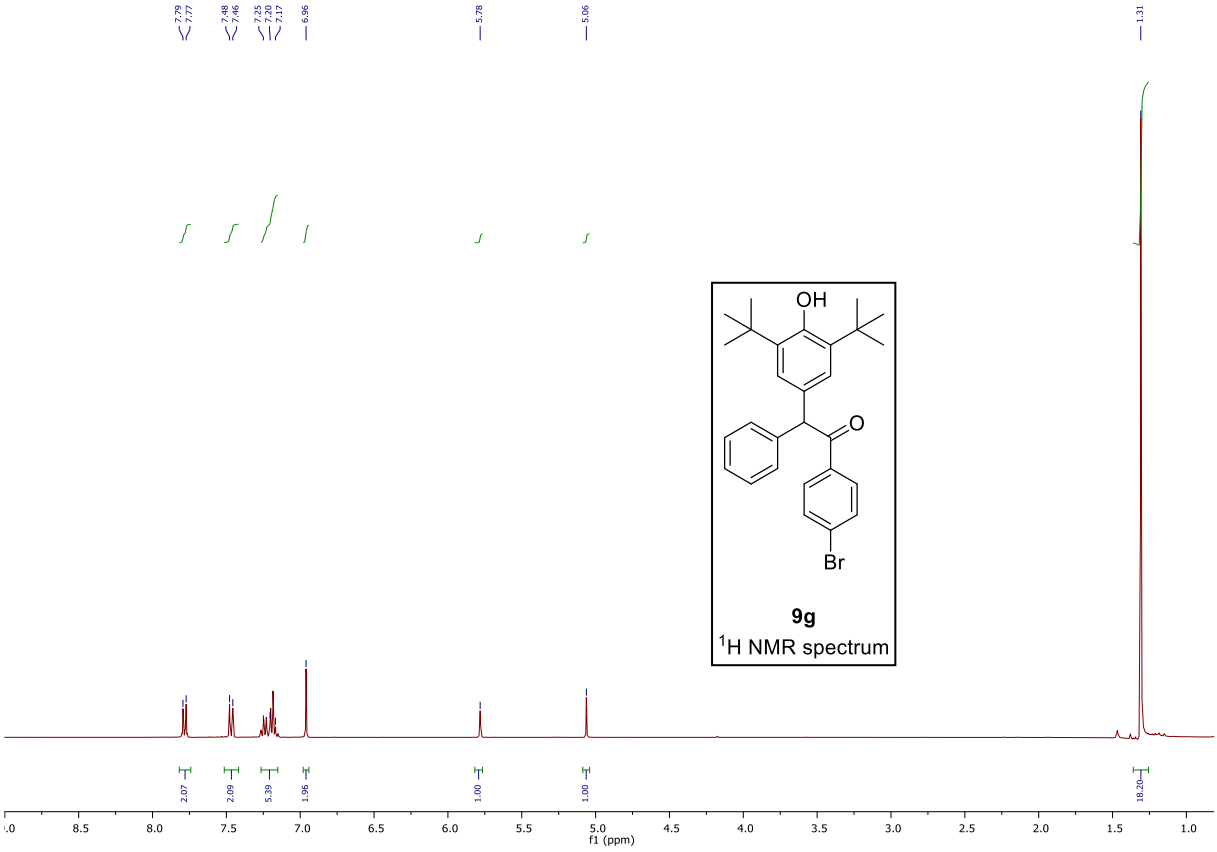

OH
O
Br
9d
13C NMR spectrum
f1 (ppm)

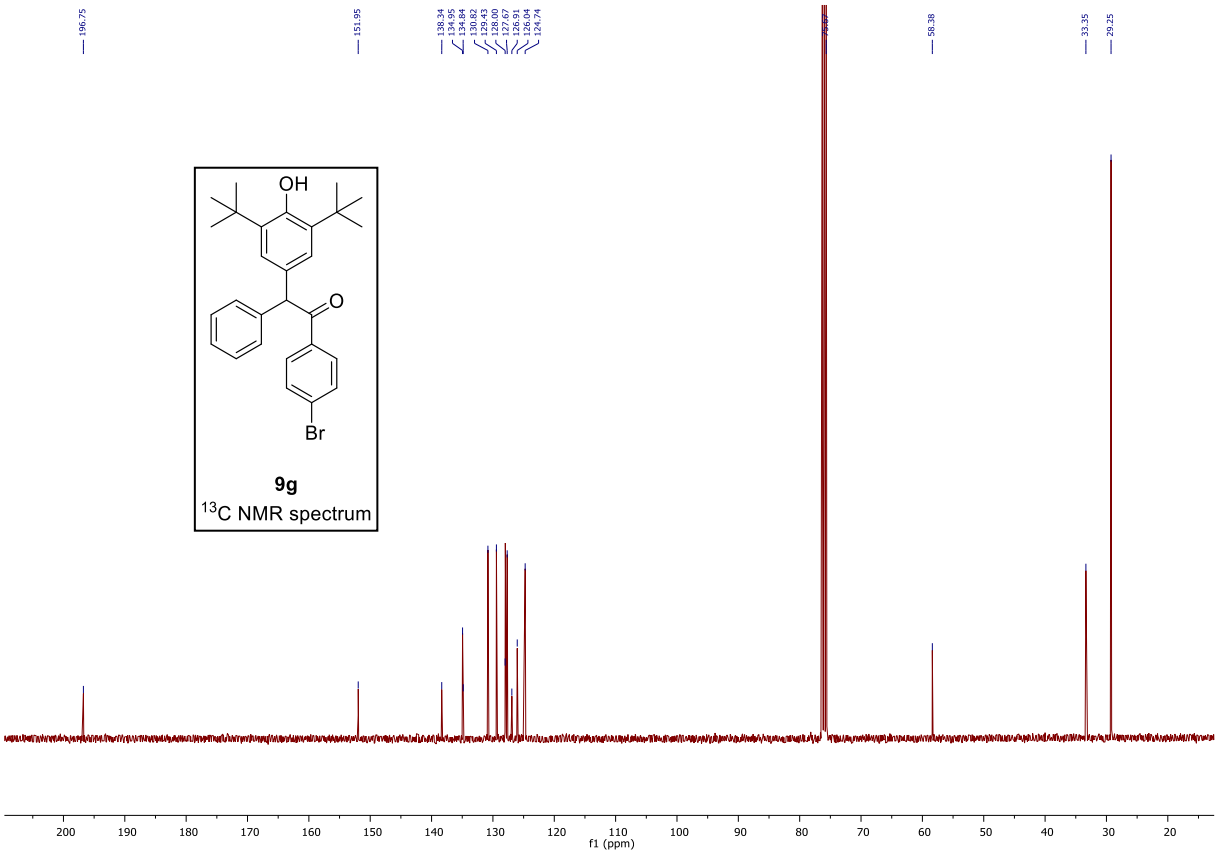

OH
O
Cl
9e
1H NMR spectrum
f1 (ppm)

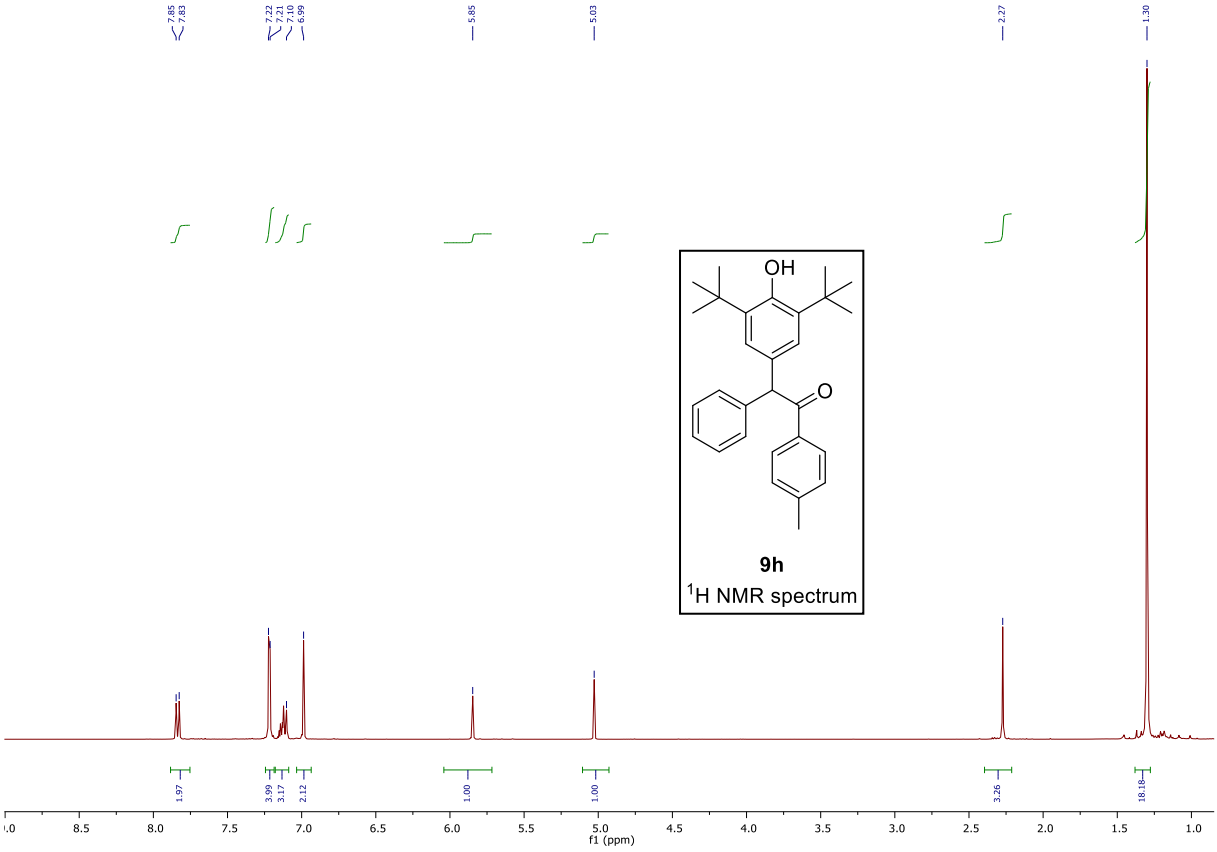

OH
O
Cl
9e
13C NMR spectrum
f1 (ppm)

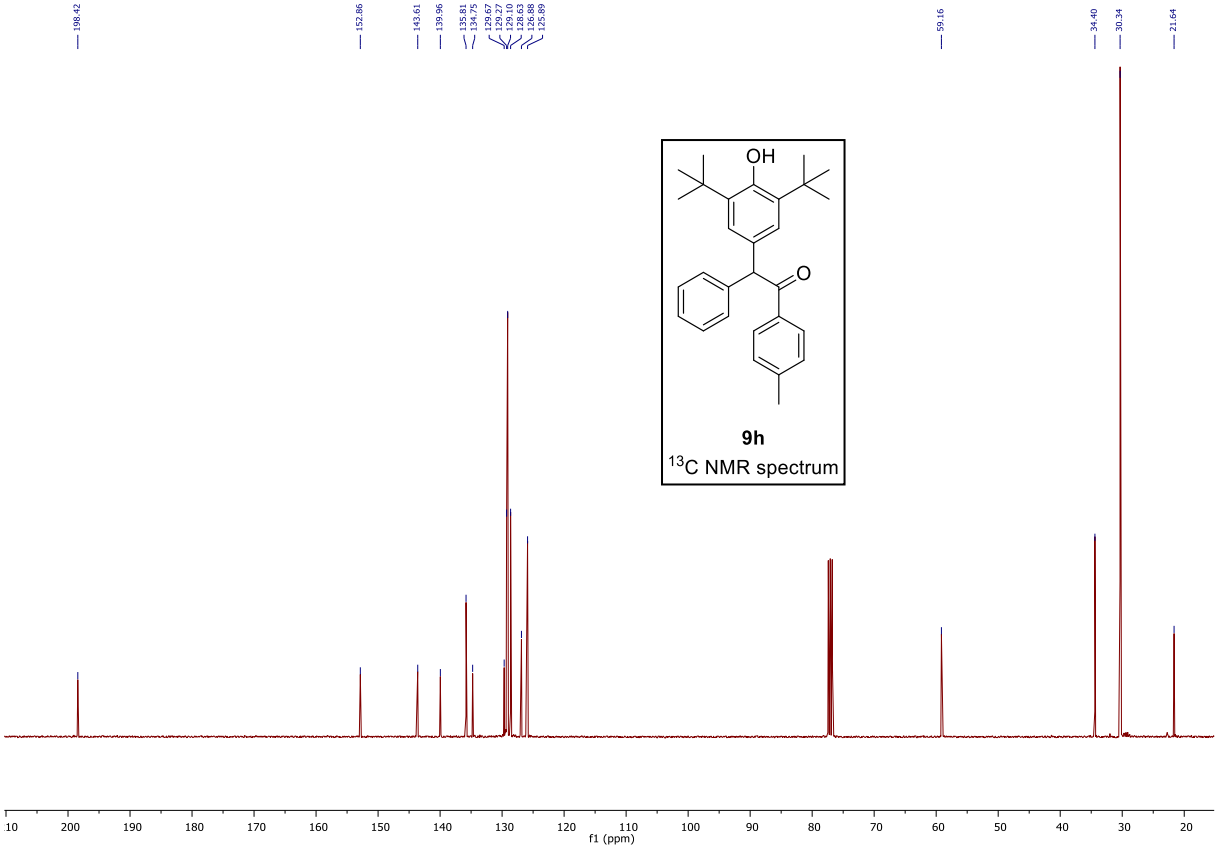

7.93
7.91
7.22
7.21
7.14
7.13
6.99
6.80
6.78
5.82
5.03
3.72
1.30
OH
O
OMe
9f
1H NMR spectrum
1.97
3.81
1.15
1.97
1.96
1.00
0.99
3.04
18.12
f1 (ppm)

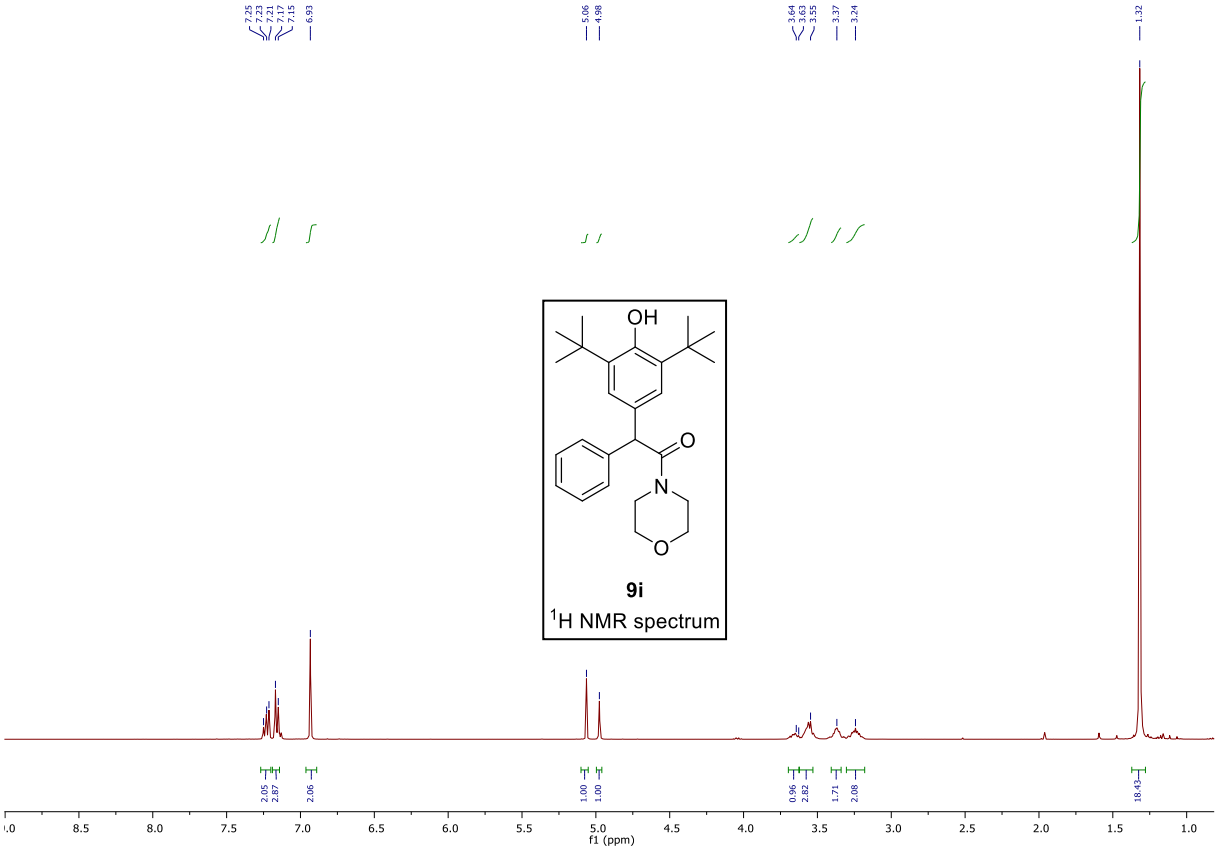

197.35
163.28
152.83
140.11
135.80
131.27
130.20
130.01
129.80
128.62
126.85
125.88
113.75
58.96
55.45
34.40
30.35
OH
O
OMe
9f
13C NMR spectrum
f1 (ppm)

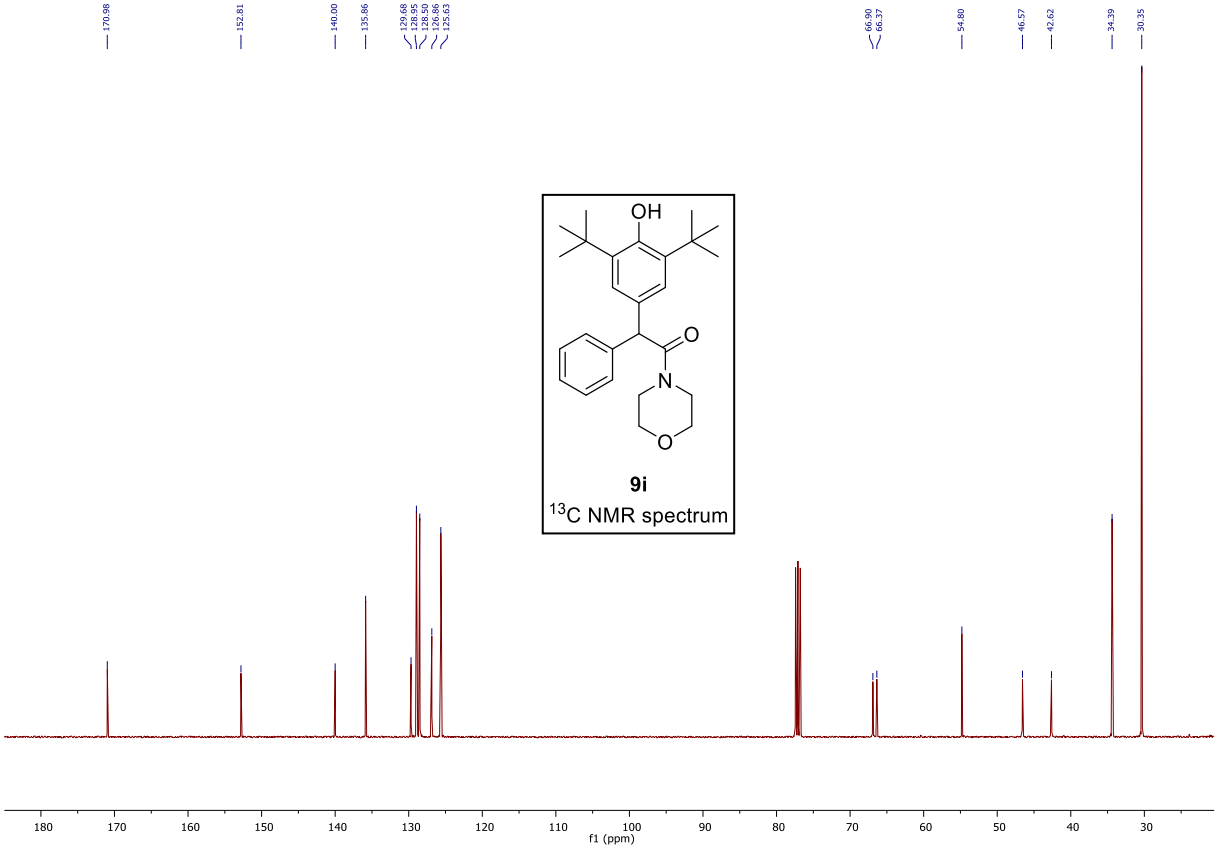

7.79
7.77
7.48
7.46
7.25
7.20
7.17
6.96
5.78
5.06
1.31
OH
O
Br
9g
1H NMR spectrum
2.07
2.09
5.39
1.96
1.00
1.00
18.20
f1 (ppm)

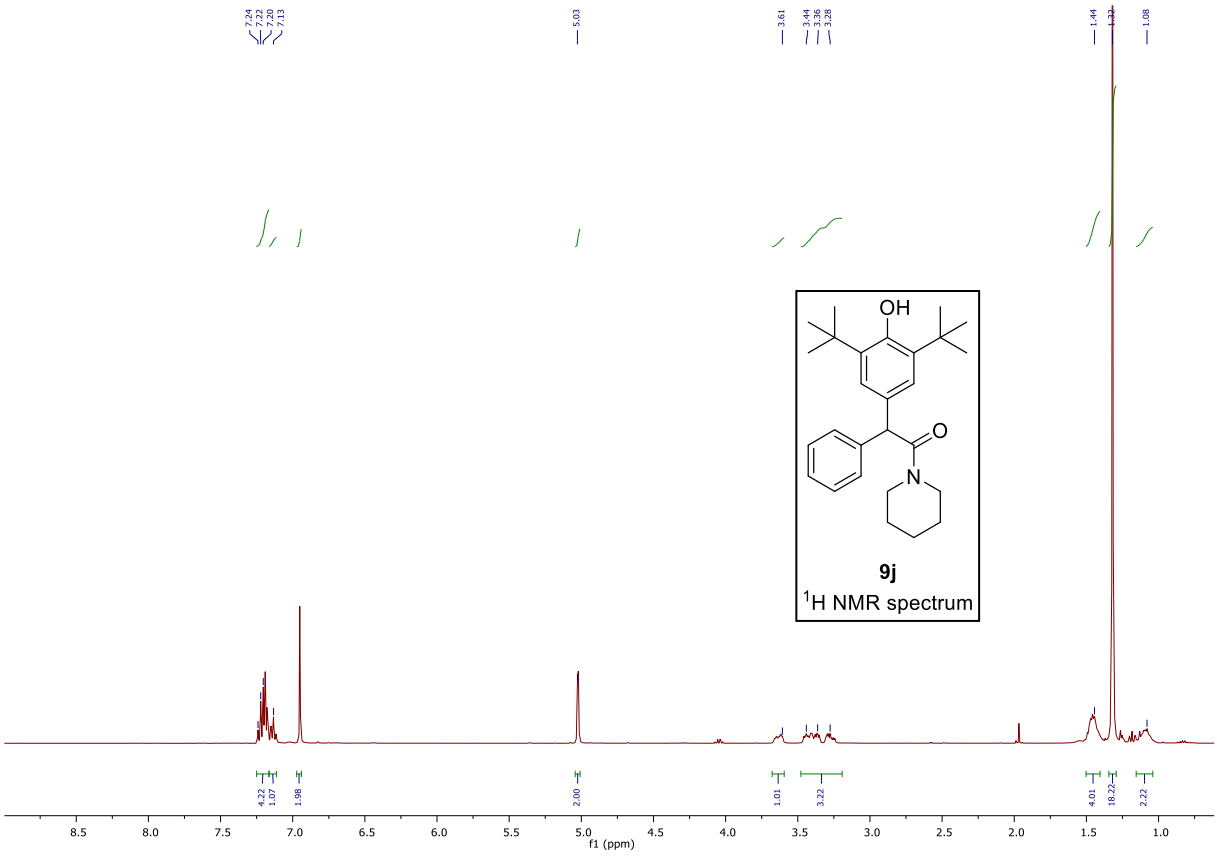

196.75
151.95
138.34
134.95
134.84
130.03
129.43
128.00
127.67
126.94
126.54
124.74
58.38
33.35
29.25
OH
O
Br
9g
13C NMR spectrum
f1 (ppm)

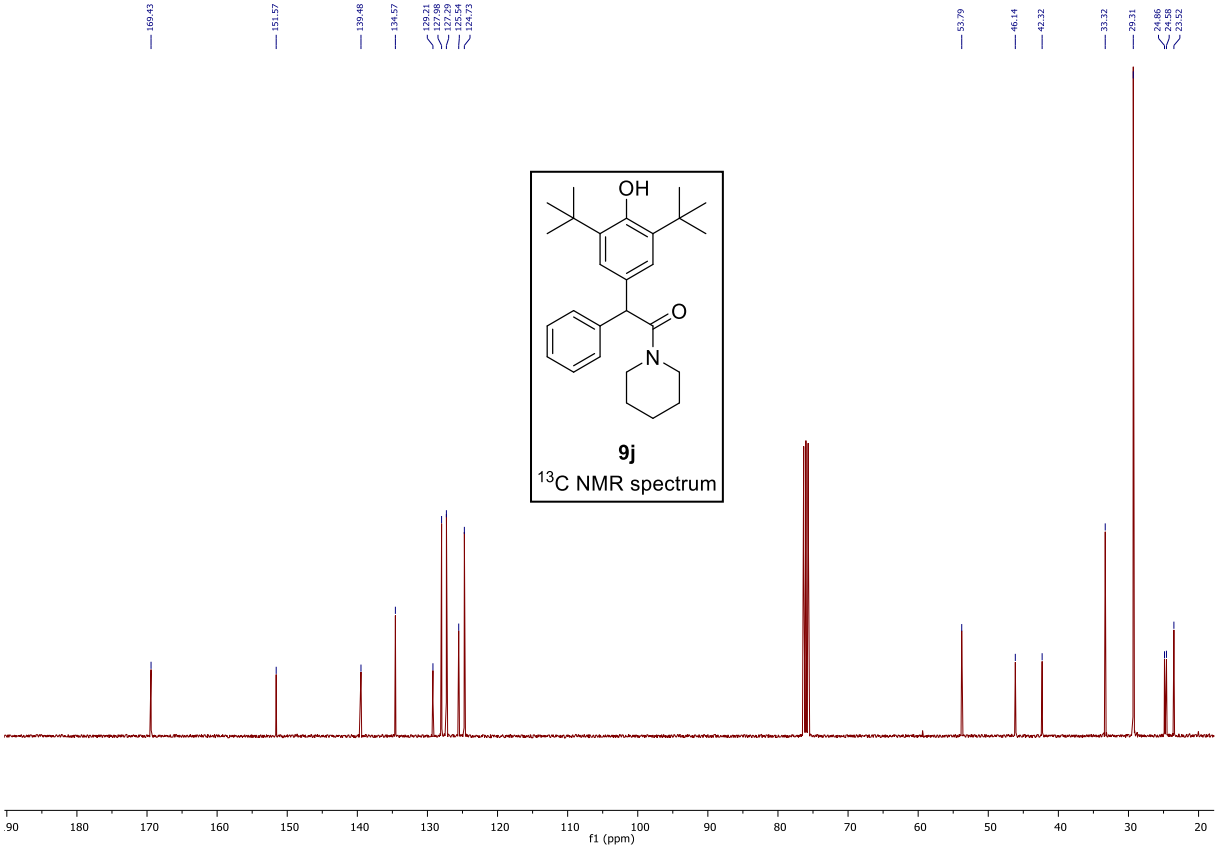

7.85
7.83
7.22
7.21
7.19
6.99
5.85
5.03
2.27
1.30
OH
O
9h
1H NMR spectrum
1.97
3.99
3.17
2.12
1.00
1.00
3.26
18.18
f1 (ppm)


198.42
152.86
143.61
139.96
135.81
134.75
129.67
129.27
129.10
128.63
126.88
125.89
59.16
34.40
30.34
21.64
OH
O
9h
13C NMR spectrum
f1 (ppm)

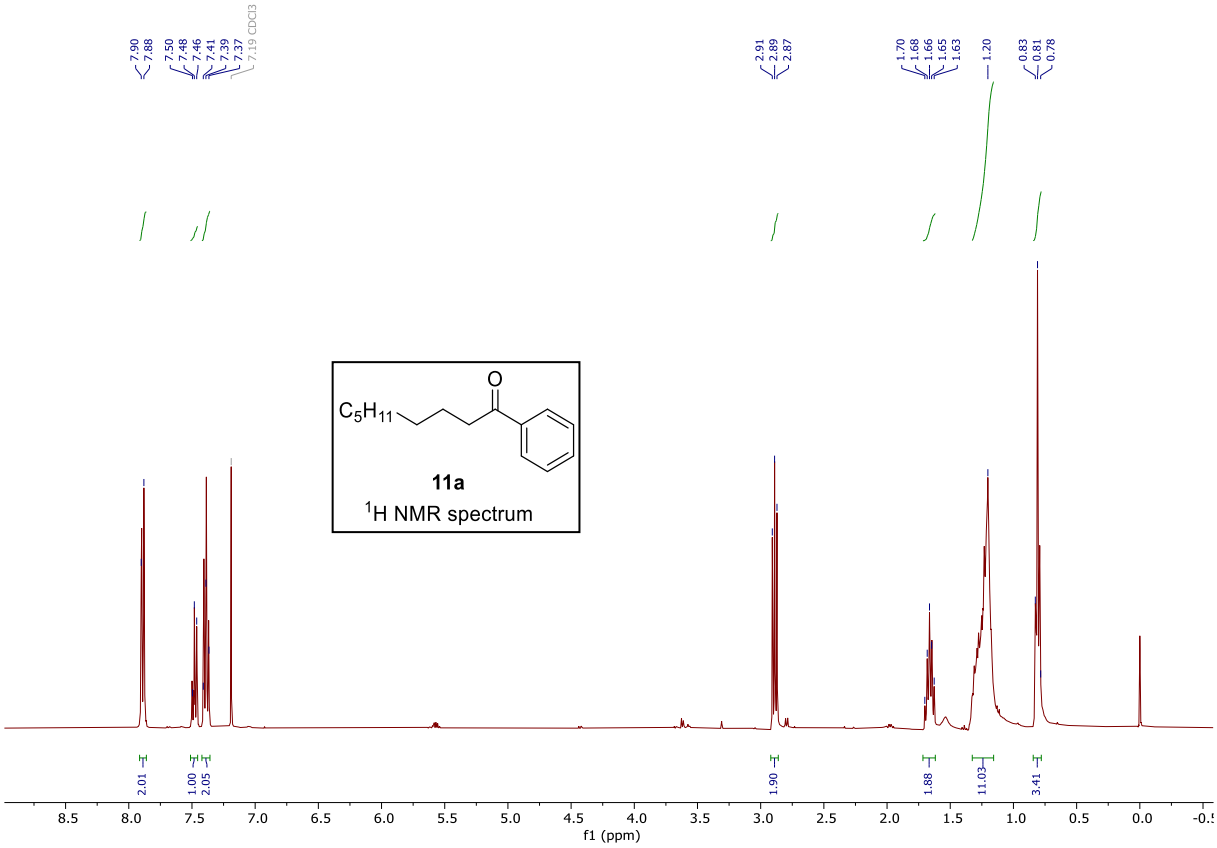

OH
O
N
O
9i
1H NMR spectrum
f1 (ppm)

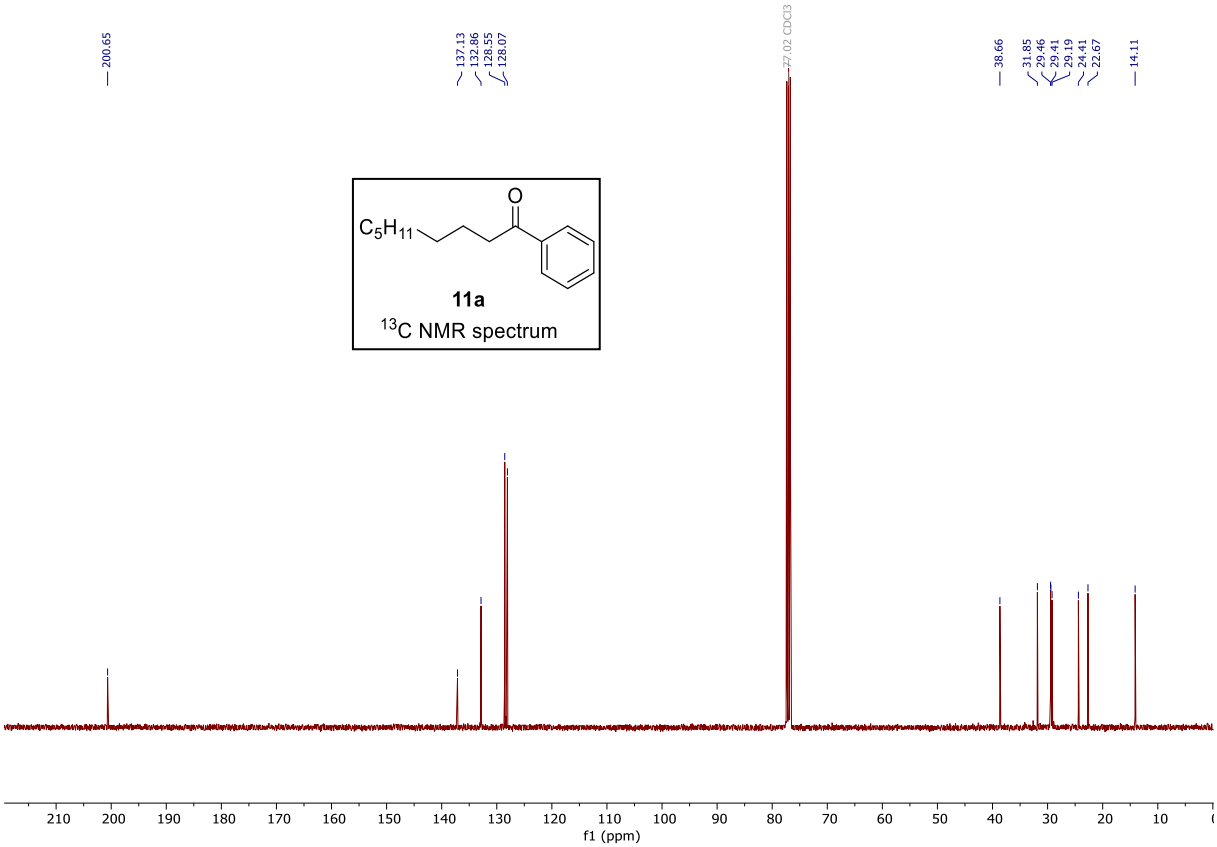

OH
O
N
O
9i
13C NMR spectrum
f1 (ppm)

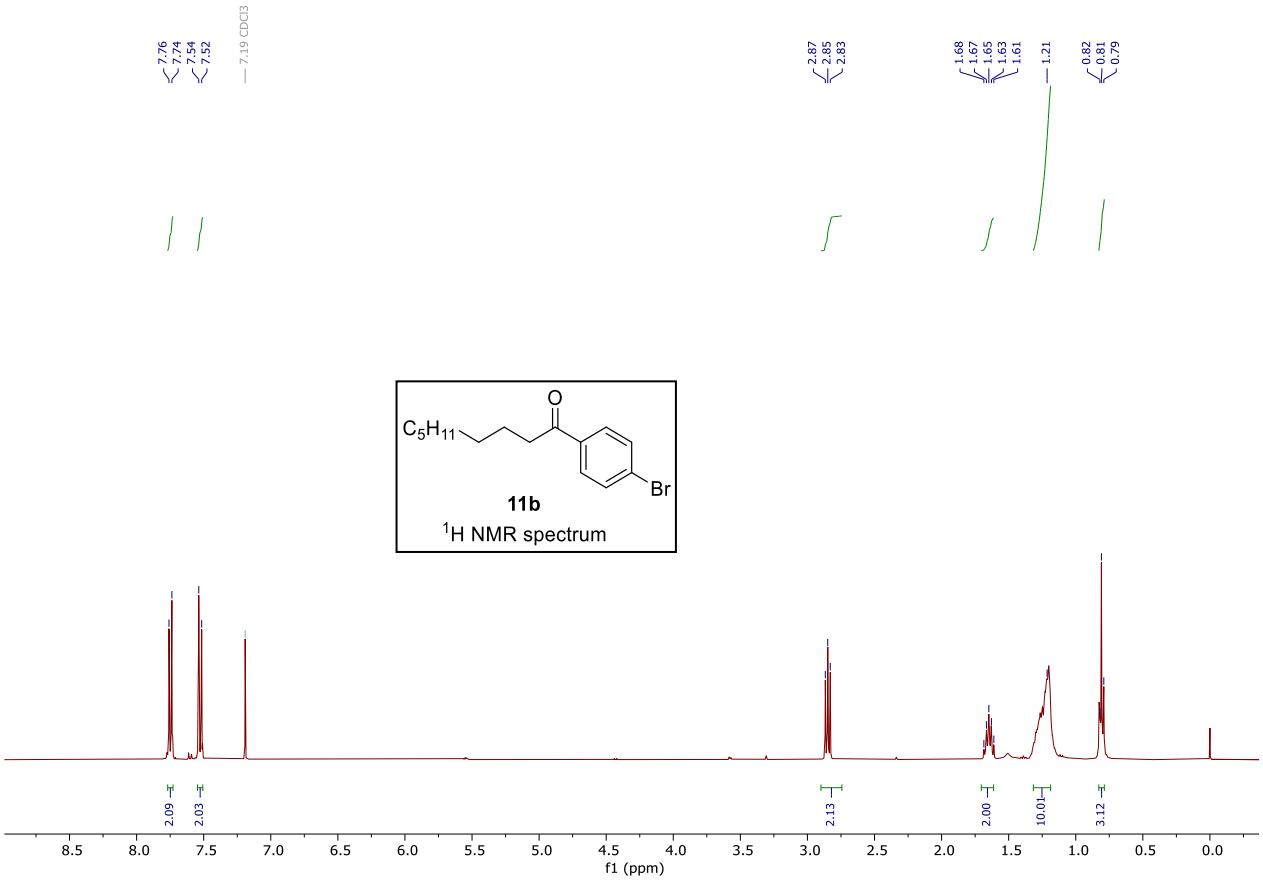

OH
O
N
9j
1H NMR spectrum
f1 (ppm)

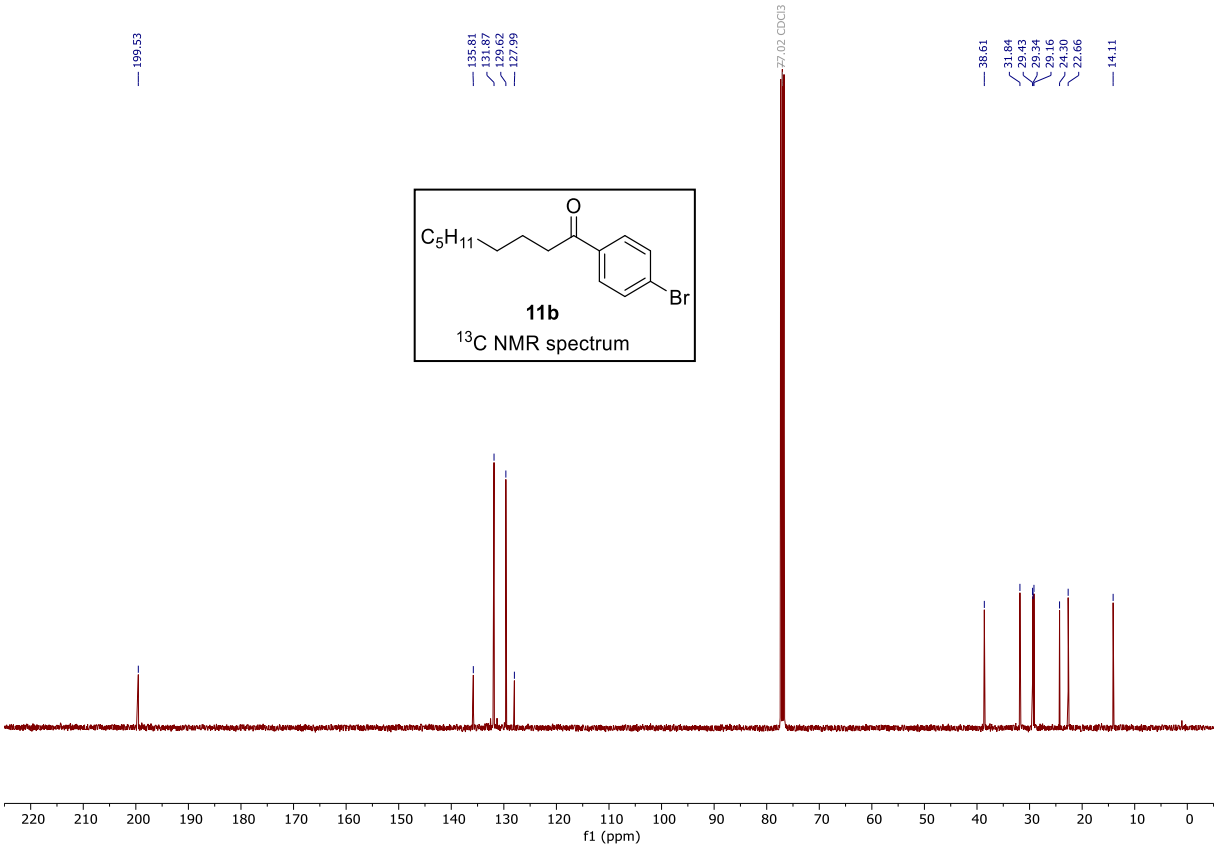

OH
O
N
9j
13C NMR spectrum
f1 (ppm)

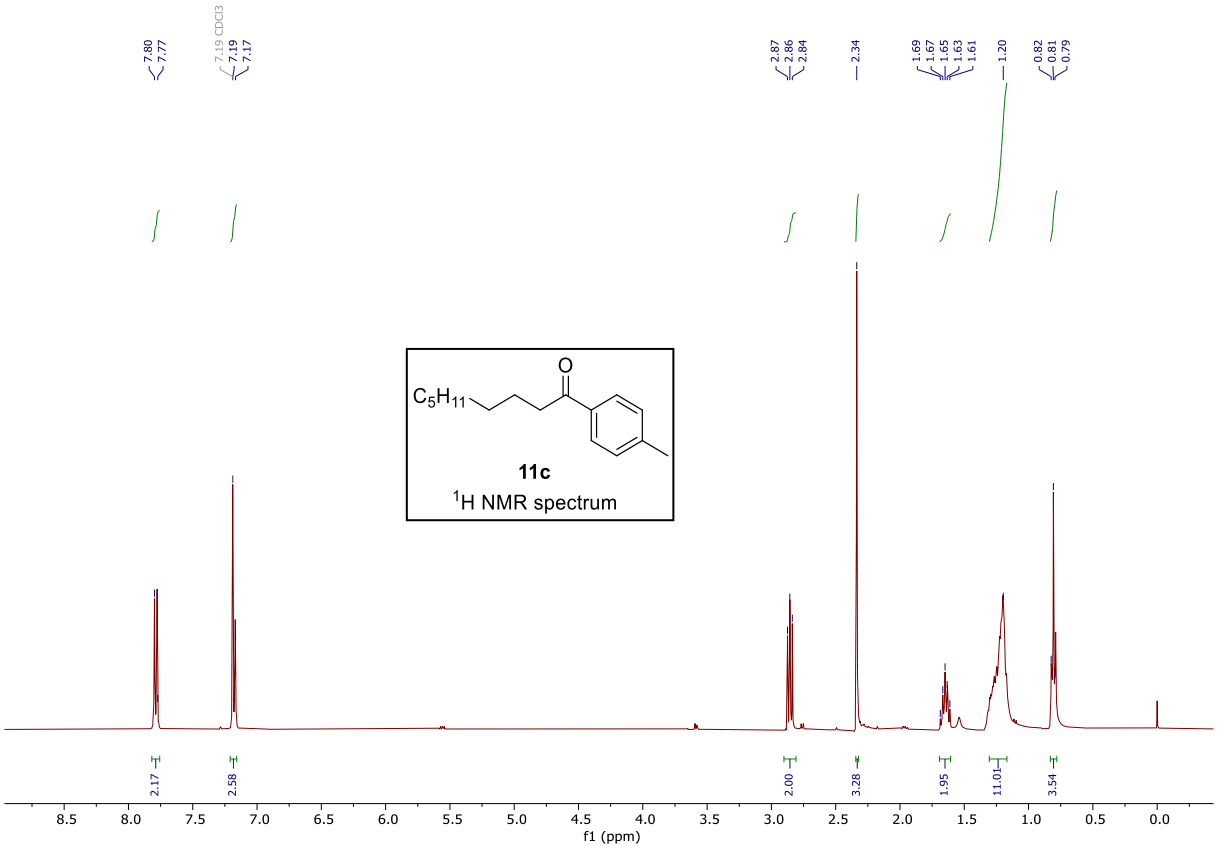
9.4. NMR spectra for the hydroacylation of unactivated alkenes

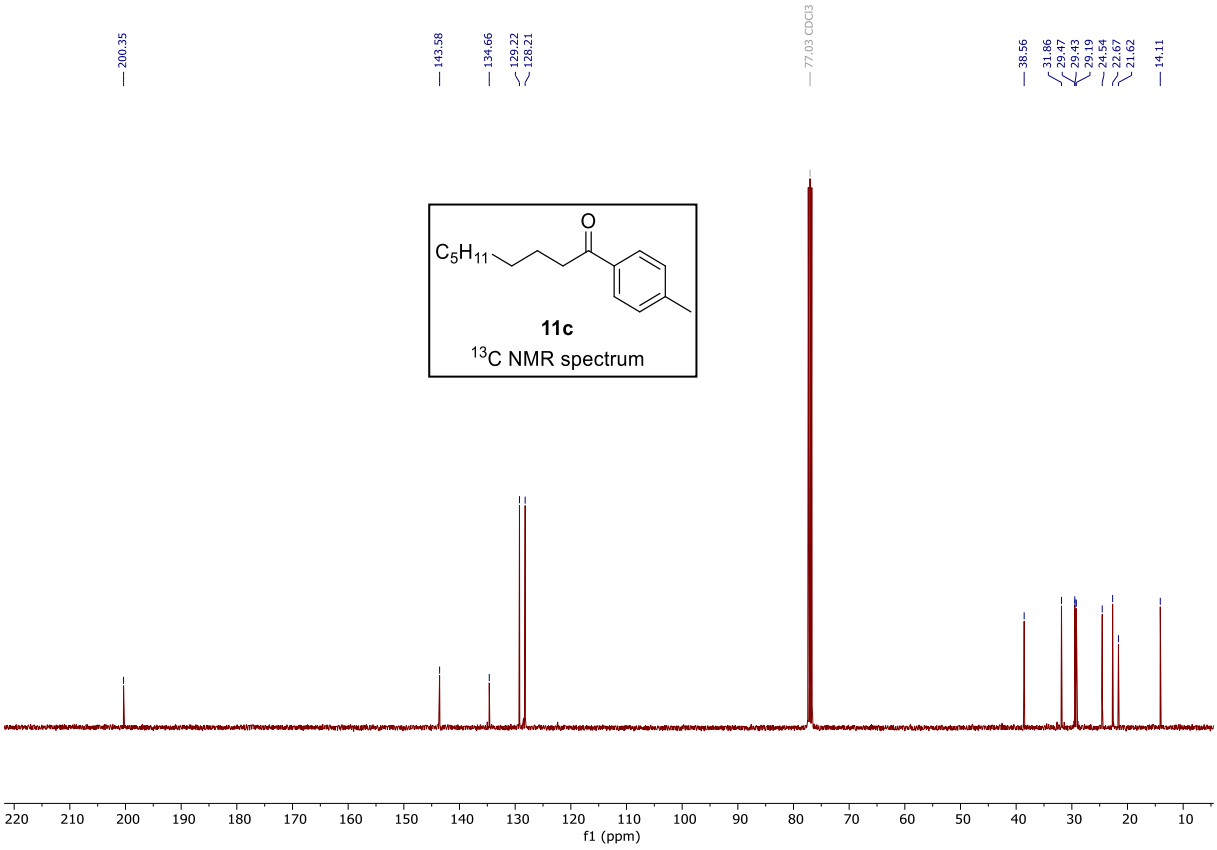


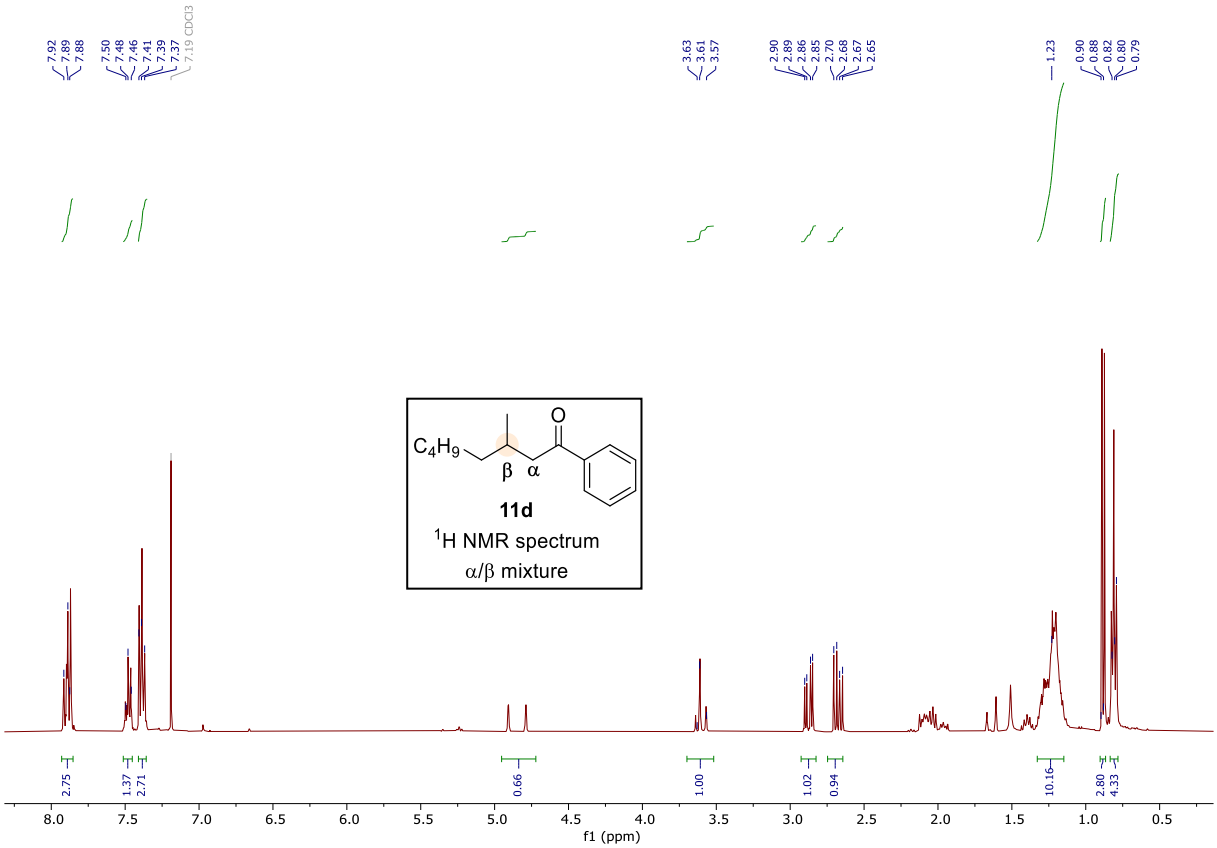


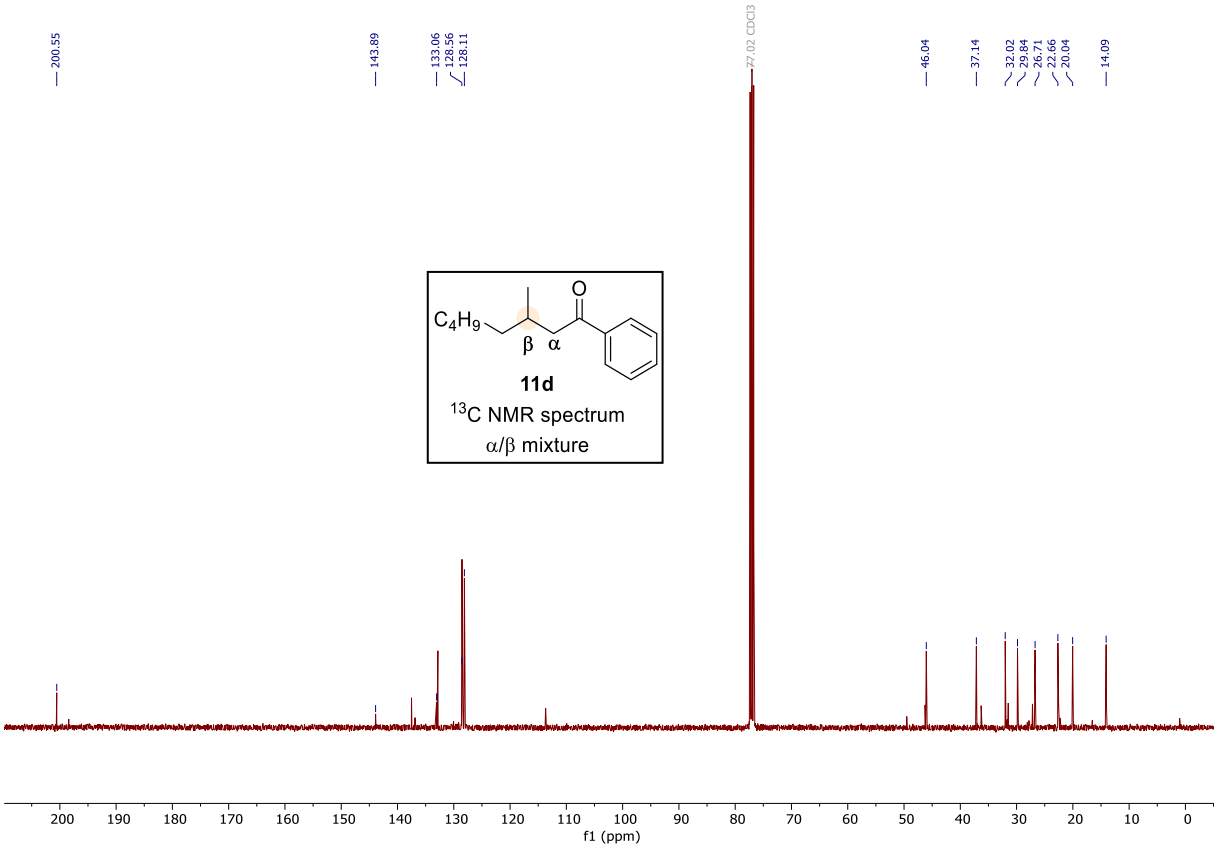

7.76
7.74
7.54
7.52
7.19 CDCl3
2.87
2.85
2.83
1.68
1.67
1.65
1.63
1.61
1.21
0.82
0.81
0.79
O
C5H11
Br
11b
1H NMR spectrum
2.09
2.03
2.13
2.00
10.01
3.12
f1 (ppm)

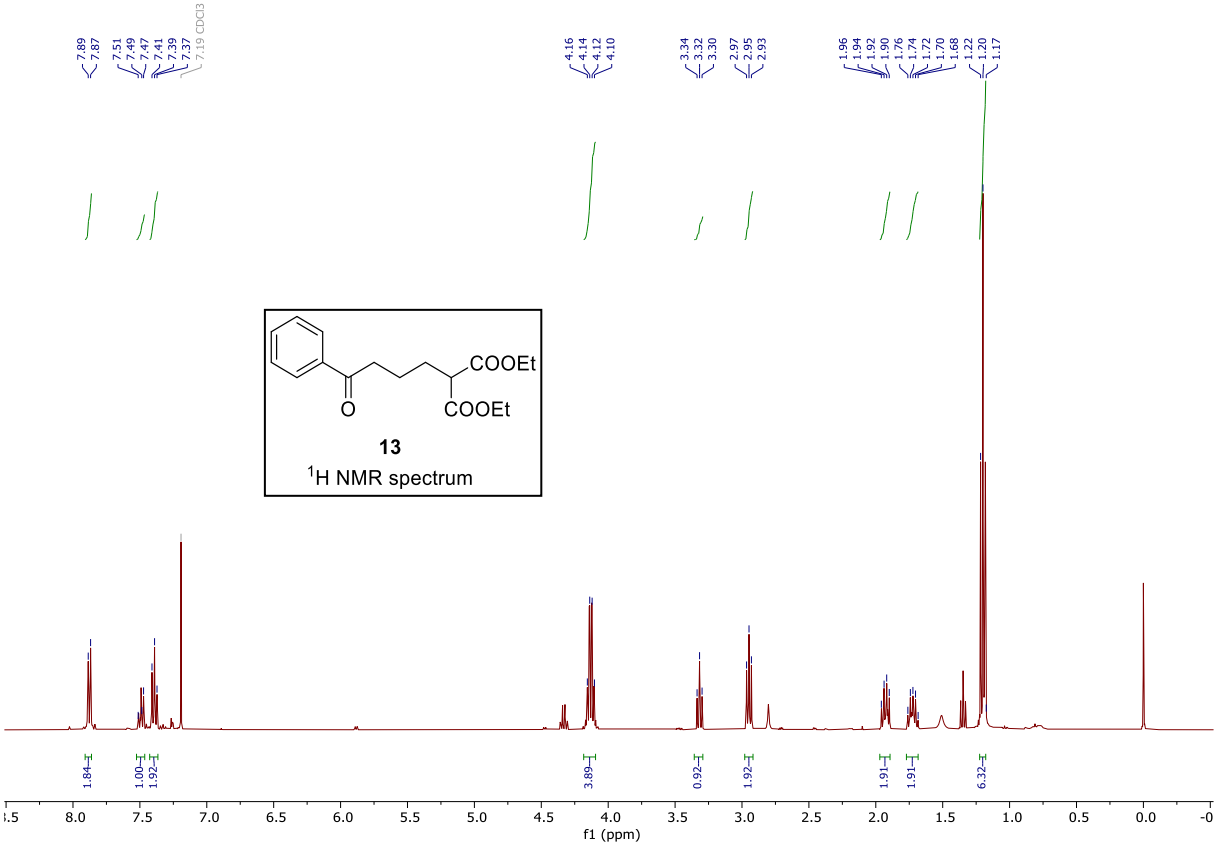

199.53
135.81
131.87
129.62
127.99
77.02 CDCl3
38.61
31.84
29.43
29.34
29.16
24.30
22.66
14.11
O
C5H11
Br
11b
13C NMR spectrum
f1 (ppm)

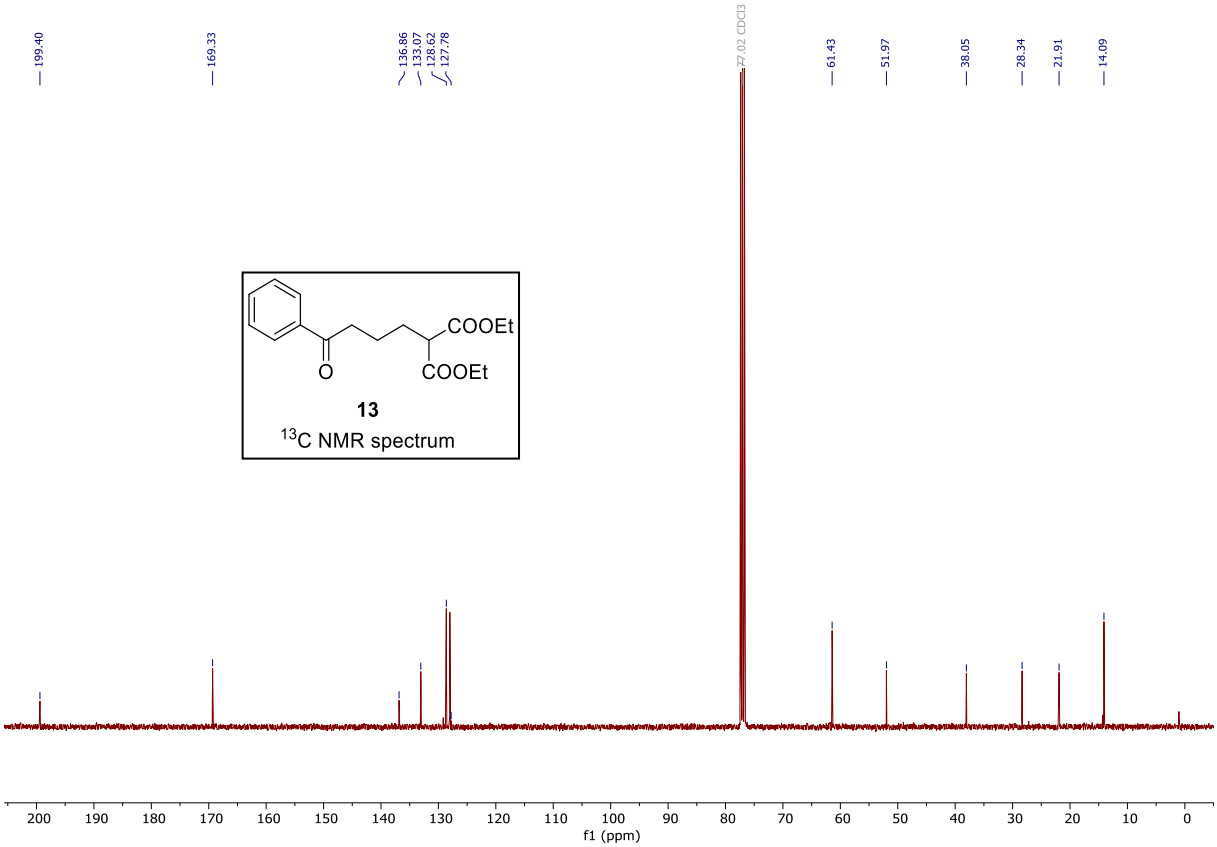

7.80
7.77
7.19 CDCl3
7.19
7.17
2.87
2.86
2.84
2.34
1.69
1.67
1.65
1.63
1.61
1.20
0.82
0.81
0.79
O
C5H11
11c
1H NMR spectrum
2.17
2.58
2.00
3.28
1.95
11.01
3.54
f1 (ppm)


200.35
143.58
134.66
129.22
128.21
77.03 CDCl3
38.56
31.86
29.47
29.43
24.19
23.54
21.67
21.62
14.11
O
C5H11
11c
13C NMR spectrum
f1 (ppm)


7.92
7.89
7.88
7.50
7.48
7.46
7.41
7.39
7.37
7.19 CDCl3
3.63
3.61
3.57
2.90
2.89
2.86
2.85
2.70
2.68
2.67
2.65
1.23
0.90
0.88
0.82
0.80
0.79
2.75
1.37
2.71
0.66
1.00
1.02
0.94
10.16
2.80
4.33
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
C4H9
β α
O
11d
1H NMR spectrum
α/β mixture


200.55
143.89
133.06
128.56
128.11
77.02 CDCl3
46.04
37.14
32.02
29.84
26.71
22.66
20.04
14.09
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
C4H9
β α
O
11d
13C NMR spectrum
α/β mixture


COOEt
O
COOEt
13
1H NMR spectrum
f1 (ppm)


COOEt
O
COOEt
13
13C NMR spectrum
f1 (ppm)

10. References

1 Y. Lou, P. Cao, T. Jia, Y. Zhang, M. Wang and J. Liao, *Angew. Chem. Int. Ed.* 2015, **54**, 12134–12138.

2 G. Goti, B. Bieszczad, A. Vega-Peñaloza and P. Melchiorre, *Angew. Chem. Int. Ed.*, 2019, **58**, 1213–1217.

3 L. Cardinale, M. O. Konev and A. Jacobi von Wangelin, *Chem.- A. Eur. J.* 2020, ***26***, 8239–8243.

4 L. Li, S. Guo, Q. Wang and J. Zhu, *Org. Lett.*, 2019, **21**, 5462–5466.

5 T. Uchikura, K. Moriyama, M. Toda, T. Mouri, I. Ibáñez and T. Akiyama, *Chem. Commun.*, 2019, **55**, 11171–11174.

6 P. Liu, M. Lei, L. Ma and L. Hu, *Synlett*, 2011, **8**, 1133–1136.

7 C. M. Wang, D. Song, P. J. Xia, J. Wang, H. Y. Xiang and H. Yang, *Chem. - An Asian J.*, 2018, **13**, 271–274.

8 G. Blay, I. Fernández, B. Monje, M. C. Muñoz, J. R. Pedro and C. Vila, *Tetrahedron*, 2006, **62**, 9174–9182.

9 G. Z. Wang, R. Shang, W. M. Cheng and Y. Fu, *Org. Lett.*, 2015, **17**, 4830–4833.

10 D. Ravelli, M. Zema, M. Mella, M. Fagnoni and A. Albini, *Org. Biomol. Chem.*, 2010, **8**, 4158–4164.

11 G. Zhang, L. Jiang, W. Shi, M. Zhou, F. Qiu, S. Sun, J. Wang and H. Guo, *Synth. Commun.*, 2017, **47**, 803–810.

12 J. F. Hooper, R. D. Young, A. S. Weller and M. C. Willis, *Chem. - A Eur. J.* 2013, **19**, 3125–3130.

13 D. R. Pye, L.-J. Cheng and N. P. Mankad, *Chem. Sci.*, 2017, **8**, 4750–4755.

14 K. Endo, D. Hamada, S. Yakeishi and T. Shibata, *Angew. Chem. Int. Ed.*, 2013, **52**, 606–610.