Electronic Supplementary Information

Direct photolysis of 4-*tert*-alkyl-1,4-dihydropyridines under blue-light irradiation for the generation of tertiary alkyl radicals

Prasadi C. Gallage[a] and Spencer P. Pitre[a]*

[a]Department of Chemistry, Oklahoma State University, 107 Physical Sciences, Stillwater, OK 74078, United States

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A. General Information

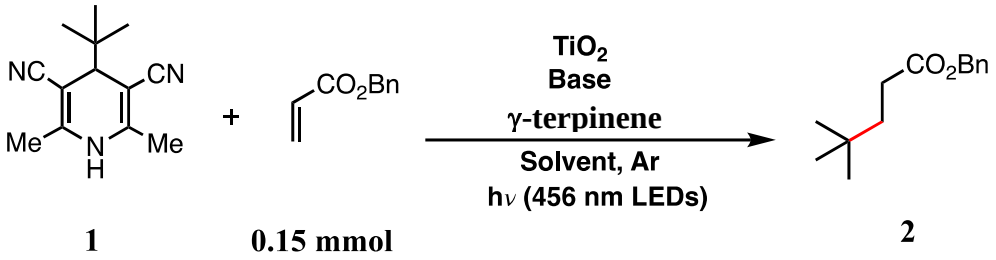
A1. Reagents

All reactions were conducted in oven-dried glassware under an inert atmosphere of argon, unless otherwise stated. All solvents and reagents were purchased from commercial suppliers (Fisher Scientific, TCI America, Sigma Aldrich, Oakwood Chemicals, Combi-Blocks Inc.) and were used as received unless otherwise noted. Irradiation of reaction vessels was performed using two Kessil PR160-456 nm LEDs at a distance of ~6 cm. A fan was employed to ensure the reaction mixtures remained at roughly 30 ^{o}C. Thin-layer chromatography (TLC) was conducted with silica gel 60 F254 pre-coated plates (0.25 μm thickness) and the analysis was performed using hexanes/EtOAc as the eluent and visualized by exposure to UV-light (254 nm) or potassium permanganate ($KMnO_4$) staining. Flash column chromatography was accomplished using a Biotage Isolera Four equipped with either Biotage SNAP, Biotage Sfär, or Sorbtech Purity flash column cartridges (60 Å porosity, 40-75 μm). Preparative thin layer chromatography was performed using Sorbtech silica gel prep TLC plates (w/UV254, glass backed, thickness: 1000 μm, dimensions: 20 x 20 cm).

A2. Analytical Methods

^{1}H NMR spectra were recorded on a 400 MHz spectrometer at 298 K and are reported relative to the signals for deuterated $CHCl_3$ (7.26 ppm). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant, *J*, (reported in *Hz*) and integration. ^{13}C NMR spectra were recorded at 101 or 101 MHz. All ^{13}C NMR spectra were reported in terms of chemical shift in ppm relative to residual $CHCl_3$ (77.2 ppm) and were obtained with ^{1}H decoupling. High-resolution mass spectra were obtained with a quadrupole-Orbitrap hybrid mass spectrometer at Oklahoma State University or a LCT spectrometer at UC Irvine. Absorption spectra were recorded on a Shimadzu UV-2600 UV-vis spectrometer. IR spectra were recorded on a Shimadzu IRAffinity-1S FT-IR spectrophotometer equipped with a QATR 10 single reflectance ATR accessory and are reported in terms of frequency of absorption (cm^{-1}).

B. Reaction Optimization



1 **0.15 mmol** **2**

Table S1. Optimization of reaction conditions.

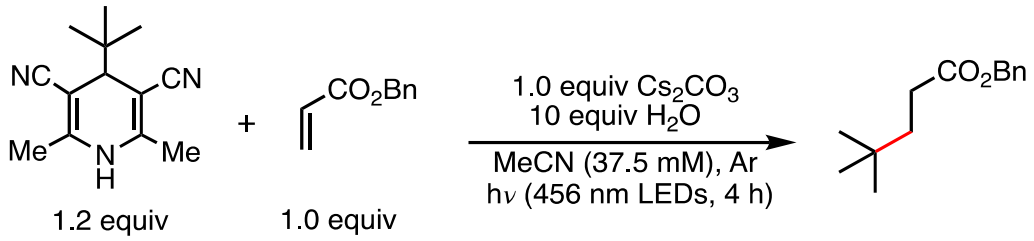
Entry	1/ (equiv)	TiO_2/ (mg/mL)	Base/ (equiv)	γ-terpinene / (equiv)	Solvent/ (mL)	Time	Yield of 2%[a]
1	1.5	0.5	Cs_2CO_3 (1.5)	1.0	MeCN (1.5)	24 h	40
2	1.5	1.0	Cs_2CO_3 (1.5)	1.0	MeCN (1.5)	24 h	41
3	1.5	2.0	Cs_2CO_3 (1.5)	1.0	MeCN (1.5)	24 h	41
4	**1.5**	**3.0**	**Cs_2CO_3 (1.5)**	**1.0**	**MeCN (1.5)**	**24 h**	**48**
5	1.5	4.0	Cs_2CO_3 (1.5)	1.0	MeCN (1.5)	24 h	39
6	1.5	5.0	Cs_2CO_3 (1.5)	1.0	MeCN (1.5)	24 h	42
7	1.5	3.0	Cs_2CO_3 (1.5)	1.0	DMA (1.5)	24 h	38
8	1.5	3.0	Cs_2CO_3 (1.5)	1.0	DMSO (1.5)	24 h	<10
9	1.5	3.0	Cs_2CO_3 (1.5)	1.0	Dioxane (1.5)	24 h	<10
10	1.5	3.0	Cs_2CO_3 (1.5)	1.0	DMF (1.5)	24 h	30
11	1.5	3.0	Cs_2CO_3 (1.5)	1.0	$CHCl_3$ (1.5)	24 h	<10
12	1.5	3.0	Cs_2CO_3 (1.5)	1.0	DCM (1.5)	24 h	<10
13	1.5	3.0	Cs_2CO_3 (1.5)	1.0	EtOH (1.5)	24 h	<10
14	1.5	3.0	Cs_2CO_3 (1.5)	1.0	THF (1.5)	24 h	30
15	1.5	3.0	Cs_2CO_3 (1.5)	1.0	$MeNO_2$ (1.5)	24 h	<10
16	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (0.5)	24 h	25
17	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (0.75)	24 h	33
18	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (1.0)	24 h	38

Entry	1/ (equiv)	TiO_2/ (mg/mL)	Base/ (equiv)	γ-terpinene / (equiv)	Solvent/ (mL)	Time	Yield of 2%[a]
19	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (1.75)	24 h	48
20	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (2.0)	24 h	42
21	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (3.0)	24 h	47
22	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (4.0)	24 h	58
23	**1.5**	**3.0**	**Cs_2CO_3 (1.5)**	**1.0**	**MeCN (5.0)**	24 h	**62**
24	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (6.0)	24 h	25
25	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (7.0)	24 h	34
26	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (8.0)	24 h	31
27	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (9.0)	24 h	26
28	1.5	3.0	Cs_2CO_3 (1.5)	1.0	MeCN (10.0)	24 h	30
29	**1.5**	**3.0**	Cs_2CO_3 (1.5)	**-**	**MeCN (5.0)**	24 h	**63**
30	1.5	3.0	Cs_2CO_3 (1.5)	2.0	MeCN (5.0)	24 h	62
31	1.5	3.0	-	-	MeCN (5.0)	24 h	11
32	1.5	3.0	-	1.0	MeCN (5.0)	24 h	<10
33	1.5	3.0	-	2.0	MeCN (5.0)	24 h	13
34	1.5	3.0	-	3.0	MeCN (5.0)	24 h	10
35	**1.5**	**-**	**Cs_2CO_3 (1.5)**	**-**	**MeCN (5.0)**	24 h	**62**
36	1.5	-	$NaHCO_3$ (1.5)	-	MeCN (5.0)	24 h	<10
37	1.5	-	K_2CO_3 (1.5)	-	MeCN (5.0)	24 h	30
38	1.5	-	K_3PO_4 (1.5)	-	MeCN (5.0)	24 h	50
39	1.5	-	K_2HPO_4 (1.5)	-	MeCN (5.0)	24 h	<10
40	1.5	-	CH_3COOK (1.5)	-	MeCN (5.0)	24 h	<10
41	1.5	-	$KHCO_3$ (1.5)	-	MeCN (5.0)	24 h	<10
42	1.5	-	$CsHCO_3$ (1.5)	-	MeCN (5.0)	24 h	<10
43	1.5	-	CH_3COONa (1.5)	-	MeCN (5.0)	24 h	<10
44	1.5	-	Li_2CO_3 (1.5)	-	MeCN (5.0)	24 h	<10

Entry	1/ (equiv)	TiO_2/ (mg/mL)	Base/ (equiv)	γ-terpinene / (equiv)	Solvent/ (mL)	Time	Yield of 2%[a]
45	1.0	-	Cs_2CO_3 (1.5)	-	MeCN (5.0)	24 h	50
46	1.1	-	Cs_2CO_3 (1.5)	-	MeCN (5.0)	24 h	54
47	**1.2**	**-**	**Cs_2CO_3 (1.5)**	**-**	**MeCN (5.0)**	24 h	**63**
48	2.0	-	Cs_2CO_3 (1.5)	-	MeCN (5.0)	24 h	48
49	2.2	-	Cs_2CO_3 (1.5)	-	MeCN (5.0)	24 h	60
50	2.5	-	Cs_2CO_3 (1.5)	-	MeCN (5.0)	24 h	54
51	3.0	-	Cs_2CO_3 (1.5)	-	MeCN (5.0)	24 h	42
52	1.2	-	Cs_2CO_3 (0.3)	-	MeCN (5.0)	24 h	26
53	**1.2**	**-**	**Cs_2CO_3 (1.0)**	**-**	**MeCN (5.0)**	24 h	**64**
54	1.2	-	Cs_2CO_3 (1.5)	-	MeCN (5.0)	24 h	63
55	1.2	-	Cs_2CO_3 (2.0)	-	MeCN (5.0)	24 h	62
56	1.2	-	Cs_2CO_3 (3.0)	-	MeCN (5.0)	24 h	63
57	1.2	-	Cs_2CO_3 (5.0)	-	MeCN (5.0)	24 h	63
58	1.2	-	Cs_2CO_3 (1.0)	-	MeCN (5.0)	1 h	52
59	1.2	-	Cs_2CO_3 (1.0)	-	MeCN (5.0)	2 h	58
60	1.2	-	Cs_2CO_3 (1.0)	-	MeCN (5.0)	3 h	62
61	**1.2**	**-**	**Cs_2CO_3 (1.0)**	**-**	**MeCN (5.0)**	**4 h**	**64**
62	1.2	-	Cs_2CO_3 (1.0)	-	MeCN (5.0)	5 h	63
63	1.2	-	Cs_2CO_3 (1.0)	-	MeCN (1.5)	4 h	51
64	1.2	-	Cs_2CO_3 (1.0)	-	MeCN (3.0)	4 h	56
65	**1.2**	**-**	**Cs_2CO_3 (1.0)**	**-**	**MeCN (4.0)**	**4 h**	**65**
66	1.2	-	Cs_2CO_3 (1.0)	-	MeCN (6.0)	4 h	63
67	**1.2**	**-**	**Cs_2CO_3 (1.0)**	**-**	**MeCN (4.0)**	**4 h**	**73[b,c]**

[a] Yields determined by ^1H NMR using methyl 4-clorobenzoate as an external standard. All reactions were irradiated using two PR160-456 nm LEDs, and the reaction temperatures were maintained at ~ 30 °C. Up to 6 reactions were performed in parallel at any given time in our photochemical setup. [b] H_2O (10 equiv) was added. [c] Average of 3 trials.

Table S2. Variations from standard conditions.



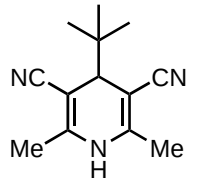
1 **2**

Entry	Variation from the standard conditions	Yield of **2** (%) [a]
1	none	73
2	without H_2O	52
3	50 equiv. H_2O	60
4	without light (T = 25°C)	N.R
5	without Cs_2CO_3	N.R
6	without Ar	51
7	γ-terpinene instead of H_2O	56

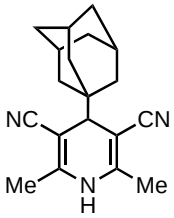
Standard Conditions: 4-*tert*-Butyl-1,4-DHP (0.18 mmol), benzyl acrylate (0.15 mmol), Cs_2CO_3(0.15 mmol), H_2O (1.5 mmol) and MeCN (4.0 mL) were irradiated under Ar with 2 X Kessil PR160-456 nm LEDs lamps for 4 hrs. [a]Yields were determined by ^1H NMR using methyl 4-chlorobenzoate as an external standard. N.R = No Reaction.

C. Experimental Procedures

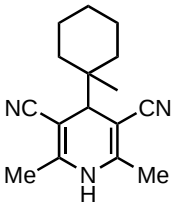
C1. General Procedure for Synthesis of 4 -Alkyl-1,4-Dihydropyridines (DHPs)



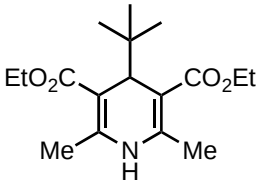
1



S1



S2



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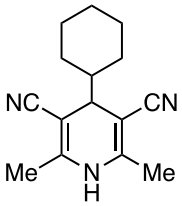
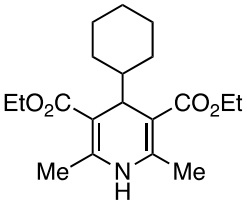
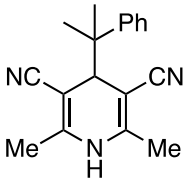


S3



S4



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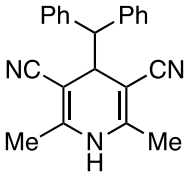

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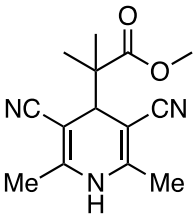
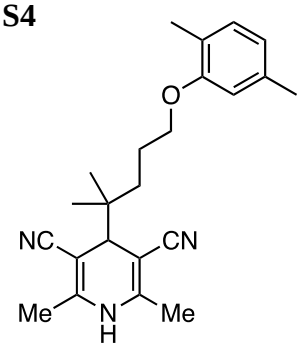
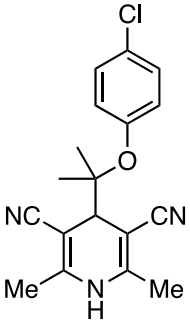


S7



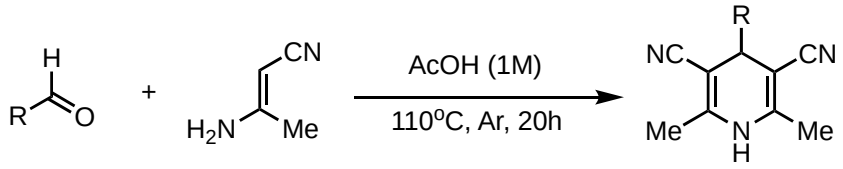
S8



S9

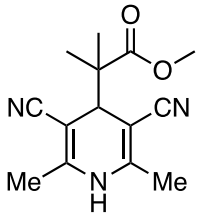
Scheme S1. 4-Alkyl-1,4-DHPs used in this study.

Procedure A:

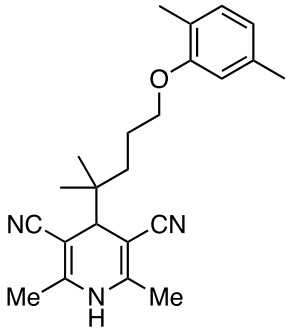


1 equiv 2 equiv

In an oven-dried round bottom flask with a PTFE-coated stir bar, the required aldehyde (1.0 equiv.), 3-aminocrotononitrile (2.0 equiv.) and glacial acetic acid (1.0 M) were charged under argon, and then the mixture was heated at 110 °C for 20 hours. The reaction was allowed to cool to room temperature, diluted with distilled water and extracted three times with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography (Hex → 30% EtOAc). The spectral data for **1**, **S1**, **S2**, **S3, S5** and **S6** agreed with those previously reported.[1,2]



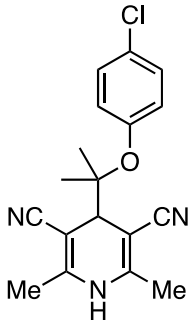
Methyl 2-(3,5-dicyano-2,6-dimethyl-1,4-dihydropyridin-4-yl)-2-methylpropanoate (S7).
Following Procedure A using methyl 2,2-dimethyl-3-oxopropanoate (1.2 g, 9 mmol, 1.0 equiv.), **S7** was isolated as a white solid in 22% yield (514 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 1H), 3.76 (s, 3H), 3.67 (s, 1H), 2.19 (s, 6H), 1.20 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.1, 149.3, 119.6, 81.2, 52.9, 51.0, 44.0, 21.4, 19.3. **Rf:** 0.44 (2:3 Hex:EtOAc). **HRMS:** calculated **m/z** for $[M+H]^+$: 260.1399, measured **m/z** for $[M+H]^+$: 260.1396. **IR (neat, cm^{-1}):** 3316, 3246, 3118, 2978, 2199, 1712, 1653, 1501, 1452, 1388, 1286, 1263, 1194, 1136, 1019, 990, 863, 773, 700.



4-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile (S8).

Following Procedure A using 5-(2,5-dimethylphenoxy)-2,2-dimethyl pentanal (718 mg, 3 mmol, 1.0 equiv.), **S8** was isolated as as a pale-yellow solid in 46% yield (332 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.5 Hz, 1H), 6.66 – 6.62 (m, 2H), 5.95 (s, 1H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.07 (s, 1H), 2.30 (s, 3H), 2.19 (s, 6H), 2.17 (s, 3H), 1.87 – 1.75 (m, 2H), 1.51 – 1.46 (m, 2H), 0.97 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.5, 148.2, 136.7, 130.4, 123.6, 120.7, 120.3, 112.2, 82.1, 68.4, 45.1, 43.2, 34.3, 24.1, 23.8, 21.5, 19.0, 16.0. **R_f:** 0.39 (1:1 Hex:EtOAc). **HRMS:** calculated **m/z** for $[M+H]^+$: 364.2389, measured **m/z** for $[M+H]^+$: 364.2388. **IR (neat, cm^{-1}):** 3294, 3235, 3116, 2961, 2873, 2197, 1652, 1506, 1387, 1285, 1265, 1157, 1129, 1021, 803, 730.



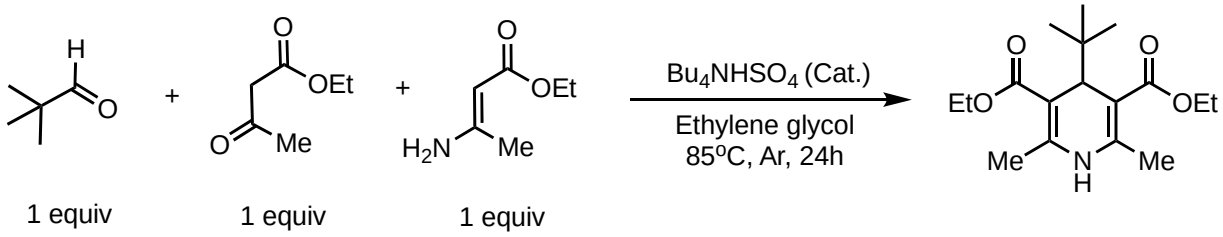
4-(2-(4-Chlorophenoxy)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile (S9).

Following Procedure A using 2-(4-Chlorophenoxy)-2-methylpropanal (1.3 g, 7 mmol, 1.0 equiv), **S9** was isolated as a white solid in 52% yield (1.2 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 2H), 6.96 – 6.88 (m, 2H), 6.23 (s, 1H), 3.45 (s, 1H), 2.23 (s, 6H), 1.27 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.2, 148.5, 129.2, 129.0, 125.1, 120.0, 86.1, 81.8, 47.1, 22.9, 19.0. **R_f:** 0.31 (1:1 Hex:EtOAc). **HRMS:** calculated **m/z** for $[M+H]^+$:

328.1216, measured **m/z** for $[M+H]^+$: 328.1218. **IR (neat, cm^{-1}):** 3290, 3224, 3114, 3008, 2973, 2204, 1653, 1506, 1486, 1383, 1287, 1226, 1129, 1090, 1027, 907, 829, 737.

Procedure B:



1 equiv 1 equiv 1 equiv

A solution of ethyl-3-aminocrotonate (3.6 mL, 29 mmol, 1.0 equiv) in ethylene glycol (11.6 mL, 2.5 M) was added to an oven dried round bottom flask equipped with a magnetic stir bar under argon. Next, ethyl acetoacetate (3.6 mL, 29 mmol, 1.0 equiv) was added followed by pivaldehyde (3.1 mL, 29 mmol, 1.0 equiv.) and tetrabutylammonium hydrogen sulfate (1.18 g, 3.5 mmol, 12 mol%). The reaction mixture was then heated to 85 °C and stirred for 20 hours. The mixture was allowed to cool to room temperature and then diluted with ethyl acetate and distilled water. The aqueous layer was extracted with ethyl acetate and the organic layer was washed with brine. The organic layers were combined, dried over $MgSO_4$, and concentrated. The crude material was purified by flash column chromatography to furnish the desired Hantzsch ester as a light-yellow solid (600 mg, 1.95 mmol, 7%). The spectral data for **23** and **S4** agreed with those previously reported.[3]

C2. General Procedure for the Giese Reaction of 4-*tert*-alkyl-DHPs.

An oven-dried Pyrex tube (10 mL) equipped with a magnetic stir bar was charged with a 4-*tert*-alkyl-1,4-DHP (0.18 mmol, 1.2 equiv), Michael acceptor (0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 µL, 1.5 mmol, 10 equiv). Dry MeCN (dried over 3 Å molecular sieves) was added (4 mL, 37.5 mM), and the reaction mixture was degassed by sparging with argon for 5-6 minutes. The reaction mixture was then sonicated and irradiated with two Kessil PR160-456 nm LEDs for 4 h at 30 °C. The reaction mixture was transferred into a separatory funnel and diluted with 15 mL of anhydrous ethyl ether and washed with 15 mL of 1 M HCl, then 15 mL of brine. The aqueous phase was extracted with 15 mL of anhydrous ethyl ether. The combined organic phases were dried over $MgSO_4$, and the filtrate was concentrated *in vacuo*. The purified product was obtained by flash column chromatography using a Biotage Isolera Four. Yields were reported as isolated yield of the purified products averaged over two trials.

D. Picture of the Photochemical Reaction Set-Up

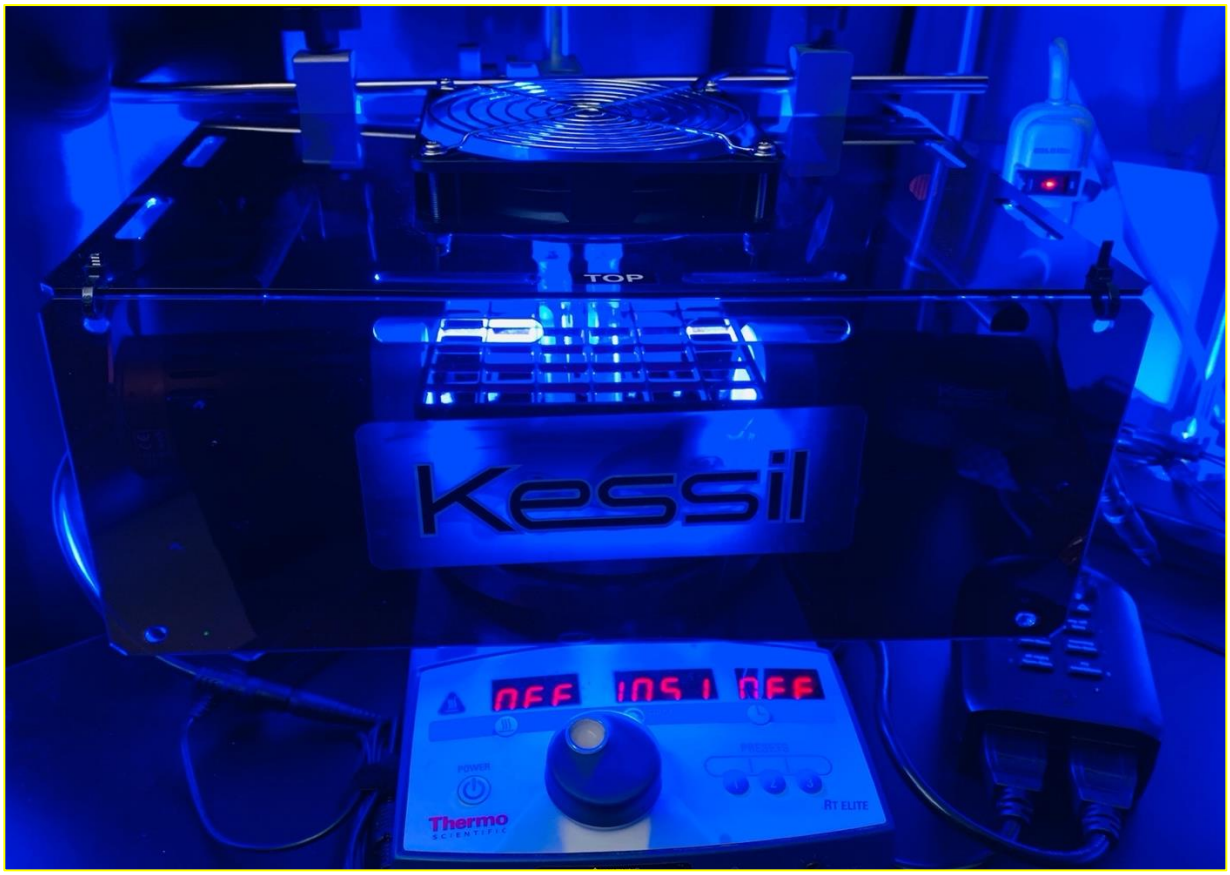
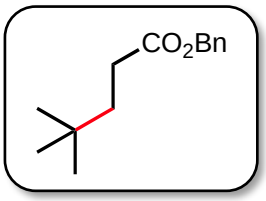


Figure S1. Picture of the photochemistry set-up employed in this work.

E. Characterization of Products

Benzyl 4,4-dimethylpentanoate (2)

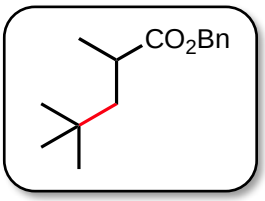


Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), benzyl acrylate (23 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 71% yield (23 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 5.11 (s, 2H), 2.37 – 2.30 (m, 2H), 1.60 – 1.56 (m, 2H), 0.89 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 136.2, 128.7, 128.4, 128.3, 66.3, 38.7, 30.3, 30.2, 29.2. **R_f:** 0.74 (4:1 Hex:EtOAc).

Reference: *J. Org. Chem.* 2018, **83**, 253-259.

Benzyl 2,4,4-trimethylpentanoate (3)

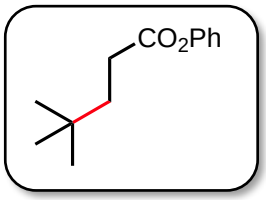


Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), benzyl methacrylate (25 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 86% yield (30 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 5.10 (s, 2H), 2.62 – 2.50 (m, 1H), 1.88 (dd, *J*=14.1, 9.1 Hz, 1H), 1.22 – 1.16 (m, 4H), 0.86 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.9, 136.3, 128.7, 128.3, 128.3, 66.3, 47.9, 36.4, 30.9, 29.5, 20.5. **R_f:** 0.70 (4:1 Hex:EtOAc).

Reference: *J. Org. Chem.* 2018, **83**, 253-259.

Phenyl 4,4-dimethylpentanoate (4)

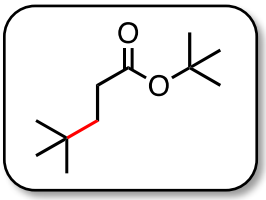


Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), phenyl acrylate (20 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 68% yield (21 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.25 – 7.20 (m, 1H), 7.08 (d, *J* = 6.3 Hz, 2H), 2.57 – 2.50 (m, 2H), 1.73 – 1.65 (m, 2H), 0.96 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 150.9, 129.5, 125.9, 121.7, 38.7, 30.4, 30.3, 29.2. **R_f:** 0.72 (4:1 Hex:EtOAc).

Reference: *Org. Lett.* 2021, **23**, 6046-6051.

***tert*-Butyl 4,4-dimethylpentanoate (5)**



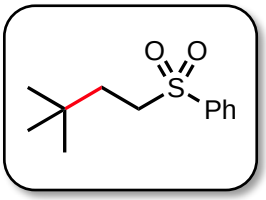
Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), *tert*-butylacrylate (22 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 64% yield (22 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 – 2.15 (m, 2H), 1.53 – 1.47 (m, 2H), 1.44 (s, 9H), 0.88 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 80.1, 38.8, 31.5, 29.9, 29.2, 28.3.

R_f: 0.90 (4:1 Hex:EtOAc)

Reference: *J. Am. Chem. Soc.* 2008, **130**, 11546-11560.

((3,3-dimethylbutyl)sulfonyl)benzene (6)

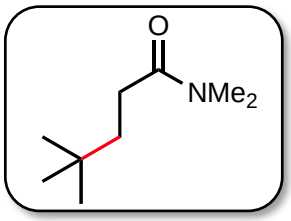


Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), phenyl vinyl sulfone (25 mg, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a white solid in 73% yield (25 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.70 – 7.61 (m, 1H), 7.62 – 7.53 (m, 2H), 3.09 – 3.02 (m, 2H), 1.63 – 1.55 (m, 2H), 0.86 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.3, 133.8, 129.4, 128.2, 53.1, 35.7, 30.2, 29.0. **R_f:** 0.45 (4:1 Hex:EtOAc).

Reference: *Chem. Eur. J.* 2020, **26**, 3226-3230.

***N, N*,4,4-tetramethylpentanamide (7)**

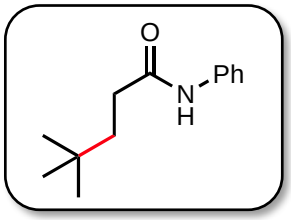


Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), *N*,*N*-dimethylacrylamide (17 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 66% yield (16 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.01 (s, 3H), 2.94 (s, 3H), 2.32 – 2.23 (m, 2H), 1.58 – 1.50 (m, 2H), 0.91 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 39.1, 37.5, 35.6, 30.3, 29.3, 29.2. **R_f:** 0.54 (1:1 Hex:EtOAc)**.**

Reference: *Org. Lett.* 2018, **20**, 2208-2212.

4,4-Dimethyl-*N*-phenylpentanamide (8)

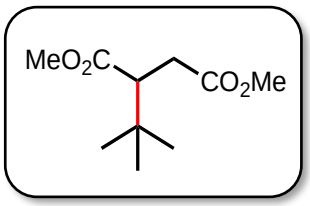


Prepared according to the general procedure described above using **1** (38.75 mg, 0.18 mmol, 1.2 equiv), *N*-phenylacrylamide (22 mg, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a white solid in 61% yield (18 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.14 (brs, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.37 – 2.29 (m, 2H), 1.69 – 1.62 (m, 2H), 0.94 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 138.1, 129.2, 124.3, 119.9, 39.4, 33.7, 30.3, 29.3. **R_f:** 0.61 (1:1 Hex:EtOAc).

Reference: *Org. Lett.* 2016, **18**, 6400-6403.

Dimethyl 2-(*tert*-butyl) succinate (9)

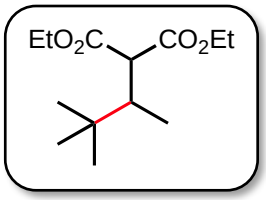


Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), dimethyl fumarate (22 mg, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a white solid in 72% yield (22 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.66 (s, 3H), 2.83 – 2.75 (m, 1H), 2.64 (dd, *J* = 11.8, 2.9 Hz, 1H), 2.48 (dd, *J* = 16.5, 2.9 Hz, 1H), 0.96 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 173.3, 51.9, 51.5, 51.3, 32.8, 27.9. **R_f:** 0.49 (4:1 Hex:EtOAc).

Reference: *J. Am. Chem. Soc.* 2020, **142**, 9938-9943.

Diethyl 2-(3,3-dimethylbutan-2-yl) malonate (10)

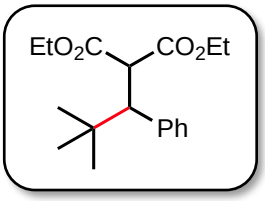


Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), diethyl ethylidenemalonate (28 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27.0 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 35% yield (13 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 – 4.12 (m, 4H), 3.51 (d, *J* = 5.4 Hz, 1H), 2.29 – 2.19 (m, 1H), 1.29 – 1.23 (m, 6H), 1.01 (d, *J* = 7.2 Hz, 3H), 0.90 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 169.7, 61.5, 61.1, 53.5, 42.8, 33.8, 27.7, 14.2, 14.2, 12.2. **R_f:** 0.68 (4:1 Hex:EtOAc).

Reference: *Angew. Chem. Int. Ed.* 2018, **57**, 6667-6671.

Diethyl 2-(2,2-dimethyl-1-phenylpropyl) malonate (11)



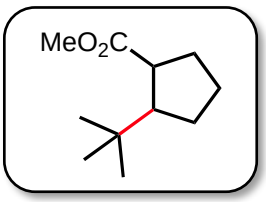
Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), diethyl benzylidenemalonate (34 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified

by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 53% yield (22 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.11 (m, 5H), 4.29 – 4.12 (m, 2H), 3.97 (d, *J* = 10.9 Hz, 1H), 3.75 – 3.66 (m, 2H), 3.47 (d, *J* = 10.9 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.79 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 168.3, 140.3, 127.5, 126.6, 61.9, 61.3, 55.3, 55.1, 34.6, 28.4, 14.1, 13.6. **R_f:** 0.61 (4:1 Hex:EtOAc).

Reference: *Angew. Chem. Int. Ed.* 2018, **57**, 6667-6671.

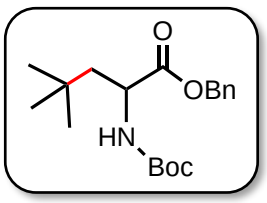
Methyl 2-(*tert*-butyl) cyclopentane-1-carboxylate (12)



Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), methyl cyclopentane-1-carboxylate (19 µL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 µL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 56% yield as a 7:1 mixture of diastereomers (15 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H, major *diast.*), 3.62 (s, 3H, minor *diast.*), 2.59 – 2.49 (m, 1H), 2.19 (q, *J* = 8.5 Hz, 1H), 1.89 – 1.58 (m, 5H), 1.45 – 1.31 (m, 1H), 0.91 (s, 9H, minor *diast.*), 0.85 (s, 9H, major *diast.*). **^{13}C NMR** (101 MHz, $CDCl_3$, major *diast.*) δ 178.7, 54.2, 51.7, 45.4, 32.9, 30.3, 28.6, 27.7, 26.3. **R_f:** 0.83 (4:1 Hex:EtOAc). **HRMS:** calculated **m/z** for $[M+H]^+$: 185.1542, measured **m/z** for $[M+H]^+$: 185.1543. **IR (neat, cm^{-1}):** 2988, 2929, 2865, 1729, 1436, 1265, 1167, 1152, 1069, 896, 737, 705.

Benzyl 2-((*tert*-butoxycarbonyl)amino)-4,4-dimethylpentanoate (13)

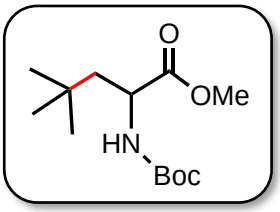


Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), Boc-Gly-OBzl (42 mg, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 µL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 51% yield (26 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 5H), 5.15 (dd, *J* = 6.2 Hz, 2H), 4.81 (d, *J* = 9.1 Hz, 1H), 4.49 – 4.21 (m, 1H), 1.73 (dd, *J* = 14.4, 3.5 Hz, 2H), 1.43 (s, 9H), 0.96 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 155.3, 135.7, 128.7, 128.4, 128.2, 80.0, 67.0, 51.6, 46.4, 30.8, 29.7, 28.5. **R_f:** 0.70 (7:3 Hex:EtOAc).

Reference: *J. Org. Chem.* 1995, **60**, 8262-8266.

Methyl 2-((*tert*-butoxycarbonyl) amino)-4,4-dimethylpentanoate (14)

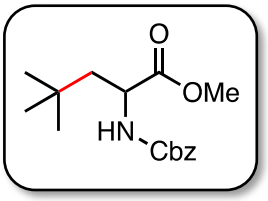


Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), Boc-Gly-OMe (30 mg, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 46% yield (18 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (d, *J* = 8.5 Hz, 1H), 4.33 (td, *J* = 9.1, 4.8 Hz, 1H), 3.72 (s, 3H), 1.71 (dd, *J* = 14.3, 3.7 Hz, 1H), 1.44 (s, 9H), 0.97 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 155.3, 80.0, 52.4, 51.4, 46.5, 30.8, 29.7, 28.5. **R_f:** 0.66 (3:2 Hex:EtOAc).

Reference: *J. Org. Chem.* 2019, **84**, 4558-4565.

Methyl 2-(((benzyloxy)carbonyl)amino)-4,4-dimethylpentanoate (15)

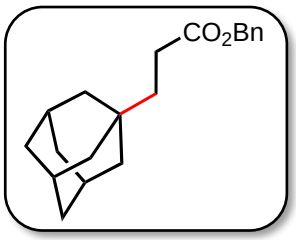


Prepared according to the general procedure described above using **1** (39 mg, 0.18 mmol, 1.2 equiv), Bzl-Gly-OMe (35 mg, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 67% yield (30 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 5.11 (s, 2H), 5.06 (d, *J* = 12.7 Hz, 1H, NH), 4.42 (td, *J* = 9.0, 3.7 Hz, 1H), 3.72 (s, 3H), 1.76 (dd, *J* = 14.4, 3.7 Hz, 1H), 1.48 – 1.41 (m, 1H), 0.96 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 155.8, 136.4, 128.7, 128.3, 128.2, 67.1, 52.5, 51.9, 46.4, 30.8, 29.7. **R_f:** 0.67 (4:1 Hex:EtOAc) **HRMS:** calculated **m/z** for $[M+H]^+$: 294.1705,

measured **m/z** for $[M+H]^+$: 294.1697. **IR (neat, cm^{-1}):** 2954, 2917, 2849,1715, 1533, 1456, 1436, 1369, 1274, 1245, 1206, 1178, 1051, 909, 733.

Benzyl 3-((1*R*,3*s*)-adamantan-1-yl) propanoate (16)

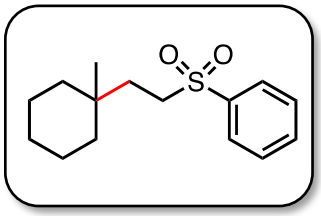


Prepared according to the general procedure described above using **S1** (53 mg, 0.18 mmol, 1.2 equiv), benzyl acrylate (23 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 60% yield (27 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 5.11 (s, 2H), 2.35 – 2.28 (m, 2H), 1.97 – 1.91 (m, 3H), 1.73 – 1.66 (m, 3H), 1.65 – 1.56 (m, 3H), 1.50 – 1.40 (m, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 136.3, 128.7, 128.4, 128.3, 66.3, 42.2, 39.0, 37.2, 32.1, 28.7, 28.3. **R_f:** 0.86 (1:1 Hex:EtOAc).

Reference: *J. Am. Chem. Soc*. 2020, **142**, 20143-20151.

((2-(1-methylcyclohexyl)ethyl)sulfonyl)benzene (17)

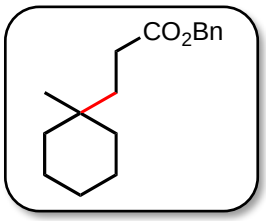


Prepared according to the general procedure described above using **S2** (46 mg, 0.18 mmol, 1.2 equiv), phenyl vinyl sulfone (25 mg, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 20% EtOAc in hexane) to afford the title compound as a colorless oil in 52% yield (20 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.69 – 7.63 (m, 1H), 7.62 – 7.53 (m, 2H), 3.08 – 3.00 (m, 2H), 1.65 – 1.60 (m, 2H), 1.43 – 1.35 (m, 5H), 1.26 – 1.14 (m, 5H), 0.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.4, 133.7, 129.4, 128.2, 52.1, 37.5, 33.7, 32.5, 26.3, 24.8, 21.9. **R_f:** 0.56 (4:1 Hex:EtOAc).

Reference: *J. Am. Chem. Soc*. 2020, **142**, 20143-20151.

Benzyl 3-(1-methylcyclohexyl) propanoate (18)

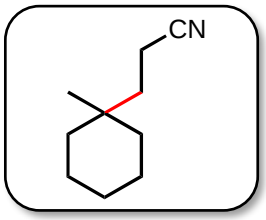


Prepared according to the general procedure described above using **S2** (46 mg, 0.18 mmol, 1.2 equiv), benzyl acrylate (23 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 69% yield (27 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 5.11 (s, 2H), 2.35 – 2.28 (m, 2H), 1.63 – 1.56 (m, 2H), 1.49 – 1.37 (m, 5H), 1.33 – 1.19 (m, 5H), 0.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 136.3, 128.7, 128.4, 128.3, 66.3, 37.6, 36.8, 32.5, 29.1, 26.6, 24.6, 22.1. **R_f:** 0.91 (1:1 Hex:EtOAc)

Reference: *J. Am. Chem. Soc*. 2020, **142**, 20143-20151.

3-(1-Methylcyclohexyl) propanenitrile (19)

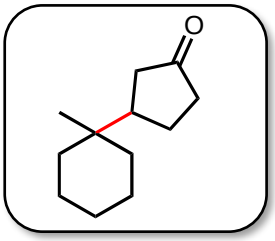


Prepared according to the general procedure described above using **S2** (46 mg, 0.18 mmol, 1.2 equiv), benzyl acrylate (23 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27.0 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 80% yield (18 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 – 2.22 (m, 2H), 1.69 – 1.60 (m, 2H), 1.51 – 1.40 (m, 5H), 1.28 – 1.23 (m, 5H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 120.9, 37.6, 37.3, 32.7, 26.3, 24.2, 21.9, 11.9. **R_f:** 0.55 (4:1 Hex:EtOAc).

Reference: *J. Am. Chem. Soc*. 2020, **142**, 20143-20151.

3-(1-Methylcyclohexyl)cyclopentan-1-one (20)

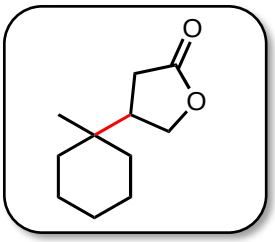


Prepared according to the general procedure described above using **S2** (46 mg, 0.18 mmol, 1.2 equiv), 2-cyclopentenone (13 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 49% yield (13 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 – 2.27 (m, 1H), 2.24 – 2.04 (m, 3H), 2.02 – 1.90 (m, 2H), 1.66 – 1.58 (m, 1H), 1.58 – 1.38 (m, 5H), 1.37 – 1.32 (m, 1H), 1.30 – 1.23 (m, 4H), 0.87 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.2, 39.7, 39.4, 36.6, 36.0, 34.2, 26.5, 23.3, 21.9, 21.9. **R_f:** 0.81 (4:1 Hex:EtOAc).

Reference: *J. Am. Chem. Soc.* 2013, **135**, 15342-15345.

4-(1-Methylcyclohexyl)dihydrofuran-2(3*H*)-one (21)

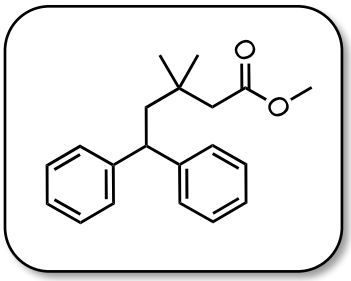


Prepared according to the general procedure described above using **S2** (45.9 mg, 0.18 mmol, 1.2 equiv), 2(5H)-furanone (13 mg 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 42% yield (12 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (t, *J* = 8.1 Hz, 1H), 4.13 (t, *J* = 8.8 Hz, 1H), 2.54 (p, *J* = 8.3 Hz, 1H), 2.46 – 2.32 (m, 2H), 1.62 – 1.56 (m, 1H), 1.53 – 1.49 (m, 1H), 1.50 – 1.42 (m, 2H), 1.35 – 1.27 (m, 2H), 1.27 – 1.11 (m, 4H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.7, 69.3, 35.9, 35.4, 33.9, 29.2, 26.2, 21.6, 21.6. **R_f:** 0.48 (7:3 Hex:EtOAc).

Reference: *J. Am. Chem.* Soc. 2013, **135**, 15342-15345.

Methyl 3,3-dimethyl-5,5-diphenylpentanoate (22)

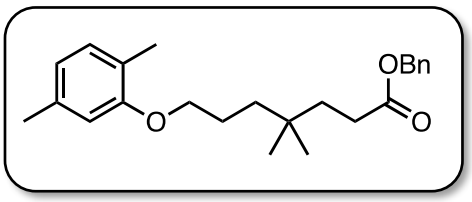


Prepared according to the general procedure described above using **S7** (46.7 mg, 0.18 mmol, 1.2 equiv), 1,1-Diphenylethylene (27 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 25% yield (11 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 8H), 7.18 – 7.08 (m, 2H), 4.01 (t, *J* = 6.9 Hz, 1H), 3.20 (s, 3H), 2.42 (d, *J* = 7.0 Hz, 2H), 1.19 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.7, 145.2, 128.5, 128.0, 126.3, 51.4, 48.3, 46.5, 42.1, 26.2. **R_f:** 0.63 (4:1 Hex:EtOAc).

Reference: *Org. Lett.* 2019, **21**, 1, 56-59.

Benzyl 7-(2,5-dimethylphenoxy)-4,4-dimethylheptanoate (23)

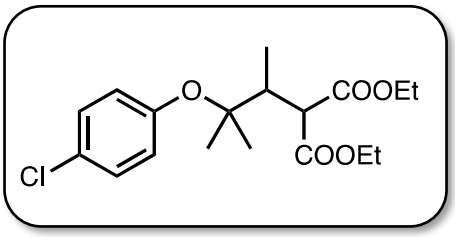


Prepared according to the general procedure described above using **S8** (65.4 mg, 0.18 mmol, 1.2 equiv), Benzyl acrylate (27 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil in 36% yield (20 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 1H), 6.61 (s, 1H), 5.12 (s, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.37 – 2.32 (m, 2H), 2.31 (s, 3H), 2.17 (s, 3H), 1.80 – 1.69 (m, 2H), 1.66 – 1.58 (m, 2H), 1.40 – 1.33 (m, 2H), 0.90 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 157.2, 136.6, 136.2, 130.4, 128.7, 128.4, 128.3, 123.7, 120.8, 112.1, 68.5, 66.4, 38.0, 36.5, 32.4, 29.7, 26.9, 24.4, 21.6, 15.9. **R_f:** 0.75 (4:1 Hex:EtOAc).

Reference: *ACS Catal.* 2020, **10**, 19, 11448-11457.

Diethyl 2-(3-(4-chlorophenoxy)-3-methylbutan-2-yl)malonate (24)



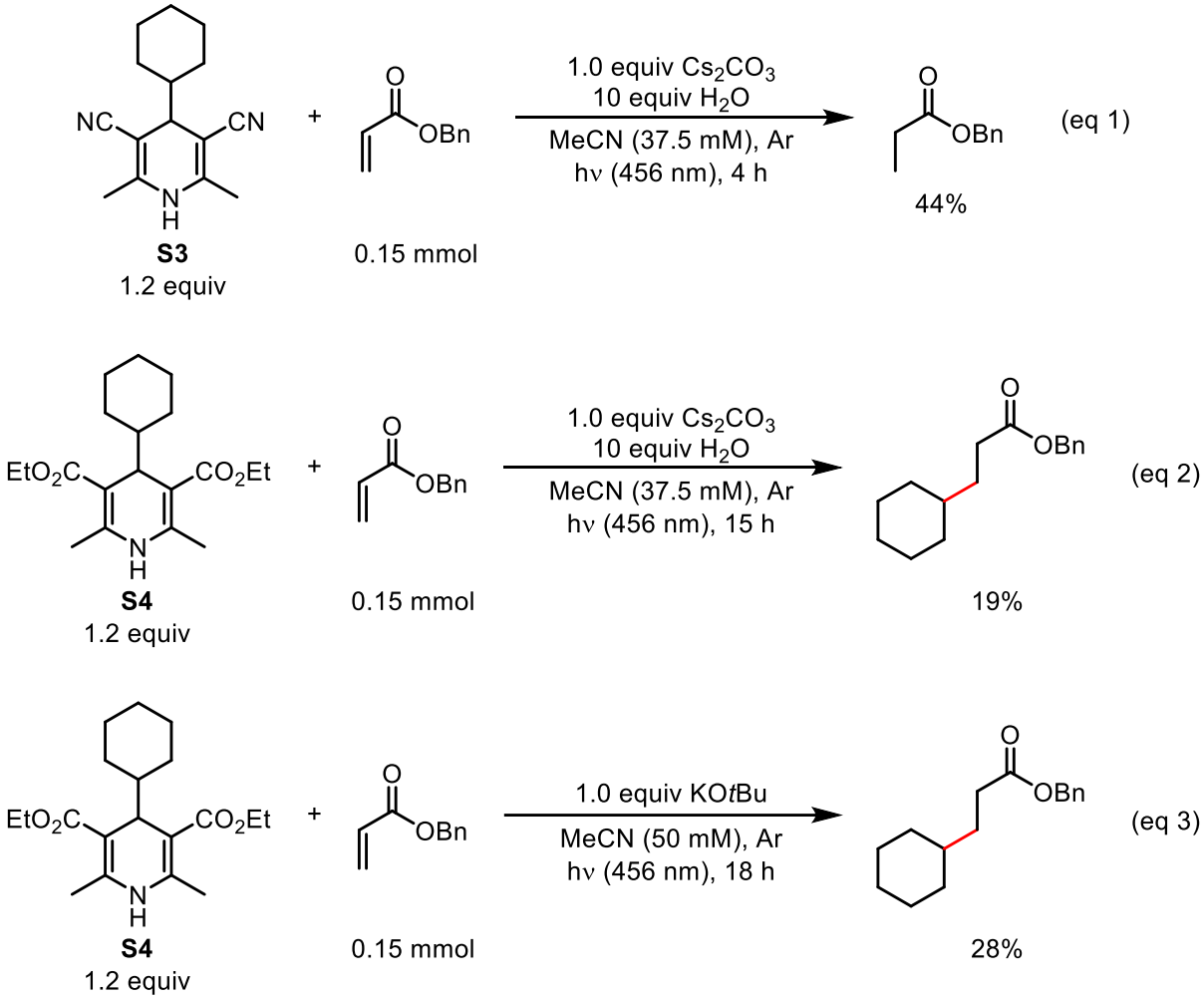
Prepared according to the general procedure described above using **S9** (59.0 mg, 0.18 mmol, 1.2 equiv), Diethyl ethylidenemalonate (28 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 10% EtOAc in hexane) to afford the title compound as a colorless oil in 38% yield (20 mg). Spectral data are in accordance with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 6.93 – 6.86 (m, 2H), 4.26 – 4.13 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.77 (d, *J* = 6.8 Hz, 1H), 2.77 (p, *J* = 7.0 Hz, 1H), 1.30 – 1.23 (m, 6H), 1.22 – 1.16 (m, 6H), 1.11 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 169.4, 153.4, 129.0, 125.8, 83.0, 61.5, 61.3, 53.7, 43.7, 25.8, 21.9, 14.2, 14.2, 13.3. **R_f:** 0.34 (9:1 Hex:EtOAc).

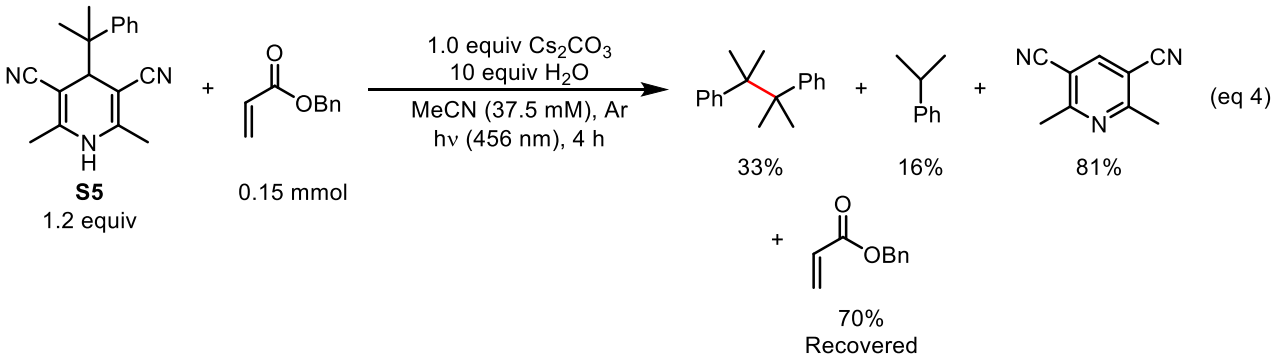
Reference: *Eur. J. Org. Chem.* 2017, **15**, 2154-2163.

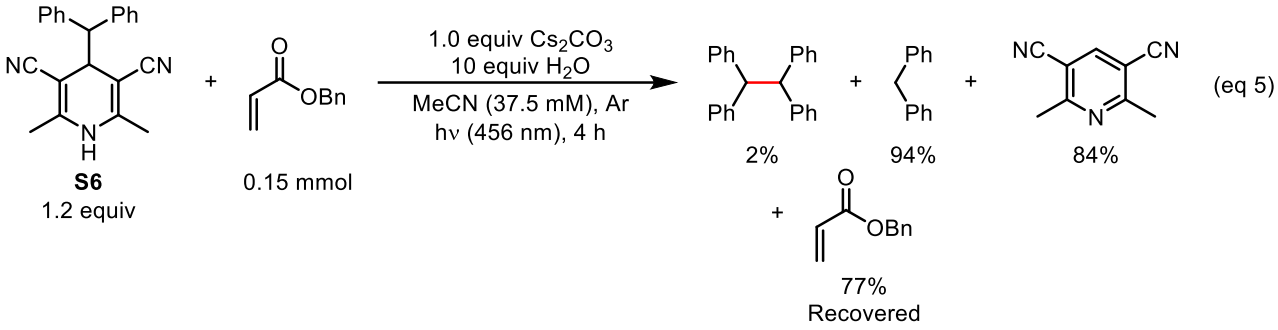
F. Unsuccessful or Low Yielding Scope Examples

For DHPs bearing secondary alkyl group substituents at C4, the 3,5-diCN DHP **S3** did not result in the formation of the Giese adduct. Instead, reduction of the Michael acceptor (benzyl acrylate in this case) was observed (eq 1). By switching to the 3,5-di(CO_2Et) DPH **S4**, the Giese adduct could be produced, albeit in low yield and extended irradiation times were required (eq 2). The reaction could be slightly improved by switching to a stronger base (KO*t*Bu); however, this result remains unoptimized (eq 3).



DHPs **S5** and **S6** bearing benzylic substituents at C4 could be photolyzed efficiently under our reaction conditions. However, the corresponding benzyl radicals did not participate in the Giese reaction, instead yielding either the radical homodimer or gaining a hydrogen atom (eq 4 and 5).

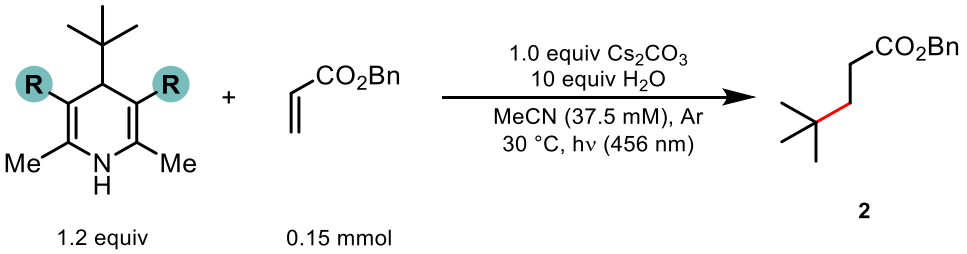

Ph
NC
CN
N
H
S5
1.2 equiv
O
OBn
0.15 mmol
1.0 equiv Cs2CO3
10 equiv H2O
MeCN (37.5 mM), Ar
hν (456 nm), 4 h
Ph
Ph
33%
Ph
16%
NC
CN
N
81%
O
OBn
70%
Recovered
(eq 4)


Ph
Ph
NC
CN
N
H
S6
1.2 equiv
O
OBn
0.15 mmol
1.0 equiv Cs2CO3
10 equiv H2O
MeCN (37.5 mM), Ar
hν (456 nm), 4 h
Ph
Ph
Ph
Ph
2%
Ph
Ph
94%
NC
CN
N
84%
O
OBn
77%
Recovered
(eq 5)

G. Procedure for Initial Rate Studies

An oven-dried Pyrex tube (10 mL) equipped with a magnetic stir bar was charged with a 4-*tert*-alkyl-1,4-DHP (**1** or **23**, 0.18 mmol, 1.2 equiv), benzyl acrylate (23 µL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 µL, 1.5 mmol, 10 equiv). Dry MeCN (dried over 3 Å molecular sieves) was added (4 mL, 37.5 mM), and the reaction mixture was degassed by sparging with argon for 5-6 minutes. The reaction mixture was then sonicated and irradiated with two Kessil PR160-456 nm LEDs lamps for 2 or 4 h at 30 °C. The reaction mixture was transferred into a separatory funnel and diluted with 15 mL of anhydrous ethyl ether and washed with 15 mL of 1M HCl, then 15 mL of brine. The aqueous phase was extracted with 15 mL of anhydrous ethyl ether. The combined organic phases were dried over $MgSO_4$, and the filtrate was concentrated *in vacuo*. Yields were determined by ^{1}H NMR analysis using methyl 4-chlorobenzoate as an external standard.

Table S3. Initial rate studies for the Giese reactions of **1** and **23**.



R Group	DHP pK_a[a]	t = 2 h	t = 4 h
CN (**1**)	16.7	33%	73%
CO_2Et (**23**)	20.1	3%	8%

[a] pK_a values correspond to DHPs bearing no substituents at C4.[4]

H. Mechanistic Experiments

H1. Radical Trap Experiment with TEMPO

Performed according to General Procedure C2 using **1** (39 mg, 0.18 mmol, 1.2 equiv), benzyl acrylate (23 μL, 0.15 mmol, 1 equiv), TEMPO (23 mg, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. Yields were determined by ^1H NMR analysis using methyl 4-chlorobenzoate as an external standard. No Giese adduct was observed in the reaction crude, and 44% yield of the *tert*-butyl–TEMPO adduct was observed. The chemical shifts of the *tert*-butyl–TEMPO adduct are consistent with those previously reported.[5]

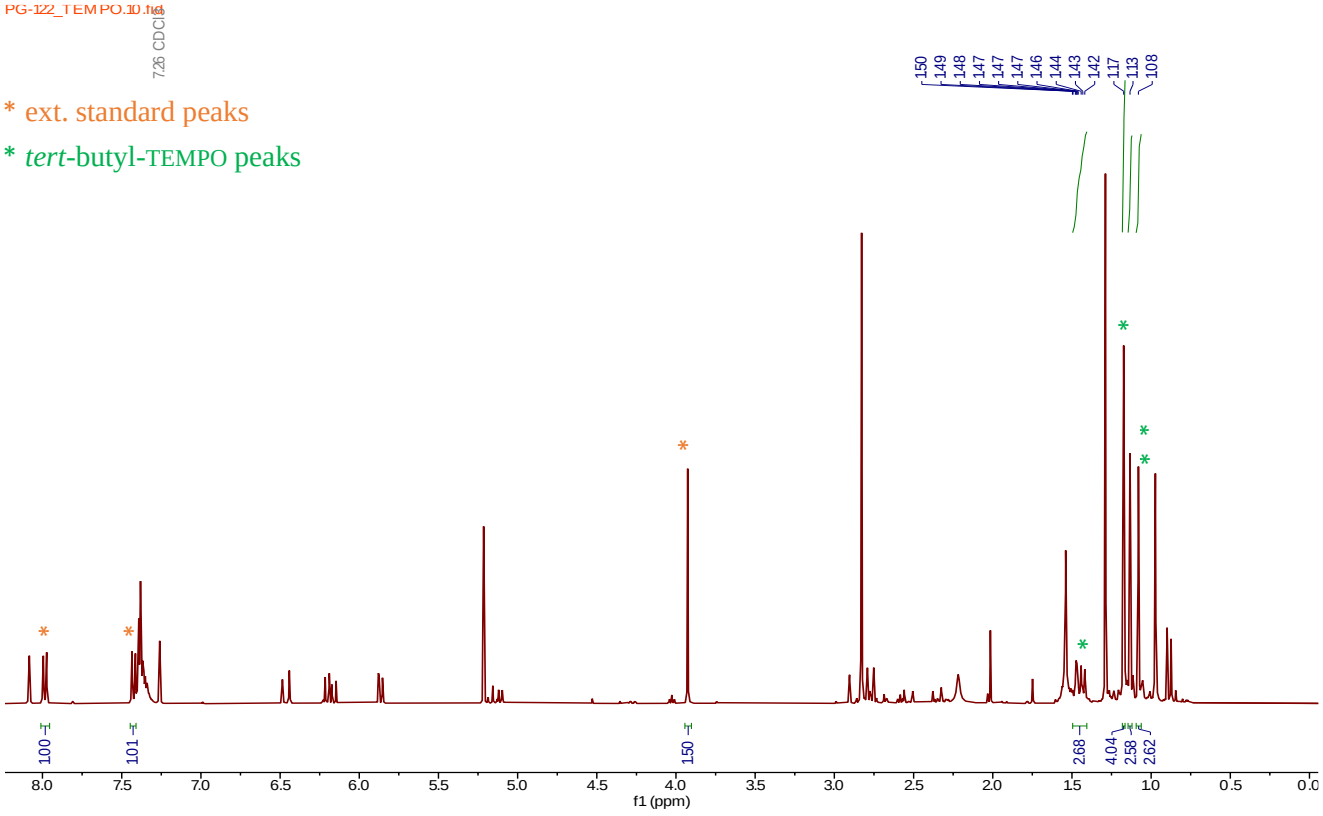
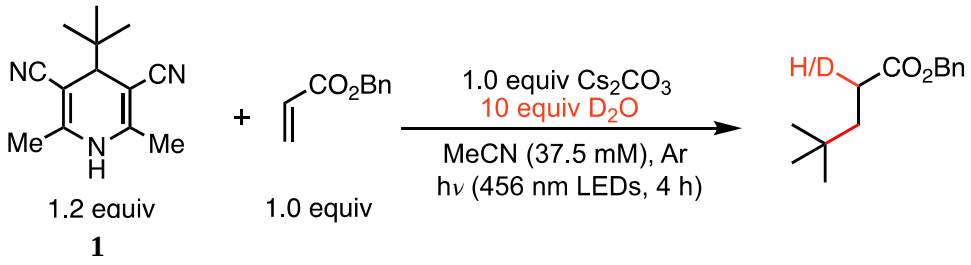


Figure S2. Crude ^1H NMR for the control reaction with TEMPO.

H2. Deuterium Incorporation Study



Performed according to General Procedure C2 using **1** (39 mg, 0.18 mmol, 1.2 equiv), benzyl acrylate (23 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and D_2O (30 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil. (50% isolated yield, 29% deuterium incorporation).

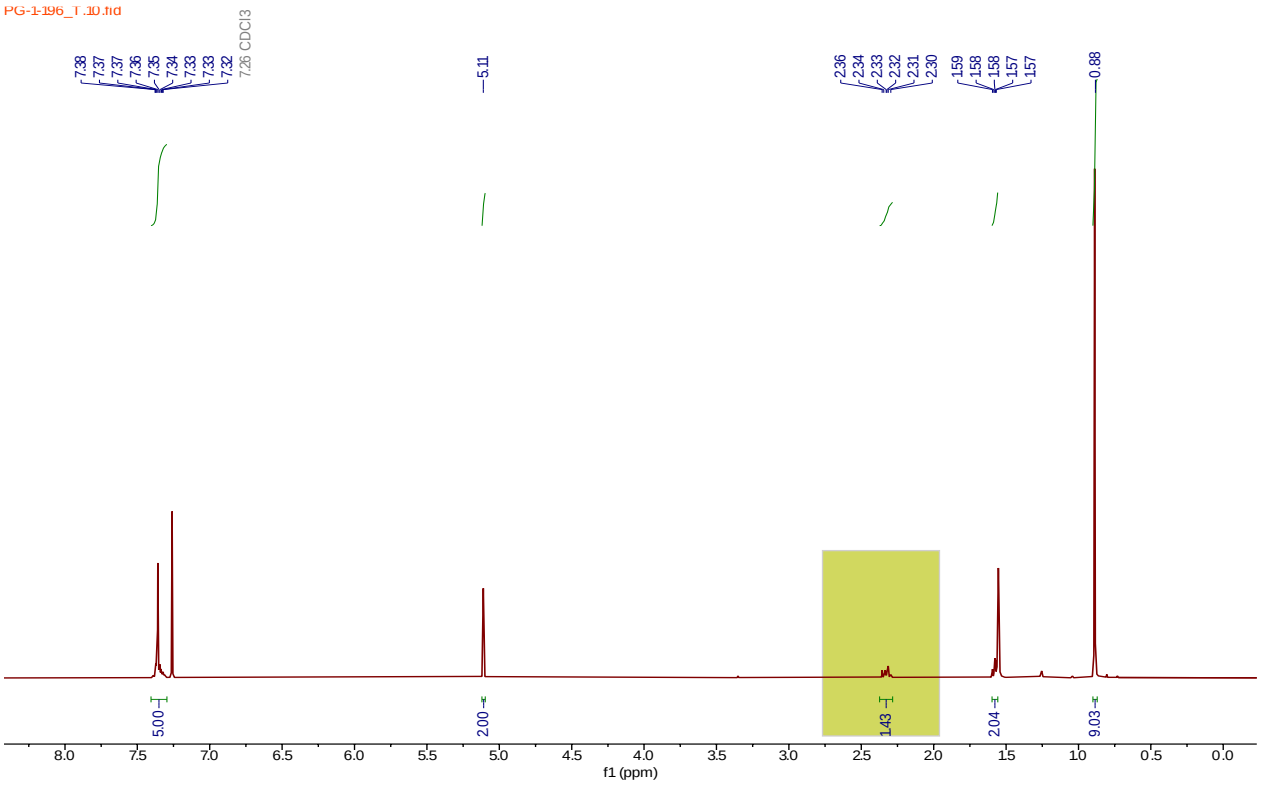
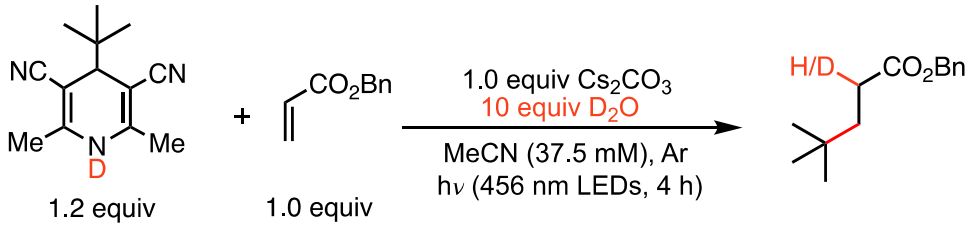


Figure S3. ^{1}H NMR spectrum for deuterium incorporation study using **1**.



Performed according to General Procedure C2 using **1 ND** (39 mg, 0.18 mmol, 1.2 equiv), benzyl acrylate (23 μL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and D_2O (30 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. The crude material was purified by flash column chromatography (0 → 15% EtOAc in hexane) to afford the title compound as a colorless oil. (63% isolated yield, 37% deuterium incorporation).

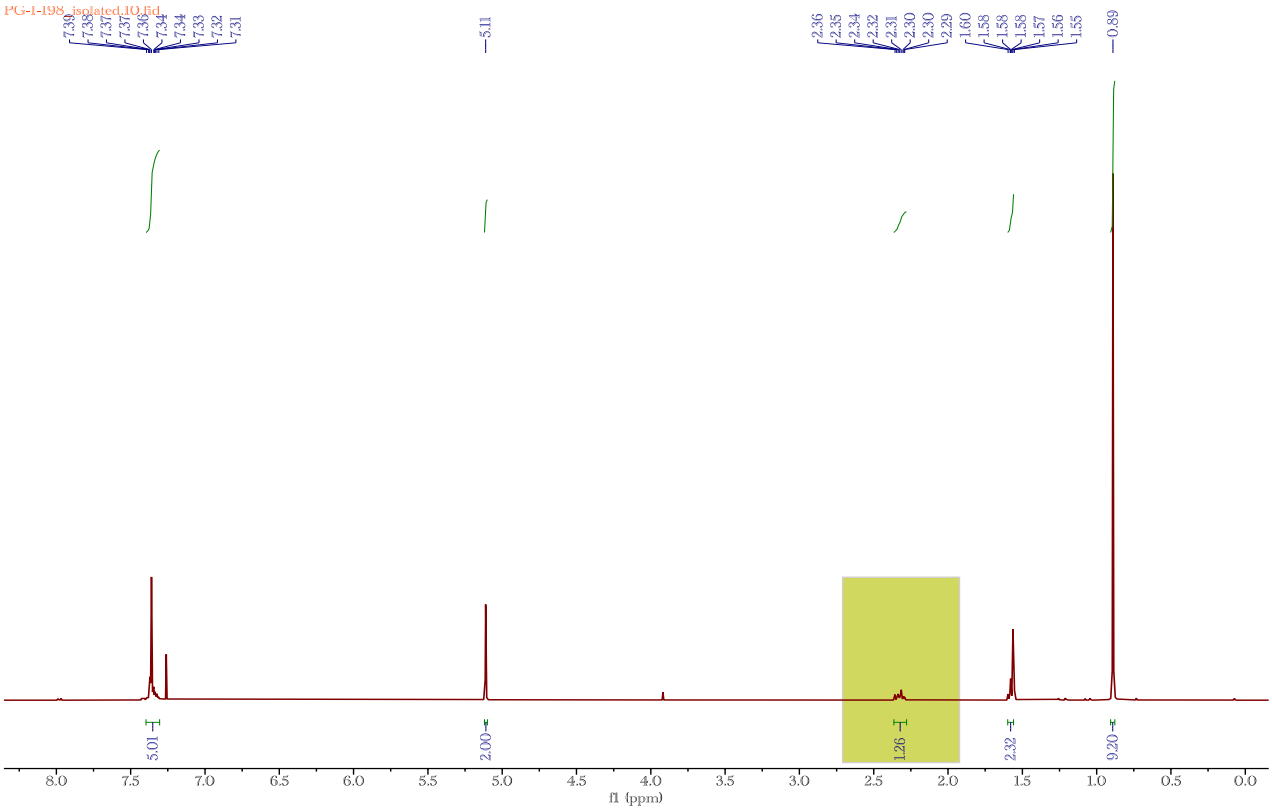
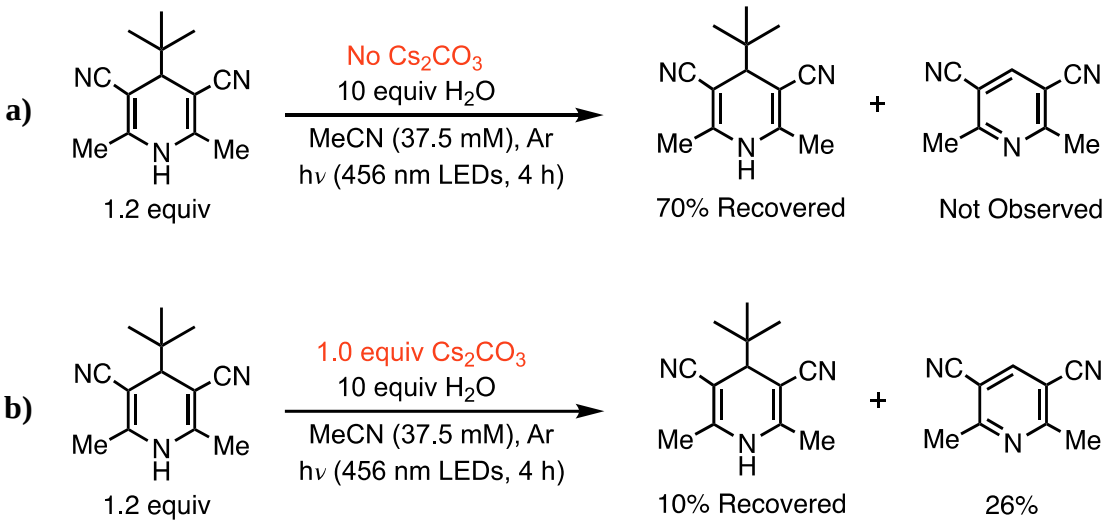


Figure S4. ^{1}H NMR spectrum for deuterium incorporation study using **1 ND**.

H3. Control Reactions in the Absence of Michael Acceptors



Both reactions, **a)** no Cs_2CO_3 **b)** with Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv), were performed according to General Procedure C2 using **1** (39 mg, 0.18 mmol, 1.2 equiv), H_2O (27 μL, 1.5 mmol, 10 equiv) in 4 mL of dry MeCN. Yields were determined by ^1H NMR using 4-(chloromethyl) benzoic acid as an external standard.

H4. Determination of Giese Reaction Quantum Yield

To determine the quantum yield for the Giese reaction of DHP anions, we employed the $Ru(bpy)_3Cl_2$/9,10-diphenylanthracene (DPA) actinometer previously reported by Scaiano and coworkers.[6] To facilitate spectral matching between the $Ru(bpy)_3Cl_2$/DPA actinometer and the DHP anion, we performed the quantum yield studies using a 427 nm Kessil LED to ensure the actinometer and the reaction mixture absorbed >99% of the photons in the region of the LED emission. To determine the moles of photons absorbed per unit time (Nhν/t), a 100 mL stock solution of the actinometer was made with 0.5 mM $Ru(bpy)_3Cl_2$ (18.7 mg) and 0.10 mM 9,10-diphenylanthracene (DPA, 3.3 mg) in MeCN. 3 mL of the stock solution was added to a quartz cuvette, and a UV-Vis spectrum was recorded from 450-350 nm ($A_{initial}$). 4 mL of the stock solution was then transferred into a 10 mL Pyrex tube then placed in front of the 427 nm Kessil LED and was irradiated at 25% power for 10 seconds. Following irradiation, 3 mL of this solution was transferred into a quartz cuvette and the absorption spectrum was recorded again from 450-350 nm (A_{final}). This was repeated in triplicate, and by employing equations (6) and (7):

$$moles\ of\ DPA\ consumed = \frac{\left(A_{initial} - A_{final}\right)}{(\varepsilon_{372\ nm})(l)}(V) \quad (eq\ 6)$$

$$\frac{Nh\nu}{t} = \frac{moles\ of\ DPA\ consumed}{(\Phi)(t)} \quad (eq\ 7)$$

where $A_{initial}$ and A_{final} are the absorbances at 372 nm before and after irradiation, $\varepsilon_{372\ nm}$ is the extinction coefficient of DPA at 372 nm (11,100 $M^{-1}\ cm^{-1}$)[5], l is the path length and Φ is the quantum yield of the actinometer (0.019)[5], it was calculated that the moles of photons absorbed per unit time (Nhν/t) for the 427 nm Kessil LED setup employed was 4.07±0.42 x 10^{-7} mol hν s^{-1}. A typical example of the UV-vis spectra from one of our $Ru(bpy)_3Cl_2$/DPA actinometry experiments is shown in Figure S5.

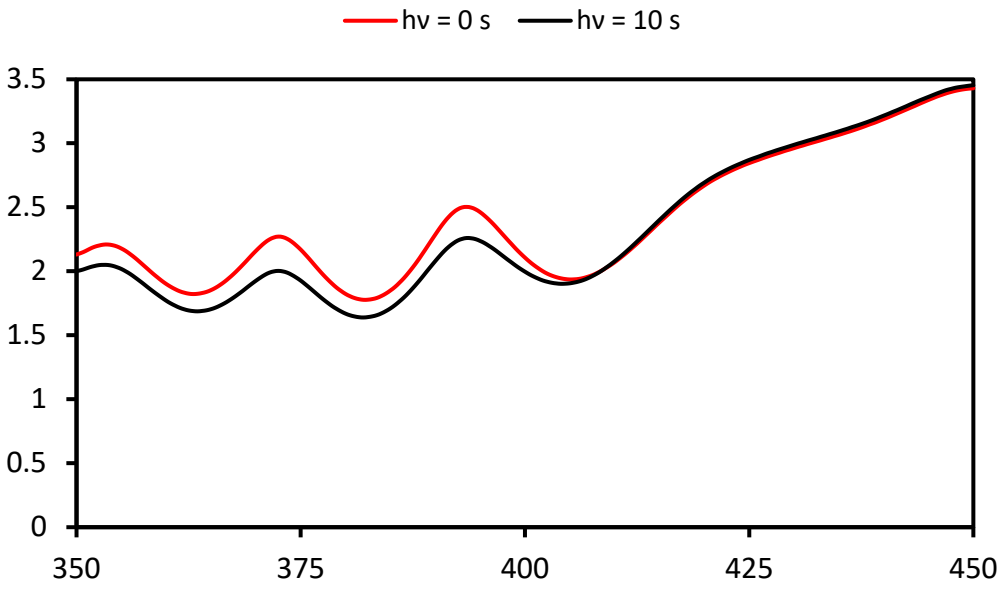


Figure S5. Typical example of UV-vis spectra from one $Ru(bpy)_3Cl_2$/DPA actinometry trial.

To calculate the quantum yield for the Giese reaction, an oven-dried Pyrex tube (10 mL) equipped with a magnetic stir bar was charged with **1** (39 mg, 0.18 mmol, 1.2 equiv), benzyl acrylate (23 µL, 0.15 mmol, 1 equiv), Cs_2CO_3 (49 mg, 0.15 mmol, 1 equiv) and H_2O (27 µL, 1.5 mmol, 10 equiv). Dry MeCN (dried over 3 Å molecular sieves) was added (4 mL, 37.5 mM), and the reaction mixture was degassed by sparging with argon for 5-6 minutes. The reaction mixture was then sonicated and irradiated with the same setup using a single 427 nm Kessil LED at 25% power for 2 h. The reaction mixture was transferred into a separatory funnel and diluted with 15 mL of anhydrous ethyl ether and washed with 15 mL of 1 M HCl, then 15 mL of brine. The aqueous phase was extracted with 15 mL of anhydrous ethyl ether. The combined organic phases were dried over $MgSO_4$, and the filtrate was concentrated *in vacuo*. The yield of the reaction was calculated by ^{1}H NMR analysis using methyl 4-chlorobenzoate as an external standard. The yield of product was calculated to be 8%, equivalent to 0.012 mmol of product produced. Using equation 8,

$$\Phi = \frac{(moles\ of\ product\ produced)}{t \times F} \times \left(\frac{Nh\nu}{t}\right)^{-1} \quad (eq\ 8)$$

where t = 7200 s, F = 1.0, and Nhν/t = 4.07 x 10^{-7} mol hν s^{-1}, the quantum yield (Φ) was calculated to be 4.1 x 10^{-3}, *indicating that chain propagation is likely not part of the underlying mechanism*.

I. Absorption Spectra

All DHP solutions were transferred to 3.5 mL macro fluorescence cuvettes and scanned from the 300–700 nm region using a Shimadzu UV-2600 UV-vis spectrometer.

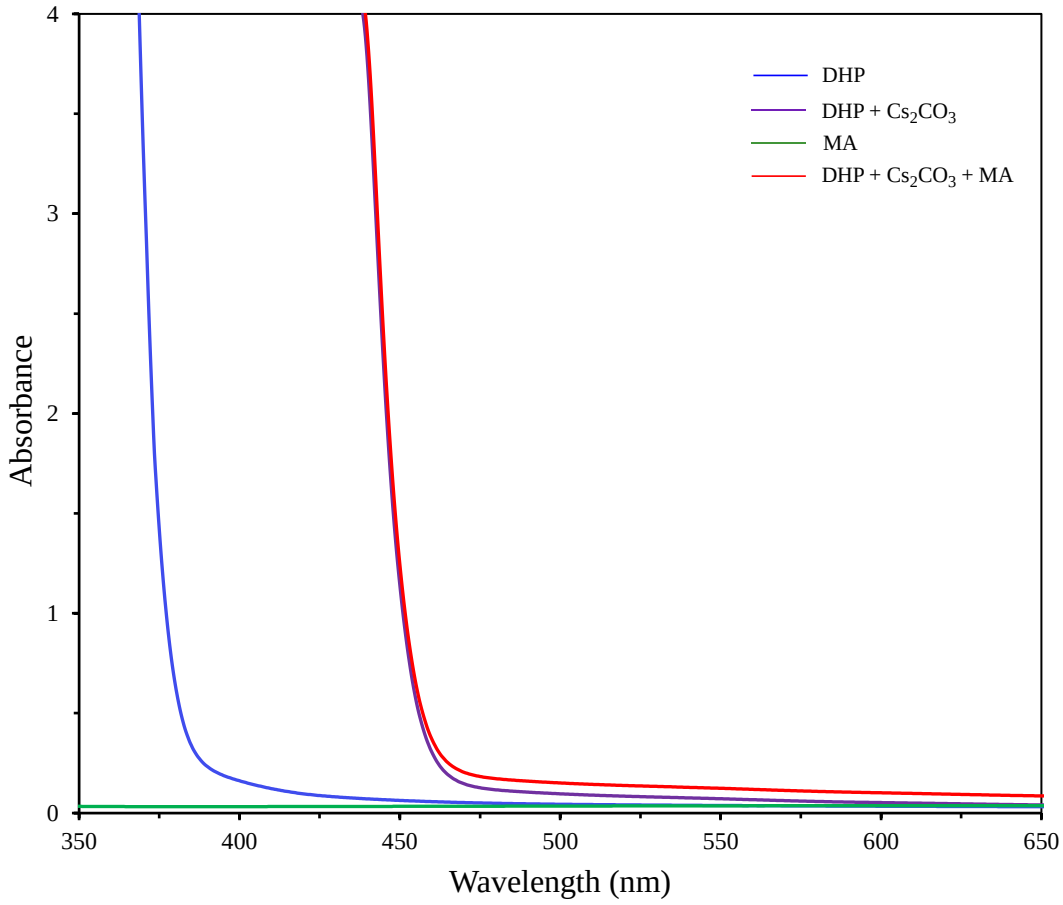


Figure S6. UV-Vis spectra of DHP **1, 1** + Cs_2CO_3, **MA** (benzyl acrylate) and **1** + Cs_2CO_3 + **MA**. [**1**] = 45 mM, [Cs_2CO_3] = 37.5 mM, [**MA]** = 37.5 mM in MeCN.

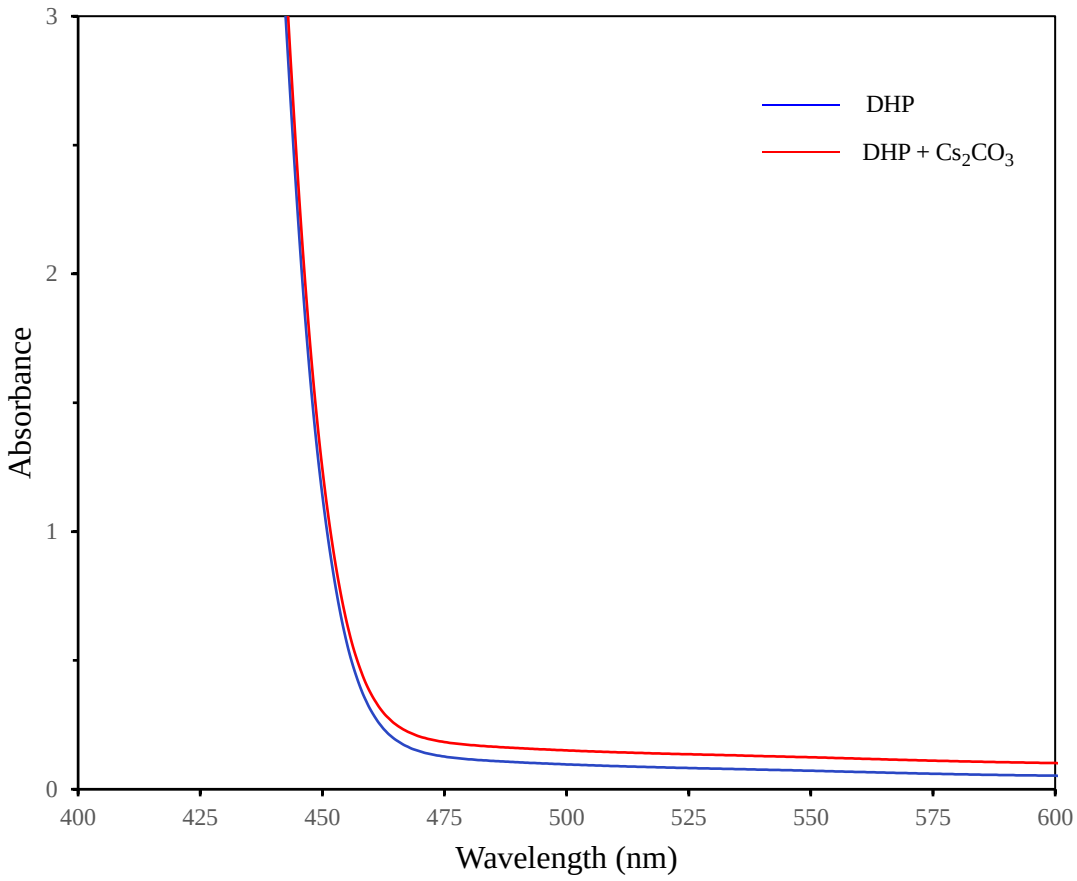


Figure S7. UV-Vis spectra of DHP **23** and **23** + Cs_2CO_3. [**23**] = 45 mM, [Cs_2CO_3] = 37.5 mM in MeCN.

J. References

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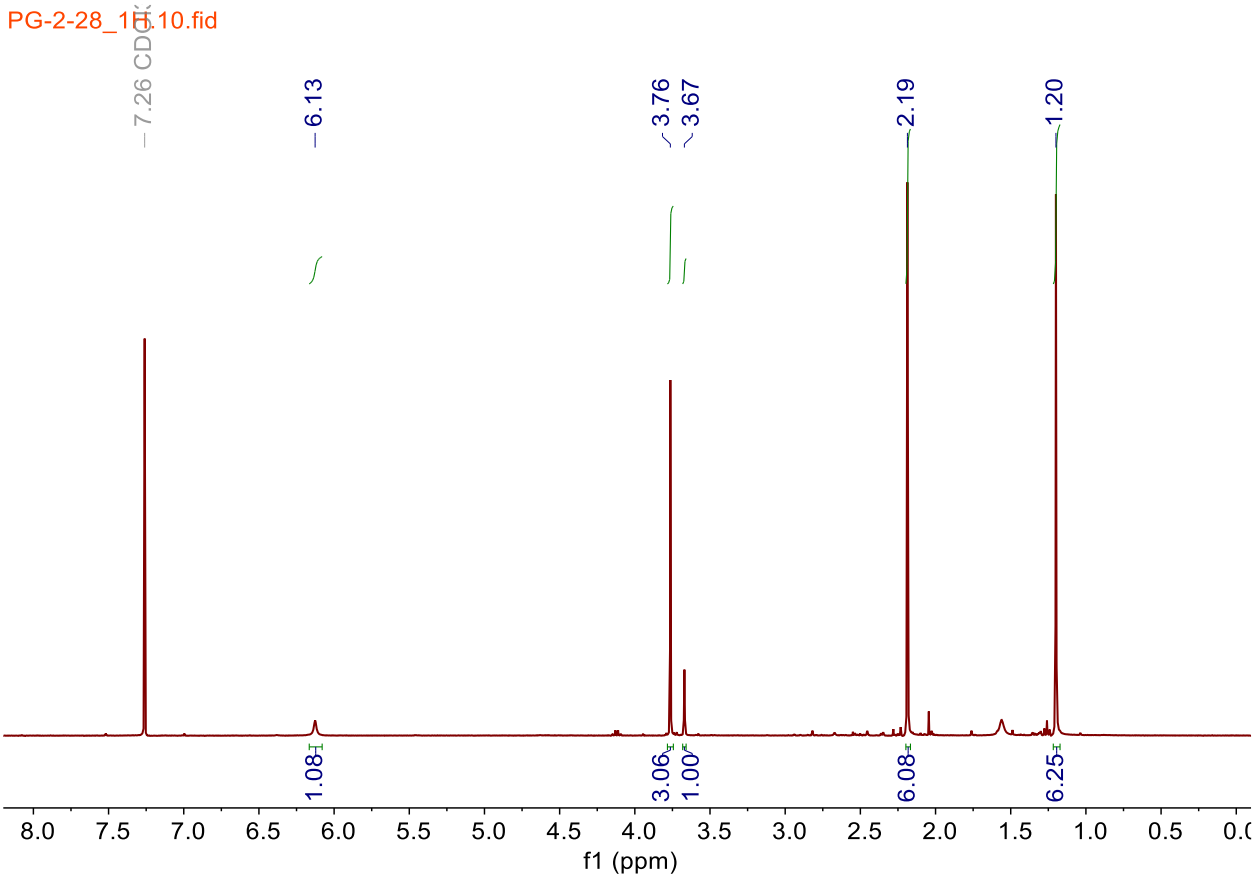
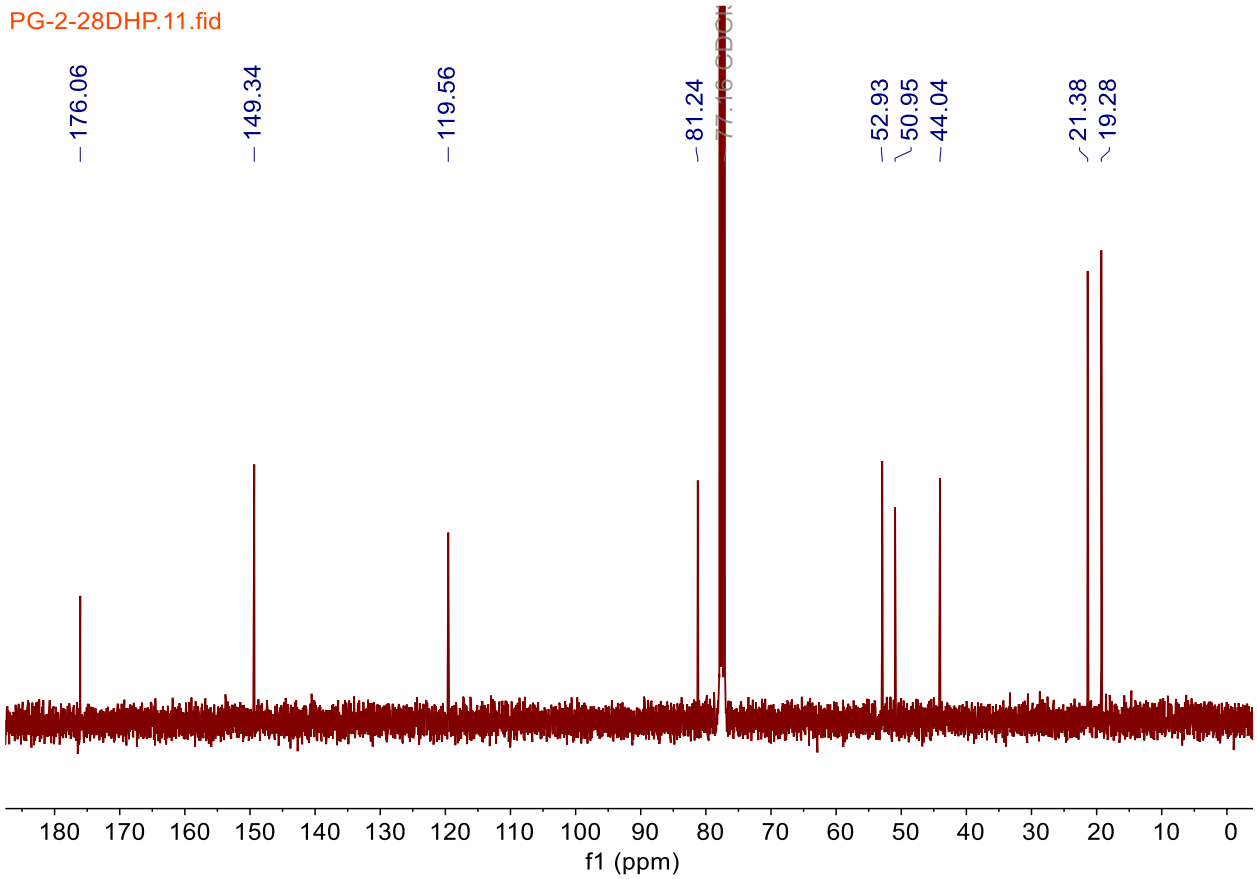
K. NMR Spectra

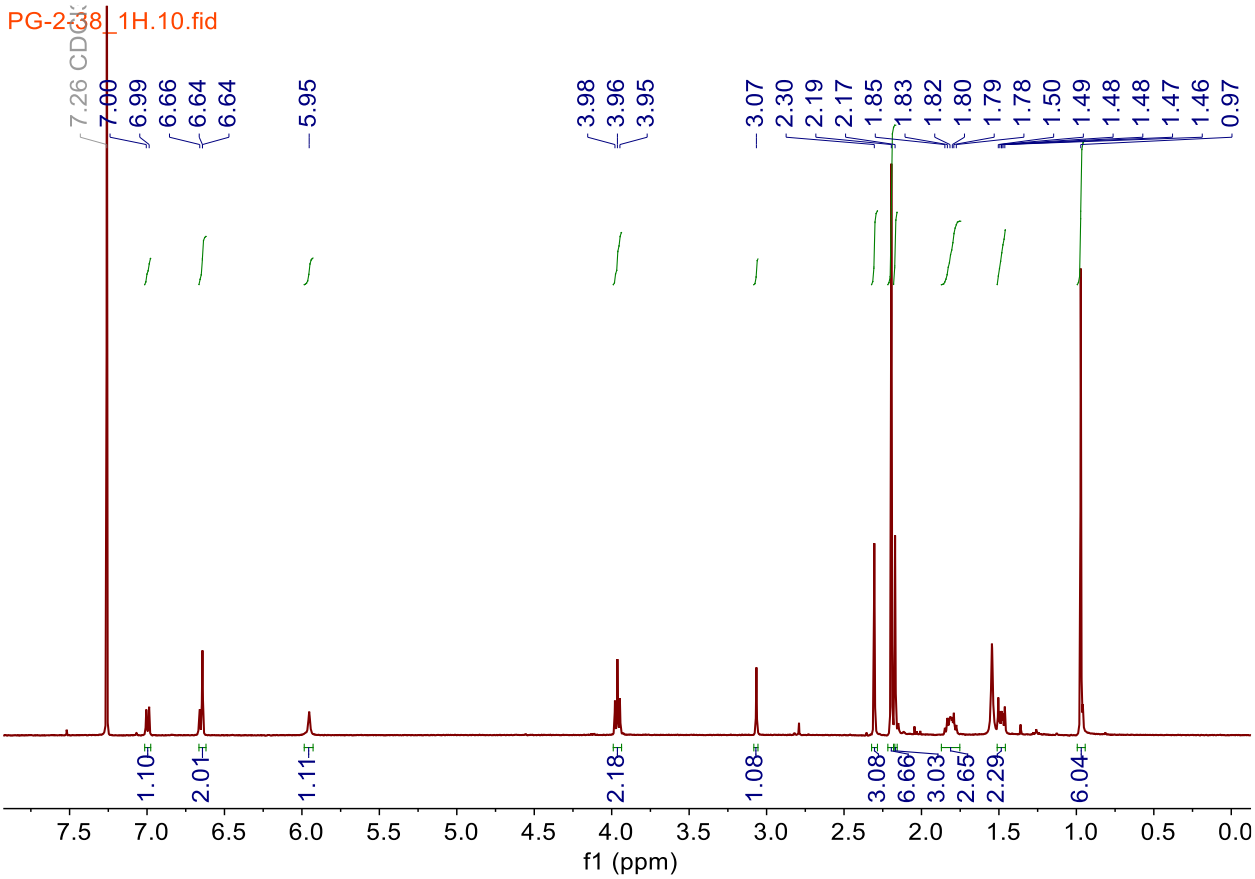
Methyl 2-(3,5-dicyano-2,6-dimethyl-1,4-dihydropyridin-4-yl)-2-methylpropanoate (S7): ^{1}H NMR (400 MHz, $CDCl_3$)



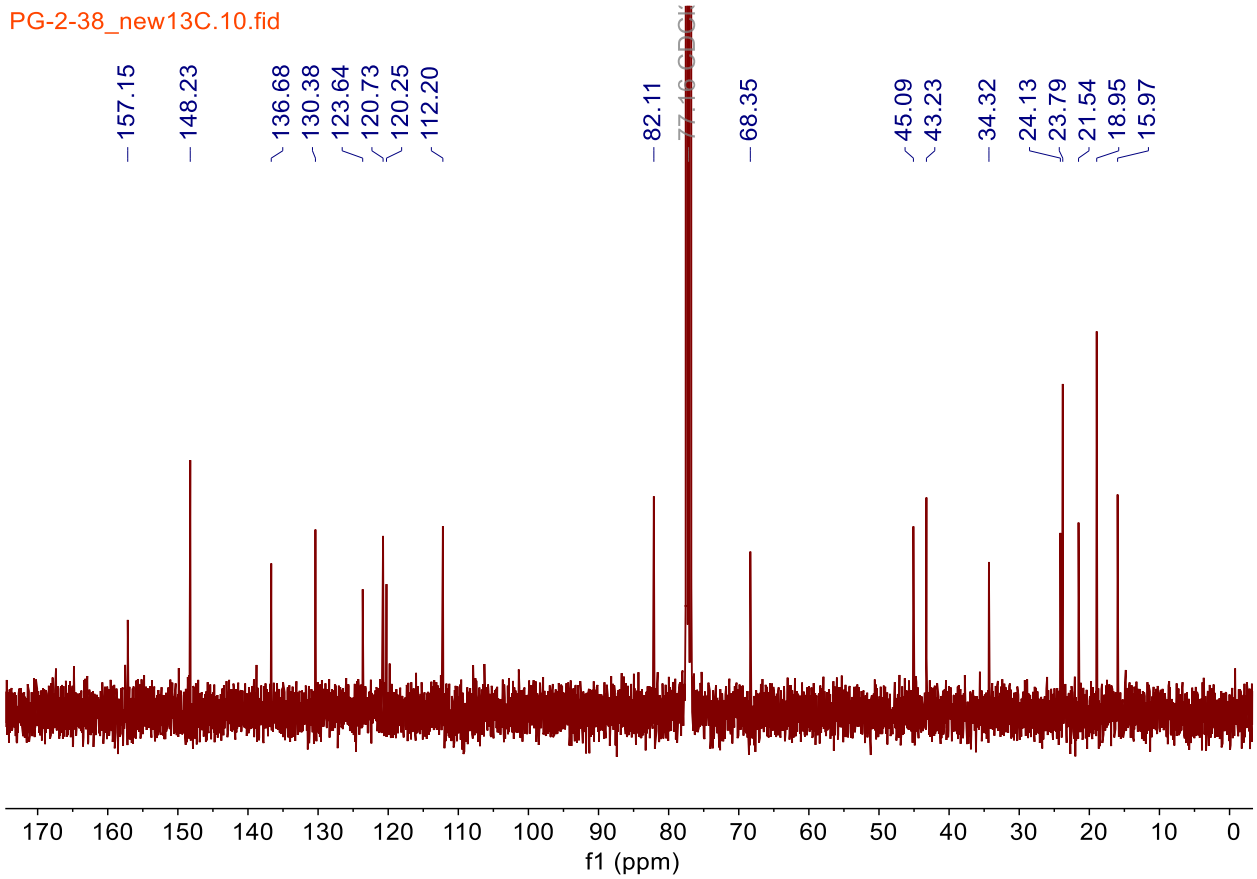
Methyl 2-(3,5-dicyano-2,6-dimethyl-1,4-dihydropyridin-4-yl)-2-methylpropanoate (S7):
^{13}C NMR (101 MHz, $CDCl_3$)



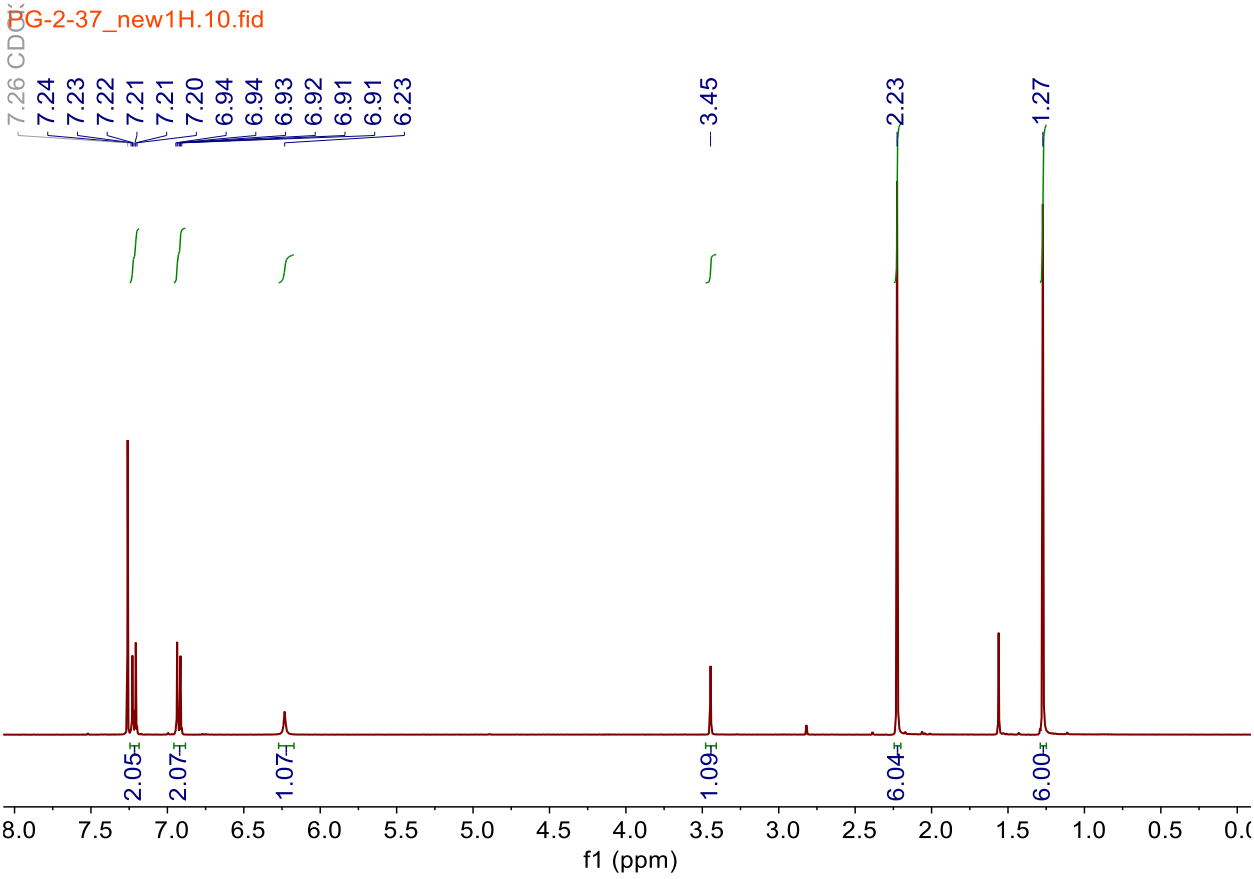
4-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile (S8): ^{1}H NMR (400 MHz, $CDCl_3$)



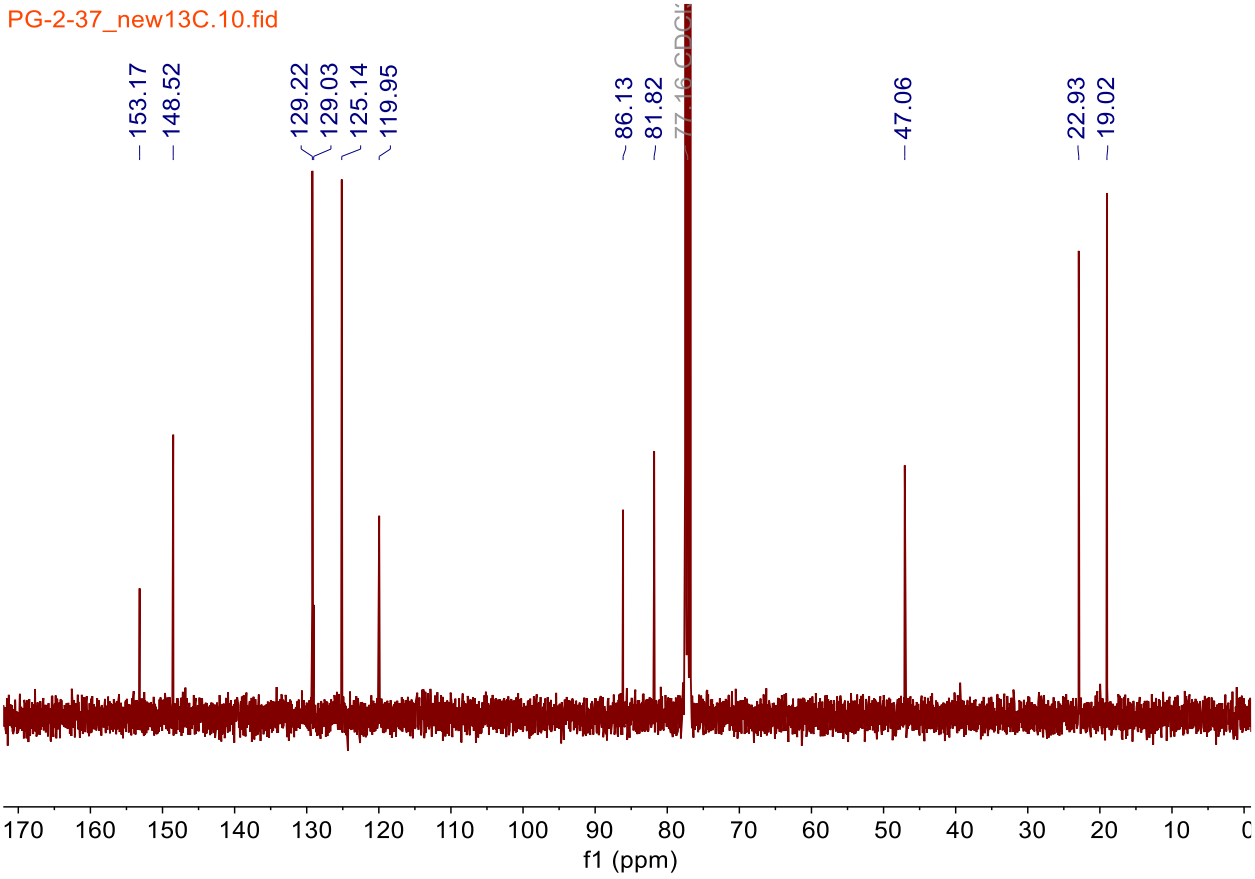
4-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile (S8): ^{13}C NMR (101 MHz, $CDCl_3$)



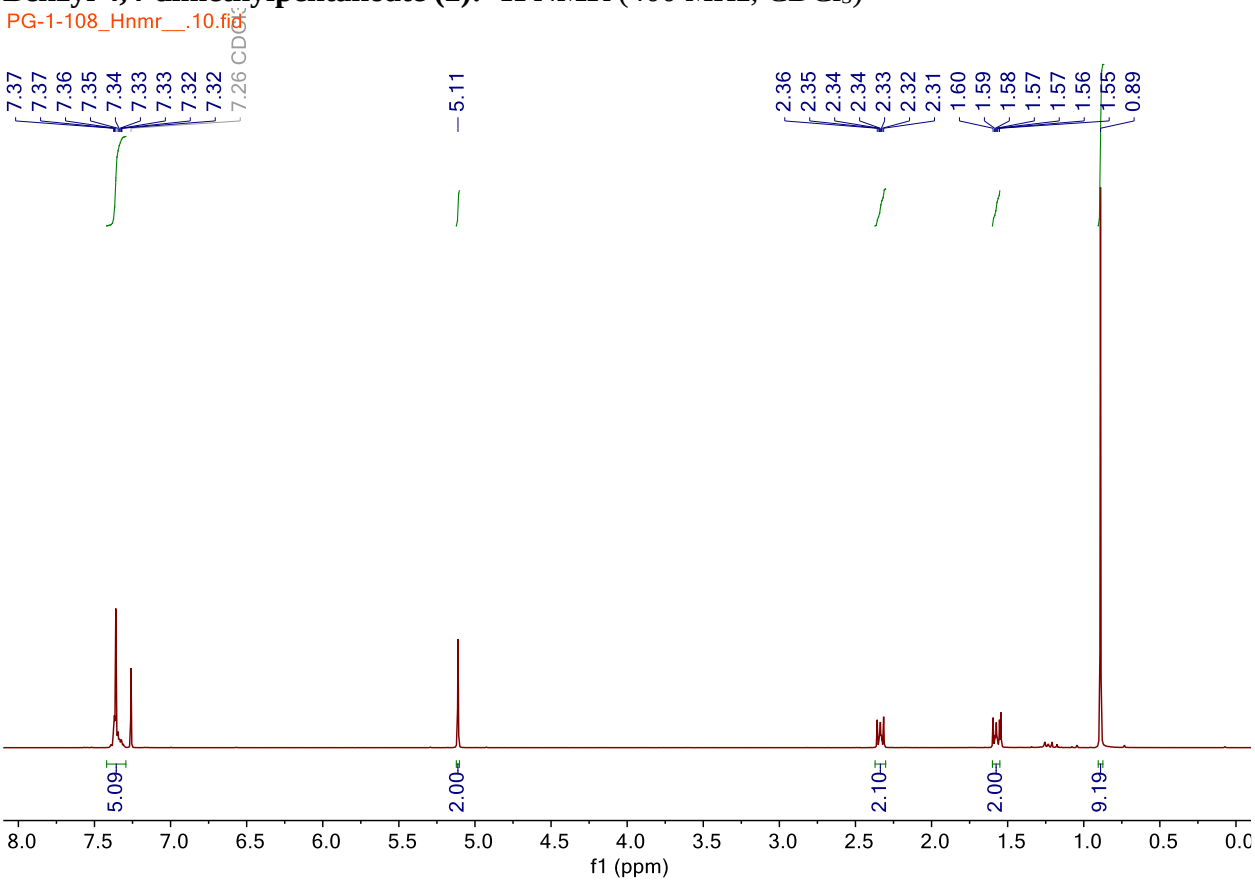
4-(2-(4-Chlorophenoxy)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile (S9): ^{1}H NMR (101 MHz, $CDCl_3$)



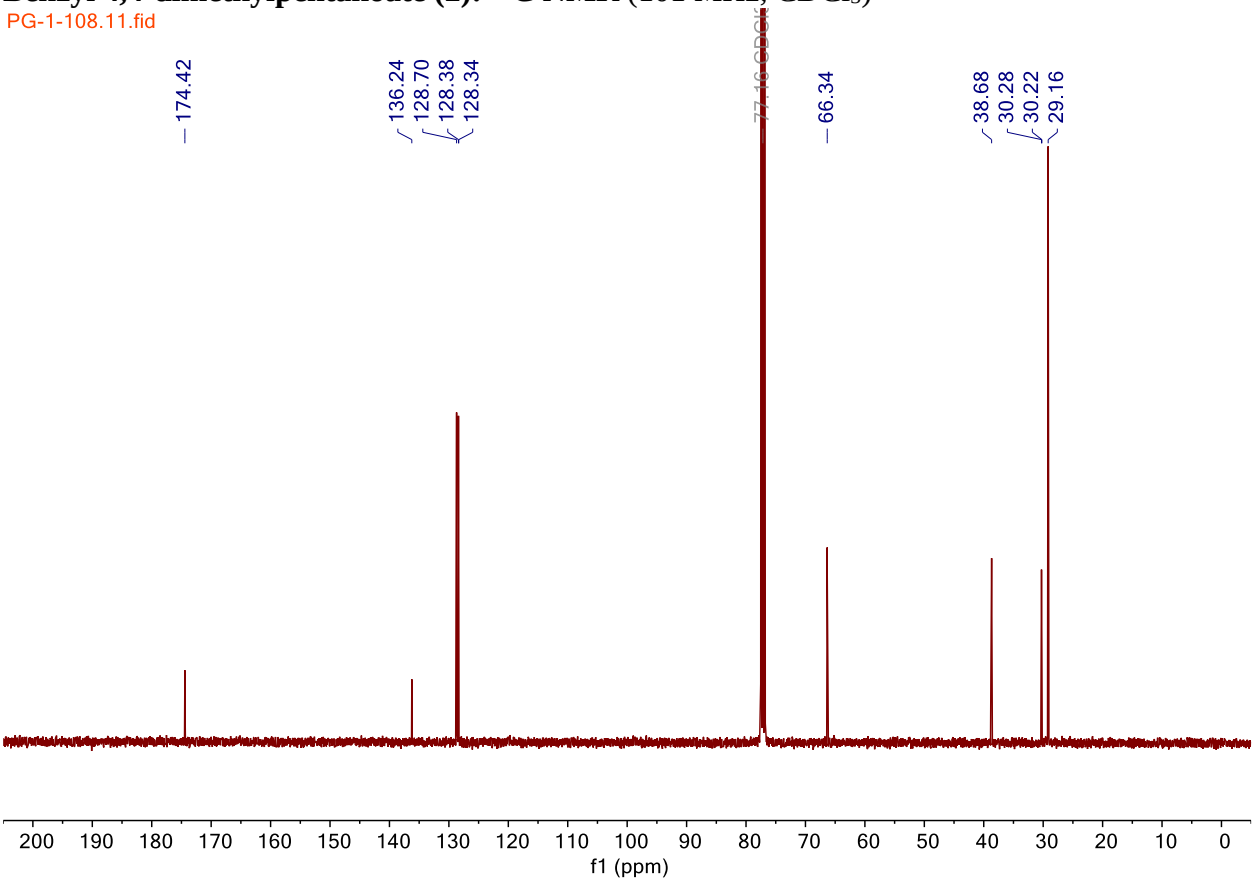
4-(2-(4-Chlorophenoxy)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile (S9): ^{13}C NMR (101 MHz, $CDCl_3$)



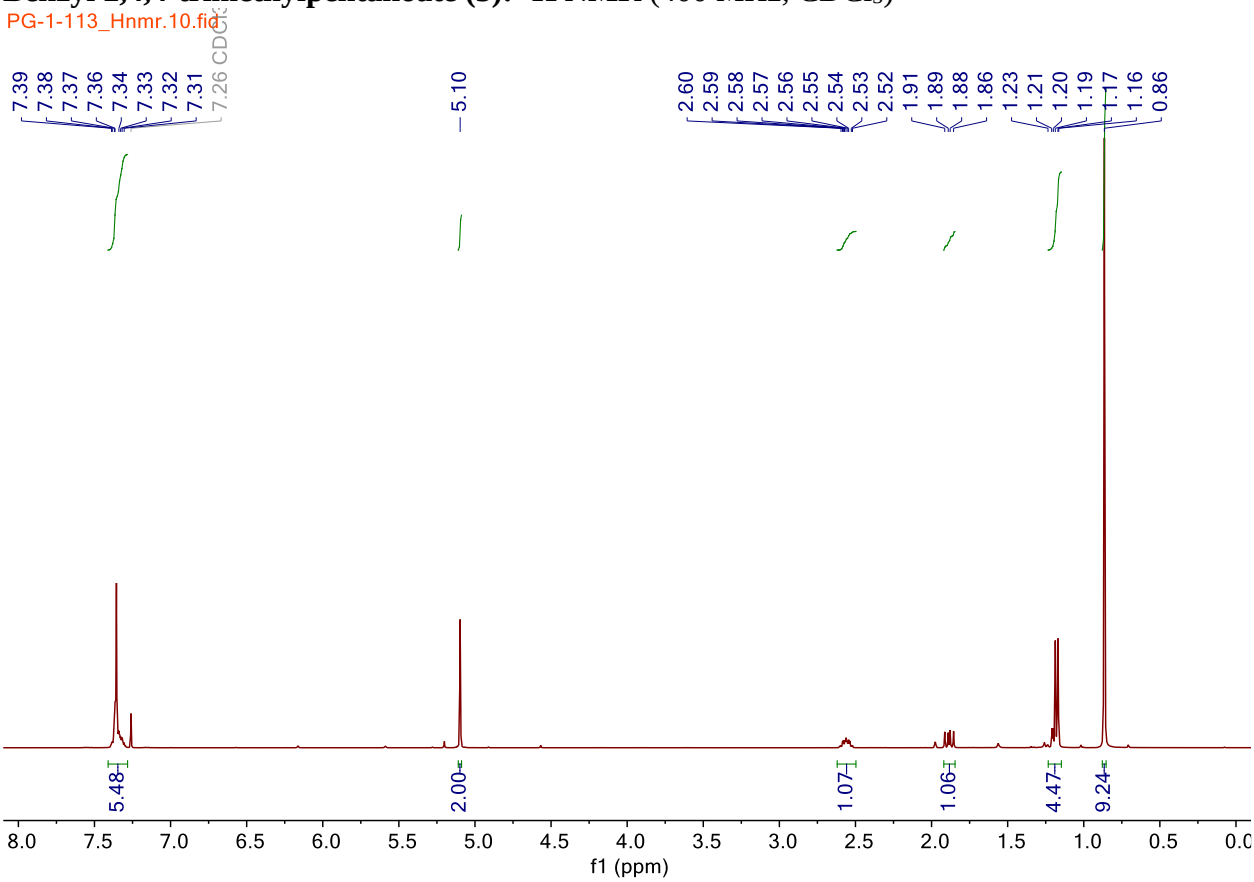
Benzyl 4,4-dimethylpentanoate (2): ^{1}H NMR (400 MHz, $CDCl_3$)



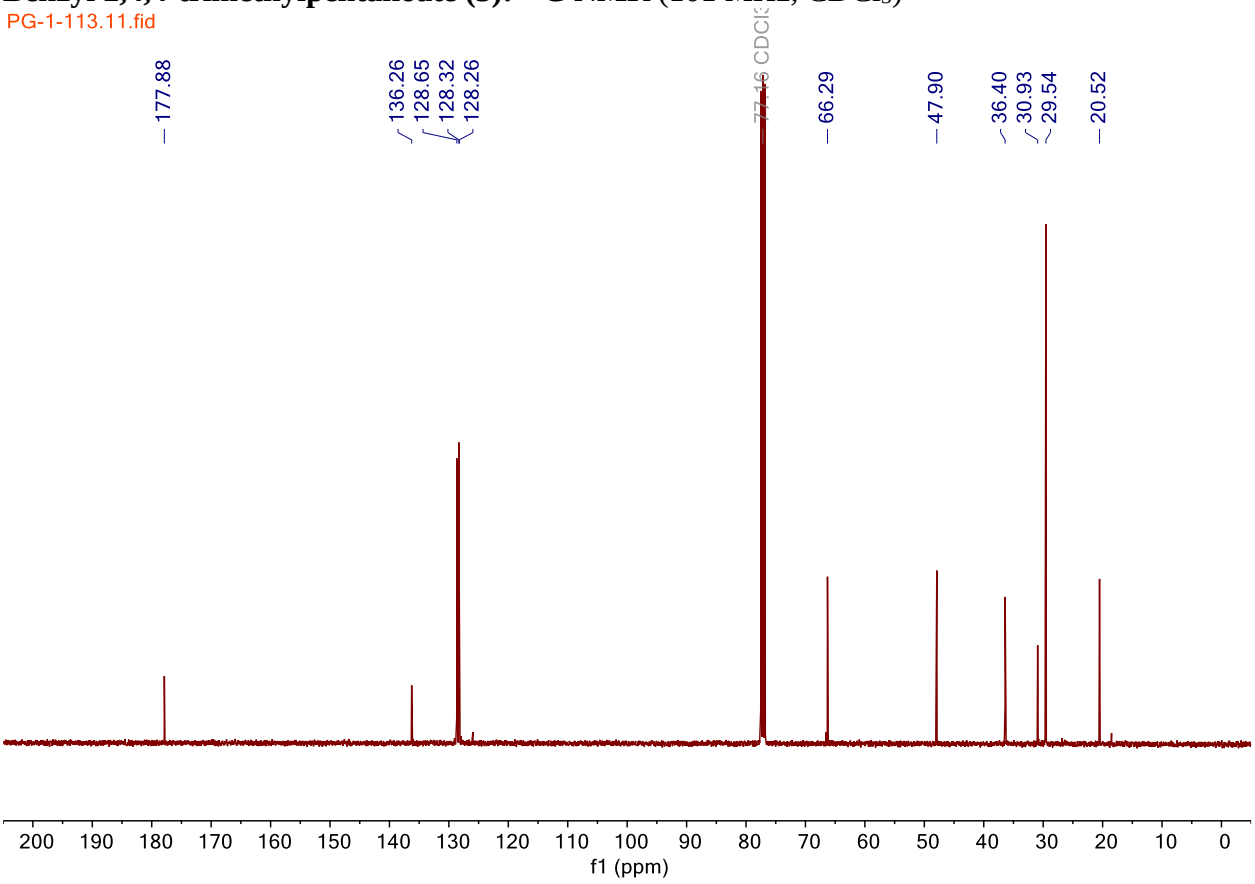
Benzyl 4,4-dimethylpentanoate (2): ^{13}C NMR (101 MHz, $CDCl_3$)



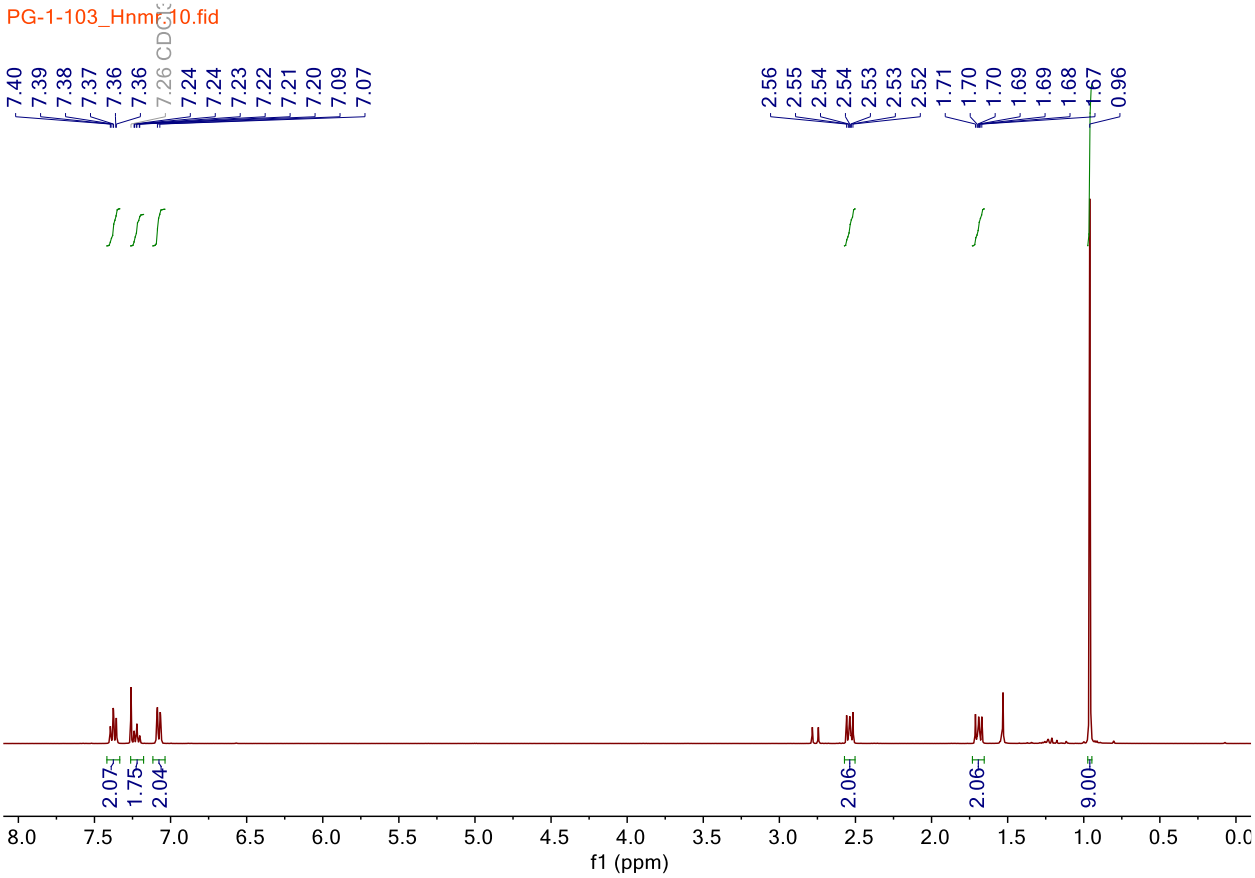
Benzyl 2,4,4-trimethylpentanoate (3): ^{1}H NMR (400 MHz, $CDCl_3$)



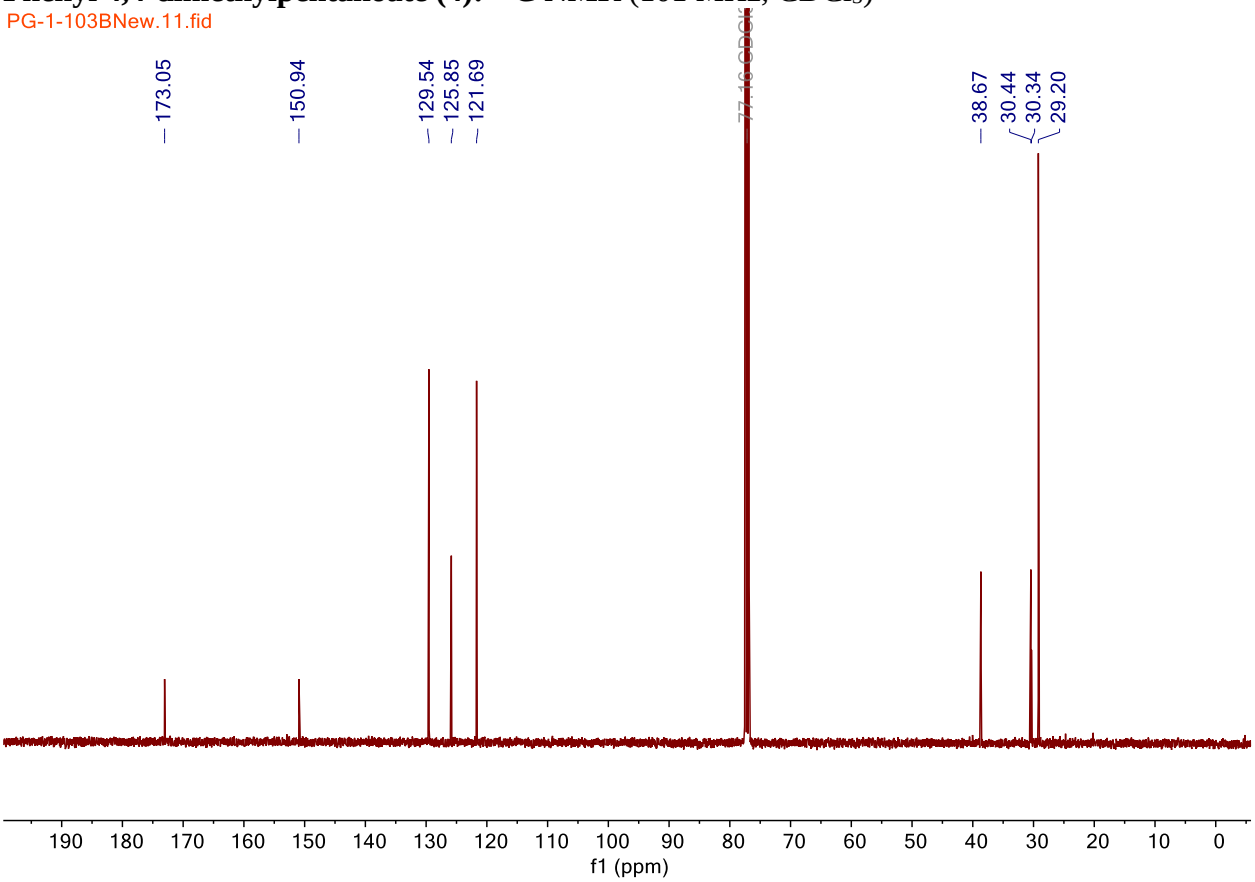
Benzyl 2,4,4-trimethylpentanoate (3): ^{13}C NMR (101 MHz, $CDCl_3$)



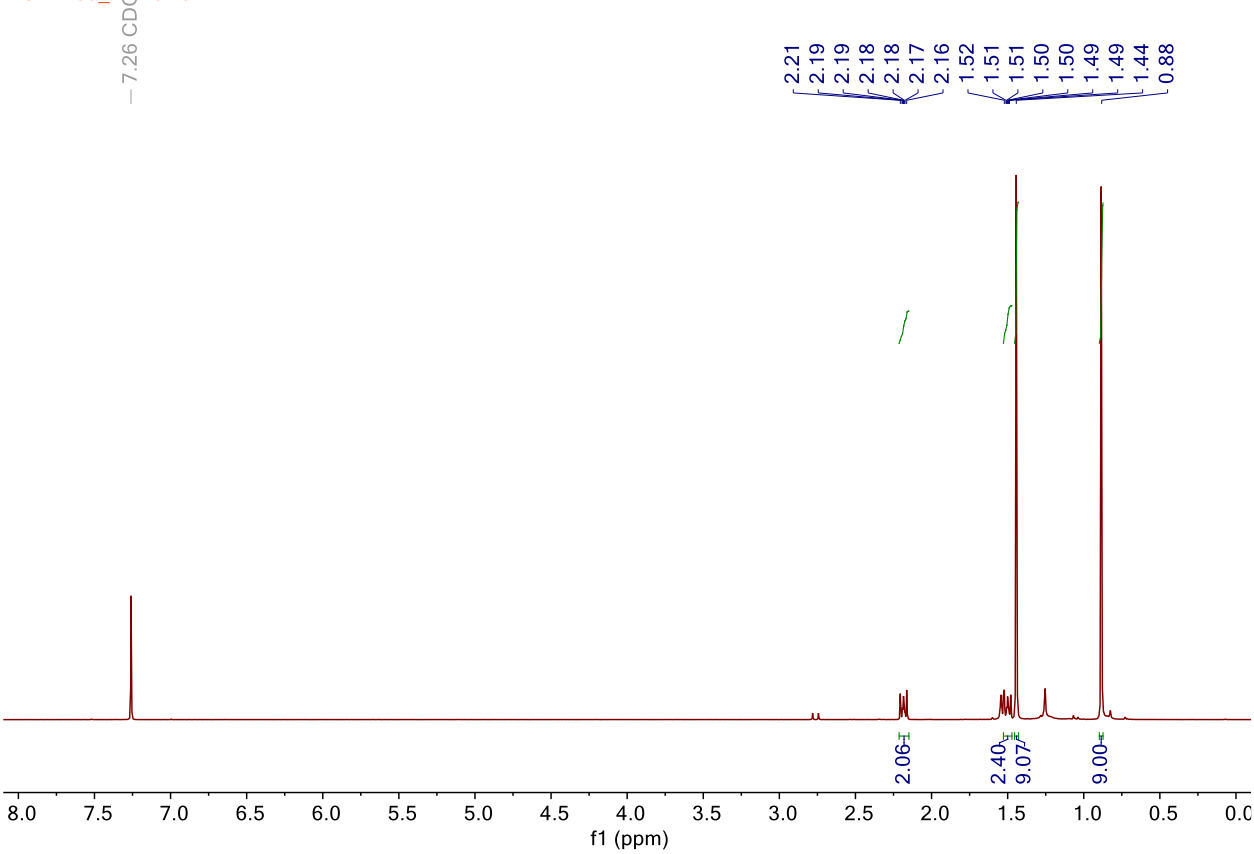
Phenyl 4,4-dimethylpentanoate (4): ^{1}H NMR (400 MHz, $CDCl_3$)



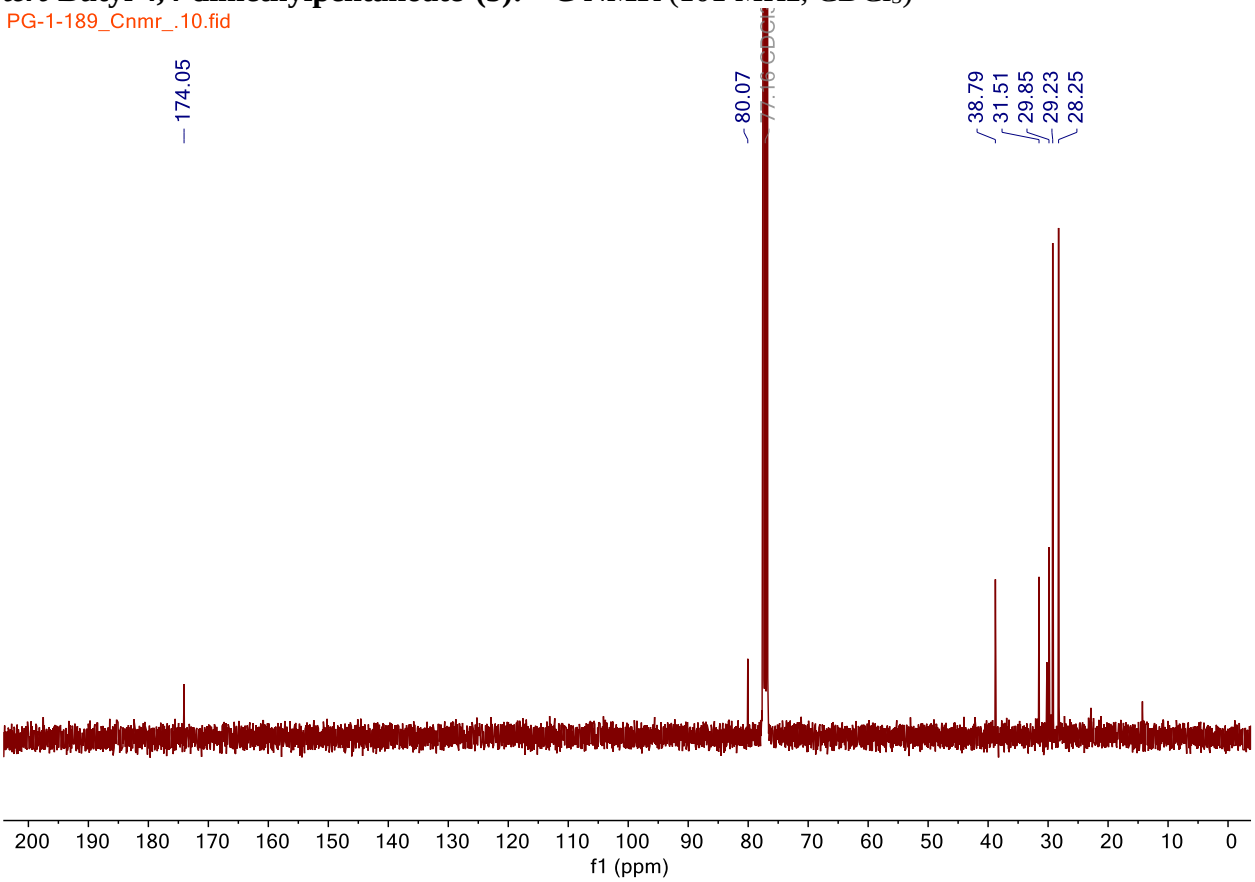
Phenyl 4,4-dimethylpentanoate (4): ^{13}C NMR (101 MHz, $CDCl_3$)



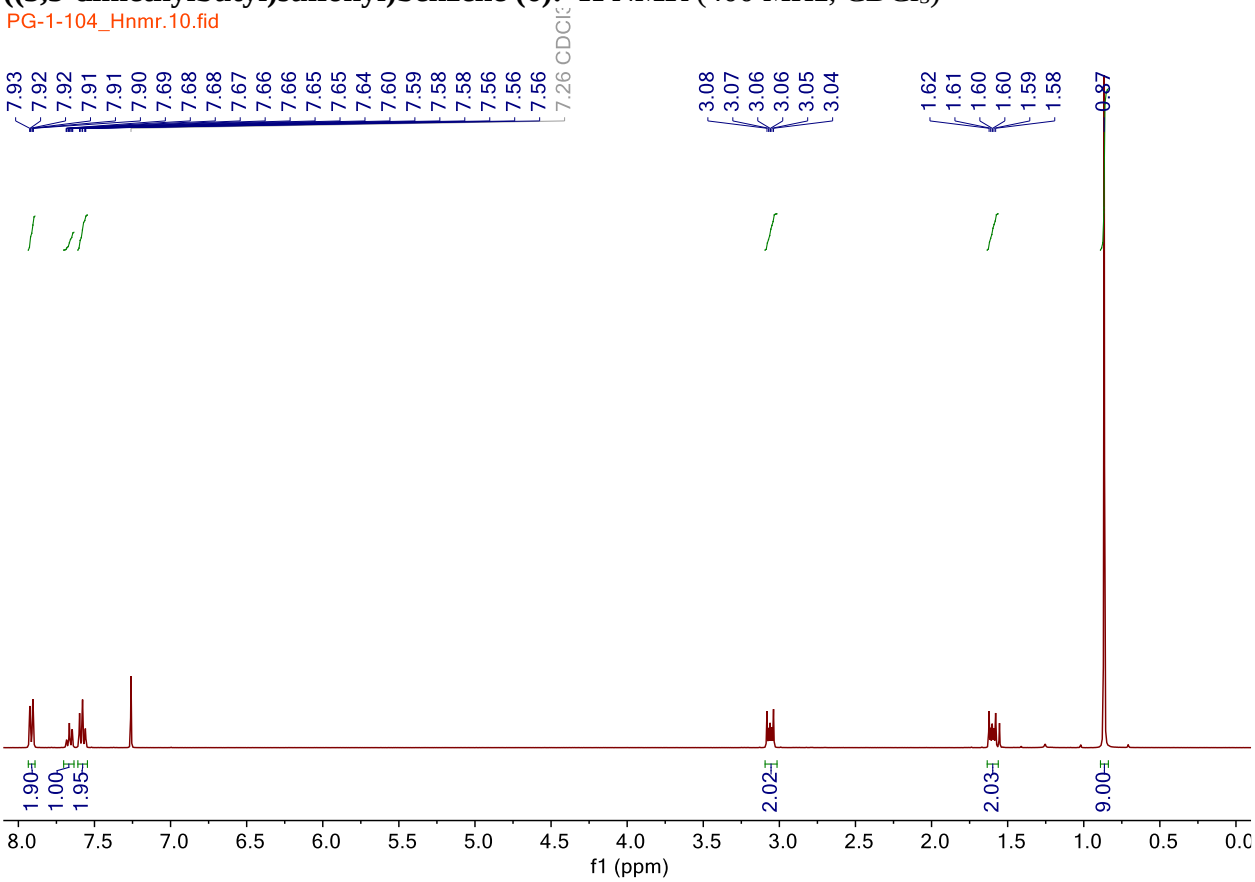
***tert*-Butyl 4,4-dimethylpentanoate (5): ^{1}H NMR** (400 MHz, $CDCl_3$)



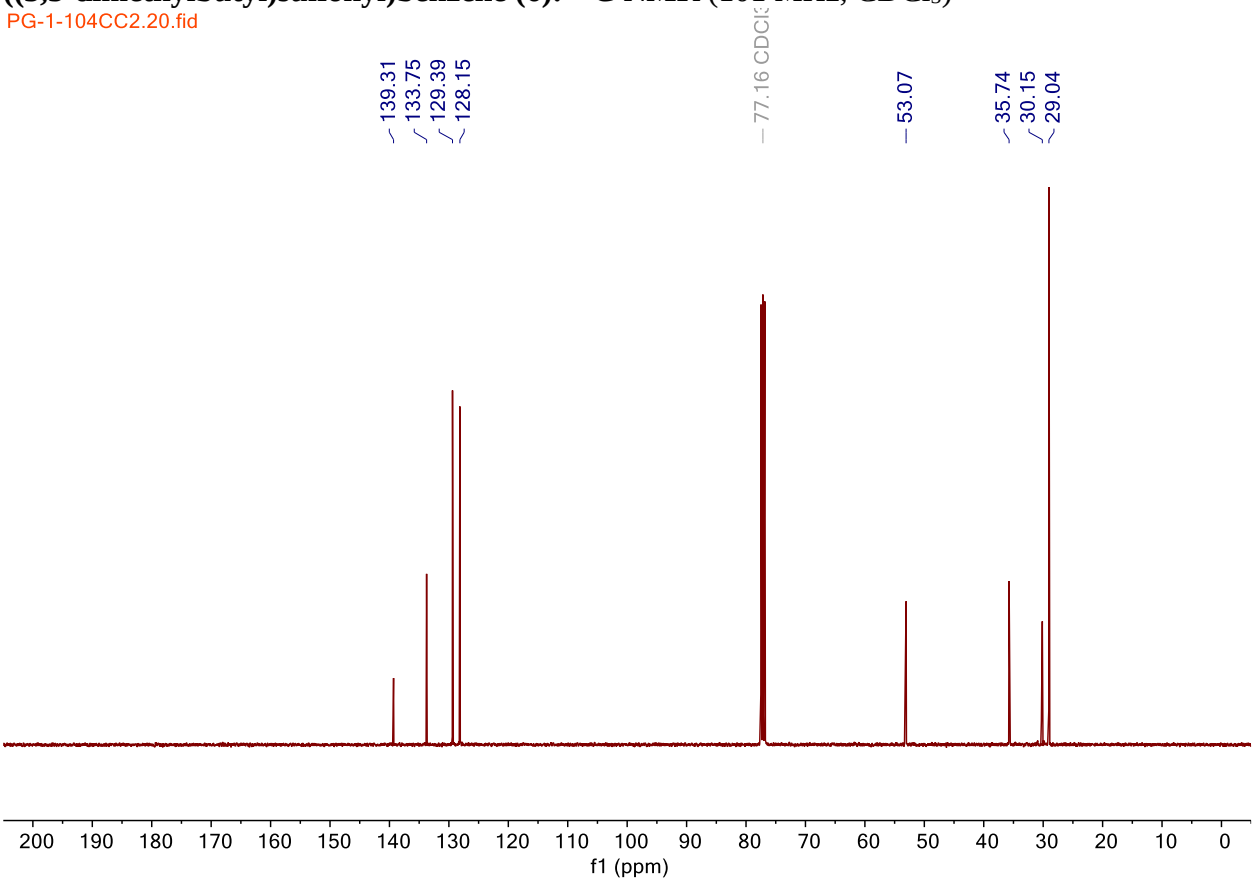
***tert*-Butyl 4,4-dimethylpentanoate (5): ^{13}C NMR** (101 MHz, $CDCl_3$)



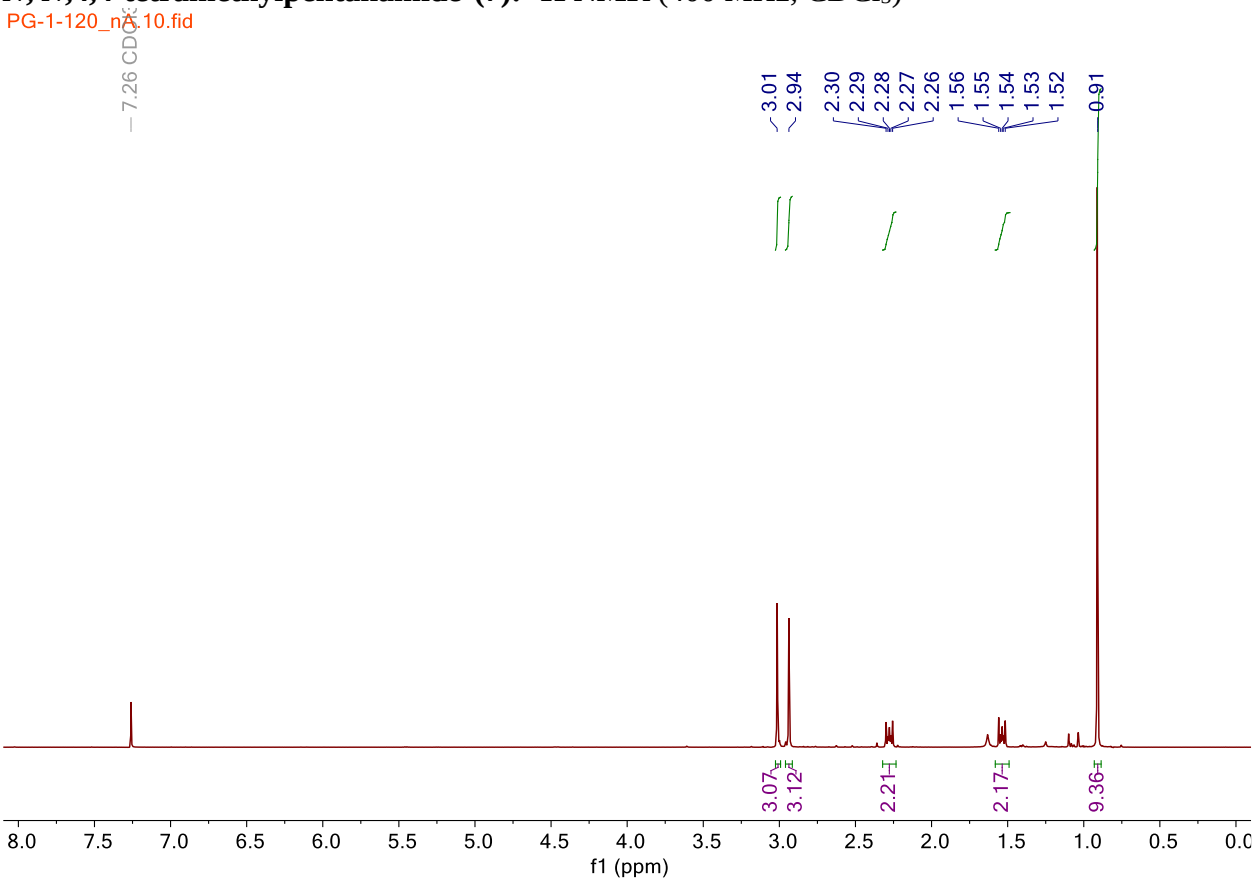
((3,3-dimethylbutyl)sulfonyl)benzene (6): ^{1}H NMR (400 MHz, $CDCl_3$)



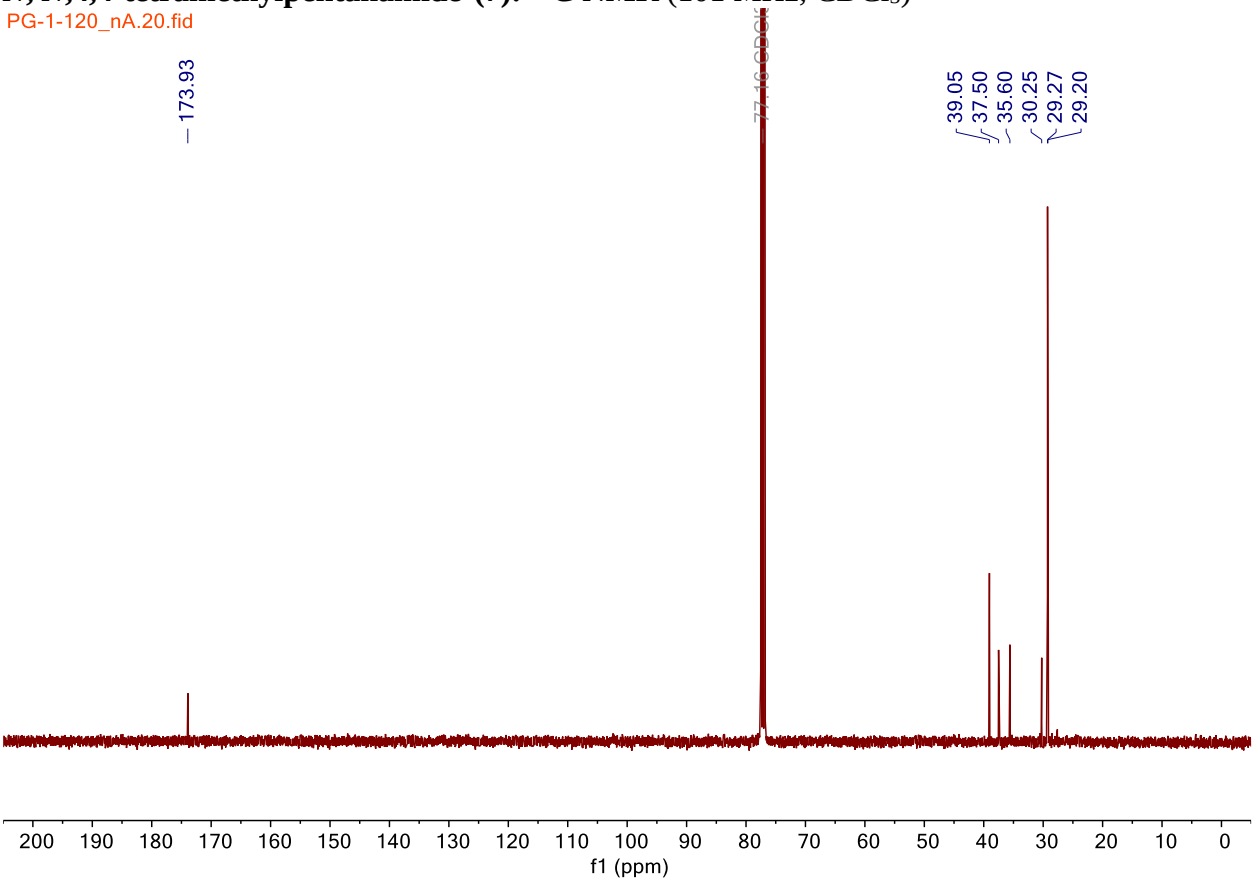
((3,3-dimethylbutyl)sulfonyl)benzene (6): ^{13}C NMR (101 MHz, $CDCl_3$)



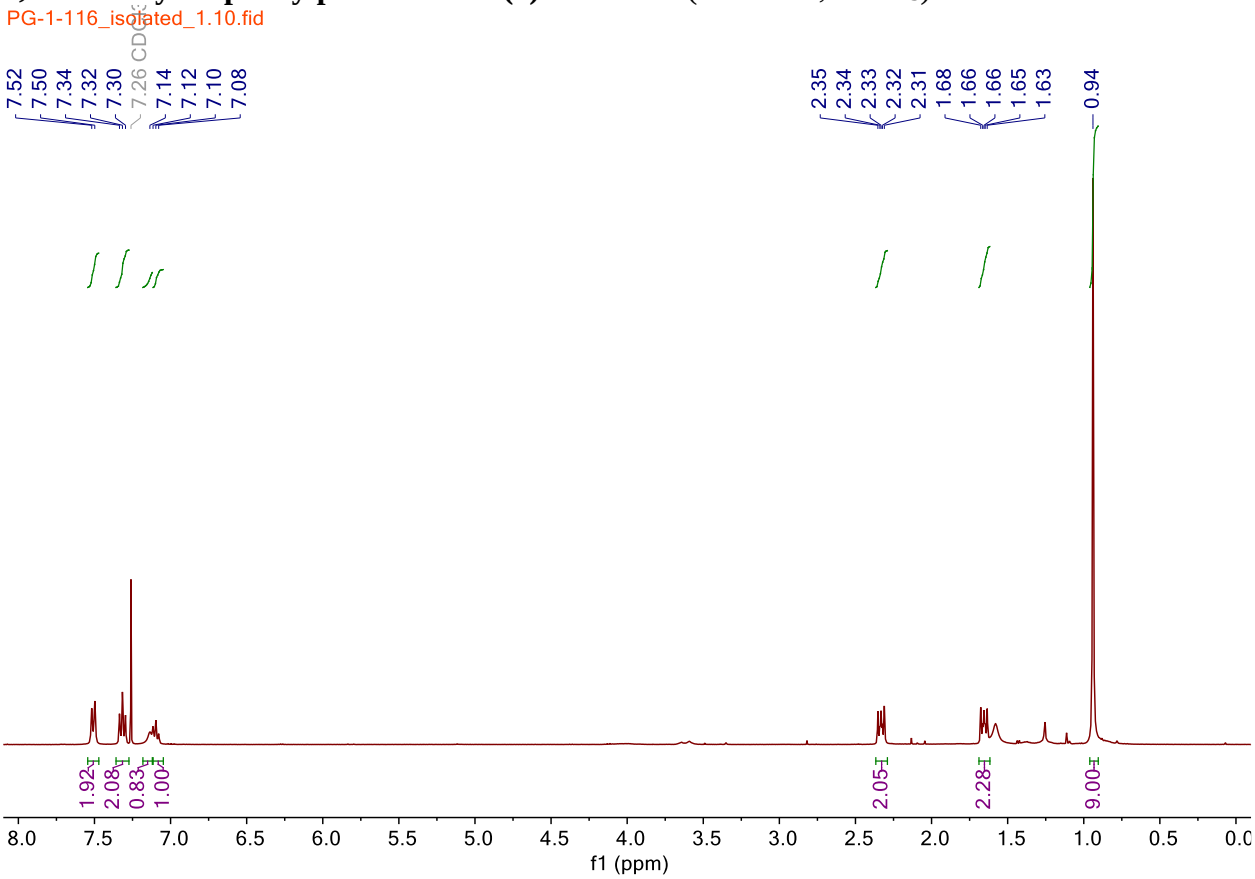
***N, N*,4,4-tetramethylpentanamide (7): ^{1}H NMR** (400 MHz, $CDCl_3$)



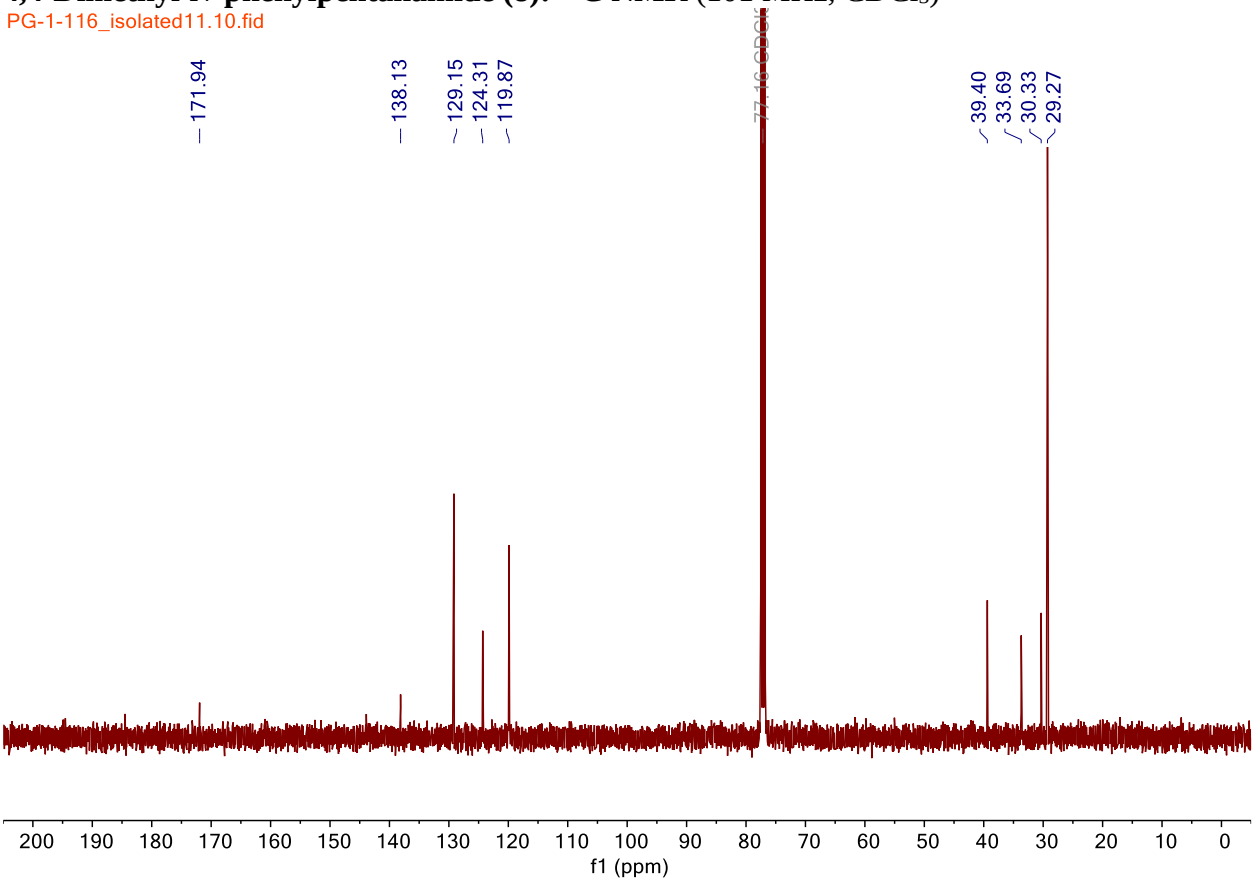
***N*, *N*,4,4-tetramethylpentanamide (7): ^{13}C NMR** (101 MHz, $CDCl_3$)



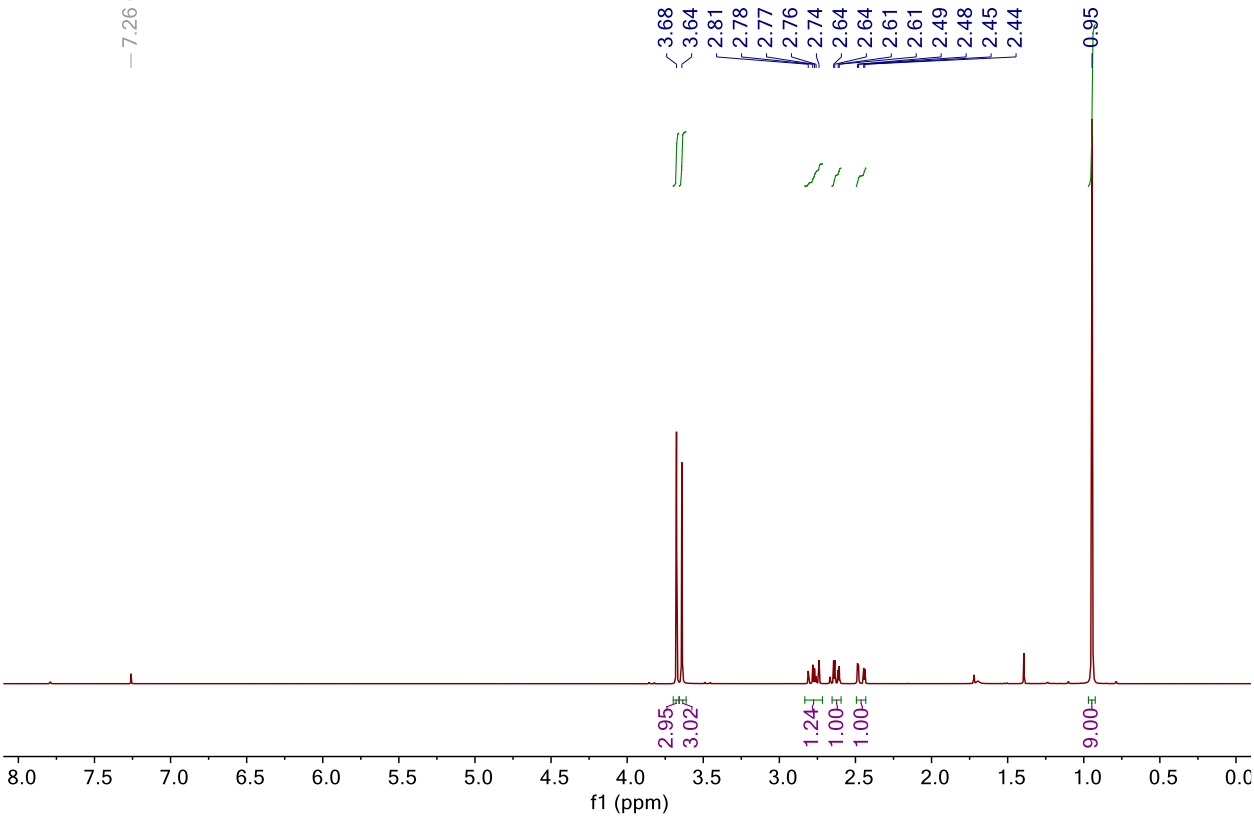
4,4-Dimethyl-*N*-phenylpentanamide (8): ^{1}H NMR (400 MHz, $CDCl_3$)



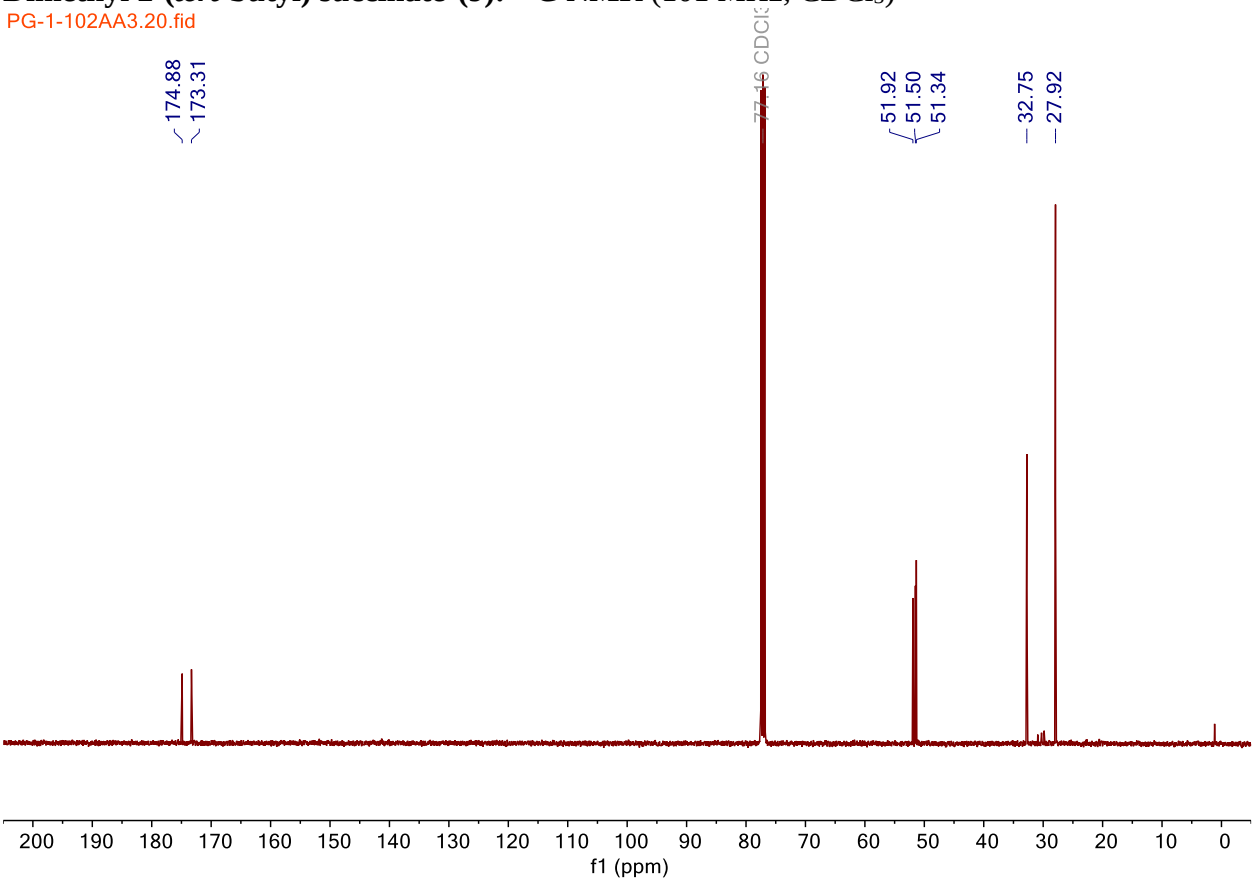
4,4-Dimethyl-*N*-phenylpentanamide (8): ^{13}C NMR (101 MHz, $CDCl_3$)



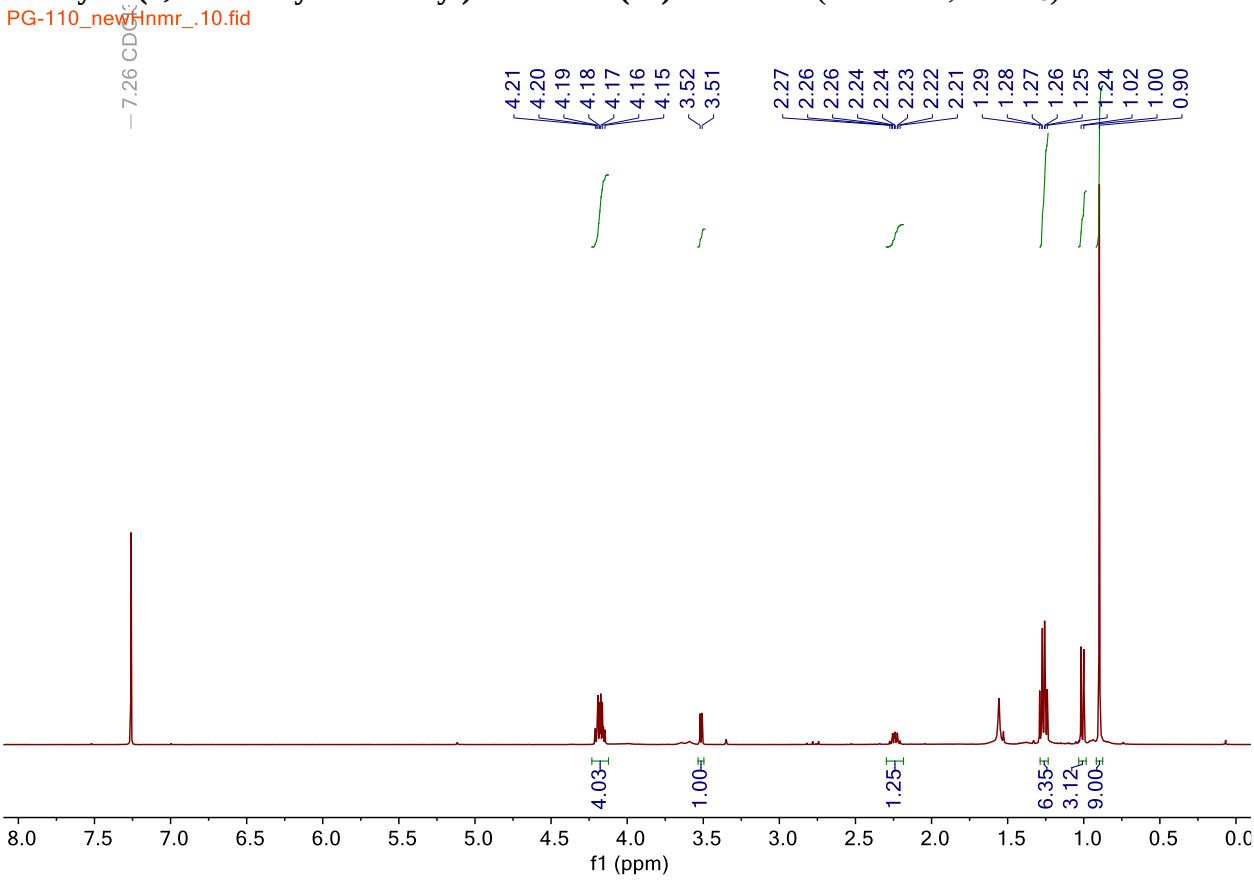
Dimethyl 2-(*tert*-butyl) succinate (9): ^{1}H NMR (400 MHz, $CDCl_3$)



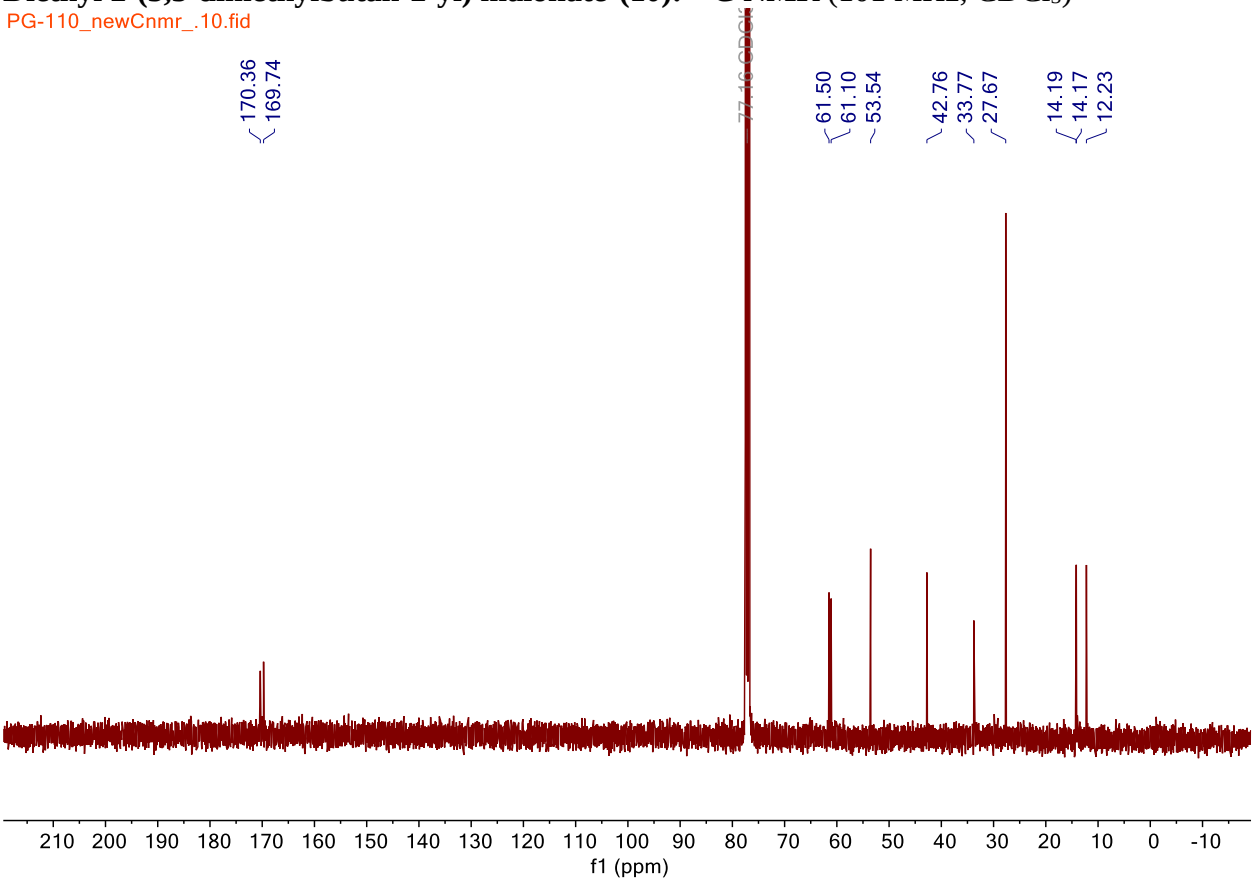
Dimethyl 2-(*tert*-butyl) succinate (9): ^{13}C NMR (101 MHz, $CDCl_3$)



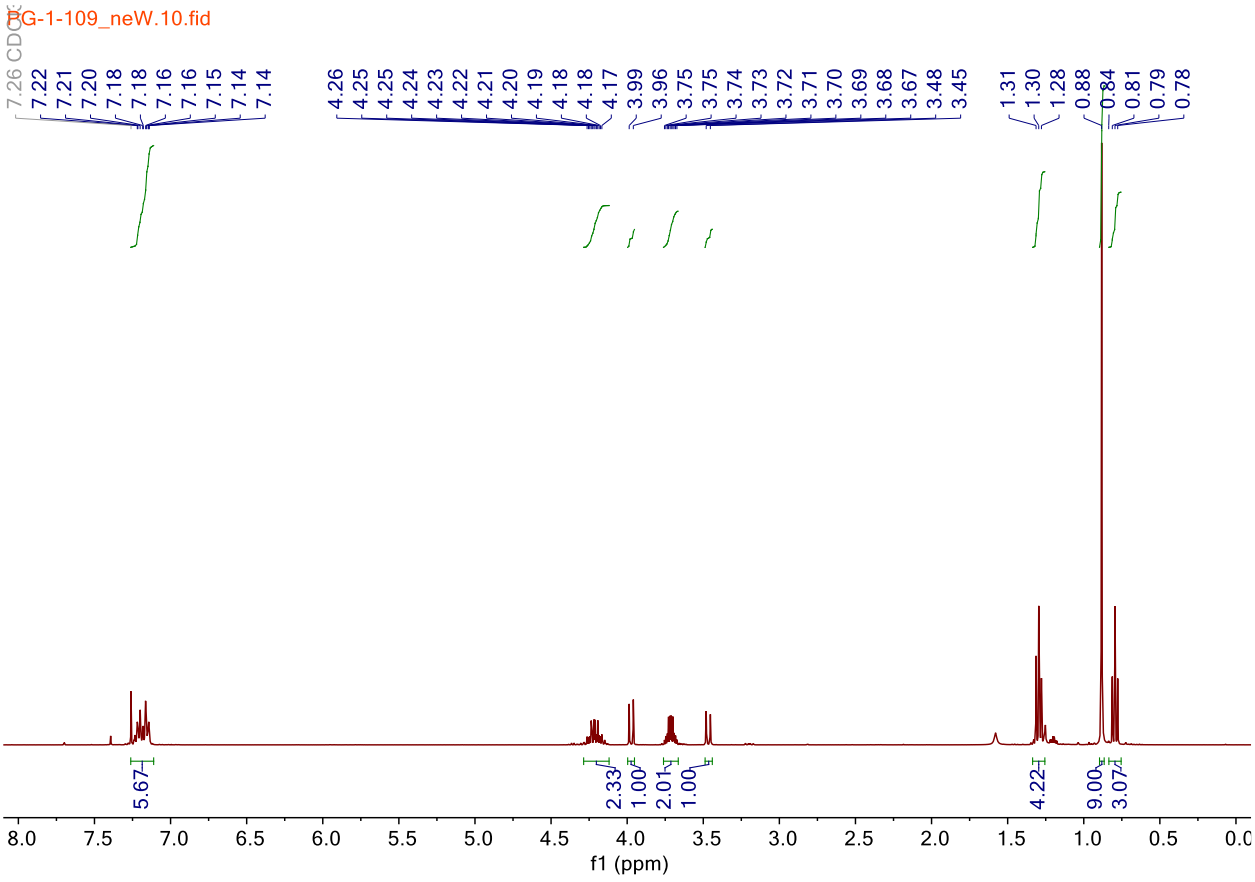
Diethyl 2-(3,3-dimethylbutan-2-yl) malonate (10): ^{1}H NMR (400 MHz, $CDCl_3$)



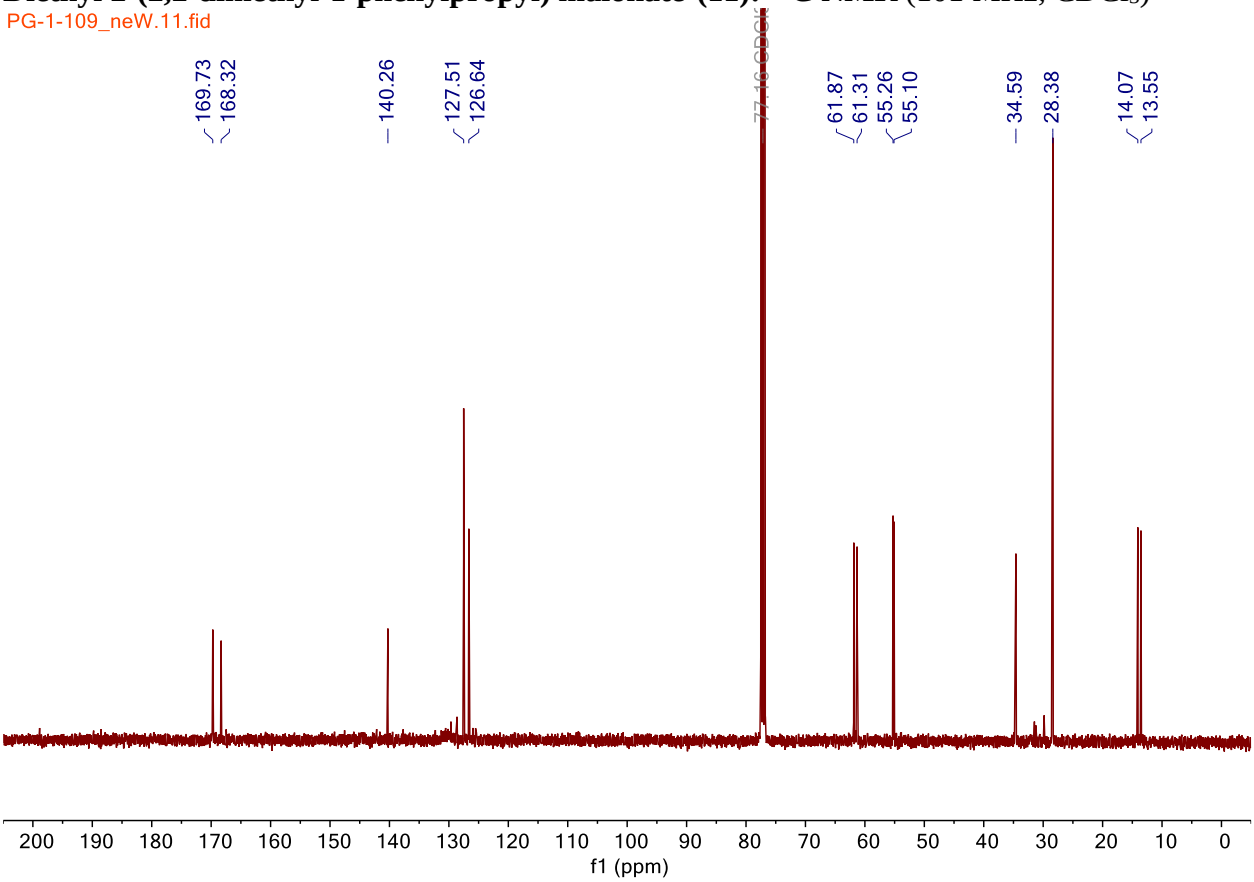
Diethyl 2-(3,3-dimethylbutan-2-yl) malonate (10): ^{13}C NMR (101 MHz, $CDCl_3$)



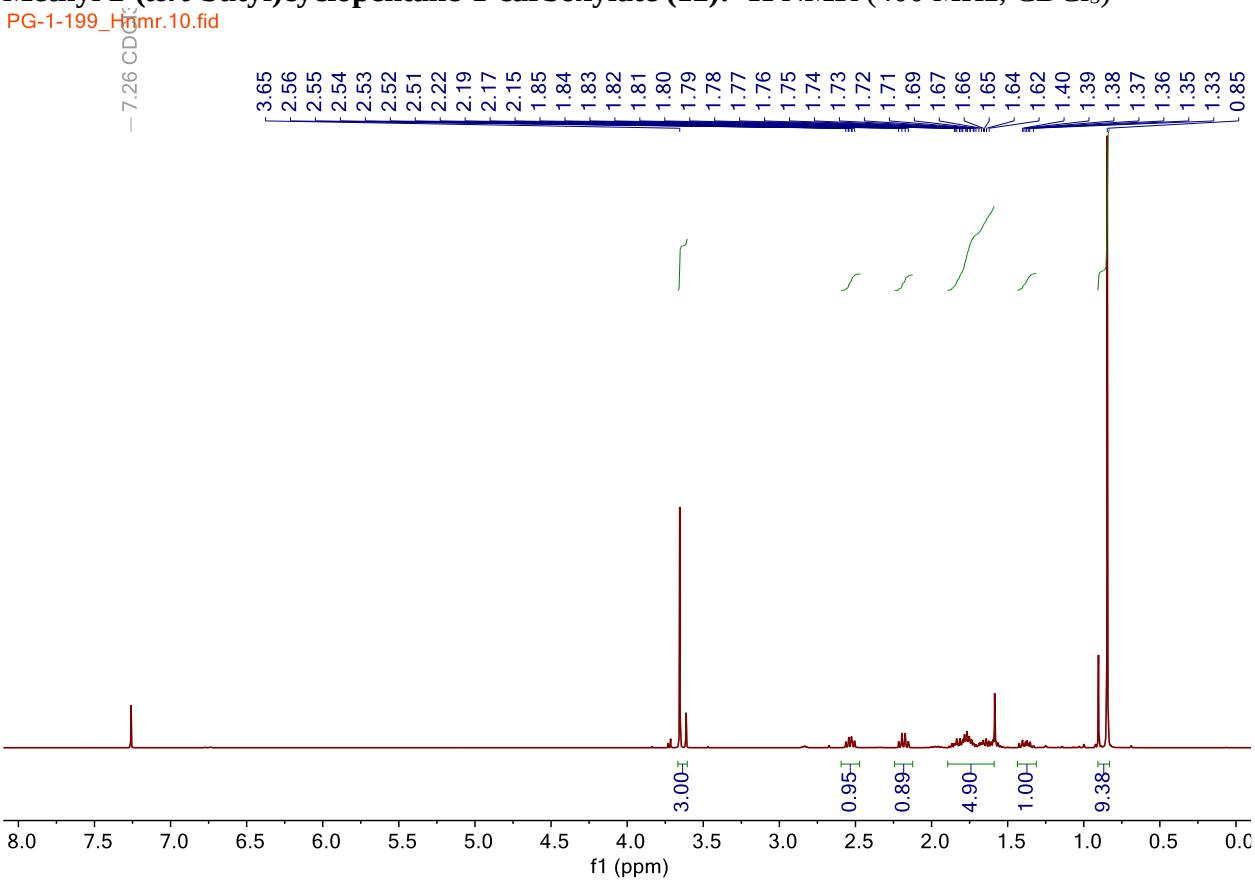
Diethyl 2-(2,2-dimethyl-1-phenylpropyl) malonate (11): ^{1}H NMR (400 MHz, $CDCl_3$)



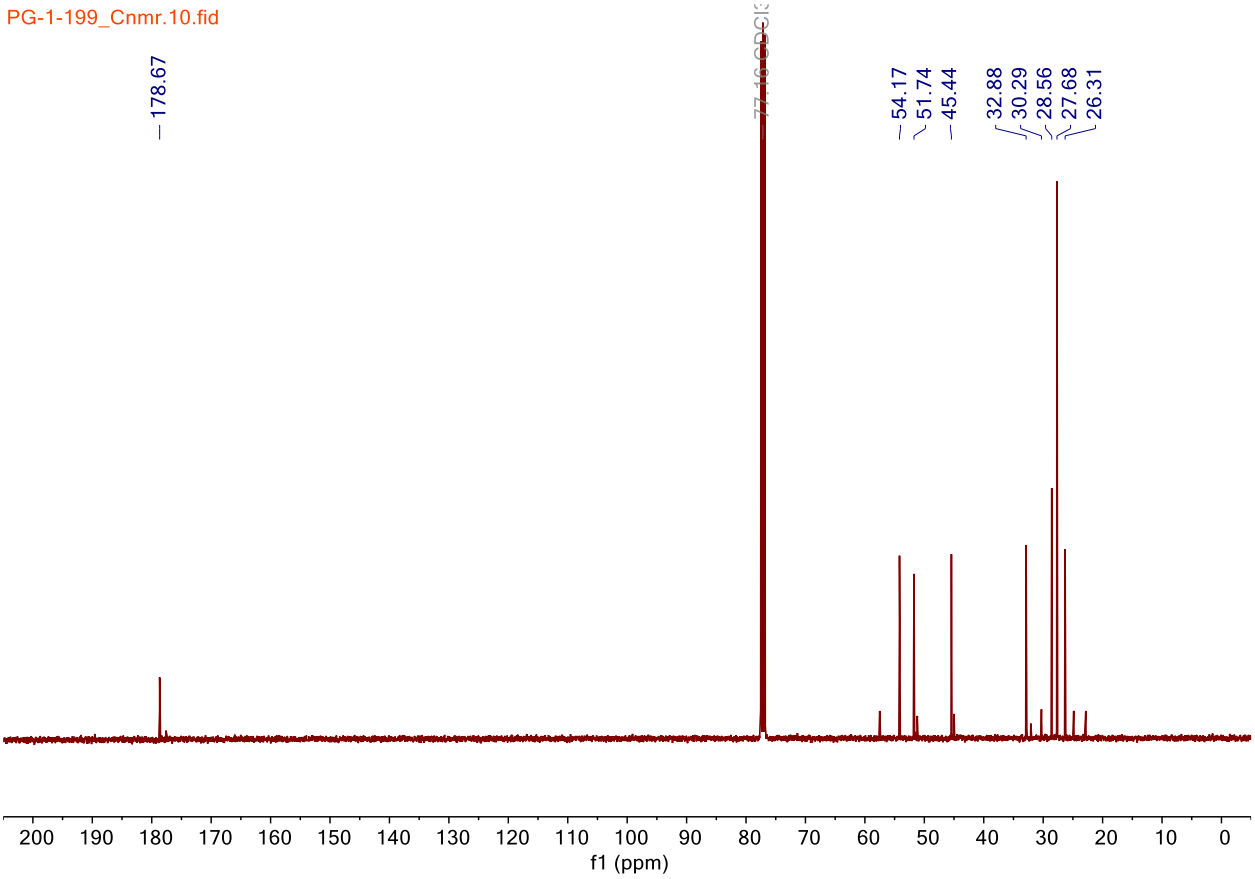
Diethyl 2-(2,2-dimethyl-1-phenylpropyl) malonate (11): ^{13}C NMR (101 MHz, $CDCl_3$)



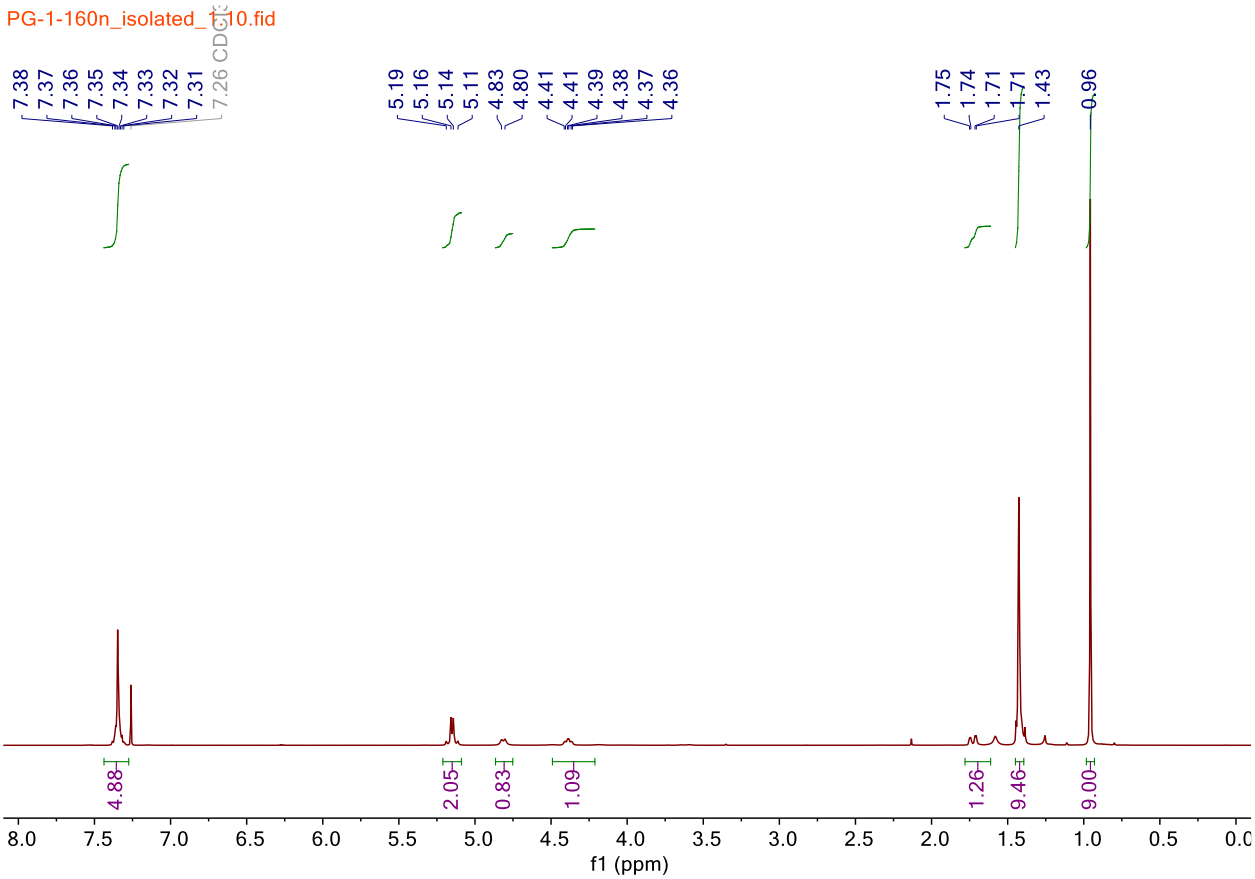
Methyl 2-(*tert*-butyl)cyclopentane-1-carboxylate (12): ^{1}H NMR (400 MHz, $CDCl_3$)



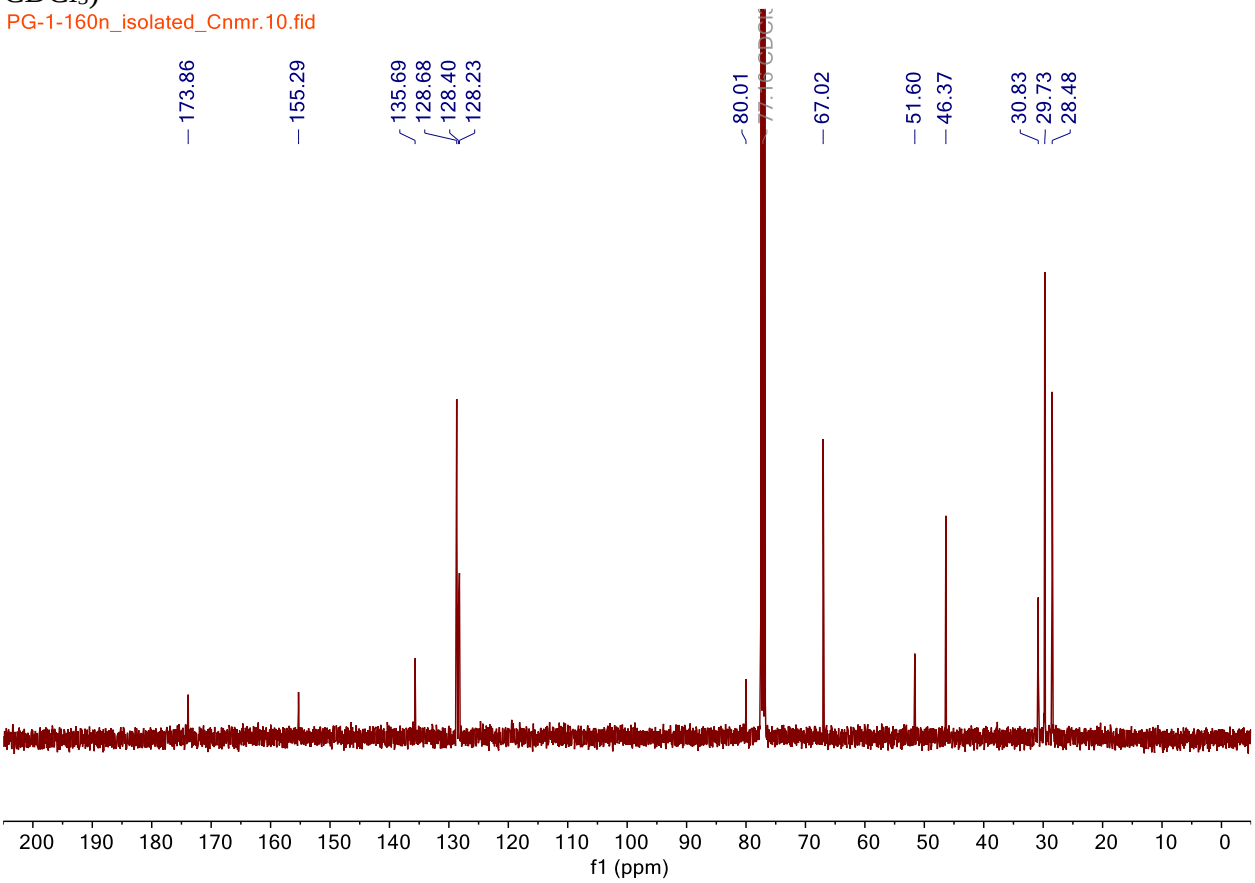
Methyl 2-(*tert*-butyl)cyclopentane-1-carboxylate (12): ^{13}C NMR (101 MHz, $CDCl_3$)



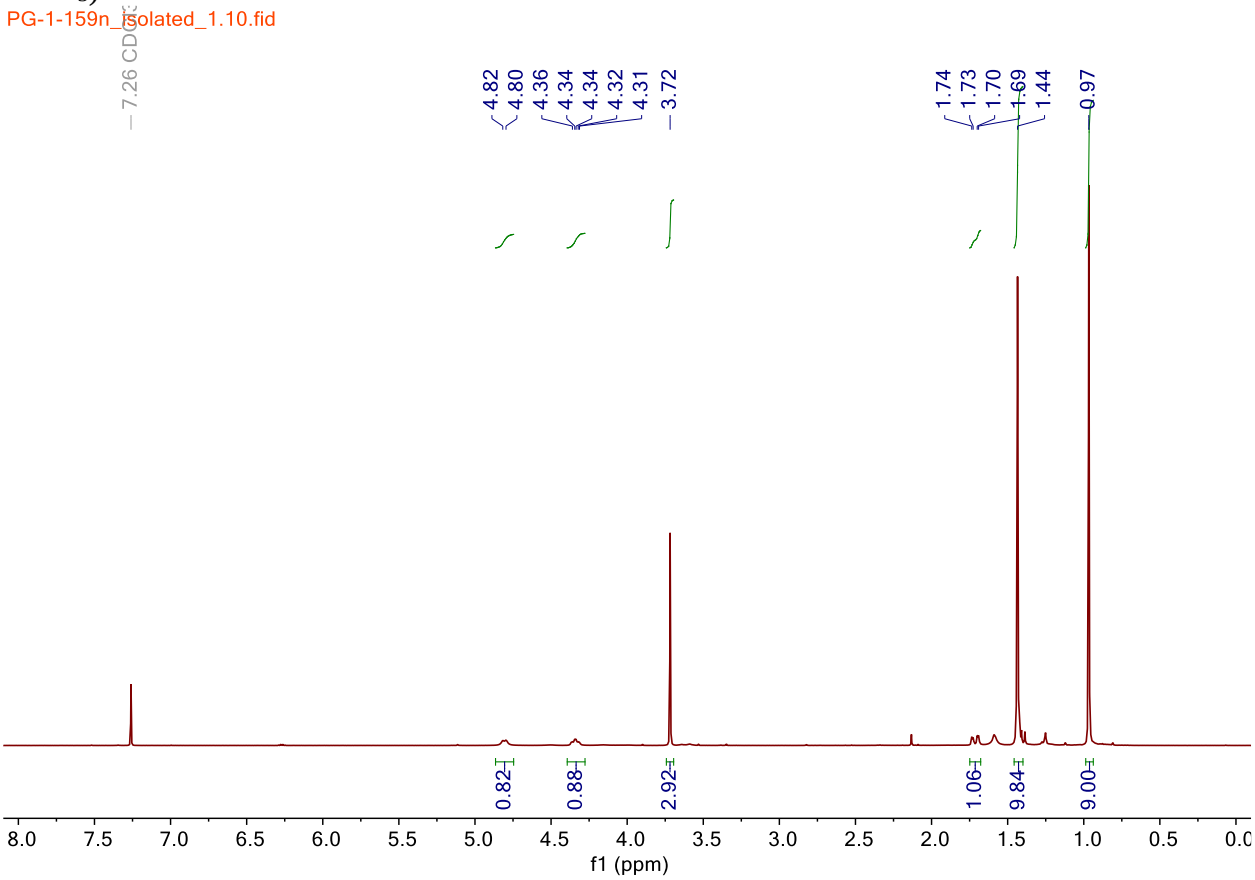
Benzyl 2-((*tert*-butoxycarbonyl)amino)-4,4-dimethylpentanoate (13): ^{1}H NMR (400 MHz, $CDCl_3$)



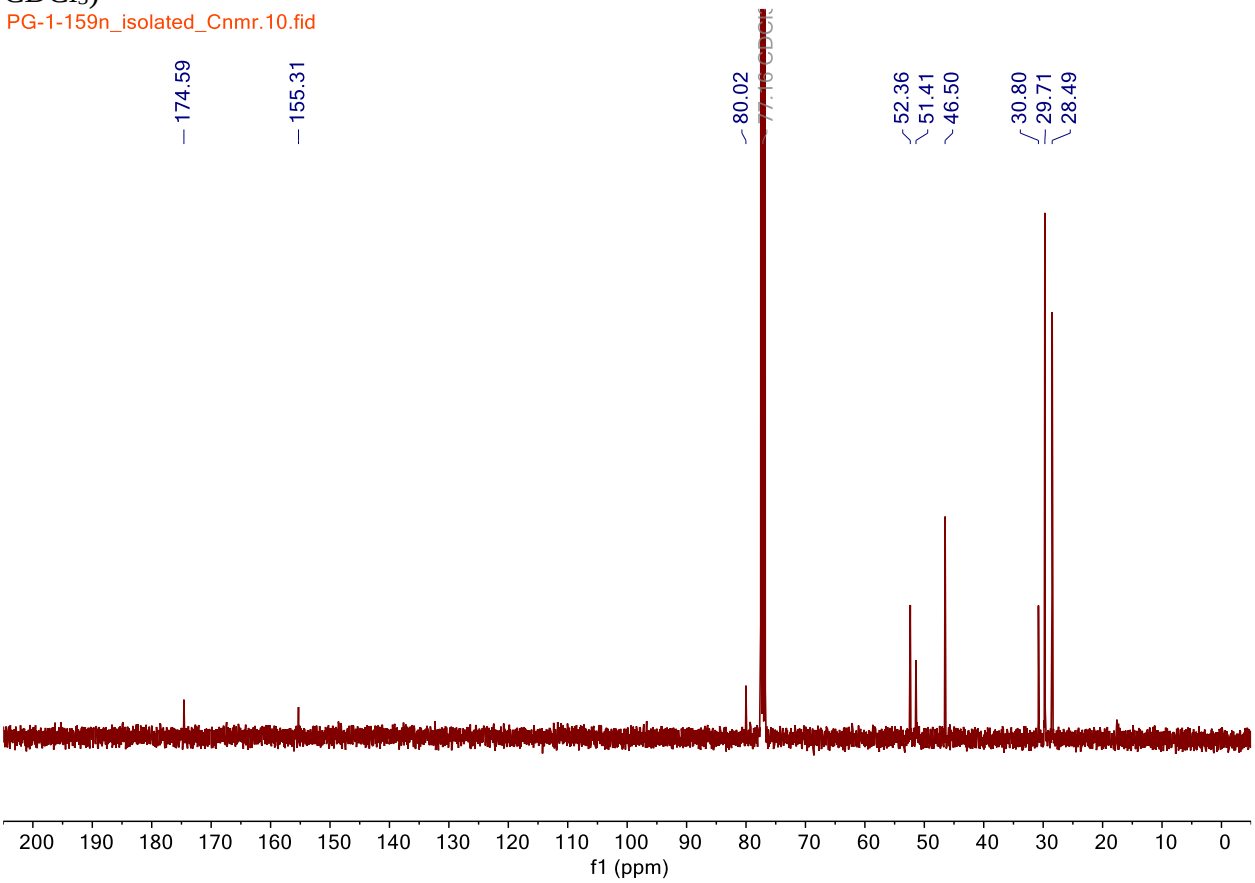
Benzyl 2-((*tert*-butoxycarbonyl)amino)-4,4-dimethylpentanoate (13): ^{13}C NMR (101 MHz, $CDCl_3$)



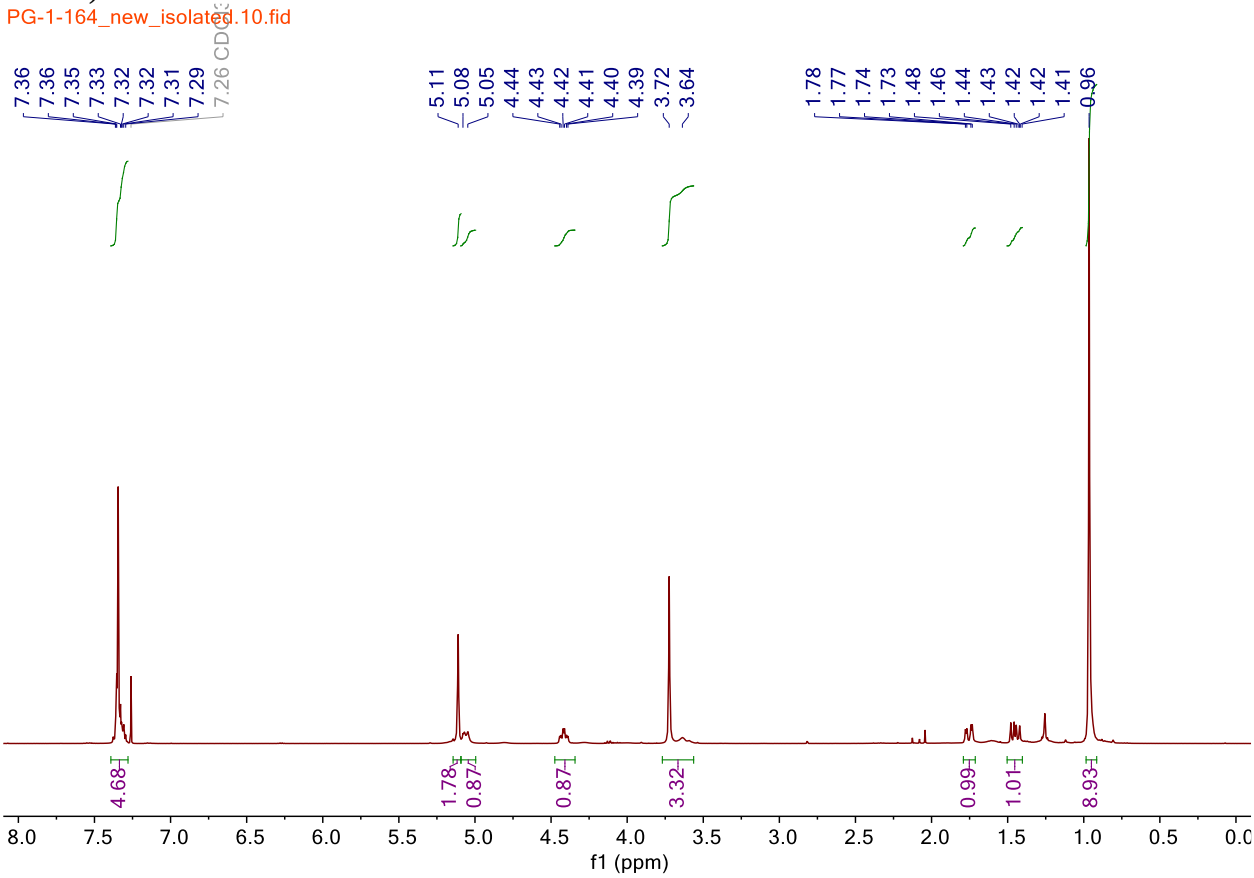
Methyl 2-((*tert*-butoxycarbonyl)amino)-4,4-dimethylpentanoate (14): ^{1}H NMR (400 MHz, $CDCl_3$)



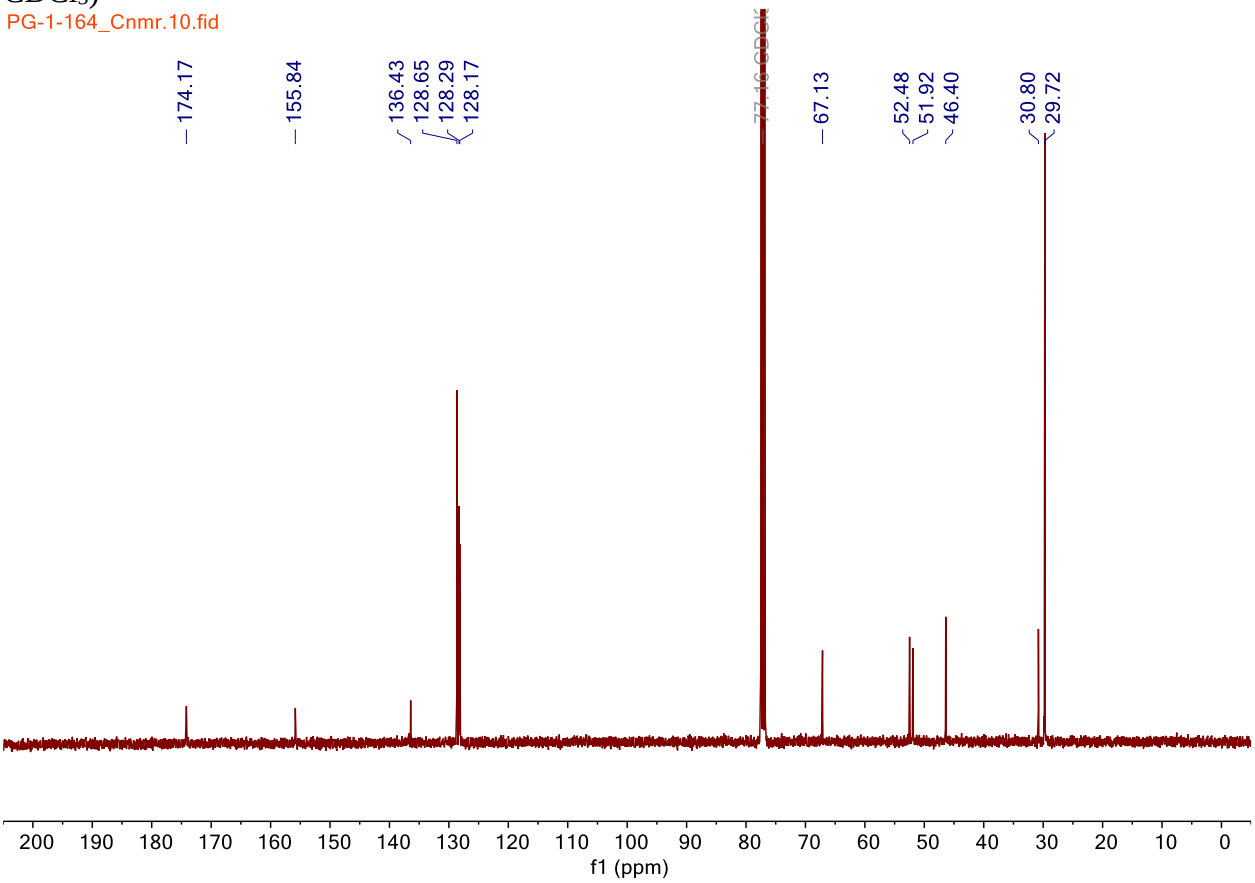
Methyl 2-((*tert*-butoxycarbonyl)amino)-4,4-dimethylpentanoate (14): ^{13}C NMR (101 MHz, $CDCl_3$)



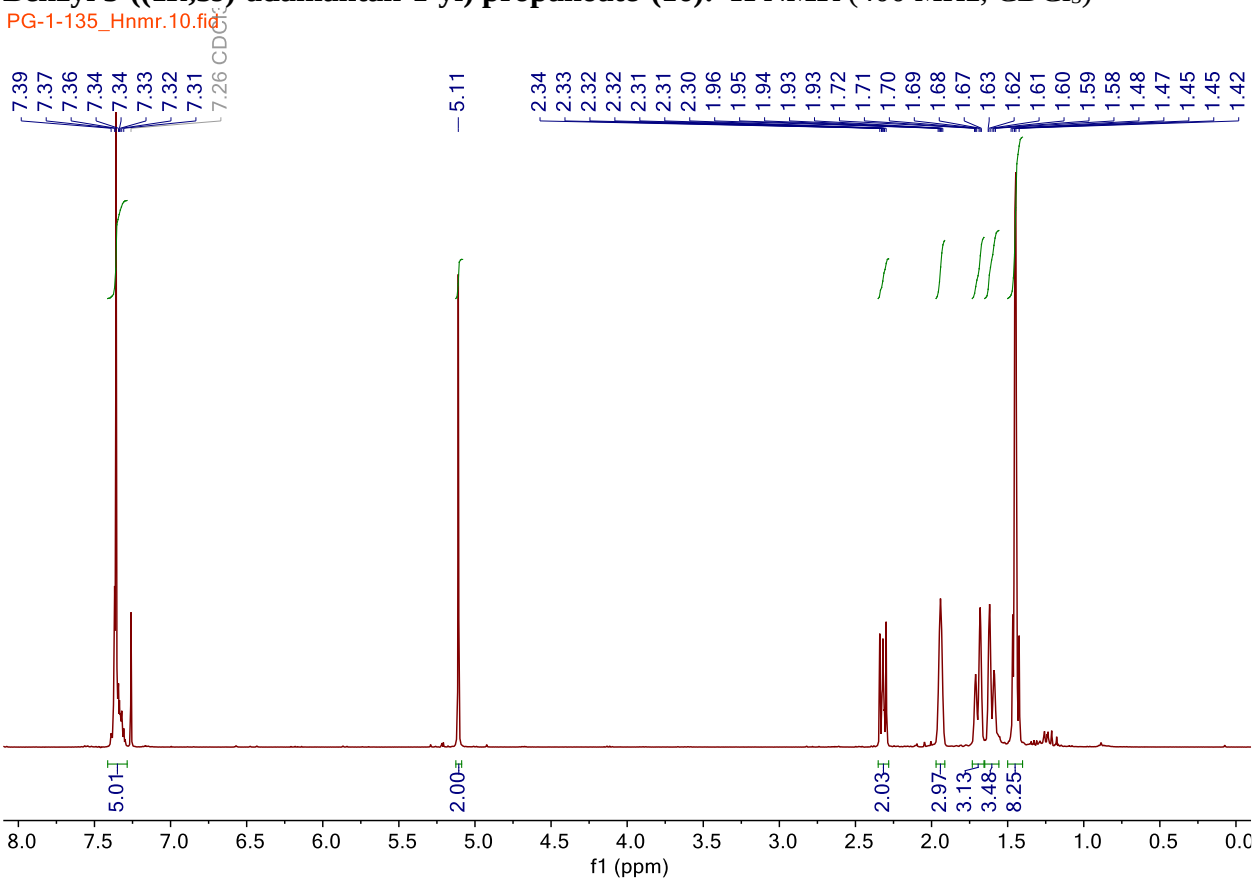
Methyl 2-(((benzyloxy)carbonyl)amino)-4,4-dimethylpentanoate (15): ^{1}H NMR (400 MHz, $CDCl_3$)



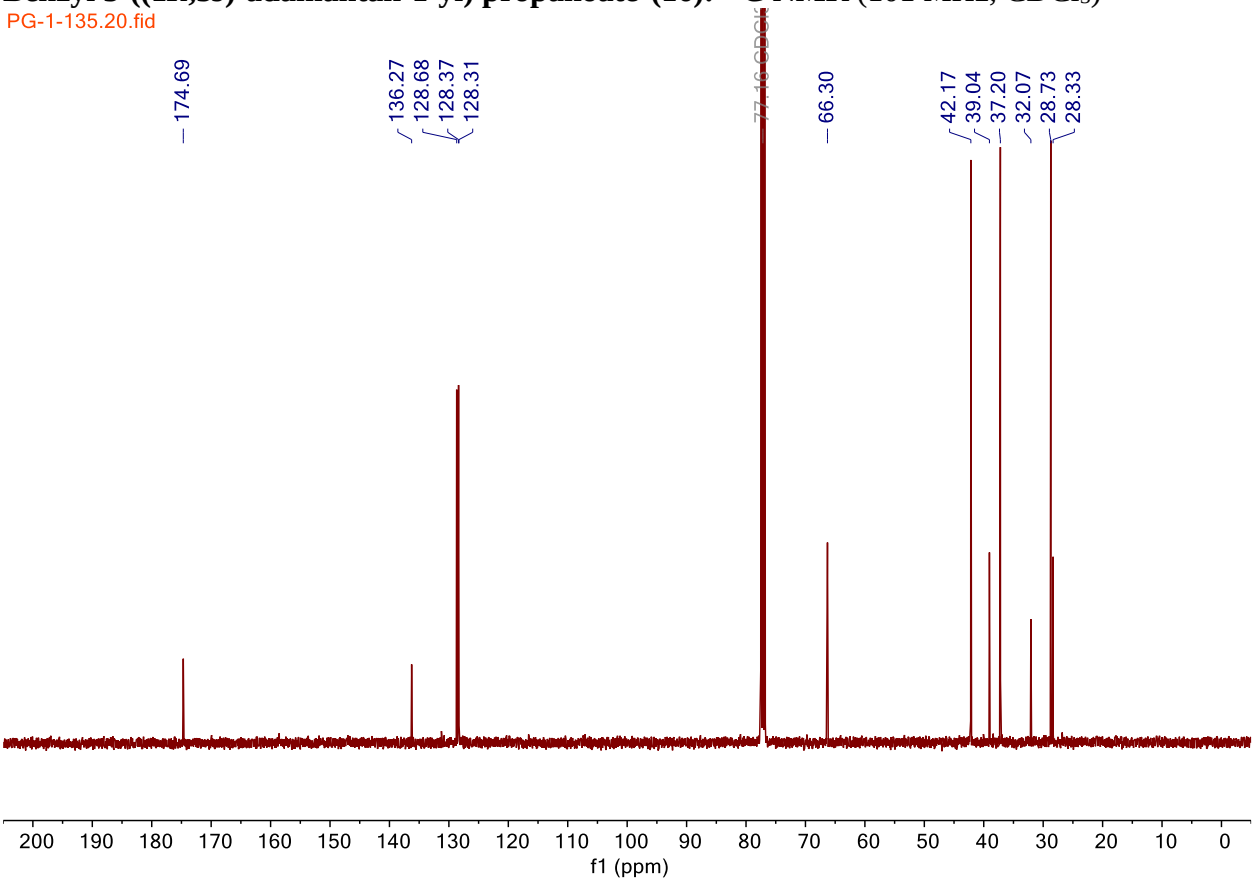
Methyl 2-(((benzyloxy)carbonyl)amino)-4,4-dimethylpentanoate (15): ^{13}C NMR (101 MHz, $CDCl_3$)



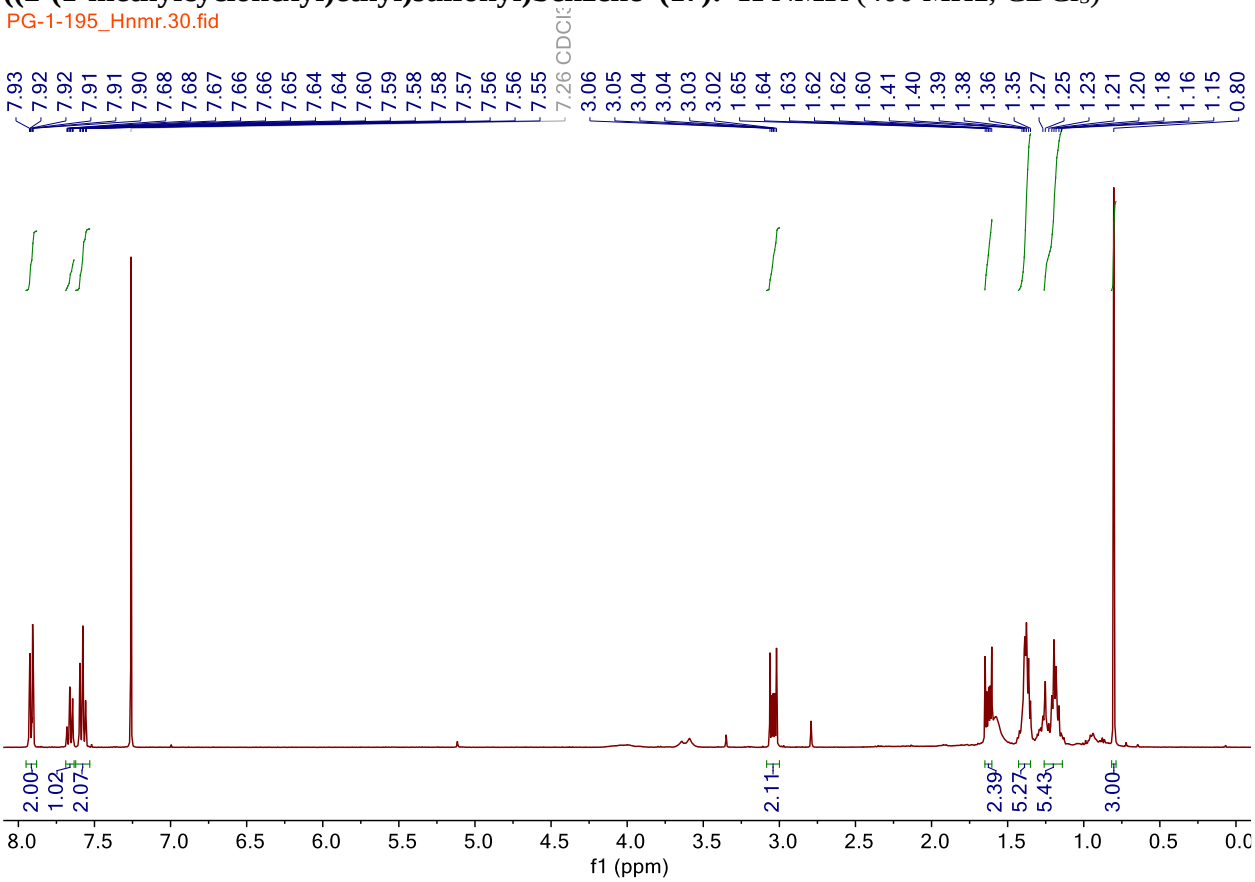
Benzyl 3-((1*R*,3*s*)-adamantan-1-yl) propanoate (16): ^{1}H NMR (400 MHz, $CDCl_3$)



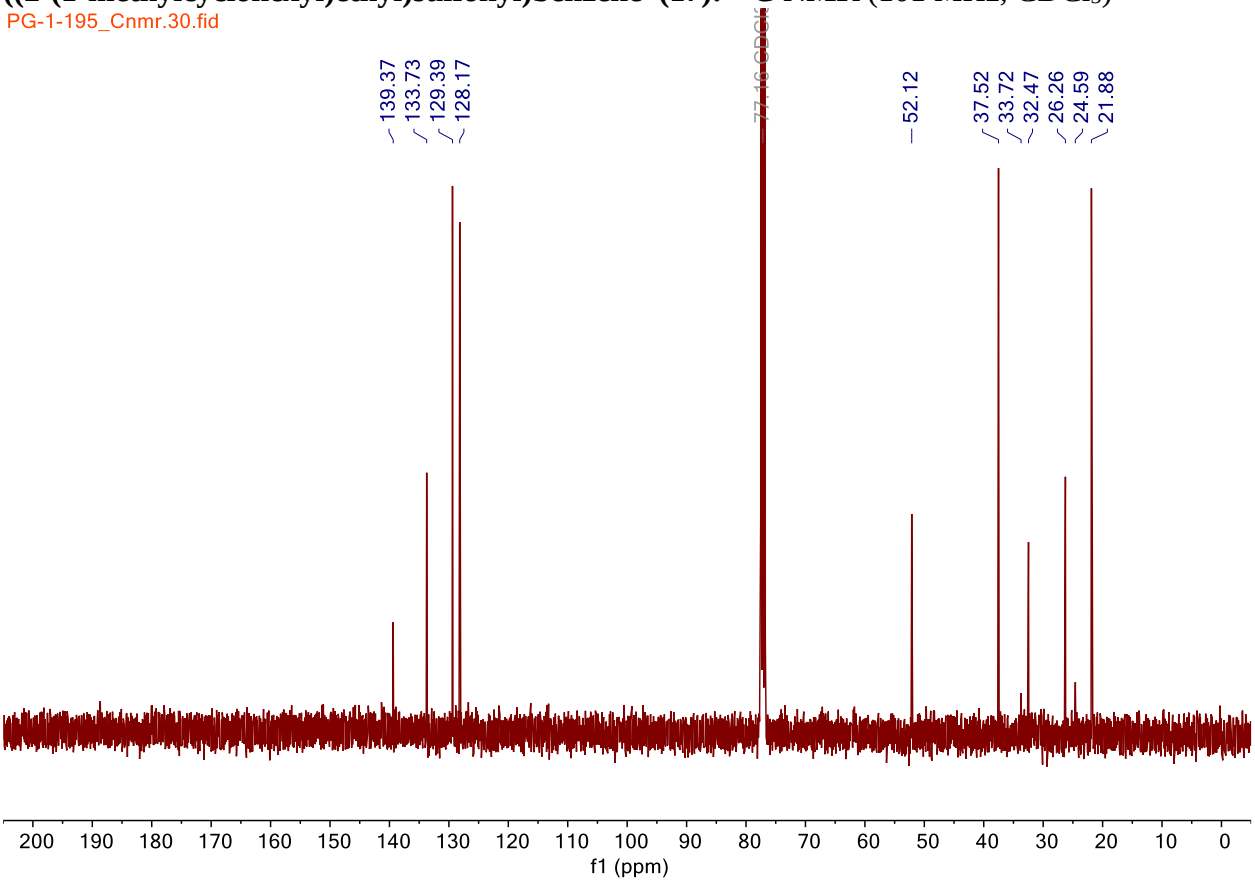
Benzyl 3-((1*R*,3*s*)-adamantan-1-yl) propanoate (16): ^{13}C NMR (101 MHz, $CDCl_3$)



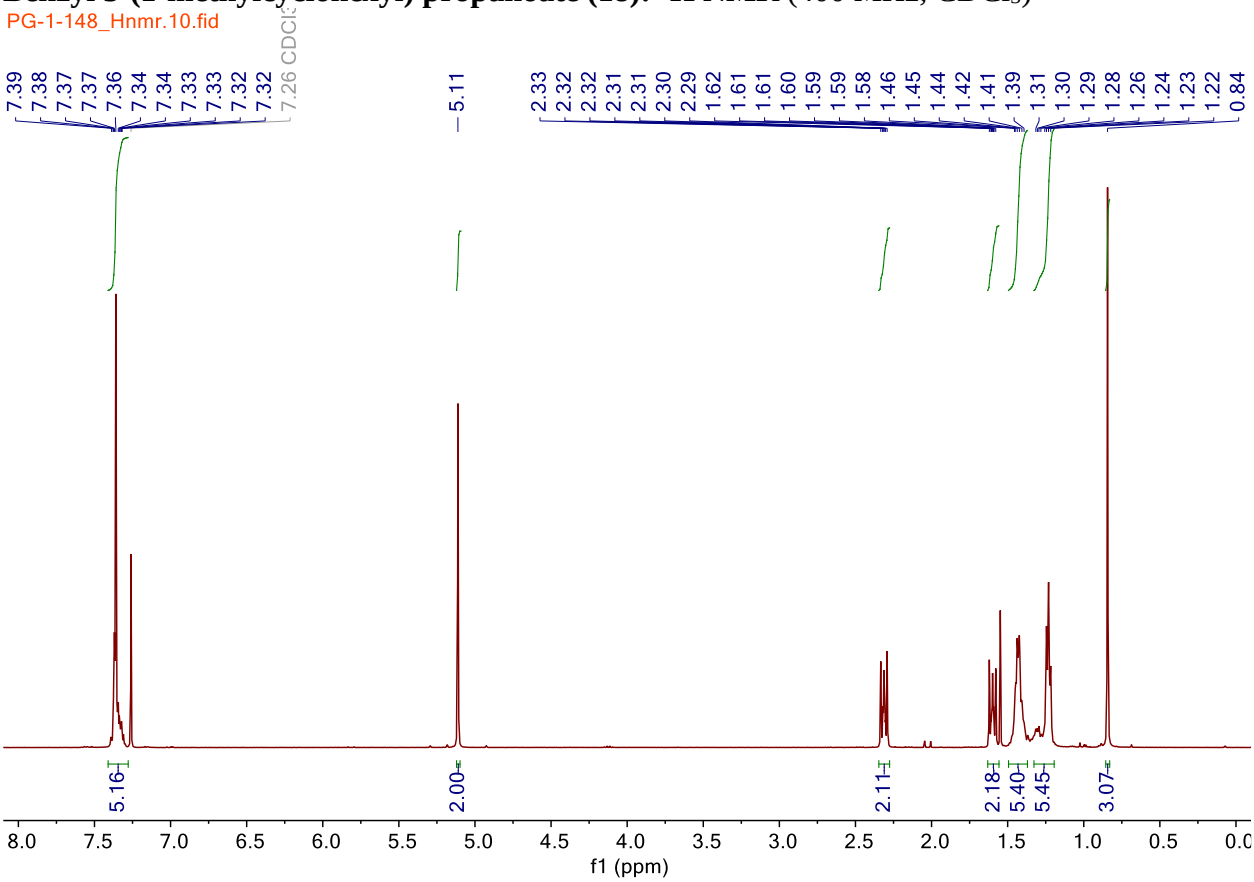
((2-(1-methylcyclohexyl)ethyl)sulfonyl)benzene (17): ^{1}H NMR (400 MHz, $CDCl_3$)



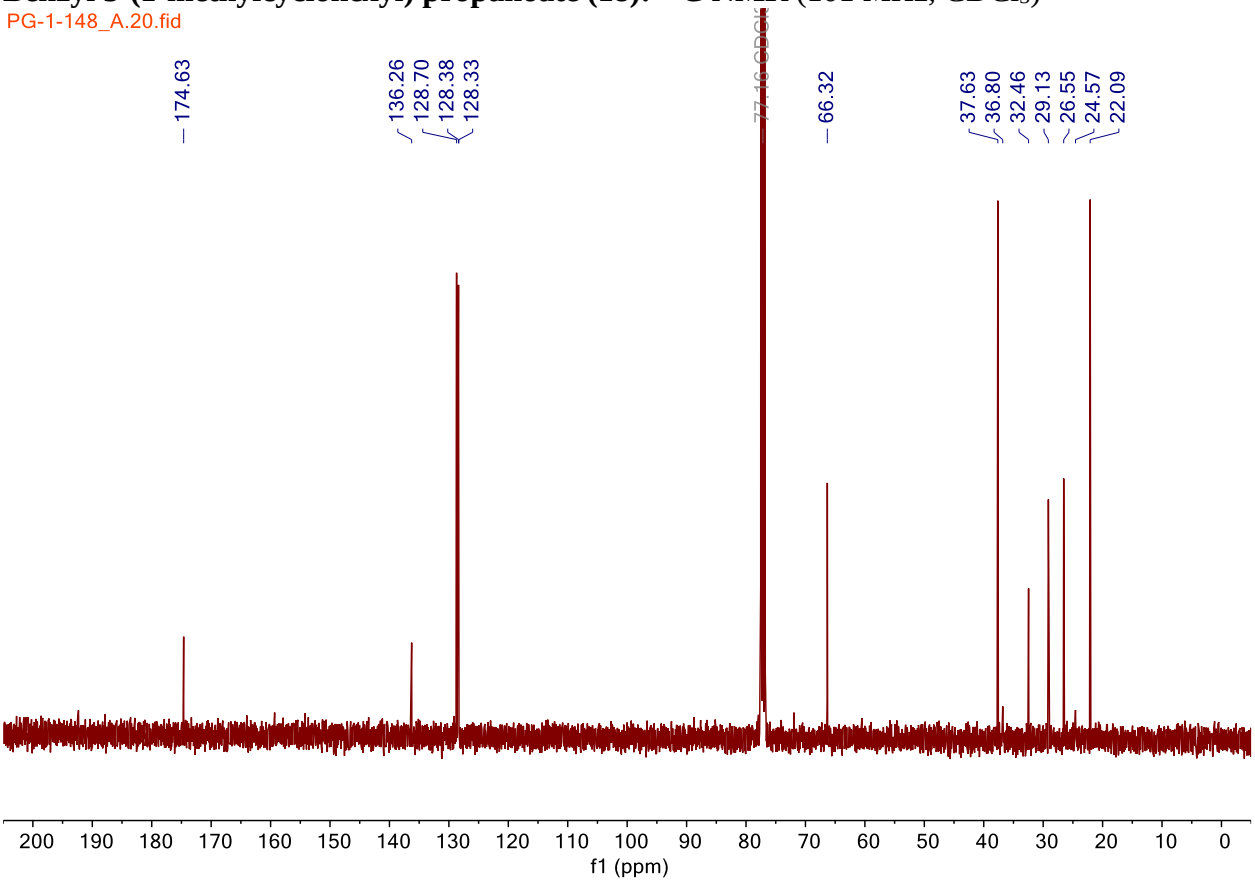
((2-(1-methylcyclohexyl)ethyl)sulfonyl)benzene (17): ^{13}C NMR (101 MHz, $CDCl_3$)



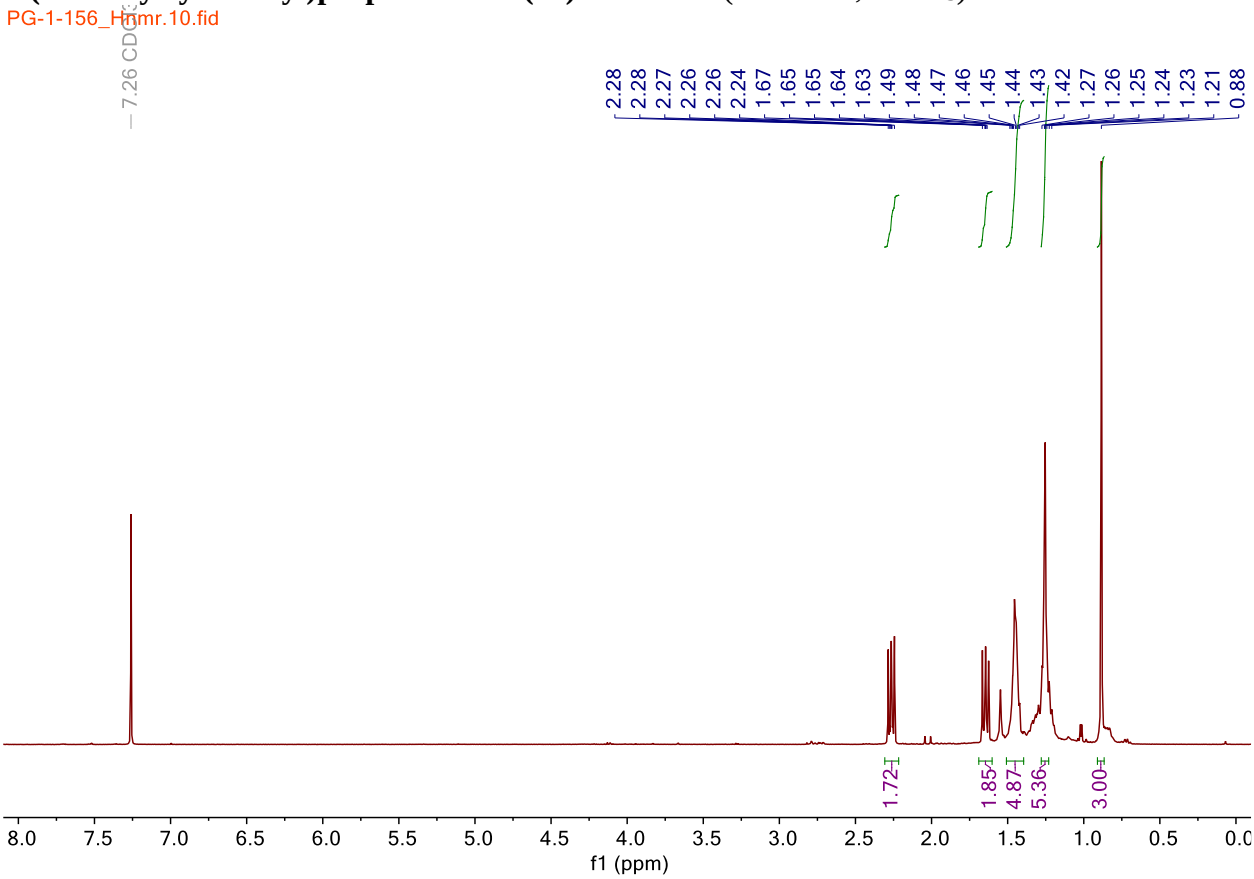
Benzyl 3-(1-methylcyclohexyl) propanoate (18): ^{1}H NMR (400 MHz, $CDCl_3$)



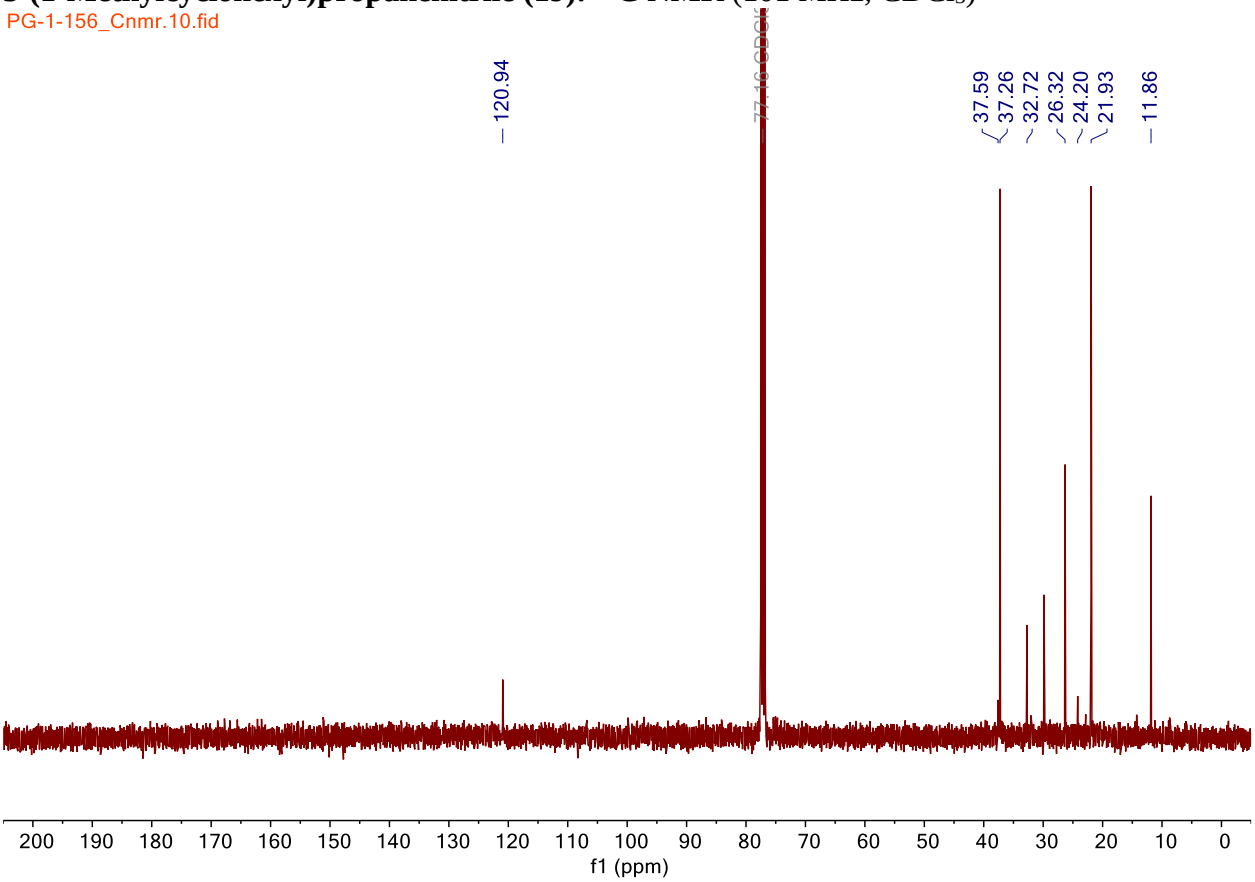
Benzyl 3-(1-methylcyclohexyl) propanoate (18): ^{13}C NMR (101 MHz, $CDCl_3$)



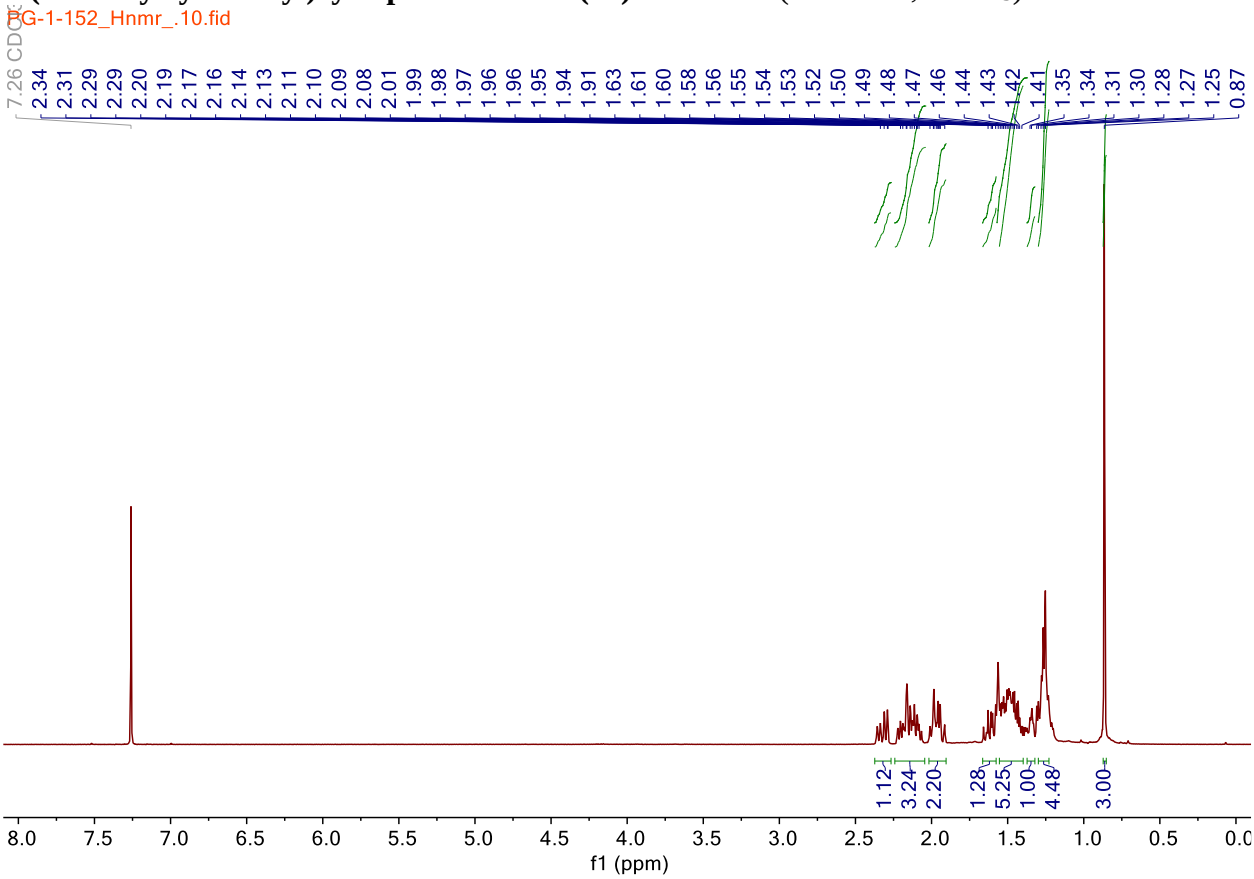
3-(1-Methylcyclohexyl)propanenitrile (19): ^{1}H NMR (400 MHz, $CDCl_3$)



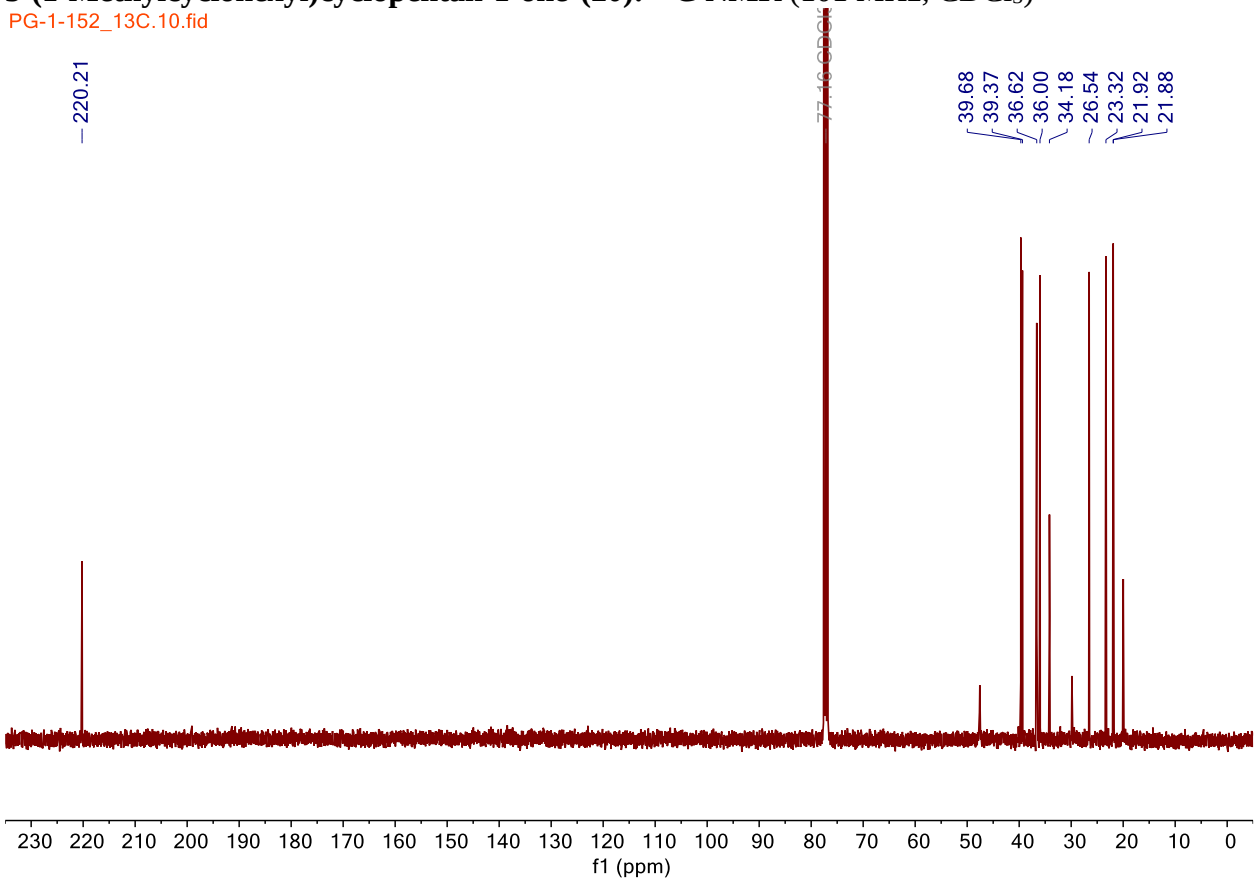
3-(1-Methylcyclohexyl)propanenitrile (19): ^{13}C NMR (101 MHz, $CDCl_3$)



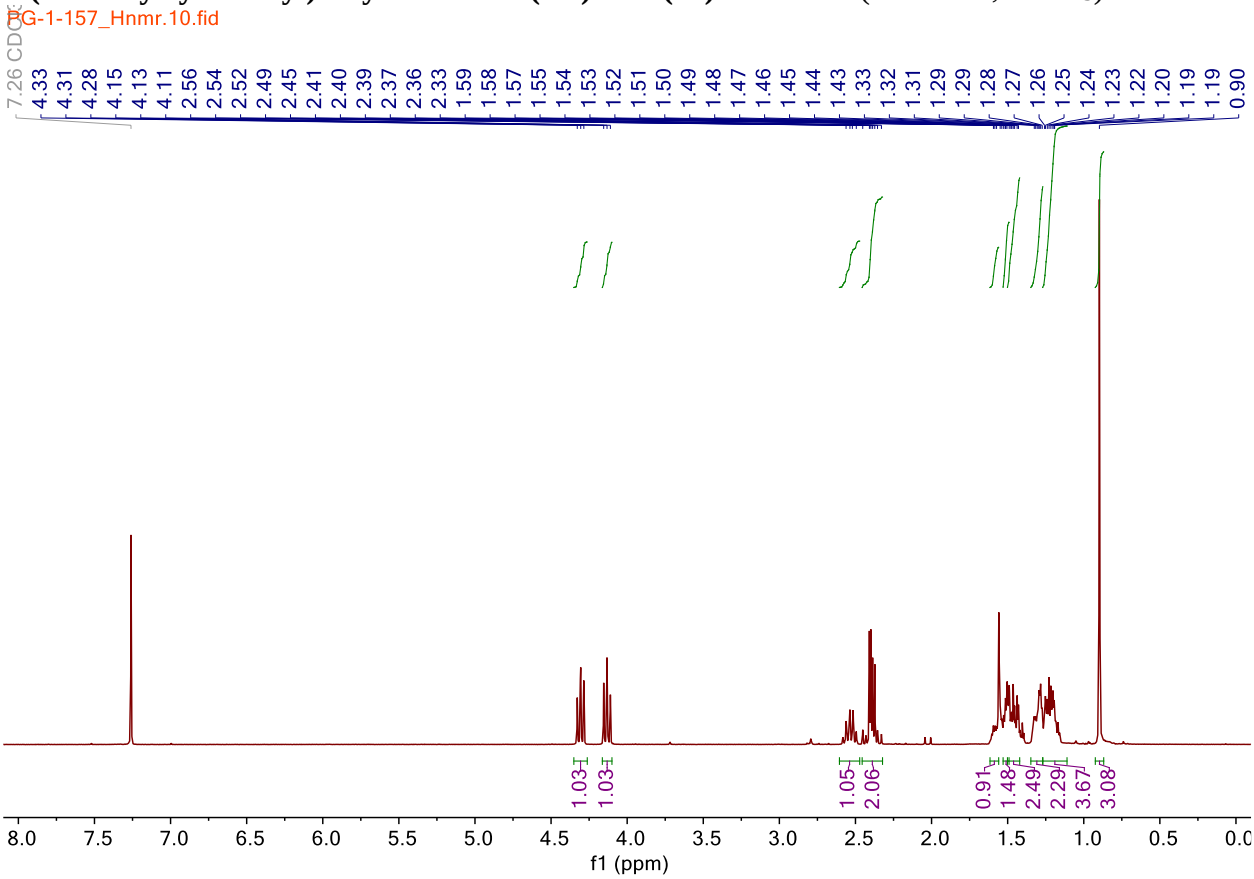
3-(1-Methylcyclohexyl)cyclopentan-1-one (20): ^{1}H NMR (400 MHz, $CDCl_3$)



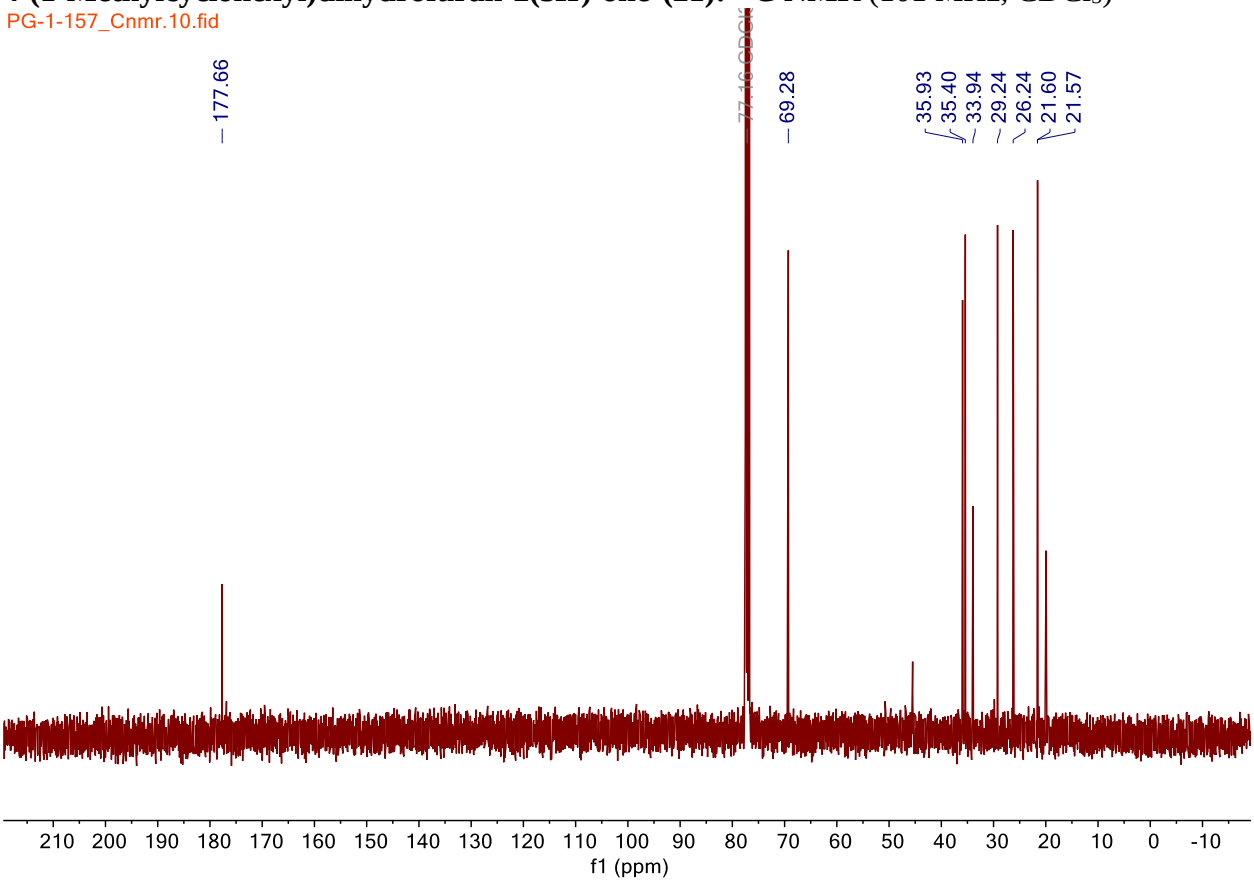
3-(1-Methylcyclohexyl)cyclopentan-1-one (20): ^{13}C NMR (101 MHz, $CDCl_3$)



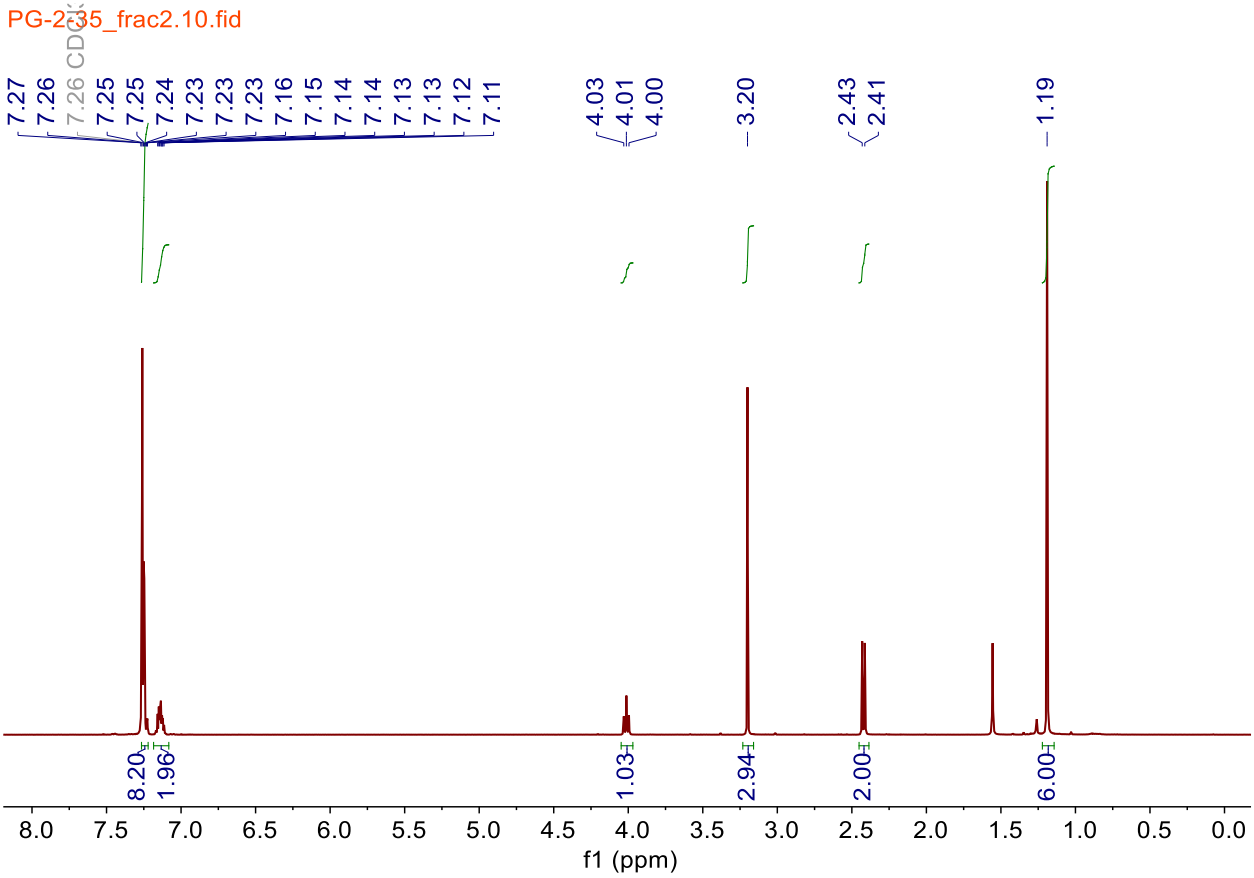
4-(1-Methylcyclohexyl)dihydrofuran-2(3*H*)-one (21): ^{1}H NMR (400 MHz, $CDCl_3$)



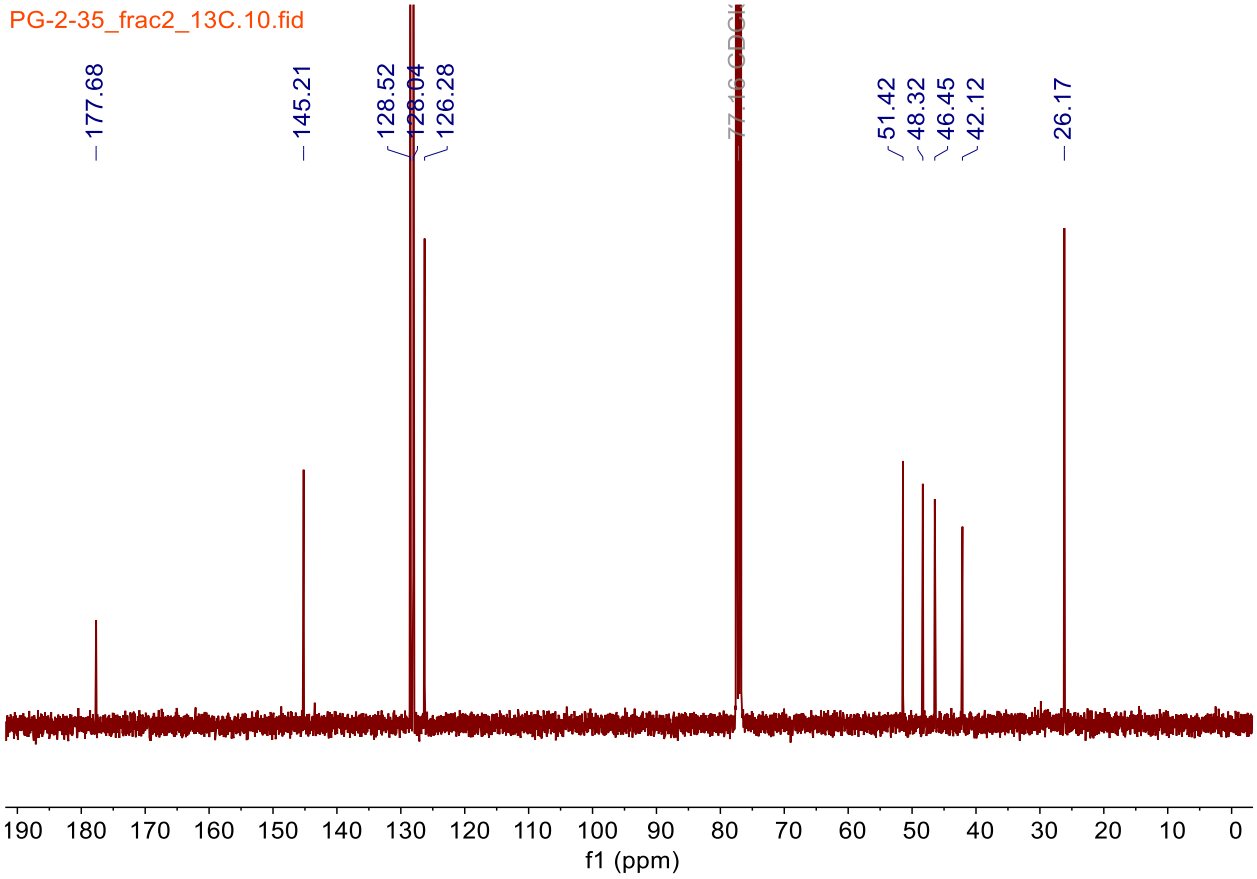
4-(1-Methylcyclohexyl)dihydrofuran-2(3*H*)-one (21): ^{13}C NMR (101 MHz, $CDCl_3$)



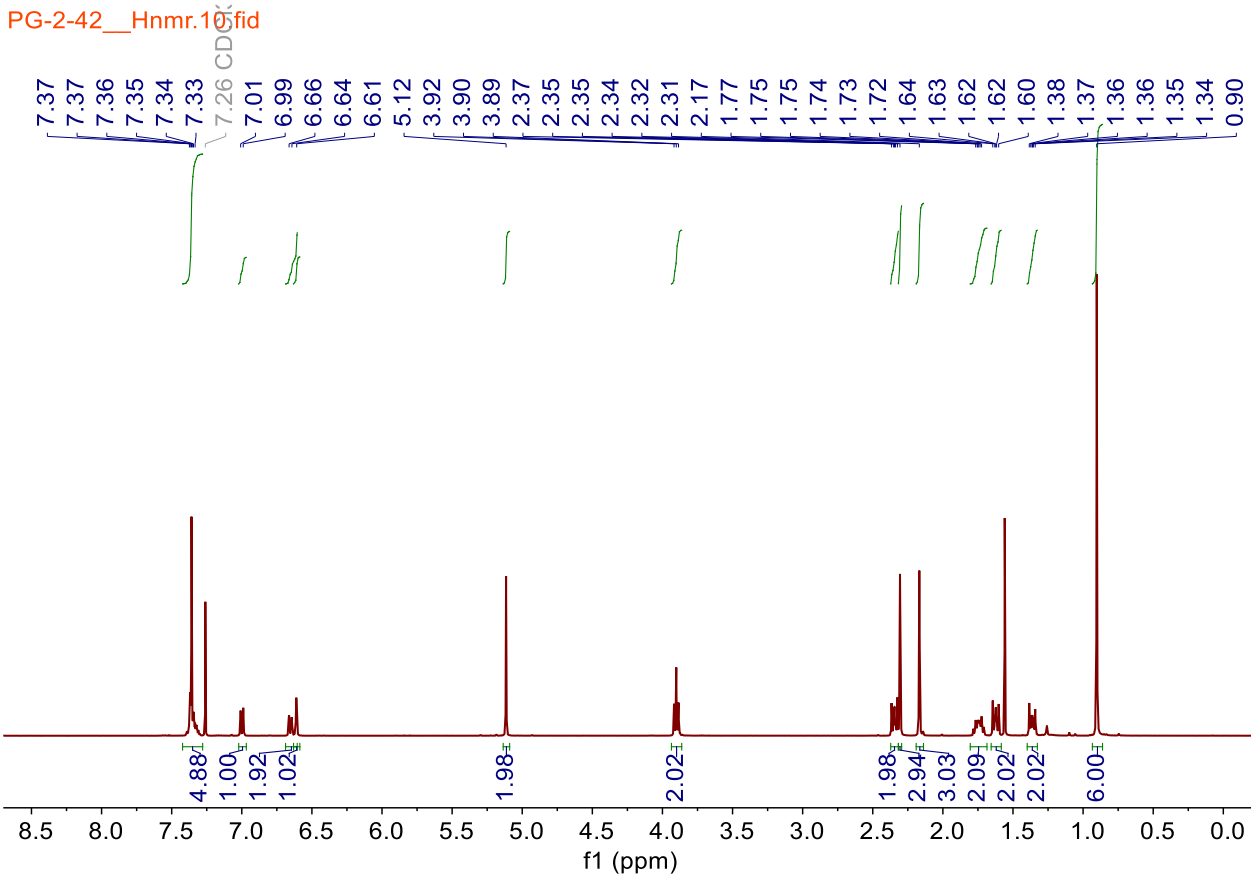
Methyl 3,3-dimethyl-5,5-diphenylpentanoate (22): ^{1}H NMR (400 MHz, $CDCl_3$)



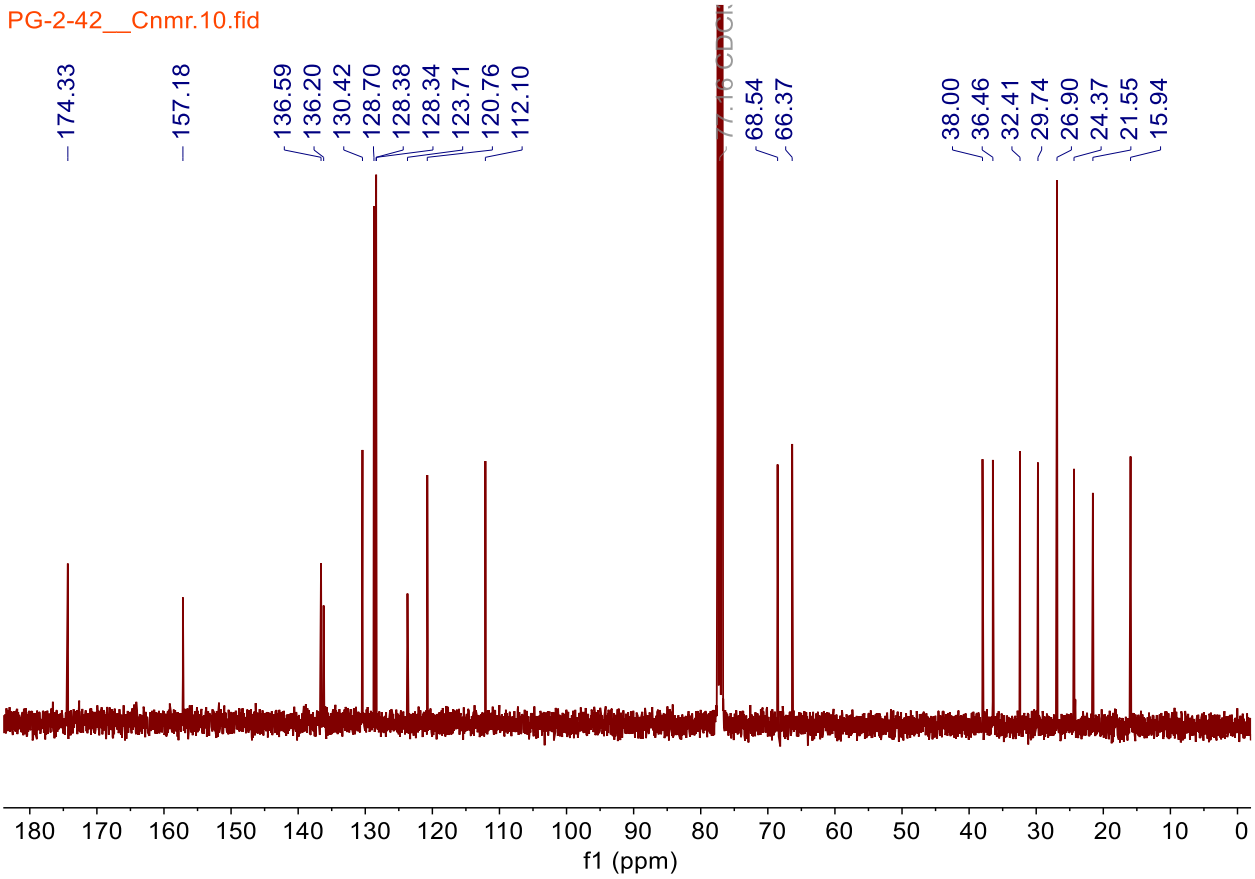
Methyl 3,3-dimethyl-5,5-diphenylpentanoate (22): ^{13}C NMR (101 MHz, $CDCl_3$)



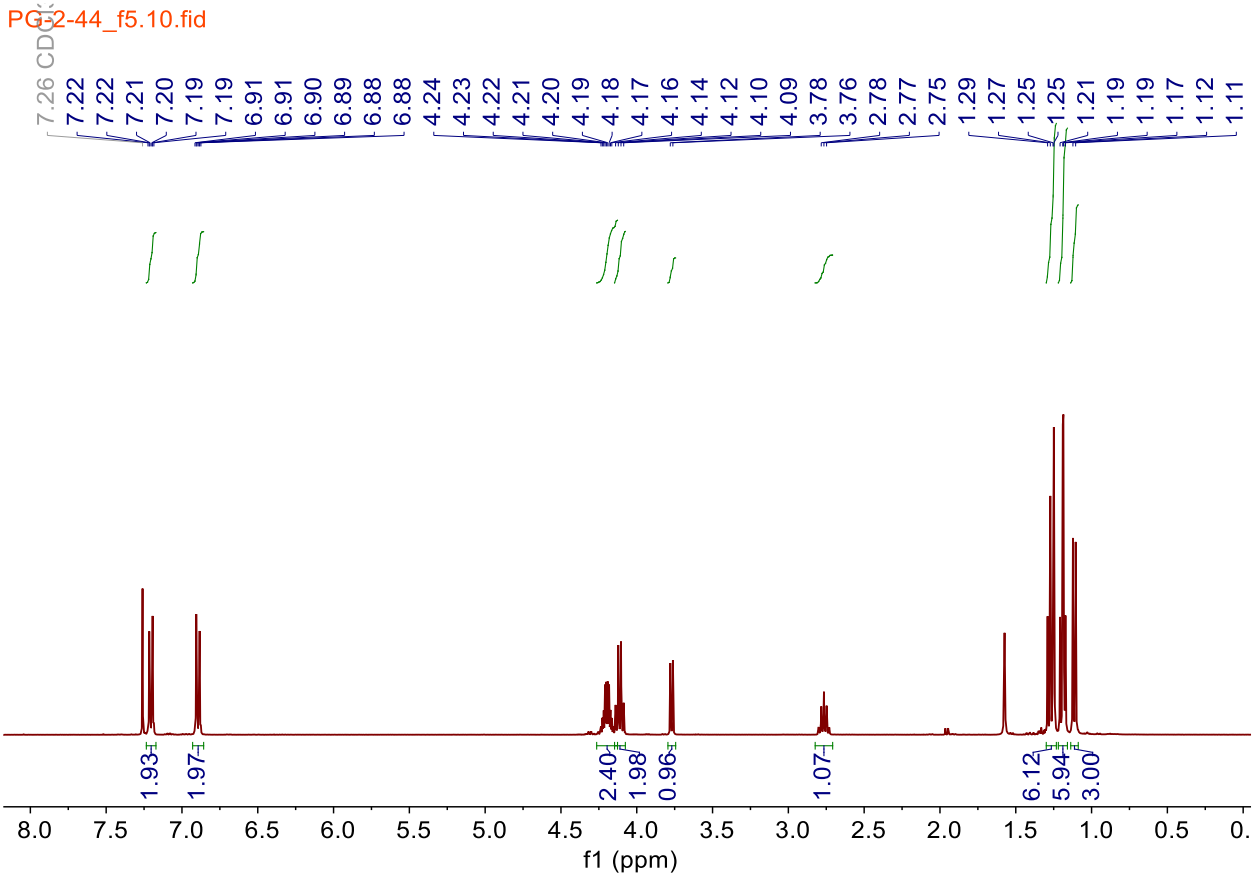
Benzyl 7-(2,5-dimethylphenoxy)-4,4-dimethylheptanoate (23): ^{1}H NMR (400 MHz, $CDCl_3$)



Benzyl 7-(2,5-dimethylphenoxy)-4,4-dimethylheptanoate (23): ^{13}C NMR (101 MHz, $CDCl_3$)



Diethyl 2-(3-(4-chlorophenoxy)-3-methylbutan-2-yl)malonate (24): ^{1}H NMR (400 MHz, $CDCl_3$



Diethyl 2-(3-(4-chlorophenoxy)-3-methylbutan-2-yl)malonate (24): ^{13}C NMR (101 MHz, $CDCl_3$