Pd^{II}-Catalyzed Site-selective β- and γ-C(sp^3)−H Arylation of Primary Aldehydes Controlled by Transient Directing Groups

Yi-Hao Li, Yuxin Ouyang, Nikita Chekshin and Jin-Quan Yu*

Department of Chemistry, The Scripps Research Institute, 10550 N. Torrey Pines Road, La Jolla, California 92037, United States

Table of Contents

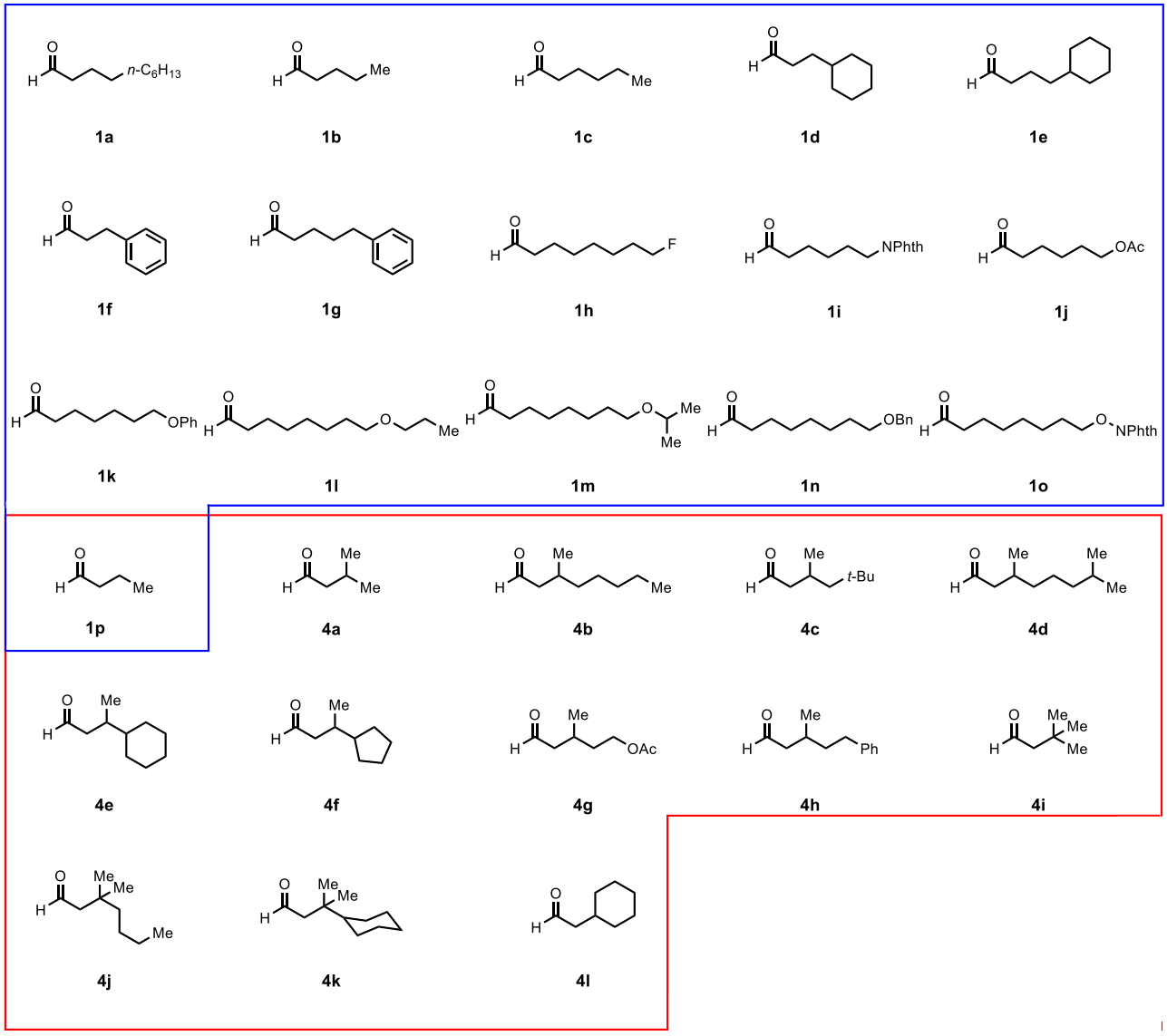
1. General Information

Substrates were obtained from the commercial sources or synthesized following literature procedures. Solvents were obtained from Sigma-Aldrich, Oakwood and Acros and used directly without further purification. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light, and Bromocresol Green Stain and Vogel's permanganate. ^{1}H NMR was recorded on Bruker DRX-600 instrument (600 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker DRX-600 instrument (151 MHz), and were fully decoupled by broad band proton decoupling. ^{19}F NMR spectra were recorded on Bruker AMX-400 instrument (376 MHz), and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Substrate Structures

β-C(sp^3)-H arylation

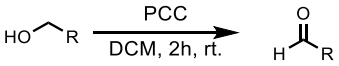
γ-C(sp^3)-H arylation



3. Substrate Preparation

3.1 Substrates **1a**, **1b**, **1c**, **1p**, **4a**, **4c** and **4i** are commercially available and used after distillation.

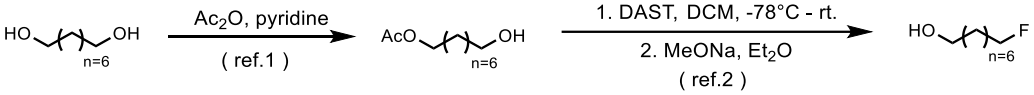
3.2 Substrates **1d-o**, **4d, 4g** and **4l** were synthesized from the corresponding alcohol with the following procedure:



Alcohol (5.0 mmol) was dissolved in DCM (20 mL), cone. Pyridinium chlorochromate (PCC, 7.5 mmol, 1.62g) added in proportion with stirring and the reaction mixture was stirred at room temperature for 2 h before filtered through a pad of silica gel and concentrated under reduced pressure. The crude aldehyde was then purified by chromatography to give the title compounds.

The corresponding alcohol for substrates **1d-g**, **4d** and **4l** are commercially available.

The corresponding alcohol for substrates **1h** were prepared according to literature procedures[1,2].



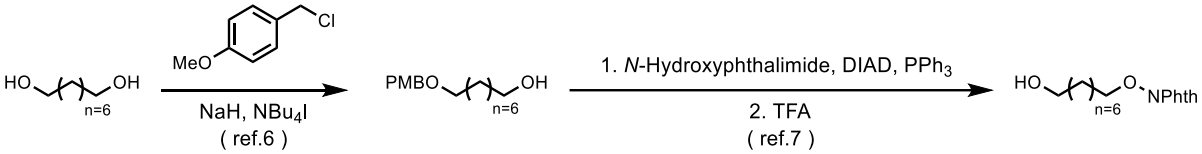
The corresponding alcohol for substrates **1i** were prepared according to literature procedures[3].

The corresponding alcohol for substrates **1j** and **4g** were prepared according to literature procedures[1].

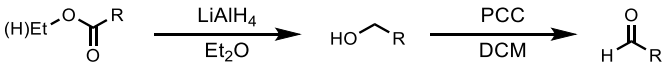
The corresponding alcohol for substrates **1k** were prepared according to literature procedures[4].

The corresponding alcohol for substrates **1l-n** were prepared according to literature procedures[5].

The corresponding alcohol for substrates **1o** were prepared according to literature procedures[6,7].

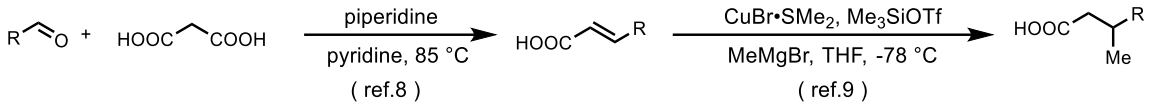


3.3 Substrates **4b**, **4e-f** and **4h** were synthesized from the corresponding carboxylic acid, **4j-k** were synthesized form the corresponding ethyl ester with the following procedure:



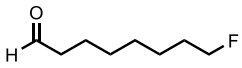
To a stirring suspension of $LiAlH_4$ (6.5 mmol) in 19 mL Et_2O at 0° C was added a solution of ester/acid (5 mmol) in 4 mL Et_2O dropwise. The reaction was stirred for 5 min before being brough to reflux for 1 h. The mixture was cooled to 0° C and 0.3 mL water was carefully added dropwise followed by 0.3 mL 6M NaOH solution, and $MgSO_4$ sufficient to sequester excess water. The slurry was stirred for 30-60 min and filter through celite. The filtrate was concentrated to give corresponding alcohol. The alcohol was dissolved in DCM (20 mL), cone. Pyridinium chlorochromate (PCC, 7.5 mmol, 1.62g) added in proportion with stirring and the reaction mixture was stirred at room temperature for 2 h before filtered through a pad of silica gal and concentrated under reduced pressure. The crude aldehyde was then purified by chromatography to give the title compounds.

The corresponding carboxylic acid for substrates **4b**, **4e-f** and **4h** were prepared according to literature procedures[8,9].



The corresponding ethyl ester for substrates **4j-k** were prepared according to literature procedures[10].

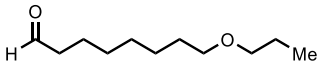
Spectroscopic characterization of aldehyde substrates



1h

8-fluorooctanal (1h)

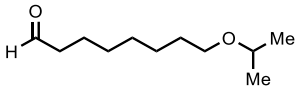
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.9 Hz, 1H), 4.48 (t, *J* = 6.1 Hz, 1H), 4.40 (t, *J* = 6.1 Hz, 1H), 2.43 (td, *J* = 7.3, 1.8 Hz, 2H), 1.77 – 1.62 (m, 4H), 1.47 – 1.32 (m, 6H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.75, 84.11 (d, J_{CF} = 164.2 Hz), 43.85, 30.38, 30.25, 28.99 (d, J_{CF} = 7.7 Hz), 25.01 (d, J_{CF} = 5.5 Hz), 21.95. ^{19}**F NMR** (376 MHz, $CDCl_3$) δ -220.88.



1l

8-propoxyoctanal (1l)

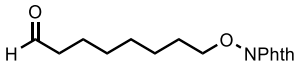
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.9 Hz, 1H), 3.39 (t, *J* = 6.7 Hz, 2H), 3.36 (t, *J* = 6.8 Hz, 2H), 2.42 (td, *J* = 7.3, 1.8 Hz, 2H), 1.65 – 1.53 (m, 6H), 1.39 – 1.30 (m, 6H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.88, 72.59, 70.79, 43.90, 29.71, 29.21, 29.12, 26.02, 22.95, 22.03, 10.60.



1m

8-isopropoxyoctanal (1m)

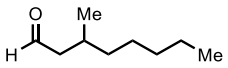
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.8 Hz, 1H), 3.58 – 3.50 (m, 1H), 3.39 (t, *J* = 6.7 Hz, 2H), 2.42 (td, *J* = 7.4, 1.8 Hz, 2H), 1.65 – 1.61 (m, 2H), 1.55 (p, *J* = 6.7 Hz, 2H), 1.39-1.30 (m, 6H), 1.15 (d, *J* = 6.1 Hz, 6H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.91, 71.28, 68.11, 43.90, 30.10, 29.21, 29.11, 26.05, 22.16, 22.02.



1o

8-((1,3-dioxoisoindolin-2-yl)oxy)octanal (1o)

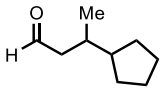
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.9 Hz, 1H), 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.20 (t, *J* = 6.7 Hz, 2H), 2.44 (td, *J* = 7.4, 1.9 Hz, 2H), 1.79 (p, *J* = 6.8 Hz, 2H), 1.66 (q, *J* = 7.4 Hz, 2H), 1.54 – 1.48 (m, 2H), 1.39 (hd, *J* = 8.9, 8.5, 2.8 Hz, 4H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.85, 163.68, 134.46, 128.97, 123.49, 78.46, 43.84, 28.97, 28.06, 25.36, 21.96, 21.95.



4b

3-methyloctanal (4b)

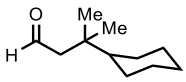
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.76 (t, *J* = 2.3 Hz, 1H), 2.39 (ddd, *J* = 16.1, 5.8, 1.9 Hz, 1H), 2.22 (ddd, *J* = 16.0, 7.9, 2.7 Hz, 1H), 2.04 (q, *J* = 5.9, 4.0 Hz, 1H), 1.34 – 1.19 (m, 8H), 0.96 (dd, *J* = 6.7, 1.1 Hz, 3H), 0.89 (td, *J* = 7.1, 1.1 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 203.22, 51.11, 36.88, 31.92, 28.19, 26.61, 22.62, 20.00, 14.06.



4f

3-cyclopentylbutanal (4f)

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.94 – 9.64 (m, 1H), 2.50 (ddd, *J* = 15.9, 4.3, 1.8 Hz, 1H), 2.22 (ddd, *J* = 15.9, 9.0, 3.1 Hz, 1H), 1.92 (dddd, *J* = 13.1, 8.7, 4.3, 1.9 Hz, 1H), 1.80 – 1.71 (m, 2H), 1.67 – 1.58 (m, 3H), 1.58 – 1.44 (m, 2H), 1.18 – 1.09 (m, 2H), 0.97 (d, *J* = 6.7 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 203.41, 50.25, 46.23, 33.53, 30.82, 30.29, 25.37, 18.83.



4k

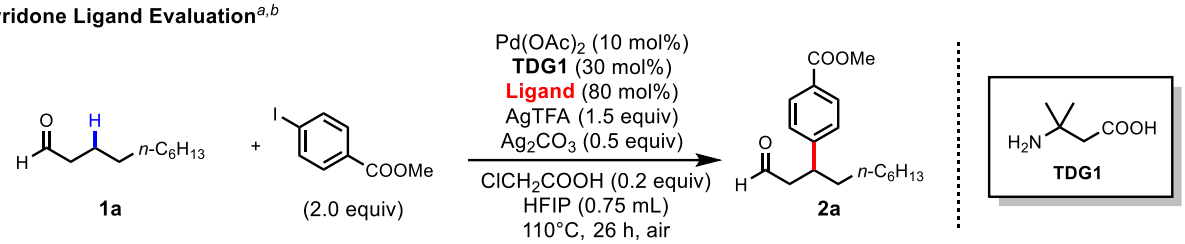
3-cyclohexyl-3-methylbutanal (4k)

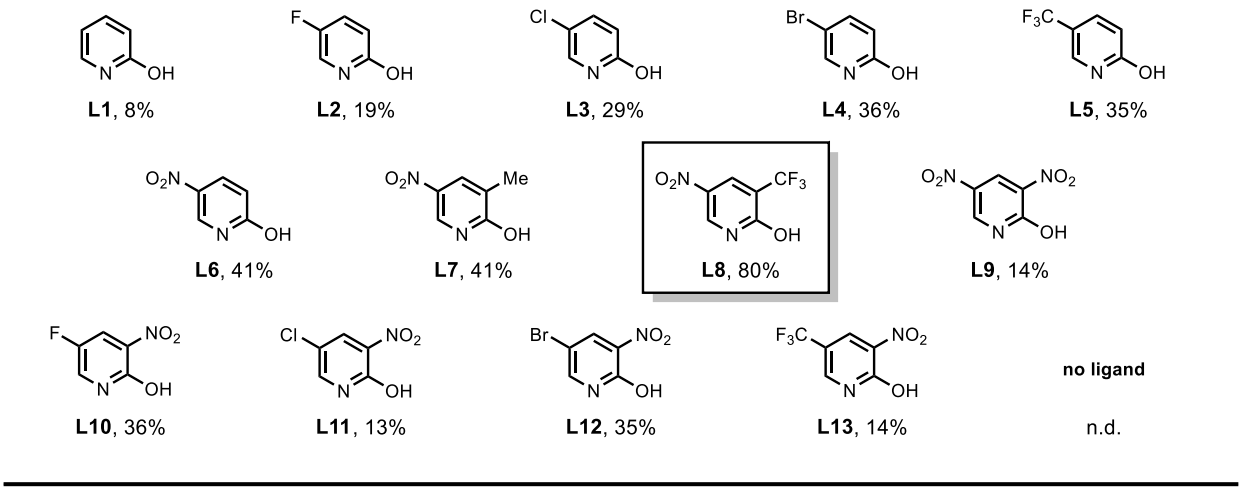
^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.86 (t, *J* = 3.3 Hz, 1H), 2.27 (d, *J* = 3.3 Hz, 2H), 1.77 (t, *J* = 12.7 Hz, 4H), 1.66 (d, *J* = 11.9 Hz, 1H), 1.23 – 1.08 (m, 4H), 1.02 (s, 6H), 1.01-0.91 (m, 2H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 203.91, 52.94, 47.03, 35.65, 26.77, 26.49, 26.07, 24.83.

4. Reaction Conditions Optimization

Part 1: Conditions Optimization for *β*-methylene C(sp^3)−H Arylation

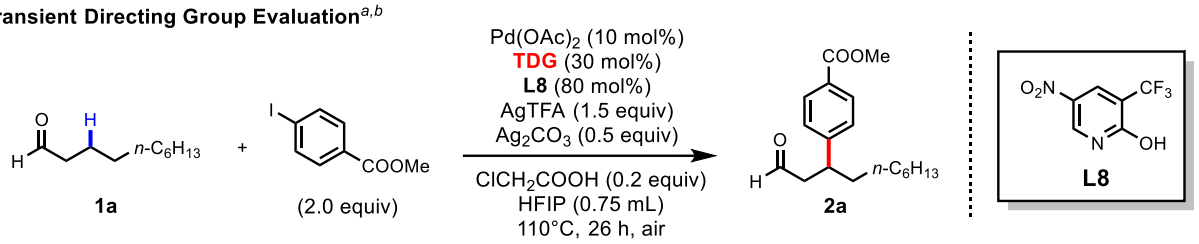
Pyridone Ligand Evaluation[a,b]





[a] Conditions: **1a** (0.1 mmol, 1.0 equiv), aryl iodide (2.0 equiv), $Pd(OAc)_2$ (10 mol%), **TDG1** (30 mol%), **Ligand** (80 mol%), AgTFA (1.5 equiv), Ag_2CO_3 (0.5 equiv), $ClCH_2COOH$ (0.2 equiv), HFIP (0.75 mL), 110 °C, under air, 26 h. [b]Yield determined by ^{1}**H NMR** analysis of the crude product using CH_2Br_2 as internal standard.

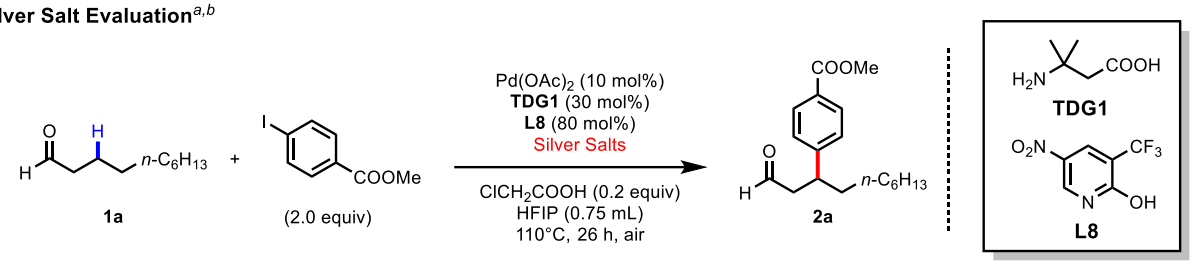
Transient Directing Group Evaluation[a,b]



no TDG n.d.	**TDG1**, 80%	**TDG3,** <5%	**TDG4,** <5%
TDG5, 6%	**TDG6,** 9%	**TDG7,** 10%	**TDG8,** 49%
TDG9, 60%	**TDG10**, 68%	**TDG1** (20 mol%) 46%	**TDG1** (40 mol%) 56%

[a] Conditions: **1a** (0.1 mmol, 1.0 equiv), aryl iodide (2.0 equiv), $Pd(OAc)_2$ (10 mol%), **TDG** (30 mol%), **L8** (80 mol%), AgTFA (1.5 equiv), Ag_2CO_3 (0.5 equiv), $ClCH_2COOH$ (0.2 equiv), HFIP (0.75 mL), 110 °C, under air, 26 h. [b]Yield determined by ^{1}**H NMR** analysis of the crude product using CH_2Br_2 as internal standard.

Silver Salt Evaluation[a,b]



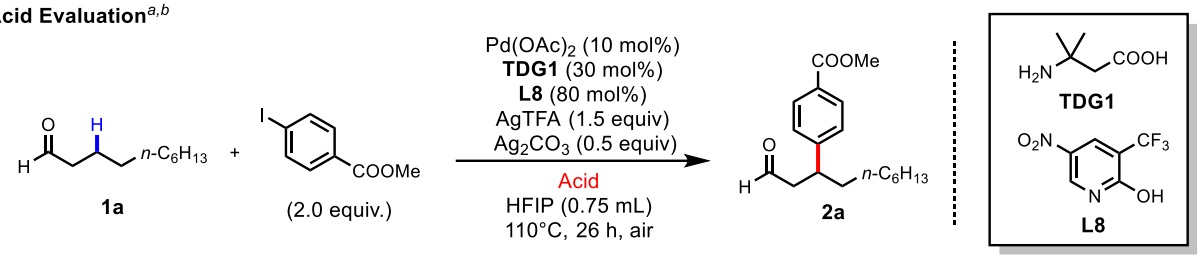
AgTFA (1.5 equiv)	Ag_2CO_3 (1.5 equiv)	AgOAc (1.5 equiv)	Ag_2O (1.5 equiv)	$AgNO_3$ (1.5 equiv)
49%	<5%	<5%	<5%	<5%

AgTFA (1.5 equiv) + Ag_2CO_3 (0.5 equiv)	AgTFA (1.5 equiv) + AgOAc (0.5 equiv)	AgTFA (1.5 equiv) + Ag_2O (0.5 equiv)
80%	36%	61%
AgTFA (1.5 equiv) + $AgNO_3$ (0.5 equiv)	AgTFA (1.5 equiv) + Li_2CO_3 (0.5 equiv)	AgTFA (1.5 equiv) + Na_2CO_3 (0.5 equiv)
24%	58%	13%

AgTFA (1.5 equiv.) + K_2CO_3 (0.5 equiv.)	AgTFA (1.5 equiv.) + Cs_2CO_3 (0.5 equiv.)
9%	<5%

[a] Conditions: **1a** (0.1 mmol, 1.0 equiv), aryl iodide (2.0 equiv), $Pd(OAc)_2$ (10 mol%), **TDG1** (30 mol%), **L8** (80 mol%), silver salts, $ClCH_2COOH$ (0.2 equiv), HFIP (0.75 mL), 110 °C, under air, 26 h. [b]Yield determined by ^{1}**H NMR** analysis of the crude product using CH_2Br_2 as internal standard.

Acid Evaluation[a,b]

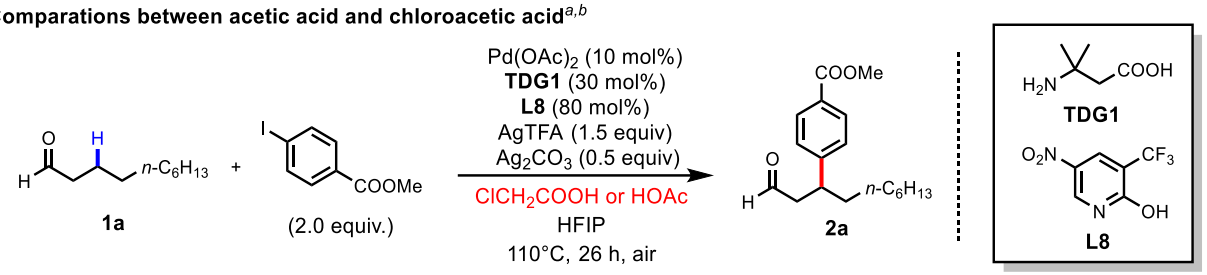


1a **2a**

$ClCH_2COOH$ (0.05 equiv) 56%	$ClCH_2COOH$ (0.1 equiv) 66%	$ClCH_2COOH$ (0.2 equiv) 80%	$ClCH_2COOH$ (0.3 equiv) 58%
F_3CCOOH (0.05 equiv) 37%	F_3CCOOH (0.1 equiv) 50%	F_3CCOOH (0.2 equiv) 57%	F_3CCOOH (0.3 equiv) 55%
$F_2CHCOOH$ (0.05 equiv) 40%	$F_2CHCOOH$ (0.1 equiv) 53%	$F_2CHCOOH$ (0.2 equiv) 48%	
Cl_3CCOOH (0.05 equiv) 34%	Cl_3CCOOH (0.1 equiv) 36%	Cl_3CCOOH (0.2 equiv) 35%	

[a] Conditions: **1a** (0.1 mmol, 1.0 equiv), aryl iodide (2.0 equiv), $Pd(OAc)_2$ (10 mol%), **TDG1** (30 mol%), **L8** (80 mol%), AgTFA (1.5 equiv), Ag_2CO_3 (0.5 equiv), acid , HFIP (0.75 mL), 110 °C, under air, 26 h. [b]Yield determined by ^{1}**H NMR** analysis of the crude product using CH_2Br_2 as internal standard.

Comparations between acetic acid and chloroacetic acid[a,b]

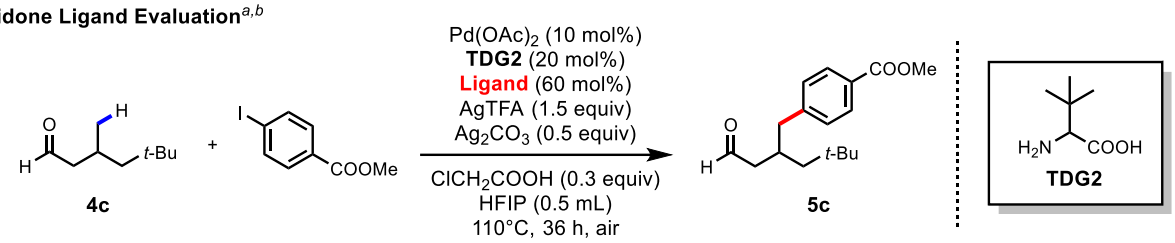


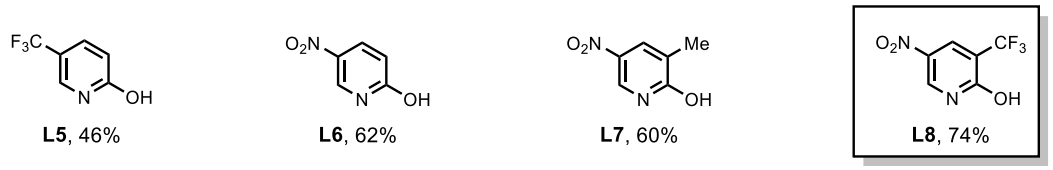
Entry	L8 (Y/N)	$ClCH_2COOH$ (equiv)	HOAc (equiv)	Solvent [0.133M]	Yield (%)	Mass Balance (%)
1[c]	N	--	19.8	HFIP/HOAc (5:1, v/v)	4	47
2[c]	Y	--	19.8	HFIP/HOAc (5:1 v/v)	40	60
3	Y	--	--	HFIP	46	96
4	Y	--	0.2	HFIP	54	92
5	Y	--	5.7	HFIP/HOAc (20:1, v/v)	62	72
6	Y	--	19.8	HFIP/HOAc (5:1, v/v)	45	52
7	Y	0.2	--	HFIP	80	96

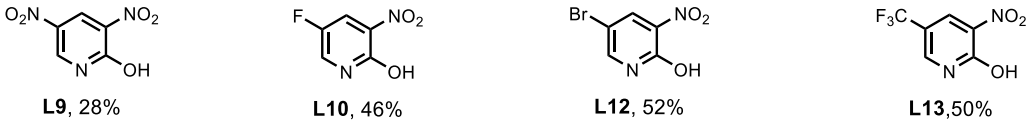
[a] Conditions: **1a** (0.1 mmol, 1.0 equiv), aryl iodide (2.0 equiv), $Pd(OAc)_2$ (10 mol%), **TDG1** (30 mol%), **L8** (80 mol%), AgTFA (1.5 equiv), Ag_2CO_3 (0.5 equiv), acid , solvent (0.75 mL), 110 °C, under air, 26 h. [b]Yield and mass balance determined by ^{1}**H NMR** analysis of the crude product using CH_2Br_2 as internal standard. [c]Conditions: **1a** (0.1 mmol, 1.0 equiv), aryl iodide (1.5 equiv), $Pd(OAc)_2$ (10 mol%), **TDG1** (40 mol%), **L8** (80 mol% or None), AgTFA (1.5 equiv), HFIP/HOAc (5:1, v/v, 0.7 mL), 100 °C, under N_2, 24 h.

Part 2: Conditions Optimization for γ-C(sp^3)−H Arylation

Pyridone Ligand Evaluation[a,b]

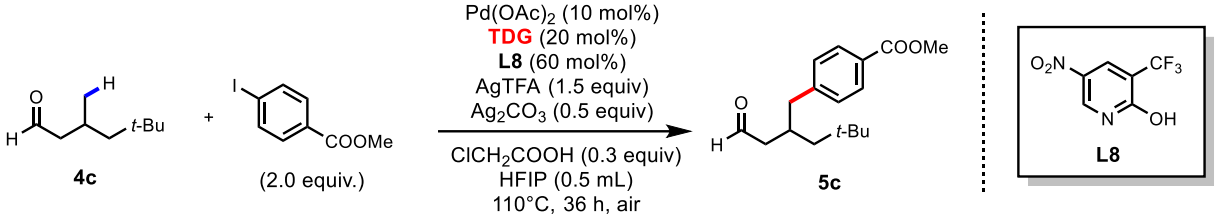






[a] Conditions: **4c** (0.1 mmol, 1.0 equiv), aryl iodide (2.0 equiv), $Pd(OAc)_2$ (10 mol%), **TDG2** (20 mol%), **Ligand** (60 mol%), AgTFA (1.5 equiv), Ag_2CO_3 (0.5 equiv), $ClCH_2COOH$ (0.3 equiv), HFIP (0.5 mL), 110 °C, under air, 36 h. [b]Yield determined by ^{1}**H NMR** analysis of the crude product using CH_2Br_2 as internal standard.

Transient Directing Group Evaluation[a,b]



TDG1, 9%	**TDG2**, 74%	**TDG2** (30 mol%) 52%	**TDG2** (40 mol%) 28%
TDG3, 12%	**TDG4**, 34%	**TDG5**, 40%	**TDG6**, 36%
TDG7, 38%	**TDG8**, 18%	**TDG9,** 20%	**TDG10**, 25%

[a] Conditions: **4c** (0.1 mmol, 1.0 equiv), aryl iodide (2.0 equiv), $Pd(OAc)_2$ (10 mol%), **TDG** (20 mol%), **L8** (60 mol%), AgTFA (1.5 equiv), Ag_2CO_3 (0.5 equiv), $ClCH_2COOH$ (0.3 equiv), HFIP (0.5 mL), 110 °C, under air, 36 h. [b]Yield determined by ^{1}**H NMR** analysis of the crude product using CH_2Br_2 as internal standard.

5. General Procedure for the *β*-Methylene and *γ*-C(sp^3)−H Arylation.

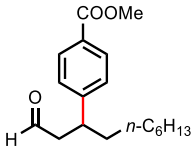
General Procedure A (for *β*-Methylene C(sp^3)−H Arylation of Primary Aldehydes)

In air, to an oven-dried reaction tube (10 mL) equipped with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%), transient directing groups (**TDG1**, 0.03 mmol, 30 mol%), ligand (**L8**, 0.08 mmol, 80 mol%), ArI (0.2 mmol, 2.0 equiv), AgTFA (0.15 mmol, 1.5 equiv), Ag_2CO_3 (0.05 mmol, 0.5 equiv), and solvent (HFIP, 0.75 mL and 0.02 mmol of $ClCH_2COOH$), followed by the aldehyde substrate (0.1 mmol, 1.0 equiv). The tube was sealed and stirred at room temperature for 20 min before heating to 110 °C for 26 h under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature and the dark brown suspension was diluted with 2 mL of ethyl acetate and was passed through a pad of Celite and washed with ethyl acetate (1.0 mL × 3). The crude reaction mixture was purified on silica gel using hexanes/EtOAc as the eluent to afford the desired product.

General Procedure B (for γ-C(sp^3)−H Arylation of Primary Aldehydes)

In air, to an oven-dried reaction tube (10 mL) equipped with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%), transient directing groups (**TDG2**, 0.02 mmol, 20 mol%), ligand (**L8**, 0.06 mmol, 60 mol%), ArI (0.2 mmol, 2.0 equiv), AgTFA (0.15 mmol, 1.5 equiv), Ag_2CO_3 (0.05 mmol, 0.5 equiv), and solvent (HFIP, 0.5 mL and 0.03 mmol of $ClCH_2COOH$), followed by the aldehyde substrate (0.1 mmol, 1.0 equiv). The tube was sealed and stirred at room temperature for 20 min before heating to 110 °C for 24 h under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature and the dark brown suspension was diluted with 2 mL of ethyl acetate and was passed through a pad of Celite and washed with ethyl acetate (1.0 mL × 3). The crude reaction mixture was purified on silica gel using hexanes/EtOAc as the eluent to afford the desired product.

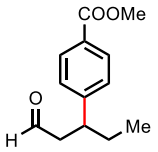
Spectroscopic characterization of *β*-arylation products



2a

Methyl 4-(1-oxodecan-3-yl)benzoate (2a)

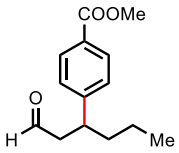
Following the **General Procedure A**, **2a** was obtained as a colorless oil in 74% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (t, *J* = 1.9 Hz, 1H), 7.99 – 7.96 (d, *J* =8.3 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 3.27 – 3.20 (m, 1H), 2.74 (dd, *J* = 7.3, 1.9 Hz, 2H), 1.70 – 1.58 (m, 2H), 1.27 – 1.07 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H).^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.23, 166.95, 149.52, 129.98, 128.57, 127.55, 52.05, 50.38, 39.96, 36.37, 31.75, 29.40, 29.08, 27.25, 22.60, 14.06. HRMS (ESI-TOF) Calcd for $C_{18}H_{25}O_3^-$ [M-H]$^-$: 289.1804, found: 289.1803.



2b

Methyl 4-(1-oxopentan-3-yl)benzoate (2b)

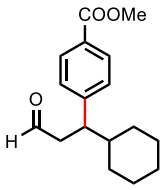
Following the **General Procedure A**, **2b** was obtained as a colorless oil in 71% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.68 (t, *J* = 1.9 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 3.16 (dtd, *J* = 9.2, 7.2, 5.5 Hz, 1H), 2.79 – 2.70 (m, 2H), 1.78 – 1.61 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.21, 166.95, 149.20, 129.96, 128.61, 127.62, 52.05, 49.98, 41.60, 29.29, 11.81. Spectroscopic data for this compound is consistent with that shown in the literature.[11]



2c

Methyl 4-(1-oxohexan-3-yl)benzoate (2c)

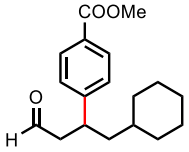
Following the **General Procedure A**, **2c** was obtained as a colorless oil in 70% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.9, 2H), 3.90 (s, 3H), 3.26 (p, *J* = 7.2 Hz, 1H), 2.74 (dd, *J* = 7.3, 1.9 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.25 – 1.11 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}**C NMR** (151 MHz, CDCl3) δ 201.21, 166.93, 149.47, 129.98, 128.58, 127.55, 52.05, 50.34, 39.70, 38.54, 20.39, 13.88. HRMS (ESI-TOF) Calcd for $C_{14}H_{19}O_3^+$ [M+H]$^+$: 235.1334, found: 235.1335.



2d

Methyl 4-(1-cyclohexyl-3-oxopropyl)benzoate (2d)

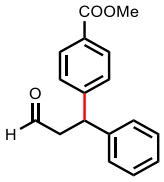
Following the **General Procedure A**, **2d** was obtained as a colorless oil in 41% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 3.06 (ddd, *J* = 9.4, 7.8, 5.3 Hz, 1H), 2.92 – 2.71 (m, 2H), 1.84 – 1.71 (m, 2H), 1.67 – 1.58 (m, 2H), 1.54 – 1.47 (m, 1H), 1.46 – 1.39 (m, 1H), 1.22 (qt, *J* = 12.8, 3.5 Hz, 1H), 1.16 – 1.03 (m, 2H), 0.94 (qd, *J* = 12.5, 3.5 Hz, 1H), 0.81 (qd, J = 12.3, 3.6 Hz, 1H).^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.73, 166.96, 148.45, 129.72, 128.50, 128.33, 52.04, 47.00, 45.98, 42.97, 31.04, 30.70, 26.35, 26.24, 26.23. HRMS (ESI-TOF) Calcd for $C_{17}H_{23}O_3^+$ $[M+H]^+$: 275.1647, found: 275.1649



2e

Methyl 4-(1-cyclohexyl-4-oxobutan-2-yl)benzoate (2e)

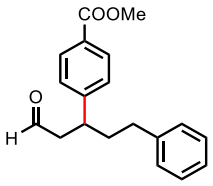
Following the **General Procedure A**, **2e** was obtained as a colorless oil in 69% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.65 (t, *J* = 1.9 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 3.39 (dtd, *J* = 9.9, 7.2, 5.5 Hz, 1H), 2.70 (dt, *J* = 7.0, 1.9 Hz, 2H), 1.83 – 1.76 (m, 1H), 1.69 – 1.60 (m, 2H), 1.59 – 1.44 (m, 4H), 1.12-1.05 (m, 3H), 1.00 (tddd, *J* = 11.7, 8.3, 4.9, 2.4 Hz, 1H), 0.94 – 0.84 (m, 2H).^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.24, 166.96, 149.64, 130.02, 128.55, 127.54, 52.05, 50.86, 44.11, 36.94, 34.71, 33.91, 32.57, 26.47, 26.10, 26.01. HRMS (ESI-TOF) Calcd for $C_{18}H_{25}O_3^+$ $[M+H]^+$: 289.1804, found: 289.1810.



2f

Methyl 4-(3-oxo-1-phenylpropyl)benzoate (2f)

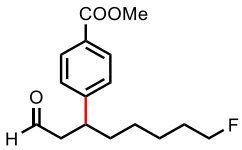
Following the **General Procedure A**, **2f** was obtained as a colorless oil in 50% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.75 (d, *J* = 1.4 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 4H), 7.21 (d, *J* = 8.1 Hz, 3H), 4.68 (t, *J* = 7.7 Hz, 1H), 3.89 (s, 3H), 3.21 (d, *J* = 7.6 Hz, 2H). ^{13}**C NMR** (151 MHz, $CDCl_3$) 200.27, 166.79, 148.48, 142.39, 130.07, 128.89, 128.65, 127.78, 127.72, 127.00, 52.10, 49.15, 44.79. HRMS (ESI-TOF) Calcd for $C_{17}H_{17}O_3^+$ $[M+H]^+$: 269.1178, found: 269.1180.



2g

Methyl 4-(1-oxo-5-phenylpentan-3-yl)benzoate (2g)

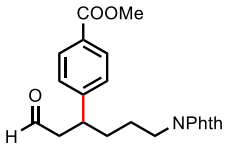
Following the **General Procedure A**, **2g** was obtained as a colorless oil in 56% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.64 (t, *J* = 1.8 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.20 – 7.16 (m, 1H), 7.08 (d, *J* = 6.7 Hz, 2H), 3.92 (s, 3H), 3.28 (dtd, *J* = 9.8, 7.2, 5.0 Hz, 1H), 2.77 (dd, *J* = 7.2, 1.8 Hz, 2H), 2.46 (t, *J* = 8.0 Hz, 2H), 2.07 – 1.92 (m, 2H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 200.83, 166.89, 148.86, 141.31, 130.12, 128.81, 128.44, 128.30, 127.69, 126.02, 52.09, 50.43, 39.41, 37.79, 33.35. HRMS (ESI-TOF) Calcd for $C_{19}H_{21}O_3^+$ $[M+H]^+$: 297.1491, found: 297.1489.



2h

Methyl 4-(8-fluoro-1-oxooctan-3-yl)benzoate (2h)

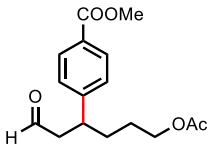
Following the **General Procedure A**, **2h** was obtained as a colorless oil in 81% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (t, *J* = 1.8 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.41 (t, *J* = 6.1 Hz, 1H), 4.33 (t, *J* = 6.1 Hz, 1H), 3.91 (s, 3H), 3.30 – 3.21 (m, 1H), 2.76 (dd, *J* = 7.2, 1.8 Hz, 2H), 1.74 – 1.58 (m, 4H), 1.42 – 1.29 (m, 2H), 1.24 (ddt, *J* = 11.7, 9.5, 5.7 Hz, 1H), 1.18 – 1.10 (m, 1H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.01, 166.90, 149.24, 130.03, 128.68, 127.53, 83.93 (d, J_{CF} = 164.2 Hz), 52.08 (d, J_{CF} = 2.7 Hz), 50.38, 39.79, 36.16, 30.17 (d, J_{CF} = 19.3 Hz), 26.87, 25.05 (d, J_{CF} = 5.4 Hz). ^{19}**F NMR** (376 MHz, $CDCl_3$) δ -221.05. HRMS (ESI-TOF) Calcd for $C_{16}H_{22}FO_3^+$ $[M+H]^+$: 281.1553, found: 281.1553.



2i

Methyl 4-(6-(1,3-dioxoisoindolin-2-yl)-1-oxohexan-3-yl)benzoate (2i)

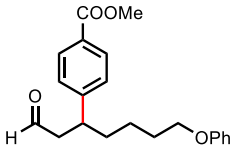
Following the **General Procedure A**, reaction time 32 h, **2i** was obtained as a pale-yellow solid in 62% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.82 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 3.63 (t, *J* = 7.1 Hz, 2H), 3.35 – 3.26 (m, 1H), 2.76 (d, *J* = 7.1 Hz, 2H), 1.78 – 1.66 (m, 2H), 1.63-1.55 (m, 1H), 1.53-1.44 (m, 1H).^{13}**C NMR** (151 MHz, $CDCl_3$) δ 200.69, 168.34, 166.81, 148.60, 133.96, 132.01, 130.11, 128.80, 127.54, 123.23, 52.05, 50.21, 39.38, 37.53, 33.31, 26.34. HRMS (ESI-TOF) Calcd for $C_{22}H_{22}NO_5^+$ $[M+H]^+$: 380.1498, found: 380.1495.



2j

Methyl 4-(6-acetoxy-1-oxohexan-3-yl)benzoate (2j)

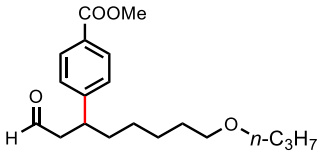
Following the **General Procedure A**, reaction time 72 h, **2j** was obtained as a colorless oil in 70% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.68 (t, *J* = 1.7 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.28 (s, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 3.91 (s, 3H), 3.28 (dtd, *J* = 9.7, 7.1, 5.2 Hz, 1H), 2.78 (dd, *J* = 6.9, 1.4 Hz, 2H), 2.02 (s, 3H), 1.82 – 1.63 (m, 2H), 1.57 – 1.38 (m, 2H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 200.65, 171.08, 166.84, 148.67, 130.12, 127.54, 127.53, 63.95, 52.10, 50.36, 39.48, 32.51, 26.44, 20.94. HRMS (ESI-TOF) Calcd for $C_{16}H_{21}O_5^+$ $[M+H]^+$: 293.1384, found: 293.1384.



2k

Methyl 4-(1-oxo-7-phenoxyheptan-3-yl)benzoate (2k)

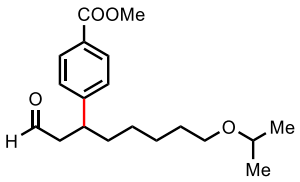
Following the **General Procedure A**, **2k** was obtained as a colorless oil in 61% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.23 (m, 4H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 2H), 3.92 – 3.85 (m, 5H), 3.32 – 3.25 (m, 1H), 2.77 (dd, *J* = 7.2, 1.8 Hz, 2H), 1.81 – 1.67 (m, 4H), 1.39 – 1.22 (m, 2H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 200.97, 166.90, 158.90, 149.14, 130.05, 129.41, 128.70, 127.56, 120.58, 114.44, 67.36, 52.07, 50.35, 39.83, 35.99, 29.03, 23.86. HRMS (ESI-TOF) Calcd for $C_{21}H_{23}O_4^-$ $[M-H]^-$: 339.1596, found: 339.1603.



2l

Methyl 4-(1-oxo-8-propoxyoctan-3-yl)benzoate (2l)

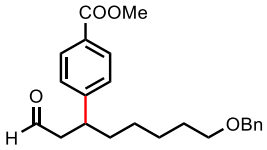
Following the **General Procedure A**, **2l** was obtained as a colorless oil in 69% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.66 (t, *J* = 1.8 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 3.35 – 3.30 (m, 4H), 3.27 – 3.21 (m, 1H), 2.74 (dd, *J* = 7.2, 1.9 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.56 (dt, *J* = 14.3, 7.1 Hz, 2H), 1.48 (tdd, *J* = 10.4, 5.5, 3.0 Hz, 2H), 1.37 – 1.25 (m, 2H), 1.25 – 1.18 (m, 1H), 1.12 (tdd, *J* = 13.1, 10.2, 5.3 Hz, 1H), 0.89 (t, *J* = 7.4 Hz, 3H).^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.13, 166.92, 149.41, 129.99, 128.60, 127.55, 72.55, 70.60, 52.05, 50.37, 39.88, 36.29, 29.53, 27.07, 26.05, 22.94, 10.58. HRMS (ESI-TOF) Calcd for $C_{19}H_{27}O_4^-$ $[M-H]^-$: 319.1909, found: 319.1913.



2m

Methyl 4-(8-isopropoxy-1-oxooctan-3-yl)benzoate (2m)

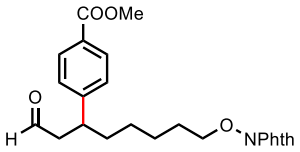
Following the **General Procedure A**, **2m** was obtained as a colorless oil in 65% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 3.90 (s, 3H), 3.49 (hept, *J* = 6.1 Hz, 1H), 3.32 (t, *J* = 6.6 Hz, 2H), 3.28 – 3.21 (m, 1H), 2.74 (dd, *J* = 7.2, 1.9 Hz, 2H), 1.66 (ttd, *J* = 18.2, 9.1, 8.6, 5.1 Hz, 2H), 1.47 (ddt, *J* = 9.6, 6.6, 4.8 Hz, 2H), 1.39 – 1.13 (m, 4H), 1.11 (d, *J* = 6.2 Hz, 6H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.16, 166.92, 149.41, 129.99, 128.59, 127.54, 71.26, 67.92, 52.05, 50.35, 39.89, 36.28, 29.91, 27.07, 26.09, 22.13. HRMS (ESI-TOF) Calcd for $C_{19}H_{27}O_4^-$ [M-H]$^-$: 319.1909, found: 319.1910.



2n

Methyl 4-(8-(benzyloxy)-1-oxooctan-3-yl)benzoate (2n)

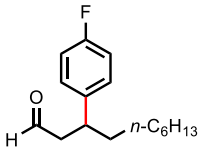
Following the **General Procedure A**, **2n** was obtained as a colorless oil in 72% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.32 (dt, *J* = 13.2, 7.3 Hz, 4H), 7.25 (d, *J* = 8.1 Hz, 3H), 4.46 (s, 2H), 3.90 (s, 3H), 3.40 (t, *J* = 6.5 Hz, 2H), 3.27 – 3.17 (m, 1H), 2.73 (d, *J* = 5.3 Hz, 2H), 1.67 – 1.48 (m, 4H), 1.42 – 1.28 (m, 2H), 1.23 – 1.06 (m, 2H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.12, 166.91, 149.38, 138.60, 129.98, 128.59, 128.34, 127.60, 127.53, 127.49, 72.85, 70.18, 52.04, 50.35, 39.86, 36.25, 29.50, 27.04, 26.03. HRMS (ESI-TOF) Calcd for $C_{23}H_{29}O_4^+$ [M+H]$^+$: 369.2066, found: 369.2058.



2o

Methyl 4-(8-((1,3-dioxoisoindolin-2-yl)oxy)-1-oxooctan-3-yl)benzoate (2o)

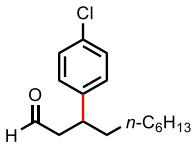
Following the **General Procedure A**, **2o** was obtained as a pale-yellow solid in 71% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (t, *J* = 1.8 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.82 (dt, *J* = 7.0, 3.6 Hz, 2H), 7.76 – 7.73 (m, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 4.14 (t, *J* = 6.6 Hz, 2H), 3.90 (s, 3H), 3.27 (ddt, *J* = 12.7, 9.3, 6.1 Hz, 1H), 2.76 (dt, *J* = 7.7, 1.4 Hz, 2H), 1.77 – 1.65 (m, 4H), 1.56 – 1.41 (m, 2H), 1.31 – 1.15 (m, 2H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.11, 166.91, 163.64, 149.29, 134.46, 130.02, 128.95, 128.62, 127.56, 123.49, 52.04, 50.32, 39.81, 36.14, 27.91, 26.86, 25.42. HRMS (ESI-TOF) Calcd for $C_{24}H_{26}NO_6^+$ [M+H]$^+$: 424.1760, found: 424.1757.



3a

3-(4-fluorophenyl)decanal (3a)

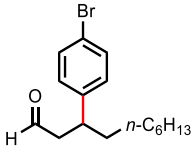
Following the **General Procedure A**, reaction time 28 h, **3a** was obtained as a colorless oil in 80% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.66 (t, *J* = 2.0 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.03 – 6.95 (m, 2H), 3.20 – 3.10 (m, 1H), 2.74 – 2.64 (m, 2H), 1.67 – 1.55 (m, 2H), 1.28 – 1.09 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.71, 161.49 (d, J_{CF} = 244.3 Hz), 139.63 (d, J_{CF} = 3.3 Hz), 128.82 (d, J_{CF} = 7.7 Hz), 115.40 (d, J_{CF} = 20.9 Hz), 50.76, 39.32, 36.70, 31.77, 29.40, 29.12, 27.24, 22.61, 14.07. ^{19}**F NMR** (376 MHz, $CDCl_3$) δ -119.23. HRMS (ESI-TOF) Calcd for $C_{16}H_{23}FNaO^+$ $[M+Na]^+$: 273.1625, found: 273.1610.



3b

3-(4-chlorophenyl)decanal (3b)

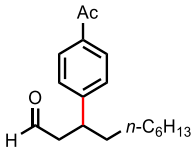
Following the **General Procedure A**, reaction time 28 h, **3b** was obtained as a colorless oil in 69% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.66 (t, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.15 (dq, *J* = 9.4, 6.9 Hz, 1H), 2.74 – 2.65 (m, 2H), 1.67 – 1.56 (m, 2H), 1.26 – 1.07 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.48, 142.50, 132.18, 128.82, 128.75, 50.58, 39.41, 36.51, 31.77, 29.40, 29.11, 27.23, 22.61, 14.06. HRMS (ESI-TOF) Calcd for $C_{16}H_{23}ClNaO^+$ $[M+Na]^+$: 289.1329, found: 289.1329.



3c

3-(4-bromophenyl)decanal (3c)

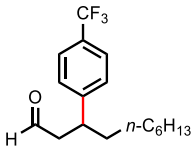
Following the **General Procedure A**, reaction time 28 h, **3c** was obtained as a colorless oil in 70% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.66 (t, *J* = 1.9 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 3.17 – 3.09 (m, 1H), 2.73 – 2.66 (m, 2H), 1.68 – 1.56 (m, 2H), 1.26 – 1.08 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.42, 143.04, 131.70, 129.22, 120.22, 50.52, 39.46, 36.45, 31.77, 29.40, 29.10, 27.23, 22.60, 14.06. HRMS (ESI-TOF) Calcd for $C_{16}H_{23}BrNaO^+$ $[M+Na]^+$: 333.0824, found: 333.0808.



3d

3-(4-acetylphenyl)decanal (3d)

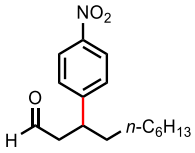
Following the **General Procedure A**, reaction time 28 h, **3d** was obtained as a colorless oil in 69% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (t, *J* = 1.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.25 (dtd, *J* = 9.3, 7.2, 5.6 Hz, 1H), 2.79 – 2.72 (m, 2H), 2.59 (s, 3H), 1.70 – 1.59 (m, 2H), 1.25 – 1.04 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.15, 197.71, 149.80, 135.71, 128.79, 127.74, 50.35, 39.93, 36.35, 31.76, 29.40, 29.09, 27.26, 26.58, 22.60, 14.06. HRMS (ESI-TOF) Calcd for $C_{18}H_{27}O_2^+$ $[M+H]^+$: 275.2011, found: 275.2018.



3e

3-(4-(trifluoromethyl)phenyl)decanal (3e)

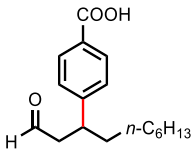
Following the **General Procedure A**, reaction time 24 h, **3e** was obtained as a colorless oil in 71% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.68 (d, *J* = 1.8 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 3.29 – 3.21 (m, 1H), 2.75 (dq, *J* = 7.6, 1.6 Hz, 2H), 1.72 – 1.58 (m, 2H), 1.28 – 1.05 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.04, 148.25, 128.88 (q, J_{CF} = 32.5 Hz), 127.85, 125.58 (q, J_{CF} = 3.9 Hz), 125.57 (q, J_{CF} = 270.2 Hz), 50.42, 39.74, 36.37, 31.76, 29.39, 29.08, 27.24, 22.60, 14.06. ^{19}**F NMR** (376 MHz, $CDCl_3$) δ -65.07. HRMS (ESI-TOF) Calcd for $C_{17}H_{23}F_3NaO_3^+$ $[M+Na]^+$: 323.1593, found: 323.1599.



3f

3-(4-nitrophenyl)decanal (3f)

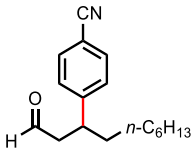
Following the **General Procedure A**, reaction time 28 h, **3f** was obtained as a colorless oil in 83% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.69 (t, *J* = 1.6 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 3.35 – 3.28 (m, 1H), 2.86 – 2.73 (m, 2H), 1.72 – 1.58 (m, 2H), 1.27 – 1.05 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H).^{13}**C NMR** (151 MHz, $CDCl_3$) δ 200.33, 152.02, 146.73, 128.38, 123.91, 50.28, 39.65, 36.26, 31.72, 29.35, 29.05, 27.24, 22.58, 14.05. HRMS (ESI-TOF) Calcd for $C_{16}H_{24}NO_3^+$ $[M+H]^+$: 278.1751, found: 278.1751.



3g

4-(1-oxodecan-3-yl)benzoic acid (3g)

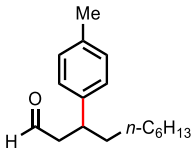
Following the **General Procedure A**, reaction time 36 h, **3g** was obtained as a white solid in 57% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.68 (t, *J* = 1.8 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.26 (p, *J* = 6.9 Hz, 1H), 2.76 (dd, *J* = 7.3, 1.8 Hz, 2H), 1.65 (ttd, *J* = 17.7, 8.8, 8.4, 4.8 Hz, 2H), 1.26 – 1.05 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.12, 170.92, 150.56, 130.63, 127.70, 127.58, 50.35, 40.00, 36.35, 31.75, 29.40, 29.08, 27.26, 22.60, 14.06. HRMS (ESI-TOF) Calcd for $C_{17}H_{24}NaO_3^+$ $[M+Na]^+$: 299.1617, found: 299.1622.



3h

4-(1-oxodecan-3-yl)benzonitrile (3h)

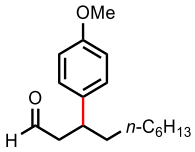
Following the **General Procedure A**, reaction time 28 h, **3h** was obtained as a colorless oil in 45% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (t, *J* = 1.6 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.25 (tt, *J* = 8.0, 5.9 Hz, 1H), 2.81 – 2.69 (m, 2H), 1.70 – 1.58 (m, 2H), 1.26 – 1.03 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 200.52, 149.83, 132.47, 128.36, 118.84, 110.49, 50.23, 39.88, 36.20, 31.73, 29.35, 29.05, 27.22, 22.58, 14.05. HRMS (ESI-TOF) Calcd for $C_{17}H_{24}NO^+$ $[M+H]^+$: 258.1853, found: 258.1847.



3i

3-(p-tolyl)decanal (3i)

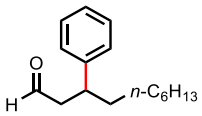
Following the **General Procedure A**, reaction time 28 h, **3i** was obtained as a colorless oil in 60% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.65 (t, *J* = 2.1 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 6.4 Hz, 2H), 3.12 (p, *J* = 7.4 Hz, 1H), 2.68 (d, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 1.60 (dq, *J* = 13.8, 7.9, 6.6 Hz, 2H), 1.29 – 1.09 (m, 10H), 0.88 – 0.83 (m, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.35, 140.89, 136.03, 129.29, 127.31, 50.69, 39.75, 36.68, 31.81, 29.48, 29.13, 27.31, 22.62, 21.01, 14.08. HRMS (ESI-TOF) Calcd for $C_{17}H_{26}NaO^+$ $[M+Na]^+$: 269.1876, found: 269.1868.



3j

3-(4-methoxyphenyl)decanal (3j)

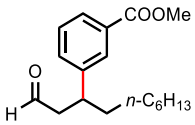
Following the **General Procedure A**, reaction time 28 h, **3j** was obtained as a colorless oil in 52% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.65 (t, *J* = 2.2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.11 (dtd, *J* = 9.2, 7.3, 5.6 Hz, 1H), 2.67 (dd, *J* = 7.4, 2.2 Hz, 2H), 1.65 – 1.56 (m, 2H), 1.29 – 1.08 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.36, 158.16, 135.96, 128.35, 113.98, 55.23, 50.80, 39.36, 36.80, 31.81, 29.46, 29.15, 27.29, 22.62, 14.08. HRMS (ESI-TOF) Calcd for $C_{17}H_{26}NaO_2^+$ $[M+Na]^+$: 285.1825, found: 285.1824.



3k

3-phenyldecanal (3k)

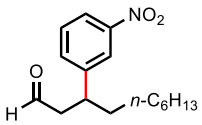
Following the **General Procedure A**, reaction time 28 h, **3k** was obtained as a colorless oil in 55% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.66 (d, *J* = 3.4 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.20 (dd, *J* = 17.9, 7.8 Hz, 3H), 3.16 (p, *J* = 7.3 Hz, 1H), 2.76 – 2.66 (m, 2H), 1.63 (dtd, *J* = 13.2, 7.8, 6.9, 3.4 Hz, 2H), 1.30 – 1.09 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.15, 143.97, 128.61, 127.46, 126.54, 50.62, 40.12, 36.62, 31.79, 29.46, 29.12, 27.30, 22.61, 14.07. HRMS (ESI-TOF) Calcd for $C_{16}H_{24}NaO^+$ $[M+Na]^+$: 255.1719, found: 255.1718.



3l

Methyl 3-(1-oxodecan-3-yl)benzoate (3l)

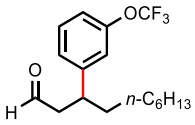
Following the **General Procedure A**, reaction time 28 h, **3l** was obtained as a colorless oil in 72% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (t, *J* = 1.9 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.41 – 7.35 (m, 2H), 3.92 (s, 3H), 3.23 (dtd, *J* = 9.1, 7.2, 5.7 Hz, 1H), 2.75 (dd, *J* = 7.2, 1.9 Hz, 2H), 1.72 – 1.60 (m, 2H), 1.27 – 1.06 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.43, 167.09, 144.50, 132.33, 130.51, 128.68, 128.42, 127.87, 52.14, 50.51, 39.84, 36.49, 31.76, 29.40, 29.09, 27.27, 22.60, 14.06. HRMS (ESI-TOF) Calcd for $C_{18}H_{27}O_3^+$ $[M+H]^+$: 291.1960, found: 291.1967.



3m

3-(3-nitrophenyl)decanal (3m)

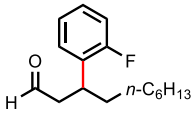
Following the **General Procedure A**, reaction time 28 h, **3m** was obtained as a colorless oil in 78% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.70 (t, *J* = 1.5 Hz, 1H), 8.11 – 8.04 (m, 2H), 7.54 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 3.36 – 3.28 (m, 1H), 2.86 – 2.75 (m, 2H), 1.73 – 1.60 (m, 2H), 1.28 – 1.06 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 200.43, 148.53, 146.40, 134.10, 129.50, 122.17, 121.74, 50.37, 39.48, 36.32, 31.73, 29.33, 29.06, 27.24, 22.58, 14.05. HRMS (ESI-TOF) Calcd for $C_{16}H_{23}NNaO_3^+$ $[M+Na]^+$: 300.1570, found: 300.1573.



3n

3-(3-(trifluoromethoxy)phenyl)decanal (3n)

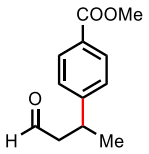
Following the **General Procedure A**, reaction time 28 h, **3n** was obtained as a colorless oil in 63% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.68 (t, *J* = 1.8 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.12 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.07 (ddt, *J* = 8.1, 2.2, 1.1 Hz, 1H), 7.03 (t, *J* = 1.3 Hz, 1H), 3.20 (dtd, *J* = 9.3, 7.1, 5.5 Hz, 1H), 2.72 (ddd, *J* = 7.5, 1.8, 1.0 Hz, 2H), 1.68 – 1.56 (m, 2H), 1.27 – 1.08 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.15, 149.49 (q, J_{CF} = 1.7 Hz), 146.55, 129.90, 125.93, 120.46 (q, J_{CF} = 257.0 Hz), 119.98, 118.89, 50.44, 39.65, 36.36, 31.74, 29.35, 29.06, 27.17, 22.59, 14.05. ^{19}**F NMR** (376 MHz, $CDCl_3$) δ -60.41. HRMS (ESI-TOF) Calcd for $C_{17}H_{23}NaF_3O_2^+$ $[M+Na]^+$: 339.1542, found: 339.1546.



3o

3-(2-fluorophenyl)decanal (3o)

Following the **General Procedure A**, reaction time 28 h, **3o** was obtained as a colorless oil in 58% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.68 (t, *J* = 2.1 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.12 – 7.07 (m, 1H), 7.04 – 6.98 (m, 1H), 3.49 (dq, *J* = 8.8, 7.2 Hz, 1H), 2.75 (dd, *J* = 7.3, 2.1 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.28 – 1.09 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.69, 160.91 (d, J_{CF} = 244.9 Hz), 130.52 (d, J_{CF} = 13.8 Hz), 128.85 (d, J_{CF} = 5.0 Hz), 128.00 (d, J_{CF} = 8.8 Hz), 124.27 (d, J_{CF} = 3.8 Hz), 115.66 (d, J_{CF} = 23.1 Hz), 49.37 (d, J_{CF} = 1.7 Hz), 35.22 (d, J_{CF} = 1.7 Hz), 33.53, 31.77, 29.39, 29.12, 27.32, 22.61, 14.07. ^{19}**F NMR** (376 MHz, $CDCl_3$) δ -120.39. HRMS (ESI-TOF) Calcd for $C_{16}H_{23}FNaO^+$ $[M+Na]^+$: 273.1625, found: 273.1621.

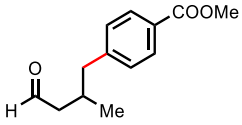


2p

methyl 4-(4-oxobutan-2-yl)benzoate (2p)

Following the **General Procedure A**, reaction time 18 h, **2p** was obtained as a colorless oil in 77% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.72 (t, *J* = 1.8 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 3H), 3.43 (h, *J* = 7.0 Hz, 1H), 2.81 – 2.67 (m, 2H), 1.33 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.02, 166.92, 150.85, 130.07, 128.55, 126.86, 52.07, 51.44, 34.19, 21.91. Spectroscopic data for this compound is consistent with that shown in the literature.[12]

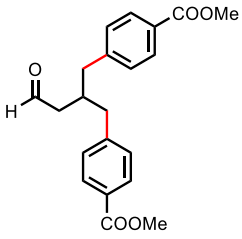
Spectroscopic characterization of γ-arylation products



5a$_{mono}$

Methyl 4-(2-methyl-4-oxobutyl)benzoate (5a$_{mono}$)

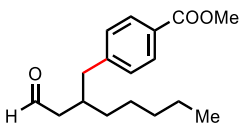
Following the **General Procedure B**, **5a$_{mono}$** was obtained as a colorless oil in 40% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.73 (dd, *J* = 2.3, 1.4 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 3H), 2.68 (dd, *J* = 13.4, 6.7 Hz, 1H), 2.59 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.45 – 2.37 (m, 2H), 2.32 – 2.26 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.04, 167.04, 145.53, 129.73, 129.21, 128.28, 52.04, 50.23, 43.07, 29.97, 19.85. HRMS (ESI-TOF) Calcd for $C_{13}H_{16}NaO_3^+$ $[M+Na]^+$: 243.0991, found: 243.0992.



5a$_{di}$

Dimethyl 4,4'-(2-(2-oxoethyl)propane-1,3-diyl)dibenzoate (5a$_{di}$)

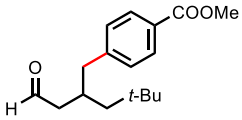
Following the **General Procedure B**, **5a$_{di}$** was obtained as a colorless oil in 32% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.61 (t, *J* = 1.5 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 4H), 7.22 (d, *J* = 8.3 Hz, 4H), 3.91 (s, 6H), 2.73 (dd, *J* = 13.2, 6.1 Hz, 2H), 2.69 – 2.59 (m, 3H), 2.35 (dd, *J* = 5.9, 1.5 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.32, 166.95, 145.07, 129.88, 129.22, 128.50, 52.08, 46.93, 40.30, 36.84. HRMS (ESI-TOF) Calcd for $C_{21}H_{23}O_5^+$ $[M+H]^+$: 355.1540, found: 355.1537.



5b

Methyl 4-(2-(2-oxoethyl)heptyl)benzoate (5b)

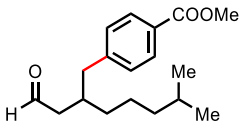
Following the **General Procedure B**, **5b** was obtained as a colorless oil in 60% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 3.90 (s, 3H), 2.75 (dd, *J* = 13.6, 6.3 Hz, 1H), 2.58 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.33 (tq, *J* = 12.2, 6.1 Hz, 3H), 1.28 (dtd, *J* = 25.3, 13.4, 12.6, 6.6 Hz, 8H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.33, 167.04, 145.73, 129.74, 129.27, 128.23, 52.03, 47.82, 40.59, 34.96, 33.92, 31.88, 26.41, 22.56, 14.03. HRMS (ESI-TOF) Calcd for $C_{18}H_{27}O_2^+$ $[M+H]^+$: 277.1804, found: 277.1805.



5c

Methyl 4-(4,4-dimethyl-2-(2-oxoethyl)pentyl)benzoate (5c)

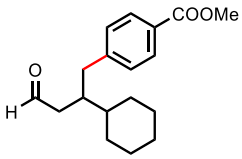
Following the **General Procedure B**, reaction time 36 h, **5c** was obtained as a colorless oil in 72% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (t, *J* = 1.9 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 3H), 2.73 (dd, *J* = 13.5, 6.7 Hz, 1H), 2.61 (dd, *J* = 13.5, 7.8 Hz, 1H), 2.43 – 2.35 (m, 2H), 2.32 (td, *J* = 12.3, 6.5 Hz, 1H), 1.33 (dd, *J* = 14.3, 4.5 Hz, 1H), 1.24 (dd, *J* = 14.2, 5.3 Hz, 1H), 0.86 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.27, 167.05, 145.89, 129.72, 129.37, 128.25, 52.03, 50.15, 47.39, 42.91, 31.44, 31.18, 29.81. HRMS (ESI-TOF) Calcd for $C_{17}H_{25}O_3^+$ $[M+H]^+$: 277.1804, found: 277.1799.



5d

Methyl 4-(6-methyl-2-(2-oxoethyl)heptyl)benzoate (5d)

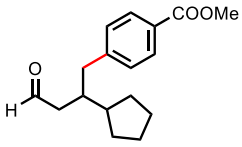
Following the **General Procedure B**, **5d** was obtained as a colorless oil in 61% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.69 (t, *J* = 1.9 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 3H), 2.75 (dd, *J* = 13.6, 6.3 Hz, 1H), 2.59 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.39 – 2.25 (m, 3H), 1.50 (dp, *J* = 13.3, 6.6 Hz, 1H), 1.38 – 1.24 (m, 4H), 1.15-1.12 (m, 2H), 0.85 (d, *J* = 6.6 Hz, 6H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.33, 167.05, 145.72, 129.75, 129.27, 128.24, 52.04, 47.84, 40.62, 38.96, 34.99, 34.22, 27.87, 24.51, 22.59, 22.56. HRMS (ESI-TOF) Calcd for $C_{18}H_{26}NaO_3^+$ $[M+Na]^+$: 313.1774, found: 313.1771.



5e

Methyl 4-(2-cyclohexyl-4-oxobutyl)benzoate (5e)

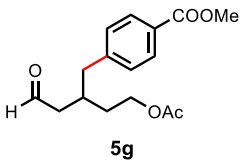
Following the **General Procedure B**, **5e** was obtained as a colorless oil in 60% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.59 (t, *J* = 1.9 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.81 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.50 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.46 – 2.39 (m, 1H), 2.24 (dddd, *J* = 17.1, 12.3, 6.6, 2.9 Hz, 2H), 1.82 – 1.62 (m, 5H), 1.35 (tq, *J* = 11.8, 3.3 Hz, 1H), 1.23 – 1.02 (m, 5H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.46, 167.04, 146.26, 129.79, 129.22, 128.20, 52.02, 45.17, 40.43, 37.85, 30.25, 29.36, 26.56, 26.55. HRMS (ESI-TOF) Calcd for $C_{18}H_{24}NaO_3^+$ $[M+Na]^+$: 311.1617, found: 311.1615.



5f

Methyl 4-(2-cyclopentyl-4-oxobutyl)benzoate (5f)

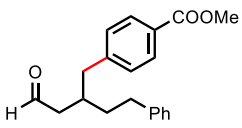
Following the **General Procedure B**, **5f** was obtained as a colorless oil in 59% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.61 (d, *J* = 2.1 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 3.90 (s, 3H), 2.89 (dd, *J* = 13.7, 5.3 Hz, 1H), 2.57 (dd, *J* = 13.7, 8.9 Hz, 1H), 2.35 (qd, *J* = 17.0, 4.7 Hz, 2H), 2.25 (h, *J* = 6.0 Hz, 1H), 1.84 (h, *J* = 8.1 Hz, 2H), 1.77 – 1.71 (m, 1H), 1.64 – 1.48 (m, 4H), 1.24 – 1.14 (m, 2H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.42, 167.03, 145.88, 129.77, 129.32, 128.23, 52.03, 46.29, 43.94, 40.12, 39.63, 30.77, 30.26, 25.34, 25.31. HRMS (ESI-TOF) Calcd for $C_{17}H_{22}NaO_3^+$ $[M+H]^+$: 297.1461, found: 297.1455.



5g

Methyl 4-(4-acetoxy-2-(2-oxoethyl)butyl)benzoate (5g)

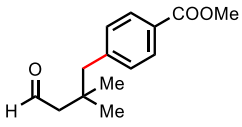
Following the **General Procedure B**, **5g** was obtained as a colorless oil in 56% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.70 (t, *J* = 1.3 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 4.17 – 4.07 (m, 2H), 3.91 (s, 3H), 2.77 (dd, *J* = 13.5, 5.9 Hz, 1H), 2.66 (dd, *J* = 13.5, 6.7 Hz, 1H), 2.51 – 2.34 (m, 3H), 2.05 (s, 3H), 1.76 – 1.64 (m, 2H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.35, 171.02, 166.96, 144.91, 129.86, 129.25, 128.50, 62.07, 52.08, 47.46, 40.38, 32.55, 31.93, 20.96. HRMS (ESI-TOF) Calcd for $C_{16}H_{20}NaO_5^+$ $[M+Na]^+$: 315.1203, found: 315.1206.



5h

Methyl 4-(4-oxo-2-phenethylbutyl)benzoate (5h)

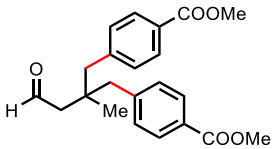
Following the **General Procedure B**, **5h** was obtained as a colorless oil in 45% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.68 (t, *J* = 1.8 Hz, 1H), 7.98 – 7.94 (m, 2H), 7.27 (d, *J* = 6.1 Hz, 2H), 7.23 – 7.20 (m, 2H), 7.20 – 7.17 (m, 1H), 7.14 – 7.11 (m, 2H), 3.91 (s, 3H), 2.82 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.71 – 2.60 (m, 3H), 2.45 – 2.32 (m, 3H), 1.75 – 1.62 (m, 2H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.94, 167.01, 145.35, 141.57, 129.80, 129.26, 128.48, 128.35, 128.27, 126.01, 52.05, 47.72, 40.40, 35.60, 34.45, 33.08. HRMS (ESI-TOF) Calcd for $C_{20}H_{23}O_3^+$ $[M+H]^+$: 311.1647, found: 311.1646.



5i$_{mono}$

Methyl 4-(2,2-dimethyl-4-oxobutyl)benzoate (5i$_{mono}$)

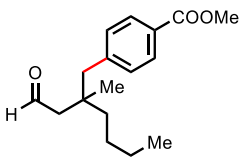
Following the **General Procedure B**, **5i$_{mono}$** was obtained as a colorless oil in 60% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.86 (t, *J* = 2.8 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H), 2.70 (s, 2H), 2.27 (d, *J* = 2.8 Hz, 2H), 1.08 (s, 6H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.96, 167.07, 143.47, 130.61, 129.26, 128.37, 54.31, 52.06, 48.57, 34.71, 27.39. HRMS (ESI-TOF) Calcd for $C_{14}H_{18}NaO_3^+$ $[M+Na]^+$: 257.1148, found: 257.1138.



5i$_{di}$

Dimethyl 4,4'-(2-methyl-2-(2-oxoethyl)propane-1,3-diyl)dibenzoate (5i$_{di}$)

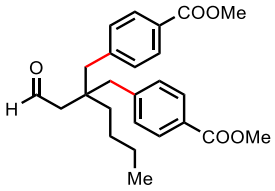
Following the **General Procedure B**, **5i$_{di}$** was obtained as a colorless oil in 23% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.81 (t, *J* = 2.1 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 4H), 7.20 (d, *J* = 8.3 Hz, 4H), 3.91 (s, 6H), 2.92 (d, *J* = 13.1 Hz, 2H), 2.77 (d, *J* = 13.1 Hz, 2H), 2.23 (d, *J* = 2.1 Hz, 2H), 1.03 (s, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.46, 166.99, 143.05, 130.77, 129.38, 128.58, 52.09, 50.76, 46.54, 38.49, 24.56. HRMS (ESI-TOF) Calcd for $C_{22}H_{25}O_3^+$ $[M+H]^+$: 369.1697, found: 369.1691.



5j$_{mono}$

Methyl 4-(2-methyl-2-(2-oxoethyl)hexyl)benzoate (5j$_{mono}$)

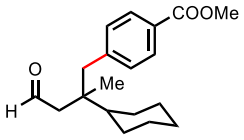
Following the **General Procedure B**, **5j$_{mono}$** was obtained as a colorless oil in 44% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.84 (t, *J* = 2.8 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 3H), 2.73 (q, *J* = 13.2 Hz, 2H), 2.32 – 2.20 (m, 2H), 1.44 – 1.28 (m, 6H), 1.04 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 203.16, 167.08, 143.53, 130.68, 129.26, 128.32, 52.05, 51.97, 46.23, 39.62, 37.47, 26.05, 25.05, 23.28, 14.10. HRMS (ESI-TOF) Calcd for $C_{17}H_{24}NaO_3^+$ $[M+Na]^+$: 299.1617, found: 299.1613.



5j$_{di}$

Dimethyl 4,4'-(2-butyl-2-(2-oxoethyl)propane-1,3-diyl)dibenzoate (5j$_{di}$)

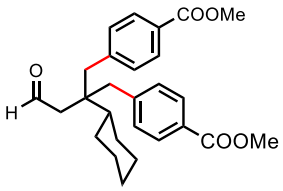
Following the **General Procedure B**, **5j$_{di}$** was obtained as a colorless oil in 16% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.73 – 9.69 (m, 1H), 7.96 (d, *J* = 8.3 Hz, 4H), 7.19 (d, *J* = 8.3 Hz, 4H), 3.91 (s, 6H), 2.93 – 2.84 (m, 4H), 2.20 (d, *J* = 2.0 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.33 (h, *J* = 6.8 Hz, 4H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.49, 166.97, 143.28, 130.69, 129.45, 128.55, 52.10, 49.49, 43.06, 41.47, 35.42, 25.88, 23.10, 14.15. HRMS (ESI-TOF) Calcd for $C_{25}H_{31}O_5^+$ $[M+H]^+$: 411.2166, found: 411.2168.



5k$_{mono}$

Methyl 4-(2-cyclohexyl-2-methyl-4-oxobutyl)benzoate (5k$_{mono}$)

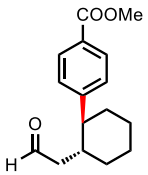
Following the **General Procedure B**, **5k$_{mono}$** was obtained as a colorless oil in 37% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.79 (t, *J* = 2.8 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H), 2.82 – 2.72 (m, 2H), 2.32 (dd, *J* = 15.4, 3.1 Hz, 1H), 2.19 (dd, *J* = 15.4, 2.5 Hz, 1H), 1.89 – 1.78 (m, 4H), 1.69 (d, *J* = 12.4 Hz, 1H), 1.36 (tt, *J* = 11.7, 2.8 Hz, 1H), 1.23 – 1.05 (m, 5H), 1.02 (s, 3H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 203.50, 167.07, 143.96, 130.81, 129.24, 128.28, 52.05, 50.31, 45.30, 43.42, 40.32, 27.57, 27.27, 26.91, 26.53, 22.63. HRMS (ESI-TOF) Calcd for $C_{19}H_{26}NaO_3^+$ $[M+Na]^+$: 325.1774, found: 325.1766.



5k$_{di}$

Dimethyl 4,4'-(2-cyclohexyl-2-(2-oxoethyl)propane-1,3-diyl)dibenzoate (5k$_{di}$)

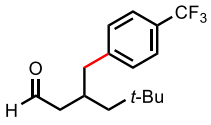
Following the **General Procedure B**, **5k$_{di}$** was obtained as a colorless oil in 9% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.09 (t, *J* = 2.3 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 4H), 7.19 (d, *J* = 8.4 Hz, 4H), 3.91 (s, 6H), 3.00 (d, *J* = 13.4 Hz, 2H), 2.78 (d, *J* = 13.4 Hz, 2H), 2.31 (d, *J* = 2.4 Hz, 2H), 1.86 (dd, *J* = 17.8, 10.7 Hz, 4H), 1.69 (dd, *J* = 32.4, 10.2 Hz, 2H), 1.27 – 1.16 (m, 5H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.45, 166.91, 143.36, 131.00, 129.52, 128.65, 52.10, 48.61, 44.03, 42.31, 41.80, 27.54, 26.89, 26.52. HRMS (ESI-TOF) Calcd for $C_{27}H_{33}O_5^+$ $[M+H]^+$: 437.2323, found: 437.2328.



5l

Methyl 4-(2-(2-oxoethyl)cyclohexyl)benzoate (5l)

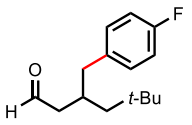
Following the **General Procedure B**, **5l** was obtained as a colorless oil in 20% yield. The relative stereochemistry was determined by NOESY analysis. ^{1}**H NMR** (600 MHz, $CDCl_3$) ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.50 (dt, *J* = 2.3, 1.1 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.34 (td, *J* = 11.5, 3.5 Hz, 1H), 2.22 – 2.11 (m, 2H), 2.10 – 2.04 (m, 1H), 1.96 – 1.90 (m, 1H), 1.88 – 1.78 (m, 3H), 1.53 – 1.48 (m, 1H), 1.48 – 1.32 (m, 2H), 1.22 – 1.10 (m, 1H). ^{13}**C NMR** (151 MHz, $CDCl_3$) ^{13}**C NMR** (151 MHz, $CDCl_3$) ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.08, 166.97, 150.75, 130.04, 128.52, 127.62, 52.03, 50.36, 49.02, 37.75, 35.25, 33.18, 26.45, 26.11. HRMS (ESI-TOF) Calcd for $C_{16}H_{20}NaO_3^+$ $[M+Na]^+$: 283.1304, found: 283.1303.



6a

5,5-dimethyl-3-(4-(trifluoromethyl)benzyl)hexanal (6a)

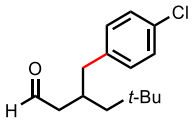
Following the **General Procedure B**, reaction time 36 h, **6a** was obtained as a colorless oil in 64% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.69 (t, *J* = 1.9 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.32 – 7.27 (m, 2H), 2.74 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.61 (dd, *J* = 13.5, 7.8 Hz, 1H), 2.40 (dt, *J* = 6.1, 1.8 Hz, 2H), 2.34 – 2.28 (m, 1H), 1.33 (dd, *J* = 14.3, 4.6 Hz, 1H), 1.25 (dd, *J* = 14.3, 5.3 Hz, 1H), 0.87 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.20, 144.49, 129.61, 128.53 (q, J_{CF}= 96.3 Hz), 125.30 (q, J_{CF} = 3.9 Hz), 124.27 (q, J_{CF} = 272.0 Hz), 50.00, 47.36, 42.63, 31.38, 31.19, 29.81. ^{19}**F NMR** (376 MHz, $CDCl_3$) δ -65.01. HRMS (ESI-TOF) Calcd for $C_{16}H_{21}F_3NaO^+$ $[M+Na]^+$: 309.1436, found: 309.1440.



6b

3-(4-fluorobenzyl)-5,5-dimethylhexanal (6b)

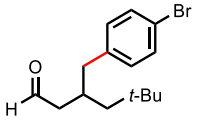
Following the **General Procedure B**, reaction time 36 h, **6b** was obtained as a colorless oil in 57% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.66 (t, *J* = 2.0 Hz, 1H), 7.12 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 2.67 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.50 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.41 – 2.34 (m, 2H), 2.28 – 2.21 (m, 1H), 1.33 (dd, *J* = 14.3, 4.6 Hz, 1H), 1.23 (dd, *J* = 14.2, 5.2 Hz, 1H), 0.87 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.51, 161.49 (d, J_{CF} = 244.3 Hz), 135.95 (d, J_{CF} = 2.8 Hz), 130.66 (d, J_{CF} = 7.7 Hz), 115.15 (d, J_{CF} = 21.1 Hz), 50.10, 47.41, 42.15, 31.77, 31.21, 29.82. ^{19}**F NMR** (376 MHz, $CDCl_3$) δ -119.65. HRMS (ESI-TOF) Calcd for $C_{15}H_{21}FNaO^+$ $[M+Na]^+$: 259.1468, found: 259.1467.



6c

3-(4-chlorobenzyl)-5,5-dimethylhexanal (6c)

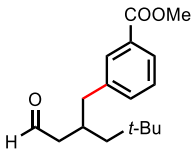
Following the **General Procedure B**, reaction time 36 h, **6c** was obtained as a colorless oil in 64% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.66 (t, *J* = 2.0 Hz, 1H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 2.66 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.50 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.38 (dd, *J* = 6.1, 2.1 Hz, 2H), 2.26 (ddt, *J* = 12.8, 7.9, 3.0 Hz, 1H), 1.32 (dd, *J* = 14.3, 4.6 Hz, 1H), 1.23 (dd, *J* = 14.3, 5.3 Hz, 1H), 0.87 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.40, 138.77, 132.01, 130.64, 128.49, 50.04, 47.40, 42.25, 31.56, 31.19, 29.82. HRMS (ESI-TOF) Calcd for $C_{15}H_{21}ClNaO^+$ $[M+Na]^+$: 275.1173, found: 275.1172.



6d

3-(4-bromobenzyl)-5,5-dimethylhexanal (6d)

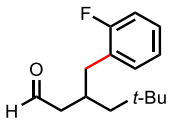
Following the **General Procedure B**, reaction time 36 h, **6d** was obtained as a colorless oil in 63% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (t, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 2.65 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.49 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.38 (dd, *J* = 6.4, 1.9 Hz, 2H), 2.26 (dddd, *J* = 12.9, 7.9, 6.3, 3.2 Hz, 1H), 1.32 (dd, *J* = 14.2, 4.6 Hz, 1H), 1.23 (dd, *J* = 14.3, 5.3 Hz, 1H), 0.87 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.39, 139.29, 131.44, 131.04, 120.04, 50.02, 47.39, 42.30, 31.49, 31.19, 29.83. HRMS (ESI-TOF) Calcd for $C_{15}H_{21}BrNaO^+$ $[M+Na]^+$: 319.0668, found: 319.0669.



6e

Methyl 3-(4,4-dimethyl-2-(2-oxoethyl)pentyl)benzoate (6e)

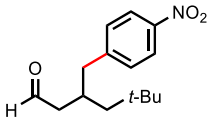
Following the **General Procedure B**, reaction time 36 h, **6e** was obtained as a colorless oil in 69% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (t, *J* = 2.0 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.84 (s, 1H), 7.39 – 7.35 (m, 2H), 3.92 (s, 3H), 2.76 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.59 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.41 – 2.36 (m, 2H), 2.36 – 2.27 (m, 1H), 1.34 (dd, *J* = 14.3, 4.6 Hz, 1H), 1.25 (dd, *J* = 14.3, 5.2 Hz, 1H), 0.87 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.39, 167.16, 140.69, 133.96, 130.31, 130.25, 128.47, 127.59, 52.14, 50.05, 47.42, 42.71, 31.55, 31.21, 29.84. HRMS (ESI-TOF) Calcd for $C_{17}H_{24}NaO_3^+$ $[M+Na]^+$: 299.1617, found: 299.1621.



6f

3-(2-fluorobenzyl)-5,5-dimethylhexanal (6f)

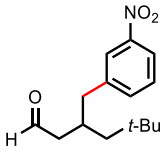
Following the **General Procedure B**, reaction time 36 h, **6f** was obtained as a colorless oil in 61% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.65 (t, *J* = 2.0 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.06 (td, *J* = 7.5, 1.2 Hz, 1H), 7.02 (ddd, *J* = 9.7, 8.2, 1.2 Hz, 1H), 2.80 (dd, *J* = 13.5, 5.4 Hz, 1H), 2.54 (dd, *J* = 13.5, 7.6 Hz, 1H), 2.42 – 2.30 (m, 3H), 1.34 (dd, *J* = 14.2, 4.4 Hz, 1H), 1.27 (dd, *J* = 14.2, 4.3 Hz, 1H), 0.89 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.65, 161.38 (d, J_{CF} = 244.8 Hz), 131.71 (d, J_{CF} = 5.0 Hz), 128.11 (d, J_{CF} = 8.2 Hz), 127.18 (d, J_{CF} = 15.9 Hz), 123.96 (d, J_{CF} = 3.4 Hz), 115.37 (d, J_{CF} = 22.5 Hz), 50.11, 47.85, 36.26, 31.19, 30.63, 29.74. ^{19}**F NMR** (376 MHz, $CDCl_3$) δ -120.03. HRMS (ESI-TOF) Calcd for $C_{15}H_{21}FNaO^+$ $[M+H]^+$: 259.1468, found: 259.1470.



6g

5,5-dimethyl-3-(4-nitrobenzyl)hexanal (6g)

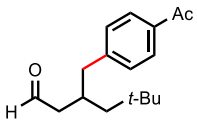
Following the **General Procedure B**, reaction time 36 h, **6g** was obtained as a colorless oil in 70% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.72 (t, *J* = 1.7 Hz, 1H), 8.16 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 2.76 – 2.65 (m, 2H), 2.51 – 2.39 (m, 2H), 2.34 (dtdd, *J* = 7.2, 5.8, 4.8, 2.9 Hz, 1H), 1.33 – 1.24 (m, 2H), 0.85 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.78, 148.34, 146.63, 130.14, 123.65, 50.18, 47.24, 42.63, 31.25, 31.14, 29.76. HRMS (ESI-TOF) Calcd for $C_{15}H_{22}NO_3^+$ $[M+H]^+$: 264.1594, found: 264.1592.



6h

5,5-dimethyl-3-(3-nitrobenzyl)hexanal (6h)

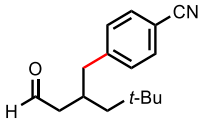
Following the **General Procedure B**, reaction time 36 h, **6h** was obtained as a colorless oil in 71% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.72 (t, *J* = 1.7 Hz, 1H), 8.08 (ddd, *J* = 8.1, 2.3, 1.1 Hz, 1H), 8.05 (t, *J* = 2.0 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 2.77 – 2.66 (m, 2H), 2.50 – 2.39 (m, 2H), 2.37 – 2.30 (m, 1H), 1.30 (qd, *J* = 14.3, 4.9 Hz, 2H), 0.86 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.83, 148.28, 142.45, 135.60, 129.30, 124.01, 121.51, 50.09, 47.19, 42.41, 31.25, 31.17, 29.78. HRMS (ESI-TOF) Calcd for $C_{15}H_{22}NO_3^+$ $[M+H]^+$: 264.1594, found: 264.1596.



6i

3-(4-acetylbenzyl)-5,5-dimethylhexanal (6i)

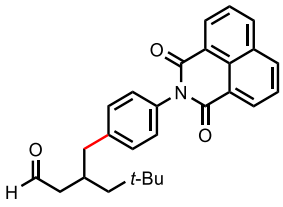
Following the **General Procedure B**, reaction time 36 h, **6i** was obtained as a colorless oil in 59% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.68 (t, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.74 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.64 – 2.59 (m, 1H), 2.59 (s, 3H), 2.40 (dt, *J* = 6.0, 1.5 Hz, 2H), 2.36 – 2.29 (m, 1H), 1.34 (dd, *J* = 14.3, 4.5 Hz, 1H), 1.25 (dd, *J* = 14.3, 5.3 Hz, 1H), 0.87 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.25, 197.82, 146.17, 135.41, 129.55, 128.54, 50.12, 47.44, 42.88, 31.40, 31.19, 29.82, 26.58. HRMS (ESI-TOF) Calcd for $C_{17}H_{25}O_2^+$ $[M+H]^+$: 261.1849, found: 261.1853.



6j

4-(4,4-dimethyl-2-(2-oxoethyl)pentyl)benzonitrile (6j)

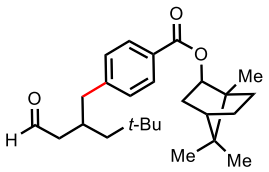
Following the **General Procedure B**, reaction time 36 h, **6j** was obtained as a colorless oil in 48% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.70 (t, *J* = 1.7 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 2.72 – 2.61 (m, 2H), 2.50 – 2.37 (m, 2H), 2.30 (qtd, *J* = 7.1, 5.6, 4.4 Hz, 1H), 1.31 – 1.23 (m, 2H), 0.85 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 201.87, 146.12, 132.20, 130.11, 118.94, 110.21, 50.14, 47.24, 42.91, 31.22, 31.14, 29.75. HRMS (ESI-TOF) Calcd for $C_{16}H_{22}NO^+$ $[M+H]^+$: 244.1696, found: 244.1704.



6k

3-(4-(1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)benzyl)-5,5-dimethylhexanal (6k)

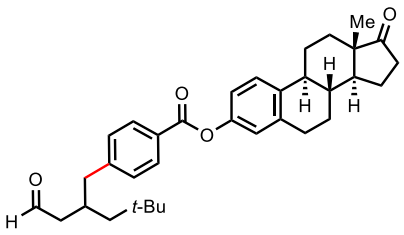
Following the **General Procedure B**, reaction time 36 h, **6k** was obtained as white solid in 56% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.73 (dd, *J* = 2.3, 1.7 Hz, 1H), 8.65 (dd, *J* = 7.2, 1.1 Hz, 2H), 8.28 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.80 (dd, *J* = 8.2, 7.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 2.86 (dd, *J* = 13.5, 5.6 Hz, 1H), 2.62 (dd, *J* = 13.5, 8.2 Hz, 1H), 2.50 (ddd, *J* = 16.2, 5.8, 1.8 Hz, 1H), 2.44 – 2.33 (m, 2H), 1.41 (dd, *J* = 14.3, 5.0 Hz, 1H), 1.32 – 1.29 (m, 1H), 0.93 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.79, 164.42, 140.90, 134.28, 133.54, 131.77, 131.62, 130.23, 128.57, 128.56, 127.05, 122.86, 49.82, 47.54, 42.58, 31.58, 31.31, 29.90. HRMS (ESI-TOF) Calcd for $C_{27}H_{28}NO_3^+$ $[M+H]^+$: 414.2064, found: 414.2064.



6l

(2*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(4,4-dimethyl-2-(2-oxoethyl)pentyl)benzoate (6l)

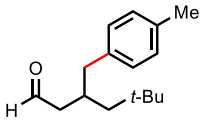
Following the **General Procedure B**, reaction time 36 h, **6l** was obtained as a colorless oil in 65% yield (d.r. =1:1). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.67 (t, *J* = 1.9 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.10 (dddd, *J* = 10.0, 3.5, 2.1, 1.3 Hz, 1H), 2.77 (dd, *J* = 13.5, 6.3 Hz, 1H), 2.60 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.50 – 2.44 (m, 1H), 2.39 (dd, *J* = 6.4, 1.9 Hz, 2H), 2.37 – 2.29 (m, 1H), 2.13 (ddd, *J* = 12.9, 9.5, 4.5 Hz, 1H), 1.86 – 1.77 (m, 1H), 1.74 (t, *J* = 4.5 Hz, 1H), 1.41 (dddd, *J* = 14.3, 12.2, 4.5, 2.2 Hz, 1H), 1.37 – 1.28 (m, 2H), 1.26 (dd, *J* = 14.3, 5.2 Hz, 1H), 1.12 (ddd, *J* = 13.8, 3.5, 1.5 Hz, 1H), 0.97 (s, 3H), 0.92 (d, *J* = 3.1 Hz, 6H), 0.88 (d, *J* = 0.8 Hz, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.32, 166.75, 145.66, 129.67, 129.31, 128.99, 80.43, 50.00, 49.09, 47.88, 47.49, 45.00, 42.90, 36.92, 31.48, 31.21, 29.86, 28.10, 27.40, 19.74, 18.93, 13.63. HRMS (ESI-TOF) Calcd for $C_{26}H_{38}NaO_3^+$ $[M+Na]^+$: 421.2713, found: 421.2712.



6m

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl 4-(4,4-dimethyl-2-(2-oxoethyl)pentyl)benzoate (6m)

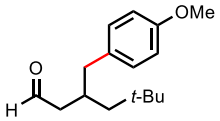
Following the **General Procedure B**, reaction time 36 h, **6m** was obtained as a white solid in 57% yield (d.r. =1:1). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.69 (t, *J* = 1.9 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.29 (m, 3H), 6.98 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.96 – 6.93 (m, 1H), 2.97 – 2.90 (m, 2H), 2.77 (dd, *J* = 13.4, 6.7 Hz, 1H), 2.65 (dd, *J* = 13.4, 7.7 Hz, 1H), 2.52 (ddd, *J* = 19.1, 8.8, 1.0 Hz, 1H), 2.46 – 2.39 (m, 3H), 2.33 (ddd, *J* = 15.5, 9.7, 4.8 Hz, 2H), 2.16 (dt, *J* = 19.0, 9.0 Hz, 1H), 2.09 – 1.96 (m, 3H), 1.65 – 1.48 (m, 6H), 1.36 (dd, *J* = 14.3, 4.4 Hz, 1H), 1.27 (dd, *J* = 14.2, 5.5 Hz, 1H), 0.93 (s, 3H), 0.88 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 220.80, 202.18, 165.37, 148.87, 146.64, 138.07, 137.40, 130.30, 129.55, 127.72, 126.46, 121.74, 118.90, 50.46, 50.17, 47.97, 47.42, 44.20, 42.97, 38.04, 35.87, 31.57, 31.43, 31.19, 29.83, 29.44, 26.37, 25.79, 21.61, 13.85. HRMS (ESI-TOF) Calcd for $C_{34}H_{43}O_4^+$ $[M+H]^+$: 515.3156, found: 515.3155.



6n

5,5-dimethyl-3-(4-methylbenzyl)hexanal (6n)

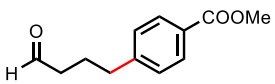
Following the **General Procedure B**, reaction running at 105 °C, **6n** was obtained as a colorless oil in 22% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.61 (t, *J* = 2.2 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 7.7 Hz, 2H), 2.74 (dd, *J* = 13.6, 5.7 Hz, 1H), 2.44 (dd, *J* = 13.6, 8.5 Hz, 1H), 2.38 (ddd, *J* = 16.3, 6.3, 2.0 Hz, 1H), 2.34 – 2.25 (m, 5H), 1.35 (dd, *J* = 14.2, 4.9 Hz, 1H), 1.23 (dd, *J* = 14.2, 4.8 Hz, 1H), 0.90 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.94, 137.13, 135.72, 129.18, 129.06, 49.99, 47.69, 42.64, 31.85, 31.26, 29.90, 21.03. HRMS (ESI-TOF) Calcd for $C_{16}H_{23}^+$ $[M-OH]^+$: 215.1800, found: 215.1798.



6o

3-(4-methoxybenzyl)-5,5-dimethylhexanal (6o)

Following the **General Procedure B**, reaction running at 105 °C, **6o** was obtained as a colorless oil in 36% yield. ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.62 (t, *J* = 2.2 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.70 (dd, *J* = 13.7, 6.0 Hz, 1H), 2.44 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.35 (qdd, *J* = 16.5, 6.3, 2.2 Hz, 2H), 2.29 – 2.21 (m, 1H), 1.34 (dd, *J* = 14.2, 4.9 Hz, 1H), 1.23 (dd, *J* = 14.2, 4.9 Hz, 1H), 0.89 (s, 9H). ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 202.90, 158.07, 132.32, 130.23, 113.77, 55.24, 50.06, 47.60, 42.19, 31.97, 31.25, 29.88. HRMS (ESI-TOF) Calcd for $C_{16}H_{23}O^+$ $[M-OH]^+$: 231.1749, found: 231.1753.

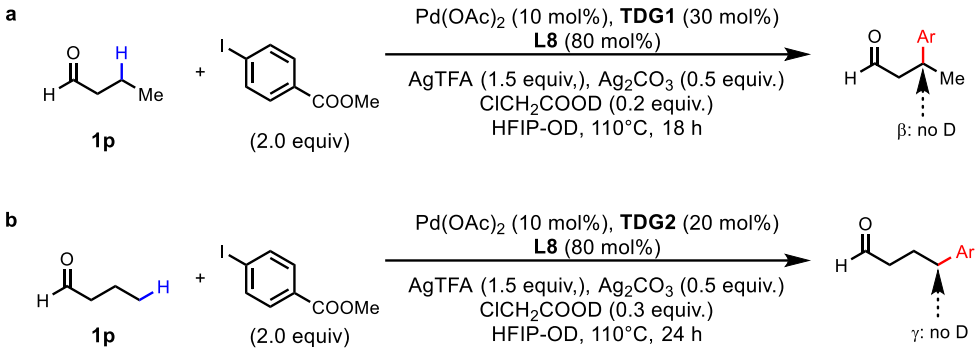


5m

methyl 4-(4-oxobutyl)benzoate (5m)

Following the **General Procedure B**, with slightly modification of solvent volume to 0.65 mL and **L8** loading to 80 mol%, **5m** was obtained as a colorless oil in 62% yield (**5m**/**2p** = 9/1). ^{1}**H NMR** (600 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.5 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H), 2.73 – 2.70 (m, 2H), 2.47 (td, *J* = 7.2, 1.5 Hz, 2H), 1.98 (p, *J* = 7.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.89, 167.05, 146.74, 129.84, 128.49, 128.16, 52.04, 43.03, 34.99, 23.26. Spectroscopic data for this compound is consistent with that shown in the literature.[13]

6. Deuterium Incorporation Experiments

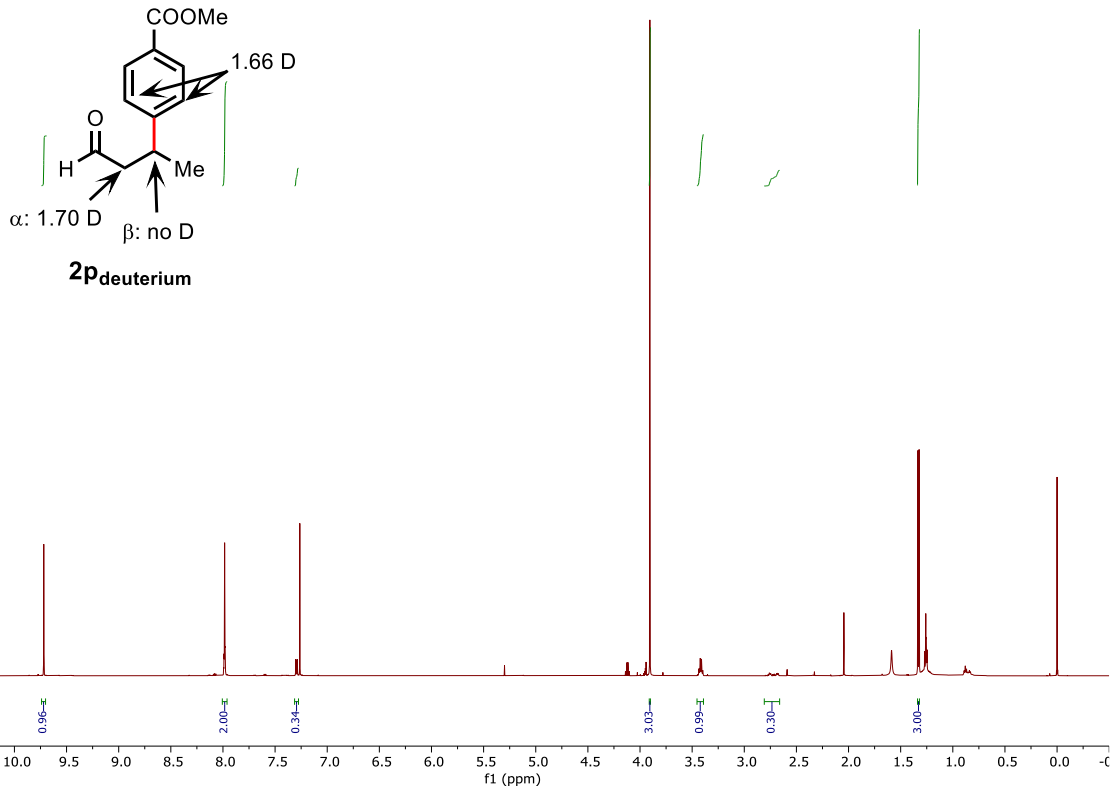


Deuterium Incorporation Experiments a:

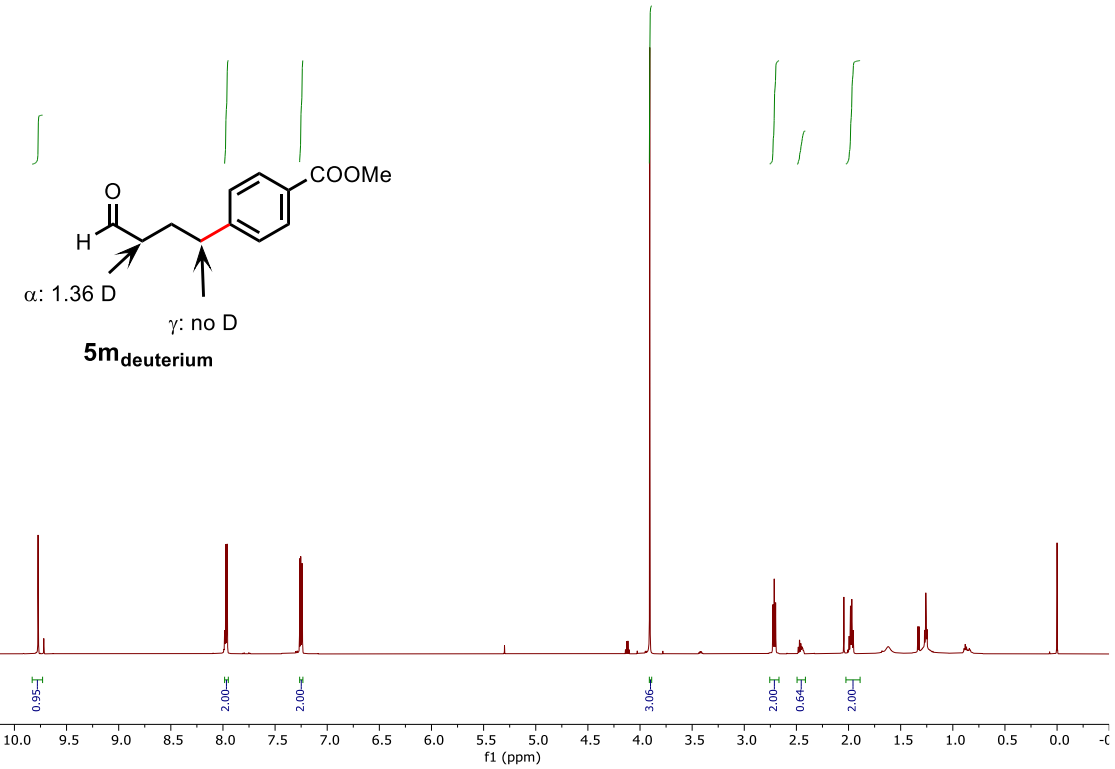
In air, to an oven-dried reaction tube (10 mL) equipped with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%), transient directing groups (**TDG1**, 0.03 mmol, 30 mol%), ligand (**L8**, 0.08 mmol, 80 mol%), ArI (0.2 mmol, 2.0 equiv), AgTFA (0.15 mmol, 1.5 equiv), Ag_2CO_3 (0.05 mmol, 0.5 equiv), and solvent (HFIP-OD, 0.75 mL and 0.02 mmol of $ClCH_2COOD$), followed by the aldehyde substrate **1p** (0.1 mmol, 1.0 equiv). The tube was sealed and stirred at room temperature for 20 min before heating to 110 °C for 18 h under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature and the dark brown suspension was diluted with 2 mL of ethyl acetate and was passed through a pad of Celite and washed with ethyl acetate (1.0 mL × 3). The crude reaction mixture was purified on silica gel using hexanes/EtOAc as the eluent to to get the arylation product (no deuteration at the *β*-position). This result indicated that the *β*-methylene C(sp^3)–H activation was not reversible under the reaction conditions.

Deuterium Incorporation Experiments b:

In air, to an oven-dried reaction tube (10 mL) equipped with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%), transient directing groups (**TDG2**, 0.02 mmol, 20 mol%), ligand (**L8**, 0.08 mmol, 80 mol%), ArI (0.2 mmol, 2.0 equiv), AgTFA (0.15 mmol, 1.5 equiv), Ag_2CO_3 (0.05 mmol, 0.5 equiv), and solvent (HFIP-OD, 0.65 mL and 0.03 mmol of $ClCH_2COOD$), followed by the aldehyde substrate **1p** (0.1 mmol, 1.0 equiv). The tube was sealed and stirred at room temperature for 20 min before heating to 110 °C for 24 h under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature and the dark brown suspension was diluted with 2 mL of ethyl acetate and was passed through a pad of Celite and washed with ethyl acetate (1.0 mL × 3). The crude reaction mixture was purified on silica gel using hexanes/EtOAc as the eluent to to get the arylation product (no deuteration at the *γ*-position). This result indicated that the *γ*-C(sp^3)–H activation was not reversible under the reaction conditions.

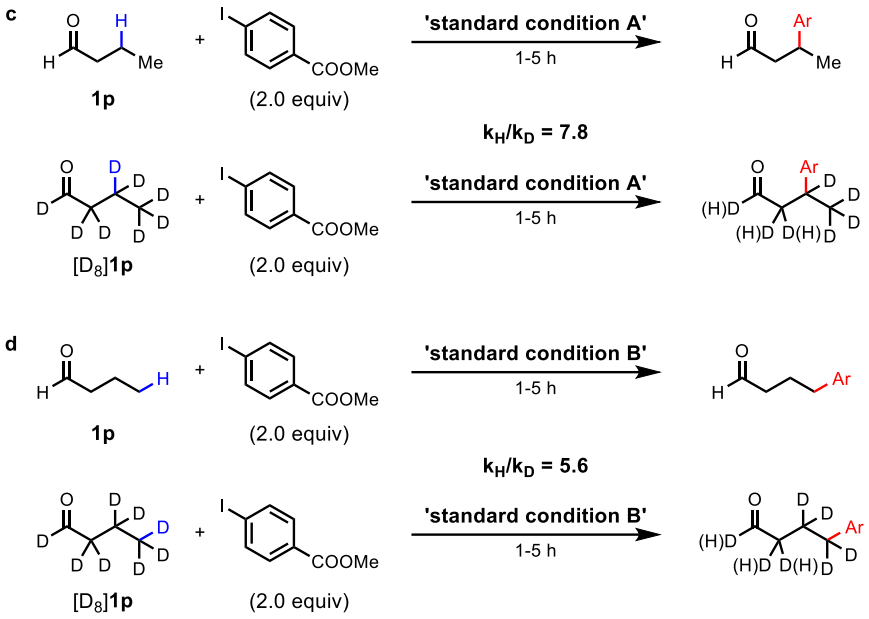


2p$_{deuterium}$



5m$_{deuterium}$

7. KIE Experiments



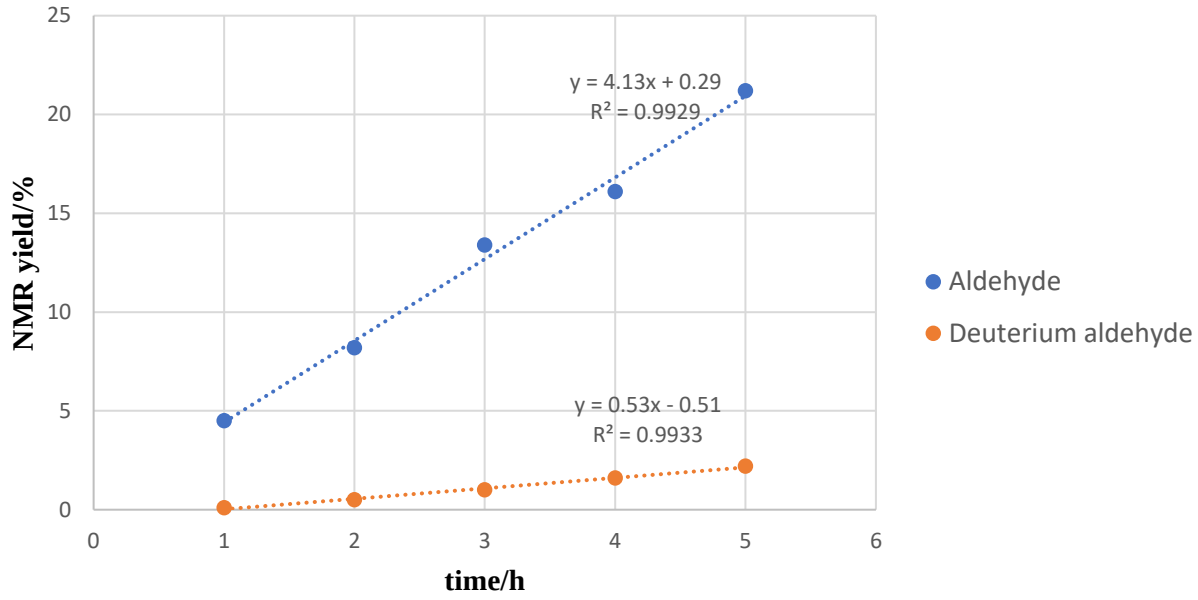
Standard condition A:

In air, to an oven-dried reaction tube (10 mL) equipped with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%), transient directing groups (**TDG1**, 0.03 mmol, 30 mol%), ligand (**L8**, 0.08 mmol, 80 mol%), ArI (0.2 mmol, 2.0 equiv), AgTFA (0.15 mmol, 1.5 equiv), Ag_2CO_3 (0.05 mmol, 0.5 equiv), and solvent (HFIP, 0.75 mL and 0.02 mmol of $ClCH_2COOH$), followed by the aldehyde substrate **1p** or **1p-d8** (0.1 mmol, 1.0 equiv). The tube was sealed and stirred at room temperature for 20 min before heating to 110 °C for 1-5 h under vigorous stirring. The reaction was quenched by freezing the vial in a dry ice-acetone bath at the indicated time, after then the mixture was diluted with 2 mL of ethyl acetate and was passed through a pad of Celite and washed with ethyl acetate (1.0 mL × 3). The yield of β-arylation product was determined by ^1H NMR using CH_2Br_2 as internal standard. The result indicated that the KIE were 7.8 for the β position respectively.

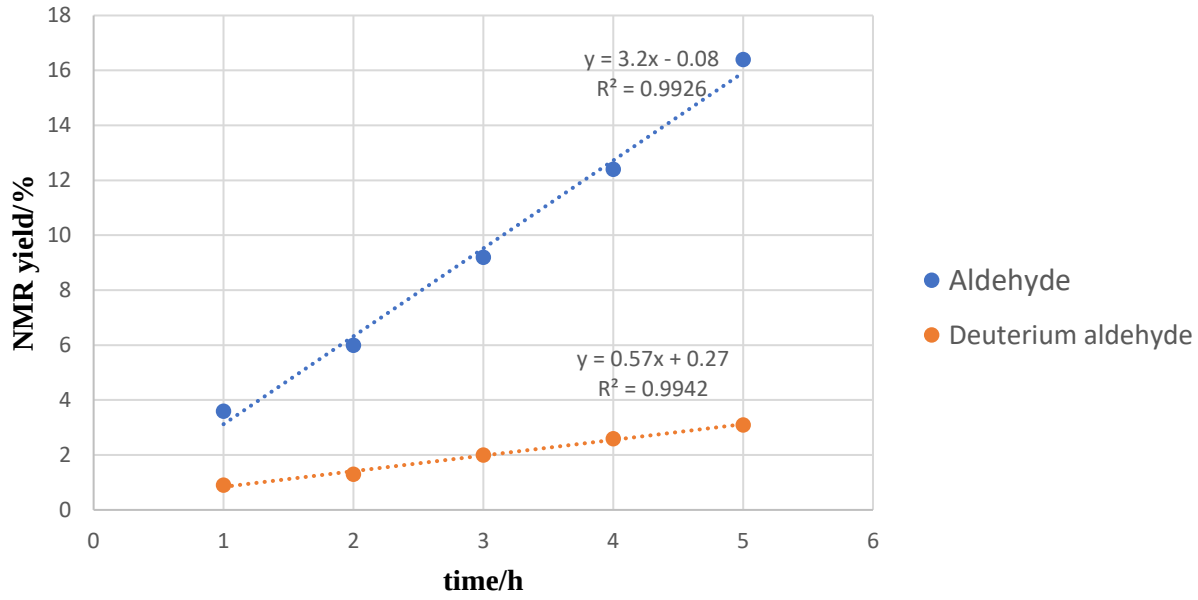
Standard condition B:

In air, to an oven-dried reaction tube (10 mL) equipped with a magnetic stir bar was added $Pd(OAc)_2$ (0.01 mmol, 10 mol%), transient directing groups (**TDG2**, 0.02 mmol, 20 mol%), ligand (**L8**, 0.08 mmol, 80 mol%), ArI (0.2 mmol, 2.0 equiv), AgTFA (0.15 mmol, 1.5 equiv), Ag_2CO_3 (0.05 mmol, 0.5 equiv), and solvent (HFIP, 0.65 mL and 0.03 mmol of $ClCH_2COOH$), followed by the aldehyde substrate **1p** or **1p-d8** (0.1 mmol, 1.0 equiv). The tube was sealed and stirred at room temperature for 20 min before heating to 110 °C for 1-5 h under vigorous stirring. The reaction was quenched by freezing the vial in a dry ice-acetone bath at the indicated time, after then the mixture was diluted with 2 mL of ethyl acetate and was passed through a pad of Celite and washed with ethyl acetate (1.0 mL × 3). The yield of γ-arylation product was determined by ^1H NMR using CH_2Br_2 as internal standard. The result indicated that the KIE were 5.6 for the γ position respectively.

KIE for β-C−H arylation: k_H/k_D = 7.8



KIE for γ-C−H arylation: k_H/k_D = 5.6



8. Computational Data and Analysis

A. Computational methods

DFT calculations were performed with *Gaussian16 (Rev. B.01)* suite of quantum chemical programs[14] with a pruned (99,590)-quadrature integration grid. Geometry optimizations were carried out with tight convergence thresholds using the B3LYP[15–18] density functional, combined with Grimme's D3 empirical dispersion correction[19] with Becke-Johnson damping.[20] The SDD basis set was used on Pd with Stuttgart-Dresden ECPs,[21] and a split-valence 6-31G(d,p) basis set[22-24] was used for all other atoms, augmented with diffuse functions on O atoms. Frequency analysis was carried out for all calculated transition state (TS) structures at the optimization level of theory to verify them as saddle points by the presence of precisely one imaginary vibrational frequency corresponding to the appropriate reactive vibrational mode. Single point electronic energies were computed at the PBE0[25]-$D3_{BJ}$/6-311++G(2d,p)/SDD(Pd) level. Bulk solvation effects of HFIP were implemented implicitly as a generic solvent (ε=17.8, n^2=1.629452)[26,27] for all calculations using the integral equation formalism polarizable continuum (IEF-PCM) solvation model.[28] The quasi-RRHO (rigid-rotor-harmonic-oscillator) approximation was applied to vibrational entropies, as proposed by Grimme,[29] switching to a free rotor description of vibrational modes below 100 cm^{-1}, with a smooth damping function applied to interpolate between the two limiting descriptions at the cut-off frequency (*GoodVibes v.3.0.1)*.[30] Enthalpies, quasi-harmonic Gibbs free energies, and Boltzmann weights population factors were evaluated at the reaction temperature (as indicated) and adjusted to the standard state concentration of 1 $mol \cdot dm^{-3}$.[30] All presented structures were visualized with *CylView 1.0b*.[31]

TS conformations were searched both systematically and via the xTB[32]-based conformer-rotamer ensemble sampling tool,[33] utilizing the GFN2-xTB[34] semiempirical tight binding quantum mechanical method with the iMTD-GC algorithm, where iterative (up to 5 cycles) RMSD-based molecular meta-dynamic sampling (MTD) is combined with an extra genetic z-matrix crossing (GC) step at the end.[35]

All located TS were separated into two groups based on the TDG, which were further split according to the C−H cleavage site (4 TS ensembles in total). Boltzmann-weighed relative TS ensemble free energies were calculated for each ensemble as sums of the relative free energies of constituent TS multiplied by their corresponding Boltzmann weights (population factors). Theoretical β/γ selectivities for each TDG were calculated as ratios between the sums of TS Boltzmann weights corresponding to the β and γ TS.

B. Energy span of TS ensembles based on the transient directing group (TDG)

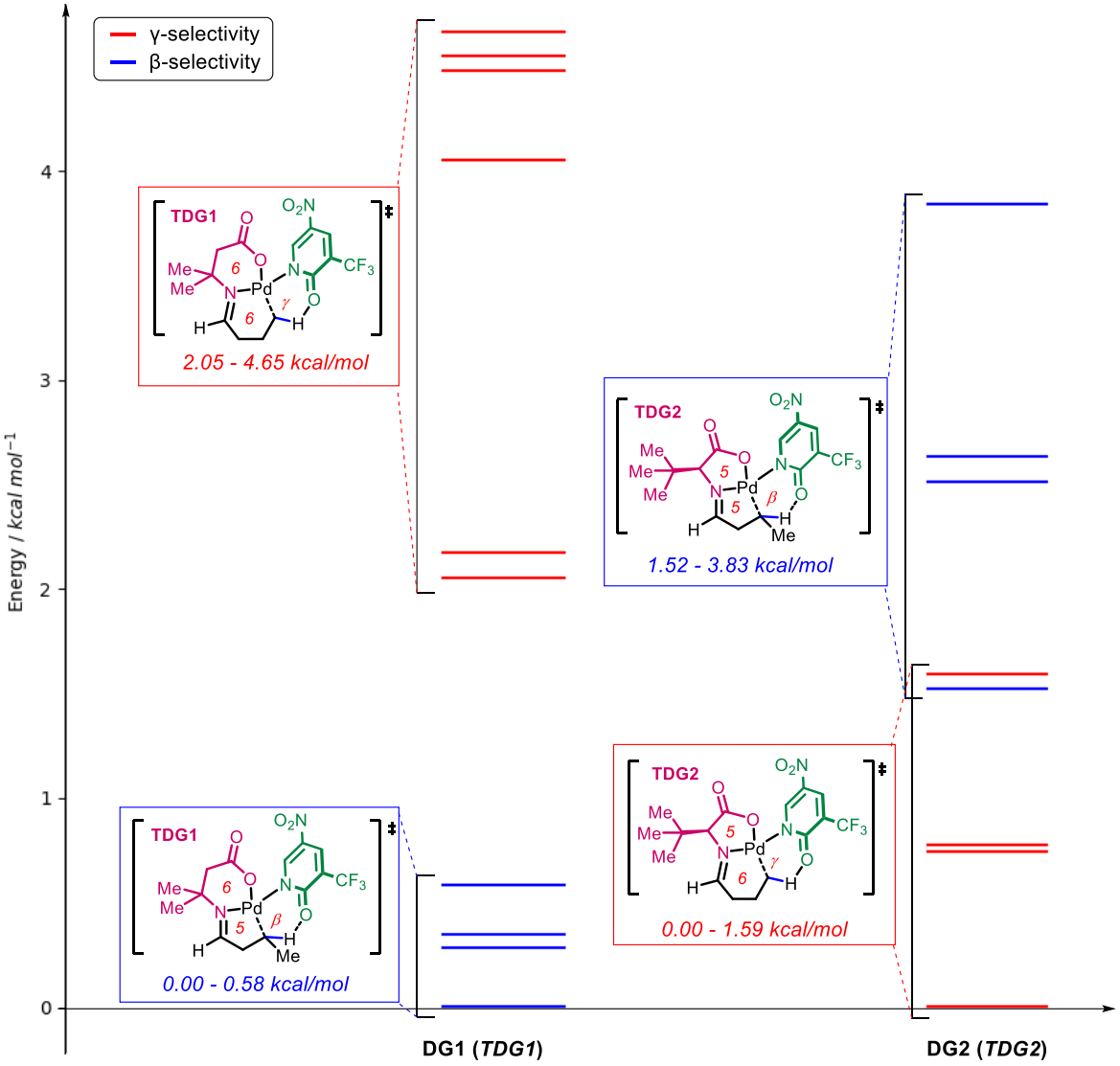


Figure S1. Relative quasi-harmonic Gibbs free energies (Δqh-G_{383}) are plotted in kcal/mol for the C(sp^3)−H cleavage TS in the analyzed ensembles for structures within 5 kcal/mol (corresponding to >99.9% of Boltzmann population).

C. Energies of the calculated structures

Notation

The following structure descriptors were used:

TS1[*C(sp^3)-H activation TS*]_**DG1/DG2**[*6-membered **TDG1** or 5-membered **TDG2**, respectively*]_**L1**[*3-nitro-5-trifluoromethyl-2-pyridone ligand (**L8**)*]-[*conformation number*]_**B/G**[*β or γ-C(sp^3)-H activation, respectively*]. All TS were separated into 2 groups according to the DG and further split according to site selectivity, comprising 4 ensembles for analysis (based on the **DG1**, **DG2**, **B**, and **G** descriptors). Lowest free energy TS structures within each ensemble are highlighted in bold. Predicted regioselectivities were computed for each TDG as the difference between the sums of Boltzmann factors corresponding to the *β* (**B**) and *γ* (**G**) TS.

Structure	E	ZPE	H	qh-G_{383}	$f_{Boltz.}$	Δqh-G_{383}
TS1_DG1_L1_2_B	-1549.140373	0.330572	-1548.767618	-1548.881500	0.340	**0.00**
TS1_DG1_L1_4_B	-1549.140299	0.330653	-1548.767558	-1548.881052	0.235	0.28
TS1_DG1_L1_3_B	-1549.139656	0.330479	-1548.766940	-1548.880963	0.218	0.34
TS1_DG1_L1_1_B	-1549.139487	0.330483	-1548.766825	-1548.880580	0.159	0.58
TS1_DG1_L1_2-1_G	-1549.137933	0.331137	-1548.764960	-1548.878241	0.023	**2.05**
TS1_DG1_L1_2-2_G	-1549.138219	0.331351	-1548.765115	-1548.878044	0.020	2.17
TS1_DG1_L1_1-2_G	-1549.134154	0.330837	-1548.761303	-1548.875065	0.002	4.04
TS1_DG1_L1_4-2_G	-1549.133755	0.330844	-1548.760962	-1548.874376	0.001	4.47
TS1_DG1_L1_1-1_G	-1549.134042	0.331110	-1548.761040	-1548.874263	0.001	4.54
TS1_DG1_L1_4-1_G	-1549.133553	0.330896	-1548.760702	-1548.874094	0.001	4.65
TS1_DG2_L1_3-4_G	-1588.415902	0.358808	-1588.012927	-1588.130526	0.481	**0.00**
TS1_DG2_L1_3-3_G	-1588.414989	0.359144	-1588.011766	-1588.129346	0.182	0.74
TS1_DG2_L1_2-1-2_G	-1588.414824	0.358967	-1588.011706	-1588.129301	0.175	0.77
TS1_DG2_L1_1-2_B	-1588.412556	0.358335	-1588.009751	-1588.128098	0.065	**1.52**
TS1_DG2_L1_1-1_G	-1588.413683	0.359068	-1588.010468	-1588.127996	0.060	1.59
TS1_DG2_L1_2-2_B	-1588.411112	0.358271	-1588.008386	-1588.126541	0.018	2.50
TS1_DG2_L1_1-1_B	-1588.410670	0.358181	-1588.007989	-1588.126343	0.015	2.62
TS1_DG2_L1_2-1_B	-1588.409129	0.358278	-1588.006449	-1588.124429	0.003	3.83

Table S1. Electronic energies (E), zero-point energy corrections (ZPE), enthalpies (H), and quasi-harmonic Gibbs free energies (qh-G (T=383.15 K)) are given in Hartree at the IEFPCM$_{HFIP}$-PBE0-D3$_{BJ}$/6-311++G(2d,p)/SDD(Pd)//B3LYP-D3$_{BJ}$/6-31G(d,p)/6-31+G(d)(O)/SDD(Pd) level of theory. Boltzmann population factors are calculated for TS grouped by TDG based on the relative Gibbs free energies at 383.15 K. Imaginary frequencies are in cm^{-1} and relative free energies (Δqh-G) are in kcal/mol. Only TS within 5 kcal/mol (corresponding to >99.9% of Boltzmann population) are reported.

D. Coordinates of the calculated structures (Å)

TS1_DG1_L1_1-1_G E = -1549.134042

C	-3.788113	-1.427196	-0.665231
C	-3.328203	-2.238740	-1.831894
C	-1.969228	-1.897004	-2.432088
C	-0.784093	-2.081950	-1.475377
H	-4.112349	-2.167627	-2.597488
H	-1.986993	-0.884985	-2.850825
Pd	-1.091205	-0.153126	-0.368530
H	-0.192824	-1.766313	-0.270703
H	-1.814820	-2.574420	-3.282057
O	1.038334	-1.938178	0.402036
H	0.147105	-2.008267	-2.041720
H	-0.831250	-3.096754	-1.059098
H	-4.814555	-1.614362	-0.353078
H	-3.345922	-3.290715	-1.507183
N	0.931343	0.208630	-0.347378
C	1.657071	-0.858208	0.148458
C	1.493908	1.391818	-0.609996
C	3.063473	-0.681844	0.344889
C	2.857118	1.572906	-0.435286
H	0.836955	2.193277	-0.926304
C	3.652824	0.525074	0.053614
C	3.865249	-1.840592	0.869049
N	3.456176	2.854444	-0.759058
H	4.714699	0.678150	0.196155
F	3.432331	-2.242938	2.079939
F	5.169511	-1.509898	0.994361
F	3.797757	-2.904241	0.041230
O	2.732064	3.721998	-1.252341
O	4.661150	2.994099	-0.526213
N	-3.090972	-0.568180	-0.027787
C	-3.673062	0.211674	1.116357
C	-3.669020	1.695756	0.696647
C	-5.118973	-0.189920	1.442516
C	-2.799603	-0.038046	2.357034
C	-2.333366	2.437728	0.570274
H	-4.184787	1.788018	-0.267646
H	-4.258020	2.261895	1.421201
H	-5.806129	0.011536	0.614732
H	-5.198315	-1.243744	1.727451
H	-5.454782	0.403858	2.294927
H	-3.186334	0.551567	3.192633
H	-2.824773	-1.095299	2.637020
H	-1.761687	0.252148	2.188507
O	-1.274818	1.789921	0.147425
O	-2.301472	3.632982	0.834322

TS1_DG1_L1_1-2_G E = -1549.134154

C	-3.815584	-1.216452	-0.847839
C	-3.342792	-2.017996	-2.014946
C	-1.881463	-1.879418	-2.434975
C	-0.856071	-2.181620	-1.326815
H	-4.006222	-1.782683	-2.858302
H	-1.707631	-0.893695	-2.879754
Pd	-1.070339	-0.158116	-0.368095
H	-0.157916	-1.766700	-0.207692
H	-1.718652	-2.604658	-3.242663
O	1.062780	-1.920419	0.464378
H	0.107559	-2.372439	-1.806359
H	-1.149069	-3.099312	-0.802646
H	-4.881702	-1.308423	-0.627549
H	-3.564237	-3.068165	-1.769125
N	0.949446	0.200707	-0.347263
C	1.680539	-0.848624	0.175822
C	1.509130	1.375066	-0.654198
C	3.087768	-0.665025	0.357583
C	2.872746	1.564164	-0.491797
H	0.850323	2.163043	-1.000245
C	3.673138	0.533186	0.025141
C	3.895011	-1.806606	0.910713
N	3.467371	2.836542	-0.857594
H	4.735676	0.692153	0.155976
F	3.469242	-2.173850	2.135086
F	5.199083	-1.469774	1.018897
F	3.824611	-2.893658	0.114426
O	2.735681	3.691585	-1.361771
O	4.675405	2.981671	-0.646156
N	-3.095594	-0.476455	-0.097717
C	-3.761961	0.234555	1.063530
C	-2.706041	1.048763	1.836725
C	-4.347297	-0.824811	2.010653
C	-4.850138	1.173749	0.522024
C	-2.088997	2.182715	1.014284
H	-3.192088	1.493679	2.706687
H	-1.917745	0.374830	2.191733
H	-4.775024	-0.334182	2.888456
H	-5.143219	-1.405307	1.535283
H	-3.567076	-1.513913	2.347092
H	-5.665669	0.618872	0.049315
H	-5.271563	1.755772	1.345050
H	-4.433064	1.874635	-0.204915
O	-1.341009	1.807847	0.000021
O	-2.307855	3.355557	1.285895

TS1_DG1_L1_1_B E = -1549.139487

Pd	-1.117150	-0.168696	-0.238559
O	-1.436219	1.744513	0.330626
N	-3.050250	-0.765797	0.041034
O	-2.744448	3.528338	0.552428
C	-2.191373	-2.946564	-0.502519
C	-1.032112	-2.204909	-1.180155
C	-3.282808	-2.017992	-0.089844
C	-2.598930	2.351057	0.248874
C	-3.801611	1.541469	-0.254227
C	1.695159	-0.712365	0.131999
O	1.165107	-1.860349	0.322633
C	3.088442	-0.461664	0.306151
H	-0.004947	-1.809882	-0.229874
C	3.587125	0.801938	0.088040
H	4.640434	1.017678	0.211687
C	2.706426	1.821051	-0.300883
C	1.353676	1.558445	-0.451274

H	0.633453	2.331270	-0.691048
N	0.879535	0.322585	-0.257750
N	3.207600	3.163260	-0.546656
O	2.410462	4.009411	-0.954838
O	4.406687	3.368498	-0.336271
H	-3.669470	1.326912	-1.321835
H	-4.672428	2.190738	-0.153398
H	-2.607519	-3.727692	-1.155750
H	-1.840577	-3.474581	0.397371
C	-4.079604	0.217978	0.490660
C	-0.011664	-3.179751	-1.797190
H	0.435922	-3.839443	-1.050508
H	-0.514635	-3.796803	-2.552119
H	0.800747	-2.640500	-2.289888
H	-1.432287	-1.630250	-2.025393
C	-5.502287	-0.252510	0.156394
H	-5.615907	-0.451871	-0.913895
H	-5.789161	-1.146984	0.716770
H	-6.207293	0.534562	0.431874
C	-3.916647	0.388699	2.010297
H	-4.583872	1.179510	2.363122
H	-4.170283	-0.541183	2.528279
H	-2.892319	0.665983	2.266566
C	3.981642	-1.599547	0.717243
H	-4.277059	-2.418975	0.105206
F	3.612616	-2.123252	1.902517
F	5.263122	-1.190121	0.835046
F	3.958995	-2.598194	-0.190660

TS1_DG1_L1_2-1_G E = -1549.137933

C	-2.394426	-2.885069	0.878656
C	-1.629497	-3.360257	-0.380681
C	-0.982208	-2.217555	-1.168475
Pd	-1.048898	-0.217974	-0.117478
O	1.346874	-1.964389	0.009256
H	-1.697162	-1.722746	-1.830853
H	-0.855985	-4.057135	-0.043679
H	-2.312357	-3.929184	-1.023186
H	-1.668107	-2.487467	1.598191
H	-2.904864	-3.727807	1.352183
H	0.117967	-1.854437	-0.416063
C	-3.388484	-1.805321	0.577480
N	0.954651	0.270526	-0.181988
C	1.827553	-0.783141	-0.033884
C	1.390064	1.536030	-0.224735
C	3.226097	-0.511062	0.064042
C	2.744090	1.820404	-0.150392
C	3.677883	0.786017	0.003773
H	4.733034	1.016553	0.072661
C	4.176207	-1.666409	0.222501
F	3.915854	-2.378298	1.336573
F	4.106212	-2.513415	-0.825025
F	5.452917	-1.233231	0.306852
H	-4.448461	-2.013217	0.737566
H	-0.216112	-2.603266	-1.850769
H	0.640501	2.315008	-0.283275
N	3.190259	3.201014	-0.229153
O	2.340819	4.070408	-0.432981
O	4.398467	3.415511	-0.093084
N	-3.041049	-0.658624	0.129328
C	-4.080287	0.395066	-0.150406
C	-3.362410	1.663841	-0.647232
C	-5.011203	-0.119135	-1.259318
C	-4.856033	0.699525	1.140053
C	-2.432790	2.291307	0.397307
H	-2.792403	1.422622	-1.552280
H	-4.117792	2.407128	-0.907546
H	-4.440478	-0.368916	-2.158785
H	-5.566409	-1.006894	-0.942750
H	-5.738412	0.654747	-1.517600
H	-5.545640	1.528622	0.964369
H	-5.441422	-0.163065	1.471085
H	-4.175825	0.993102	1.942968
O	-1.354371	1.605105	0.710354
O	-2.700534	3.372340	0.904794

TS1_DG1_L1_2-2_G E = -1549.138219

C	2.409606	-2.955412	-0.734322
C	1.615261	-3.372327	0.524912
C	0.958188	-2.187029	1.236661
Pd	1.074140	-0.221003	0.134063
O	-1.304824	-1.966971	-0.073206
H	1.659444	-1.671731	1.898174
H	0.845882	-4.080751	0.203071
H	2.279423	-3.911901	1.210869
H	1.700293	-2.585801	-1.485221
H	2.925650	-3.819713	-1.160747
H	-0.084867	-1.848829	0.402943
C	3.406867	-1.869403	-0.461469
N	-0.932234	0.262602	0.200959
C	-1.795408	-0.791432	0.005489
C	-1.372896	1.523404	0.291542
C	-3.194200	-0.523331	-0.097538
C	-2.728538	1.801187	0.216354
C	-3.653764	0.768106	0.010218
H	-4.709514	0.995351	-0.060285
C	-4.135496	-1.676635	-0.310729
F	-3.857626	-2.345519	-1.447243
F	-4.073479	-2.562277	0.705230
F	-5.413812	-1.247962	-0.394647
H	4.464173	-2.096321	-0.590323
H	0.158913	-2.523188	1.906305
H	-0.622825	2.300321	0.383865
N	-3.186910	3.174036	0.347503
O	-2.348452	4.039897	0.602646
O	-4.394936	3.385066	0.201022
N	3.058215	-0.697465	-0.083258
C	4.034438	0.411507	0.128294
C	3.747660	1.466549	-0.963064
C	5.492580	-0.047439	-0.002832
C	3.804807	0.977822	1.537987
C	2.448141	2.275763	-0.868738
H	4.560382	2.195368	-0.961877
H	3.760874	0.968037	-1.940379
H	6.143897	0.803019	0.208708
H	5.736552	-0.836663	0.715437
H	5.729281	-0.396835	-1.012507
H	4.032525	0.223020	2.296961
H	4.460634	1.837835	1.696197
H	2.772993	1.308404	1.672993

O	1.328449	1.657379	-0.574129
O	2.480154	3.475395	-1.113106

TS1_DG1_L1_2_B E = -1549.140373

Pd	1.081982	-0.265485	0.089933
C	2.257509	-2.998046	0.196112
C	1.015880	-2.393065	0.870163
C	3.344581	-2.004398	-0.023746
C	-1.782053	-0.791268	-0.174095
O	-1.286605	-1.944637	-0.381792
C	-3.182049	-0.512308	-0.245586
H	-0.010419	-1.888046	0.073623
C	-3.641196	0.758230	0.007657
H	-4.696926	0.992152	-0.036599
C	-2.715881	1.762155	0.329871
C	-1.360309	1.477450	0.375676
H	-0.609781	2.236178	0.566526
N	-0.920372	0.235501	0.140787
N	-3.174346	3.110521	0.615809
O	-2.334945	3.945157	0.958423
O	-4.383822	3.334620	0.503133
H	2.648162	-3.841924	0.782512
H	1.990990	-3.416366	-0.785394
O	1.382567	1.695006	-0.268554
N	3.062533	-0.757384	-0.078060
O	2.526395	3.420997	-1.072902
C	2.420315	2.216638	-0.884097
C	3.519203	1.265589	-1.365419
C	4.083945	0.306794	-0.293034
H	4.329876	1.892706	-1.739227
C	1.209245	-2.067018	2.359168
H	0.298086	-1.638974	2.785622
H	1.436457	-2.984871	2.917773
H	2.022348	-1.358279	2.537080
H	0.255317	-3.183989	0.841037
H	3.140189	0.673209	-2.206898
H	4.369570	-2.349470	-0.152835
C	-4.123056	-1.634340	-0.586442
C	5.421702	-0.258957	-0.787286
H	6.107195	0.571969	-0.965665
H	5.894600	-0.911920	-0.047536
H	5.306782	-0.808381	-1.727138
C	4.282640	1.021698	1.054081
H	4.732085	0.340709	1.783130
H	4.947685	1.878744	0.919762
H	3.333365	1.386060	1.451046
F	-3.850772	-2.167229	-1.793924
F	-4.054868	-2.631703	0.320120
F	-5.402480	-1.201259	-0.613759

TS1_DG1_L1_3_B E = -1549.139656

Pd	1.080473	-0.270253	0.068837
O	1.384057	1.663361	-0.414978
N	3.054382	-0.777977	-0.108995
O	2.612083	3.514511	-0.438724
C	2.256990	-3.001418	0.301443
C	1.005137	-2.368914	0.929730
H	0.246673	-3.162412	0.923701
C	3.340834	-2.017012	0.032787
C	2.506174	2.317435	-0.207998
C	3.703193	1.534352	0.339634
C	-1.787676	-0.794081	-0.156557
O	-1.297710	-1.956028	-0.325595
C	-3.187359	-0.514813	-0.233694
H	-0.017402	-1.891825	0.114014
C	-3.642940	0.766027	-0.031724
H	-4.698216	1.000703	-0.082351
C	-2.713798	1.779716	0.245080
C	-1.359109	1.492762	0.300262
H	-0.608093	2.258252	0.454903
N	-0.921520	0.240898	0.118410
N	-3.167200	3.140521	0.474461
O	-2.324496	3.985809	0.780951
O	-4.376002	3.363906	0.353552
H	3.510194	1.265505	1.385462
H	4.552750	2.218481	0.326241
H	2.644751	-3.810879	0.936011
H	2.001725	-3.472382	-0.659198
C	4.074606	0.258730	-0.445737
C	1.178326	-1.980792	2.406195
H	0.261990	-1.535248	2.802505
H	1.398457	-2.874121	3.005817
H	1.989844	-1.265383	2.565238
H	4.368697	-2.364084	-0.067043
C	5.491279	-0.176263	-0.044689
H	5.845738	-1.032859	-0.625182
H	6.179829	0.647858	-0.242239
H	5.549921	-0.419454	1.021052
C	4.001563	0.494229	-1.963820
H	4.659299	1.323450	-2.237533
H	4.323575	-0.401270	-2.503800
H	2.985895	0.745906	-2.274509
C	-4.132060	-1.647587	-0.525656
F	-3.867503	-2.227801	-1.712749
F	-4.060676	-2.608799	0.418975
F	-5.410867	-1.213332	-0.562880

TS1_DG1_L1_4-1_G E = -1549.133553

Pd	-1.098636	-0.130772	-0.425048
C	-3.373806	-2.051263	-1.919866
C	-2.107060	-2.865736	-1.615656
C	-0.834678	-2.033134	-1.559355
O	1.014831	-1.940835	0.356548
H	-4.187785	-2.717472	-2.218660
H	-3.183844	-1.384736	-2.773067
H	-2.243665	-3.427988	-0.684434
H	-2.004614	-3.610499	-2.414253
H	-0.134981	-1.818932	-0.361531
C	-3.851257	-1.229176	-0.762631
N	0.936505	0.197154	-0.417422
C	1.645630	-0.861698	0.108453
C	1.512241	1.373526	-0.683433
C	3.044871	-0.691758	0.343731
C	2.871864	1.550009	-0.478341
C	3.648858	0.507871	0.049055
H	4.707287	0.658151	0.217823
H	0.026545	-2.709068	-1.625008
H	-0.733981	-1.398556	-2.448427

H	-4.903966	-1.316684	-0.500778
C	3.825743	-1.847382	0.905411
F	3.352854	-2.235415	2.105837
F	3.780392	-2.919593	0.086817
F	5.126168	-1.519386	1.068051
H	0.868906	2.175343	-1.024457
N	3.486288	2.823405	-0.809112
O	2.781261	3.682270	-1.342836
O	4.683632	2.963291	-0.541246
N	-3.101885	-0.463553	-0.066864
C	-3.649970	0.313279	1.096423
C	-3.594583	1.806365	0.717709
C	-5.107580	-0.046141	1.420786
C	-2.780376	-0.002094	2.324702
C	-2.230230	2.492795	0.597907
H	-4.114553	1.944984	-0.238730
H	-4.154600	2.374595	1.463417
H	-5.797019	0.225854	0.615545
H	-5.225112	-1.109750	1.650885
H	-5.408489	0.516143	2.306991
H	-3.138398	0.580780	3.177654
H	-2.846039	-1.064333	2.577994
H	-1.733012	0.251076	2.155573
O	-1.206645	1.806354	0.153243
O	-2.142396	3.679460	0.888505

TS1_DG1_L1_4-2_G E = -1549.133755

Pd	-1.079209	-0.139929	-0.435145
C	-3.356747	-1.939462	-1.994886
C	-2.174604	-2.832754	-1.580814
C	-0.840634	-2.106580	-1.466705
O	1.027505	-1.920941	0.426578
H	-4.188039	-2.554564	-2.350384
H	-3.057818	-1.297893	-2.835560
H	-2.414951	-3.348055	-0.643516
H	-2.079830	-3.612602	-2.346284
H	-0.130158	-1.829355	-0.275719
C	-3.858321	-1.079039	-0.878129
N	0.951265	0.186806	-0.422157
C	1.661024	-0.853914	0.136600
C	1.527744	1.351386	-0.735444
C	3.061976	-0.679647	0.356969
C	2.888505	1.532809	-0.542287
C	3.666402	0.507801	0.016917
H	4.726125	0.661581	0.174135
H	-0.052164	-2.867636	-1.413180
H	-0.609419	-1.553039	-2.384919
H	-4.933432	-1.083438	-0.689086
C	3.844041	-1.816740	0.954127
F	3.378488	-2.159425	2.171105
F	3.789402	-2.917251	0.175019
F	5.146298	-1.486732	1.095555
H	0.884680	2.139544	-1.108558
N	3.503147	2.793501	-0.918728
O	2.793313	3.639640	-1.466469
O	4.704492	2.936164	-0.672049
N	-3.104259	-0.380877	-0.120342
C	-3.740491	0.381323	1.024098
C	-2.643431	1.101154	1.831317
C	-4.438067	-0.627909	1.950761
C	-4.733573	1.407197	0.457287
C	-1.951734	2.216372	1.046268
H	-3.106262	1.549596	2.711992
H	-1.902344	0.367676	2.169815
H	-4.851485	-0.103468	2.815690
H	-5.263064	-1.143290	1.451019
H	-3.726352	-1.377182	2.309815
H	-5.579973	0.920099	-0.035471
H	-5.125084	2.023736	1.270013
H	-4.242195	2.068544	-0.260173
O	-1.272998	1.828212	-0.009710
O	-2.059303	3.389322	1.378407

TS1_DG1_L1_4_B E = -1549.140299

Pd	-1.119625	-0.169838	-0.254495
C	-2.193959	-2.949963	-0.407326
C	-1.040743	-2.236914	-1.124693
C	-3.289101	-2.006062	-0.039756
C	1.689804	-0.711582	0.147411
O	1.155489	-1.851700	0.370944
C	3.083809	-0.459109	0.312144
H	-0.011282	-1.811150	-0.188734
C	3.584998	0.795742	0.052676
H	4.639051	1.012659	0.167643
C	2.706513	1.804316	-0.367933
C	1.352618	1.541241	-0.507291
H	0.631955	2.306353	-0.772019
N	0.876932	0.313399	-0.271391
N	3.211651	3.136384	-0.657618
O	2.416000	3.972323	-1.088819
O	4.412330	3.343545	-0.458306
H	-2.611059	-3.762130	-1.021172
H	-1.838465	-3.434770	0.514567
O	-1.441417	1.774283	0.193701
N	-3.063650	-0.746788	0.013444
O	-2.626610	3.428070	1.090233
C	-2.467672	2.233776	0.871869
C	-3.488426	1.219411	1.401807
C	-4.101343	0.269765	0.345970
H	-4.292429	1.799659	1.856921
H	-3.021825	0.617895	2.191191
H	-1.447414	-1.697717	-1.989682
C	-0.022553	-3.234404	-1.708254
H	0.788585	-2.714137	-2.223111
H	0.427179	-3.866450	-0.939299
H	-0.527983	-3.878569	-2.438493
H	-4.279631	-2.401909	0.180508
C	-4.430186	1.018670	-0.956202
H	-4.911347	0.345490	-1.672087
H	-5.110968	1.846254	-0.740708
H	-3.527461	1.429997	-1.411939
C	-5.373753	-0.362979	0.923618
H	-6.076810	0.433432	1.175777
H	-5.873728	-1.017632	0.203278
H	-5.165722	-0.929805	1.836795
C	3.974767	-1.585717	0.757486
F	3.604707	-2.072010	1.958404
F	5.257129	-1.175767	0.862536
F	3.949561	-2.611691	-0.119263

TS1_DG2_L1_1-1-2_G E = -1588.398682

C	3.296873	-1.798052	-0.424582
C	2.690820	-3.144334	-0.675148
C	1.171675	-3.305527	-0.589819
C	0.529702	-2.624512	0.631057
C	2.528159	1.589101	-0.556681
C	3.322313	0.548529	0.304927
H	3.063433	-3.492787	-1.647394
H	0.709541	-2.935493	-1.511371
Pd	0.662904	-0.452734	0.092292
O	1.233566	1.382547	-0.544469
O	3.063505	2.517823	-1.136703
H	-0.636643	-1.997990	0.338273
H	0.970825	-4.382483	-0.569896
N	2.682243	-0.759679	-0.008747
O	-1.954526	-1.948586	0.115023
H	-0.229567	-3.281560	1.073068
H	1.227210	-2.457054	1.456103
H	4.370963	-1.747363	-0.571550
H	3.175092	-3.806375	0.060422
N	-1.289403	0.222771	0.100064
C	-2.289067	-0.723579	0.084660
C	-1.569602	1.533066	0.069172
C	-3.650497	-0.287201	0.037324
C	-2.881827	1.975437	0.036388
H	-0.729452	2.217034	0.047052
C	-3.940625	1.055225	0.015051
C	-4.738895	-1.325233	0.020946
N	-3.154333	3.401785	0.021881
H	-4.963049	1.408399	-0.017945
F	-4.705162	-2.098970	1.124721
F	-5.958143	-0.744806	-0.028351
F	-4.635907	-2.139668	-1.047877
O	-2.195569	4.174056	0.087960
O	-4.335903	3.753322	-0.051510
H	2.982617	0.751759	1.329618
C	4.870724	0.683610	0.337614
C	5.486007	-0.338592	1.321993
C	5.531822	0.593034	-1.050919
C	5.174811	2.081013	0.931060
H	4.970611	-0.310371	2.288567
H	5.476800	-1.372785	0.971745
H	6.533106	-0.077037	1.500324
H	5.119053	1.351666	-1.717439
H	6.607617	0.769323	-0.951796
H	5.411147	-0.383075	-1.530318
H	6.257548	2.195531	1.040044
H	4.801139	2.878272	0.291055
H	4.728868	2.189819	1.926516

TS1_DG2_L1_1-1_B E = -1588.410670

Pd	-0.846693	-0.324555	-0.369305
C	-2.113099	-2.987623	-0.739721
C	-0.681148	-2.479323	-1.033913
H	-0.025497	-3.307869	-0.736476
C	-3.159471	-1.923031	-0.711201
C	1.984456	-0.725159	0.192383
O	1.521899	-1.899206	0.355181
C	3.356757	-0.382579	0.398592
H	0.254042	-1.902923	-0.136078
C	3.775804	0.912423	0.206424
H	4.809725	1.194607	0.357211
C	2.839773	1.879299	-0.191872
C	1.512817	1.529374	-0.386540
H	0.754605	2.250950	-0.671132
N	1.113279	0.264369	-0.207096
N	3.256299	3.254814	-0.400735
O	2.404349	4.065313	-0.770699
O	4.443251	3.526473	-0.195403
H	-2.386305	-3.770283	-1.460398
H	-2.144184	-3.471528	0.247873
C	-0.421171	-2.239291	-2.528408
H	0.602021	-1.891590	-2.694369
H	-0.548320	-3.174533	-3.089274
H	-1.098630	-1.496287	-2.958974
H	-4.215195	-2.162745	-0.850525
C	4.314109	-1.463310	0.819609
F	3.957558	-2.016722	1.995375
F	4.373984	-2.454736	-0.093154
F	5.564112	-0.972114	0.965398
N	-2.790875	-0.728252	-0.447184
C	-3.660193	0.436246	-0.238056
C	-2.817251	1.704992	-0.532422
H	-4.501674	0.397798	-0.937217
C	-4.239600	0.471089	1.226717
O	-1.516151	1.582663	-0.356638
O	-3.365783	2.745772	-0.852289
C	-5.027235	-0.819517	1.509342
C	-3.115699	0.616820	2.266758
C	-5.209359	1.662339	1.332977
H	-5.804721	-0.993890	0.756651
H	-4.382479	-1.701981	1.559852
H	-5.524315	-0.732971	2.479842
H	-2.554300	1.543614	2.126823
H	-3.547795	0.628779	3.272110
H	-2.406822	-0.215859	2.215667
H	-5.650449	1.677112	2.334522
H	-4.707529	2.613927	1.157273
H	-6.023547	1.576225	0.605955

TS1_DG2_L1_1-1_G E = -1588.413683

C	-3.675659	-1.154206	-1.174767
C	-3.178294	-2.256747	-2.053021
C	-1.757947	-2.096219	-2.601953
C	-0.613441	-2.181734	-1.578196
C	-2.596341	2.011296	0.061865
C	-3.469306	0.751259	0.270318
H	-3.887398	-2.362331	-2.882678
H	-1.694026	-1.169059	-3.181235
H	-4.487731	0.977322	-0.061990
Pd	-0.898316	-0.145880	-0.668821
O	-1.345699	1.782346	-0.269889
O	-3.069296	3.122540	0.238148
H	-0.025298	-1.750696	-0.407220
H	-1.604011	-2.914110	-3.317691
N	-2.916795	-0.320934	-0.579565
O	1.159398	-1.897783	0.347202
H	0.334581	-2.212704	-2.121241

H	-0.707070	-3.134136	-1.039946
H	-4.756010	-1.070946	-1.028784
H	-3.262978	-3.193056	-1.479184
C	-3.547958	0.335654	1.785366
C	-4.317562	-0.989641	1.913110
C	-2.156028	0.177497	2.420220
C	-4.329638	1.434334	2.529336
H	-5.308402	-0.928888	1.448130
H	-3.774150	-1.828918	1.468762
H	-4.466938	-1.222713	2.971332
H	-1.581096	1.105609	2.369317
H	-2.267193	-0.093872	3.474663
H	-1.570679	-0.610533	1.935399
H	-4.424645	1.159304	3.584381
H	-3.830425	2.401807	2.462797
H	-5.337947	1.550272	2.118167
N	1.104063	0.225945	-0.462856
C	1.791919	-0.820469	0.122576
C	1.678281	1.409304	-0.701614
C	3.173773	-0.624780	0.439194
C	3.016495	1.612268	-0.402737
H	1.052701	2.194209	-1.110068
C	3.774879	0.582938	0.177641
C	3.936051	-1.762979	1.059599
N	3.626711	2.896790	-0.690833
H	4.817817	0.751329	0.412871
F	3.399777	-2.141081	2.236302
F	5.220699	-1.414910	1.292436
F	3.951087	-2.845173	0.254416
O	2.932277	3.754675	-1.241537
O	4.809090	3.049948	-0.369828

TS1_DG2_L1_1-2_B E = -1588.412556

Pd	-0.804023	-0.389483	-0.290871
C	-1.965591	-3.041042	-0.789408
C	-0.804427	-2.629777	0.151189
H	-0.051126	-3.415708	0.006693
C	-3.042257	-2.009881	-0.880800
C	2.104126	-0.717870	-0.087353
O	1.731060	-1.927802	-0.202429
C	3.473417	-0.324867	0.032726
H	0.378766	-1.955149	-0.172956
C	3.796490	1.005783	0.149639
H	4.826000	1.326559	0.241821
C	2.765548	1.957904	0.147494
C	1.444516	1.558307	0.024819
H	0.623681	2.265999	-0.009739
N	1.134782	0.259297	-0.078204
N	3.076995	3.370724	0.274524
O	2.137298	4.168156	0.304843
O	4.268730	3.685289	0.348631
H	-2.394212	-3.999231	-0.463595
H	-1.586017	-3.212759	-1.806579
C	-1.178135	-2.665373	1.638116
H	-0.323665	-2.378443	2.256992
H	-1.475280	-3.680425	1.932773
H	-2.004574	-1.993119	1.880934
H	-4.060410	-2.266040	-1.181024
C	4.532878	-1.392363	0.029644
F	4.519452	-2.105593	-1.113714
F	4.367153	-2.259049	1.049567
F	5.764349	-0.851104	0.155169
N	-2.723606	-0.801914	-0.616173
C	-3.599906	0.370966	-0.662640
C	-2.712234	1.593412	-1.018328
O	-1.433385	1.482746	-0.719269
O	-3.213669	2.596316	-1.497011
C	-4.355902	0.594923	0.699773
C	-5.388665	1.717976	0.494337
C	-5.104183	-0.689672	1.093415
C	-3.380559	0.985984	1.823010
H	-4.915067	2.654938	0.200295
H	-6.113041	1.450488	-0.282238
H	-5.938160	1.877507	1.427391
H	-4.425328	-1.510741	1.341793
H	-5.714819	-0.495886	1.979972
H	-5.779524	-1.023424	0.297183
H	-3.931444	1.108259	2.760543
H	-2.614193	0.221290	1.981538
H	-2.872616	1.928453	1.603986
H	-4.350664	0.234496	-1.447863

TS1_DG2_L1_2-1-2_G E = -1588.414824

C	-2.174889	-3.136965	-1.024229
C	-1.437744	-3.469969	0.294601
C	-0.758602	-2.296446	1.013026
Pd	-0.827895	-0.362709	-0.109436
O	1.674666	-1.933479	0.030086
H	-1.457614	-1.769239	1.668926
H	-0.684863	-4.224728	0.047358
H	-2.147982	-3.950226	0.978340
H	-1.427554	-2.903868	-1.795228
H	-2.723765	-4.017047	-1.369981
H	0.391671	-1.910502	0.324597
C	-3.109947	-1.964885	-0.968638
N	1.113512	0.272172	0.079642
C	2.067288	-0.720468	0.052822
C	1.446577	1.568737	0.089226
C	3.445520	-0.344630	0.052563
C	2.777859	1.952908	0.101112
C	3.793290	0.985405	0.077406
H	4.830893	1.293198	0.078797
C	4.488854	-1.428147	0.029823
F	4.377084	-2.205139	-1.065255
F	4.392298	-2.231572	1.108760
F	5.732453	-0.900854	0.028322
H	-4.132110	-2.070333	-1.342637
H	0.000344	-2.677805	1.706288
H	0.636596	2.288247	0.061026
N	3.114703	3.365517	0.134435
O	2.189105	4.176689	0.206308
O	4.311473	3.665234	0.093878
N	-2.732348	-0.820466	-0.545248
C	-3.571551	0.382420	-0.613686
C	-2.677892	1.533170	-1.151633
O	-1.384197	1.389410	-0.966935
O	-3.192476	2.506687	-1.677542
H	-4.383929	0.210456	-1.328110
C	-4.221710	0.740604	0.770001
C	-4.883024	-0.516675	1.358482

C	-3.188944	1.292552	1.766888
C	-5.305645	1.803756	0.515678
H	-5.592104	-0.966237	0.653673
H	-4.147371	-1.276909	1.637754
H	-5.441310	-0.249681	2.260491
H	-2.727285	2.212494	1.398540
H	-3.682368	1.519815	2.716871
H	-2.390255	0.572025	1.969651
H	-5.778139	2.077209	1.464342
H	-4.887170	2.701591	0.058668
H	-6.085310	1.419165	-0.150554

TS1_DG2_L1_2-1_B E = -1588.409129

Pd	-0.874820	-0.186846	-0.574935
C	-2.102517	-2.855147	-1.052006
C	-0.730129	-2.257995	-1.427731
C	-3.165102	-1.829598	-0.825947
C	1.875805	-0.660776	0.128898
O	1.345271	-1.812773	0.285279
C	3.237070	-0.378322	0.449519
H	0.207201	-1.801976	-0.356429
C	3.732720	0.891573	0.263601
H	4.761454	1.130963	0.499777
C	2.883128	1.887167	-0.240829
C	1.562607	1.591991	-0.543299
H	0.866416	2.341581	-0.902260
N	1.092112	0.351291	-0.373150
N	3.381632	3.236632	-0.446081
O	2.607801	4.069293	-0.922554
O	4.553562	3.463179	-0.131754
H	-2.432369	-3.573051	-1.816231
H	-2.020199	-3.438978	-0.122017
C	0.281272	-3.388344	-1.700835
H	0.480441	-3.990465	-0.810710
H	-0.121978	-4.046171	-2.480956
H	1.236743	-2.994135	-2.051095
H	-0.836342	-1.716246	-2.376188
C	4.100675	-1.489091	0.981300
H	-4.221469	-2.100133	-0.865378
F	3.614467	-1.992583	2.132603
F	5.354456	-1.051461	1.226591
F	4.192952	-2.507382	0.100871
N	-2.808456	-0.635880	-0.539698
C	-3.678499	0.489169	-0.171131
C	-2.886384	1.798860	-0.438995
H	-4.574712	0.481392	-0.799472
C	-4.132855	0.405521	1.335368
O	-1.574774	1.703669	-0.364548
O	-3.485516	2.841046	-0.646989
C	-4.878017	-0.916058	1.589065
C	-2.928418	0.496879	2.287778
C	-5.105691	1.567513	1.609014
H	-5.712072	-1.052904	0.891159
H	-4.219842	-1.787734	1.526496
H	-5.295059	-0.905615	2.600244
H	-2.391757	1.441103	2.169887
H	-3.276115	0.428782	3.323221
H	-2.216358	-0.317316	2.118584
H	-5.461735	1.501051	2.641850
H	-4.632678	2.538688	1.463308
H	-5.976481	1.519248	0.947037

TS1_DG2_L1_2-1_G E = -1588.402549

C	-2.560754	-3.094032	-0.449817
C	-1.406210	-3.325808	-1.443831
C	-0.431488	-2.161322	-1.634685
Pd	-0.810379	-0.279723	-0.516438
O	1.503115	-1.929819	0.181326
H	-0.764346	-1.505375	-2.447914
H	-0.861400	-4.203374	-1.082037
H	-1.828619	-3.602935	-2.417332
H	-2.143611	-3.093900	0.566920
H	-3.260966	-3.931908	-0.505796
H	0.373106	-1.898922	-0.489416
C	-3.338853	-1.812851	-0.561593
N	1.161766	0.257300	-0.362955
C	1.991095	-0.755173	0.068302
C	1.592942	1.517672	-0.494613
C	3.352198	-0.441552	0.364151
C	2.912927	1.838343	-0.219313
C	3.805252	0.848867	0.218925
H	4.833040	1.108967	0.436511
C	4.263967	-1.546218	0.824318
F	3.821574	-2.117322	1.961512
F	4.369886	-2.519035	-0.103857
F	5.508153	-1.077438	1.062571
H	-4.426188	-1.870307	-0.630796
H	0.531450	-2.539429	-1.995914
H	0.862396	2.260004	-0.796610
N	3.366287	3.209525	-0.381115
O	2.555628	4.038352	-0.798952
O	4.540382	3.457103	-0.090746
N	-2.796142	-0.660272	-0.453774
C	-3.591509	0.568956	-0.231096
C	-2.696570	1.792897	-0.531198
H	-4.450027	0.576648	-0.909712
C	-4.131560	0.649206	1.251843
O	-1.422882	1.633678	-0.237952
O	-3.186405	2.833588	-0.938821
C	-5.099122	-0.511492	1.543641
C	-2.981688	0.604216	2.273242
C	-4.915649	1.966924	1.407393
H	-5.905842	-0.568458	0.804018
H	-4.595543	-1.481502	1.591953
H	-5.561288	-0.351402	2.522117
H	-2.287082	1.435120	2.136649
H	-3.393806	0.661229	3.285542
H	-2.410268	-0.326501	2.196517
H	-5.353185	2.005733	2.409740
H	-4.279645	2.842050	1.273369
H	-5.729189	2.034802	0.678348

TS1_DG2_L1_2-2_B E = -1588.411112

Pd	-0.837945	-0.317187	-0.062198
C	-1.853655	-3.078609	-0.279624
C	-0.812045	-2.454009	0.677798
C	-2.934085	-2.110463	-0.645039
C	2.041180	-0.623379	-0.078161

O	1.647078	-1.827007	-0.246652
C	3.417378	-0.247045	-0.086172
H	0.392652	-1.879372	0.054570
C	3.764771	1.072419	0.089327
H	4.801311	1.383789	0.086775
C	2.750490	2.023549	0.273384
C	1.419970	1.635393	0.272345
H	0.608974	2.347271	0.370627
N	1.090514	0.347564	0.118471
N	3.087737	3.423861	0.465497
O	2.164830	4.214572	0.672208
O	4.281451	3.732833	0.414670
H	-2.306045	-3.978453	0.162347
H	-1.369241	-3.419414	-1.206549
C	0.117839	-3.542054	1.250861
H	0.686152	-4.054605	0.471048
H	-0.488488	-4.285054	1.783896
H	0.835988	-3.120121	1.956887
H	-1.338762	-2.031798	1.541679
C	4.458471	-1.314773	-0.283252
H	-3.898464	-2.453265	-1.025522
F	4.309699	-1.945524	-1.464398
F	5.701583	-0.787972	-0.257308
F	4.395438	-2.250572	0.686590
N	-2.699908	-0.863198	-0.496850
C	-3.609226	0.251160	-0.772410
C	-2.739237	1.473605	-1.181596
O	-1.494723	1.471205	-0.752414
O	-3.237921	2.383408	-1.823570
C	-4.510444	0.580158	0.475368
C	-5.531894	1.655839	0.064081
C	-5.278087	-0.682205	0.903031
C	-3.665229	1.088023	1.655689
H	-5.045223	2.579847	-0.248397
H	-6.156070	1.310338	-0.766639
H	-6.188490	1.871620	0.912862
H	-5.857378	-1.102933	0.073064
H	-4.616925	-1.459944	1.296974
H	-5.983873	-0.425859	1.698450
H	-4.316766	1.298537	2.509325
H	-2.925979	0.345765	1.973335
H	-3.131525	2.007312	1.401951
H	-4.268169	-0.009775	-1.607088

TS1_DG2_L1_3-3_G E = -1588.414989

C	-0.730152	-2.534700	0.727860
Pd	-0.824727	-0.466421	-0.134622
H	0.433873	-1.983349	0.293270
O	1.752138	-1.971011	0.064245
C	-2.841926	-3.303073	-0.542962
C	-1.332052	-3.457081	-0.344110
H	-3.376186	-3.732135	0.320443
H	-3.179610	-3.896034	-1.402256
H	-1.156148	-4.505405	-0.078509
H	-0.820035	-3.301751	-1.299994
C	-3.405521	-1.926640	-0.697269
N	1.113363	0.207551	0.024520
C	2.102800	-0.749306	0.054982
C	1.403355	1.515264	0.012526
C	3.467978	-0.324432	0.078503
C	2.719278	1.946271	0.051737
C	3.769351	1.016134	0.078563
H	4.795105	1.360597	0.099566
H	-1.456546	-2.212082	1.479336
H	0.018358	-3.077002	1.318401
H	-4.459527	-1.873146	-0.986503
H	0.571364	2.205596	-0.057089
N	-2.800601	-0.827205	-0.461913
C	-3.533180	0.451499	-0.563301
C	-2.591535	1.505700	-1.182264
O	-1.309553	1.304968	-0.979234
O	-3.049638	2.469109	-1.775661
N	3.004073	3.370179	0.062550
O	4.190310	3.712292	0.043644
O	2.049248	4.149549	0.095829
C	4.547138	-1.371576	0.112353
F	4.490315	-2.181876	-0.962738
F	5.772116	-0.801880	0.126578
F	4.450908	-2.148297	1.210751
C	-4.091598	0.922723	0.830701
C	-4.887622	-0.221110	1.481284
C	-2.968161	1.365503	1.783153
C	-5.045181	2.105184	0.578065
H	-5.677959	-0.592530	0.818919
H	-4.248559	-1.062639	1.765282
H	-5.370385	0.144430	2.392225
H	-2.405479	2.210000	1.377272
H	-3.401472	1.676961	2.738632
H	-2.261064	0.554276	1.985270
H	-5.460235	2.446564	1.531536
H	-4.534342	2.940716	0.098024
H	-5.879418	1.808465	-0.066391
H	-4.390058	0.317223	-1.231756

TS1_DG2_L1_3-4_G E = -1588.415902

C	-0.657539	-2.174993	-1.596848
H	0.181955	-2.881007	-1.604818
Pd	-0.875551	-0.163000	-0.684287
H	0.099093	-1.837548	-0.464946
O	1.224980	-1.924361	0.283127
C	-3.207981	-2.272607	-2.016807
C	-1.957554	-2.967395	-1.460319
H	-3.031921	-1.963697	-3.058852
H	-4.041486	-2.981824	-2.056412
H	-1.855481	-3.909615	-2.011817
H	-2.128866	-3.242527	-0.413087
C	-3.675681	-1.074230	-1.252541
N	1.131205	0.210901	-0.489970
C	1.836875	-0.826155	0.081697
C	1.685699	1.407626	-0.711773
C	3.210281	-0.612110	0.413720
C	3.018688	1.630280	-0.403579
C	3.791938	0.609614	0.170263
H	4.830091	0.793884	0.414520
H	1.046481	2.186607	-1.110043
H	-4.750191	-0.872258	-1.226540
H	-0.581601	-1.676863	-2.571317
N	-2.901187	-0.283186	-0.618304
C	-3.452883	0.837746	0.166987
C	-2.522659	2.058609	-0.006239

H	-4.440995	1.097793	-0.227401
C	-3.634306	0.448803	1.680686
O	-1.266679	1.775977	-0.262247
O	-2.960761	3.189941	0.130170
C	-4.492722	-0.823297	1.782894
C	-2.285271	0.209787	2.379211
C	-4.379671	1.601881	2.377840
H	-5.452570	-0.705745	1.266668
H	-3.983872	-1.701948	1.375579
H	-4.710045	-1.031614	2.834497
H	-1.652805	1.100599	2.349838
H	-2.459268	-0.048046	3.428542
H	-1.729079	-0.614856	1.921696
H	-4.548793	1.340390	3.427068
H	-3.815295	2.534076	2.335439
H	-5.354579	1.781599	1.912757
C	3.988927	-1.745378	1.023159
F	3.448113	-2.153884	2.187451
F	4.033587	-2.813330	0.200022
F	5.263562	-1.375587	1.274879
N	3.608242	2.929404	-0.674055
O	2.903853	3.778378	-1.224780
O	4.783926	3.100929	-0.338664

9. References

(1) Zong, Q.-S.; Wu, J.-Y. A New Approach to the Synthesis of Royal Jelly Acid. *Chem. Nat. Compd.* **2014**, *50*, 399-401.

(2) Cormanich, R. A.; Rittner, R.; Freitas, M. P.; Bühl, M. The seeming lack of CF···HO intramolecular hydrogen bonds in linear aliphatic fluoroalcohols in solution. *Phys. Chem. Chem. Phys.* **2014**, *16*, 19212-19217.

(3) Olsen, E. P. K.; Madsen, R. Iridium-Catalyzed Dehydrogenative Decarbonylation of Primary Alcohols with the Liberation of Syngas. *Chem. Eur. J.* **2012**, *18*, 16023-16029.

(4) Fallek, A.; Weiss-Shtofman, M.; Kramer, M.; Dobrovetsky, R.; Portnoy, M. Phosphorylation Organocatalysts Highly Active by Design. *Org. Lett.* **2020**, *22*, 3722-3727.

(5) Zhu, Y.; Huang, K.; Pan, J.; Qiu, X.; Luo, X.; Qin, Q.; Wei, J.; Wen, X.; Zhang, L.; Jiao, N. Silver-catalyzed remote Csp^3−H functionalization of aliphatic alcohols. *Nature Communications* **2018**, *9*, 2625.

(6) Komine, K.; Urayama, Y.; Hosaka, T.; Yamashita, Y.; Fukuda, H.; Hatakeyama, S.; Ishihara, J. Formal Synthesis of (−)-Haliclonin A: Stereoselective Construction of an Azabicyclo[3.3.1]nonane Ring System by a Tandem Radical Reaction. *Org. Lett.* **2020**, *22*, 5046-5050.

(7) Chen, F.; Song, K.-S.; Wu. Y.-D.; Yang, D. Synthesis and Conformational Studies of γ−Aminoxy Peptides. *J. Am. Chem. Soc.* **2008**, *130*, 743-755.

(8) Xu. G.-F.; Yang. X.-L.; Lei, P.; Liu, X.-L.; Zhang, X.-B.; Ling Y. Synthesis and fungicidal activity study of novel daphneolone analogs with 2,6-dimethylmorpholine. *Chinese Chemical Letters*, **2016**, *27*, 555-558.

(9) Yan, X.-C.; Harutyunyan, S. R. Double-slit photoelectron interference in strong-field ionization of the neon dimer. *Nature Communications* **2019**, *10*, 1.

(10) Park, H. S.; Fan, Z.-L.; Zhu, R.-Y.; Yu, J.-Q. Distal γ-C(sp^3)−H Olefination of Ketone Derivatives and Free Carboxylic Acids. *Angew. Chem. Int. Ed.* **2020**, *59*, 12853-12859.

(11) García, J. M.; González, A.; Kardak, B. G.; Odriozola, J. M.; Oiarbide, M.; Razkin J.; Palomo, C. Copper-Catalyzed Enantioselective Conjugate Addition of Dialkylzinc Reagents to α′-Oxy Enones. *Chem. Eur. J.* **2008**, *14*, 8768-8771.

(12) You, C.; Li, S.; Li, X.; Lan, J.; Yang, Y.; Chung, L. W.; Lv, H.; Zhang, X. Design and Application of Hybrid Phosphorus Ligands for Enantioselective Rh-Catalyzed Anti-Markovnikov Hydroformylation of Unfunctionalized 1,1-Disubstituted Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 4977-4981.

(13) Ohno, H.; Okumura, M.; Maeda S.; Iwasaki H.; Wakayama, R.; Tanaka. T. Samarium(II)-Promoted Radical Spirocyclization onto an Aromatic Ring. *J. Org. Chem.* **2003**, 68, 7722-7732.

(14) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. S.; M. A. Robb, J. R. Cheeseman, G. Scalmani, V. B.; G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. M.; J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. H.; J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. W.-Y.; F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. P.; T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. R.; G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. F.; J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H.

N.; T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. P.; et al. Gaussian 16, Revision B.01.. Gaussian, Inc.: Wallingford CT **2016**.

(15) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(16) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1998**, *37*, 785–789.

(17) Becke, A. D. A New Mixing of Hartree-Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.

(18) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.*, **1994**, *98*, 11623–11627.

(19) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(20) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.

(21) (a) Martin, J. M. L.; Sundermann, A., Correlation consistent valence basis sets for use with the Stuttgart–Dresden–Bonn relativistic effective core potentials: The atoms Ga–Kr and In–Xe. *J. Chem. Phys.* **2001**, *114*, 3408-3420; (b) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H., Energy-adjusted *ab initio* pseudopotentials for the second and third row transition elements. *Theor. Chim. Acta* **1990**, *77*, 123-141; (c) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H., Energy-adjusted *ab initio* pseudopotentials for the first row transition elements. *J. Chem. Phys.* **1987**, *86*, 866-872.

(22) Ditchfield, R.; Hehre, W. J.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1971**, *54*, 720–723.

(23) Hehre, W. J.; Ditchfield, K.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, *56*, 2257–2261.

(24) Hariharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. *Theor. Chim. Acta*, **1973**, *28*, 213–222.

(25) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999,** *110*, 6158-6170.

(26) M Hong, D. P.; Hoshino, M.; Kuboi, R.; Goto, Y. Clustering of Fluorine-Substituted Alcohols as a Factor Responsible for Their Marked Effects on Proteins and Peptides. *J. Am. Chem. Soc.* **1999**, *121*, 8427–8433.

(27) Wohlfarth C, Wohlfarth B, Lechner MD. Optical constants. *Springer*; **1996**.

(28) (a) Cances, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032−3041.; (b) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151−5158.; (c) Scalmani, G.; Frisch, M. J. *J. Chem. Phys.* **2010**, *132*, 114110−114124.

(29) Grimme, S. Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory. *Chem. - A Eur. J.* **2012**, *18*, 9955–9964.

(30) Luchini, G.; Alegre-Requena, J. V; Funes-Ardoiz, I.; Paton, R. S. GoodVibes: Automated Thermochemistry for Heterogeneous Computational Chemistry Data. *F1000Research* **2020**, *9*, 291.

(31) Legault, C. Y. CYLView, 1.0b. Université de Sherbrooke **2009**.

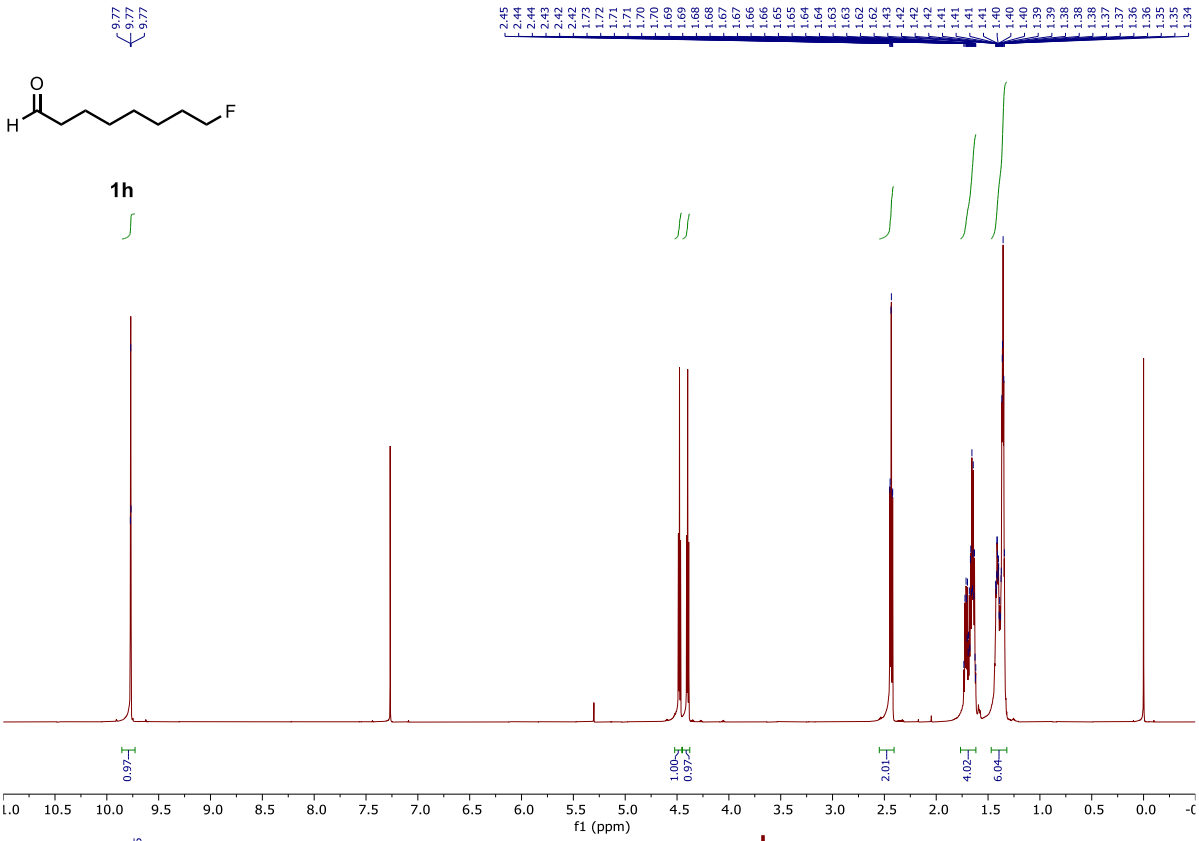
(32) Grimme, S.; et al. xTB, Version 6.3.1. University Bonn **2020**.

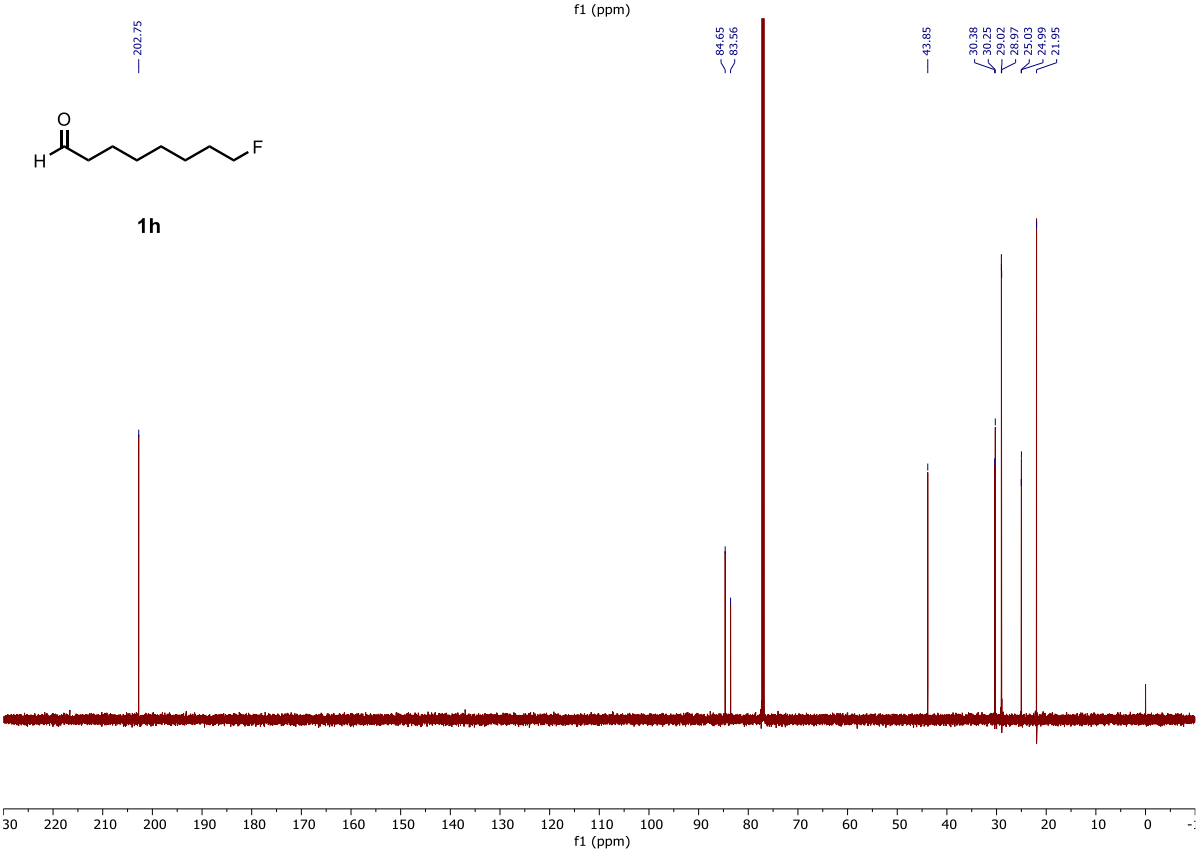
(33) Pracht, P.; Bohle, F.; Grimme, S. Automated Exploration of the Low-Energy Chemical Space with Fast Quantum Chemical Methods. *Phys. Chem. Chem. Phys.* **2020**, *22* (14), 7169–7192.

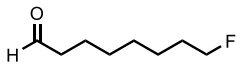
(34) Bannwarth, C.; Ehlert, S.; Grimme, S. GFN2-XTB — An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **2019**, *15* (3), 1652–1671.

(35) Grimme, S. Exploration of Chemical Compound, Conformer, and Reaction Space with Meta-Dynamics Simulations Based on Tight-Binding Quantum Chemical Calculations. *J. Chem. Theory Comput.* **2019**, *15* (5), 2847–2862.

10. ^{1}H, ^{13}C and ^{19}F NMR Spectra

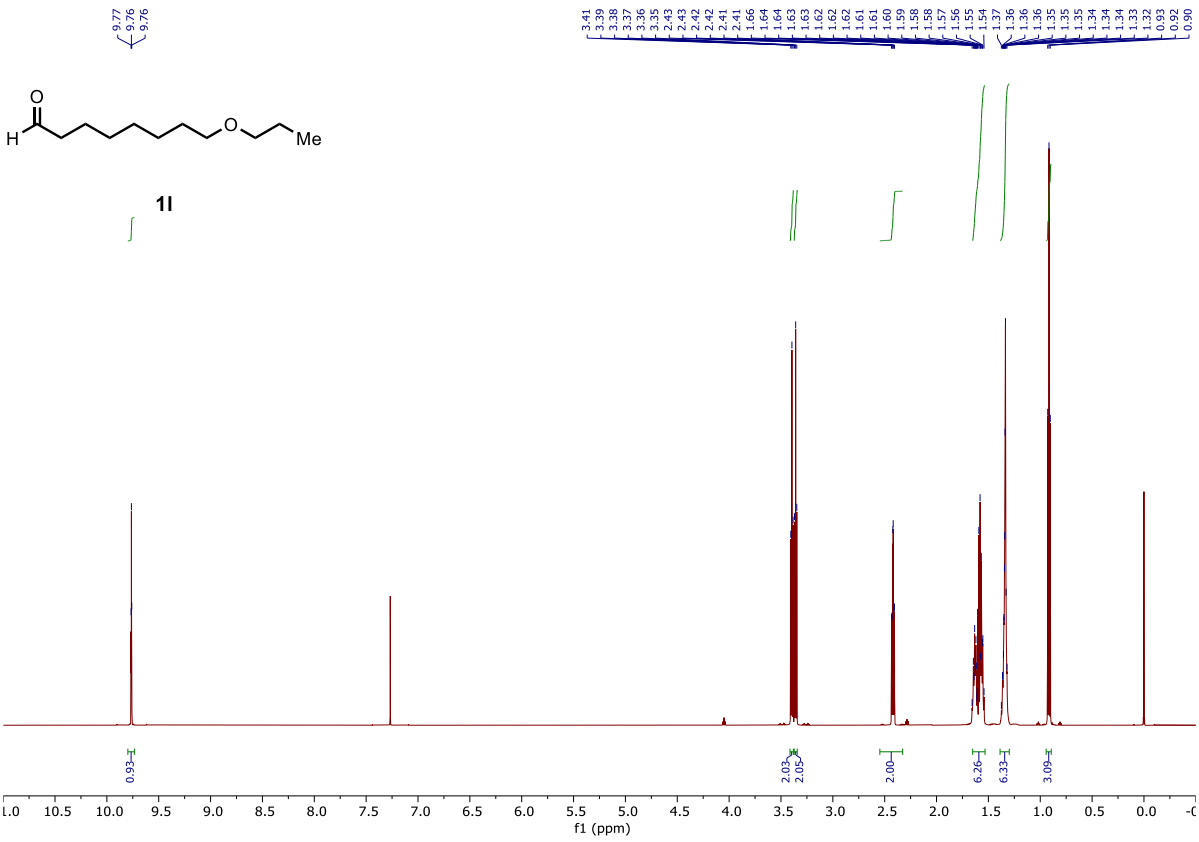


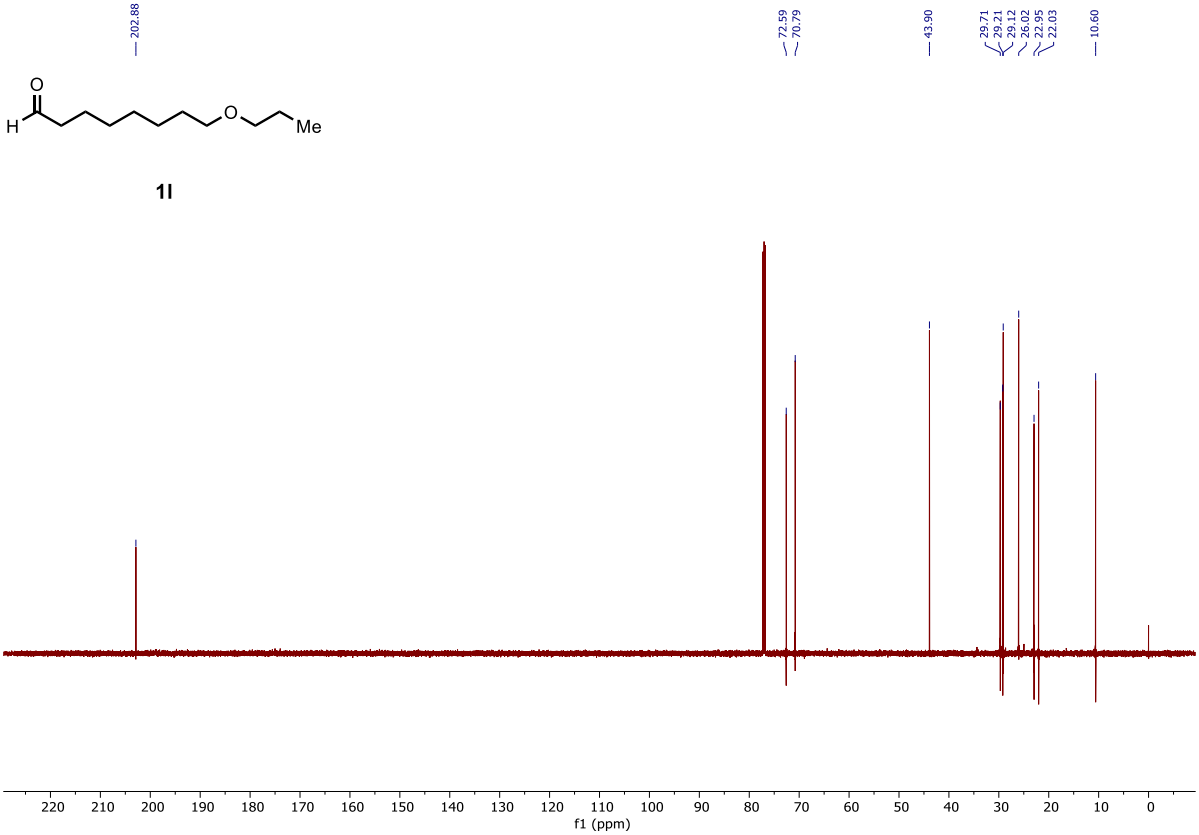


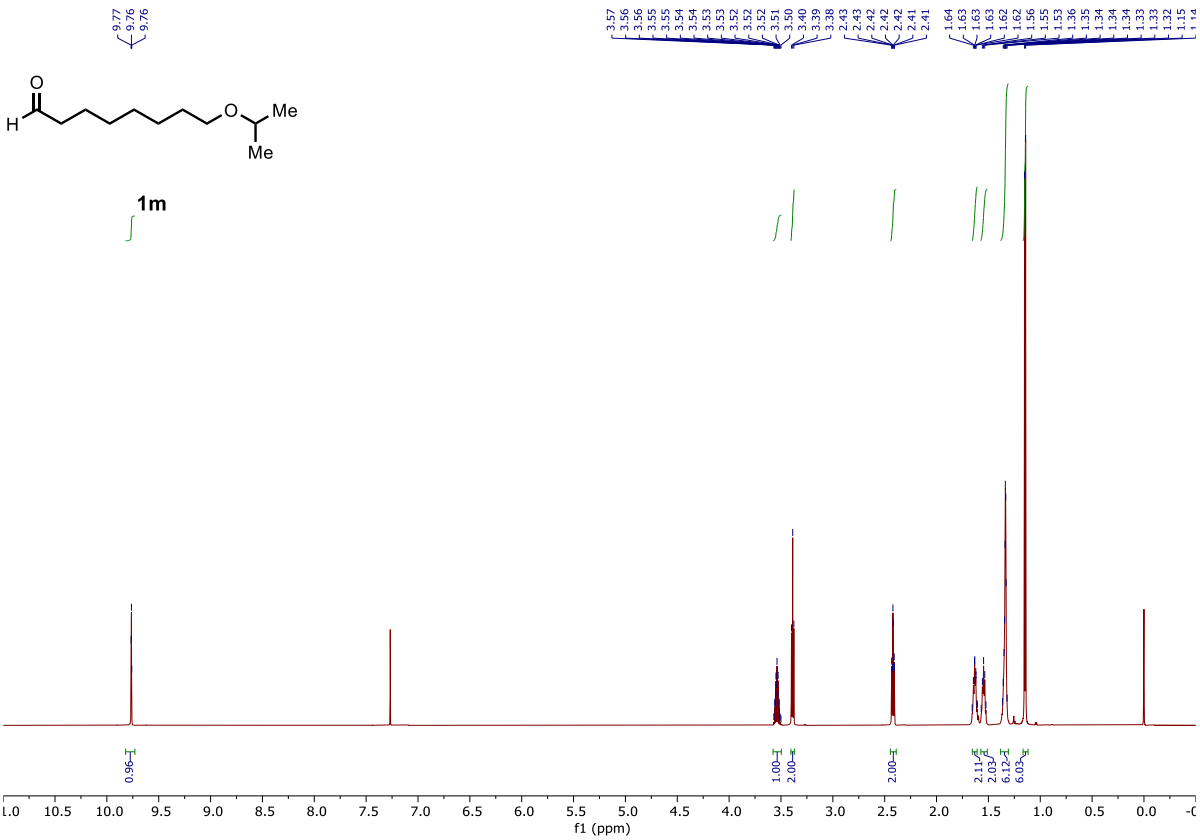

O
H
F

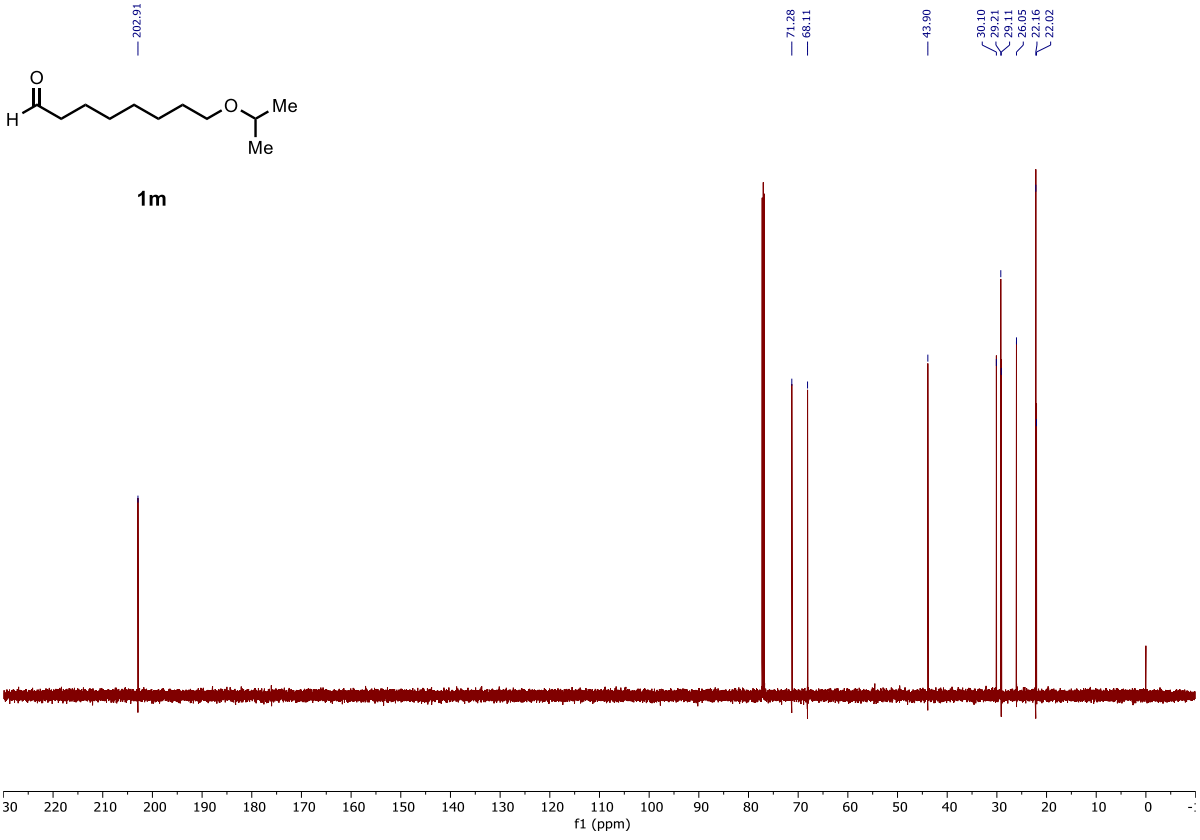
1h

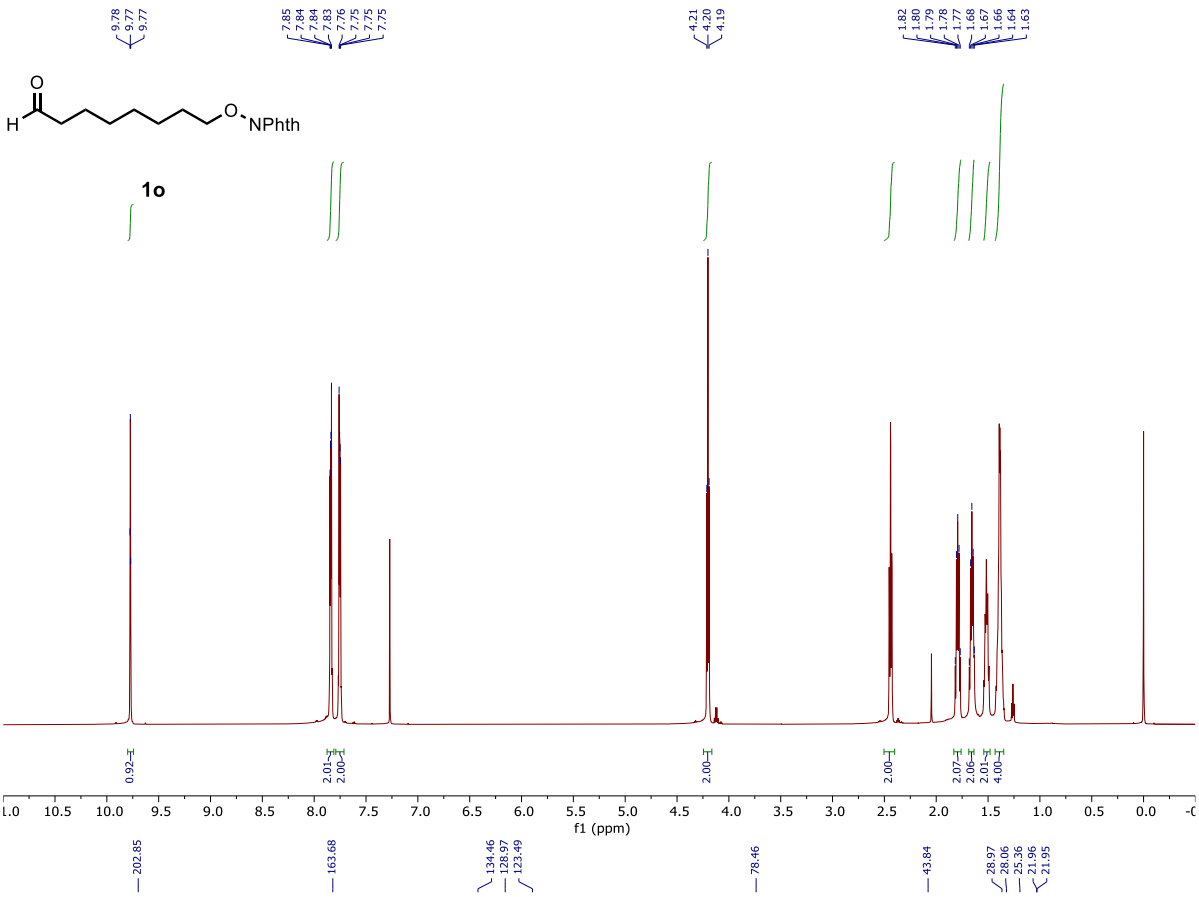
-220.68
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)

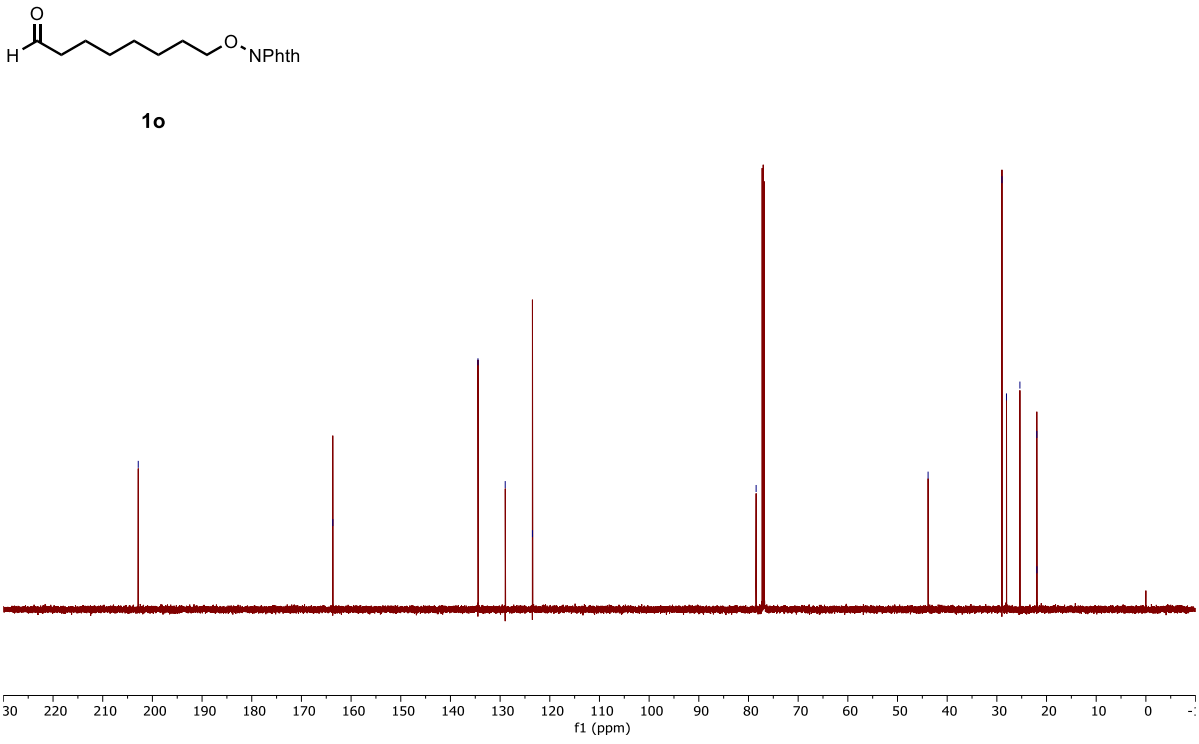

9.77
9.76
9.76
3.41
3.39
3.38
3.37
3.36
3.35
2.43
2.43
2.42
2.42
2.41
2.41
1.66
1.64
1.64
1.63
1.63
1.62
1.62
1.61
1.61
1.60
1.59
1.58
1.58
1.57
1.56
1.55
1.54
1.37
1.36
1.36
1.36
1.35
1.35
1.35
1.34
1.34
1.34
1.33
1.32
0.93
0.92
0.90
O
H
O
Me
1l
0.93
2.03
2.05
2.00
6.26
6.33
3.09
f1 (ppm)

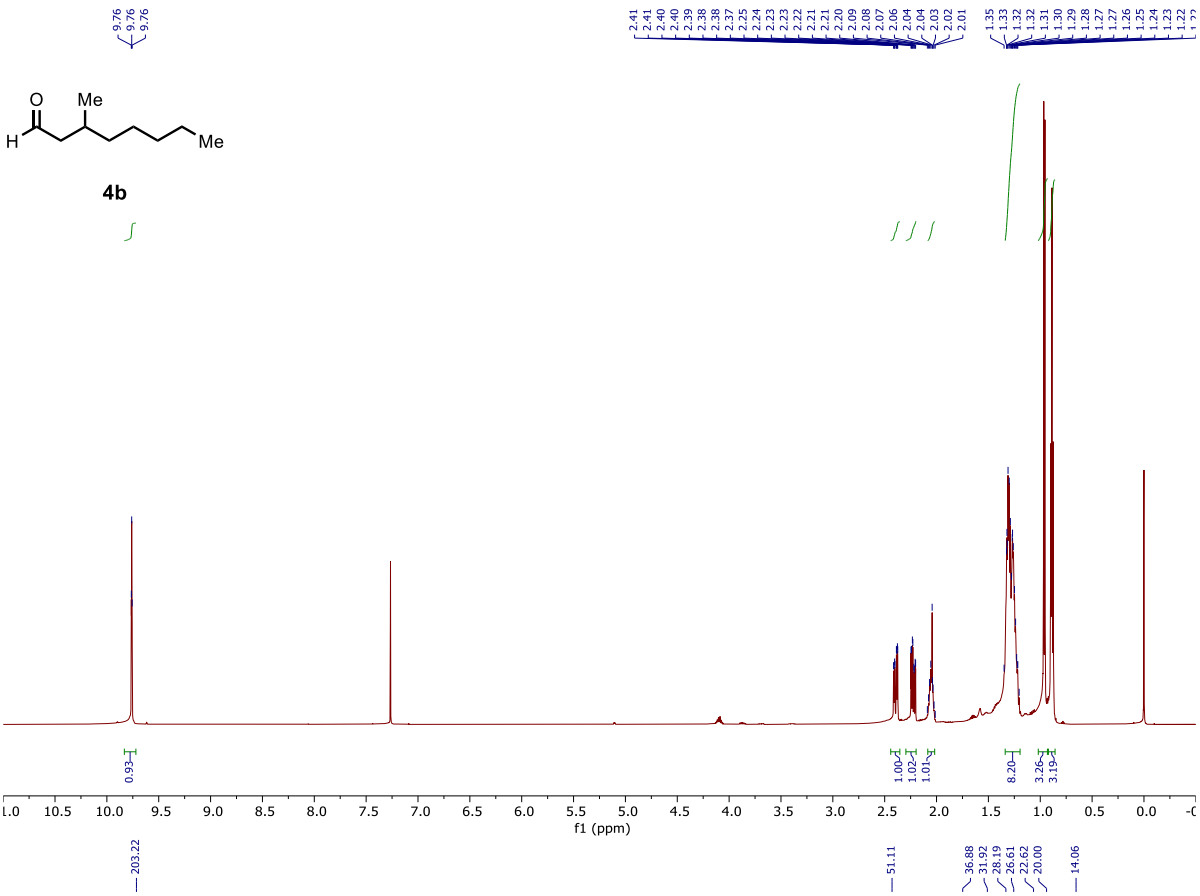

202.88
72.59
70.79
43.90
29.71
29.21
29.12
26.02
22.95
22.03
10.60
O
H
O
Me
1l
f1 (ppm)

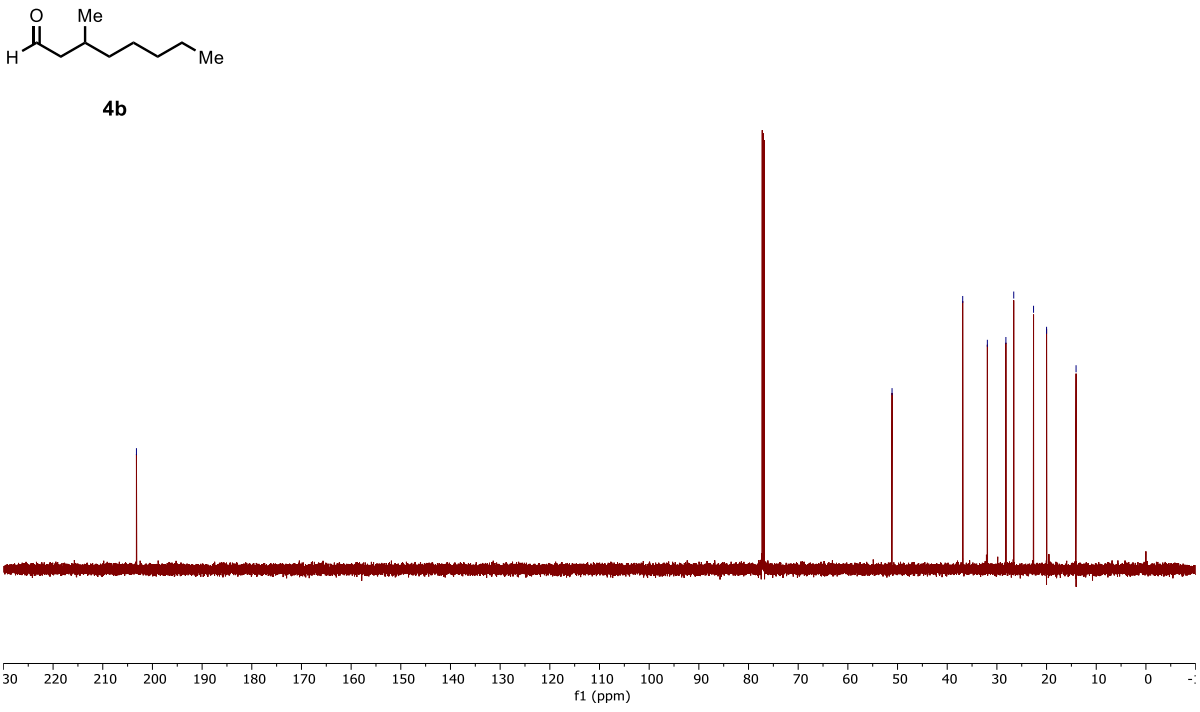

1m
f1 (ppm)

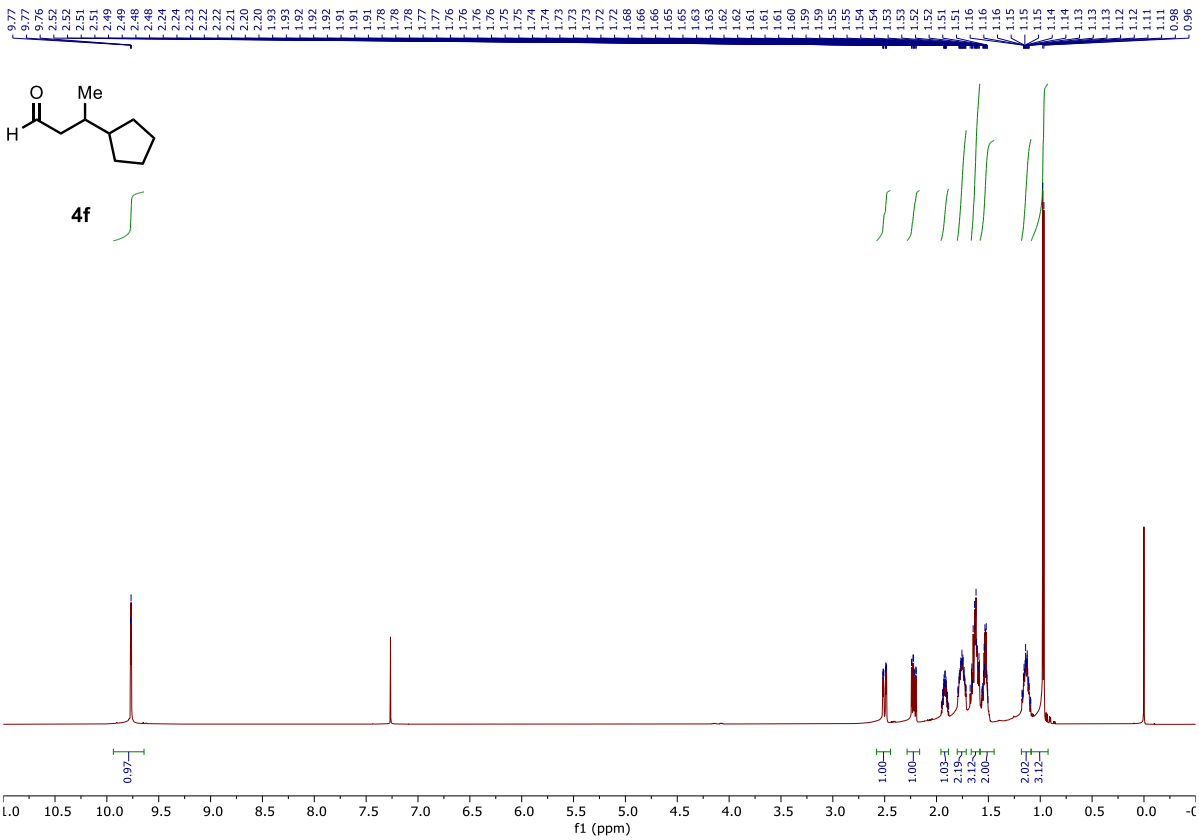

1m
f1 (ppm)

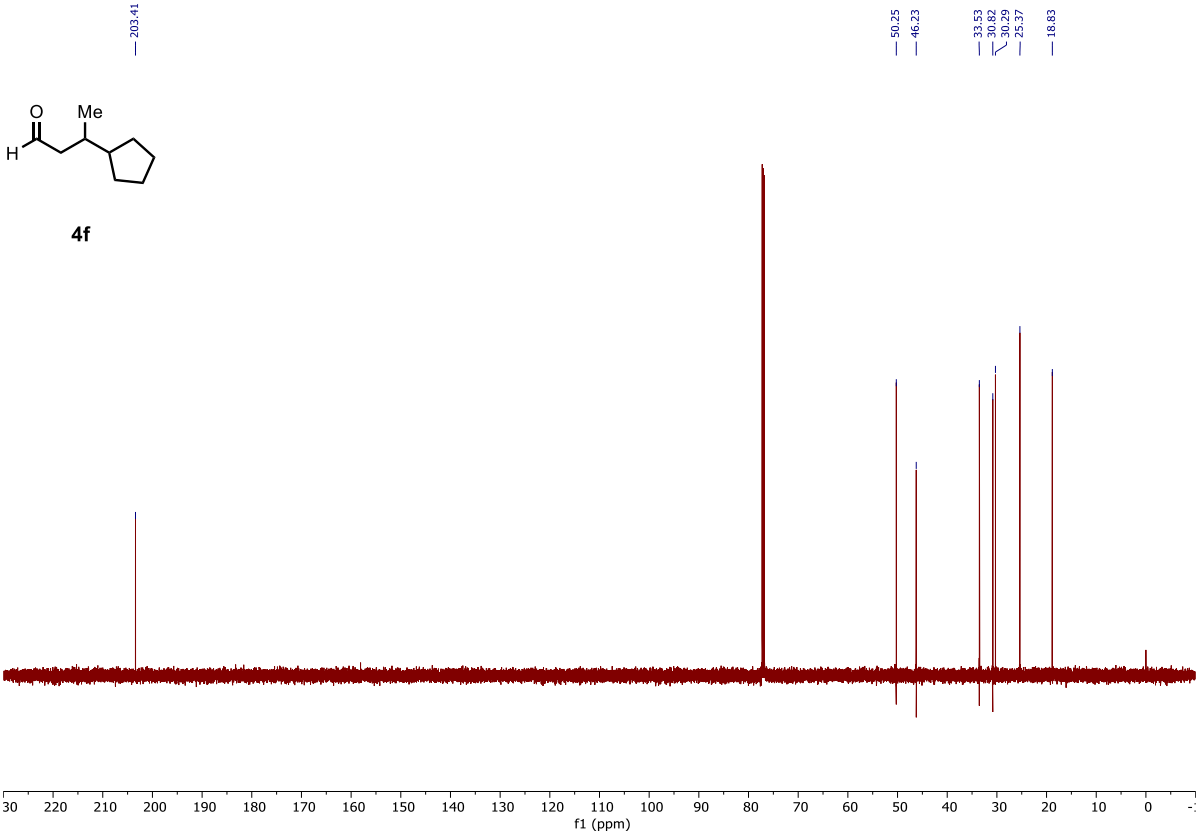

9.78
9.77
9.77
7.85
7.84
7.84
7.83
7.76
7.75
7.75
7.75
4.21
4.20
4.19
1.82
1.80
1.79
1.78
1.77
1.68
1.67
1.66
1.64
1.63
O
H
O
NPhth
1o
0.92
2.01
2.00
2.00
2.00
2.07
2.06
2.01
4.00
f1 (ppm)

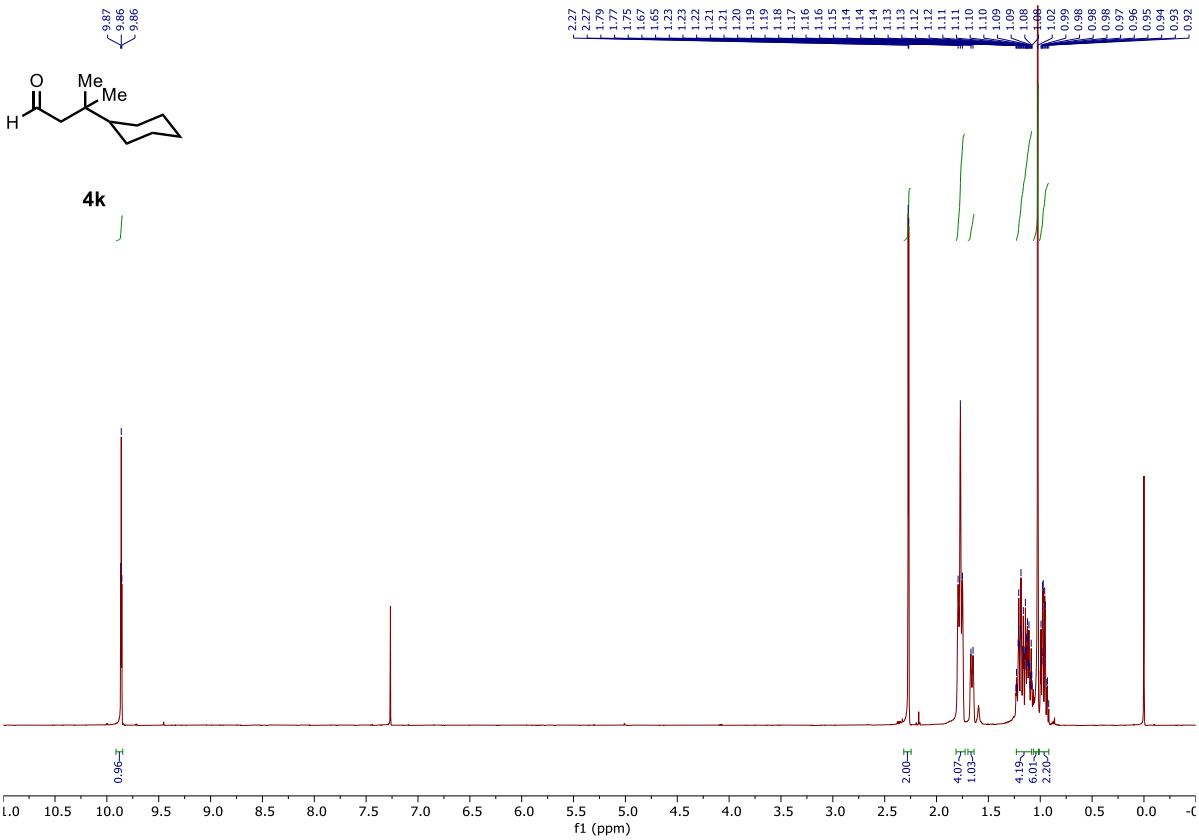

202.85
163.68
134.46
128.97
123.49
78.46
43.84
28.97
28.06
25.36
21.96
21.95
O
H
O
NPhth
1o
f1 (ppm)

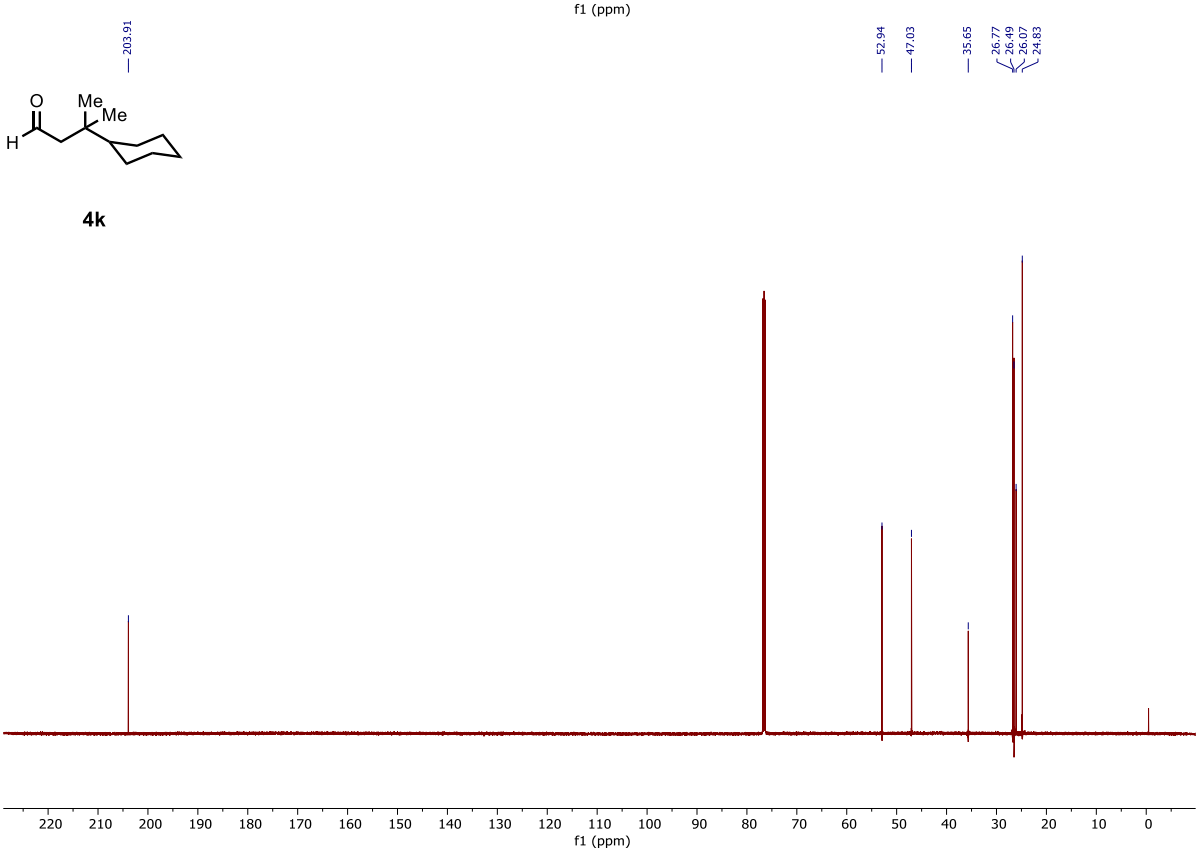

9.76
9.76
9.76
2.41
2.41
2.40
2.40
2.40
2.39
2.38
2.38
2.37
2.25
2.24
2.23
2.23
2.22
2.21
2.21
2.20
2.09
2.08
2.07
2.06
2.04
2.04
2.03
2.02
2.01
1.35
1.33
1.32
1.32
1.31
1.30
1.29
1.28
1.27
1.27
1.26
1.25
1.24
1.23
1.22
O
Me
H
Me
4b
0.93
1.00
1.02
1.01
8.20
3.26
3.19
f1 (ppm)
203.22
51.11
36.88
31.92
28.19
26.61
22.62
20.00
14.06

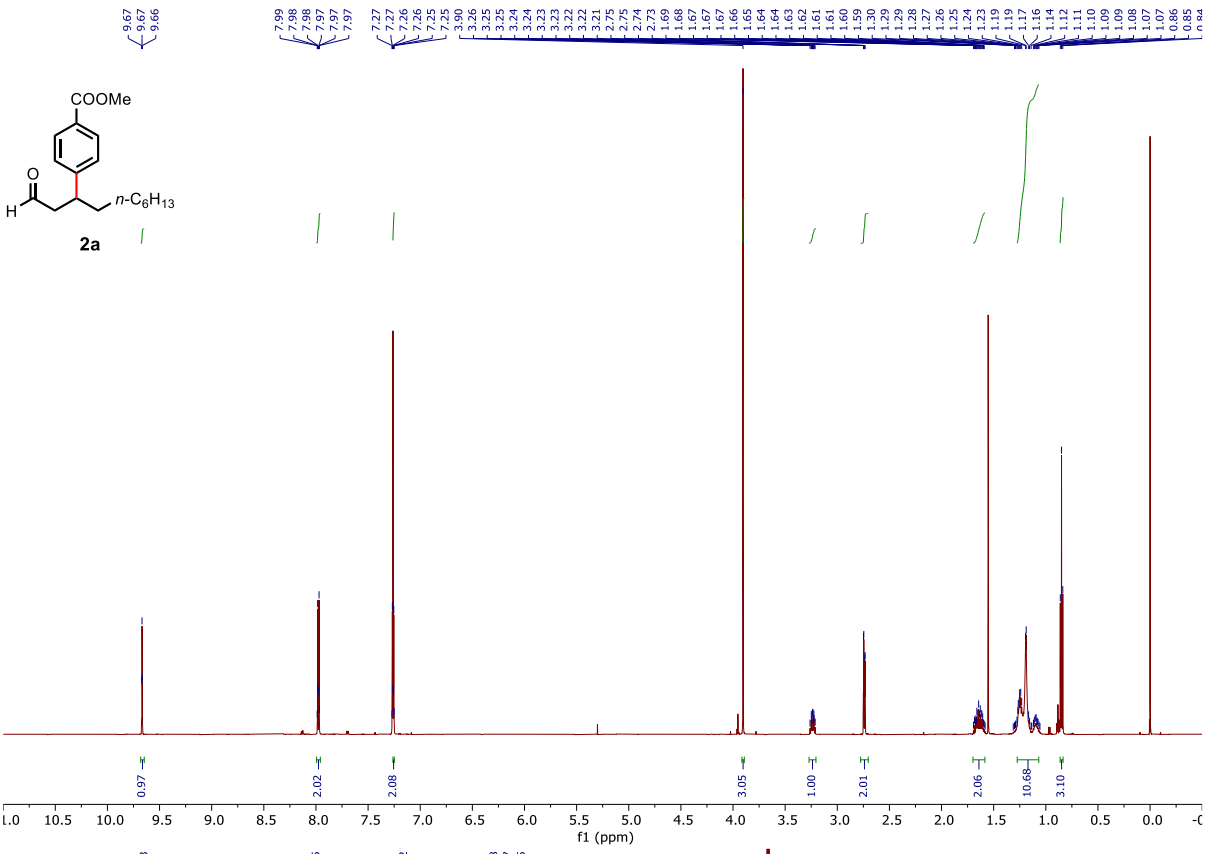

O
Me
H
Me
4b
f1 (ppm)

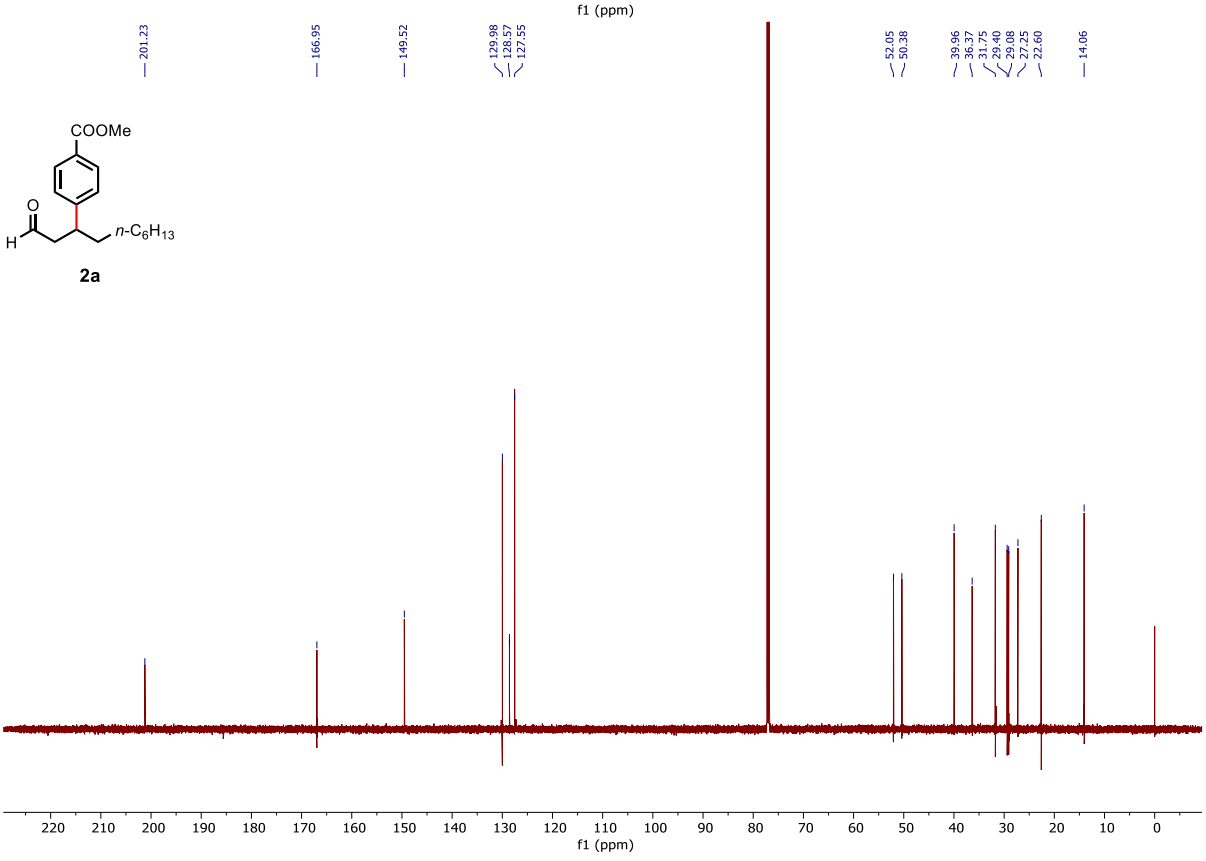

O
Me
H
4f
f1 (ppm)

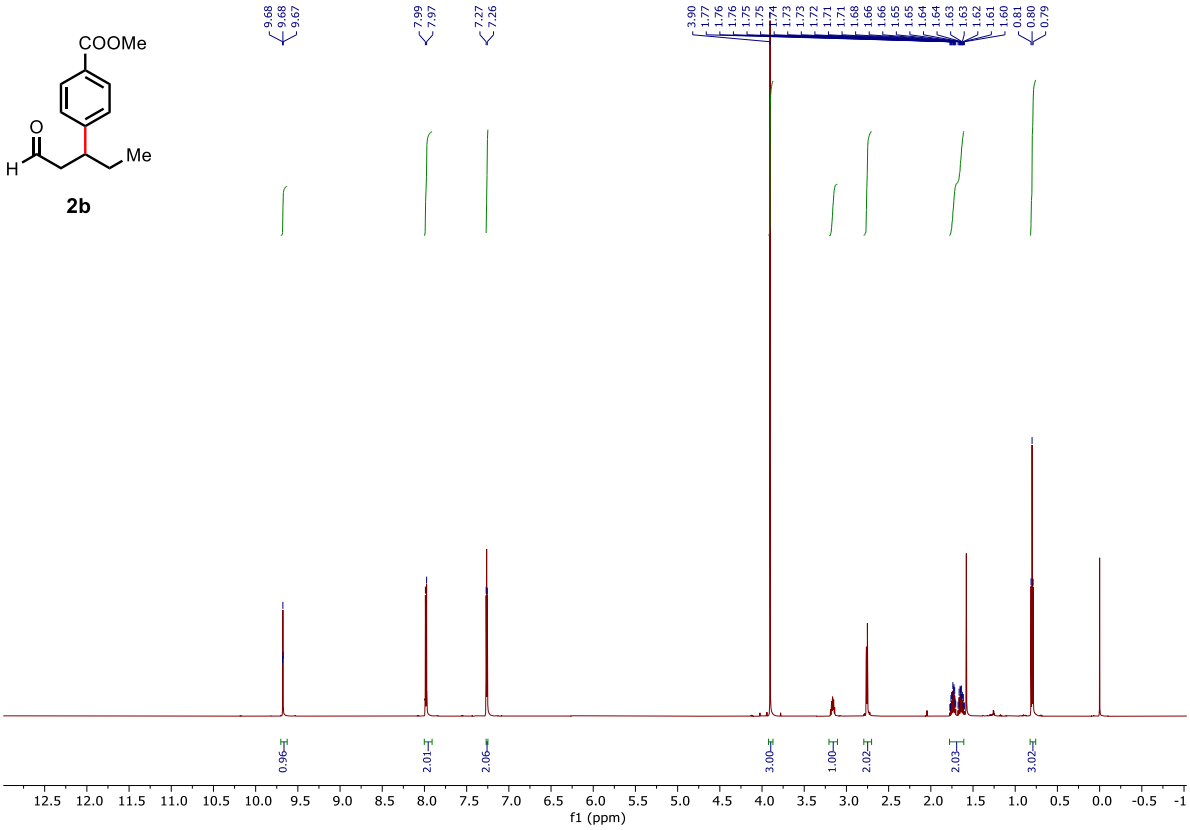

O
Me
H
4f
f1 (ppm)

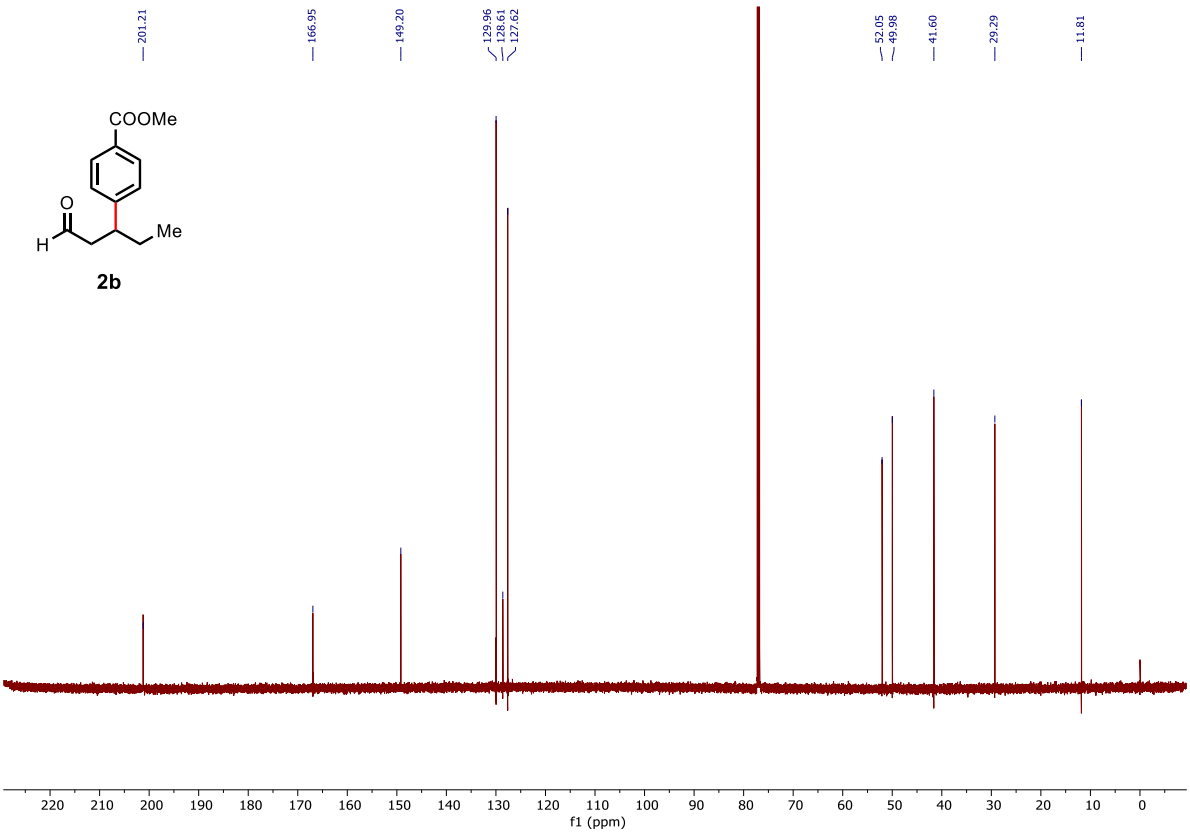

9.87
9.86
9.86
O
Me
Me
H
4k
2.27
2.27
1.79
1.77
1.75
1.67
1.65
1.23
1.23
1.22
1.21
1.21
1.20
1.19
1.19
1.18
1.17
1.16
1.16
1.15
1.14
1.14
1.14
1.13
1.13
1.12
1.12
1.11
1.11
1.10
1.10
1.09
1.09
1.08
1.08
1.02
0.99
0.98
0.98
0.98
0.98
0.97
0.96
0.95
0.94
0.93
0.92
0.96
2.00
4.07
1.03
4.19
6.01
2.20
f1 (ppm)

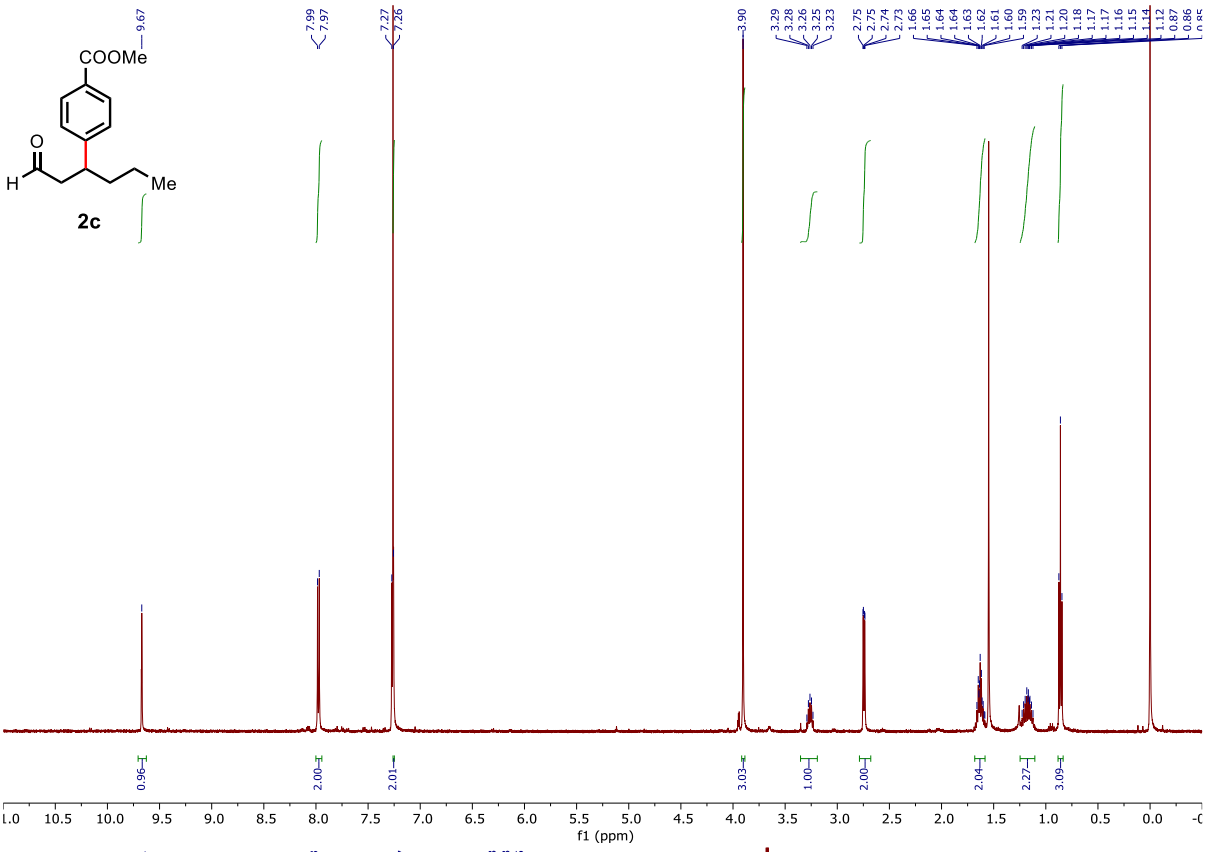

203.91
52.94
47.03
35.65
26.77
26.49
26.07
24.83
O
Me
Me
H
4k
f1 (ppm)

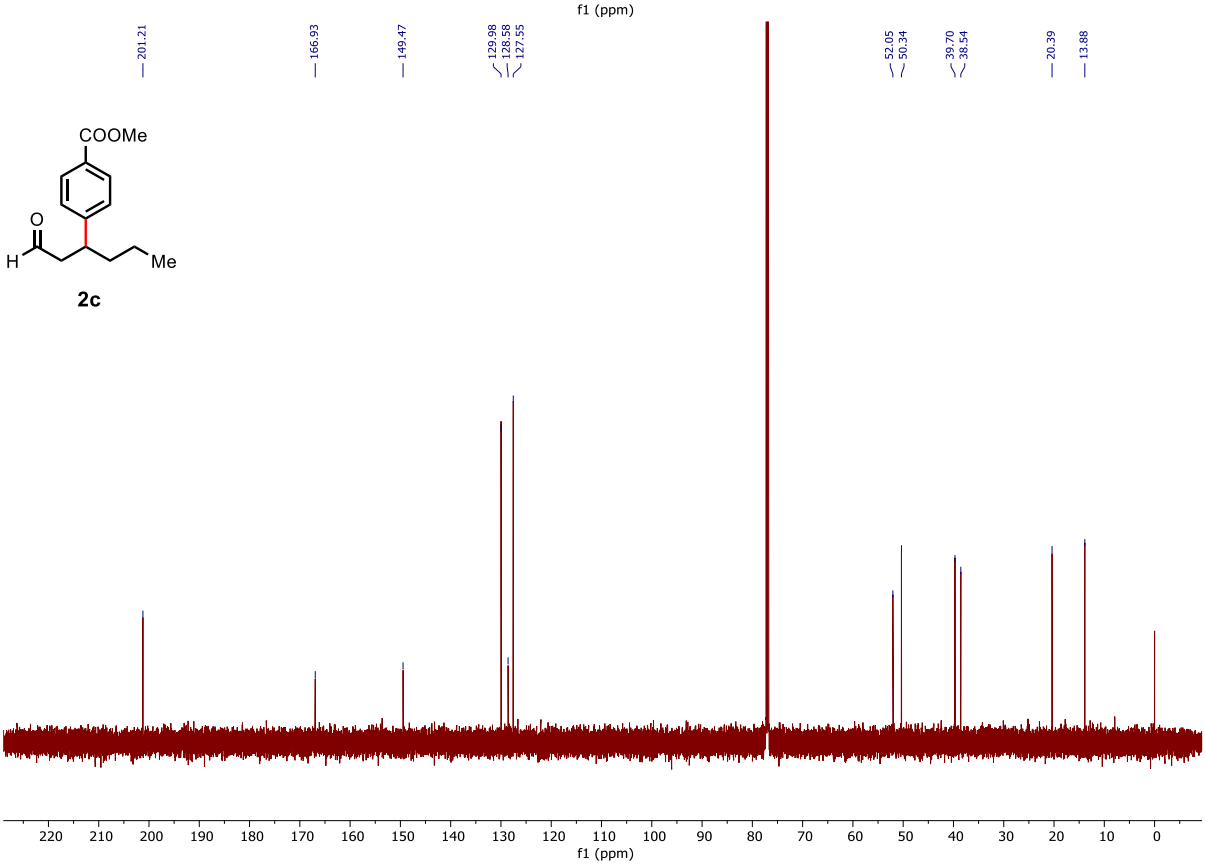

COOMe
O
H
n-C6H13
2a
f1 (ppm)

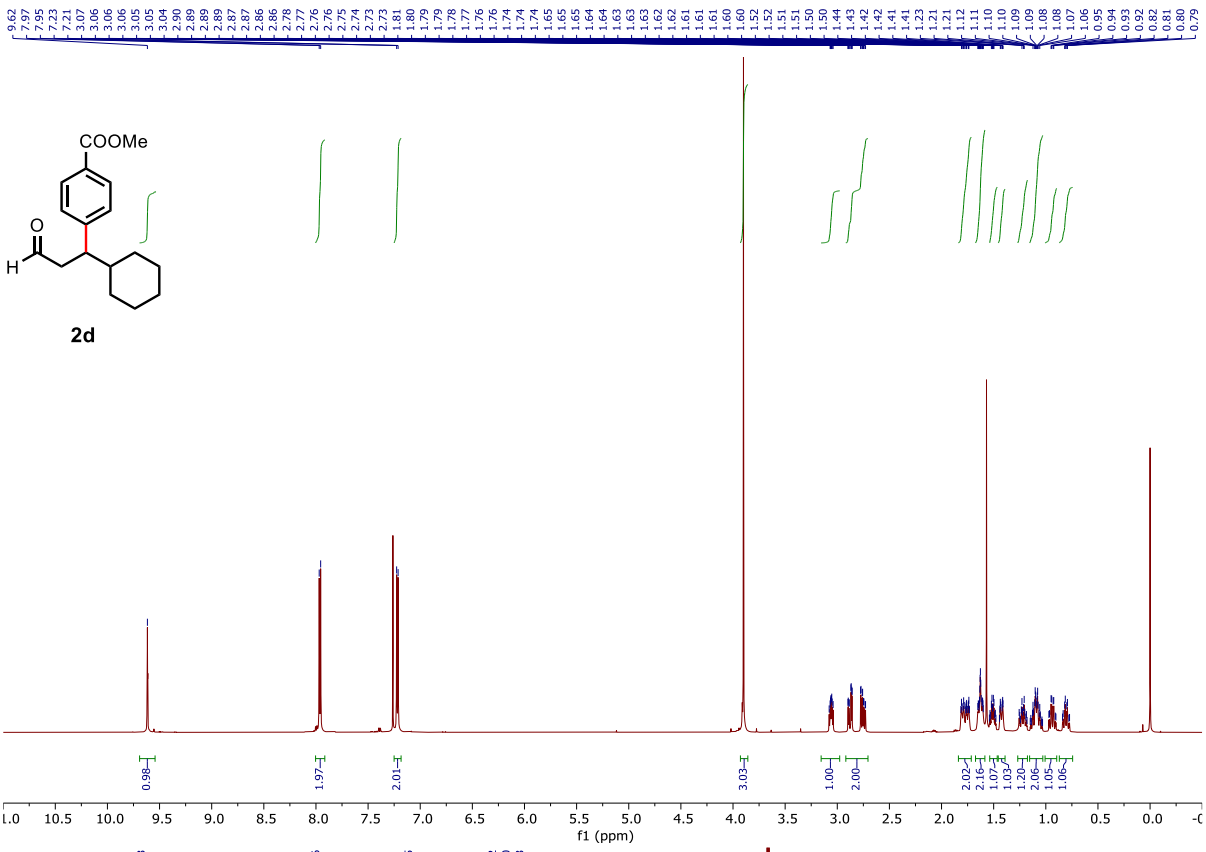

COOMe
O
H
n-C6H13
2a
f1 (ppm)

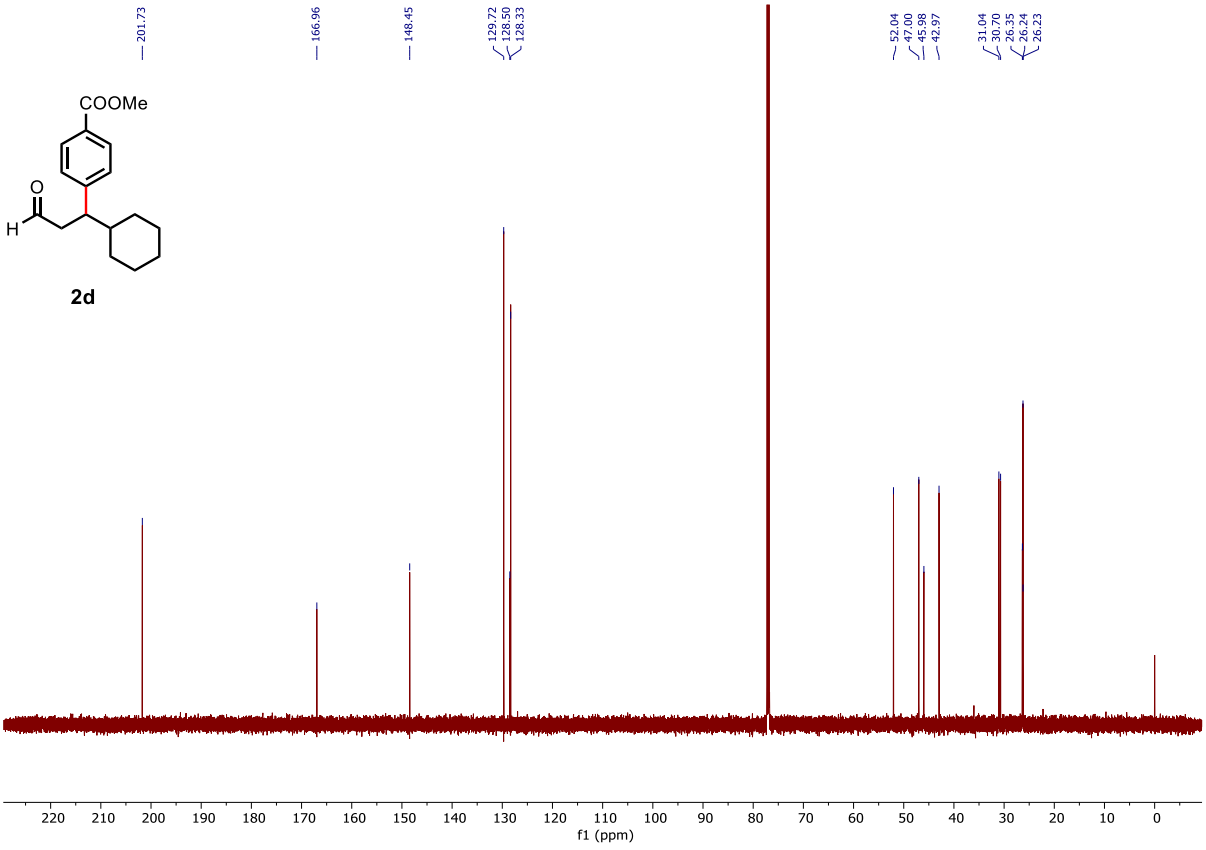

COOMe
O
H
Me
2b
9.68
9.68
9.67
7.99
7.97
7.27
7.26
3.90
1.77
1.76
1.76
1.75
1.75
1.74
1.73
1.73
1.72
1.71
1.71
1.68
1.66
1.66
1.65
1.65
1.64
1.64
1.63
1.63
1.62
1.61
1.60
0.81
0.80
0.79
0.96
2.01
2.06
3.00
1.00
2.02
2.03
3.02
f1 (ppm)

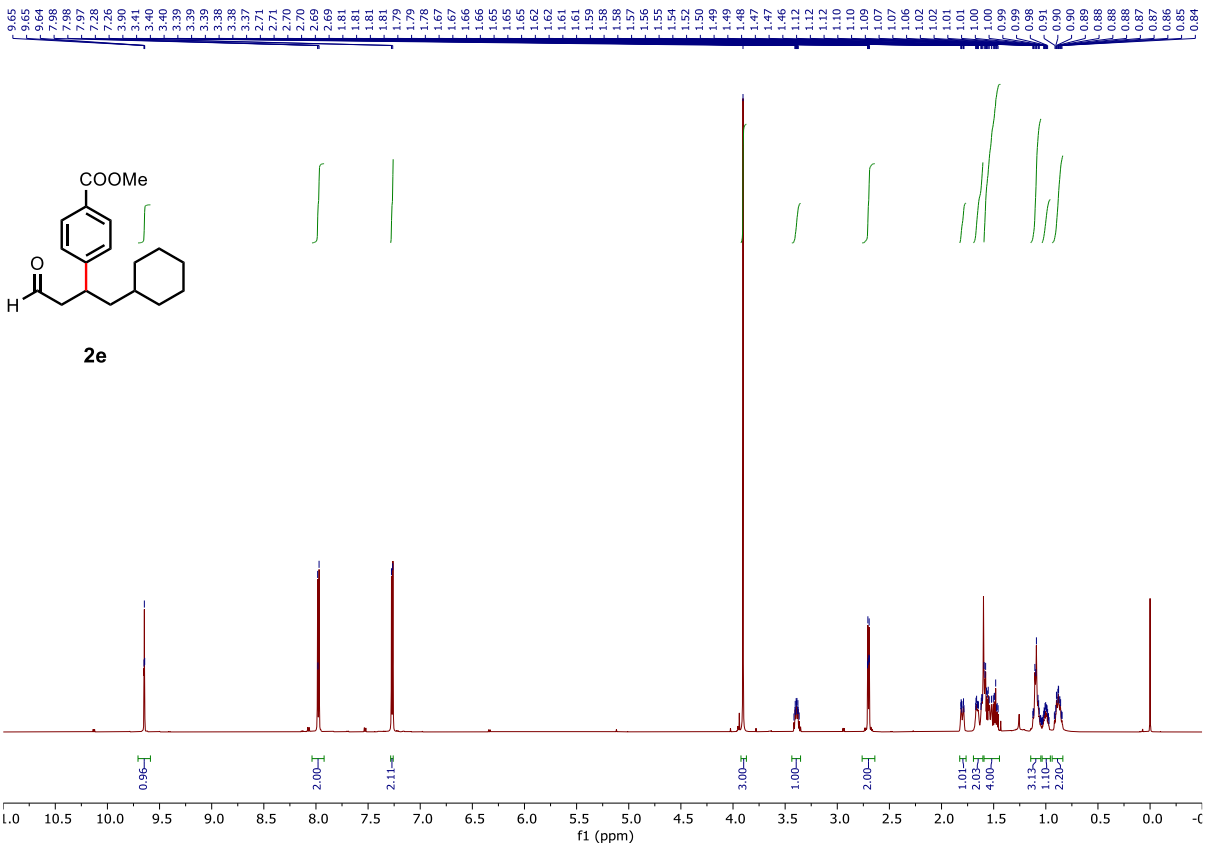

201.21
166.95
149.20
129.96
128.61
127.62
52.05
49.98
41.60
29.29
11.81
COOMe
O
H
Me
2b
f1 (ppm)

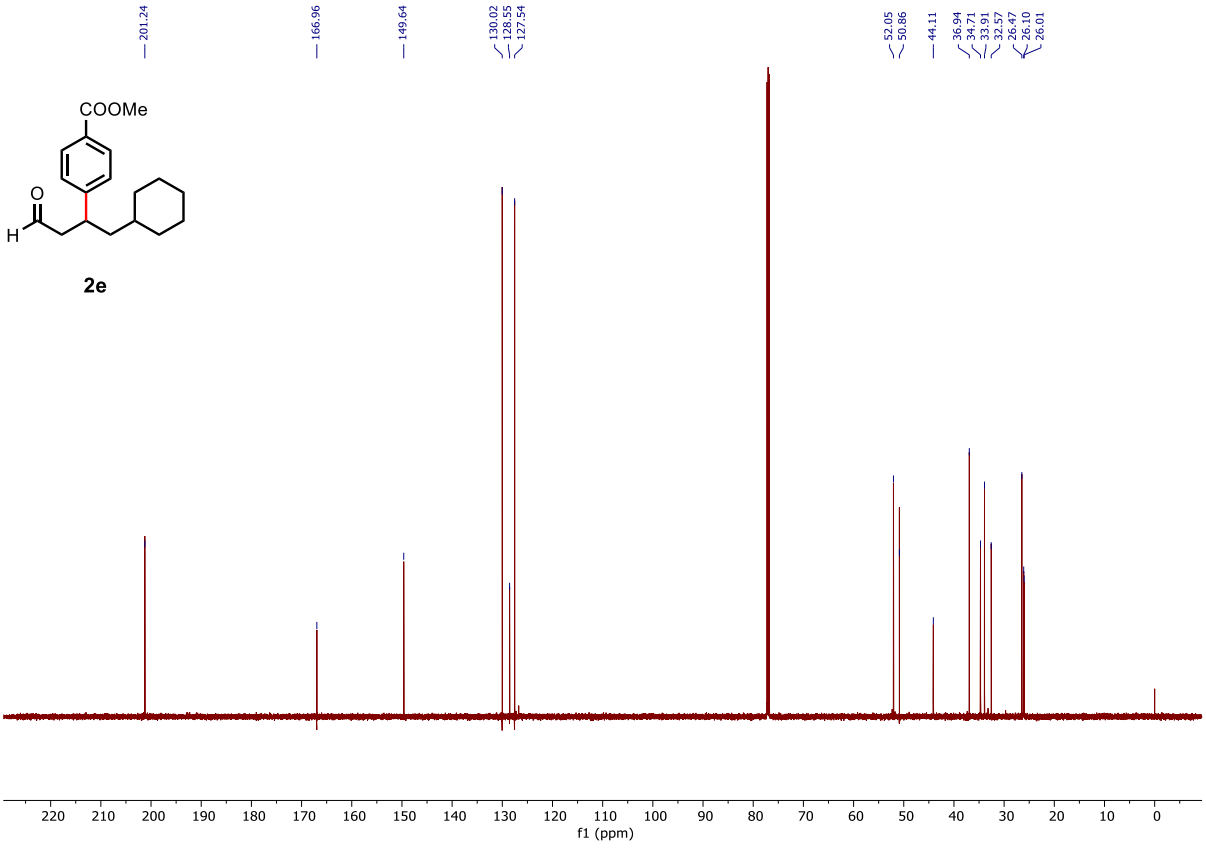

COOMe
O
H
Me
2c
9.67
7.99
7.97
7.27
7.26
3.90
3.29
3.28
3.26
3.25
3.23
2.75
2.75
2.74
2.73
1.66
1.65
1.64
1.64
1.63
1.62
1.61
1.60
1.59
1.23
1.21
1.20
1.18
1.17
1.17
1.16
1.15
1.14
1.12
0.87
0.86
0.96
2.00
2.01
3.03
1.00
2.00
2.04
2.27
3.09
f1 (ppm)

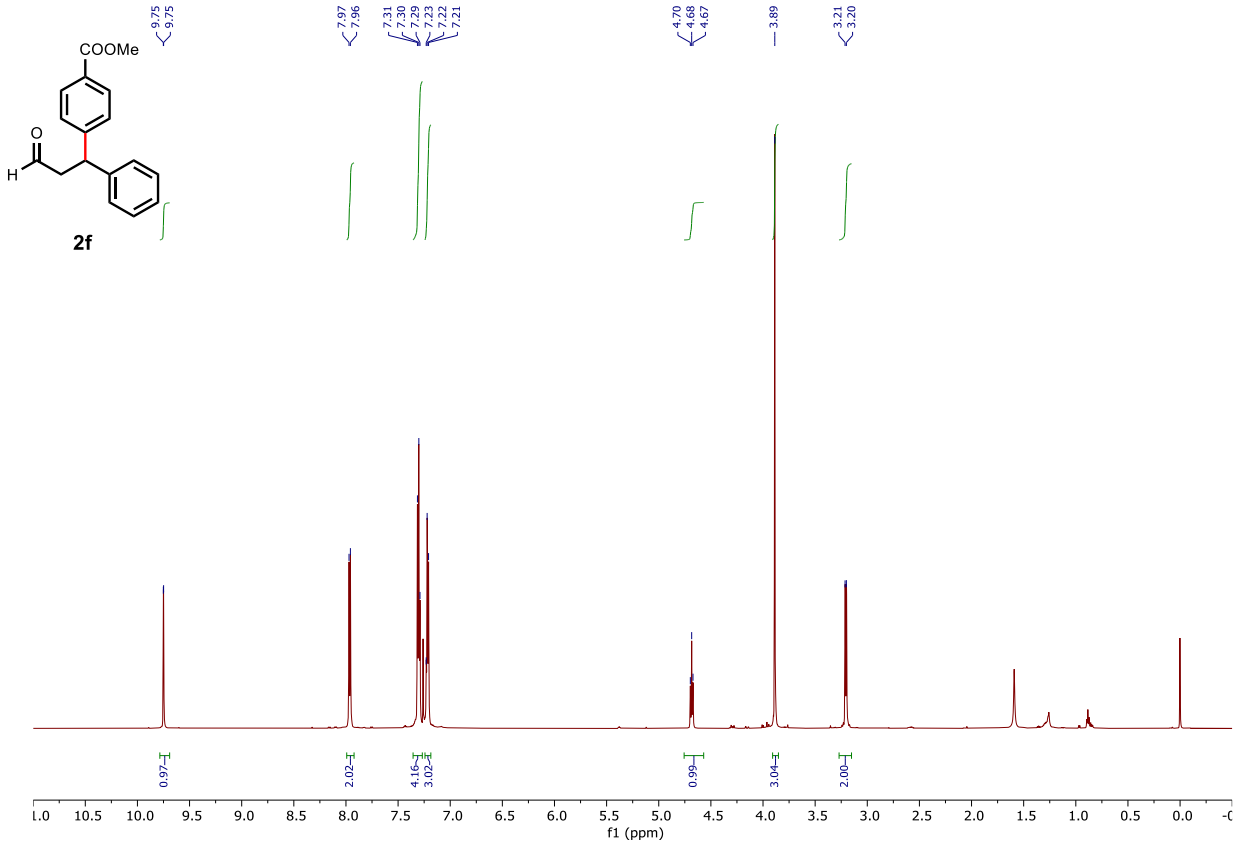

201.21
166.93
149.47
129.98
128.58
127.55
52.05
50.34
39.70
38.54
20.39
13.88
COOMe
O
H
Me
2c
f1 (ppm)

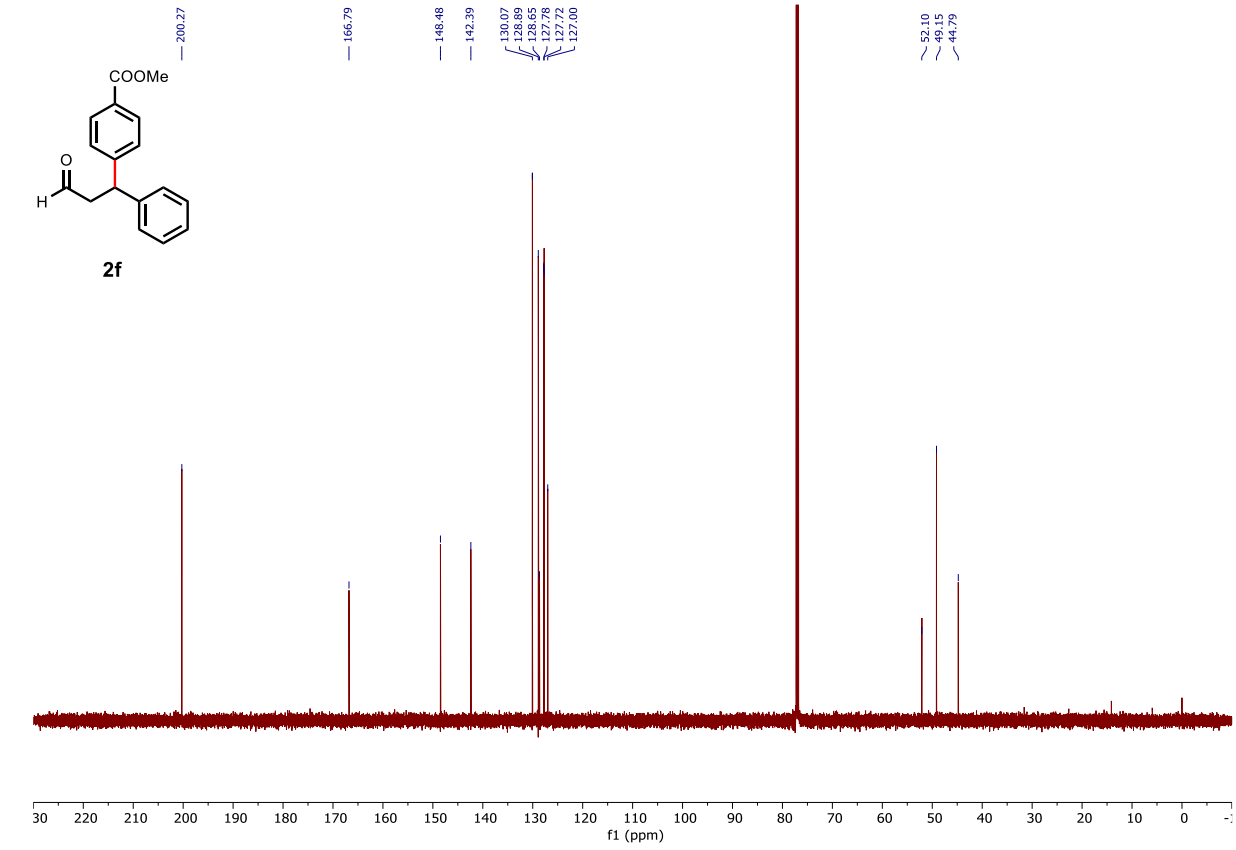

COOMe
O
H
2d
f1 (ppm)

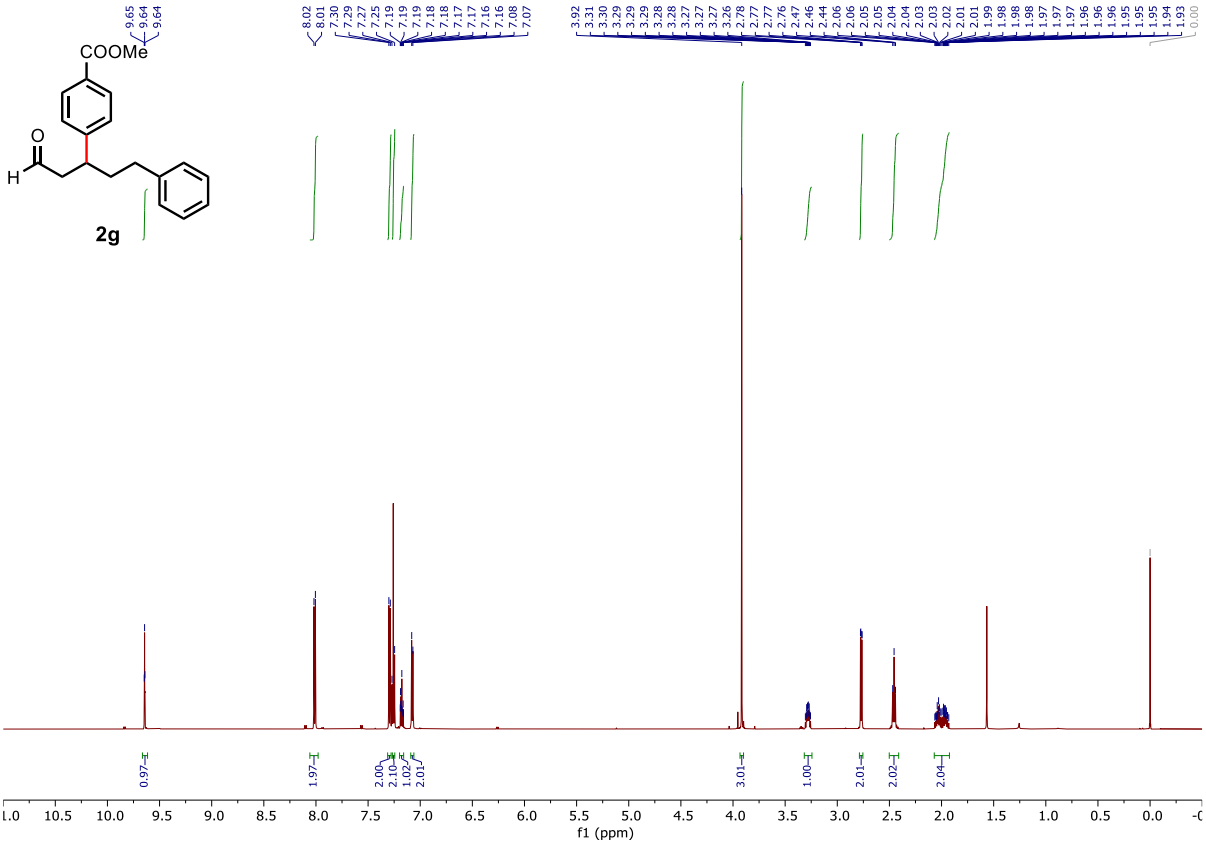

COOMe
O
H
2d
f1 (ppm)

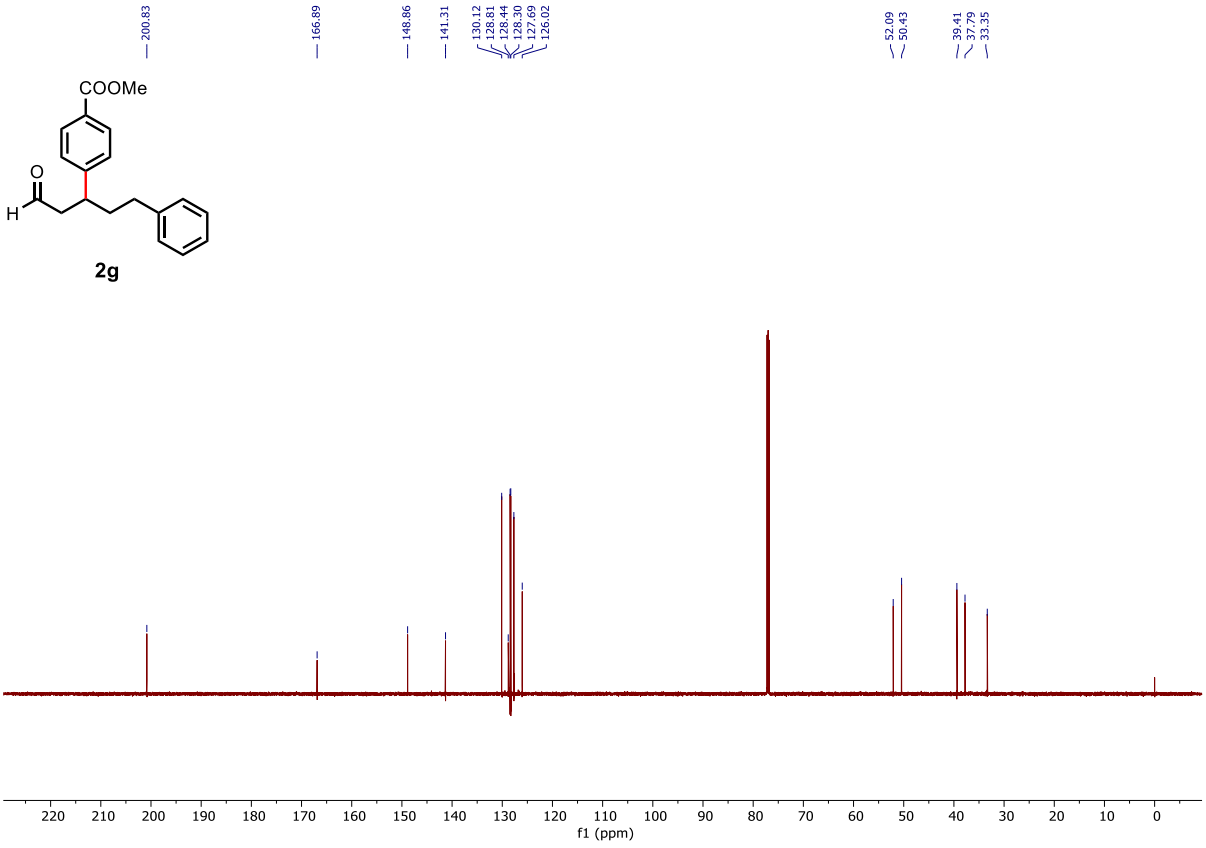

COOMe
O
H
2e
f1 (ppm)

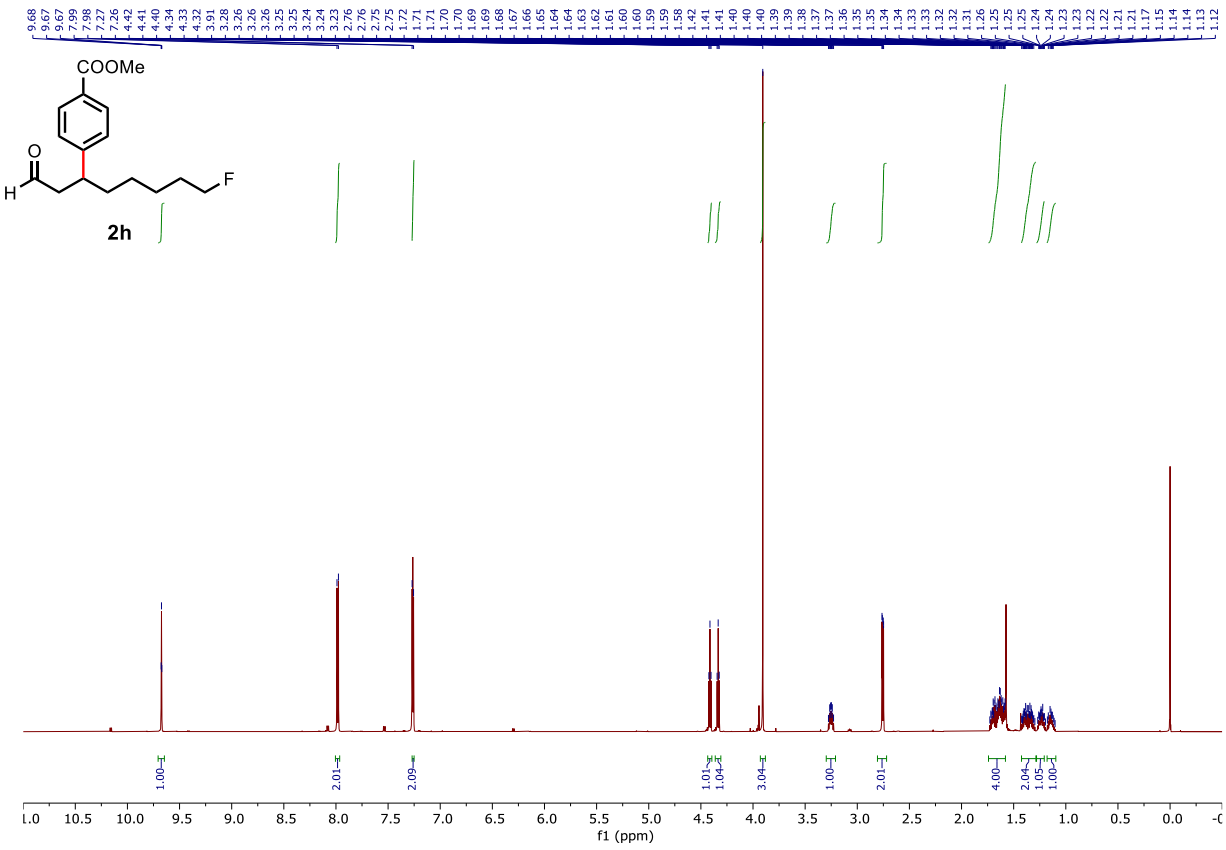

COOMe
O
H
2e
f1 (ppm)

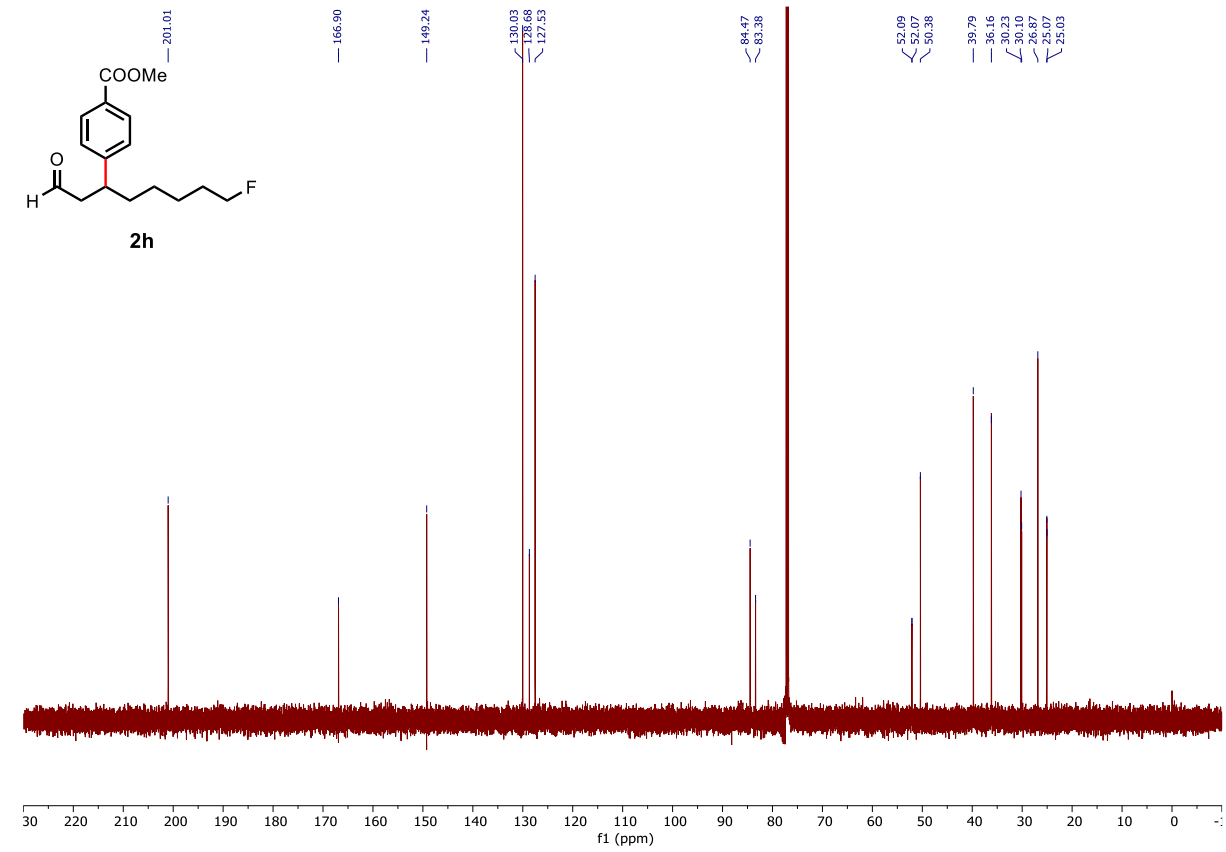

9.75
9.75
7.97
7.96
7.31
7.30
7.29
7.23
7.22
7.21
4.70
4.68
4.67
3.89
3.21
3.20
COOMe
O
H
2f
0.97
2.02
4.16
3.02
0.99
3.04
2.00
f1 (ppm)

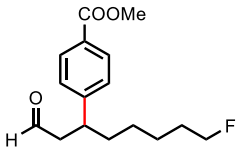

200.27
166.79
148.48
142.39
130.07
128.89
128.65
127.78
127.72
127.00
52.10
49.15
44.79
COOMe
O
H
2f
f1 (ppm)


COOMe
O
H
2g
f1 (ppm)


COOMe
O
H
2g
f1 (ppm)

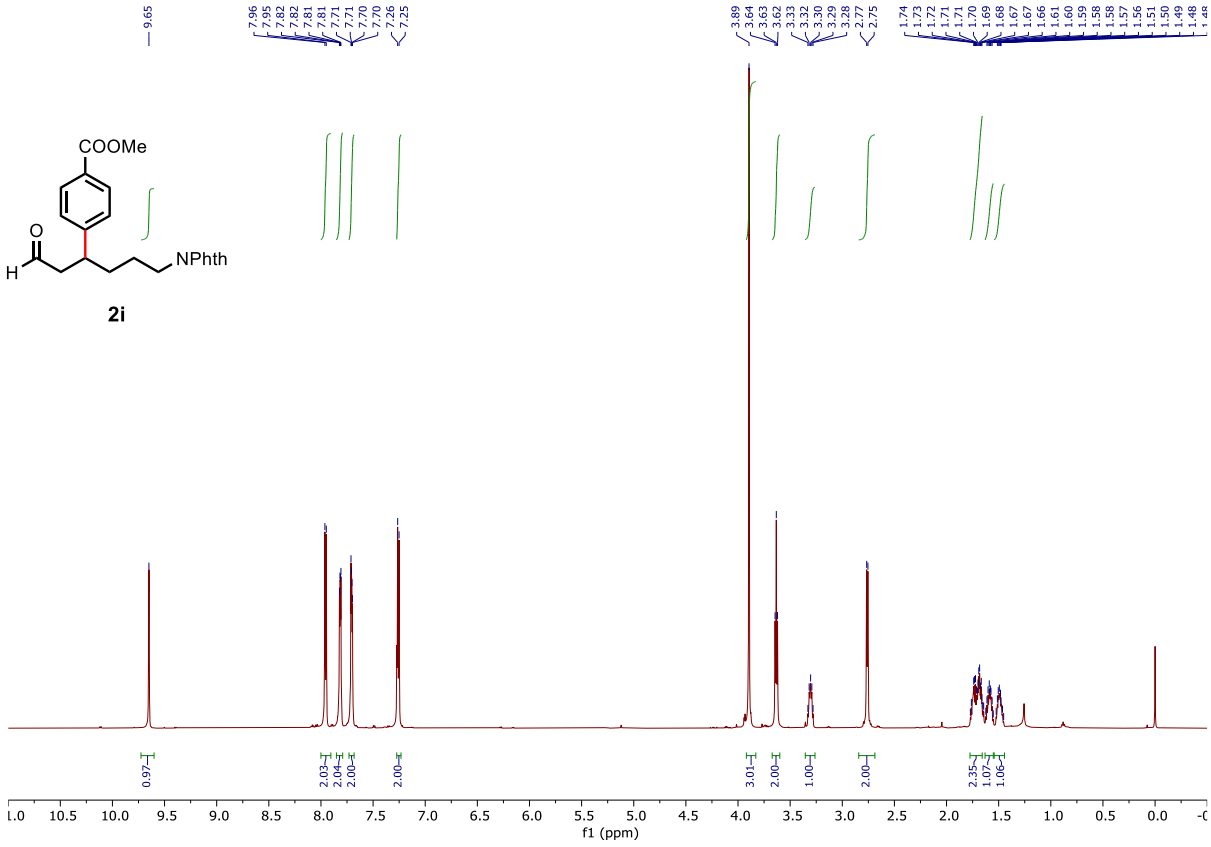

COOMe
O
H
F
2h
f1 (ppm)

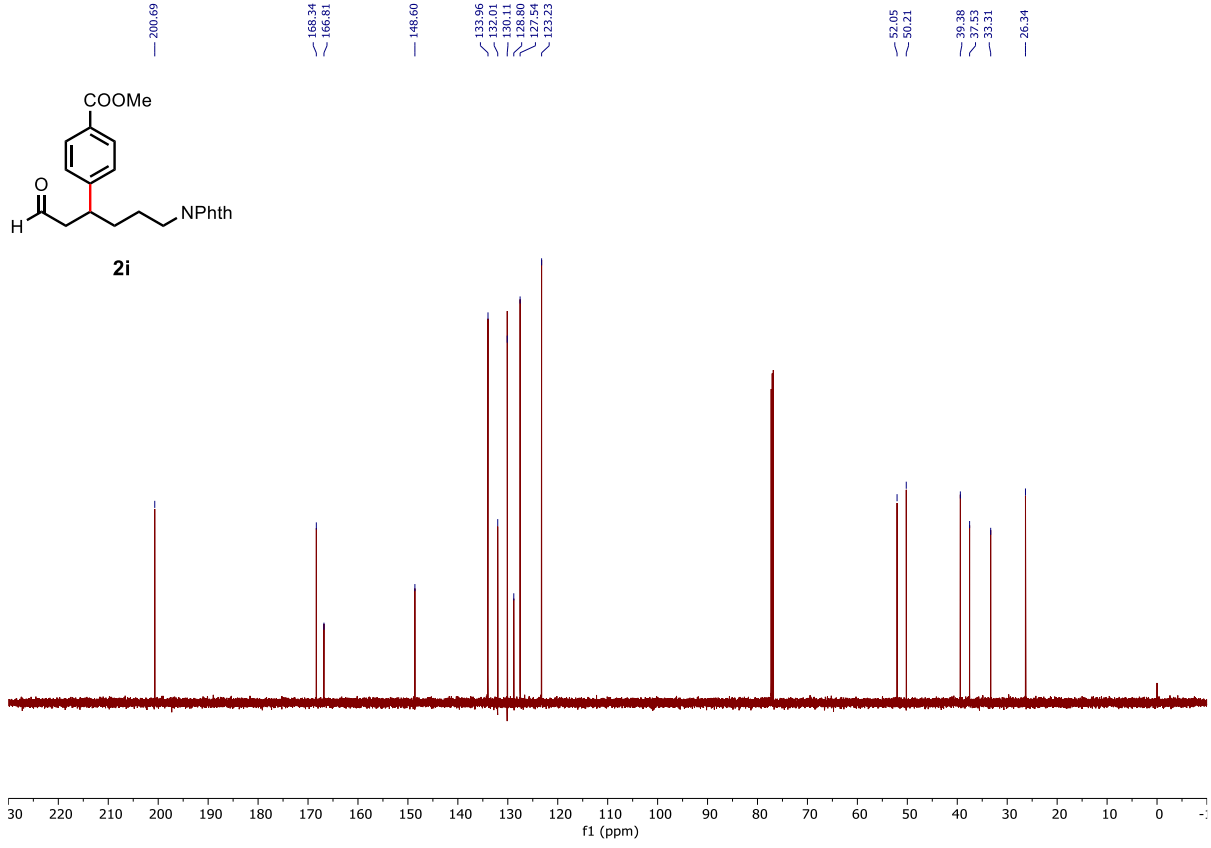

COOMe
O
H
F
2h
f1 (ppm)

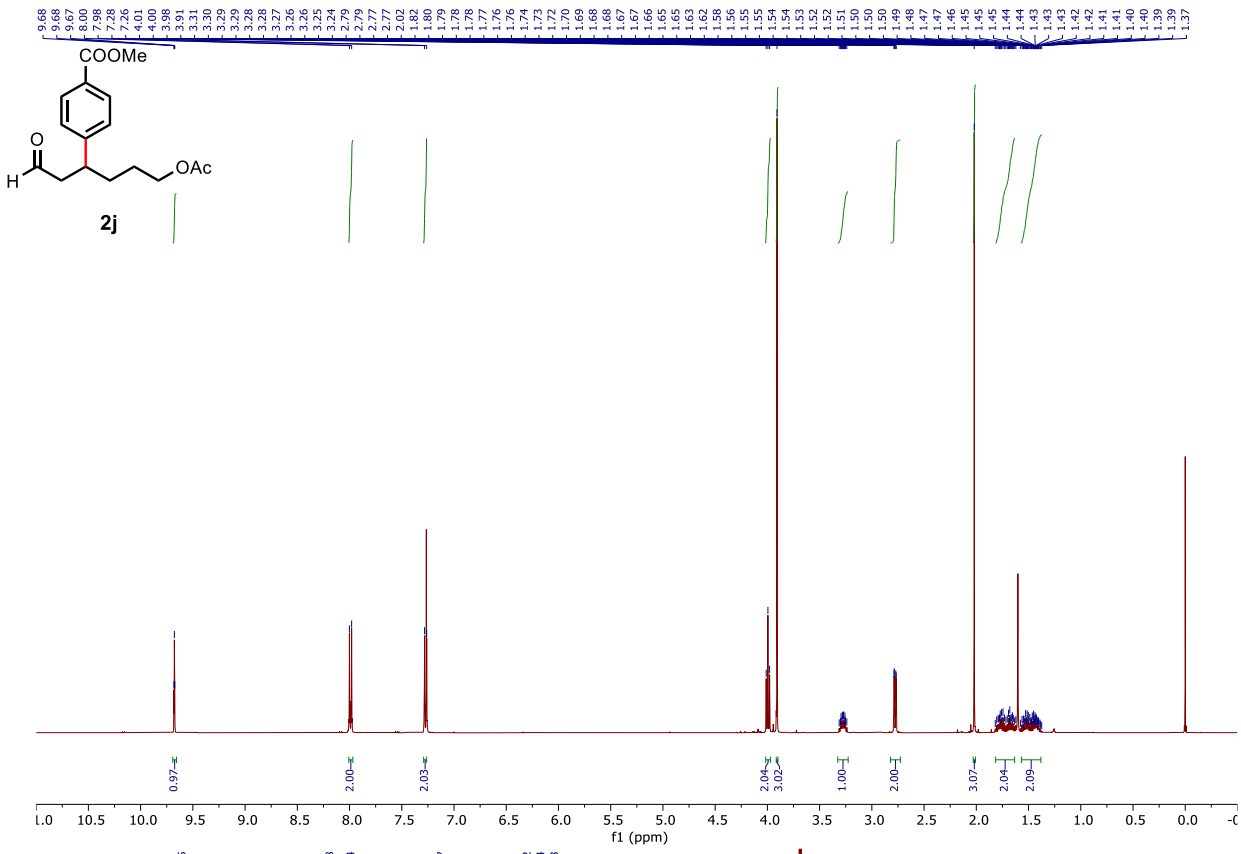

COOMe
O
H
F

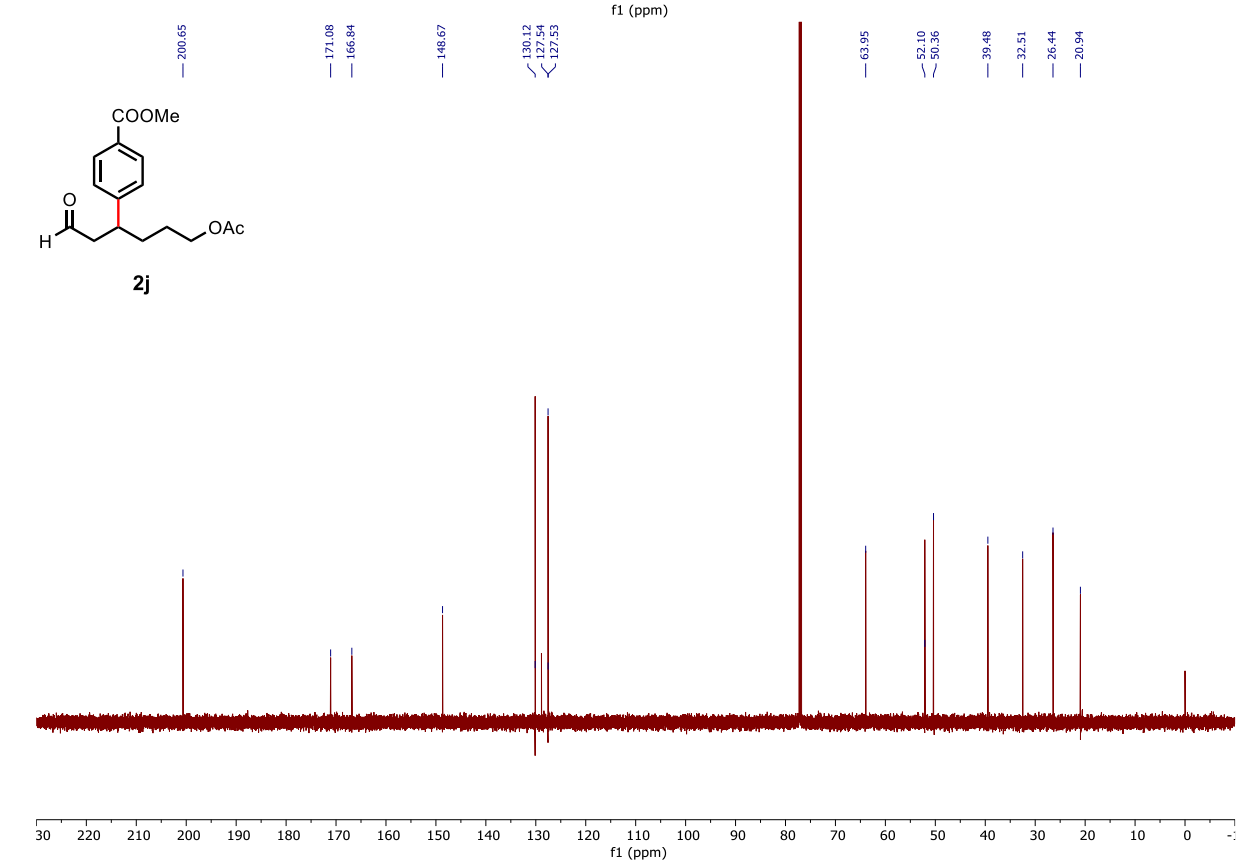
2h

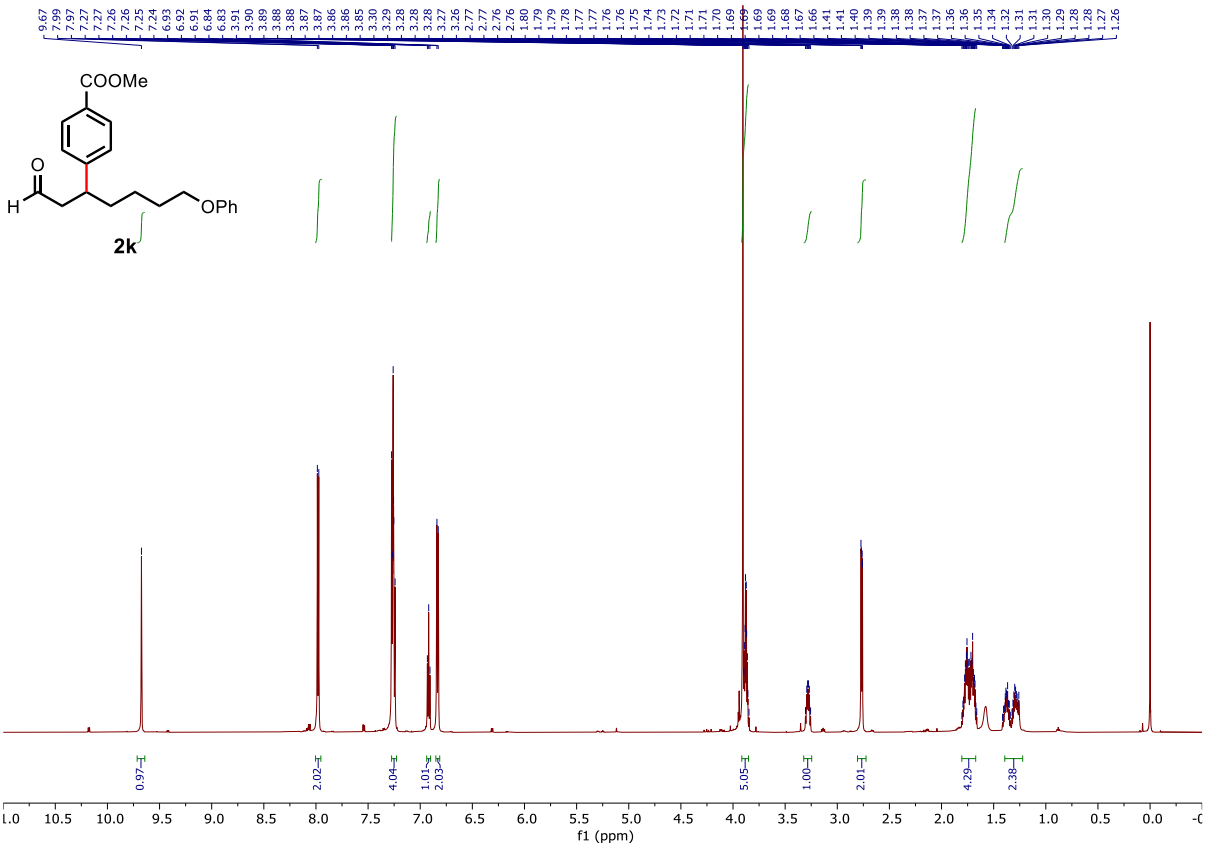
-221.05
-206 -207 -208 -209 -210 -211 -212 -213 -214 -215 -216 -217 -218 -219 -220 -221 -222 -223 -224 -225 -226 -227 -228 -229 -230 -231
f1 (ppm)

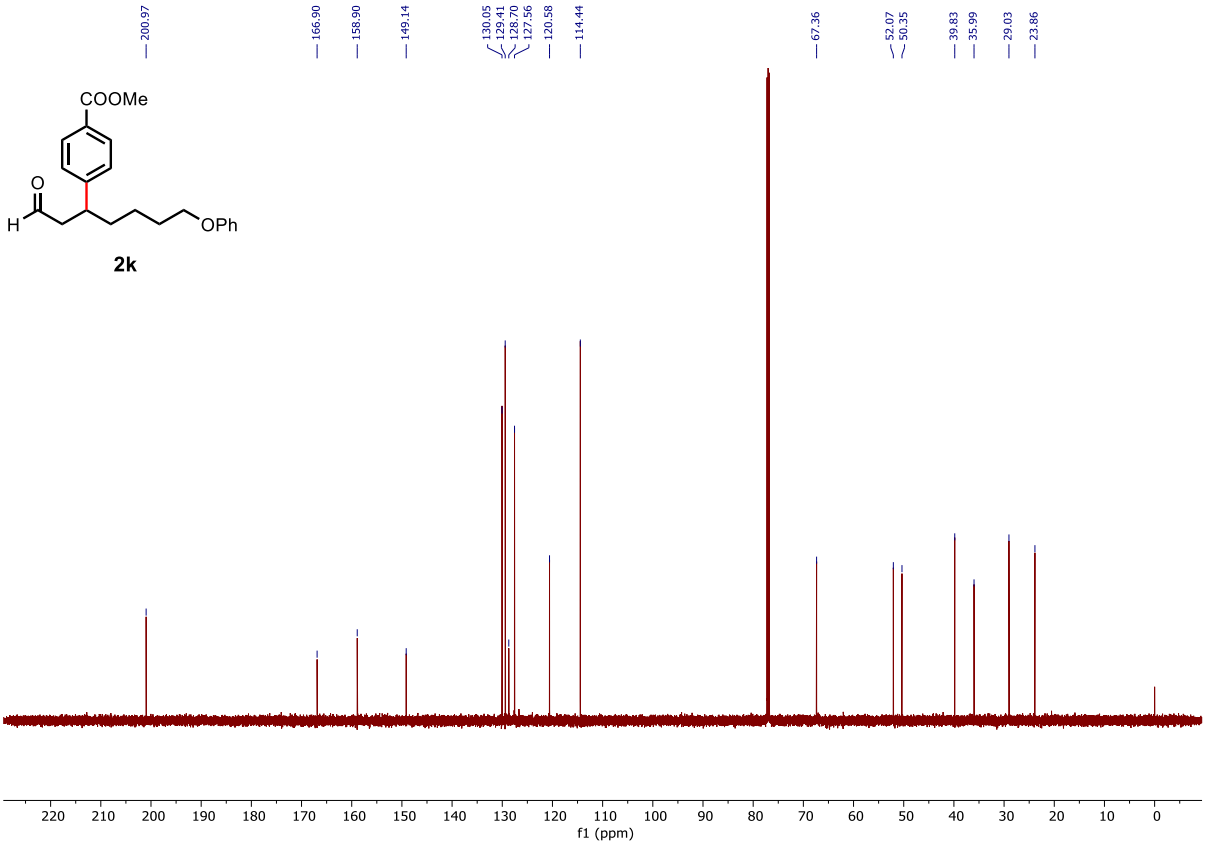

COOMe
O
H
NPhth
2i
f1 (ppm)

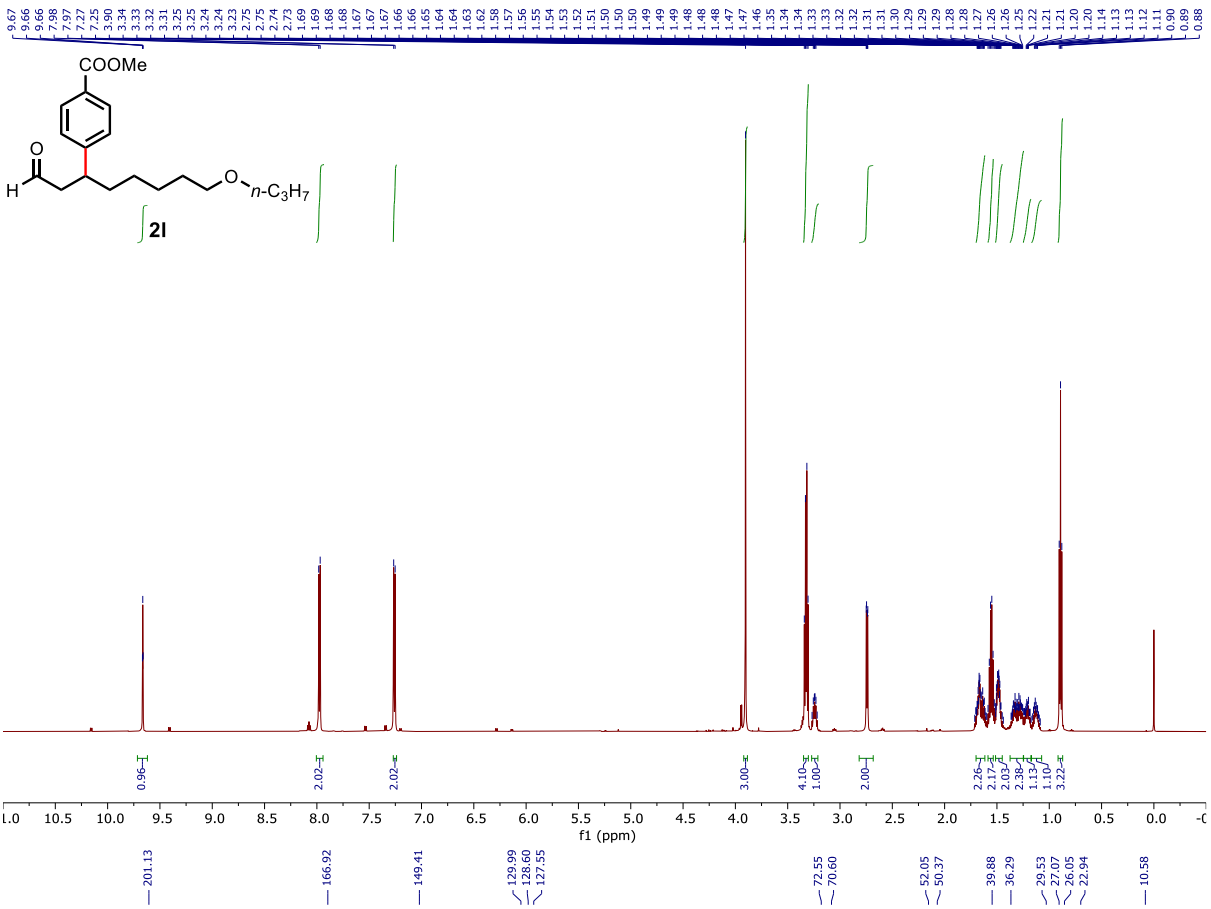

COOMe
O
H
NPhth
2i
f1 (ppm)

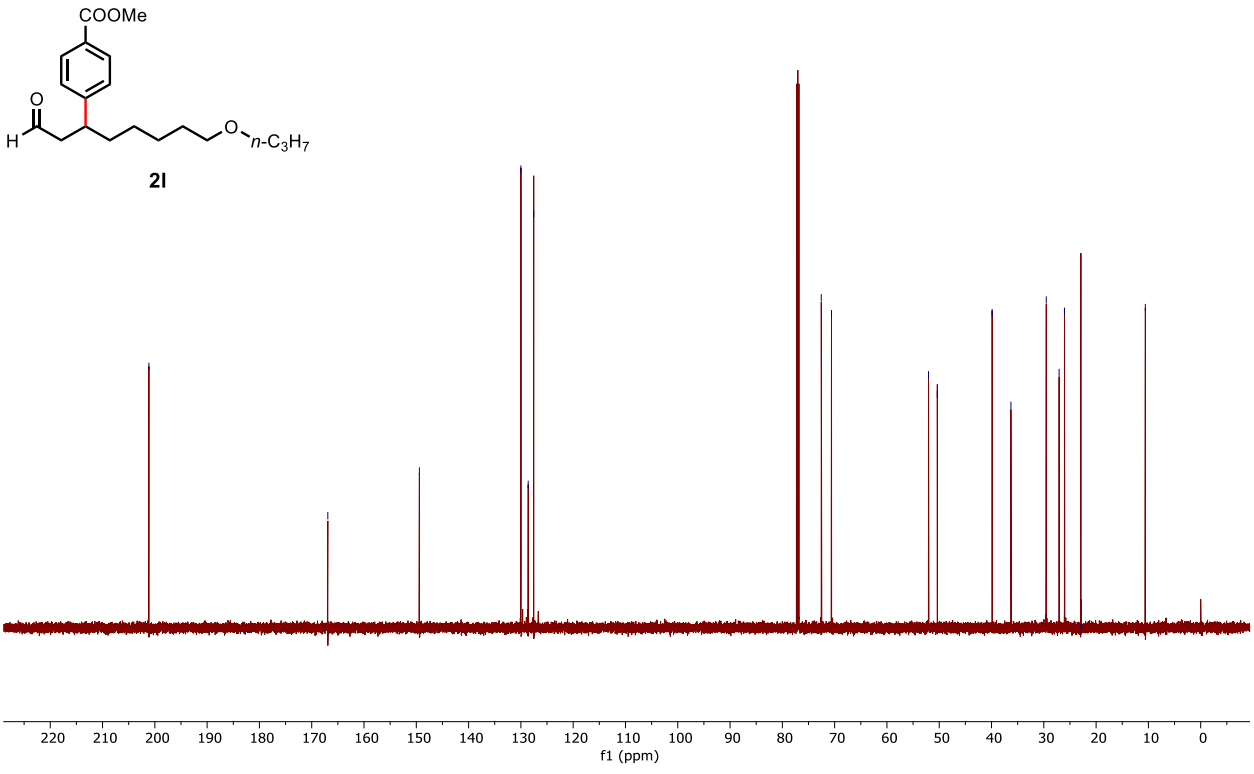

COOMe
O
H
OAc
2j
f1 (ppm)

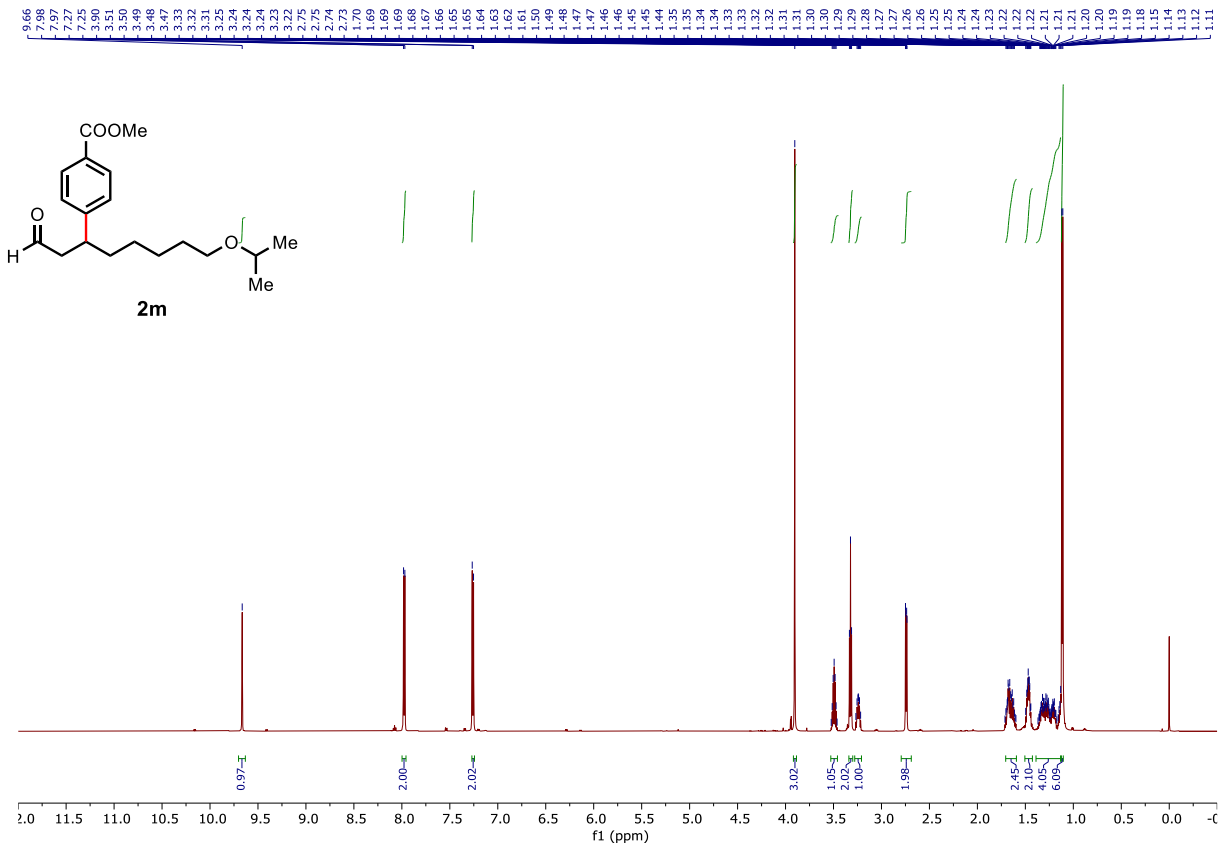

COOMe
O
H
OAc
2j
f1 (ppm)

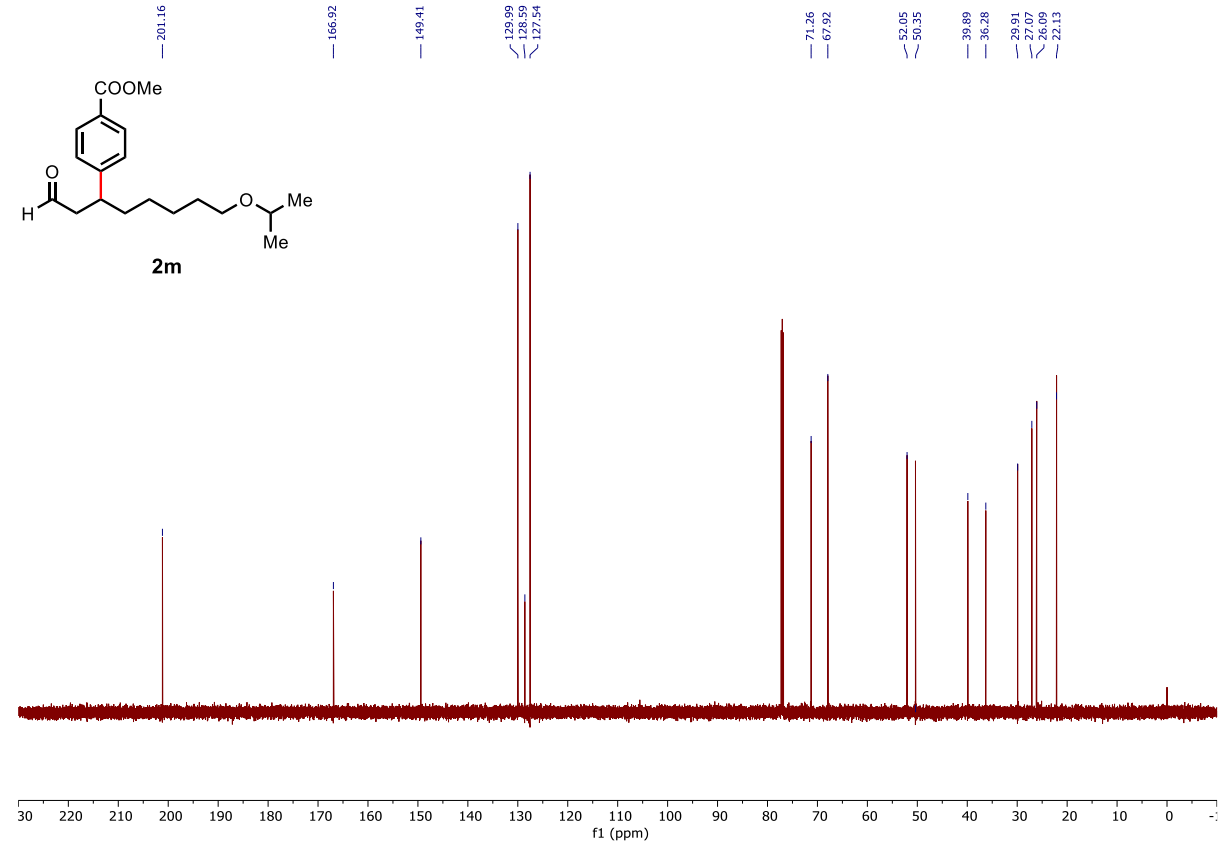

COOMe
O
H
OPh
2k
f1 (ppm)

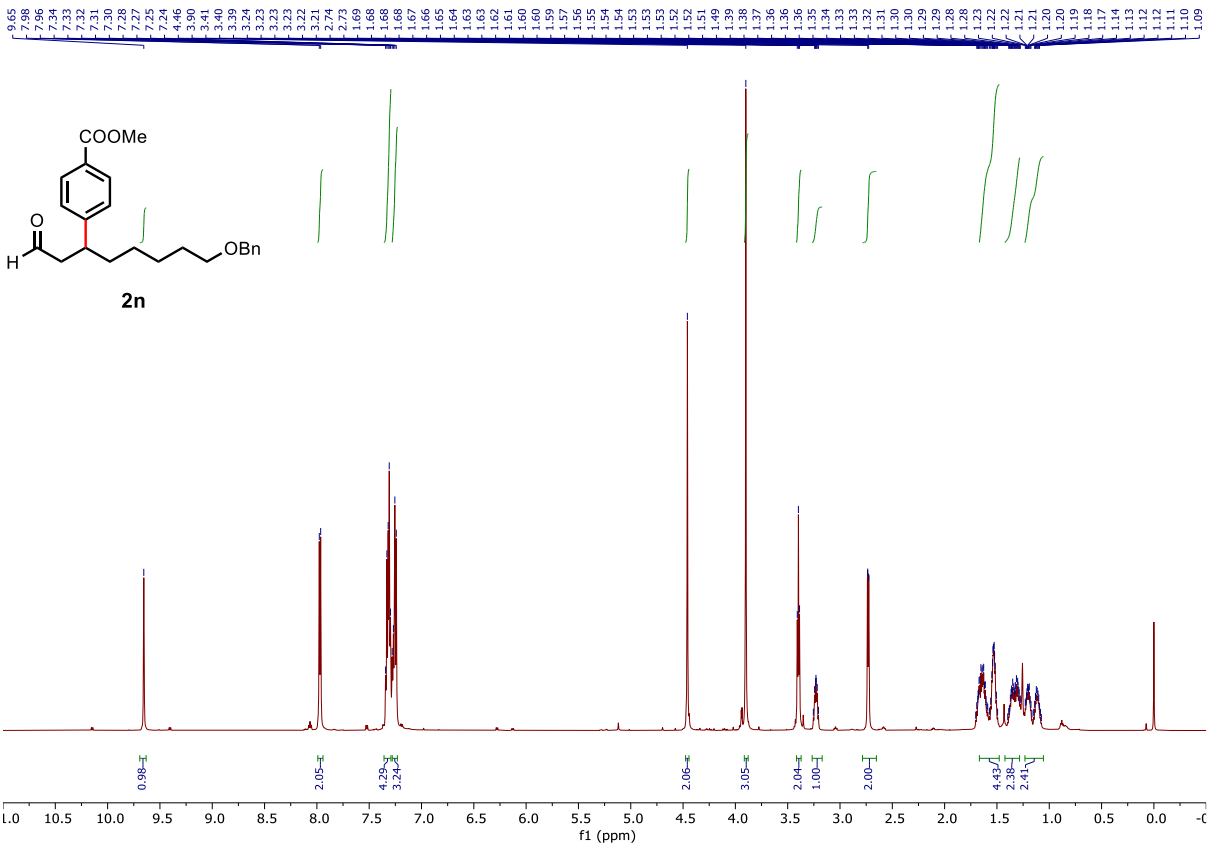

COOMe
O
H
OPh
2k
f1 (ppm)

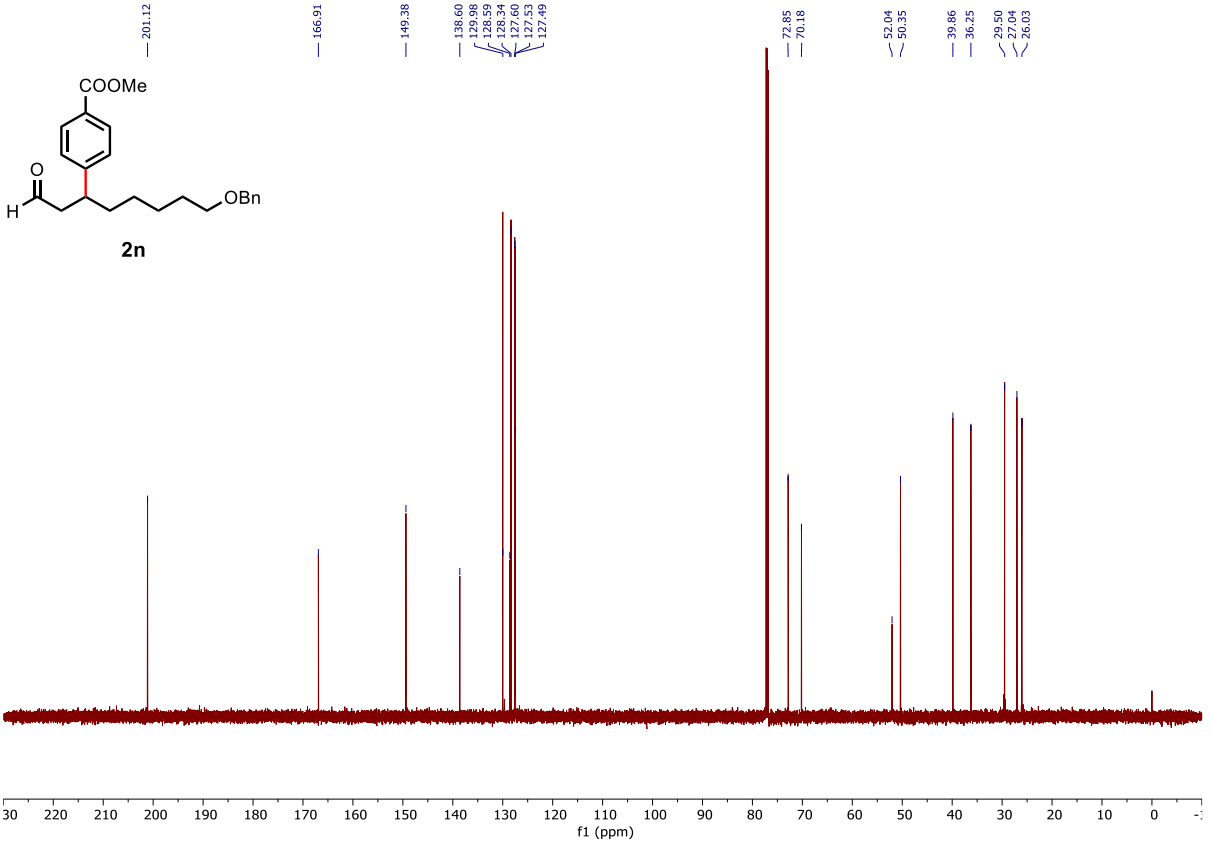

COOMe
O
H
O
n-C3H7
2l
f1 (ppm)

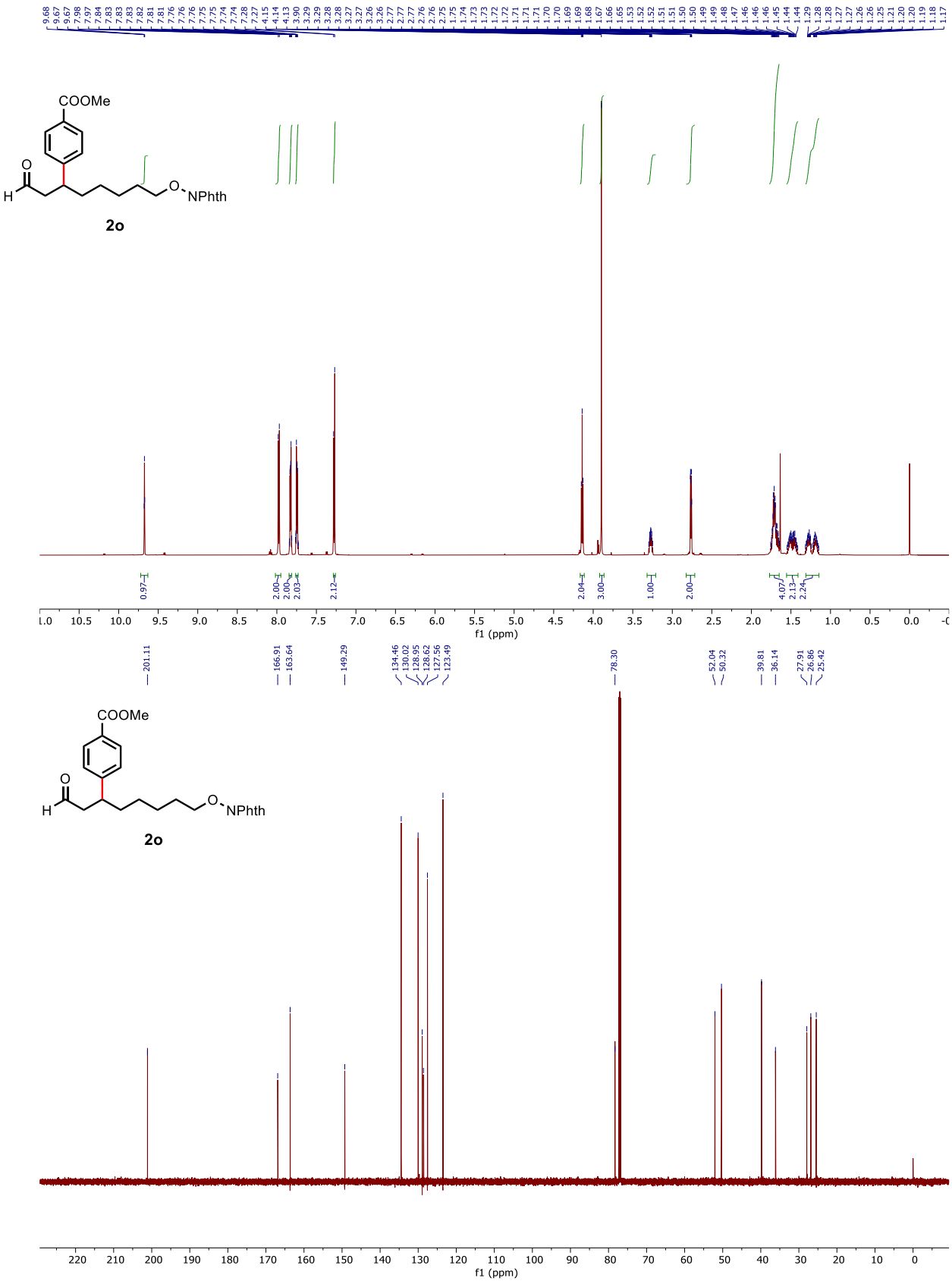

COOMe
O
H
O
n-C3H7
2l
f1 (ppm)

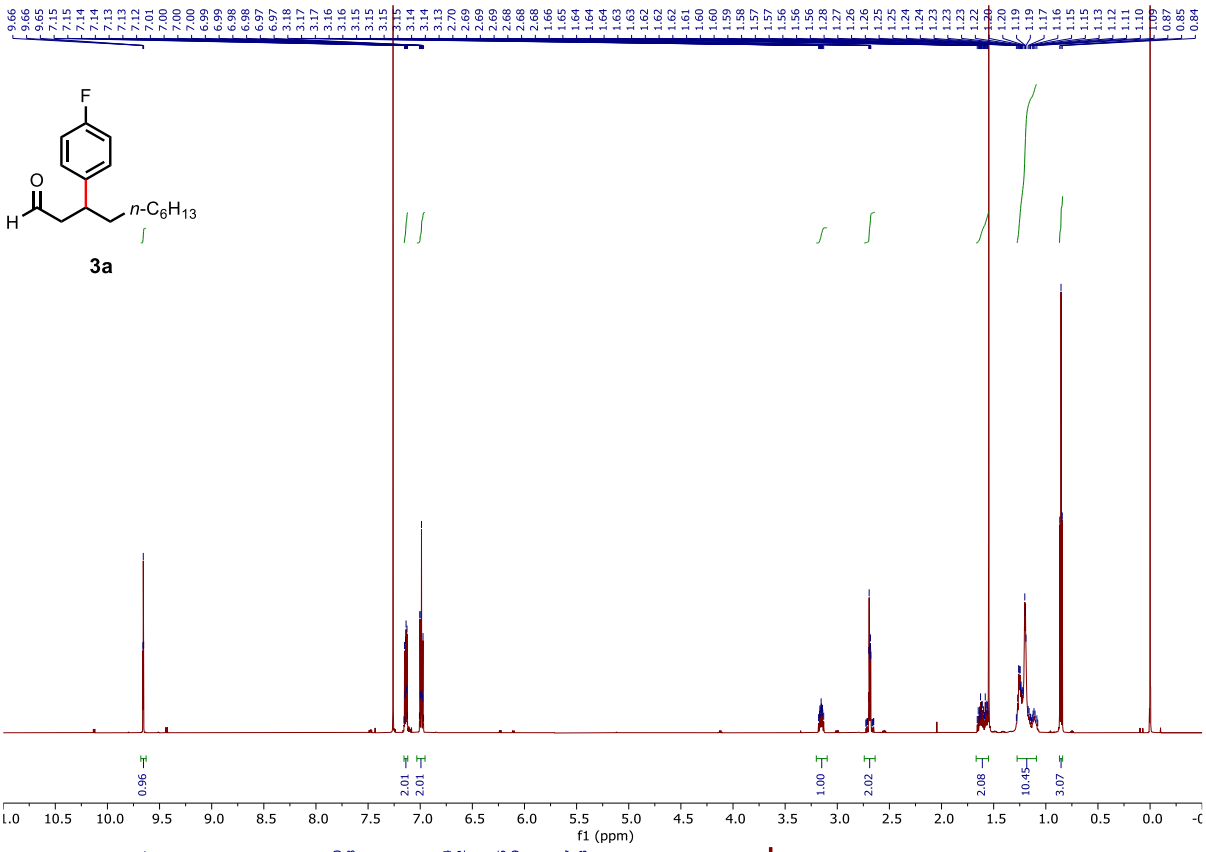

COOMe
O
H
O
Me
Me
2m
f1 (ppm)

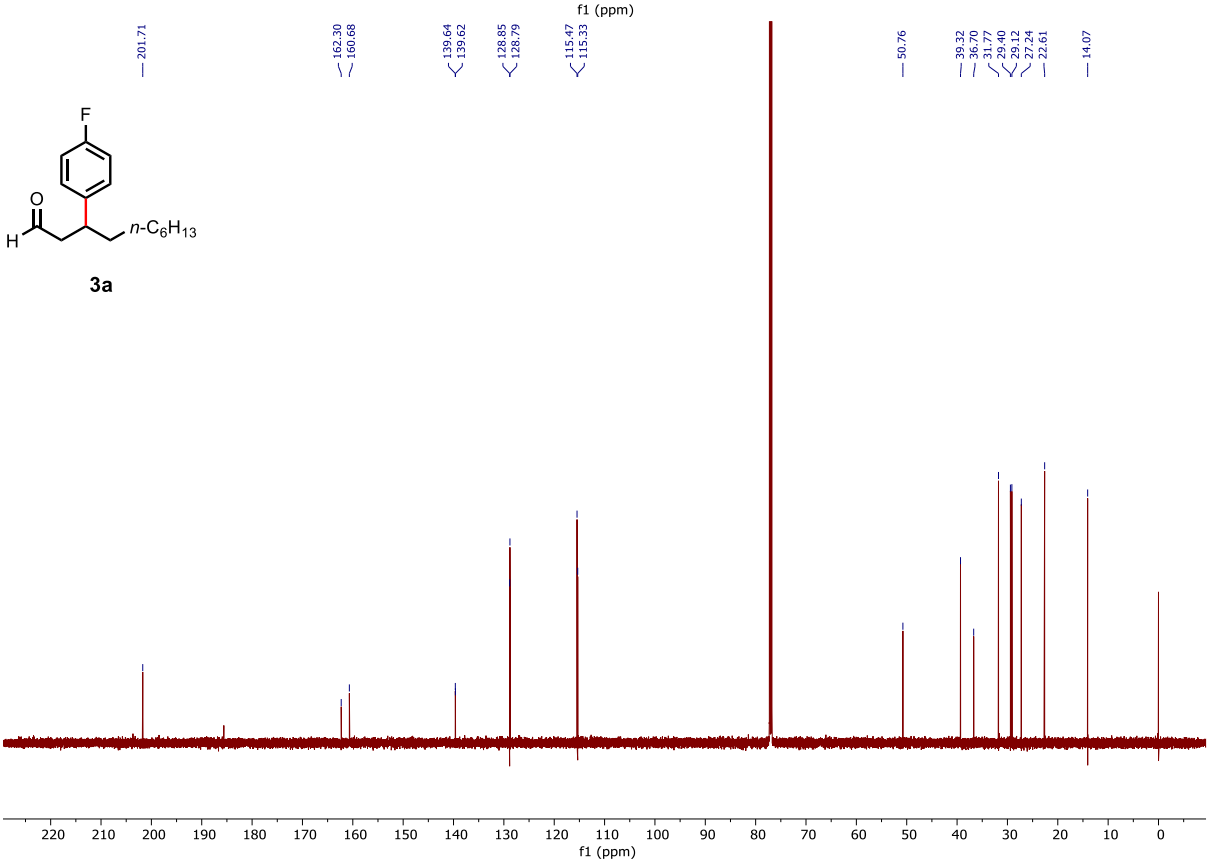

COOMe
O
H
O
Me
Me
2m
f1 (ppm)

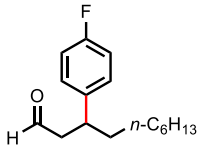

COOMe
O
H
OBn
2n
f1 (ppm)


COOMe
O
H
OBn
2n
f1 (ppm)


COOMe
O
H
O
NPhth
2o
f1 (ppm)
COOMe
O
H
O
NPhth
2o
f1 (ppm)

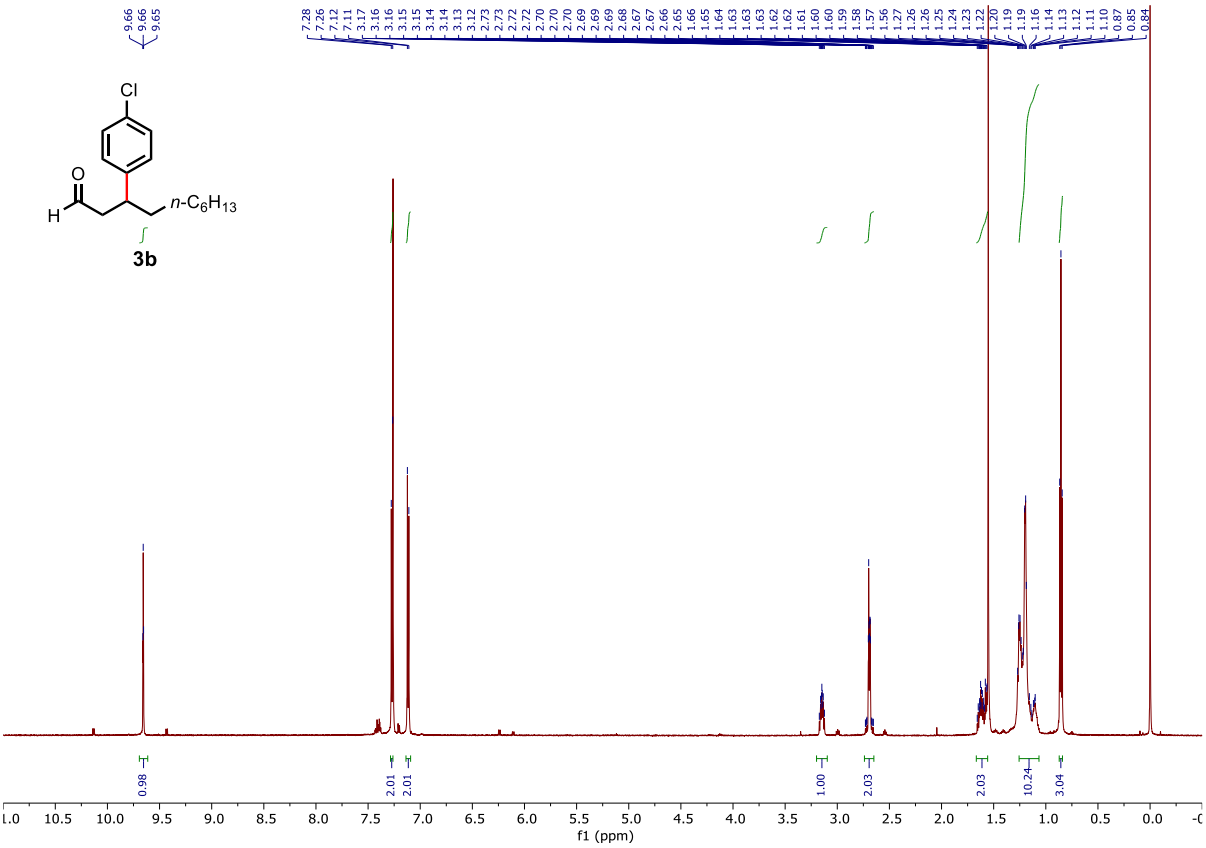

F
O
H
n-C6H13
3a
f1 (ppm)

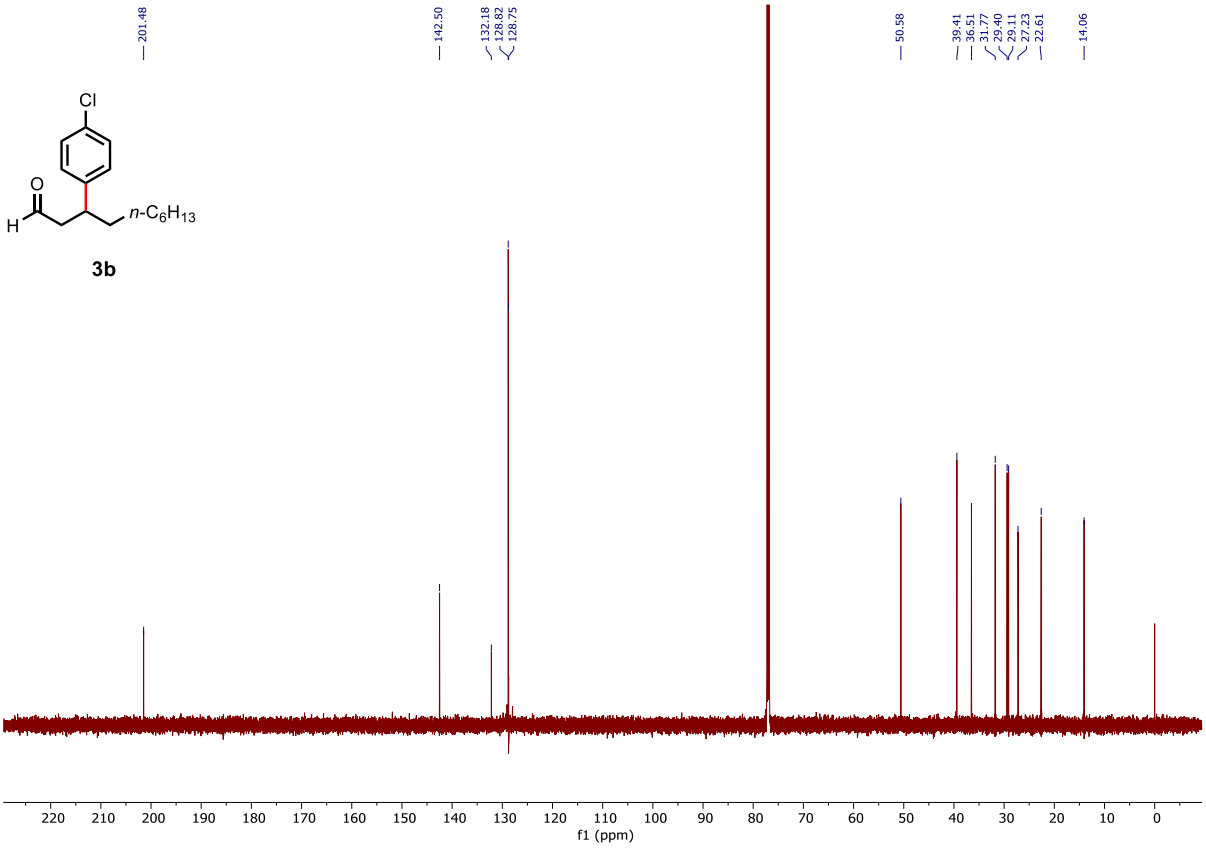

F
O
H
n-C6H13
3a
f1 (ppm)

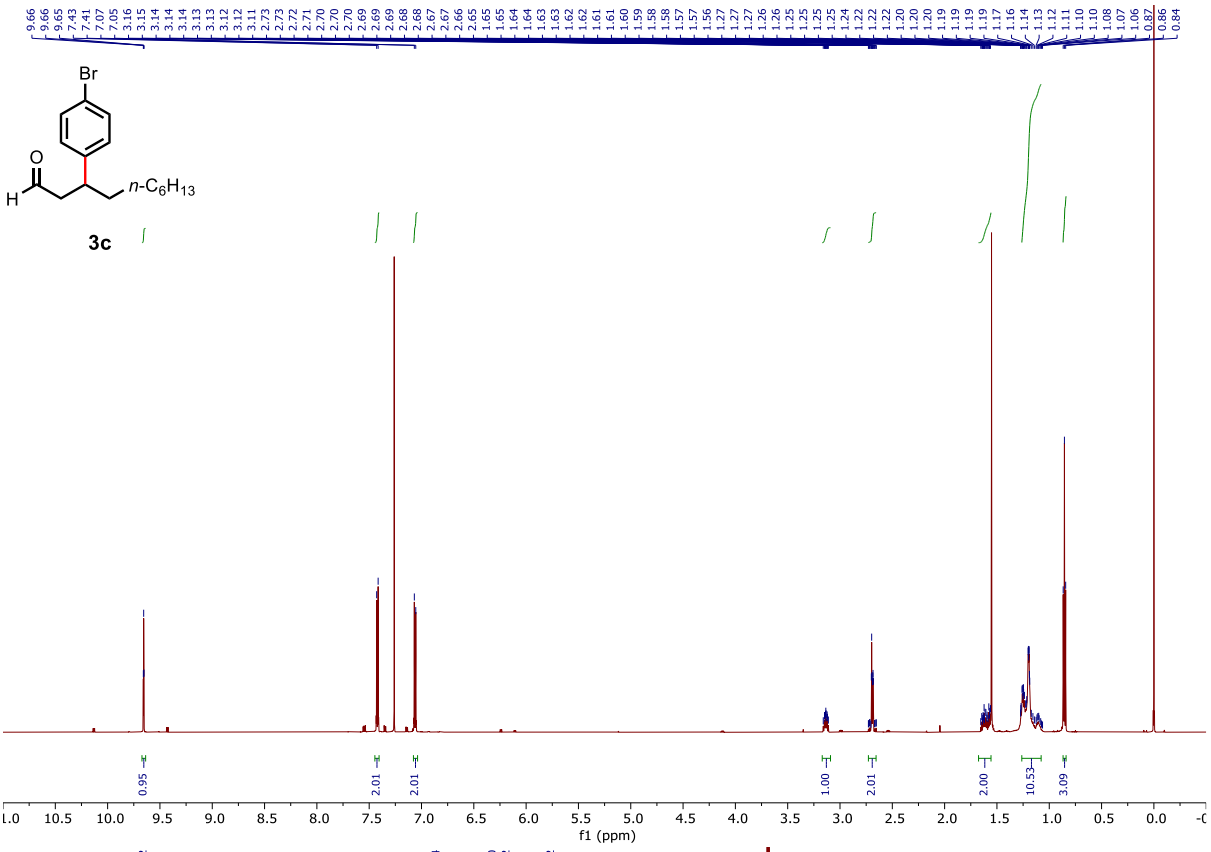

F
O
H
n-C6H13

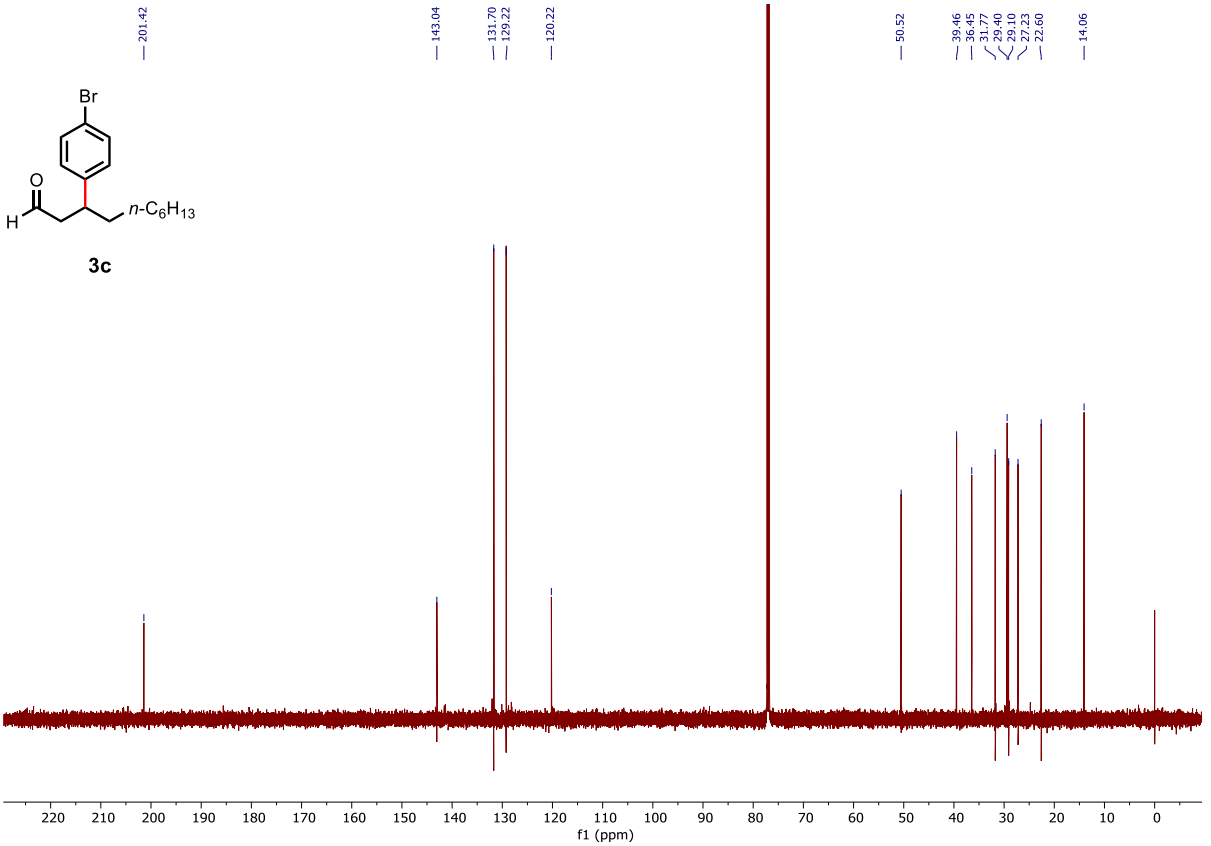
3a

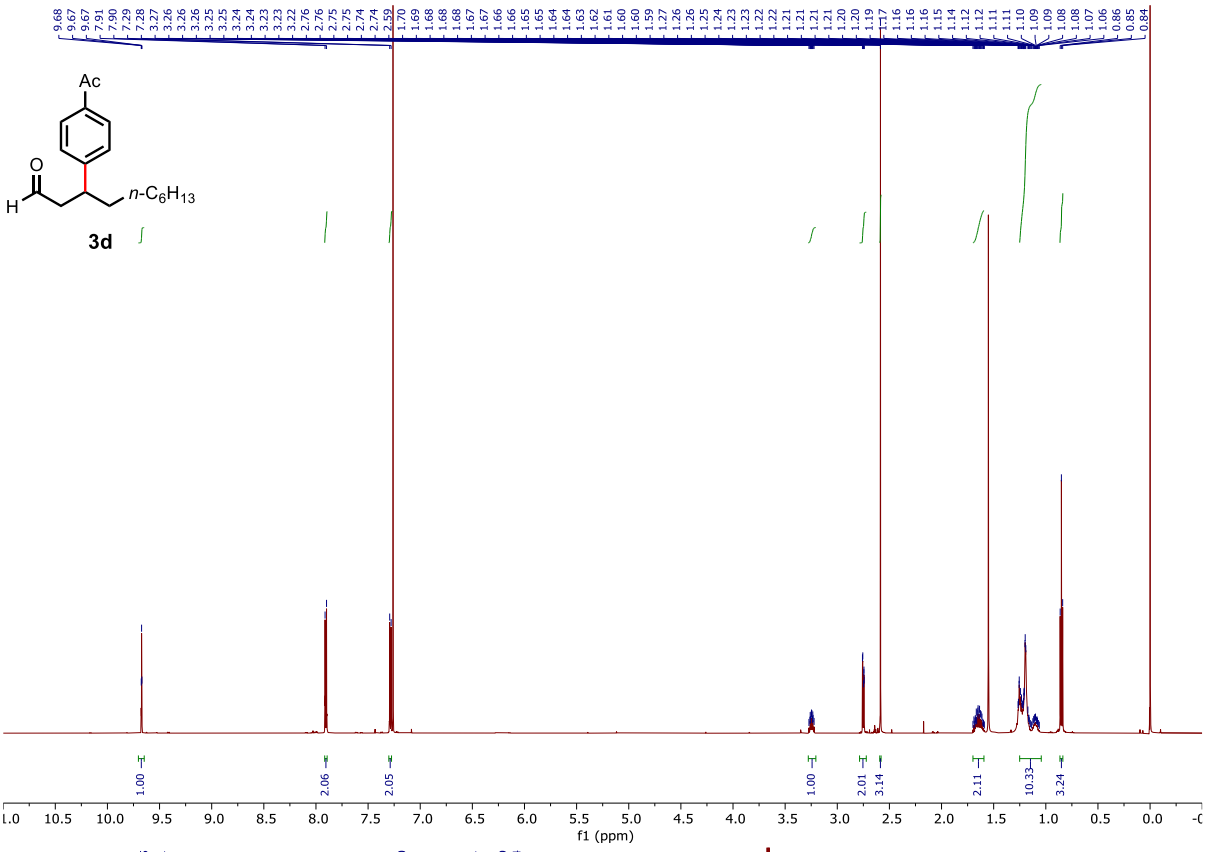
-119.23
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-19
f1 (ppm)

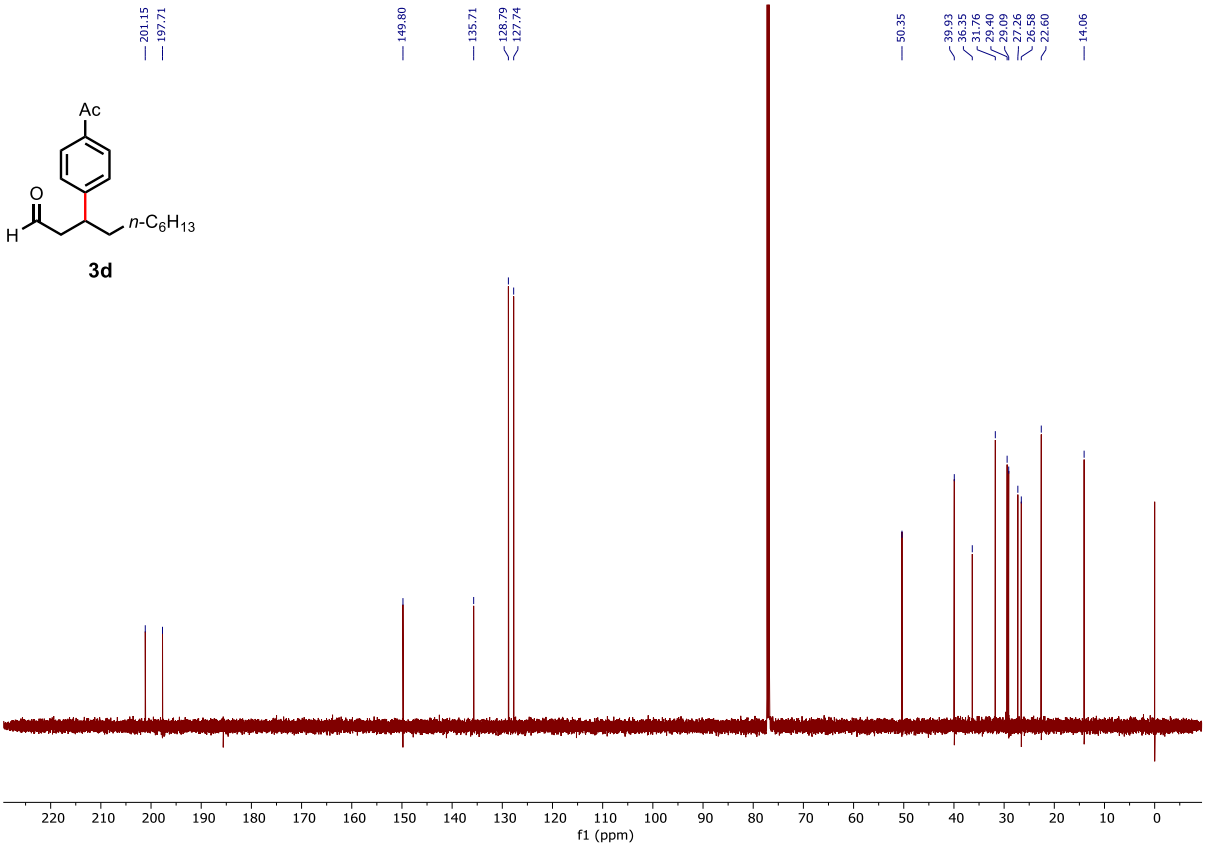

Cl
O
H
n-C6H13
3b
f1 (ppm)

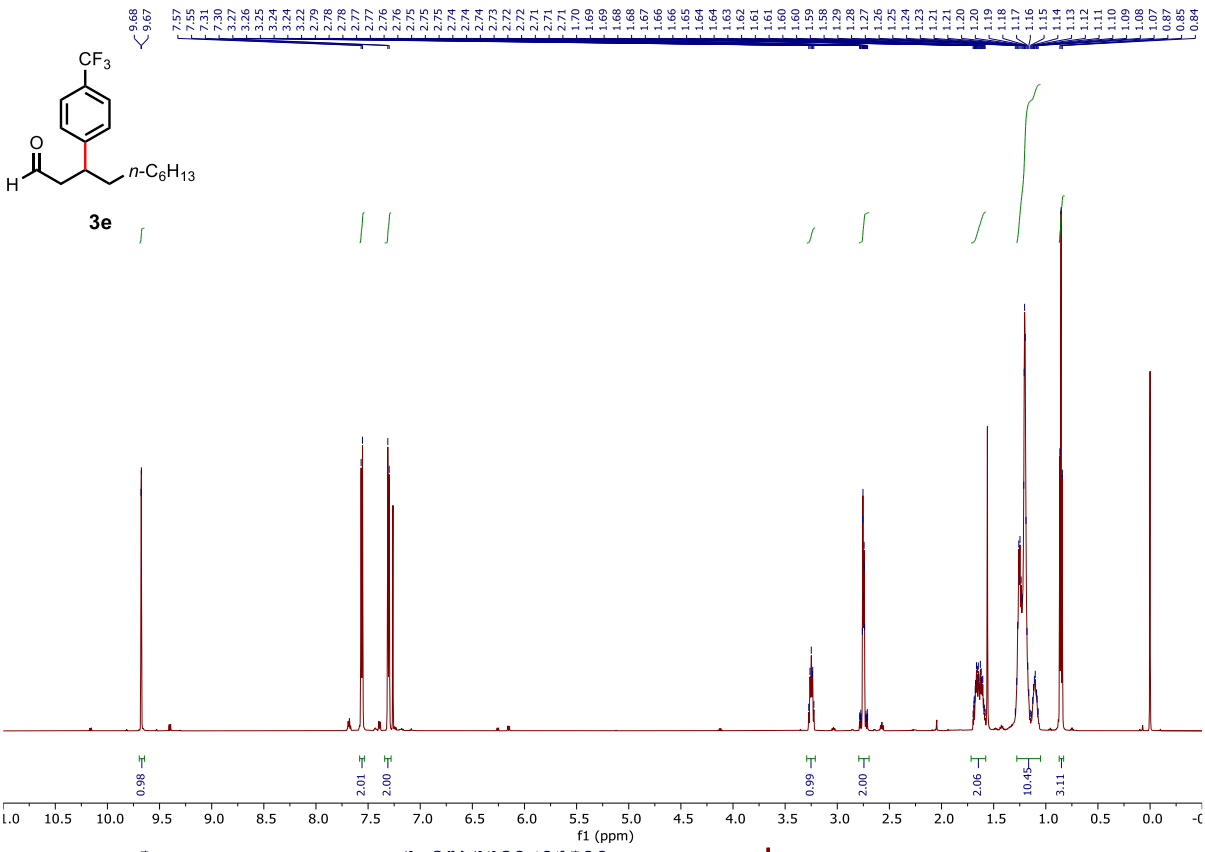

Cl
O
H
n-C6H13
3b
f1 (ppm)

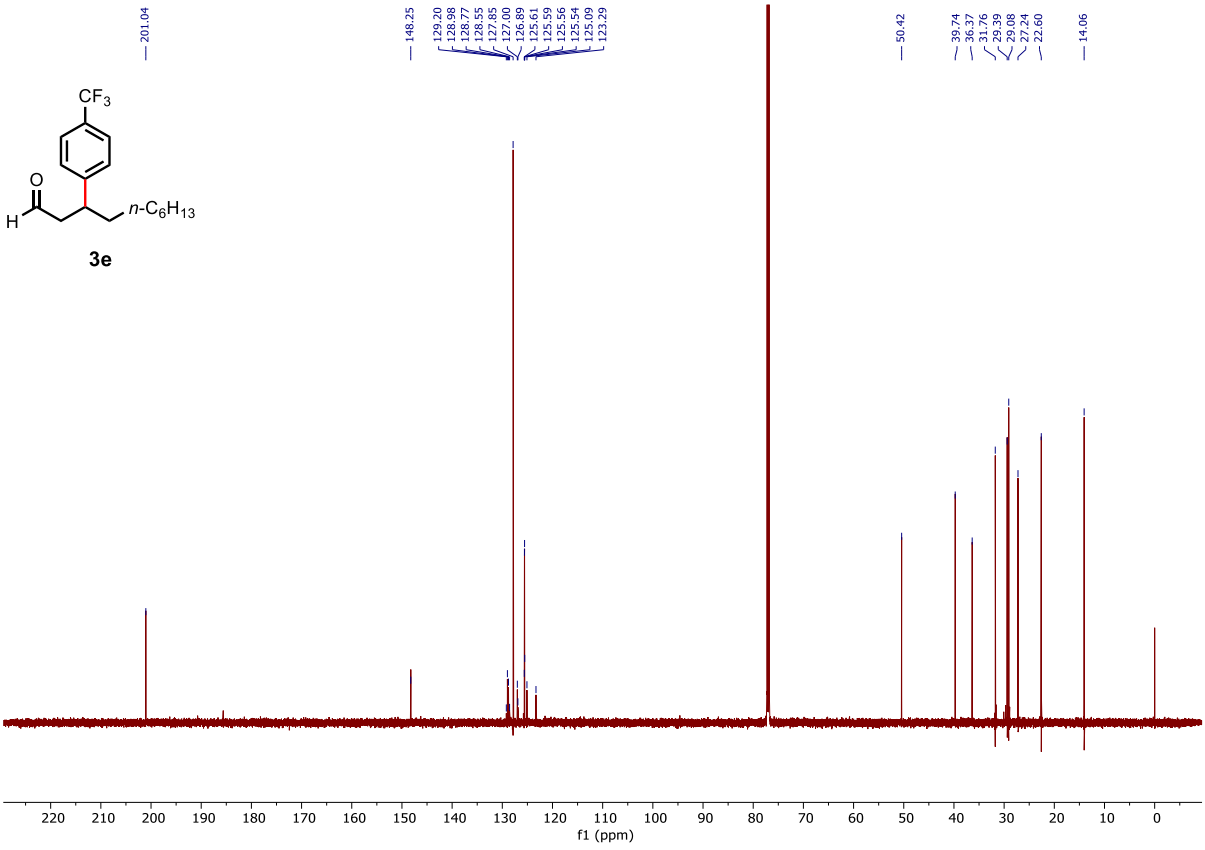

Br
O
H
n-C6H13
3c
f1 (ppm)

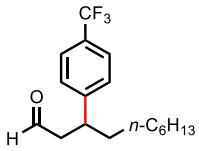

Br
O
H
n-C6H13
3c
f1 (ppm)


Ac
O
H
n-C6H13
3d
f1 (ppm)


Ac
O
H
n-C6H13
3d
f1 (ppm)

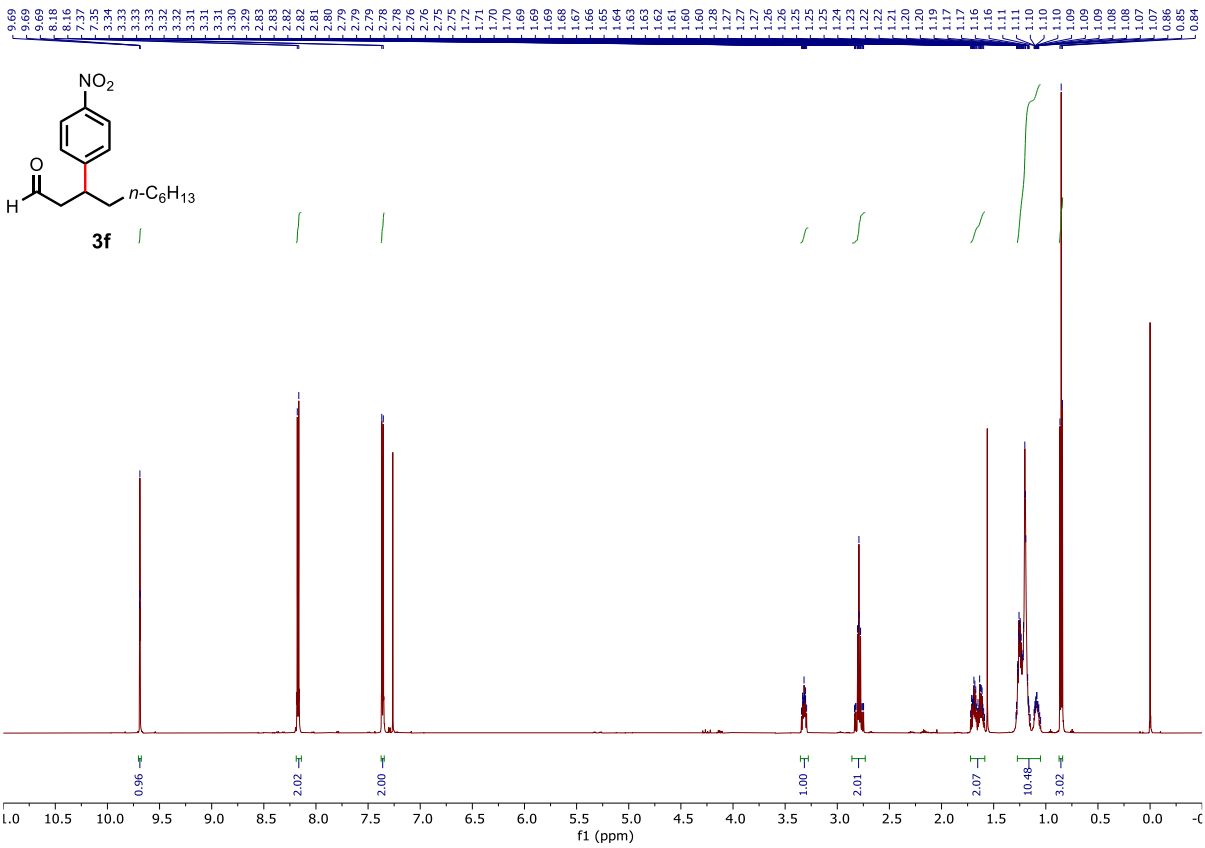

CF3
O
H
n-C6H13
3e
f1 (ppm)

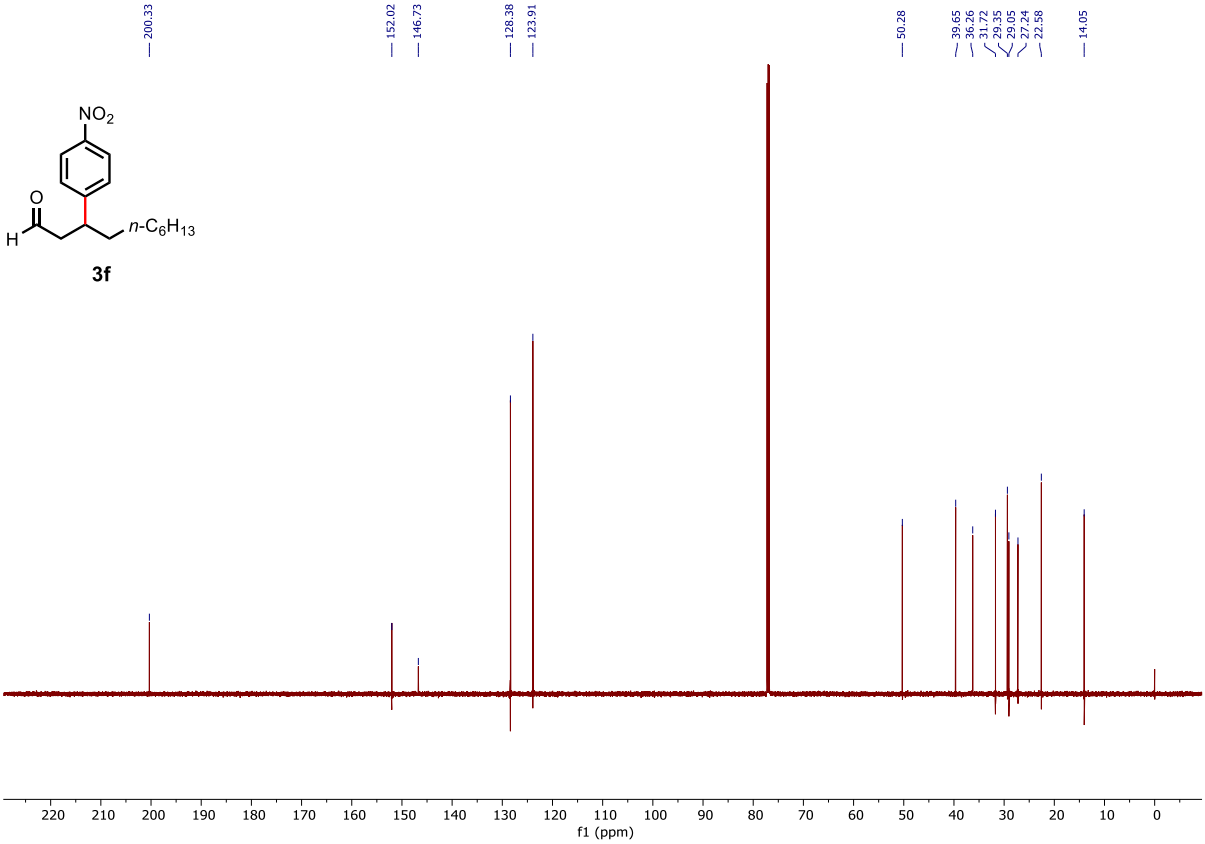

CF3
O
H
n-C6H13
3e
f1 (ppm)

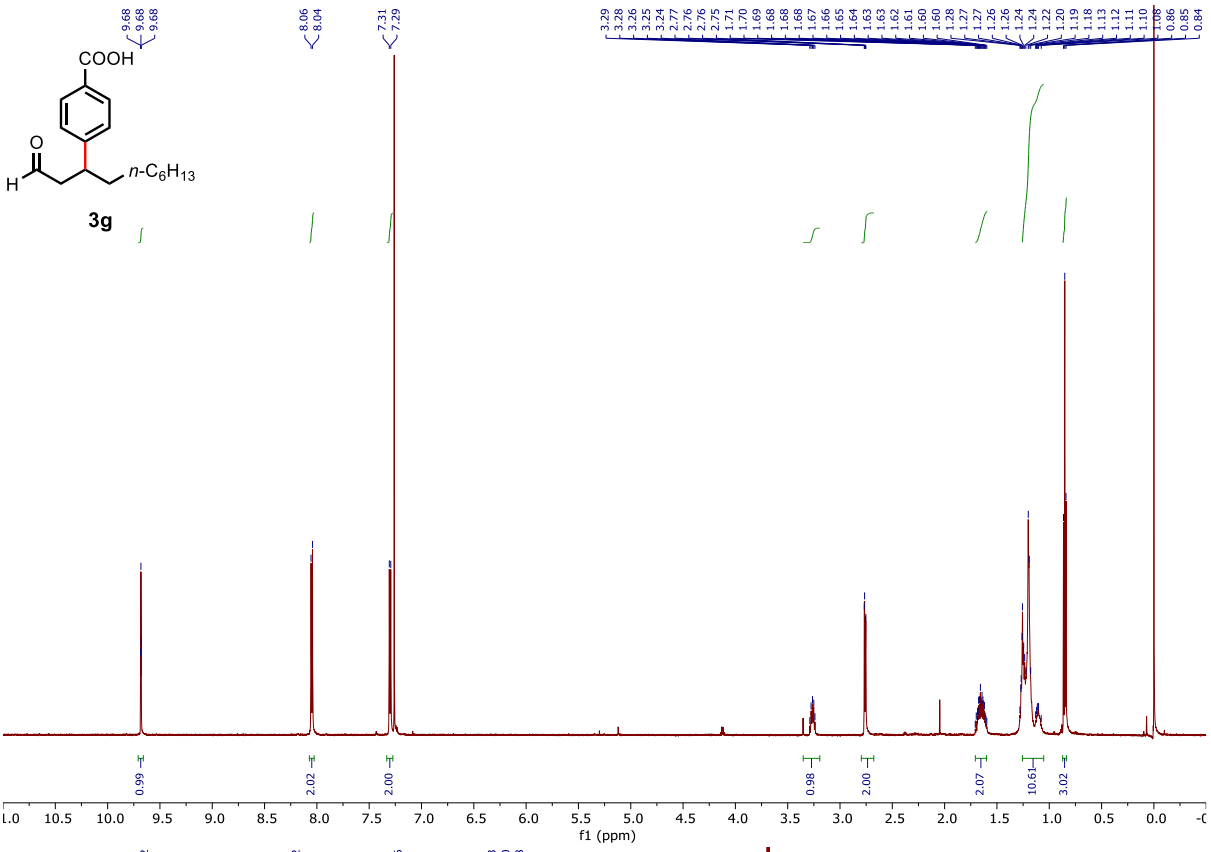

CF3
O
H
n-C6H13

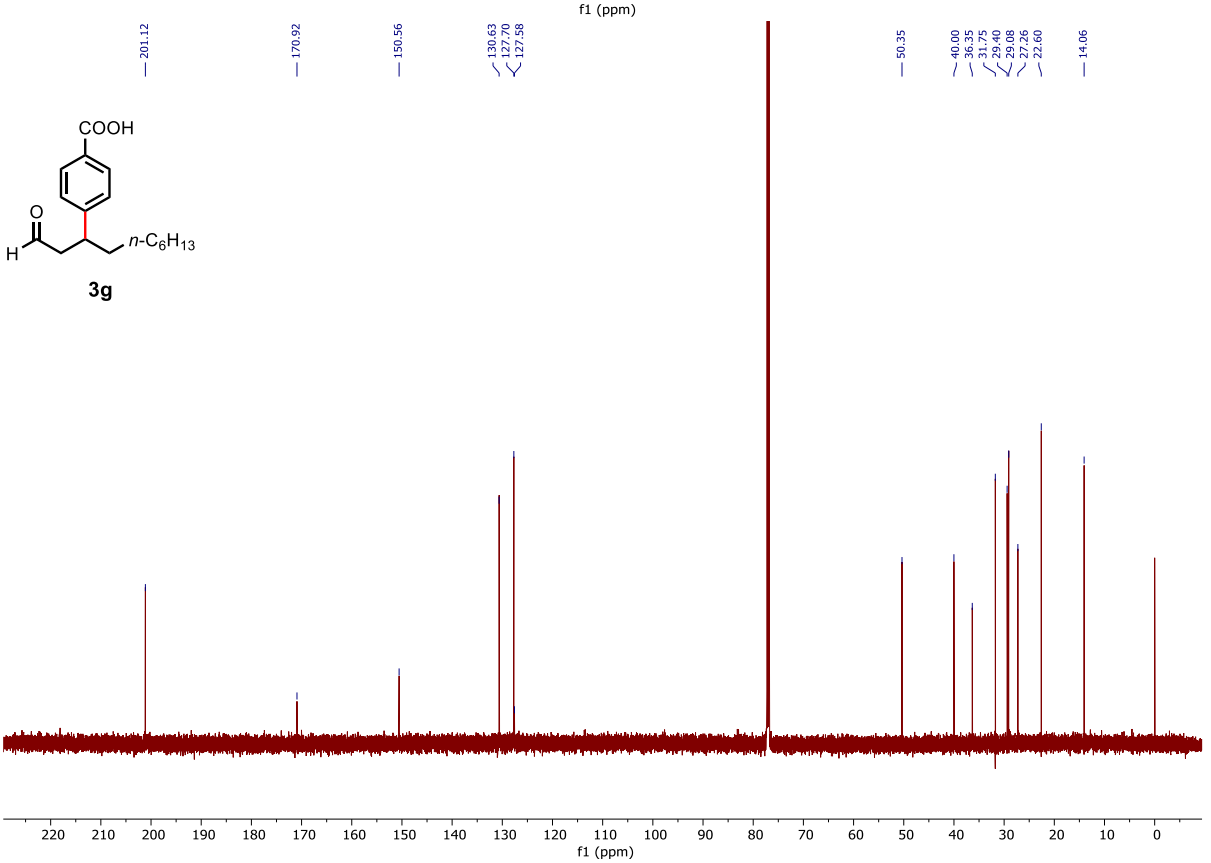
3e

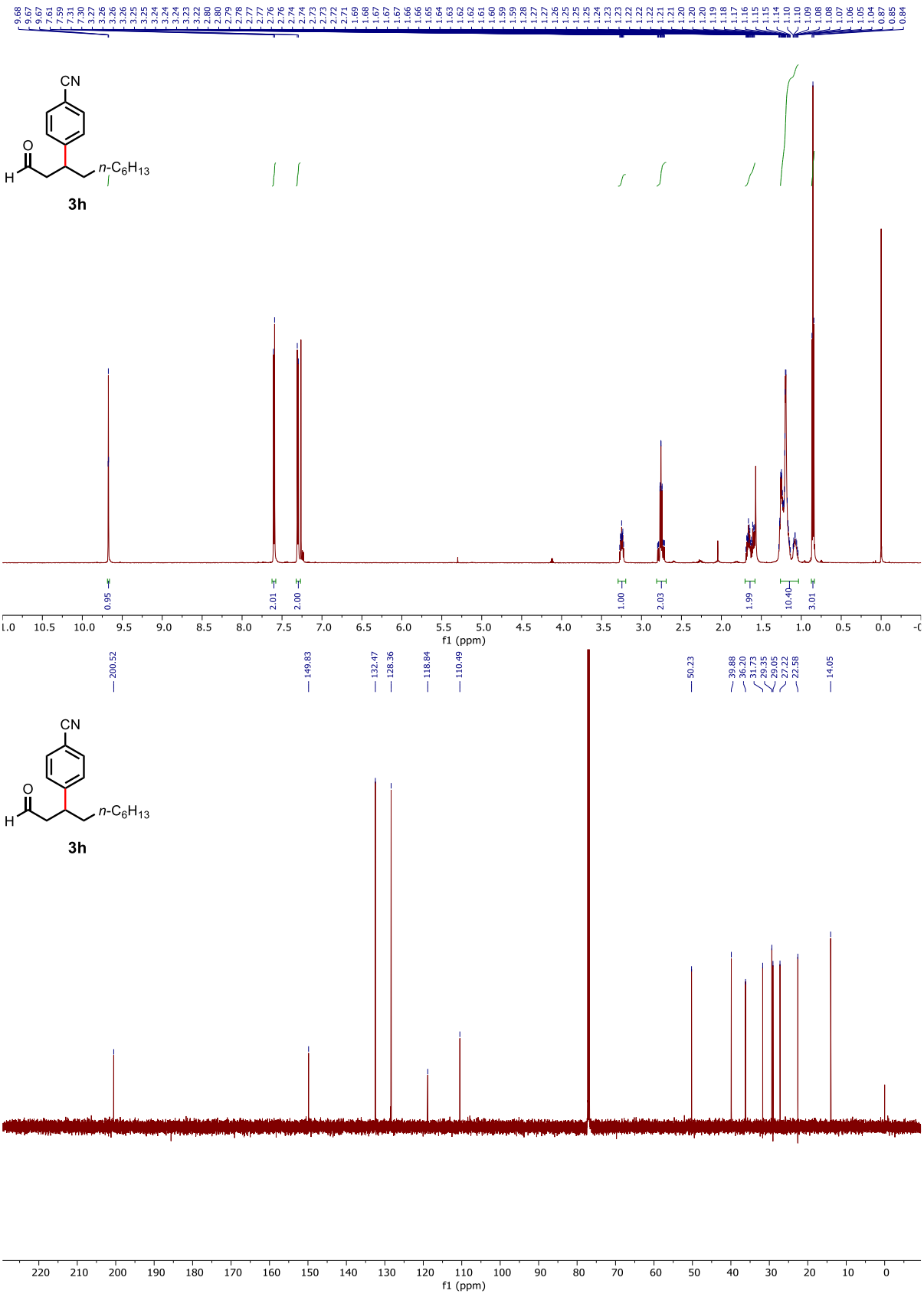
-65.07
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)

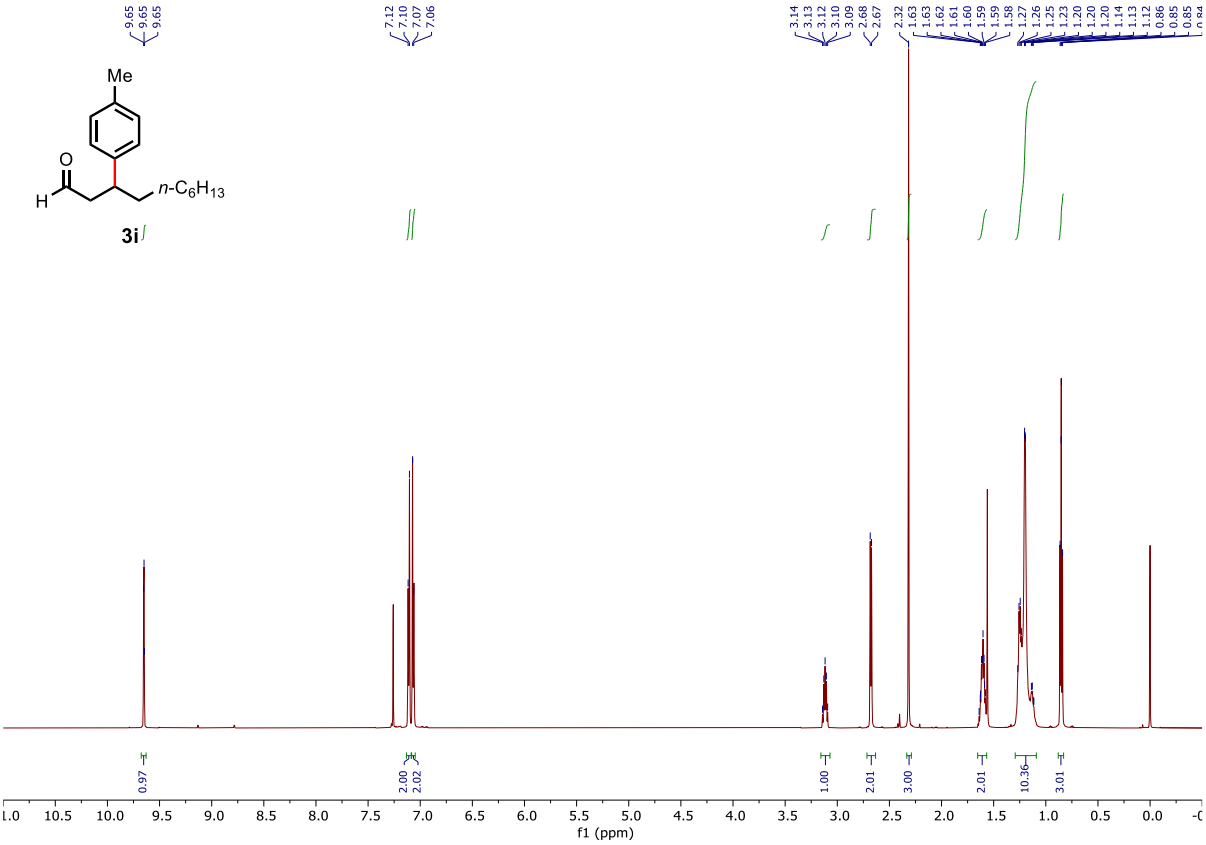

NO2
O
H
n-C6H13
3f
0.96
2.02
2.00
1.00
2.01
2.07
10.48
3.02
f1 (ppm)

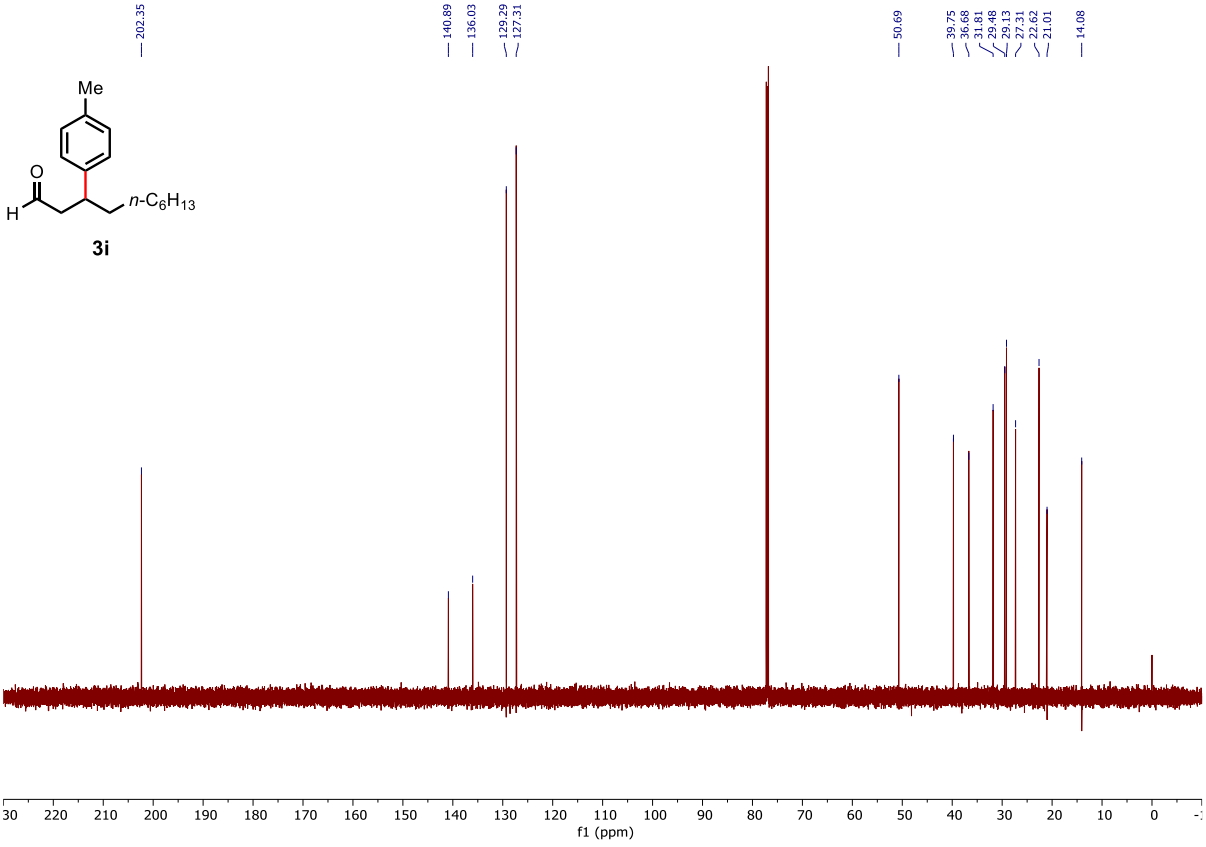

200.33
152.02
146.73
128.38
123.91
50.28
39.65
36.26
31.72
29.35
29.05
27.24
22.58
14.05
NO2
O
H
n-C6H13
3f
f1 (ppm)

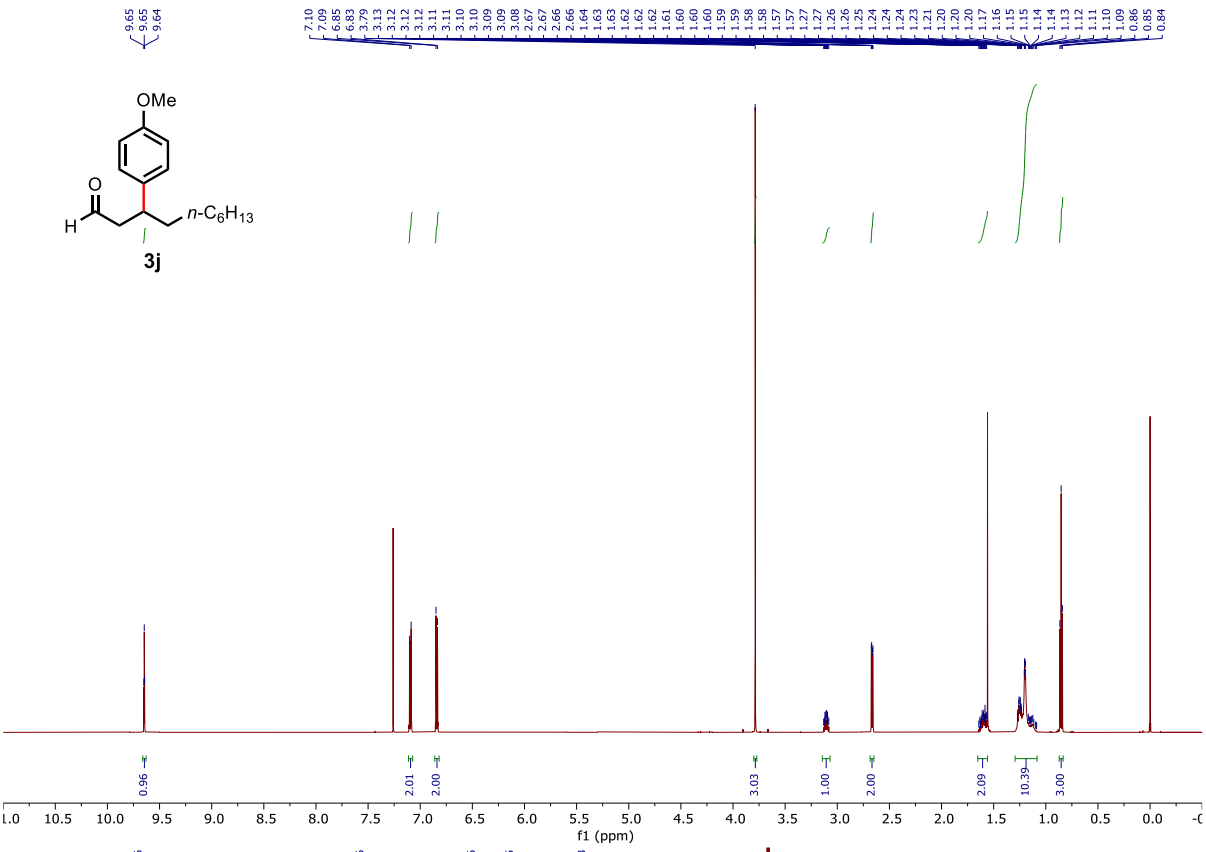

COOH
O
H
n-C6H13
3g
f1 (ppm)

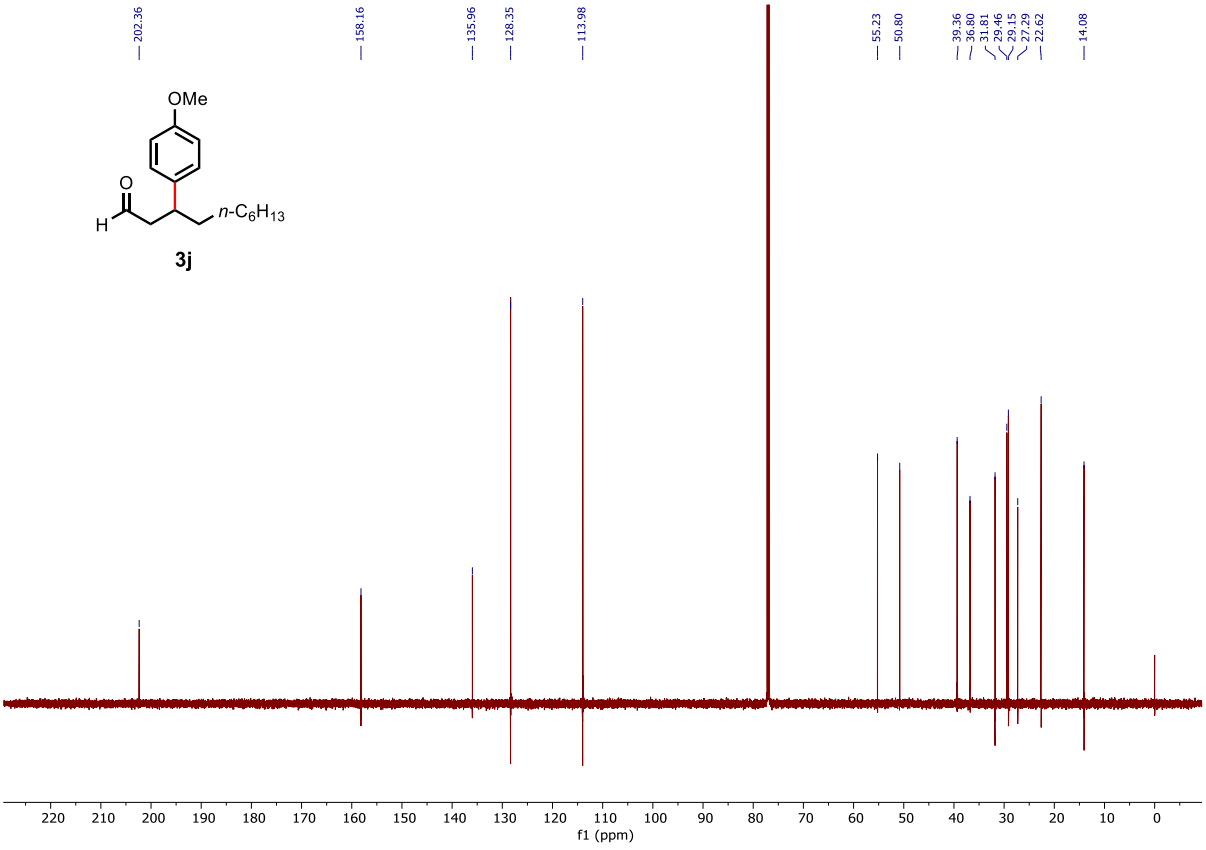

COOH
O
H
n-C6H13
3g
f1 (ppm)

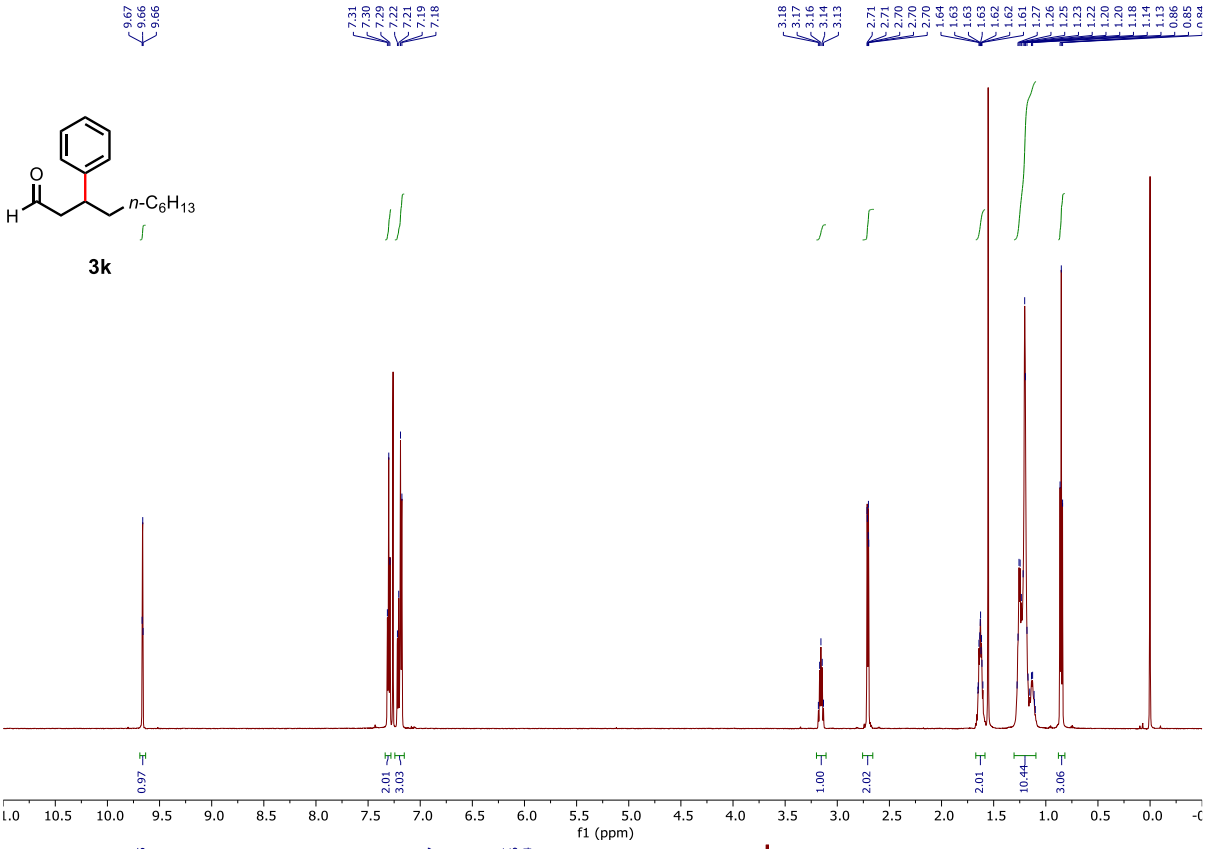

CN
O
H
n-C6H13
3h
f1 (ppm)
CN
O
H
n-C6H13
3h
f1 (ppm)

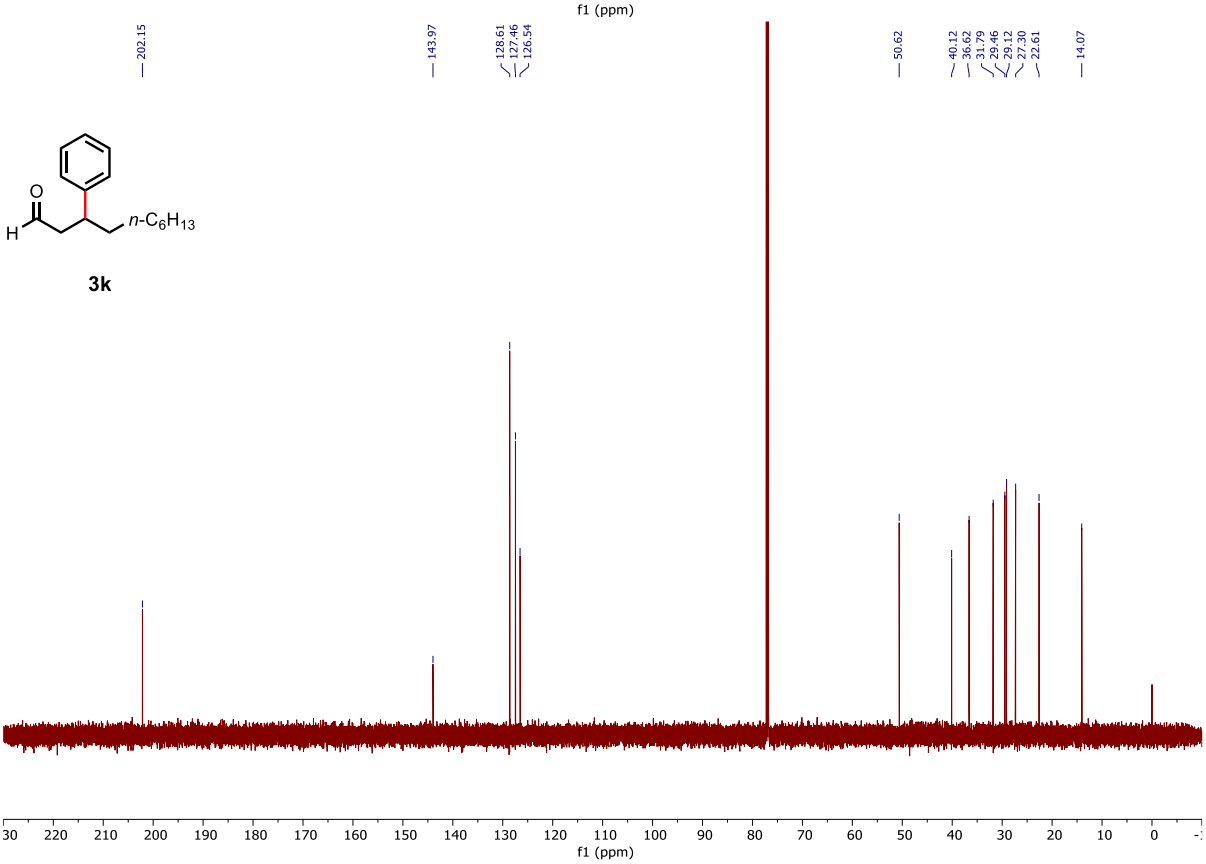

Me
O
H
n-C6H13
3i
f1 (ppm)

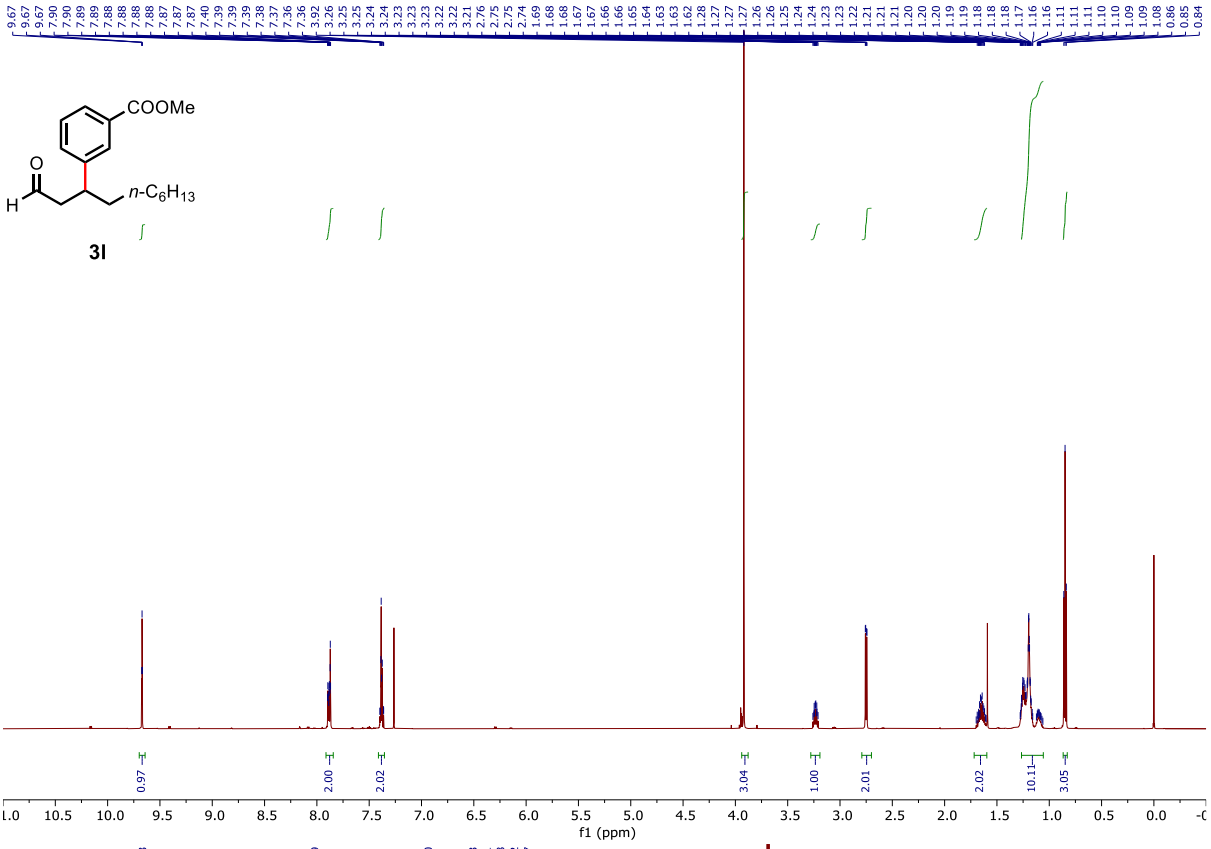

Me
O
H
n-C6H13
3i
f1 (ppm)

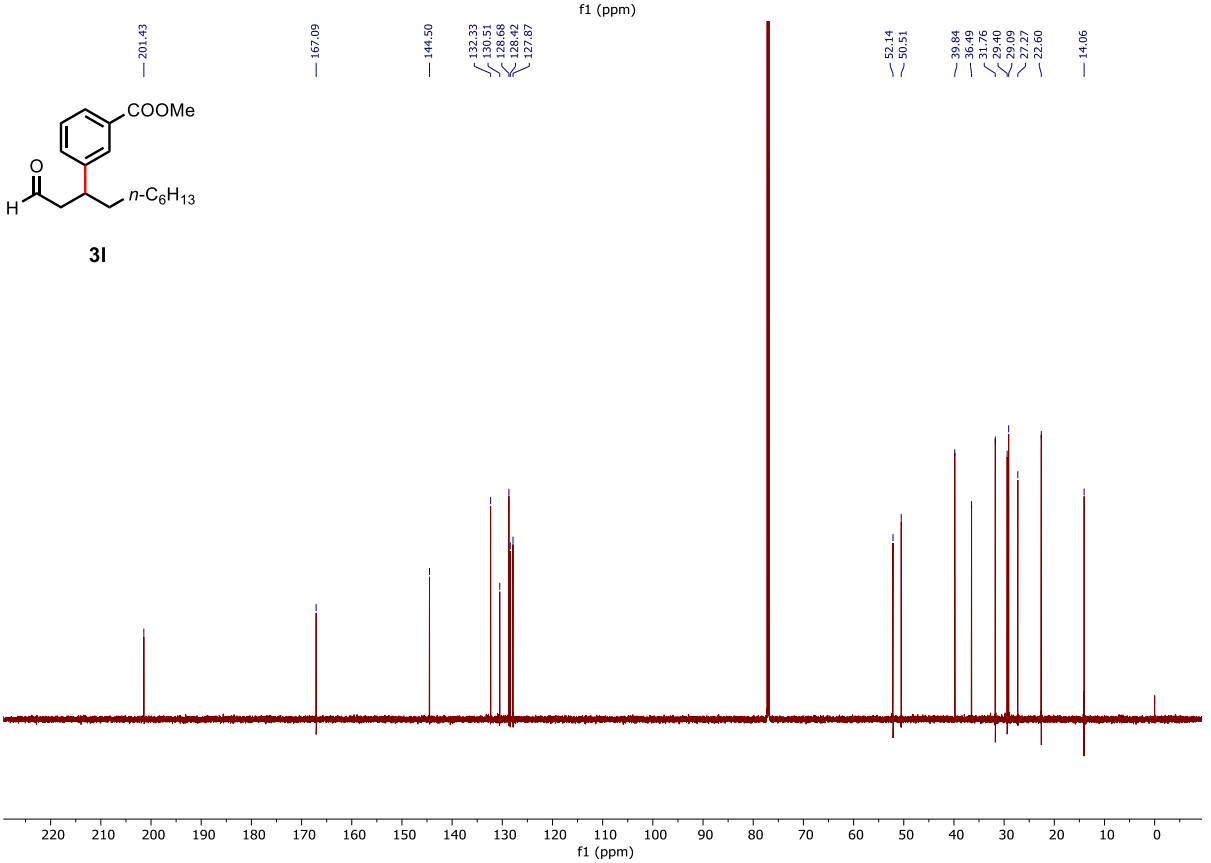

OMe
O
H
n-C6H13
3j
f1 (ppm)

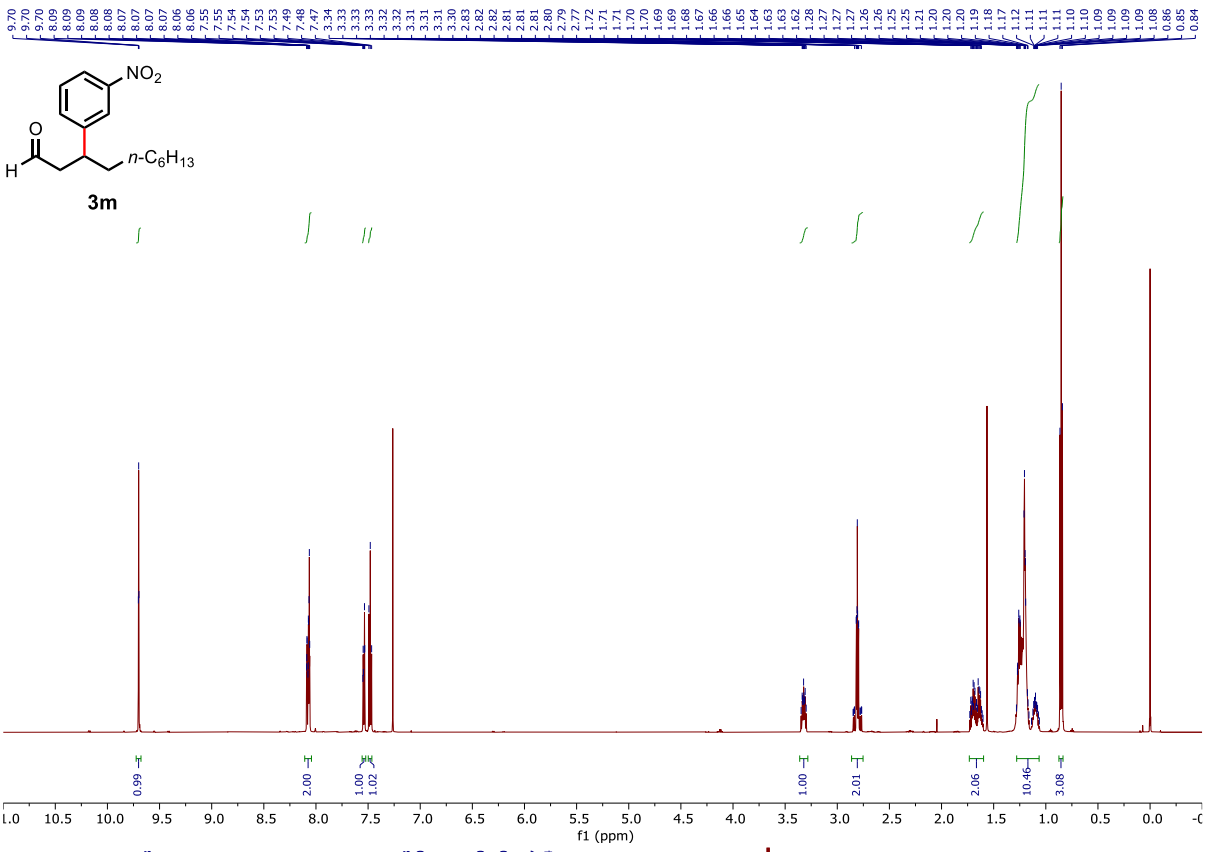

OMe
O
H
n-C6H13
3j
f1 (ppm)

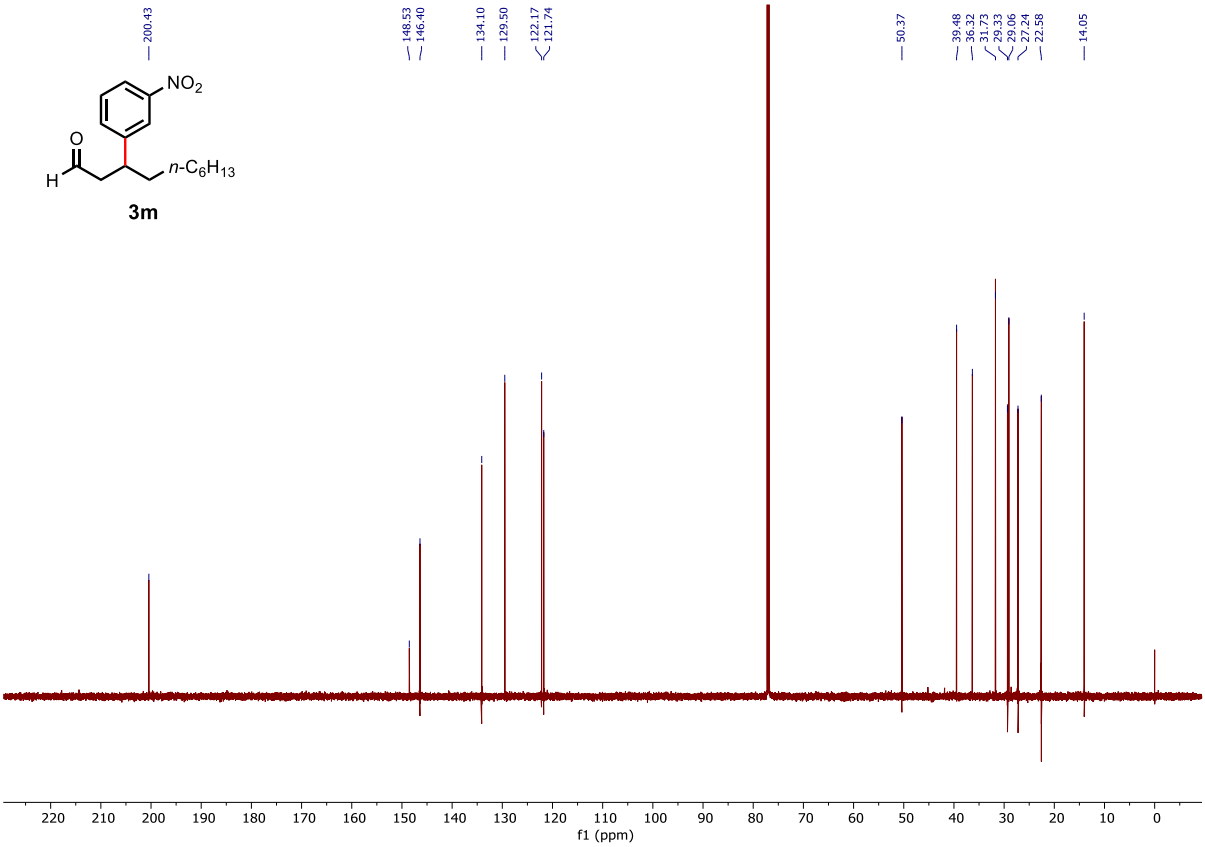

9.67
9.66
9.66
7.31
7.30
7.29
7.22
7.21
7.19
7.18
3.18
3.17
3.16
3.14
3.13
2.71
2.71
2.70
2.70
2.70
1.64
1.63
1.63
1.63
1.62
1.62
1.61
1.27
1.26
1.25
1.23
1.22
1.20
1.20
1.18
1.14
1.13
0.86
0.85
O
H
n-C6H13
3k
0.97
2.01
3.03
1.00
2.02
2.01
10.44
3.06
f1 (ppm)

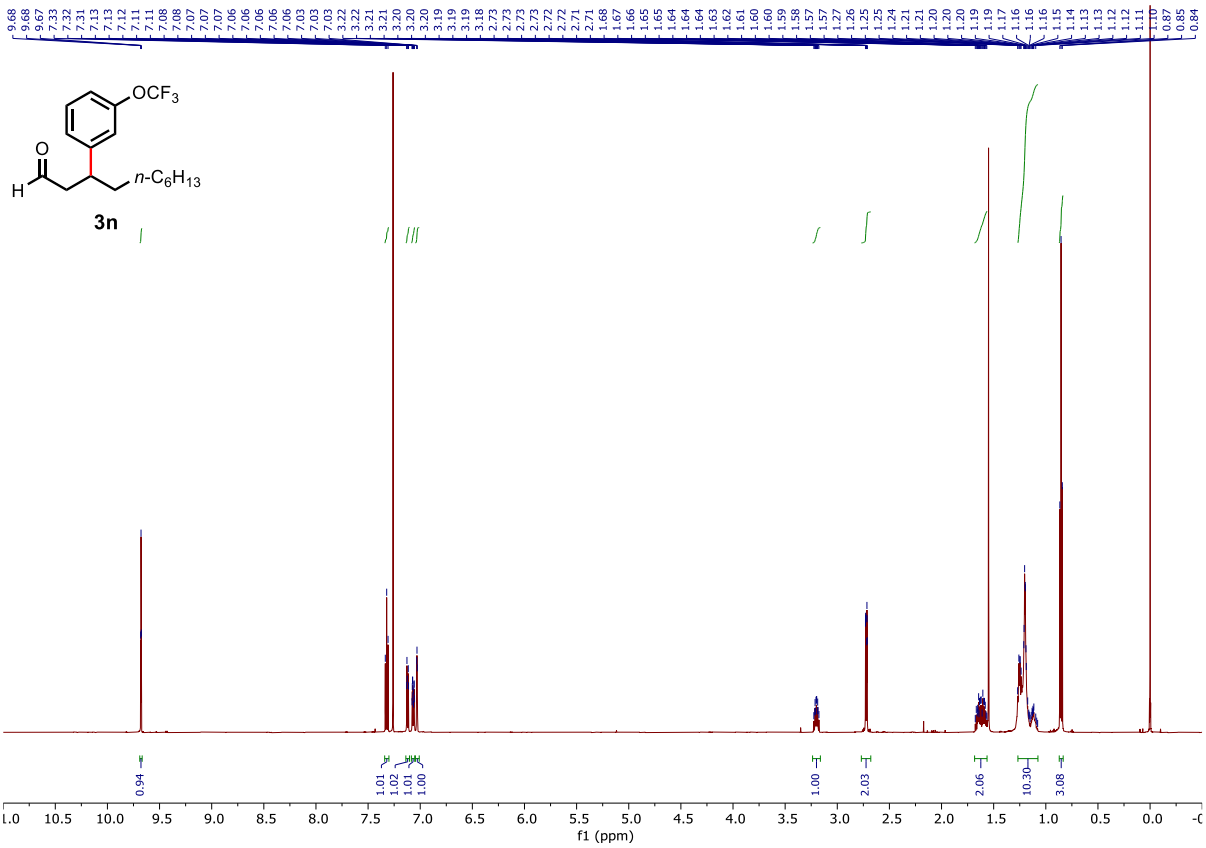

202.15
143.97
128.61
127.46
126.54
50.62
40.12
36.62
31.79
29.46
29.12
27.30
22.61
14.07
O
H
n-C6H13
3k
f1 (ppm)

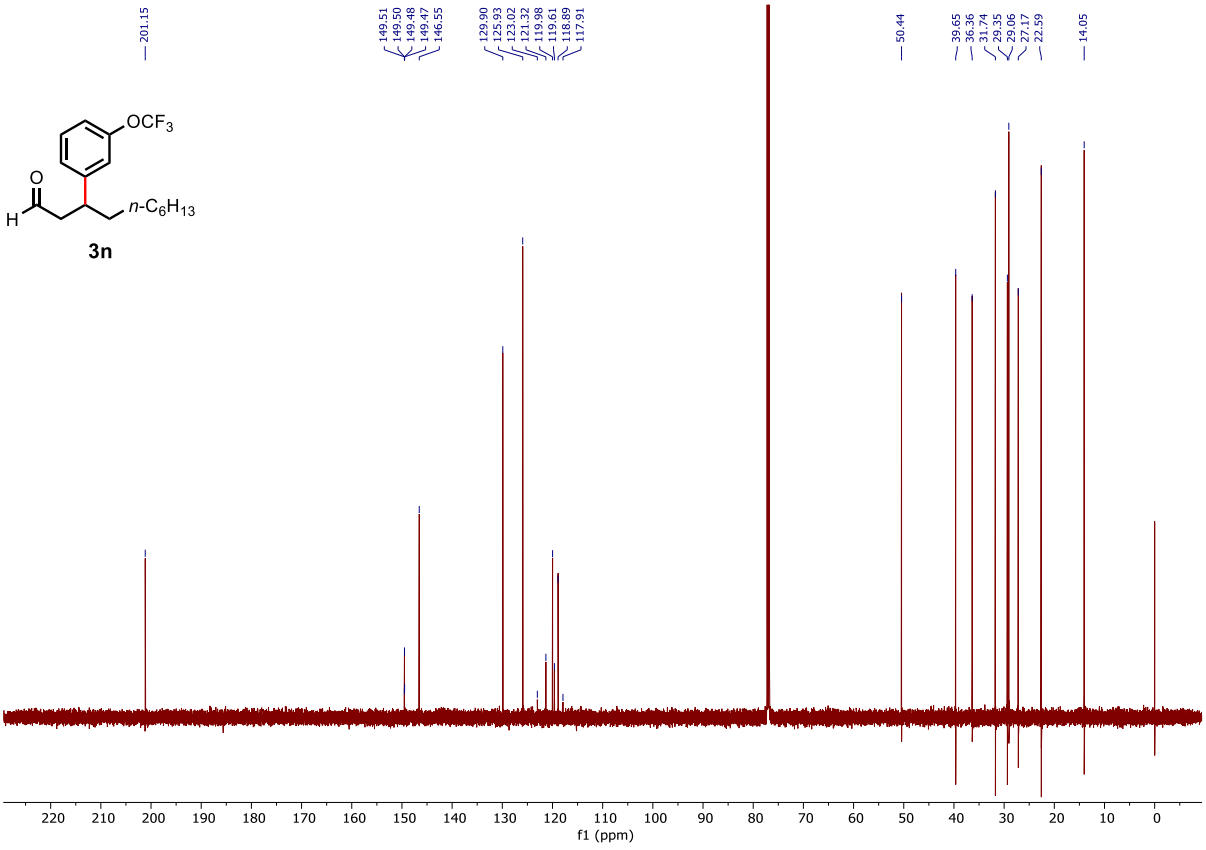

COOMe
O
H
n-C6H13
3l
f1 (ppm)

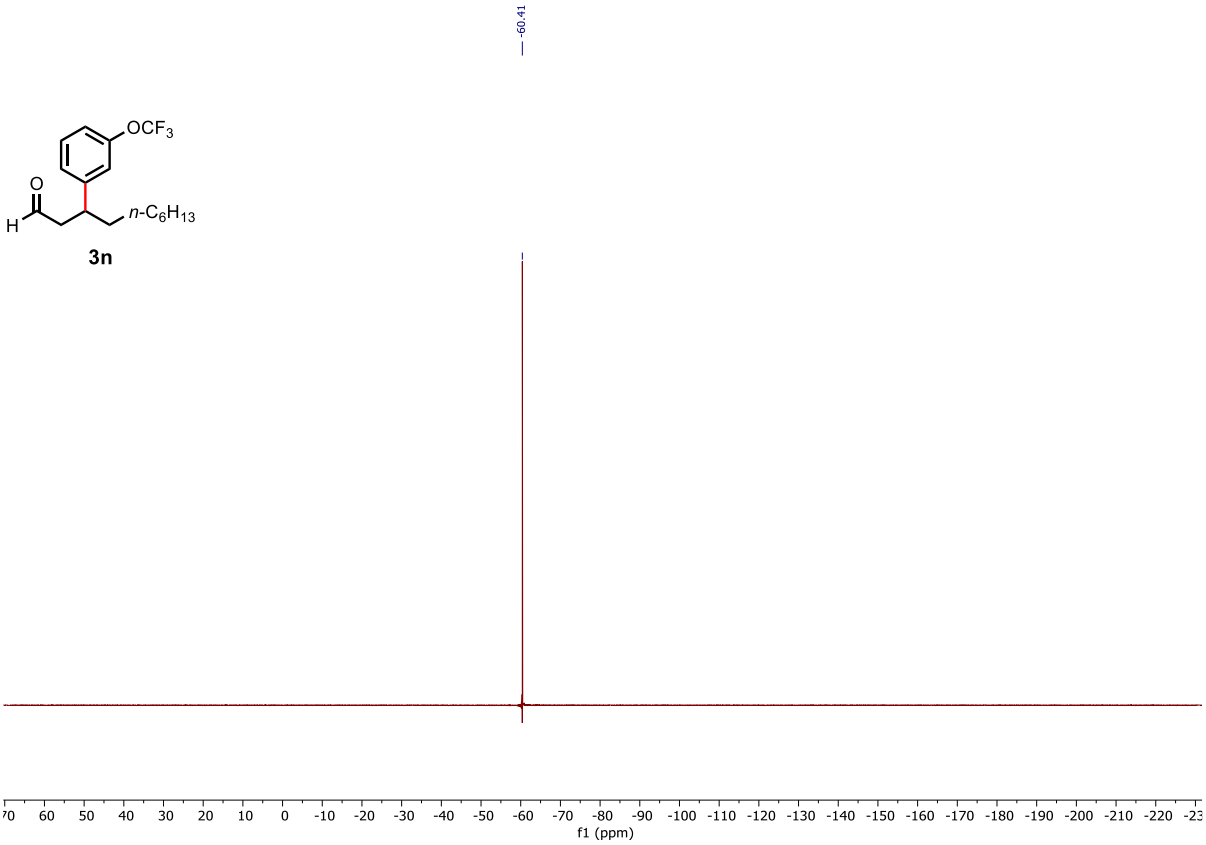

COOMe
O
H
n-C6H13
3l
f1 (ppm)

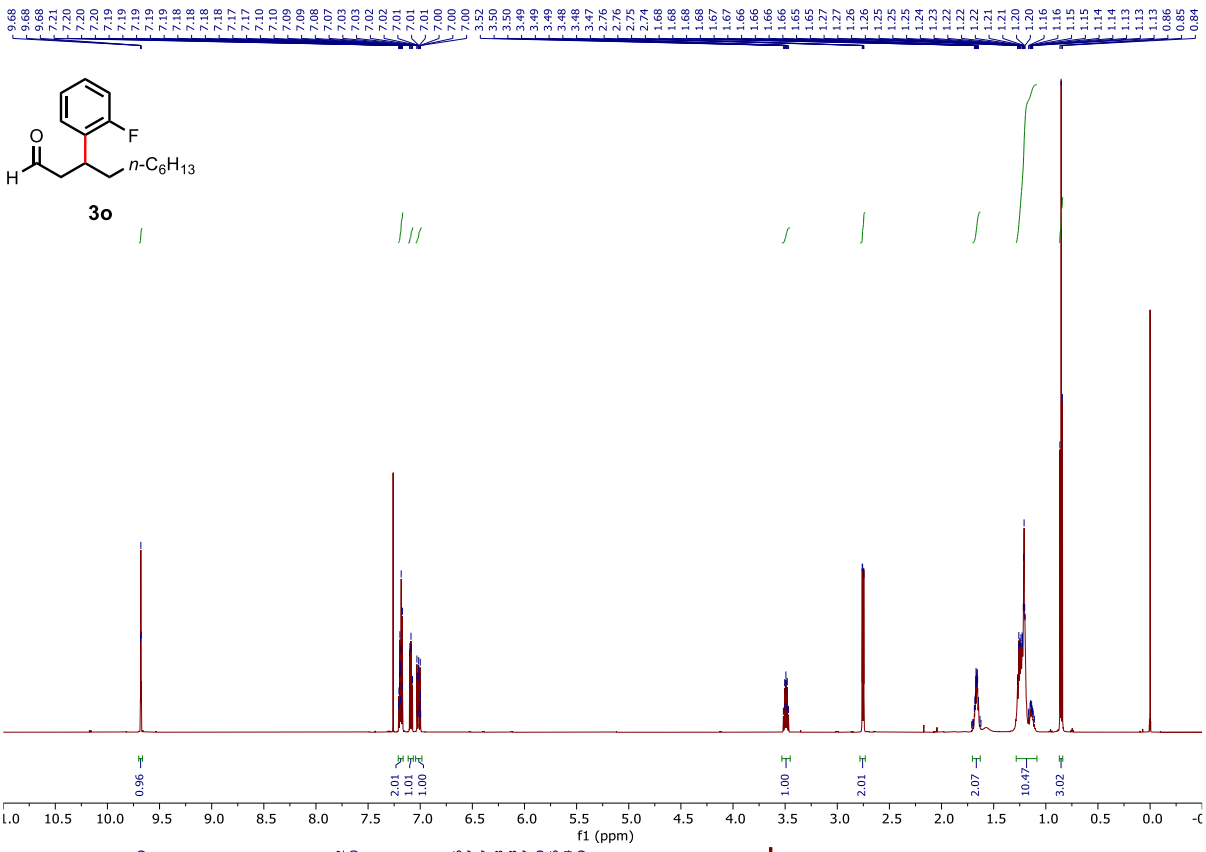

NO2
O
H
n-C6H13
3m
f1 (ppm)

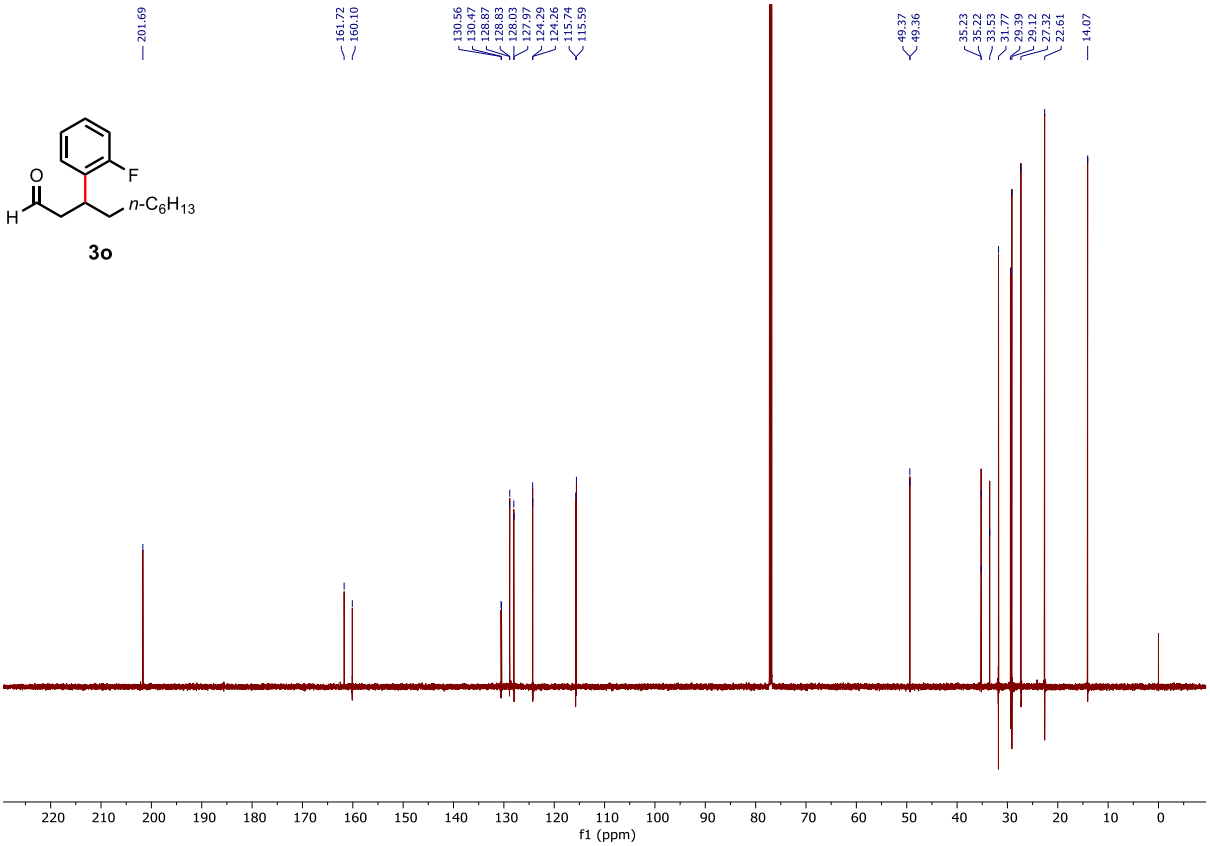

NO2
O
H
n-C6H13
3m
f1 (ppm)

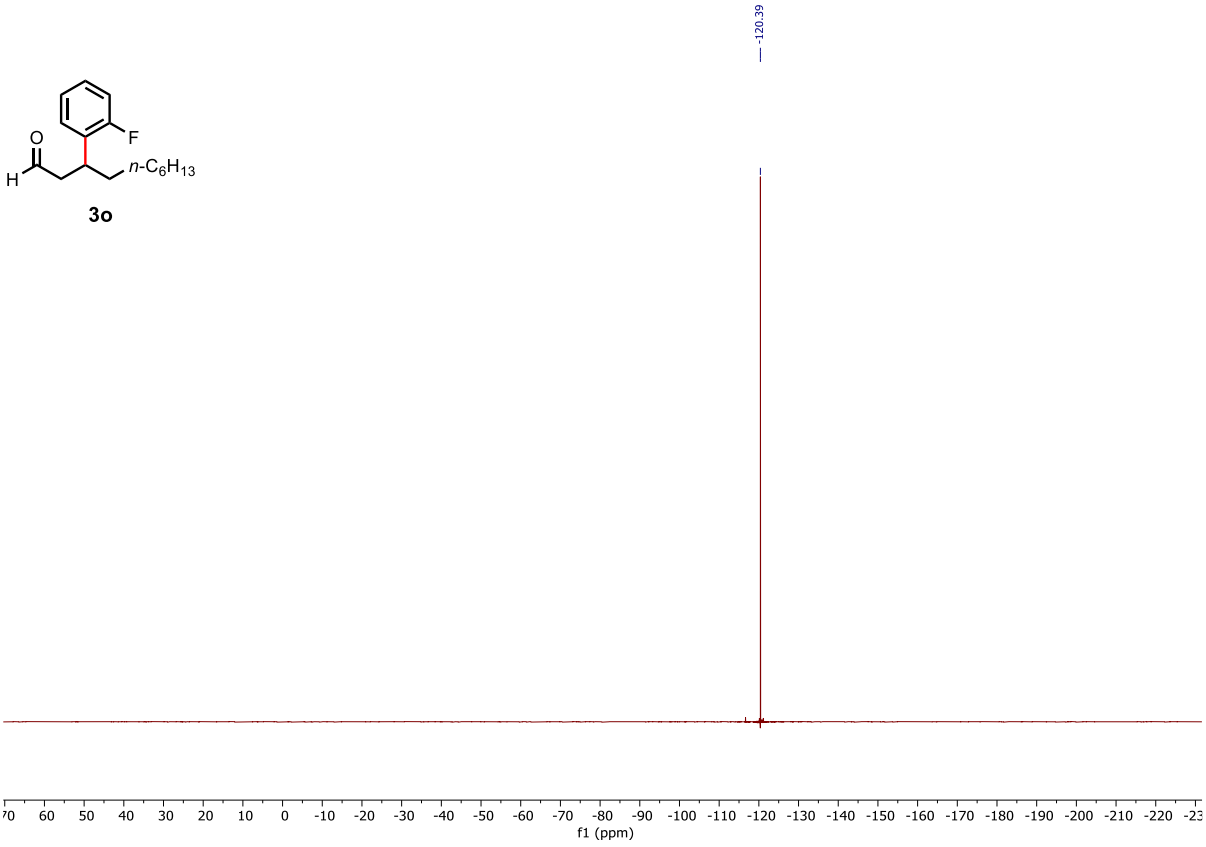

OCF3
O
H
n-C6H13
3n
f1 (ppm)


OCF3
O
H
n-C6H13
3n
f1 (ppm)

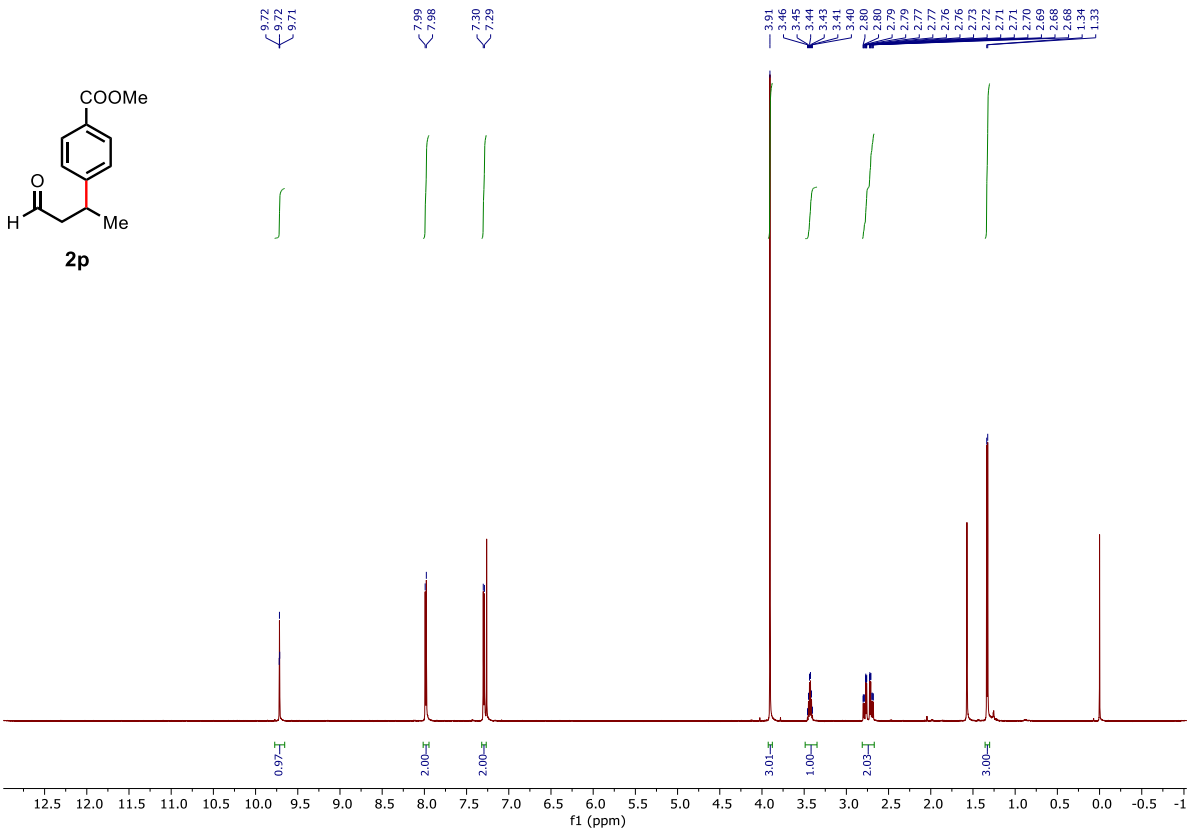

-60.41
OCF3
O
H
n-C6H13
3n
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)

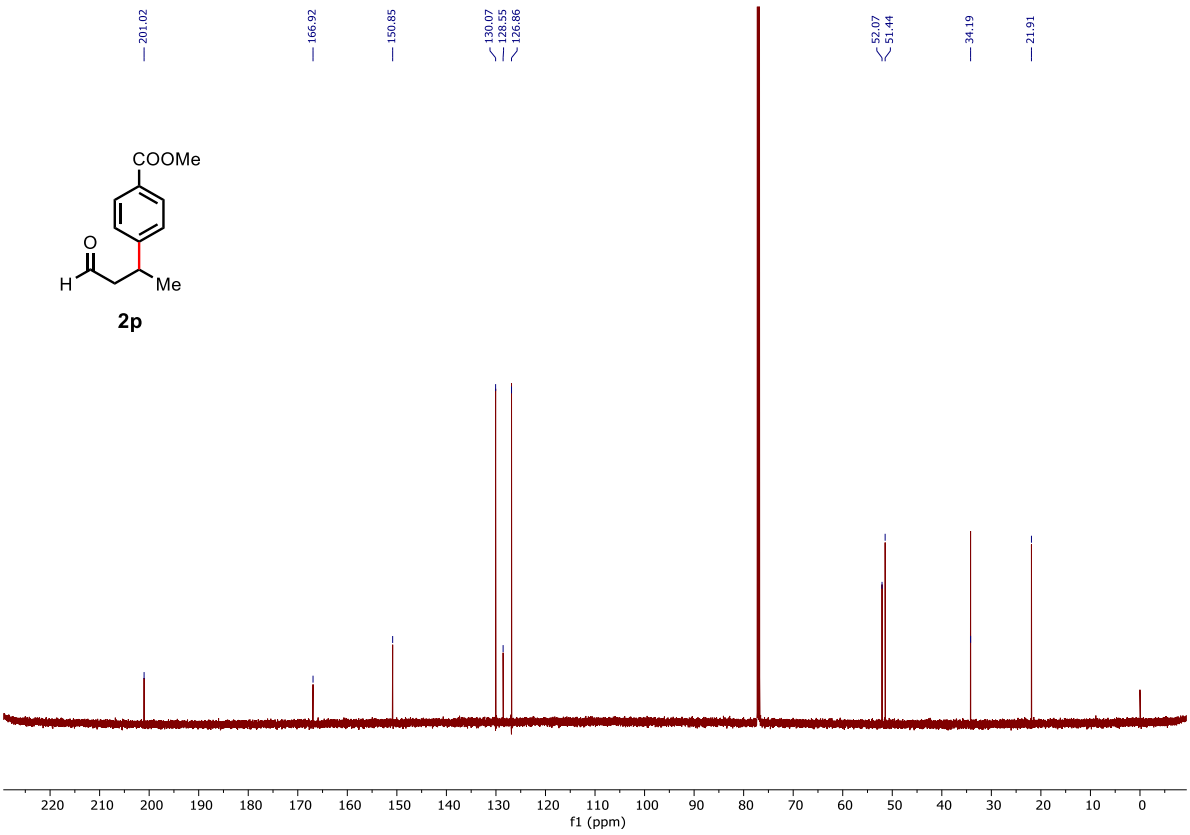

O
H
F
n-C6H13
3o
0.96
2.01
1.01
1.00
1.00
2.01
2.07
10.47
3.02
f1 (ppm)

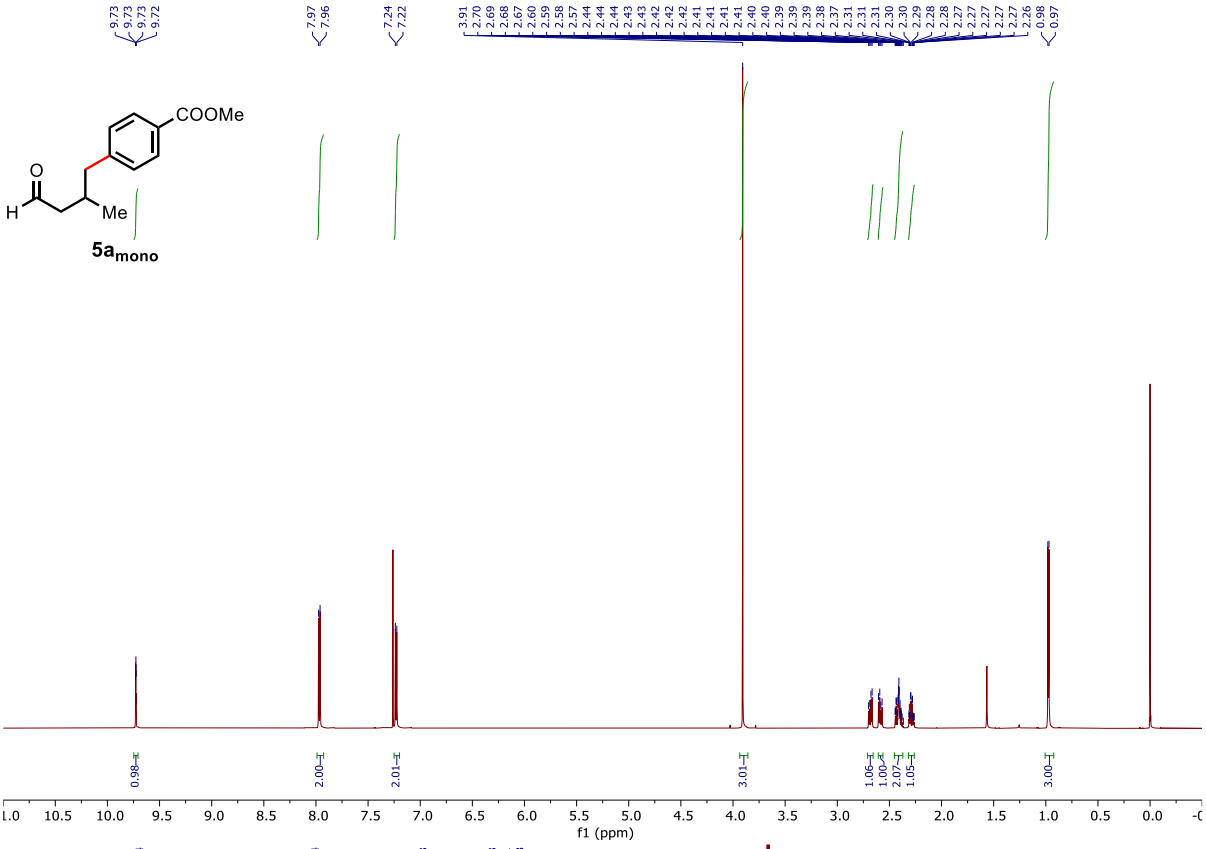

201.69
161.72
160.10
130.56
130.47
128.87
128.83
128.03
127.97
124.29
124.26
115.74
115.59
49.37
49.36
35.23
35.22
33.53
31.77
29.39
29.12
27.32
22.61
14.07
O
H
F
n-C6H13
3o
f1 (ppm)

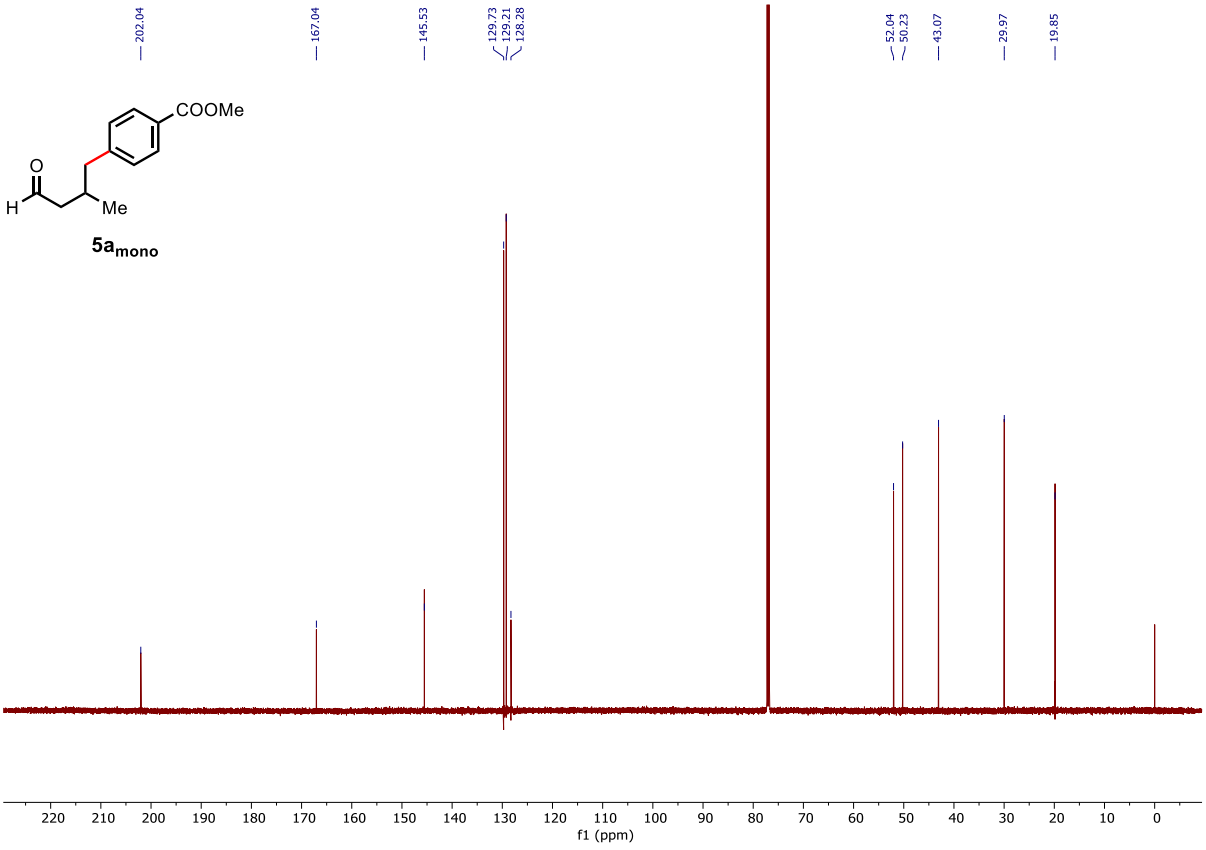

O
H
F
n-C6H13
-120.39
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)

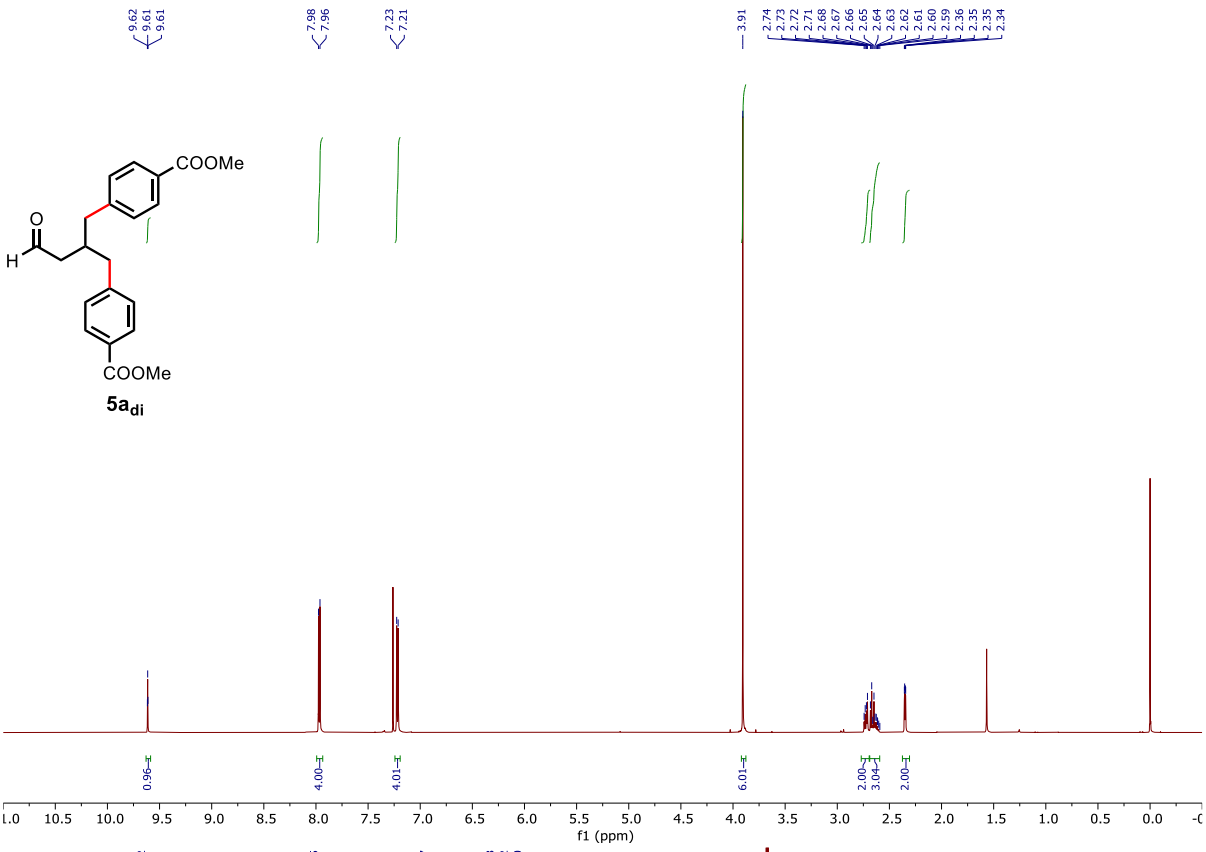
3o

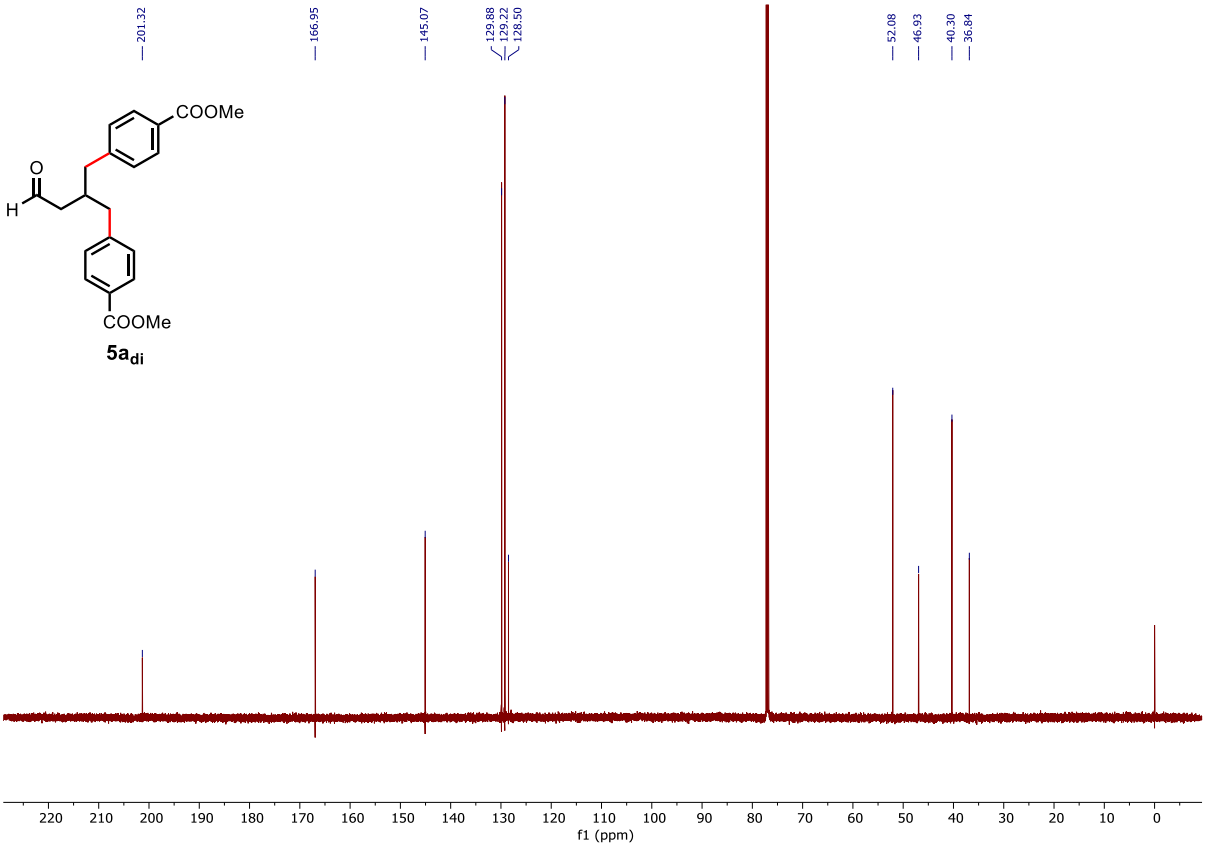

COOMe
O
H
Me
2p
9.72
9.72
9.71
7.99
7.98
7.30
7.29
3.91
3.46
3.45
3.44
3.43
3.41
3.40
2.80
2.80
2.79
2.79
2.77
2.77
2.76
2.76
2.73
2.72
2.71
2.71
2.70
2.69
2.68
2.68
1.34
1.33
0.97
2.00
2.00
3.01
1.00
2.03
3.00
f1 (ppm)

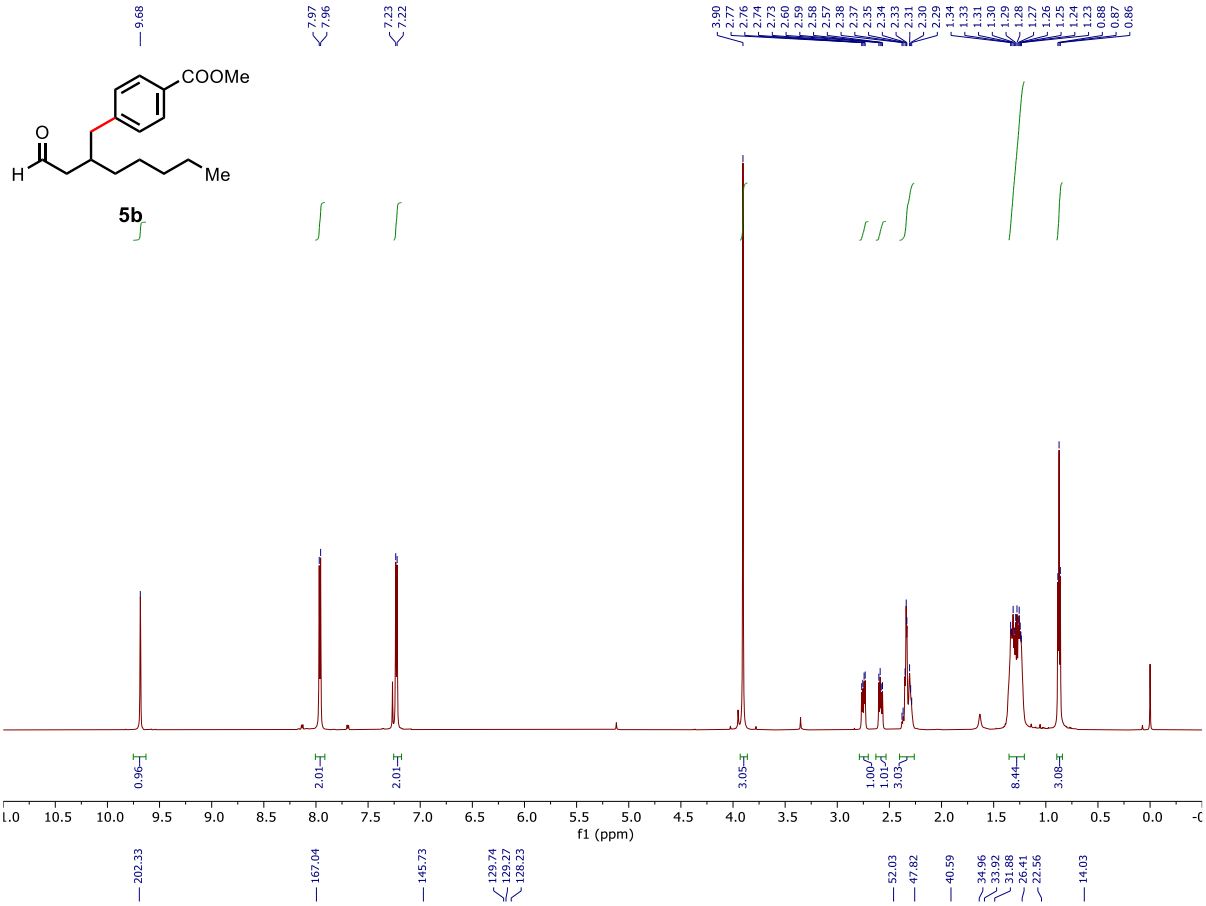

COOMe
O
H
Me
2p
201.02
166.92
150.85
130.07
128.55
126.86
52.07
51.44
34.19
21.91
f1 (ppm)

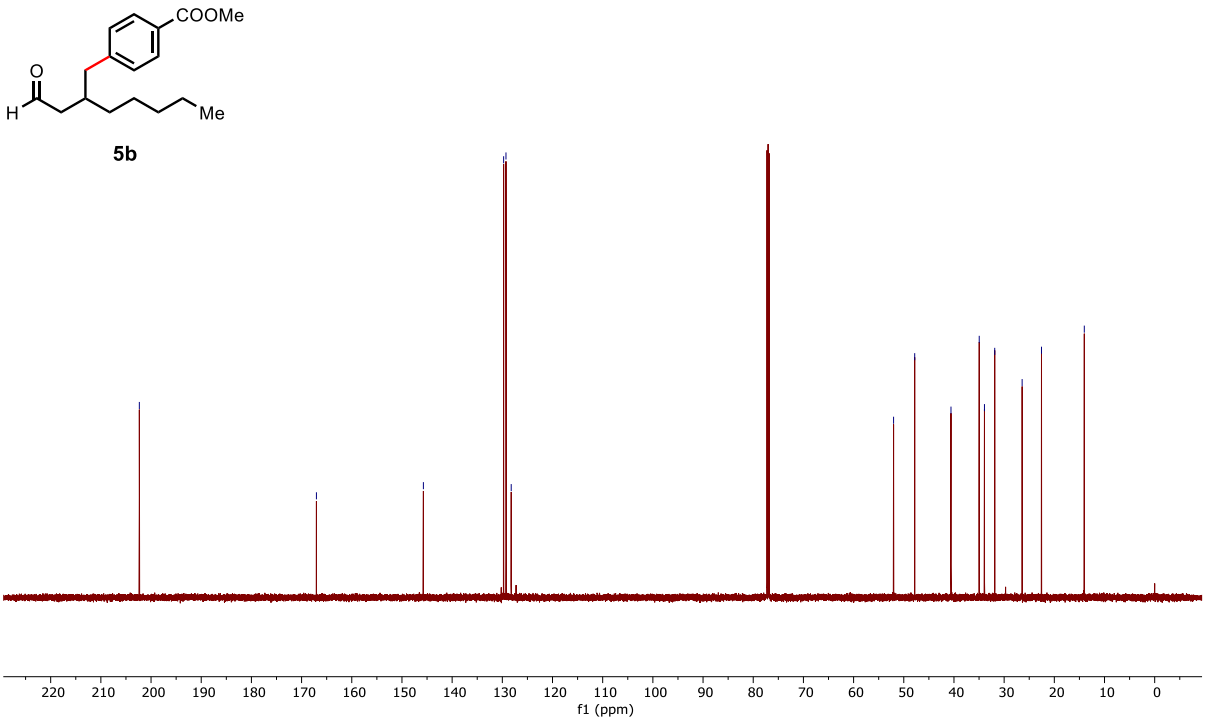

COOMe
O
H
Me
5a mono
f1 (ppm)

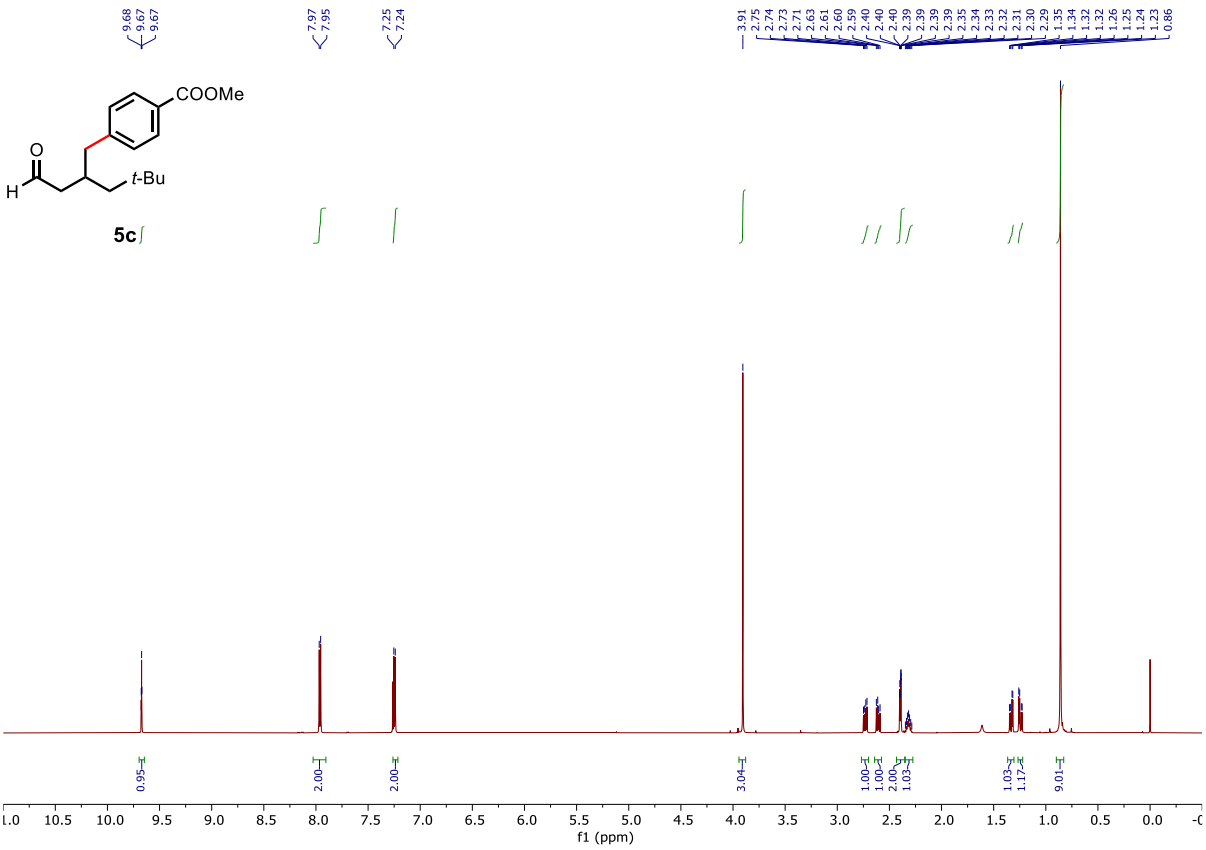

COOMe
O
H
Me
5a mono
f1 (ppm)

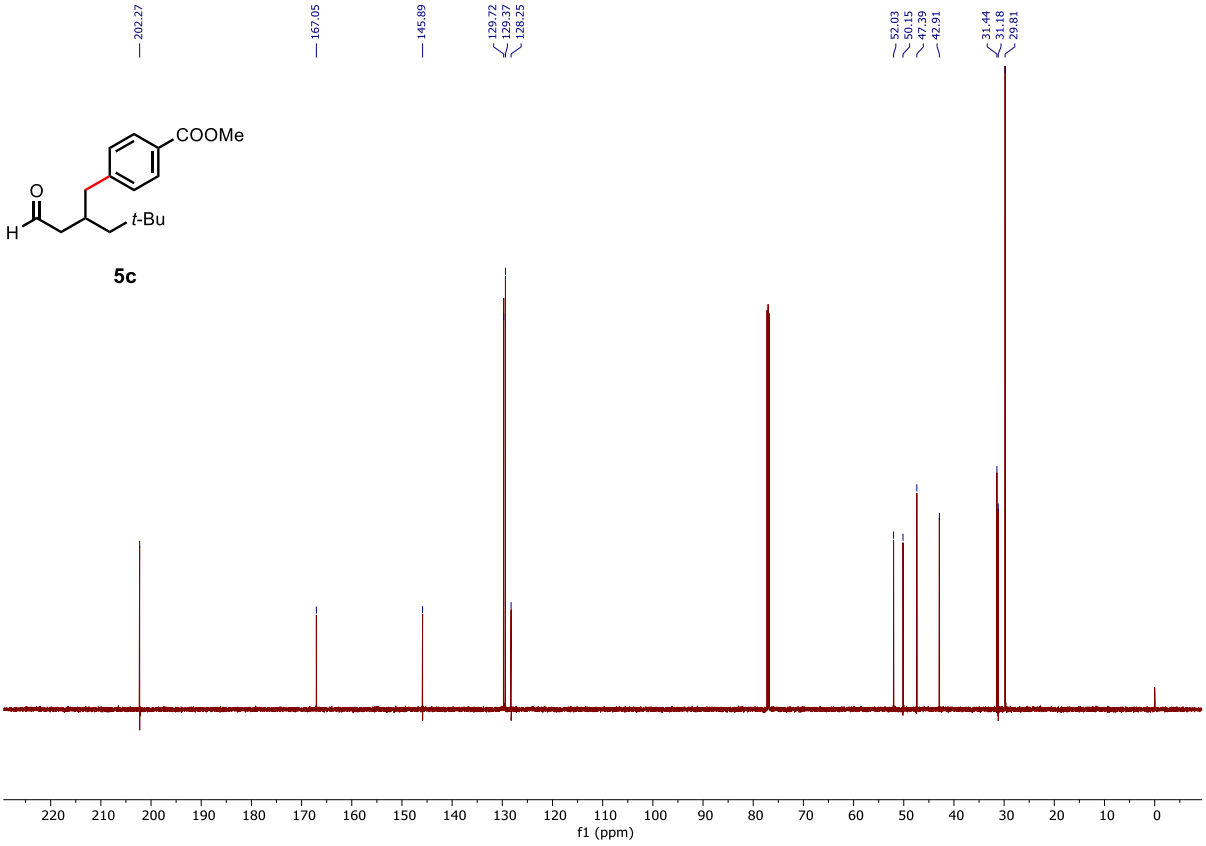

9.62
9.61
9.61
7.98
7.96
7.23
7.21
3.91
2.74
2.73
2.72
2.71
2.68
2.67
2.66
2.65
2.64
2.63
2.62
2.61
2.60
2.59
2.36
2.35
2.35
2.34
COOMe
O
H
COOMe
5a_di
0.96
4.00
4.01
6.01
2.00
3.04
2.00
f1 (ppm)

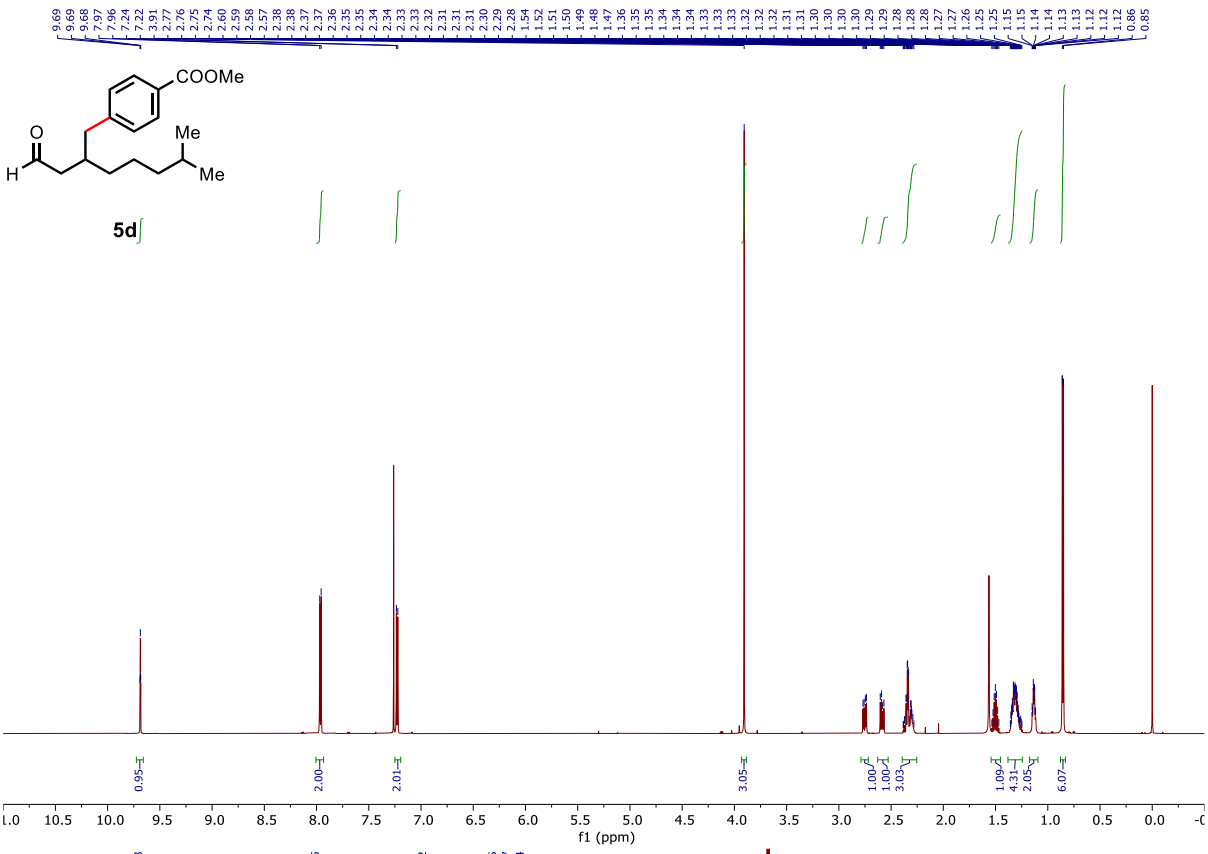

201.32
166.95
145.07
129.88
129.22
128.50
52.08
46.93
40.30
36.84
COOMe
O
H
COOMe
5a_di
f1 (ppm)

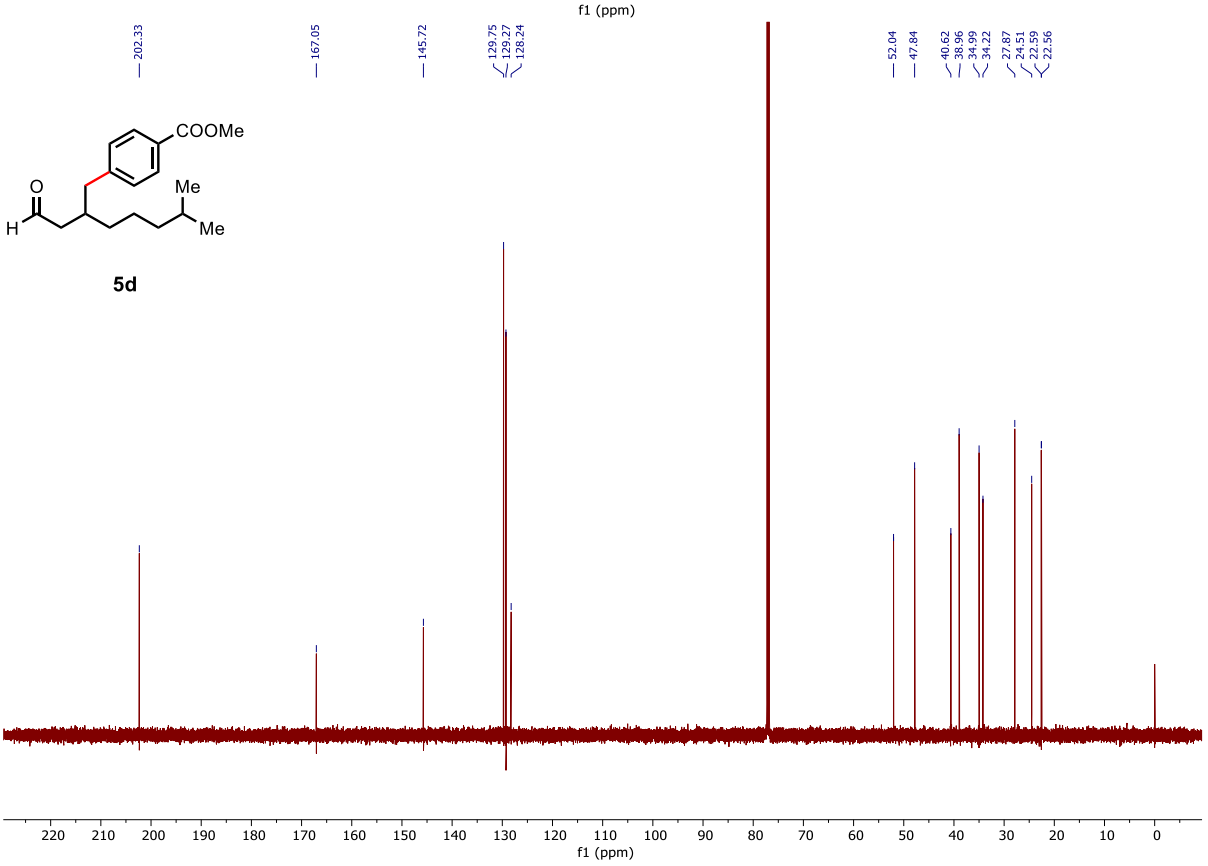

9.68
7.97
7.96
7.23
7.22
3.90
2.77
2.76
2.74
2.73
2.60
2.59
2.58
2.57
2.38
2.37
2.35
2.34
2.33
2.31
2.30
2.29
1.34
1.33
1.31
1.30
1.29
1.28
1.27
1.26
1.25
1.24
1.23
0.88
0.87
0.86
COOMe
O
H
Me
5b
0.96
2.01
2.01
3.05
1.00
1.01
3.03
8.44
3.08
f1 (ppm)

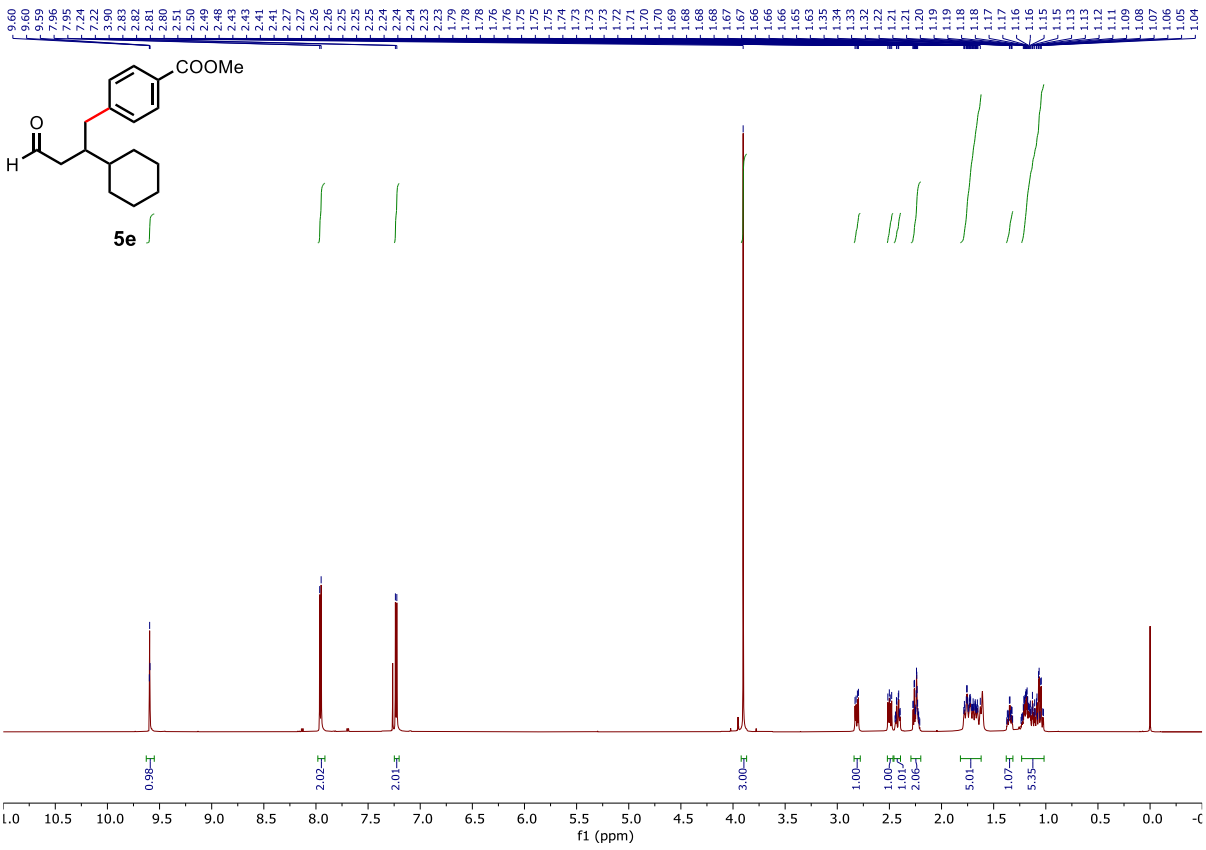

202.33
167.04
145.73
129.74
129.27
128.23
52.03
47.82
40.59
34.96
33.92
31.88
26.41
22.56
14.03
COOMe
O
H
Me
5b
f1 (ppm)

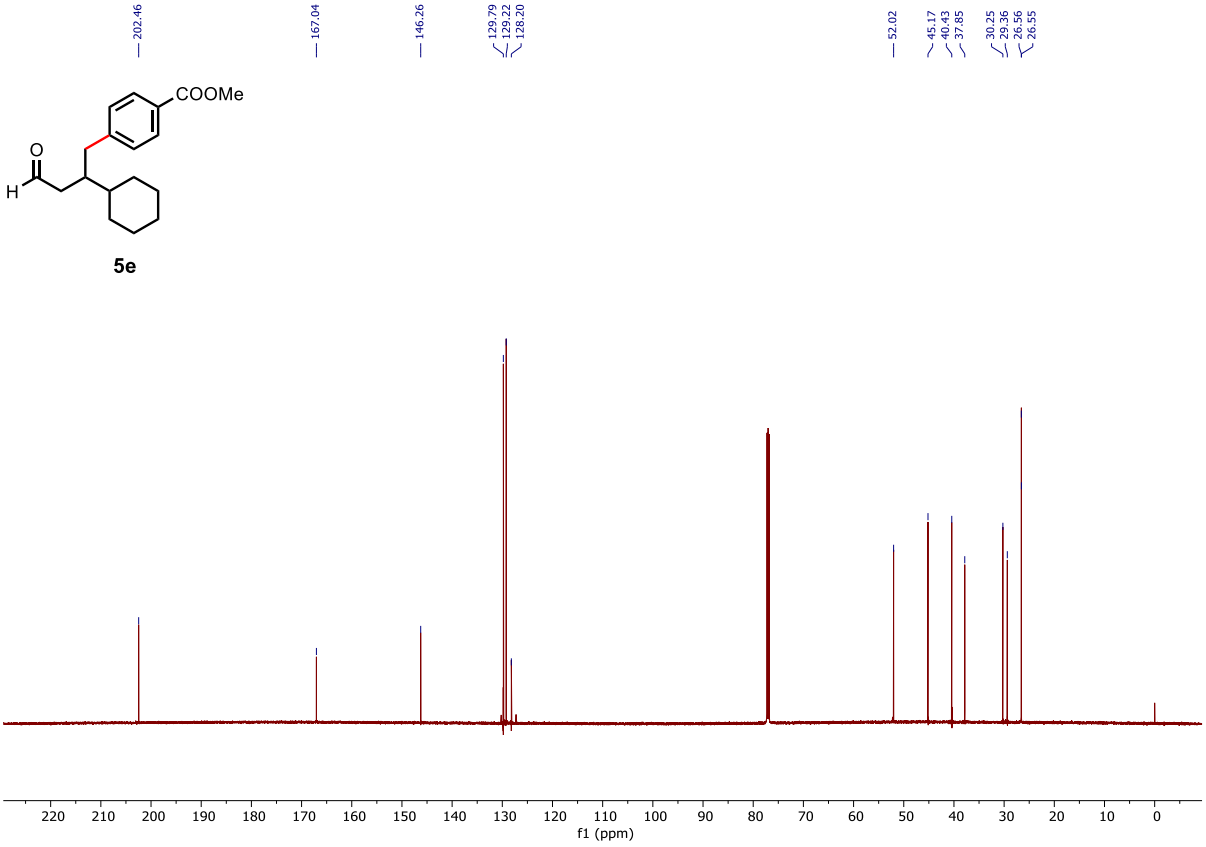

COOMe
O
H
t-Bu
5c
f1 (ppm)

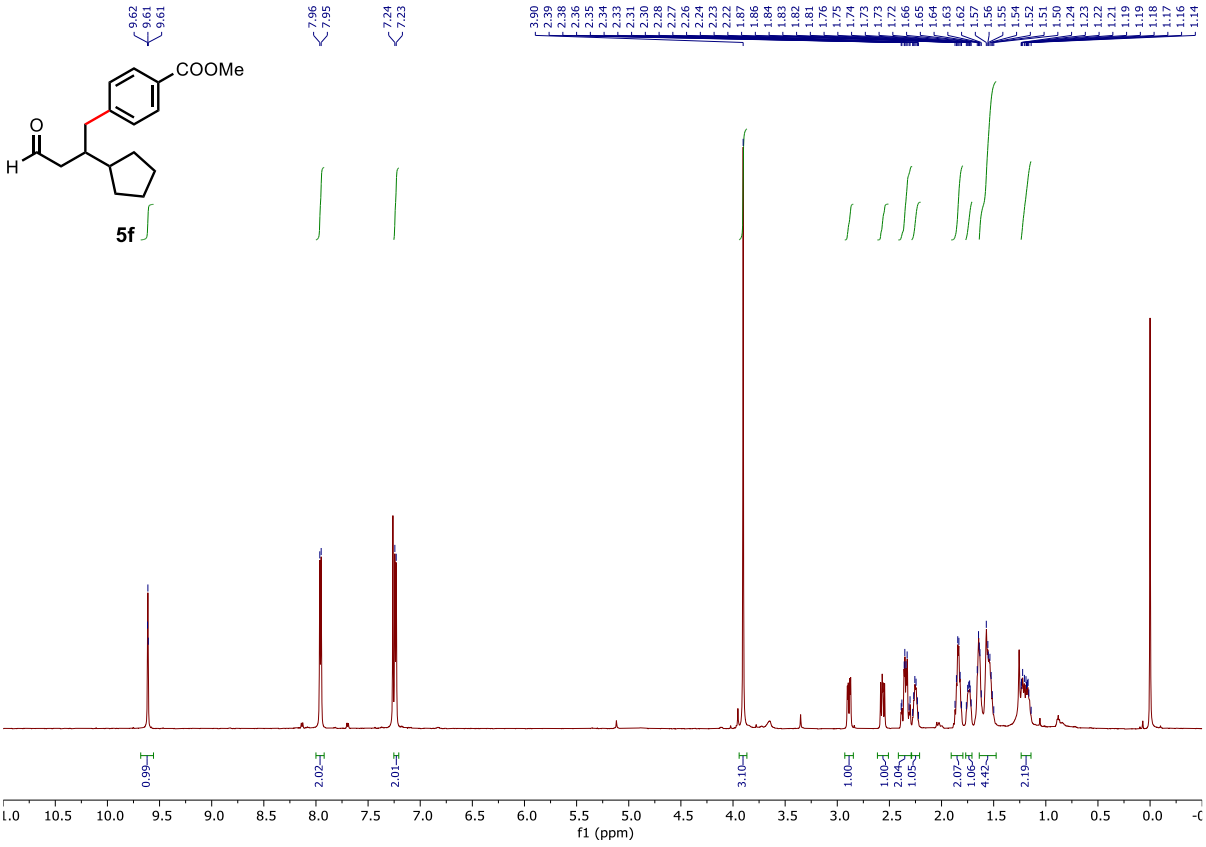

COOMe
O
H
t-Bu
5c
f1 (ppm)

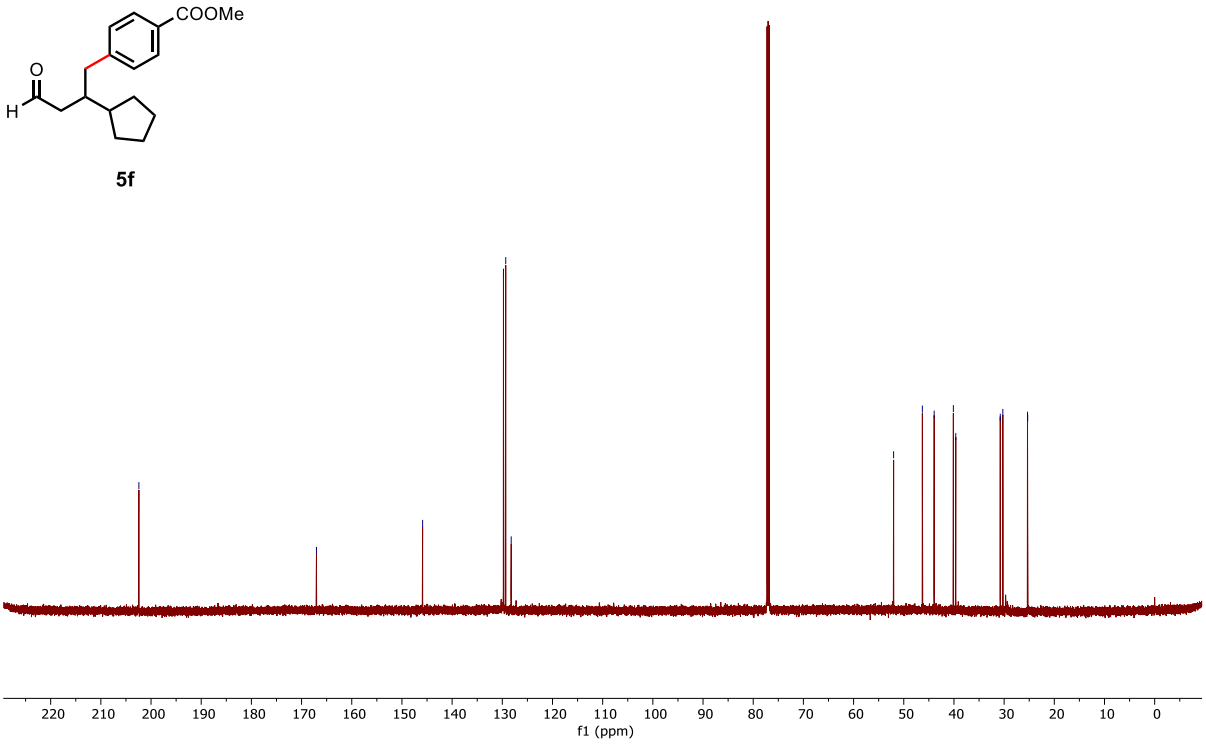

COOMe
O
H
Me
Me
5d
f1 (ppm)

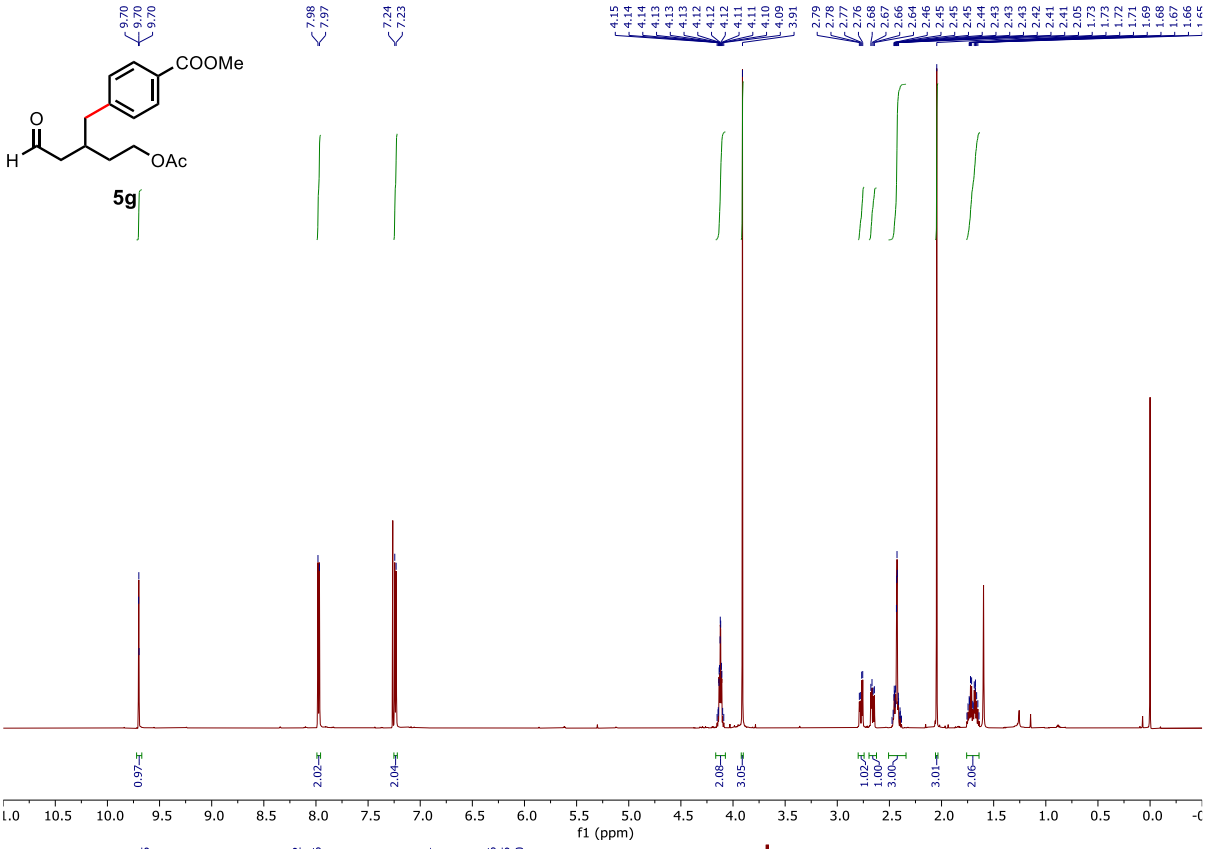

COOMe
O
H
Me
Me
5d
f1 (ppm)

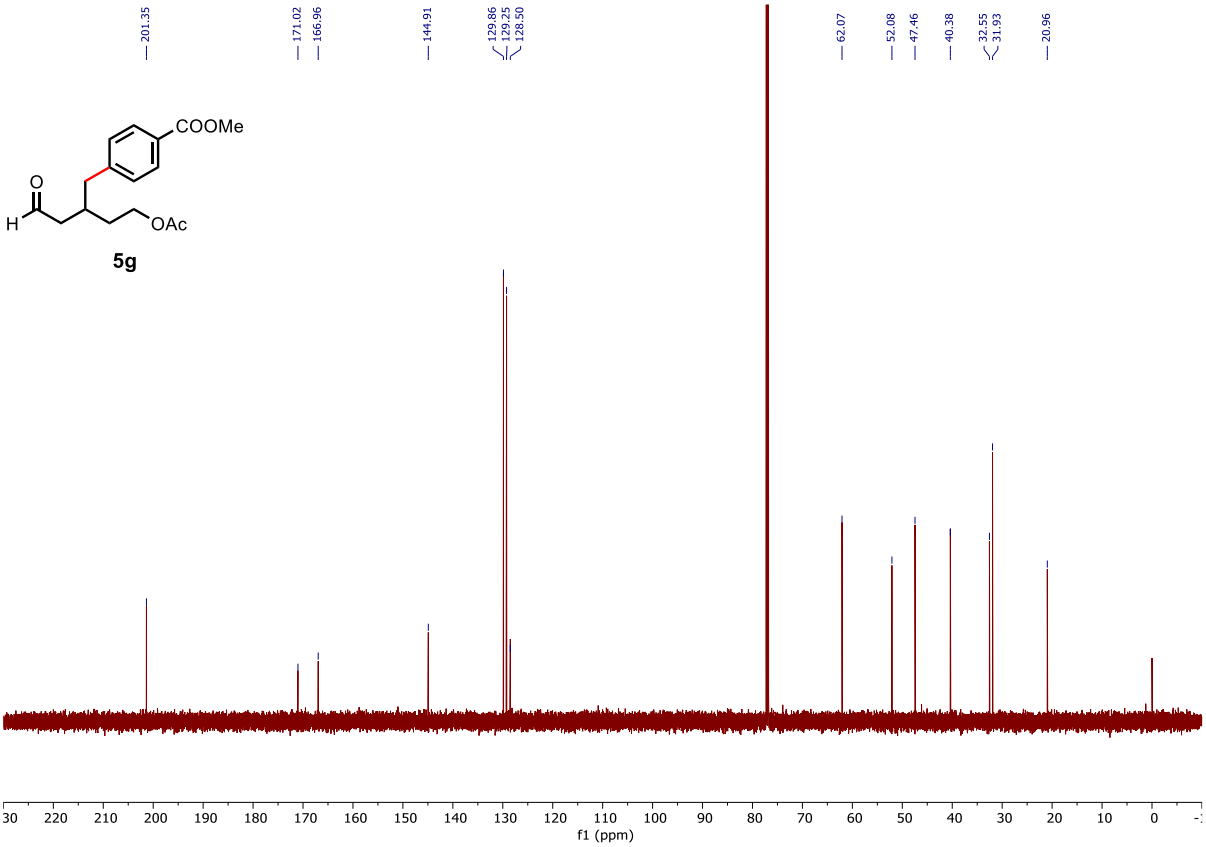

COOMe
O
H
5e
f1 (ppm)

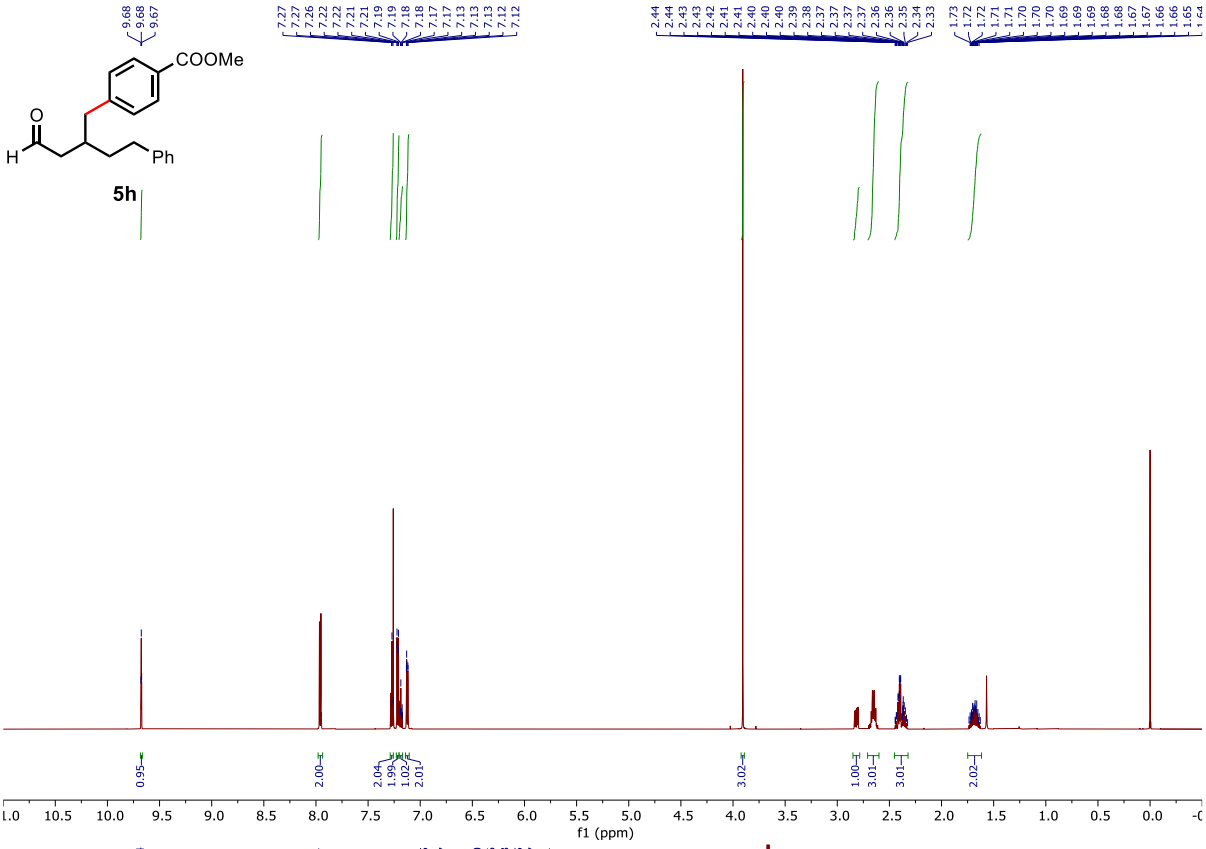

COOMe
O
H
5e
f1 (ppm)

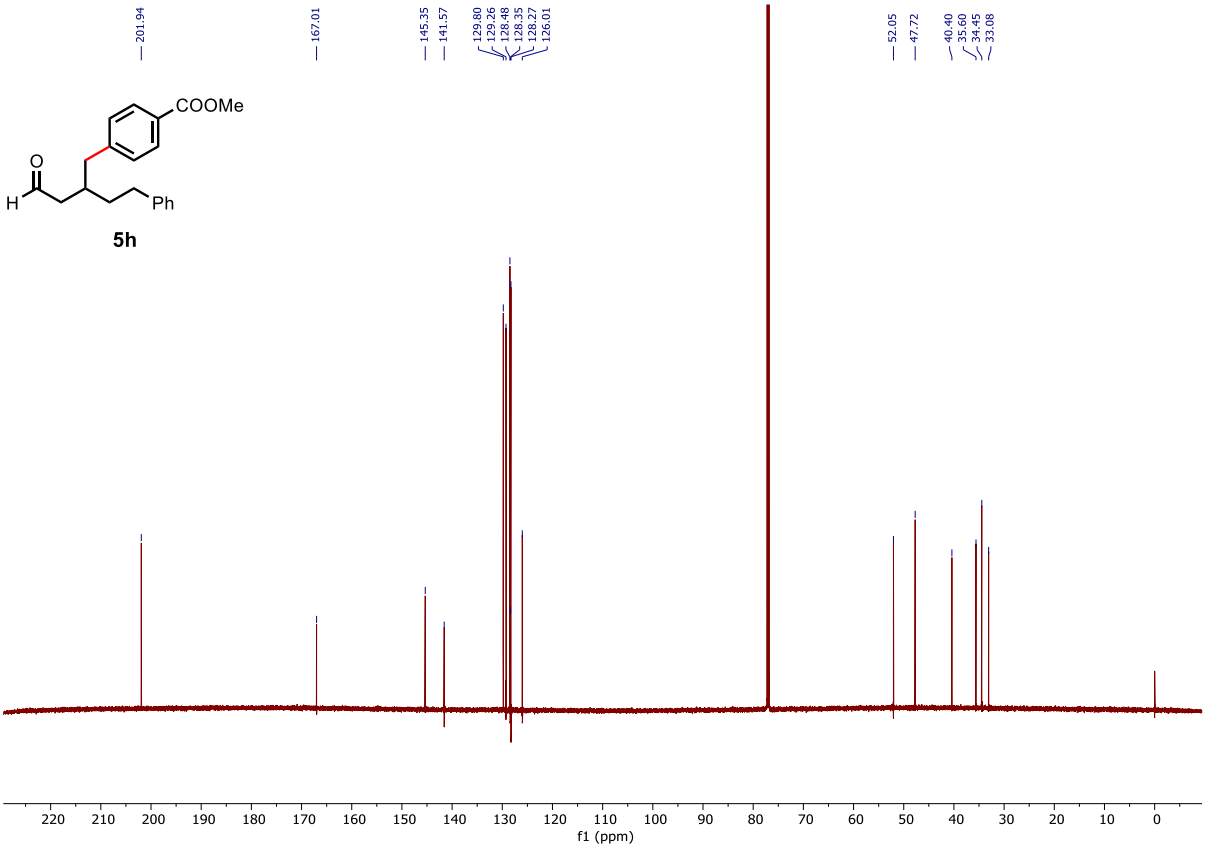

COOMe
O
H
5f
f1 (ppm)

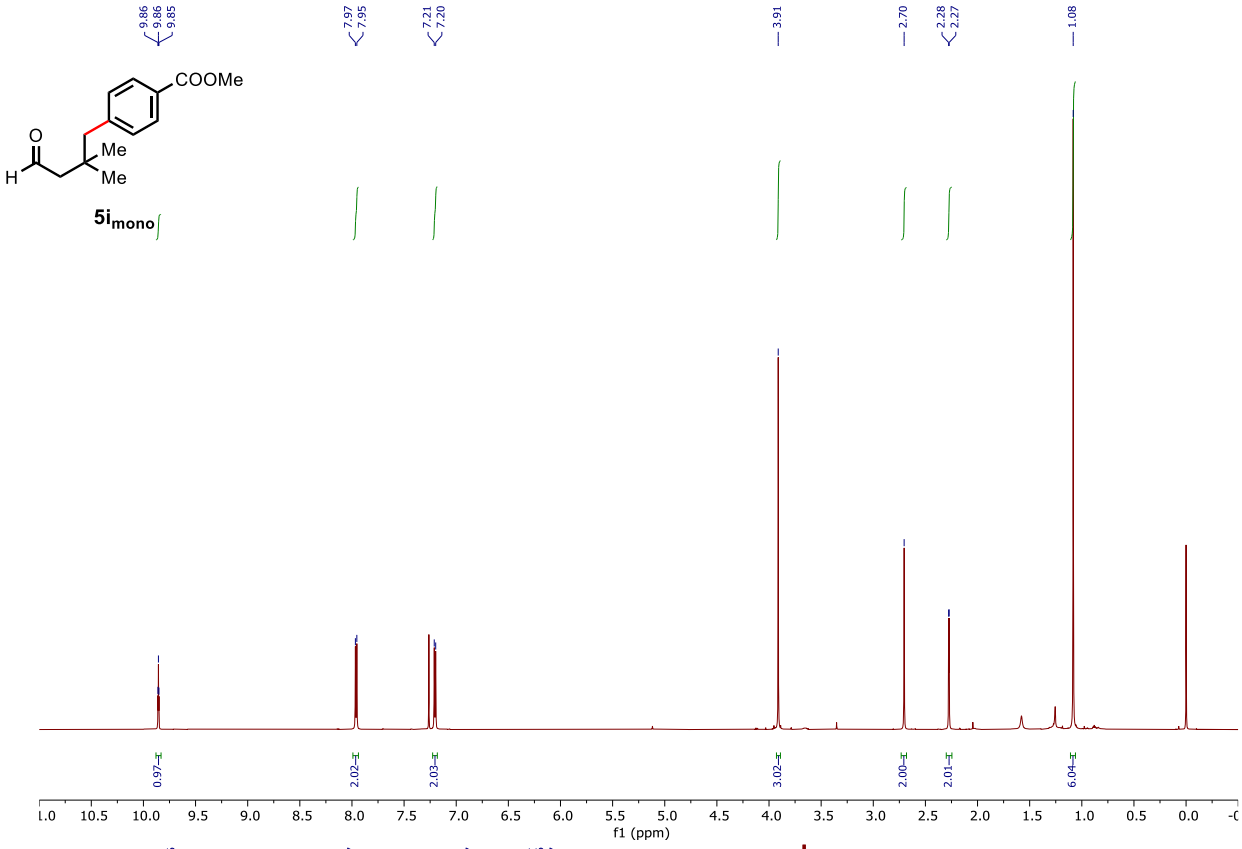

COOMe
O
H
5f
f1 (ppm)

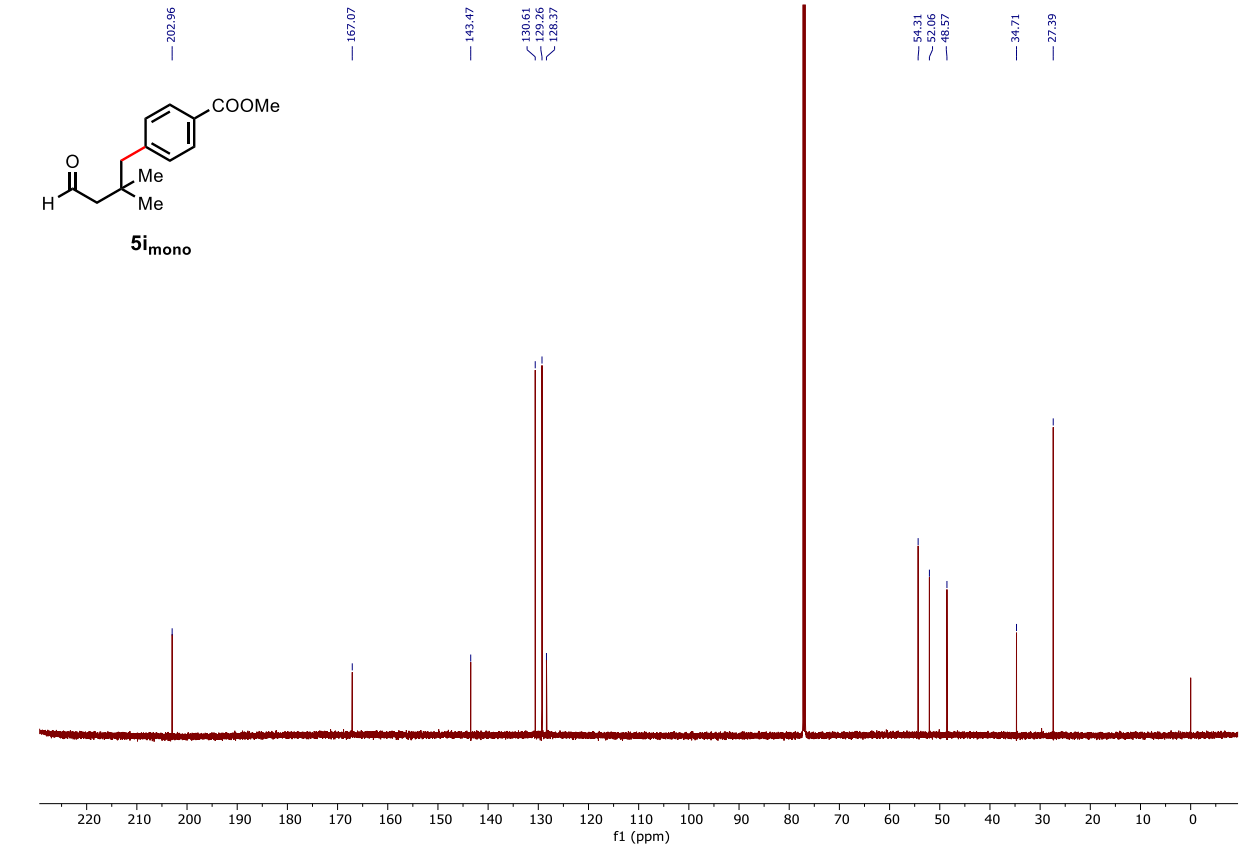

COOMe
O
H
OAc
5g
f1 (ppm)

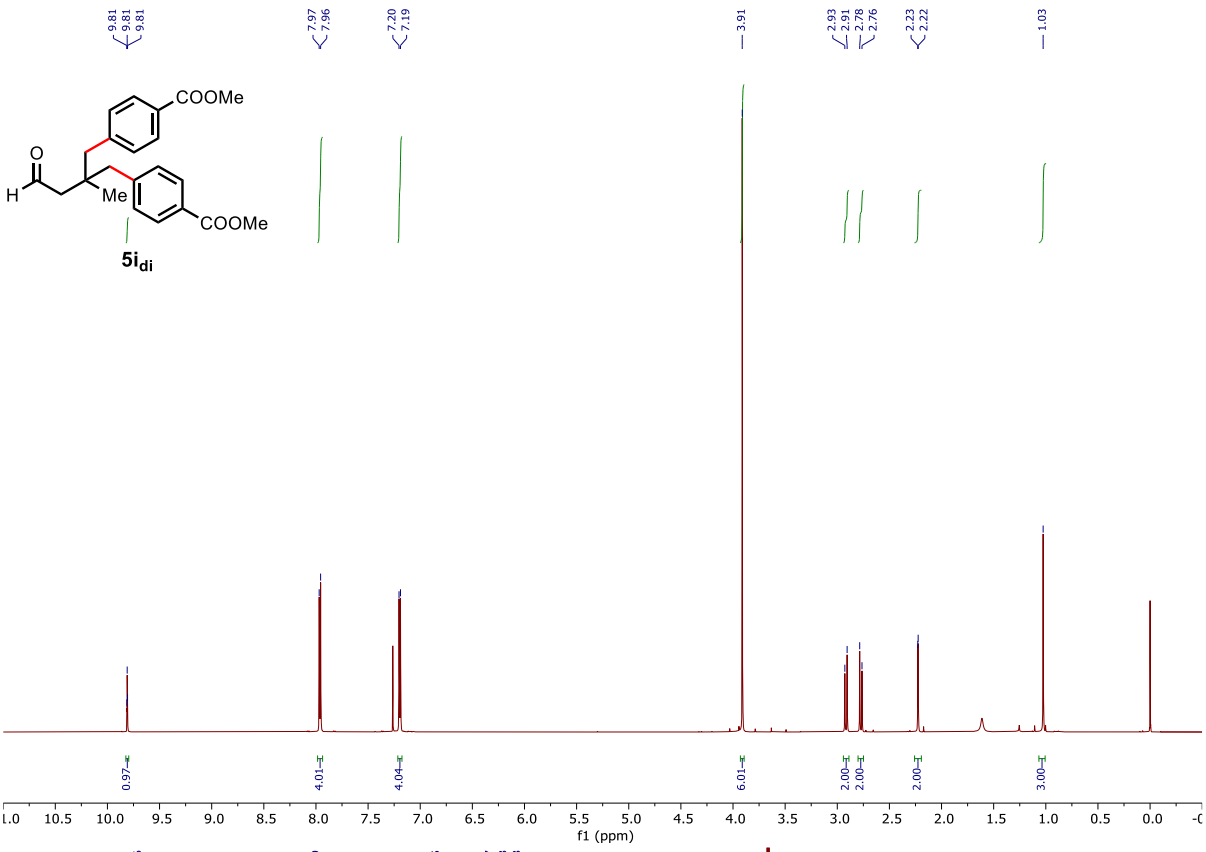

COOMe
O
H
OAc
5g
f1 (ppm)


COOMe
O
H
Ph
5h
f1 (ppm)

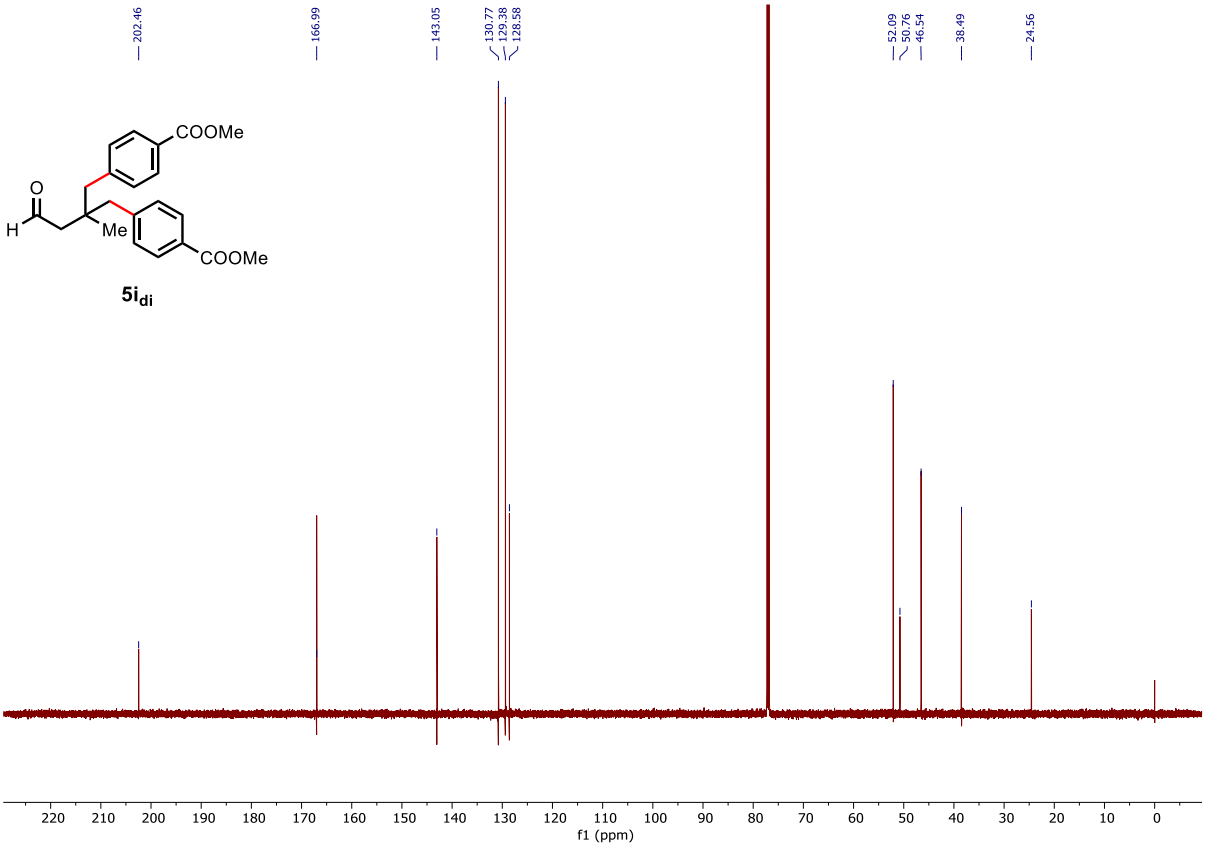

COOMe
O
H
Ph
5h
f1 (ppm)


9.86
9.86
9.85
7.97
7.95
7.21
7.20
3.91
2.70
2.28
2.27
1.08
COOMe
O
H
Me
Me
5i mono
0.97
2.02
2.03
3.02
2.00
2.01
6.04
f1 (ppm)

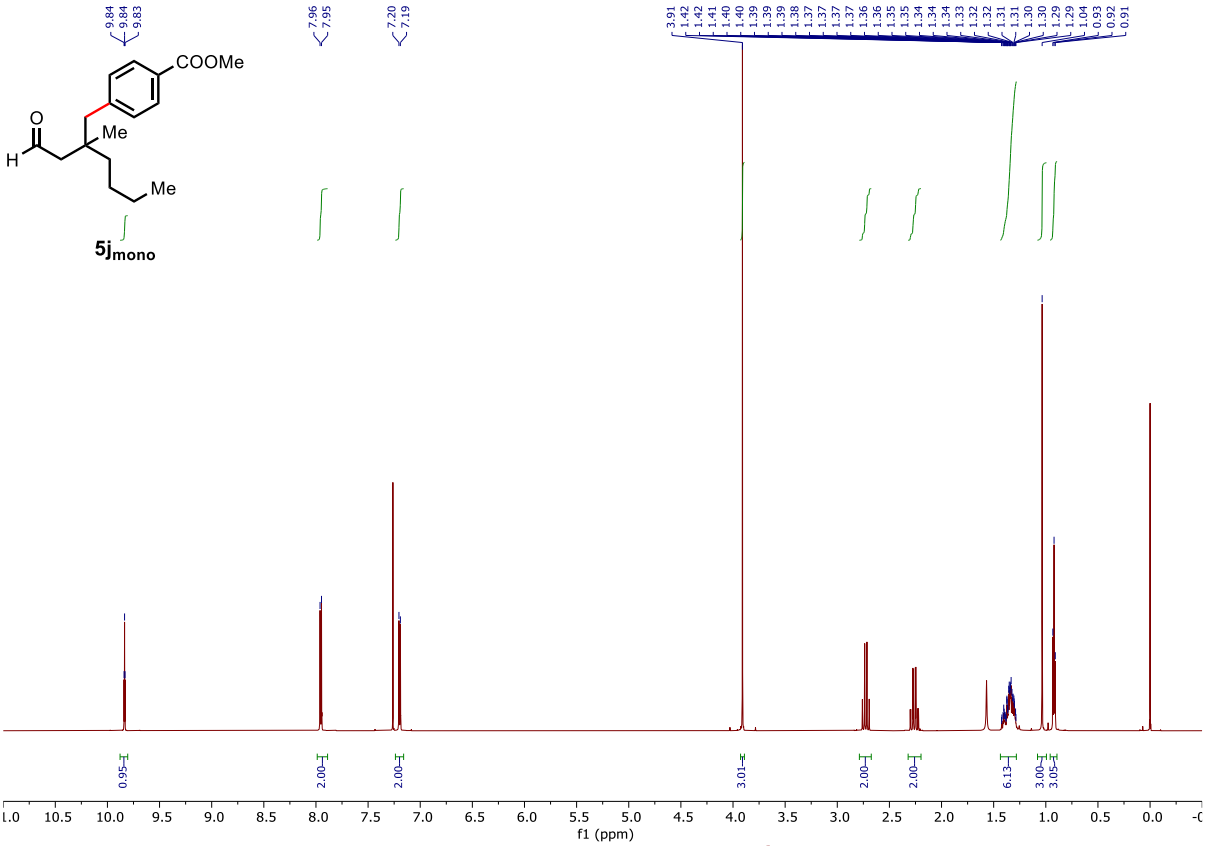

202.96
167.07
143.47
130.61
129.26
128.37
54.31
52.06
48.57
34.71
27.39
COOMe
O
H
Me
Me
5i mono
f1 (ppm)

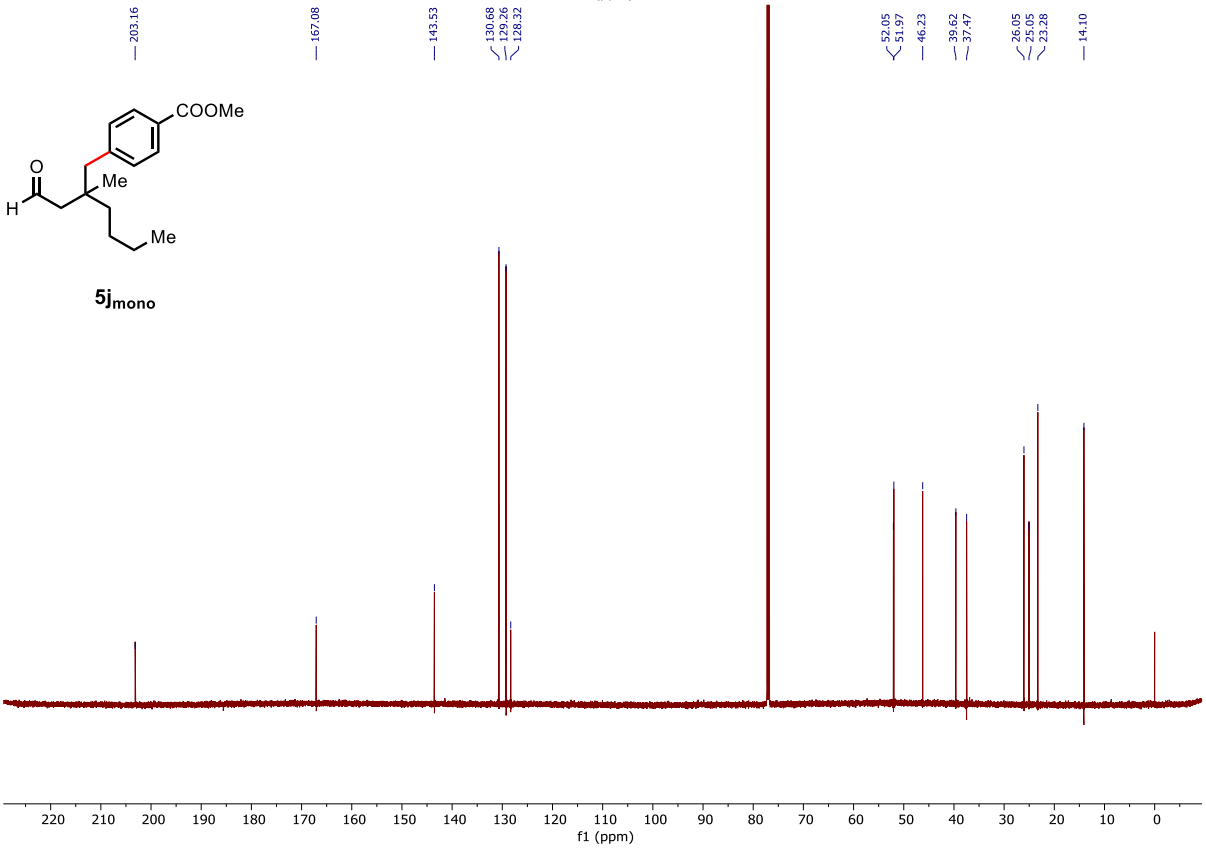

9.81
9.81
9.81
7.97
7.96
7.20
7.19
3.91
2.93
2.91
2.78
2.76
2.23
2.22
1.03
COOMe
O
H
Me
COOMe
0.97
4.01
4.04
6.01
2.00
2.00
2.00
3.00
f1 (ppm)

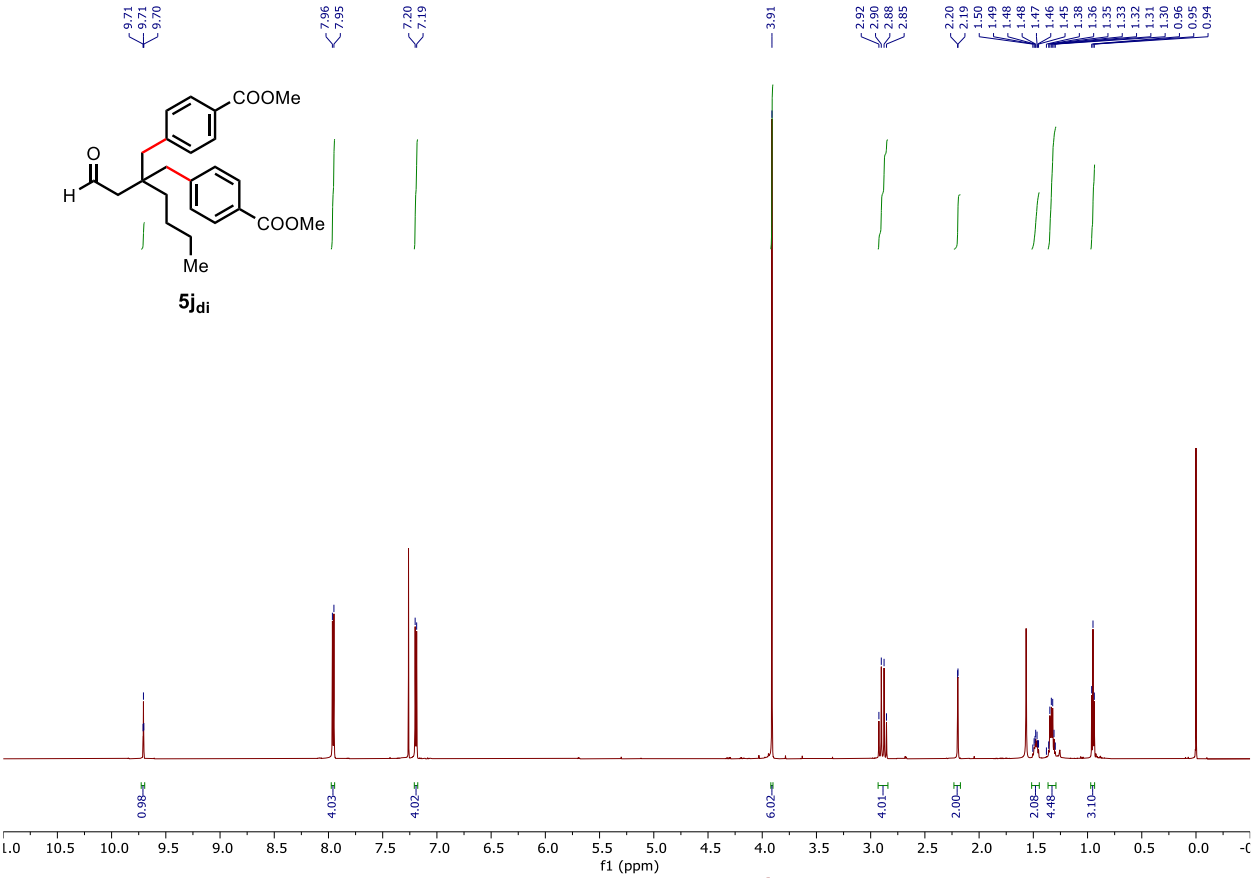
5i$_{di}$


202.46
166.99
143.05
130.77
129.38
128.58
52.09
50.76
46.54
38.49
24.56
COOMe
O
H
Me
COOMe
f1 (ppm)

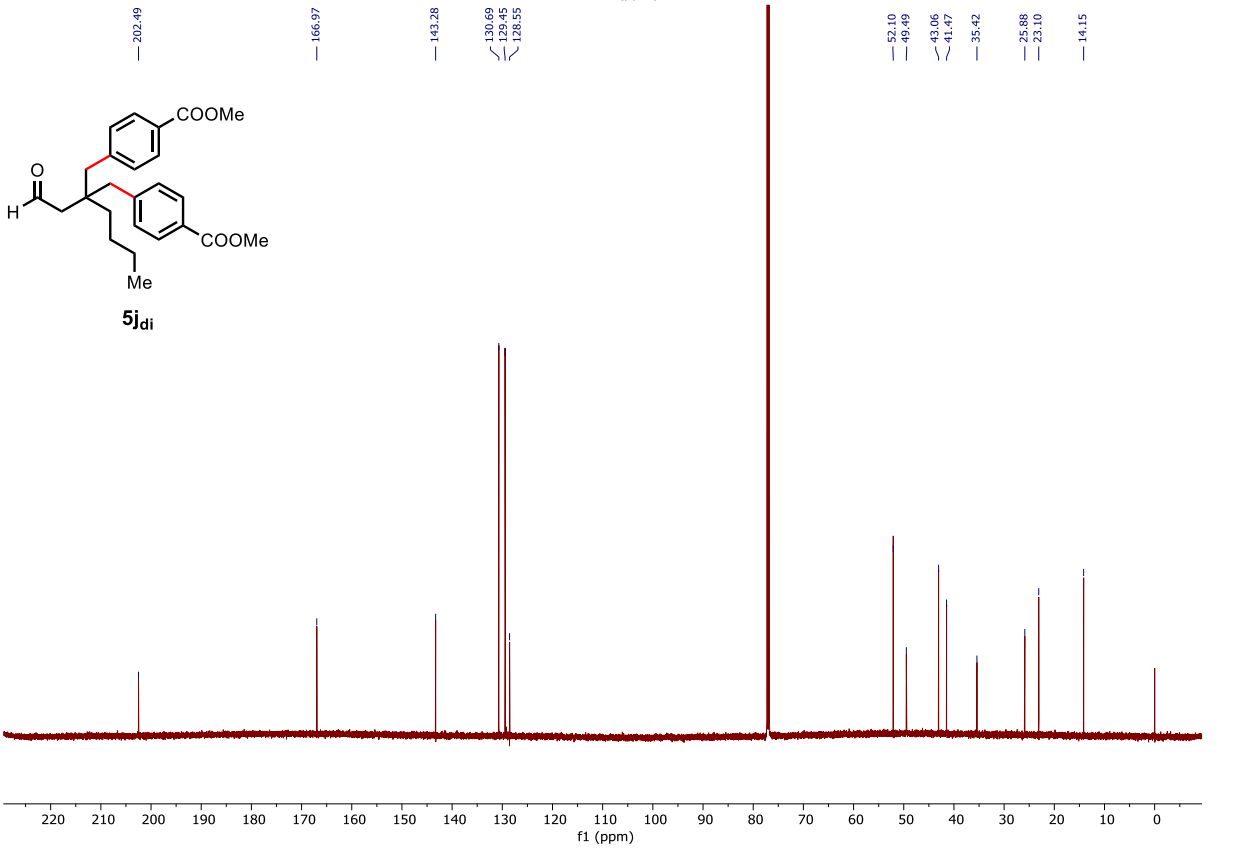
5i$_{di}$


COOMe
O
H
Me
Me
5j mono
f1 (ppm)

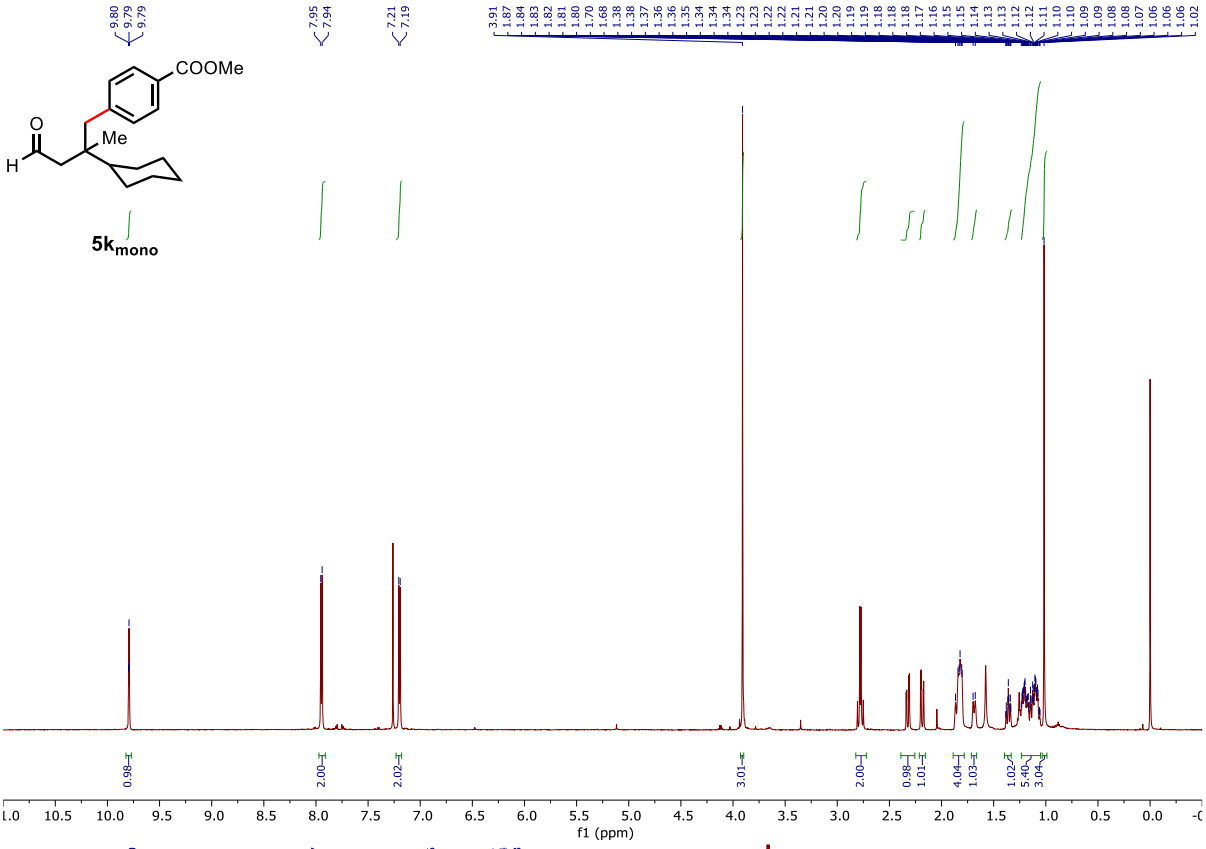

COOMe
O
H
Me
Me
5j mono
f1 (ppm)

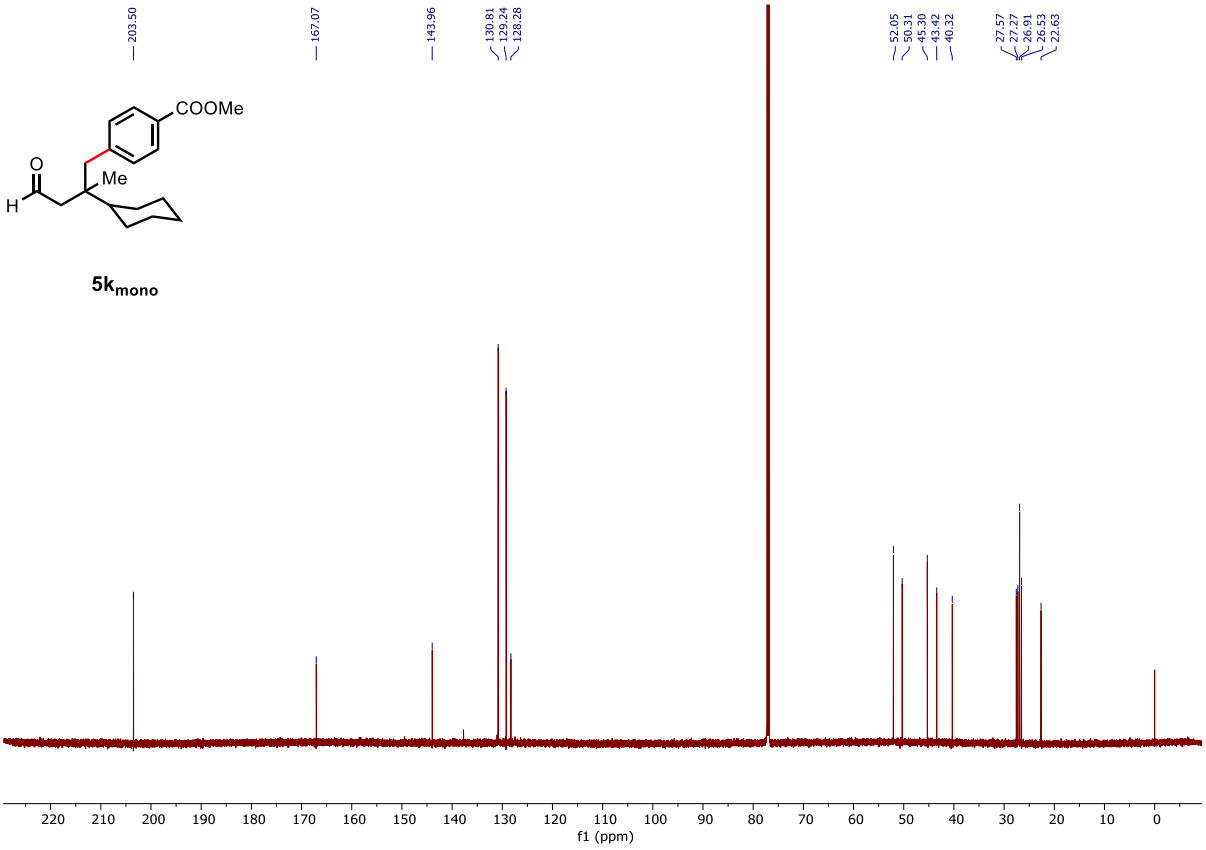

9.71
9.71
9.70
7.96
7.95
7.20
7.19
3.91
2.92
2.90
2.88
2.85
2.20
2.19
1.50
1.49
1.48
1.48
1.47
1.46
1.45
1.38
1.36
1.35
1.33
1.32
1.31
1.30
0.96
0.95
0.94
COOMe
O
H
COOMe
Me
0.98
4.03
4.02
6.02
4.01
2.00
2.08
4.48
3.10
f1 (ppm)

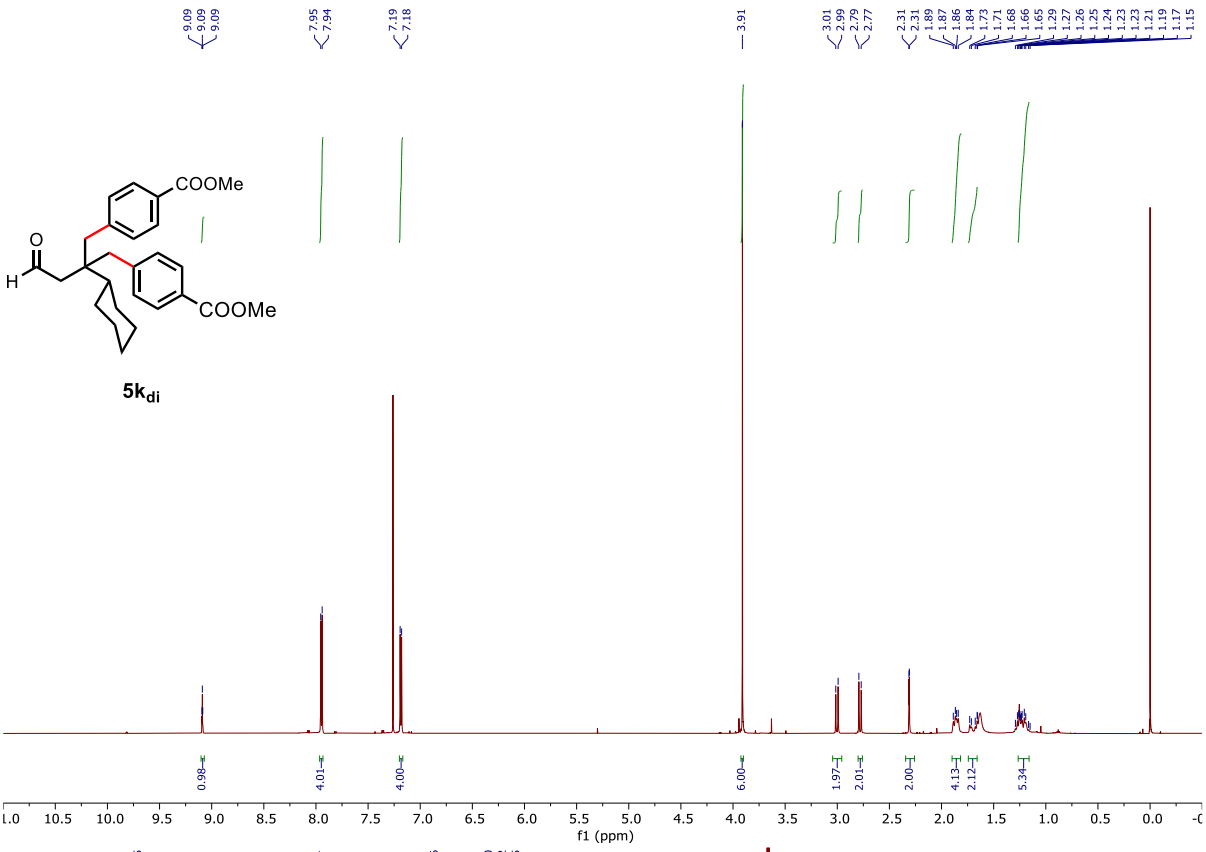
5j$_{di}$


202.49
166.97
143.28
130.69
129.45
128.55
52.10
49.49
43.06
41.47
35.42
25.88
23.10
14.15
COOMe
O
H
COOMe
Me
f1 (ppm)

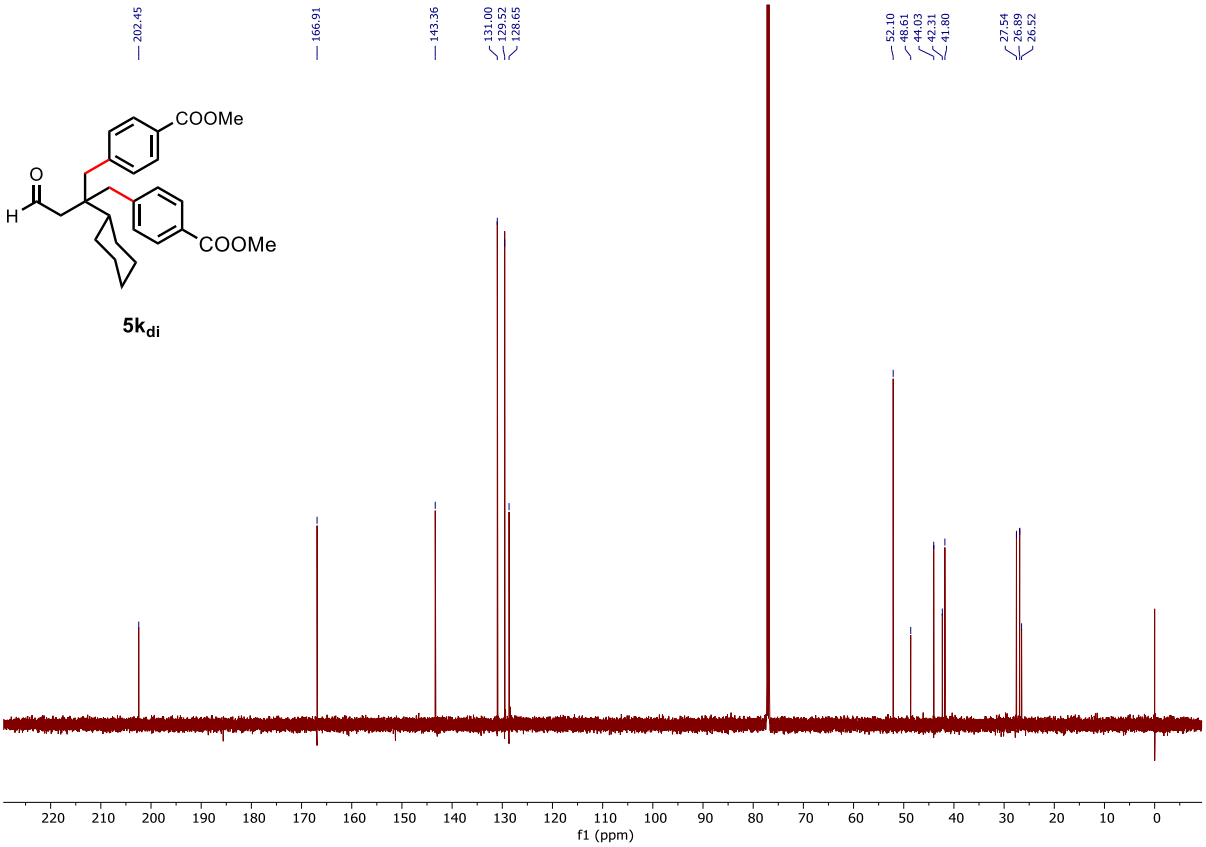
5j$_{di}$


COOMe
O
H
Me
5k mono
f1 (ppm)

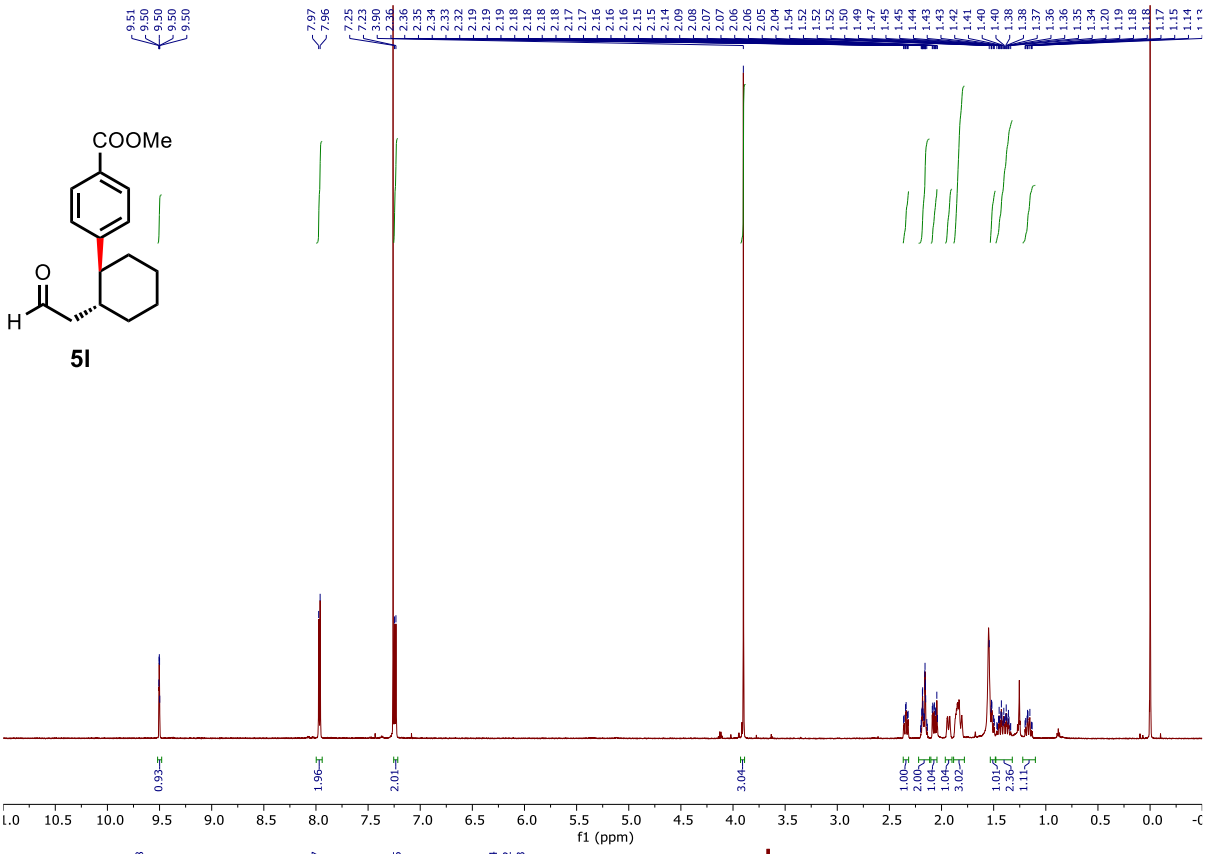

COOMe
O
H
Me
5k mono
f1 (ppm)

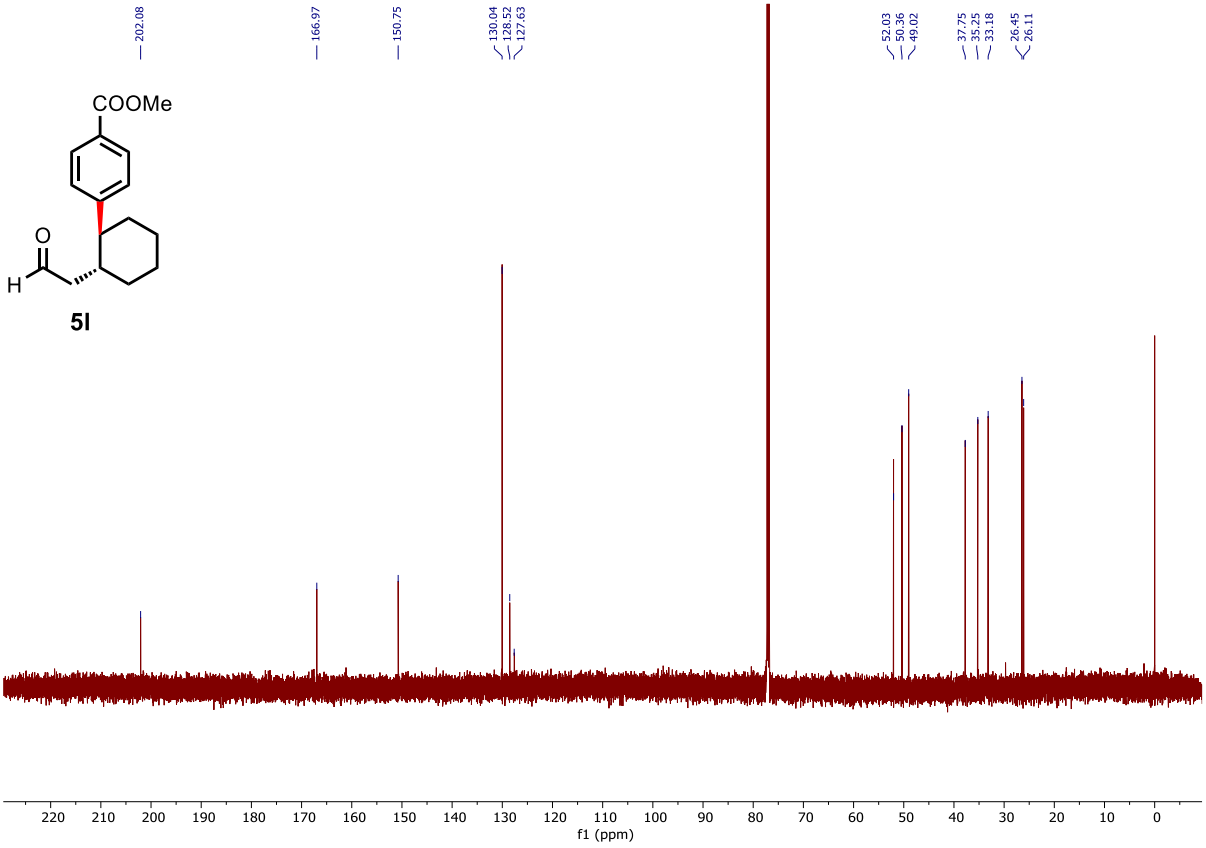

9.09
9.09
9.09
7.95
7.94
7.19
7.18
3.91
3.01
2.99
2.79
2.77
2.31
2.31
1.89
1.87
1.86
1.84
1.73
1.71
1.68
1.66
1.65
1.29
1.27
1.26
1.25
1.24
1.23
1.23
1.21
1.19
1.17
1.15
COOMe
O
H
COOMe
0.98
4.01
4.00
6.00
1.97
2.01
2.00
4.13
2.12
5.34
f1 (ppm)

5k$_{di}$

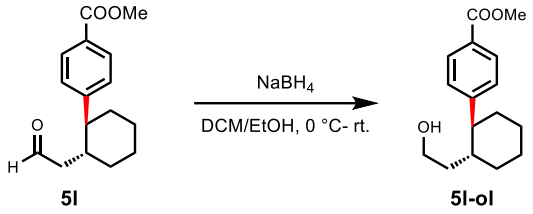

202.45
166.91
143.36
131.00
129.52
128.65
52.10
48.61
44.03
42.31
41.80
27.54
26.89
26.52
COOMe
O
H
COOMe
f1 (ppm)

5k$_{di}$

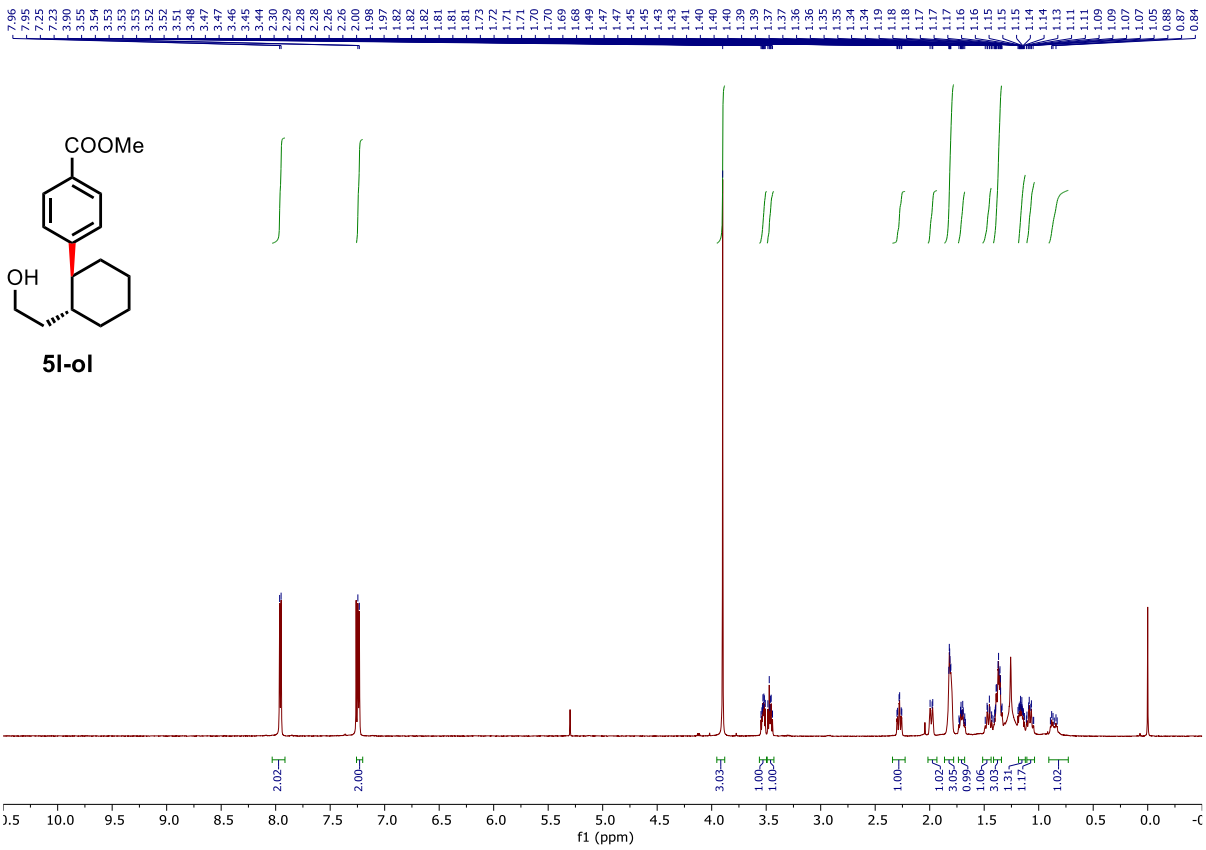

COOMe
O
H
5l
f1 (ppm)

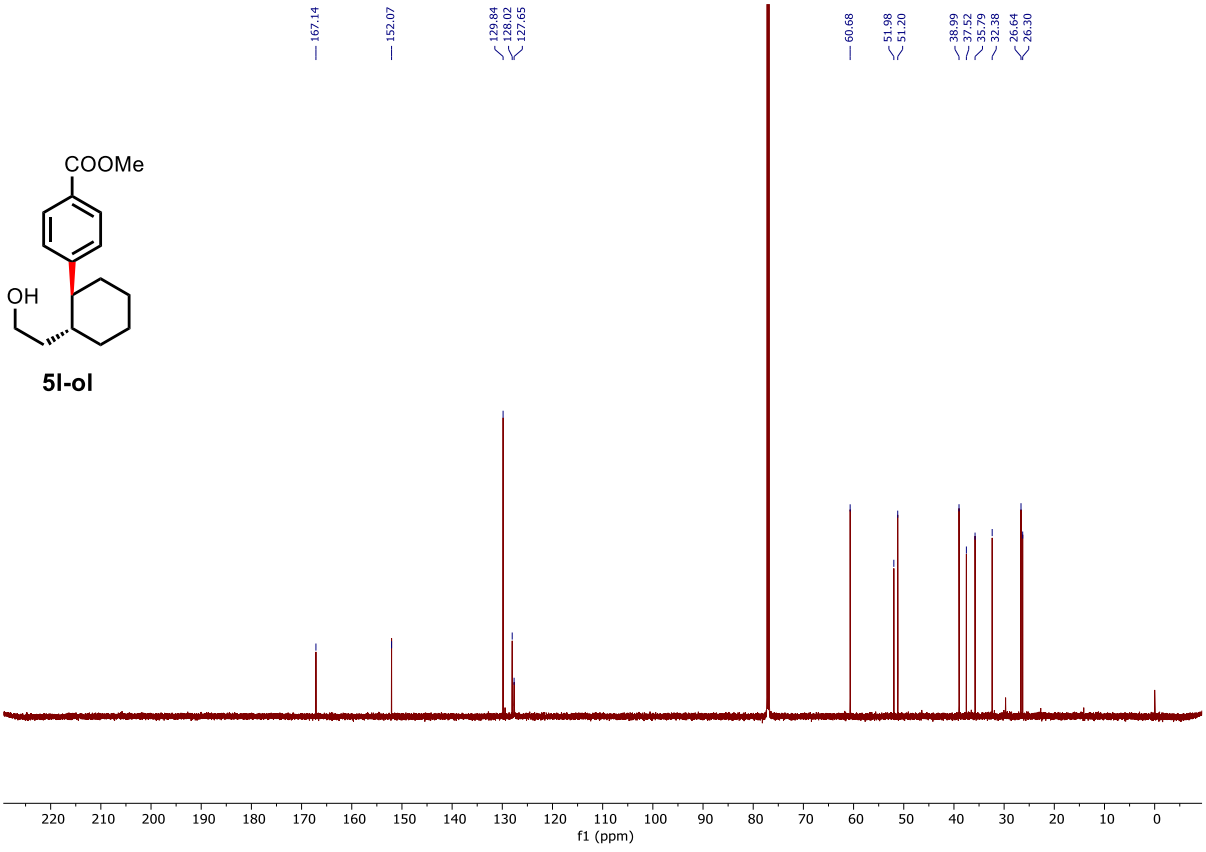

COOMe
O
H
5l
f1 (ppm)

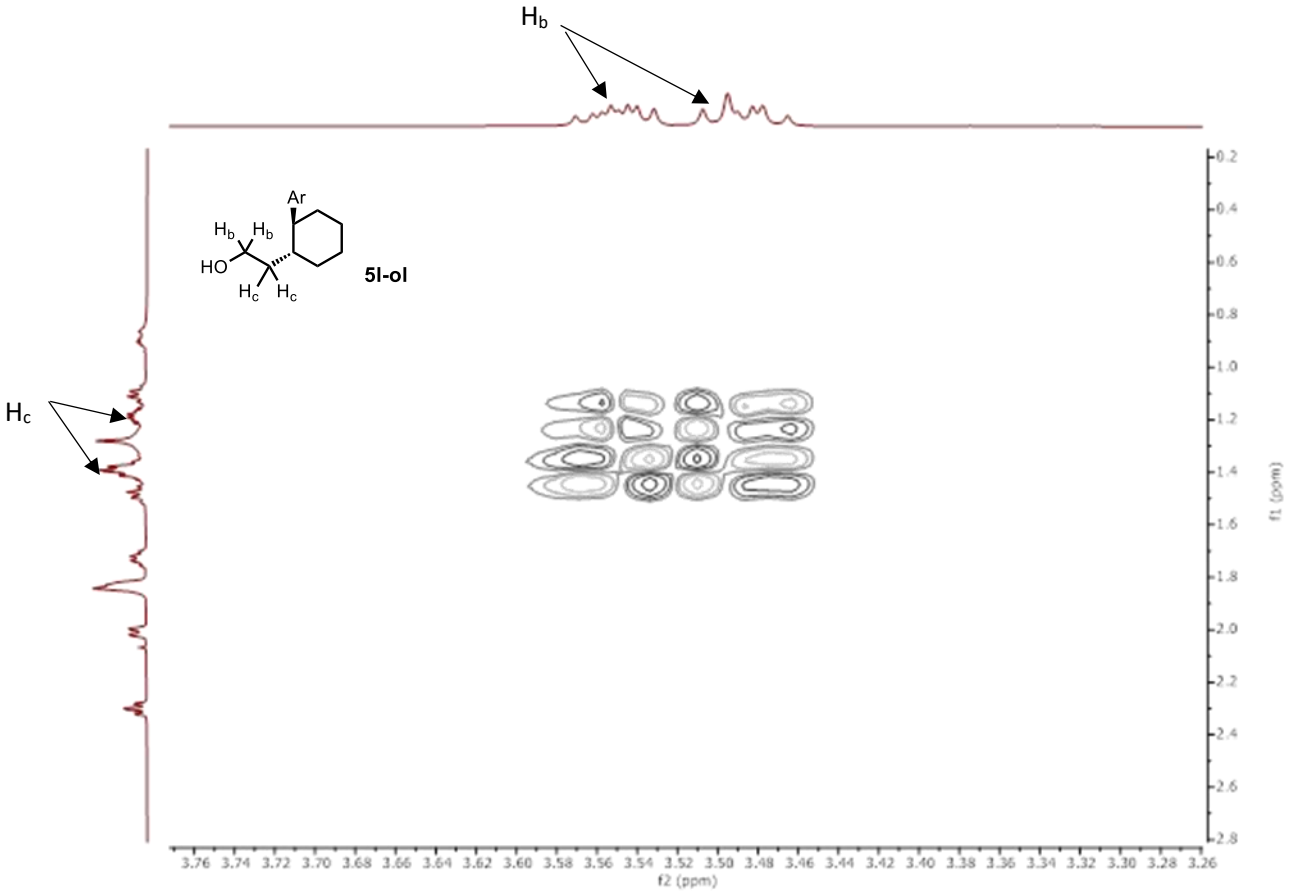
The corresponding alcohol **5l-ol** was obtained by reducing the aldehyde **5l** with the following procedure.



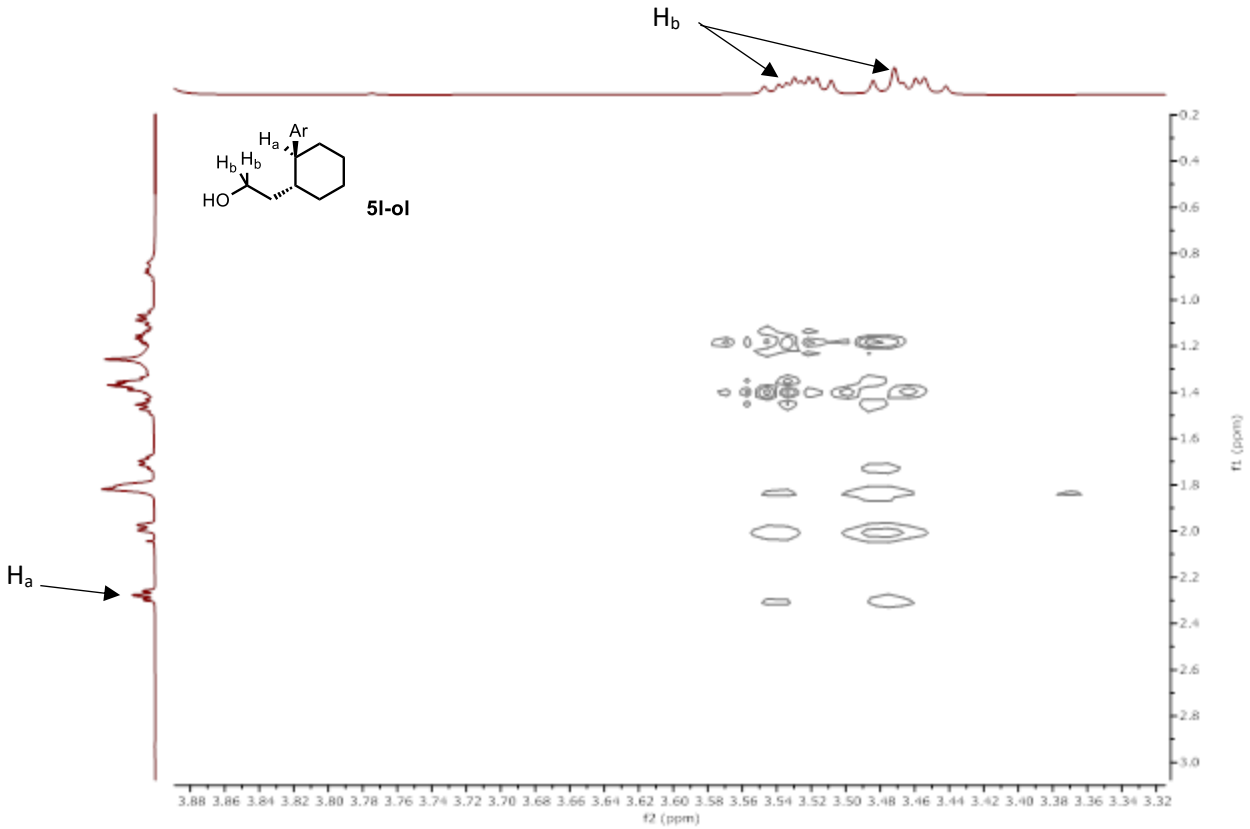
5l **5l-ol**


COOMe
OH
5l-ol
f1 (ppm)

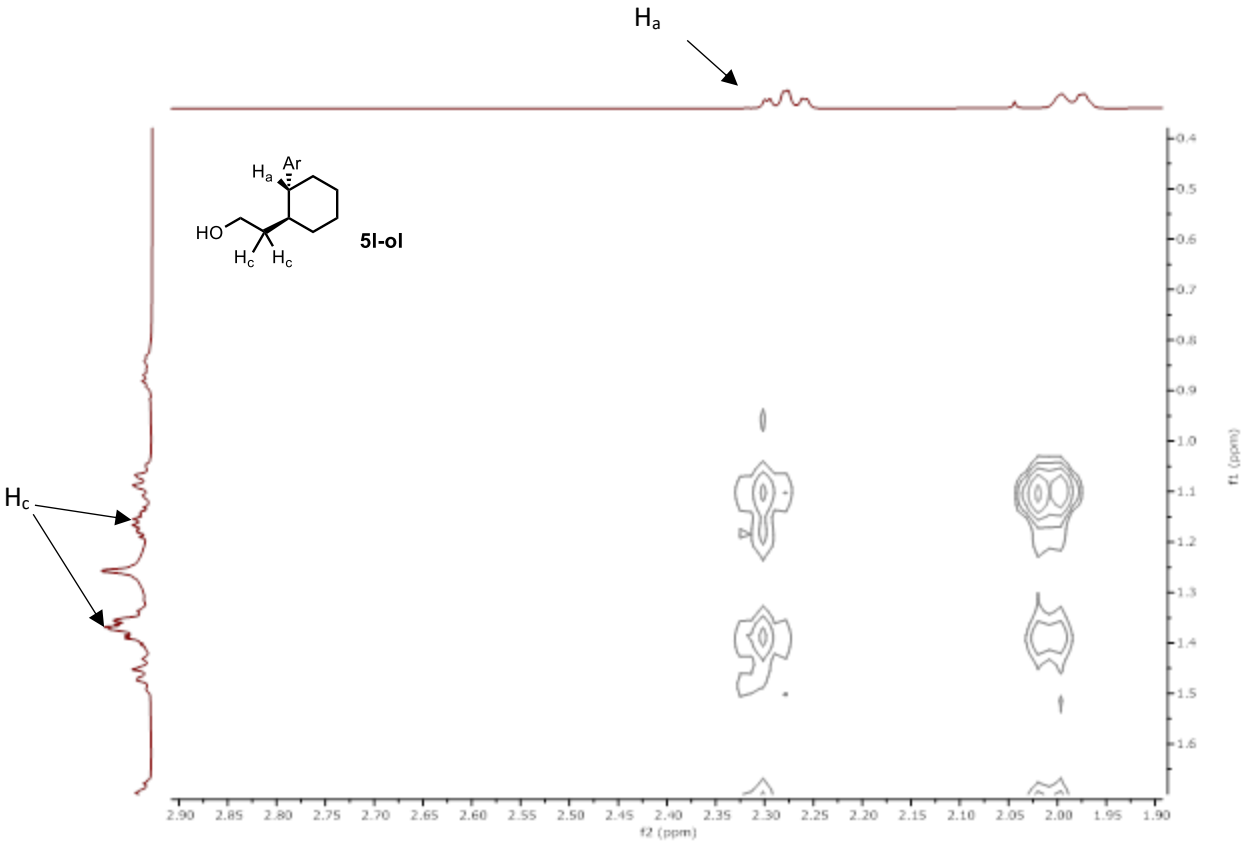

COOMe
OH
5l-ol
f1 (ppm)



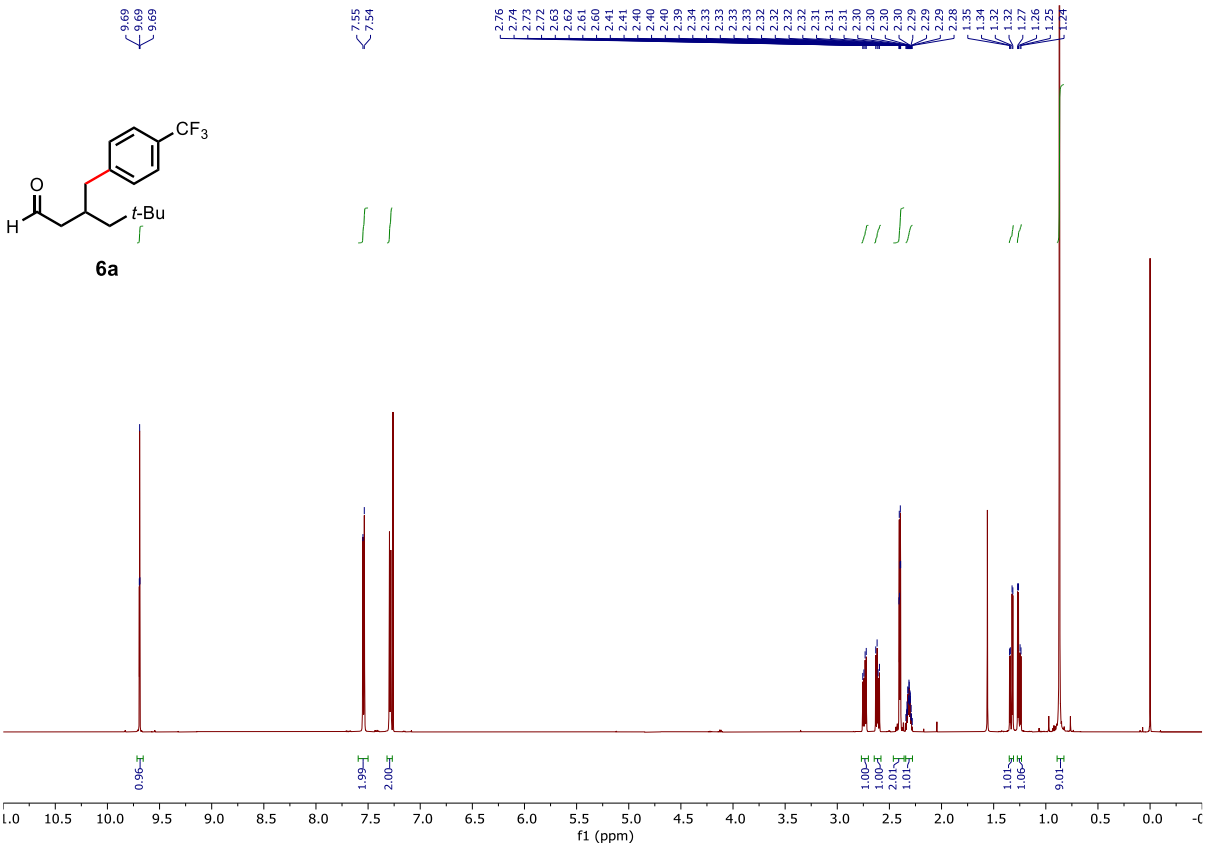
COSY 2D spectrum for **5l-ol**

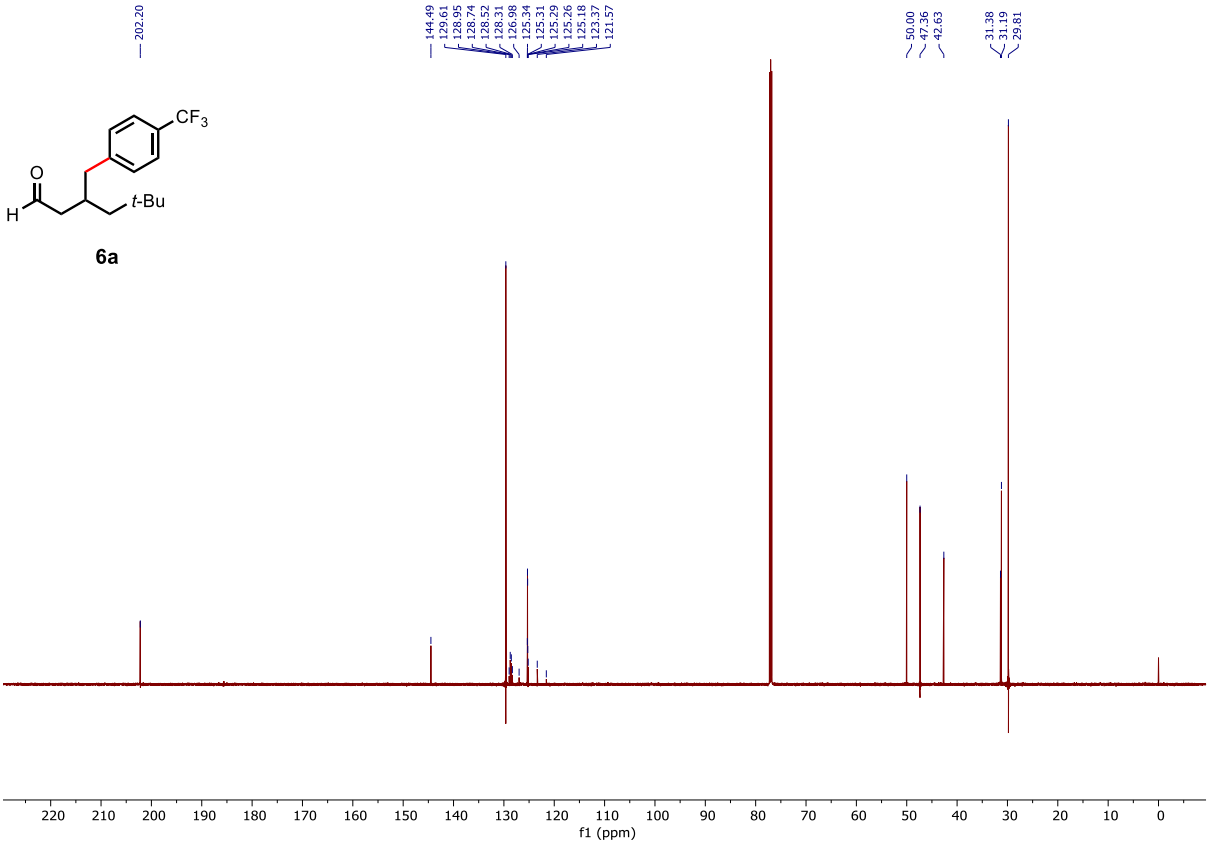


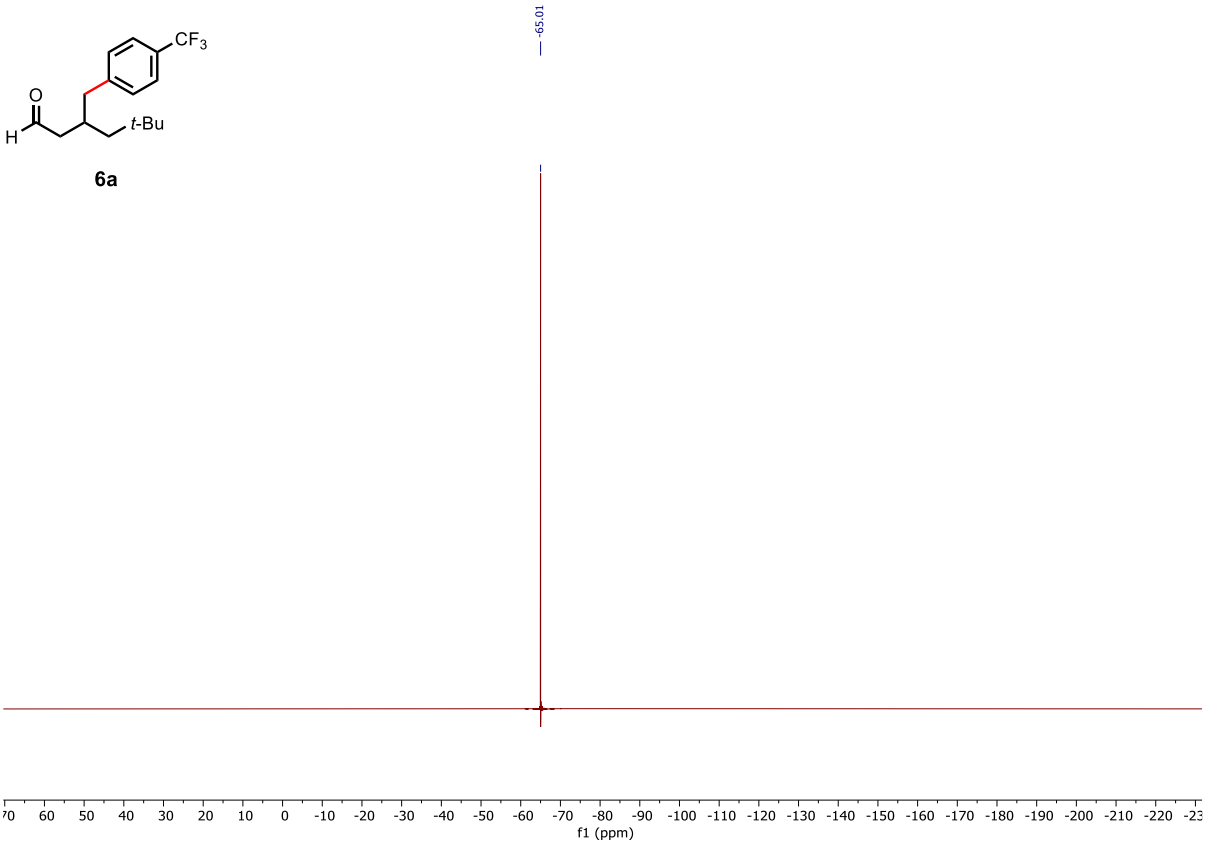
NOE 2D spectrum for **5l-ol**



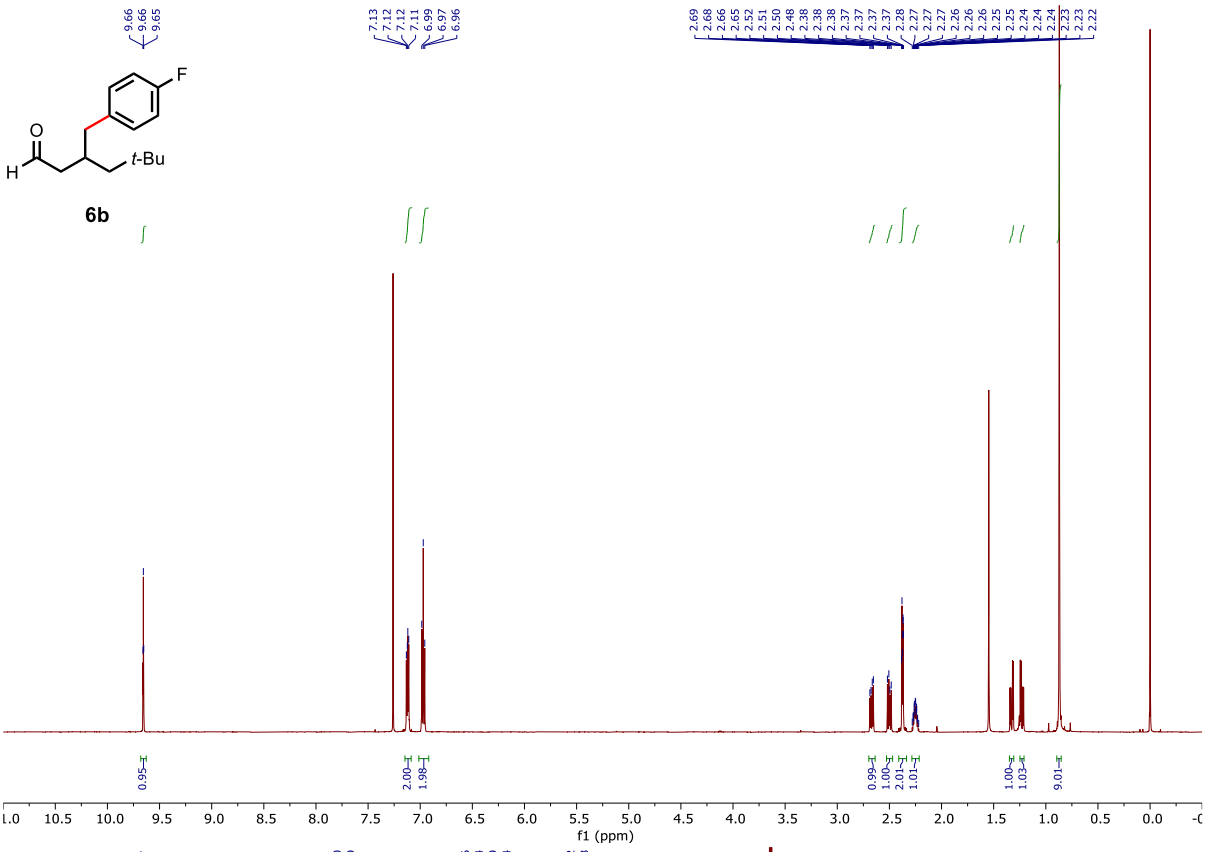
NOE 2D spectrum for **5l-ol**

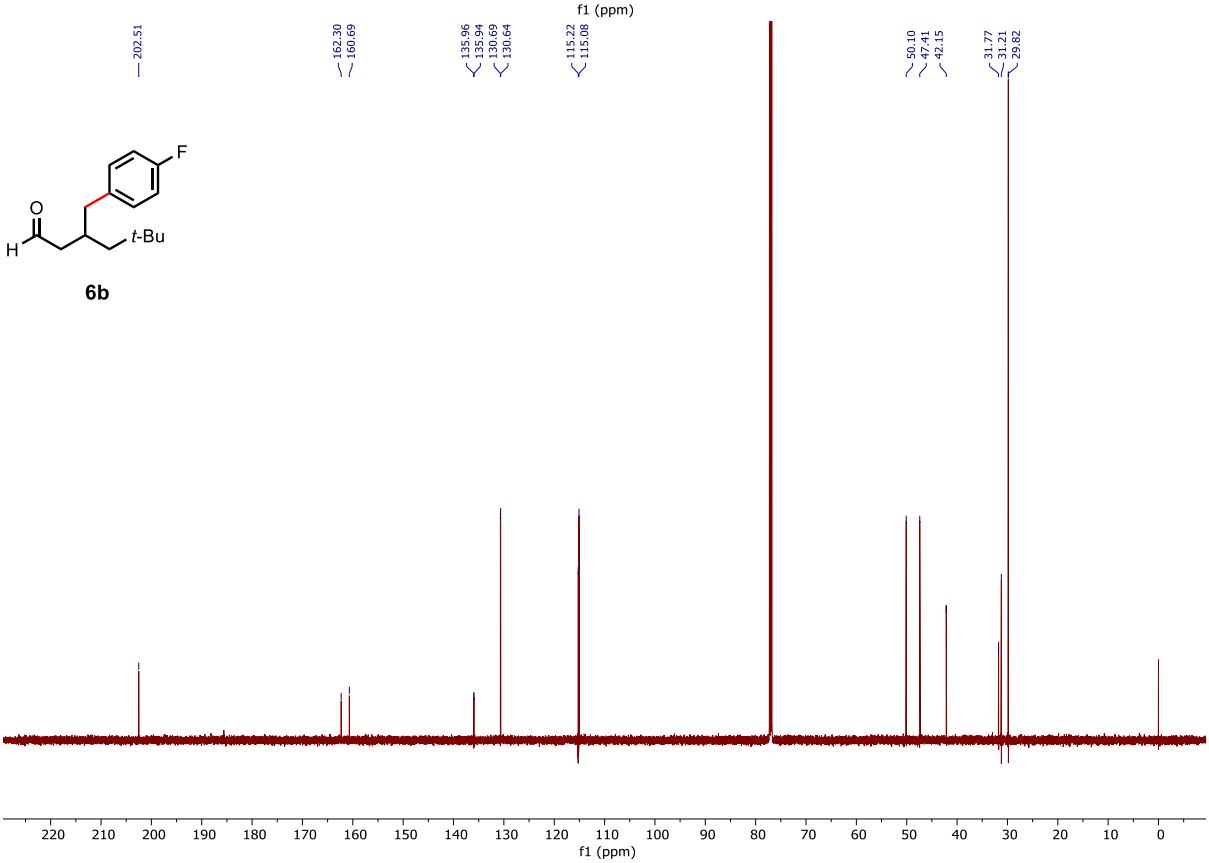

9.69
9.69
9.69
7.55
7.54
2.76
2.74
2.73
2.72
2.63
2.62
2.61
2.60
2.41
2.41
2.40
2.40
2.40
2.39
2.34
2.33
2.33
2.33
2.32
2.32
2.32
2.31
2.31
2.31
2.30
2.30
2.30
2.30
2.29
2.29
2.29
2.28
1.35
1.34
1.32
1.32
1.27
1.26
1.25
1.24
CF3
O
H
t-Bu
6a
0.96
1.99
2.00
1.00
1.00
2.01
1.01
1.01
1.06
9.01
f1 (ppm)

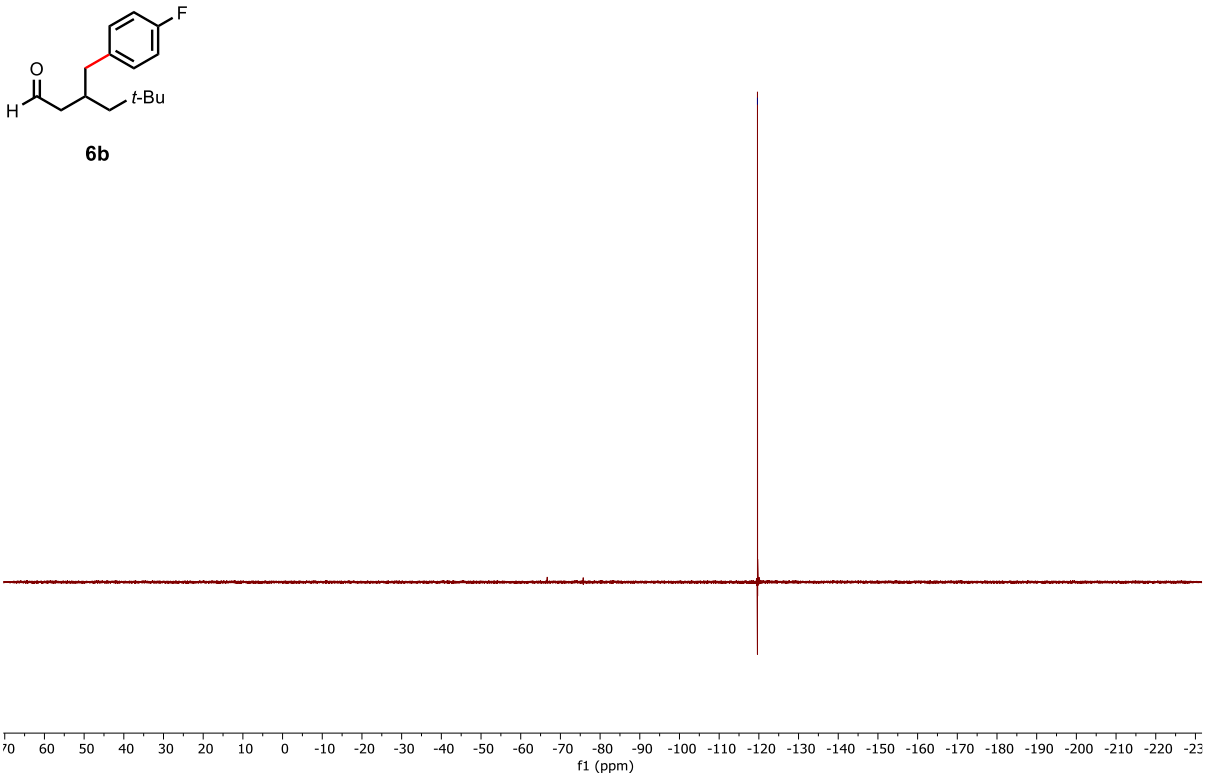

202.20
144.49
129.61
128.95
128.74
128.52
128.31
126.98
125.34
125.31
125.29
125.26
125.18
123.37
121.57
50.00
47.36
42.63
31.38
31.19
29.81
CF3
O
H
t-Bu
6a
f1 (ppm)

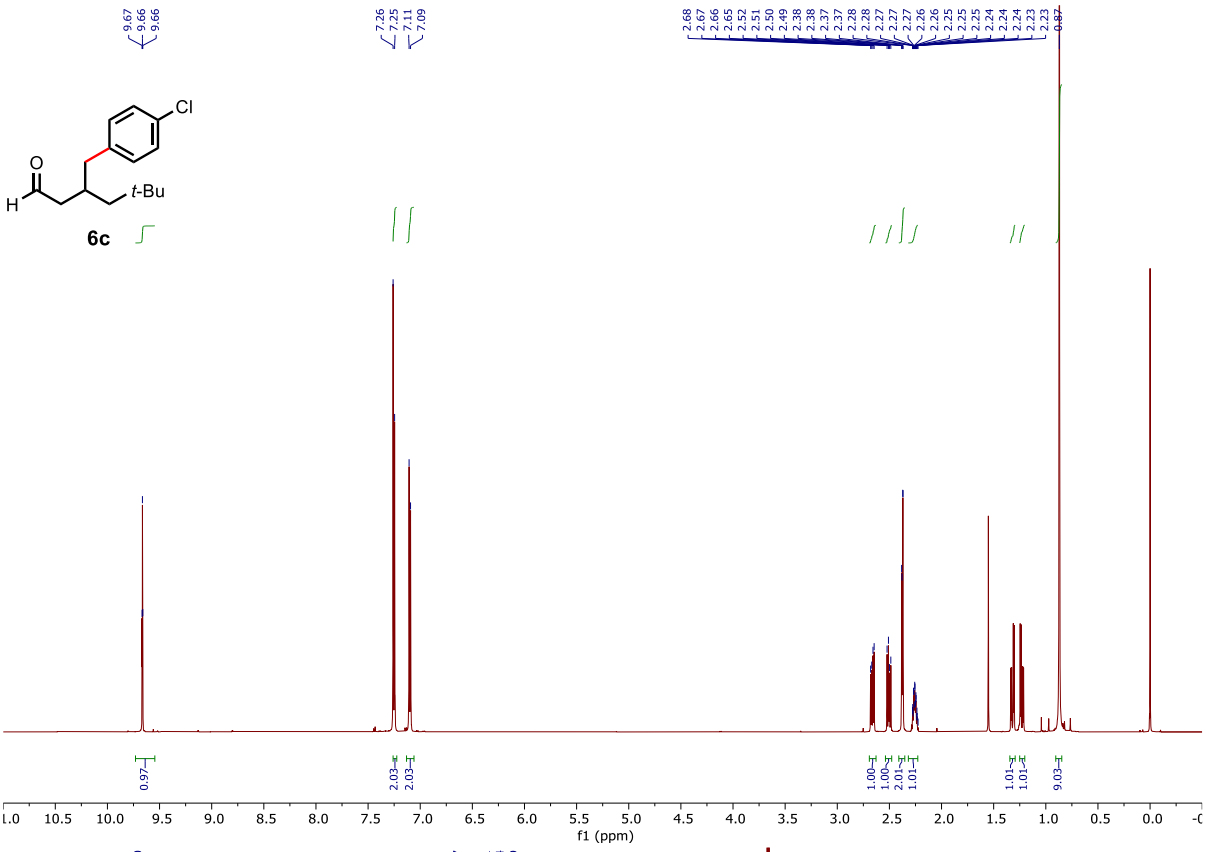

CF3
O
H
t-Bu
-65.01
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)

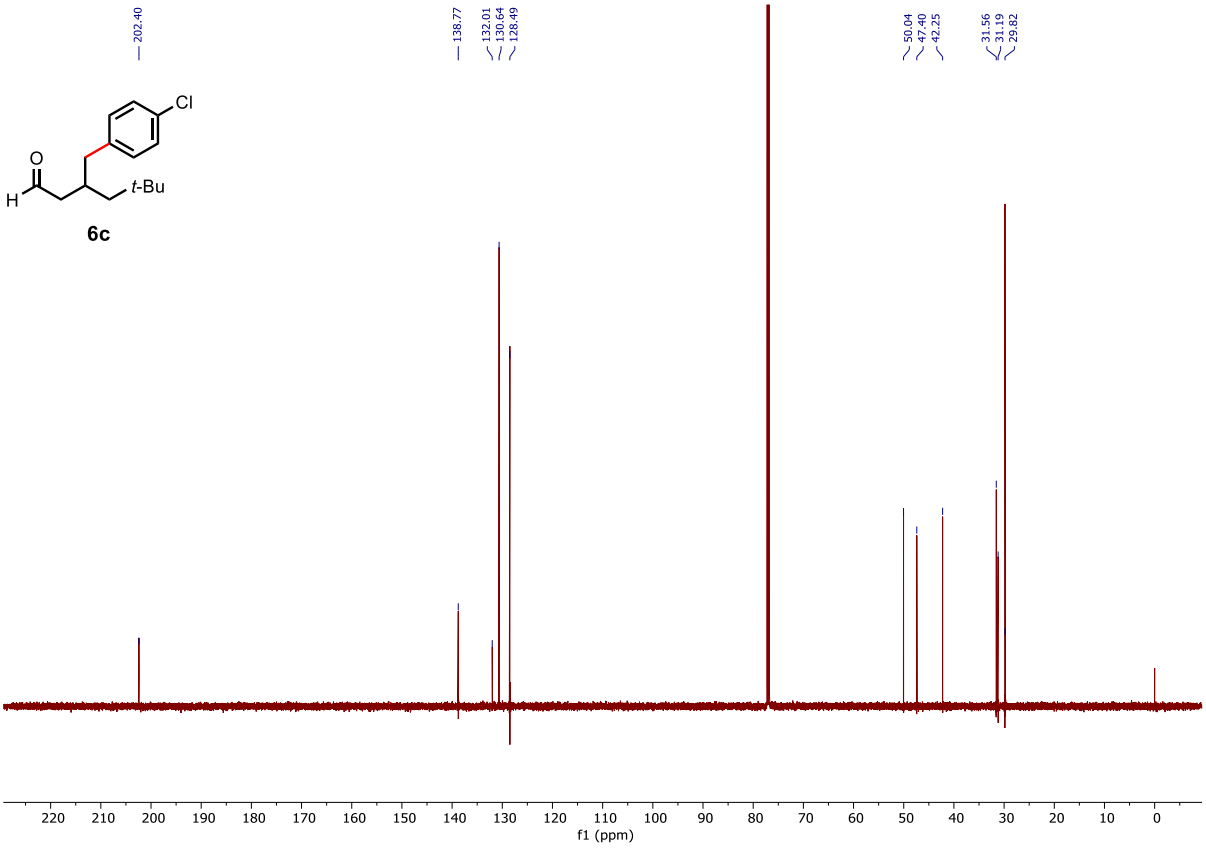
6a

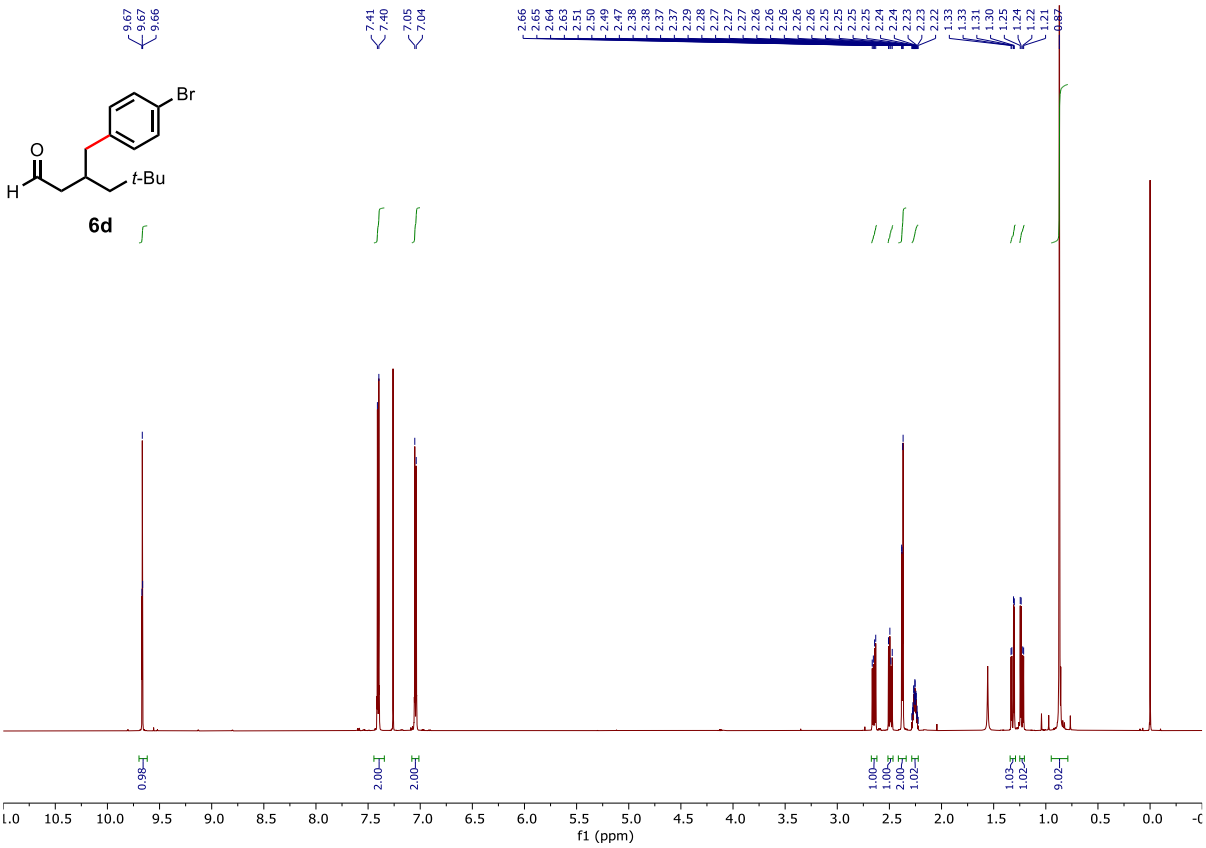

9.66
9.66
9.65
7.13
7.12
7.12
7.11
6.99
6.97
6.96
2.69
2.68
2.66
2.65
2.52
2.51
2.50
2.48
2.38
2.38
2.37
2.37
2.37
2.28
2.27
2.27
2.26
2.26
2.25
2.25
2.24
2.24
2.24
2.23
2.23
2.22
F
O
H
t-Bu
6b
0.95
2.00
1.98
0.99
1.00
2.01
1.01
1.00
1.03
9.01
f1 (ppm)

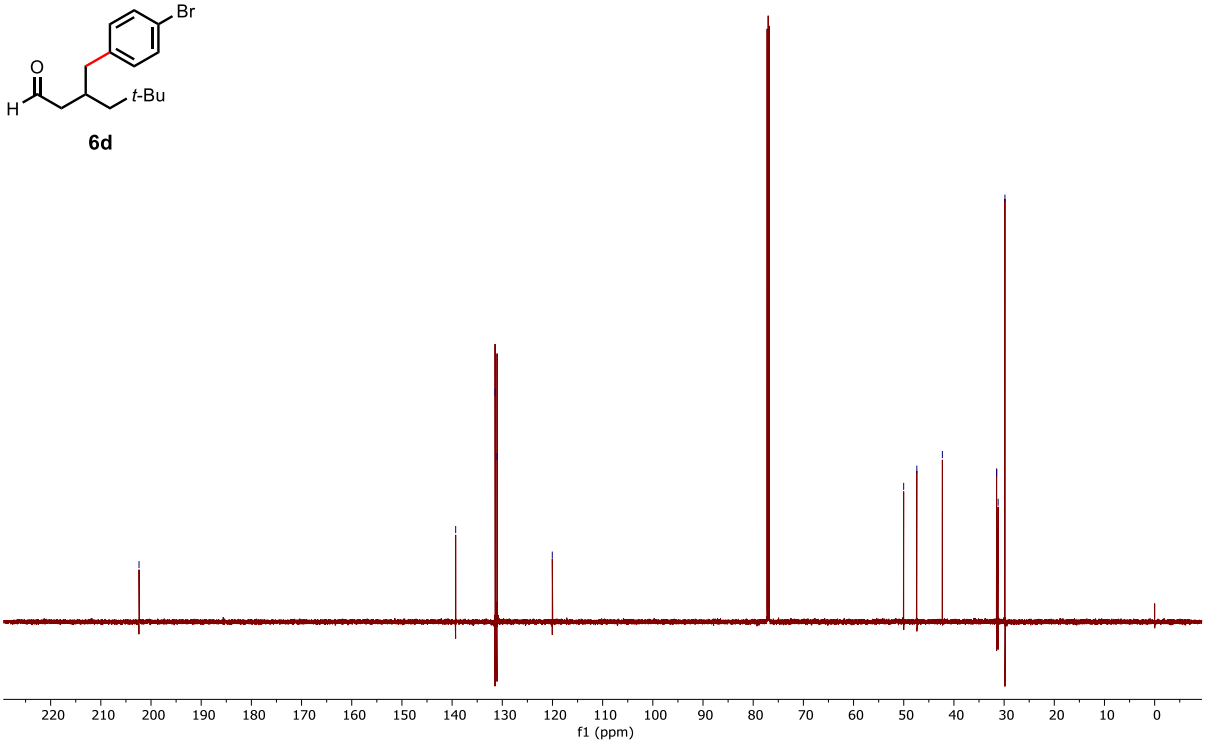

202.51
162.30
160.69
135.96
135.94
130.69
130.64
115.22
115.08
50.10
47.41
42.15
31.77
31.21
29.82
F
O
H
t-Bu
6b
f1 (ppm)

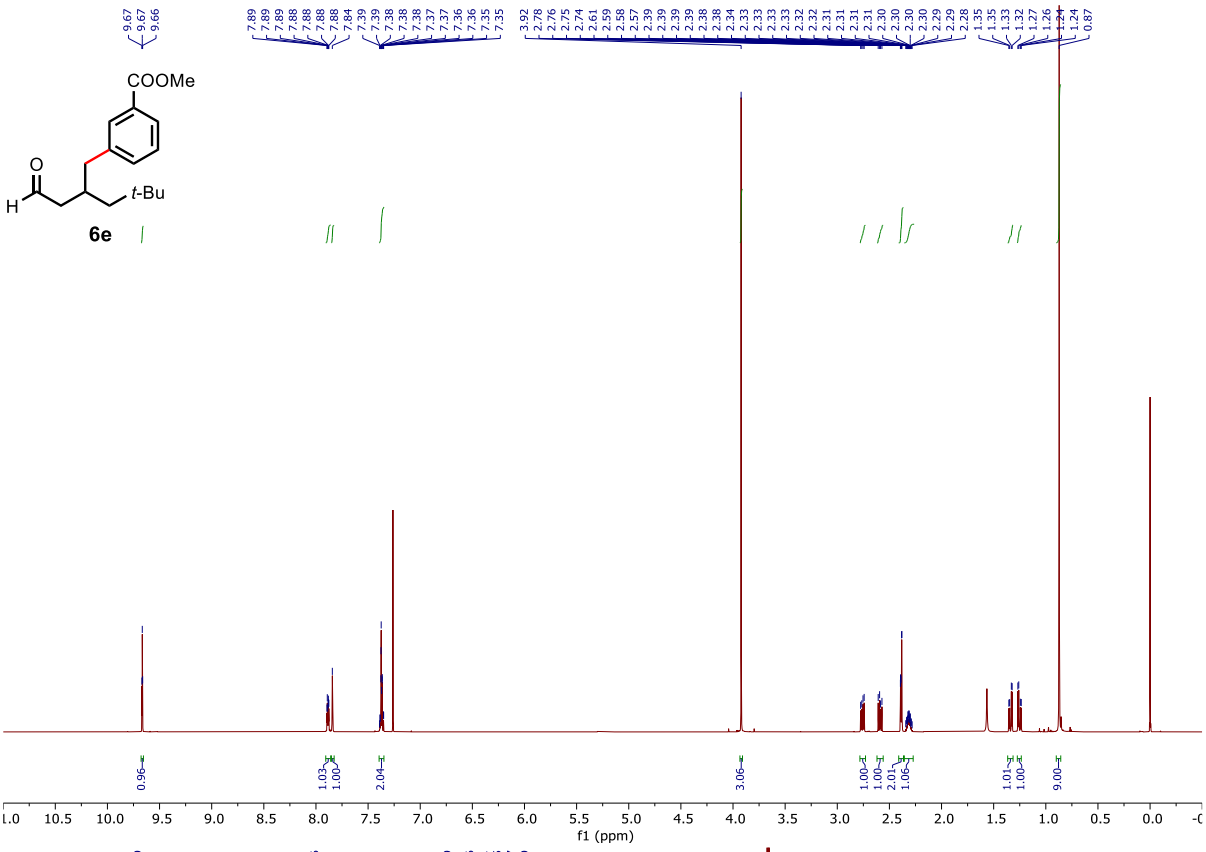

-119.65
F
O
H
t-Bu
6b
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)

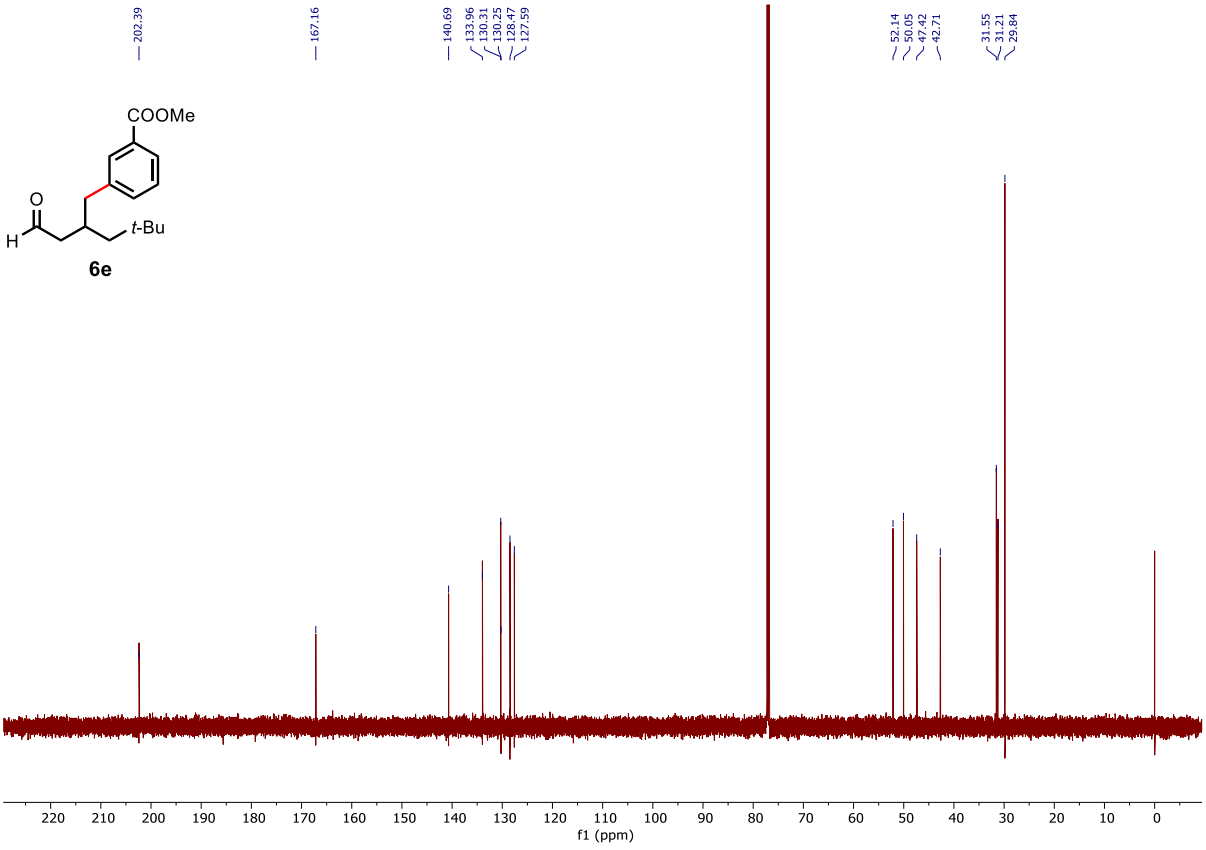

9.67
9.66
9.66
7.26
7.25
7.11
7.09
2.68
2.67
2.66
2.65
2.52
2.51
2.50
2.49
2.38
2.38
2.37
2.37
2.28
2.28
2.27
2.27
2.27
2.26
2.26
2.25
2.25
2.25
2.24
2.24
2.24
2.23
2.23
0.87
Cl
O
H
t-Bu
6c
0.97
2.03
2.03
1.00
1.00
2.01
1.01
1.01
1.01
9.03
f1 (ppm)

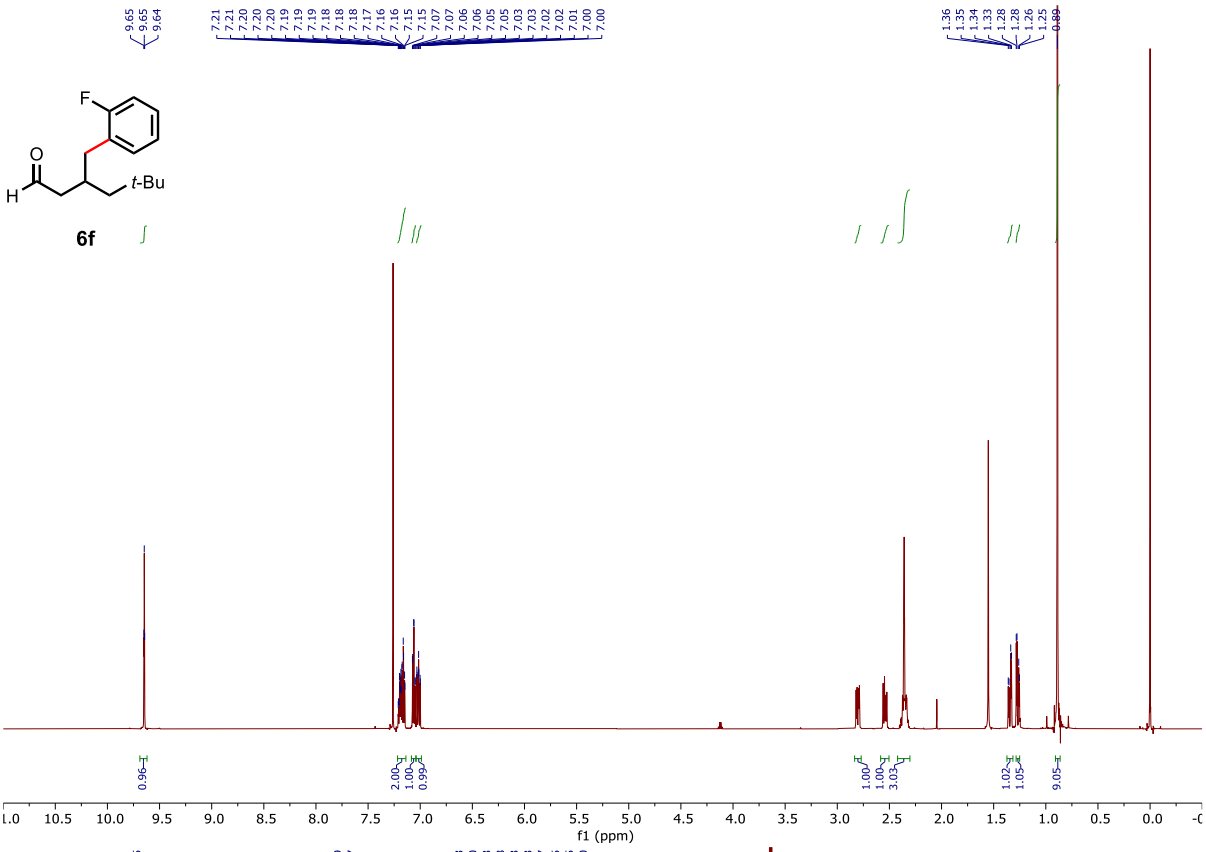

202.40
138.77
132.01
130.64
128.49
50.04
47.40
42.25
31.56
31.19
29.82
Cl
O
H
t-Bu
6c
f1 (ppm)

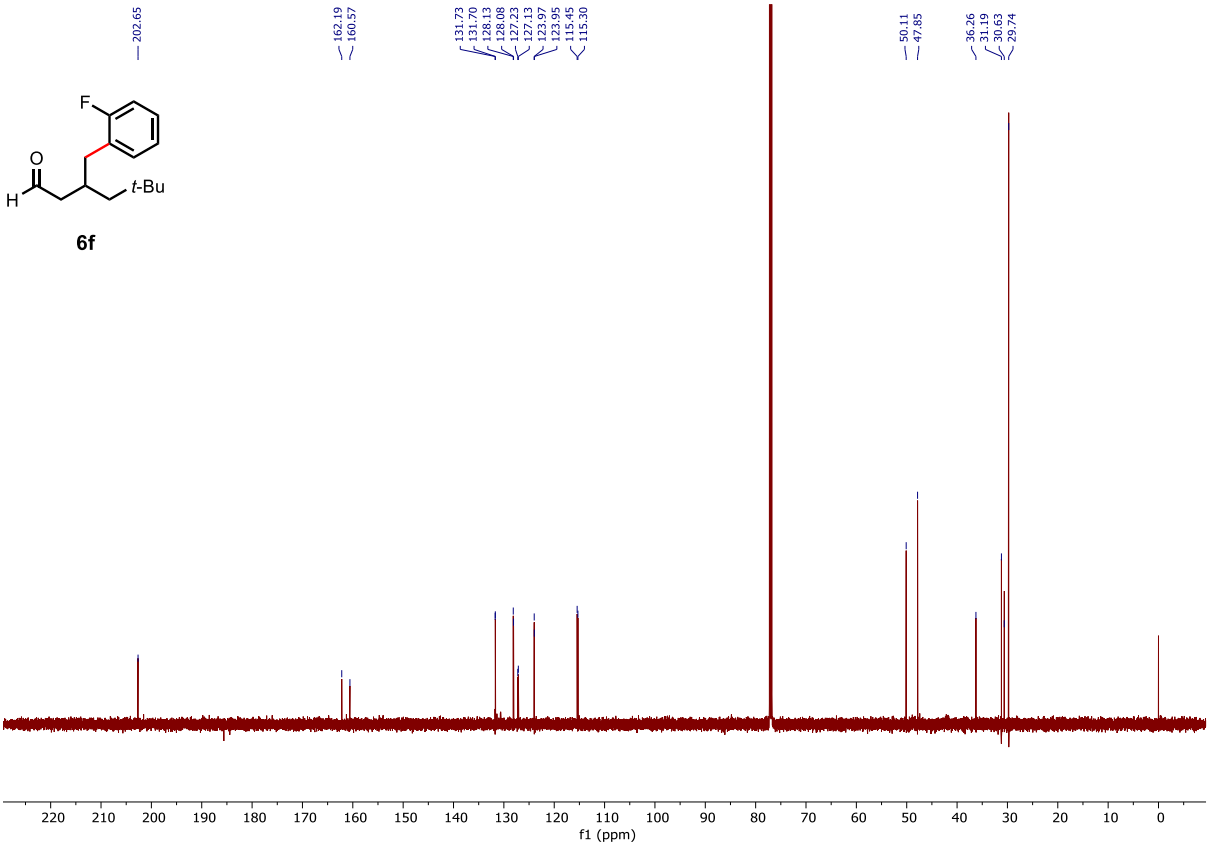

Br
O
H
t-Bu
6d
f1 (ppm)

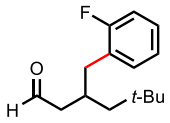

Br
O
H
t-Bu
6d
f1 (ppm)


COOMe
O
H
t-Bu
6e
f1 (ppm)


COOMe
O
H
t-Bu
6e
f1 (ppm)

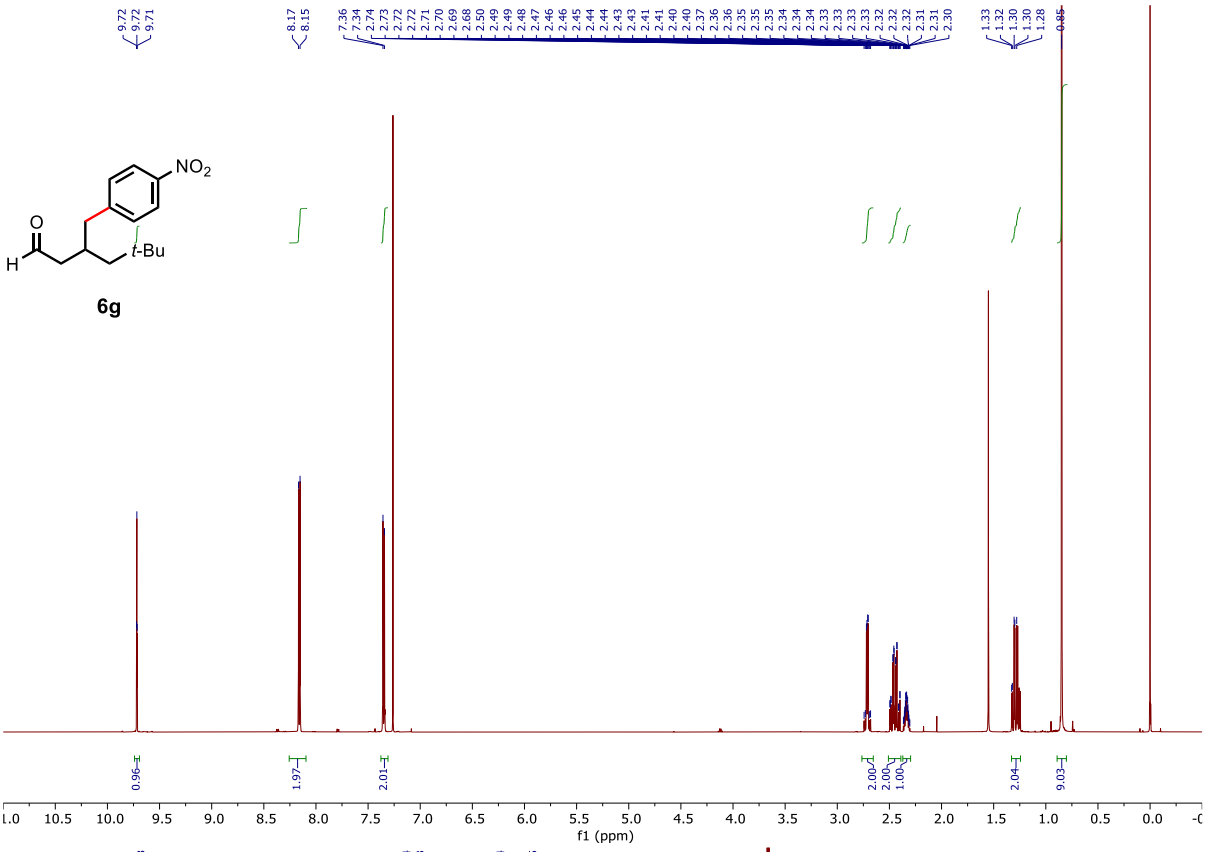

F
O
H
t-Bu
6f
f1 (ppm)

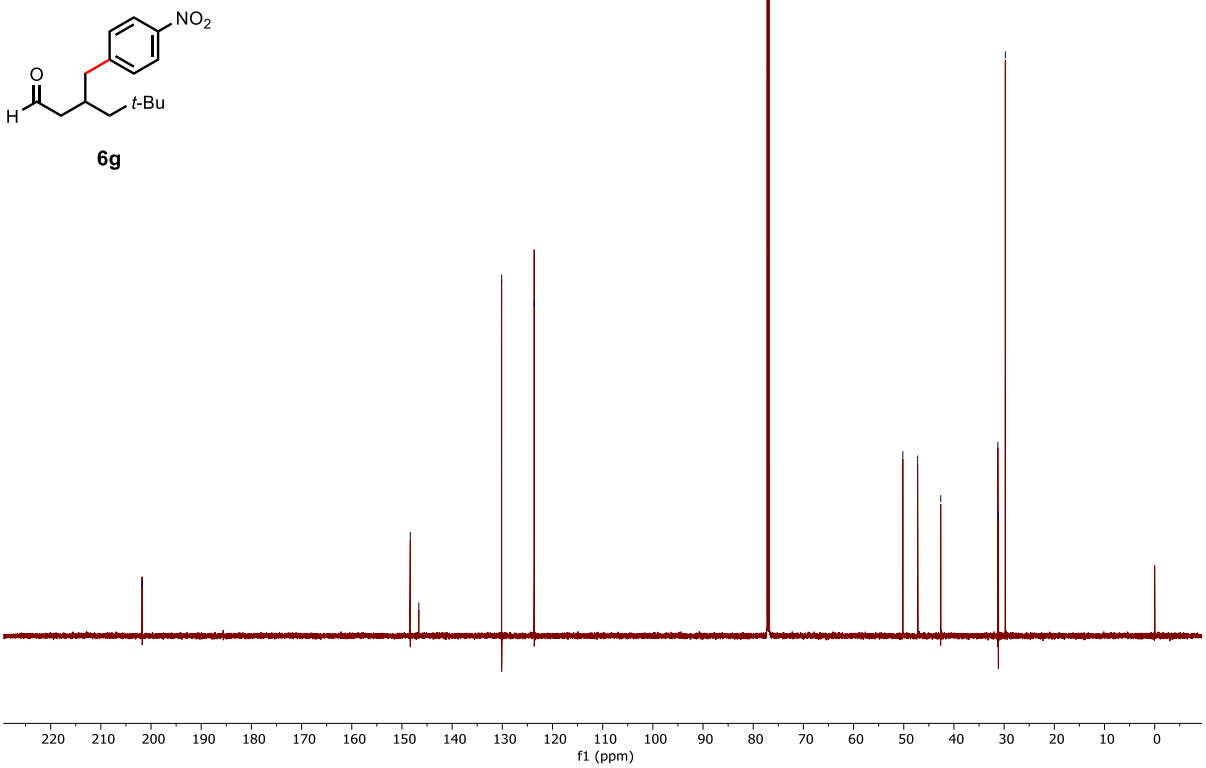

F
O
H
t-Bu
6f
f1 (ppm)


F
O
H
t-Bu

6f

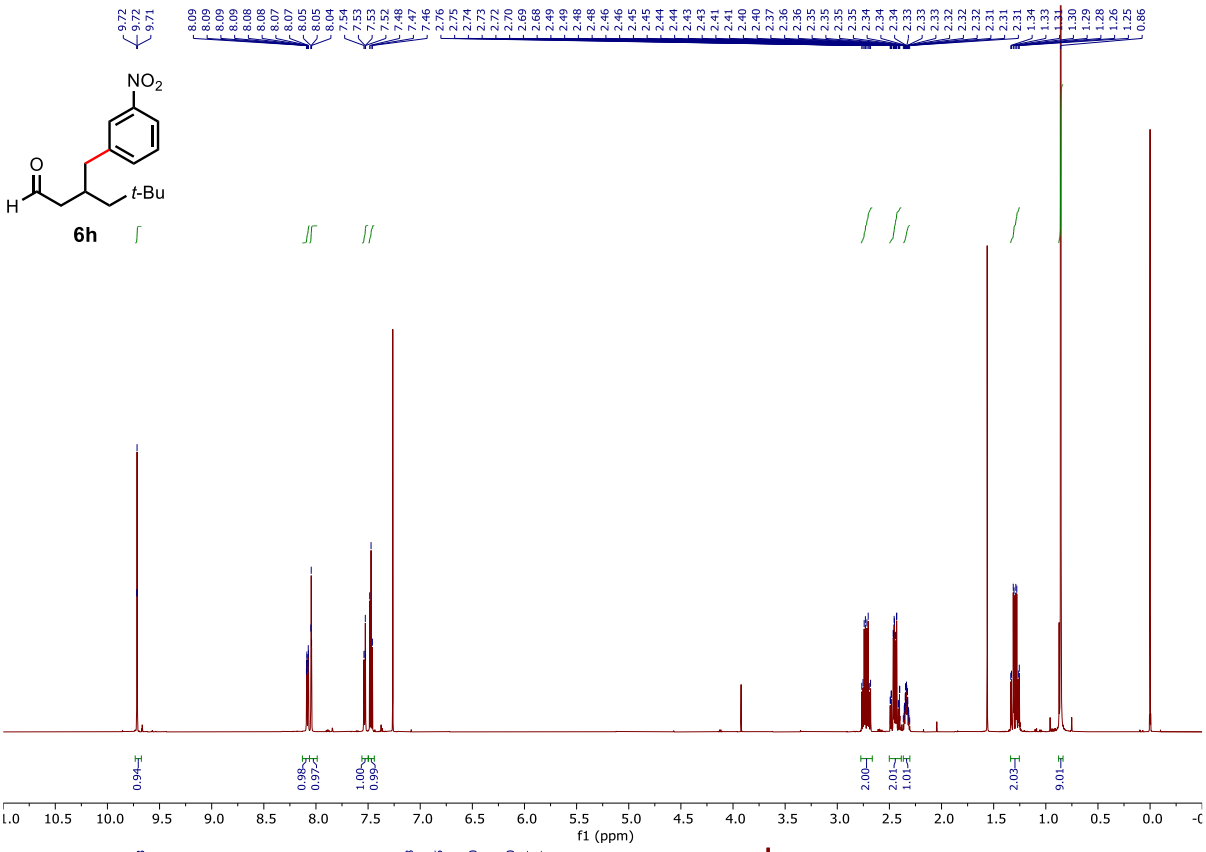
-120.03
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)

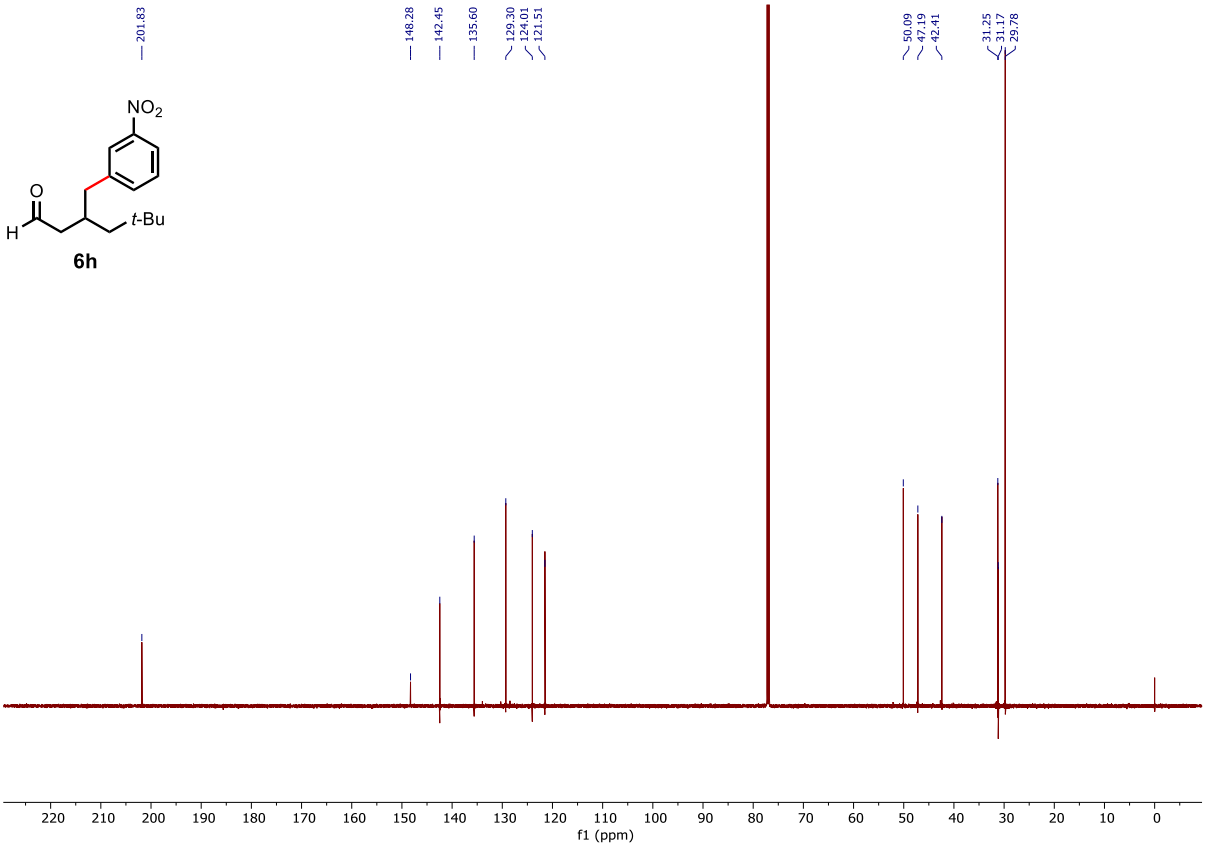

9.72
9.72
9.71
8.17
8.15
7.36
7.34
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.16
7.15
7.14
7.13
7.12
7.11
7.10
7.09
7.08
7.07
7.06
7.05
7.04
7.03
7.02
7.01
7.00
6.99
6.98
6.97
6.96
6.95
6.94
6.93
6.92
6.91
6.90
6.89
6.88
6.87
6.86
6.85
6.84
6.83
6.82
6.81
6.80
6.79
6.78
6.77
6.76
6.75
6.74
6.73
6.72
6.71
6.70
6.69
6.68
6.67
6.66
6.65
6.64
6.63
6.62
6.61
6.60
6.59
6.58
6.57
6.56
6.55
6.54
6.53
6.52
6.51
6.50
6.49
6.48
6.47
6.46
6.45
6.44
6.43
6.42
6.41
6.40
6.39
6.38
6.37
6.36
6.35
6.34
6.33
6.32
6.31
6.30
1.33
1.32
1.31
1.30
1.28
0.96
1.97
2.01
2.00
2.00
1.00
2.04
9.03
f1 (ppm)

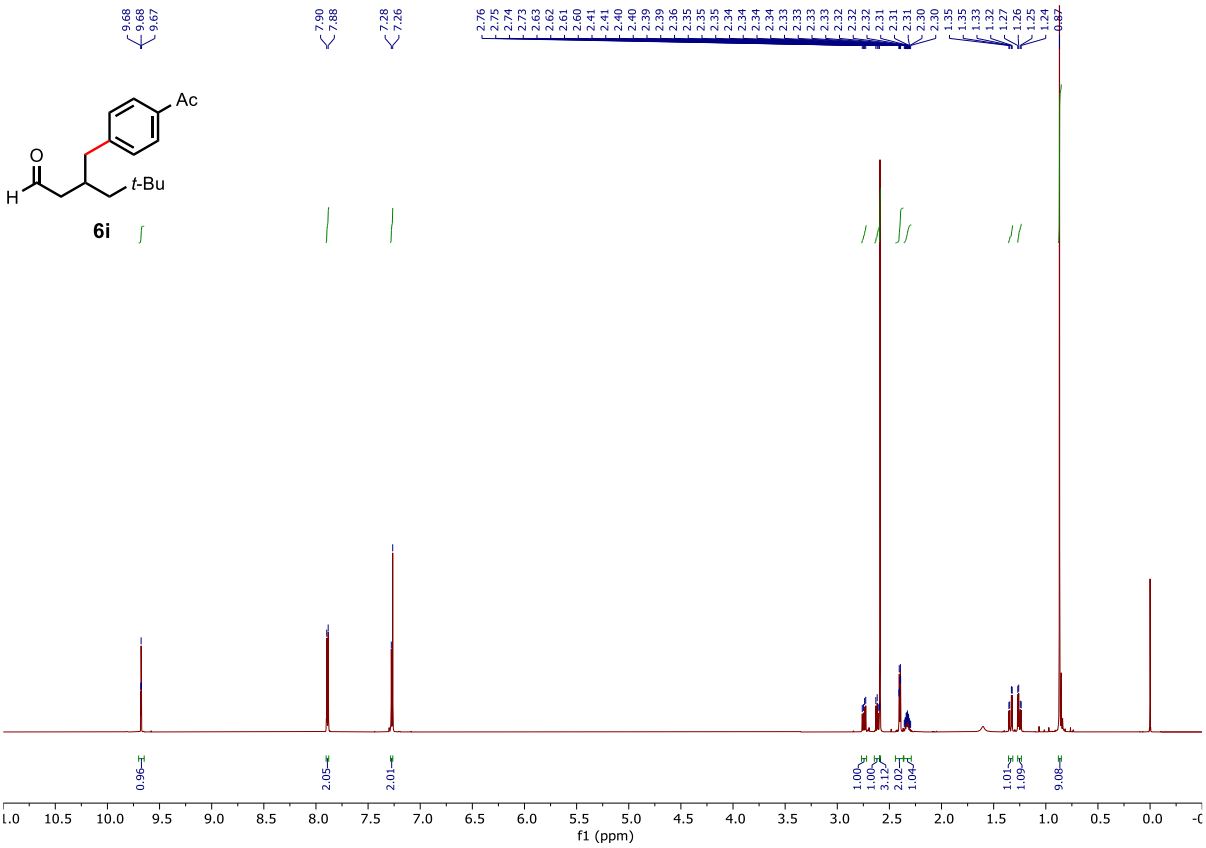

201.78
148.34
146.63
130.14
123.65
50.18
47.24
42.63
31.25
31.14
29.76
f1 (ppm)

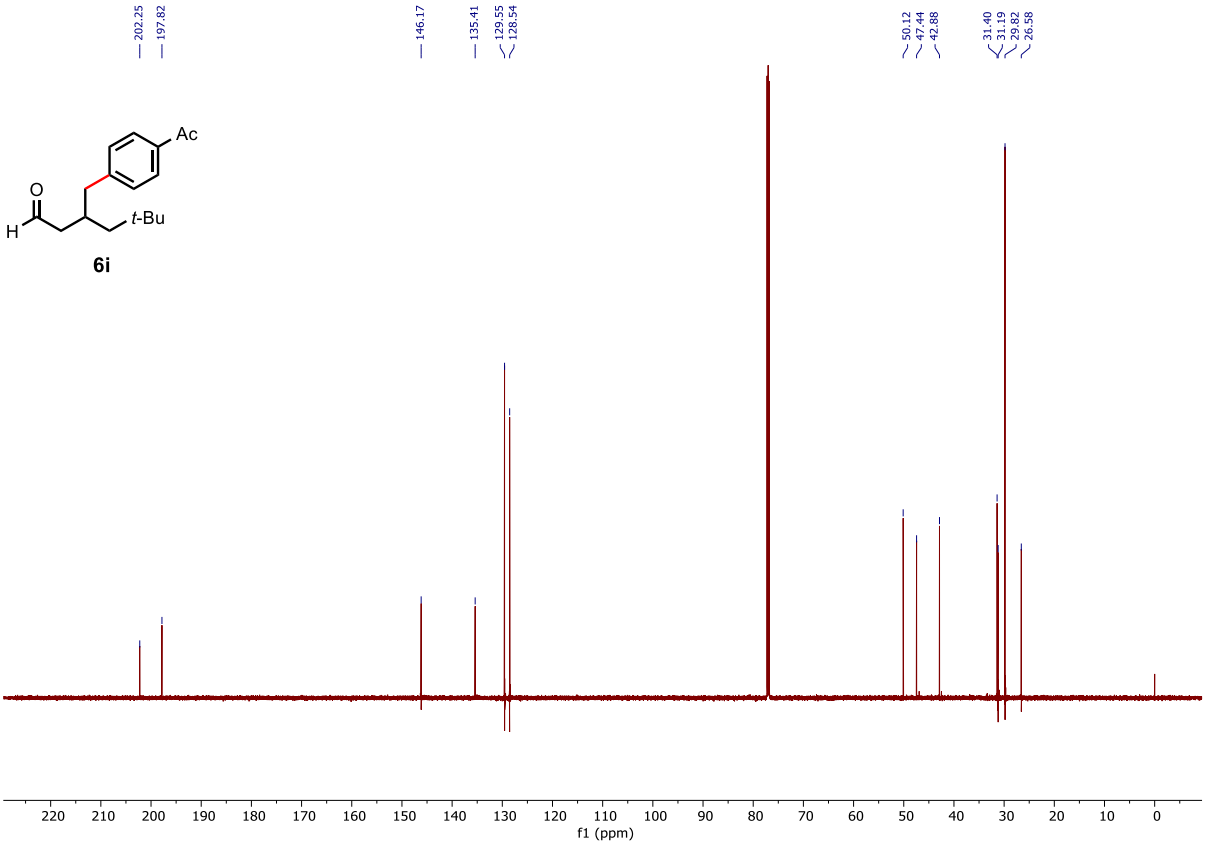
NO2
O
H
t-Bu

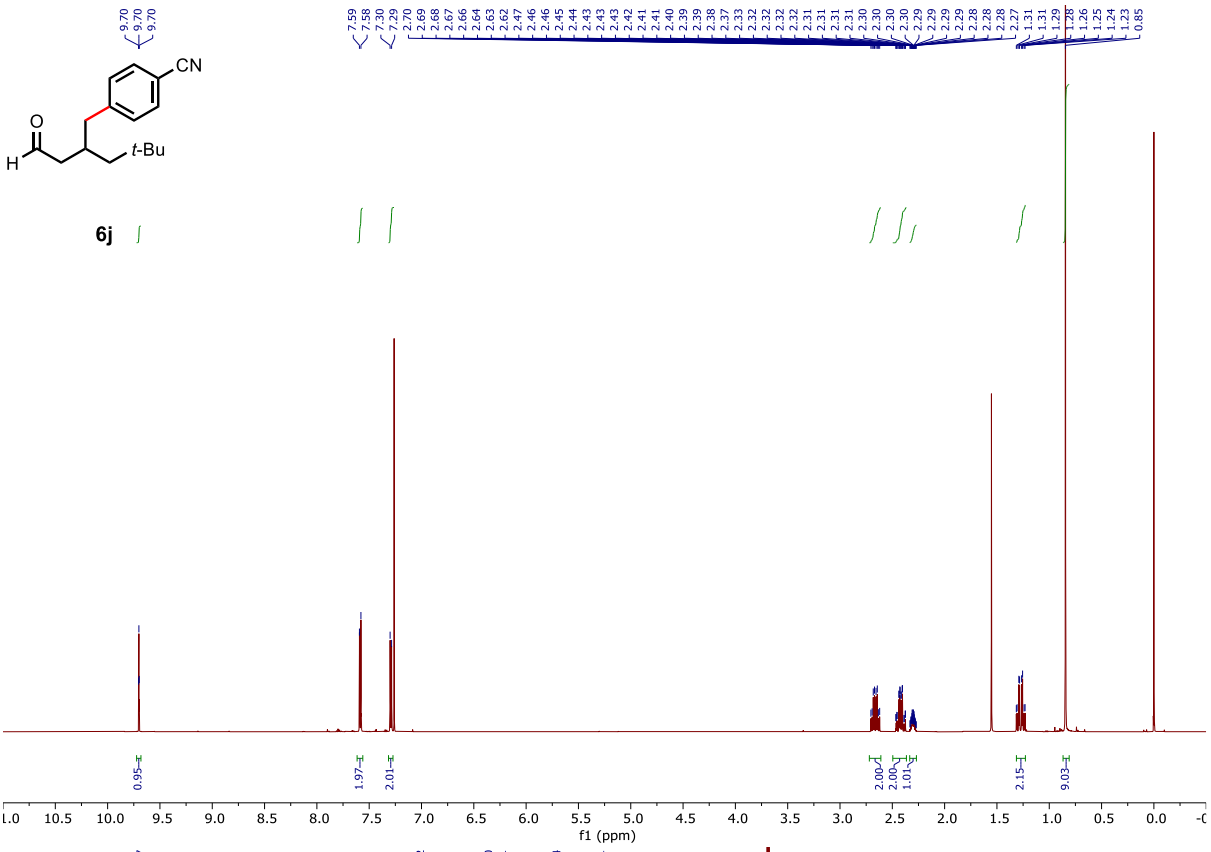
6g

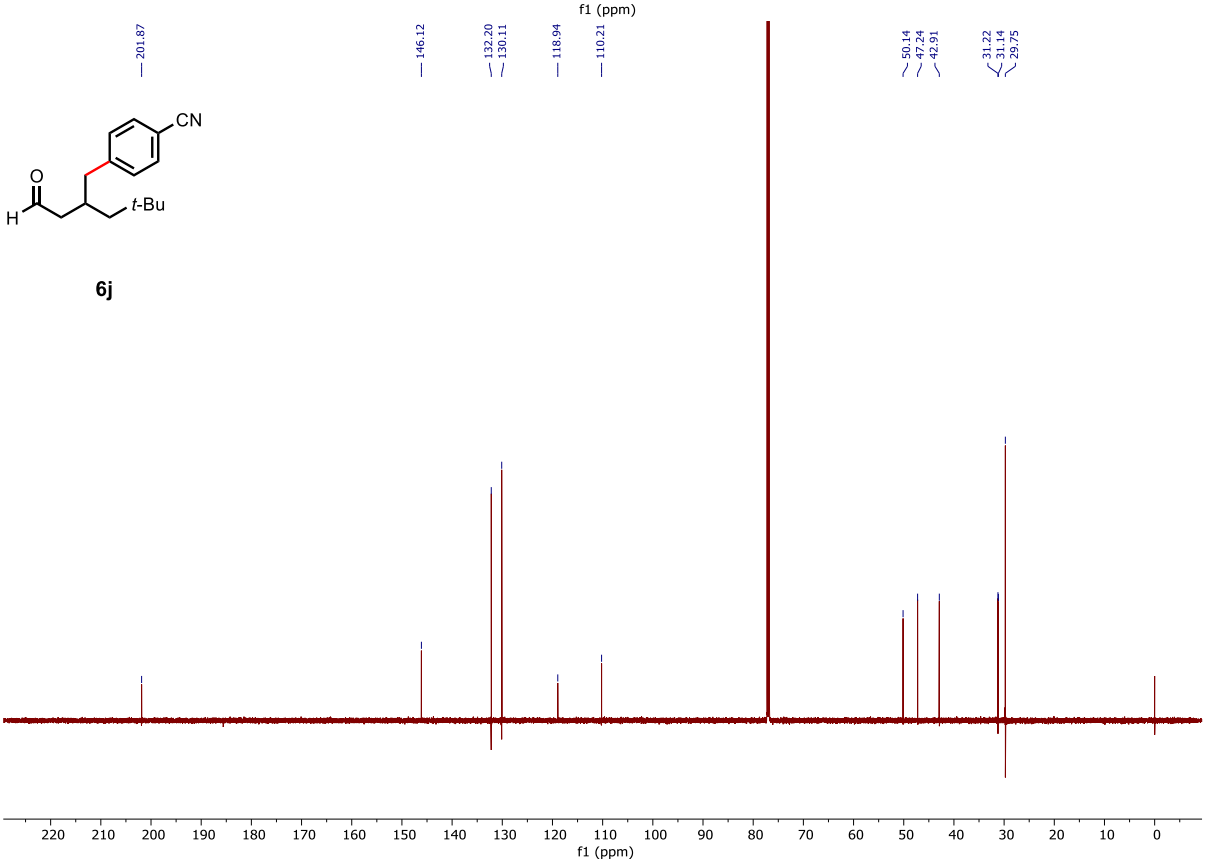

NO2
O
H
t-Bu
6h
f1 (ppm)

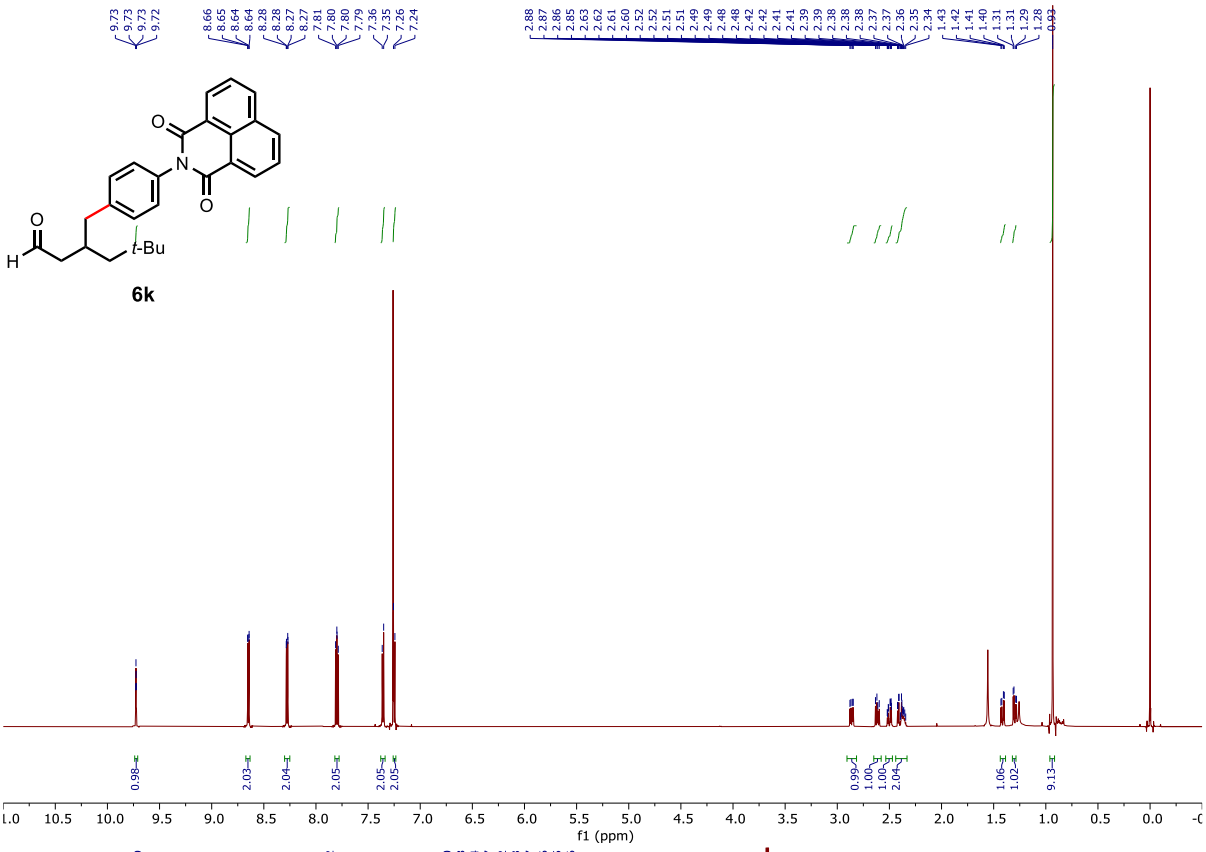

NO2
O
H
t-Bu
6h
f1 (ppm)

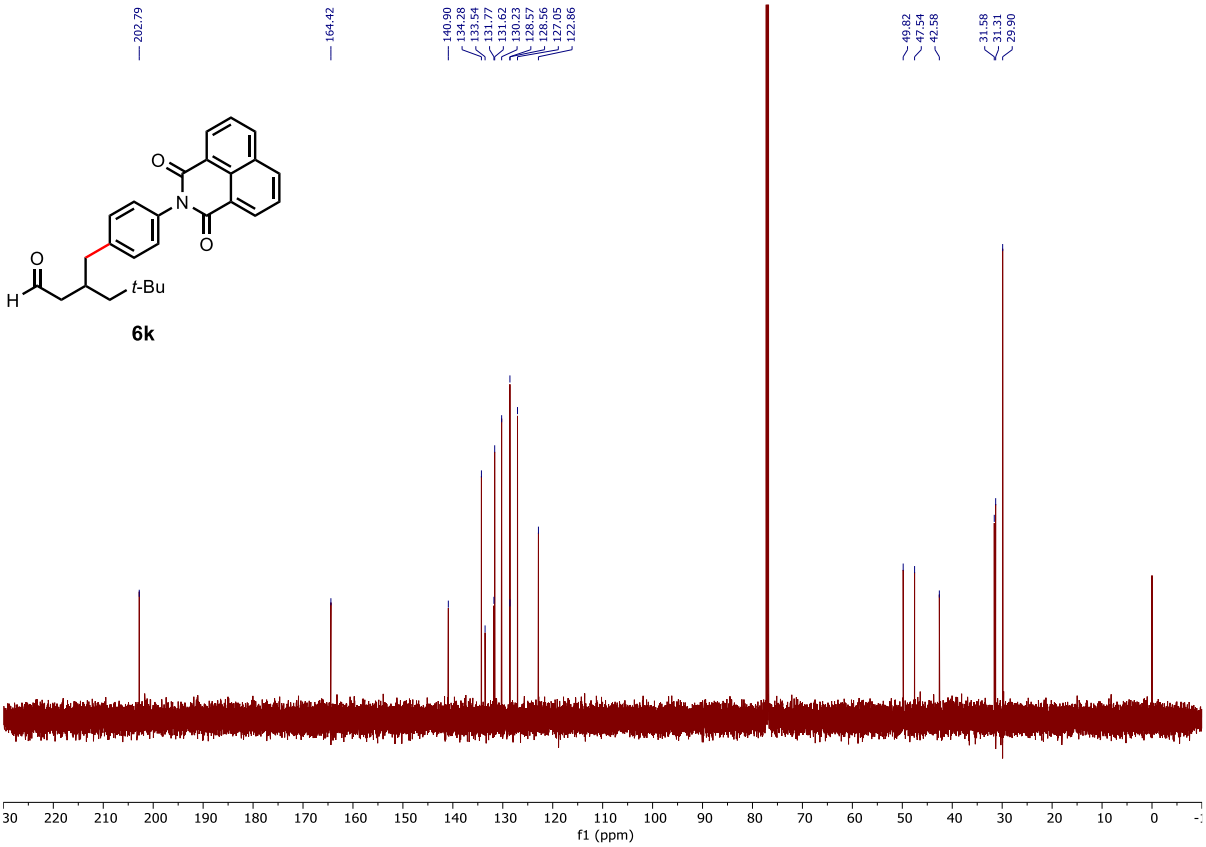

9.68
9.68
9.67
7.90
7.88
7.28
7.26
2.76
2.75
2.74
2.73
2.63
2.62
2.61
2.60
2.41
2.40
2.40
2.39
2.39
2.36
2.35
2.35
2.35
2.34
2.34
2.34
2.34
2.33
2.33
2.33
2.33
2.32
2.32
2.32
2.31
2.31
2.31
2.30
2.30
1.35
1.35
1.33
1.32
1.27
1.26
1.25
1.24
0.87
Ac
O
H
t-Bu
6i
0.96
2.05
2.01
1.00
1.00
3.12
2.02
1.04
1.01
1.09
9.08
f1 (ppm)

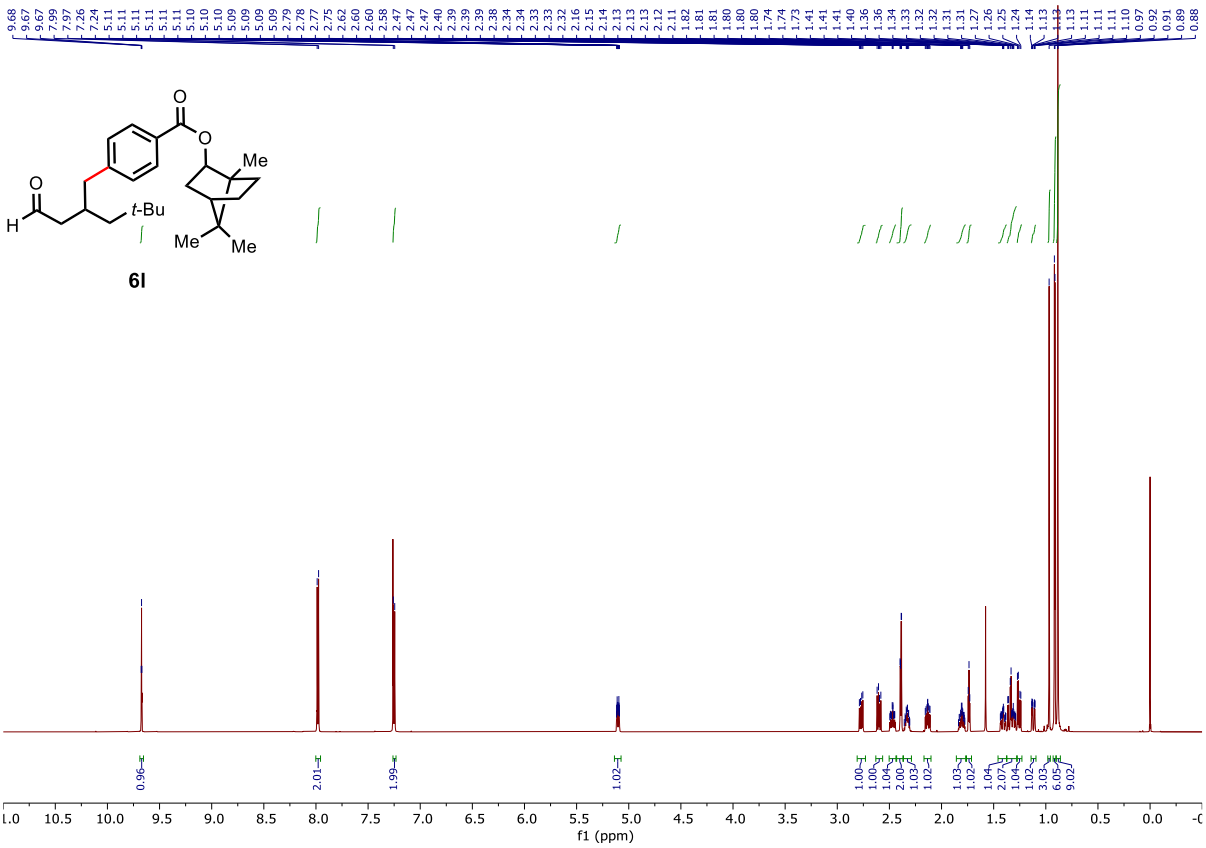

202.25
197.82
146.17
135.41
129.55
128.54
50.12
47.44
42.88
31.40
31.19
29.82
26.58
Ac
O
H
t-Bu
6i
f1 (ppm)


9.70
9.70
9.70
CN
O
H
t-Bu
6j
7.59
7.58
7.30
7.29
2.70
2.69
2.68
2.67
2.66
2.64
2.63
2.62
2.47
2.46
2.46
2.45
2.44
2.43
2.43
2.43
2.42
2.41
2.41
2.40
2.39
2.39
2.38
2.37
2.33
2.32
2.32
2.32
2.31
2.31
2.31
2.30
2.30
2.30
2.30
2.29
2.29
2.29
2.29
2.28
2.28
2.28
2.27
1.31
1.31
1.29
1.26
1.26
1.25
1.24
1.23
0.85
0.95
1.97
2.01
2.00
2.00
1.01
2.15
9.03
f1 (ppm)

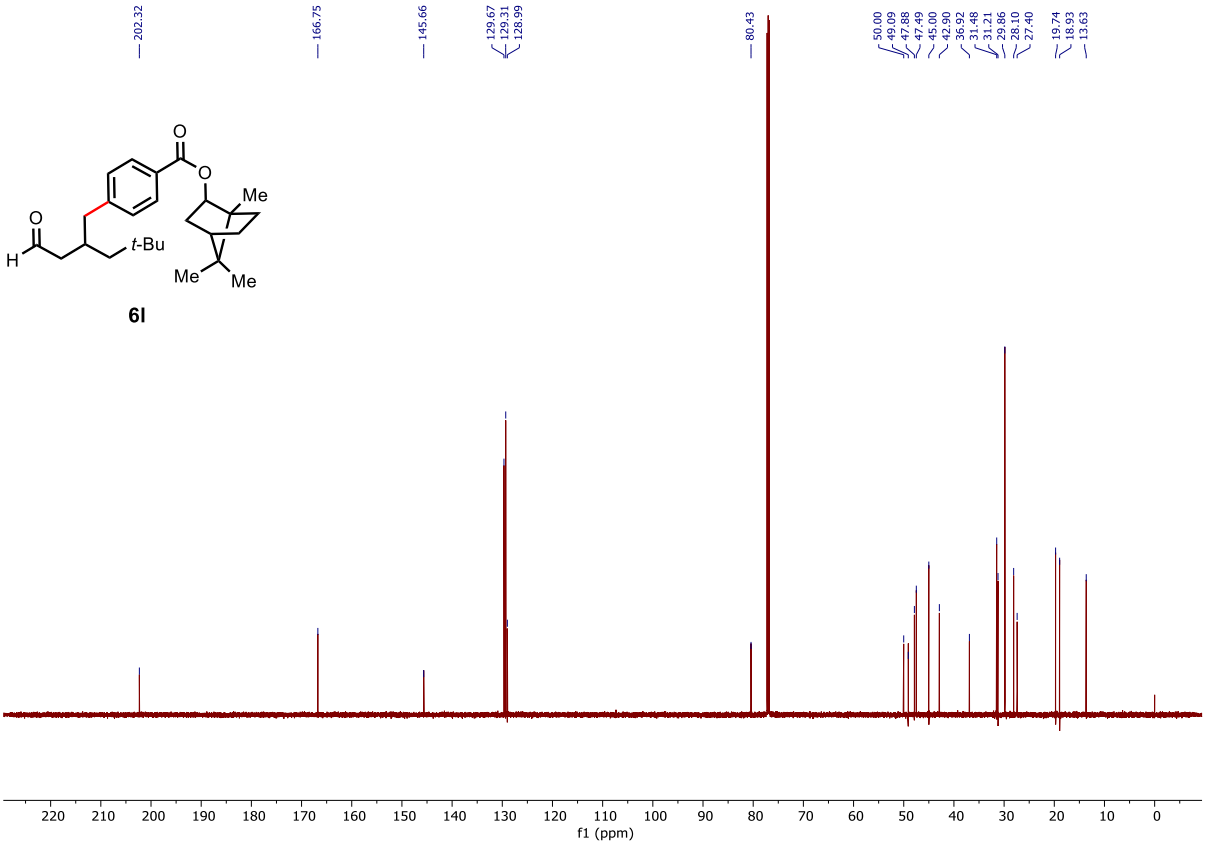

201.87
146.12
132.20
130.11
118.94
110.21
50.14
47.24
42.91
31.22
31.14
29.75
CN
O
H
t-Bu
6j
f1 (ppm)


9.73
9.73
9.73
9.72
8.66
8.65
8.64
8.64
8.28
8.28
8.27
8.27
7.81
7.80
7.80
7.79
7.36
7.35
7.26
7.24
2.88
2.87
2.86
2.85
2.63
2.62
2.61
2.60
2.52
2.52
2.51
2.51
2.49
2.49
2.48
2.48
2.42
2.42
2.41
2.41
2.39
2.39
2.38
2.38
2.37
2.37
2.36
2.35
2.34
1.43
1.42
1.41
1.40
1.31
1.31
1.29
1.28
0.93
O
N
O
O
H
t-Bu
6k
0.98
2.03
2.04
2.05
2.05
2.05
0.99
1.00
1.00
2.04
1.06
1.02
9.13
f1 (ppm)

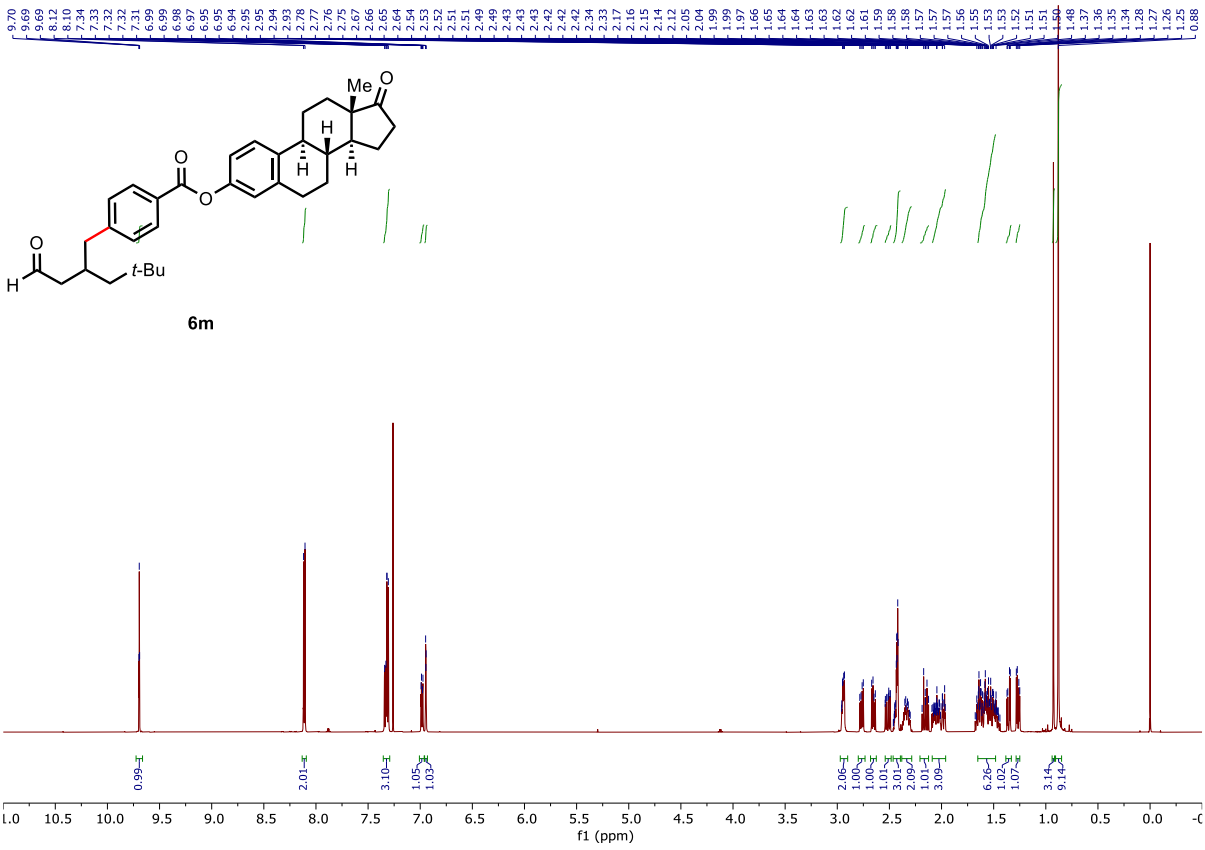

202.79
164.42
140.90
134.28
133.54
131.77
131.62
130.23
128.57
128.56
127.05
122.86
49.82
47.54
42.58
31.58
31.31
29.90
O
N
O
O
H
t-Bu
6k
f1 (ppm)

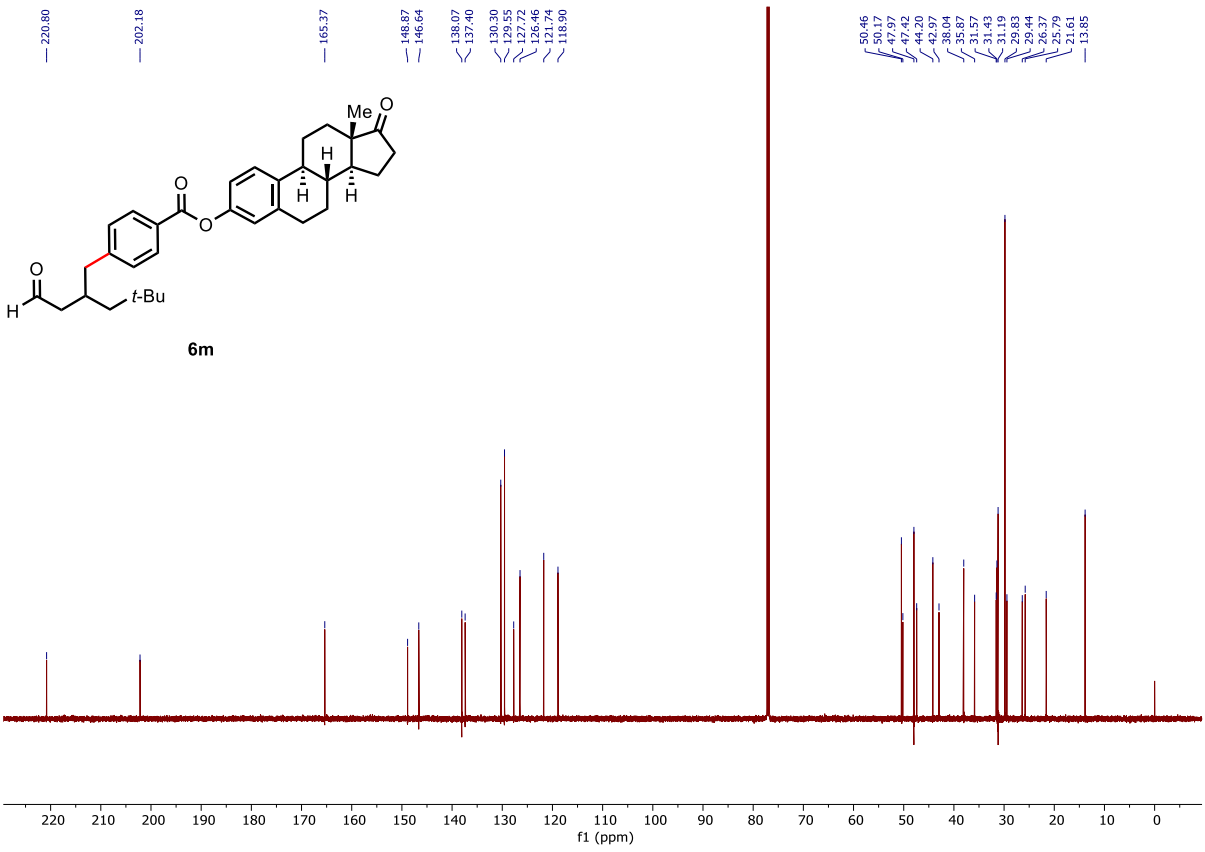


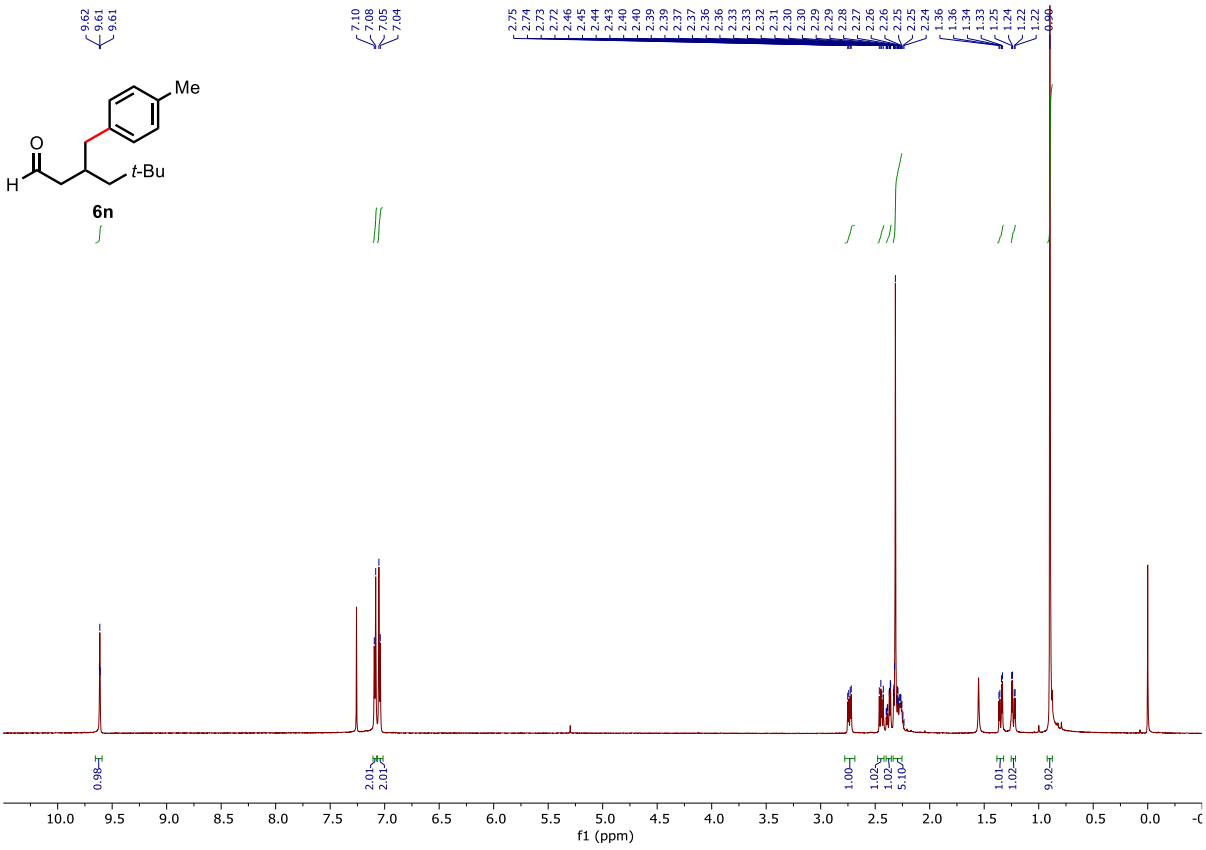
6l

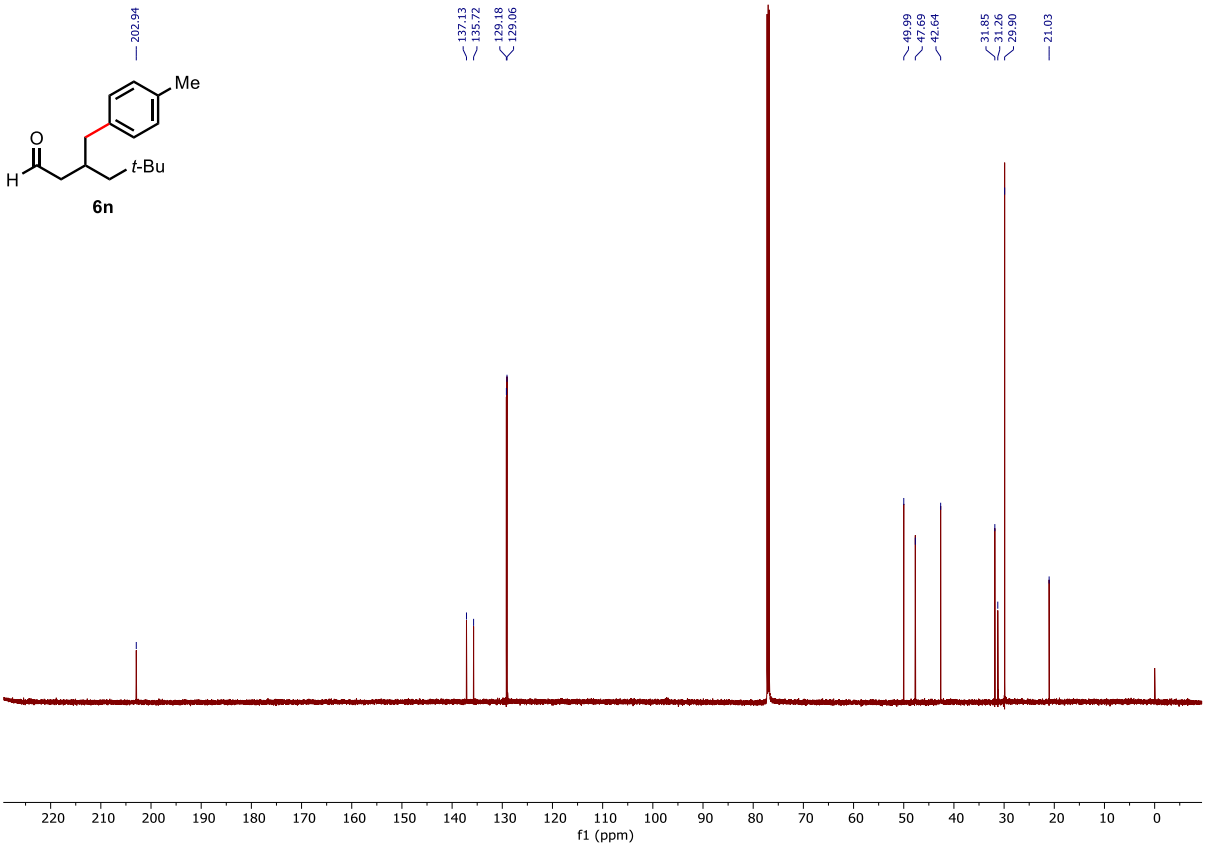


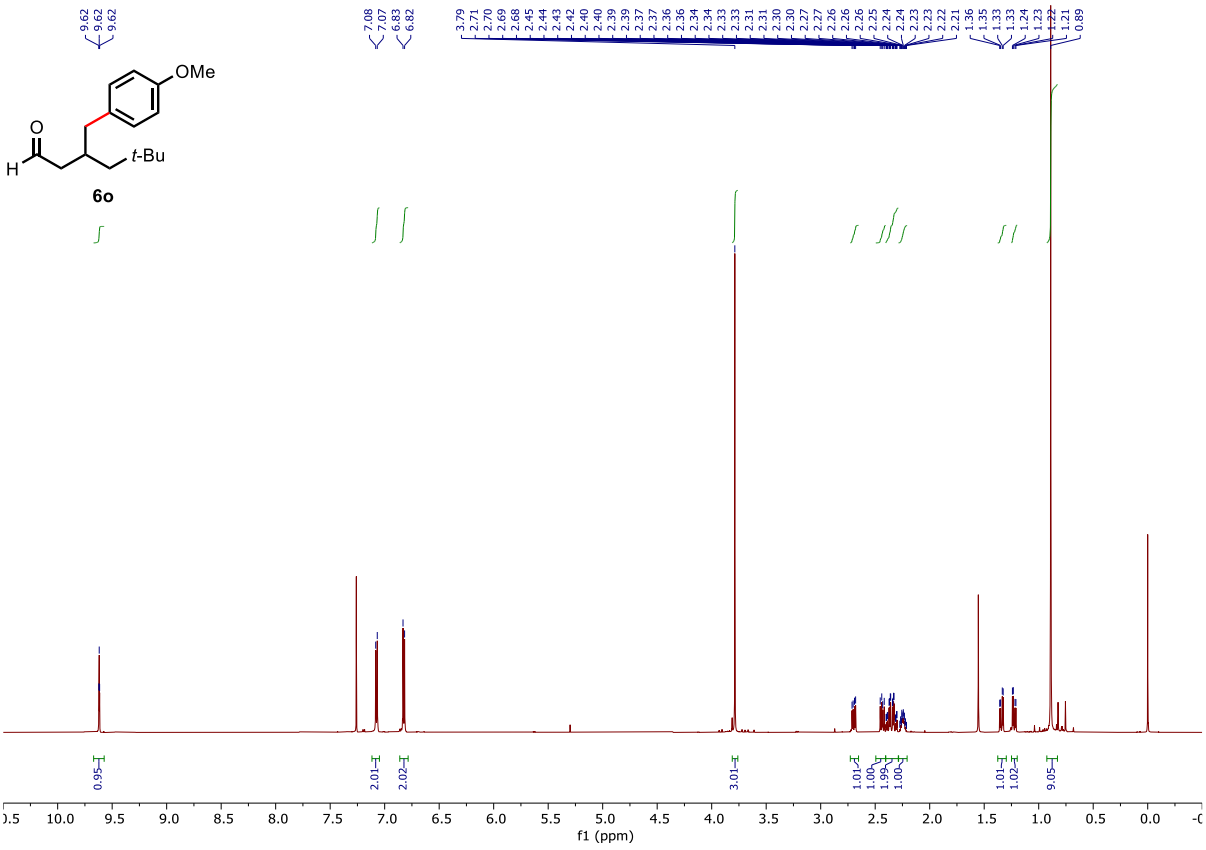
6l

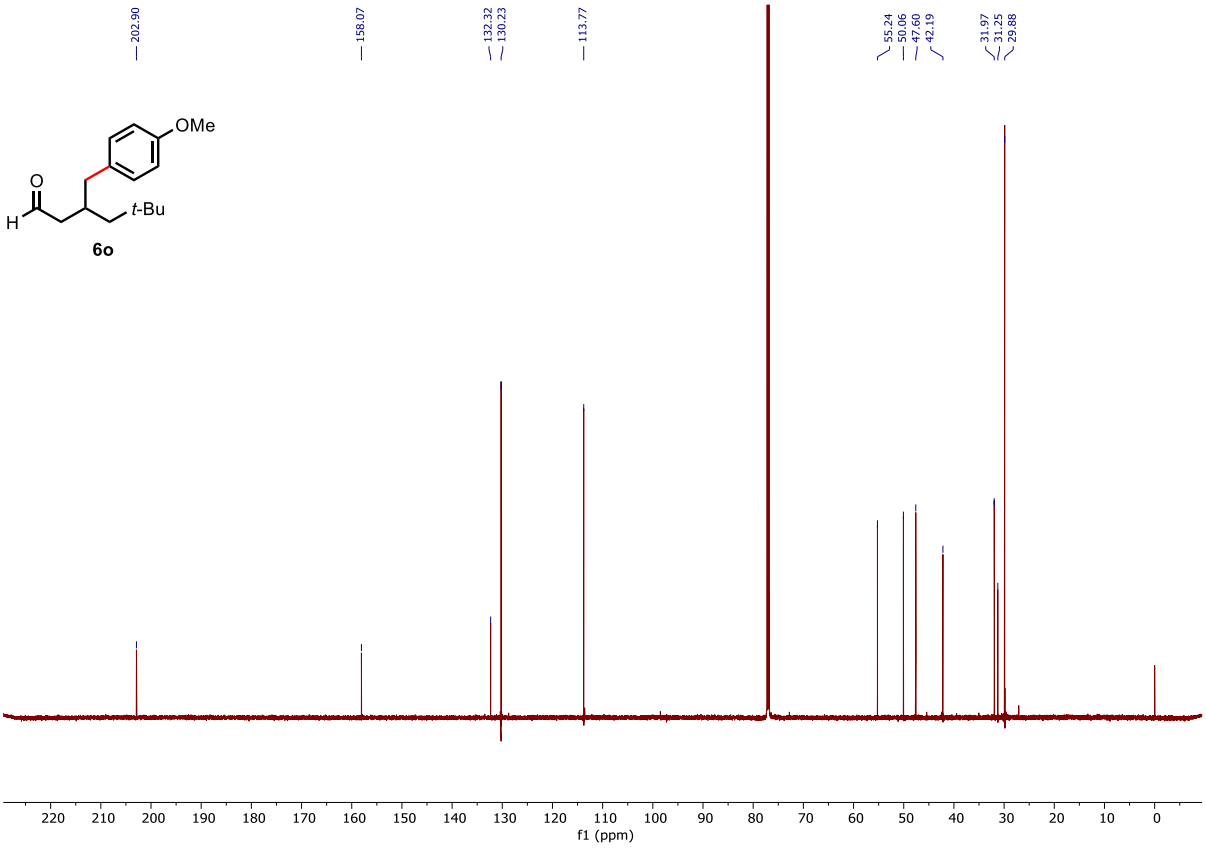

Me
O
H
H
H
O
O
O
t-Bu
6m
f1 (ppm)

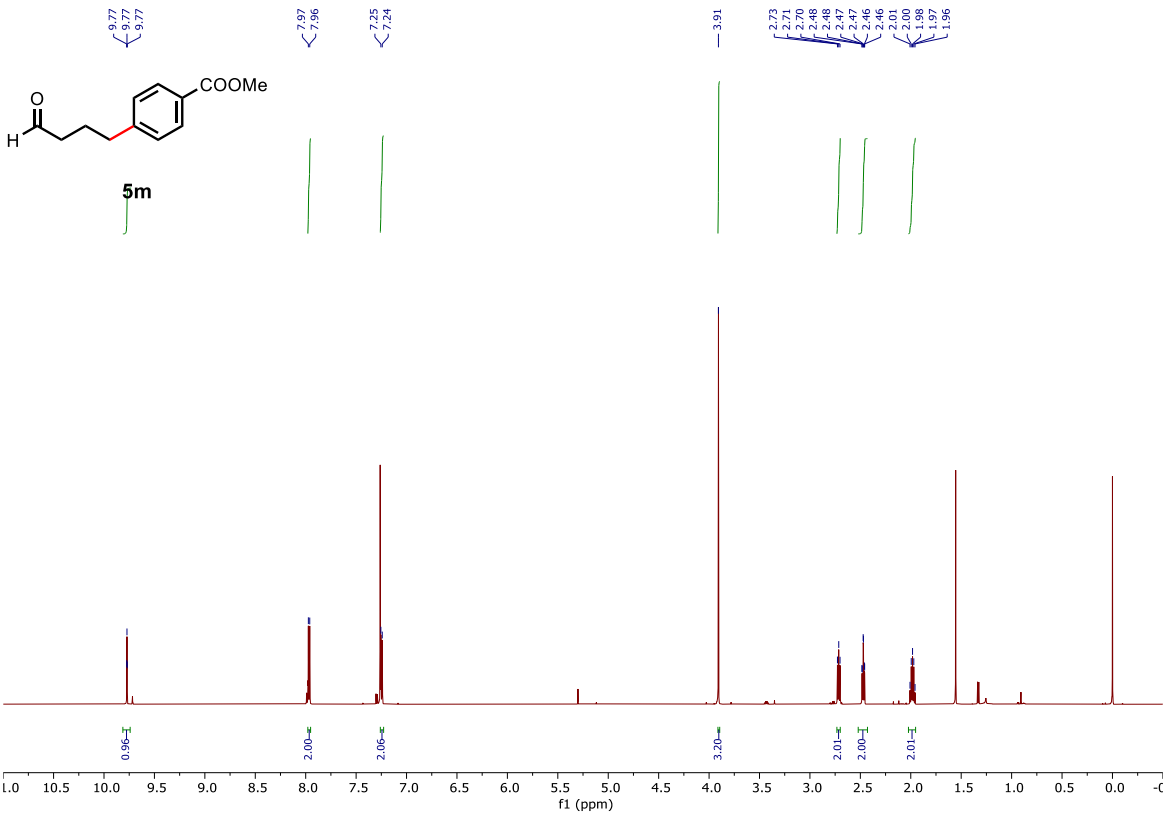

Me
O
H
H
H
O
O
O
t-Bu
6m
f1 (ppm)

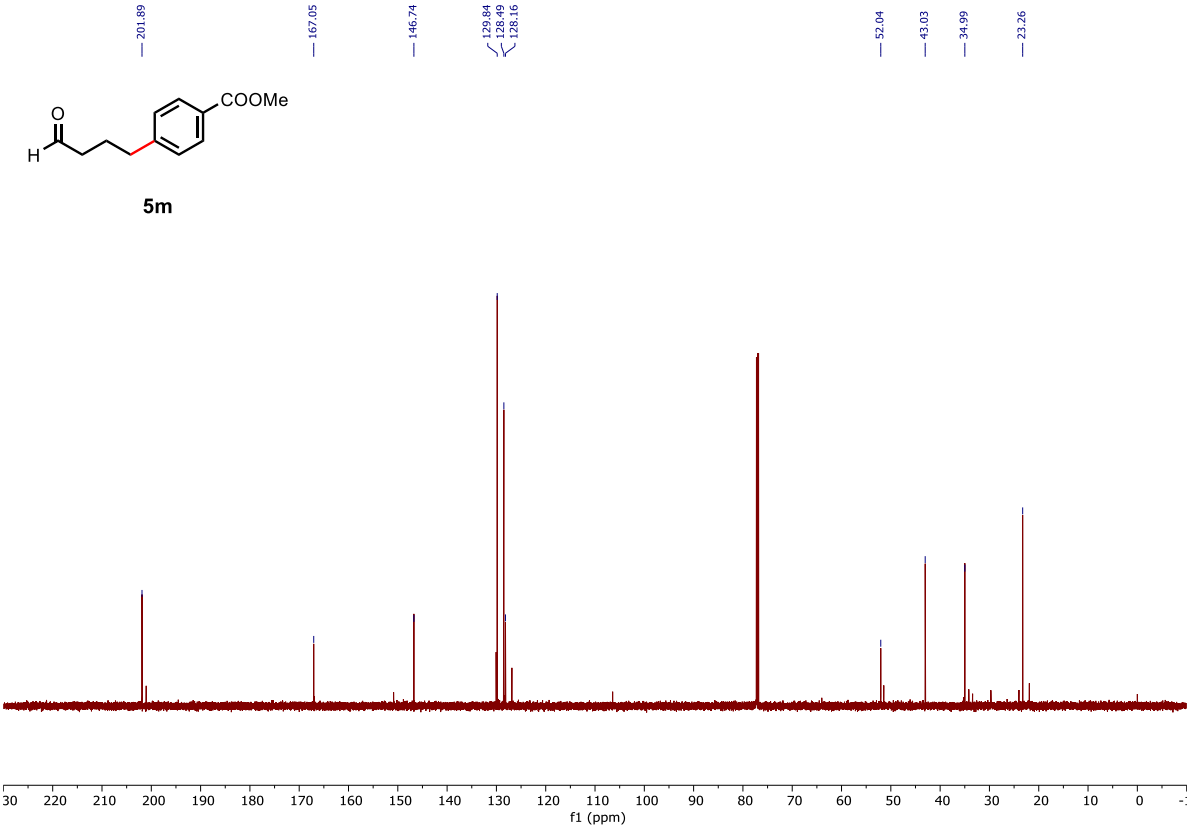

9.62
9.61
9.61
7.10
7.08
7.05
7.04
2.75
2.74
2.73
2.72
2.46
2.45
2.44
2.43
2.40
2.39
2.39
2.37
2.37
2.36
2.36
2.33
2.33
2.32
2.31
2.30
2.30
2.29
2.29
2.28
2.27
2.26
2.26
2.25
2.25
2.24
1.36
1.36
1.34
1.33
1.25
1.24
1.22
1.22
0.00
Me
O
H
t-Bu
6n
0.98
2.01
2.01
1.00
1.02
1.02
5.10
1.01
1.02
9.02
10.0
9.5
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
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


202.94
137.13
135.72
129.18
129.06
49.99
47.69
42.64
31.85
31.26
29.90
21.03
Me
O
H
t-Bu
6n
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)


OMe
O
H
t-Bu
6o
f1 (ppm)


OMe
O
H
t-Bu
6o
f1 (ppm)


9.77
9.77
9.77
7.97
7.96
7.25
7.24
3.91
2.73
2.71
2.70
2.48
2.48
2.47
2.47
2.46
2.46
2.01
2.00
1.98
1.97
1.96
COOMe
O
H
5m
0.96
2.00
2.06
3.20
2.01
2.00
2.01
f1 (ppm)


201.89
167.05
146.74
129.84
128.49
128.16
52.04
43.03
34.99
23.26
COOMe
O
H
5m
f1 (ppm)