Ligand-Enabled mono-Selective β-C(sp^3)–H Acyloxylation of Free Carboxylic Acids Using a Practical Oxidant

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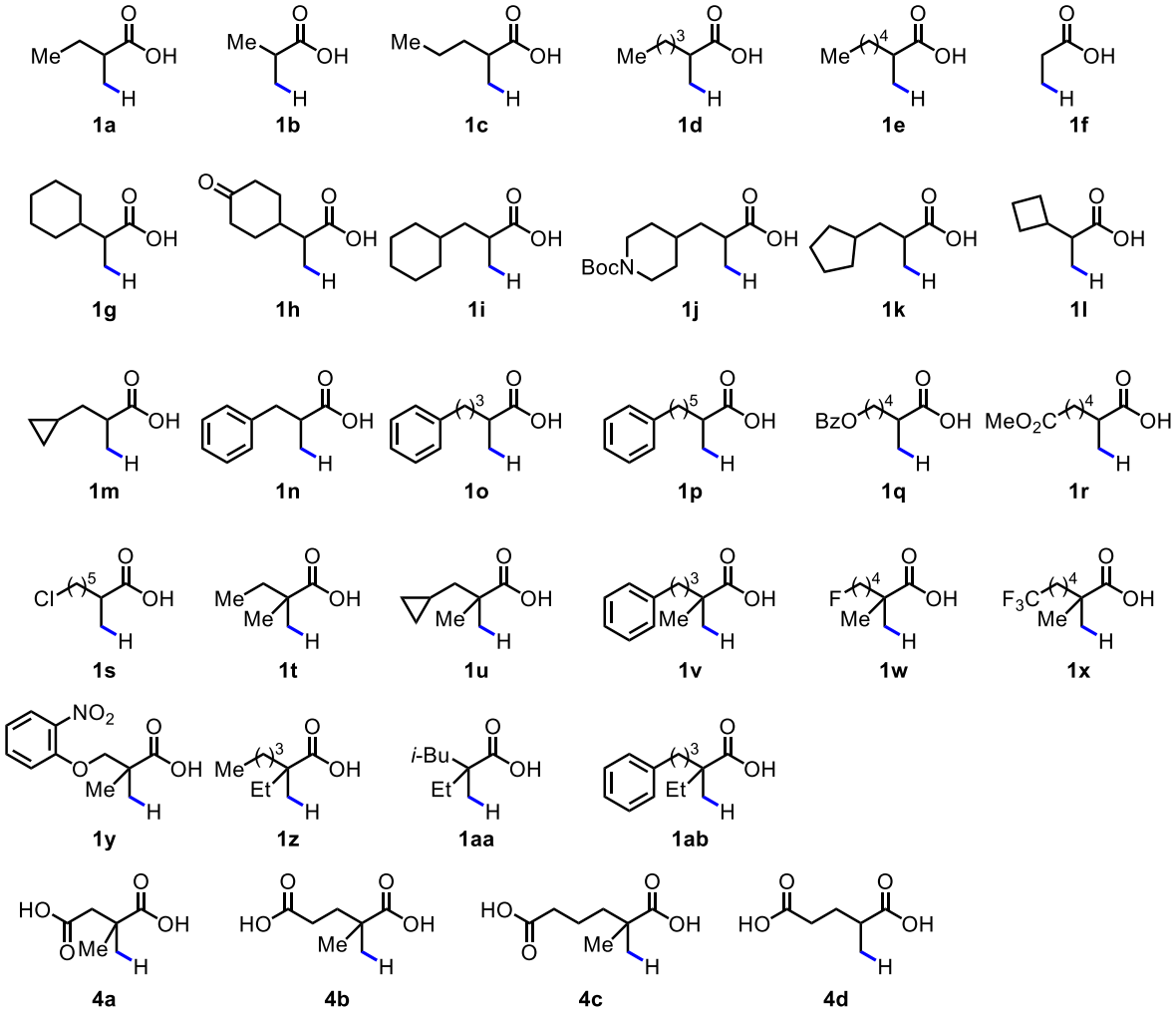
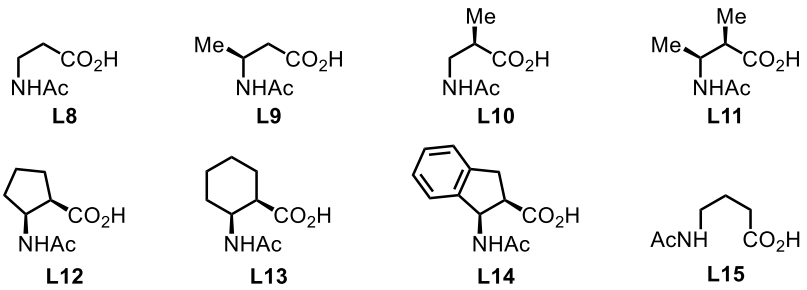
General Information: HFIP was obtained from Oakwood. $Pd(OAc)_2$ was obtained from Strem. TBHP (70% in water or ca. 5.5 M in decane) was purchased from Sigma-Aldrich. Carboxylic acids were obtained from the commercial sources or synthesized following literature procedures. Other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with short-wave UV light or $KMnO_4$ and heat as developing agents. ^1H NMR spectra were recorded on Bruker DRX-600 instrument. Chemical shifts were quoted in parts per million (ppm) referenced to 0.0 ppm for TMS. 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 and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of $CDCl_3$. Column chromatography was performed using E. Merck silica (60, particle size 0.043–0.063 mm), and pTLC was performed on Merck silica plates (60F-254). High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

Preparation of Aliphatic Carboxylic Acids



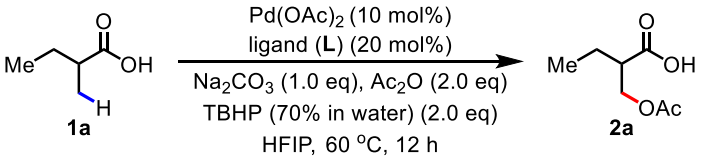
Aliphatic carboxylic acids were obtained from the commercial sources or synthesized following literature procedures[1-3].

Preparation of Mono-*N*-Protected β-Amino Acid Ligands



Mono-*N*-protected amino acid ligands were obtained from the commercial sources or synthesized following literature procedures[4-7].

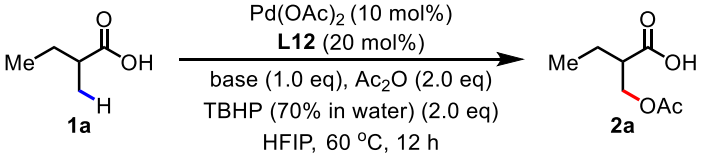
Table S1. Ligand Investigation for β-C(sp^3)–H Acetoxylation[a,b]



w/o ligand 0%	**L1**, 0%	**L2**, 13%	**L3**, 0%
L4, 25%	**L5**, 29%	**L6**, 18%	**L7**, 28%
L8, 44%	**L9**, 40%	**L10**, 28%	**L11**, 19%
L12, 61%	**L13**, 56%	**L14**, 43%	**L15**, 0%

[a]Conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **L** (20 mol%), Na_2CO_3 (1.0 eq), TBHP (70% in water) (2.0 eq), Ac_2O (2.0 eq), HFIP (1.0 mL), 60 °C, 12 h. [b]The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard.

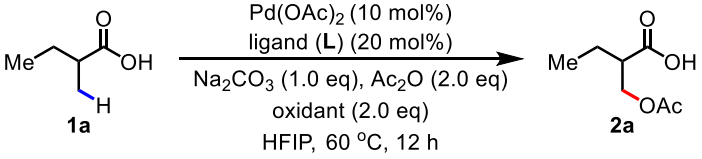
Table S2. Base Investigation for β-C(sp^3)–H Acetoxylation[a,b]



entry	base	yield (%)	entry	base	yield (%)
1	w/o	0	7	Na_3PO_4	34
2	$NaHCO_3$	13	8	NaOAc	22
3	Na_2CO_3	61	9	Li_2CO_3	0
4	NaH_2PO_4	0	10	K_2CO_3	52
5	Na_2HPO_4	10	11	Cs_2CO_3	11
6	$Na_2HPO_4.7H_2O$	14			

[a]Conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **L12** (20 mol%), base (1.0 eq), TBHP (70% in water) (2.0 eq), Ac_2O (2.0 eq), HFIP (1.0 mL), 60 ^{O}C, 12 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as the internal standard.

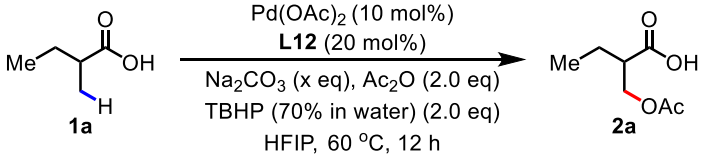
Table S3. Oxidant Investigation for β-C(sp^3)–H Acetoxylation[a,b]



entry	oxidant	yield (%)	entry	oxidant	yield (%)
1	w/o	0	7	$(BzO)_2$	0
2	H_2O_2	0	8	mCPBA	0
3	AcO*t*-Bu	34	9	CMHP	0
4	BzO*t*-Bu	0	10	TBHP (70% in water)	61
5	$(t\text{-BuO})_2$	0	11	TBHP (ca. 5.5 M in decane)	72
6	Lauroyl peroxide	0			

[a]Conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **L12** (20 mol%), Na_2CO_3 (1.0 eq), oxidant (2.0 eq), Ac_2O (2.0 eq), HFIP (1.0 mL), 60 ^{O}C, 12 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as the internal standard.

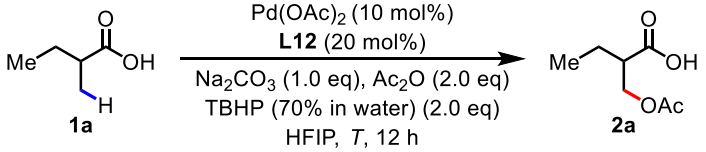
Table S4. Base Loadings Investigation for β-C(sp^3)–H Acetoxylation[a,b]



entry	x eq base	yield (%)	entry	x eq base	yield (%)
1	0.5	23	4	2.0	44
2	1.0	61	5	2.5	8
3	1.5	40	6	3.0	12

[a]Conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **L12** (20 mol%), Na_2CO_3 (x eq), TBHP (70% in water) (2.0 eq), Ac_2O (2.0 eq), HFIP (1.0 mL), 60 °C, 12 h. [b]The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard.

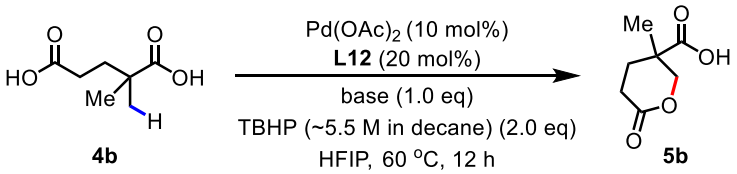
Table S5. Temperature Investigation for β-C(sp^3)–H Acetoxylation[a,b]



entry	*T* (°C)	yield (%)	entry	*T* (°C)	yield (%)
1	50	55	4	80	22
2	60	61	5	90	21
3	70	30			

[a]Conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **L12** (20 mol%), Na_2CO_3 (1.0 eq), TBHP (70% in water) (2.0 eq), Ac_2O (2.0 eq), HFIP (1.0 mL), *T* °C, 12 h. [b]The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard.

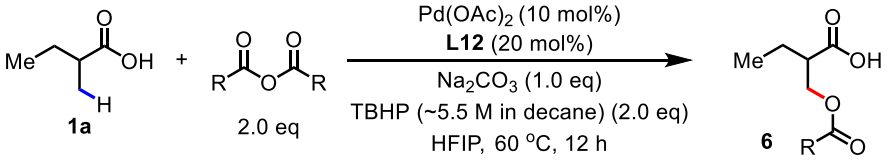
Table S6. Base Investigation for Intramolecular β-C(sp^3)–H Acyloxylation[a,b]

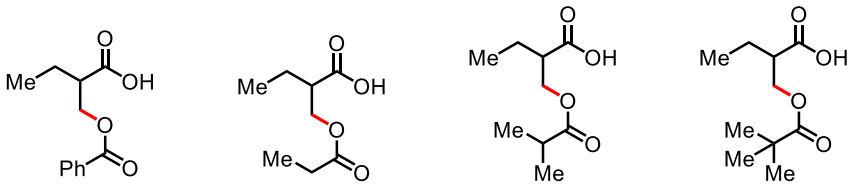


entry	base	yield (%)	entry	base	yield (%)
1	w/o	0	7	NaOAc	45
2	$NaHCO_3$	8	8	$KHCO_3$	68
3	Na_2CO_3	32	9	K_2CO_3	67
4	NaH_2PO_4	0	10	K_2HPO_4	45
5	Na_2HPO_4	16	11	K_3PO_4	75
6	Na_3PO_4	49	12	KOAc	34

[a]Conditions: **4b** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **L12** (20 mol%), base (1.0 eq), TBHP (ca. 5.5 M in decane) (2.0 eq), HFIP (1.0 mL), 60 °C, 12 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as the internal standard.

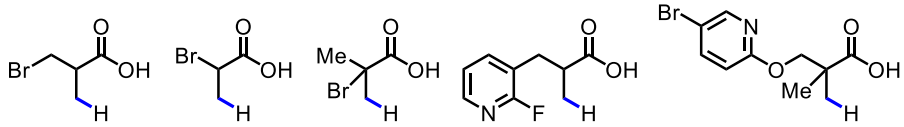
Table S7. Acid Anhydride Scope for β-C(sp^3)–H Acyloxylation[a,b]



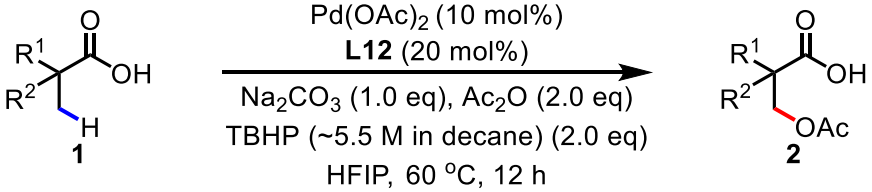


[a]Conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), **L12** (20 mol%), Na_2CO_3 (1.0 eq), TBHP (ca. 5.5 M in decane) (2.0 eq), $(RCO)_2O$ (2.0 eq), HFIP (1.0 mL), 60 °C, 12 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as the internal standard.

Table S8. Selected Unsuccessful Substrates

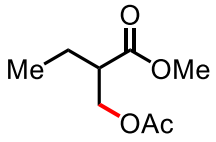


General Procedure for β-C(sp^3)–H Acetoxylation



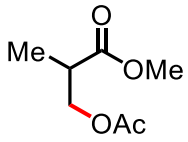
General Procedure: In the culture tube, $Pd(OAc)_2$ (10 mol%, 2.2 mg), ligand **L12** (20 mol%, 3.4 mg), Na_2CO_3 (1.0 eq, 10.6 mg), and carboxylic acid **1** (0.1 mmol) in order were weighed in air and placed with a magnetic stir bar. Then HFIP (1.0 mL), Ac_2O (2.0 eq, 19 μL), and TBHP (ca. 5.5 M in decane) (2.0 eq, 36 μL) were added. The reaction mixture was stirred at rt for 3 minutes, and then heated to 60 ^oC for 12 hours (600 rpm). After being allowed to cool to room temperature, the mixture was treated with AcOH (0.05 mL) and concentrated *in vacuo*. The resulting mixture was dissolved in MeOH (1.0 mL), treated with $TMSCHN_2$ (2.0 eq), and concentrated *in vacuo* after 1 hour. The crude mixture was purified by pTLC or column chromatography to afford corresponding methyl esters **2'**.

Substrate Scope for β-C(sp^3)–H Acetoxylation



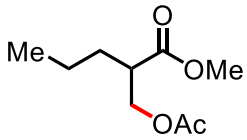
Methyl 2-(acetoxymethyl)butanoate (2a')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 12.5 mg, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.25 – 4.17 (m, 2H), 3.71 (s, 3H), 2.69 – 2.60 (m, 1H), 2.04 (s, 3H), 1.73 – 1.63 (m, 1H), 1.63 – 1.56 (m, 1H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.11, 170.93, 64.43, 51.92, 46.38, 22.14, 20.98, 11.58; HRMS (ESI-TOF) Calcd for $C_8H_{14}NaO_4$ $[M+Na]^+$: 197.0784; found: 197.0786.



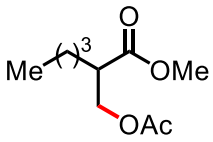
Methyl 3-acetoxy-2-methylpropanoate (2b')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 11.5 mg, 72%, mono/di > 20/1). The NMR data matches the reported data[8].



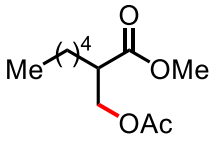
Methyl 2-(acetoxymethyl)pentanoate (2c')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 14.0 mg, 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.26 – 4.12 (m, 2H), 3.70 (s, 3H), 2.72 (tt, *J* = 8.4, 5.6 Hz, 1H), 2.03 (s, 3H), 1.67 – 1.55 (m, 1H), 1.54 – 1.42 (m, 1H), 1.40 – 1.29 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.31, 170.91, 64.77, 51.93, 44.74, 31.03, 20.97, 20.41, 14.02; HRMS (ESI-TOF) Calcd for $C_9H_{16}NaO_4$ $[M+Na]^+$: 211.0941; found: 211.0943.



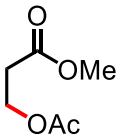
Methyl 2-(acetoxymethyl)hexanoate (2d')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 13.0 mg, 64%). The NMR data matches the reported data[9].



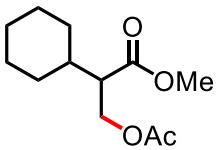
Methyl 2-(acetoxymethyl)heptanoate (2e')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 14.5 mg, 67%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.31 – 4.12 (m, 2H), 3.71 (s, 3H), 2.77 – 2.64 (m, 1H), 2.04 (s, 3H), 1.67 – 1.58 (m, 1H), 1.53 – 1.45 (m, 1H), 1.36 – 1.21 (m, 6H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.34, 170.94, 64.78, 44.97, 31.73, 29.85, 28.90, 26.82, 22.54, 20.99, 14.11; HRMS (ESI-TOF) Calcd for $C_{11}H_{21}O_4$ $[M+H]^+$: 217.1434; found: 217.1438.



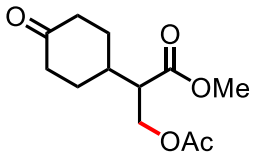
Methyl 3-acetoxypropanoate (2f')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 7.5 mg, 51%). The NMR data matches the reported data[10].



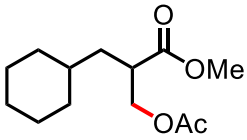
Methyl 3-acetoxy-2-cyclohexylpropanoate (2g')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 10.0 mg, 44%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.32 (dd, *J* = 10.8, 4.6 Hz, 1H), 4.19 (dd, *J* = 10.8, 9.9 Hz, 1H), 3.70 (s, 3H), 2.55 (dtd, *J* = 9.9, 4.6, 2.3 Hz, 1H), 2.02 (s, 3H), 1.79 – 1.67 (m, 2H), 1.67 – 1.55 (m, 3H), 1.29 – 1.18 (m, 2H), 1.18 – 1.09 (m, 1H), 1.10 – 1.00 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.96, 170.95, 63.73, 51.72, 50.93, 38.02, 30.93, 30.82, 26.28, 26.25, 21.02; HRMS (ESI-TOF) Calcd for $C_{12}H_{21}O_4$ $[M+H]^+$: 229.1434; found: 229.1440.



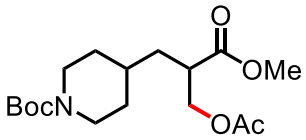
Methyl 3-acetoxy-2-(4-oxocyclohexyl)propanoate (2h')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 9.0 mg, 37%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.37 (dd, *J* = 11.0, 4.9 Hz, 1H), 4.26 (dd, *J* = 11.0, 9.0 Hz, 1H), 3.73 (s, 3H), 2.69 (ddd, *J* = 9.0, 7.4, 4.9 Hz, 1H), 2.47 – 2.38 (m, 2H), 2.38 – 2.29 (m, 2H), 2.20 – 2.07 (m, 2H), 2.05 (s, 3H), 2.02 – 1.92 (m, 1H), 1.65 – 1.51 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.43, 173.14, 170.81, 63.36, 52.10, 49.32, 40.62, 40.60, 36.07, 30.29, 30.20, 20.98; HRMS (ESI-TOF) Calcd for $C_{12}H_{19}O_5$ $[M+H]^+$: 243.1227; found: 243.1229.



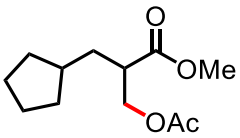
Methyl 3-acetoxy-2-(cyclohexylmethyl)propanoate (2i')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 13.0 mg, 54%). The NMR data matches the reported data[9].



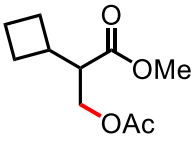
***tert*-Butyl 4-(2-(acetoxymethyl)-3-methoxy-3-oxopropyl)piperidine-1-carboxylate (2j')**

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 14.0 mg, 41%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.20 (dd, *J* = 10.9, 5.2 Hz, 1H), 4.16 (dd, *J* = 10.9, 8.3 Hz, 1H), 4.07 (br s, 2H), 3.72 (s, 3H), 2.82 (tt, *J* = 8.7, 5.3 Hz, 1H), 2.66 (br s, 2H), 2.04 (s, 3H), 1.71 (d, *J* = 13.2 Hz, 1H), 1.68 – 1.54 (m, 3H), 1.45 (s, 9H), 1.40 – 1.32 (m, 1H), 1.18 – 0.99 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.19, 170.90, 154.97, 79.59, 65.01, 52.14, 52.12, 43.89 (br), 42.27, 35.59, 33.96, 28.61, 20.95; HRMS (ESI-TOF) Calcd for $C_{17}H_{30}NO_6$ $[M+H]^+$: 344.2068; found: 344.2068.



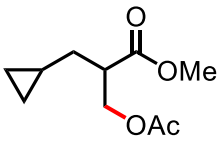
Methyl 3-acetoxy-2-(cyclopentylmethyl)propanoate (2k')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 10.5 mg, 46%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.22 (dd, *J* = 10.9, 5.0 Hz, 1H), 4.16 (dd, *J* = 10.9, 8.7 Hz, 1H), 3.71 (s, 3H), 2.80 – 2.72 (m, 1H), 2.04 (s, 3H), 1.86 – 1.73 (m, 3H), 1.73 – 1.66 (m, 1H), 1.66 – 1.56 (m, 2H), 1.56 – 1.50 (m, 2H), 1.50 – 1.41 (m, 1H), 1.15 – 1.01 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.56, 170.91, 65.08, 51.96, 44.48, 38.01, 35.23, 32.87, 32.70, 25.21, 25.19, 20.98; HRMS (ESI-TOF) Calcd for $C_{12}H_{21}O_4$ $[M+H]^+$: 229.1434; found: 229.1439.



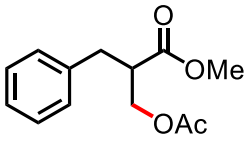
Methyl 3-acetoxy-2-cyclobutylpropanoate (2l')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 10.0 mg, 50%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.16 (dd, *J* = 11.0, 4.6 Hz, 1H), 4.12 (dd, *J* = 11.0, 8.7 Hz, 1H), 3.69 (s, 3H), 2.70 (ddd, *J* = 10.1, 8.7, 4.6 Hz, 1H), 2.55 – 2.45 (m, 1H), 2.13 – 2.05 (m, 1H), 2.05 – 1.97 (m, 4H), 1.94 – 1.71 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.27, 170.96, 63.30, 51.84, 51.02, 35.07, 27.31, 26.91, 21.00, 18.53; HRMS (ESI-TOF) Calcd for $C_{10}H_{17}O_4$ $[M+H]^+$: 201.1121; found: 201.1124.



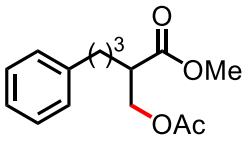
Methyl 3-acetoxy-2-(cyclopropylmethyl)propanoate (2m')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 8.5 mg, 43%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.26 – 4.13 (m, 2H), 3.71 (s, 3H), 2.74 – 2.66 (m, 1H), 2.04 (s, 3H), 1.67 – 1.60 (m, 1H), 1.54 – 1.48 (m, 1H), 1.36 – 1.26 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.33, 170.92, 64.78, 51.95, 44.95, 29.31, 28.65, 22.65, 20.98, 13.98; HRMS (ESI-TOF) Calcd for $C_{10}H_{17}O_4$ $[M+H]^+$: 201.1121; found: 201.1127.



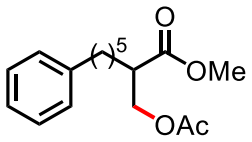
Methyl 3-acetoxy-2-benzylpropanoate (2n')

Following **General Procedure** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 9.5 mg, 40%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.20 (m, 1H), 7.19 – 7.13 (m, 2H), 4.25 – 4.15 (m, 2H), 3.66 (s, 3H), 3.05 – 2.97 (m, 2H), 2.88 – 2.79 (m, 1H), 2.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.40, 170.82, 138.05, 128.98, 128.73, 126.86, 64.01, 52.06, 46.59, 34.89, 20.94; HRMS (ESI-TOF) Calcd for $C_{13}H_{17}O_4$ $[M+H]^+$: 237.1121; found: 237.1122.



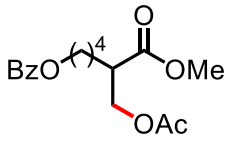
Methyl 2-(acetoxymethyl)-5-phenylpentanoate (2o')

Following **General Procedure** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 13.5 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.15 (m, 3H), 4.24 – 4.18 (m, 2H), 3.73 (s, 3H), 2.80 – 2.73 (m, 1H), 2.65 (t, J = 7.4 Hz, 3H), 2.05 (s, 3H), 1.77 – 1.62 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.11, 170.89, 141.83, 128.52, 128.51, 126.05, 64.66, 52.00, 44.80, 35.73, 28.91, 28.45, 20.96; HRMS (ESI-TOF) Calcd for $C_{15}H_{21}O_4$ $[M+H]^+$: 265.1434; found: 265.1445.



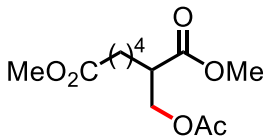
Methyl 2-(acetoxymethyl)-7-phenylheptanoate (2p')

Following **General Procedure** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 12.0 mg, 41%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 4.25 – 4.15 (m, 2H), 3.70 (s, 3H), 2.73 – 2.66 (m, 1H), 2.63 – 2.56 (m, 2H), 2.03 (s, 3H), 1.68 – 1.44 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.29, 170.94, 142.85, 128.53, 128.39, 125.76, 64.76, 51.97, 44.94, 36.04, 31.50, 29.15, 28.91, 27.09, 20.99; HRMS (ESI-TOF) Calcd for $C_{17}H_{25}O_4$ $[M+H]^+$: 293.1747; found: 293.1750.



5-(Acetoxymethyl)-6-methoxy-6-oxohexyl benzoate (2q')

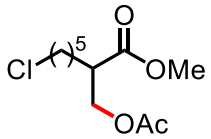
Following **General Procedure** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 21.0 mg, 66%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.59 – 7.52 (m, 1H), 7.47 – 7.41 (m, 2H), 4.35 – 4.28 (m, 2H), 4.26 – 4.19 (m, 2H), 3.70 (s, 3H), 2.74 (ddt, *J* = 8.6, 7.8, 5.7 Hz, 1H), 2.03 (s, 3H), 1.87 – 1.67 (m, 3H), 1.67 – 1.55 (m, 1H), 1.55 – 1.45 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.97, 170.88, 166.73, 133.05, 130.47, 129.67, 128.50, 64.65, 64.60, 52.03, 44.85, 28.69, 28.54, 23.79, 20.95; HRMS (ESI-TOF) Calcd for $C_{17}H_{23}O_6$ $[M+H]^+$: 323.1489; found: 323.1497.



Dimethyl 2-(acetoxymethyl)heptanedioate (2r')

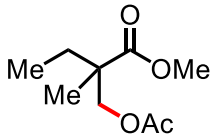
Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 16.0 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.25 – 4.15 (m, 2H), 3.71 (s, 3H), 3.67 (s, 3H), 2.76 – 2.67 (m, 1H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.04 (s, 3H), 1.72 – 1.57 (m, 3H), 1.57 – 1.49 (m, 1H), 1.39 – 1.32 (m, 2H); ^{13}C NMR (150

MHz, $CDCl_3$) δ 174.02, 173.99, 170.89, 64.59, 52.02, 51.67, 44.75, 33.87, 28.53, 26.66, 24.81, 20.95; HRMS (ESI-TOF) Calcd for $C_{12}H_{21}O_6$ $[M+H]^+$: 261.1333; found: 261.1335.



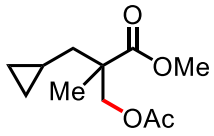
Methyl 2-(acetoxymethyl)-7-chloroheptanoate (2s')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 13.0 mg, 52%). ^1H NMR (600 MHz, $CDCl_3$) δ 4.25 – 4.16 (m, 2H), 3.72 (s, 3H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.76 – 2.66 (m, 1H), 2.04 (s, 3H), 1.82 – 1.73 (m, 2H), 1.70 – 1.61 (m, 2H), 1.58 – 1.50 (m, 2H), 1.50 – 1.41 (m, 2H), 1.39 – 1.31 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.09, 170.90, 64.65, 52.03, 45.01, 44.85, 32.42, 28.73, 26.81, 26.47, 20.98; HRMS (ESI-TOF) Calcd for $C_{11}H_{20}ClO_4$ $[M+H]^+$: 251.1045; found: 251.1044.



Methyl 2-(acetoxymethyl)-2-methylbutanoate (2t')

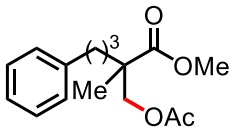
Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 8.5 mg, 45%, mono/di > 20/1). ^1H NMR (600 MHz, $CDCl_3$) δ 4.20 (d, *J* = 10.9 Hz, 1H), 4.08 (d, *J* = 10.9 Hz, 1H), 3.70 (s, 3H), 2.05 (s, 3H), 1.68 (dq, *J* = 13.7, 7.5 Hz, 1H), 1.53 (dq, *J* = 13.7, 7.5 Hz, 1H), 1.19 (s, 3H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.65, 171.01, 68.90, 52.04, 46.67, 28.84, 20.97, 19.26, 8.72; HRMS (ESI-TOF) Calcd for $C_9H_{17}O_4$ $[M+H]^+$: 189.1121; found: 189.1124.



Methyl 3-acetoxy-2-(cyclopropylmethyl)-2-methylpropanoate (2u')

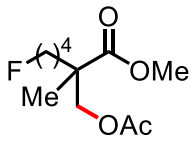
Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 7.0 mg, 33%, mono/di > 20/1). ^1H NMR (600

MHz, $CDCl_3$) δ 4.29 (d, *J* = 10.8 Hz, 1H), 4.17 (d, *J* = 10.8 Hz, 1H), 3.73 (s, 3H), 2.07 (s, 3H), 1.57 – 1.48 (m, 2H), 1.30 (s, 3H), 0.70 – 0.62 (m, 1H), 0.54 – 0.41 (m, 2H), 0.12 – 0.04 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.77, 171.02, 68.94, 52.03, 46.93, 40.95, 21.01, 20.08, 6.37, 4.59, 4.43.



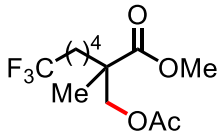
Methyl 2-(acetoxymethyl)-2-methyl-5-phenylpentanoate (2v')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 12.0 mg, 43%, mono/di > 20/1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.14 (m, 3H), 4.20 (d, *J* = 10.9 Hz, 1H), 4.09 (d, *J* = 10.9 Hz, 1H), 3.70 (s, 3H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.04 (s, 3H), 1.77 – 1.65 (m, 1H), 1.65 – 1.60 (m, 1H), 1.61 – 1.51 (m, 2H), 1.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.60, 170.96, 141.92, 128.49, 126.03, 68.98, 52.10, 46.24, 36.20, 35.55, 26.10, 20.95, 19.80 1 carbon signal was not assigned due to overlaps).



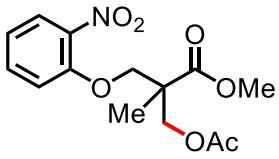
Methyl 2-(acetoxymethyl)-6-fluoro-2-methylhexanoate (2w')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 12.0 mg, 51%, mono/di > 20/1). ^1H NMR (600 MHz, $CDCl_3$) δ 4.43 (dt, *J* = 47.3, 6.0 Hz, 2H), 4.19 (d, *J* = 10.9 Hz, 1H), 4.09 (d, *J* = 10.9 Hz, 1H), 3.70 (s, 3H), 2.05 (s, 3H), 1.73 – 1.62 (m, 3H), 1.55 – 1.48 (m, 1H), 1.45 – 1.36 (m, 1H), 1.36 – 1.28 (m, 1H), 1.21 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.51, 170.95, 83.81 (d, *J* = 164.6 Hz), 68.97, 52.17, 46.28, 35.59, 30.84 (d, *J* = 19.8 Hz), 20.96, 20.27 (d, *J* = 5.2 Hz), 19.76.



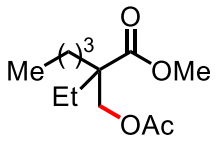
Methyl 2-(acetoxymethyl)-7,7,7-trifluoro-2-methylheptanoate (2x')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 11.5 mg, 40%, mono/di > 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.20 (d, *J* = 10.9 Hz, 1H), 4.11 (d, *J* = 10.9 Hz, 1H), 3.72 (s, 3H), 2.13 – 2.08 (m, 2H), 2.08 (s, 3H), 1.72 – 1.64 (m, 2H), 1.56 – 1.48 (m, 2H), 1.42 – 1.28 (m, 2H), 1.23 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.39, 170.92, 127.20 (q, *J* = 276.3 Hz), 68.87, 52.19, 46.18, 35.51, 33.63 (q, *J* = 28.6 Hz), 23.55, 22.38 (q, *J* = 3.2 Hz), 20.96, 19.84.



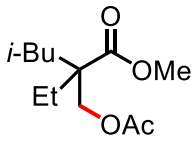
Methyl 3-acetoxy-2-methyl-2-((2-nitrophenoxy)methyl)propanoate (2y')

Following **General Procedure** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 17.0 mg, 55%, mono/di > 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.3, 7.5, 1.7 Hz, 1H), 7.12 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.06 (ddd, *J* = 8.5, 7.5, 1.1 Hz, 1H), 4.42 (d, *J* = 11.1 Hz, 1H), 4.34 (d, *J* = 11.1 Hz, 1H), 4.30 (d, *J* = 8.7 Hz, 1H), 4.20 (d, *J* = 8.7 Hz, 1H), 3.75 (s, 3H), 2.03 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.57, 170.50, 152.15, 134.37, 125.98, 120.98, 114.84, 70.73, 65.48, 52.60, 47.18, 20.89, 18.03 (1 carbon signal was not assigned due to overlaps); HRMS (ESI-TOF) Calcd for $C_{14}H_{18}NO_7$ $[M+H]^+$: 312.1078; found: 312.1085.



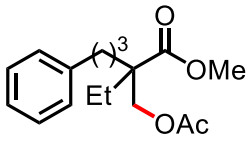
Methyl 2-(acetoxymethyl)-2-ethylhexanoate (2z')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 12.0 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.20 (d, *J* = 11.3 Hz, 1H), 4.19 (d, *J* = 11.3 Hz, 1H), 3.69 (s, 3H), 2.04 (s, 3H), 1.65 (qd, *J* = 7.5, 3.2 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.29 (q, *J* = 7.5 Hz, 2H), 1.22 – 1.09 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.45, 170.97, 64.87, 51.86, 49.80, 32.64, 26.19, 25.96, 23.22, 21.00, 14.06, 8.48; HRMS (ESI-TOF) Calcd for $C_{12}H_{23}O_4$ $[M+H]^+$: 231.1591; found: 231.1589.



Methyl 2-(acetoxymethyl)-2-ethyl-4-methylpentanoate (2aa')

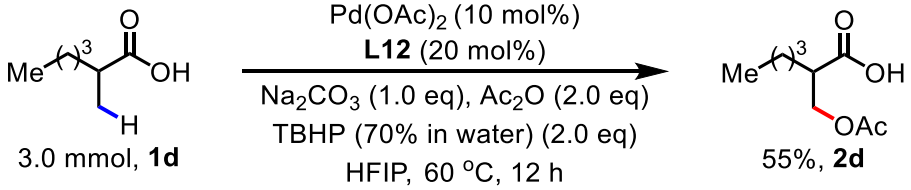
Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 12.5 mg, 54%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.24 (d, *J* = 11.4 Hz, 1H), 4.19 (d, *J* = 11.4 Hz, 1H), 3.68 (s, 3H), 2.05 (s, 3H), 1.75 – 1.51 (m, 5H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.85, 170.99, 64.33, 51.73, 49.07, 42.59, 26.80, 24.35, 24.19, 23.49, 21.00, 8.39; HRMS (ESI-TOF) Calcd for $C_{12}H_{23}O_4$ $[M+H]^+$: 231.1591; found: 231.1593.



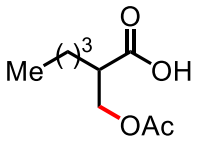
Methyl 2-(acetoxymethyl)-2-ethyl-5-phenylpentanoate (2ab')

Following **General Procedure** on 0.1 mmol scale. Purification by pTLC afforded the title compound (colorless oil, 16.0 mg, 55%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.20 – 7.12 (m, 3H), 4.22 – 4.13 (m, 2H), 3.67 (s, 3H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.99 (s, 3H), 1.68 – 1.57 (m, 4H), 1.55 – 1.45 (m, 2H), 0.78 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.25, 170.91, 142.01, 128.50, 128.45, 125.98, 64.72, 51.90, 49.79, 36.19, 32.32, 26.06, 25.74, 20.94, 8.46; HRMS (ESI-TOF) Calcd for $C_{17}H_{24}NaO_4$ $[M+Na]^+$: 315.1567; found: 315.1575.

Scale-up Reaction for β-C(sp^3)–H Acetoxylation



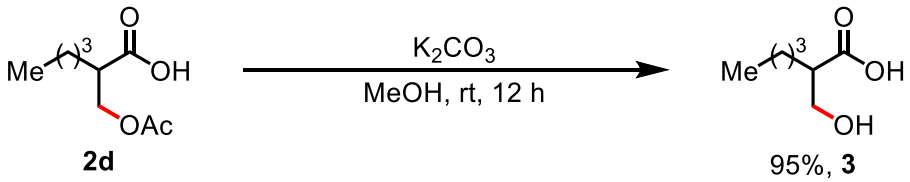
In the sealed tube, $Pd(OAc)_2$ (10 mol%, 66.0 mg), ligand **L12** (20 mol%, 102.0 mg), and Na_2CO_3 (1.0 eq, 318.0 mg) in order were weighed in air and placed with a magnetic stir bar. Then HFIP (30.0 mL), carboxylic acid **1d** (3.0 mmol, 0.43 mL), Ac_2O (2.0 eq, 0.57 mL), and TBHP (70% in water) (2.0 eq, 0.83 mL) were added. The reaction mixture was stirred at rt for 3 minutes, and then heated to 60 °C for 24 hours (600 rpm). After being allowed to cool to room temperature, the mixture was treated with AcOH (1.0 mL) and concentrated *in vacuo*. The crude mixture was purified by column chromatography to afford corresponding β-acetoxylation free carboxylic acid **2d** (55%, 310 mg).



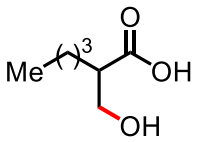
2-(Acetoxymethyl)hexanoic acid (2d)

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.25 (dd, *J* = 11.0, 5.2 Hz, 1H), 4.21 (dd, *J* = 11.0, 8.3 Hz, 1H), 2.78 – 2.70 (m, 1H), 2.06 (s, 3H), 1.71 – 1.64 (m, 1H), 1.60 – 1.51 (m, 1H), 1.41 – 1.29 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.50, 171.01, 64.46, 44.63, 29.21, 28.47, 22.64, 20.98, 13.95; HRMS (ESI-TOF) Calcd for $C_9H_{17}O_4$ $[M+H]^+$: 189.1121; found: 189.1130.

Experimental Procedure for Deprotection of Acetyl Group



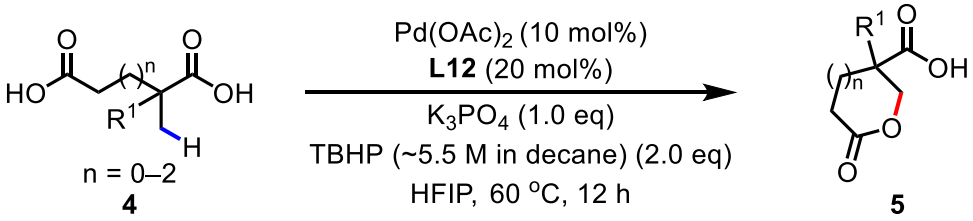
In the culture tube, **2d** (0.1 mmol, 18.8 mg) and K_2CO_3 (2.0 eq, 27.6 mg) were weighed in air and placed with a magnetic stir bar. Then MeOH (1.0 mL) was added. The reaction mixture was stirred at rt for 12 hours. The resulting mixture was diluted with EA, washed with saturated NH_4Cl solution, dried with $MgSO_4$, and concentrated *in vacuo* to afford pure β-hydroxy acid **3** (95%, 14.0 mg).



2-(Hydroxymethyl)hexanoic acid (3)

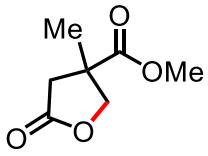
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.31 (br s, 2H), 3.86 – 3.74 (m, 2H), 2.67 – 2.56 (m, 1H), 1.72 – 1.61 (m, 1H), 1.59 – 1.49 (m, 1H), 1.41 – 1.30 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.37, 63.14, 47.68, 29.42, 28.10, 22.70, 13.94; HRMS (ESI-TOF) Calcd for $C_7H_{15}O_3$ $[M+H]^+$: 147.1016; found: 147.1018.

General Procedure for Intramolecular β-C(sp^3)–H Acyloxylation



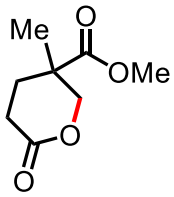
General Procedure: In the culture tube, $Pd(OAc)_2$ (10 mol%, 2.2 mg), ligand **L12** (20 mol%, 3.4 mg), Na_2CO_3 (1.0 eq, 10.6 mg), and carboxylic acid **4** (0.1 mmol) in order were weighed in air and placed with a magnetic stir bar. Then HFIP (1.0 mL) and TBHP (ca. 5.5 M in decane) (2.0 eq, 36 μL) were added. The reaction mixture was stirred at rt for 3 minutes, and then heated to 60 °C for 12 hours (600 rpm). After being allowed to cool to room temperature, the mixture was treated with AcOH (0.05 mL) and concentrated *in vacuo*. The resulting mixture was dissolved in MeOH (1.0 mL), treated with $TMSCHN_2$ (2.0 eq), and concentrated *in vacuo* after 1 hour. The crude mixture was purified by column chromatography to afford corresponding methyl esters **5'**.

Substrate Scope for β-C(sp^3)–H Intramolecular β-C(sp^3)–H Acyloxylation



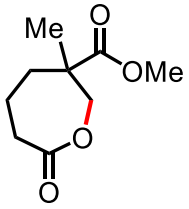
Methyl 3-methyl-5-oxotetrahydrofuran-3-carboxylate (5a')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 8.0 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.55 (d, *J* = 9.3 Hz, 1H), 4.08 (d, *J* = 9.3 Hz, 1H), 3.77 (s, 3H), 3.06 (d, *J* = 17.6 Hz, 1H), 2.43 (d, *J* = 17.6 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.06, 173.98, 75.43, 53.06, 46.41, 39.14, 22.75; HRMS (ESI-TOF) Calcd for $C_7H_{11}O_4$ $[M+H]^+$: 159.0652; found: 159.0660.



Methyl 3-methyl-6-oxotetrahydro-2H-pyran-3-carboxylate (5b')

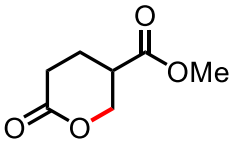
Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 12.5 mg, 73%). The NMR data matches the reported data[11].



Methyl 3-methyl-7-oxooxepane-3-carboxylate (5c')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 11.0 mg, 59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.41 (d, *J* = 12.8 Hz, 1H), 4.14 (d, *J* = 12.8 Hz, 1H), 3.74 (s, 3H), 2.71 – 2.60 (m, 2H), 2.24 – 2.16 (m, 1H), 1.97 – 1.87 (m, 1H), 1.87 – 1.79 (m, 1H), 1.65 – 1.59 (m, 1H), 1.23 (s, 3H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 175.04, 174.71, 72.63, 68.06, 52.48, 45.89, 37.67, 33.88, 19.45; HRMS (ESI-TOF) Calcd for $C_9H_{15}O_4$ $[M+H]^+$: 187.0965; found: 187.0964.



Methyl 6-oxotetrahydro-2H-pyran-3-carboxylate (5d')

Following **General Procedure** on 0.1 mmol scale. Purification by column chromatography afforded the title compound (colorless oil, 8.5 mg, 54%). The NMR data matches the reported data[12].

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1. H. Park, N. Chekshin, P.-X. Shen, J.-Q. Yu, Ligand-enabled, palladium-catalyzed β-C(sp^3)–H arylation of weinreb amides. *ACS Catal.* **8**, 9292−9297 (2018).
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7. F. Fülöp, M. Palkó, J. Kámán, L. Lázár, R. Sillanpää, Synthesis of all four enantiomers of 1-aminoindane-2-carboxylic acid, a new cispentacin benzologue. *Tetrahedron: Asymmetry* **11**, 4179−4187 (2000).
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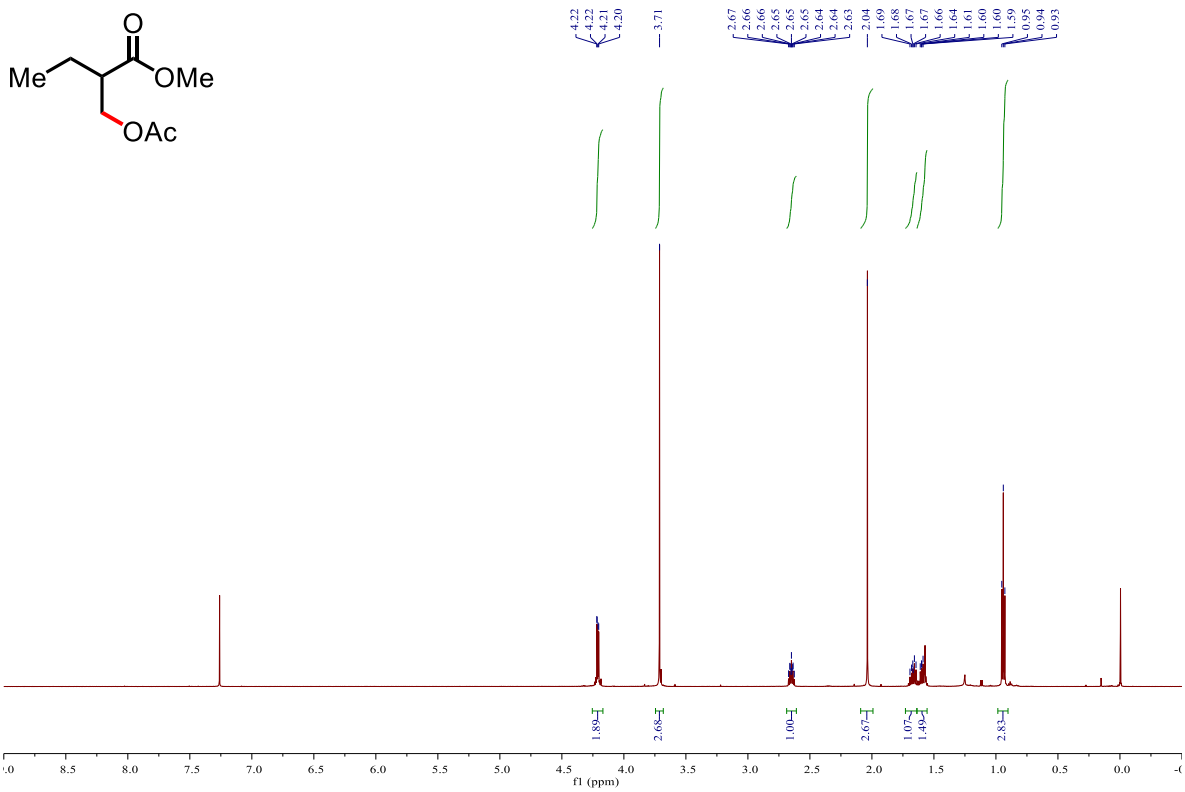
11. T. Mitsudo, N. Suzuki, T. Kobayashi, T. Kondo, $Ru_3(CO)_{12}$/1,10-phenanthroline-catalyzed hydroformylation of styrene and acrylic esters. *J. Mol. Catal. A* **137**, 253−262 (1999).
12. G. W. Fahnhorst, D. E. Stasiw, W. B. Tolman, T. R. Hoye, Isomerization of linear to hyperbranched polymers: two isomeric lactones converge via metastable isostructural polyesters to a highly branched analogue. *ACS Macro Lett.* **7**, 1144−1148 (2018).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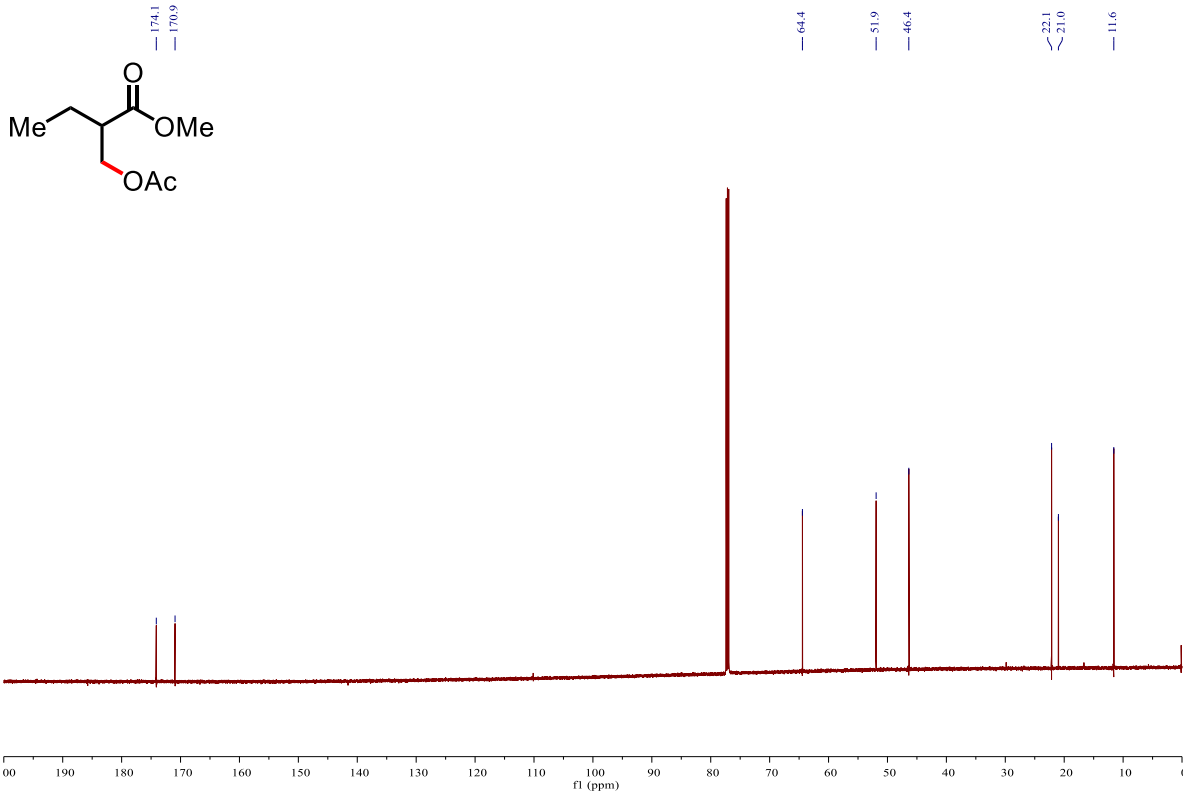
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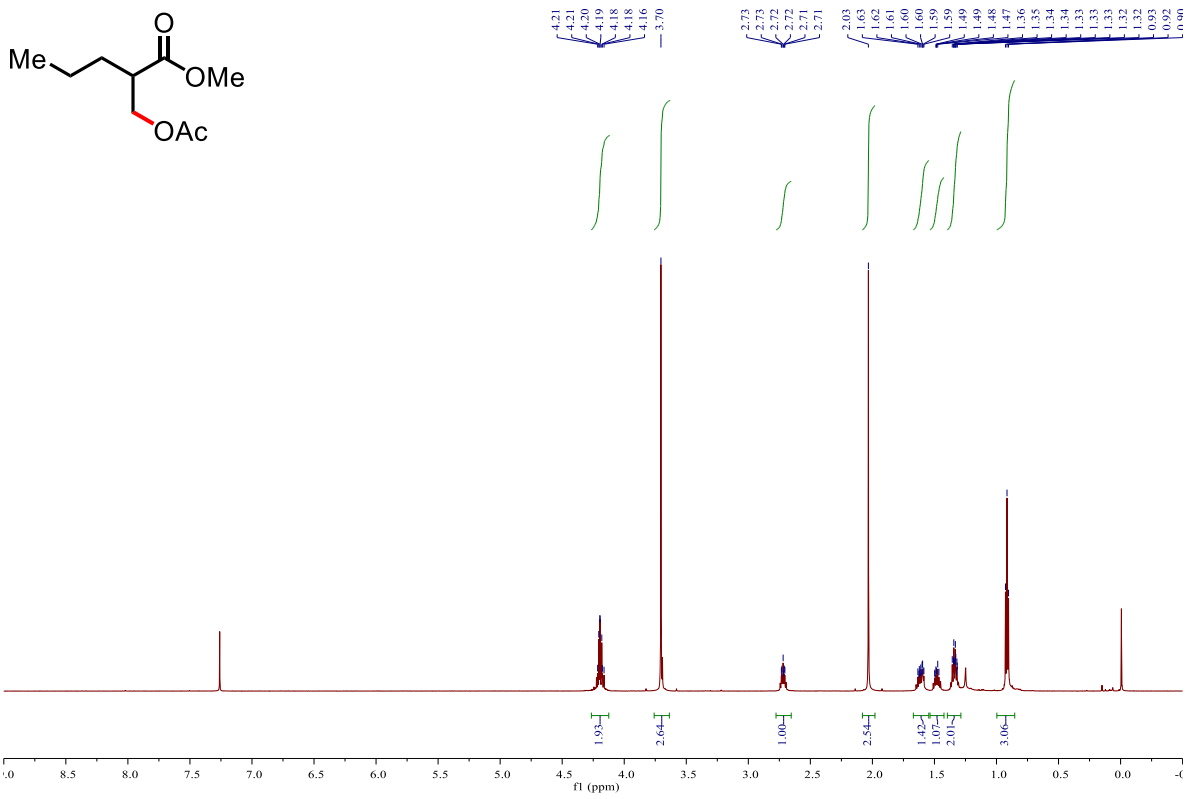
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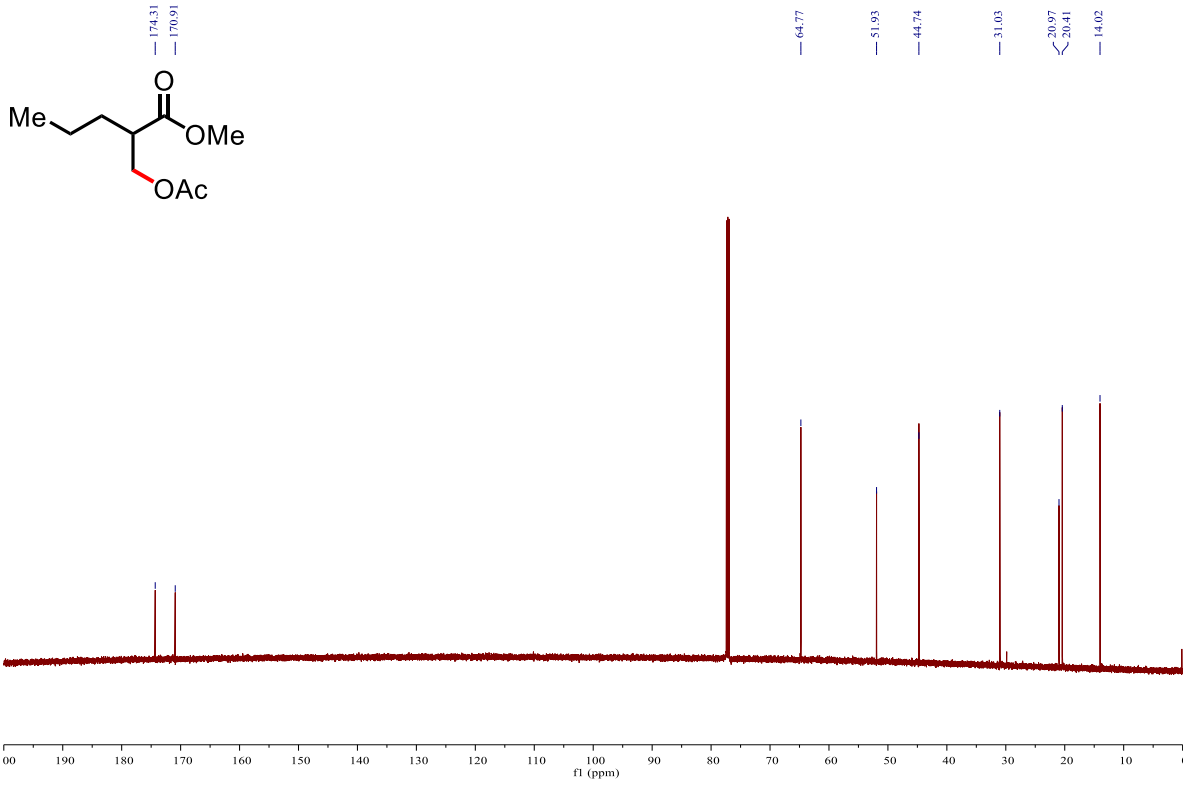
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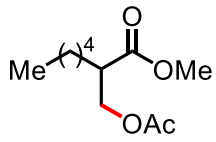
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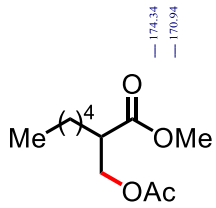
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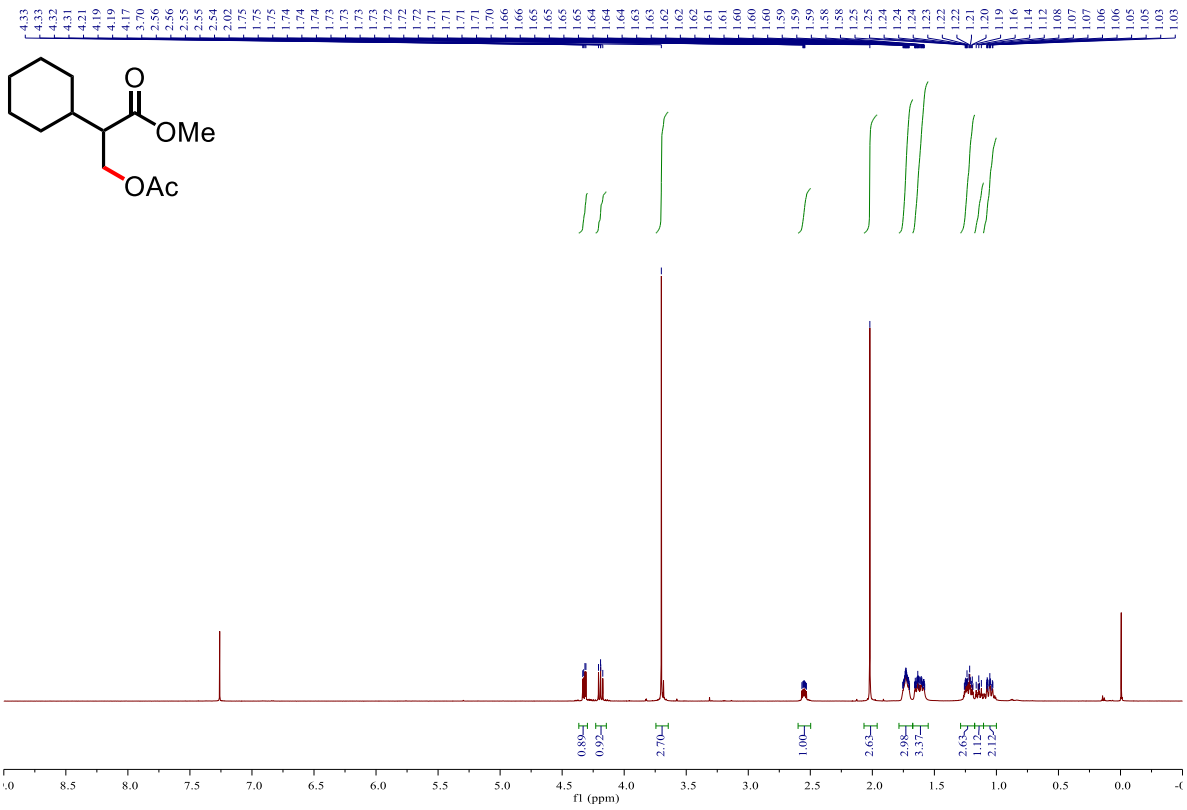
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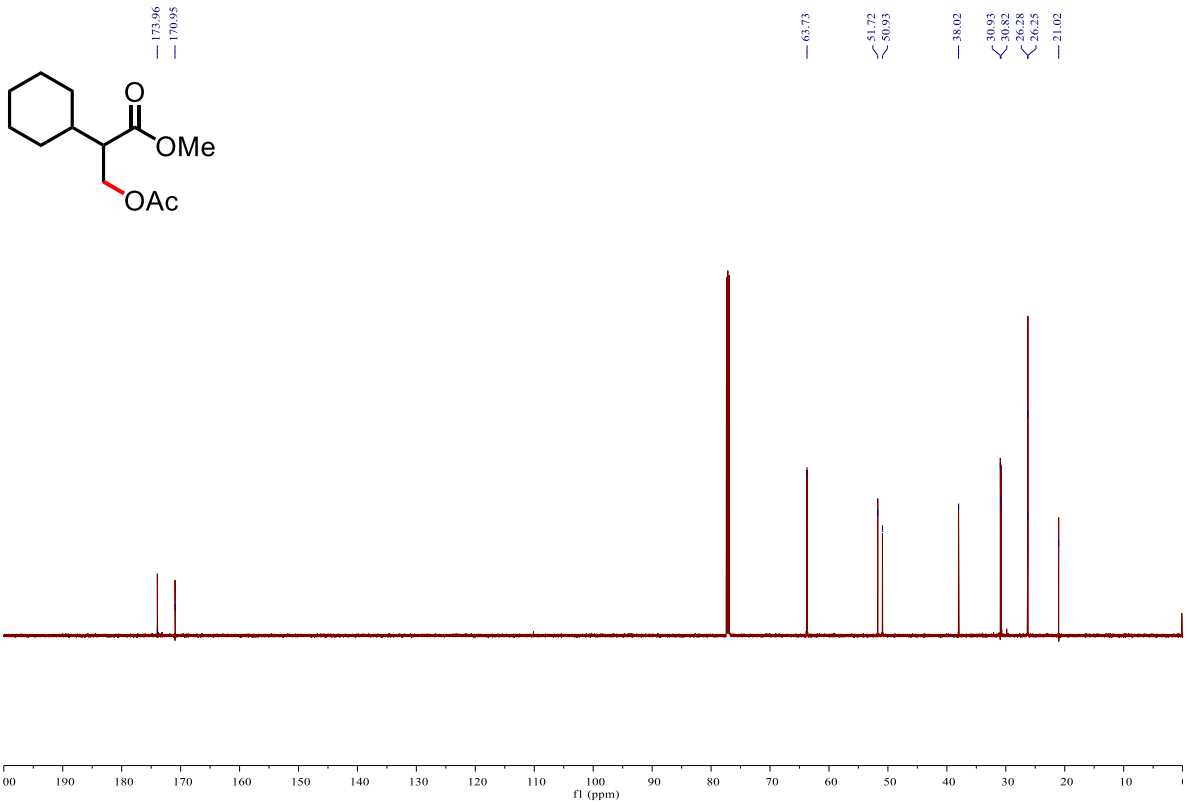
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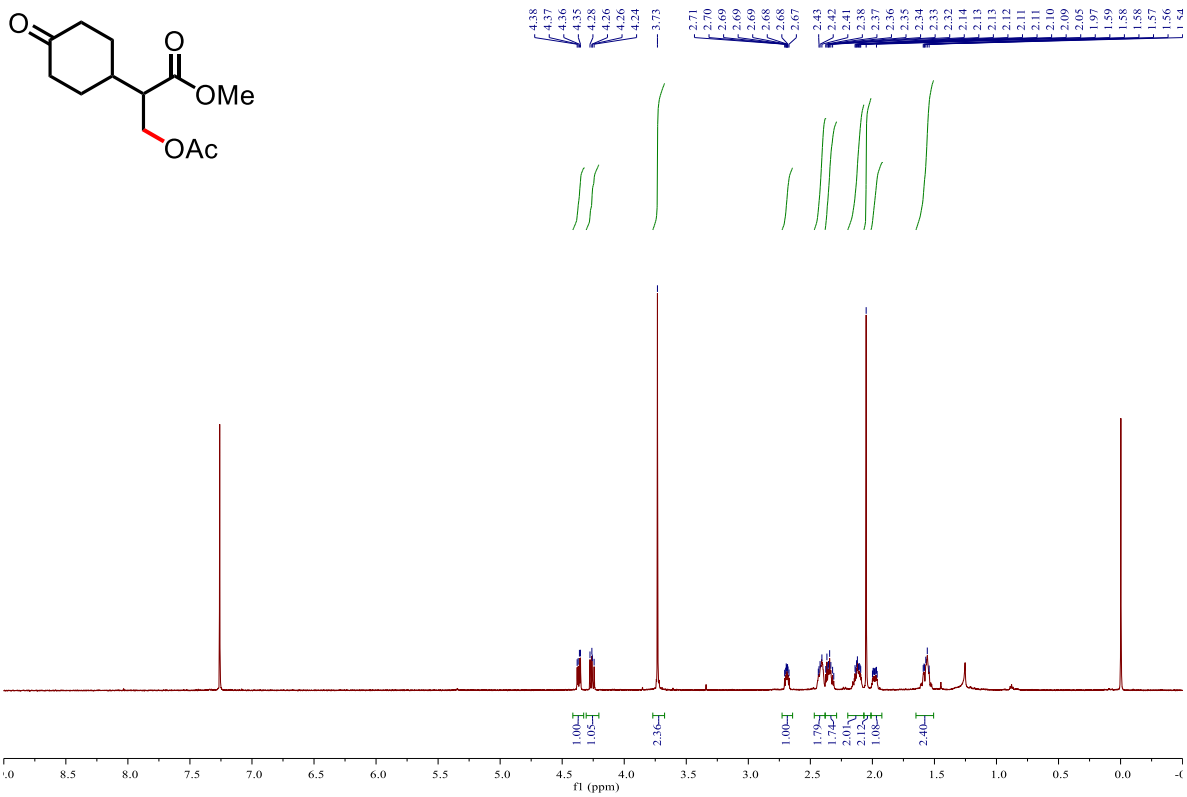
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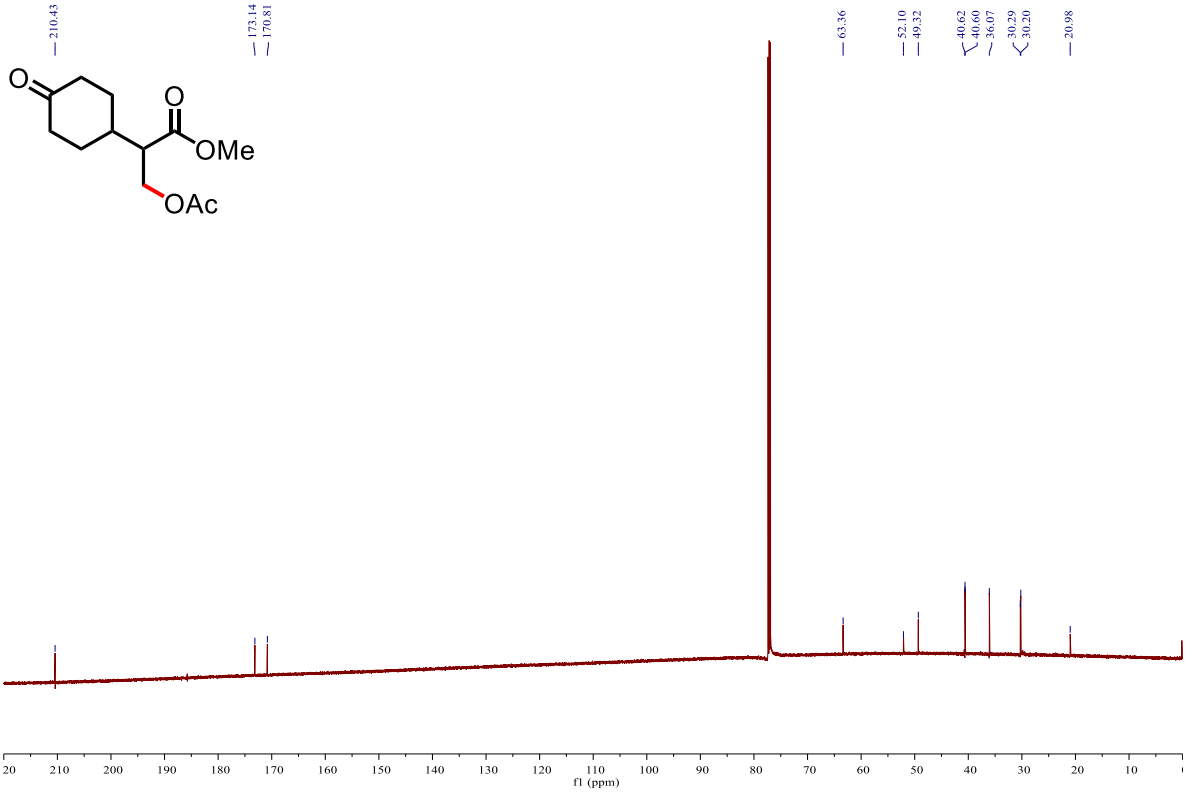
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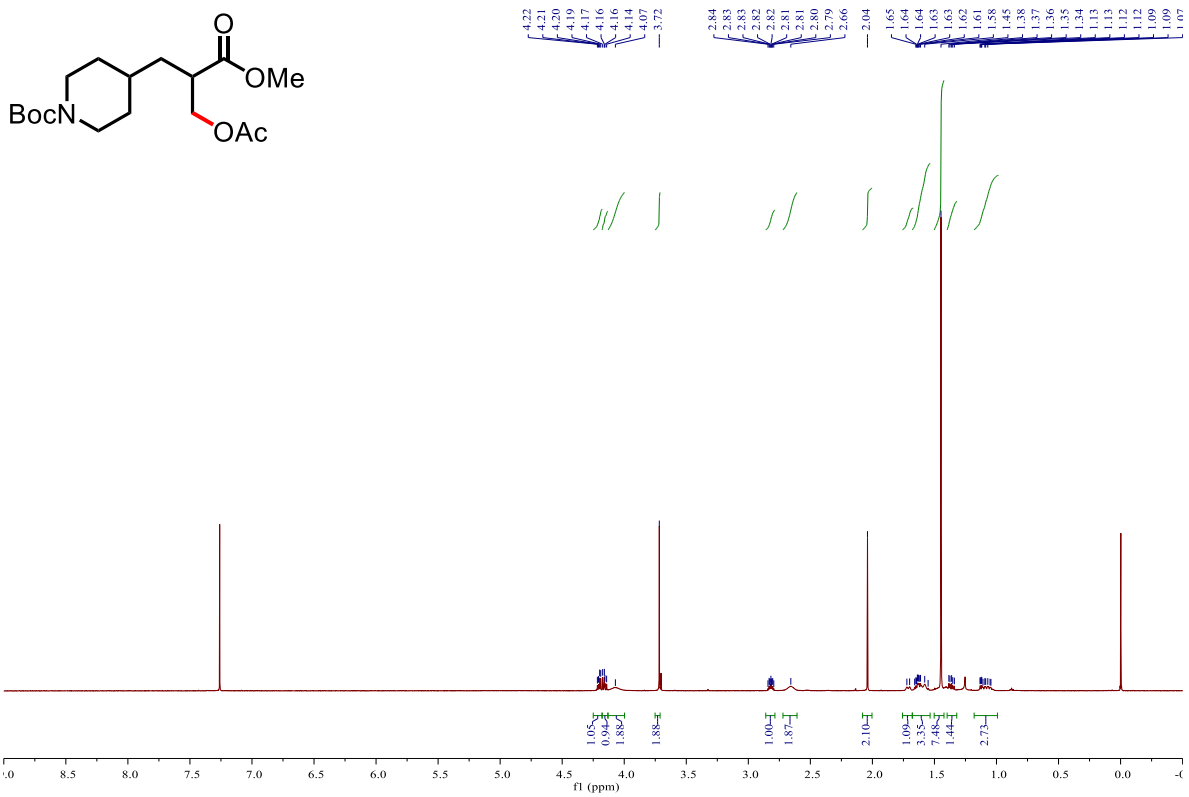
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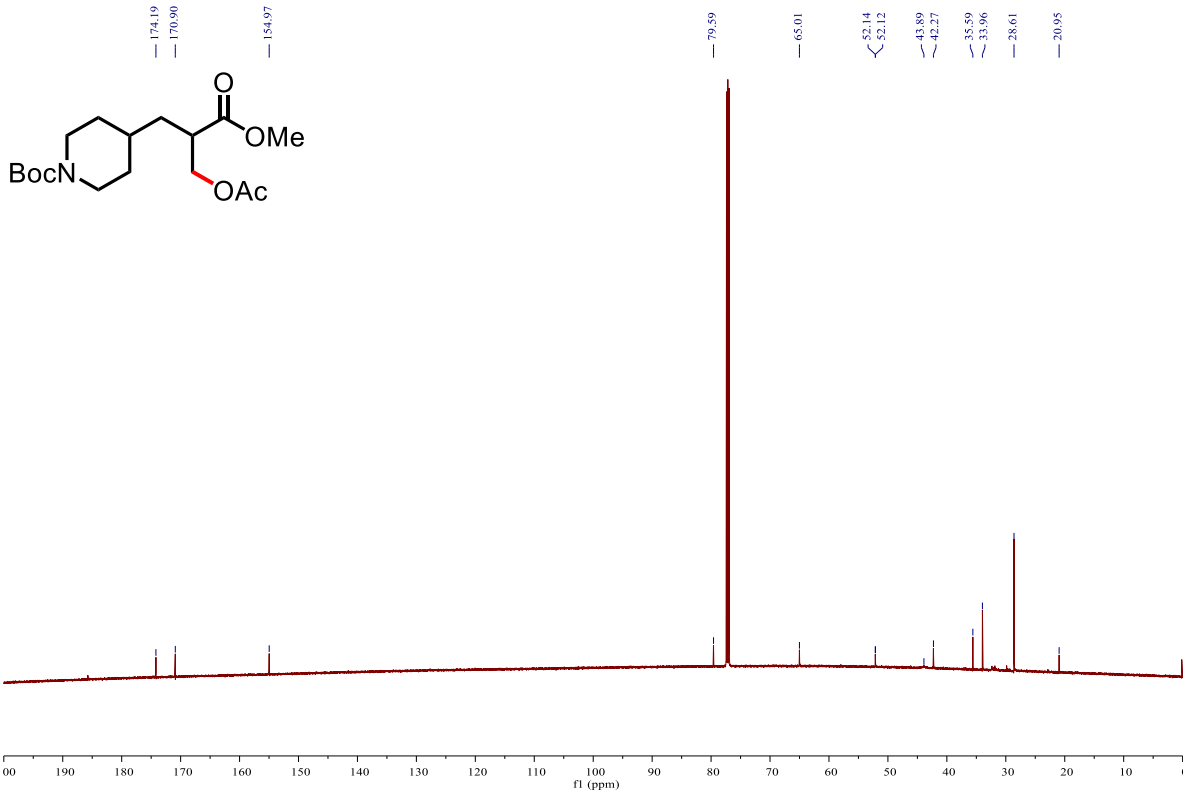
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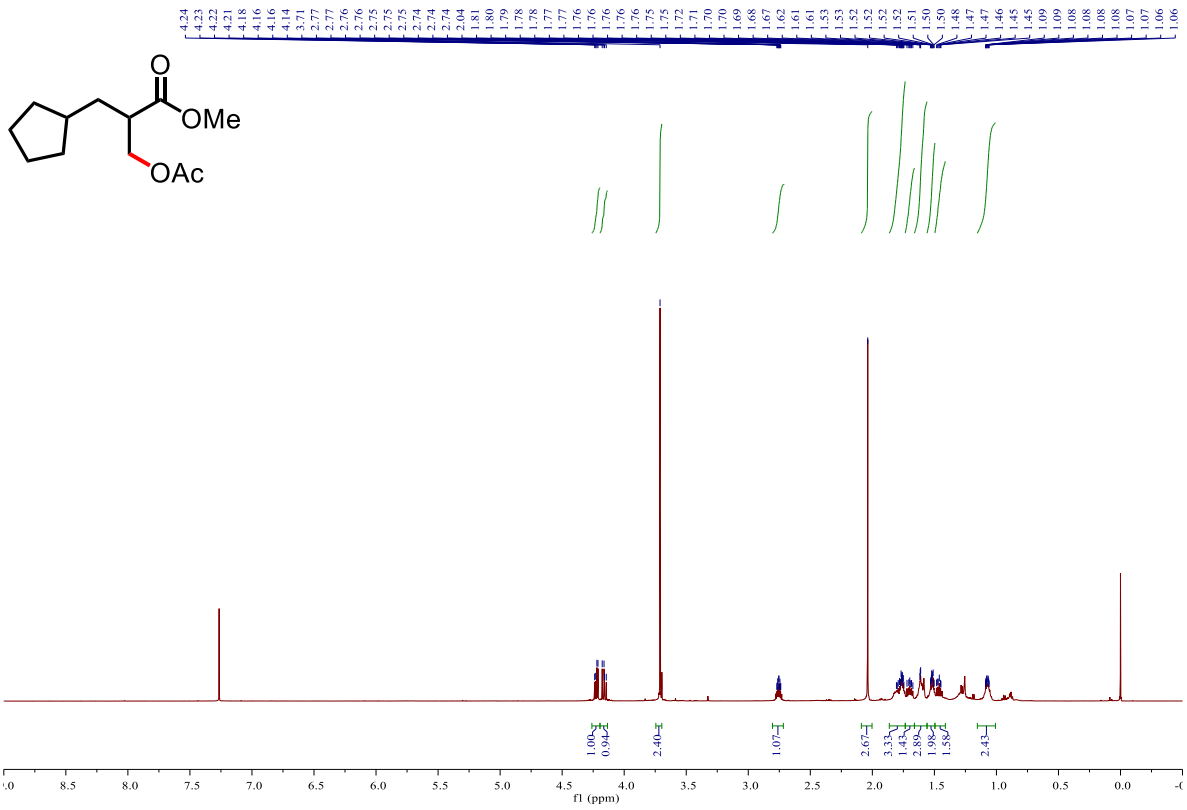
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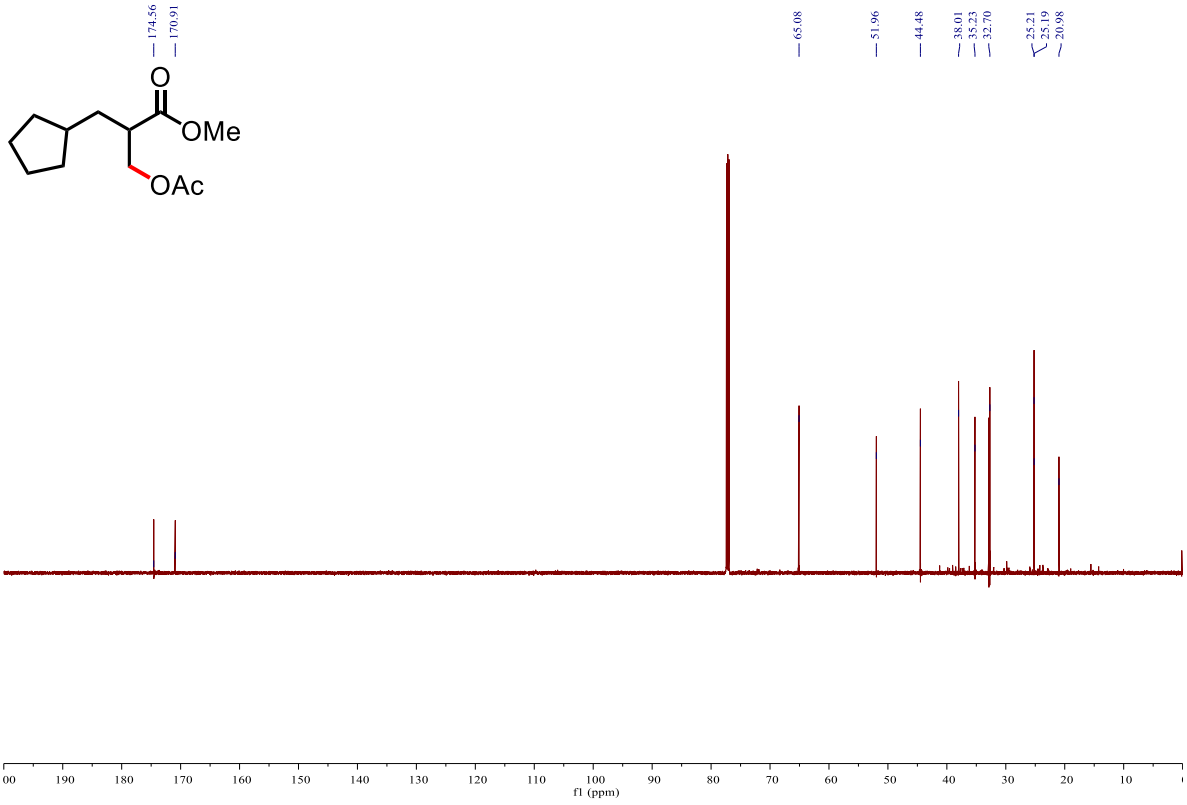
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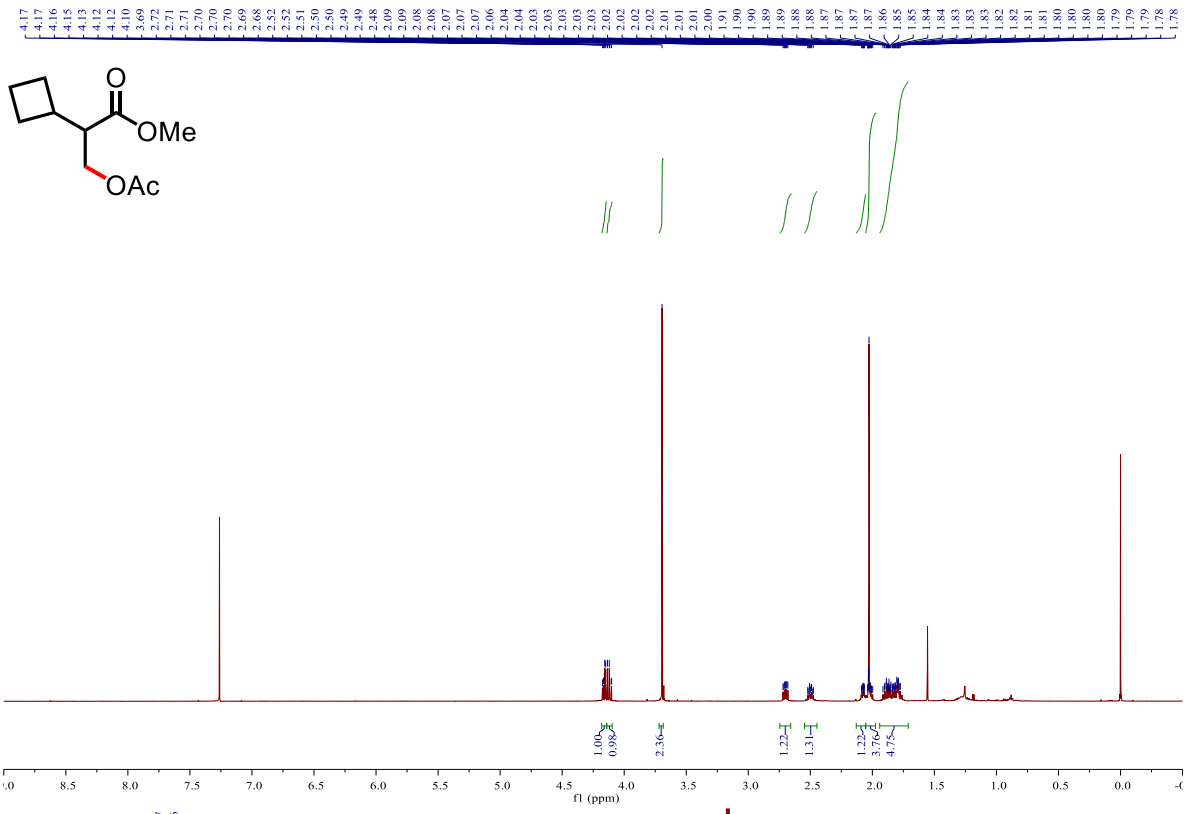
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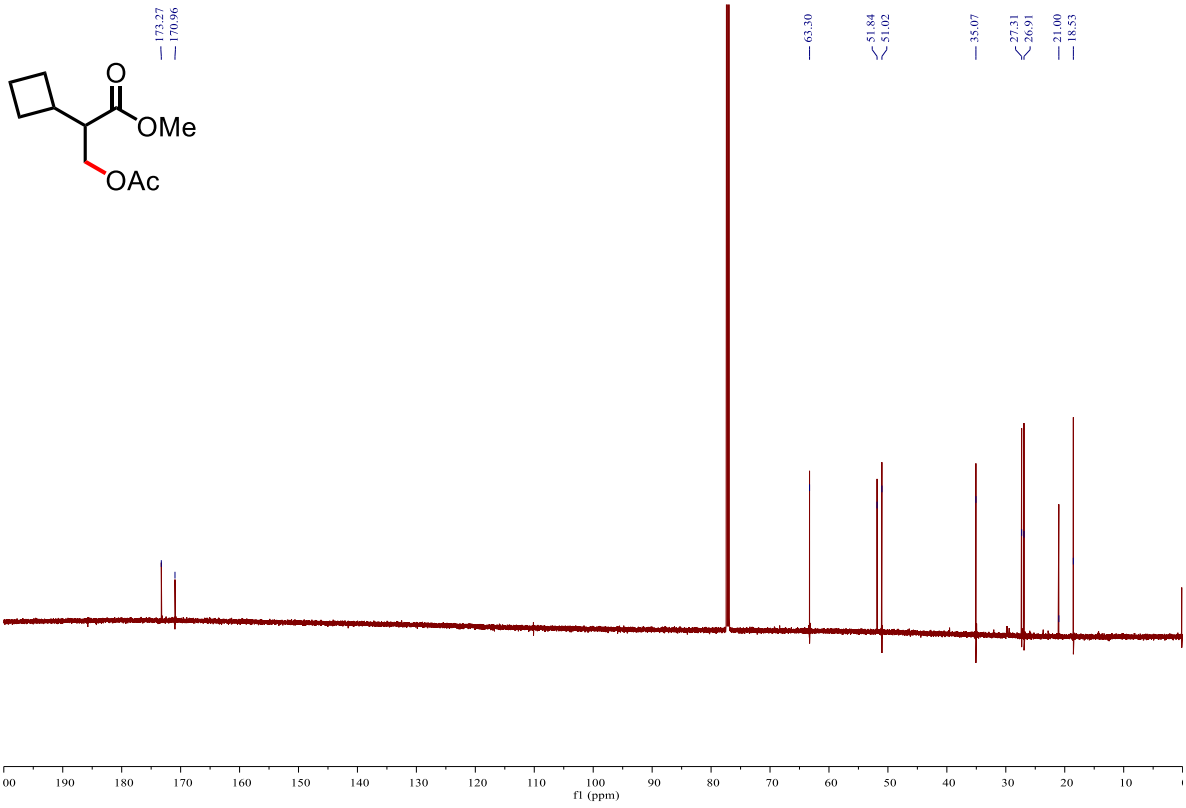
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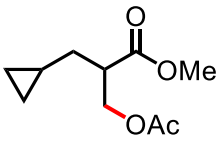
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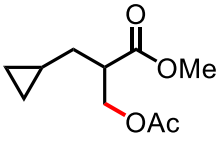
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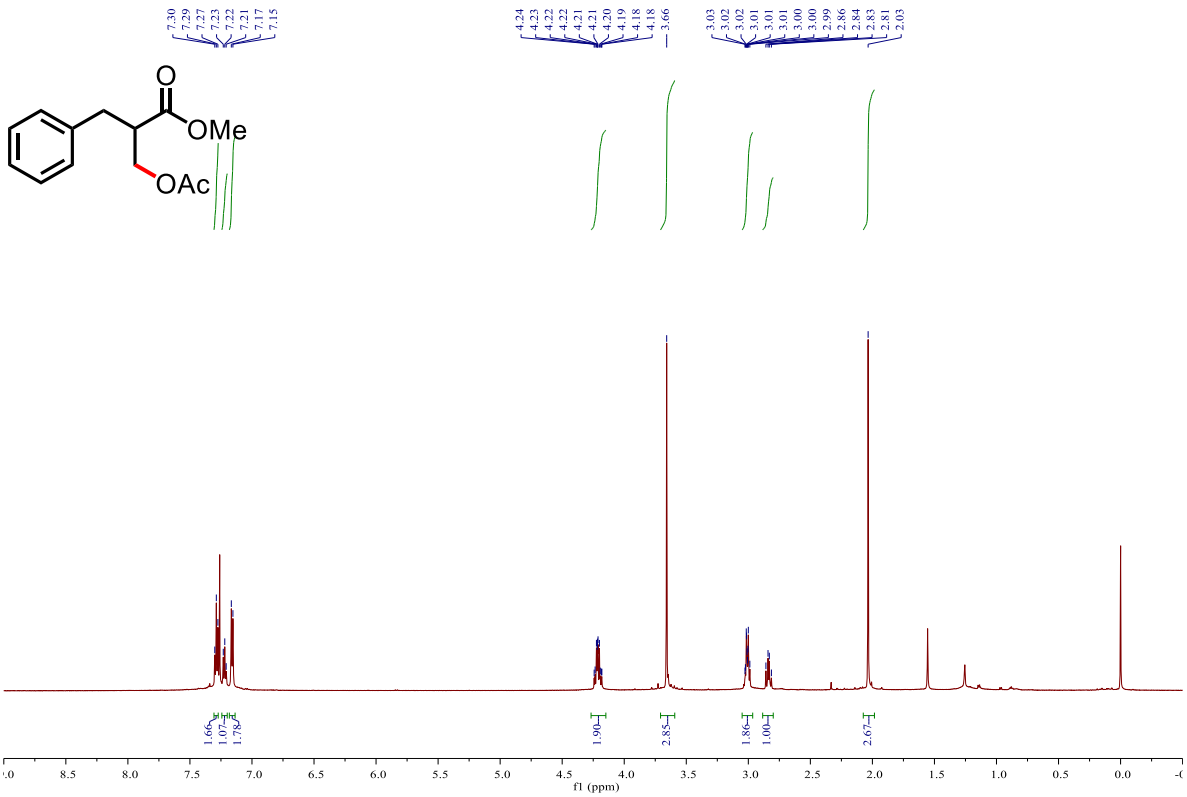
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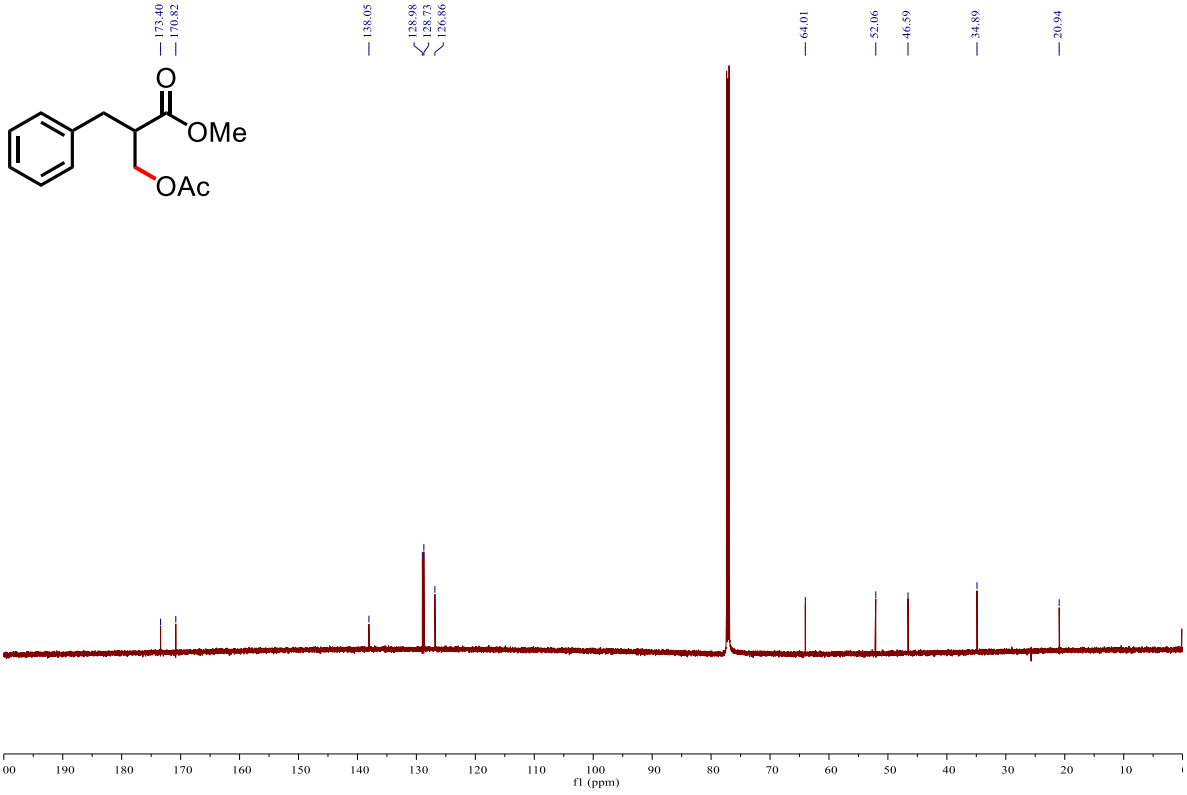
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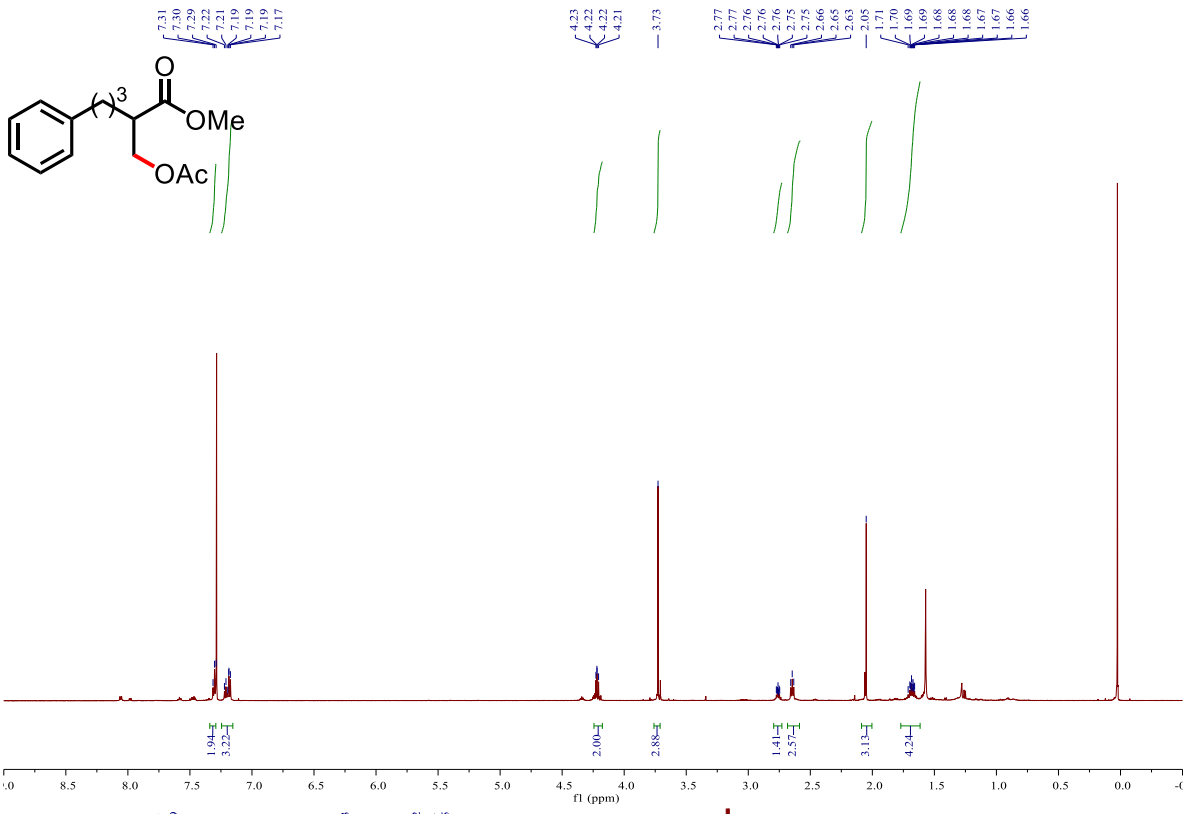
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4.22
4.21
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2.77
2.77
2.76
2.76
2.76
2.75
2.75
2.66
2.65
2.63
2.05
1.71
1.70
1.69
1.69
1.68
1.68
1.68
1.67
1.67
1.66
1.66
O
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OAc
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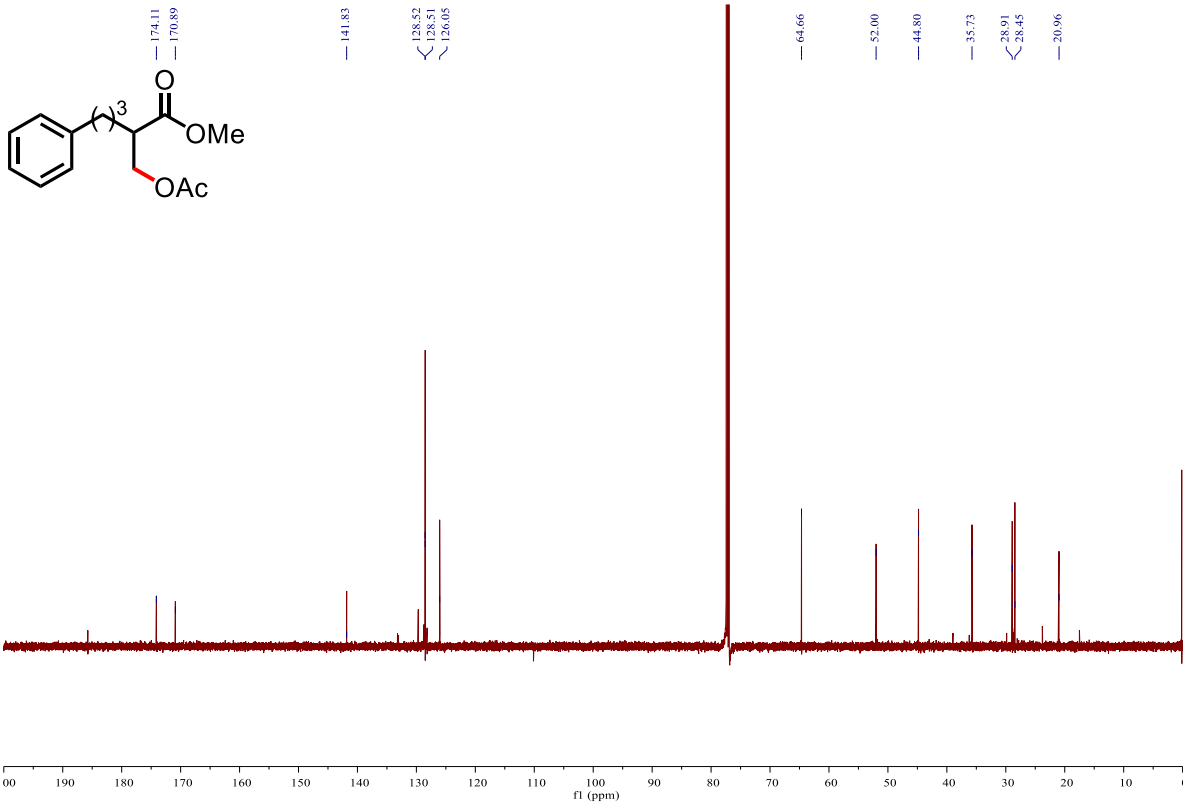
1.41
2.57
3.13
4.24
f1 (ppm)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141.83
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28.45
20.96
O
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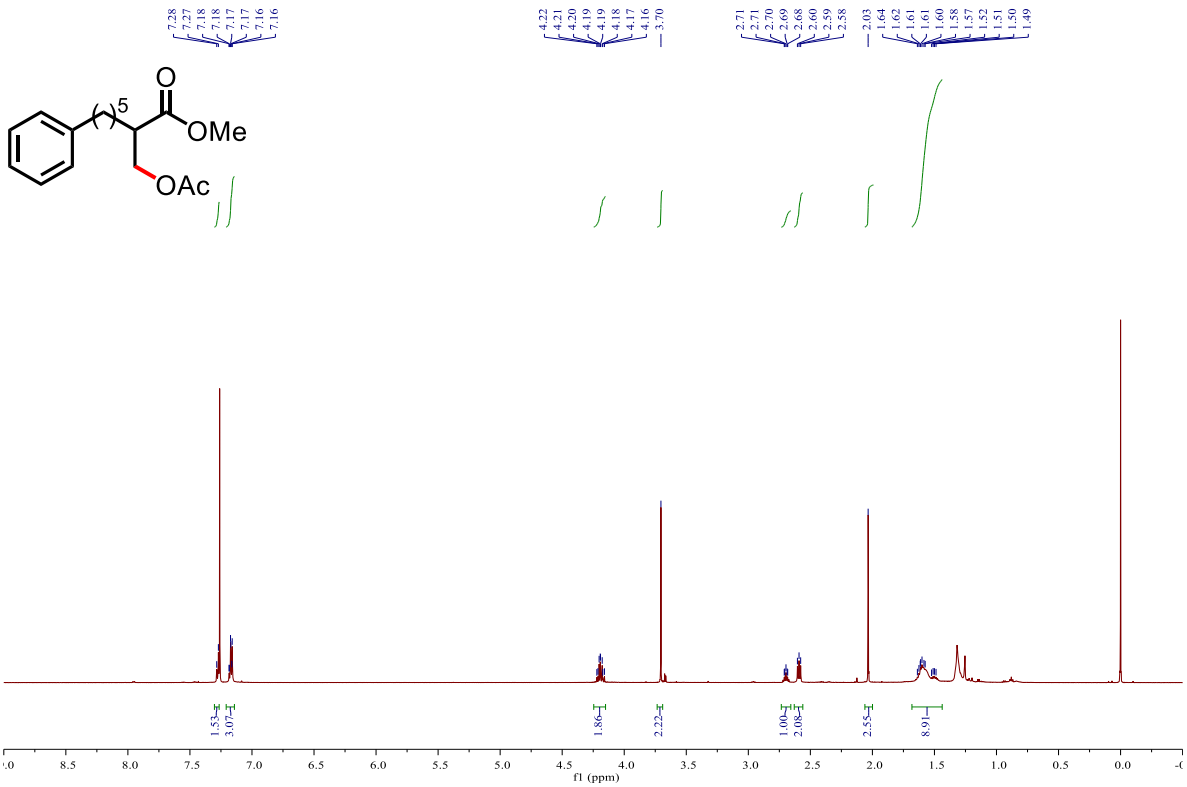
OMe
OAc
f1 (ppm)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2.69
2.68
2.66
2.59
2.58
2.03
1.64
1.62
1.61
1.61
1.60
1.58
1.57
1.52
1.51
1.50
1.49
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OAc
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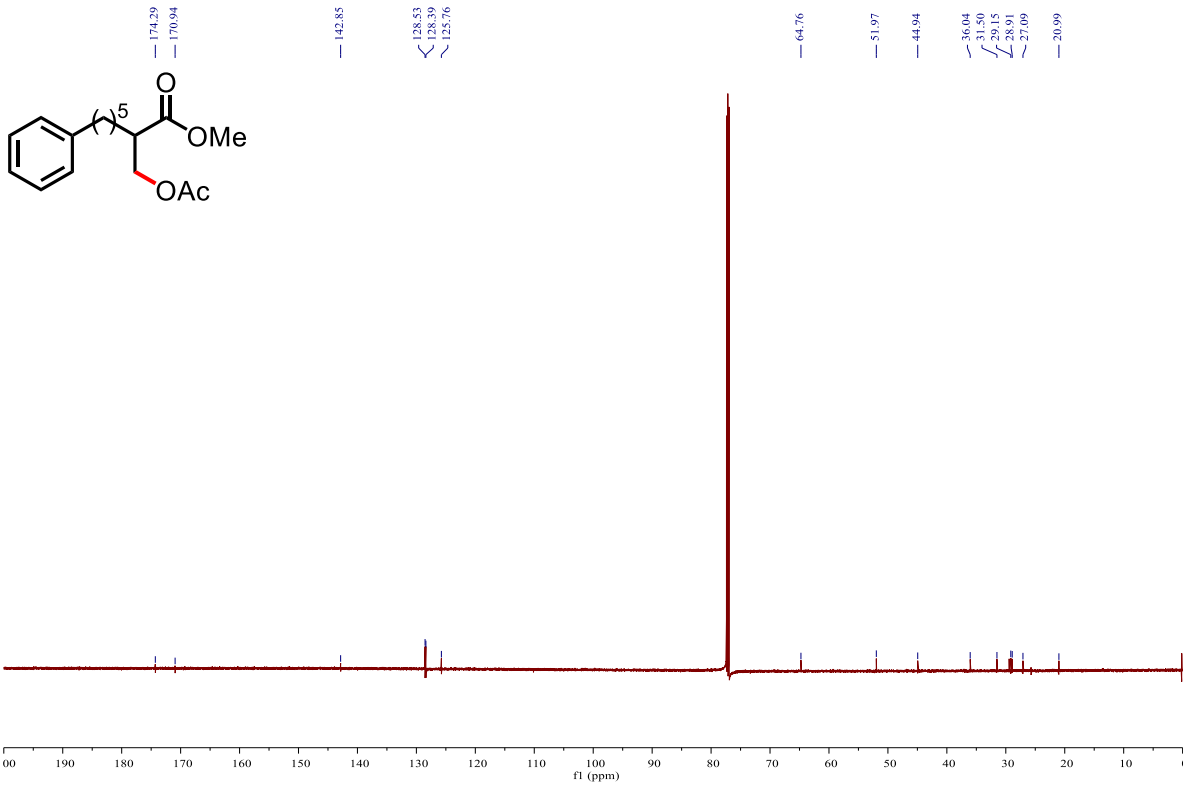
2.08
2.55
8.91
f1 (ppm)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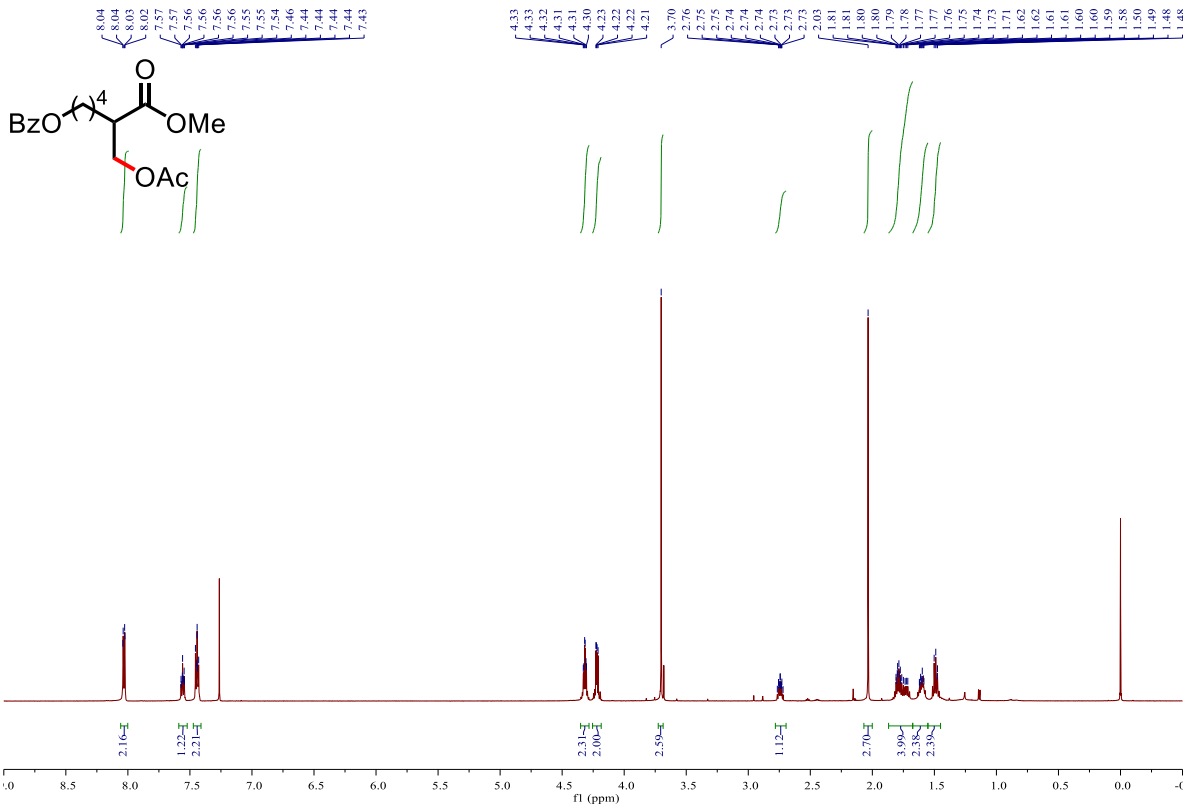
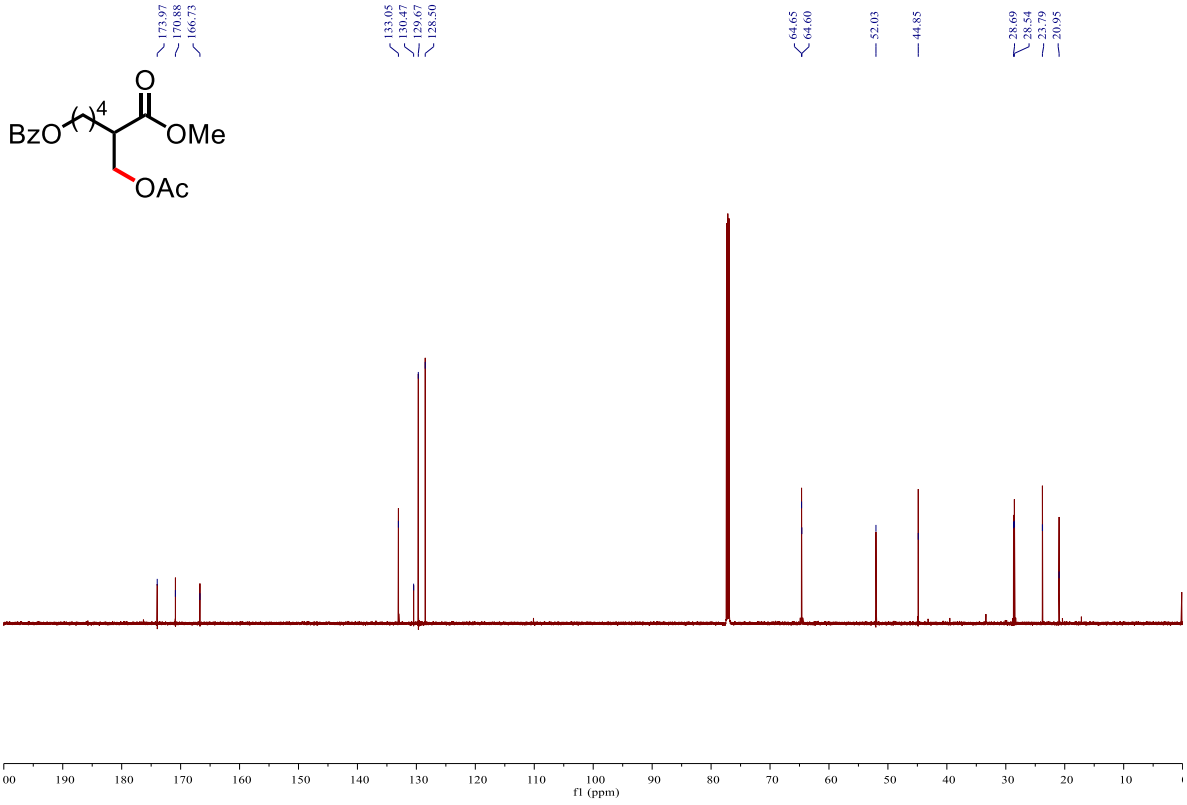
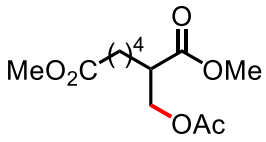
31.50
29.15
28.91
27.09
20.99
O
OMe
OAc
5
f1 (ppm)


BzO
OMe
OAc
fl (ppm)


BzO
OMe
OAc
fl (ppm)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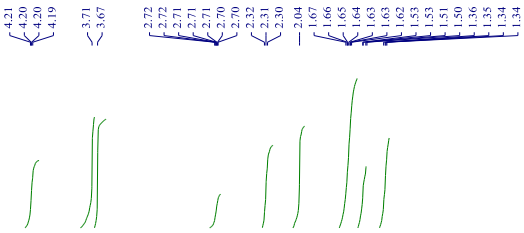
MeO2C
4
OMe
OAc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2.72
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2.71
2.71
2.70
2.70
2.32
2.31
2.30
2.04
1.67
1.66
1.65
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1.51
1.50
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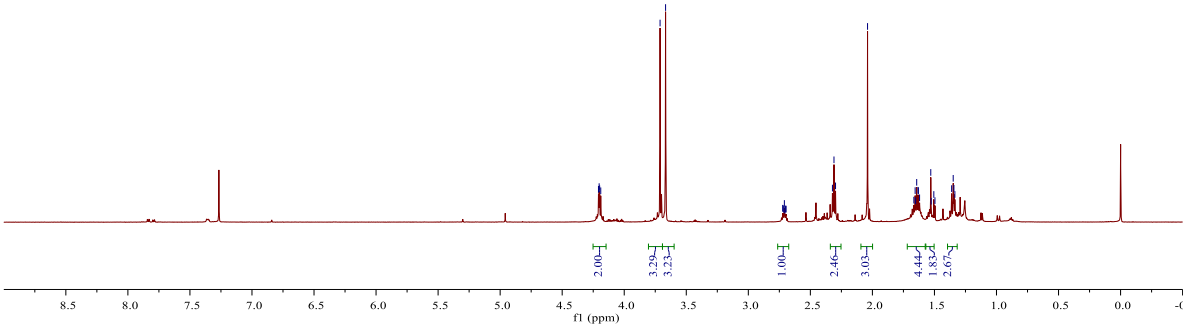
1.34
1.34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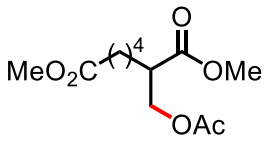
3.23
1.00
2.46
3.03
4.44
1.83
2.67
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


174.02
173.99
170.89


O
MeO2C
4
OMe
OAc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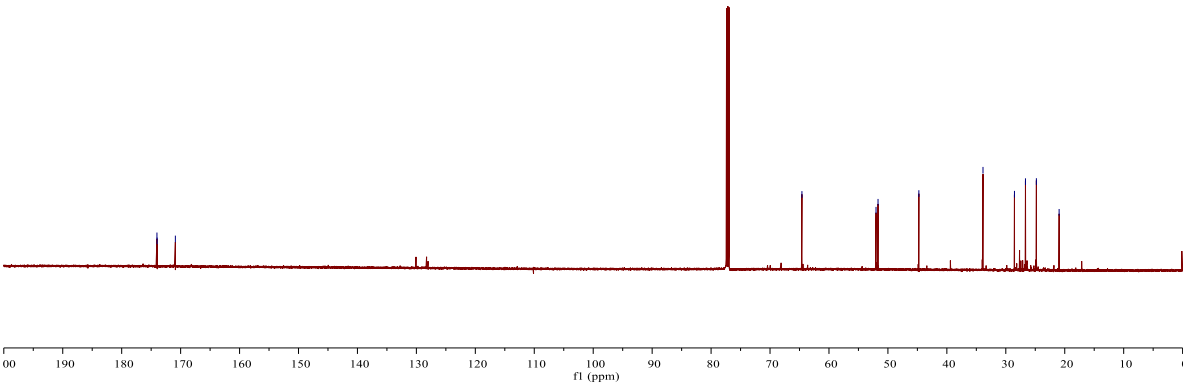
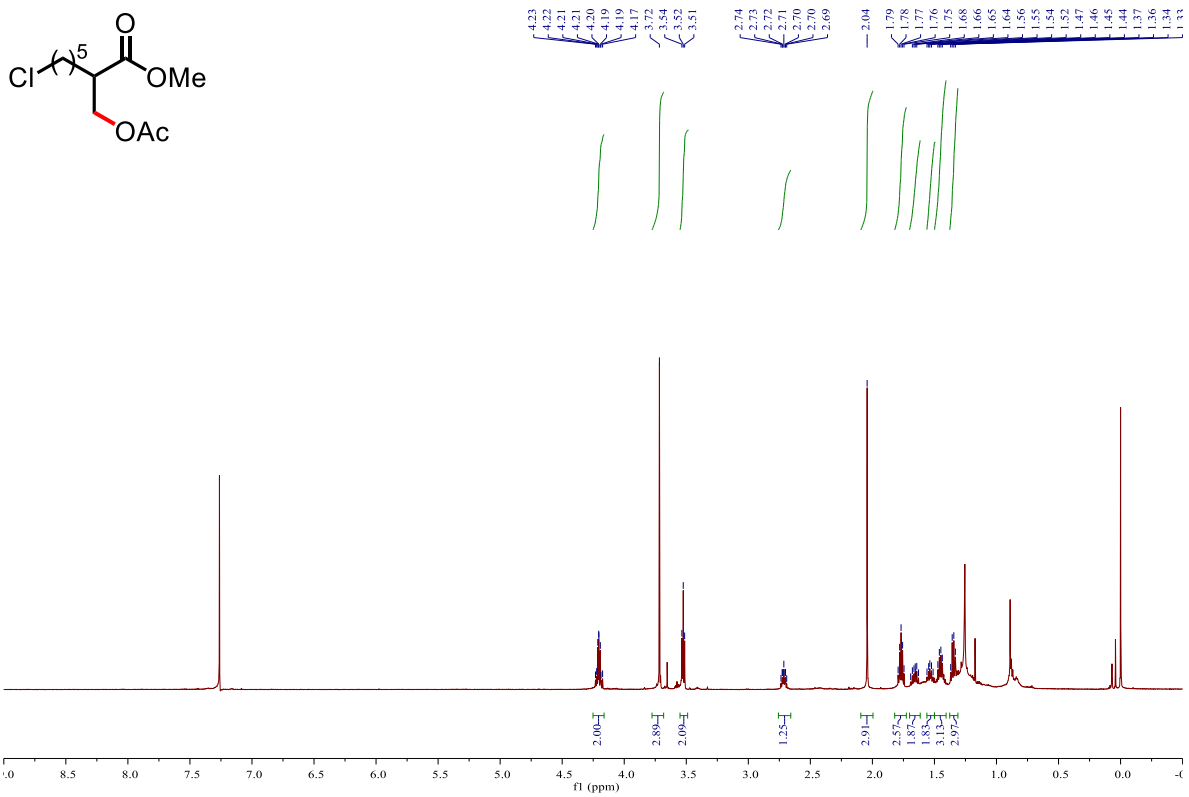
51.67
44.75
33.87
28.53
26.66
24.81
20.95


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Cl
5
O
OMe
OAc
4.23
4.22
4.21
4.21
4.20
4.19
4.19
4.17
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3.54
3.52
3.51
2.74
2.73
2.72
2.71
2.70
2.70
2.69
2.04
1.79
1.78
1.77
1.76
1.75
1.68
1.66
1.65
1.64
1.56
1.55
1.54
1.52
1.47
1.46
1.45
1.44
1.37
1.36
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2.00
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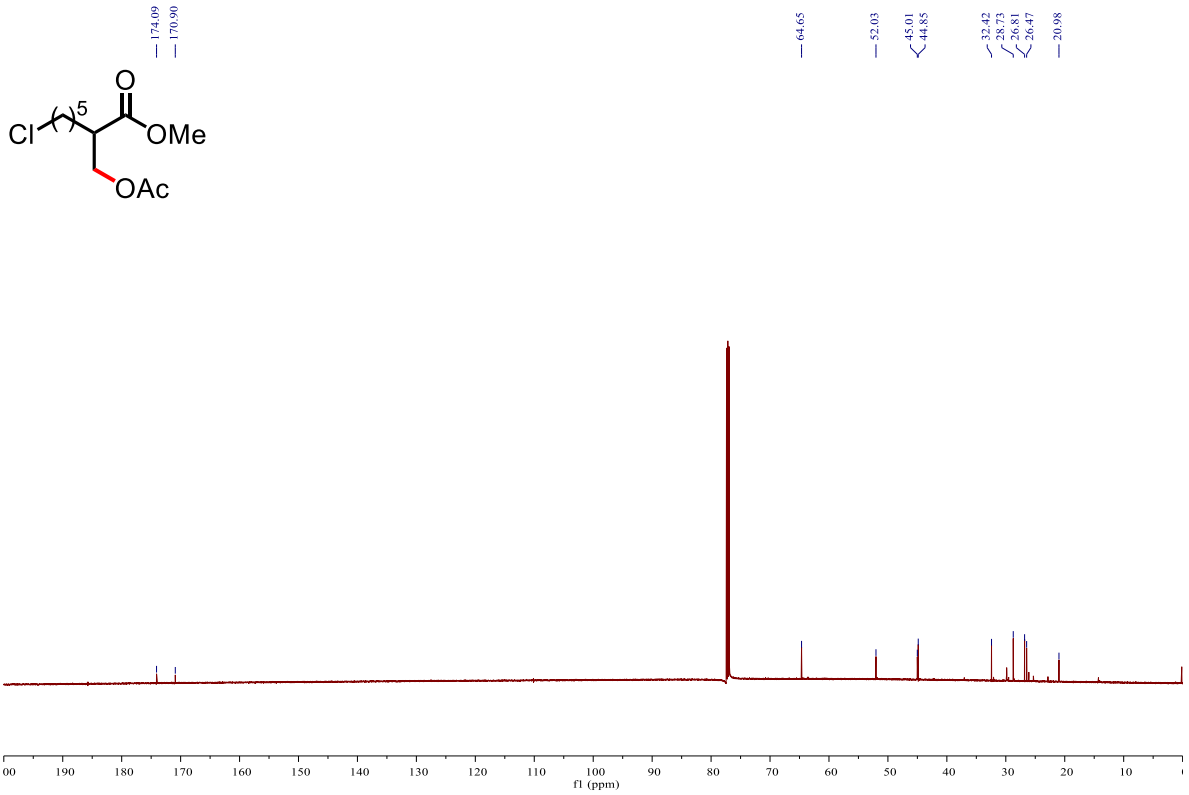
2.57
1.87
1.83
3.13
2.97
f1 (ppm)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170.90
64.65
52.03
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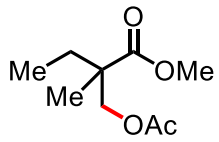
32.42
28.73
26.81
26.47
20.98
Cl
5
O
OMe
OAc
f1 (ppm)


O
Me
OMe
Me
OAc

4.21
4.19
4.09
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2.05
1.71
1.70
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1.69
1.68
1.68
1.67
1.67
1.66
1.65
1.57
1.56
1.55
1.54
1.54
1.53
1.52
1.51
1.50
1.19
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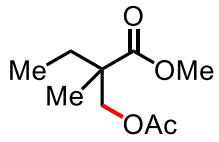
1.00
0.97
2.67
2.62
1.19
1.30
2.88
3.37
f1 (ppm)


O
Me
OMe
Me
OAc

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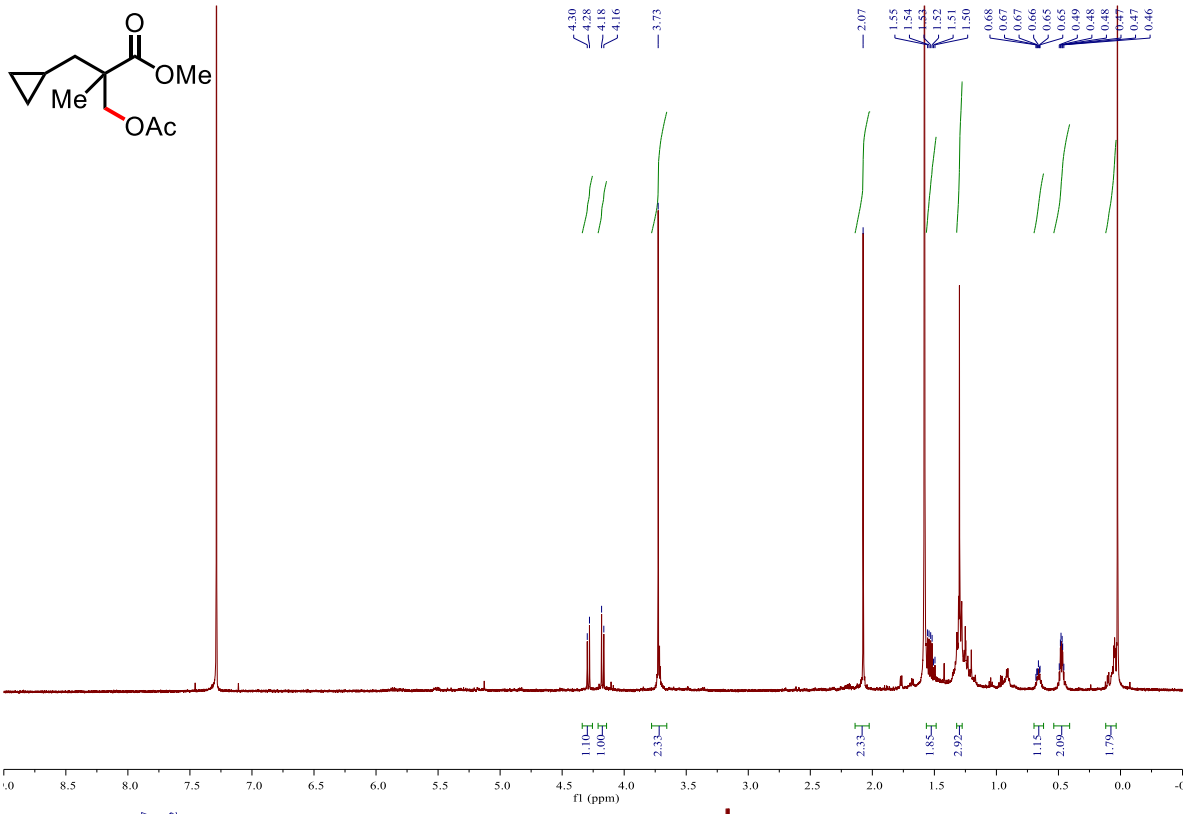
52.04
46.67
28.84
20.97
19.26
8.72
f1 (ppm)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OMe
Me
OAc
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4.18
4.16
3.73
2.07
1.55
1.54
1.53
1.52
1.51
1.50
0.68
0.67
0.67
0.66
0.65
0.65
0.49
0.48
0.48
0.47
0.46
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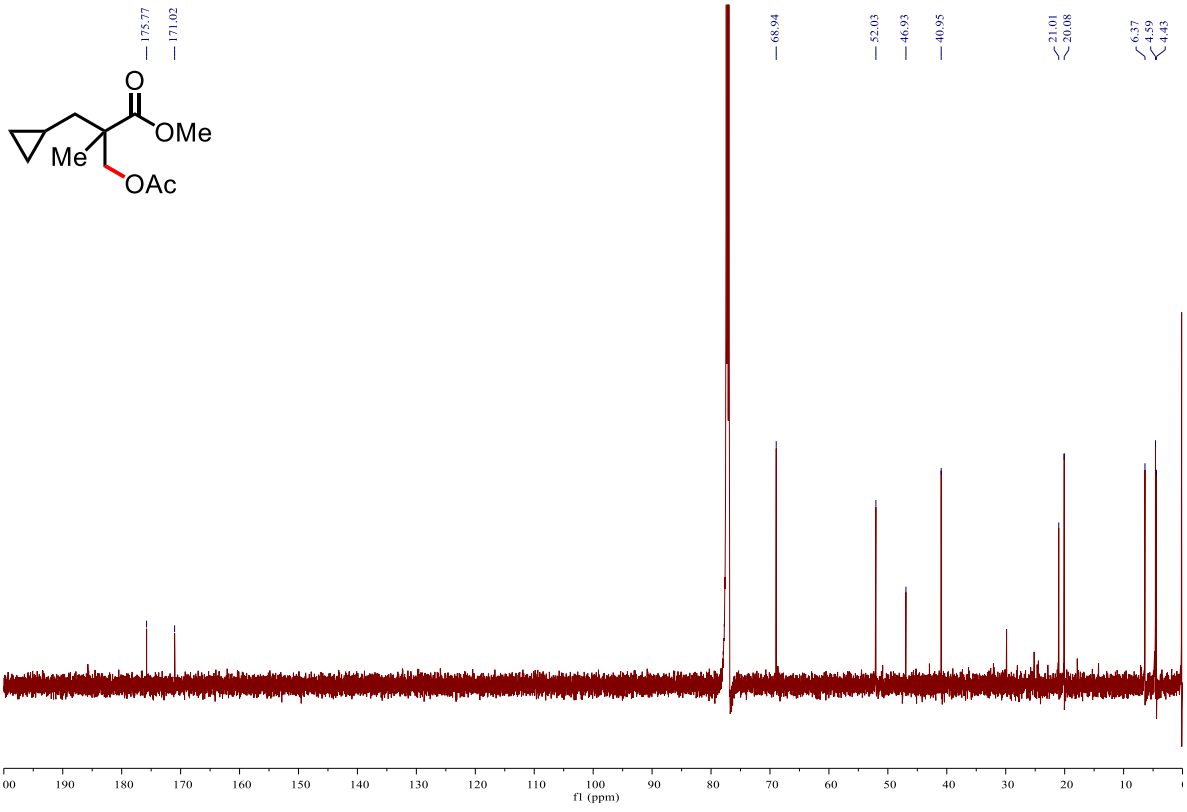
1.00
2.33
2.33
1.85
2.92
1.15
2.09
1.79
f1 (ppm)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Me
OAc
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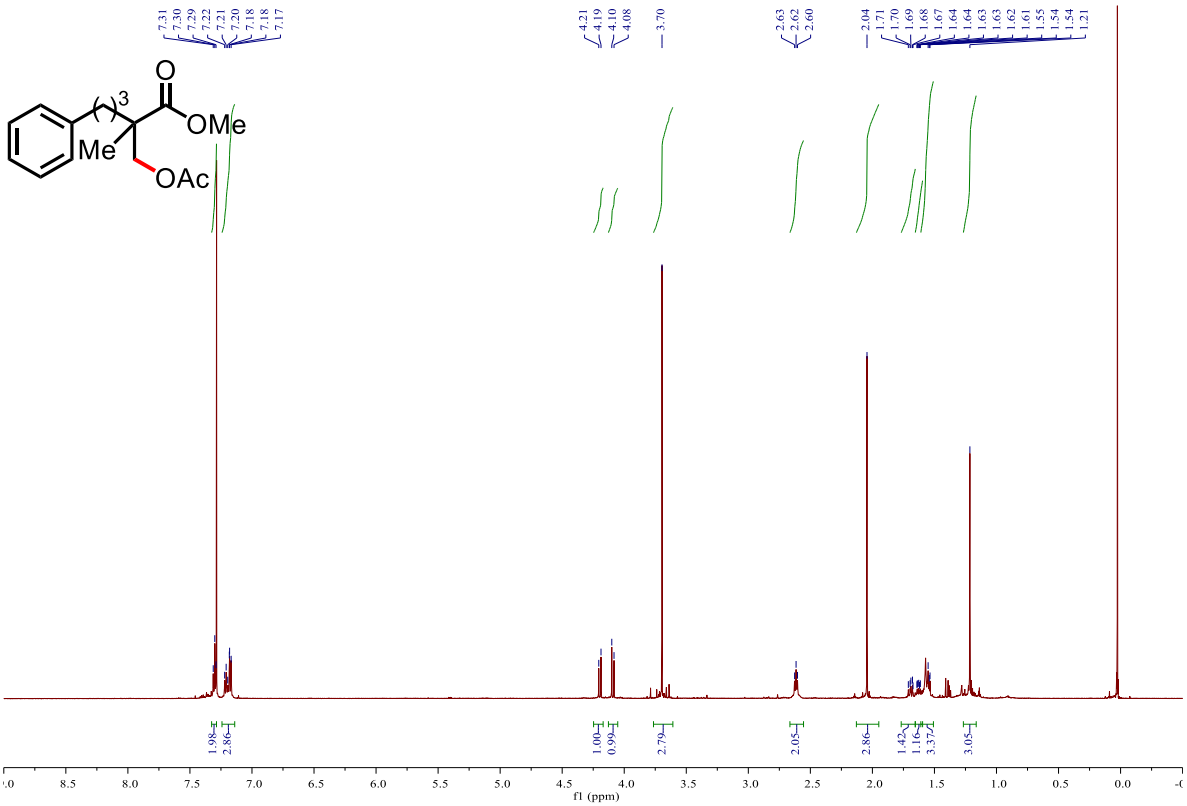
21.01
20.08
6.37
4.59
4.43
f1 (ppm)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4.19
4.10
4.08
3.70
2.63
2.62
2.60
2.04
1.71
1.70
1.69
1.68
1.67
1.64
1.64
1.63
1.62
1.61
1.55
1.54
1.54
1.21
O
OMe
3
Me
OAc
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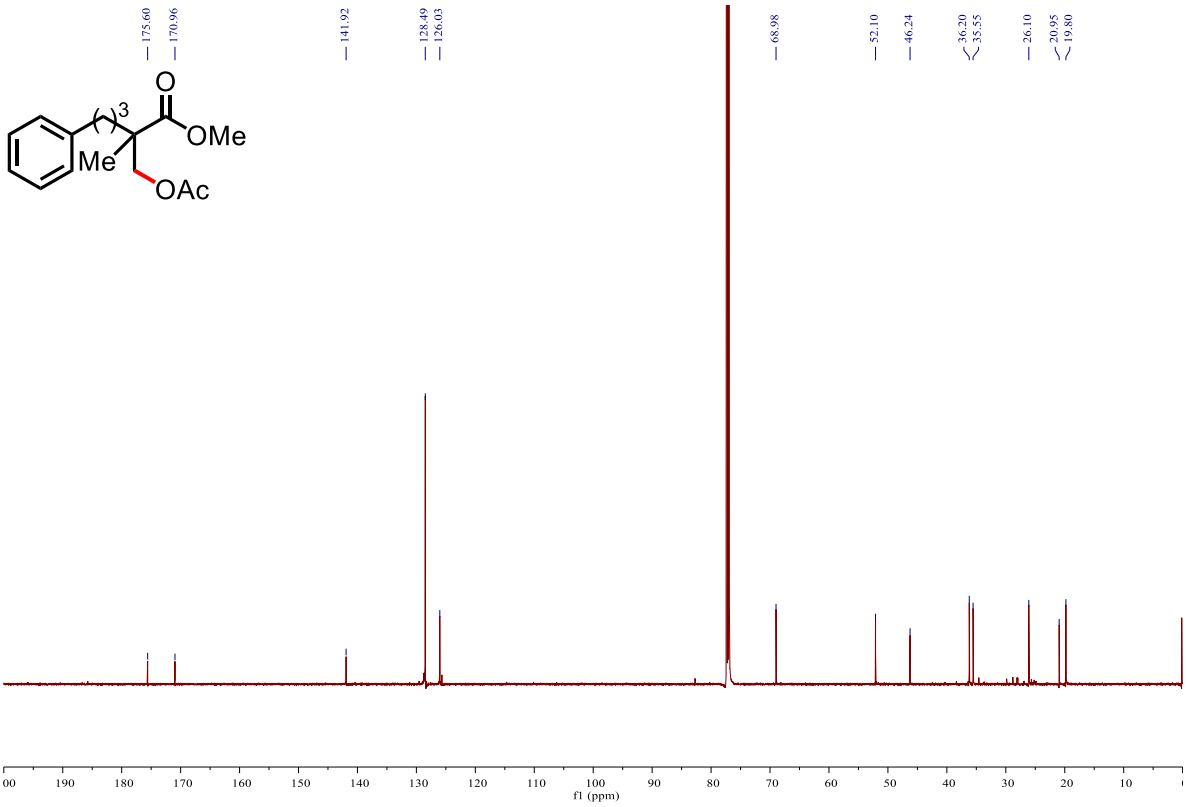
2.86
1.00
0.99
2.79
2.05
2.86
1.42
1.16
3.37
3.05
f1 (ppm)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128.49
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68.98
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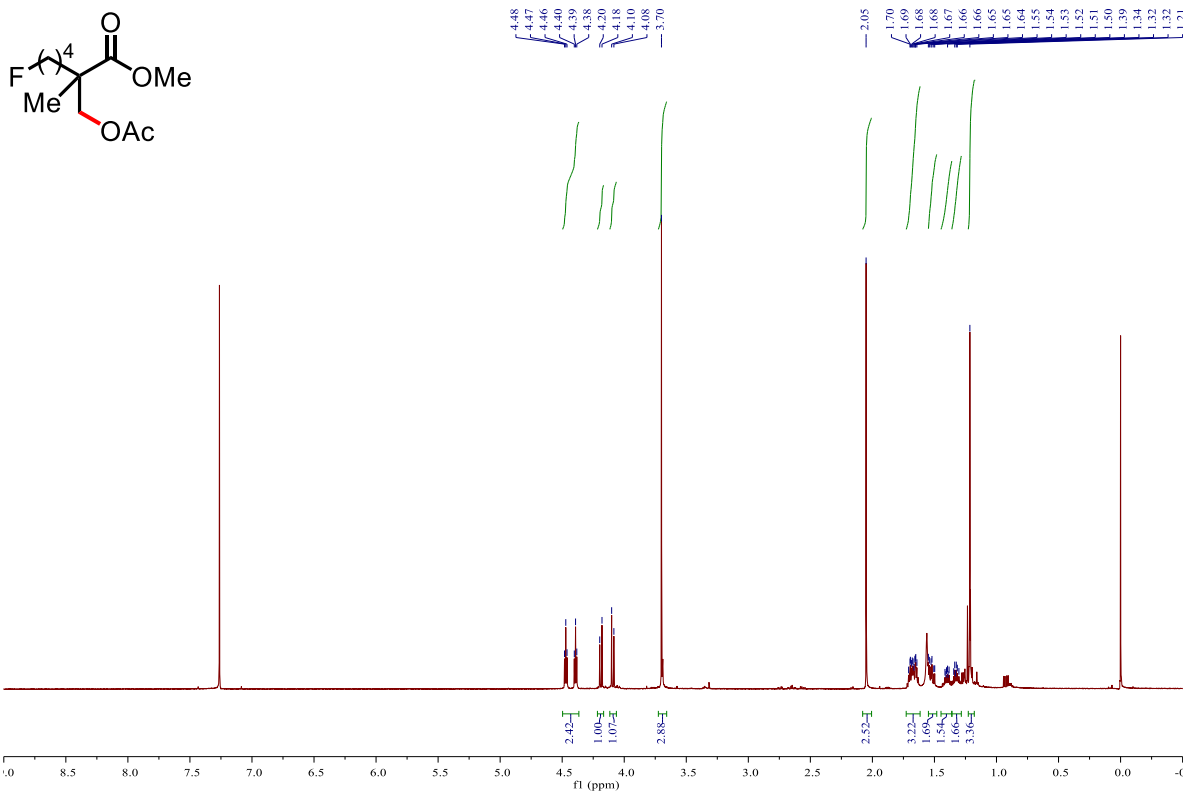
36.20
35.55
26.10
20.95
19.80
O
OMe
3
Me
OAc
f1 (ppm)


F
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O
OMe
OAc
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4.20
4.18
4.10
4.08
3.70
2.05
1.70
1.69
1.68
1.68
1.67
1.66
1.66
1.65
1.65
1.64
1.55
1.54
1.53
1.52
1.51
1.50
1.39
1.34
1.32
1.32
2.42
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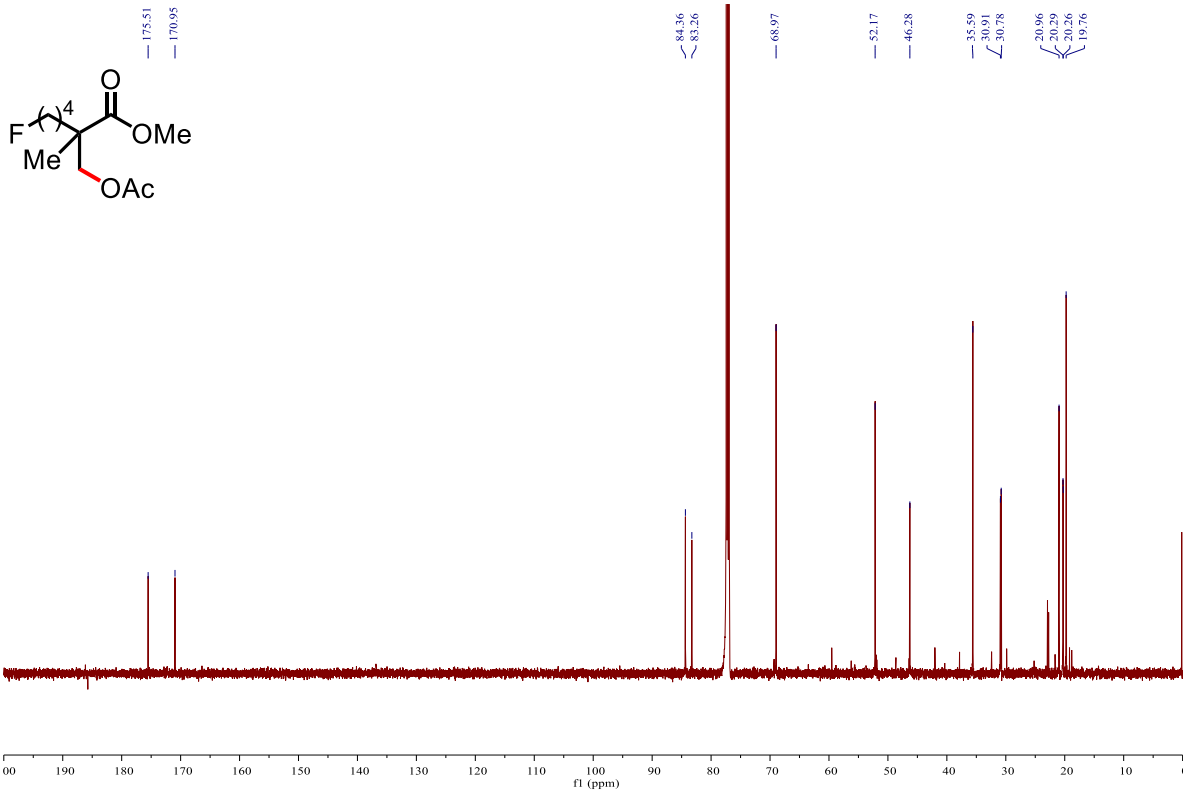
2.88
2.52
3.22
1.69
1.54
1.66
3.36
f1 (ppm)


F
4
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O
OMe
OAc
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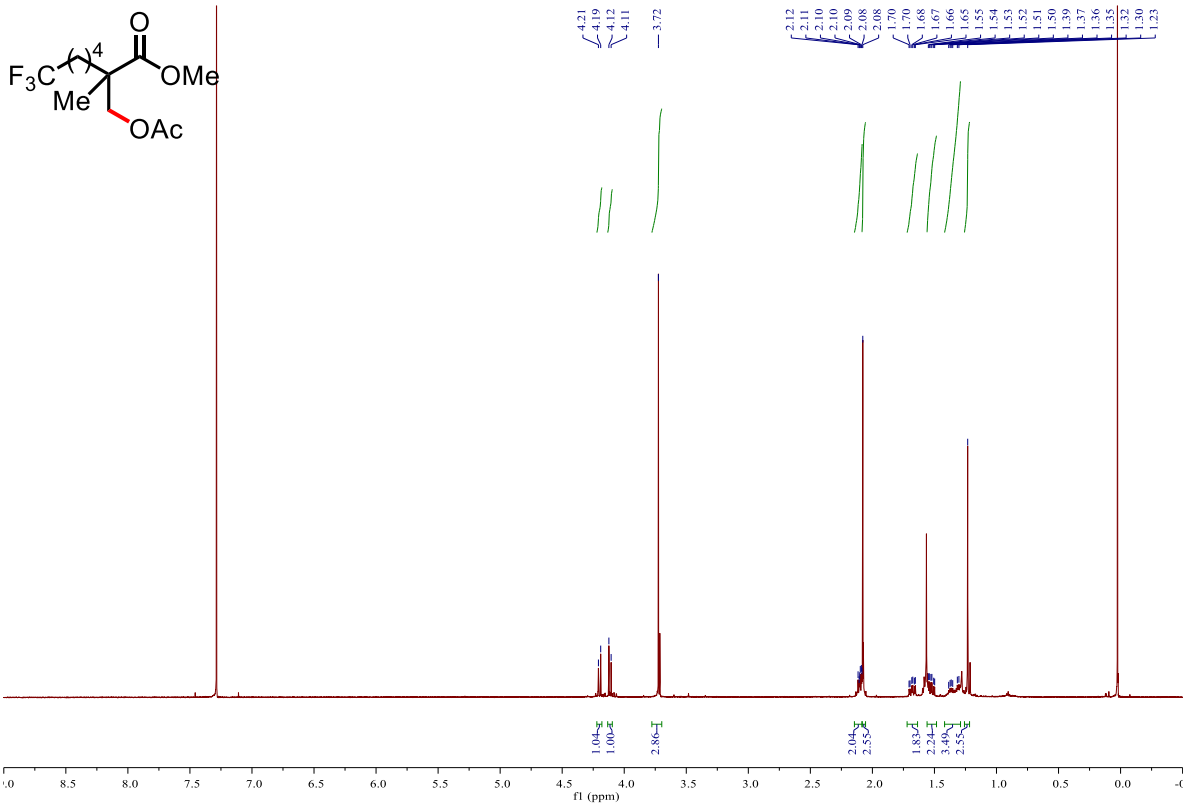
30.91
30.78
20.96
20.29
20.26
19.76
f1 (ppm)


F3C
4
Me
O
OMe
OAc
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2.11
2.10
2.10
2.09
2.08
2.08
1.70
1.70
1.68
1.67
1.66
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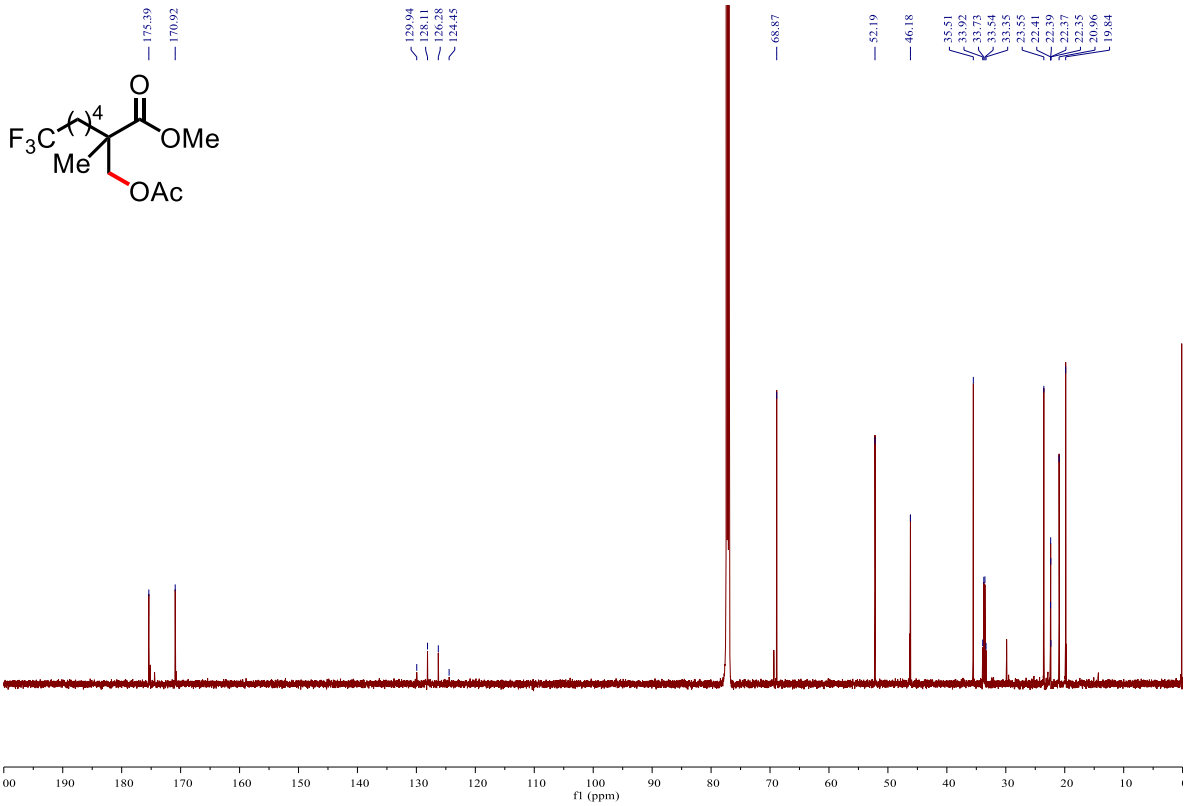
1.54
1.53
1.52
1.51
1.50
1.39
1.37
1.36
1.35
1.32
1.30
1.23
1.04
1.00
2.86
2.04
2.55
1.83
2.24
3.49
2.55
f1 (ppm)


F3C
4
Me
O
OMe
OAc
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170.92
129.94
128.11
126.28
124.45
68.87
52.19
46.18
35.51
33.92
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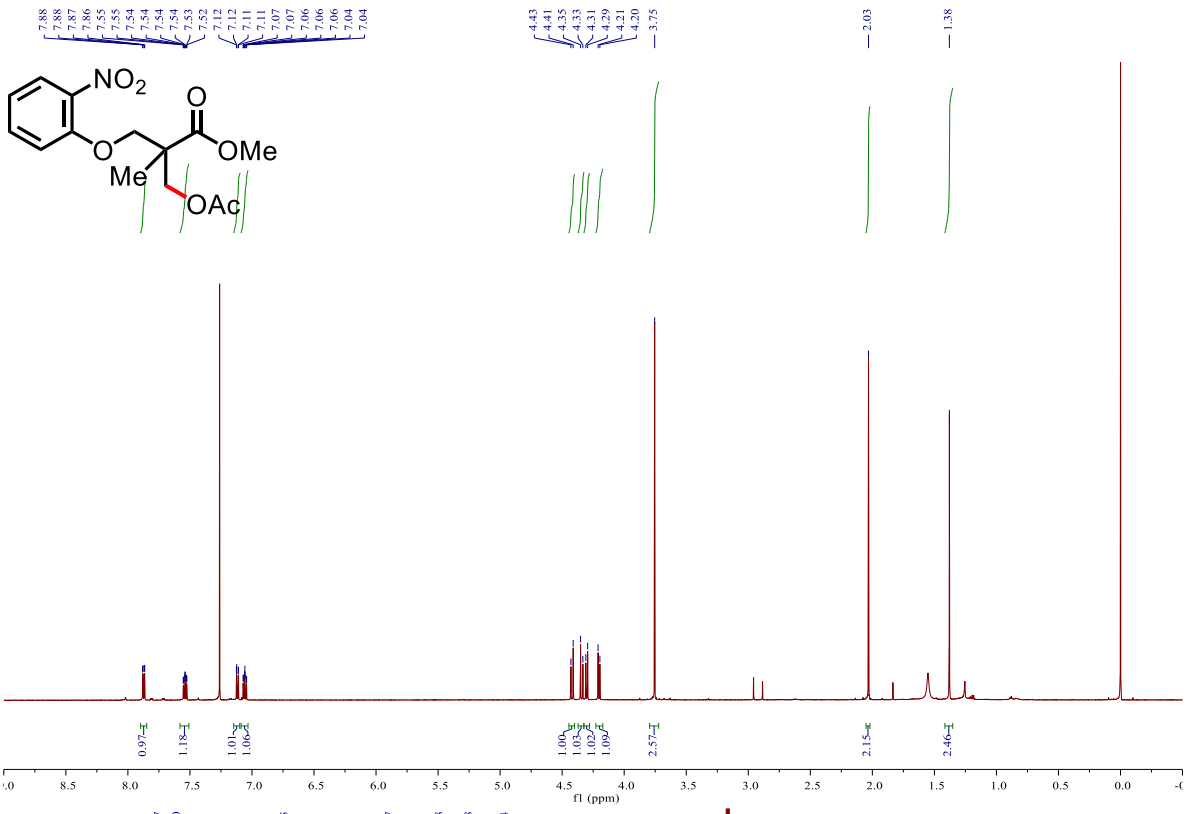
33.35
23.55
22.41
22.39
22.37
22.35
20.96
19.84
f1 (ppm)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7.04
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4.41
4.35
4.33
4.31
4.29
4.21
4.20
3.75
2.03
1.38
NO2
O
O
OMe
Me
OAc
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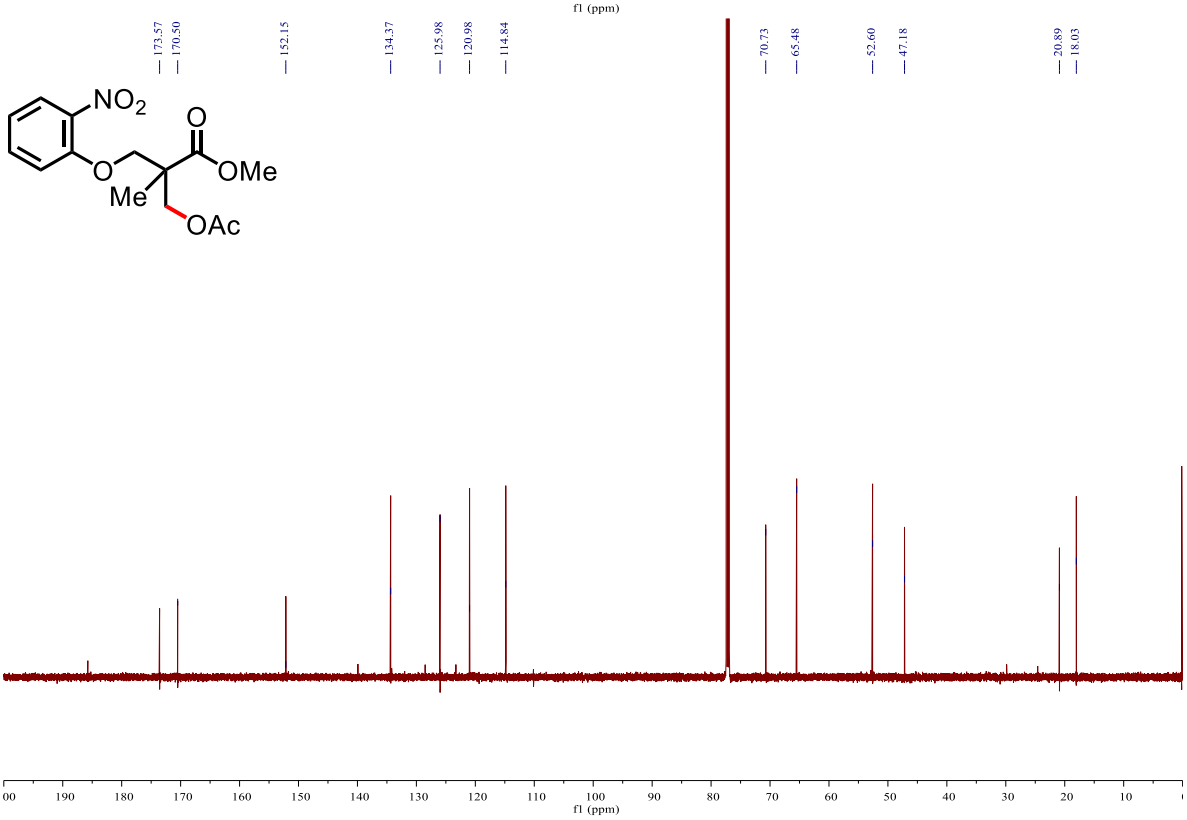
1.06
1.00
1.03
1.02
1.09
2.57
2.15
2.46
f1 (ppm)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120.98
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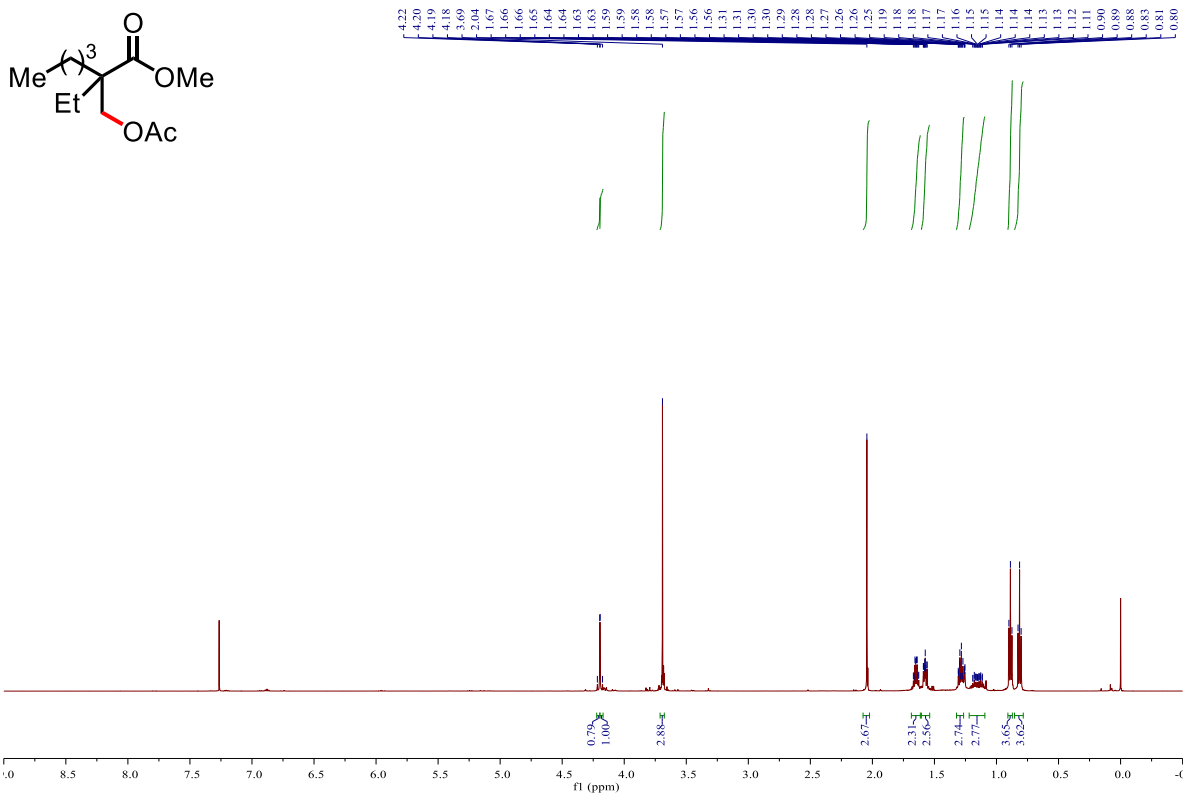
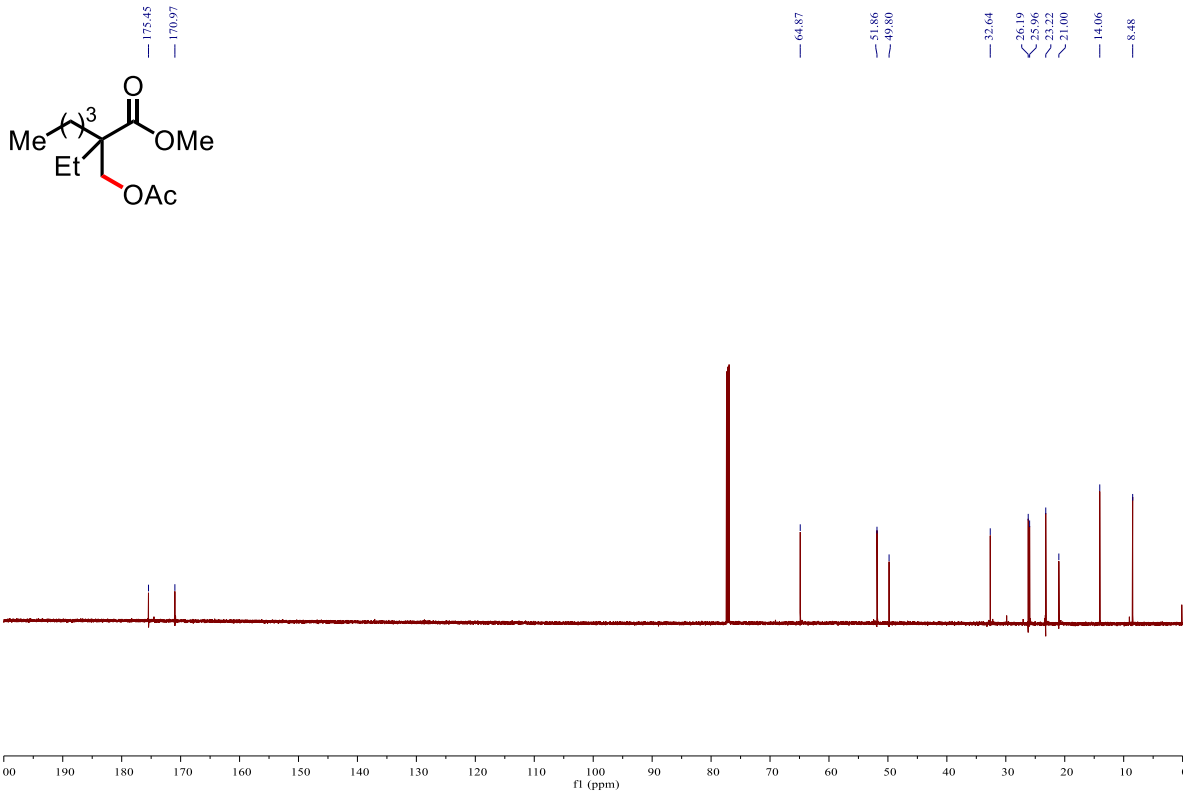
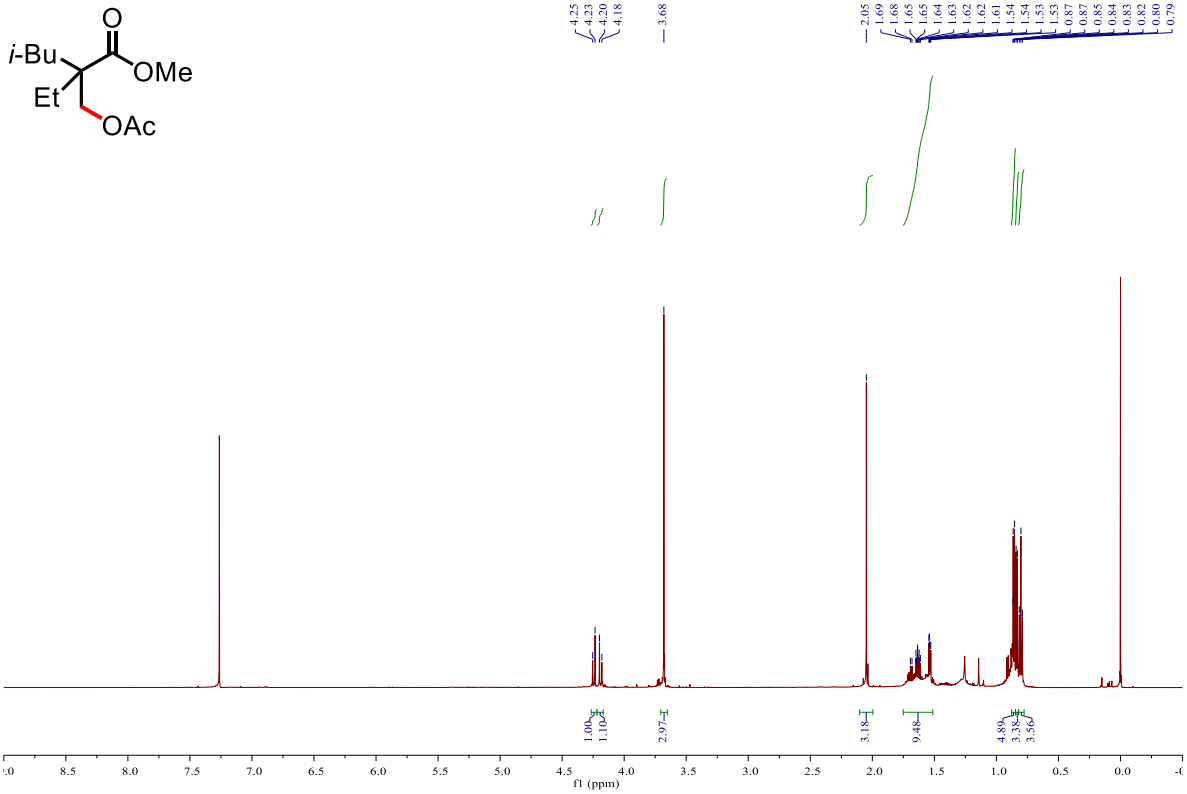
52.60
47.18
20.89
18.03
NO2
O
O
OMe
Me
OAc
f1 (ppm)


Me
3
Et
O
OMe
OAc
fl (ppm)


Me
3
Et
O
OMe
OAc
fl (ppm)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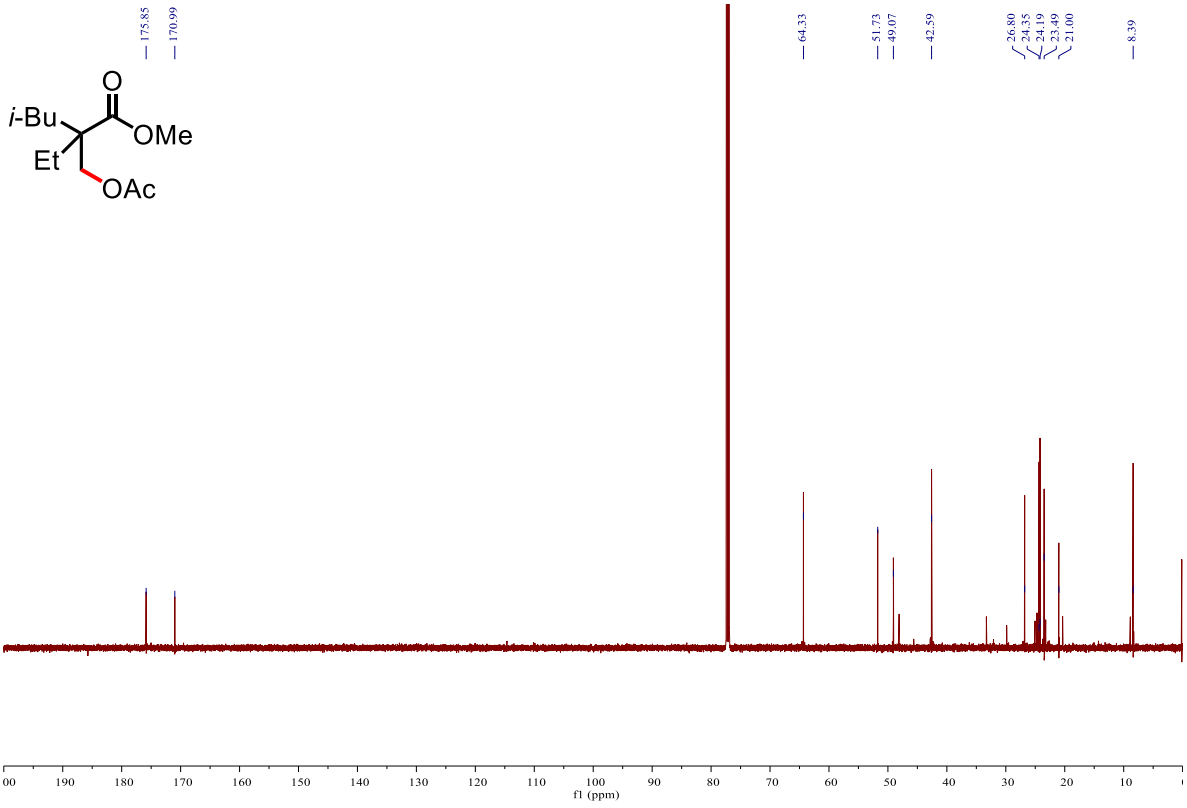
Et
O
OMe
OAc
4.25
4.23
4.20
4.18
3.68
2.05
1.69
1.68
1.65
1.65
1.64
1.63
1.62
1.62
1.61
1.54
1.54
1.53
1.53
0.87
0.87
0.85
0.84
0.83
0.82
0.80
0.79
1.00
1.10
2.97
3.18
9.48
4.89
3.38
3.56
f1 (ppm)


i-Bu
Et
O
OMe
OAc
175.85
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64.33
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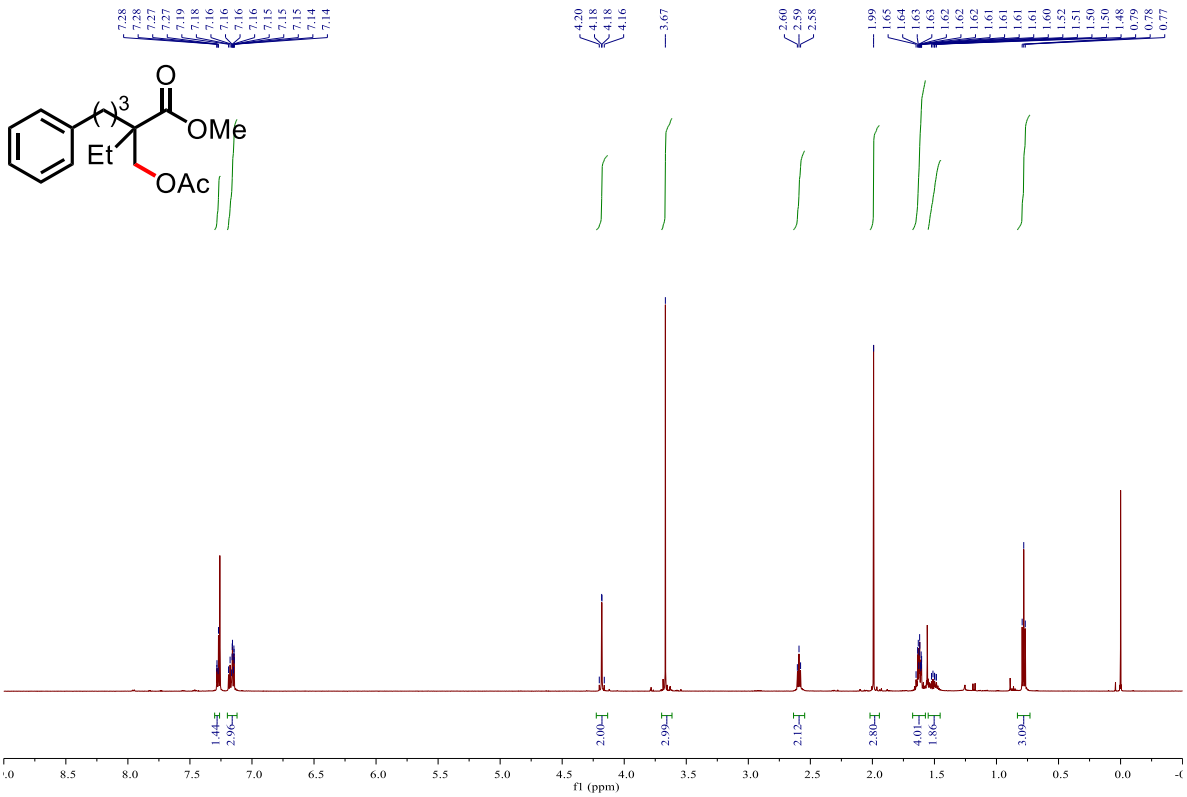
42.59
26.80
24.35
24.19
23.49
21.00
8.39
f1 (ppm)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7.27
7.27
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7.16
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7.15
7.14
7.14
4.20
4.18
4.18
4.16
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2.59
2.58
1.99
1.65
1.64
1.63
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1.62
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1.61
1.61
1.61
1.61
1.60
1.52
1.51
1.50
1.50
1.48
0.79
0.78
0.77
O
OMe
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OAc
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2.99
2.12
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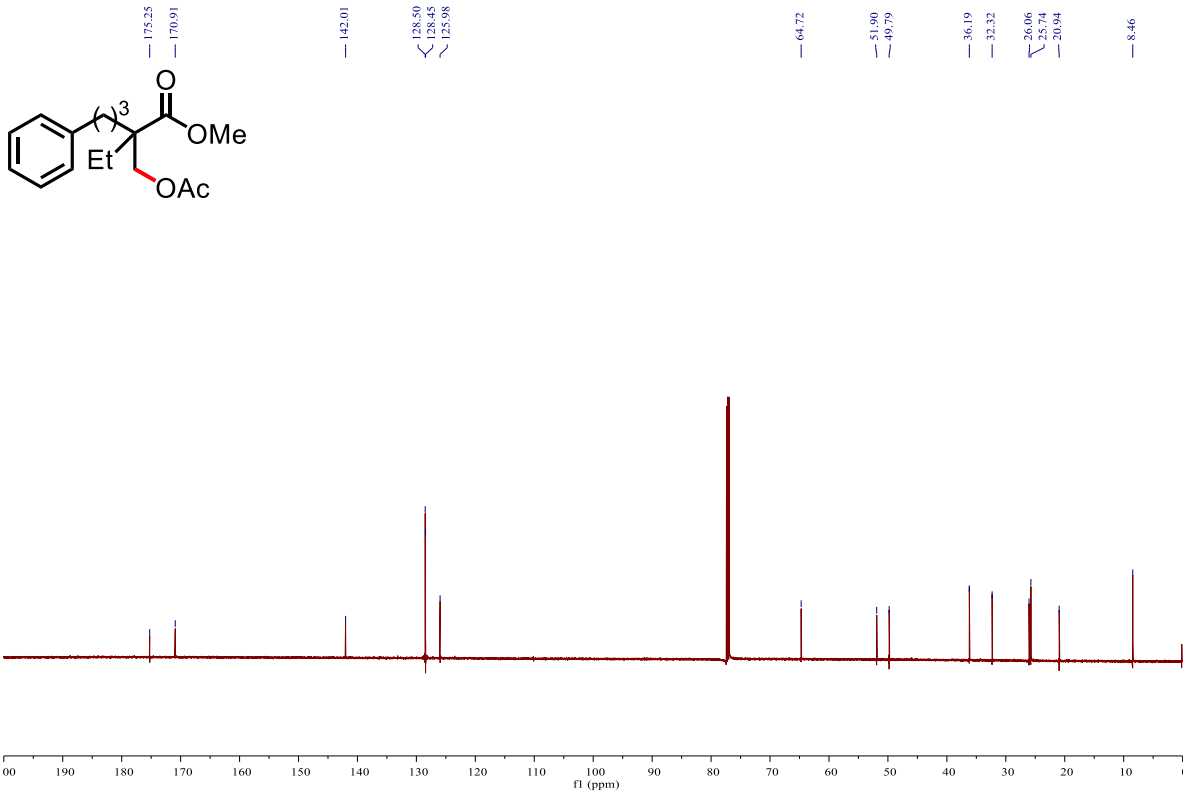
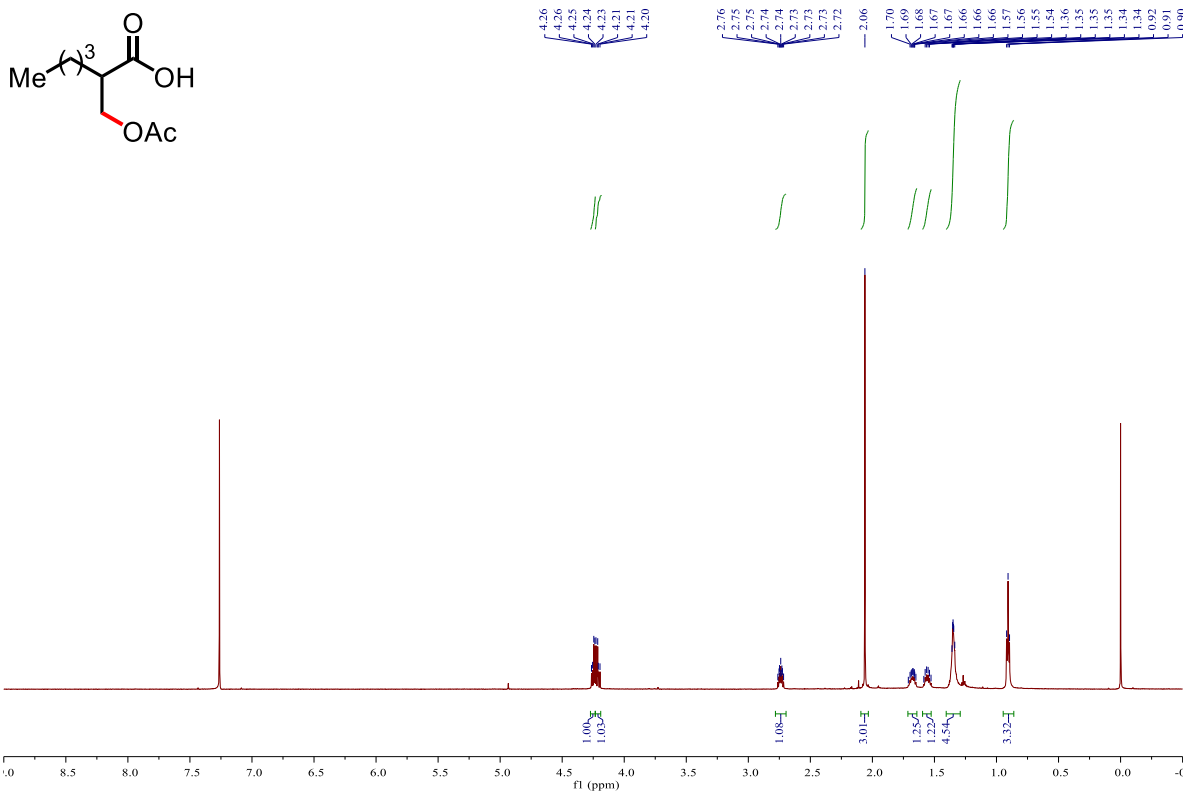
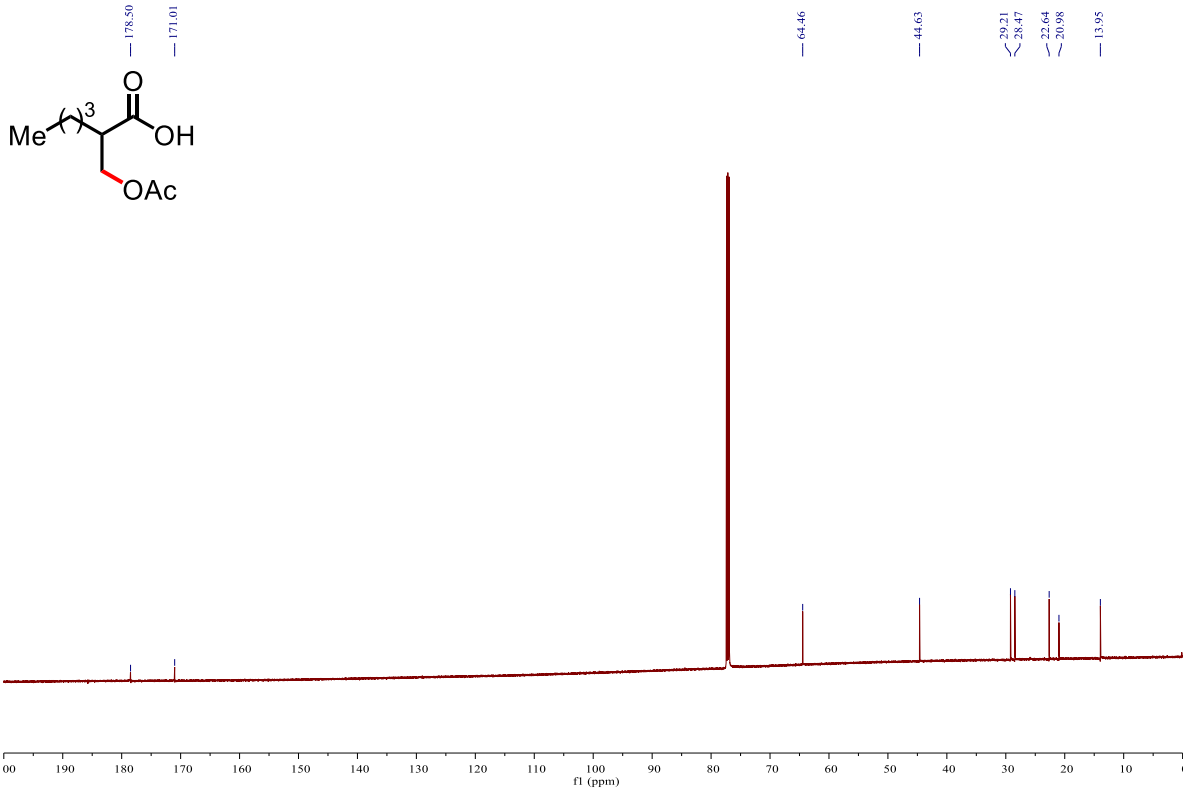
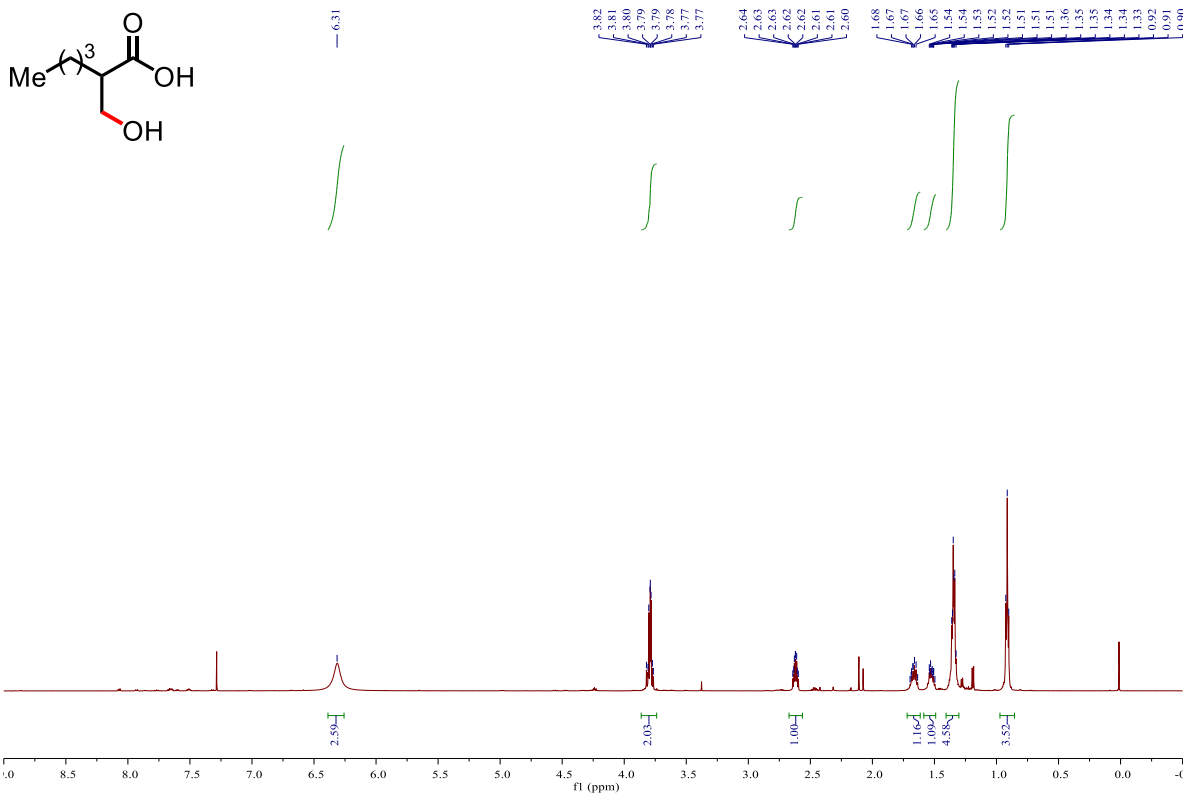
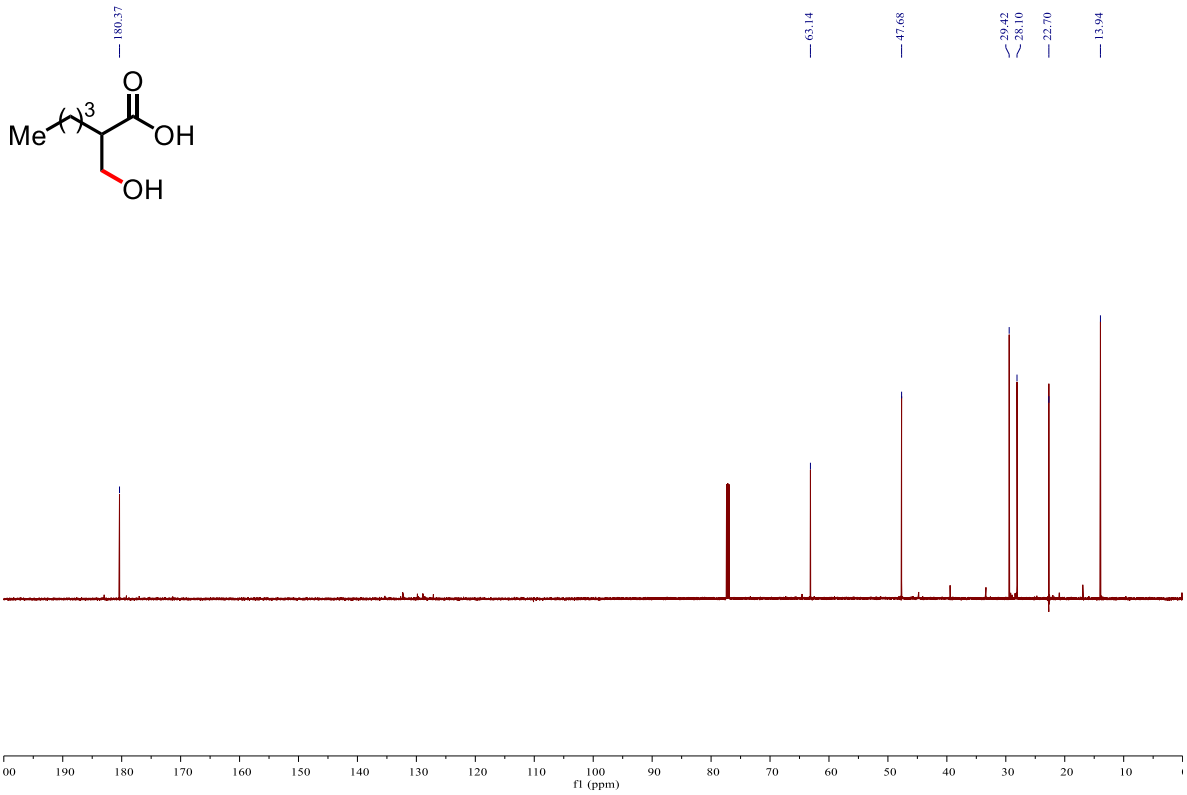
4.01
1.86
3.09
f1 (ppm)

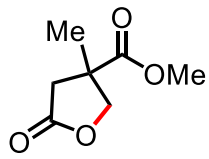

175.25
170.91
142.01
128.50
128.45
125.98
64.72
51.90
49.79
36.19
32.32
26.06
25.74
20.94
8.46
O
OMe
3
Et
OAc
f1 (ppm)


Me
3
O
OH
OAc
4.26
4.26
4.25
4.24
4.23
4.21
4.21
4.20
2.76
2.75
2.75
2.74
2.74
2.73
2.73
2.73
2.72
2.06
1.70
1.69
1.68
1.67
1.67
1.66
1.66
1.66
1.57
1.56
1.55
1.54
1.36
1.35
1.35
1.35
1.34
1.34
0.92
0.91
1.00
1.03
1.08
3.01
1.25
1.22
4.54
3.32
f1 (ppm)

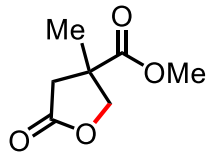

178.50
171.01
64.46
44.63
29.21
28.47
22.64
20.98
13.95
Me
3
O
OH
OAc
f1 (ppm)


Me
3
O
OH
OH
6.31
3.82
3.81
3.80
3.79
3.79
3.78
3.77
3.77
2.64
2.63
2.63
2.62
2.62
2.61
2.61
2.60
1.68
1.67
1.67
1.66
1.65
1.54
1.54
1.53
1.52
1.52
1.51
1.51
1.51
1.36
1.35
1.35
1.34
1.34
1.33
0.92
0.91
2.59
2.03
1.00
1.16
1.09
4.58
3.52
f1 (ppm)

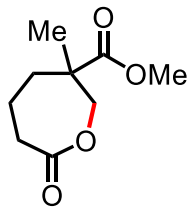

Me
3
O
OH
OH
180.37
63.14
47.68
29.42
28.10
22.70
13.94
f1 (ppm)


Me
O
OMe
O
O

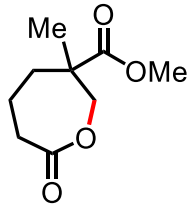
4.56
4.55
4.09
4.07
3.77
3.07
3.04
2.44
2.42
1.47
1.00
1.04
3.20
0.93
1.20
2.83
f1 (ppm)


Me
O
OMe
O
O

175.06
173.98
75.43
53.06
46.41
39.14
22.75
f1 (ppm)


Me
O
OMe
O
O

4.42
4.40
4.15
4.13
3.74
2.69
2.67
2.65
2.64
2.61
2.22
2.20
2.19
1.93
1.92
1.90
1.85
1.84
1.82
1.64
1.62
1.60
1.23
1.00
1.10
3.17
2.22
1.39
1.62
1.76
1.83
3.12
f1 (ppm)


Me
O
OMe
O
O

175.04
174.71
72.63
68.06
52.48
45.89
37.67
33.88
19.45
f1 (ppm)