Supplementary Materials for

Functionalization of C(sp^3)–H bonds Using a Transient Directing Group

Fang-Lin Zhang,* Kai Hong,* Tuan-Jie Li,* Hojoon Park, Jin-Quan Yu†

The Scripps Research Institute, 10550 N. Torrey Pines Road, La Jolla, California 92037, USA.

*These authors contributed equally to this work.

†Corresponding author. Email: yu200@scripps.edu

Table of Contents

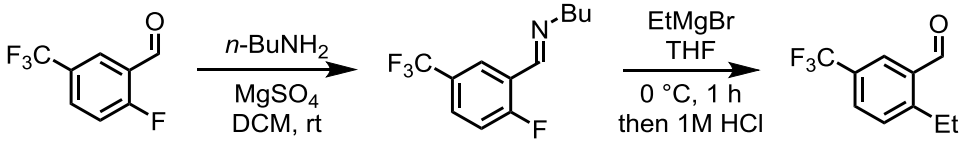
General Information

Unless otherwise noted all commercial materials were used without further purification. Solvents were obtained from 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. ^{1}H NMR spectra were recorded on Bruker DPX-400 instrument (400 MHz), Bruker DRX-500 (500 MHz) or 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 DPX-400 instrument (100 MHz), Bruker DRX-500 (125 MHz) or Bruker DRX-600 instrument (150 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. ^{19}F NMR spectra were recorded on Bruker DPX-400 instrument (376 MHz) and Chemical shifts were reported in ppm. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). Enantiomeric ratios (er) were determined on a Hitachi LaChrom Elite HPLC system using commercially available chiral columns. IR spectrums were recorded on Thermo Scientific Nicolet 380 Fourier transform infrared spectrometer. The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Mo K_{α} radiation (λ = 0.71073).

Experimental Section

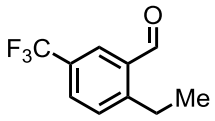
I. Substrate Preparation (Fig. 4)

Method A:



The aldehyde **5a** was prepared according to the literature procedure with modification (*31*). To a solution of 2-fluoro-5-(trifluoromethyl)benzaldehyde (1.92 g, 10.0 mmol) in DCM (10 mL) was added butylamine (1.04 mL, 10.5 mmol) and anhydrous $MgSO_4$ (1.0 g). The reaction was allowed to stir overnight at ambient temperature. Upon completion, the reaction mixture was filtered, concentrated and the crude product was used in the next step without further purification.

To a solution of *N*-butyl-1-(2-fluoro-5-(trifluoromethyl)phenyl)methanimine (max. 10.0 mmol) in THF (15 mL) was added ethylmagnesium bromide (6.7 mL, 20.0 mmol, 3.0 M in diethyl ether) dropwise at 0 ℃. After stirring for 1 h, the reaction was quenched at 0 ℃ with 1 M HCl, and stirred for 30 min. The layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel to afford the desired product as a pale yellow oil.



2-ethyl-5-(trifluoromethyl)benzaldehyde (5a)

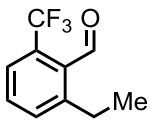
^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.33 (s, 1H), 8.09 (d, *J* =1.5 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 3.14 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.78, 150.72, 133.73, 130.96, 130.15 (q, J_{CF} = 3.4 Hz), 129.21 (q, J_{CF} = 33.3 Hz), 128.22 (q, J_{CF} = 3.8 Hz), 123.70 (d, J_{CF} = 272.3 Hz), 25.66, 16.07;

^{19}F NMR ($CDCl_3$, 376 MHz): δ – 63.08;

IR (neat): 1703, 1618, 1330, 1200, 1163, 1117, 1083, 1049, 899, 843 cm^{-1};

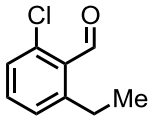
HRMS (ESI-TOF): *m/z* calculated for $C_{10}H_{10}F_3O^+$ $[M+H]^+$ 203.0678, found 203.0683.



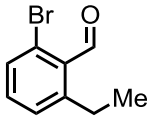
2-ethyl-6-(trifluoromethyl)benzaldehyde (5c)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.54 (q, *J* = 2.7 Hz, 1H); 7.63 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 2.94 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H);

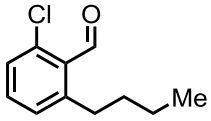
^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.07, 146.89, 134.30, 132.88, 131.81, 130.96 (q, J_{CF} = 31.5 Hz), 123.98 (q, J_{CF} = 5.9 Hz), 123.93 (q, J_{CF} = 274.5 Hz), 26.94, 15.89;
^{19}F NMR ($CDCl_3$, 376 MHz): δ – 55.82;
IR (neat): 2360.9, 2341.3, 1705.6, 1309.3, 1163.1, 1118.9, 1087.7, 809.3, 719.8, 669.5 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{10}H_{10}F_3O^+$ $[M+H]^+$ 203.0678, found 203.0680.



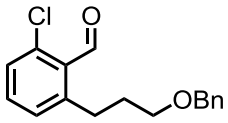
2-chloro-6-ethylbenzaldehyde (5e)
^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.64 (s, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 2.97 (q, *J* = 7.5 Hz, 2H), 1.21 (t, *J* = 7.5 Hz, 3H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.35, 148.54, 138.73, 133.67, 130.55, 129.18, 128.25, 26.83, 15.61;
IR (neat): 2972.6, 2872.0, 2360.2, 2341.4, 1693.1, 1588.8, 1560.4, 1453.6, 1404.2, 1265.0, 1182.8, 785.1, 683.6 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_9H_{10}ClO^+$ $[M+H]^+$ 169.0415, found 169.0412.



2-bromo-6-ethylbenzaldehyde (5f)
^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.51 (s, 1H), 7.51 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.25-7.24 (m, 1H), 2.96 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 194.36, 148.65, 133.77, 131.65, 131.60, 129.90, 127.82, 26.81, 15.71;
IR (neat): 2970.8, 2871.8, 2359.0, 2340.7, 1692.9, 1587.5, 1557.4, 1450.7, 1401.7, 1262.8, 1183.5, 854.5, 770.6, 669.5 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_9H_{10}BrO^+$ $[M+H]^+$ 212.9910, found 212.9913.



2-butyl-6-chlorobenzaldehyde (5g)
^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.62 (s, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 2.95-2.92 (m, 2H), 1.56-1.51 (m, 2H), 1.43-1.36 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.35, 147.27, 138.68, 133.42, 130.71, 129.93, 128.24, 33.71, 33.33, 22.69, 13.90;
IR (neat): 2957.1, 2929.9, 2869.8, 2359.0, 2341.4, 1696.9, 1589.4, 1558.9, 1454.1, 1404.3, 1182.5, 786.3 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{11}H_{14}ClO^+$ $[M+H]^+$ 197.0728, found 197.0730.



2-(3-(benzyloxy)propyl)-6-chlorobenzaldehyde (5h)

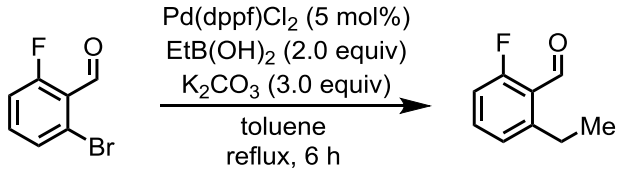
^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.61 (s, 1H), 7.35-7.32 (m, 5H), 7.30-7.27 (m, 2H), 7.16 (d, *J* = 7.5 Hz, 1H), 4.51 (s, 2H), 3.51 (t, *J* = 6.2 Hz, 2H), 3.04-3.02 (m, 2H), 1.91-1.87 (m, 2H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.27, 146.33, 138.89, 138.49, 133.51, 130.70, 130.15, 128.46, 128.31, 127.65, 127.48, 72.80, 69.46, 31.15, 30.28;

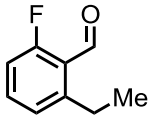
IR (neat): 2856.2, 1694.1, 1588.8, 1453.4, 1181.7, 1099.8, 1027.6, 787.5, 734.0, 696.7 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{18}ClO_2^+$ $[M+H]^+$ 289.0990, found 289.0988.

Method B:



To a mixture of ethylboronic acid (0.734 g, 10.0 mmol), 2-bromo-6-fluorobenzaldehyde (1.02 g, 5.0 mmol), and K_2CO_3 (2.08 g, 15.0 mmol) in dry toluene (15 mL) was added $PdCl_2$(dppf) (183 mg, 0.25 mmol). The resulting reaction mixture was heated under reflux for 6 h. Upon completion, the reaction mixture was cooled to room temperature. The solvent was removed and the crude mixture was diluted with DCM, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash chromatography to afford aldehyde **5d** as a colorless oil.



2-fluoro-6-ethylbenzaldehyde (5d)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.54 (s, 1H), 7.45-7.49 (m, 1H), 7.07 (d, J = 7.4 Hz, 1H), 7.03-6.99 (m, 1H), 3.03 (q, J = 7.2 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H);

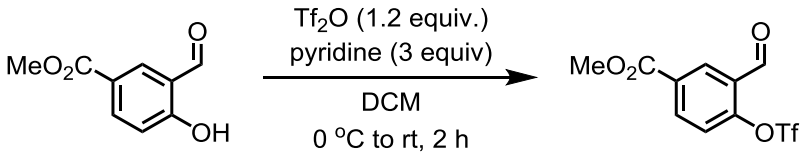
^{13}C NMR ($CDCl_3$, 150 MHz): δ 189.05 (d, J_{CF} = 11.1 Hz), 166.28 (d, J_{CF} = 257.6 Hz), 148.79, 135.21 (d, J_{CF} = 10.5 Hz), 125.94 (d, J_{CF} = 3.2 Hz), 122.03 (d, J_{CF} = 4.8 Hz), 113.75 (d, J_{CF} = 21.8 Hz), 26.71, 15.35;

^{19}F NMR ($CDCl_3$, 376 MHz): δ −121.25;

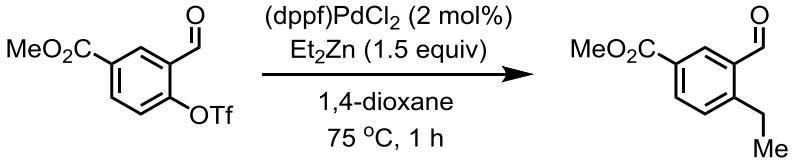
IR (neat): 1697, 1610, 1571, 1472, 1416, 1272, 1244, 1189, 829, 799 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_9H_{10}FO^+$ $[M+H]^+$ 153.0710, found 153.0712.

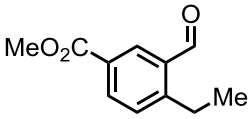
Method C:



To a solution of methyl 3-formyl-4-hydroxybenzoate (607.8 mg, 3.37 mmol) in DCM was added pyridine at room temperature. After cooling the reaction mixture to 0 ^{o}C with ice bath, Tf_2O was added dropwise. The reaction mixture was stirred for 1 h at 0 ^{o}C, and 1 h at room temperature. After removing solvent *in vacuo*, the crude residue was purified by flash column chromatography (hexanes : ethyl acetate = 10:1).



An oven-dried round-bottom flask was charged with methyl 3-formyl-4-(((trifluoromethyl)sulfonyl)oxy) benzoate (862.5 mg, 2.76 mmol) and 1,4-dioxane under N_2 atmosphere. After adding (dppf)$PdCl_2$ (40.4 mg, 55.2 μmol) to the stirring solution, Et_2Zn solution(1.5 M in toluene, 2.76 ml, 4.14 mmol) was added dropwise. The reaction mixture was heated to 75 ^{o}C and stirred for 1 h. After cooling down to room temperature, reaction was quenched with dropwise addition of water. 1,4-Dioxane was removed *in vacuo*, and the aqueous layer was extracted with ethyl acetate. After drying the combined organic layers with $MgSO_4$, the residue was purified by flash column chromatography (hexanes : ethyl acetate = 10 : 1).



methyl 4-ethyl-3-formylbenzoate (5b)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.29 (s, 1H), 8.48 (d, *J* = 1.9 Hz, 1H), 8.16 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 3.13 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 191.70, 166.10, 151.83, 134.43, 133.57, 133.54, 130.57, 128.67, 52.33, 26.03, 15.81;

IR (neat): 1720, 1695, 1285, 1266, 1234, 1195, 1173, 1127, 1108, 764 cm^{-1};

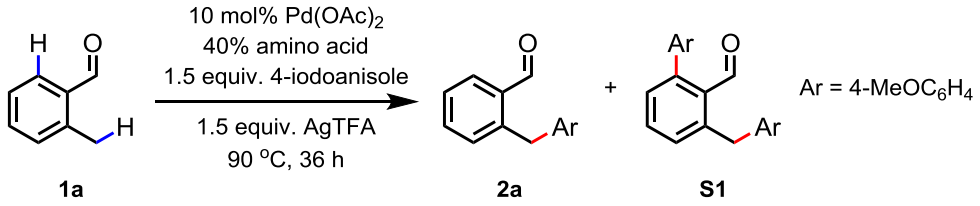
HRMS (ESI-TOF): *m/z* calculated for $C_{11}H_{13}O_3^+$ $[M+H]^+$ 193.0859, found 193.0864.

II. Pd(II)-Catalyzed Benzylic C(sp^3)–H Arylation of Aldehydes (Fig. 2)

General Procedure

A reaction tube (10 mL) with magnetic stir bar was charged with aldehyde substrate (0.24 mmol), aryl iodide (0.20 mmol), silver trifluoroacetate (66.3 mg, 0.30 mmol), palladium acetate (4.5 mg, 0.02 mmol), glycine (6.0 mg, 0.08 mmol), acetic acid (1.8 mL) and H_2O (0.2 mL) in air. The reaction tube was sealed and allowed to stir at ambient temperature for 10 minutes, then heated to 90 ℃ for 36 hours. Upon completion, the reaction mixture was cooled to room temperature, filtered through a silica gel plug, and concentrated *in vacuo*. The crude reaction mixture was purified on preparative TLC using hexanes/ EtOAc as the eluent to afford the desired product.

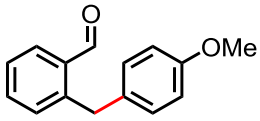
Table S1. Optimization of Pd(II)-Catalyzed Benzylic C(sp^3)–H Arylation of Aldehydes[*,†]



entry	solvent	amino acid	conversion (%)	**2a** (%)	**S1** (%)
1	DCE	glycine	-	<2	<2
2	toluene	glycine	-	<2	<2
3	dioxane	glycine	-	<2	<2
4	MeCN	glycine	-	<2	<2
5	HFIP	glycine	60	18	11
6	AcOH	glycine	90	52	10
7	AcOH:HFIP (9:1)	glycine	94	59	6
8	AcOH:H_2O (9:1)	glycine	93	71	11
9	AcOH:H_2O (4:1)	glycine	84	63	11
10‡	**AcOH:H_2O (9:1)**	**glycine**	**95**	**81 (72)**§	**<3**
11‡	AcOH:H_2O (9:1)	L-alanine	-	76	<3
12‡	AcOH:H_2O (9:1)	L-valine	-	78	<3
13‡	AcOH:H_2O (9:1)	L-norvaline	-	76	<3
14‡	AcOH:H_2O (9:1)	Ac-Gly-OH	-	<2	<2

*Conditions: 0.1 mmol of **1a**, 1.5 equiv of 4-iodoanisole, 10 mol% of $Pd(OAc)_2$, 40 mol% of amino acid, 1.5 equiv of AgTFA, 1.0 mL of solvent, 90 °C, 36 h. †The yield was determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. ‡0.12 mmol of **1a** and 0.1 mmol of 4-iodoanisole were used. §isolated yield.

Full Characterization of Reaction Products



2-(4-methoxybenzyl)benzaldehyde (2a)

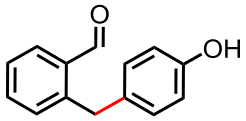
The compound **2a** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 72% yield (33 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.26 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.38 (s, 2H), 3.77 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.37, 158.03, 143.48, 133.87, 133.84, 132.34, 131.89, 131.46, 129.70, 126.87, 113.96, 55.21, 37.13;

IR (neat): 2930, 1693, 1598, 1715, 1509, 1244, 1177, 1304, 772, 753 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{15}O_2^+$ $[M+H]^+$ 227.1067, found 227.1073.



2-(4-hydroxybenzyl)benzaldehyde (2b)

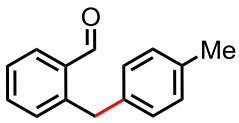
The compound **2b** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 82% yield (35 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.23 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 5.45 (s, 1H), 4.36 (s, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.84, 154.11, 143.60, 134.07, 133.72, 132.30, 131.98, 131.53, 129.83, 126.93, 115.43, 37.19.

IR (neat): 3337 (br), 29271684, 1597, 1511, 1442, 1210, 906, 725, 647 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{13}O_2^+$ $[M+H]^+$ 213.0910, found 213.0907.

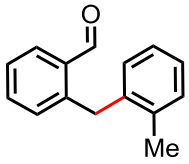


2-(4-methylbenzyl)benzaldehyde (2c)

The compound **2c** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 74% yield (31 mg).

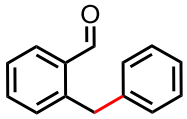
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.26 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J*

= 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.40 (s, 2H), 2.30 (s, 3H);
^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.33, 143.30, 137.20, 135.79, 133.89, 133.87, 131.78, 131.56, 129.24, 128.62, 126.88, 37.57, 20.97;
IR (neat): 2920, 1695, 1598, 1513, 1451, 1290, 1208, 750 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{15}O^+$ $[M+H]^+$ 211.1117, found 211.1113.



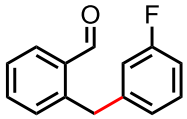
2-(2-methylbenzyl)benzaldehyde (2d)

The compound **2d** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 43% yield (18 mg).
^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.24 (s, 1H), 7.88 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.48 (td, *J* = 7.5, 1.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.16 (td, *J* = 7.4, 1.1 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 4.43 (s, 2H), 2.27 (s, 3H).
^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.60, 142.64, 138.19, 136.49, 134.02, 133.92, 132.34, 130.75, 130.23, 129.42, 126.77, 126.59, 126.17, 35.70, 19.64;
IR (neat): 2362, 2339, 2017, 1694, 1599, 1194, 743 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{15}O^+$ $[M+H]^+$ 211.1117, found 211.1110.



2-benzylbenzaldehyde (2e)

The compound **2e** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 70% yield (27 mg).
^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.26 (s, 1H), 7.87 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.53 (td, *J* = 7.5, 1.5 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.29-7.26 (m, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 4.46 (s, 2H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.37, 142.98, 140.26, 133.91, 132.03, 131.65, 128.77, 128.56, 126.99, 126.28, 38.03;
IR (neat): 2360, 2341, 1695, 1597, 1195, 755, 730 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{13}O^+$ $[M+H]^+$ 197.0961, found 197.0956.



2-(3-fluorobenzyl)benzaldehyde (2f)

The compound **2f** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 81% yield (35 mg).

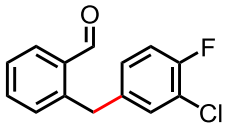
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.20 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.54 (td, *J* = 7.6, 1.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.27-7.20 (m, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.90-6.86 (m, 1H), 6.82 (d, *J* = 10.0 Hz, 1H), 4.45 (s, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.41, 162.95 (d, J_{CF} = 245.9 Hz), 142.81 (d, J_{CF} = 7.3 Hz), 141.95, 133.93, 133.88, 132.96, 131.69, 129.88 (d, J_{CF} = 8.3 Hz), 127.25, 124.41 (d, J_{CF} = 2.7 Hz), 115.65 (d, J_{CF} = 21.4 Hz), 113.15 (d, J_{CF} = 21.0 Hz), 37.82 (d, J_{CF} = 1.8 Hz);

^{19}F NMR ($CDCl_3$, 376 MHz): δ −113.58;

IR (neat): 2829, 1697, 1614, 1589, 1486, 1448, 1247, 770, 749 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{12}FO^+$ $[M+H]^+$ 215.0867, found 215.0869.



2-(3-chloro-4-fluorobenzyl)benzaldehyde (2g)

The compound **2g** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 79% yield (39 mg).

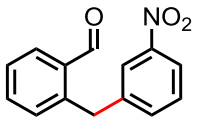
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.16 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.16 (d, *J* = 6.8 Hz, 1H), 7.02-7.03 (m, 2H), 4.40 (s, 2H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.60, 156.69 (d, J_{CF} = 246.5 Hz), 141.65, 137.28 (d, J_{CF} = 3.8 Hz), 133.99, 133.84, 133.78, 131.65, 130.68, 128.43 (d, J_{CF} = 6.6 Hz), 127.39, 120.80 (d, J_{CF} = 17.6 Hz), 116.43 (d, J_{CF} = 20.9 Hz), 37.22;

^{19}F NMR ($CDCl_3$, 376 MHz): δ −119.55;

IR (neat): 2924, 1697, 1599, 1498, 1406, 1246, 783, 753 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{11}ClFO^+$ $[M+H]^+$ 249.0477, found 249.0480.



2-(3-nitrobenzyl)benzaldehyde (2h)

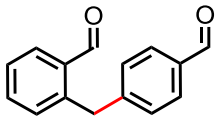
The compound **2h** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 83% yield (40 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.13 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.57-7.61 (m, 1H), 7.49-7.53 (m, 2H), 7.41-7.45 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 4.55 (s, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.72, 148.34, 142.36, 140.69, 135.07, 134.69, 134.06, 133.81, 131.87, 129.22, 127.65, 123.49, 121.35, 38.01;

IR (neat): 2923, 1692, 1522, 1344, 1192, 1096, 803, 754, 726 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{12}NO_3^+$ $[M+H]^+$ 242.0812, found 242.0816.



2-(4-formylbenzyl)benzaldehyde (2i)

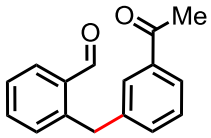
The compound **2i** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 81% yield (36 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.16 (s, 1H), 9.96 (s, 1H), 7.86 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.57 (td, *J* = 7.6, 1.5 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 4.54 (s, 2H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.56, 191.87, 147.57, 141.28, 134.69, 133.97, 133.89, 133.81, 131.85, 129.98, 129.41, 127.43, 38.48;

IR (neat): 1686, 1598, 1573, 1304, 1210, 1167, 1108, 848, 751 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{13}O_2^+$ $[M+H]^+$ 225.0910, found 225.0908.



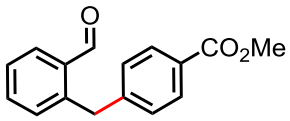
2-(3-acetylbenzyl)benzaldehyde (2j)

The compound **2j** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 76% yield (36 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.20 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.78-7.89 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.34-7.39 (m, 2H), 7.27 (d, *J* = 6.8 Hz, 1H), 4.51 (s, 2H), 2.56 (s, 3H);

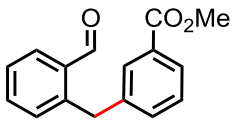
^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.11, 192.53, 142.02, 140.86, 137.35, 133.96, 133.83, 133.56, 133.33,

131.66, 128.72, 128.51, 127.23, 126.41, 38.00, 26.64;
IR (neat): 2923, 1679, 1597, 1434, 1357, 1269, 1193, 755, 692 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{15}O_2^+$ $[M+H]^+$ 239.1067, found 239.1066.



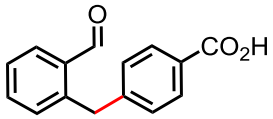
methyl 4-(2-formylbenzyl)benzoate (2k)

The compound **2k** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 74% yield (38 mg).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.18 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.53-7.57 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.51 (s, 2H), 3.89 (s, 3H);
^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.45, 166.94, 145.65, 141.76, 133.93, 133.91, 133.26, 131.74, 129.82, 128.80, 128.22, 127.28, 52.01, 38.21;
IR (neat): 2925, 1717, 1696, 1610, 1434, 1279, 1193, 1109, 749 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{15}O_3^+$ $[M+H]^+$ 255.1016, found 255.1018.



methyl 3-(2-formylbenzyl)benzoate (2l)

The compound **2l** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 78% yield (40 mg).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.21 (s, 1H), 7.88-7.84 (m, 3H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.37-7.32 (m, 2H), 7.26 (d, *J* = 7.6 Hz, 1H), 4.50 (s, 2H), 3.88 (s, 3H);
^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.46, 167.01, 142.11, 140.61, 133.95, 133.83, 133.42, 133.09, 131.65, 130.38, 129.84, 128.56, 127.55, 127.19, 52.07, 37.90;
IR (neat): 2922, 1716, 1692, 1597, 1433, 1280, 1195, 1106, 987, 741 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{15}O_3^+$ $[M+H]^+$ 255.1016, found 255.1014.



4-(2-formylbenzyl)benzoic acid (2m)

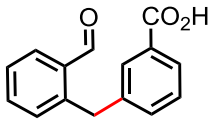
The compound **2m** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 73% yield (35 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.18 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.28-7.24 (m, 3H), 4.53 (s, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.56, 171.97, 146.69, 141.56, 133.97, 133.88, 133.49, 131.78, 130.45, 128.91, 127.34, 38.30;

IR (neat): 2920, 1686, 1610, 1418, 1279, 1178, 1046, 749 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{11}O_3^-$ $[M-H]^-$ 239.0714, found 239.0711.



3-(2-formylbenzyl)benzoic acid (2n)

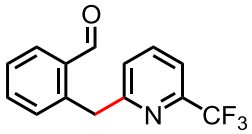
The compound **2n** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 74% yield (36 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.20 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.91 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.47-7.36 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 4.52 (s, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.59, 172.01, 141.96, 140.79, 134.34, 134.00, 133.83, 133.35, 131.69, 130.41, 129.52, 128.68, 128.19, 127.27, 37.90.

IR (neat): 2922, 1692, 1598, 1451, 1411, 1289, 1196, 744 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{11}O_3^-$ $[M-H]^-$ 239.0714, found 239.0715.



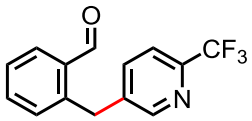
2-((6-(trifluoromethyl)pyridin-2-yl)methyl)benzaldehyde (2o)

The compound **2o** was prepared according to the general procedure for 48 h and was purified by preparative TLC to give a colorless oil in 71% yield (38 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.27 (s, 1H), 7.87 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.56 (td, *J* = 7.5, 1.5 Hz, 1H), 7.49 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.46 (td, *J* = 7.6, 1.2 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 4.69 (s, 2H);

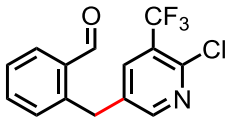
^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.75, 160.89, 147.75 (q, J_{CF} = 34.4 Hz), 140.09, 137.79, 134.11,

133.97, 133.00, 132.05, 127.50, 125.84, 121.44 (q, J_{CF} = 274.0 Hz), 118.03 (q, J_{CF} = 2.5 Hz), 40.53;
^{19}F NMR ($CDCl_3$, 376 MHz): δ −68.31;
IR (neat): 2945, 1693, 1461, 1341, 1182, 1134, 1022, 748 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{11}F_3NO^+$ $[M+H]^+$ 266.0787, found 266.0787.



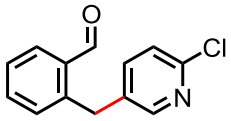
2-((6-(trifluoromethyl)pyridin-3-yl)methyl)benzaldehyde (2p)

The compound **2p** was prepared according to the general procedure for 48 h and was purified by preparative TLC to give a colorless oil in 68% yield (36 mg).
^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.10 (s, 1H), 8.58 (d, *J* = 1.3 Hz, 1H), 7.85 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.64 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.59 (td, *J* = 7.5, 1.5 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.52 (td, *J* = 7.5, 1.1 Hz, 1H); 7.30 (d, *J* = 7.5 Hz, 1H), 4.53 (s, 2H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.91, 150.34, 146.10 (q, J_{CF} = 35.1 Hz), 140.00, 139.18, 137.41, 135.45, 134.07, 133.79, 131.88, 127.81, 121.61 (q, J_{CF} = 273.7 Hz), 120.13 (q, J_{CF} = 2.8 Hz), 35.73;
^{19}F NMR ($CDCl_3$, 376 MHz): δ −68.05;
IR (neat): 2937, 1449, 1337, 1127, 1085, 1019, 746, 686 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{11}F_3NO^+$ $[M+H]^+$ 266.0787, found 266.0781.



2-((6-chloro-5-(trifluoromethyl)pyridin-3-yl)methyl)benzaldehyde (2q)

The compound **2q** was prepared according to the general procedure for 48 h and was purified by preparative TLC to give a colorless oil in 52% yield (31 mg).
^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.07 (s, 1H), 8.41 (d, *J* = 2.1 Hz, 1H), 7.85 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.80 (d, *J* = 2.3 Hz, 1H), 7.62 (td, *J* = 7.5, 1.5 Hz, 1H), 7.55 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 4.48 (s, 2H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 193.08, 152.39, 146.57, 139.39, 136.79 (q, J_{CF} = 4.7 Hz), 136.11, 135.05, 134.18, 133.69, 131.85, 128.06, 124.81 (q, J_{CF} = 33.0 Hz), 122.13 (d, J_{CF} = 272.9 Hz), 35.15;
^{19}F NMR ($CDCl_3$, 376 MHz): δ −63.91;
IR (neat): 2926, 1696, 1575, 1436, 1322, 1241, 1131, 1047, 752, 659 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{10}ClF_3NO^+$ $[M+H]^+$ 300.0398, found 300.0394.



2-((6-chloropyridin-3-yl)methyl)benzaldehyde (2r)

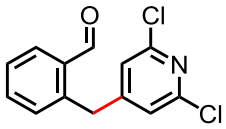
The compound **2n** was prepared according to the general procedure for 48 h and was purified by preparative TLC to give a colorless oil in 57% yield (26 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.16 (s, 1H), 8.24 (d, *J* = 2.4 Hz, 1H), 7.84 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.57 (td, *J* = 7.6, 1.6 Hz, 1H), 7.49 (td, *J* = 7.6, 1.6 Hz, 1H), 7.44 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 4.43 (s, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.81, 149.84, 149.32, 140.69, 139.18, 134.98, 134.74, 134.00, 133.74, 131.66, 127.60, 123.94, 34.98;

IR (neat): 2983, 1734, 1460, 1373, 1238, 1044, 915, 731, 647 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{13}H_{11}ClNO^+$ $[M+H]^+$ 232.0524, found 232.0523.



2-((2,6-dichloropyridin-4-yl)methyl)benzaldehyde (2s)

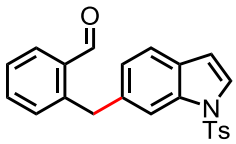
The compound **2s** was prepared according to the general procedure for 48 h and was purified by preparative TLC to give a colorless oil in 47% yield (25 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.06 (s, 1H), 7.86 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.72 (td, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.03 (s, 2H), 4.41 (s, 2H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.91, 155.35, 138.30, 135.80, 134.16, 133.81, 132.21, 132.20, 128.22, 122.99, 37.62;

IR (neat): 2922, 1697, 1581, 1541, 1377, 1168, 774, 732, 649 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{13}H_{10}Cl_2NO^+$ $[M+H]^+$ 266.0134, found 266.0131.

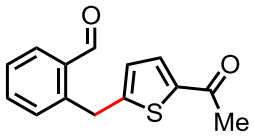


2-((1-tosyl-1H-indol-6-yl)methyl)benzaldehyde (2t)

The compound **2t** was prepared according to the general procedure for 48 h and was purified by preparative TLC to give a colorless oil in 72% yield (56 mg).

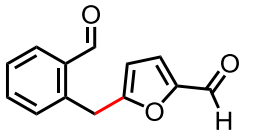
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.22 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.72 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 3.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 3.6 Hz, 1H), 4.56

(s, 2H), 2.34 (s, 3H);
^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.19, 144.86, 143.16, 137.11, 135.07, 134.92, 133.93, 133.85, 132.06, 131.63, 129.80, 129.14, 127.05, 126.76, 126.22, 124.38, 121.29, 113.76, 108.80, 38.36, 21.54;
HRMS (ESI-TOF): *m/z* calculated for $C_{23}H_{20}NO_3S^+$ $[M+H]^+$ 390.1158, found 390.1154.



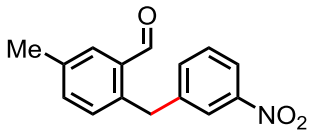
2-((5-acetylthiophen-2-yl)methyl)benzaldehyde (2u)

The compound **2u** was prepared according to the general procedure for 48 h and was purified by preparative TLC to give a colorless oil in 58% yield (28 mg).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.16 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.51-7.49 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.63 (s, 2H), 2.48 (s, 3H);
^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.56, 190.43, 153.06, 142.94, 140.64, 134.19, 134.08, 133.54, 132.67, 131.43, 127.79, 126.62, 33.50, 26.45;
IR (neat): 2923, 1694, 1651, 1448, 1359, 1276, 1195, 1209, 909, 751, 659 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{13}O_2S^+$ $[M+H]^+$ 245.0631, found 245.0632.



5-(2-formylbenzyl)furan-2-carbaldehyde (2v)

The compound **2v** was prepared according to the general procedure for 48 h and was purified by preparative TLC to give a colorless oil in 54% yield (23 mg).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.16 (s, 1H), 9.53 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 3.6 Hz, 1H), 6.20 (d, *J* = 3.2 Hz, 1H), 4.55 (s, 2H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ 192.64, 177.17, 160.89, 152.19, 137.74, 134.38, 134.07, 133.77, 131.75, 127.91, 110.15, 31.76;
IR (neat): 2937, 1672, 1599, 1513, 1398, 1248, 1194, 1022, 790, 755 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{13}H_{11}O_3^+$ $[M+H]^+$ 215.0703, found 215.0699.



5-methyl-2-(3-nitrobenzyl)benzaldehyde (2w)

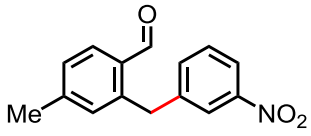
The compound **2w** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 77% yield (39 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.09 (s, 1H), 8.05-8.02 (m, 1H), 7.97 (s, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 4.50 (s, 2H), 2.44 (s, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.84, 148.31, 142.70, 137.69, 137.52, 135.12, 135.01, 134.80, 133.62, 131.87, 129.16, 123.39, 121.25, 37.59, 20.77;

IR (neat): 2928, 1692, 1610, 1526, 1350, 1156, 909, 729 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{14}NO_3^+$ $[M+H]^+$ 256.0968, found 256.0974.



4-methyl-2-(3-nitrobenzyl)benzaldehyde (2x)

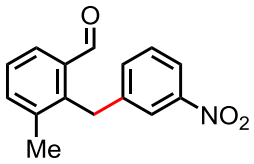
The compound **2x** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 84% yield (43 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.06 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 4.51 (s, 2H), 2.43 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.31, 148.34, 145.19, 142.53, 140.65, 135.08, 135.02, 132.71, 131.57, 129.17, 128.34, 123.46, 121.30, 37.99, 21.78;

IR (neat): 2925, 1693, 1607, 1527, 1348, 1218, 1096, 804, 729 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{14}NO_3^+$ $[M+H]^+$ 256.0968, found 256.0970.

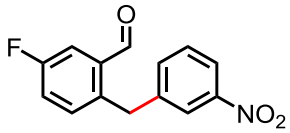


3-methyl-2-(3-nitrobenzyl)benzaldehyde (2y)

The compound **2y** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 73% yield (37 mg).

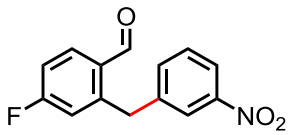
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.14 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.51-7.37 (m, 4H), 4.62 (s, 2H), 2.31 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.17, 148.41, 141.79, 139.00, 138.23, 136.31, 134.62, 134.31, 132.64, 129.21, 127.57, 122.81, 121.20, 33.31, 19.55;
IR (neat): 2982, 1735, 1696, 1529, 1372, 1349, 1236, 1043, 847, 786, 729, 634, 607 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{14}NO_3^+$ $[M+H]^+$ 256.0968, found 256.0973.



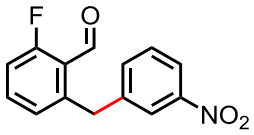
5-fluoro-2-(3-nitrobenzyl)benzaldehyde (2z)

The compound **2z** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 64% yield (33 mg).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.10 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.97 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.50-7.43 (m, 2H), 7.31-7.29 (m, 2H), 4.51 (s, 2H);
^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.88, 161.90 (d, J_{CF} = 247.9 Hz), 148.43, 142.08, 136.51 (d, J_{CF} = 3.6 Hz), 135.29 (d, J_{CF} = 5.6 Hz), 134.86, 133.67 (d, J_{CF} = 7.0 Hz), 129.42, 123.37, 121.57, 121.16 (d, J_{CF} = 21.0 Hz), 119.89 (d, J_{CF} = 21.9 Hz), 37.20;
^{19}F NMR ($CDCl_3$, 376 MHz): δ −113.80;
IR (neat): 2926, 1696, 1575, 1436, 1322, 1241, 1131, 1047, 752, 659 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{11}FNO_3^+$ $[M+H]^+$ 260.0717, found 260.0710.



4-fluoro-2-(3-nitrobenzyl)benzaldehyde (2aa)

The compound **2aa** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 76% yield (39 mg).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.09 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.01 (s, 1H), 7.89 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.17 (td, *J* = 8.0, 2.4 Hz, 1H), 6.97 (dd, *J* = 9.2, 2.4 Hz, 1H), 4.56 (s, 2H);
^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.99, 165.68 (d, J_{CF} = 256.7 Hz), 148.43, 144.30 (d, J_{CF} = 8.8 Hz), 141.39, 137.35 (d, J_{CF} = 10.1 Hz), 135.06, 130.44 (d, J_{CF} = 2.7 Hz), 129.45, 123.55, 121.67, 118.91 (d, J_{CF} = 22.2 Hz), 114.73 (d, J_{CF} = 21.6 Hz), 37.82 (d, J_{CF} = 1.6 Hz);
^{19}F NMR ($CDCl_3$, 376 MHz): δ −102.63;
IR (neat): 2868, 1696, 1605, 1583, 1528, 1349, 1244, 805, 727 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{11}FNO_3^+$ $[M+H]^+$ 260.0717, found 260.0722.



2-fluoro-6-(3-nitrobenzyl)benzaldehyde (2ab)

The compound **2ab** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 81% yield (42 mg).

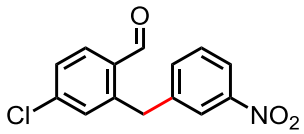
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.49 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 1H), 7.59-7.53 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 10.7, 8.4 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 4.51 (s, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.61 (d, J_{CF} = 11.9 Hz), 166.83 (d, J_{CF} = 257.3 Hz), 148.32, 142.52, 141.84, 135.67 (d, J_{CF} = 10.3 Hz), 135.22, 129.17, 127.62 (d, J_{CF} = 3.4 Hz), 123.52, 122.09 (d, J_{CF} = 5.5 Hz), 121.41, 115.27 (d, J_{CF} = 21.7 Hz), 38.38 (d, J_{CF} = 2.2 Hz);

^{19}F NMR ($CDCl_3$, 376 MHz): δ −120.44;

IR (neat): 2887, 1697, 1611, 1572, 1527, 1350, 1255, 910, 818,727 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{11}FNO_3^+$ $[M+H]^+$ 260.0717, found 260.0720.



4-chloro-2-(3-nitrobenzyl)benzaldehyde (2ac)

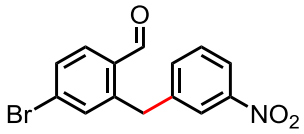
The compound **2ac** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 60% yield (33 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.09 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.00 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.52-7.44 (m, 3H), 7.27-7.26 (m, 1H), 4.53 (s, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.31, 148.44, 142.55, 141.42, 140.53, 135.75, 135.01, 132.21, 131.87, 129.45, 127.97, 123.53, 121.69, 37.68;

IR (neat): 2926, 1590, 1561, 1528, 1349, 1196, 1092, 913, 804, 728 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{11}ClNO_3^+$ $[M+H]^+$ 276.0422, found 276.0425.



4-bromo-2-(3-nitrobenzyl)benzaldehyde (2ad)

The compound **2ad** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 68% yield (44 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.09 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.00 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.51-7.44 (m, 3H), 4.52 (s, 2H);

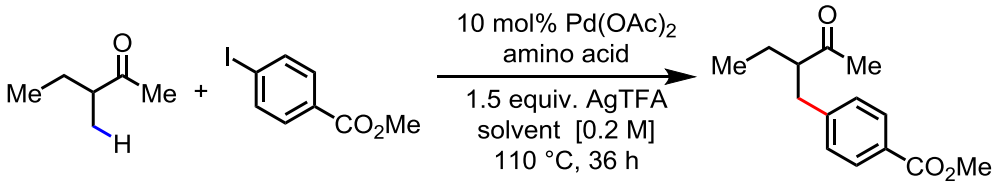
^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.50, 148.42, 142.53, 141.43, 135.71, 134.98, 134.83, 132.58, 131.02, 129.45, 129.41, 123.51, 121.69, 37.60;
IR (neat): 2851, 1697, 1585, 1557, 1526, 1348, 1195, 1080, 879, 805, 727 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{14}H_{11}BrNO_3^+$ $[M+H]^+$ 319.9917, found 319.9916.

III. Pd(II)-Catalyzed C(sp^3)–H Arylation of Ketones (Fig. 3)

General Procedure

In air, a reaction tube (10 mL) with magnetic stir bar was charged with ketone substrate (0.20 mmol), aryl iodide (0.40 mmol), silver trifluoroacetate (66.3 mg, 0.30 mmol), palladium acetate (4.5 mg, 0.020 mmol) and glycine (7.5 mg, 0.10 mmol), followed by the mixture of HFIP (0.75 mL) and acetic acid (0.25 mL). The reaction tube was sealed and allowed to stir at ambient temperature for 10 minutes, then heated to 110 ℃ for 36 hours. Upon completion, the reaction mixture was cooled to room temperature, filtered through a silica gel plug, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel using hexanes/ EtOAc as the eluent to afford the desired product.

Table S2. Optimization of Pd(II)-Catalyzed C(sp^3)–H Arylation of Ketones[*,†]

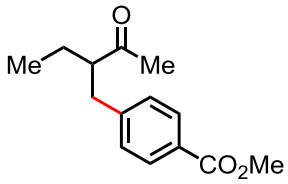


3a 2.0 equiv. **4a**

entry	solvent	amino acid	NMR yield (%)
1	HOAc/H_2O (9:1)	glycine (40%)	<2
2	HOAc	glycine (40%)	25
3	HFIP	glycine (40%)	19
4	HFIP/HOAc (1:1)	glycine (40%)	53
5	HFIP/HOAc (3:1)	glycine (40%)	62
6	HFIP/HOAc (5:1)	glycine (40%)	57
7	**HFIP/HOAc (3:1)**	**glycine (50%)**	**71 (71)[‡]**
8	HFIP/HOAc (3:1)	glycine (60%)	55
9	HFIP/HOAc (3:1)	L-alanine (50%)	60
10	HFIP/HOAc (3:1)	L-valine (50%)	48
11	HFIP/HOAc (3:1)	L-*tert*-leucine (50%)	44

[*]Conditions: 0.2 mmol of **3a**, 2.0 equiv of methyl 4-iodobenzoate, 10 mol% of $Pd(OAc)_2$, 40-60 mol% amino acid, 1.5 equiv of AgTFA, 1.0 mL of solvent, 110 ^oC, 36 h. [†]The yield was determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. [‡]isolated yield.

Full Characterization of Reaction Products and Proof of Stereochemistry



methyl 4-(2-ethyl-3-oxobutyl)benzoate (4a)

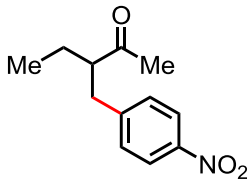
The compound **4a** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 71% yield (33 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.21(d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 2.93 (dd, *J* = 12.4, 7.6 Hz, 1H), 2.79-2.69 (m, 2H), 2.01 (s, 3H), 1.68-1.62 (m, 1H), 1.56-1.51 (m, 1H), 0.90 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 211.64, 166.96, 145.30, 129.75, 128.87, 128.24, 55.71, 51.98, 37.10, 30.19, 24.57, 11.43;

IR (neat): 2960, 1715, 1610, 1435, 1278, 1179, 1109, 1020, 764, 706 cm^{-1};

HRMS (ESI-TOF): m/z calculated for $C_{14}H_{19}O_3$ $[M+H]^+$: 235.1329; found: 235.1329.



3-(4-nitrobenzyl)pentan-2-one (4b)

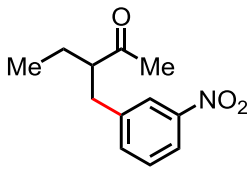
The compound **4b** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 65% yield (29 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.02 (dd, *J* = 12.4, 7.6 Hz, 1H), 2.83-2.73 (m, 2H), 2.04 (s, 3H), 1.73-1.64 (m, 1H), 1.59-1.53 (m, 1H), 0.92 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 210.89, 147.80, 146.58, 129.71, 123.67, 55.50, 36.50, 30.09, 24.67, 11.32;

IR (neat): 2929, 1707, 1599, 1514, 1342, 1165, 1109, 853, 800,731, 695 cm^{-1};

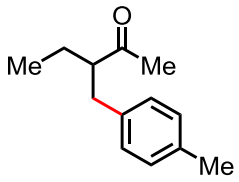
HRMS (ESI-TOF): m/z calculated for $C_{12}H_{16}NO_3$ $[M+H]^+$: 222.1125; found: 222.1131.



3-(3-nitrobenzyl)pentan-2-one (4c)

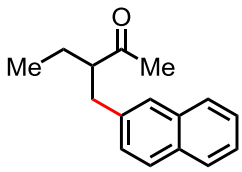
The compound **4c** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 62% yield (27 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.02 (m, 2H), 7.49-7.41 (m, 2H), 3.03 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.84-2.73 (m, 2H), 2.06 (s, 3H), 1.74-1.64 (m, 1H), 1.59-1.53 (m, 1H), 0.92 (t, *J* = 7.6 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 210.94, 148.31, 141.95, 135.26, 129.30, 123.56, 121.42, 55.51, 36.19, 30.03, 24.53, 11.29;
IR (neat): 2928, 1707, 1524, 1459, 1346, 1162, 1098, 806, 729, 686 cm^{-1};
HRMS (ESI-TOF): m/z calculated for $C_{12}H_{16}NO_3$ $[M+H]^+$: 222.1125; found: 222.1131.



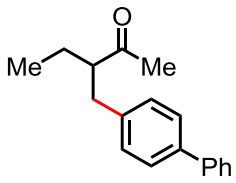
3-(4-methylbenzyl)pentan-2-one (4d)

The compound **4d** was prepared according to the general procedure with 3 equiv. of aryl iodide at 130 ℃ and was purified by preparative TLC to give a colorless oil in 60% yield (23 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.84 (dd, *J* = 13.0, 7.6 Hz, 1H), 2.76-2.70 (m, 1H), 2.64 (dd, *J* = 13.0, 6.4 Hz, 1H), 2.03 (s, 3H), 2.01 (s, 3H), 1.68-1.61 (m, 1H), 1.55-1.48 (m, 1H), 0.88 (t, *J* = 7.6 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 212.46, 136.52, 135.66, 129.09, 128.67, 56.25, 37.02, 30.10, 24.45, 20.96, 11.58;
IR (neat): 2923, 1709, 1514, 1458, 1349, 1159, 1021, 800, 751 cm^{-1};
HRMS (ESI-TOF): m/z calculated for $C_{13}H_{19}O$ $[M+H]^+$: 191.1430; found: 191.1424.



3-(naphthalen-2-ylmethyl)pentan-2-one (4e)

The compound **4e** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 53% yield (24 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.76 (m, 3H), 7.59 (s, 1H), 7.48-7.41 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 3.09-3.02 (m, 1H), 2.90-2.82 (m, 2H), 2.02 (s, 3H), 1.74-1.67 (m, 1H), 1.61-1.52 (m, 1H), 0.91(t, *J* = 8.0 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 212.26, 137.24, 133.51, 132.11, 128.08, 127.59, 127.49, 127.29, 127.21, 126.01, 125.38, 56.07, 37.56, 30.24, 24.60, 11.60;
IR (neat): 2931, 1709, 1508, 1459, 1359, 1163, 856, 820, 751 cm^{-1};
HRMS (ESI-TOF): m/z calculated for $C_{16}H_{19}O$ $[M+H]^+$: 227.1430; found: 227.1432.



3-([1,1'-biphenyl]-4-ylmethyl)pentan-2-one (4f)

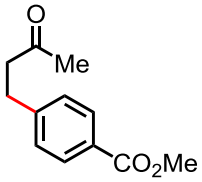
The compound **4f** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 47% yield (24 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.94 (dd, *J* = 13.0, 7.8 Hz, 1H), 2.84-2.77 (m, 1H), 2.73 (dd, *J* = 13.0, 6.3 Hz, 1H), 2.05 (s, 3H), 1.76-1.64 (m, 1H), 1.60-1.53 (m, 1H), 0.92 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.23, 140.85, 139.13, 138.81, 129.25, 128.71, 127.13, 127.11, 126.94, 56.10, 36.96, 30.15, 24.55, 11.57;

IR (neat): 2931, 1709, 1486, 1409, 1351, 1160, 841, 763, 698 cm^{-1};

HRMS (ESI-TOF): m/z calculated for $C_{18}H_{21}O$ $[M+H]^+$: 253.1587; found: 253.1593.



methyl 4-(3-oxobutyl)benzoate (4g)

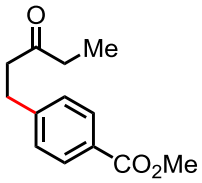
The compound **4g** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 47% yield (19 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 3.89 (s, 3H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.13 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.20, 166.95, 146.48, 129.78, 128.32, 128.10, 51.95, 44.51, 30.02, 29.57;

IR (neat): 2952, 1709, 1610, 1434, 1355, 1273, 1161, 1104, 764, 703 cm^{-1};

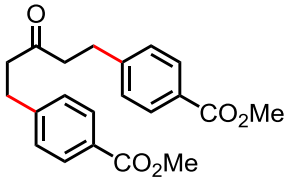
HRMS (ESI-TOF): m/z calculated for $C_{14}H_{19}O_3$ $[M+H]^+$: 207.1016; found: 207.1012.



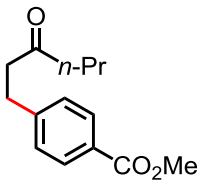
methyl 4-(3-oxopentyl)benzoate (4h)

The compound **4h** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 59% yield (26 mg).

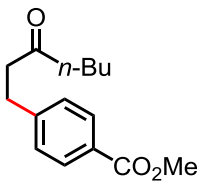
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 8.0 Hz, 2H), 1.04 (t, *J* = 8.0 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 210.08, 167.04, 146.69, 129.81, 128.37, 128.10, 51.99, 43.26, 36.14, 29.73, 7.72;
IR (neat): 2950, 1709, 1610, 1434, 1274, 1178, 1103, 762, 703 cm^{-1};
HRMS (ESI-TOF): m/z calculated for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.1172; found: 221.1166.



dimethyl 4,4'-(3-oxopentane-1,5-diyl)dibenzoate (4h')
The compound **4h'** was isolated in 26% yield (18 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 4H), 7.21 (d, *J* = 8.0 Hz, 4H), 3.90 (s, 6H), 2.93 (t, *J* = 7.2 Hz, 4H), 2.72 (t, *J* = 7.2 Hz, 4H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 207.90, 166.96, 146.35, 129.83, 128.35, 128.19, 51.99, 43.89, 29.56;
IR (neat): 2952, 1714, 1608, 1436, 1274, 1177, 1105, 765, 707 cm^{-1};
HRMS (ESI-TOF): m/z calculated for $C_{21}H_{23}O_5$ $[M+H]^+$: 355.1540; found: 355.1546.



methyl 4-(3-oxohexyl)benzoate (4i)
The compound **4i** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 60% yield (28 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.61-1.56 (m, 2H), 0.89 (t, *J* = 7.6 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 209.61, 167.02, 146.71, 129.80, 128.38, 128.08, 51.98, 44.93, 43.65, 29.64, 17.21, 13.69;
IR (neat): 2955, 1714, 1610, 1435, 1278, 1179, 1108, 765, 707 cm^{-1};
HRMS (ESI-TOF): m/z calculated for $C_{14}H_{19}O_3$ $[M+H]^+$: 235.1329; found: 235.1325.



methyl 4-(3-oxoheptyl)benzoate (4j)

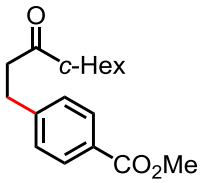
The compound **4j** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 48% yield (24 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.57-1.50 (m, 2H), 1.33-1.23 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 209.71, 167.01, 146.71, 129.80, 128.37, 128.08, 51.98, 43.62, 42.75, 29.67, 25.85, 22.29, 13.79;

IR (neat): 2954, 1713, 1610, 1434, 1274, 1179, 1105, 763, 704 cm^{-1};

HRMS (ESI-TOF): m/z calculated for $C_{15}H_{21}O_3$ [M+H]$^+$: 249.1485; found: 249.1480.



methyl 4-(3-cyclohexyl-3-oxopropyl)benzoate (4k)

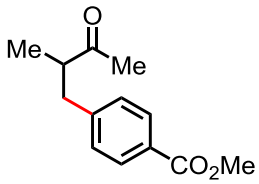
The compound **4k** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 40% yield (22 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 2.92 (t, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.32-2.26 (m, 1H), 1.79-1.74 (m, 4H), 1.65-1.62 (m, 1H), 1.33-1.14 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 212.51, 166.99, 146.93, 129.72, 128.35, 127.97, 51.92, 50.89, 41.56, 29.58, 28.32, 25.74, 25.55;

IR (neat): 2930, 1709, 1610, 1435, 1278, 1109, 1019, 732, 702 cm^{-1};

HRMS (ESI-TOF): m/z calculated for $C_{17}H_{23}O_3$ [M+H]$^+$: 275.1642; found: 275.1638.



methyl 4-(2-methyl-3-oxobutyl)benzoate (4l)

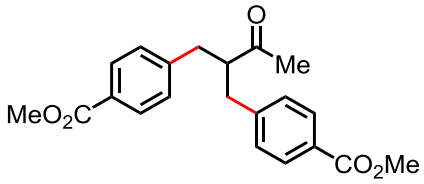
The compound **4l** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 57% yield (25 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91(d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 3.01 (dd, *J* = 13.2, 7.4 Hz, 1H), 2.86-2.77 (m, 1H), 2.57 (dd, *J* = 13.2, 7.4 Hz, 1H), 2.06 (s, 3H), 1.06 (d, *J* = 7.2, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 211.35, 166.86, 145.16, 129.63, 128.88, 128.16, 51.88, 48.34, 38.57, 28.72, 16.22;

IR (neat): 2952, 1709, 1610, 1434, 1273, 1104, 1019, 766, 702 cm^{-1};

HRMS (ESI-TOF): m/z calculated for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.1172; found: 221.1168.



dimethyl 4,4'-(2-acetylpropane-1,3-diyl)dibenzoate (4l')

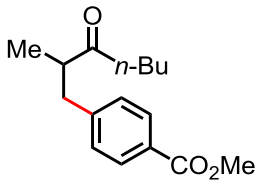
The compound **4l'** was isolated in 21% yield (15 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 4H), 7.20 (d, *J* = 8.4 Hz, 4H), 3.90 (s, 6H), 3.21-3.13 (m, 1H), 3.01-2.96 (m, 2H), 2.77-2.72 (m, 2H), 1.78 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 210.89, 166.88, 144.42, 129.92, 128.90, 128.57, 55.75, 52.06, 37.99, 31.58;

IR (neat): 2950, 1712, 1609, 1434, 1274, 1103, 1020, 765, 706 cm^{-1};

HRMS (ESI-TOF): m/z calculated for $C_{21}H_{23}O_5$ $[M+H]^+$: 355.1540; found: 355.1537.



methyl 4-(2-methyl-3-oxoheptyl)benzoate (4m)

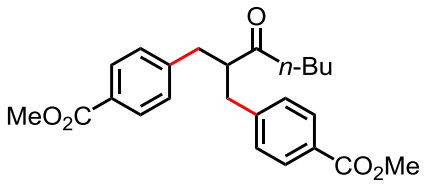
The compound **4m** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 38% yield (20 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 3.02 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.88-2.79 (m, 1H), 2.59 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.44-2.36 (m, 1H), 2.28-2.20 (m, 1H), 1.49-1.42 (m, 2H), 1.26-1.16 (m, 2H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.84 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 213.70, 166.98, 145.42, 129.67, 128.97, 128.17, 51.96, 47.72, 41.64, 38.88, 25.53, 22.22, 16.64, 13.77;

IR (neat): 2959, 1714, 1611, 1435, 1277, 1108, 1020, 733, 702 cm^{-1};

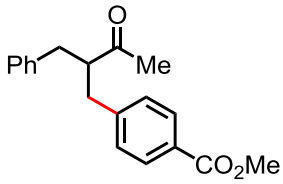
HRMS (ESI-TOF): m/z calculated for $C_{16}H_{23}O_3$ $[M+H]^+$: 263.1642; found: 263.1638.



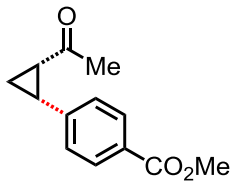
dimethyl 4,4'-(2-pentanoylpropane-1,3-diyl)dibenzoate (4m')

The compound **4m'** was isolated in 15% yield (12 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 4H), 3.90 (s, 6H), 3.16-3.10 (m, 1H), 2.97 (dd, *J* = 12.0, 8.0 Hz, 2H), 2.72 (dd, *J* = 12.0, 8.0 Hz, 2H), 1.91 (t, *J* = 8.0 Hz, 2H), 1.25-1.18 (m, 2H), 1.05-0.95 (m, 2H), 0.69 (t, *J* = 8.0 Hz, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 212.98, 166.90, 144.59, 129.85, 128.96, 128.49, 55.26, 52.05, 44.47, 38.28, 24.85, 21.92, 13.63;
IR (neat): 2952, 1719, 1610, 1435, 1278, 1107, 1020, 764, 706 cm^{-1};
HRMS (ESI-TOF): m/z calculated for $C_{24}H_{29}O_5$ $[M+H]^+$: 397.2010; found: 397.2005.

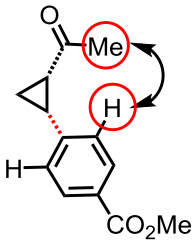


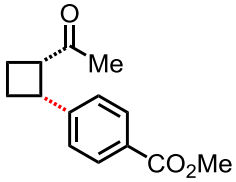
methyl 4-(2-benzyl-3-oxobutyl)benzoate (4n)
The compound **4n** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 55% yield (33 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.18-7.15 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 3H), 3.16-3.09 (m, 1H), 2.97-2.87 (m, 2H), 2.75-2.65 (m, 2H), 1.74 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 211.45, 166.92, 144.87, 138.89, 129.83, 128.90, 128.82, 128.60, 128.38, 126.53, 56.09, 52.03, 38.28, 37.84, 31.57;
IR (neat): 2951, 1709, 1609, 1435, 1276, 1103, 1020, 908, 727, 699 cm^{-1};
HRMS (ESI-TOF): m/z calculated for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1485; found: 297.1484.



methyl 4-(2-acetylcyclopropyl)benzoate (4o)
The compound **4o** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 39% yield (17 mg). Analysis of crude reaction mixture by ^{1}H NMR showed a 20:1 diastereomer ratio. The relative stereochemistry was determined by NOESY analysis.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 2.73-2.67 (m, 1H), 2.52-2.46 (m, 1H), 2.04 (s, 3H), 1.90-1.85 (m, 1H), 1.39-1.33 (m, 1H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 203.74, 166.96, 141.49, 129.27, 129.07, 128.53, 51.98, 31.39, 30.40, 28.16, 12.00;
IR (neat): 2952, 1718, 1611, 1435, 1279, 1111, 1018, 778, 737, 705 cm^{-1};
HRMS (ESI-TOF): m/z calculated for $C_{13}H_{15}O_3$ $[M+H]^+$: 219.1016; found: 219.1013.

The following NOEs were observed:





methyl 4-(2-acetylcyclobutyl)benzoate (4p)

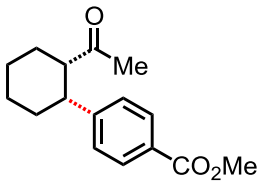
The compound **4p** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 52% yield (24 mg). Analysis of crude reaction mixture by ^{1}H NMR showed a > 20:1 diastereomer ratio. The relative stereochemistry was assigned by analogy to compound **4o** and **4q**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 3.80-3.72 (m, 1H), 3.34-3.27 (m, 1H), 2.27-2.12 (m, 4H), 2.05 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 208.34, 166.97, 148.99, 129.82, 128.33, 126.62, 53.53, 52.02, 42.06, 27.74, 24.54, 21.42;

IR (neat): 2951, 1718, 1610, 1435, 1278, 1110, 738, 685 cm^{-1};

HRMS (ESI-TOF): m/z calculated for $C_{14}H_{17}O_3$ $[M+H]^+$: 233.1172; found: 233.1176.



methyl 4-(2-acetylcyclohexyl)benzoate (4q)

The compound **4q** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 54% yield (29 mg). Analysis of crude reaction mixture by ^{1}H NMR showed a > 20:1 diastereomer ratio. The relative stereochemistry was determined by NOESY analysis.

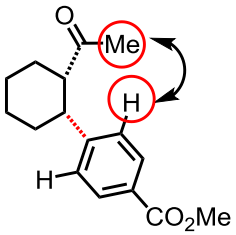
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 2.86-2.75 (m, 2H), 1.97-1.86 (m, 4H), 1.82 (s, 3H), 1.53-1.36 (m, 4H);

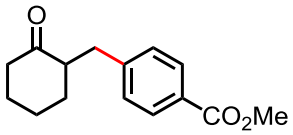
^{13}C NMR (125 MHz, $CDCl_3$) δ 211.44, 166.97, 150.35, 129.87, 128.34, 127.36, 56.95, 51.97, 46.20, 34.08, 29.88, 29.51, 26.05, 25.50;

IR (neat): 2927, 1709, 1609, 1434, 1273, 1108, 768, 706 cm^{-1};

HRMS (ESI-TOF): m/z calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485; found: 261.1482.

The following NOEs were observed:





methyl 4-((2-oxocyclohexyl)methyl)benzoate (4r)

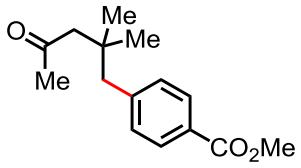
The compound **4r** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 60% yield (30 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 3.26 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.61-2.53 (m, 1H), 2.48-2.41 (m, 2H), 2.36-2.28 (m, 1H), 2.09-1.96 (m, 2H), 1. 88-1.81 (m, 1H), 1.71-1.54 (m, 2H), 1.41-1.31 (m, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 211.92, 167.06, 146.04, 129.61, 129.14, 127.99, 52.16, 51.96, 42.14, 35.54, 33.53, 27.96, 25.08;

IR (neat): 2939, 1708, 1611, 1435, 1265, 1109, 731, 701 cm^{-1};

HRMS (ESI-TOF): m/z calculated for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329; found: 247.1327.



methyl 4-(2,2-dimethyl-4-oxopentyl)benzoate (4s)

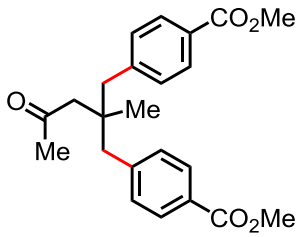
The compound **4s** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 49% yield (24 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.75 (s, 2H), 2.27 (s, 2H), 2.11 (s, 3H), 1.01 (s, 6H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 208.62, 167.16, 144.41, 130.56, 129.08, 128.05, 52.92, 51.97, 47.26, 34.50, 32.38, 27.39;

IR (neat): 2954, 1714, 1610, 1434, 1275, 1110, 744, 707 cm^{-1};

HRMS (ESI-TOF): m/z calculated for $C_{15}H_{21}O_3$ $[M+H]^+$: 249.1485; found: 249.1485.



dimethyl 4,4'-(2-methyl-2-(2-oxopropyl)propane-1,3-diyl)dibenzoate (4s')

The compound **4s'** was isolated in 12% yield (9.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 4H), 7.17 (d, *J* = 8.0 Hz, 4H), 3.90 (s, 6H), 3.08 (d, *J* = 12.0 Hz, 2H), 2.76 (d, *J* = 12.0 Hz, 2H), 2.10 (s, 2H), 2.06 (s, 3H), 0.90 (s, 3H) ;

^{13}C NMR (125 MHz, $CDCl_3$) δ 208.59, 167.08, 143.95, 130.65, 129.22, 128.27, 52.03, 48.90, 45.41, 38.06, 31.85, 24.93;

IR (neat): 2953, 1713, 1434, 1276, 1108, 782, 762, 712 cm^{-1};

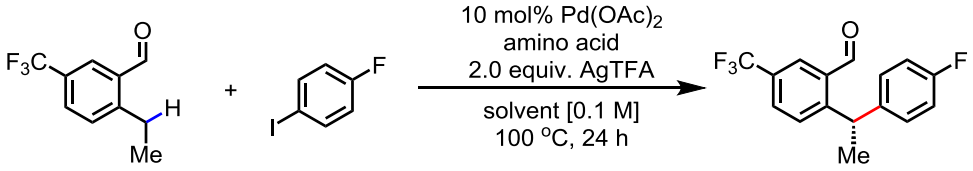
HRMS (ESI-TOF): *m/z* calculated for $C_{23}H_{27}O_5$ $[M+H]^+$: 383.1853; found: 383.1847.

IV. Pd(II)-Catalyzed Enantioselective Benzylic C(sp^3)–H Arylation of Aldehydes (Fig. 4)

General Procedure

In air, a reaction tube (10 mL) with magnetic stir bar was charged with aldehyde substrate (0.20 mmol), aryl iodide (0.60 mmol), silver trifluoroacetate (88.4 mg, 0.40 mmol), palladium acetate (4.5 mg, 0.020 mmol) and L-*tert*-leucine (5.2 mg, 0.040 mmol), followed by the mixture of HFIP (0.9 mL), acetic acid (0.1 mL) and H_2O (10.8 μL). The reaction tube was sealed and allowed to stir at ambient temperature for 10 minutes, then heated to 100 ℃ for 24 hours. Upon completion, the reaction mixture was cooled to room temperature, diluted with EtOAc, filtered through a silica gel plug, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel using hexanes/ EtOAc as the eluent to afford the desired product.

Table S3. Optimization of Pd(II)-Catalyzed Enantioselective Benzylic C(sp^3)–H Arylation of Aldehydes[*,†]

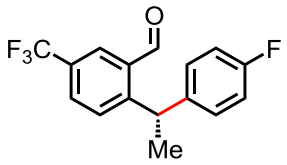


5a (1.0 equiv.) 3.0 equiv. **6a**

entry	amino acid	solvent	additive	conversion (%)	NMR yield (%)	er
1	L-valine (40%)	AcOH:H_2O (9:1)	-	42	10	-
2	L-valine (40%)	AcOH	-	70	21	-
3	L-valine (40%)	HFIP	-	10	<2	-
4	L-valine (40%)	HFIP:AcOH (9:1)	-	96	88	85:15
5	L-*tert*-leucine (40%)	HFIP:AcOH (9:1)	-	60	30	98:2
6	L-*tert*-leucine (20%)	HFIP:AcOH (9:1)	-	96	87	98:2
7	**L-*tert*-leucine (20%)**	**HFIP:AcOH (9:1)‡**	**-**	**98**	**90**	**98:2**
8	**L-*tert*-leucine (20%)**	**HFIP:AcOH (9:1)‡**	**H_2O (3.0)**	**96**	**88 (80)§**	**98:2**

[*]Conditions: 0.2 mmol of **5a**, 3.0 equiv of 4-fluoroiodobenzene, 10 mol% of $Pd(OAc)_2$, 40 mol% or 20 mol% of amino acid, 3.0 equiv of AgTFA, 1.0 or 2.0 mL solvent, 100 °C, 24 h. [†]The yield was determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. [‡][0.2 M] instead of [0.1 M]. [§]isolated yield.

Full Characterization of Reaction Products and Proof of Stereochemistry



(*S*)-2-(1-(4-fluorophenyl)ethyl)-5-(trifluoromethyl)benzaldehyde (6a)

The compound **6a** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 80% yield (47 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.31 (s, 1H), 8.08 (d, *J* = 2.1 Hz, 1H), 7.77 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.17-7.13 (m, 2H), 7.01-6.97 (m, 2H), 5.27 (q, *J* = 7.1 Hz, 1H), 1.67 (d, *J* = 7.1 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 190.83, 161.49 (d, J_{CF} = 245.4 Hz), 152.03, 140.21 (d, J_{CF} = 3.3 Hz), 133.45, 130.18 (q, J_{CF} = 3.6 Hz), 129.43 (q, J_{CF} = 33.4 Hz), 129.19 (d, J_{CF} = 8.5 Hz), 129.15, 128.99 (q, J_{CF} = 3.9 Hz), 123.52 (q, J_{CF} = 272.1 Hz), 115.50 (d, J_{CF} = 21.0 Hz), 38.27, 22.14;

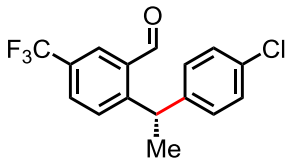
^{19}F NMR ($CDCl_3$, 376 MHz): δ –63.14, –116.44;

HPLC Chiralpak® AS-H column (1% isopropanol in hexanes, 0.5 mL/min) t_r= 12.77 min (minor), 13.51 min (major): 98:2 er.

IR (neat): 1705, 1618, 1508, 1330, 1225, 1162, 1124, 1085, 901, 836, 550 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{13}F_4O^+$ $[M+H]^+$ 297.0897, found 297.0899.

The absolute stereochemistry was assigned by analogy to compound **6c**.



(*S*)-2-(1-(4-chlorophenyl)ethyl)-5-(trifluoromethyl)benzaldehyde (6b)

The compound **6b** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 72% yield (45 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.29 (s, 1H), 8.08 (d, *J* = 1.6 Hz, 1H), 7.77 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.29-7.23 (m, 2H), 7.15-7.10 (m, 2H), 5.27 (q, *J* = 7.2 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H);

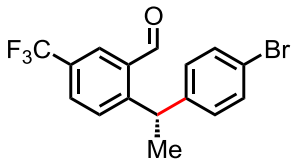
^{13}C NMR ($CDCl_3$, 150 MHz): δ 190.86, 151.67, 142.99, 133.47, 132.49, 130.21 (q, J_{CF} = 3.4 Hz), 129.53 (q, J_{CF} = 33.2 Hz), 129.25 (q, J_{CF} = 3.0 Hz), 129.19, 129.09, 128.82, 123.50 (q, J_{CF} = 272.1 Hz), 38.42, 21.94;

^{19}F NMR ($CDCl_3$, 376 MHz): δ – 63.15;

HPLC Chiralpak® AS-H column (1% isopropanol in hexanes, 0.5 mL/min) t_r= 12.81 min (minor), 13.81 min (major): 97:3 er.

IR (neat): 1698, 1618, 1492, 1330, 1165, 1127, 1088, 1014, 848, 831 cm^{-1};

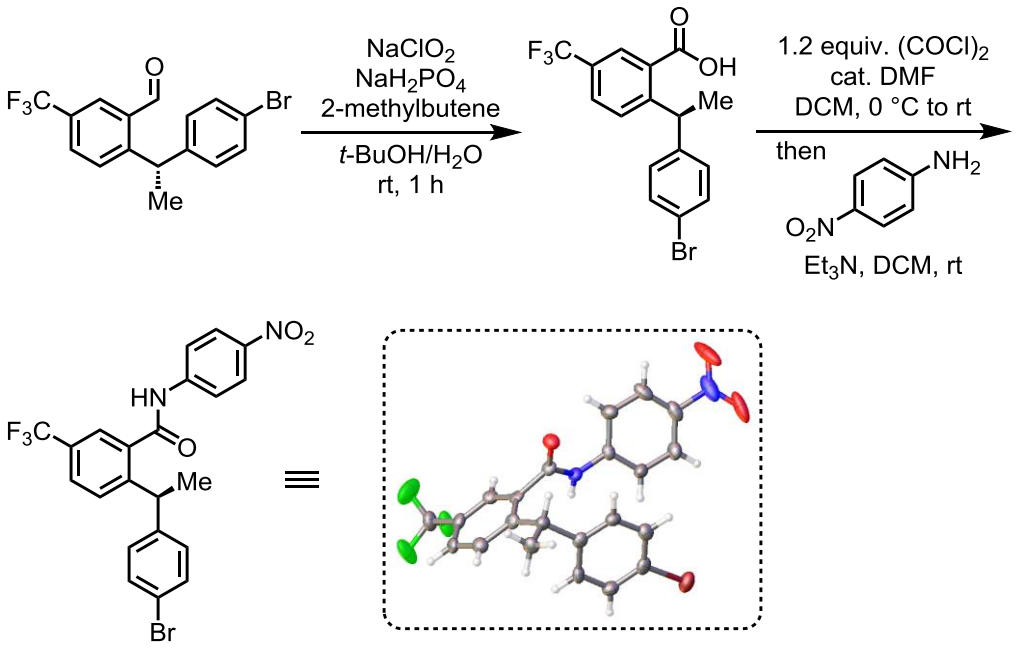
HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{13}ClF_3O^+$ $[M+H]^+$ 313.0602, found 313.0597.
The absolute stereochemistry was assigned by analogy to compound **6c**.



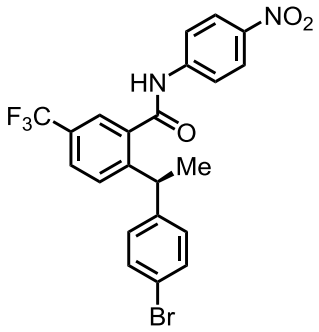
(*S*)-2-(1-(4-bromophenyl)ethyl)-5-(trifluoromethyl)benzaldehyde (6c)

The compound **6c** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 77% yield (55 mg).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.29 (s, 1H), 8.08 (s, 1H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 5.26 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 190.85, 151.55, 143.52, 133.46, 131.75, 130.20 (q, J_{CF} = 3.1 Hz), 129.52 (q, J_{CF} = 33.4 Hz), 129.47, 129.27 (q, J_{CF} = 3.7 Hz), 129.19, 123.48 (q, J_{CF} = 272.2 Hz), 120.53, 38.47, 21.86;
^{19}F NMR ($CDCl_3$, 376 MHz): δ –63.14;
HPLC Chiralpak® AS-H column (1% isopropanol in hexanes, 0.5 mL/min) t_r= 12.65 min (minor), 13.73 min (major): 98:2 er.
IR (neat): 1696, 1618, 1488, 1328, 1164, 1123, 1076, 1009, 901, 825, 768, 731, 692, 640, 539 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{13}BrF_3O^+$ $[M+H]^+$ 357.0096, found 357.0090.

The absolute stereochemistry was assigned by X-ray crystallography:



Metrical parameters for the structure are available free of charge from the Cambridge Crystallographic Data Centre under reference number CCDC 1434263.



(*S*)-2-(1-(4-bromophenyl)ethyl)-N-(4-nitrophenyl)-5-(trifluoromethyl)benzamide (S2)

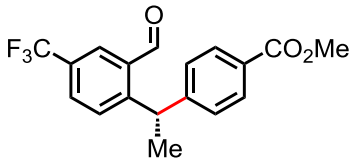
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.24-8.22 (m, 2H), 7.75-7.74 (m, 1H), 7.69 (s, 1H), 7.60-7.58 (m, 3H), 7.38 (s, 1H), 7.32-7.30 (m, 2H), 7.02-7.00 (m, 2H), 4.69 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 166.82, 147.72, 144.03, 143.79, 142.84, 136.48, 131.75, 129.48, 129.13 (q, J_{CF} = 33.2 Hz), 128.66, 127.61 (q, J_{CF} = 3.9 Hz), 125.07, 123.75 (q, J_{CF} = 3.6 Hz), 123.48 (q, J_{CF} = 272.5 Hz), 120.59, 119.32, 40.28, 21.66;

^{19}F NMR ($CDCl_3$, 376 MHz): δ −62.88.

IR (neat): 2017, 1667, 1615, 1597, 1549, 1509, 1405, 1337, 1304, 1256, 1173, 1129, 1088, 853 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{22}H_{17}BrF_3N_2O_3^+$ $[M+H]^+$ 493.0369, found 383.493.0372.



methyl (*S*)-4-(1-(2-formyl-4-(trifluoromethyl)phenyl)ethyl)benzoate (6d)

The compound **6d** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 73% yield (49 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.29 (s, 1H), 8.09 (d, *J* = 2.0 Hz, 1H), 7.98-7.96 (m, 2H), 7.78 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.36 (q, *J* = 7.1 Hz, 1H), 3.90 (s, 3H), 1.71 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 190.84, 166.75, 151.28, 149.69, 133.50, 130.22 (q, J_{CF} = 3.2 Hz), 129.98, 129.59 (q, J_{CF} = 33.6 Hz), 129.38 (q, J_{CF} = 3.6 Hz), 129.31, 128.59, 127.79, 123.47 (q, J_{CF} = 272.3 Hz), 52.09, 39.03, 21.76;

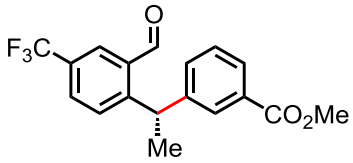
^{19}F NMR ($CDCl_3$, 376 MHz): δ −63.15;

HPLC Chiralpak® AS-H column (10% isopropanol in hexanes, 0.5 mL/min) t_r= 15.22 min (major), 19.73 min (minor): 98:2 er.

IR (neat): 1713.1, 1609.8, 1436.2, 1331.3, 1279.5, 1166.3, 1126.9, 1018.9, 850.5, 730.9 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{18}H_{16}F_3O_3^+$ $[M+H]^+$ 337.1046, found 337.1042.

The absolute stereochemistry was assigned by analogy to compound **6c**.



methyl (*S*)-3-(1-(2-formyl-4-(trifluoromethyl)phenyl)ethyl)benzoate (6e)

The compound **6e** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 88% yield (59 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.32 (s, 1H), 8.09 (d, *J* = 2.1 Hz, 1H), 7.91-7.89 (m, 2H), 7.77 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.38-7.37 (m, 2H), 5.36 (q, *J* = 7.1 Hz, 1H), 3.90 (s, 2H), 1.72 (d, *J* = 7.1 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 190.85, 166.89, 151.59, 144.83, 133.44, 132.49, 130.59, 130.24 (q, J_{CF} = 3.5 Hz), 129.49 (q, J_{CF} = 33.1 Hz), 129.32, 129.22 (q, J_{CF} = 3.4 Hz), 128.76, 128.64, 127.93, 123.49 (q, J_{CF} = 272.1 Hz), 52.17, 38.81, 21.93;

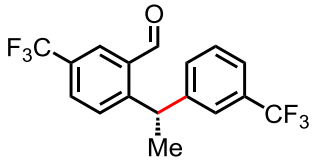
^{19}F NMR ($CDCl_3$, 376 MHz): δ –63.14;

HPLC Chiralpak® AS-H column (5% isopropanol in hexanes, 0.5 mL/min) t_r= 13.96 min (minor), 16.10 min (major): 98:2 er.

IR (neat): 1715, 1618, 1435, 1329, 1283, 1164, 1122, 1084, 970, 902, 845, 749, 731, 695 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{18}H_{16}F_3O_3^+$ $[M+H]^+$ 337.1046, found 337.1053.

The absolute stereochemistry was assigned by analogy to compound **6c**.



(*S*)-5-(trifluoromethyl)-2-(1-(3-(trifluoromethyl)phenyl)ethyl)benzaldehyde (6f)

The compound **6f** was prepared according to the general procedure at 110 ℃ and was purified by preparative TLC to give a colorless oil in 77% yield (53 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.28 (s, 1H), 8.09 (d, *J* = 2.0 Hz, 1H), 7.79 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.50-7.45 (m, 3H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 5.40 (q, *J* = 7.2 Hz, 1H), 1.71 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 190.98, 151.18, 145.38, 133.46, 131.34, 131.02 (q, J_{CF} = 32.1 Hz), 130.31 (q, J_{CF} = 3.4 Hz), 129.85 (q, J_{CF} = 3.4 Hz), 129.68 (q, J_{CF} = 33.6 Hz), 129.29, 129.12, 124.02 (q, J_{CF} = 272.6 Hz), 124.31 (q, J_{CF} = 3.4 Hz), 123.59 (q, J_{CF} = 3.6 Hz), 123.45 (q, J_{CF} = 272.5 Hz), 38.73, 21.87;

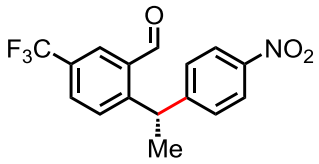
^{19}F NMR ($CDCl_3$, 376 MHz): δ –62.85, –63.17;

HPLC Chiralpak® AS-H column (1% isopropanol in hexanes, 0.5 mL/min) t_r= 9.45 min (minor), 10.41 min (major): 98:2 er.

IR (neat): 1704, 1619, 1325, 1161, 1115, 1074, 900, 846, 804, 771, 702 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{13}F_6O^+$ $[M+H]^+$ 347.0865, found 347.0866.

The absolute stereochemistry was assigned by analogy to compound **6c**.



(*S*)-2-(1-(4-nitrophenyl)ethyl)-5-(trifluoromethyl)benzaldehyde (6g)

The compound **6g** was prepared according to the general procedure at 110 ℃ and was purified by preparative TLC to give a colorless oil in 63% yield (41 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.22 (s, 1H), 8.17-8.14 (m, 2H), 8.09 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.38-7.35 (m, 2H), 5.48 (q, *J* = 7.2 Hz, 1H), 1.72 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 191.14, 152.06, 150.18, 146.61, 133.51, 130.75 (q, J_{CF} = 3.4 Hz), 130.37 (q, J_{CF} = 3.4 Hz), 129.97 (q, J_{CF} = 33.6 Hz), 129.25, 128.66, 123.84, 123.35 (q, J_{CF} = 272.3 Hz), 38.93, 21.68;

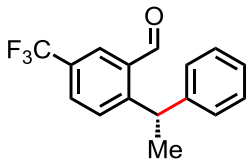
^{19}F NMR ($CDCl_3$, 376 MHz): δ −63.19;

HPLC Chiralpak® AS-H column (20% isopropanol in hexanes, 0.5 mL/min) t_r= 17.96 min (minor), 24.87 min (major): 98:2 er.

IR (neat): 2360, 2341, 1706, 1598, 1519, 1332, 1167, 1128, 1087, 857 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{13}F_3NO_3^+$ $[M+H]^+$ 324.0842, found 324.0850.

The absolute stereochemistry was assigned by analogy to compound **6c**.



(*S*)-2-(1-phenylethyl)-5-(trifluoromethyl)benzaldehyde (6h)

The compound **6h** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 62% yield (35 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.35 (s, 1H), 8.10 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.23-7.18 (m, 3H), 5.25 (q, *J* = 7.1 Hz, 1H), 1.70 (d, *J* = 7.1 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 190.76, 152.26, 144.49, 133.48, 130.13 (q, J_{CF} = 3.7 Hz), 129.27 (q, J_{CF} = 33.3 Hz), 129.25, 128.72, 128.29 (q, J_{CF} = 3.9 Hz), 127.68, 126.66, 123.56 (q, J_{CF} = 272.5 Hz), 39.01, 22.02;

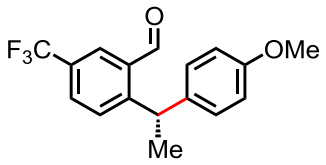
^{19}F NMR ($CDCl_3$, 376 MHz): δ −63.12;

HPLC Chiralcel® AS-H column (1% isopropanol in hexanes, 0.5 mL/min) t_r= 10.68 min (minor), 11.76 min (major): 98:2 er.

IR (neat): 1694, 1618, 1328, 1163, 1119, 1083, 900, 846, 752, 720, 699 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{14}F_3O^+$ $[M+H]^+$ 279.0991, found 279.0997.

The absolute stereochemistry was assigned by analogy to compound **6c**.



(*S*)-2-(1-(4-methoxyphenyl)ethyl)-5-(trifluoromethyl)benzaldehyde (6i)

The compound **6i** was prepared according to the general procedure and was purified by preparative TLC to give a colorless oil in 63% yield (39 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.36 (s, 1H), 8.09 (d, *J* = 1.6 Hz, 1H), 7.75 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.12-7.07 (m, 2H), 6.87-6.82 (m, 2H), 5.18 (q, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 1.67 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 190.76, 158.24, 152.73, 136.63, 133.46, 130.11 (q, J_{CF} = 3.5 Hz), 129.21 (q, J_{CF} = 33.3 Hz), 129.14, 128.67, 128.19 (q, J_{CF} = 3.6 Hz), 123.60 (q, J_{CF} = 272.4 Hz), 114.09, 55.26, 38.26, 22.22;

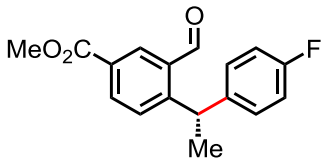
^{19}F NMR ($CDCl_3$, 376 MHz): δ – 63.11;

HPLC Chiralcel® OD-H column (3% isopropanol in hexanes, 0.5 mL/min) t_r= 15.85 min (minor), 16.79 min (major): 95:5 er.

IR (neat): 1702, 1615, 1510, 1246, 1330, 1163, 1121, 1084, 1032, 832 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{16}F_3O_2^+$ $[M+H]^+$ 309.1097, found 309.1098.

The absolute stereochemistry was assigned by analogy to compound **6c**.



methyl (*S*)-3-(1-(4-fluorophenyl)ethyl)-4-formylbenzoate (6j)

The compound **6j** was prepared according to the general procedure with 0.5 mL of solvent and was purified by preparative TLC to give a colorless oil in 71% yield (41 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.27 (s, 1H), 8.47 (d, *J* =1.9 Hz, 1H), 8.17 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.18-7.04 (m, 2H), 7.02-6.91 (m, 2H), 5.32 (q, *J* = 7.1 Hz, 1H), 3.95 (s, 3H), 1.65 (d, *J* = 7.1 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 191.79, 165.86, 161.41 (d, J_{CF} = 245.2 Hz), 153.06, 140.46, 134.38 (d, J_{CF} = 12.1 Hz), 133.27, 129.23 (d, J_{CF} = 7.9 Hz), 128.92, 128.74, 115.36 (d, J_{CF} = 21.1 Hz), 52.40, 38.35, 22.05;

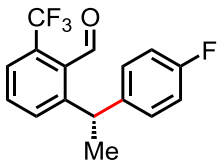
^{19}F NMR ($CDCl_3$, 376 MHz): δ –116.74.

HPLC Chiralpak® AS-H column (5% isopropanol in hexanes, 0.5 mL/min) t_r= 23.81 min (minor), 26.61 min (major): 96:4 er.

IR (neat): 1720, 1695, 1508, 1288, 1221, 1195, 1173, 1160, 835, 746 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{16}FO_3^+$ $[M+H]^+$ 287.1078, found 287.1079.

The absolute stereochemistry was assigned by analogy to compound **6c**.



(*S*)-2-(1-(4-fluorophenyl)ethyl)-6-(trifluoromethyl)benzaldehyde (6k)

The compound **6k** was prepared according to the general procedure with 0.5 mL of solvent at 110 ℃ and was purified by preparative TLC to give a colorless oil in 69% yield (41 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.50 (q, *J* = 2.9 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.17-7.14 (m, 2H), 7.00-6.96 (m, 2H), 4.94 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.92, 161.40 (d, J_{CF} = 245.4 Hz), 148.24, 140.41 (d, J_{CF} = 3.2 Hz), 133.45, 132.43, 131.61, 130.41 (q, J_{CF} = 31.6 Hz), 129.32 (d, J_{CF} = 7.7 Hz), 124.17 (q, J_{CF} = 5.8 Hz), 123.83 (q, J_{CF} = 274.7 Hz), 115.27 (d, J_{CF} = 21.3 Hz), 38.48, 22.14;

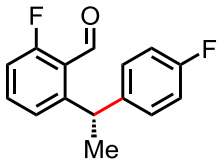
^{19}F NMR ($CDCl_3$, 376 MHz): δ –55.93, – 116.86;

HPLC Chiralpak® AS-H column (1% isopropanol in hexanes, 0.5 mL/min) t_r= 9.42 min (minor), 11.01 min (major): 97:3 er.

IR (neat): 1707, 1602, 1509, 1308, 1225, 1162, 1121, 838, 809 cm^{-1};

HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{13}F_4O^+$ $[M+H]^+$ 297.0897, found 297.0893.

The absolute stereochemistry was assigned by analogy to compound **6c**.



(*S*)-2-fluoro-6-(1-(4-fluorophenyl)ethyl)benzaldehyde (6l)

The compound **6l** was prepared according to the general procedure with 5 mol% $Pd(OAc)_2$, 10 mol% L-*tert*-leucine and 1 mL of solvent. The crude residue was purified by preparative TLC to give a colorless oil in 64% yield (32 mg).

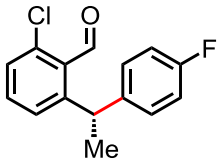
^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.52 (s, 1H), 7.47 (td, *J* = 8.1, 5.8 Hz, 1H), 7.18-7.15 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 1H), 7.04-7.00 (m, 1H), 6.97-6.94 (m, 2H), 5.34 (q, *J* = 7.2 Hz, 1H), 1.58 (d, J = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ 189.30 (d, J_{CF} = 12.0 Hz), 166.26 (d, J_{CF} = 257.9 Hz), 161.29 (d, J_{CF} = 244.4 Hz), 150.39, 140.84 (d, J_{CF} = 3.3 Hz), 135.22 (d, J_{CF} = 10.5 Hz), 129.31 (d, J_{CF} = 7.9 Hz), 124.22 (d, J_{CF} = 3.3 Hz), 121.76 (d, J_{CF} = 5.0 Hz), 115.05 (d, J_{CF} = 21.2 Hz), 114.05 (d, J_{CF} = 21.8 Hz), 38.05 (d, J_{CF} = 2.0 Hz), 22.05;

^{19}F NMR ($CDCl_3$, 376 MHz): δ –117.25, –120.78;

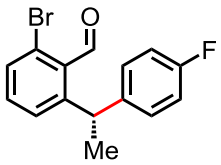
HPLC Chiralpak® AS-H column (3% isopropanol in hexanes, 0.5 mL/min) t_r= 9.55 min (minor), 10.29 min (major): 96:4 er.

IR (neat): 1694, 1609, 1570, 1507, 1496, 1417, 1284, 1221, 1158, 825, 797, 735 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{13}F_2O^+$ $[M+H]^+$ 247.0929, found 247.0930.
The absolute stereochemistry was assigned by analogy to compound **6c**.



(*S*)-2-chloro-6-(1-(4-fluorophenyl)ethyl)benzaldehyde (6m)

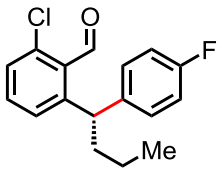
The compound **6m** was prepared according to the general procedure with 5 mol% $Pd(OAc)_2$, 10 mol% L-*tert*-leucine and 1 mL of solvent. The crude residue was purified by preparative TLC to give a colorless oil in 67% yield (35 mg).
^1H NMR ($CDCl_3$, 600 MHz): δ 10.59 (s, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.31 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.17-7.14 (m, 2H), 6.98-6.94 (m, 2H), 5.19 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.88, 161.29 (d, J_{CF} = 244.4 Hz), 150.04, 140.85 (d, J_{CF} = 3.4 Hz), 138.36, 133.53, 130.78, 129.33 (d, J_{CF} = 7.8 Hz), 128.47, 127.40, 115.08 (d, J_{CF} = 21.1 Hz), 37.96, 22.13;
^{19}F NMR ($CDCl_3$, 376 MHz): δ −117.20;
HPLC Chiralpak® AS-H column (3% isopropanol in hexanes, 0.5 mL/min) t_r= 9.23 min (minor), 9.95 min (major): 97:3 er.
IR (neat): 1694, 1587, 1559, 1506, 1450, 1405, 1221, 1178, 1159, 1138, 835, 791, 746, 548 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{13}ClFO^+$ $[M+H]^+$ 263.0633, found 263.0627.
The absolute stereochemistry was assigned by analogy to compound **6c**.



(*S*)-2-bromo-6-(1-(4-fluorophenyl)ethyl)benzaldehyde (6n)

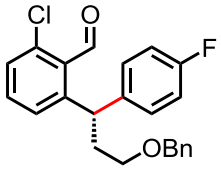
The compound **6n** was prepared according to the general procedure with 5 mol% $Pd(OAc)_2$, 10 mol% L-*tert*-leucine and 1 mL of solvent. The crude residue was purified by preparative TLC to give a colorless oil in 60% yield (37 mg).
^1H NMR ($CDCl_3$, 500 MHz): δ 10.45 (s, 1H), 7.51 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.16-7.14 (m, 2H), 6.97-6.94 (m, 2H), 5.15 (q, *J* = 7.2 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 194.75, 161.30 (d, J_{CF} = 244.9 Hz), 150.07, 140.82 (d, J_{CF} = 3.1 Hz), 133.58, 131.99, 131.75, 129.33 (d, J_{CF} = 7.8 Hz), 128.07, 127.22, 115.10 (d, J_{CF} = 21.0 Hz), 37.97, 22.15;
^{19}F NMR ($CDCl_3$, 376 MHz): δ −117.17;
HPLC Chiralpak® AS-H column (3% isopropanol in hexanes, 0.5 mL/min) t_r= 9.77 min (minor), 10.61

min (major): 97:3 er.
IR (neat): 1693.4, 1554.4, 1505.8, 1446.0, 1220.4, 1181.2, 1158.7, 834.5, 781.5, 746.2, 723.7, 545.7 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{13}BrFO^+$ $[M+H]^+$ 307.0128, found 307.0129.
The absolute stereochemistry was assigned by analogy to compound **6c**.



(*S*)-2-chloro-6-(1-(4-fluorophenyl)butyl)benzaldehyde (6o)

The compound **6o** was prepared according to the general procedure with 0.5 mL of solvent and was purified by preparative TLC to give a colorless oil in 68% yield (40 mg).
^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.59 (s, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.32-7.29 (m, 2H), 7.22-7.20 (m, 2H), 6.97-6.93 (m, 2H), 5.06 (t, *J* = 7.7 Hz, 1H), 1.98-1.87 (m, 2H), 1.30-1.23 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 1H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 193.07, 161.30 (d, J_{CF} = 244.7 Hz), 148.81, 139.59 (d, J_{CF} = 3.3 Hz), 138.32, 133.44, 131.24, 129.74 (d, J_{CF} = 7.8 Hz), 128.34, 127.16, 115.09 (d, J_{CF} = 21.1 Hz), 43.01, 38.46, 20.91, 14.01;
^{19}F NMR ($CDCl_3$, 376 MHz): δ −117.13;
HPLC Chiralcel® OD-H column (1% isopropanol in hexanes, 0.5 mL/min) t_r= 9.34 min (minor), 10.70 min (major): 97:3 er.
IR (neat): 2957, 2930, 2871, 2361, 2340, 1695, 1587, 1559, 1506, 1452, 1405, 1221, 1178, 1158, 836, 794, 743 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{17}ClFO^+$ $[M+H]^+$ 291.0946, found 291.0948.
The absolute stereochemistry was assigned by analogy to compound **6c**.

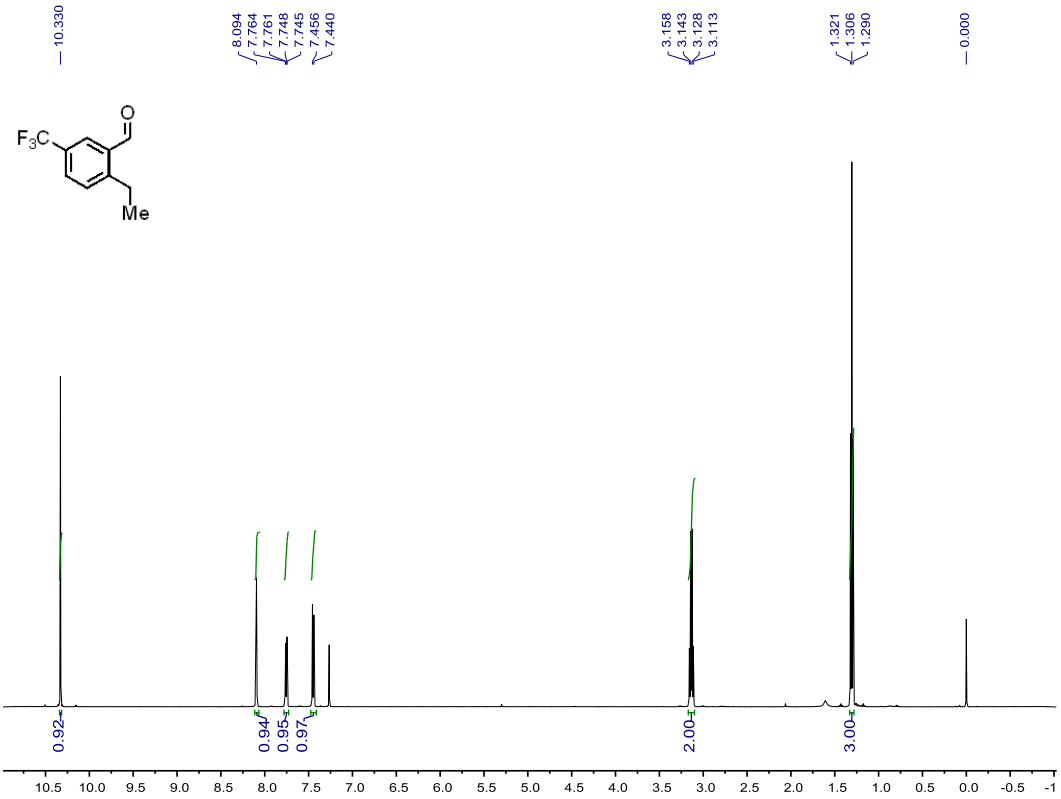


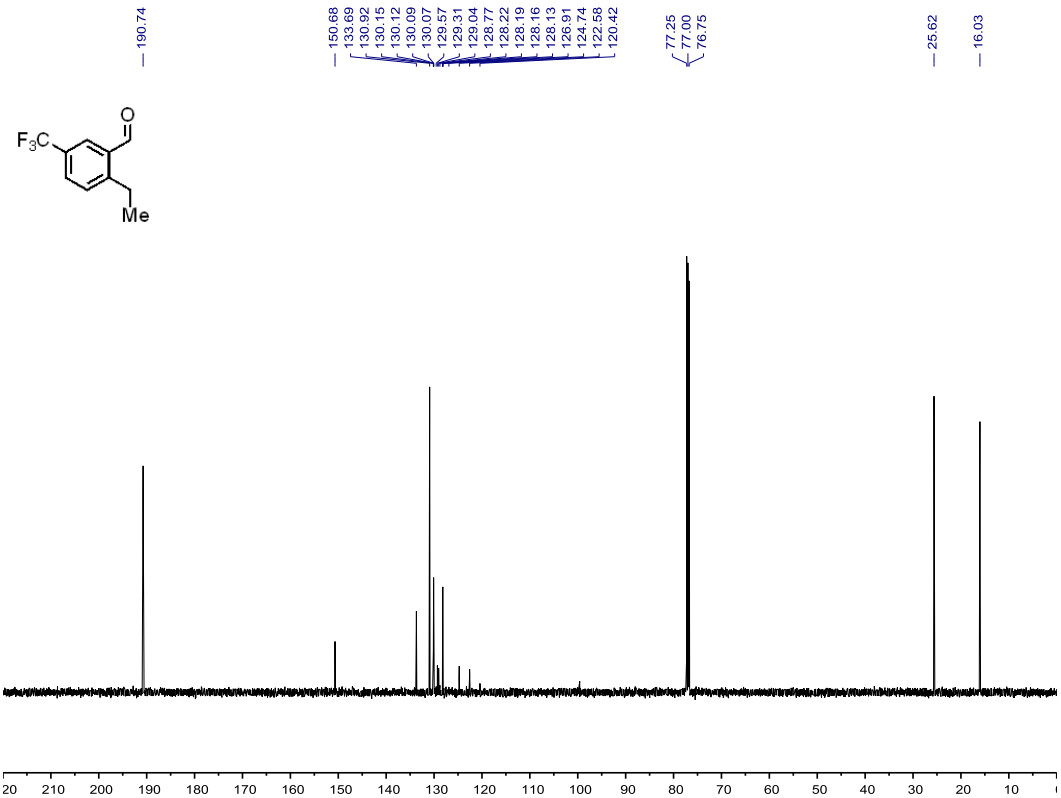
(*S*)-2-(3-(benzyloxy)-1-(4-fluorophenyl)propyl)-6-chlorobenzaldehyde (6p)

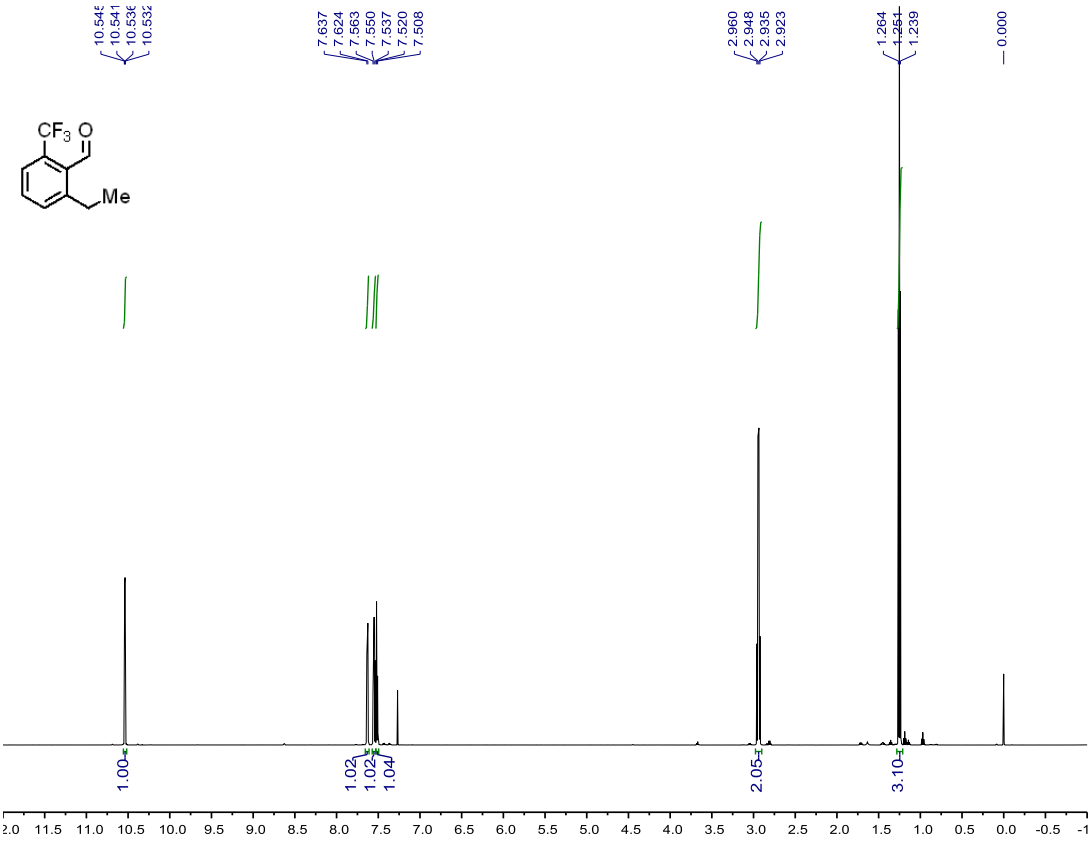
The compound **6p** was prepared according to the general procedure with 0.5 mL of solvent at 110 ℃ and was purified by preparative TLC to give a colorless oil in 54% yield (41 mg).
^{1}H NMR ($CDCl_3$, 600 MHz): δ 10.52 (s, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.34-7.27 (m, 7H), 7.22-7.20 (m, 2H), 6.95-6.92 (m, 2Hz), 5.19 (t, *J* = 7.7 Hz, 1H), 4.42 (s, 2H), 3.43-3.36 (m, 2H), 2.34-2.24 (m, 2H);
^{13}C NMR ($CDCl_3$, 150 MHz): δ 192.83, 161.35 (d, J_{CF} = 244.3 Hz), 147.86, 139.06 (d, J_{CF} = 3.3 Hz), 138.19, 138.10, 133.36, 131.47, 129.71 (d, J_{CF} = 8.0 Hz), 128.53, 128.32, 127.62, 127.55, 127.07, 115.16

(d, J_{CF} = 21.0 Hz), 72.92, 67.91, 39.85, 35.93;
^{19}F NMR ($CDCl_3$, 376 MHz): δ −116.87.
HPLC Chiralcel® OD-H column (1% isopropanol in hexanes, 0.5 mL/min) t_r= 26.57 min (minor), 28.09 min (major): 98:2 er.
IR (neat): 1697, 1587, 1507, 1453, 1221, 1159, 1099, 835, 804, 733, 696 cm^{-1};
HRMS (ESI-TOF): *m/z* calculated for $C_{23}H_{21}ClFO_2^+$ $[M+H]^+$ 383.1209, found 383.1211.
The absolute stereochemistry was assigned by analogy to compound **6c**.

^{1}H and ^{13}C NMR Spectra



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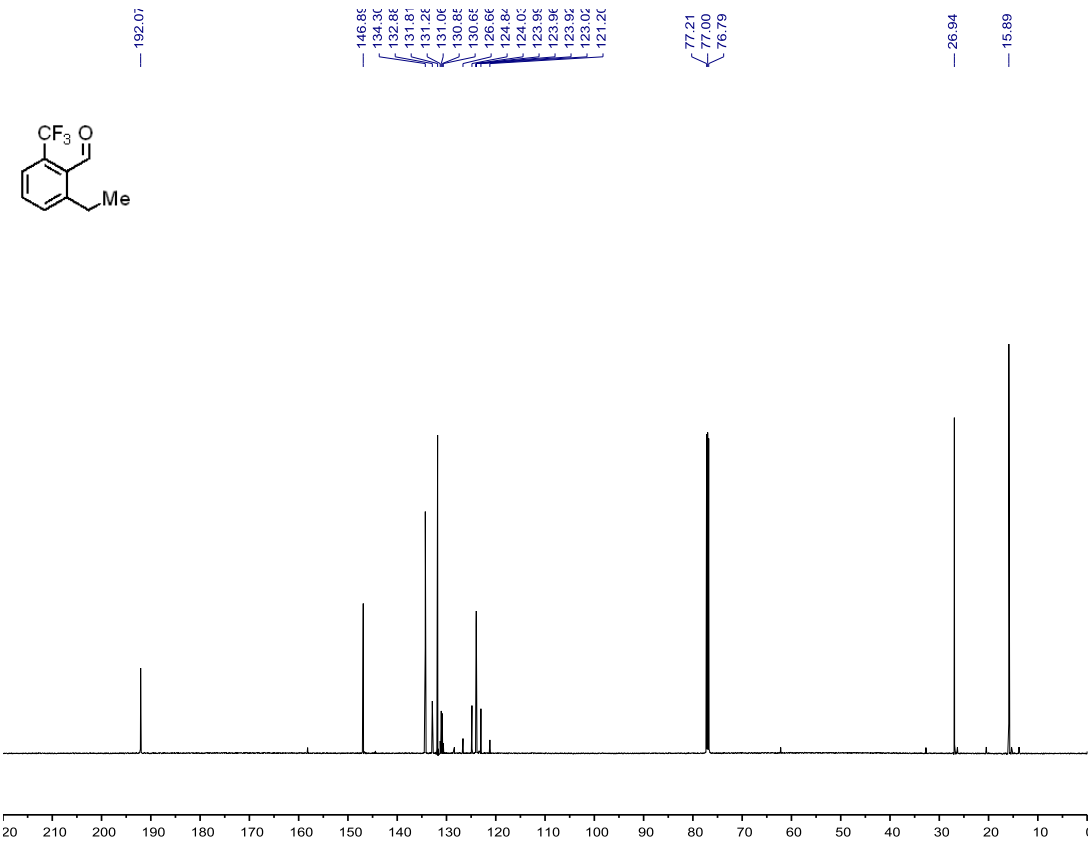
3.10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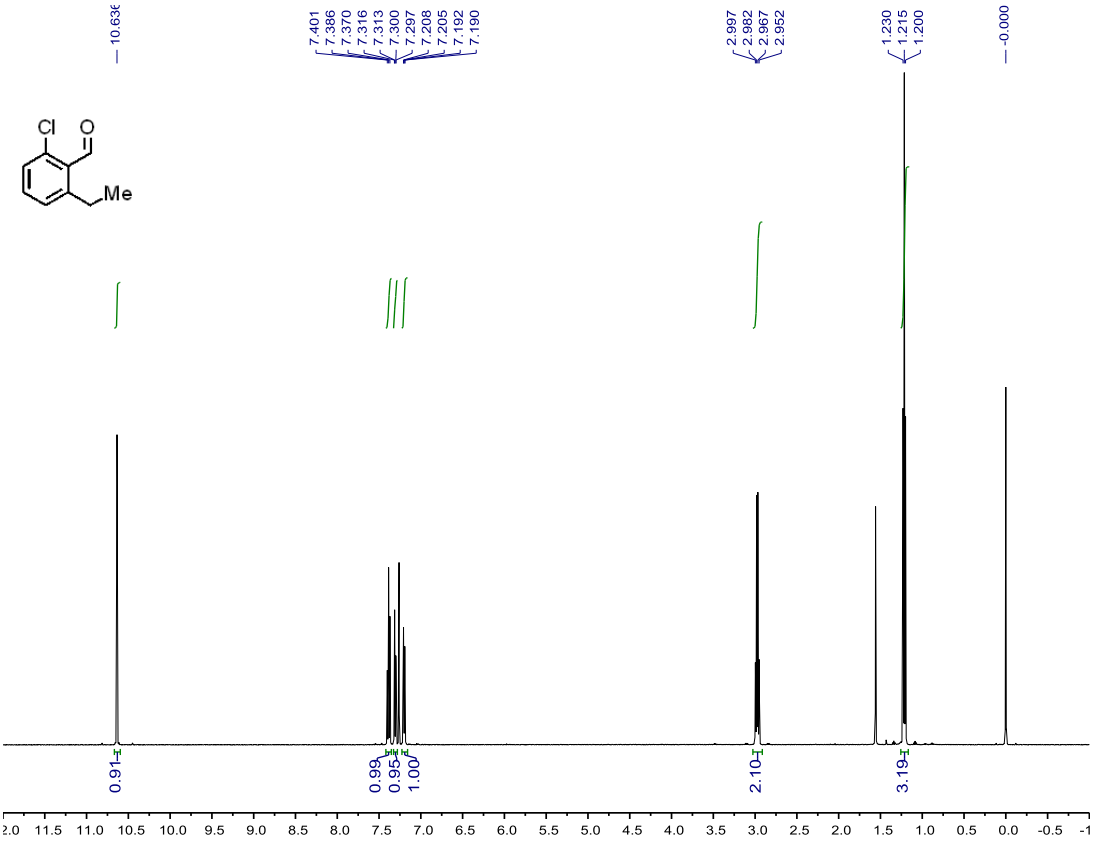
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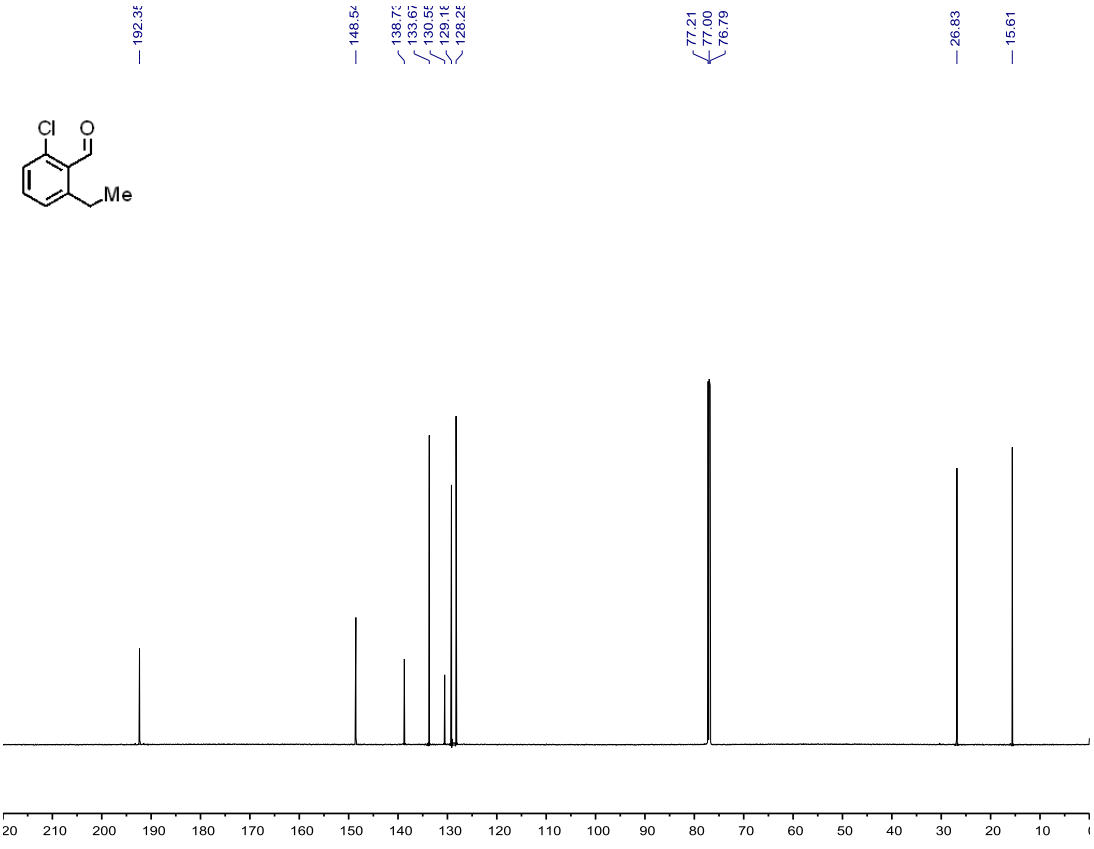
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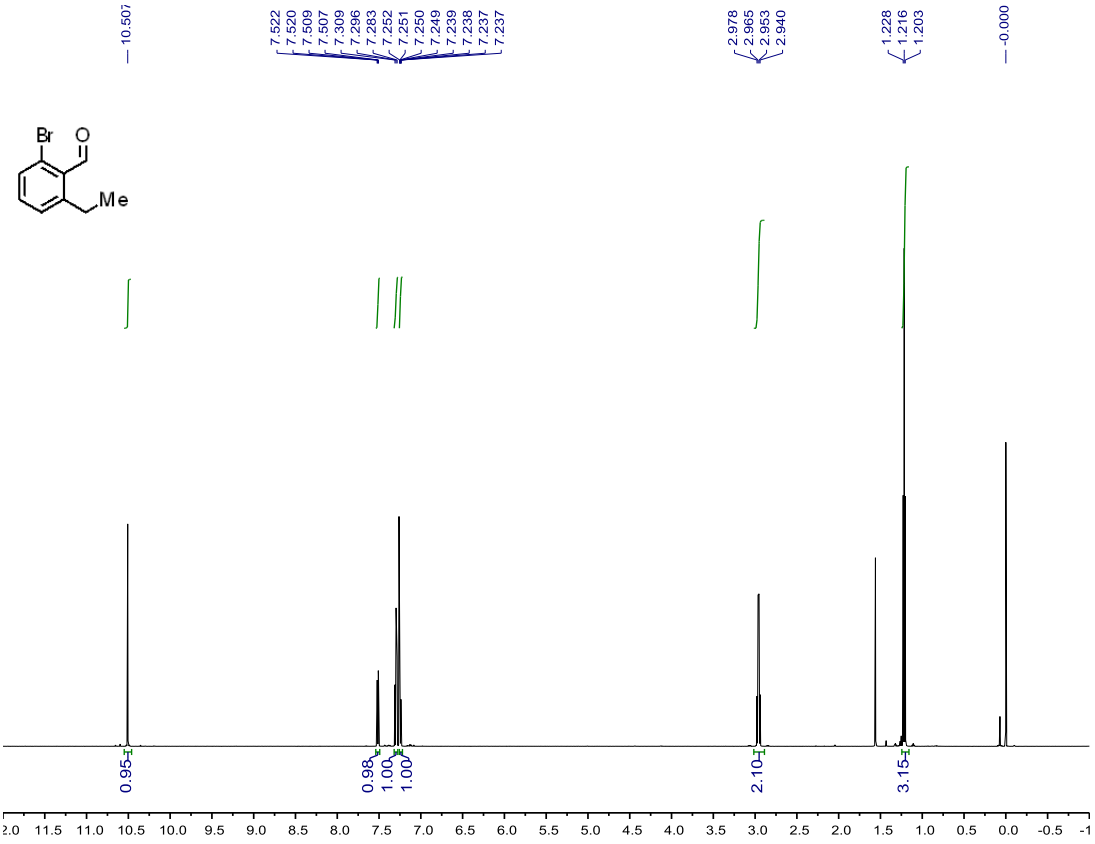
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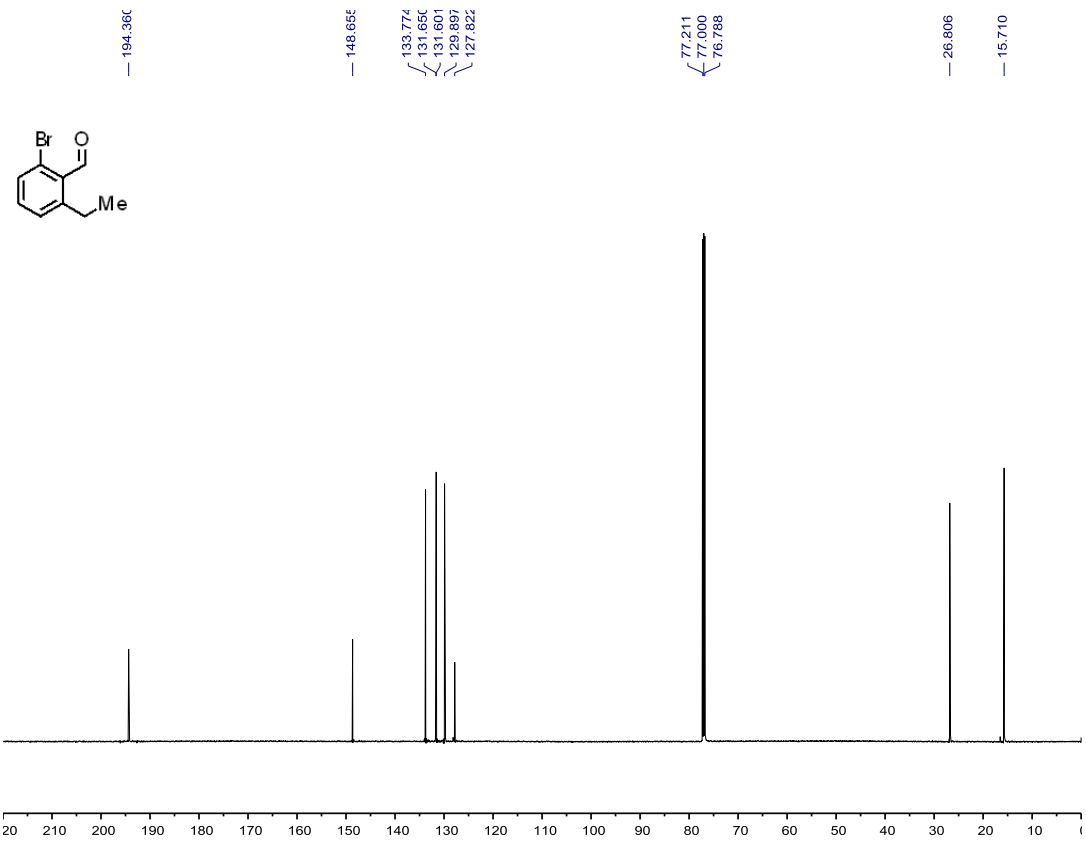
2.10
3.15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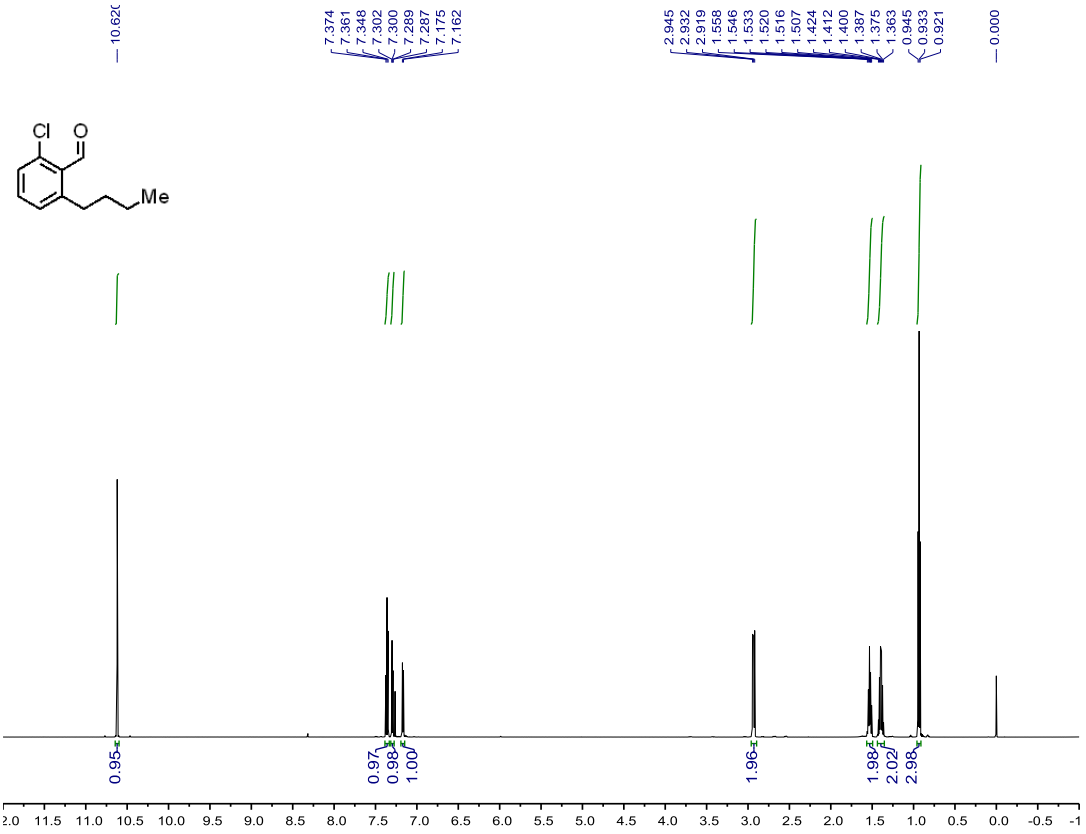
Br
O
Me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7.287
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7.162
2.945
2.932
2.919
1.558
1.546
1.533
1.520
1.516
1.507
1.424
1.412
1.400
1.387
1.375
1.363
0.945
0.933
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Cl
O
Me
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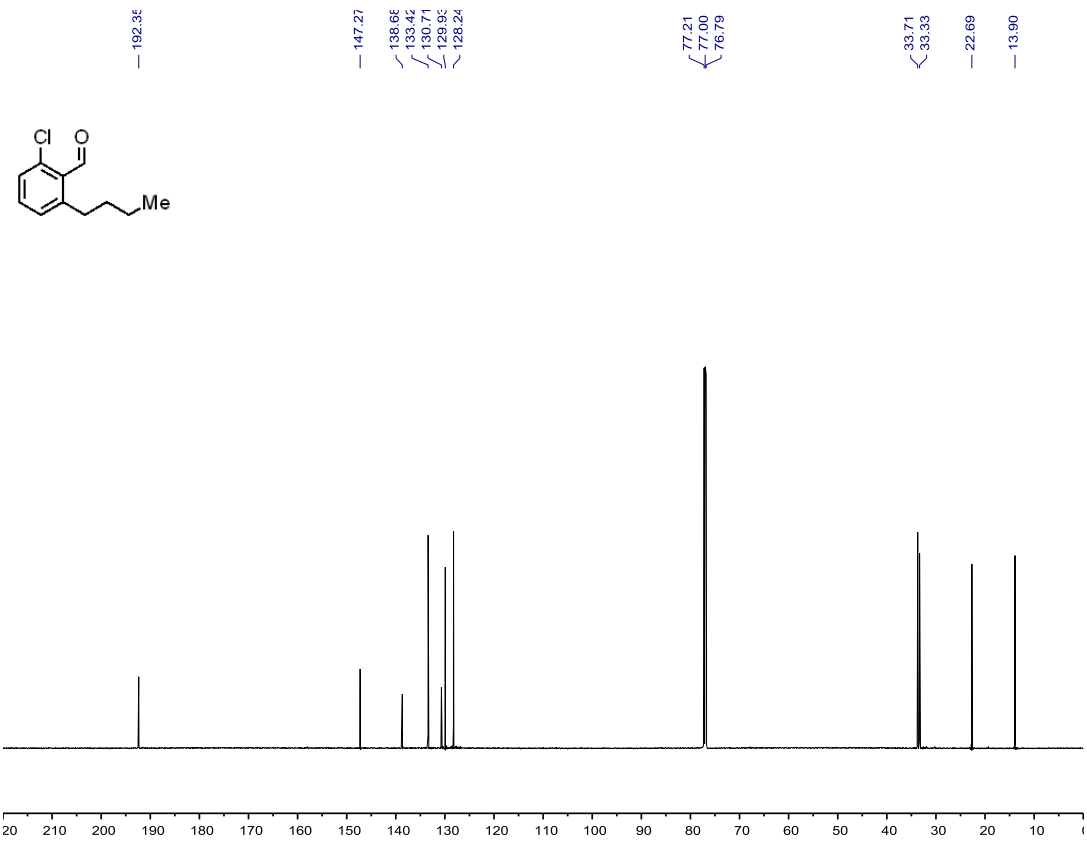
1.98
2.02
2.98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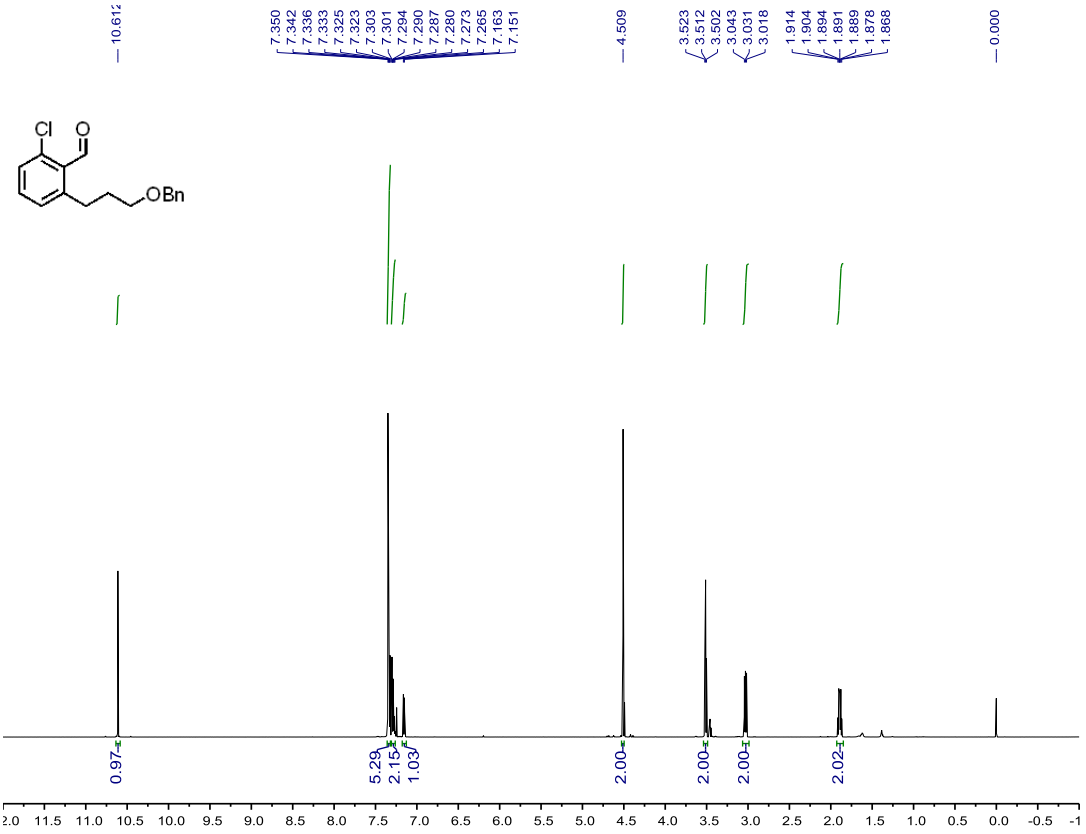
13.90
Cl
O
Me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7.303
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7.287
7.280
7.273
7.265
7.163
7.151
4.509
3.523
3.512
3.502
3.043
3.031
3.018
1.914
1.904
1.894
1.891
1.889
1.878
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O
OBn
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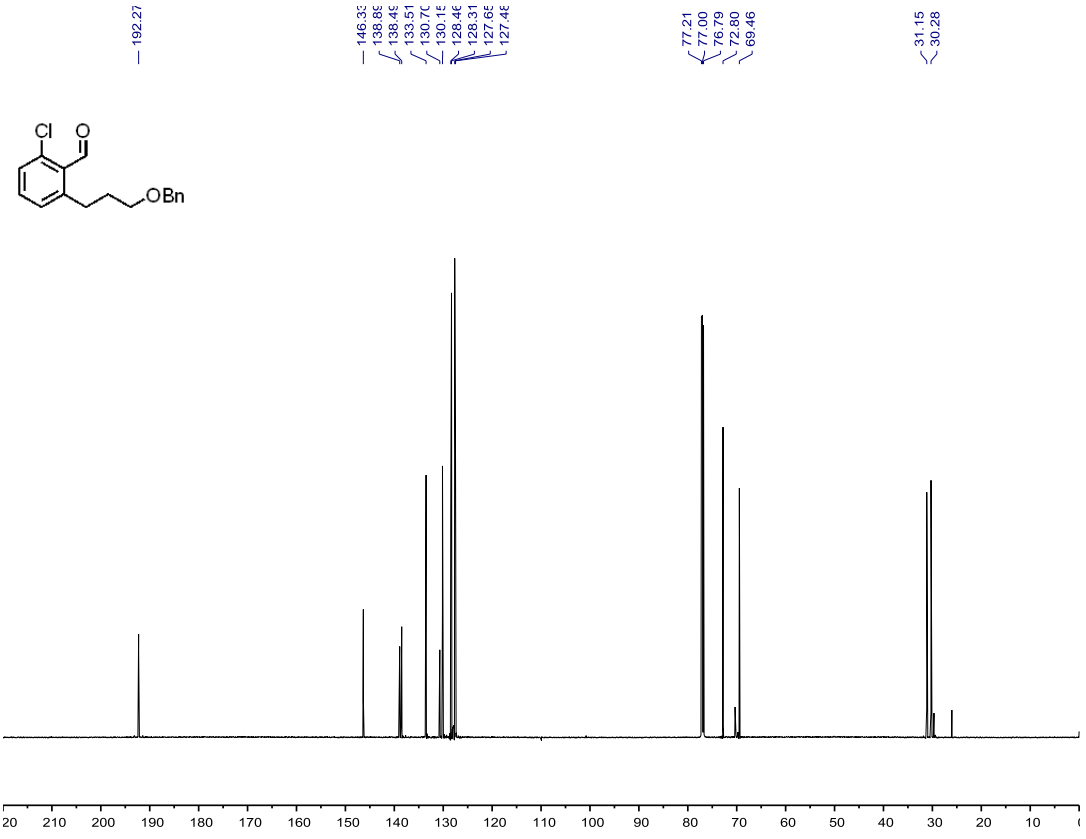
1.03
2.00
2.00
2.00
2.02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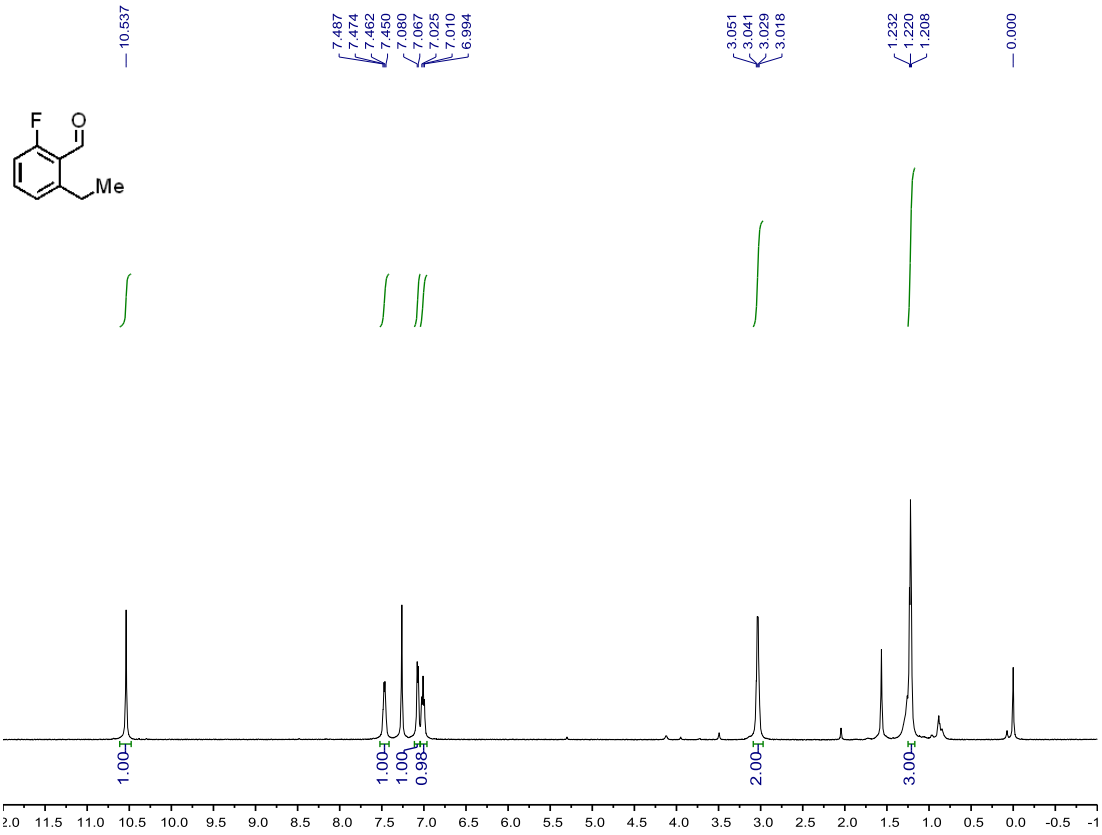
69.46
31.15
30.28
Cl
O
OBn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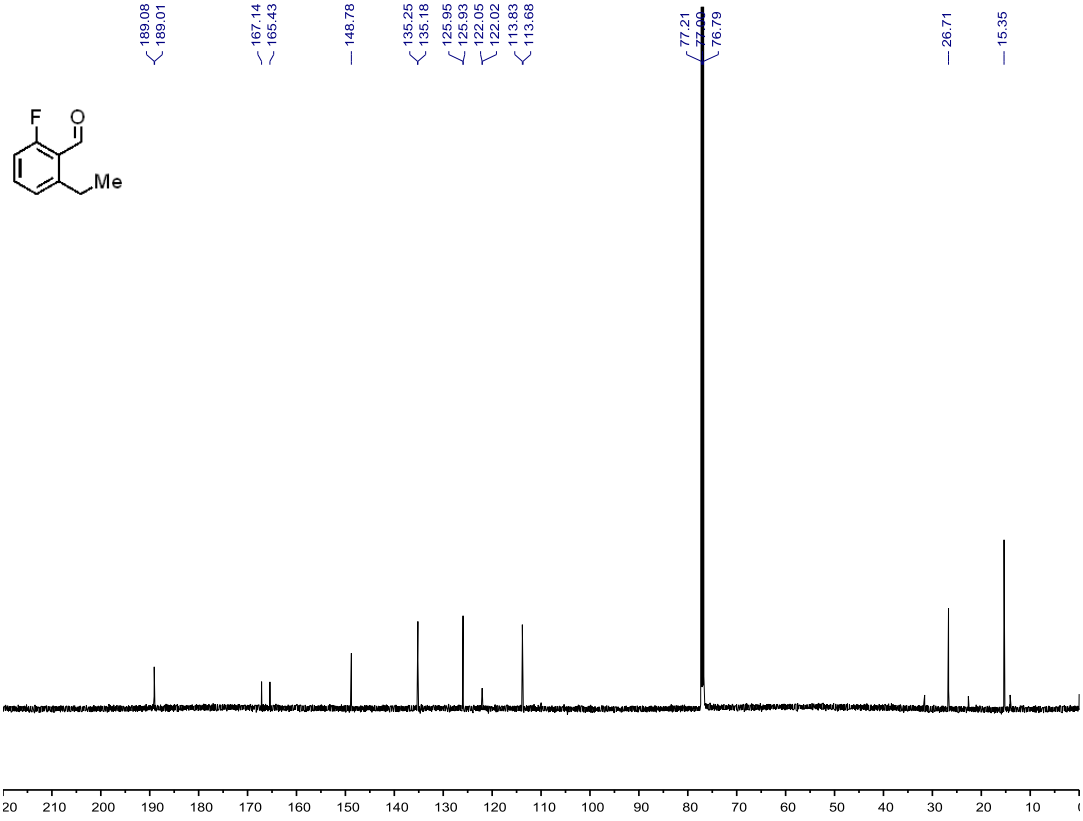
7.450
7.080
7.067
7.025
7.010
6.994
3.051
3.041
3.029
3.018
1.232
1.220
1.208
0.000
F
O
Me
1.00
1.00
0.98
2.00
3.00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189.01
167.14
165.43
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135.25
135.18
125.95
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122.02
113.83
113.68
77.21
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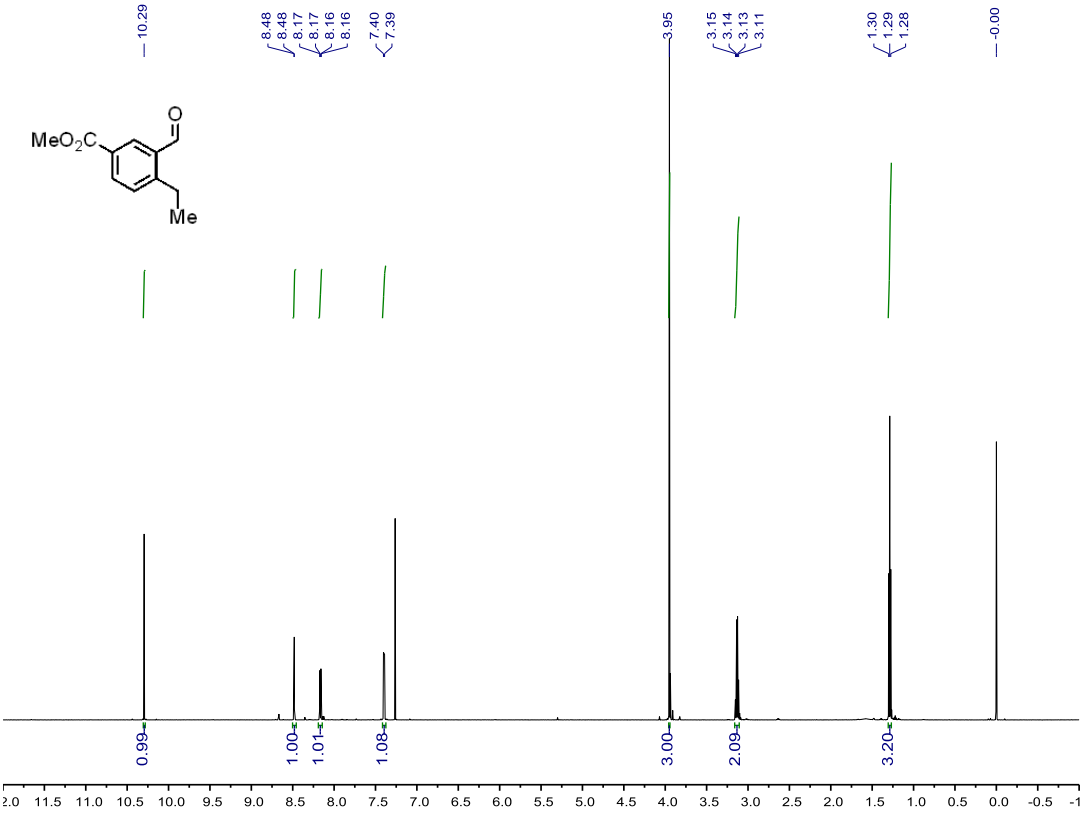
76.79
26.71
15.35
F
O
Me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8.48
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8.16
8.16
7.40
7.39
3.95
3.15
3.14
3.13
3.11
1.30
1.29
1.28
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MeO2C
O
Me
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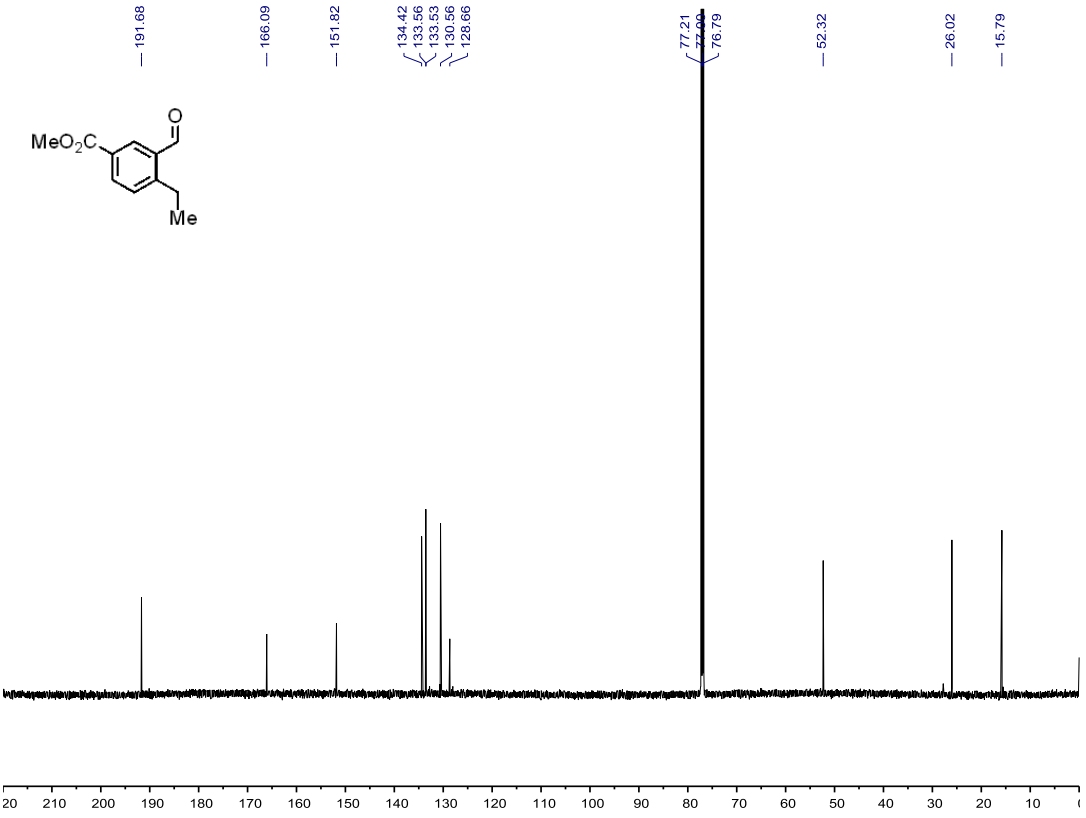
1.00
1.01
1.08
3.00
2.09
3.20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134.42
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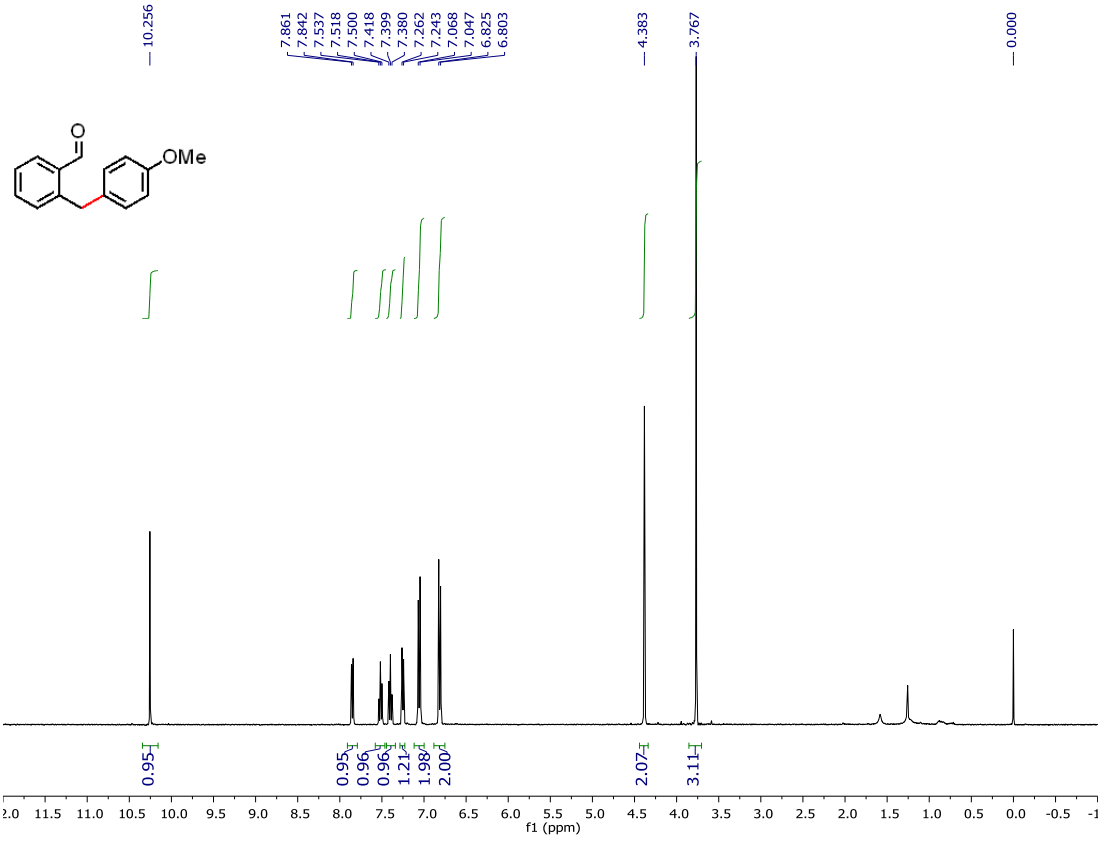
76.79
52.32
26.02
15.79
MeO2C
O
Me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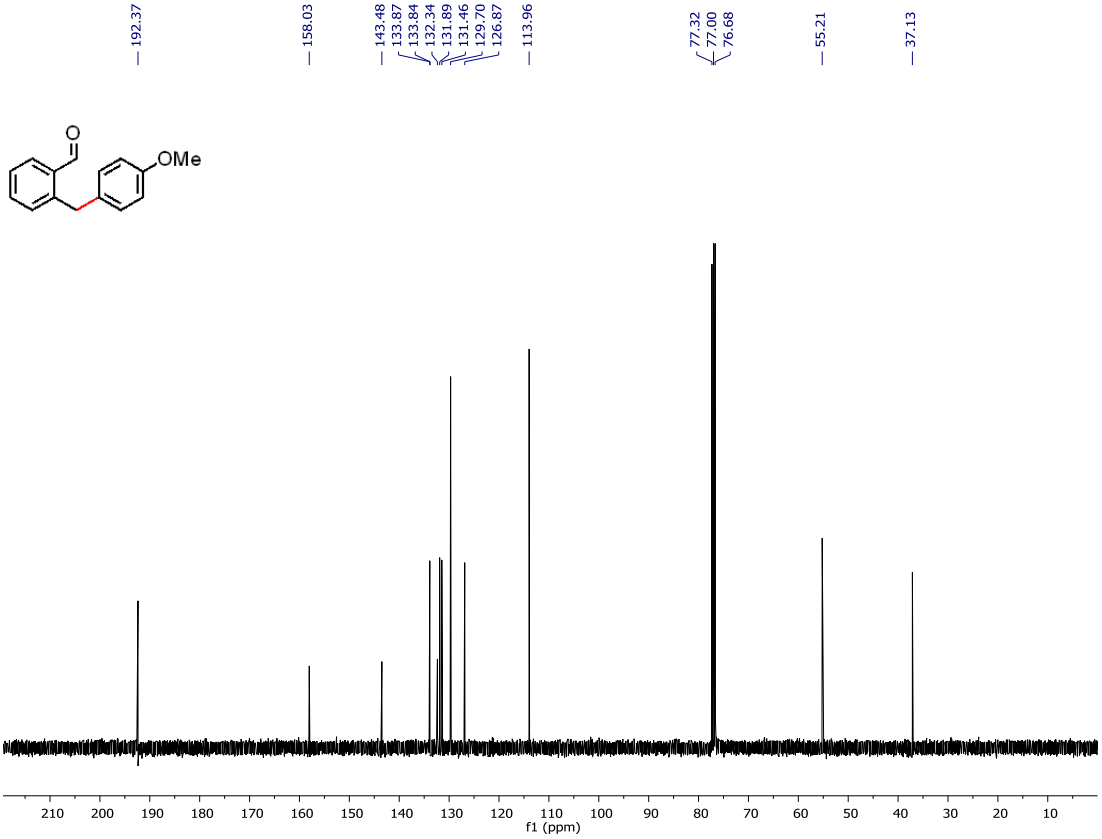
7.842
7.537
7.518
7.500
7.418
7.399
7.380
7.262
7.243
7.068
7.047
6.825
6.803
4.383
3.767
0.000
O
OMe
0.95
0.95
0.96
0.96
1.21
1.98
2.00
2.07
3.11
f1 (ppm)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143.48
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133.84
132.34
131.89
131.46
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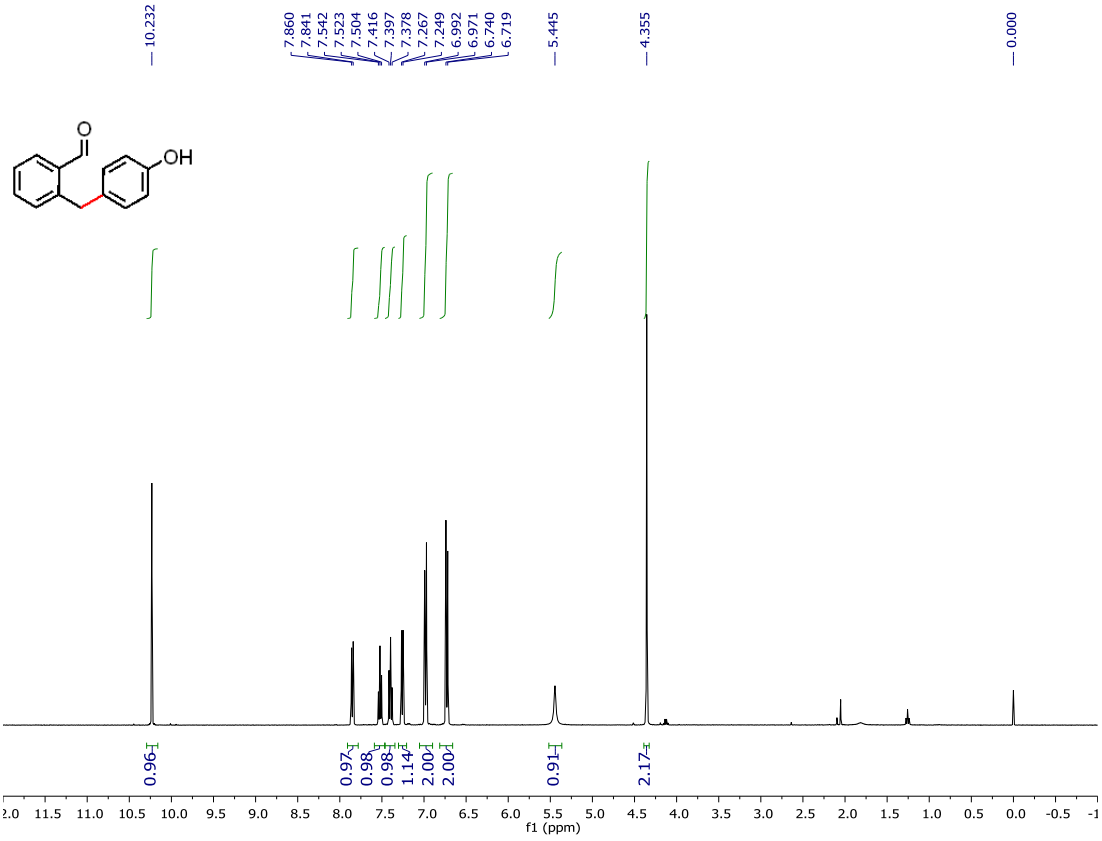
126.87
113.96
77.32
77.00
76.68
55.21
37.13
O
OMe
f1 (ppm)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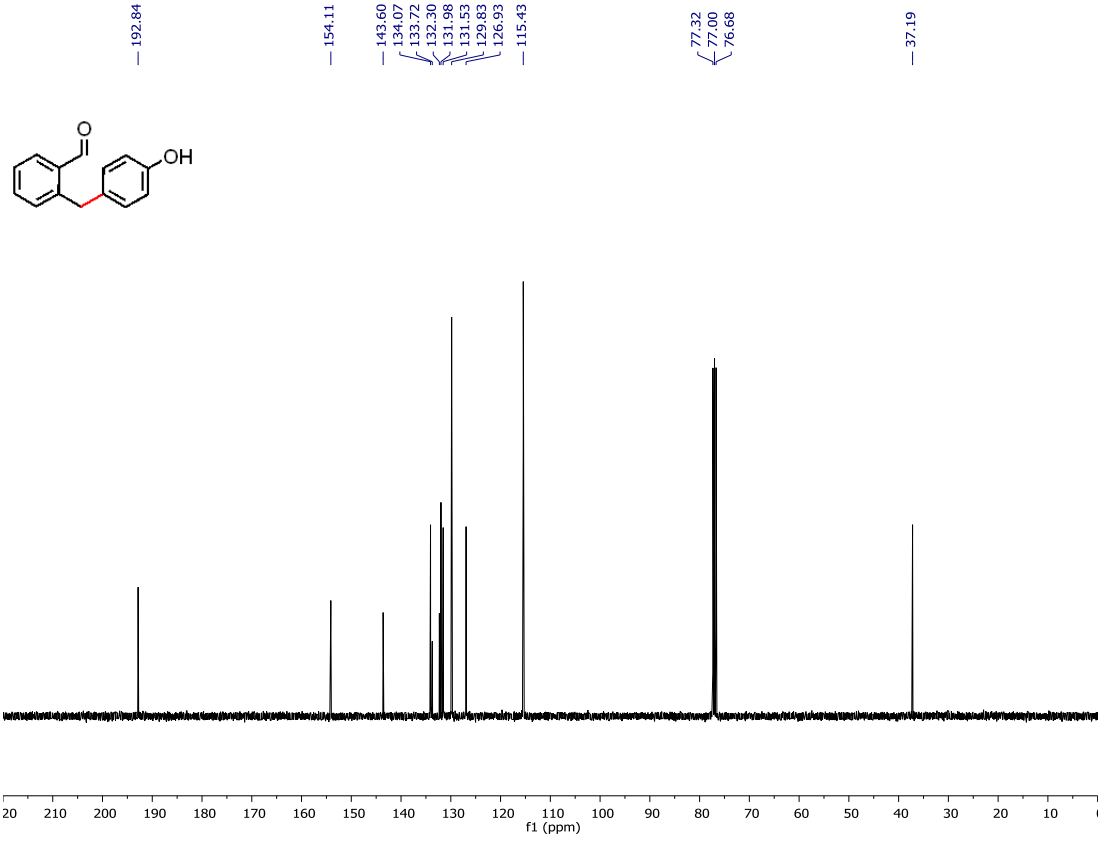
7.841
7.542
7.523
7.504
7.416
7.397
7.378
7.267
7.249
6.992
6.971
6.740
6.719
5.445
4.355
0.000
O
OH
0.96
0.97
0.98
0.98
1.14
2.00
2.00
0.91
2.17
f1 (ppm)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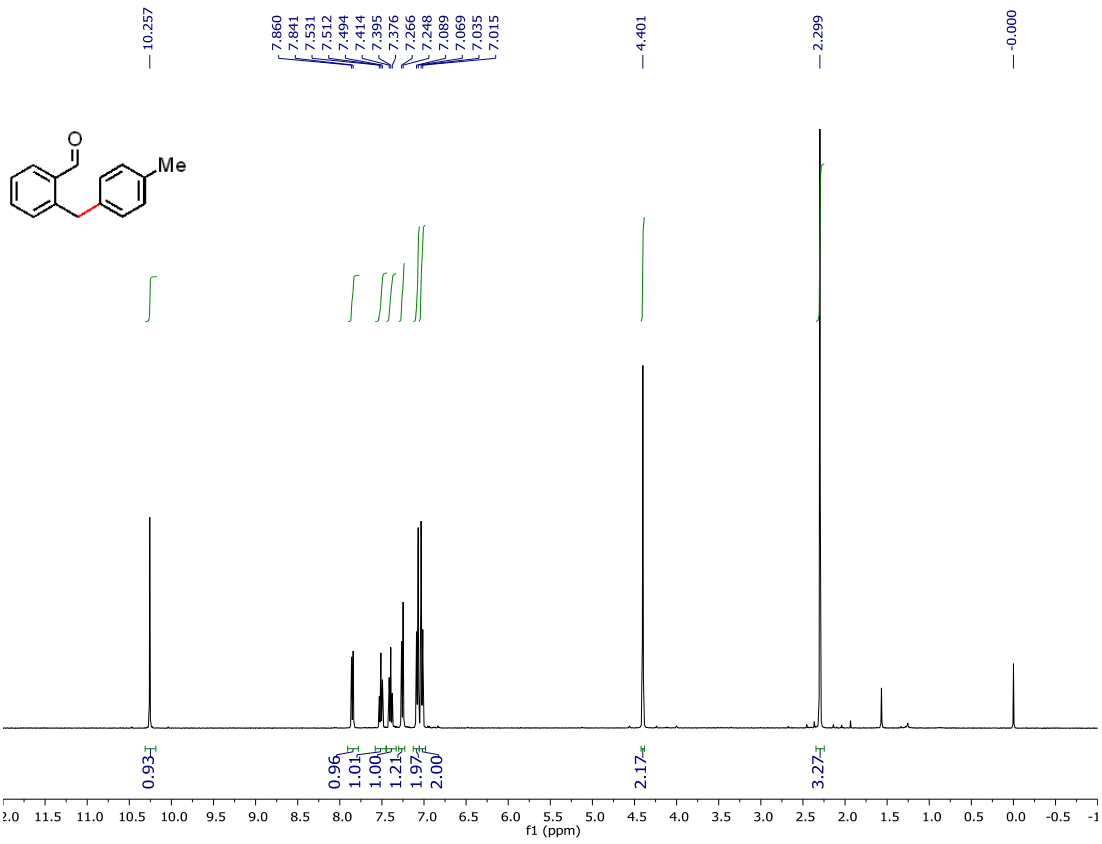
143.60
134.07
133.72
132.30
131.98
131.53
129.83
126.93
115.43
77.32
77.00
76.68
37.19
O
OH
f1 (ppm)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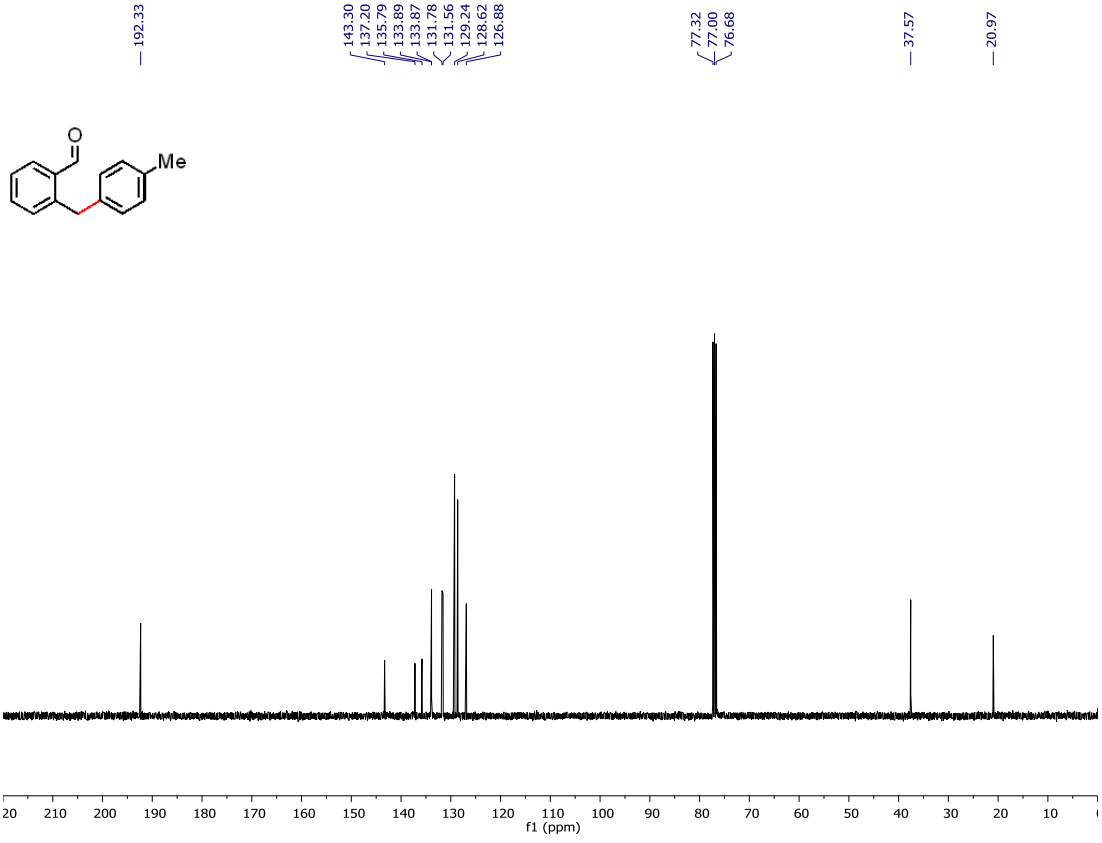
7.841
7.531
7.512
7.494
7.414
7.395
7.376
7.266
7.248
7.089
7.069
7.035
7.015
4.401
2.299
-0.000
O
Me
0.93
0.96
1.01
1.00
1.21
1.97
2.00
2.17
3.27
f1 (ppm)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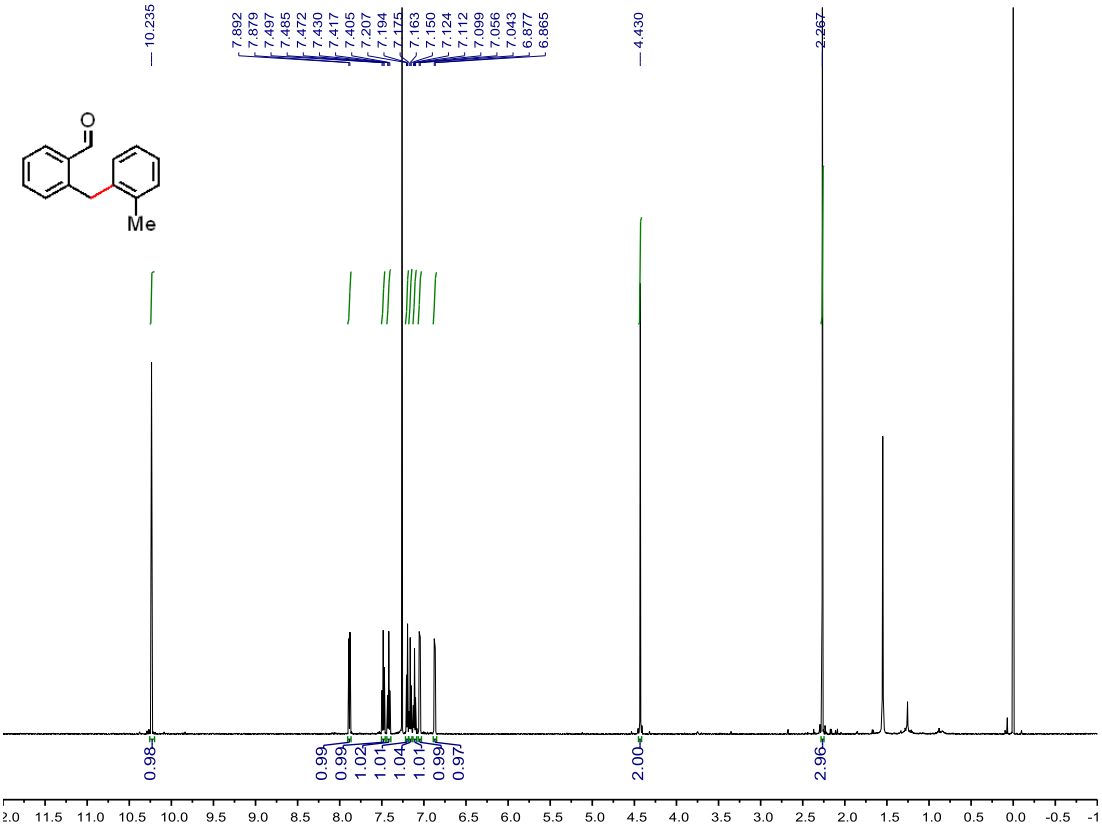
135.79
133.89
133.87
131.78
131.56
129.24
128.62
126.88
77.32
77.00
76.68
37.57
20.97
O
Me
f1 (ppm)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7.472
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7.417
7.405
7.207
7.194
7.175
7.163
7.150
7.124
7.112
7.099
7.056
7.043
6.877
6.865
4.430
2.267
O
Me
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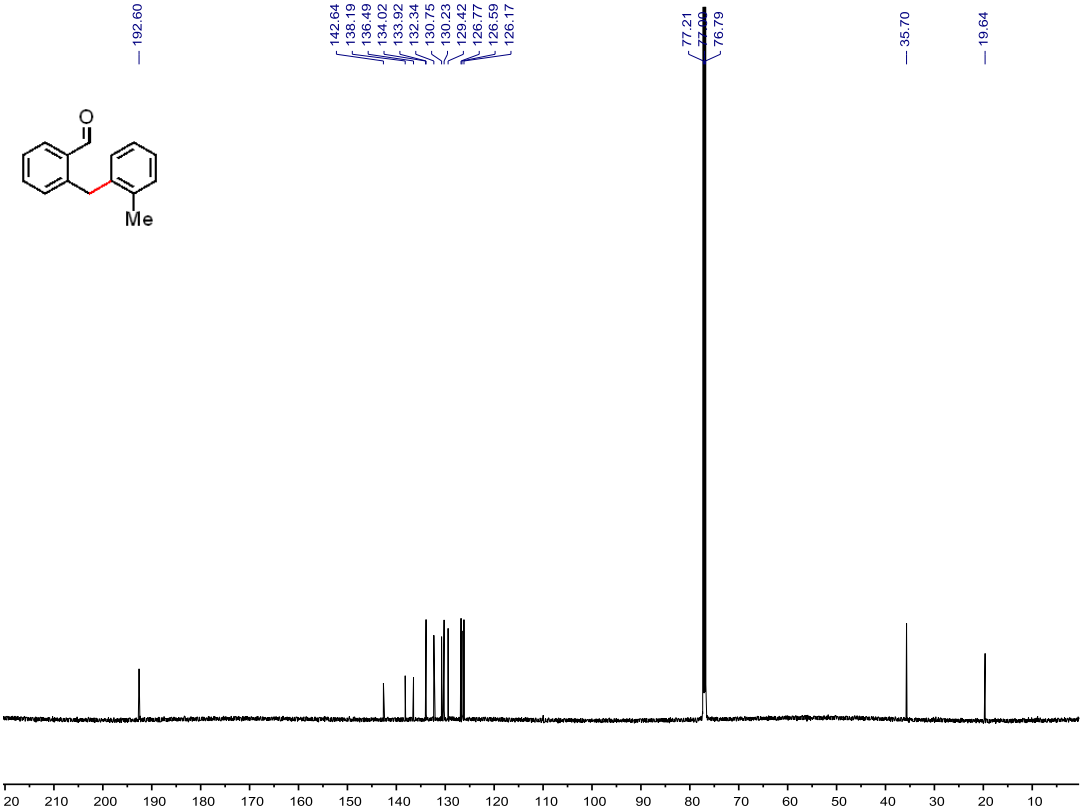
0.99
0.99
1.02
1.01
1.04
1.01
0.99
0.97
2.00
2.96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136.49
134.02
133.92
132.34
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126.59
126.17
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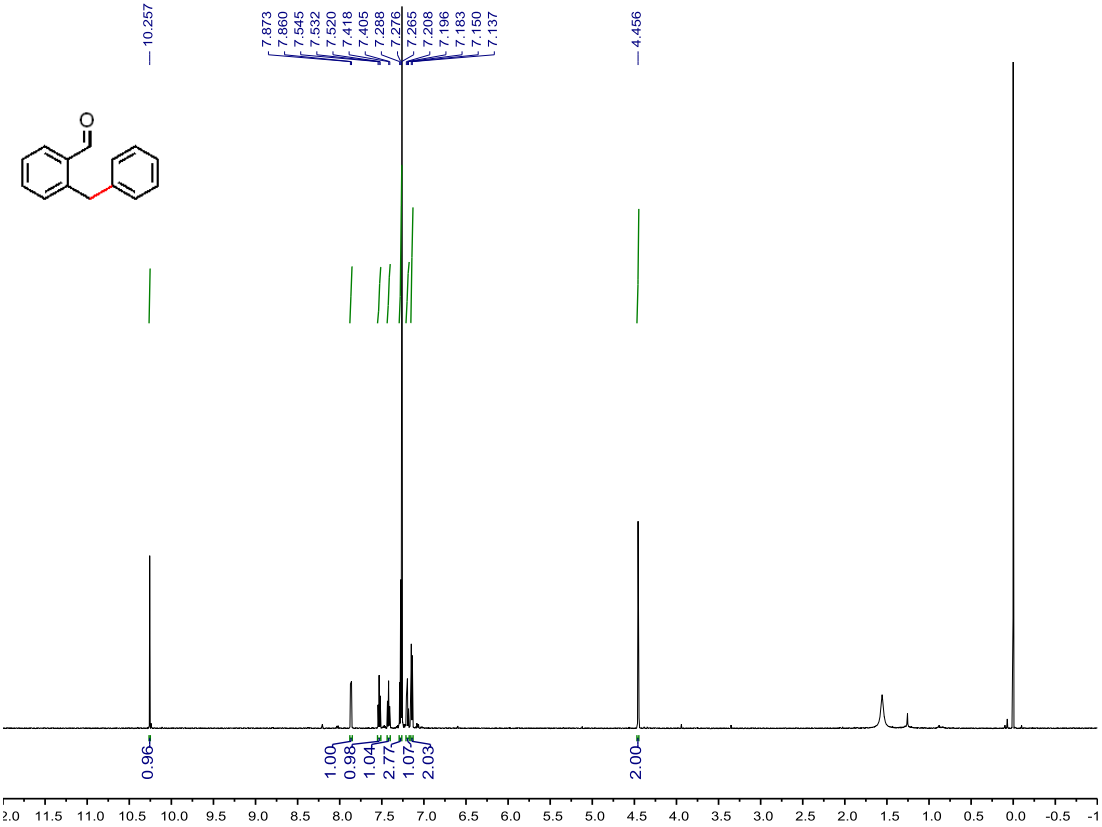
77.00
76.79
35.70
19.64
O
Me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7.418
7.405
7.288
7.276
7.265
7.208
7.196
7.183
7.150
7.137
4.456
0.96
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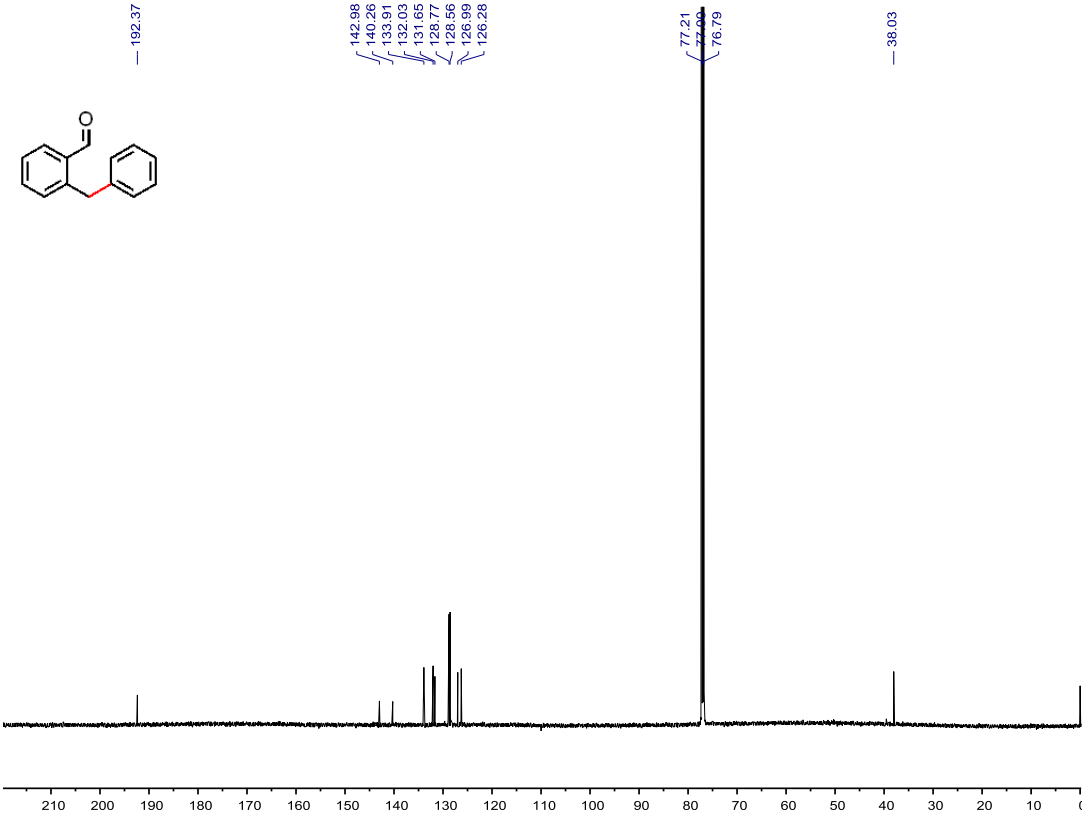
0.98
1.04
2.77
1.07
2.03
2.00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128.77
128.56
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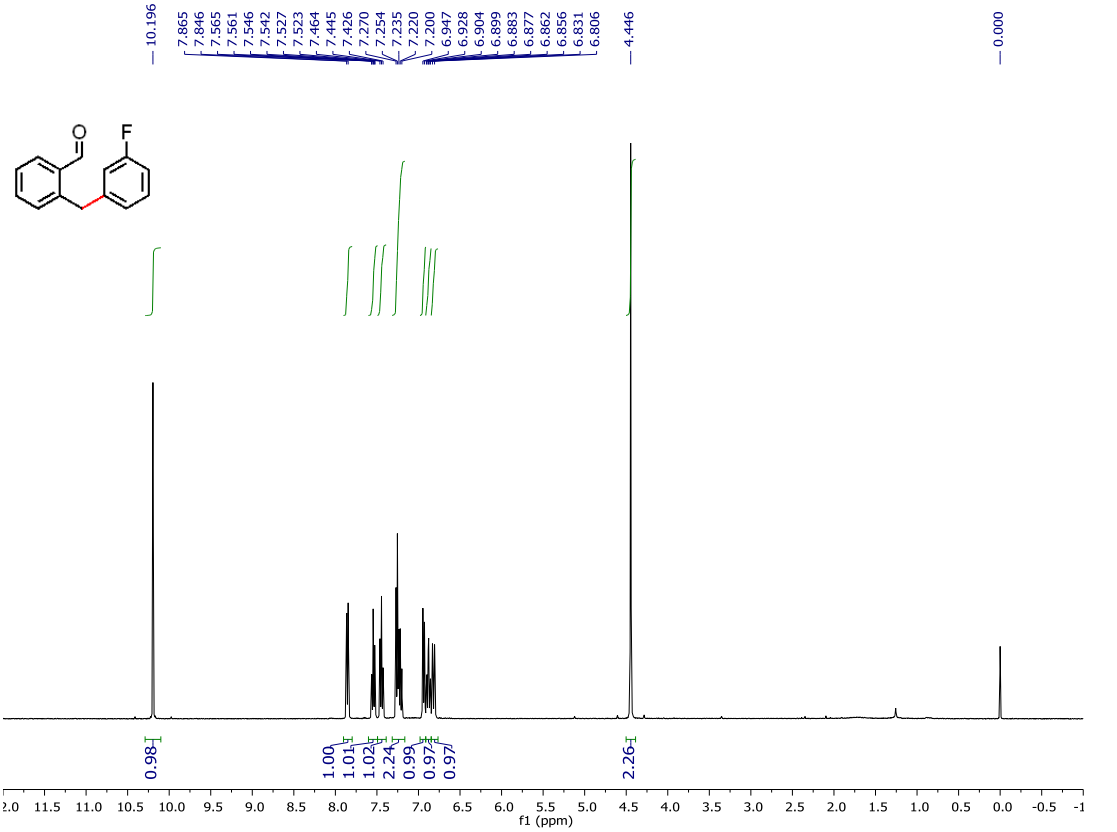
126.28
77.21
77.00
76.79
38.03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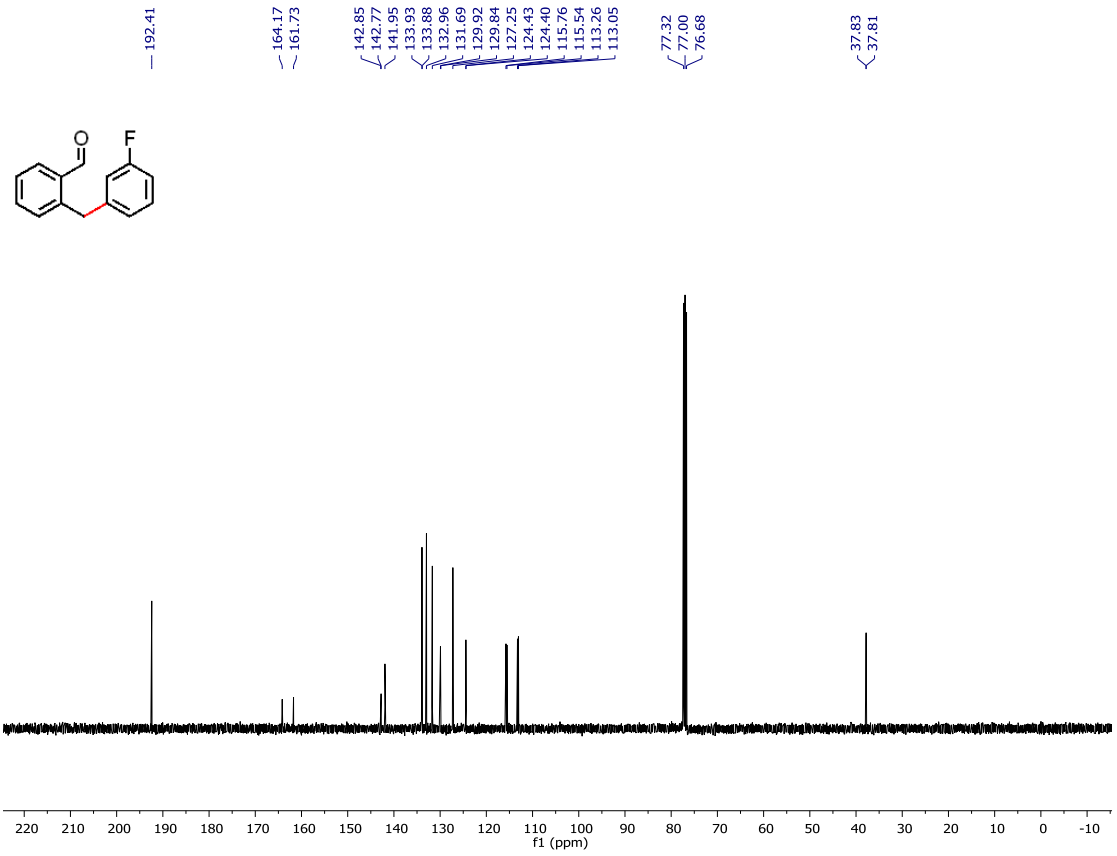
7.561
7.546
7.542
7.527
7.523
7.464
7.445
7.426
7.270
7.254
7.235
7.220
7.200
6.947
6.928
6.904
6.899
6.883
6.877
6.862
6.856
6.831
6.806
4.446
0.000
O
F
0.98
1.00
1.01
1.02
2.24
0.99
0.97
0.97
2.26
f1 (ppm)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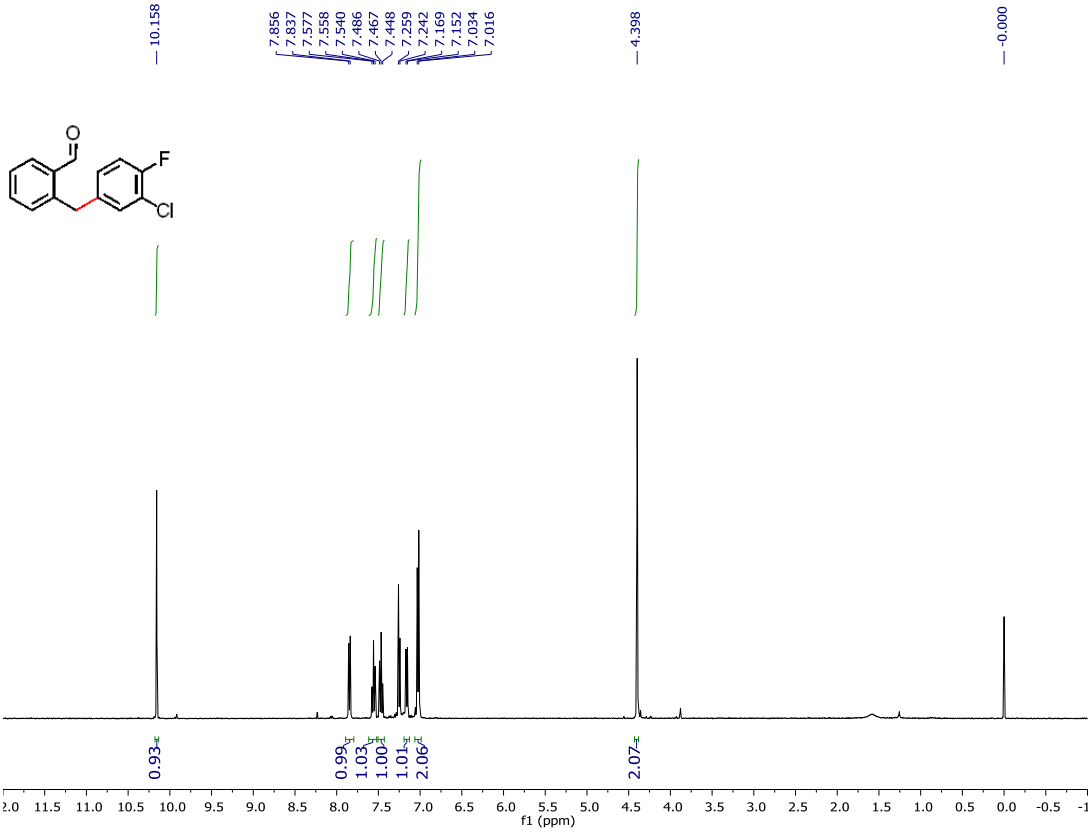
141.95
133.93
133.88
132.96
131.69
129.92
129.84
127.25
124.43
124.40
115.76
115.54
113.26
113.05
77.32
77.00
76.68
37.83
37.81
O
F
f1 (ppm)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7.486
7.467
7.448
7.259
7.242
7.169
7.152
7.034
7.016
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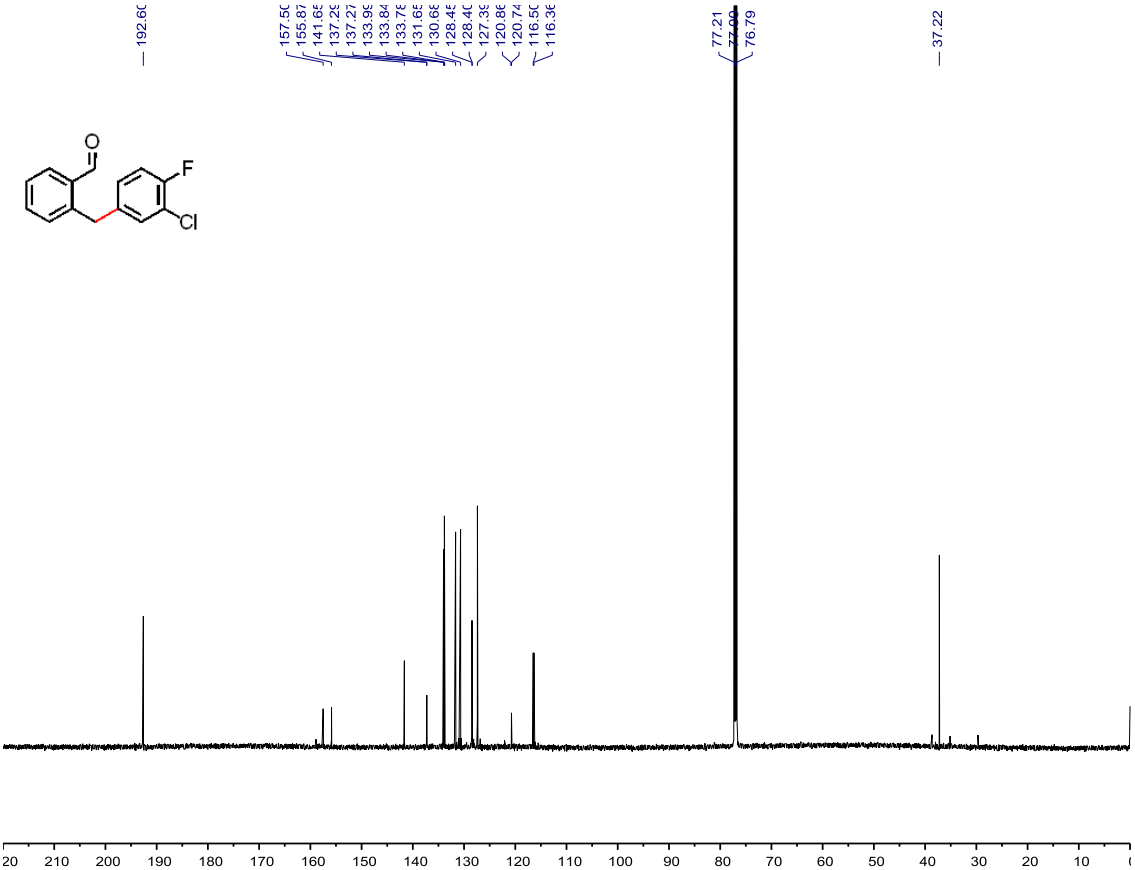
O
F
Cl
0.93
0.99
1.03
1.00
1.01
2.06
2.07
f1 (ppm)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155.87
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137.27
133.99
133.84
133.78
131.65
130.68
128.45
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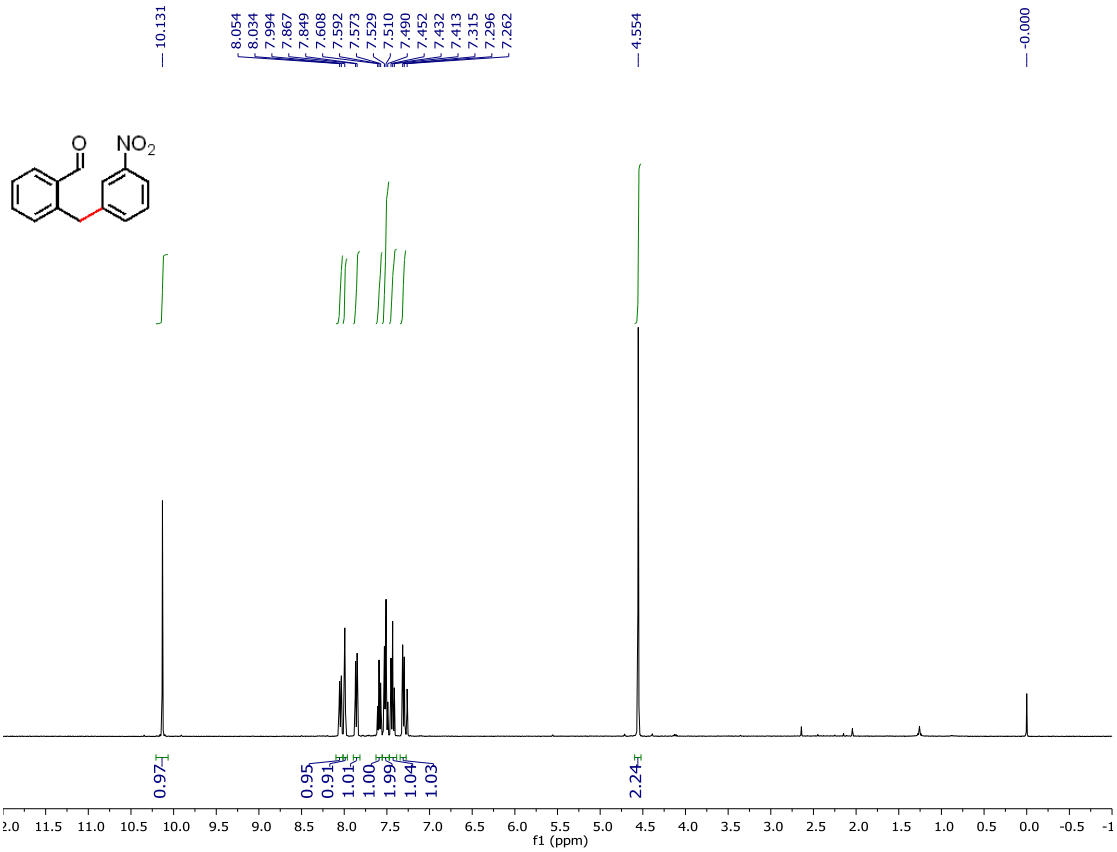
120.88
120.74
116.50
116.36
77.21
77.00
76.79
37.22
O
F
Cl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7.849
7.608
7.592
7.573
7.529
7.510
7.490
7.452
7.432
7.413
7.315
7.296
7.262
4.554
-0.000
O
NO2
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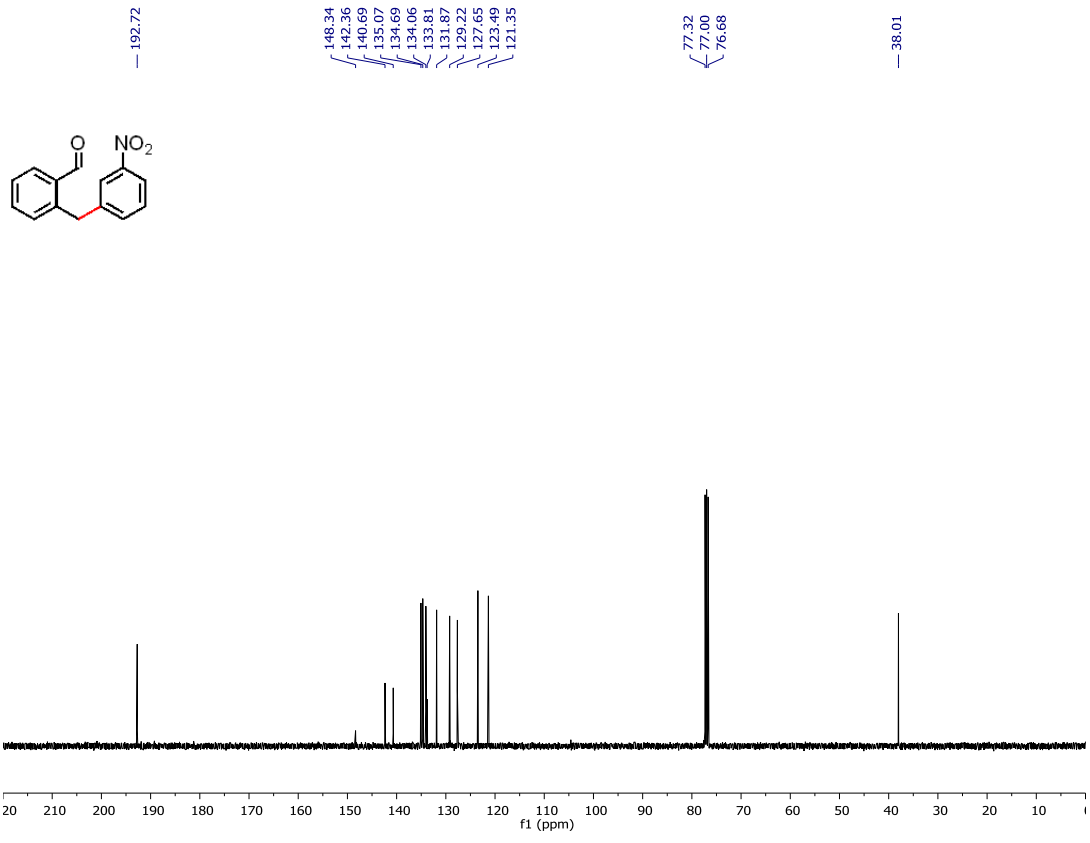
0.95
0.91
1.01
1.00
1.99
1.04
1.03
2.24
f1 (ppm)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135.07
134.69
134.06
133.81
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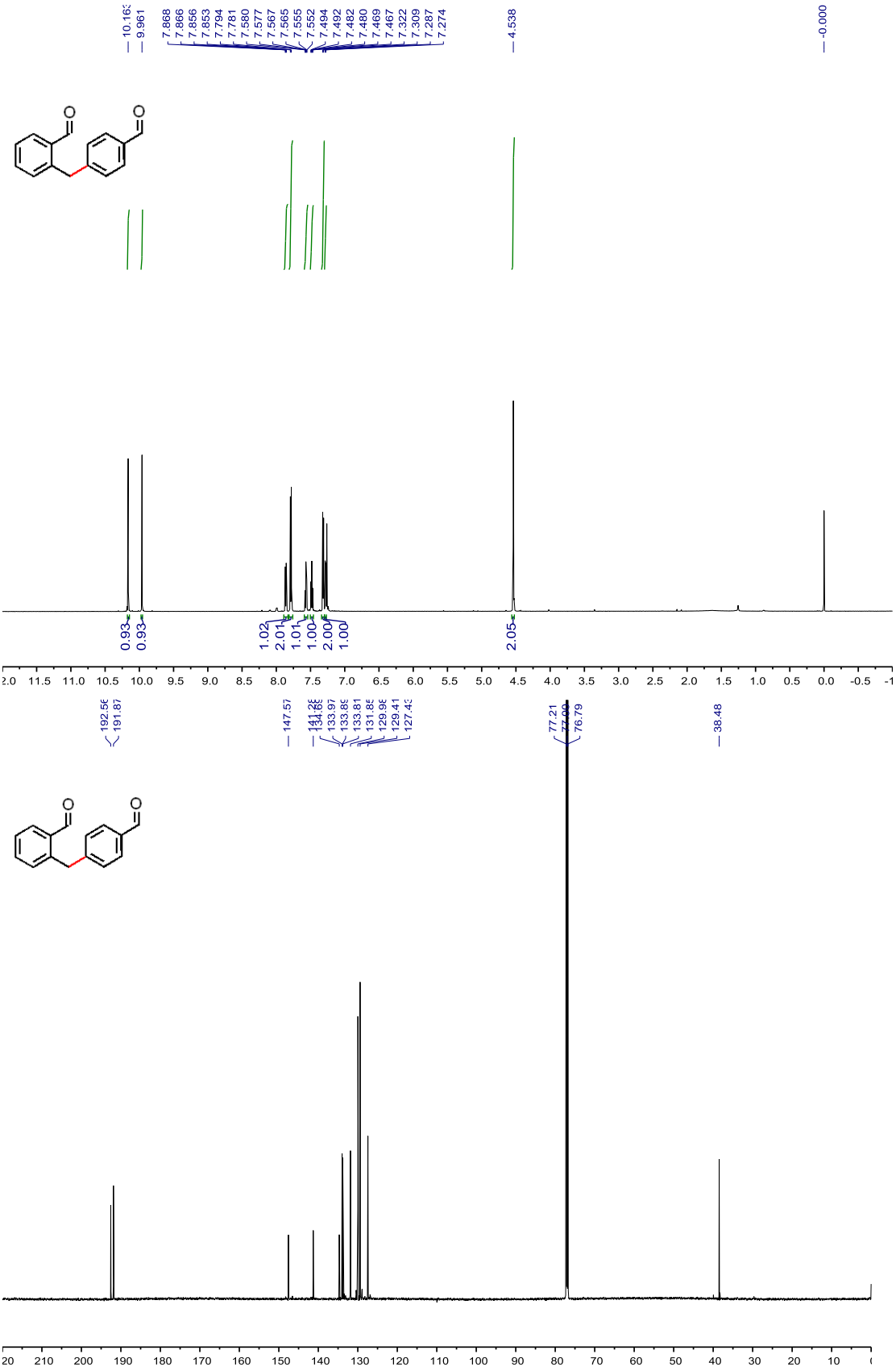
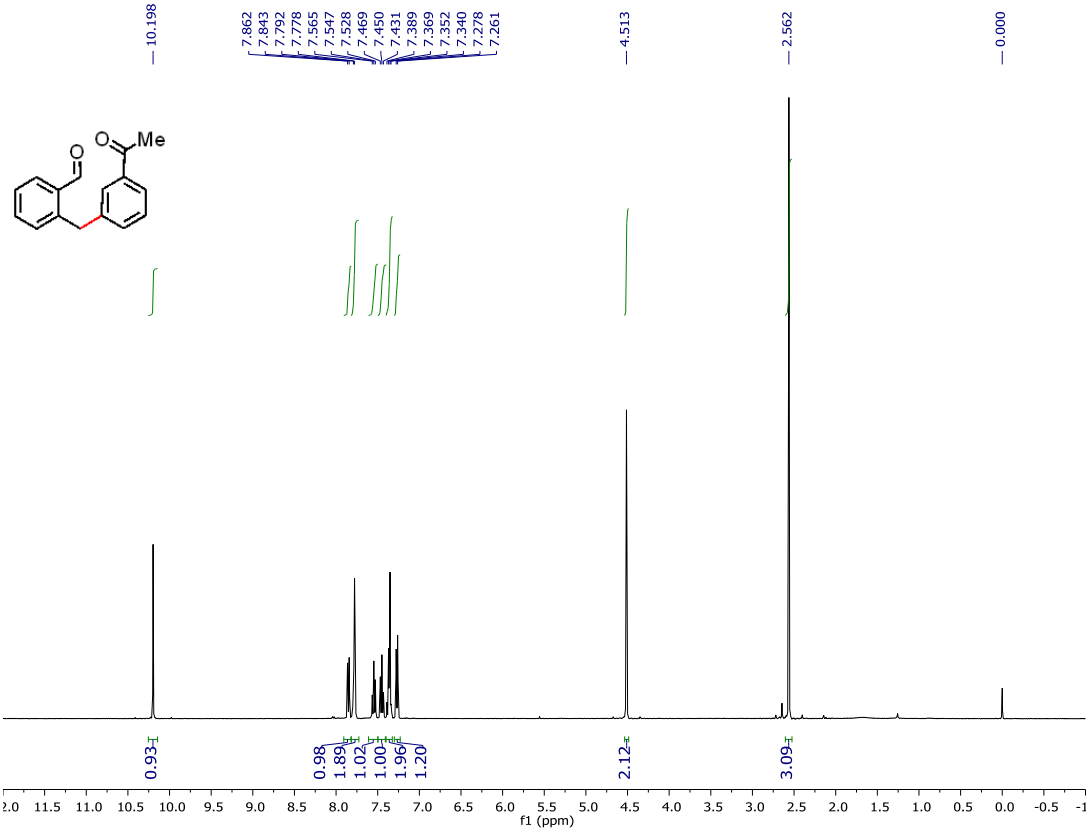
123.49
121.35
77.32
77.00
76.68
38.01
O
NO2
f1 (ppm)

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7.528
7.469
7.450
7.431
7.389
7.369
7.352
7.340
7.278
7.261
4.513
2.562
0.000
O
Me
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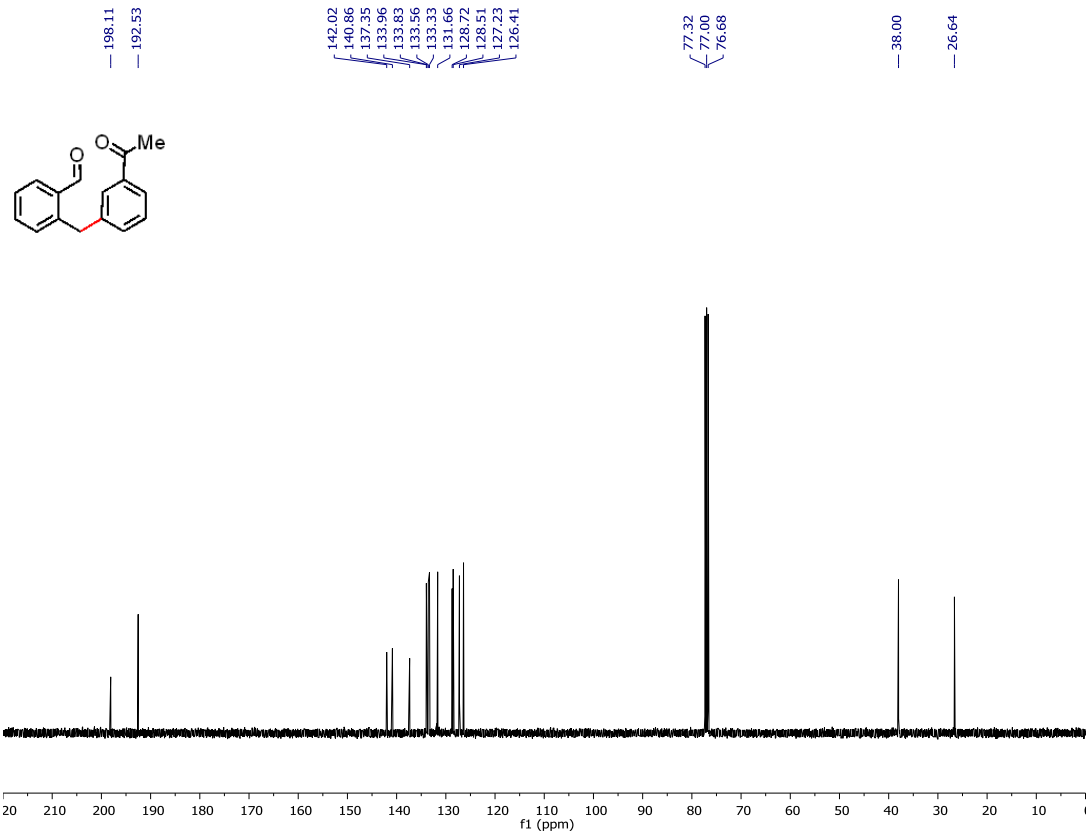
0.98
1.89
1.02
1.00
1.96
1.20
2.12
3.09
f1 (ppm)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133.33
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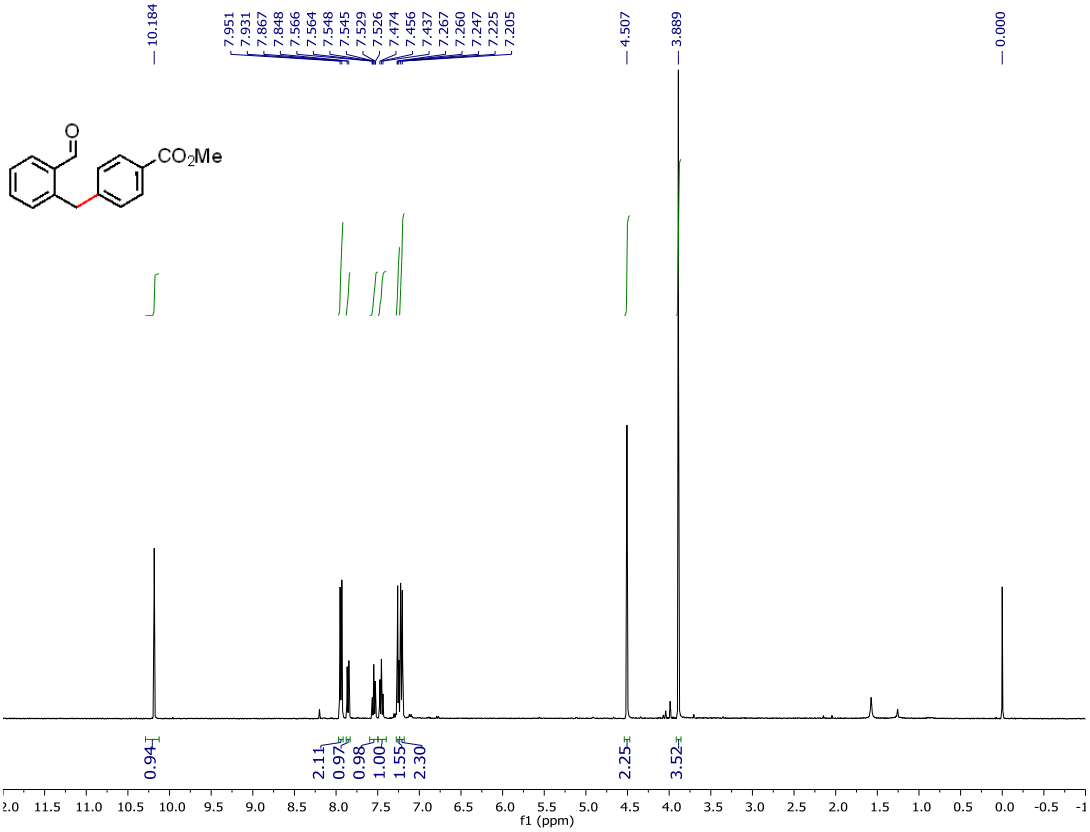
127.23
126.41
77.32
77.00
76.68
38.00
26.64
O
Me
f1 (ppm)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7.545
7.529
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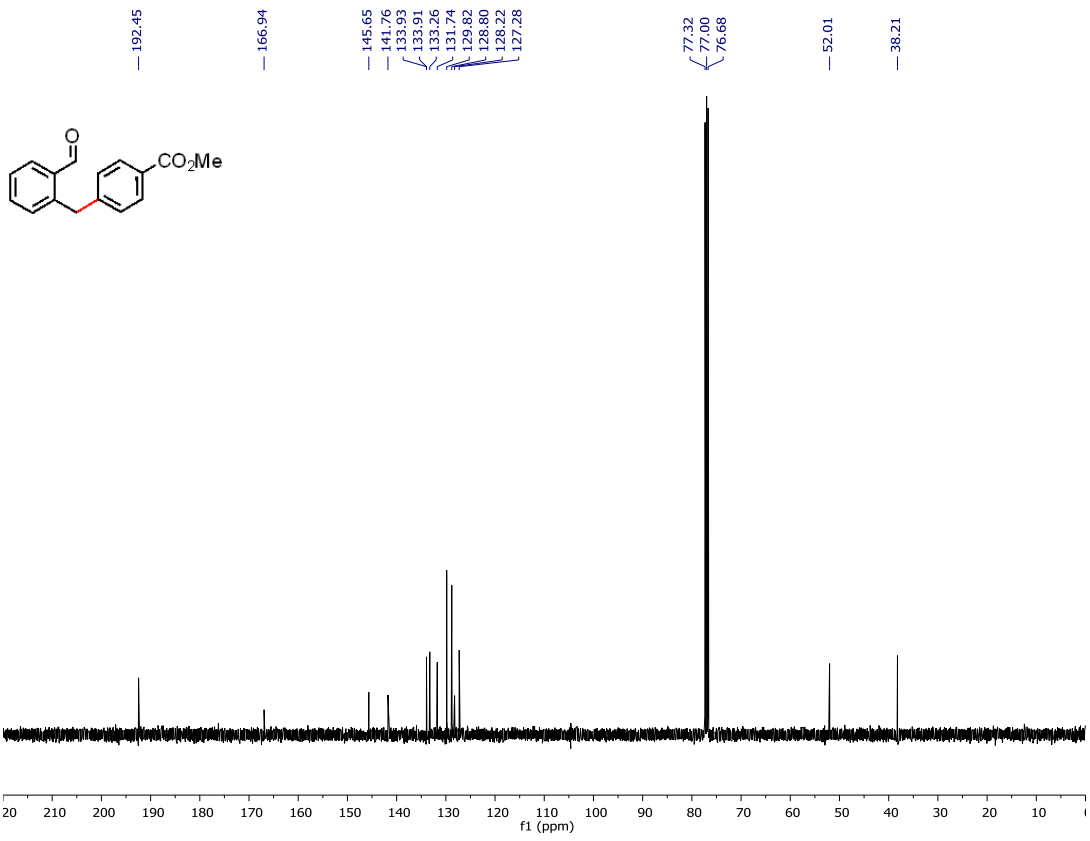
7.474
7.456
7.437
7.267
7.260
7.247
7.225
7.205
4.507
3.889
0.000
CO2Me
0.94
2.11
0.97
0.98
1.00
1.55
2.30
2.25
3.52
f1 (ppm)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133.91
133.26
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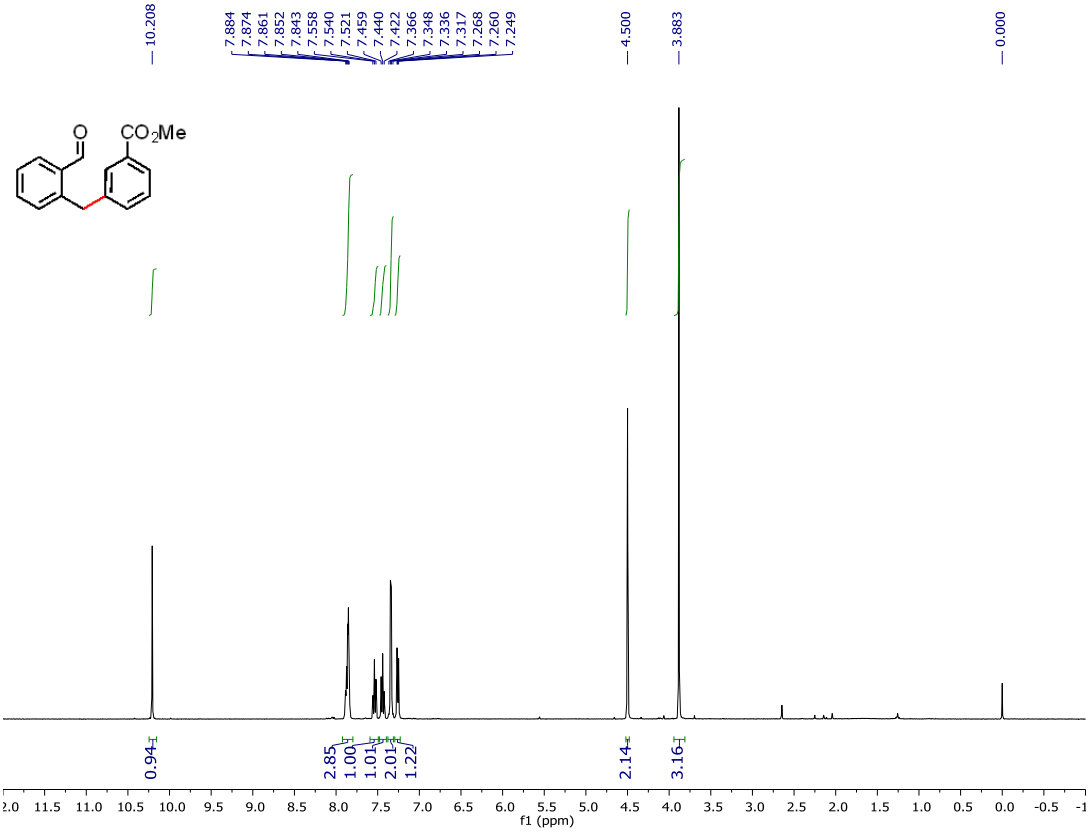
128.22
127.28
77.32
77.00
76.68
52.01
38.21
CO2Me
f1 (ppm)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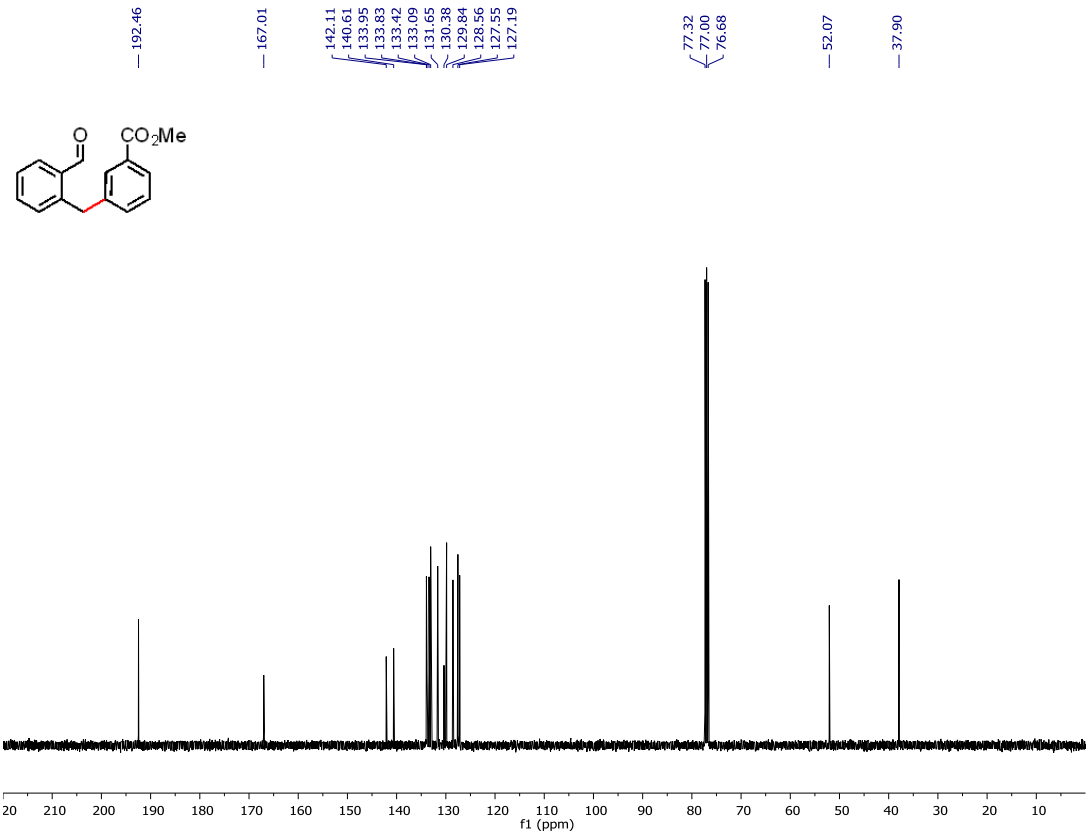
7.348
7.336
7.317
7.268
7.260
7.249
4.500
3.883
0.000
O
CO2Me
0.94
2.85
1.00
1.01
2.01
1.22
2.14
3.16
f1 (ppm)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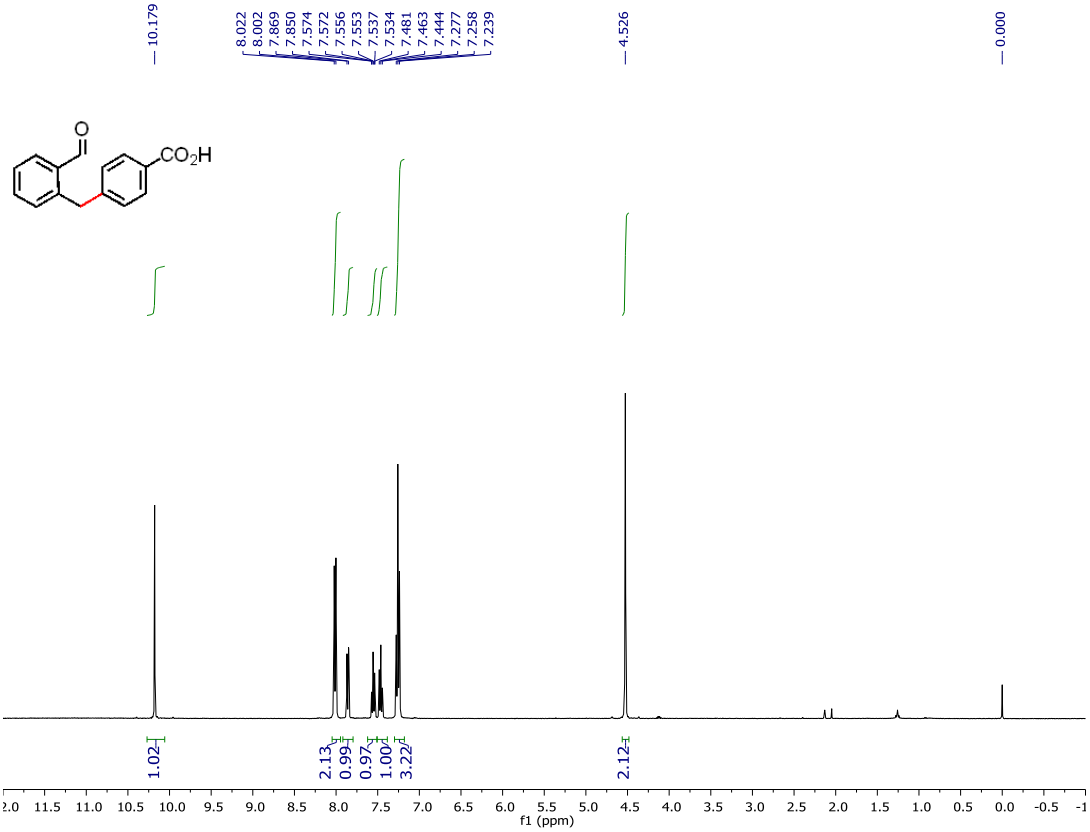
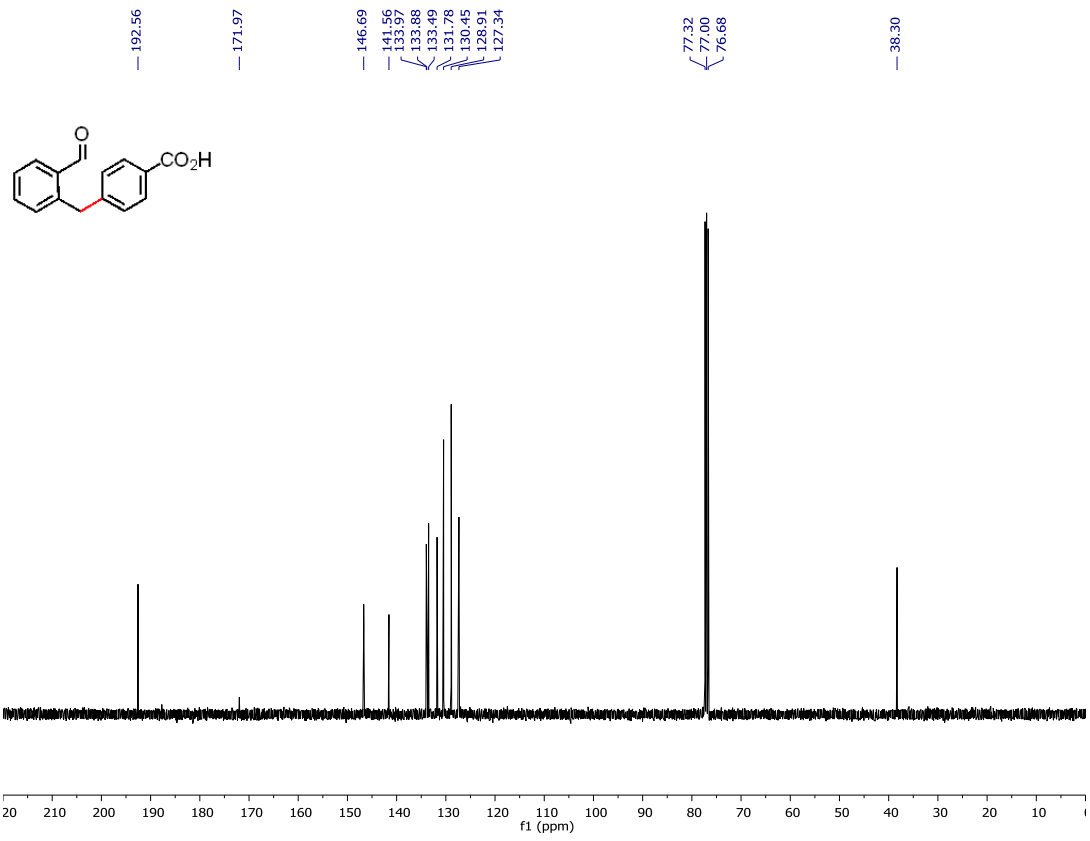
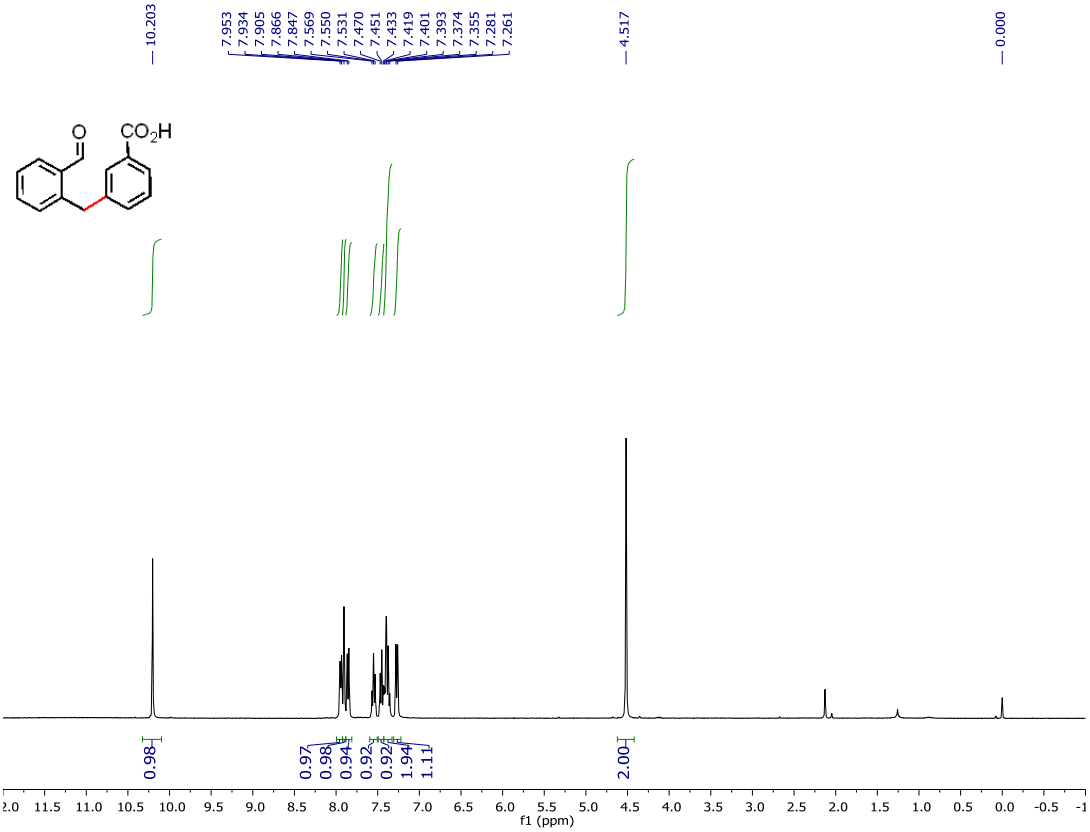
127.55
127.19
77.32
77.00
76.68
52.07
37.90
O
CO2Me
f1 (ppm)


10.179
8.022
8.002
7.869
7.850
7.574
7.572
7.556
7.553
7.537
7.534
7.481
7.463
7.444
7.277
7.258
7.239
4.526
0.000
O
CO2H
1.02
2.13
0.99
0.97
1.00
3.22
2.12
f1 (ppm)


192.56
171.97
146.69
141.56
133.97
133.88
133.49
131.78
130.45
128.91
127.34
77.32
77.00
76.68
38.30
O
CO2H
f1 (ppm)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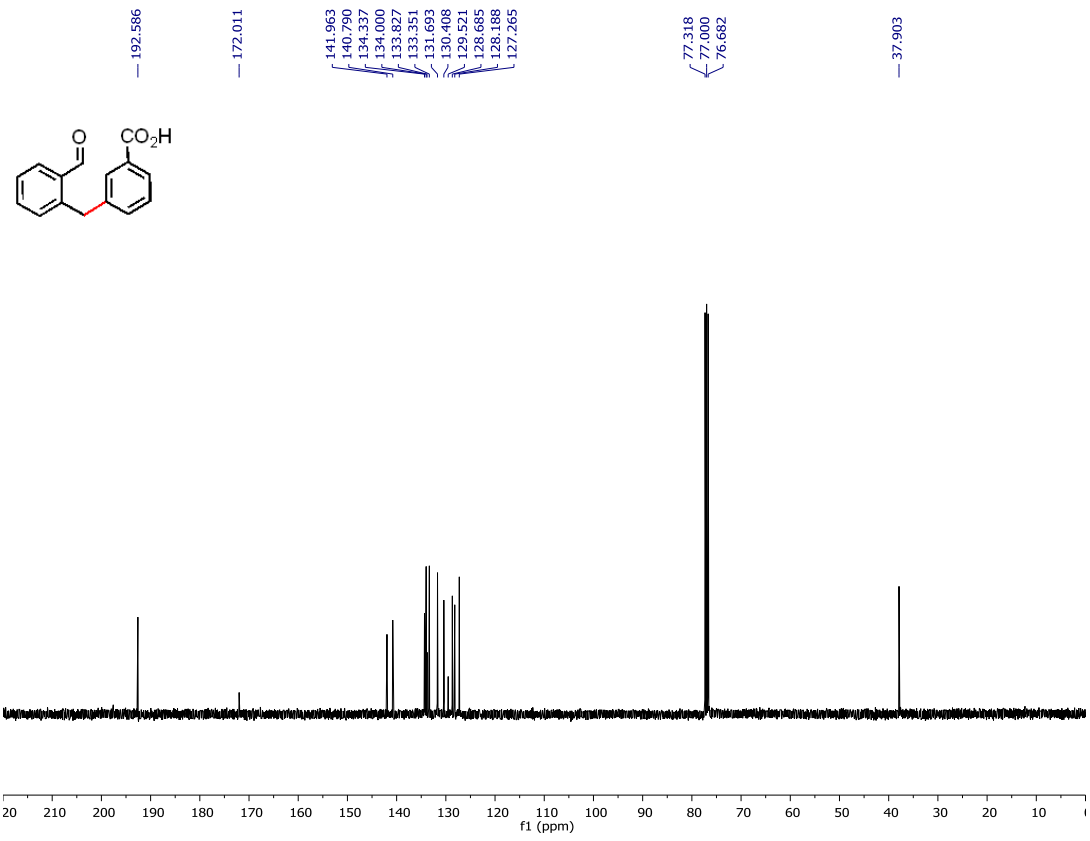
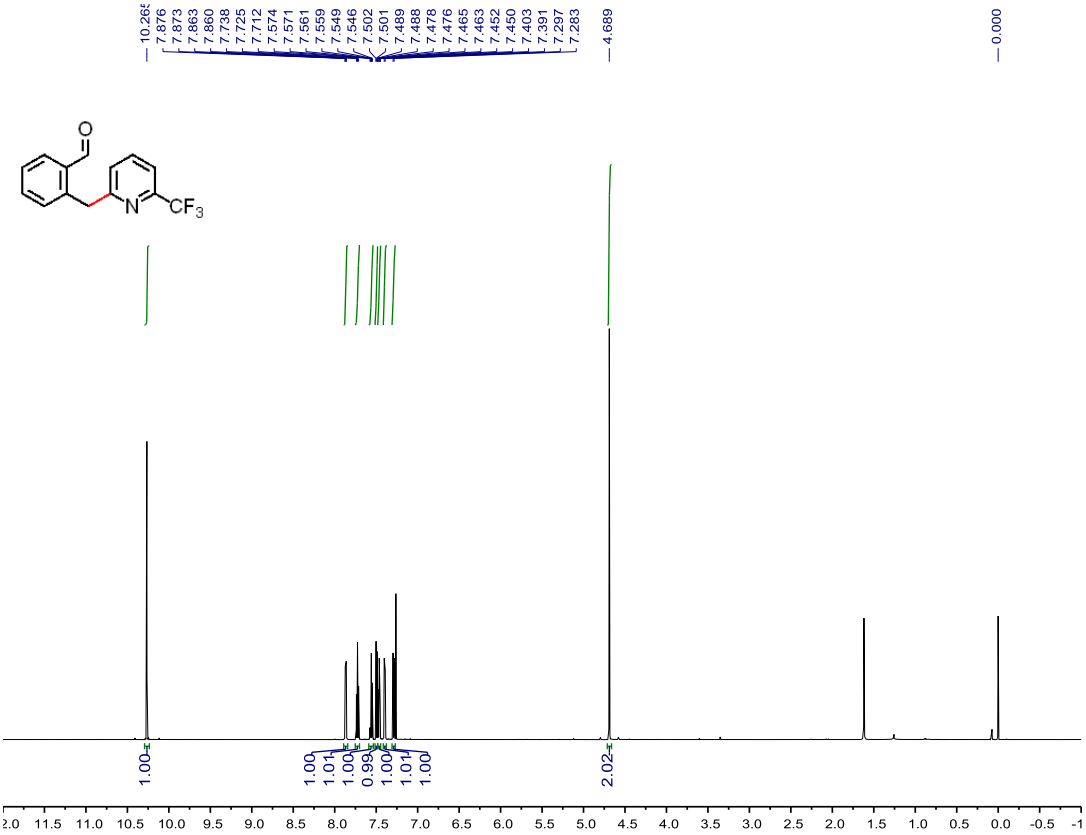
7.953
7.934
7.905
7.866
7.847
7.569
7.550
7.531
7.470
7.451
7.433
7.419
7.401
7.393
7.374
7.355
7.281
7.261
4.517
0.000
O
CO2H
0.98
0.97
0.98
0.94
0.92
0.92
1.94
1.11
2.00
f1 (ppm)


192.586
172.011
141.963
140.790
134.337
134.000
133.827
133.351
131.693
130.408
129.521
128.685
128.188
127.265
77.318
77.000
76.682
37.903
O
CO2H
f1 (ppm)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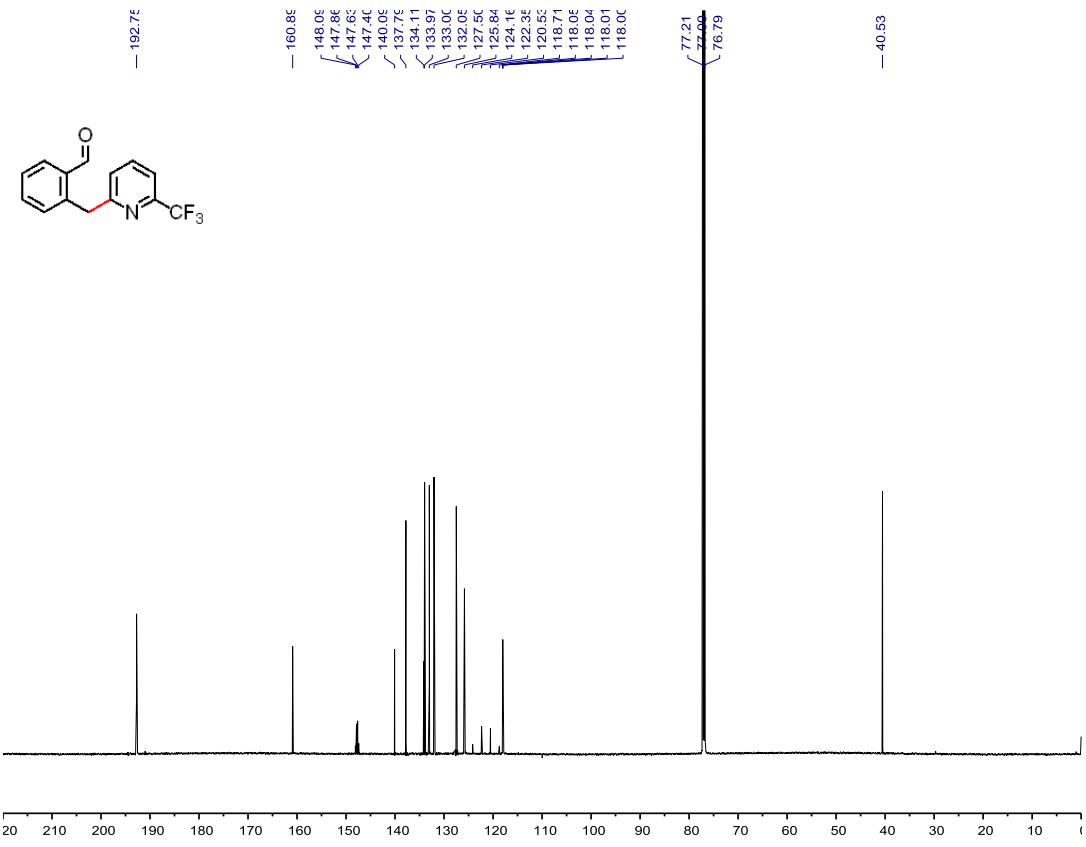
7.876
7.873
7.863
7.860
7.738
7.725
7.712
7.574
7.571
7.561
7.559
7.549
7.546
7.502
7.501
7.489
7.488
7.478
7.476
7.465
7.463
7.452
7.450
7.403
7.391
7.297
7.283
4.689
0.000
O
N
CF3
1.00
1.00
1.01
1.00
0.99
1.00
1.01
1.00
2.02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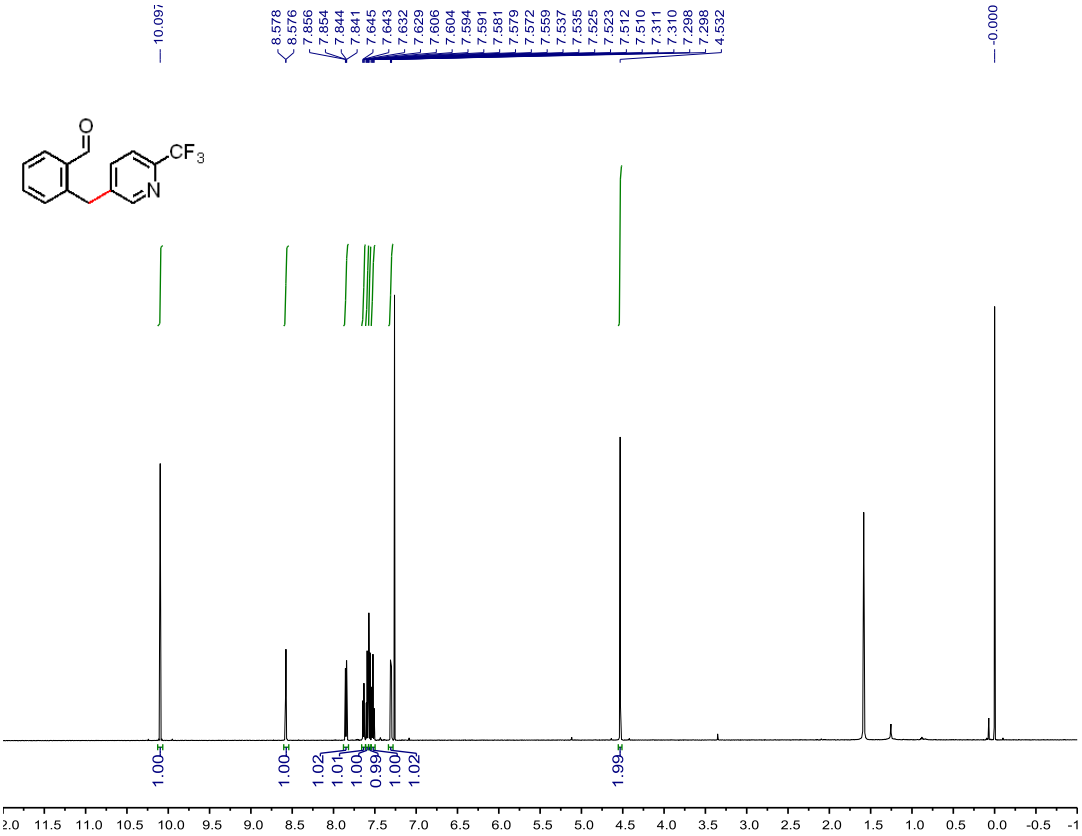
160.85
148.05
147.86
147.63
147.46
140.05
137.75
134.11
133.97
133.06
132.05
127.56
125.84
124.16
122.38
120.55
118.71
118.05
118.04
118.01
118.00
77.21
77.00
76.79
40.53
O
N
CF3


10.097
8.578
8.576
7.856
7.854
7.844
7.841
7.645
7.643
7.632
7.629
7.606
7.604
7.594
7.591
7.581
7.579
7.572
7.559
7.537
7.535
7.525
7.523
7.512
7.510
7.311
7.310
7.298
7.298
4.532
-0.000
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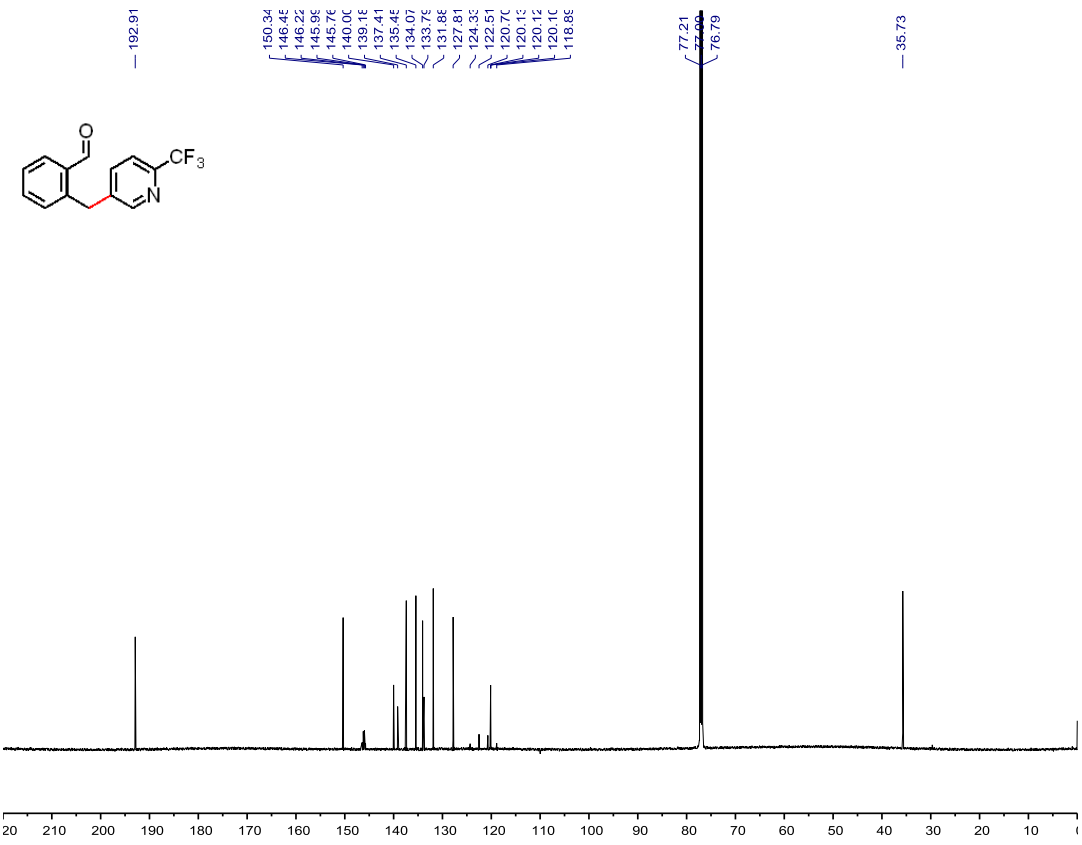
CF3
N
1.00
1.00
1.02
1.01
1.00
0.99
1.00
1.02
1.99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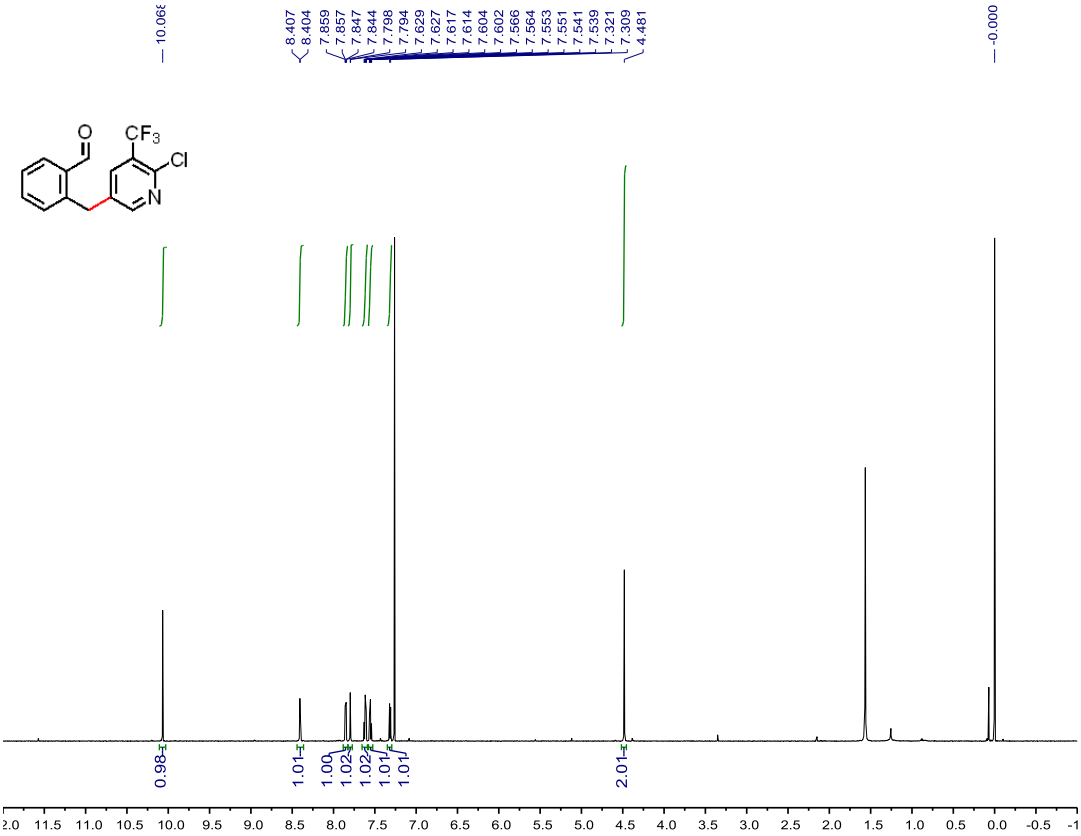
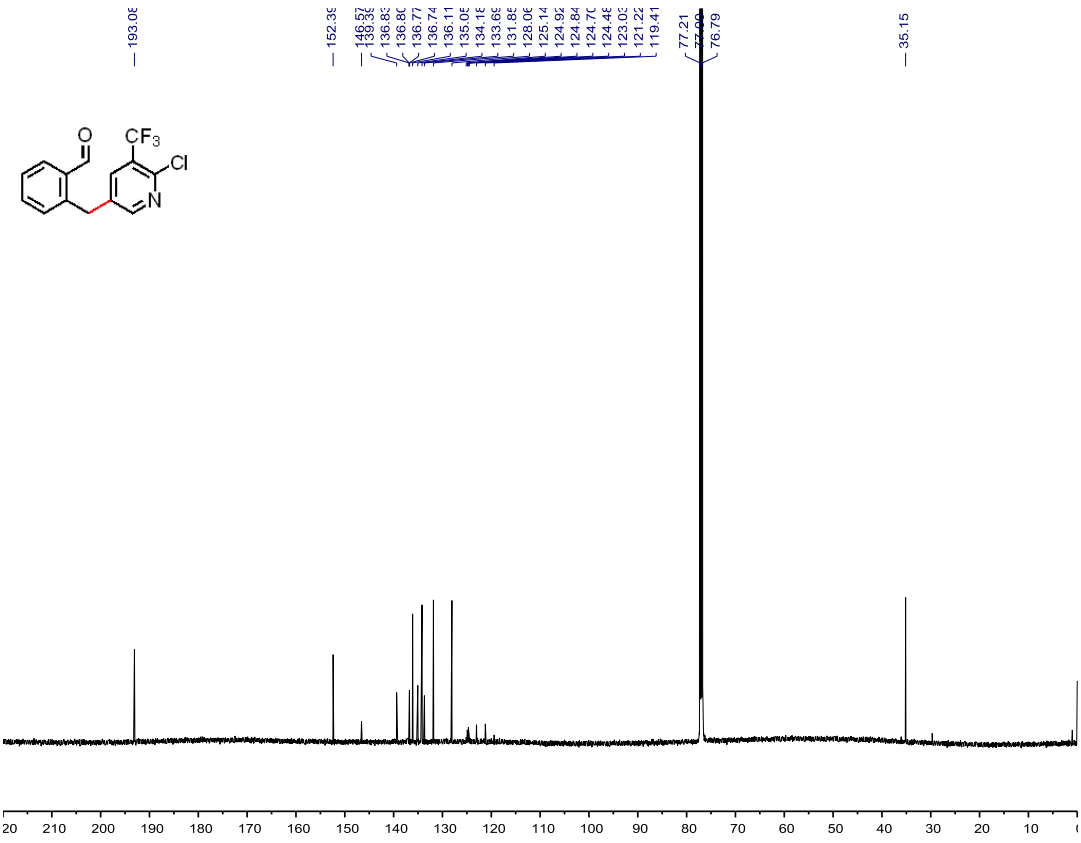
146.45
146.22
145.96
145.76
140.00
139.18
137.41
135.45
134.07
133.75
131.88
127.81
124.33
122.51
120.76
120.13
120.12
120.10
118.85
77.21
77.00
76.79
35.73
O
CF3
N


10.068
8.407
8.404
7.859
7.857
7.847
7.844
7.798
7.794
7.629
7.627
7.617
7.614
7.604
7.602
7.566
7.564
7.553
7.551
7.541
7.539
7.321
7.309
4.481
-0.000
O
CF3
Cl
N
0.98
1.01
1.00
1.02
1.02
1.01
1.01
2.01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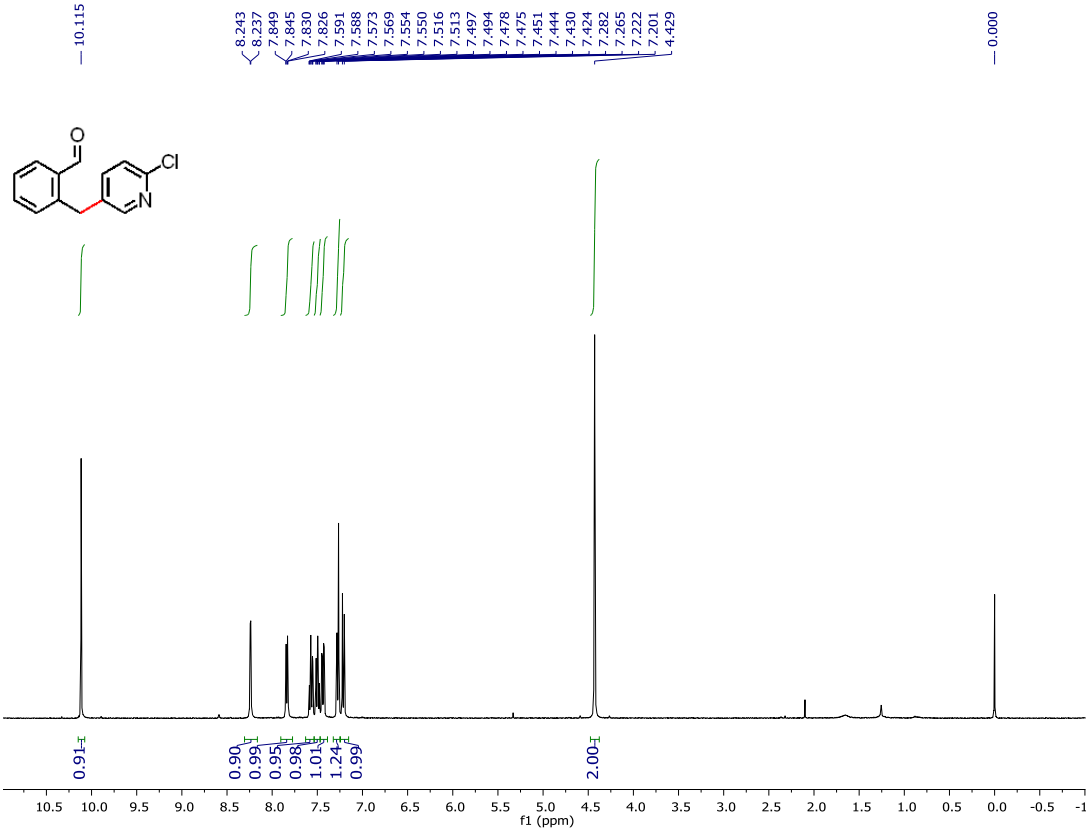
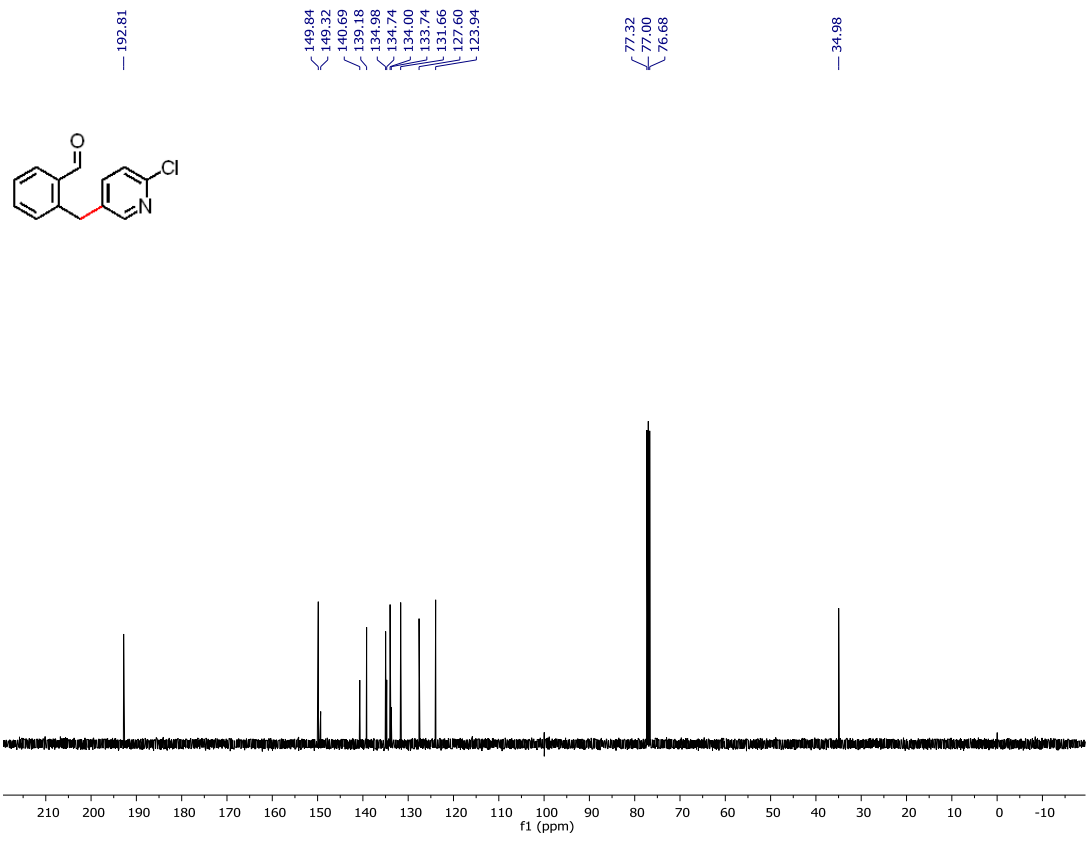
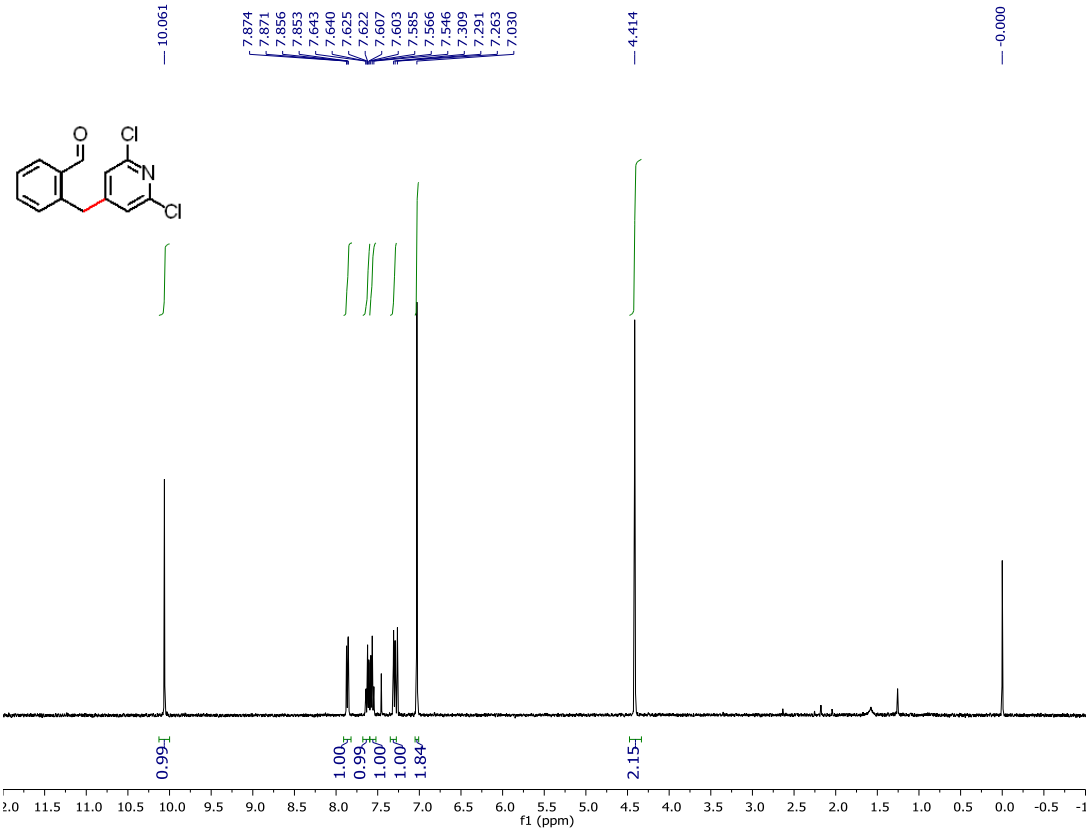
152.38
146.57
138.88
136.86
136.77
136.74
136.11
135.05
134.18
133.65
131.88
128.06
125.14
124.92
124.84
124.70
124.46
123.00
121.22
119.41
77.21
77.00
76.79
35.15
O
CF3
Cl
N


10.115
8.243
8.237
7.849
7.845
7.830
7.826
7.591
7.588
7.573
7.569
7.554
7.550
7.516
7.513
7.497
7.494
7.478
7.475
7.451
7.444
7.430
7.424
7.282
7.265
7.222
7.201
4.429
0.000
O
Cl
N
0.91
0.90
0.99
0.95
0.98
1.01
1.24
0.99
2.00
f1 (ppm)


192.81
149.84
149.32
140.69
139.18
134.98
134.74
134.00
133.74
131.66
127.60
123.94
77.32
77.00
76.68
34.98
O
Cl
N
f1 (ppm)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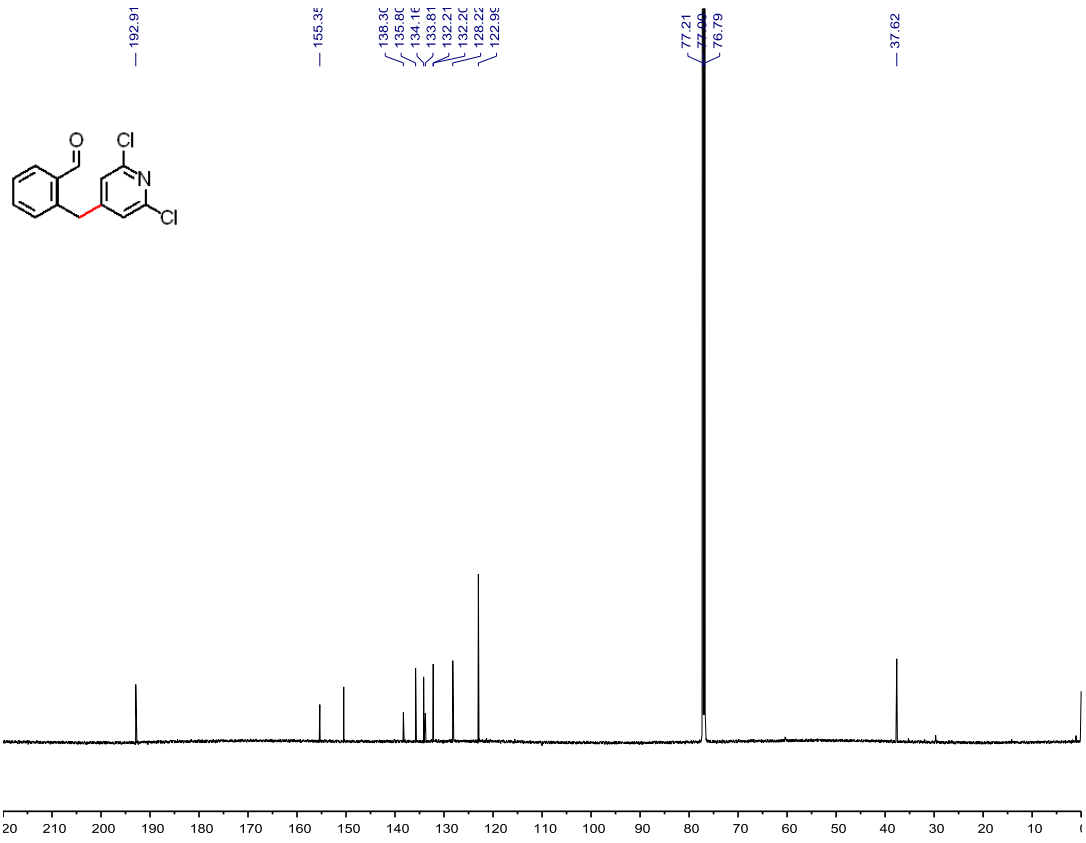
7.871
7.856
7.853
7.643
7.640
7.625
7.622
7.607
7.603
7.585
7.566
7.546
7.309
7.291
7.263
7.030
4.414
-0.000
O
Cl
N
Cl
0.99
1.00
0.99
1.00
1.00
1.84
2.15
f1 (ppm)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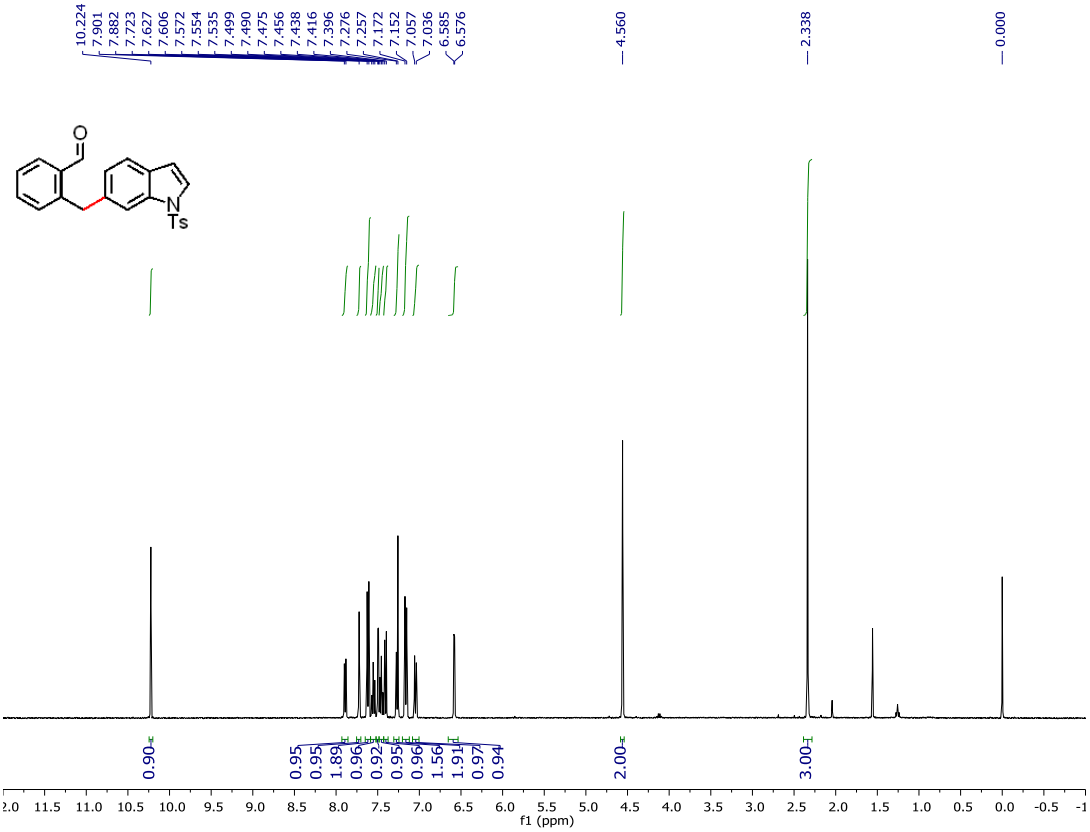
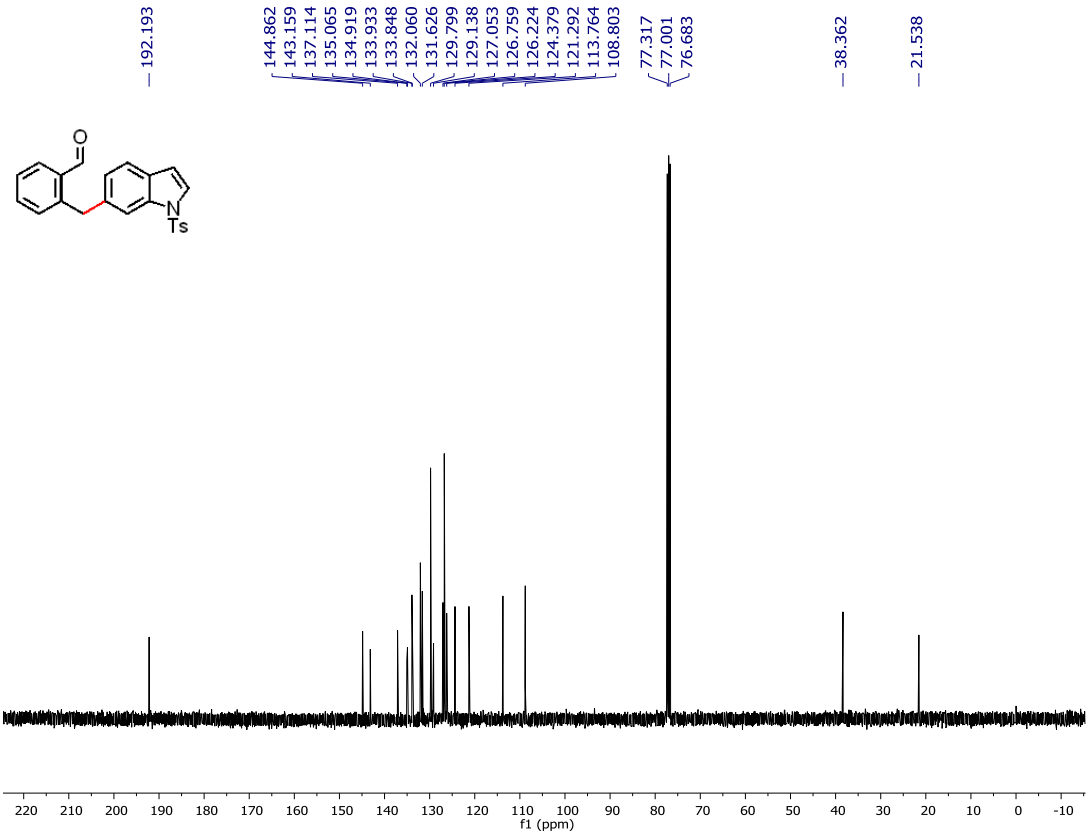
155.38
138.36
135.86
134.16
133.81
132.21
132.26
128.22
122.98
77.21
76.79
37.62
O
Cl
N
Cl


10.224
7.901
7.882
7.723
7.627
7.606
7.572
7.554
7.535
7.499
7.490
7.475
7.456
7.438
7.416
7.396
7.276
7.257
7.172
7.152
7.057
7.036
6.585
6.576
4.560
2.338
0.000
O
N
Ts
0.90
0.95
0.95
1.89
0.96
0.92
0.95
0.96
1.56
1.91
0.97
0.94
2.00
3.00
f1 (ppm)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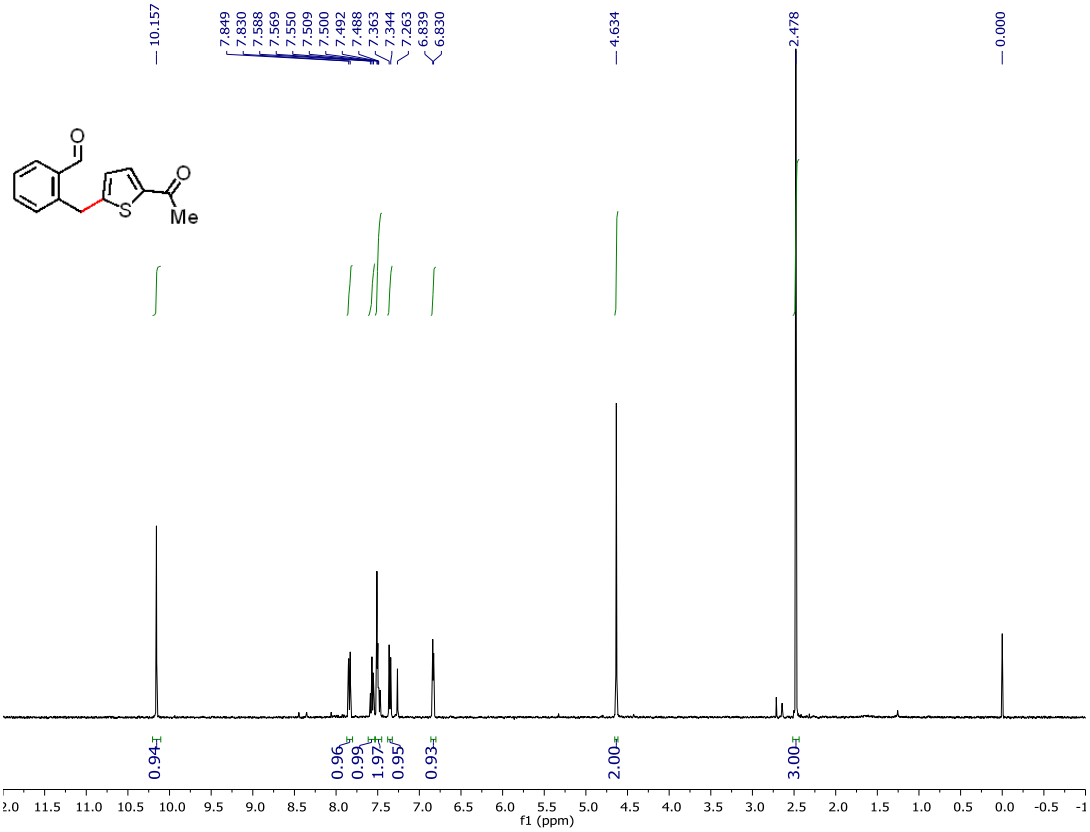
144.862
143.159
137.114
135.065
134.919
133.933
133.848
132.060
131.626
129.799
129.138
127.053
126.759
126.224
124.379
121.292
113.764
108.803
77.317
77.001
76.683
38.362
21.538
O
N
Ts
f1 (ppm)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7.849
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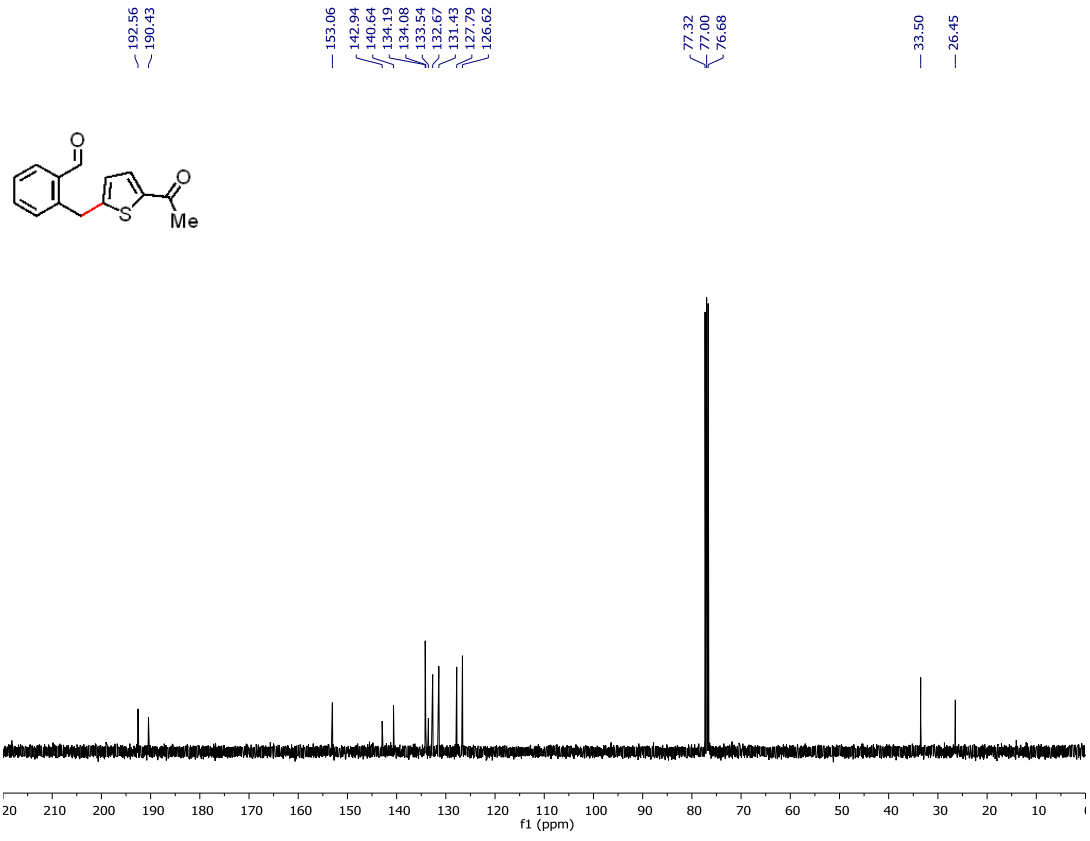
7.588
7.569
7.550
7.509
7.500
7.492
7.488
7.363
7.344
7.263
6.839
6.830
4.634
2.478
0.000
O
O
S
Me
0.94
0.96
0.99
1.97
0.95
0.93
2.00
3.00
f1 (ppm)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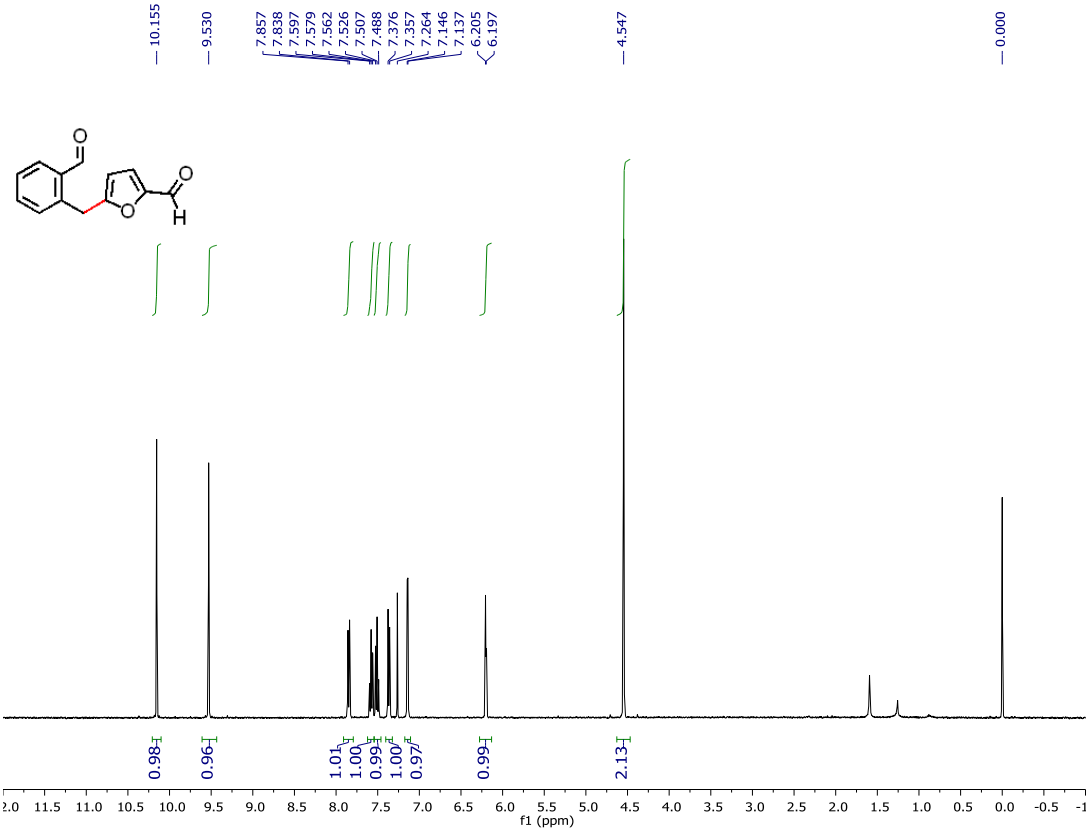
190.43
153.06
142.94
140.64
134.19
134.08
133.54
132.67
131.43
127.79
126.62
77.32
77.00
76.68
33.50
26.45
O
O
S
Me
f1 (ppm)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7.838
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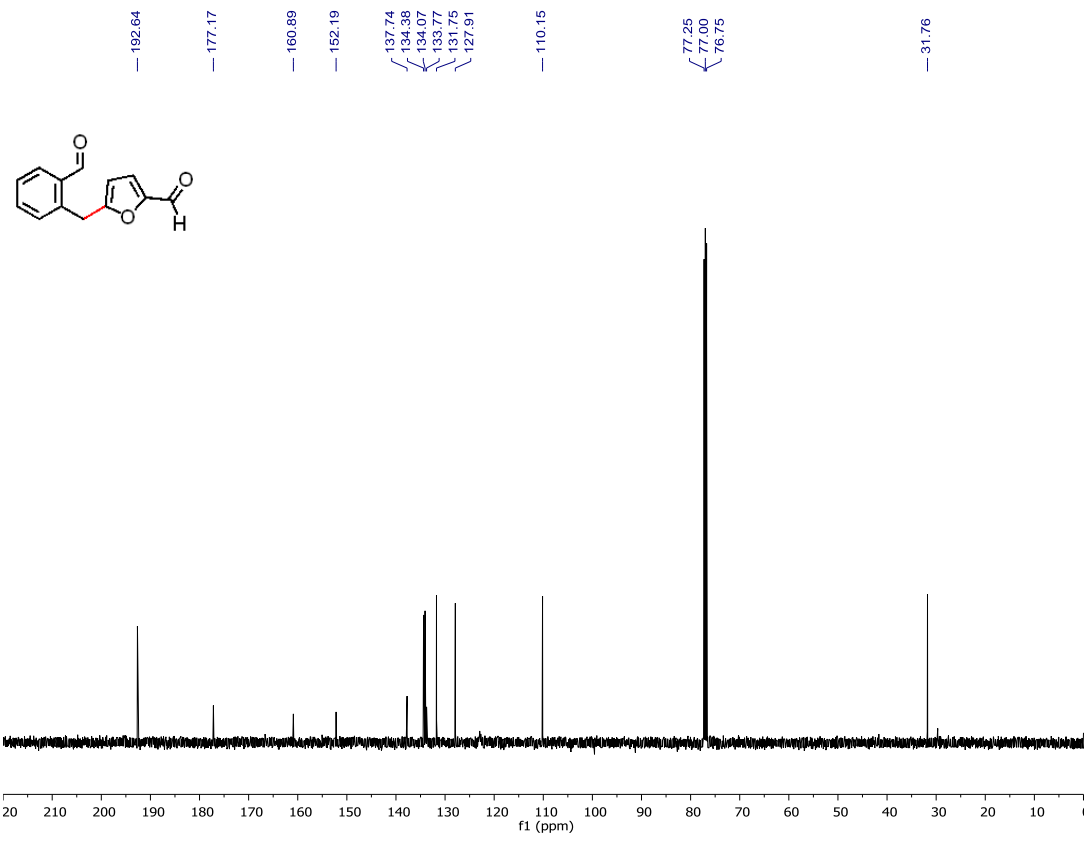
7.579
7.562
7.526
7.507
7.488
7.376
7.357
7.264
7.146
7.137
6.205
6.197
4.547
0.000
0.98
0.96
1.01
1.00
0.99
1.00
0.97
0.99
2.13
f1 (ppm)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152.19
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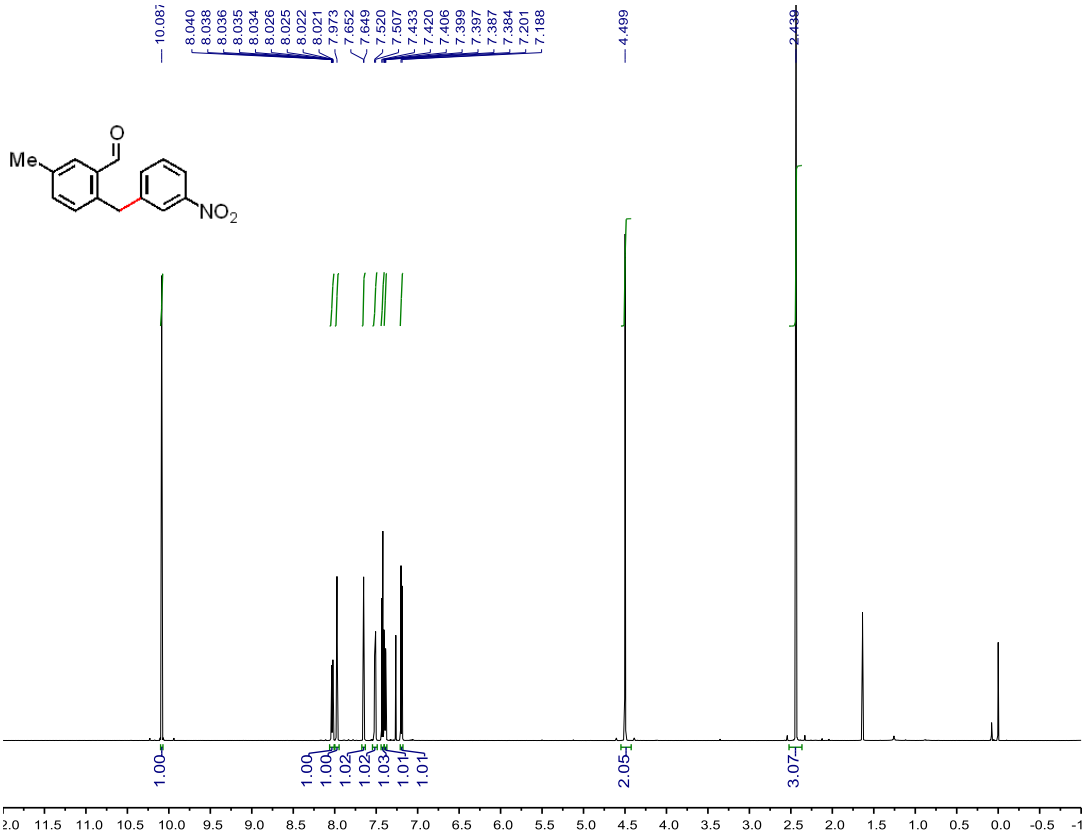
133.77
131.75
127.91
110.15
77.25
77.00
76.75
31.76
f1 (ppm)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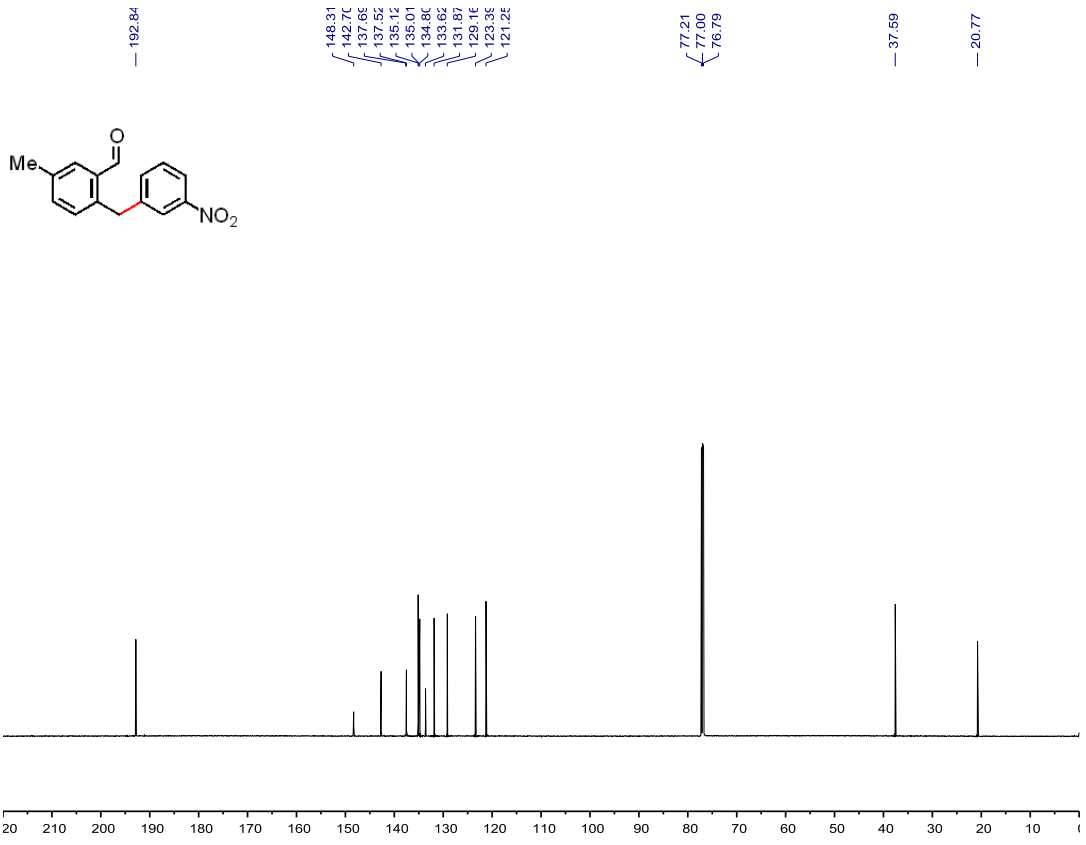
8.038
8.036
8.035
8.034
8.026
8.025
8.022
8.021
7.973
7.652
7.649
7.520
7.507
7.433
7.420
7.406
7.399
7.397
7.387
7.384
7.201
7.188
4.499
2.439
Me
O
NO2
1.00
1.00
1.00
1.02
1.02
1.03
1.01
1.01
2.05
3.07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148.31
142.70
137.68
137.52
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135.01
134.86
133.62
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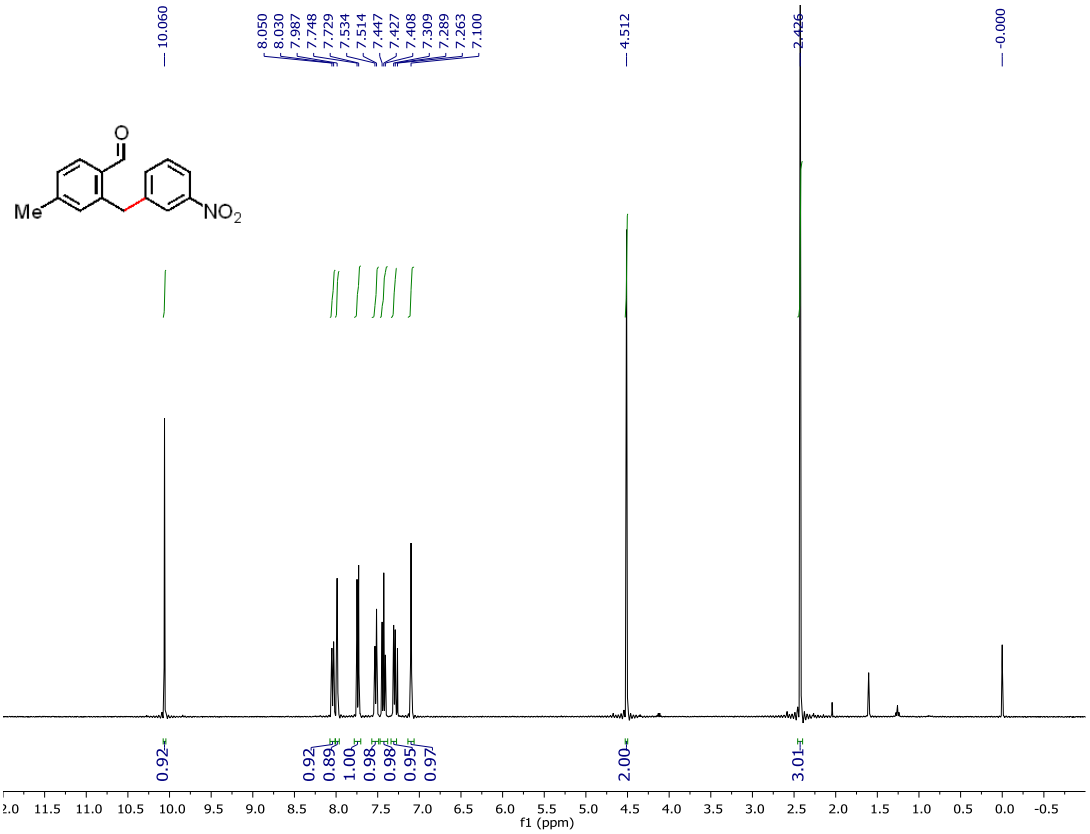
129.16
123.36
121.25
77.21
77.00
76.79
37.59
20.77
Me
O
NO2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8.030
7.987
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7.729
7.534
7.514
7.447
7.427
7.408
7.309
7.289
7.263
7.100
4.512
2.426
-0.000
O
Me
NO2
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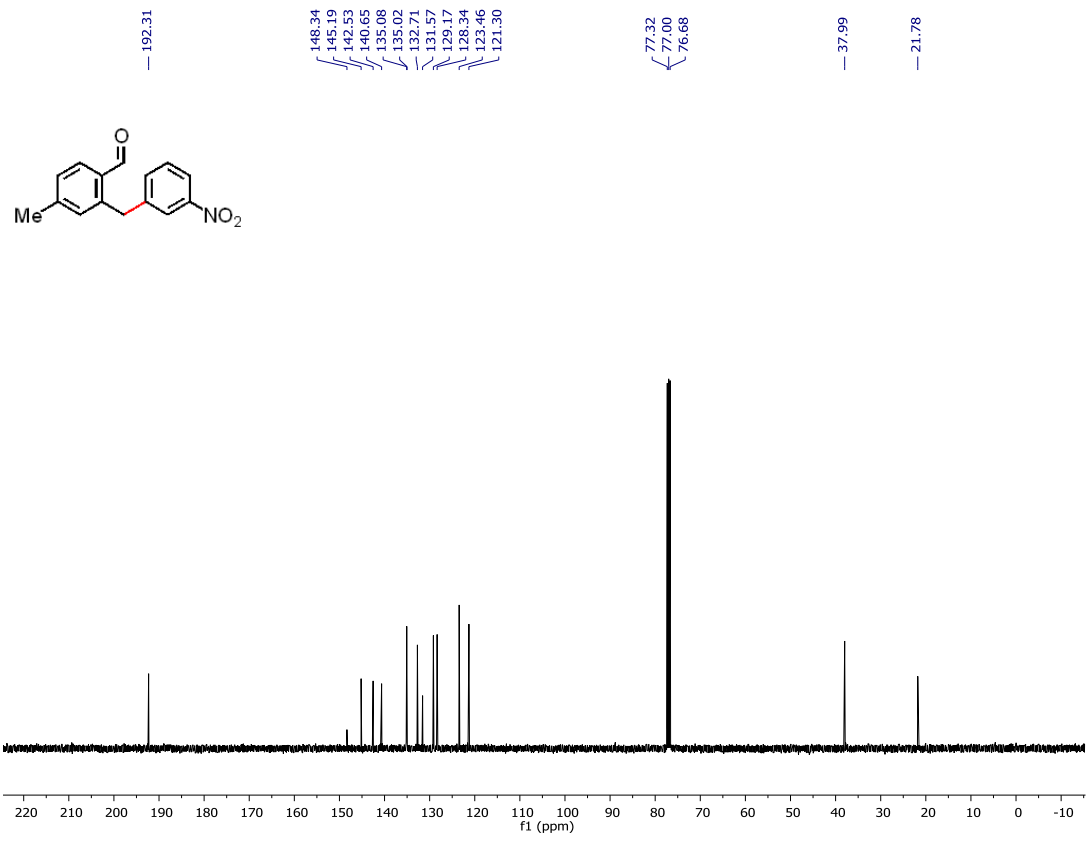
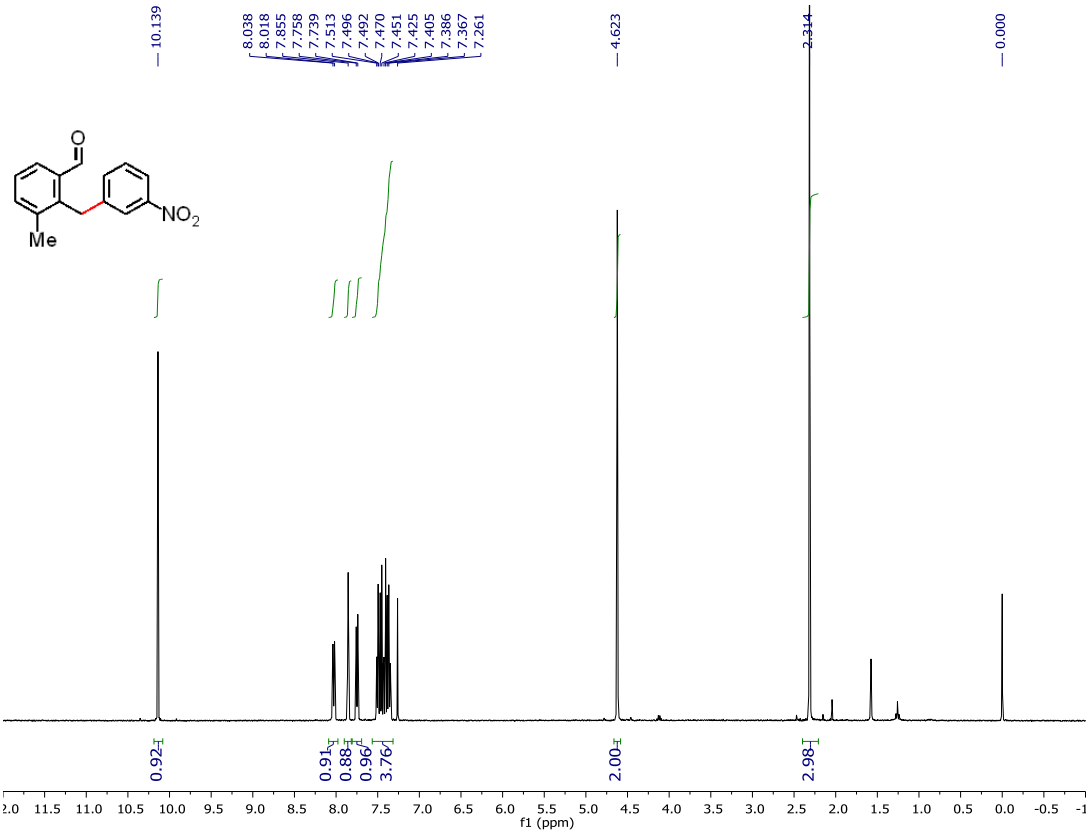
0.92
0.89
1.00
0.98
0.98
0.95
0.97
2.00
3.01
f1 (ppm)


192.31
148.34
145.19
142.53
140.65
135.08
135.02
132.71
131.57
129.17
128.34
123.46
121.30
77.32
77.00
76.68
37.99
21.78
O
Me
NO2
f1 (ppm)


10.139
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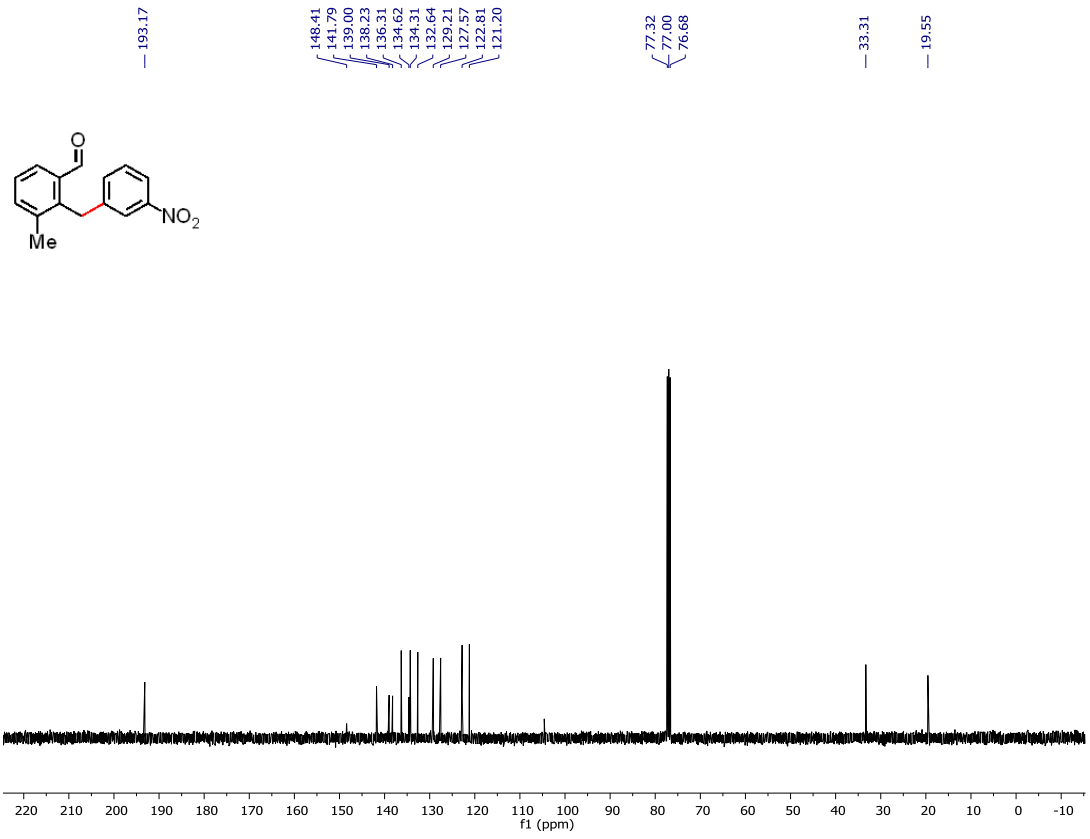
7.758
7.739
7.513
7.496
7.492
7.470
7.451
7.425
7.405
7.386
7.367
7.261
4.623
2.314
0.000
O
NO2
Me
0.92
0.91
0.88
0.96
3.76
2.00
2.98
f1 (ppm)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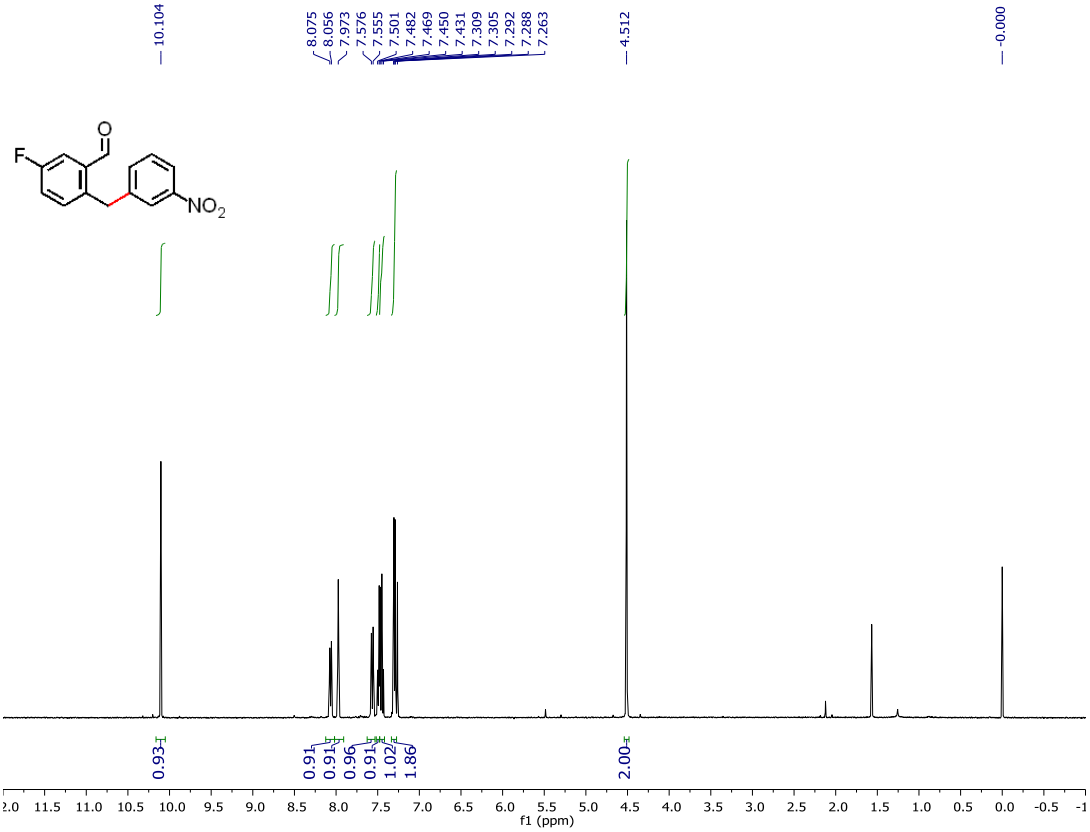
148.41
141.79
139.00
138.23
136.31
134.62
134.31
132.64
129.21
127.57
122.81
121.20
77.32
77.00
76.68
33.31
19.55
O
NO2
Me
f1 (ppm)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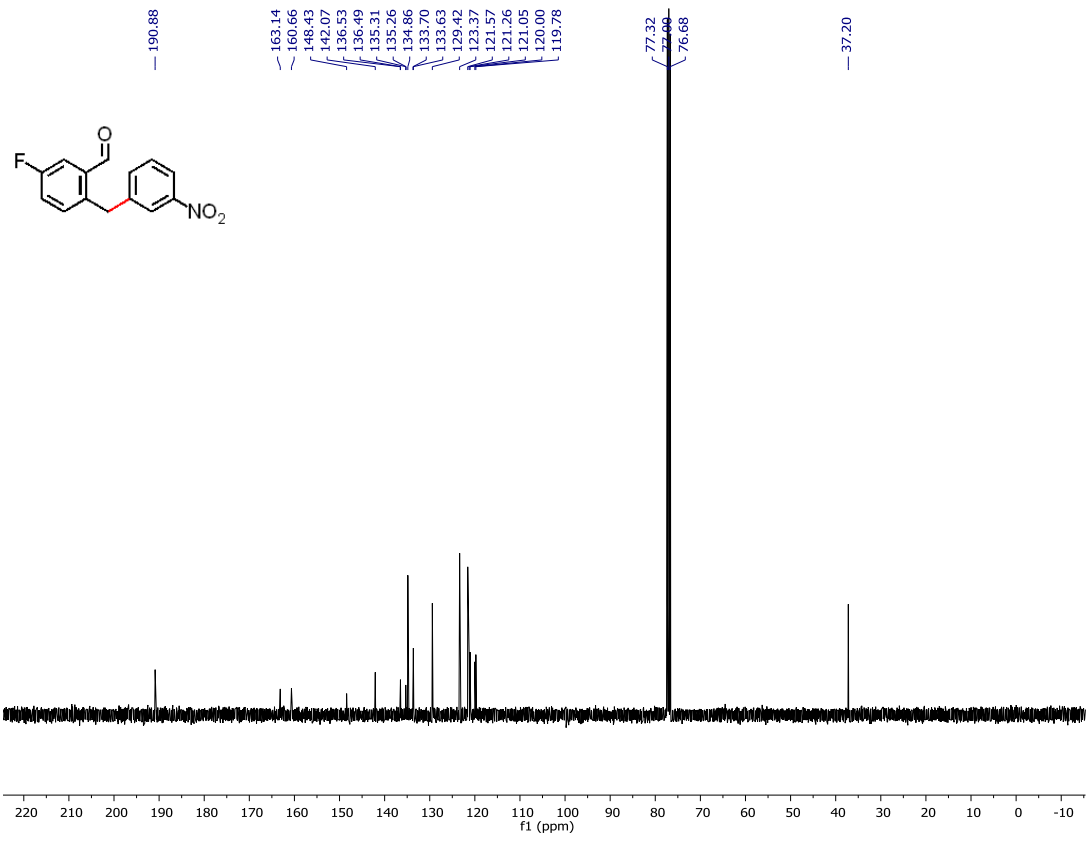
7.555
7.501
7.482
7.469
7.450
7.431
7.309
7.305
7.292
7.288
7.263
4.512
-0.000
O
F
NO2
0.93
0.91
0.91
0.96
0.91
1.02
1.86
2.00
f1 (ppm)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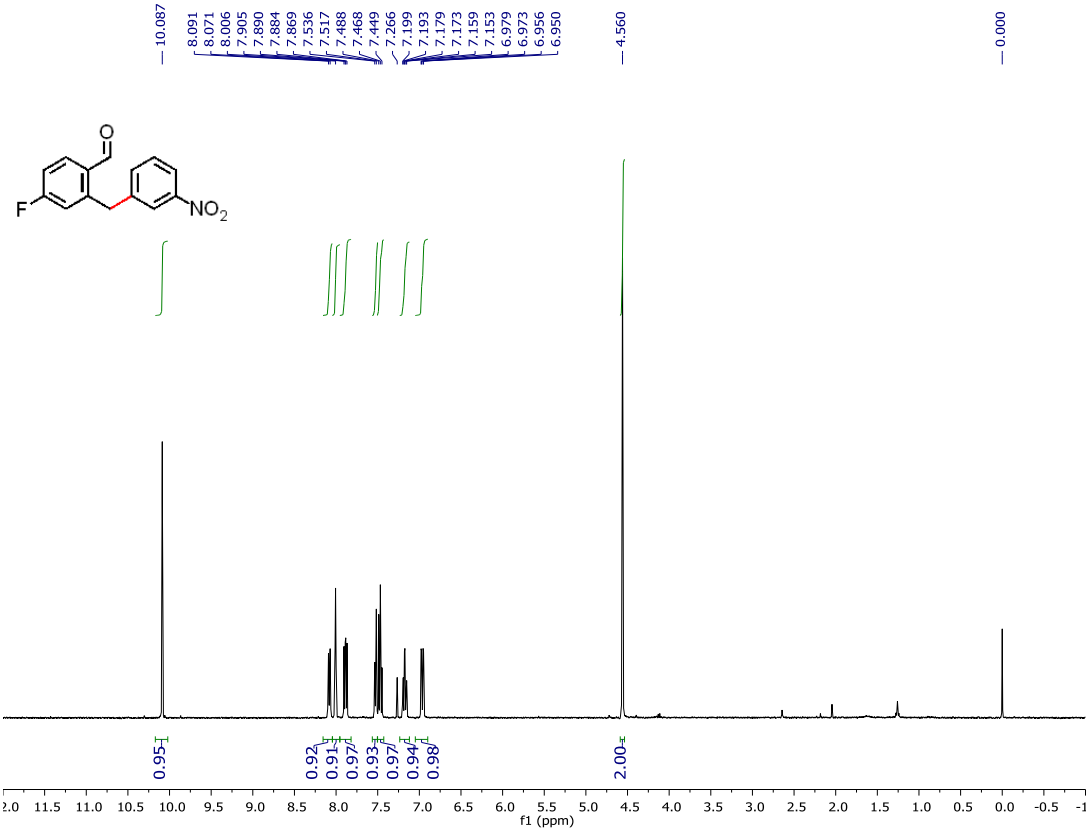
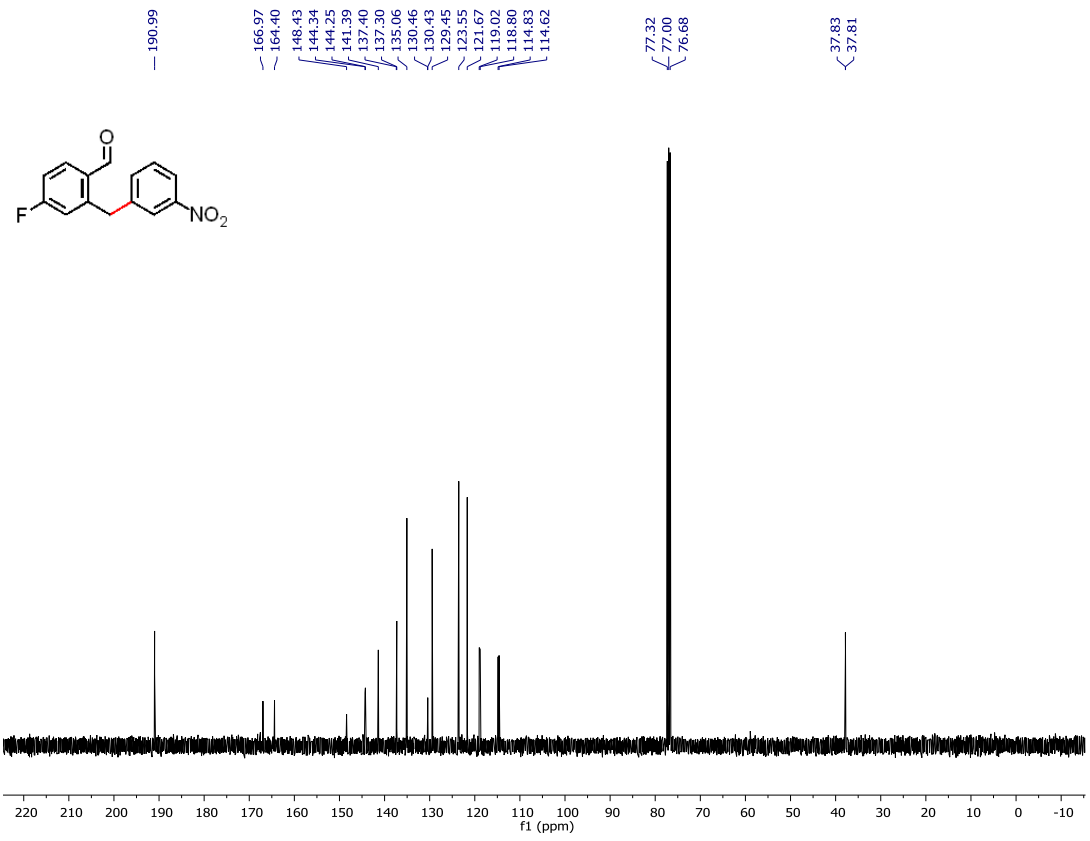
163.14
160.66
148.43
142.07
136.53
136.49
135.31
135.26
134.86
133.70
133.63
129.42
123.37
121.57
121.26
121.05
120.00
119.78
77.32
77.00
76.68
37.20
O
F
NO2
f1 (ppm)


10.087
8.091
8.071
8.006
7.905
7.890
7.884
7.869
7.536
7.517
7.488
7.468
7.449
7.266
7.199
7.193
7.179
7.173
7.159
7.153
6.979
6.973
6.956
6.950
4.560
0.000
O
F
NO2
0.95
0.92
0.91
0.97
0.93
0.97
0.94
0.98
2.00
f1 (ppm)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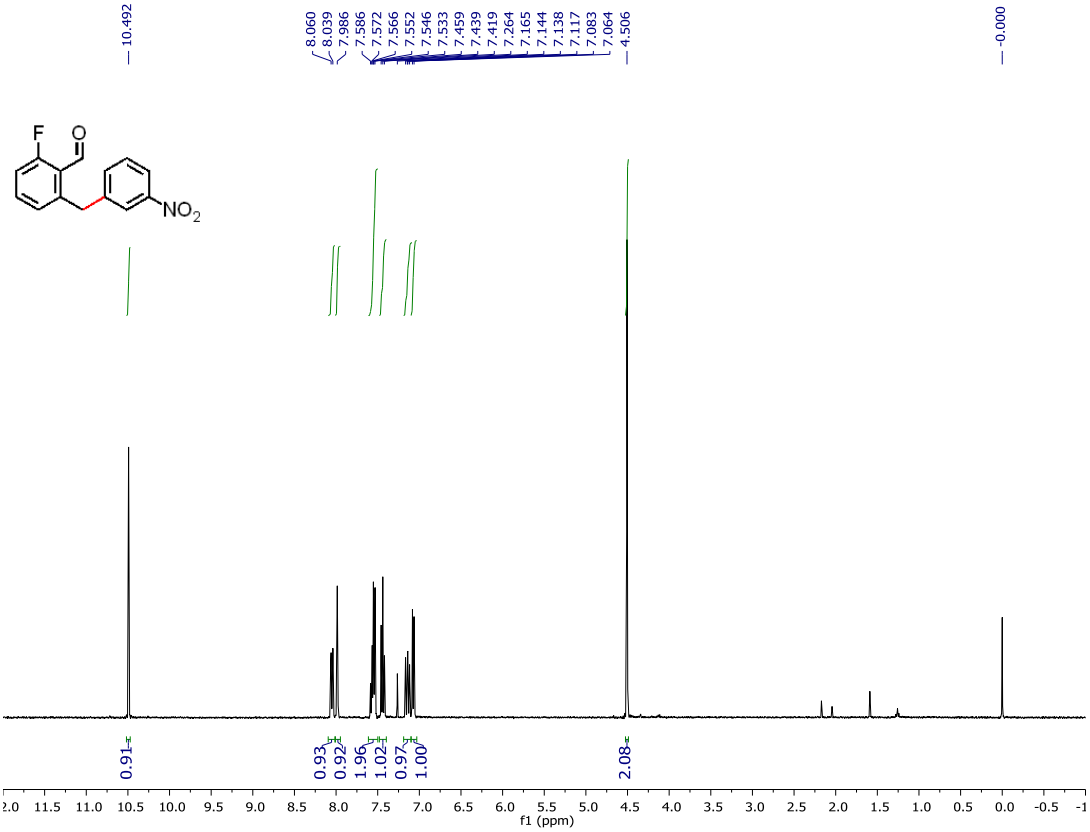
144.34
144.25
141.39
137.40
137.30
135.06
130.46
130.43
129.45
123.55
121.67
119.02
118.80
114.83
114.62
77.32
77.00
76.68
37.83
37.81
O
F
NO2
f1 (ppm)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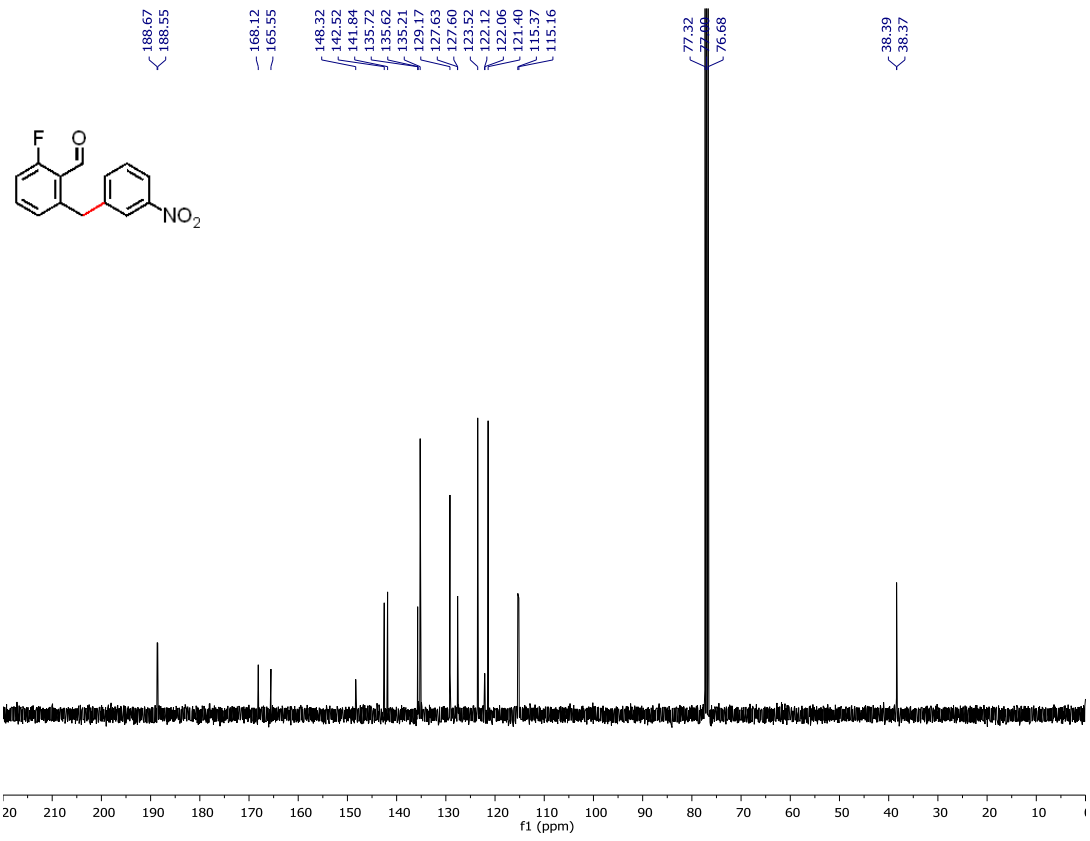
8.060
8.039
7.986
7.586
7.572
7.566
7.552
7.546
7.533
7.459
7.439
7.419
7.264
7.165
7.144
7.138
7.117
7.083
7.064
4.506
-0.000
F
O
NO2
0.91
0.93
0.92
1.96
1.02
0.97
1.00
2.08
f1 (ppm)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165.55
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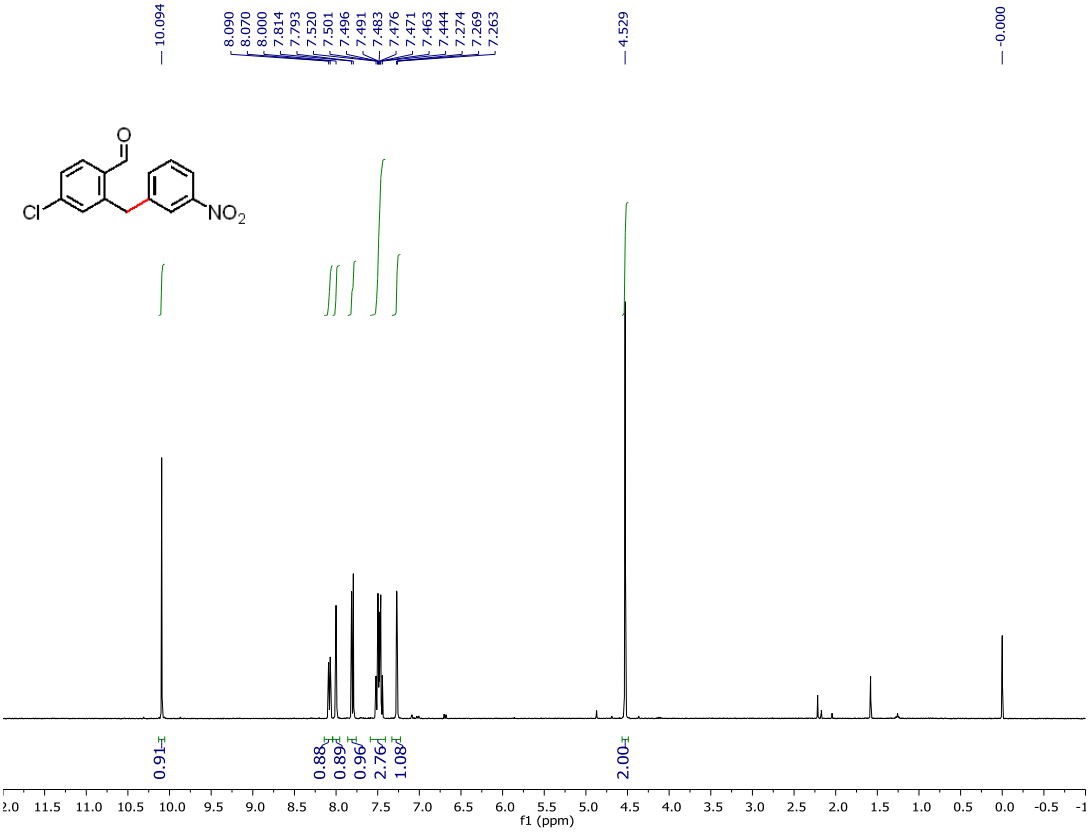
142.52
141.84
135.72
135.62
135.21
129.17
127.63
127.60
123.52
122.12
122.06
121.40
115.37
115.16
77.32
77.00
76.68
38.39
38.37
F
O
NO2
f1 (ppm)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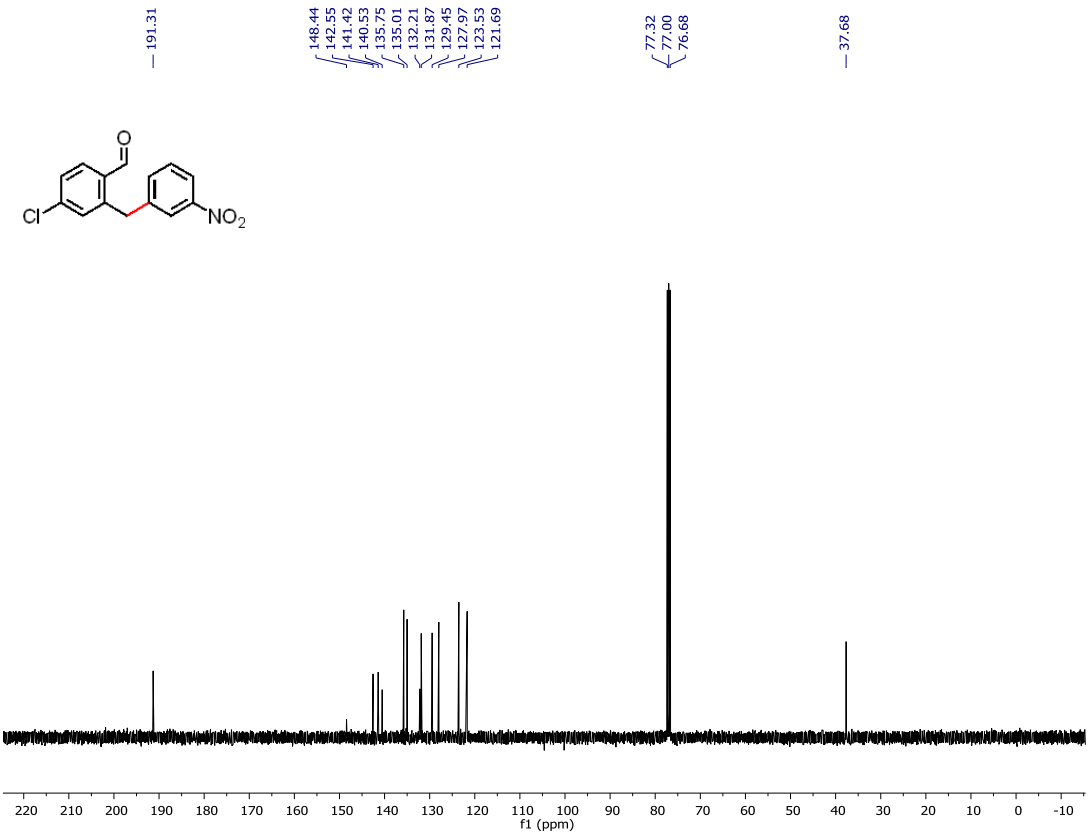
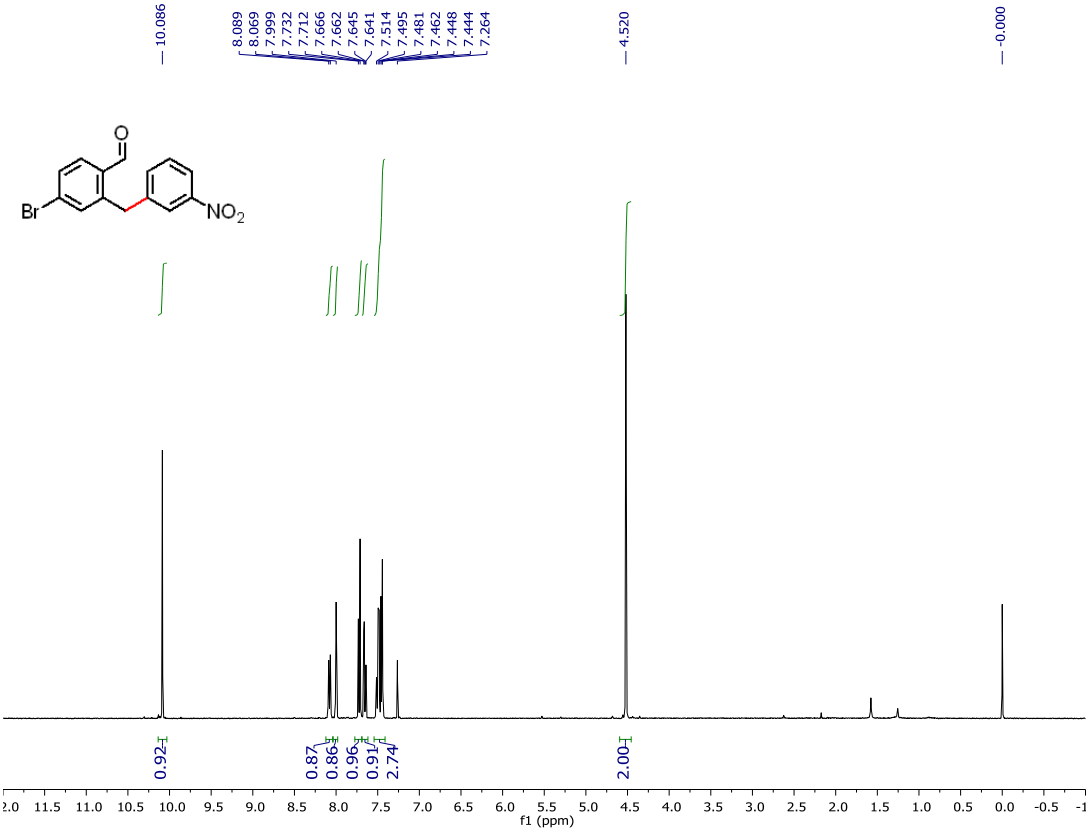
8.070
8.000
7.814
7.793
7.520
7.501
7.496
7.491
7.483
7.476
7.471
7.463
7.444
7.274
7.269
7.263
4.529
-0.000
Cl
O
NO2
0.91
0.88
0.89
0.96
2.76
1.08
2.00
f1 (ppm)


191.31
148.44
142.55
141.42
140.53
135.75
135.01
132.21
131.87
129.45
127.97
123.53
121.69
77.32
77.00
76.68
37.68
Cl
O
NO2
f1 (ppm)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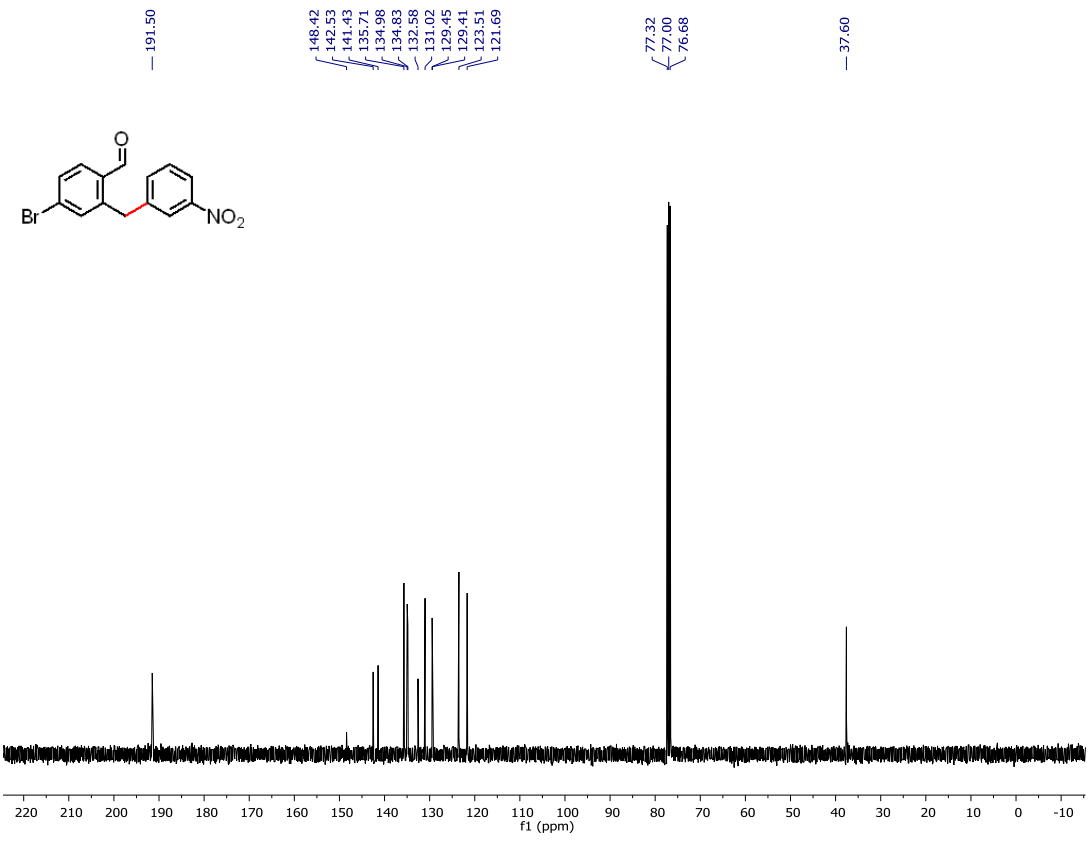
8.089
8.069
7.999
7.732
7.712
7.666
7.662
7.645
7.641
7.514
7.495
7.481
7.462
7.448
7.444
7.264
4.520
-0.000
Br
NO2
0.92
0.87
0.86
0.96
0.91
2.74
2.00
f1 (ppm)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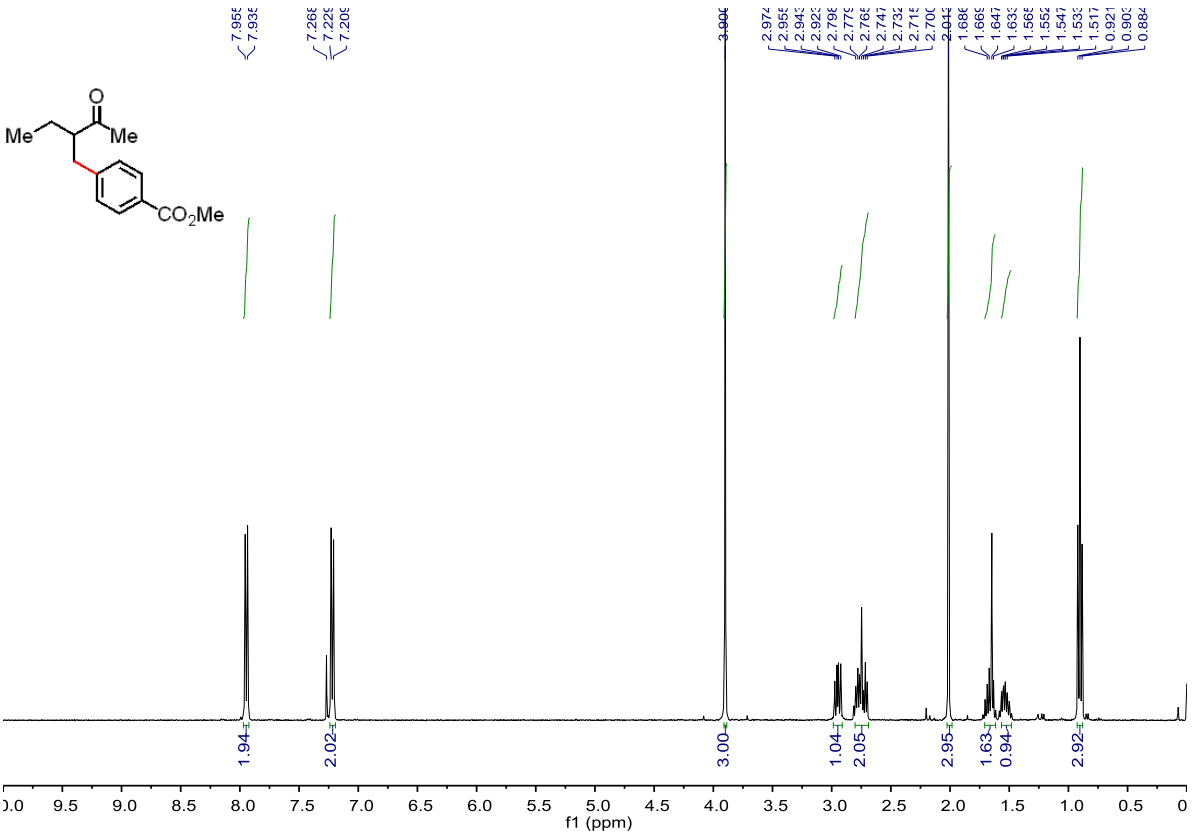
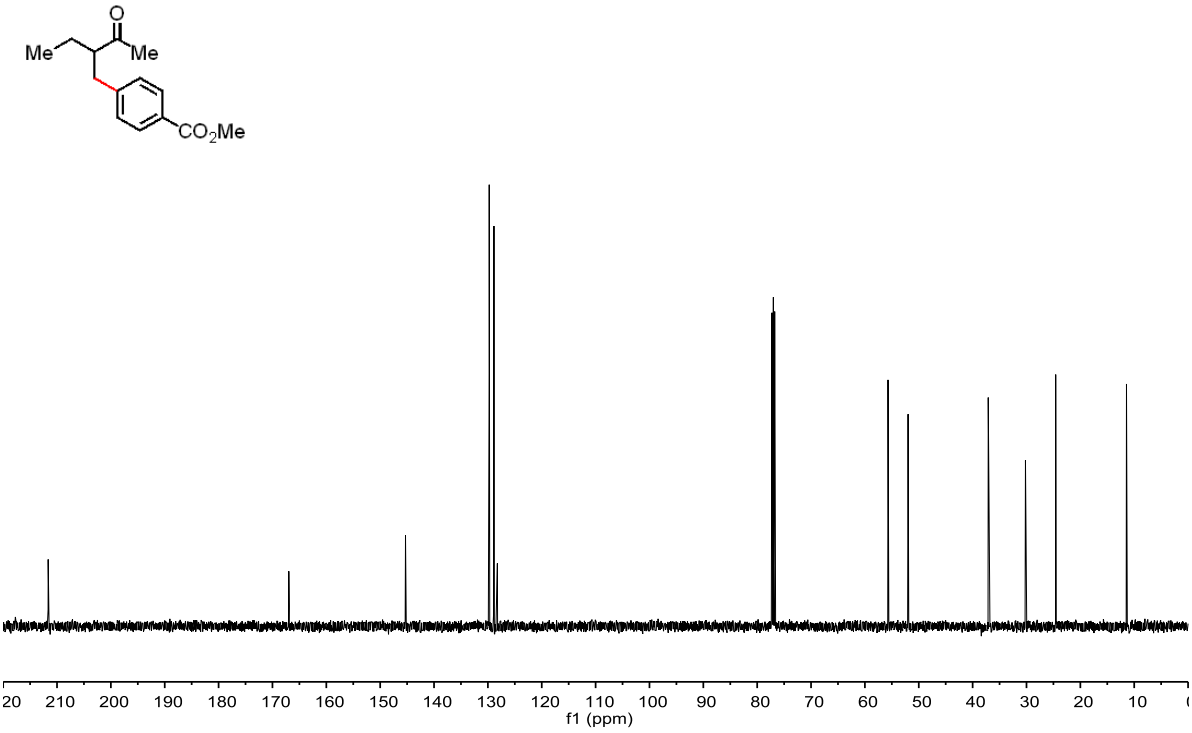
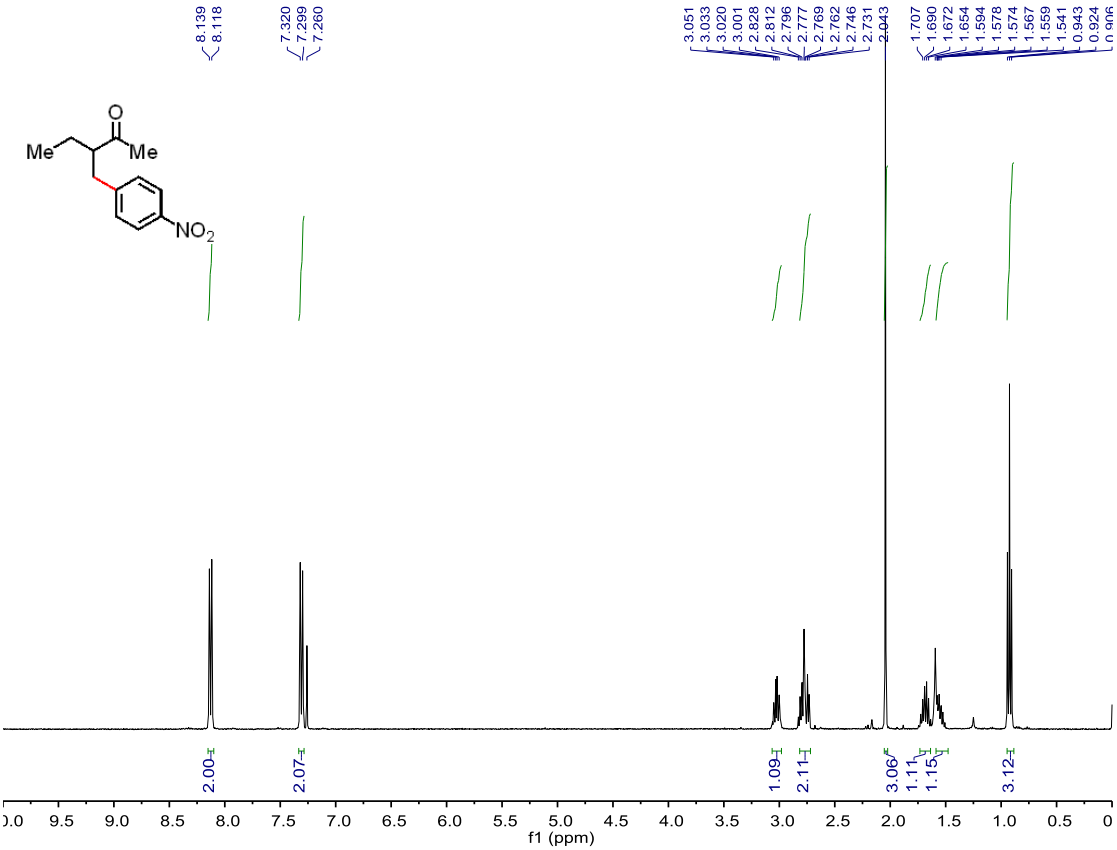
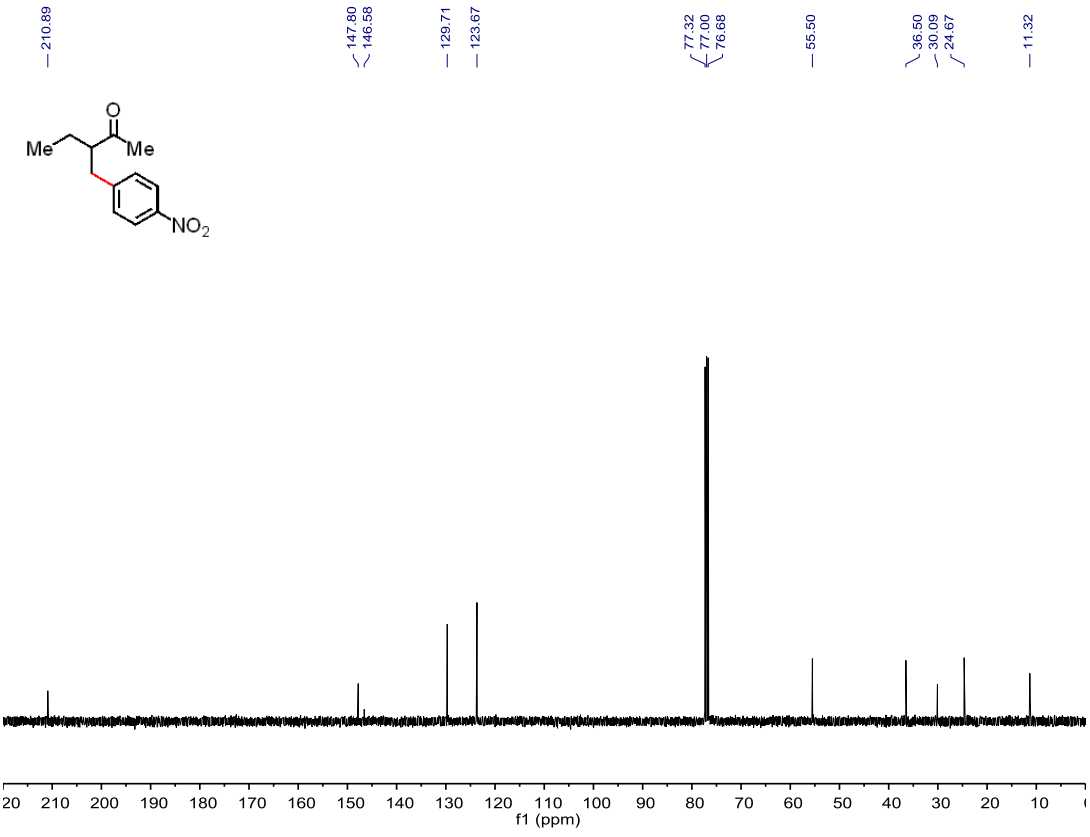
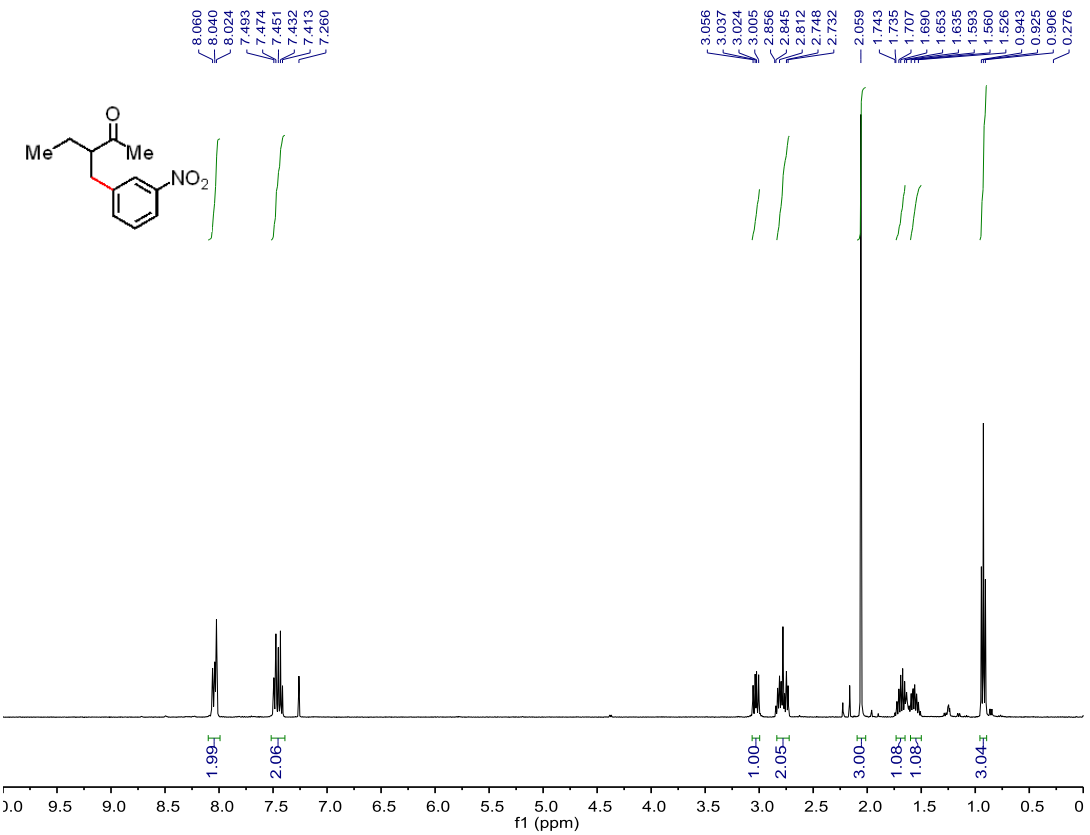
142.53
141.43
135.71
134.98
134.83
132.58
131.02
129.45
129.41
123.51
121.69
77.32
77.00
76.68
37.60
Br
NO2
f1 (ppm)


Me
O
Me
CO2Me
f1 (ppm)


Me
O
Me
CO2Me
f1 (ppm)


8.139
8.118
7.320
7.299
7.260
3.051
3.033
3.020
3.001
2.828
2.812
2.796
2.777
2.769
2.762
2.746
2.731
2.043
1.707
1.690
1.672
1.654
1.594
1.578
1.574
1.567
1.559
1.541
0.943
0.924
Me
O
Me
NO2
2.00
2.07
1.09
2.11
3.06
1.11
1.15
3.12
f1 (ppm)


210.89
147.80
146.58
129.71
123.67
77.32
77.00
76.68
55.50
36.50
30.09
24.67
11.32
Me
O
Me
NO2
f1 (ppm)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8.040
8.024
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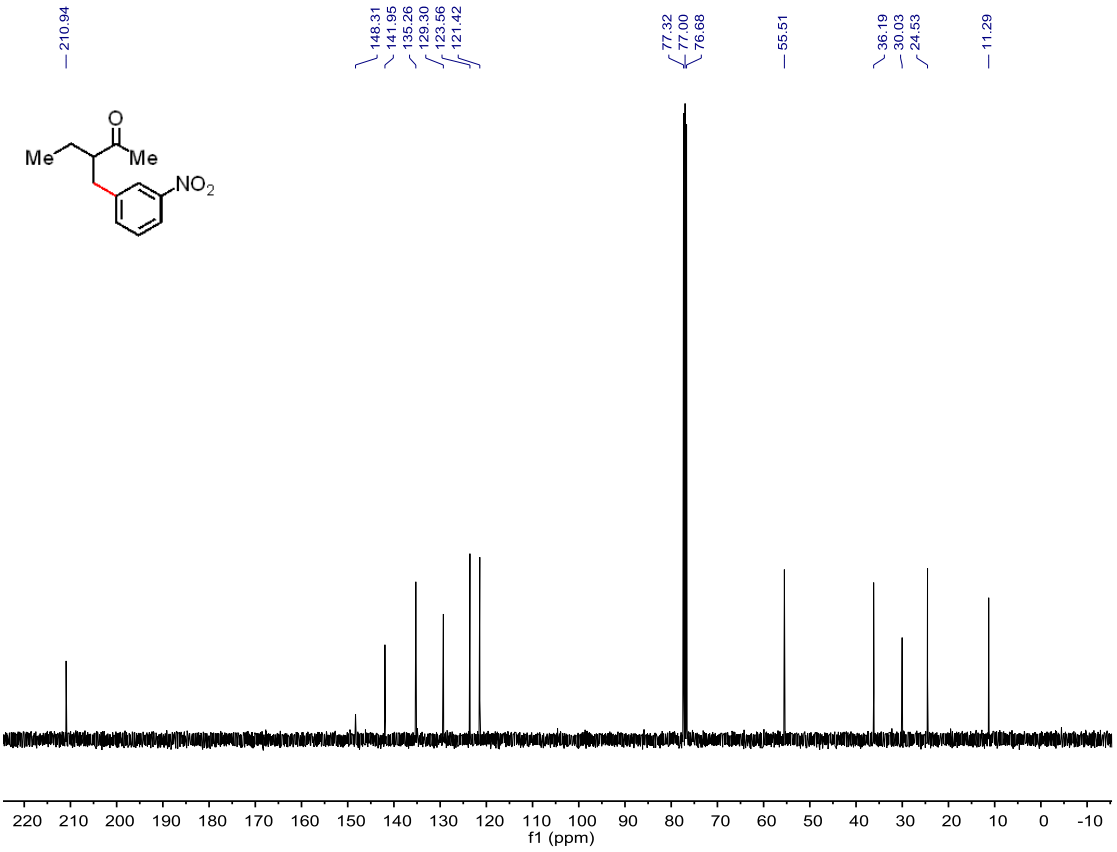
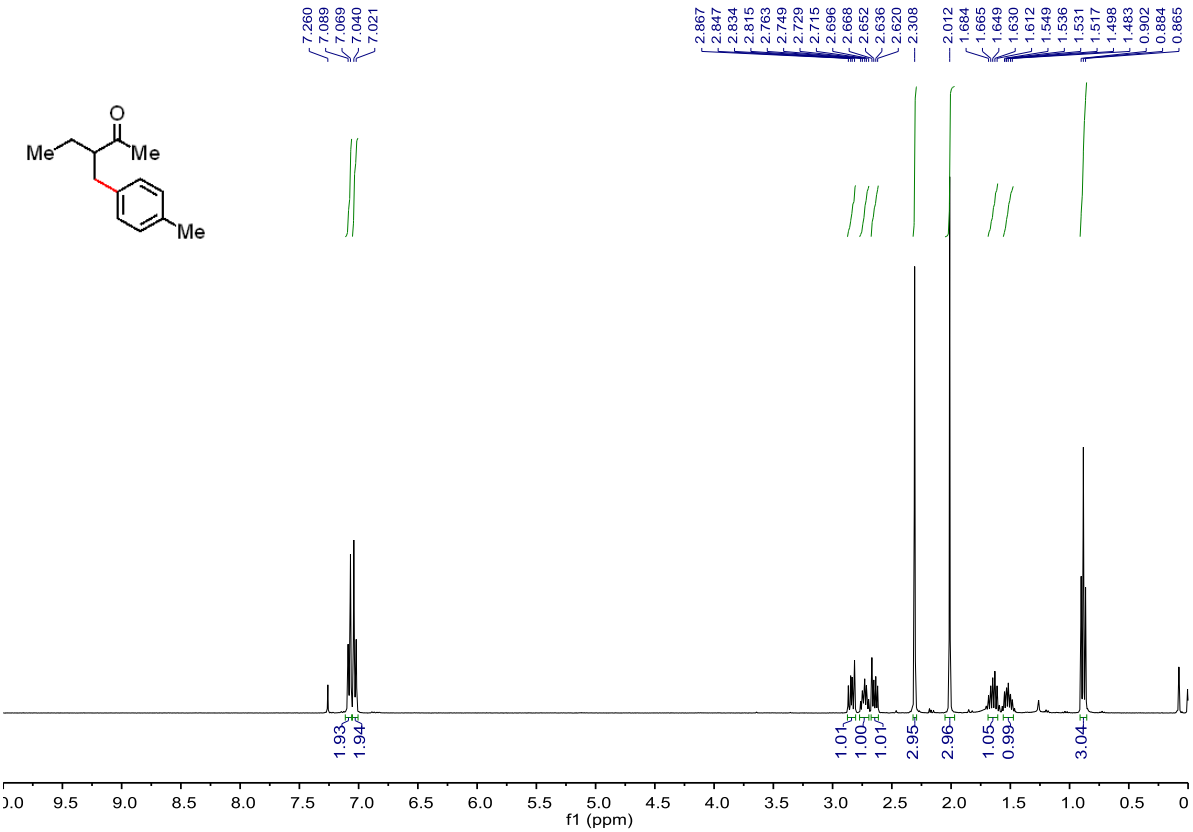
7.474
7.451
7.432
7.413
7.260
3.056
3.037
3.024
3.005
2.856
2.845
2.812
2.748
2.732
2.059
1.743
1.735
1.707
1.690
1.653
1.635
1.593
1.560
1.526
0.943
0.925
0.906
0.276
O
Me
Me
NO2
1.99
2.06
1.00
2.05
3.00
1.08
1.08
3.04
f1 (ppm)


210.94
148.31
141.95
135.26
129.30
123.56
121.42
77.32
77.00
76.68
55.51
36.19
30.03
24.53
11.29
O
Me
Me
NO2
f1 (ppm)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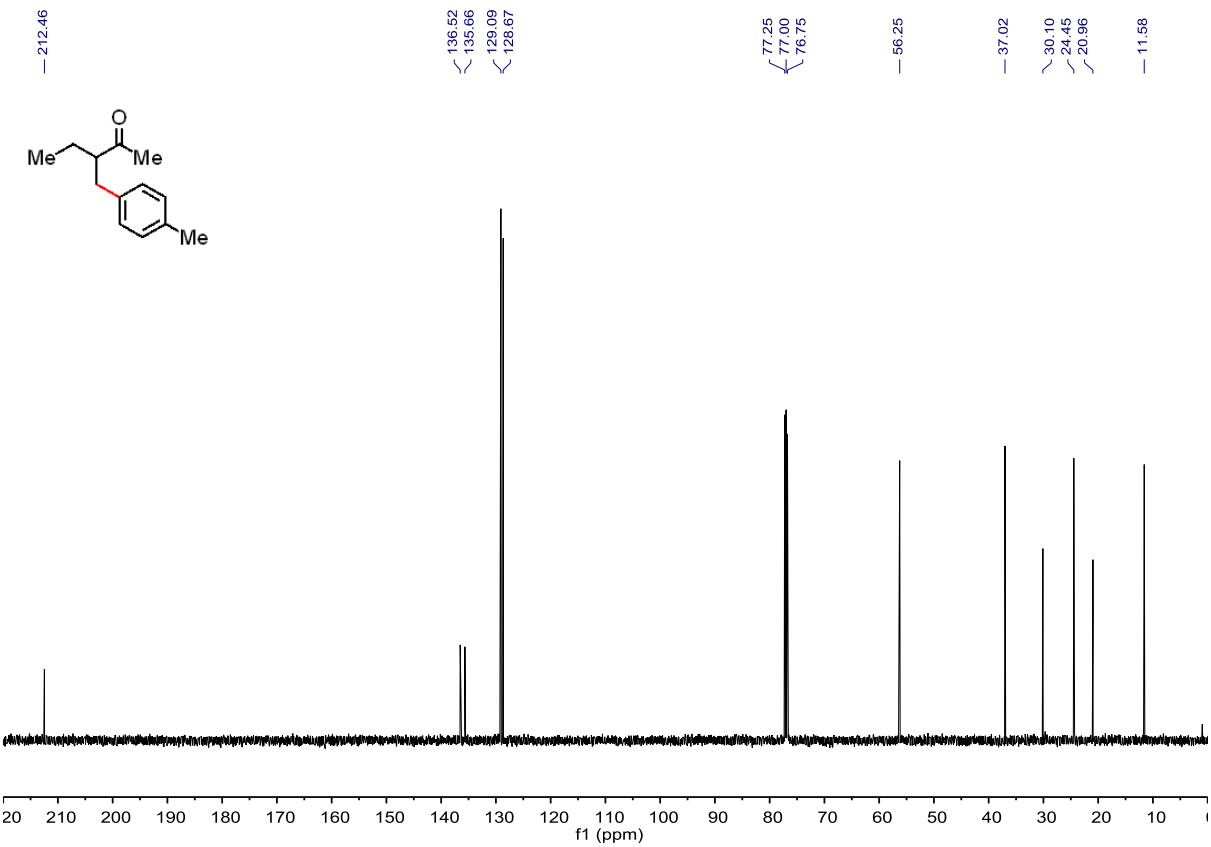
7.069
7.040
7.021
2.867
2.847
2.834
2.815
2.763
2.749
2.729
2.715
2.696
2.668
2.652
2.636
2.620
2.308
2.012
1.684
1.665
1.649
1.630
1.612
1.549
1.536
1.531
1.517
1.498
1.483
0.902
0.884
0.865
Me
Me
Me
1.93
1.94
1.01
1.00
1.01
2.95
2.96
1.05
0.99
3.04
f1 (ppm)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136.52
135.66
129.09
128.67
77.25
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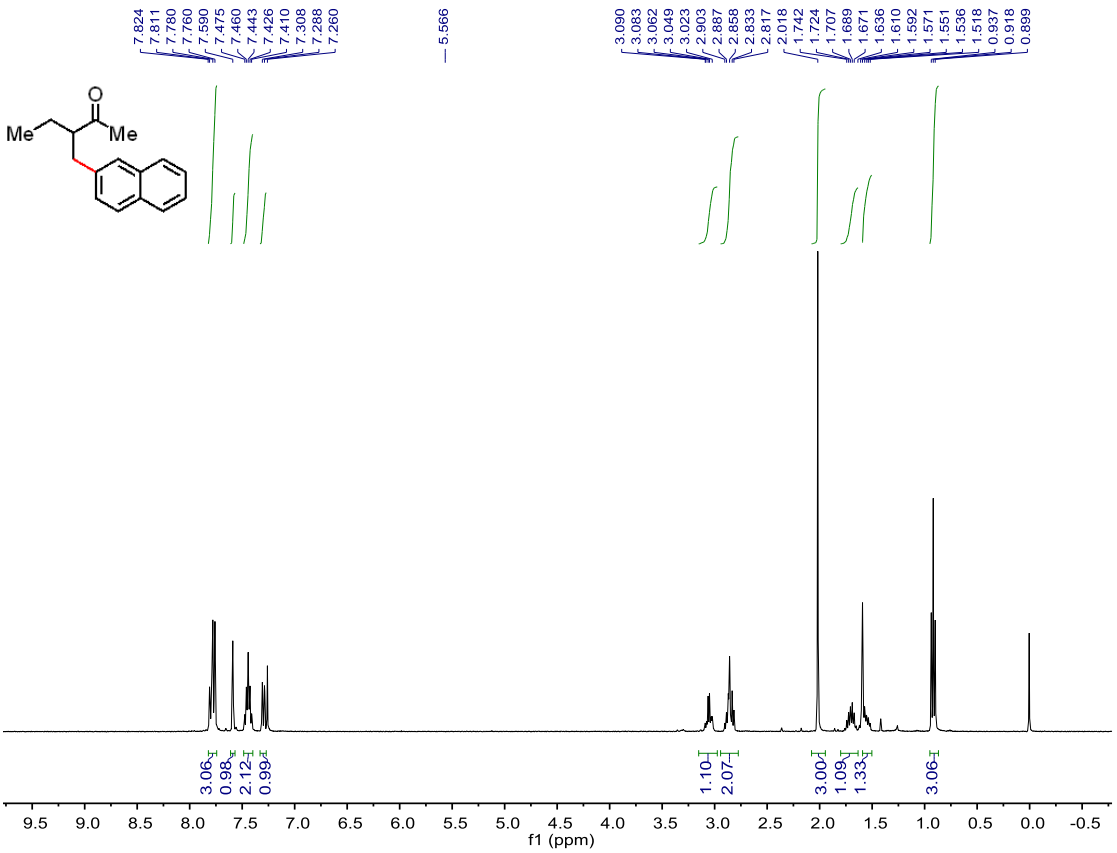
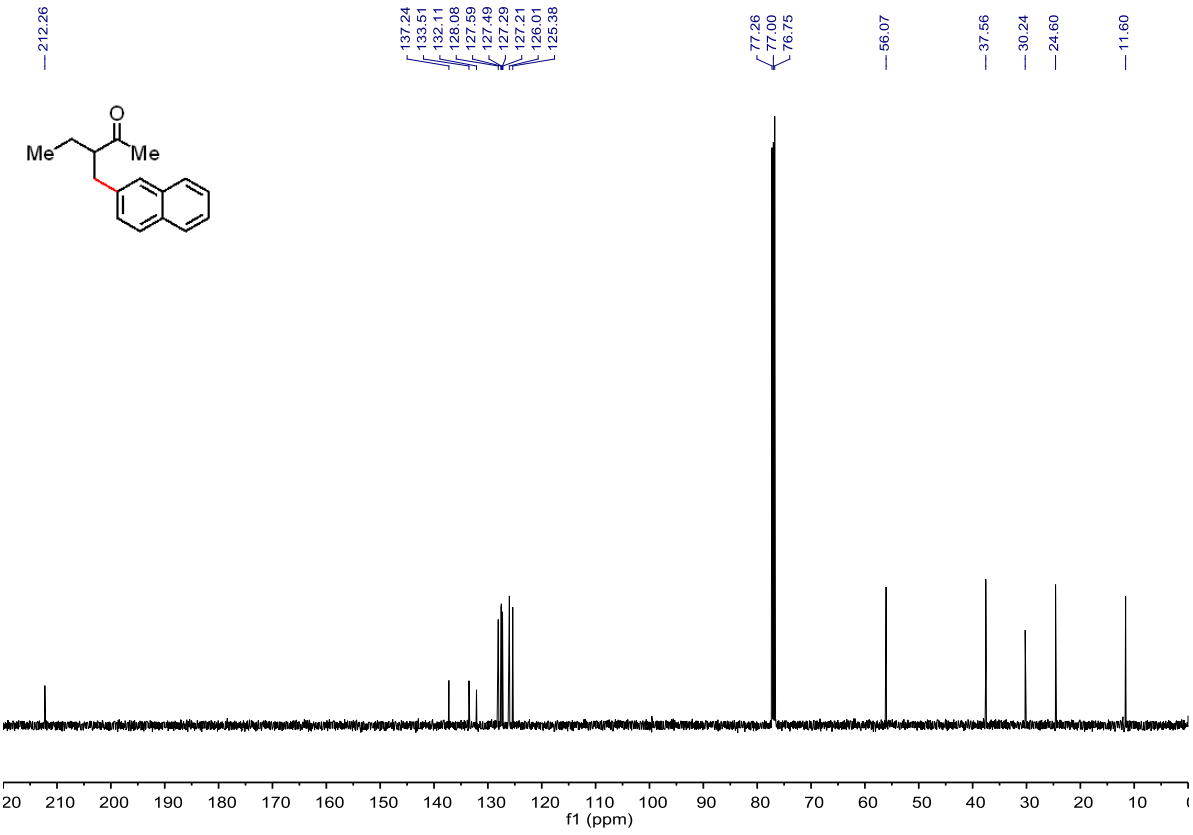
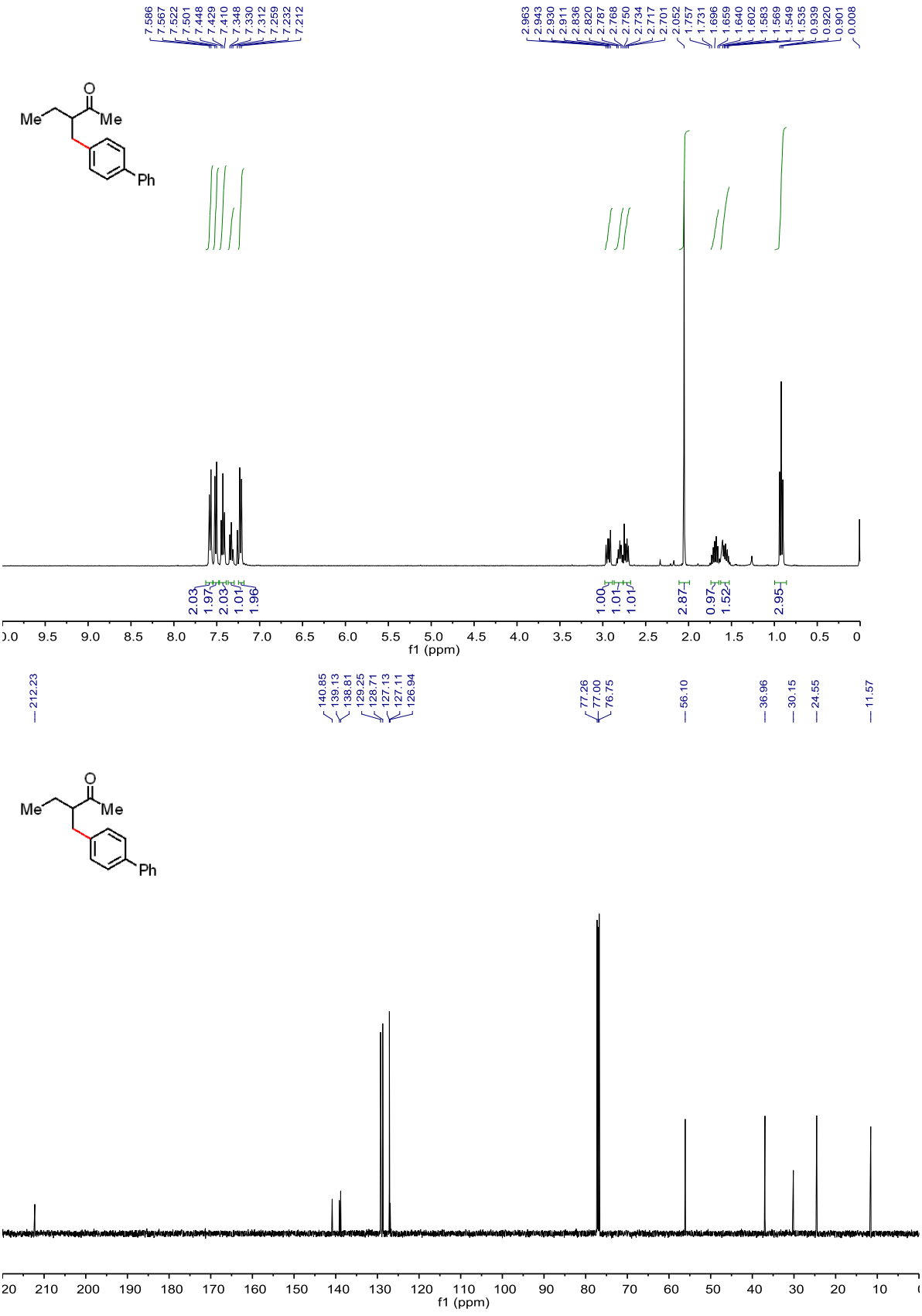
76.75
56.25
37.02
30.10
24.45
20.96
11.58
Me
Me
Me
f1 (ppm)


7.824
7.811
7.780
7.760
7.590
7.475
7.460
7.443
7.426
7.410
7.308
7.288
7.260
5.566
3.090
3.083
3.062
3.049
3.023
2.903
2.887
2.858
2.833
2.817
2.018
1.742
1.724
1.707
1.689
1.671
1.636
1.610
1.592
1.571
1.551
1.536
1.518
0.937
0.918
0.899
Me
O
Me
3.06
0.98
2.12
0.99
1.10
2.07
3.00
1.09
1.33
3.06
f1 (ppm)


212.26
137.24
133.51
132.11
128.08
127.59
127.49
127.29
127.21
126.01
125.38
77.26
77.00
76.75
56.07
37.56
30.24
24.60
11.60
Me
O
Me
f1 (ppm)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7.501
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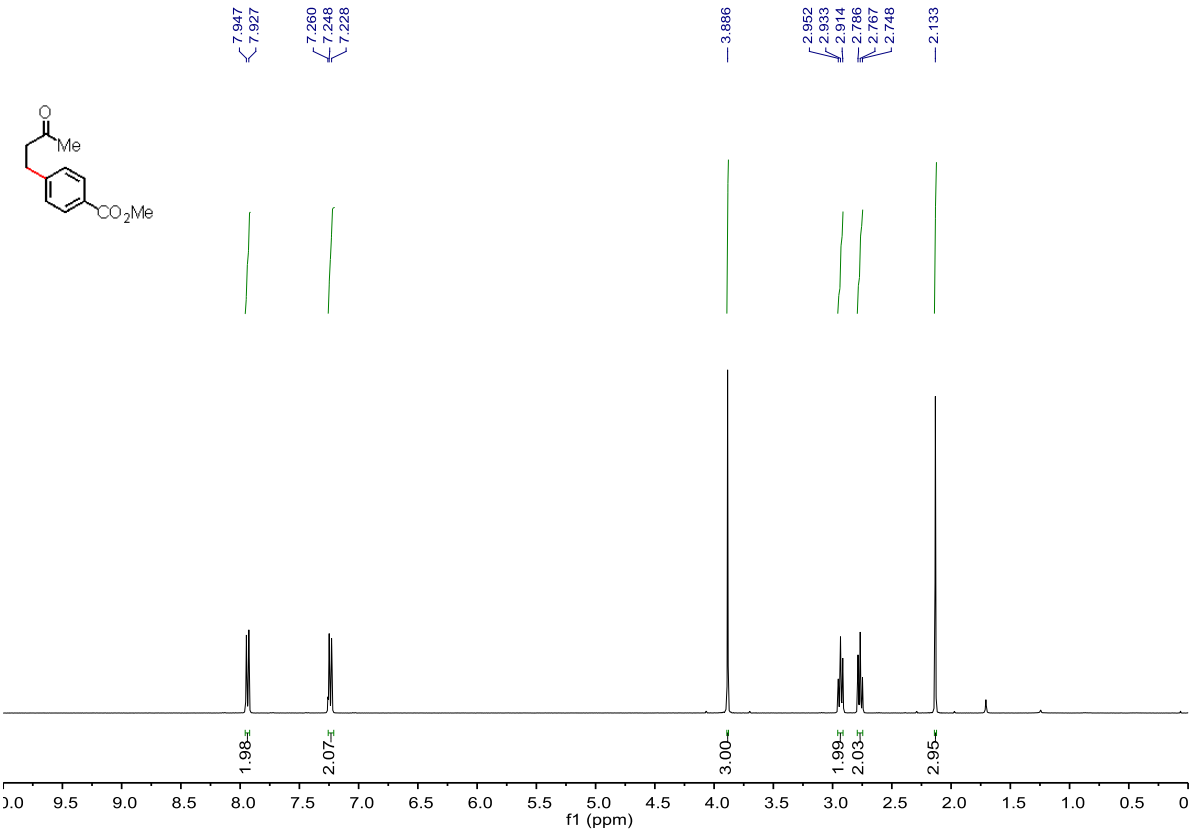
7.429
7.410
7.348
7.330
7.312
7.259
7.232
7.212
2.963
2.943
2.930
2.911
2.836
2.820
2.787
2.768
2.750
2.734
2.717
2.701
2.052
1.757
1.731
1.696
1.659
1.640
1.602
1.583
1.569
1.549
1.535
0.939
0.920
0.901
0.008
O
Me
Me
Ph
2.03
1.97
2.03
1.01
1.96
1.00
1.01
1.01
2.87
0.97
1.52
2.95
f1 (ppm)
212.23
140.85
139.13
138.81
129.25
128.71
127.13
127.11
126.94
77.26
77.00
76.75
56.10
36.96
30.15
24.55
11.57
f1 (ppm)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7.248
7.228
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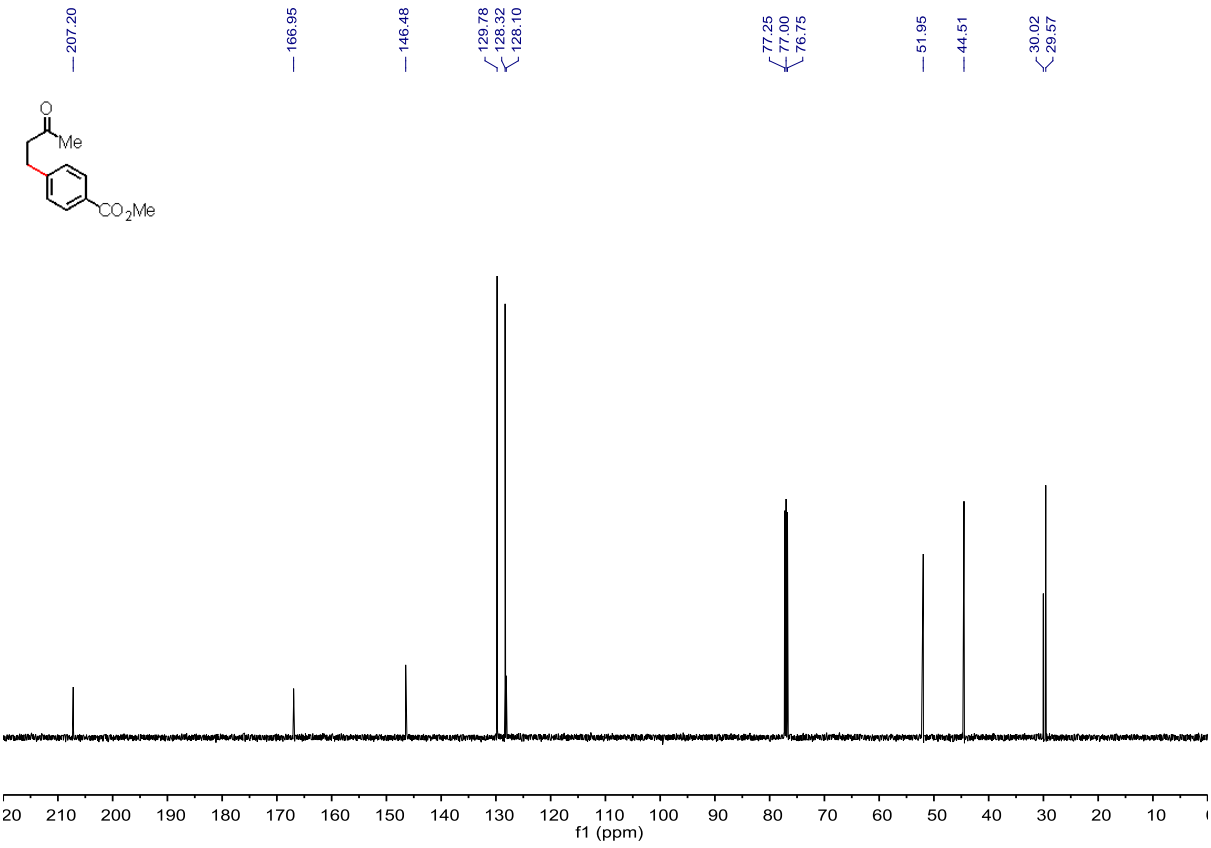
2.952
2.933
2.914
2.786
2.767
2.748
2.133
O
Me
CO2Me
1.98
2.07
3.00
1.99
2.03
2.95
f1 (ppm)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166.95
146.48
129.78
128.32
128.10
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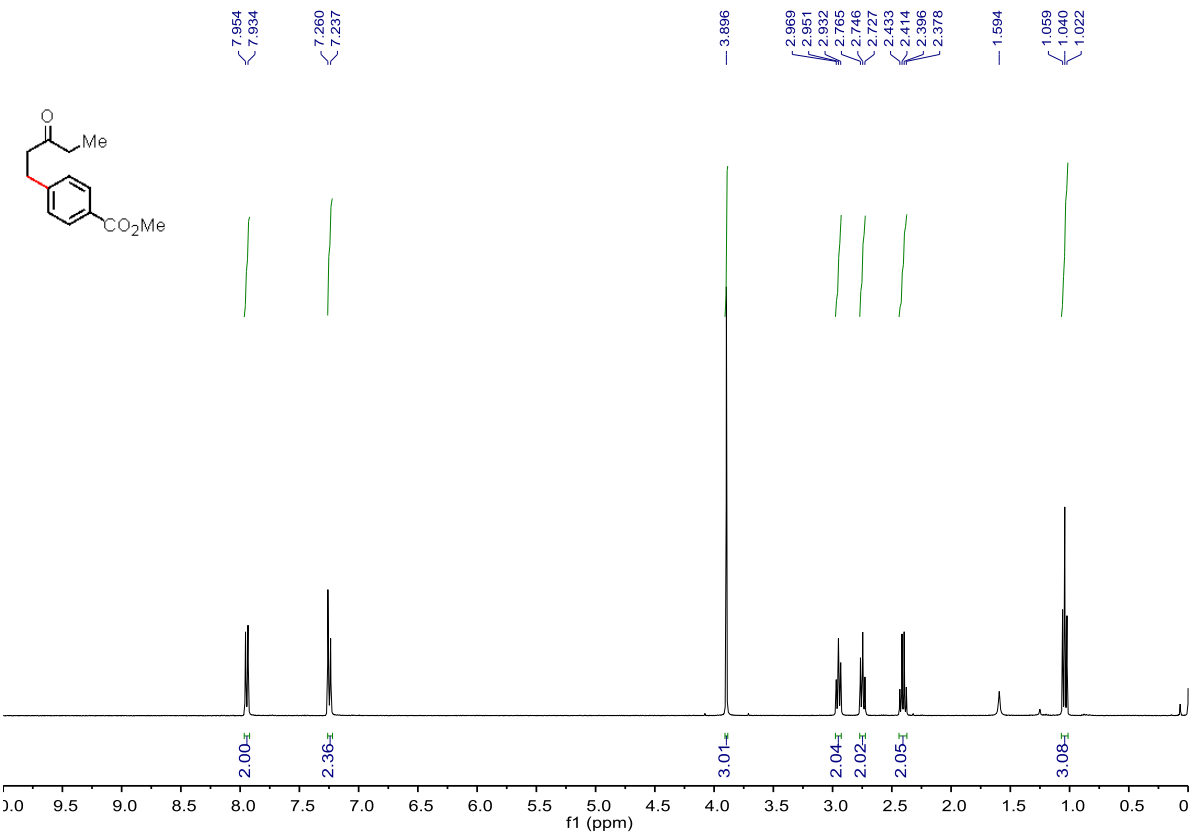
77.00
76.75
51.95
44.51
30.02
29.57
O
Me
CO2Me
f1 (ppm)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7.260
7.237
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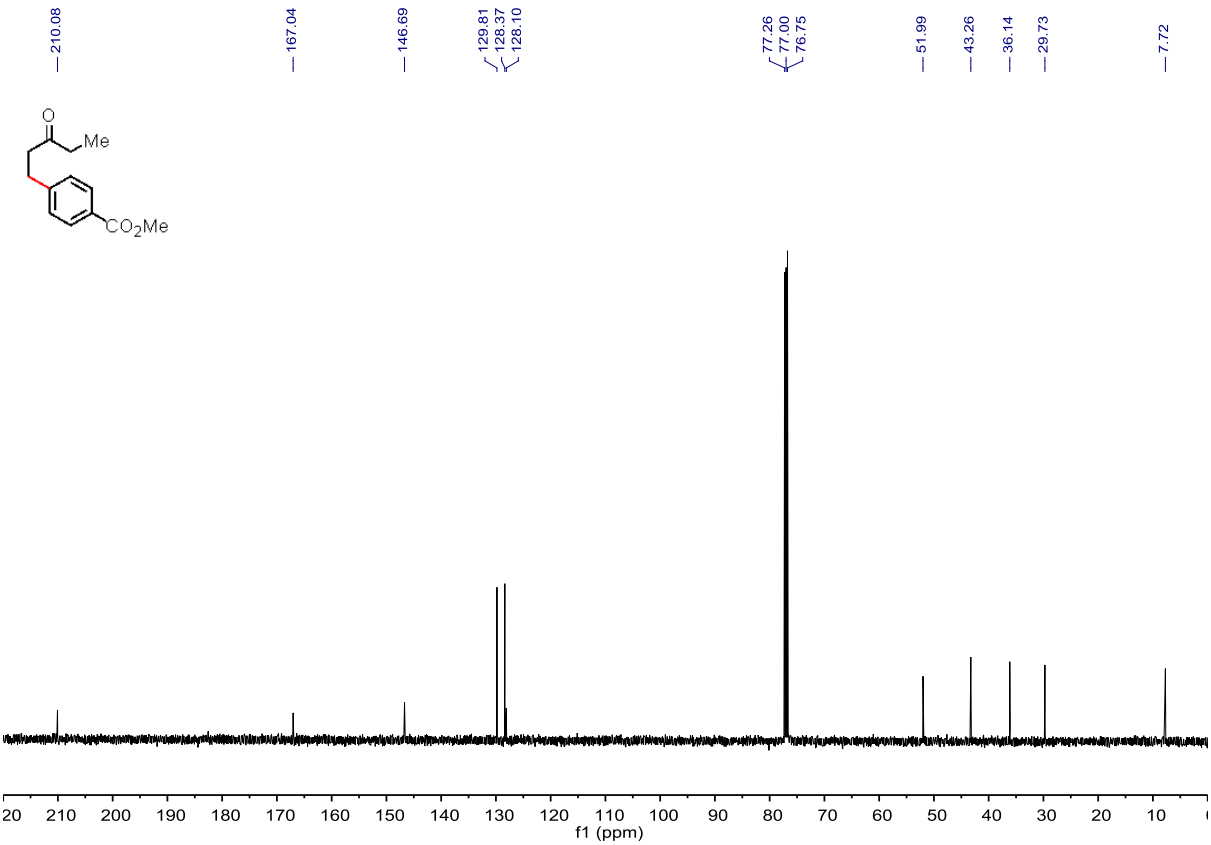
2.969
2.951
2.932
2.765
2.746
2.727
2.433
2.414
2.396
2.378
1.594
1.059
1.040
1.022
Me
CO2Me
2.00
2.36
3.01
2.04
2.02
2.05
3.08
f1 (ppm)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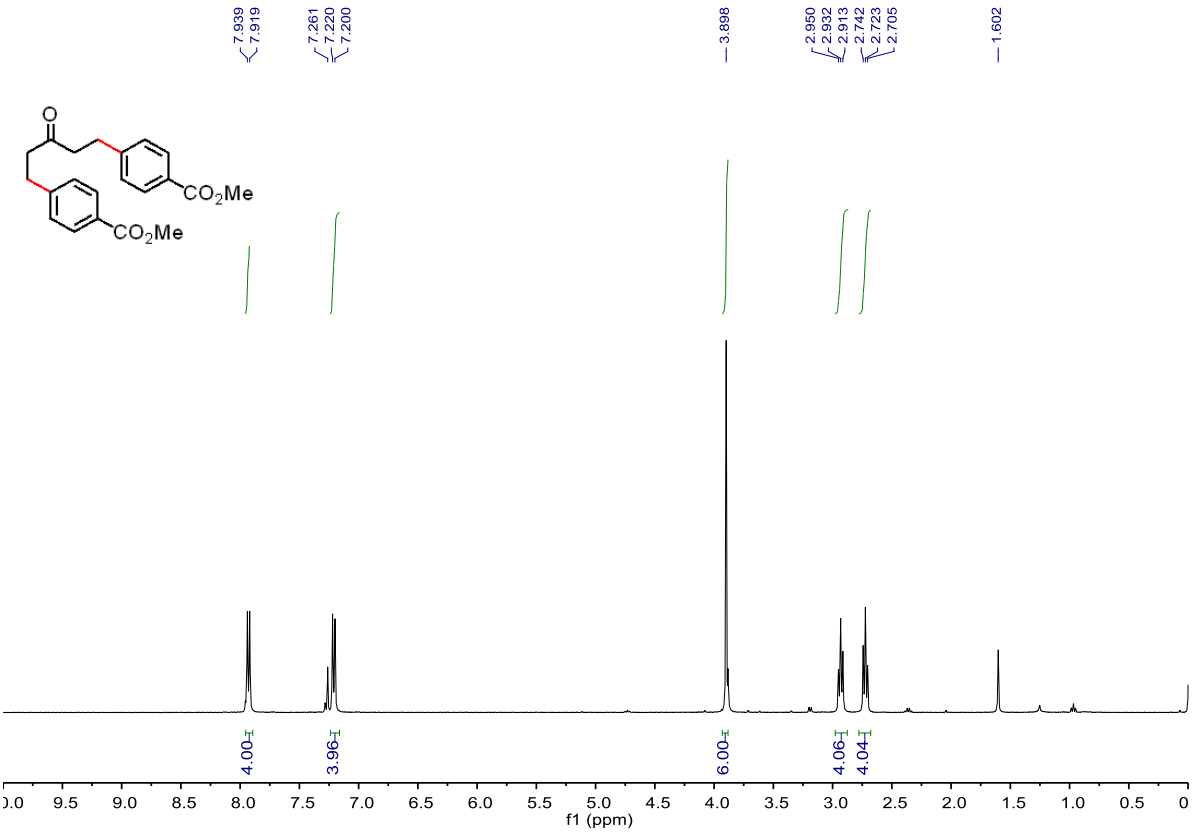
167.04
146.69
129.81
128.37
128.10
77.26
77.00
76.75
51.99
43.26
36.14
29.73
7.72
Me
CO2Me
f1 (ppm)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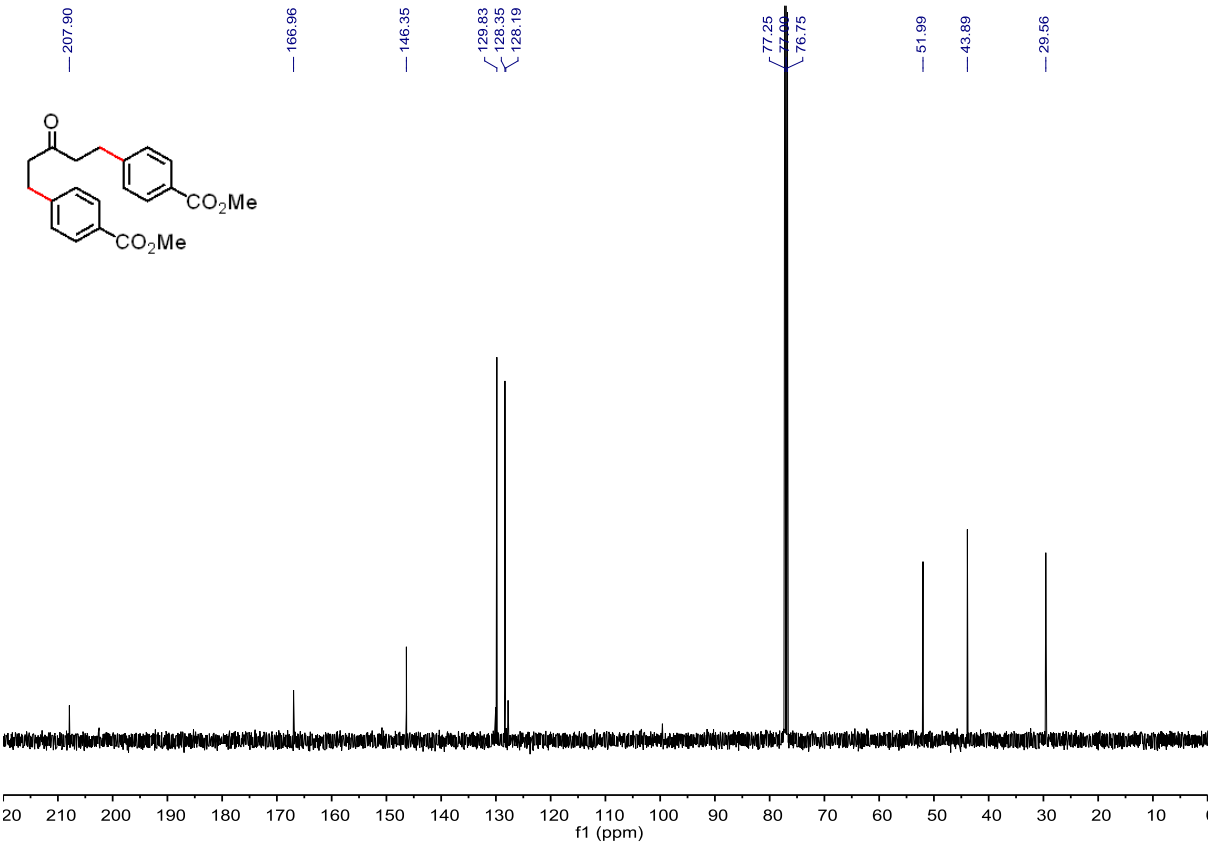
7.919
7.261
7.220
7.200
3.898
2.950
2.932
2.913
2.742
2.723
2.705
1.602
CO2Me
CO2Me
4.00
3.96
6.00
4.06
4.04
f1 (ppm)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77.00
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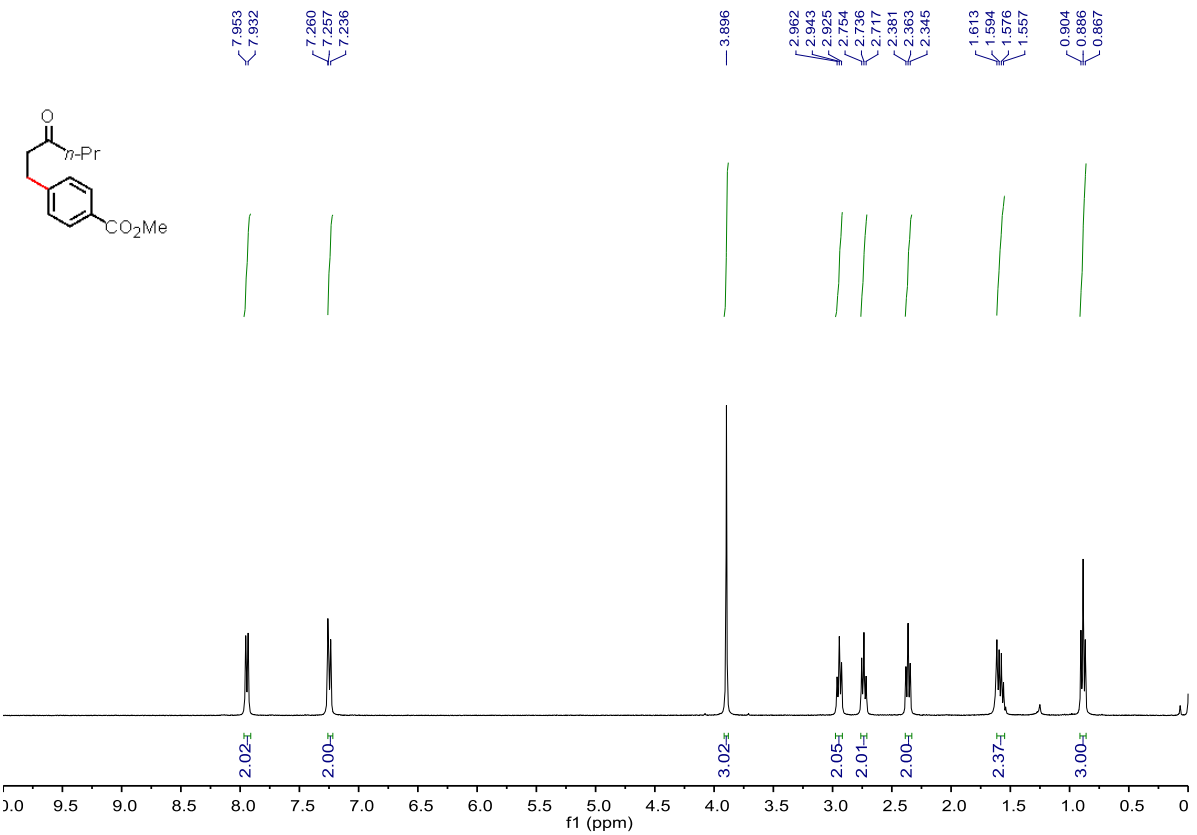
51.99
43.89
29.56
CO2Me
CO2Me
f1 (ppm)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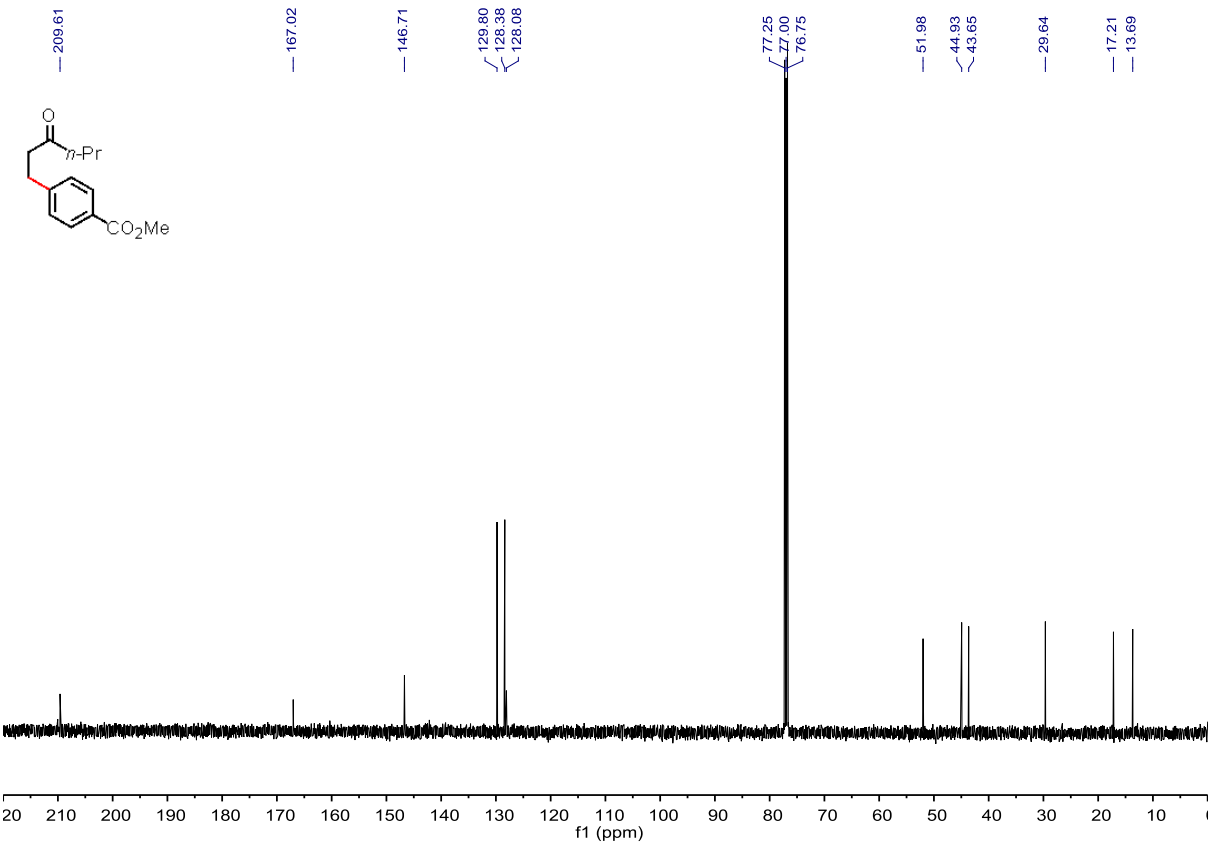
2.943
2.925
2.754
2.736
2.717
2.381
2.363
2.345
1.613
1.594
1.576
1.557
0.904
0.886
0.867
O
n-Pr
CO2Me
2.02
2.00
3.02
2.05
2.01
2.00
2.37
3.00
f1 (ppm)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128.38
128.08
77.25
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76.75
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44.93
43.65
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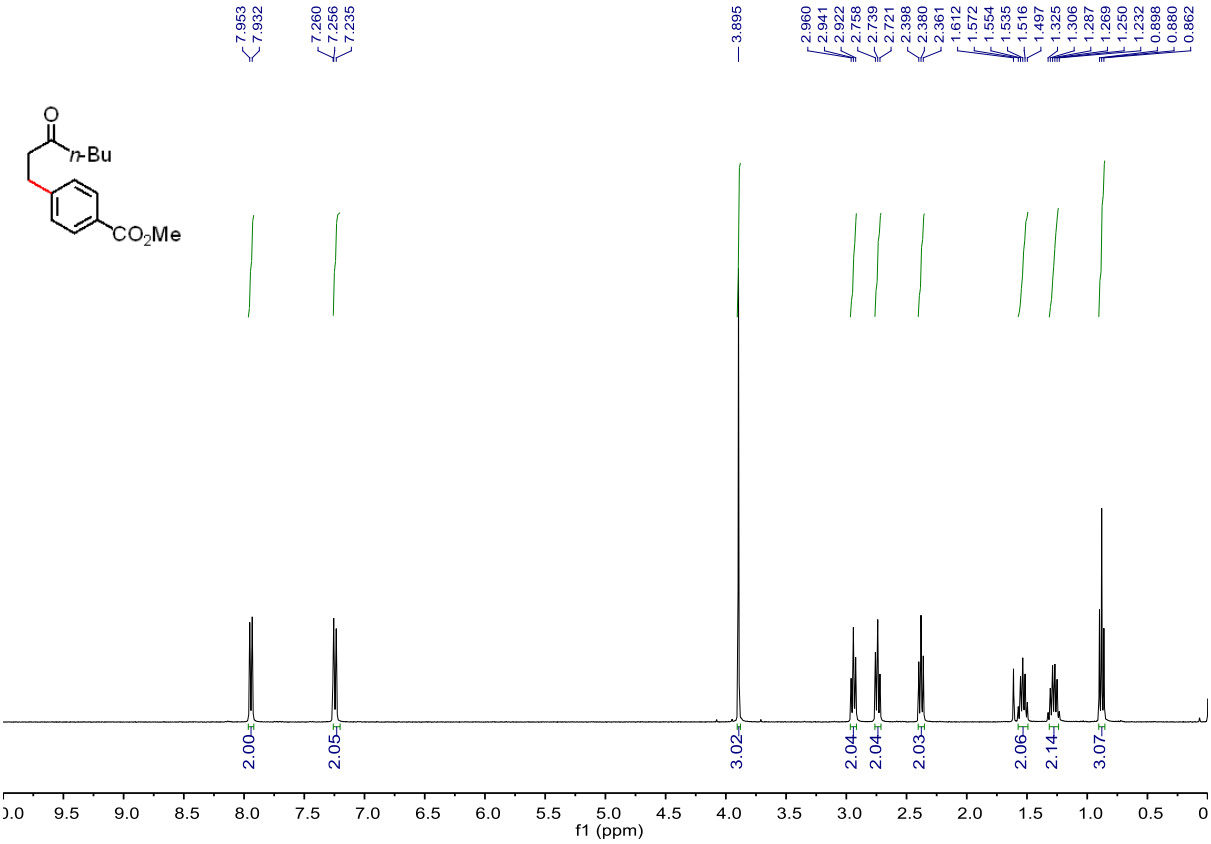
17.21
13.69
O
n-Pr
CO2Me
f1 (ppm)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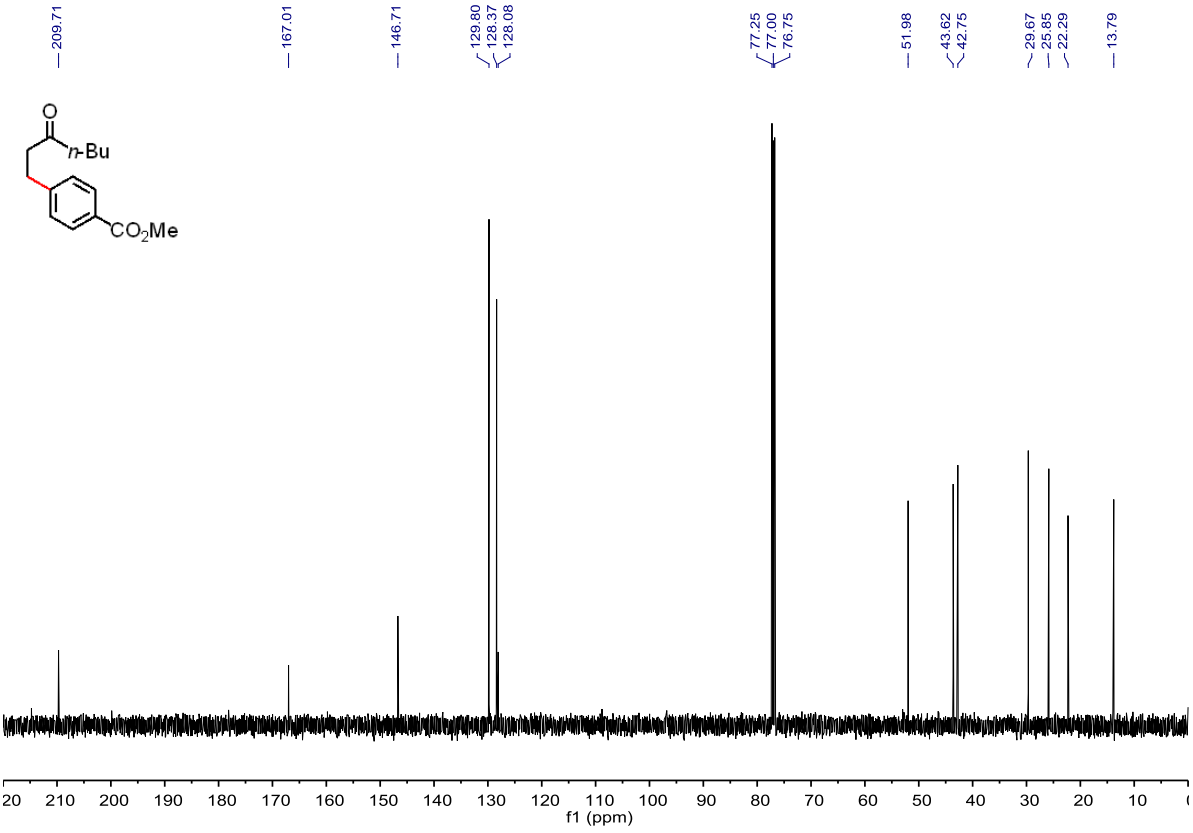
7.932
7.260
7.256
7.235
3.895
2.960
2.941
2.922
2.758
2.739
2.721
2.398
2.380
2.361
1.612
1.572
1.554
1.535
1.516
1.497
1.325
1.306
1.287
1.269
1.250
1.232
0.898
0.880
0.862
n-Bu
CO2Me
2.00
2.05
3.02
2.04
2.04
2.03
2.06
2.14
3.07
f1 (ppm)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128.37
128.08
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77.00
76.75
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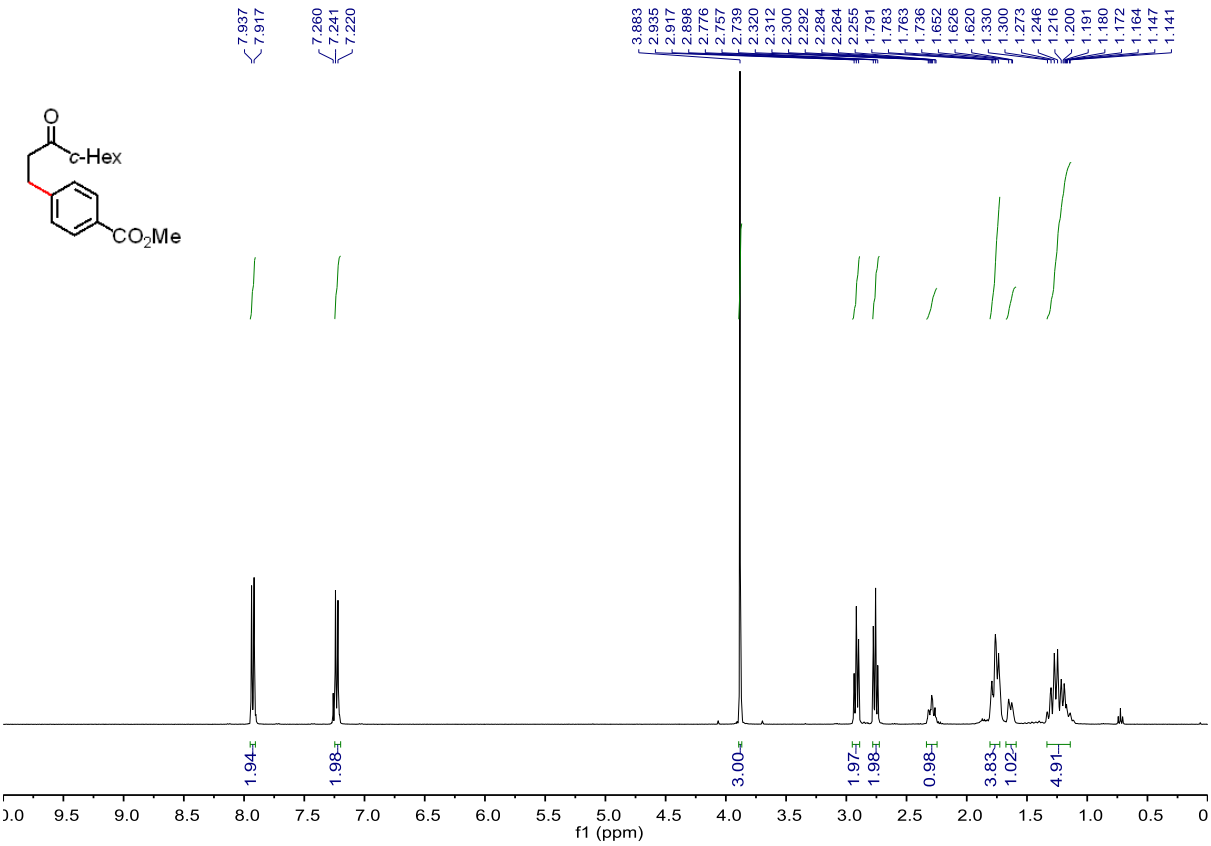
43.62
42.75
29.67
25.85
22.29
13.79
n-Bu
CO2Me
f1 (ppm)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2.739
2.320
2.312
2.300
2.292
2.284
2.264
2.255
1.791
1.783
1.763
1.736
1.652
1.626
1.620
1.330
1.300
1.273
1.246
1.216
1.200
1.191
1.180
1.172
1.164
1.147
1.141
c-Hex
CO2Me
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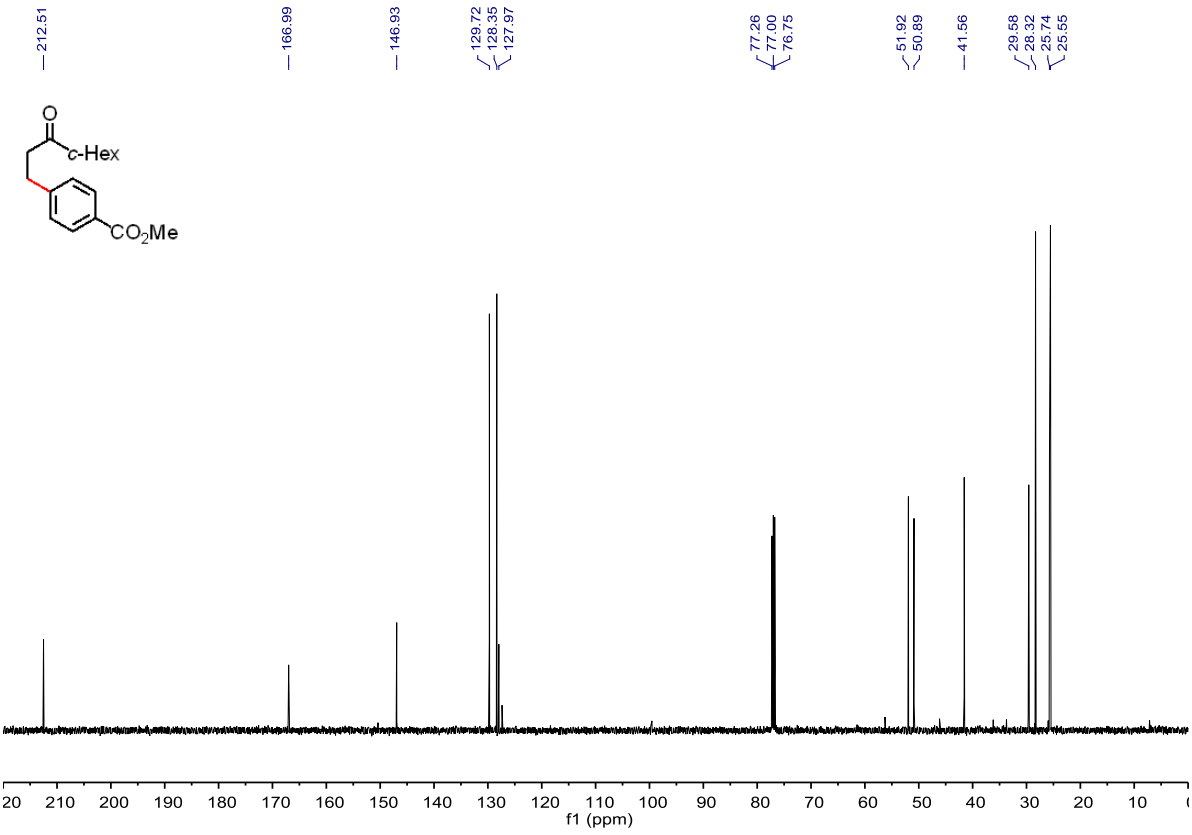
0.98
3.83
1.02
4.91
f1 (ppm)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129.72
128.35
127.97
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77.00
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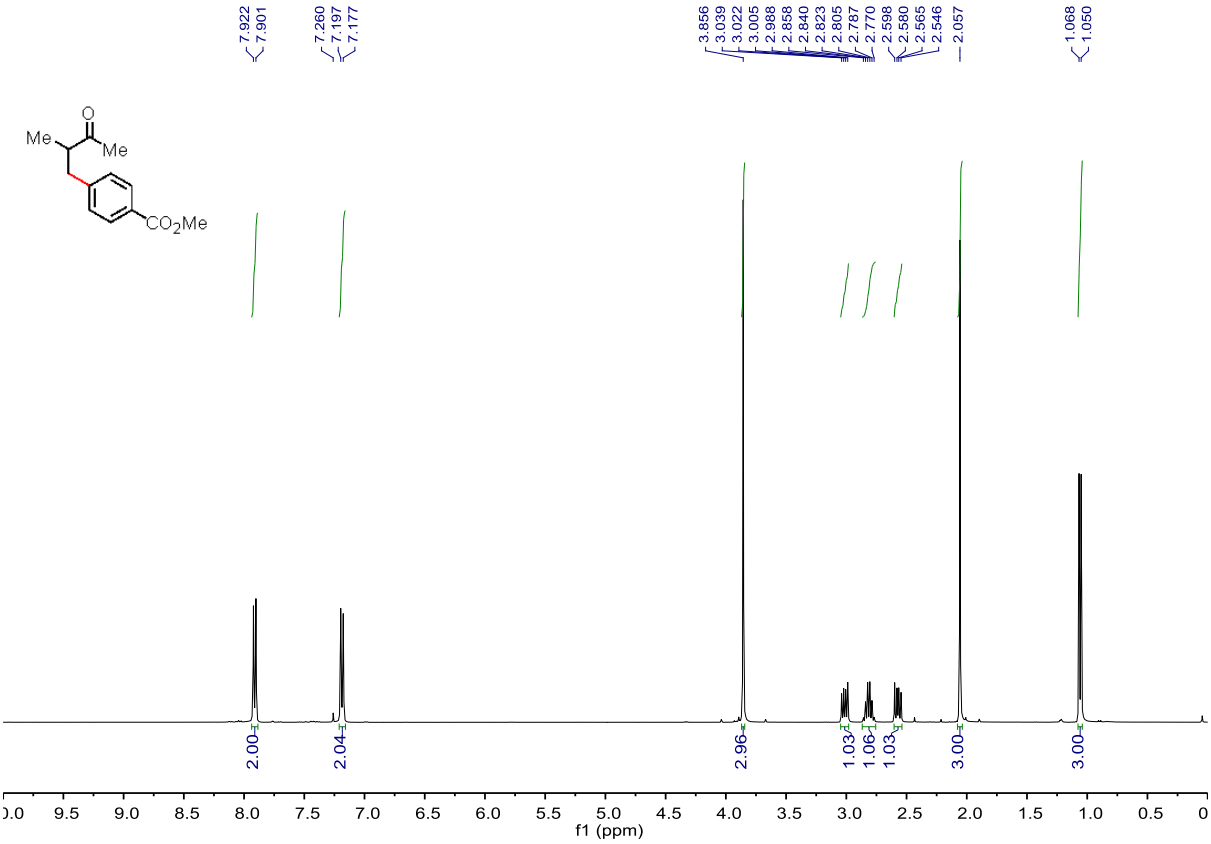
41.56
29.58
28.32
25.74
25.55
c-Hex
CO2Me
f1 (ppm)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7.177
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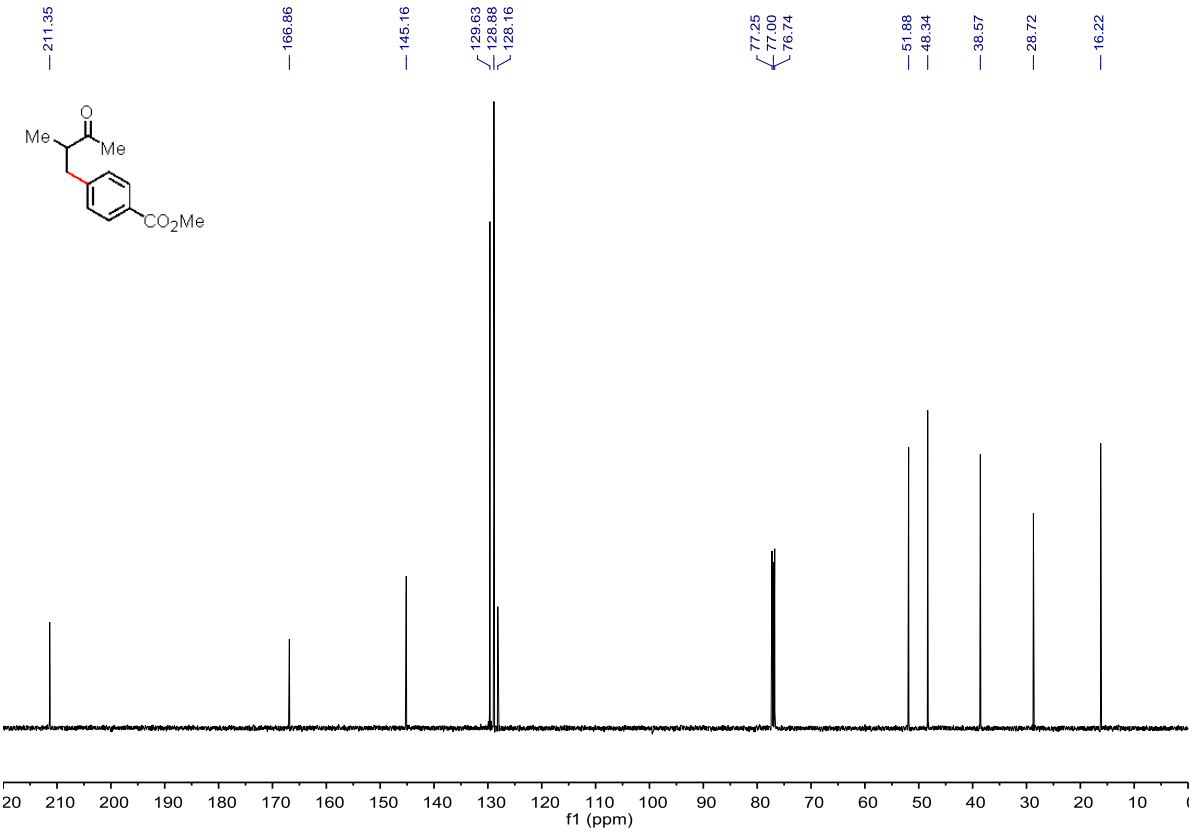
3.039
3.022
3.005
2.988
2.858
2.840
2.823
2.805
2.787
2.770
2.598
2.580
2.565
2.546
2.057
1.068
1.050
Me
O
Me
CO2Me
2.00
2.04
2.96
1.03
1.06
1.03
3.00
3.00
f1 (ppm)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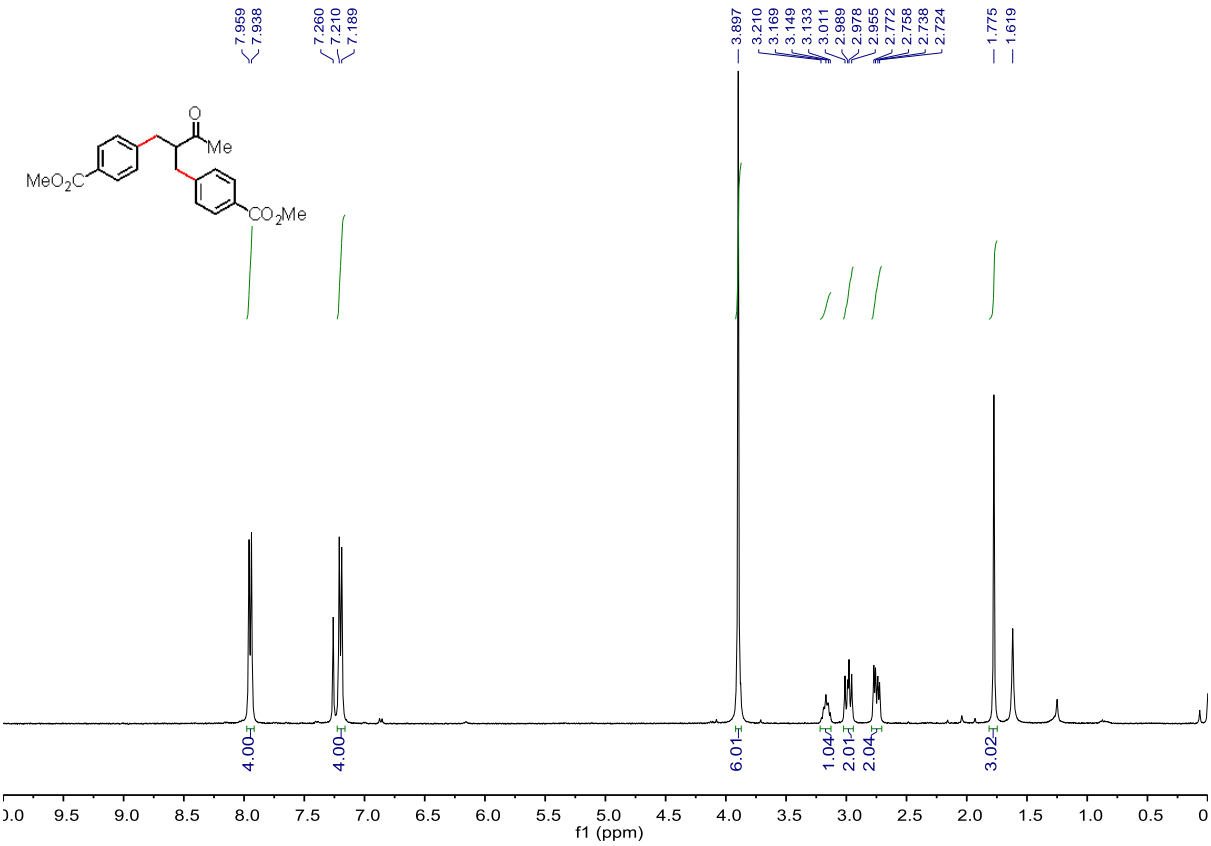
145.16
129.63
128.88
128.16
77.25
77.00
76.74
51.88
48.34
38.57
28.72
16.22
Me
O
Me
CO2Me
f1 (ppm)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7.189
3.897
3.210
3.169
3.149
3.133
3.011
2.989
2.978
2.955
2.772
2.758
2.738
2.724
1.775
1.619
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Me
MeO2C
CO2Me
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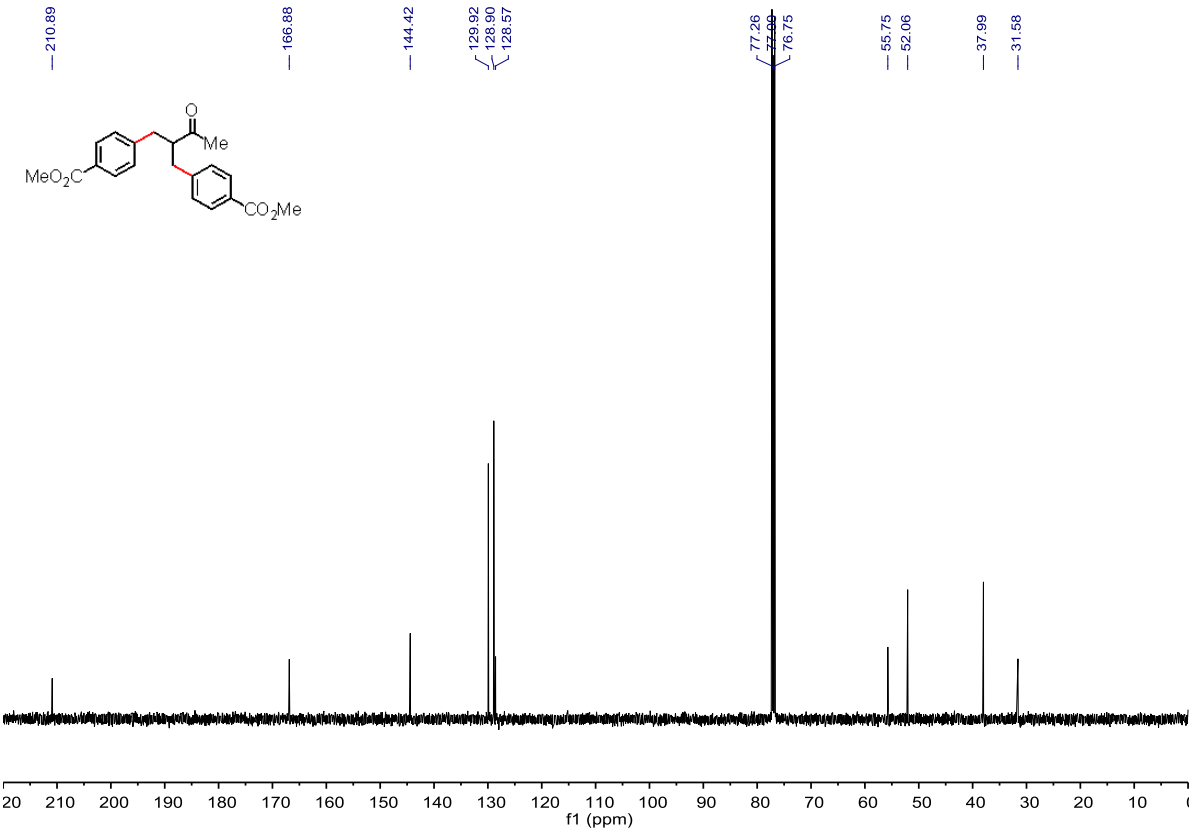
4.00
6.01
1.04
2.01
2.04
3.02
f1 (ppm)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128.90
128.57
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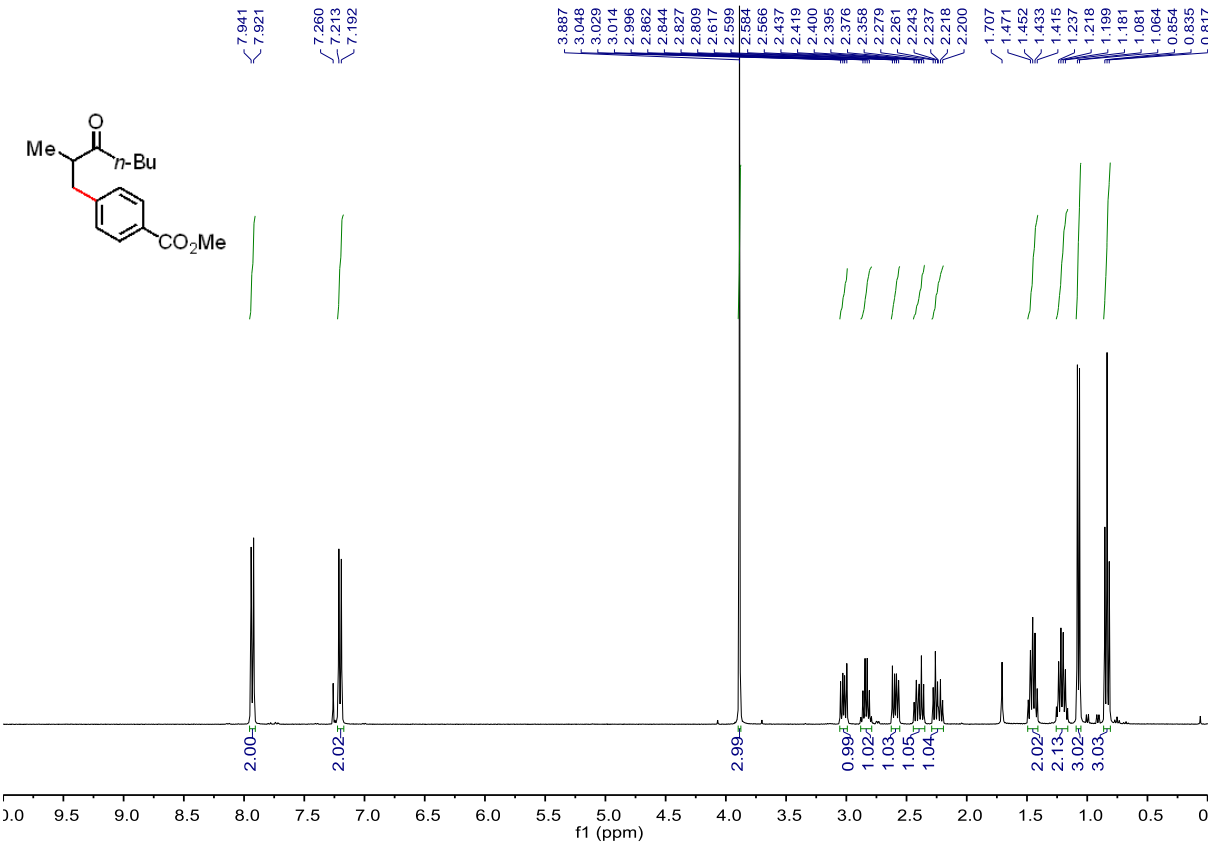
76.75
55.75
52.06
37.99
31.58
O
Me
MeO2C
CO2Me
f1 (ppm)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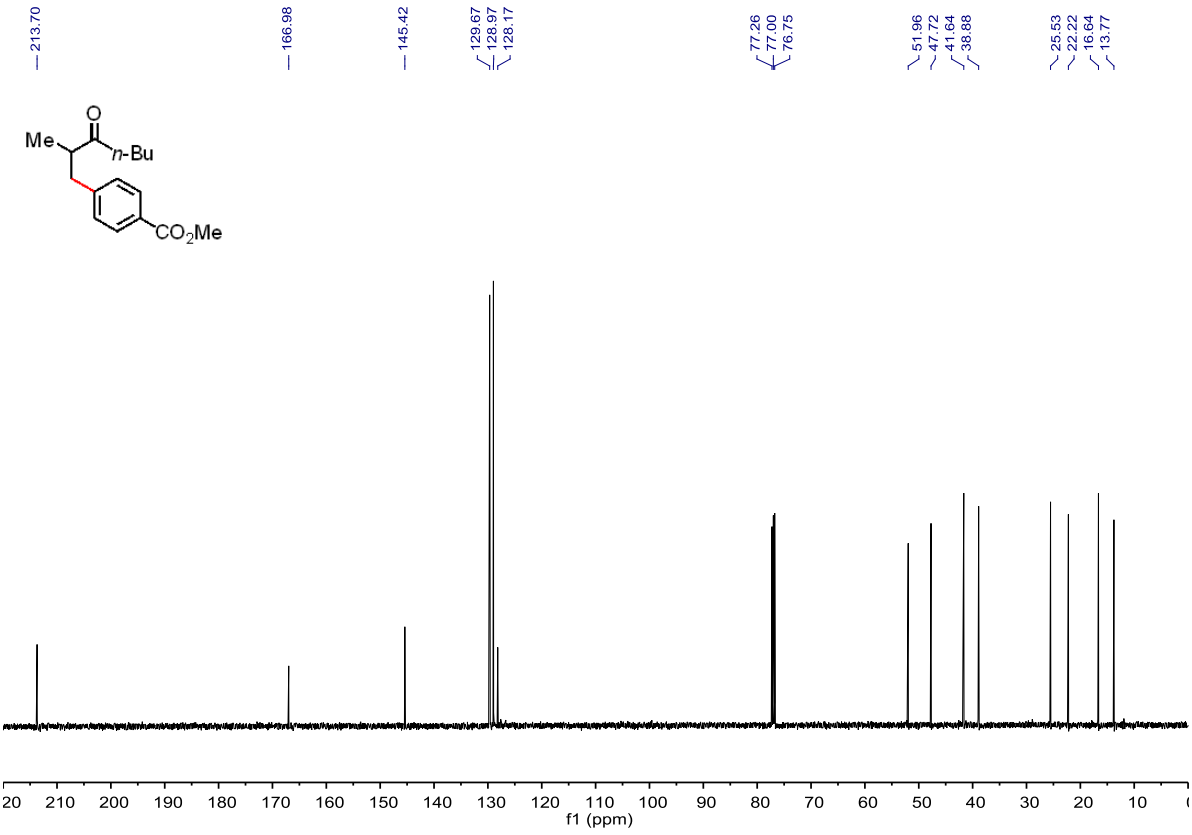
2.809
2.617
2.599
2.584
2.566
2.437
2.419
2.400
2.395
2.376
2.358
2.279
2.261
2.243
2.237
2.218
2.200
1.707
1.471
1.452
1.433
1.415
1.237
1.218
1.199
1.181
1.081
1.064
0.854
0.835
Me
n-Bu
CO2Me
2.00
2.02
2.99
0.99
1.02
1.03
1.05
1.04
2.02
2.13
3.02
3.03
f1 (ppm)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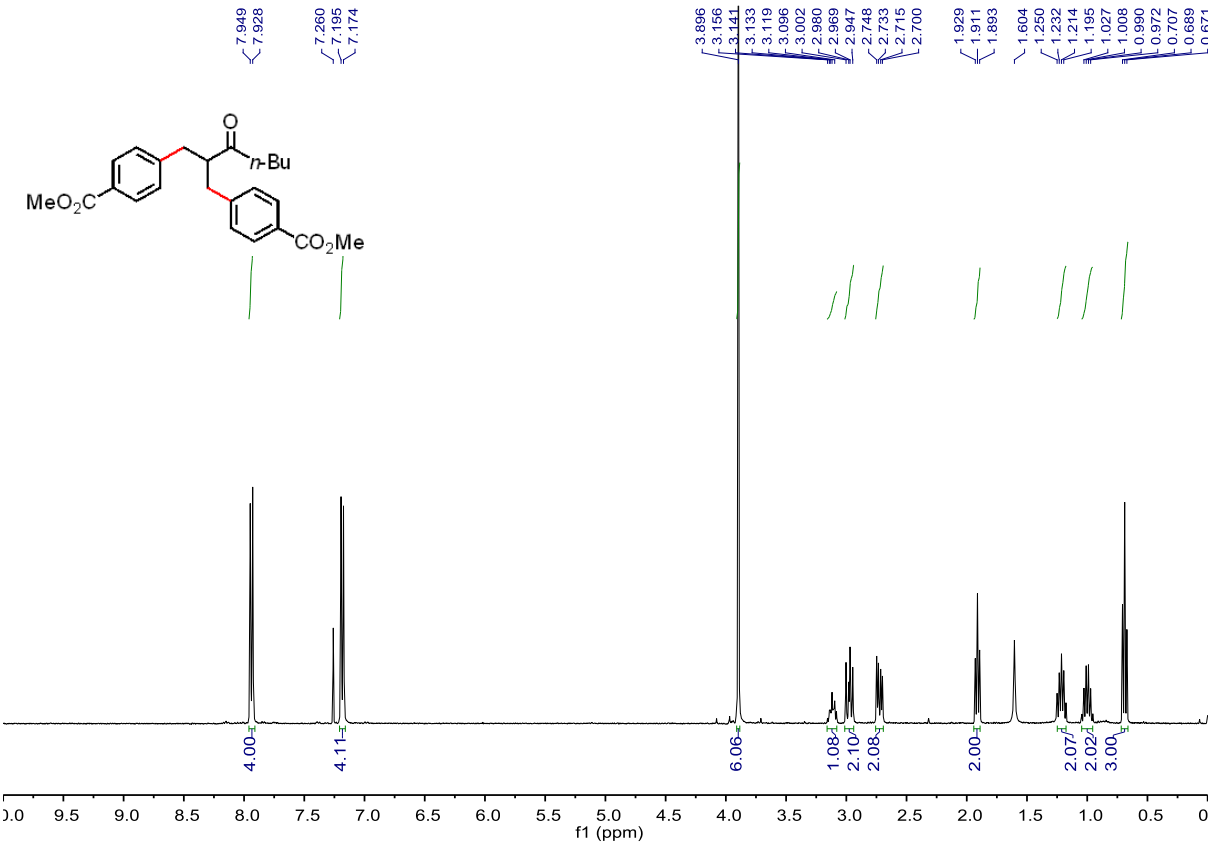
22.22
16.64
13.77
Me
n-Bu
CO2Me
f1 (ppm)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3.141
3.133
3.119
3.096
3.002
2.980
2.969
2.947
2.748
2.733
2.715
2.700
1.929
1.911
1.893
1.604
1.250
1.232
1.214
1.195
1.027
1.008
0.990
0.972
0.707
0.689
O
n-Bu
MeO2C
CO2Me
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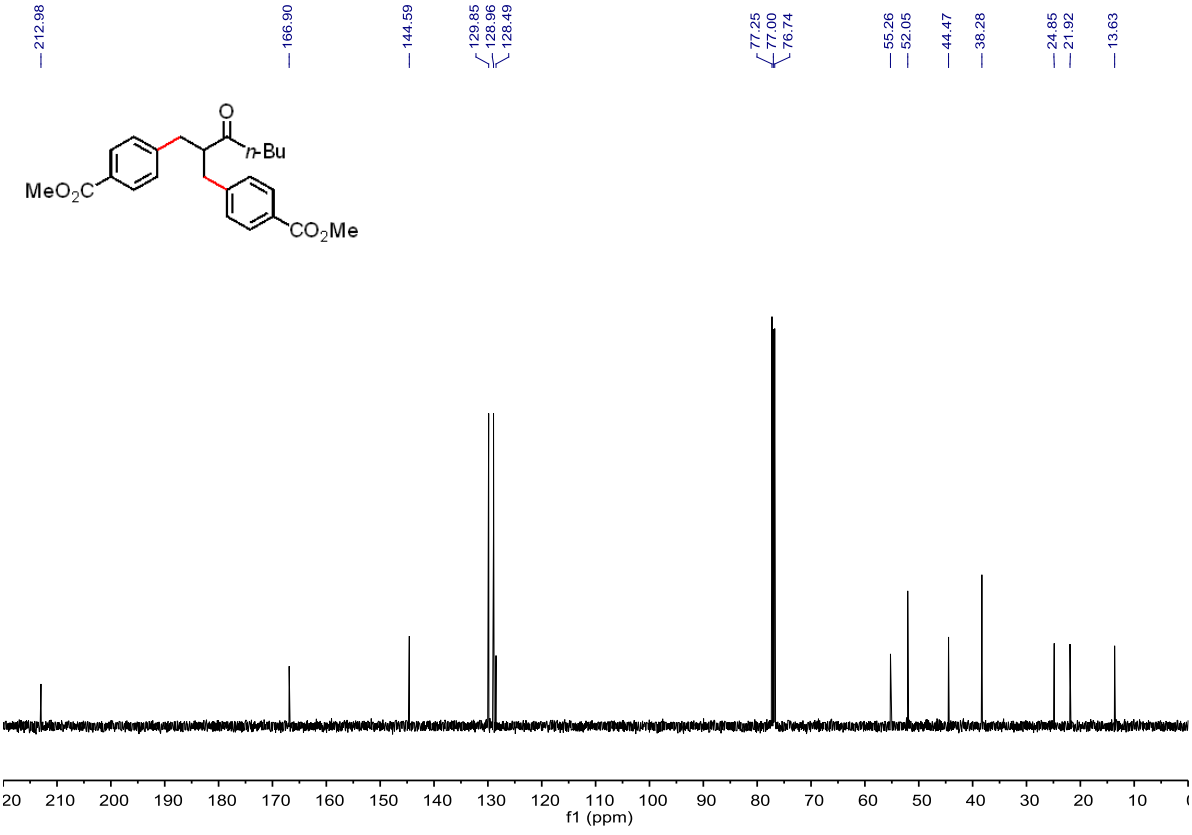
1.08
2.10
2.08
2.00
2.07
2.02
3.00
f1 (ppm)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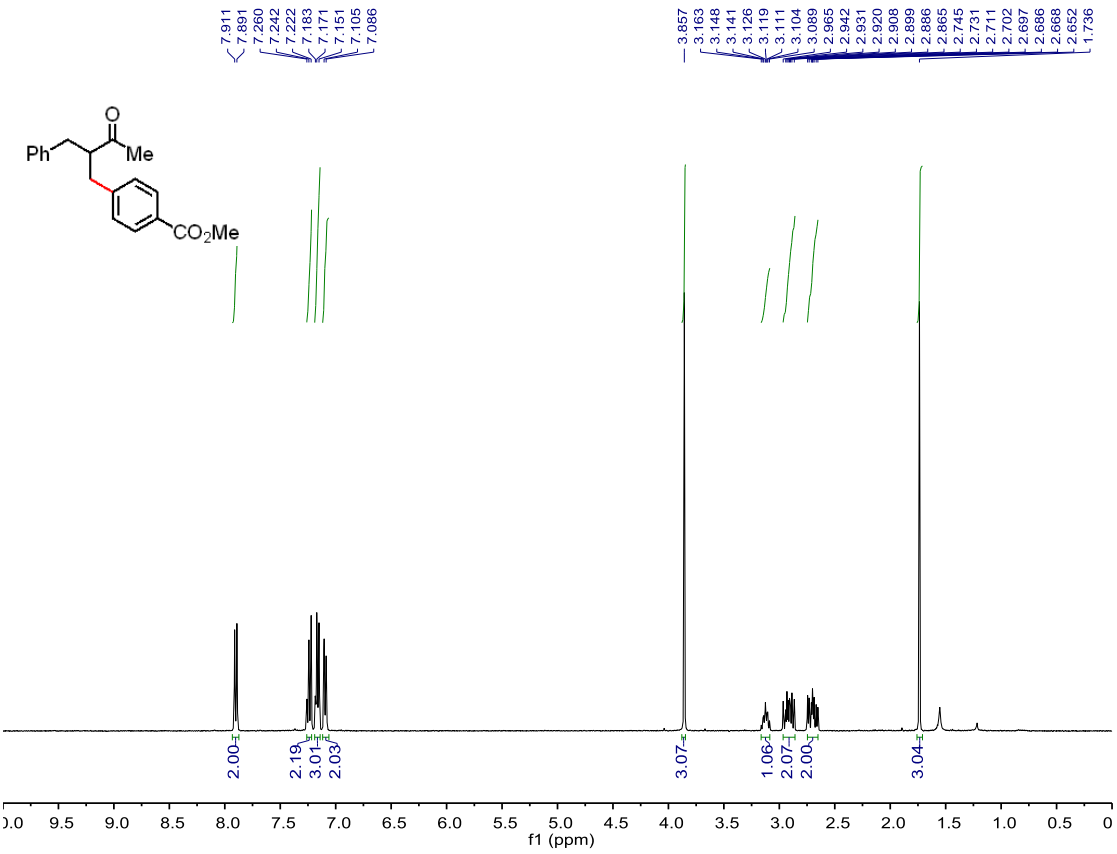
128.49
77.25
77.00
76.74
55.26
52.05
44.47
38.28
24.85
21.92
13.63
O
n-Bu
MeO2C
CO2Me
f1 (ppm)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7.171
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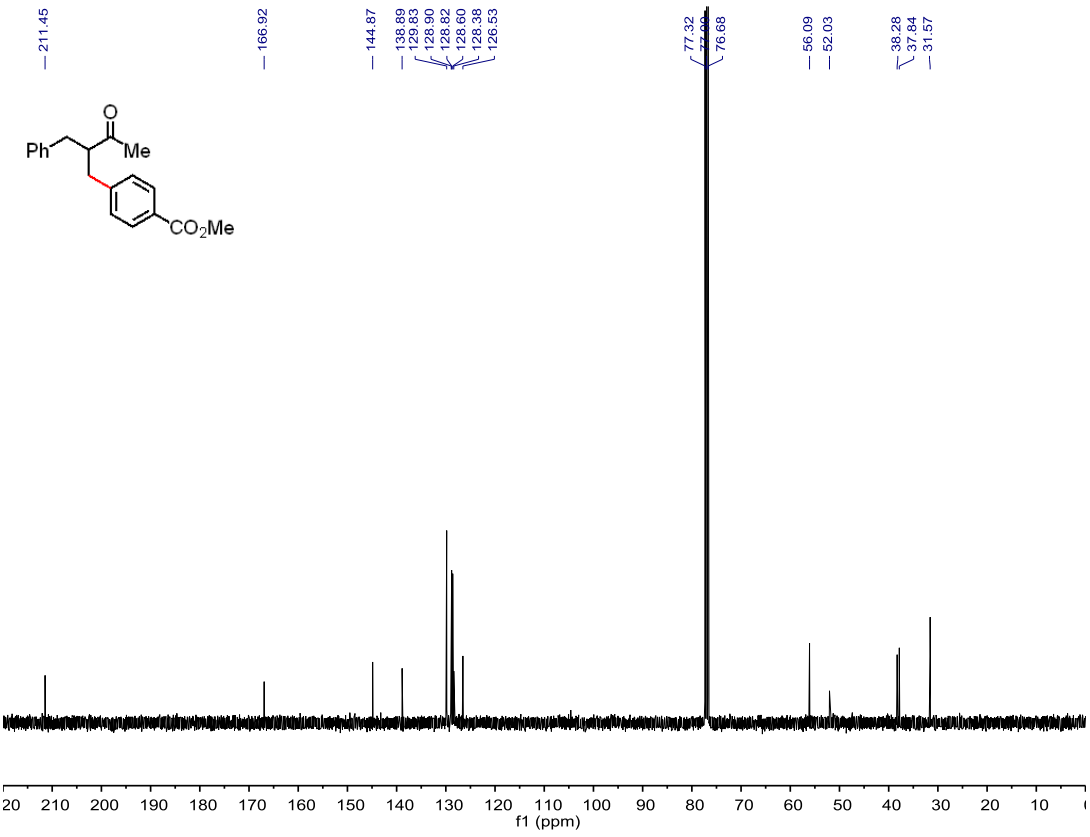
7.105
7.086
3.857
3.163
3.148
3.141
3.126
3.119
3.111
3.104
3.089
2.965
2.942
2.931
2.920
2.908
2.899
2.886
2.865
2.745
2.731
2.711
2.702
2.697
2.686
2.668
2.652
1.736
Ph
O
Me
CO2Me
2.00
2.19
3.01
2.03
3.07
1.06
2.07
2.00
3.04
f1 (ppm)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128.90
128.82
128.60
128.38
126.53
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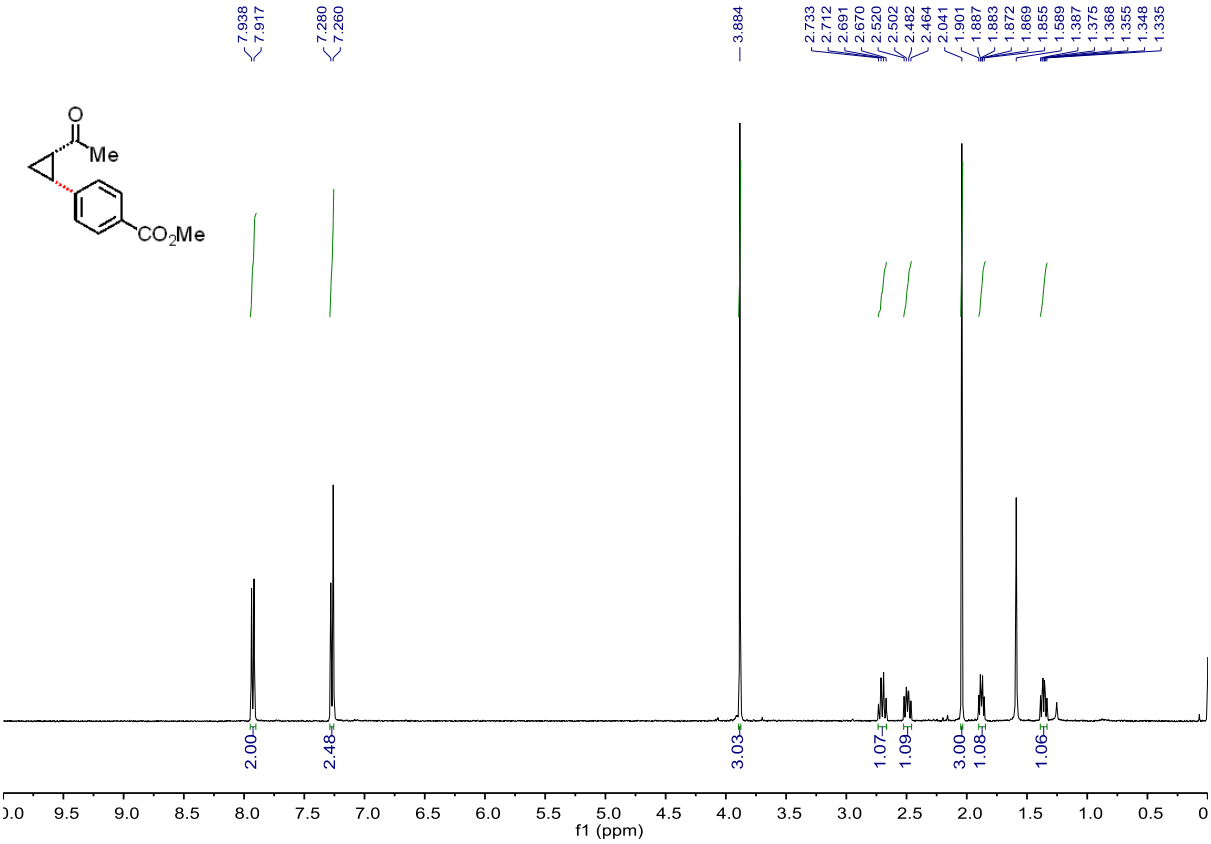
77.00
76.68
56.09
52.03
38.28
37.84
31.57
Ph
O
Me
CO2Me
f1 (ppm)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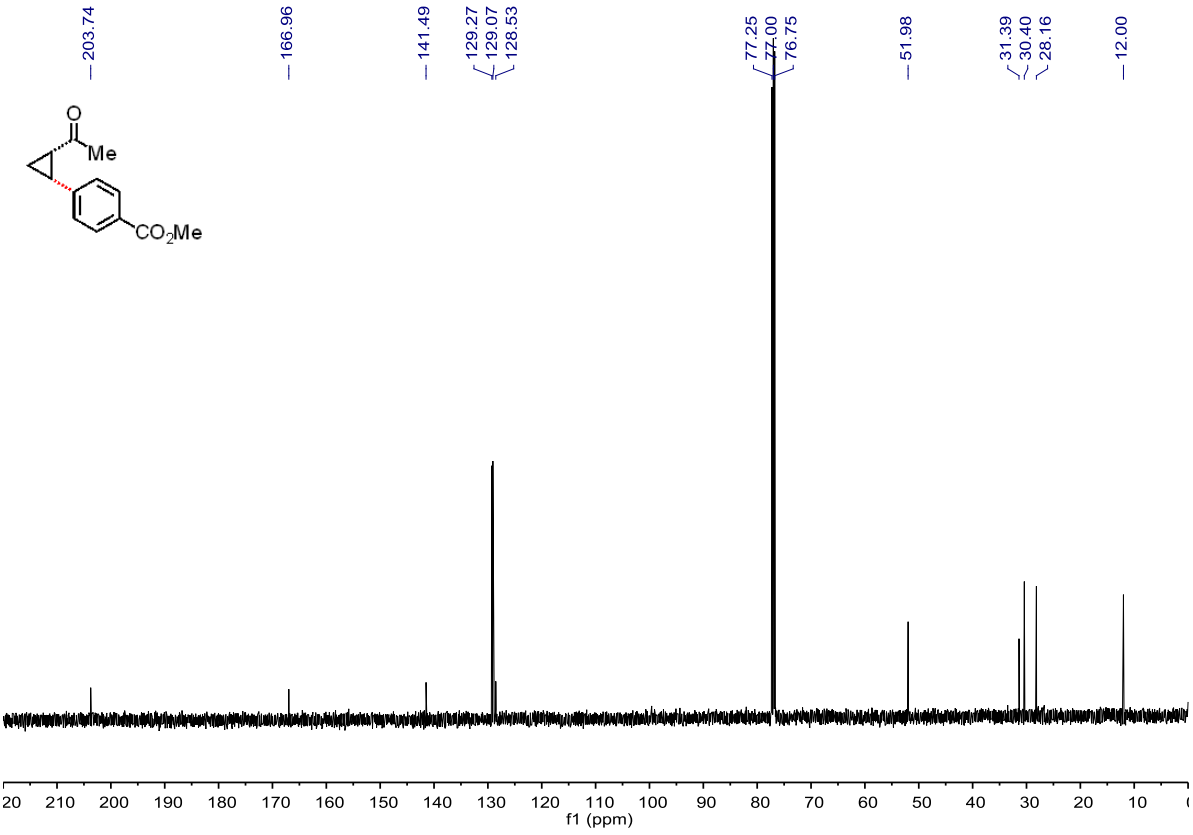
2.691
2.670
2.520
2.502
2.482
2.464
2.041
1.901
1.887
1.883
1.872
1.869
1.855
1.589
1.387
1.375
1.368
1.355
1.348
1.335
O
Me
CO2Me
2.00
2.48
3.03
1.07
1.09
3.00
1.08
1.06
f1 (ppm)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129.07
128.53
77.25
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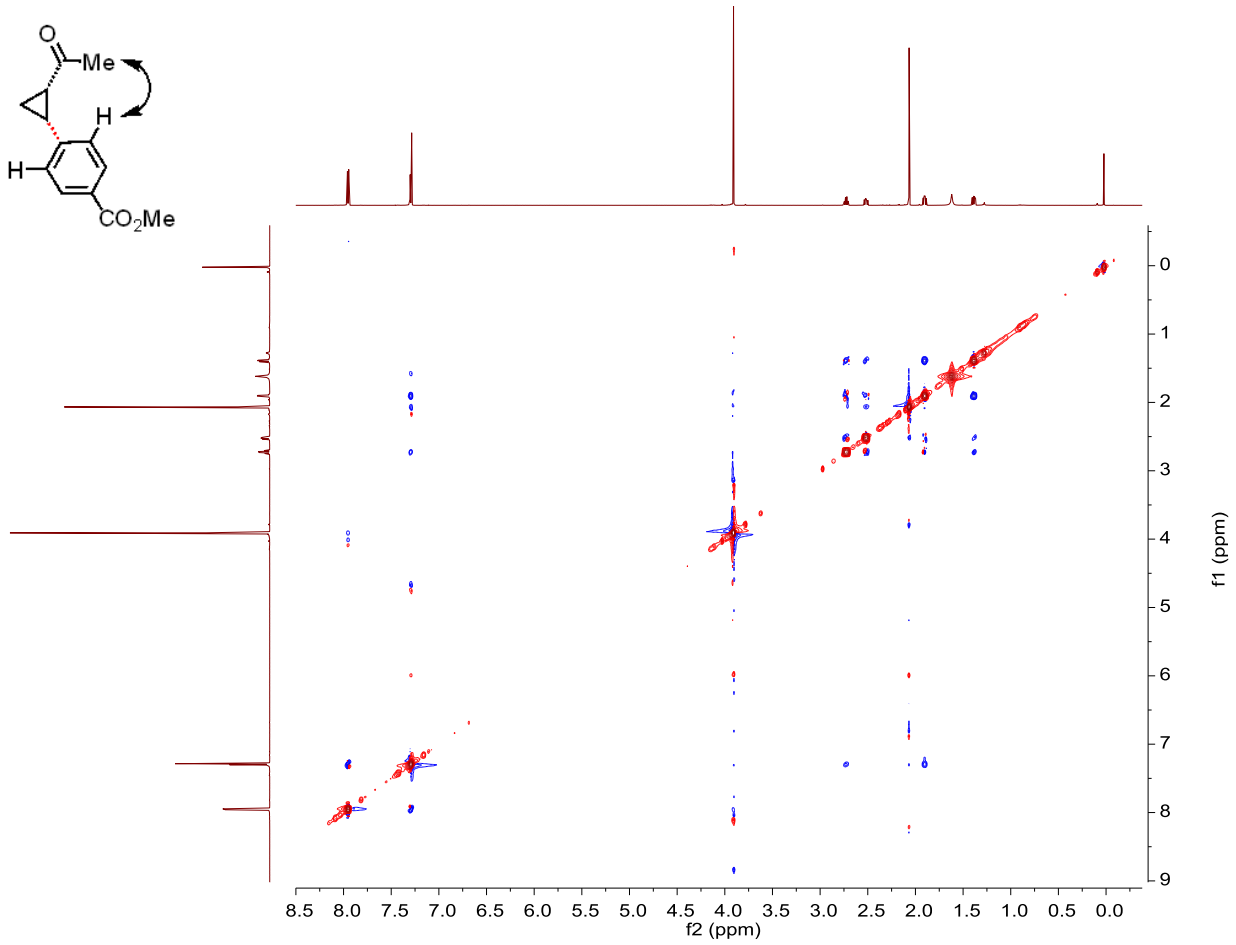
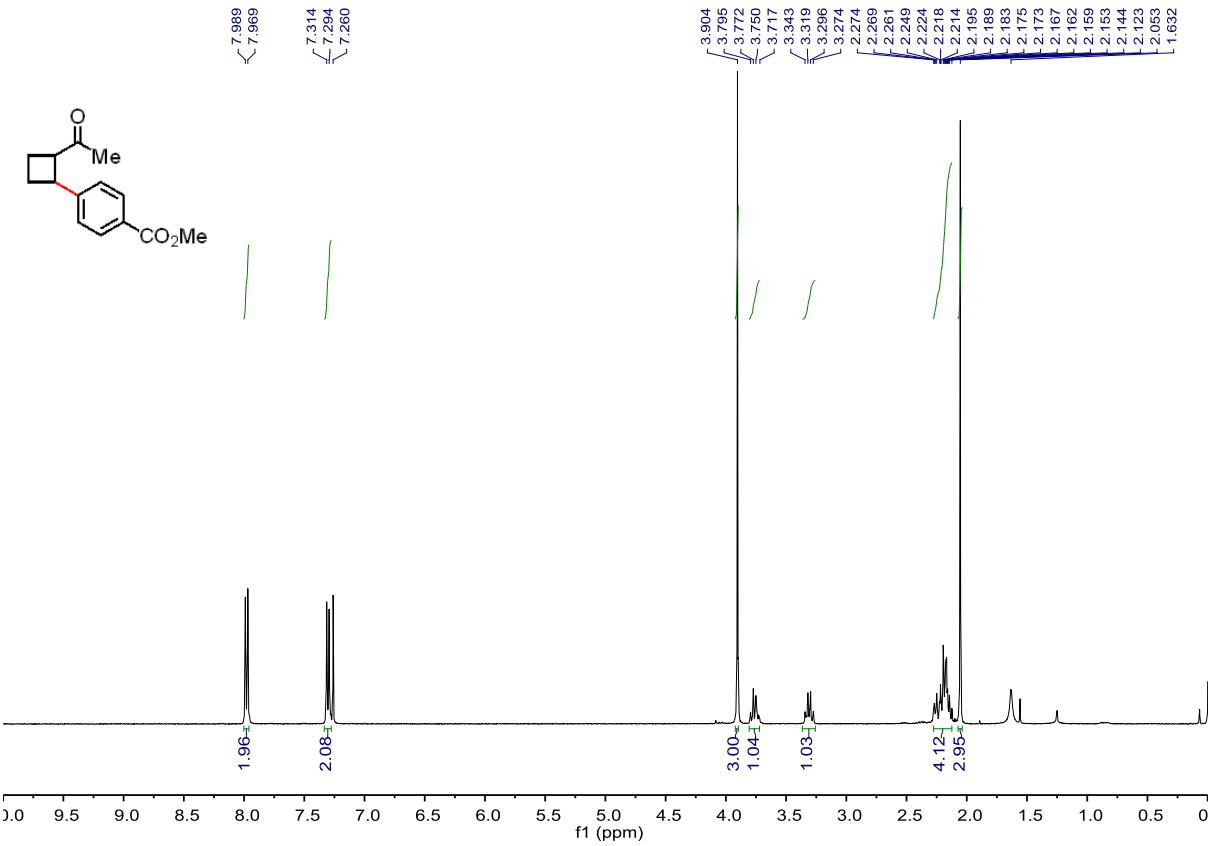
51.98
31.39
30.40
28.16
12.00
O
Me
CO2Me
f1 (ppm)


O
Me
H
H
CO2Me
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
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)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3.772
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3.319
3.296
3.274
2.274
2.269
2.261
2.249
2.224
2.218
2.214
2.195
2.189
2.183
2.175
2.173
2.167
2.162
2.159
2.153
2.144
2.123
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Me
CO2Me
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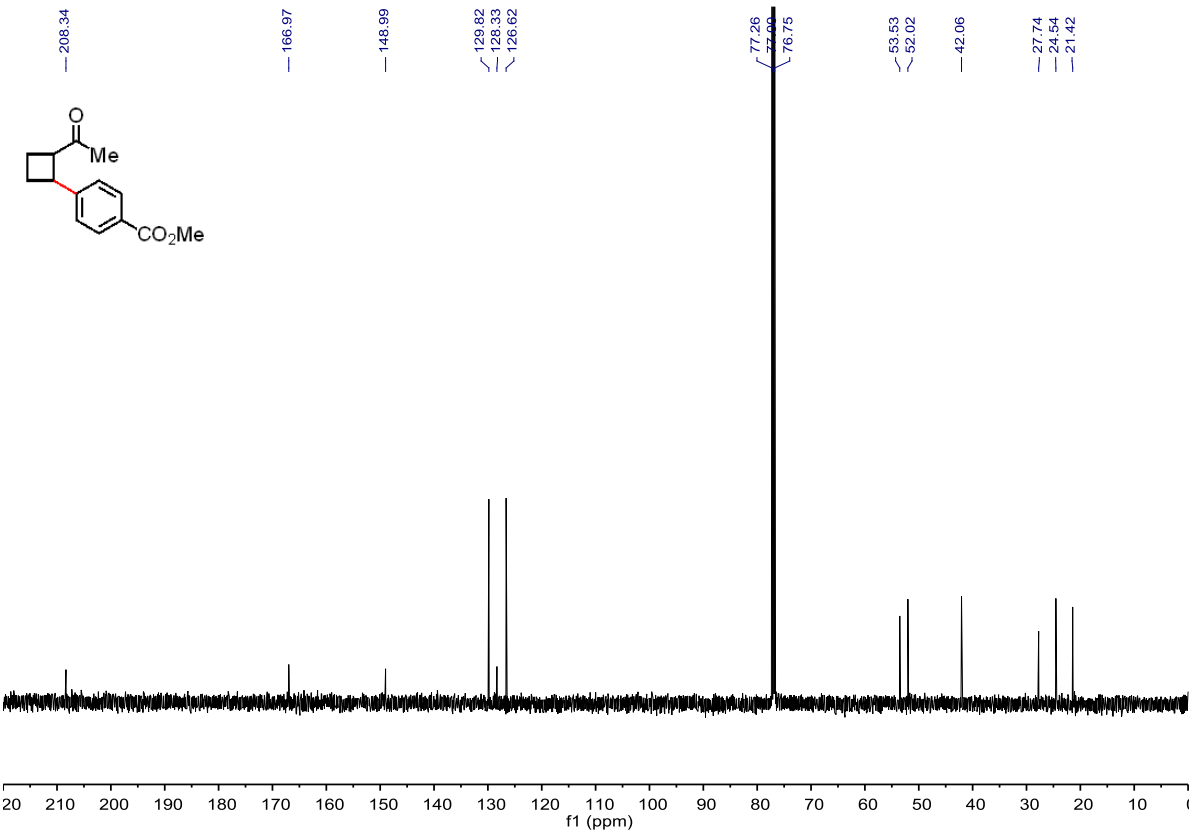
3.00
1.04
1.03
4.12
2.95
f1 (ppm)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129.82
128.33
126.62
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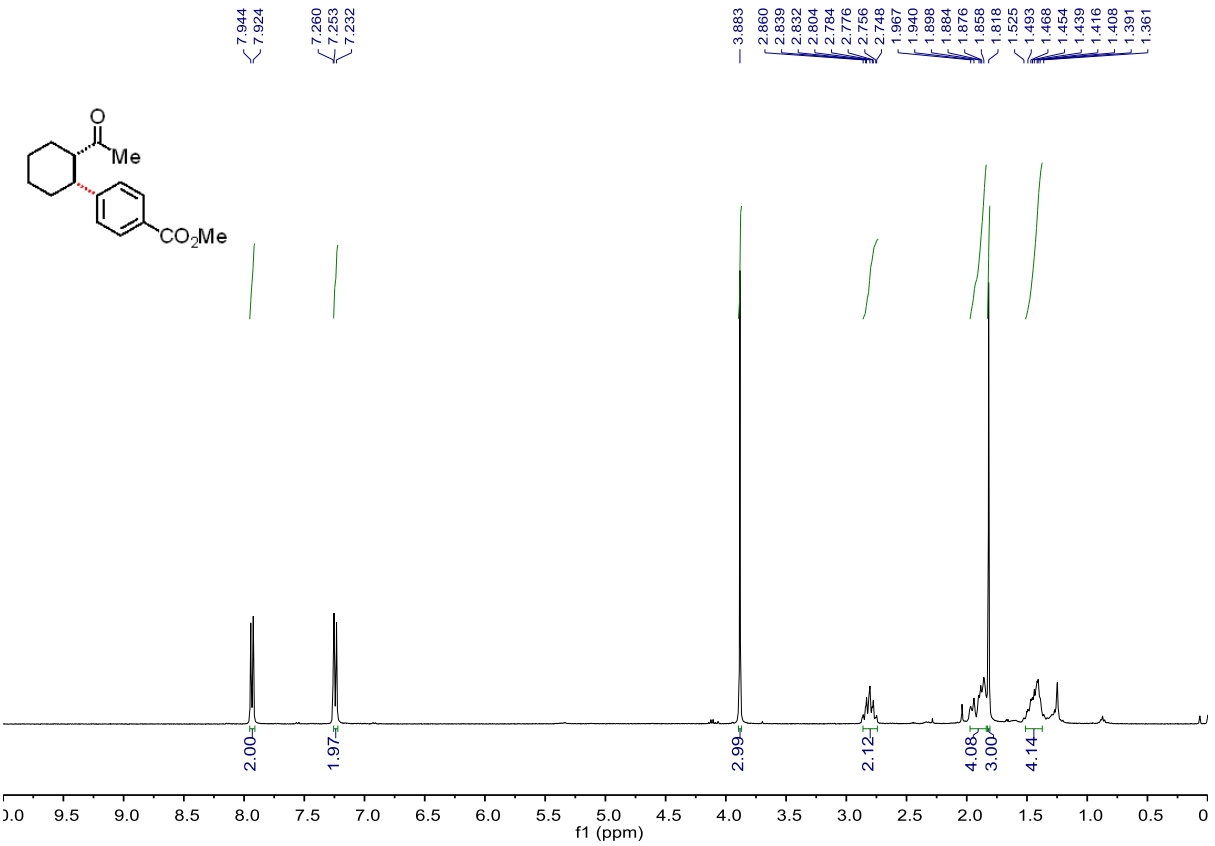
77.00
76.75
53.53
52.02
42.06
27.74
24.54
21.42
Me
CO2Me
f1 (ppm)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2.776
2.756
2.748
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1.940
1.898
1.884
1.876
1.858
1.818
1.525
1.493
1.468
1.454
1.439
1.416
1.408
1.391
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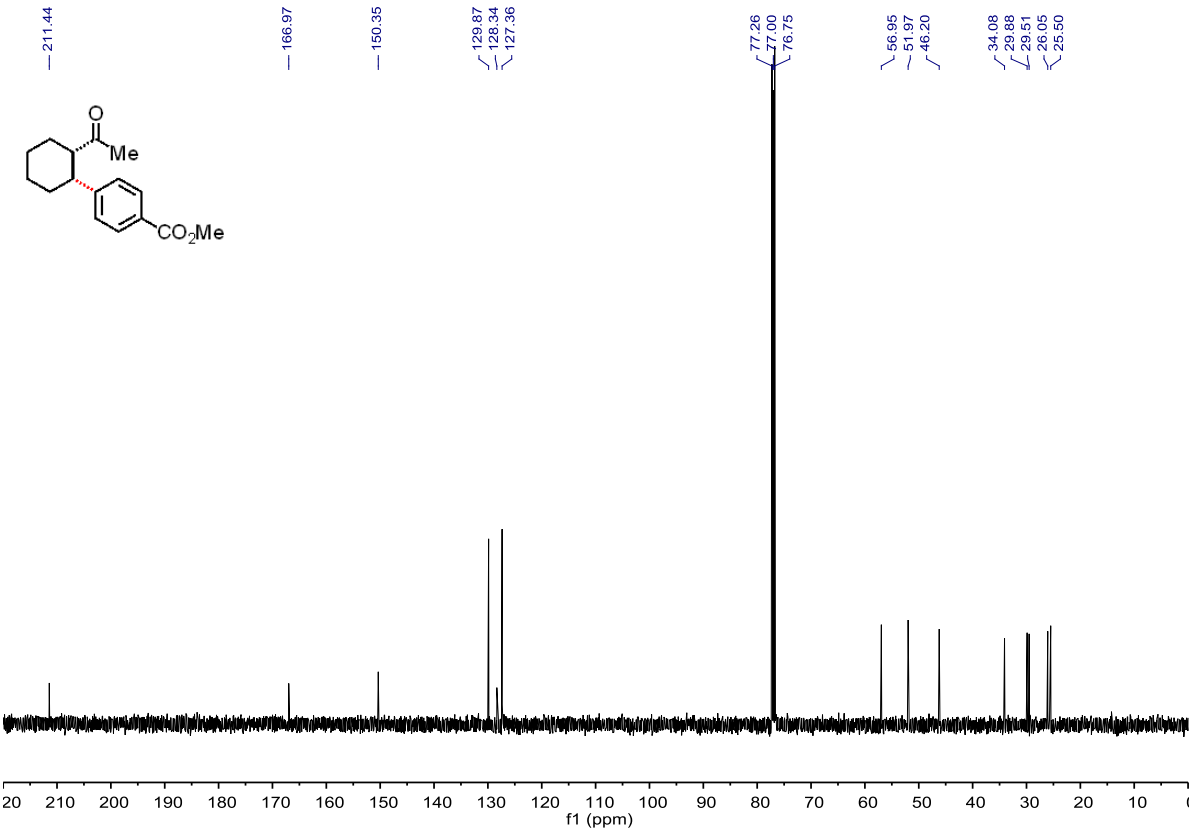
O
Me
CO2Me
2.00
1.97
2.99
2.12
4.08
3.00
4.14
f1 (ppm)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77.00
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29.51
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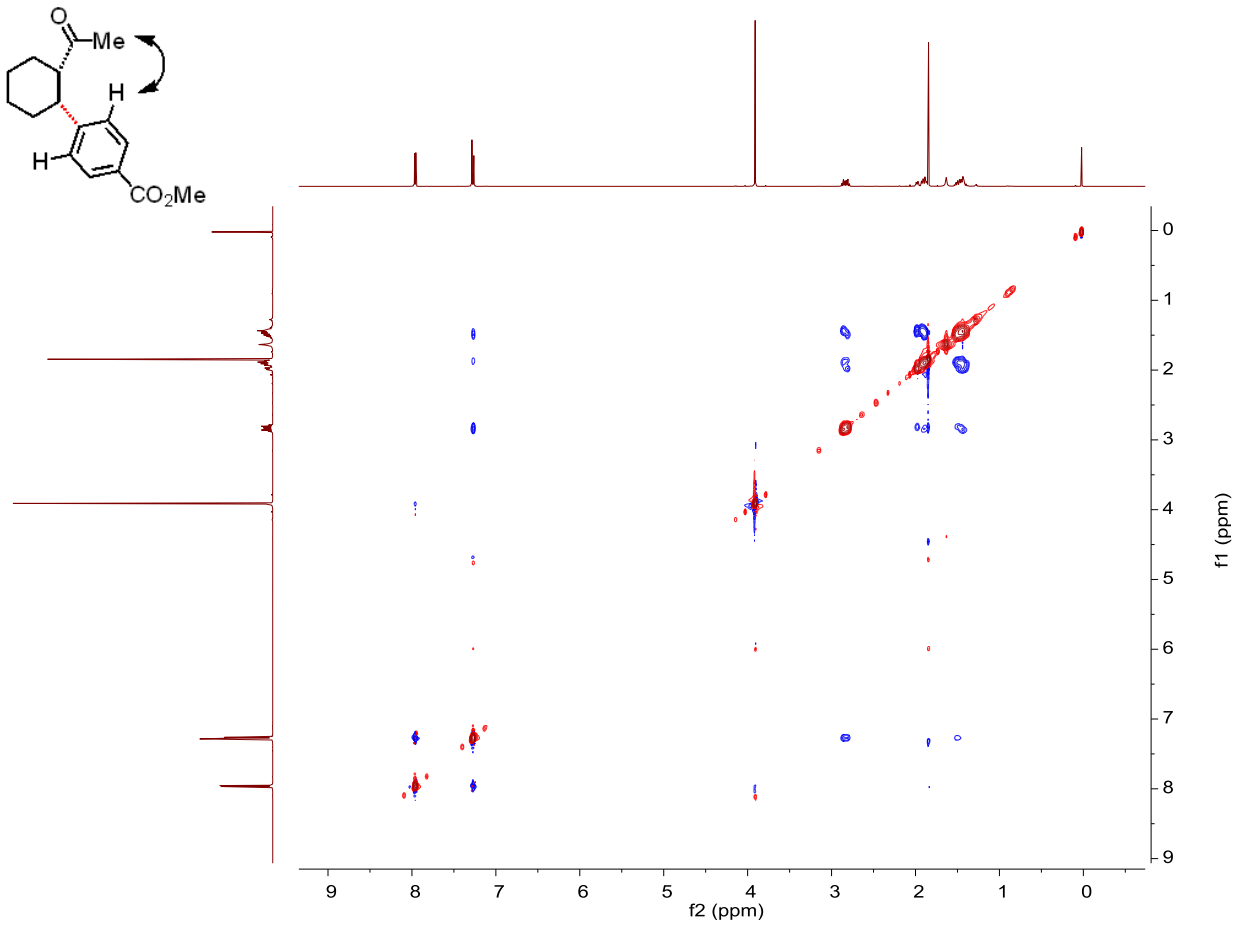
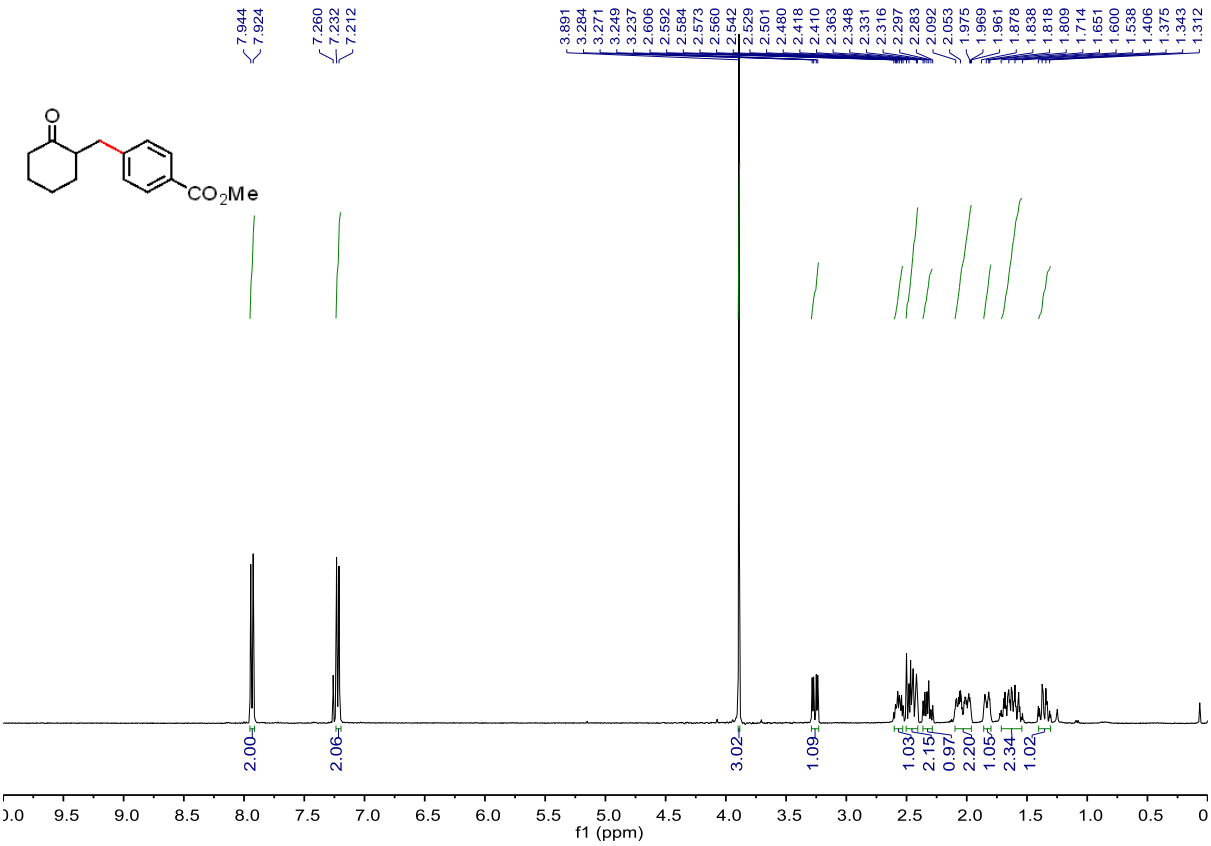
25.50
O
Me
CO2Me
f1 (ppm)


O
Me
H
H
CO2Me
f2 (ppm)
f1 (ppm)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2.573
2.560
2.542
2.529
2.501
2.480
2.418
2.410
2.363
2.348
2.331
2.316
2.297
2.283
2.092
2.053
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1.969
1.961
1.878
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1.818
1.809
1.714
1.651
1.600
1.538
1.406
1.375
1.343
1.312
O
CO2Me
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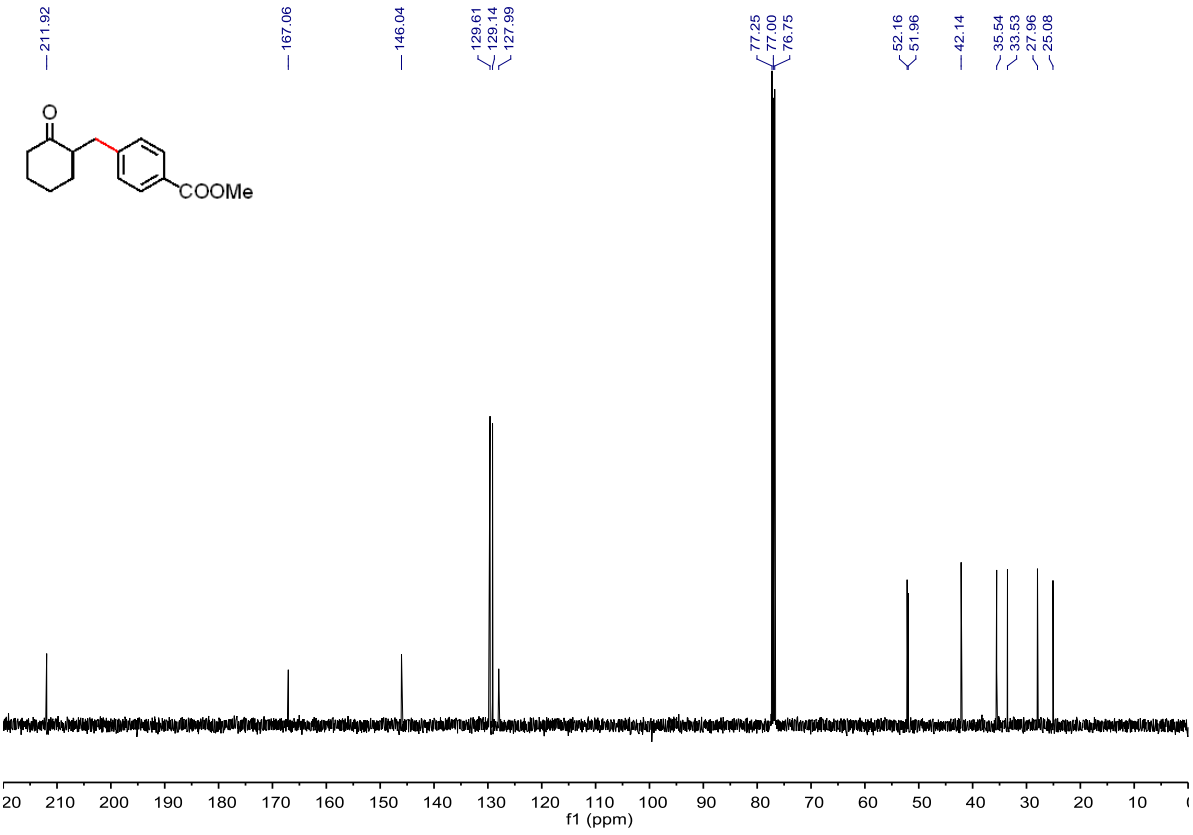
1.03
2.15
0.97
2.20
1.05
2.34
1.02
f1 (ppm)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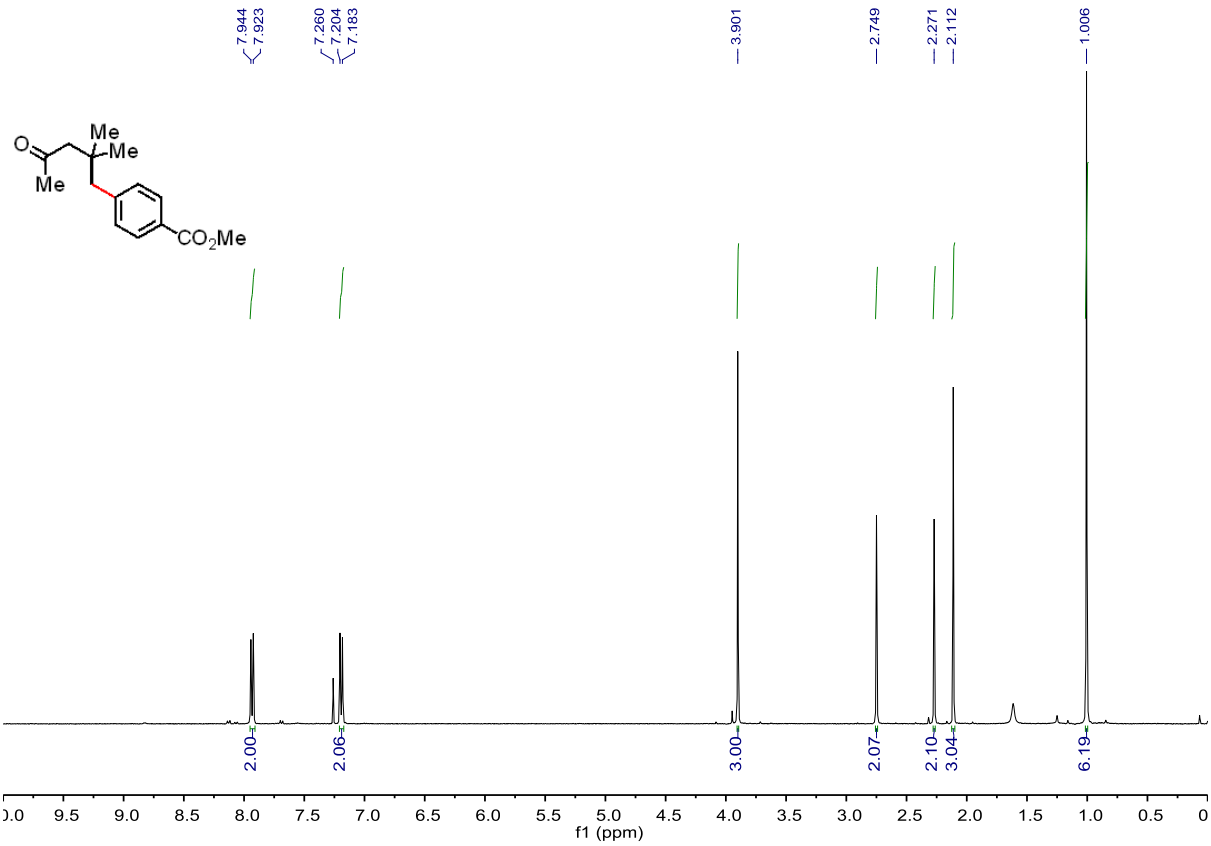
51.96
42.14
35.54
33.53
27.96
25.08
O
COOMe
f1 (ppm)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2.271
2.112
1.006
Me
Me
Me
O
CO2Me
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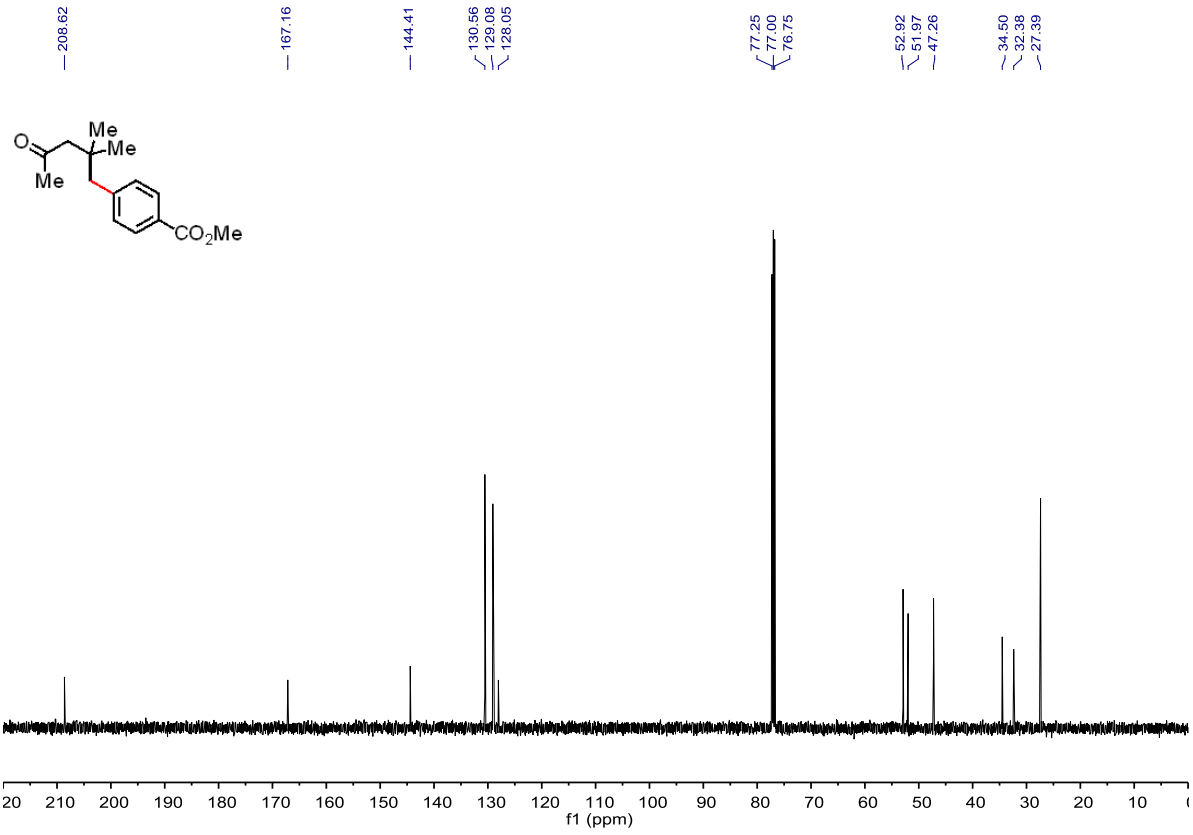
2.06
3.00
2.07
2.10
3.04
6.19
f1 (ppm)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77.00
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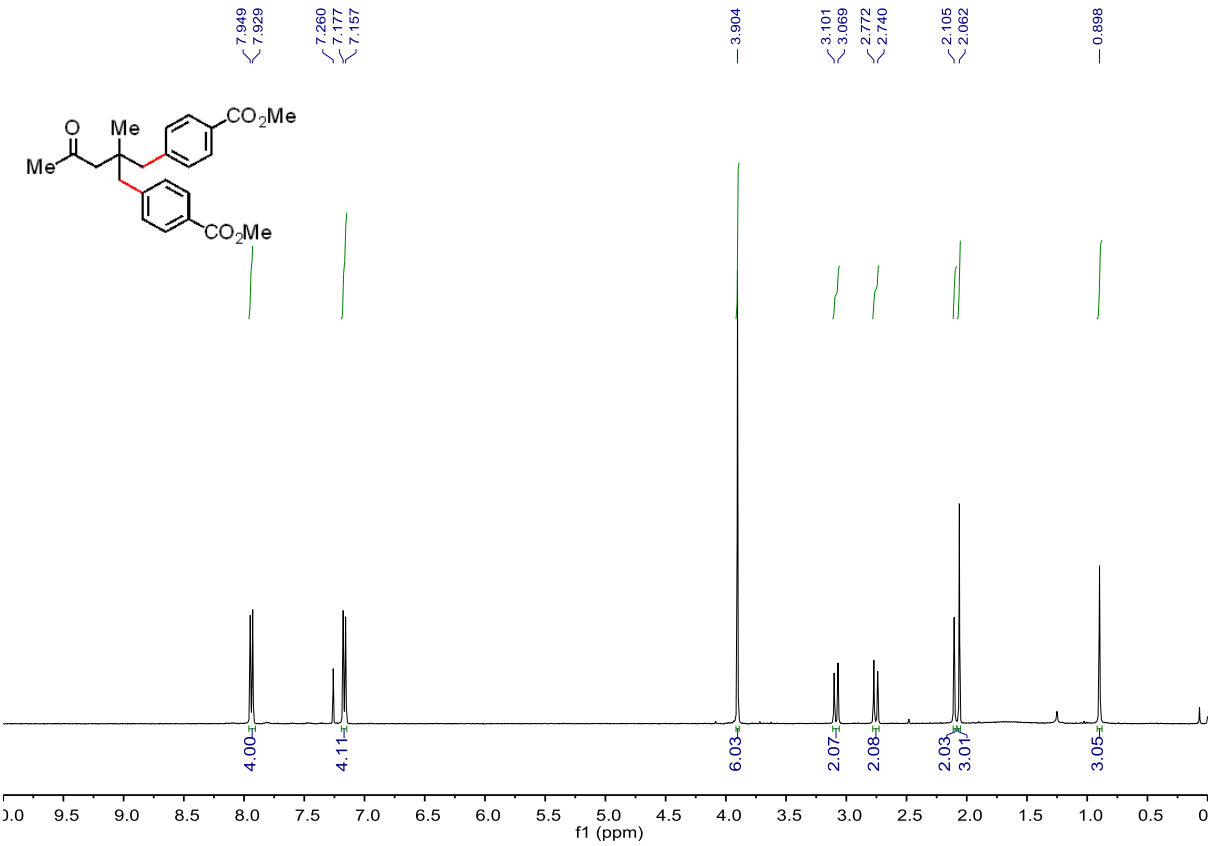
32.38
27.39
Me
Me
Me
O
CO2Me
f1 (ppm)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3.069
2.772
2.740
2.105
2.062
0.898
O
Me
Me
CO2Me
CO2Me
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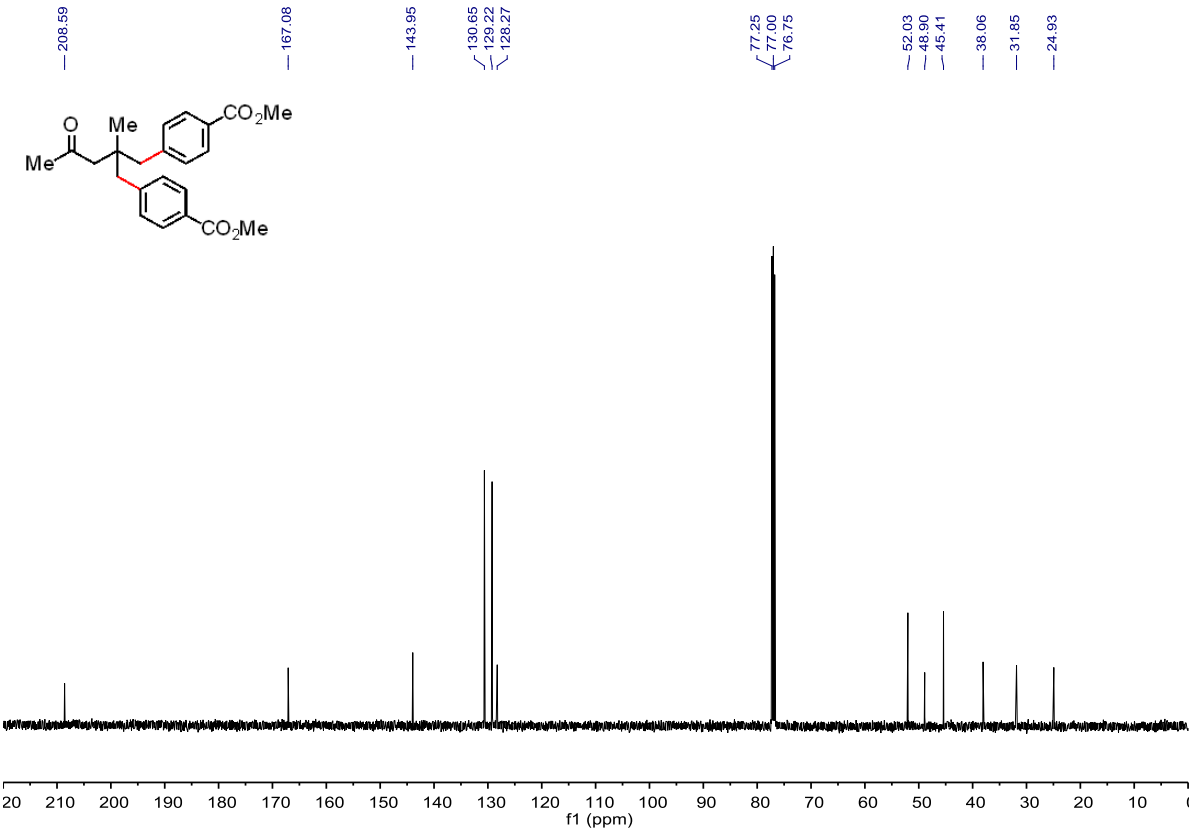
4.11
6.03
2.07
2.08
2.03
3.01
3.05
f1 (ppm)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77.00
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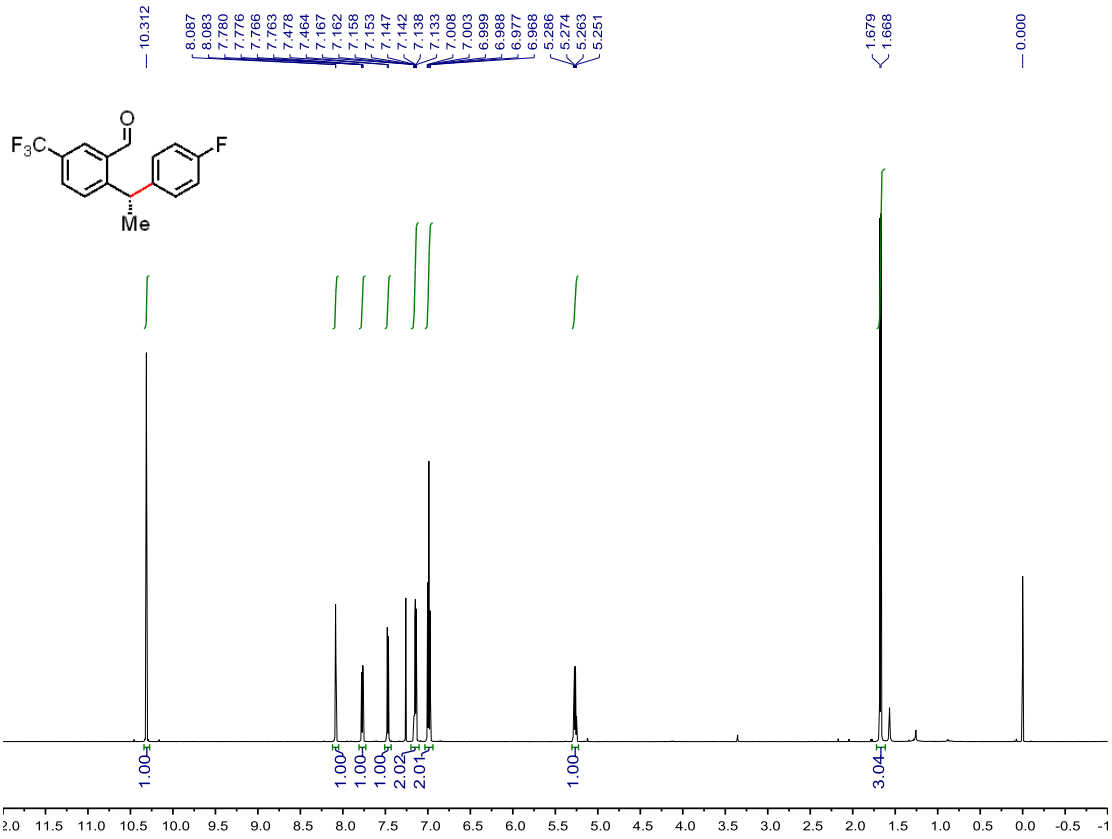
O
Me
Me
CO2Me
CO2Me
f1 (ppm)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7.158
7.153
7.147
7.142
7.138
7.133
7.008
7.003
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6.988
6.977
6.968
5.286
5.274
5.263
5.251
1.679
1.668
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O
F
Me
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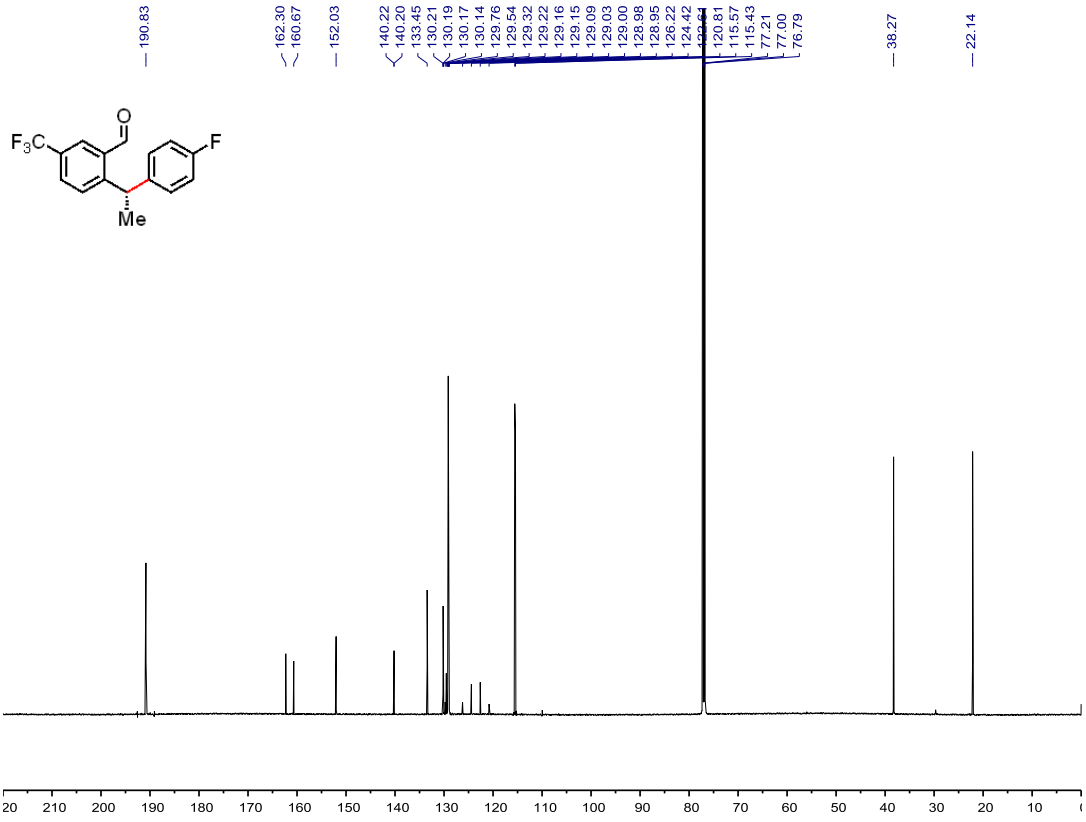
1.00
1.00
1.00
2.02
2.01
1.00
3.04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129.54
129.32
129.22
129.16
129.15
129.09
129.03
129.00
128.98
128.95
126.22
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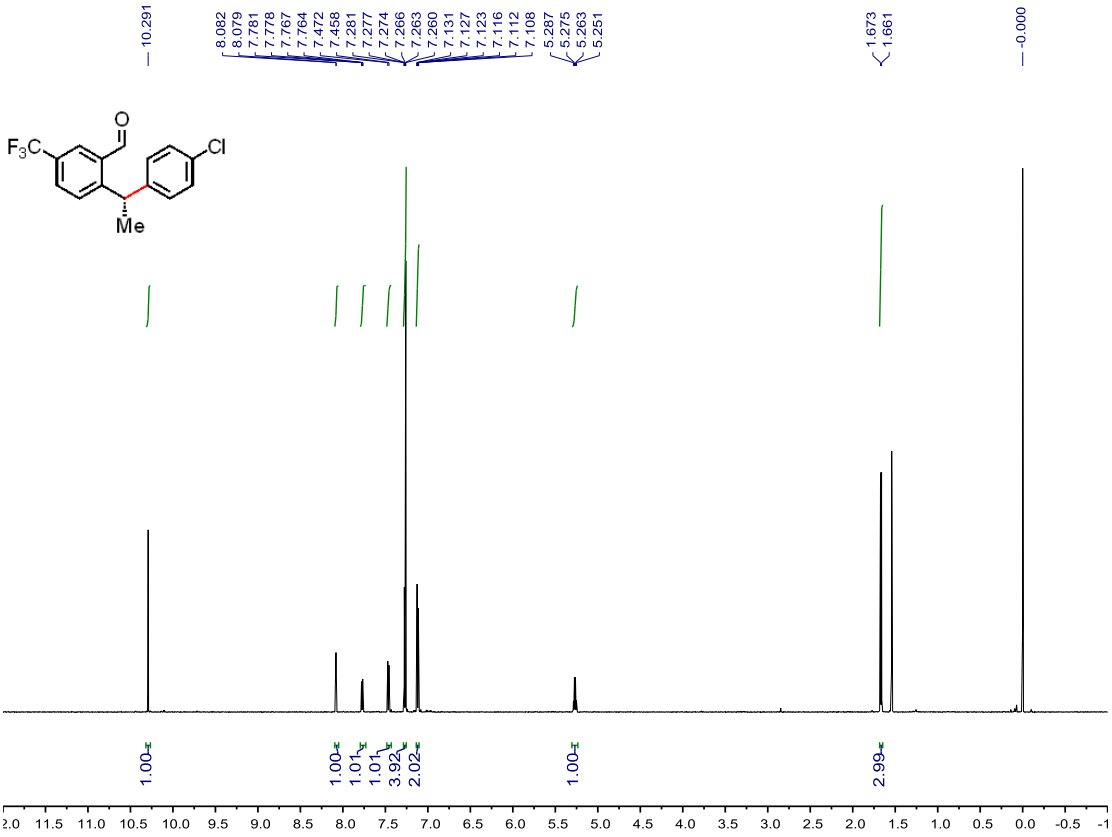
76.79
38.27
22.14
F3C
O
F
Me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7.266
7.263
7.260
7.131
7.127
7.123
7.116
7.112
7.108
5.287
5.275
5.263
5.251
1.673
1.661
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F3C
Cl
Me
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1.01
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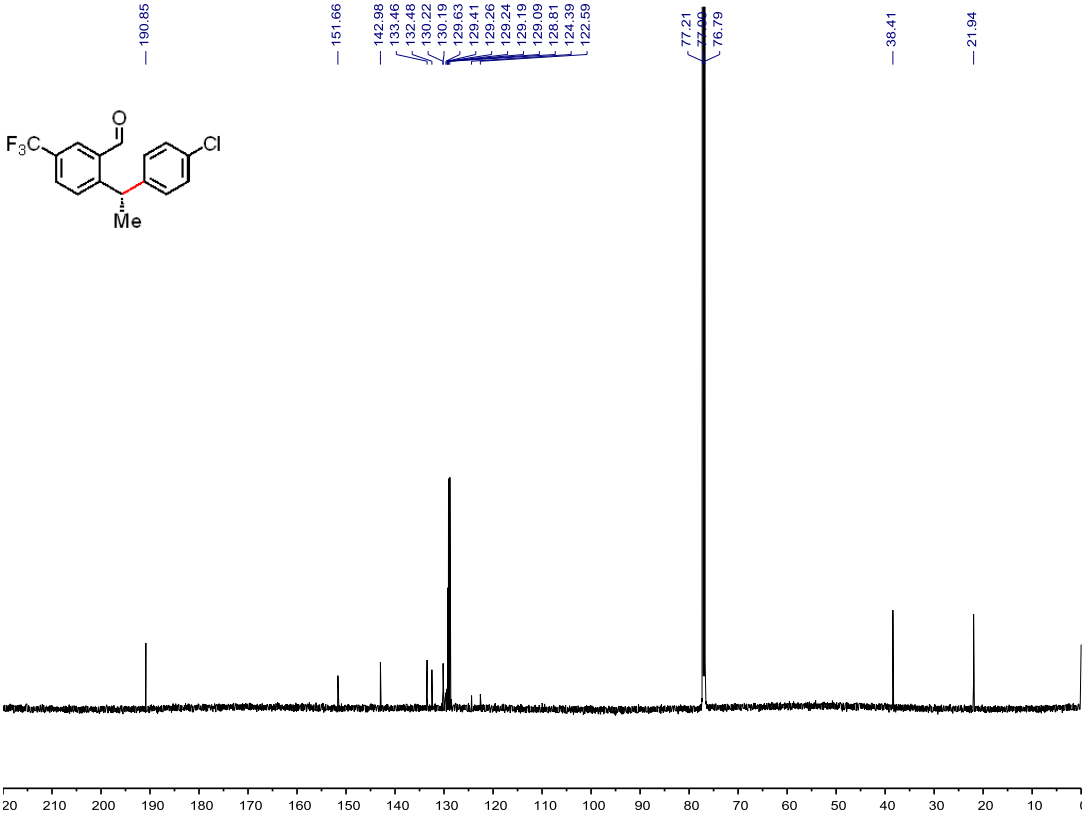
2.02
1.00
2.99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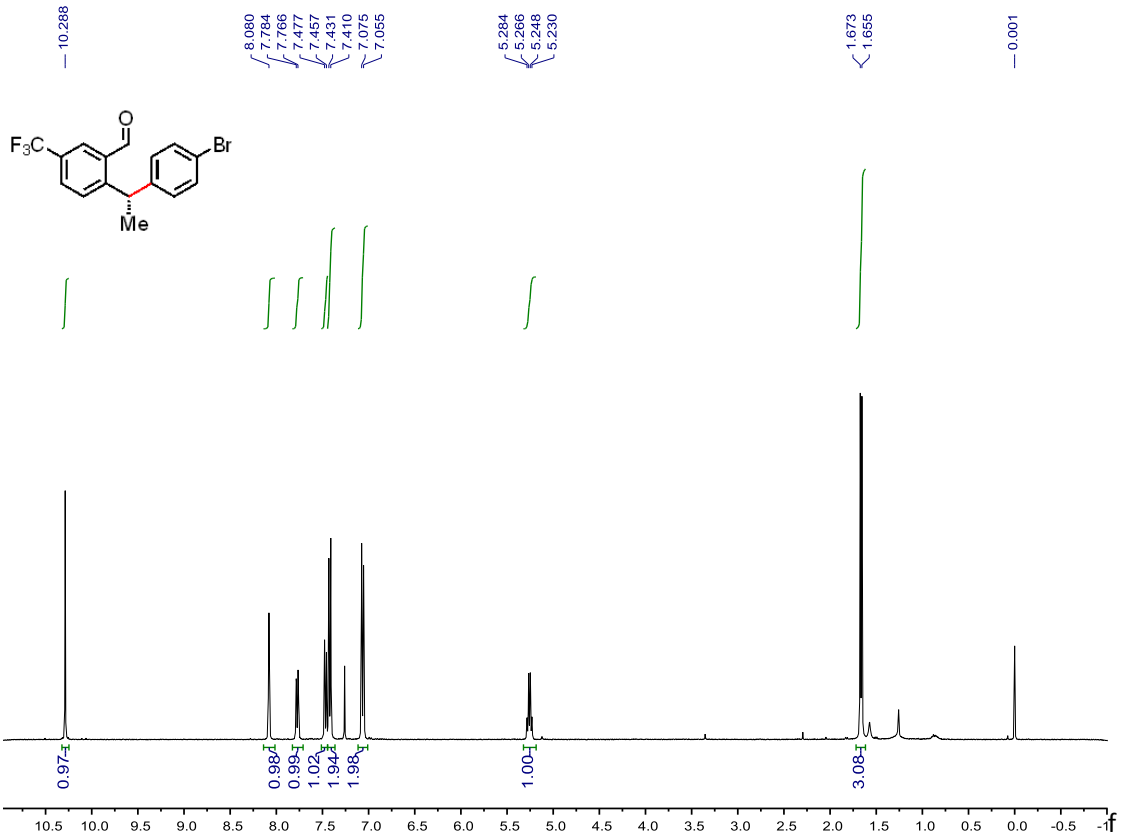
76.79
38.41
21.94
O
F3C
Cl
Me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7.055
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5.266
5.248
5.230
1.673
1.655
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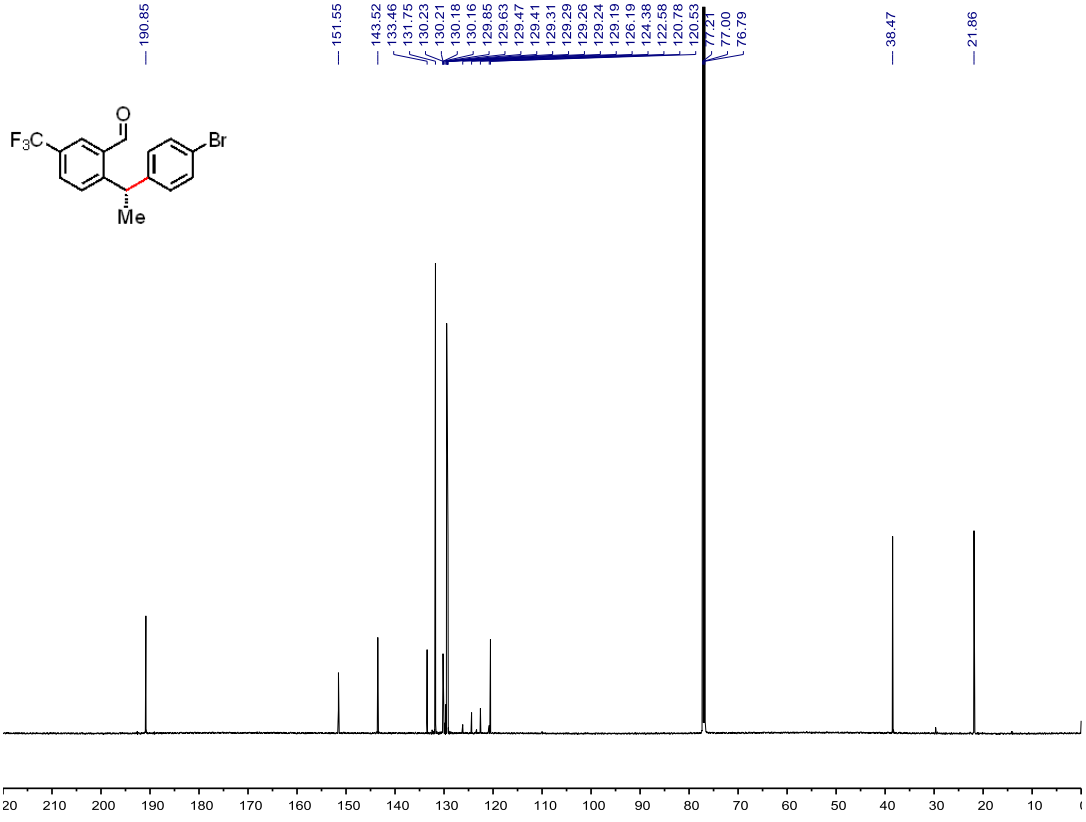
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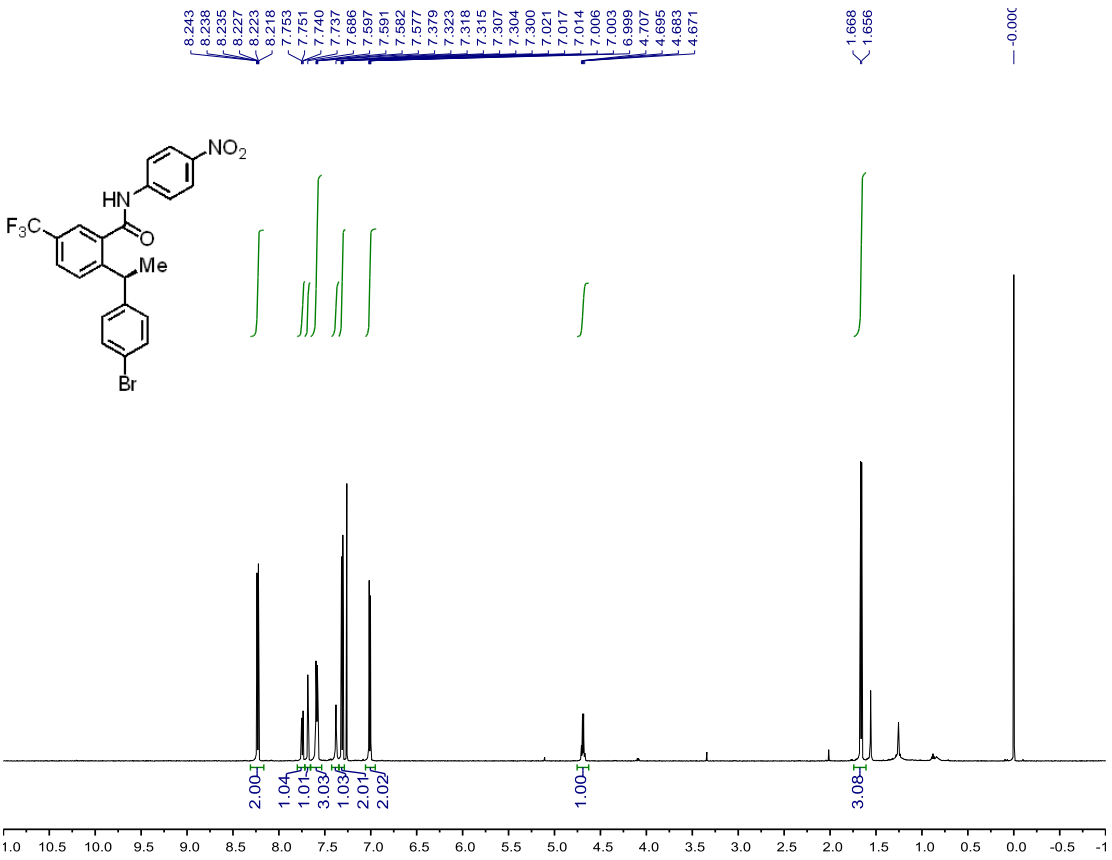
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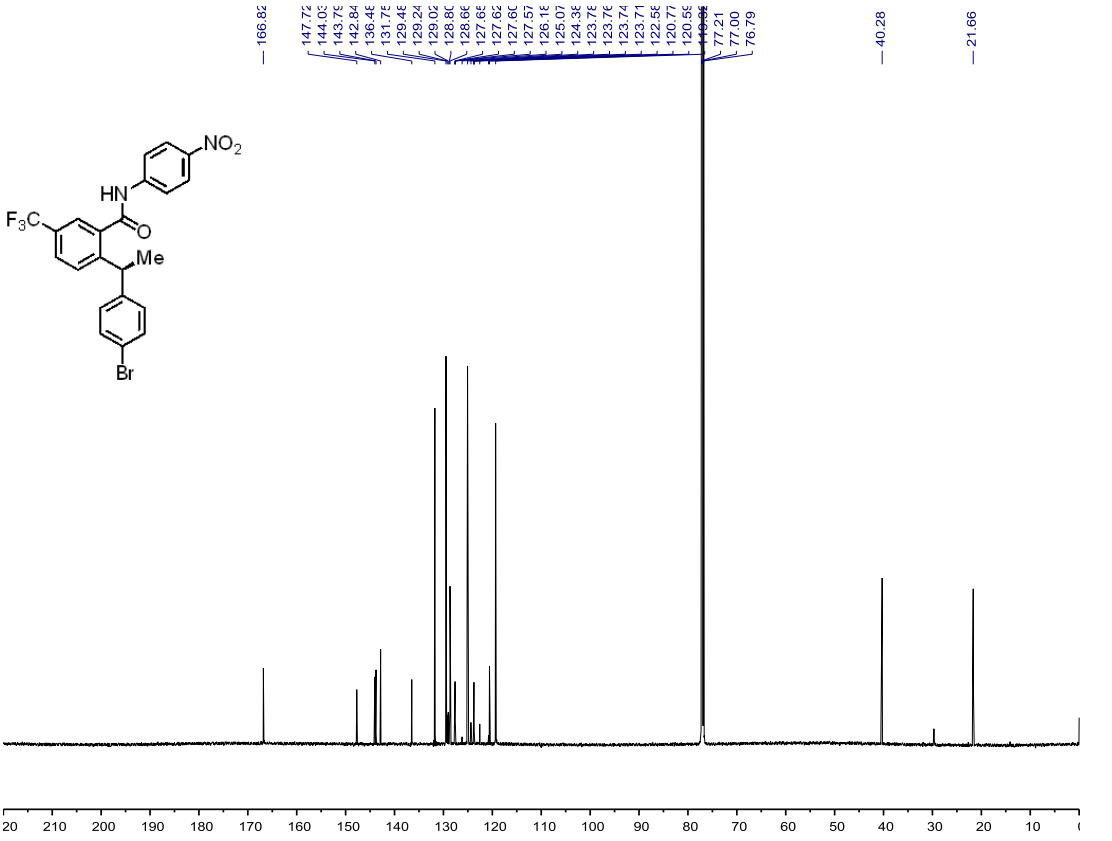
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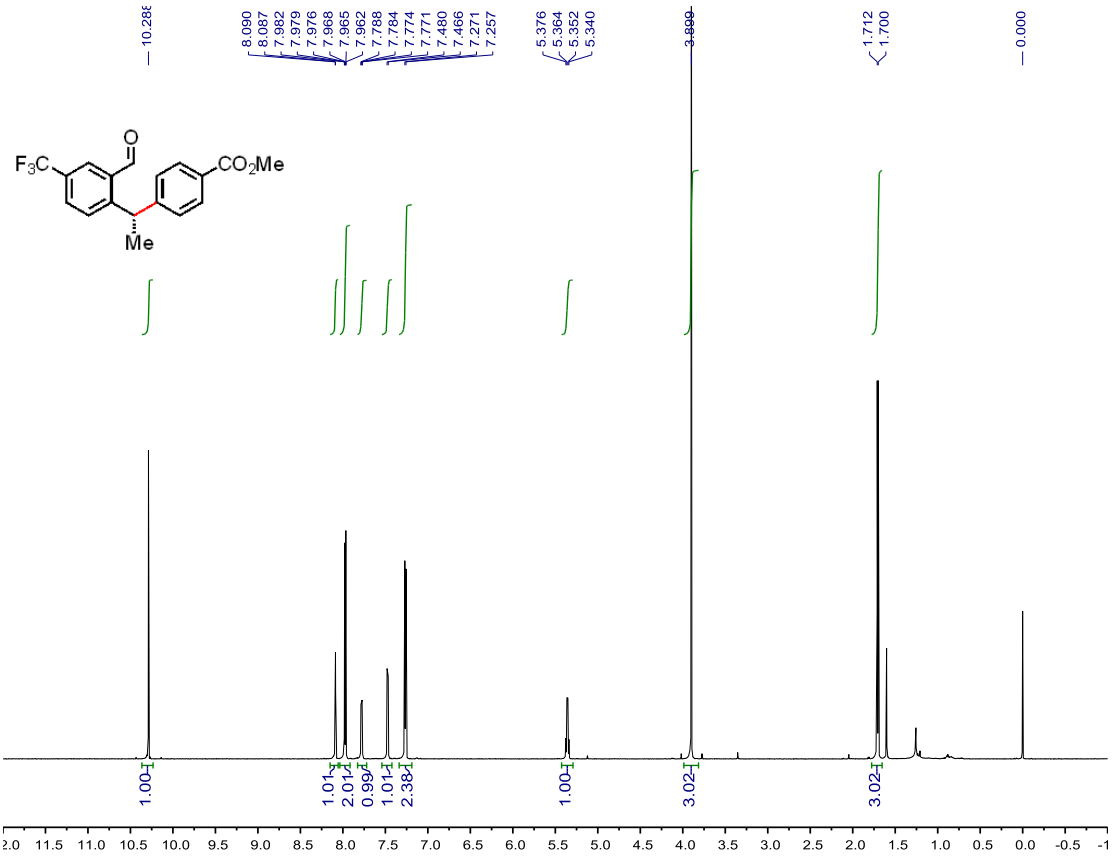
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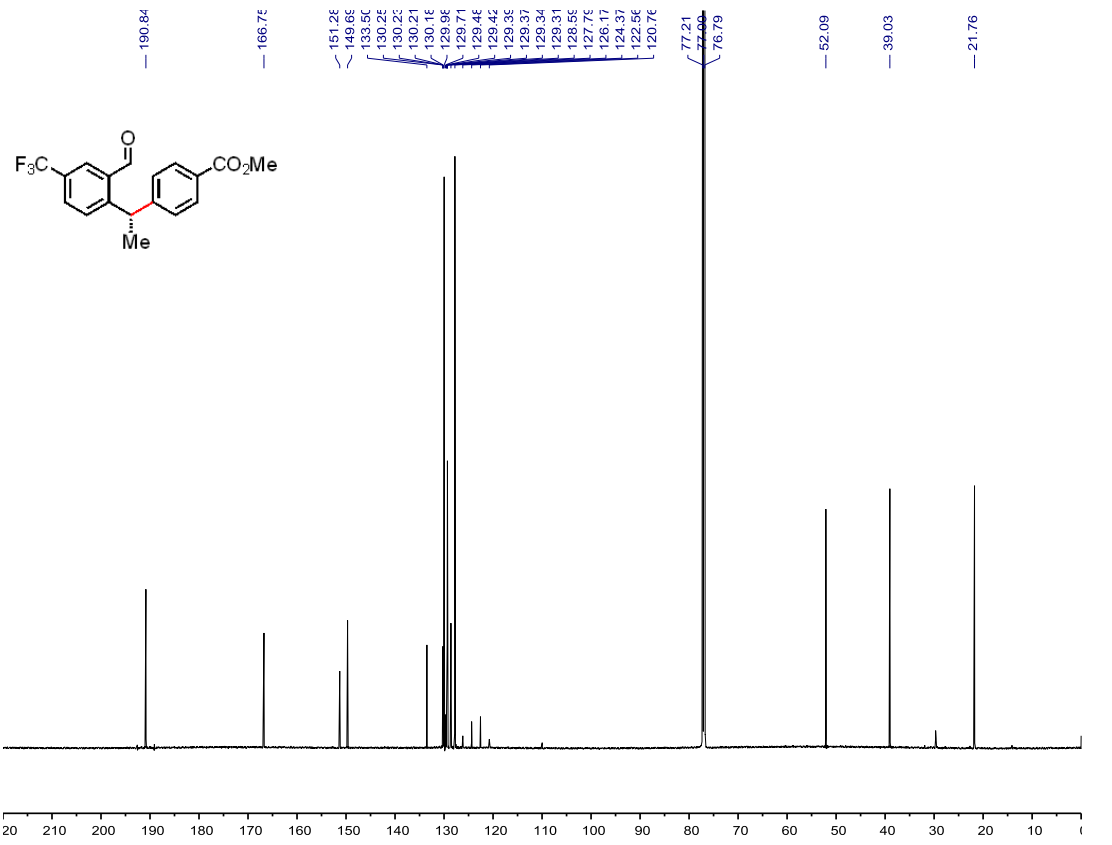
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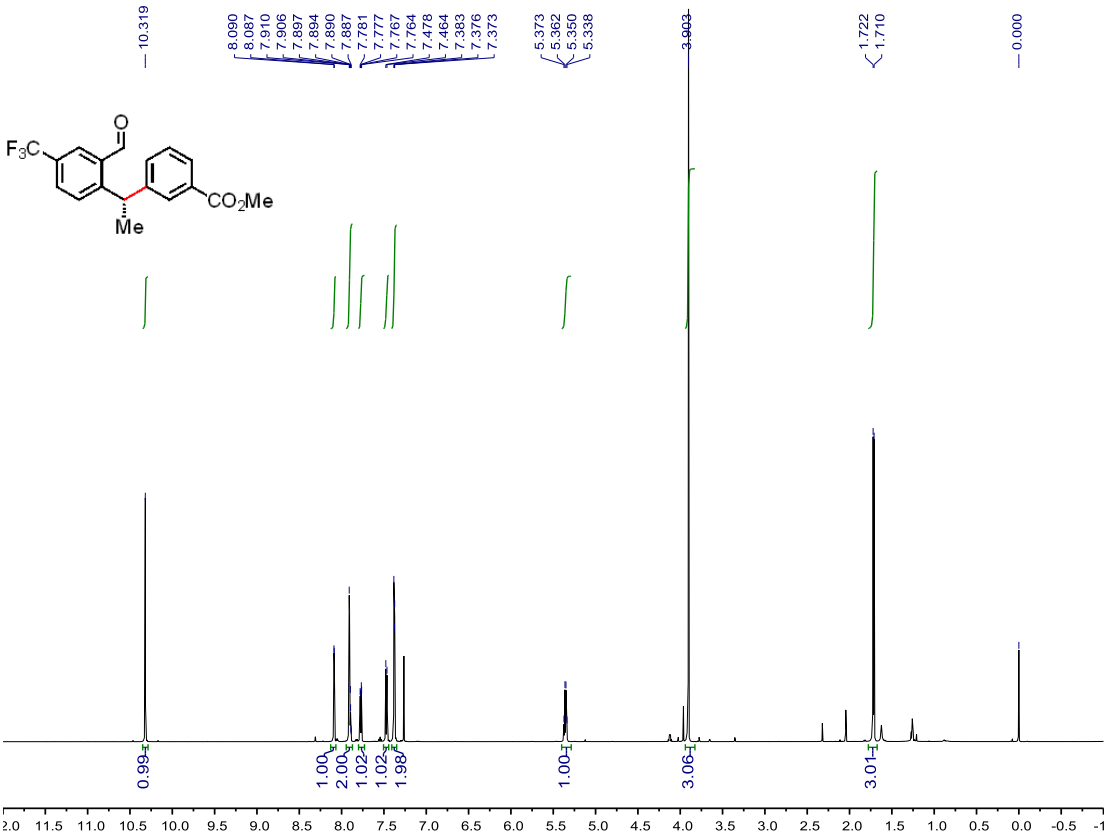
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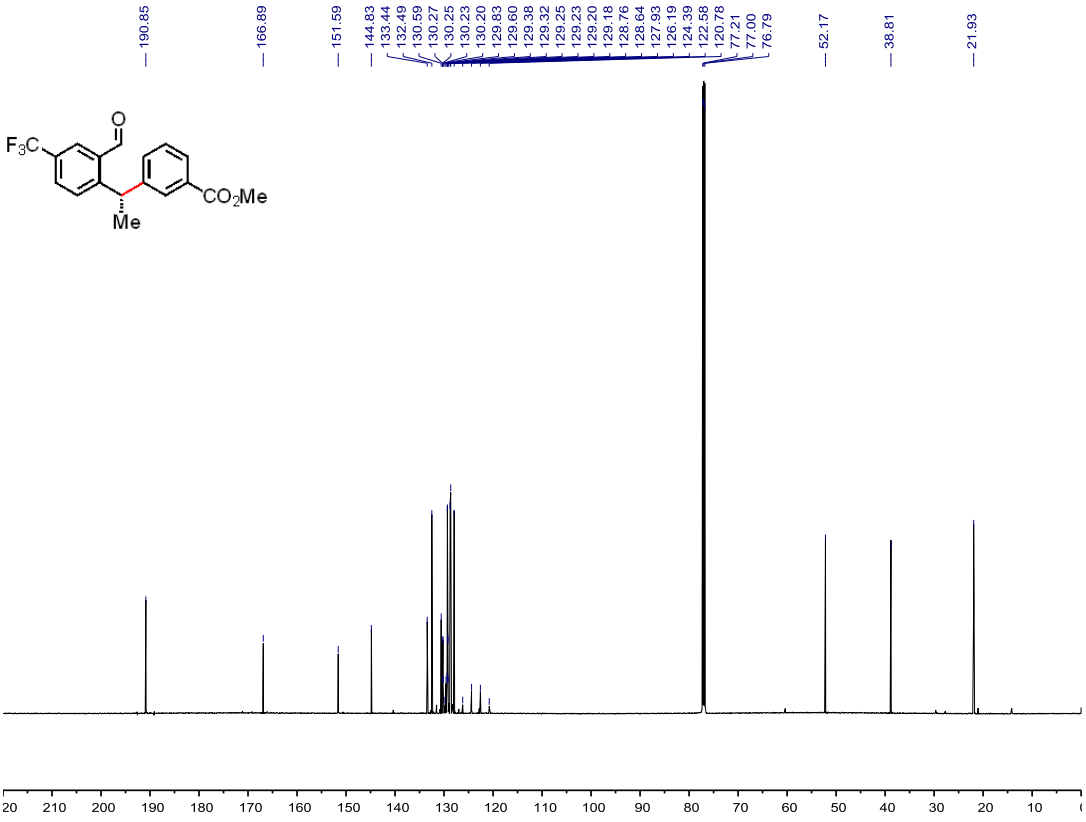
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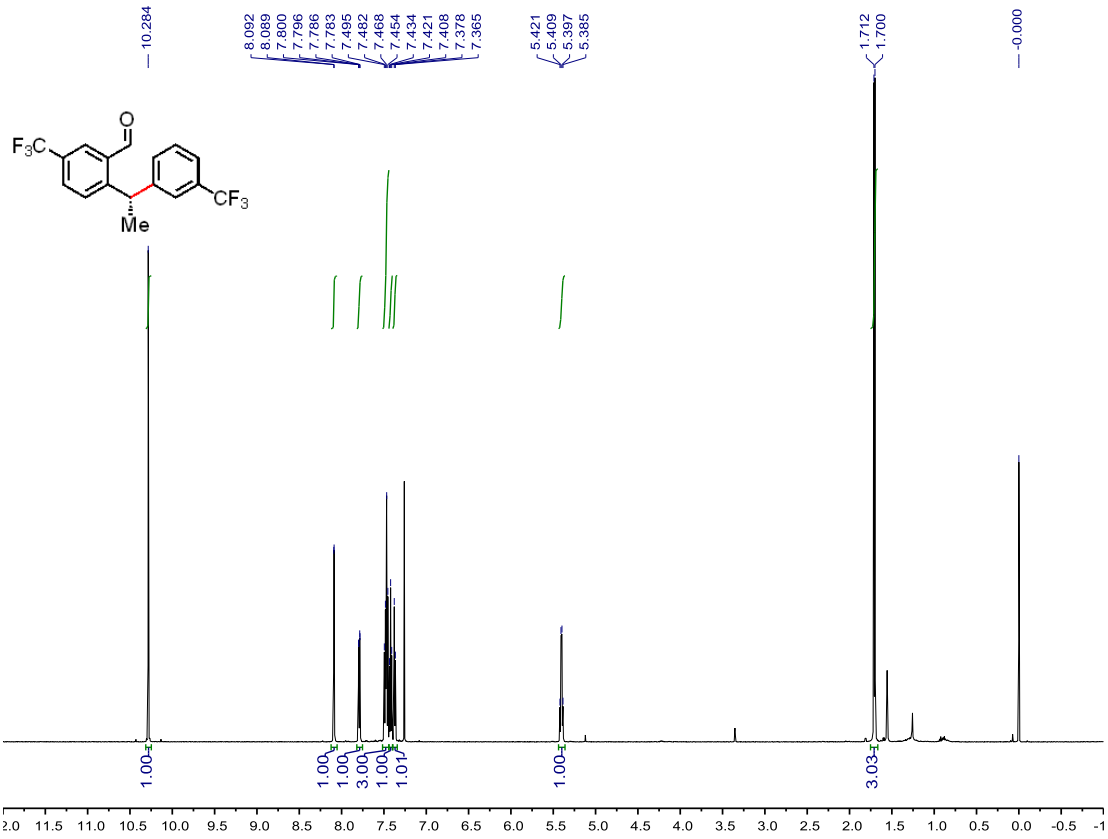
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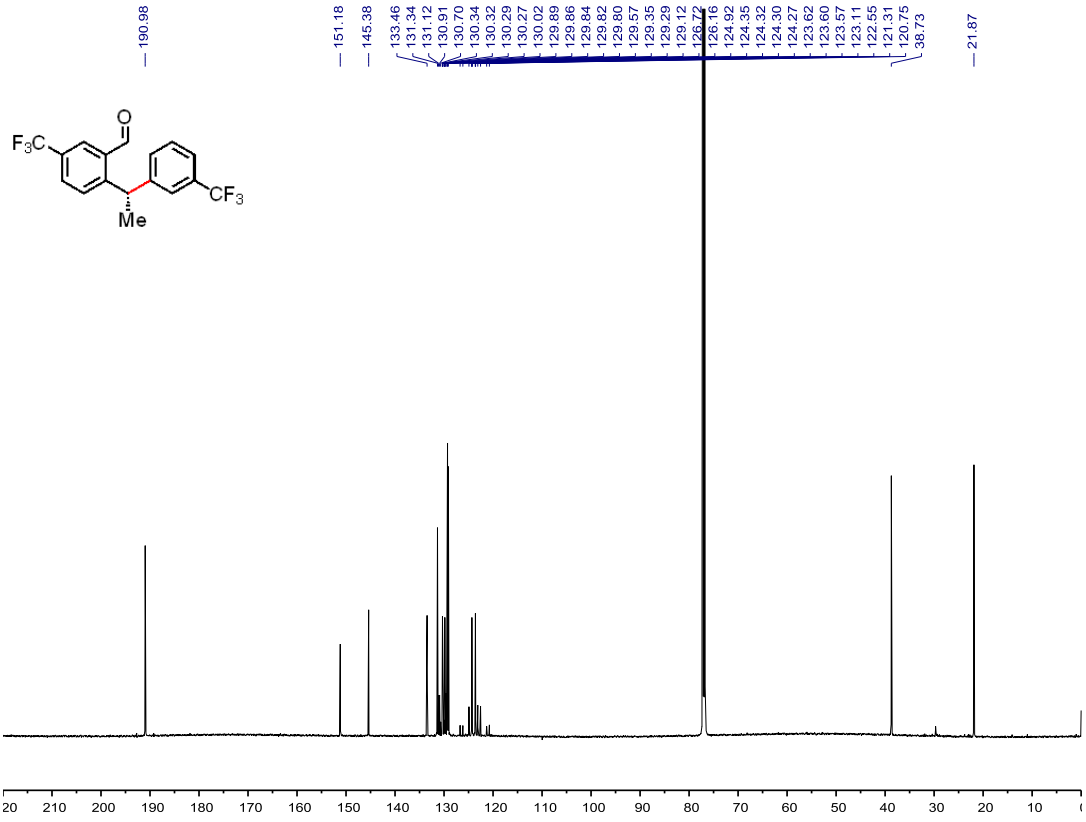
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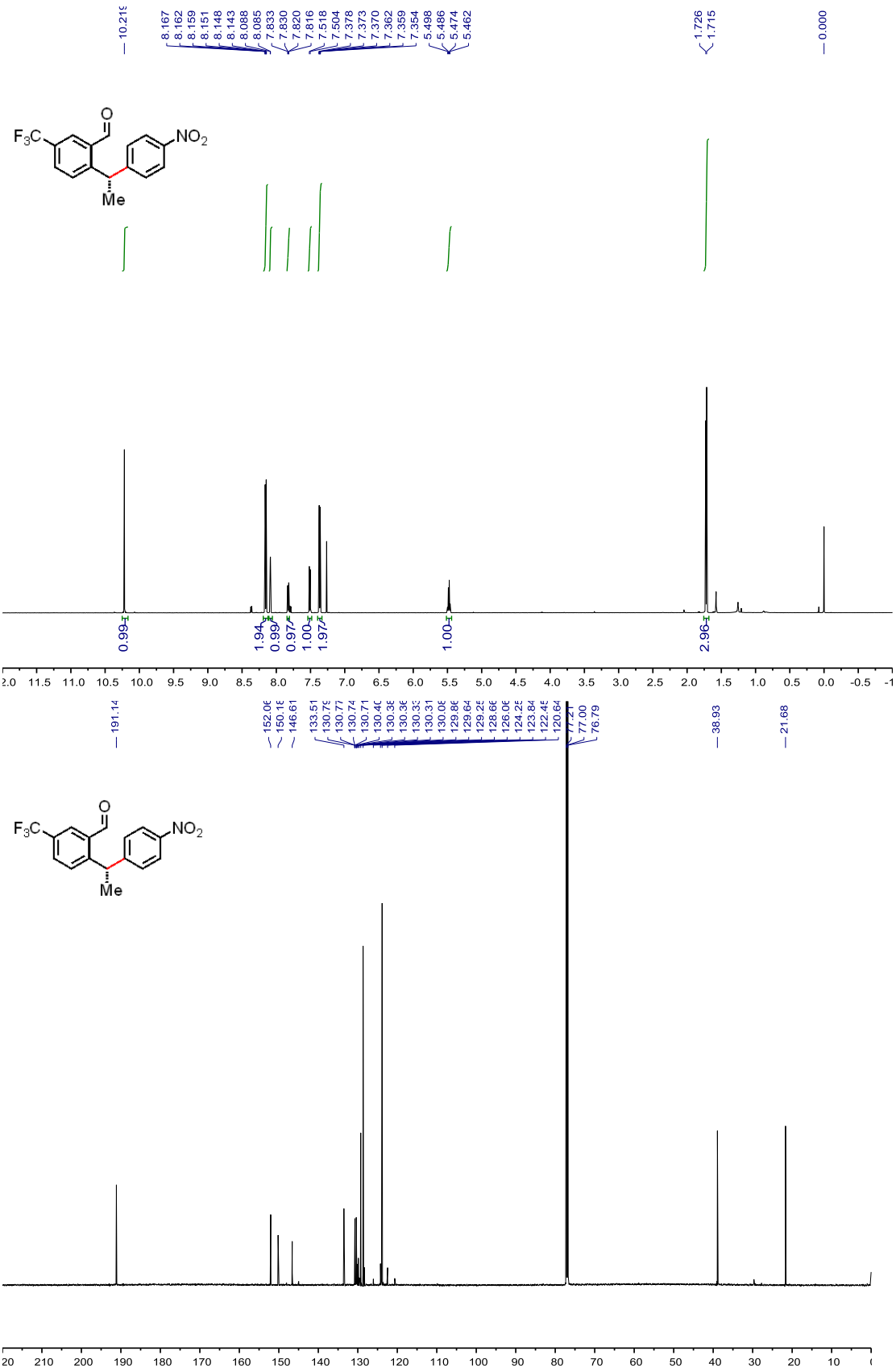
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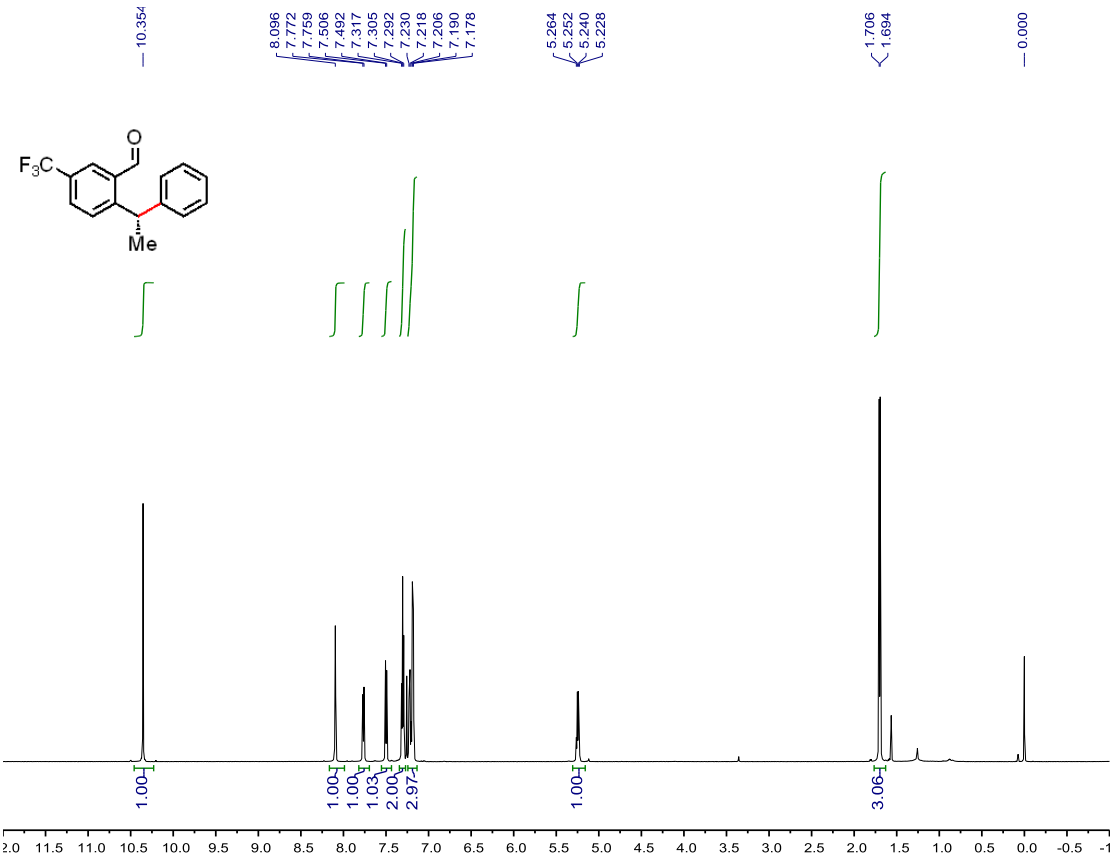
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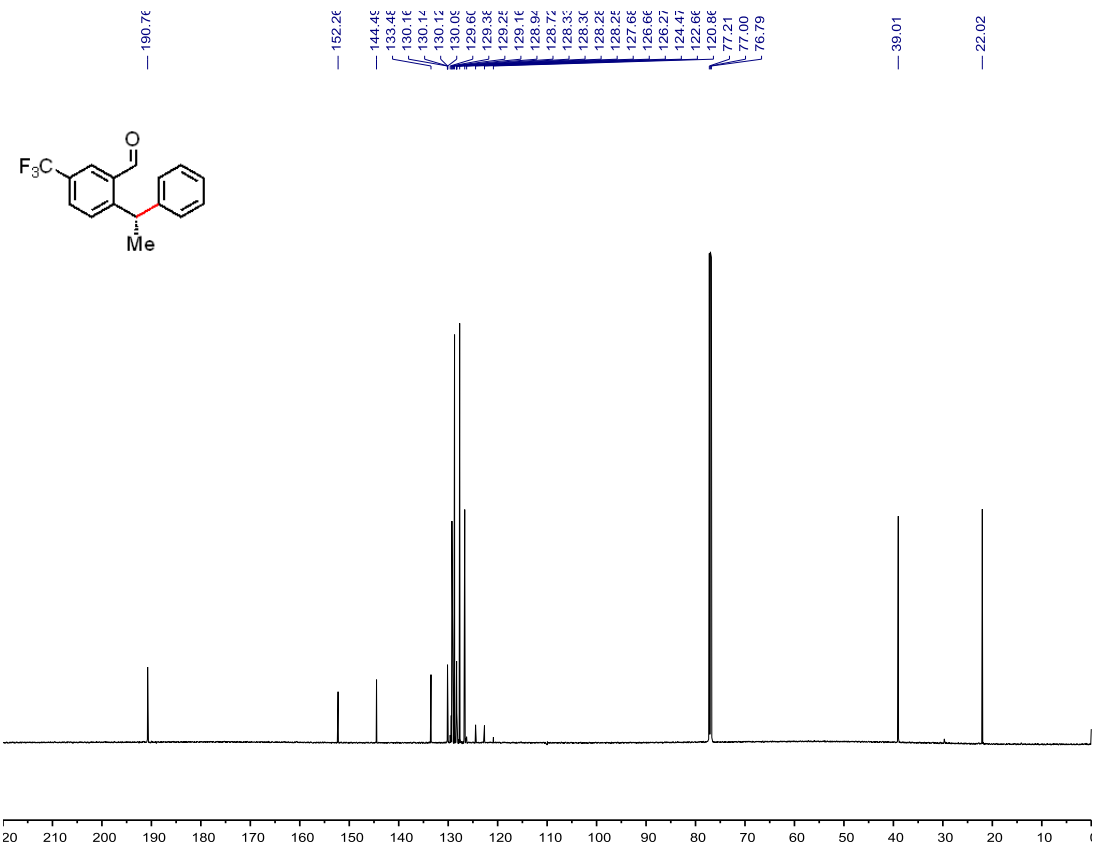
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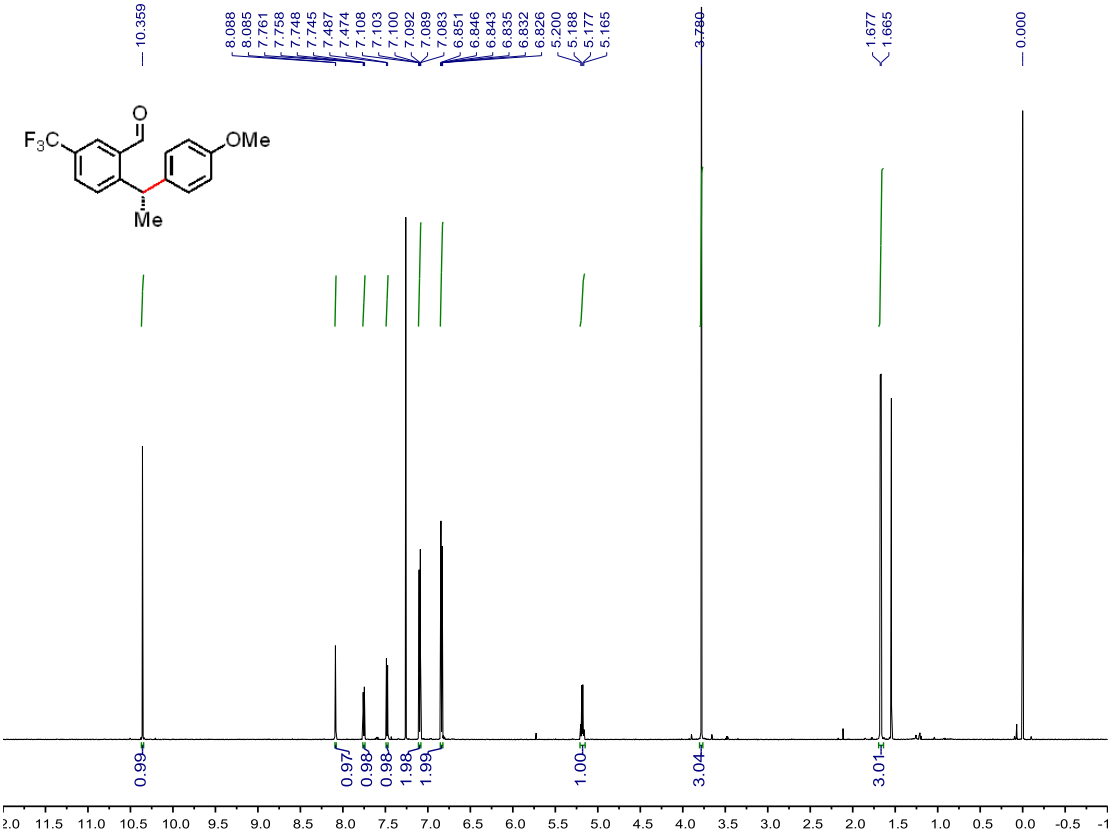
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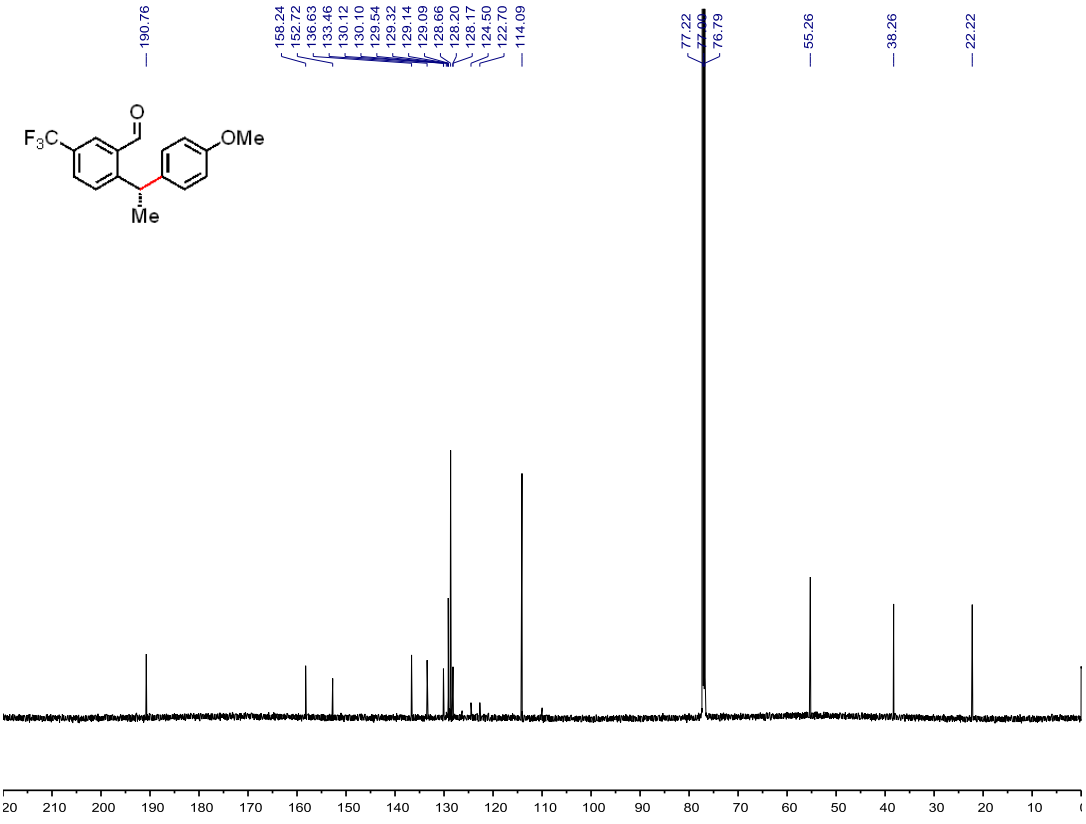
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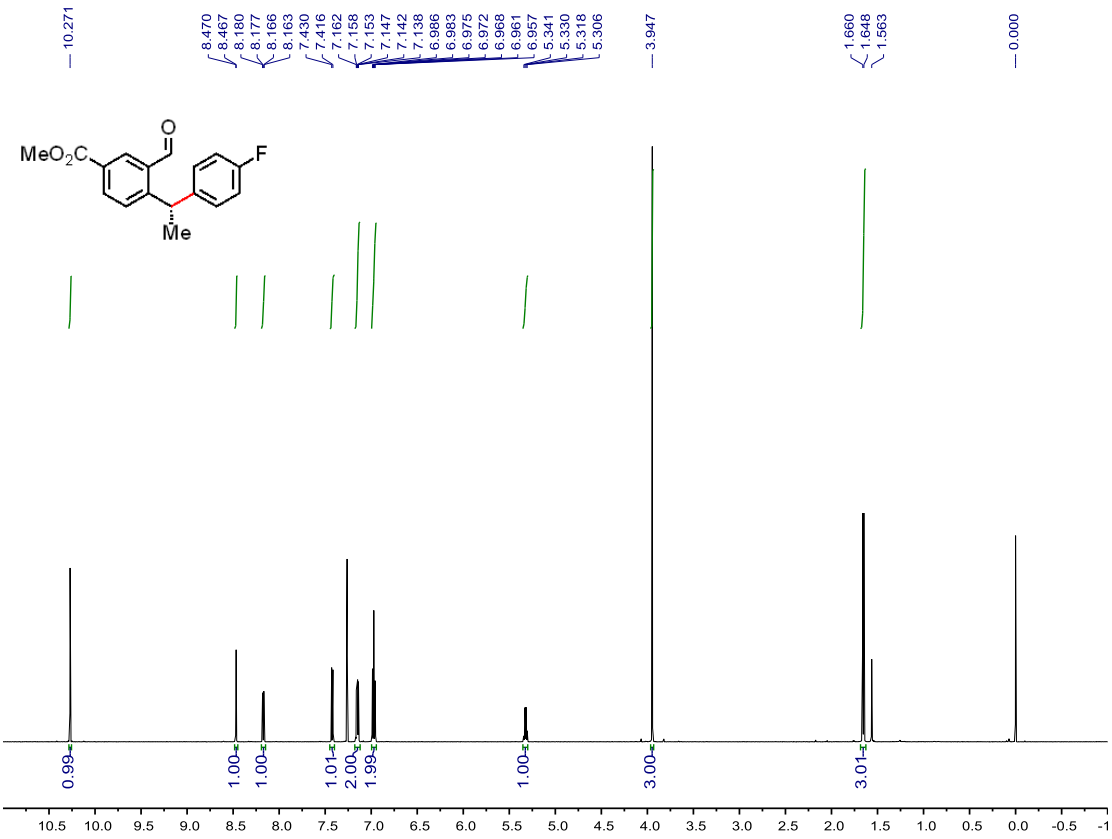
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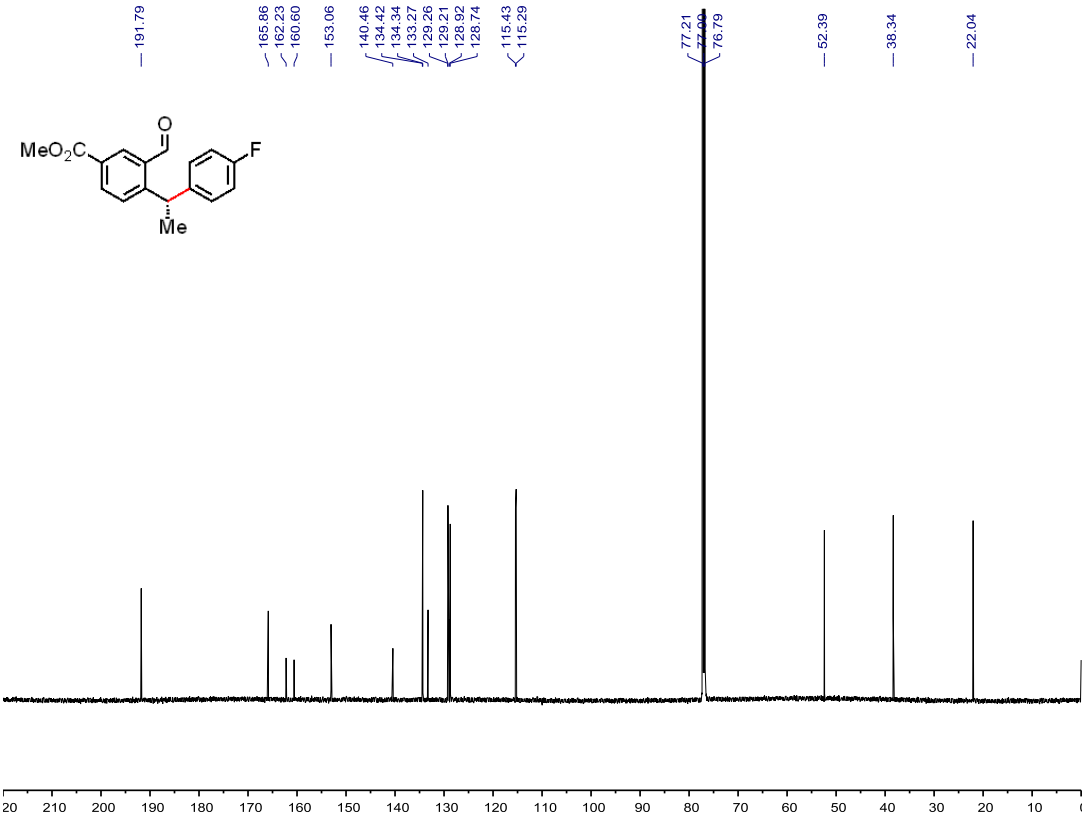
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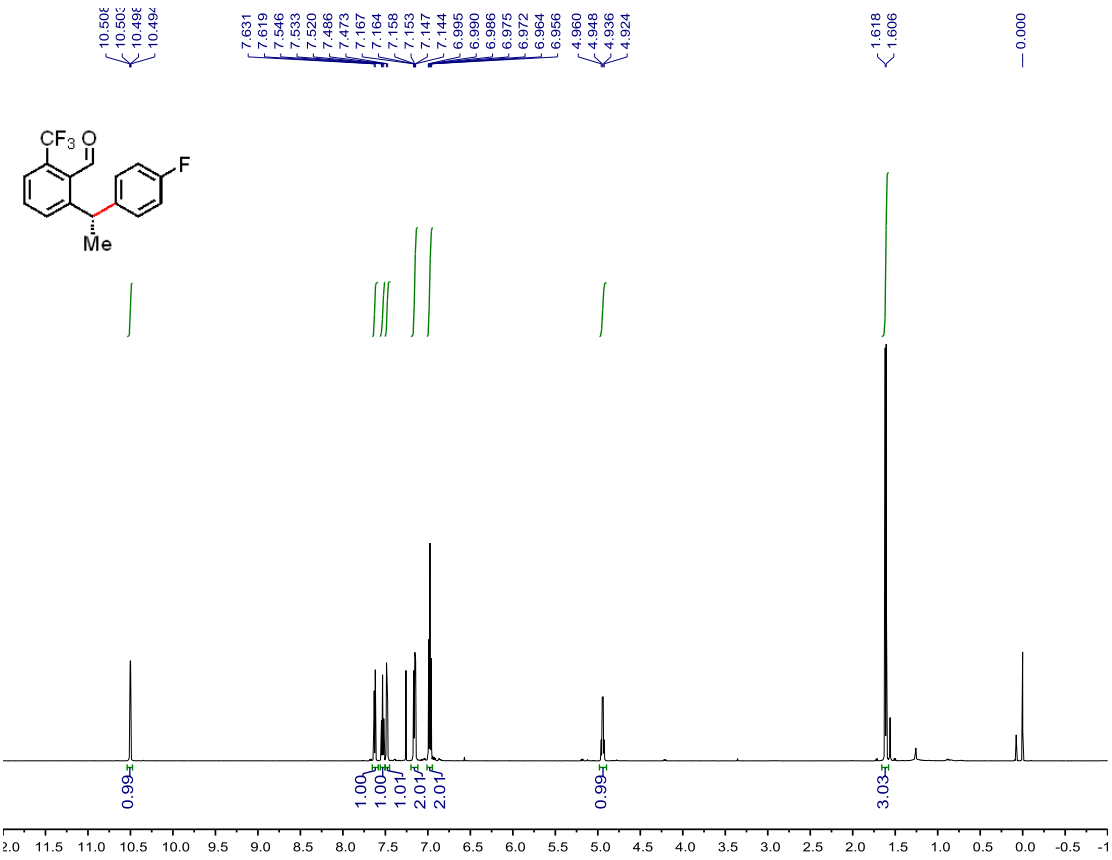
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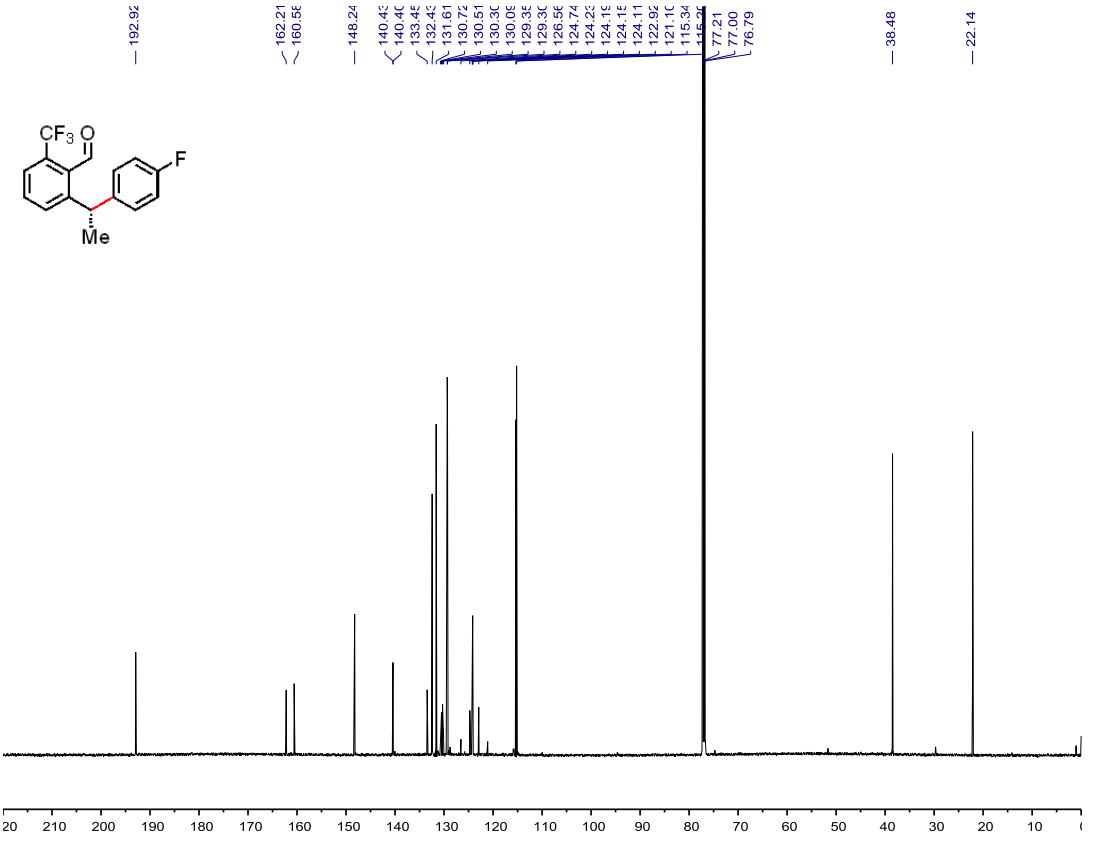
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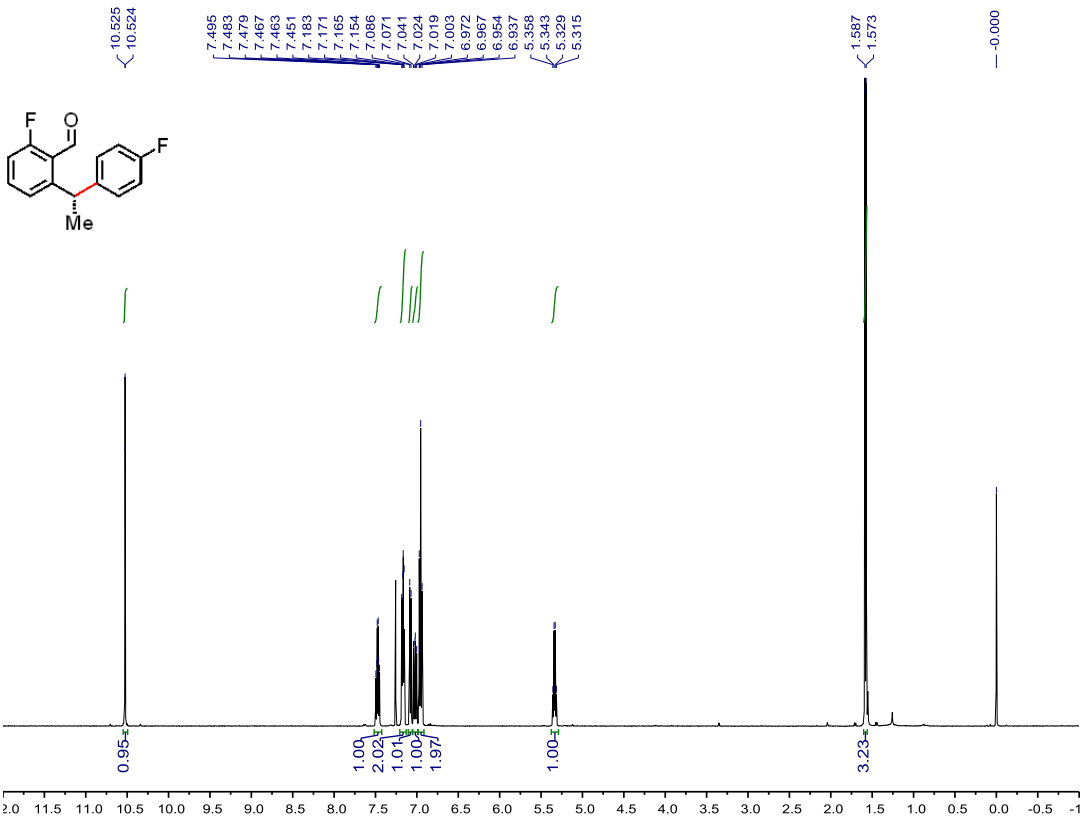
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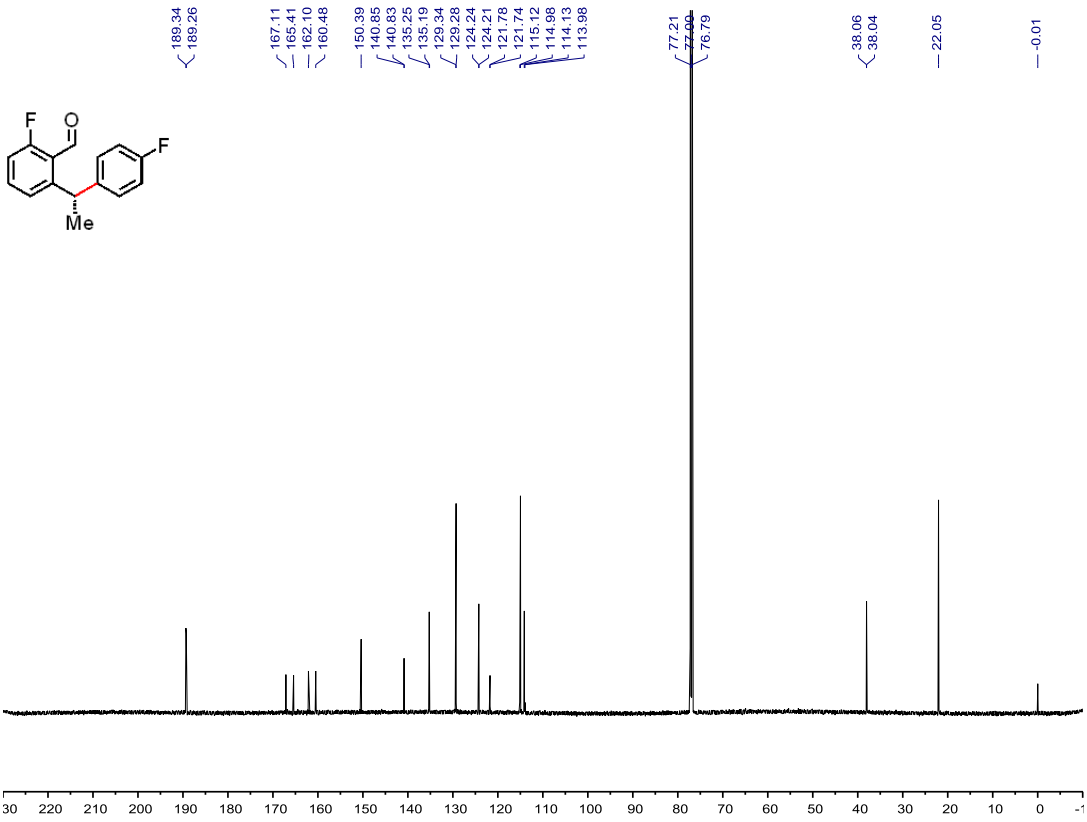
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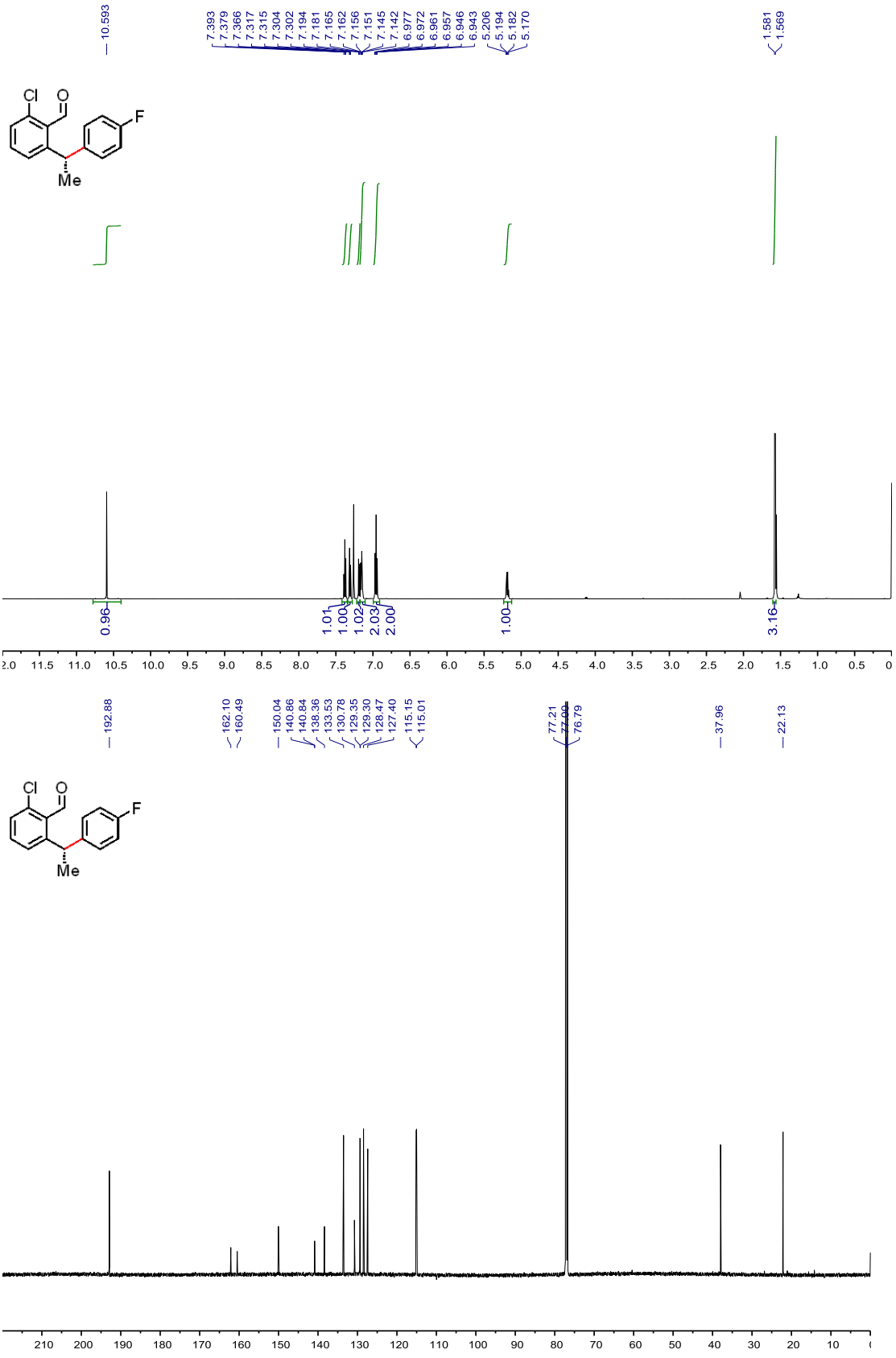
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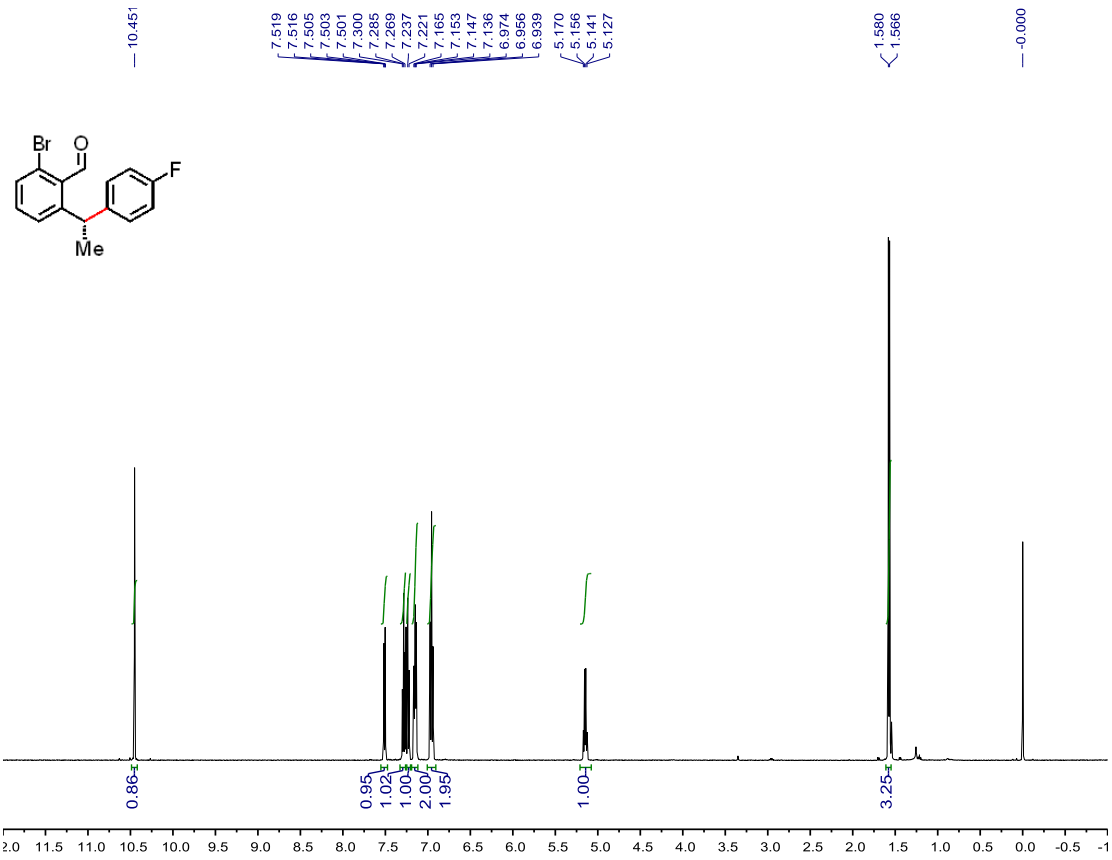
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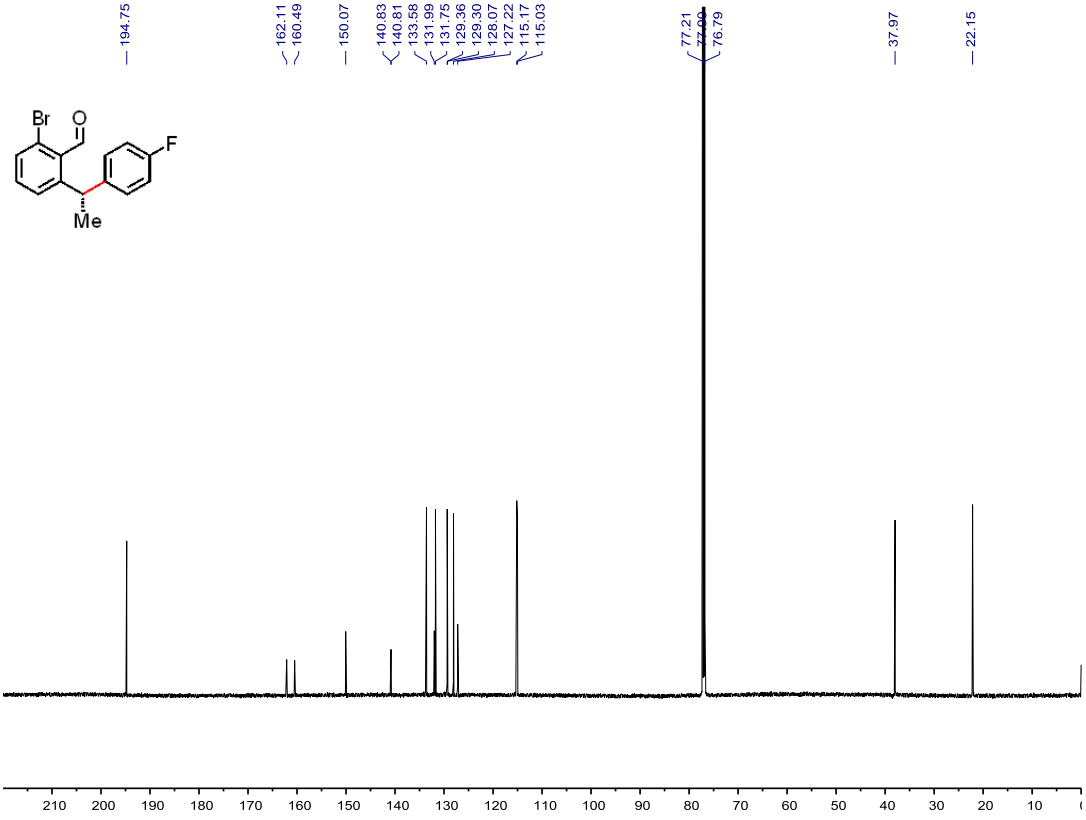
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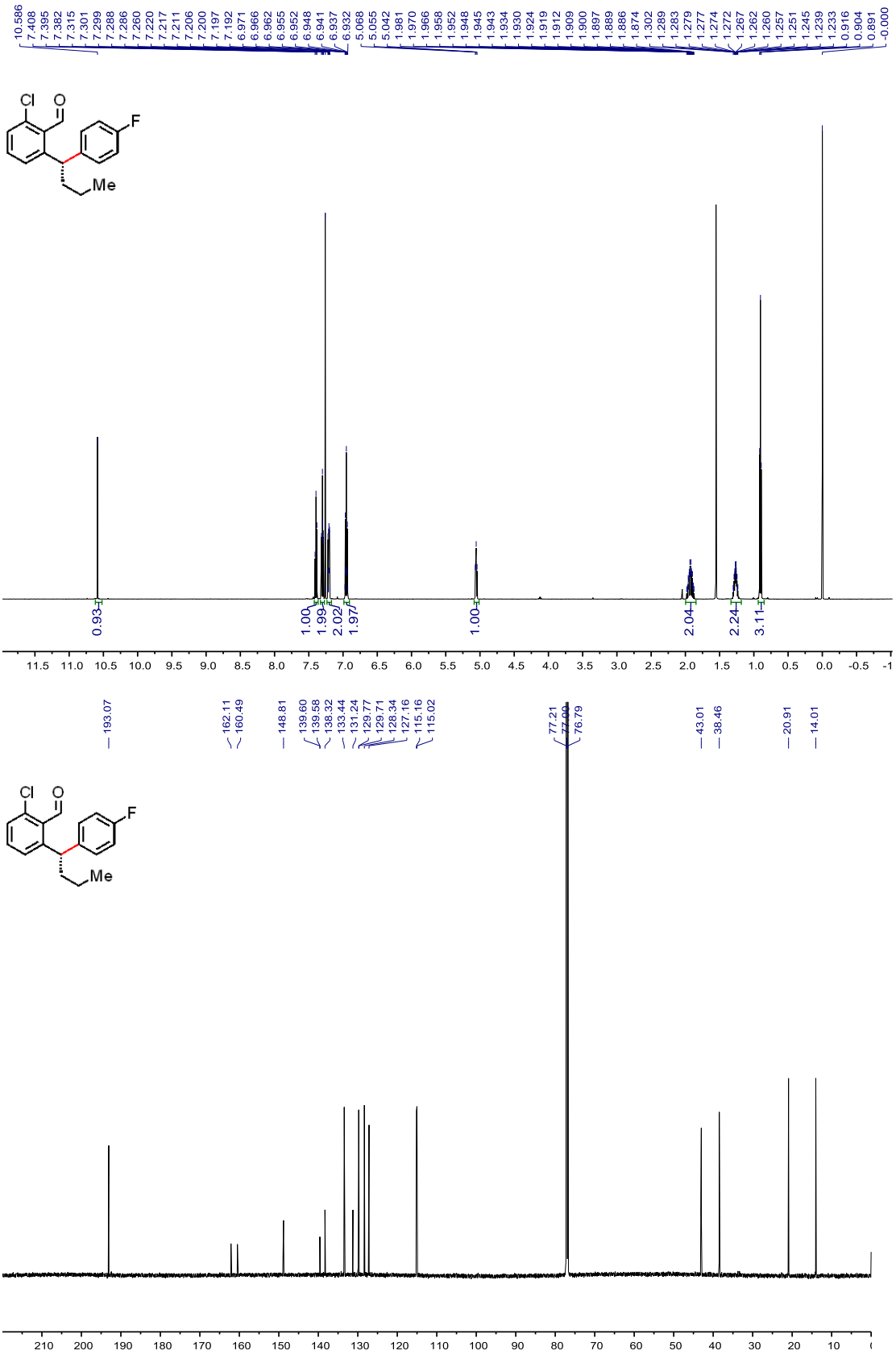
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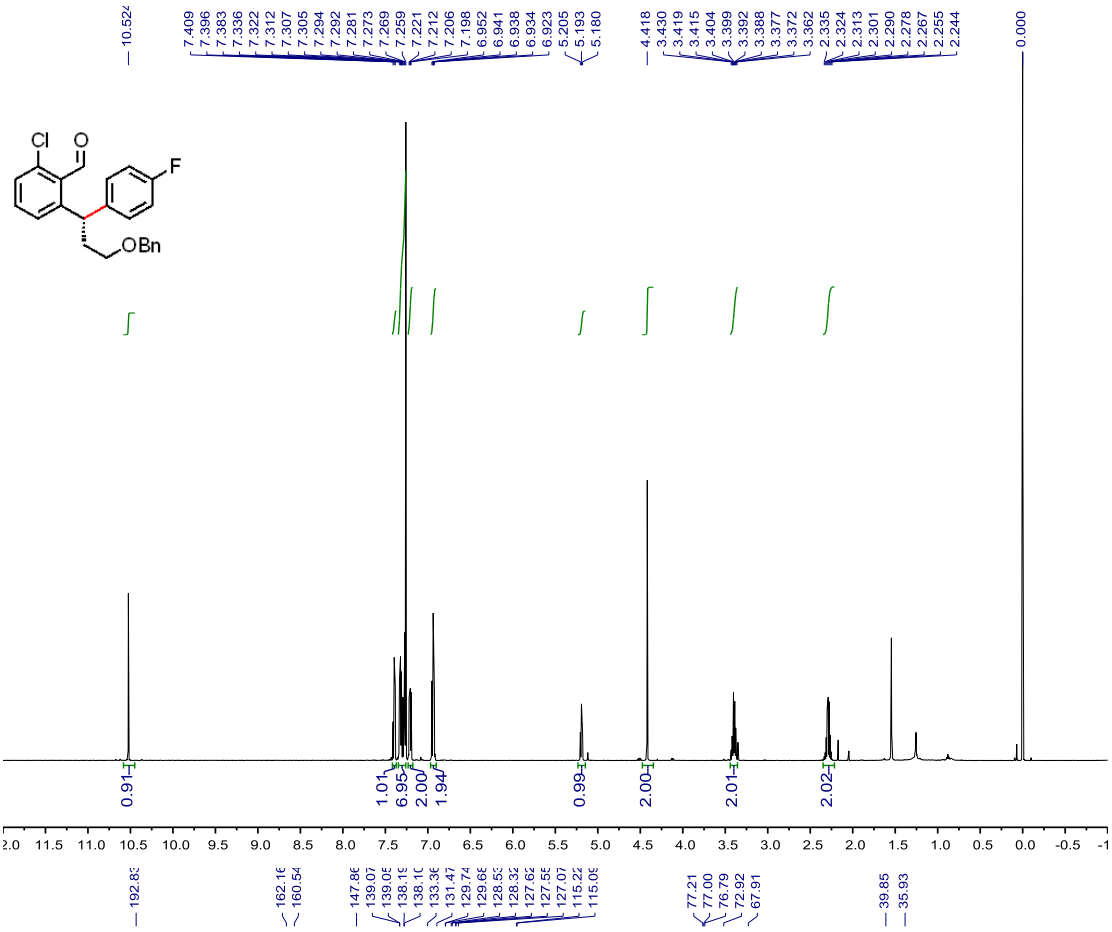
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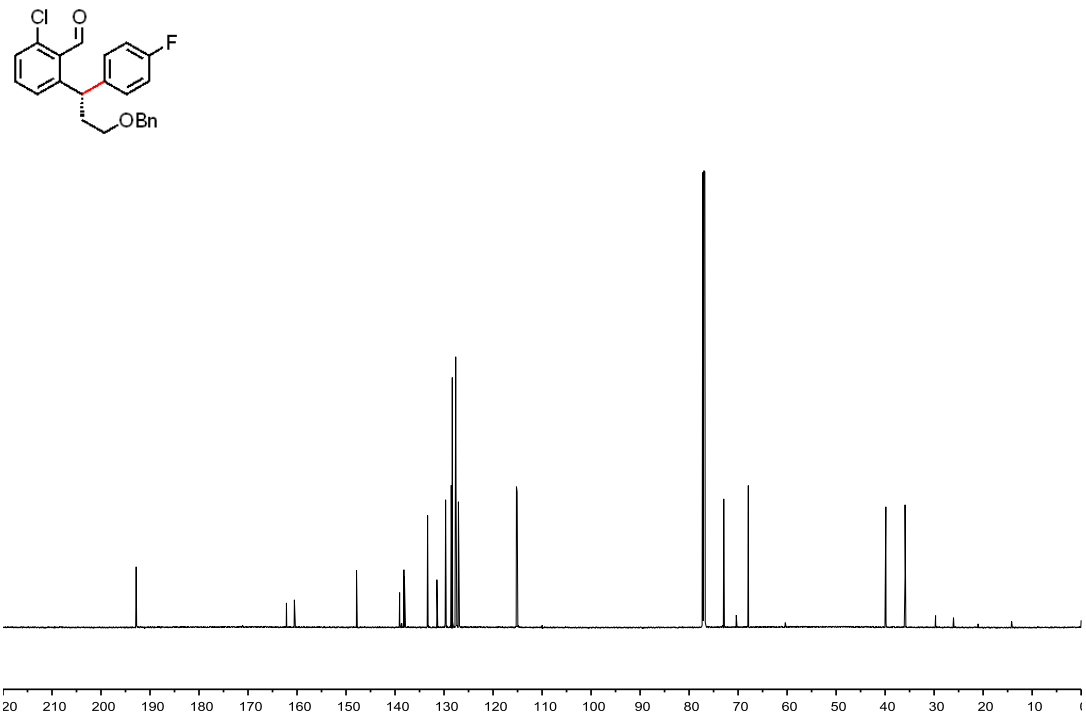
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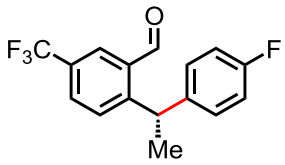
OBn

HPLC Spectra



Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-135-dilute-1%IPA-0.5ml-min-20min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 20 min without fc 0.5 ml per min.met
Acquired: 9/12/2015 9:45:39 PM
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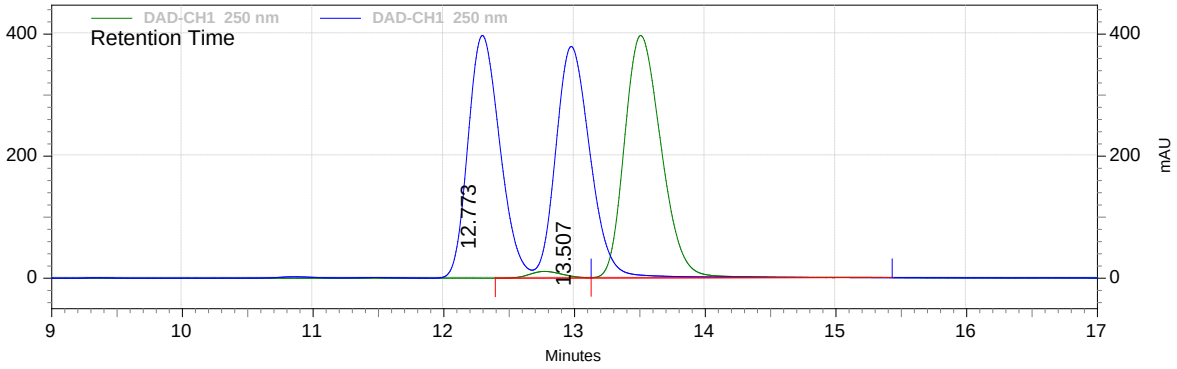
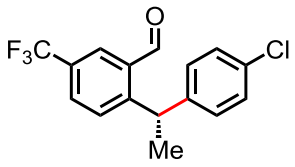


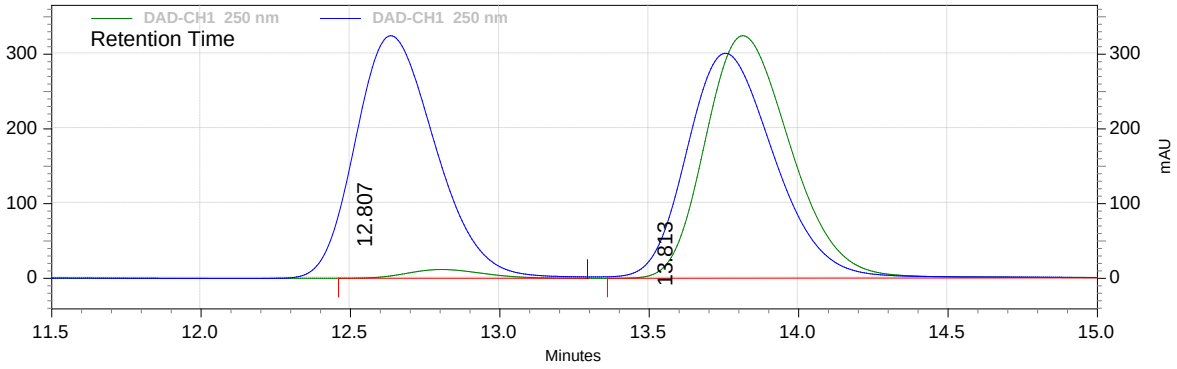
DAD-CH1 250 nm Results

Retention Time	Area	Area %	Height	Height %
12.773	753849	2.37	43391	2.66
13.507	31040381	97.63	1588913	97.34
Totals	31794230	100.00	1632304	100.00



Area % Report

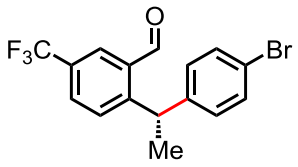
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\HP\HP-1-043-5-report-1%IPA-0.5ml-30min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 20 min without fc 0.5 ml per min.met
Acquired: 9/22/2015 2:21:20 PM
Printed: 9/22/2015 2:42:11 PM



DAD-CH1 250 nm Results

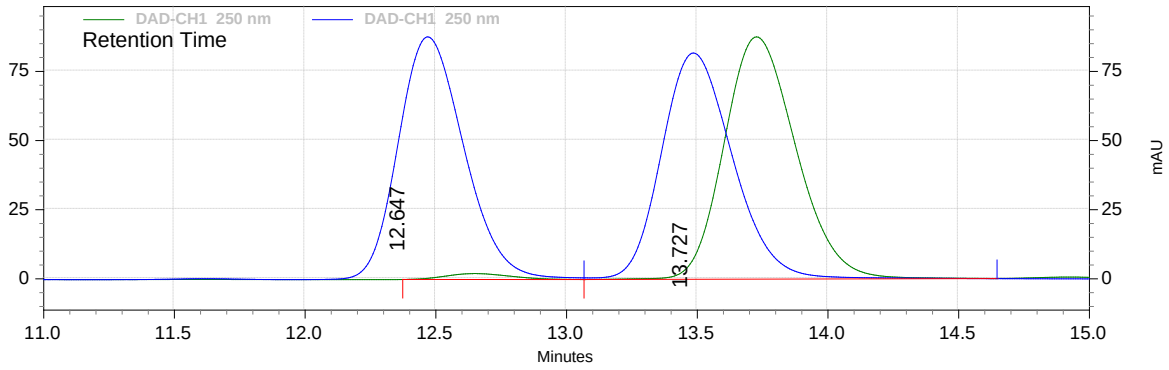
Retention Time	Area	Area %	Height	Height %
12.807	833113	3.13	46902	3.49
13.813	25822746	96.87	1297870	96.51

Totals				
	26655859	100.00	1344772	100.00



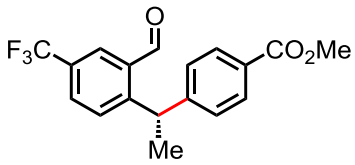
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-134-1%IPA-0.5ml-20min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 20 min without fc 0.5 ml per min.met
Acquired: 9/22/2015 12:14:02 AM
Printed: 9/22/2015 10:52:40 AM



DAD-CH1 250 nm Results

Retention Time	Area	Area %	Height	Height %
12.647	146092	2.14	8530	2.38
13.727	6692957	97.86	350195	97.62
Totals	6839049	100.00	358725	100.00



Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-132-A-10%IPA-0.5ml-min-30min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 30 min without fc 0.5 ml per min.met
Acquired: 9/15/2015 3:20:38 PM
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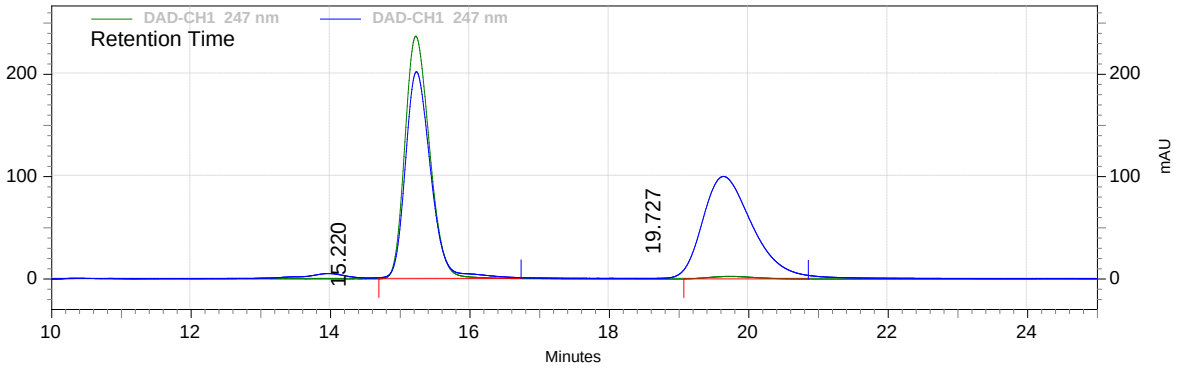
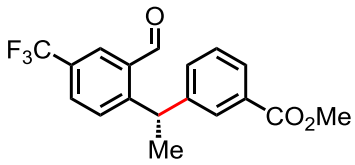


DAD-CH1 247 nm Results

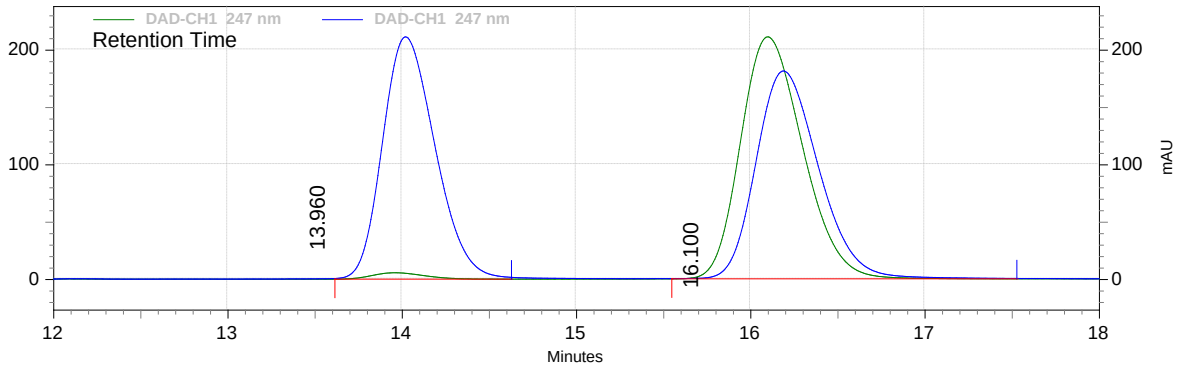
Retention Time	Area	Area %	Height	Height %
15.220	23241654	98.12	947263	98.98
19.727	445905	1.88	9791	1.02

Totals				
	23687559	100.00	957054	100.00



Area % Report

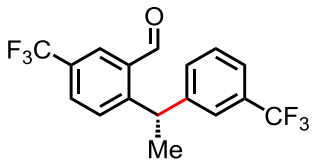
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-132-B-5%IPA-0.5ml-min-30min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 30 min without fc 0.5 ml per min.met
Acquired: 9/12/2015 11:59:54 PM
Printed: 9/20/2015 4:28:11 PM



DAD-CH1 247 nm Results

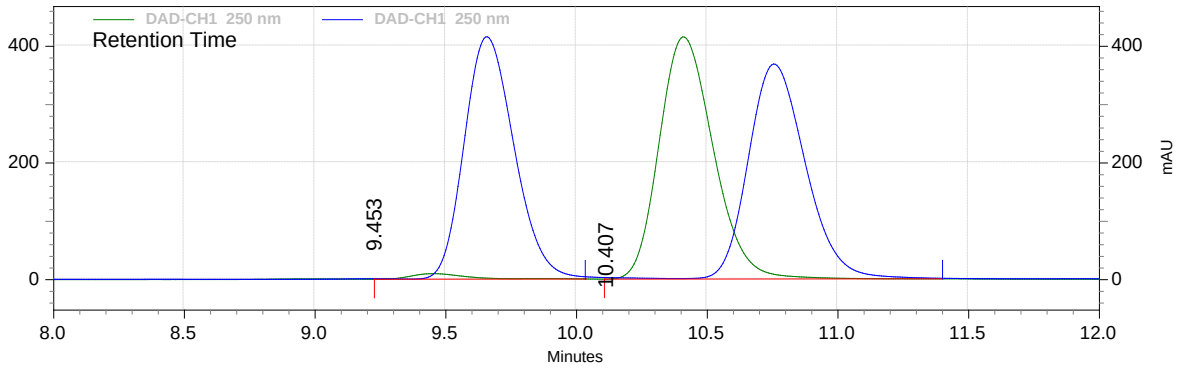
Retention Time	Area	Area %	Height	Height %
13.960	463549	2.17	22385	2.58
16.100	20944361	97.83	843898	97.42

Totals				
	21407910	100.00	866283	100.00



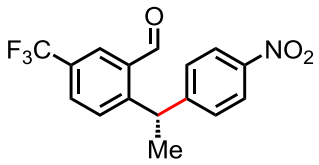
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-149-B-1%IPA-0.5ml-min-20min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 20 min without fc 0.5 ml per min.met
Acquired: 9/14/2015 9:02:34 PM
Printed: 9/20/2015 4:52:49 PM



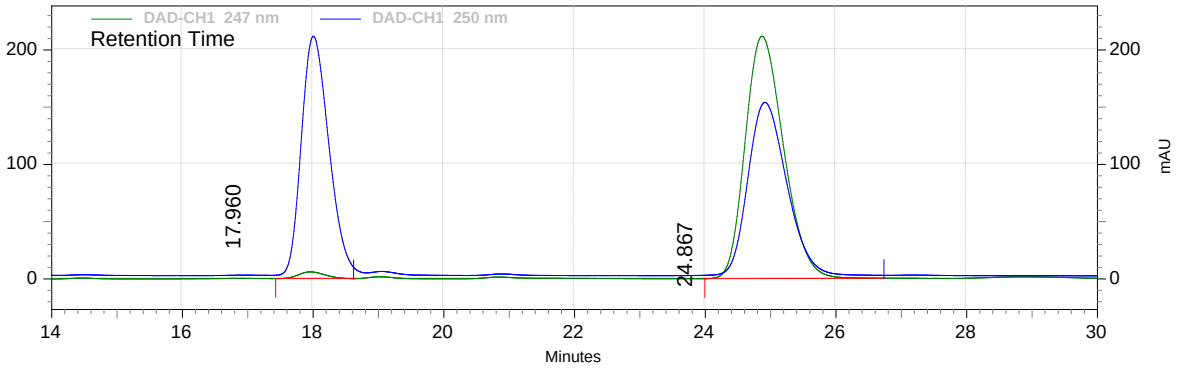
DAD-CH1 250 nm Results

Retention Time	Area	Area %	Height	Height %
9.453	561320	2.29	38231	2.25
10.407	23949861	97.71	1660094	97.75
Totals	24511181	100.00	1698325	100.00



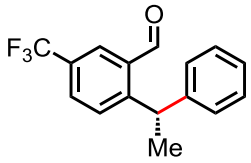
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-154-C-20%IPA-0.5ml-min-30min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 30 min without fc 0.5 ml per min.met
Acquired: 9/18/2015 8:36:05 PM
Printed: 9/18/2015 10:53:35 PM



DAD-CH1 247 nm Results

Retention Time	Area	Area %	Height	Height %
17.960	657590	1.86	23477	2.70
24.867	34618590	98.14	846528	97.30
Totals	35276180	100.00	870005	100.00



Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-3-075-A-1%IPA-0.5ml-min-30min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 30 min without fc 0.5 ml per min.met
Acquired: 11/27/2015 6:25:56 PM
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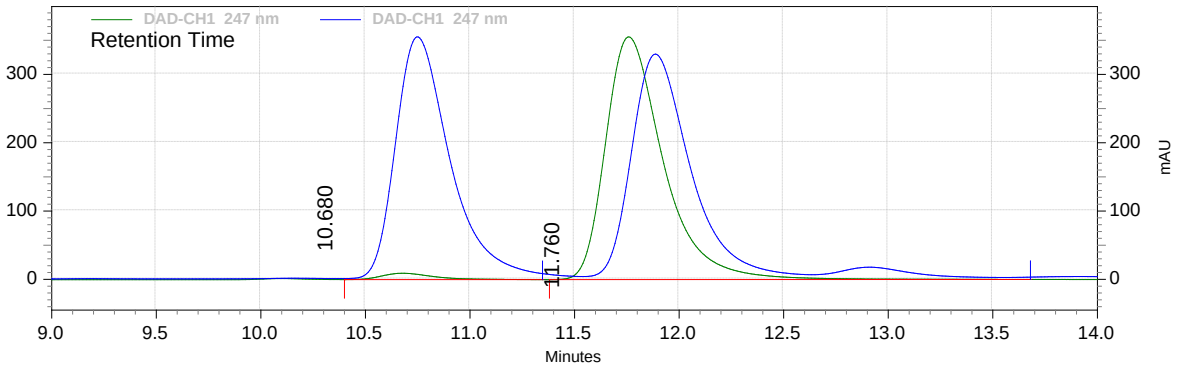
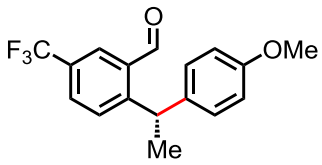


DAD-CH1 247 nm Results

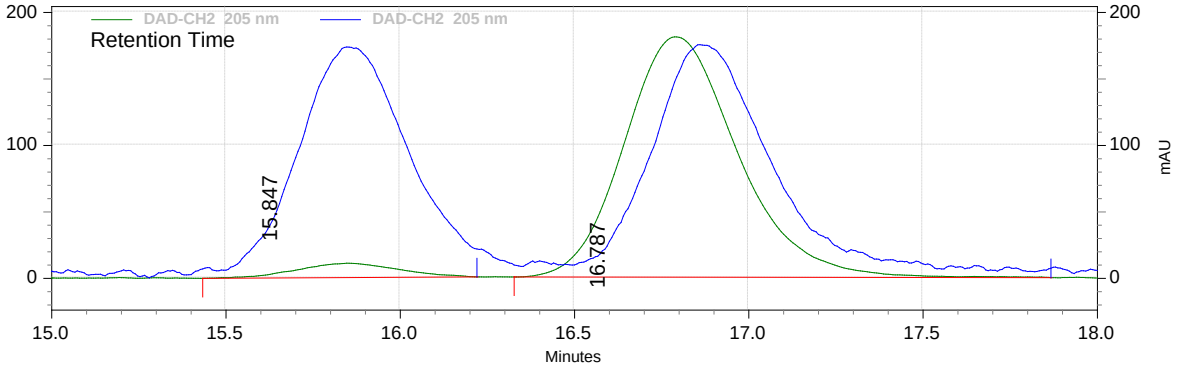
Retention Time	Area	Area %	Height	Height %
10.680	632406	2.26	37047	2.54
11.760	27319853	97.74	1420980	97.46

Totals				
	27952259	100.00	1458027	100.00



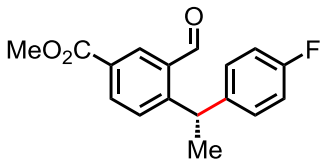
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\HP\HP-1-052-report-3%IPA-0.5ml-30min-OD-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 40 min without fc 0.5 ml per min.met
Acquired: 9/22/2015 4:09:22 PM
Printed: 9/22/2015 5:08:15 PM



DAD-CH1 250 nm Results

Retention Time	Area	Area %	Height	Height %
15.847	253676	5.00	12143	5.34
16.793	4821634	95.00	215333	94.66
Totals	5075310	100.00	227476	100.00



Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\HP\HP-1-041-2-5%IPA-0.5ml-30min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 30 min without fc 0.5 ml per min.met
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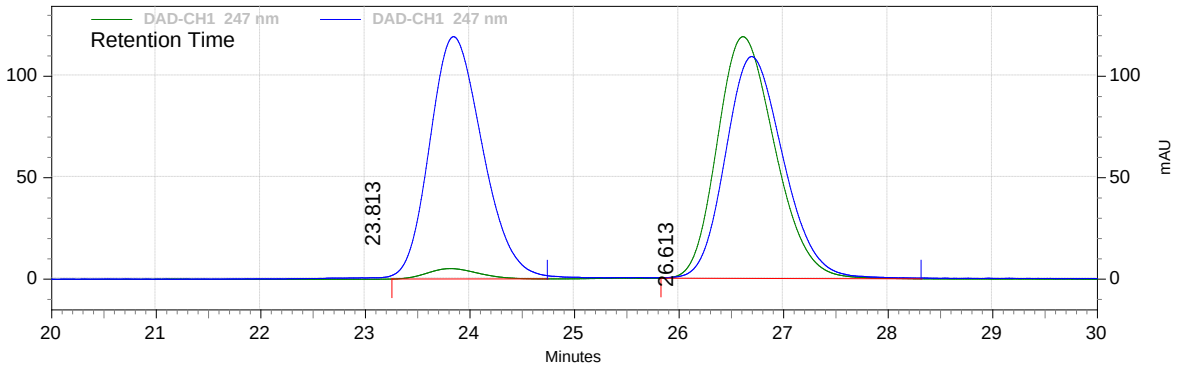
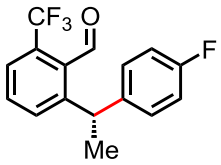


DAD-CH1 247 nm Results

Retention Time	Area	Area %	Height	Height %
23.813	697192	3.67	20523	4.13
26.613	18298532	96.33	476628	95.87
Totals	18995724	100.00	497151	100.00



Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-150-A-1%IPA-0.5ml-min-20min-AS-H
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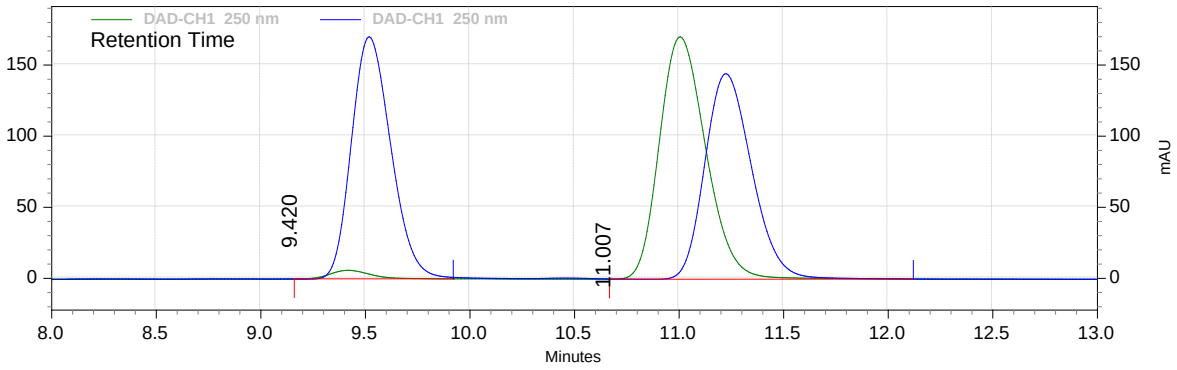
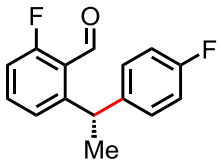


DAD-CH1 250 nm Results

Retention Time	Area	Area %	Height	Height %
9.420	317834	2.93	23919	3.39
11.007	10535448	97.07	681885	96.61
Totals	10853282	100.00	705804	100.00



Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-091-B-3%IPA-0.5ml-min-40min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 40 min without fc 0.5 ml per min.met
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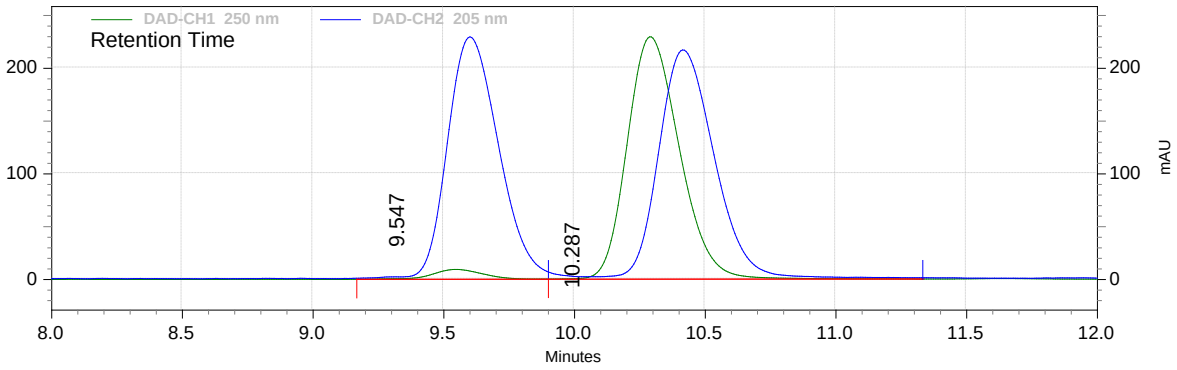
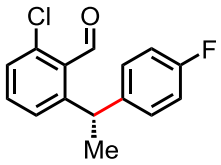


DAD-CH1 250 nm Results

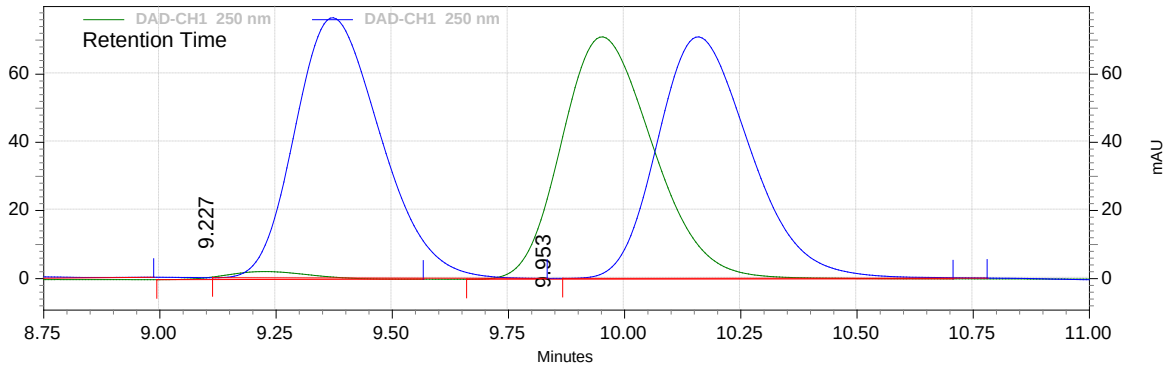
Retention Time	Area	Area %	Height	Height %
9.547	502990	3.79	37240	3.90
10.287	12759456	96.21	917668	96.10

Totals				
	13262446	100.00	954908	100.00



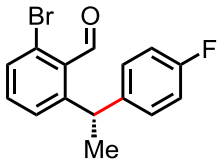
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-088-B -3%IPA-0.5ml-min-20min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 20 min without fc 0.5 ml per min.met
Acquired: 8/18/2015 5:46:32 PM
Printed: 9/19/2015 11:08:05 PM



DAD-CH1 250 nm Results

Retention Time	Area	Area %	Height	Height %
9.227	115704	2.88	9269	3.16
9.953	3904117	97.12	284443	96.84
Totals	4019821	100.00	293712	100.00



Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-104-3%IPA-0.5ml-min-20min-AS-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 20 min without fc 0.5 ml per min.met
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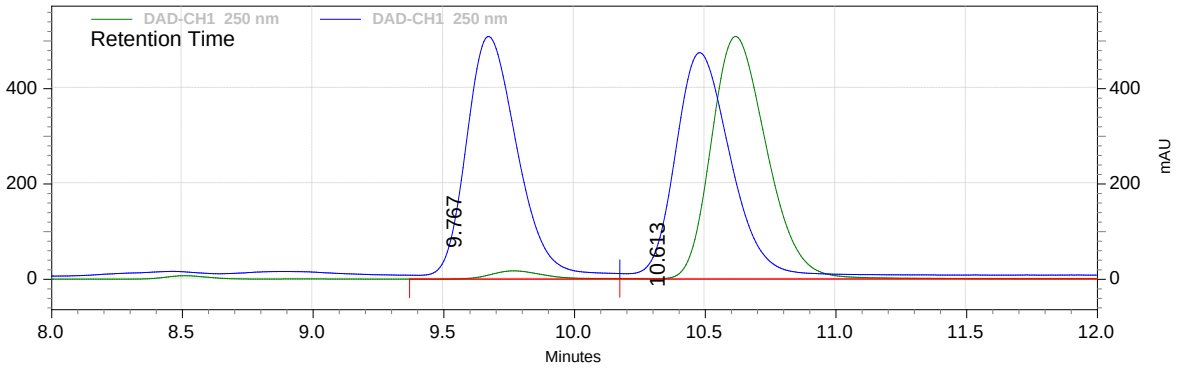
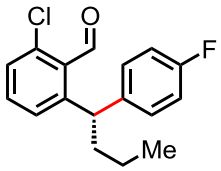


DAD-CH1 250 nm Results

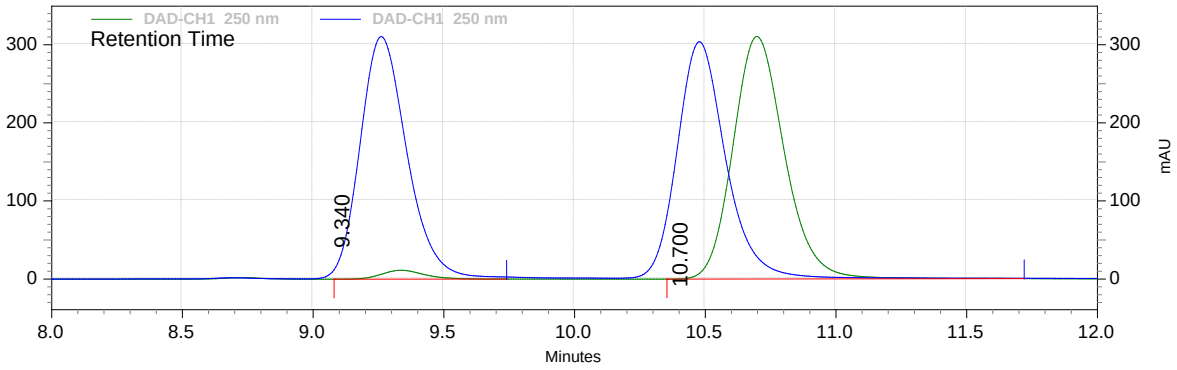
Retention Time	Area	Area %	Height	Height %
9.767	978432	3.14	68694	3.26
10.613	30229310	96.86	2035371	96.74

Totals				
	31207742	100.00	2104065	100.00



Area % Report

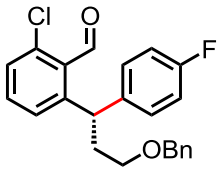
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-093-B-1%IPA-0.5ml-min-90min-OD-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 90 min without fc 0.5 ml per min.met
Acquired: 8/20/2015 3:12:37 PM
Printed: 9/19/2015 11:33:10 PM



DAD-CH1 250 nm Results

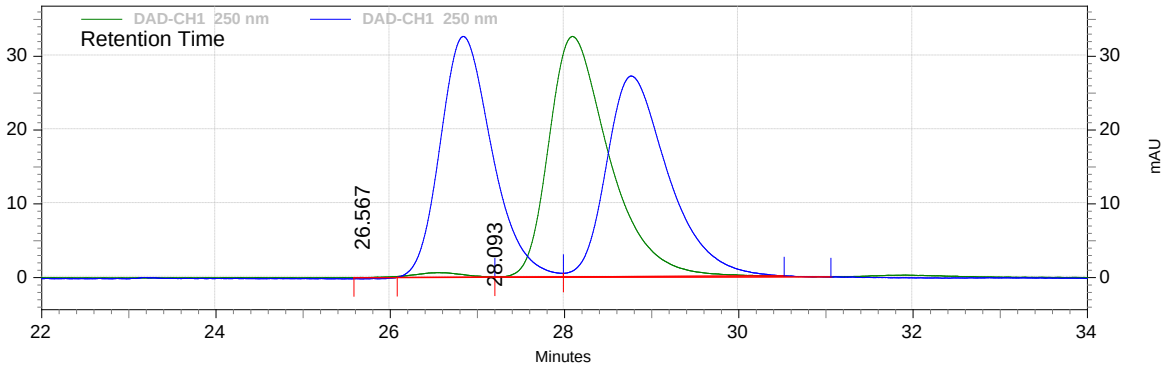
Retention Time	Area	Area %	Height	Height %
9.340	517110	2.95	45223	3.51
10.700	16982876	97.05	1241936	96.49

Totals				
	17499986	100.00	1287159	100.00



Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\KH\Transient Template\Supporting Information\KH-2-101-C-1%IPA-0.5ml-min-45min-OD-H
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 45 min without fc 0.5 ml per min.met
Acquired: 8/24/2015 9:53:48 PM
Printed: 9/20/2015 8:46:18 PM



DAD-CH1 250 nm Results

Retention Time	Area	Area %	Height	Height %
26.567	107170	1.67	2603	1.96
28.093	6323075	98.33	130525	98.04

Totals				
	6430245	100.00	133128	100.00

X-Ray Crystallographic Data

Table S4. Crystal data and structure refinement for KH-3-008.

Report date	2015-10-05	
Identification code	yu48	
Empirical formula	C22.80 H16 Br Cl2.39 D0.80 F3 N2 O3	
Molecular formula	C22 H16 Br F3 N2 O3, 0.8(C D Cl3)	
Formula weight	589.28	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.5997(4) Å	α= 90 °.
	b = 15.9813(6) Å	β= 90 °.
	c = 16.1869(6) Å	γ = 90 °.
Volume	2483.32(17) $Å^3$	
Z	4	
Density (calculated)	1.576 Mg/m^3	
Absorption coefficient	1.963 mm^{-1}	
F(000)	1177	
Crystal size	0.22 x 0.13 x 0.08 mm^3	
Crystal color, habit	colourless block	
Theta range for data collection	2.467 to 27.162 °.	
Index ranges	-12<=h<=10, -19<=k<=20, -20<=l<=20	
Reflections collected	24771	
Independent reflections	5494 [R(int) = 0.0397]	
Completeness to theta = 26.000 °	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4912 and 0.3754	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5494 / 124 / 362	

Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0859
R indices (all data)	R1 = 0.0430, wR2 = 0.0899
Absolute structure parameter	0.012(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.354 and -0.302 e.$Å^{-3}$

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for KH-3-008. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2426(1)	4649(1)	6008(1)	39(1)
F(1A)	4460(5)	10900(3)	5282(4)	87(2)
F(1B)	2445(16)	10451(9)	5944(16)	87(2)
F(2A)	2581(4)	10190(2)	5281(2)	54(1)
F(2B)	4198(16)	11140(7)	5918(10)	54(1)
F(3A)	3225(6)	10812(3)	6348(2)	70(1)
F(3B)	3530(20)	10487(9)	4861(8)	70(1)
O(1)	7286(2)	7630(2)	4762(1)	27(1)
O(2)	6197(4)	4891(3)	1594(2)	83(1)
O(3)	4874(4)	4086(2)	2335(2)	66(1)
N(1)	5002(3)	7289(2)	4596(2)	22(1)
N(2)	5488(4)	4752(3)	2209(3)	55(1)
C(1)	6068(4)	6022(2)	6085(2)	28(1)
C(2)	5100(4)	5403(2)	5931(2)	30(1)
C(3)	3802(4)	5459(2)	6284(2)	28(1)
C(4)	3465(4)	6108(2)	6818(2)	30(1)
C(5)	4443(4)	6720(2)	6968(2)	28(1)
C(6)	5761(4)	6695(2)	6596(2)	23(1)
C(7)	6777(4)	7415(2)	6700(2)	25(1)
C(8)	7405(4)	7454(2)	7567(2)	32(1)
C(9)	6039(3)	8220(2)	6435(2)	23(1)
C(10)	5686(4)	8847(2)	7002(2)	28(1)
C(11)	4935(4)	9540(2)	6769(2)	28(1)
C(12)	4511(3)	9633(2)	5954(2)	27(1)
C(13)	4852(4)	9027(2)	5373(2)	24(1)
C(14)	5619(4)	8328(2)	5608(2)	20(1)
C(15)	3704(4)	10384(3)	5699(2)	34(1)
C(16)	6060(4)	7719(2)	4957(2)	21(1)
C(17)	5164(3)	6652(2)	3991(2)	21(1)
C(18)	4228(4)	5997(2)	3998(2)	25(1)
C(19)	4332(4)	5366(2)	3420(2)	32(1)
C(20)	5362(4)	5412(3)	2833(2)	36(1)
C(21)	6302(4)	6074(3)	2796(2)	36(1)
C(22)	6212(4)	6698(2)	3386(2)	30(1)

Cl(1A)	2301(9)	2557(3)	5294(3)	83(2)
Cl(1B)	1584(7)	2553(4)	5370(4)	45(1)
Cl(2A)	966(10)	1856(6)	3900(6)	71(3)
Cl(2B)	1057(11)	1697(8)	3834(7)	39(2)
Cl(3A)	3255(8)	2966(4)	3647(4)	69(2)
Cl(3B)	3044(12)	3041(8)	3899(5)	73(3)
C(1A)	2494(11)	2218(5)	4297(5)	47(2)
D(1A)	3147	1731	4315	56
C(1B)	1539(16)	2605(8)	4311(8)	47(2)
D(1B)	781	3014	4180	56

Table S6. Bond lengths [Å] and angles [°] for KH-3-008.

Br(1)-C(3)	1.903(4)
F(1A)-C(15)	1.290(5)
F(1B)-C(15)	1.276(15)
F(2A)-C(15)	1.309(5)
F(2B)-C(15)	1.346(13)
F(3A)-C(15)	1.335(5)
F(3B)-C(15)	1.377(14)
O(1)-C(16)	1.227(4)
O(2)-N(2)	1.226(6)
O(3)-N(2)	1.233(6)
N(1)-H(1)	0.94(3)
N(1)-C(16)	1.358(4)
N(1)-C(17)	1.421(4)
N(2)-C(20)	1.465(5)
C(1)-H(1A)	0.9500
C(1)-C(2)	1.381(5)
C(1)-C(6)	1.389(5)
C(2)-H(2)	0.9500
C(2)-C(3)	1.373(5)
C(3)-C(4)	1.388(5)
C(4)-H(4)	0.9500
C(4)-C(5)	1.378(5)
C(5)-H(5)	0.9500
C(5)-C(6)	1.401(5)
C(6)-C(7)	1.518(5)
C(7)-H(7)	1.0000
C(7)-C(8)	1.529(5)
C(7)-C(9)	1.530(5)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.400(5)
C(9)-C(14)	1.410(5)
C(10)-H(10)	0.9500

C(10)-C(11)	1.375(5)
C(11)-H(11)	0.9500
C(11)-C(12)	1.388(5)
C(12)-C(13)	1.390(5)
C(12)-C(15)	1.487(5)
C(13)-H(13)	0.9500
C(13)-C(14)	1.390(5)
C(14)-C(16)	1.496(5)
C(17)-C(18)	1.380(5)
C(17)-C(22)	1.406(5)
C(18)-H(18)	0.9500
C(18)-C(19)	1.379(5)
C(19)-H(19)	0.9500
C(19)-C(20)	1.374(6)
C(20)-C(21)	1.392(6)
C(21)-H(21)	0.9500
C(21)-C(22)	1.384(5)
C(22)-H(22)	0.9500
Cl(1A)-C(1A)	1.713(10)
Cl(1B)-C(1B)	1.717(13)
Cl(2A)-C(1A)	1.703(13)
Cl(2B)-C(1B)	1.708(15)
Cl(3A)-C(1A)	1.752(11)
Cl(3B)-C(1B)	1.737(16)
C(1A)-D(1A)	1.0000
C(1B)-D(1B)	1.0000

C(16)-N(1)-H(1)	116(4)
C(16)-N(1)-C(17)	125.2(3)
C(17)-N(1)-H(1)	115(4)
O(2)-N(2)-O(3)	123.8(4)
O(2)-N(2)-C(20)	118.3(5)
O(3)-N(2)-C(20)	117.9(4)
C(2)-C(1)-H(1A)	119.4
C(2)-C(1)-C(6)	121.3(3)
C(6)-C(1)-H(1A)	119.4

C(1)-C(2)-H(2)	120.4
C(3)-C(2)-C(1)	119.3(3)
C(3)-C(2)-H(2)	120.4
C(2)-C(3)-Br(1)	119.2(3)
C(2)-C(3)-C(4)	121.3(3)
C(4)-C(3)-Br(1)	119.5(3)
C(3)-C(4)-H(4)	120.6
C(5)-C(4)-C(3)	118.8(4)
C(5)-C(4)-H(4)	120.6
C(4)-C(5)-H(5)	119.4
C(4)-C(5)-C(6)	121.3(3)
C(6)-C(5)-H(5)	119.4
C(1)-C(6)-C(5)	118.0(3)
C(1)-C(6)-C(7)	121.1(3)
C(5)-C(6)-C(7)	120.7(3)
C(6)-C(7)-H(7)	107.3
C(6)-C(7)-C(8)	112.7(3)
C(6)-C(7)-C(9)	108.0(3)
C(8)-C(7)-H(7)	107.3
C(8)-C(7)-C(9)	114.0(3)
C(9)-C(7)-H(7)	107.3
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(7)	122.0(3)
C(10)-C(9)-C(14)	117.7(3)
C(14)-C(9)-C(7)	120.2(3)
C(9)-C(10)-H(10)	119.2
C(11)-C(10)-C(9)	121.6(3)
C(11)-C(10)-H(10)	119.2
C(10)-C(11)-H(11)	120.0
C(10)-C(11)-C(12)	120.0(3)
C(12)-C(11)-H(11)	120.0

C(11)-C(12)-C(13)	120.0(3)
C(11)-C(12)-C(15)	120.2(3)
C(13)-C(12)-C(15)	119.8(3)
C(12)-C(13)-H(13)	120.0
C(12)-C(13)-C(14)	119.9(3)
C(14)-C(13)-H(13)	120.0
C(9)-C(14)-C(16)	120.5(3)
C(13)-C(14)-C(9)	120.7(3)
C(13)-C(14)-C(16)	118.7(3)
F(1A)-C(15)-F(2A)	110.1(4)
F(1A)-C(15)-F(3A)	106.1(4)
F(1A)-C(15)-C(12)	111.6(4)
F(1B)-C(15)-F(2B)	100.2(11)
F(1B)-C(15)-F(3B)	100.4(13)
F(1B)-C(15)-C(12)	118.4(6)
F(2A)-C(15)-F(3A)	104.1(4)
F(2A)-C(15)-C(12)	112.5(3)
F(2B)-C(15)-F(3B)	101.3(10)
F(2B)-C(15)-C(12)	117.9(6)
F(3A)-C(15)-C(12)	112.0(3)
F(3B)-C(15)-C(12)	115.7(6)
O(1)-C(16)-N(1)	123.3(3)
O(1)-C(16)-C(14)	121.8(3)
N(1)-C(16)-C(14)	114.9(3)
C(18)-C(17)-N(1)	117.8(3)
C(18)-C(17)-C(22)	120.8(3)
C(22)-C(17)-N(1)	121.4(3)
C(17)-C(18)-H(18)	119.9
C(17)-C(18)-C(19)	120.1(3)
C(19)-C(18)-H(18)	119.9
C(18)-C(19)-H(19)	120.6
C(20)-C(19)-C(18)	118.9(4)
C(20)-C(19)-H(19)	120.6
C(19)-C(20)-N(2)	119.9(4)
C(19)-C(20)-C(21)	122.4(4)
C(21)-C(20)-N(2)	117.7(4)

C(20)-C(21)-H(21)	120.7
C(22)-C(21)-C(20)	118.6(4)
C(22)-C(21)-H(21)	120.7
C(17)-C(22)-H(22)	120.4
C(21)-C(22)-C(17)	119.2(4)
C(21)-C(22)-H(22)	120.4
Cl(1A)-C(1A)-Cl(3A)	113.3(6)
Cl(1A)-C(1A)-D(1A)	106.7
Cl(2A)-C(1A)-Cl(1A)	111.7(7)
Cl(2A)-C(1A)-Cl(3A)	111.4(6)
Cl(2A)-C(1A)-D(1A)	106.7
Cl(3A)-C(1A)-D(1A)	106.7
Cl(1B)-C(1B)-Cl(3B)	112.4(8)
Cl(1B)-C(1B)-D(1B)	105.2
Cl(2B)-C(1B)-Cl(1B)	114.6(9)
Cl(2B)-C(1B)-Cl(3B)	113.1(9)
Cl(2B)-C(1B)-D(1B)	105.2
Cl(3B)-C(1B)-D(1B)	105.2

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for KH-3-008. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	40(1)	30(1)	49(1)	4(1)	-10(1)	-10(1)
F(1A)	55(2)	44(2)	161(5)	55(3)	29(3)	17(2)
F(1B)	55(2)	44(2)	161(5)	55(3)	29(3)	17(2)
F(2A)	55(2)	36(2)	72(2)	-13(2)	-34(2)	17(2)
F(2B)	55(2)	36(2)	72(2)	-13(2)	-34(2)	17(2)
F(3A)	103(3)	53(2)	52(2)	-21(2)	-17(2)	50(2)
F(3B)	103(3)	53(2)	52(2)	-21(2)	-17(2)	50(2)
O(1)	15(1)	38(1)	29(1)	-7(1)	0(1)	0(1)
O(2)	35(2)	125(3)	90(3)	-81(3)	10(2)	-1(2)
O(3)	48(2)	48(2)	103(3)	-50(2)	-32(2)	16(2)
N(1)	15(1)	25(2)	25(1)	-5(1)	-1(1)	0(1)
N(2)	24(2)	66(3)	75(3)	-46(2)	-15(2)	17(2)
C(1)	26(2)	26(2)	31(2)	1(2)	3(2)	6(2)
C(2)	34(2)	22(2)	34(2)	3(2)	-3(2)	4(2)
C(3)	28(2)	20(2)	34(2)	5(2)	-6(2)	-3(2)
C(4)	25(2)	31(2)	35(2)	7(2)	2(2)	0(2)
C(5)	29(2)	23(2)	31(2)	0(2)	1(2)	3(2)
C(6)	25(2)	23(2)	23(2)	6(1)	-1(1)	3(2)
C(7)	23(2)	28(2)	24(2)	3(2)	1(1)	1(2)
C(8)	29(2)	35(2)	31(2)	-1(2)	-7(2)	-2(2)
C(9)	18(2)	24(2)	27(2)	-2(1)	-1(1)	-3(1)
C(10)	26(2)	31(2)	26(2)	-3(2)	-1(2)	-3(2)
C(11)	29(2)	26(2)	30(2)	-9(2)	2(1)	-6(2)
C(12)	20(2)	22(2)	39(2)	-3(2)	-4(2)	-2(2)
C(13)	21(2)	25(2)	25(2)	-3(1)	-2(1)	-3(1)
C(14)	14(2)	22(2)	25(2)	-2(1)	1(1)	-4(1)
C(15)	37(2)	27(2)	39(2)	-7(2)	-3(2)	5(2)
C(16)	21(2)	20(2)	22(2)	2(1)	-1(1)	-1(1)
C(17)	17(2)	22(2)	23(2)	-1(1)	-3(1)	6(1)

C(18)	19(2)	25(2)	31(2)	-1(2)	-4(2)	5(1)
C(19)	23(2)	24(2)	50(2)	-10(2)	-10(2)	4(2)
C(20)	24(2)	39(2)	44(2)	-21(2)	-12(2)	13(2)
C(21)	25(2)	50(2)	33(2)	-13(2)	1(2)	8(2)
C(22)	25(2)	33(2)	31(2)	-6(2)	2(2)	0(2)
Cl(1A)	134(4)	62(2)	54(2)	-24(2)	-40(3)	29(3)
Cl(1B)	64(3)	37(2)	36(2)	0(2)	-1(2)	-2(2)
Cl(2A)	103(4)	53(4)	58(3)	2(3)	-31(3)	-11(3)
Cl(2B)	45(3)	40(4)	32(2)	-7(2)	-6(2)	-14(2)
Cl(3A)	87(4)	48(2)	73(4)	7(2)	-36(3)	-14(2)
Cl(3B)	84(4)	83(5)	50(4)	5(3)	5(3)	-44(3)
C(1A)	58(5)	34(4)	48(3)	0(3)	-20(4)	7(4)
C(1B)	58(5)	34(4)	48(3)	0(3)	-20(4)	7(4)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for KH-3-008.

	x	y	z	U(eq)
H(1)	4160(40)	7260(40)	4890(40)	104
H(1A)	6963	5987	5836	33
H(2)	5328	4942	5586	36
H(4)	2576	6129	7075	37
H(5)	4220	7168	7331	33
H(7)	7562	7320	6305	30
H(8A)	8056	7925	7601	48
H(8B)	7902	6931	7683	48
H(8C)	6659	7530	7974	48
H(10)	5972	8791	7561	33
H(11)	4705	9956	7166	34
H(13)	4561	9090	4815	29
H(18)	3510	5980	4402	30
H(19)	3701	4908	3427	39
H(21)	6990	6097	2374	43
H(22)	6852	7151	3383	36

Table S9. Hydrogen bonds for KH-3-008 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.94(3)	1.89(3)	2.810(4)	164(6)

Symmetry transformations used to generate equivalent atoms:
#1 x-1/2,-y+3/2,-z+1

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