Supporting Information

Methylene C(sp^3)–H Arylation of Aliphatic Ketones Using a Transient Directing Group

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General Information

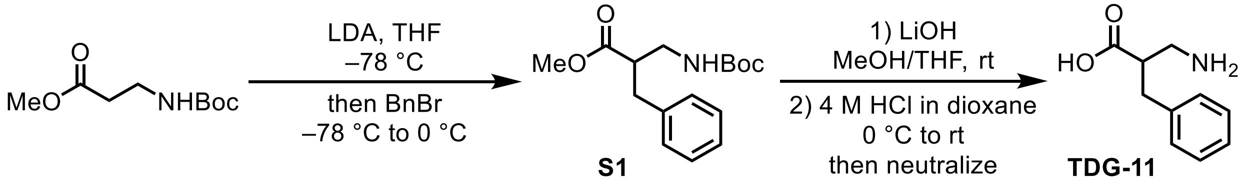
Unless otherwise noted all commercial materials were used without further purification. Solvents were obtained from Oakwood and Acros and used directly without further purification. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light and Vogel's permanganate. ^{1}H NMR spectra were recorded on 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, qi = quintet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on 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).

Experimental Section

I. Synthesis of β-Amino Acids

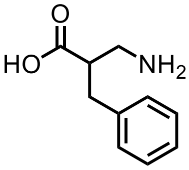
β-Amino acids in **Table 1** were either purchased or prepared according to literature procedures or the following methods:

Method A:



To a solution of lithium diisopropylamide in THF (40 mL, 0.66 M, 2.2 equiv.) was added a THF solution (10 mL) of methyl 3-((tert-butoxycarbonyl)amino)propanoate (2.43 g, 12.0 mmol, 1.0 equiv.) dropwise at –78 ºC. The reaction was stirred at –78 ºC for 1 h, followed by the addition of benzyl bromide (5.71 mL, 4.0 equiv.). After being stirred at –78 ºC for 2 h, the reaction was allowed to warm to 0 ºC, then quenched with saturated aqueous solution of NH_4Cl. The reaction mixture was concentrated *in vacuo*, then extracted with EtOAc (50 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude mixture was purified on silica gel to afford **S1** in 73% yield.

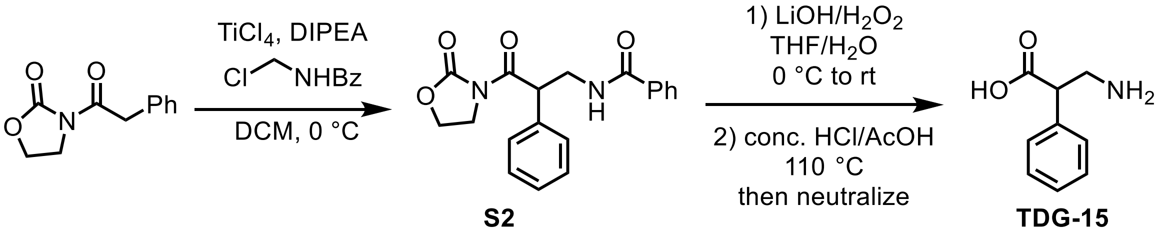
To a solution of **S1** (2.50 g, 8.50 mmol) in THF/H_2O (1:1, 40 mL) was added LiOH·H_2O (714 mg, 2.0 equiv.) at rt. The reaction was stirred at rt and monitored by TLC. Upon completion, the reaction mixture was acidified by an aqueous solution of citric acid, then extracted with EtOAc (50 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was then added into a solution of HCl in 1,4-dioxane (4 M, 6 equiv.) at 0 ºC. The reaction mixture was allowed to warm to rt and stir for 3 h. Upon completion, 40 mL of diethyl ether was added, and a white precipitate was formed. The white solid was filtered and washed with diethyl ether, then dissolve in a minimal amount of water. Triethylamine was added dropwise to carefully tune the pH of the solution to 7–8. The volatiles were removed *in vacuo*, and the resulting white solid was washed with copious amounts of DCM to remove the residual $Et_3N·HCl$ to afford the desired β-amino acid **TDG-11**in 80% yield.



3-Amino-2-benzylpropanoic acid (TDG-11)

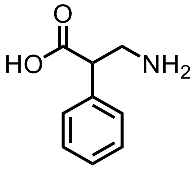
^{1}H NMR (D_2O, 600 MHz): δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.24-7.19 (m, 3H), 3.00 (dd, *J* = 12.7, 9.3 Hz, 1H), 2.94-2.90 (m, 2H), 2.80-2.72 (m, 2H); ^{13}C NMR (D_2O, 150 MHz): δ 179.13, 138.04, 128.49, 128.22, 126.27, 46.49, 40.18, 35.70; HRMS (ESI-TOF): *m/z* calculated for $C_{10}H_{13}NO_2^+$ $[M+H]^+$ 180.1019, found 180.1024.

Method B:



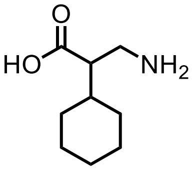
To a solution of 3-(2-phenylacetyl)oxazolidin-2-one (877 mg, 4.0 mmol, 1.0 equiv.) in DCM (16 mL) was added a solution of $TiCl_4$ (1 M in DCM, 4.4 mL, 1.1 equiv.) dropwise at 0 °C. The reaction was stirred for 10 min, followed by the slow addition of *N*,*N*-diisopropylethylamine (0.73 mL, 4.2 mmol, 1.05 equiv.). After stirred at 0 °C for 45 min, *N*-(chloromethyl)benzamide was added in one portion. The reaction was allowed to stir at 0 °C for 1 h, then quenched with a saturated aqueous solution of NH_4Cl. The reaction mixture was extracted with DCM (20 mL×3). The combined organic layers were washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude mixture was purified on silica gel to afford **S2** in 75% yield.

To a solution of **S2** (1.06 g, 3.00 mmol) in THF/H_2O (4:1, 20 mL) was added H_2O_2 (35 wt%, 2.2 mL) and an aqueous solution of LiOH•H_2O (380 mg, 2.4 equiv., in a minimal amount of water) at 0 °C. The reaction was stirred at 0 °C for 2 h and monitored by TLC. Upon completion, the reaction was quenched with an aqueous solution of Na_2SO_3. After removal of the volatiles *in vacuo*, the reaction mixture was washed with DCM (20 mL×3), acidified by 1 M HCl, then extracted with EtOAc (50 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was then purified on silica gel or recrystallized in hot EtOAc/AcOH to afford the desired acid product. To remove the Bz protecting group, the acid was refluxed in a mixture of conc. HCl and AcOH at 110 °C for 48 h. Upon completion, the volatiles were removed *in vacuo*, and the solid was dissolved in 10 mL of water, and washed with DCM (20 mL×3). Triethylamine was added dropwise to the aqueous solution to carefully tune the pH to 7–8. The volatiles were removed *in vacuo*, and the resulting white solid was washed with copious amounts of DCM to remove the residual Et_3N•HCl to afford the desired β-amino acid in 70% yield.



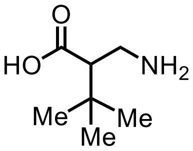
3-Amino-2-phenylpropanoic acid (TDG-15)

^{1}H NMR (D_2O, 600 MHz): δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 2H), 3.72 (t, *J* = 7.5 Hz, 1H), 3.39 (dd, *J* = 12.9, 7.8 Hz, 1H), 3.21 (dd, *J* = 12.9, 7.1 Hz, 1H); ^{13}C NMR (D_2O, 150 MHz): δ 177.76, 136.72, 128.77, 127.65, 127.46, 50.89, 41.83; HRMS (ESI-TOF): *m/z* calculated for $C_9H_{12}NO_2$ $[M+H]^+$ 166.0863, found 166.0865.



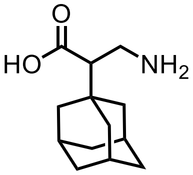
3-Amino-2-cyclohexylpropanoic acid (TDG-12)

TDG-12 was prepared according to **Method B**. ^{1}H NMR (D_2O, 600 MHz): δ 3.09-3.01 (m, 2H), 2.26 (ddd, *J* = 9.7, 6.3, 3.9 Hz, 1H), 1.66-1.64 (m, 2H), 1.58-1.51 (m, 4H), 1.21-1.11 (m, 2H), 1.08-0.91 (m, 3H); ^{13}C NMR (D_2O, 150 MHz): δ 179.92, 50.93, 38.47, 37.73, 30.20, 28.97, 25.54, 25.44, 25.24; HRMS (ESI-TOF): *m/z* calculated for $C_9H_{18}NO_2^+$ $[M+H]^+$ 172.1332, found 172.1337.



2-(Aminomethyl)-3,3-dimethylbutanoic acid (TDG-13)

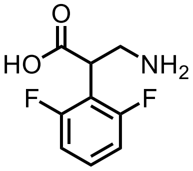
TDG-13 was prepared according to **Method B**. ^{1}H NMR (D_2O, 600 MHz): δ 3.13-3.06 (m, 2H), 2.24 (dd, *J* = 10.9, 4.0 Hz, 1H), 0.90 (s, 9H); ^{13}C NMR (D_2O, 150 MHz): δ 178.54, 55.97, 38.76, 31.06, 26.92; HRMS (ESI-TOF): *m/z* calculated for $C_7H_{16}NO_2^+$ $[M+H]^+$ 146.1175, found 146.1173.



2-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-3-aminopropanoic acid (TDG-14)

TDG-14 was prepared according to **Method B**. ^{1}H NMR (D_2O, 600 MHz): δ 3.11 (d, *J* = 7.5 Hz, 2H), 2.12-2.09 (m, 1H), 1.88 (s, 3H), 1.64-1.54 (m, 9H), 1.47 (d, *J* = 12.2 Hz, 3H); ^{13}C NMR (D_2O, 150 MHz): δ 185.13, 57.13, 39.29, 37.62, 35.71, 33.36, 27.84. HRMS (ESI-TOF): *m/z* calculated for $C_{13}H_{22}NO_2^+$

$[M+H]^+$ 224.1645, found 224.1653.



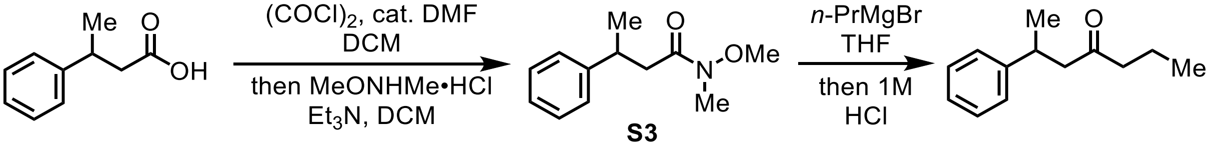
3-Amino-2-(2,6-difluorophenyl)propanoic acid (TDG-16)

TDG-16 was prepared according to **Method B**. ^{1}H NMR (D_2O, 600 MHz): δ 7.34-7.29 (m, 1H), 6.98-6.95 (m, 2H), 4.10 (dd, J = 8.4, 6.6 Hz, 1H), 3.50 (dd, J = 12.9, 8.4 Hz, 1H), 3.18 (dd, J = 12.8, 6.6 Hz, 1H); ^{13}C NMR (D_2O, 150 MHz): δ 176.38, 160.59 (dd, J_{CF} = 246.0, 8.2 Hz), 129.71 (t, J_{CF} = 10.6 Hz), 112.98 (t, J_{CF} = 19.3 Hz), 111.26 (dd, J_{CF} = 21.9, 4.0 Hz), 39.82 (t, J_{CF} = 1.8 Hz), 38.78 (t, J_{CF} = 1.6 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): δ –114.92; HRMS (ESI-TOF): *m/z* calculated for $C_9H_{10}F_2NO_2^+$ $[M+H]^+$ 202.0674, found 202.0681.

II. Substrate Preparation

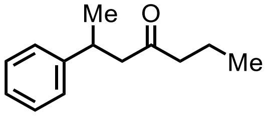
The ketone substrates were prepared according to either literature procedures or the following methods:

Method A:



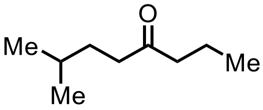
To a solution of 3-phenylbutanoic acid (1.00 g, 6.09 mmol) in DCM (12 mL) was added $(COCl)_2$ (0.57 mmol, 1.1 equiv.) and one drop of DMF at 0 °C. The reaction was allowed to warm to rt and stir for 3 h, then concentrated *in vacuo*. The reaction mixture was dissolved in 24 mL of DCM and cooled to 0 °C. MeONHMe·HCl (536 mg, 1.2 equiv.) was added in one portion, followed by triethylamine (1.92 mmol, 3.0 equiv.). The reaction was allowed to warm to rt and stirred overnight. Upon completion, 100 mL of diethyl ether was added, and a white precipitate was formed. The white solid (**S3**) was filtered and washed with diethyl ether, then used in the next step without further purification.

To a solution of amide **S3** in THF was added *n*-propylmagnesium chloride (2.0 M in ether, 1.5 equiv.) at 0 °C. The reaction was slowly warmed to rt and stirred for 1h, then quenched with 1 M HCl solution. The reaction mixture was extracted with EtOAc (30 mL×3), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was then purified on silica gel to afford the desired ketone product.



2-Phenylheptan-4-one (3n)

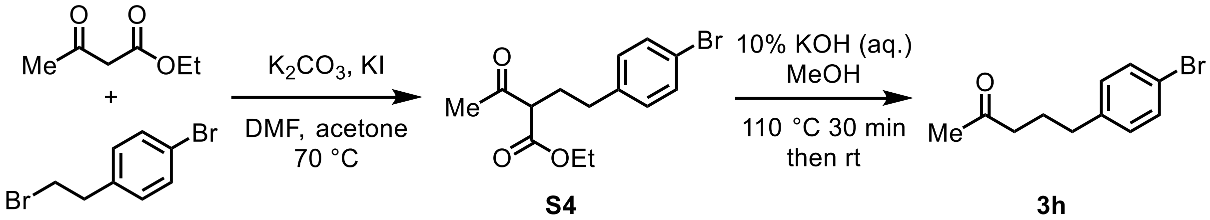
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.30-7.27 (m, 2H), 7.22-7.17 (m, 3H), 3.35-3.29 (m, 1H), 2.71 (dd, *J* = 16.2, 6.4 Hz, 1H), 2.62 (dd, *J* = 16.2, 7.9 Hz, 1H), 2.33-2.23 (m, 2H), 1.57-1.50 (m, 2H), 1.26 (d, *J* = 6.9 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 210.02, 146.31, 128.48, 126.77, 126.23, 51.12, 45.43, 35.40, 21.94, 17.06, 13.66; HRMS (ESI-TOF): *m/z* calculated for $C_{13}H_{19}O^+$ $[M+H]^+$ 191.1430, found 191.1430.



7-Methyloctan-4-one (3p)

^{1}H NMR (CDCl$_3$, 600 MHz): δ 2.39 (t, *J* = 7.8 Hz, 1H), 1.63-1.57 (m, 2H), 1.56-1.50 (m, 1H), 1.46 (q, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 211.67, 44.68, 40.86, 32.65, 27.73, 22.34, 17.33, 13.77; HRMS (ESI-TOF): *m/z* calculated for $C_9H_{19}O^+$ $[M+H]^+$ 143.1430, found 143.1426.

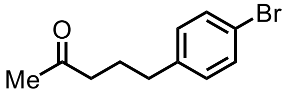
Method B:



A 250 mL round-bottom flask with magnetic stir bar was charged with ethyl acetoacetate (0.95 mL, 7.5 mmol), 1-bromo-4-(2-bromoethyl)benzene (0.99 g, 3.75 mmol), K_2CO_3 (1.56 g, 11.25 mmol), KI (0.62 g, 3.75 mmol), DMF (3.75 mL) and acetone (50 mL). The reaction mixture was stirred at 70 °C for 16 h, then the volatiles were removed *in vacuo*. Water was added to dissolve the solids and the mixture was extracted with EtOAc (30 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was then purified on silica gel to afford **S4** with ethyl acetoacetate as the impurity.

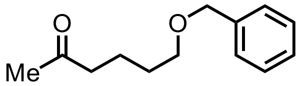
The mixture of **S4** and ethyl acetoacetate were added into a mixture of MeOH (4 mL) and 10% KOH aqueous solution (4 mL). After refluxed for 30 min, the reaction was cooled to rt and stirred overnight. The mixture were concentrated *in vacuo*, and diluted with water and EtOAc. After extracted with EtOAc (30 mL×3), the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated.

The crude product was then purified on silica gel to afford **3h**.



5-(4-Bromophenyl)pentan-2-one (3h)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.41-7.39 (m, 2H), 7.06-7.03 (m, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.12 (s, 3H), 1.90-1.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 208.43, 140.51, 131.41, 130.18, 119.67, 42.59, 34.37, 29.98, 24.94; HRMS (ESI-TOF): *m/z* calculated for $C_{11}H_{14}BrO^+$ $[M+H]^+$ 241.0222, found 241.0228.



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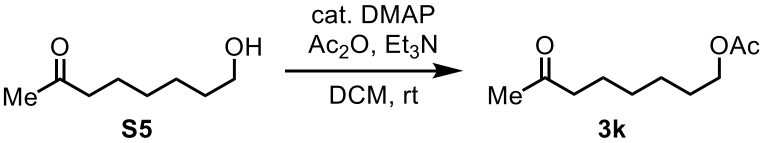
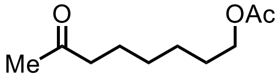
6-(Benzyloxy)hexan-2-one (3j)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.36-7.32 (m, 4H), 7.30-7.27 (m, 1H), 4.49 (s, 2H), 3.47 (t, *J* = 6.2 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.12 (s, 3H), 1.70-1.65 (m, 2H), 1.64-1.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 208.91, 138.49, 128.35, 127.62, 127.52, 72.91, 69.95, 43.39, 29.86, 29.15, 20.60; HRMS (ESI-TOF): *m/z* calculated for $C_{13}H_{19}O_2^+$ $[M+H]^+$ 207.1379, found 207.1378.



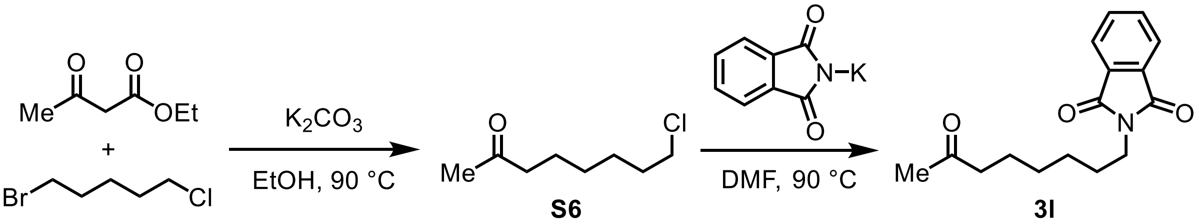
Compound **S5** was prepared according to **Method B**. It was then acylated using the general condition.



7-Oxooctyl acetate (3k)

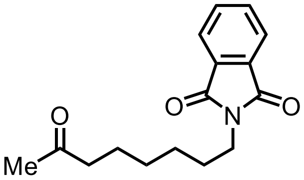
^{1}H NMR ($CDCl_3$, 600 MHz): δ 4.05 (t, *J* = 6.7 Hz, 1H), 2.43 (t, *J* = 7.4 Hz, 1H), 2.14 (s, 1H), 2.05 (s, 1H), 1.65-1.56 (m, 4H), 1.39-1.29 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 209.01, 171.19, 64.42, 43.57, 29.88, 28.75, 28.41, 25.72, 23.61, 20.99. HRMS (ESI-TOF): *m/z* calculated for $C_{10}H_{19}O_3^+$ $[M+H]^+$ 187.1329, found 187.1332.

Method C:



A 50 mL round-bottom flask with magnetic stir bar was charged with ethyl acetoacetate (0.51 mL, 4.0 mmol), 1-bromo-5-chloropentane (0.53 mL, 4.0 mmol), K_2CO_3 (1.66 g, 12.0 mmol) and ethanol (20 mL). The reaction mixture was stirred at 90 °C for 12 h, then the volatiles were removed *in vacuo*. Water was added to dissolve the solids and the mixture was extracted with EtOAc (30 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was then purified on silica gel to afford **S6**.

To a solution of **S6** (317 mg, 1.3 equiv.) in DMF (1.5 mL) was added phthalimide potassium salt (278 mg, 1.5 mmol). The reaction mixture was stirred at 90 °C and monitored by TLC. Upon completion, the reaction was diluted with diethyl ether, filtered and concentrated. The crude mixture was purified on silica gel to afford the desired product **3l**.

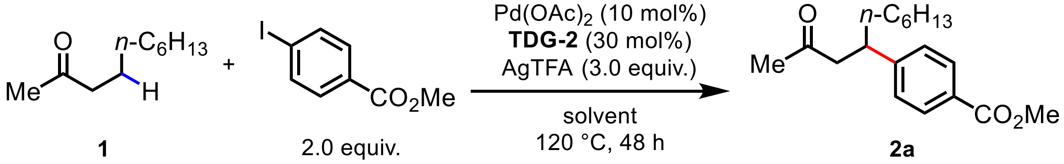


2-(7-Oxooctyl)isoindoline-1,3-dione (3l)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.86-7.82 (m, 2H), 7.73-7.70 (m, 2H), 3.67 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.13 (s, 3H), 1.68 (qi, *J* = 7.4 Hz, 2H), 1.57 (qi, *J* = 7.4 Hz, 2H), 1.38-1.30 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 208.98, 168.38, 133.82, 132.09, 123.11, 43.55, 37.83, 29.82, 28.62, 28.37, 26.56, 23.57; HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{20}NO_3^+$ [M+H]$^+$ 274.1438, found 274.1443.

III. Preliminary Optimization Using β-Alanine (TDG-2)

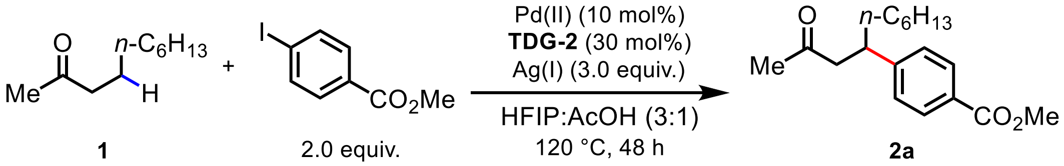
Table S1. Screening of Solvents[a,b]



entry	solvent	conversion (%)	NMR yield (%)
1	HFIP:AcOH (1:1)	56	19
2	HFIP:AcOH (3:1)	47	41
3	HFIP:AcOH (5:1)	32	26
4	HFIP:AcOH (9:1)	30	10
5	HFIP	-	<2
6	AcOH	25	3
7	TFA	-	<2
8	HFIP:TFA (3:1)	-	<2
9	C_6F_6:AcOH (3:1)	40	9
10	C_7F_8:AcOH (3:1)	43	11
11	toluene:AcOH (3:1)	-	<2
12	DCE:AcOH (3:1)	-	<2
13	MeCN:AcOH (3:1)	-	<2
14	dioxane:AcOH (3:1)	-	<2

[a] Conditions: 0.2 mmol of **1**, 2.0 equiv. of methyl 4-iodobenzoate, 10 mol% of $Pd(OAc)_2$, 30 mol% of **TDG-2**, 3.0 equiv. of AgTFA, 2.0 mL of solvent, 120 °C, under air, 48 h. [b] The yield was determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard.

Table S2. Screening of Silver Salt and Palladium Catalyst[a,b]

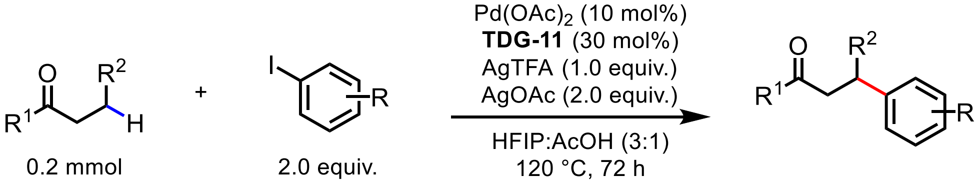


entry	Pd(II) catalyst	Ag(I) salt	conversion (%)	NMR yield (%)
1	$Pd(OAc)_2$	AgTFA	47	41
2	$Pd(MeCN)Cl_2$	AgTFA	47	39
3	$Pd(TFA)_2$	AgTFA	49	41
4	$Pd(OAc)_2$	AgOAc	38	25
5	$Pd(OAc)_2$	AgF	15	10
6	$Pd(OAc)_2$	AgOTs	-	<2
7	$Pd(OAc)_2$	AgOBz	-	<2
8	$Pd(OAc)_2$	Ag_2O	20	12
9	$Pd(OAc)_2$	$AgBF_4$	-	<2
10	$Pd(OAc)_2$	Ag_2CO_3	20	14
11	$Pd(OAc)_2$	AgTFA:AgOAc (2:1)	52	45
12	$Pd(OAc)_2$	AgTFA:AgOAc (1:1)	58	49
13	$Pd(OAc)_2$	AgTFA:AgOAc (1:2)	63	57
14	$Pd(OAc)_2$	AgTFA:AgOAc (1:5)	57	48

[a] Conditions: 0.2 mmol of **1**, 2.0 equiv. of methyl 4-iodobenzoate, 10 mol% of Pd(II) catalyst, 30 mol% of **TDG-2**, 3.0 equiv. of Ag(I) salt, 1.5 mL of HFIP, 0.5 mL of acetic acid, 120 °C, under air, 48 h. [b] The yield was determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard.

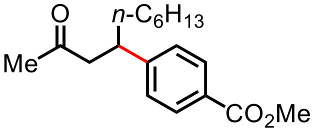
IV. Pd-Catalyzed Methylene C(sp^3)–H Arylation of Ketones

General Procedure



In air, a reaction tube (15 mL) with magnetic stir bar was charged with ketone substrate (0.20 mmol), aryl iodide (0.40 mmol), silver trifluoroacetate (44 mg, 0.20 mmol), silver acetate (67 mg, 0.40 mmol), palladium acetate (4.5 mg, 0.020 mmol) and the transient directing group **TDG-11** (10.8 mg, 0.060 mmol), followed by the mixture of HFIP (1.5 mL) and acetic acid (0.5 mL). The reaction tube was sealed and allowed to stir at ambient temperature for 10 minutes, then heated to 120 °C for 72 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 or toluene/EtOAc as the eluent to afford the desired product.

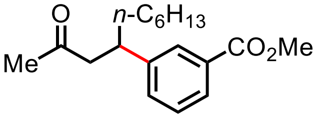
Full Characterization of Reaction Products



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

The compound **2a** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 76% yield (44.2 mg).

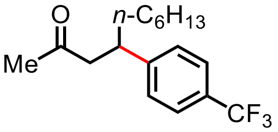
^{1}H NMR ($CDCl_3$, 600 MHz): δ ; 7.96 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.19 (dtd, *J* = 9.5, 7.1, 5.3 Hz, 1H), 2.73 (d, *J* = 7.1 Hz, 2H), 2.02 (s, 3H), 1.66-1.60 (m, 1H), 1.58-1.52 (m, 1H), 1.27-1.11 (m, 7H), 1.08-1.02 (m, 1H), 0.83 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 207.30, 166.99, 150.21, 129.78, 127.52, 51.97, 50.45, 41.09, 36.21, 31.60, 30.62, 29.09, 27.24, 22.52, 13.99; HRMS (ESI-TOF): *m/z* calculated for $C_{18}H_{27}O_3^+$ $[M+H]^+$ 291.1955, found 291.1951.



Methyl 3-(2-oxodecan-4-yl)benzoate (2b)

The compound **2b** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 77% yield (44.7 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.88-7.86 (m, 2H), 7.39-7.34 (m, 2H), 3.92 (s, 3H), 3.18 (dtd, *J* = 9.5, 7.1, 5.4 Hz, 1H), 2.75 (d, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.66-1.53 (m, 2H), 1.28-1.02 (m, 8H), 0.83 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 207.46, 167.16, 145.11, 132.51, 130.29, 128.45, 128.25, 127.59, 52.06, 50.61, 40.90, 36.34, 31.62, 30.62, 29.10, 27.27, 22.53, 14.00; HRMS (ESI-TOF): *m/z* calculated for $C_{18}H_{27}O_3^+$ $[M+H]^+$ 291.1955, found 291.1950.

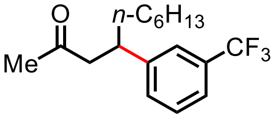


4-(4-(Trifluoromethyl)phenyl)decan-2-one (2c)

The compound **2c** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 77% yield (46.0 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.20 (dtd, *J* = 9.5, 7.1, 5.4 Hz, 1H), 2.74 (d, *J* = 7.1 Hz, 2H), 2.04 (s, 3H), 1.66-1.60 (m, 1H), 1.58-1.52 (m, 1H), 1.27-1.03 (m, 8H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 207.13, 148.90, 128.56 (q, J_{CF} = 32.4 Hz), 125.36 (q, J_{CF} = 3.8 Hz), 124.23 (q, J_{CF} = 271.7 Hz), 50.46, 40.83, 36.23, 31.62, 30.59, 29.11, 27.25, 22.55, 14.00; ^{19}F NMR ($CDCl_3$, 376 MHz): δ –62.65; HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{24}F_3O^+$

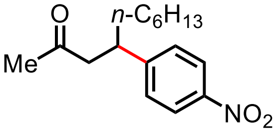
$[M+H]^+$ 301.1774, found 301.1776.



4-(3-(Trifluoromethyl)phenyl)decan-2-one (2d)

The compound **2d** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 76% yield (45.7 mg).

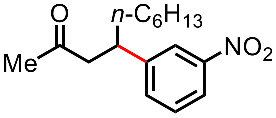
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.46-7.44 (m, 1H), 7.42-7.36 (m, 3H), 3.21 (dtd, *J* = 9.4, 7.1, 5.5 Hz, 1H), 2.78-2.70 (m, 2H), 2.04 (s, 3H), 1.66-1.60 (m, 1H), 1.58-1.52 (m, 1H), 1.30-1.13 (m, 7H), 1.09-1.03 (m, 1H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 207.12, 145.77, 131.13 (q, J_{CF} = 1.3 Hz), 130.72 (q, J_{CF} = 31.9 Hz), 128.83, 124.19 (q, J_{CF} = 272.2 Hz), 123.97 (q, J_{CF} = 3.8 Hz), 123.18 (q, J_{CF} = 3.7 Hz), 50.50, 40.80, 36.24, 31.60, 30.60, 29.07, 27.23, 22.53, 13.99; ^{19}F NMR (CDCl$_3$, 376 MHz): δ –62.79; HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{24}F_3O^+$ $[M+H]^+$ 301.1774, found 301.1775.



4-(4-Nitrophenyl)decan-2-one (2e)

The compound **2e** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 66% yield (36.6 mg).

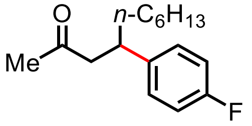
^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.16-8.14 (m, 2H), 7.36-7.34 (m, 2H), 3.29-3.25 (m, 1H), 2.81-2.73 (m, 2H), 2.06 (s, 3H), 1.68-1.62 (m, 1H), 1.59-1.53 (m, 1H), 1.28-1.13 (m, 7H), 1.08-1.01 (m, 1H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 206.59, 152.74, 146.53, 128.37, 123.72, 50.18, 40.75, 36.13, 31.58, 30.55, 29.05, 27.24, 22.52, 13.99; HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{24}NO_3^+$ $[M+H]^+$ 278.1751, found 278.1750.



4-(3-Nitrophenyl)decan-2-one (2f)

The compound **2f** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 76% yield (42.2 mg).

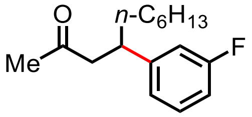
^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.07-8.04 (m, 2H), 7.54 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 3.30-3.25 (m, 1H), 2.82-2.75 (m, 2H), 2.07 (s, 3H), 1.69-1.63 (m, 1H), 1.60-1.54 (m, 1H), 1.29-1.13 (m, 7H), 1.10-1.03 (m, 1H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 206.68, 148.42, 147.03, 134.34, 129.26, 121.98, 121.47, 50.23, 40.51, 36.20, 31.58, 30.56, 29.04, 27.23, 22.52, 13.99; HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{24}NO_3^+$ $[M+H]^+$ 278.1751, found 278.1749.



4-(4-Fluorophenyl)decan-2-one (2g)

The compound **2g** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 65% yield (32.4 mg).

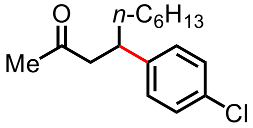
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.14-7.11 (m, 2H), 6.98-6.95 (m, 2H), 3.10 (dtd, J = 9.6, 7.2, 5.3 Hz, 1H), 2.68 (d, J = 7.2 Hz, 2H), 2.01 (s, 3H), 1.62-1.56 (m, 1H), 1.54-1.47 (m, 1H), 1.27-1.03 (m, 8H), 0.84 (t, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 207.74, 161.33 (d, J_{CF} = 243.9 Hz), 140.22 (d, J_{CF} = 3.3 Hz), 128.78 (d, J_{CF} = 7.7 Hz), 115.18 (d, J_{CF} = 21.2 Hz), 50.97, 40.47, 36.54, 31.66, 30.65, 29.12, 27.26, 22.56, 14.02; ^{19}F NMR (CDCl$_3$, 376 MHz): δ –117.29; HRMS (ESI-TOF): m/z calculated for $C_{16}H_{24}FO^+$ $[M+H]^+$ 251.1806, found 251.1805.



4-(3-Fluorophenyl)decan-2-one (2h)

The compound **2h** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 79% yield (39.7 mg).

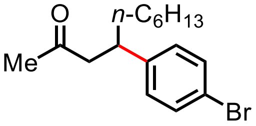
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.25-7.21 (m, 1H), 6.95 (d, J = 7.7 Hz, 1H), 6.89-6.86 (m, 2H), 3.12 (dtd, J = 9.6, 7.0, 5.2 Hz, 1H), 2.73-2.66 (m, 2H), 2.03 (s, 3H), 1.62-1.57 (m, 1H), 1.55-1.49 (m, 1H), 1.27-1.05 (m, 8H), 0.84 (t, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 207.44, 162.92 (d, J_{CF} = 245.4 Hz), 147.39 (d, J_{CF} = 6.9 Hz), 129.81 (d, J_{CF} = 8.2 Hz), 123.26 (d, J_{CF} = 2.7 Hz), 114.12 (d, J_{CF} = 21.1 Hz), 113.14 (d, J_{CF} = 21.1 Hz), 50.63, 40.90 (d, J_{CF} = 2.0 Hz), 36.30, 31.64, 30.62, 29.12, 27.25, 22.55, 14.01; ^{19}F NMR (CDCl$_3$, 376 MHz): δ –113.68; HRMS (ESI-TOF): m/z calculated for $C_{16}H_{24}FO^+$ $[M+H]^+$ 251.1806, found 251.1808.



4-(4-Chlorophenyl)decan-2-one (2i)

The compound **2i** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 78% yield (41.5 mg).

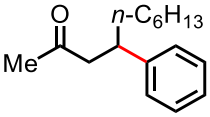
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.26-7.24 (m, 2H), 7.11-7.09 (m, 2H), 3.10 (dtd, J = 9.6, 7.2, 5.3 Hz, 1H), 2.69 (d, J = 7.2 Hz, 2H), 2.02 (s, 3H), 1.62-1.56 (m, 1H), 1.54-1.47 (m, 1H), 1.27-1.03 (m, 8H), 0.84 (t, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 207.50, 143.12, 131.85, 128.81, 128.54, 50.74, 40.54, 36.36, 31.64, 30.65, 29.12, 27.25, 22.56, 14.02; HRMS (ESI-TOF): m/z calculated for $C_{16}H_{24}ClO^+$ $[M+H]^+$ 267.1510, found 267.1508.



4-(4-Bromophenyl)decan-2-one (2j)

The compound **2j** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 83% yield (51.4 mg).

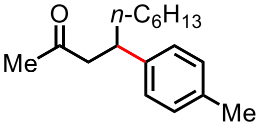
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.41-7.39 (m, 2H), 7.06-7.04 (m, 2H), 3.09 (dtd, *J* = 9.6, 7.2, 5.3 Hz, 1H), 2.68 (d, *J* = 7.2 Hz, 2H), 2.02 (s, 3H), 1.62-1.56 (m, 1H), 1.53-1.47 (m, 1H), 1.28-1.03 (m, 8H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 207.46, 143.66, 131.49, 129.23, 119.91, 77.22, 40.59, 36.30, 31.64, 30.65, 29.12, 27.25, 22.56, 14.02; HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{24}BrO^+$ $[M+H]^+$ 311.1005, found 311.1000.



4-Phenyldecan-2-one (2k)

The compound 2**k** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 75% yield (35.0 mg).

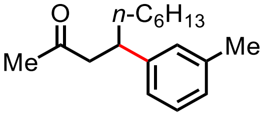
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.29-7.26 (m, 2H), 7.19-7.16 (m, 3H), 3.10 (dtd, *J* = 9.4, 7.2, 5.4 Hz, 1H), 2.74-2.67 (m, 2H), 2.01 (s, 3H), 1.63-1.52 (m, 2H), 1.27-1.05 (m, 8H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 208.06, 144.58, 128.41, 127.43, 126.26, 50.94, 41.30, 36.47, 31.66, 30.63, 29.18, 27.32, 22.57, 14.02; HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{25}O^+$ $[M+H]^+$ 233.1900, found 233.1899.



4-(*p*-Tolyl)decan-2-one (2l)

The compound **2l** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 68% yield (33.7 mg).

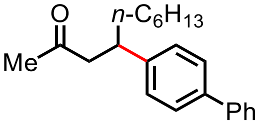
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.09 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 3.06 (dtd, *J* = 9.5, 7.2, 5.3 Hz, 1H), 2.72-2.65 (m, 2H), 2.31 (s, 3H), 2.01 (s, 3H), 1.61-1.49 (m, 2H), 1.27-1.05 (m, 8H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 208.23, 141.49, 135.70, 129.10, 127.28, 51.07, 40.94, 36.55, 31.69, 30.63, 29.21, 27.35, 22.60, 21.00, 14.04; HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{27}O^+$ $[M+H]^+$ 247.2056, found 247.2056.



4-(*m*-Tolyl)decan-2-one (2m)

The compound **2m** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 70% yield (34.7 mg).

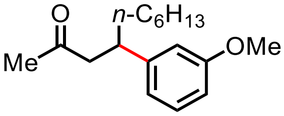
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.16 (t, *J* = 7.5 Hz, 1H), 7.00-6.95 (m, 3H), 3.06 (dtd, *J* = 9.3, 7.2, 5.4 Hz, 1H), 2.73-2.65 (m, 2H), 2.32 (s, 3H), 2.01 (s, 3H), 1.62-1.50 (m, 2H), 1.28-1.06 (m, 8H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 208.15, 144.57, 137.89, 128.27, 128.25, 127.02, 124.37, 109.96, 50.97, 41.25, 36.49, 31.68, 30.64, 29.21, 27.37, 22.59, 21.48, 14.04; HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{27}O^+$ [M+H]$^+$ 247.2056, found 247.2055.



4-([1,1'-Biphenyl]-4-yl)decan-2-one (2n)

The compound **2n** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 48% yield (29.8 mg).

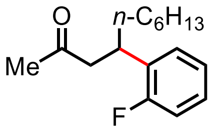
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.58-7.57 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.16 (dtd, *J* = 9.3, 7.2, 5.5 Hz, 1H), 2.78-2.71 (m, 2H), 2.04 (s, 3H), 1.66-1.65 (m, 2H), 1.30-1.10 (m, 8H), 0.84 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 207.99, 143.75, 140.90, 139.10, 128.68, 127.85, 127.11, 127.04, 126.93, 50.90, 40.90, 36.47, 31.69, 30.67, 29.21, 27.37, 22.60, 14.04; HRMS (ESI-TOF): *m/z* calculated for $C_{22}H_{29}O^+$ [M+H]$^+$ 309.2213, found 309.2214.



4-(3-Methoxyphenyl)decan-2-one (2o)

The compound **2o** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 39% yield (20.5 mg).

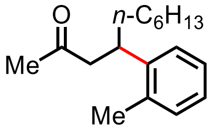
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.20 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.74-6.71 (m, 2H), 3.79 (s, 3H), 3.08 (dtd, *J* = 9.4, 7.2, 5.4 Hz, 1H), 2.73-2.65 (m, 2H), 2.02 (s, 3H), 1.62-1.50 (m, 2H), 1.28-1.06 (m, 8H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 208.01, 159.60, 146.36, 129.36, 119.85, 113.46, 111.21, 55.11, 50.89, 41.33, 36.40, 31.67, 30.65, 29.20, 27.34, 22.59, 14.03; HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{27}O_2^+$ [M+H]$^+$ 263.2005, found 263.2000.



4-(2-Fluorophenyl)decan-2-one (2p)

The compound **2p** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 50% yield (25.2 mg).

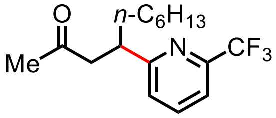
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.18-7.14 (m, 2H), 7.08-7.05 (m, 1H), 7.01-6.98 (m, 1H), 3.44-3.40 (m, 1H), 2.81-2.74 (m, 2H), 2.06 (3H), 1.63-1.60 (m, 2H), 1.29-1.06 (m, 8H), 0.84 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 207.62, 160.97 (d, J = 244.9 Hz), 131.05 (d, J = 14.4 Hz), 129.12 (d, J = 5.3 Hz), 127.70 (d, J = 8.3 Hz), 124.07 (d, J = 3.4 Hz), 115.55 (d, J = 22.8 Hz), 49.39 (d, J = 1.7 Hz), 35.14 (d, J = 1.6 Hz), 31.66, 30.27, 29.12, 27.36, 22.56, 14.02; ^{19}F NMR ($CDCl_3$, 376 MHz): δ –117.96; HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{24}FO^+$ $[M+H]^+$ 251.1806, found 251.1804.



4-(*o*-Tolyl)decan-2-one (2q)

The compound **2q** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 33% yield (16.6 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.17-7.11 (m, 3H), 7.07 (td, J = 7.5, 1.6 Hz, 1H), 3.46-3.41 (m, 1H), 2.74-2.65 (m, 2H), 2.36 (s, 3H), 2.01 (s, 3H), 1.62-1.51 (m, 2H), 1.26-1.06 (m, 8H), 0.84 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 208.14, 143.06, 136.03, 130.35, 126.15, 125.80, 125.46, 50.57, 36.51, 35.65, 31.69, 30.65, 29.40, 27.23, 22.60, 19.85, 14.04; HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{27}O^+$ $[M+H]^+$ 247.2056, found 247.2053.

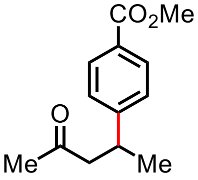


4-(6-(Trifluoromethyl)pyridin-2-yl)decan-2-one (2r)

The compound **2r** was prepared according to the general procedure with 1.0 equiv. of 2-iodo-6-(trifluoromethyl)pyridine and was purified on silica gel to give a colorless oil in 35% yield (21.2 mg).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.73 (t, J = 7.8 Hz, 1H), 7.46 (dd, J = 7.8, 0.9 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 3.39 (dddd, J = 9.3, 8.1, 6.3, 4.8 Hz, 1H), 3.22 (dd, J = 17.2, 9.3 Hz, 1H), 2.69 (dd, J = 17.2, 4.8 Hz, 1H), 2.10 (s, 3H), 1.72-1.66 (m, 1H), 1.61-1.56 (m, 1H), 1.26-1.18 (m, 7H), 1.14-1.07 (m, 1H), 0.85 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 208.33, 164.78, 147.50 (q, J_{CF} = 34.1 Hz), 137.09, 126.34, 121.58 (q, J_{CF} = 274.0 Hz), 117.76 (q, J_{CF} = 2.8 Hz), 47.46, 42.17, 35.46, 31.61, 30.58, 29.16, 27.09, 22.53, 14.01. ^{19}F NMR ($CDCl_3$, 376 MHz): δ –68.44; HRMS (ESI-TOF): *m/z* calculated for $C_{16}H_{23}F_3NO^+$

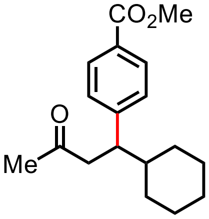
$[M+H]^+$ 302.1726, found 302.1724.



Methyl 4-(4-oxopentan-2-yl)benzoate (4a)

The compound **4a** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 74% yield (32.6 mg).

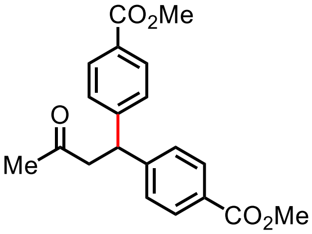
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.40-3.35 (m, 1H), 2.77 (dd, *J* = 16.7, 6.6 Hz, 1H), 2.69 (dd, *J* = 16.7, 7.6 Hz, 1H), 2.07 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 207.12, 166.94, 151.56, 129.88, 128.25, 126.82, 51.98, 51.45, 35.28, 30.54, 21.72; HRMS (ESI-TOF): *m/z* calculated for $C_{13}H_{17}O_3^+$ $[M+H]^+$ 221.1172, found 221.1175.



Methyl 4-(1-cyclohexyl-3-oxobutyl)benzoate (4b)

The compound **4b** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 39% yield (22.7 mg).

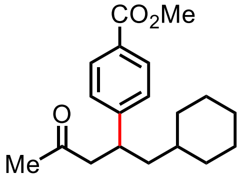
^{1}H NMR ($CDCl_3$, 600 MHz): δ ;7.94 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 3H), 3.04-3.01 (m, 1H), 2.87 (dd, *J* = 16.4, 5.1 Hz, 1H), 2.77 (dd, *J* = 16.4, 9.3 Hz, 1H), 1.99 (s, 3H), 1.79-1.72 (m, 2H), 1.63-1.59 (m, 2H), 1.50-1.43 (m, 1H), 1.40-1.38 (m, 1H), 1.26-1.17 (m, 1H), 1.13-1.02 (m, 2H), 0.96-0.89 (m, 1H), 0.82-0.75 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 207.72, 167.02, 149.20, 129.50, 128.30, 128.18, 51.97, 47.13, 47.01, 42.86, 31.08, 30.73, 30.61, 26.38, 26.25; HRMS (ESI-TOF): *m/z* calculated for $C_{18}H_{25}O_3^+$ $[M+H]^+$ 289.1798, found 289.1808.



Dimethyl 4,4'-(3-oxobutane-1,1-diyl)dibenzoate (4c)

The compound **4c** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 41% yield (27.7 mg).

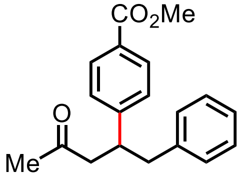
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.95 (d, *J* = 8.3 Hz, 4H), 7.28 (d, *J* = 8.3 Hz, 4H), 4.71 (t, *J* = 7.4 Hz, 1H), 3.89 (s, 6H), 3.22 (d, *J* = 7.4 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 205.66, 166.72, 148.22, 130.03, 128.67, 127.75, 52.07, 48.89, 45.68, 30.62; HRMS (ESI-TOF): *m/z* calculated for $C_{20}H_{21}O_5^+$ [M+H]$^+$ 341.1384, found 341.1383.



Methyl 4-(1-cyclohexyl-4-oxopentan-2-yl)benzoate (4d)

The compound **4d** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 72% yield (42.1 mg).

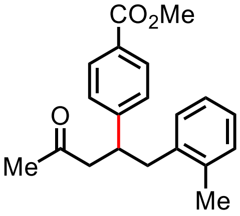
^{1}H NMR (CDCl$_3$, 600 MHz): δ ;7.96 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H), 3.38-3.30 (m, 1H), 2.74-2.63 (m, 2H), 2.00 (s, 3H), 1.80 (d, *J* = 11.9 Hz, 1H), 1.66-1.40 (m, 6H), 1.12-0.82 (m, 6H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 207.31, 167.01, 150.31, 129.82, 128.25, 127.54, 51.98, 50.98, 43.91, 38.13, 34.74, 33.98, 32.47, 30.66, 26.48, 26.11, 26.00; HRMS (ESI-TOF): *m/z* calculated for $C_{19}H_{27}O_3^+$ [M+H]$^+$ 303.1955, found 303.1965.



Methyl 4-(4-oxo-1-phenylpentan-2-yl)benzoate (4e)

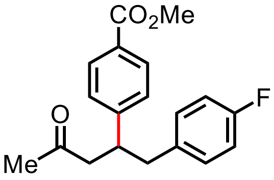
The compound **4e** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 50% yield (29.8 mg). The starting material **3e** was recovered in 25% yield.

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.21-7.19 (m, 4H), 7.16-7.14 (m, 1H), 7.01 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 3H), 3.56-3.51 (m, 1H), 2.91 (dd, *J* = 13.5, 7.1 Hz, 1H), 2.86 (dd, *J* = 13.5, 7.9 Hz, 1H), 2.84-2.75 (m, 2H), 2.01 (s, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 206.94, 166.96, 149.27, 139.05, 129.72, 129.13, 128.39, 128.24, 127.64, 126.27, 51.99, 48.74, 42.80, 42.73, 30.60; HRMS (ESI-TOF): *m/z* calculated for $C_{19}H_{21}O_3^+$ [M+H]$^+$ 297.1485, found 297.1484.



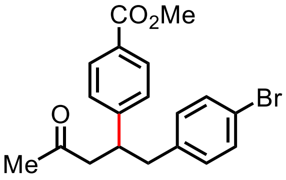
Methyl 4-(4-oxo-1-(*o*-tolyl)pentan-2-yl)benzoate (4f)

The compound **4f** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 50% yield (31.2 mg). The starting material **3f** was recovered in 36% yield.
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.12-7.05 (m, 2H), 7.01 (td, *J* = 7.3, 1.6 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 1H), 3.89 (s, 3H), 3.61-3.42 (m, 1H), 2.91 (dd, *J* = 13.7, 7.4 Hz, 1H), 2.88-2.77 (m, 3H), 2.24 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 206.88, 166.95, 149.55, 137.31, 136.34, 130.34, 130.01, 129.73, 128.39, 127.53, 126.43, 125.66, 51.99, 48.70, 41.53, 40.27, 30.57, 19.37; HRMS (ESI-TOF): *m/z* calculated for $C_{20}H_{23}O_3^+$ [M+H]$^+$ 311.1642, found 311.1637.



Methyl 4-(1-(4-fluorophenyl)-4-oxopentan-2-yl)benzoate (4g)

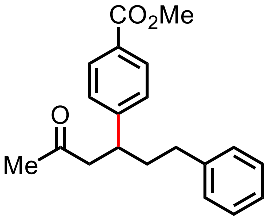
The compound **4g** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 55% yield (34.5 mg). The starting material **3g** was recovered in 27% yield.
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.95-6.91 (m, 2H), 6.89-6.85 (m, 2H), 3.89 (s, 3H), 3.51-3.46 (m, 1H), 2.91 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.84-2.76 (m, 3H), 2.03 (s, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 206.79, 166.90, 161.43 (d, J_{CF} = 244.4 Hz), 148.90, 134.73 (d, J_{CF} = 3.1 Hz), 130.47 (d, J_{CF} = 7.7 Hz), 129.75, 128.49, 127.65, 115.01 (d, J_{CF} = 21.0 Hz), 52.02, 48.73, 42.89, 41.83, 30.63; ^{19}F NMR (CDCl$_3$, 376 MHz): δ –117.09; HRMS (ESI-TOF): *m/z* calculated for $C_{19}H_{20}FO_3^+$ [M+H]$^+$ 315.1391, found 315.1388.



Methyl 4-(1-(4-bromophenyl)-4-oxopentan-2-yl)benzoate (4h)

The compound **4h** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 50% yield (37.8 mg). The starting material **3h** was recovered in 37% yield.
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H),

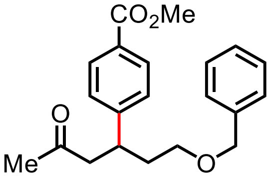
6.85 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H), 3.51-3.46 (m, 1H), 2.90 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.84-2.75 (m, 3H), 2.04 (s, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 206.68, 166.87, 148.70, 138.05, 131.29, 130.81, 129.78, 128.55, 127.63, 120.13, 52.03, 48.74, 42.60, 41.98, 30.63; HRMS (ESI-TOF): *m/z* calculated for $C_{19}H_{20}BrO_3^+$ $[M+H]^+$ 375.0590, found 375.0593.



Methyl 4-(5-oxo-1-phenylhexan-3-yl)benzoate (4i)

The compound **4i** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 70% yield (43.6 mg).

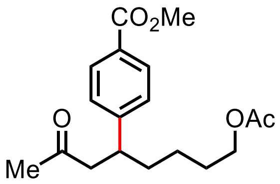
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.26-7.23 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 2H), 3.91 (s, 3H), 3.25 (dtd, *J* = 9.9, 7.1, 4.8 Hz, 1H), 2.79-2.72 (m, 2H), 2.47-2.38 (m, 2H), 2.03-1.97 (m, 1H), 2.01 (s, 3H), 1.92-1.86 (m, 1H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 206.95, 166.95, 149.56, 141.55, 129.93, 128.52, 128.34, 128.25, 127.67, 125.87, 52.03, 50.47, 40.68, 37.73, 33.50, 30.58; HRMS (ESI-TOF): *m/z* calculated for $C_{20}H_{23}O_3^+$ $[M+H]^+$ 311.1642, found 311.1641.



Methyl 4-(1-(benzyloxy)-5-oxohexan-3-yl)benzoate (4j)

The compound **4j** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 56% yield (38.0 mg).

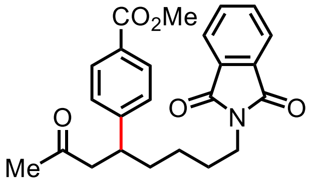
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.34-7.31 (m, 2H), 7.28-7.24 (m, 5H), 4.41-4.36 (m, 2H), 3.90 (s, 3H), 3.44 (dtd, *J* = 9.6, 7.2, 5.4 Hz, 1H), 3.35-3.31 (m, 1H), 3.26-3.22 (m, 1H), 2.81-2.74 (m, 2H), 2.04-1.98 (m, 1H), 2.01 (s, 3H), 1.85-1.80 (m, 1H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 206.88, 166.94, 149.41, 138.22, 129.85, 128.44, 128.33, 127.66, 127.59, 127.57, 72.92, 67.69, 52.01, 50.13, 37.88, 36.04, 30.45; HRMS (ESI-TOF): *m/z* calculated for $C_{21}H_{25}O_4^+$ $[M+H]^+$ 341.1747, found 341.1745.



Methyl 4-(8-acetoxy-2-oxooctan-4-yl)benzoate (4k)

The compound **4k** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 60% yield (38.4 mg).

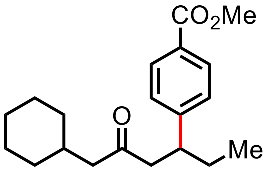
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 4.02-3.92 (m, 2H), 3.90 (s, 3H), 3.28-3.12 (m, 1H), 2.78-2.71 (m, 2H), 2.04 (s, 3H), 2.00 (s, 3H), 1.70-1.64 (m, 1H), 1.63-1.50 (m, 3H), 1.27-1.19 (m, 1H), 1.17-1.09 (m, 1H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 207.02, 171.09, 166.91, 149.72, 129.86, 128.44, 127.51, 64.08, 52.01, 50.36, 40.86, 35.61, 30.63, 28.33, 23.65, 20.92; HRMS (ESI-TOF): *m/z* calculated for $C_{18}H_{25}O_5^+$ [M+H]$^+$ 321.1697, found 321.1697.



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

The compound **4l** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 71% yield (58.1 mg).

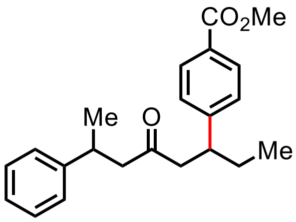
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.83-7.80 (m, 2H), 7.71-7.68 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 3H), 3.59 (t, *J* = 7.3 Hz, 2H), 3.22-3.17 (m, 1H), 2.74 (d, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.73-1.64 (m, 2H), 1.63-1.55 (m, 2H), 1.24-1.17 (m, 1H), 1.16-1.09 (m, 1H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 207.01, 168.29, 166.85, 149.63, 133.80, 131.99, 129.80, 128.31, 127.48, 123.09, 51.93, 50.27, 40.72, 37.51, 35.40, 30.55, 28.12, 24.35; HRMS (ESI-TOF): *m/z* calculated for $C_{24}H_{26}NO_5^+$ [M+H]$^+$ 408.1807, found 408.1805.



Methyl 4-(6-cyclohexyl-5-oxohexan-3-yl)benzoate (4m)

The compound **4m** was prepared according to the general procedure with 60 mol% of **TDG-12** and was purified on silica gel to give a colorless oil in 41% yield (25.8 mg).

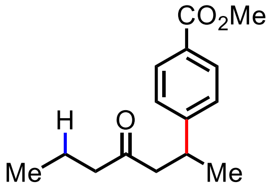
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.13 (dtd, *J* = 9.4, 7.1, 5.3 Hz, 1H), 2.80-2.59 (m, 2H), 2.17 (dd, *J* = 15.7, 7.1 Hz, 1H), 2.12 (dd, *J* = 15.7, 6.6 Hz, 1H), 1.75-1.65 (m, 2H), 1.62-1.49 (m, 6H), 1.24-1.15 (m, 2H), 1.12-1.04 (m, 1H), 0.85-0.78 (m, 2H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 209.26, 167.04, 150.11, 129.72, 128.21, 127.66, 51.97, 51.29, 49.78, 42.67, 33.69, 33.13, 33.07, 29.08, 26.12, 26.02, 26.00, 11.90; HRMS (ESI-TOF): *m/z* calculated for $C_{20}H_{29}O_3^+$ $[M+H]^+$ 317.2111, found 317.2115.



Methyl 4-(5-oxo-7-phenyloctan-3-yl)benzoate (4n)

The compound **4n** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 40% yield (25.8 mg).

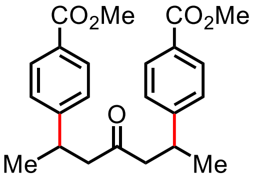
^{1}H NMR (CDCl$_3$, 600 MHz, 1:1 mixture of diastereomers): δ 7.95-7.91 (m, 2H), 7.29-7.24 (m, 2H), 7.22-7.12 (m, 5H), 3.90 (s, 3H), 3.35-3.29 (m, 1H), 3.28-3.22 (m, 1H), 2.69-2.49 (m, 4H), 1.20 (d, *J* = 7.0 Hz, 1.5H), 1.20 (d, *J* = 7.0 Hz, 1.5H), 1.17 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz, 1:1 mixture of diastereomers): δ 208.11, 208.05, 166.97, 151.63, 151.57, 145.99, 145.95, 129.84, 129.84, 128.50, 128.48, 128.18, 128.15, 126.83, 126.79, 126.74, 126.69, 126.30, 126.27, 51.98, 51.98, 51.76, 51.71, 51.35, 51.27, 35.36, 35.30, 35.07, 35.06, 21.92, 21.91, 21.64, 21.60; HRMS (ESI-TOF): *m/z* calculated for $C_{21}H_{25}O_3^+$ $[M+H]^+$ 325.1798, found 325.1794.



Methyl 4-(4-oxoheptan-2-yl)benzoate (4o$_{mono}$)

The compound **4o$_{mono}$** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 29% yield (14.5 mg).

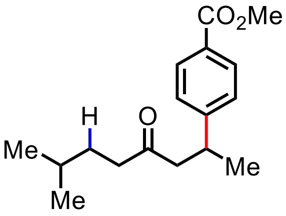
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.42-3.36 (m, 1H), 2.73 (dd, *J* = 16.5, 6.7 Hz, 1H), 2.65 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.34-2.24 (m, 2H), 1.57-1.50 (m, 2H), 1.27 (d, *J* = 7.0 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 209.41, 167.00, 151.76, 129.86, 128.21, 126.86, 52.00, 50.63, 45.42, 35.28, 21.73, 17.06, 13.64; HRMS (ESI-TOF): *m/z* calculated for $C_{15}H_{21}O_3^+$ $[M+H]^+$ 249.1485, found 249.1492.



Dimethyl 4,4'-(4-oxoheptane-2,6-diyl)dibenzoate ($4o_{di}$)

The compound **$4o_{di}$** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 25% yield (19.1 mg).

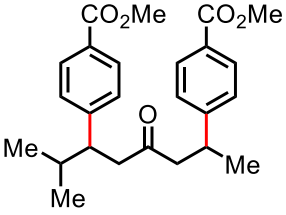
^{1}H NMR (CDCl$_3$, 600 MHz, 1:1 mixture of diastereomers): δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 6H), 3.36-3.28 (m, 2H), 2.70-2.51 (m, 4H), 1.21 (d, *J* = 7.0 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz, 1:1 mixture of diastereomers): δ 207.52, 166.94, 151.45, 151.37, 129.87, 129.85, 128.26, 128.24, 126.83, 126.78, 52.01, 51.31, 51.29, 35.15, 21.68; HRMS (ESI-TOF): *m/z* calculated for $C_{23}H_{27}O_5^+$ [M+H]$^+$ 383.1853, found 383.1857.



Methyl 4-(7-methyl-4-oxooctan-2-yl)benzoate ($4p_{mono}$)

The compound **$4p_{mono}$** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 30% yield (16.9 mg).

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 3.42-3.36 (m, 1H), 2.74 (dd, *J* = 16.5, 6.7 Hz, 1H), 2.66 (dd, *J* = 16.6, 7.6 Hz, 1H), 2.38-2.23 (m, 2H), 1.49-1.42 (m, 1H), 1.41-1.37 (m, 1H), 1.27 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 1.8 Hz, 3H), 0.83 (d, *J* = 1.8 Hz, 3H); ^{13}C NMR (CDCl$_3$, 150 MHz): δ 209.66, 167.00, 151.77, 129.87, 128.21, 126.87, 52.00, 50.61, 41.56, 35.30, 32.38, 27.60, 22.27, 21.72; HRMS (ESI-TOF): *m/z* calculated for $C_{17}H_{25}O_3^+$ [M+H]$^+$ 277.1798, found 277.1807.

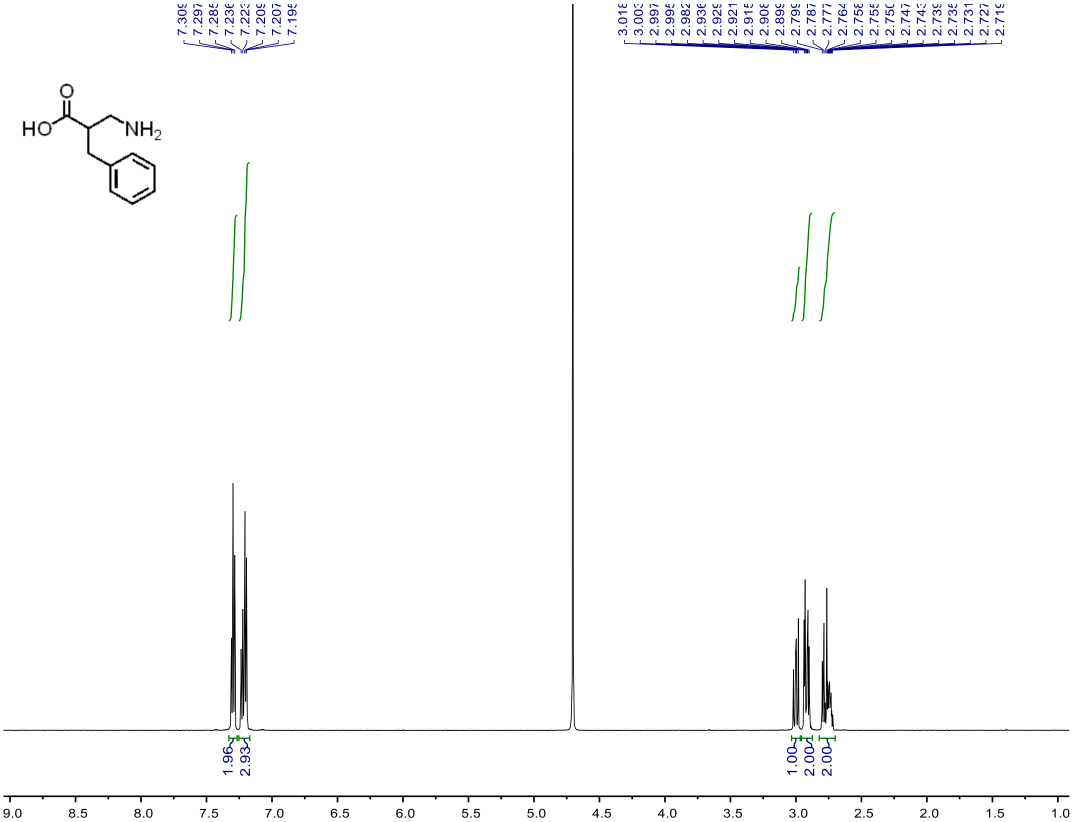


Dimethyl 4,4'-(7-methyl-4-oxooctane-2,6-diyl)dibenzoate ($4p_{di}$)

The compound **$4p_{di}$** was prepared according to the general procedure and was purified on silica gel to give a colorless oil in 10% yield (8.2 mg).

^{1}H NMR (CDCl$_3$, 600 MHz, 1:1 mixture of diastereomers): δ 7.93-7.91 (m, 2H), 7.89-7.87 (m, 2H), 7.17-7.16 (m, 2H), 7.13-7.11 (m, 2H), 3.90 (s, 6H), 3.28-3.20 (m, 1H), 2.96-2.92 (m, 1H), 2.76-2.63 (m, 2.5H), 2.58-2.49 (m, 1H), 2.43 (dd, *J* = 16.9, 7.2 Hz, 0.5H), 1.82-1.74 (m, 1H), 1.12 (d, *J* = 6.9 Hz, 1.5H), 1.08 (d, *J* = 7.0 Hz, 1.5H), 0.90 (d, *J* = 6.7 Hz, 1.5H), 0.86 (d, *J* = 6.7 Hz, 1.5H), 0.69 (d, *J* = 6.7 Hz, 1.5H), 0.67 (d, *J* = 6.7 Hz, 1.5H); ^{13}C NMR ($CDCl_3$, 150 MHz, 1:1 mixture of diastereomers): δ 207.89, 207.88, 167.01, 166.97, 166.95, 166.93, 151.53, 151.42, 148.94, 148.82, 129.82, 129.80, 129.49, 129.47, 128.26, 128.22, 128.20, 128.18, 126.80, 126.71, 52.00, 51.99, 51.46, 51.34, 47.74, 47.73, 47.07, 47.05, 34.94, 34.92, 33.03, 33.00, 21.60, 21.53, 20.66, 20.61, 20.30, 20.26; HRMS (ESI-TOF): *m/z* calculated for $C_{25}H_{31}O_5^+$ $[M+H]^+$ 411.2166, found 411.2171.

NMR Spectra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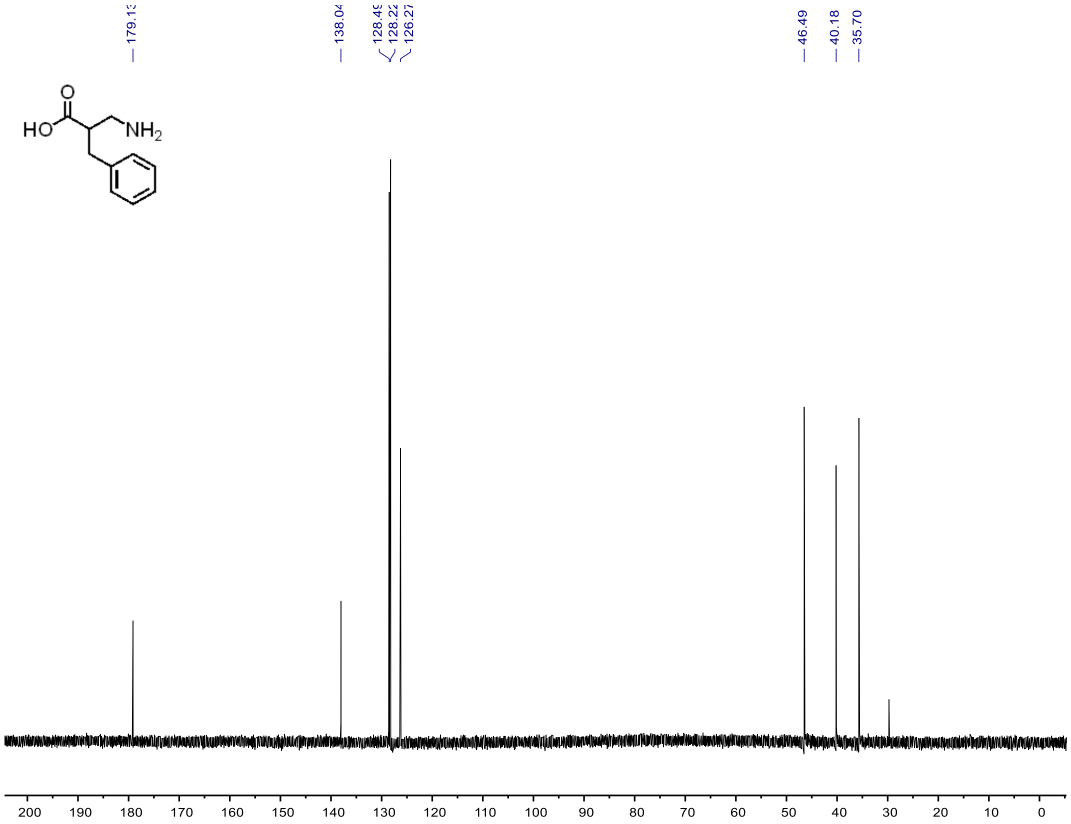
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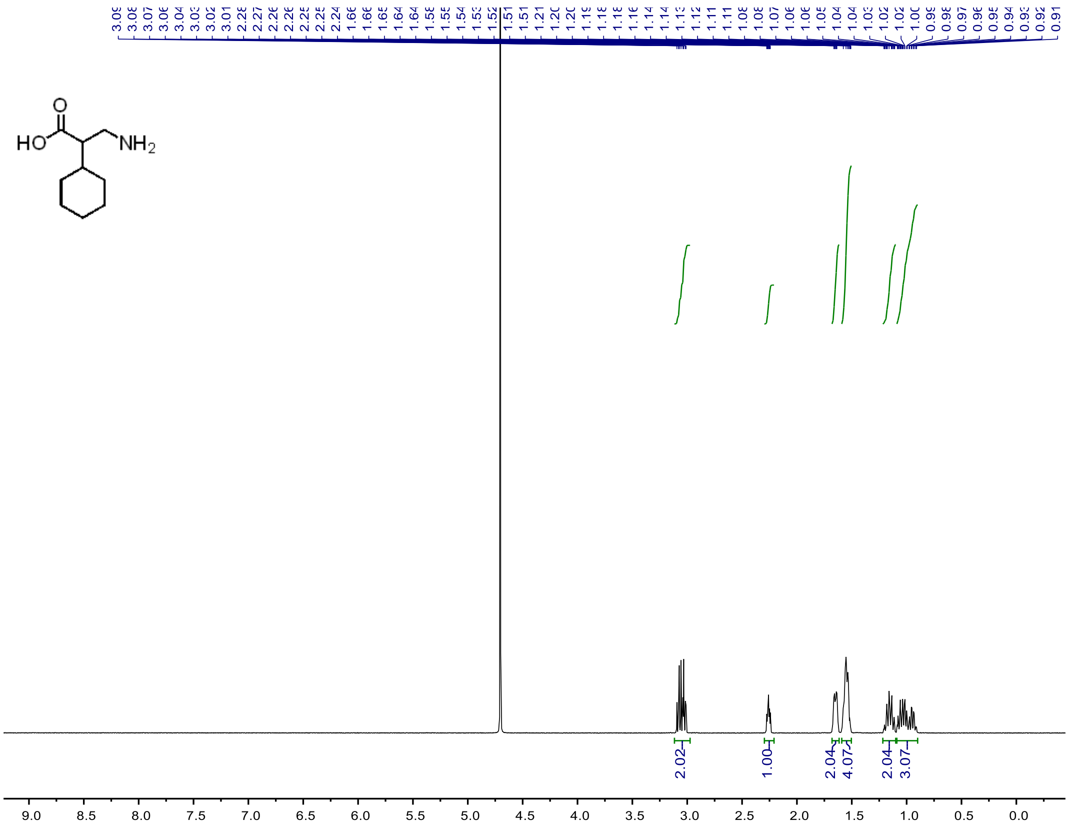
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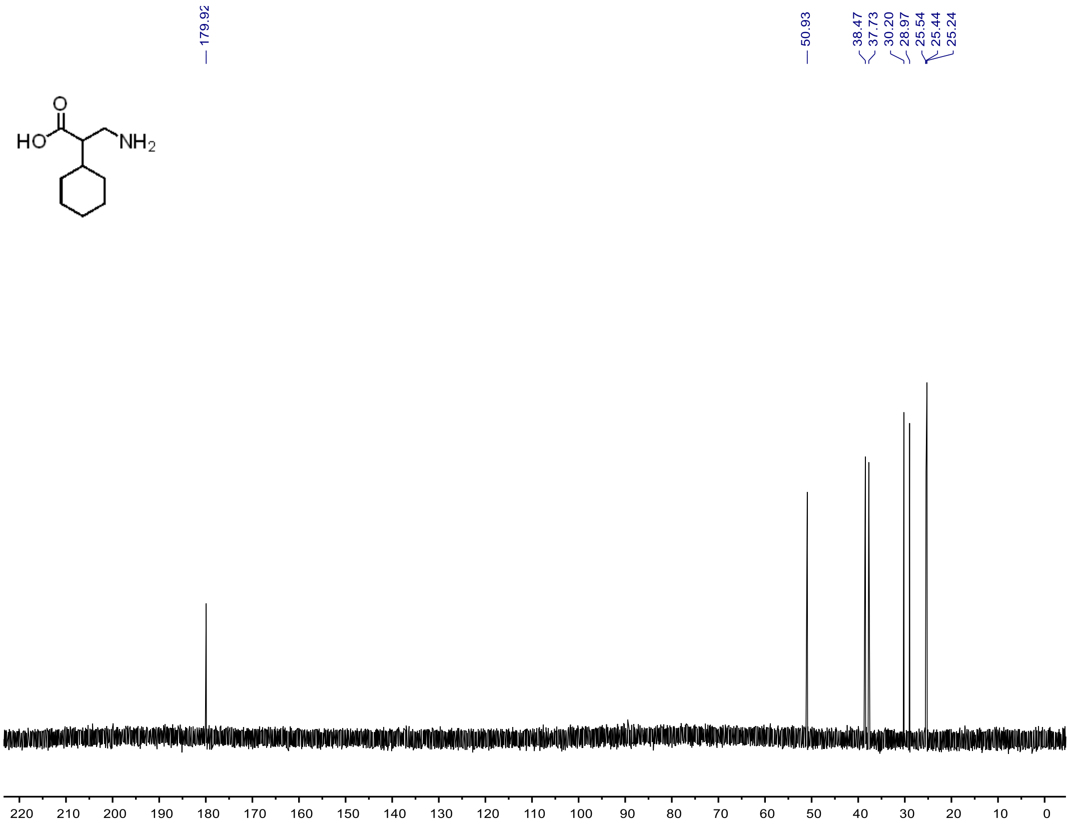
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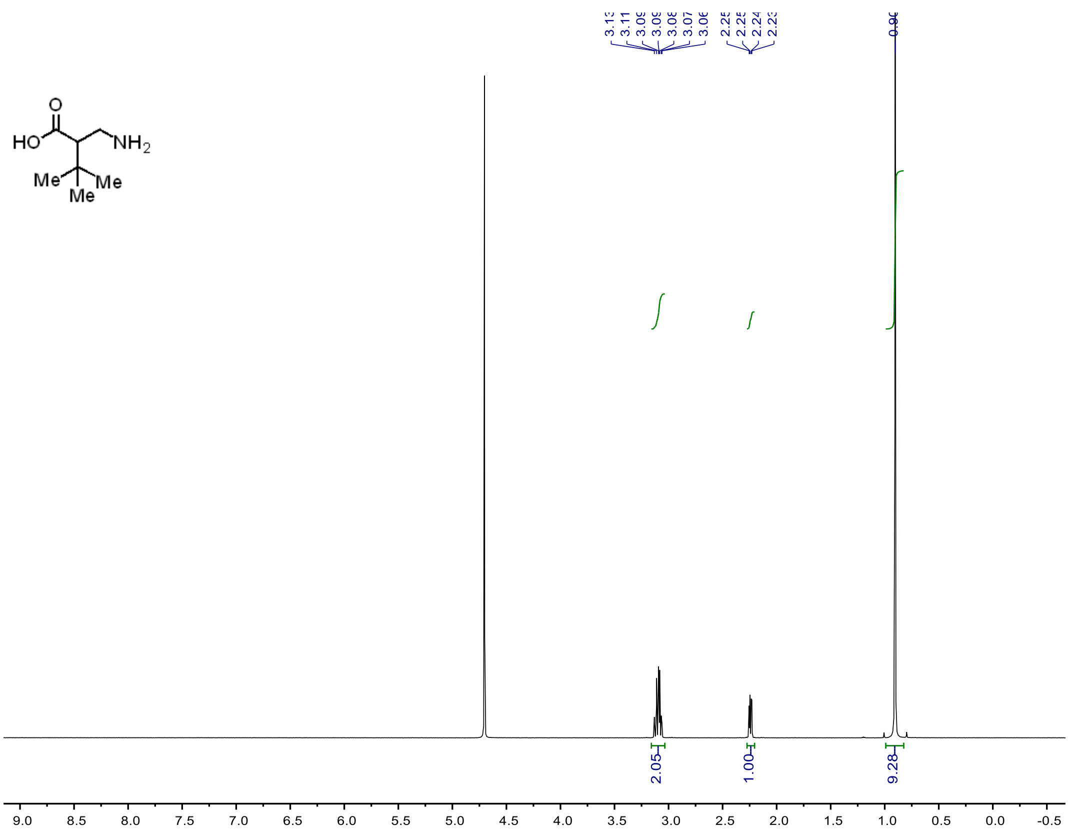
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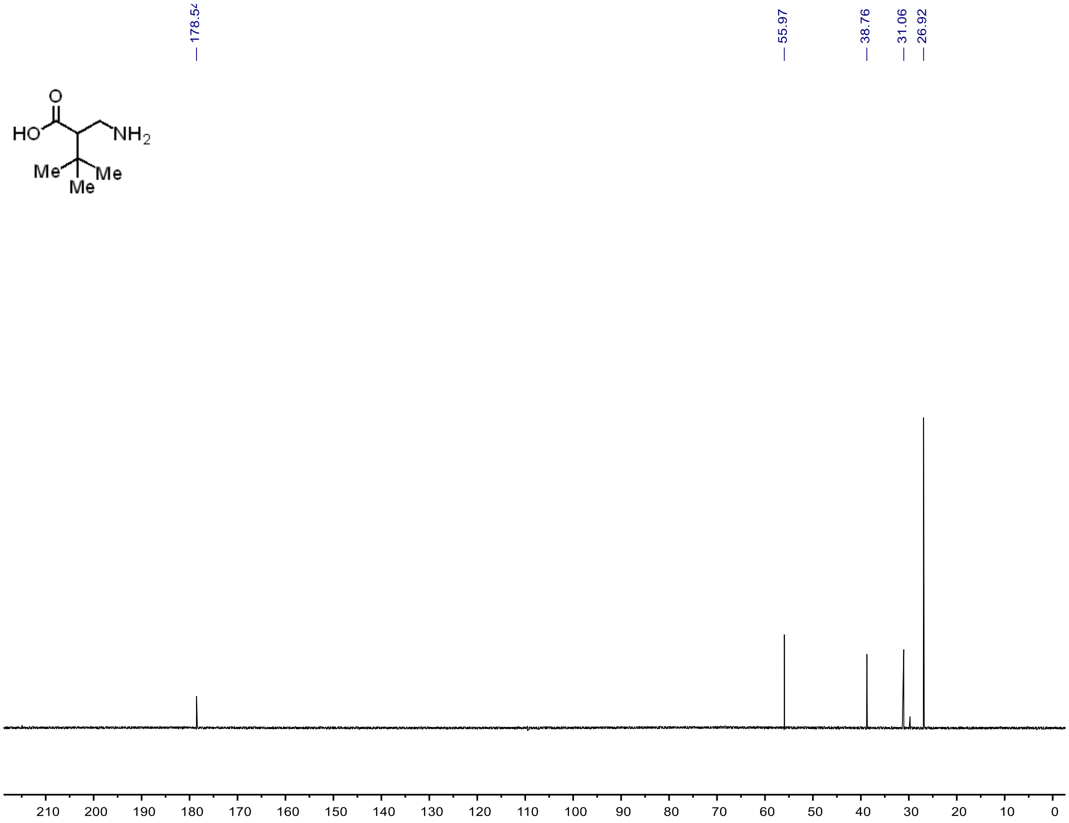
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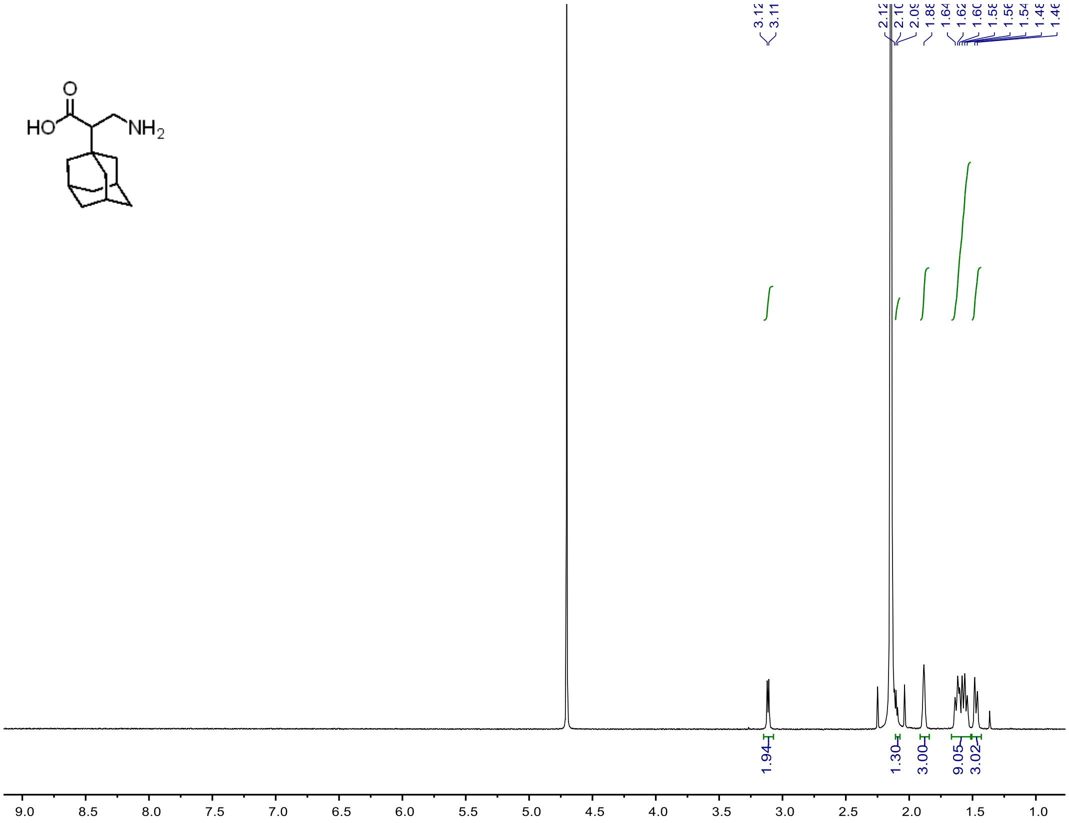
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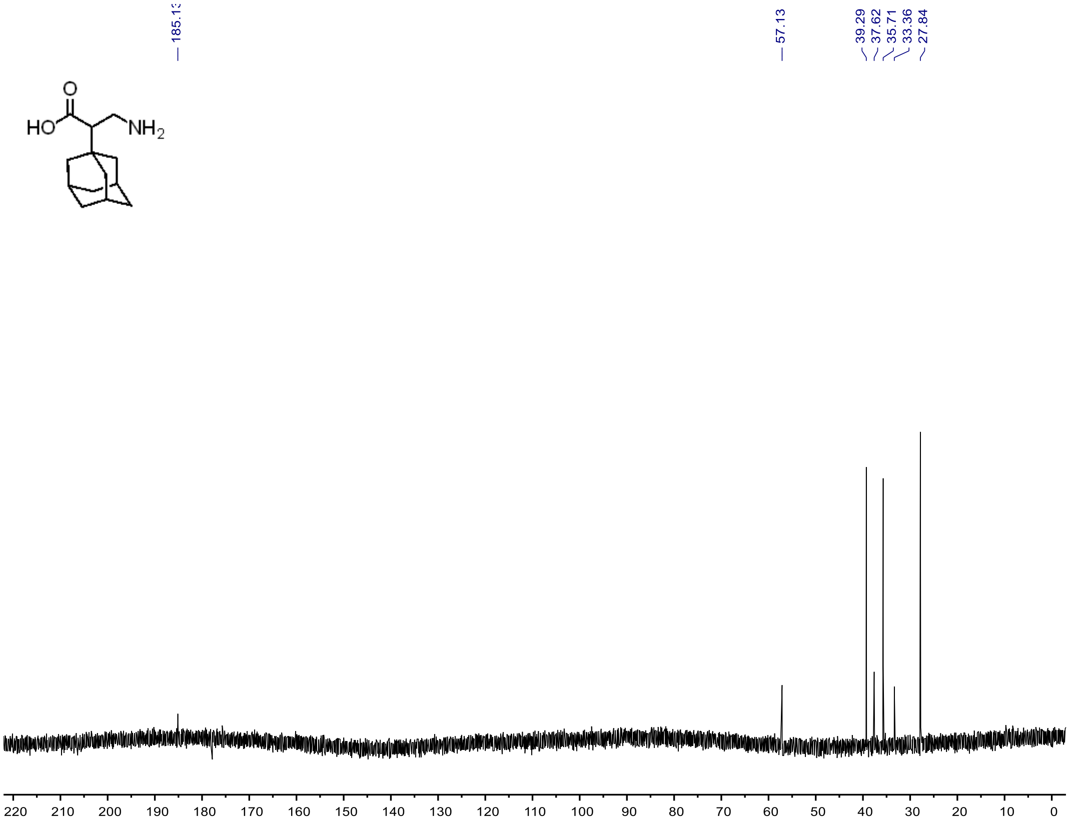
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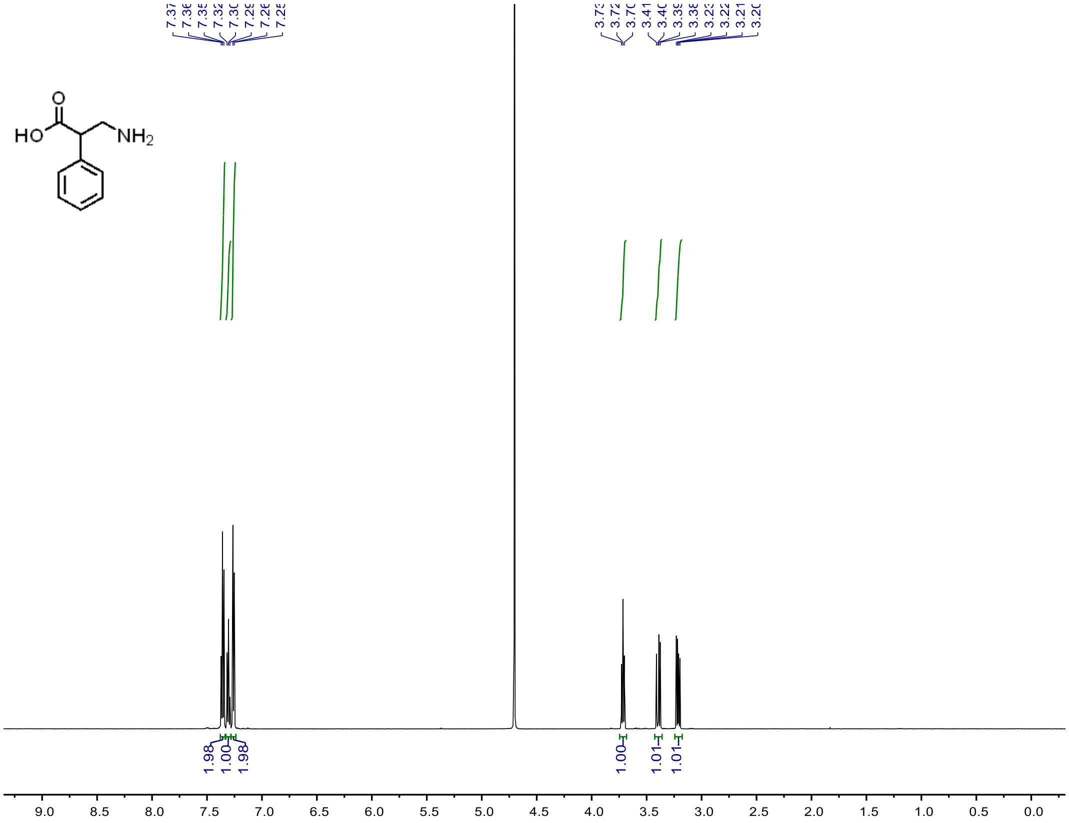
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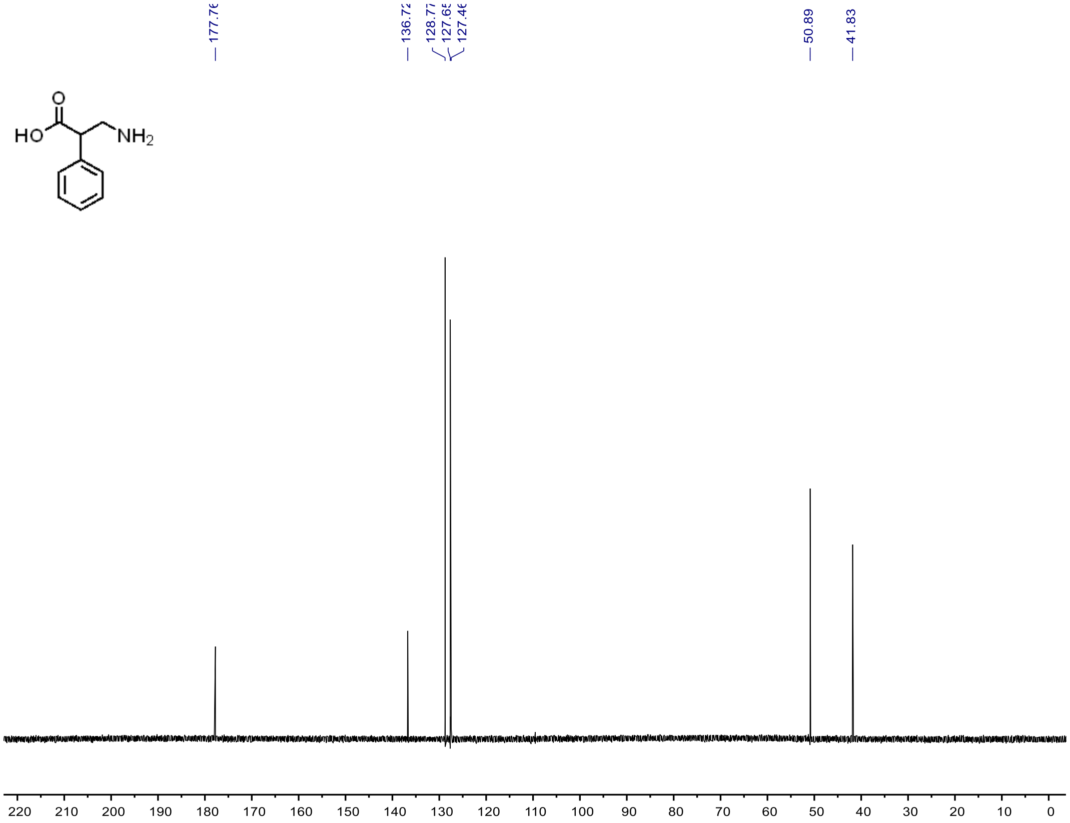
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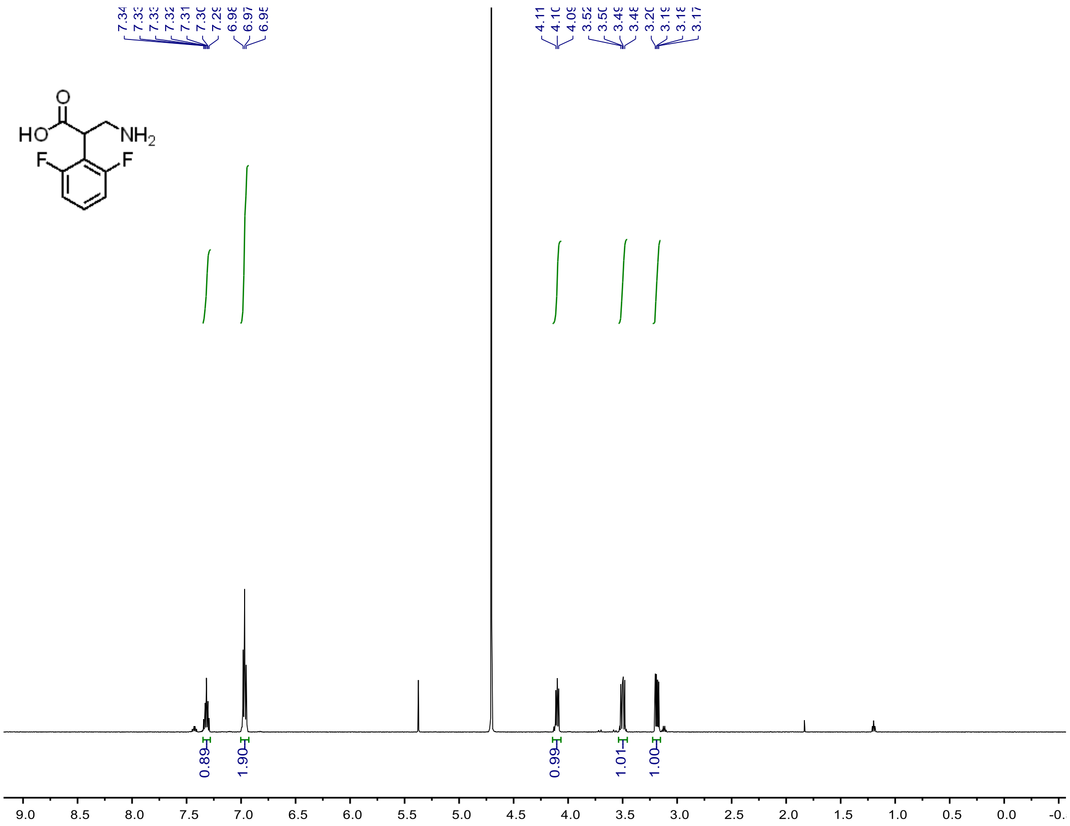
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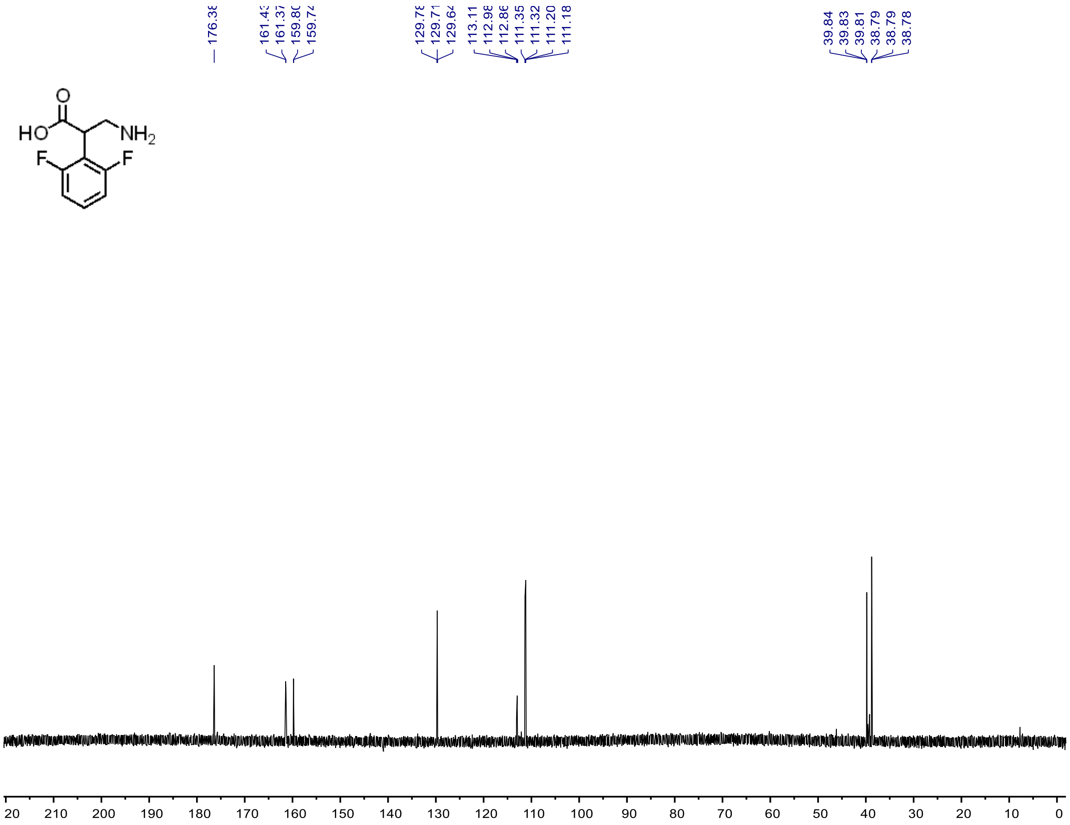
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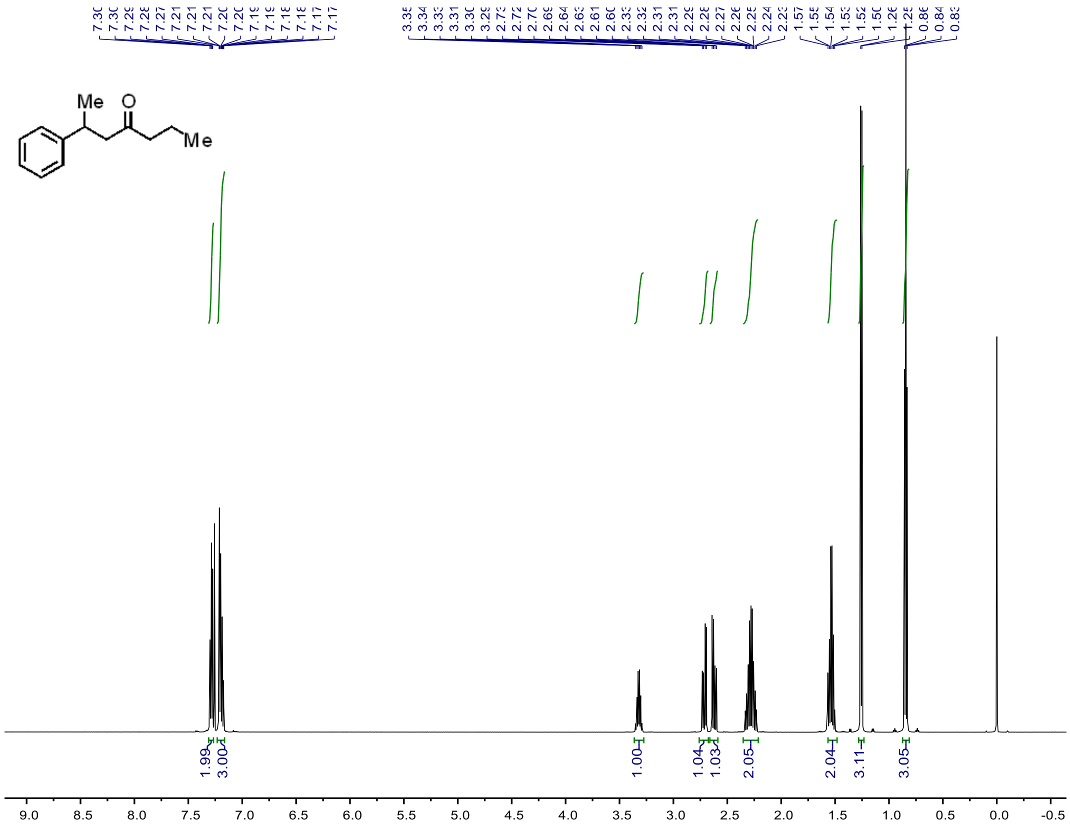
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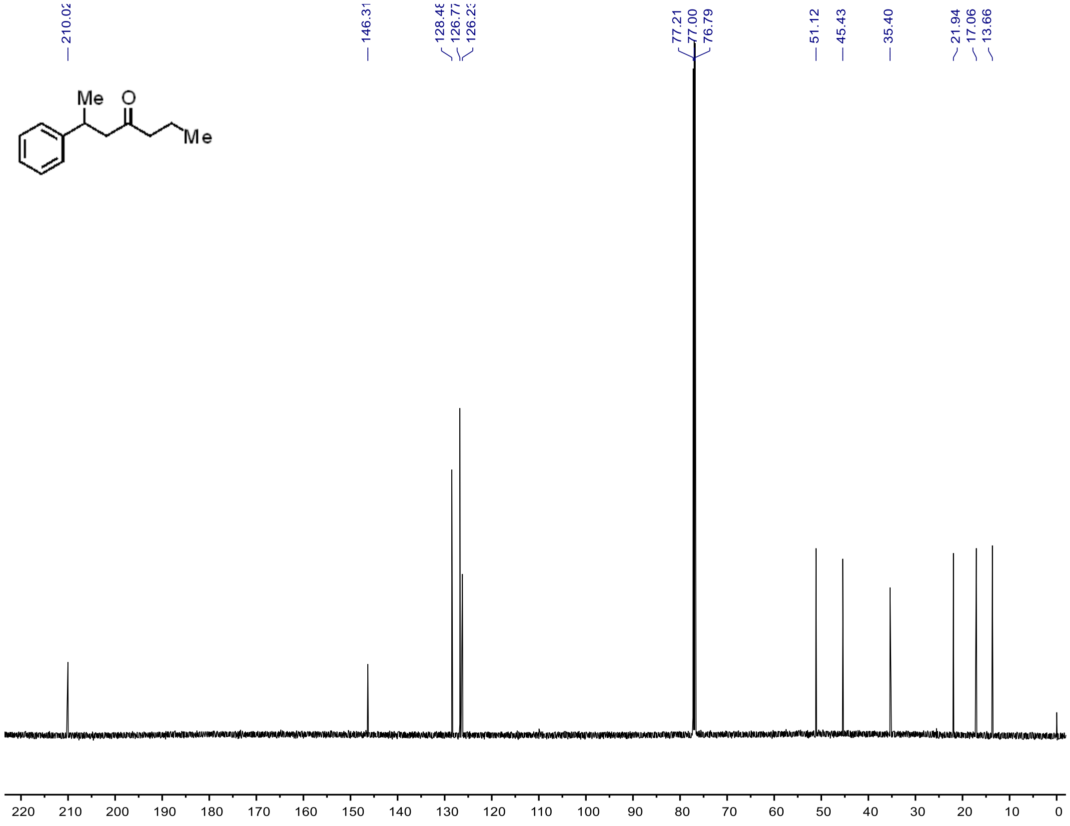
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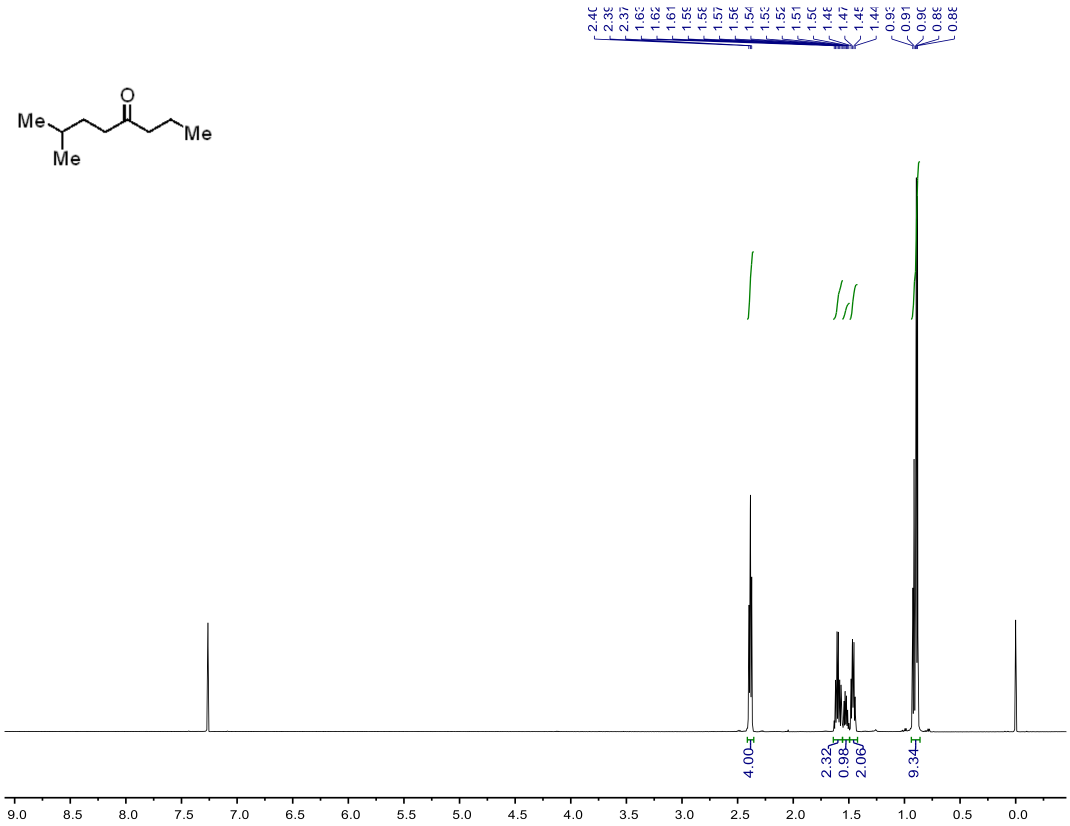
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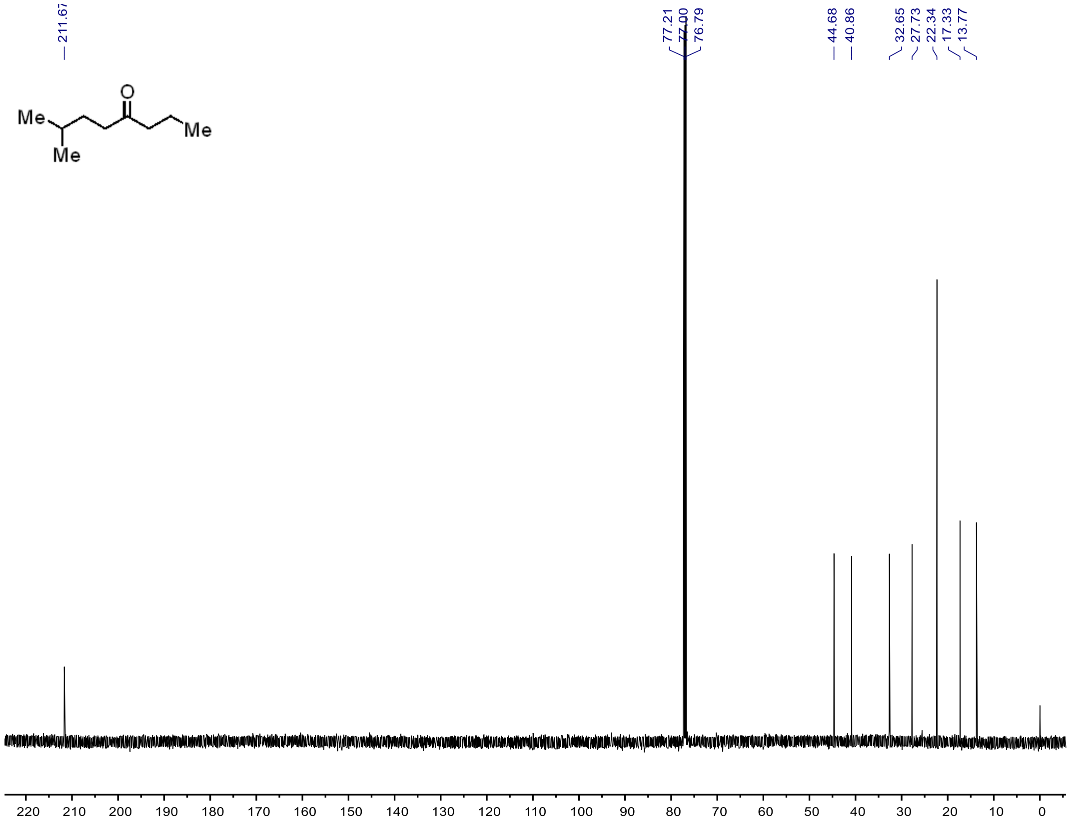
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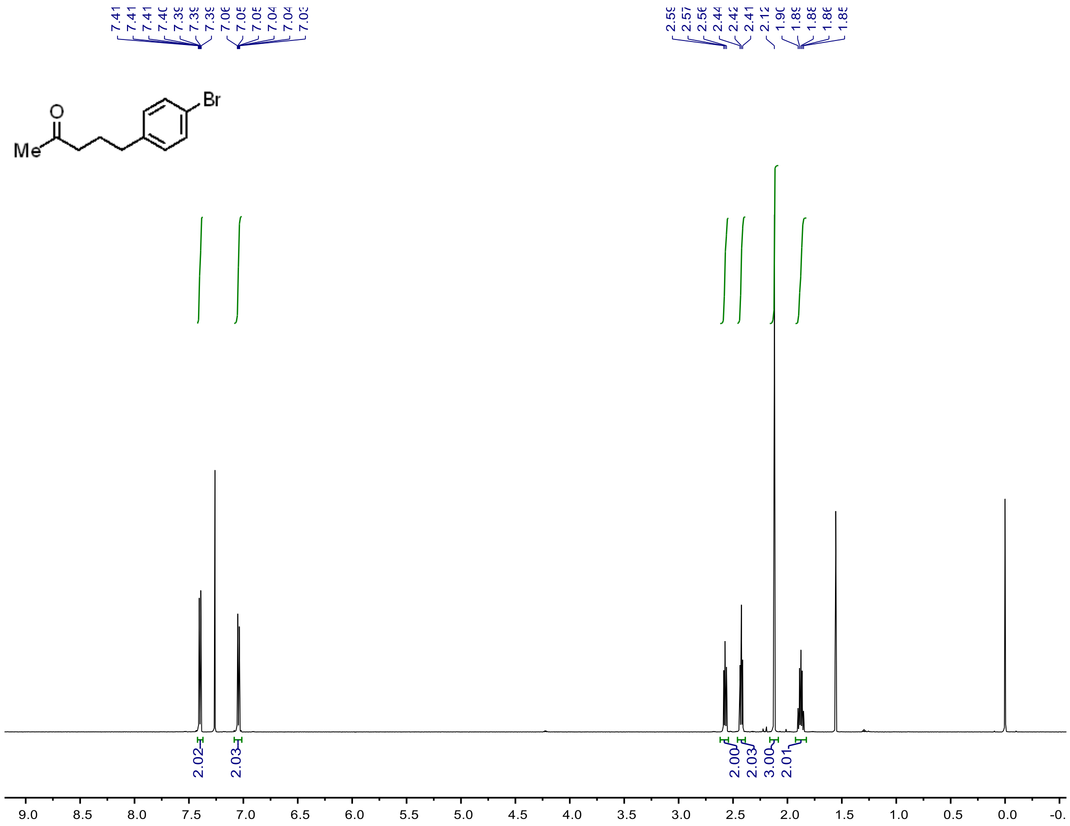
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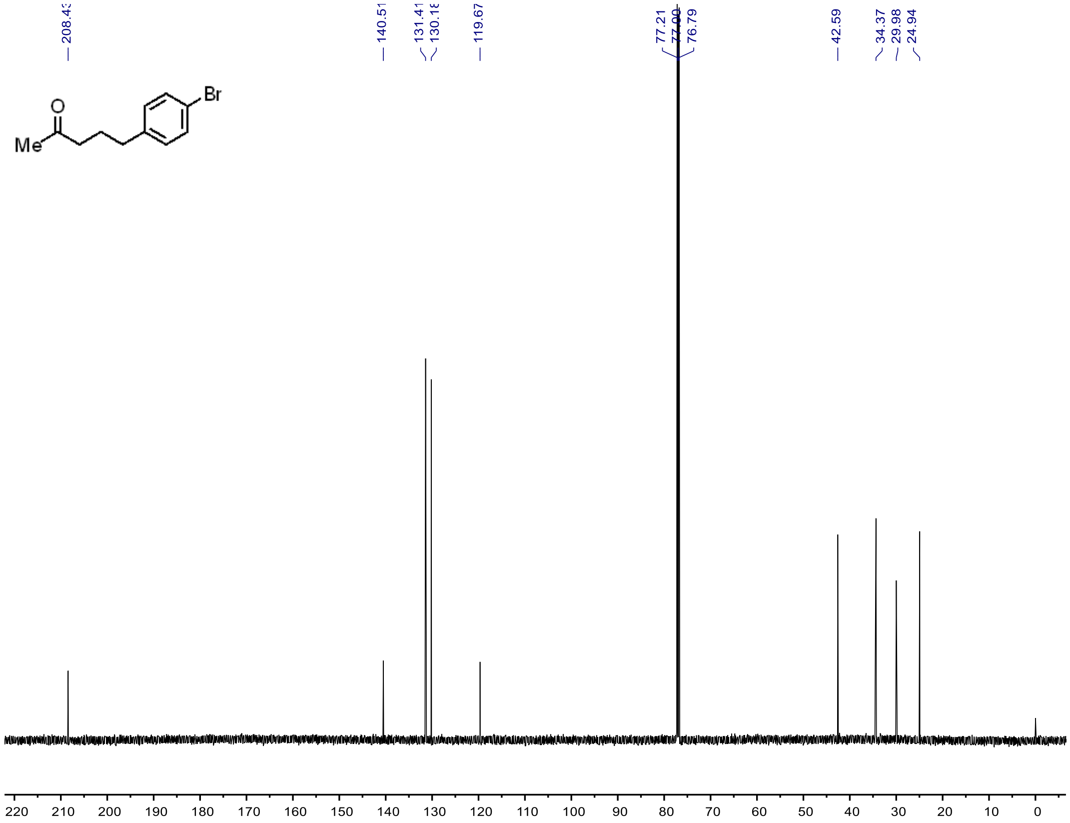
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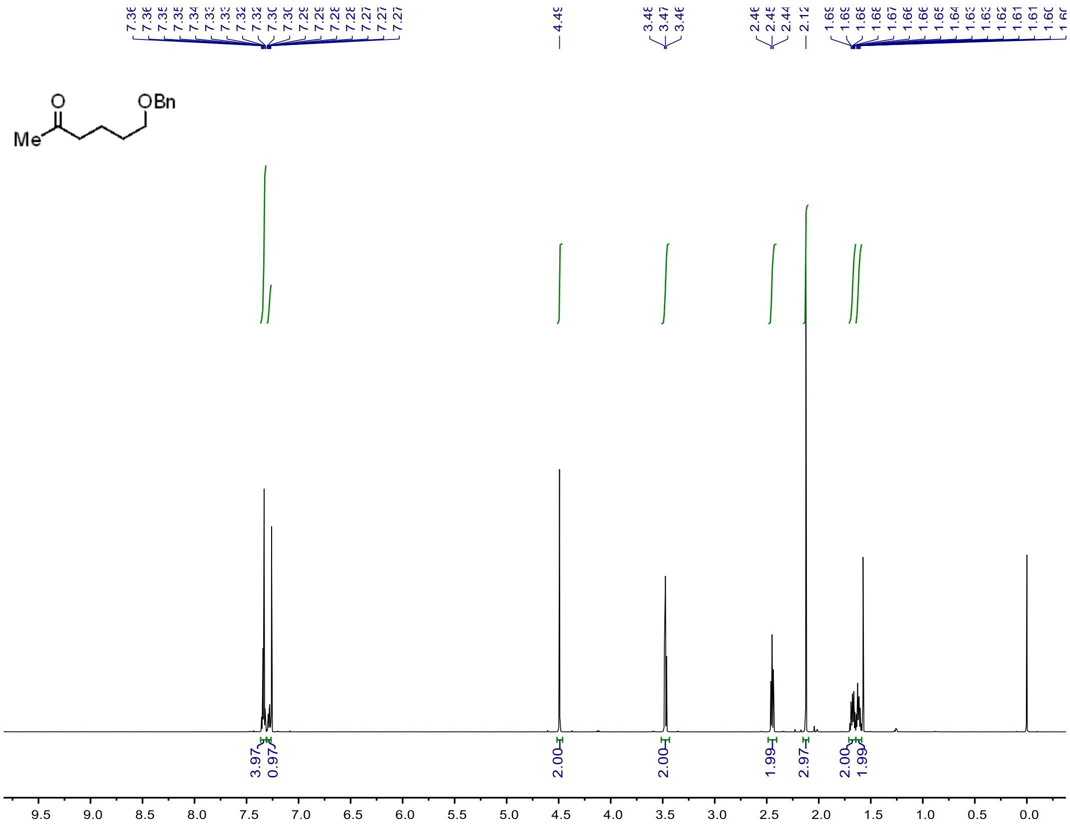
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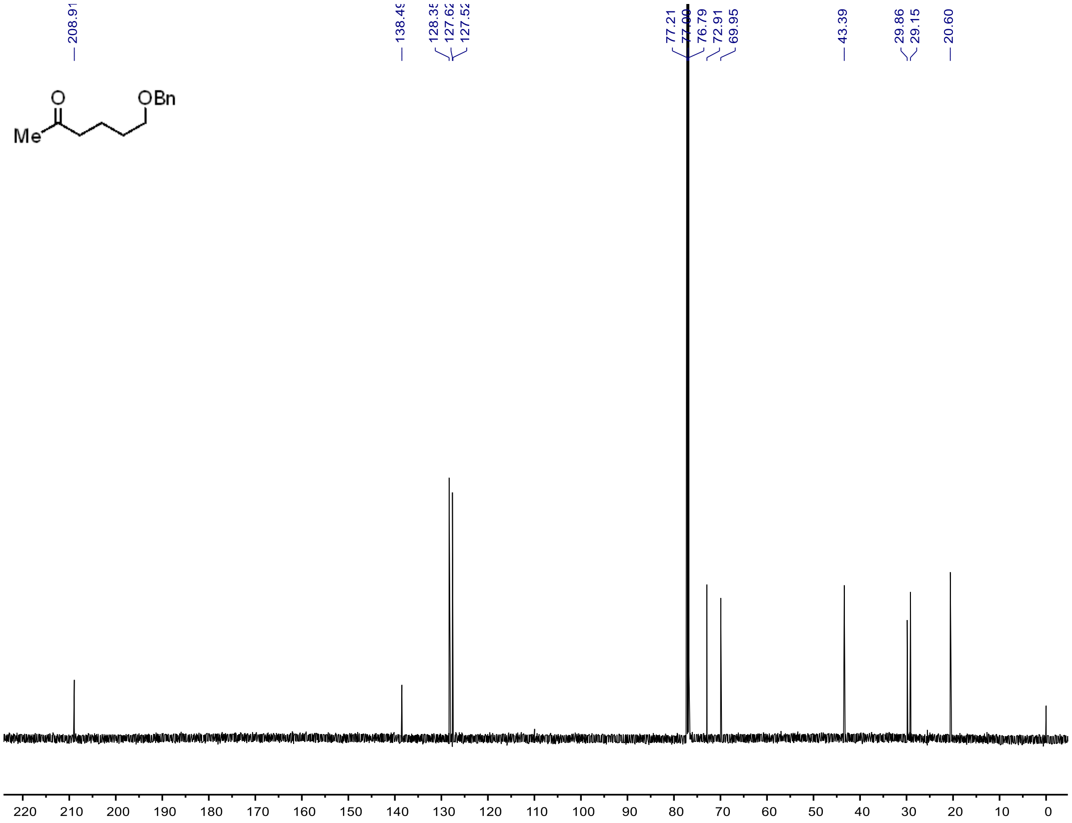
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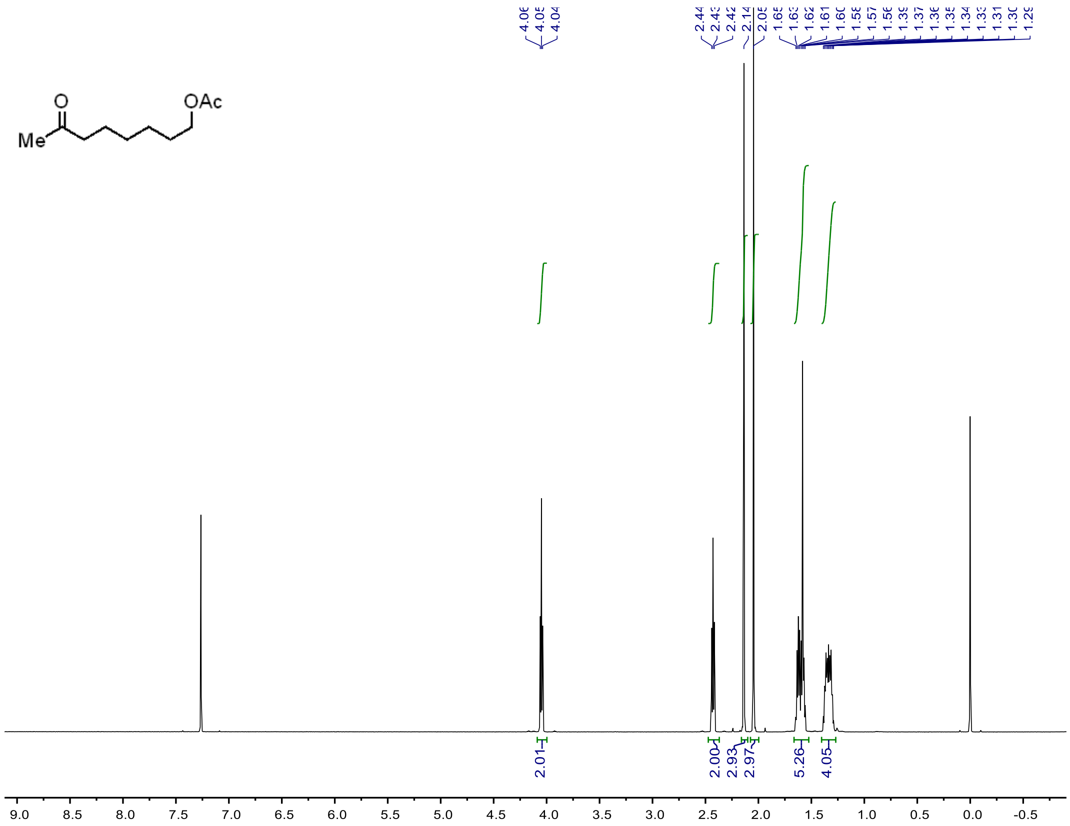
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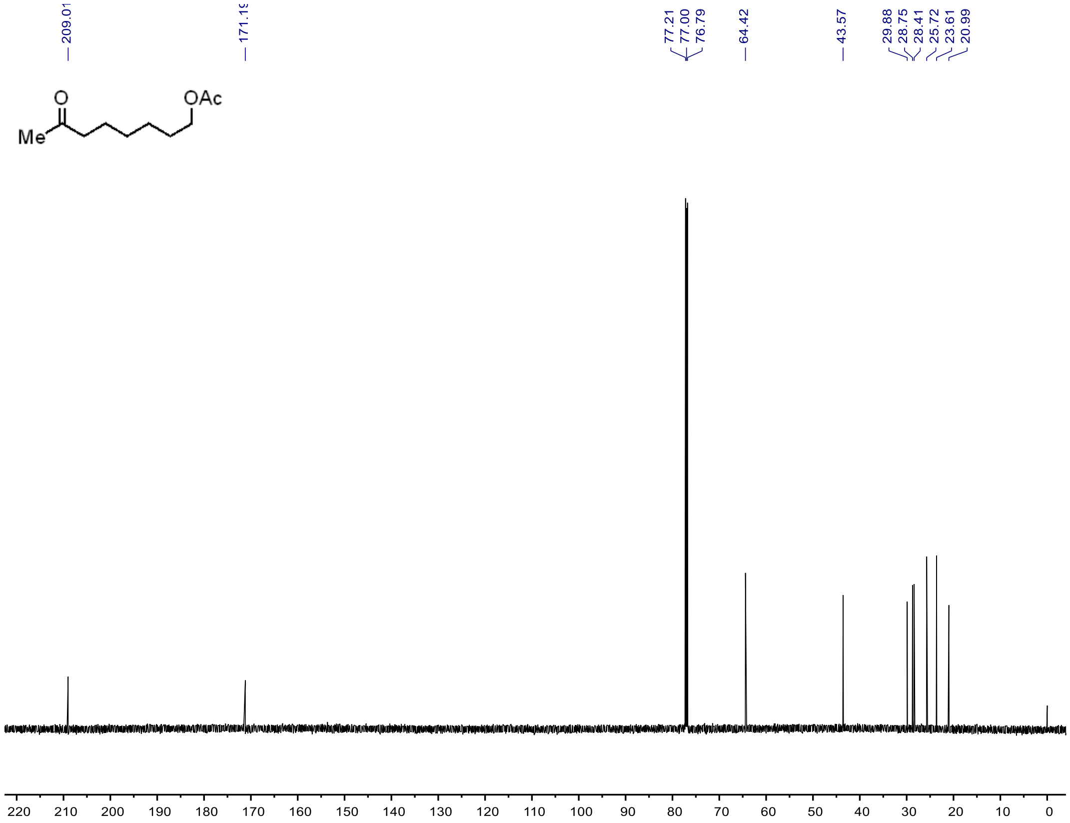
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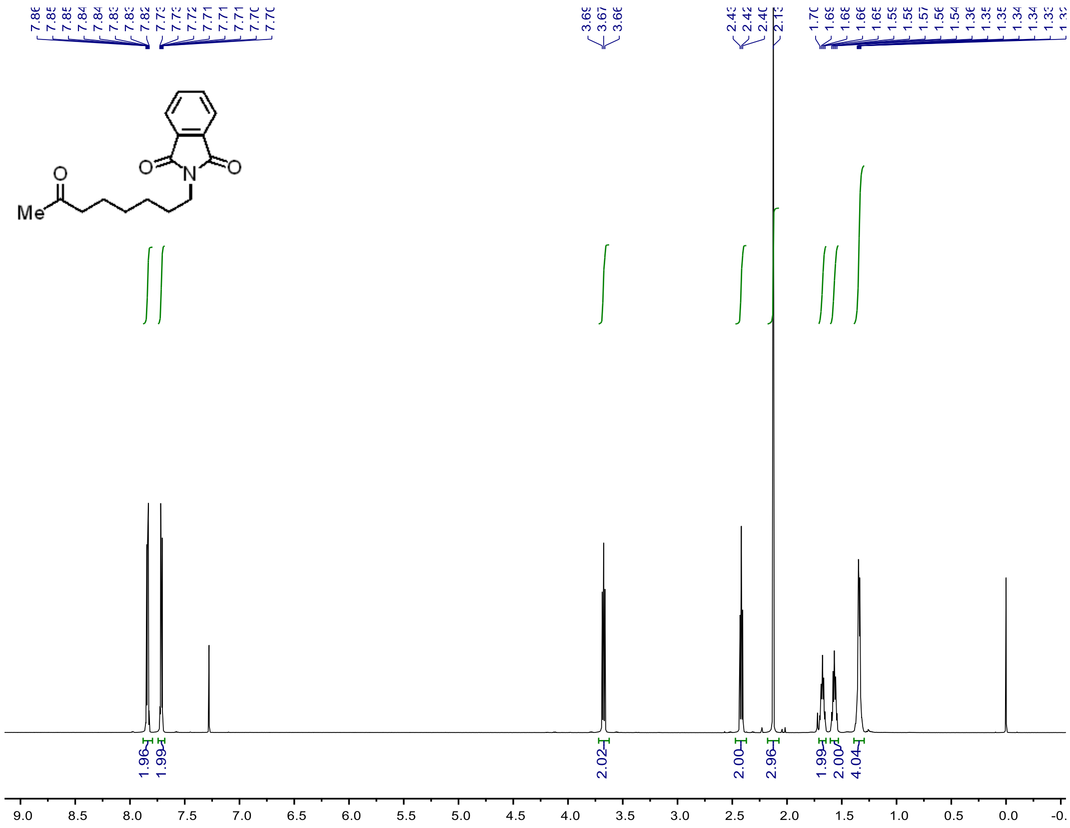

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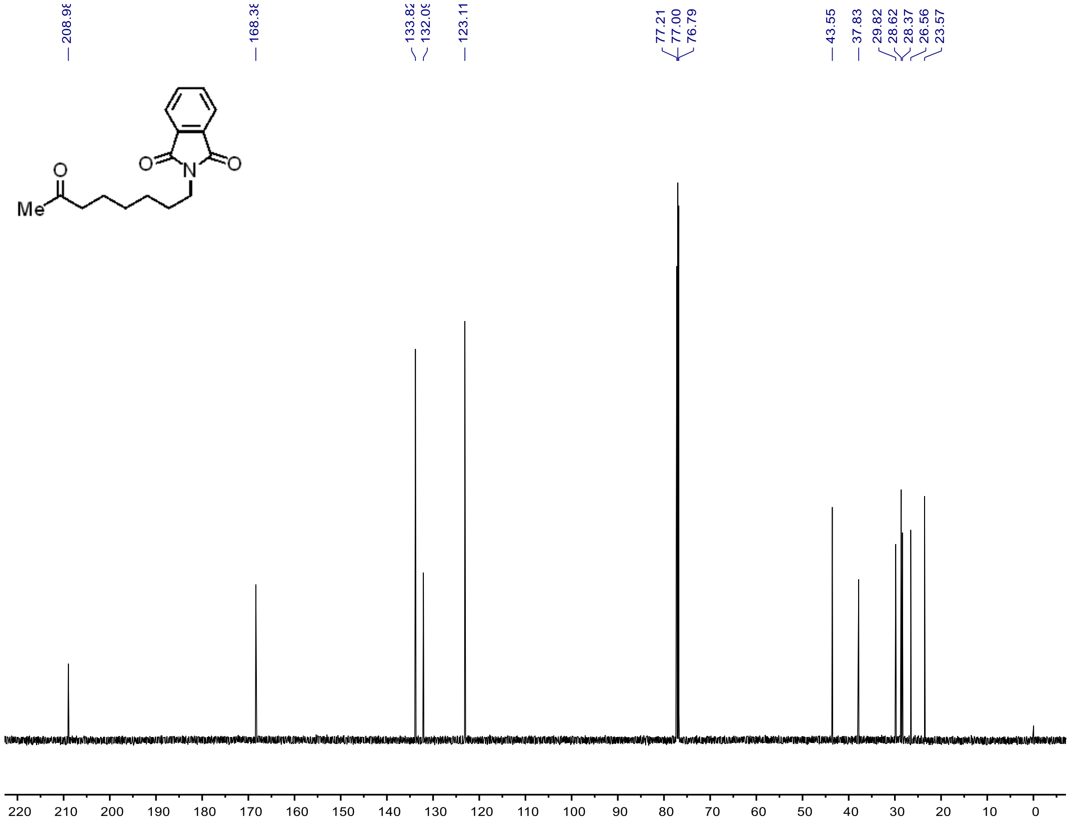

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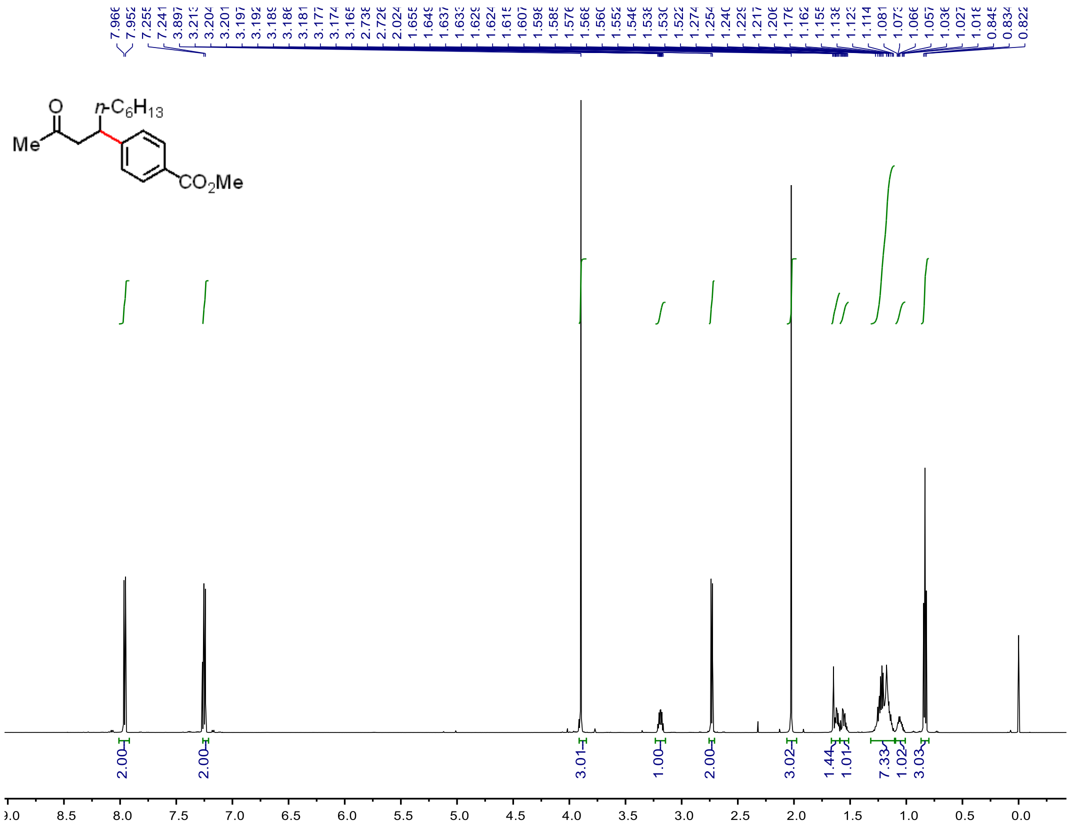
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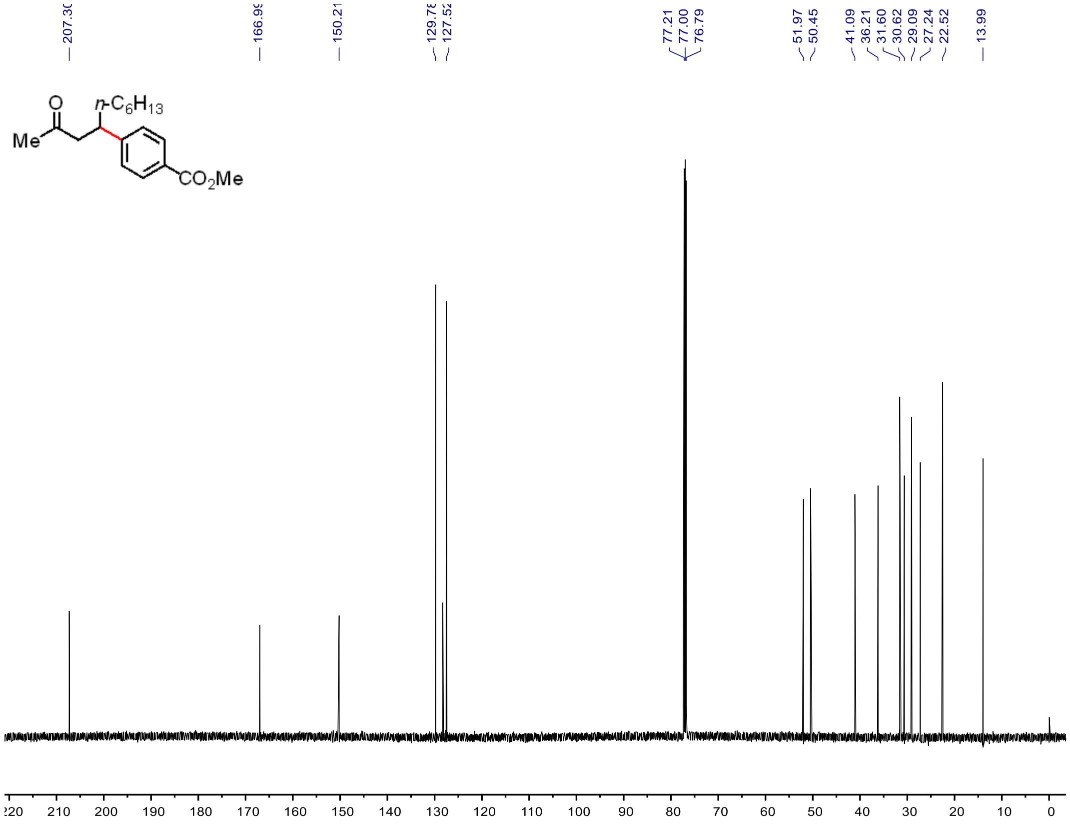
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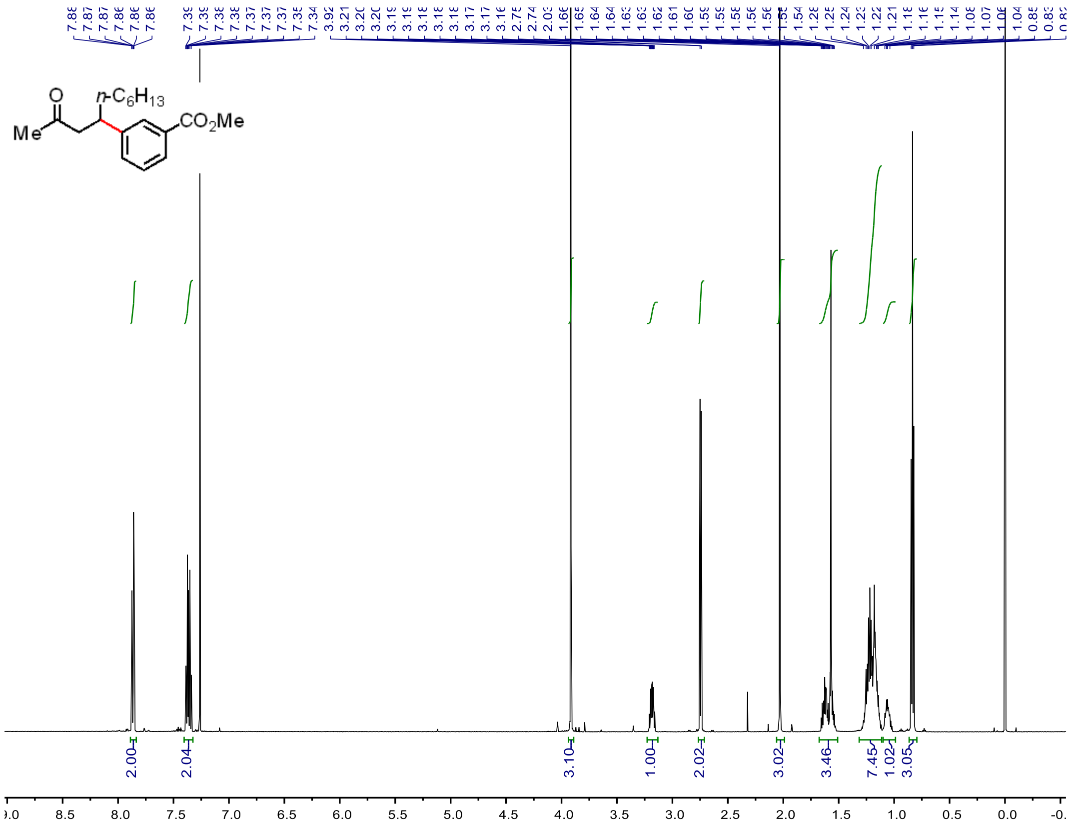
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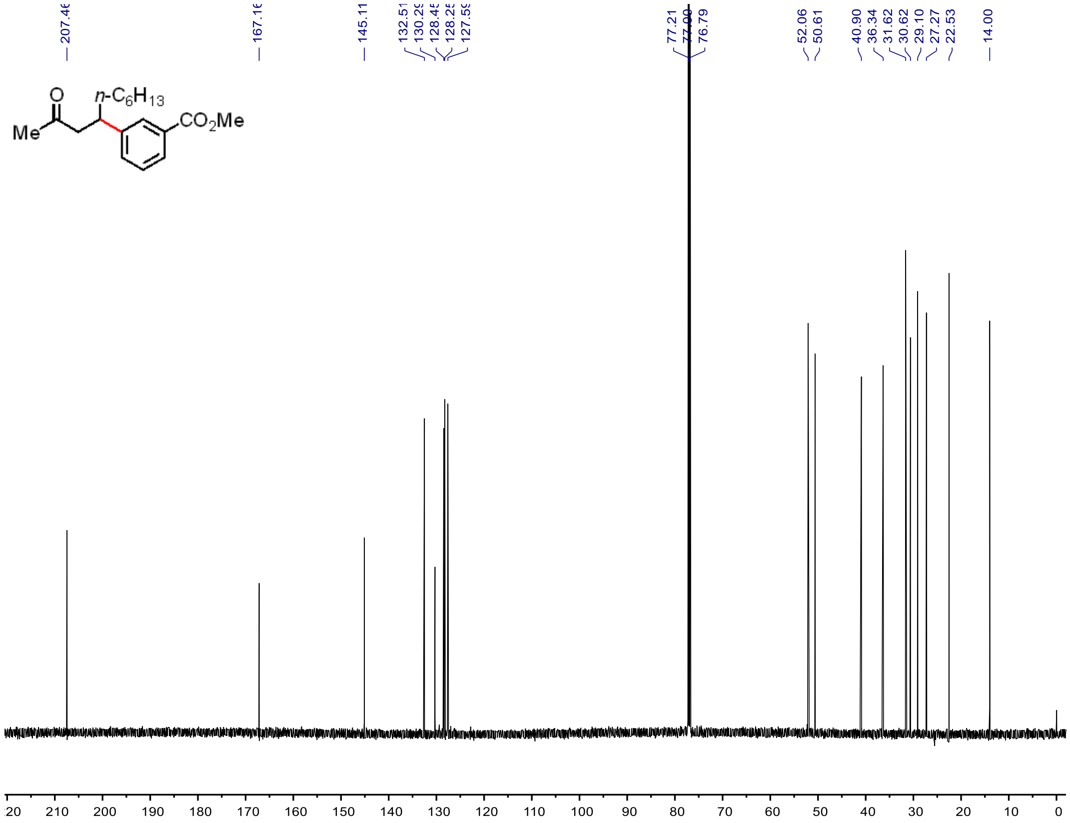
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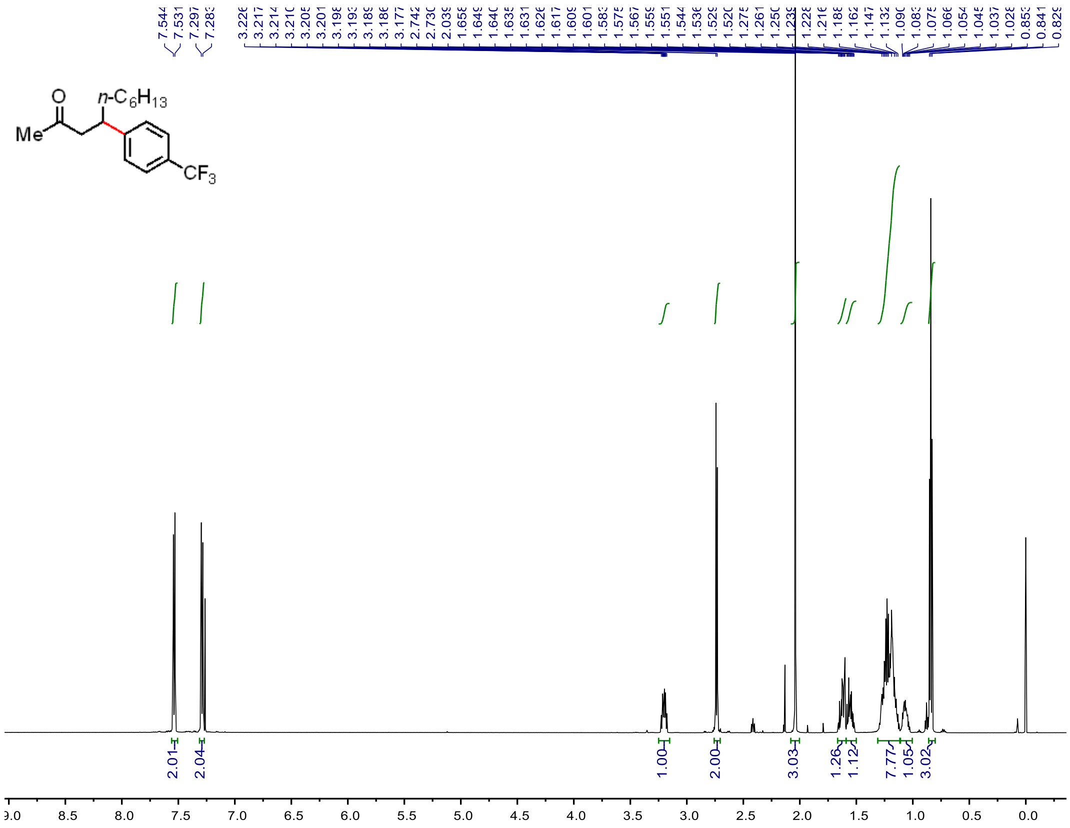
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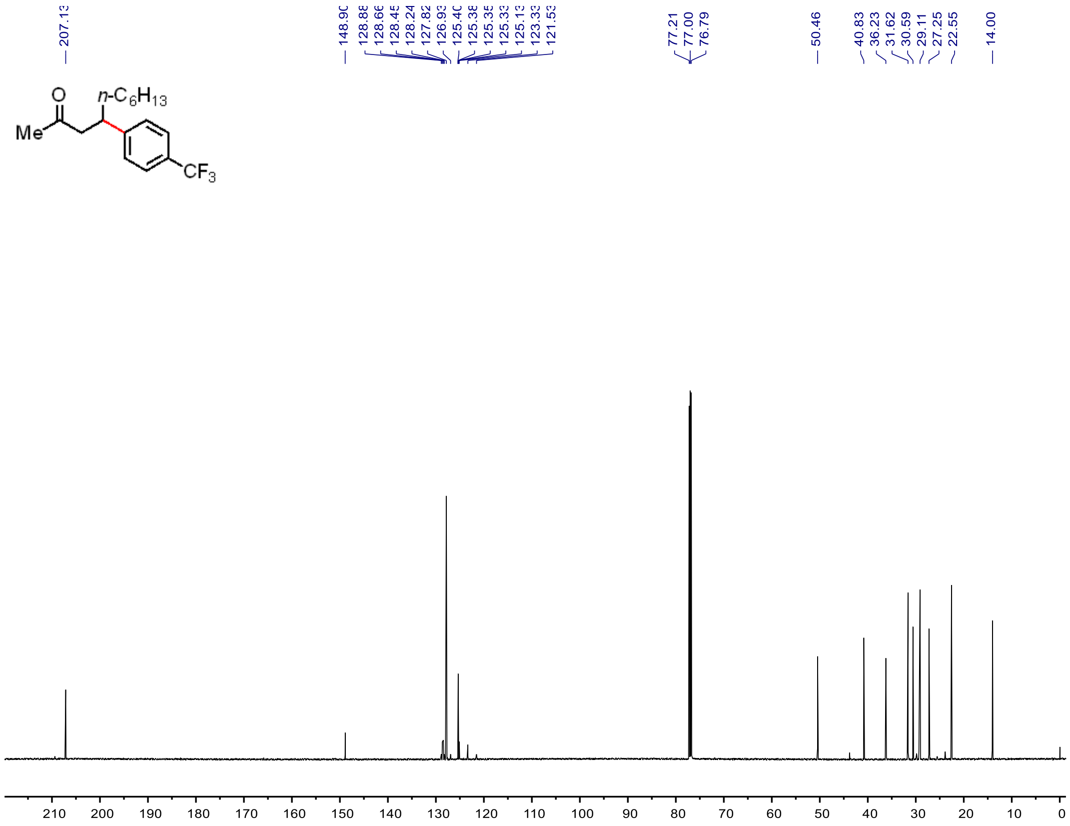
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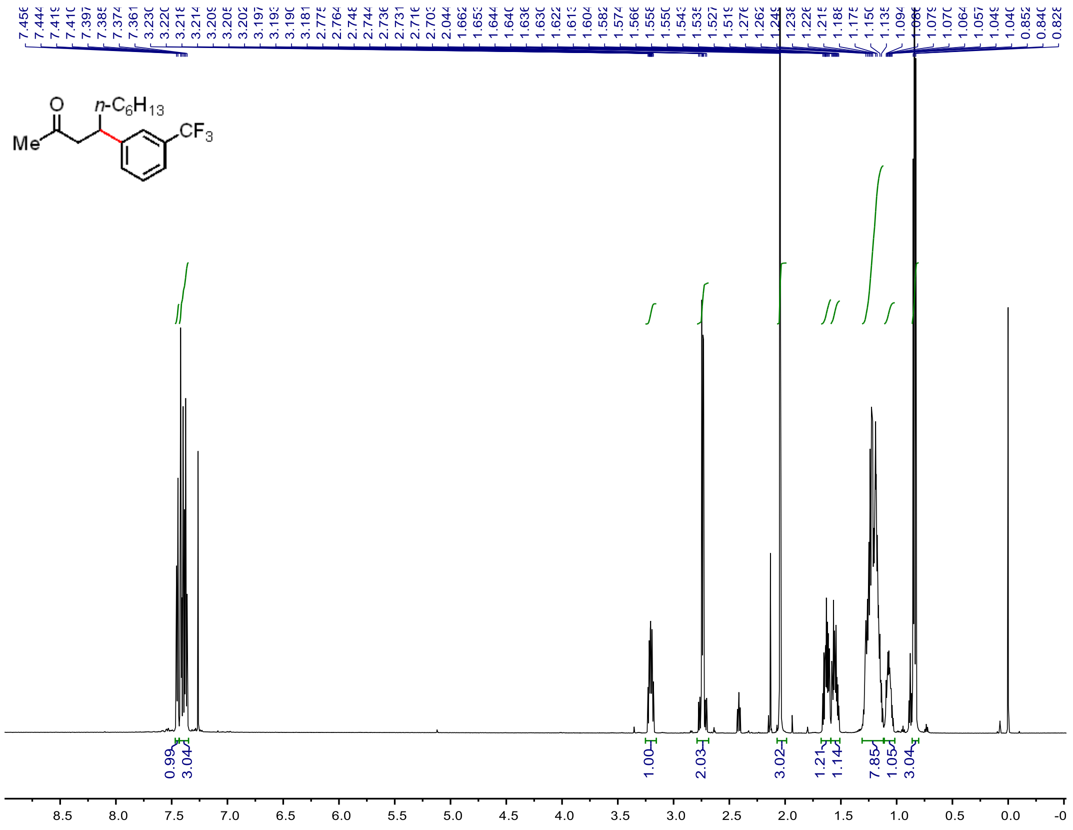
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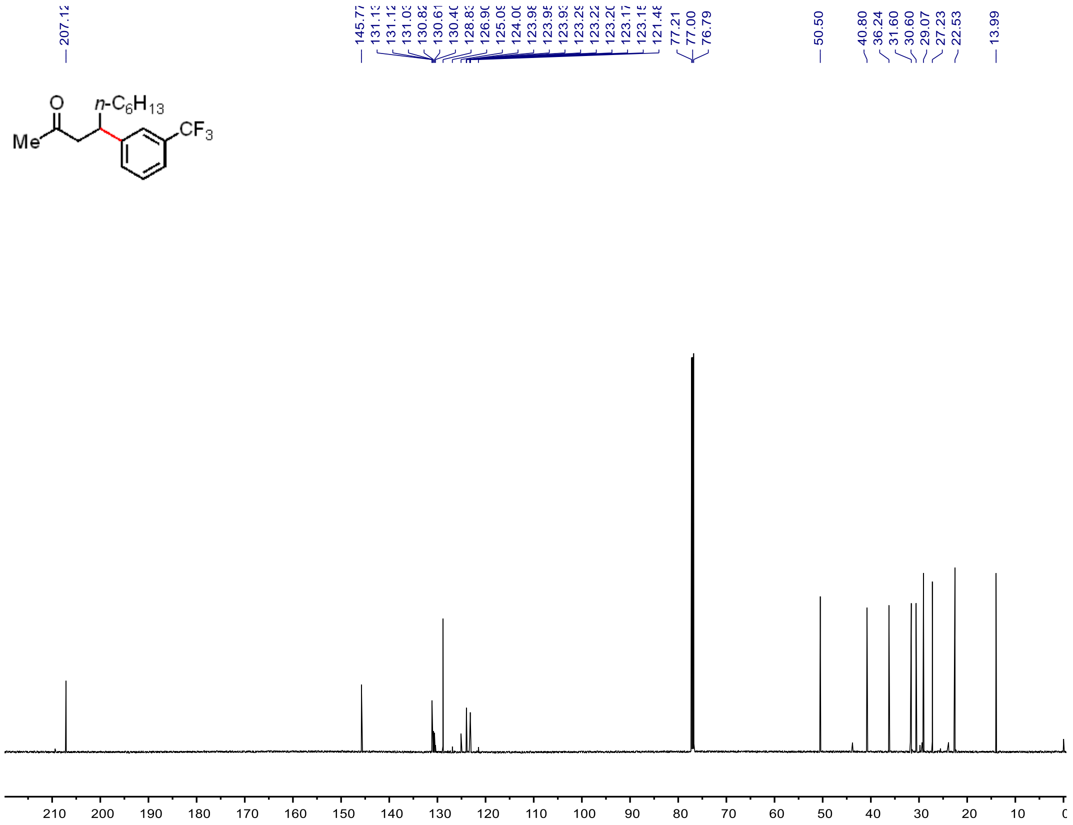
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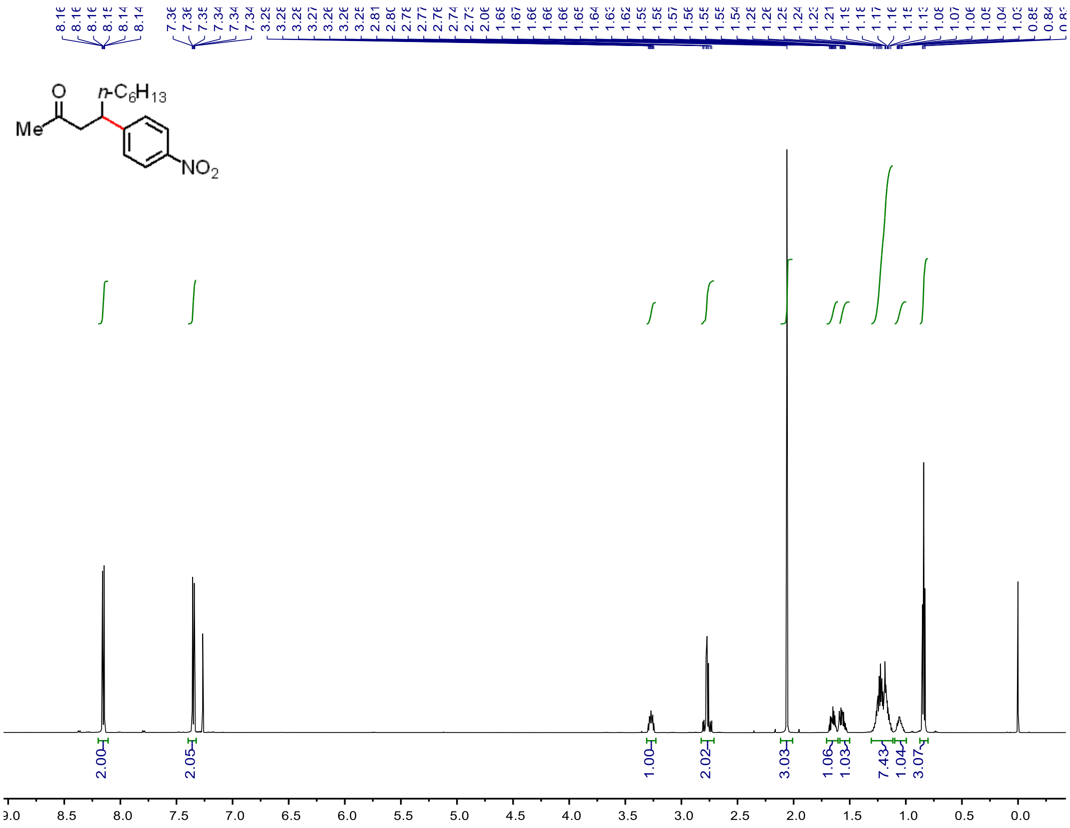

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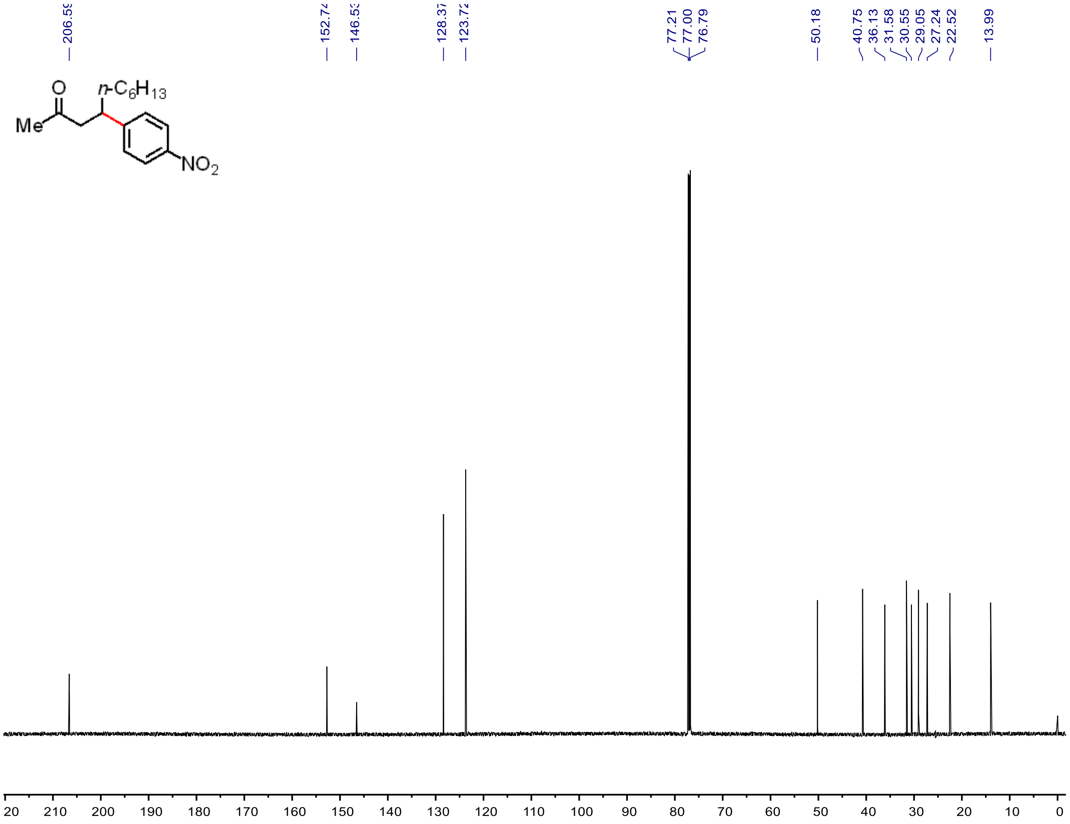

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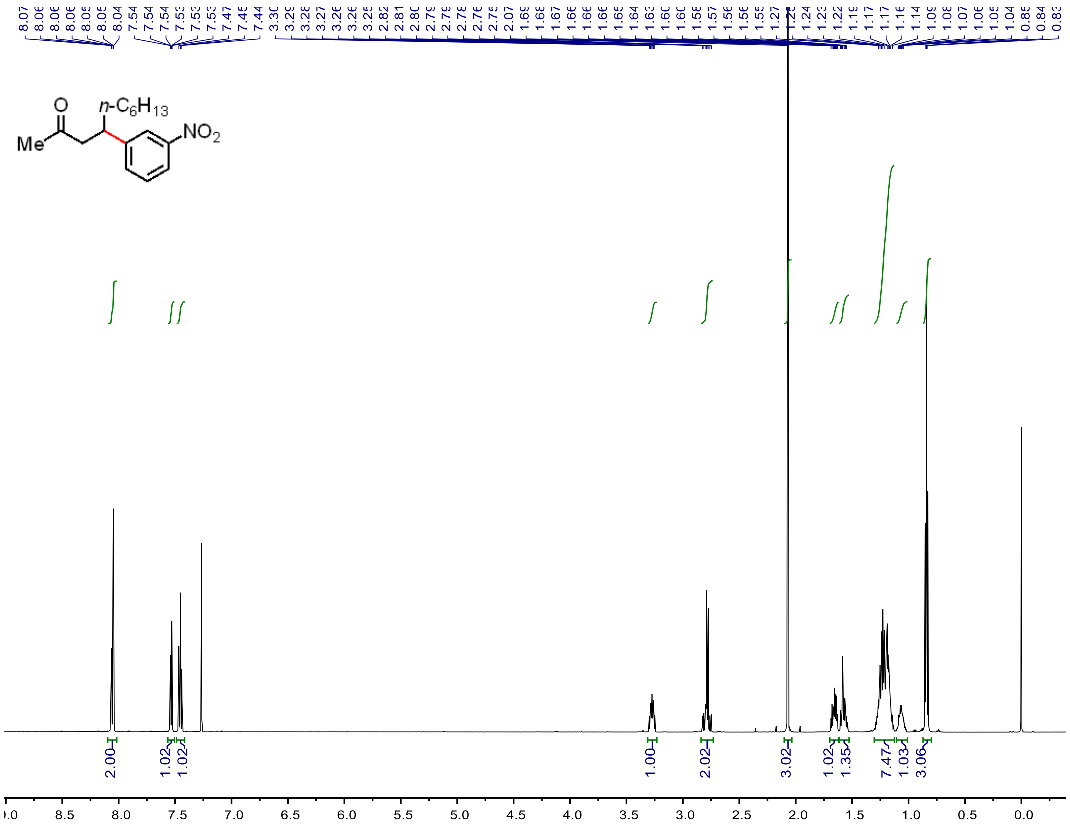
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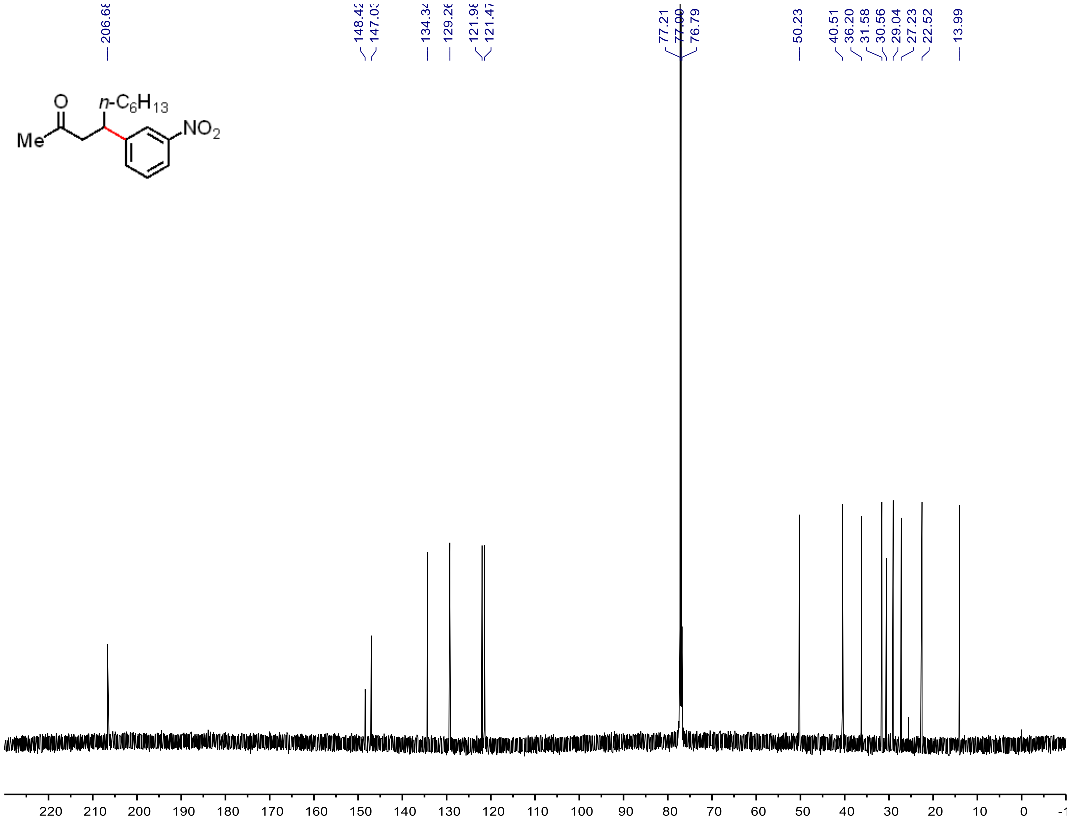
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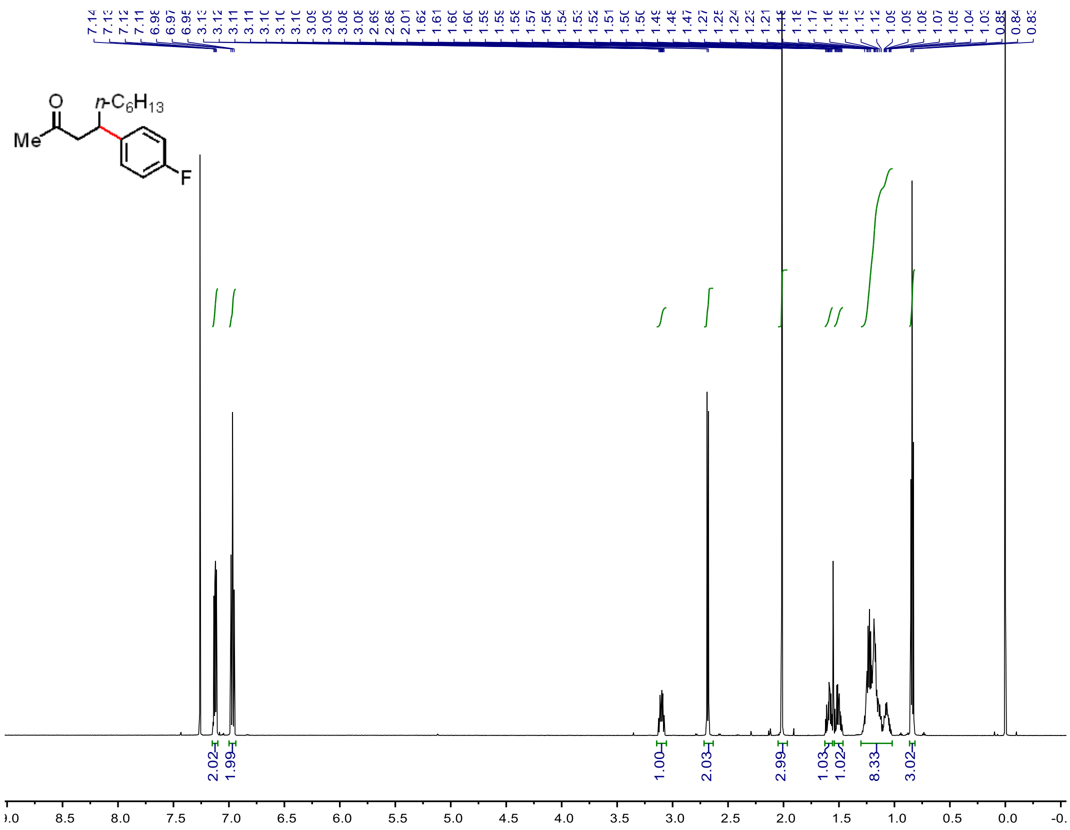
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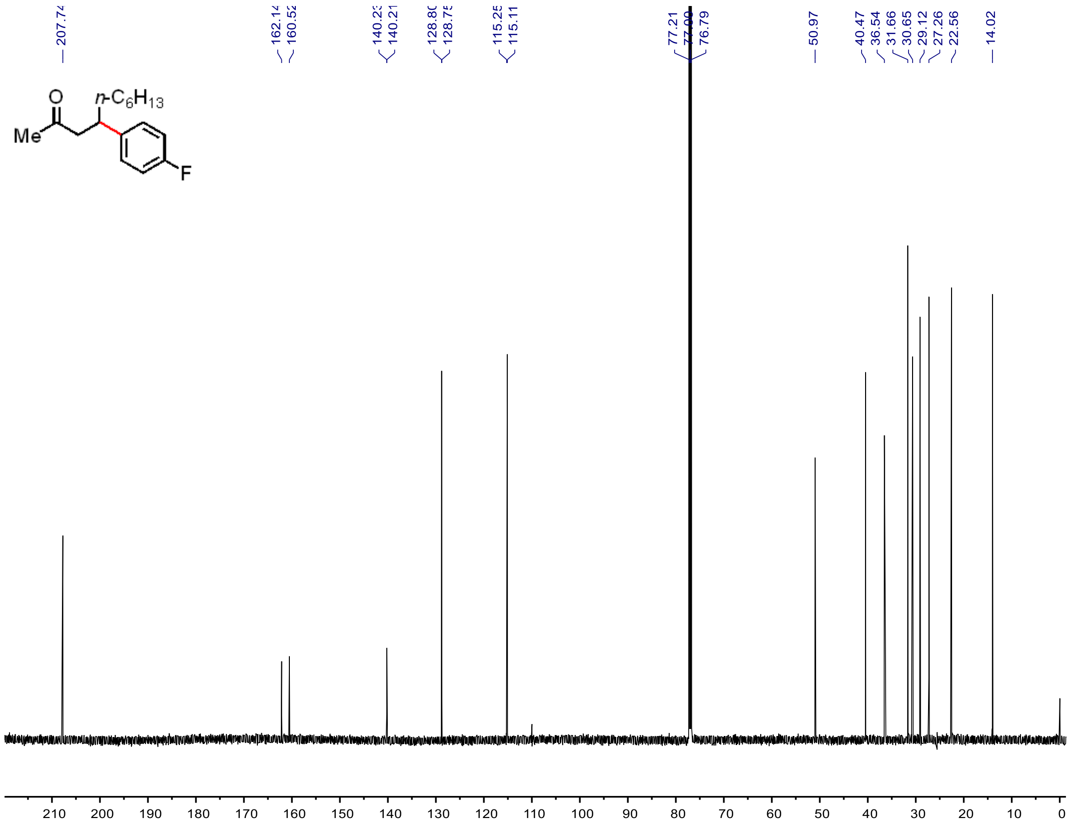
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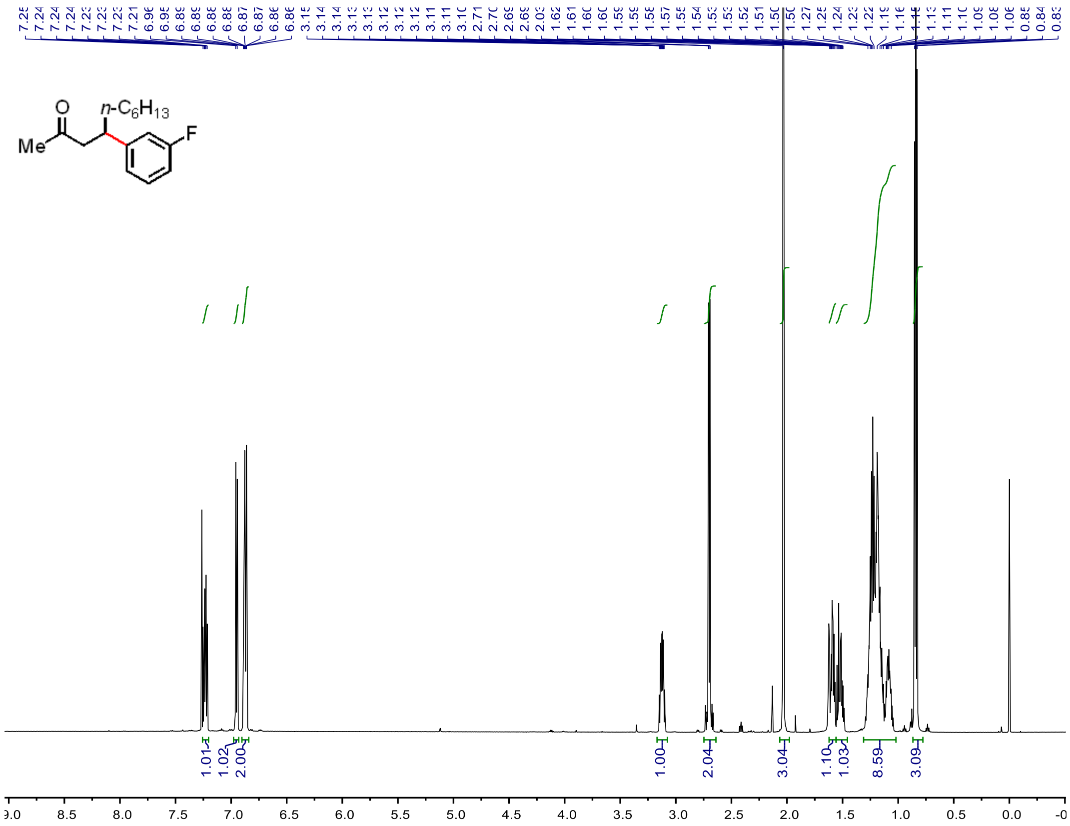
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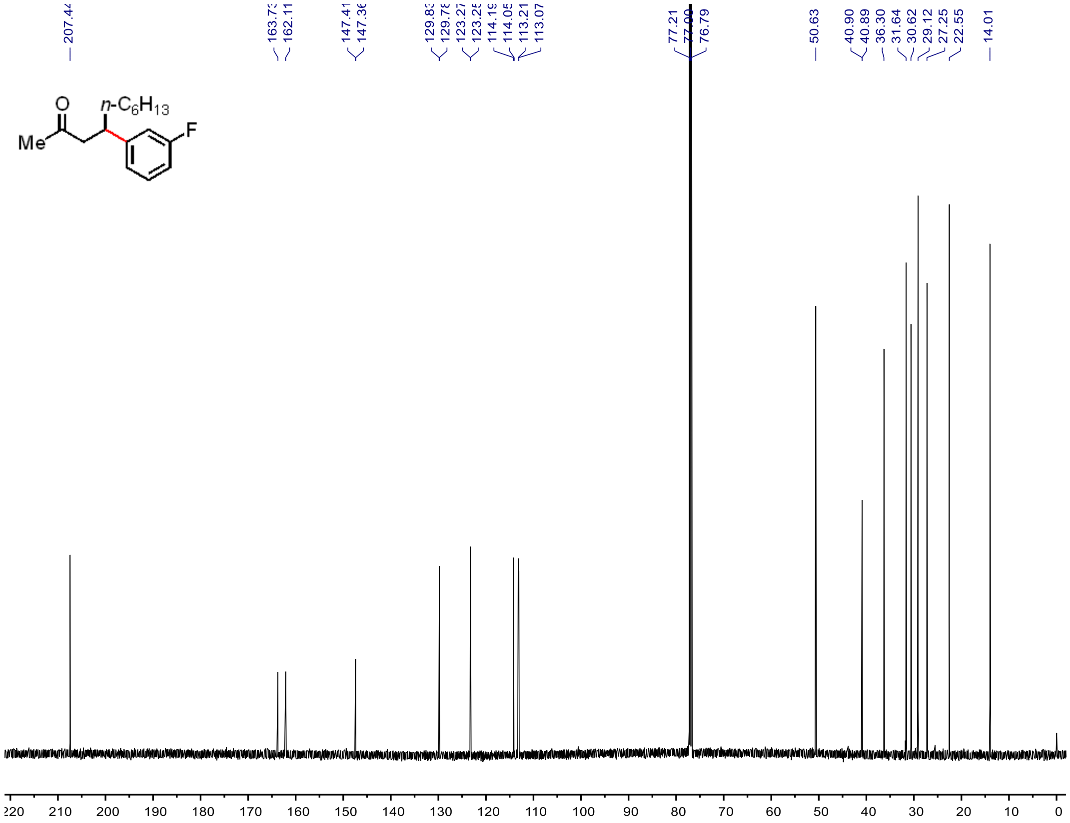
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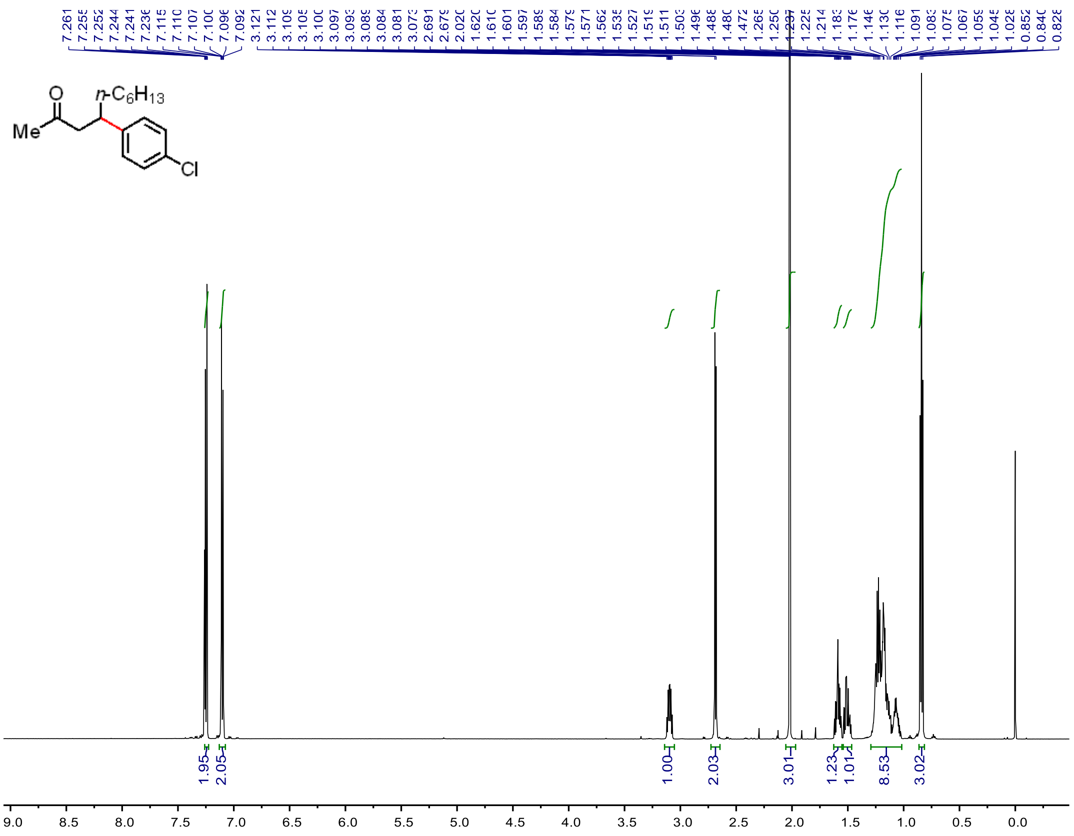
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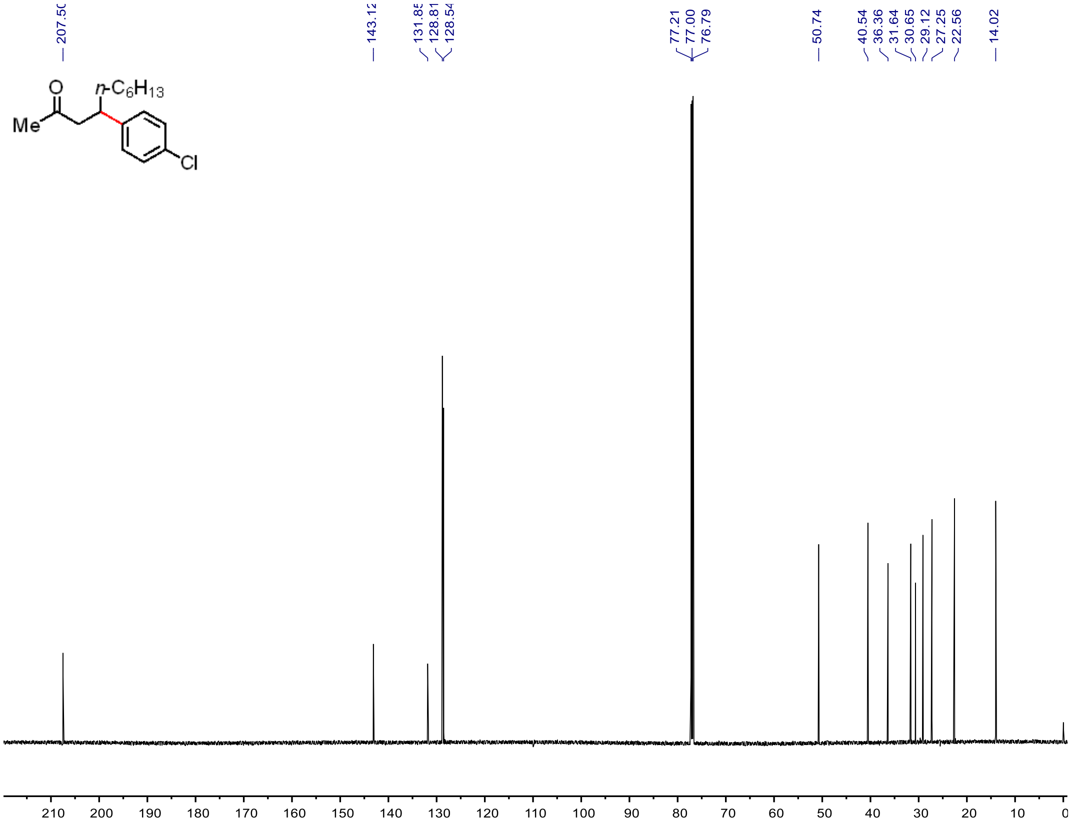
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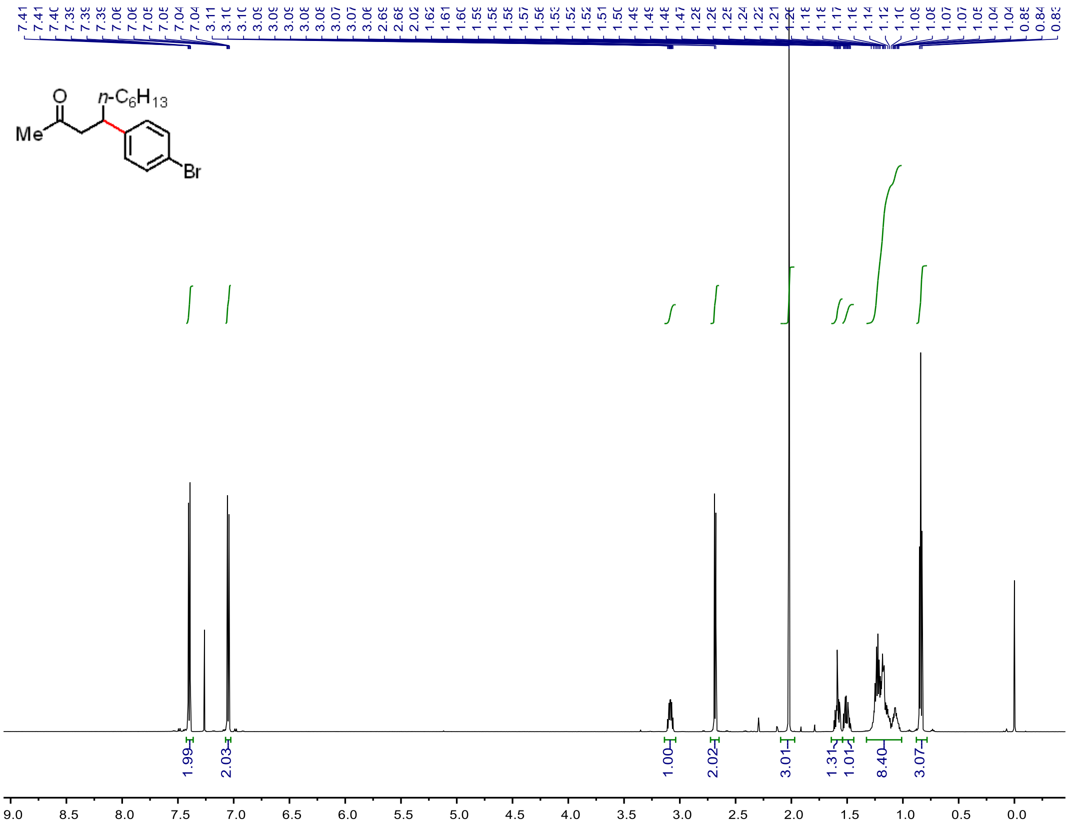
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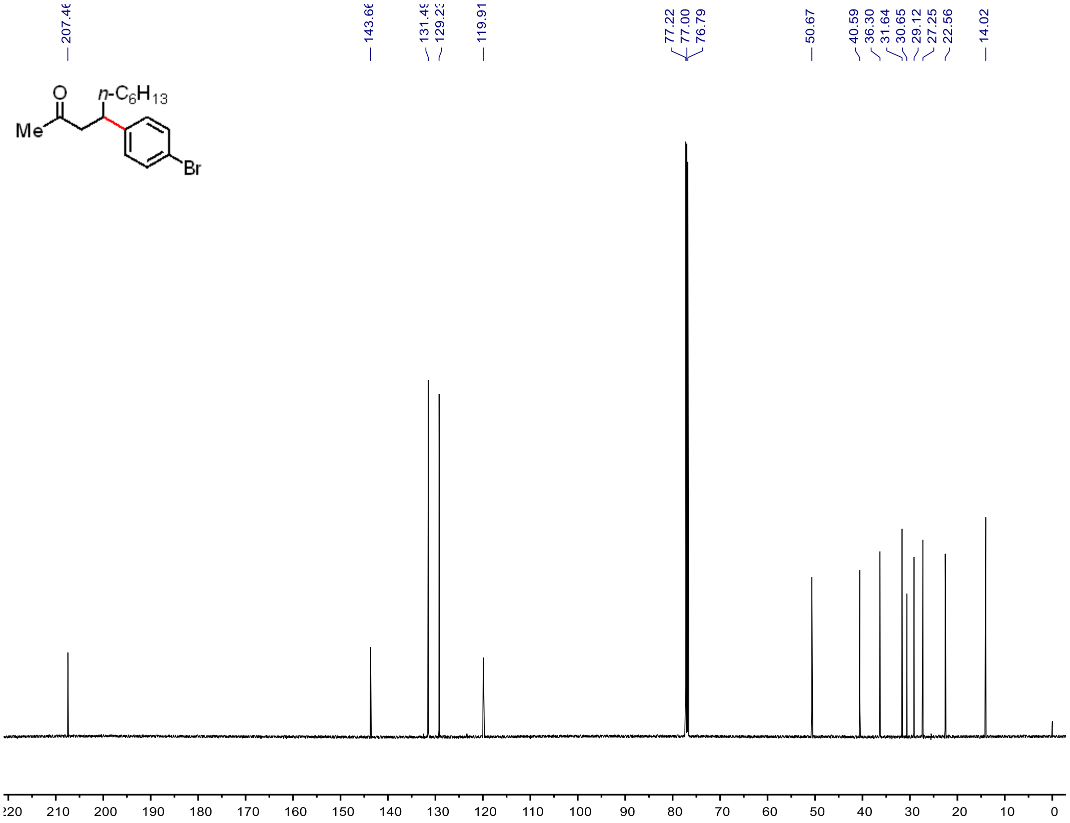
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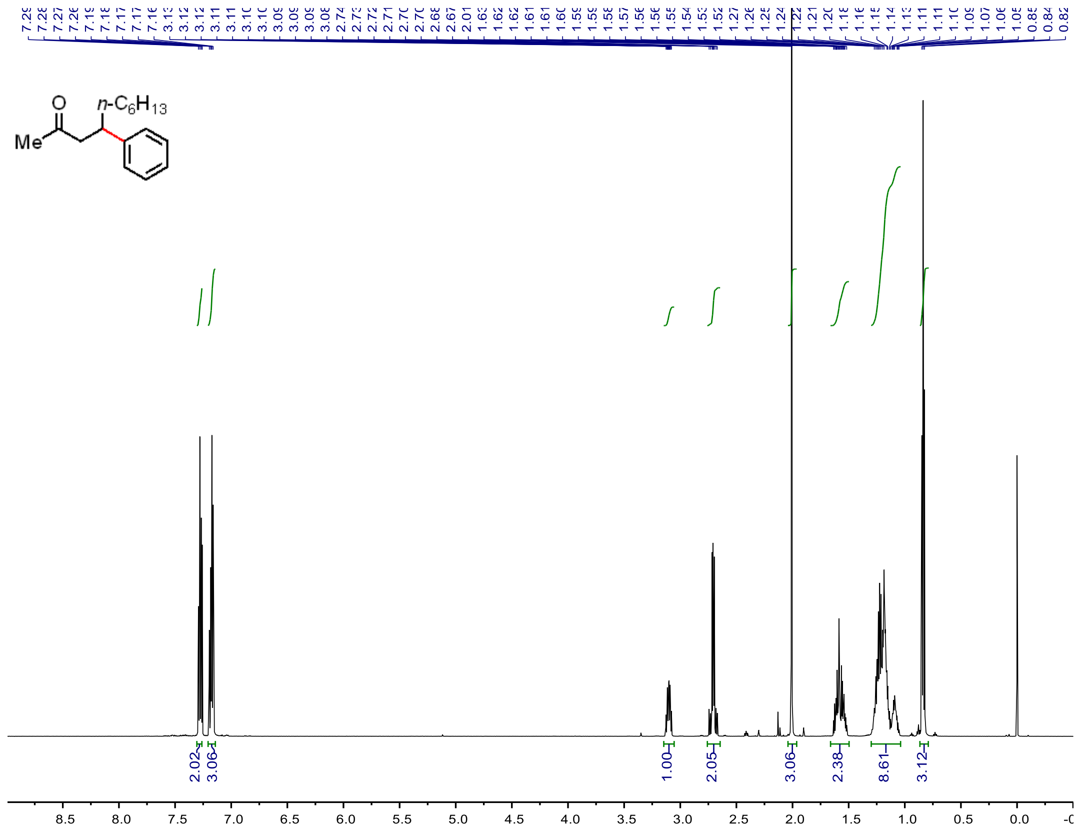
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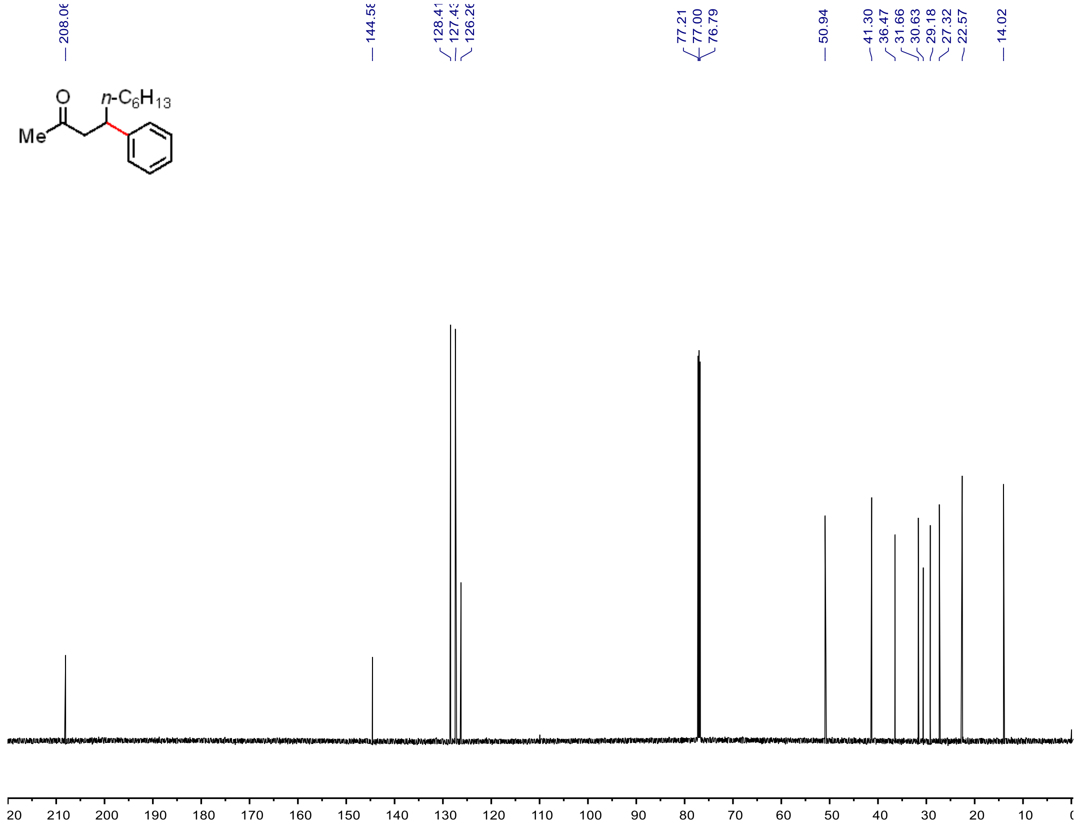
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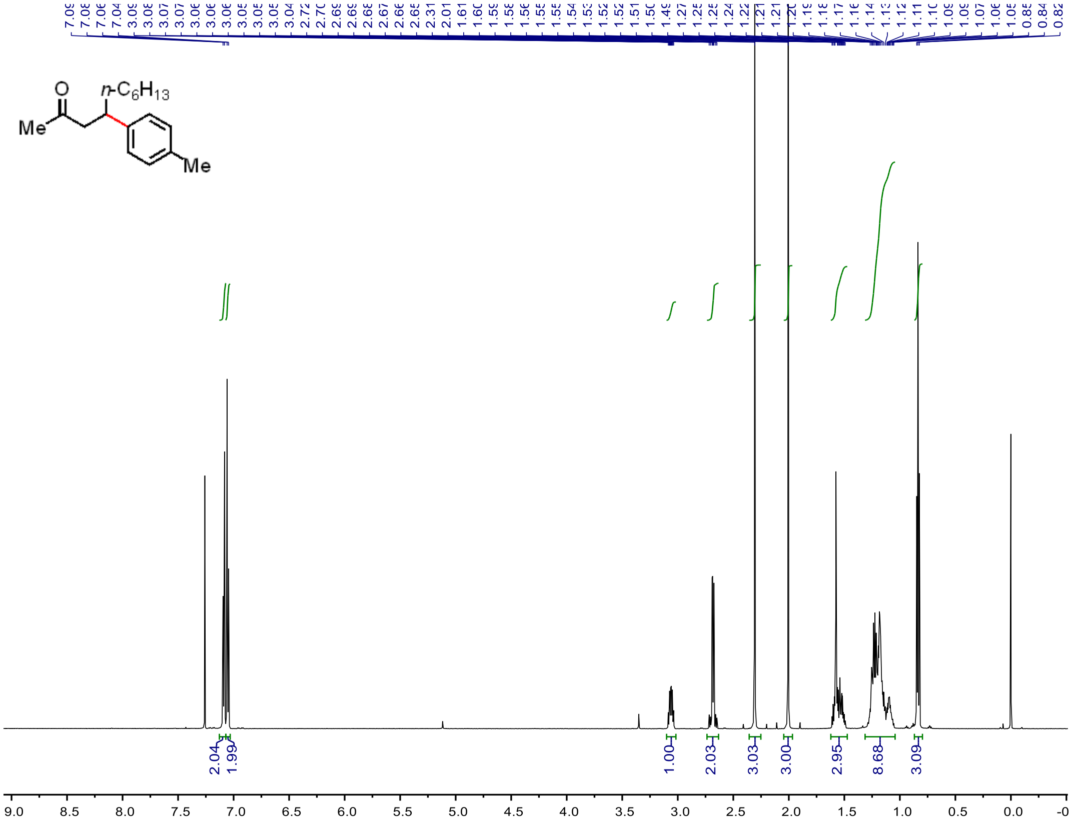
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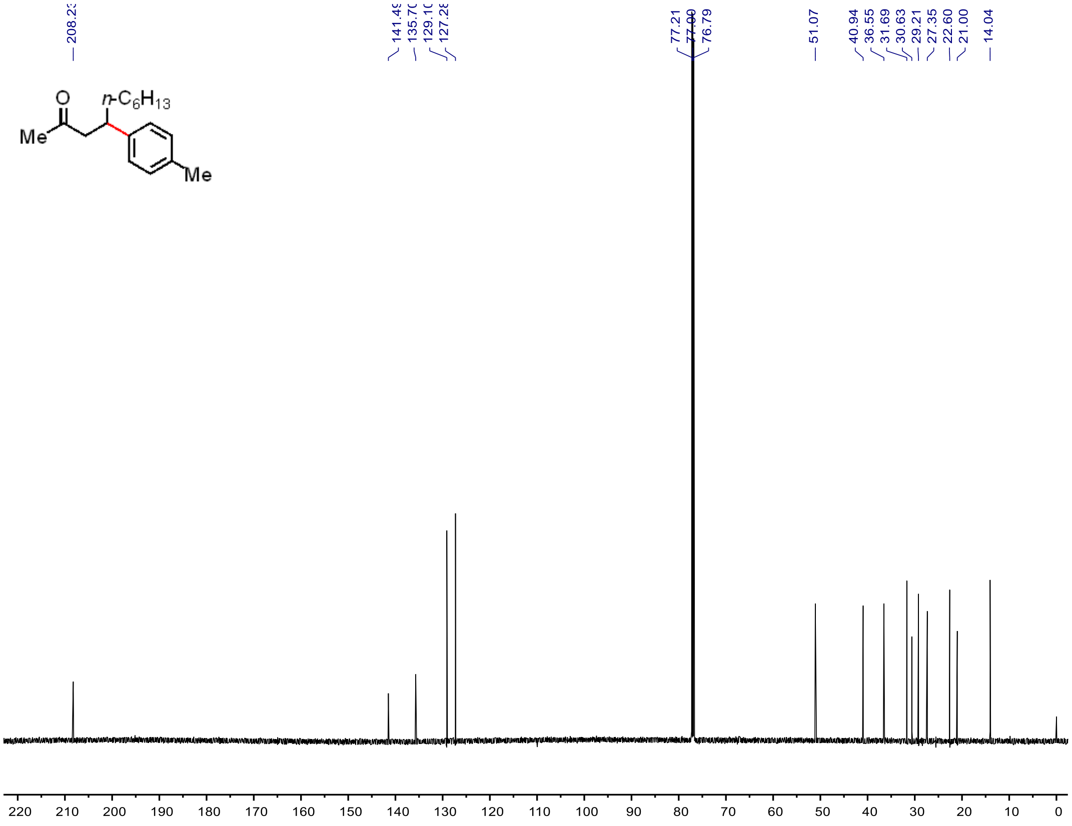
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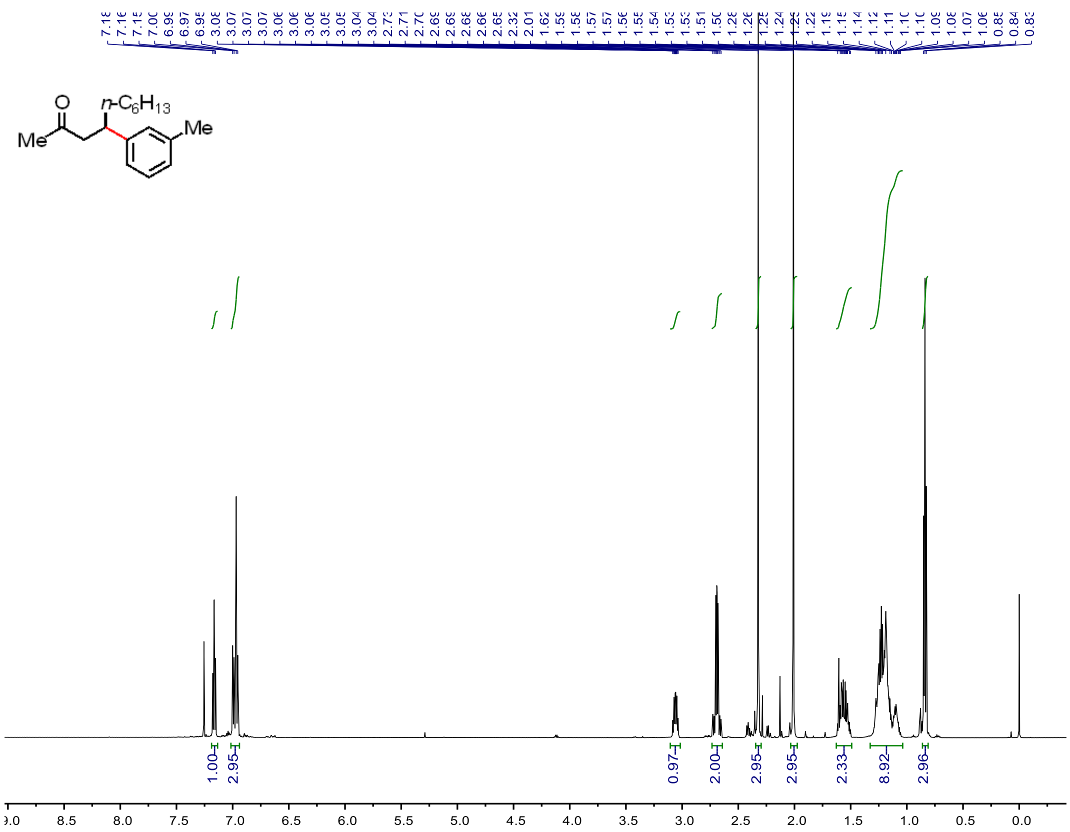
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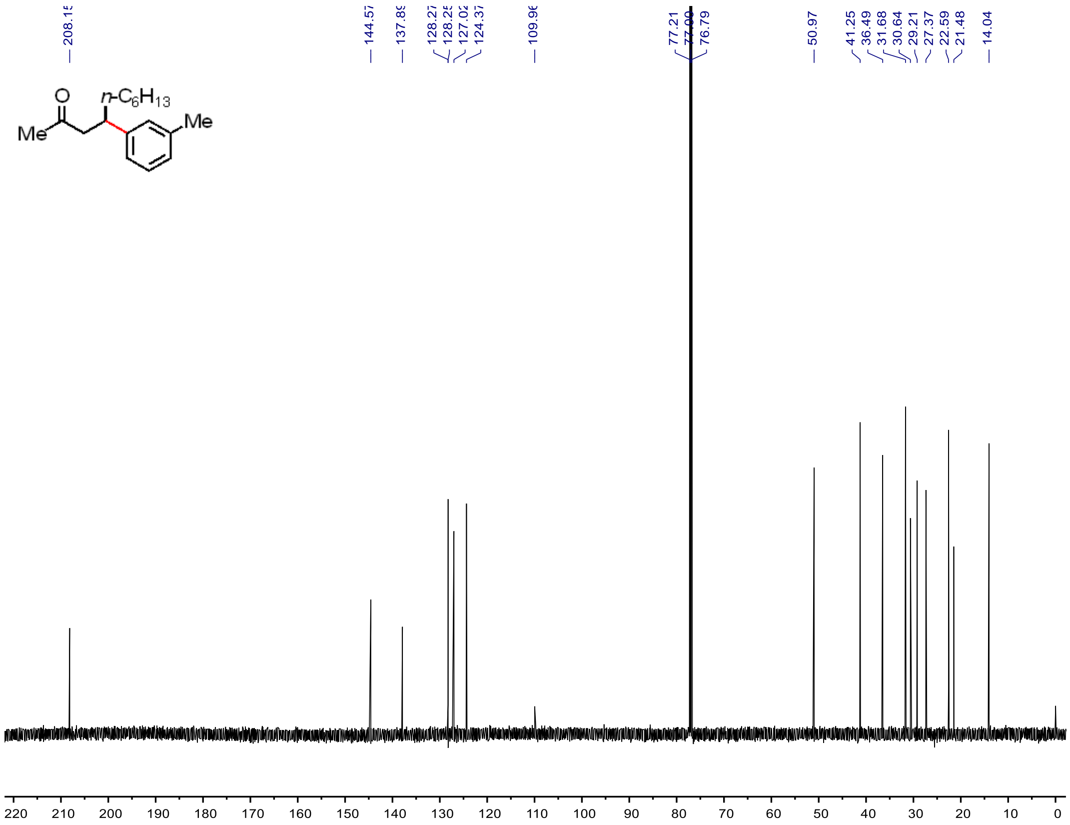
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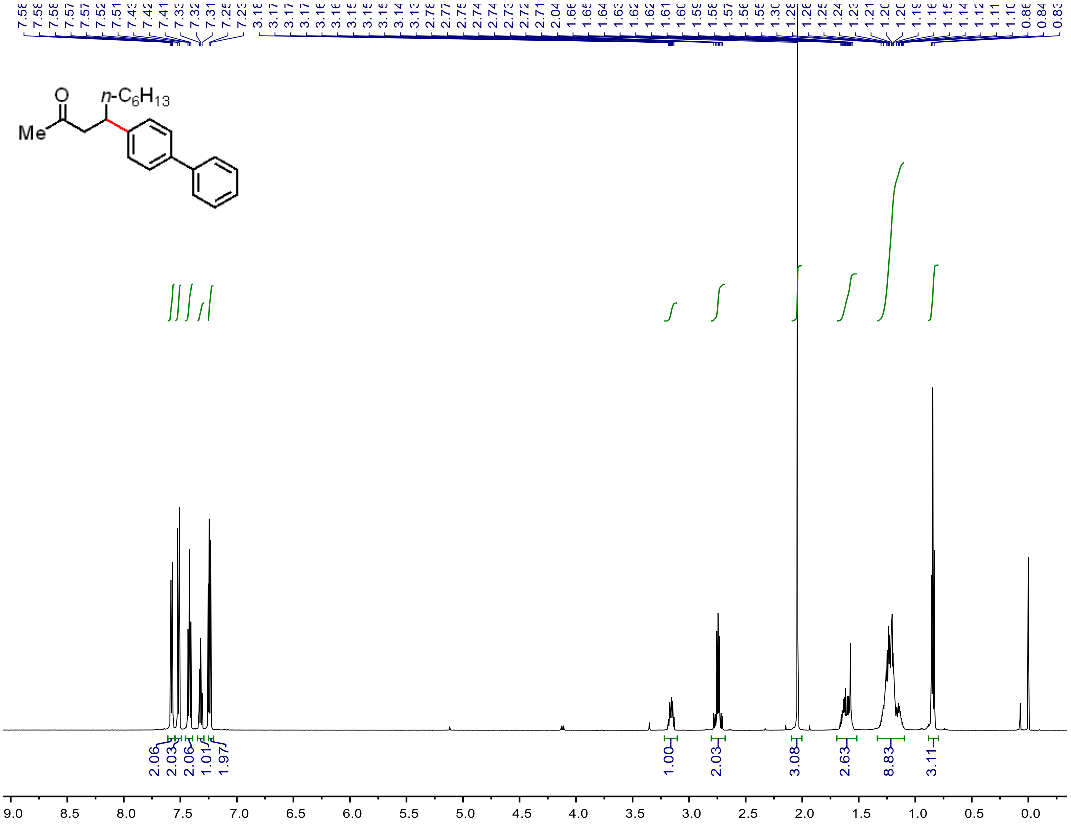
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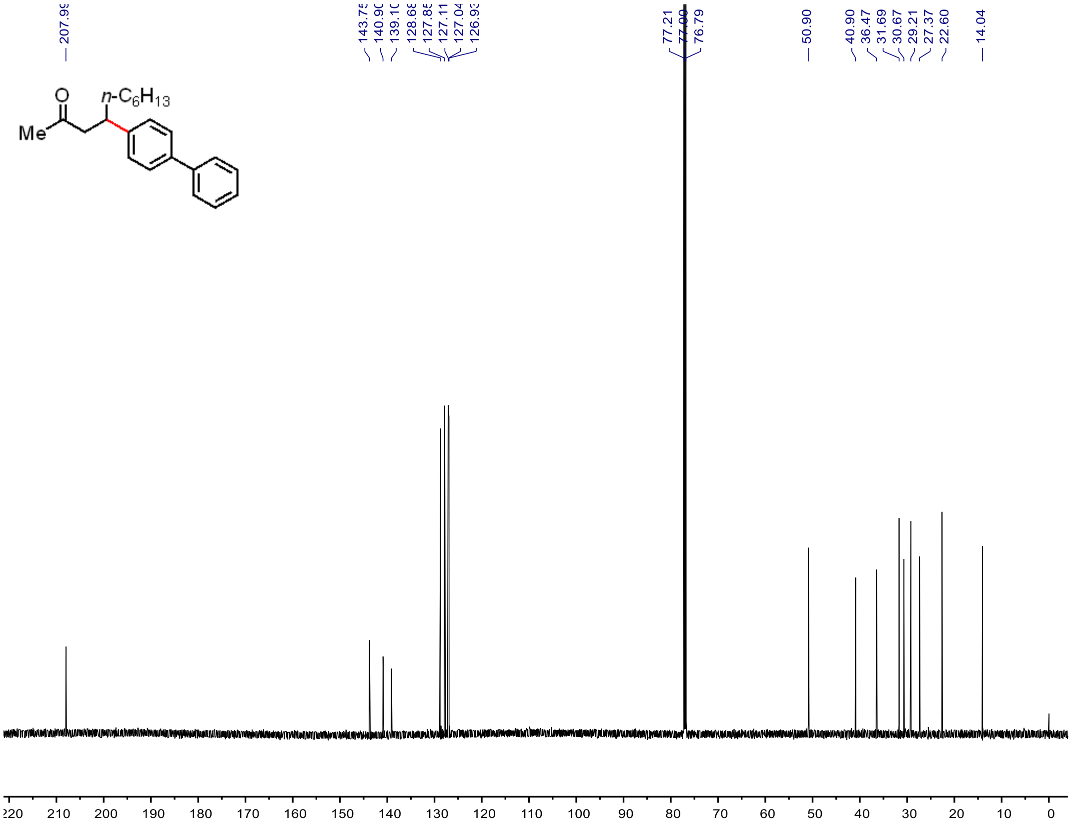
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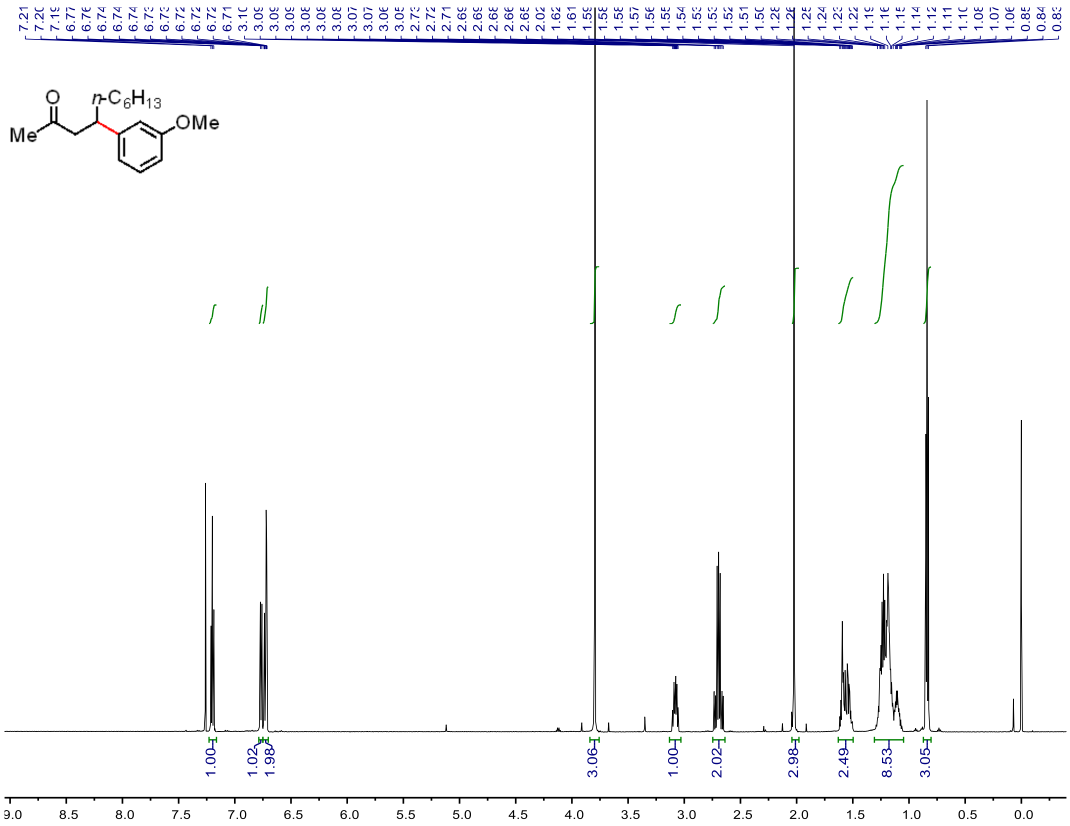
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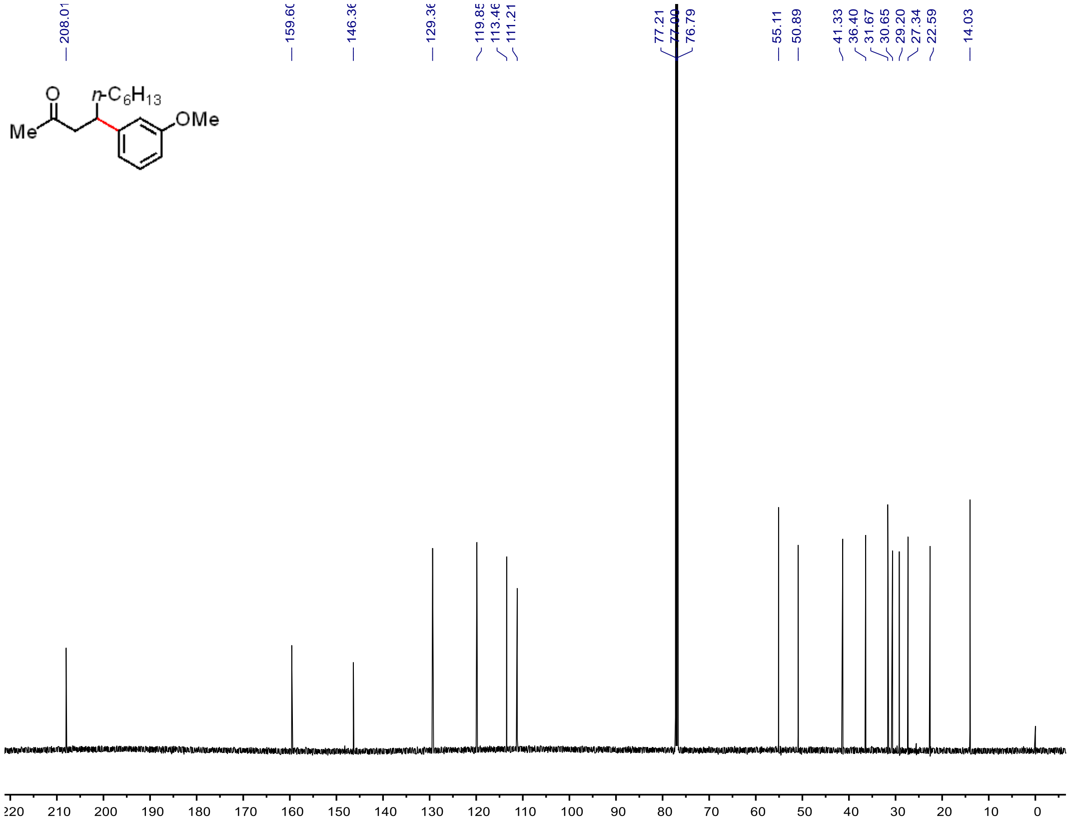
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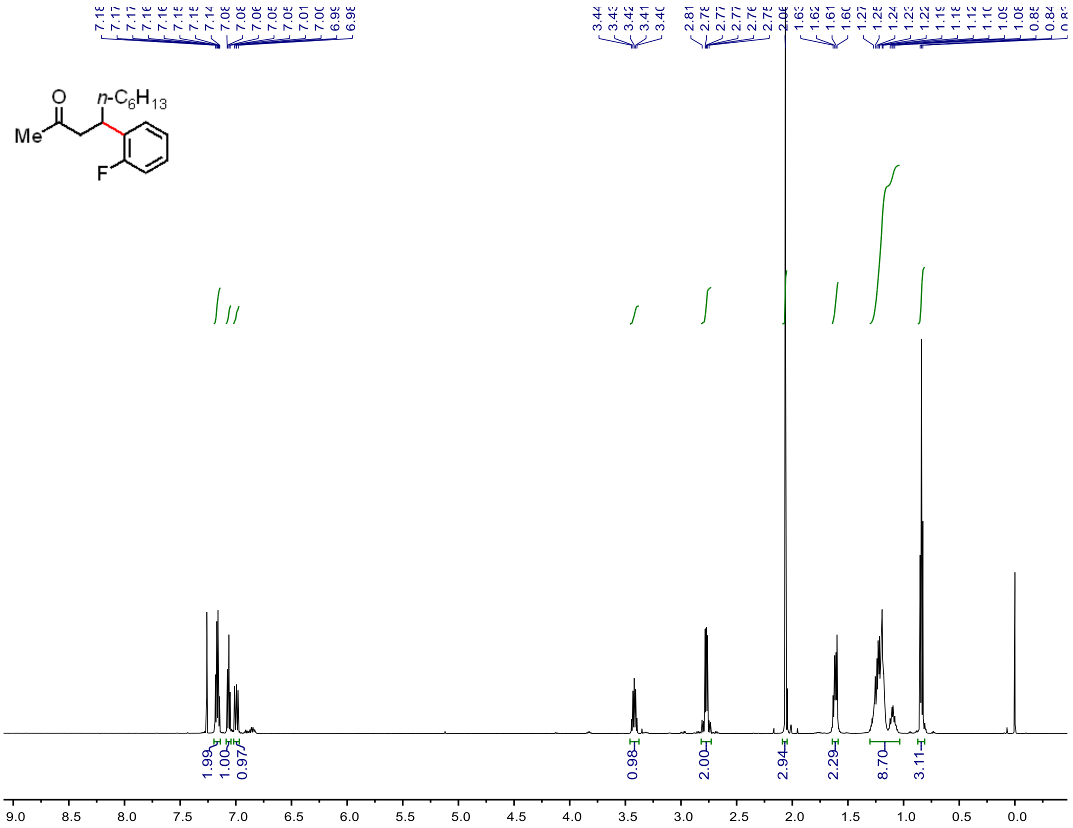
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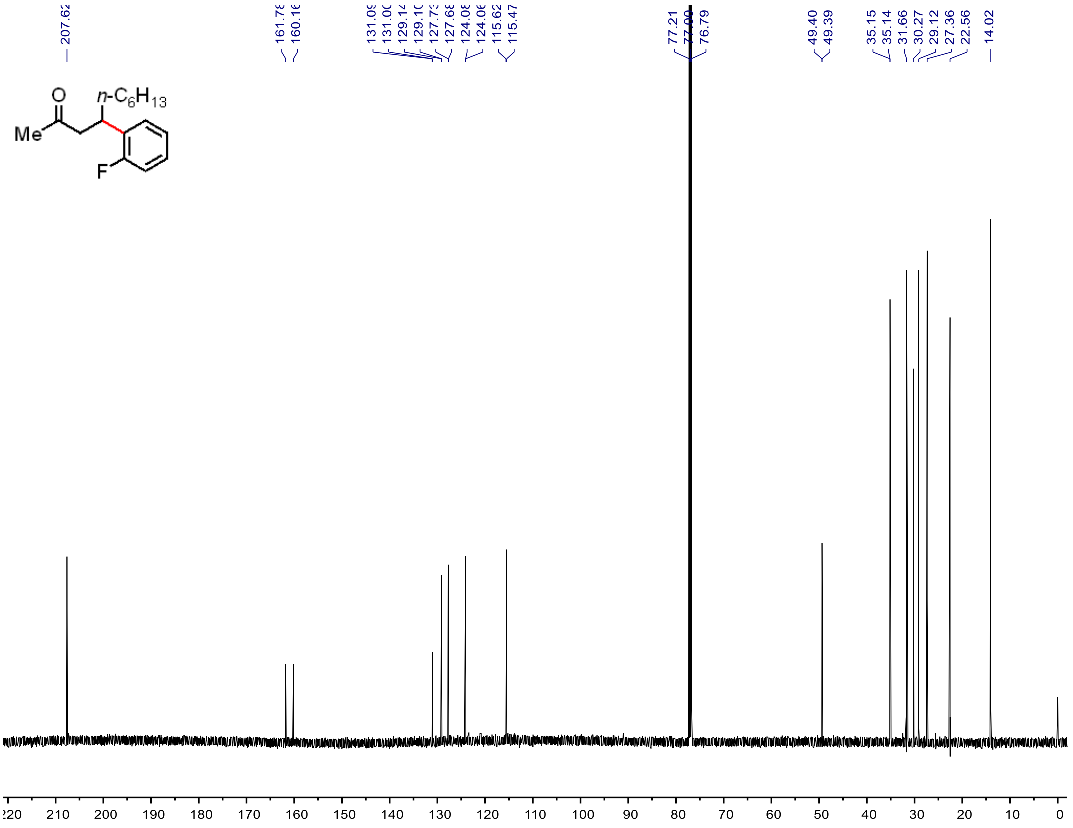
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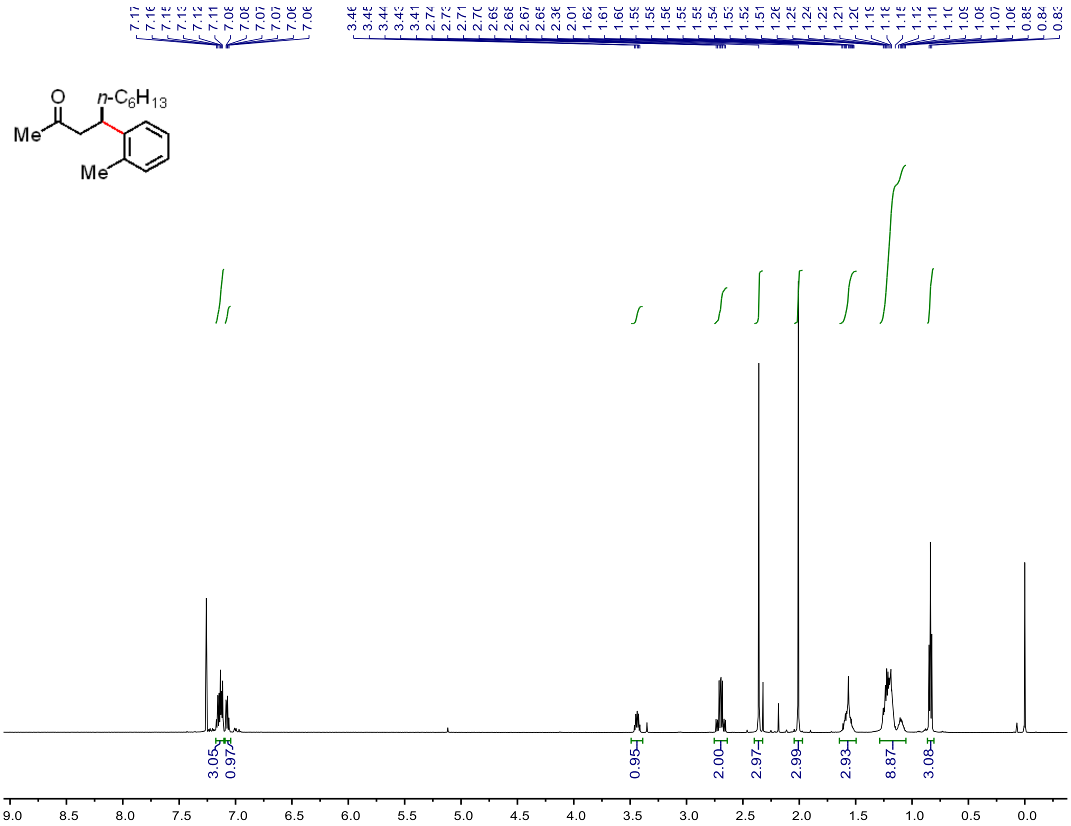
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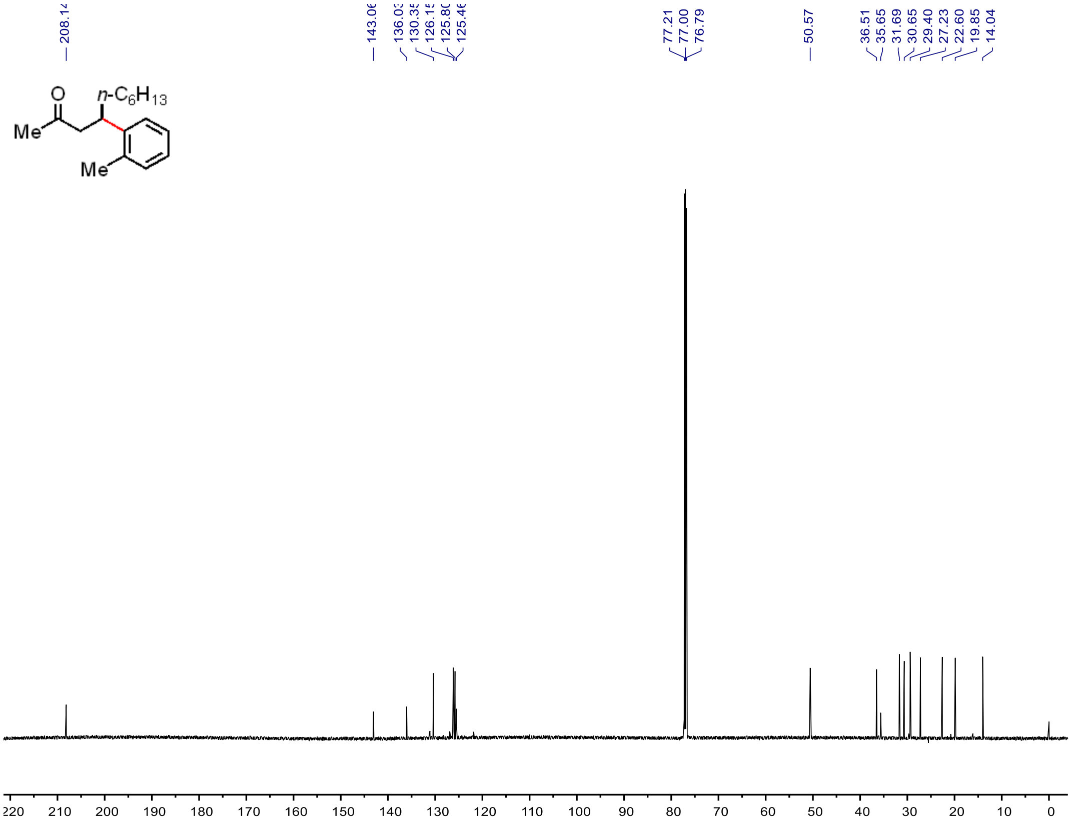
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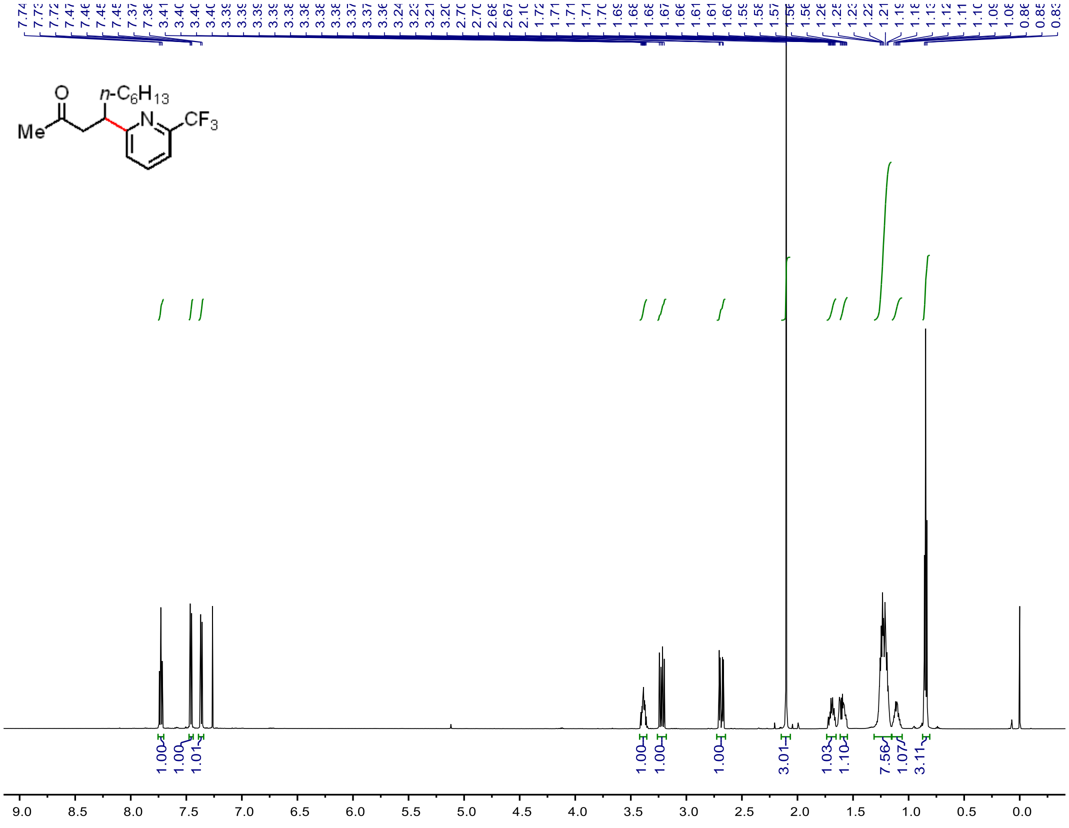
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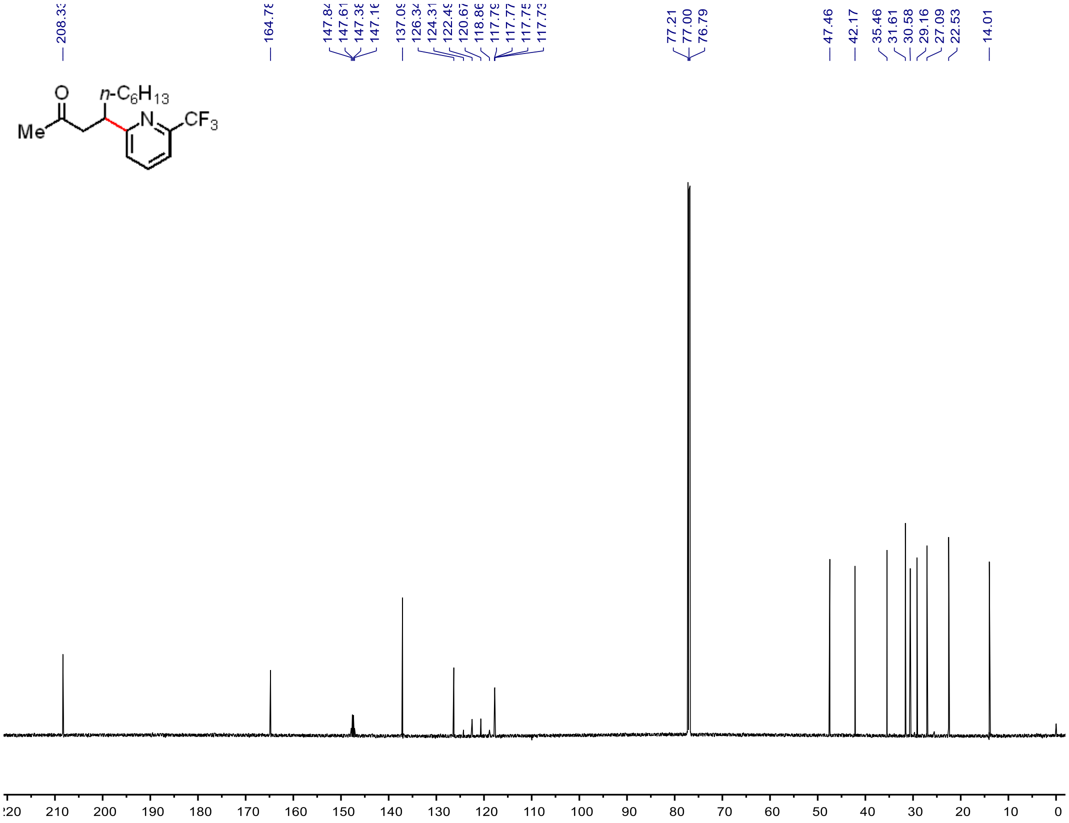
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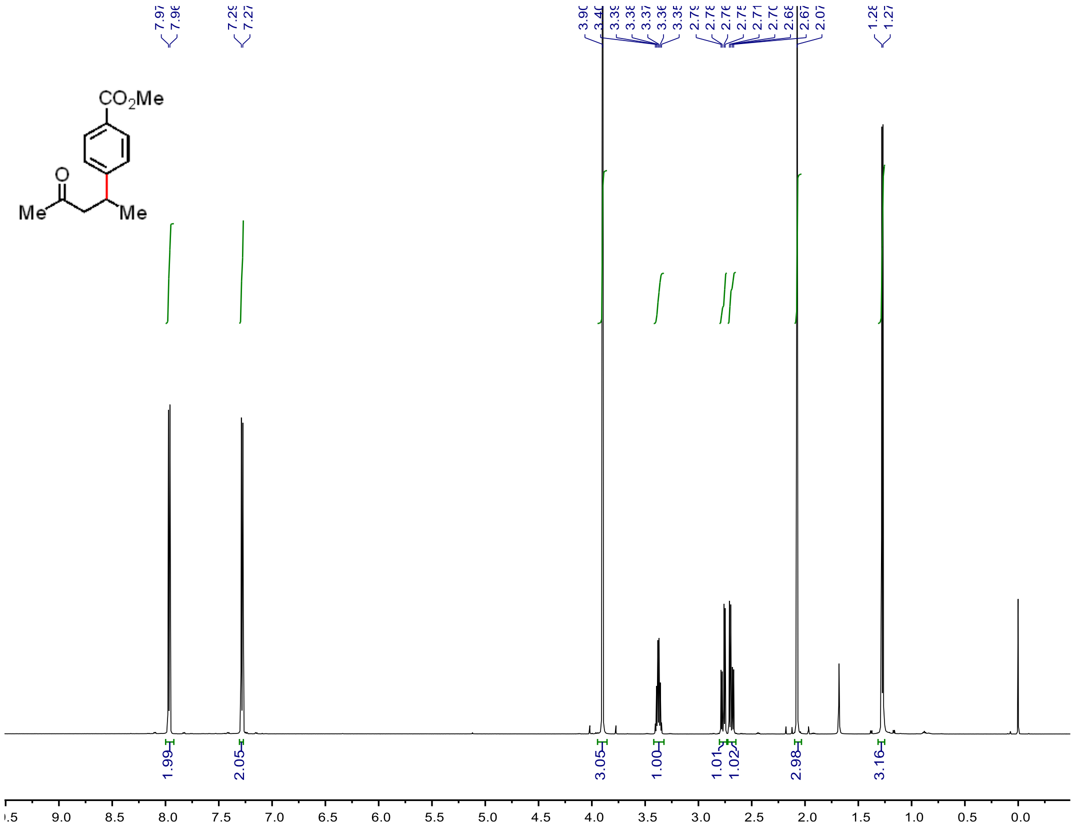
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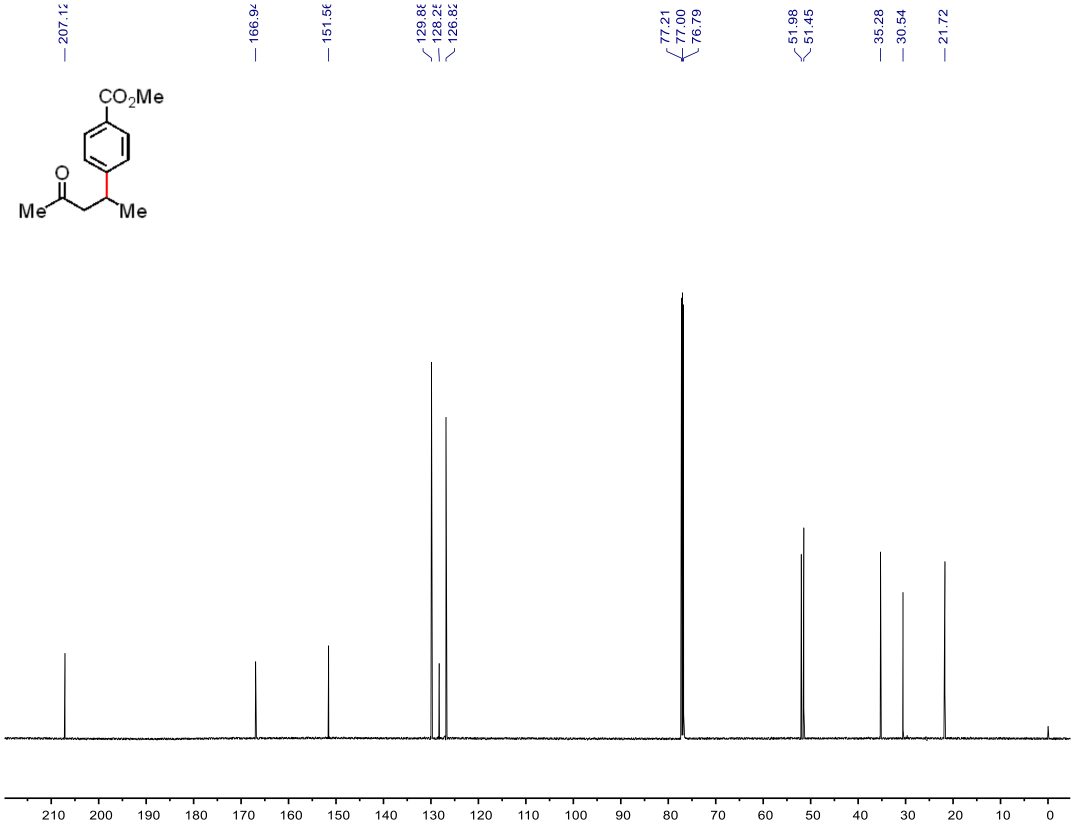
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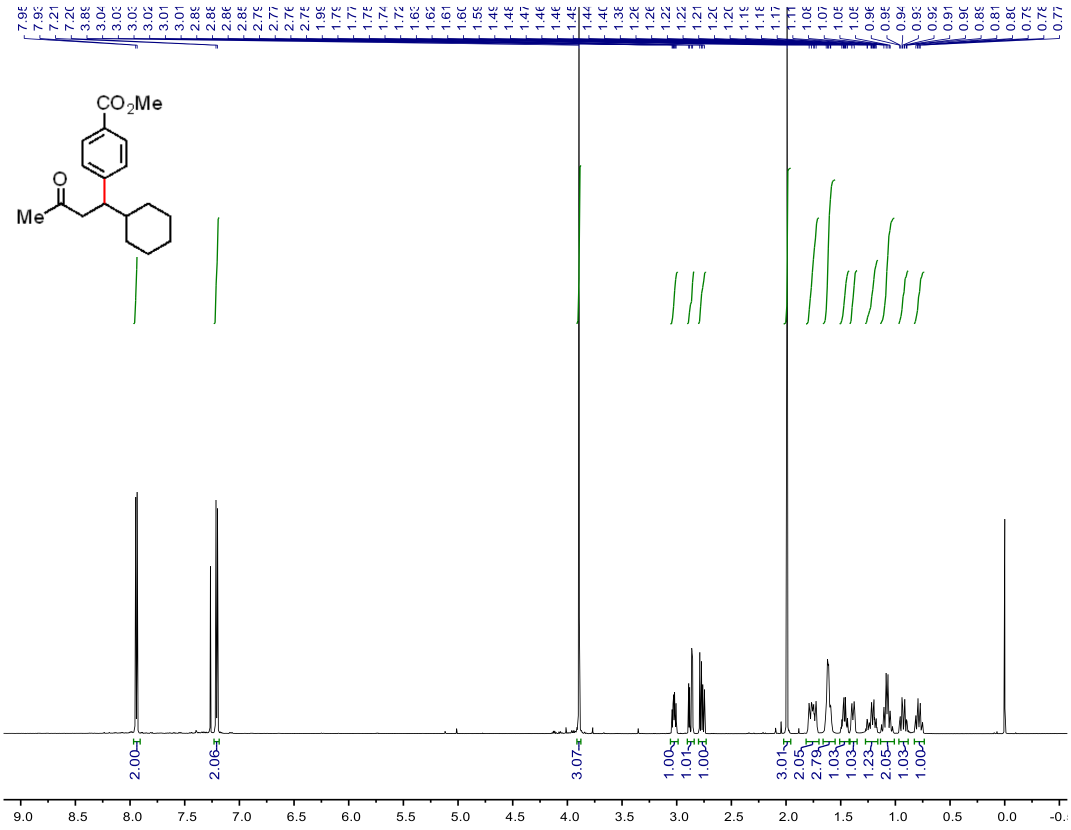
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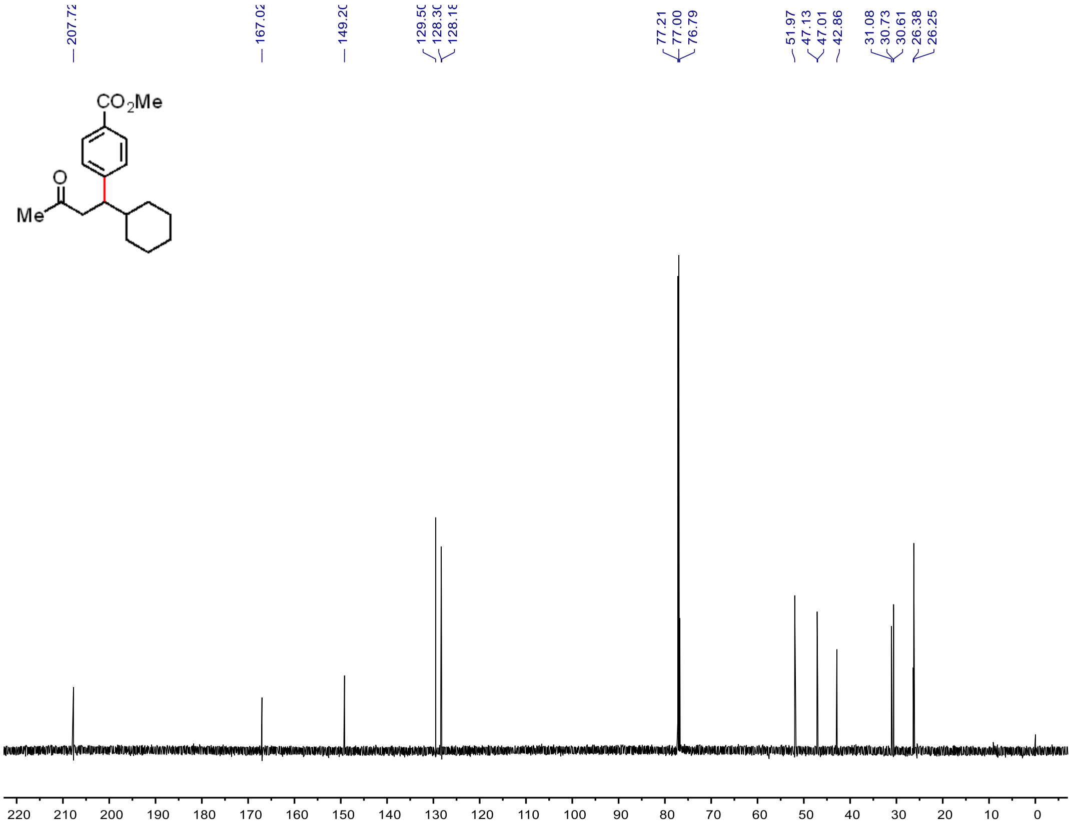
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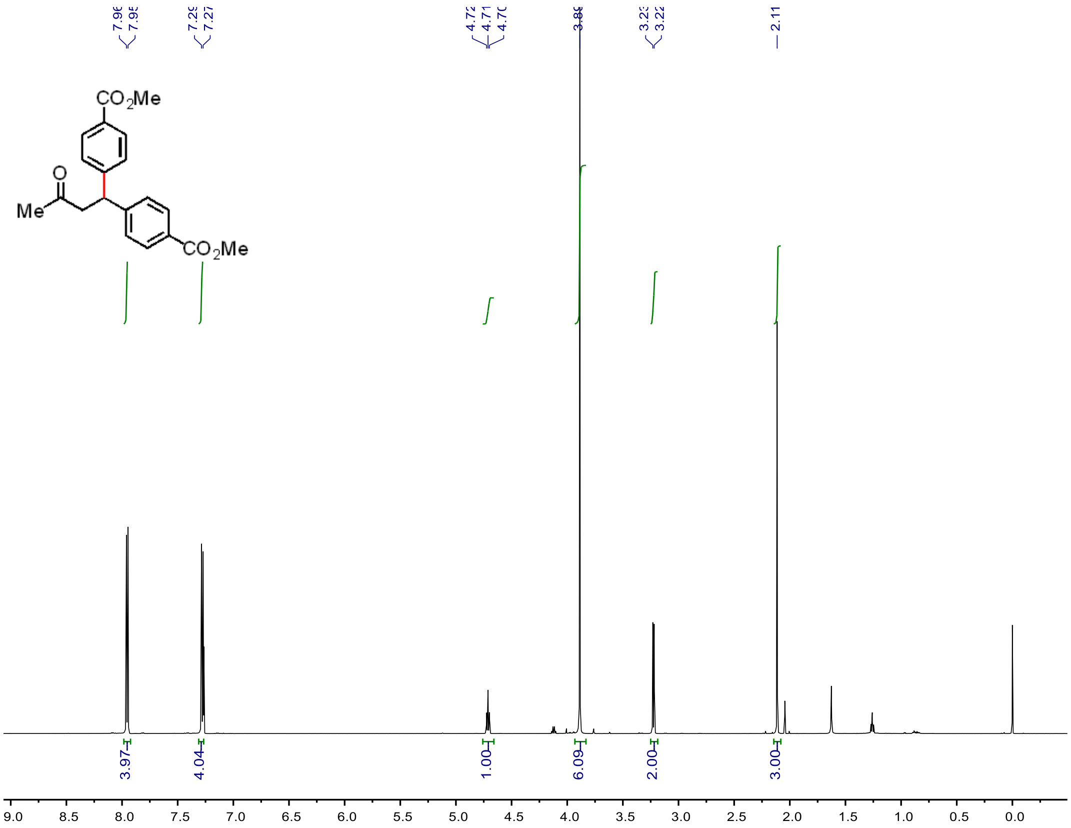
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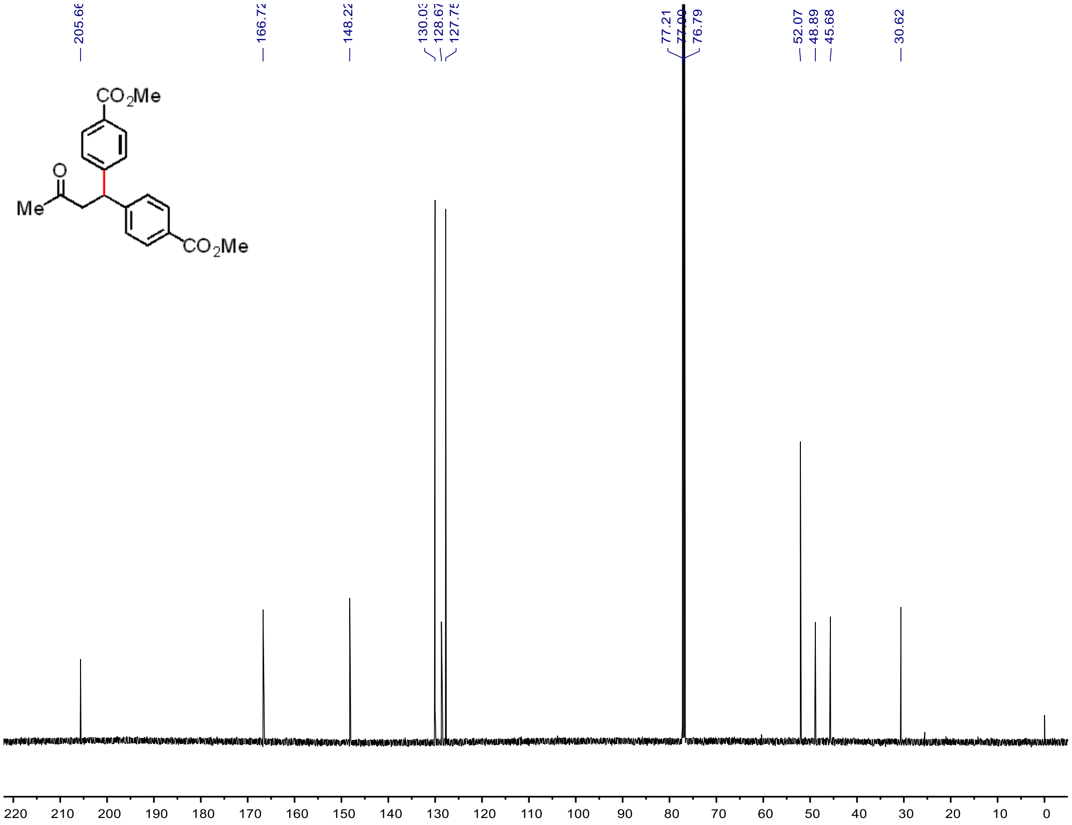
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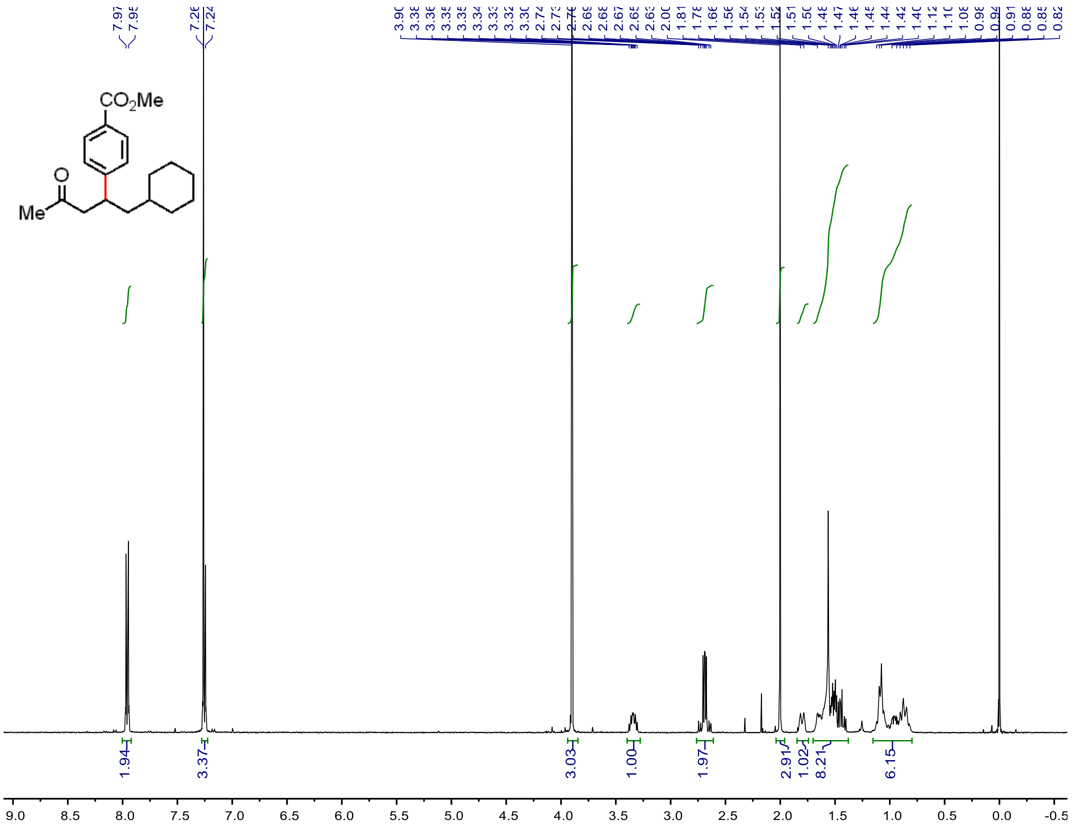
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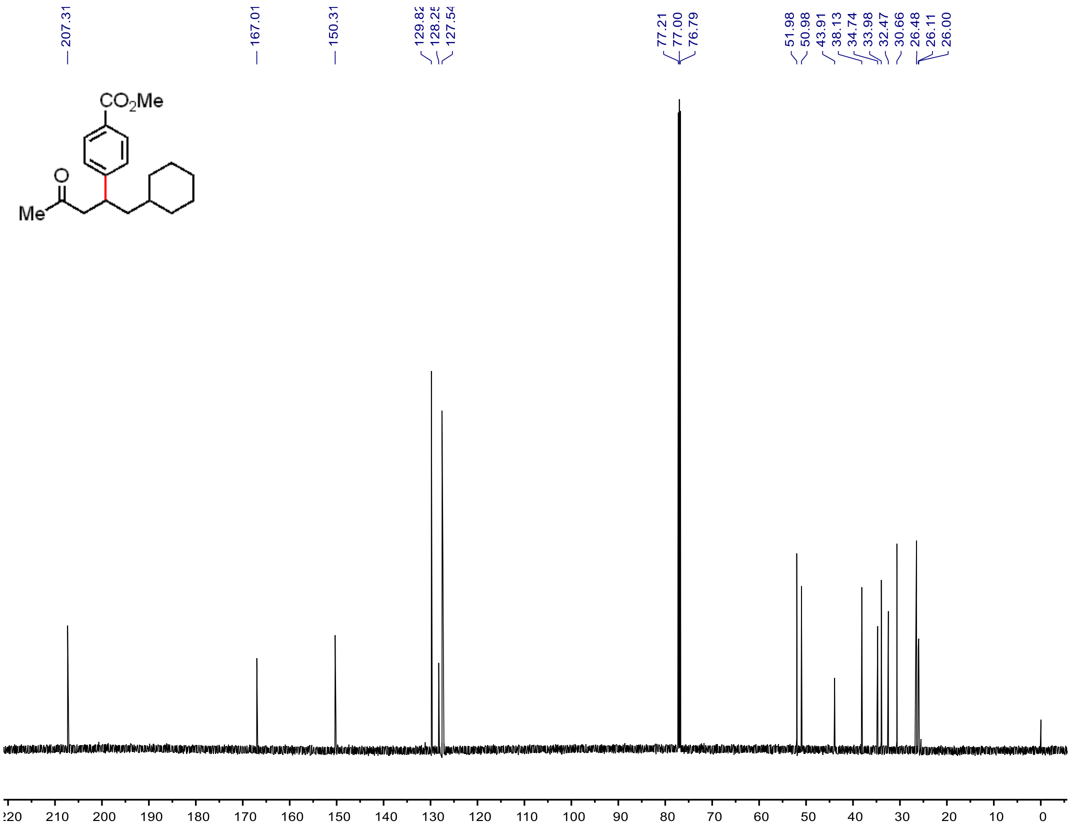
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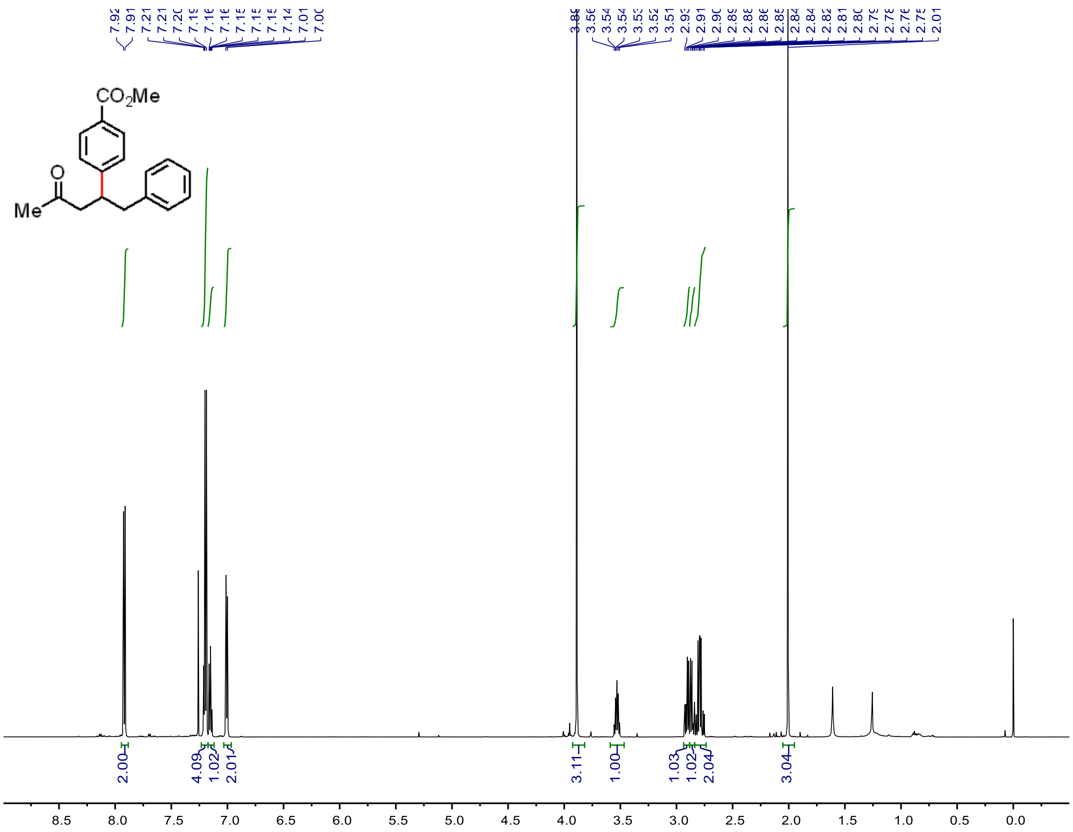
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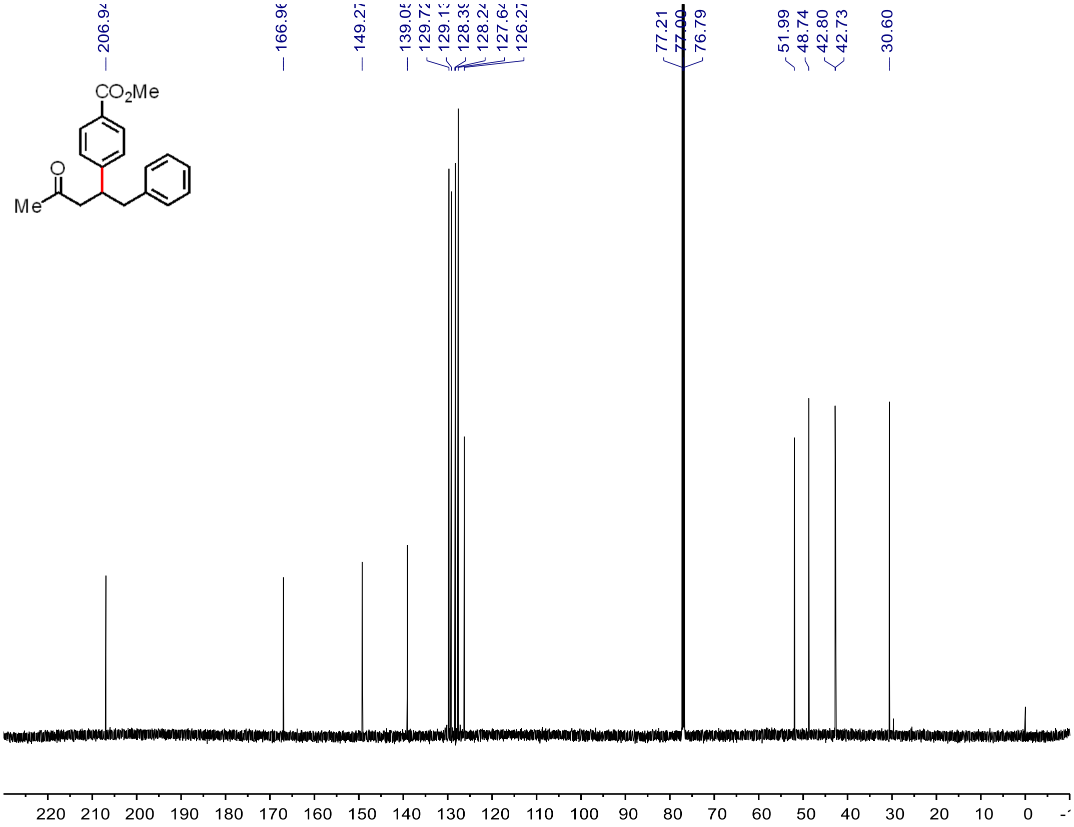
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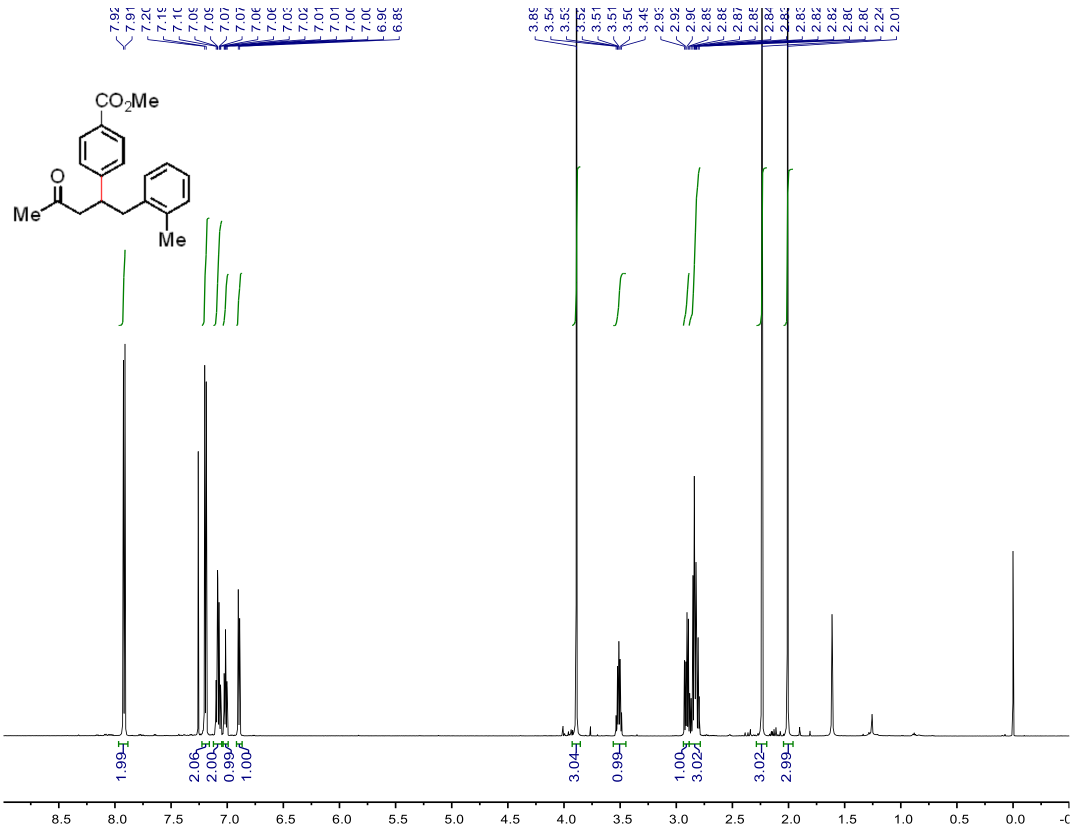
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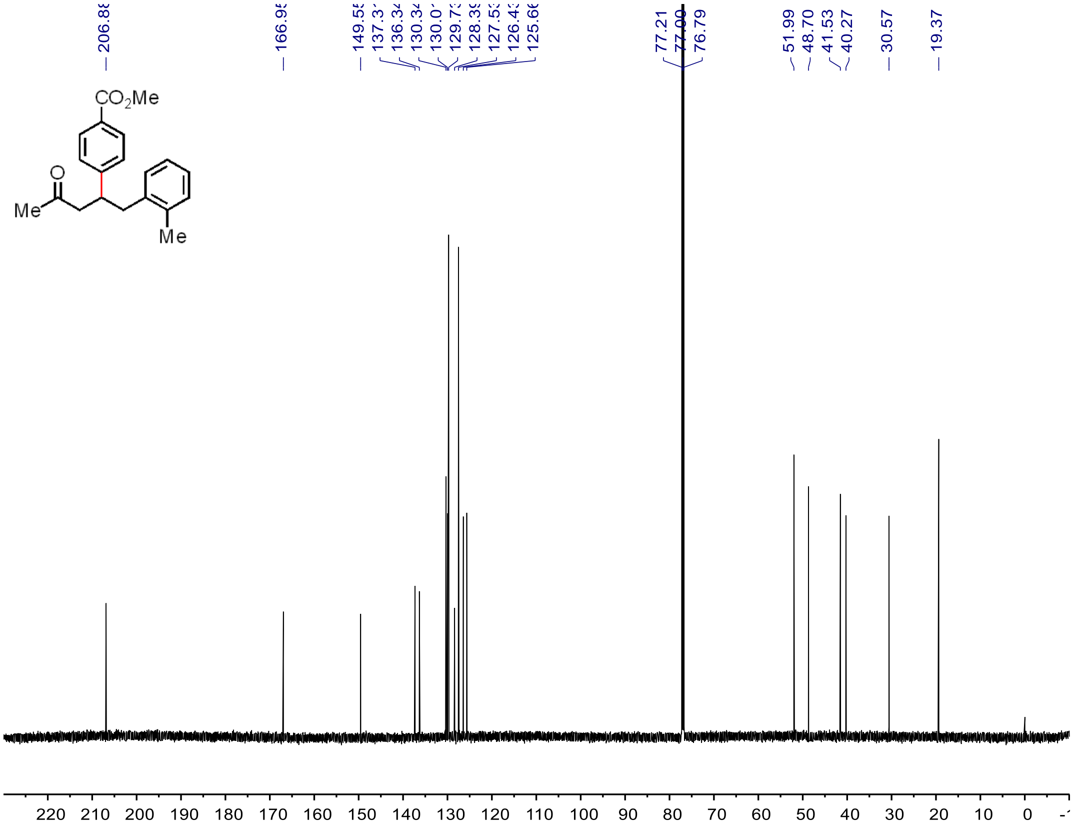
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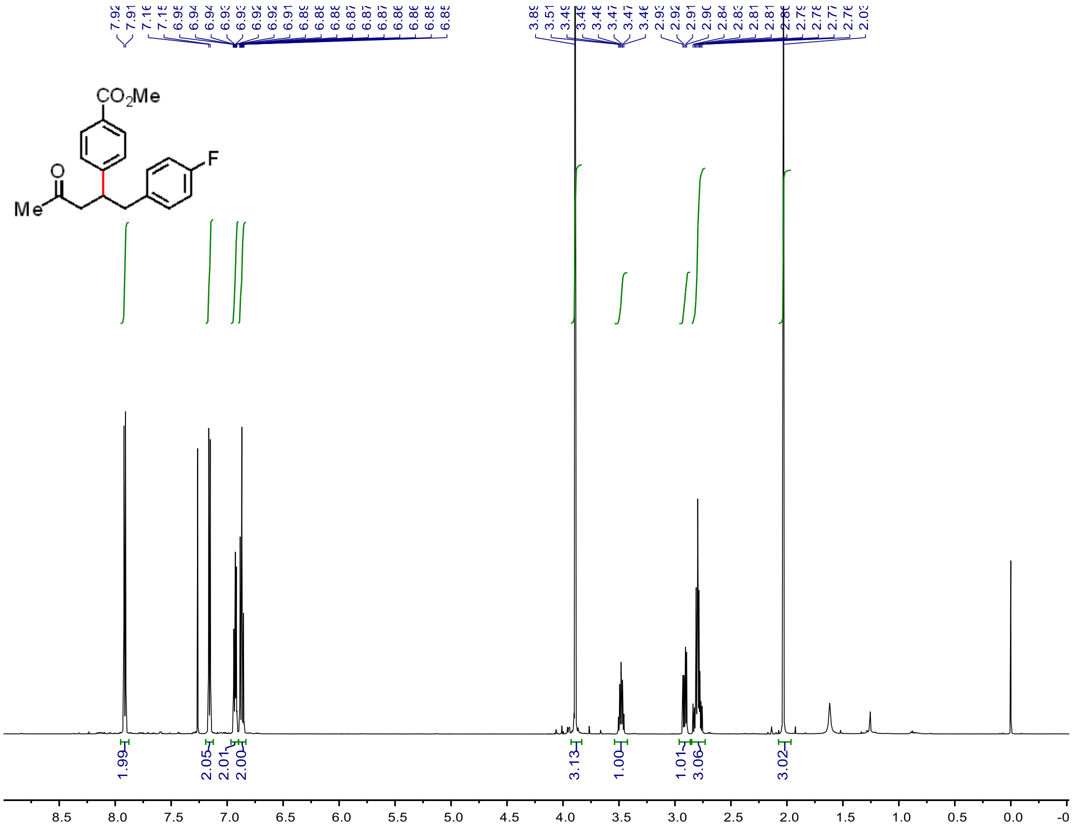
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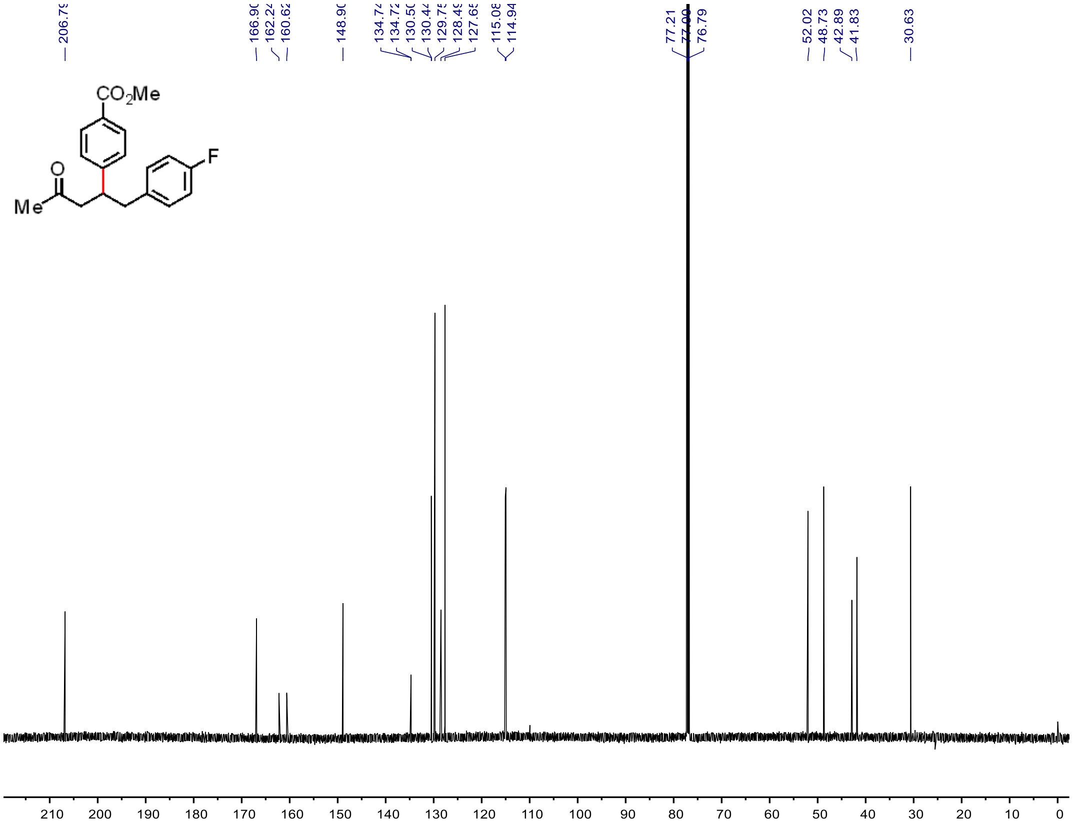
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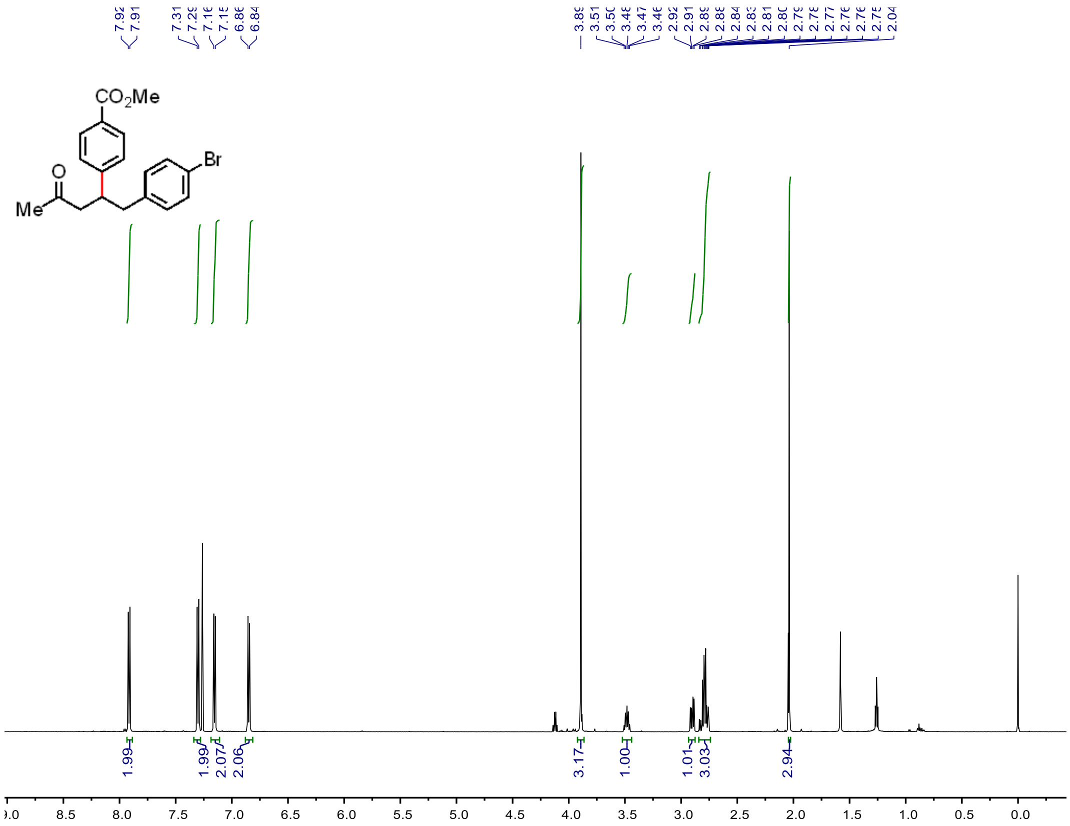
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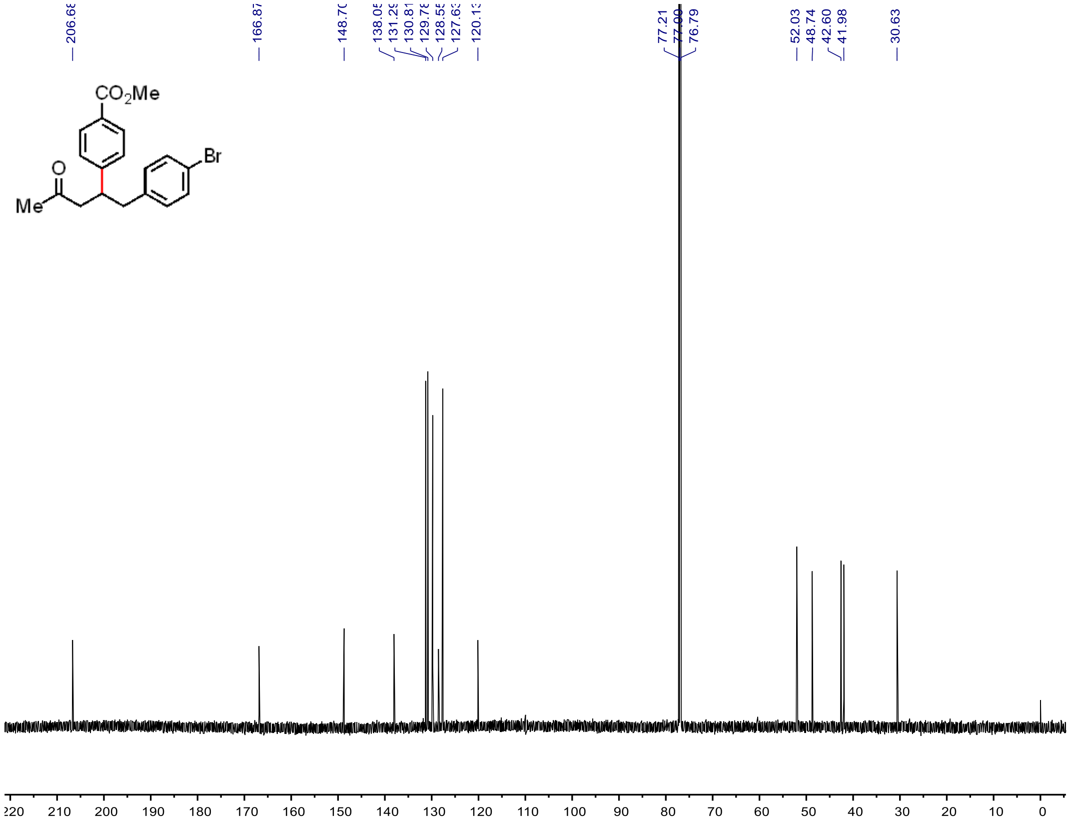
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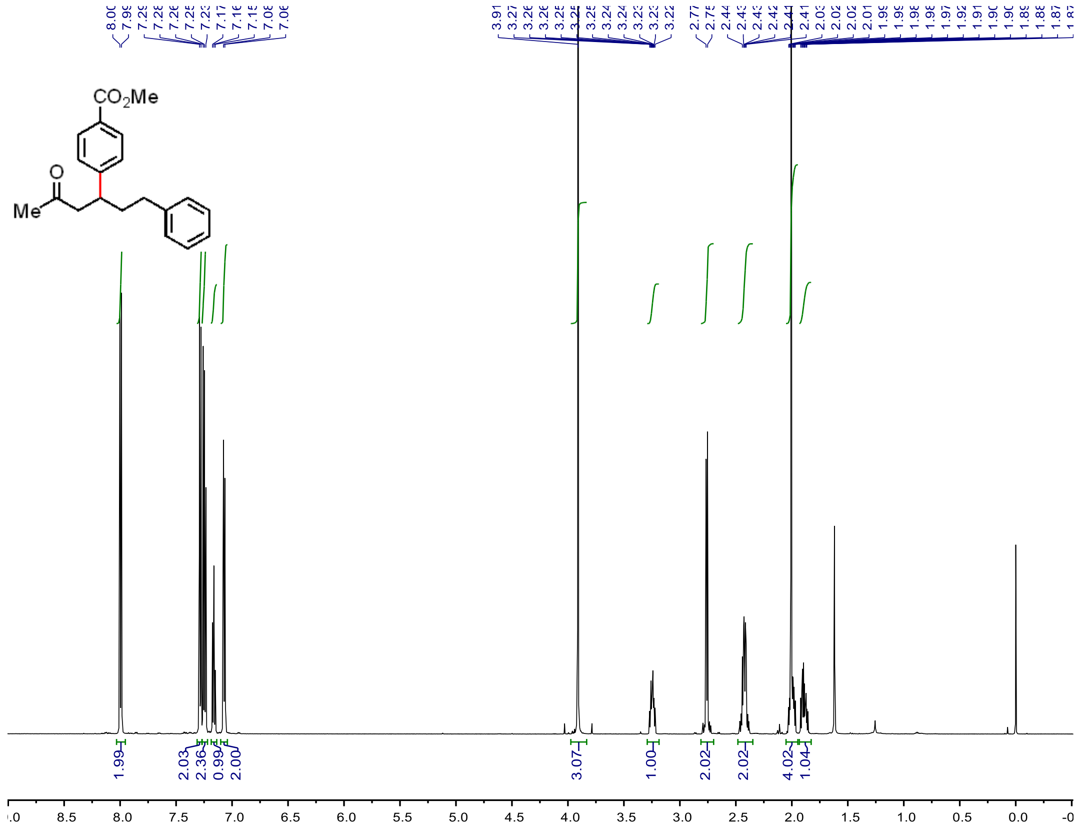
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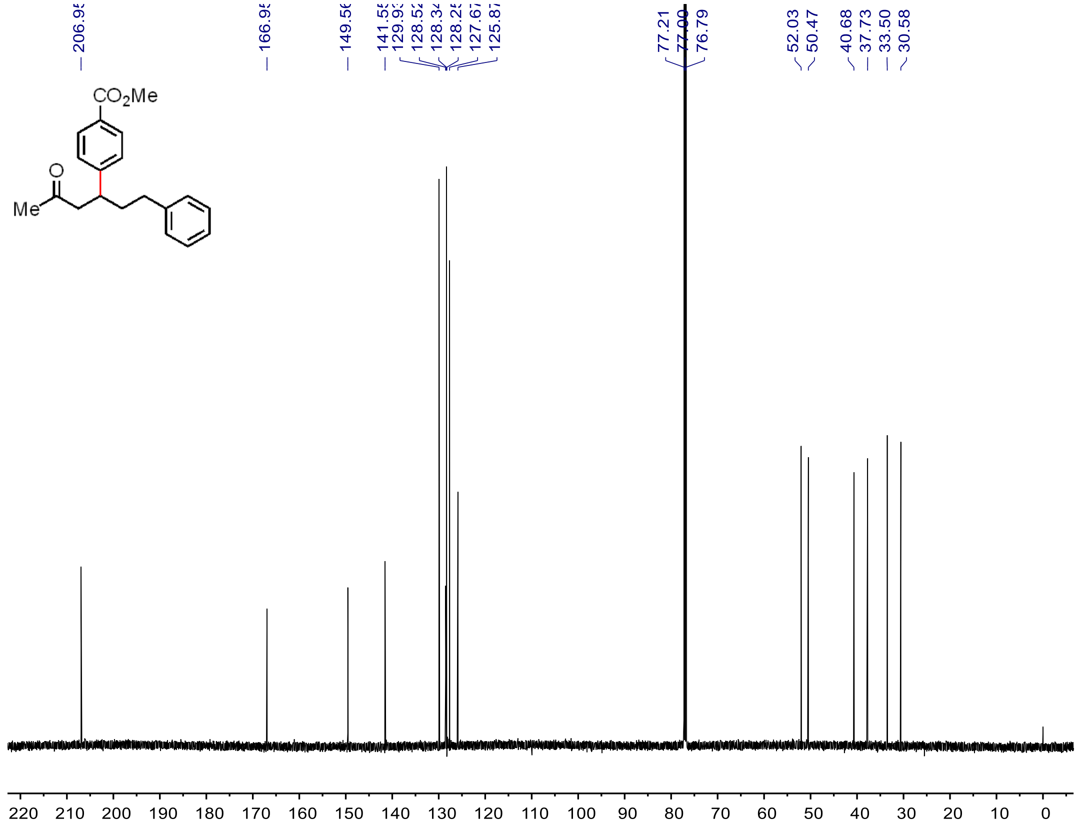
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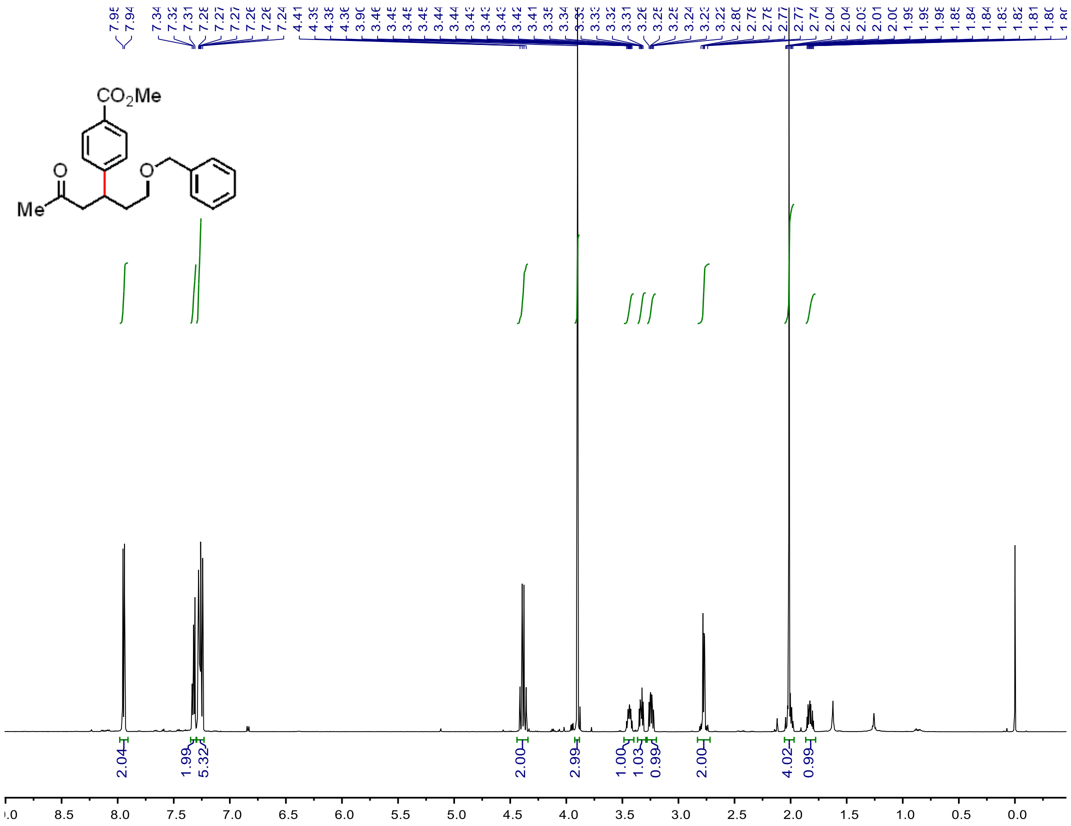
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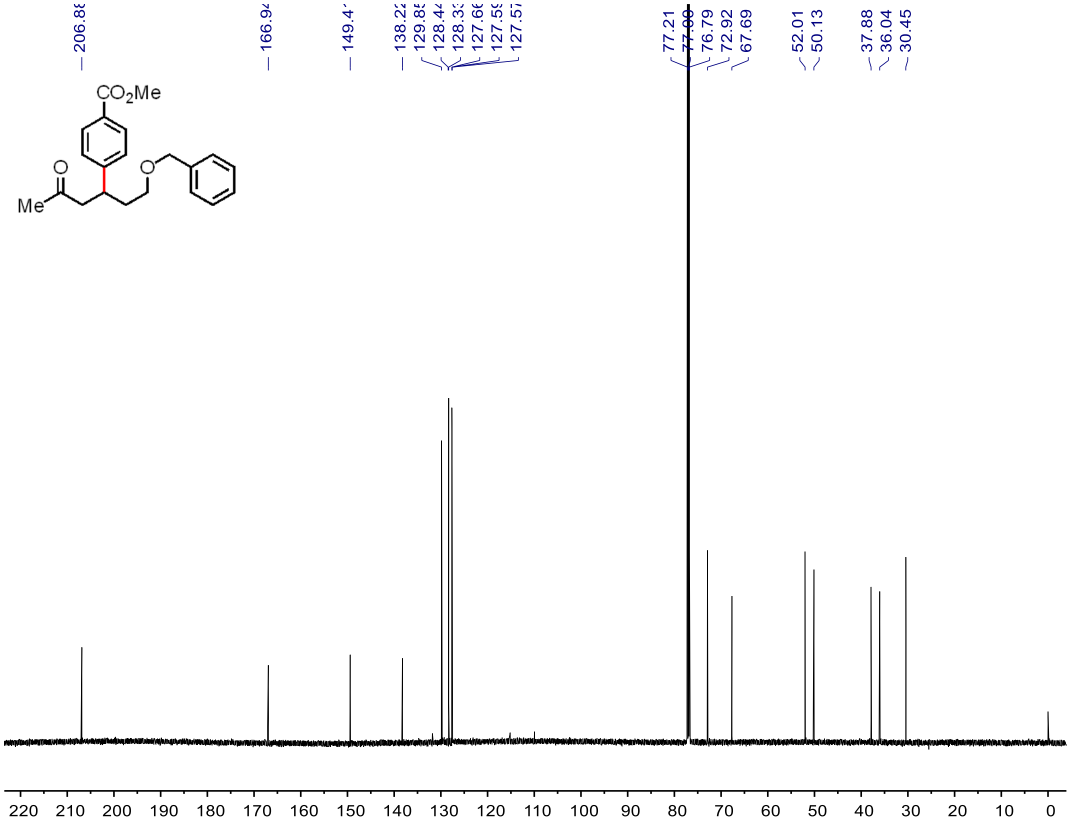
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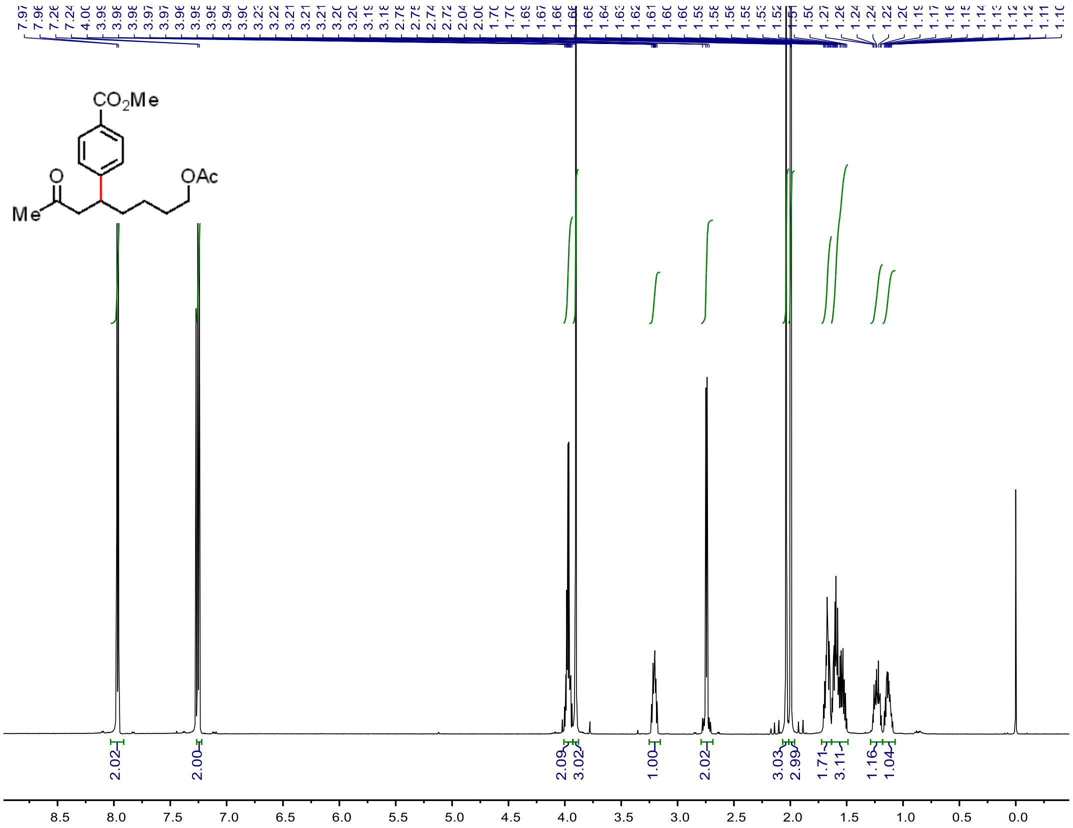
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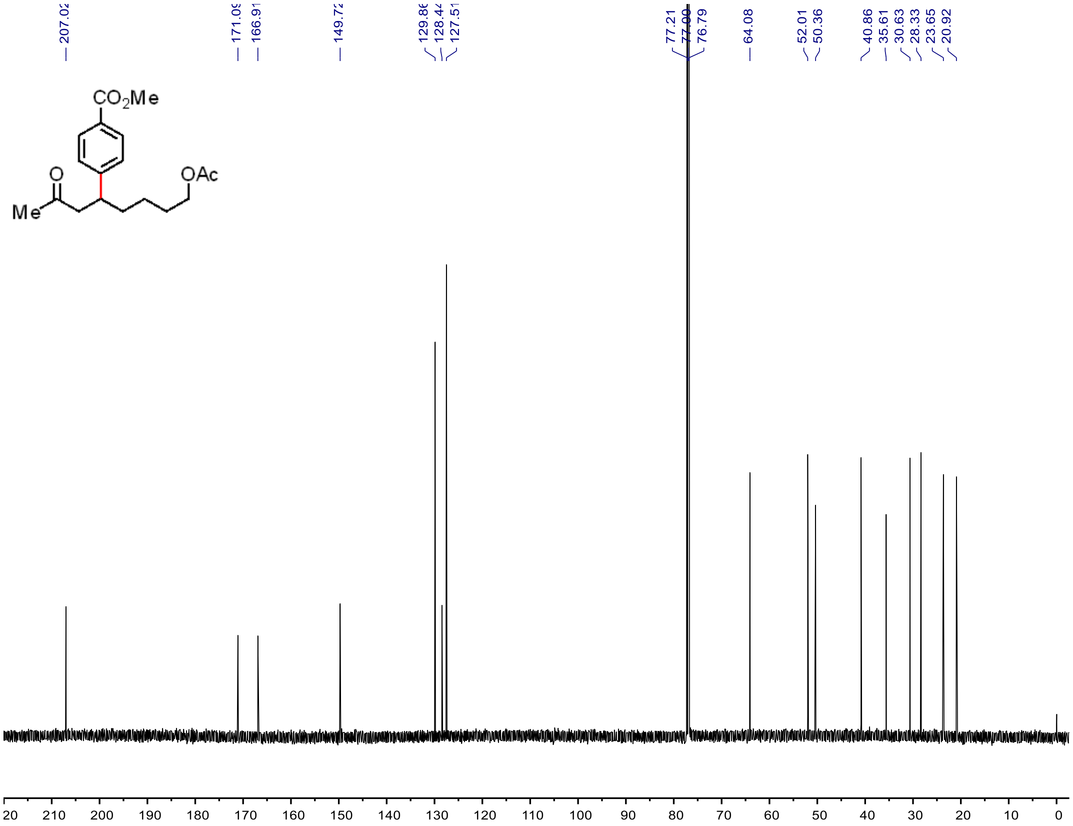
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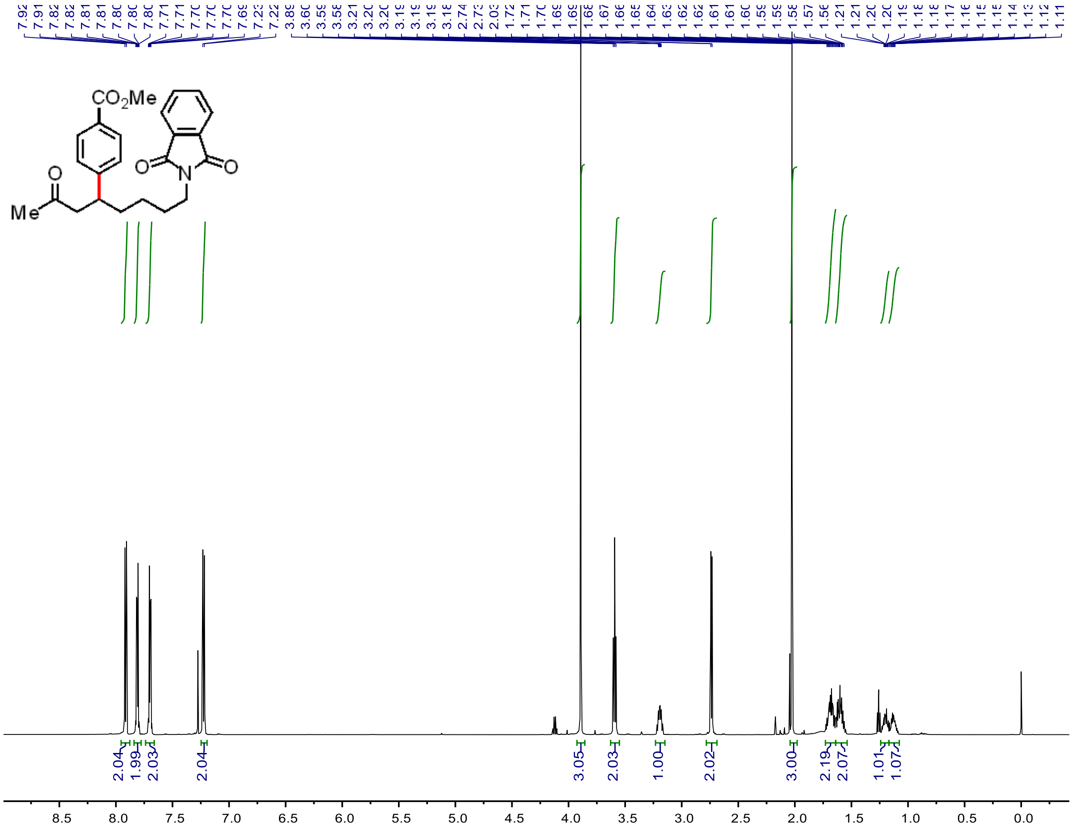
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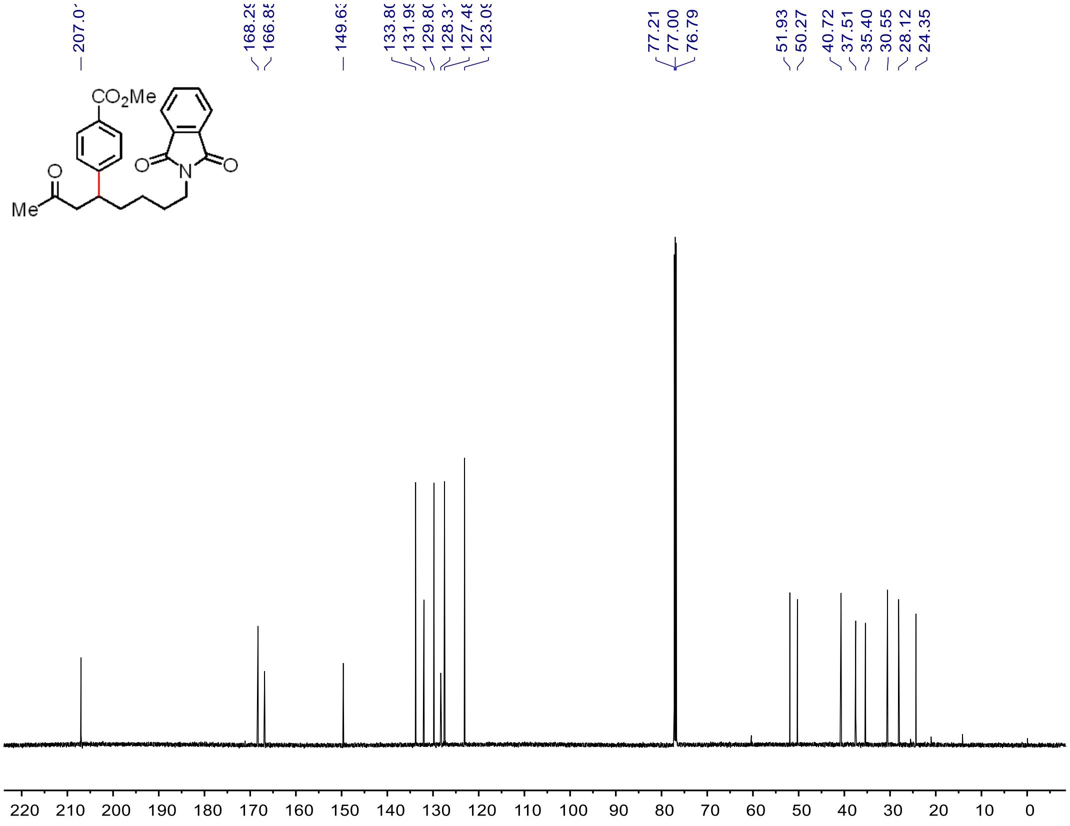
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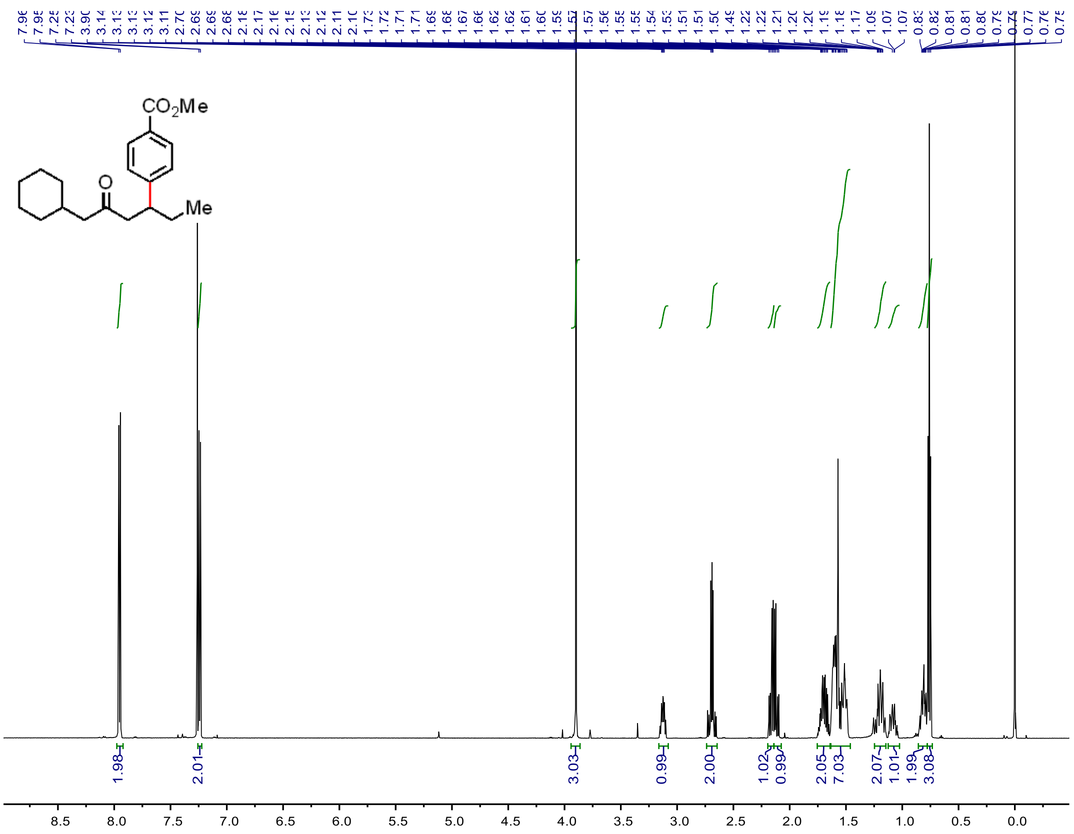
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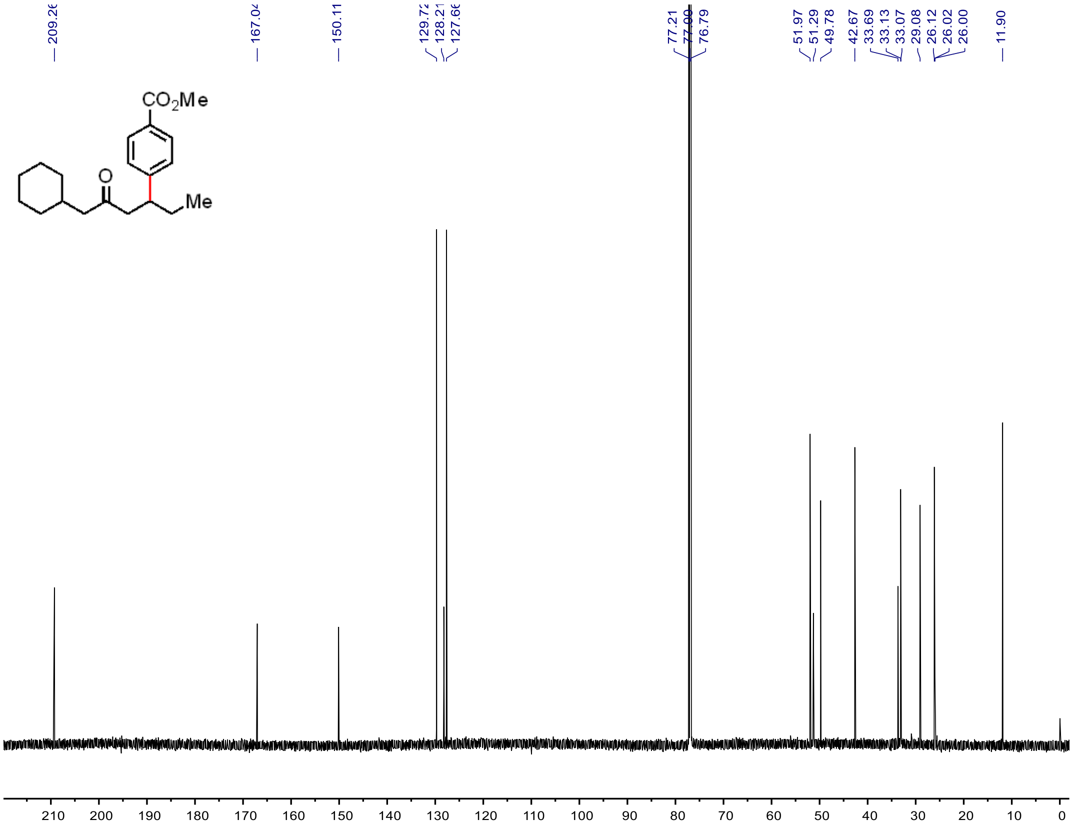
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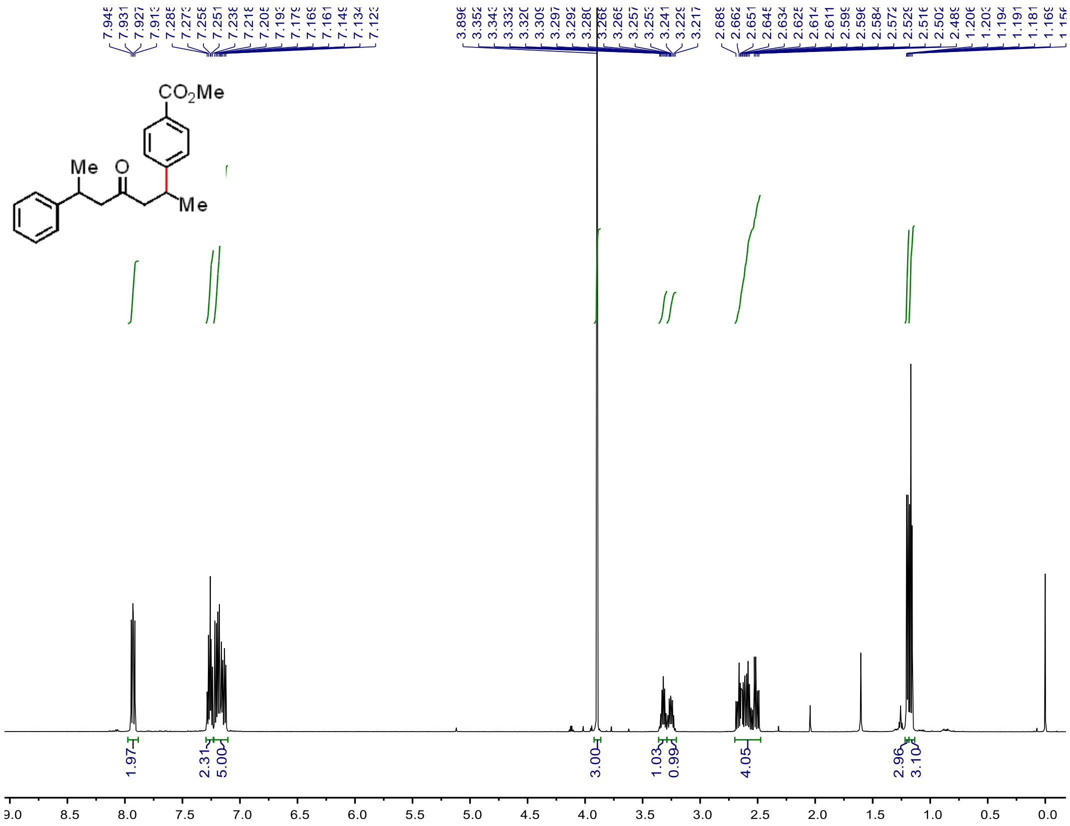
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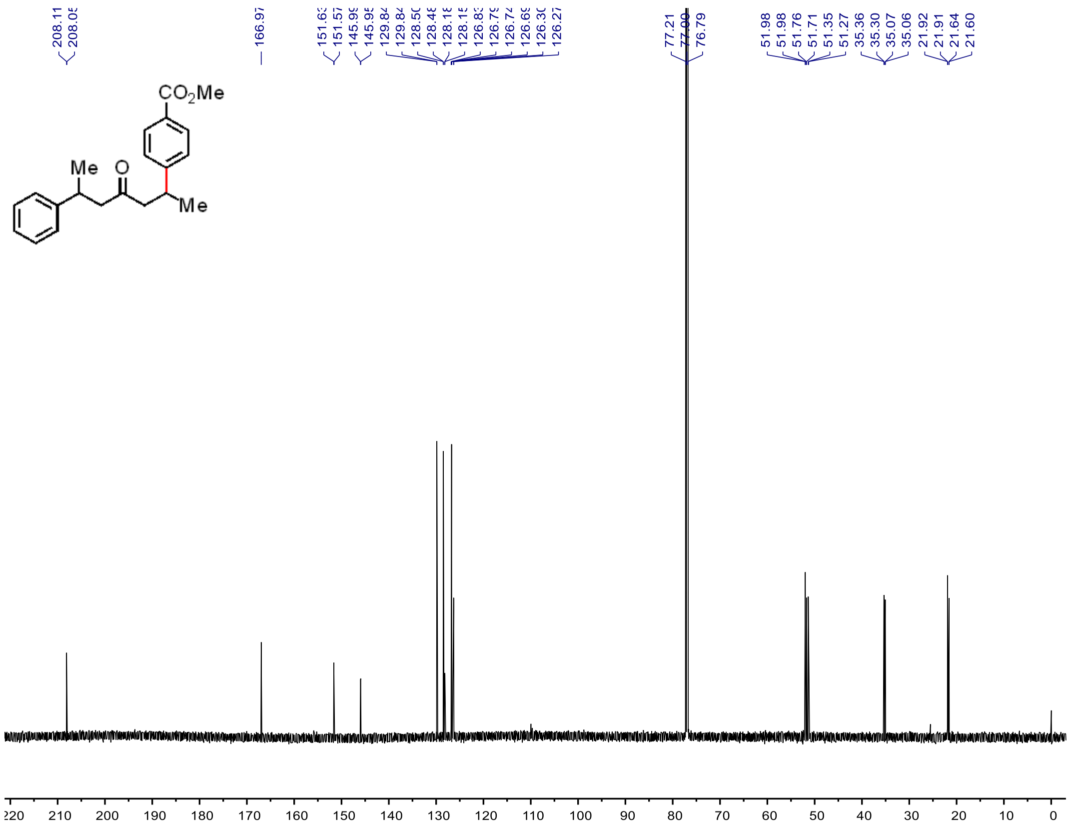
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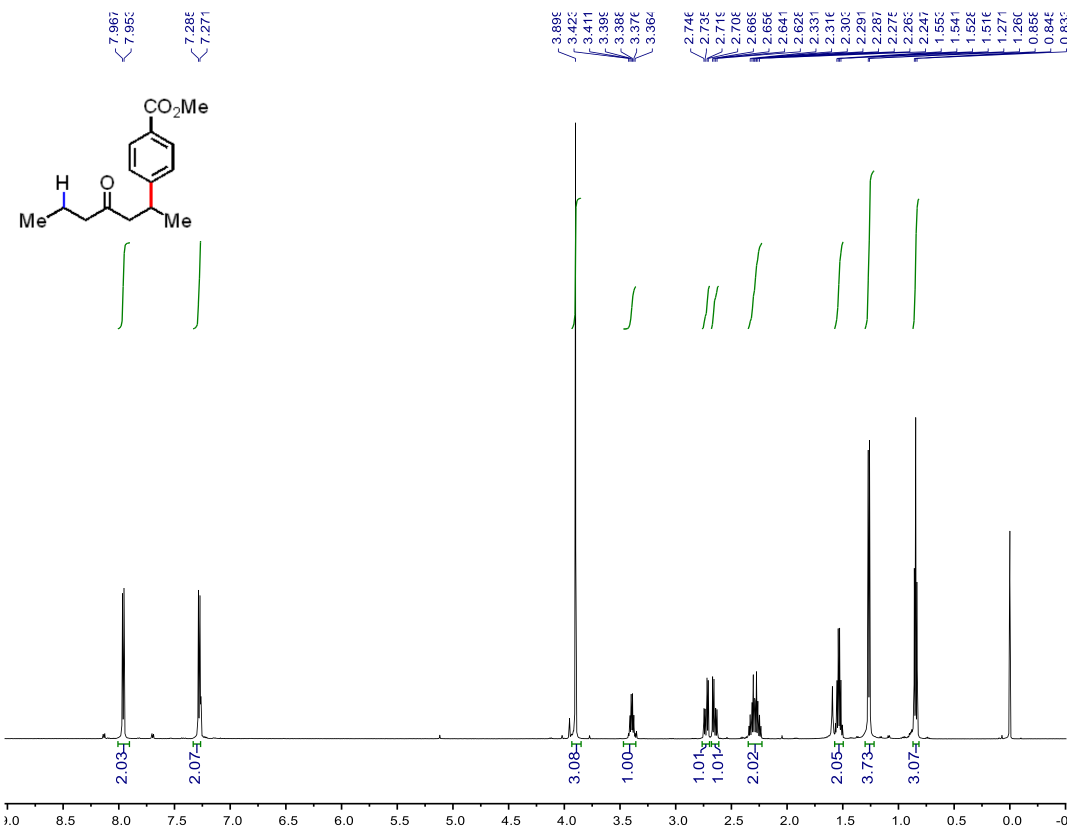
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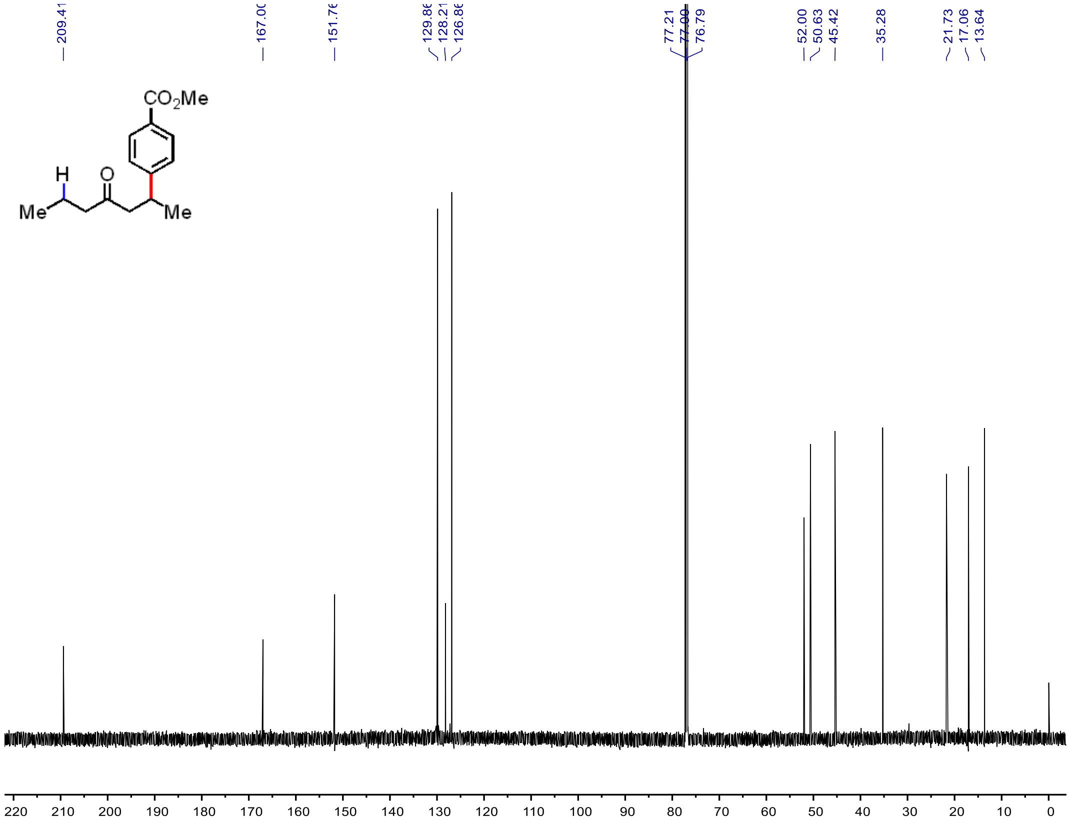
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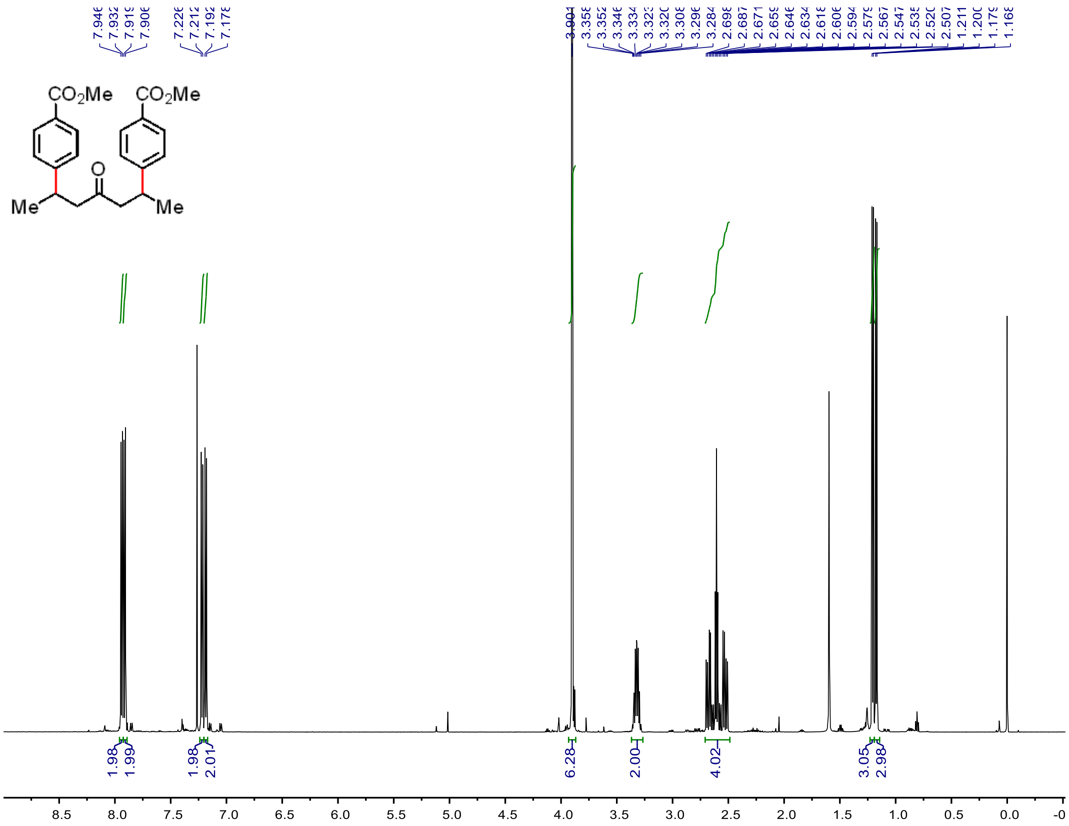
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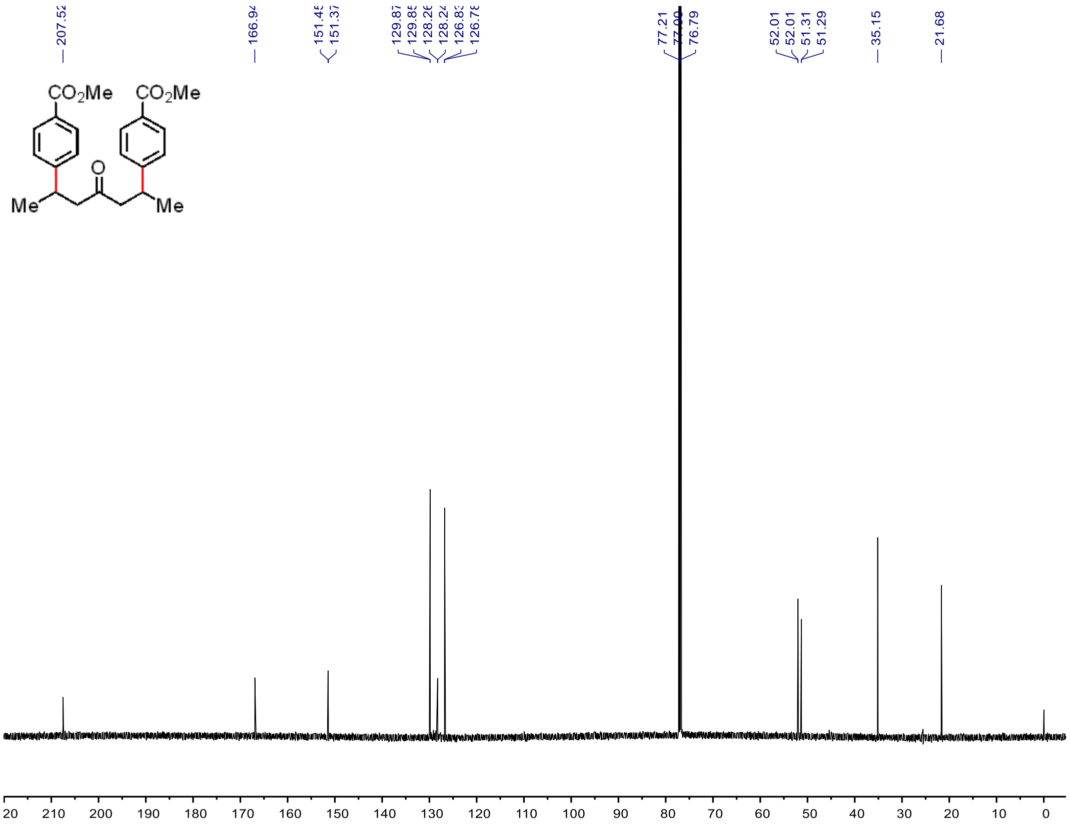
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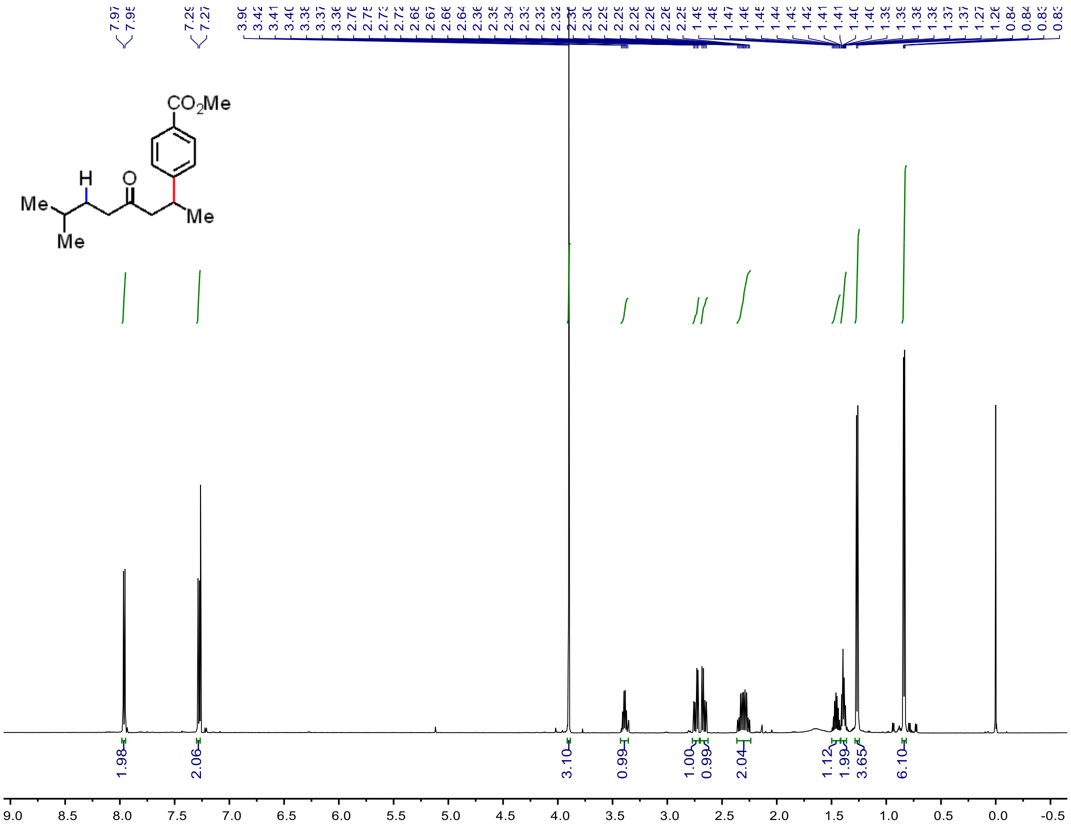
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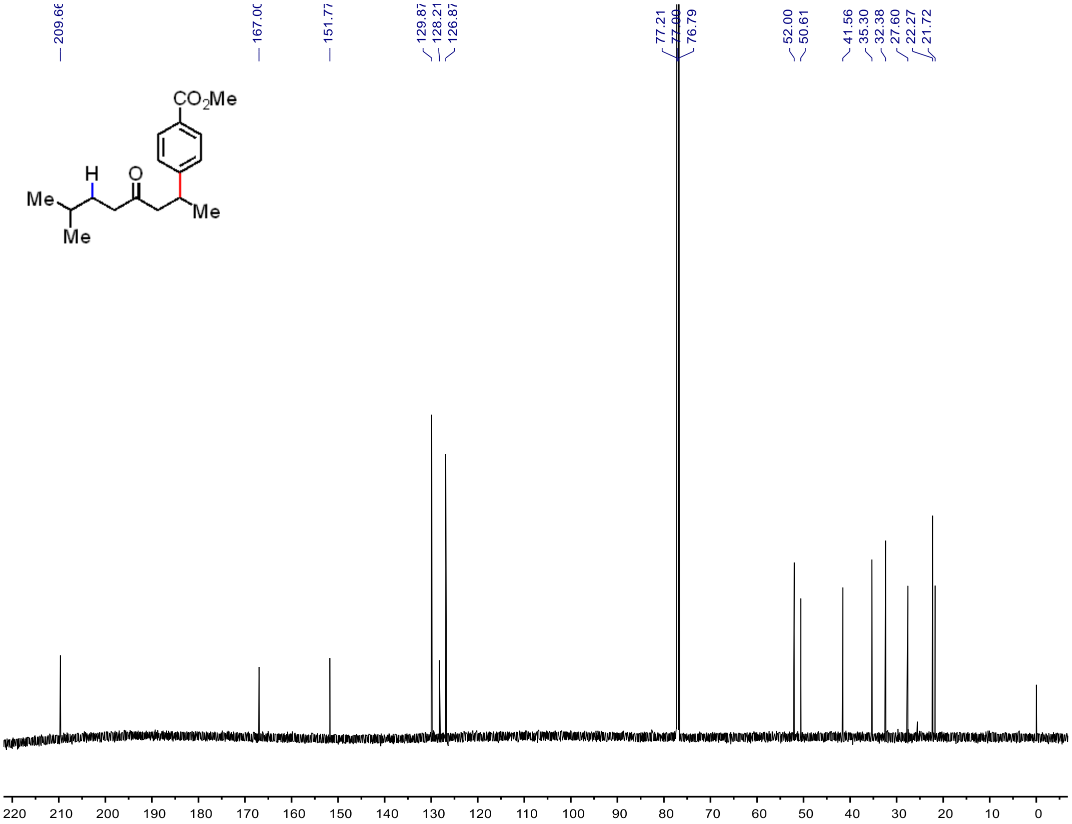
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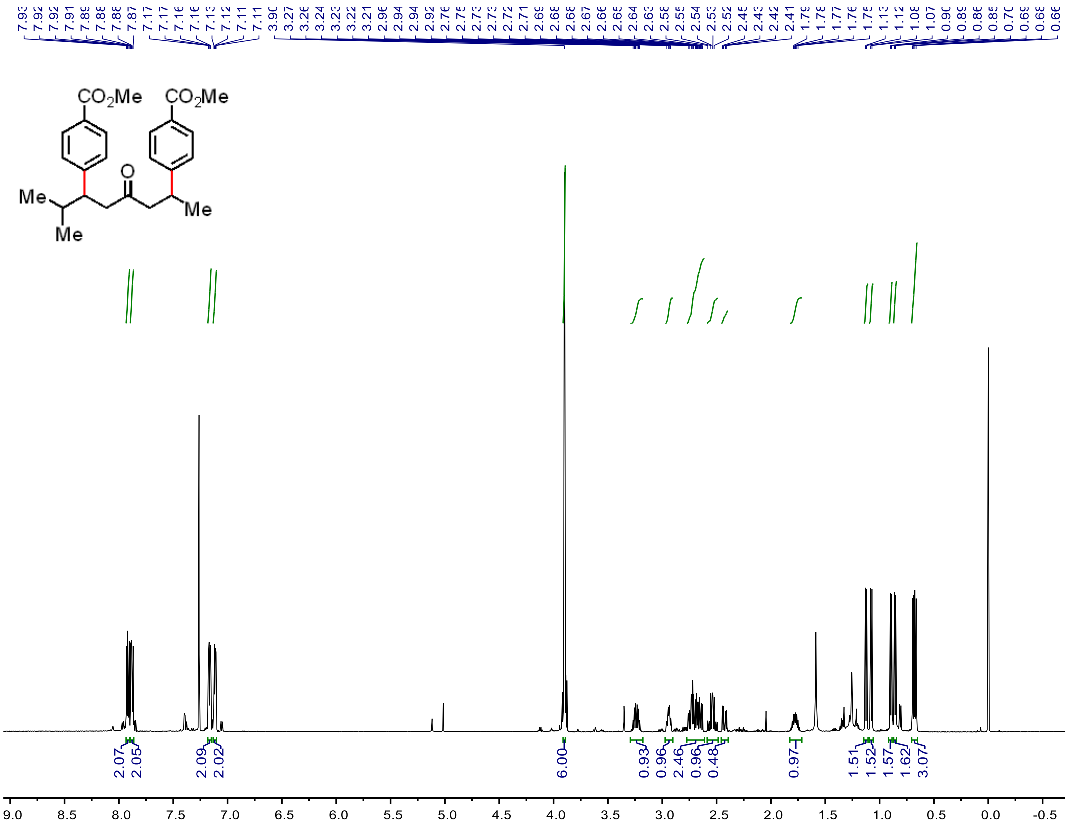
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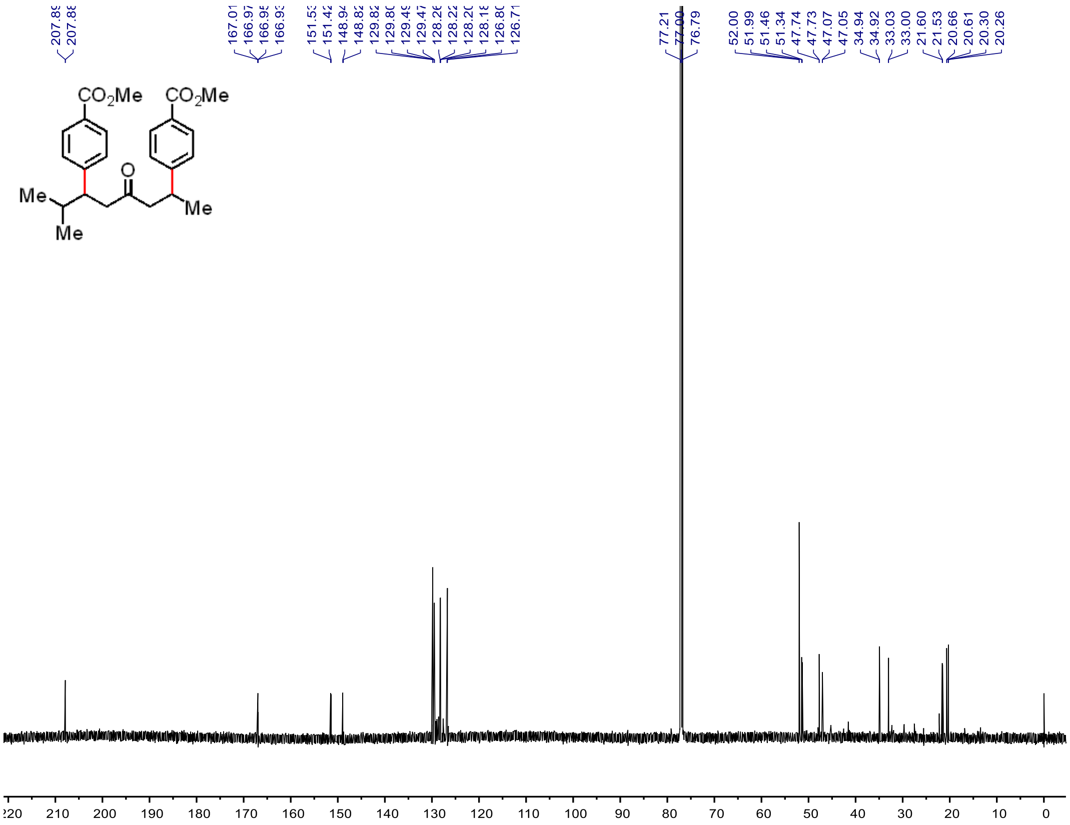
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