Supporting information for

Visible-light-induced hydroalkylation of alkenes with aromatic β-ketoesters

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1. General Information

All reactions were performed using quartz tube. Commercial grade reagents **1** and **2** and EtOH (OCEANPAK, GC ≥ 99.9%) were obtained from commercial sources without further purification unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminum plates with F-254 indicator, visualized by irradiation with UV light. Flash chromatography columns were packed with 200-300 mesh silica gel and silica gel was purchased from Qing Dao Hai Yang Chemical Industry. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz relative to tetramethylsilane as internal standard (δ = 0 ppm). For the ^{19}F spectra, α-trifluorotoluene served as external standard (δ = -63.9 ppm). High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionization (ESI). The UV-Vis absorption spectra were recorded in EtOH on a Perkin Elmer Lambda 35 spectrometer. The LCD Digital Hotplate Magnetic Stirrer MS-H-Pro^{+} and Digital Single Channel Adjustable Automatic Electronic Pipette Micropipette dPettee^{+} were purchased from Dragon Laboratory Instruments Limited. The cyclic voltammetry (CV) curves were performed using a CHI650A Instruments. And the Luminescence Quenching Experiments were recorded using a F-4500 FL Spectrophotometer. All reactions were carried out with photoreactor (Serial No: D243V12) which was purchased from LUOYANG JINFENG ELECTROMECHANICAL EQUIPMENT CO., LTD.

2. Experimental Procedures

2.2 Optimization of the reaction conditions

Styrene **1a**, benzoylacetate **2a**, photocatalyst and base were combined in solvent (2.0 mL) under Ar atmosphere. The mixture was stirred at room temperature under blue LED lamp (5 W). After the reaction, the mixture was extracted with ethyl acetate and saturated salt water, organic phase was purified by chromatography on silica gel (elute: ethyl acetate/petroleum ether = 1/5-1/7, v/v) to give the desired products **3a**.

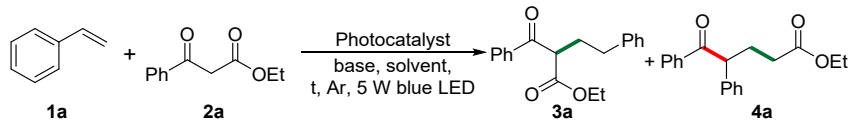


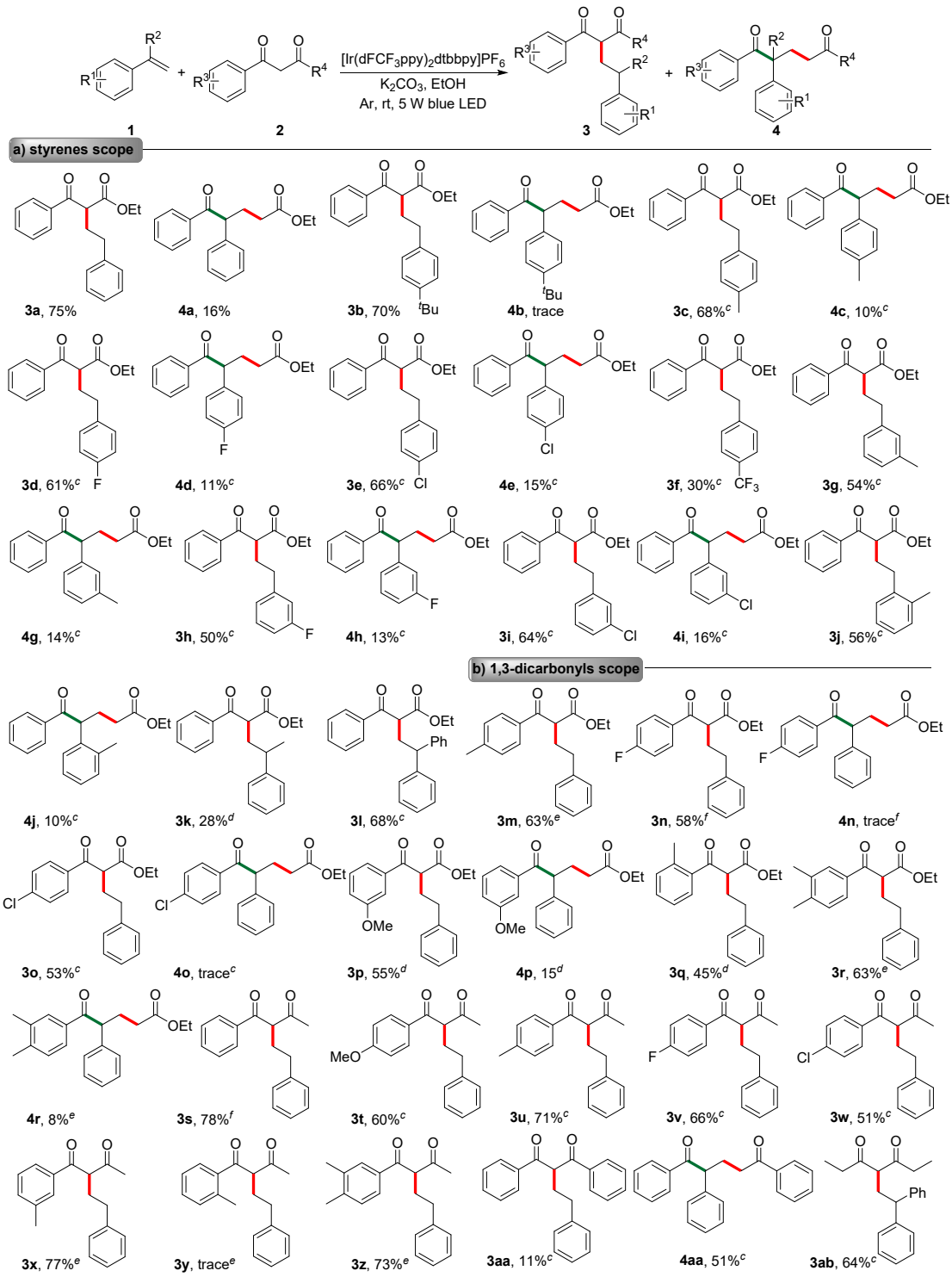
Table S1: Optimization of the reaction conditions in the visible light mediated hydroalkylation.

entry	photocatalyst	base	solvent	yield[b] (%)	
				3a	**4a**
1	RB	Cs_2CO_3	CH_3CN/H_2O (1:1)	--	--
2	EY	Cs_2CO_3	CH_3CN/H_2O (1:1)	--	--
3	Na_2-EY	Cs_2CO_3	CH_3CN/H_2O (1:1)	--	--
4	EB	Cs_2CO_3	CH_3CN/H_2O (1:1)	--	--
5	ARS	Cs_2CO_3	CH_3CN/H_2O (1:1)	--	--
6	FI	Cs_2CO_3	CH_3CN/H_2O (1:1)	--	--
7[c]	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	Na_2CO_3	CH_3CN/H_2O (1:1)	--	--
8	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	CsOAc	CH_3CN/H_2O (1:1)	--	--
9	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	$NaHCO_3$	CH_3CN/H_2O (1:1)	trace	19%
10	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	^{t}BuOK	CH_3CN/H_2O (1:1)	28%	trace
11	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	DBU	CH_3CN/H_2O (1:1)	--	--

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (3.0 equiv.), photocatalyst (3 mol %), base (3.0 equiv.), solvent (2 mL) in a quartz-tube under Ar at room temperature, under 5 W blue LED for 8 h. [b]Isolated yield. [c]no light irradiation.

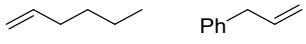
2.1 General procedure for the hydroalkylation of alkenes with aromatic β-diketones

Styrenes **1** (0.3 mmol), aromatic β-diketones **2** (0.9 mmol, 3.0 equiv.), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (0.009 mmol, 3 mol %) and K_2CO_3 (0.9 mmol, 3 equiv.) were combined in EtOH (2.0 mL) under Ar atmosphere. The mixture was stirred at room temperature under blue LED lamp (5 W). After the reaction, the mixture was extracted with ethyl acetate and saturated salt water, organic phase was purified by chromatography on silica gel (elute: ethyl acetate/petroleum ether = 1/5-1/7, v/v) to give the desired products **3**.

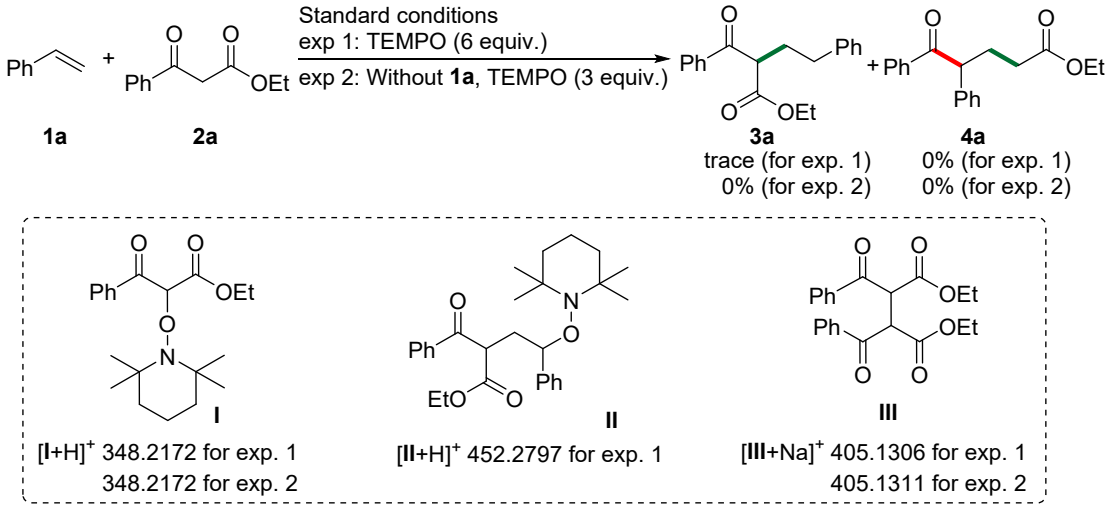


Scheme S1. Scope of styrenes and 1,3-dicarbonyls. [a]Reaction conditions: **1** (0.3 mmol), **2** (3.0 equiv.), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (3 mol %), K_2CO_3 (3.0 equiv.), EtOH (2 mL) in a quartz-tube under Ar at room temperature, 5 W blue LED, for 26 h. [b]Isolated yield. [c]For 10 h. [d]For 11 h. [e]For 8 h. [f]For 7 h.

Failed substrate:



3. Radical Scavenger Experiments



Scheme S2. Control experiments.

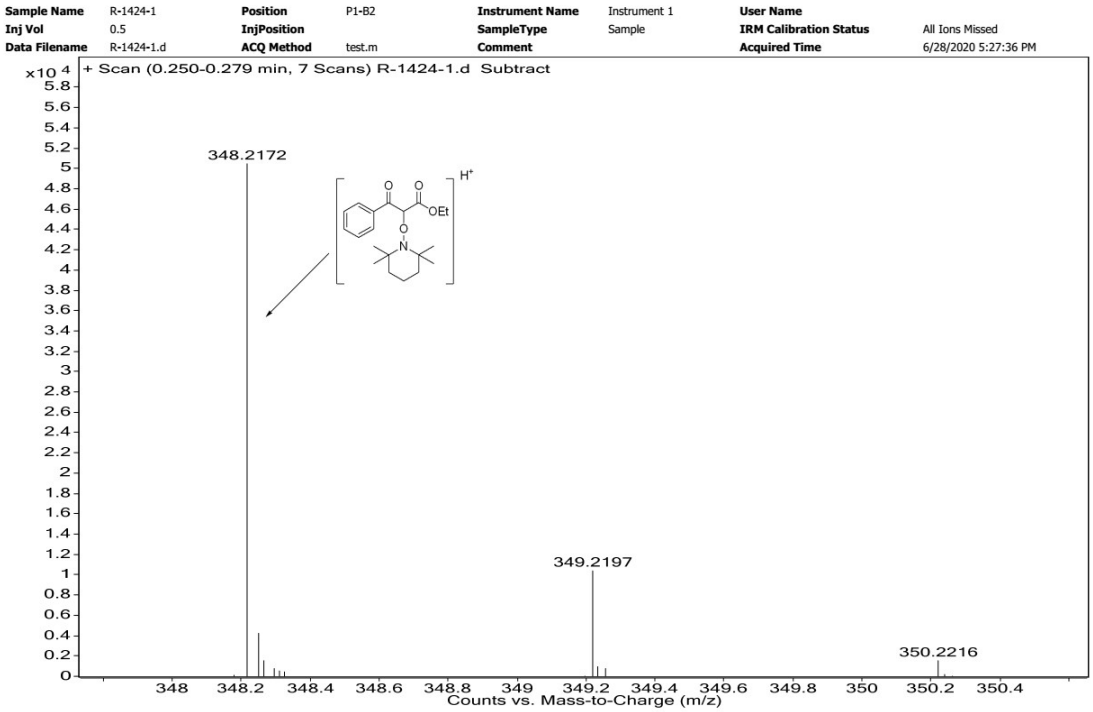


Figure S1. HRMS spectrum of compound compound [**I**+H]+ for exp 1

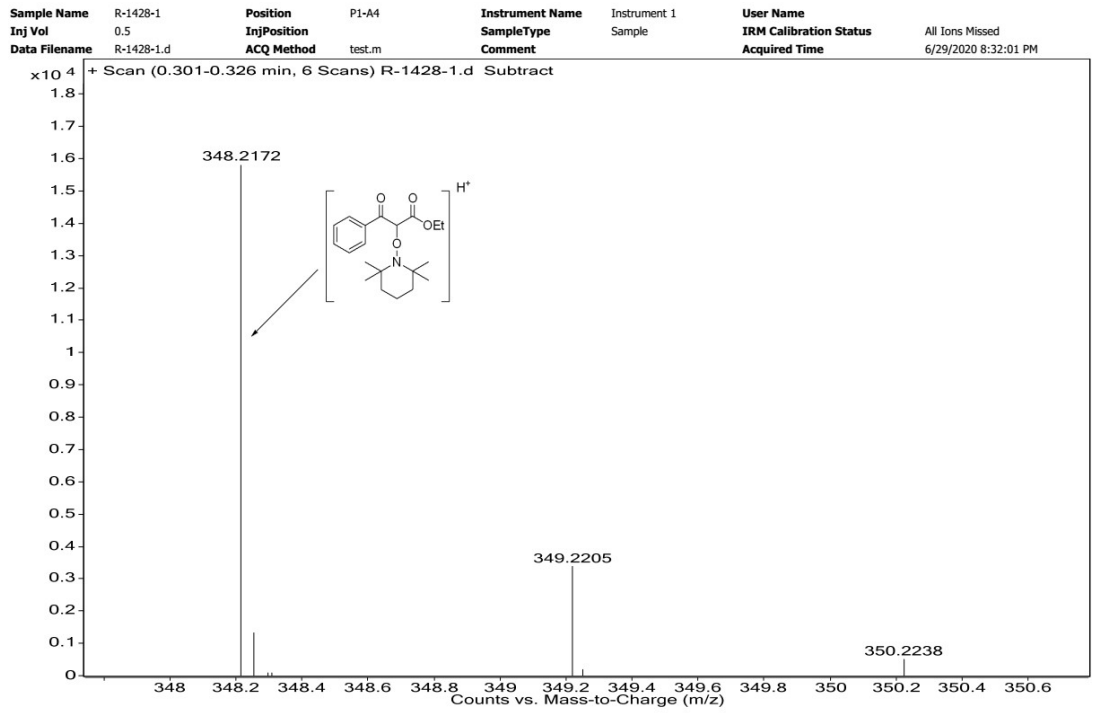


Figure S2. HRMS spectrum of compound compound [**I**+H]$^+$ for exp 2

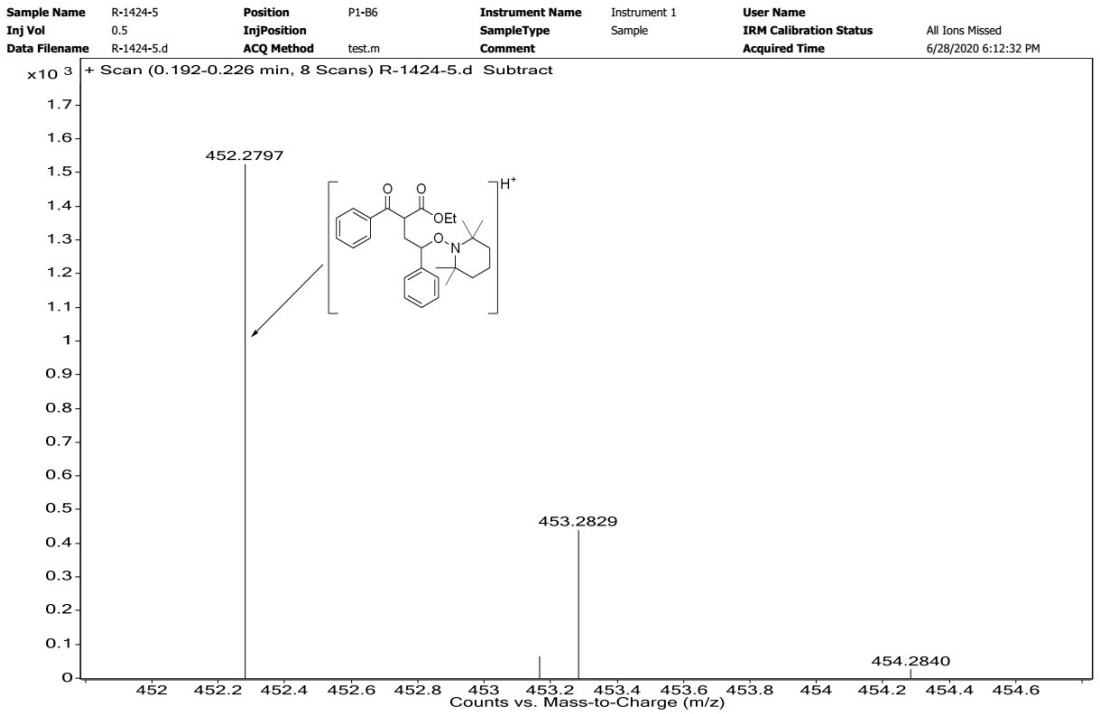


Figure S3. HRMS spectrum of compound compound [**II**+H]$^+$ for exp 1

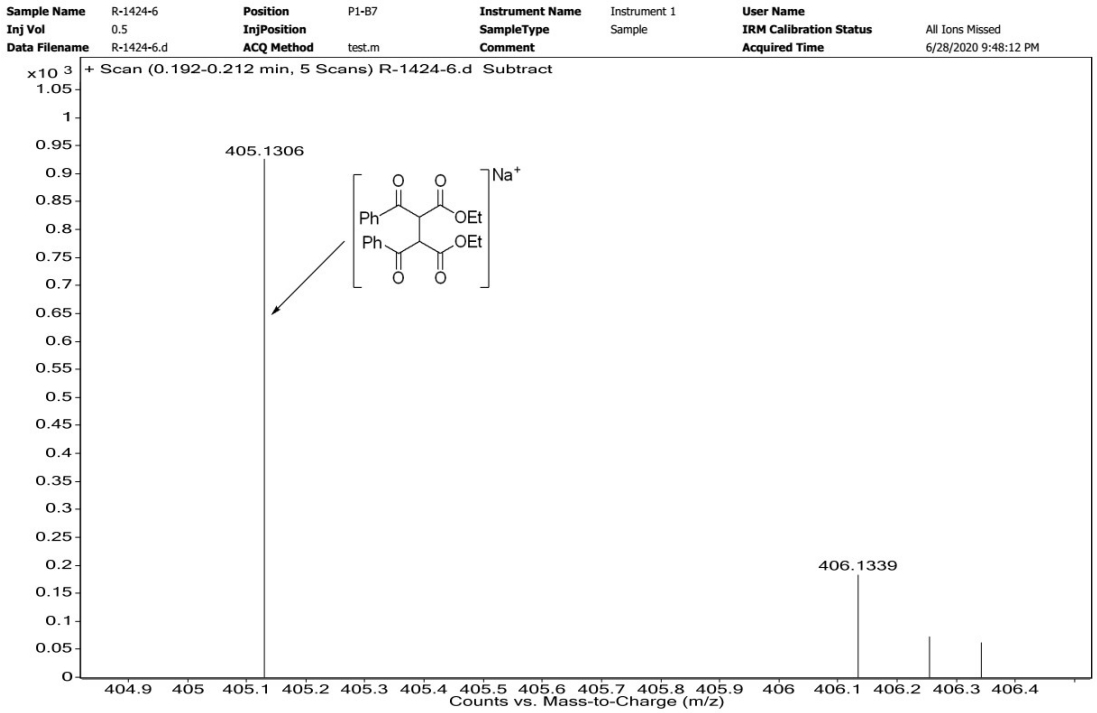


Figure S4. HRMS spectrum of compound compound [**III**+Na]$^+$ for exp 1

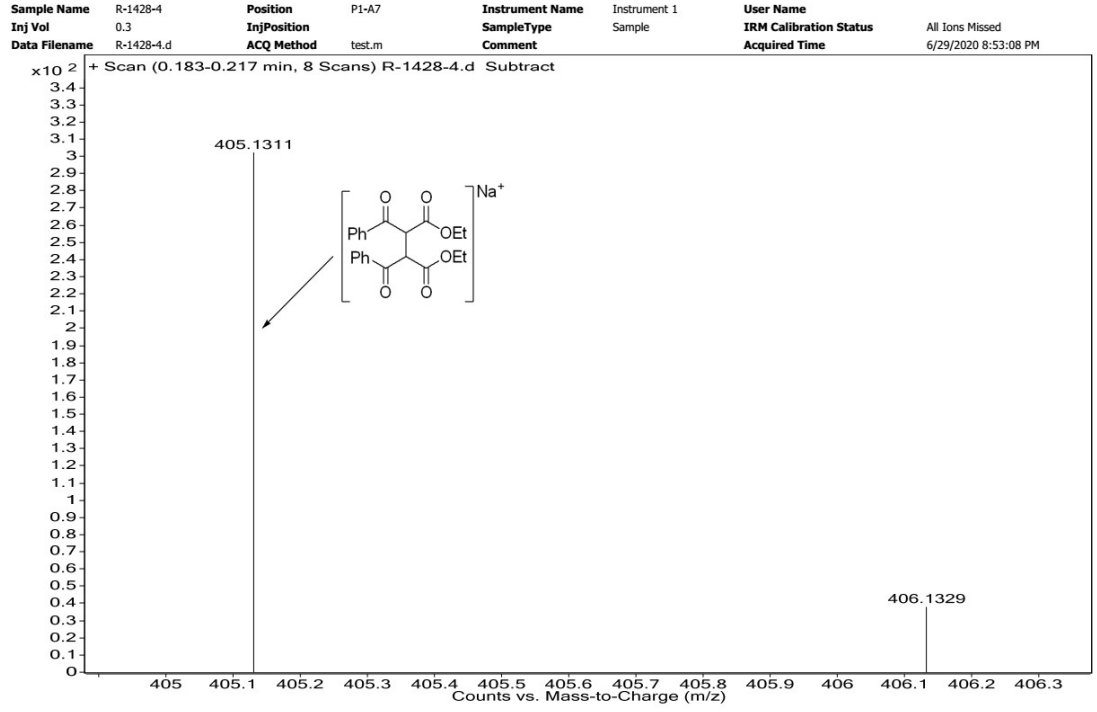


Figure S5. HRMS spectrum of compound compound [**III**+Na]$^+$ for exp 2

4. Property Test

1) UV/VIS Absorption spectra

The UV/VIS Absorption spectra were recorded in EtOH of a 0.05 mM solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.

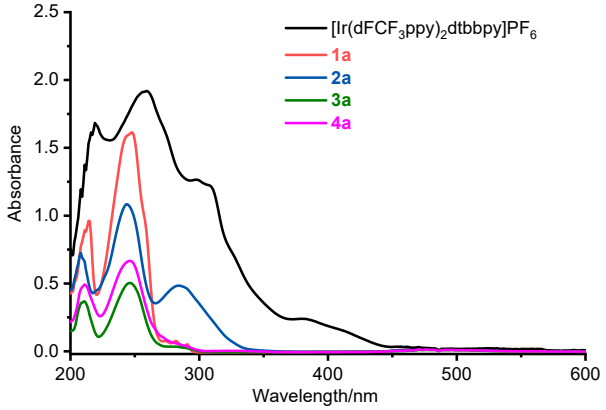


Figure S6. The UV/Vis absorption spectra of styrene **1a** (λ_{max} = 296 nm), ethyl benzoylacetate **2a** (λ_{max} = 340 nm), $Ir(dFCF_3ppy)_3(dtbbpy)PF_6$ (λ_{max} = 466 nm), **3a** (λ_{max} = 298 nm), **4a** (λ_{max} = 299 nm) in EtOH (0.05 mM).

2) Luminescence quenching experiments

Emission intensities were recorded using a F-4500 FL Spectrophotometer. First, $Ir(dFCF_3ppy)_3(dtbbpy)PF_6$ solutions were excited at 305 nm, the emission spectrum of a 5×10^{-5} M solution of $Ir(dFCF_3ppy)_3(dtbbpy)PF_6$ and different concentration of (0.5 mM-10 mM) ethyl benzoylacetate **2a** in EtOH in 10 mm path length quartz cuvette was collected.

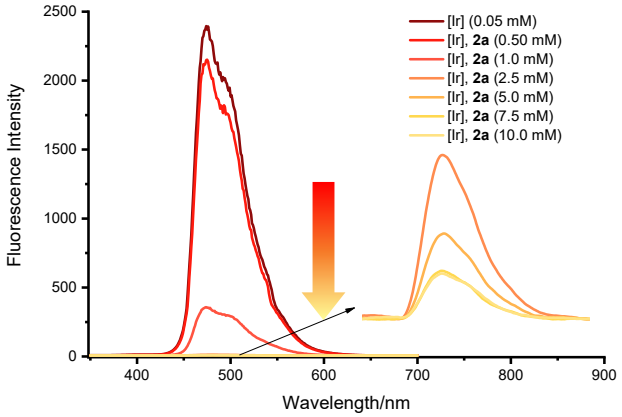


Figure S7. Luminescence quenching experiments of $Ir(dFCF_3ppy)_3(dtbbpy)PF_6$ with **2a**.

3) Cyclic voltammetry experiments

Cyclic voltammetry was measured in a glass cell with a CHI650A electrochemical workstation under Ar balloon protection with conventional three-electrode system. The working electrode was a steady glassy carbon disk electrode, and the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 5 mL of EtOH containing 0.1 M *n*-Bu_4NPF_6

were poured into the electrochemical cell. The CV of substrates were measured at the concentration of 1 mM. The scan rate was 0.05 V/s.

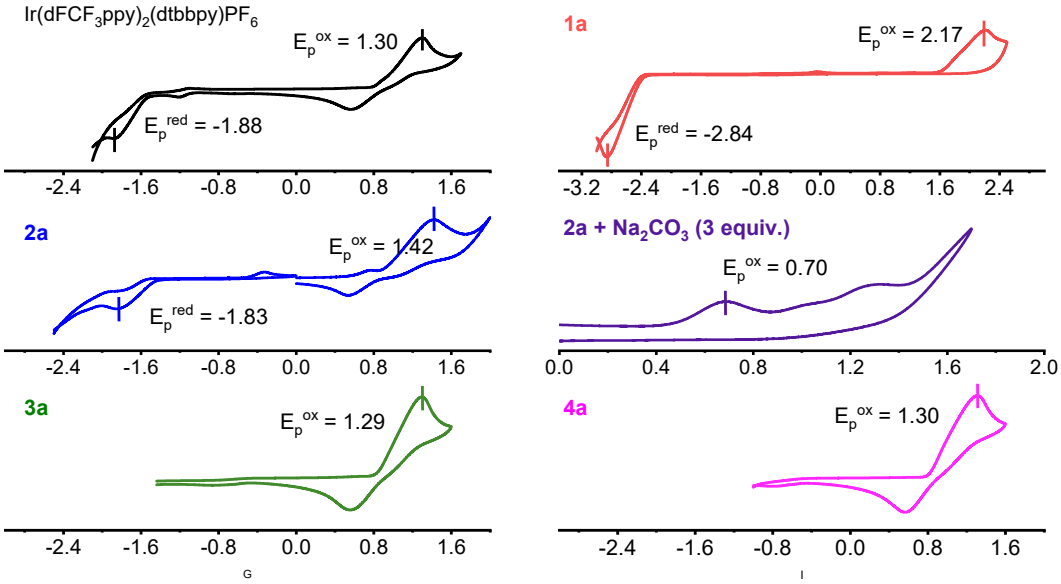


Figure S8. The CV of reaction reagents (1 mM in EtOH).

4) Data processing

With the reversible waves of all the reagents in hand, we calculated the excited redox potential, Eg of different reagents.

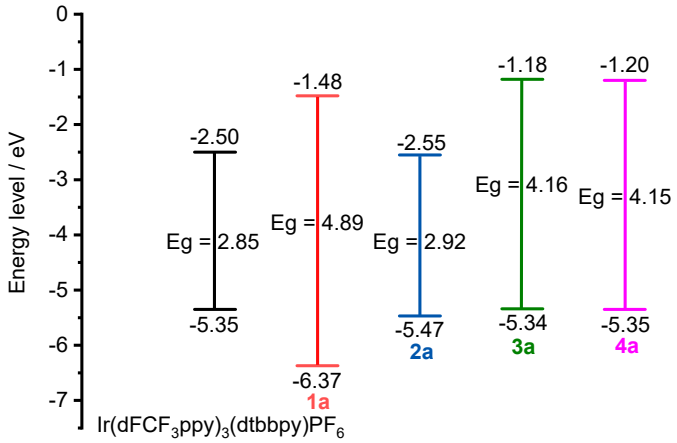


Figure S9. The E_{HOMO}, E_{LUMO} and Eg of different reagents

5. Computational Details

All the calculations were conducted by using the Gaussian 16 program package.[1] The B3LYP functional together with Becke-Johnson damping corrections[2] (abbreviated as B3LYP-D3BJ) and the 6-311+G(d,p) basis sets[3] were used for all the calculations. The polarizable continuum model (PCM) was employed to consider the solvent effect of EtOH. The intrinsic reaction coordinate (IRC)[4] analysis was carried out to confirm that all the saddle point connected the correct reactant and product on the potential energy surface. With the help of Multiwfn 3.7-dew[5] and VMD version 1.9.3 programs[6], we drawn and analyzed **TS1**, **TS2**. **TS3**, **TS4** and **TS5**.

1a

Sum of electronic and zero-point Energies= -309.625466

Sum of electronic and thermal Energies= -309.618685

Sum of electronic and thermal Enthalpies= -309.617741

Sum of electronic and thermal Free Energies= -309.657031

C	-1.35591500	1.32859500	0.00000200
C	0.01243700	1.09004700	-0.00000200
C	0.51370000	-0.22239700	-0.00000500
C	-0.40653400	-1.28119100	-0.00000500
C	-1.77853300	-1.04330900	-0.00000100
C	-2.25929400	0.26353900	0.00000300
H	-1.72252800	2.34865000	0.00000300
H	0.69580800	1.93048900	-0.00000500
H	-0.03695300	-2.30100600	-0.00000800
H	-2.47007100	-1.87784800	0.00000000
H	-3.32604800	0.45382800	0.00000600
C	1.95173500	-0.53200300	-0.00000800
H	2.18445400	-1.59432200	-0.00002800
C	2.96637200	0.33668800	0.00001300
H	2.81909200	1.41089300	0.00003600
H	3.99243100	-0.01049400	0.00000900

2a

Sum of electronic and zero-point Energies= -652.104209

Sum of electronic and thermal Energies= -652.090758

Sum of electronic and thermal Enthalpies= -652.089814

Sum of electronic and thermal Free Energies= -652.147022

C	2.34241400	-0.98487700	0.59531200
C	1.75689800	0.07990900	-0.10136700
C	2.55793900	1.15402500	-0.51372800
C	3.91744000	1.16367100	-0.23510100
C	4.49367300	0.09854500	0.45968500
C	3.70575800	-0.97364400	0.87375600
H	1.74447700	-1.82468900	0.92403600

H	2.09277700	1.96986200	-1.05156500
H	4.53036300	1.99690700	-0.55693600
H	5.55513200	0.10519600	0.67739800
H	4.15224700	-1.80016100	1.41287100
C	0.30418300	0.11962100	-0.42810000
C	-0.56116400	-1.06184400	0.01040100
H	-0.18840300	-1.97726100	-0.45236100
H	-0.49618600	-1.17427600	1.09470600
C	-1.99580200	-0.84958200	-0.40936800
O	-0.18966100	1.05545000	-1.03069700
O	-2.49082200	-1.29548300	-1.41751400
O	-2.64648100	-0.08532200	0.47590700
C	-4.01615000	0.26941700	0.14469400
H	-4.01359300	0.77791600	-0.82108500
H	-4.59811500	-0.64881600	0.04705300
C	-4.53187500	1.15706300	1.25525900
H	-5.56211600	1.45086400	1.04176000
H	-4.51467500	0.63199800	2.21262500
H	-3.92607200	2.06147500	1.34128100

3a

Sum of electronic and zero-point Energies=	-961.758720
Sum of electronic and thermal Energies=	-961.738028
Sum of electronic and thermal Enthalpies=	-961.737084
Sum of electronic and thermal Free Energies=	-961.812721

C	1.52918700	2.22508700	-0.91559300
C	2.00868900	1.65734100	0.27221800
C	2.82216300	2.42585300	1.11716400
C	3.14889900	3.73261500	0.78311800
C	2.66663400	4.28994900	-0.40243200
C	1.85800000	3.53509200	-1.24971300
H	0.90126900	1.65569100	-1.58760800
H	3.18641500	1.97665300	2.03189700
H	3.77731600	4.31899300	1.44250100

H	2.92100000	5.31013500	-0.66439600
H	1.48381400	3.96542400	-2.17053700
C	1.69605700	0.25937800	0.68705600
C	0.69399100	-0.54672400	-0.14588300
H	0.89202900	-0.37963100	-1.20680200
C	0.92194900	-2.02360100	0.13318200
O	2.18728900	-0.22842000	1.69006400
O	0.21994000	-2.72249100	0.82491100
O	2.02685700	-2.45122200	-0.48932700
C	2.42043900	-3.82956900	-0.24714800
H	2.55348000	-3.96296200	0.82785900
H	1.61057600	-4.48296600	-0.57641000
C	3.69982700	-4.07373300	-1.01540400
H	4.03184900	-5.10226400	-0.85681000
H	3.54552600	-3.92264800	-2.08584400
H	4.48985100	-3.40019300	-0.67698100
C	-0.74162400	-0.11319300	0.19966600
H	-0.80265800	0.97717800	0.20140700
H	-0.97004900	-0.45199300	1.21250400
C	-3.18053100	-0.25036900	-0.40809300
C	-3.72828200	0.93457800	-0.90924200
C	-3.93841100	-1.01046800	0.48861600
C	-5.00228800	1.35002300	-0.52715200
H	-3.15179400	1.53352700	-1.60672400
C	-5.21250700	-0.59913400	0.87367100
H	-3.52469400	-1.93179600	0.88530700
C	-5.74882100	0.58361900	0.36636200
H	-5.41303000	2.26928100	-0.92904900
H	-5.78760200	-1.20267600	1.56665800
H	-6.74087400	0.90379300	0.66283900
C	-1.78222000	-0.67450100	-0.78246900
H	-1.71691100	-1.76482800	-0.79057100
H	-1.54511200	-0.32511200	-1.79196900

4a

Sum of electronic and zero-point Energies= -961.755905

Sum of electronic and thermal Energies= -961.735229

Sum of electronic and thermal Enthalpies= -961.734285

Sum of electronic and thermal Free Energies= -961.809916

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C	-1.57275100	1.52477500	0.27177300
C	-1.89952400	2.84414900	0.61689600
C	-2.33139900	3.74177300	-0.35000600
C	-2.45693400	3.32832800	-1.67708000
C	-2.14686200	2.01629200	-2.02910700
H	-1.48670900	0.10029400	-1.34961500
H	-1.79980300	3.14670300	1.65114000
H	-2.57093800	4.76153500	-0.07344000
H	-2.79707500	4.02641000	-2.43290000
H	-2.25293800	1.68957100	-3.05650200
C	-1.10273000	0.62107400	1.36558900
C	3.15050000	0.84084000	0.26434500
O	3.54663900	1.90952600	-0.14310700
O	3.83771400	-0.30509200	0.12883700
C	5.11521800	-0.22481900	-0.55768700
H	4.94810700	0.19301900	-1.55204000
H	5.76236000	0.45874400	-0.00486500
C	5.68446800	-1.62490200	-0.61624700
H	6.65166400	-1.60667500	-1.12380500
H	5.83020000	-2.02743000	0.38833600
H	5.01897100	-2.29262700	-1.16747000
C	-0.35443600	-0.67936600	1.03745800
H	-0.07353400	-1.06376500	2.02290700
C	-1.28415500	-1.70604100	0.39952300
C	-0.94532500	-2.42278500	-0.75097400
C	-2.52536900	-1.95347600	0.99919500
C	-1.82817200	-3.35688400	-1.29263500
H	0.00586700	-2.25651600	-1.23949600

C	-3.40799100	-2.88293200	0.45919000
H	-2.80132400	-1.41194100	1.89719300
C	-3.06280600	-3.58845700	-0.69303200
H	-1.54700400	-3.90190000	-2.18629200
H	-4.36481700	-3.05651700	0.93767300
H	-3.74915500	-4.31192200	-1.11681200
C	0.94757100	-0.40886700	0.26512000
H	1.49706200	-1.34640100	0.17027000
H	0.73275500	-0.05635200	-0.74597300
O	-1.27259300	0.92950100	2.53393400
C	1.83916800	0.61724300	0.97967600
H	2.05810000	0.26834800	1.99390300
H	1.34854400	1.58786100	1.05594600

A

Sum of electronic and zero-point Energies=	-652.105315
Sum of electronic and thermal Energies=	-652.092330
Sum of electronic and thermal Enthalpies=	-652.091386
Sum of electronic and thermal Free Energies=	-652.146670

C	3.48976100	-1.72642500	-0.14345400
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C	1.86959800	0.07105500	-0.02582600
C	2.91725400	0.97913700	0.18230100
C	4.23452900	0.53616300	0.23447900
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H	3.71007500	-2.77832700	-0.27952600
H	1.38369200	-2.00470100	-0.38062500
H	2.68894600	2.02855900	0.30708300
H	5.03407600	1.24799500	0.40123700
H	5.55170600	-1.16170000	0.11143800
C	0.48055900	0.56464200	-0.06508000
C	-0.62279000	-0.23800500	0.01872200
H	-0.53294600	-1.30548200	0.13294900
C	-1.94437700	0.33814300	-0.02506600
O	0.37550700	1.89260300	-0.17338200

H	-0.59629900	2.09879300	-0.17159600
O	-2.17815300	1.54966300	-0.12571500
O	-2.92493200	-0.57037200	0.05830000
C	-4.28794200	-0.07069300	0.02699400
H	-4.42118500	0.62936900	0.85376600
H	-4.43793200	0.47280900	-0.90769700
C	-5.20612200	-1.26722700	0.14198500
H	-5.03343700	-1.80091800	1.07889900
H	-6.24621200	-0.93387900	0.12170500
H	-5.04950000	-1.95857100	-0.68865000

B

Sum of electronic and zero-point Energies=	-652.215012
Sum of electronic and thermal Energies=	-652.201566
Sum of electronic and thermal Enthalpies=	-652.200622
Sum of electronic and thermal Free Energies=	-652.257608

C	-1.18568500	0.77077700	-0.76804300
C	-1.37050900	-0.49701100	-0.13018700
C	-2.57382000	-0.65048600	0.63299400
C	-3.50723700	0.36701600	0.72910000
C	-3.31001800	1.59896300	0.08192200
C	-2.13106100	1.77742100	-0.66338900
H	-0.28086900	0.96511600	-1.32772800
H	-2.73968500	-1.59466500	1.13684700
H	-4.40731400	0.20812300	1.31620100
H	-4.04284800	2.39323900	0.16166200
H	-1.95045600	2.72448900	-1.16328000
C	-0.45301100	-1.59392100	-0.23067300
C	0.82329400	-1.44387300	-1.07929000
H	1.11153900	-2.43909900	-1.41928000
H	0.67305800	-0.79301800	-1.94167500
C	1.93183000	-0.90028800	-0.21881600
O	-0.62822000	-2.71017400	0.36933100
O	2.64415100	-1.56242500	0.51509700

O	2.02361900	0.44327500	-0.30232900
C	2.96171300	1.09965600	0.58569300
H	2.71265700	0.83134100	1.61441700
H	3.96646100	0.73002300	0.37050300
C	2.84455100	2.58973300	0.34718900
H	3.53943300	3.12125500	1.00203100
H	3.08882200	2.84029500	-0.68765600
H	1.83252400	2.93957800	0.56216500

C

Sum of electronic and zero-point Energies=	-652.211770
Sum of electronic and thermal Energies=	-652.198404
Sum of electronic and thermal Enthalpies=	-652.197460
Sum of electronic and thermal Free Energies=	-652.253487

C	3.48852900	-1.74833300	-0.00007300
C	2.17676500	-1.30872900	-0.00007300
C	1.85911400	0.08735400	0.00001200
C	2.96792600	0.99200400	0.00009100
C	4.27432900	0.53248300	0.00009000
C	4.56354900	-0.84216600	0.00001000
H	3.68656300	-2.81587400	-0.00014200
H	1.37979900	-2.04210500	-0.00014600
H	2.77089400	2.05606700	0.00015500
H	5.08749100	1.25214800	0.00015400
H	5.58766400	-1.19564700	0.00001000
C	0.52285000	0.56715300	0.00002200
C	-0.64884800	-0.22925200	-0.00001100
H	-0.56646500	-1.30533000	-0.00002400
C	-1.93065900	0.33175400	0.00000500
O	0.37454200	1.93741400	0.00007800
H	-0.60312300	2.09671000	0.00007300
O	-2.20924100	1.56784900	0.00001700
O	-2.95885200	-0.59372900	0.00001200
C	-4.29894100	-0.07854800	-0.00001700

H	-4.45116600	0.54841100	0.88297900
H	-4.45108600	0.54852200	-0.88294600
C	-5.24511800	-1.26324500	-0.00013400
H	-5.09463600	-1.88376100	0.88676800
H	-6.27991700	-0.91063300	-0.00014300
H	-5.09457600	-1.88363300	-0.88711600

D

Sum of electronic and zero-point Energies=	-651.648440
Sum of electronic and thermal Energies=	-651.635336
Sum of electronic and thermal Enthalpies=	-651.634392
Sum of electronic and thermal Free Energies=	-651.690010

C	1.03744800	-0.42272400	-1.05451700
C	1.18690300	0.60768100	-0.12222400
C	2.17919000	0.49463000	0.85539000
C	2.98597300	-0.64045600	0.92141500
C	2.82945400	-1.66495500	-0.01281600
C	1.85759200	-1.54743300	-1.00751900
H	0.26806300	-0.34293700	-1.81324900
H	2.31090000	1.29770300	1.57170000
H	3.73883100	-0.72399500	1.69748200
H	3.46114400	-2.54493300	0.03158600
H	1.73487600	-2.33594600	-1.74188500
C	0.36382000	1.87027400	-0.21535800
C	-1.04149200	1.83758400	-0.19666900
C	-1.94094700	0.78244800	0.12697300
O	1.02174700	2.94261900	-0.36206000
O	-3.17156700	0.83735000	-0.01583200
O	-1.36372800	-0.33700200	0.67999800
C	-2.18630700	-1.50743600	0.82629000
H	-1.68830100	-2.09651200	1.59790300
H	-3.17435000	-1.21758200	1.18604700
C	-2.28381600	-2.29021700	-0.47439400
H	-2.86681400	-3.20256000	-0.31793500

H	-2.77739300	-1.69658800	-1.24646000
H	-1.29024500	-2.57152400	-0.82999600
H	-1.53521900	2.77477200	-0.43147600

E

C	-3.30892000	-1.74782000	-0.40476500
C	-2.05503800	-1.14391600	-0.48986600
C	-1.86149800	0.17333100	-0.05438500
C	-2.96041300	0.87025900	0.46330000
C	-4.21024600	0.26492800	0.56670100
C	-4.39047900	-1.04830600	0.12999000
H	-3.44217200	-2.76329900	-0.76096700
H	-1.22695000	-1.69565500	-0.91776700
H	-2.81661200	1.89488300	0.78346200
H	-5.04521300	0.81693700	0.98406300
H	-5.36440000	-1.51912000	0.20047700
C	-0.52715300	0.89367900	-0.15200100
C	0.62213300	0.09177700	-0.01334000
H	0.49157000	-0.96166500	0.18688900
C	1.97206200	0.53886800	-0.07842000
O	-0.57239100	2.14043100	-0.32457300
O	2.42896800	1.66462900	-0.28526800
O	2.84601600	-0.52547200	0.13342000
C	4.24977700	-0.22756200	0.09784500
H	4.50373000	0.22603700	-0.86399200
H	4.48950400	0.49923200	0.87946000
C	5.00227700	-1.52733900	0.30796100
H	6.07921000	-1.33987700	0.28981500
H	4.74889900	-1.97497700	1.27221500
H	4.76666800	-2.24660700	-0.48041200

F

Sum of electronic and zero-point Energies= -651.457810

Sum of electronic and thermal Energies= -651.444432

Sum of electronic and thermal Enthalpies= -651.443488

Sum of electronic and thermal Free Energies= -651.500630

C	-0.95223600	-0.19642000	1.12363100
C	-1.16590700	0.67465000	0.04951000
C	-2.27340100	0.48519500	-0.78432800
C	-3.13813000	-0.58028800	-0.56619400
C	-2.91636500	-1.44985000	0.50243500
C	-1.82889200	-1.25072500	1.35272000
H	-0.11584400	-0.04176500	1.79416400
H	-2.43547000	1.17421400	-1.60342400
H	-3.98467000	-0.73383100	-1.22448600
H	-3.59280000	-2.27854300	0.67521800
H	-1.66480400	-1.91660900	2.19108900
C	-0.27433600	1.83772000	-0.19770100
C	1.12178300	1.84241400	0.24150300
C	2.03216400	0.69730500	0.31115500
O	-0.67189100	2.84098700	-0.79352400
O	3.04919000	0.71006800	0.97984000
O	1.62352900	-0.34208900	-0.42578100
C	2.39564400	-1.56834700	-0.32489200
H	3.39609900	-1.38098600	-0.71981800
H	2.48670900	-1.82993400	0.73080500
C	1.65384300	-2.62411100	-1.11349700
H	2.20114400	-3.56820600	-1.06684200
H	0.65482300	-2.78074200	-0.70177500
H	1.55912600	-2.33139800	-2.16108500
H	1.56406000	2.81081300	0.43582300

G

Sum of electronic and zero-point Energies= -651.457470

Sum of electronic and thermal Energies= -651.444056

Sum of electronic and thermal Enthalpies= -651.443112

Sum of electronic and thermal Free Energies= -651.500685

C	-3.33981000	-1.75081900	0.32772700
C	-2.06375700	-1.19606800	0.29742200
C	-1.88804100	0.15334600	-0.03590500
C	-3.01171700	0.93601900	-0.33399800
C	-4.28285000	0.37888800	-0.31332400
C	-4.44933900	-0.96731200	0.01772700
H	-3.46692900	-2.79301300	0.59397400
H	-1.21556200	-1.81728600	0.55422200
H	-2.86505400	1.97936700	-0.58135200
H	-5.14506100	0.98919900	-0.55359300
H	-5.44150900	-1.40240900	0.03577300
C	-0.54789200	0.81411300	-0.05780000
C	0.63850400	-0.03474400	-0.06795500
H	0.55372100	-1.08264000	-0.31803600
C	1.99802300	0.45672900	0.19111800
O	-0.44823200	2.04025500	-0.11335000
O	2.30159500	1.52850900	0.66991700
O	2.89214700	-0.49034300	-0.15799600
C	4.29043000	-0.16563200	0.05766400
H	4.52424200	0.74282800	-0.50119500
H	4.43577000	0.04264200	1.11969100
C	5.10664600	-1.34985700	-0.40959800
H	4.93745400	-1.54394900	-1.47072300
H	6.16896900	-1.14275400	-0.26217200
H	4.84871100	-2.24733200	0.15636400

H

Sum of electronic and zero-point Energies= -961.126277

Sum of electronic and thermal Energies= -961.105963

Sum of electronic and thermal Enthalpies= -961.105019

Sum of electronic and thermal Free Energies= -961.178109

C	-3.05059500	0.84125000	-0.66797900
C	-3.14676200	-0.43090200	-0.08814900
C	-4.38243200	-0.86304200	0.41301600

C	-5.49828500	-0.04104500	0.33965100
C	-5.39373300	1.22547900	-0.23823200
C	-4.17044000	1.66412100	-0.74086700
H	-2.11106700	1.20244700	-1.06501300
H	-4.44373600	-1.84778600	0.85773400
H	-6.44891100	-0.38229500	0.73139000
H	-6.26423200	1.86811500	-0.29612700
H	-4.08778500	2.64592800	-1.19071500
C	-1.98165800	-1.35725600	0.01946400
C	-0.61451700	-0.85551200	-0.45994300
H	-0.71110000	-0.46555900	-1.47479100
C	-0.14530600	0.26613700	0.45119200
O	-2.10527600	-2.48017300	0.46943100
O	-0.26825200	0.24625600	1.65541800
O	0.46476600	1.23449300	-0.23573300
C	1.11938800	2.28727800	0.53059500
H	0.35525400	3.01160300	0.81980500
H	1.54047200	1.84246800	1.43098300
C	2.18511600	2.89179900	-0.35544500
H	2.68484000	3.70360500	0.17843200
H	2.93077700	2.14015100	-0.61969700
H	1.75041500	3.29861500	-1.27098200
C	1.71296700	-1.59287800	-1.13708600
C	0.44646200	-1.99320900	-0.45666900
H	-0.00071500	-2.84419600	-0.97397300
H	0.61065900	-2.30549500	0.57614500
H	1.73667500	-1.68587300	-2.21830100
C	2.83793300	-1.00849700	-0.51630800
C	2.92802600	-0.78943200	0.88725600
C	3.94206000	-0.58535400	-1.31111300
C	4.03536400	-0.17040300	1.44257300
H	2.11482600	-1.09397700	1.53267000
C	5.04403400	0.02813300	-0.74419800
H	3.90044300	-0.74348300	-2.38317600

C	5.10095800	0.24661500	0.63797100
H	4.07327500	-0.00691500	2.51359500
H	5.86624200	0.34588300	-1.37524100
H	5.96227300	0.73245100	1.07995900

TS1

Sum of electronic and zero-point Energies=	-961.110919
Sum of electronic and thermal Energies=	-961.090290
Sum of electronic and thermal Enthalpies=	-961.089346
Sum of electronic and thermal Free Energies=	-961.163782

C	3.38736800	-0.52490100	1.08707400
C	3.31571000	0.14674000	-0.14162800
C	4.49360900	0.32598200	-0.88078400
C	5.71089300	-0.14520000	-0.40430200
C	5.77032700	-0.81480900	0.81910000
C	4.60575600	-1.00557000	1.56044000
H	2.50086100	-0.69276400	1.68363000
H	4.43434700	0.84078000	-1.83085100
H	6.61338100	0.00659900	-0.98456300
H	6.71806600	-1.18592800	1.19109800
H	4.64384800	-1.52867900	2.50844600
C	2.03580100	0.67388600	-0.73006600
C	0.84475700	0.64444300	0.10681900
H	0.95909700	0.43052900	1.15717000
C	-0.40377100	1.33662400	-0.22851800
O	2.02587800	1.09569500	-1.88947700
O	-0.75911800	1.74756700	-1.31631500
O	-1.16951400	1.44055800	0.88258000
C	-2.47826300	2.04631900	0.72432500
H	-2.34746600	3.05791300	0.33507700
H	-3.04146900	1.46587800	-0.00709700
C	-3.14530100	2.04389500	2.08198500
H	-4.14136500	2.48515900	1.99767500
H	-3.25367100	1.02495400	2.45781700

H	-2.57025500	2.62857200	2.80352900
C	-0.93373500	-1.75126200	0.29572400
C	0.17632100	-1.53748600	-0.47277000
H	1.13254500	-1.92137400	-0.14519900
H	0.10564500	-1.24807600	-1.51313700
H	-0.78608400	-2.12647700	1.30419400
C	-2.30287600	-1.44718800	-0.06438700
C	-2.68024500	-1.02904800	-1.35711400
C	-3.30422900	-1.55923300	0.92057100
C	-4.00298800	-0.72348800	-1.64192300
H	-1.93605900	-0.93959500	-2.13737800
C	-4.62661600	-1.24853500	0.63350400
H	-3.02666000	-1.88003400	1.91830800
C	-4.98134400	-0.82709200	-0.64895800
H	-4.27651200	-0.39969700	-2.63897300
H	-5.38097800	-1.32996300	1.40681800
H	-6.01229300	-0.58281600	-0.87541500

I

Sum of electronic and zero-point Energies=			-961.251650
Sum of electronic and thermal Energies=			-961.231043
Sum of electronic and thermal Enthalpies=			-961.230098
Sum of electronic and thermal Free Energies=			-961.304220
C	-1.17050100	1.56555000	-0.67115700
C	-0.05247600	2.20708800	-0.11172700
C	-0.06748700	3.60846500	0.01610100
C	-1.16452400	4.34744200	-0.39856900
C	-2.27538600	3.69782300	-0.95353600
C	-2.27230500	2.31408700	-1.09029700
H	-1.18942000	0.49562700	-0.80121800
H	0.79319600	4.09628600	0.45598300
H	-1.16529100	5.42581900	-0.28957600
H	-3.13406800	4.27464600	-1.27797500
H	-3.12714900	1.80756100	-1.52312300

C	1.11547900	1.46033500	0.40460000
C	0.98006900	-0.03086800	0.55437400
H	0.49829600	-0.46446000	-0.32259300
C	2.35703100	-0.64563000	0.65842500
O	2.13735800	2.04751400	0.78409600
O	2.91075100	-0.98769600	1.68100300
O	2.91321100	-0.78278000	-0.55882200
C	4.25732100	-1.32992600	-0.61228800
H	4.91371000	-0.69050500	-0.01905700
H	4.24527600	-2.32324700	-0.15967100
C	4.67293100	-1.37505200	-2.06632600
H	5.68382000	-1.78276600	-2.14367100
H	4.00084400	-2.01201200	-2.64564800
H	4.67197900	-0.37443800	-2.50416400
C	-1.39248600	-0.44630100	1.59193500
C	0.06807900	-0.39257900	1.83303300
H	0.32012100	0.32060100	2.62094900
H	0.46628400	-1.35762900	2.16345800
H	-1.99668400	0.39667900	1.90882600
C	-1.99118400	-1.41261400	0.77280200
C	-1.26971300	-2.50657600	0.17714700
C	-3.38761800	-1.35476900	0.42714800
C	-1.89358600	-3.44039600	-0.64206200
H	-0.21327700	-2.62758800	0.38933200
C	-3.98843800	-2.29185100	-0.39071900
H	-3.98092800	-0.53868200	0.83093500
C	-3.25781600	-3.36158100	-0.94470000
H	-1.29952900	-4.25072300	-1.05698200
H	-5.04799100	-2.19550600	-0.61310300
H	-3.73409300	-4.09185600	-1.58801700

J

Sum of electronic and zero-point Energies= -961.117053

Sum of electronic and thermal Energies= -961.096793

Sum of electronic and thermal Enthalpies= -961.095849

Sum of electronic and thermal Free Energies= -961.169101

C	-2.23010700	2.57292100	-1.17234600
C	-0.99753300	1.92849500	-1.18831700
C	-0.24756400	1.81466500	-0.01375000
C	-0.72708700	2.38926300	1.16686800
C	-1.95674600	3.04190400	1.17847300
C	-2.71465700	3.12635900	0.01149100
H	-2.81506100	2.63749500	-2.08188200
H	-0.62066600	1.49265500	-2.10518600
H	-0.13576600	2.32743800	2.07226500
H	-2.32149500	3.48433200	2.09768800
H	-3.67603200	3.62583700	0.02393000
C	1.05114300	1.09821100	-0.05430800
C	1.31903800	-0.01769500	0.68491500
C	2.59239900	-0.74274900	0.62301600
O	2.83777400	-1.76508300	1.23191000
O	1.88898500	1.66589900	-0.94055700
O	3.52060300	-0.16878100	-0.20034300
C	5.64794000	-0.01535100	-1.27823800
H	5.78760700	1.00152400	-0.90539200
H	6.63039600	-0.47951600	-1.38857100
H	5.17812400	0.03231400	-2.26300900
C	4.81000100	-0.83073400	-0.31889200
H	4.64099600	-1.84657500	-0.67842100
H	5.25695700	-0.88590800	0.67449400
C	0.26597600	-0.70057700	1.55291700
H	0.77006100	-1.09501100	2.43920700
H	-0.47119000	0.01720200	1.89778600
C	-0.38282700	-1.82786800	0.80901100
H	0.24166500	-2.69262400	0.60986200
C	-1.69188700	-1.83495400	0.28297600
C	-2.60960900	-0.75587200	0.43634100
C	-2.14880900	-2.97194900	-0.44787200

C	-3.88213900	-0.81865100	-0.10514200
H	-2.31047500	0.13526500	0.96955100
C	-3.42295500	-3.02237800	-0.98223800
H	-1.47103700	-3.80821600	-0.58130600
C	-4.30468400	-1.94620200	-0.81758000
H	-4.55402900	0.02278200	0.02135800
H	-3.73992900	-3.90061600	-1.53354000
H	-5.30180500	-1.98600200	-1.23924400
H	2.71342900	1.14030800	-0.96161400

TS2

Sum of electronic and zero-point Energies=	-961.221283
Sum of electronic and thermal Energies=	-961.202075
Sum of electronic and thermal Enthalpies=	-961.201131
Sum of electronic and thermal Free Energies=	-961.269586

C	1.06189600	-1.74400600	-1.14287000
C	0.71590300	-1.41584600	0.17828100
C	1.69582600	-1.56670600	1.17874500
C	2.97186800	-2.01311800	0.86331100
C	3.30651000	-2.33533000	-0.45597700
C	2.34176600	-2.19845800	-1.45269800
H	0.31082100	-1.66861400	-1.91873700
H	1.44630900	-1.31802600	2.20239600
H	3.71335700	-2.11264100	1.64874700
H	4.30222200	-2.68773100	-0.69906400
H	2.58243300	-2.45432100	-2.47895700
C	-0.62855100	-0.93725700	0.52216000
C	-1.61176600	-0.46774300	-0.44174000
C	-2.96025600	-0.54994800	-0.13127700
O	-3.46410200	-1.14663000	0.87871900
O	-3.80882900	0.10172500	-1.01399100
C	-5.12696600	0.42055500	-0.53598200
H	-5.71388600	0.59295000	-1.43985900
H	-5.54183300	-0.43753000	-0.00592100

C	-5.12015200	1.65758700	0.34994300
H	-6.14044100	1.90515700	0.65790500
H	-4.52360100	1.48511700	1.24829700
H	-4.70525900	2.51525400	-0.18582000
C	-0.10651000	1.19574500	0.07128800
C	-0.96118600	0.73534200	-1.10284700
H	-1.69422400	1.47081200	-1.45444700
H	-0.33936000	0.48083400	-1.96676000
O	-1.05621100	-1.36278700	1.73491700
H	-2.05702900	-1.28771800	1.69370700
C	1.26314900	1.58488700	0.01680500
C	2.06156500	1.47775200	-1.15388400
C	1.93649400	1.98869800	1.20444600
C	3.42782100	1.73092500	-1.12458400
H	1.60025700	1.18858300	-2.08899200
C	3.29841100	2.24142700	1.22375700
H	1.35973700	2.08166200	2.11971200
C	4.06705100	2.10979400	0.05854500
H	4.00488900	1.63052500	-2.03861900
H	3.77340600	2.54070900	2.15277900
H	5.13257000	2.30719400	0.07376400
H	-0.67447000	1.54353900	0.93018100

K

Sum of electronic and zero-point Energies=	-961.258528
Sum of electronic and thermal Energies=	-961.238885
Sum of electronic and thermal Enthalpies=	-961.237941
Sum of electronic and thermal Free Energies=	-961.308232

C	1.33010400	-2.04650500	-0.82862900
C	0.90181000	-1.36987900	0.31867300
C	1.78860600	-1.30943600	1.40219700
C	3.05438700	-1.88487300	1.34074300
C	3.46698700	-2.55522500	0.18737900
C	2.59435800	-2.63688400	-0.89458500

H	0.68751100	-2.12340600	-1.69608900
H	1.45768800	-0.79970200	2.29770300
H	3.72135800	-1.81361300	2.19370500
H	4.45037900	-3.00908800	0.13618500
H	2.89429700	-3.15980900	-1.79659700
C	-0.43864200	-0.62348000	0.47277500
C	-1.44736200	-1.00996100	-0.78243800
C	-2.85353000	-0.98830700	-0.31121400
O	-3.46359200	-1.97424700	0.06957100
O	-3.39910000	0.24405900	-0.28997600
C	-4.72617600	0.36834200	0.27191100
H	-5.41679500	-0.23746200	-0.31878900
H	-4.71248600	-0.02687100	1.28943900
C	-5.09722200	1.83576200	0.24236100
H	-6.09791700	1.96950700	0.66081900
H	-4.39537100	2.42683000	0.83493000
H	-5.09924400	2.21857600	-0.78087100
C	-0.31574100	0.82838800	-0.27929400
C	-0.91936000	0.21497800	-1.55422400
H	-1.66535800	0.82349800	-2.06672100
H	-0.16410600	-0.08737400	-2.28010700
O	-0.91832700	-0.62522400	1.70093900
C	0.99146000	1.54294200	-0.26987800
C	1.99122500	1.31717800	-1.22756800
C	1.28866500	2.42161900	0.78473500
C	3.23608500	1.93534100	-1.13168100
H	1.80232800	0.64113200	-2.05161900
C	2.53400900	3.03686500	0.88930100
H	0.52860700	2.61644800	1.53415600
C	3.51798000	2.79606500	-0.07036000
H	3.99036200	1.74159300	-1.88679600
H	2.73584700	3.70778300	1.71736500
H	4.48737200	3.27542000	0.00478200
H	-1.07056700	1.43291900	0.22451200

H	-1.27163200	-1.99065200	-1.22150700

L

Sum of electronic and zero-point Energies= -961.730266

Sum of electronic and thermal Energies= -961.710603

Sum of electronic and thermal Enthalpies= -961.709659

Sum of electronic and thermal Free Energies= -961.780804

C	0.73275400	-2.12455000	-0.72327300
C	0.71714100	-1.29371600	0.39841500
C	1.76971500	-1.39194800	1.31692100
C	2.80895300	-2.29294300	1.11628700
C	2.81819100	-3.11549000	-0.01021200
C	1.77501000	-3.02916500	-0.92647100
H	-0.05985400	-2.07781200	-1.45820100
H	1.76665100	-0.74971300	2.18662200
H	3.61586600	-2.35079500	1.83780200
H	3.62959000	-3.81592400	-0.16976100
H	1.76649100	-3.66506100	-1.80409100
C	-0.32226200	-0.21680900	0.62264200
C	-1.56966600	-0.30038000	-0.32510200
C	-2.82278900	0.28381000	0.26403300
O	-2.86169100	1.07569400	1.19084100
O	-3.90947800	-0.13446900	-0.38382800
C	-5.18898300	0.41425600	0.04802200
H	-5.32795800	0.16856400	1.10184600
H	-5.14567600	1.50009700	-0.04961900
C	-6.25714400	-0.19792100	-0.82931500
H	-7.23544500	0.19062600	-0.53752600
H	-6.08710200	0.04974500	-1.87905000
H	-6.27224300	-1.28449100	-0.72299900
C	0.06717300	1.14018700	-0.10955500
C	-0.86530500	0.72859000	-1.27078100
H	-1.48858100	1.51441400	-1.69592200
H	-0.35132500	0.21013800	-2.07803600

O	-0.55741500	-0.12129000	2.00669500
C	1.51458300	1.46732200	-0.30383700
C	2.25854600	0.97873000	-1.38240600
C	2.17748300	2.21670500	0.67559200
C	3.62587300	1.22668000	-1.47634700
H	1.77560900	0.38793300	-2.15010800
C	3.54493600	2.46269600	0.58836100
H	1.61284400	2.60152400	1.51811000
C	4.27569000	1.96651200	-0.49017900
H	4.18503400	0.83755700	-2.31961000
H	4.03910500	3.04279100	1.35938700
H	5.34018400	2.15672600	-0.56258800
H	-0.41341900	1.93685700	0.46215700
H	-1.80439000	-1.27046000	-0.75651400
H	-1.27610400	0.52242800	2.11167800

TS3

Sum of electronic and zero-point Energies=	-961.093066
Sum of electronic and thermal Energies=	-961.073602
Sum of electronic and thermal Enthalpies=	-961.072657
Sum of electronic and thermal Free Energies=	-961.143112

C	-3.35471000	0.34607200	-1.10233700
C	-2.89995100	0.04043600	0.20025500
C	-3.80487400	-0.59151300	1.08350300
C	-5.08404700	-0.93351800	0.66854200
C	-5.50874700	-0.64848500	-0.63100800
C	-4.63641400	0.00057800	-1.50759700
H	-2.71672300	0.89876800	-1.77870900
H	-3.48012600	-0.81599600	2.09066200
H	-5.75560600	-1.42853300	1.36090700
H	-6.50828000	-0.91595300	-0.95207000
H	-4.96453600	0.25468700	-2.50901100
C	-1.58237000	0.40412400	0.66843700
C	-0.39296200	0.44890800	-0.13176100

C	0.72421500	1.27283900	0.36853500
O	0.86133500	1.58968100	1.54808500
O	1.59022700	1.63164500	-0.57705100
C	2.79771100	2.33066600	-0.15663300
H	3.13038300	1.90434500	0.78871200
H	3.52047800	2.09262100	-0.93466200
C	2.55126000	3.82275900	-0.04940100
H	3.49031300	4.33014100	0.18572000
H	2.17302800	4.22045700	-0.99353700
H	1.83310900	4.04169800	0.74179300
C	0.33507400	-1.20583000	-0.54564500
C	-0.25876700	-0.22121500	-1.47431700
H	0.41292500	0.27643500	-2.16282600
H	-1.18366800	-0.52186900	-1.94859300
O	-1.47980800	0.55135800	2.01708700
H	-0.56892600	0.87269500	2.19828100
C	1.74617100	-1.48926800	-0.35208200
C	2.75310600	-1.00164900	-1.20650800
C	2.13492000	-2.29023800	0.74116300
C	4.09041300	-1.29415900	-0.96727200
H	2.48569800	-0.39565100	-2.06131000
C	3.47150700	-2.58053100	0.97622300
H	1.37108300	-2.67473200	1.40813400
C	4.45926200	-2.07967400	0.12521900
H	4.84958200	-0.91062600	-1.63924200
H	3.74723600	-3.19593900	1.82479200
H	5.50329700	-2.30344500	0.30913100
H	-0.35809100	-1.89238200	-0.07703400

M

Sum of electronic and zero-point Energies= -961.098690

Sum of electronic and thermal Energies= -961.078727

Sum of electronic and thermal Enthalpies= -961.077783

Sum of electronic and thermal Free Energies= -961.149773

C	-3.29754800	0.81618000	-0.81291700
C	-2.95544800	-0.17076400	0.15210400
C	-4.01558600	-0.94994500	0.69443000
C	-5.32157500	-0.76833400	0.27210500
C	-5.63535400	0.19471500	-0.69312300
C	-4.61020200	0.98683800	-1.22099400
H	-2.53228200	1.47073500	-1.20563000
H	-3.78337300	-1.69596700	1.44224800
H	-6.10821300	-1.38220600	0.69688700
H	-6.65901500	0.33269100	-1.01939800
H	-4.84264800	1.75428500	-1.95088100
C	-1.62622700	-0.36674800	0.60843700
C	-0.38305600	0.10667000	-0.04290100
C	0.55463900	0.82448800	0.87537000
O	0.64800900	0.53911700	2.05944900
O	1.31477900	1.73162000	0.27660100
C	2.42163700	2.28185300	1.05069800
H	2.00736000	2.83544700	1.89410300
H	3.00804000	1.44637300	1.43528700
C	3.22213400	3.16264000	0.11960300
H	4.05720900	3.60554500	0.66705900
H	3.62380100	2.58061800	-0.71165400
H	2.60529000	3.97036000	-0.27951800
C	0.39002800	-0.94724100	-0.93007200
C	-0.23681000	0.25886300	-1.53715900
H	0.40371000	1.06279600	-1.87185000
H	-1.12195600	0.10332700	-2.13672100
O	-1.45152700	-1.16778200	1.70288700
H	-0.60625900	-0.89997100	2.10915700
C	1.85716300	-1.13894200	-0.75920300
C	2.80035600	-0.40899400	-1.48689400
C	2.30793900	-2.06348800	0.19185700
C	4.16357700	-0.59172500	-1.26451400
H	2.47020800	0.30711900	-2.22875200

C	3.66850700	-2.24836100	0.41444500
H	1.58137100	-2.62836100	0.76568100
C	4.60214100	-1.50906300	-0.31206700
H	4.88235300	-0.01690100	-1.83685900
H	4.00086300	-2.96483800	1.15656700
H	5.66246700	-1.64904200	-0.13788200
H	-0.17690700	-1.86750400	-1.01456900

TS4

Sum of electronic and zero-point Energies=	-961.074480
Sum of electronic and thermal Energies=	-961.055214
Sum of electronic and thermal Enthalpies=	-961.054270
Sum of electronic and thermal Free Energies=	-961.123613

C	-0.94696300	2.03237200	-0.86949400
C	-0.78966200	1.32108900	0.32267000
C	-1.86157000	1.25192300	1.22167900
C	-3.07010500	1.86795400	0.92363800
C	-3.22709400	2.56355200	-0.27595700
C	-2.16120600	2.64703200	-1.16788400
H	-0.11351700	2.12018700	-1.55490300
H	-1.74237700	0.70326900	2.14633600
H	-3.89404000	1.80130700	1.62440300
H	-4.17150300	3.04100900	-0.50913000
H	-2.26841400	3.19952400	-2.09403200
C	0.48071000	0.61849600	0.65238400
C	1.54012600	0.44353400	-0.33817200
C	2.91963000	0.43763600	0.06031800
O	3.32279300	0.73833200	1.19391700
O	3.75654400	0.06152900	-0.92820000
C	5.16781100	-0.03111200	-0.60268500
H	5.66872100	0.07375700	-1.56389000
H	5.43644800	0.80788300	0.03871200
C	5.49336900	-1.36040900	0.05475100
H	6.57140900	-1.43364800	0.22016500

H	4.99057500	-1.44818300	1.01895600
H	5.18597300	-2.19195700	-0.58321100
C	0.14228500	-1.18153700	-0.14620600
C	0.94810500	-0.57623800	-1.28375700
H	1.69008600	-1.23824600	-1.72990700
H	0.33532200	-0.15936600	-2.08313500
O	0.79157800	0.72993700	1.97032600
H	1.76666200	0.62795100	2.03995500
C	-1.26905800	-1.54397200	-0.19655200
C	-2.11517500	-1.16740300	-1.25234000
C	-1.83072200	-2.23622400	0.89245000
C	-3.46993100	-1.47697400	-1.22109900
H	-1.71689600	-0.62057600	-2.09632600
C	-3.18477000	-2.54142600	0.92358200
H	-1.19043600	-2.52647500	1.71831500
C	-4.01282700	-2.16100800	-0.13410200
H	-4.10664300	-1.17724800	-2.04537800
H	-3.59765200	-3.07557100	1.77152000
H	-5.07040900	-2.39561000	-0.11027500
H	0.74164800	-1.79009600	0.52413300

N

Sum of electronic and zero-point Energies= -961.087020

Sum of electronic and thermal Energies= -961.066686

Sum of electronic and thermal Enthalpies= -961.065741

Sum of electronic and thermal Free Energies= -961.139420

C	-0.15511200	1.81846600	-0.81473300
C	-0.52848600	1.18176800	0.36852300
C	-1.67778900	1.61162600	1.04010200
C	-2.44423900	2.65241600	0.52937300
C	-2.07106900	3.27942000	-0.66080200
C	-0.92358200	2.86243700	-1.32932800
H	0.73471500	1.49662400	-1.34329300
H	-1.96520400	1.11995000	1.96065600

H	-3.33579500	2.97361600	1.05543700
H	-2.67038100	4.08914700	-1.06029700
H	-0.62249000	3.34931400	-2.24957800
C	0.23492000	-0.00283100	0.91655200
C	1.46682600	-0.42269200	0.15846200
C	2.79824600	0.08583900	0.32959200
O	3.05902900	1.04017200	1.05534700
O	3.72015900	-0.58926500	-0.38439800
C	5.09209500	-0.13424400	-0.26323500
H	5.14078900	0.91057200	-0.57698300
H	5.38449500	-0.18667700	0.78754400
C	5.94294500	-1.02997500	-1.13592600
H	6.98810200	-0.71849600	-1.07309700
H	5.87289000	-2.06979600	-0.80980200
H	5.62709800	-0.96874300	-2.17947400
C	-0.36859700	-1.42825800	0.52940400
C	0.84072600	-1.63658300	-0.44251800
H	1.39070700	-2.57476100	-0.33854100
H	0.58555900	-1.51449300	-1.50071600
O	0.42447500	0.08843600	2.32465400
H	1.03544400	0.82435900	2.46830700
C	-1.78173000	-1.50205300	0.03697700
C	-2.14594800	-1.07619500	-1.24484600
C	-2.78803600	-1.94135700	0.90349600
C	-3.47858900	-1.08503300	-1.64670700
H	-1.39073900	-0.71648700	-1.93226300
C	-4.12301700	-1.95099300	0.50595600
H	-2.52040000	-2.27347400	1.90078500
C	-4.47305400	-1.52057000	-0.77215200
H	-3.74122900	-0.74703800	-2.64251300
H	-4.88765400	-2.29509700	1.19286100
H	-5.51062600	-1.52565900	-1.08502400
H	-0.24364700	-2.05473100	1.41202900

CO_3^{2-}

Sum of electronic and zero-point Energies= -264.130361

Sum of electronic and thermal Energies= -264.127156

Sum of electronic and thermal Enthalpies= -264.126212

Sum of electronic and thermal Free Energies= -264.155914

C	0.00000000	0.00013000	0.00000000
O	-0.23275000	-1.27836200	0.00000000
O	-0.99077500	0.84016900	0.00000000
O	1.22352500	0.43809500	0.00000000

HCO_3^-

Sum of electronic and zero-point Energies= -264.629126

Sum of electronic and thermal Energies= -264.625589

Sum of electronic and thermal Enthalpies= -264.624645

Sum of electronic and thermal Free Energies= -264.654893

C	-0.14275600	0.05430500	-0.00000900
O	-1.16831100	-0.64810300	-0.00007000
O	-0.01051400	1.29792100	-0.00000300
O	1.06397400	-0.68632600	0.00006600
H	1.77534400	-0.03376500	0.00011500

Ir(III)

Sum of electronic and zero-point Energies= -2943.105227

Sum of electronic and thermal Energies= -2943.053989

Sum of electronic and thermal Enthalpies= -2943.053045

Sum of electronic and thermal Free Energies= -2943.196513

C	-2.25211600	-0.03677400	-1.40557600
C	-3.05455900	-1.14319900	-1.68797900
H	-2.97530800	-2.06401300	-1.12613600
C	-3.98139900	-1.06696900	-2.71441900
C	-4.16222400	0.06931600	-3.49099800
H	-4.89167800	0.10626900	-4.28732300
C	-3.36598300	1.15923000	-3.19995700
C	-2.40974200	1.15033300	-2.17698800

C	-1.53558500	2.26082900	-1.82273200
C	-1.49579900	3.52793100	-2.42104700
H	-2.16493100	3.75394900	-3.23392100
C	-0.60075600	4.48088000	-1.97204100
H	-0.56631400	5.45743500	-2.43718100
C	0.26035500	4.16393200	-0.92076100
C	0.18710500	2.90459100	-0.35660400
H	0.83206600	2.61617900	0.45839900
C	1.22303100	5.17717400	-0.37923000
C	-2.23260200	0.50162400	1.36260900
C	-2.77431800	1.75919500	1.63166100
H	-2.47345300	2.63962400	1.08013100
C	-3.72453700	1.89064100	2.63079600
C	-4.17821300	0.82215700	3.39210700
H	-4.92040900	0.94822700	4.16726400
C	-3.63804900	-0.41798300	3.11465200
C	-2.67423200	-0.62151000	2.11935200
C	-2.05807600	-1.89794500	1.78188800
C	-2.32582100	-3.14470900	2.36490600
H	-3.06028300	-3.21903000	3.14891300
C	-1.65222500	-4.27141900	1.93393300
H	-1.86084700	-5.23406100	2.38267600
C	-0.70572300	-4.15139700	0.91466200
C	-0.47339900	-2.90575600	0.36471400
H	0.24307800	-2.76545500	-0.42923800
C	0.05700900	-5.35006200	0.43774800
C	0.77823800	-0.84429300	-2.54476700
H	-0.22004400	-0.86257800	-2.96029800
C	1.88271000	-1.18926700	-3.29939600
H	1.73351100	-1.48113800	-4.32956200
C	3.16118000	-1.16164700	-2.72705800
C	3.24066700	-0.76775700	-1.39239700
H	4.19843600	-0.72839200	-0.90030800
C	2.09447600	-0.42767200	-0.67700500

C	2.12173200	-0.00764100	0.74171200
C	3.29250900	0.12542100	1.47562200
H	4.23941300	-0.08044300	1.00068700
C	3.26413500	0.52985300	2.81466800
C	2.00639100	0.77534000	3.36793900
H	1.88971700	1.08517000	4.39543600
C	0.86808400	0.63143500	2.58943000
H	-0.11693300	0.82745500	2.99110200
C	4.38625300	-1.55618600	-3.54879300
F	-4.75086300	-2.14442000	-2.98102500
F	-3.54351900	2.26613600	-3.96039600
F	0.60259300	6.08702600	0.40672000
F	1.82683500	5.86804300	-1.36894700
F	2.19253000	4.60800200	0.36796700
F	-4.24032700	3.11265800	2.88502900
F	-4.08060500	-1.45826500	3.86094000
F	-0.77127100	-6.35183100	0.06914400
F	0.85680400	-5.84811400	1.40805800
F	0.84384600	-5.06799500	-0.62069500
Ir	-0.80567200	0.07341500	-0.00050400
N	-0.68119900	1.98206600	-0.79097600
N	-1.12827200	-1.81376800	0.78230400
N	0.87384000	-0.47645800	-1.25727000
N	0.91642200	0.26020000	1.30458400
C	4.48050900	-0.62803100	-4.77911900
H	3.59764400	-0.70655400	-5.41630300
H	5.35237300	-0.90123700	-5.37815000
H	4.58881500	0.41487200	-4.47129800
C	4.21669800	-3.02000100	-4.01084100
H	4.13645300	-3.69114900	-3.15218900
H	5.08483200	-3.32088700	-4.60204600
H	3.32658100	-3.14914600	-4.62945200
C	5.68836800	-1.44068900	-2.74266000
H	5.86547100	-0.41709500	-2.40280400

H	6.52941500	-1.72957900	-3.37593400
H	5.68718600	-2.10211600	-1.87258700
C	4.56966500	0.69106400	3.59083200
C	5.43603500	1.75558500	2.88230000
H	5.68668200	1.46245800	1.86080900
H	6.37072000	1.89219200	3.43126200
H	4.91641600	2.71609600	2.84404700
C	5.31449800	-0.66135900	3.60704600
H	4.71058100	-1.43177800	4.09250600
H	6.24942100	-0.55757900	4.16278300
H	5.56011500	-1.00410400	2.59995700
C	4.32594200	1.13802000	5.03961200
H	3.82312300	2.10717100	5.08491900
H	5.28534800	1.23764500	5.55101400
H	3.72837100	0.40951200	5.59307300

Ir(II)

Sum of electronic and zero-point Energies=	-2943.218010
Sum of electronic and thermal Energies=	-2943.166372
Sum of electronic and thermal Enthalpies=	-2943.165428
Sum of electronic and thermal Free Energies=	-2943.311629

C	2.19760800	-0.70310300	1.36140300
C	2.68624700	-1.99692800	1.56581600
H	2.36093300	-2.82785100	0.95331200
C	3.60406800	-2.22961500	2.57468700
C	4.08184900	-1.23002800	3.41284600
H	4.79858500	-1.43464600	4.19518100
C	3.59938800	0.04619500	3.19975200
C	2.66990100	0.35124100	2.19833100
C	2.11996300	1.67268400	1.92380700
C	2.41593300	2.86851700	2.59422800
H	3.12109000	2.86161700	3.40824800
C	1.80318000	4.04797900	2.21502000
H	2.02654600	4.97034800	2.73523900

C	0.88650900	4.03030100	1.16212200
C	0.62409900	2.83149100	0.52542300
H	-0.07813000	2.75969500	-0.29102500
C	0.22656000	5.29042300	0.69495000
C	2.28026300	-0.02649600	-1.40523200
C	3.16957400	1.02968300	-1.62459200
H	3.15793200	1.91711200	-1.00515300
C	4.08674000	0.94834800	-2.65739700
C	4.18006400	-0.14734400	-3.50623700
H	4.90367200	-0.18908900	-4.30766100
C	3.30321200	-1.18950500	-3.27819000
C	2.35121500	-1.17268300	-2.25188500
C	1.39995500	-2.23739100	-1.95889400
C	1.26623600	-3.46168600	-2.63043600
H	1.91601600	-3.68797500	-3.45900300
C	0.30688300	-4.37259600	-2.23042800
H	0.20562500	-5.31886700	-2.74583500
C	-0.52278900	-4.05791500	-1.15229500
C	-0.35707200	-2.84223500	-0.51530900
H	-0.96822700	-2.54891400	0.32439300
C	-1.60797000	-4.99403800	-0.71905600
C	-0.91120700	-0.79786100	2.52079300
H	0.05601100	-1.07400100	2.92301400
C	-2.05779000	-0.95346600	3.26340900
H	-1.98445900	-1.35041100	4.26589400
C	-3.31723400	-0.59997700	2.68779300
C	-3.30429400	-0.08978900	1.41226400
H	-4.23056300	0.18646800	0.93244000
C	-2.09550500	0.07347400	0.67942600
C	-2.02405300	0.59812100	-0.64247500
C	-3.13270000	1.10671500	-1.36786700
H	-4.10025400	1.11258200	-0.88570600
C	-3.00620100	1.60330100	-2.64704200
C	-1.70837200	1.58140500	-3.22858000

H	-1.52347200	1.94225800	-4.22845000
C	-0.65064900	1.09198300	-2.49130000
H	0.35171700	1.07470600	-2.90187000
C	-4.59982100	-0.81451200	3.49026000
F	4.06583600	-3.48751200	2.76594200
F	4.06868100	1.02035000	4.02045900
F	1.05725300	6.03968100	-0.06975300
F	-0.15014900	6.07206100	1.73048300
F	-0.87365300	5.04627400	-0.04797400
F	4.93870000	1.97991100	-2.86270500
F	3.39762000	-2.25855900	-4.10947400
F	-1.18175800	-6.27616400	-0.69190700
F	-2.66765200	-4.95940000	-1.56241900
F	-2.07800400	-4.69909600	0.51135900
Ir	0.82236000	-0.12267700	-0.00417400
N	1.22204300	1.69052500	0.89109800
N	0.57538800	-1.96236500	-0.90214100
N	-0.89800800	-0.31667500	1.26457200
N	-0.76963100	0.62209000	-1.24003900
C	-4.52303400	0.00156400	4.79845000
H	-3.66733800	-0.29373500	5.40878800
H	-5.42911900	-0.15272600	5.39109100
H	-4.43288400	1.06934800	4.58188100
C	-4.73221100	-2.31546300	3.82900500
H	-4.78146000	-2.91339600	2.91502900
H	-5.64480800	-2.49217900	4.40520300
H	-3.88580800	-2.67085400	4.42009500
C	-5.85397800	-0.37820700	2.71870600
H	-5.82228400	0.68486700	2.46638600
H	-6.73947400	-0.54872300	3.33570600
H	-5.97699300	-0.94793400	1.79408900
C	-4.22817200	2.17006800	-3.37974000
C	-4.76764400	3.38393900	-2.59302400
H	-5.08016400	3.10049100	-1.58583900

H	-5.63159000	3.81418000	-3.10800300
H	-4.00076300	4.15801900	-2.50393100
C	-5.32471100	1.08818200	-3.47002000
H	-4.96136500	0.21442500	-4.01740400
H	-6.19936300	1.48226100	-3.99551100
H	-5.64733700	0.75757200	-2.48077600
C	-3.88495200	2.62995300	-4.80541600
H	-3.13805800	3.42762000	-4.80361600
H	-4.78483100	3.01721500	-5.28929500
H	-3.50600900	1.80535100	-5.41447100

Ir(IV)

Sum of electronic and zero-point Energies= -2942.151301

Sum of electronic and thermal Energies= -2942.100017

Sum of electronic and thermal Enthalpies= -2942.099072

Sum of electronic and thermal Free Energies= -2942.241996

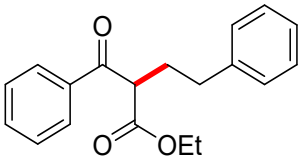
C	2.16412000	-0.42659900	1.47652700
C	2.62972300	-1.67803900	1.90797600
H	2.31878300	-2.59770900	1.42969100
C	3.52125000	-1.73108200	2.96824000
C	3.96721300	-0.58602300	3.63167300
H	4.66376800	-0.65122600	4.45799000
C	3.49078100	0.64714300	3.20320600
C	2.58702500	0.77124600	2.14472200
C	2.03063800	2.02272000	1.64276100
C	2.27315700	3.30998900	2.13561600
H	2.94077100	3.44608300	2.97204700
C	1.64968100	4.40268100	1.54678600
H	1.82766100	5.40200900	1.92583200
C	0.78683100	4.19914100	0.47020700
C	0.57476800	2.90568400	0.01389000
H	-0.08453100	2.69739400	-0.81709700
C	0.12501300	5.35000100	-0.23820000
C	2.23631000	-0.13794000	-1.43962200

C	3.02122100	0.95029300	-1.85234500
H	2.94758300	1.91960700	-1.37672300
C	3.92281200	0.77087900	-2.88969000
C	4.07549600	-0.45115900	-3.54834600
H	4.78577700	-0.56862600	-4.35703400
C	3.28715200	-1.51968100	-3.13801600
C	2.35599500	-1.40583200	-2.10266500
C	1.48637500	-2.47223700	-1.61909800
C	1.40793200	-3.78193300	-2.10619100
H	2.04652600	-4.09017900	-2.91922300
C	0.50721200	-4.67566400	-1.54057800
H	0.44255000	-5.69219200	-1.90979900
C	-0.30651000	-4.25273000	-0.49007100
C	-0.19088200	-2.94671600	-0.03429700
H	-0.79067400	-2.57593000	0.78504100
C	-1.34450900	-5.15636500	0.11875800
C	-0.84389700	-0.27388600	2.64402000
H	0.12783800	-0.48490400	3.07022300
C	-1.97558300	-0.20987900	3.43680600
H	-1.86684900	-0.37168200	4.50180600
C	-3.22706900	0.05864200	2.86134800
C	-3.25069400	0.24712500	1.47707500
H	-4.18481300	0.45887400	0.98003200
C	-2.08125300	0.17011800	0.72180400
C	-2.05080500	0.35844800	-0.74252000
C	-3.18910800	0.57582600	-1.50952900
H	-4.15422000	0.60972400	-1.02451500
C	-3.10685500	0.74678200	-2.89869400
C	-1.82771200	0.68763400	-3.46137200
H	-1.66807700	0.81048600	-4.52364100
C	-0.72177000	0.46689400	-2.65228400
H	0.27548000	0.42384900	-3.07003700
C	-4.48111600	0.13057700	3.72932700
F	3.98094700	-2.91692000	3.38194900

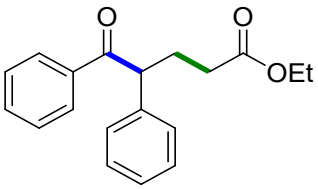
F	3.93165800	1.73482600	3.85634400
F	0.90026500	5.81567900	-1.24002800
F	-0.10770700	6.37439600	0.60267500
F	-1.05243100	4.97776000	-0.78257800
F	4.68242100	1.79801000	-3.28540800
F	3.44968200	-2.68499000	-3.78566800
F	-0.97686300	-6.44816400	0.04377800
F	-2.52812400	-5.03333300	-0.51918700
F	-1.55682300	-4.85370700	1.41644400
Ir	0.86481700	-0.10928200	0.00228900
N	1.18006400	1.85543500	0.58258700
N	0.68012700	-2.08960200	-0.58037500
N	-0.88825400	-0.08973000	1.31017500
N	-0.82233200	0.30751300	-1.32215600
C	-4.28073500	1.22653200	4.80029900
H	-3.42640600	1.01381800	5.44839100
H	-5.17235700	1.28708900	5.43113000
H	-4.12256300	2.20398300	4.33473300
C	-4.68087600	-1.23998300	4.41559300
H	-4.81405100	-2.03285000	3.67338500
H	-5.57453100	-1.20574100	5.04562300
H	-3.83180300	-1.50512000	5.05129500
C	-5.73731600	0.46306700	2.90907000
H	-5.65364700	1.43476200	2.41220300
H	-6.60108600	0.50711900	3.57749500
H	-5.94426900	-0.30044200	2.15273300
C	-4.37582100	0.97601700	-3.71686000
C	-5.09330900	2.23732400	-3.18514100
H	-5.38822500	2.13159000	-2.13756300
H	-6.00063100	2.41374100	-3.77011100
H	-4.45142900	3.11897100	-3.27292900
C	-5.29531800	-0.25594200	-3.55331400
H	-4.80221800	-1.16253000	-3.91674300
H	-6.21097800	-0.10719200	-4.13313200

H	-5.58164600	-0.41732000	-2.51036000
C	-4.06915000	1.17209600	-5.20969400
H	-3.42857500	2.04254800	-5.38169900
H	-5.00483800	1.33661400	-5.75041100
H	-3.58617300	0.29173000	-5.64446700

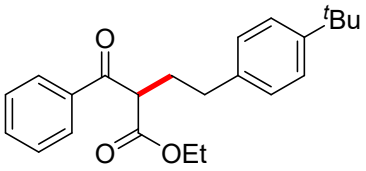
6. Characterization Data



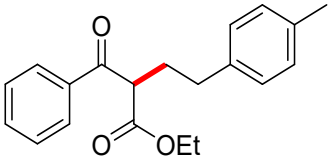
ethyl 2-benzoyl-4-phenylbutanoate (3a)[7] Yellow oil (66.7 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.85 (m, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.30-7.23 (m, 2H), 7.22-7.14 (m, 3H), 4.29 (t, J = 6.8 Hz, 1H), 4.14 (q, J = 7.0 Hz, 2H), 2.74-2.65 (m, 2H), 2.41-2.25 (m, 2H), 1.16 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 169.8, 140.8, 136.1, 133.5, 128.7, 128.6, 128.6, 128.5, 126.2, 61.4, 53.2, 33.5, 30.5, 14.0. HRMS (ESI), calcd. for $C_{19}H_{21}O_3$ $(M+H)^+$: 297.1485, found: 297.1484.



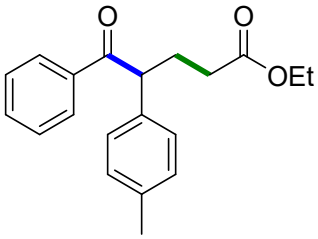
ethyl 5-oxo-4,5-diphenylpentanoate (4a)[8] Yellow oil (14.2 mg, 16 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.92 (m, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.32-7.26 (m, 4H), 7.24-7.17 (m, 1H), 4.68 (t, J = 7.3 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 2.52-2.40 (m, 1H), 2.32-2.25 (m, 2H), 2.23-2.12 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 173.3, 138.8, 136.6, 132.9, 129.1, 128.7, 128.5, 128.3, 127.3, 60.4, 52.4, 31.8, 28.8, 14.2. HRMS (ESI), calcd. for $C_{19}H_{21}O_3$ $(M+H)^+$: 297.1485, found: 297.1482.



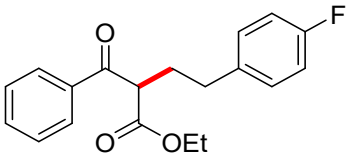
ethyl 2-benzoyl-4-(4-(tert-butyl)phenyl)butanoate (3b) Colorless oil (74.2 mg, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.82 (m, 2H), 7.58-7.52 (m, 1H), 7.47-7.39 (m, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 4.34-4.26 (m, 1H), 4.19-4.10 (m, 2H), 2.72-2.59 (m, 2H), 2.41-2.23 (m, 2H), 1.31 (s, 9H), 1.17 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 169.9, 149.0, 137.7, 136.1, 133.4, 128.6, 128.6, 128.3, 125.3, 61.3, 53.3, 34.3, 32.9, 31.4, 30.5, 14.0. HRMS (ESI), calcd. for $C_{23}H_{29}O_3$ $(M+H)^+$: 353.2111, found: 353.2110.



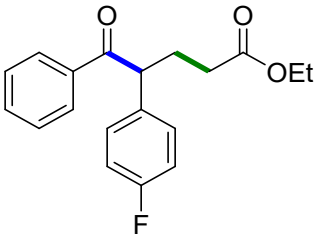
ethyl 2-benzoyl-4-(*p*-tolyl)butanoate (3c) Yellow oil (63.4 mg, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.84 (m, 2H), 7.60-7.52 (m, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.12-7.03 (m, 4H), 4.28 (t, J = 7.3 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 2.70-2.61 (m, 2H), 2.37-2.25 (m, 5H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 169.9, 137.7, 136.2, 135.7, 133.5, 129.2, 128.7, 128.6, 128.5, 61.4, 53.3, 33.1, 30.6, 21.0, 14.0. HRMS (ESI), calcd. for $C_{20}H_{23}O_3$ $(M+H)^+$: 311.1642, found: 311.1639.



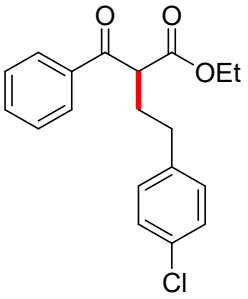
ethyl 5-oxo-5-phenyl-4-(*p*-tolyl)pentanoate (4c) Colorless oil (9.3 mg, 10 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.92 (m, 2H), 7.49-7.43 (m, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 4.63 (t, J = 7.3 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 2.48-2.38 (m, 1H), 2.32-2.25 (m, 5H), 2.20-2.11 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 173.3, 136.9, 136.7, 135.7, 132.9, 129.8, 128.7, 128.5, 128.2, 60.3, 52.0, 31.9, 28.8, 21.0, 14.2. HRMS (ESI), calcd. for $C_{20}H_{23}O_3$ $(M+H)^+$: 311.1642, found: 311.1639.



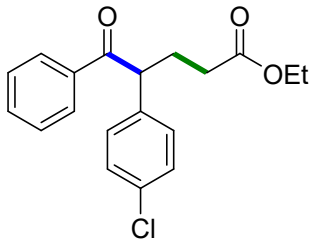
ethyl 2-benzoyl-4-(4-fluorophenyl)butanoate (3d) Colorless oil (57.6 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.86 (m, 2H), 7.62-7.55 (m, 1H), 7.49-7.42 (m, 2H), 7.17-7.08 (m, 2H), 7.01-6.92 (m, 2 H), 4.27 (t, J = 7.1 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.71-2.62 (m, 2H), 2.37-2.24 (m, 2H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 169.8, 161.5 (d, J = 244.3 Hz), 136.4 (d, J = 2.9 Hz), 136.2, 133.6, 130.0 (d, J = 8.1 Hz), 128.7, 128.6, 115.2 (d, J = 21.3 Hz), 61.5, 53.2, 32.7, 30.6, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -117.1. HRMS (ESI), calcd. for $C_{19}H_{20}FO_3$ $(M+H)^+$: 315.1391, found: 315.1390.



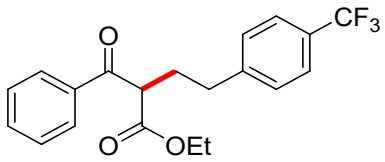
ethyl 4-(4-fluorophenyl)-5-oxo-5-phenylpentanoate (4d) Colorless oil (10.4 mg, 11 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.92 (m, 2H), 7.54-7.48 (m, 1H), 7.44-7.37 (m, 2H), 7.30-7.24 (m, 2H), 7.03-6.96 (m, 2H), 4.70 (t, J = 7.5 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 2.50-2.39 (m, 1H), 2.29 (t, J = 7.0 Hz, 2H), 2.20-2.09 (m, 1H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 173.2, 162.0 (d, J = 245.8 Hz), 136.4, 134.5 (d, J = 2.9 Hz), 133.1, 128.9 (d, J = 8.1 Hz), 128.7, 128.6, 115.9 (d, J = 21.3 Hz), 60.4, 51.4, 31.7, 28.8, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.2. HRMS (ESI), calcd. for $C_{19}H_{20}FO_3$ $(M+H)^+$: 315.1391, found: 315.1390.



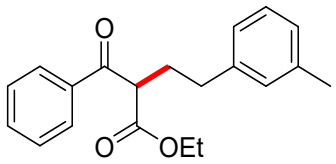
ethyl 2-benzoyl-4-(4-chlorophenyl)butanoate (3e) Colorless oil (65.3 mg, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.86 (m, 2H), 7.63-7.54 (m, 1H), 7.50-7.42 (m, 2H), 7.30-7.21 (m, 2H), 7.10 (d, J = 8.4 Hz, 2H), 4.26 (t, J = 7.0 Hz, 1H), 4.15 (q, J = 7.0 Hz, 2H), 2.66 (t, J = 7.7 Hz, 2H), 2.36-2.25 (m, 2H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 169.7, 139.2, 136.1, 133.6, 132.0, 129.9, 128.7, 128.6, 128.6, 61.5, 53.1, 32.8, 30.3, 14.0. HRMS (ESI), calcd. for $C_{19}H_{20}ClO_3$ $(M+H)^+$: 331.1095, found: 331.1099.



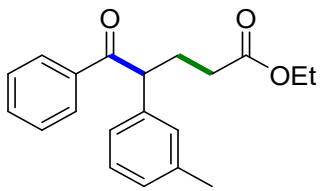
ethyl 4-(4-chlorophenyl)-5-oxo-5-phenylpentanoate (4e) Colorless oil (15.0 mg, 15 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.94 (m, 2H), 7.56-7.51 (m, 1H), 7.46-7.40 (m, 2H), 7.33-7.24 (m, 4H), 4.72 (t, J = 7.3 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 2.52-2.41 (m, 1H), 2.31 (t, J = 7.1 Hz, 2H), 2.21-2.11 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0, 173.1, 137.3, 136.3, 133.2, 133.2, 129.7, 129.2, 128.7, 128.6, 60.5, 51.5, 31.7, 28.7, 14.2. HRMS (ESI), calcd. for $C_{19}H_{20}ClO_3$ $(M+H)^+$: 331.1095, found: 311.1095.



ethyl 2-benzoyl-4-(4-(trifluoromethyl)phenyl)butanoate (3f) Colorless oil (32.9 mg, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.88 (m, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.51-7.44 (m, 2H), 7.33-7.28 (m, 2 H), 4.29 (t, J = 7.1 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.82-2.73 (m, 2H), 2.42-2.30 (m, 2H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.7, 169.7, 145.0, 136.1, 133.6, 128.9, 128.8, 128.6, 128.5, 125.4 (d, J = 3.7 Hz), 124.3 (d, J = 272.2 Hz), 61.6, 53.2, 33.3, 30.1, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.4. HRMS (ESI), calcd. for $C_{20}H_{20}F_3O_3$ $(M+H)^+$: 365.1359, found: 365.1356.

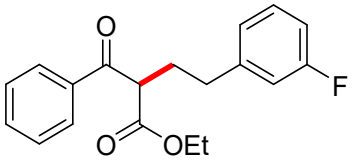


ethyl 2-benzoyl-4-(*m*-tolyl)butanoate (3g) Colorless oil (50.4 mg, 54 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.87 (m, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.49-7.41 (m, 2H), 7.17-7.09 (m, 4H), 4.33 (t, J = 7.1 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.74-2.63 (m, 2H), 2.35-2.20 (m, 5H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 169.9, 139.0, 136.1, 136.1, 133.5, 130.4, 129.1, 128.7, 128.6, 126.4, 126.0, 61.4, 53.7, 31.1, 29.3, 19.2, 14.0. HRMS (ESI), calcd. for $C_{20}H_{23}O_3$ $(M+H)^+$: 311.1642, found: 311.1639.

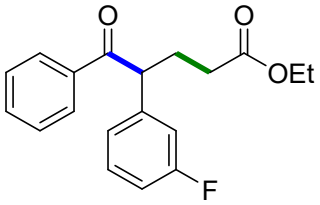


ethyl 5-oxo-5-phenyl-4-(*m*-tolyl)pentanoate (4g) Colorless oil (13.0 mg, 14 %). ^{1}H NMR (400 MHz,

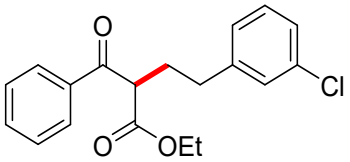
$CDCl_3$): δ 8.01-7.91 (m, 2H), 7.48 (t, J = 7.1 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.22-7.14 (m, 1H), 7.12-7.06 (m, 2H), 7.02 (d, J = 7.5 Hz, 1H), 4.63 (t, J = 7.3 Hz, 1H), 4.16-4.06 (m, 2H), 2.50-2.39 (m, 1H), 2.34-2.25 (m, 5H), 2.21-2.10 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 173.3, 138.7, 136.7, 132.9, 128.9, 128.8, 128.8, 128.5, 128.1, 125.5, 60.4, 52.4, 31.9, 28.8, 21.4, 14.2. HRMS (ESI), calcd. for $C_{20}H_{23}O_3$ $(M+H)^+$: 311.1642, found: 311.1644.



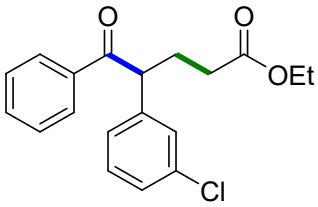
ethyl 2-benzoyl-4-(3-fluorophenyl)butanoate (3h) Yellow oil (47.3 mg, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.6 Hz, 2H), 7.66-7.55 (m, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.32-7.18 (m, 1H), 7.10-6.81 (m, 3 H), 4.41-4.05 (m, 3H), 2.69 (t, J = 7.8 Hz, 2H), 2.51-2.23 (m, 2H), 1.17 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 169.7, 162.9 (d, J = 245.8 Hz), 143.4 (d, J = 7.3 Hz), 136.1, 133.6, 129.9 (d, J = 8.1 Hz), 128.8, 128.6, 124.3 (d, J = 2.9 Hz), 115.4 (d, J = 20.5 Hz), 113.2 (d, J = 20.5 Hz), 61.5, 53.2, 33.2, 30.2, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.5. HRMS (ESI), calcd. for $C_{19}H_{20}FO_3$ $(M+H)^+$: 315.1391, found: 315.1392.



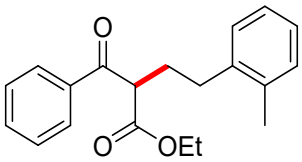
ethyl 4-(3-fluorophenyl)-5-oxo-5-phenylpentanoate (4h) Colorless oil (12.3 mg, 13 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.91 (m, 2H), 7.54-7.47 (m, 1H), 7.44-7.37 (m, 2H), 7.32-7.18 (m, 1H), 7.11-7.05 (m, 1 H), 7.02 (dt, J = 9.8 Hz, 2.3 Hz, 1H), 6.91 (tdd, J = 8.4, 2.6, 0.9 Hz, 1H), 4.71 (t, J = 7.3 Hz, 1H), 4.12 (qd, J = 7.1, 1.0 Hz, 2H), 2.50-2.39 (m, 1H), 2.29 (t, J = 6.9 Hz, 2H), 2.22-2.10 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 173.1, 163.1 (d, J = 247.2 Hz), 141.2 (d, J = 7.3 Hz), 136.4, 133.2, 130.5 (d, J = 8.8 Hz), 128.7, 128.6, 124.1 (d, J = 2.9 Hz), 115.2 (d, J = 22.0 Hz), 114.3 (d, J = 21.3 Hz), 60.4, 51.9, 31.7, 28.7, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.1. HRMS (ESI), calcd. for $C_{19}H_{19}FNaO_3$ $(M+Na)^+$: 337.1210, found: 337.1209.



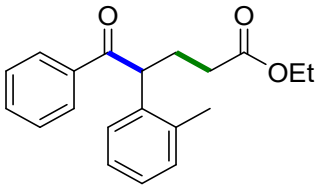
ethyl 2-benzoyl-4-(3-chlorophenyl)butanoate (3i) Yellow oil (63.6 mg, 64 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.87 (m, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.50-7.42 (m, 2H), 7.25-7.14 (m, 3H), 7.05 (dt, J = 6.9, 1.6 Hz, 1H), 4.27 (t, J = 7.0 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.67 (t, J = 7.6 Hz, 2H), 2.37-2.26 (m, 5H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 169.7, 142.9, 136.1, 134.3, 133.6, 129.8, 128.8, 128.7, 128.6, 126.8, 126.5, 61.5, 53.1, 33.1, 30.2, 14.0. HRMS (ESI), calcd. for $C_{19}H_{20}ClO_3$ $(M+H)^+$: 331.1095, found: 331.1096.



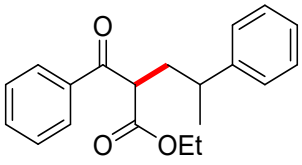
ethyl 4-(3-chlorophenyl)-5-oxo-5-phenylpentanoate (4i) Colorless oil (15.9 mg, 16 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.92 (m, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.45-7.39 (m, 2H), 7.33-7.29 (m, 1H), 7.25-7.17 (m, 3H), 4.69 (t, J = 7.3 Hz, 1H), 4.13 (qd, J = 7.2, 1.6 Hz, 2H), 2.50-2.40 (m, 1H), 2.30 (t, J = 7.2 Hz, 2H), 2.21-2.10 (m, 1H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 173.1, 140.8, 136.3, 134.8, 133.2, 130.3, 128.7, 128.7, 128.4, 127.6, 126.5, 60.5, 51.8, 31.7, 28.8, 14.2. HRMS (ESI), calcd. for $C_{19}H_{20}ClO_3$ $(M+H)^+$: 331.1095, found: 331.1098.



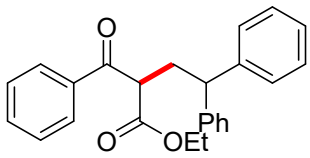
ethyl 2-benzoyl-4-(*o*-tolyl)butanoate (3j) Yellow oil (52.3 mg, 56 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.85 (m, 2H), 7.61-7.53 (m, 1H), 7.48-7.40 (m, 2H), 7.21-7.13 (m, 1H), 7.06-6.93 (m, 3H), 4.28 (t, J = 7.2 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.71-2.60 (m, 2H), 2.38-2.26 (m, 5H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 169.9, 140.7, 138.1, 136.2, 133.5, 129.4, 128.7, 128.6, 128.4, 126.9, 125.6, 61.4, 53.2, 33.4, 30.5, 21.4, 14.0. HRMS (ESI), calcd. for $C_{20}H_{23}O_3$ $(M+H)^+$: 311.1642, found: 311.1642.



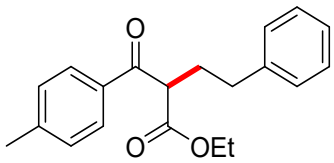
ethyl 5-oxo-5-phenyl-4-(*o*-tolyl)pentanoate (4j) Colorless oil (9.4 mg, 10 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.80 (m, 2H), 7.49-7.43 (m, 1H), 7.39-7.33 (m, 2H), 7.22-7.18 (m, 1H), 7.14-7.05 (m, 3H), 4.89-4.81 (m, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.53 (s, 3H), 2.49-2.33 (m, 3H), 2.10-2.00 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.0, 173.5, 138.7, 137.0, 135.3, 132.8, 131.1, 128.5, 128.4, 127.3, 127.2, 126.7, 60.4, 48.5, 32.0, 28.3, 19.8, 14.2. HRMS (ESI), calcd. for $C_{20}H_{23}O_3$ $(M+H)^+$: 311.1642, found: 311.1639.



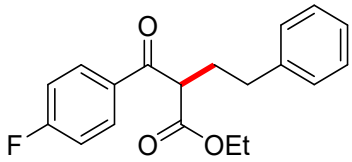
ethyl 2-benzoyl-4-phenylpentanoate (3k) Colorless oil (26.4 mg, 28 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.42 (m, 2H), 7.39-7.33 (m, 3H), 7.32-7.27 (m, 3H), 7.24-7.18 (m, 2H), 4.05 (q, J = 7.0 Hz, 2H), 2.43-2.31 (m, 2H), 2.21-2.10 (m, 2H), 1.61 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.9, 173.5, 143.1, 136.4, 131.8, 129.6, 129.1, 128.0, 127.2, 126.3, 60.4, 54.0, 35.2, 29.8, 23.5, 14.2. HRMS (ESI), calcd. for $C_{20}H_{23}O_3$ $(M+H)^+$: 311.1642, found: 311.1643.



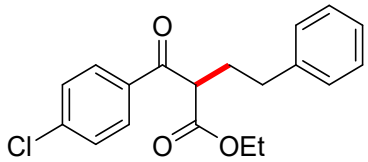
ethyl 2-benzoyl-4,4-diphenylbutanoate (3l) Colorless oil (76.5 mg, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.74 (m, 2H), 7.62-7.55 (m, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.37-7.20 (m, 10H), 4.24 (t, J = 7.2 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.04 (t, J = 7.7 Hz, 1H), 2.87-2.70 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 169.8, 143.6, 143.4, 136.0, 133.5, 128.6, 128.6, 128.6, 128.6, 128.1, 127.9, 126,6, 126.5, 61.4, 52.1, 48.7, 34.7, 14.0. HRMS (ESI), calcd. for $C_{25}H_{25}O_3$ $(M+H)^+$: 373.1798, found: 373.1795.



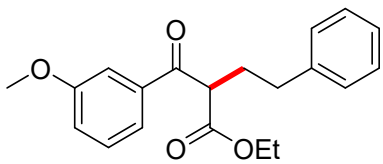
ethyl 2-(4-methylbenzoyl)-4-phenylbutanoate (3m) Colorless oil (58.8 mg, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.3 Hz, 2H), 7.31-7.26 (m, 2H), 7.25-7.15 (m, 5H), 4.26 (t, J = 7.1 Hz, 1H), 4.15 (qd, J = 7.2, 1.0 Hz, 2H), 2.74-2.64 (m, 2H), 2.40 (s, 3H), 2.38-2.26 (m, 2H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.7, 170.0, 144.4, 140.9, 133.7, 129.4, 128.8, 128.6, 128.5, 126.2, 61.4, 53.1, 33.5, 30.6, 21.7, 14.1. HRMS (ESI), calcd. for $C_{20}H_{22}NaO_3$ $(M+Na)^+$: 333.1461, found: 333.1463.



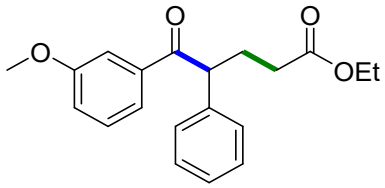
ethyl 2-(4-fluorobenzoyl)-4-phenylbutanoate (3n) Yellow oil (54.9 mg, 58 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.85 (m, 2H), 7.32-7.26 (m, 2H), 7.24-7.14 (m, 3H), 7.13-7.07 (m, 2H), 4.23 (t, J = 7.2 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.74-2.64 (m, 2H), 2.41-2.24 (m, 2H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 169.7, 166.0 (d, J = 256.0 Hz), 140.7, 132.5 (d, J = 2.9 Hz), 131.3 (d, J = 9.5 Hz), 128.6, 128.5, 126.3, 115.9 (d, J = 22.0 Hz), 61.5, 53.1, 33.4, 30.4, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.3. HRMS (ESI), calcd. for $C_{19}H_{20}FO_3$ $(M+H)^+$: 315.1391, found: 315.1390.



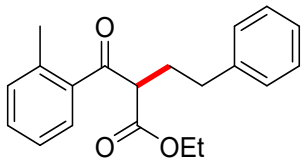
ethyl 2-(4-chlorobenzoyl)-4-phenylbutanoate (3o) Yellow oil (52.6 mg, 53 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.77 (m, 2H), 7.44-7.37 (m, 2H), 7.32-7.26 (m, 2H), 7.24-7.18 (m, 1H), 7.18-7.13 (m, 2H), 4.22 (t, J = 6.9 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.74-2.64 (m, 2H), 2.41-2.23 (m, 2H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.9, 169.6, 140.6, 140.0, 134.4, 130.0, 129.0, 128.6, 128.6, 126.3, 61.6, 53.1, 33.4, 30.4, 14.0. HRMS (ESI), calcd. for $C_{19}H_{20}ClO_3$ $(M+H)^+$: 331.1095, found: 331.1096.



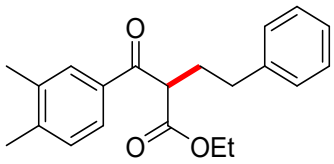
ethyl 2-(3-methoxybenzoyl)-4-phenylbutanoate (3p) Yellow oil (54.0 mg, 55 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.41 (m, 2H), 7.37-7.26 (m, 3H), 7.24-7.15 (m, 3H), 7.11 (ddd, J = 8.2, 2.5, 1.0 Hz, 1H), 4.26 (t, J = 7.2 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 2.75-2.64 (m, 2H), 2.40-2.26 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 169.8, 159.9, 140.8, 137.5, 129.7, 128.6, 128.5, 126.2, 121.2, 120.3, 112.6, 61.4, 55.4, 53.3, 33.5, 30.6, 14.0. HRMS (ESI), calcd. for $C_{20}H_{23}O_4$ $(M+H)^+$: 327.1591, found: 327.1592.



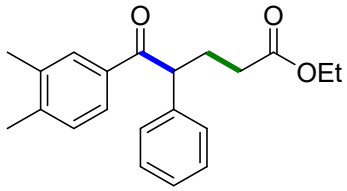
ethyl 5-(3-methoxyphenyl)-5-oxo-4-phenylpentanoate (4p)[9] Colorless oil (14.7 mg, 15 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.52 (m, 1H), 7.51-7.47 (m, 1H), 7.34-7.28 (m, 5H), 7.25-7.19 (m, 1H), 7.03 (ddd, J = 8.2, 2.6, 0.7 Hz, 1H), 4.66 (t, J = 7.3 Hz, 1H), 4.16-4.07 (m, 2H), 3.81 (s, 3H), 2.51-2.40 (m, 1H), 2.33-2.26 (m, 2H), 2.23-2.12 (m, 1H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 173.3, 159.7, 138.8, 137.9, 129.5, 129.1, 128.3, 127.3, 121.4, 119.5, 113.0, 60.4, 55.4, 52.6, 31.8, 28.8, 14.2. HRMS (ESI), calcd. for $C_{20}H_{23}O_4$ $(M+H)^+$: 327.1591, found: 327.1592.



ethyl 2-(2-methylbenzoyl)-4-phenylbutanoate (3q) Colorless oil (42.1 mg, 45%), keto-enol (10:1). ^{1}H NMR (400 MHz, $CDCl_3$): keto tautomer: δ 7.50 (d, J = 7.8 Hz, 1H), 7.36 (td, J = 7.5, 1.1 Hz, 1H), 7.31-7.26 (m, 2H), 7.24-7.13 (m, 5H), 4.21-4.07 (m, 3H), 2.76-2.64 (m, 2H), 2.47 (s, 3H), 2.32-2.24 (m, 2H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.08, 169.9, 140.8, 138.8, 137.2, 132.0, 131.6, 128.6, 128.5, 128.4, 126.2, 125.6, 61.3, 55.7, 33.5, 30.3, 21.0, 14.0. HRMS (ESI), calcd. for $C_{20}H_{22}NaO_3$ $(M+Na)^+$: 333.1461, found: 333.1466.

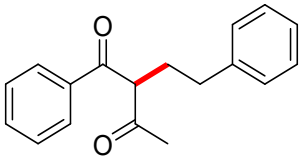


ethyl 2-(3,4-dimethylbenzoyl)-4-phenylbutanoate (3r) Yellow oil (61.5 mg, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.58 (m, 2H), 7.32-7.26 (m, 2H), 7.24-7.14 (m, 4H), 4.27 (t, J = 7.0 Hz, 1H), 4.20-4.10 (m, 2H), 2.76-2.61 (m, 2H), 2.38-2.23 (m, 8H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 170.1, 143.2, 140.9, 137.1, 134.0, 129.9, 129.7, 128.7, 128.5, 126.4, 126.2, 61.3, 53.0, 33.5, 30.6, 20.1, 19.8, 14.1. HRMS (ESI), calcd. for $C_{21}H_{25}O_3$ $(M+H)^+$: 325.1798, found: 325.1799.

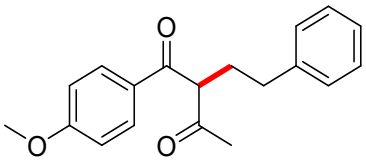


ethyl 5-(3,4-dimethylphenyl)-5-oxo-4-phenylpentanoate (4r) Colorless oil (7.8 mg, 8 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 1.5 Hz, 1H), 7.68 (dd, J = 7.8, 1.7 Hz, 1H), 7.31-7.27 (m, 4H), 7.23-7.17 (m, 1H), 7.12 (d, J = 8.0 Hz, 1H), 4.66 (t, J = 7.3 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 2.50-2.39 (m,

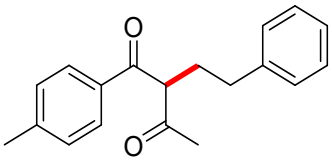
1H), 2.32-2.23 (m, 8H), 2.21-2.12 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 173.4, 142.6, 139.2, 136.9, 134.5, 129.9, 129.7, 129.0, 128.3, 127.2, 126.5, 60.4, 52.2, 31.9, 28.8, 20.0, 19.8, 14.2. HRMS (ESI), calcd. for $C_{21}H_{25}O_3$ $(M+H)^+$: 325.1798, found: 325.1797.



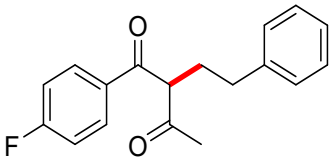
2-phenethyl-1-phenylbutane-1,3-dione (3s)[10] Yellow oil (62.5 mg, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.86 (m, 2H), 7.61-7.54 (m, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.31-7.24 (m, 2H), 7.23-7.18 (m, 1H), 7.17-7.11 (m, 2H), 4.43 (t, J = 7.0 Hz, 1H), 2.69-2.60 (m, 2H), 2.40-2.24 (m, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.1, 196.4, 140.7, 136.3, 133.8, 128.9, 128.7, 128.6, 128.6, 126.3, 62.2, 33.6, 30.5, 28.2. HRMS (ESI), calcd. for $C_{18}H_{19}O_2$ $(M+H)^+$: 267.1380, found: 267.1378.



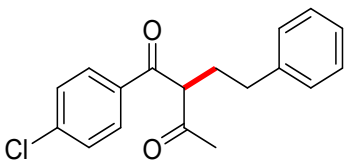
1-(4-methoxyphenyl)-2-phenethylbutane-1,3-dione (3t) Yellow oil (53.4 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.83 (m, 2H), 7.31-7.25 (m, 2H), 7.23-7.18 (m, 1H), 7.17-7.12 (m, 2H), 6.95-6.89 (m, 2H), 4.37 (t, J = 7.0 Hz, 1H), 3.86 (s, 3H), 2.70-2.57 (m, 2H), 2.39-2.20 (m, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.4, 194.7, 164.1, 140.9, 131.2, 129.4, 128.6, 128.5, 126.3, 114.0, 62.0, 55.6, 33.6, 30.5, 28.0. HRMS (ESI), calcd. for $C_{19}H_{21}O_3$ $(M+H)^+$: 297.1485, found: 297.1487.



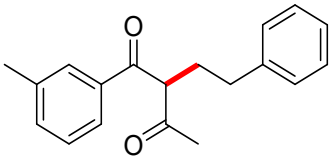
2-phenethyl-1-(*p*-tolyl)butane-1,3-dione (3u) Yellow oil (60.0 mg, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.3 Hz, 2H), 7.30-7.18 (m, 5H), 7.17-7.12 (m, 2H), 4.40 (t, J = 6.8 Hz, 1H), 2.67-2.57 (m, 2H), 2.40 (s, 3H), 2.36-2.22 (m, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.2, 196.0, 144.8, 140.8, 133.9, 129.6, 128.9, 128.6, 128.5, 126.3, 62.1, 33.6, 30.5, 28.1, 21.7. HRMS (ESI), calcd. for $C_{19}H_{21}O_2$ $(M+H)^+$: 281.1536, found: 281.1537.



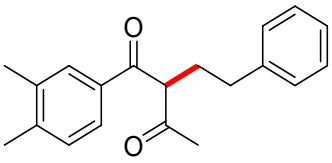
1-(4-fluorophenyl)-2-phenethylbutane-1,3-dione (3v) Yellow oil (56.4 mg, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.85 (m, 2H), 7.32-7.25 (m, 2H), 7.25-7.18 (m, 1H), 7.17-7.07 (m, 4H), 4.37 (t, J = 7.0 Hz, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.40-2.22 (m, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.0, 194.7, 166.1 (d, J = 256.8 Hz), 140.6, 132.7 (d, J = 2.9 Hz), 131.5 (d, J = 9.5 Hz), 128.6, 126.4, 116.0 (d, J = 22.0 Hz), 62.2, 33.5, 30.5, 28.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.8. HRMS (ESI), calcd. for $C_{18}H_{18}FO_2$ $(M+H)^+$: 285.1285, found: 285.1288.



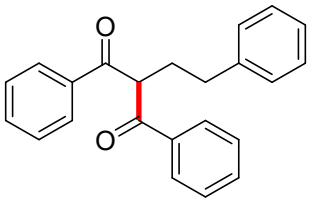
1-(4-chlorophenyl)-2-phenethylbutane-1,3-dione (3w) Orange oil (46.2 mg, 51 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.77 (m, 2H), 7.45-7.38 (m, 2H), 7.32-2.26 (m, 2H), 7.24-7.19 (m, 1H), 7.16-7.12 (m, 2H), 4.35 (t, J = 6.9 Hz, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.37-2.24 (m, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.8, 195.1, 140.5, 140.4, 134.6, 130.1, 129.2, 128.6, 128.6, 126.4, 62.2, 33.5, 30.4, 28.0. HRMS (ESI), calcd. for $C_{18}H_{17}ClNaO_2$ $(M+Na)^+$: 323.0809, found: 323.0810.



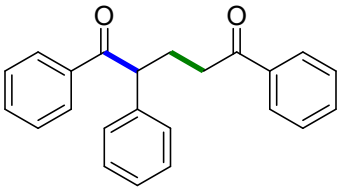
2-phenethyl-1-(*m*-tolyl)butane-1,3-dione (3x) Yellow oil (64.9 mg, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.63 (m, 2H), 7.41-7.37 (m, 1H), 7.36-7.25 (m, 3H), 7.24-7.18 (m,1H), 7.17-7.12 (m, 2H), 4.42 (t, J = 6.8 Hz, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.38 (s, 3H), 2.34-2.24 (m, 2H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.1, 196.7, 140.8, 138.8, 136.4, 134.6, 129.2, 128.7, 128.6, 128.6, 126.3, 126.0, 62.0, 33.6, 30.5, 28.3, 21.4. HRMS (ESI), calcd. for $C_{19}H_{21}O_2$ $(M+H)^+$: 281.1536, found: 281.1535.



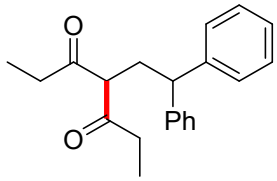
1-(3,4-dimethylphenyl)-2-phenethylbutane-1,3-dione (3z) Yellow oil (64.6 mg, 73 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.58 (m, 2H), 7.32-7.25 (m, 2H), 7.24-7.18 (m, 2H), 7.17-7.13 (m, 2H), 4.40 (t, J = 7.0 Hz, 1H), 2.66-2.59 (m, 2H), 2.33-2.26 (m, 8H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.3, 196.3, 143.6, 140.9, 137.3, 134.3, 130.1, 129.8, 128.6, 128.5, 126.5, 126.3, 61.9, 33.6, 30.5, 28.2, 20.1, 19.8. HRMS (ESI), calcd. for $C_{20}H_{23}O_2$ $(M+H)^+$: 295.1693, found: 295.1694.



2-phenethyl-1,3-diphenylpropane-1,3-dione (3aa)[10] colorless oil (10.9 mg, 11 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.80 (m, 4H), 7.63-7.55 (m, 2H), 7.45 (t, J = 7.6 Hz, 4H), 7.40-7.31 (m,3H), 7.25-7.18 (m, 2H), 5.21 (t, J = 6.5 Hz, 1H), 2.81 (t, J = 7.2 Hz, 2H), 2.52-2.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 140.9, 135.9, 133.5, 128.8, 128.8, 128.6, 128.5, 126.4, 55.3, 34.0, 30.8. HRMS (ESI), calcd. for $C_{23}H_{20}NaO_2$ $(M+Na)^+$: 351.1356, found: 351.1360.



1,2,5-triphenylpentane-1,5-dione (4aa)[11] colorless oil (50.0 mg, 51 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.85 (m, 4H), 7.57-7.50 (m, 1H), 7.50-7.35 (m, 5H), 7.34-7.26 (m, 4H), 7.24-7.18 (m, 1H), 4.78 (t, J = 7.3 Hz, 1H), 3.07-2.87 (m, 2H), 2.65-2.52 (m, 1H), 2.35-2.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 199.6, 139.1, 136.8, 136.6, 133.1, 132.9, 129.0, 128.8, 128.6, 128.5, 128.3, 128.0, 127.2, 52.4, 36.0, 28.3. HRMS (ESI), calcd. for $C_{23}H_{20}NaO_2$ $(M+Na)^+$: 351.1356, found: 351.1358.



4-(2,2-diphenylethyl)heptane-3,5-dione (4ab) colorless oil (59.2 mg, 64 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.25 (m, 4H), 7.22-7.16 (m, 6H), 3.82 (t, J = 8.1 Hz, 1H), 3.58 (t, J = 7.0 Hz, 1H), 2.62-2.56 (m, 2H), 2.46-2.35 (m, 2H), 2.33-2.24 (m, 2H), 0.97 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.7, 143.4, 128.7, 127.9, 126.7, 65.2, 49.1, 35.5, 34.1, 7.6. HRMS (ESI), calcd. for $C_{21}H_{24}NaO_2$ $(M+Na)^+$: 331.1669, found: 331.1668.

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

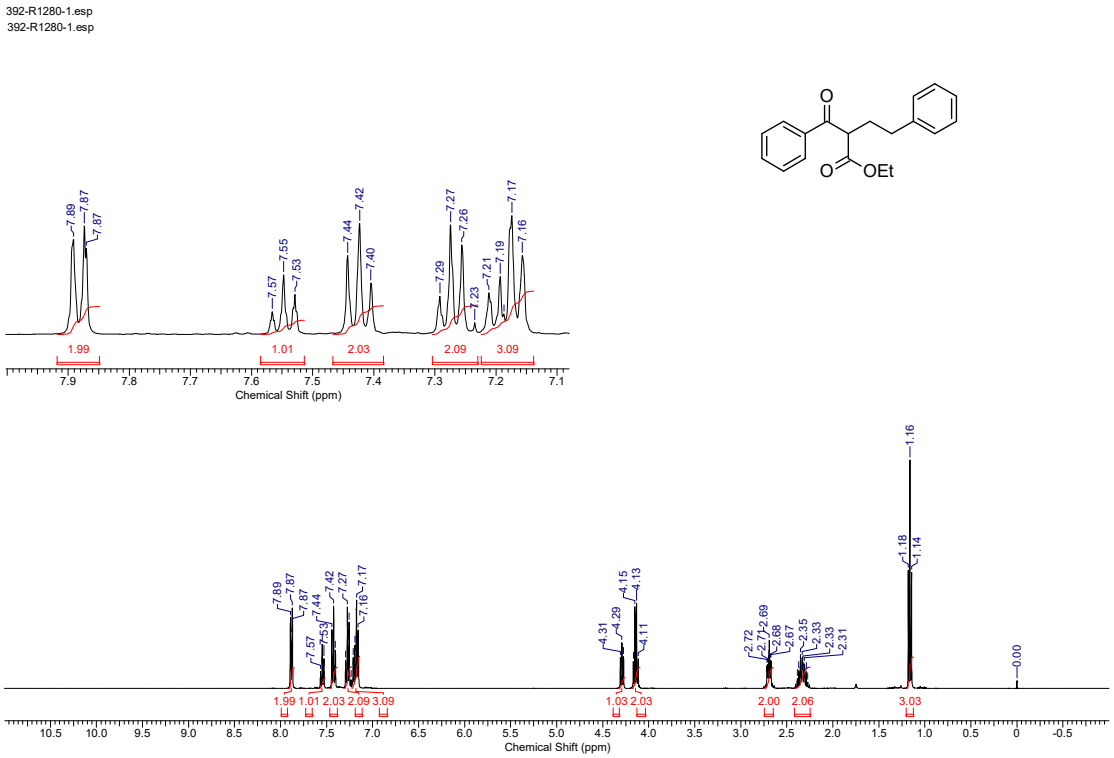


Figure S10. ^{1}H NMR spectrum of compound **3a**

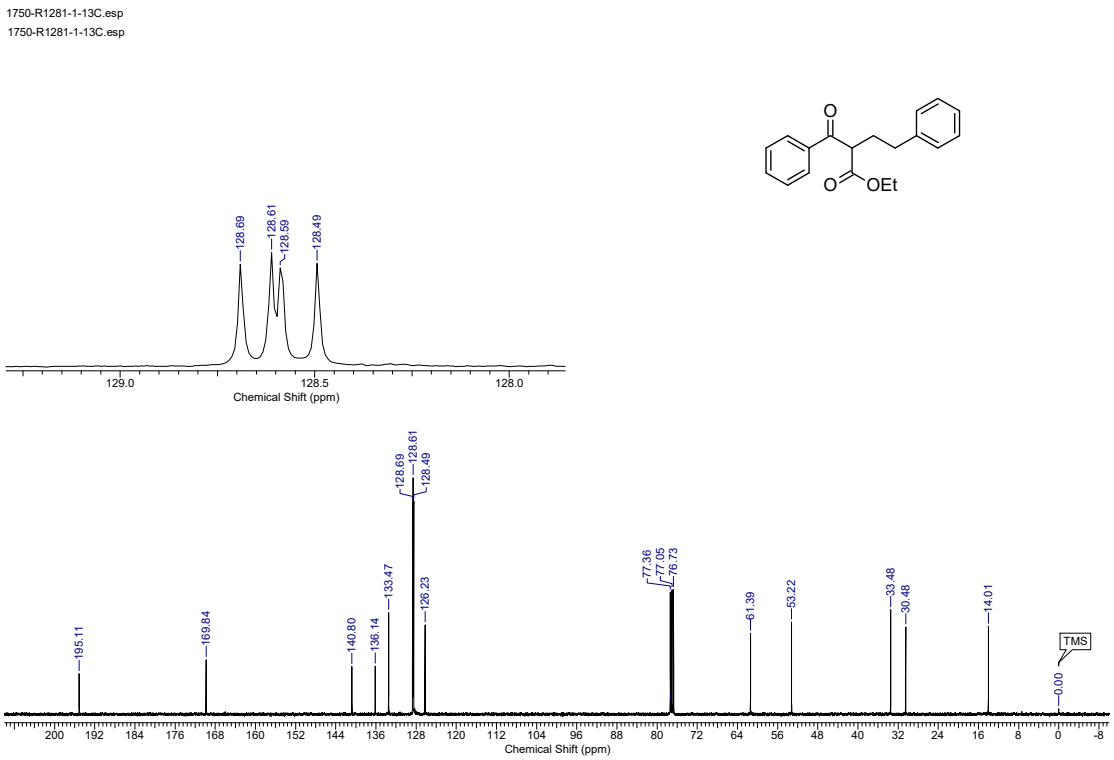


Figure S11. ^{13}C NMR spectrum of compound **3a**

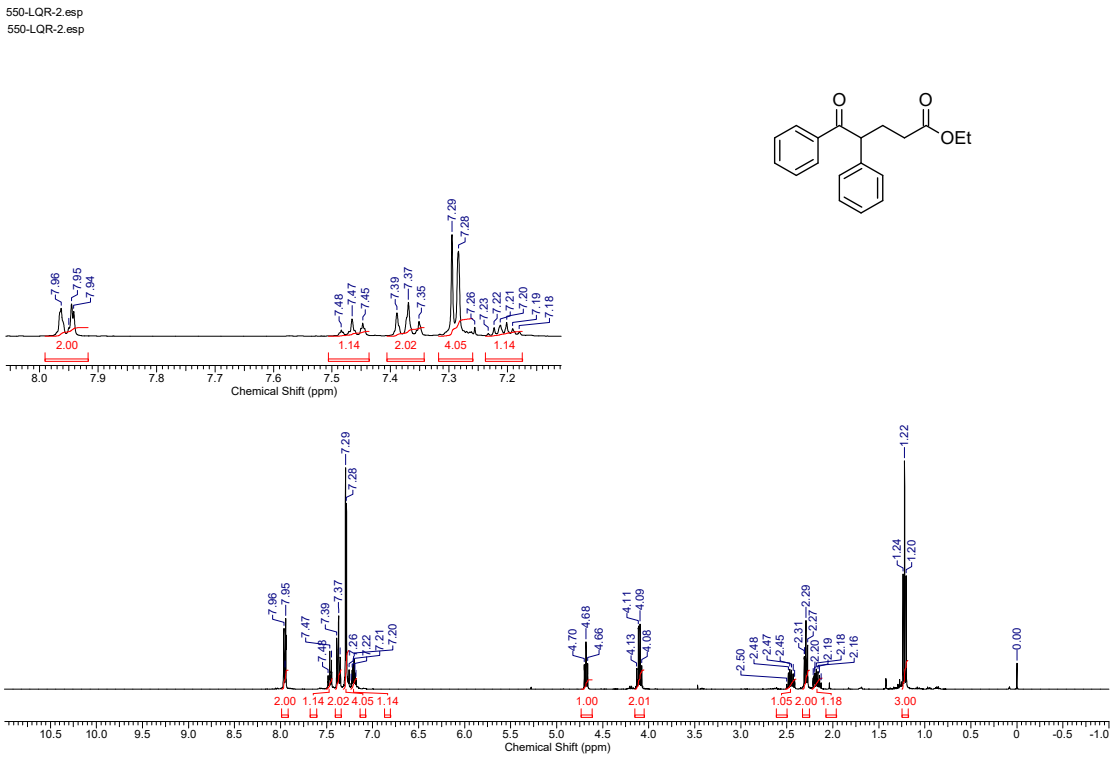


Figure S12. [1]H NMR spectrum of compound **4a**

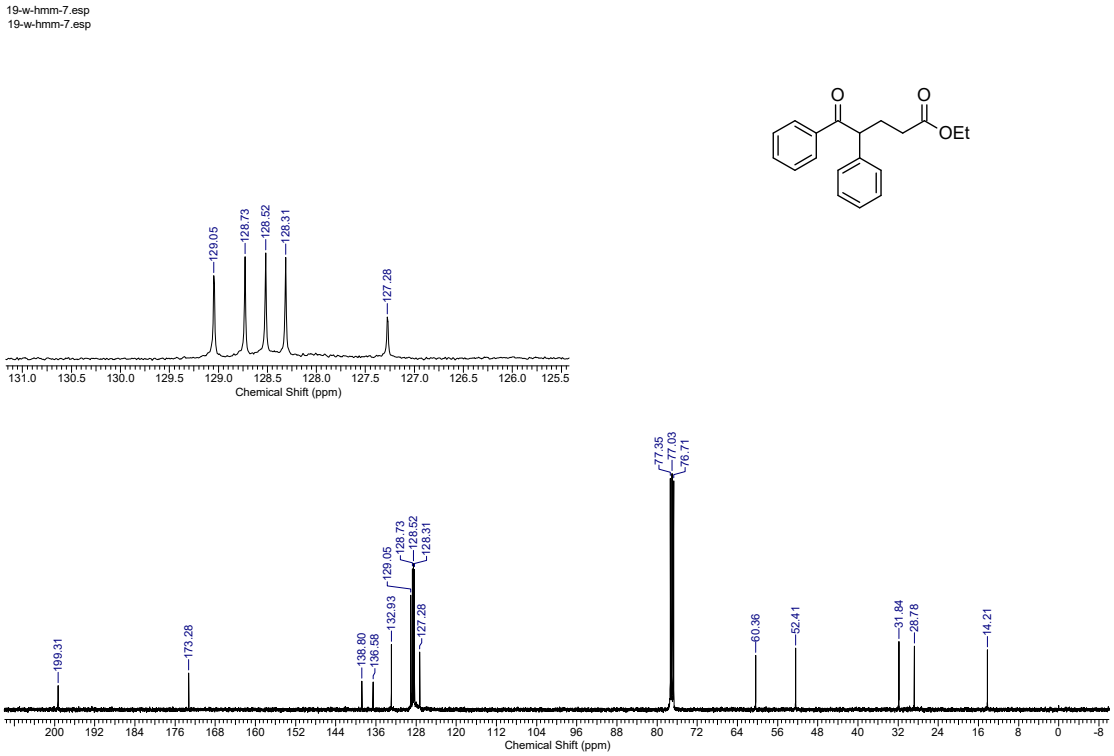


Figure S13. [13]C NMR spectrum of compound **4a**

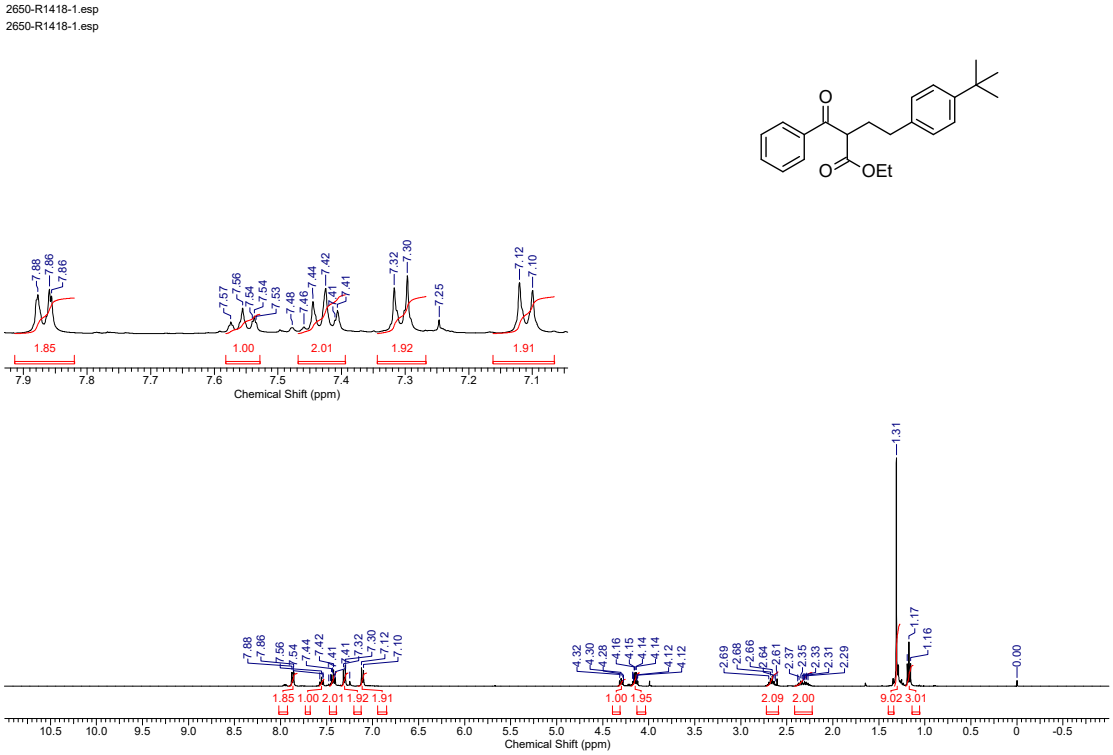


Figure S14. ^{1}H NMR spectrum of compound **3b**

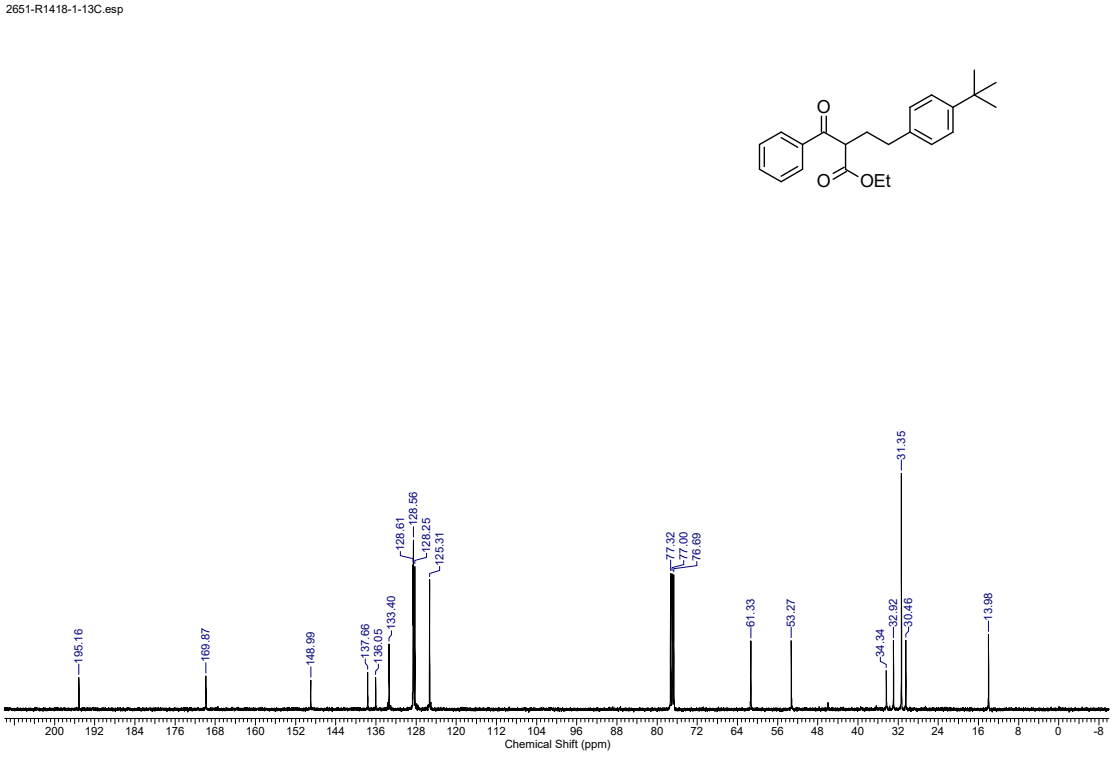


Figure S15. ^{13}C NMR spectrum of compound **3b**

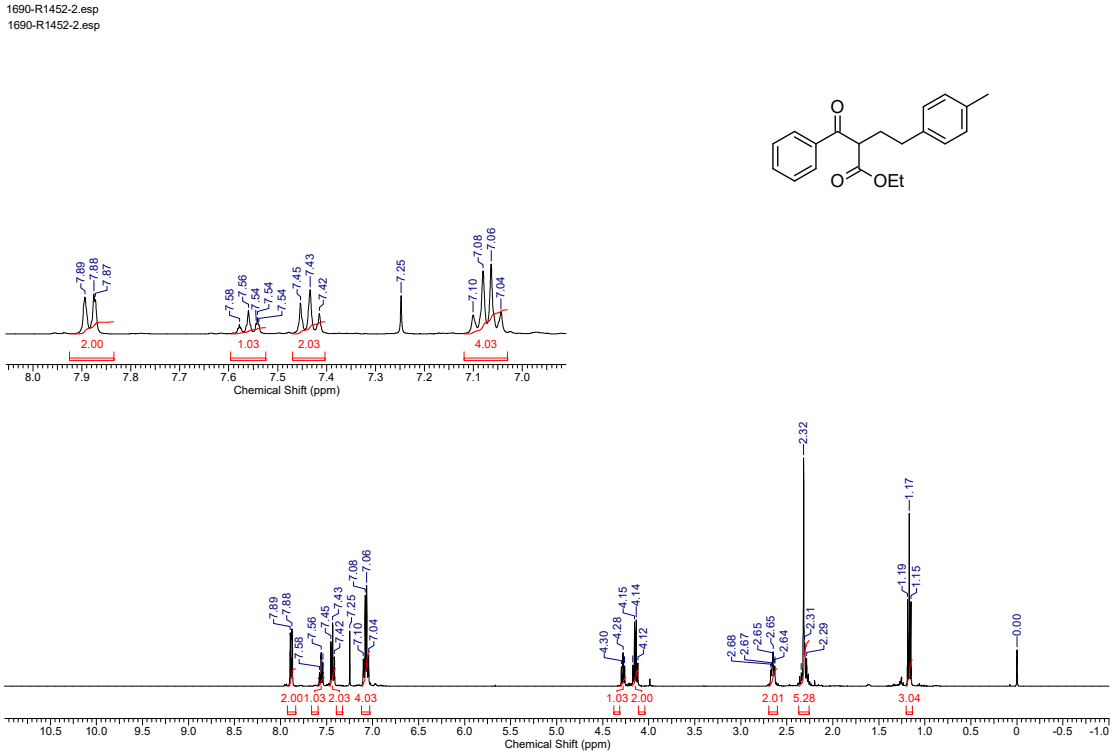


Figure S16. ^{1}H NMR spectrum of compound **3c**

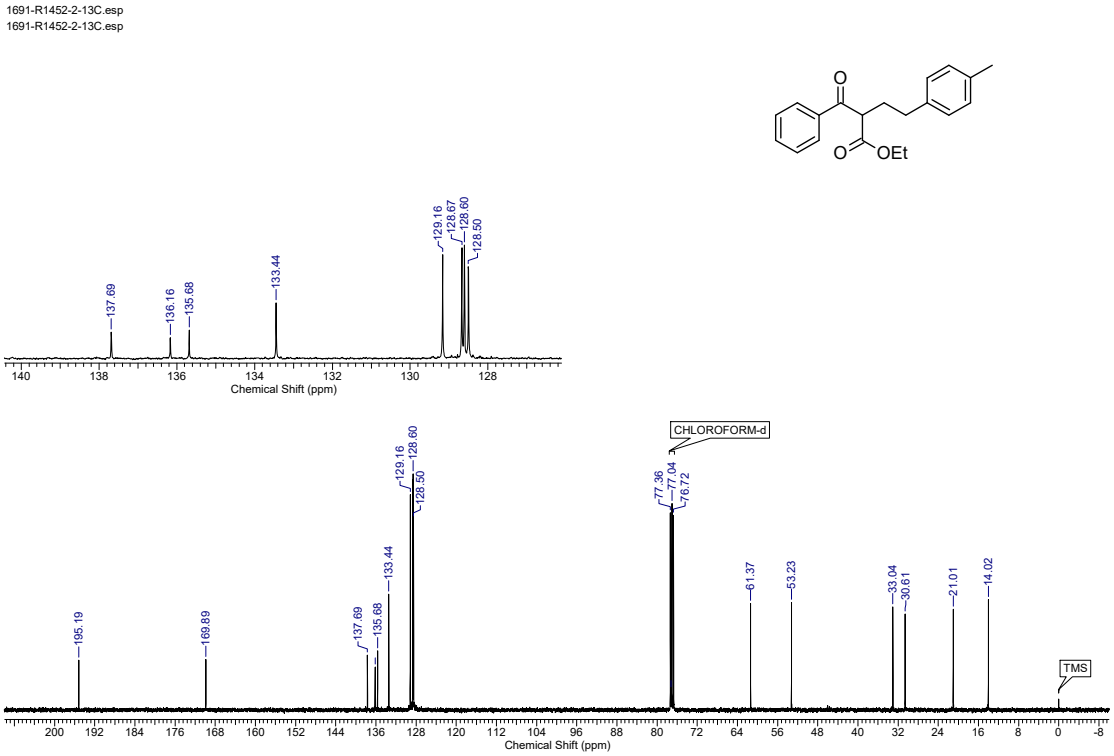


Figure S17. ^{13}C NMR spectrum of compound **3c**

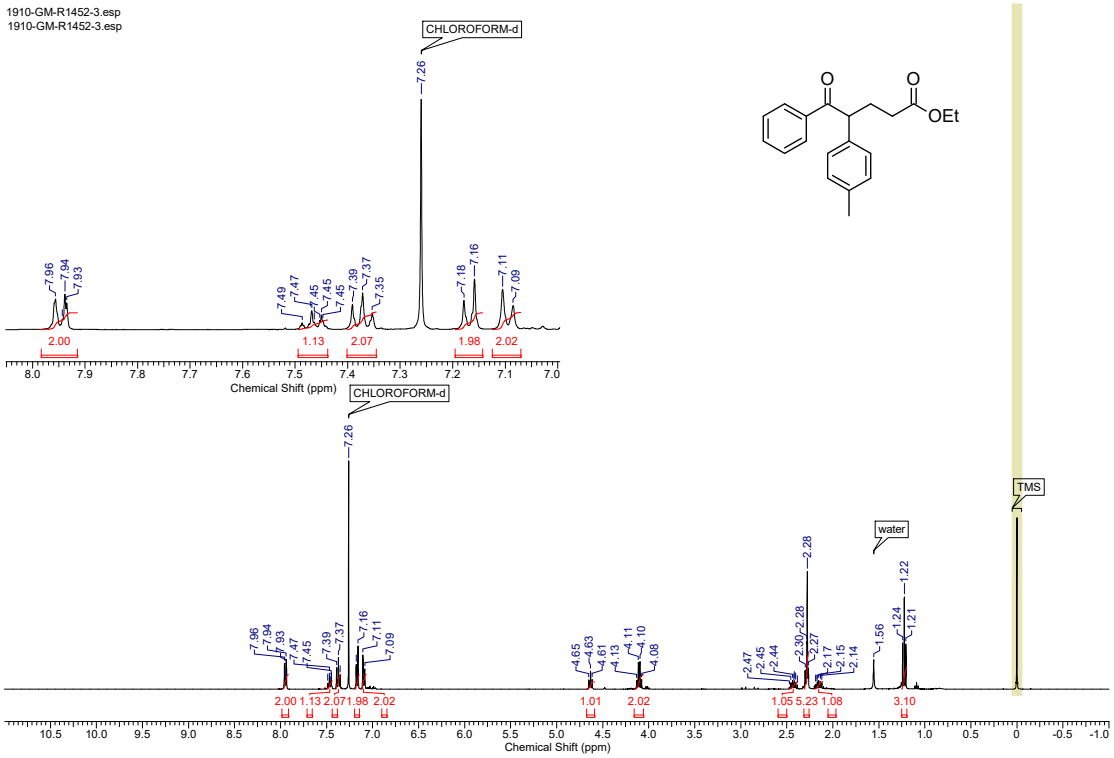


Figure S18. ^{1}H NMR spectrum of compound **4c**

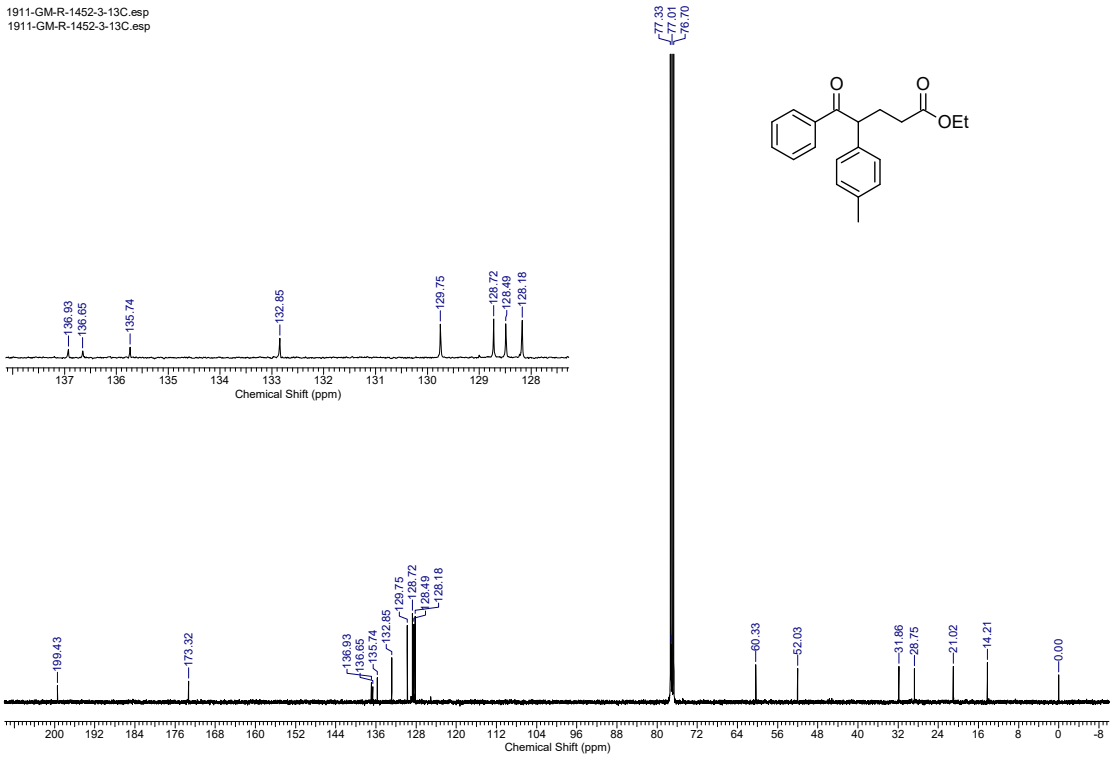


Figure S19. ^{13}C NMR spectrum of compound **4c**

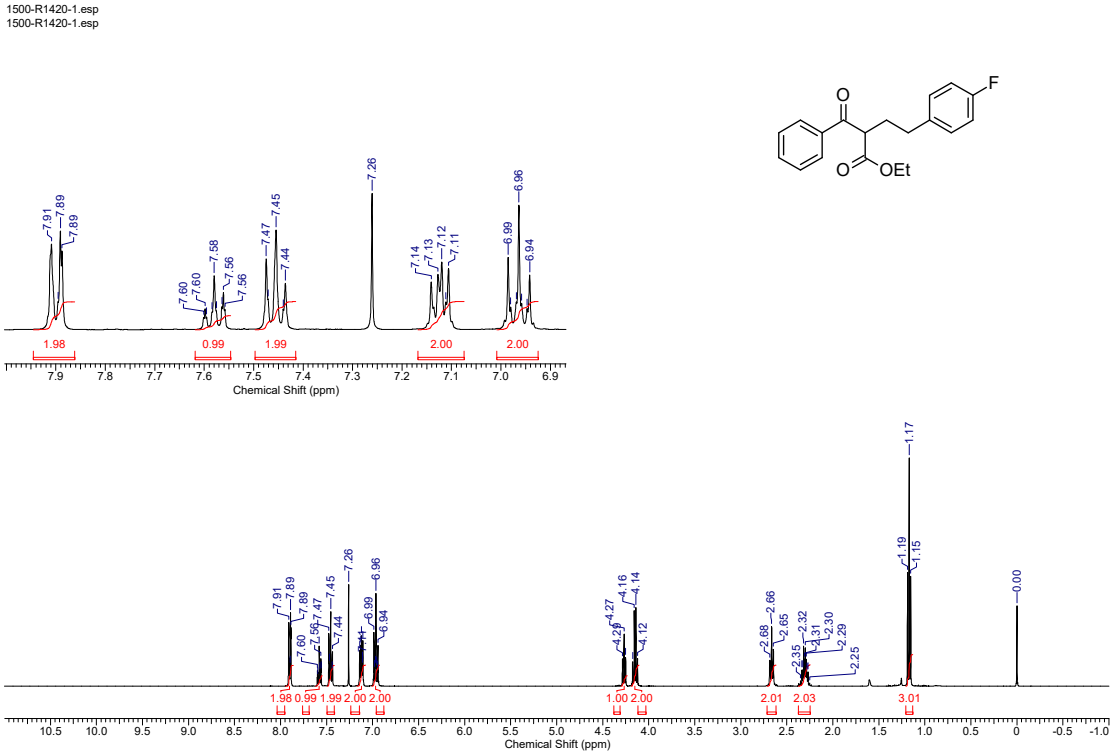


Figure S20. [1]H NMR spectrum of compound **3d**

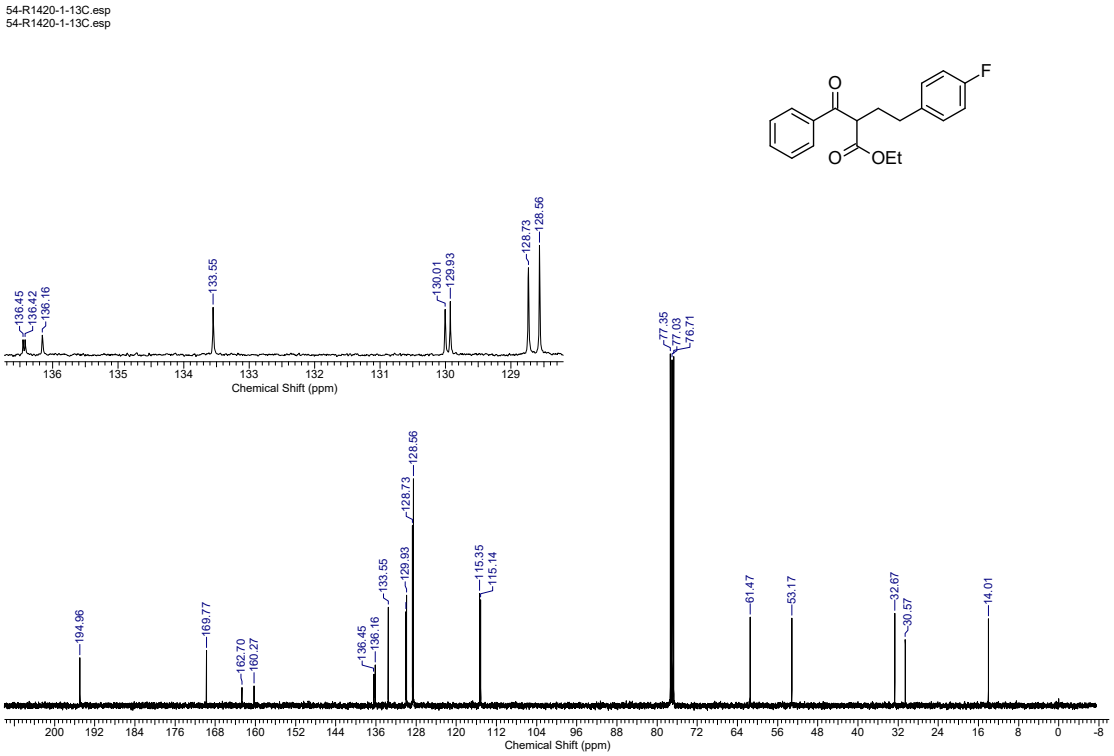


Figure S21. [13]C NMR spectrum of compound **3d**

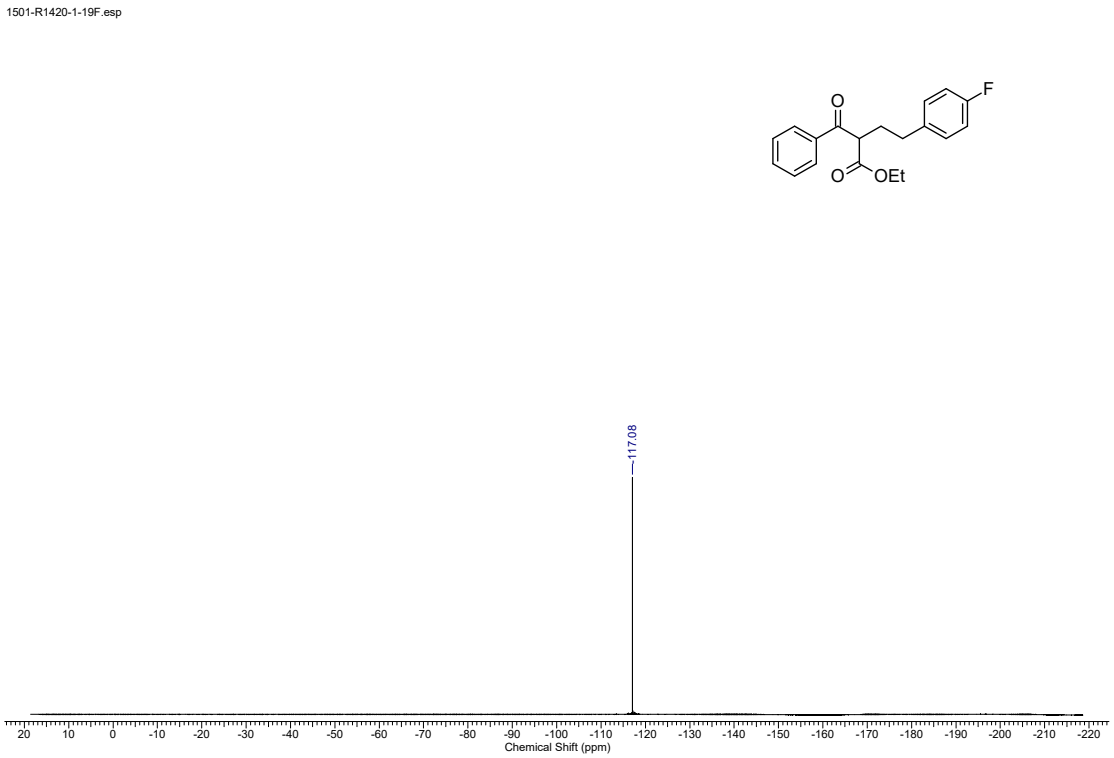


Figure S22. ^{19}F NMR spectrum of compound **3d**

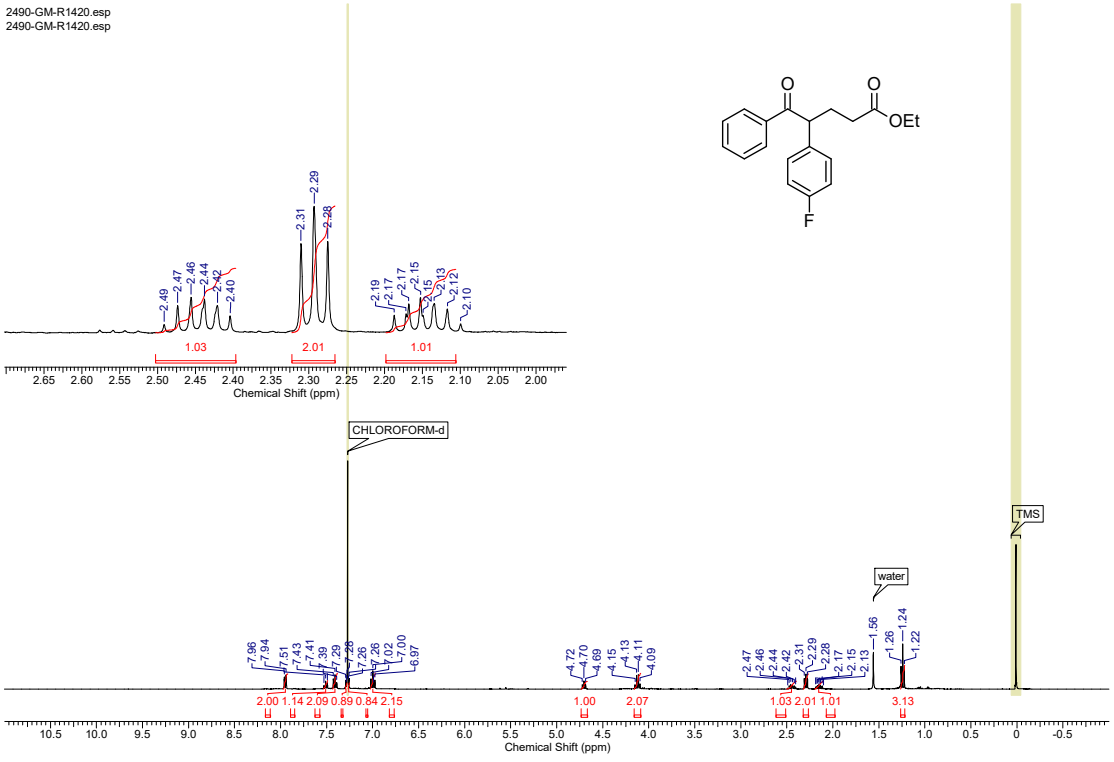


Figure S23. ^{1}H NMR spectrum of compound **4d**

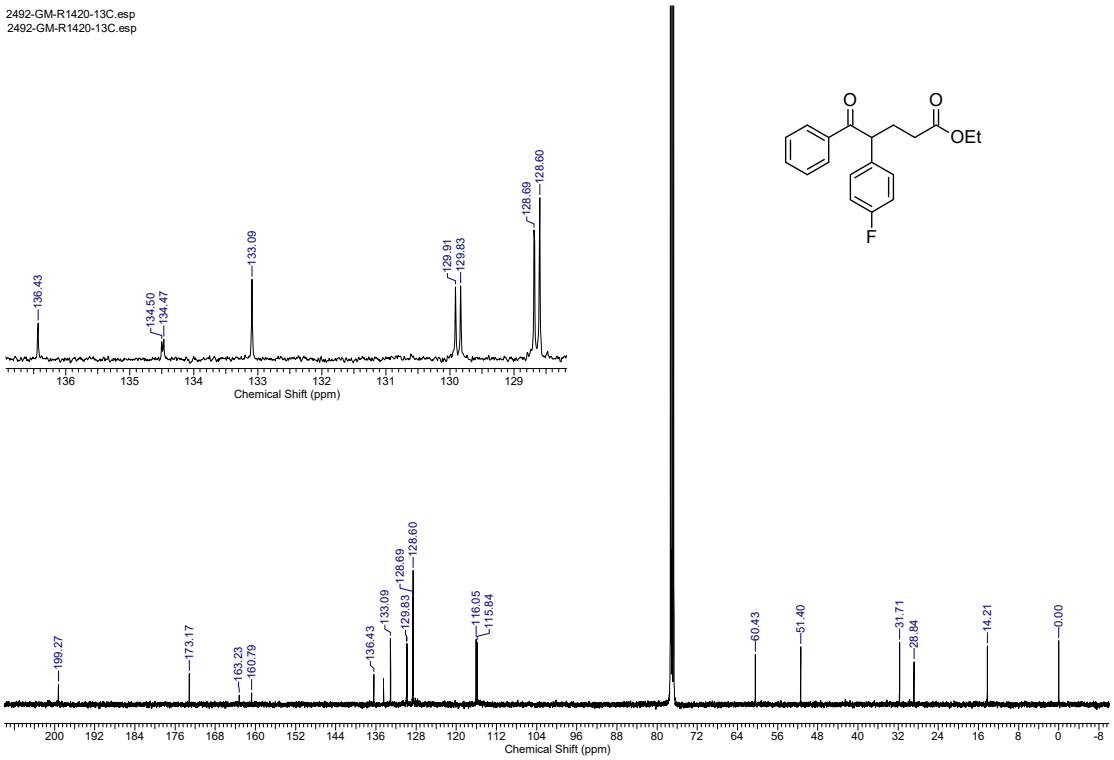


Figure S24. ^{13}C NMR spectrum of compound **4d**

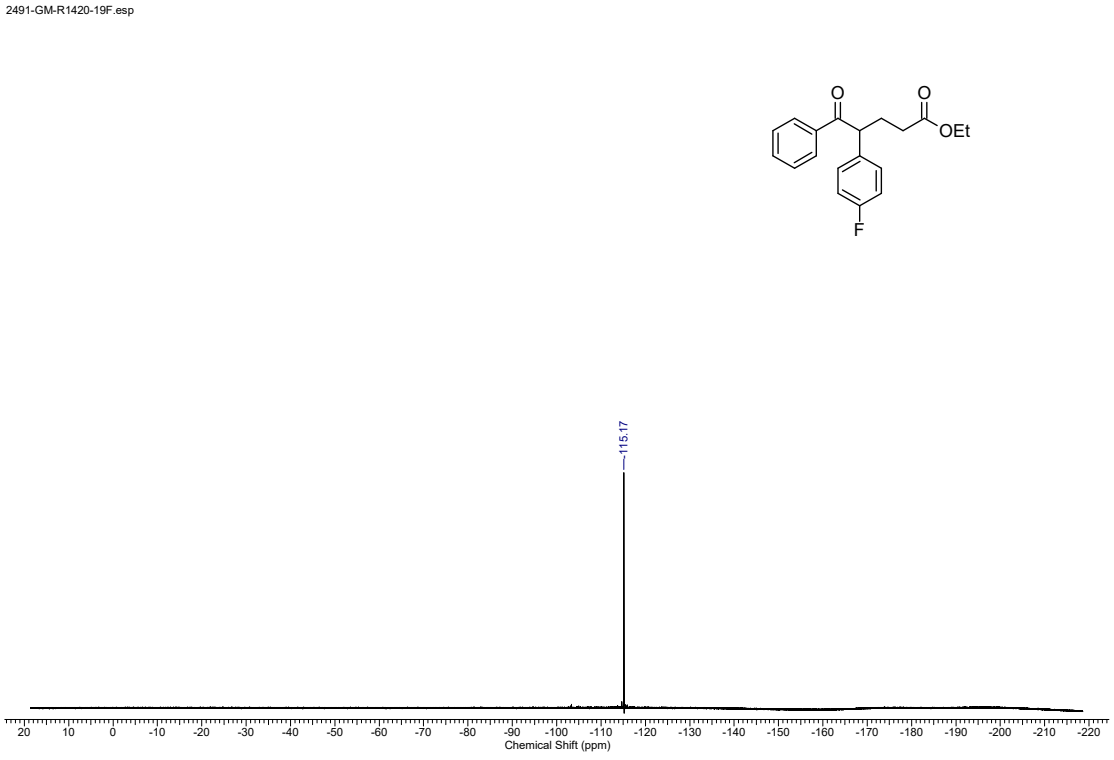


Figure S25. ^{19}F NMR spectrum of compound **4d**

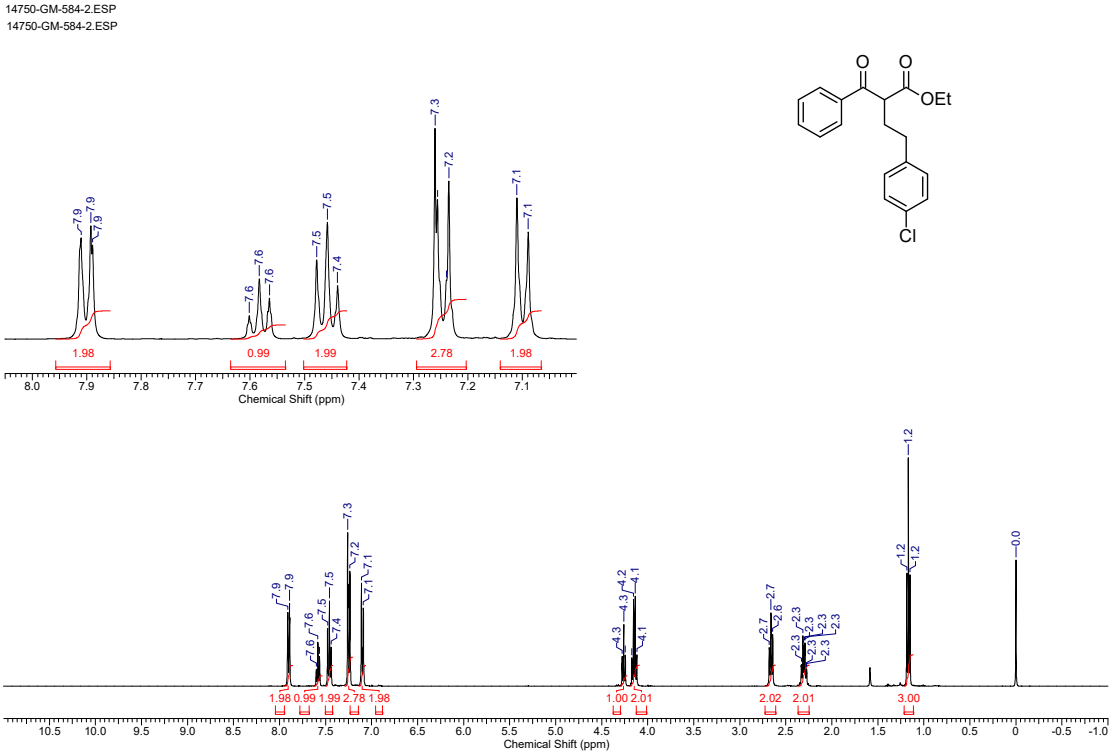


Figure S26. ^{1}H NMR spectrum of compound **3e**

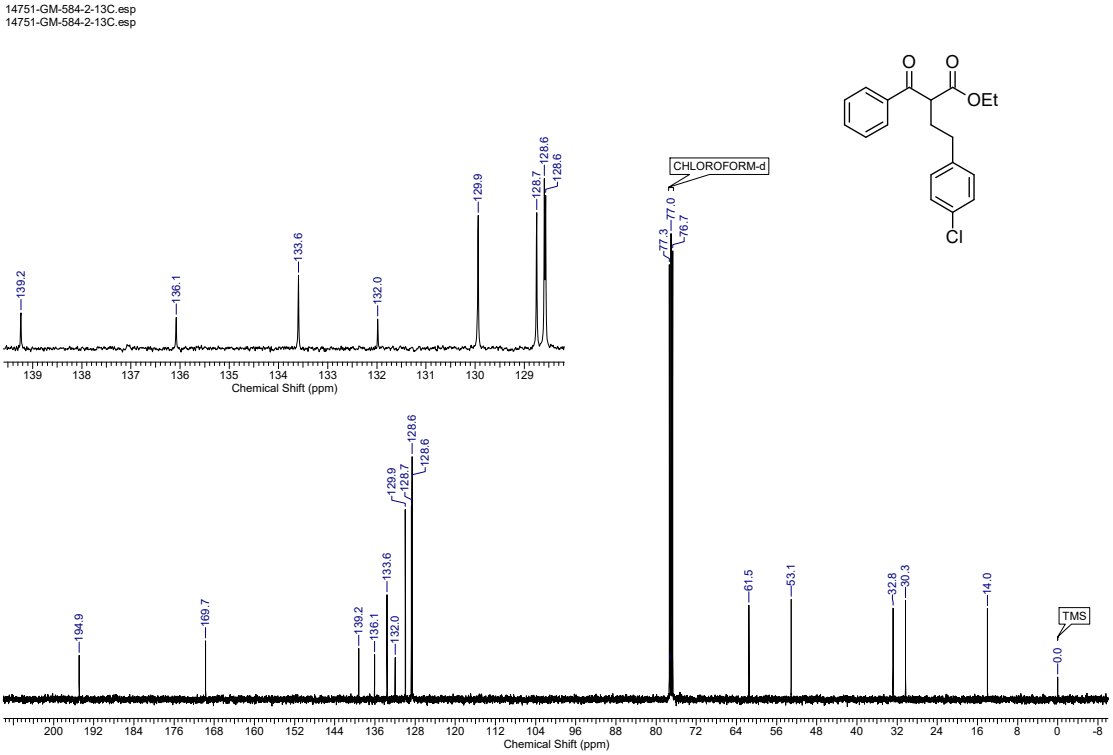


Figure S27. ^{13}C NMR spectrum of compound **3e**

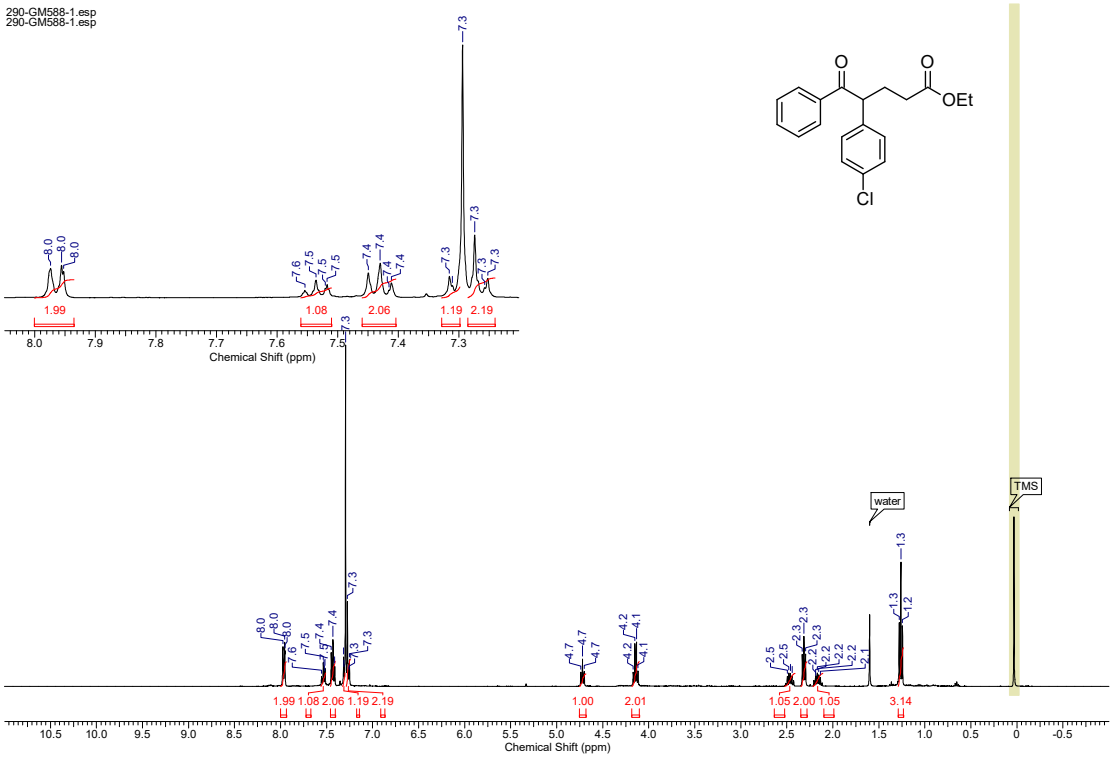


Figure S28. ^{1}H NMR spectrum of compound **4e**

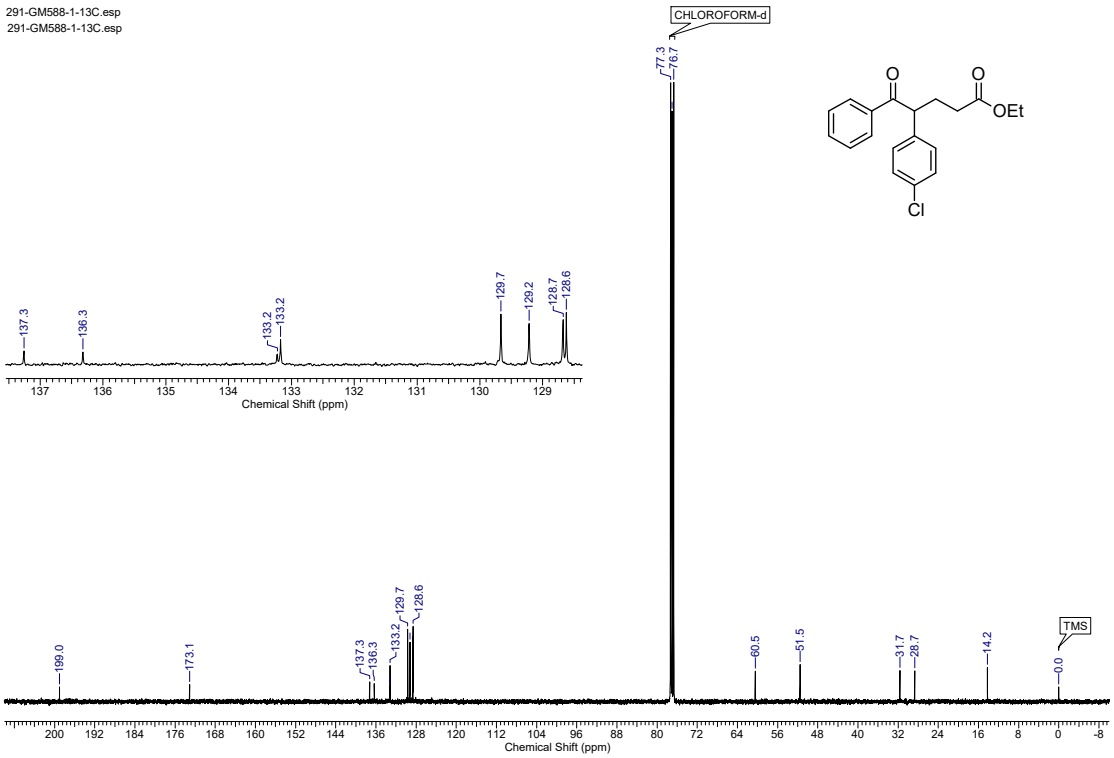


Figure S29. ^{13}C NMR spectrum of compound **4e**

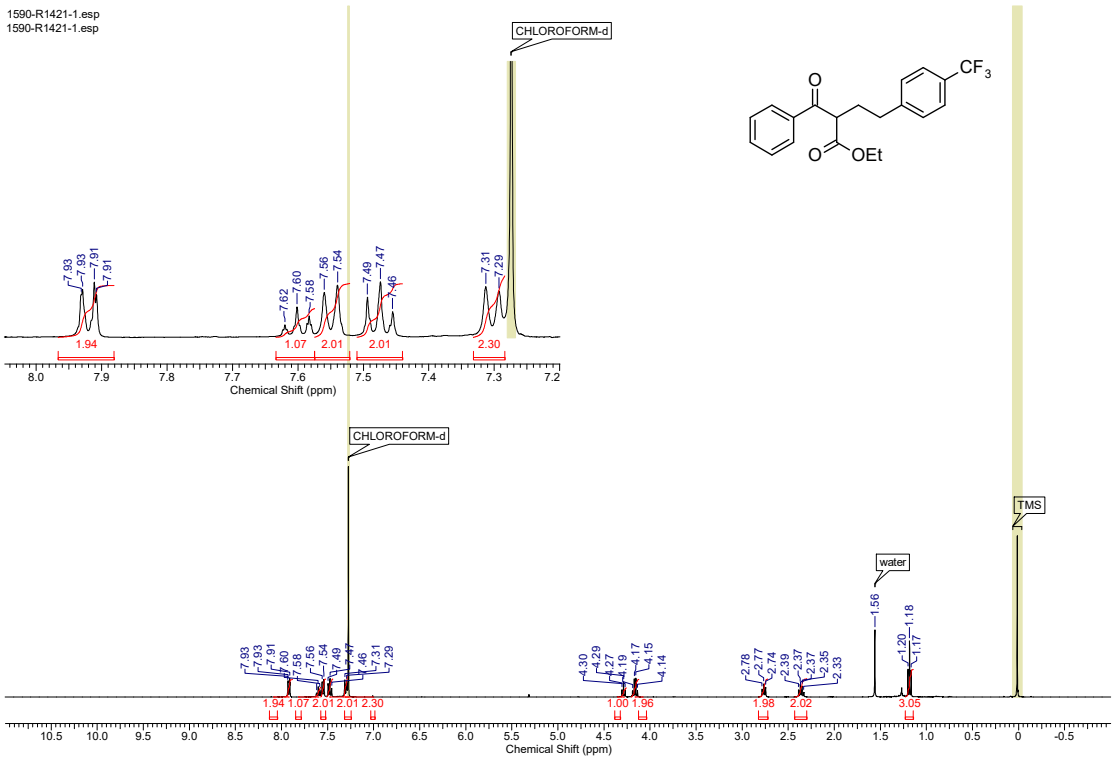


Figure S30. ^{1}H NMR spectrum of compound **3f**

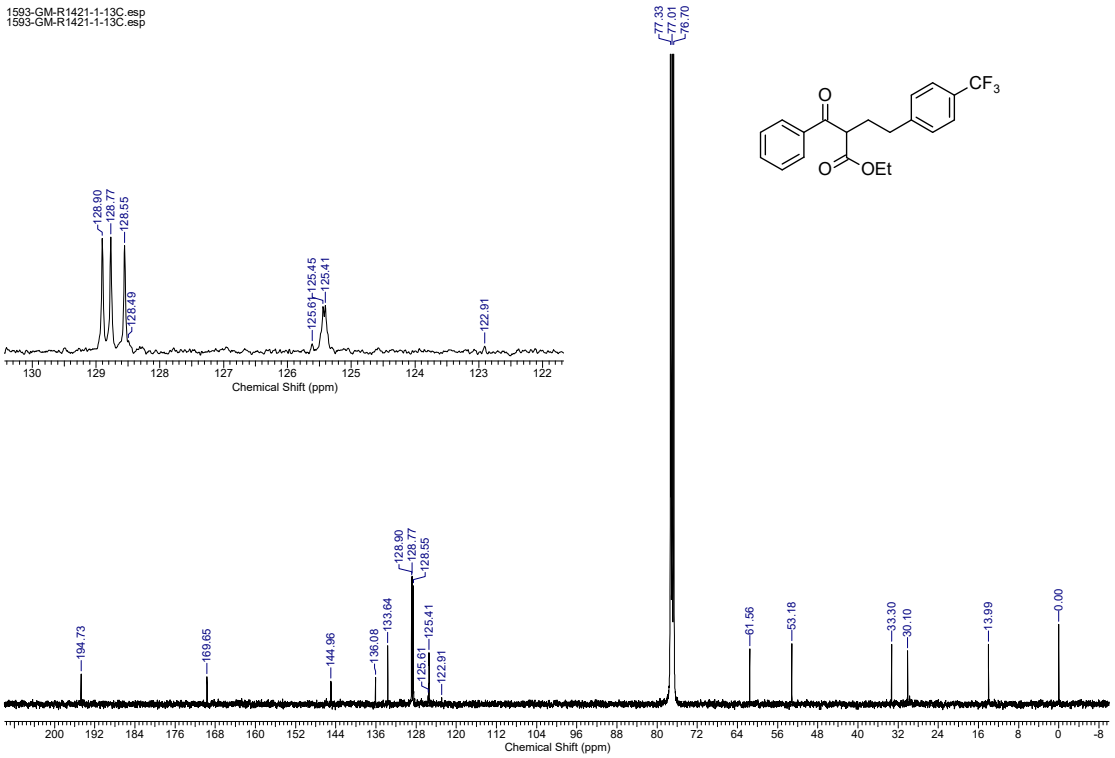


Figure S31. ^{13}C NMR spectrum of compound **3f**

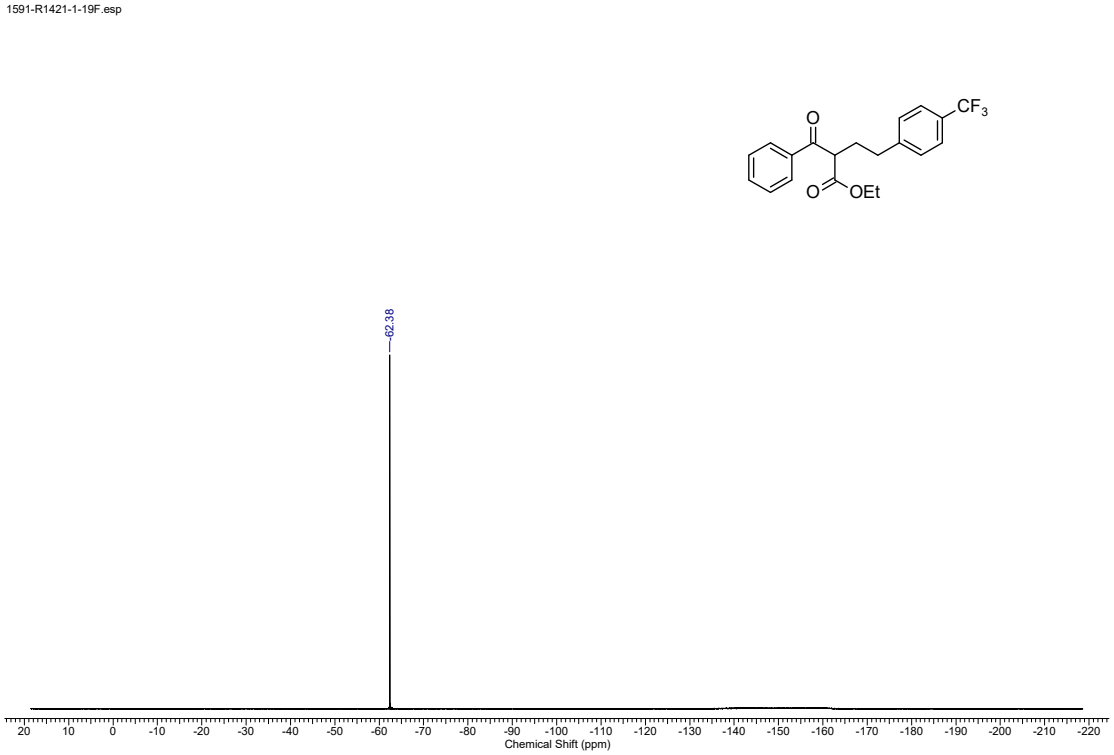


Figure S32. ^{19}F NMR spectrum of compound **3f**

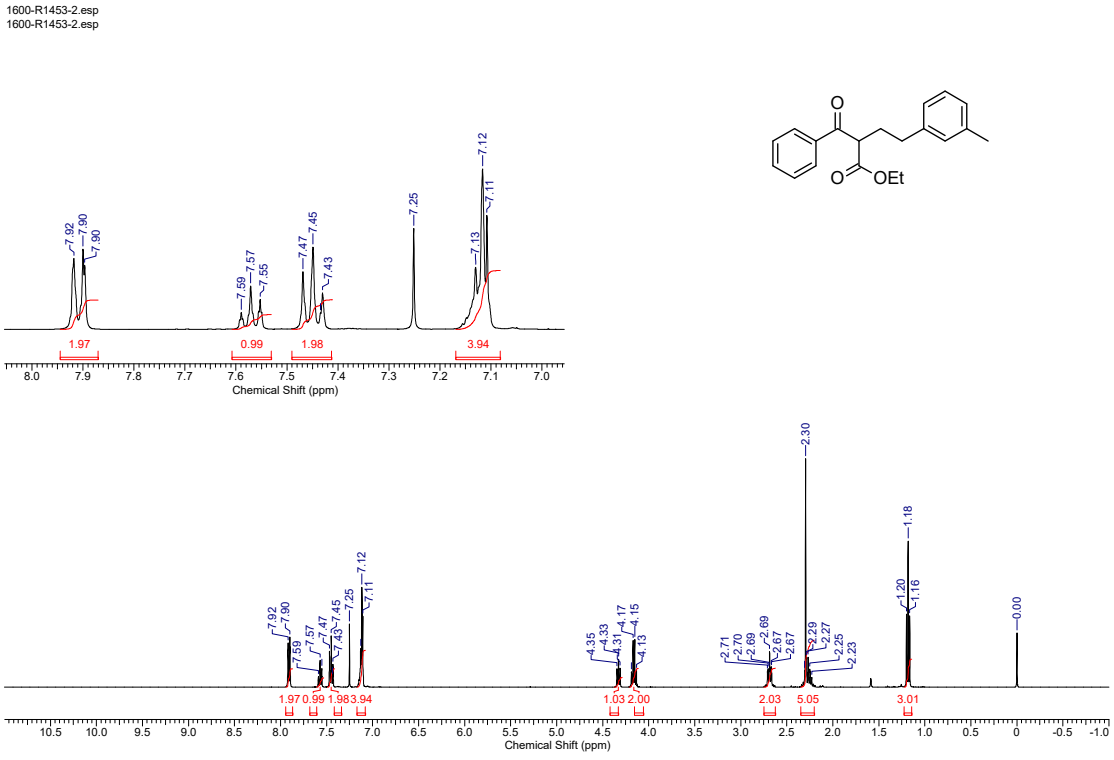


Figure S33. ^{1}H NMR spectrum of compound **3g**

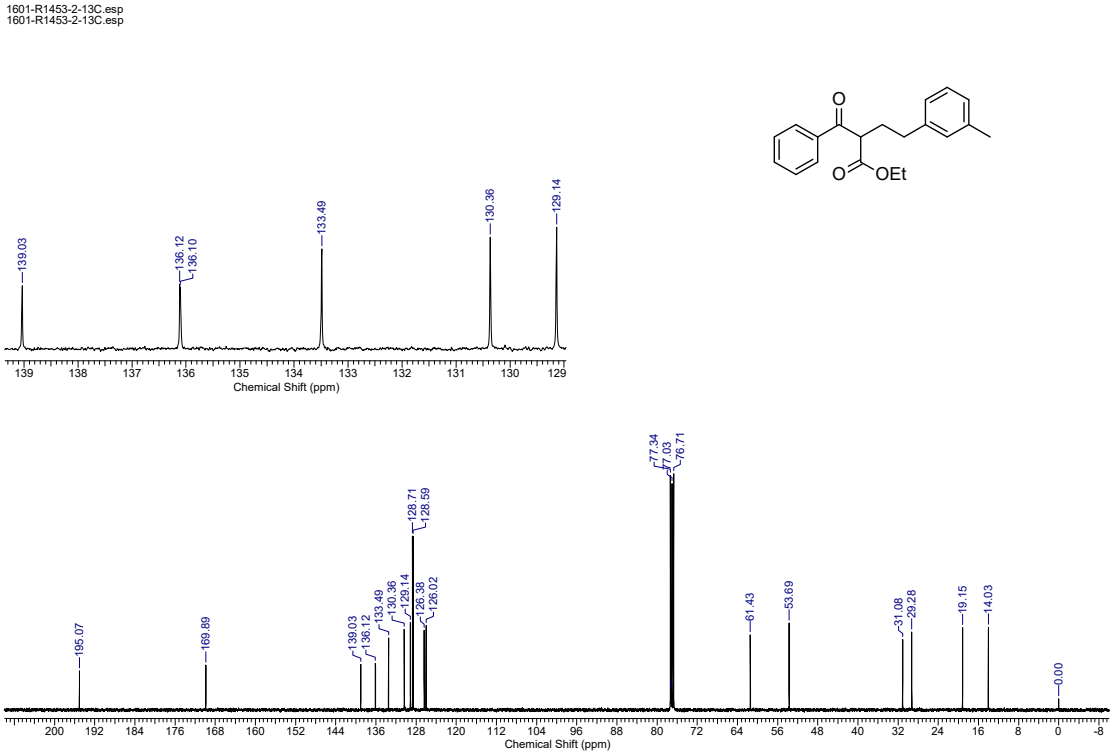


Figure S34. ^{13}C NMR spectrum of compound **3g**

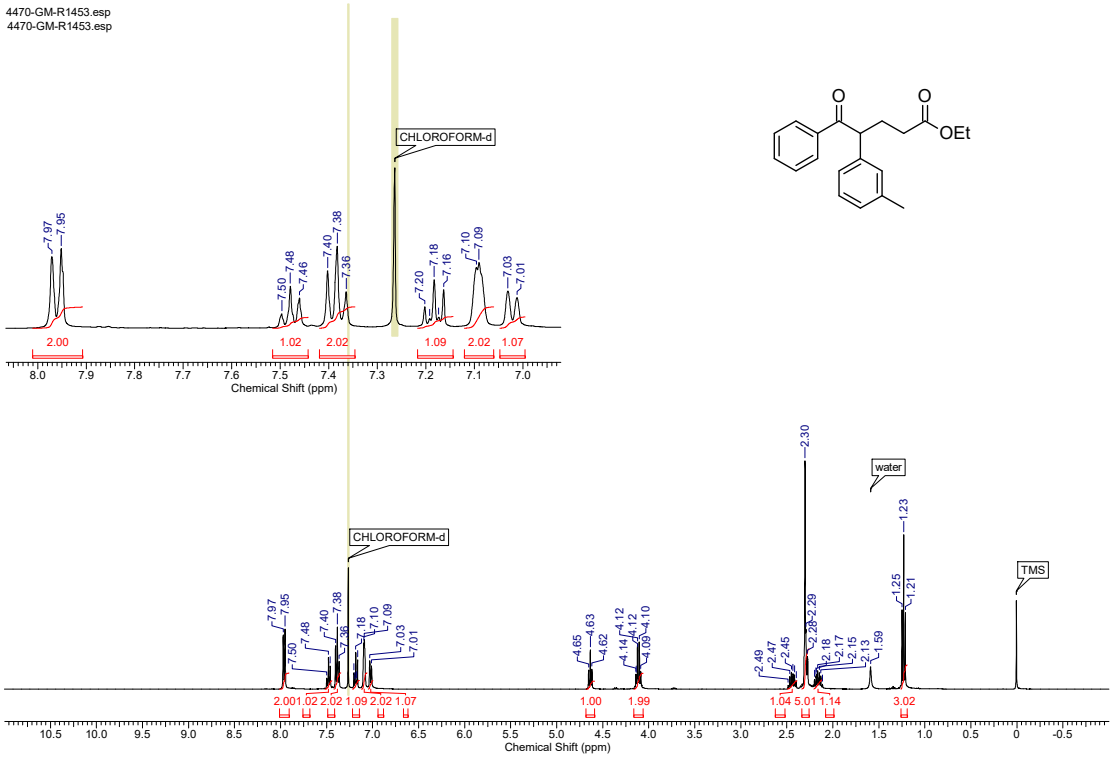


Figure S35. ^{1}H NMR spectrum of compound **4g**

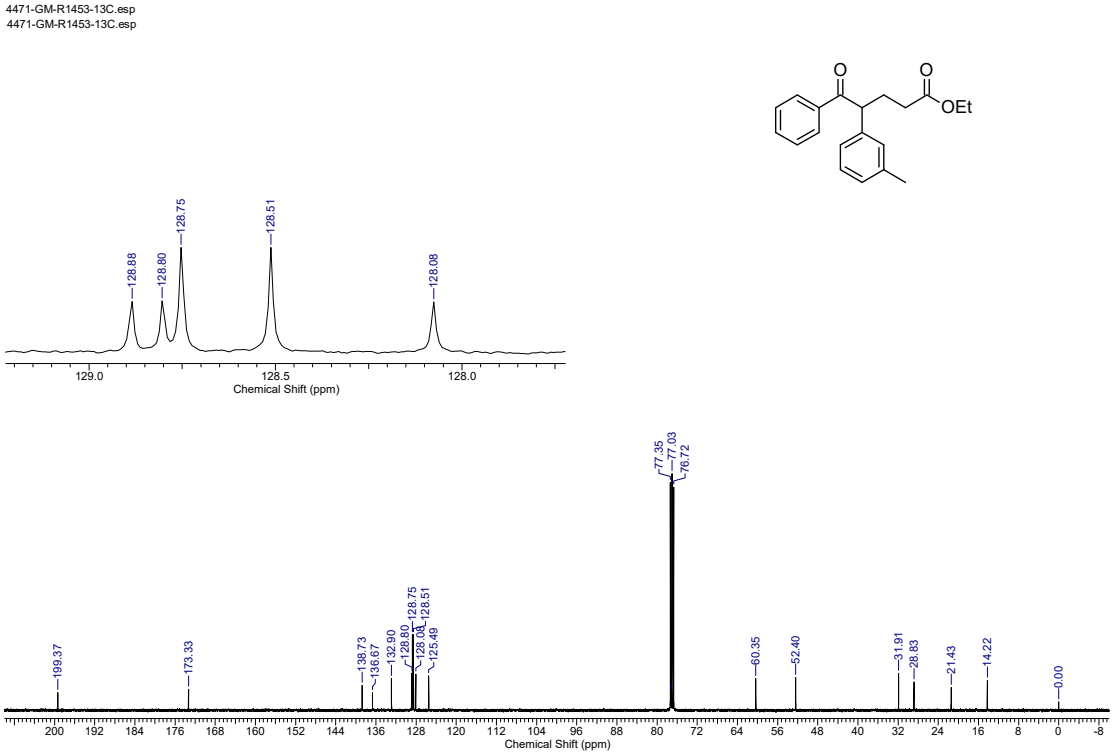


Figure S36. ^{13}C NMR spectrum of compound **4g**

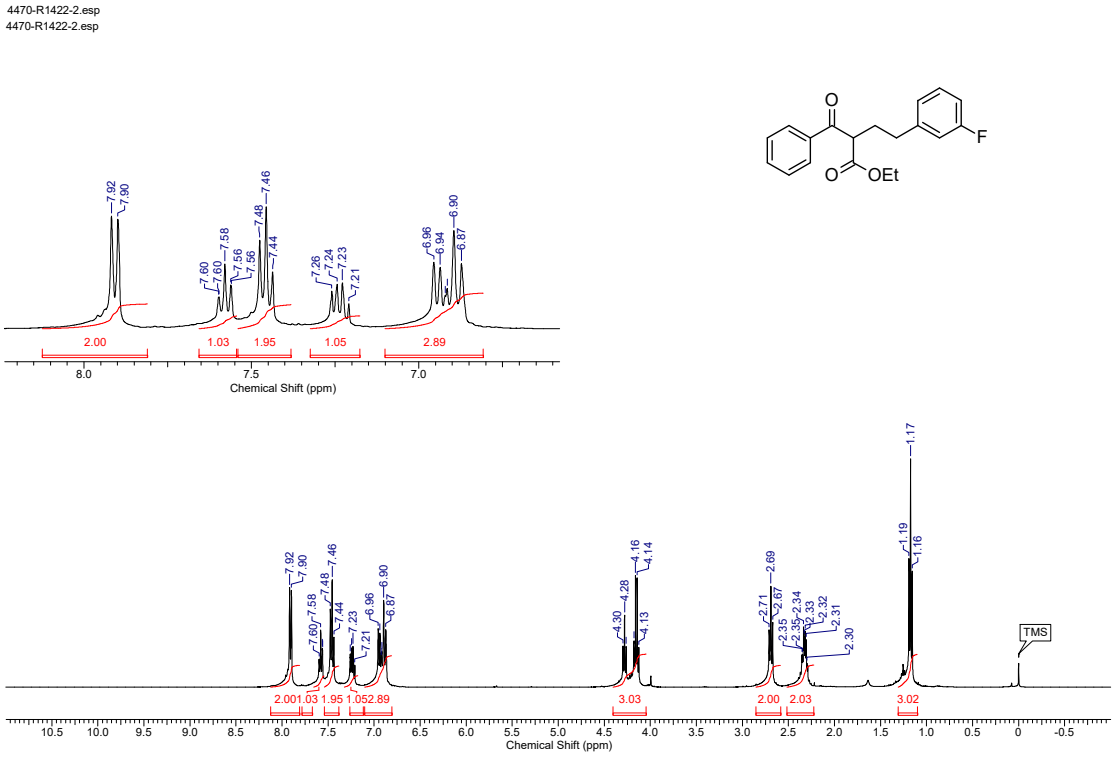


Figure S37. ^{1}H NMR spectrum of compound **3h**

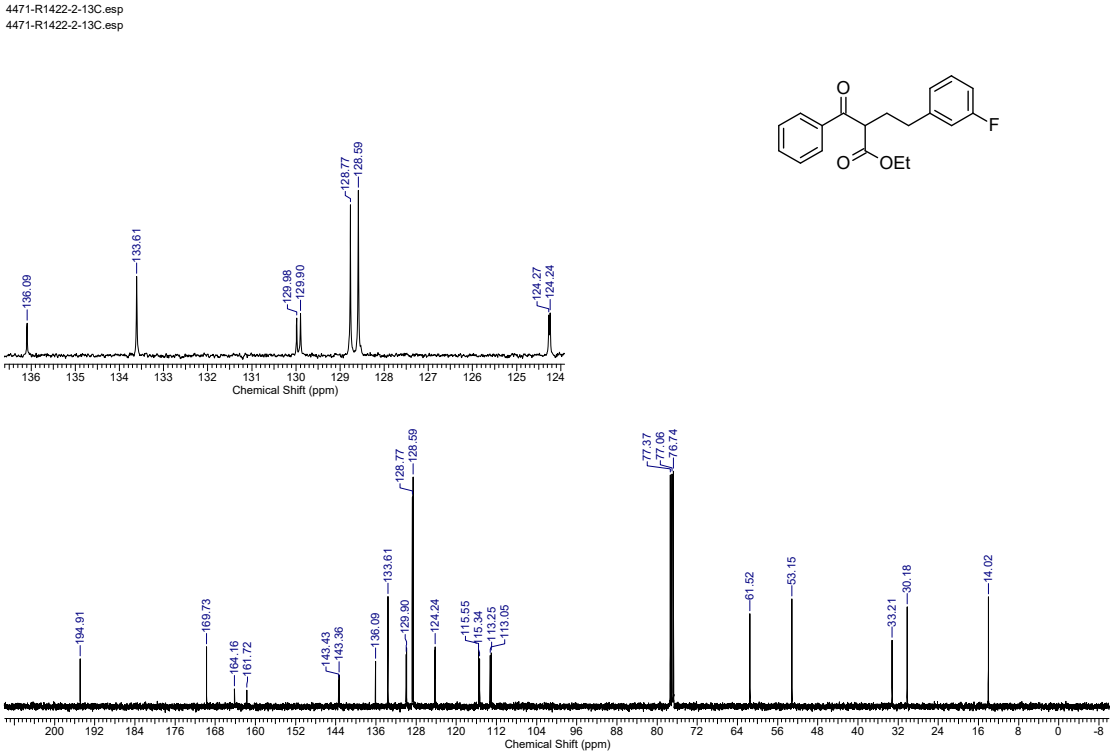


Figure S38. ^{13}C NMR spectrum of compound **3h**

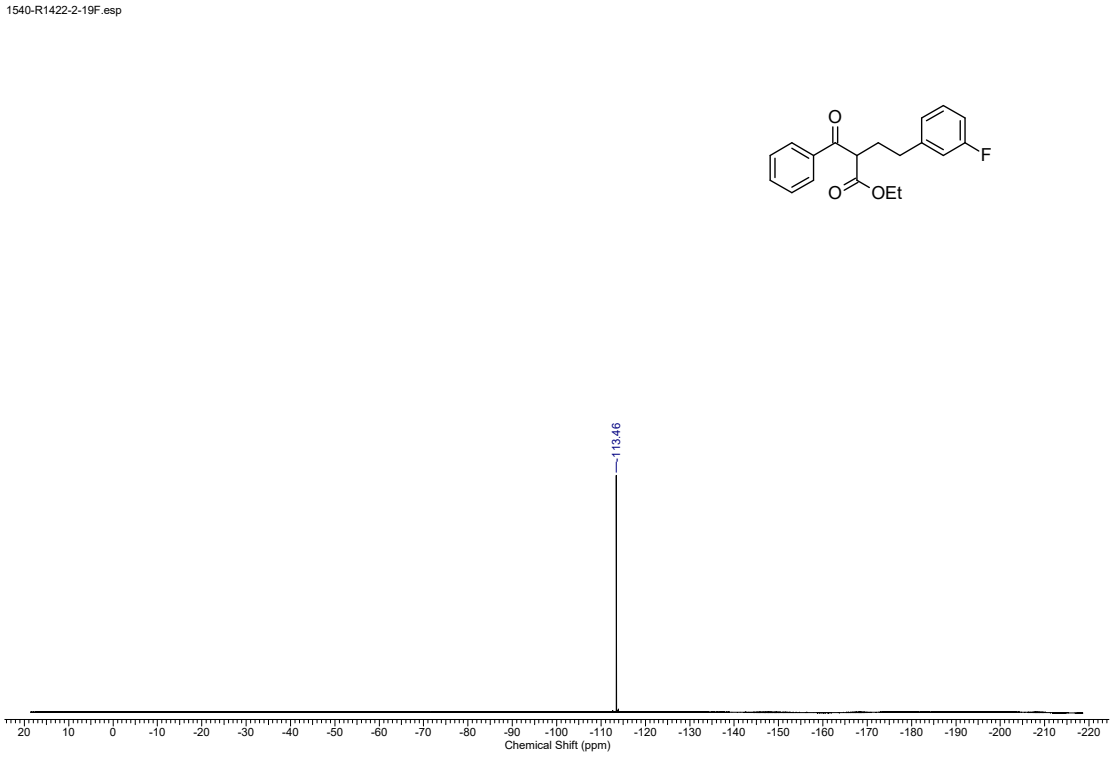


Figure S39. ^{19}F NMR spectrum of compound **3h**

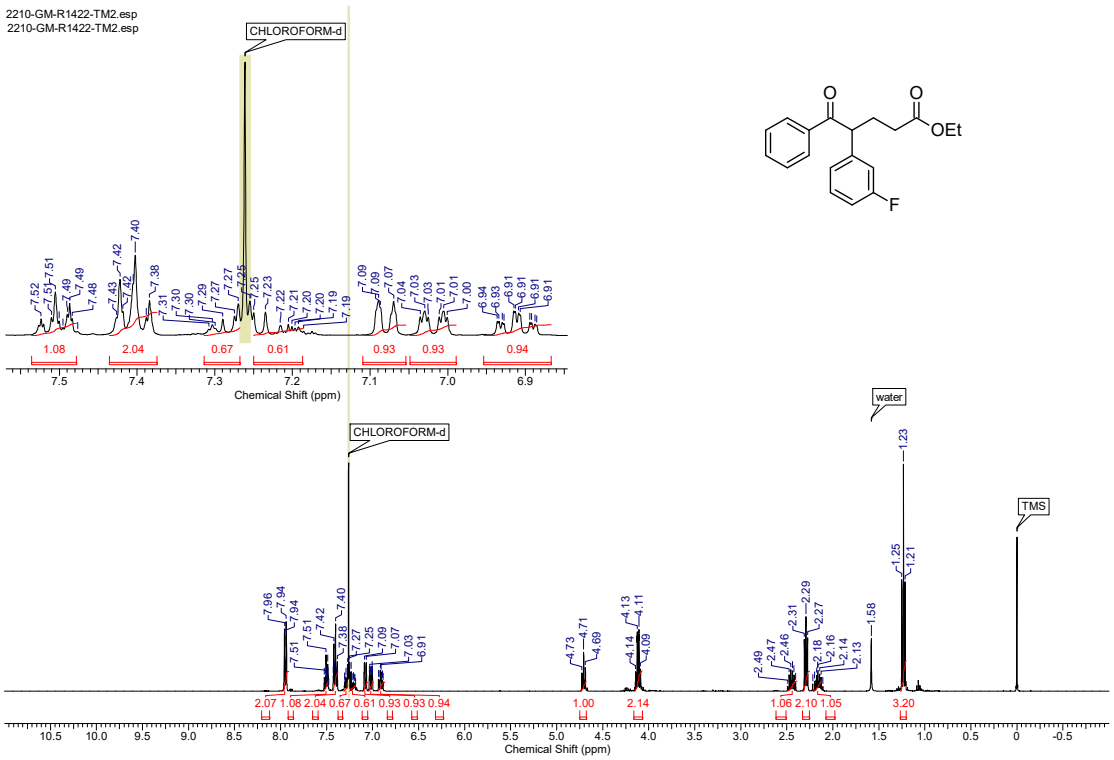


Figure S40. ^{1}H NMR spectrum of compound **4h**

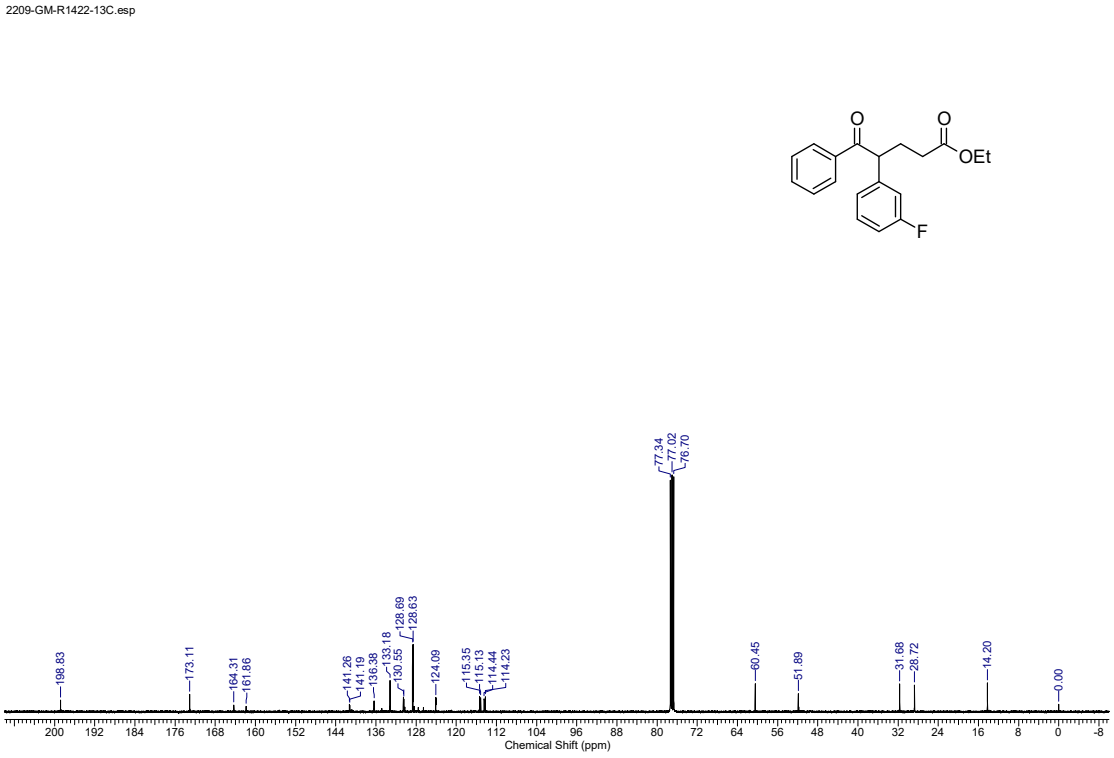


Figure S41. ^{13}C NMR spectrum of compound **4h**

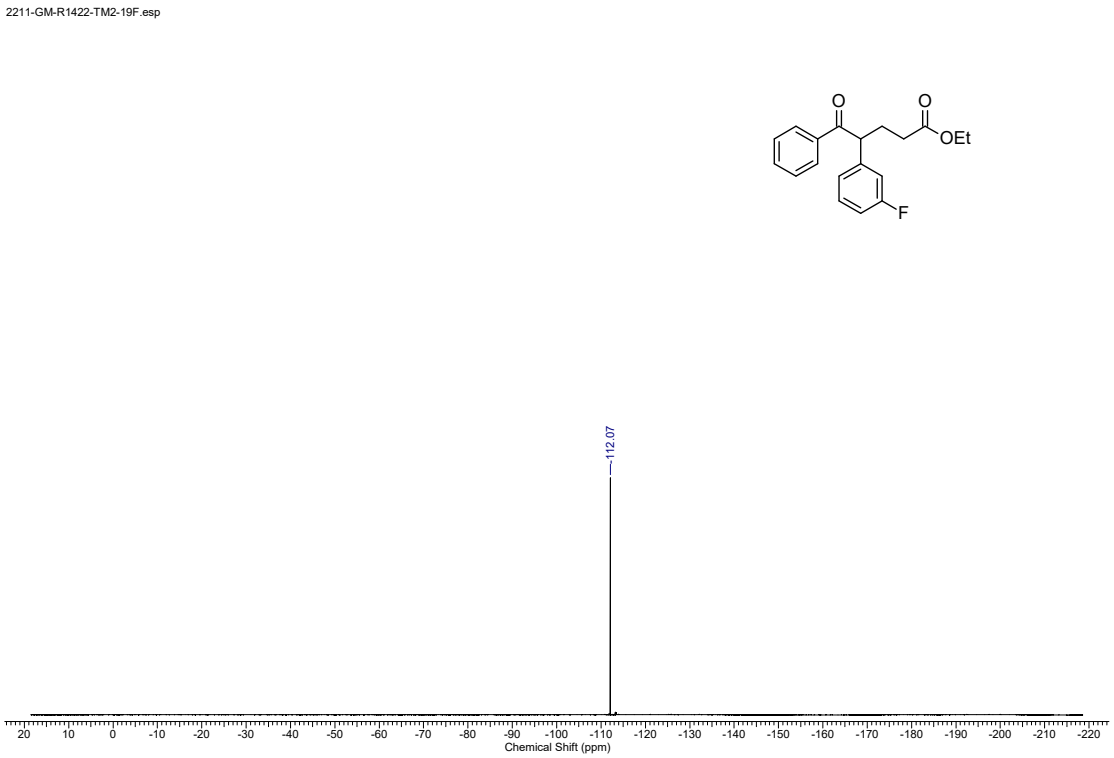


Figure S42. ^{19}F NMR spectrum of compound **4h**

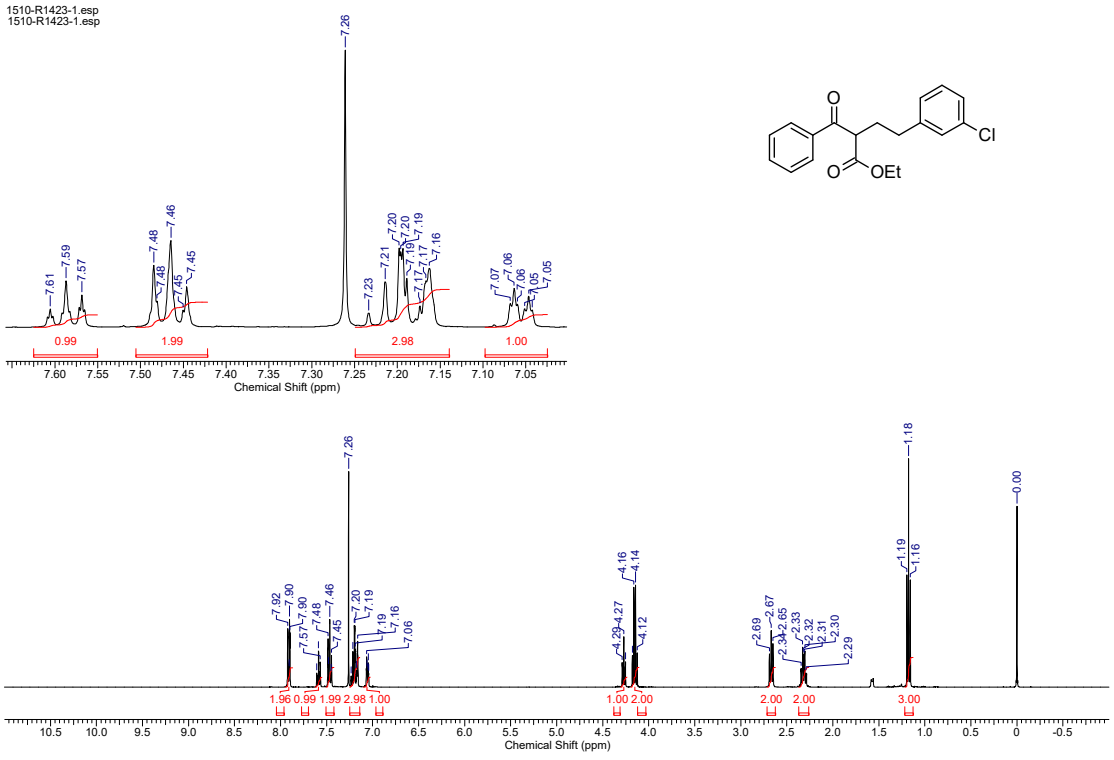


Figure S43. ^{1}H NMR spectrum of compound **3i**

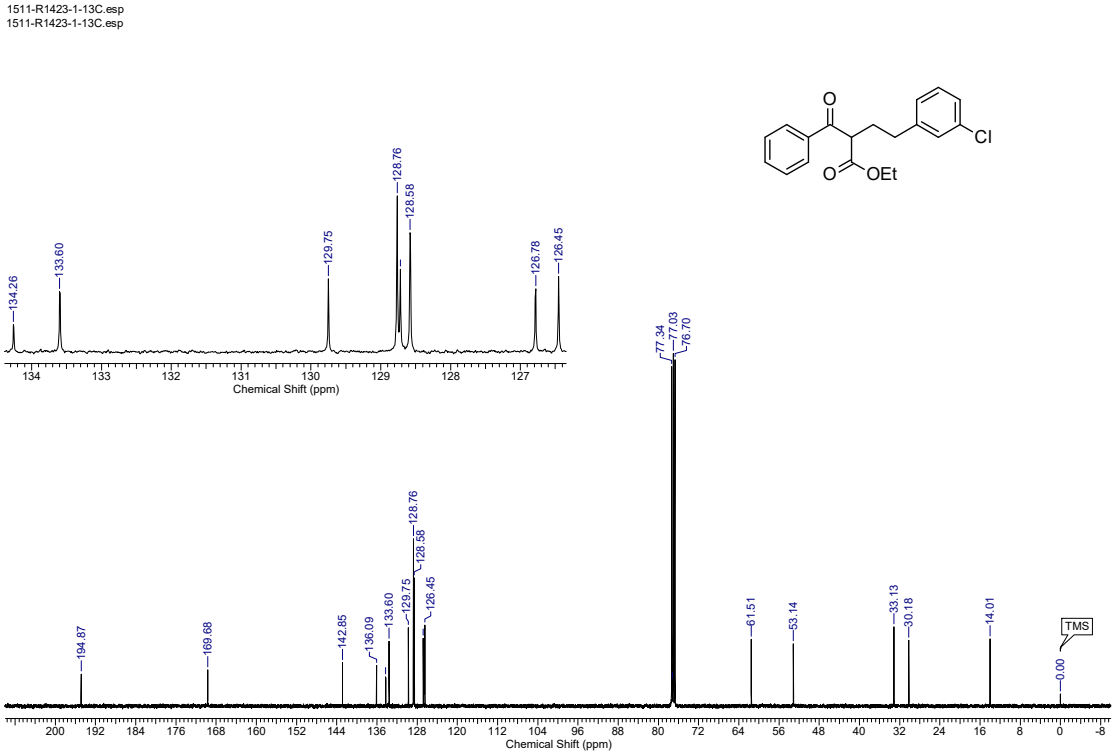


Figure S44. ^{13}C NMR spectrum of compound **3i**

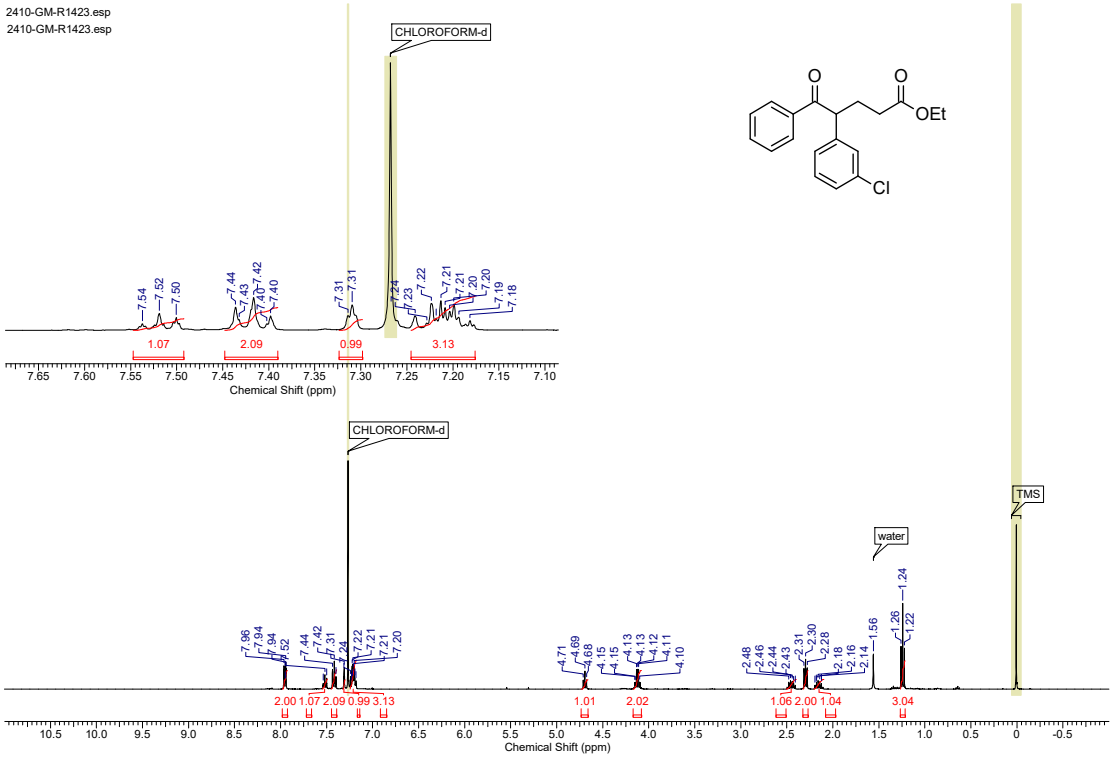


Figure S45. ^{1}H NMR spectrum of compound **4i**

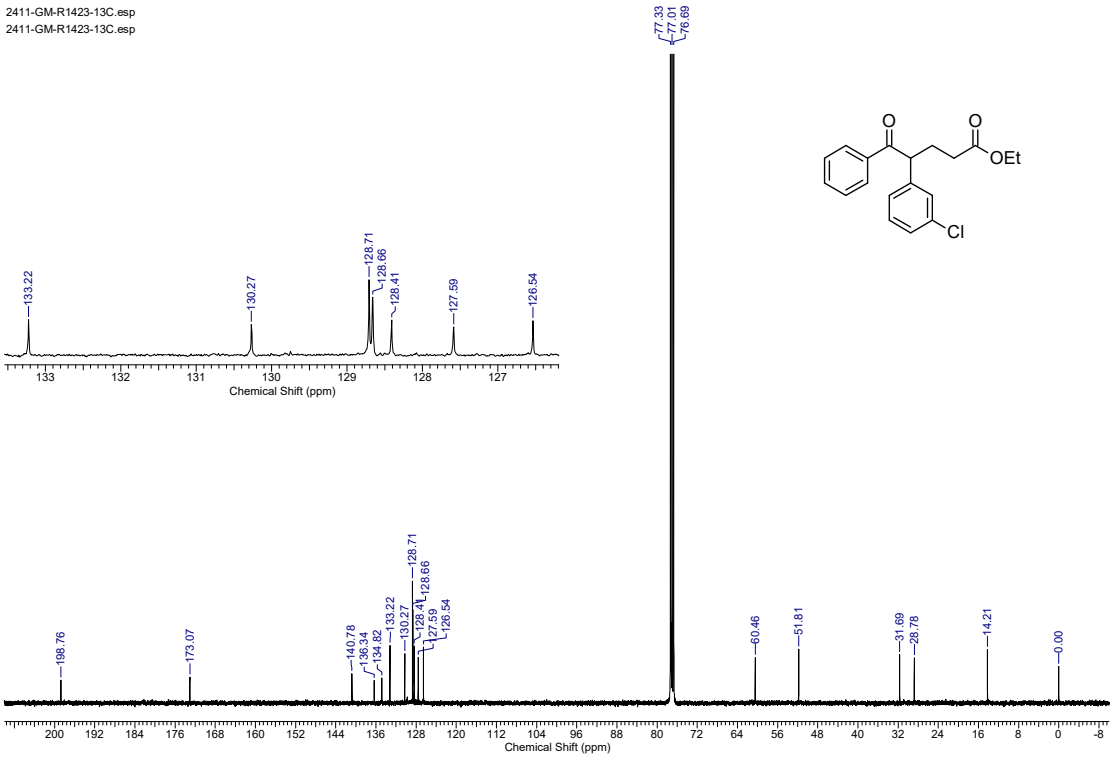


Figure S46. ^{13}C NMR spectrum of compound **4i**

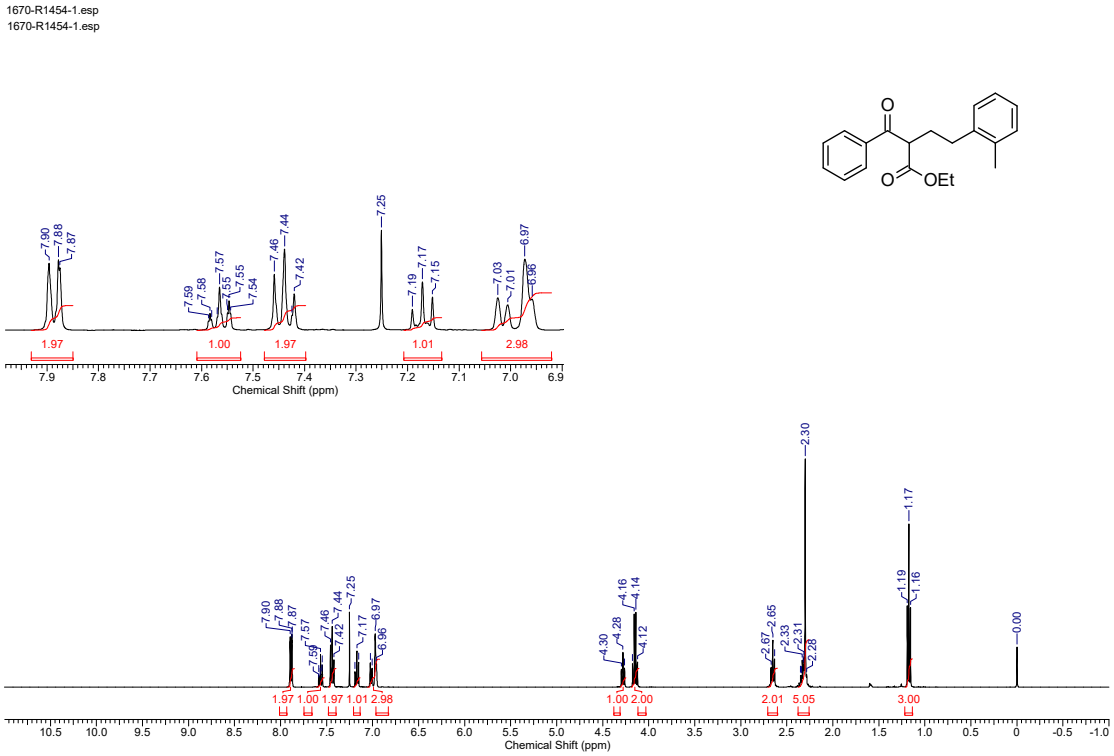


Figure S47. ^{1}H NMR spectrum of compound **3j**

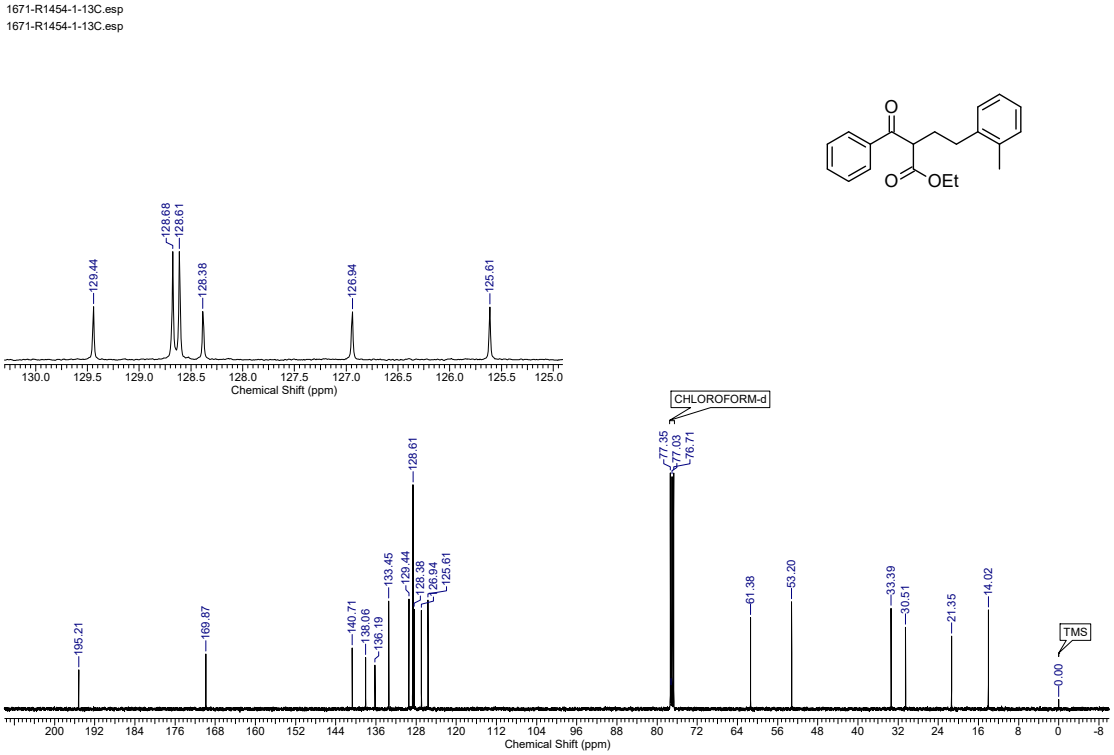


Figure S48. ^{13}C NMR spectrum of compound **3j**

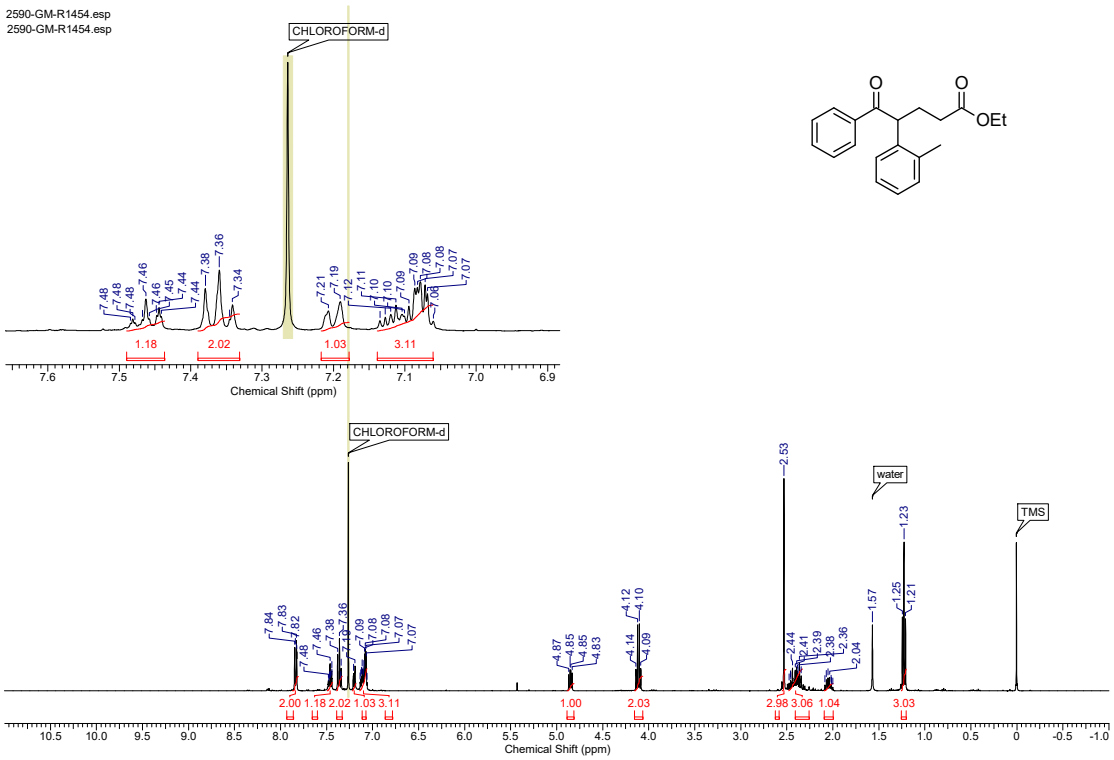


Figure S49. ^{1}H NMR spectrum of compound **4j**

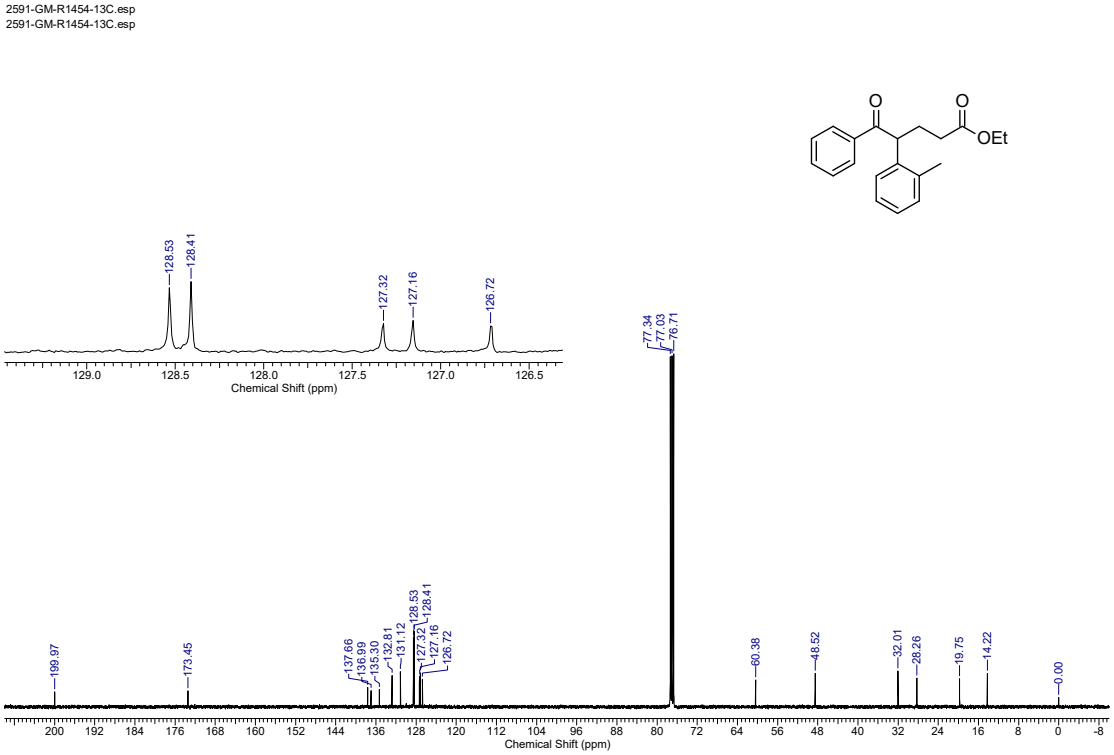


Figure S50. ^{13}C NMR spectrum of compound **4j**

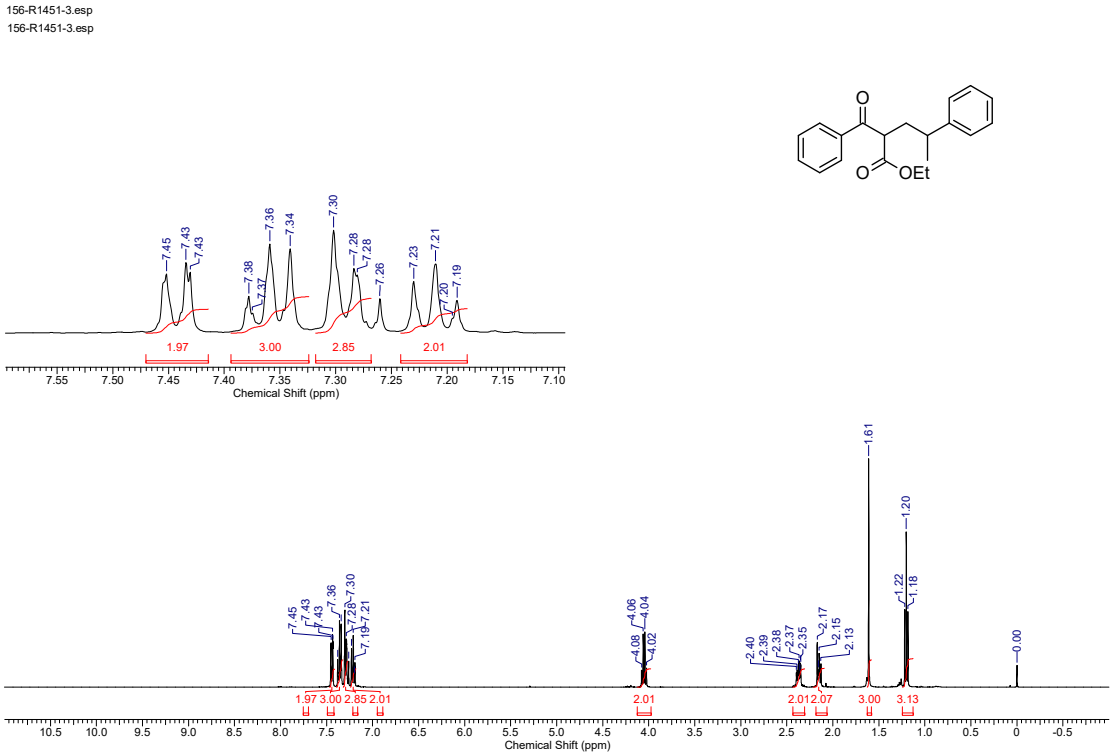


Figure S51. ^{1}H NMR spectrum of compound **3k**

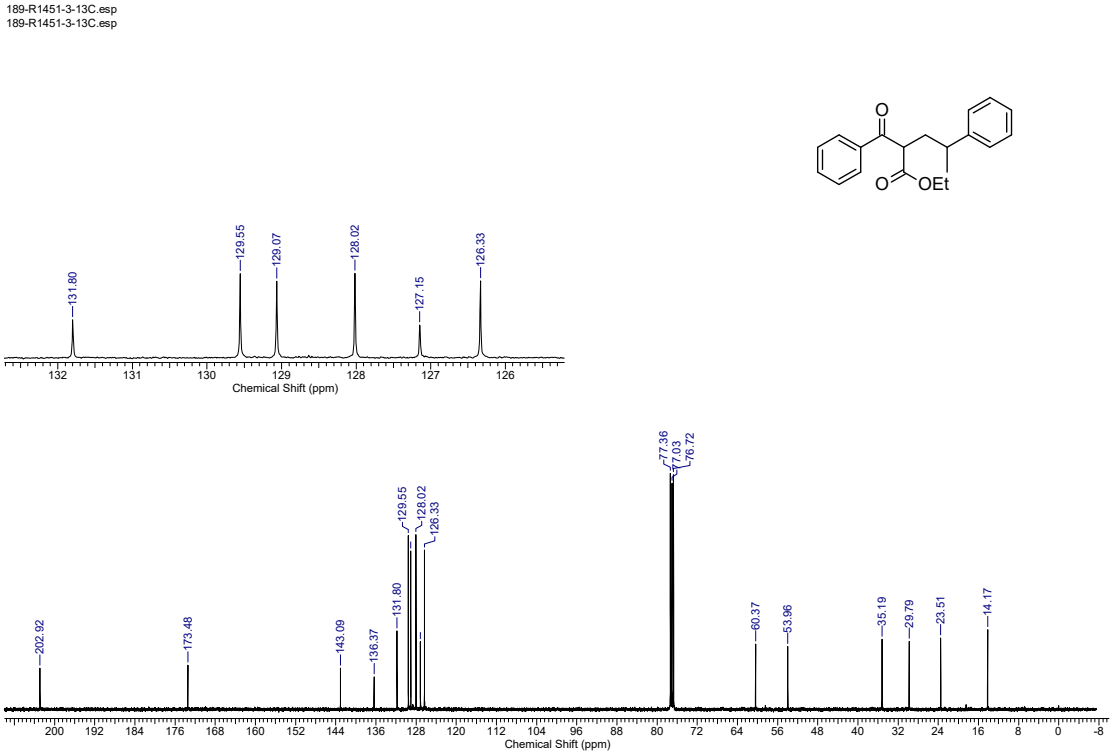


Figure S52. ^{13}C NMR spectrum of compound **3k**

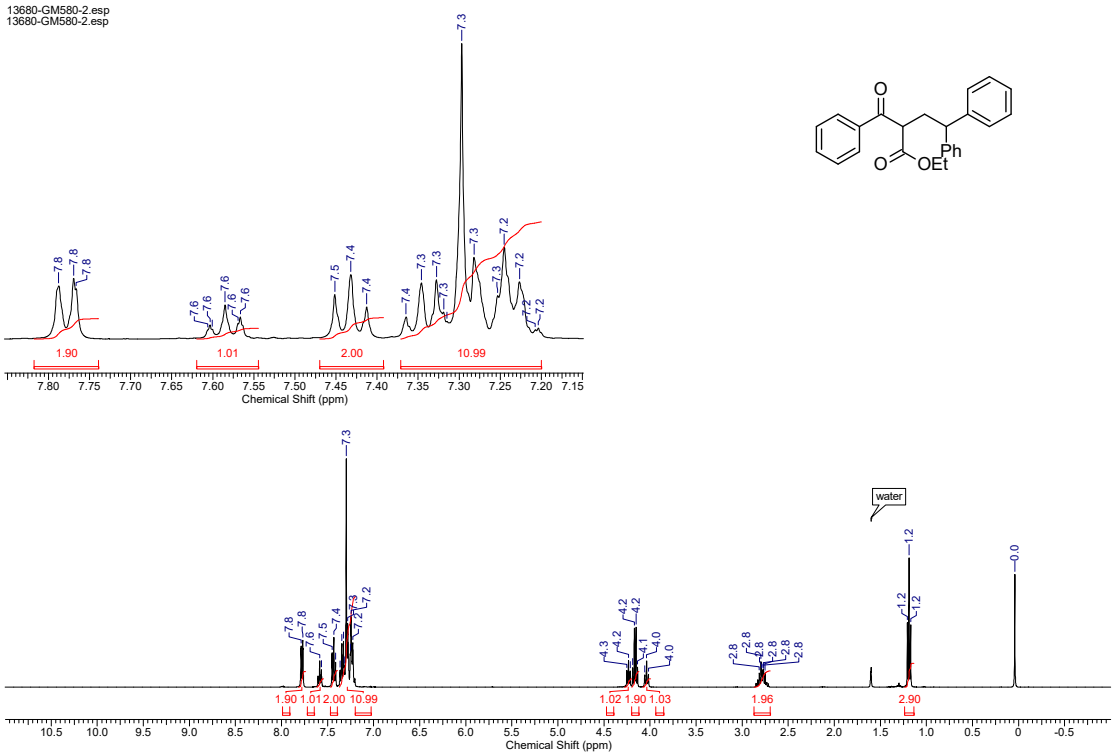


Figure S53. ^{1}H NMR spectrum of compound **3l**

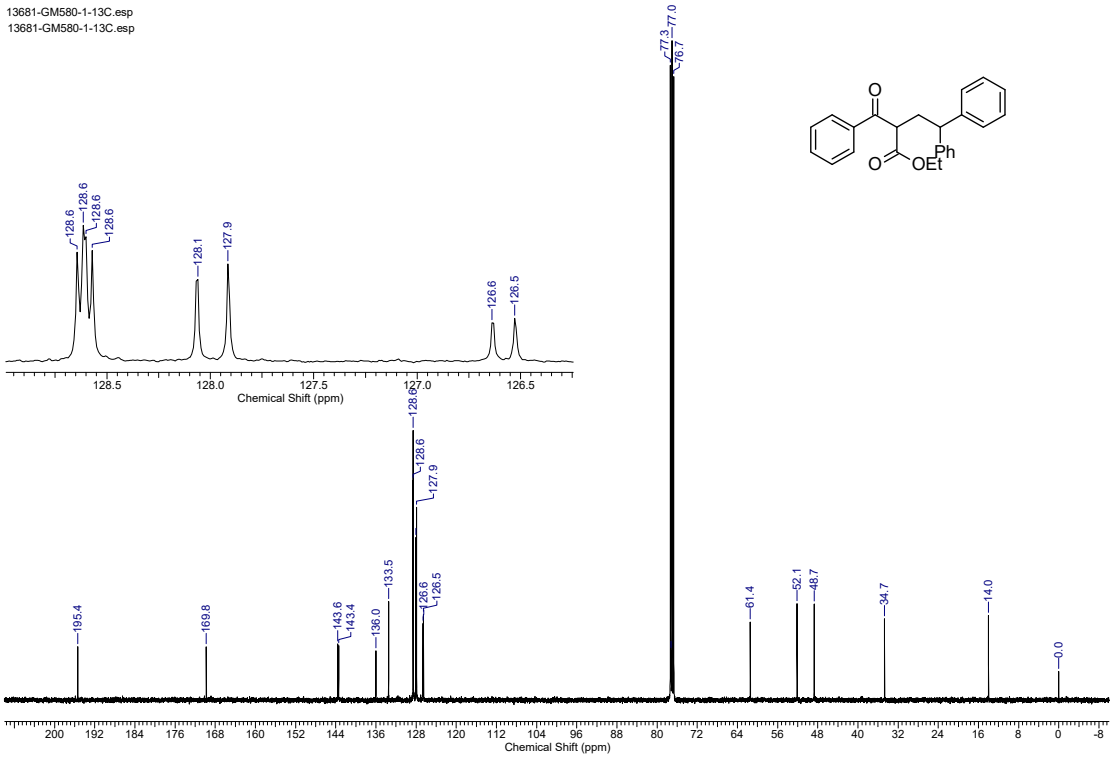


Figure S54. ^{13}C NMR spectrum of compound **3l**

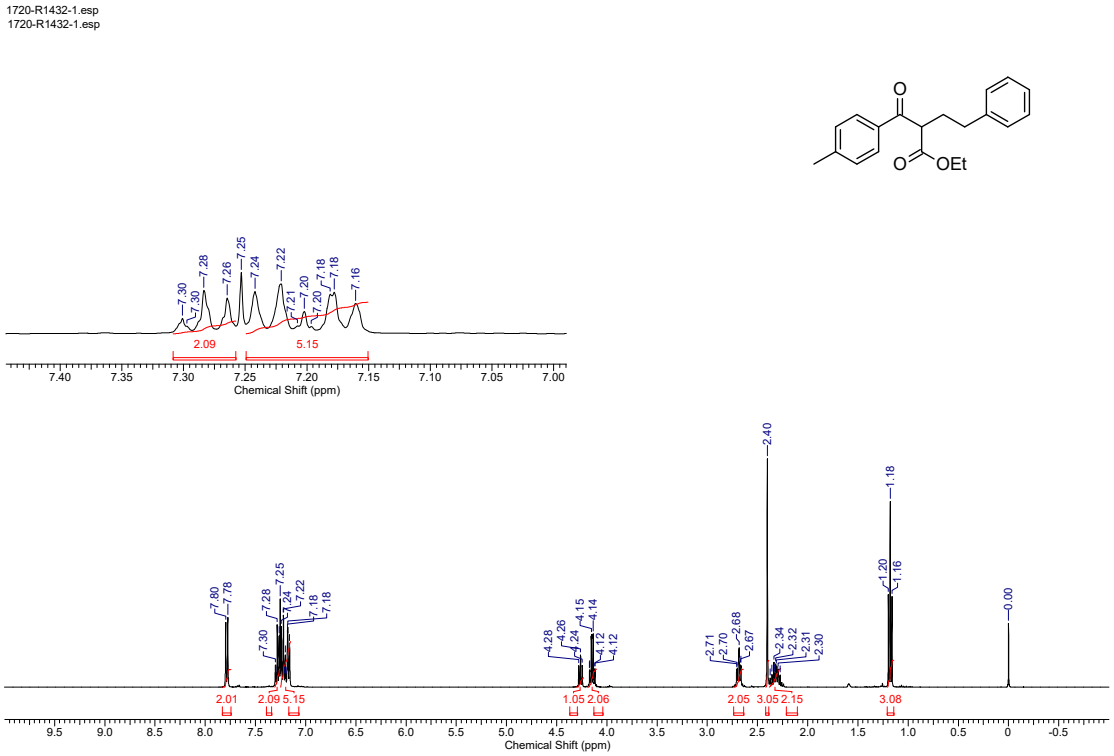


Figure S55. ^{1}H NMR spectrum of compound **3m**

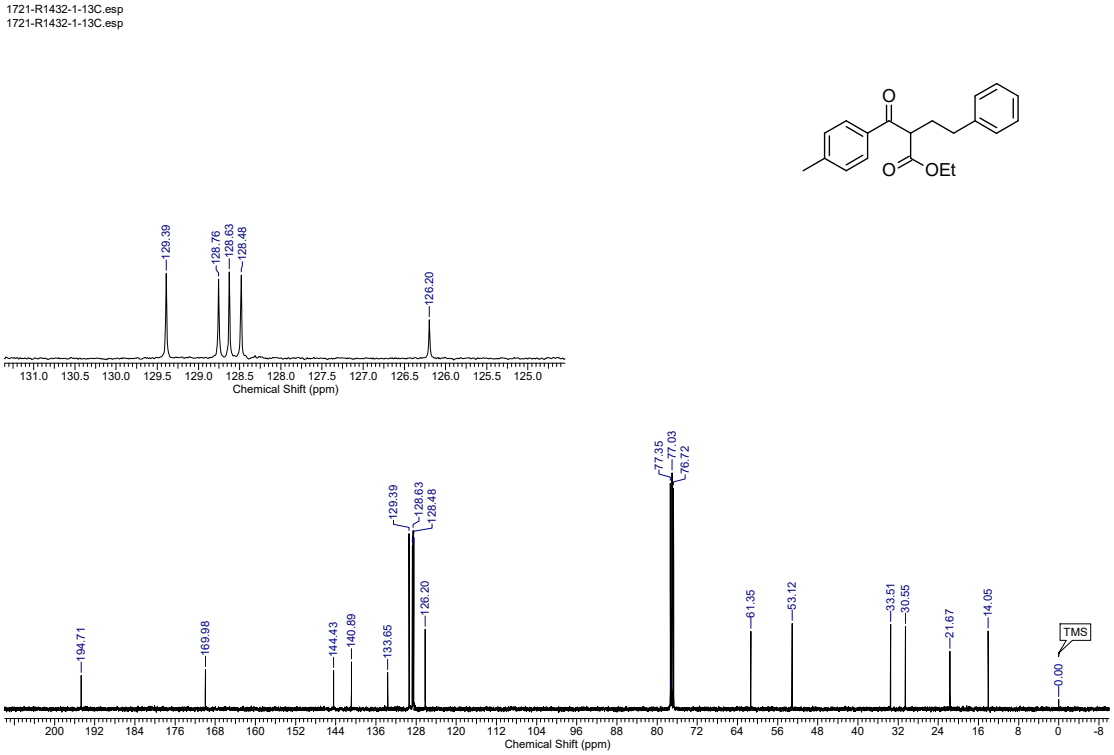


Figure S56. ^{13}C NMR spectrum of compound **3m**

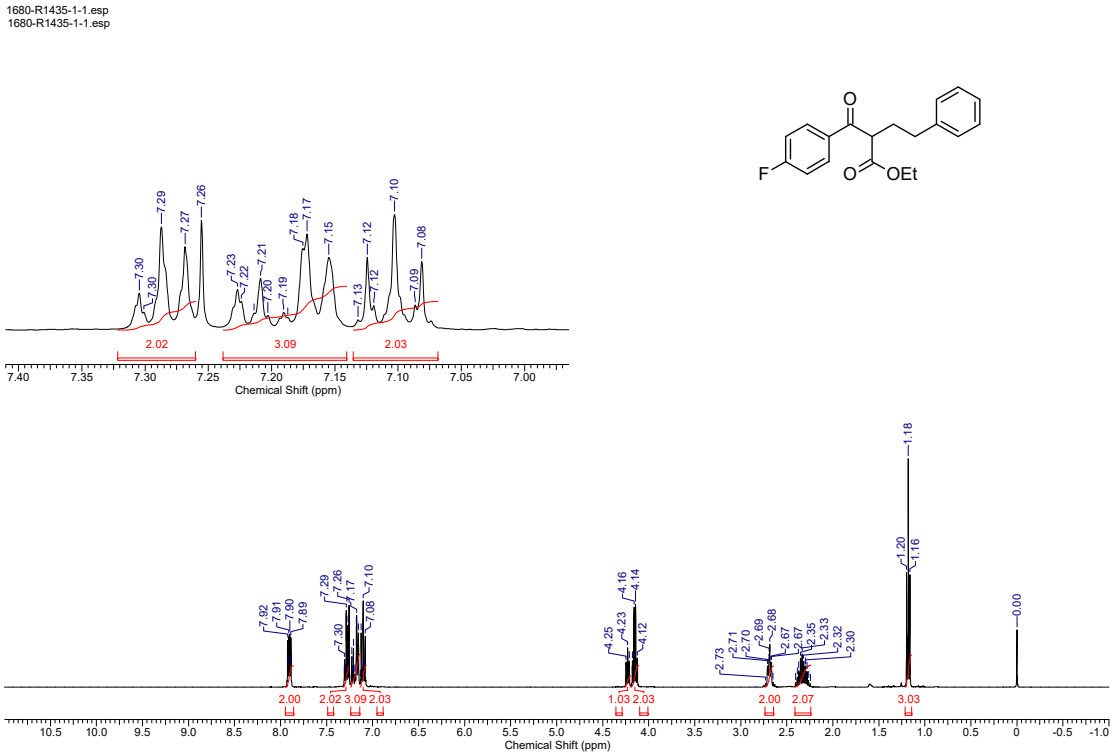


Figure S57. ^{1}H NMR spectrum of compound **3n**

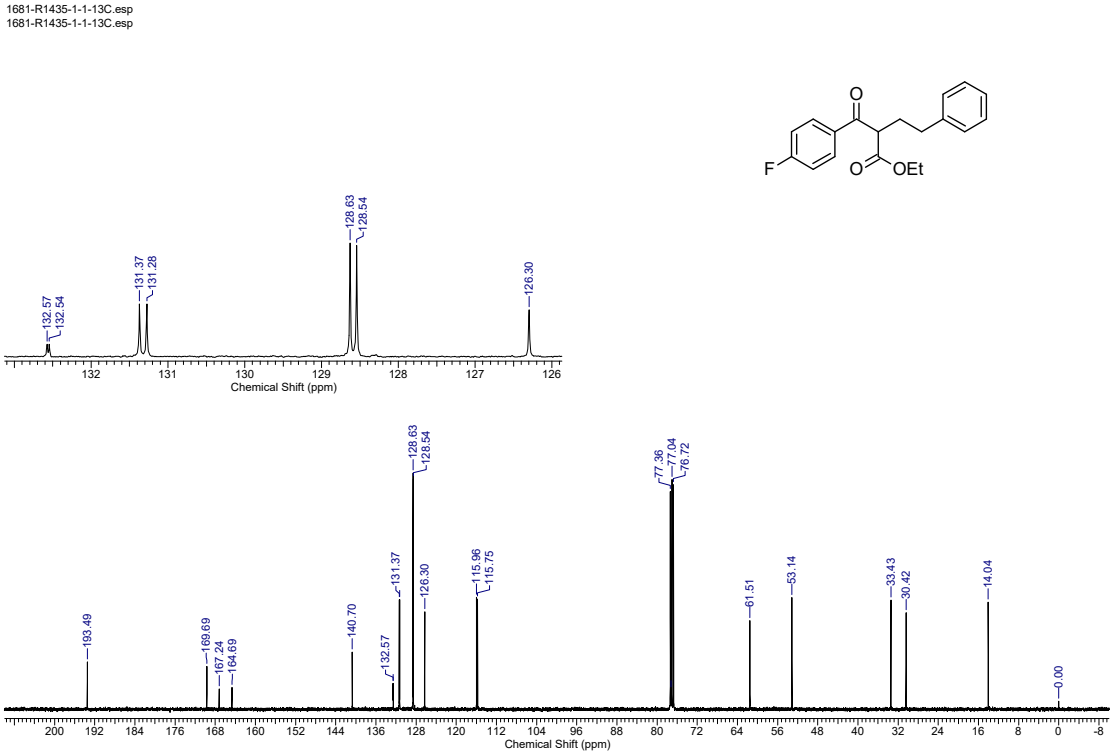


Figure S58. ^{13}C NMR spectrum of compound **3n**

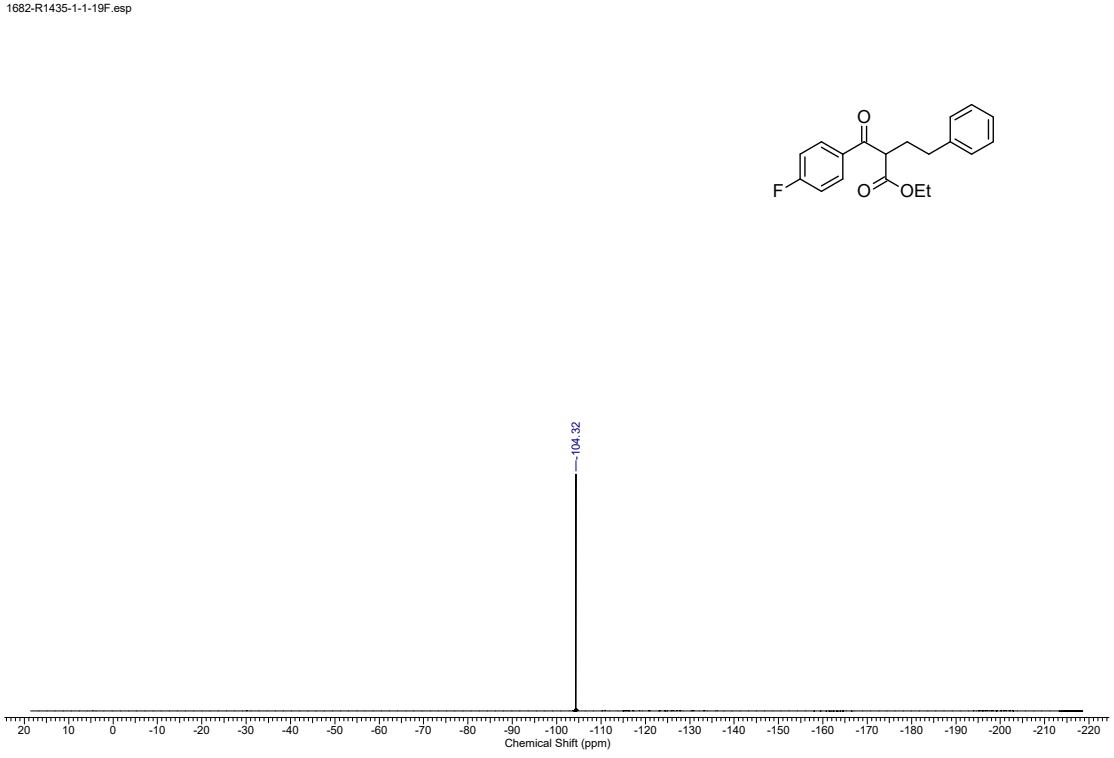


Figure S59. ^{19}F NMR spectrum of compound **3n**

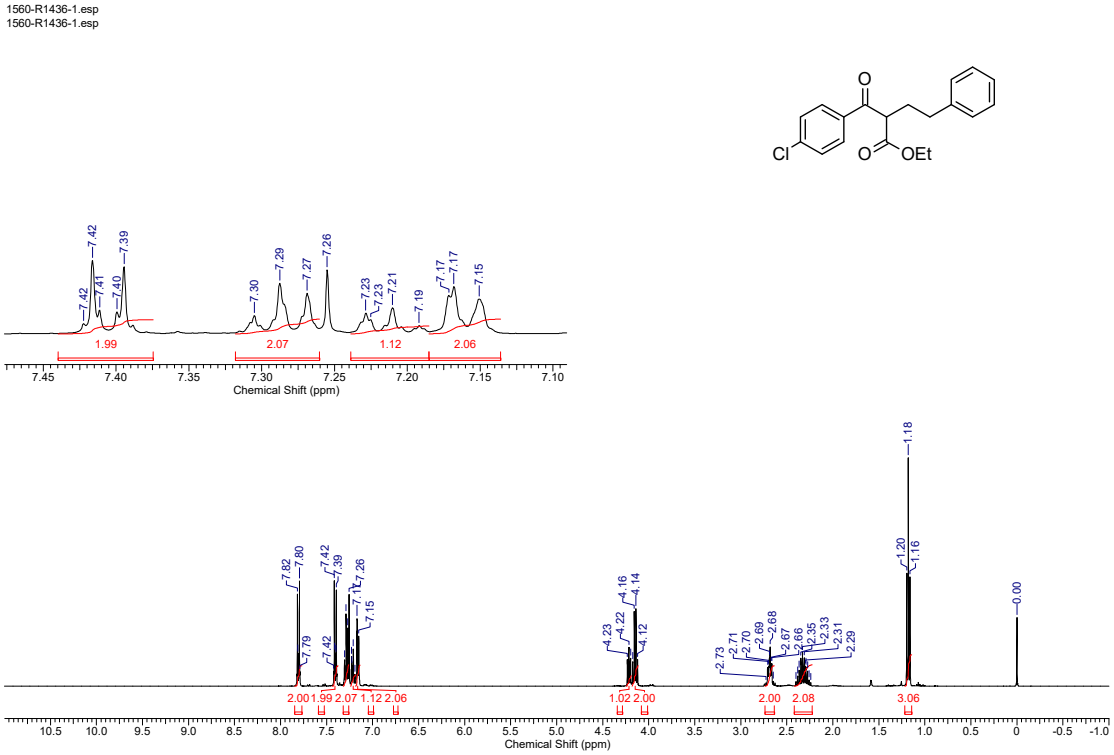


Figure S60. ^{1}H NMR spectrum of compound **3o**

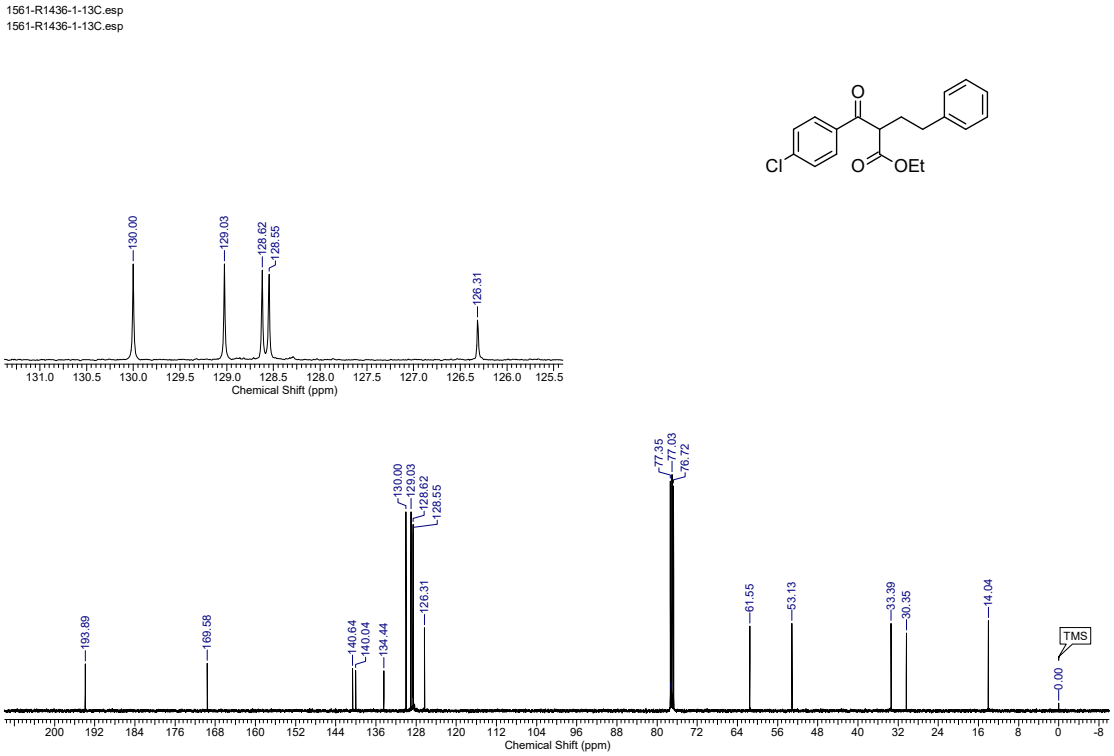


Figure S61. ^{13}C NMR spectrum of compound **3o**

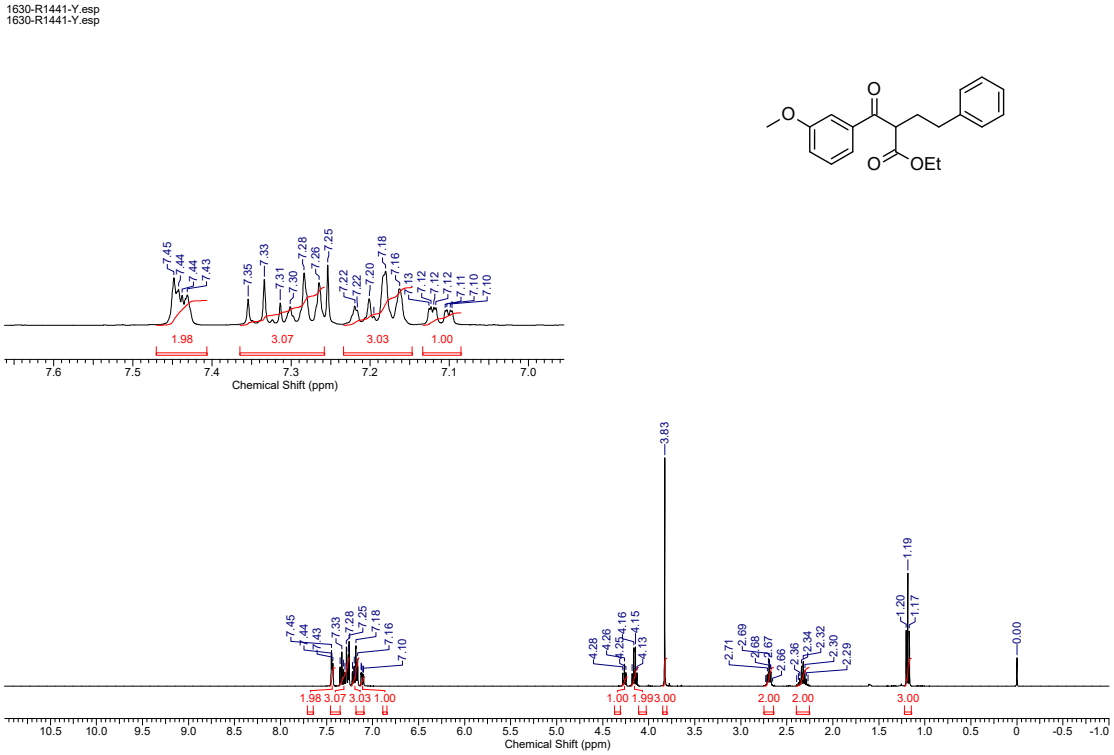


Figure S62. ^{1}H NMR spectrum of compound **3p**

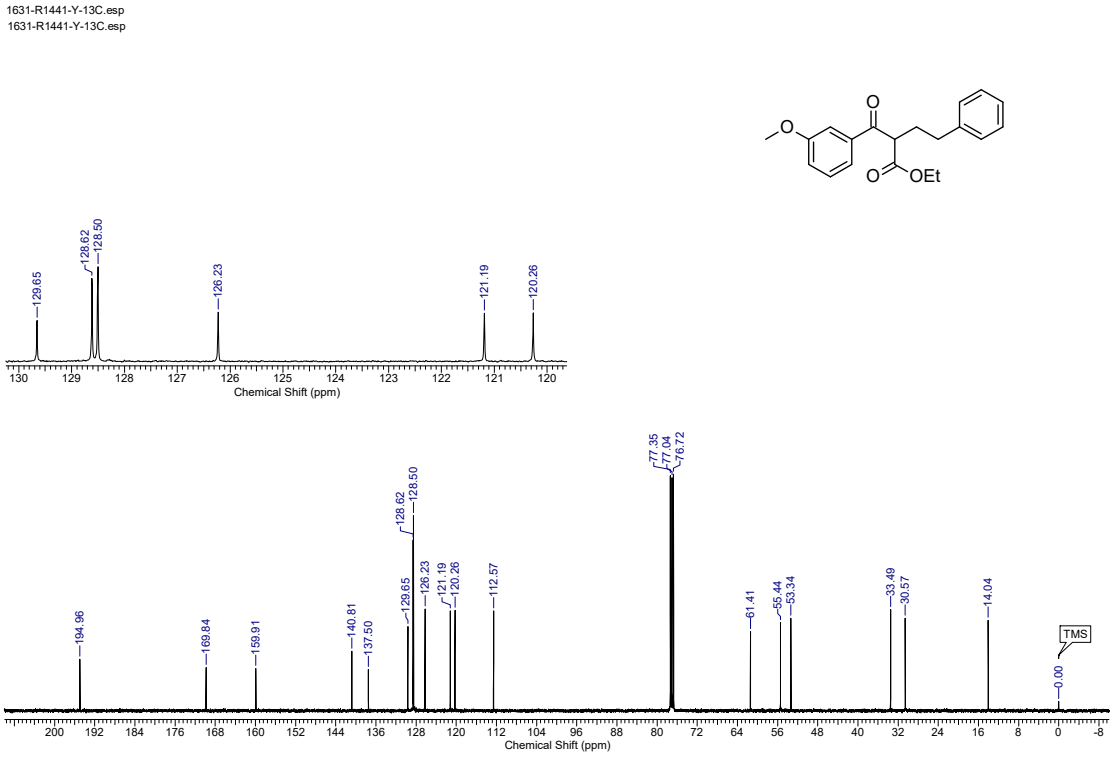


Figure S63. ^{13}C NMR spectrum of compound **3p**

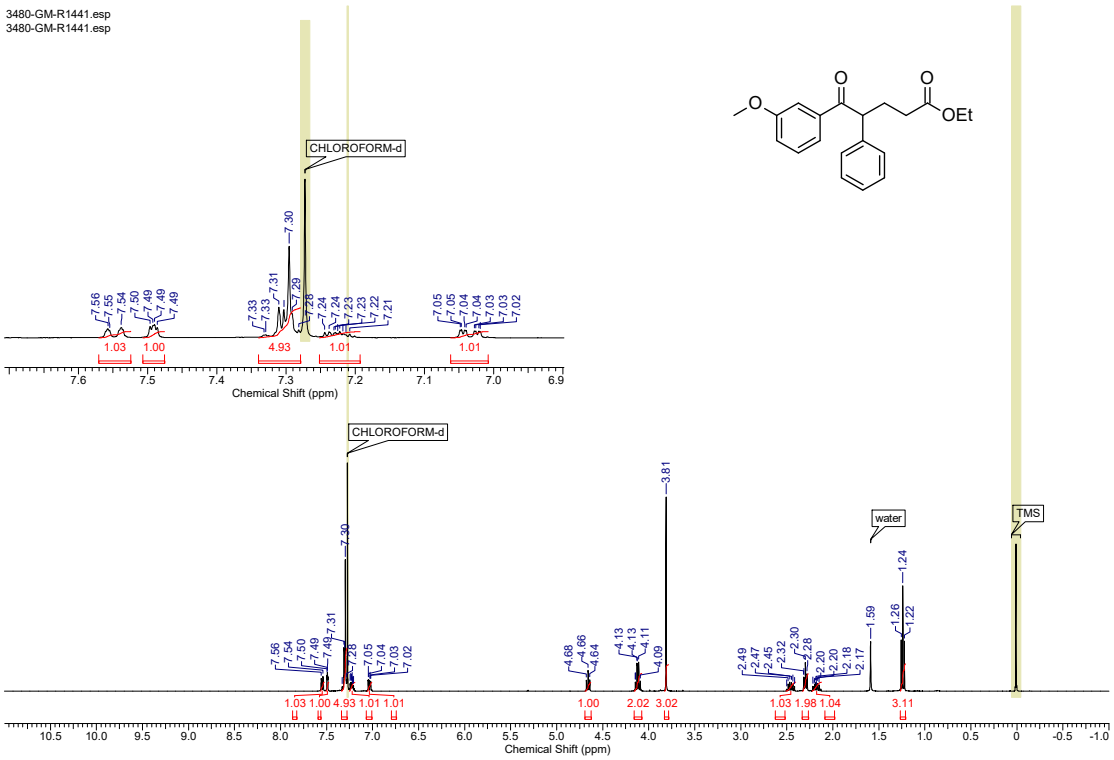


Figure S64. [1]H NMR spectrum of compound **4p**

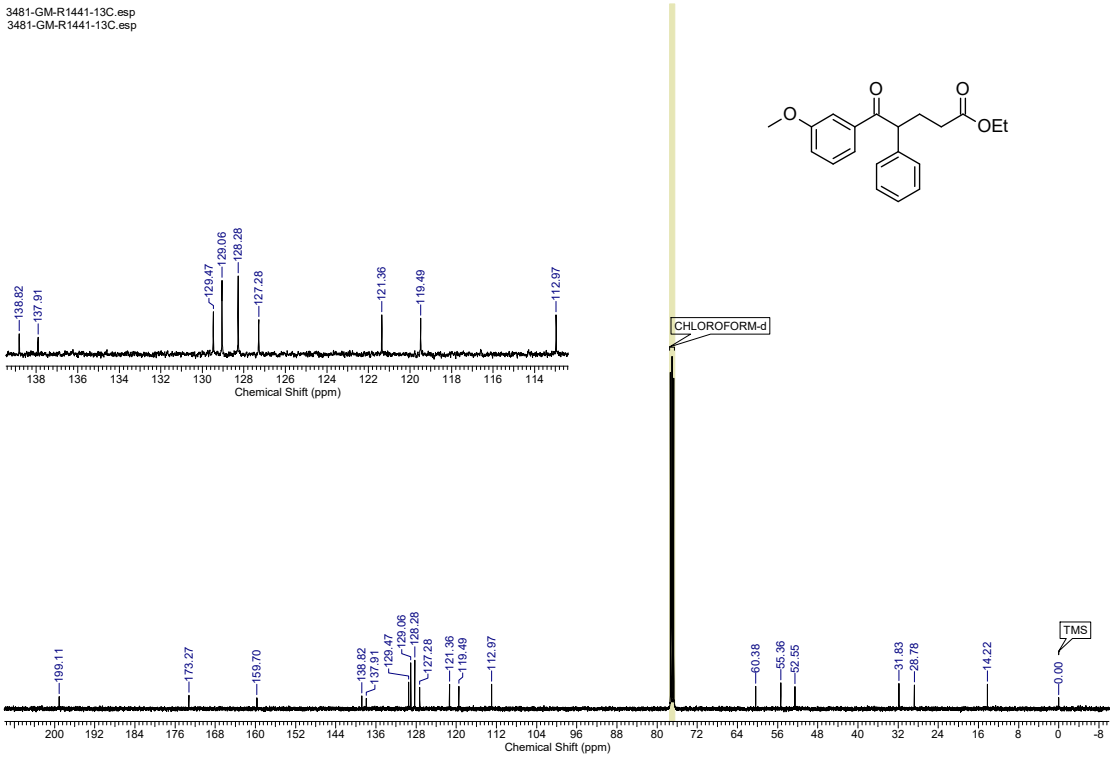


Figure S65. [13]C NMR spectrum of compound **4p**

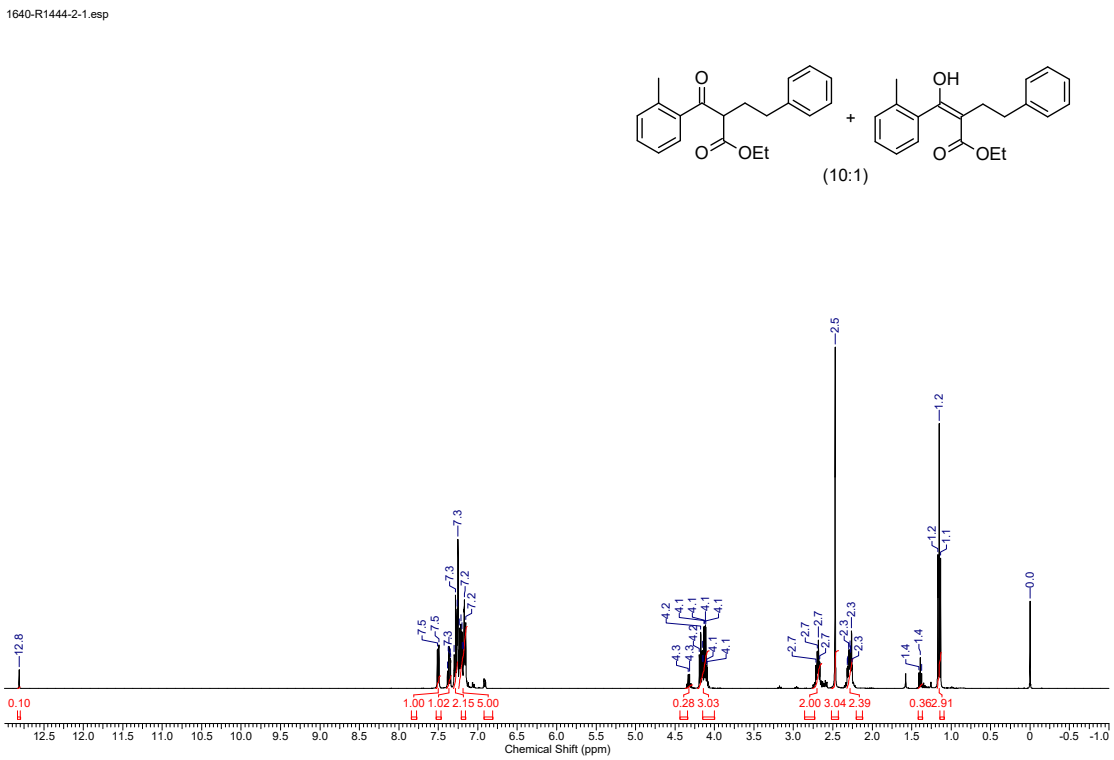


Figure S66. ^{1}H NMR spectrum of compound **3q**

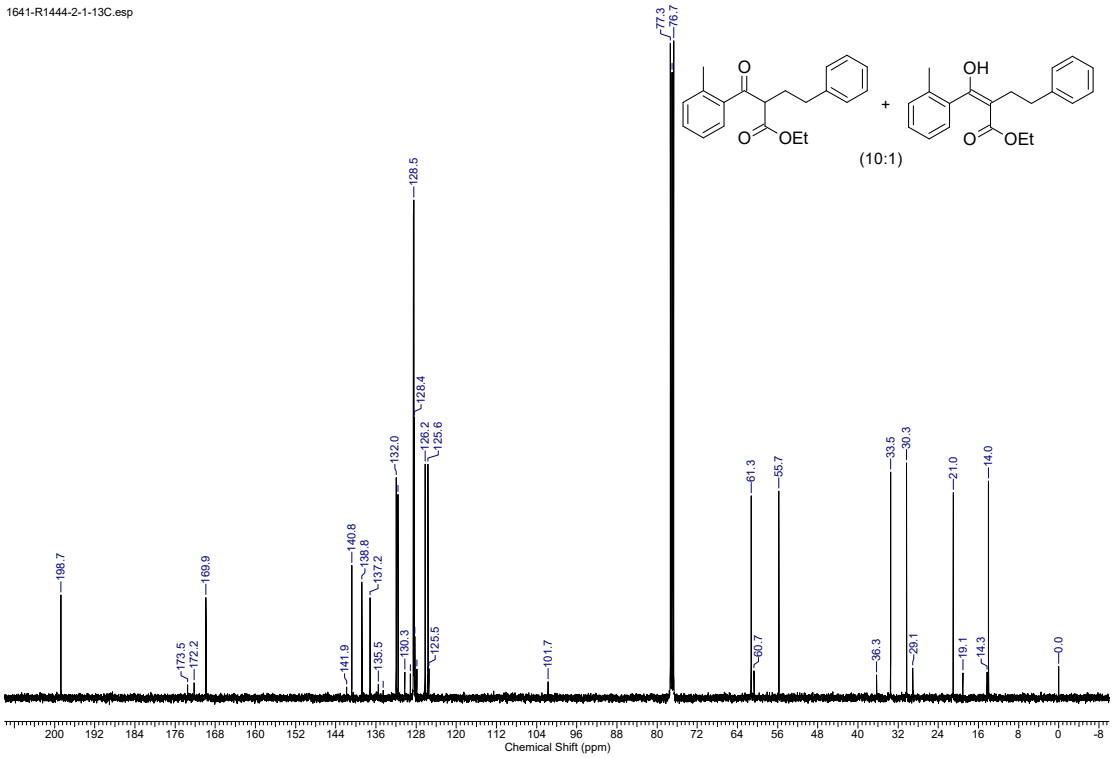


Figure S67. ^{13}C NMR spectrum of compound **3q**

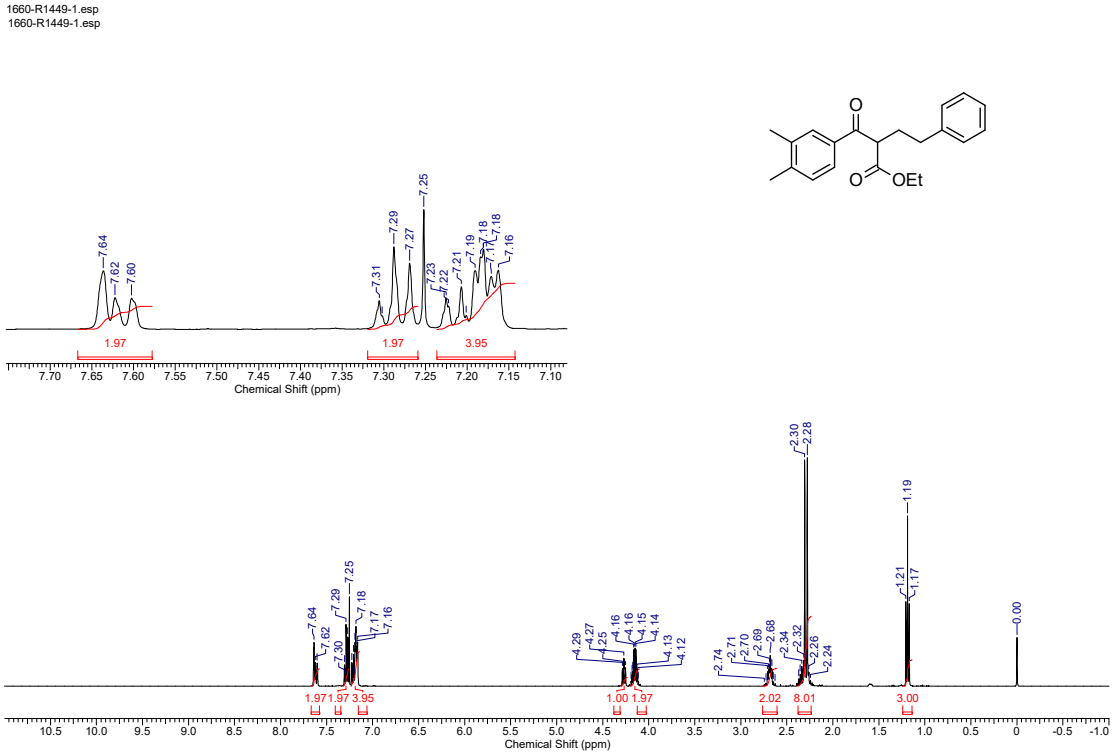


Figure S68. [1]H NMR spectrum of compound **3r**

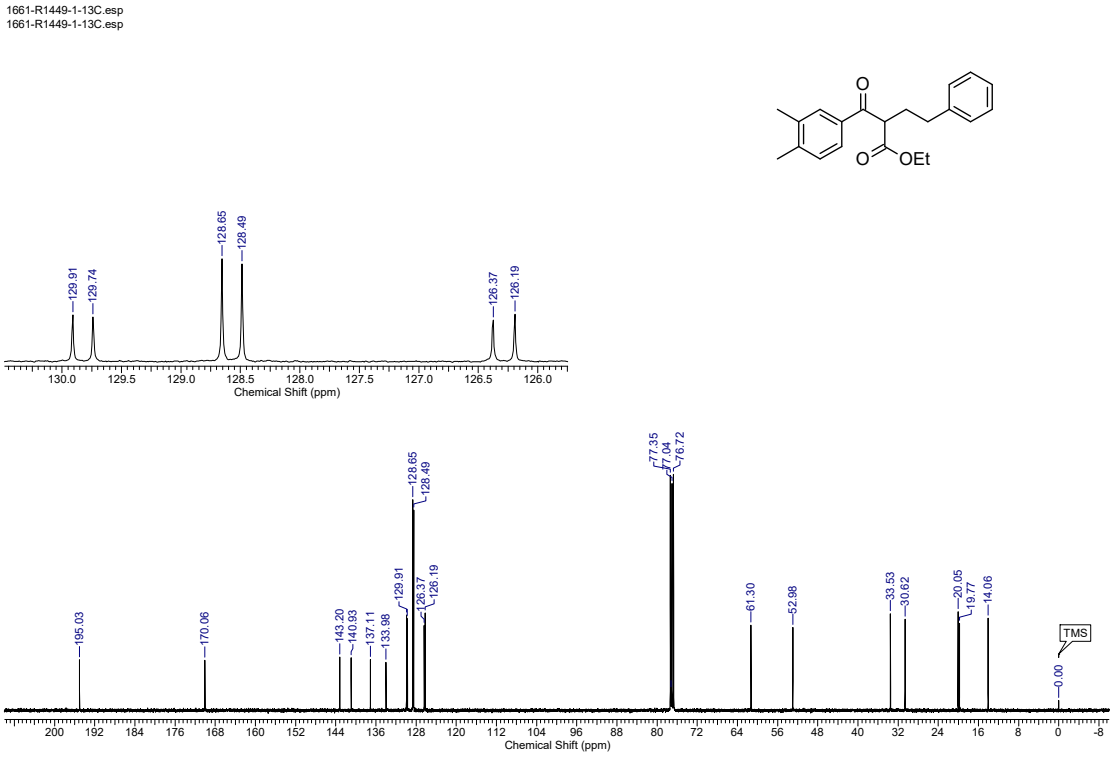


Figure S69. [13]C NMR spectrum of compound **3r**

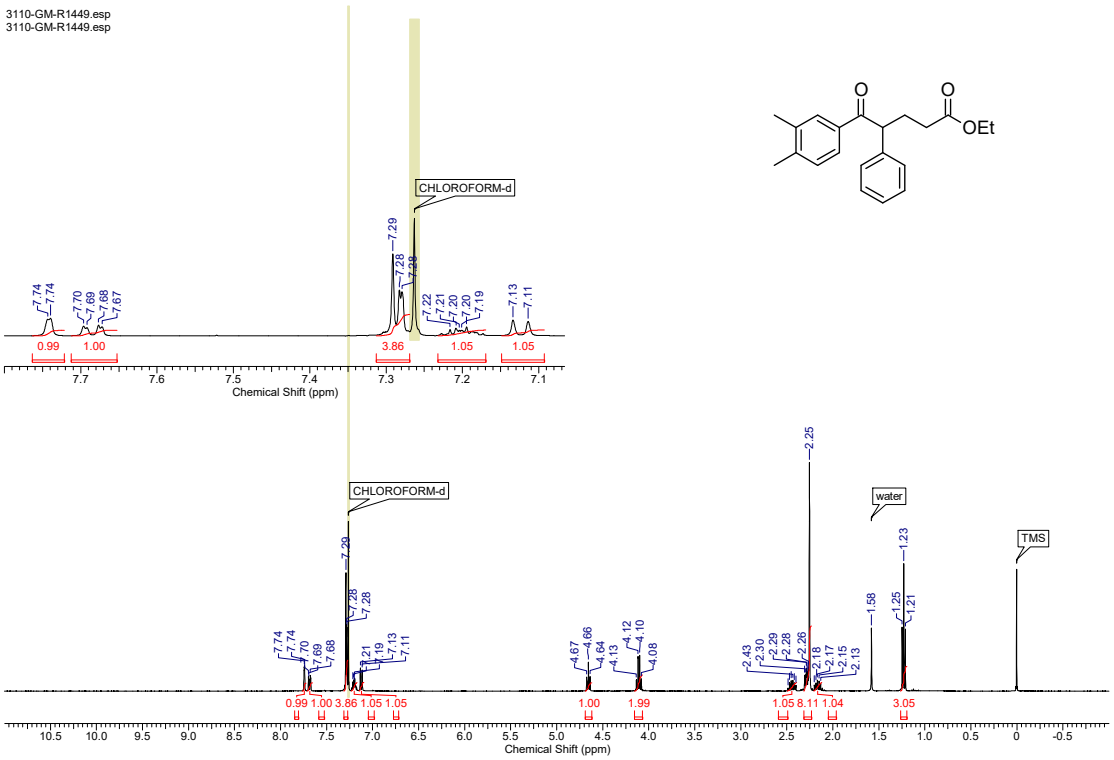


Figure S70. ^{1}H NMR spectrum of compound **4r**

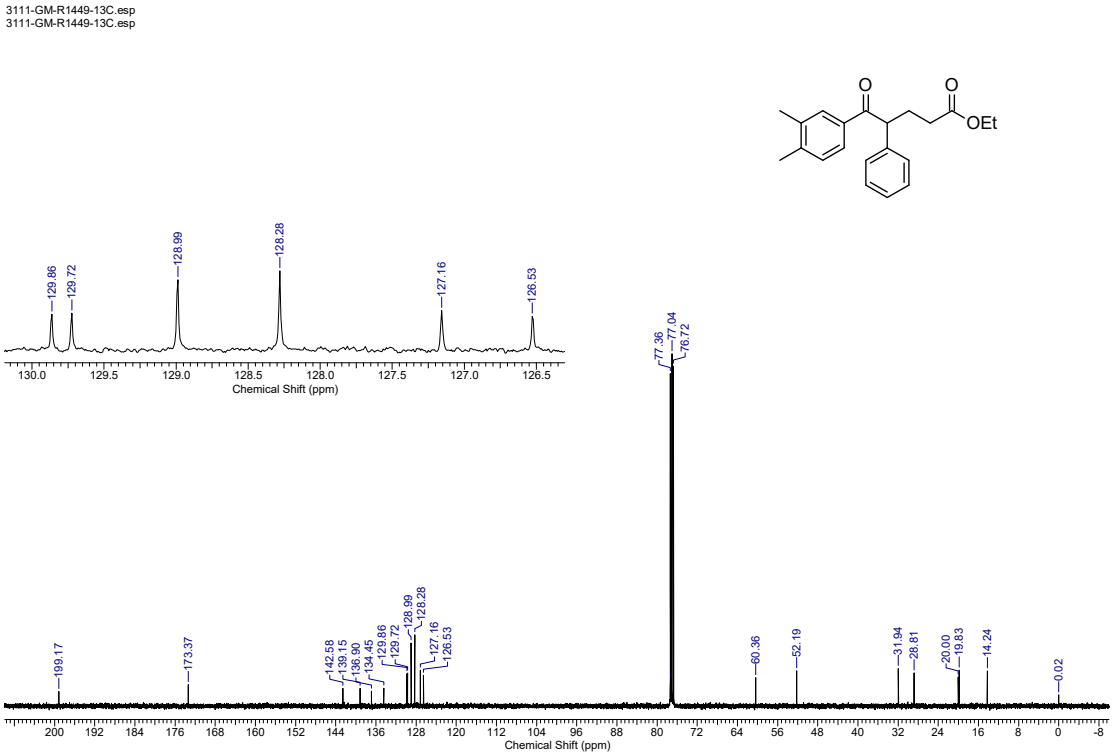


Figure S71. ^{13}C NMR spectrum of compound **4r**

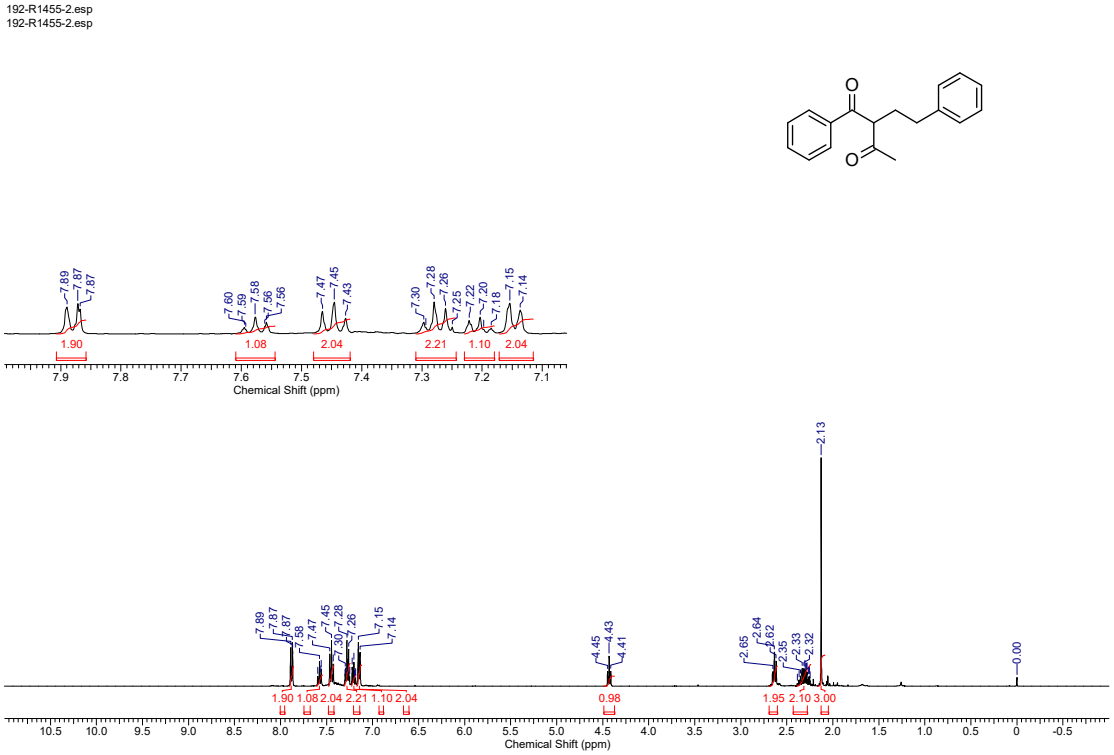


Figure S72. ^{1}H NMR spectrum of compound **3s**

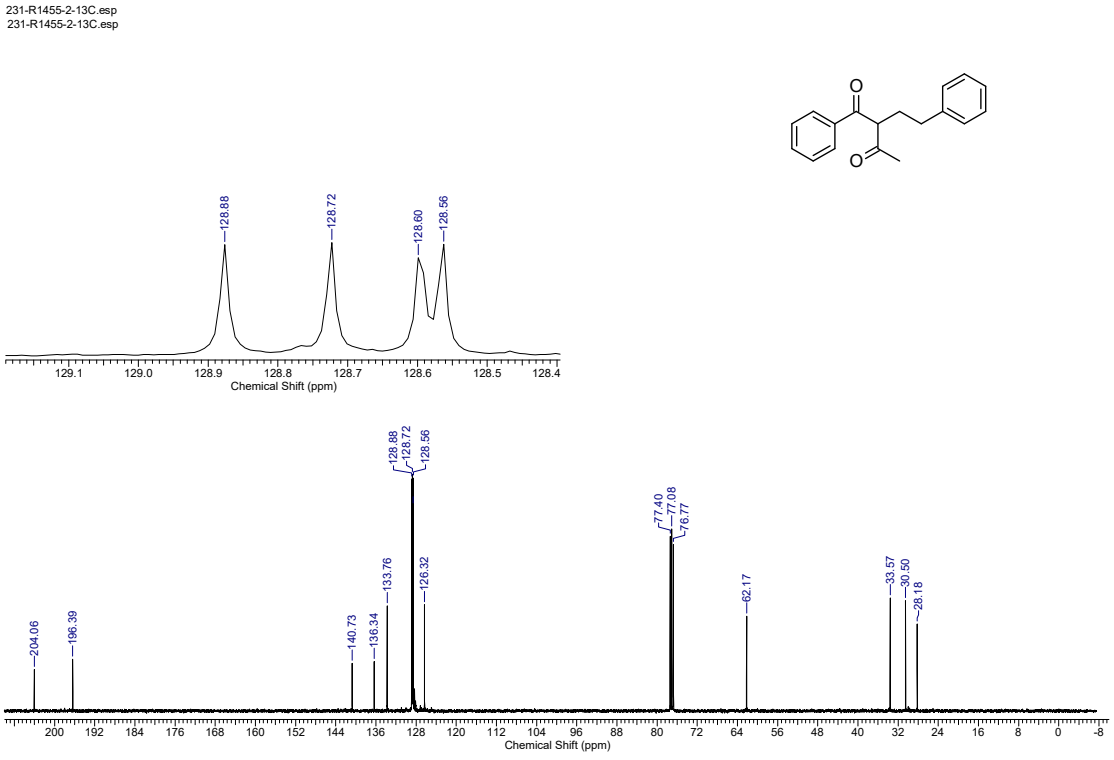


Figure S73. ^{13}C NMR spectrum of compound **3s**

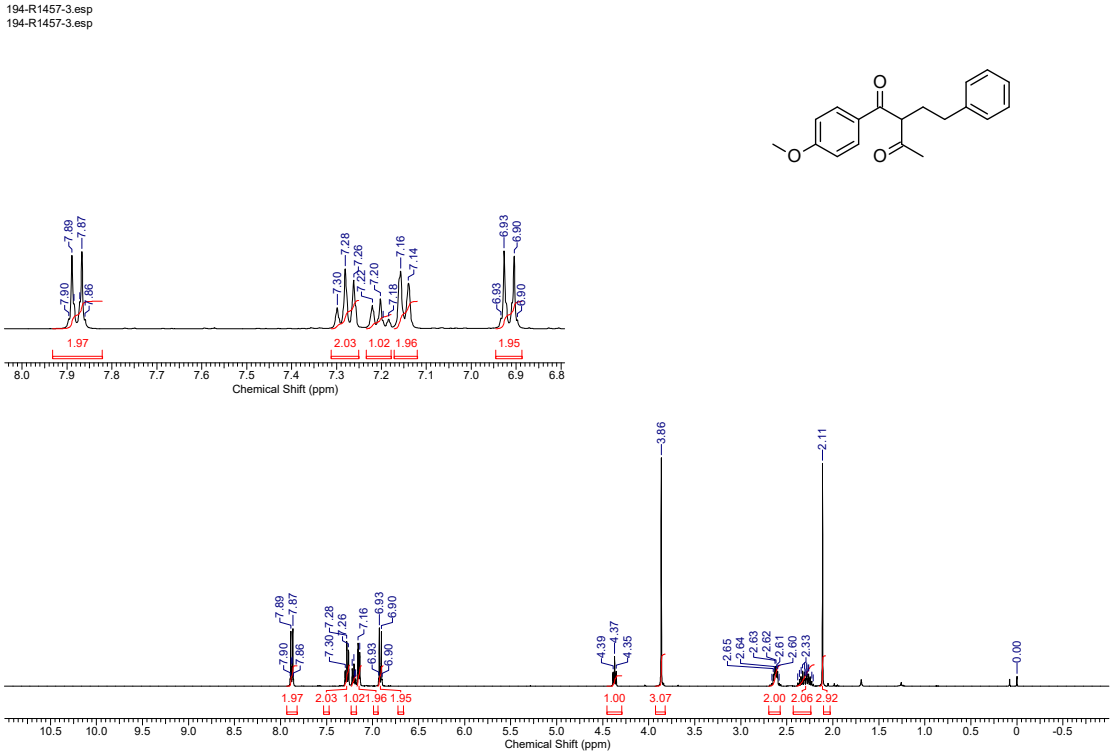


Figure S74. ^{1}H NMR spectrum of compound **3t**

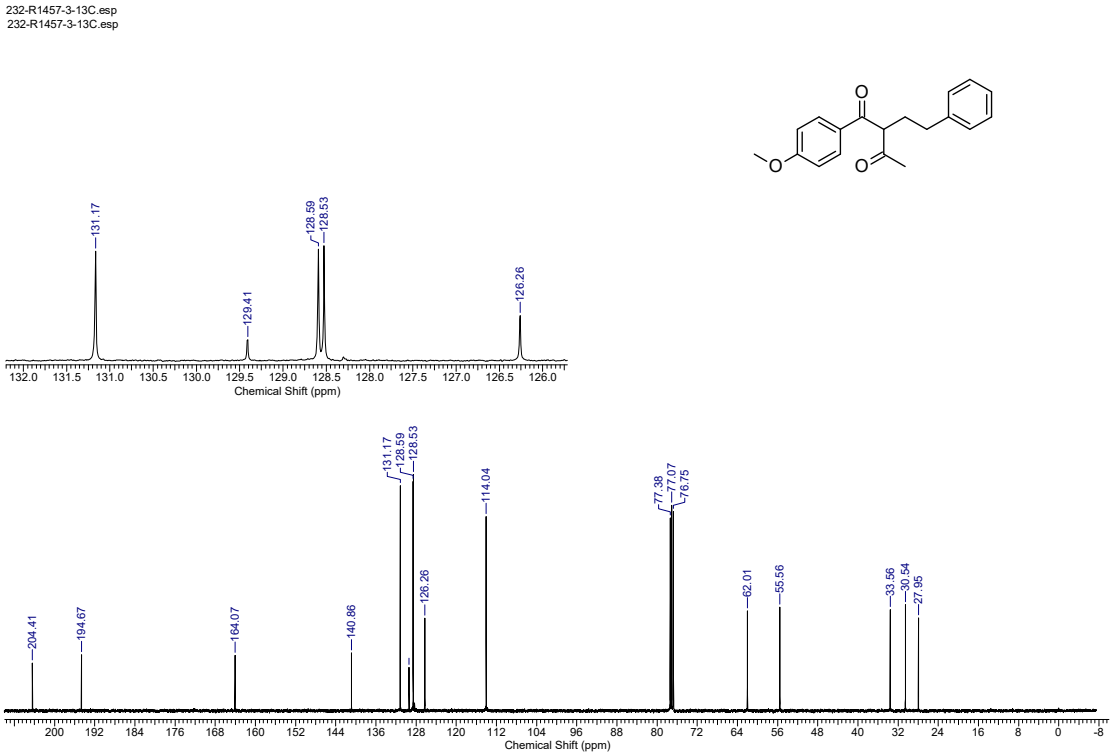


Figure S75. ^{13}C NMR spectrum of compound **3t**

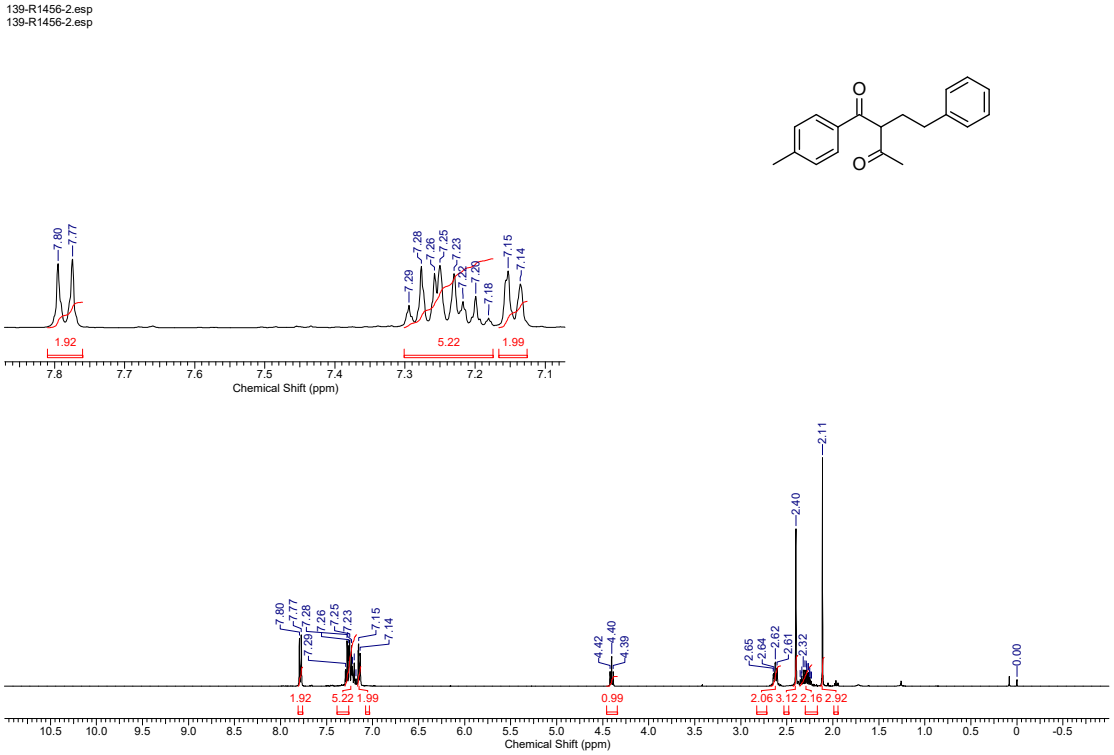


Figure S76. ^{1}H NMR spectrum of compound **3u**

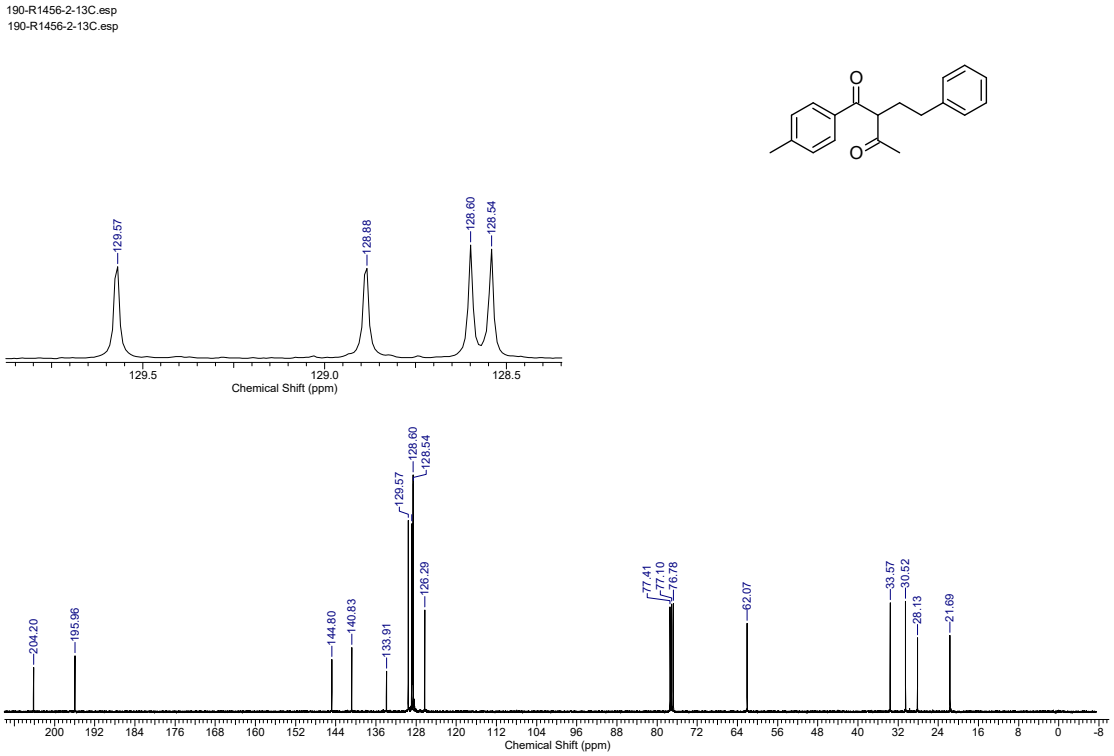


Figure S77. ^{13}C NMR spectrum of compound **3u**

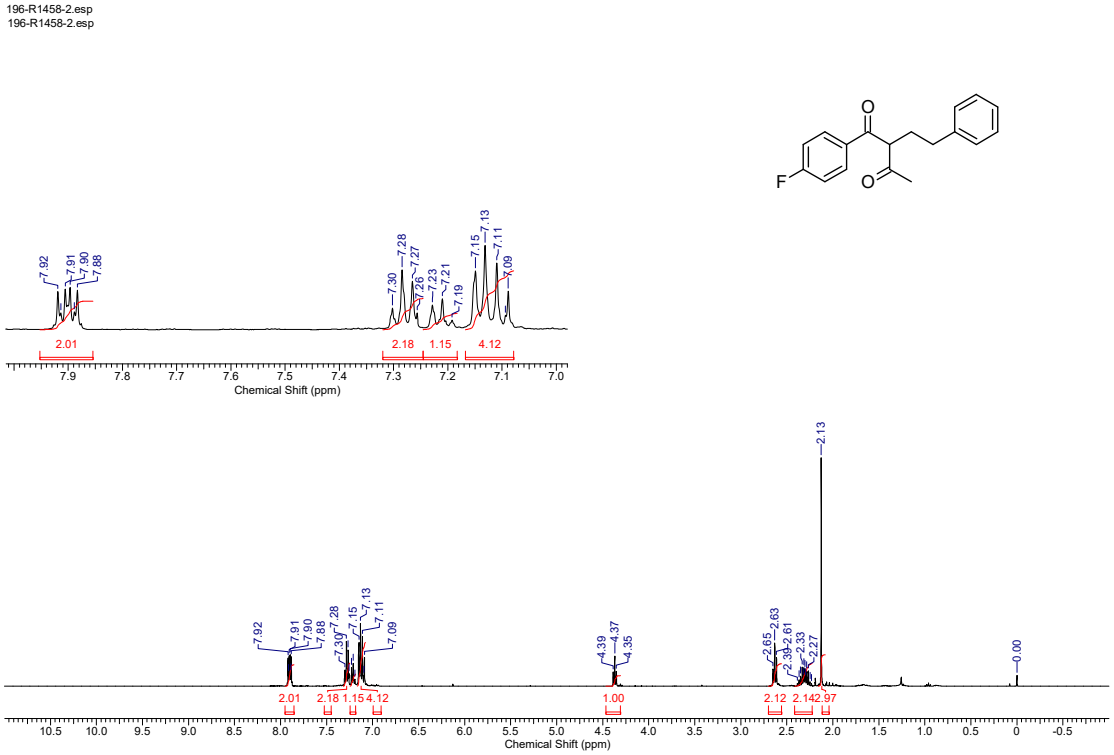


Figure S78. ^{1}H NMR spectrum of compound **3v**

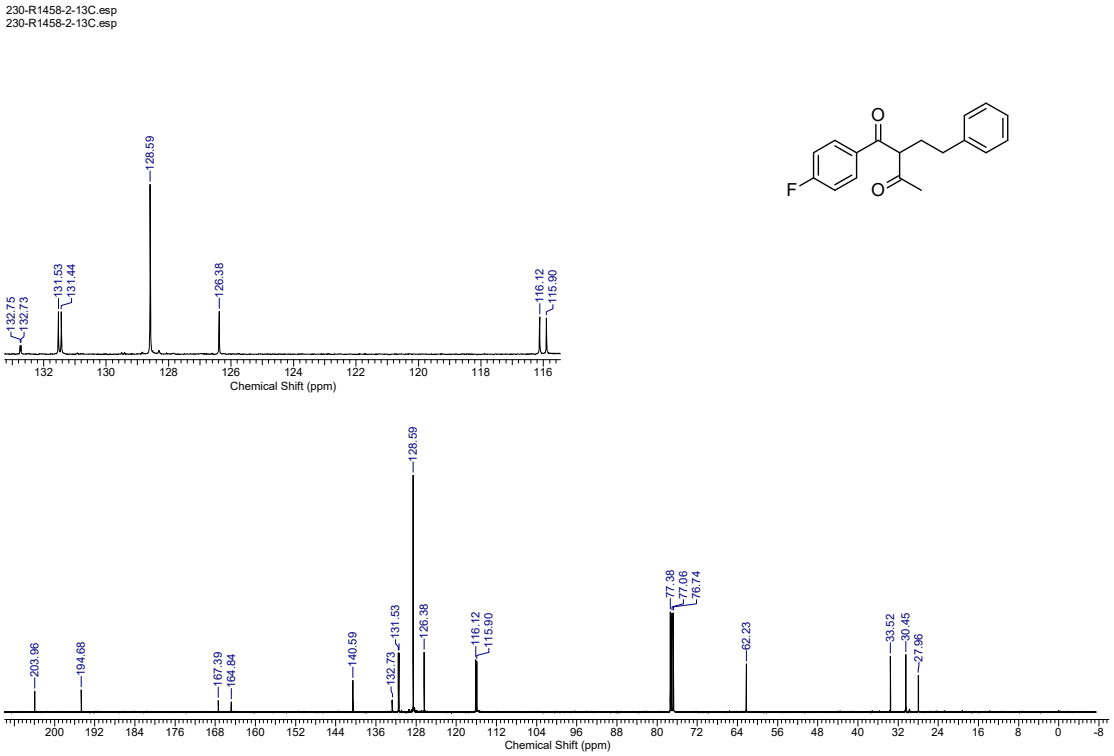


Figure S79. ^{13}C NMR spectrum of compound **3v**

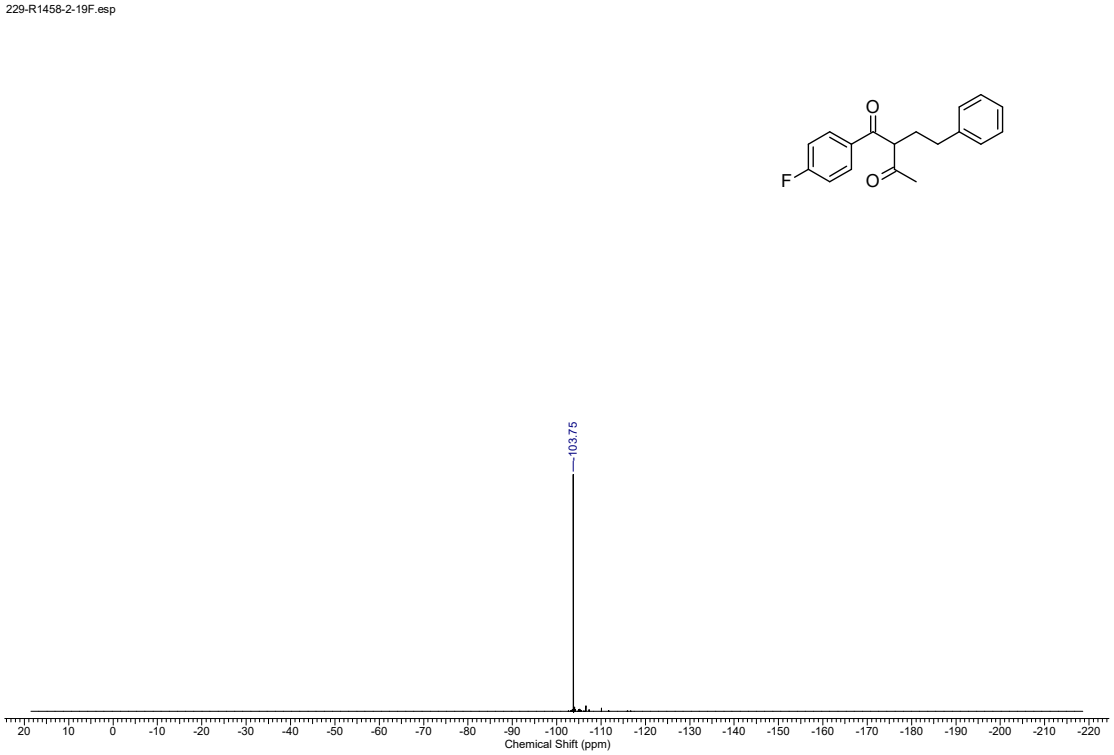


Figure S80. ^{19}F NMR spectrum of compound **3v**

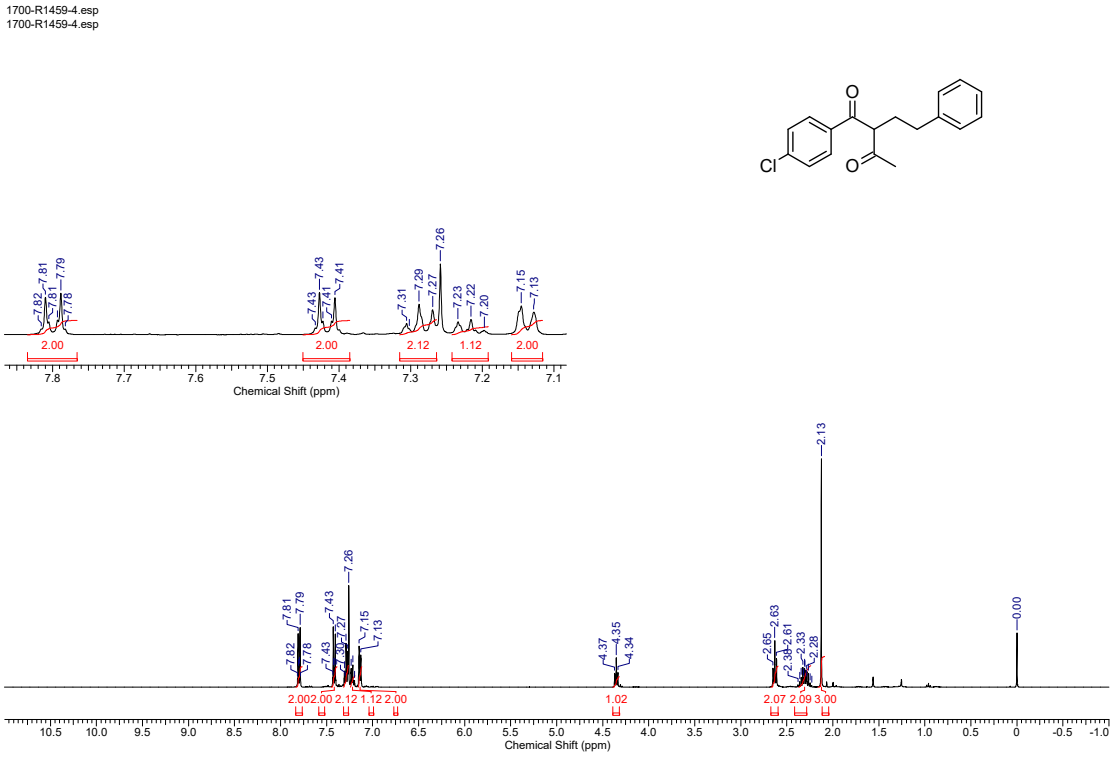


Figure S81. ^{1}H NMR spectrum of compound **3w**

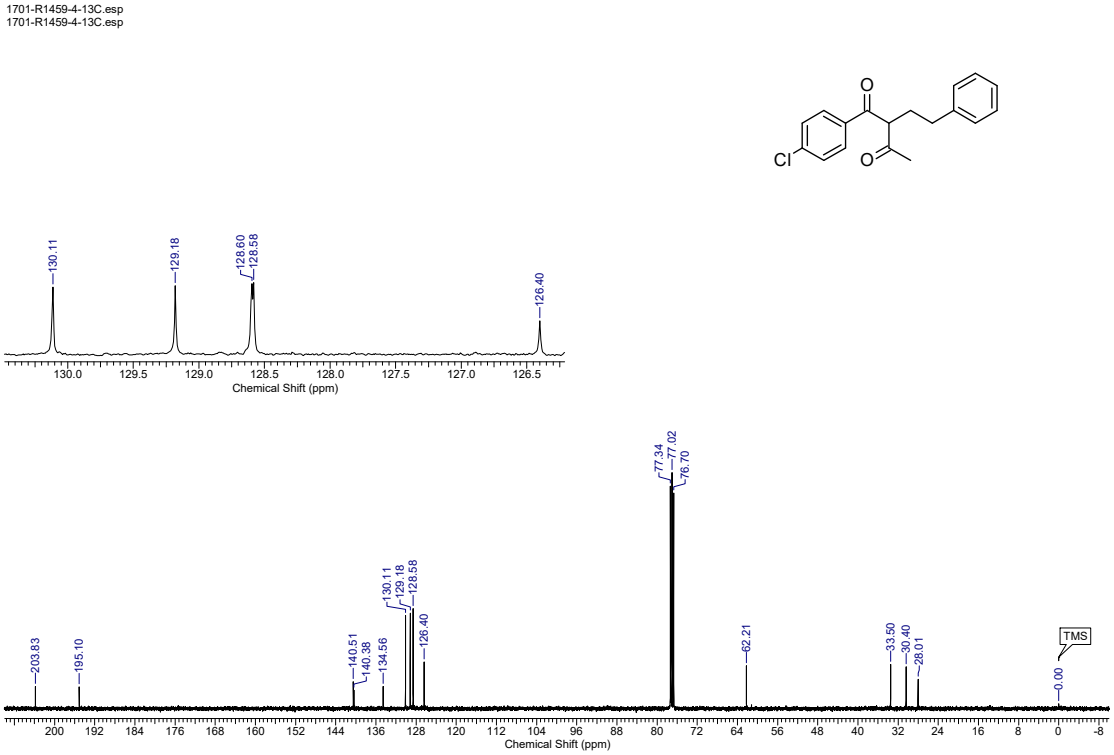


Figure S82. ^{13}C NMR spectrum of compound **3w**

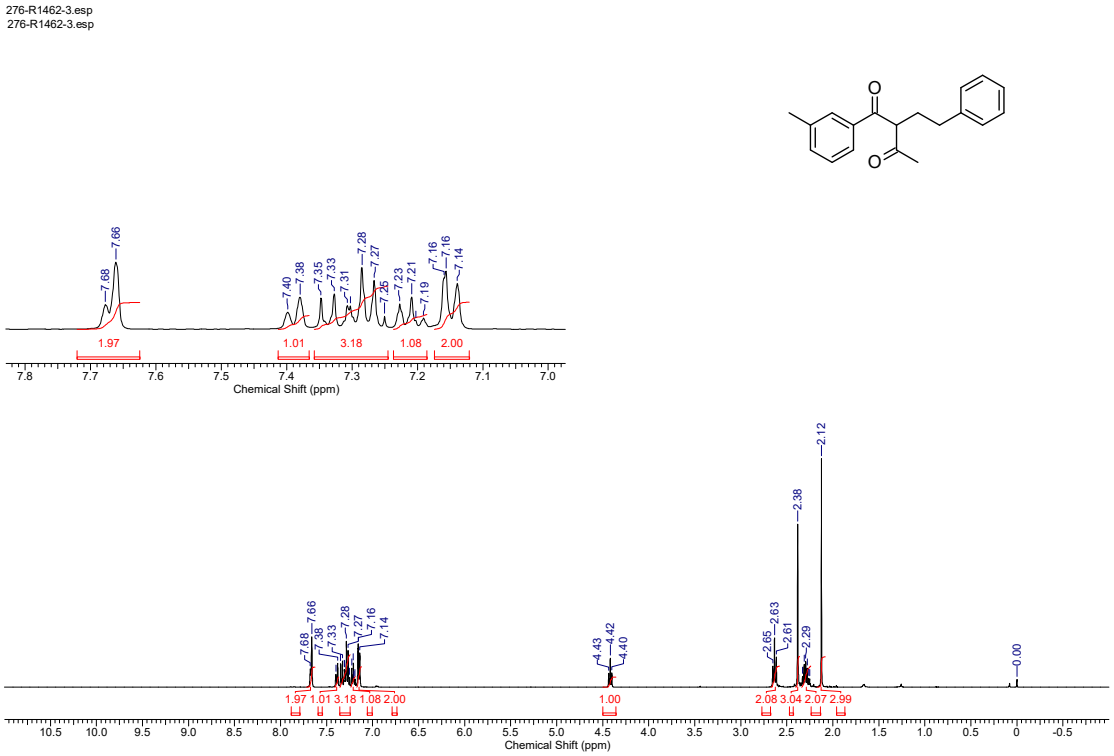


Figure S83. ^{1}H NMR spectrum of compound **3x**

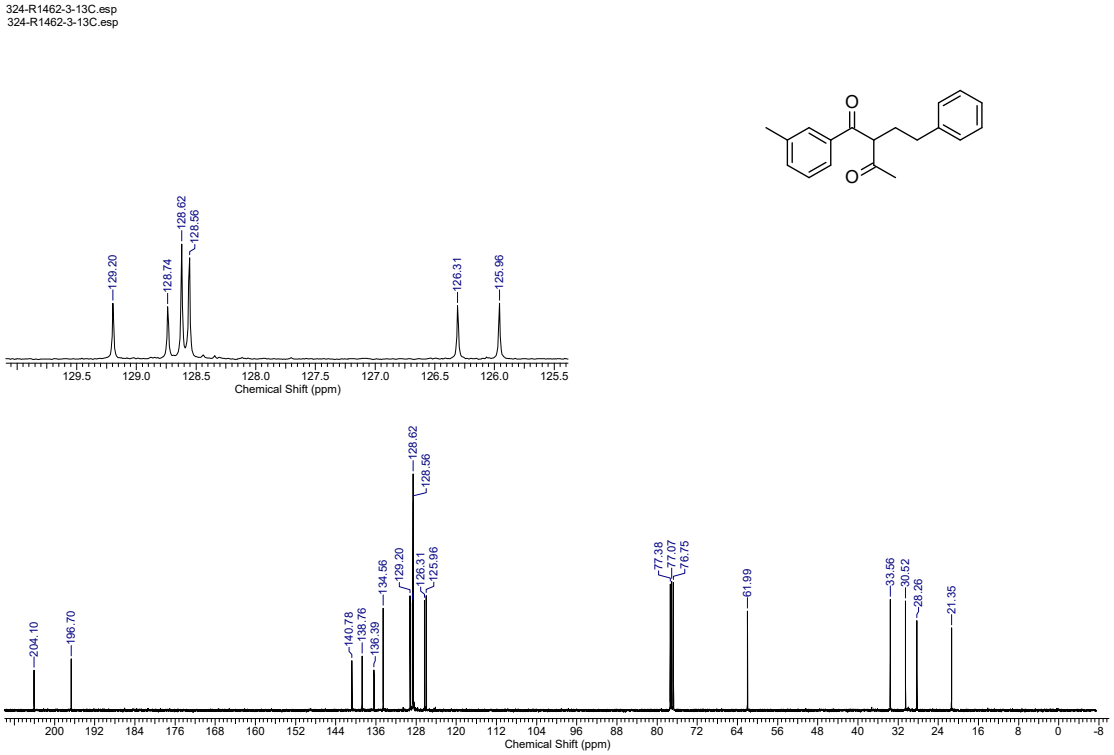


Figure S84. ^{13}C NMR spectrum of compound **3x**

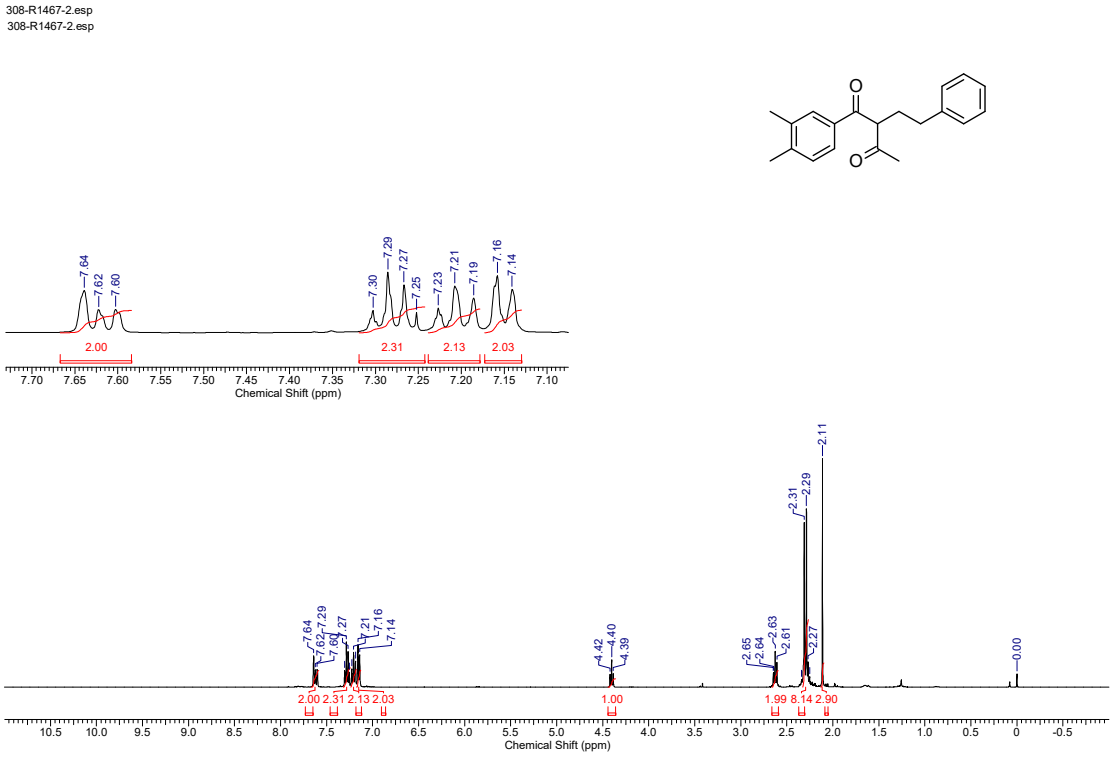


Figure S85. ^{1}H NMR spectrum of compound **3z**

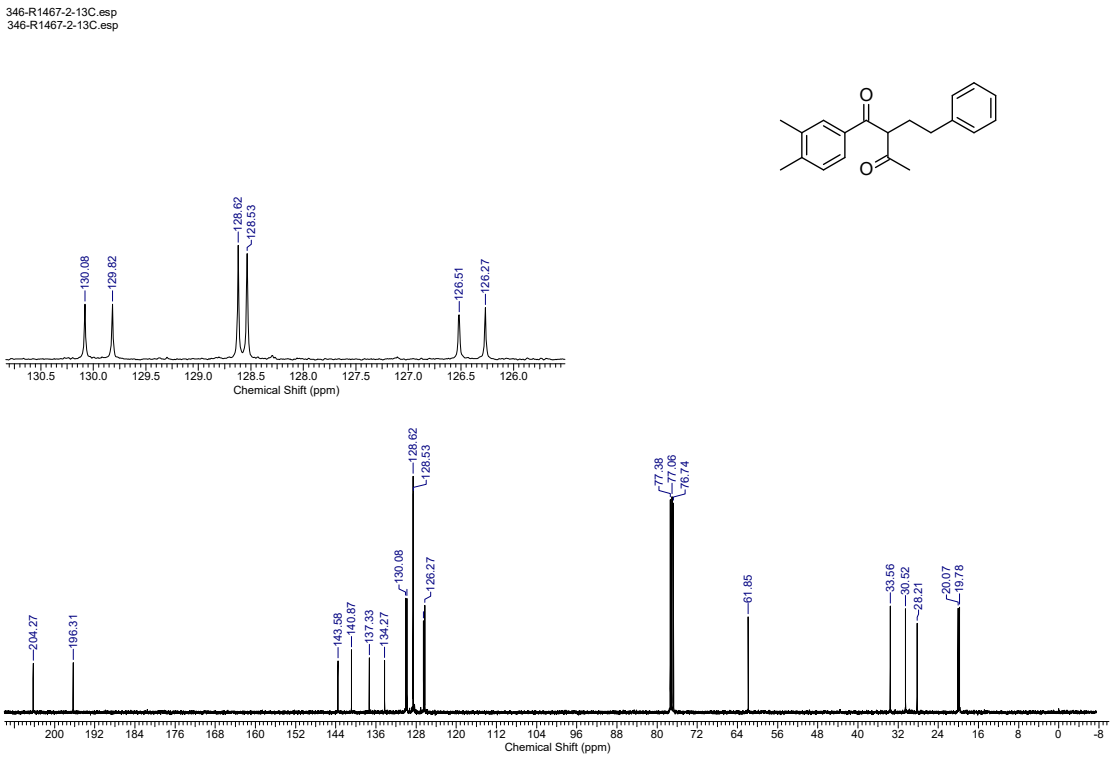


Figure S86. ^{13}C NMR spectrum of compound **3z**

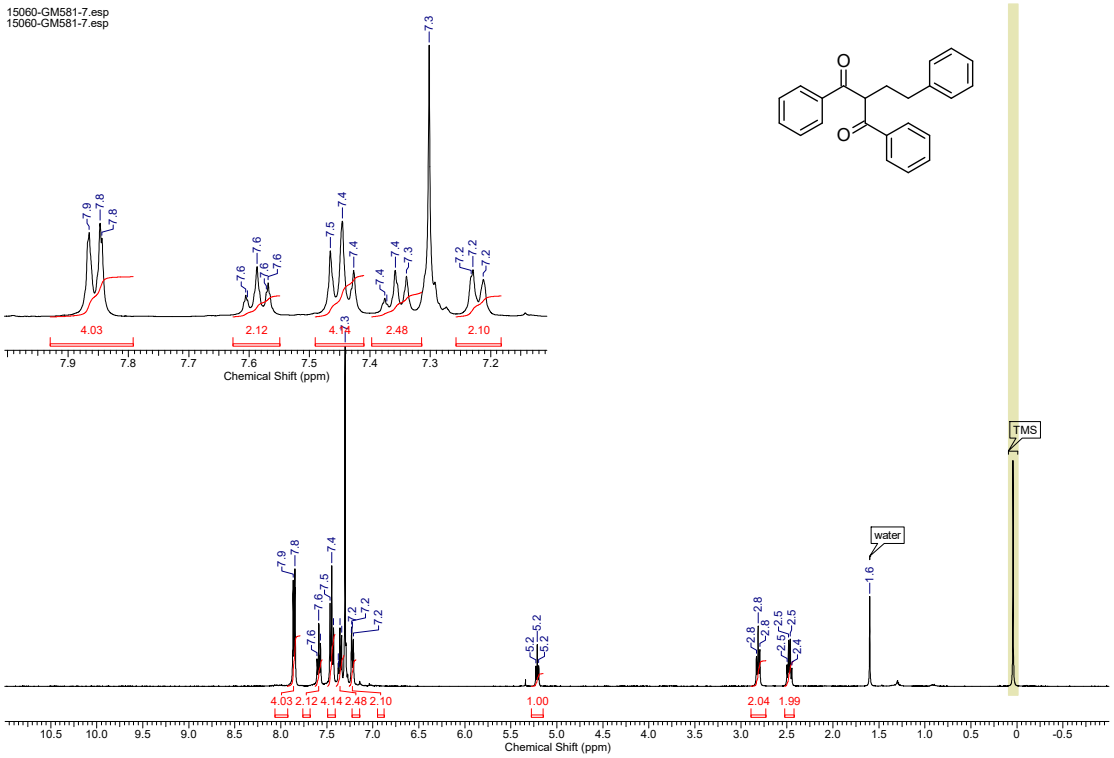


Figure S87. ^{1}H NMR spectrum of compound **3aa**

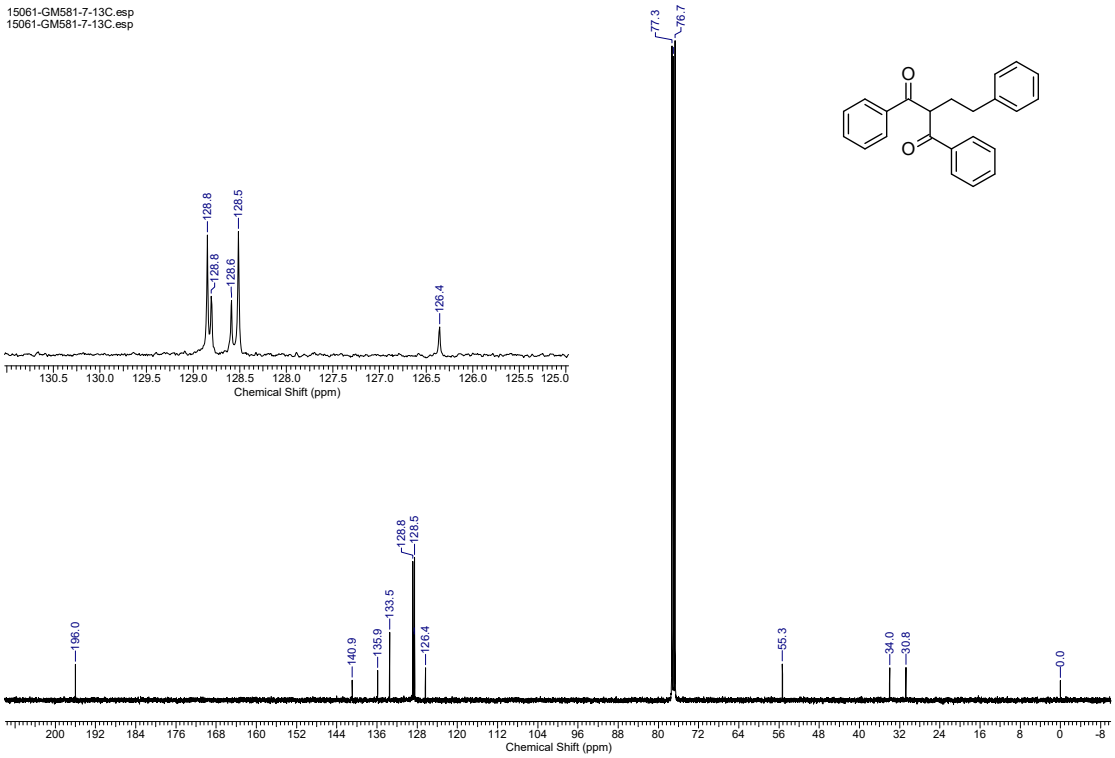


Figure S88. ^{13}C NMR spectrum of compound **3aa**

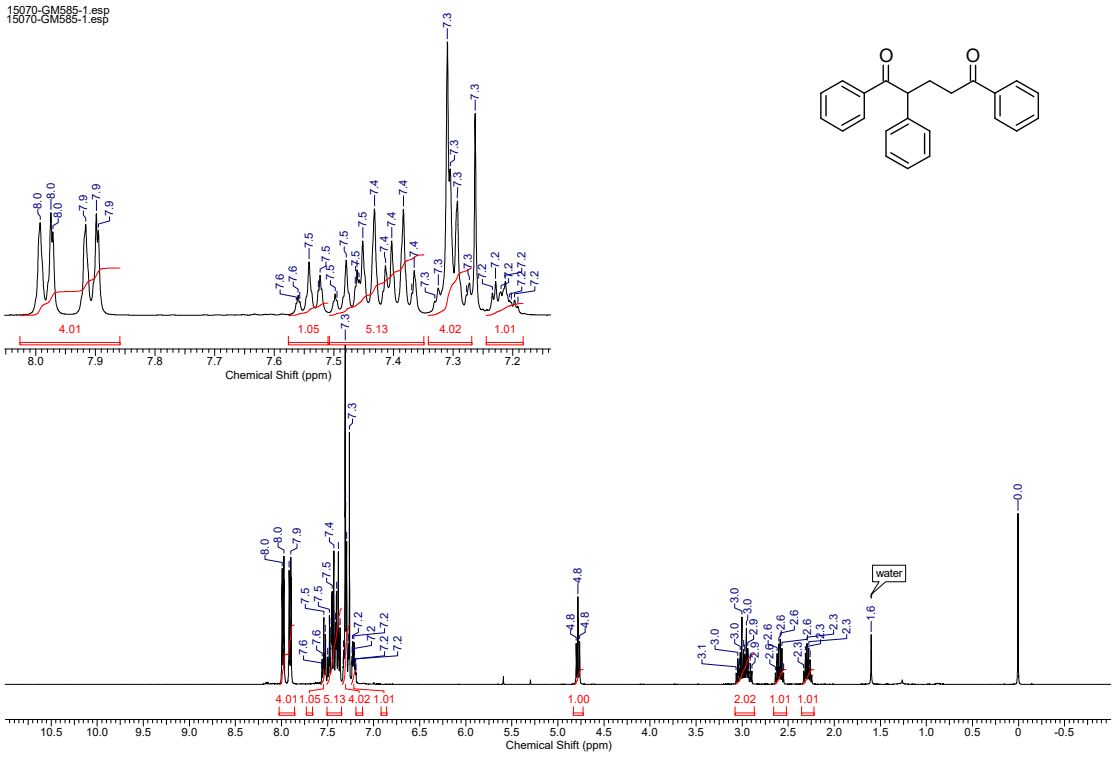


Figure S89. ^{1}H NMR spectrum of compound **4aa**

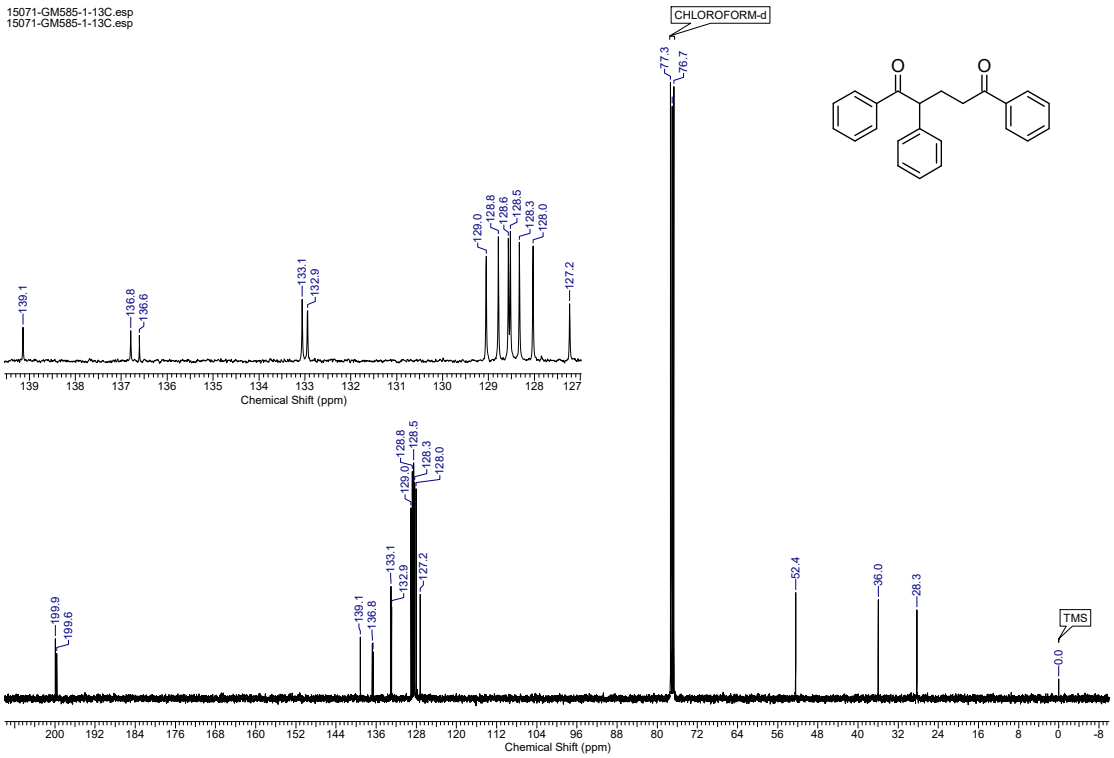


Figure S90. ^{13}C NMR spectrum of compound **4aa**

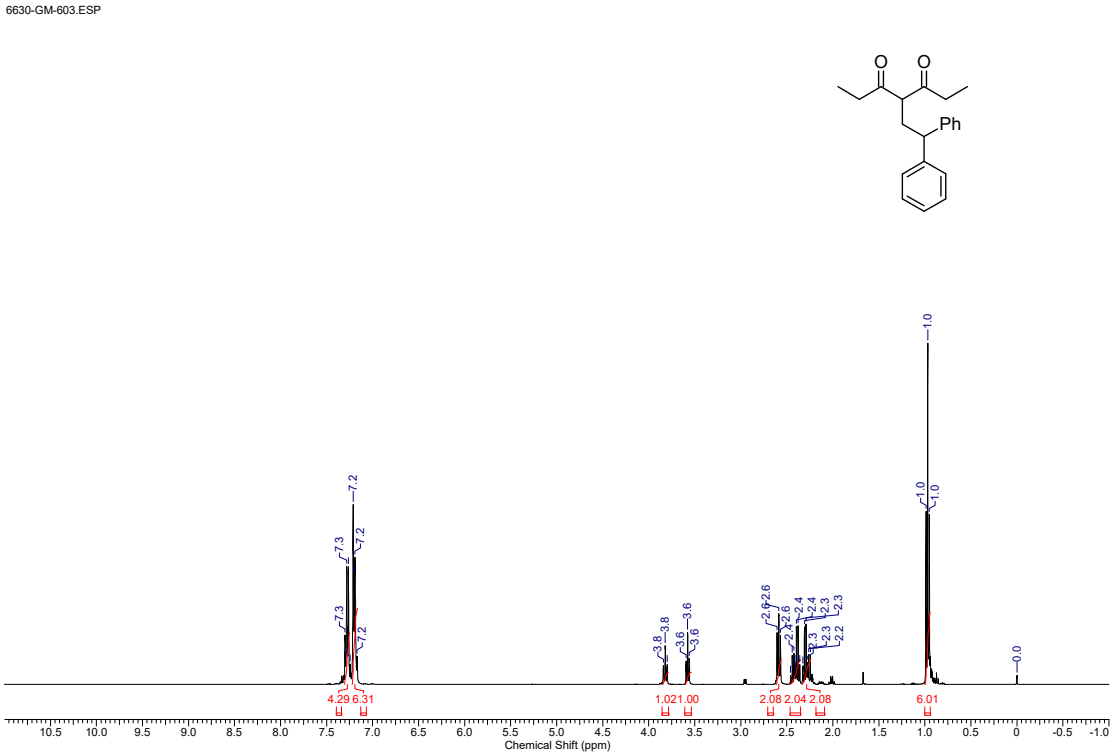


Figure S91. ^{1}H NMR spectrum of compound **3ab**

6631-GM-603-13C.ESP

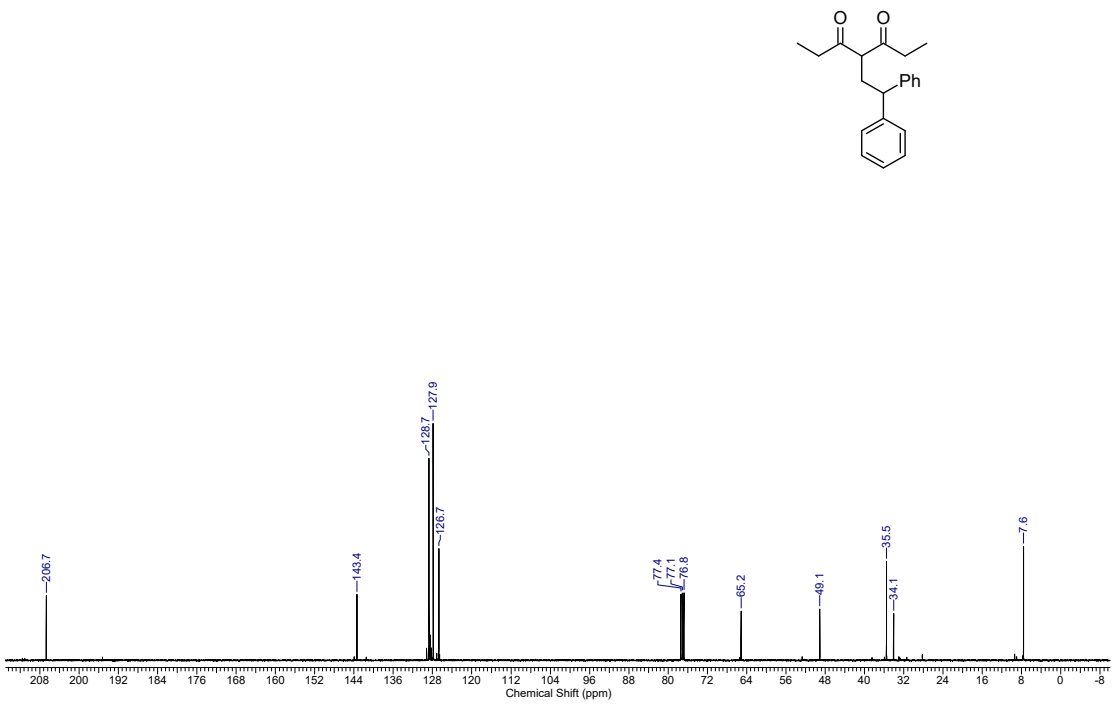


Figure S92. ^{13}C NMR spectrum of compound **3ab**

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