Supporting Information for

Catalytic O-H Bond Insertion Reactions Using Surface Modified Sewage Sludge as Catalyst

Zhipeng Zhang[1,4,⊥], Yang Yu[3,⊥], Fei Huang*[,1,2], Xiangyan Yi,[2] Yao Xu[5], Yide He[3], Jonathan B. Baell[2,6] and He Huang*[,1,2]

[1]School of Food Science and Pharmaceutical Engineering, Nanjing Normal University, Nanjing, 210023, China.
[2]School of Pharmaceutical Sciences, Nanjing Tech University, Nanjing, 211816, China
[3]School of Environmental Science and Engineering, Nanjing Tech University, Nanjing, 211816, China
[4]School of Biology and Biological Engineering, South China University of Technology, Guangzhou, 510006, China
[5]The First Affiliated Hospital of Soochow University, Suzhou, 215006, China
[6]Medicinal Chemistry, Monash Institute of Pharmaceutical Sciences, Monash University, Parkville, Victoria 3052, Australia
[⊥]These authors contributed equally to this work.
Email: huangfei0208@yeah.net; huang_h@njnu.edu.cn

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1. General considerations

All reactions and manipulations were performed using standard Schlenk techniques. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX-400 MHz spectrometer and all chemical shift values refer to $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm, $(CD_3)_2SO$ ($\delta(^{1}H)$, 2.50 ppm, $\delta(^{13}C)$, 39.52 ppm). X-ray Crystallographic analysis was achieved by the Analysis Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The GC analysiswas obtained on Agilent 7890/5975C. The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All the melting points were uncorrected. Column chromatographic purifications were performed on SDZF silica gel 160. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Compounds **3a**,[1,4] **3c**,[2] **3d**,[3] **3e**,[4] **3h**,[5] **3i**,[4] **3r**,[6,7] **3s**,[7,8] **3u**,[7] **3w**,[6] **3x**,[6] **9**,[8] **B**[9] were known and their spectroscopic features were in good agreement with that reported in the literatures.

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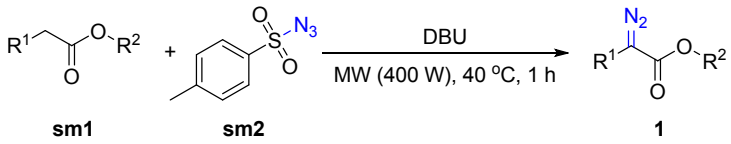
Chem. 2019, **39**, 544.

2. Experimental procedures

2.1 Preparation of SWs, SW-Cu and Soil-Ⅰ catalysts.[10]

The surface of SW was modified by different kinds of acids or bases to gain SW catalysts. SW was prepared by using municipal sewage sludge from wastewater treatment plant (WWTP) in China. Sewage sludge was dried to constant weight at 105 °C and carbonized at 600 °C for 4 h under a heating rate of 3 °C min^{-1} and a high purity nitrogen (99.999 wt%) flow of 500 mL min^{-1}. After the furnace had cooled to room temperature, SW was obtained. Different kinds of acids or bases were used to treat the SW. In the acid or base treatment process, 50 mL of SW were produced by immersing carbonized SW with the same volume of $HClO_4$ (35.4 wt%), HCl (20.5 wt%), H_2SO_4 (63.4 wt%), H_3PO_4 (45.4 wt%), HNO_3 (40.5 wt%) and NaOH (39.5 wt%) for 24 h, respectively. Then, SW-Ⅰ ($HClO_4$), SW-Ⅱ (HCl), SW-Ⅲ (H_2SO_4), SW-Ⅳ (H_3PO_4), SW-Ⅴ (HNO_3) and SW-Ⅶ (NaOH) were washed with deionized water until the pH of the washing water reached 6-7 and the recovered solids were dried at room temperature. Soil-Ⅰ (common soil treated by $HClO_4$) was prepared by the same method of SW-Ⅰ. SW-Cu (Cu-loaded SW) was prepared via adding 10 g SW to 20 mL of a 0.08 mol/L $CuCl_2$ solution and stirred for 18 h at room temperature, then, after filtrating, the sludge residue was carbonized at 600 °C for 4 h under a heating rate of 3 °C min^{-1} in a high purity nitrogen (99.999 wt%, 500 mL/min) atmosphere. When the furnace was cooled to room temperature, the SW-Cu was obtained.

2.2 Preparation for synthesis of α-diazoesters.[11]

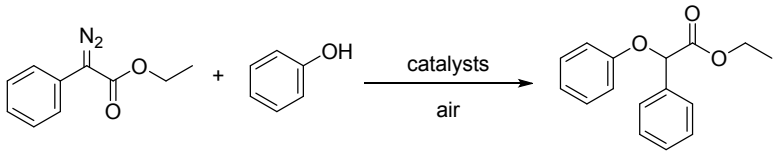


sm1 sm2 1

A typical procedure for the synthesis of α-diazoesters 1 – *Synthesis of 1a*: DBU (2.24 mL, 15 mmol) was added slowly to a stirred solution of ethyl 2-phenylacetate

(**sm1a**, 1.41 mL, 10.0 mmol) and tosylazide (**sm2**, 2.42 mL, 11.0 mmol) in the CH_3CN (20 mL) at 0 ºC. After that, it was placed in microwave reactor that was heated to 40 °C (400 W, monitored by IR temperature sensor) and maintained at this temperature for 30 min. After cooling to room temperature, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (5 mL), extracted with CH_2Cl_2 (3×30 mL), washed with brine (3×10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the product. The residue was purified by flash chromatography (petroleum ether (60-90 ºC)/AcOEt, 10:1) to afford the corresponding ethyl-2-diazo-2-phenylacetate **1a** as a yellow oil (1.65 g, 87%).

2.3 Screening the optimum reaction conditions for O-H bond insertion of 3a[a]



1a **2a** **3a**

Table S1. Screening the optimum reaction conditions of **3a**[a]

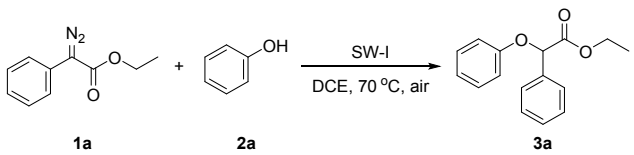
Entry	Catalyst	1a:2a (equiv)	Solvent	Temp. (ºC)	Yield[b] (%)
1	—	1:1.5	DCE	70	trace
2	SW[c]	1:1.5	DCE	70	8
3	**SW-Ⅰ[c]**	**1:1.5**	**DCE**	**70**	**87**
4	SW-Ⅱ[c]	1:1.5	DCE	70	10
5	SW-Ⅲ[c]	1:1.5	DCE	70	13
6	SW-Ⅳ[c]	1:1.5	DCE	70	12
7	SW-Ⅴ[c]	1:1.5	DCE	70	10
8	SW-Cu[c]	1:1.5	DCE	70	41
9	Soil-Ⅰ[c]	1:1.5	DCE	70	70
10	$HClO_4$[d]	1:1.5	DCE	70	64
11	SW[c]+$HClO_4$[d]	1:1.5	DCE	70	75
12	**SW-Ⅰ**	**1:1.5**	**DCE**	**70**	**94**
13	SW-Ⅰ[e]	1:1.5	DCE	70	89
14	SW-Ⅰ[f]	1:1.5	DCE	70	84
15	SW-Ⅰ[g]	1:1.5	DCE	70	83
16	SW-Ⅰ	1:1.5	DMF	70	16
17	SW-Ⅰ	1:1.5	Toluene	70	26
18	SW-Ⅰ	1:1.5	Dioxane	70	31
19	SW-Ⅰ	1:1.5	CH_3CN	70	35
20	SW-Ⅰ	1:1.5	DMSO	70	trace

21	SW-Ⅰ	1:1.5	1,4-dioxane	70	31
22	SW-Ⅰ	1:1.5	DCE:DMF=2:1 (v:v)	70	33
23	SW-Ⅰ	1:1.5	DCE	rt	36
24	SW-Ⅰ	1:1.5	DCE	40	53
25	SW-Ⅰ	1:1.5	DCE	50	67
26	SW-Ⅰ	1:1.5	DCE	60	70
27	SW-Ⅰ	1:1.5	DCE	reflux	47
28	SW-Ⅰ	1:0.8	DCE	70	69
29	SW-Ⅰ	1:1	DCE	70	84
30	SW-Ⅰ	1:1.2	DCE	70	91
31	SW-Ⅰ	1:1.4	DCE	70	94
32	**SW-Ⅰ**	**1:1.6**	**DCE**	**70**	**95(63[h])**
33	SW-Ⅰ	1:1.7	DCE	70	95
34	SW-Ⅰ	1:2	DCE	70	94
35[i]	SW-Ⅰ	1:1.6	DCE	70	90(53[h])

[a]Conditions: **1a** (0.5 mmol), **2a**, catalyst (50 mg), solvent (5 mL), 0.1 MPa air, 4 h; symbol "-" means no catalyst. [b]GC yield with mesitylene as the internal standard. [c]75 mg. [d]$HClO_4$ (3 μL). [e]25 mg. [f]100 mg. [g]150 mg. [h]Isolated yield given in parentheses. [i]Catalyst recycling, 7 h.

2.4 Catalyst recycling experiments

Table S2. The SW-Ⅰ catalyst reusability[a]



1a **2a** **3a**

Entry	Catalyst	Recycling times	Time (h)	Yield[b] (%)
1	SW-Ⅰ	0	4	95(63[c])
2	SW-Ⅰ	1	7	90(54[c])
3	SW-Ⅰ	2	11	75(40[c])
4	SW-Ⅰ	3	24	69(35[c])

[a]Conditions: **1a** (0.5 mmol), **2a** (0.8 mmol), catalyst (50 mg), solvent (5 mL), 0.1 MPa air, 4 h; [b]GC yield with mesitylene as the internal standard. [c]Isolated yield given in parentheses.

2.5 The PH value of SW-Ⅰ

Table S3. The PH value of SW-Ⅰ

Entry	Solvent	SW-Ⅰ (mg)	PH value
1	water	0	7.17
2[a]	water	50	6.70

3	DCE	0	6.14
4[b]	DCE	50	6.01

Conditions: [a]Water (5 mL) + SW-Ⅰ (50 mg); [b]DCE (5 mL) + SW-Ⅰ (50 mg).

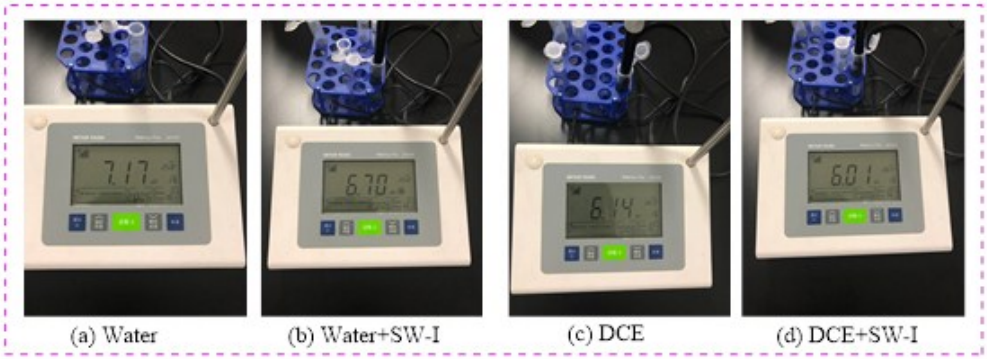
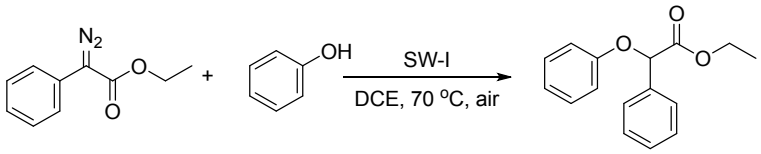


Figure S1. PH value (a) The PH value of water. (b) The PH value of SW-Ⅰ (50 mg) in water (5 mL). (c) The PH value of DCE. (d) The PH value of SW-Ⅰ (50 mg) in DCE (5 mL).

2.6 Typical O-H insertion procedures

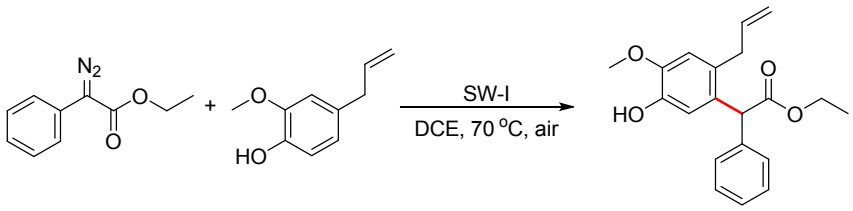


1a **2a** **3a**

A typical procedure for the synthesis of O-H insertion procedures (3, 6, 7, 8)

– *Synthesis of* ***3a***: A mixture of SW-Ⅰ (50 mg), phenol (**2a**, 75 mg, 0.8 mmol) and ethyl 2-diazo-2-phenylacetate (**1a**, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under 0.1 Mpa air for 1 h, then the resulting mixture was stirred at 70 °C for 4 h. After filtrating and removing solvent in vacuum the product was purified by flash chromatography with petroleum ether (60-90 ℃)/AcOEt (10:1) to afford the corresponding **3a** as a Colorless oil (80 mg, 63%).

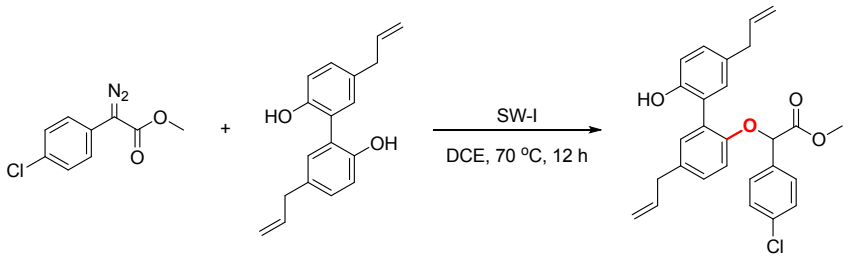
2.7 Typical C-H bond functionalization procedures



1a **2s** **4a**

A typical procedure for the synthesis of C-H insertion procedures (4) – *Synthesis of* ***4a****:* A mixture of SW-Ⅰ (50 mg), eugenol (**2s**, 131 mg, 0.8 mmol) and ethyl 2-diazo-2-phenylacetate (**1a**, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under 0.1 Mpa air for 1 h, then the resulting mixture was stirred at 70 °C for 12 h. After filtrating and removing solvent in vacuum the product was purified by flash chromatography with petroleum ether (60-90 ℃)/AcOEt (5:1) to afford the corresponding **4a** as a Colorless oil (57 mg, 35%).

2.8 A gram-scale experiment



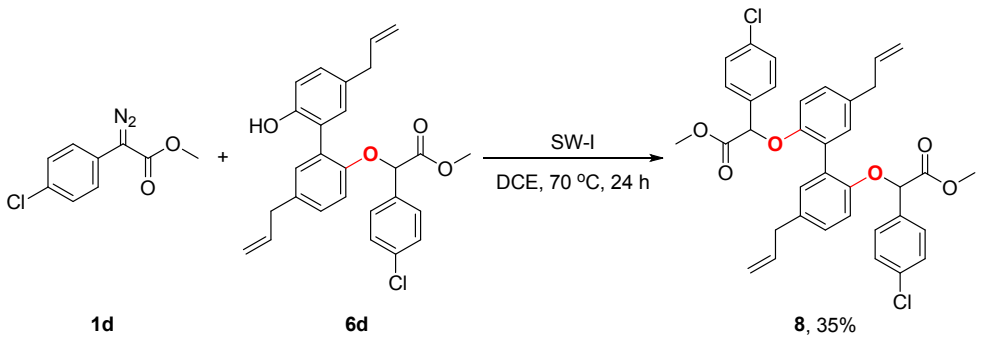
1d, 1.05 g
5 mmol

5a, 2.13 g
8 mmol

6d, 1.61g
72%

A mixture of SW-Ⅰ (500 mg), magnolol (**5a**, 2.13 g, 8 mmol) and methyl 2-(4-chlorophenyl)-2-diazoacetate (**1d**, 1.05 g, 5 mmol) in DCE (50 mL) was stirred at room temperature under 0.1 Mpa air for 1 h, then the resulting mixture was stirred at 70 °C for 12 h. After filtrating and removing solvent in vacuum the product was purified by flash chromatography with petroleum ether (60-90 ℃)/A_COEt (10:1) to afford the corresponding **6d** as a white solid (1.61 g, 72%).

2.9 The synthesis of compound 8 (The secondary O-H insertion product of natural phenol **5a**).



1d

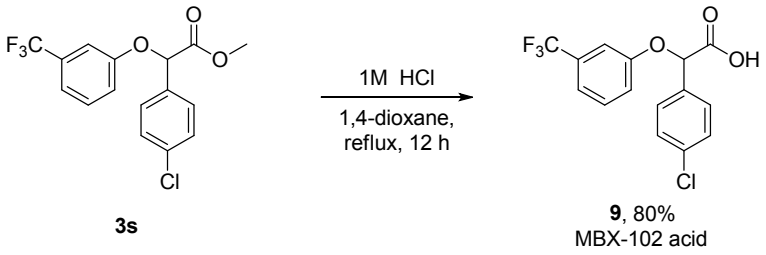
6d

8, 35%

A mixture of SW-Ⅰ (25 mg), **6d** (179 mg, 0.4 mmol) and methyl 2-(4-

chlorophenyl)-2-diazoacetate (**1d**, 53 mg, 0.25 mmol) in DCE (2.5 mL) was stirred at room temperature under 0.1 Mpa air for 1 h, then the resulting mixture was stirred at 70 °C for 24 h. After filtrating and removing solvent in vacuum the product was purified by flash chromatography with petroleum ether (60-90 ºC)/A_COEt (10:1) to afford the corresponding **8** as a Colorless oil (55 mg, 35%).

2.10 The synthesis of MBX-102 acid (9)

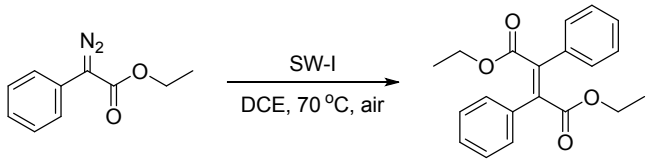


3s

9, 80%
MBX-102 acid

A mixture of **3s** (172 mg, 0.5 mmol) and 1M HCl (0.5 mL) in 1,4-dioxane (5 mL) was stirred at 100 °C reflux for 12 h. After filtrating and removing solvent in vacuum the product was purified by flash chromatography with petroleum ether (60-90 ºC)/A_COEt (2:1) to afford the corresponding **9** (MBX-102 acid) as a white syrup (132 mg, 80%).

2.11 The synthesis of B (self-coupling product of ethyl 2-diazo-2-phenylacetate **1a**)



1a

B, 19%
self-coupling
product

A mixture of SW-Ⅰ (50 mg), ethyl 2-diazo-2-phenylacetate (**1a**, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under 0.1 Mpa air for 1 h, then the resulting mixture was stirred at 70 °C for 4 h. After filtrating and removing solvent in vacuum the product was purified by flash chromatography with petroleum ether (60-90 ºC)/AcOEt (10:1) to afford the corresponding **B** as a yellow oil (31 mg, 19%).

3. Control experiments

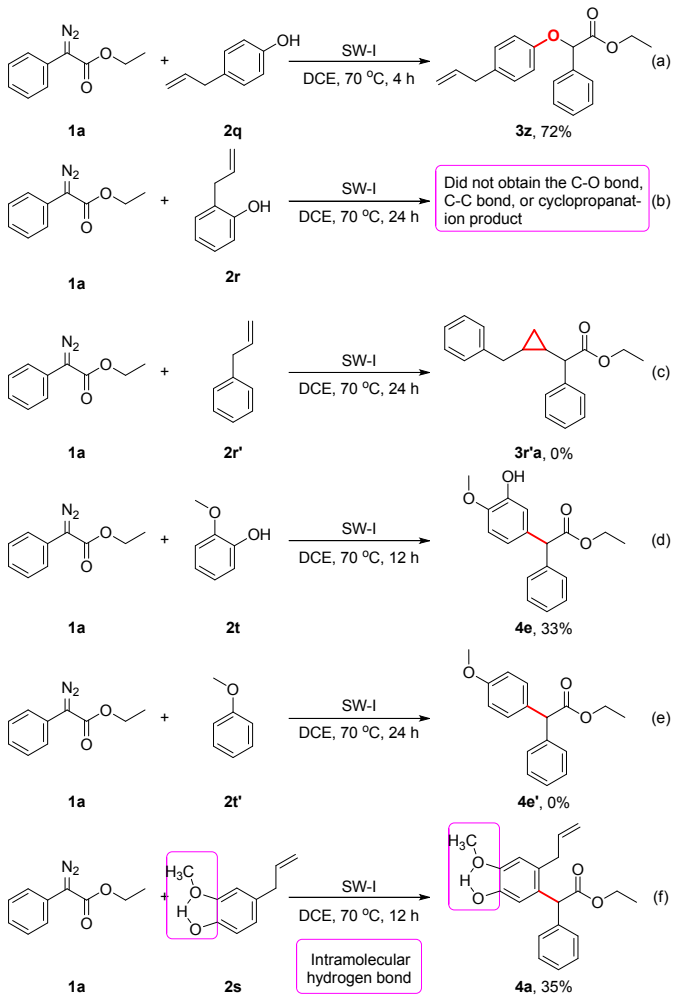


Figure S2. Control experiments. (To know the reason for C−H bond functionalization of eugenol **2s)**

Under the optimal reaction conditions, several control experiments (reactions a-e) were carried out. The reaction procedures followed the typical O-H insertion and C-H bond functionalization.

4. X-Ray crystallographic studies

Single crystals of compounds **4d** and **6d** were grown in petroleum ether (60-90 °C)/CH_2Cl_2 (v/v, 5/1) at 25 °C and their X-ray diffraction studies were carried out on a SMART APEX diffractometer with graphite-monochromated Mo radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure

solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1917686 for **4d** and CCDC 1869826 for **6d**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

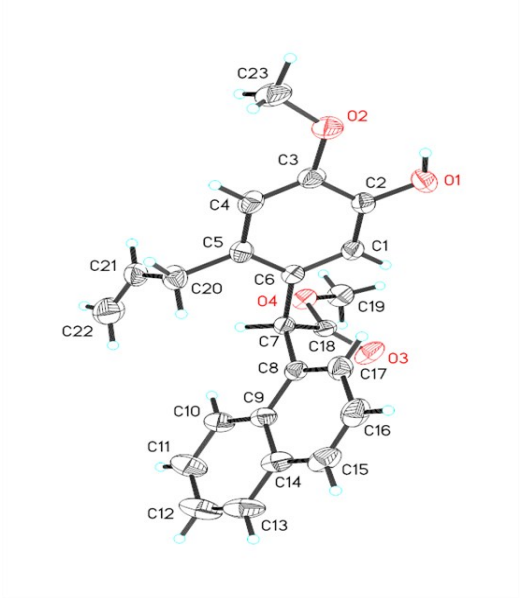


Figure S3. Molecular structure of compound **4d**

Table S4. Crystal data and structure refinement for **4d**

Empirical formula	$C_{23}H_{22}O4$	
Formula weight	362.40	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.0906(5) Å	□α = 90°
	b = 7.9886(2) Å	□β = 95.5440(10)°
	c = 15.7975(5) Å	□γ = 90°
Volume	1895.52(10) $Å^3$	
Z, Calculated density	4, 1.270 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	768	
Crystal size	0.180 x 0.150 x 0.130 mm^3	

Theta range for data collection	2.888 to 25.997°
Index ranges	-18<=h<=18, -9<=k<=9, -19<=l<=19
Reflections collected	27913
Independent reflections	3693 [R(int) = 0.0322]
Completeness to theta = 25.242°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6709
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3693 / 0 / 256
Goodness-of-fit on F^2	1.013
Final R indices [I > 2 sigma(I)]	R1 = 0.0421, wR2 = 0.1089
R indices (all data)	R1 = 0.0531, wR2 = 0.1192
Extinction coefficient	0.030(5)
Largest diff. peak and hole	0.149 and -0.137 e.Å^{-3}

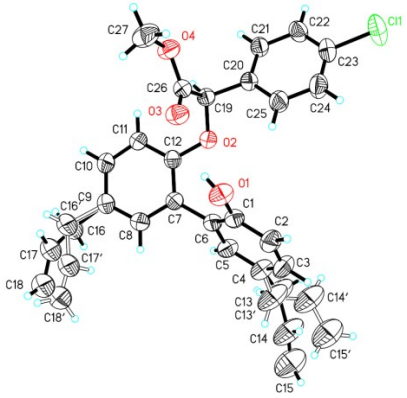


Figure S4. Molecular structure of compound **6d**

Table S5. Crystal data and structure refinement for **6d**

Empirical formula	$C_{27}H_{25}ClO_4$	
Formula weight	448.92	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.4738(2) Å	□α = 90°
	b = 24.4748(6) Å	□β = 91.0510(10)°
	c = 11.8708(3) Å	□γ = 90°
Volume	2461.52(10) Å^3	
Z, Calculated density	4, 1.211 Mg/m^3	
Absorption coefficient	0.184 mm^{-1}	
F(000)	944	

Crystal size	0.220 x 0.170 x 0.130 mm^3
Theta range for data collection	2.391 to 24.999°
Index ranges	-10<=h<=10, -29<=k<=29, -14<=l<=14
Reflections collected	29317
Independent reflections	4295 [R(int) = 0.0422]
Completeness to theta = 25.242°	96.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6652
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4295 / 138 / 346
Goodness-of-fit on F^2	1.046
Final R indices [I > 2 sigma(I)]	R1 = 0.0684, wR2 = 0.1953
R indices (all data)	R1 = 0.0900, wR2 = 0.2209
Extinction coefficient	0.030(8)
Largest diff. peak and hole	0.368 and -0.464 e.$Å^{-3}$

5. NMR titration experiments

^{1}H-NMR titration experiments.

The preparation of mother liquor: (a) phenol (0.3 mmol), (b) Phenol (0.3 mmol) with SW-Ⅰ (20 mg), (c) Phenol (0.3 mmol) with SW-Ⅰ (40 mg), (d) Phenol (0.3 mmol) with HCl (4 μL), (e) Phenol (0.3 mmol) with $HClO_4$ (4 μL), (f) Phenol (0.3 mmol) with Et_3N (4 μL), (g) Phenol (0.3 mmol) with NaOH (5 mg) were added in $CDCl_3$ (2 mL) respectively, stirred at room temperature under 0.1 Mpa air for 1 h. Then, the mother liquor of (a) 30 μL, (b) 50 μL, (c) 50 μL, (d) 50 μL, (e) 50 μL, (f) 50 μL, (g) 50 μL were moved in $CDCl_3$ (0.5 mL), respectively. Last, conducted a ^{1}H NMR analysis to show the ^{1}H of OH in phenol, as shown in Fig. S5-7.

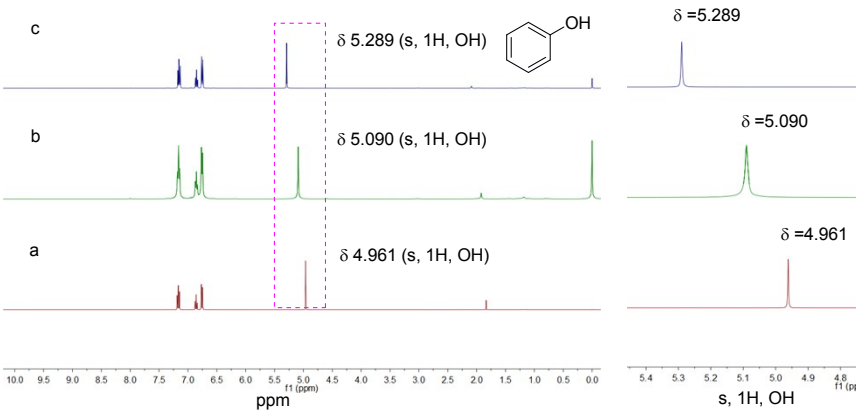


Figure S5. ^{1}H NMR spectra of the phenol signals in $CDCl_3$. (a) phenol. (b) Phenol

(0.3 mmol) with SW-Ⅰ (20 mg). (c) Phenol (0.3 mmol) with SW-Ⅰ (40 mg).

The results showed that the single ^{1}H resonance of phenol was shifted downfield when more SW-Ⅰ was mixed, which further indicated that the predominant interaction between phenol and SW-Ⅰ was hydrogen bonding.

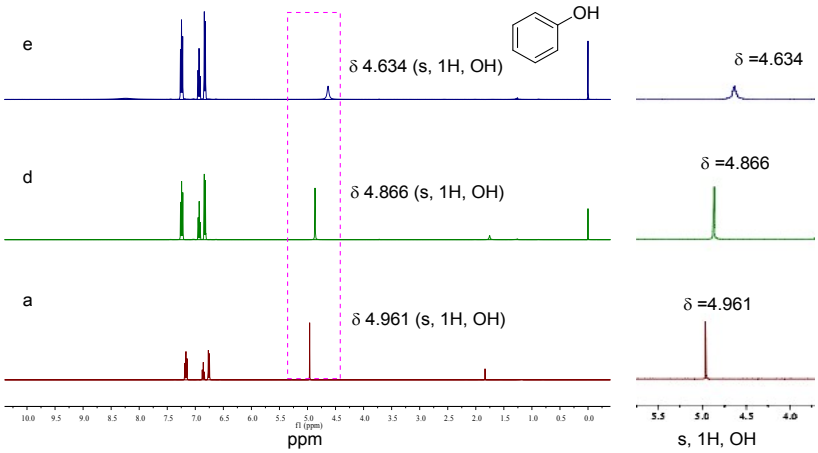


Figure S6. ^{1}H NMR spectra of the phenol signals in $CDCl_3$. (a) phenol. (d) Phenol (0.3 mmol) with HCl (4 μL). (e) Phenol (0.3 mmol) with $HClO_4$ (4 μL).

The results showed that the single ^{1}H resonance of phenol was shifted upfield when HCl or $HClO_4$ was added.

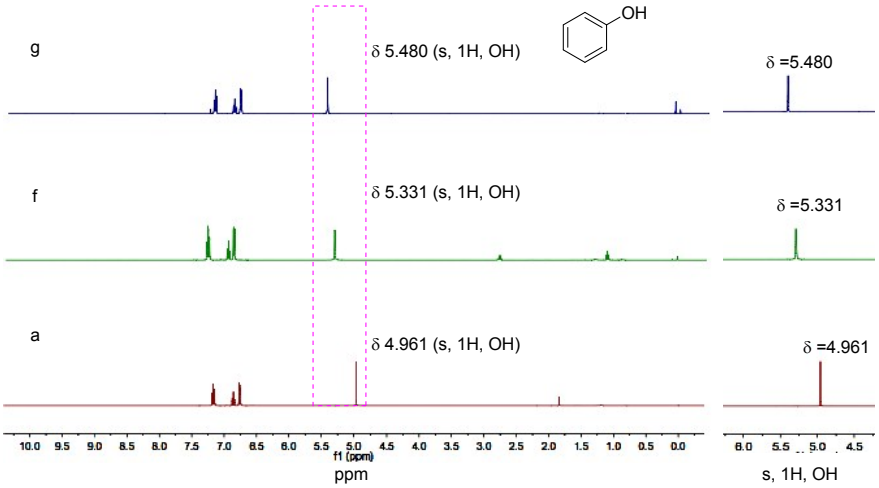


Figure S7. ^{1}H NMR spectra of the phenol signals in $CDCl_3$. (a) phenol. (f) Phenol (0.3 mmol) with Et_3N (4 μL). (e) Phenol (0.3 mmol) with NaOH (5 mg).

The results showed that the single ^{1}H resonance of phenol was shifted downfield when Et_3N or NaOH was added.

Combined with the above results, the single ^1H resonance of phenol was shifted downfield (SW-Ⅰ was mixed) or shifted upfield ($HClO_4$ was added). The single ^1H resonance of phenol was shifted in the opposite direction, which further indicated that the predominant interaction between phenol and SW-Ⅰ, phenol and $HClO_4$ was different. Meanwhile, we could infer that the O-H insertion of phenols was not caused by $HClO_4$ (protonation of $HClO_4$), but caused by the hydrogen bond between SW-Ⅰ and the hydroxy group of phenol. Further, when NaOH or Et_3N was added. the single 1H resonance of phenol was shifted in consistent with SW-Ⅰ, which all could be shifted in the opposite direction with acid. The results supported our hypothesis that the SW-Ⅰ might act as a Lewis or Bronsted base.

6. The characterization of SW-Ⅰ, SW and Soil-Ⅰ

Catalyst characterization. X-ray Fluorescence (XRF, Magix 601) was used to analyse the element content in the SW catalysts. The morphology and microstructure of SW-Ⅰ catalyst were examined by scanning electron microscope (SEM, HITACHI S4800), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010 UHR) and transmission electron microscopy (TEM, JSM7500F).

Table S6. XRF analysis of elements in SW, SW-Ⅰ and Soil-Ⅰ

Chemical composition	SW (wt%)	SW-Ⅰ (wt%)	Soil-Ⅰ (wt%)	Chemical composition	SW (wt%)	SW-Ⅰ (wt%)	Soil-Ⅰ (wt%)
C	13.800	12.180	5.9513	TiO_2	0.618	0.720	1.2612
Na_2O	1.154	1.016	0.2101	Cr_2O_3	0.047	0.040	0.0285
MgO	2.490	1.527	0.8788	MnO	0.109	0.040	0.0902
Al_2O_3	15.207	15.043	19.8577	Fe_2O_3	5.050	2.308	6.1935
SiO_2	46.269	58.201	62.5152	CuO	0.027	0.029	0.0058
P_2O_5	2.059	0.458	0.0704	ZnO	0.087	0.032	0.0092
SO_3	1.377	1.396	0.036	Rb_2O	0.009	0.011	0.0091
Cl	0.166	3.815	0.0574	SrO	0.029	0.011	0.0042
K_2O	1.796	2.123	2.3094	Y_2O_3	0.003	0.002	0.0012
CaO	9.683	1.018	0.0771	ZrO_2	0.021	0.021	0.0248

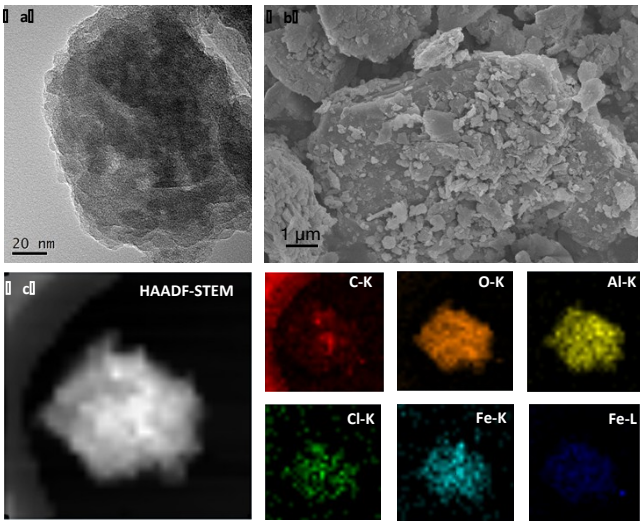


Figure S8. Properties of SW-Ⅰ. (aⅡ, bⅡ) HRTEM and SEM images. (cⅡ) HAADF-STEM and EDS elemental mapping images

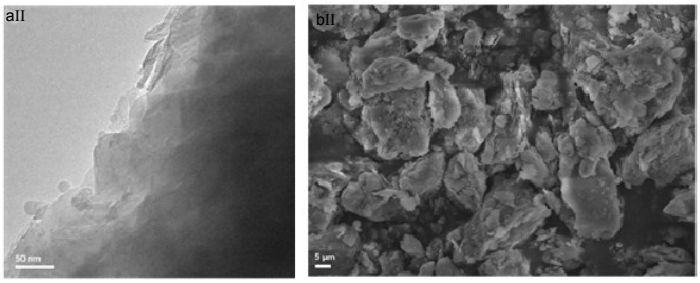


Figure S9. Properties of Soil-Ⅰ. (aⅡ, bⅡ) HRTEM and SEM images.

7. Anti-tumor and anti-inflammatory bioactivities in vitro

7.1 Anti-tumor

Tumors are the most common disease and cause a major public health problem in many parts of the world.[12] There is a critical need for designing, synthesizing new and reliable anti-tumor agents to improve the survival rates of tumor patients.[13] According to the reported biological activities of magnolol and honokiol,[14] compounds **6a-6f**, **7a-7c**, **5a** and **5b** may have anti-tumor effects. Then, these compounds were evaluated for anti-tumor bioactivities in vitro.

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EXPERIMENTAL SECTION

Chemicals. The human tumor cell lines HL-60, SMMC-7721, A-549, MCF-7, and SW-480 were obtained from ATCC (Manassas, VA, USA). Dulbecco's Modified Eagle's Medium (DMEM) and fetal bovine serum (FBS) were purchased from BI company (Biological Industries, Israel). 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxyme-thoxyphe-

enyl)-2-(4-sulfophenyl)-2H-tetrazolium, inner salt (MTS) was purchased from Promega company (Madison, WI, USA). **DDP** (Cisplatin: positive control) was purchased from Sigma-Aldrich (Sigma, USA).

General Experimental Procedures. O-H bond insertion products (**6a**-**6f**, **7a**-**7c**) have been confirmed by NMR and HRMS.

Source of magnolol 5a and **honokiol 5b.** Compounds **5a** and **5b** were purchased from Sigma-Aldrich (Sigma, USA).

In vitro antiproliferative activity assay. The human tumor cell lines HL-60, SMMC-7721, A-549, MCF-7, and SW-480 were used in the cytotoxic assay. Cells were cultured in RMPI-1640 or DMEM medium supplemented with 10% fetal bovine serum at 37 °C in a humidified atmosphere with 5% CO_2. The cytotoxicity assay was evaluated by the 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulf-ophenyl)-

2H-tetrazolium, inner salt (MTS) assay.[15] Briefly, cells were seeded into each well of a 96-well cell culture plate. After 12 h of incubation at 37 °C, the test compound (40 μM) was added. After incubated for 48 h, cells were subjected to the MTS assay. Most compounds exhibited moderate to good antiproliferative activity against HL-60, SMMC-7721, A-549, MCF-7 and SW-480 cell lines (Table S7). Then, compounds (**5b**, **6d**, **7a** and **7c**) with a growth inhibition rate of 50% were further evaluated at

concentrations of 0.064, 0.32, 1.6, 8, and 40 μM in triplicate, with cisplatin as positive controls. The IC_{50} values were gave in Table S8.

Table S7. Cell inhibition (%) of compounds towards five selected tumor cell lines.

	HL-60		A-549		SMMC-7721		MCF-7		SW-480	
	Cell Inhibition (%)									
Compounds	**Average**	**SD**	**Average**	**SD**	**Average**	**SD**	**Average**	**SD**	**Average**	**SD**
5a	61.55	1.38	15.92	1.01	10.52	1.99	59.13	0.43	-8.44	1.10
5b	98.89	0.23	73.21	0.43	69.81	0.61	98.09	0.47	93.96	0.68
6a	21.24	2.63	46.86	0.12	57.70	2.23	70.81	3.57	57.78	1.69
6b	77.56	1.03	39.09	2.88	64.43	2.34	94.46	1.51	48.55	1.27
6c	1.92	2.74	15.78	0.75	29.25	2.66	22.41	1.01	20.51	0.22
6d	99.34	0.57	50.20	0.98	75.38	2.16	100.25	0.36	74.15	1.29
6e	99.47	0.85	21.83	1.10	45.27	2.96	94.55	0.32	87.82	0.65
6f	15.25	2.17	44.86	0.19	43.34	2.42	69.37	3.85	44.77	4.18
7a	100.67	0.23	99.74	0.05	99.98	0.10	100.40	0.26	99.55	0.12
7b	6.30	0.69	2.64	1.16	3.28	2.32	25.38	1.23	10.00	1.15
7c	99.69	0.44	90.61	0.75	94.63	0.43	98.12	0.21	92.17	1.23

Table S8. IC_{50} values (μM) of compounds towards five selected tumor cell lines.

	IC_{50} μM				
Compounds	**HL-60**	**A-549**	**SMMC-7721**	**MCF-7**	**SW-480**
DDP	2.87±0.08	20.62±2.70	17.40±0.51	14.96±0.45	14.34±1.15
5b	16.18±0.19	21.18±0.63	21.89±0.94	20.71±0.68	23.56±1.19
6d	16.82±0.50	27.86±0.78	26.61±0.20	15.32±0.40	34.39±3.29
7a	15.13±0.22	16.80±0.47	16.84±0.15	16.03±0.41	16.78±0.48
7c	14.76±0.11	16.48±0.31	17.44±0.39	14.84±0.67	17.37±0.66

Reference

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7.2 Anti-inflammatory

Inflammation is recognized as a very complex pathophysiological process in response to tissue injuries induced by different injurious stimuli, such as pathogens, damaged cells and irritation.[16] Nitric oxide (NO) is a free radical which could be involved in many physiological and pathogical processes, and as a cytotoxic agent in pathological processes, particularly in inflammatory disorders.[17] NO is endogenously synthesized by oxidation of L-arginine catalyzed by nitric oxide synthase (NOS).

There are three NOS isoforms: neuronal NOS (nNOS/NOS1), inducible NOS (iNOS/NOS2), and endothelial NOS (eNOS/NOS3).[18] Macrophages play a key role in inflammation, which are the main producers of NO at the inflammatory site when activated by inflammatory mediators.[19] Inflammatory mediator stimuli such as lipopolysaccharide (LPS) will produce a lot of iNOS and lead to trigger NO production.[20] So inhibition of NO production is a direct anti-inflammatory activity indicator of the compound. Herein, compounds **5a**, **5b**, **6a-6f** and **7a-7c** were evaluated for anti-inflammatory activity by using LPS- stimulated RAW 264.7 murine macrophage cells to produce iNOS and trigger NO production.

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EXPERIMENTAL SECTION

Chemicals. RAW 264.7 cells were purchased from the Cell Bank of Chinese Academic of Sciences (Shanghai, China). Dulbecco's Modified Eagle's Medium (DMEM) and fetal bovine serum (FBS) were purchased from BI company (Biological Industries, Israel). Lipopolysaccharide (LPS), Griess Reagent and L-NMMA (positive control) were purchased from Sigma-Aldrich (Sigma, USA). 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium, inner salt (MTS) was purchased from Promega company (Madison, WI, USA).

General Experimental Procedures. O-H insertion products (**6a-6f**, **7a-7c**) have been confirmed by NMR and HRMS.

Source of magnolol 5a and **honokiol 5b.** Compounds **5a** and **5b** were purchased from Sigma-Aldrich (Sigma, USA).

Measurement of Cell Viability and Nitrite. RAW 264.7 cells were cultured in Dulbecco's modified Eagle's medium supplemented with 10% fetal bovine serum, 100 units/mL penicillin, 100 μg/mL streptomycin, 2 mM L- glutamine, and 1 mM nonessential amino acids. Then, cells (4×10^5 cells/well) were seeded and incubated in 96-well culture plates at 37 °C, 5% CO_2 in humidified air for 24 h. test compounds, drug-free group and L-NMMA (positive control) dissolved in 0.1% DMSO, with the final concentrations ranging from 12.5 μM to 50 μM, were added to the plates. Following by LPS stimulation (1 μg/mL) for 18 h. NO production in the supernatant was assessed by Griess reagents. The absorbance at 570 nm was measured with a microplate reader (Thermo, Waltham, MA, USA). N^G-Methyl-L-arginine acetate salt (L-NMMA, Sigma), a well-known nitric oxide synthase (NOS) inhibitor, was used as a positive control.[21] The viability of RAW264.7 cells was evaluated by the MTS assay simultaneously to exclude the interference of the cytotoxicity of the test compounds. All samples were assayed in at least triplicate. The NO inhibition (%) of compounds on NO production in LPS-stimulated RAW 264.7 cells were showed in Table S9.

Table S9. NO inhibition (%) of compounds on NO production in LPS-stimulated RAW 264.7 cells.

Compound	Concentration（μM）	NO inhibition（%）
L-NMMA	50	53.32±0.95
L-NMMA	25	43.6±0.44
L-NMMA	12.5	27.56±1.34
5a	50	58.16±1.97 (cytotoxicity)
5a	12.5	5.12±1.14
5b	12.5	22.98±1.81
6a	12.5	12.78±1.93
6b	50	49.73±1.93 (cytotoxicity)
6b	12.5	31.28±1.78
6c	50	16.03±3.22

6d	50	80.02±0.47 (cytotoxicity)
6d	12.5	30.36±3.82
6e	50	88.68±0.22 (cytotoxicity)
6e	12.5	21.85±0.91
6f	50	-1.23±1.10
7a	50	90.64±0.13 (cytotoxicity)
7a	12.5	36.88±0.25
7b	50	-13.93±0.85
7c	12.5	19.36±0.37

Reference

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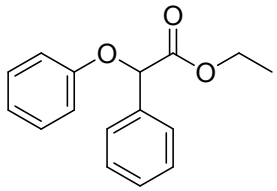
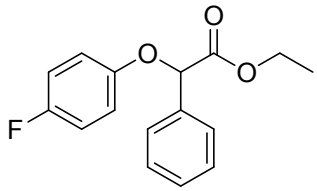
8. Analytical Date for known compounds

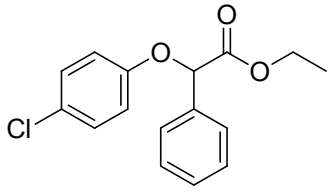


Ethyl 2-phenoxy-2-phenylacetate (3a): Colorless oil; 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.35-7.26 (m, 3H), 7.22-7.17 (m, 2H), 6.97-6.79 (m, 3H), 5.55 (s, 1H), 4.18-4.04 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.06, 157.40, 135.59, 129.65 (2C), 129.02, 128.86 (2C), 127.16 (2C), 121.87, 115.55 (2C), 78.71, 61.74, 14.13.

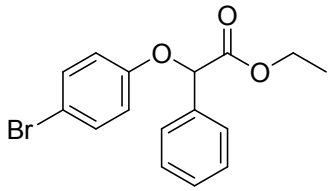


Ethyl 2-(4-fluorophenoxy)-2-phenylacetate (3c): Yellow oil; 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.45-7.32 (m, 3H), 7.05-6.84 (m, 4H), 5.55 (s, 1H), 4.28-4.08 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.90, 157.95 (d, *J* = 239.7 Hz), 153.52 (d, *J* = 2.3 Hz), 135.44,

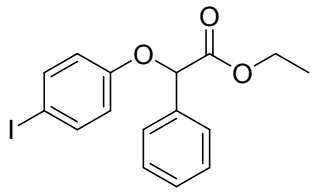
129.16, 128.93, 127.18, 116.98 (d, J = 8.1 Hz), 116.10 (d, J = 23.3 Hz), 79.57, 61.83, 14.16.



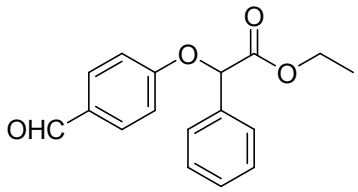
Ethyl 2-(4-chlorophenoxy)-2-phenylacetate (3d): Colorless oil; 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 7.6, 1.4 Hz, 2H), 7.44-7.34 (m, 3H), 7.22 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 5.57 (s, 1H), 4.26-4.12 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.70, 155.98, 135.19, 129.59 (2C), 129.22, 128.96 (2C), 127.17, 126.88 (2C), 116.97 (2C), 79.04, 61.90, 14.15.



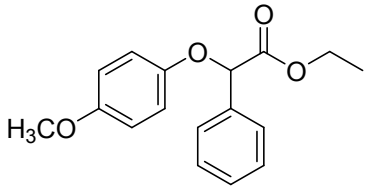
Ethyl 2-(4-bromophenoxy)-2-phenylacetate (3e): Colorless oil; 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 7.6, 1.7 Hz, 2H), 7.44-7.32 (m, 5H), 6.97-6.68 (m, 2H), 5.57 (s, 1H), 4.32-4.09 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.66, 156.50, 135.16, 132.54 (2C), 129.24, 128.97 (2C), 127.18 (2C), 117.46 (2C), 114.25, 78.96, 61.93, 14.17.



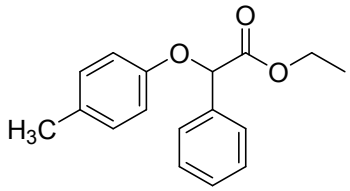
Ethyl 2-(4-iodophenoxy)-2-phenylacetate (3f): Colorless oil; 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.51 (m, 4H), 7.43-7.39 (m, 1H), 7.39-7.35 (m, 2H), 6.73 (d, J = 8.9 Hz, 2H), 5.57 (s, 1H), 4.27-4.10 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.64, 157.29, 138.49 (2C), 135.13, 129.24, 128.97(2C), 127.17 (2C), 117.97 (2C), 84.33, 78.79, 61.93, 14.16. HRMS (EI) calcd for $C_{16}H_{15}O_3INa$ $[M+Na]^+$: 404.9958; Found: 404.9972.



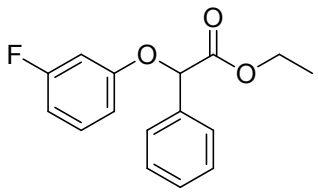
Ethyl 2-(4-formylphenoxy)-2-phenylacetate (3g): Colorless oil; 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.58 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.45-7.37 (m, 3H), 7.06 (d, *J* = 8.7 Hz, 2H), 5.71 (s, 1H), 4.28-4.15 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.88, 169.23, 162.24, 134.69, 132.12 (2C), 130.83, 129.44, 129.07 (2C), 127.21 (2C), 115.73 (2C), 78.70, 62.11, 14.15. HRMS (EI) calcd for $C_{17}H_{16}O_4Na$ $[M+Na]^+$: 307.0941; Found: 307.0942.



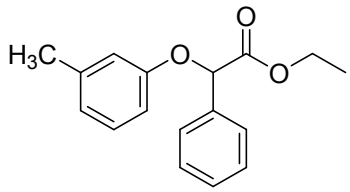
Ethyl 2-(4-methoxyphenoxy)-2-phenylacetate (3h): Colorless oil; 30% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.44-7.32 (m, 3H), 6.95-6.89 (m, 2H), 6.84-6.78 (m, 2H), 5.55 (s, 1H), 4.28-4.13 (m, 2H), 3.75 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.19, 154.69, 151.55, 135.86, 128.94, 128.79 (2C), 127.16 (2C), 116.98 (2C), 114.72 (2C), 79.80, 61.62, 55.69, 14.12. HRMS (EI) calcd for $C_{17}H_{22}O_4N$ $[M+NH_4]^+$: 304.1543; Found: 304.1544.



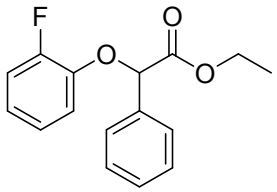
Ethyl 2-phenyl-2-(*p*-tolyloxy) acetate (3i): Colorless oil; 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.43-7.34 (m, 3H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.90-6.83 (m, 2H), 5.59 (s, 1H), 4.28-4.12 (m, 2H), 2.27 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.21, 155.37, 135.81, 131.21, 130.11(2C), 128.97, 128.85 (2C), 127.19 (2C), 115.54 (2C), 79.02, 61.69, 20.63, 14.17. HRMS (EI) calcd for $C_{17}H_{22}O_3N$ $[M+NH_4]^+$: 288.1594; Found: 288.1599.



Ethyl 2-(3-fluorophenoxy)-2-phenylacetate (3k)： Colorless oil; 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ[1] 7.57 (d, *J* = 6.3 Hz, 2H), 7.43-7.36 (m, 3H), 7.21 (dd, *J* = 15.1, 8.2 Hz, 1H), 6.77-6.71 (m, 1H), 6.71-6.65 (m, 2H), 5.59 (s, 1H), 4.28-4.13 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.64, 163.61 (d, *J* = 245.9 Hz), 158.67 (d, *J* = 10.9 Hz), 135.13, 130.49 (d, *J* = 9.9 Hz), 129.24, 128.97, 127.19, 111.15 (d, *J* = 3.0 Hz), 108.81 (d, *J* = 21.3 Hz), 103.58 (d, *J* = 25.1 Hz), 78.92, 61.93, 14.15. HRMS (EI) calcd for $C_{16}H_{15}O_3FNa$ $[M+Na]^+$: 297.0897; Found: 297.0911.

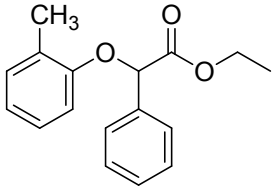


Ethyl 2-phenyl-2-(*m*-tolyloxy) acetate (3l): Colorless oil; 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.44-7.34 (m, 3H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.75 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.63 (s, 1H), 4.29-4.13 (m, 2H), 2.32 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.17, 157.47, 139.77, 135.71, 129.36, 128.99, 128.85 (2C), 127.17 (2C), 122.73, 116.56, 112.19, 78.67, 61.71, 21.63, 14.16. HRMS (EI) calcd for $C_{17}H_{22}O_3N$ $[M+NH_4]^+$: 288.1594; Found: 288.1592.

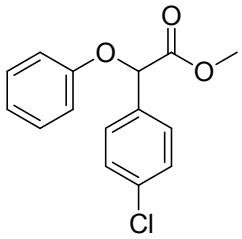


Ethyl 2-(2-fluorophenoxy)-2-phenylacetate (3m)： Colorless oil; 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.4 Hz, 2H), 7.45-7.34 (m, 3H), 7.14-7.06 (m, 1H), 7.04-6.91 (m, 3H), 5.65 (s, 1H), 4.28-4.13 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.66, 153.42 (d,

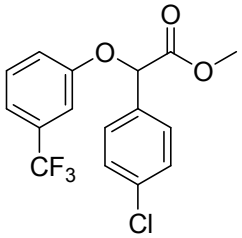
J = 246.9 Hz), 145.31 (d, *J* = 10.6 Hz), 135.29, 129.19, 128.87, 127.28, 124.36 (d, *J* = 3.9 Hz), 122.94 (d, *J* = 7.0 Hz), 117.78, 116.79 (d, *J* = 18.4 Hz), 80.26, 61.81, 14.12. HRMS (EI) calcd for $C_{16}H_{15}O_3FNa$ $[M+Na]^+$: 297.0897; Found: 297.0910.



Ethyl 2-phenyl-2-(*o*-tolyloxy) acetate (3o): Colorless oil; 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.44-7.35 (m, 3H), 7.18 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.14-7.06 (m, 1H), 6.94-6.87 (m, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 5.65 (s, 1H), 4.26-4.10 (m, 2H), 2.38 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.25, 155.70, 136.02, 131.17, 128.91, 128.80 (2C), 127.86, 127.03 (2C), 126.78, 121.59, 112.17, 78.78, 61.64, 16.57, 14.12. HRMS (EI) calcd for $C_{17}H_{22}O_3N$ $[M+NH_4]^+$: 288.1594; Found: 288.1597.

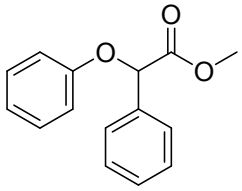


Methyl 2-(4-chlorophenyl)-2-phenoxyacetate (3r): Colorless oil; 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.58 (m, 2H), 7.48-7.43 (m, 2H), 7.38-7.33 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.03-6.97 (m, 2H), 5.70 (s, 1H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.18, 157.16, 135.08, 134.07, 129.77 (2C), 129.15 (2C), 128.53 (2C), 122.19, 115.58 (2C), 78.03, 52.87.

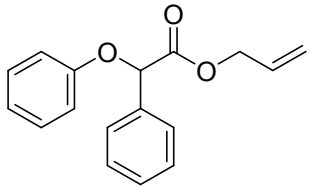


Methyl 2-(4-chlorophenyl)-2-(3-(trifluoromethyl) phenoxy) acetate (3s): White solid, m.p.: 83-85 ^{o}C; 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.35-7.28 (m, 3H), 7.21-7.16 (m, 1H), 7.13 (s, 1H), 7.01 (dd, *J* = 8.4, 2.5

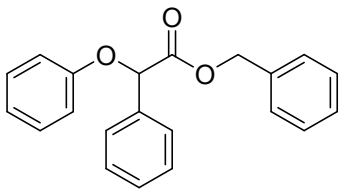
Hz, 1H), 5.58 (s, 1H), 3.68 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.58, 157.21, 135.42, 133.35, 132.23 (q, *J* = 32.6 Hz), 130.38, 129.29, 128.54, 127.90, 123.84 (q, *J* = 272.4 Hz), 119.77, 118.90 (q, *J* = 3.8 Hz), 118.57, 112.87 (q, *J* = 3.9 Hz), 78.11, 53.01.



Methyl 2-phenoxy-2-phenylacetate (3u): Colorless oil; 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.41-7.33 (m, 3H), 7.29-7.22 (m, 2H), 7.00-6.89 (m, 3H), 5.64 (s, 1H), 3.71 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.52, 157.33, 135.48, 129.68 (2C), 129.09, 128.90 (2C), 127.16 (2C), 121.93, 115.52 (2C), 78.63, 52.72.

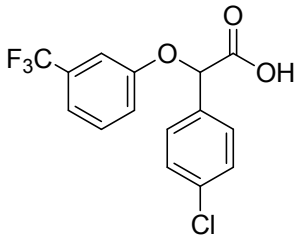


Allyl 2-phenoxy-2-phenylacetate (3w): Colorless oil; 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.49-7.39 (m, 3H), 7.31 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.05-6.96 (m, 3H), 5.86 (dd, *J* = 17.1, 10.5 Hz, 1H), 5.71 (s, 1H), 5.27-5.17 (m, 2H), 4.75-4.61 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.73, 157.41, 135.54, 131.47, 129.69 (2C), 129.12, 128.92 (2C), 127.23 (2C), 121.96, 118.75, 115.64 (2C), 78.75, 66.05. HRMS (EI) calcd for $C_{17}H_{20}O_3N$ $[M+NH_4]^+$: 286.1438; Found: 286.1438.

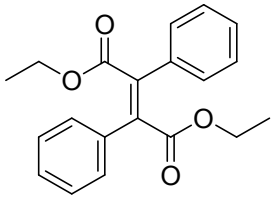


Benzyl 2-phenoxy-2-phenylacetate (3x): Colorless oil; 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.42-7.34 (m, 3H), 7.30-7.22 (m, 5H), 7.17 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.00-6.90 (m, 3H), 5.68 (s, 1H), 5.20 (d, *J* = 12.4 Hz,

1H), 5.12 (d, *J* = 12.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.89, 157.36, 135.41, 135.34, 129.67 (2C), 129.10, 128.89 (2C), 128.60 (2C), 128.41, 128.12 (2C), 127.25 (2C), 121.93, 115.59 (2C), 78.70, 67.23.

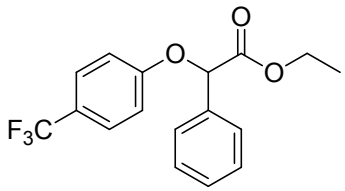


2-(4-chlorophenyl)-2-(3-(trifluoromethyl) phenoxy) acetic acid (9): White syrup; 80% yield; ^{1}H NMR (400 MHz, DMSO) δ 13.57 (s, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 9.1 Hz, 3H), 6.11 (s, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO) δ 170.75, 157.67, 135.18, 133.99, 131.29, 130.78 (q, *J* = 31.8 Hz), 129.69, 129.18, 128.42, 124.35 (q, *J* = 272.5 Hz), 120.29, 119.91, 118.40 (q, *J* = 3.7 Hz), 112.32 (q, *J* = 3.7 Hz), 76.97.



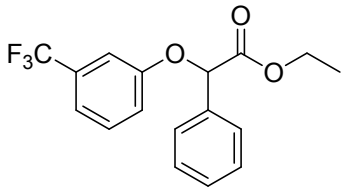
Diethyl 2,3-diphenylfumarate (B): Colorless oil; 19% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.14 (m, 6H), 7.13-7.04 (m, 4H), 4.30 (q, *J* = 7.1 Hz, 4H), 1.30 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 168.11, 138.76, 134.75, 129.87, 128.34, 128.20, 61.85, 14.16.

9. Analytical Date for unknown compounds

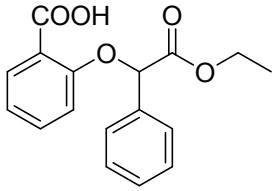


Ethyl 2-phenyl-2-(4-(trifluoromethyl) phenoxy) acetate (3b): Colorless oil; 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.46-7.36 (m, 3H), 7.02 (d, *J* = 8.6 Hz, 2H), 5.67 (s, 1H), 4.30-4.14 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.40, 159.78, 134.88, 129.36,

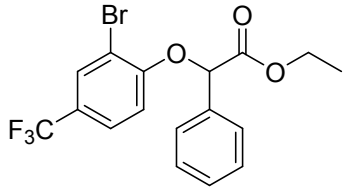
129.03, 128.41, 127.19, 127.14, 127.10, 124.37 (q, J = 271.3 Hz), 124.04 (q, J = 32.8 Hz), 120.33, 115.50 (2C), 78.71, 62.03, 14.13. HRMS (EI) calcd for $C_{17}H_{15}O_3F_3Na$ $[M+Na]^+$: 347.0866; Found: 347.0880.



Ethyl 2-phenyl-2-(3-(trifluoromethyl) phenoxy) acetate (3j)： Colorless oil; 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 2H), 7.43-7.33 (m, 4H), 7.22 (d, J = 8.4 Hz, 2H), 7.13-7.07 (m, 1H), 5.64 (s, 1H), 4.30-4.09 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.47, 157.50, 134.91, 132.08 (q, J = 32.5 Hz), 130.26, 129.33, 129.00, 127.97, 127.21, 123.91 (q, J = 272.4 Hz), 119.85, 118.75, 118.60 (q, J = 3.8 Hz), 112.69 (q, J = 3.9 Hz), 78.88, 61.98, 14.10. HRMS (EI) calcd for $C_{17}H_{15}O_3F_3Na$ $[M+Na]^+$: 347.0866; Found: 347.0881.

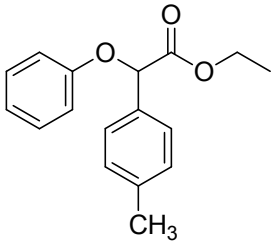


2-(2-Ethoxy-2-oxo-1-phenylethoxy) benzoic acid (3n): Colorless oil; 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.99 (dd, J = 8.0, 1.6 Hz, 1H), 7.58 (dd, J = 7.4, 2.1 Hz, 2H), 7.53-7.40 (m, 4H), 7.00 (d, J = 8.4 Hz, 1H), 6.96-6.86 (m, 1H), 6.15 (s, 1H), 4.39-4.08 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.41, 168.45, 161.93, 136.39, 133.58, 130.43, 129.59, 129.05(2C), 127.74(2C), 119.49, 117.76, 111.87, 75.26, 62.10, 14.12. HRMS (EI) calcd for $C_{17}H_{16}O_5Na$ $[M+Na]^+$: 323.0890; Found: 323.0897.

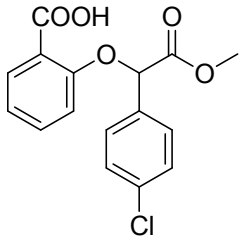


Ethyl 2-(2-bromo-4-(trifluoromethyl) phenoxy)-2-phenylacetate (3p): White solid, m.p.: 69-72 ^{o}C.; 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz,

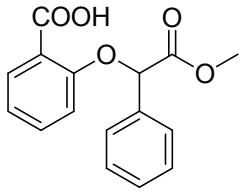
$CDCl_3$) δ 7.85 (d, *J* = 1.6 Hz, 1H), 7.65 (d, *J* = 6.5 Hz, 2H), 7.48 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.45-7.37 (m, 3H), 6.87 (d, *J* = 8.6 Hz, 1H), 5.72 (s, 1H), 4.26-4.13 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.83, 156.43, 134.40, 131.14 (q, *J*=7.4, 3.7 Hz), 129.43, 129.03, 127.50, 127.06, 125.86 (q, *J* = 3.8 Hz), 123.45 (q, *J* = 271.9 Hz), 119.40, 113.69, 113.30, 79.45, 62.17, 14.11. HRMS (EI) calcd for $C_{17}H_{14}O_3BrF_3Na$ $[M+Na]^+$: 424.9971; Found: 424.9982.



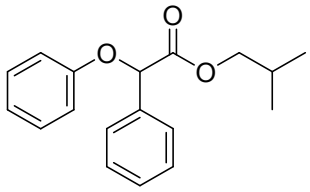
Ethyl 2-phenoxy-2-(*p*-tolyl)acetate (3q): Colorless oil; 59% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.38-7.33 (m, 2H), 7.29 (t, *J* = 9.6 Hz, 2H), 7.09-6.99 (m, 3H), 5.69 (s, 1H), 4.39-4.19 (m, 2H), 2.45 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.21, 157.54, 138.94, 132.71, 129.64 (2C), 129.58 (2C), 127.18 (2C), 121.81, 115.62 (2C), 78.68, 61.68, 21.37, 14.17. HRMS (EI) calcd for $C_{17}H_{22}O_3N$ $[M+NH_4]^+$: 288.1594; Found: 288.1599.



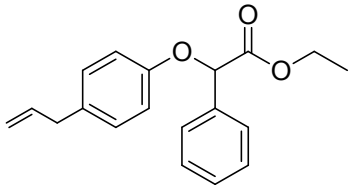
2-(1-(4-chlorophenyl)-2-methoxy-2-oxoethoxy) benzoic acid (3t): White solid, m.p.: 65-68 ^oC.; 83% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.97 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56-7.46 (m, 3H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.03-6.96 (m, 1H), 6.94-6.86 (m, 1H), 6.15 (s, 1H), 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.16, 168.54, 161.94, 136.51, 135.68, 131.96, 130.26, 129.28 (2C), 129.06 (2C), 119.50, 117.79, 111.59, 74.28, 53.03. HRMS (EI) calcd for $C_{16}H_{13}ClO_5Na$ $[M+Na]^+$: 343.0349; Found: 343.0344.



2-(2-Methoxy-2-oxo-1-phenylethoxy) benzoic acid (3v): Colorless oil; 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.00 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.59 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.52-7.41 (m, 4H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.95-6.86 (m, 1H), 6.19 (s, 1H), 3.77 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.33, 168.90, 161.92, 136.40, 133.42, 130.37, 129.63, 129.05 (2C), 127.73 (2C), 119.46, 117.73, 111.76, 75.07, 52.91. HRMS (EI) calcd for $C_{16}H_{14}O_5Na$ $[M+Na]^+$: 309.0733; Found: 309.0737.

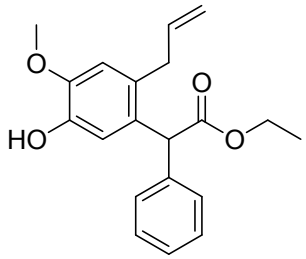


Isobutyl 2-phenoxy-2-phenylacetate (3y): Colorless oil; 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.44-7.33 (m, 3H), 7.29-7.25 (m, 2H), 7.01-6.94 (m, 3H), 5.66 (s, 1H), 3.96-3.87 (m, 2H), 1.95-1.81 (m, 1H), 0.81 (d, *J* = 2.9 Hz, 3H), 0.80 (d, *J* = 2.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.13, 157.46, 135.76, 129.66 (2C), 129.02, 128.85 (2C), 127.17 (2C), 121.85, 115.53 (2C), 78.73, 71.60, 27.79, 18.92, 18.91. HRMS (EI) calcd for $C_{18}H_{24}O_3N$ $[M+NH_4]^+$: 302.1751; Found: 302.1753.

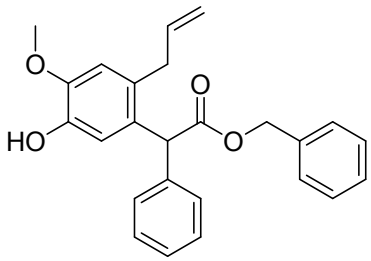


Ethyl 2-(4-allylphenoxy)-2-phenylacetate (3z): Colorless oil; 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.43-7.34 (m, 3H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.94 (dd, *J* = 17.7, 9.3 Hz, 1H), 5.60 (s, 1H), 5.09-5.05 (m, 1H), 5.03 (t, *J* = 1.4 Hz, 1H), 4.28-4.13 (m, 2H), 3.32 (d, *J* = 6.7 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.13, 155.88,

137.76, 135.75, 133.40, 129.70 (2C), 128.99, 128.85 (2C), 127.18 (2C), 115.71, 115.61 (2C), 78.96, 61.71, 39.45, 14.16. HRMS (EI) calcd for $C_{19}H_{24}O_3N$ $[M+NH_4]^+$: 314.1751; Found: 314.1743.

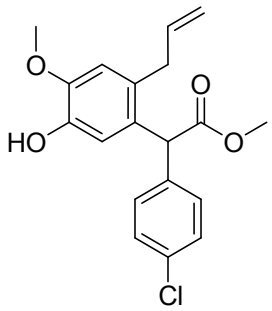


Ethyl 2-(2-allyl-5-hydroxy-4-methoxyphenyl)-2-phenylacetate (4a): Colorless oil; 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 6.9 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 3H), 6.77 (s, 1H), 6.58 (s, 1H), 5.84 (ddt, *J* = 16.3, 10.2, 6.1 Hz, 1H), 5.39 (s, 1H), 5.09 (s, 1H), 4.99 (dd, *J* = 10.1, 1.5 Hz, 1H), 4.93 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.10 (t, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.24 (dd, *J* = 5.8, 4.3 Hz, 2H), 1.17 (d, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.88, 145.74, 144.07, 138.70, 137.06, 129.92, 129.63, 128.83 (2C), 128.63 (2C), 127.16, 116.13, 115.40, 112.45, 61.27, 56.00, 52.66, 37.12, 14.28. HRMS (EI) calcd for $C_{20}H_{22}O_4Na$ $[M+Na]^+$: 349.1410; Found: 349.1424.

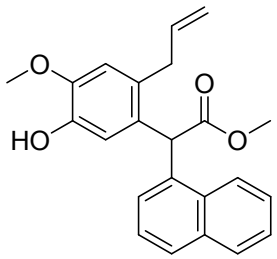


Benzyl 2-(2-allyl-5-hydroxy-4-methoxyphenyl)-2-phenylacetate (4b): Colorless oil; 39% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.16 (m, 7H), 7.13 (t, *J* = 6.0 Hz, 3H), 6.77 (s, 1H), 6.56 (s, 1H), 5.80 (dd, *J* = 16.7, 10.5 Hz, 1H), 5.45 (s, 1H), 5.16 (s, 1H), 5.08 (s, 2H), 4.95 (dd, *J* = 10.1, 1.5 Hz, 1H), 4.89 (dd, *J* = 17.1, 1.7 Hz, 1H), 3.71 (s, 3H), 3.21 (dd, *J* = 4.4, 1.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.66, 145.75, 144.05, 138.42, 136.96, 135.82, 129.63, 129.53, 128.77 (2C), 128.57 (2C), 128.50 (2C), 128.21 (2C), 128.18, 127.15, 116.08, 115.45, 112.45,

66.88, 55.89, 52.54, 37.02. HRMS (EI) calcd for $C_{25}H_{24}O_4Na$ $[M+Na]^+$: 411.1567; Found: 411.1561.

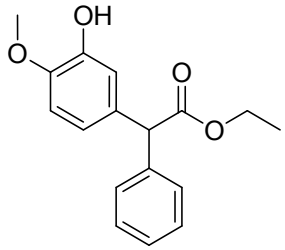


Methyl 2-(2-allyl-5-hydroxy-4-methoxyphenyl)-2-(4-chlorophenyl) acetate (4c): Colorless oil; 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.74 (s, 1H), 6.58 (s, 1H), 5.81 (dd, *J* = 17.0, 10.2 Hz, 1H), 5.43 (s, 1H), 5.07 (s, 1H), 4.99 (dd, *J* = 10.1, 1.6 Hz, 1H), 4.90 (dd, *J* = 17.1, 1.7 Hz, 1H), 3.77 (s, 3H), 3.64 (s, 3H), 3.20 (dd, *J* = 6.1, 1.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.07, 145.93, 144.20, 137.05, 136.85, 133.12, 130.20 (2C), 129.62, 129.15, 128.75 (2C), 116.25, 115.02, 112.64, 55.99, 52.57, 51.88, 37.07.HRMS (EI) calcd for $C_{19}H_{19}O_4ClNa$ $[M+Na]^+$: 369.0864; Found: 369.0857.

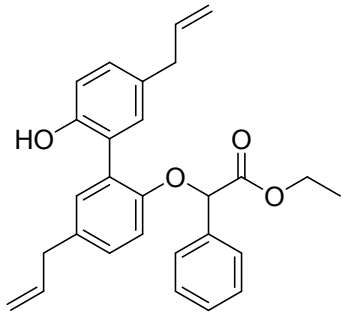


Methyl 2-(2-allyl-5-hydroxy-4-methoxyphenyl)-2-(naphthalen-1-yl) acetate (4d): White solid, m.p.: 125-127 ^{o}C.; 49% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.48 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.44-7.38 (m, 1H), 7.22 (d, *J* = 7.1 Hz, 1H), 6.76 (s, 1H), 6.74 (s, 1H), 5.93 (dd, *J* = 13.9, 7.1 Hz, 1H), 5.90 (s, 1H), 5.45 (s, 1H), 5.07 (ddd, *J* = 18.8, 13.6, 1.7 Hz, 2H), 3.88 (s, 3H), 3.76 (s, 3H), 3.34-3.22 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.70, 145.89, 144.16, 136.83, 134.50, 134.07, 131.89, 129.71, 129.26, 129.09, 128.25, 126.62, 126.49, 125.76, 125.55, 123.09, 116.28, 115.54, 112.75, 56.02, 52.59,

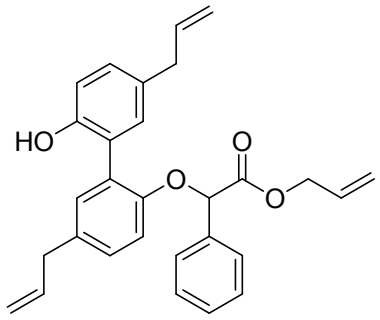
49.75, 37.25. HRMS (EI) calcd for $C_{23}H_{22}O_4Na$ $[M+Na]^+$: 385.1410; Found: 385.1397.



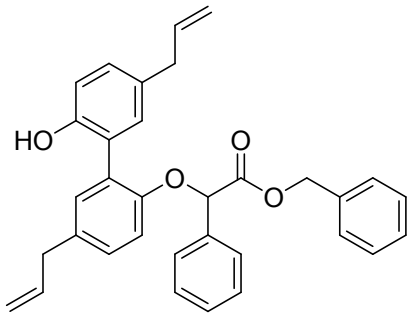
Ethyl 2-(3-hydroxy-4-methoxyphenyl)-2-phenylacetate (4e): Colorless oil; 33% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 4H), 7.28-7.26 (m, 1H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.83-6.78 (m, 1H), 5.56 (s, 1H), 4.94 (s, 1H), 4.24-4.17 (m, 2H), 3.84 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.87, 146.63, 145.00, 139.21, 130.64, 128.68 (2C), 128.51 (2C), 127.30, 121.76, 114.39, 111.23, 61.30, 56.77, 56.02, 14.30. HRMS (EI) calcd for $C_{17}H_{18}O_4Na$ $[M+Na]^+$: 309.1097; Found: 309.1097.



Ethyl 2-((5,5'-diallyl-2'-hydroxy-[1,1'-biphenyl]-2-yl) oxy)-2-phenylacetate (6 a): White solid, m.p.: 75-77 ^oC.; 85% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.33 (dd, *J* = 5.0, 1.6 Hz, 3H), 7.21-7.09 (m, 3H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.01 (dd, *J* = 13.3, 6.1 Hz, 1H), 5.96 (dd, *J* = 13.4, 6.1 Hz, 1H), 5.75 (s, 1H), 5.26-4.96 (m, 4H), 4.39-4.02 (m, 2H), 3.40 (d, *J* = 6.7 Hz, 2H), 3.36 (d, *J* = 6.7 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.93, 152.47, 151.80, 138.06, 137.43, 134.48, 134.27, 133.27, 132.02, 131.26, 129.48, 129.26, 129.12, 128.91 (2C), 128.06, 127.29 (2C), 125.79, 117.40, 116.12(2C), 115.57, 78.06, 62.55, 39.56, 39.47, 14.07. HRMS (EI) calcd for $C_{28}H_{28}O_4Na$ $[M+Na]^+$: 451.1880; Found: 451.1872.

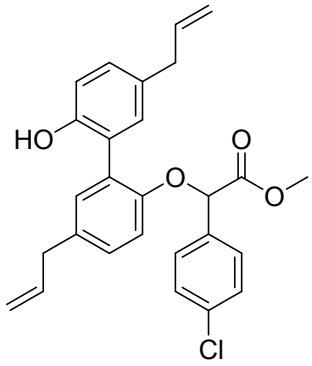


Allyl 2-((5,5'-diallyl-2'-hydroxy-[1,1'-biphenyl]-2-yl) oxy)-2-phenylacetate (6b): Colorless oil; 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) 7.50 (dd, *J* = 6.6, 2.8 Hz, 2H), 7.37-7.30 (m, 3H), 7.22-7.10 (m, 3H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.96 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.02 (dd, *J* = 13.3, 6.0 Hz, 1H), 5.97 (dd, *J* = 13.3, 6.0 Hz, 1H), 5.90-5.63 (m, 2H), 5.21-5.03 (m, 6H), 4.69-4.56 (m, 2H), 3.41 (d, *J* = 6.7 Hz, 2H), 3.37 (d, *J* = 6.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.60, 152.42, 151.79, 138.04, 137.40, 134.57, 134.19, 133.26, 132.01, 131.26, 131.00, 129.48, 129.33, 129.14, 128.92 (2C), 128.07, 127.35 (2C), 125.71, 119.31, 117.35, 116.13, 115.57, 111.72, 78.06, 66.72, 39.54, 39.45. HRMS (EI) calcd for $C_{29}H_{28}O_4Na$ $[M+Na]^+$: 463.1880; Found: 463.1872.



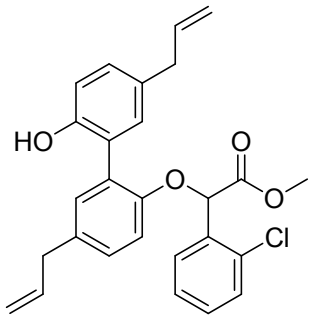
Benzyl 2-((5,5'-diallyl-2'-hydroxy-[1,1'-biphenyl]-2-yl) oxy)-2-phenylacetate (6c): White solid, m.p.: 57-59 ^{o}C; 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.35-7.27 (m, 6H), 7.19 (d, *J* = 2.0 Hz, 1H), 7.15 (dd, *J* = 6.9, 4.9 Hz, 2H), 7.13-7.05 (m, 2H), 7.02 (dd, *J* = 6.6, 5.3 Hz, 2H), 6.93 (s, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.02 (dd, *J* = 11.8, 5.0 Hz, 1H), 5.96 (dd, *J* = 11.8, 5.0 Hz, 1H), 5.79 (s, 1H), 5.21 (d, *J* = 12.2 Hz, 1H), 5.14 (s, 1H), 5.13-5.02 (m, 4H), 3.40 (d, *J* = 6.7 Hz, 2H), 3.36 (d, *J* = 6.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.77, 152.40, 151.76, 138.05, 137.41, 134.86, 134.51, 134.05, 133.22, 132.00, 131.24, 129.48, 129.33, 129.14, 128.92 (2C), 128.67 (2C), 128.64,

128.32 (2C), 128.00, 127.36 (2C), 125.66, 117.30, 116.13, 115.57,111.71, 78.13, 67.91, 39.54, 39.46. HRMS (EI) calcd for $C_{33}H_{30}O_4Na$ $[M+Na]^+$: 513.2036; Found: 513.2050.



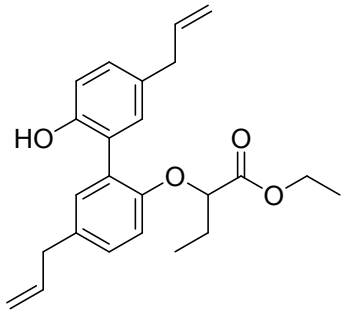
Methyl 2-(4-chlorophenyl)-2-((5,5'-diallyl-2'-hydroxy-[1,1'-biphenyl]-2-yl) oxy)

acetate (6d): White solid, m.p.: 96-99 ^oC; 75% yield; ^1H NMR (400 MHz, $CDCl_3$) δ ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.20-7.10 (m, 3H), 7.06-6.96 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.79 (s, 1H), 6.01 (dd, *J* = 13.5, 6.7 Hz, 1H), 5.96 (dd, *J* = 13.5, 6.7 Hz, 1H), 5.71 (s, 1H), 5.17-5.09 (m, 2H), 5.07 (dd, *J* = 3.9, 2.8 Hz, 2H), 3.74 (s, 3H), 3.40 (d, *J* = 6.7 Hz, 2H), 3.36 (d, *J* = 6.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.99, 152.27, 151.64, 138.00, 137.31, 135.35, 134.87, 133.26, 132.77, 132.15, 131.25, 129.60, 129.25, 129.16 (2C), 128.68 (2C), 128.06, 125.51, 117.24, 116.21, 115.62, 111.87, 100.11, 53.40, 39.53, 39.46. HRMS (EI) calcd for $C_{27}H_{25}O_4ClNa$ $[M+Na]^+$: 471.1334; Found: 471.1324.

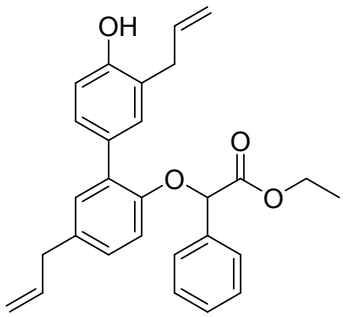


Methyl 2-(2-chlorophenyl)-2-((5,5'-diallyl-2'-hydroxy-[1,1'-biphenyl]-2-yl) oxy) acetate (6e): Yellow solid, m.p.: 77-79 ^oC; 72% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54-7.47 (m, 1H), 7.27 (dt, *J* = 5.1, 3.0 Hz, 1H), 7.17 (dd, *J* = 4.0, 3.3 Hz, 1H), 7.14 (dd, *J* = 6.3, 4.6 Hz, 1H), 7.09 (s, 2H), 7.01 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.92

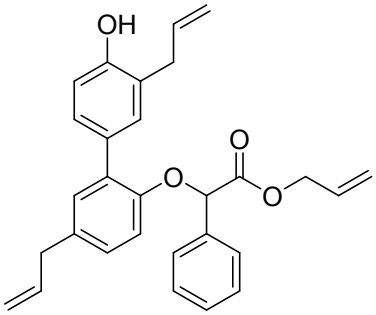
(d, *J* = 7.9 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 1H), 6.79 (s, 1H), 6.25 (s, 1H), 5.92 (dd, *J* = 11.8, 5.0 Hz, 1H), 5.86 (dd, *J* = 11.8, 5.0 Hz, 1H), 5.02 (dd, *J* = 14.8, 3.7 Hz, 2H), 4.97 (t, *J* = 9.0 Hz, 2H), 3.66 (s, 3H), 3.31 (d, *J* = 6.7 Hz, 2H), 3.26 (d, *J* = 6.7 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.89, 152.28, 151.76, 138.01, 137.35, 134.76, 133.47, 133.23, 132.38, 132.10, 131.27, 130.52, 129.70, 129.49, 129.27, 129.25, 127.96, 127.78, 125.69, 117.29, 116.17, 115.59, 112.01, 74.08, 53.37, 39.53, 39.46. HRMS (EI) calcd for $C_{27}H_{25}O_4ClNa$ $[M+Na]^+$: 471.1334; Found: 471.1343.



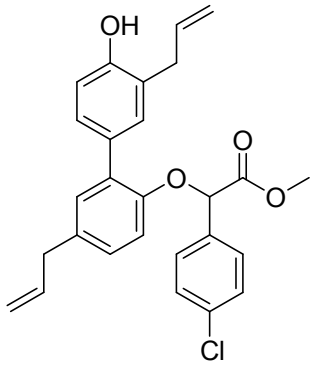
Ethyl 2-((5,5'-diallyl-2'-hydroxy-[1,1'-biphenyl]-2-yl) oxy) butanoate (6f): Colorless oil; 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 2.0 Hz, 1H), 7.11 (ddd, *J* = 7.9, 3.8, 2.3 Hz, 2H), 7.03 (d, *J* = 1.9 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.88 (s, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.02 (dd, *J* = 13.7, 6.8 Hz, 1H), 5.97 (dd, *J* = 13.8, 6.8 Hz, 1H), 5.11 (d, *J* = 1.4 Hz, 1H), 5.07 (td, *J* = 4.7, 1.5 Hz, 3H), 4.78 (t, *J* = 5.6 Hz, 1H), 4.32-4.15 (m, 2H), 3.38 (d, *J* = 6.6 Hz, 4H), 2.00-1.87 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 172.20, 152.58, 152.05, 138.11, 137.51, 134.01, 133.15, 131.91, 131.18, 129.27, 128.98, 127.83, 126.02, 117.44, 116.00, 115.53, 111.05, 76.42, 62.03, 39.56, 39.43, 25.98, 14.26, 9.21. HRMS (EI) calcd for $C_{24}H_{28}O_4Na$ $[M+Na]^+$:403.1880; Found: 403.1867.



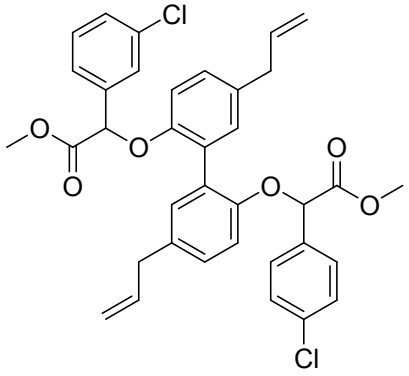
Ethyl 2-((3',5-diallyl-4'-hydroxy-[1,1'-biphenyl]-2-yl) oxy)-2-phenylacetate (7a): Light yellow oil; 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.7 Hz, 2H), 7.42 (td, *J* = 8.6, 4.4 Hz, 3H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.21 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.05 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.08 (dd, *J* = 15.3, 8.5 Hz, 1H), 5.96 (dd, *J* = 15.3, 8.4 Hz, 1H), 5.68 (s, 1H), 5.17 (d, *J* = 1.5 Hz, 1H), 5.11 (dd, *J* = 7.1, 3.6 Hz, 2H), 5.05 (d, *J* = 10.1 Hz, 2H), 4.28-4.13 (m, 2H), 3.58 (d, *J* = 6.7 Hz, 2H), 3.34 (d, *J* = 6.7 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.95, 154.83, 150.92, 137.91, 136.46, 135.62, 132.32, 131.07, 130.82, 130.33, 129.11, 129.02, 128.92 (2C), 127.95, 127.72, 127.09 (2C), 116.30(2C), 115.75, 115.71, 112.65, 78.72, 61.84, 39.53, 34.85, 14.17. HRMS (EI) calcd for $C_{28}H_{28}O_4Na$ $[M+Na]^+$: 451.1880; Found: 451.1871.



Allyl 2-((3',5-diallyl-4'-hydroxy-[1,1'-biphenyl]-2-yl) oxy)-2-phenylacetate (7b): Orange oil; 38% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.44-7.35 (m, 5H), 7.05 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.01 (d, *J* = 2.1 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.07 (dd, *J* = 13.6, 6.7 Hz, 1H), 5.96 (dd, *J* = 13.6, 6.7 Hz, 1H), 5.84 (dd, *J* = 14.1, 5.6 Hz, 1H), 5.73 (s, 1H), 5.22-5.19 (m, 2H), 5.19-5.16 (m, 2H), 5.11 (ddd, *J* = 7.6, 3.7, 1.8 Hz, 2H), 5.07 (dd, *J* = 2.9, 1.7 Hz, 1H), 4.66-4.63 (m, 2H), 3.58 (d, *J* = 6.7 Hz, 2H), 3.34 (d, *J* = 6.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.52, 169.61, 154.75, 150.91, 137.90, 136.42, 135.49, 132.32, 131.42, 131.10, 130.82, 130.32, 129.19, 129.02, 128.96, 128.75, 127.96, 127.13, 126.70, 118.92, 118.79, 116.33, 115.75, 115.71, 112.68, 78.67, 66.13, 39.53, 34.82. HRMS (EI) calcd for $C_{29}H_{28}O_4Na$ $[M+Na]^+$: 463.1880; Found: 463.1871.



Methyl 2-(4-chlorophenyl)-2-((3',5-diallyl-4'-hydroxy-[1,1'-biphenyl]-2-yl) oxy) acetate (7c): Light yellow oil; 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.43-7.39 (m, 2H), 7.28 (d, *J* = 2.2 Hz, 1H), 7.22 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.05 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.04 (dd, *J* = 13.6, 6.7 Hz, 1H), 5.96 (dd, *J* = 13.6, 6.7 Hz, 1H), 5.67 (s, 1H), 5.15 (d, *J* = 1.7 Hz, 1H), 5.12-5.04 (m, 4H), 3.75 (s, 3H), 3.56 (d, *J* = 6.7 Hz, 2H), 3.34 (d, *J* = 6.7 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.11, 154.55, 150.89, 137.88, 136.31, 135.18, 134.01, 132.38, 131.24, 130.75, 130.34, 129.23(2C), 129.09, 128.46(2C), 128.05, 127.61, 116.41(2C), 115.79, 115.74, 112.58, 77.95, 52.99, 39.53, 34.79. HRMS (EI) calcd for $C_{27}H_{25}ClO_4Na$ $[M+Na]^+$: 471.1334; Found: 471.1321.

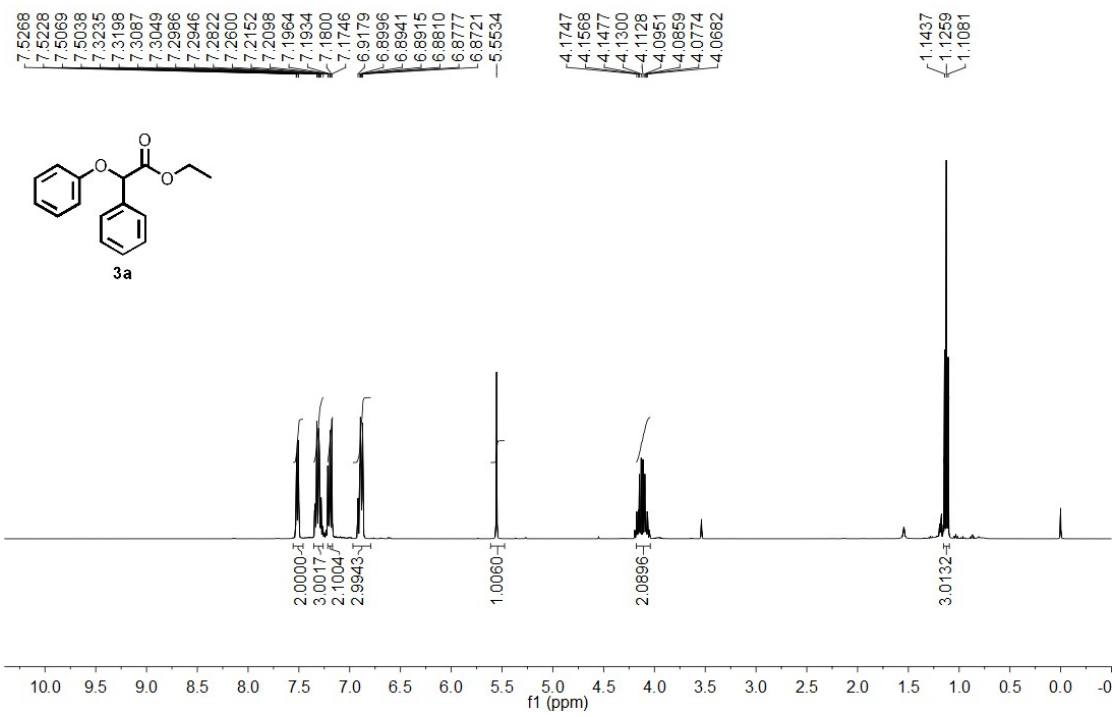


Methyl 2-(4-chlorophenyl)-2-((5,5'-diallyl-2'-(1-(3-chlorophenyl)-2-methoxy-2-oxoethoxy)-[1,1'-biphenyl]-2-yl) oxy) acetate (8): Colorless oil; 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 1.4 Hz, 1H), 7.20 (ddd, *J* = 8.8, 6.5, 3.0 Hz, 7H), 7.15-7.10 (m, 2H), 7.07 (ddd, *J* = 8.3, 3.9, 2.3 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 5.96 (dd, *J* = 13.4, 6.6 Hz, 1H), 5.90 (dd, *J* = 13.4, 6.6 Hz, 1H), 5.38 (s, 1H), 5.29 (s, 1H), 5.11-5.01 (m, 4H), 3.63 (s, 3H), 3.60 (s, 3H), 3.36 (d,

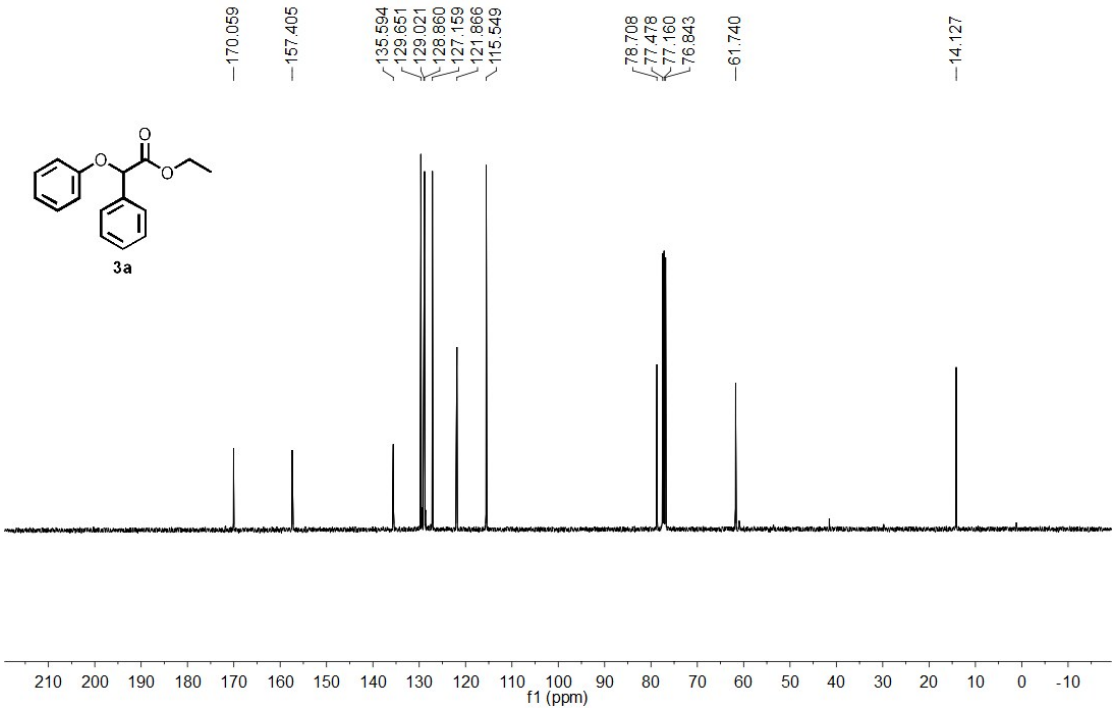
J = 6.8 Hz, 2H), 3.31 (d, *J* = 6.7 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.44, 170.41, 153.10, 153.06, 137.64, 137.59, 134.55, 134.51, 134.37, 134.29, 133.75, 133.66, 132.62(2C), 129.03, 128.70(2C), 128.64(2C), 128.58, 128.50, 128.33, 128.29(2C), 128.24(2C), 115.87, 115.85, 114.96(2C), 79.02, 78.87, 52.67, 52.61, 39.57, 39.52. HRMS (EI) calcd for $C_{36}H_{32}O_6Cl_2Na$ $[M+Na]^+$: 653.1468; Found: 653.1477.

10 Copies of NMR spectra

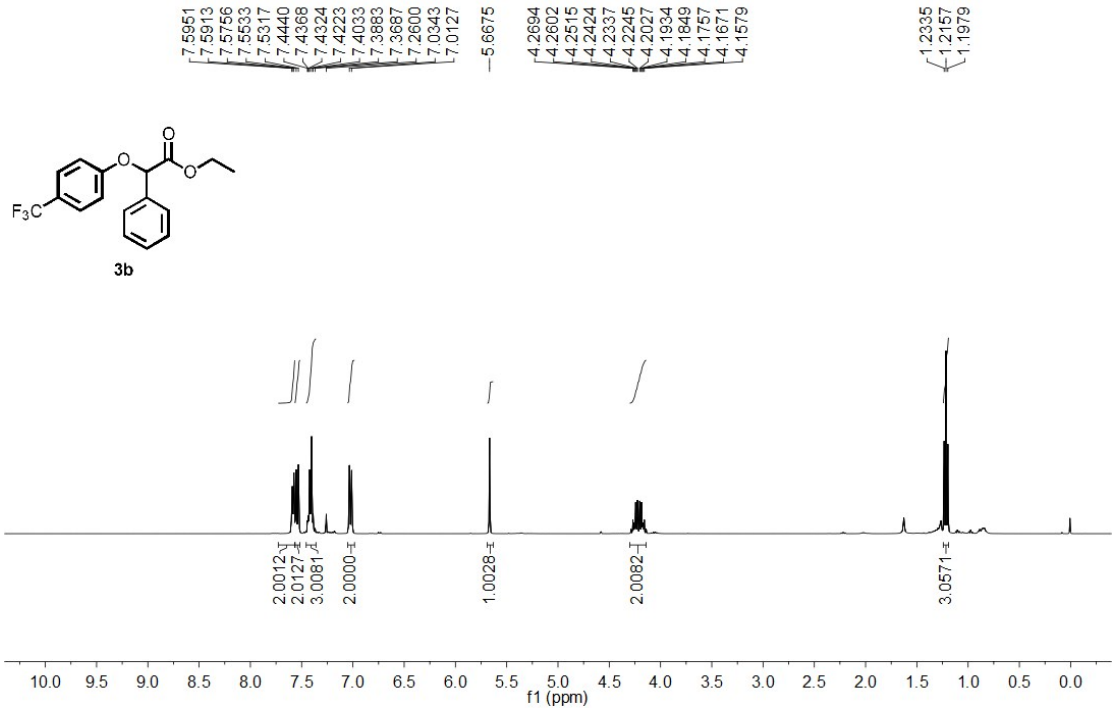
ZZP-1-H1



ZZP-1-C13



zzp-12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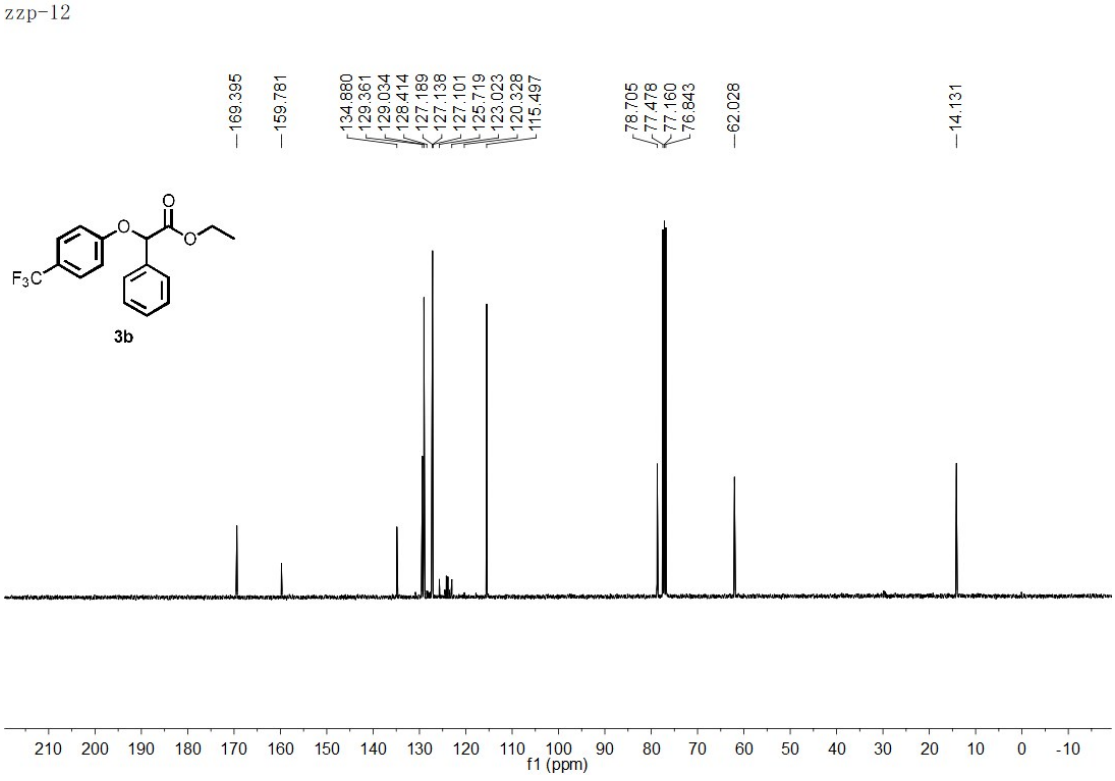
7.3687
7.2600
7.0343
7.0127
5.6675
4.2694
4.2602
4.2515
4.2424
4.2337
4.2245
4.2027
4.1934
4.1849
4.1757
4.1671
4.1579
1.2335
1.2157
1.1979
O
O
O
F3C
3b
2.0012
2.0127
3.0081
2.0000
1.0028
2.0082
3.0571
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

zzp-12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129.361
129.034
128.414
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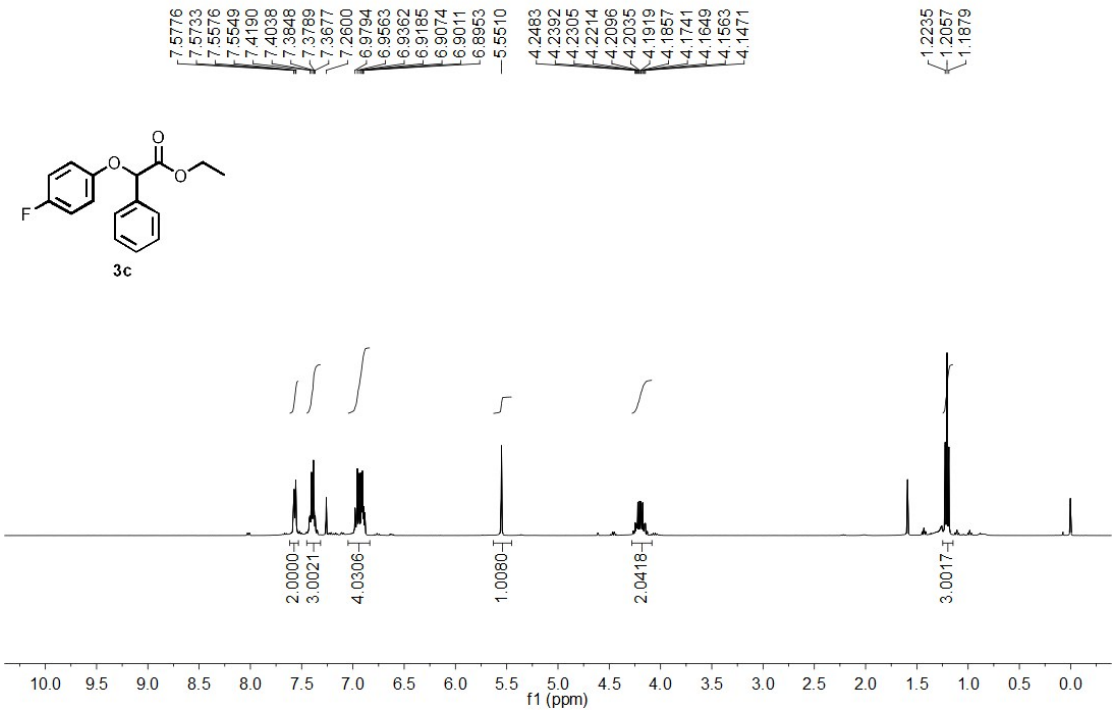
127.138
127.101
125.719
123.023
120.328
115.497
78.705
77.478
77.160
76.843
62.028
14.131
O
O
O
F3C
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

zzp-4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7.5576
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7.4190
7.4038
7.3848
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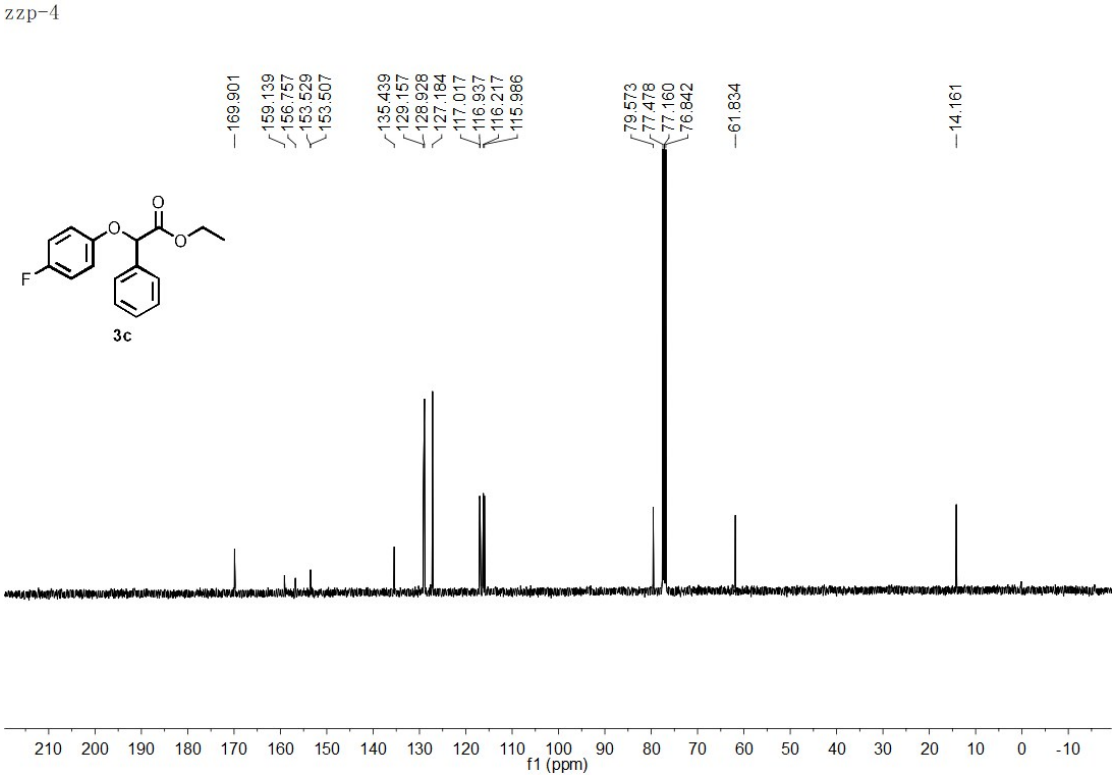
7.3677
7.2600
6.9794
6.9563
6.9362
6.9185
6.9074
6.9011
6.8953
5.5510
4.2483
4.2392
4.2305
4.2214
4.2096
4.2035
4.1919
4.1857
4.1741
4.1649
4.1563
4.1471
1.2235
1.2057
1.1879
O
O
O
F
3c
2.0000
3.0021
4.0306
1.0080
2.0418
3.0017
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

zzp-4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153.529
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135.439
129.157
128.928
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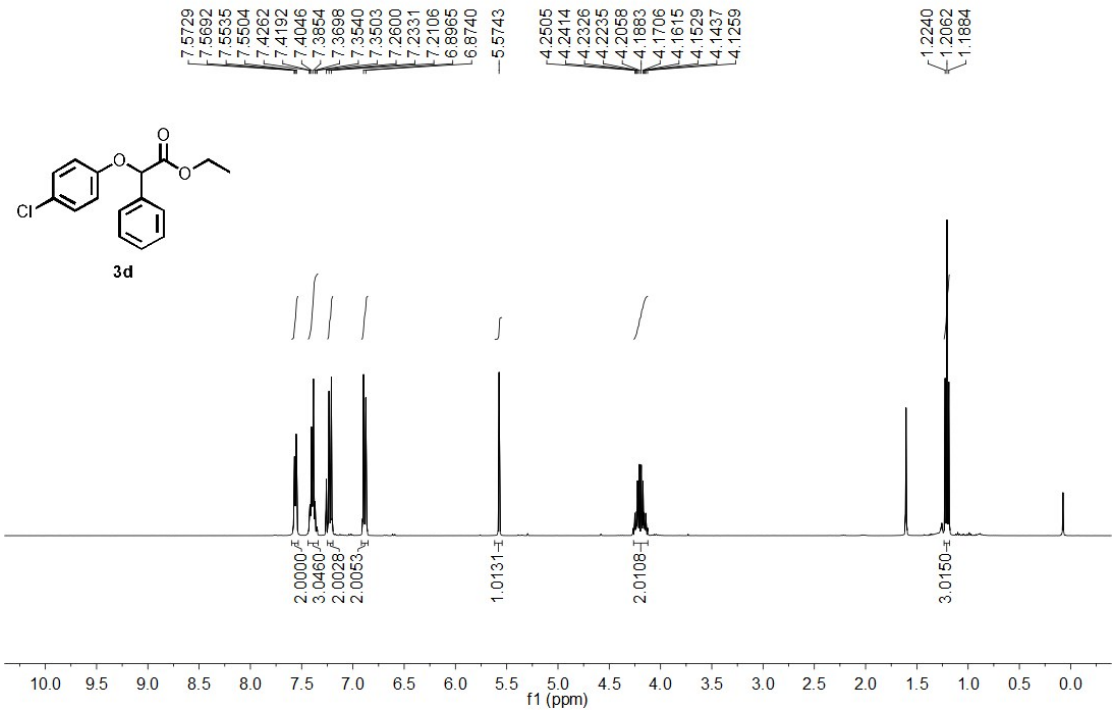
117.017
116.937
116.217
115.986
79.573
77.478
77.160
76.842
61.834
14.161
O
O
O
F
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

ZZP-3-2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7.5535
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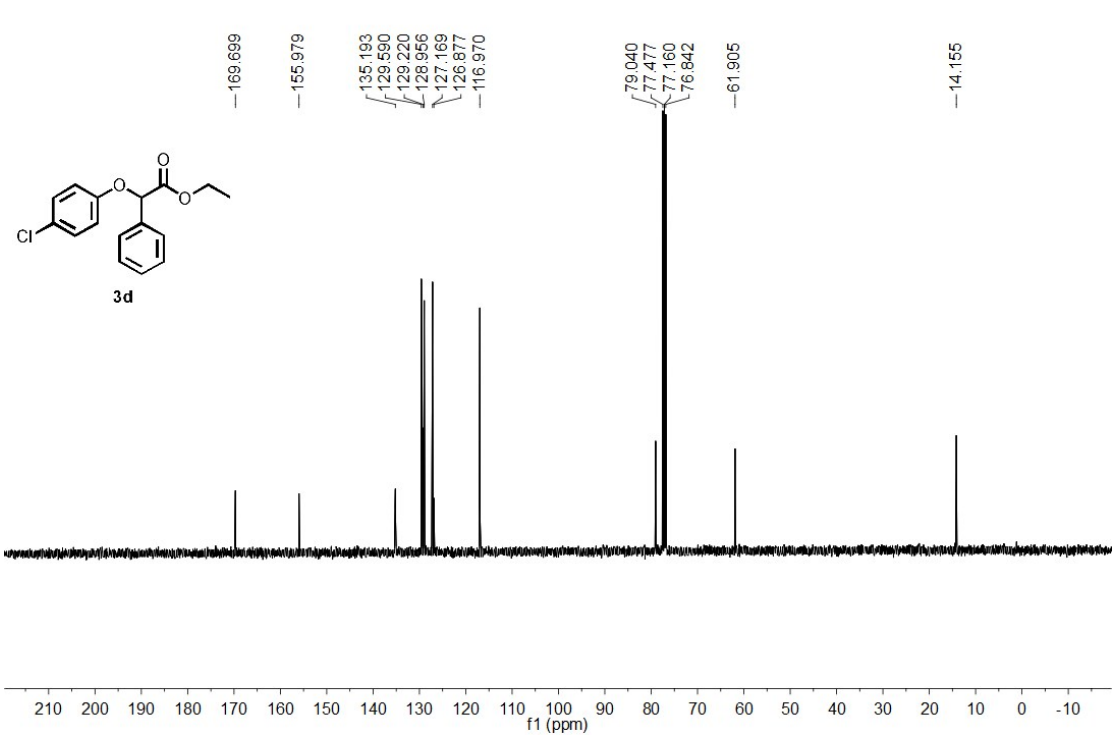
7.4046
7.3854
7.3698
7.3540
7.3503
7.2600
7.2331
7.2106
6.8965
6.8740
5.5743
4.2505
4.2414
4.2326
4.2235
4.2058
4.1883
4.1706
4.1615
4.1529
4.1437
4.1259
1.2240
1.2062
1.1884
Cl
3d
2.0000
3.0460
2.0028
2.0053
1.0131
2.0108
3.0150
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

ZZP-3-2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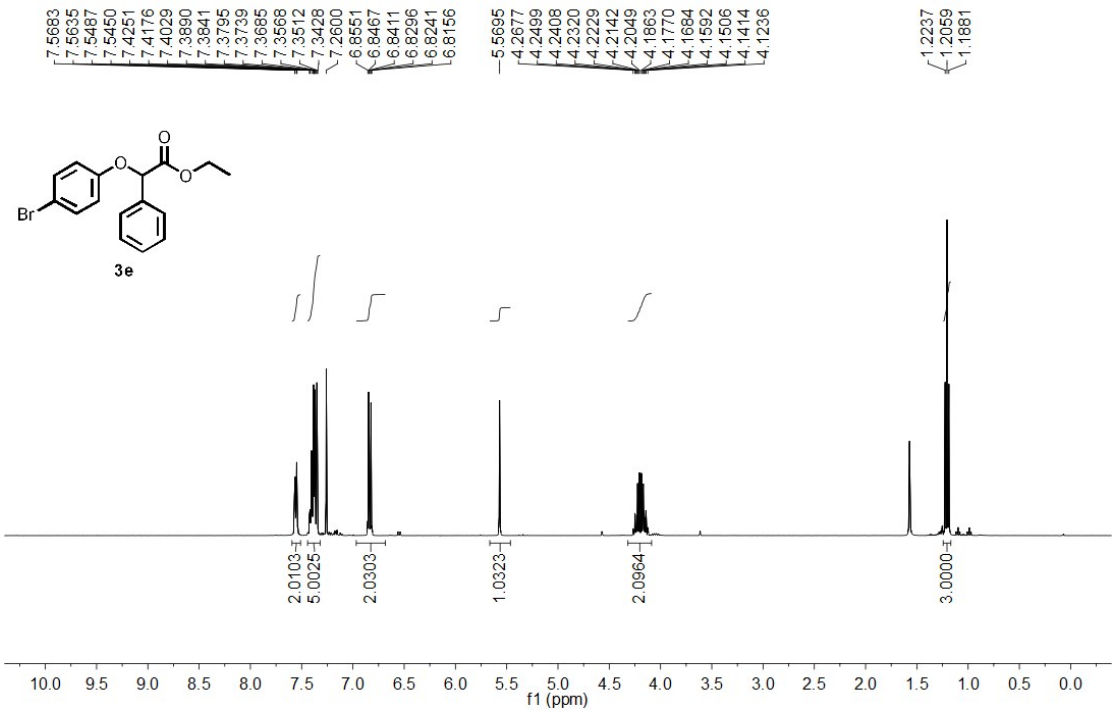
129.220
128.956
127.169
126.877
116.970
79.040
77.477
77.160
76.842
61.905
14.155
Cl
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

ZZP-2-H1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7.4029
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7.3841
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7.3428
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6.8296
6.8241
6.8156
5.5695
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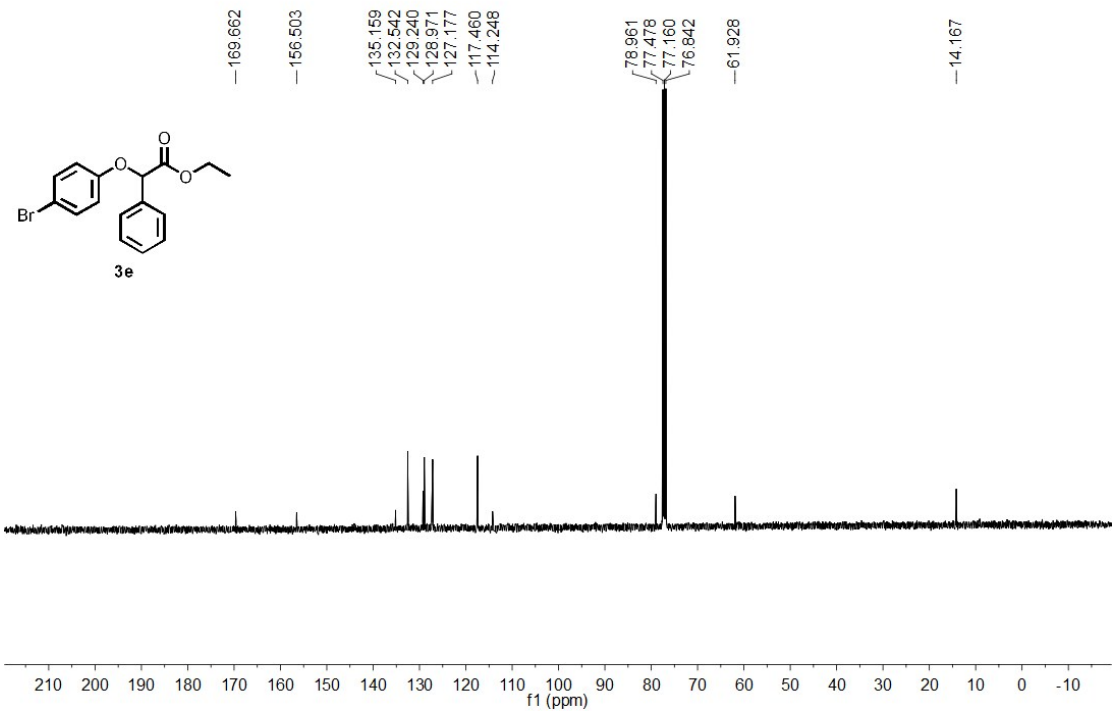
O
O
O
3e
2.0103
5.0025
2.0303
1.0323
2.0964
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

zzp-2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117.460
114.248
78.961
77.478
77.160
76.842
61.928
14.167
Br
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O
O
3e
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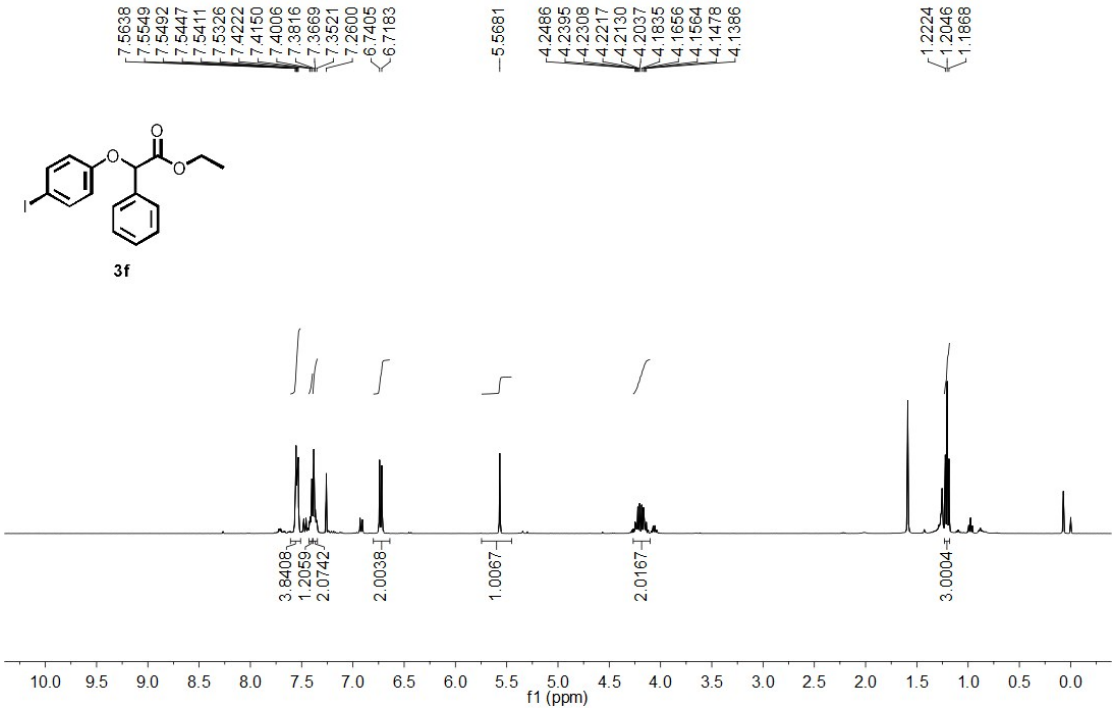
f1 (ppm)

zzp-8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7.4006
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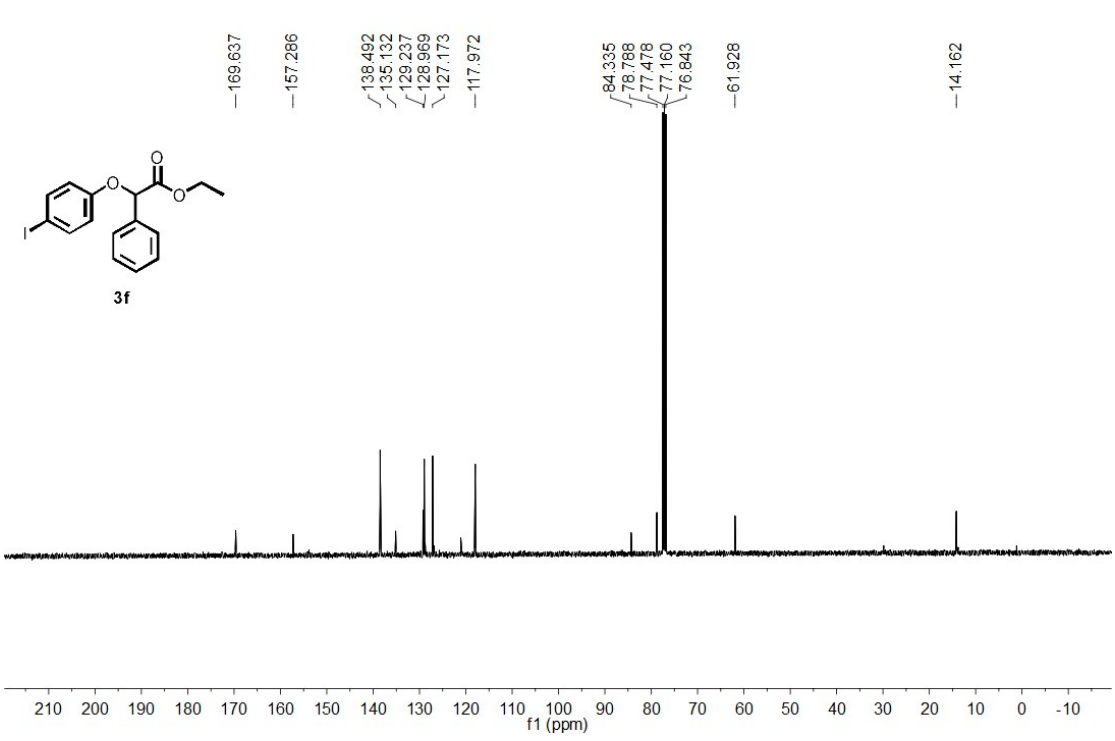
7.3521
7.2600
6.7405
6.7183
5.5681
4.2486
4.2395
4.2308
4.2217
4.2130
4.2037
4.1835
4.1656
4.1564
4.1478
4.1386
1.2224
1.2046
1.1868
3f
3.8408
1.2059
2.0742
2.0038
1.0067
2.0167
3.0004
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

zzp-8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77.160
76.843
61.928
14.162
3f
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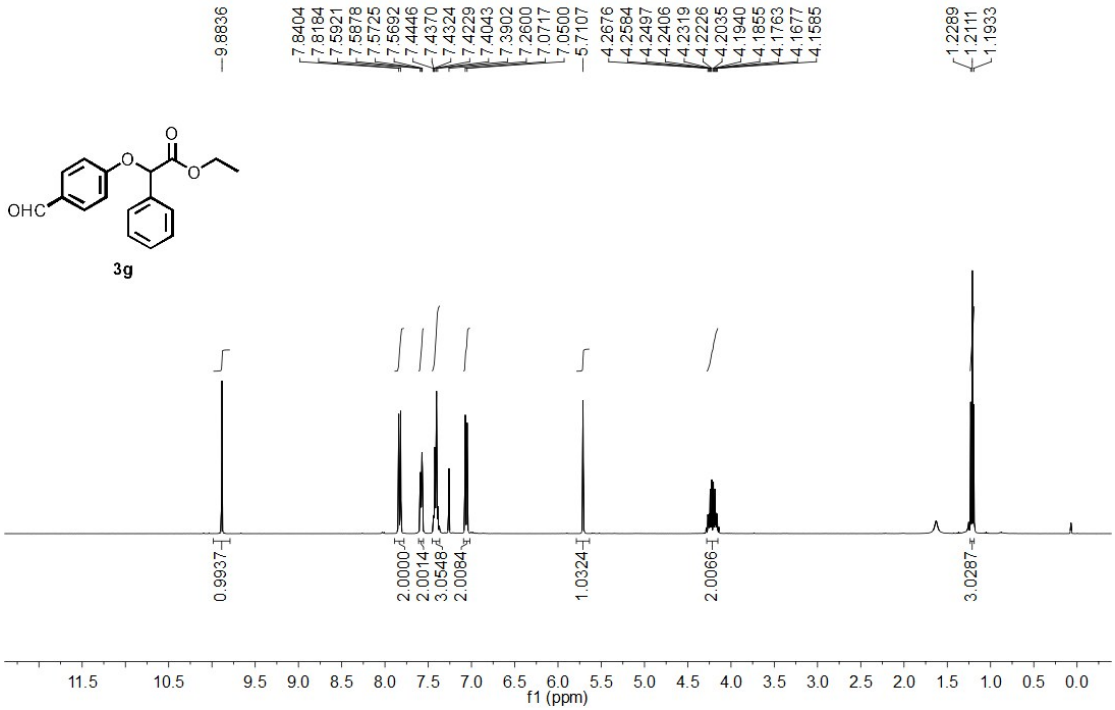
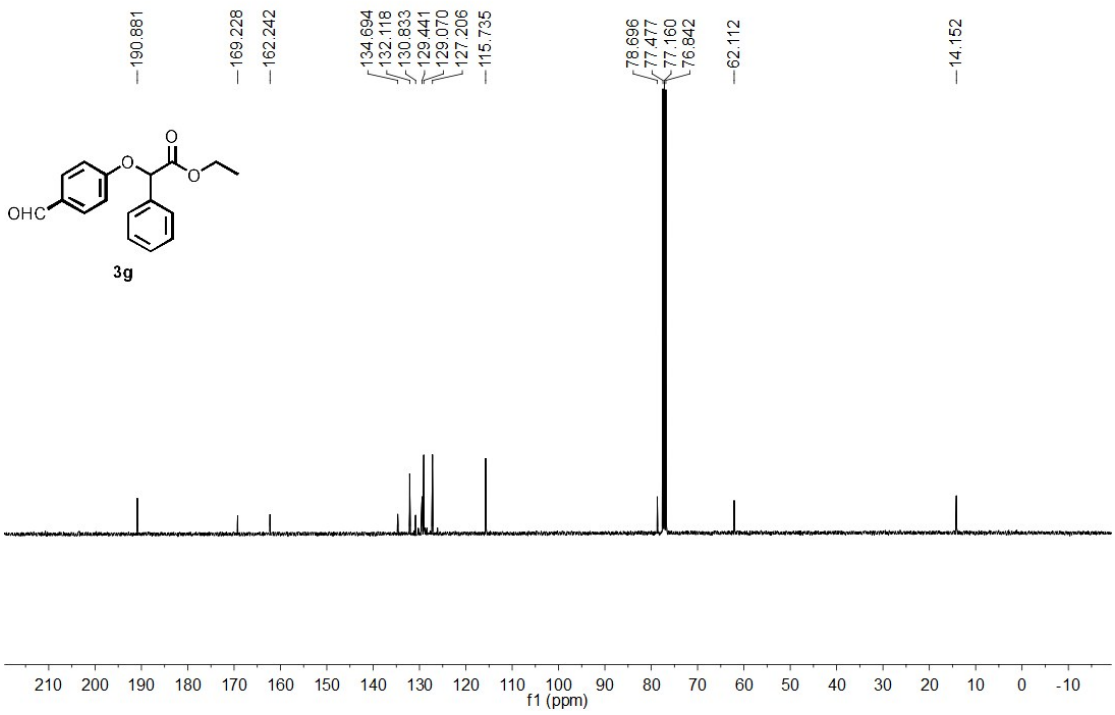
f1 (ppm)

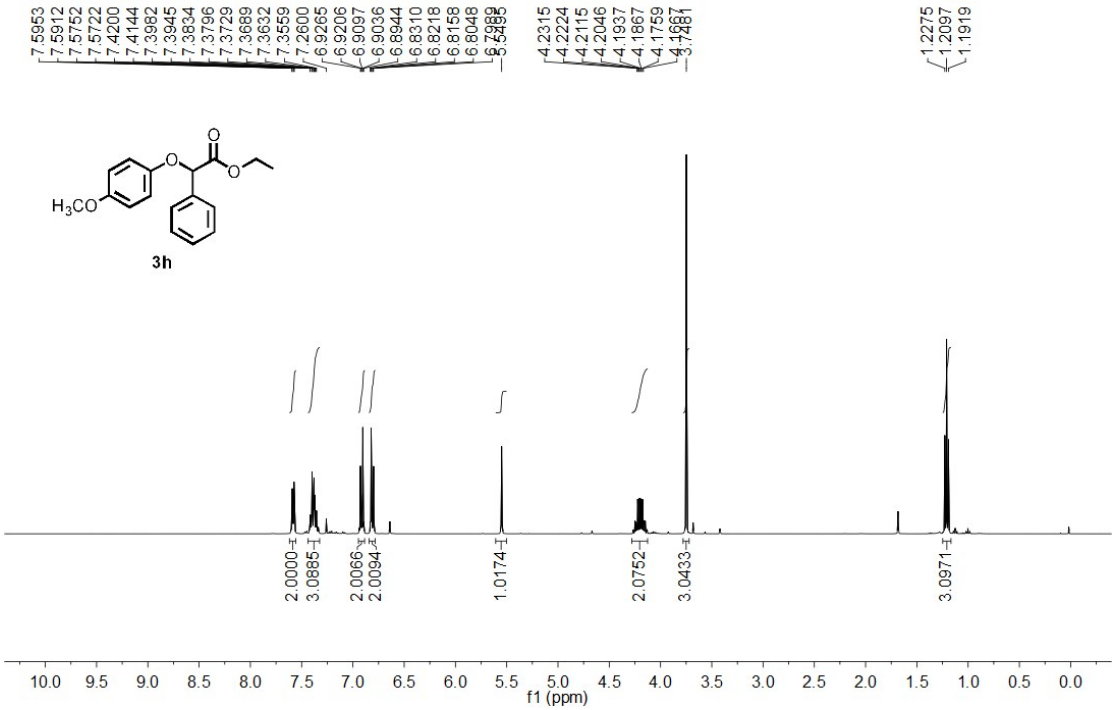
ZZP-18-2



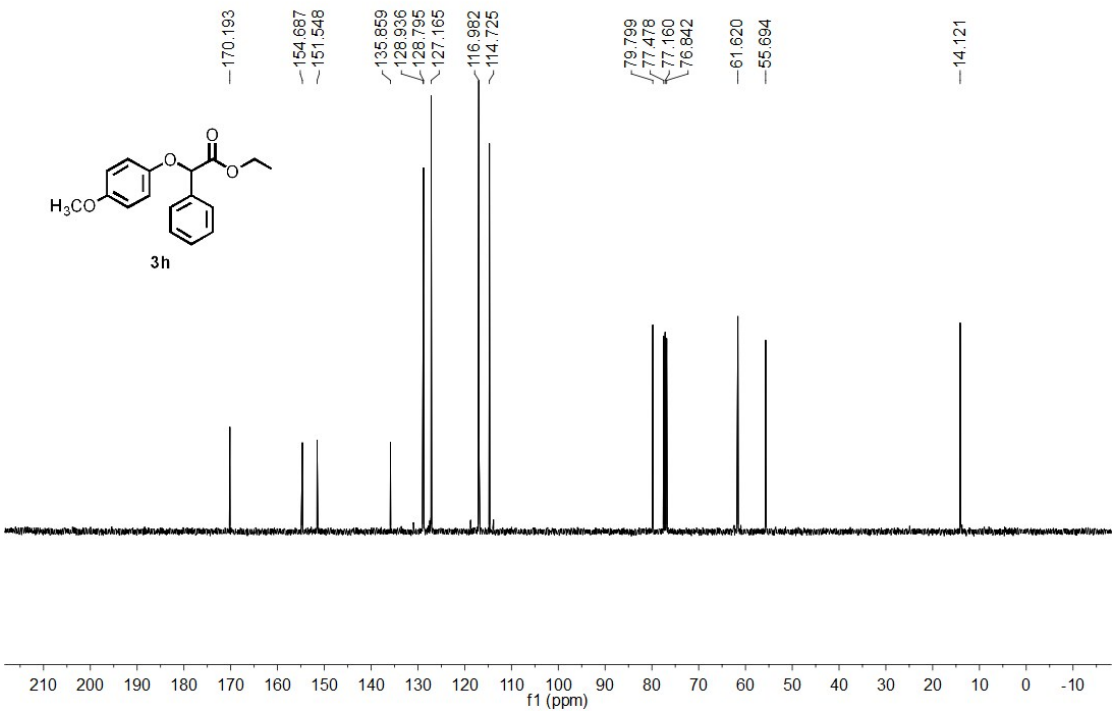
ZZP-18



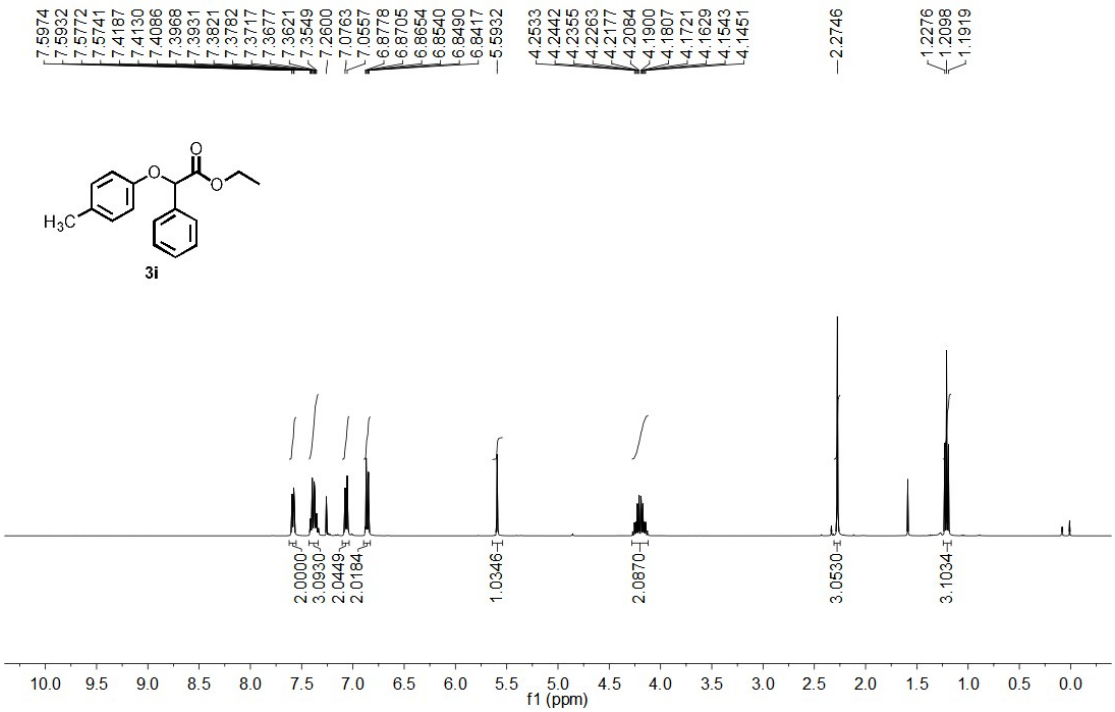
ZZP-78-1



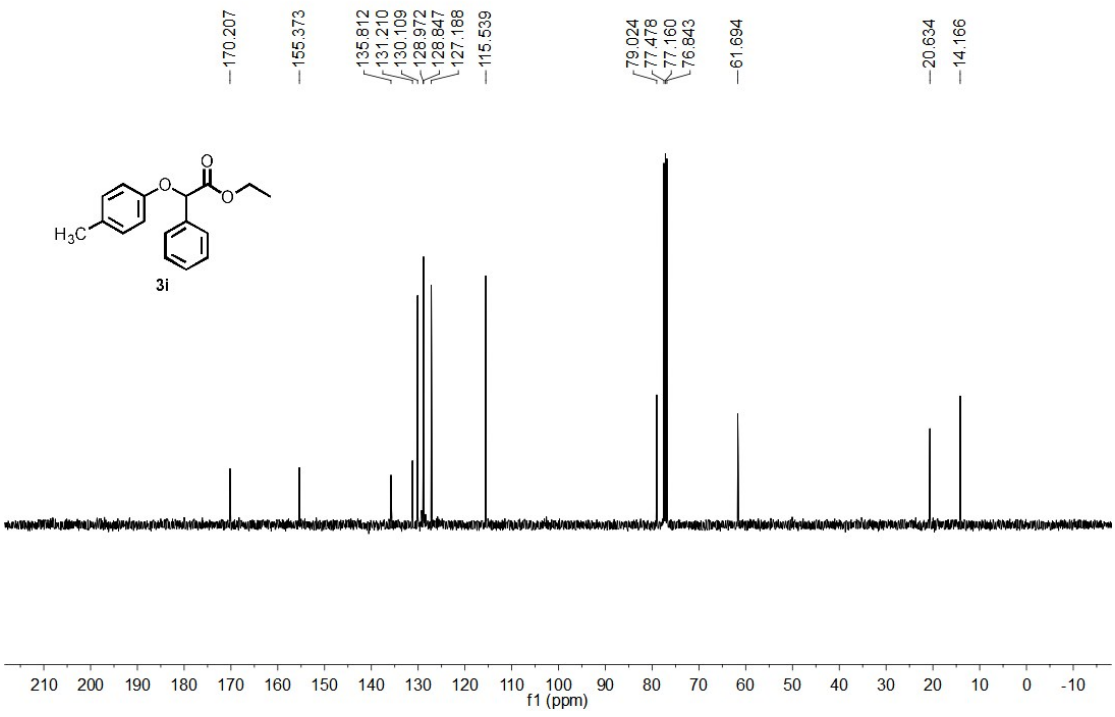
ZZP-78



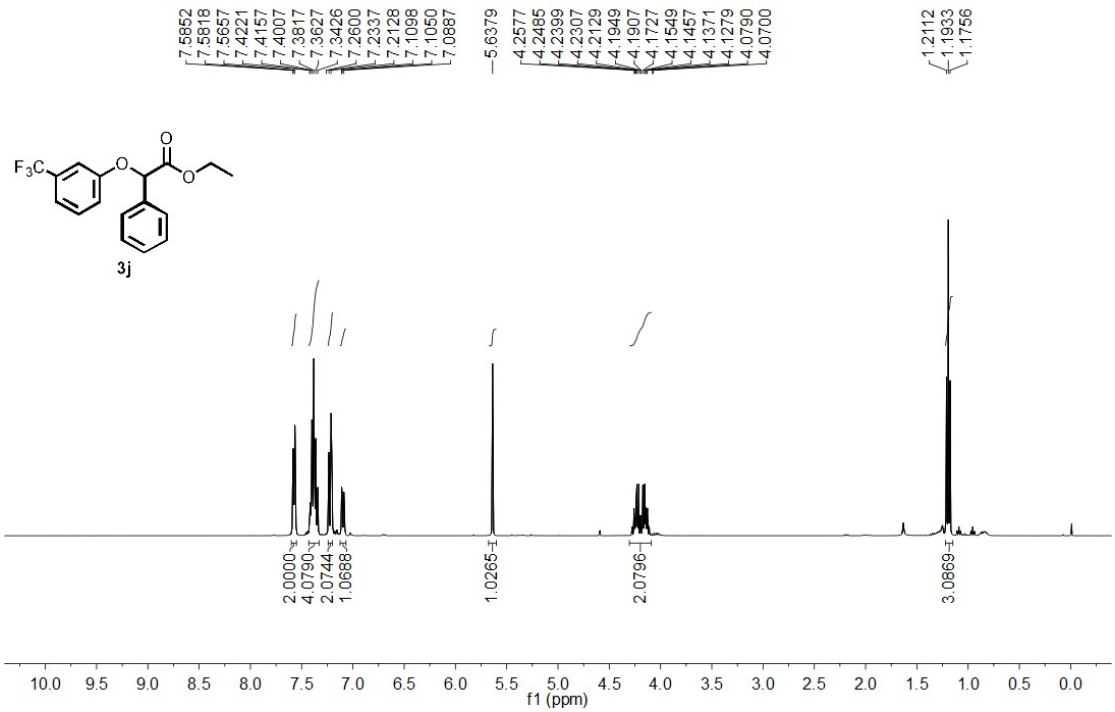
zzp-46


7.5974
7.5932
7.5772
7.5741
7.4187
7.4130
7.4086
7.3968
7.3931
7.3821
7.3782
7.3717
7.3677
7.3621
7.3549
7.2600
7.0763
7.0557
6.8778
6.8705
6.8654
6.8540
6.8490
6.8417
5.5932
4.2533
4.2442
4.2355
4.2263
4.2177
4.2084
4.1900
4.1807
4.1721
4.1629
4.1543
4.1451
2.2746
1.2276
1.2098
1.1919
H3C
O
O
O
3i
2.0000
3.0930
2.0449
2.0184
1.0346
2.0870
3.0530
3.1034
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

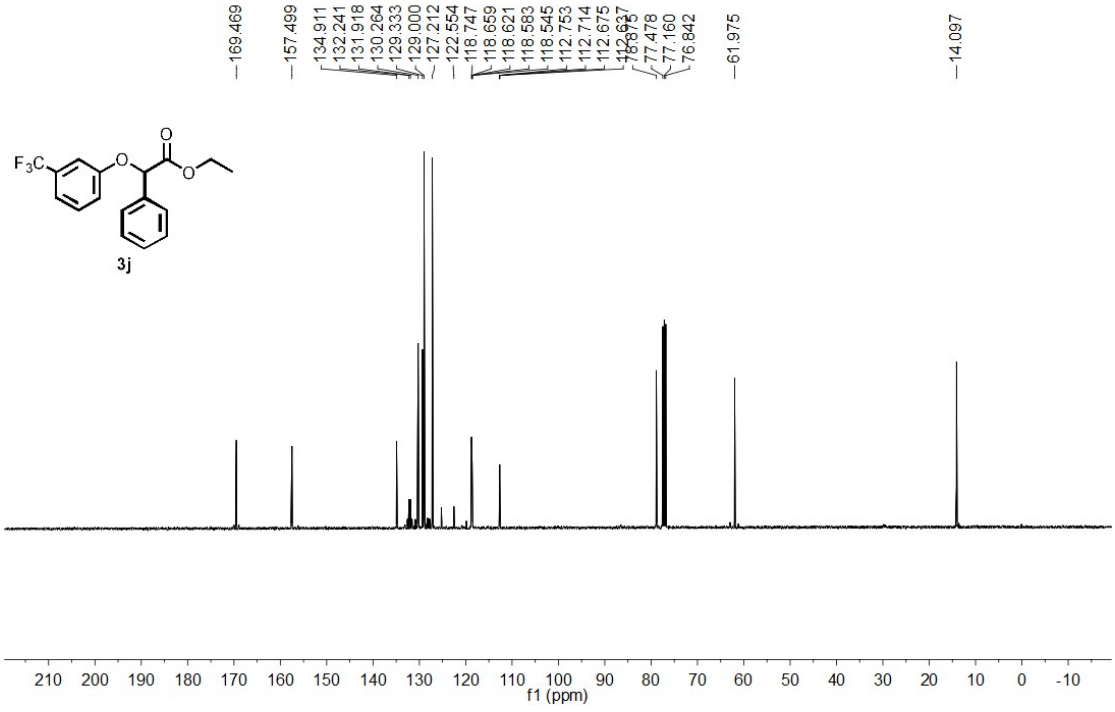
zzp-46


170.207
155.373
135.812
131.210
130.109
128.972
128.847
127.188
115.539
79.024
77.478
77.160
76.843
61.694
20.634
14.166
H3C
O
O
O
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

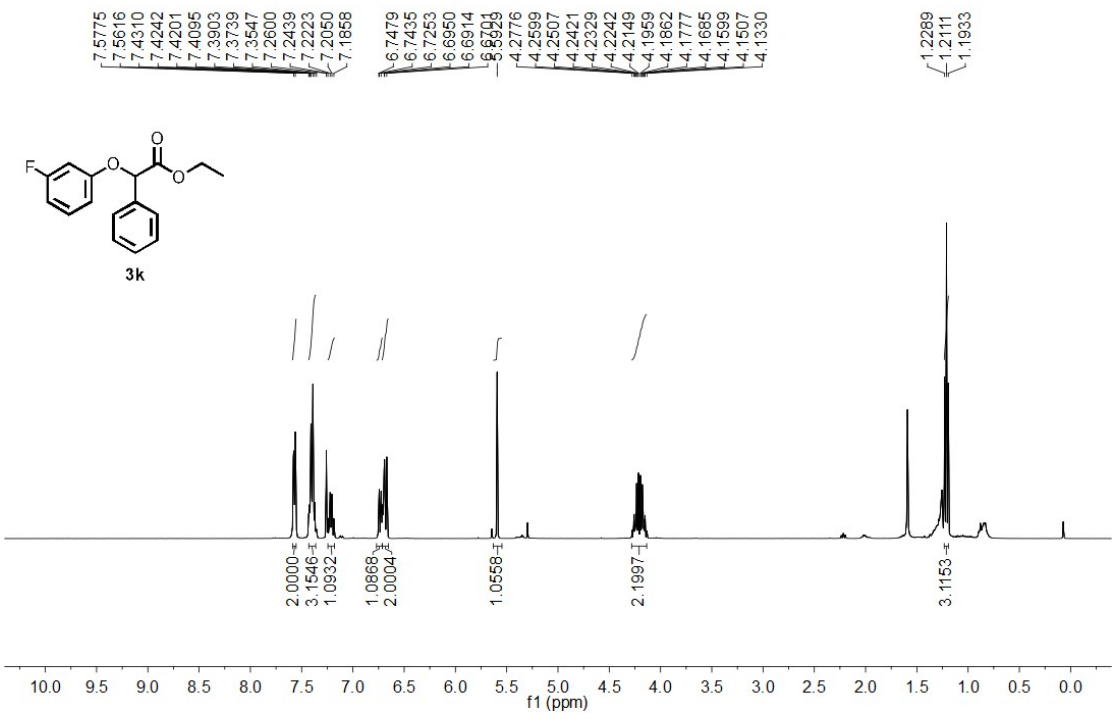
ZZP-19


7.5852
7.5818
7.5657
7.4221
7.4157
7.4007
7.3817
7.3627
7.3426
7.2600
7.2337
7.2128
7.1098
7.1050
7.0887
5.6379
4.2577
4.2485
4.2399
4.2307
4.2129
4.1949
4.1907
4.1727
4.1549
4.1457
4.1371
4.1279
4.0790
4.0700
1.2112
1.1933
1.1756
F3C
O
O
O
3j
2.0000
4.0790
2.0744
1.0688
1.0265
2.0796
3.0869
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

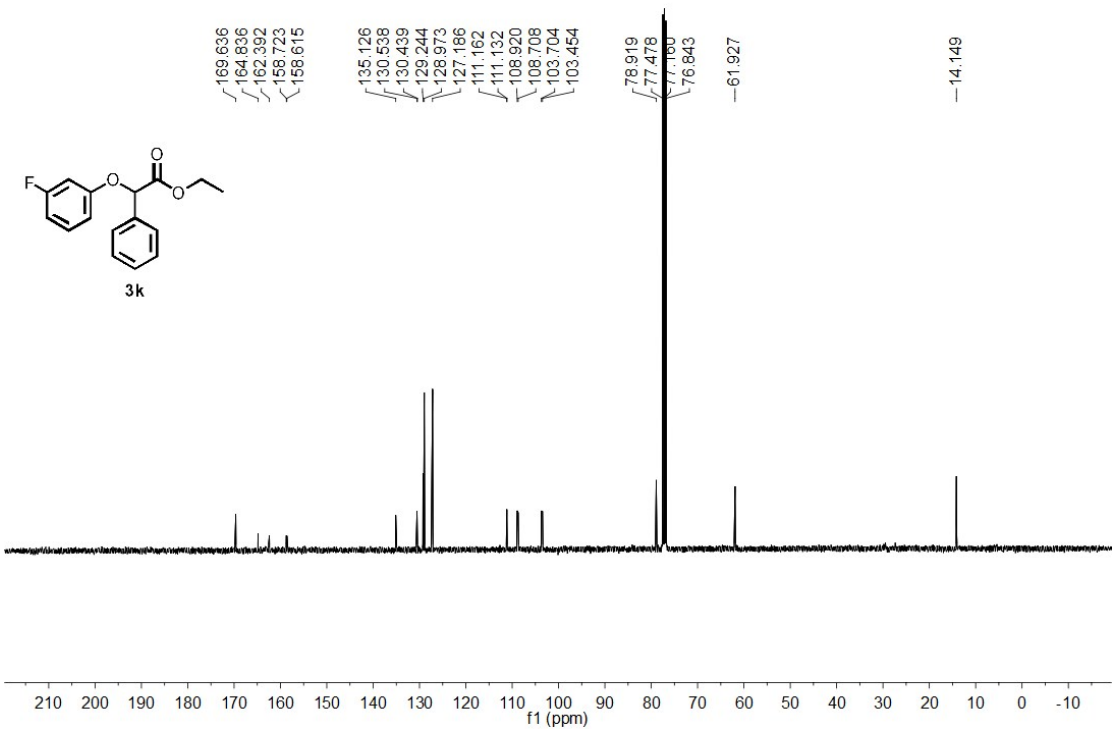
ZZP-19


169.469
157.499
134.911
132.241
131.918
130.264
129.333
129.000
127.212
122.554
118.747
118.659
118.621
118.583
118.545
112.753
112.714
112.675
112.637
77.478
77.160
76.842
61.975
14.097
F3C
O
O
O
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

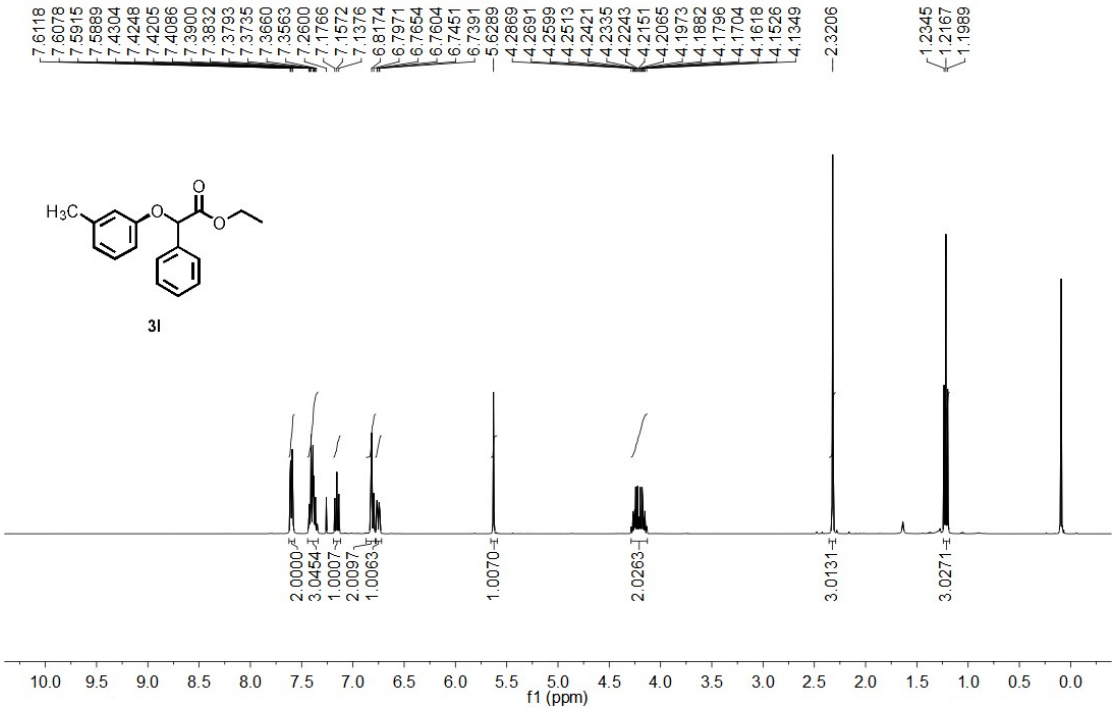
ZZP-20


7.5775
7.5616
7.4310
7.4242
7.4201
7.4095
7.3903
7.3739
7.3547
7.2600
7.2439
7.2223
7.2050
7.1858
6.7479
6.7435
6.7253
6.6950
6.6914
6.6791
6.5929
4.2776
4.2599
4.2507
4.2421
4.2329
4.2242
4.2149
4.1959
4.1862
4.1777
4.1685
4.1599
4.1507
4.1330
1.2289
1.2111
1.1933
F
O
O
O
3k
2.0000
3.1546
1.0932
1.0868
2.0004
1.0558
2.1997
3.1153
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

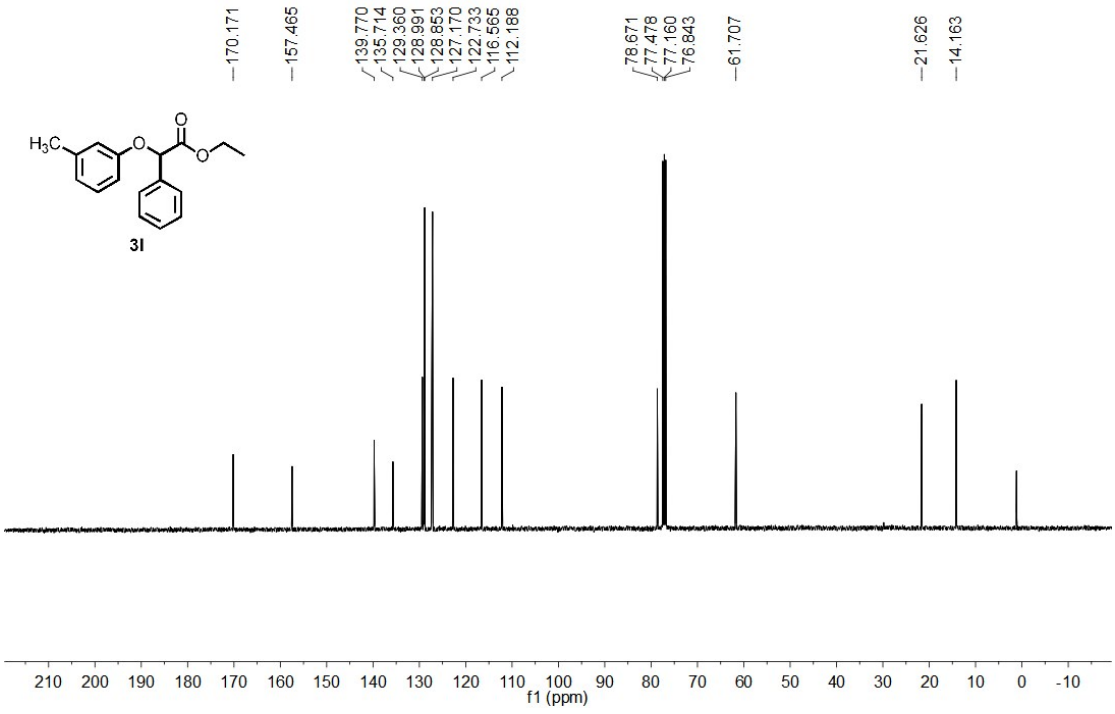
ZZP-20


169.636
164.836
162.392
158.723
158.615
135.126
130.538
130.439
129.244
128.973
127.186
111.162
111.132
108.920
108.708
103.704
103.454
78.919
77.478
77.160
76.843
61.927
14.149
F
O
O
O
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

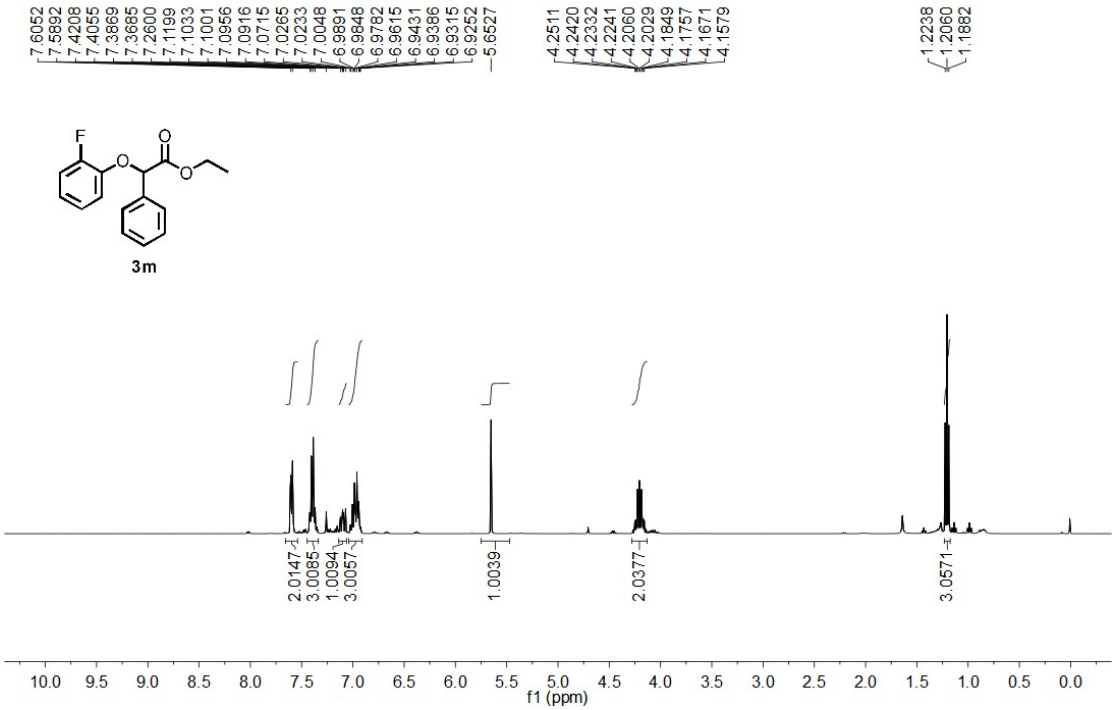
ZZP-90



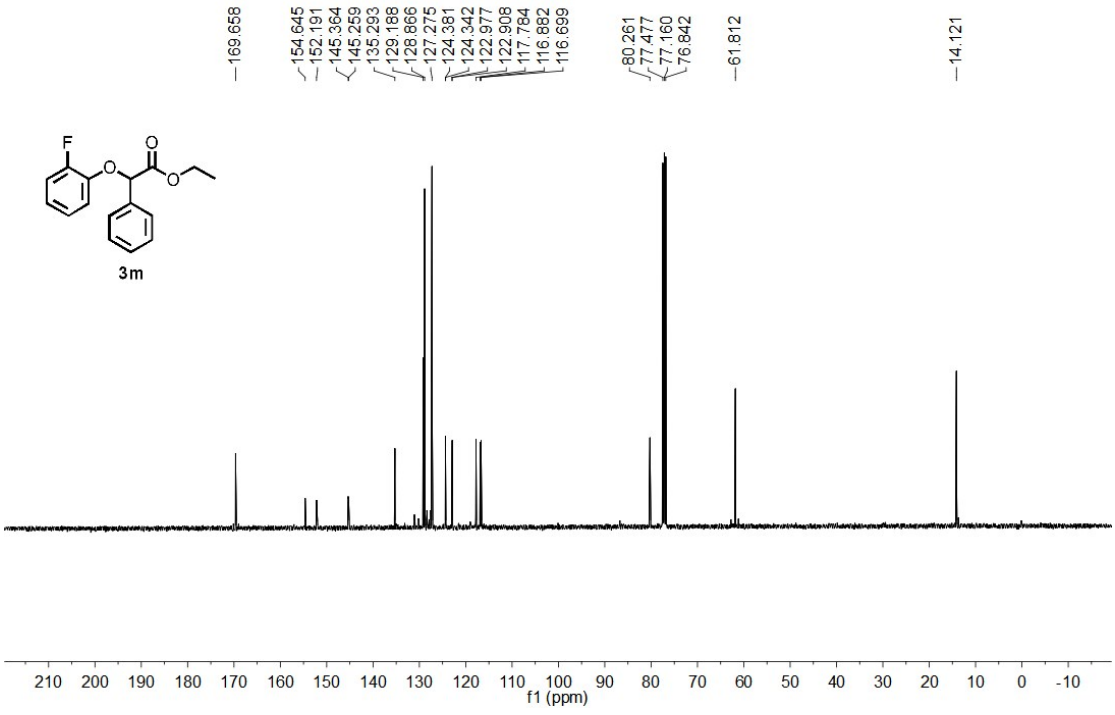
ZZP-90-3



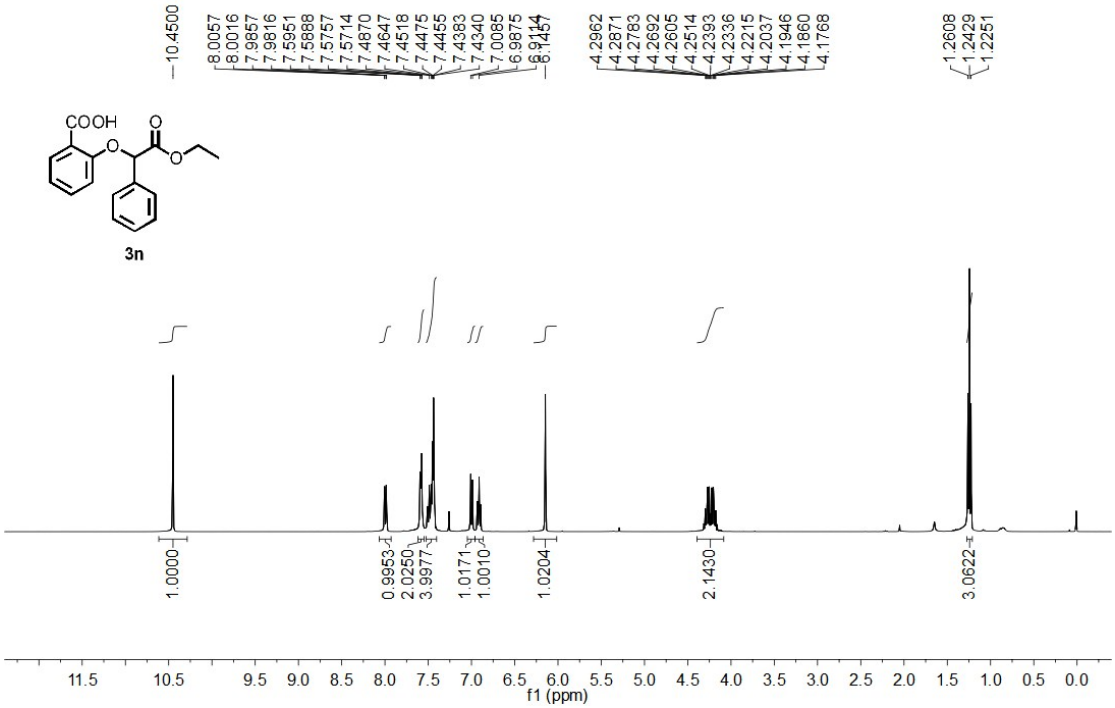
zzp-11


7.6052
7.5892
7.4208
7.4055
7.3869
7.3685
7.2600
7.1199
7.1033
7.1001
7.0956
7.0916
7.0715
7.0265
7.0233
7.0048
6.9891
6.9848
6.9782
6.9615
6.9431
6.9386
6.9315
6.9252
5.6527
4.2511
4.2420
4.2332
4.2241
4.2060
4.2029
4.1849
4.1757
4.1671
4.1579
1.2238
1.2060
1.1882
F
O
O
O
3m
2.0147
3.0085
1.0094
3.0057
1.0039
2.0377
3.0571
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

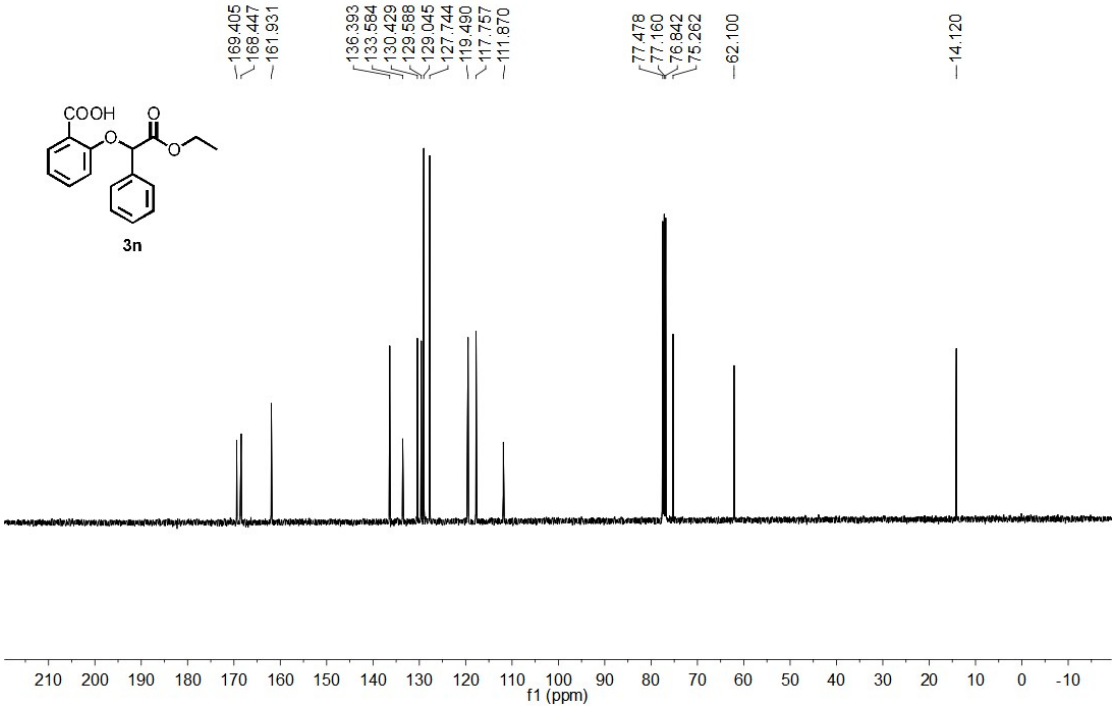
zzp-11


169.658
154.645
152.191
145.364
145.259
135.293
129.188
128.866
127.275
124.381
124.342
122.977
122.908
117.784
116.882
116.699
80.261
77.477
77.160
76.842
61.812
14.121
F
O
O
O
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

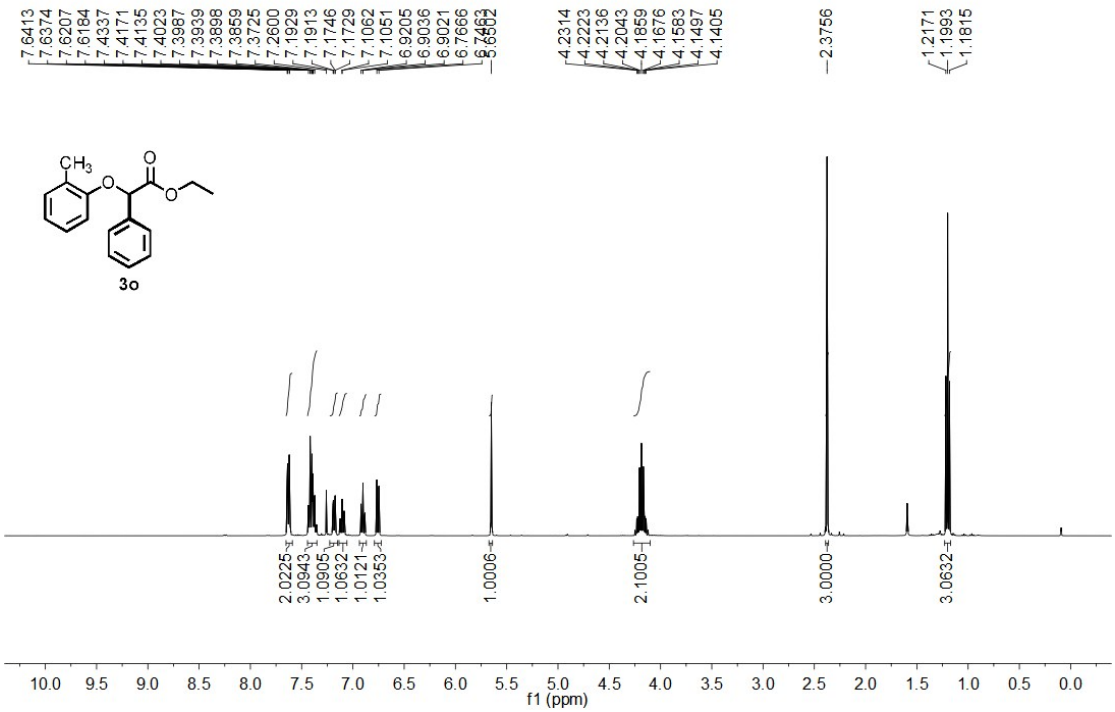
zzp-5


10.4500
8.0057
8.0016
7.9857
7.9816
7.5951
7.5888
7.5757
7.5714
7.4870
7.4647
7.4518
7.4475
7.4455
7.4383
7.4340
7.0085
6.9875
6.9414
6.9457
4.2962
4.2871
4.2783
4.2692
4.2605
4.2514
4.2393
4.2336
4.2215
4.2037
4.1946
4.1860
4.1768
1.2608
1.2429
1.2251
COOH
O
O
O
3n
1.0000
0.9953
2.0250
3.9977
1.0171
1.0010
1.0204
2.1430
3.0622
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

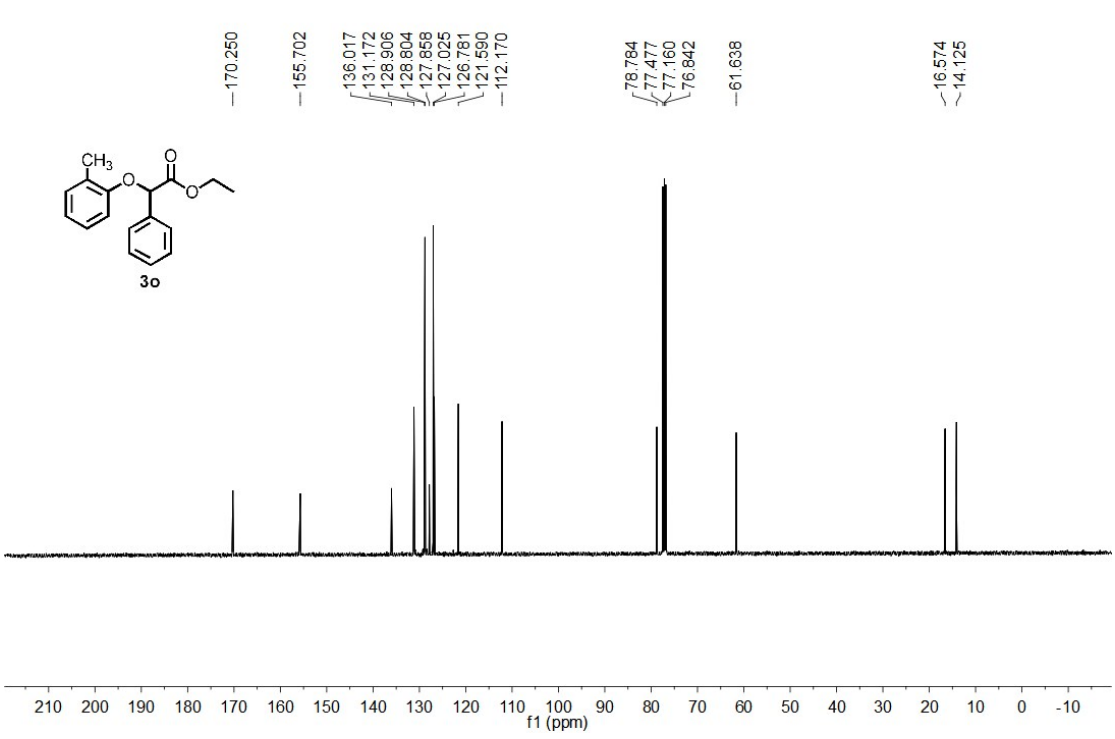
zzp-5


169.405
168.447
161.931
136.393
133.584
130.429
129.588
129.045
127.744
119.490
117.757
111.870
77.478
77.160
76.842
75.262
62.100
14.120
COOH
O
O
O
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

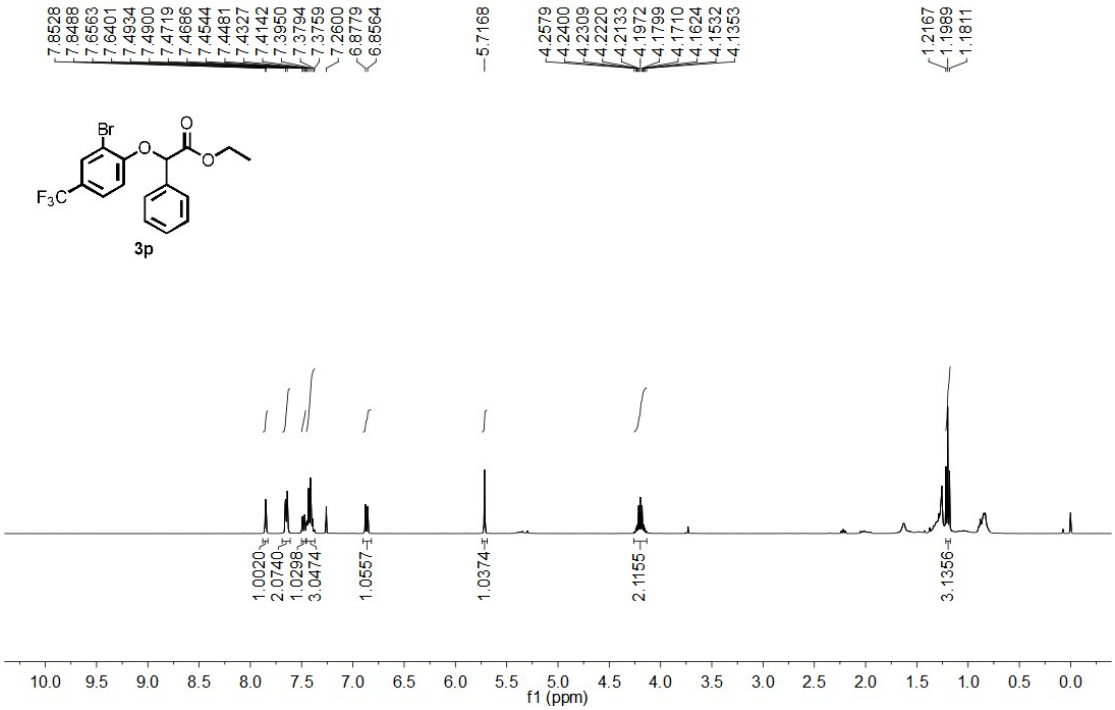
ZZP-89


7.6413
7.6374
7.6207
7.6184
7.4337
7.4171
7.4135
7.4023
7.3987
7.3939
7.3898
7.3859
7.3725
7.2600
7.1929
7.1913
7.1746
7.1729
7.1062
7.1051
6.9205
6.9036
6.9021
6.7666
4.2314
4.2223
4.2136
4.2043
4.1859
4.1676
4.1583
4.1497
4.1405
2.3756
1.2171
1.1993
1.1815
3o
2.0225
3.0943
1.0905
1.0632
1.0121
1.0353
1.0006
2.1005
3.0000
3.0632
f1 (ppm)

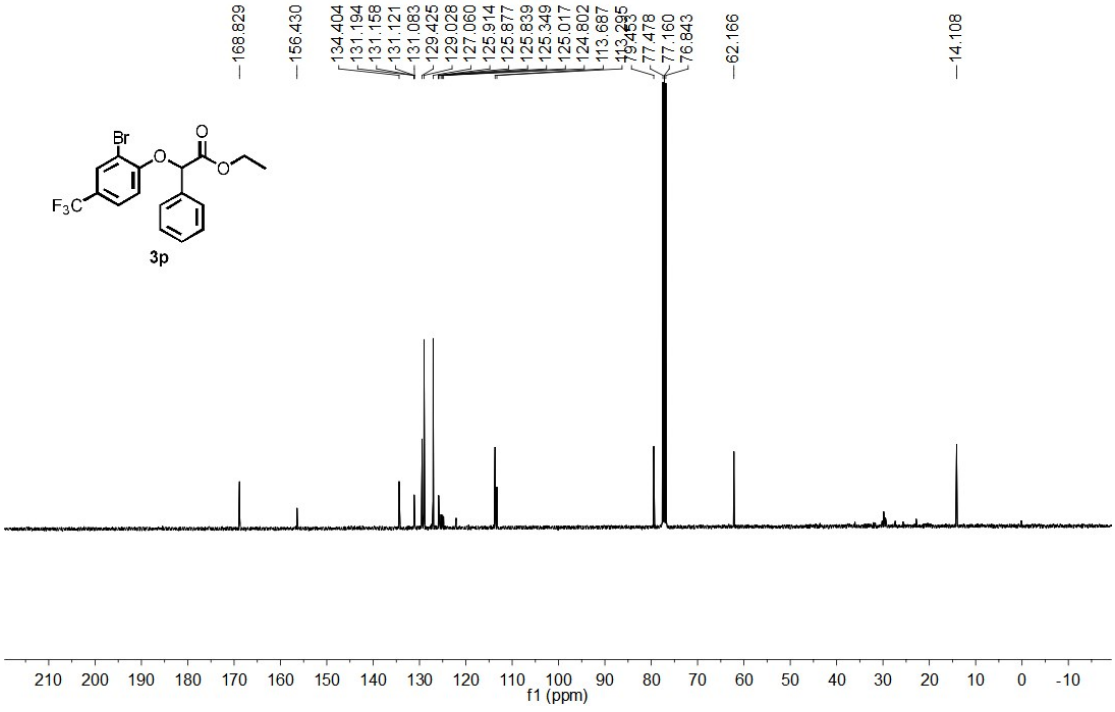
ZZP-89


170.250
155.702
136.017
131.172
128.906
128.804
127.858
127.025
126.781
121.590
112.170
78.784
77.477
77.160
76.842
61.638
16.574
14.125
3o
f1 (ppm)

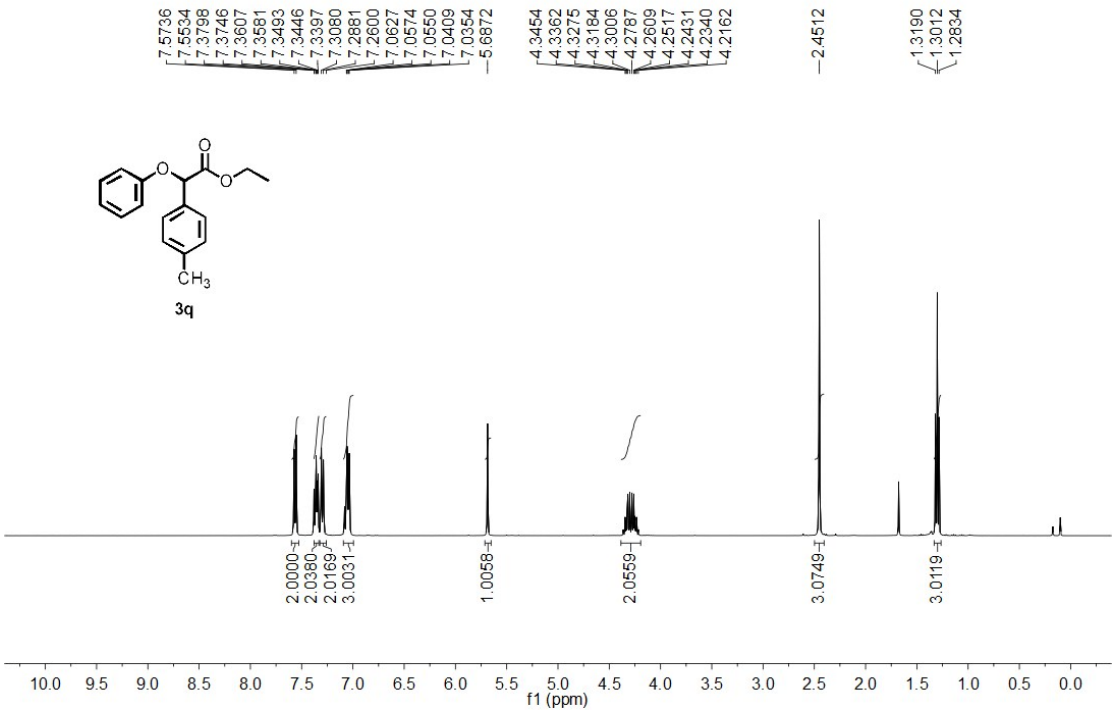
zzp-13


7.8528
7.8488
7.6563
7.6401
7.4934
7.4900
7.4719
7.4686
7.4544
7.4481
7.4327
7.4142
7.3950
7.3794
7.3759
7.2600
6.8779
6.8564
5.7168
4.2579
4.2400
4.2309
4.2220
4.2133
4.1972
4.1799
4.1710
4.1624
4.1532
4.1353
1.2167
1.1989
1.1811
Br
O
O
O
F3C
3p
1.0020
2.0740
1.0298
3.0474
1.0557
1.0374
2.1155
3.1356
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

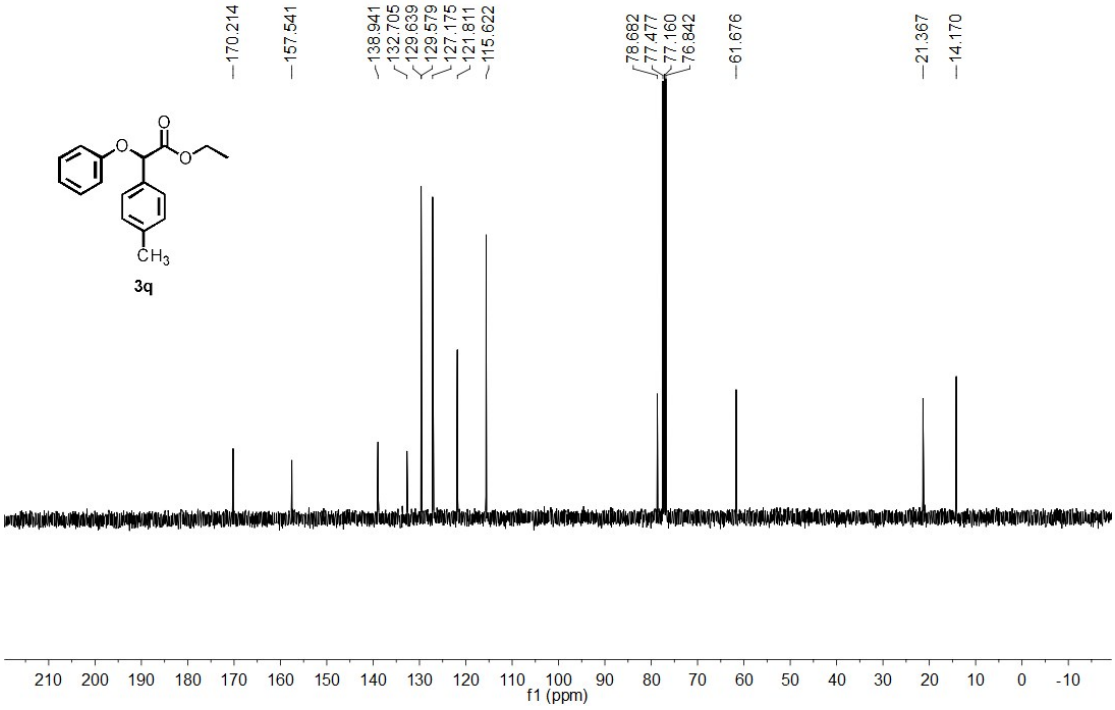
zzp-13


168.829
156.430
134.404
131.194
131.158
131.121
131.083
129.425
129.028
127.060
125.914
125.877
125.839
125.349
125.017
124.802
113.687
113.635
77.478
77.160
76.843
62.166
14.108
Br
O
O
O
F3C
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

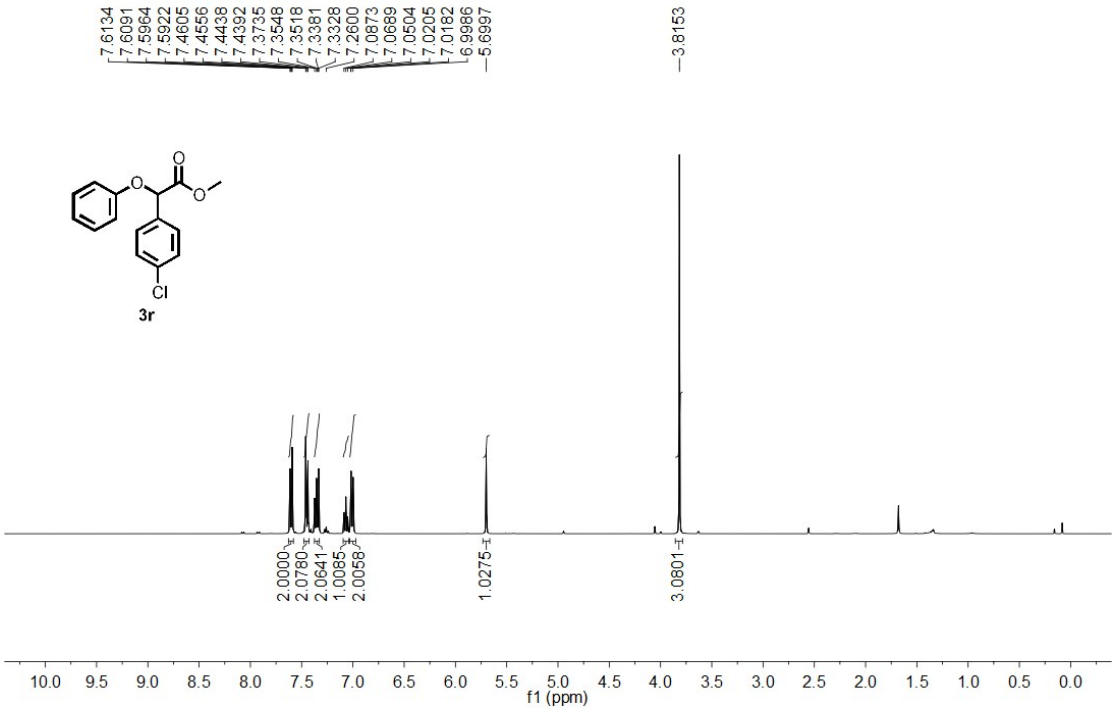
ZZP-65-1



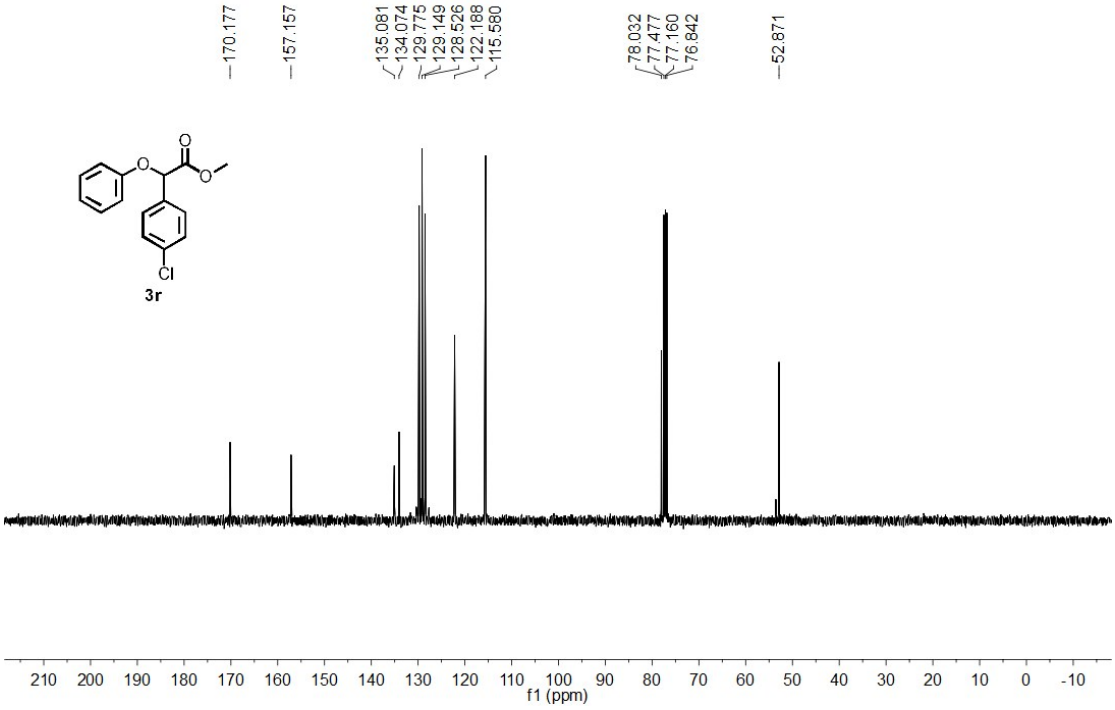
ZZP-65-1



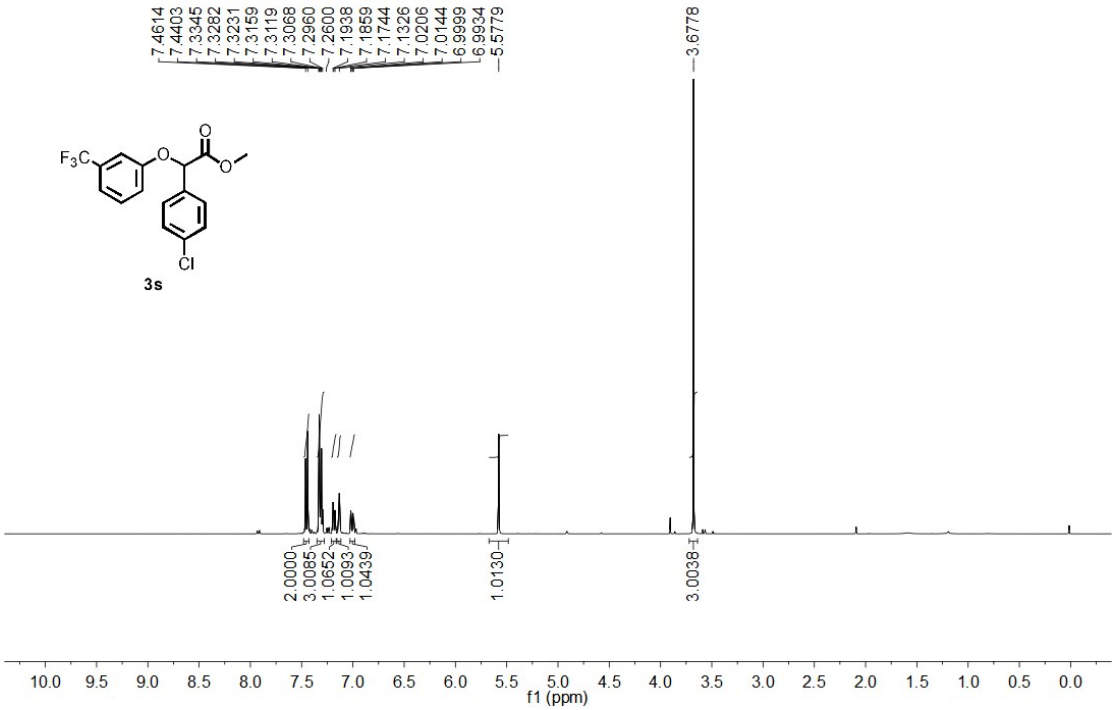
ZZP-71-1



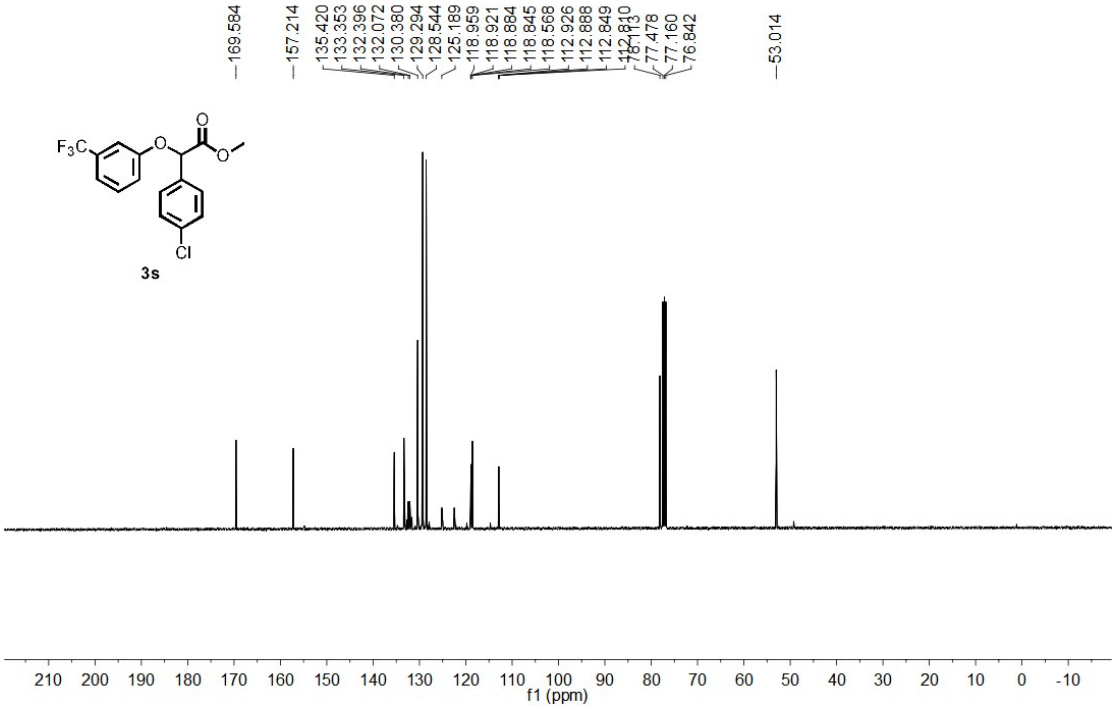
ZZP-71



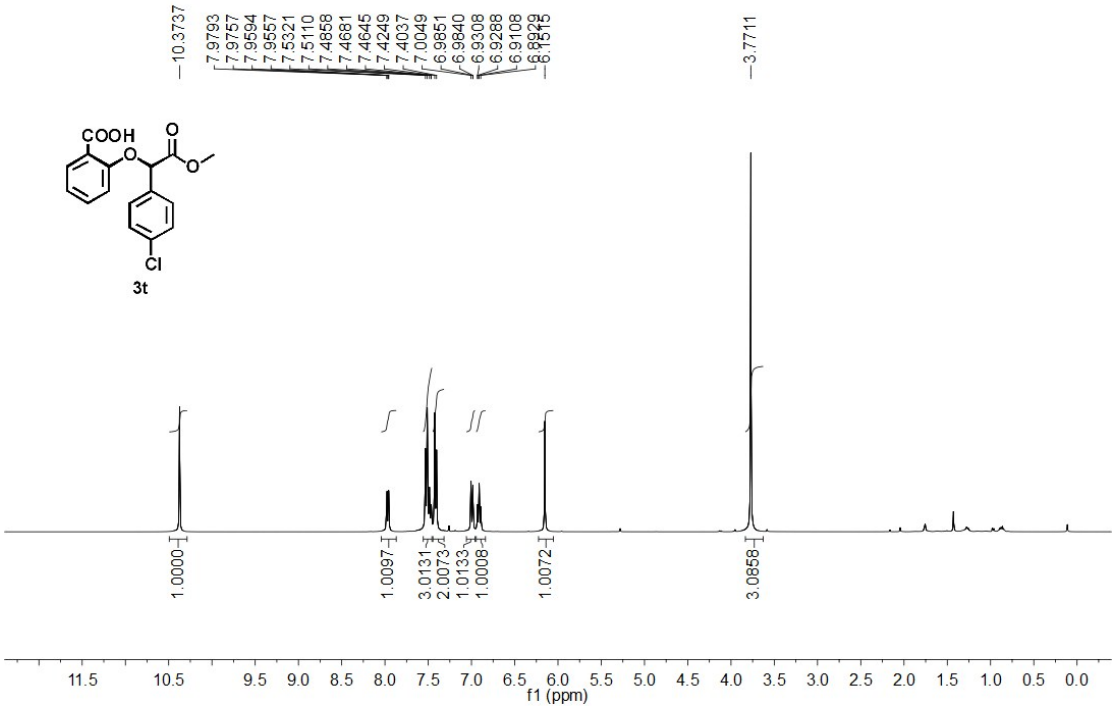
ZZP-52


7.4614
7.4403
7.3345
7.3282
7.3231
7.3159
7.3119
7.3068
7.2960
7.2600
7.1938
7.1859
7.1744
7.1326
7.0206
7.0144
6.9999
6.9934
5.5779
3.6778
F3C
O
O
O
Cl
3s
2.0000
3.0085
1.0652
1.0093
1.0439
1.0130
3.0038
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

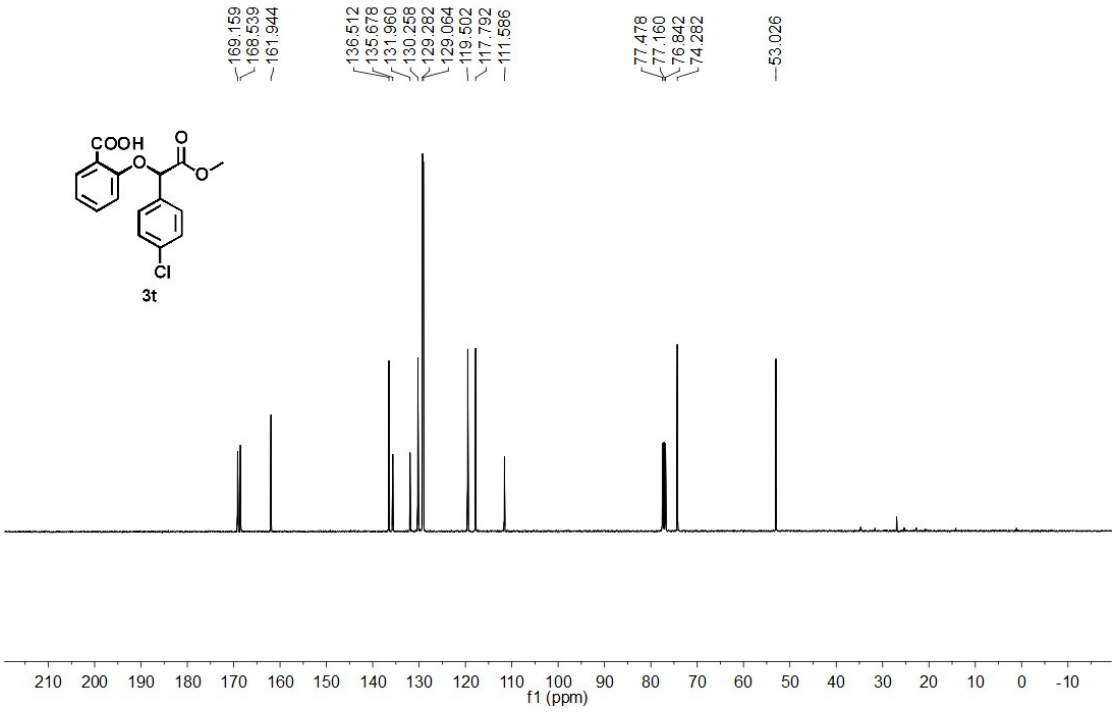
ZZP-52


169.584
157.214
135.420
133.353
132.396
132.072
130.380
129.294
128.544
125.189
118.959
118.921
118.884
118.845
118.568
112.926
112.888
112.849
112.810
78.113
77.478
77.160
76.842
53.014
F3C
O
O
O
Cl
3s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

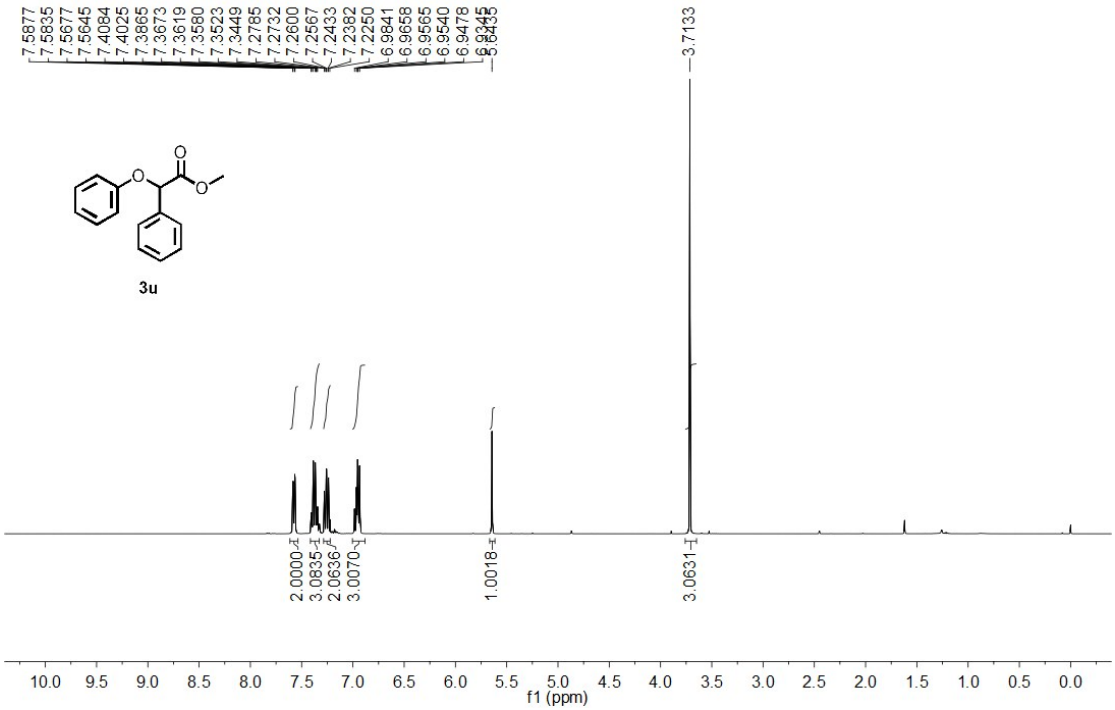
ZZP-48


10.3737
7.9793
7.9757
7.9594
7.9557
7.5321
7.5110
7.4858
7.4681
7.4645
7.4249
7.4037
7.0049
6.9851
6.9840
6.9308
6.9288
6.9108
3.7711
COOH
O
O
Cl
3t
1.0000
1.0097
3.0131
2.0073
1.0133
1.0008
1.0072
3.0858
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

ZZP-48

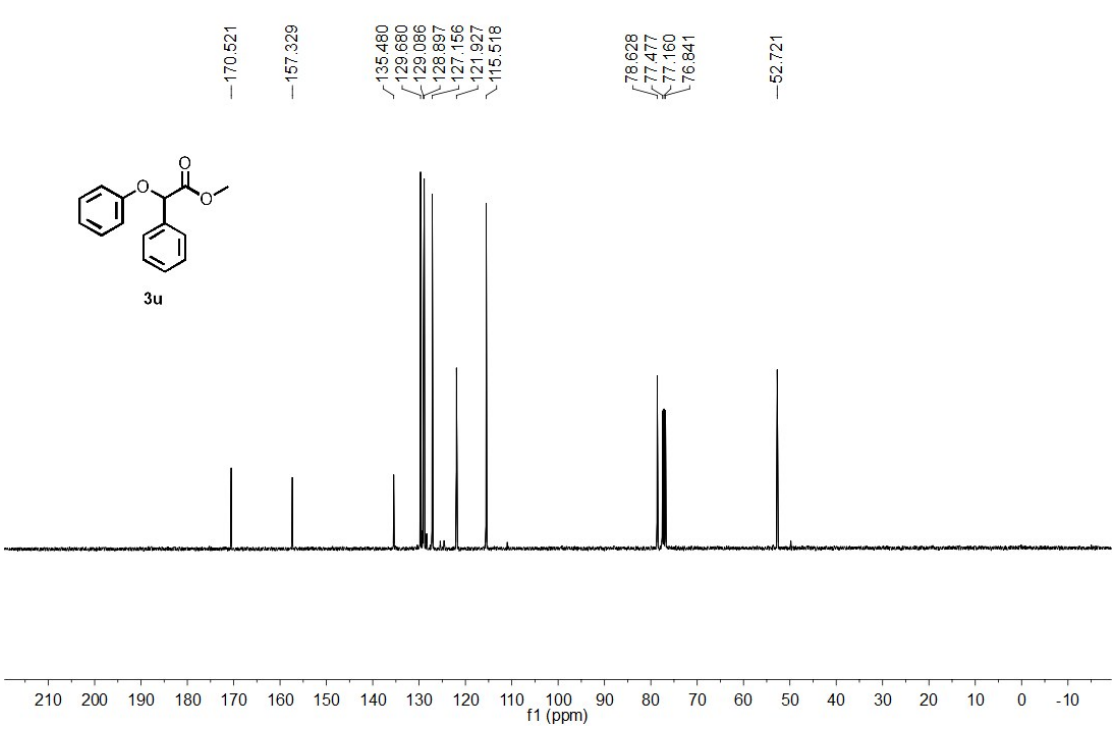

169.159
168.539
161.944
136.512
135.678
131.960
130.258
129.282
129.064
119.502
117.792
111.586
77.478
77.160
76.842
74.282
53.026
COOH
O
O
Cl
3t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

zzp-3



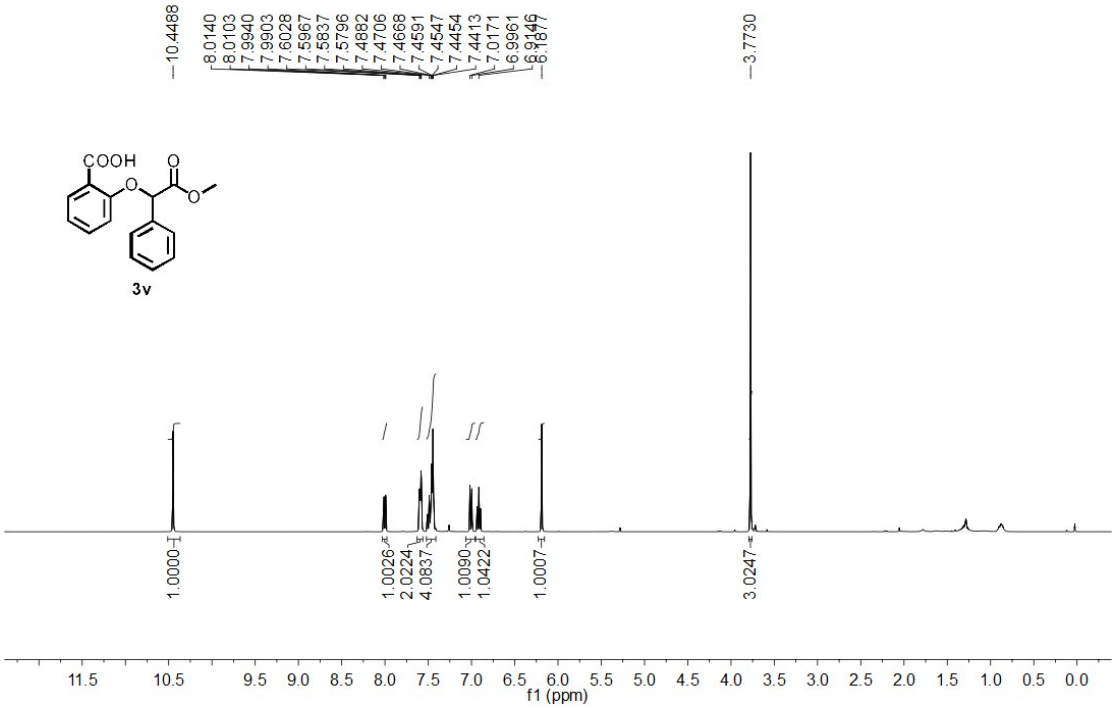
3u

zzp-1

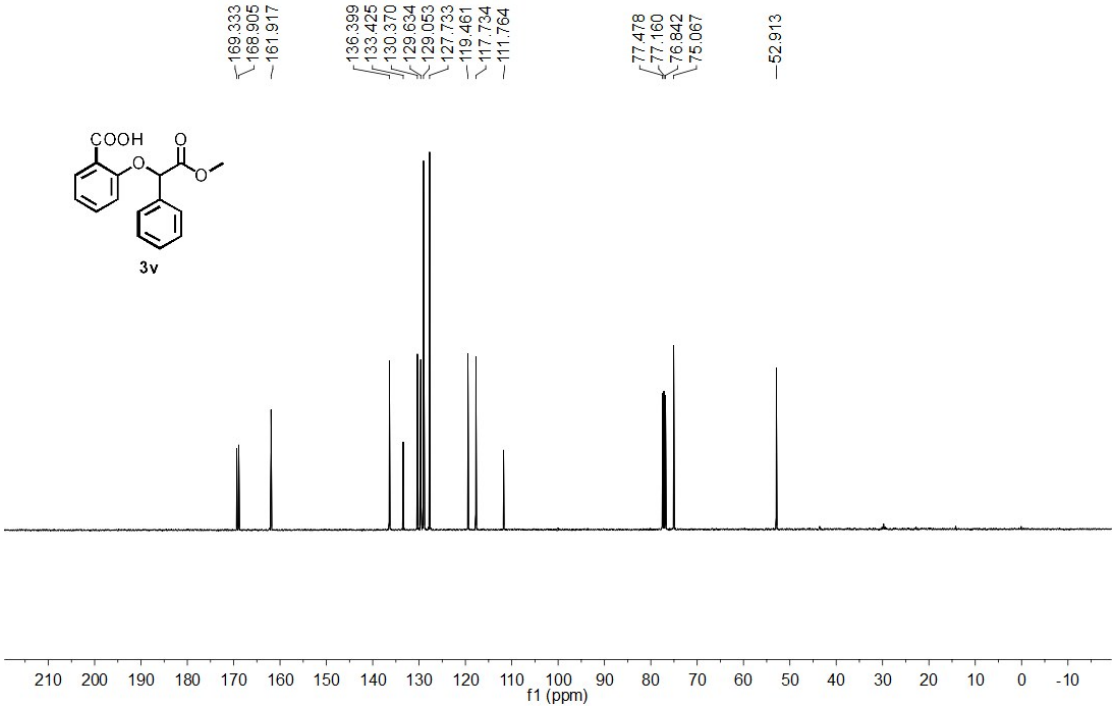


3u

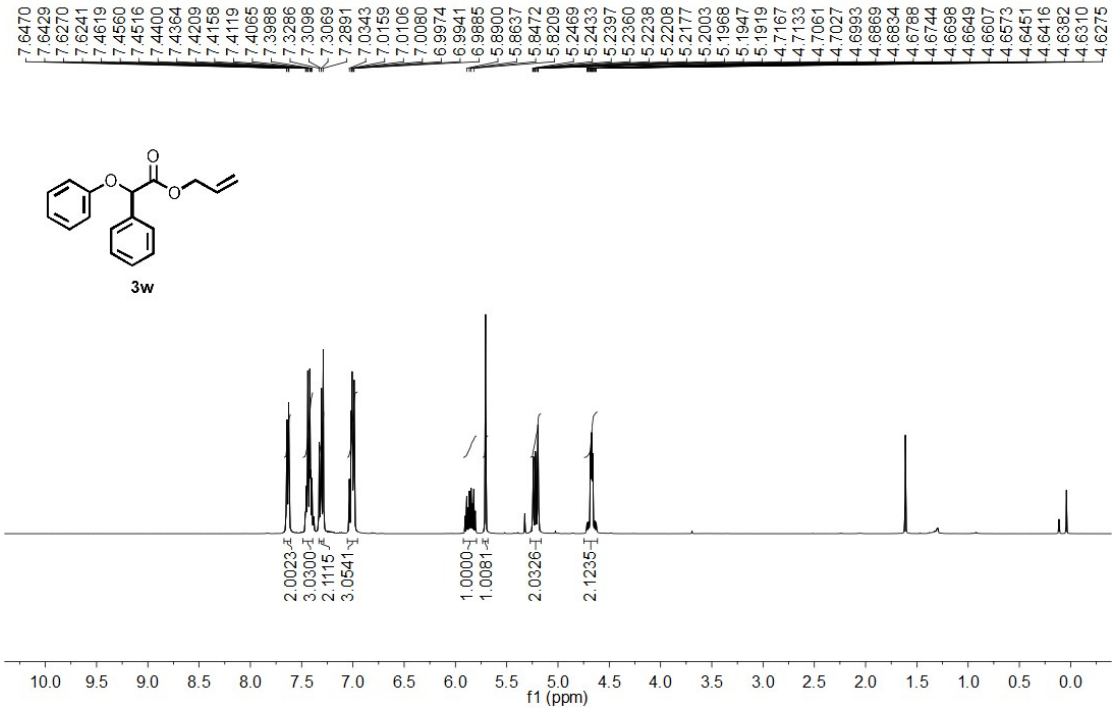
zzp-10


10.4488
8.0140
8.0103
7.9940
7.9903
7.6028
7.5967
7.5837
7.5796
7.4882
7.4706
7.4668
7.4591
7.4547
7.4454
7.4413
7.0171
6.9961
6.9146
6.1877
3.7730
COOH
O
O
O
3v
1.0000
1.0026
2.0224
4.0837
1.0090
1.0422
1.0007
3.0247
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

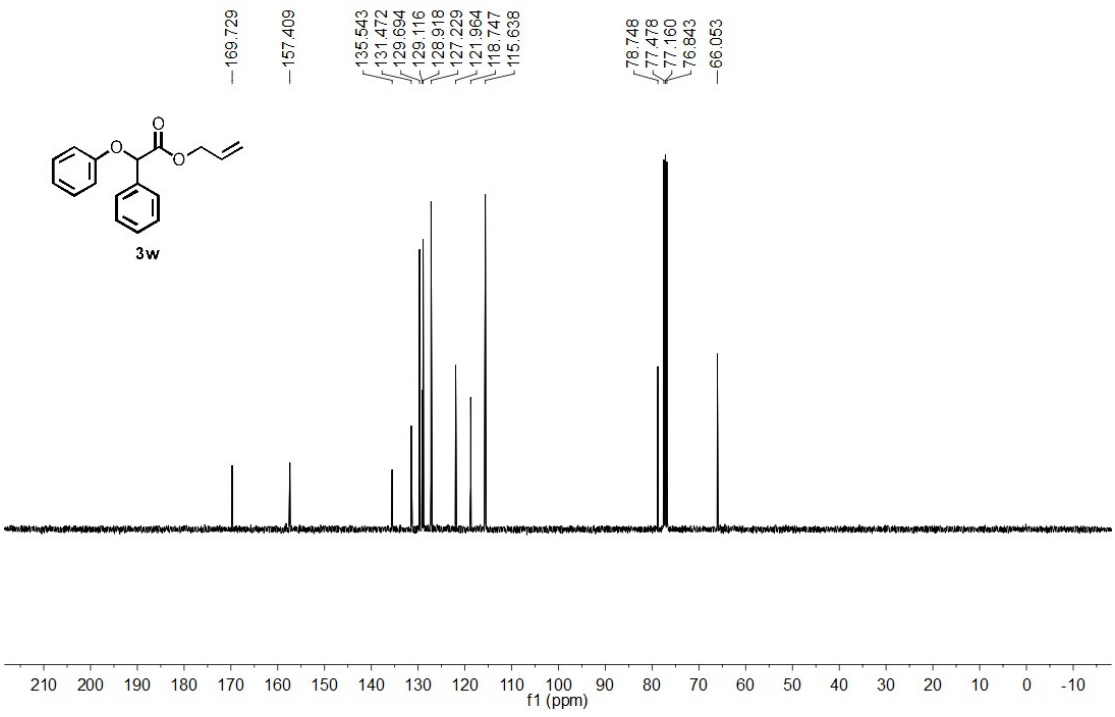
zzp-10


169.333
168.905
161.917
136.399
133.425
130.370
129.634
129.053
127.733
119.461
117.734
111.764
77.478
77.160
76.842
75.067
52.913
COOH
O
O
O
3v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

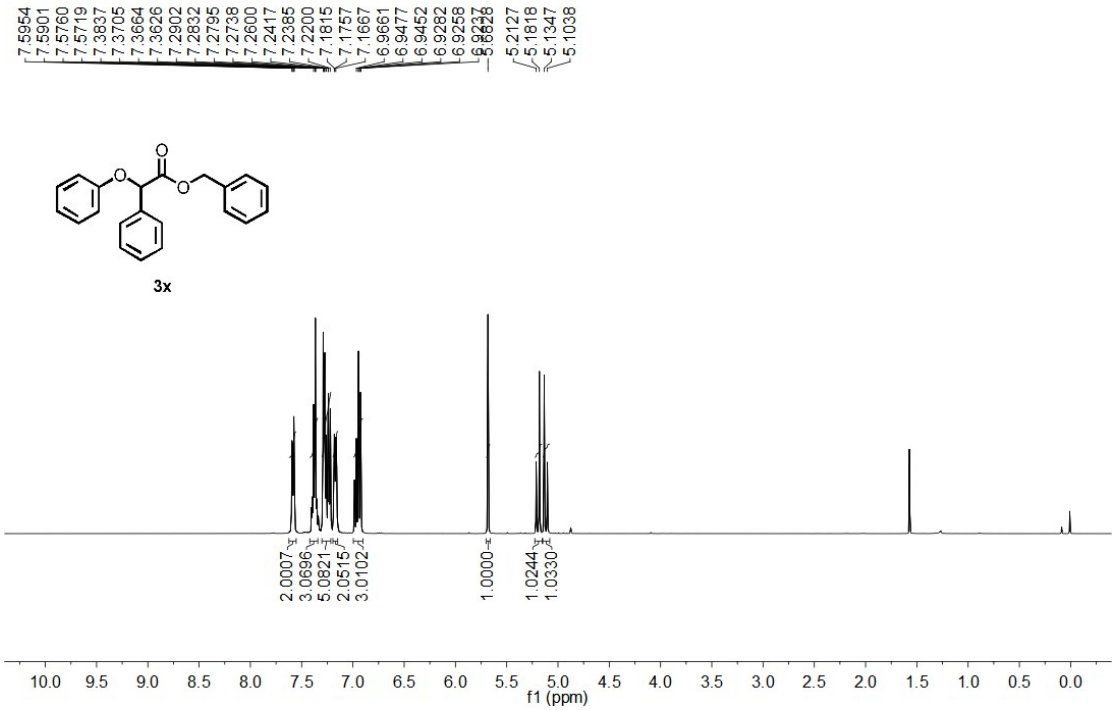
20190524
ZZP-32



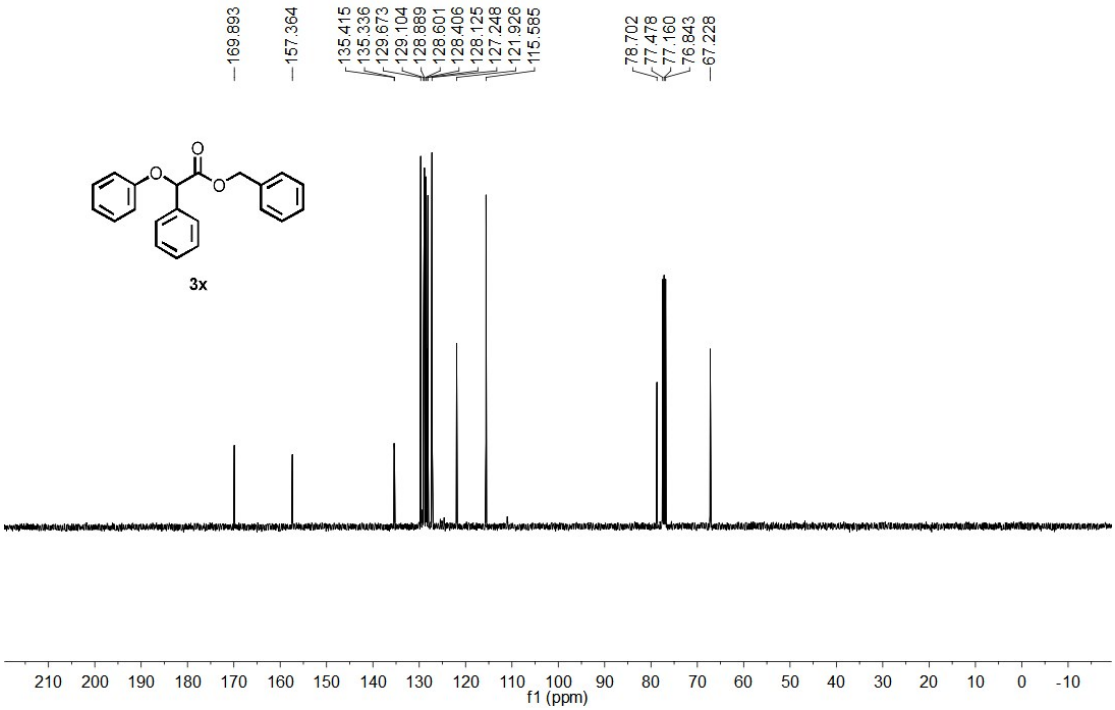
ZZP-32



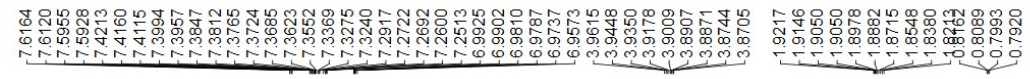
ZZ-56

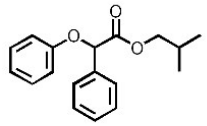

7.5954
7.5901
7.5760
7.5719
7.3837
7.3705
7.3664
7.3626
7.2902
7.2832
7.2795
7.2738
7.2600
7.2417
7.2385
7.2200
7.1815
7.1757
7.1667
6.9661
6.9477
6.9452
6.9282
6.9258
5.2127
5.1818
5.1347
5.1038
3x
2.0007
3.0696
5.0821
2.0515
3.0102
1.0000
1.0244
1.0330
f1 (ppm)

ZZ-56

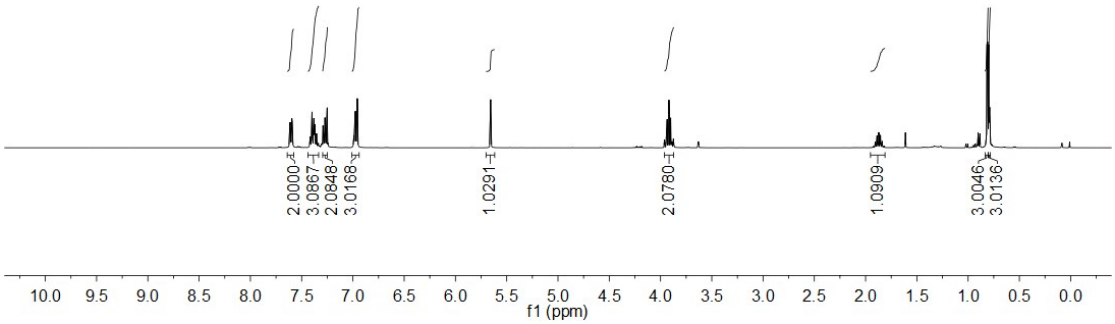

169.893
157.364
135.415
135.336
129.673
129.104
128.889
128.601
128.406
128.125
127.248
121.926
115.565
78.702
77.478
77.160
76.843
67.228
3x
f1 (ppm)

20190524
ZZP-26

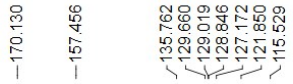


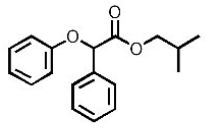


3y

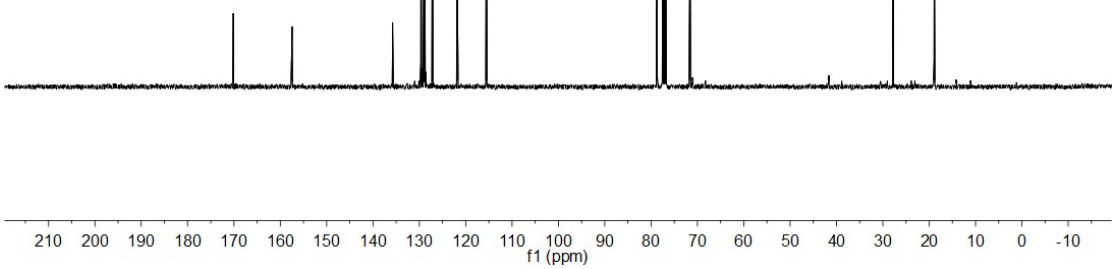


20190524
ZZP-26-C

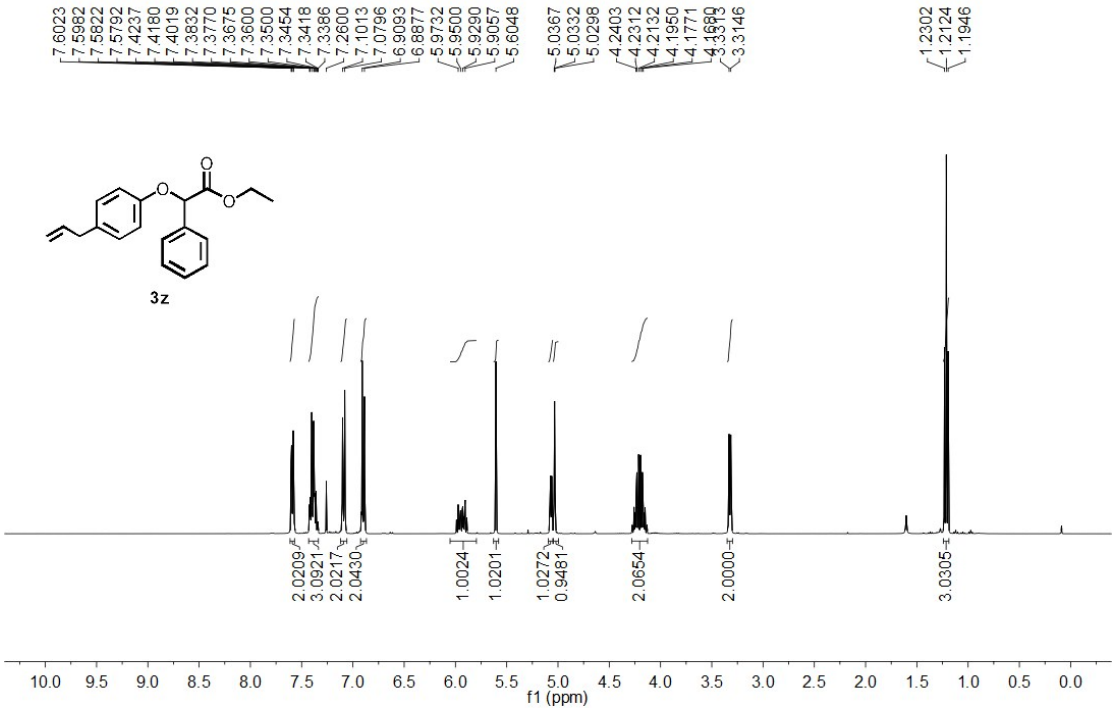




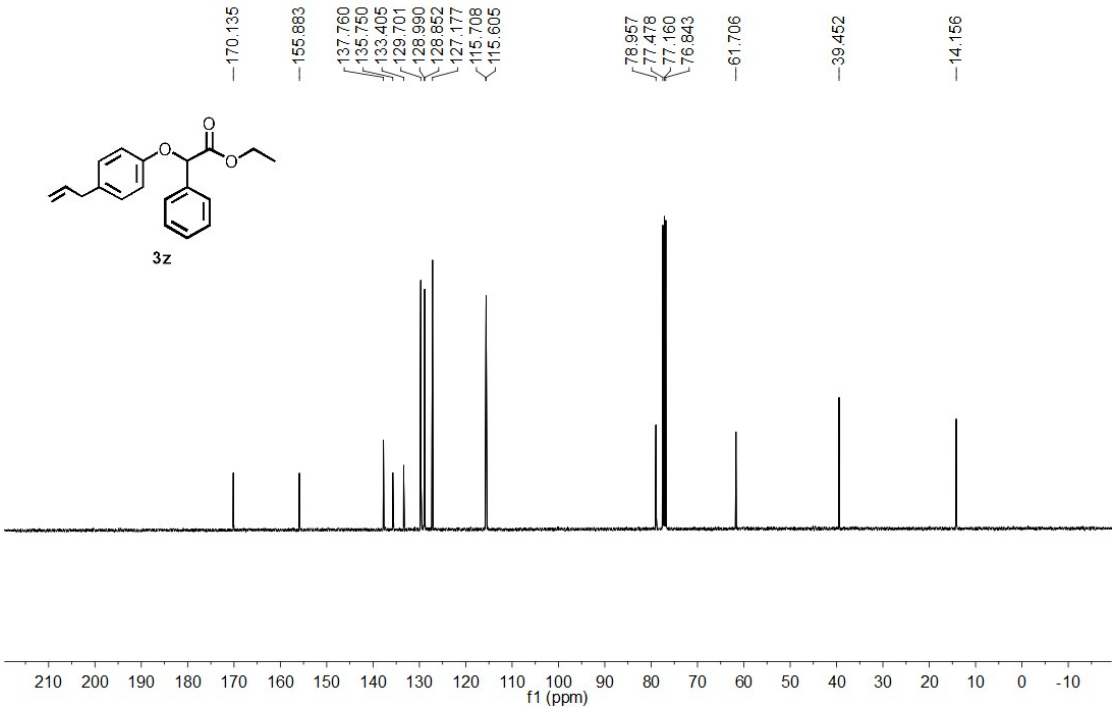
3y



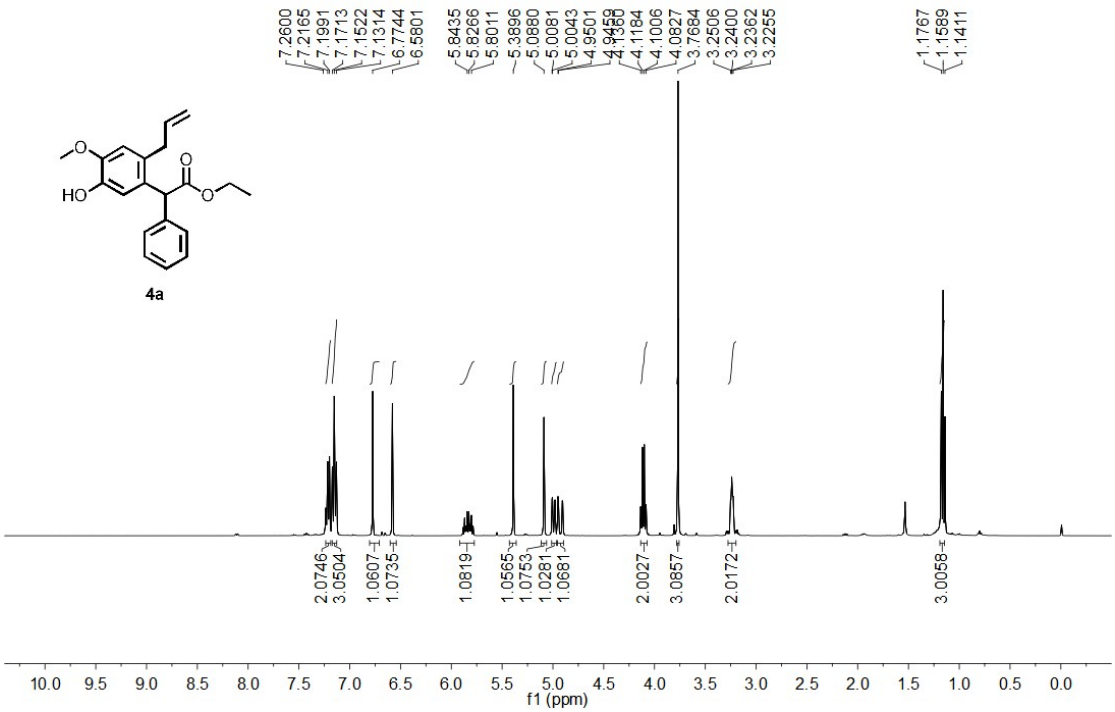
ZZP-96


7.6023
7.5982
7.5822
7.5792
7.4237
7.4180
7.4019
7.3832
7.3770
7.3675
7.3600
7.3500
7.3454
7.3418
7.3386
7.2600
7.1013
7.0796
6.9093
6.8877
5.9732
5.9500
5.9290
5.9057
5.6048
5.0367
5.0332
5.0298
4.2403
4.2312
4.2132
4.1950
4.1771
4.1689
3.3313
3.3146
1.2302
1.2124
1.1946
3z
2.0209
3.0921
2.0217
2.0430
1.0024
1.0201
1.0272
0.9481
2.0654
2.0000
3.0305
f1 (ppm)

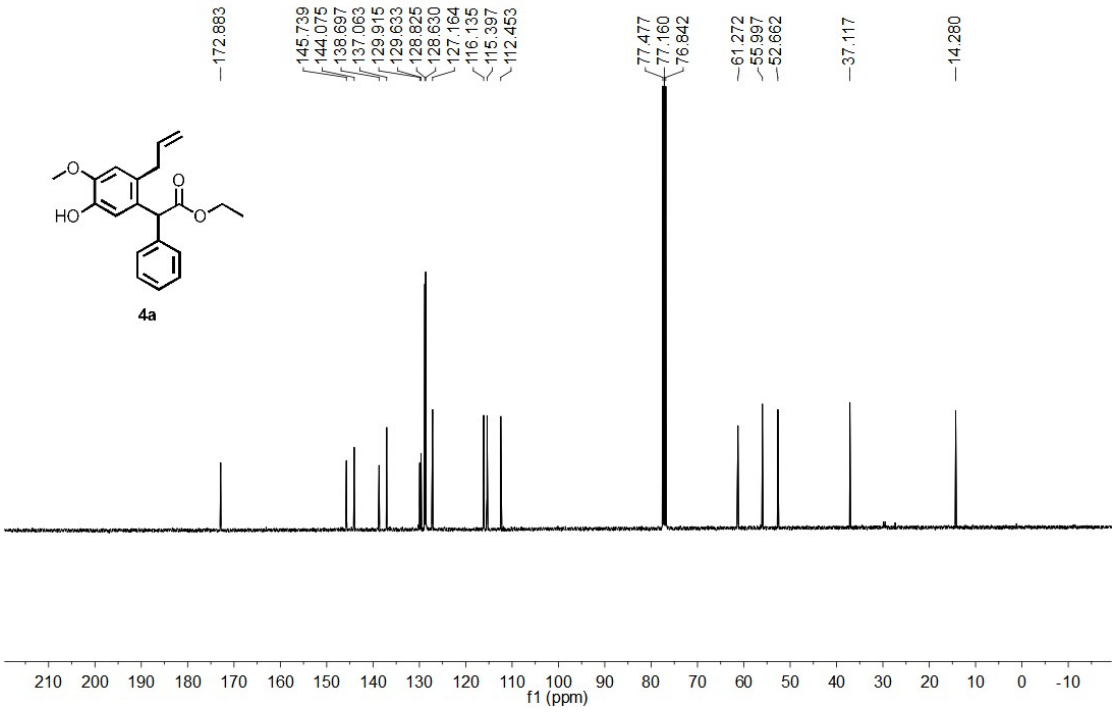
ZZP-96


170.135
155.883
137.760
135.750
133.405
129.701
128.990
128.852
127.177
115.708
115.605
78.957
77.478
77.160
76.843
61.706
39.452
14.156
3z
f1 (ppm)

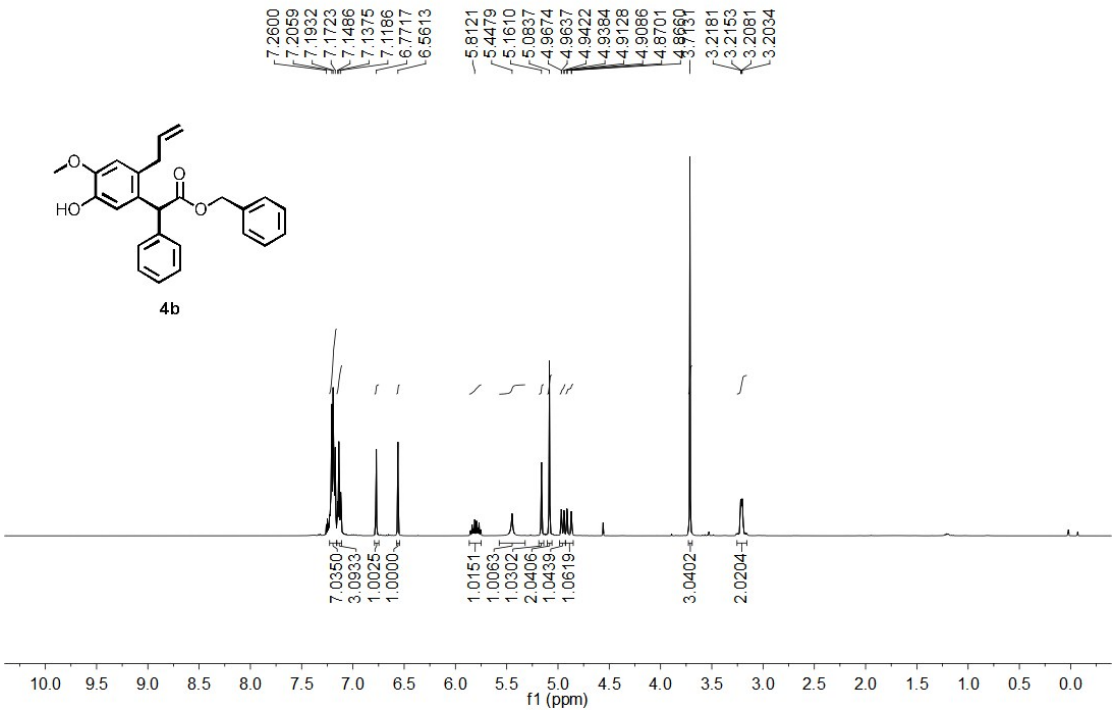
ZZP-17-1



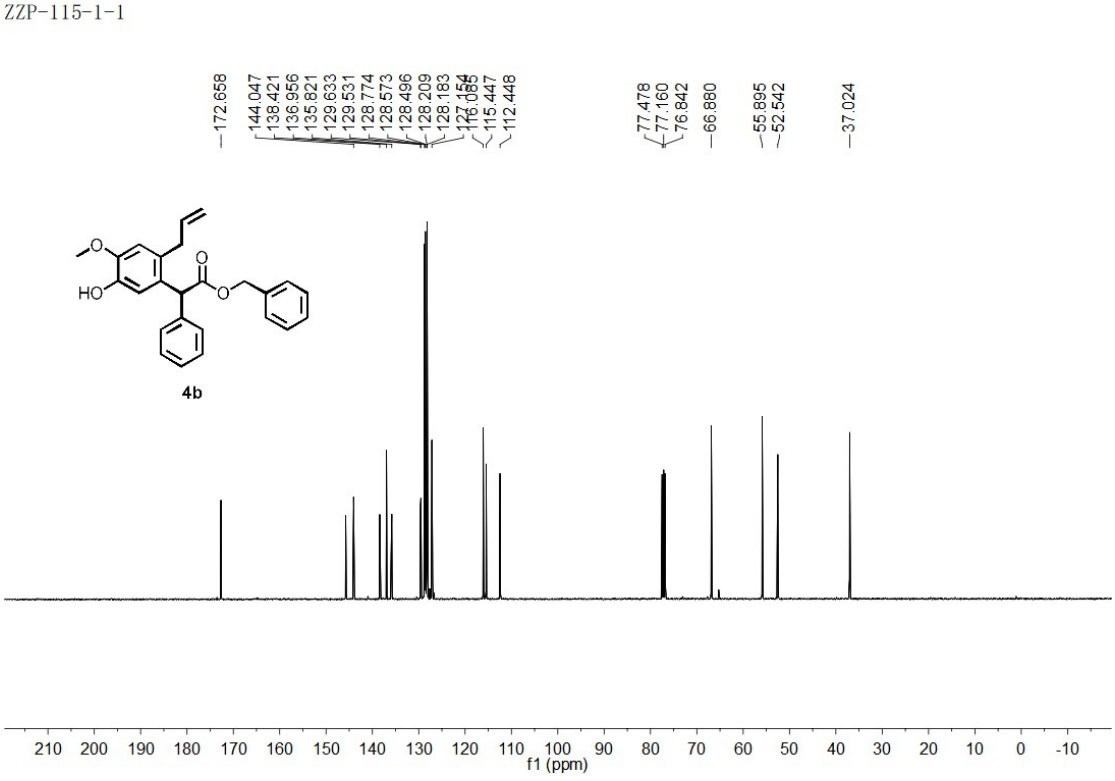
ZZP-17-1



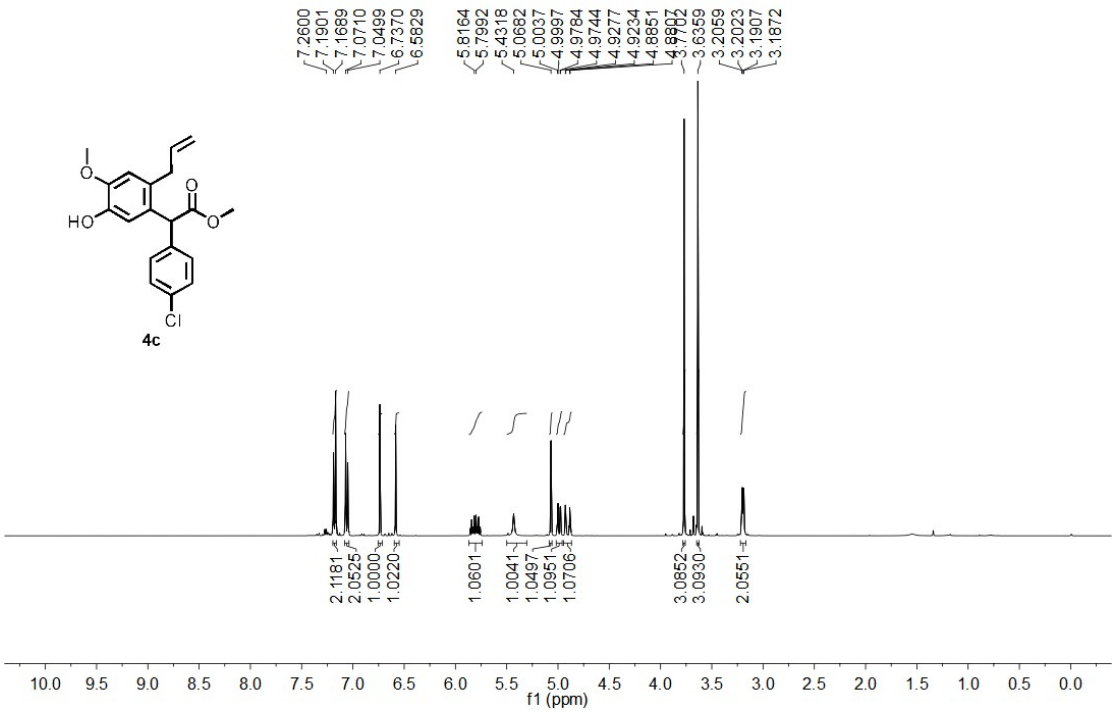
ZZP-115-1-1



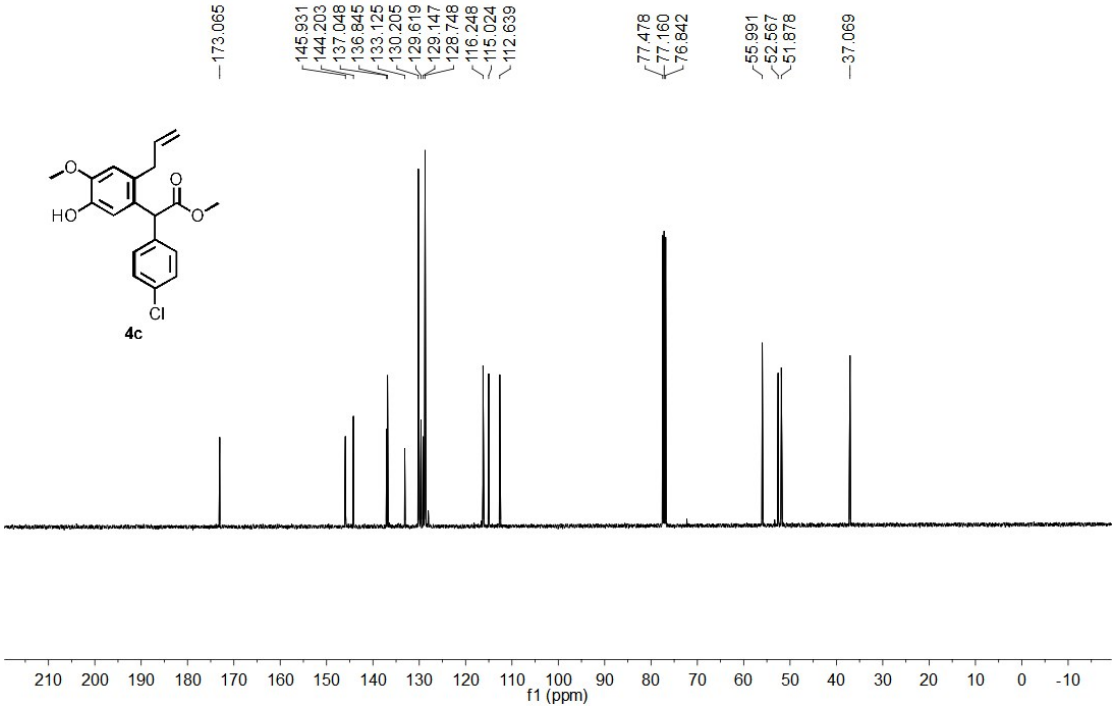
ZZP-115-1-1



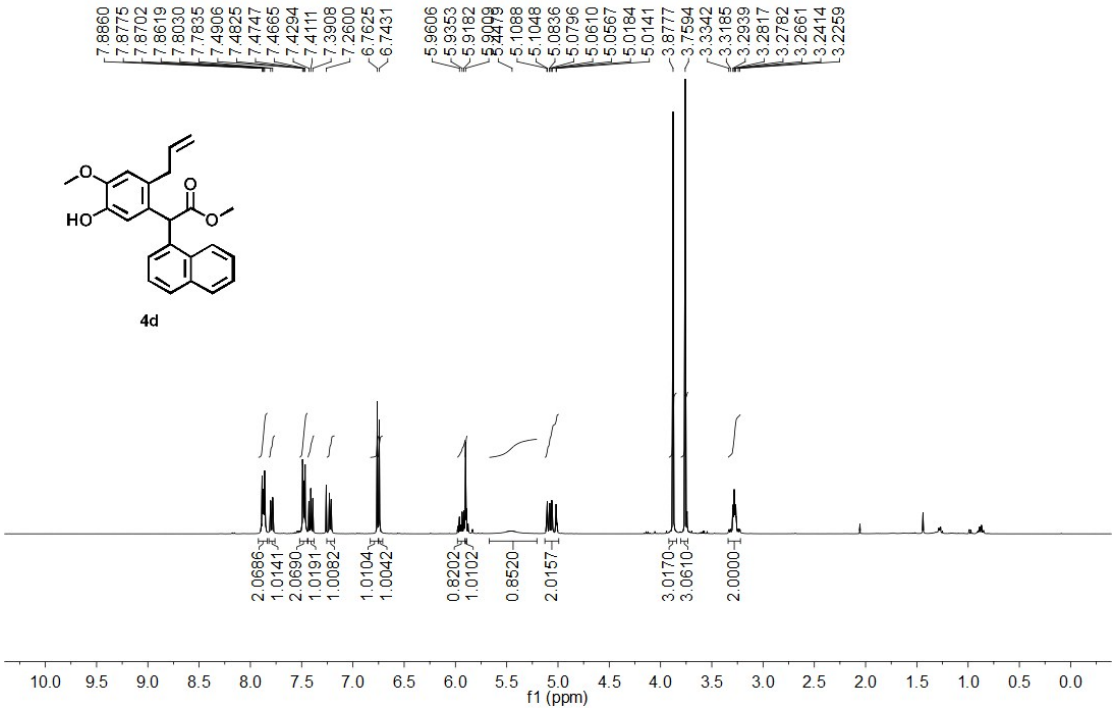
ZZP-98



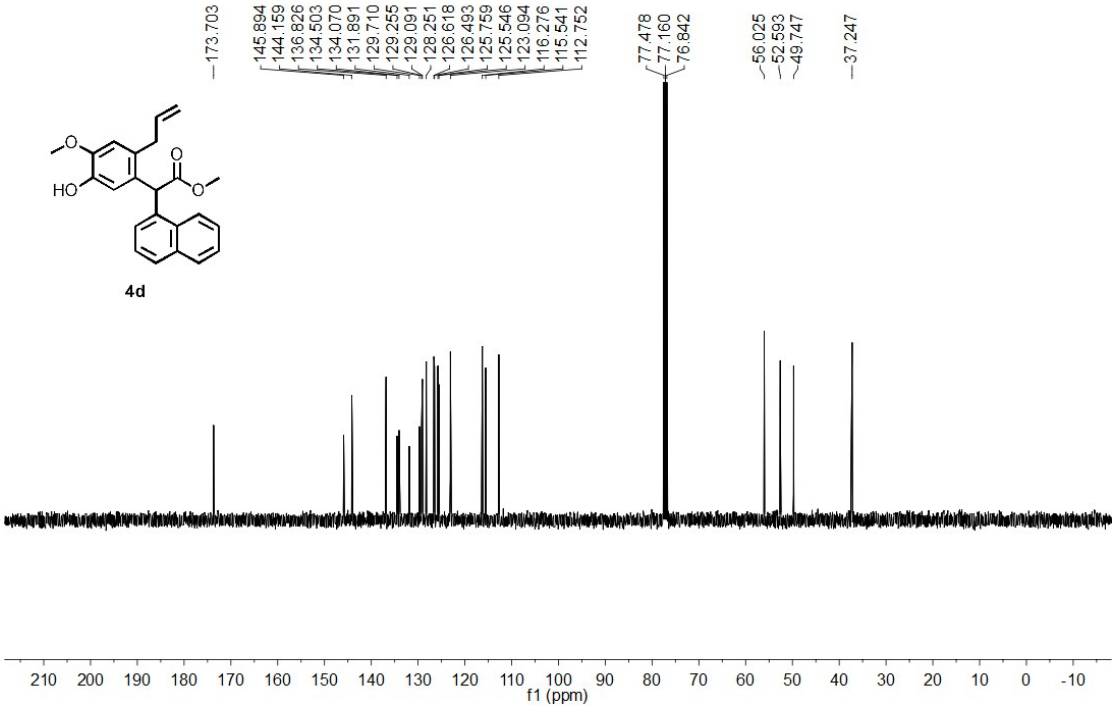
ZZP-98-1



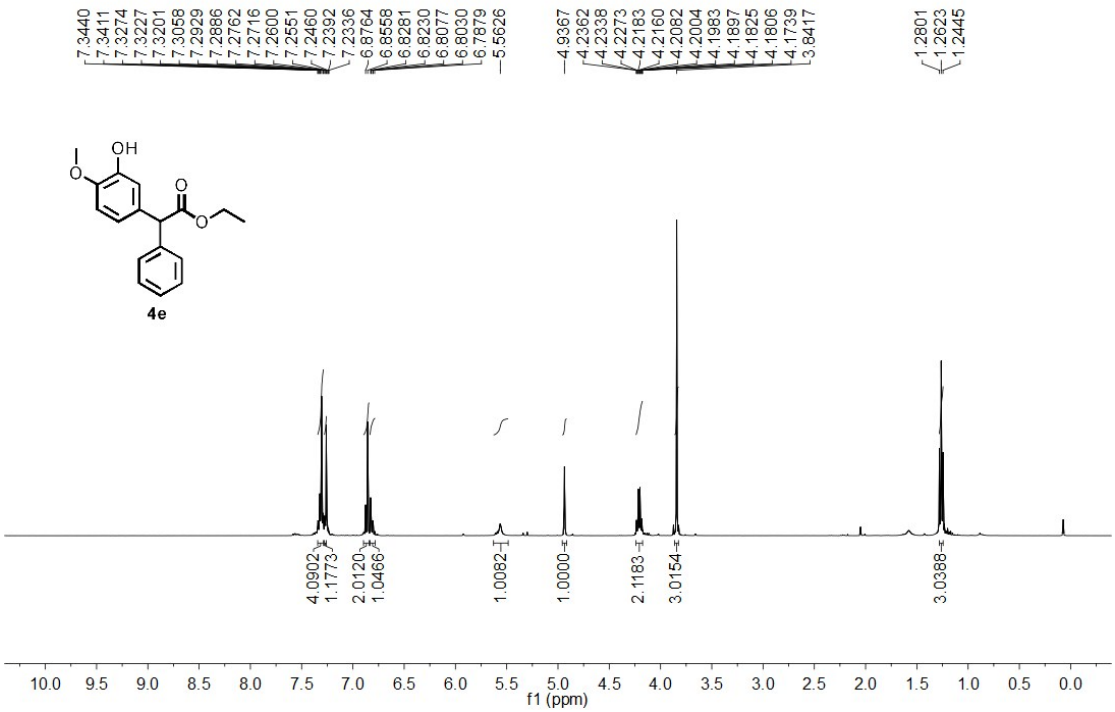
ZZP-1


7.8860
7.8775
7.8702
7.8619
7.8030
7.7835
7.4906
7.4825
7.4747
7.4665
7.4294
7.4111
7.3908
7.2600
6.7625
6.7431
5.9606
5.9353
5.9182
5.1088
5.1048
5.0836
5.0796
5.0610
5.0567
5.0184
5.0141
3.8777
3.7594
3.3342
3.3185
3.2939
3.2817
3.2782
3.2661
3.2414
3.2259
HO
O
O
O
4d
2.0686
1.0141
2.0690
1.0191
1.0082
1.0104
1.0042
0.8202
1.0102
0.8520
2.0157
3.0170
3.0610
2.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

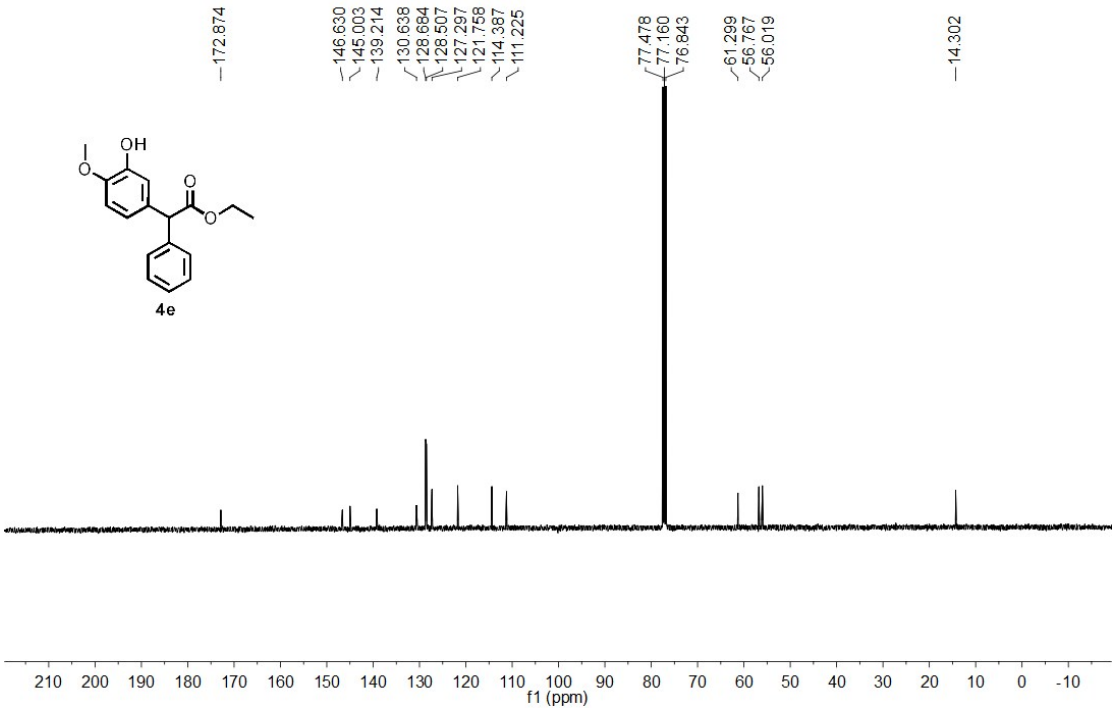
zzp-16


173.703
145.894
144.159
136.826
134.503
134.070
131.891
129.710
129.255
129.091
128.251
126.618
126.493
125.759
125.546
123.094
116.276
115.541
112.752
77.478
77.160
76.842
56.025
52.593
49.747
37.247
HO
O
O
O
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

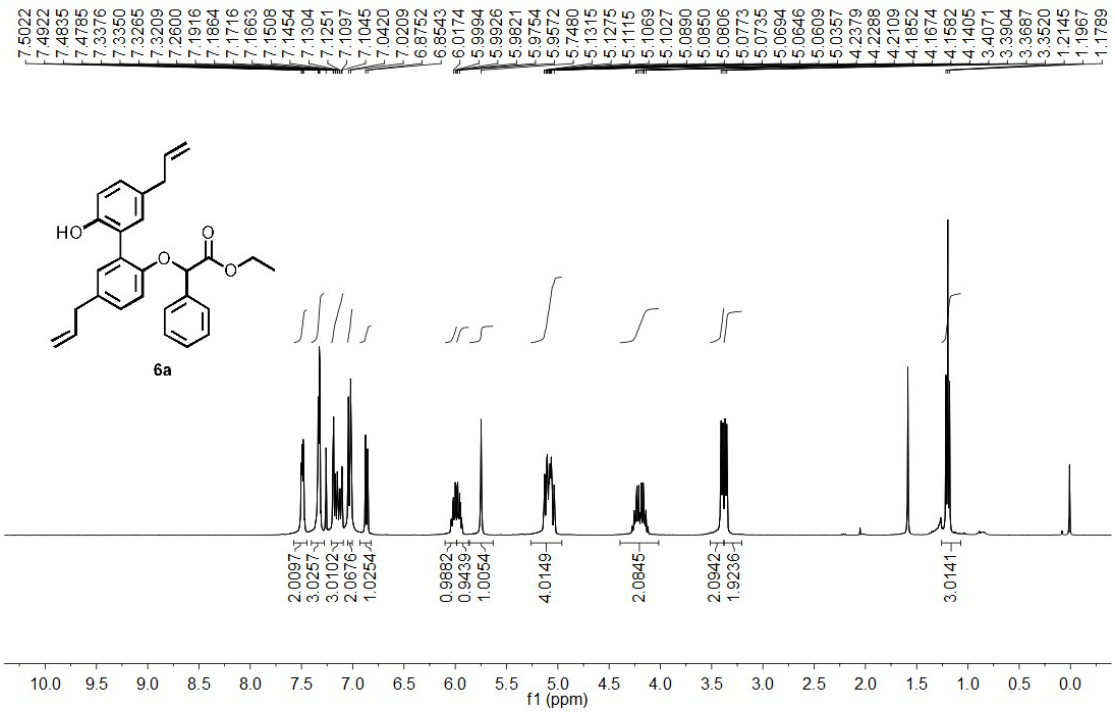
ZZP-91-3



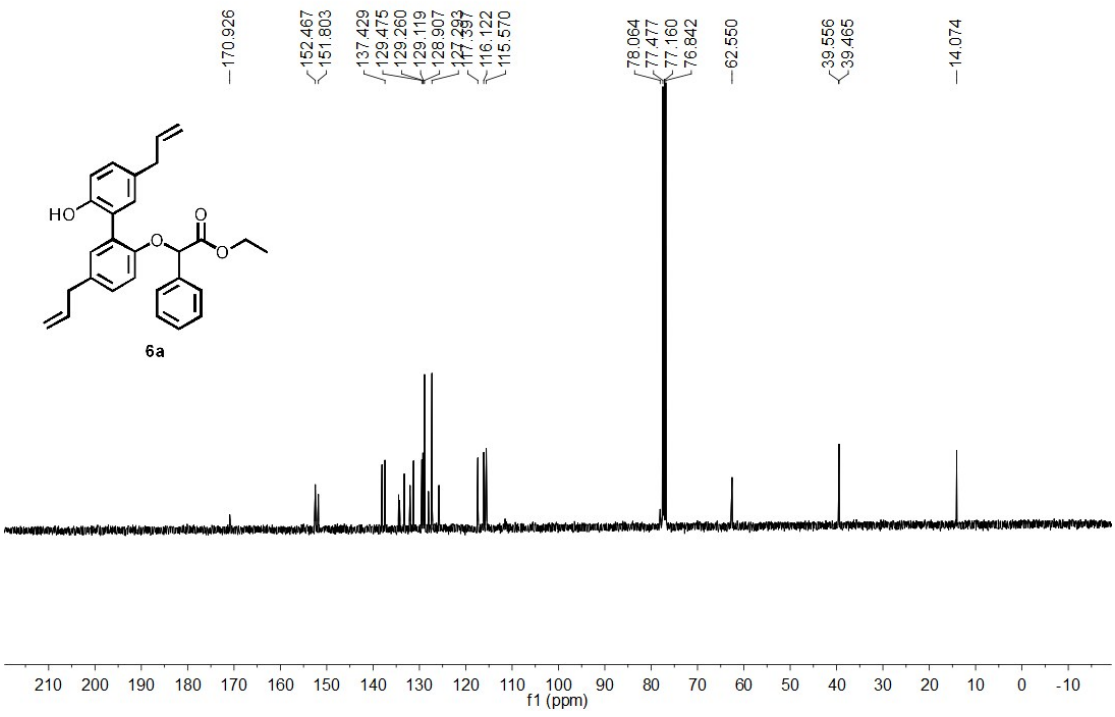
ZZP-91-3



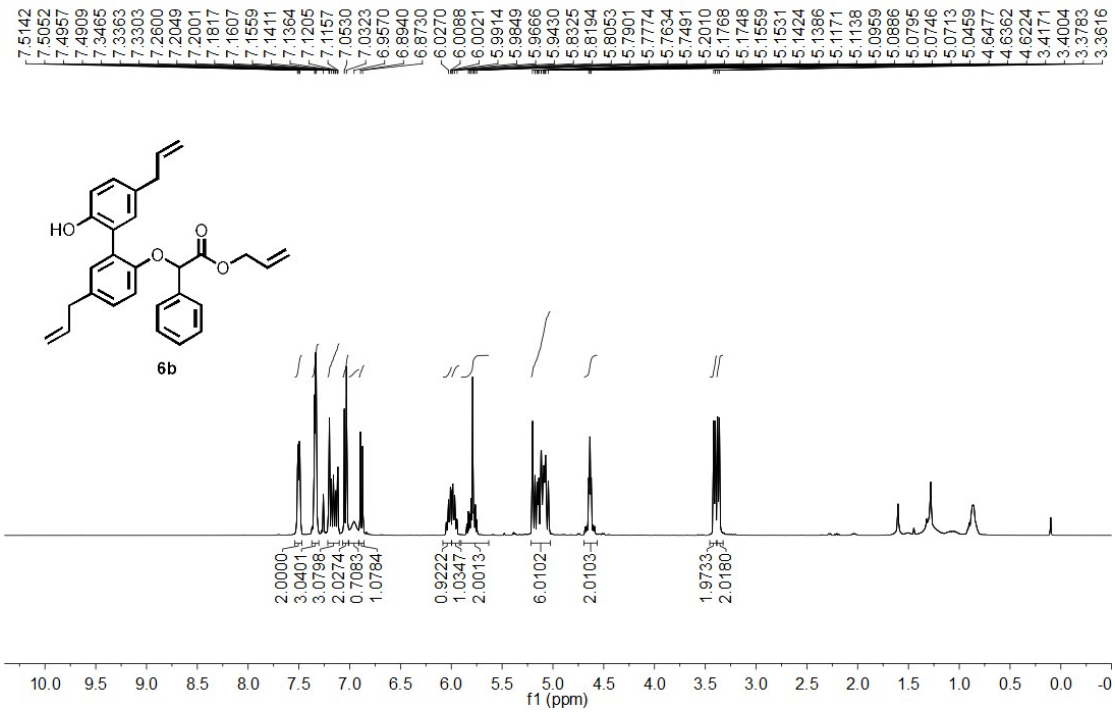
zzp-6


7.5022
7.4922
7.4835
7.4785
7.3376
7.3350
7.3265
7.3209
7.2600
7.1916
7.1864
7.1716
7.1663
7.1508
7.1454
7.1304
7.1251
7.1097
7.1045
7.0420
7.0209
6.8752
6.8543
6.0174
5.9994
5.9926
5.9821
5.9754
5.9572
5.7480
5.1315
5.1275
5.1115
5.1069
5.1027
5.0890
5.0850
5.0806
5.0773
5.0735
5.0694
5.0646
5.0609
5.0357
4.2379
4.2288
4.2109
4.1852
4.1674
4.1582
4.1405
3.4071
3.3904
3.3687
3.3520
1.2145
1.1967
1.1789
HO
O
O
O
6a
2.0097
3.0257
3.0102
2.0676
1.0254
0.9882
0.9439
1.0054
4.0149
2.0845
2.0942
1.9236
3.0141
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

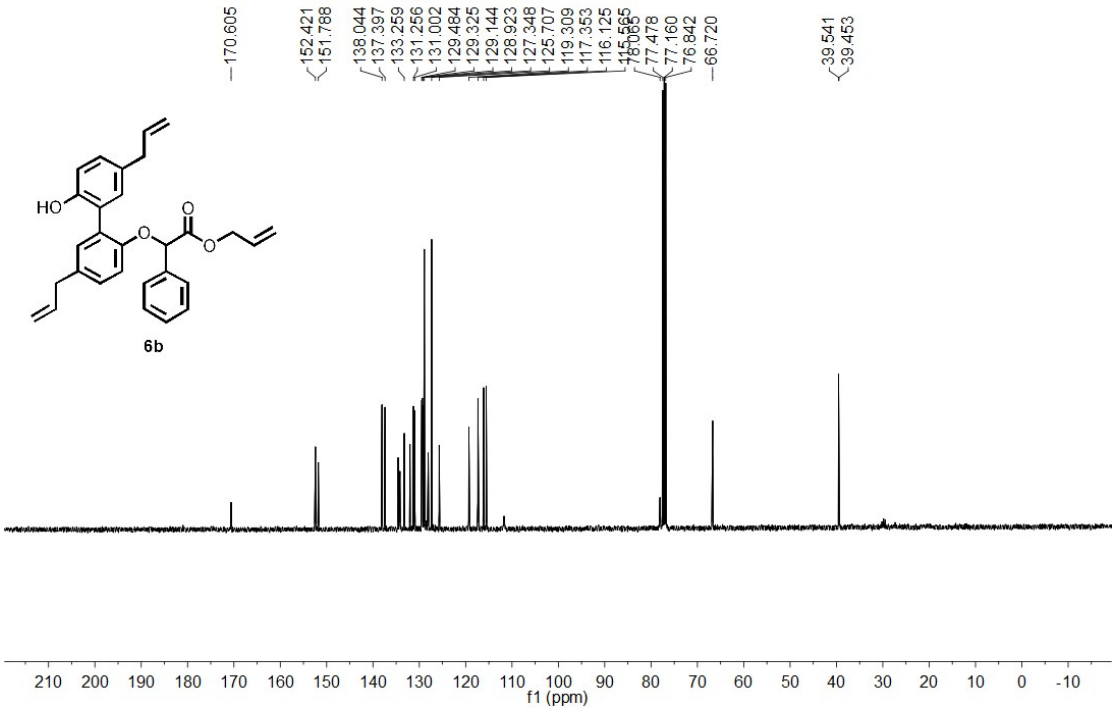
zzp-6


170.926
152.467
151.803
137.429
129.475
129.260
129.119
128.907
127.293
127.397
116.122
115.570
78.064
77.477
77.160
76.842
62.550
39.556
39.465
14.074
HO
O
O
O
6a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

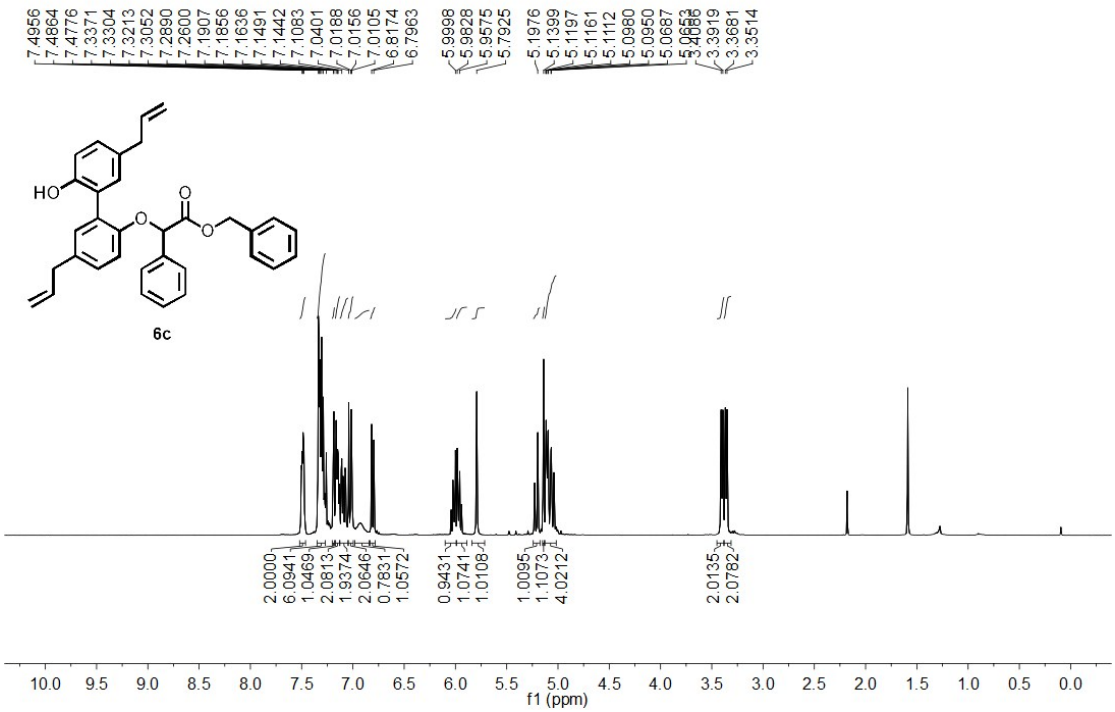
ZZP-21


7.5142
7.5052
7.4957
7.4909
7.3465
7.3363
7.3303
7.2600
7.2049
7.2001
7.1817
7.1607
7.1559
7.1411
7.1364
7.1205
7.1157
7.0530
7.0323
6.9570
6.8940
6.8730
6.0270
6.0088
6.0021
5.9914
5.9849
5.9666
5.9430
5.8325
5.8194
5.8053
5.7901
5.7774
5.7634
5.7491
5.2010
5.1768
5.1748
5.1559
5.1531
5.1424
5.1386
5.1171
5.1138
5.0959
5.0886
5.0795
5.0746
5.0713
5.0459
4.6477
4.6362
4.6224
3.4171
3.4004
3.3783
3.3616
HO
O
O
O
6b
2.0000
3.0401
3.0798
2.0274
0.7083
1.0784
0.9222
1.0347
2.0013
6.0102
2.0103
1.9733
2.0180
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

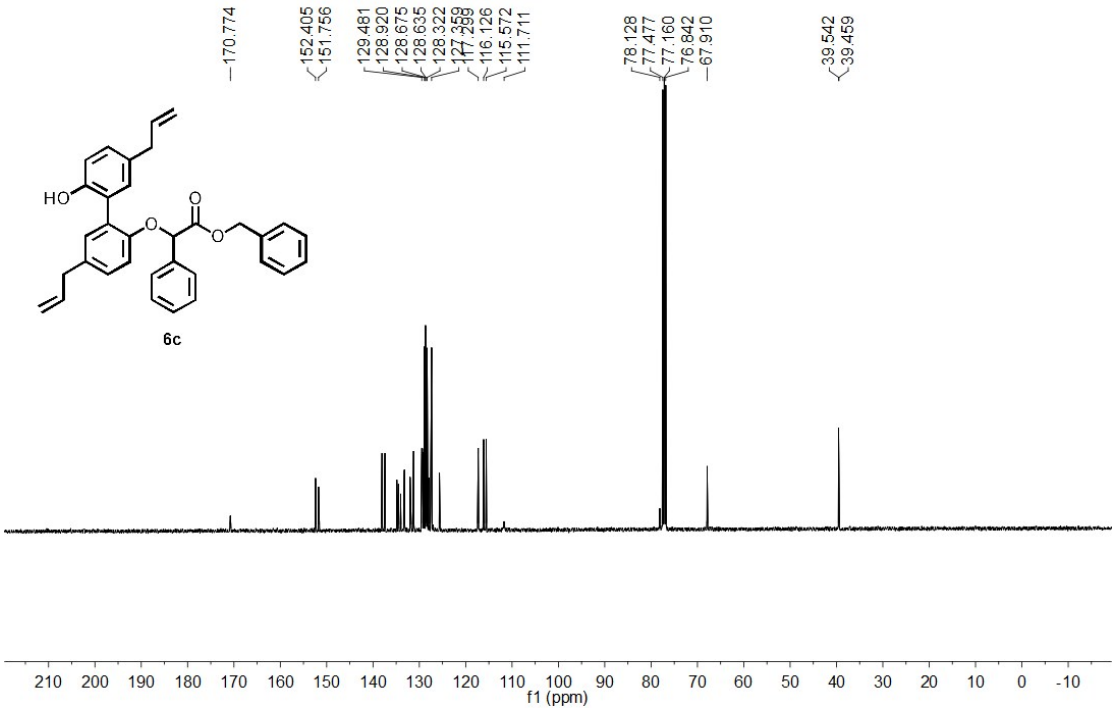
ZZP-21


170.605
152.421
151.788
138.044
137.397
133.259
131.256
131.002
129.484
129.325
129.144
128.923
127.348
125.707
119.309
117.353
116.125
115.565
78.065
77.478
77.160
76.842
66.720
39.541
39.453
HO
O
O
O
6b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

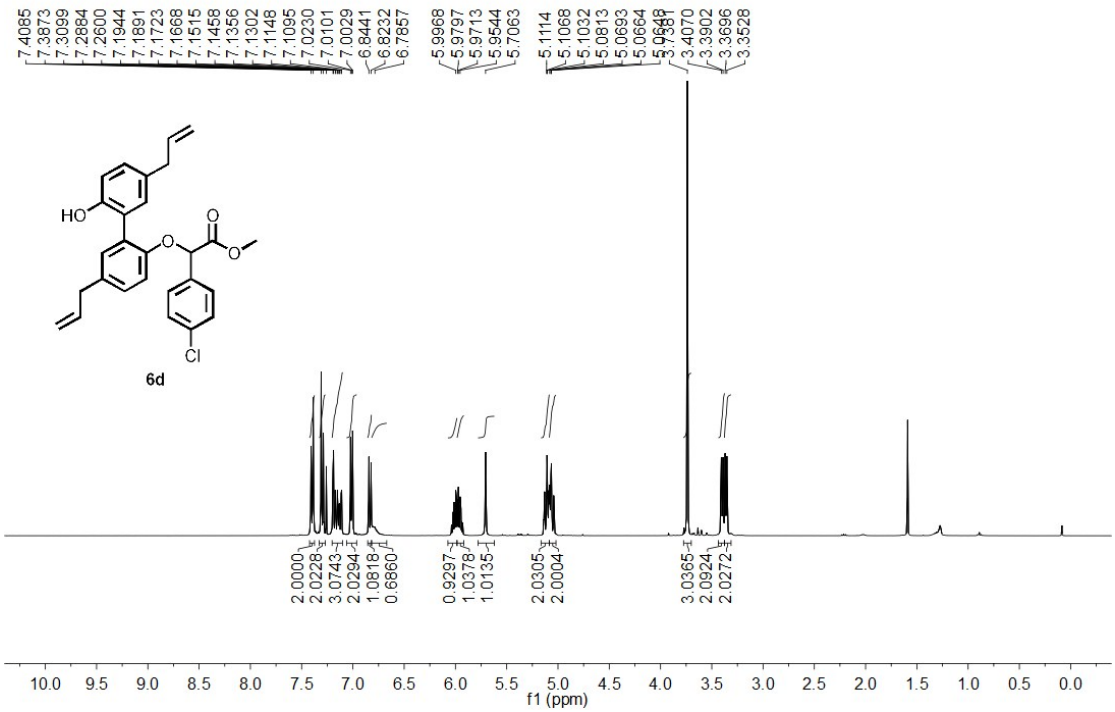
ZZP-23


7.4956
7.4864
7.4776
7.3371
7.3304
7.3213
7.3052
7.2890
7.2600
7.1907
7.1856
7.1636
7.1491
7.1442
7.1083
7.0401
7.0188
7.0156
7.0105
6.8174
6.7963
5.9998
5.9928
5.9575
5.7925
5.1976
5.1399
5.1197
5.1161
5.1112
5.0980
5.0950
5.0687
3.4086
3.3919
3.3681
3.3514
HO
O
O
O
6c
2.0000
6.0941
1.0469
2.0813
1.9374
2.0646
0.7831
1.0572
0.9431
1.0741
1.0108
1.0095
1.1073
4.0212
2.0135
2.0782
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

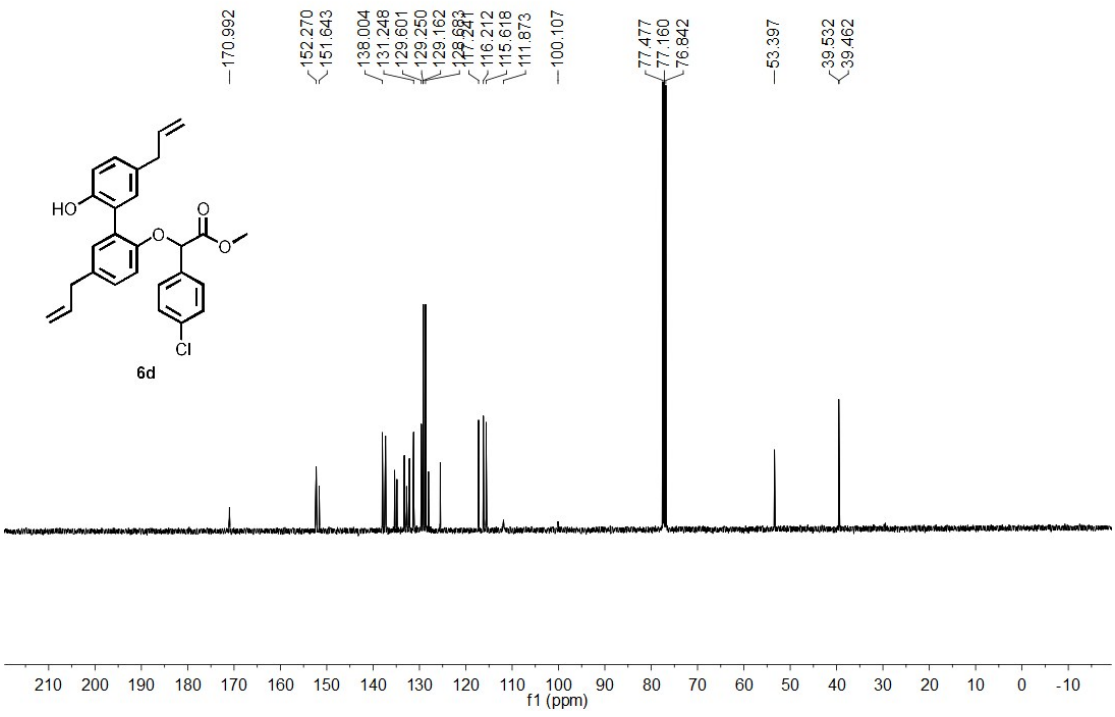
ZZP-23


170.774
152.405
151.756
129.481
128.920
128.675
128.635
128.322
127.359
127.299
116.126
115.572
111.711
78.128
77.477
77.160
76.842
67.910
39.542
39.459
HO
O
O
O
6c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

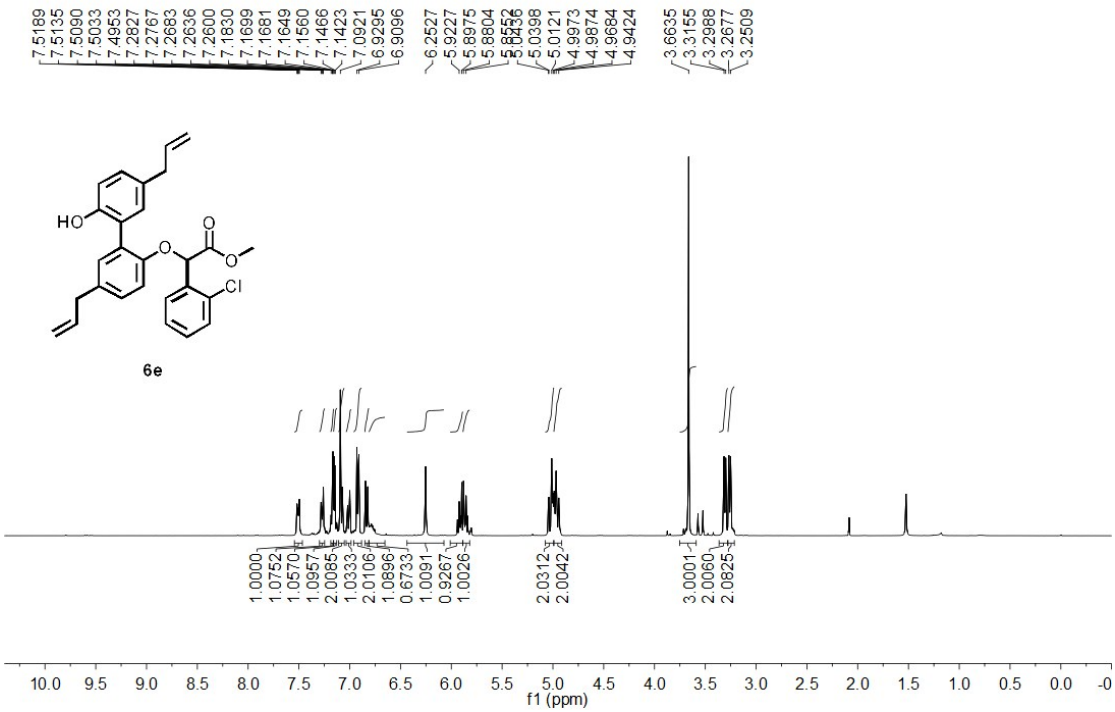
ZZP-55


7.4085
7.3873
7.3099
7.2884
7.2600
7.1944
7.1891
7.1723
7.1668
7.1515
7.1458
7.1356
7.1302
7.1148
7.1095
7.0230
7.0101
7.0029
6.8441
6.8232
6.7857
5.9968
5.9797
5.9713
5.9544
5.7063
5.1114
5.1068
5.1032
5.0813
5.0693
5.0664
3.7381
3.4070
3.3902
3.3696
3.3528
HO
O
O
O
Cl
6d
2.0000
2.0228
3.0743
2.0294
1.0818
0.6860
0.9297
1.0378
1.0135
2.0305
2.0004
3.0365
2.0924
2.0272
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

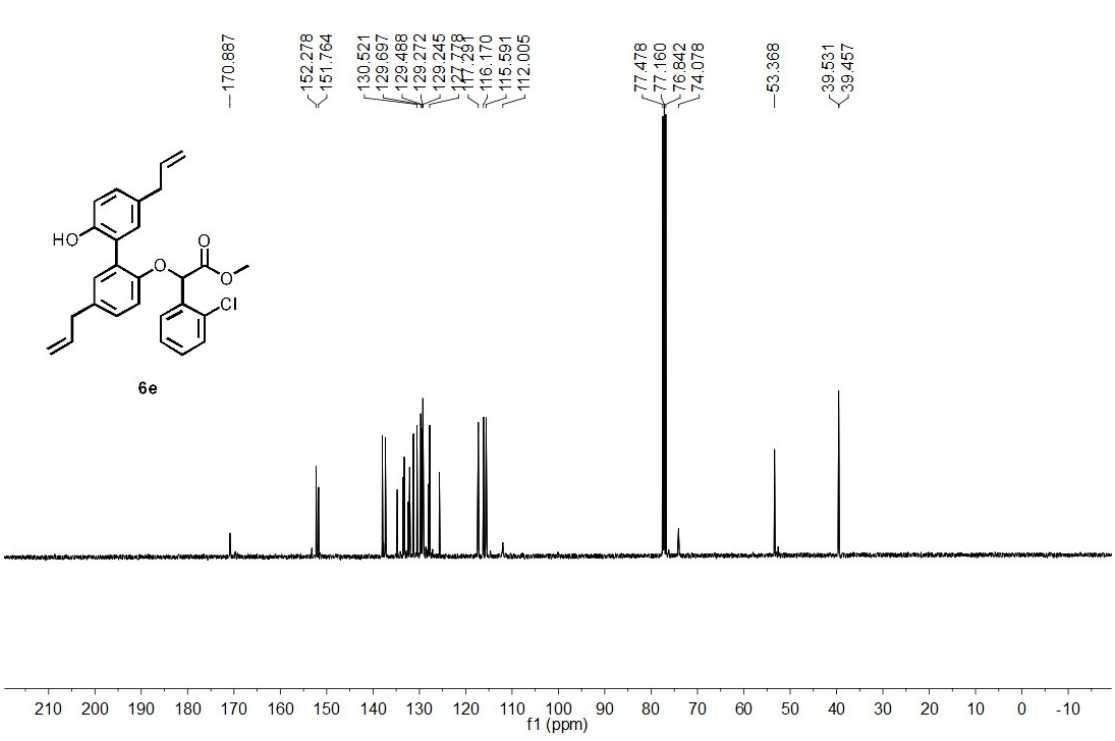
ZZP-55


170.992
152.270
151.643
138.004
131.248
129.601
129.250
129.162
128.683
127.241
116.212
115.618
111.873
100.107
77.477
77.160
76.842
53.397
39.532
39.462
HO
O
O
O
Cl
6d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

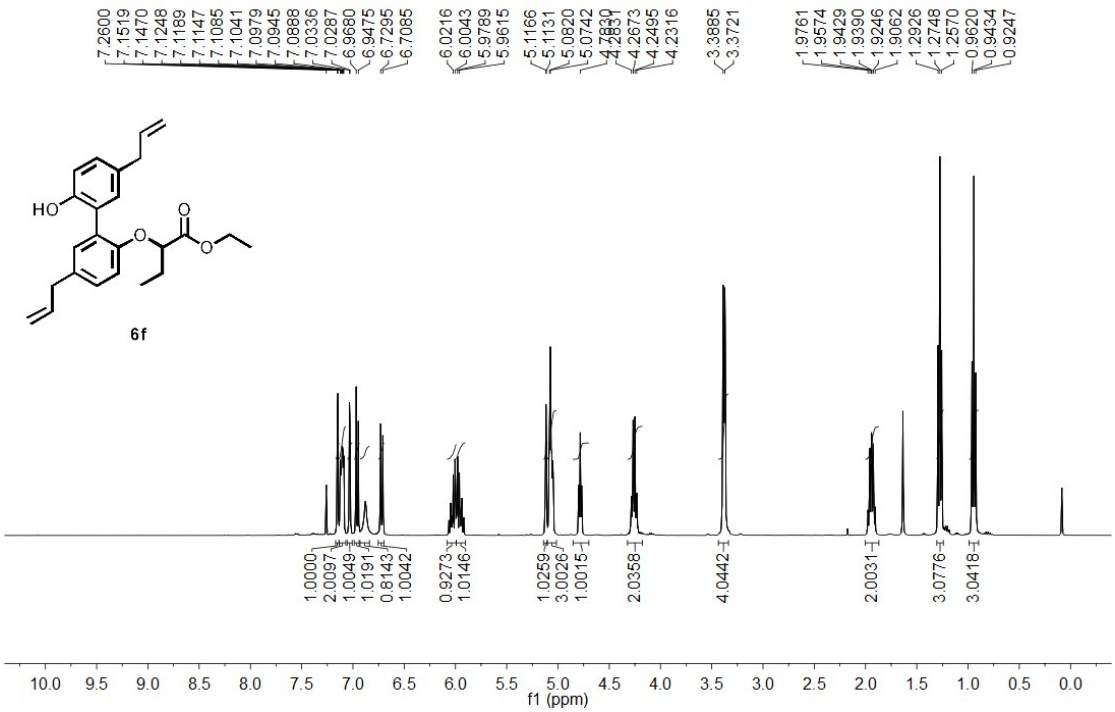
ZZP-24


7.5189
7.5135
7.5090
7.5033
7.4953
7.2827
7.2767
7.2683
7.2636
7.2600
7.1830
7.1699
7.1681
7.1649
7.1560
7.1466
7.1423
7.0921
6.9295
6.9096
6.2527
5.9227
5.8975
5.8804
5.0398
5.0121
4.9973
4.9874
4.9684
4.9424
3.6635
3.3155
3.2988
3.2677
3.2509
HO
O
O
O
Cl
6e
1.0000
1.0752
1.0570
1.0957
2.0085
1.0333
2.0106
1.0896
0.6733
1.0091
0.9267
1.0026
2.0312
2.0042
3.0001
2.0060
2.0825
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

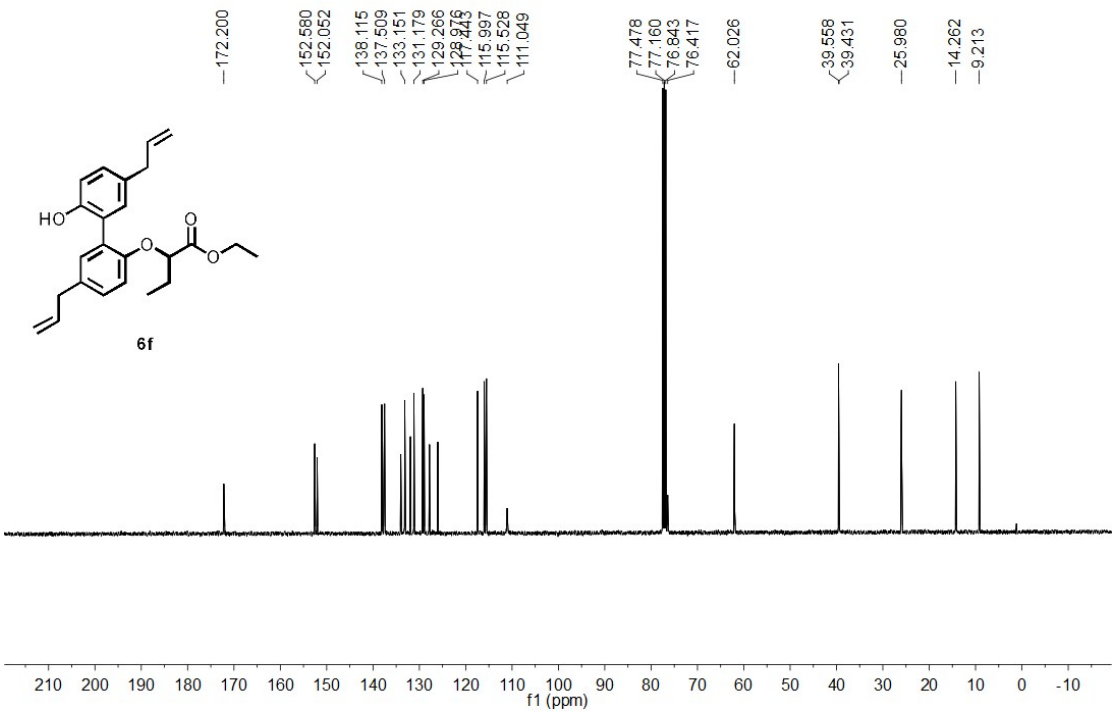
ZZP-24


170.887
152.278
151.764
130.521
129.697
129.488
129.272
129.245
127.778
127.291
116.170
115.591
112.005
77.478
77.160
76.842
74.078
53.368
39.531
39.457
HO
O
O
O
Cl
6e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

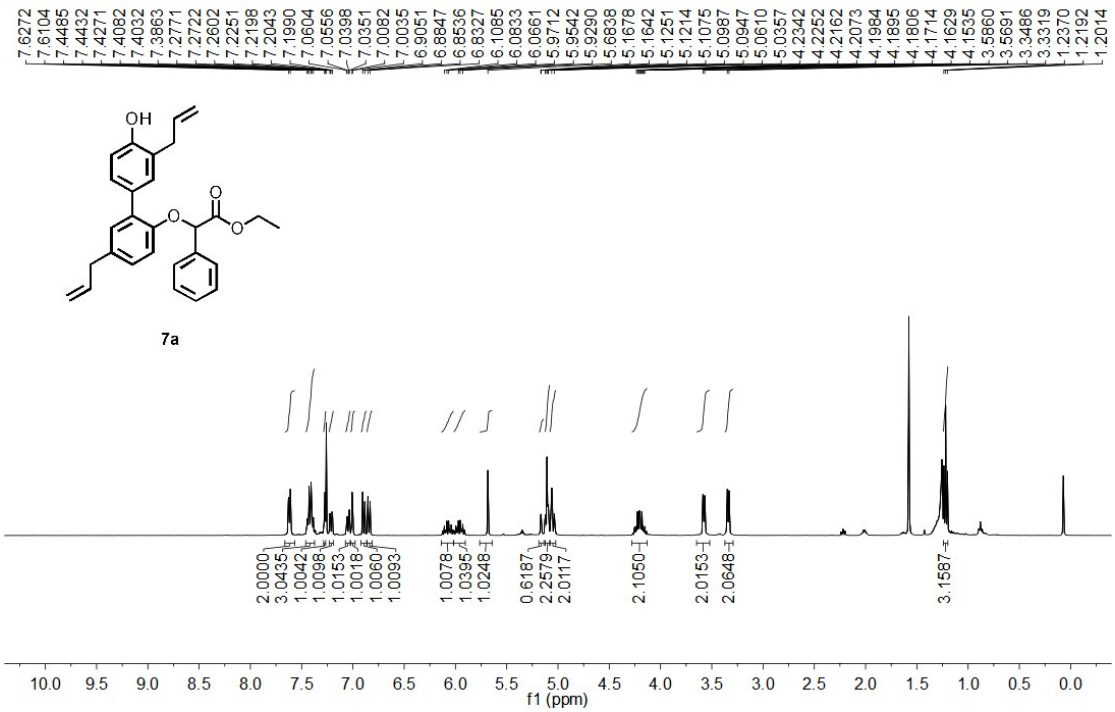
ZZP-25


7.2600
7.1519
7.1470
7.1248
7.1189
7.1147
7.1085
7.1041
7.0979
7.0945
7.0888
7.0336
7.0287
6.9680
6.9475
6.7295
6.7085
6.0216
6.0043
5.9789
5.9615
5.1166
5.1131
5.0820
5.0742
4.2673
4.2495
4.2316
3.3885
3.3721
1.9761
1.9574
1.9429
1.9390
1.9246
1.9062
1.2926
1.2748
1.2570
0.9620
0.9434
0.9247
HO
O
O
O
6f
1.0000
2.0097
1.0049
1.0191
0.8143
1.0042
0.9273
1.0146
1.0259
3.0026
1.0015
2.0358
4.0442
2.0031
3.0776
3.0418
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

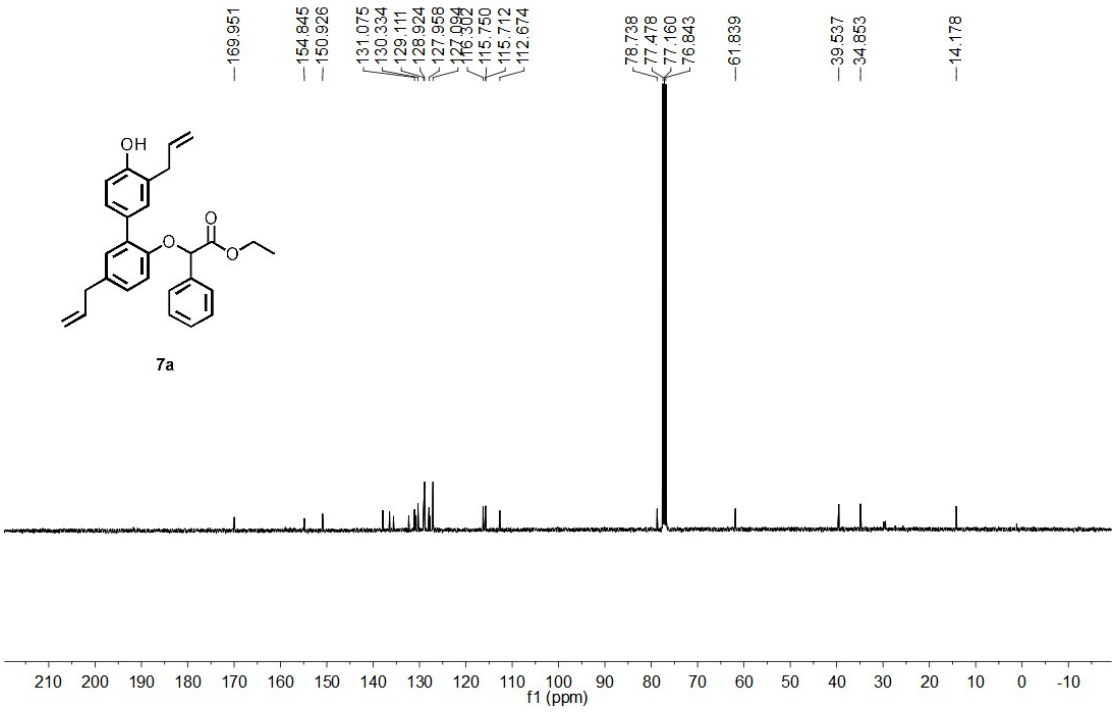
ZZP-25


172.200
152.580
152.052
138.115
137.509
133.151
131.179
129.266
128.976
128.443
115.997
115.528
111.049
77.478
77.160
76.843
76.417
62.026
39.558
39.431
25.980
14.262
9.213
HO
O
O
O
6f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

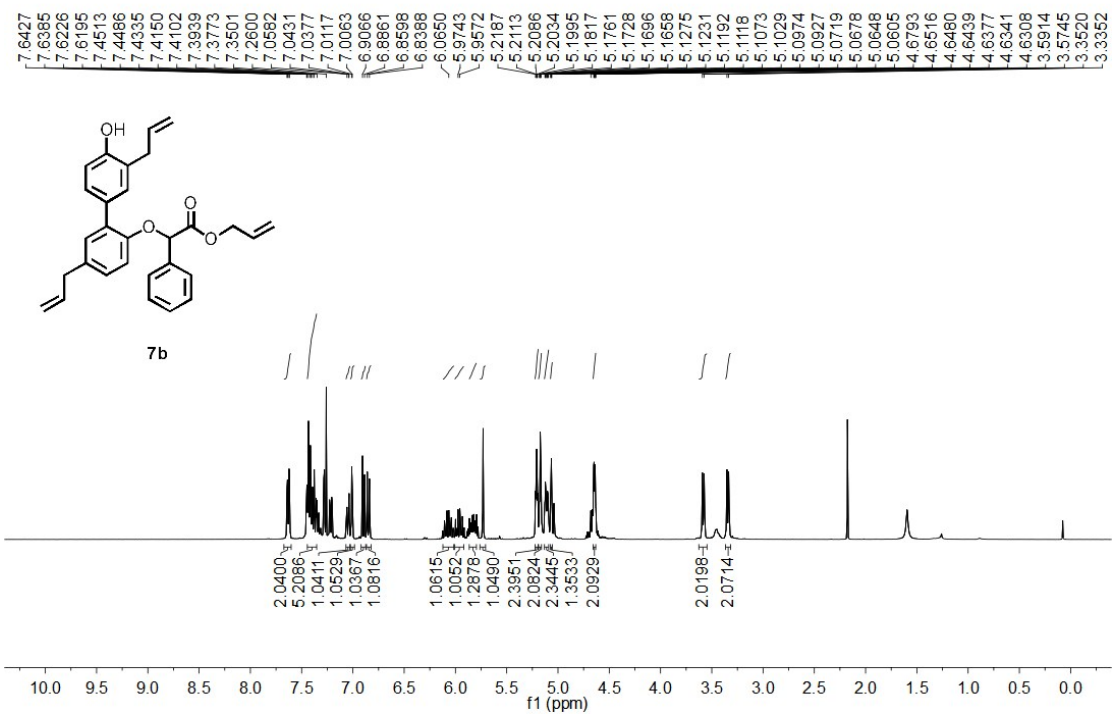
ZZP-16-2



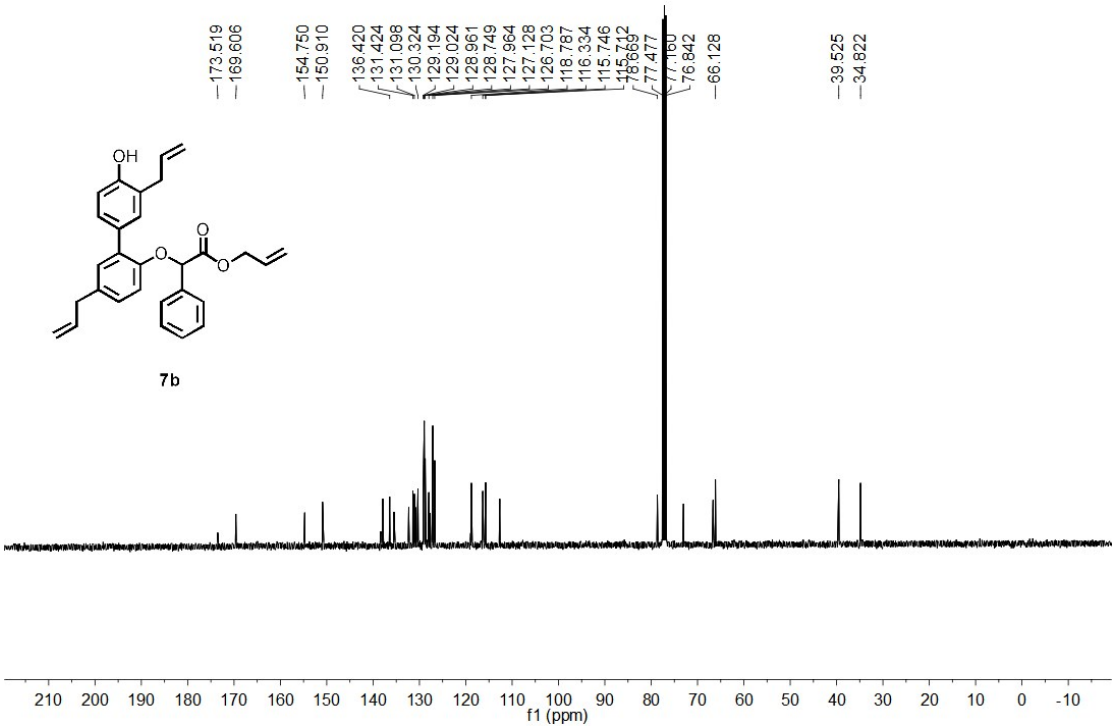
ZZP-16-2



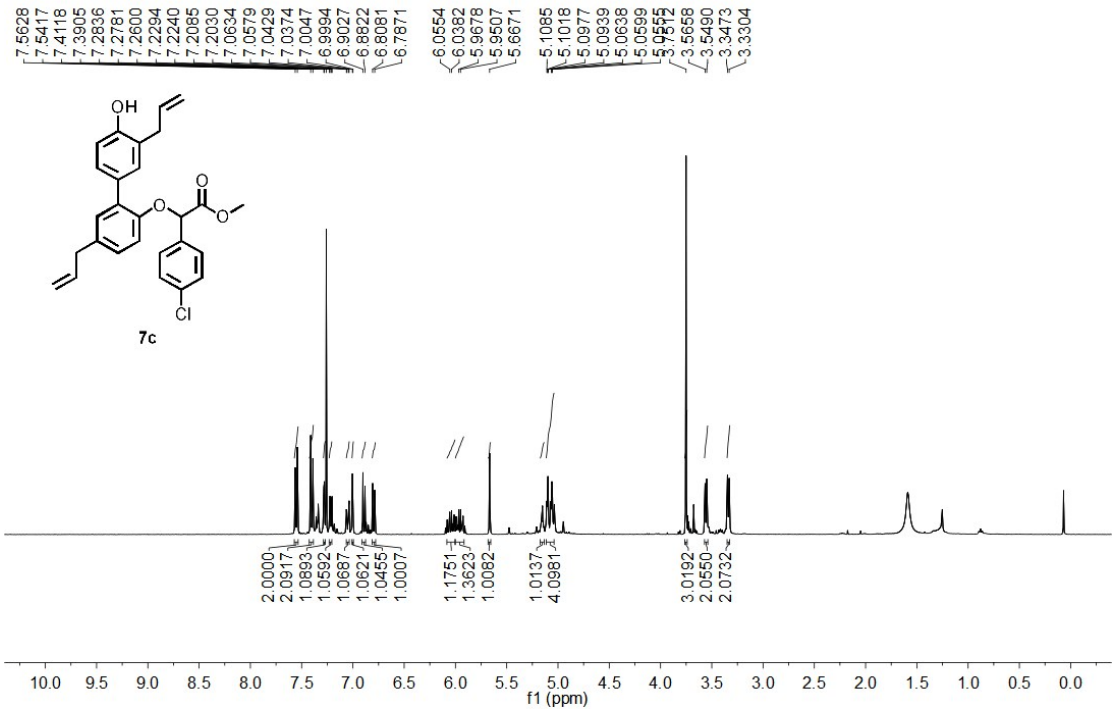
ZZP-76


7.6427
7.6385
7.6226
7.6195
7.4513
7.4486
7.4335
7.4150
7.4102
7.3939
7.3773
7.3501
7.2600
7.0582
7.0431
7.0377
7.0117
7.0063
6.9066
6.8861
6.8598
6.8388
6.0650
5.9743
5.9572
5.2187
5.2113
5.2086
5.2034
5.1995
5.1817
5.1761
5.1728
5.1696
5.1658
5.1275
5.1231
5.1192
5.1118
5.1073
5.1029
5.0974
5.0927
5.0719
5.0678
5.0648
5.0605
4.6793
4.6516
4.6480
4.6439
4.6377
4.6341
4.6308
3.5914
3.5745
3.5520
3.3352
OH
O
O
O
7b
2.0400
5.2086
1.0411
1.0529
1.0367
1.0816
1.0615
1.0052
1.2878
1.0490
2.3951
2.0824
2.3445
1.3533
2.0929
2.0198
2.0714
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

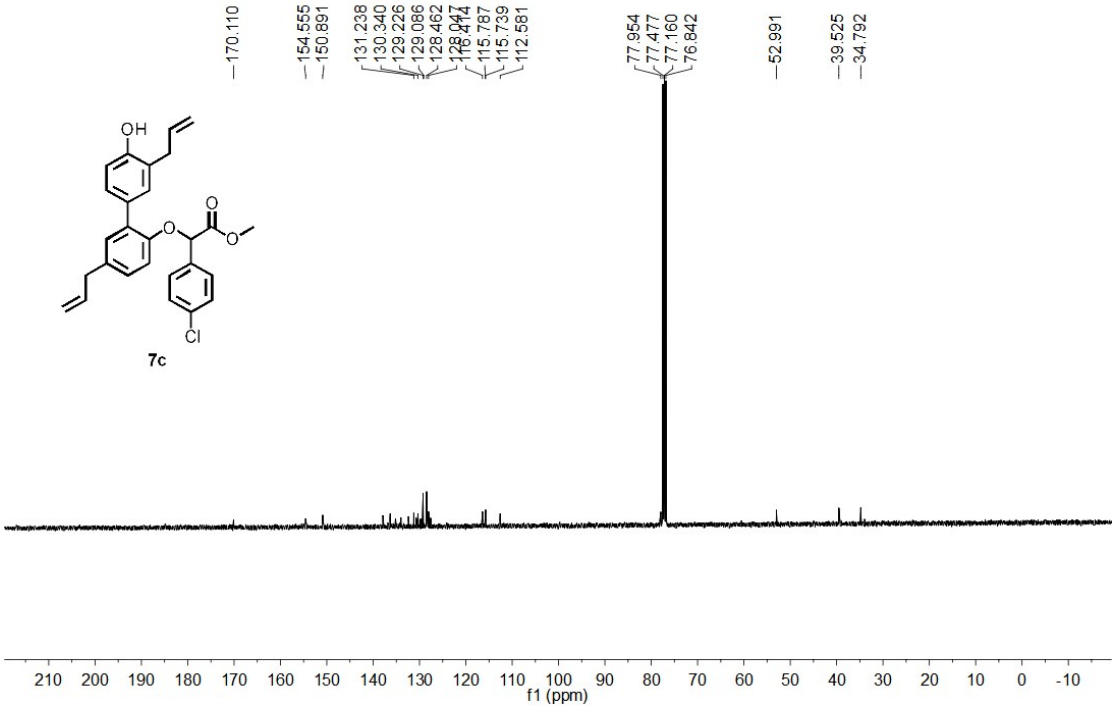
ZZP-76


173.519
169.606
154.750
150.910
136.420
131.424
131.098
130.324
129.194
129.024
128.961
128.749
127.964
127.128
126.703
118.787
116.334
115.746
77.477
76.842
66.128
39.525
34.822
OH
O
O
O
7b
f1 (ppm)

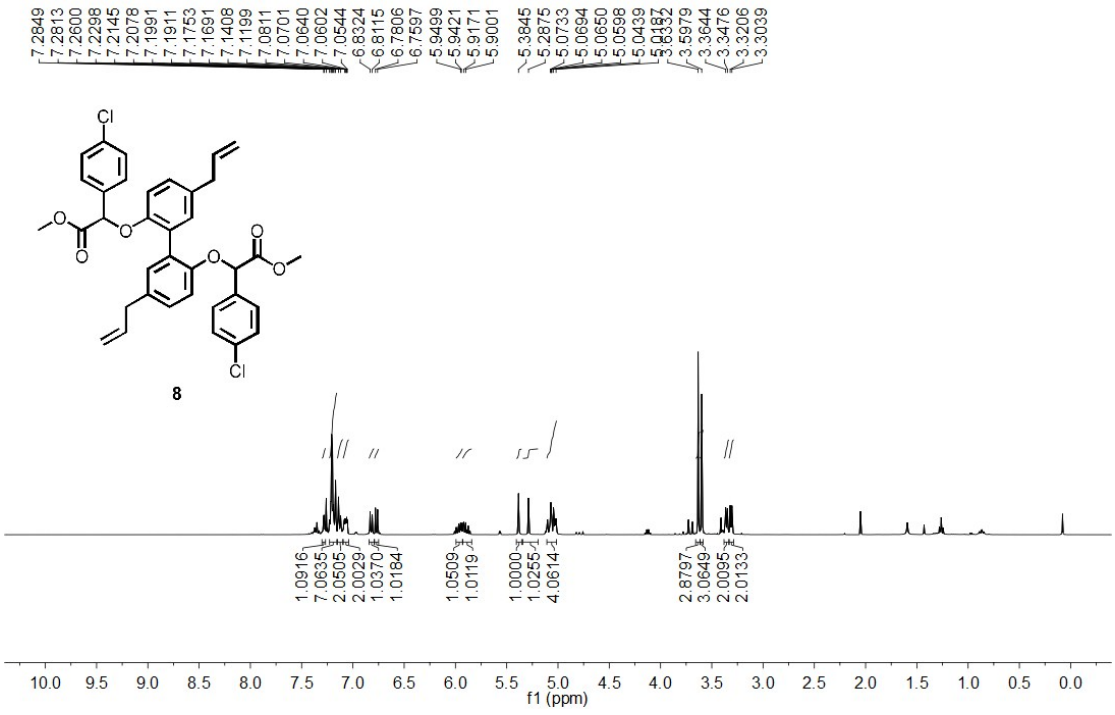
ZZP-71


7.5628
7.5417
7.4118
7.3905
7.2836
7.2781
7.2600
7.2294
7.2240
7.2085
7.2030
7.0634
7.0579
7.0429
7.0374
7.0047
6.9994
6.9027
6.8822
6.8081
6.7871
6.0554
6.0382
5.9678
5.9507
5.6671
5.1085
5.1018
5.0977
5.0939
5.0638
5.0599
5.0555
3.7512
3.5658
3.5490
3.3473
3.3304
OH
O
O
Cl
7c
2.0000
2.0917
1.0893
1.0592
1.0687
1.0621
1.0455
1.0007
1.1751
1.3623
1.0082
1.0137
4.0981
3.0192
2.0550
2.0732
f1 (ppm)

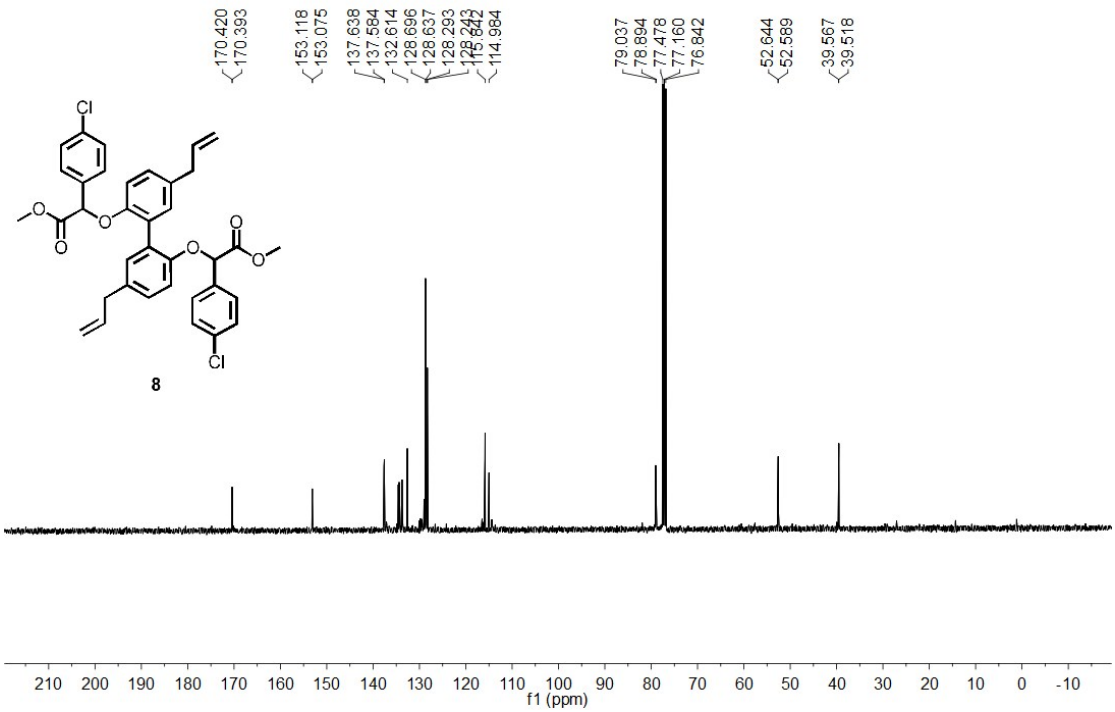
ZZP-71


170.110
154.555
150.891
131.238
130.340
129.226
129.086
128.462
116.414
115.787
115.739
112.581
77.954
77.477
77.160
76.842
52.991
39.525
34.792
OH
O
O
O
Cl
7c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

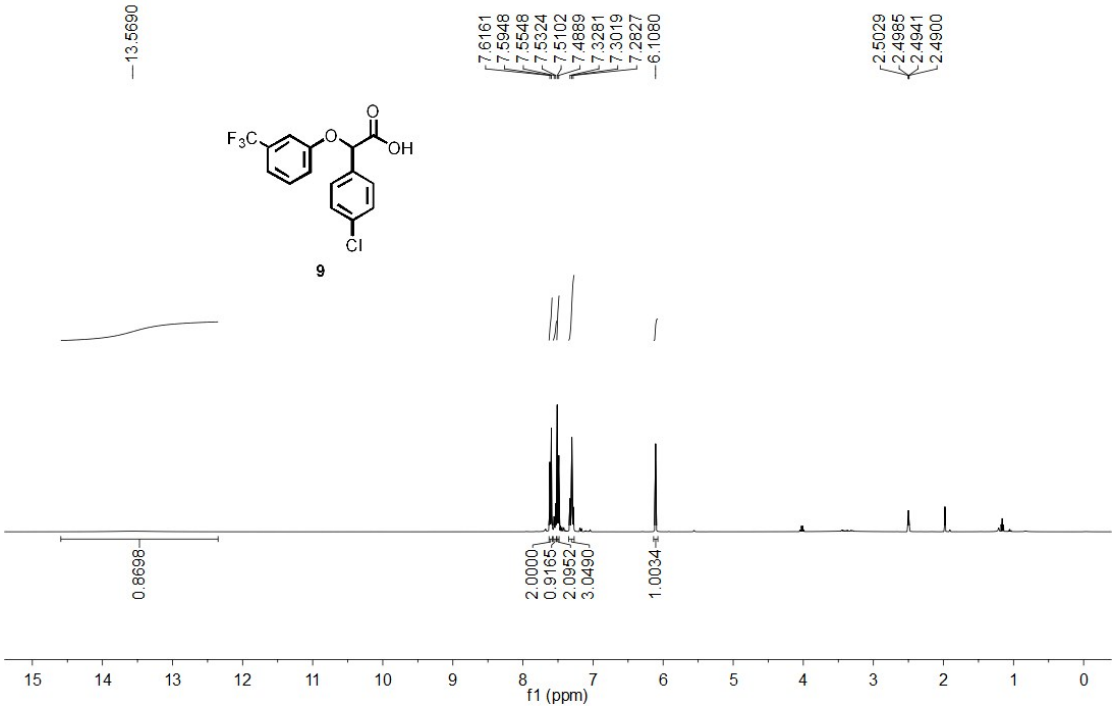
ZZP-65


7.2849
7.2813
7.2600
7.2298
7.2145
7.2078
7.1991
7.1911
7.1753
7.1691
7.1408
7.1199
7.0811
7.0701
7.0640
7.0602
7.0544
6.8324
6.8115
6.7806
6.7597
5.9499
5.9421
5.9171
5.9001
5.3845
5.2875
5.0733
5.0694
5.0650
5.0598
5.0439
3.8332
3.5979
3.3644
3.3476
3.3206
3.3039
Cl
O
O
O
O
Cl
8
1.0916
7.0635
2.0505
2.0029
1.0370
1.0184
1.0509
1.0119
1.0000
1.0255
4.0614
2.8797
3.0649
2.0095
2.0133
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

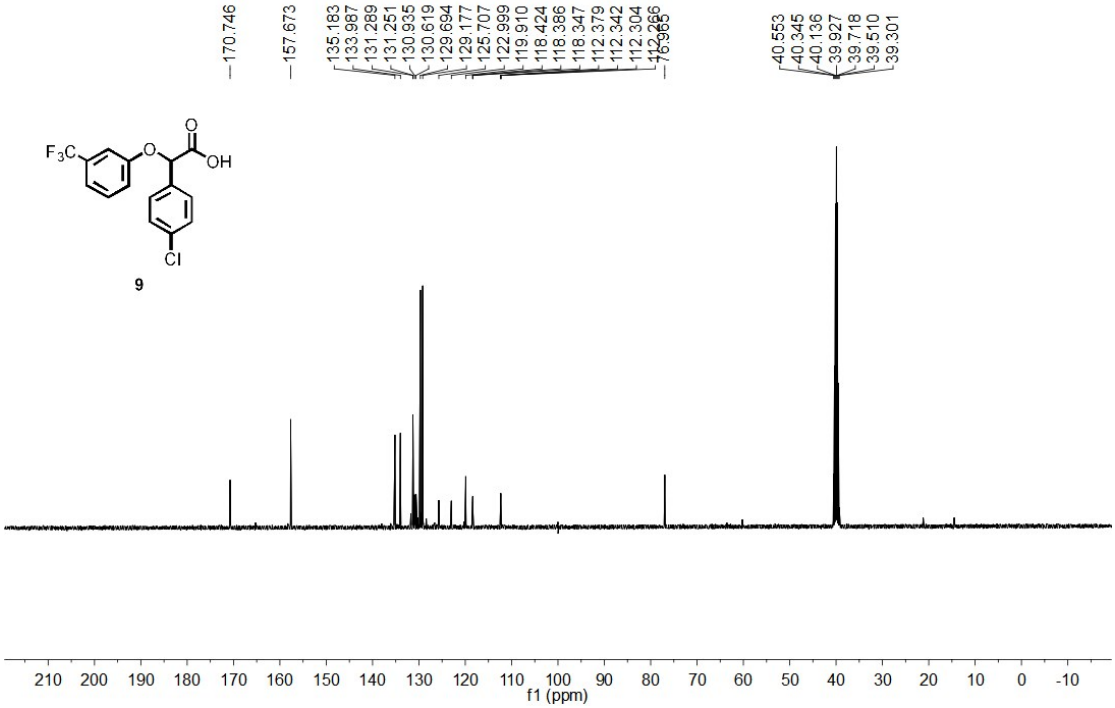
ZZP-65


170.420
170.393
153.118
153.075
137.638
137.584
132.614
128.696
128.637
128.293
115.842
114.984
79.037
78.894
77.478
77.160
76.842
52.644
52.589
39.567
39.518
Cl
O
O
O
O
O
Cl
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

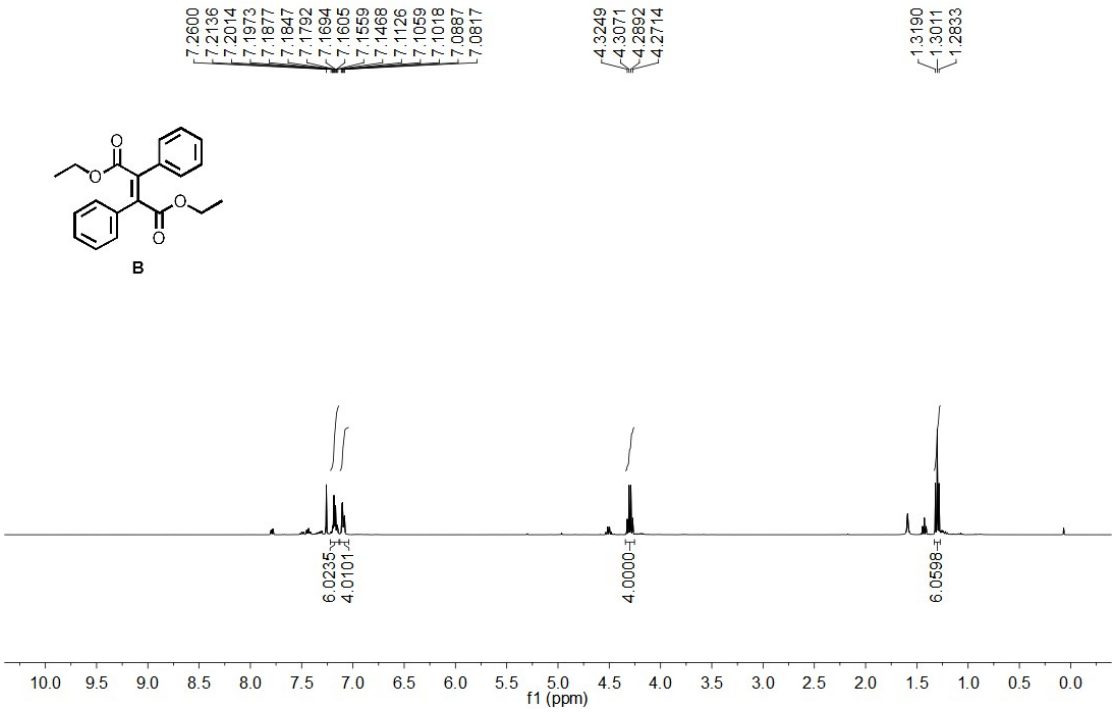
ZZP-78


13.5690
7.6161
7.5948
7.5548
7.5324
7.5102
7.4889
7.3281
7.3019
7.2827
6.1080
2.5029
2.4985
2.4941
2.4900
F3C
O
O
OH
Cl
9
0.8698
2.0000
0.9165
2.0952
3.0490
1.0034
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

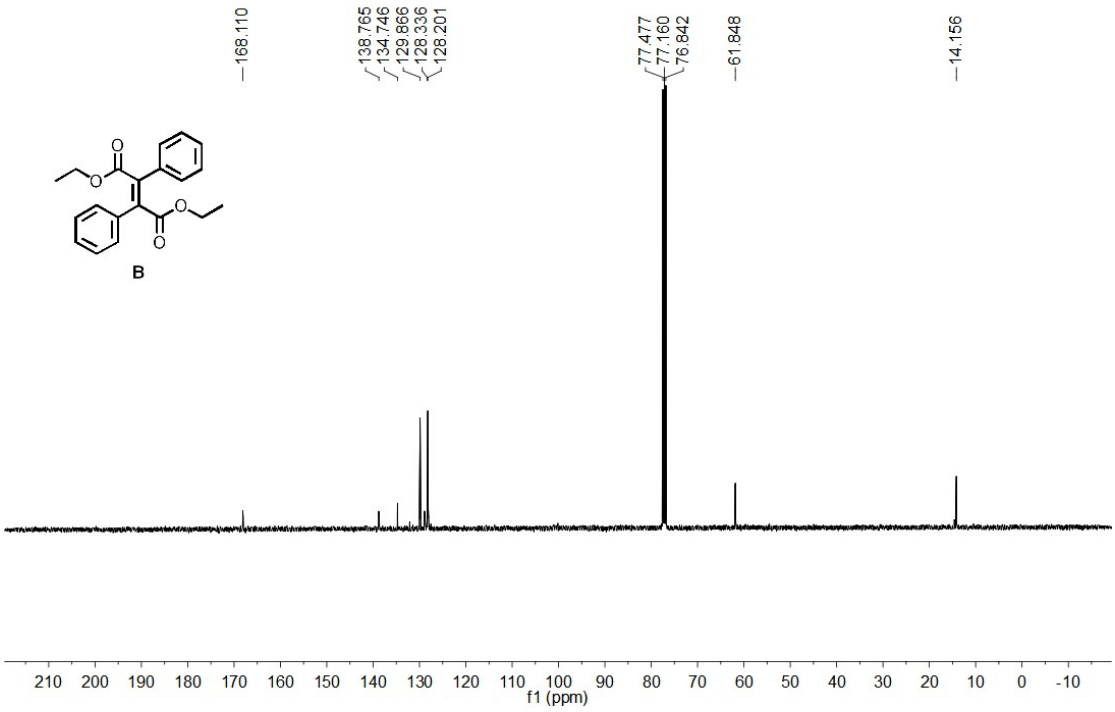
ZZP-78


170.746
157.673
135.183
133.987
131.289
131.251
130.935
130.619
129.694
129.177
125.707
122.999
119.910
118.424
118.386
118.347
112.379
112.342
112.304
40.553
40.345
40.136
39.927
39.718
39.510
39.301
F3C
O
OH
Cl
9
f1 (ppm)

ZZP-75


7.2600
7.2136
7.2014
7.1973
7.1877
7.1847
7.1792
7.1694
7.1605
7.1559
7.1468
7.1126
7.1059
7.1018
7.0887
7.0817
4.3249
4.3071
4.2892
4.2714
1.3190
1.3011
1.2833
B
6.0235
4.0101
4.0000
6.0598
f1 (ppm)

ZZP-75


168.110
138.765
134.746
129.866
128.336
128.201
77.477
77.160
76.842
61.848
14.156
B
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)