

Supporting Information for

**Brønsted acid-catalyzed homogeneous O-H and S-H insertion
reactions under metal- and ligand-free conditions**

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1. General considerations

All reactions and manipulations were performed using standard Schlenk techniques. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker DRX-400 MHz spectrometer and all chemical shift values refer to CDCl_3 ($\delta(^1\text{H})$, 7.26 ppm; $\delta(^{13}\text{C})$, 77.16 ppm), $(\text{CD}_3)_2\text{SO}$ ($\delta(^1\text{H})$, 2.50 ppm, $\delta(^{13}\text{C})$, 39.52 ppm). X-ray Crystallographic analysis was achieved by the Analysis Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The GC analysis was 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 **3b-q**,² **3v**,² **3z**,³ **3z2-z3**,⁴ **3z7**,⁵ **3z9-z12**,⁶ **3v'**,² **4a'**,⁷ **4g''**,⁸ **5k**,⁹ **7a**,¹⁰ **7c**,¹⁰ **7f**,¹¹ **7o**,¹⁰ **7p**,¹² **7s**,¹⁰ **9a**¹³ and **11a**² were known and their spectroscopic features were in good agreement with that reported in the literatures.

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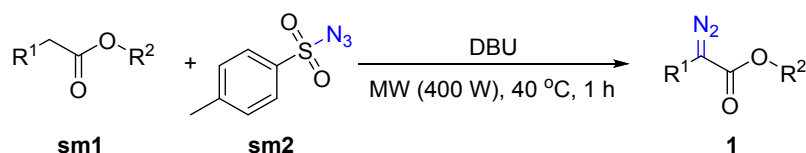
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2. Experimental procedures

2.1 Preparation for synthesis of α -diazooesters^{2,14}



A typical procedure for the synthesis of α -diazooesters 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 CH₃CN (20 mL) at 0 °C. 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 NH₄Cl (5 mL), extracted with DCM (3 × 30 mL), washed with brine (3 × 30 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give the product. The residue was purified by flash chromatography (petroleum ether (60-90 °C)/AcOEt, 10:1) to afford the corresponding ethyl-2-diazo-2-phenylacetate **1a** as a yellow oil (1.65 g, 87%).

2.2 Screening the optimum reaction conditions for the synthesis of 3a

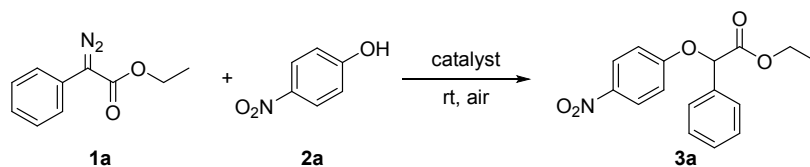


Table S1. Screening the optimum conditions for the synthesis of **3a**

Entry	Catalyst	1a:2a (equiv)	Solvent	Temp. (°C)	Yield (%)
1	—	1:1.5	DCE	rt	trace
2	HCl	1:1.5	DCE	rt	21
3	H ₂ SO ₄	1:1.5	DCE	rt	32
4	H ₃ PO ₄	1:1.5	DCE	rt	18
5	HNO ₃	1:1.5	DCE	rt	25
6	HAc	1:1.5	DCE	rt	15
7	HCOOH	1:1.5	DCE	rt	21

8	HClO ₄	1:1.5	DCE	rt	54
9	C ₆ H ₅ COOH	1:1.5	DCE	rt	19
10	C ₆ H ₅ SO ₃ H	1:1.5	DCE	rt	41
11	CF ₃ SO ₃ H	1:1.5	DCE	rt	76
12	NaOH	1:1.5	DCE	rt	26
13	KOH	1:1.5	DCE	rt	23
14	Et ₃ N	1:1.5	DCE	rt	22
15	Py	1:1.5	DCE	rt	18
16	DBU	1:1.5	DCE	rt	16
17	CF ₃ SO ₃ H ^a	1:1.5	DCE	rt	35
18	CF ₃ SO ₃ H ^b	1:1.5	DCE	rt	46
19	CF ₃ SO ₃ H ^c	1:1.5	DCE	rt	54
20	CF ₃ SO ₃ H ^d	1:1.5	DCE	rt	67
21	CF ₃ SO ₃ H	1:1.5	CH ₃ CN	rt	19
22	CF ₃ SO ₃ H	1:1.5	DMF	rt	22
23	CF ₃ SO ₃ H	1:1.5	Toluene	rt	36
24	CF ₃ SO ₃ H	1:1.5	Dioxane	rt	45
25	CF ₃ SO ₃ H	1:1.5	DCM	rt	48
26	CF ₃ SO ₃ H	1:1.5	CHCl ₃	rt	56
27	CF ₃ SO ₃ H	1:1.5	THF	rt	37
28	CF ₃ SO ₃ H	1:1.5	H ₂ O	rt	15
29	CF ₃ SO ₃ H	1:1.5	DCE	0	25
30	CF ₃ SO ₃ H	1:1.5	DCE	10	33
31	CF ₃ SO ₃ H	1:1.5	DCE	40	65
32	CF ₃ SO ₃ H	1:1.5	DCE	50	72
33 ^e	CF ₃ SO ₃ H	1:1.5	DCE	60	73
34 ^e	CF ₃ SO ₃ H	1:1.5	DCE	reflux	70
35	CF₃SO₃H	1:1.4	DCE	rt	78
36	CF ₃ SO ₃ H	1:1.3	DCE	rt	69
37	CF ₃ SO ₃ H	1:1.6	DCE	rt	75

Conditions: **1a** (0.5 mmol), **2a**, catalyst (20 mol%), solvent (5 mL), air, 20 min; symbol “-” means no catalyst, isolated yield. ^a5 mol%. ^b10 mol%. ^c15 mol%. ^d25 mol%. ^e5 min.

On the outset of this study, we chose ethyl 2-diazo-2-phenylacetate **1a** and *p*-nitrophenol **2a** as the model substrates to screen the optimum reaction conditions (Table S1). We found that the O-H insertion reaction hardly occurred in the absence of a catalyst in DCE at room temperature (entry 1). A variety of acids furnished the product **3a** (entries 2-10) with low to moderate yield (15-54%). To our delight, when CF₃SO₃H was chosen as a catalyst, the yield of **3a** obviously improved up to 76% in DCE at room temperature for 20 min (entry 11). By contrast, when bases were used as catalysts, the

desired product **3a** (entries 12-16) was got in lower yield (26%). Then, we went on to screen other reaction parameters to learn more about this catalytic system. When the amount of the CF₃SO₃H was reduced (entries 17-19) or increased (entry 20), affording the product in reduced yield. On the other hand, screening the solvent (entries 21-28) suggested that DCE was the best solvent for this transformation (entry 11). Lowering or elevating the reaction temperatures deteriorated the reaction efficiency, giving the product **3a** in diminished yield (entries 29-34). The yield was raised up to 78% when the quantity of **2a** (1.4 equiv) was decreased (entry 35), further decreasing or increasing the quantity of **2a** could not increase the yield (entry 36-37). Based on the above results, the optimum conditions for the synthesis of **3a** were identified as DCE at room temperature for 20 min, CF₃SO₃H (20 mol%) as catalyst, **1a:2a** (equiv) = 1:1.4 (entry 35).

2.3 Screening the optimum reaction conditions for the synthesis of **5a**

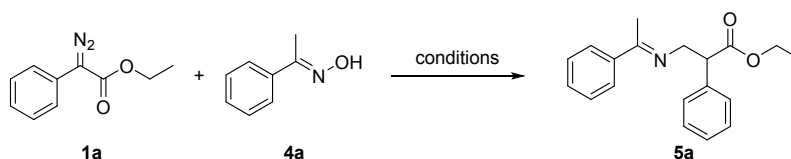


Table S2. Screening the optimum conditions for the synthesis of **5a**

Entry	Catalyst	1a:2a (equiv)	Solvent	Temp. (°C)	Yield (%)
1	CF ₃ SO ₃ H	1:1.4	DCE	rt	22
2	CF ₃ SO ₃ H	1:1.4	DCE	40	75
3	CF₃SO₃H	1:1.4	DCE	50	83
4	CF ₃ SO ₃ H	1:1.4	DCE	60	79
5	—	1:1.4	DCE	50	trace
6	HCl	1:1.4	DCE	50	30
7	H ₂ SO ₄	1:1.4	DCE	50	35
8	HNO ₃	1:1.4	DCE	50	31
9	HClO ₄	1:1.4	DCE	50	71
10	HAc	1:1.4	DCE	50	20
11	C ₆ H ₅ SO ₃ H	1:1.4	DCE	50	38
12	H ₃ PO ₄	1:1.4	DCE	50	25
13	Et ₃ N	1:1.4	DCE	50	trace
14	CF ₃ SO ₃ H ^a	1:1.4	DCE	50	35
15	CF ₃ SO ₃ H ^b	1:1.4	DCE	50	65

16	CF ₃ SO ₃ H ^c	1:1.4	DCE	50	75
17	CF ₃ SO ₃ H ^d	1:1.4	DCE	50	79
18	CF ₃ SO ₃ H	1:1.4	CH ₃ CN	50	73
19	CF ₃ SO ₃ H	1:1.4	DMF	50	15
20	CF ₃ SO ₃ H	1:1.4	CHCl ₃	50	67
21	CF ₃ SO ₃ H	1:1.5	DCE	50	80
22	CF ₃ SO ₃ H	1:1.3	DCE	50	77

Conditions: **1a** (0.5 mmol), **4a**, catalyst (20 mol%), solvent (5 mL), air, 30 min; symbol “-” means no catalyst, isolated yield. ^a5 mol%. ^b10 mol%. ^c15 mol%. ^d25 mol%.

Based on the optimized reaction conditions for O-H insertion of phenols, we optimized the reaction conditions for O-H insertion of oximes by employing ethyl 2-diazo-2-phenylacetate **1a** and (*E*)-1-phenylethan-1-one oxime **4a** as substrates (Table S2). After screening the temperature (entries 1-4), acid (entries 6-12) and base (entry 13) catalysts, the amount of acid (entries 14-17), solvent (entries 18-20), and material molar ratio (entries 21-22), we found the optimal reaction conditions for the synthesis of **5a** in DCE at 50 °C for 30 min, CF₃SO₃H (20 mol%) as catalyst, **1a**:**4a** (equiv) = 1:1.4 (entry 3).

2.4 Screening the optimum reaction conditions for the synthesis of **7a**

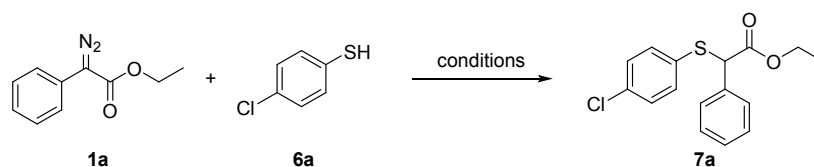


Table S3. Screening the optimum conditions for the synthesis of **7a**

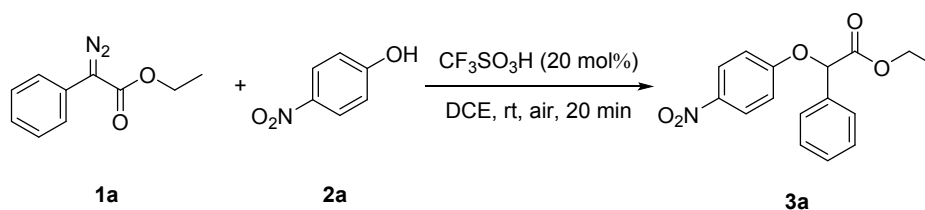
Entry	Catalyst	1a : 2a (equiv)	Solvent	Temp. (°C)	Yield (%)
1	CF₃SO₃H	1:1.4	DCE	rt	84
2	CF ₃ SO ₃ H	1:1.4	DCE	0	57
3	CF ₃ SO ₃ H	1:1.4	DCE	40	77
4	—	1:1.4	DCE	rt	trace
5	HCl	1:1.4	DCE	rt	35
6	H ₂ SO ₄	1:1.4	DCE	rt	38
7	HNO ₃	1:1.4	DCE	rt	33
8	HClO ₄	1:1.4	DCE	rt	75
9	HAc	1:1.4	DCE	rt	28

10	C ₆ H ₅ SO ₃ H	1:1.4	DCE	rt	39
11	H ₃ PO ₄	1:1.4	DCE	rt	31
12	Et ₃ N	1:1.4	DCE	rt	17
13	CF ₃ SO ₃ H ^a	1:1.4	DCE	rt	47
14	CF ₃ SO ₃ H ^b	1:1.4	DCE	rt	69
15	CF ₃ SO ₃ H ^c	1:1.4	DCE	rt	77
16	CF ₃ SO ₃ H ^d	1:1.4	DCE	rt	81
17	CF ₃ SO ₃ H	1:1.4	CH ₃ CN	rt	78
18	CF ₃ SO ₃ H	1:1.4	DMF	rt	29
19	CF ₃ SO ₃ H	1:1.4	CHCl ₃	rt	73
20	CF ₃ SO ₃ H	1:1.5	DCE	rt	82
21	CF ₃ SO ₃ H	1:1.3	DCE	rt	79

Conditions: **1a** (0.5 mmol), **6a**, catalyst (20 mol%), solvent (5 mL), air, 5 min; symbol “-” means no catalyst, isolated yield. ^a5 mol%. ^b10 mol%. ^c15 mol%. ^d25 mol%.

Based on the optimized reaction conditions for O-H insertion of phenols and oximes, we optimized the reaction conditions for S-H insertion of thiols by employing ethyl 2-diazo-2-phenylacetate **1a** and 4-chlorobenzenethiol **6a** as substrates (Table S3). After screening the temperature (entries 1-3), acid (entries 5-11) and base (entry 12) catalysts, the amount of acid (entries 13-16), solvent (entries 17-19), and material molar ratio (entries 20-21), the optimum conditions for the synthesis of **7a** were identified as DCE at room temperature for 5 min, CF₃SO₃H (20 mol%) as catalyst, **1a**:**6a** (equiv) = 1:1.4 (entry 1).

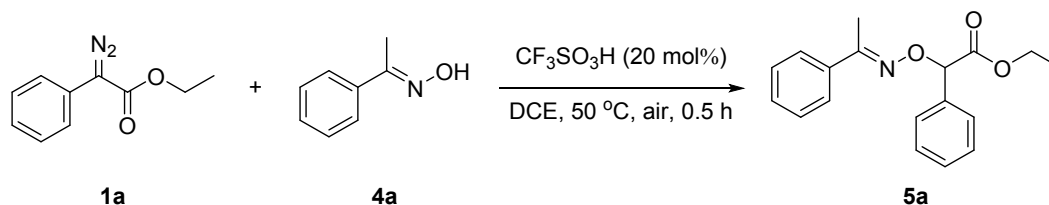
2.5 Typical procedure for O-H insertion of phenols and alcohols



A typical procedure for the synthesis of O-H insertion products (3) – Synthesis of 3a: A mixture of CF₃SO₃H (20 mol%), 4-nitrophenol (**2a**, 97 mg, 0.7 mmol) and ethyl 2-diazo-2-phenylacetate (**1a**, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under air for 20 min. Then, the crude product was got by removing

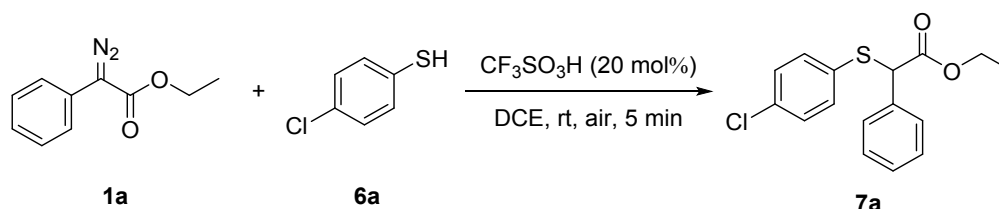
solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding **3a** as a colorless oil (117 mg, 78%).

2.6 Typical procedure for O-H insertion of oximes



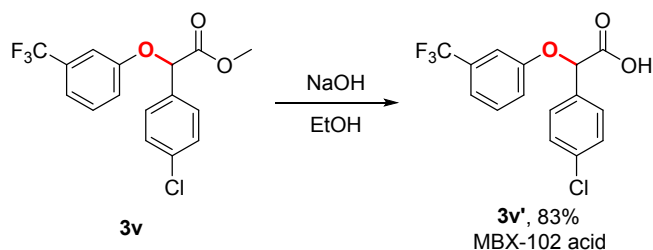
A typical procedure for the synthesis of O-H insertion products of oximes (**5**) – **Synthesis of 5a**: A mixture of $\text{CF}_3\text{SO}_3\text{H}$ (20 mol%), (E)-1-phenylethan-1-one oxime (**4a**, 95 mg, 0.7 mmol) and ethyl 2-diazo-2-phenylacetate (**1a**, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at 50 °C under air for 0.5 h. After the reaction mixture was cooled to room temperature, removing solvent under reduced pressure to get the crude product. The crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding **5a** as a colorless oil (123 mg, 83%).

2.7 Typical procedure for S-H insertion of thiols



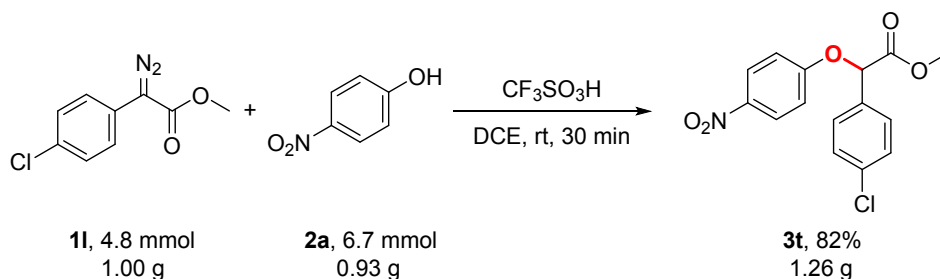
A typical procedure for the synthesis of S-H insertion products of thiols (**7**) – **Synthesis of 7a**: A mixture of $\text{CF}_3\text{SO}_3\text{H}$ (20 mol%), 4-chlorobenzenethiol (**6a**, 101 mg, 0.7 mmol) and ethyl 2-diazo-2-phenylacetate (**1a**, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under air for 5 min. Then, the crude product was got by removing solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding **7a** as a colorless oil (129 mg, 84%).

2.8 The synthesis of MBX-102 acid **3v'**

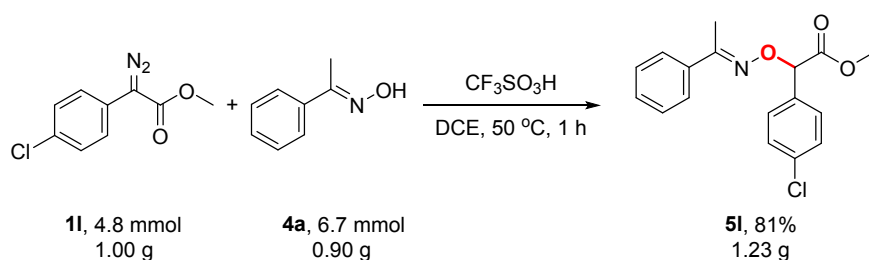


Synthesis of 3v': A mixture of **3v** (172 mg, 0.5 mmol) and NaOH (36 mg, 0.9 mmol) in EtOH (5 mL) was stirred at 90 °C reflux for 8 h. After the reaction was judged to be completed by TLC, adding slowly the 1 M HCl until the PH of reaction mixture reached 3-4. Then, 15 mL H₂O was added to the mixture. The aqueous layer was extracted with ethyl acetate (3 × 20 mL), washed with brine (3 × 20 mL), dried over anhydrous Na₂SO₄, concentrated under reduced pressure to give the crude product. The crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (2:1) to afford the corresponding **3v'** as a white syrup (137 mg, 83%).

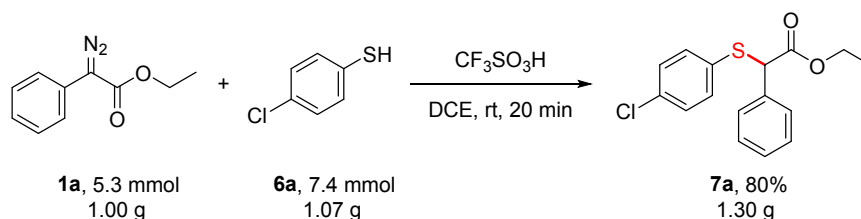
2.9 A gram-scale experiment



1 gram-scale experiment for the synthesis of 3t: A mixture of CF₃SO₃H (20 mol%), 4-nitrophenol (**2a**, 0.93 g, 6.7 mmol) and methyl 2-(4-chlorophenyl)-2-diazoacetate (**11**, 1.00 g, 4.8 mmol) in DCE (48 mL) was stirred at room temperature under air for 30 min. Then, the crude product was got by removing solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding **3t** as a white solid (1.26 g, 82%).

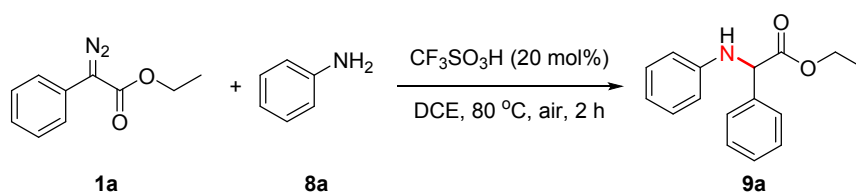


1 gram-scale experiment for the synthesis of 5i: A mixture of CF₃SO₃H (20 mol%), (*E*)-1-phenylethan-1-one oxime (**4a**, 0.90 g, 6.7 mmol) and methyl 2-(4-chlorophenyl)-2-diazoacetate (**11**, 1.00 g, 4.8 mmol) in DCE (48 mL) was stirred at 50 °C under air for 1 h. After the reaction mixture was cooled to room temperature, removing solvent under reduced pressure to get the crude product. The crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding **5i** as a white solid (1.23 g, 81%).



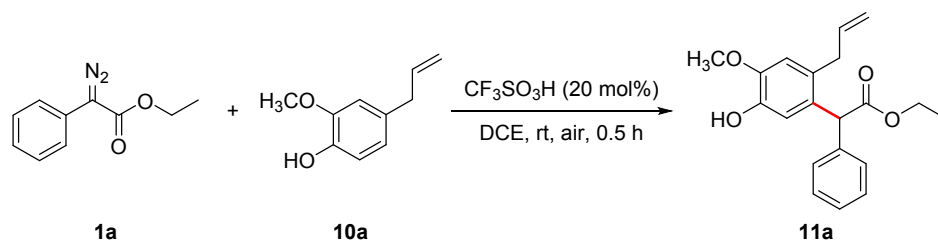
1 gram-scale experiment for the synthesis of 7a: A mixture of CF₃SO₃H (20 mol%), 4-chlorobenzenethiol (**6a**, 1.07 g, 7.4 mmol) and ethyl 2-diazo-2-phenylacetate (**1a**, 1.00 g, 5.3 mmol) in DCE (53 mL) was stirred at room temperature under air for 20 min. Then, the crude product was got by removing solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding **7a** as a colorless oil (1.30 g, 80%).

2.10 A typical procedure for the synthesis of N-H insertion product 9a



Synthesis of 9a: A mixture of CF₃SO₃H (20 mol%), aniline (**8a**, 65 mg, 0.7 mmol) and ethyl 2-diazo-2-phenylacetate (**1a**, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at 80 °C under air for 2 h. After the reaction mixture was cooled to room temperature, removing solvent under reduced pressure to get the crude product. The crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding **9a** as a colorless oil (77 mg, 60%).

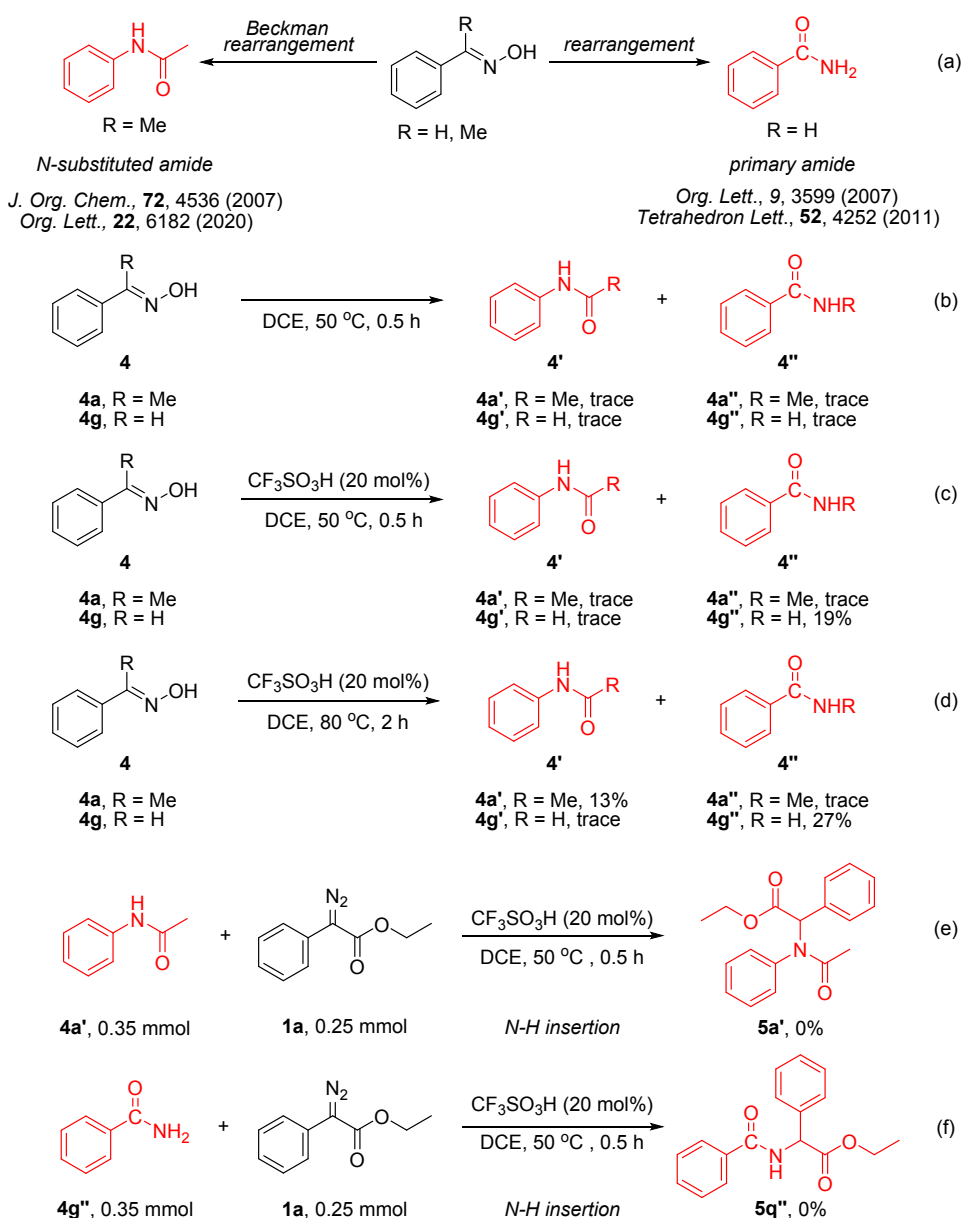
2.11 A typical procedure for the synthesis of C-H insertion product 11a



Synthesis of 11a: A mixture of $\text{CF}_3\text{SO}_3\text{H}$ (20 mol%), 4-allyl-2-methoxyphenol (**10a**, 115 mg, 0.7 mmol) and ethyl 2-diazo-2-phenylacetate (**1a**, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under air for 0.5 h. Then, the crude product was got by removing solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding **11a** as a colorless oil (99 mg, 61%).

3. Control experiments

As Shown in Scheme S1, ketoximes and aldoximes are prone to rearrangement¹⁵ and give amide products (including N-substituted amide^{15e-f} and primary amide^{15g-h}) (Scheme S1a). Based on the control experiments, acid-free, ketoxime **4a** and aldoxime **4g** did not give the rearrangement products (Scheme S1b). Under the standard conditions, **4g** was easy to rearrange and furnish the primary amide product **4g''** in 19% yield (Scheme S1c). Furthermore, increasing the temperature to 80 °C and prolonging the reaction time to 2 h, **4a** could provide the Beckmann rearrangement product **4a'** (N-substituted amide) in 13% yield, and **4g** afforded the primary amide product **4g''** in 27% yield (Scheme S1d). Significantly, the N-substituted amide product **4a'** and the primary amide product **4g''** both could not afford the N-H insertion products **5a'** or **5q''** in this catalytic system (Scheme S1e-f). Combined with the above results, we could infer that the rearrangement of aldoximes lead to the O-H insertion in reduced yield.



Scheme S1 Control experiments

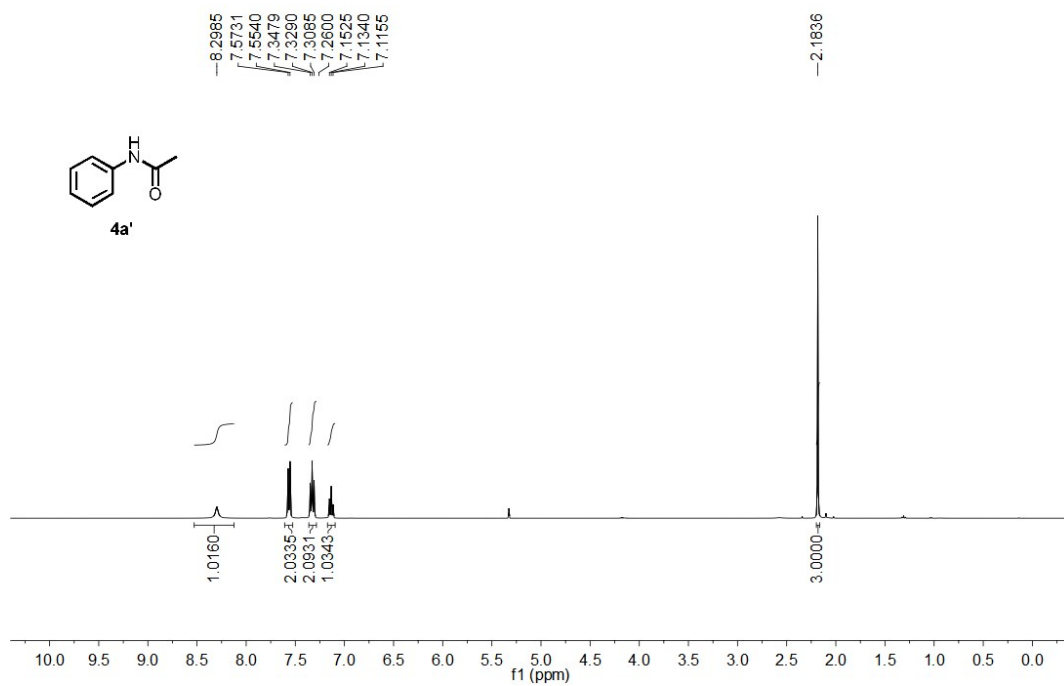
References

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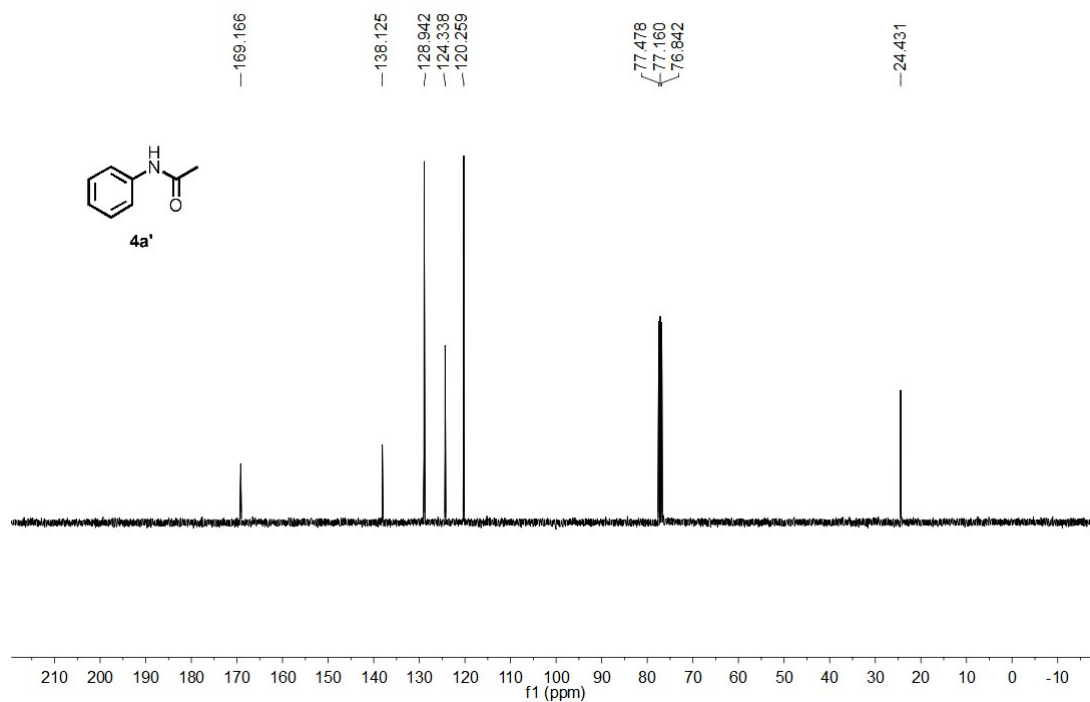
Lawrence, M. J. Bamford, A. A. Lapkin, P. Plucinski, R. J. Watson and J. M. J. Williams, *Tetrahedron Lett.*, 2011, **52**, 4252.

Copies of NMR spectra

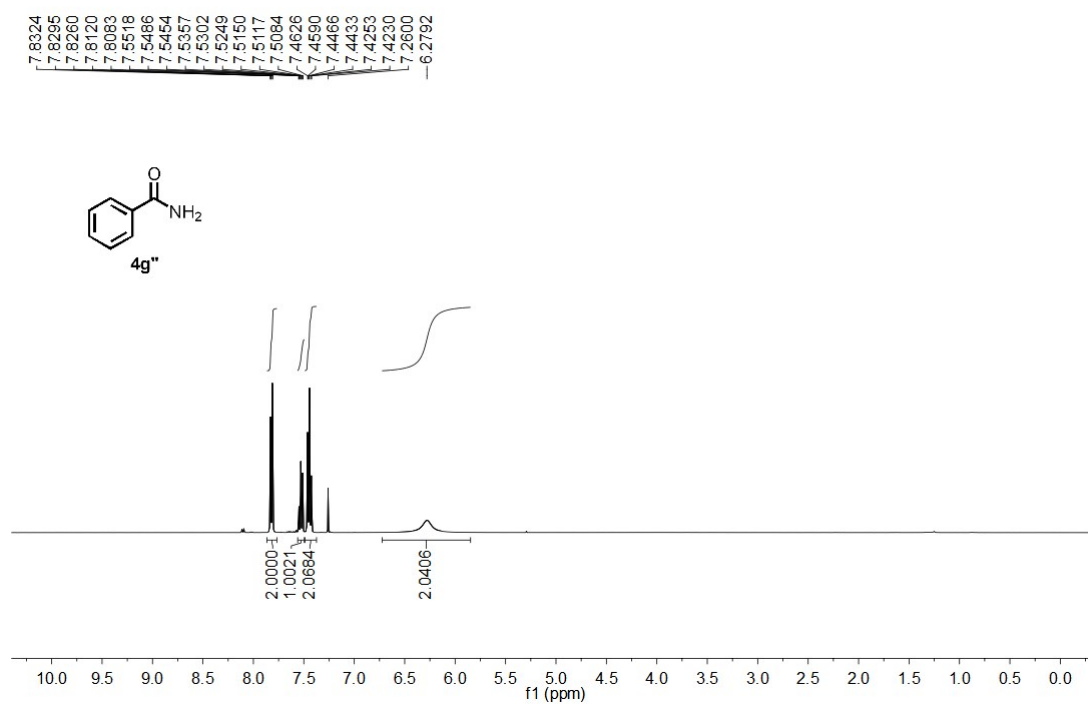
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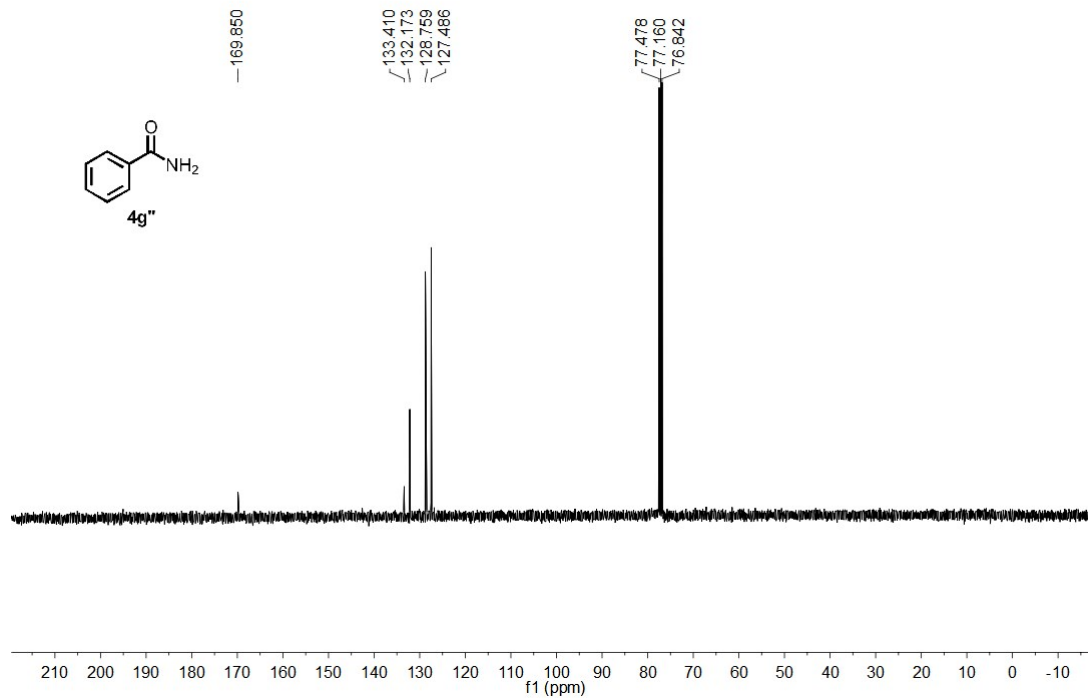
ZZP-554-8



ZZP-550-8



ZZP-550-8



4. X-Ray crystallographic studies

Single crystals of compounds **3t** and **5l** were grown in petroleum ether (60-90 °C)/CH₂Cl₂ (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 ($\lambda = 0.71073 \text{ \AA}$). 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 1975821 for **3t** and CCDC 1996648 for **5l**. 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>).

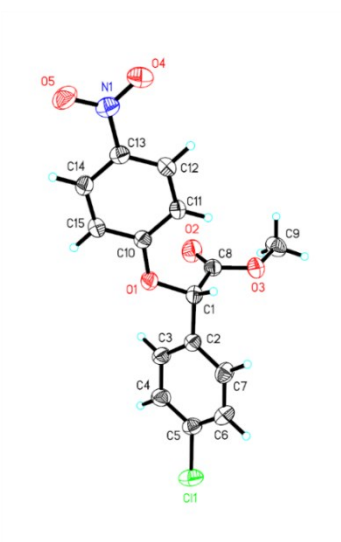


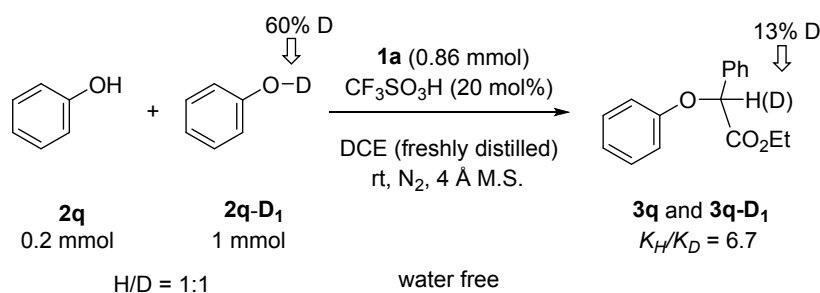
Figure S1. Molecular structure of compound **3t**

Table S4. Crystal data and structure refinement for **3t**

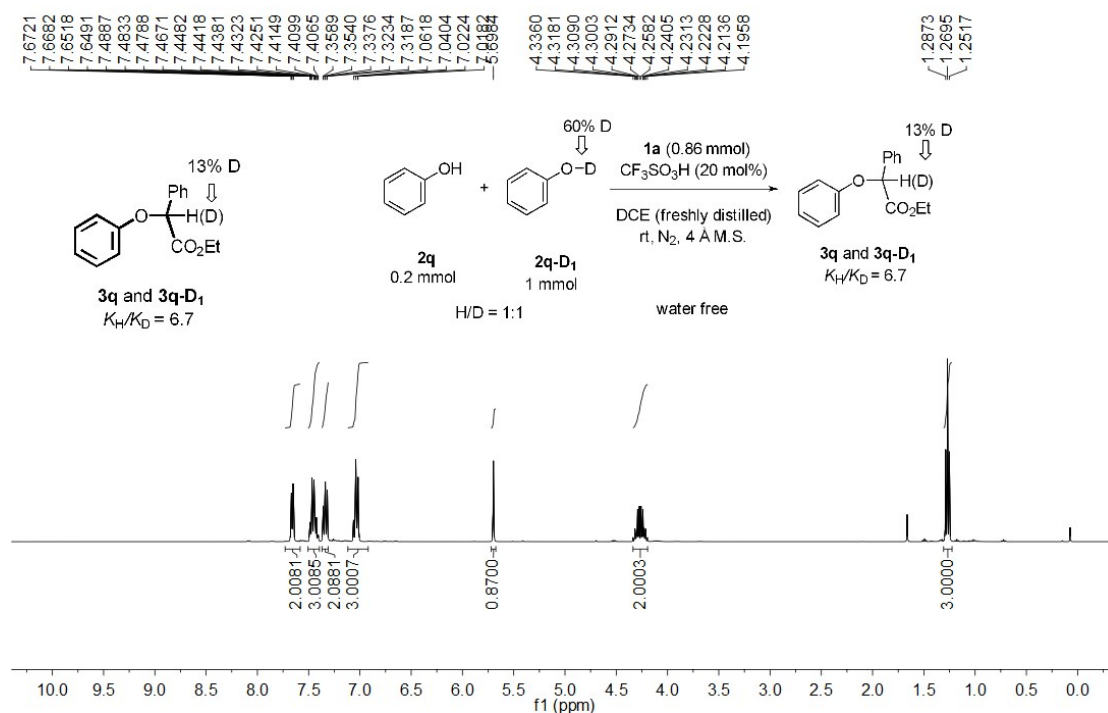
Empirical formula	$C_{15}H_{12}ClNO_5$	
Formula weight	321.71	
Temperature	293(2) K	
Wavelength	0.71073 \AA	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	$a = 16.5109(15) \text{ \AA}$	$\square\alpha = 90^\circ$
	$b = 8.7483(6) \text{ \AA}$	$\square\beta = 102.690(3)^\circ$
	$c = 10.4253(8) \text{ \AA}$	$\square\gamma = 90^\circ$

Volume	1589.03(8) Å ³
Z, Calculated density	4, 1.328 Mg/m ³
Absorption coefficient	0.252 mm ⁻¹
F(000)	664
Crystal size	0.180 x 0.160 x 0.140 mm ³
Theta range for data collection	2.985 to 25.999°
Index ranges	-17<=h<=18, -7<=k<=7, -23<=l<=21
Reflections collected	22988
Independent reflections	3101 [R(int) = 0.0293]
Completeness to theta = 25.242°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6449
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	3101 / 0 / 202
Goodness-of-fit on F ²	1.031
Final R indices [I > 2 sigma(I)]	R ¹ = 0.0386, wR ² = 0.1051
R indices (all data)	R ¹ = 0.0458, wR ² = 0.1123
Largest diff. peak and hole	0.236 and -0.200 e.Å ⁻³

5. Kinetic isotope effect of the O-H insertion reaction



A mixture of phenol (**2q**, 18.8 mg, 0.2 mmol, **2q-D₁**, 95.1 mg, 1 mmol), CF₃SO₃H (20 mol%), 4 Å M.S. (100 mg) and ethyl 2-diazo-2-phenylacetate (**1a**, 163.5 mg, 0.86 mmol) in DCE (5 mL, freshly distilled) was stirred at room temperature under N₂ for 20 min. Then, the crude product was got by removing solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford corresponding insertion product and conducted a ¹H NMR analysis to determine the H/D ratio.



6. NMR titration experiments

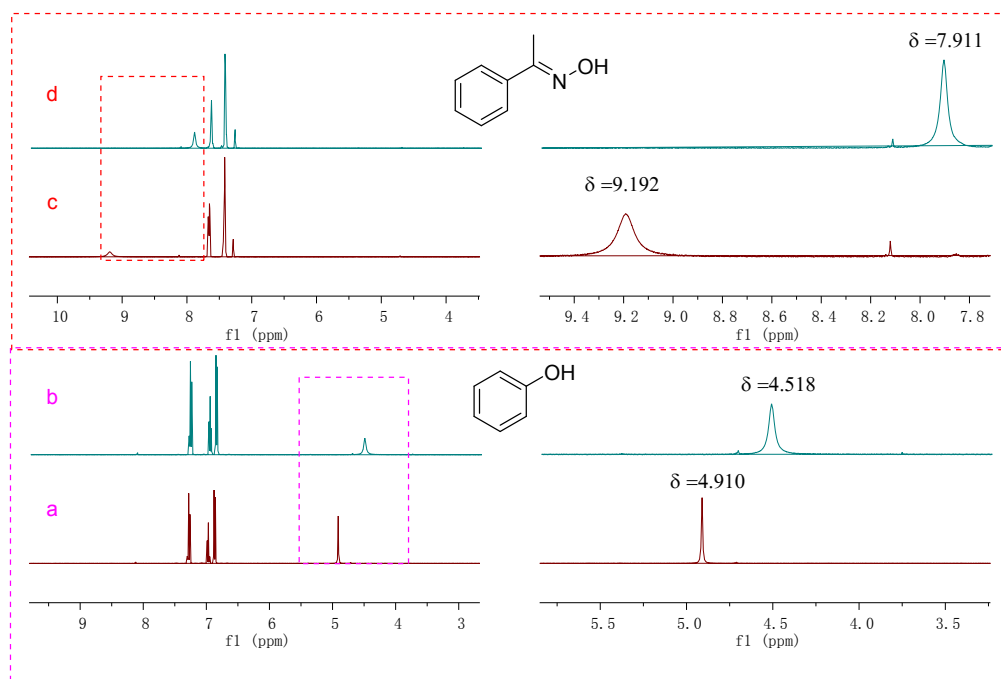
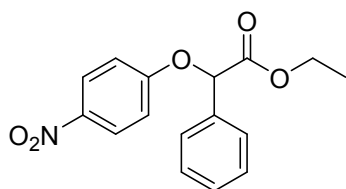


Figure S3. ^1H NMR spectra of the phenol and (*E*)-1-phenylethan-1-one oxime signals in CDCl_3 . (a) phenol (0.35 mmol), (b) phenol (0.35 mmol) with $\text{CF}_3\text{SO}_3\text{H}$ (10 mol%). (c) (*E*)-1-phenylethan-1-one oxime (0.35 mmol), (d) (*E*)-1-phenylethan-1-one oxime (0.35 mmol) with $\text{CF}_3\text{SO}_3\text{H}$ (10 mol%),

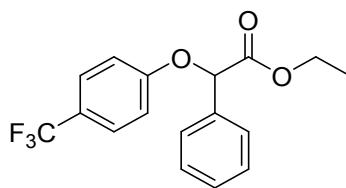
¹H-NMR titration experiments.

The preparation of mother liquor: (a) phenol (0.35 mmol), (b) phenol (0.35 mmol) with CF₃SO₃H (10 mol%), (c) (*E*)-1-phenylethan-1-one oxime (0.35 mmol), (d) (*E*)-1-phenylethan-1-one oxime (0.35 mmol) with CF₃SO₃H (10 mol%) were added in CDCl₃ (2.5 mL), respectively and stirred at room temperature under 0.1 Mpa air for 20 min. Then, the mother liquor of (a) 100 μL, (b) 100 μL, (c) 100 μL, (d) 100 μL were moved in CDCl₃ (0.5 mL), respectively. Last, conducted a ¹H NMR analysis to show the ¹H of OH in phenol and (*E*)-1-phenylethan-1-one oxime, as shown in Fig. S3.

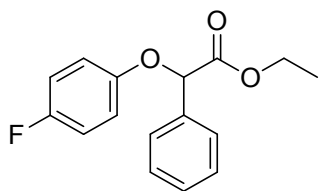
7. Analytical Data for known compounds



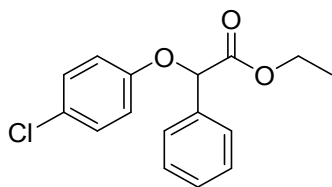
Ethyl 2-(4-nitrophenoxy)-2-phenylacetate (3a): Colorless oil; 78% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.25–8.11 (m, 2H), 7.57 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.46–7.36 (m, 3H), 7.07–6.96 (m, 2H), 5.72 (s, 1H), 4.32–4.12 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 168.79, 162.15, 142.26, 134.29, 129.50, 129.05, 127.15, 125.95, 115.46, 78.90, 77.48, 77.16, 76.84, 62.14, 14.05.



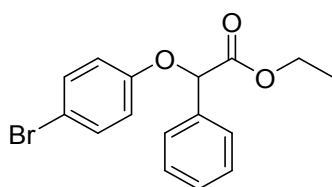
Ethyl 2-phenyl-2-(4-(trifluoromethyl)phenoxy)acetate (3b): Colorless oil; 80% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, *J* = 7.6, 1.3 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.46–7.36 (m, 3H), 7.02 (d, *J* = 8.6 Hz, 2H), 5.67 (s, 1H), 4.30–4.14 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) 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, 78.71, 62.03, 14.13.



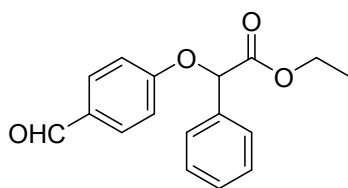
Ethyl 2-(4-fluorophenoxy)-2-phenylacetate (3c): Yellow oil; 74% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dd, $J = 7.7, 1.4$ Hz, 2H), 7.45–7.34 (m, 3H), 7.00–6.87 (m, 4H), 5.55 (s, 1H), 4.27–4.13 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 169.90, 157.95 (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.



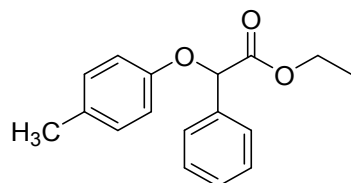
Ethyl 2-(4-chlorophenoxy)-2-phenylacetate (3d): Colorless oil; 77% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.56 (dd, $J = 7.6, 1.4$ Hz, 2H), 7.44–7.34 (m, 3H), 7.22 (d, $J = 9.0$ Hz, 2H), 6.89 (d, $J = 9.0$ Hz, 2H), 5.57 (s, 1H), 4.27–4.12 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 169.70, 155.98, 135.19, 129.59, 129.22, 128.96, 127.17, 126.88, 116.97, 79.04, 61.90, 14.15.



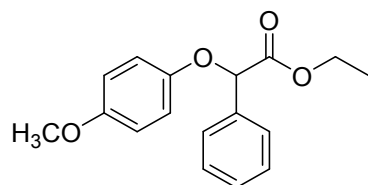
Ethyl 2-(4-bromophenoxy)-2-phenylacetate (3e): Colorless oil; 72% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dd, $J = 7.6, 1.6$ Hz, 2H), 7.42–7.35 (m, 5H), 6.92–6.79 (m, 2H), 5.58 (s, 1H), 4.29–4.13 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 169.66, 156.50, 135.16, 132.54, 129.24, 128.97, 127.18, 117.46, 114.25, 78.96, 61.93, 14.17.



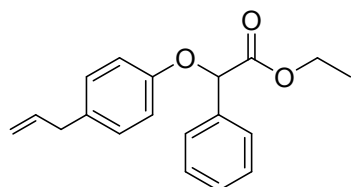
Ethyl 2-(4-formylphenoxy)-2-phenylacetate (3f): Colorless oil; 61% yield; ^1H NMR (400 MHz, CDCl_3) δ 9.88 (s, 1H), 7.83 (d, $J = 8.8$ Hz, 2H), 7.58 (dd, $J = 7.6, 1.5$ Hz, 2H), 7.45–7.37 (m, 3H), 7.06 (d, $J = 8.7$ Hz, 2H), 5.71 (s, 1H), 4.28–4.15 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.88, 169.23, 162.24, 134.69, 132.12, 130.83, 129.44, 129.07, 127.21, 115.73, 78.70, 62.11, 14.15.



Ethyl 2-phenyl-2-(*p*-tolylloxy) acetate (3g): Colorless oil; 60% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (dd, $J = 7.9, 1.5$ Hz, 2H), 7.42–7.33 (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 NMR (100 MHz, CDCl_3) δ 170.21, 155.37, 135.81, 131.21, 130.11, 128.97, 128.85, 127.19, 115.54, 79.02, 61.69, 20.63, 14.17.

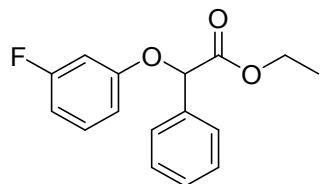


Ethyl 2-(4-methoxyphenoxy)-2-phenylacetate (3h): Colorless oil; 51% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (dd, $J = 7.8, 1.4$ Hz, 2H), 7.43–7.33 (m, 3H), 6.95–6.89 (m, 2H), 6.84–6.78 (m, 2H), 5.55 (s, 1H), 4.28–4.13 (m, 2H), 3.75 (s, 3H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.19, 154.69, 151.55, 135.86, 128.94, 128.79, 127.16, 116.98, 114.72, 79.80, 61.62, 55.69, 14.12.

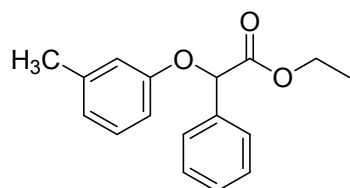


Ethyl 2-(4-allylphenoxy)-2-phenylacetate (3i): Colorless oil; 90% yield; ^1H NMR (400 MHz, CDCl_3) ^1H NMR (400 MHz, CDCl_3) δ 7.59 (dd, $J = 7.8, 1.4$ Hz, 2H), 7.43–7.34 (m, 3H), 7.09 (d, $J = 8.7$ Hz, 2H), 6.93–6.87 (m, 2H), 5.94 (dd, $J = 17.7, 9.3$ Hz, 1H), 5.60 (s, 1H), 5.09–5.05 (m, 1H), 5.03 (t, $J = 1.4$ Hz, 1H), 4.28–4.13 (m, 2H), 3.32

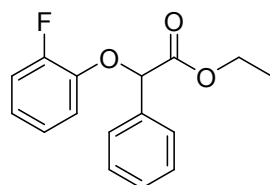
(d, $J = 6.7$ Hz, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.13, 155.88, 137.76, 135.75, 133.40, 129.70, 128.99, 128.85, 127.18, 115.71, 115.61, 78.96, 61.71, 39.45, 14.16.



Ethyl 2-(3-fluorophenoxy)-2-phenylacetate (3j): Colorless oil; 72% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dd, $J = 7.8, 1.4$ Hz, 2H), 7.43–7.37 (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), 4.26–4.13 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ 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.

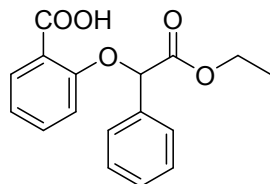


Ethyl 2-phenyl-2-(*m*-tolylloxy) acetate (3k): Colorless oil; 59% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (dd, $J = 7.8, 1.3$ Hz, 2H), 7.44–7.34 (m, 3H), 7.16 (t, $J = 7.8$ Hz, 1H), 6.81 (d, $J = 8.1$ Hz, 2H), 6.75 (dd, $J = 8.3, 2.2$ Hz, 1H), 5.63 (s, 1H), 4.29–4.13 (m, 2H), 2.32 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.17, 157.47, 139.77, 135.71, 129.36, 128.99, 128.85, 127.17, 122.73, 116.56, 112.19, 78.67, 61.71, 21.63, 14.16.

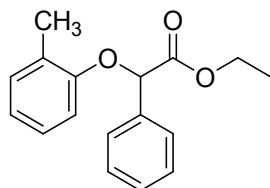


Ethyl 2-(2-fluorophenoxy)-2-phenylacetate (3l): Colorless oil; 66% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (dd, $J = 7.7, 1.6$ Hz, 2H), 7.44–7.35 (m, 3H), 7.13–7.06 (m, 1H), 7.03–6.92 (m, 3H), 5.64 (s, 1H), 4.25–4.16 (m, 2H), 1.20 (t, $J = 7.1$ Hz, 3H).

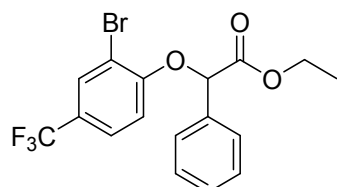
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 169.66, 153.42 (d, $J = 246.9$ Hz), 145.31 (d, $J = 10.6$ Hz), 135.29, 129.19, 128.87, 127.28, 124.36 (d, $J = 3.9$ Hz), 122.94 (d, $J = 7.0$ Hz), 117.78, 116.79 (d, $J = 18.4$ Hz), 80.26, 61.81, 14.12.



2-(2-ethoxy-2-oxo-1-phenylethoxy) benzoic acid (3m): Colorless oil; 90% yield; ^1H NMR (400 MHz, CDCl_3) δ 10.44 (s, 1H), 7.99 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.58 (dd, $J = 7.3, 2.2$ Hz, 2H), 7.51–7.41 (m, 4H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.94–6.88 (m, 1H), 6.14 (s, 1H), 4.30–4.16 (m, 2H), 1.24 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 169.42, 168.45, 161.96, 136.40, 133.63, 130.45, 129.60, 129.06, 127.76, 119.50, 117.78, 111.91, 75.28, 62.11, 14.14.

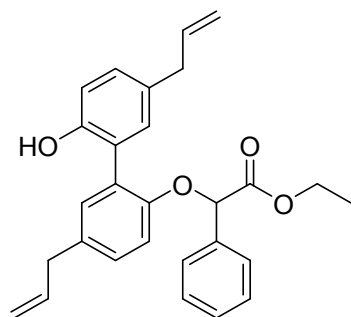


Ethyl 2-phenyl-2-(*o*-tolylloxy) acetate (3n): Colorless oil; 57% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (dd, $J = 7.9, 1.2$ Hz, 2H), 7.44–7.35 (m, 3H), 7.18 (dd, $J = 7.3, 0.7$ Hz, 1H), 7.14–7.06 (m, 1H), 6.94–6.87 (m, 1H), 6.76 (d, $J = 8.1$ Hz, 1H), 5.65 (s, 1H), 4.26–4.10 (m, 2H), 2.38 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.25, 155.70, 136.02, 131.17, 128.91, 128.80, 127.86, 127.03, 126.78, 121.59, 112.17, 78.78, 61.64, 16.57, 14.12.



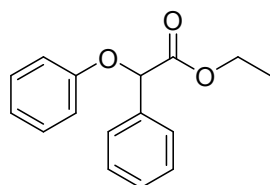
Ethyl 2-(2-bromo-4-(trifluoromethyl)phenoxy)-2-phenylacetate (3o): White solid, m.p.: 71–73 °C; 64% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 1.8$ Hz, 1H), 7.65 (dd, $J = 7.7, 1.6$ Hz, 2H), 7.51–7.37 (m, 4H), 6.87 (d, $J = 8.6$ Hz, 1H), 5.72 (s, 1H), 4.27–4.14 (m, 2H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ 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, 127.06, 125.86 (q, $J = 3.8$ Hz), 125.18 (q, $J = 33.4$ Hz), 123.45 (q, $J = 271.9$ Hz), 113.69, 113.30, 79.45, 62.17, 14.11.

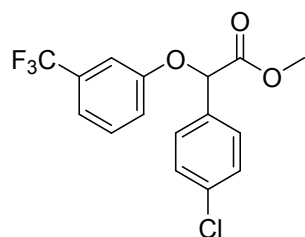


Ethyl 2-((5,5'-diallyl-2'-hydroxy-[1,1'-biphenyl]-2-yl) oxy)-2-phenylacetate (3p):

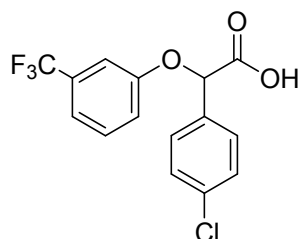
White solid, m.p.: 74-76 °C.; 88% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, $J = 6.5, 3.0$ Hz, 2H), 7.33 (dd, $J = 5.0, 1.6$ Hz, 3H), 7.20–7.09 (m, 3H), 7.03 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 1H), 6.01 (dd, $J = 13.3, 6.1$ Hz, 1H), 5.96 (dd, $J = 13.4, 6.1$ Hz, 1H), 5.75 (s, 1H), 5.20–4.97 (m, 4H), 4.30–4.11 (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). $^{13}\text{C}\{^1\text{H}\}$ 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, 128.06, 127.29, 125.79, 117.40, 116.12, 115.57, 78.06, 62.55, 39.56, 39.47, 14.07.



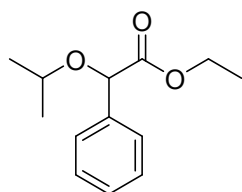
Ethyl 2-phenoxy-2-phenylacetate (3q): Colorless oil; 68% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (dd, $J = 7.8, 1.4$ Hz, 2H), 7.38–7.29 (m, 3H), 7.24–7.20 (m, 2H), 6.99–6.82 (m, 3H), 5.58 (s, 1H), 4.20–4.07 (m, 2H), 1.15 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.06, 157.40, 135.59, 129.65, 129.02, 128.86, 127.16, 121.87, 115.55, 78.71, 61.74, 14.13.



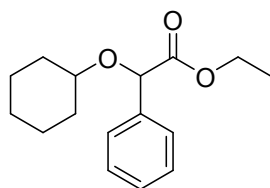
Methyl 2-(4-chlorophenyl)-2-(3-(trifluoromethyl) phenoxy) acetate (3v): White solid; m.p.: 84-86 °C; 78% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.55–7.49 (m, 2H), 7.43–7.36 (m, 3H), 7.26 (t, $J = 3.9$ Hz, 1H), 7.20 (s, 1H), 7.08 (dd, $J = 8.2, 2.4$ Hz, 1H), 5.64 (s, 1H), 3.75 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 169.60, 157.25, 135.46, 133.38, 132.29 (q, $J = 32.6$ Hz), 130.39, 129.32, 128.56, 123.85 (d, $J = 272.4$ Hz), 118.94 (q, $J = 3.9$ Hz), 118.62, 112.90 (q, $J = 3.9$ Hz), 78.18, 53.04.



2-(4-chlorophenyl)-2-(3-(trifluoromethyl) phenoxy) acetic acid (3v'): White syrup; 83% yield; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 13.57 (s, 1H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.57–7.49 (m, 3H), 7.31 (t, $J = 9.1$ Hz, 3H), 6.11 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 170.34, 157.27, 134.78, 133.58, 130.88, 130.37 (q, $J = 31.8$ Hz), 129.29, 128.77, 123.95 (q, $J = 272.4$ Hz), 119.50, 118.00 (q, $J = 3.7$ Hz), 111.92 (q, $J = 3.7$ Hz), 76.56.

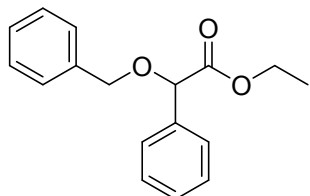


Ethyl 2-isopropoxy-2-phenylacetate (3z): Colorless oil; 54% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (dd, $J = 8.0, 1.4$ Hz, 2H), 7.38–7.29 (m, 3H), 4.97 (s, 1H), 4.22–4.11 (m, 2H), 3.74–3.62 (m, 1H), 1.26–1.23 (m, 3H), 1.23–1.17 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.68, 137.46, 128.60, 128.49, 127.22, 78.67, 71.05, 61.20, 22.21, 22.19, 14.20.

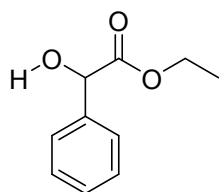


Ethyl 2-(cyclohexyloxy)-2-phenylacetate (3z3): Colorless oil; 47% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (dd, $J = 7.9, 1.1$ Hz, 2H), 7.37–7.27 (m, 3H), 5.03 (s, 1H),

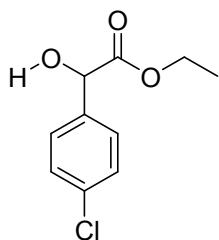
4.23–4.09 (m, 2H), 3.41–3.32 (m, 1H), 2.05–1.94 (m, 1H), 1.94–1.85 (m, 1H), 1.82–1.67 (m, 2H), 1.58–1.21 (m, 6H), 1.19 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.82, 137.69, 128.61, 128.46, 127.21, 78.38, 77.65, 61.19, 32.45, 32.30, 25.85, 24.31, 14.26.



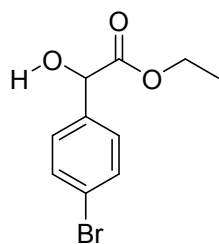
Ethyl 2-(benzyloxy)-2-phenylacetate(3z7): Colorless oil; 51% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, $J = 7.7, 1.6$ Hz, 2H), 7.41–7.30 (m, 8H), 4.94 (s, 1H), 4.62 (s, 2H), 4.26–4.11 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.89, 137.33, 136.53, 128.74, 128.69, 128.54, 128.15, 128.00, 127.47, 79.80, 71.25, 61.30, 14.18.



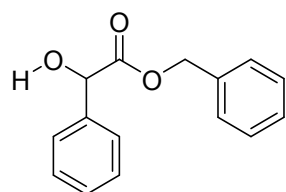
Ethyl 2-hydroxy-2-phenylacetate (3z9): Colorless oil; 50% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (dd, $J = 8.0, 1.2$ Hz, 2H), 7.40–7.29 (m, 3H), 5.16 (d, $J = 5.8$ Hz, 1H), 4.31–4.11 (m, 2H), 3.57 (d, $J = 5.8$ Hz, 1H), 1.22 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 173.78, 138.53, 128.66, 128.49, 126.63, 72.99, 62.33, 14.12.



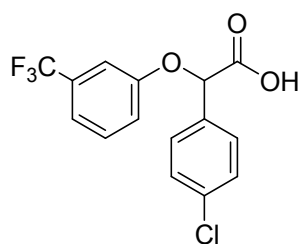
Ethyl 2-(4-chlorophenyl)-2-hydroxyacetate (3z10): White solid, 62% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 8.6$ Hz, 2H), 7.31 (d, $J = 8.5$ Hz, 2H), 5.12 (d, $J = 5.4$ Hz, 1H), 4.31–4.10 (m, 2H), 3.75–3.63 (m, 1H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 173.35, 136.97, 134.30, 128.77, 127.98, 72.28, 62.50, 14.08.



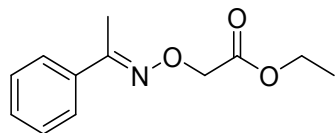
Ethyl 2-(4-bromophenyl)-2-hydroxyacetate (3z11): White solid, 65% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.51–7.43 (m, 2H), 7.29 (d, $J = 8.3$ Hz, 2H), 5.10 (d, $J = 5.4$ Hz, 1H), 4.30–4.09 (m, 2H), 3.79–3.69 (m, 1H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 173.22, 137.47, 131.69, 128.28, 122.44, 72.31, 62.48, 14.06.



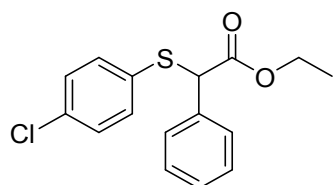
Benzyl 2-hydroxy-2-phenylacetate (3z12): White solid, 71% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.48–7.42 (m, 2H), 7.41–7.31 (m, 6H), 7.26–7.19 (m, 2H), 5.27–5.24 (m, 2H), 5.15 (d, $J = 12.4$ Hz, 1H), 3.67 (d, $J = 5.8$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 173.53, 138.27, 135.08, 128.64, 128.61, 128.54, 128.48, 128.00, 126.67, 73.06, 67.65.



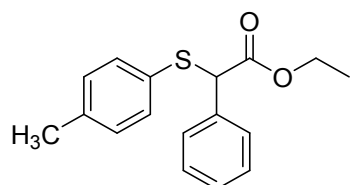
2-(4-chlorophenyl)-2-(3-(trifluoromethyl) phenoxy) acetic acid (3v'): White syrup; 83% yield; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 13.57 (s, 1H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.57–7.49 (m, 3H), 7.31 (t, $J = 9.1$ Hz, 3H), 6.11 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 170.34, 157.27, 134.78, 133.58, 130.88, 130.37 (q, $J = 31.8$ Hz), 129.29, 128.77, 123.95 (q, $J = 272.4$ Hz), 119.50, 118.00 (q, $J = 3.7$ Hz), 111.92 (q, $J = 3.7$ Hz), 76.56.



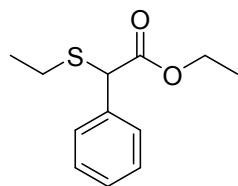
Ethyl (*E*)-2-(((1-phenylethylidene) amino) oxy) acetate (5k): Colorless oil; 50% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.69–7.59 (m, 2H), 7.40–7.32 (m, 3H), 4.74 (s, 2H), 4.24 (q, $J = 7.1$ Hz, 2H), 2.32 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.25, 156.71, 136.29, 129.46, 128.51, 126.41, 70.98, 60.98, 14.34, 13.23.



Ethyl 2-((4-chlorophenyl) thio)-2-phenylacetate (7a): Colorless oil; 84% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (dd, $J = 7.7, 1.8$ Hz, 2H), 7.35–7.28 (m, 5H), 7.25–7.21 (m, 2H), 4.86 (s, 1H), 4.19–4.09 (m, 2H), 1.18 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.24, 135.48, 134.43, 134.34, 132.23, 129.20, 128.83, 128.63, 128.52, 61.96, 56.58, 14.12.

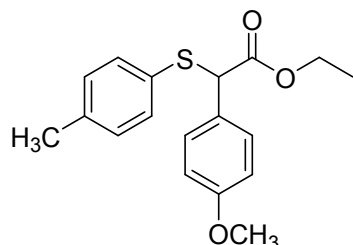


Ethyl 2-phenyl-2-(*p*-tolylthio) acetate (7c): Colorless oil; 91% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (dd, $J = 7.9, 1.6$ Hz, 2H), 7.35–7.28 (m, 5H), 7.08 (d, $J = 7.9$ Hz, 2H), 4.86 (s, 1H), 4.19–4.08 (m, 2H), 2.32 (s, 3H), 1.18 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.59, 138.38, 135.95, 133.41, 130.12, 129.79, 128.68, 128.63, 128.27, 61.72, 56.88, 21.23, 14.08.

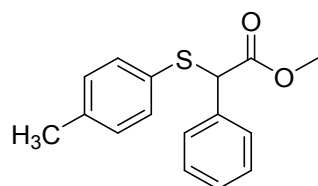


Ethyl 2-(ethylthio)-2-phenylacetate (7f): Colorless oil; 60% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (dd, $J = 8.2, 1.3$ Hz, 2H), 7.33 (dt, $J = 7.3, 6.5$ Hz, 3H), 4.59 (s,

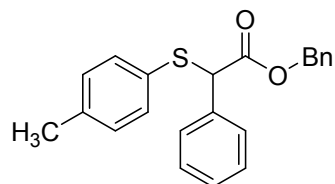
1H), 4.24–4.15 (m, 2H), 2.61–2.46 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.23 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.00, 136.38, 129.30, 128.68, 128.54, 128.11, 61.70, 52.13, 26.01, 14.19, 14.17.



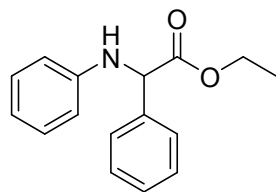
Ethyl 2-(4-methoxyphenyl)-2-(*p*-tolylthio) acetate (7o): Colorless oil; 65% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.45–7.39 (m, 2H), 7.32 (dd, $J = 6.8, 5.1$ Hz, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 6.91–6.87 (m, 2H), 4.85 (s, 1H), 4.20–4.11 (m, 2H), 3.84 (s, 3H), 2.36 (s, 3H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.84, 159.62, 138.33, 133.38, 129.86, 129.81, 127.91, 114.13, 61.68, 56.22, 55.40, 21.28, 14.13.



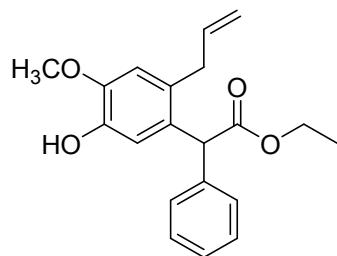
Methyl 2-phenyl-2-(*p*-tolylthio) acetate (7p): Colorless oil; 85% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (dd, $J = 9.2, 3.1$ Hz, 2H), 7.33–7.30 (m, 2H), 7.28 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 7.9$ Hz, 2H), 4.86 (s, 1H), 3.68 (s, 3H), 2.32 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.09, 138.51, 135.89, 133.47, 130.01, 129.86, 128.74, 128.64, 128.35, 56.89, 52.74, 21.26.



Benzyl 2-phenyl-2-(*p*-tolylthio) acetate (7s): Colorless oil; 75% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (dd, $J = 7.7, 1.8$ Hz, 2H), 7.37–7.29 (m, 8H), 7.25–7.21 (m, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 5.19–5.05 (m, 2H), 4.95 (s, 1H), 2.34 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.49, 138.42, 135.62, 135.43, 133.47, 129.93, 129.83, 128.70, 128.67, 128.52, 128.35, 128.29, 128.21, 67.30, 56.76, 21.24.

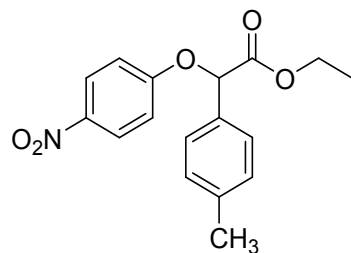


Ethyl 2-phenyl-2-(phenylamino) acetate (9a): Colorless oil; 60% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 7.1$ Hz, 2H), 7.41–7.30 (m, 3H), 7.15 (dd, $J = 8.5, 7.4$ Hz, 2H), 6.73 (t, $J = 7.3$ Hz, 1H), 6.60 (d, $J = 7.7$ Hz, 2H), 5.11 (d, $J = 5.3$ Hz, 1H), 5.02 (s, 1H), 4.32–4.08 (m, 2H), 1.24 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.91, 146.08, 137.81, 129.31, 128.90, 128.30, 127.29, 118.10, 113.48, 61.90, 60.86, 14.12.



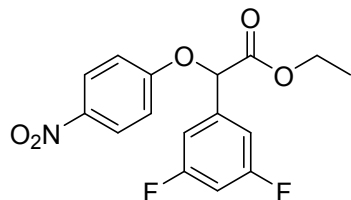
Ethyl 2-(2-allyl-5-hydroxy-4-methoxyphenyl)-2-phenylacetate (11a): Colorless oil; 61% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.17–7.12 (m, 2H), 7.08 (dd, $J = 8.7, 7.3$ Hz, 3H), 6.71 (s, 1H), 6.51 (s, 1H), 5.77 (dd, $J = 17.0, 10.2$ Hz, 1H), 5.32 (s, 1H), 5.02 (s, 1H), 4.93 (dd, $J = 10.1, 1.5$ Hz, 1H), 4.86 (dd, $J = 17.1, 1.7$ Hz, 1H), 4.04 (q, $J = 7.1$ Hz, 2H), 3.70 (s, 3H), 3.17 (dd, $J = 5.8, 4.3$ Hz, 2H), 1.10 (d, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.88, 145.74, 144.07, 138.70, 137.06, 129.92, 129.63, 128.82, 128.63, 127.16, 116.13, 115.40, 112.45, 61.27, 56.00, 52.66, 37.12, 14.28.

8. Analytical Data for unknown compounds

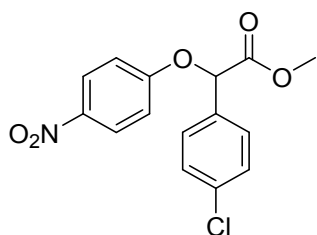


Ethyl 2-(4-nitrophenoxy)-2-(*p*-tolyl) acetate (3r): Light yellow oil; 78% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.23–8.14 (m, 2H), 7.44 (d, $J = 8.1$ Hz, 2H), 7.23 (d, $J =$

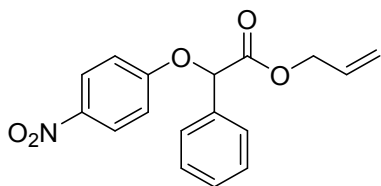
7.9 Hz, 2H), 7.03–6.97 (m, 2H), 5.67 (s, 1H), 4.28–4.15 (m, 2H), 2.37 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 168.98, 162.29, 142.28, 139.63, 131.37, 129.81, 127.18, 126.01, 115.52, 78.91, 62.13, 21.37, 14.14. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 338.0999; Found: 338.1001.



Ethyl 2-(3,5-difluorophenyl)-2-(4-nitrophenoxy) acetate (3s): Yellow oil, 68% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.23–8.17 (m, 2H), 7.44–7.34 (m, 1H), 7.11–7.04 (m, 2H), 6.98 (t, $J = 8.2$ Hz, 2H), 6.10 (s, 1H), 4.34–4.25 (m, 2H), 1.25 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 167.65, 162.28, 161.32 (d, $J = 250.6$ Hz), 161.25 (d, $J = 250.7$ Hz), 142.64, 132.06 (d, $J = 10.5$ Hz), 131.90, 126.02, 115.77, 112.19 (d, $J = 5.5$ Hz), 112.03 (d, $J = 13.3$ Hz), 69.08, 62.67, 14.12. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{13}\text{F}_2\text{NO}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 360.0654; Found: 360.0653.

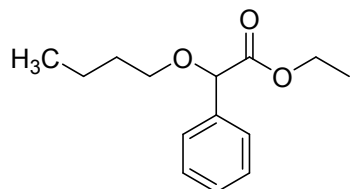


Methyl 2-(4-chlorophenyl)-2-(4-nitrophenoxy) acetate (3t): White solid, m.p.: 134–137 °C.; 85% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 9.2$ Hz, 2H), 7.51 (d, $J = 8.5$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 2H), 7.00 (d, $J = 9.2$ Hz, 2H), 5.70 (s, 1H), 3.76 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 168.97, 161.83, 142.50, 135.69, 132.70, 129.40, 128.54, 126.10, 115.46, 78.13, 53.20. HRMS (APCI) calcd for $\text{C}_{15}\text{H}_{11}\text{NClO}_5$ $[\text{M}-\text{H}]^-$: 320.0331; Found: 320.0330.

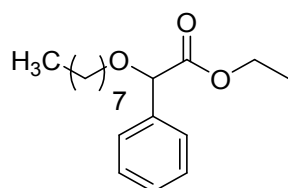


Allyl 2-(4-nitrophenoxy)-2-phenylacetate (3u): Colorless oil; 75% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.21–8.13 (m, 2H), 7.58 (dd, $J = 7.6, 1.8$ Hz, 2H), 7.47–7.37 (m,

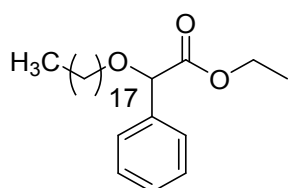
3H), 7.06–6.98 (m, 2H), 5.82 (dd, $J = 17.4, 10.2$ Hz, 1H), 5.76 (s, 1H), 5.23–5.20 (m, 1H), 5.18 (dd, $J = 2.0, 1.3$ Hz, 1H), 4.70–4.60 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 168.46, 162.08, 142.31, 134.19, 131.08, 129.60, 129.10, 127.19, 125.99, 119.17, 115.49, 78.86, 66.39. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 336.0842; Found: 336.0850.



Ethyl 2-butoxy-2-phenylacetate (3w): Colorless oil; 71% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (dd, $J = 7.8, 1.5$ Hz, 2H), 7.39–7.29 (m, 3H), 4.85 (s, 1H), 4.26–4.09 (m, 2H), 3.59–3.51 (m, 1H), 3.48–3.41 (m, 1H), 1.67–1.61 (m, 2H), 1.46–1.36 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H), 0.91 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.24, 137.03, 128.63, 128.58, 127.23, 81.26, 69.83, 61.22, 31.79, 19.38, 14.22, 13.97. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 259.1305; Found: 259.1316.

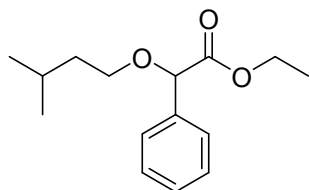


Ethyl 2-(octyloxy)-2-phenylacetate (3x): Colorless oil; 67% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (dd, $J = 7.9, 1.3$ Hz, 2H), 7.37–7.28 (m, 3H), 4.85 (s, 1H), 4.26–4.07 (m, 2H), 3.59–3.51 (m, 1H), 3.48–3.40 (m, 1H), 1.71–1.60 (m, 2H), 1.40–1.33 (m, 2H), 1.27 (d, $J = 3.4$ Hz, 8H), 1.20 (t, $J = 7.1$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.08, 136.95, 128.50, 128.46, 127.12, 81.17, 70.04, 61.06, 31.84, 29.63, 29.39, 29.25, 26.07, 22.67, 14.10. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 315.1931; Found: 315.1945.

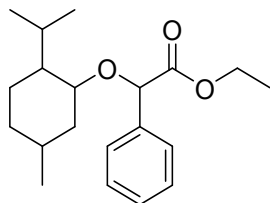


Ethyl 2-(octadecyloxy)-2-phenylacetate (3y): White solid; m.p.: 37–38 °C, 65% yield;

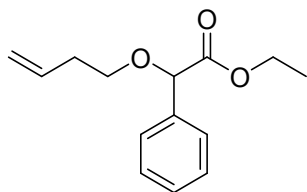
^1H NMR (400 MHz, CDCl_3) δ 7.47 (dd, $J = 8.0, 1.3$ Hz, 2H), 7.38–7.28 (m, 3H), 4.85 (s, 1H), 4.24–4.10 (m, 2H), 3.59–3.51 (m, 1H), 3.48–3.39 (m, 1H), 1.70–1.62 (m, 2H), 1.35–1.27 (m, 30 H), 1.21 (t, $J = 7.1$ Hz, 3H), 0.89 (t, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.63, 137.96, 128.47, 128.34, 127.07, 78.61, 78.20, 61.07, 48.53, 40.34, 34.52, 31.58, 25.32, 23.21, 22.39, 21.30, 16.25, 14.15. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{48}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 455.3496; Found: 455.3503.



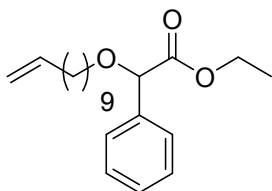
Ethyl 2-(isopentyloxy)-2-phenylacetate (3z1): Colorless oil; 55% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 6.5$ Hz, 2H), 7.37–7.29 (m, 3H), 4.85 (s, 1H), 4.22–4.12 (m, 2H), 3.62–3.55 (m, 1H), 3.53–3.36 (m, 1H), 1.83–1.70 (m, 1H), 1.67–1.43 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 3H), 0.92–0.87 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.21, 136.98, 128.60, 128.56, 127.18, 81.26, 68.46, 61.20, 38.47, 25.08, 22.70, 22.66, 14.20. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{22}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 273.1461; Found: 273.1473.



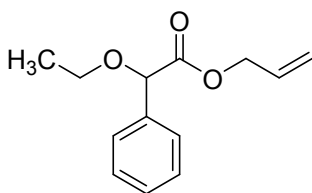
Ethyl 2-((2-isopropyl-5-methylcyclohexyl)oxy)-2-phenylacetate (3z4): Colorless oil; 47% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, $J = 7.9, 1.2$ Hz, 2H), 7.36–7.29 (m, 3H), 5.09 (s, 1H), 4.22–4.11 (m, 2H), 3.33 (td, $J = 10.5, 4.2$ Hz, 1H), 2.60–2.47 (m, 1H), 2.13–2.02 (m, 1H), 1.70–1.62 (m, 2H), 1.40–1.29 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.07–0.98 (m, 1H), 0.96 (d, $J = 7.1$ Hz, 2H), 0.94–0.77 (m, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.82, 137.69, 128.61, 128.46, 127.21, 78.38, 77.65, 61.19, 32.45, 32.30, 25.85, 24.31, 14.26. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{30}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 341.2087; Found: 341.2094.



Ethyl 2-(but-3-en-1-yloxy)-2-phenylacetate (3z5): Colorless oil; 75% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (dd, $J = 7.9, 1.5$ Hz, 2H), 7.38–7.28 (m, 3H), 5.84 (dd, $J = 17.1, 10.3$ Hz, 1H), 5.10 (dd, $J = 17.2, 1.7$ Hz, 1H), 5.06–5.00 (m, 1H), 4.87 (s, 1H), 4.26–4.11 (m, 2H), 3.66–3.56 (m, 1H), 3.54–3.45 (m, 1H), 2.48–2.37 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.92, 136.72, 134.77, 128.55, 127.15, 116.62, 81.15, 69.20, 61.15, 34.08, 14.11. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 257.1148; Found: 257.1147.

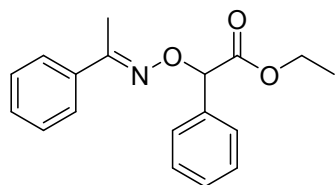


Ethyl 2-phenyl-2-(undec-10-en-1-yloxy) acetate (3z6): Colorless oil; 72% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (dd, $J = 7.8, 1.5$ Hz, 2H), 7.39–7.29 (m, 3H), 4.85 (s, 1H), 4.26–4.09 (m, 2H), 3.59–3.51 (m, 1H), 3.48–3.41 (m, 1H), 1.67–1.61 (m, 2H), 1.46–1.36 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H), 0.91 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.05, 136.98, 128.49, 128.45, 127.12, 81.19, 70.04, 61.04, 32.00, 29.78, 29.73, 29.67, 29.63, 29.48, 29.44, 26.11, 22.75, 14.15, 14.11. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{32}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 355.2244; Found: 355.2247.

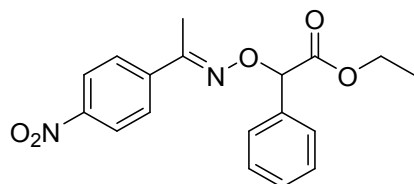


Allyl 2-ethoxy-2-phenylacetate (3z8): Colorless oil; 67% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (dd, $J = 7.9, 1.3$ Hz, 2H), 7.38–7.29 (m, 3H), 5.83 (dd, $J = 17.2, 10.5$ Hz, 1H), 5.21–5.11 (m, 2H), 4.90 (s, 1H), 4.66–4.55 (m, 2H), 3.64–3.48 (m, 2H), 1.27 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.68, 136.70, 131.66, 128.61, 128.58, 127.19, 118.30, 80.91, 65.49, 65.30, 15.12. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{Na}$

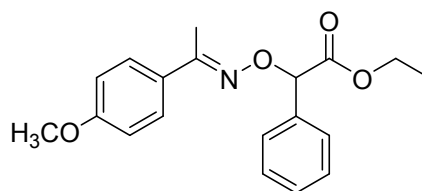
[M+Na]⁺: 243.0992; Found: 243.0994.



Ethyl (*E*)-2-phenyl-2-(((1-phenylethylidene) amino) oxy) acetate (5a): Colorless oil; 83% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.71–7.62 (m, 2H), 7.57 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.44–7.33 (m, 6H), 5.75 (s, 1H), 4.28–4.14 (m, 2H), 2.38 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 170.92, 156.91, 136.26, 135.37, 129.46, 128.96, 128.69, 128.47, 127.71, 126.41, 83.77, 61.22, 14.24, 13.35. HRMS (ESI) calcd for C₁₈H₁₉NO₃Na [M+Na]⁺: 320.1257; Found: 320.1249.

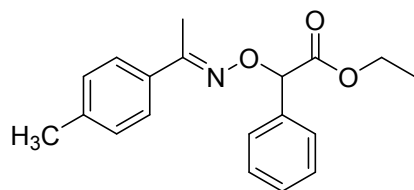


Ethyl (*E*)-2-(((1-(4-nitrophenyl) ethylidene) amino) oxy)-2-phenylacetate (5b): White solid; 61% yield; m.p 86–88 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.54 (dd, *J* = 7.3, 2.0 Hz, 2H), 7.45–7.38 (m, 3H), 5.75 (s, 1H), 4.30–4.16 (m, 2H), 2.39 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 170.54, 154.90, 148.35, 142.20, 134.83, 129.25, 128.83, 127.79, 127.18, 123.74, 84.18, 77.48, 77.16, 76.84, 61.46, 14.26, 13.16. HRMS (APCI) calcd for C₁₈H₁₉N₂O₅ [M+H]⁺: 343.1288; Found: 343.1281.

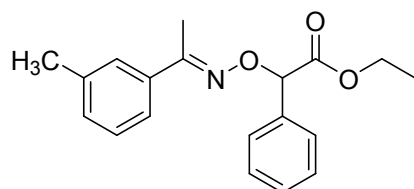


Ethyl (*E*)-2-(((1-(4-methoxyphenyl) ethylidene) amino) oxy)-2-phenylacetate (5c): Colorless oil; 70% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.66–7.53 (m, 4H), 7.46–7.36 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.72 (s, 1H), 4.27–4.16 (m, 2H), 3.82 (s, 3H), 2.35 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 171.04, 160.71, 156.43, 135.46, 128.90, 128.76, 128.67, 127.75, 127.69, 113.82, 83.67, 61.17, 55.39,

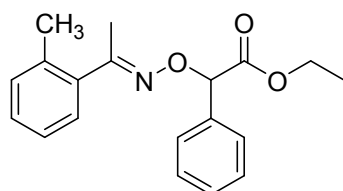
14.24, 13.20. HRMS (ESI) calcd for $C_{19}H_{21}NO_4Na$ $[M+Na]^+$: 350.1363; Found: 350.1368.



Ethyl (*E*)-2-phenyl-2-(((1-(*p*-tolyl) ethylidene) amino) oxy) acetate (5d): Colorless oil; 63% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.60–7.52 (m, 4H), 7.45–7.38 (m, 3H), 7.18 (d, $J = 8.1$ Hz, 2H), 5.73 (s, 1H), 4.28–4.18 (m, 2H), 2.37 (d, $J = 3.0$ Hz, 6H), 1.25 (t, $J = 7.1$ Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.01, 156.86, 139.51, 135.39, 133.42, 129.16, 128.93, 128.68, 127.70, 126.30, 83.69, 61.20, 21.40, 14.25, 13.31. HRMS (ESI) calcd for $C_{19}H_{22}NO_3$ $[M+H]^+$: 312.1594; Found: 312.1589.

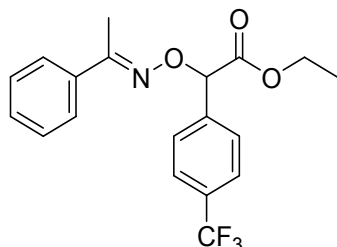


Ethyl (*E*)-2-phenyl-2-(((1-(*m*-tolyl) ethylidene) amino) oxy) acetate (5e): Colorless oil; 45% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, $J = 7.6, 1.7$ Hz, 2H), 7.48–7.38 (m, 5H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.19 (d, $J = 7.5$ Hz, 1H), 5.75 (s, 1H), 4.29–4.17 (m, 2H), 2.38 (d, $J = 3.2$ Hz, 6H), 1.25 (t, $J = 7.1$ Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.97, 157.17, 138.09, 136.21, 135.36, 130.25, 128.95, 128.70, 128.38, 127.70, 127.03, 123.60, 83.71, 61.22, 21.57, 14.25, 13.51. HRMS (ESI) calcd for $C_{19}H_{21}NO_3Na$ $[M+Na]^+$: 334.1414; Found: 334.1409.

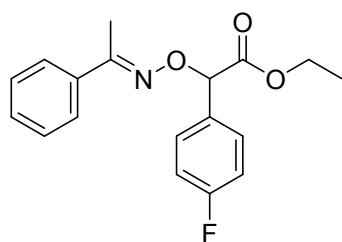


Ethyl (*E*)-2-phenyl-2-(((1-(*o*-tolyl) ethylidene) amino) oxy) acetate (5f): Light yellow oil; 27% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, $J = 7.6, 1.8$ Hz, 2H), 7.45–7.34 (m, 3H), 7.26–7.15 (m, 4H), 5.69 (s, 1H), 4.27–4.11 (m, 2H), 2.33 (d, $J = 5.6$ Hz, 6H), 1.23 (t, $J = 7.1$ Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.98, 157.19,

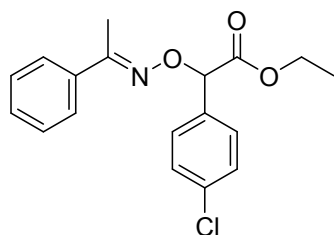
138.11, 136.26, 135.43, 130.26, 128.95, 128.71, 128.39, 127.72, 127.05, 123.63, 83.76, 61.23, 21.58, 14.26, 13.51. HRMS (ESI) calcd for C₁₉H₂₂NO₃ [M+H]⁺: 312.1594; Found: 312.1588.



Ethyl (*E*)-2-(((1-phenylethylidene) amino) oxy)-2-(4-(trifluoromethyl) phenyl) acetate (5g): Colorless oil; 60% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.70–7.61 (m, 6H), 7.37 (dd, *J* = 5.1, 1.9 Hz, 3H), 5.79 (s, 1H), 4.29–4.17 (m, 2H), 2.39 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 170.18, 157.44, 139.43, 136.04, 131.07 (q, *J* = 32.5 Hz), 129.67, 128.55, 127.94, 126.45, 125.68 (q, *J* = 3.8 Hz), 124.12 (q, *J* = 272.3 Hz), 83.10, 61.60, 14.23, 13.40. HRMS (ESI) calcd for C₁₉H₁₈F₃NO₃Na [M+Na]⁺: 388.1131; Found: 388.1136.

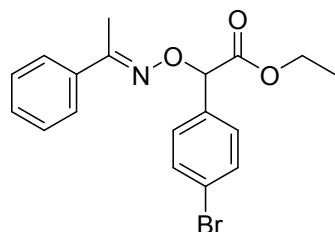


Ethyl (*E*)-2-(4-fluorophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate (5h): Colorless oil; 83% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.58–7.50 (m, 2H), 7.37 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.14–7.05 (m, 2H), 5.70 (s, 1H), 4.28–4.17 (m, 2H), 2.36 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} (100 MHz, CDCl₃) δ 170.78, 163.16 (d, *J* = 247.6 Hz), 157.09, 136.18, 131.31 (d, *J* = 3.2 Hz), 129.64, 129.56, 128.51, 126.43, 115.81, 115.59, 83.03, 61.35, 14.25, 13.37. HRMS (ESI) calcd for C₁₈H₁₈FNO₃Na [M+Na]⁺: 338.1163; Found: 338.1158.



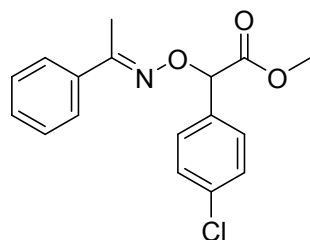
Ethyl (*E*)-2-(4-chlorophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate (5i**):**

Colorless oil; 81% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, $J = 6.8, 3.0$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.40–7.35 (m, 5H), 5.70 (s, 1H), 4.28–4.15 (m, 2H), 2.36 (s, 3H), 1.24 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.51, 157.17, 136.13, 134.91, 134.00, 129.58, 129.06, 128.93, 128.51, 126.42, 83.02, 61.41, 14.24, 13.36. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{ClNO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 354.0867; Found: 354.0867.



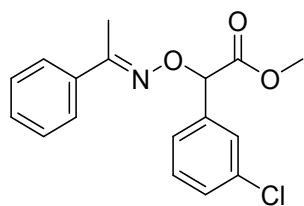
Ethyl (*E*)-2-(4-bromophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate (5j**):**

Light yellow oil; 76% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.68–7.61 (m, 2H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.40–7.33 (m, 3H), 5.68 (s, 1H), 4.28–4.14 (m, 2H), 2.36 (s, 3H), 1.24 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.43, 157.19, 136.11, 134.51, 131.88, 129.58, 129.35, 128.51, 126.42, 123.12, 83.06, 61.43, 14.24, 13.36. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{BrNO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 398.0362; Found: 398.0362.



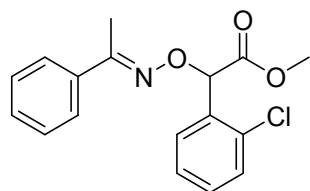
Methyl (*E*)-2-(4-chlorophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate (5l**):**

White solid; 85% yield; m.p 84–86 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (dd, $J = 6.5, 3.2$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.40–7.35 (m, 5H), 5.71 (s, 1H), 3.75 (s, 3H), 2.36 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.03, 157.28, 136.07, 135.02, 133.84, 131.64, 129.63, 129.09, 128.99, 128.53, 126.45, 82.93, 52.48, 13.40. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 340.0711; Found: 340.0721.



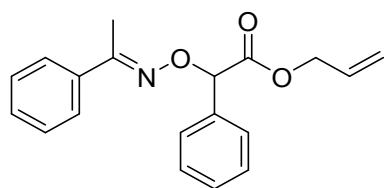
Methyl (*E*)-2-(3-chlorophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate(5m):

Colorless oil; 70% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, $J = 6.5, 3.2$ Hz, 2H), 7.55 (s, 1H), 7.46–7.41 (m, 1H), 7.39–7.30 (m, 5H), 5.72 (s, 1H), 3.76 (s, 3H), 2.38 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.82, 157.38, 137.26, 136.05, 134.66, 130.02, 129.64, 129.21, 128.53, 127.78, 126.46, 125.83, 82.98, 52.52, 13.44. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 318.0891; Found: 318.0898.



Methyl (*E*)-2-(2-chlorophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate(5n):

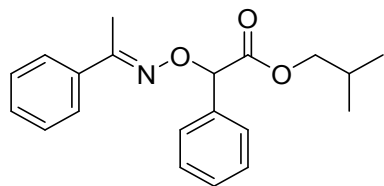
White solid; 60% yield; m.p 55-57 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.67–7.63 (m, 2H), 7.62–7.58 (m, 1H), 7.46–7.42 (m, 1H), 7.37 (dd, $J = 4.3, 2.4$ Hz, 3H), 7.33–7.29 (m, 2H), 6.24 (s, 1H), 3.77 (s, 3H), 2.35 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.75, 157.08, 136.13, 134.12, 133.57, 130.18, 129.89, 129.54, 129.43, 128.48, 127.17, 126.46, 80.21, 52.45, 13.31. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 318.0891; Found: 318.0902.



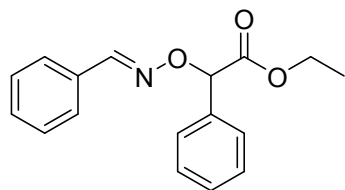
Allyl (*E*)-2-phenyl-2-(((1-phenylethylidene) amino) oxy) acetate (5o):

Yellow oil; 72% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.68–7.63 (m, 2H), 7.57 (dd, $J = 7.6, 1.7$ Hz, 2H), 7.43–7.35 (m, 6H), 5.87 (dd, $J = 17.2, 10.5$ Hz, 1H), 5.79 (s, 1H), 5.25 (dd, $J = 17.2, 1.5$ Hz, 1H), 5.18 (dd, $J = 10.5, 1.3$ Hz, 1H), 4.67 (dt, $J = 5.5, 1.4$ Hz, 2H), 2.38 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.61, 157.01, 136.22, 135.23, 131.85, 129.50, 129.06, 128.74, 128.48, 127.76, 126.44,

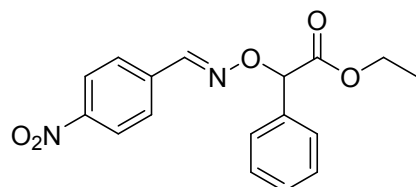
118.22, 83.77, 65.61, 13.37. HRMS (ESI) calcd for C₁₉H₂₀NO₃ [M+H]⁺: 310.1438; Found: 310.1449.



Isobutyl (*E*)-2-phenyl-2-(((1-phenylethylidene) amino) oxy) acetate (5p): Colorless oil; 79% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.68–7.63 (m, 2H), 7.57 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.42–7.35 (m, 6H), 5.76 (s, 1H), 4.00–3.90 (m, 2H), 2.38 (s, 3H), 1.97–1.87 (m, 1H), 0.86 (dd, *J* = 6.7, 1.3 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 171.01, 156.85, 136.28, 135.52, 129.46, 128.95, 128.68, 128.47, 127.69, 126.41, 83.89, 71.16, 27.89, 19.02, 19.01, 13.33. HRMS (ESI) calcd for C₂₀H₂₄NO₃ [M+H]⁺: 326.1751; Found: 326.1764.

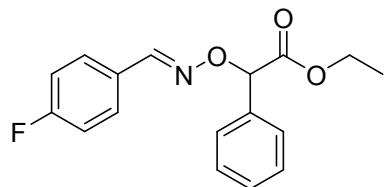


Ethyl (*E*)-2-((benzylideneamino)oxy)-2-phenylacetate (5q): Colorless oil; 63% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.28 (s, 1H), 7.64–7.57 (m, 2H), 7.55 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.43–7.36 (m, 6H), 5.73 (s, 1H), 4.35–4.16 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 170.66, 150.70, 134.93, 131.78, 130.31, 129.13, 128.78, 127.83, 127.48, 83.90, 61.38, 14.24. HRMS (ESI) calcd for C₁₇H₁₈NO₃ [M+H]⁺: 284.1281; Found: 284.1275.

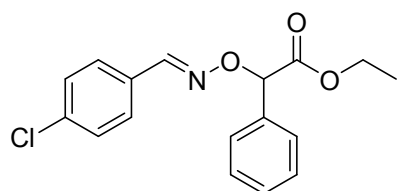


Ethyl (*E*)-2-(((4-nitrobenzylidene) amino) oxy)-2-phenylacetate (5r): White solid; 57% yield; m.p 101-104 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 1H), 8.23 (d, *J* = 8.9 Hz, 2H), 7.78–7.72 (m, 2H), 7.55–7.49 (m, 2H), 7.42–7.40 (m, 2H), 7.36–7.32 (m, 1H), 5.75 (s, 1H), 4.29–4.19 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (100

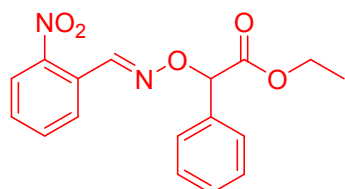
MHz, CDCl₃) δ 170.23, 148.72, 148.48, 137.86, 134.41, 129.41, 128.90, 128.10, 127.88, 124.10, 84.36, 61.60, 14.24. HRMS (ESI) calcd for C₁₇H₁₆N₂O₅Na [M+Na]⁺: 351.0951; Found: 351.0956.



Ethyl (*E*)-2-(((4-fluorobenzylidene) amino) oxy)-2-phenylacetate (5s): Colorless oil; 68% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 1H), 7.60–7.51 (m, 4H), 7.44–7.36 (m, 3H), 7.09–7.02 (m, 2H), 5.70 (s, 1H), 4.30–4.15 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 170.62, 164.01 (d, *J* = 250.6 Hz), 149.51, 134.87, 133.67 (d, *J* = 8.5 Hz), 129.39, 129.30, 129.18, 128.80, 128.02 (d, *J* = 3.2 Hz), 116.07, 115.85, 83.92, 61.41, 14.24. HRMS (ESI) calcd for C₁₇H₁₇FNO₃ [M+H]⁺: 302.1187; Found: 302.1181.

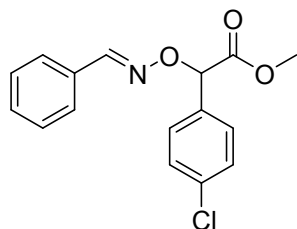


Ethyl (*E*)-2-(((4-chlorobenzylidene) amino) oxy)-2-phenylacetate (5t): Colorless oil; 59% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (s, 1H), 7.52 (dd, *J* = 8.3, 2.0 Hz, 4H), 7.43–7.37 (m, 3H), 7.36–7.32 (m, 2H), 5.70 (s, 1H), 4.29–4.18 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 170.56, 149.53, 136.25, 134.79, 130.31, 129.23, 129.11, 128.83, 128.67, 127.85, 84.00, 61.46, 14.26. HRMS (ESI) calcd for C₁₇H₁₆ClNO₃Na [M+Na]⁺: 340.0711; Found: 340.0709.

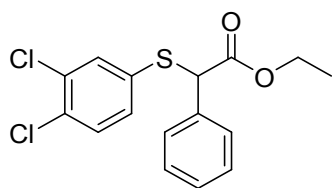


Ethyl (*E*)-2-(((2-nitrobenzylidene) amino) oxy)-2-phenylacetate (5u): Colorless oil; 31% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.84 (s, 1H), 8.06 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.94 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66–7.60 (m, 1H), 7.58–7.51 (m, 3H), 7.42–7.39 (m,

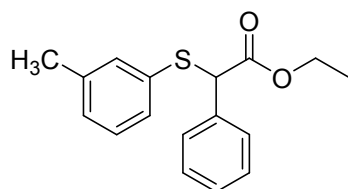
2H), 7.36–7.30 (m, 1H), 5.73 (s, 1H), 4.28–4.18 (m, 2H), 1.25 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.56, 149.53, 136.25, 134.80, 130.32, 129.22, 129.11, 128.83, 128.67, 127.85, 84.01, 61.46, 14.26. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 351.0951; Found: 351.0950.



Methyl (*E*)-2-((benzylideneamino)oxy)-2-(4-chlorophenyl) acetate (5v): White solid; 55% yield; m.p 50-52 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.26 (s, 1H), 7.58 (dd, $J = 7.4, 2.2$ Hz, 2H), 7.49–7.45 (m, 2H), 7.41–7.34 (m, 5H), 5.70 (s, 1H), 3.77 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.73, 151.03, 135.17, 133.47, 131.57, 130.47, 129.16, 129.04, 128.82, 127.53, 83.03, 52.56. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{14}\text{ClNO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 326.0554; Found: 326.0556.

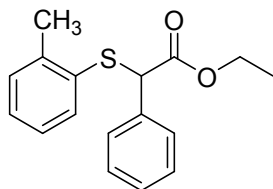


Ethyl 2-((3,4-dichlorophenyl)thio)-2-phenylacetate (7b): Colorless oil; 79% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.47–7.40 (m, 3H), 7.36–7.30 (m, 4H), 7.17 (dd, $J = 8.4, 2.1$ Hz, 1H), 4.90 (s, 1H), 4.22–4.10 (m, 2H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 169.96, 135.04, 133.99, 133.97, 132.86, 132.39, 131.70, 130.68, 128.91, 128.70, 128.60, 62.10, 56.23, 14.11. HRMS (APCI) calcd for $\text{C}_{16}\text{H}_{13}\text{Cl}_2\text{O}_2\text{S}$ $[\text{M}-\text{H}]^-$: 339.0019; Found: 339.0015.

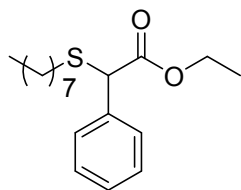


Ethyl 2-phenyl-2-(*m*-tolylthio) acetate (7d): Colorless oil; 78% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, $J = 7.9, 1.5$ Hz, 2H), 7.38–7.29 (m, 3H), 7.24–7.13 (m, 3H), 7.08 (dd, $J = 7.3, 0.6$ Hz, 1H), 4.93 (s, 1H), 4.26–4.05 (m, 2H), 2.31 (s, 3H), 1.19 (t, J

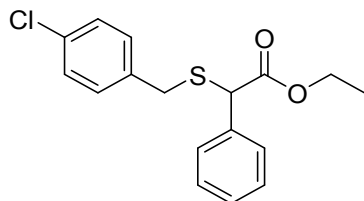
= 7.1 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.57, 138.76, 135.80, 133.67, 133.18, 129.51, 128.83, 128.79, 128.70, 128.60, 128.32, 61.74, 56.33, 21.29, 14.07. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 287.1100; Found: 287.1090.



Ethyl 2-phenyl-2-(*o*-tolylthio) acetate (7e): Colorless oil; 67% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.38–7.28 (m, 4H), 7.20–7.14 (m, 2H), 7.13–7.06 (m, 1H), 4.84 (s, 1H), 4.19–4.04 (m, 2H), 2.39 (s, 3H), 1.16 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.61, 140.57, 135.84, 133.28, 133.13, 130.49, 128.77, 128.64, 128.40, 128.16, 126.59, 61.82, 55.64, 20.73, 14.10. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 309.0920; Found: 309.0913.

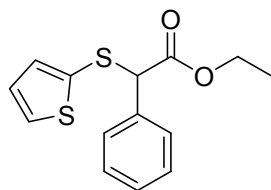


Ethyl 2-(octylthio)-2-phenylacetate (7g): Colorless oil; 65% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, $J = 7.0$ Hz, 2H), 7.38–7.26 (m, 3H), 4.56 (s, 1H), 4.28–4.10 (m, 2H), 2.61–2.42 (m, 2H), 1.63–1.45 (m, 2H), 1.36–1.19 (m, 13H), 0.87 (t, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 171.05, 136.43, 128.66, 128.55, 128.10, 61.70, 52.39, 32.04, 31.87, 29.21, 29.20, 29.06, 28.90, 22.73, 14.19. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 331.1702; Found: 331.1699.

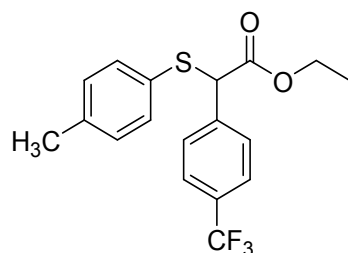


Ethyl 2-((4-chlorobenzyl) thio)-2-phenylacetate (7h): Colorless oil; 76% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (dd, $J = 7.9, 1.5$ Hz, 2H), 7.37–7.27 (m, 5H), 7.22 (d, $J = 8.4$ Hz, 2H), 4.39 (s, 1H), 4.23–4.09 (m, 2H), 3.75 (d, $J = 13.6$ Hz, 1H), 3.59 (d, $J = 13.6$ Hz, 1H), 1.25 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.63,

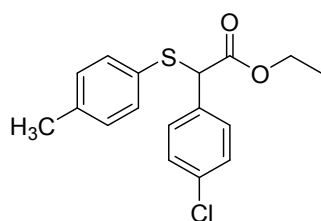
135.88, 135.78, 133.14, 130.50, 128.83, 128.80, 128.70, 128.36, 61.90, 51.73, 35.58, 14.20. HRMS (ESI) calcd for $C_{17}H_{18}ClO_2S$ $[M+H]^+$: 321.0711; Found: 321.0716.



Ethyl 2-phenyl-2-(thiophen-2-ylthio) acetate (7i): Colorless oil; 61% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.36 (m, 3H), 7.35–7.29 (m, 3H), 7.06 (dd, $J = 3.6, 1.2$ Hz, 1H), 6.94 (dd, $J = 5.3, 3.6$ Hz, 1H), 4.77 (s, 1H), 4.22–4.11 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.15, 136.34, 135.38, 131.30, 131.23, 128.74, 128.71, 128.49, 127.62, 61.93, 59.20, 14.14. HRMS (ESI) calcd for $C_{14}H_{18}NO_2S_2$ $[M+NH_4]^+$: 296.0773; Found: 296.0763.

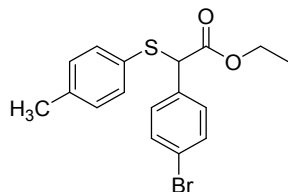


Ethyl 2-(*p*-tolylthio)-2-(4-(trifluoromethyl) phenyl) acetate (7j): Colorless oil; 62% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.65–7.53 (m, 4H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 4.88 (s, 1H), 4.26–4.07 (m, 2H), 2.35 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.97, 140.19, 138.98, 133.88, 130.41 (q, $J = 32.5$ Hz), 129.97, 129.29, 129.12, 125.60 (q, $J = 3.7$ Hz), 124.11 (q, $J = 272.2$ Hz), 62.06, 56.50, 21.26, 14.08. HRMS (ESI) calcd for $C_{18}H_{17}F_3O_2SNa$ $[M+Na]^+$: 377.0794; Found: 377.0806.

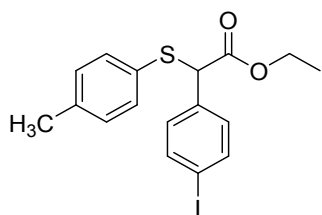


Ethyl 2-(4-chlorophenyl)-2-(*p*-tolylthio) acetate (7k): Colorless oil; 85% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.38 (m, 2H), 7.31 (dd, $J = 8.3, 6.8$ Hz, 4H), 7.11 (d,

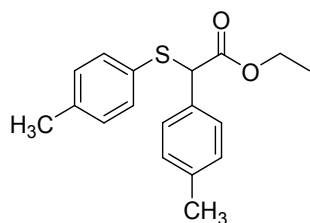
$J = 7.9$ Hz, 2H), 4.82 (s, 1H), 4.23–4.10 (m, 2H), 2.35 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.22, 138.74, 134.62, 134.19, 133.73, 130.04, 129.89, 129.54, 128.84, 61.90, 56.21, 21.27, 14.09. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{18}\text{ClO}_2\text{S}$ $[\text{M}+\text{H}]^+$: 321.0711; Found: 321.0716.



Ethyl 2-(4-bromophenyl)-2-(*p*-tolylthio) acetate (7l): Colorless oil; 81% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.46–7.40 (m, 2H), 7.32–7.23 (m, 4H), 7.07 (d, $J = 7.9$ Hz, 2H), 4.76 (s, 1H), 4.19–4.05 (m, 2H), 2.31 (s, 3H), 1.17 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.10, 138.72, 135.13, 133.70, 131.77, 130.34, 129.88, 129.49, 122.36, 61.89, 56.25, 21.26, 14.07. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{BrO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 387.0025; Found: 387.0028.

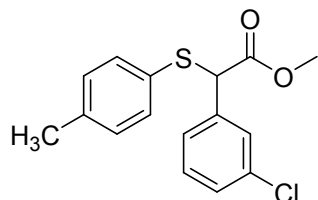


Ethyl 2-(4-iodophenyl)-2-(*p*-tolylthio) acetate (7m): Colorless oil; 70% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.66–7.61 (m, 2H), 7.28–7.24 (m, 2H), 7.20–7.15 (m, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 4.75 (s, 1H), 4.21–4.03 (m, 2H), 2.32 (s, 3H), 1.18 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.10, 138.72, 137.76, 135.80, 133.67, 130.55, 129.90, 129.52, 94.11, 61.92, 56.39, 21.28, 14.09. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{IO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 434.9886; Found: 434.9886.

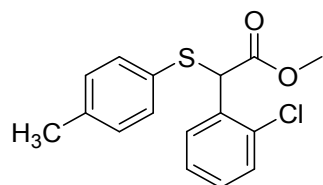


Ethyl 2-(*p*-tolyl)-2-(*p*-tolylthio) acetate (7n): Colorless oil; 80% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 8.1$ Hz, 2H), 7.33–7.28 (m, 2H), 7.14 (d, $J = 8.0$ Hz, 2H),

7.09 (d, $J = 7.9$ Hz, 2H), 4.84 (s, 1H), 4.19–4.06 (m, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 1.17 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.75, 138.24, 138.10, 133.22, 132.87, 130.37, 129.78, 129.41, 128.49, 61.66, 56.58, 21.24, 14.09. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 323.1076; Found: 323.1081.



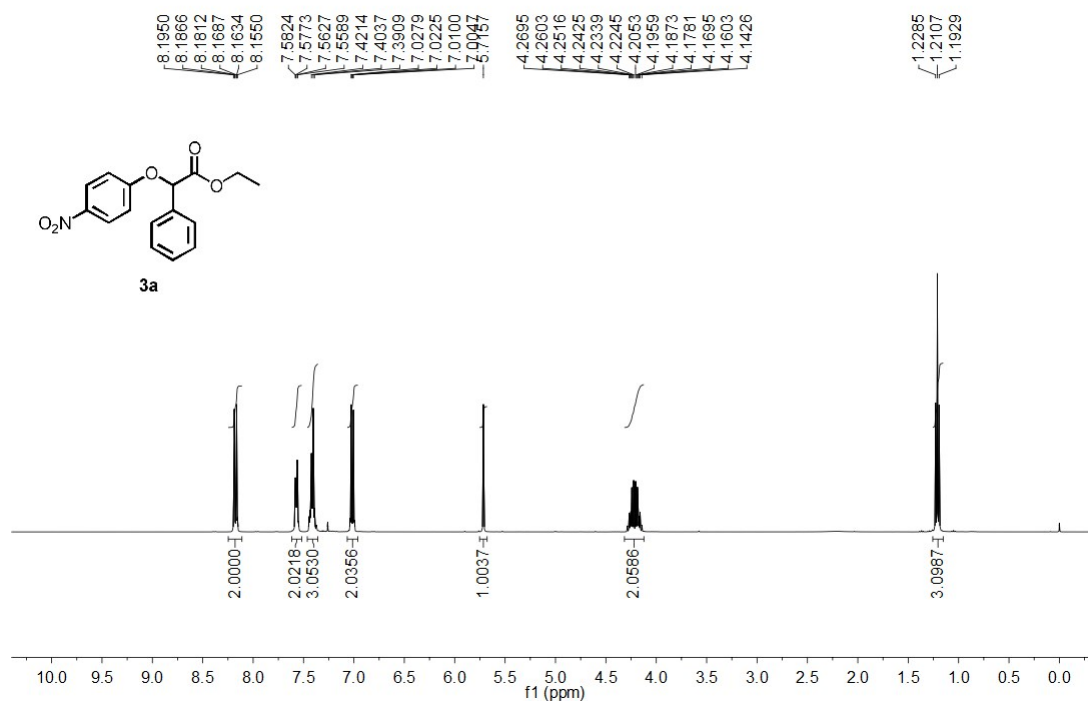
Methyl 2-(3-chlorophenyl)-2-(*p*-tolylthio) acetate (7q): Colorless oil; 78% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 1.8$ Hz, 1H), 7.38–7.27 (m, 5H), 7.13 (d, $J = 8.0$ Hz, 2H), 4.84 (s, 1H), 3.73 (s, 3H), 2.37 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.50, 138.88, 137.87, 134.49, 133.77, 129.94, 129.87, 129.32, 128.77, 128.50, 126.86, 56.31, 52.86, 21.25. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{15}\text{ClO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 329.0373; Found: 329.0386.



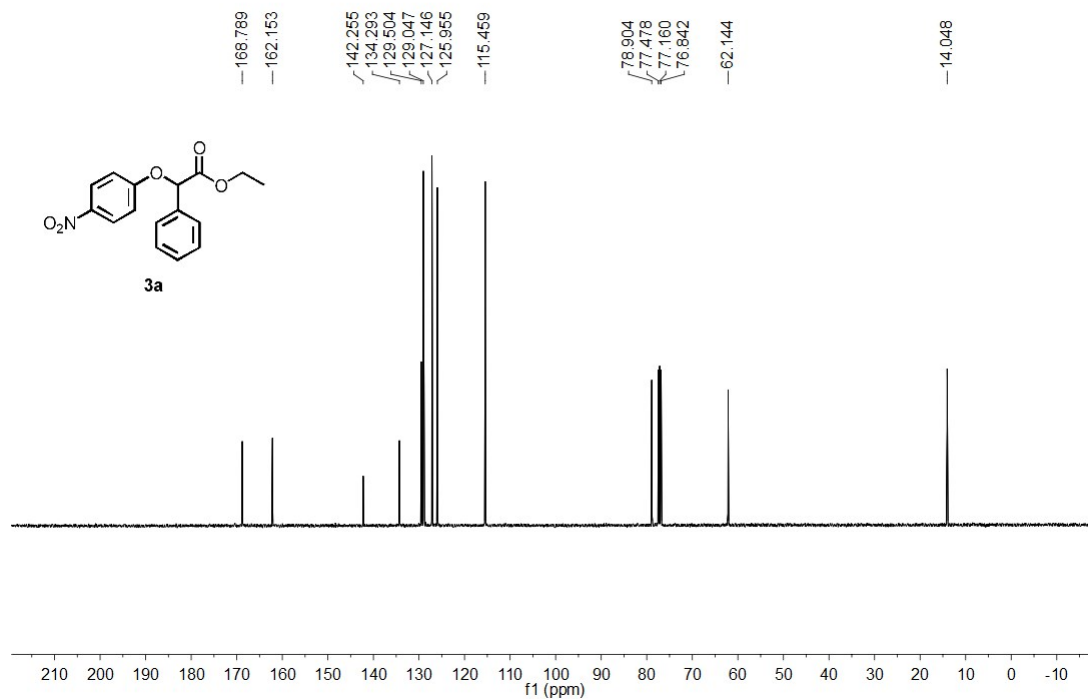
Methyl 2-(2-chlorophenyl)-2-(*p*-tolylthio) acetate (7r): Colorless oil; 70% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, $J = 7.5, 2.0$ Hz, 1H), 7.34 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.26–7.19 (m, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 5.40 (s, 1H), 3.68 (s, 3H), 2.31 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 170.64, 138.76, 133.88, 133.84, 133.77, 130.29, 129.88, 129.64, 129.53, 129.38, 127.23, 52.89, 52.78, 21.29. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{15}\text{ClO}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 329.0373; Found: 329.0385.

9. Copies of NMR spectra

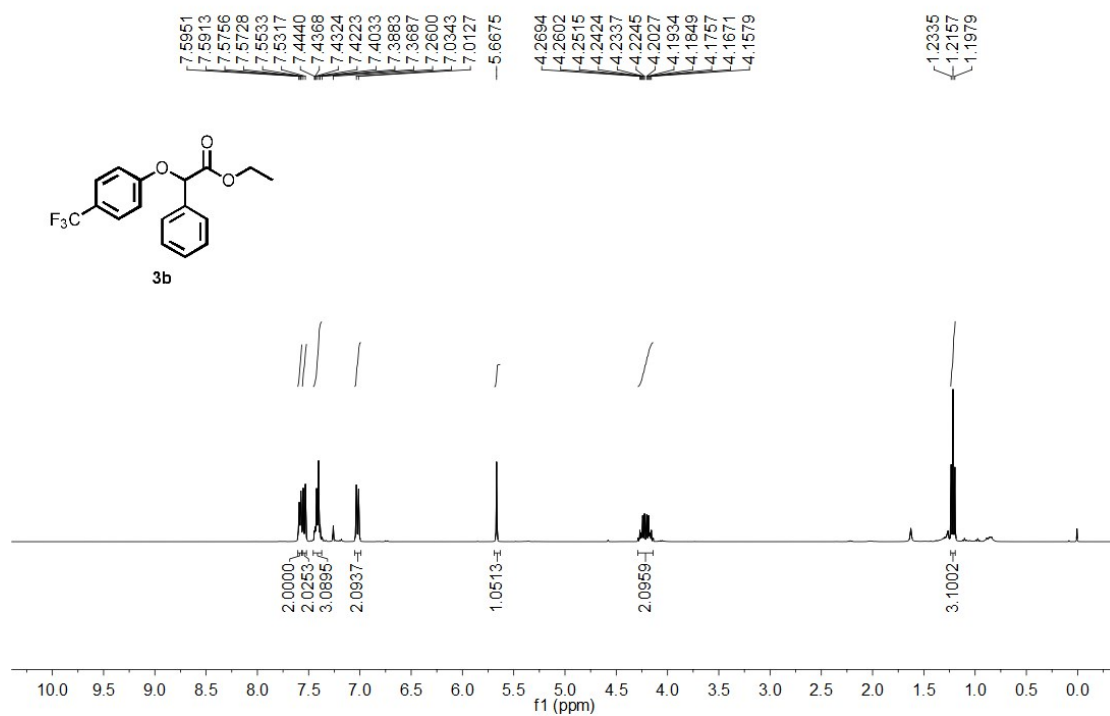
FYF-1



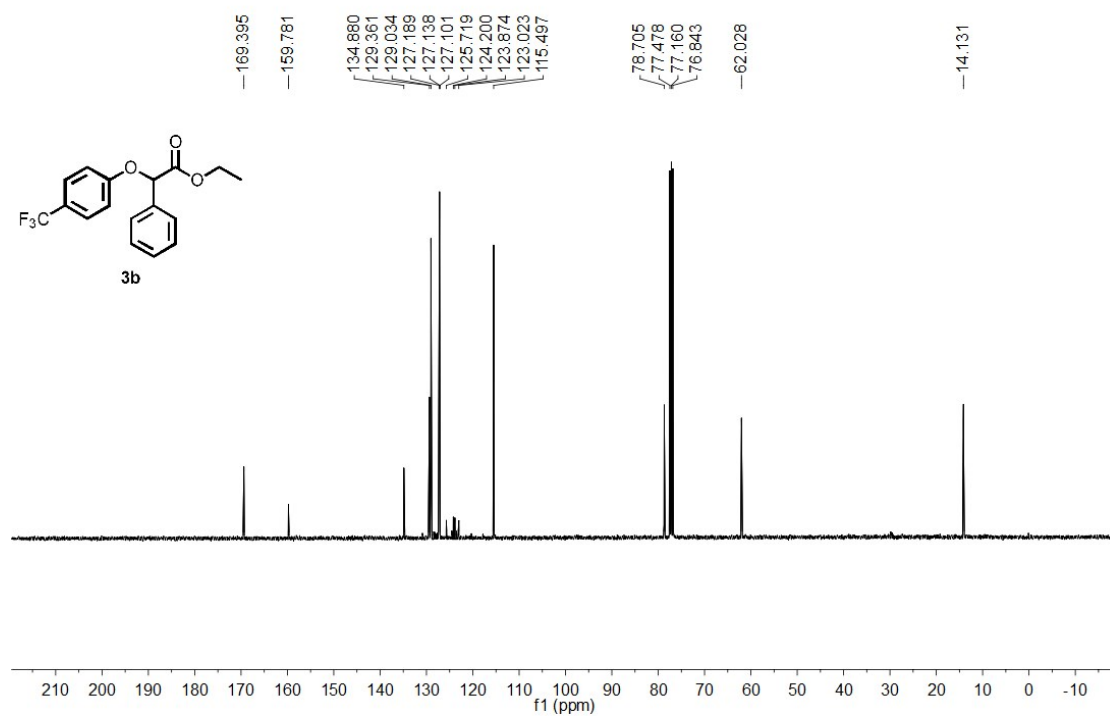
FYF-1-2



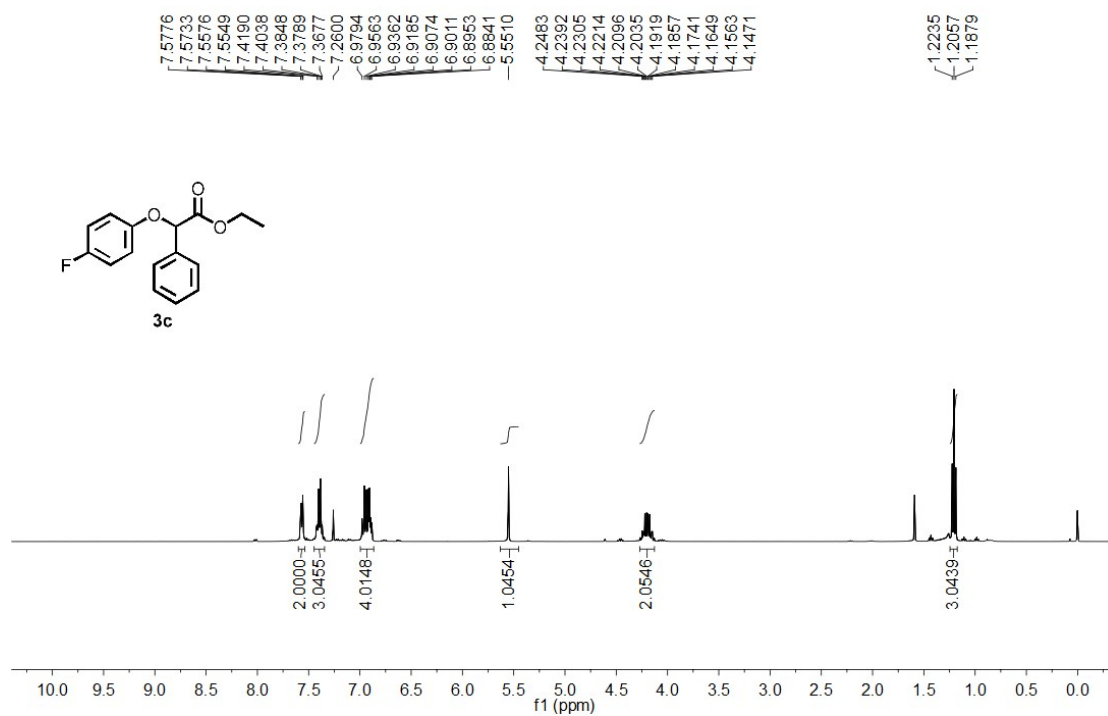
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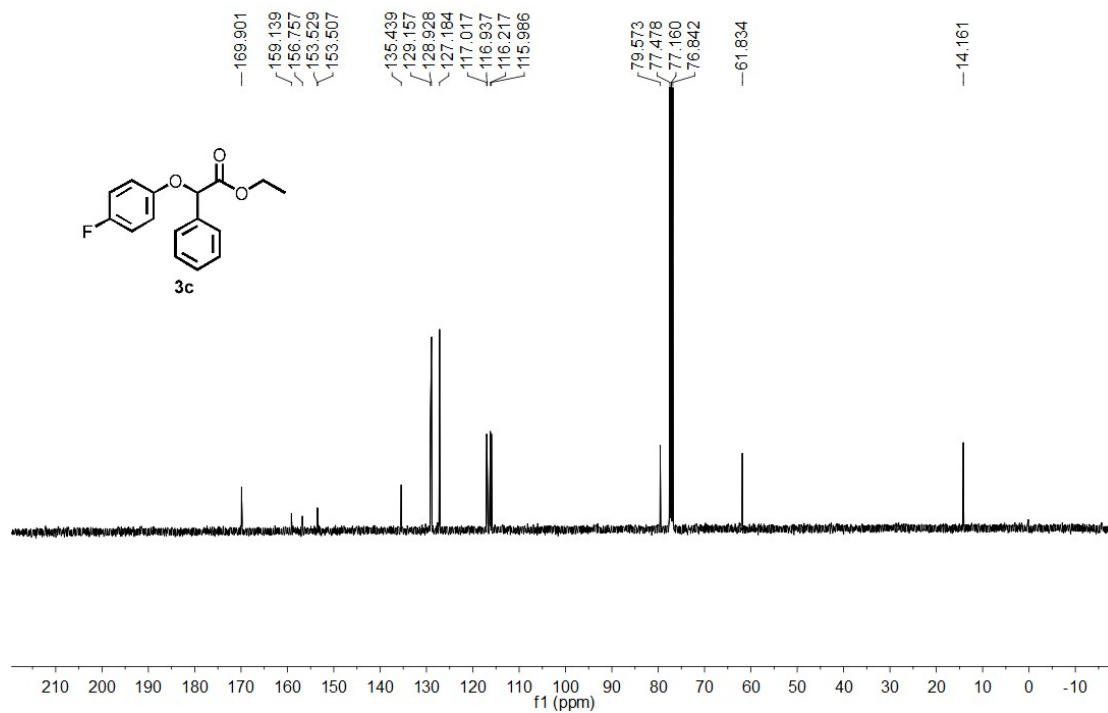
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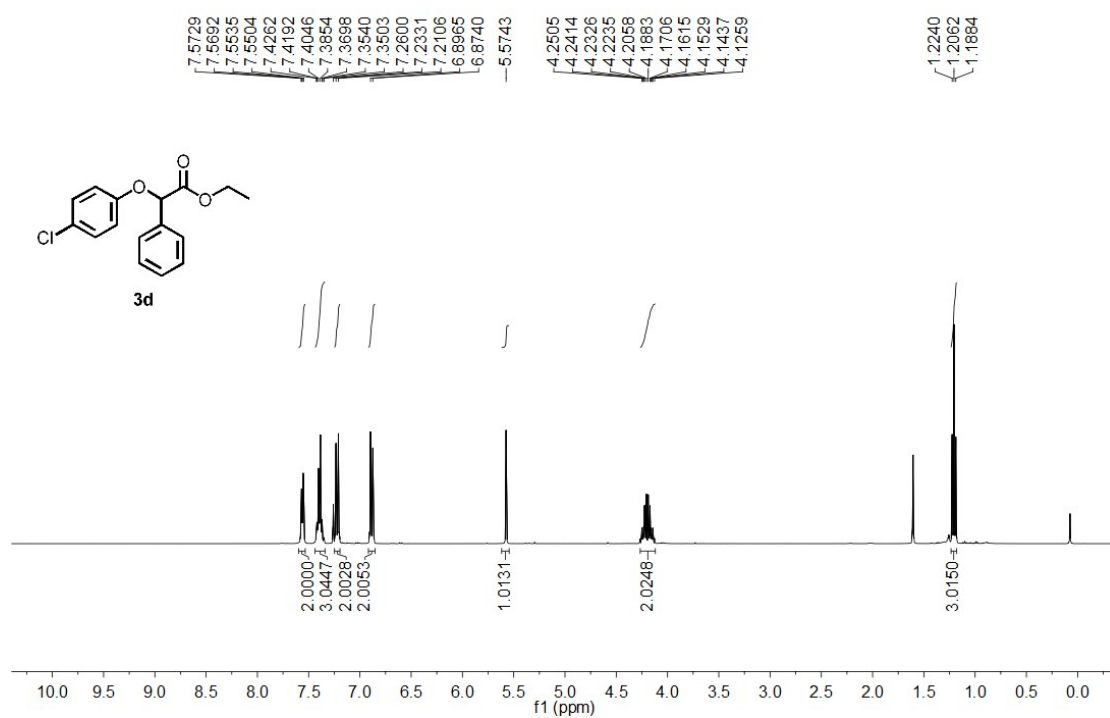
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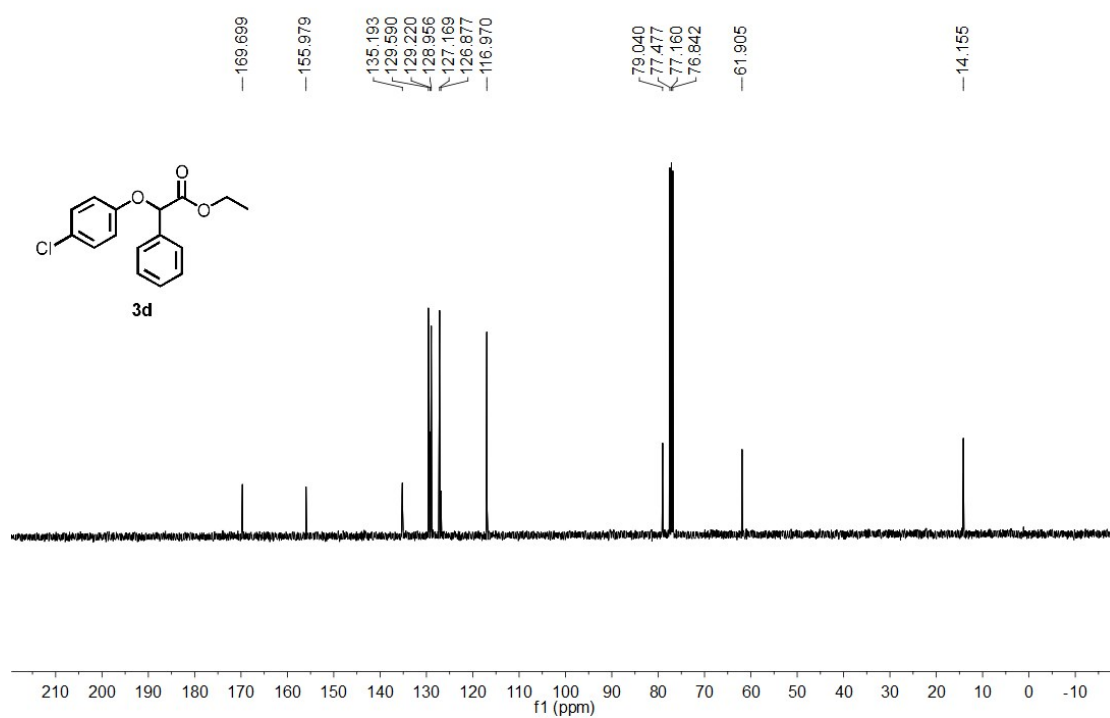
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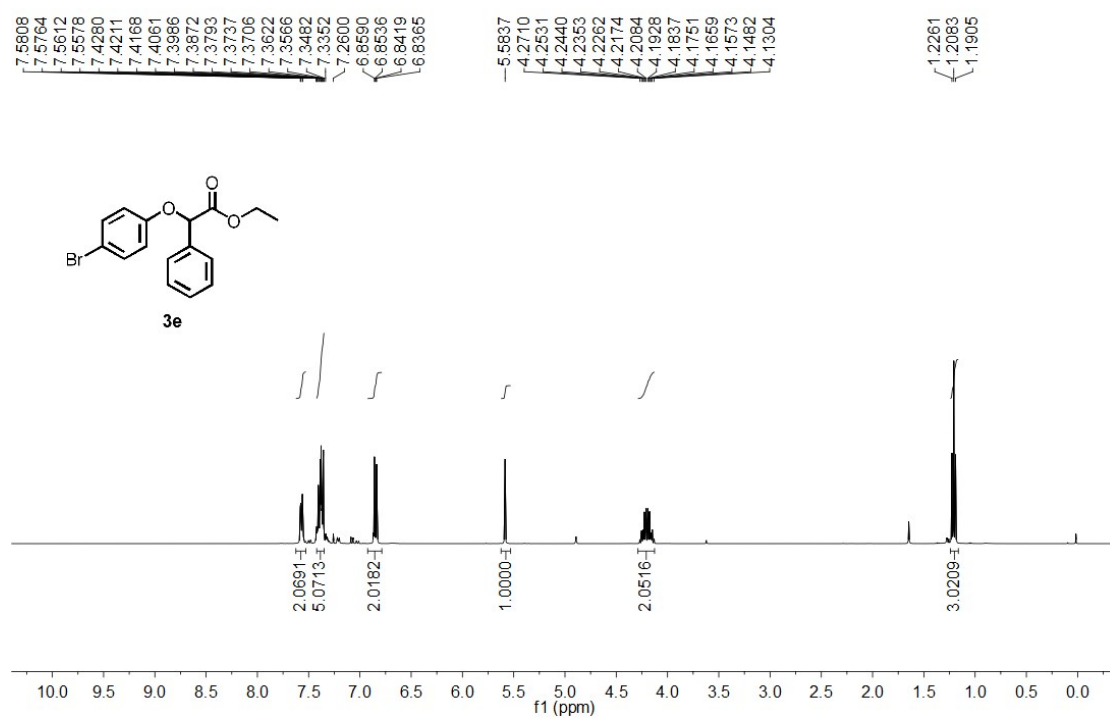
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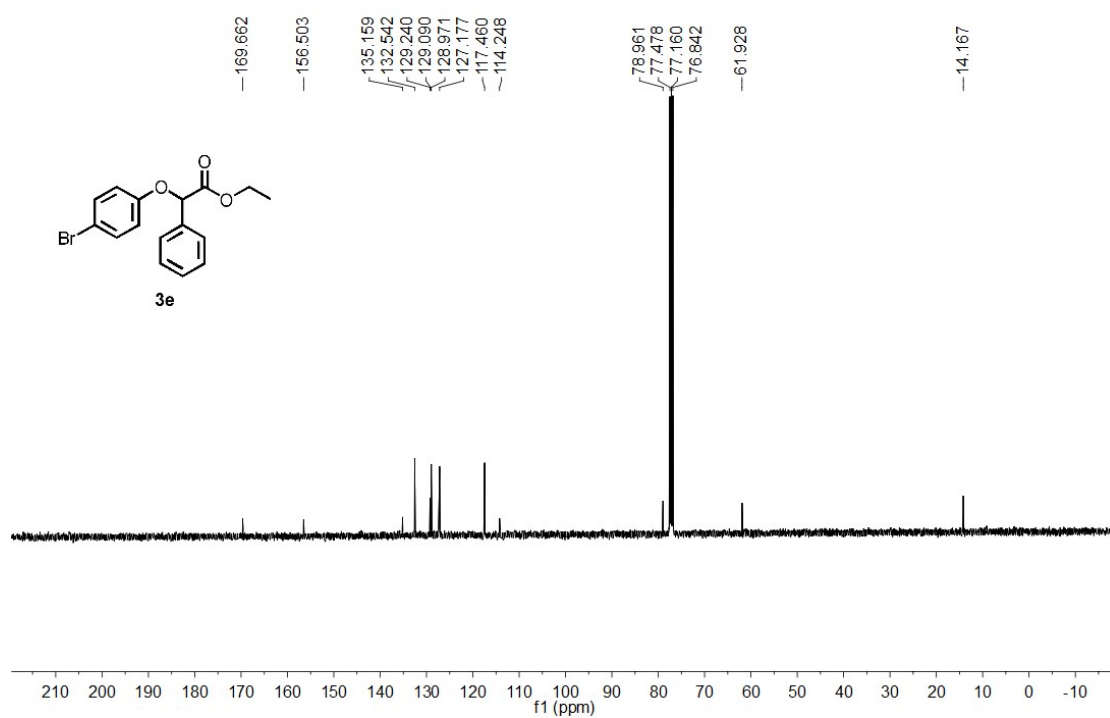
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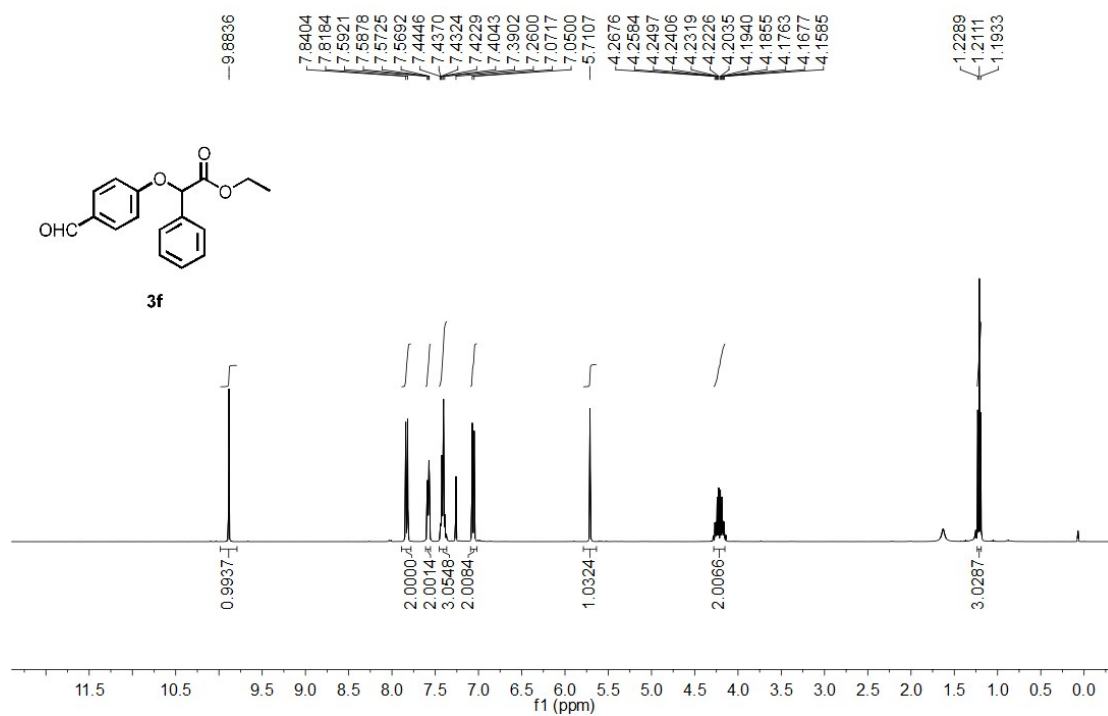
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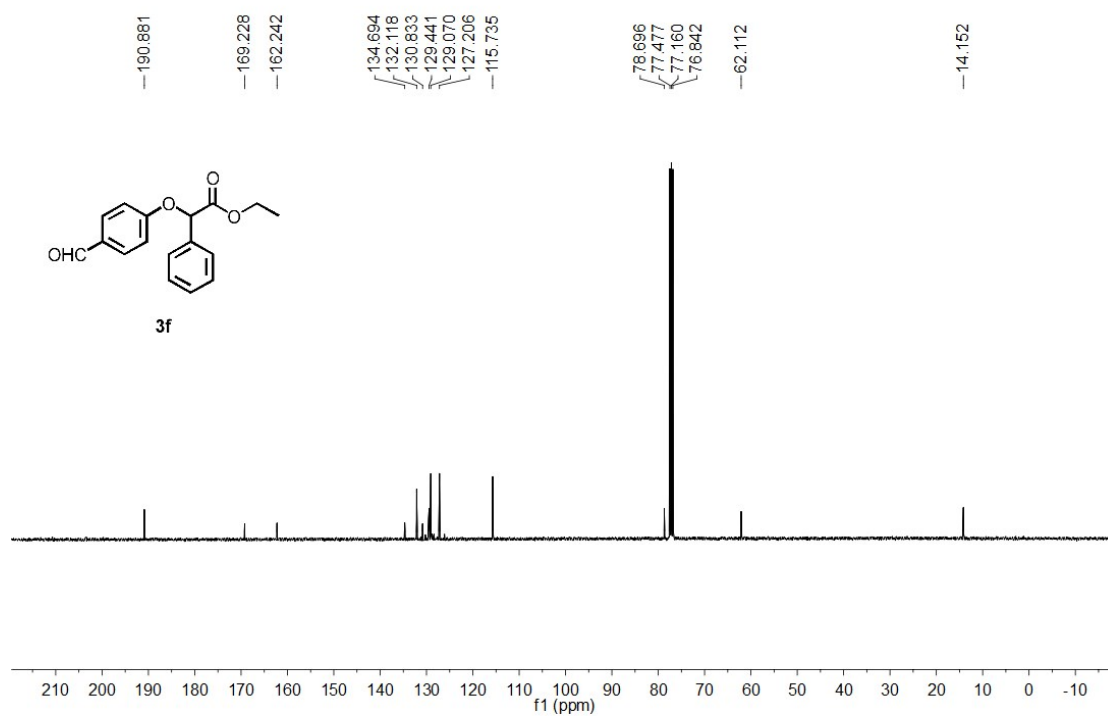
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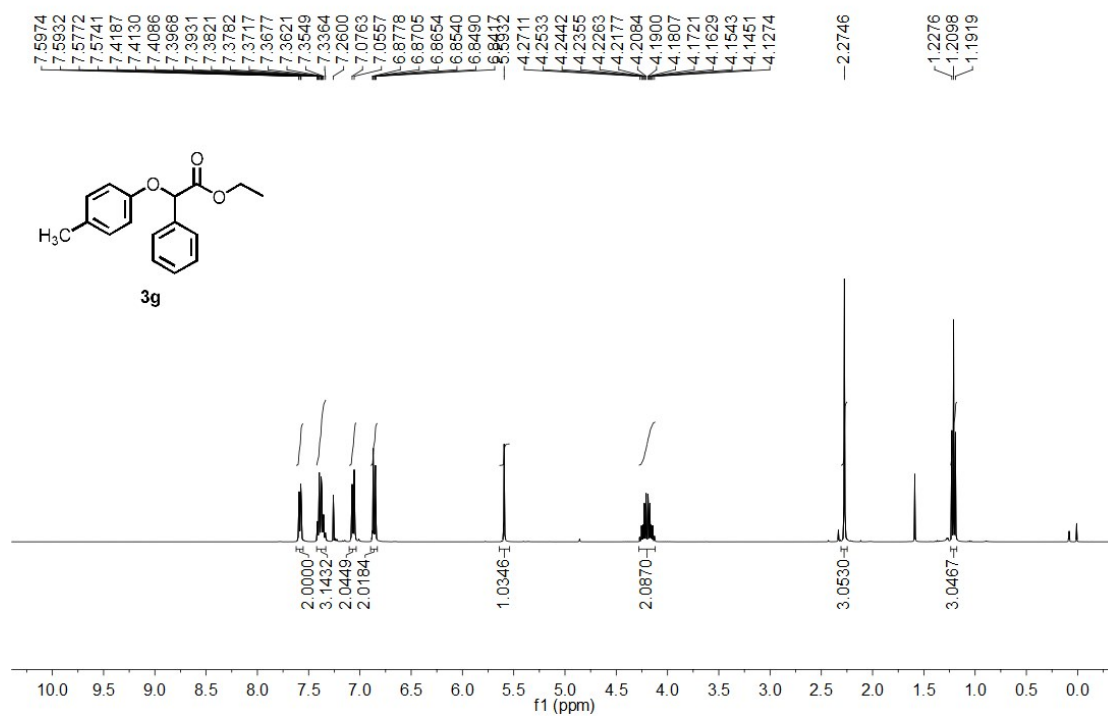
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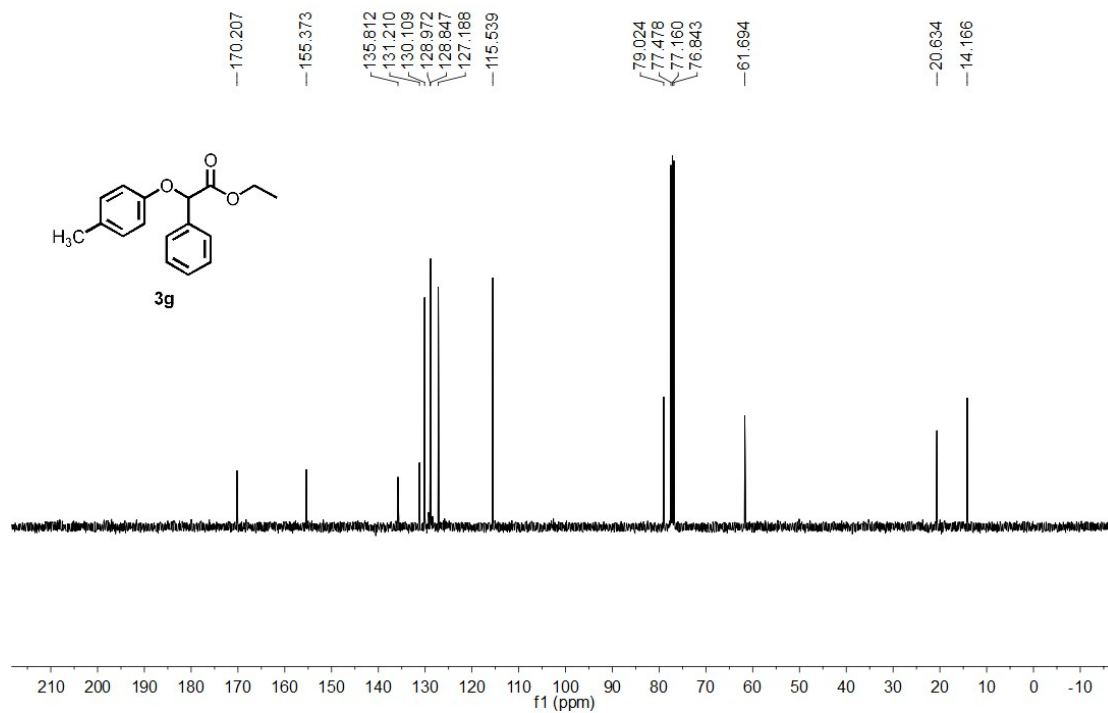
ZZP-18



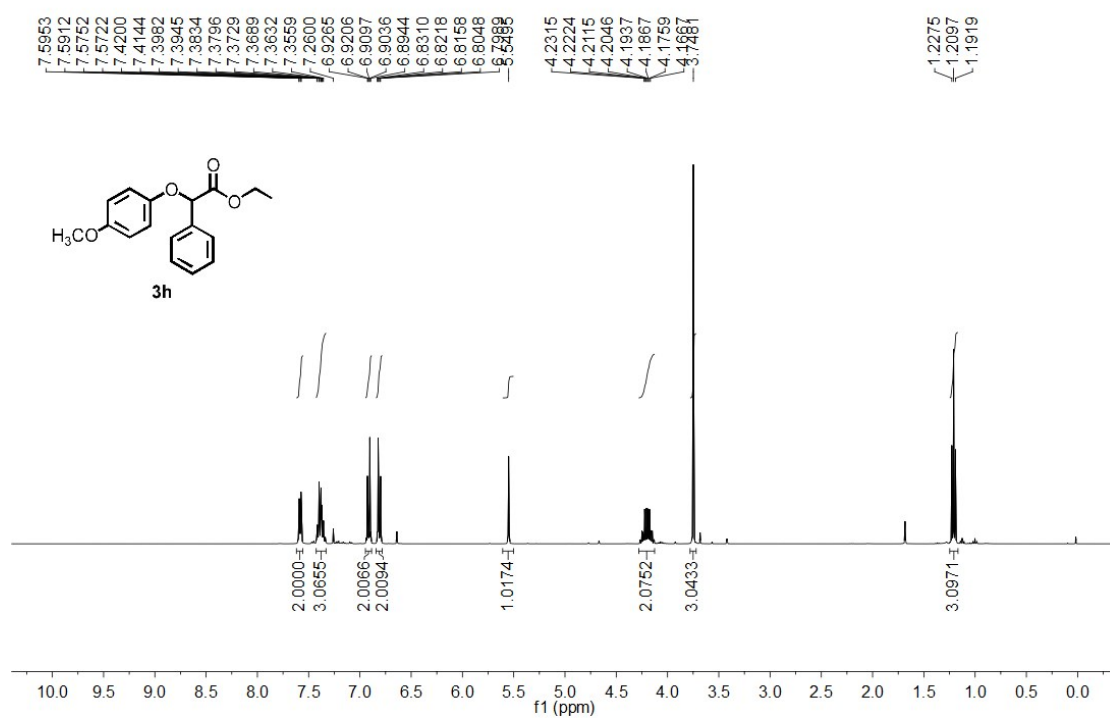
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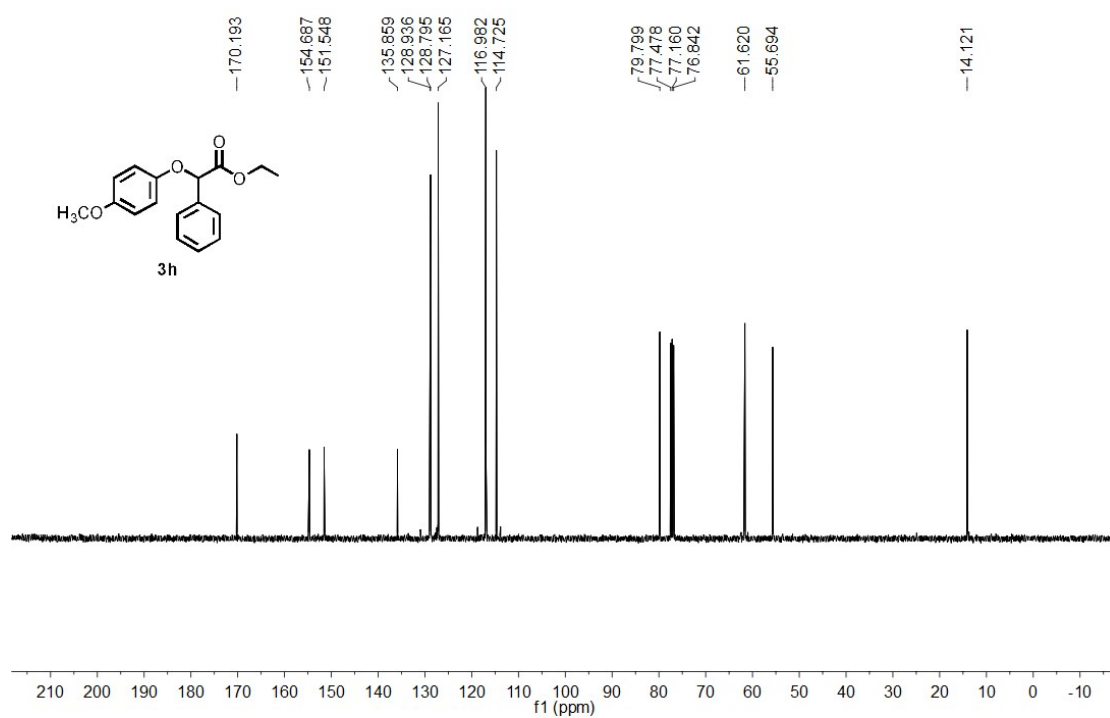
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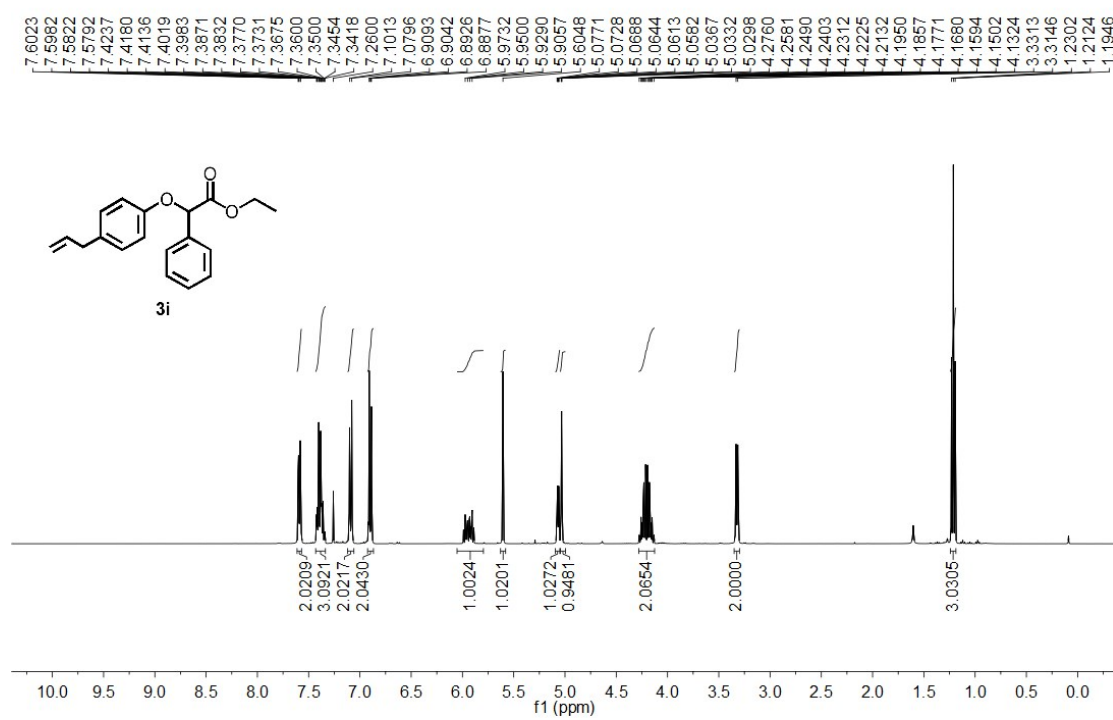
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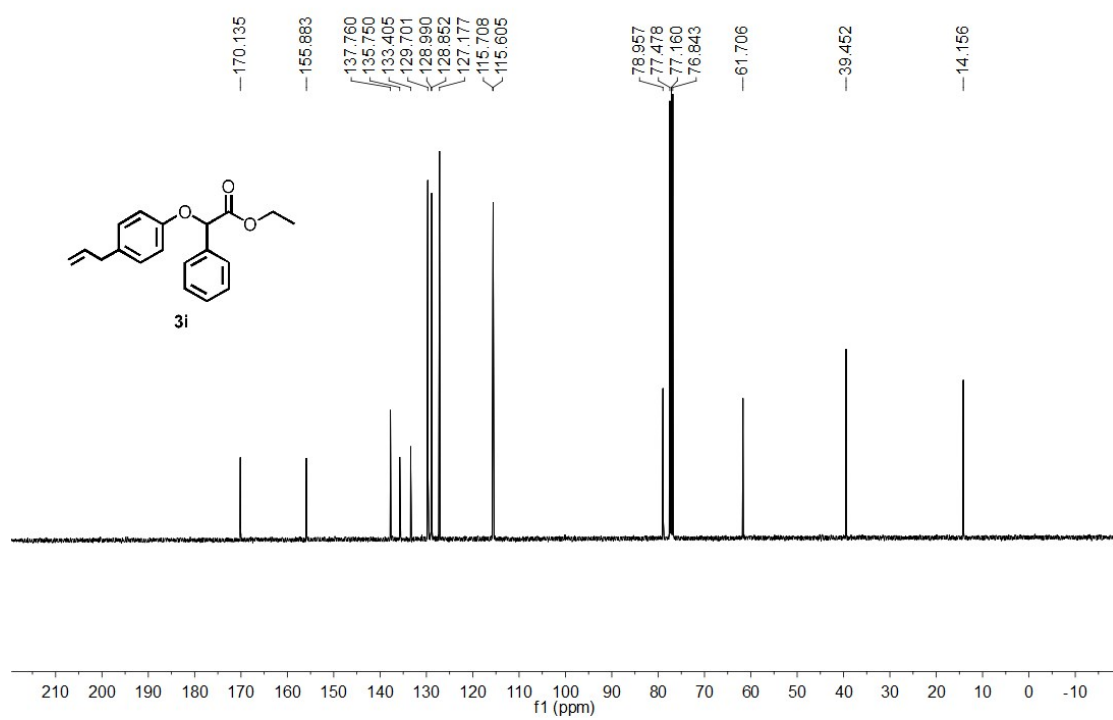
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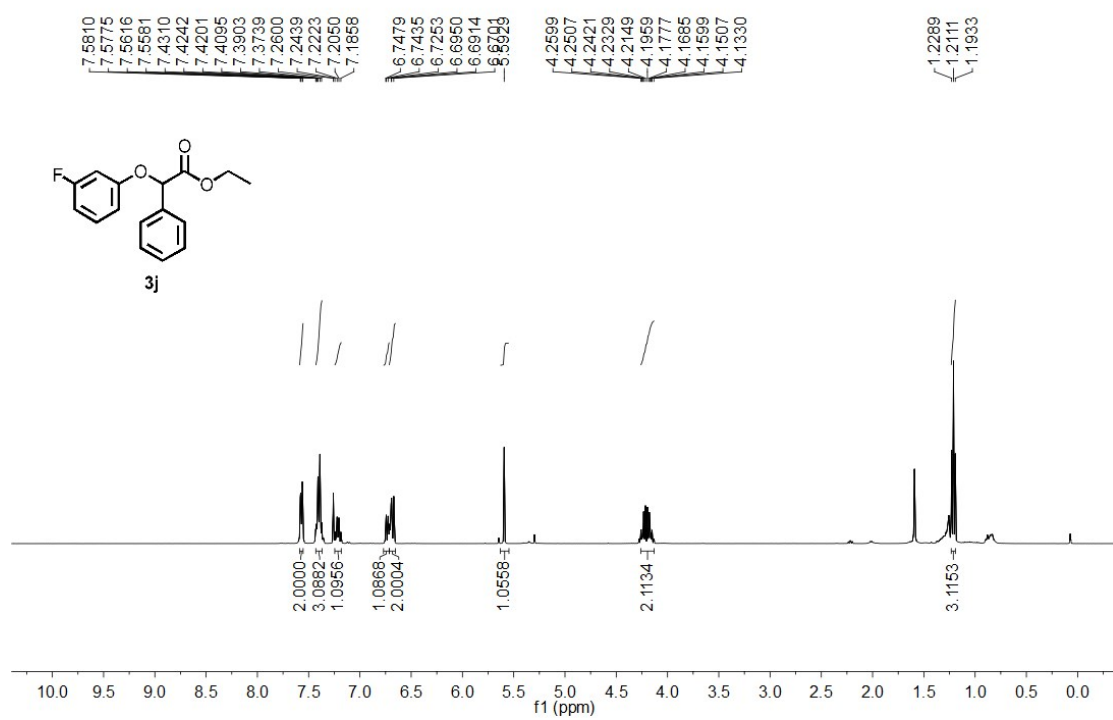
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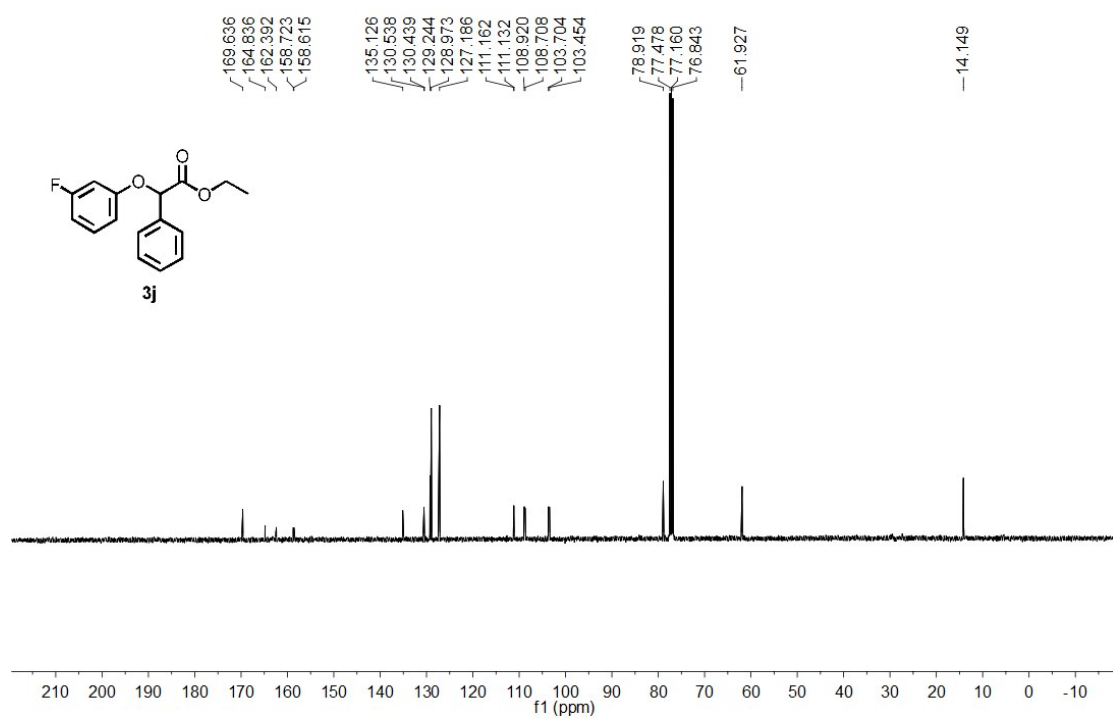
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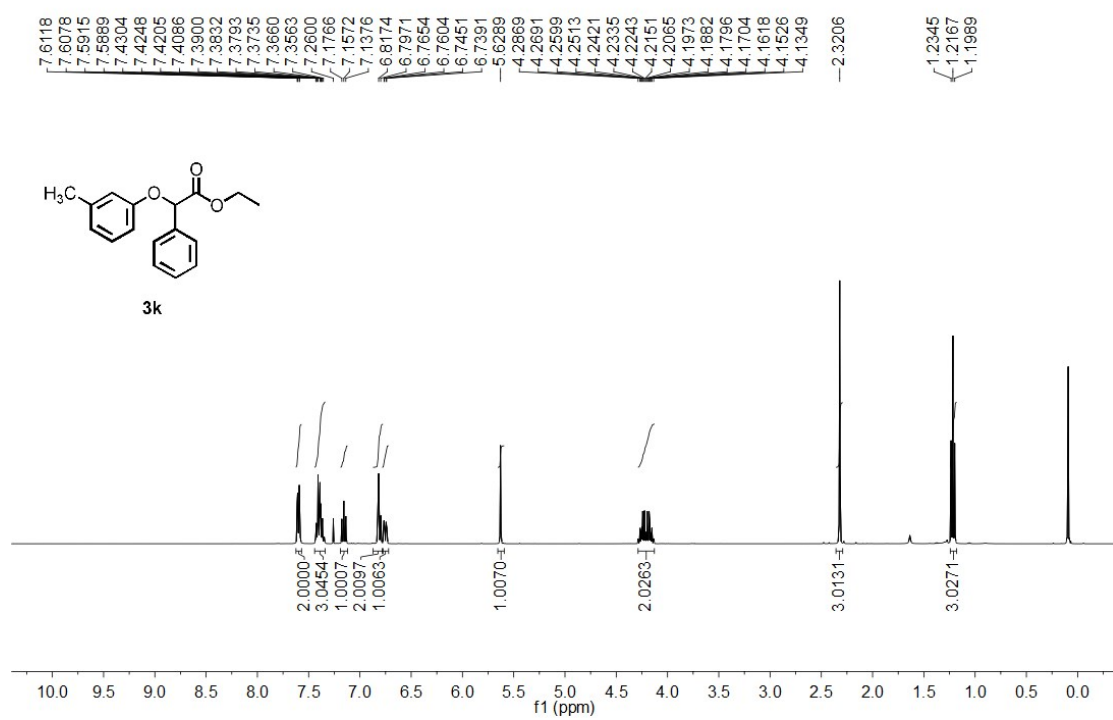
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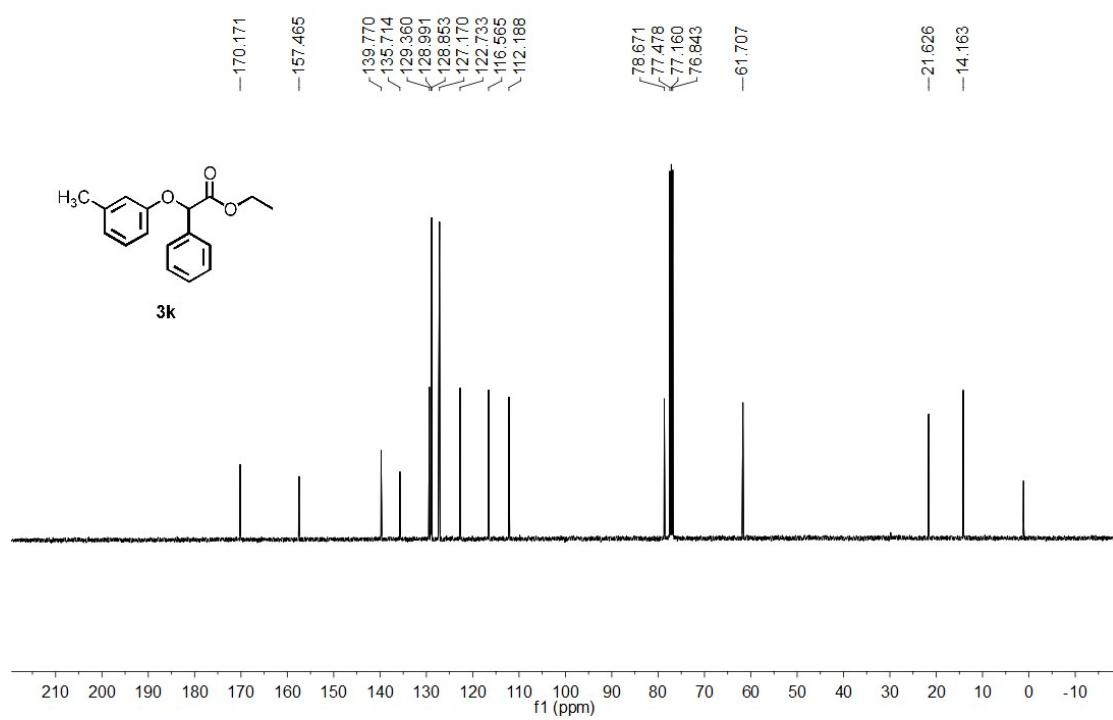
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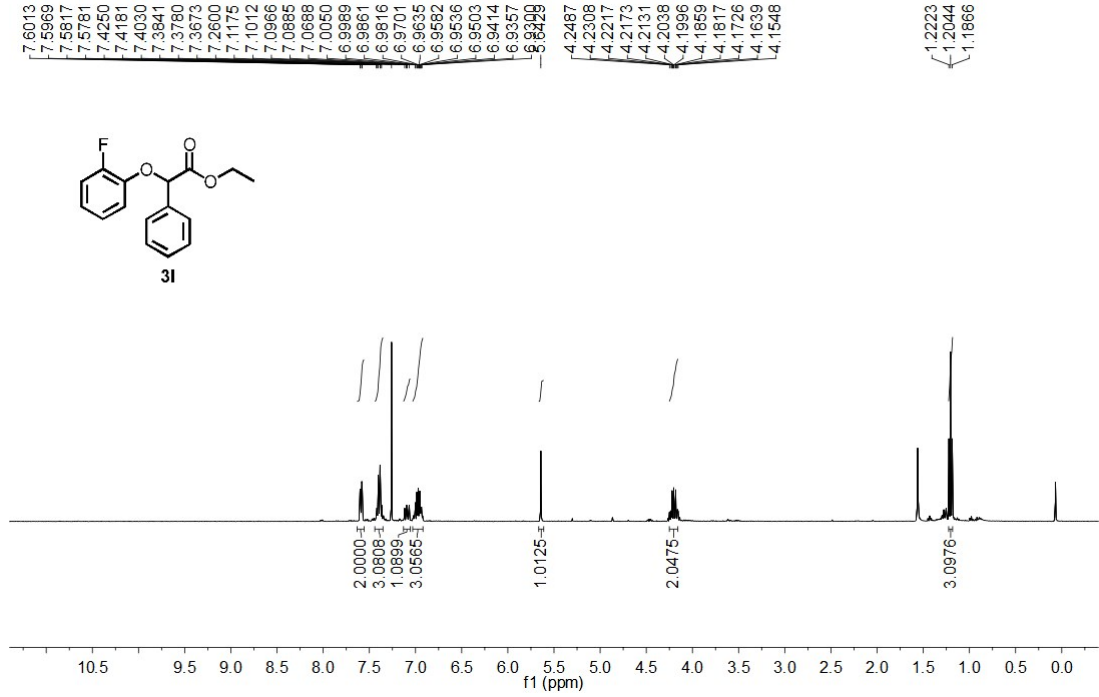
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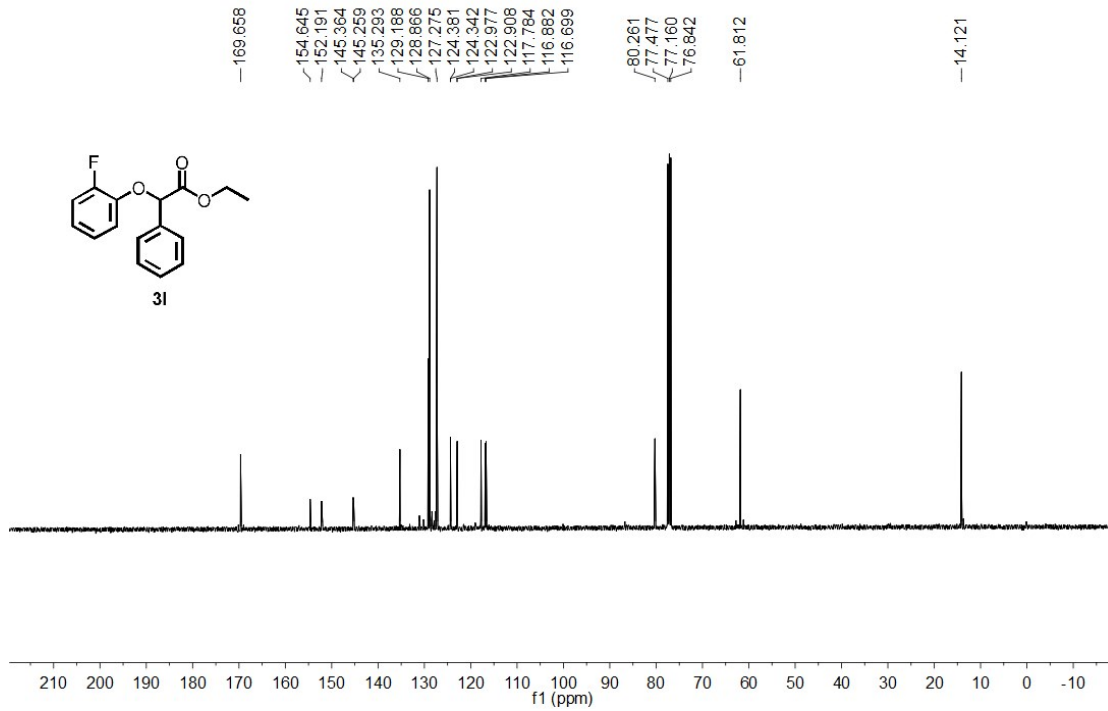
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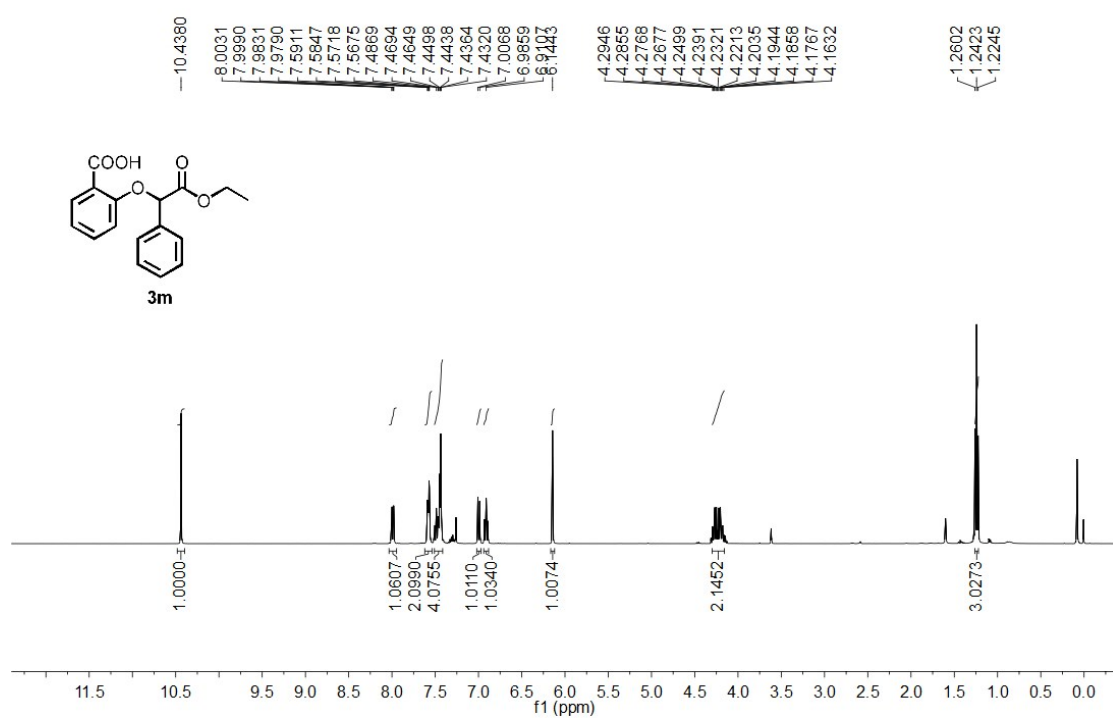
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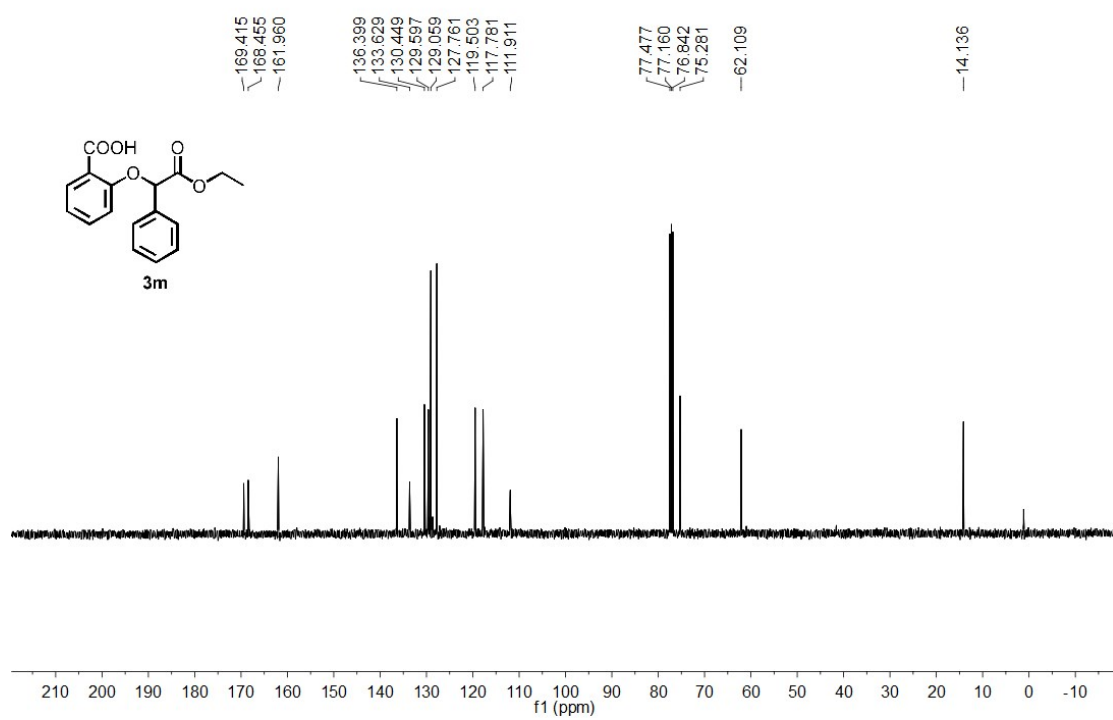
zyp-11



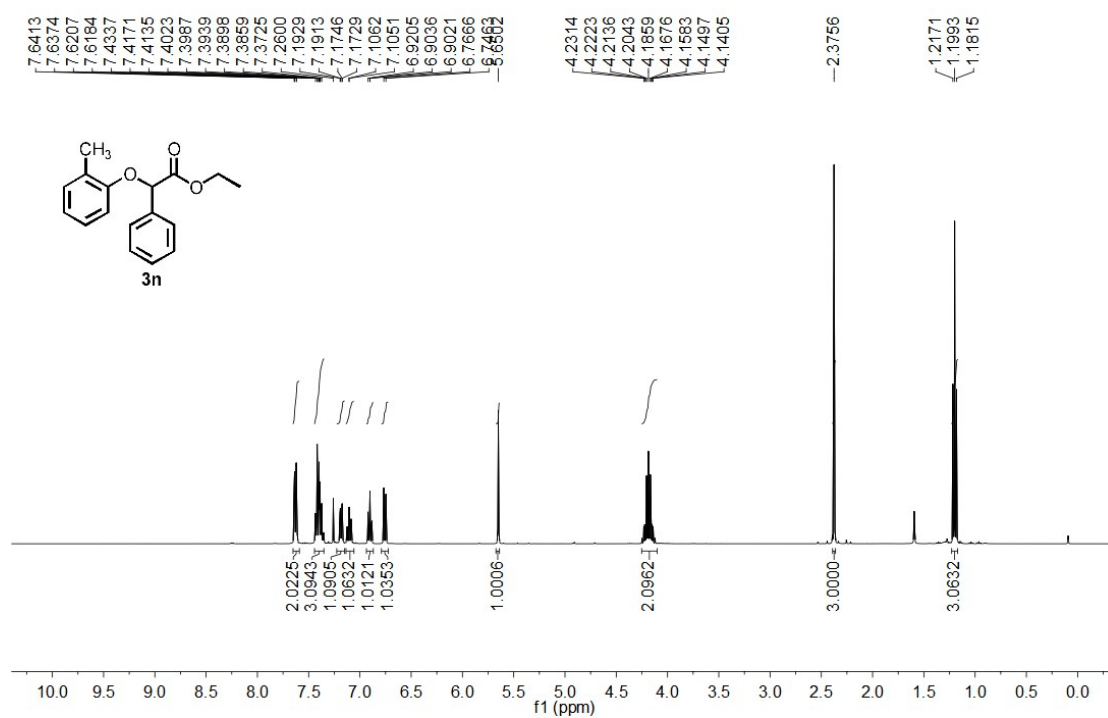
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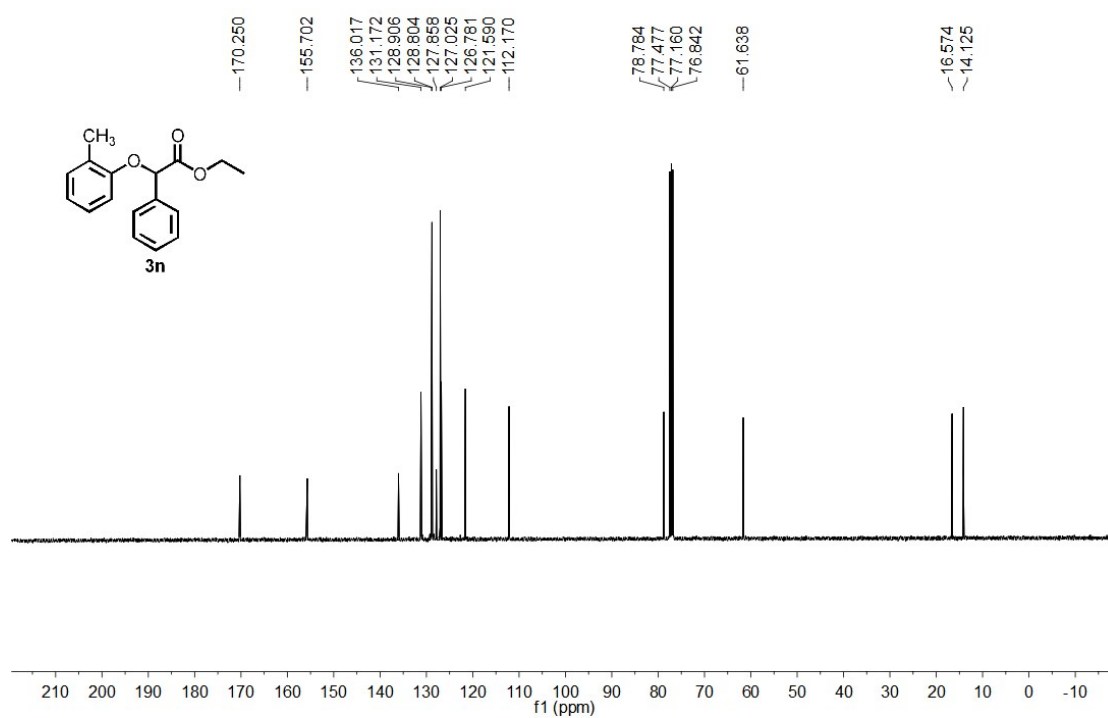
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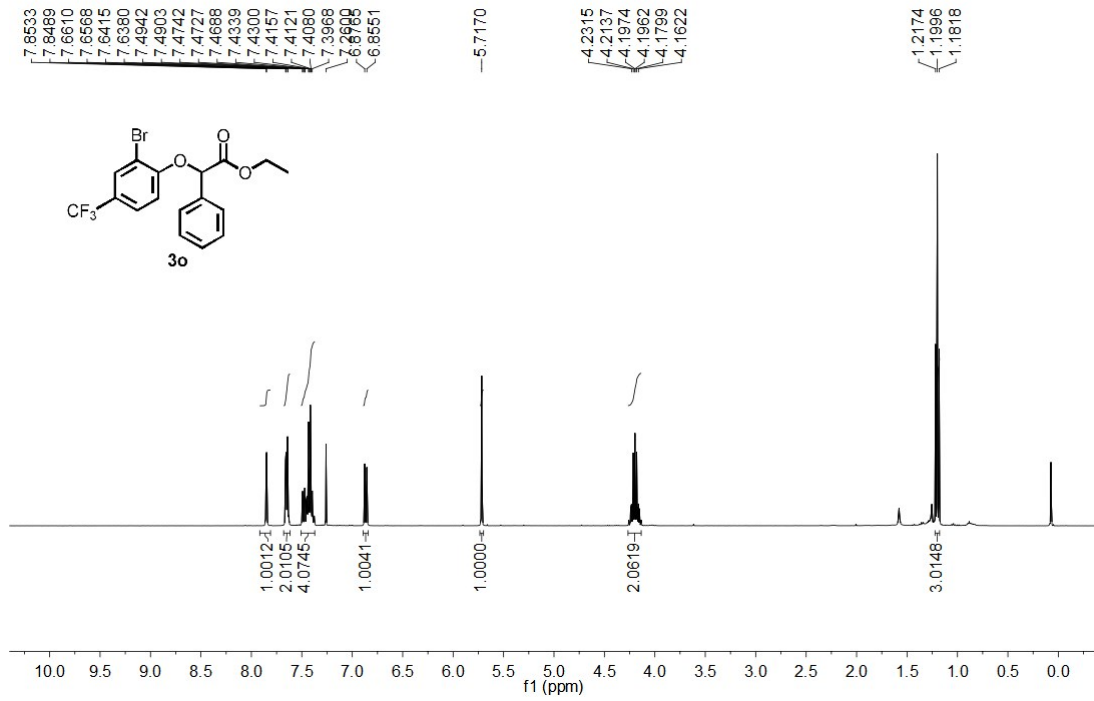
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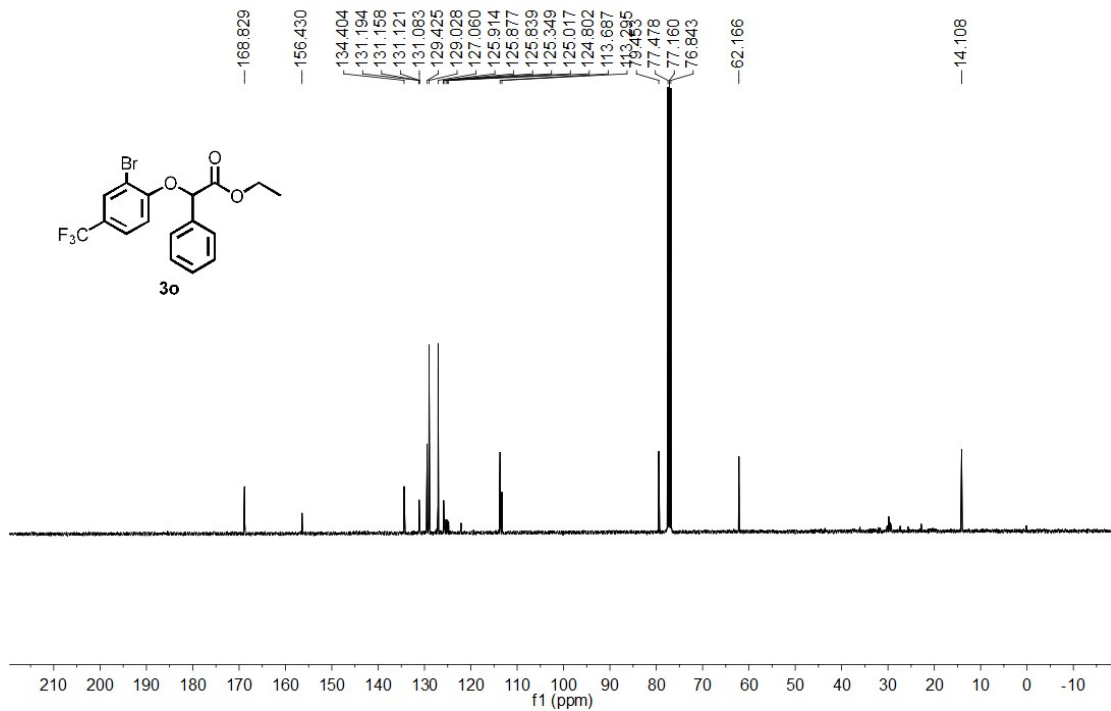
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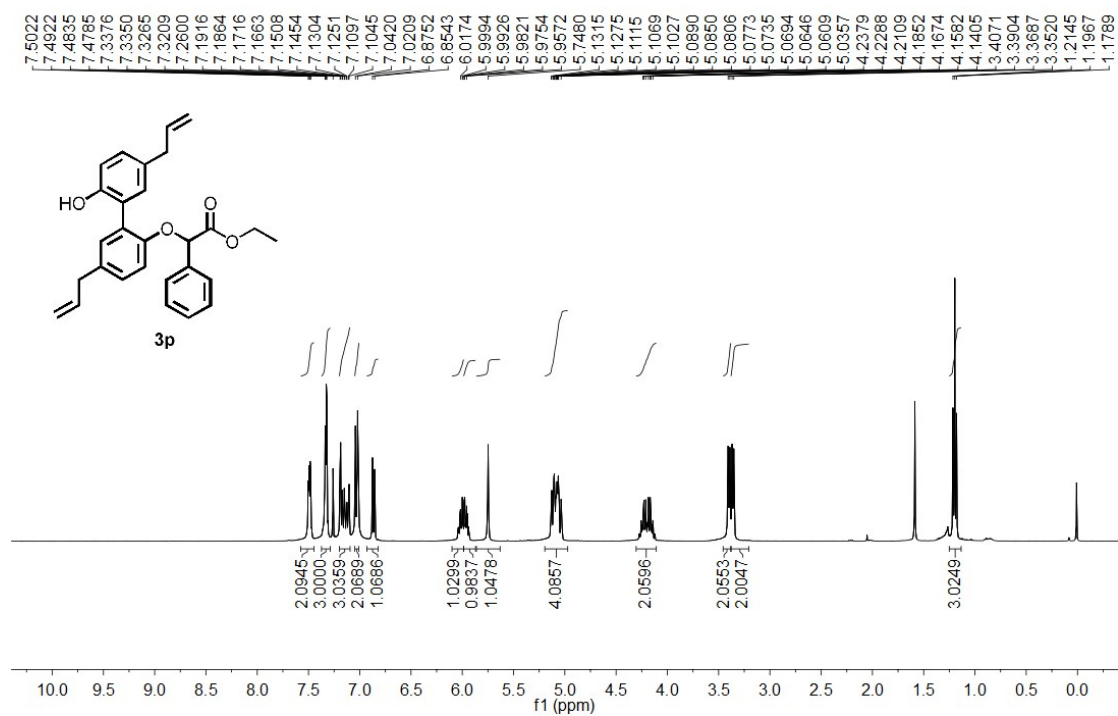
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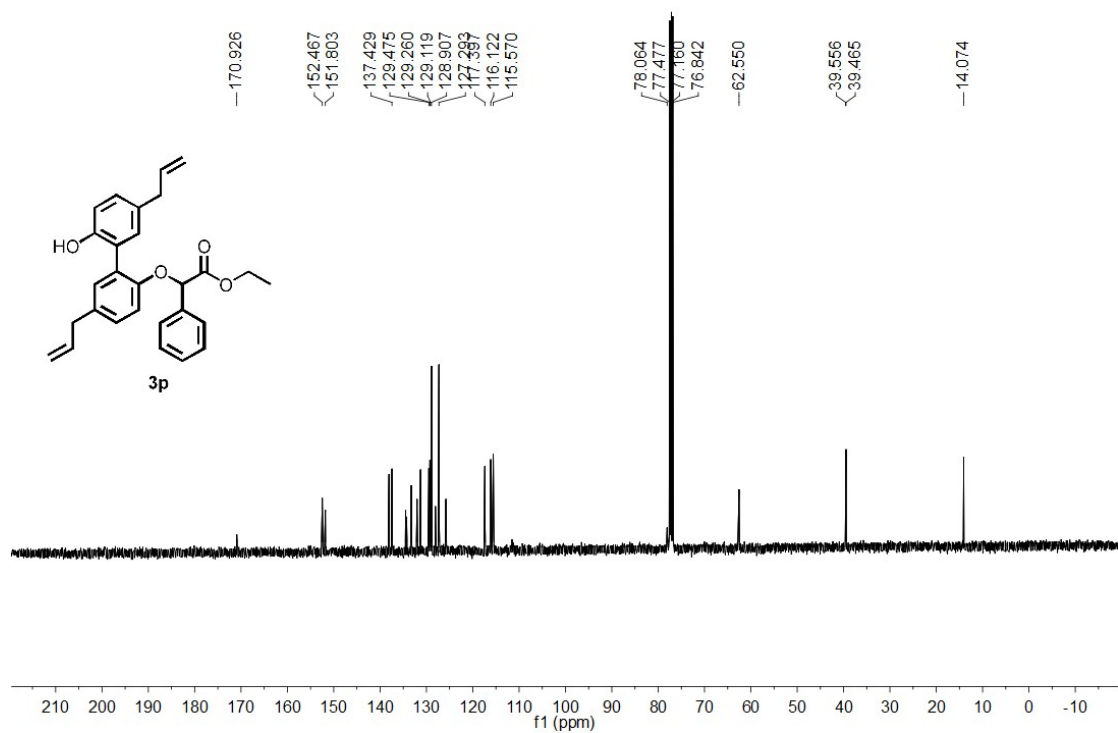
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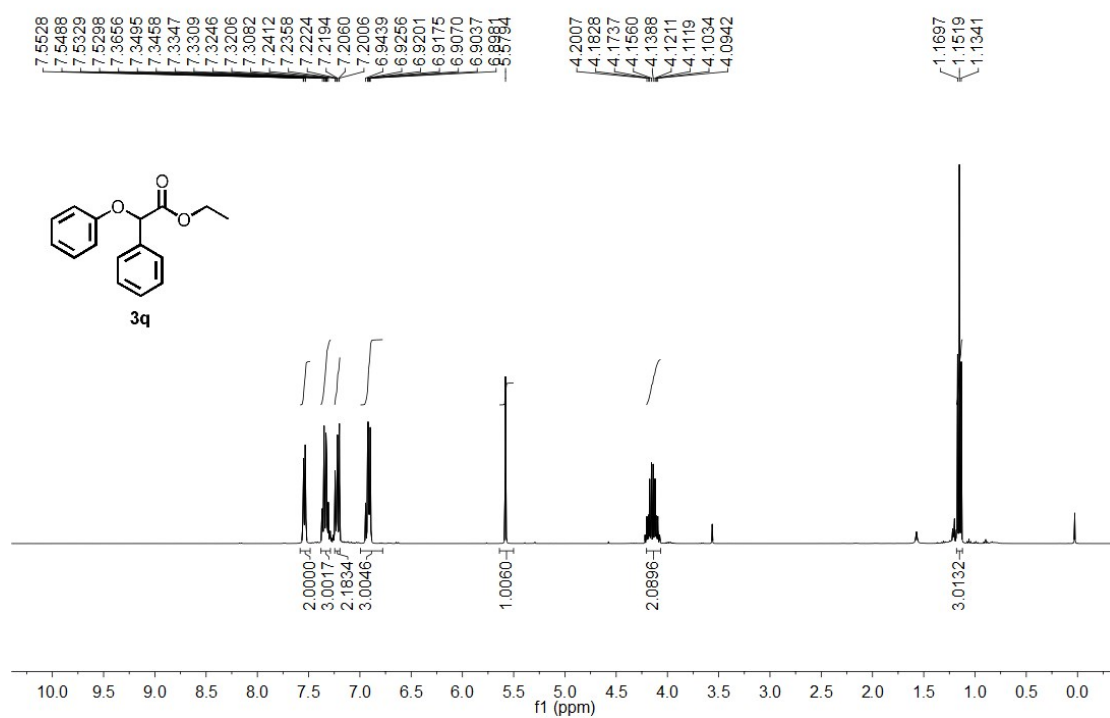
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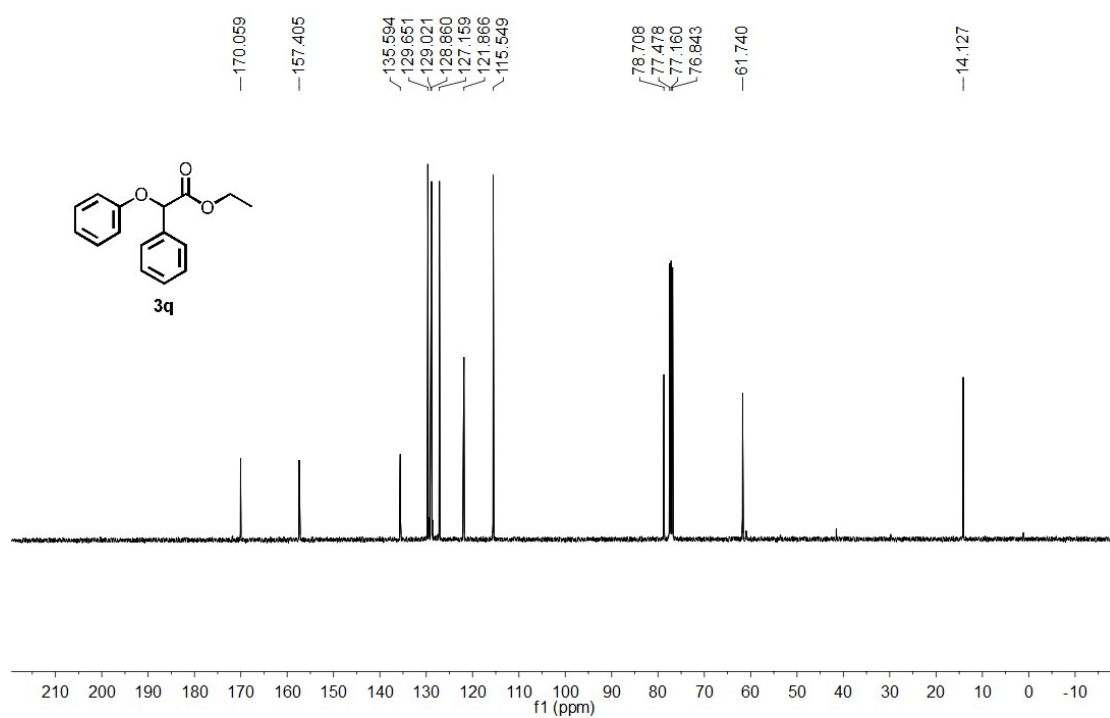
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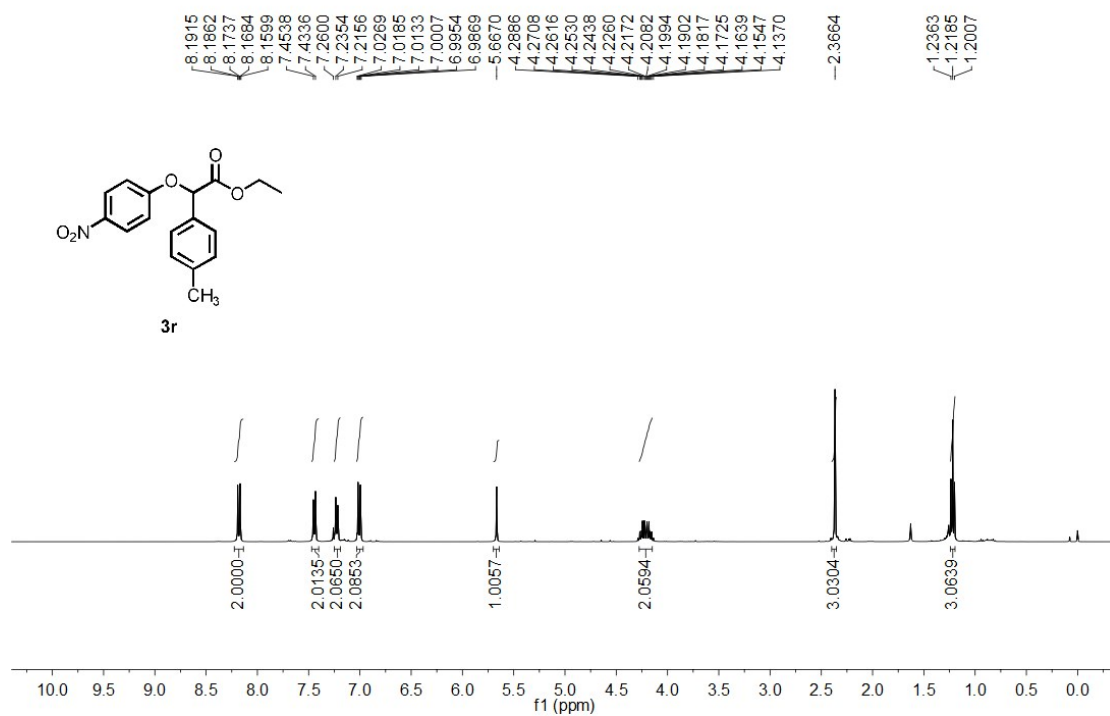
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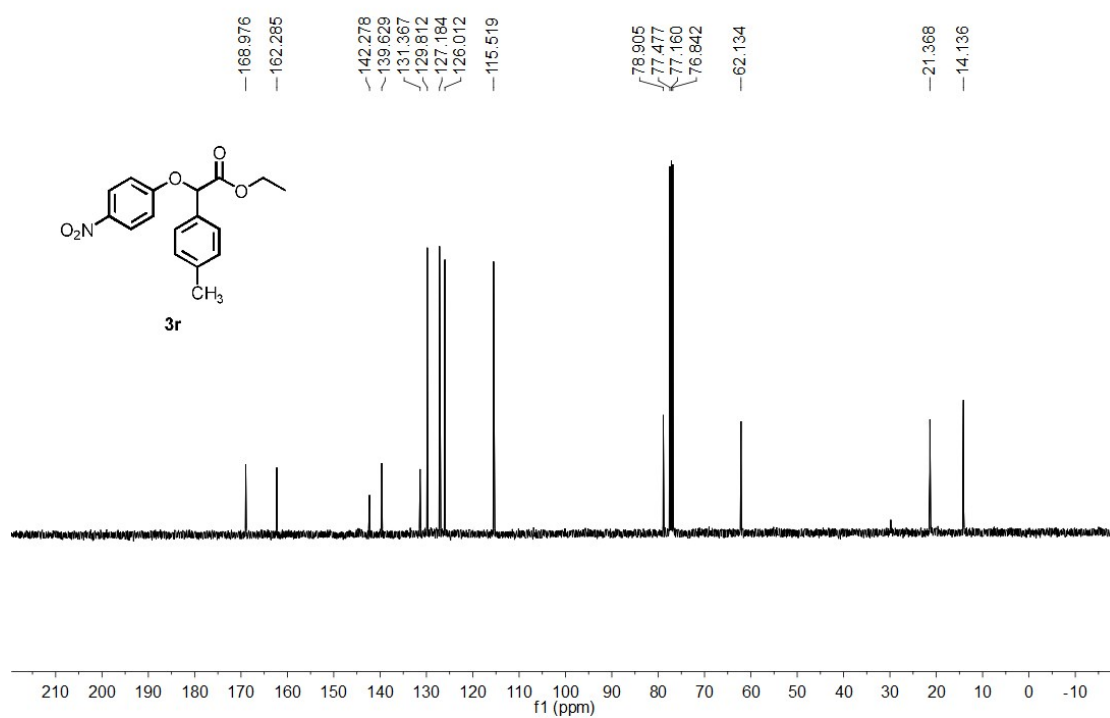
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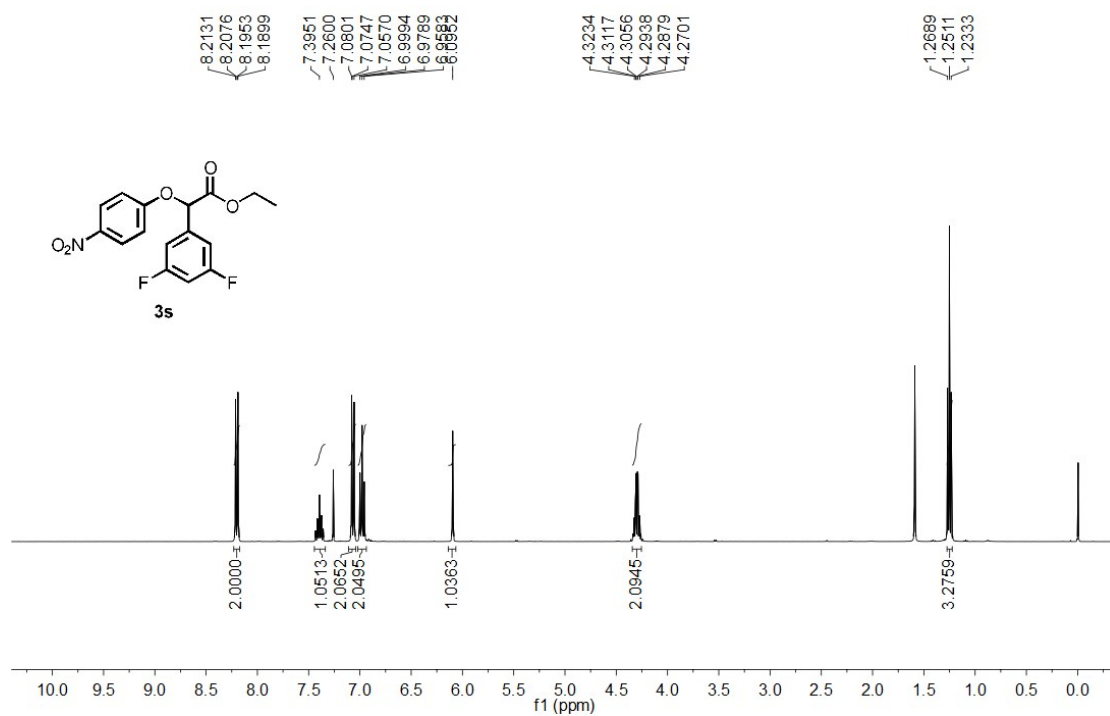
FYF-8



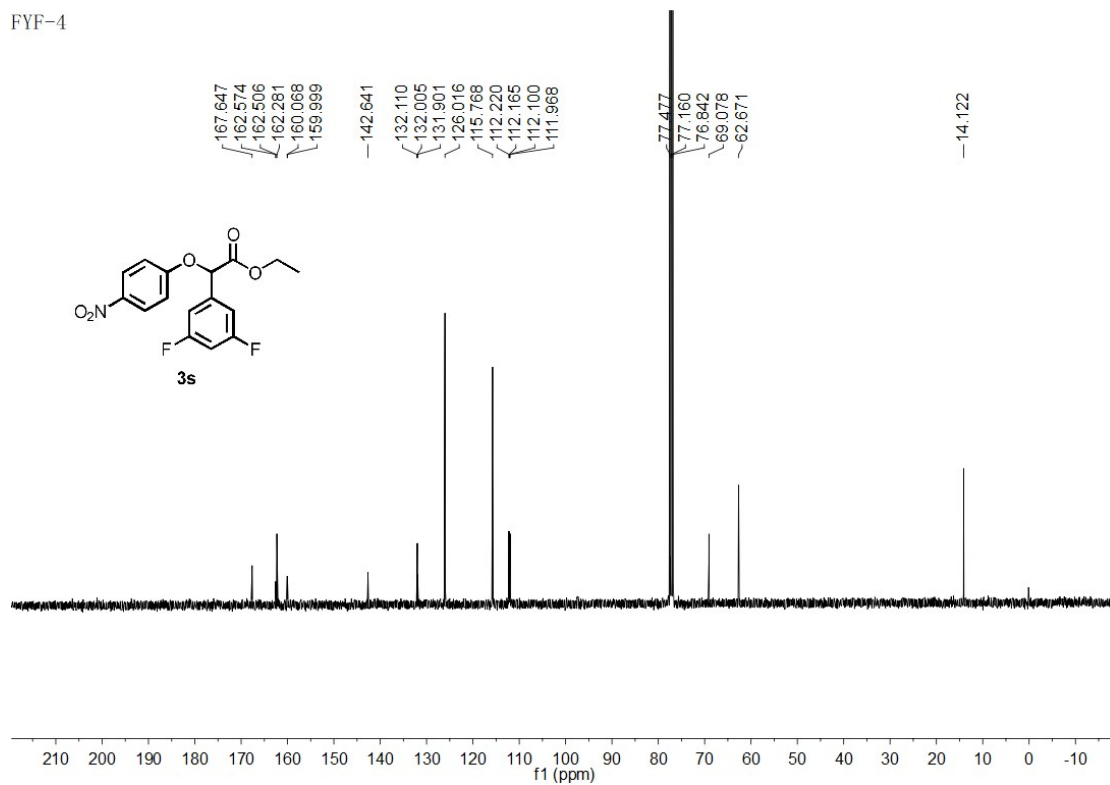
FYF-8



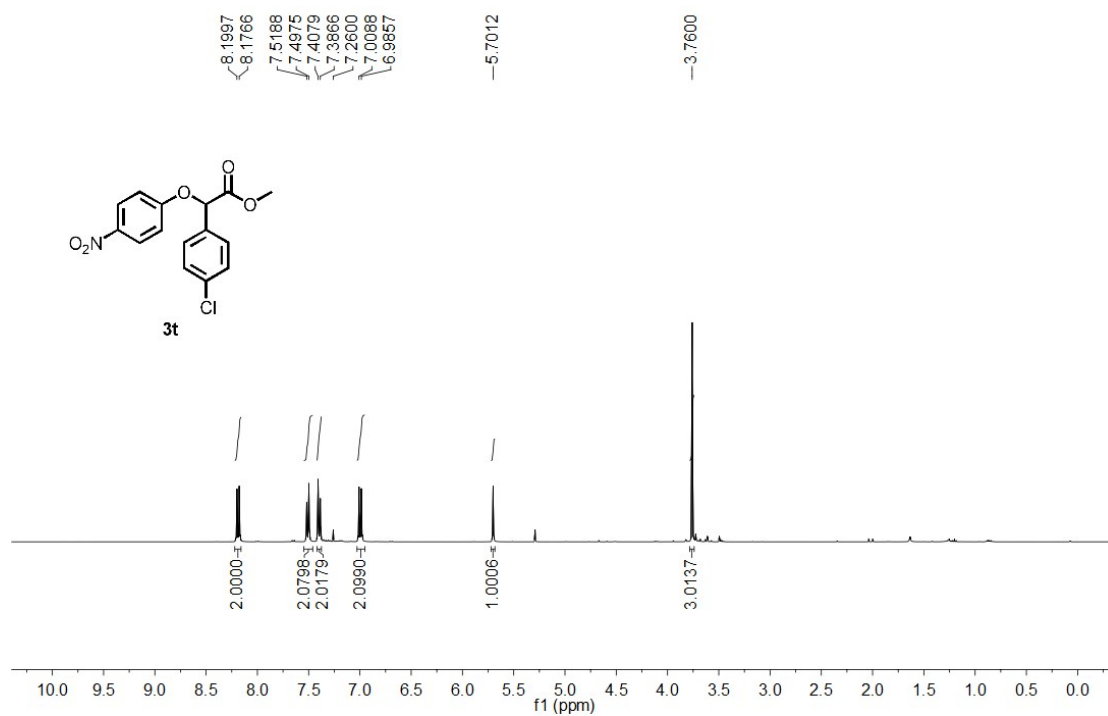
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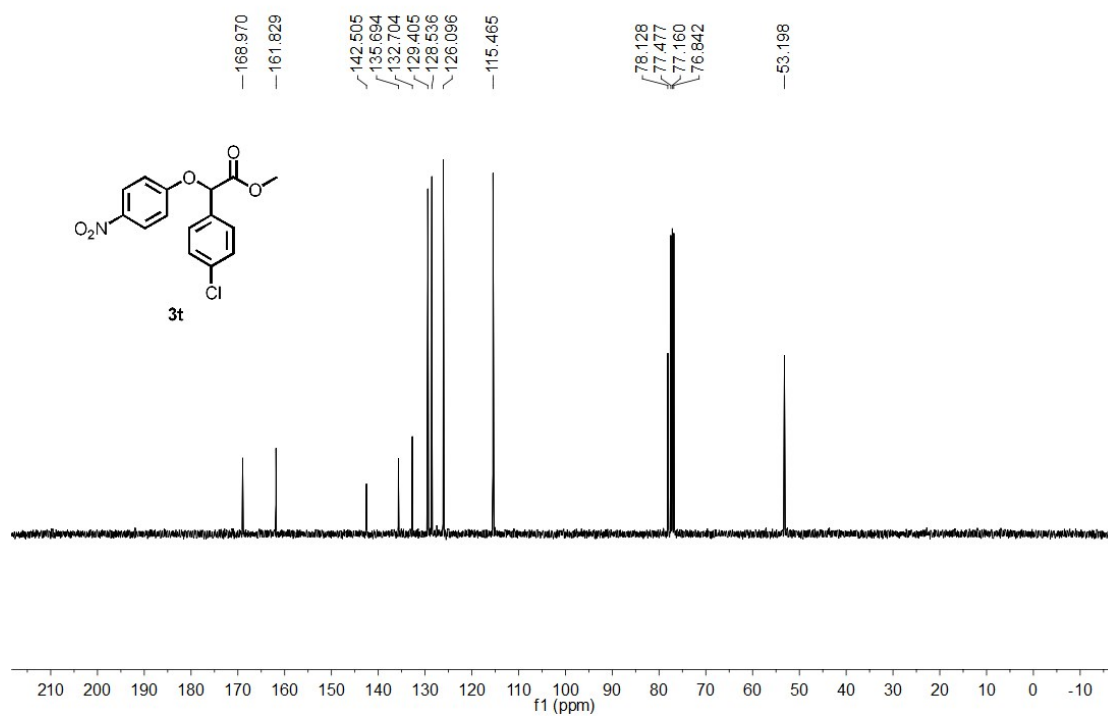
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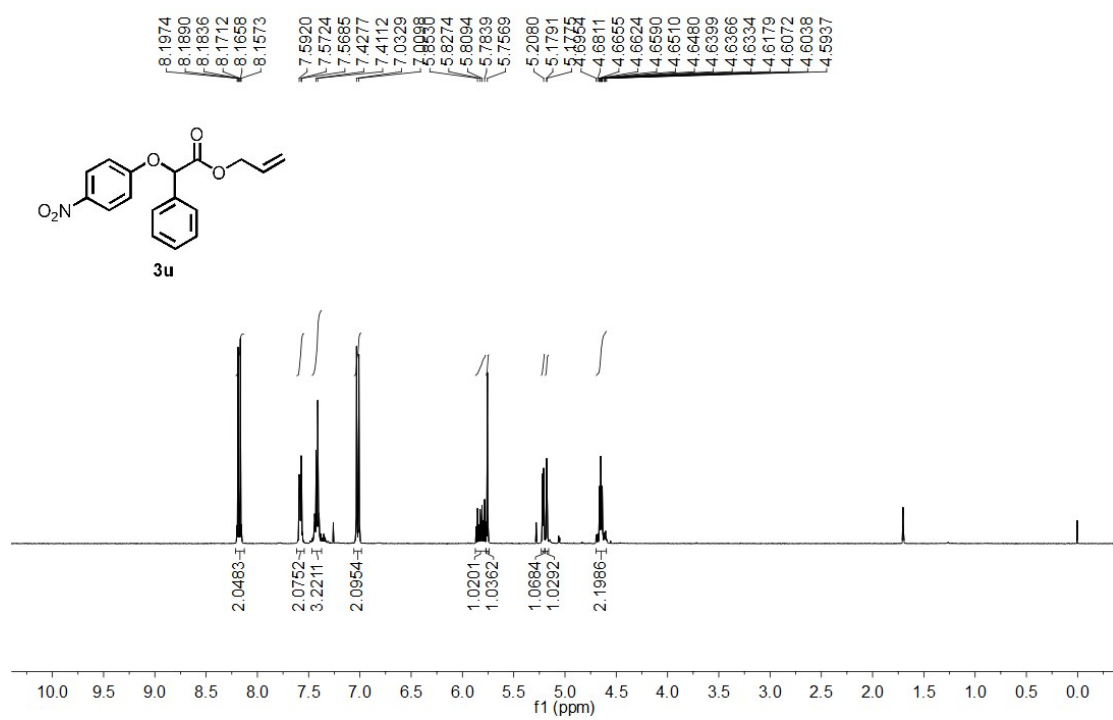
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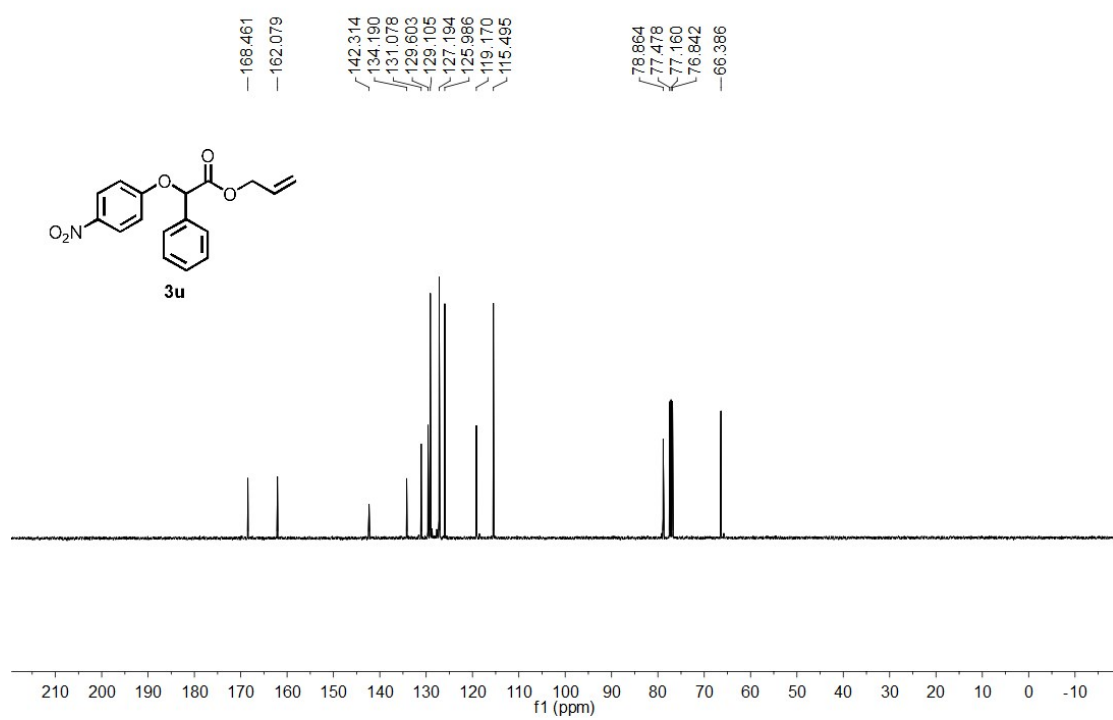
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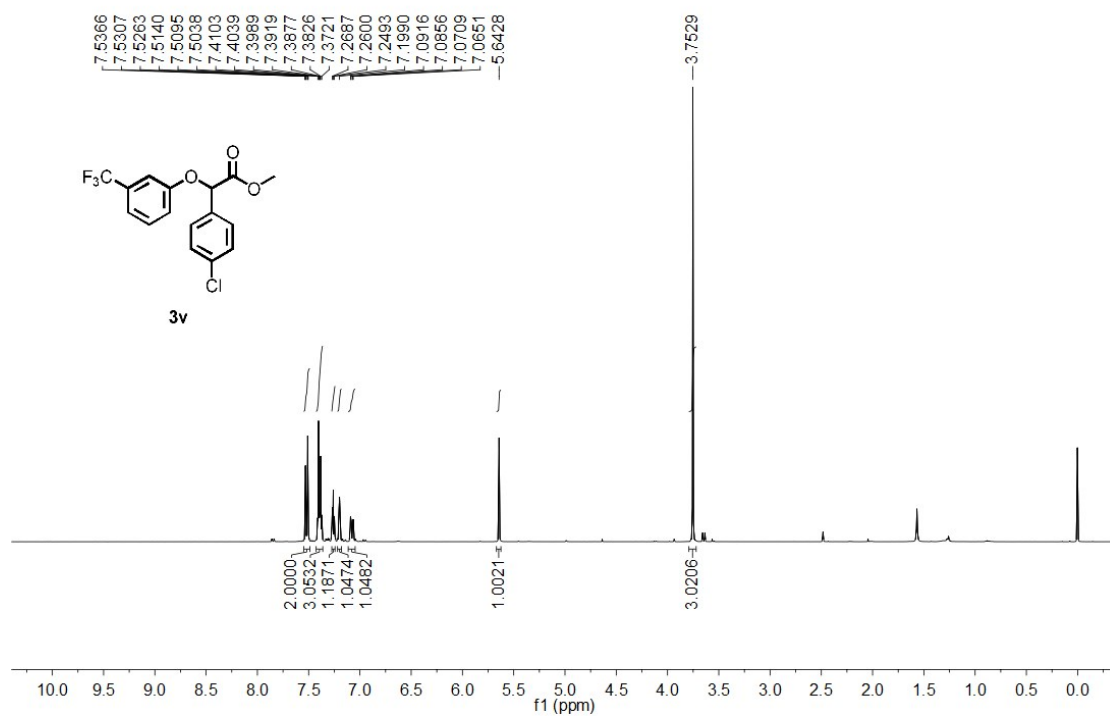
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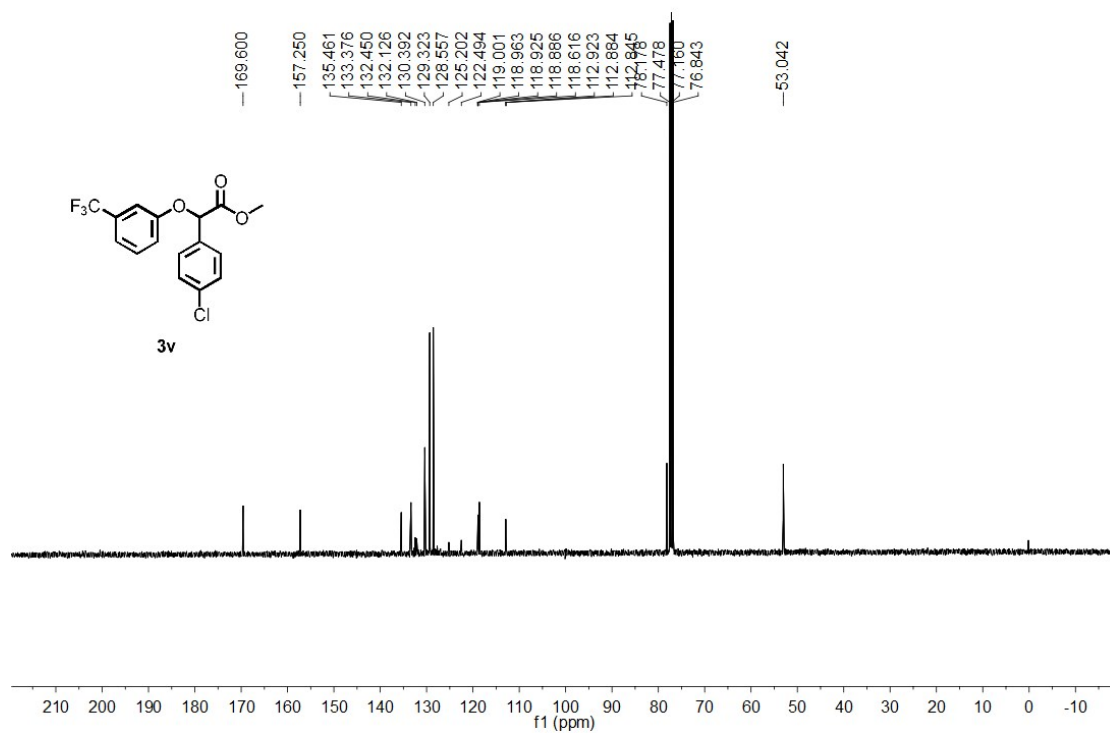
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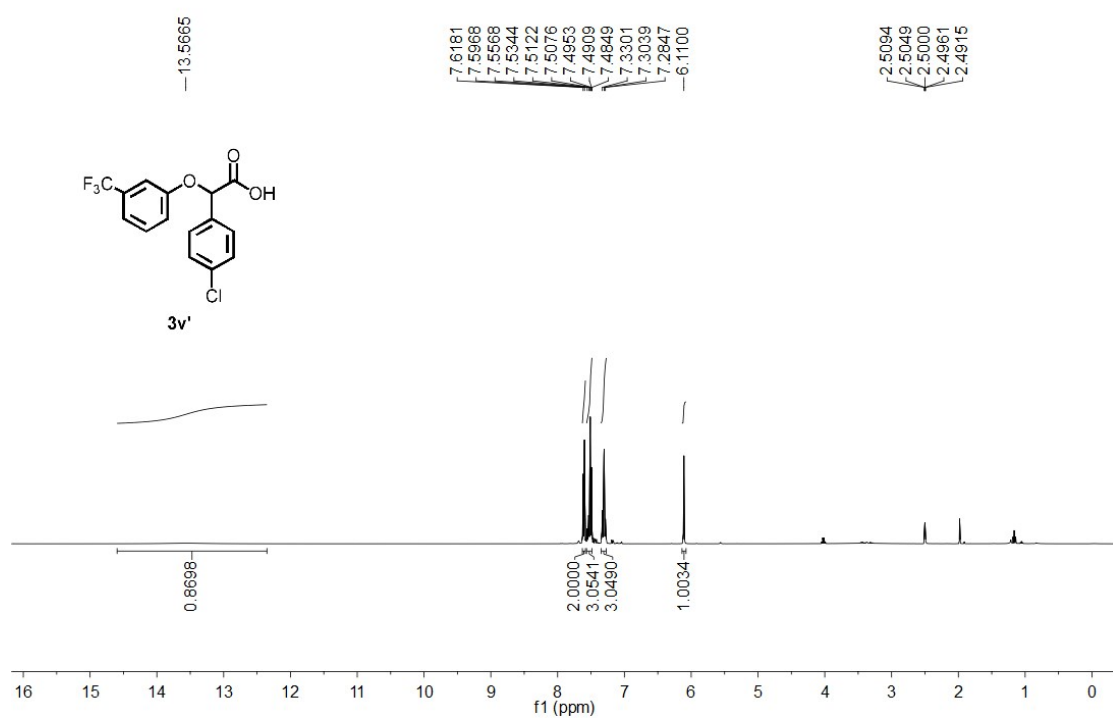
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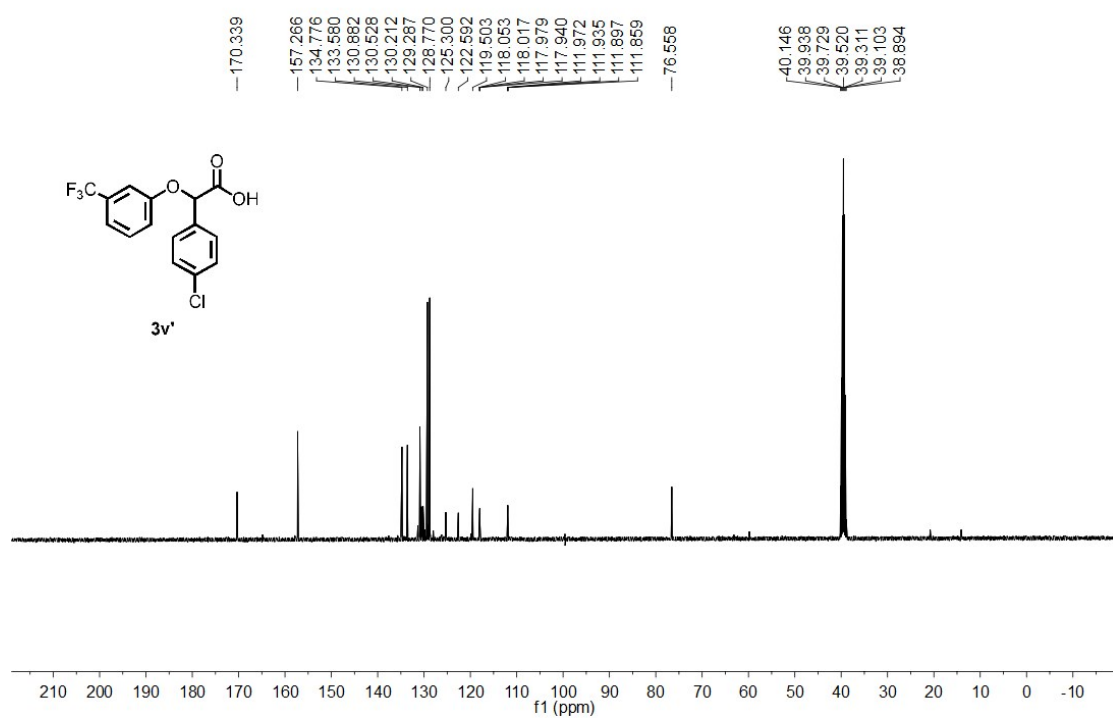
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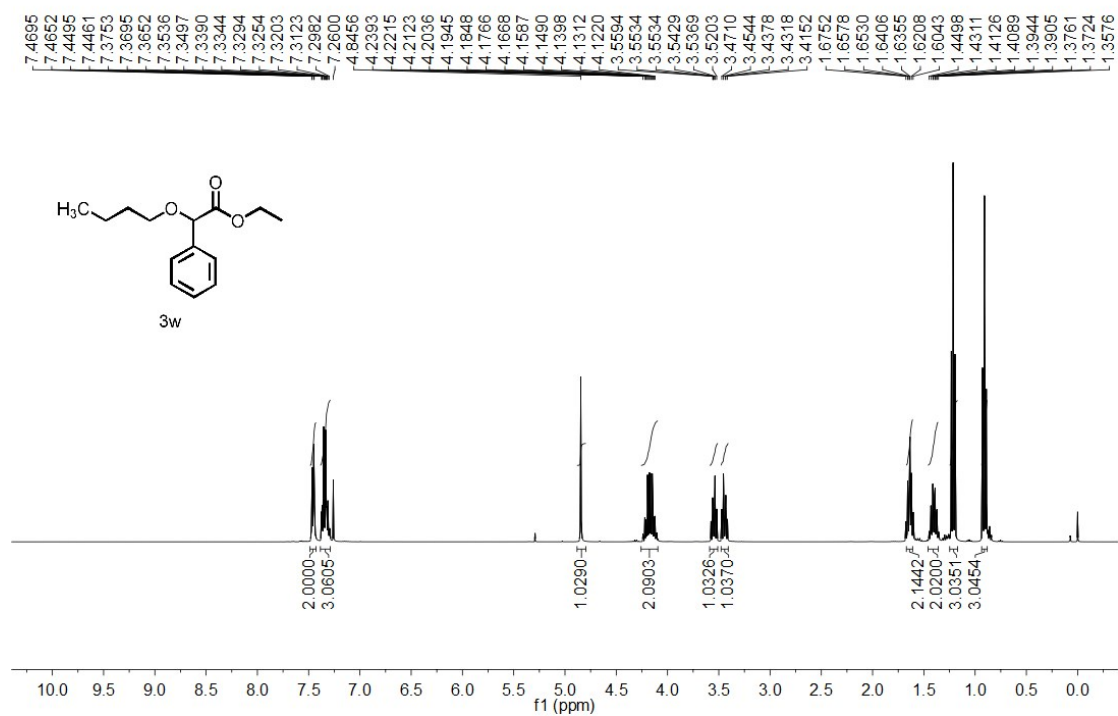
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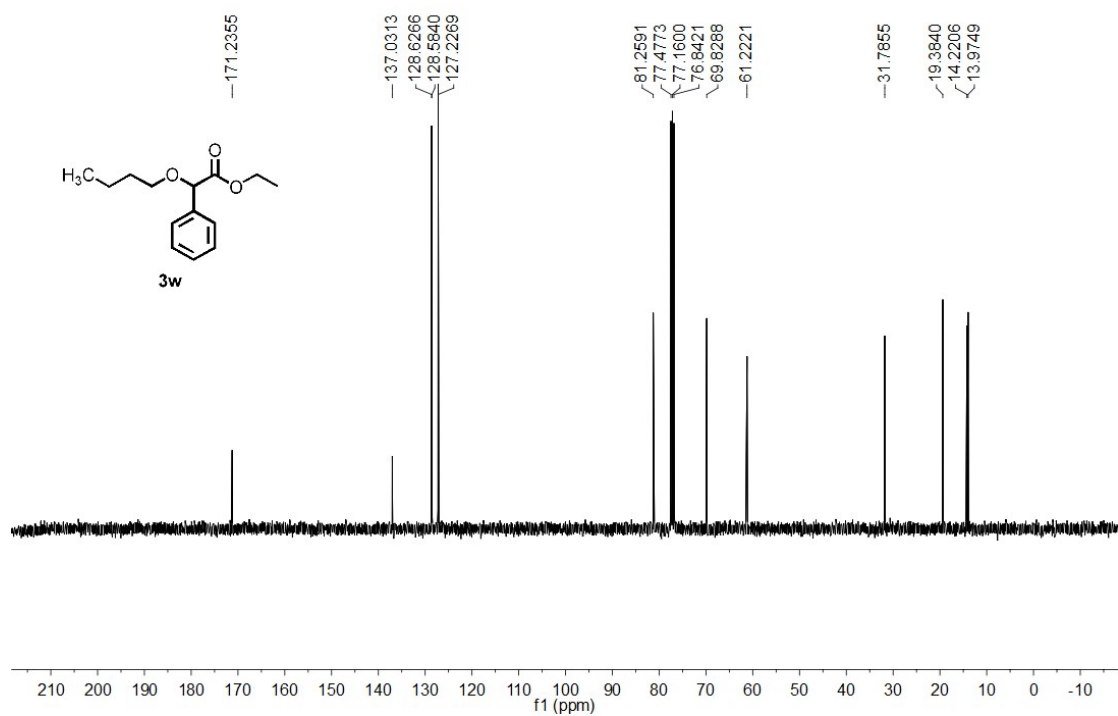
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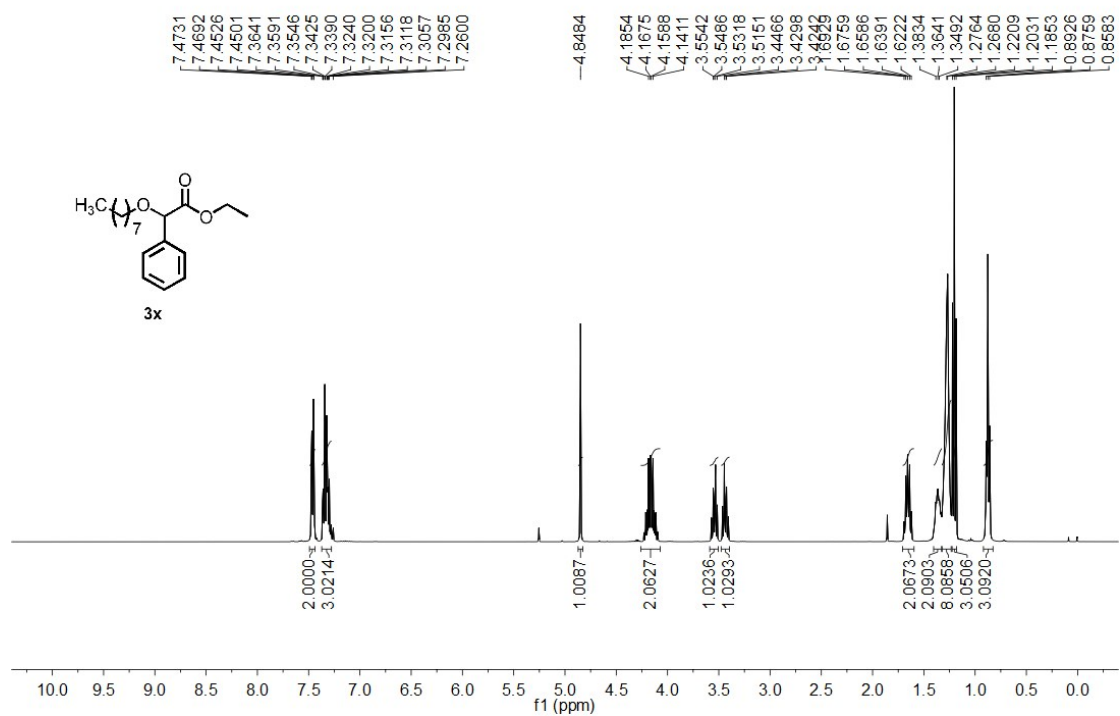
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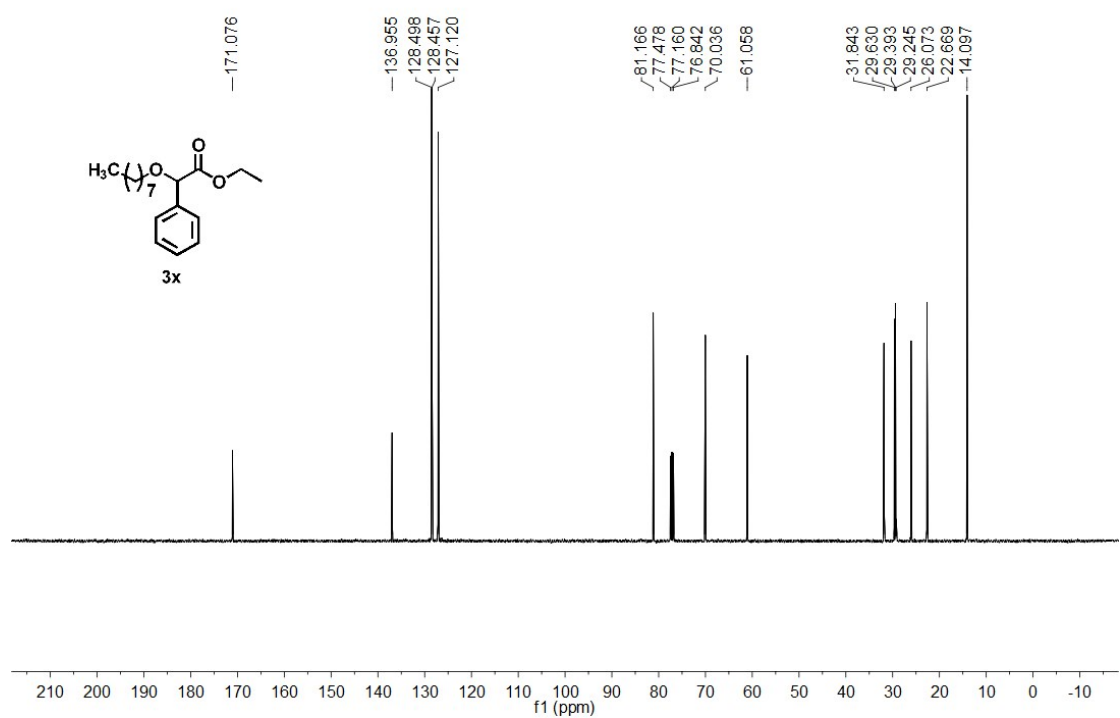
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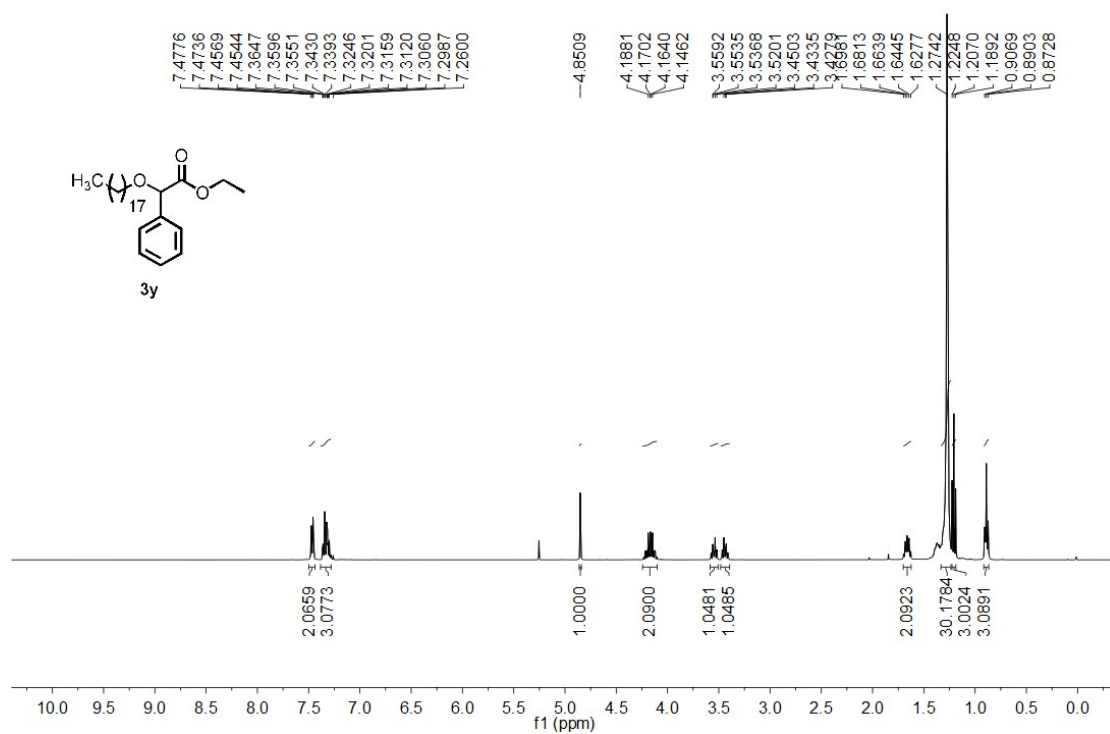
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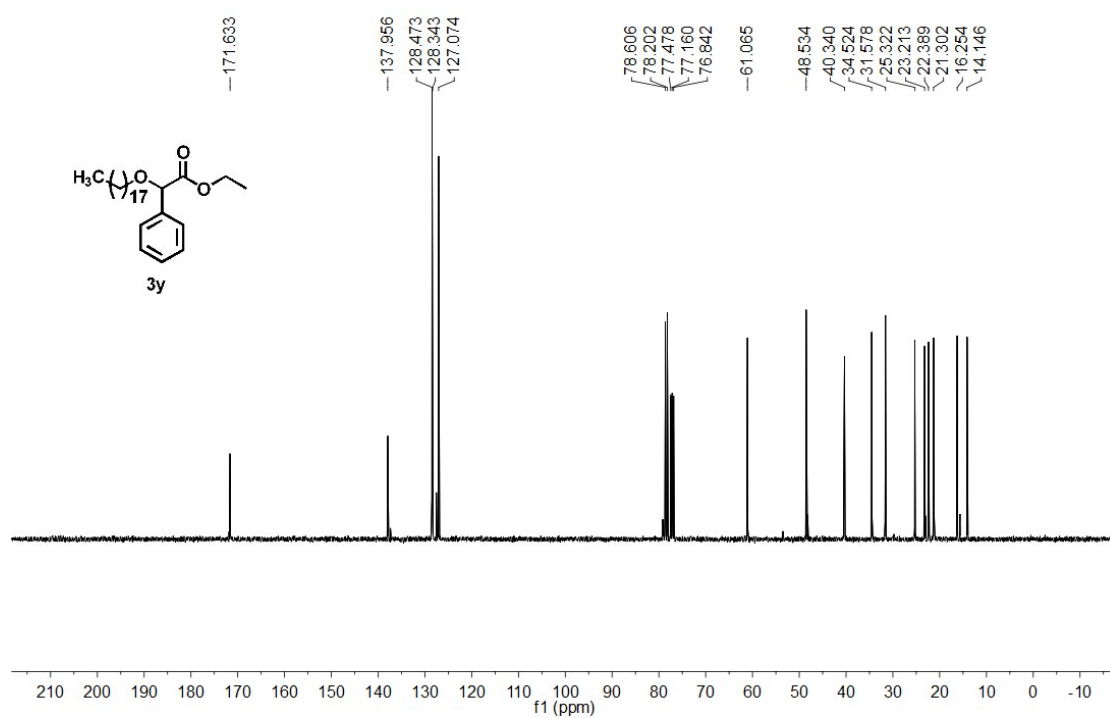
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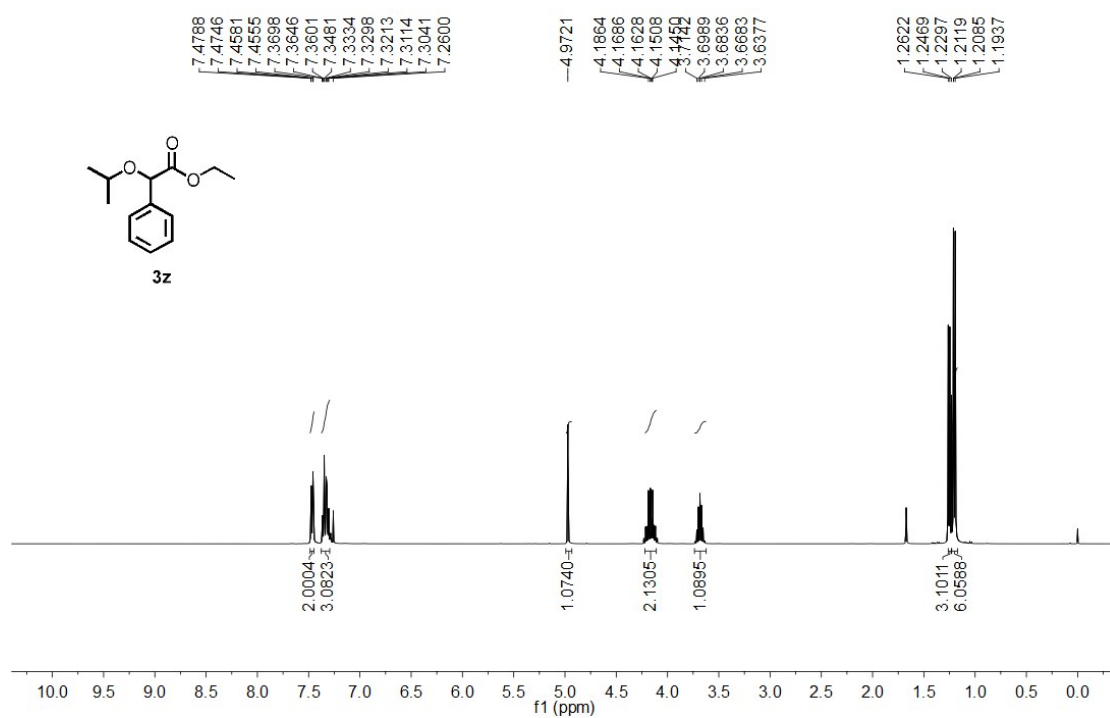
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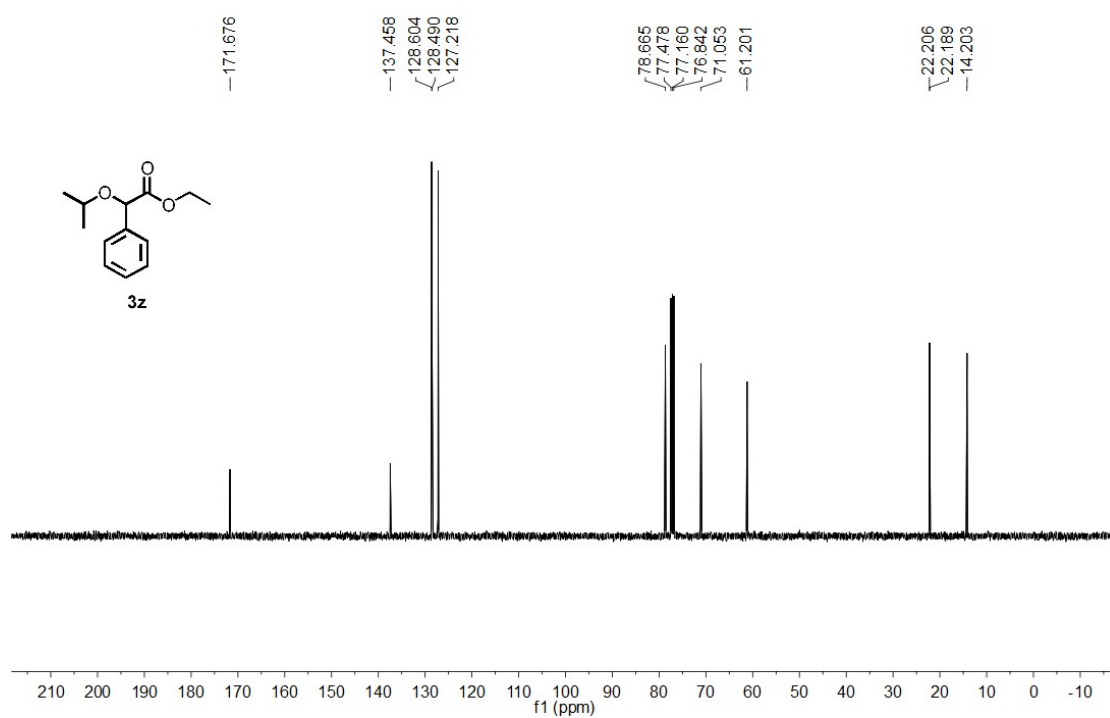
ZZP-57



ZZP-22

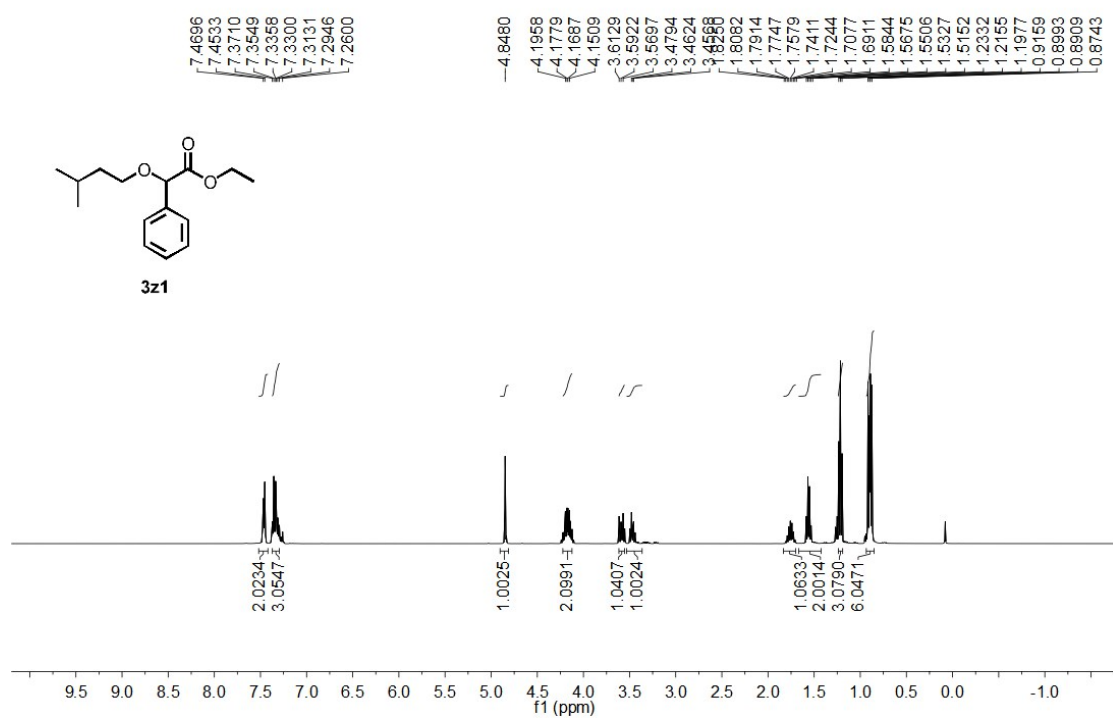


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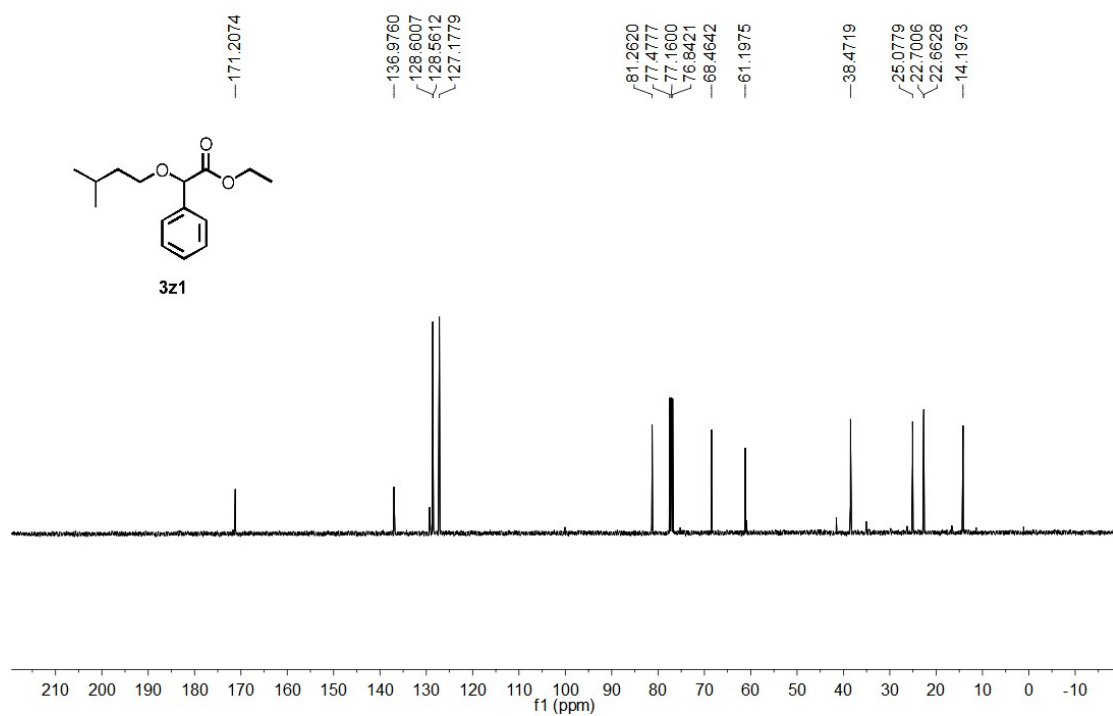
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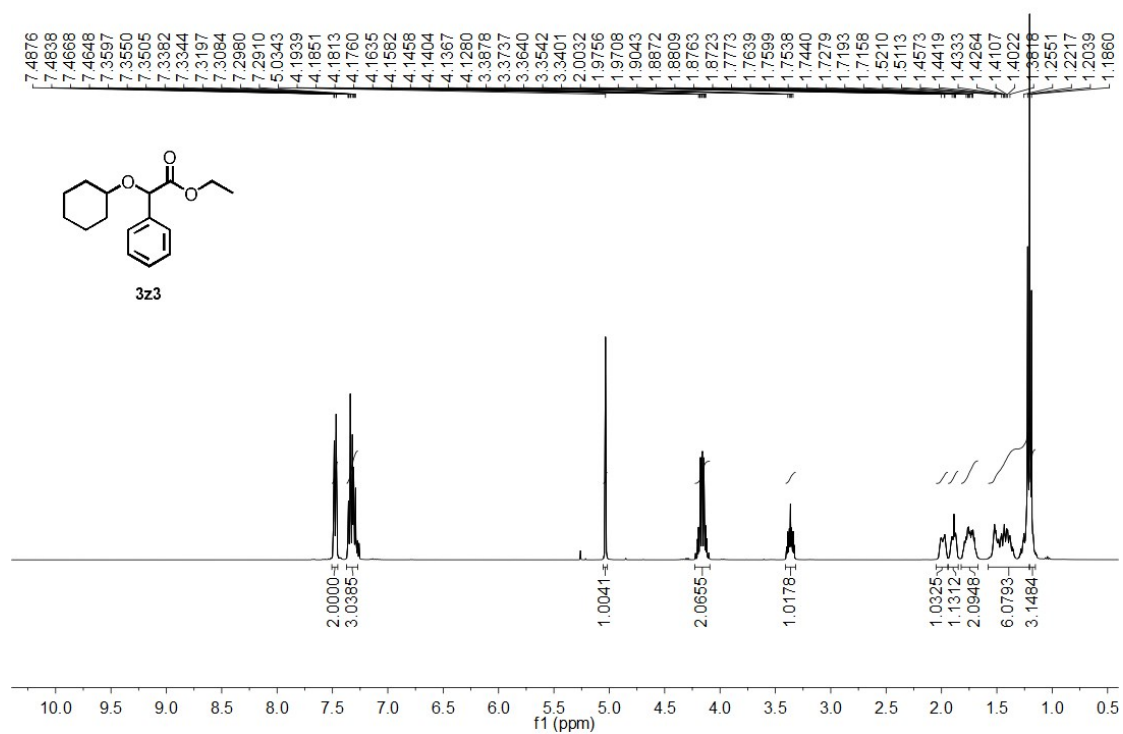


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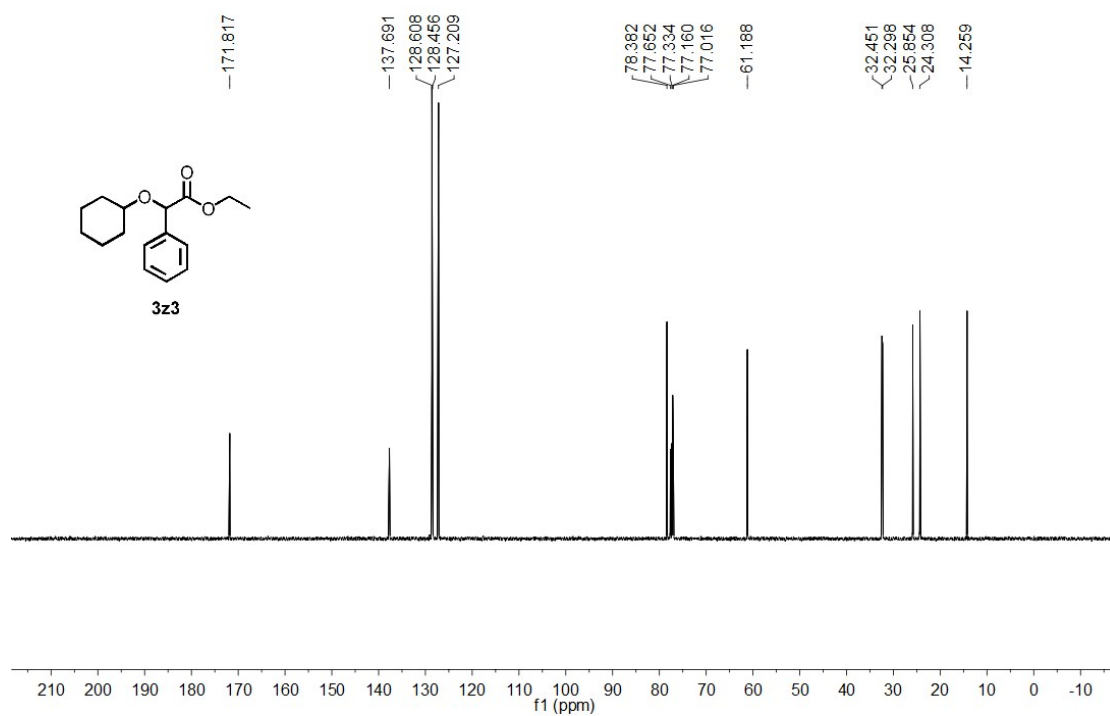
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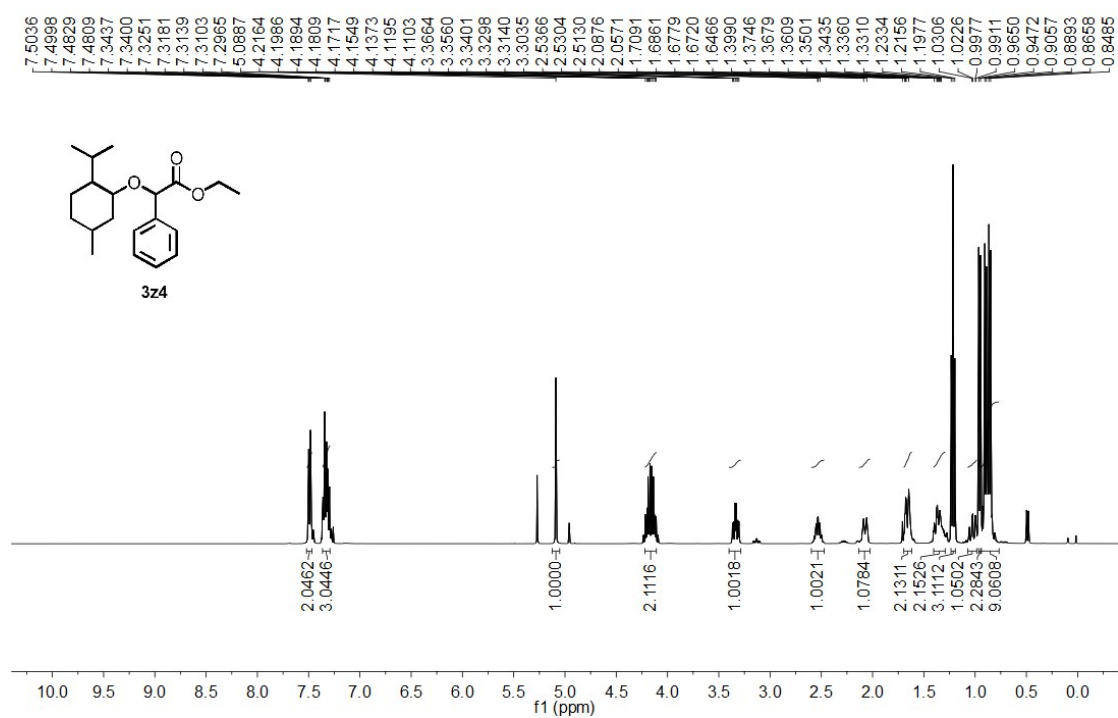
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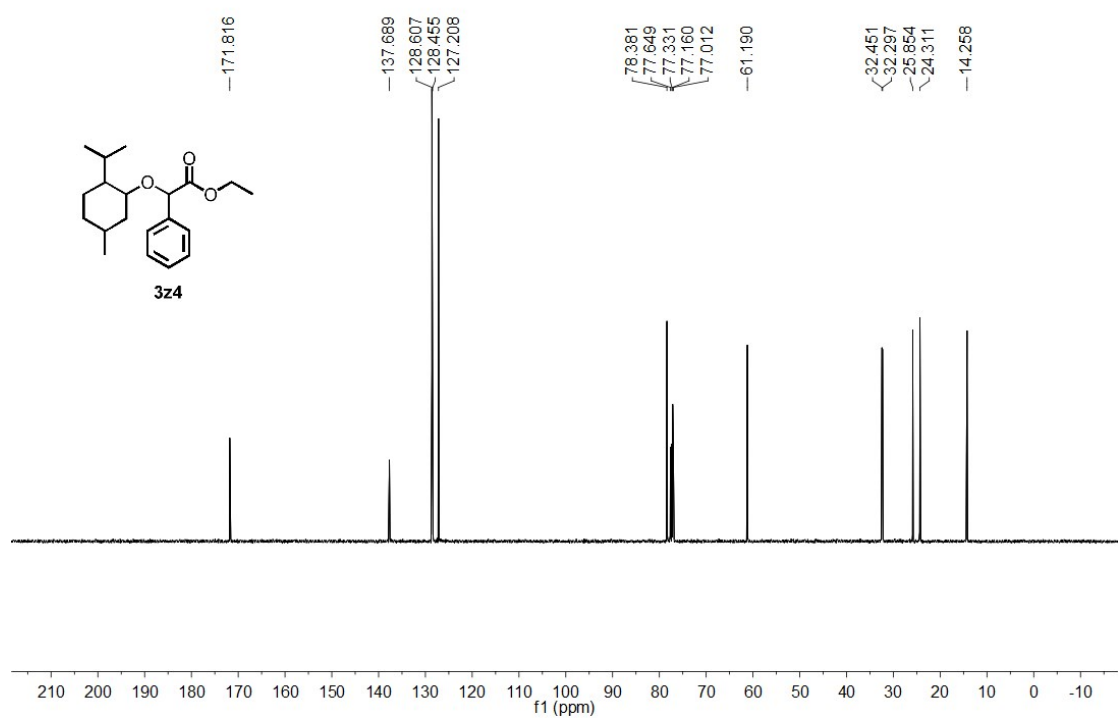
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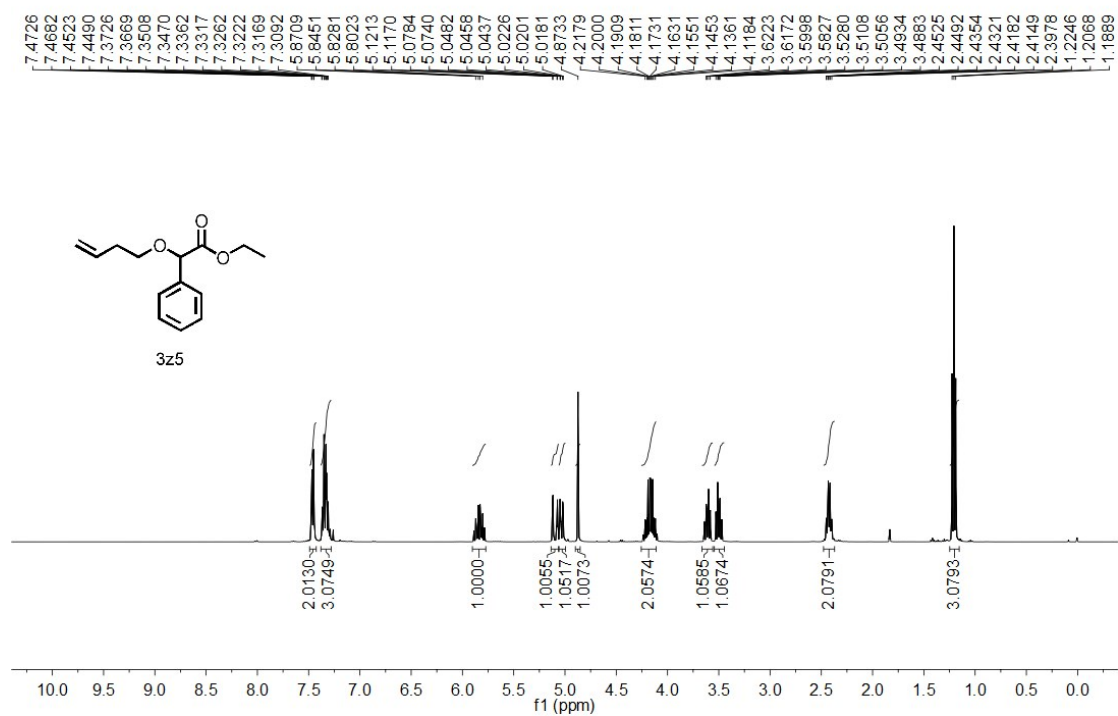
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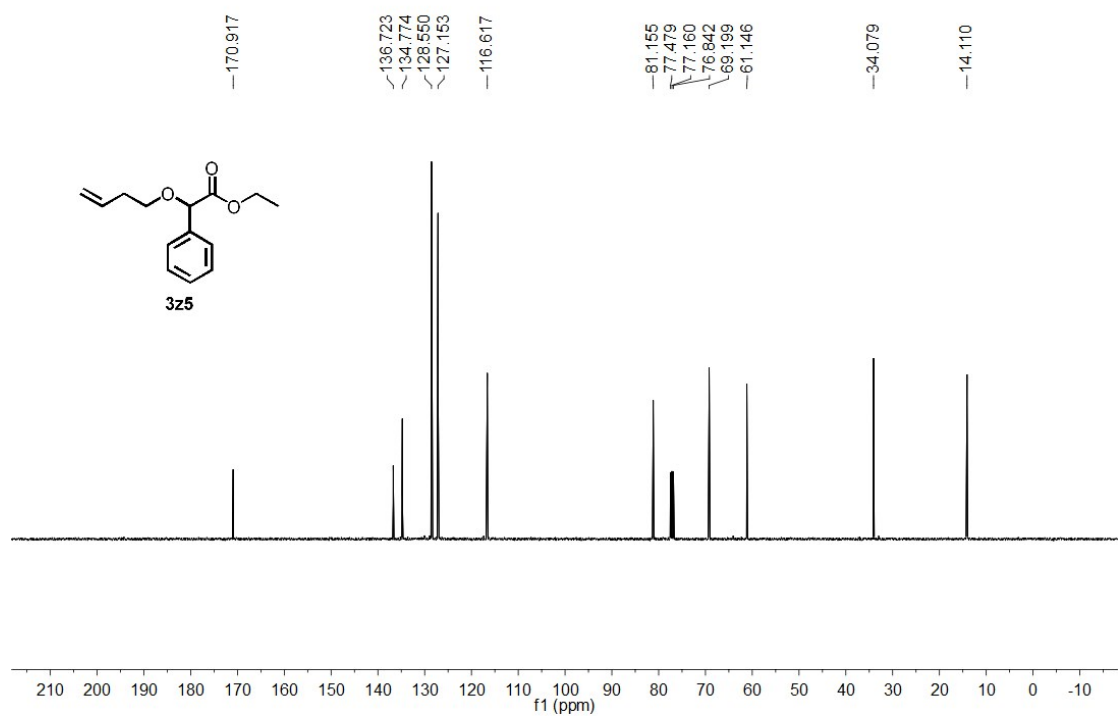
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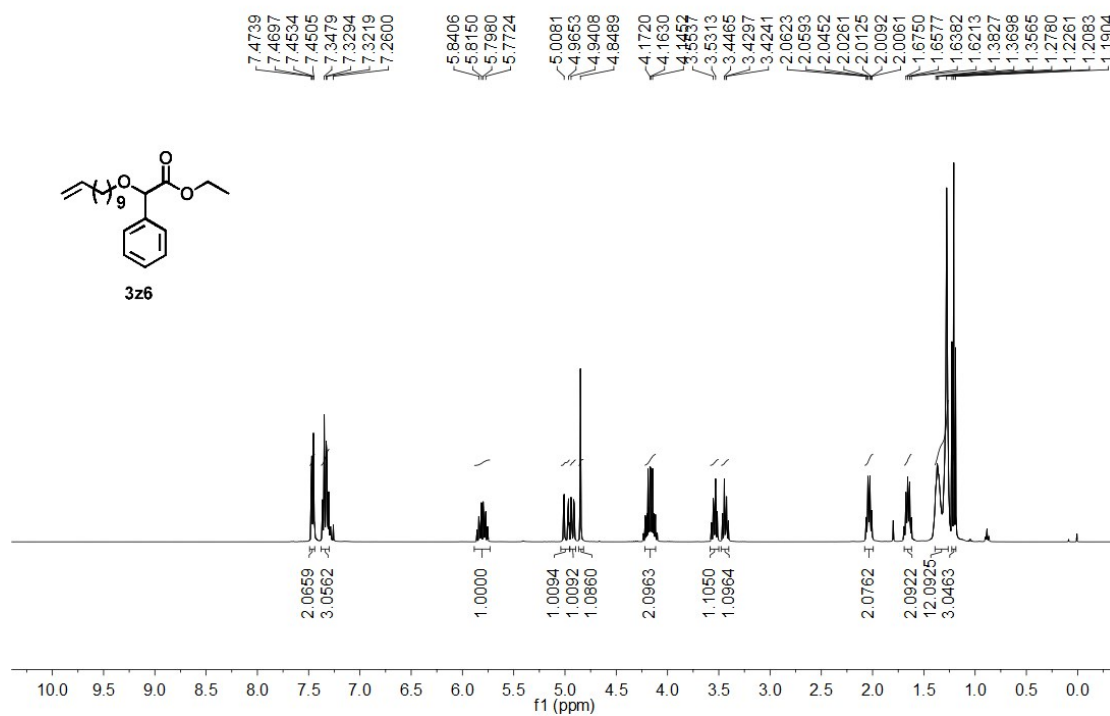
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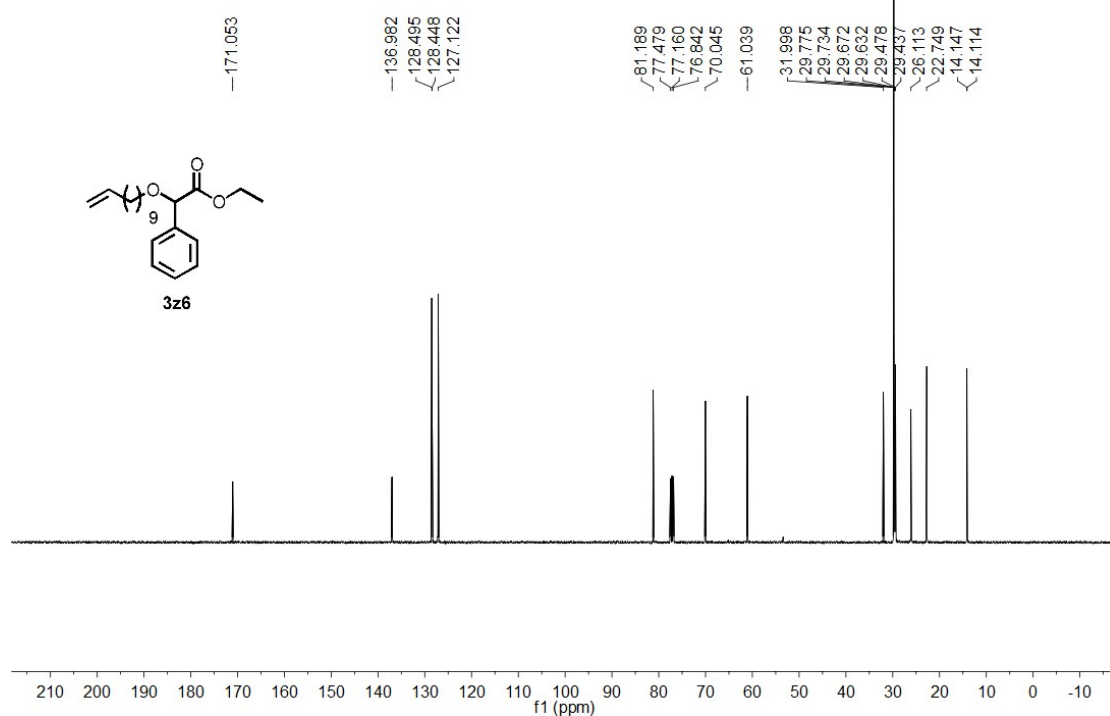
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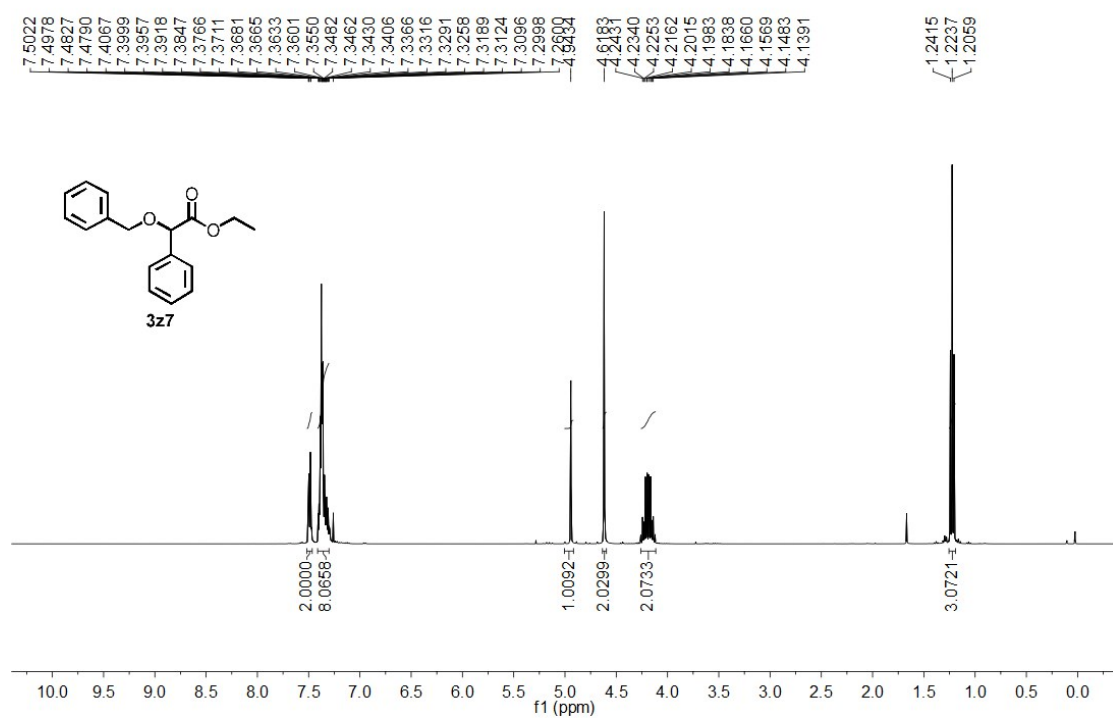
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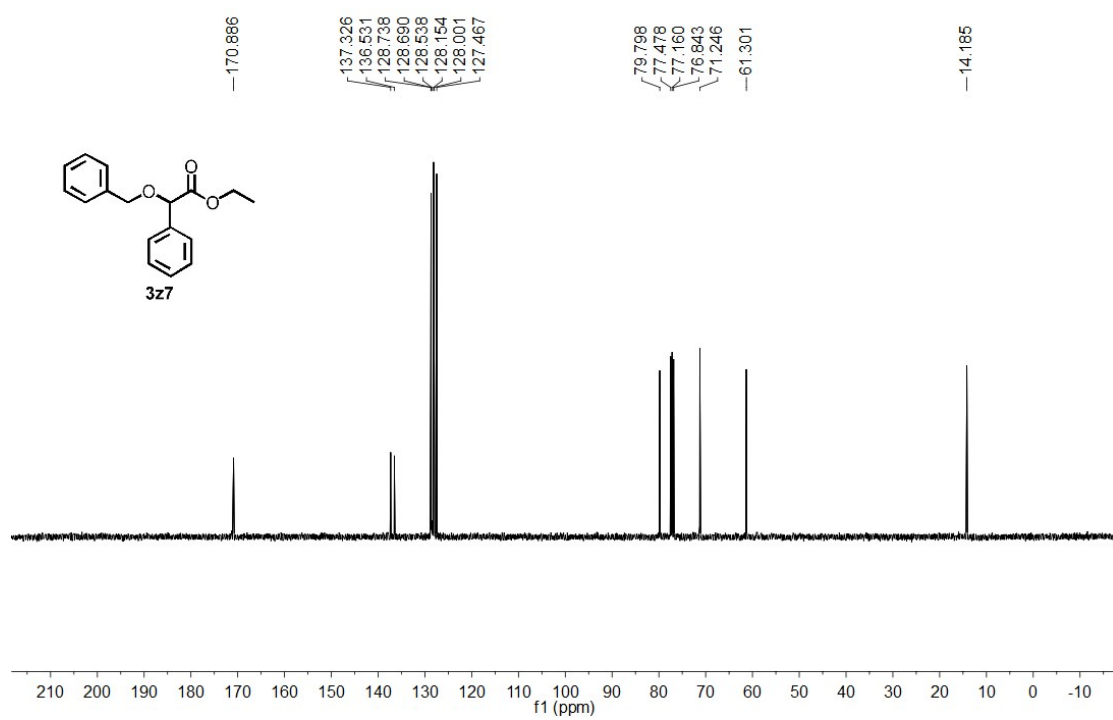
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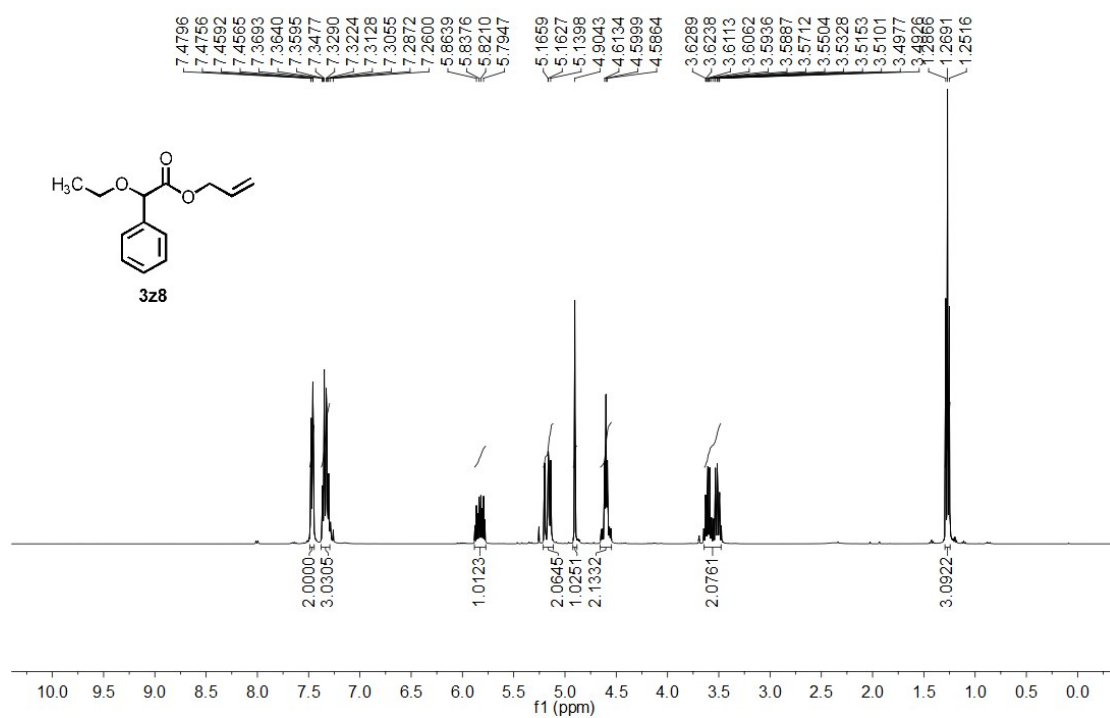
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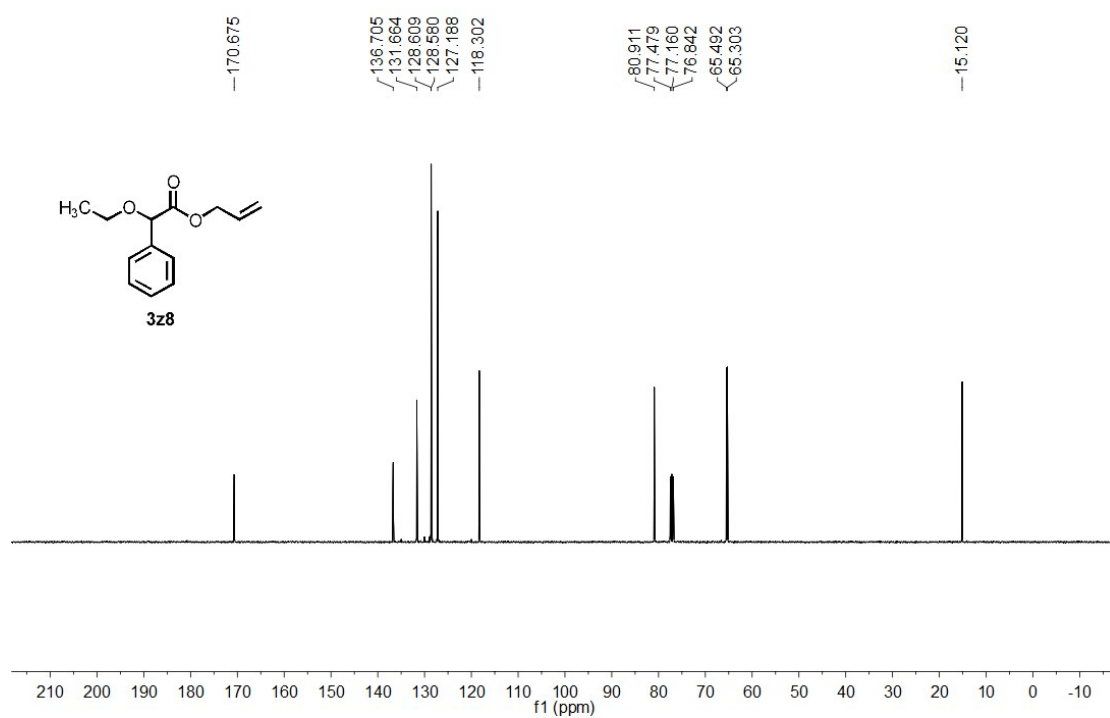
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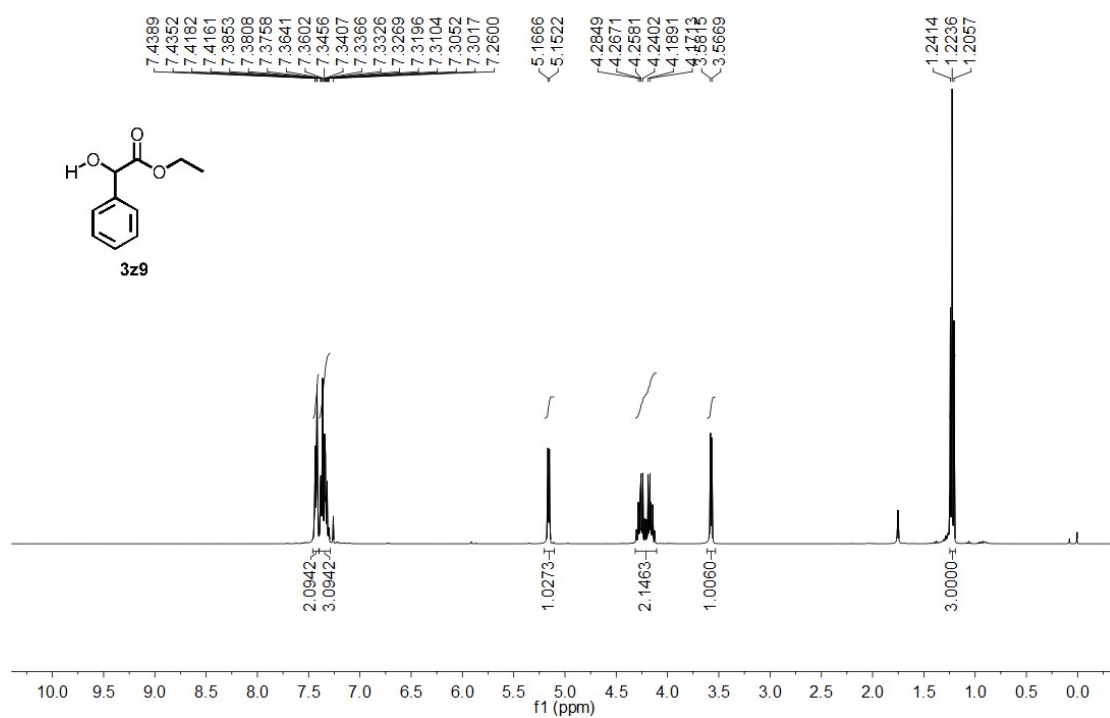
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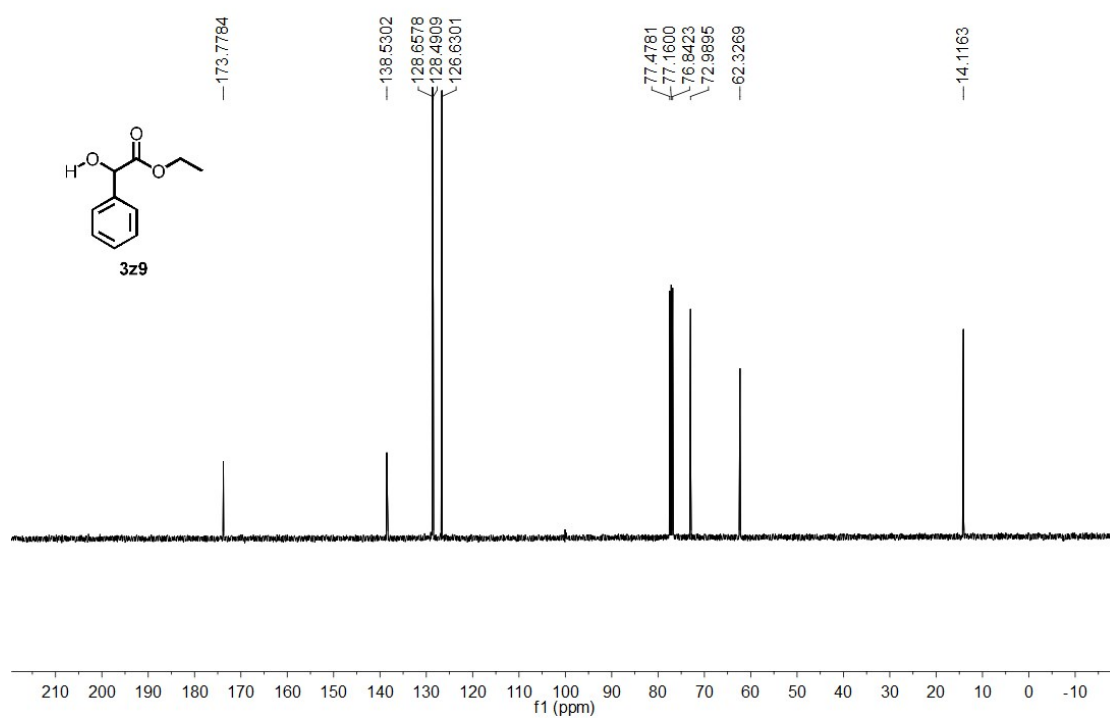
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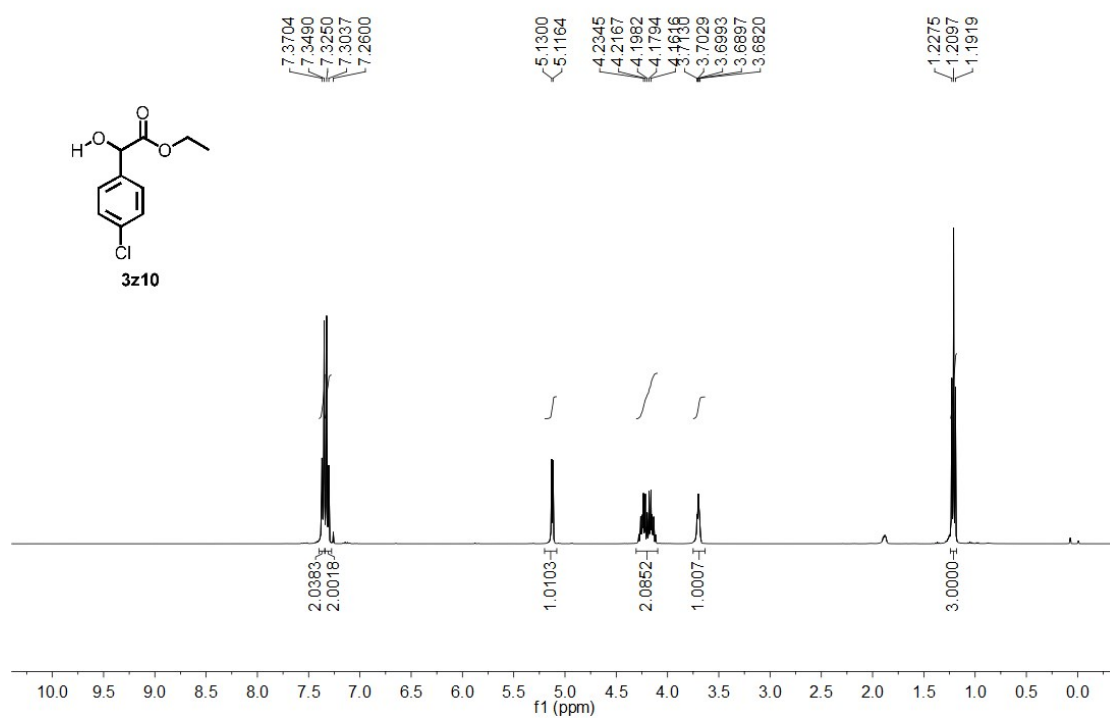
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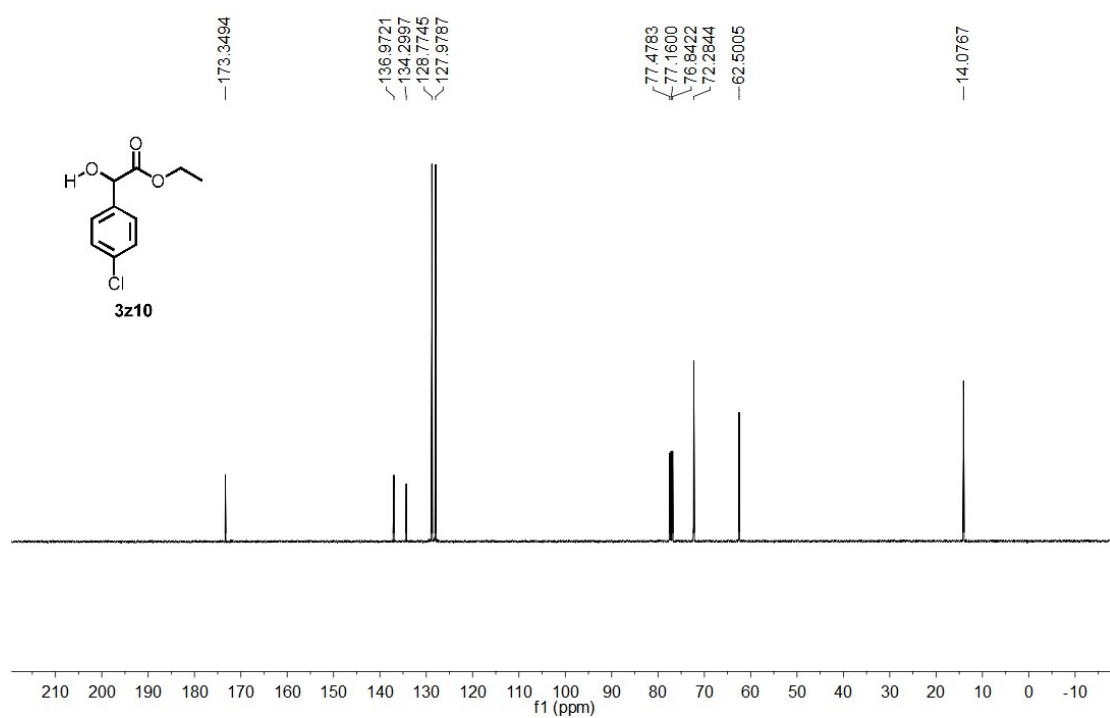
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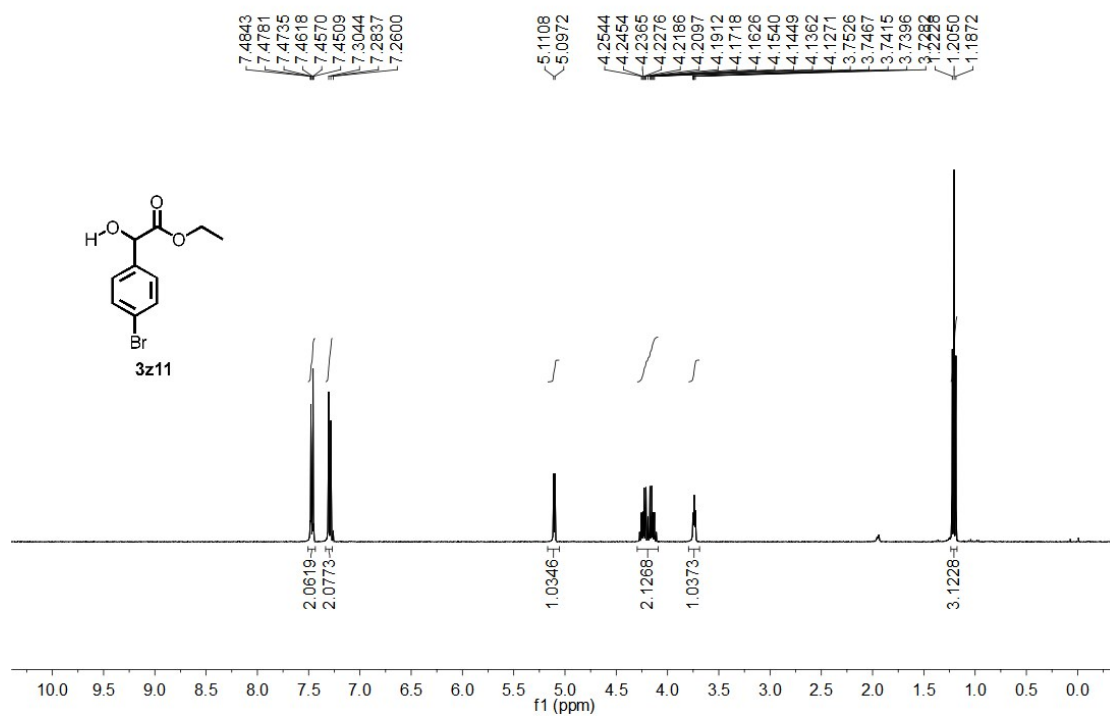
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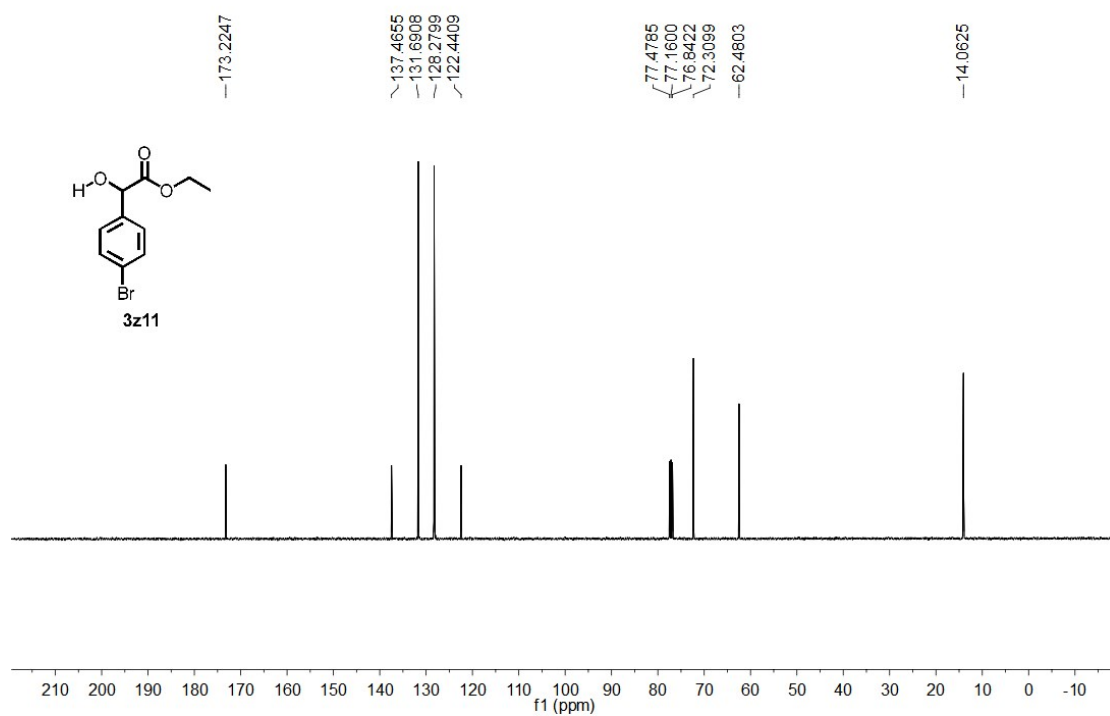
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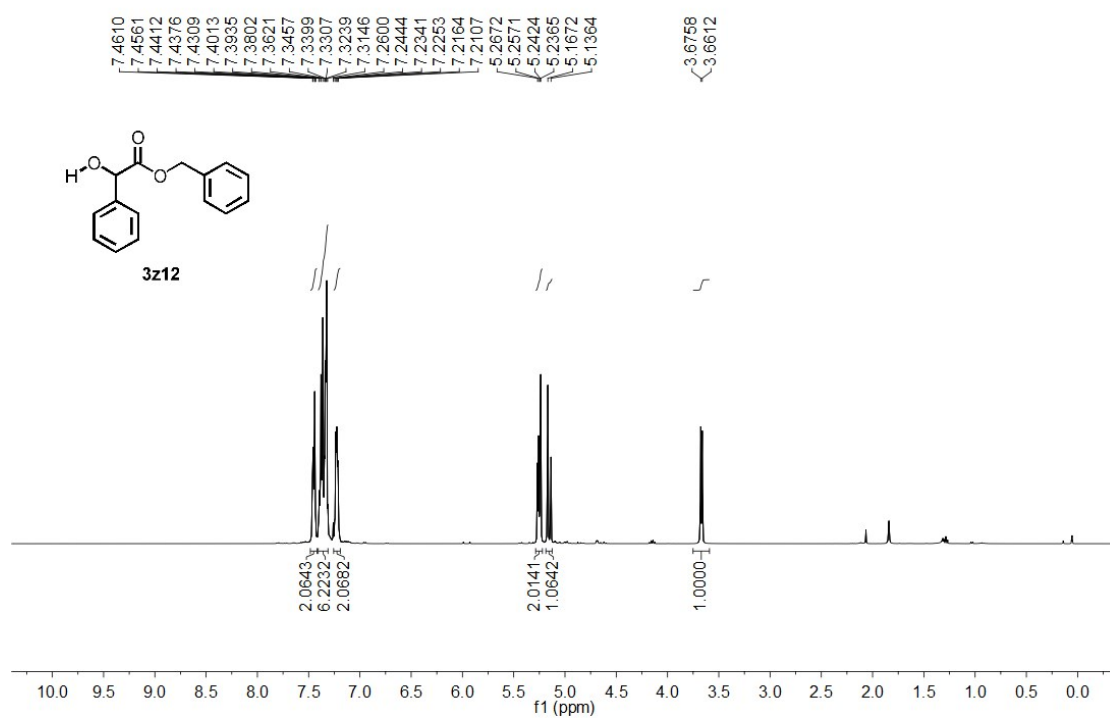
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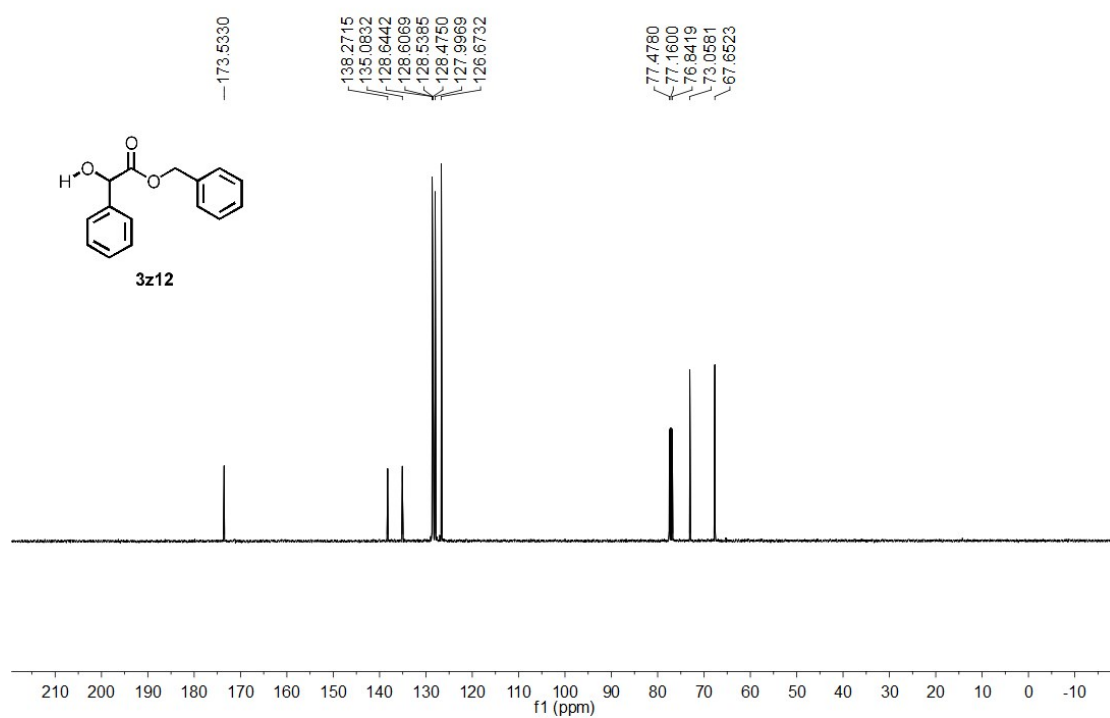
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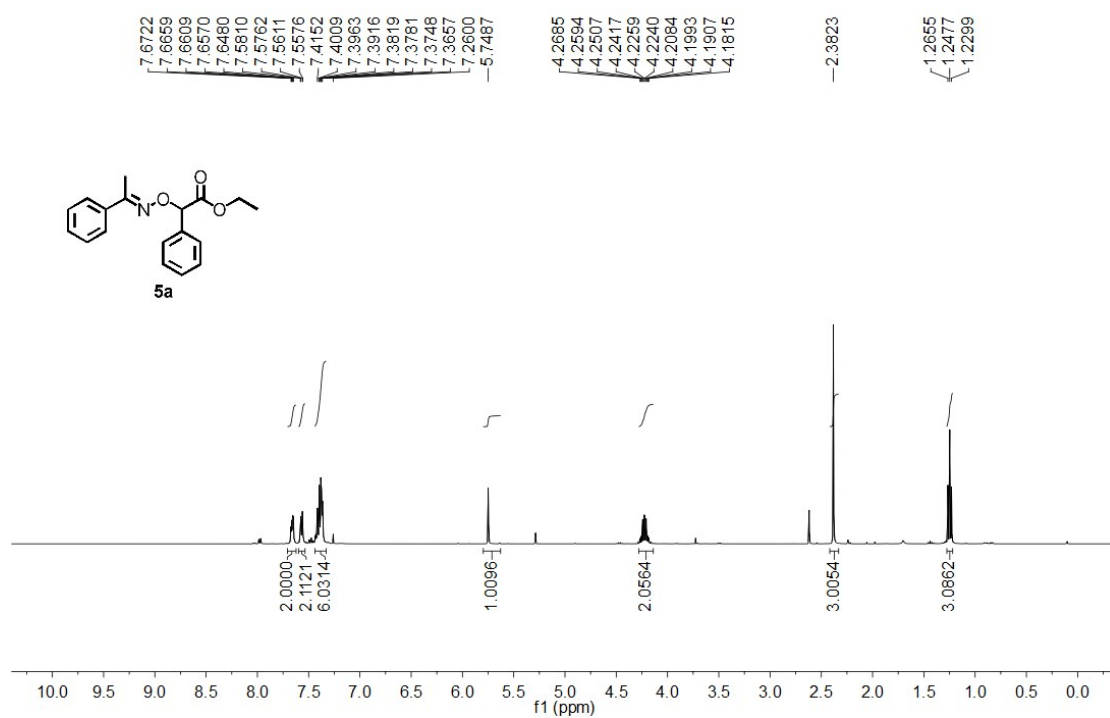
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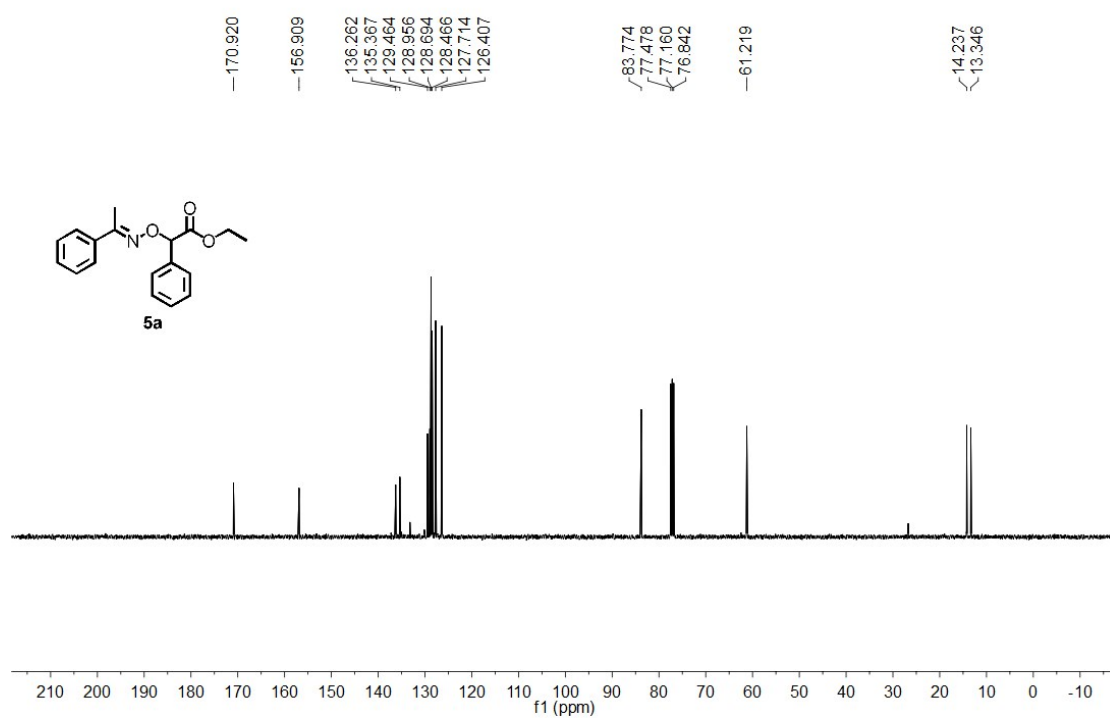
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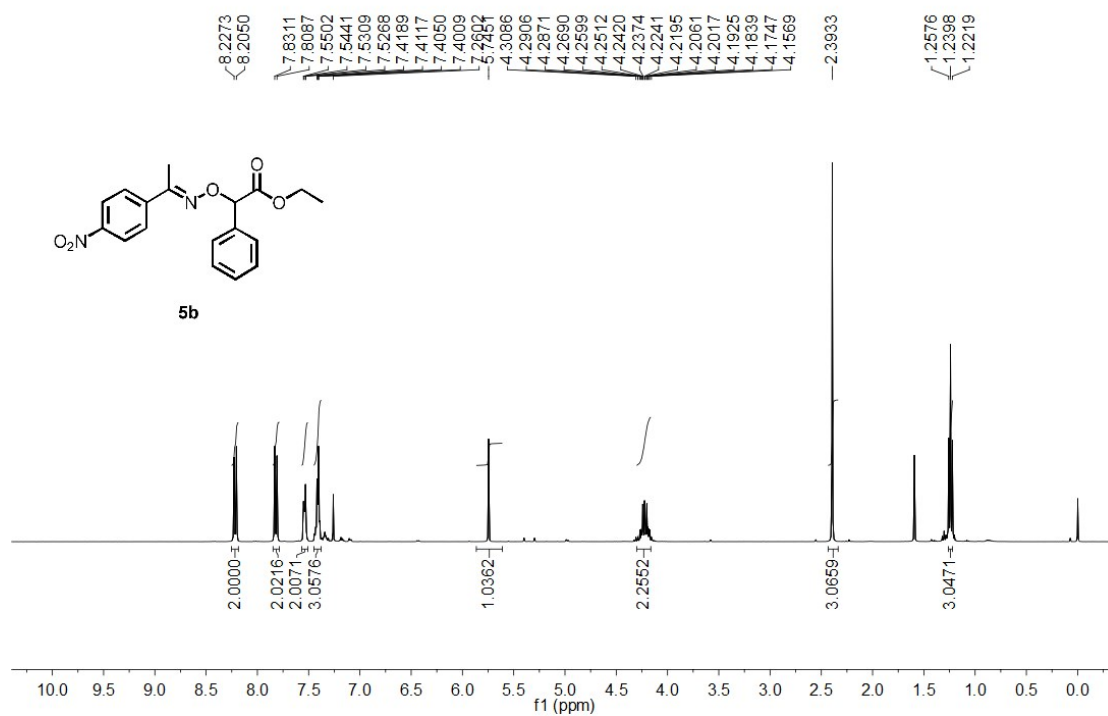
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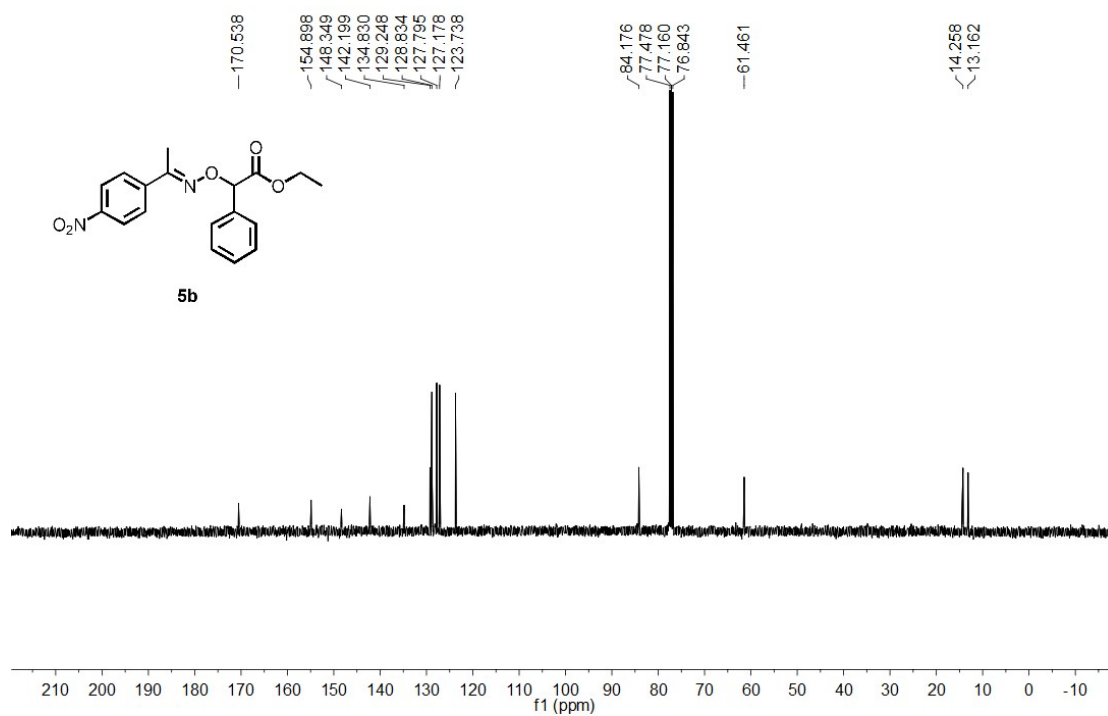
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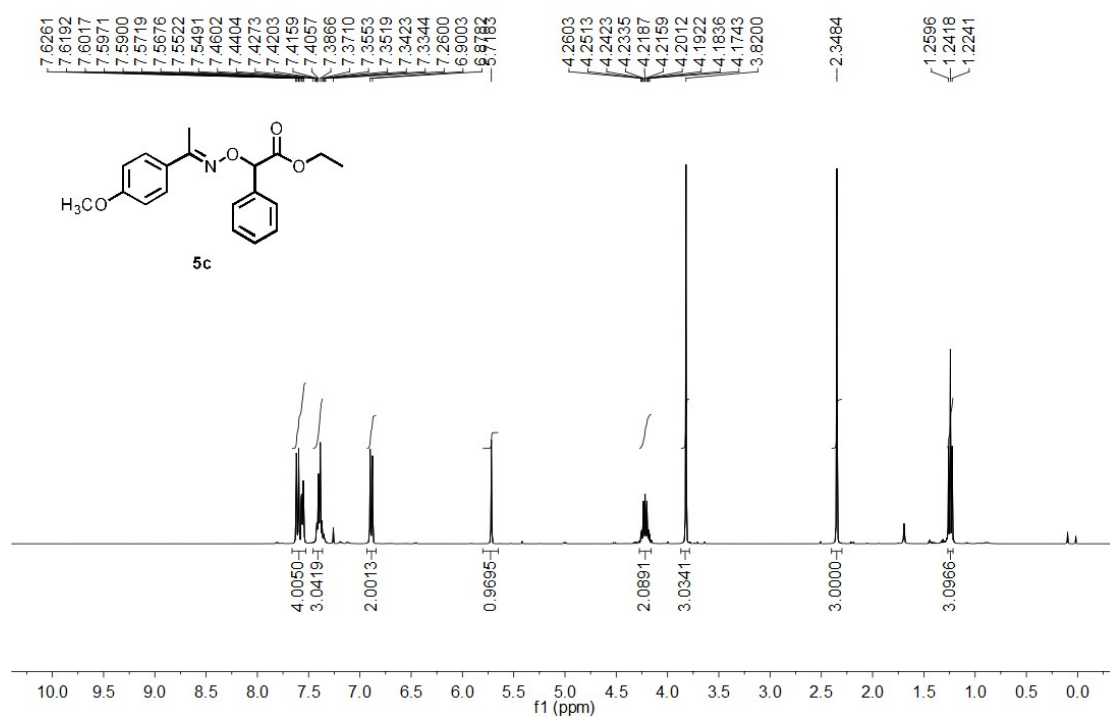
ZZP-438-1



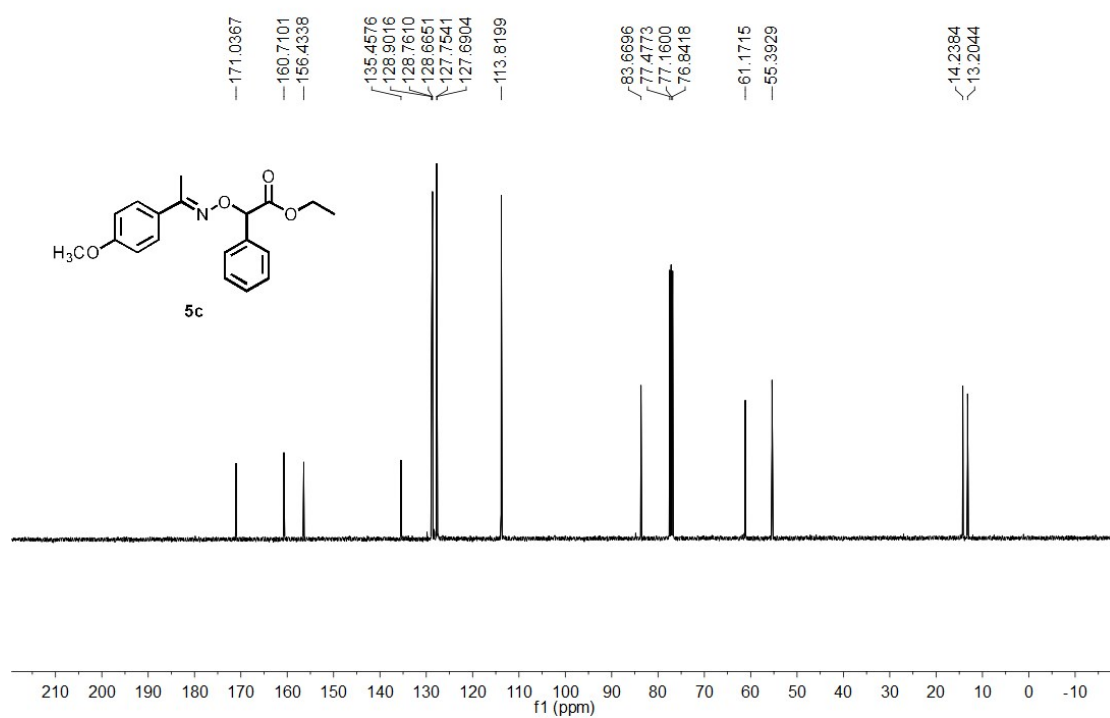
ZZP-438-1



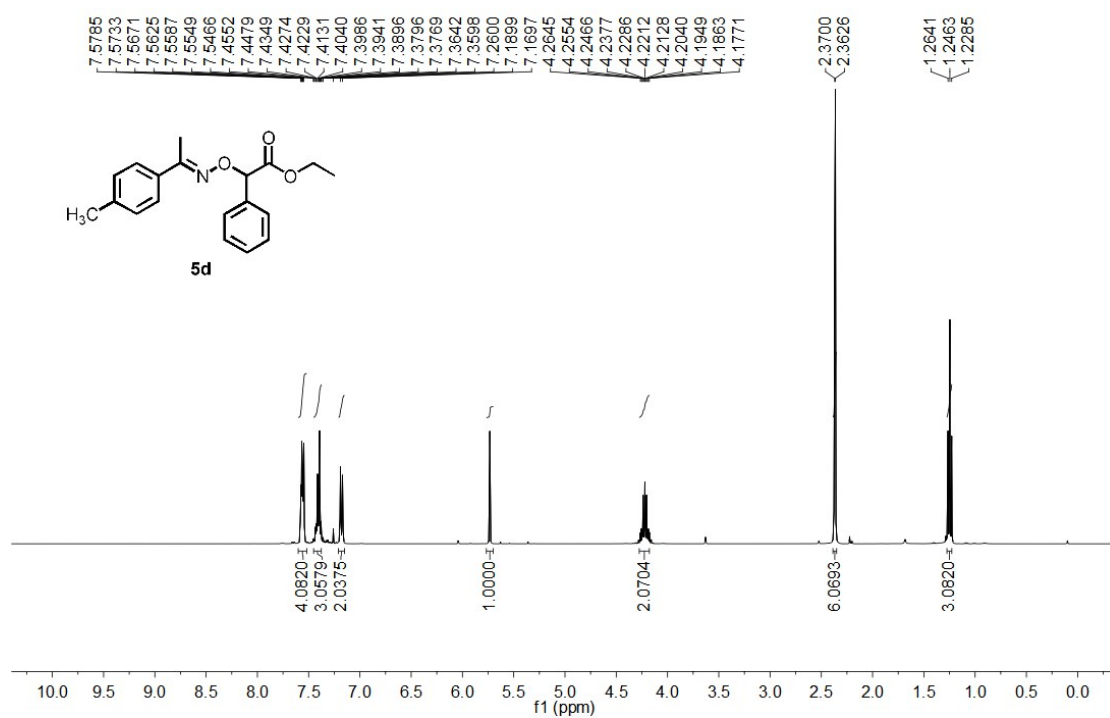
ZZP-507



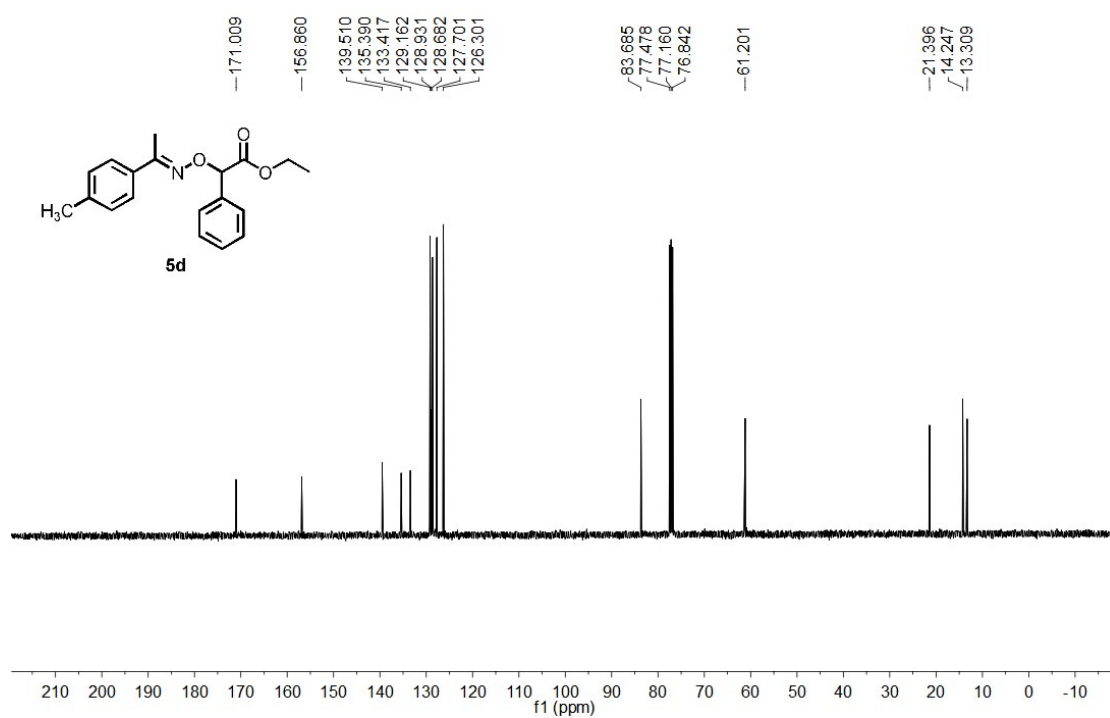
ZZP-507



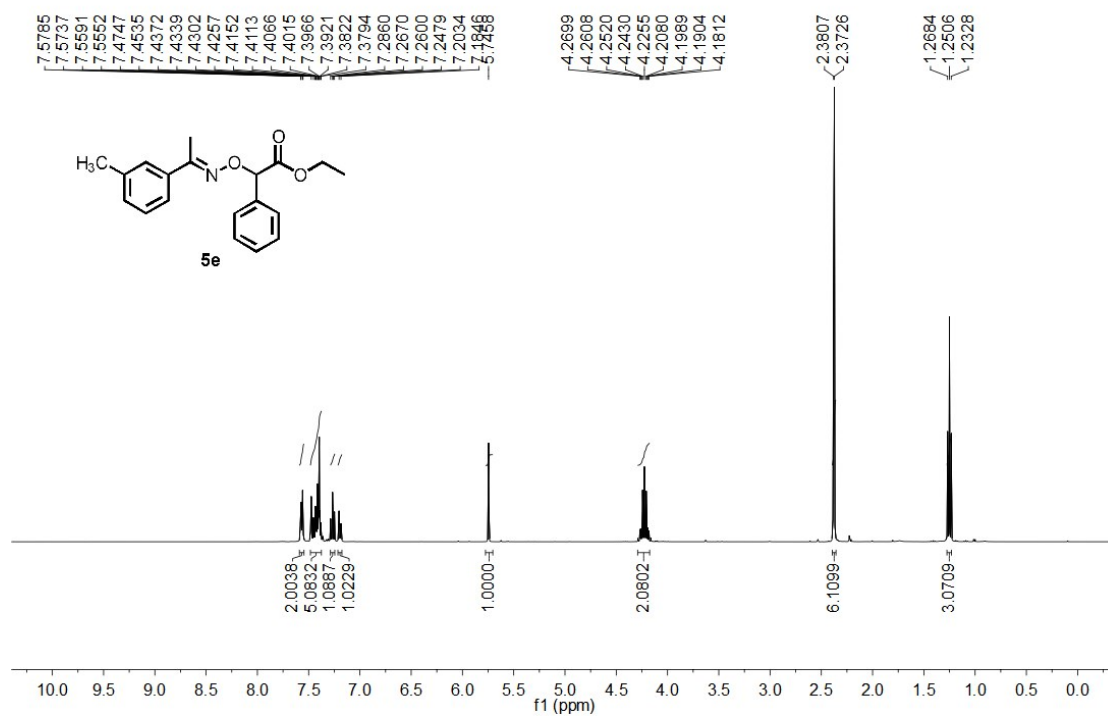
zzp-528-8



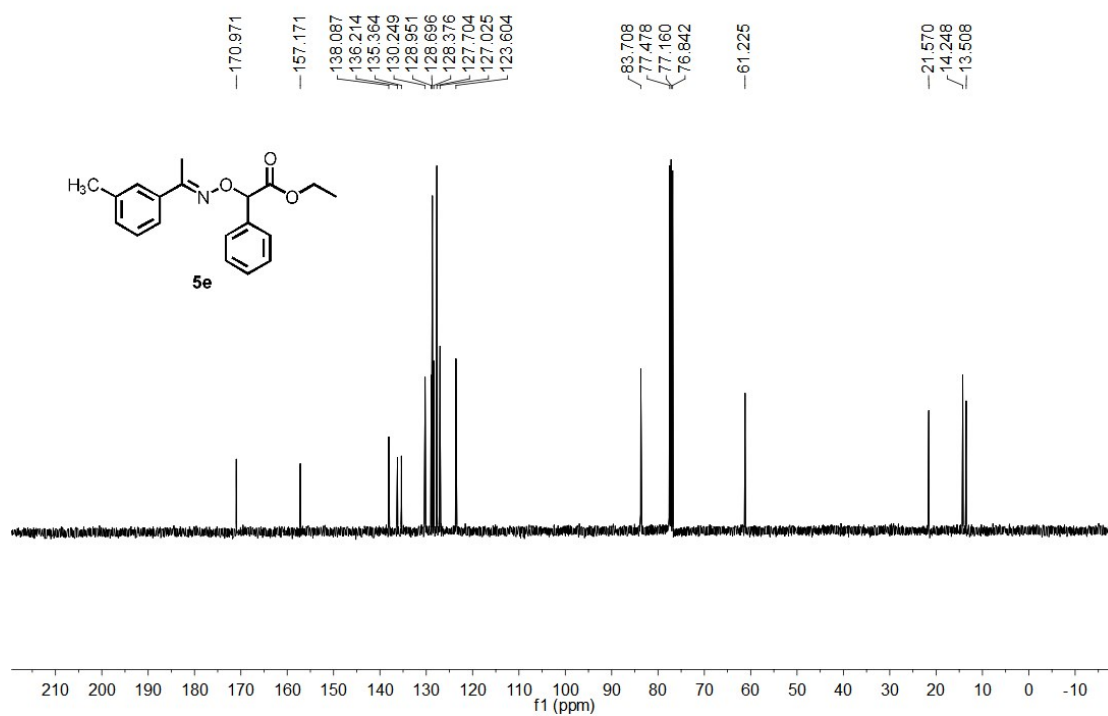
zzp-528-8



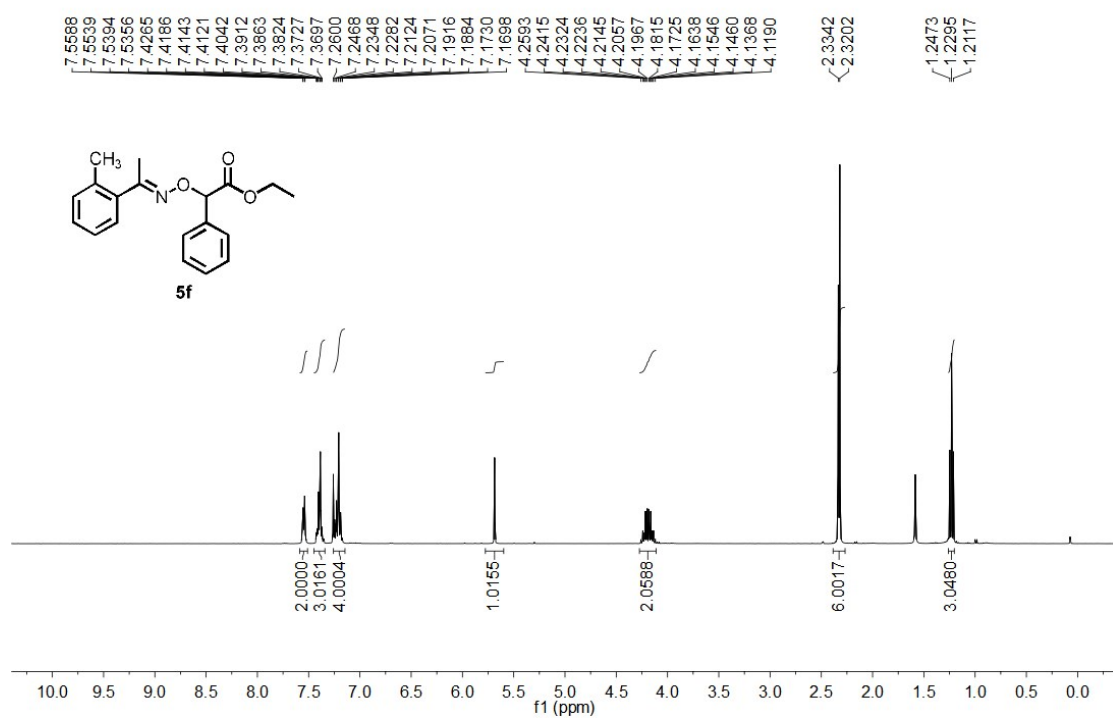
zzp-529-8



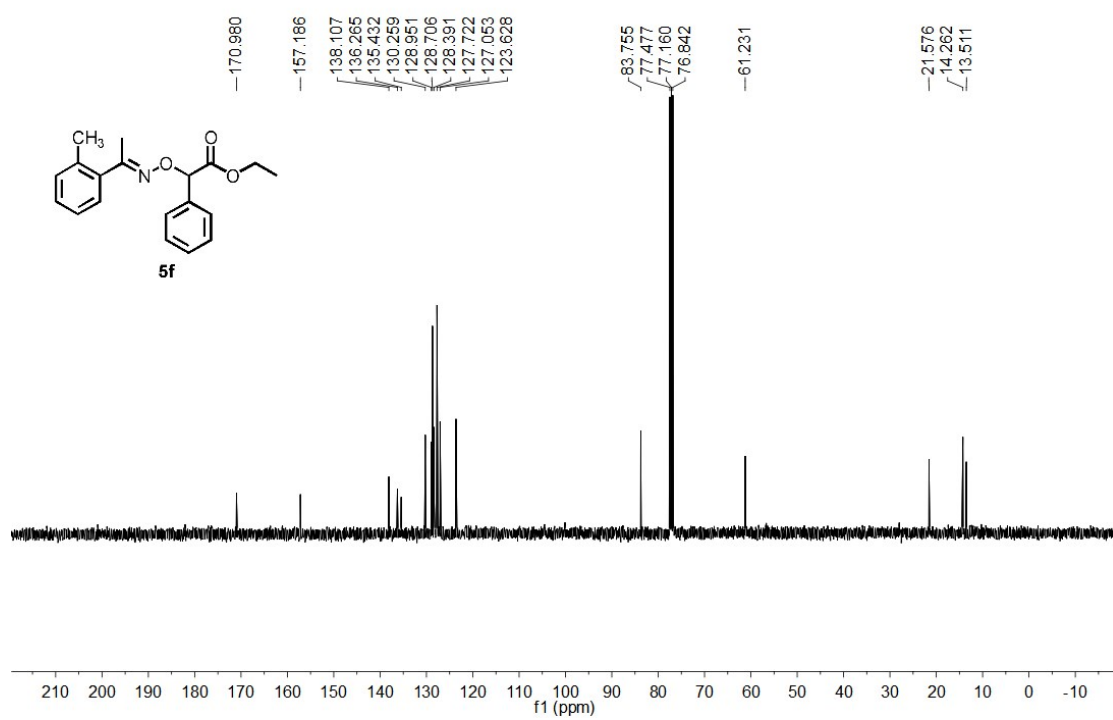
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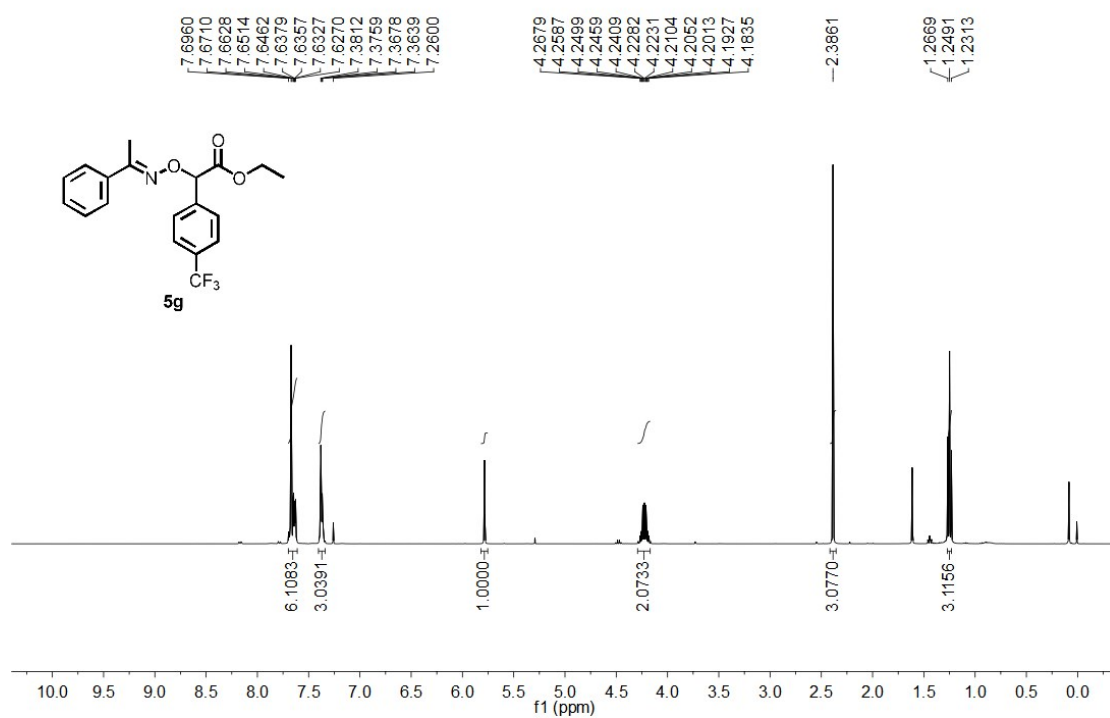
ZZP-569-8



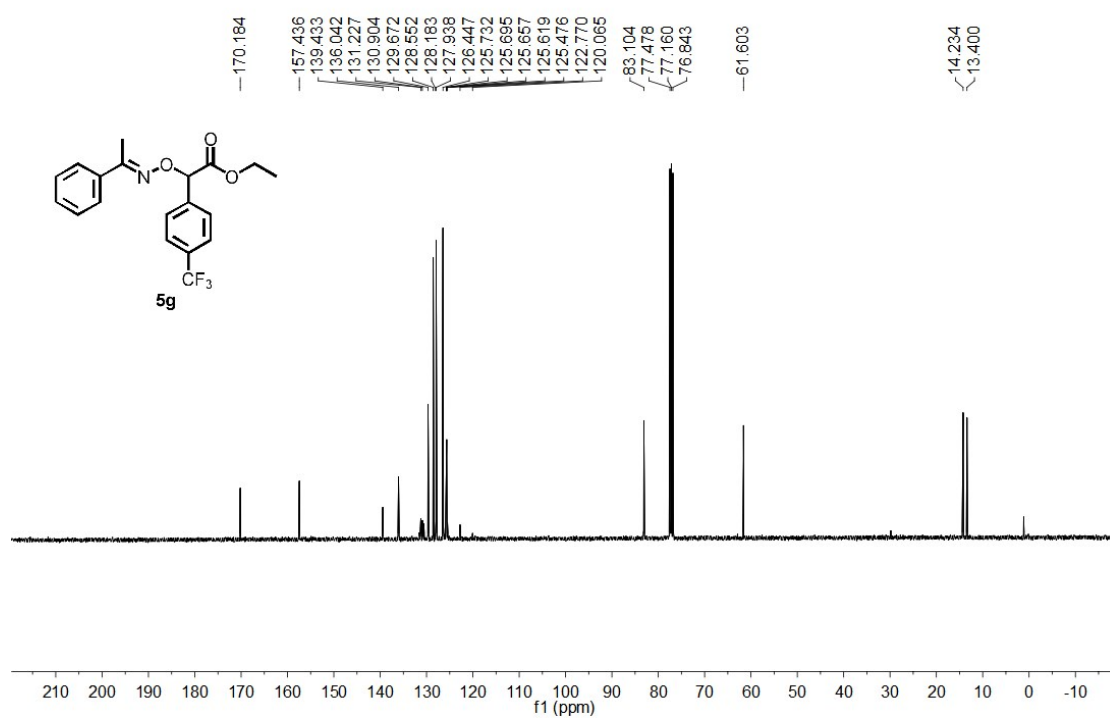
ZZP-568-8



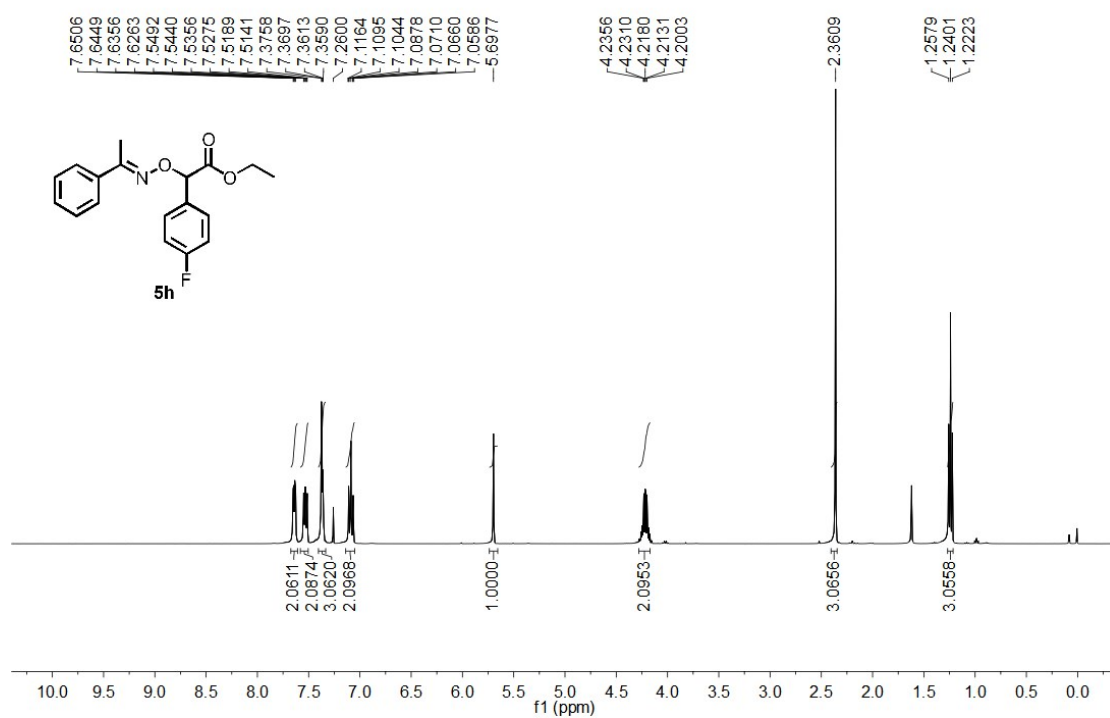
ZZP-124-2



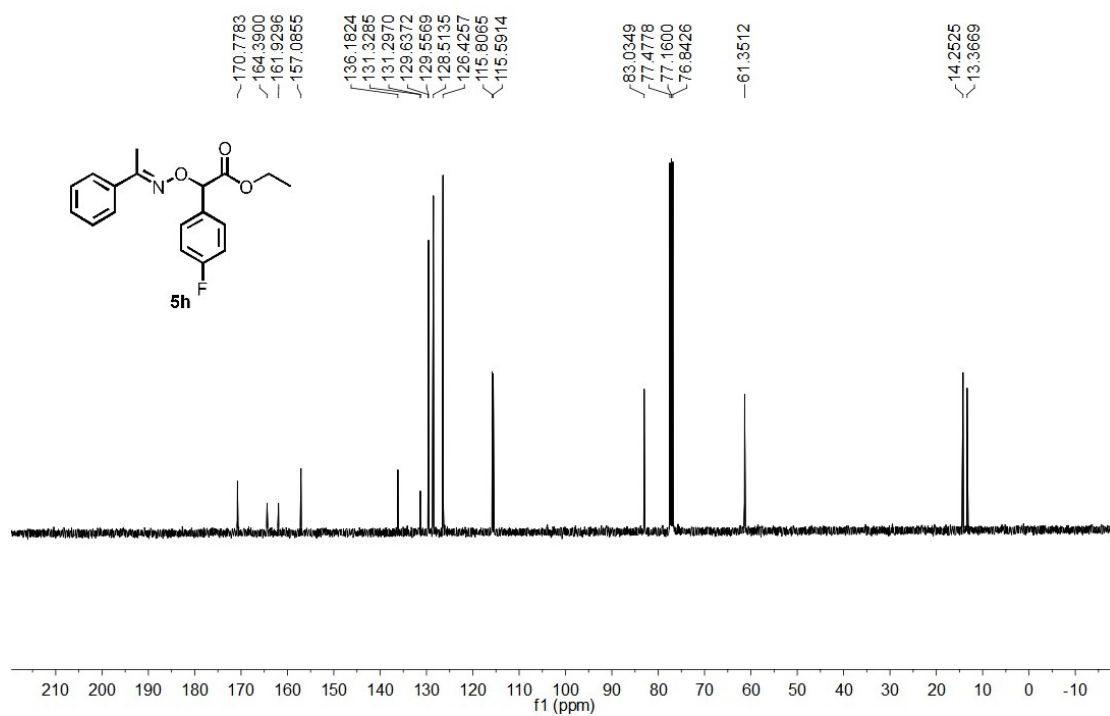
ZZP-124-2



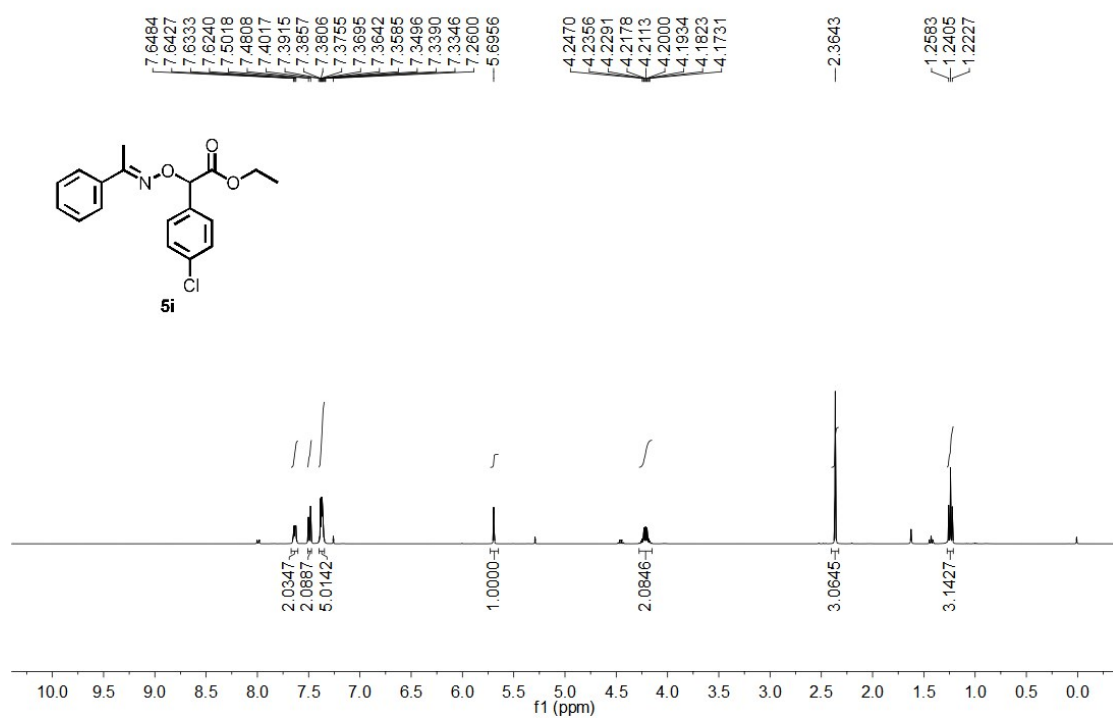
ZZP-509



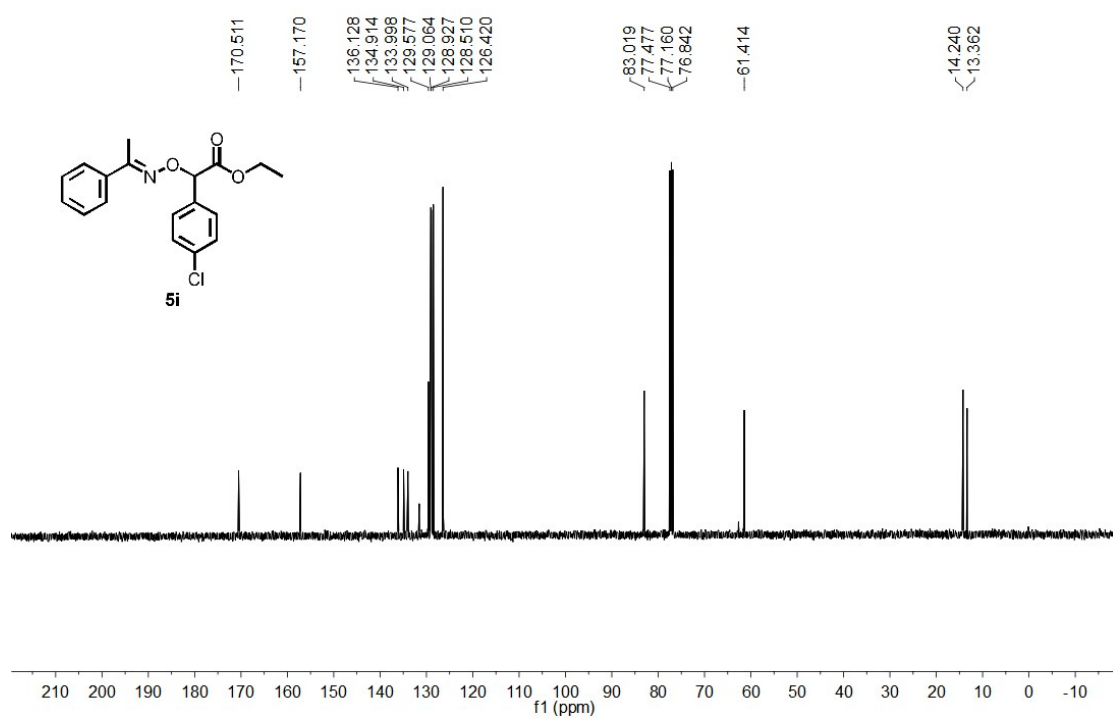
ZZP-509



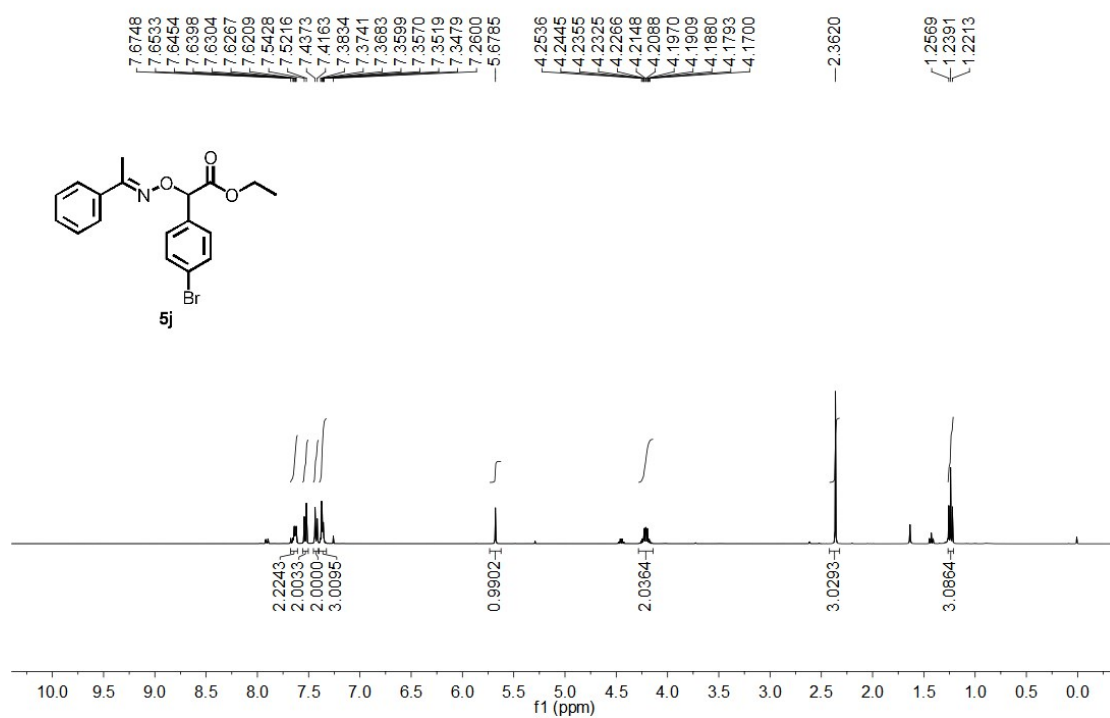
ZZP-120-3



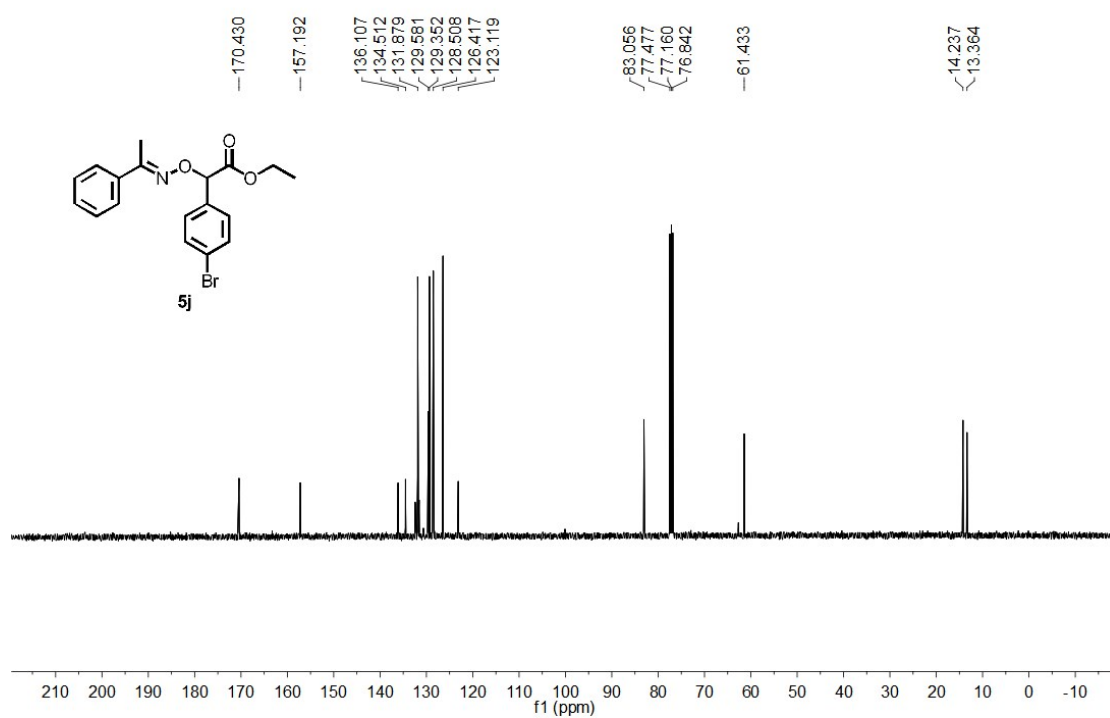
ZZP-120-3



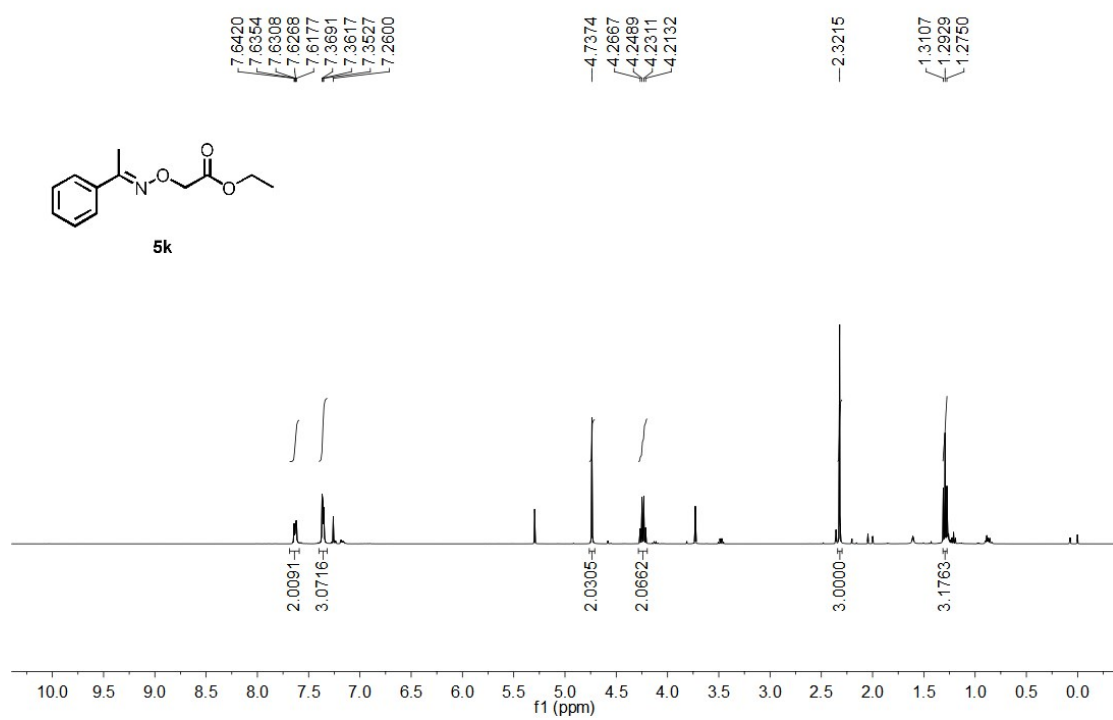
ZZP-123-2



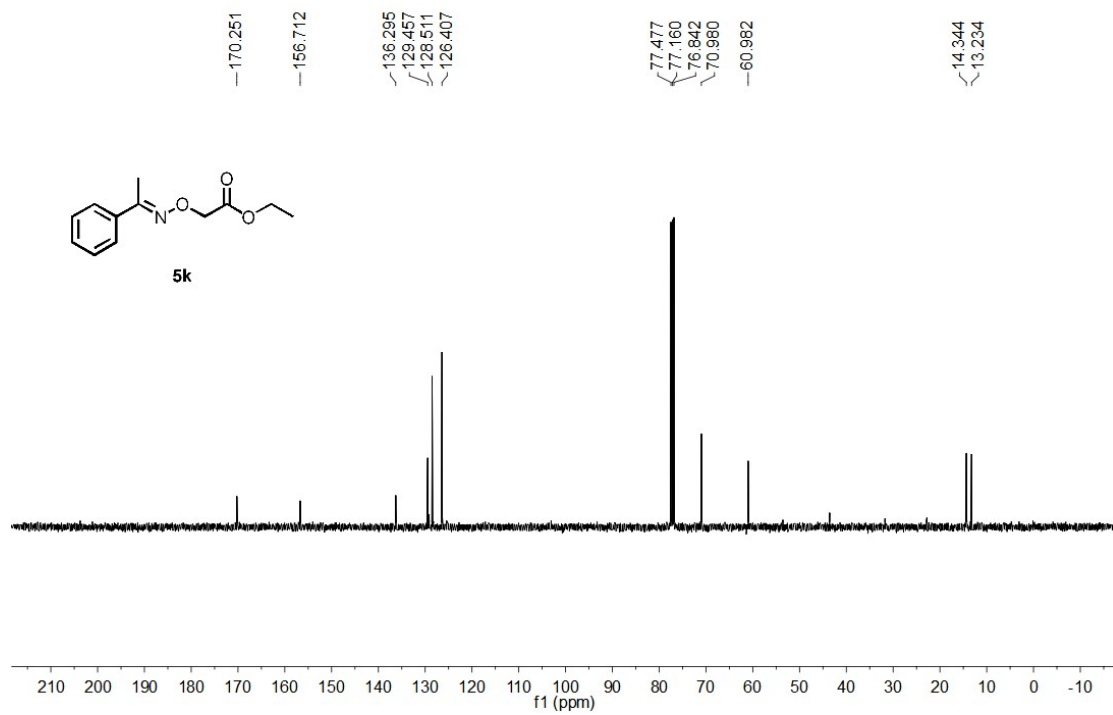
ZZP-123-2



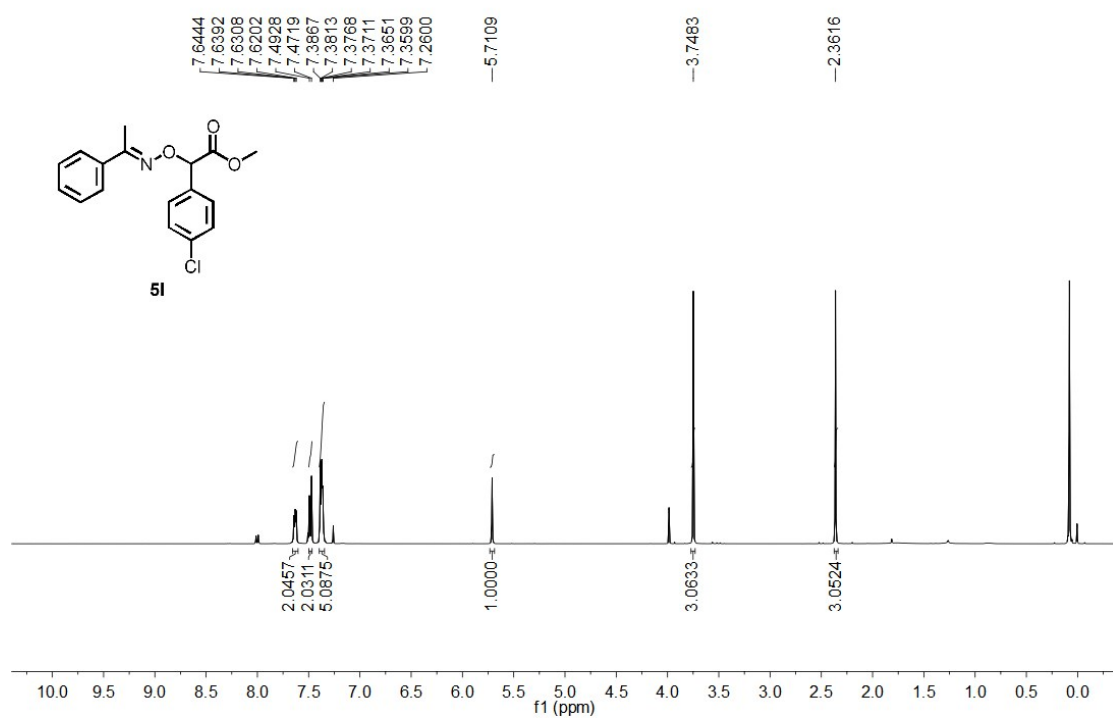
ZZP-18



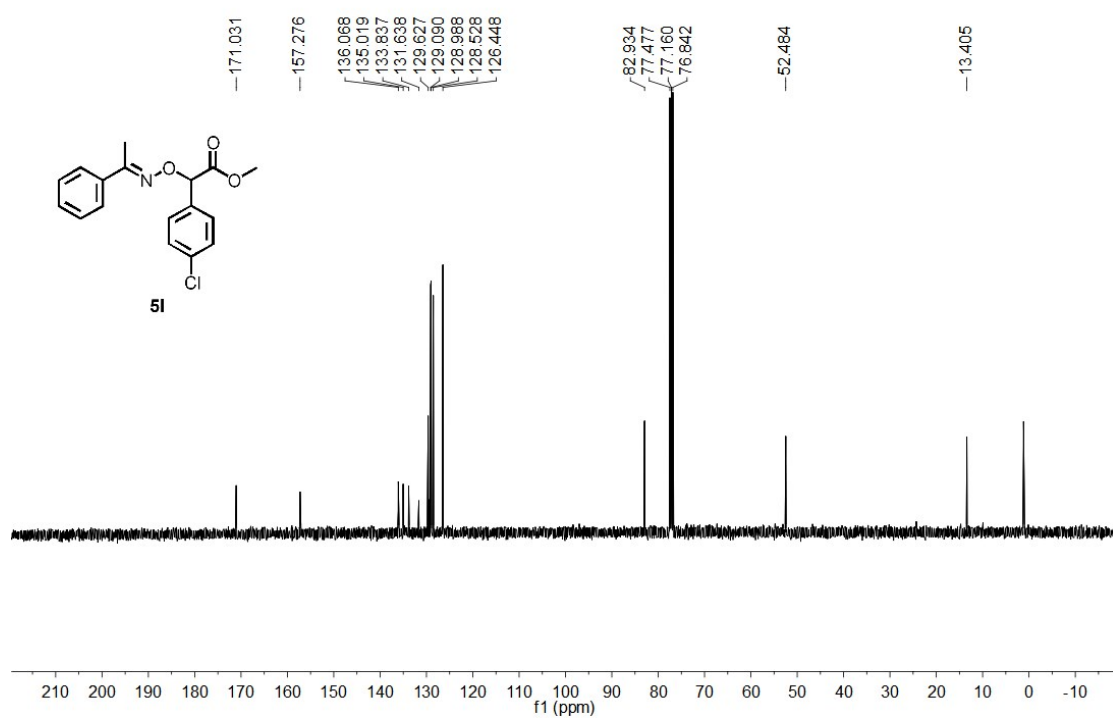
ZZP-18



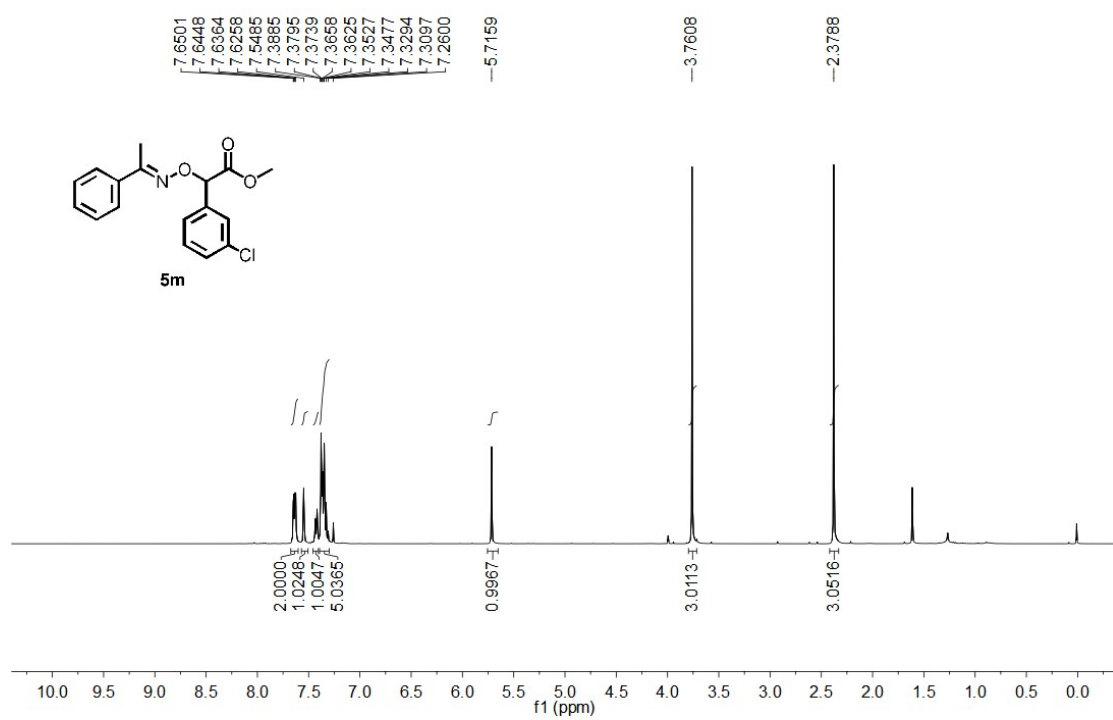
ZZP-WO



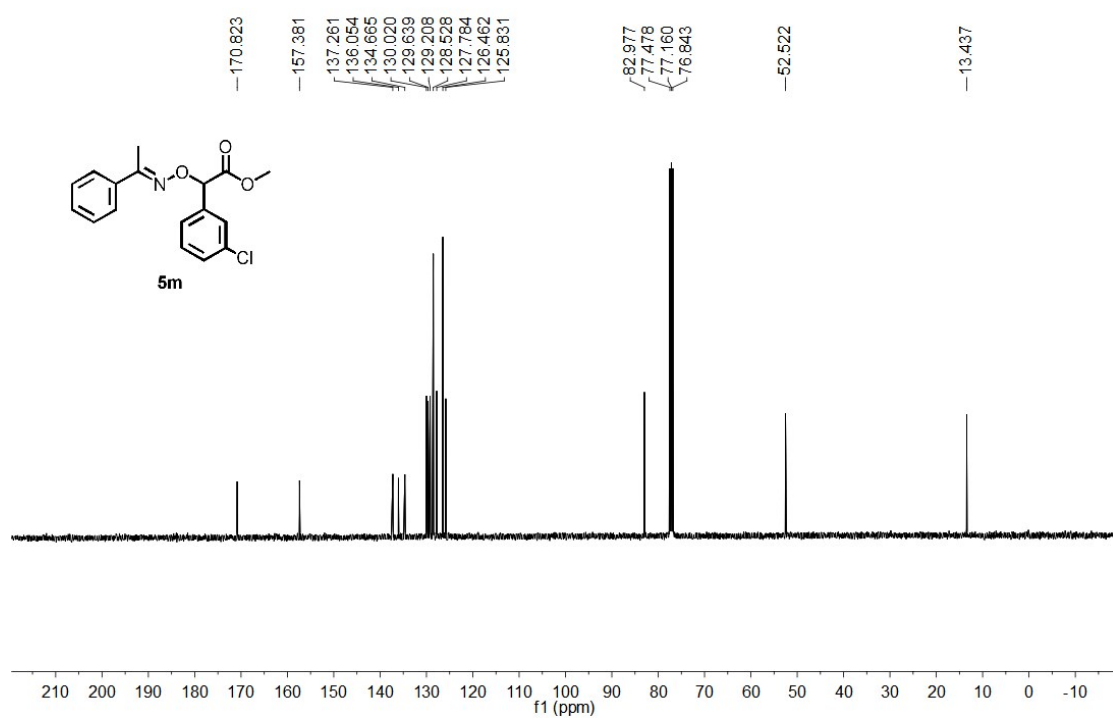
ZZP-WO



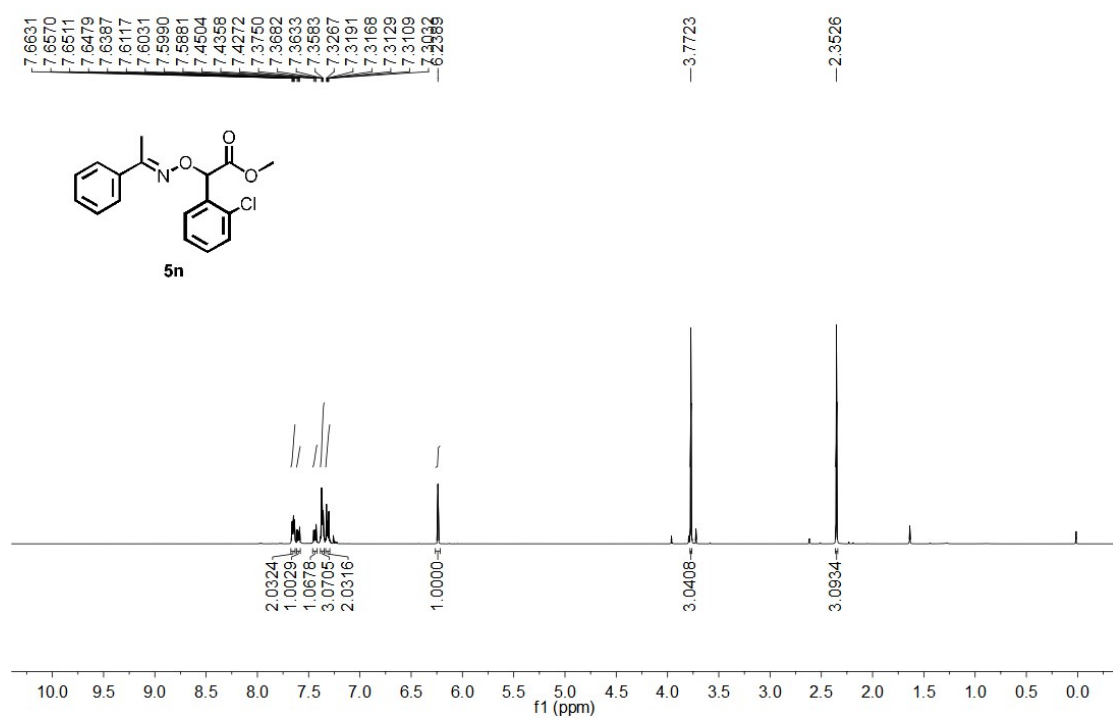
ZZP-128-1



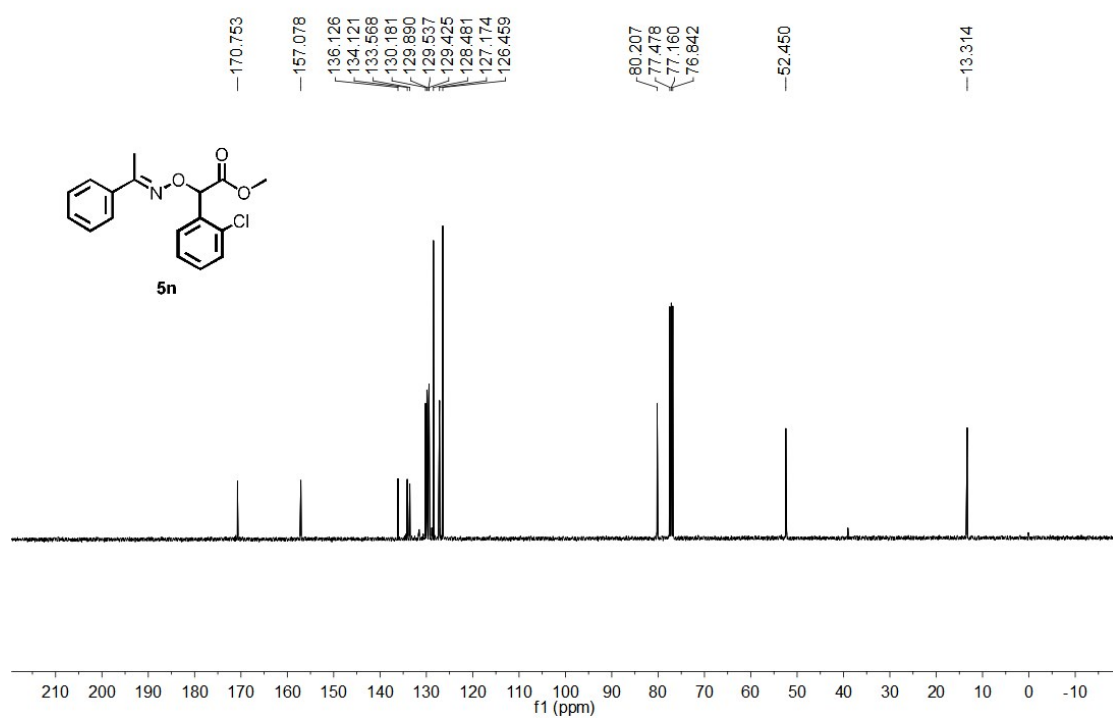
ZZP-128-1



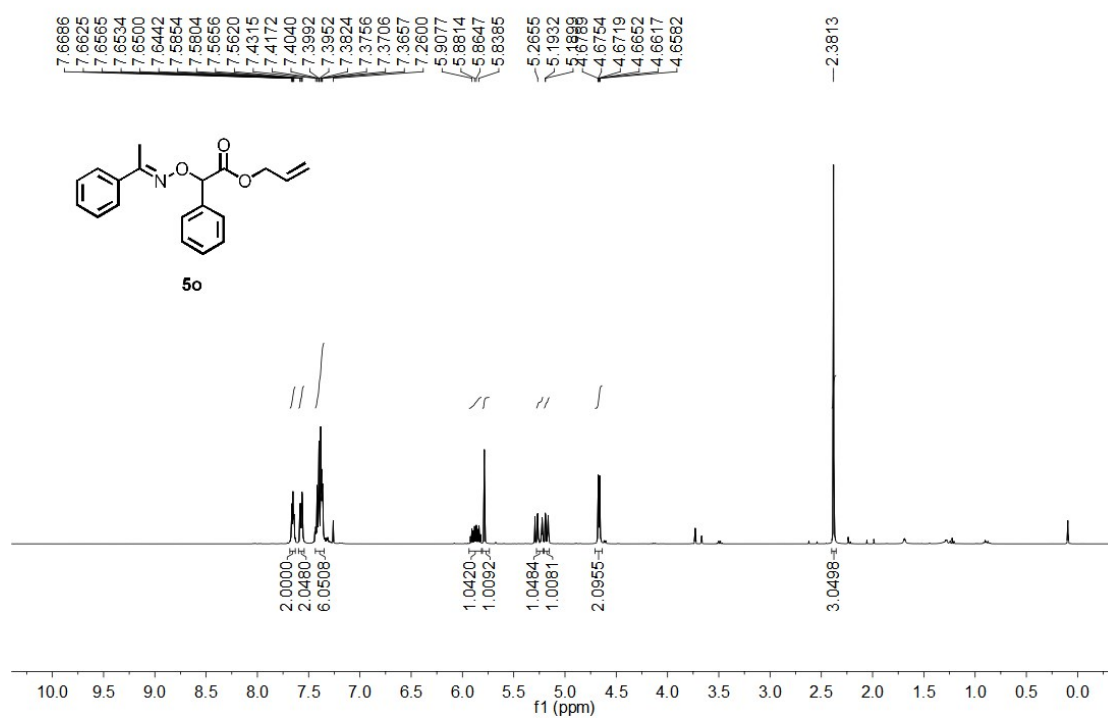
ZZP-135-1



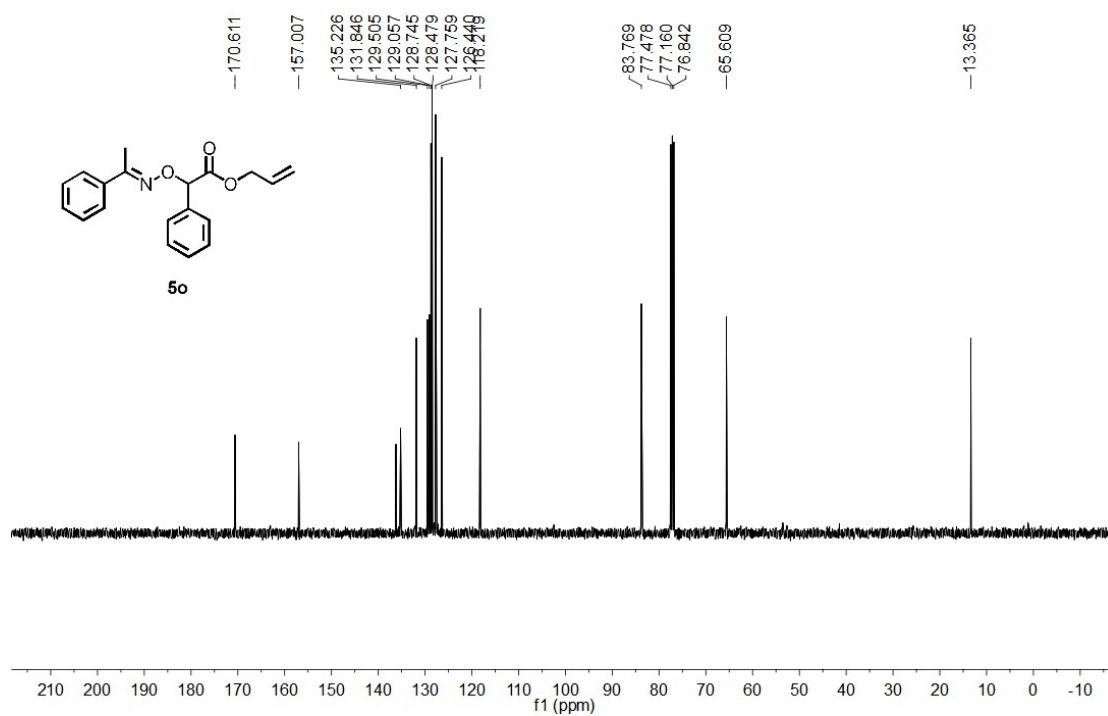
ZZP-135-1



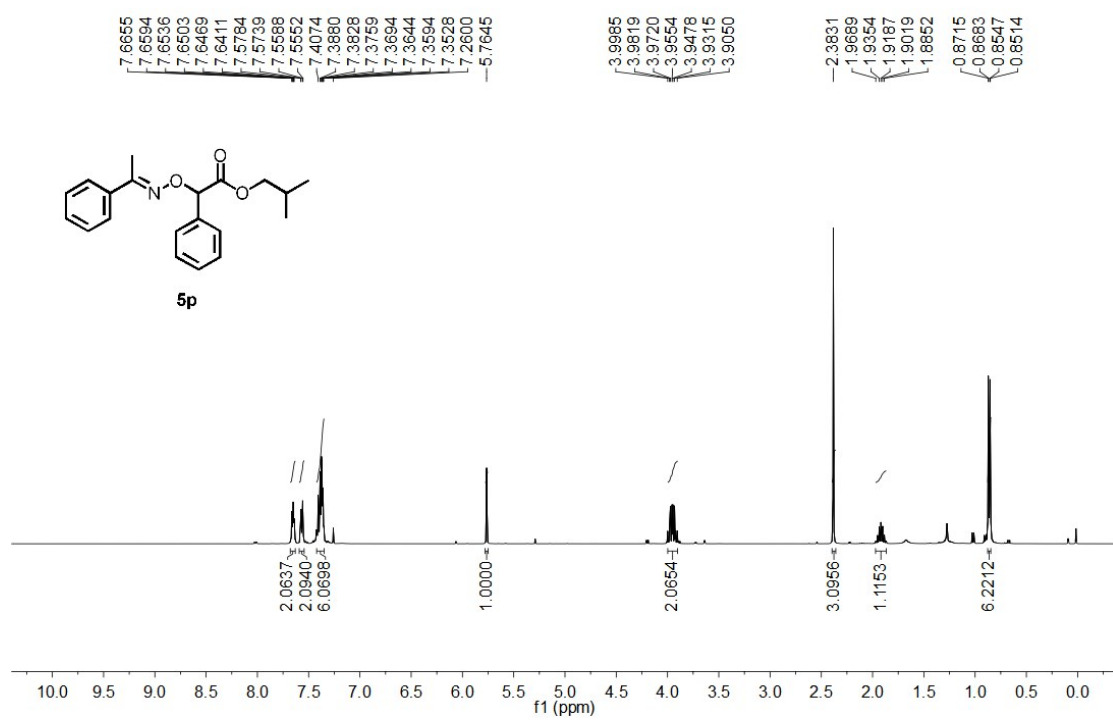
ZZP-186



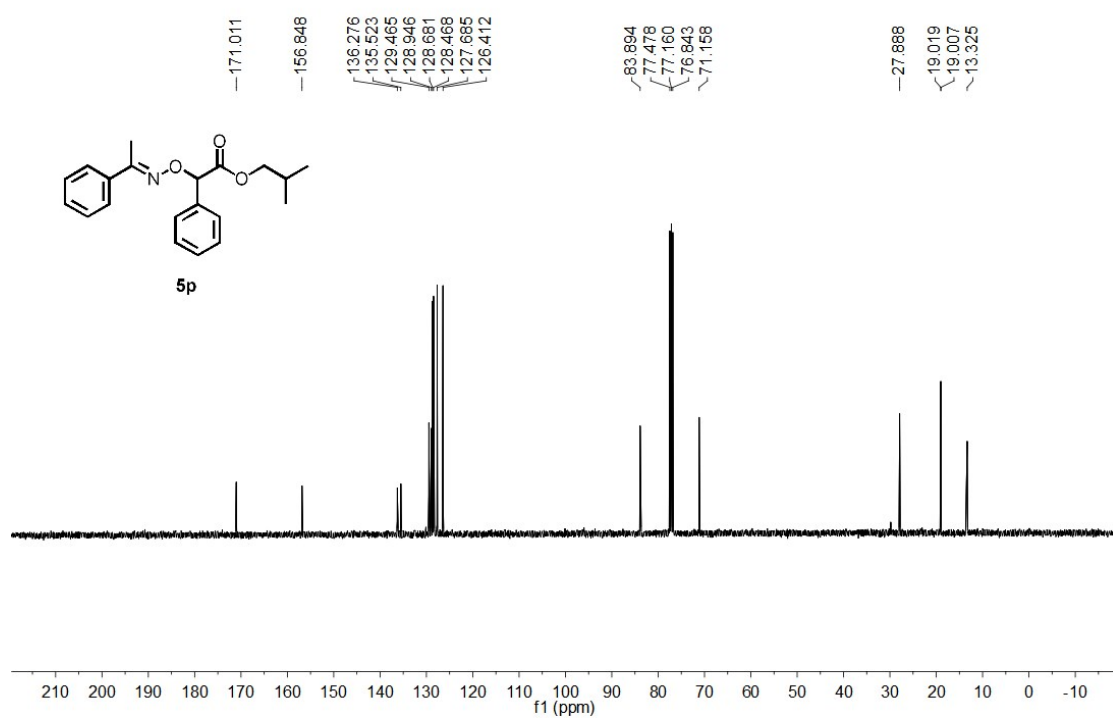
ZZP-186



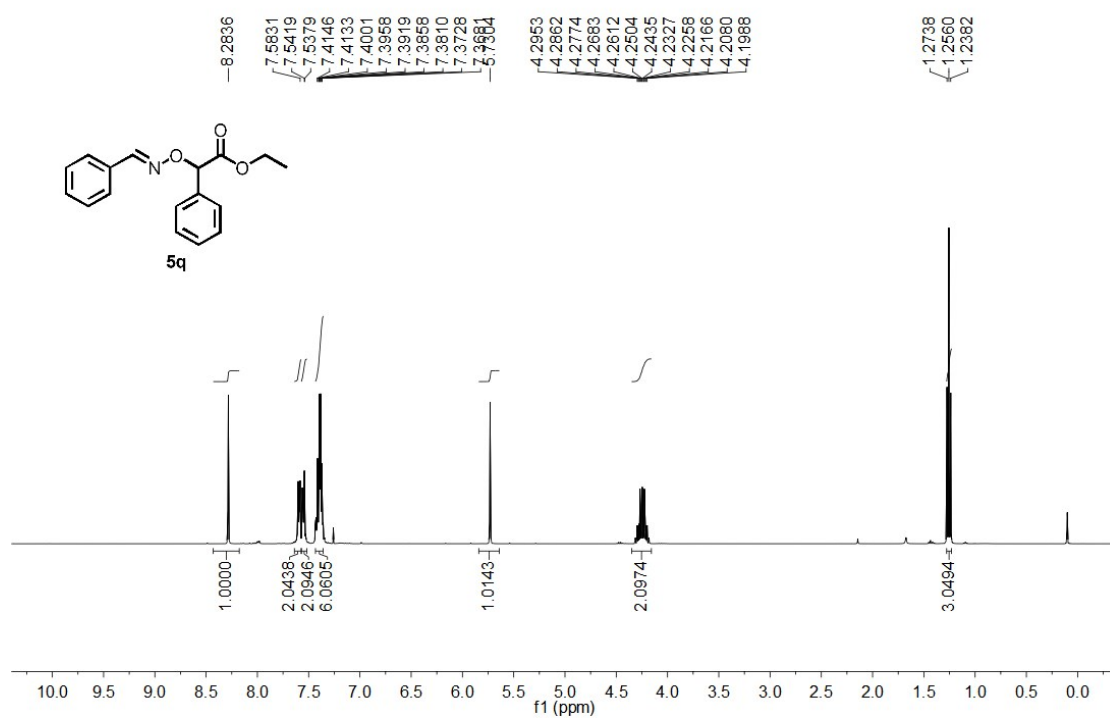
ZZP-126-1



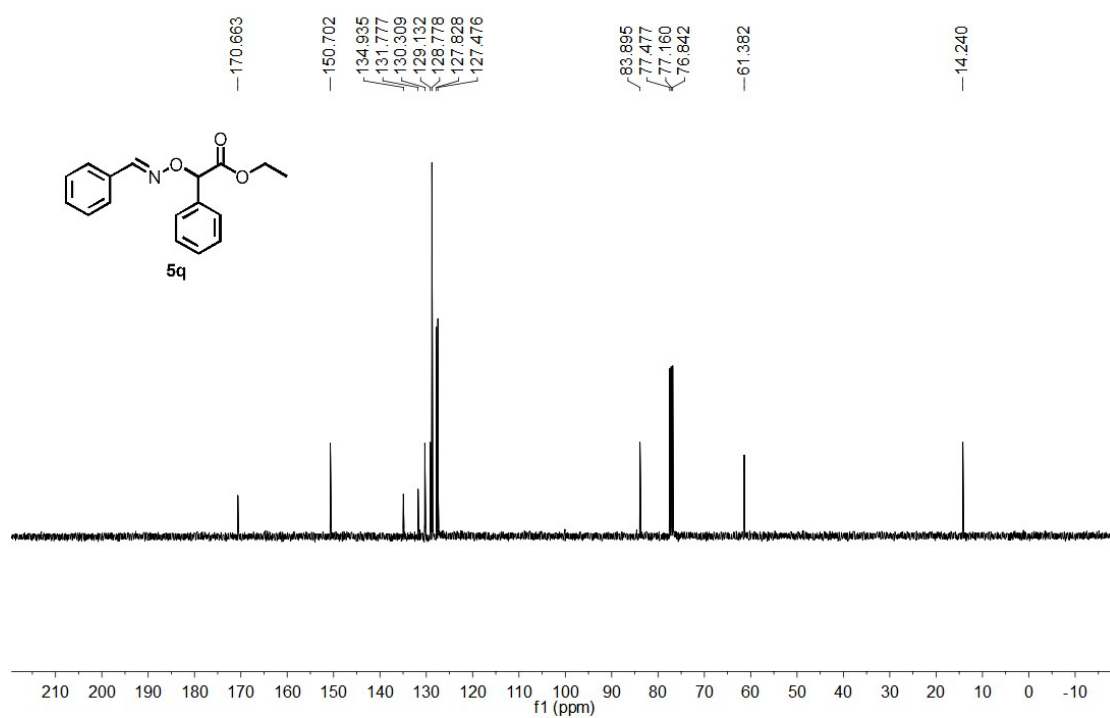
ZZP-126-1



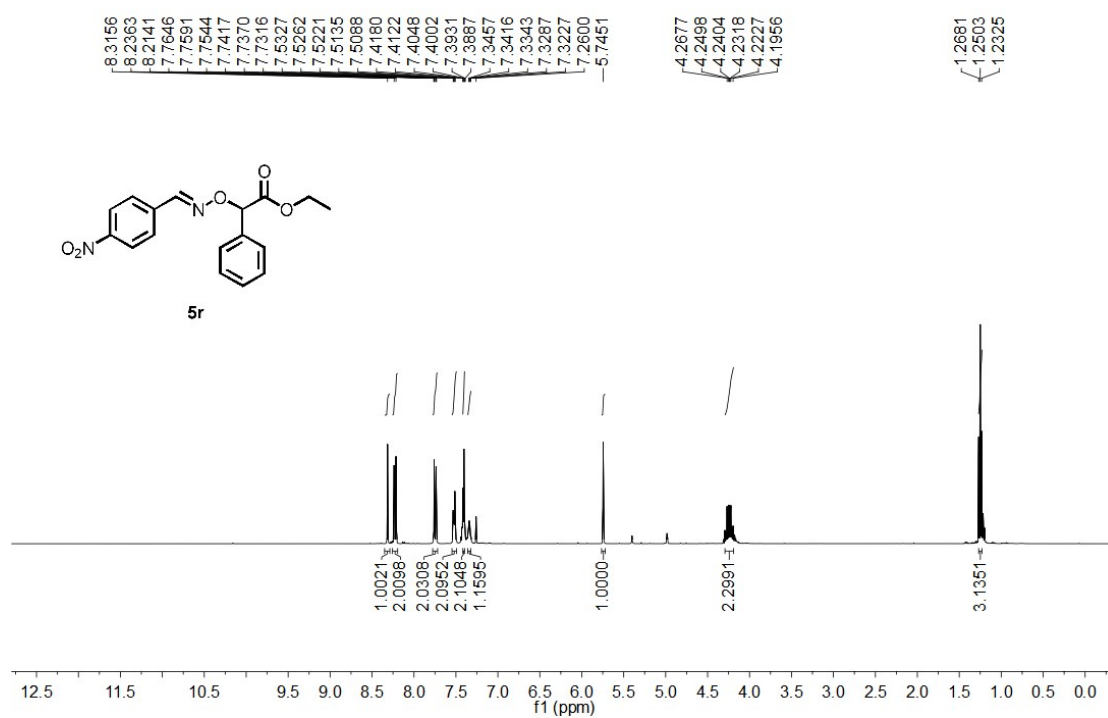
zzp-557-8



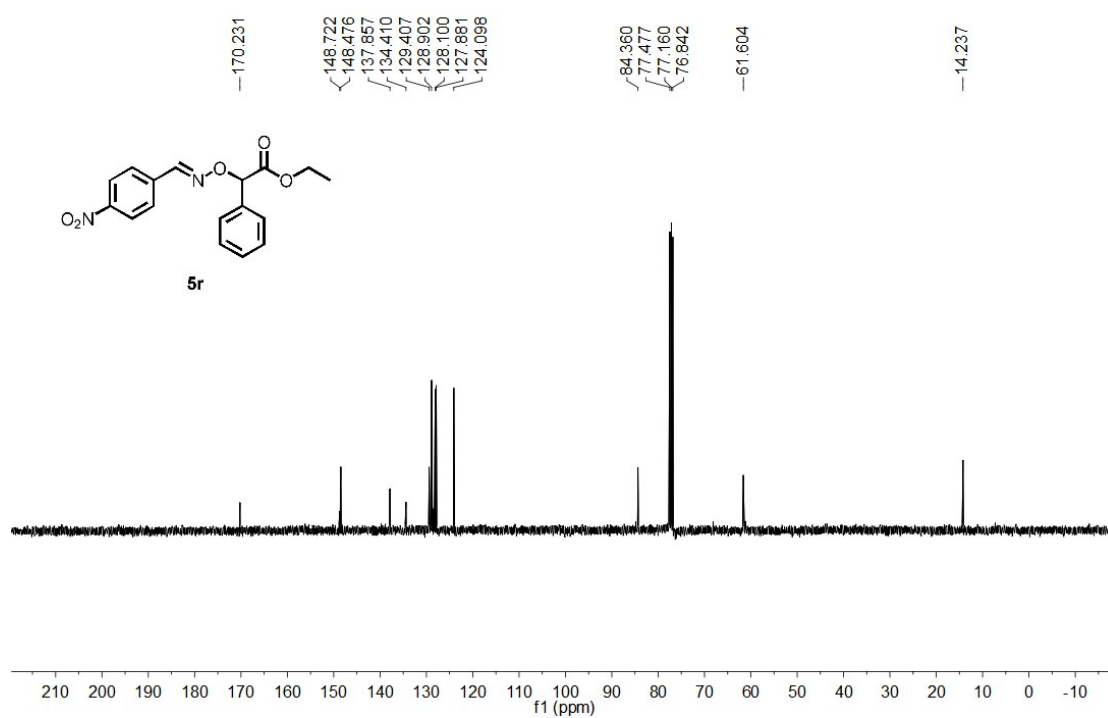
Z-557



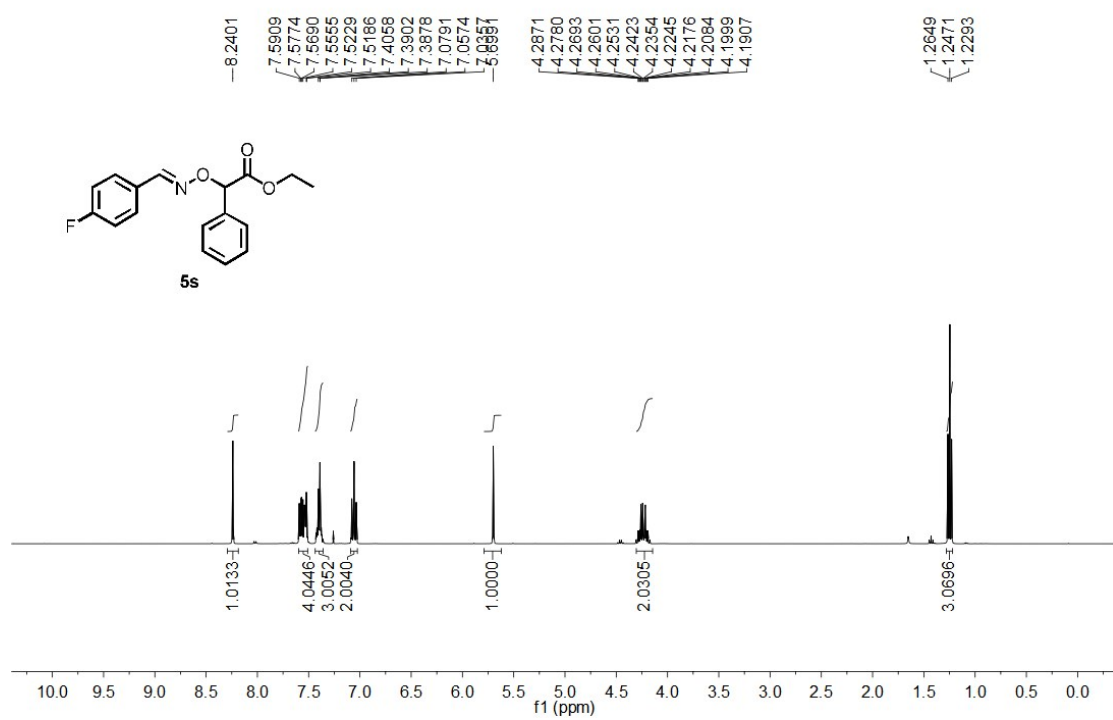
ZZP-551-8



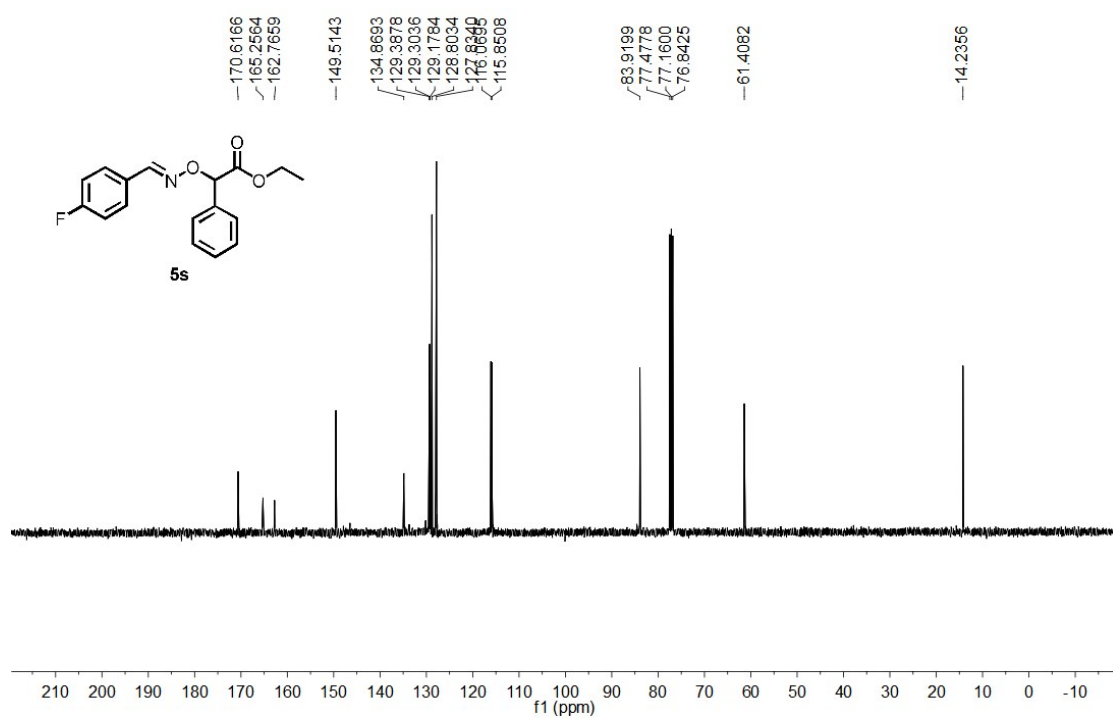
ZZP-551-8



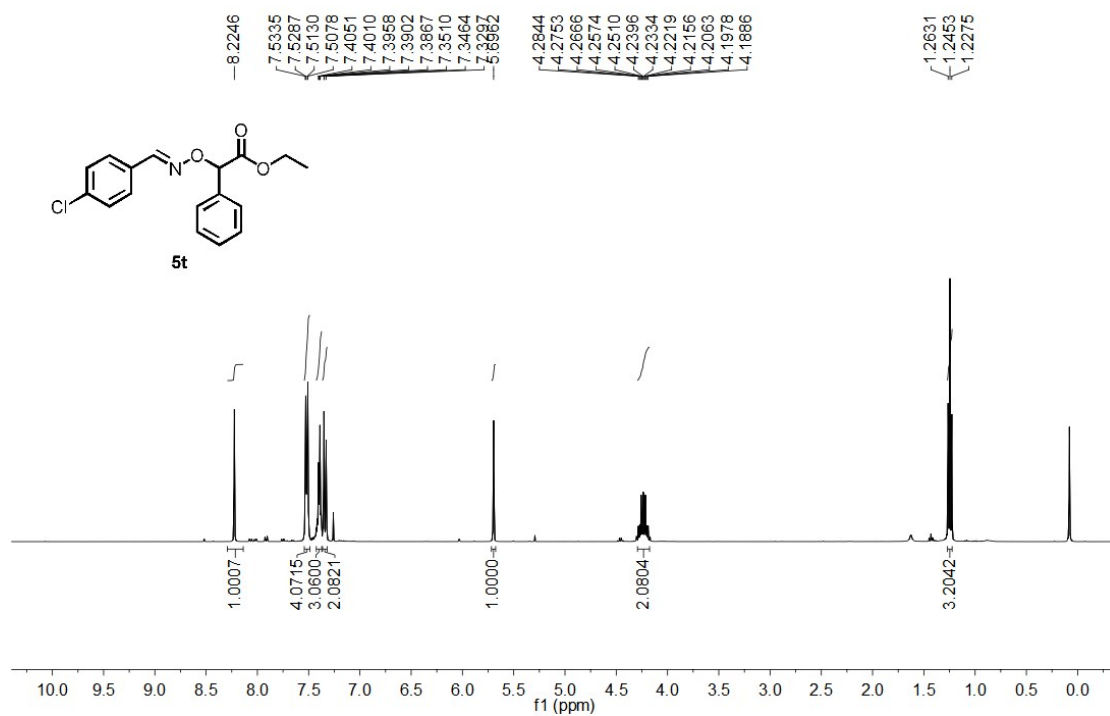
zzp-566-8



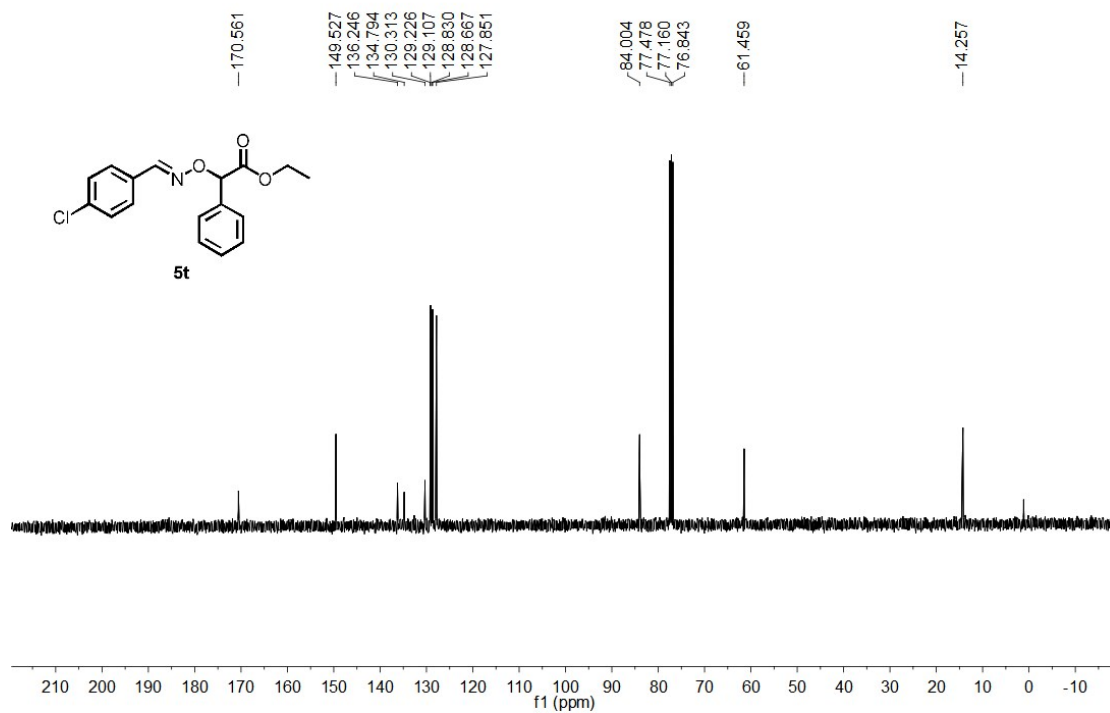
Z-566



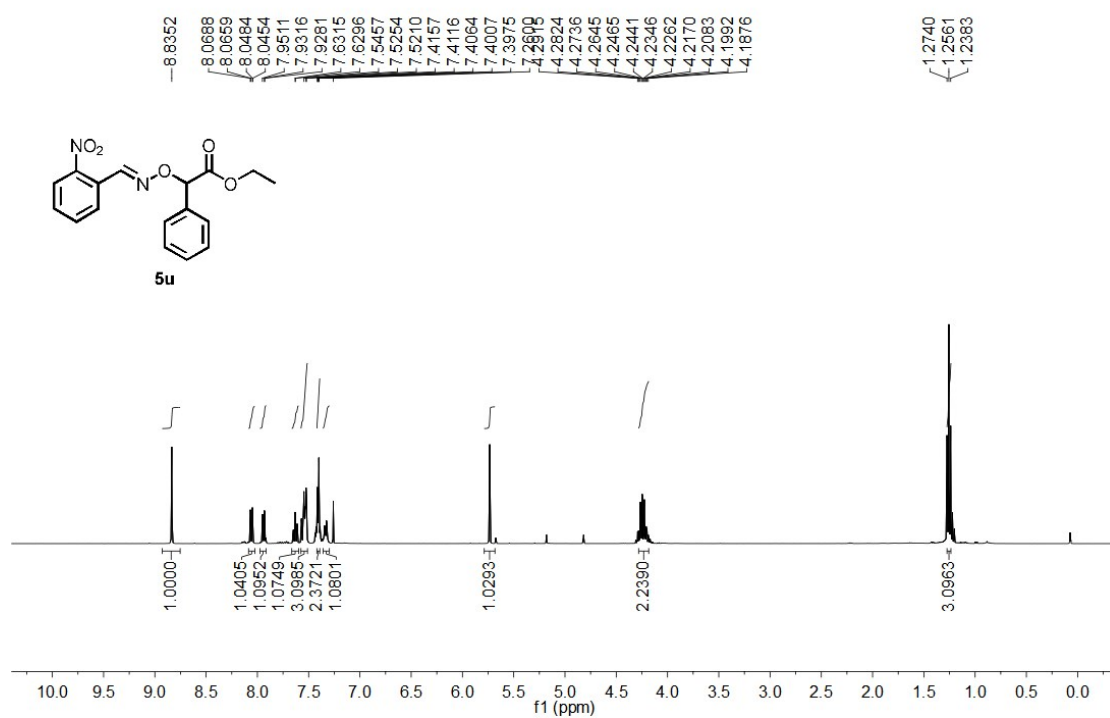
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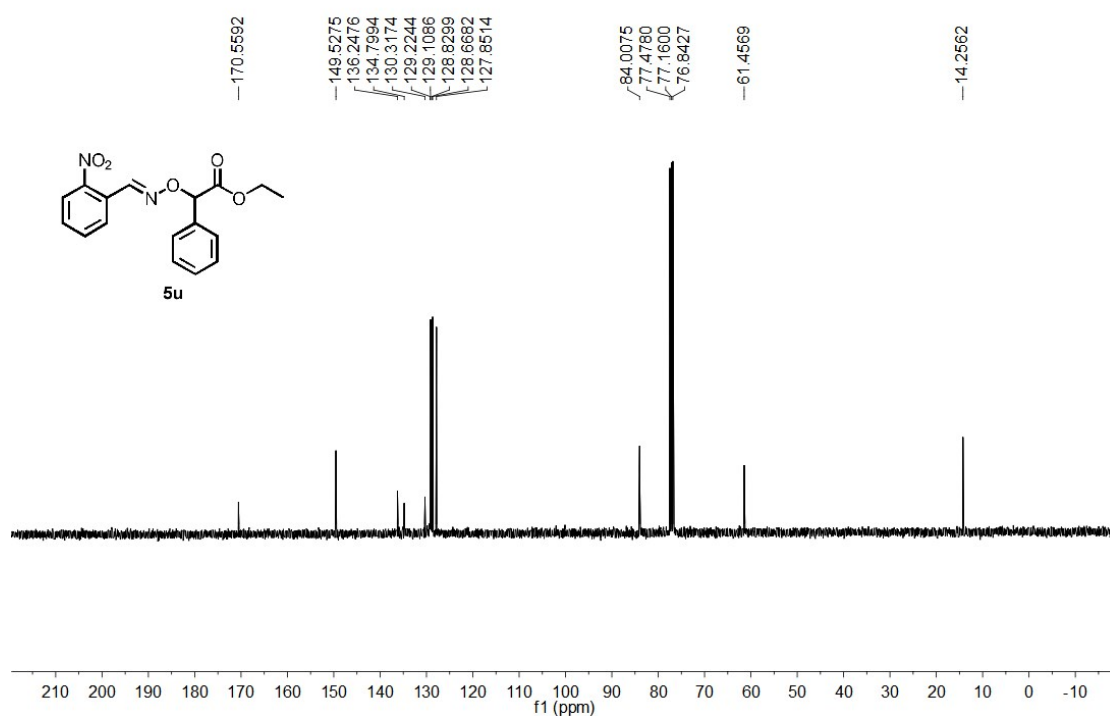
Z-555



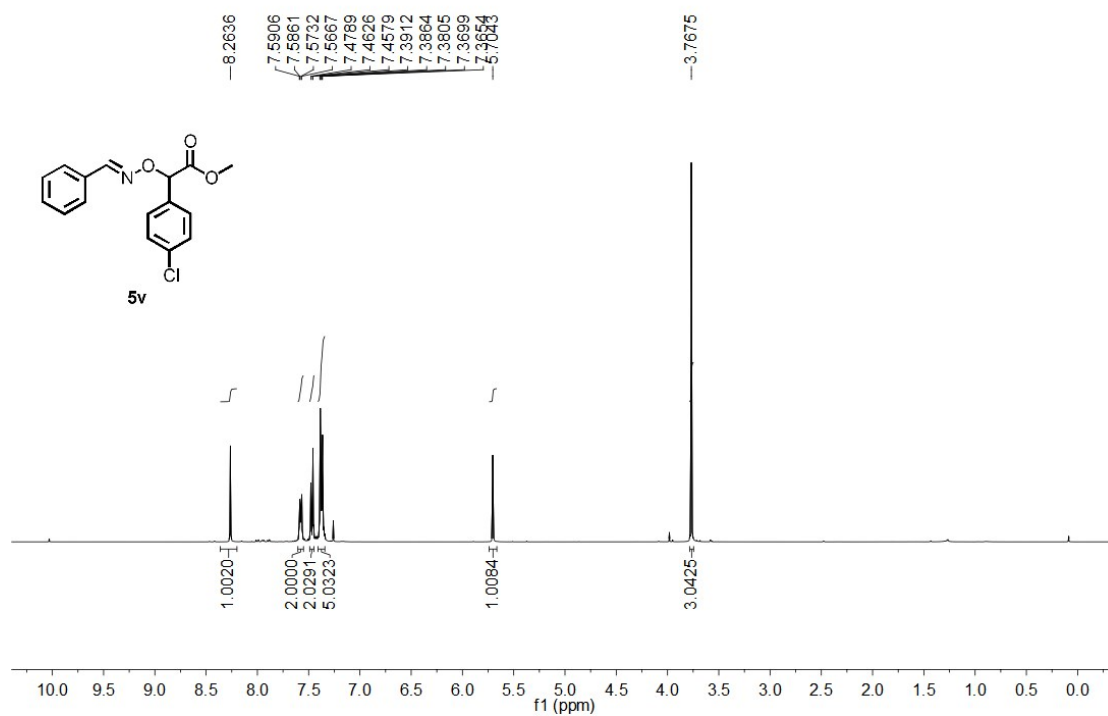
585-9



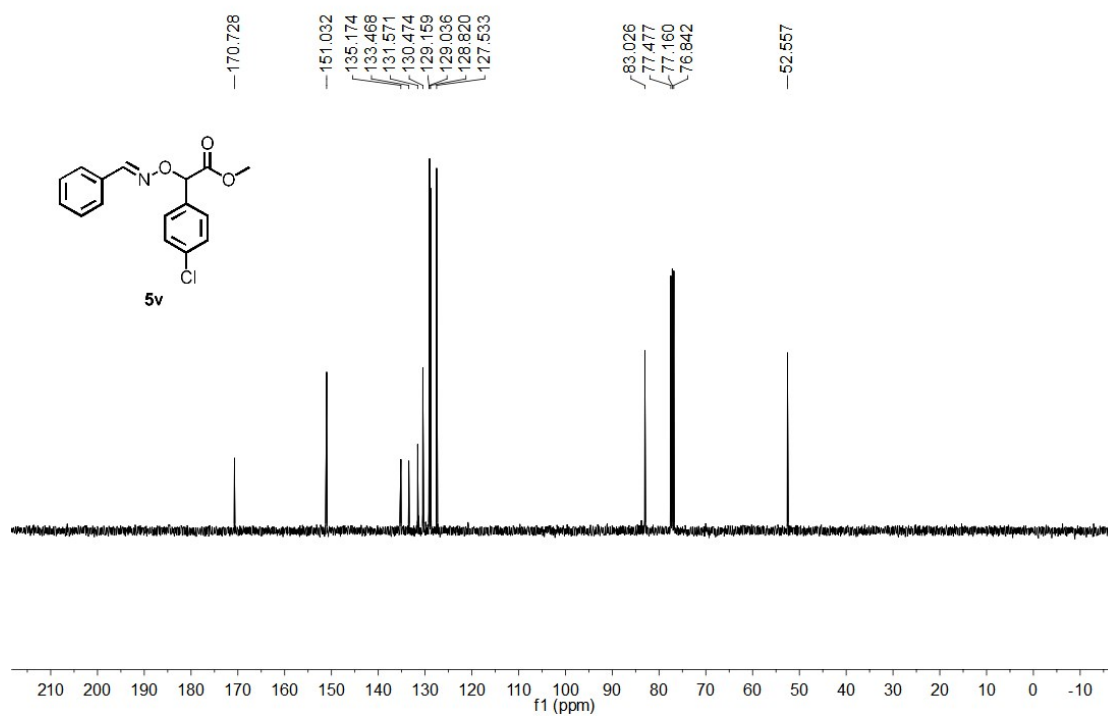
ZZP-553-8



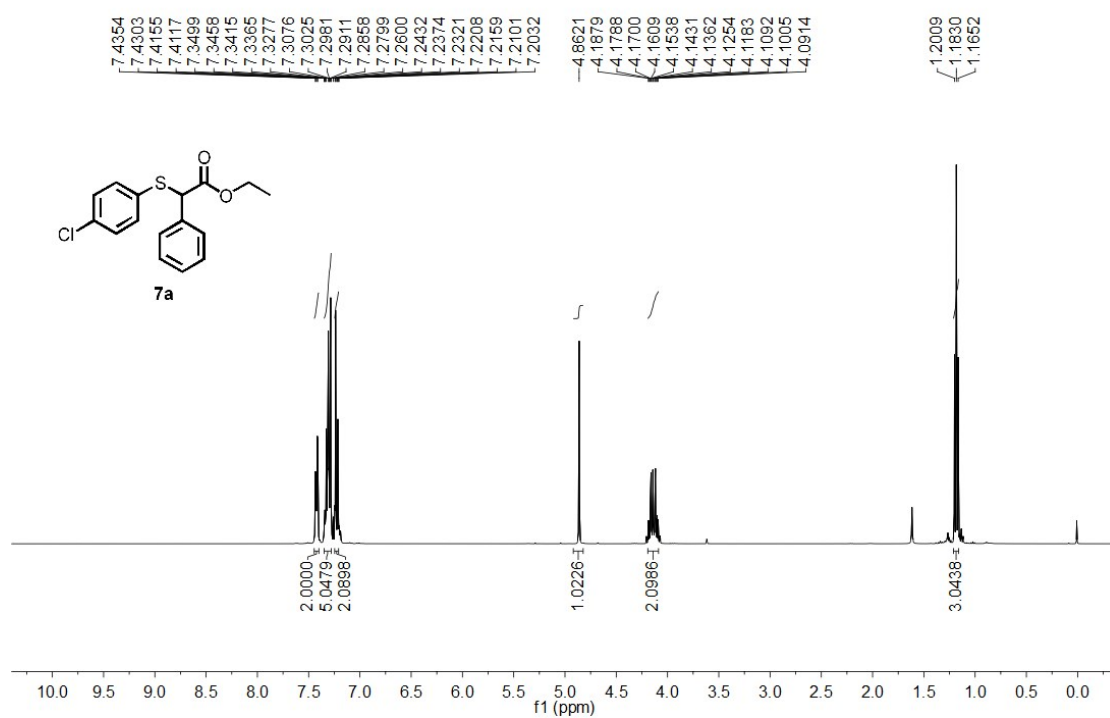
ZZP-2



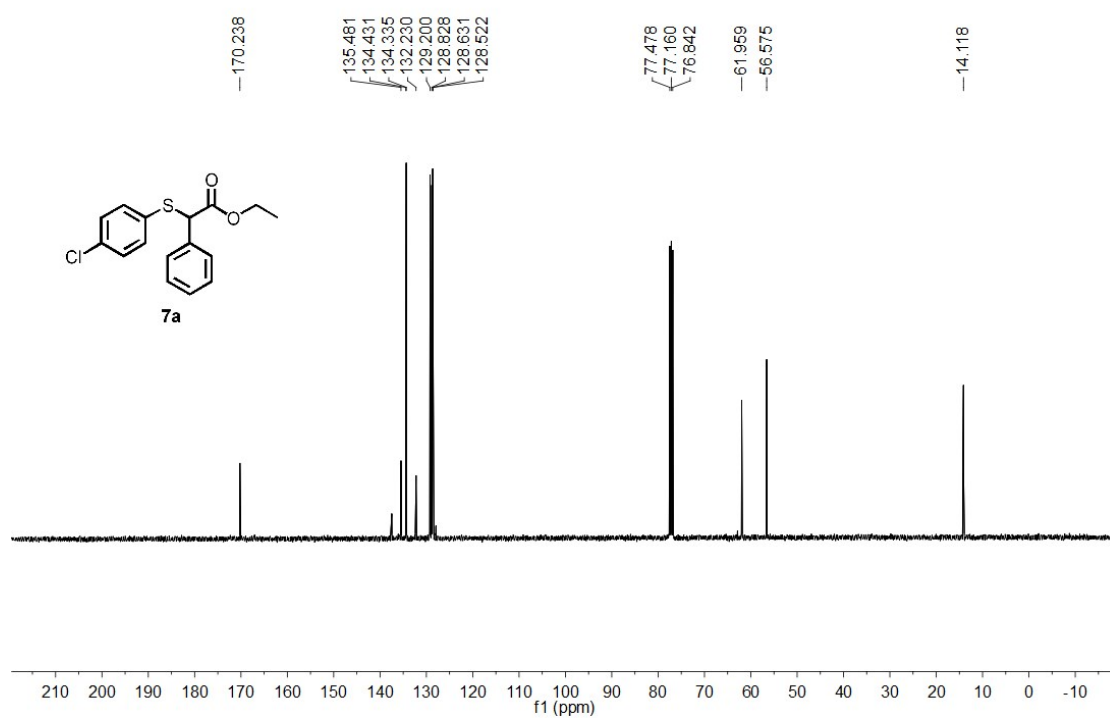
ZZP-2



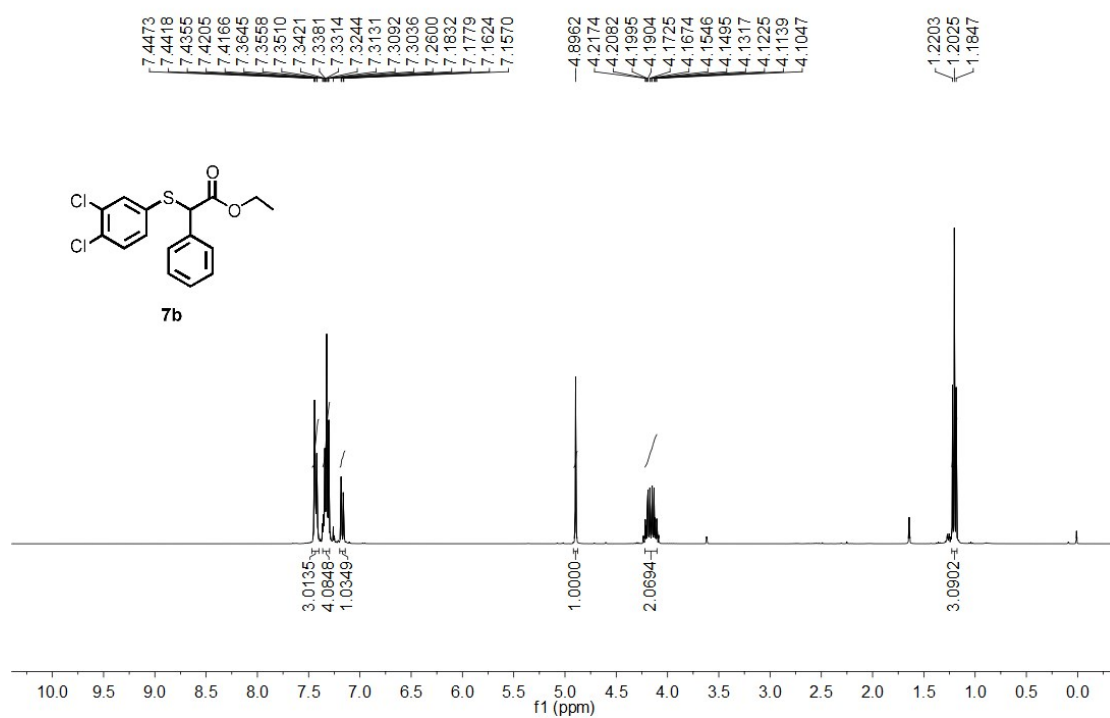
FYF-9



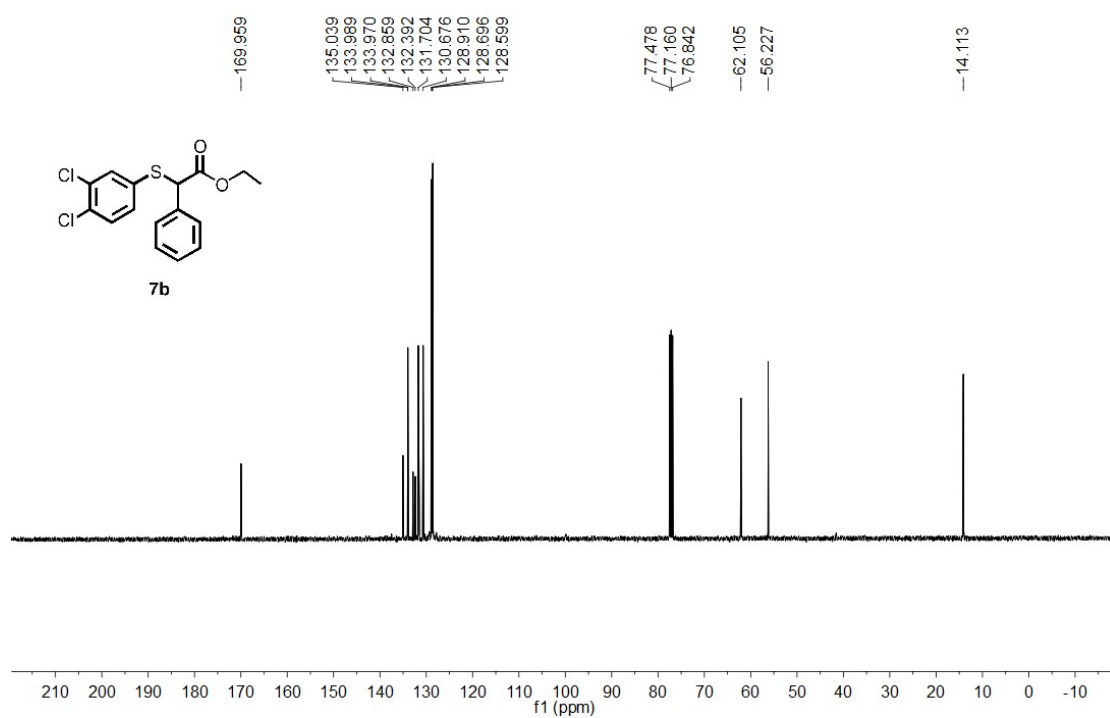
FYF-9



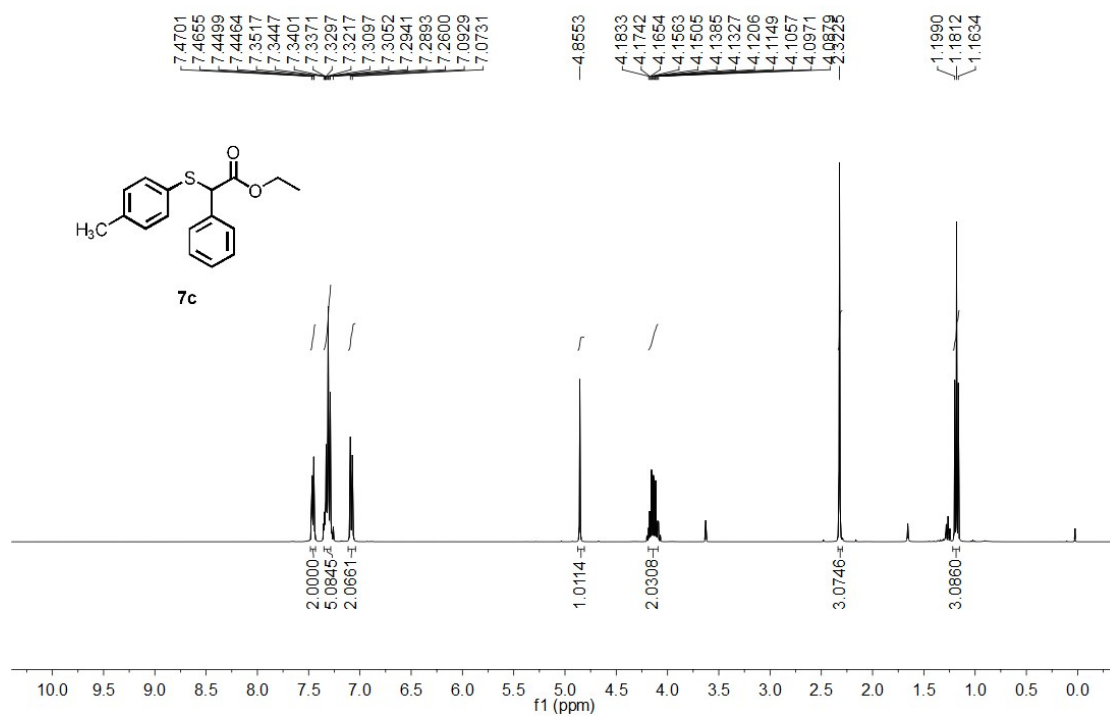
FYF-11-1



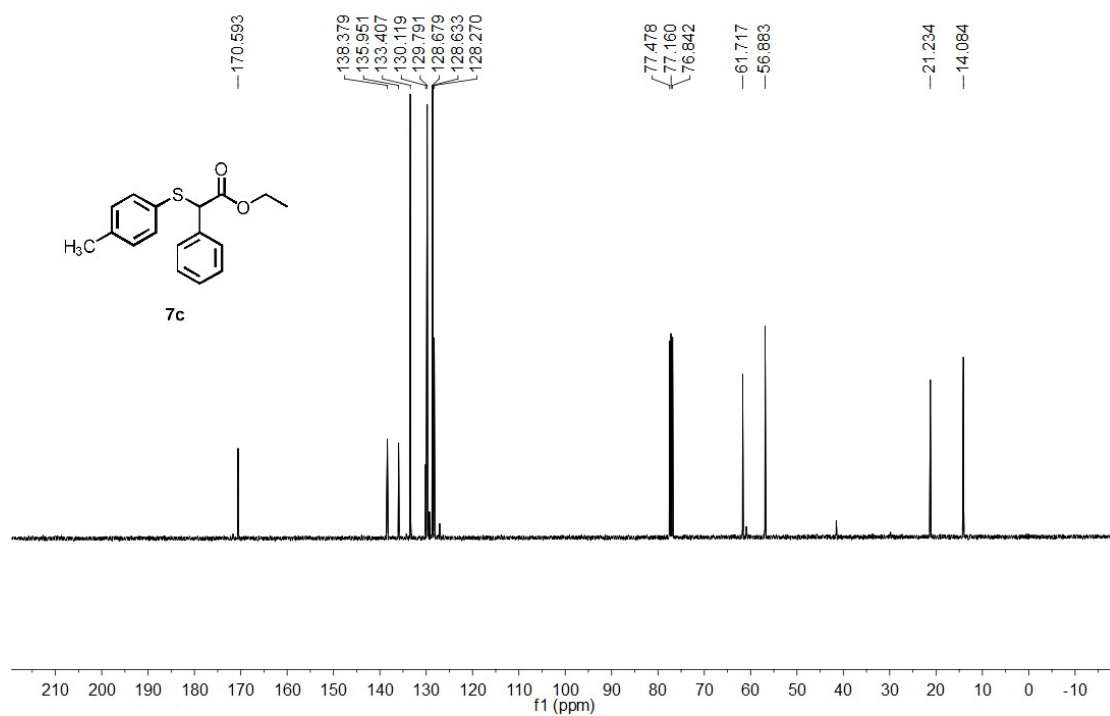
FYF-11-1



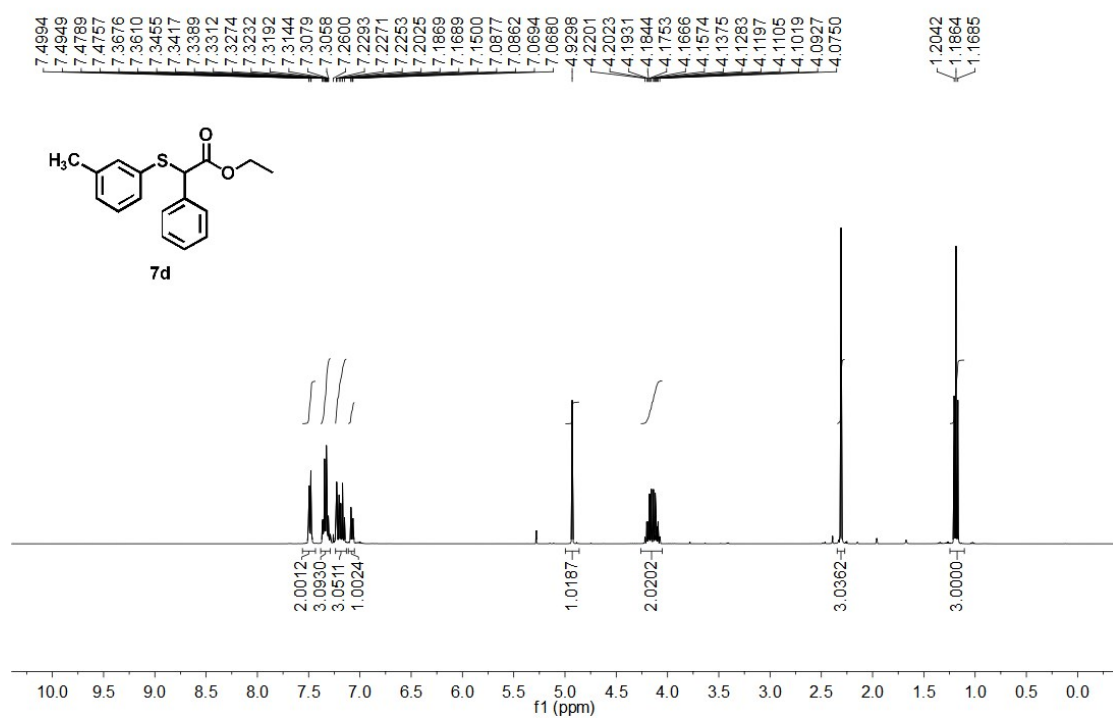
FYF-10



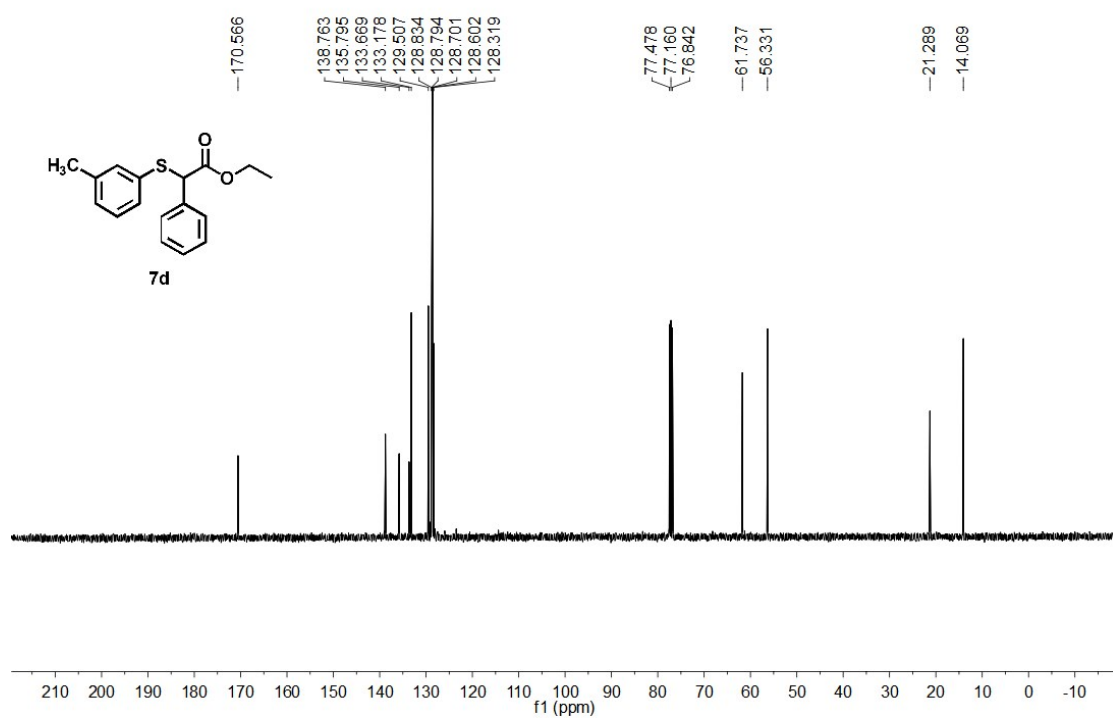
FYF-10



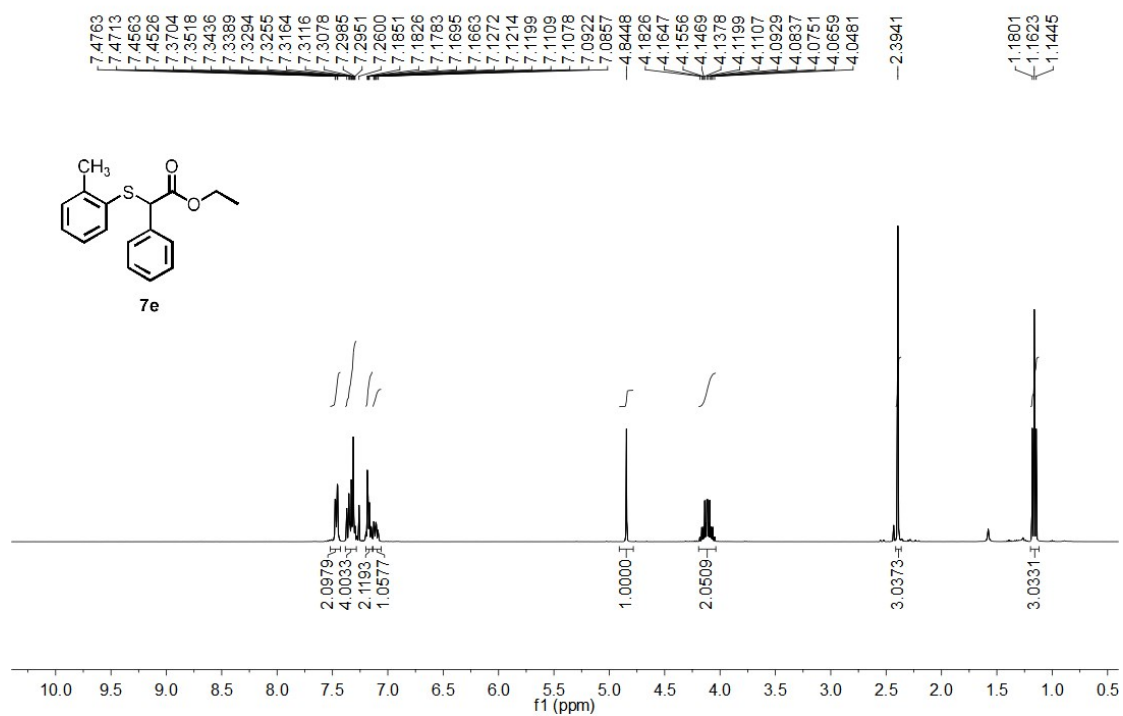
ZZP-545-8



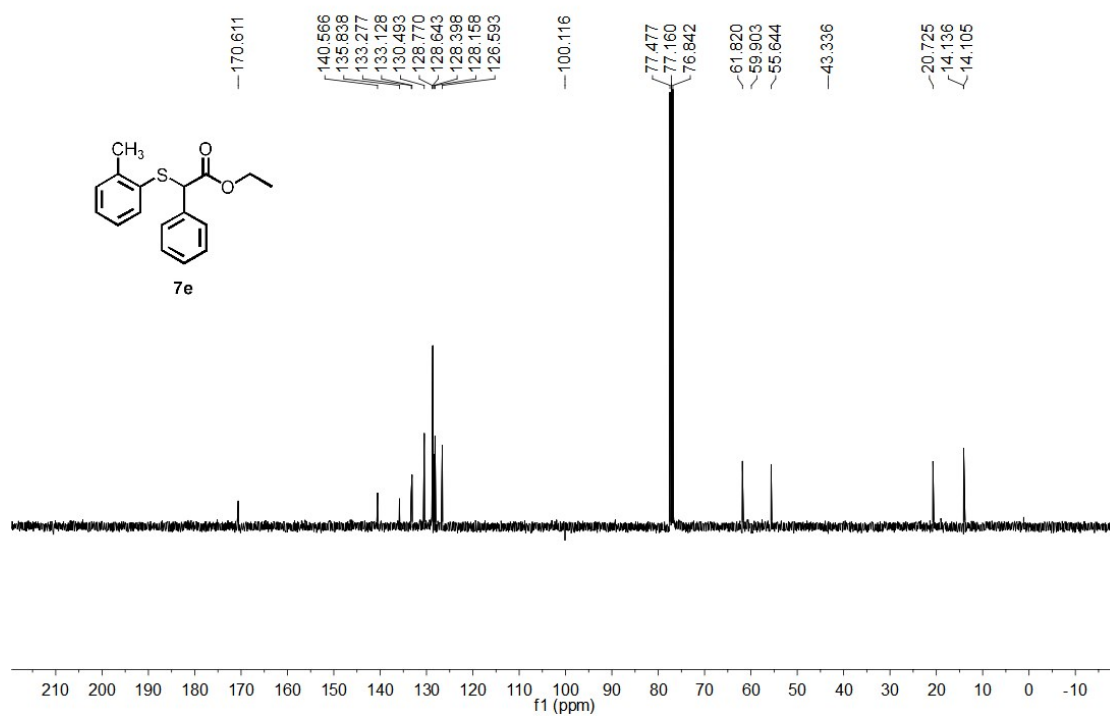
ZZP-545-8



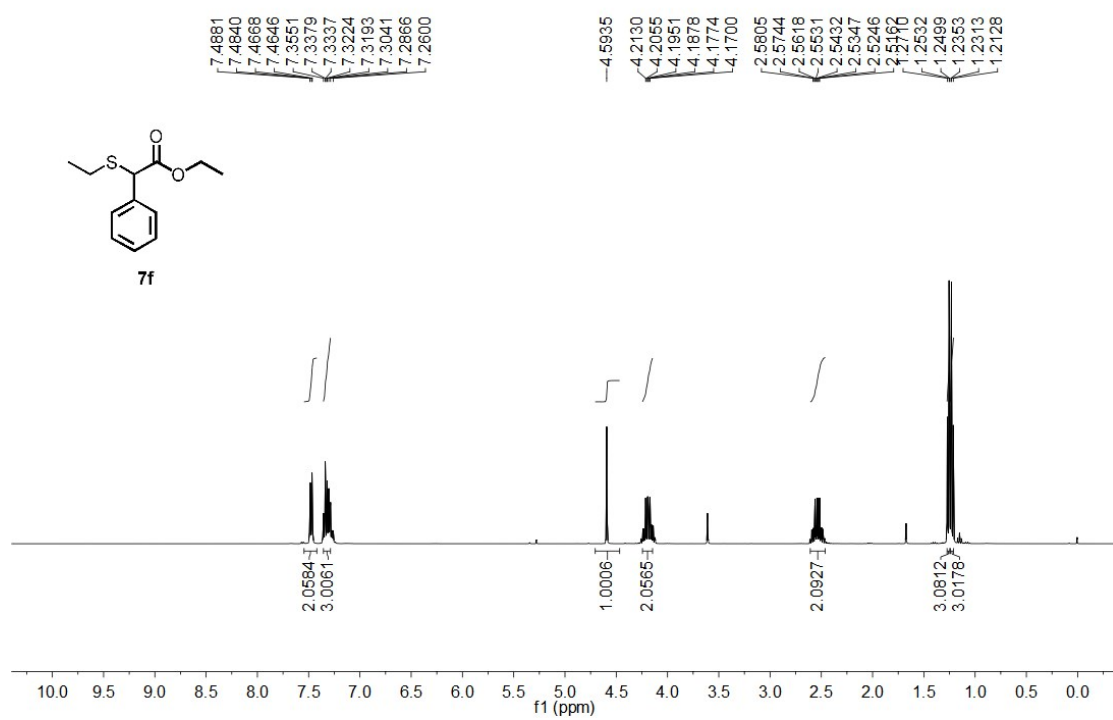
zzp-564-8



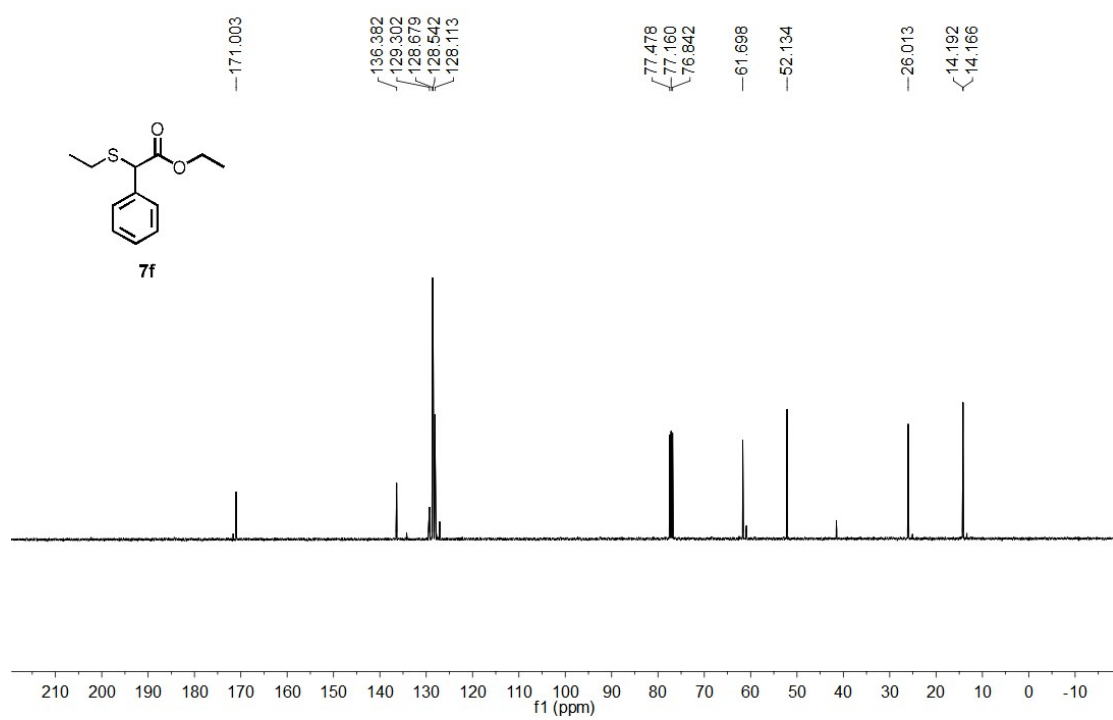
Z-564



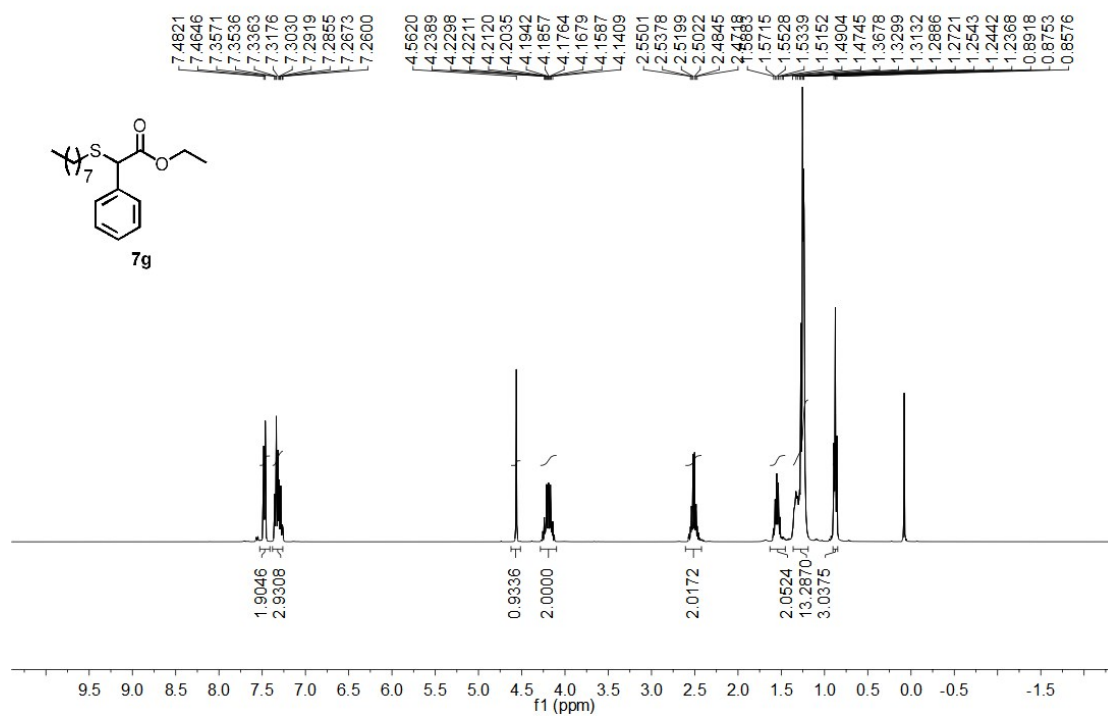
FYF-22



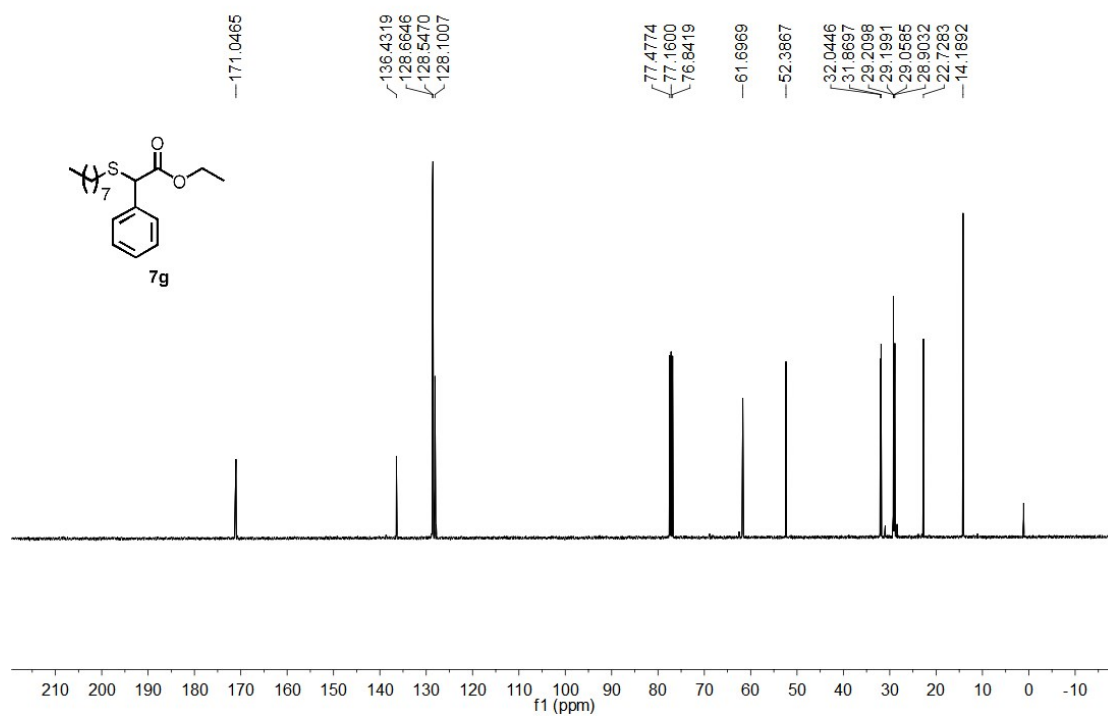
FYF-22



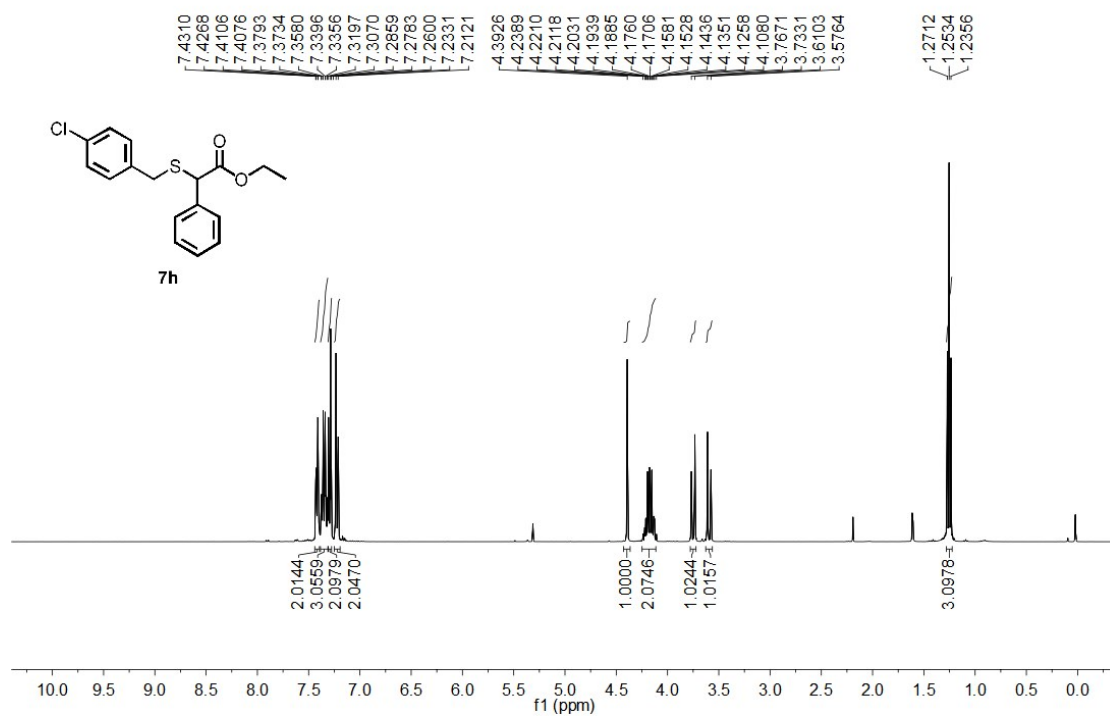
ZZP-506-8



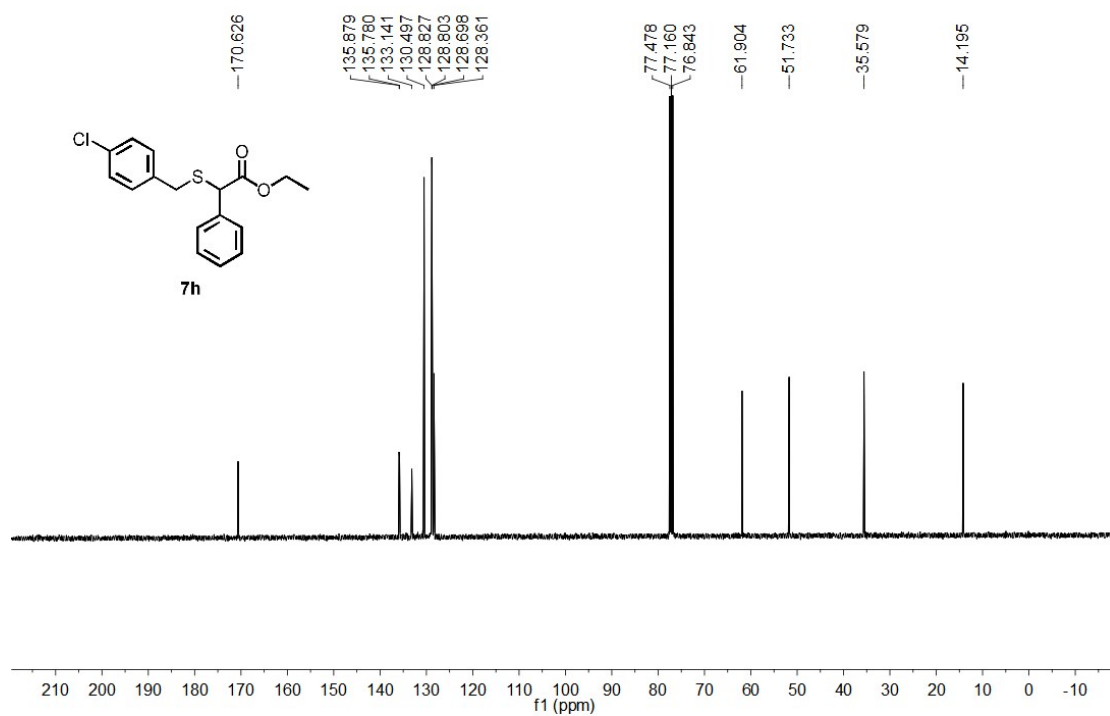
ZZP-506-8



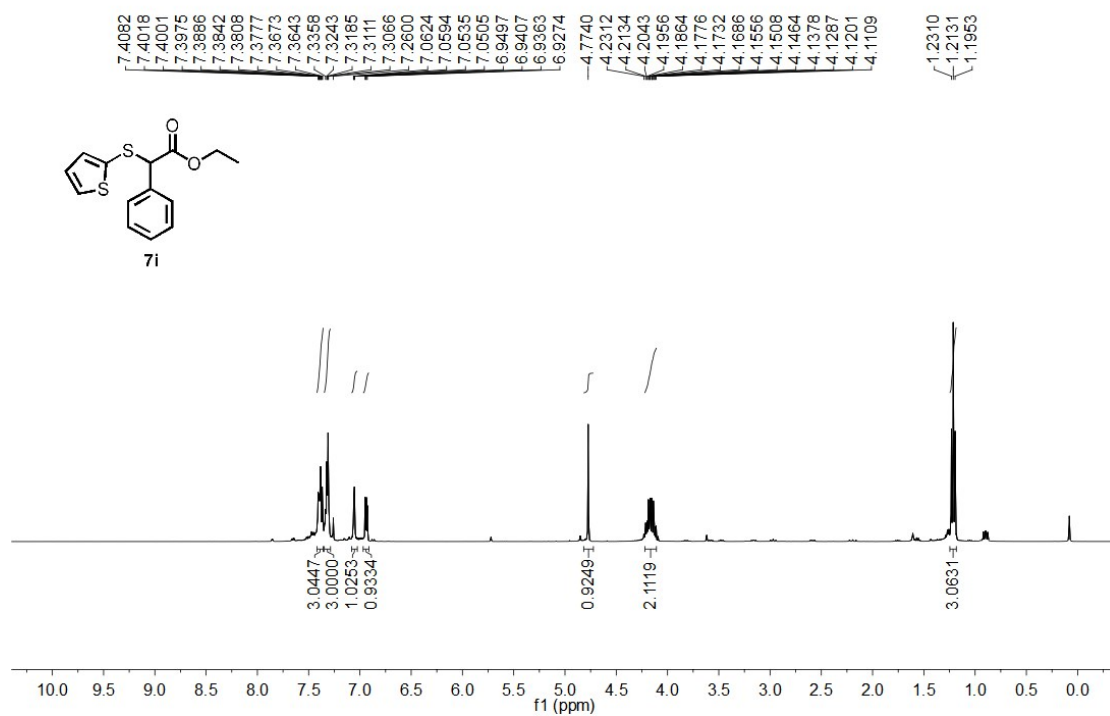
ZZP-119



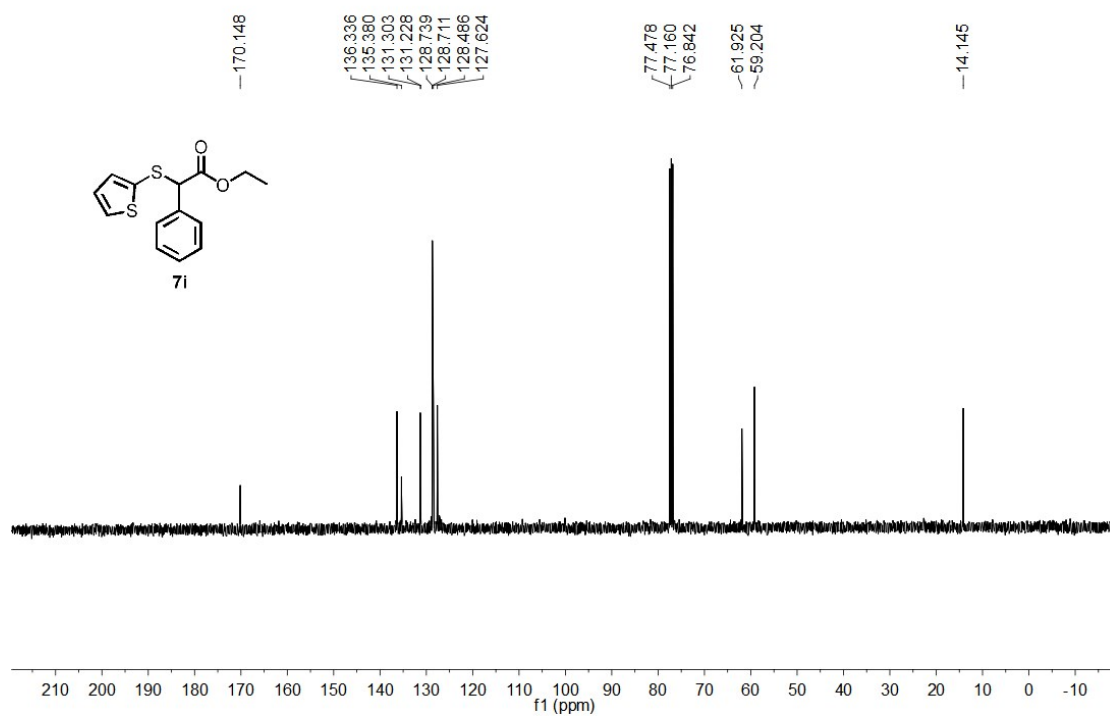
ZZP-119



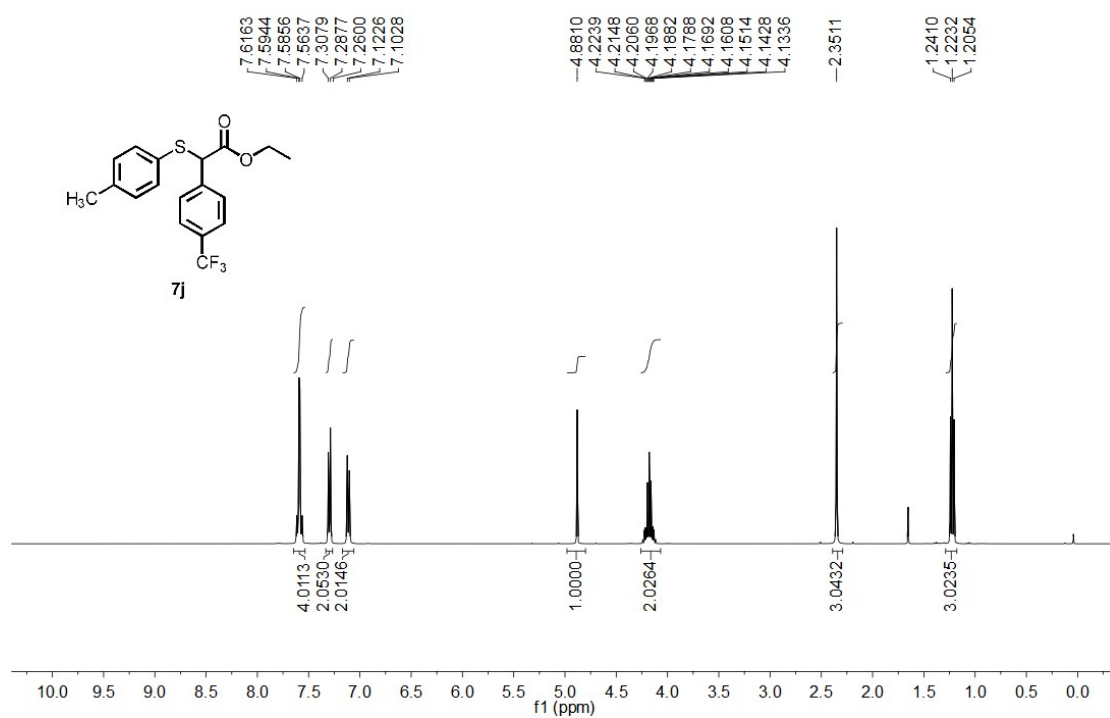
ZZP-505-9
XS-20201218-3



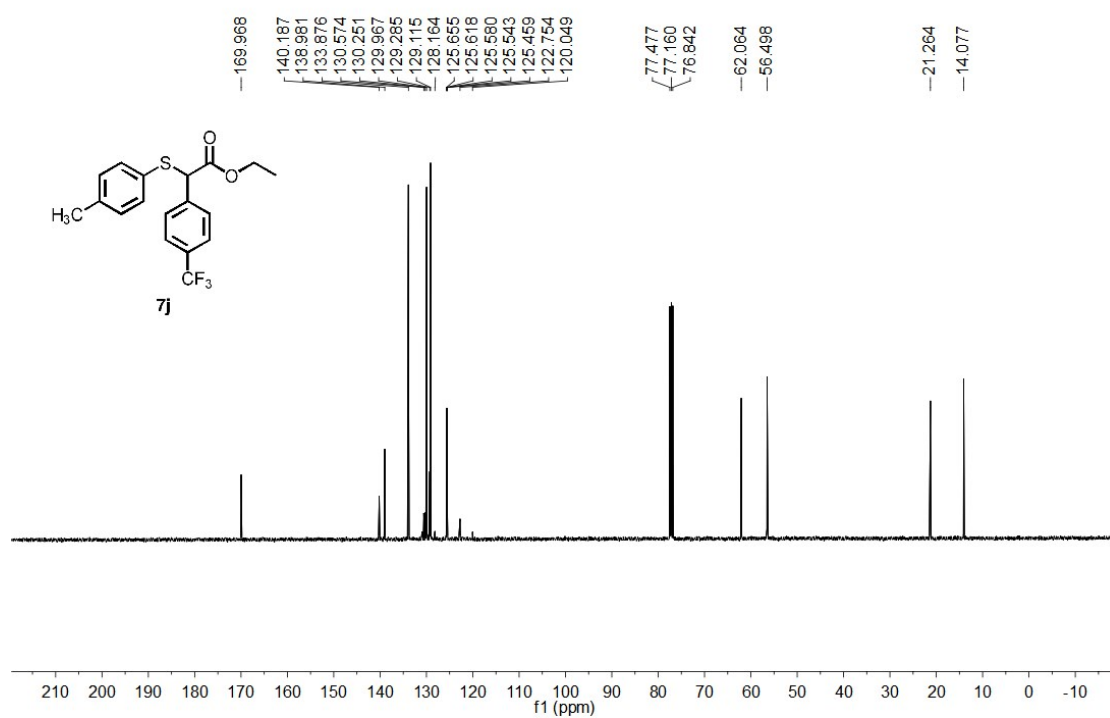
ZZP-505-9
XS-20201218-3



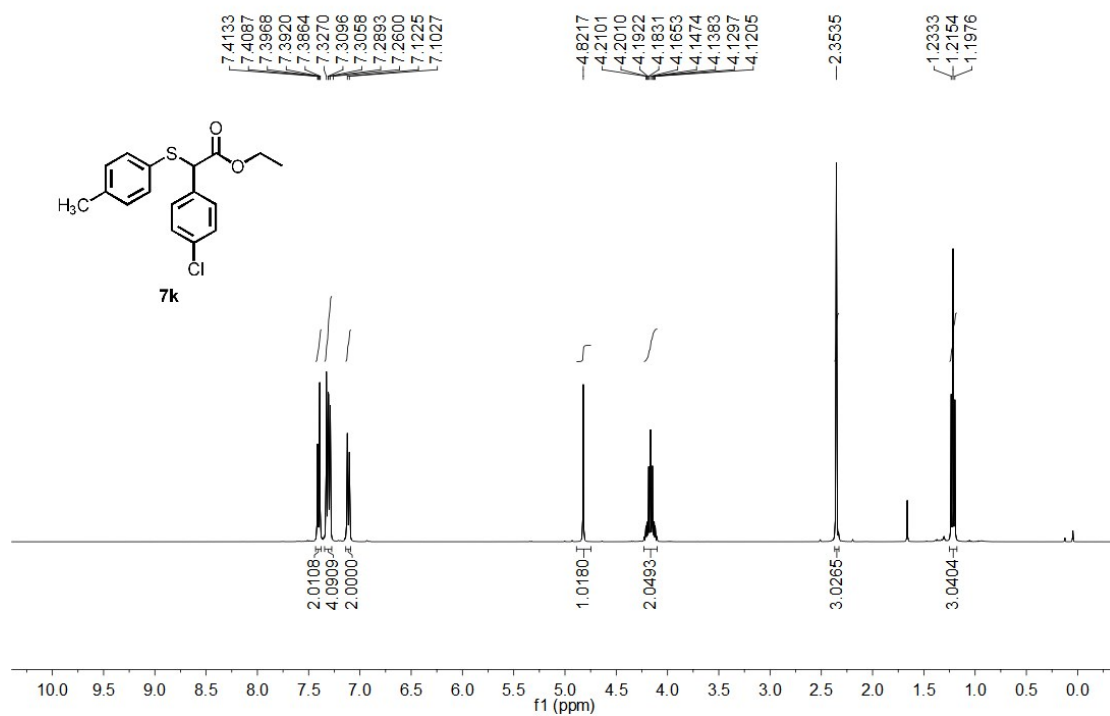
FYF-21



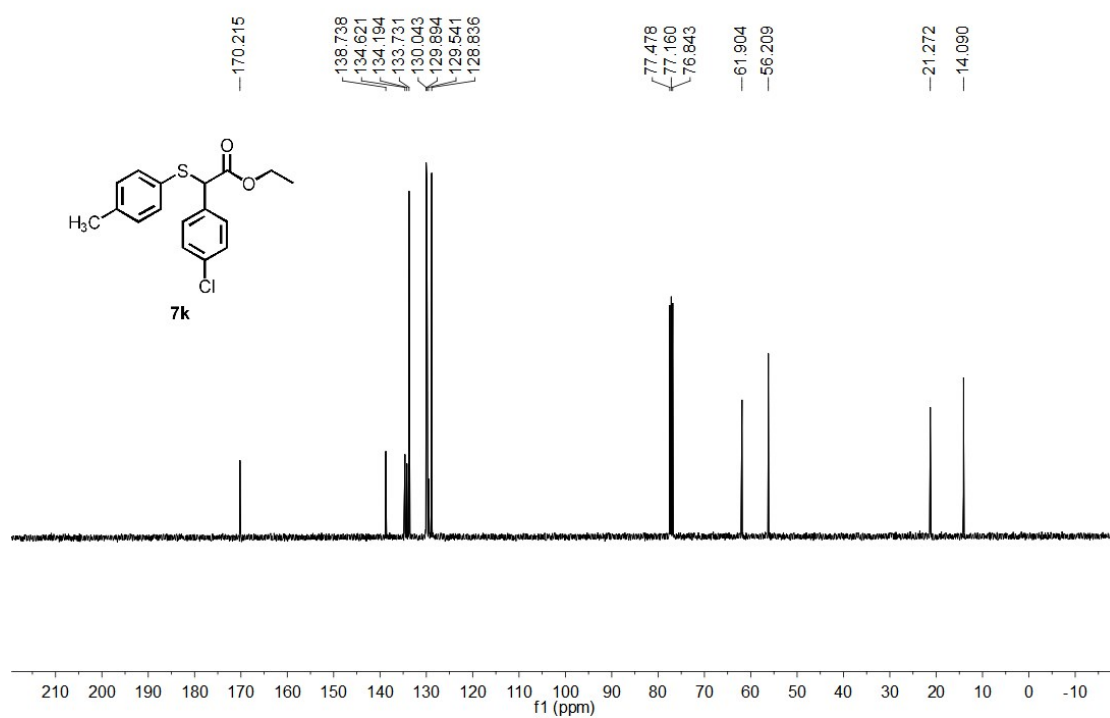
FYF-21



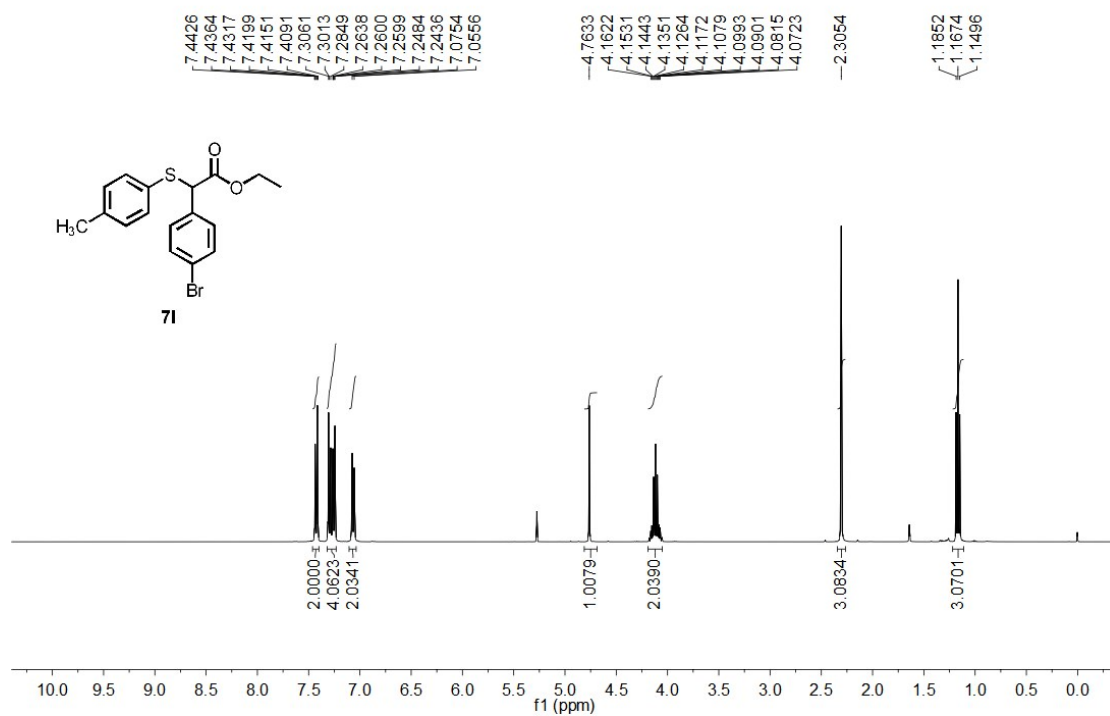
FYF-18



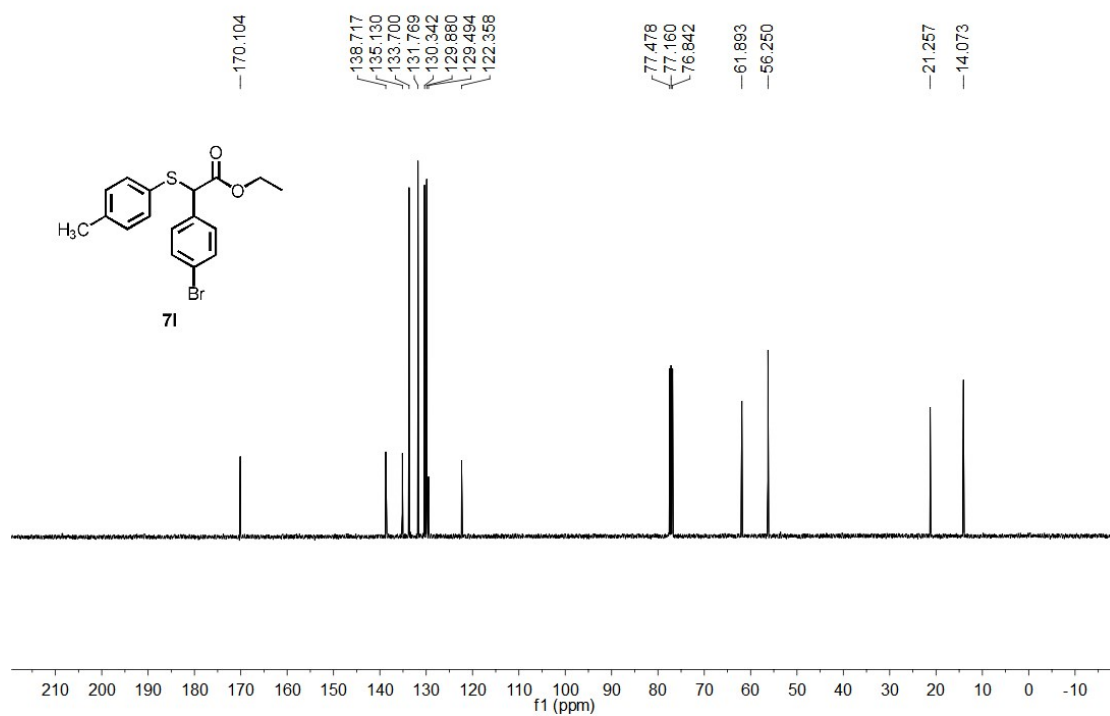
FYF-18



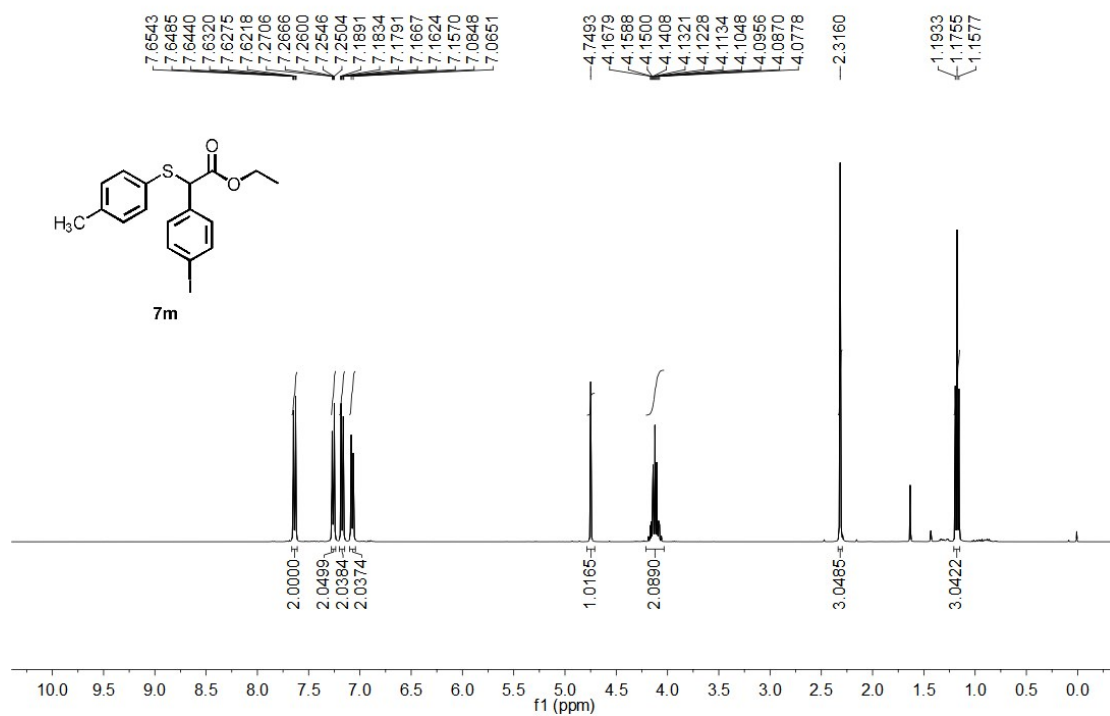
FYF-13



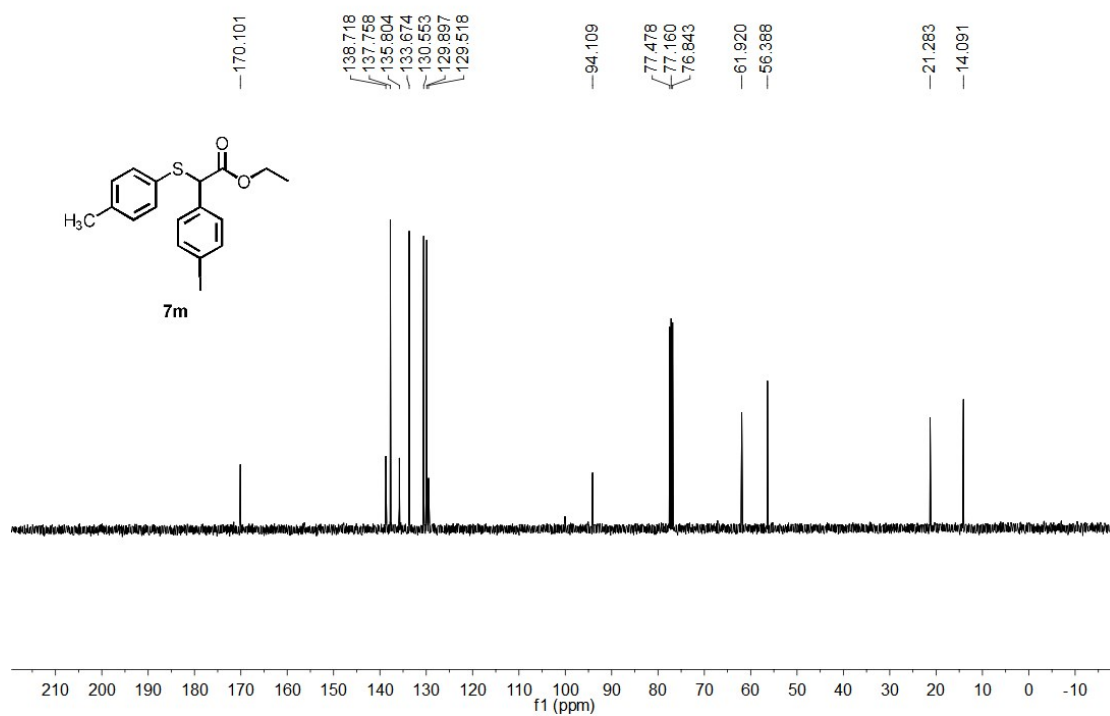
FYF-13



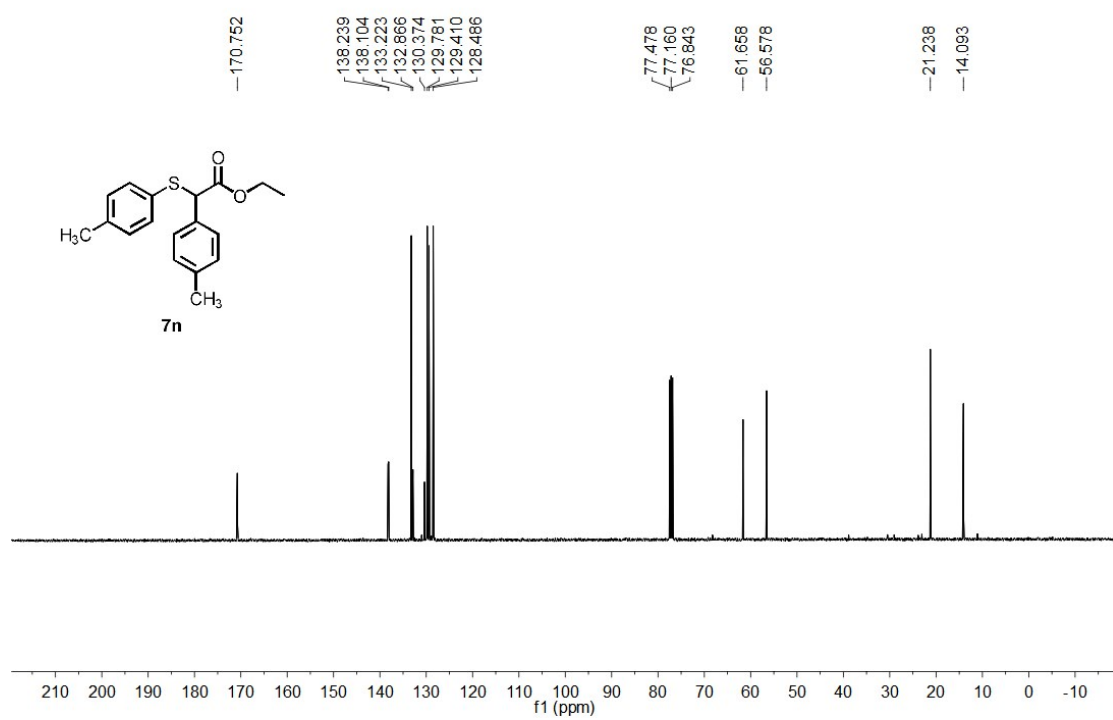
FYF-24



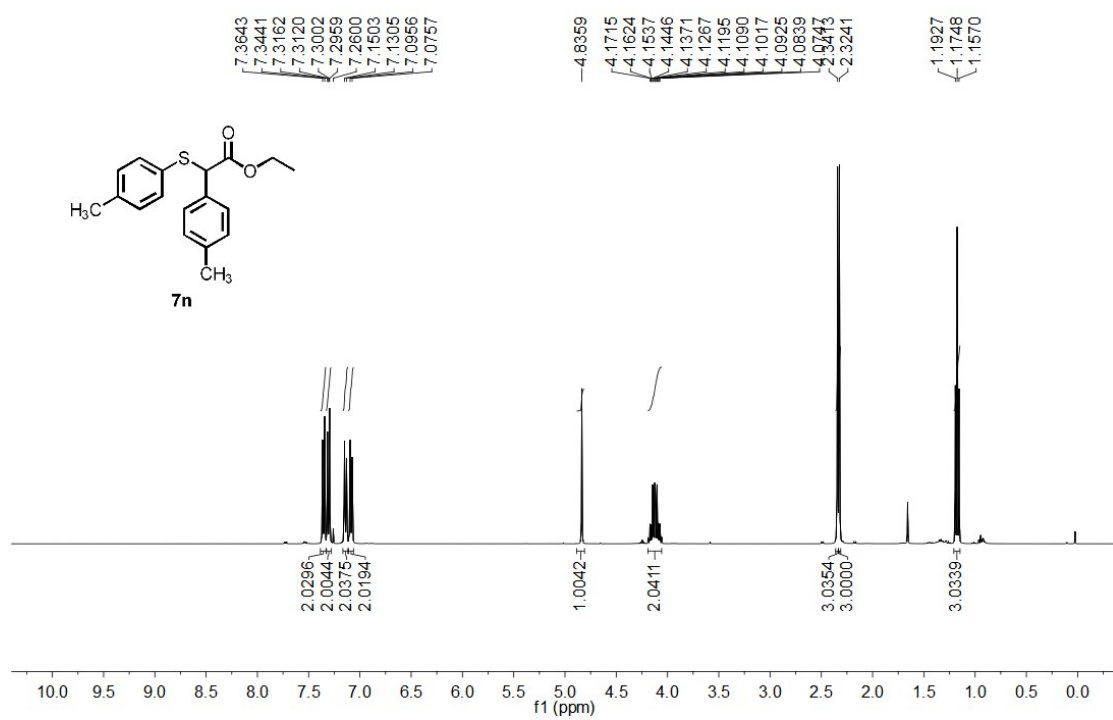
FYF-24



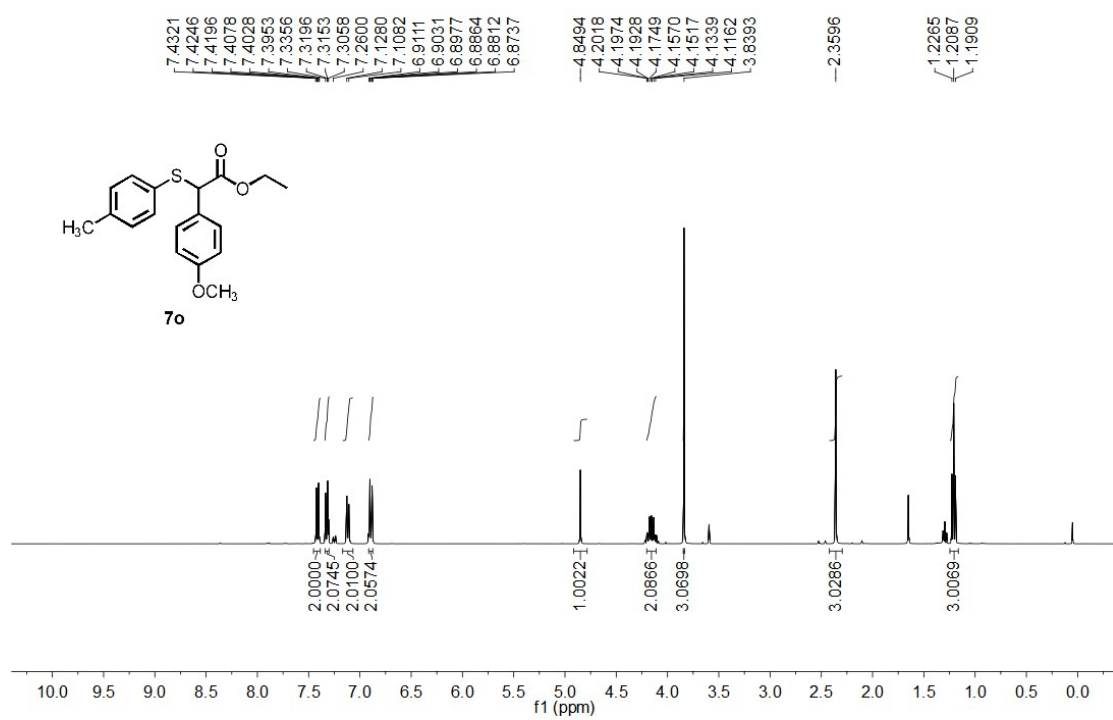
FYF-12



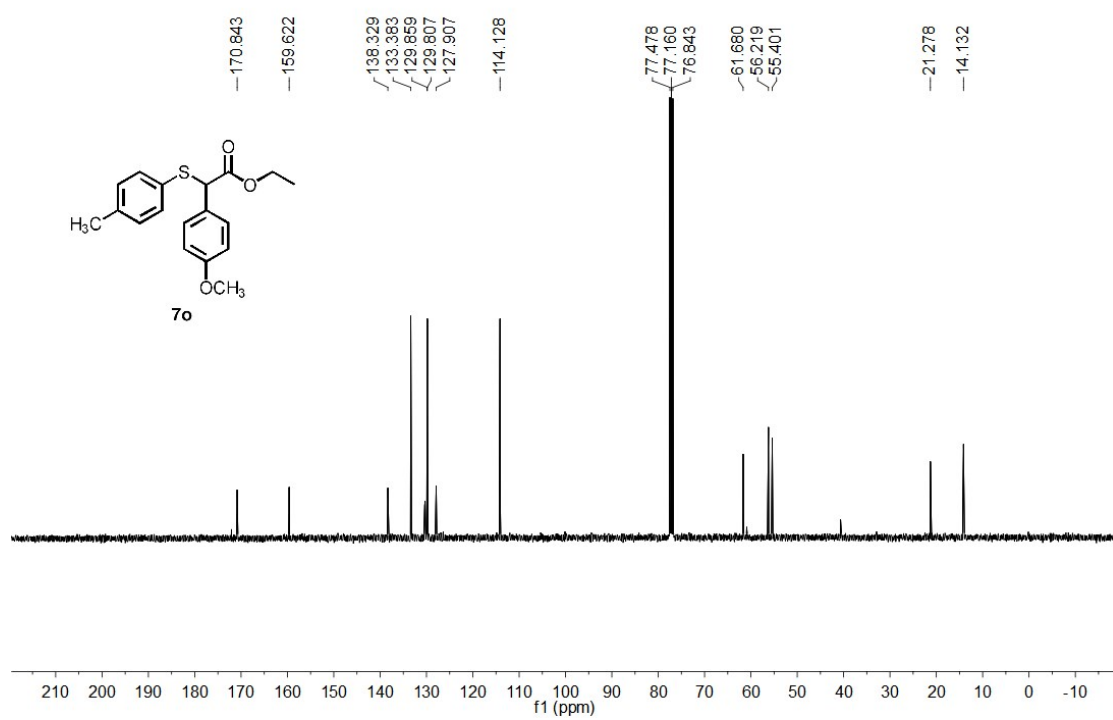
FYF-12



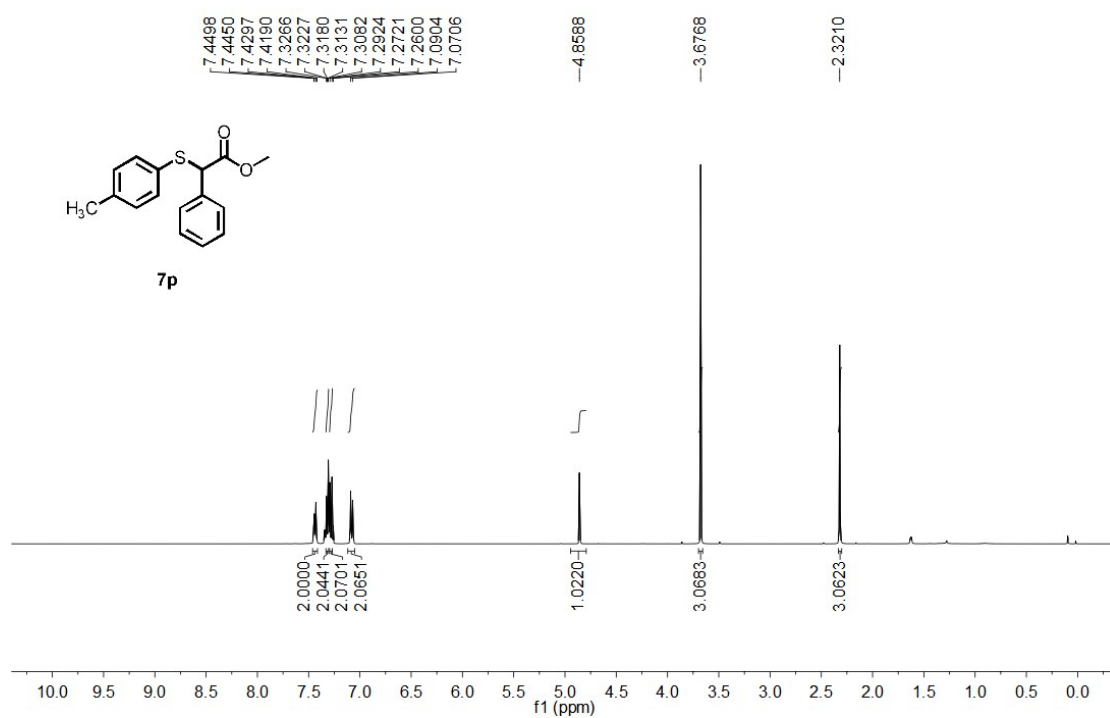
FYF-16



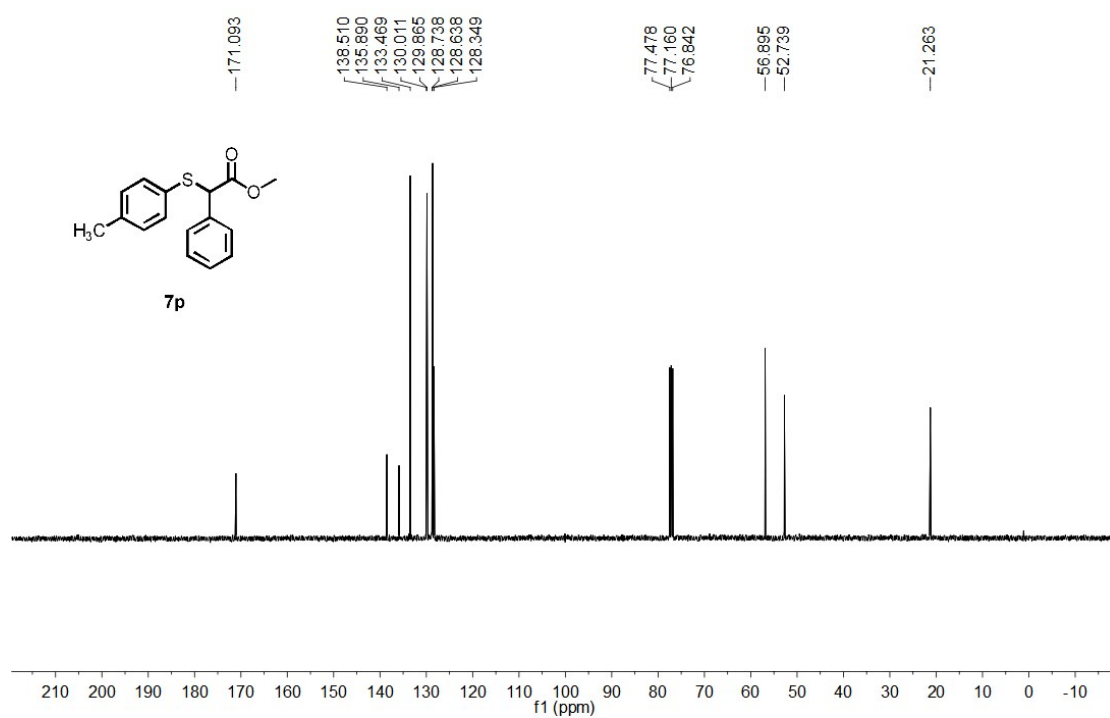
FYF-16



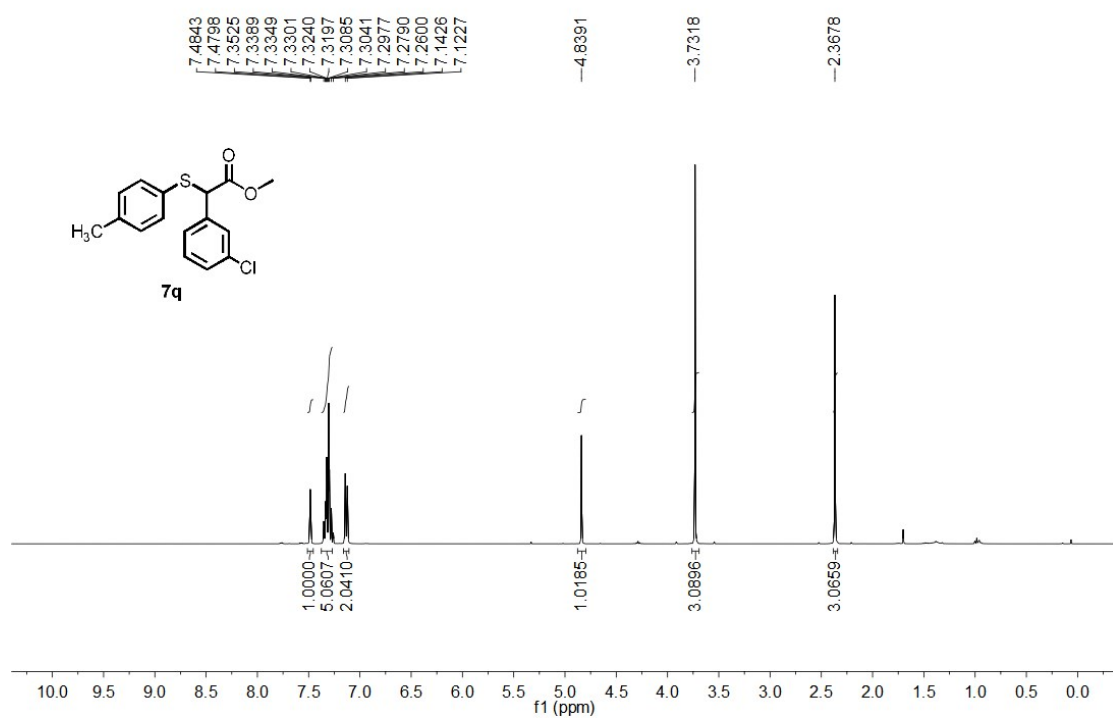
ZZP-206



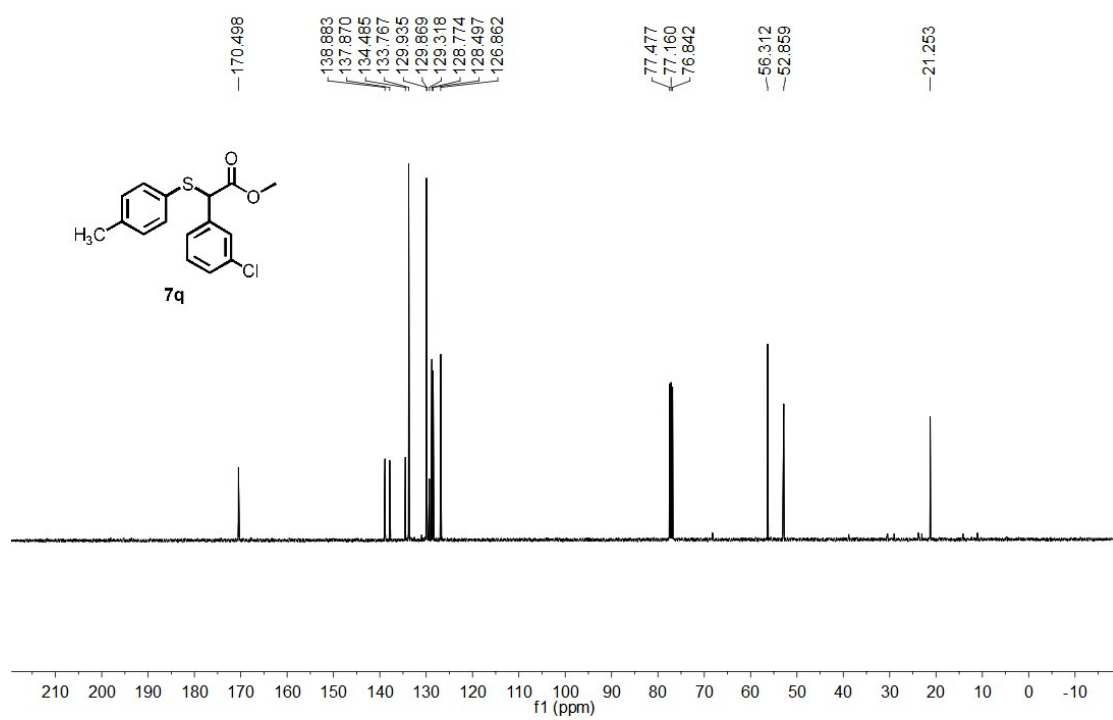
ZZP-206



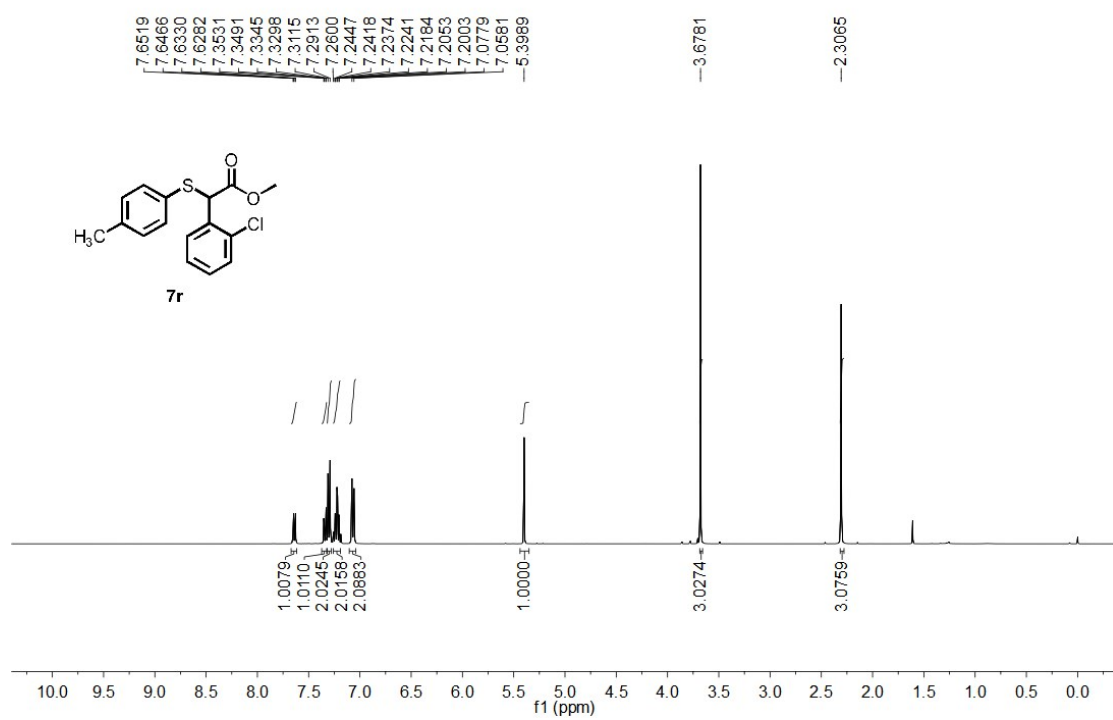
FYF-19



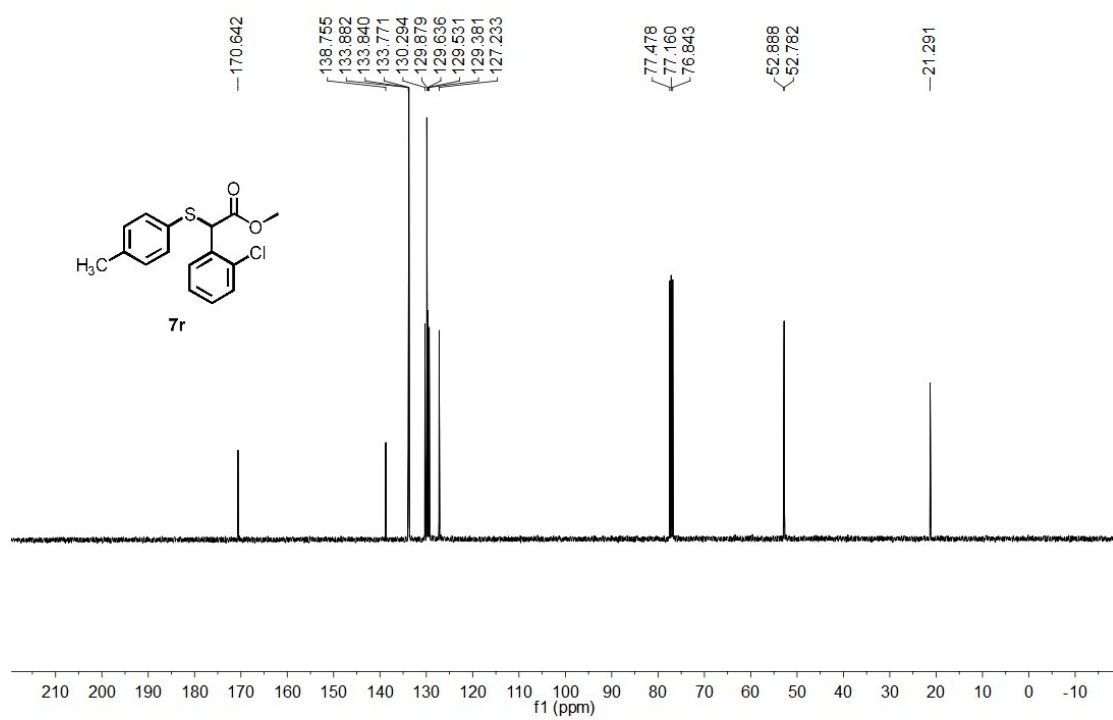
FYF-19



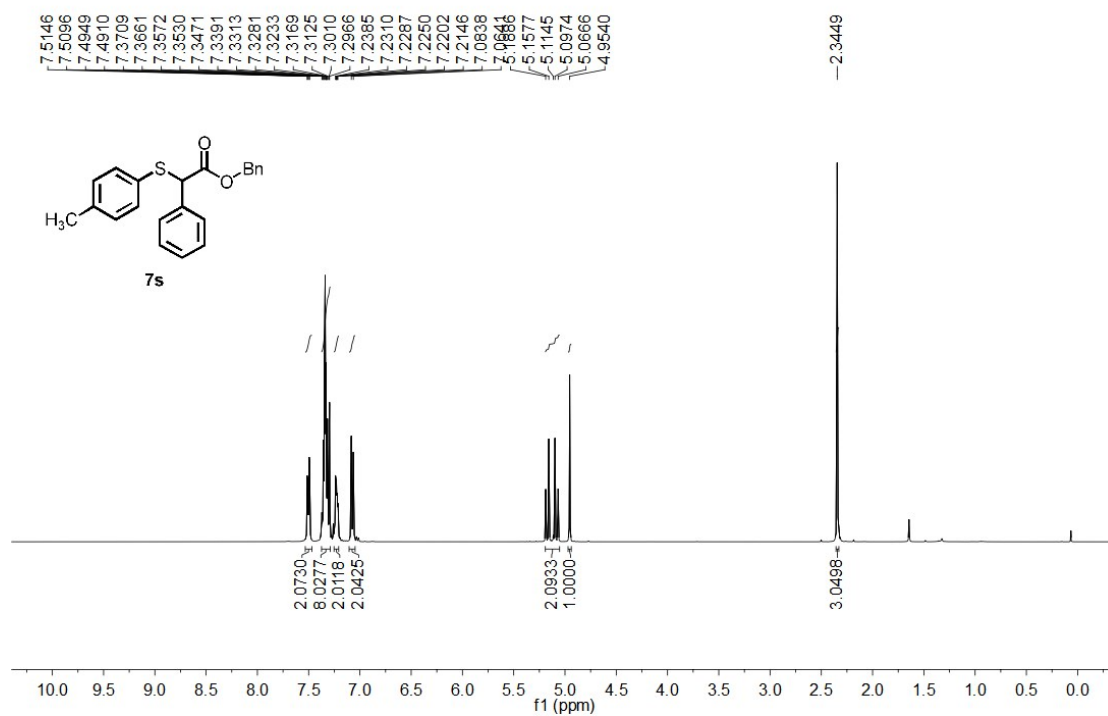
FYF-20



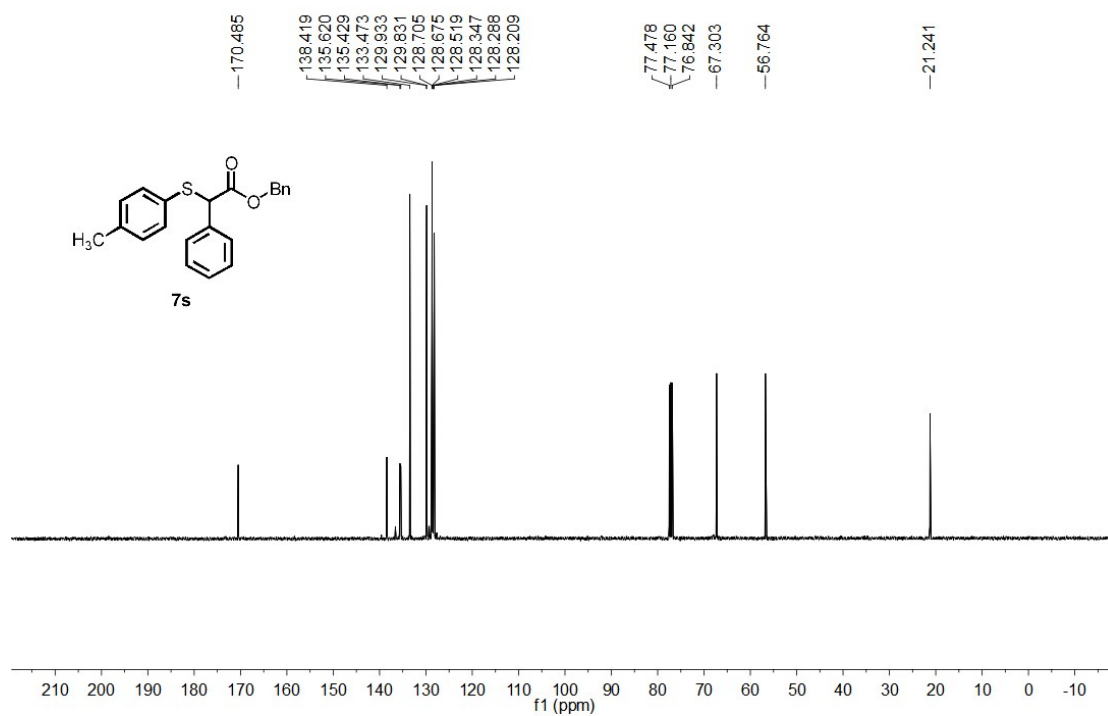
FYF-20



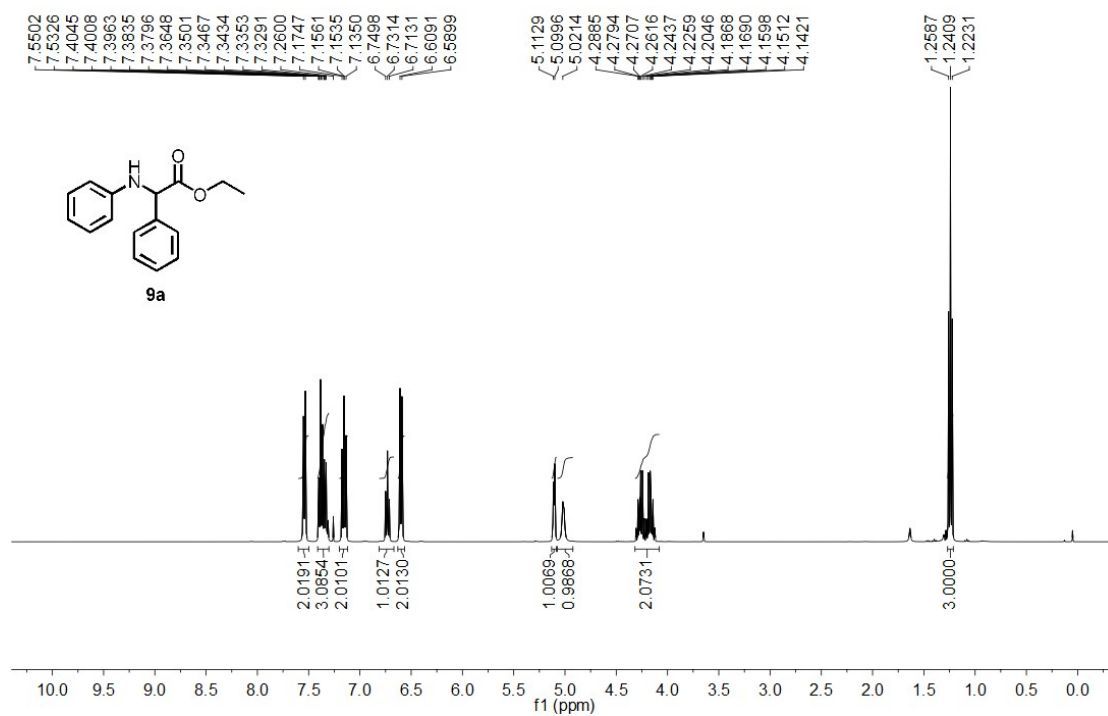
FYF-14



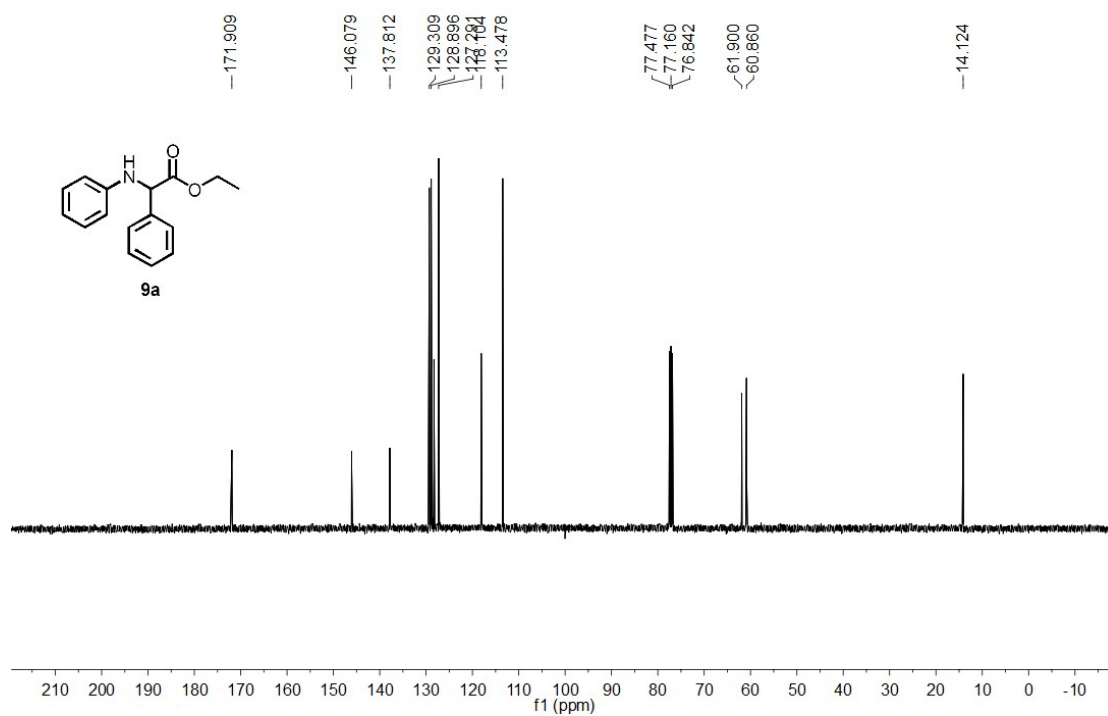
FYF-14



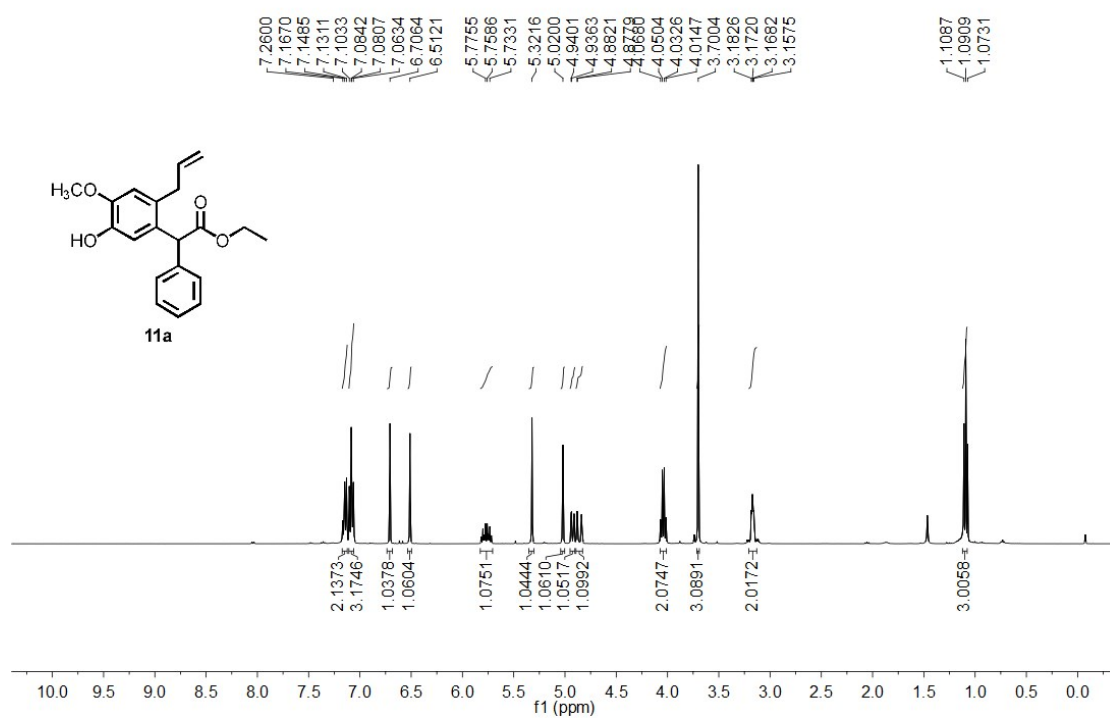
D-435



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ZZP-17-1



ZZP-17-1

