

Supporting Information

Silyl-mediated Photoredox-catalyzed Radical–Radical Cross- Coupling Reaction of Alkyl Bromides and ketoesters

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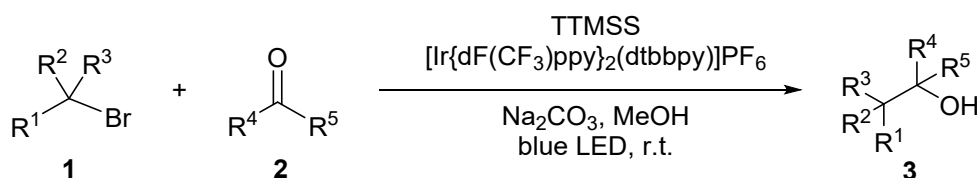
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1. General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. All light-promoted reactions were performed in two-necked schlenk tube made of borosilicate glass. The light source was a 40 W blue LEDs (Kessil, PR160-440nm, placed approximately 5 cm from the reaction tube) without any filters. All air- and moisture-sensitive reactions were performed using oven-dried glassware, including standard Schlenk techniques under an argon atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light, phosphomolybdic acid and vanillic aldehyde as visualizing agents. ^1H NMR spectra, ^{13}C NMR spectra and ^{19}F were respectively recorded on 600 MHz NMR Bruker spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants (J) were reported in Hz. High-resolution mass spectra (HRMS) were obtained by using ESI ionization sources (Varian 7.0 T FTICR-MS) and ESI-TOF.

2. Experimental procedures

2.1 General procedure for photoredox cross-coupling reactions

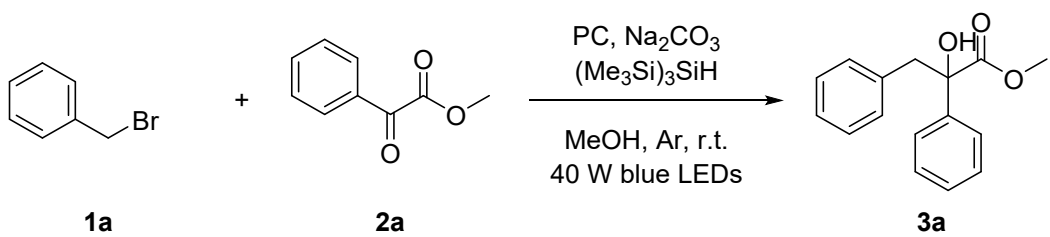


A 10 mL two-necked schlenk tube containing a stirring bar was charged with alkyl bromide **1** (0.3 mmol, 1.5 *equiv.*) (if solid), ketone **2** (0.2 mmol, 1.0 *equiv.*) (if solid), Na₂CO₃ (0.4 mmol, 2 *equiv.*) and [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (0.2 mol%). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon

balloon. Then, alkyl bromide **1** (0.3 mmol, 1.5 *equiv.*) (if liquid), ketone **2** (0.2 mmol, 1.0 *equiv.*) (if liquid), tris(trimethylsilyl)silane (TTMSS) (0.2 mmol, 1.0 *equiv.*) and MeOH (1 mL) were added via syringe. The resulting mixture was first stirred for 5 minutes and then irradiated with 40 W blue LEDs (5 cm away) with continued stirring. The reaction was monitored by TLC. The reaction was quenched by exposure to air and concentrated in vacuo. Product **3** was purified via silica gel chromatography with ethyl acetate and petroleum ether as eluents.

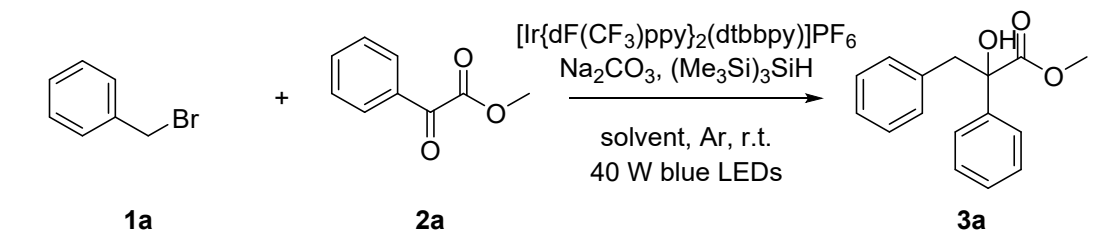
3. Optimization of reaction conditions

Table S1. Photocatalyst screening ^a



Entry	Photocatalyst (PC)	Yield (%) ^b
1	[Ir{dF(CF ₃)ppy} ₂ (dtbbpy)]PF ₆	75
2	Ru(bpy) ₃ Cl ₂ ·6H ₂ O	n.d.
3	Mes-Acr-CIO- 4	n.d.
4	4Cz-IPN	62
5	None	n.d.
6 ^c	[Ir{dF(CF ₃)ppy} ₂ (dtbbpy)]PF ₆	n.d.
6 ^d	[Ir{dF(CF ₃)ppy} ₂ (dtbbpy)]PF ₆	27

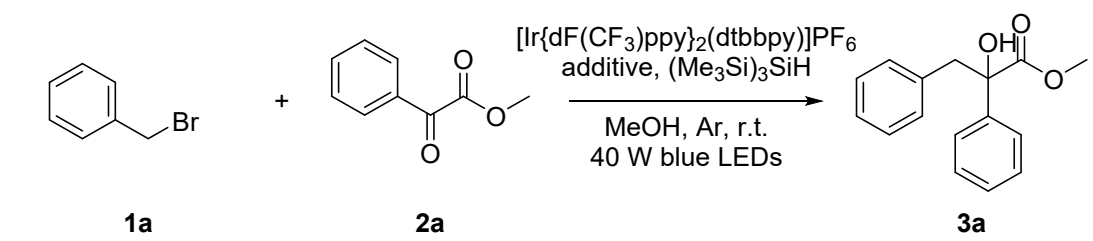
^aReaction conditions: a mixture of **1a** (0.3 mmol, 1.5 *equiv.*), **2a** (0.2 mmol, 1.0 *equiv.*), Na₂CO₃ (0.4 mmol, 2.0 *equiv.*), (Me₃Si)₃SiH (0.2 mmol, 1.0 *equiv.*) and PC (0.002 mol, 0.01 *equiv.*) in MeOH (1 mL) was irradiated with 40 W blue LEDs under Ar atmosphere (Ar balloon) at room temperature for 2 h. ^bYield of the isolated product after chromatography on silica gel. n.d. = not detected. ^cReaction performed without light irradiation. ^dReaction performed under air.

Table S2. Solvent screening ^a

1a + **2a** $\xrightarrow[\text{solvent, Ar, r.t.}]{[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6, \text{Na}_2\text{CO}_3, (\text{Me}_3\text{Si})_3\text{SiH}}$ **3a**
40 W blue LEDs

Entry	Solvent	Yield (%) ^b
1	MeCN	43
2	Acetone	61
3	MeOH	75
4	DMF	44
5	DMSO	35

^aReaction conditions: a mixture of **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), Na_2CO_3 (0.4 mmol, 2.0 equiv.), $(\text{Me}_3\text{Si})_3\text{SiH}$ (0.2 mmol, 1.0 equiv.) and $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6$ (0.002 mol, 0.01 equiv.) in solvent (1 mL) was irradiated with 40 W blue LEDs under Ar atmosphere (Ar balloon) at room temperature for 2 h.

Table S3. Additive screening^a

1a + **2a** $\xrightarrow[\text{MeOH, Ar, r.t.}]{[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6, \text{additive}, (\text{Me}_3\text{Si})_3\text{SiH}}$ **3a**
40 W blue LEDs

Entry	Additive	Yield (%) ^b
1	NaHCO_3	32
2	Na_2CO_3	75
3	$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	55
4	Cs_2CO_3	11
5	LiOH	27
6	CF_3COOH	55

7	none	39
8	Na ₂ CO ₃ +LiBr (1 equiv.)	74

^aReaction conditions: a mixture of **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), additive (0.4 mmol, 2.0 equiv.), (Me₃Si)₃SiH (0.2 mmol, 1.0 equiv.) and [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (0.002 mol, 0.01 equiv.) in MeOH (1 mL) was irradiated with 40 W blue LEDs under Ar atmosphere (Ar balloon) at room temperature for 2 h.

Table S4. Screening of equivalents of benzyl bromide^a

Entry	1a (x mmol)	1a:2a	Yield (%) ^b
1	0.2	1:1	59
2	0.3	1.5:1	75
3	0.4	2:1	74
3	0.6	3:1	76

^aReaction conditions: a mixture of **1a** (x mmol), **2a** (0.2 mmol, 1.0 equiv.), Na₂CO₃ (0.4 mmol, 2.0 equiv.), (Me₃Si)₃SiH (0.2 mmol, 1.0 equiv.) and [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (0.002 mol, 0.01 equiv.) in MeOH (1 mL) was irradiated with 40 W blue LEDs under Ar atmosphere (Ar balloon) at room temperature for 2 h.

Table S5. Screening of equivalents of (Me₃Si)₃SiH ^a

Entry	(Me ₃ Si) ₃ SiH (x equiv.)	Yield (%) ^b
1	0	6

2	0.1	30
3	0.4	53
4	0.7	70
5	1	75

^aReaction conditions: a mixture of **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), Na₂CO₃ (0.4 mmol, 2.0 equiv.), (Me₃Si)₃SiH (x equiv.) and [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (0.002 mol, 0.01 equiv.) in MeOH (1 mL) was irradiated with 40 W blue LEDs under Ar atmosphere (Ar balloon) at room temperature for 2 h.

Table S6. silane screening ^a

$$\text{1a} + \text{2a} \xrightarrow[\text{MeOH, Ar, r.t., 40 W blue LEDs}]{[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6, \text{Na}_2\text{CO}_3, \text{silane}} \text{3a}$$

Entry	Silane	Yield (%) ^b
1	Ph ₃ SiH	28
2	(MeO) ₃ SiH	26
3	(Me₃Si)₃SiH	75%

^aReaction conditions: a mixture of **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), Na₂CO₃ (0.4 mmol, 2.0 equiv.), silane (0.2 mmol, 1.0 equiv.) and [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (0.002 mol, 0.01 equiv.) in MeOH (1 mL) was irradiated with 40 W blue LEDs under Ar atmosphere (Ar balloon) at room temperature for 2 h.

4. Mechanistic investigation

4.1 Stern-Volmer luminescence quenching experiments

The measurements were performed using a 0.05 mM solution of

$[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6$ in acetone with varying concentration of a quencher. The samples were excited at 380 nm and emission intensity was recorded at 480 nm.

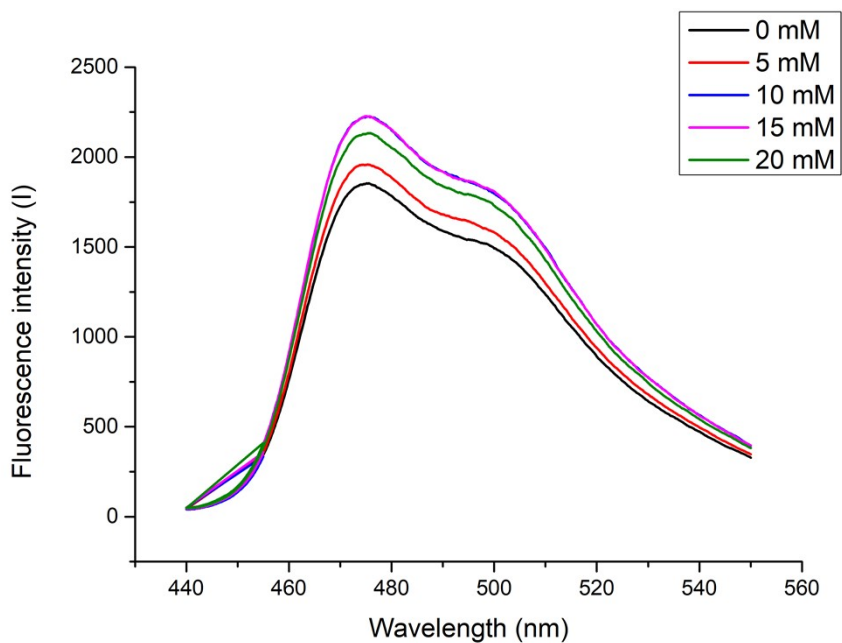


Figure S1. Fluorescence quenching of 0.05 mM $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6$ (in acetone) by increasing concentration of benzyl bromide (**1a**).

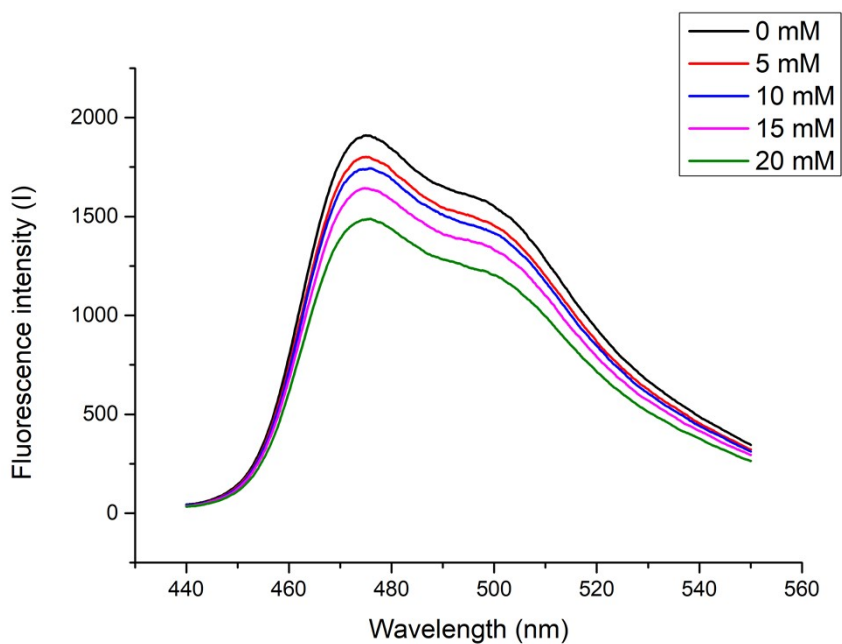


Figure S2. Fluorescence quenching of 0.05 mM $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6$ (in acetone)

by increasing concentration of methyl benzoylformate (**2a**).

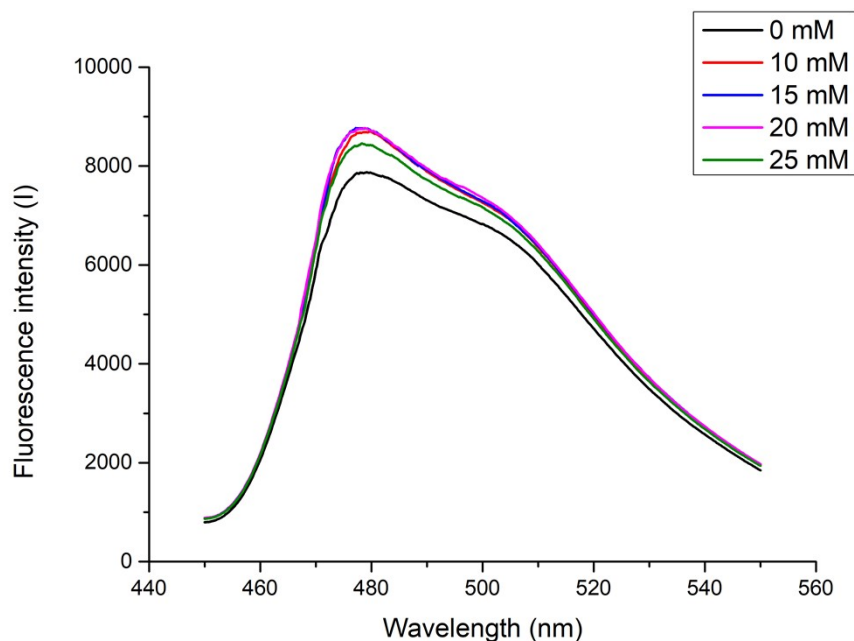


Figure S3. Fluorescence quenching of 0.05 mM $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6$ (in acetone) by increasing concentration of tris(trimethylsilyl)silane (TTMSS).

4.2 Cyclic voltammetry measurements

The cyclic voltammetry experiments were performed, and the redox potentials of **2a** were determined. The data indicated that **2a** ($E_{\text{red},1/2} = -1.26$ V vs SCE in MeCN) (**Figure S4**) can be reduced by $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6^-$ ($E_{\text{red},1/2} [\text{Ir}^{\text{III}}/\text{Ir}^{\text{II}}] = -1.37$ V vs SCE in MeCN).^[1] The literature reports, tris(trimethylsilyl)silane ($E_{\text{ox},1/2} (\text{TTMSS}/\text{TTMSS}^+) = +0.73$ V vs SCE)^[2] has low oxidation potential, it can be oxidized by excited $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6^*$ ($E_{\text{ox},1/2} = +1.21$ V vs SCE). Cyclic voltammetry was performed in a three-electrode cell (volume 10 mL, acetonitrile as solvent, tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) 0.1 M as the supporting electrolyte, 2 mM LiBr and 2 mM **2a** respectively as the tested compounds) with glassy carbon (diameter 3 mm) as the working electrode, Pt wire as the auxiliary electrode, and SCE (saturated calomel

electrode) as the reference electrode. The scan speed was $100 \text{ mV}\cdot\text{s}^{-1}$.

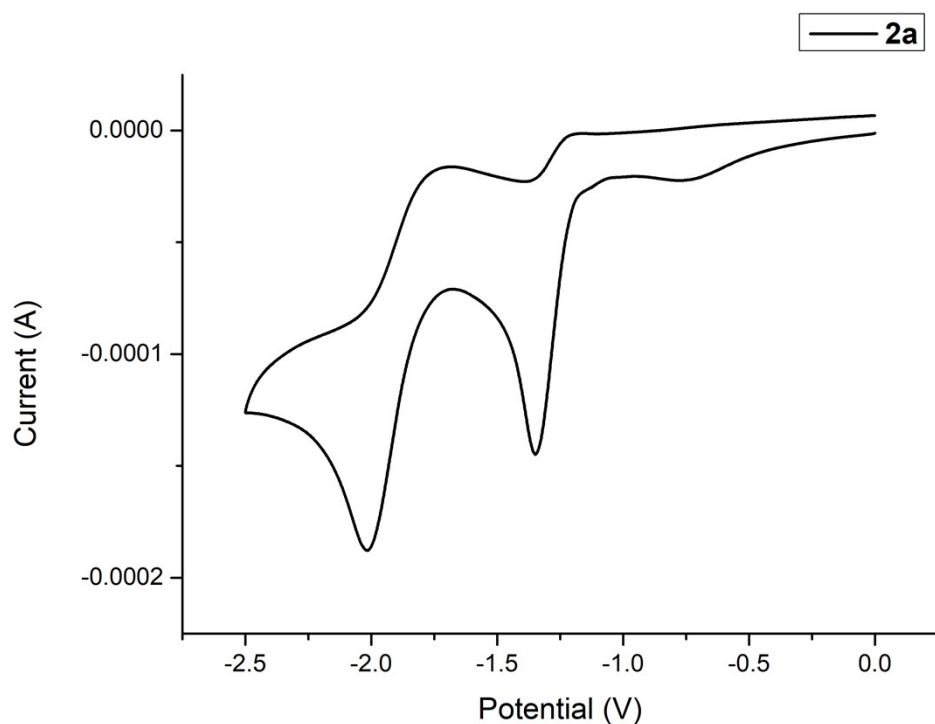


Figure S4. Cyclic voltammetry (CV) of **2a**. **2a** ($E_{\text{red},1/2} = -1.26 \text{ V}$ vs SCE in MeCN).

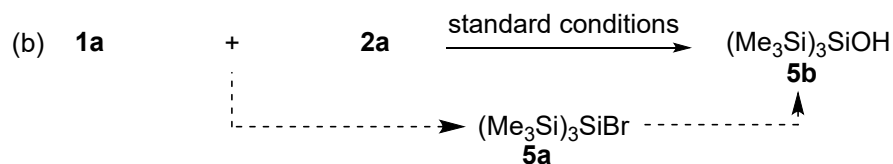
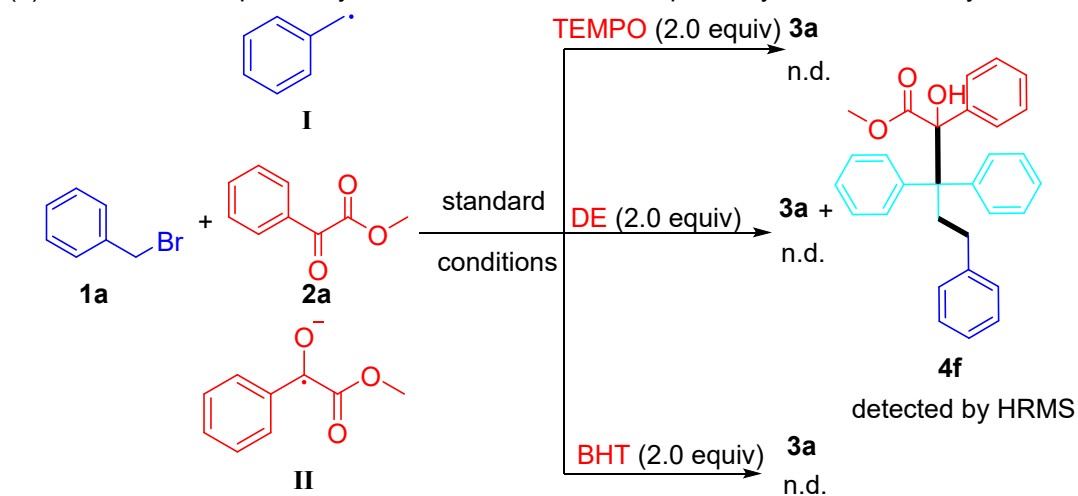
4.3 Radical trapping experiments and control experiments

In order to confirm if the reaction undergoes a radical mechanism, common radical scavengers, 2,2,6,6-tetramethylpiperidinoxy (TEMPO), 1,1-diphenylethylene (DE) and 2,6-di-tert-butyl-4-methylphenol (BHT) were employed for the radical trapping and inhibition experiments. When TEMPO (2.0 equivalents to **2a**), (DE) (2.0 equivalents to **2a**) and BHT (2.0 equivalents to **2a**) were added separately into the model reaction system at the beginning of the reaction under the standard conditions (**Table S1**, entry 1), no product **3a** was detected after 2 h, suggesting that the reaction might go through a radical pathway (**Table S7**, a). The addition products of radical intermediates **I** or **II** to the three radical scavengers, respectively, were detected by high-resolution mass spectrometry (HRMS) (**Table S8**). In addition, the diradical addition product **4f** of **1**, **2** and DE was also detected by HRMS (**Table S8**). In conclusion, benzyl radicals and ketyl radicals may be generated during the reaction. Under

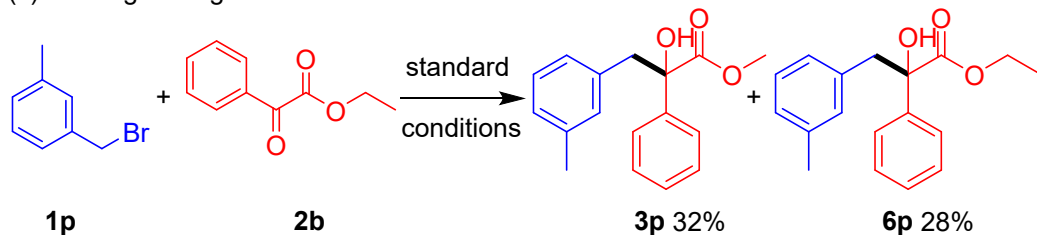
standard reaction conditions, the silanol **5b** was isolated indicating that silicon bromide **5a** is formed during the reaction (**Table S7**, b). Since when the substrates were ketoesters, the final products obtained were all methyl esters. We conducted a control experiment, in order to explore whether the substrate and methanol undergo transesterification first, or whether the coupling product is transesterified (**Table S7**, c and d). When the light source and stirring were turned on at the same time, **3p** and **6p** were obtained, and the amount of **6p** did not decrease when the reaction time was prolonged. However, after stirring for 5 minutes, and then turning on the light source, only **3p** was generated. These results indicated that the transesterification occurred first, and then the photoreaction occurred.

Table S7. Radical trapping and control experiments

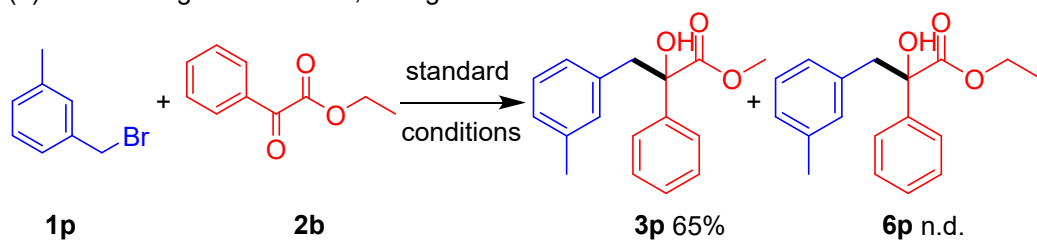
(a) **I** and **II** were captured by TEMPO, DE and BHT, respectively, and detected by HRMS.



(c) Stirring and light source were turned on at the same time

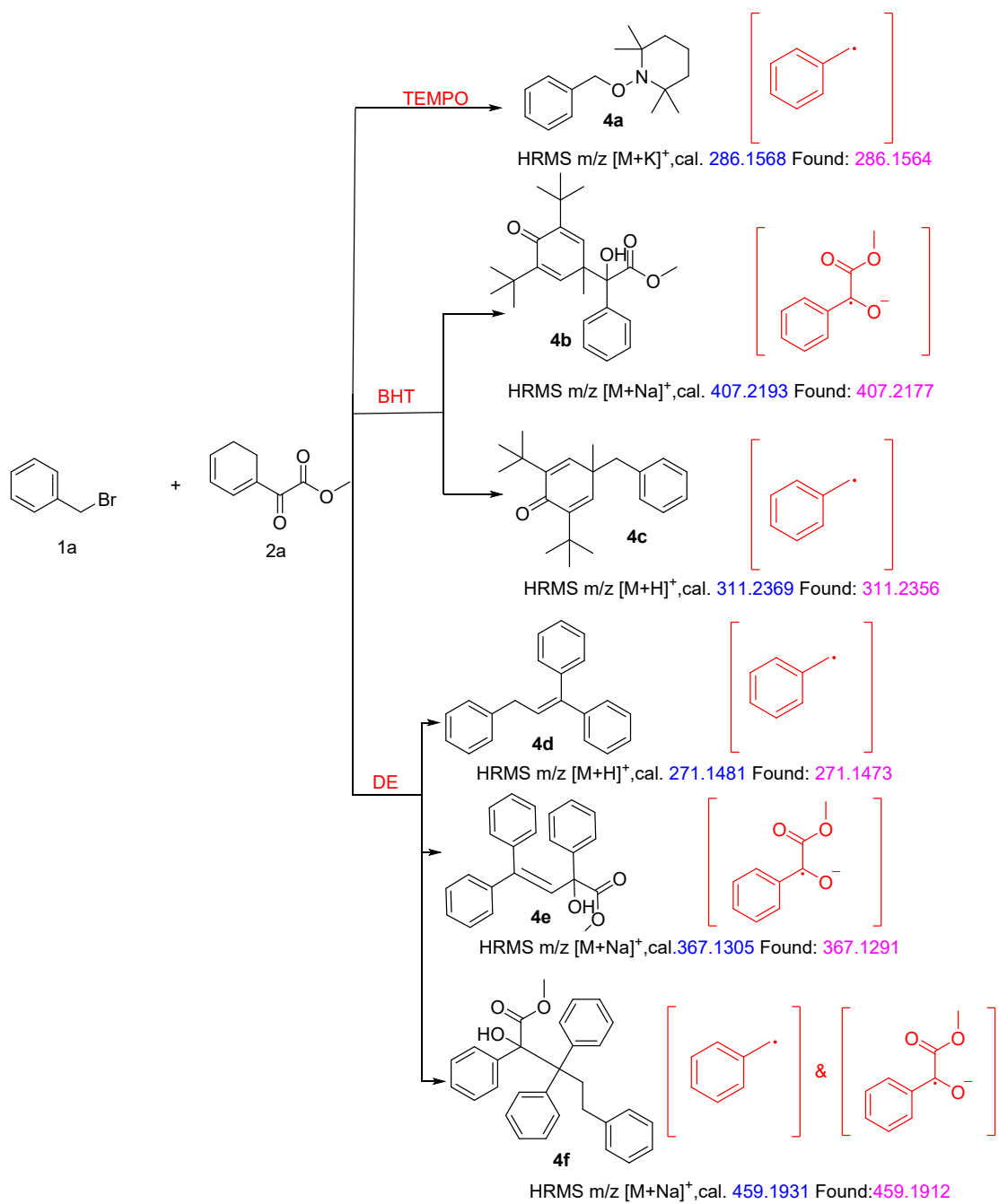


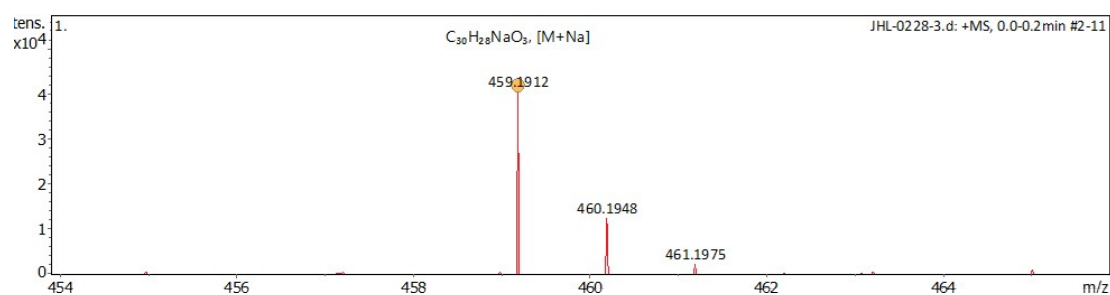
(d) After stirring for 5 minutes, the light source was turned on



Reaction conditions: a mixture of **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), Na₂CO₃ (0.4 mmol, 2.0 equiv.), (Me₃Si)₃SiH (0.2 mmol, 1.0 equiv.) and PC (0.002 mol, 0.01 equiv.) in MeOH (1 mL) was irradiated with 40 W blue LEDs under Ar atmosphere (Ar balloon) at room temperature for 2 h. ^bYield of the isolated product after chromatography on silica gel. n.d. = not detected.

Table S8. Radical addition products detected by HRMS



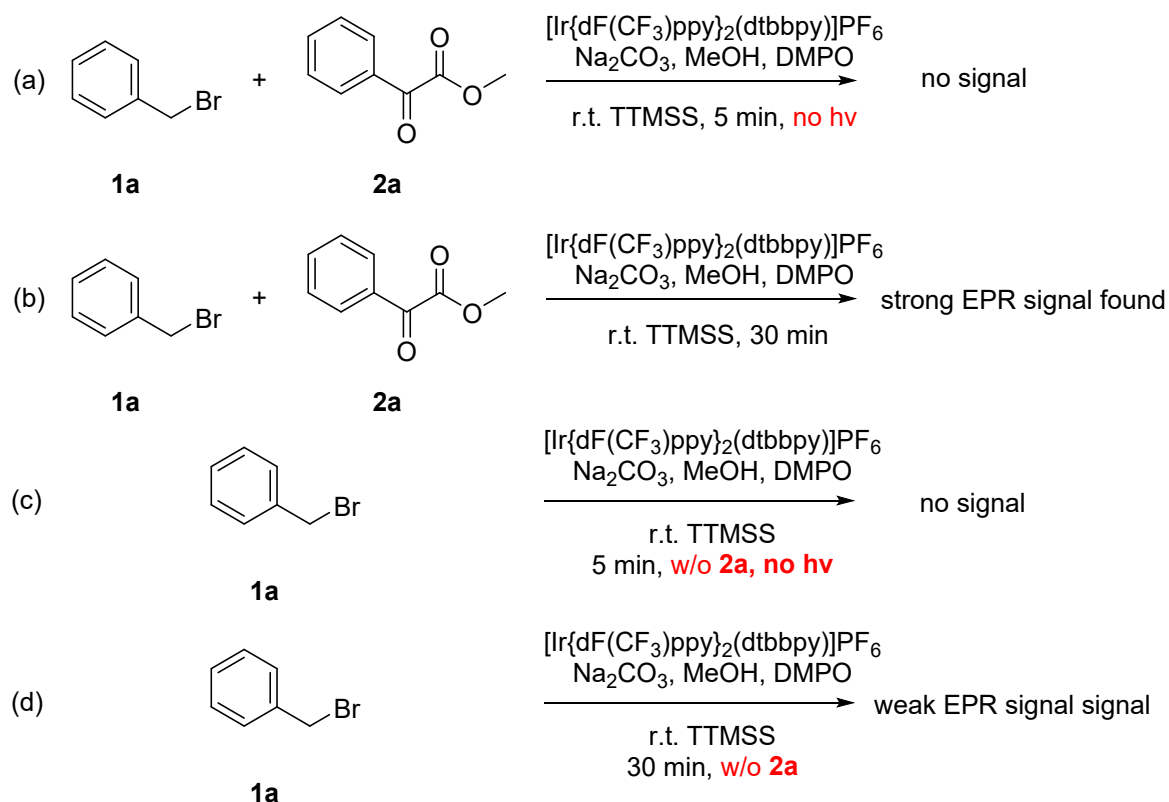


Meas. m/z	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
459.1912	C ₃₀ H ₂₈ NaO ₃	459.1931	4.0	11.1	1	100.00	17.0	even	ok

Figure S5. HRMS (ESI-TOF) m/z of **4f**

4.4 EPR experiments

To get a deeper insight into the mechanism, electron paramagnetic resonance (EPR) experiments were performed (**Table S9**). When the control experiments were performed according to a, b, c and d, significant free radical signal could only be detected in experiment b. That means that irradiation is a necessary condition for free radical generation. Furthermore, the free radical signal was detected only when **1a** and **2a** were present at the same time, suggesting that **2a** is a necessary condition for generating free radicals in this system. The observed g-factors (**Figure S6**) for the spin adducts were very close to 2.0023 for free electrons, which provided more conclusive evidence for the existence of radicals^[3].

Table S9. EPR control experiments

Unless otherwise specified, experiments were performed as follows. A 10 mL two-necked schlenk tube containing a stirring bar was charged with Na_2CO_3 (0.4 mmol, 2 *equiv.*) and $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6$ (0.002 mol, 0.01 *equiv.*). Then, **1a** (0.3 mmol, 1.5 *equiv.*), **2a** (0.2 mmol, 1.0 *equiv.*) (If **2a** is added.), TTMS (0.2 mmol, 1.0 *equiv.*), DMPO (0.2 mmol, 1.0 *equiv.*) and MeOH (1 mL) were added via syringe. The mixture was first stirred for 5 minutes in the absence of light. The 0.1 mL of the reaction solution was directly used for EPR testing without any purification. Then, the resulting mixture was stirred under irradiation of 40 W blue LEDs for thirty minutes. The 0.1 mL of the reaction solution was directly used for EPR testing without any purification. EPR spectra was recorded at room temperature on an EPR spectrometer operated at 9.828268 GHz. Typical spectrometer parameters were shown as follows, sweep width: 150.0 G; center field set: 3511.15 G; time constant: 81.92 ms; sweep time: 100.02 s; modulation amplitude: 1.000 G; modulation frequency: 100.00 kHz; power: 6.325 mW.

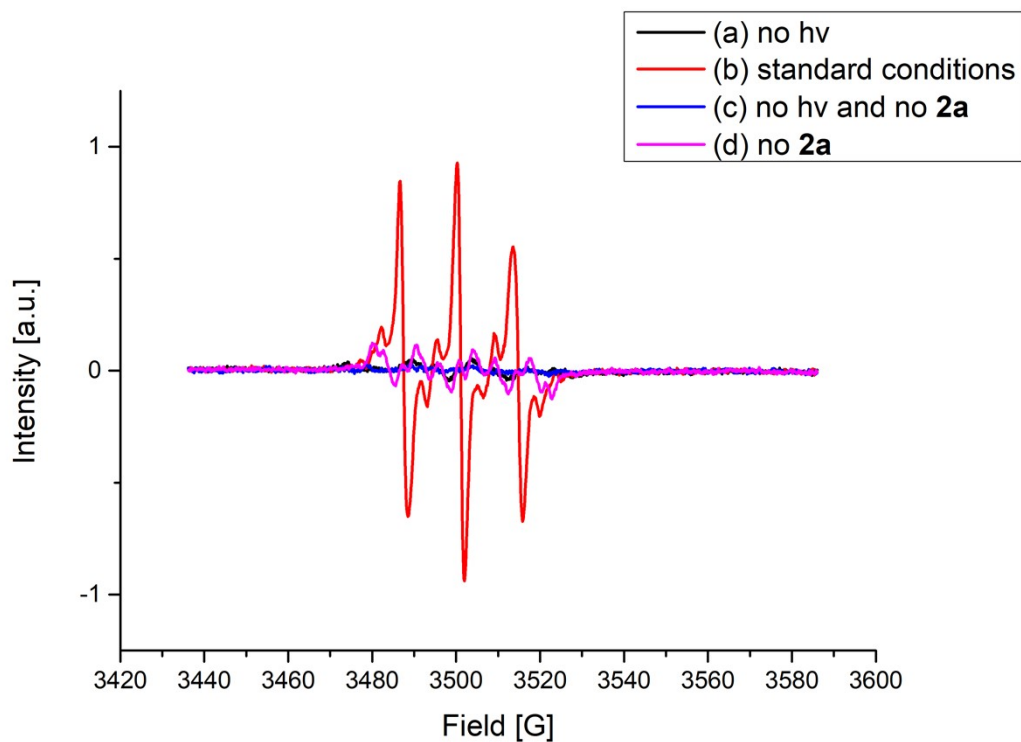
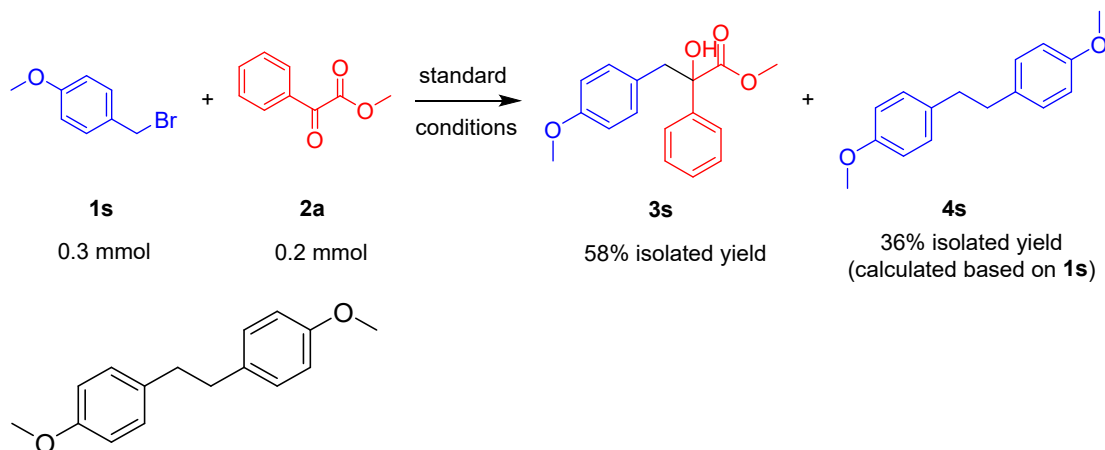


Figure S6. EPR experiment (g-factor 2.00657)

4.5 By-product separation

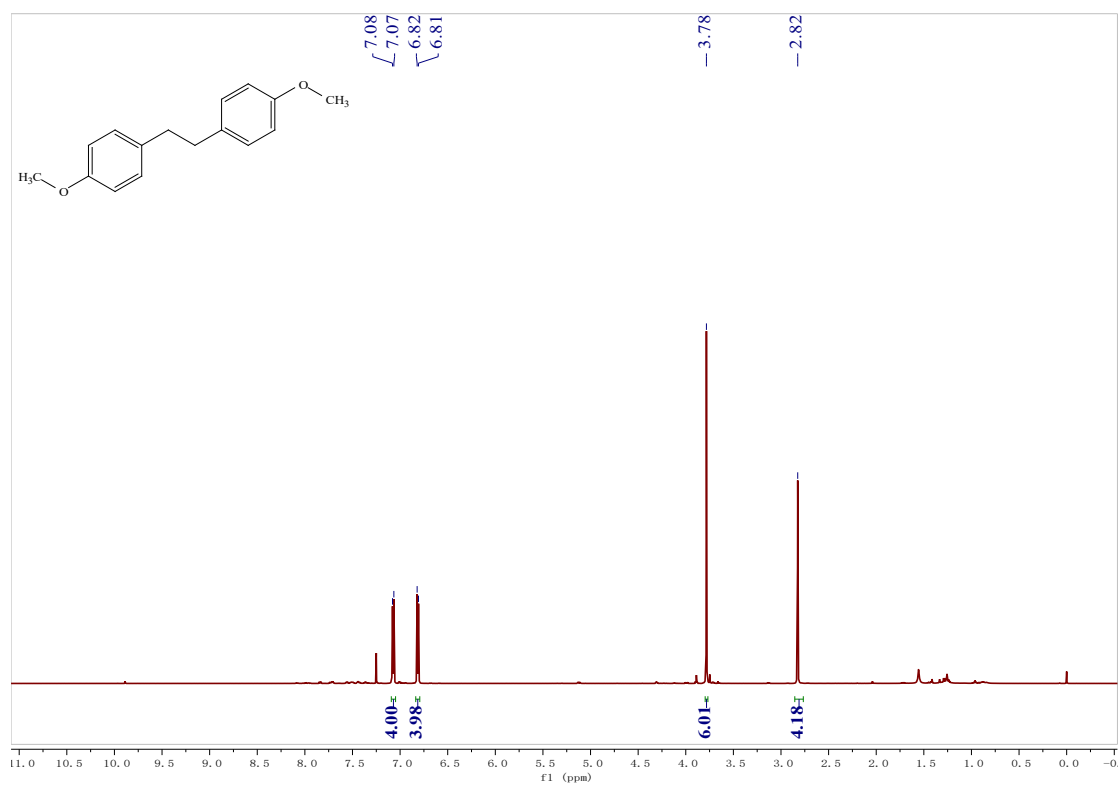
When *p*-methoxybenzyl bromide (**1s**) was used as a substrate, the self-coupling product (**4s**) of benzyl radical was isolated. This result further proved the existence of free radical intermediates.



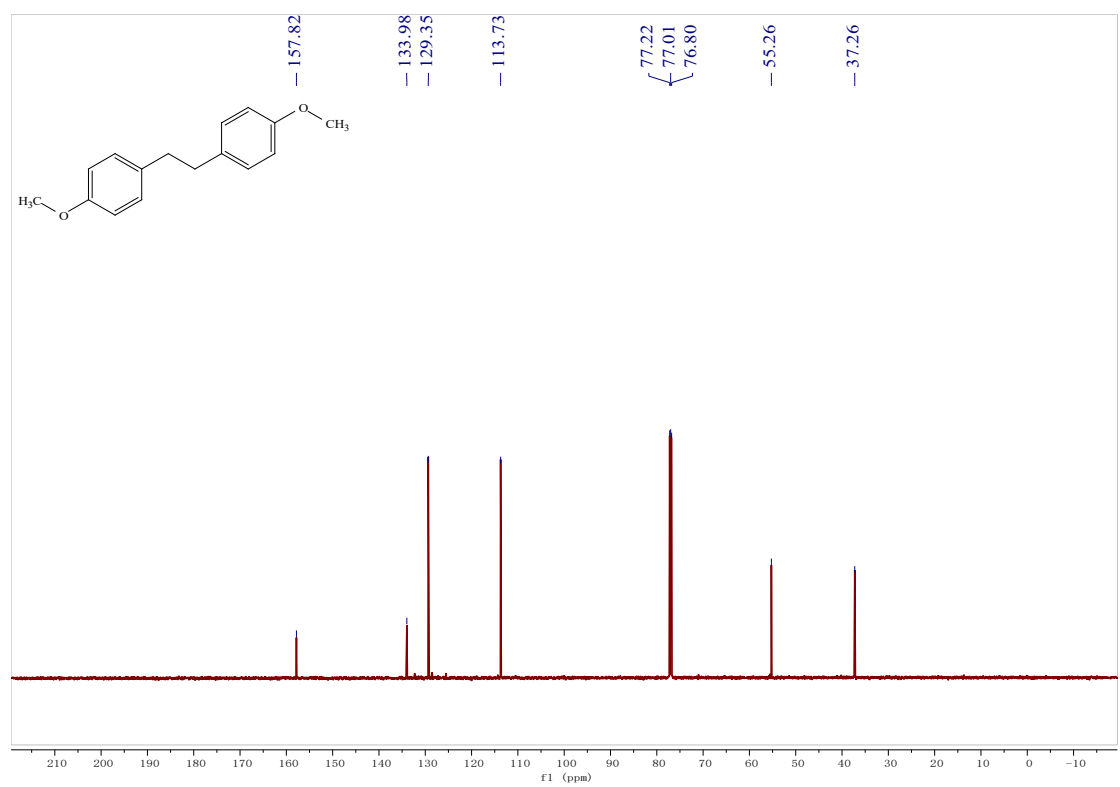
1,2-bis(4-methoxyphenyl)ethane (4s)^[4]: White solid, 13 mg (36% isolated yield) (calculated

based on **1s**); Eluent: petroleum ether/ethyl acetate = 100/1. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 8.5 Hz, 4H), 6.81 (d, *J* = 8.6 Hz, 4H), 3.78 (s, 6H), 2.82 (s, 4H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 157.8, 134.0, 129.4, 113.7, 55.3, 37.3.

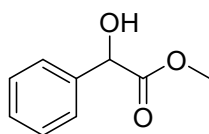
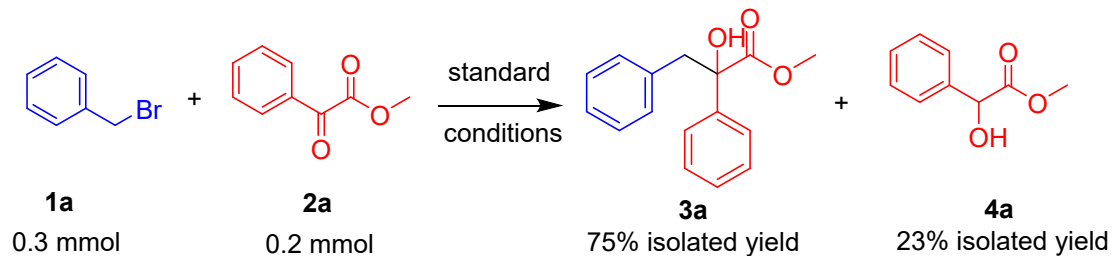
¹H NMR (600 MHz, Chloroform-*d*) of **4s**



¹³C NMR (151 MHz, Chloroform-*d*) of **4s**

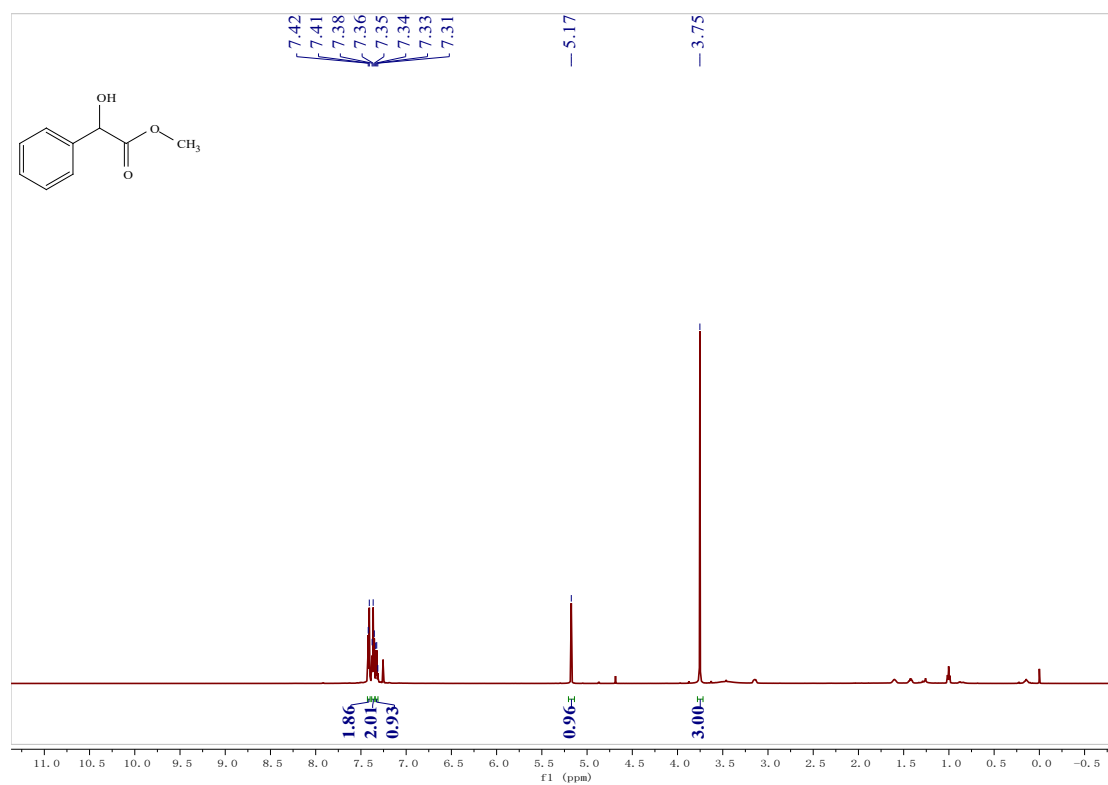


The conversion of ketone ester has also been explored. In addition to the target product, the main by-product is the reduction product of ketone ester. For example, ketone ester (**4a**) was isolated in 23% yield from the reaction below:

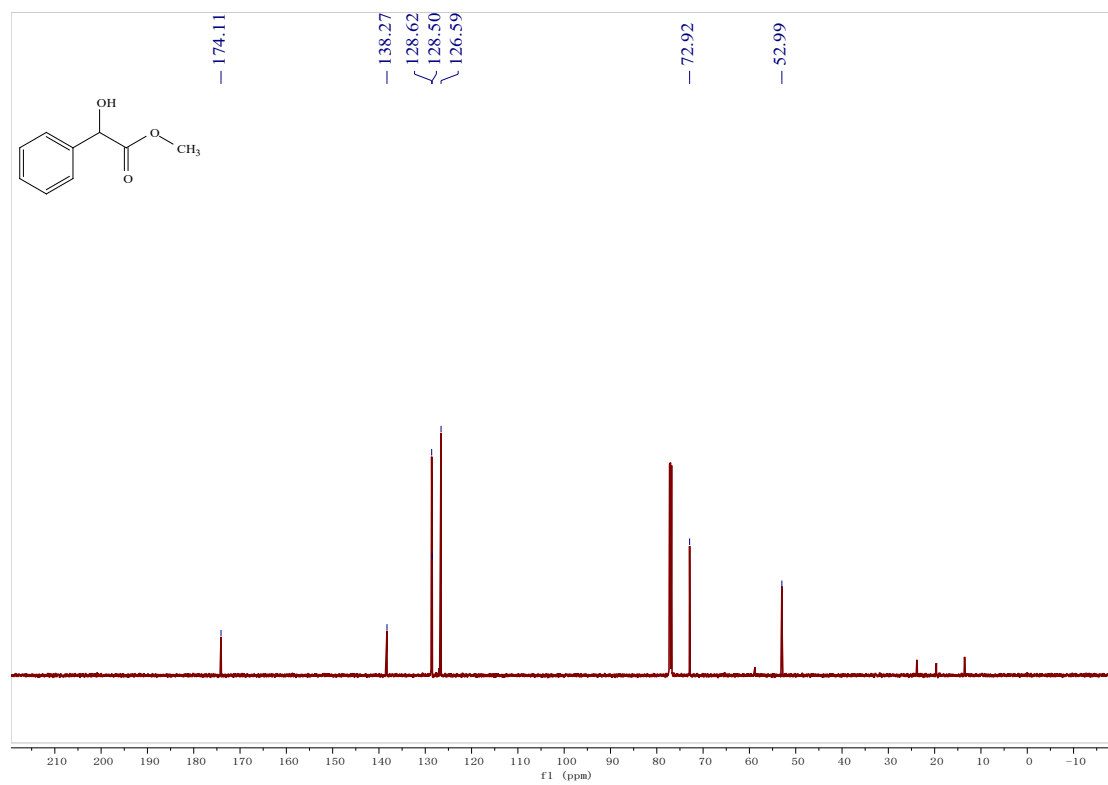


methyl 2-hydroxy-2-phenylacetate^[5]: White solid, 8 mg (23% yield); Eluent: (petroleum ether/ethyl acetate = 5/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.43 – 7.40 (m, 2H), 7.38 – 7.35 (m, 2H), 7.34 – 7.31 (m, 1H), 5.17 (s, 1H), 3.75 (s, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 174.1, 138.3, 128.6, 128.5, 126.6, 72.9, 53.0.

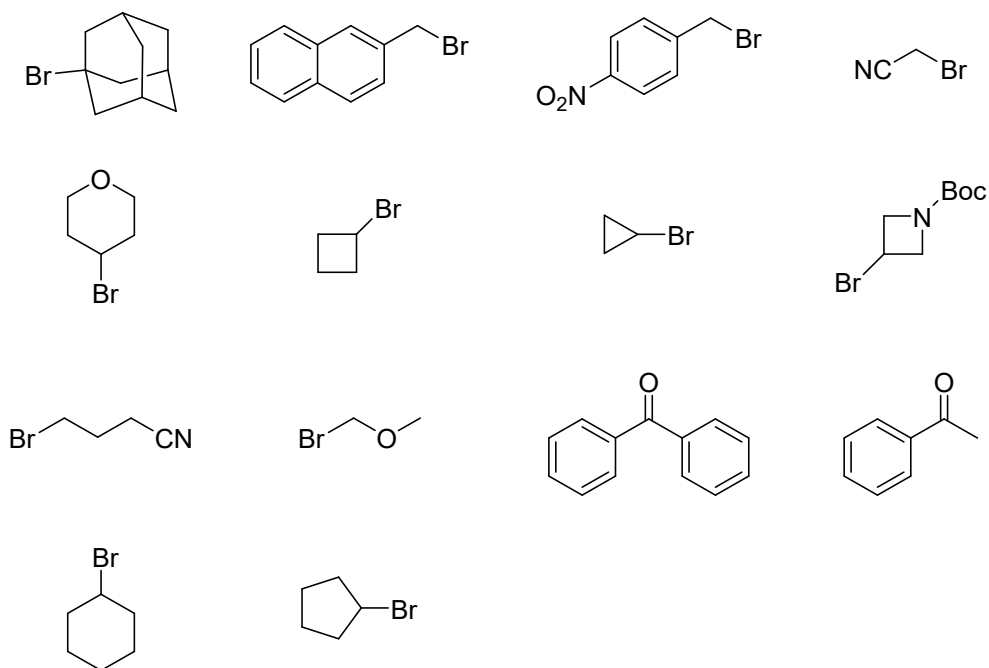
^1H NMR (600 MHz, Chloroform-*d*) of **4a**



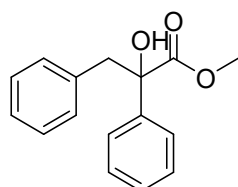
^{13}C NMR (151 MHz, Chloroform-*d*) of **4a**



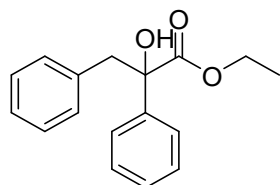
4.6 Unsuccessful substrates



5. Characterization data of the products

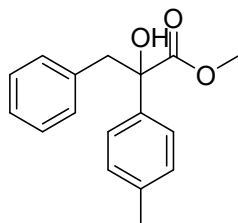


Methyl 2,3-diphenyl-2-hydroxypropanoate (3a)^[6]: White solid, 39 mg (75% yield); Eluent: (petroleum ether/ethyl acetate = 50/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.67 (d, J = 8.6 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 7.3 Hz, 1H), 7.28 – 7.19 (m, 5H), 3.72 (s, 3H), 3.59 (m, 2H), 3.20 (d, J = 13.6 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 174.7, 141.5, 135.7, 130.5, 128.3, 128.1, 127.9, 127.0, 125.7, 78.9, 53.0, 46.0.

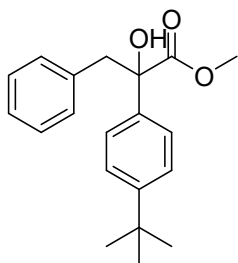


ethyl 2-hydroxy-2,3-diphenylpropanoate (3b)^[7]: White solid, 34 mg (62% yield); Eluent:

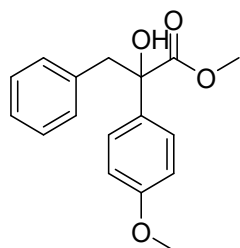
(petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, $J = 7.9$ Hz, 2H), 7.37 (t, $J = 7.5$ Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 1H), 7.24 (s, 5H), 4.21 – 4.11 (m, 2H), 3.65 (br, 1H), 3.57 (d, $J = 13.6$ Hz, 1H), 3.21 (d, $J = 13.6$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.3, 141.8, 135.8, 130.6, 128.2, 128.0, 127.8, 126.9, 125.7, 78.7, 62.5, 46.0, 14.1.



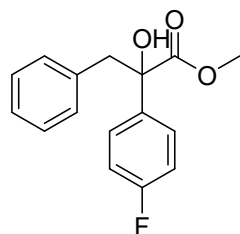
methyl 2-hydroxy-3-phenyl-2-(p-tolyl)propanoate (3c)^[6]: White solid, 38 mg (70% yield); Eluent: (petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.55 (d, $J = 8.2$ Hz, 2H), 7.27 – 7.20 (m, 5H), 7.18 (d, $J = 8.1$ Hz, 2H), 3.71 (s, 3H), 3.57 (d, $J = 13.6$ Hz, 1H), 3.55 (s, 1H), 3.19 (d, $J = 13.6$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.8, 138.7, 137.6, 135.8, 130.5, 129.0, 128.1, 126.9, 125.6, 78.8, 52.9, 45.9, 21.0.



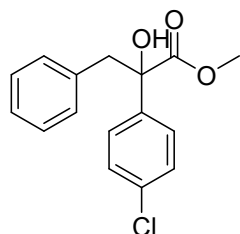
methyl 2-(4-(tert-butyl)phenyl)-2-hydroxy-3-phenylpropanoate (3d): White solid, 37 mg (60% yield); Eluent: (petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.60 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.28 – 7.21 (m, 5H), 3.71 (s, 3H), 3.59 (d, $J = 13.5$ Hz, 1H), 3.56 (s, 1H), 3.18 (d, $J = 13.6$ Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.4, 151.4, 139.2, 136.5, 131.0, 128.7, 127.5, 126.0, 125.8, 79.4, 53.5, 46.6, 35.1, 31.9. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_3\text{Na}$ 335.1618; Found 335.1616.



methyl 2-hydroxy-2-(4-methoxyphenyl)-3-phenylpropanoate (3e)^[8]: White solid, 39 mg (68% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.44 (d, J = 8.5 Hz, 2H), 7.14 – 7.03 (m, 5H), 6.75 (d, J = 8.5 Hz, 2H), 3.65 (s, 3H), 3.57 (s, 3H), 3.42 (d, J = 13.2 Hz, 2H), 3.04 (d, J = 13.6 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 175.0, 159.3, 135.8, 133.7, 130.5, 128.1, 127.0, 127.0, 113.6, 78.6, 55.3, 53.0, 46.0.

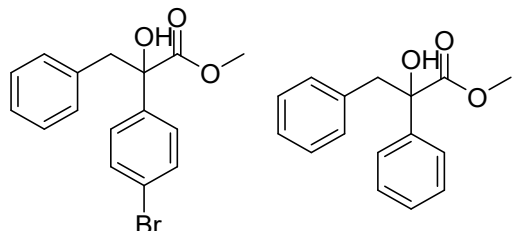


methyl 2-(4-fluorophenyl)-2-hydroxy-3-phenylpropanoate (3f): White solid, 36 mg (65% yield); Eluent: (petroleum ether/ethyl acetate = 20/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.67 – 7.63 (m, 2H), 7.27 – 7.21 (m, 3H), 7.21 – 7.17 (m, 2H), 7.06 – 7.02 (m, 2H), 3.73 (s, 3H), 3.61 (s, 1H), 3.55 (d, J = 13.6 Hz, 1H), 3.17 (d, J = 13.6 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 174.6, 162.5 (d, J = 246.8 Hz), 137.2 (d, J = 3.2 Hz), 135.4, 130.4, 128.2, 127.7 (d, J = 8.2 Hz), 127.1, 115.1 (d, J = 21.4 Hz), 78.5, 53.1, 46.2. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -114.9. HRMS (ESI-TOF) m/z : [M+Na]⁺ Calcd for C₁₆H₁₅FO₃Na 297.0897; Found 297.0896.

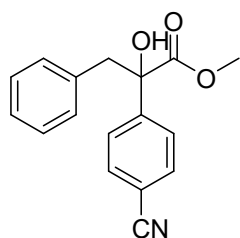


methyl 2-(4-chlorophenyl)-2-hydroxy-3-phenylpropanoate (3g)^[6]: White solid, 35 mg (60% yield); Eluent: (petroleum ether/ethyl acetate = 20/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.62 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.28 – 7.21 (m, 3H), 7.19 (d, J = 7.4 Hz,

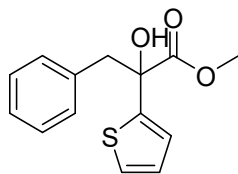
2H), 3.73 (s, 3H), 3.61 (s, 1H), 3.54 (d, $J = 13.6$ Hz, 1H), 3.16 (d, $J = 13.6$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform- d) δ 174.4, 140.0, 135.3, 133.9, 130.4, 128.4, 128.2, 127.3, 127.1, 78.5, 53.2, 46.1.



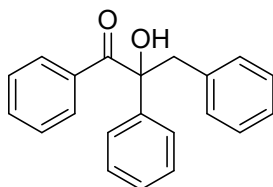
methyl 2-(4-bromophenyl)-2-hydroxy-3-phenylpropanoate (3h) and methyl 2-hydroxy-2,3-diphenylpropanoate (3a) (inseparable mixture=3h:3a=2.3:1): White solid, 32 mg (50% yield); Eluent: (petroleum ether/ethyl acetate = 20/1). ^1H NMR (600 MHz, Chloroform- d) δ 7.68 (d, $J = 7.5$ Hz, 0.83H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.37 (t, $J = 7.6$ Hz, 0.85H), 7.33 – 7.28 (m, 0.43H), 7.28 – 7.17 (m, 7.15H), 3.74 – 3.72 (m, 4.16H), 3.59 (d, $J = 13.4$ Hz, 1.56H), 3.53 (d, $J = 13.6$ Hz, 1H), 3.21 (d, $J = 13.6$ Hz, 0.43H), 3.16 (d, $J = 13.6$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform- d) δ 174.7, 174.3, 141.5, 140.5, 135.7, 135.3, 131.4, 130.5, 130.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.1, 127.0, 125.7, 122.1, 78.9, 78.6, 53.2, 53.0, 46.1, 46.0. HRMS of **3a** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{Na}$ 279.0992; Found 279.0987; HRMS of **3h** (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{15}\text{BrO}_3\text{Na}$ 357.0097; Found 357.0091.



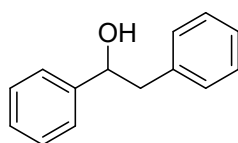
methyl 2-(4-cyanophenyl)-2-hydroxy-3-phenylpropanoate (3i): Light yellow liquid, 33 mg (58% yield); Eluent: (petroleum ether/ethyl acetate = 10/1). ^1H NMR (600 MHz, Chloroform- d) δ 7.83 (d, $J = 8.1$ Hz, 2H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.28 – 7.22 (m, 3H), 7.18 (d, $J = 7.1$ Hz, 2H), 3.77 (s, 3H), 3.70 (br, 1H), 3.54 (d, $J = 13.6$ Hz, 1H), 3.17 (d, $J = 13.6$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform- d) δ 173.7, 146.4, 134.8, 132.1, 130.4, 128.3, 127.3, 126.8, 118.6, 111.9, 78.7, 53.5, 46.2. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_3\text{Na}$ 304.0944; Found 304.0939.



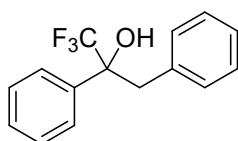
methyl 2-hydroxy-3-phenyl-2-(thiophen-2-yl)propanoate (3j): Yellow liquid, 43 mg (82% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.28 – 7.21 (m, 6H), 7.19 – 7.18 (m, 1H), 7.01 – 6.96 (m, 1H), 3.88 (br, 1H), 3.76 (s, 3H), 3.52 (d, $J = 13.6$ Hz, 1H), 3.29 (d, $J = 13.6$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.7, 146.3, 135.2, 130.3, 128.1, 127.2, 127.0, 125.2, 124.4, 77.9, 53.2, 47.4. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3\text{SNa}$ 285.0556; Found 285.0554.



2-hydroxy-1,2,3-triphenylpropan-1-one (3k)^[9]: White solid, 42 mg (70% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.70 (d, $J = 7.6$ Hz, 2H), 7.52 (d, $J = 7.4$ Hz, 2H), 7.45 – 7.36 (m, 3H), 7.33 – 7.25 (m, 3H), 7.17 – 7.14 (m, 3H), 6.97 – 6.93 (m, 2H), 4.01 (s, 1H), 3.77 (d, $J = 13.5$ Hz, 1H), 3.52 (d, $J = 13.5$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 200.6, 142.1, 135.1, 132.7, 134.9, 130.7, 130.3, 128.9, 128.1, 128.1, 128.1, 127.0, 125.8, 82.3, 45.1.

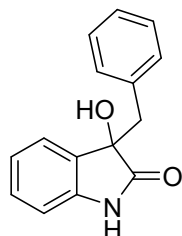


1,2-diphenylethan-1-ol (3l)^[10]: White solid, 8 mg (20% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.37 – 7.25 (m, 7H), 7.24 – 7.17 (m, 3H), 4.93 – 4.87 (m, 1H), 3.07 – 2.96 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.9, 138.0, 129.5, 128.5, 128.4, 127.6, 126.6, 125.9, 75.3, 46.1.

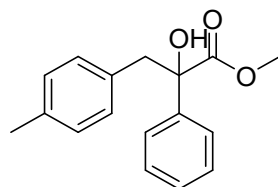


1,1,1-trifluoro-2,3-diphenylpropan-2-ol (3m)^[11]: Yellow liquid, 23 mg (43 % yield); Eluent:

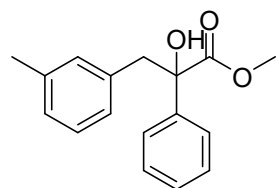
(petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.53 (d, J = 7.3 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.22 – 7.14 (m, 3H), 6.97 (d, J = 6.2 Hz, 2H), 3.46 – 3.38 (m, 2H), 2.42 (br, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.2, 133.1, 130.7, 128.5, 128.4, 128.2, 127.5, 126.4, 125.6 (q, J = 286.2 Hz), 77.3 (q, J = 27.8 Hz), 41.9. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -78.3.



3-benzyl-3-hydroxyindolin-2-one (3n)^[12]: Yellow solid, 14 mg (30 % yield); Eluent: (petroleum ether/ethyl acetate = 2/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.93 (br, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.17 – 7.09 (m, 4H), 7.02 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 6.7 Hz, 2H), 6.71 (d, J = 7.7 Hz, 1H), 3.30 (d, J = 13.1 Hz, 1H), 3.13 (d, J = 13.1 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 179.8, 140.2, 133.9, 130.4, 129.7, 129.7, 127.9, 126.9, 125.0, 122.8, 110.1, 77.5, 44.7.

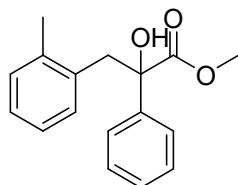


methyl 2-hydroxy-2-phenyl-3-(p-tolyl)propanoate (3o)^[6]: White solid, 33 mg (61% yield); Eluent: (petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.32 – 7.29 (m, 1H), 7.13 – 7.05 (m, 4H), 3.73 (s, 3H), 3.56 (d, J = 13.5 Hz, 2H), 3.16 (d, J = 13.6 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.8, 141.6, 136.5, 132.5, 130.3, 128.9, 128.3, 127.8, 125.7, 78.9, 53.0, 45.6, 21.0.

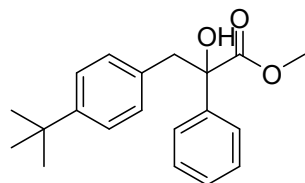


methyl 2-hydroxy-2-phenyl-3-(mfcfc-tolyl)propanoate (3p): White solid, 35 mg (65% yield); Eluent: (petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ

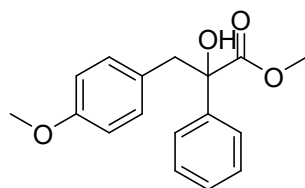
7.68 (d, $J = 7.8$ Hz, 2H), 7.37 (t, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 6.9$ Hz, 1H), 7.15 (t, $J = 7.4$ Hz, 1H), 7.04 (d, $J = 8.6$ Hz, 2H), 7.00 (d, $J = 7.4$ Hz, 1H), 3.73 (s, 3H), 3.57 (d, $J = 13.9$ Hz, 2H), 3.15 (d, $J = 13.5$ Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.7, 141.6, 137.6, 135.6, 131.3, 128.3, 128.0, 127.9, 127.7, 127.3, 125.7, 78.9, 52.9, 46.0, 21.4. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{Na}$ 293.1148; Found 293.1147.



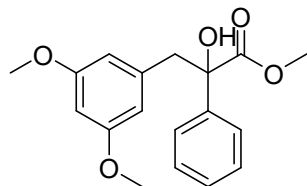
methyl 2-hydroxy-2-phenyl-3-(*o*-tolyl)propanoate (3q): Colorless liquid, 30 mg (55% yield); Eluent: (petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.29 (m, 1H), 7.16 – 7.09 (m, 3H), 7.08 – 7.04 (m, 1H), 3.76 (s, 3H), 3.61 (d, $J = 14.0$ Hz, 1H), 3.53 (br, 1H), 3.32 (d, $J = 14.0$ Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.0, 142.0, 138.3, 134.2, 130.4, 130.2, 128.3, 127.9, 126.9, 125.7, 125.5, 79.5, 53.0, 42.2, 20.1. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{Na}$ 293.1148; Found 293.1148.



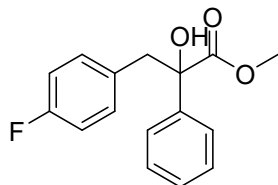
methyl 3-(4-(*tert*-butyl)phenyl)-2-hydroxy-2-phenylpropanoate (3r): White solid, 39 mg (62% yield); Eluent: (petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, $J = 7.7$ Hz, 2H), 7.37 (t, $J = 7.6$ Hz, 2H), 7.32 – 7.27 (m, 3H), 7.14 (d, $J = 8.1$ Hz, 2H), 3.73 (s, 3H), 3.58 (d, $J = 13.7$ Hz, 1H), 3.54 (s, 1H), 3.16 (d, $J = 13.6$ Hz, 1H), 1.30 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.8, 149.8, 141.7, 132.5, 130.1, 128.3, 127.8, 125.7, 125.1, 78.9, 52.9, 45.5, 34.4, 31.4. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_3\text{Na}$ 335.1618; Found 335.1619.



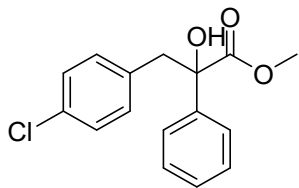
methyl 2-hydroxy-3-(4-methoxyphenyl)-2-phenylpropanoate (3s)^[6]: White solid, 33 mg (58% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.53 (d, $J = 7.5$ Hz, 2H), 7.23 (t, $J = 7.5$ Hz, 2H), 7.16 (t, $J = 7.3$ Hz, 1H), 6.99 (d, $J = 8.3$ Hz, 2H), 6.66 (d, $J = 8.4$ Hz, 2H), 3.63 (s, 3H), 3.59 (s, 3H), 3.43 (s, 1H), 3.40 (d, $J = 13.8$ Hz, 1H), 3.01 (d, $J = 13.7$ Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 174.8, 158.7, 141.6, 131.4, 128.3, 127.8, 127.7, 125.7, 113.6, 79.0, 55.2, 52.9, 45.2.



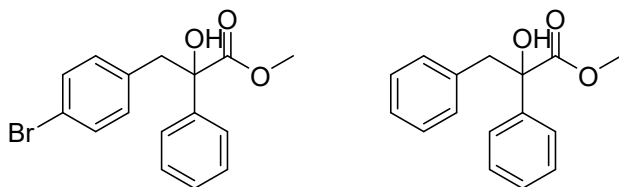
methyl 3-(3,5-dimethoxyphenyl)-2-hydroxy-2-phenylpropanoate (3t): Yellow liquid, 30 mg (48% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.67 (d, $J = 7.6$ Hz, 2H), 7.37 (t, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 1H), 6.37 (d, $J = 2.0$ Hz, 2H), 6.34 (d, $J = 2.1$ Hz, 1H), 3.74 (s, 3H), 3.72 (s, 6H), 3.61 (br, 1H), 3.53 (d, $J = 13.5$ Hz, 1H), 3.15 (d, $J = 13.5$ Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 174.6, 160.5, 141.5, 137.8, 128.3, 127.9, 125.7, 108.6, 99.3, 78.8, 55.2, 53.0, 46.3. HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd for C₁₈H₂₀O₅Na 339.1203; Found 339.1204.



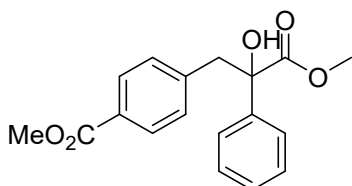
methyl 3-(4-fluorophenyl)-2-hydroxy-2-phenylpropanoate (3u): White solid, 41 mg (75% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, $J = 7.8$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 1H), 7.19 – 7.14 (m, 2H), 6.93 (t, $J = 8.6$ Hz, 2H), 3.62 (br, 1H), 3.52 (d, $J = 13.8$ Hz, 1H), 3.18 (d, $J = 13.8$ Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 174.6, 162.0 (d, $J = 245.0$ Hz), 141.4, 132.0 (d, $J = 7.9$ Hz), 131.4 (d, $J = 3.1$ Hz), 128.3, 128.0, 125.6, 114.8 (d, $J = 21.1$ Hz), 78.9, 53.0, 45.0. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -116.1. HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd for C₁₆H₁₅FO₃Na 297.0897; Found 297.0898.



methyl 3-(4-chlorophenyl)-2-hydroxy-2-phenylpropanoate (3v)^[13]: White solid, 43 mg (74% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.63 (d, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 1H), 7.21 (d, $J = 8.3$ Hz, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 3.73 (s, 3H), 3.63 (br, 1H), 3.51 (d, $J = 13.7$ Hz, 1H), 3.19 (d, $J = 13.7$ Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 174.5, 141.3, 134.3, 132.9, 131.8, 128.3, 128.2, 128.0, 125.6, 78.8, 53.1, 45.2.

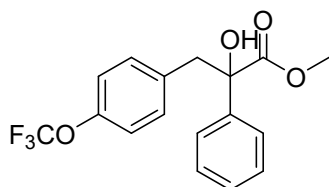


methyl 3-(4-bromophenyl)-2-hydroxy-2-phenylpropanoate (3w) and methyl 2-hydroxy-2,3-diphenylpropanoate (3a) (inseparable mixture of **3w** : **3a** = 2.3:1): White solid, 39 mg (63% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.68 – 7.65 (m, 0.86H), 7.63 (d, $J = 7.7$ Hz, 2H), 7.38 – 7.35 (m, 4.6H), 7.32 – 7.29 (m, 1.41H), 7.28 – 7.19 (m, 2.42H), 7.08 (d, $J = 8.2$ Hz, 2H), 3.74 – 3.72 (m, 4.29H), 3.64 – 3.56 (m, 1.62H), 3.49 (d, $J = 13.7$ Hz, 1H), 3.21 (d, $J = 13.6$ Hz, 0.43H), 3.17 (d, $J = 13.7$ Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 174.7, 174.5, 141.6, 141.3, 135.7, 134.8, 132.2, 131.1, 130.5, 128.3, 128.3, 128.1, 128.0, 127.9, 126.9, 125.7, 125.6, 121.0, 78.9, 78.7, 53.1, 53.0, 46.0, 45.2. HRMS of **3a** (ESI-TOF) m/z : $[M+Na]^+$ Calcd for C₁₆H₁₆O₃Na 279.0992; Found 279.0991; HRMS of **3w** (ESI-TOF) m/z : $[M+Na]^+$ Calcd for C₁₆H₁₅BrO₃Na 357.0097; Found 357.0095.

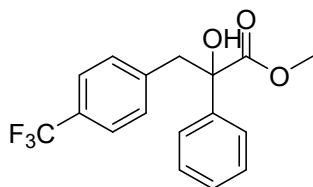


methyl 4-(2-hydroxy-3-methoxy-3-oxo-2-phenylpropyl)benzoate (3x)^[9]: White solid, 41 mg (65% yield); Eluent: (petroleum ether/ethyl acetate = 20/1). ¹H NMR (600 MHz,

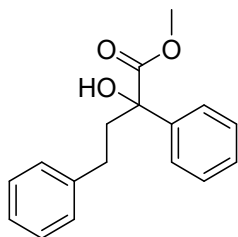
Chloroform-*d*) δ 7.91 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 7.8$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.32 – 7.27 (m, 3H), 3.88 (s, 3H), 3.73 (s, 3H), 3.67 (br, 1H), 3.59 (d, $J = 13.6$ Hz, 1H), 3.28 (d, $J = 13.6$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.4, 167.0, 141.3, 141.2, 130.6, 129.2, 128.8, 128.3, 128.0, 125.6, 78.8, 53.1, 51.9, 45.8.



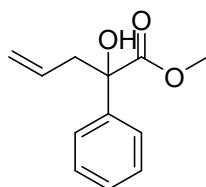
methyl 2-hydroxy-2-phenyl-3-(4-(trifluoromethoxy)phenyl)propanoate (3y): White solid, 41 mg (60% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, $J = 7.5$ Hz, 2H), 7.37 (t, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.3$ Hz, 1H), 7.23 (d, $J = 8.5$ Hz, 2H), 7.09 (d, $J = 8.1$ Hz, 2H), 3.74 (s, 3H), 3.63 (s, 1H), 3.54 (d, $J = 13.8$ Hz, 1H), 3.22 (d, $J = 13.8$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.5, 148.3, 141.3, 134.5, 131.8, 128.3, 128.0, 125.5, 120.5 (q, $J = 257.0$ Hz), 120.3, 78.8, 53.1, 45.1. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -57.8. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_4\text{Na}$ 363.0815; Found 363.0813.



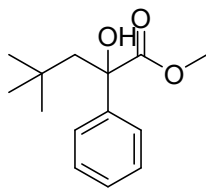
methyl 2-hydroxy-2-phenyl-3-(4-(trifluoromethyl)phenyl)propanoate (3z)^[9]: White solid, 40 mg (62% yield); Eluent: (petroleum ether/ethyl acetate = 30/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, $J = 7.6$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.18 (t, $J = 7.5$ Hz, 2H), 7.14 (d, $J = 7.6$ Hz, 3H), 3.57 (s, 3H), 3.47 (s, 1H), 3.40 (d, $J = 13.6$ Hz, 1H), 3.10 (d, $J = 13.6$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.2, 141.9, 140.7, 131.6, 129.9 (q, $J = 32.3$ Hz), 129.1, 128.8, 126.3, 125.6 (q, $J = 3.6$ Hz), 125.0 (q, $J = 272.1$ Hz), 79.5, 53.9, 46.3. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.5.



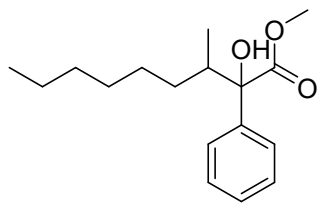
methyl 2-hydroxy-2,4-diphenylbutanoate (3aa): White solid, 16 mg (30% yield); Eluent: (petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.55 – 7.53 (m, 2H), 7.30 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 7.14 – 7.13 (m, 1H), 7.11 – 7.08 (m, 2H), 3.66 (s, 3H), 2.67 – 2.61 (m, 1H), 2.55 – 2.49 (m, 1H), 2.45 – 2.37 (m, 1H), 2.29 – 2.23 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.7, 139.7, 126.5, 126.4, 126.4, 125.9, 124.0, 123.5, 76.2, 51.3, 39.6, 28.2. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{Na}$ 293.1148; Found 293.1146.



methyl 2-hydroxy-2-phenylpent-4-enoate (3ab)^[6]: Colorless liquid, 34 mg (82% yield); Eluent: (petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.61 – 7.58 (m, 2H), 7.38 – 7.34 (m, 2H), 7.31 – 7.28 (m, 1H), 5.83 – 5.75 (m, 1H), 5.20 – 5.11 (m, 2H), 3.77 (s, 3H), 2.97 (dd, $J = 13.9, 7.6$ Hz, 1H), 2.77 (dd, $J = 14.0, 6.5$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.0, 141.3, 132.4, 128.3, 127.8, 125.5, 119.3, 78.2, 53.1, 44.2.



methyl 2-hydroxy-4,4-dimethyl-2-phenylpentanoate (3ac): Colorless liquid, 21 mg (44% yield); Eluent: (petroleum ether/ethyl acetate = 50/1). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.63 – 7.59 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.24 (m, 1H), 3.77 (s, 3H), 2.33 (d, $J = 14.7$ Hz, 1H), 1.96 (d, $J = 14.7$ Hz, 1H), 0.97 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.6, 144.0, 128.1, 127.4, 125.3, 78.5, 53.0, 51.1, 31.6, 30.8. HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{Na}$ 259.1305; Found 259.1305.



3ad d.r.=1.1:1

methyl 2-hydroxy-3-methyl-2-phenylnonanoate (3ad): White solid, 29 mg (52% yield, d.r.=1.1:1); Eluent: (petroleum ether/ethyl acetate = 50/1). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.61 (m, 4H), 7.36 – 7.31 (m, 4H), 7.27 – 7.24 (m, 2H), 3.78 – 3.75 (m, 6H), 2.44 – 2.34 (m, 2H), 1.32 – 1.04 (m, 20H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H), 0.68 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 176.2, 176.2, 141.3, 141.1, 128.1, 127.4, 127.4, 126.0, 126.0, 81.8, 81.7, 53.1, 53.0, 40.8, 40.5, 31.8, 31.8, 31.7, 29.4, 29.4, 29.1, 27.5, 27.4, 22.6, 22.5, 14.1, 14.0, 14.0, 12.7. HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₆O₃Na 301.1774; Found 301.1773.

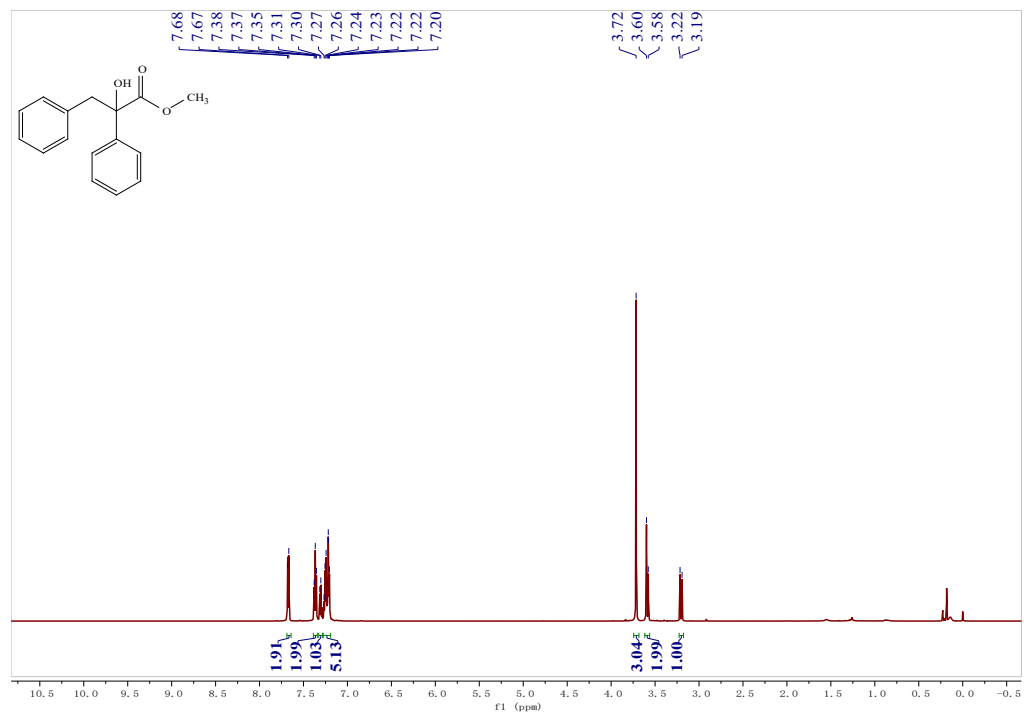
6. References

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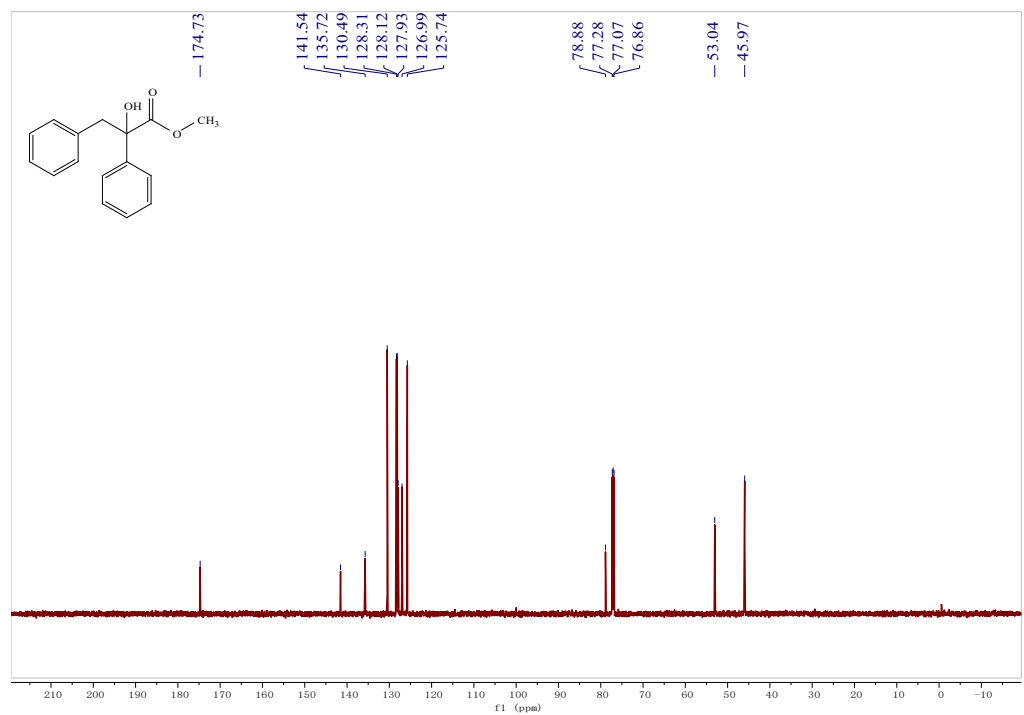
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7. NMR of Products

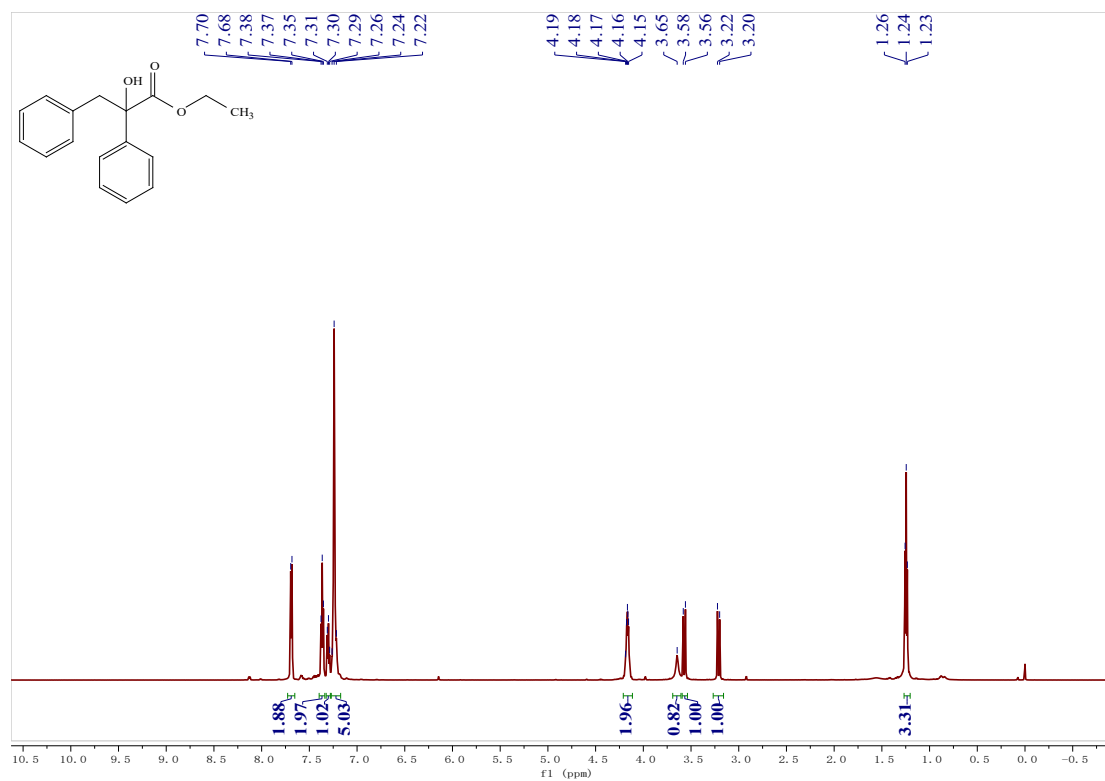
^1H NMR (600 MHz, Chloroform-*d*) of **3a**



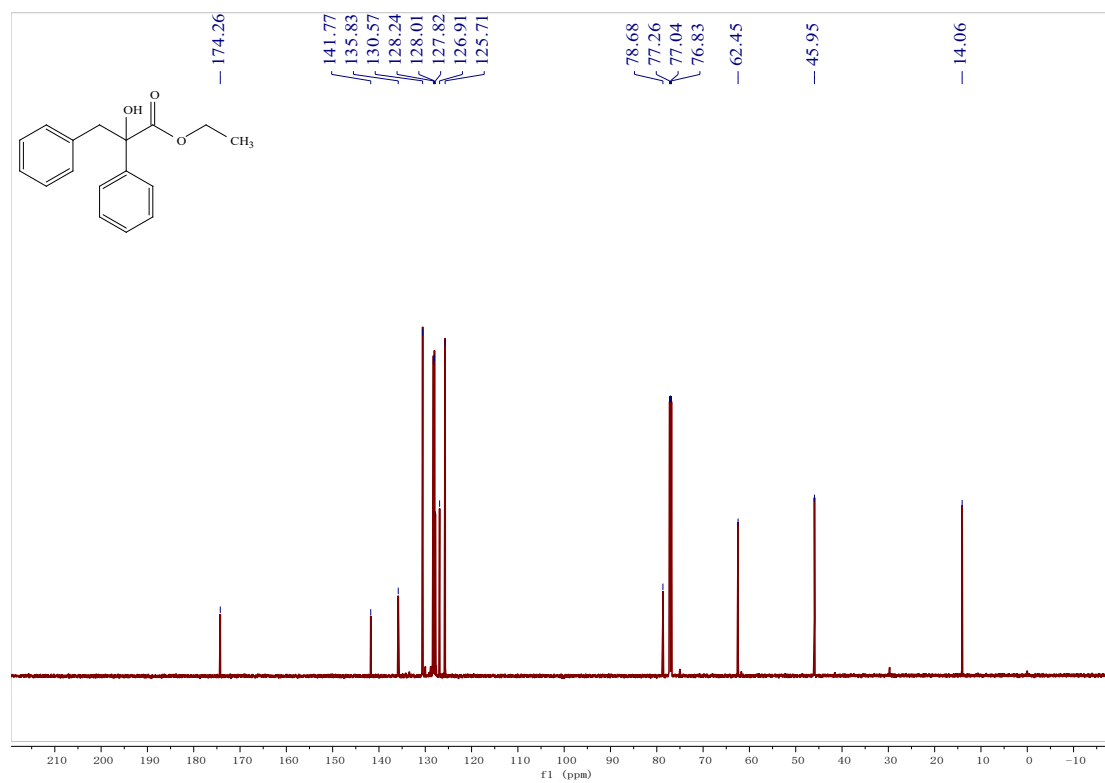
^{13}C NMR (151 MHz, Chloroform-*d*) of **3a**



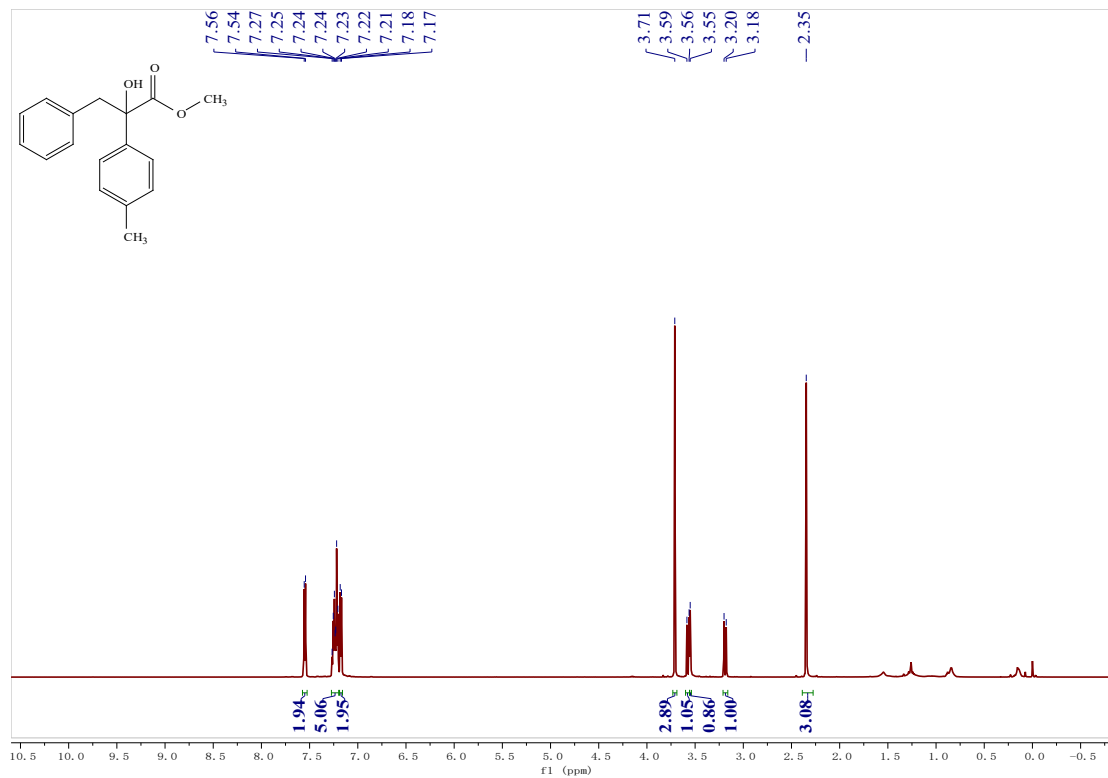
¹H NMR (600 MHz, Chloroform-*d*) of **3b**



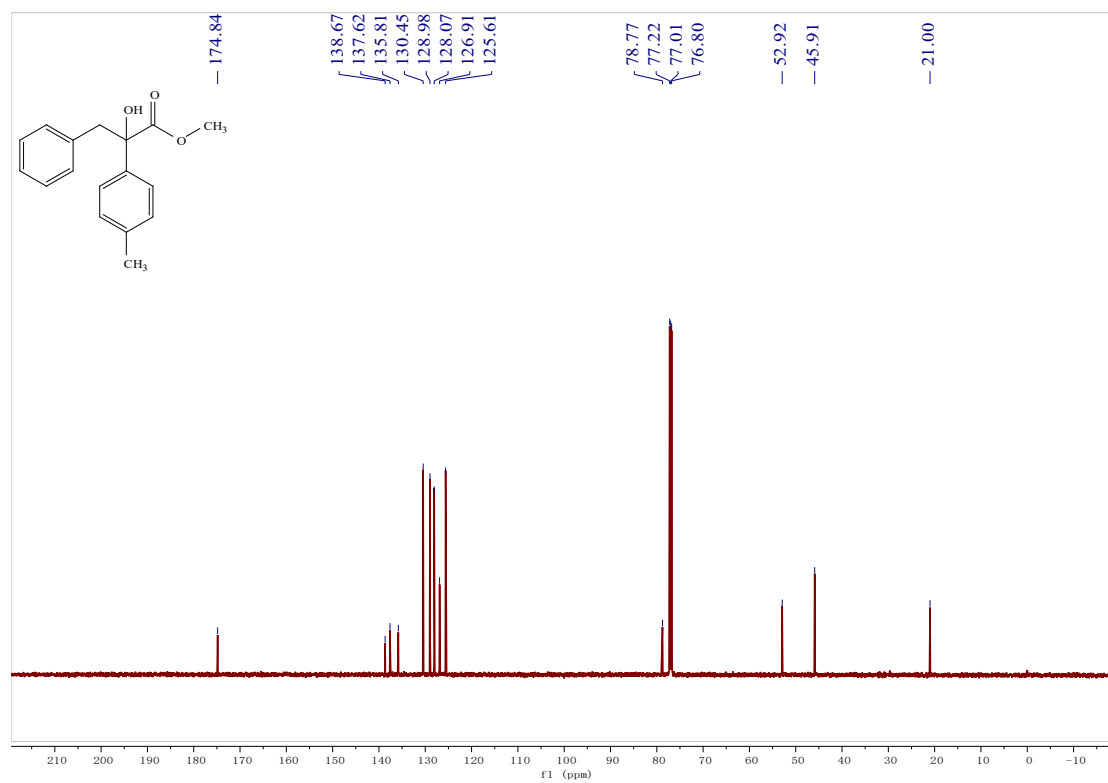
¹³C NMR (151 MHz, Chloroform-*d*) of **3b**



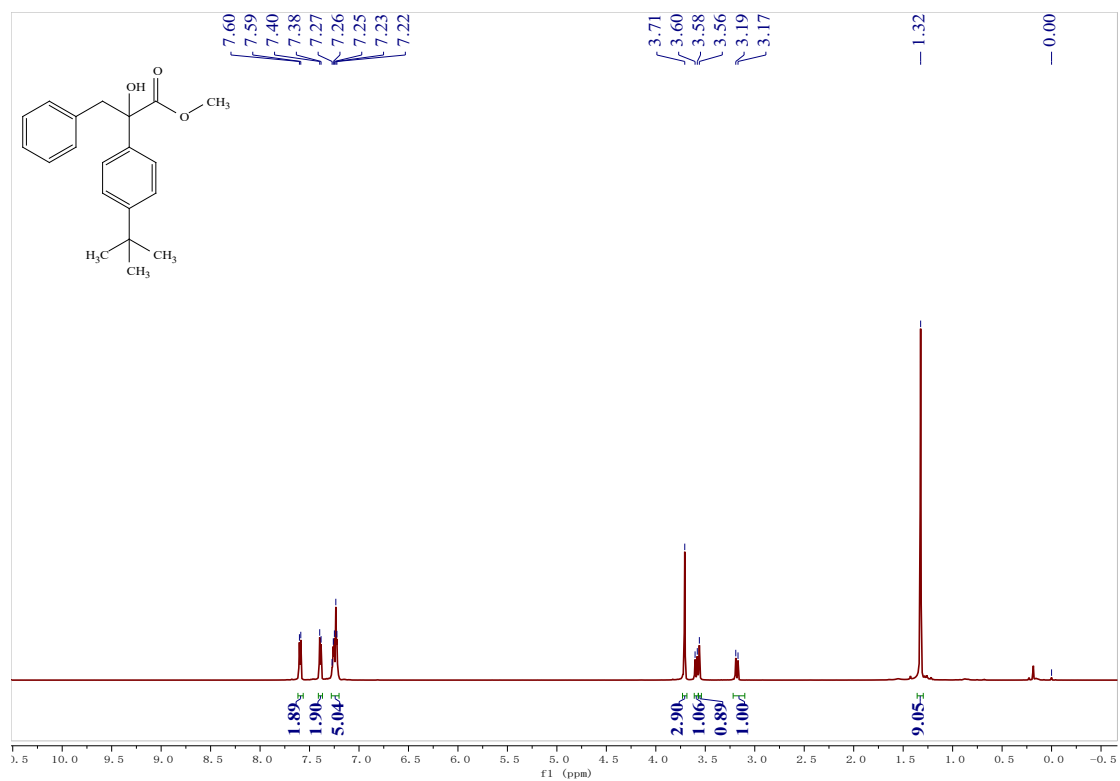
¹H NMR (600 MHz, Chloroform-*d*) of **3c**



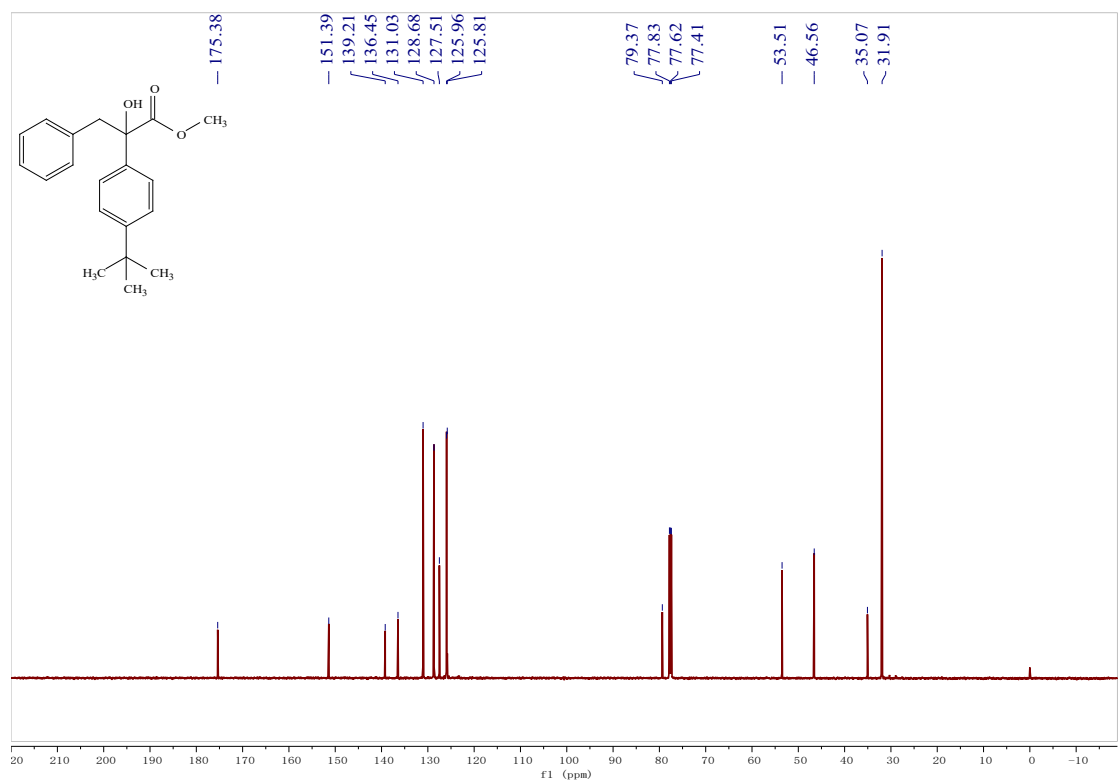
¹³C NMR (151 MHz, Chloroform-*d*) of **3c**



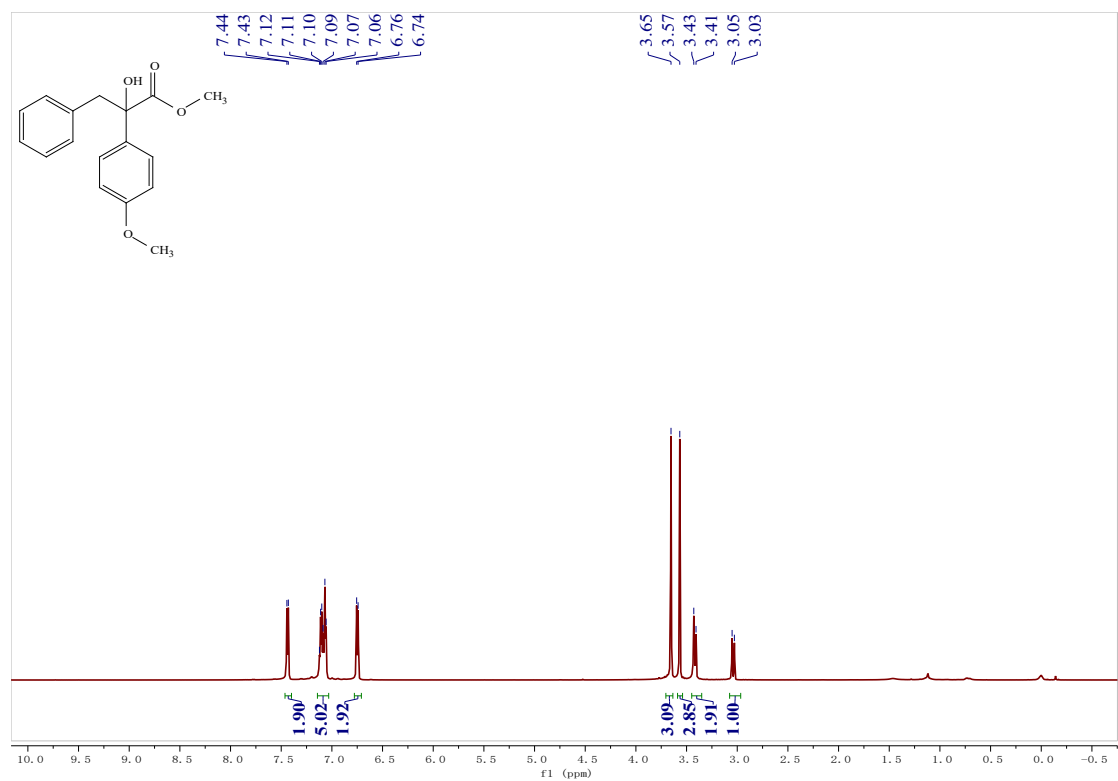
¹H NMR (600 MHz, Chloroform-*d*) of **3d**



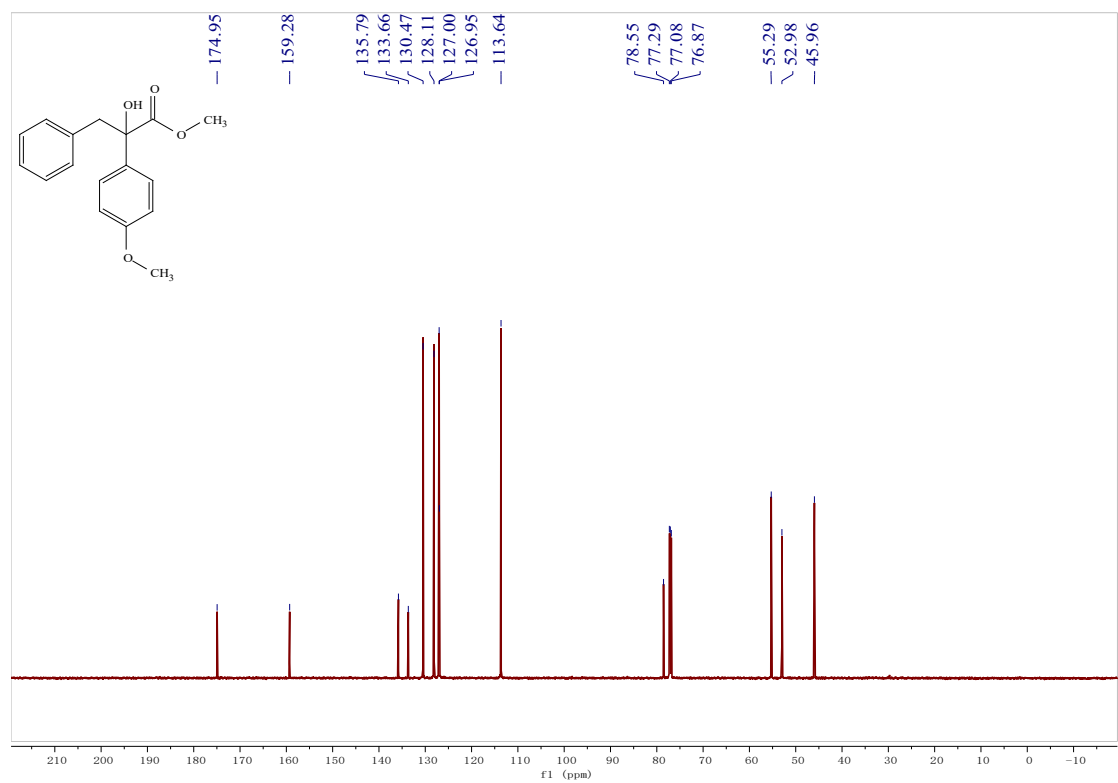
¹³C NMR (151 MHz, Chloroform-*d*) of **3d**



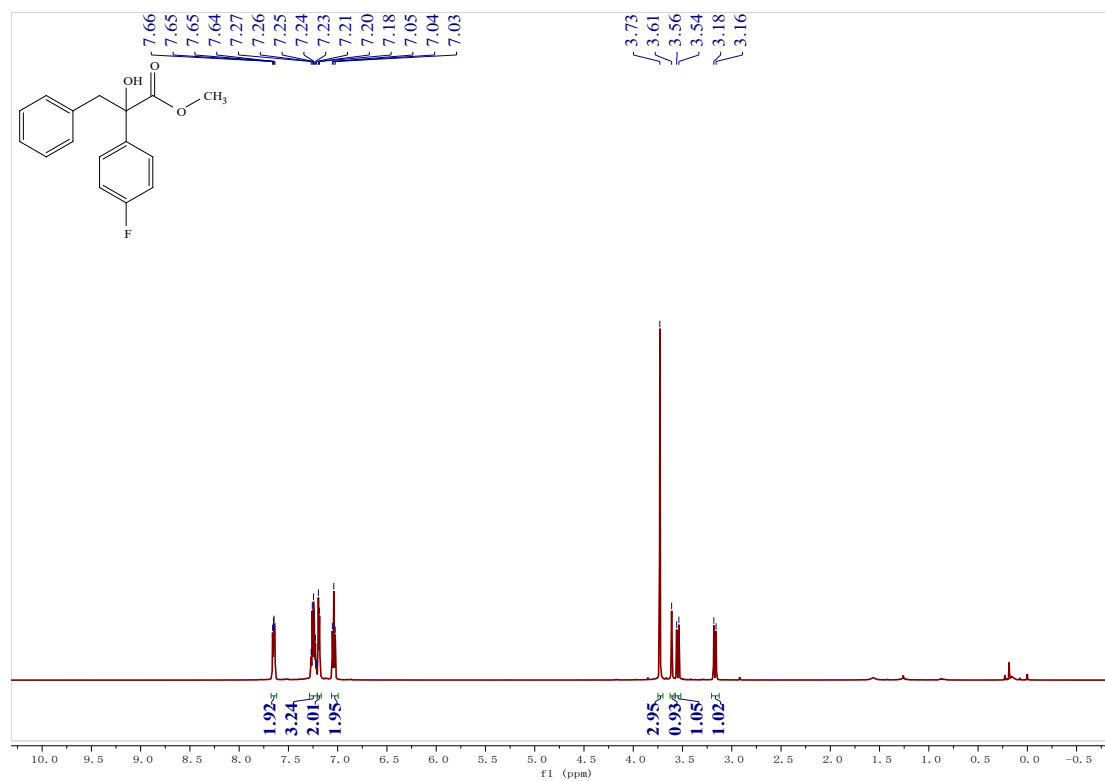
¹H NMR (600 MHz, Chloroform-*d*) of **3e**



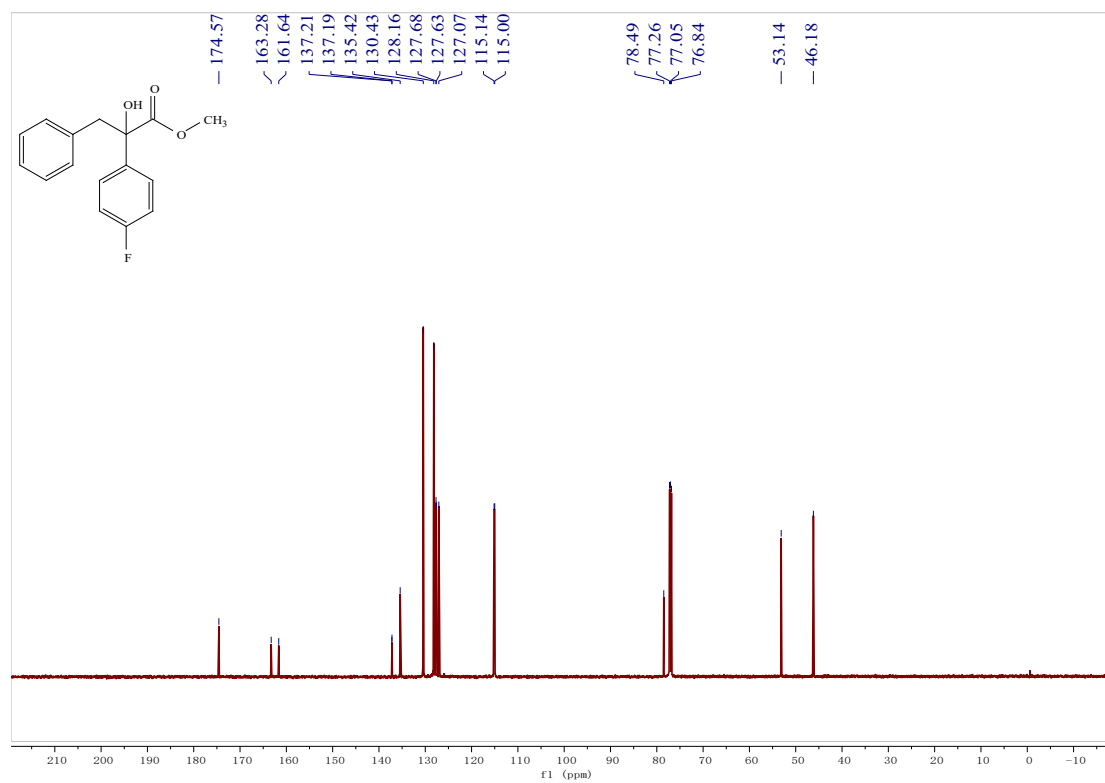
¹³C NMR (151 MHz, Chloroform-*d*) of **3e**



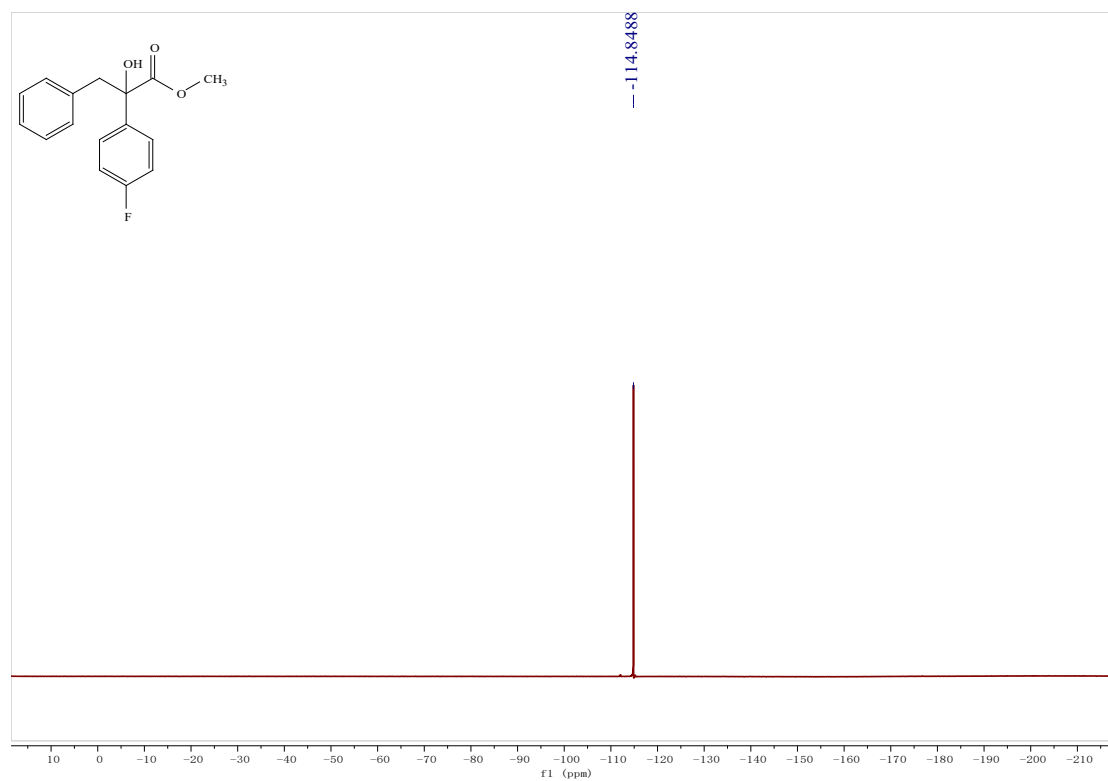
¹H NMR (600 MHz, Chloroform-*d*) of **3f**



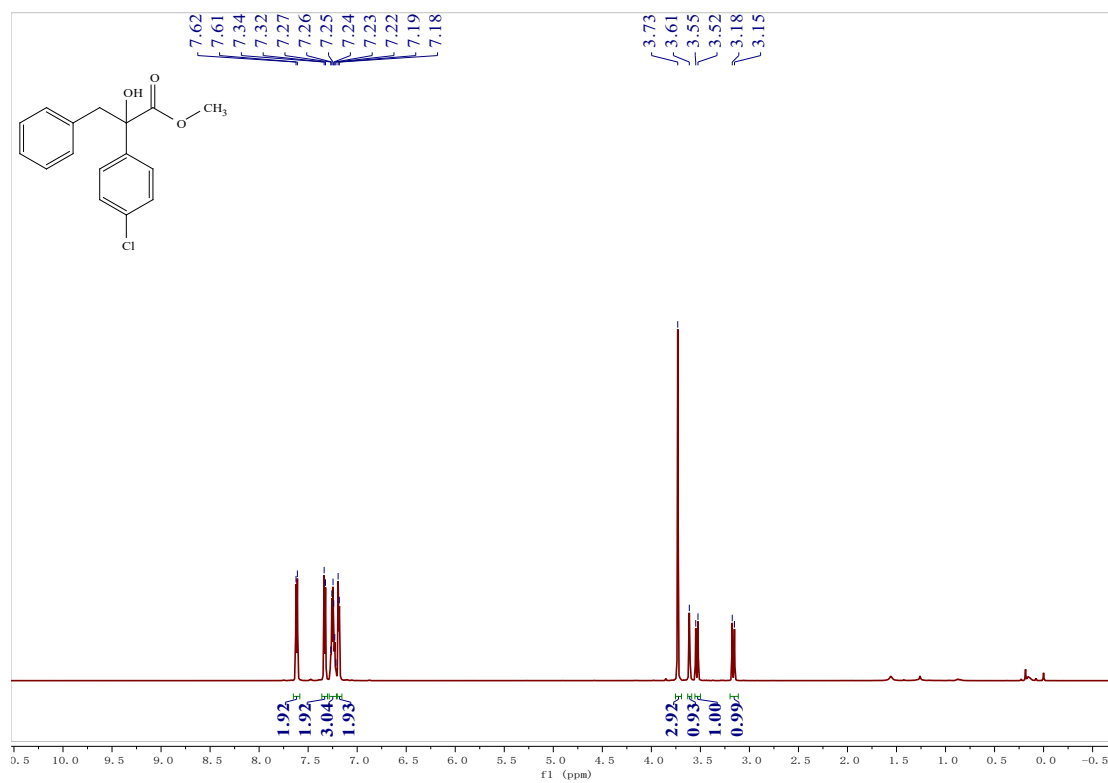
¹³C NMR (151 MHz, Chloroform-*d*) of **3f**



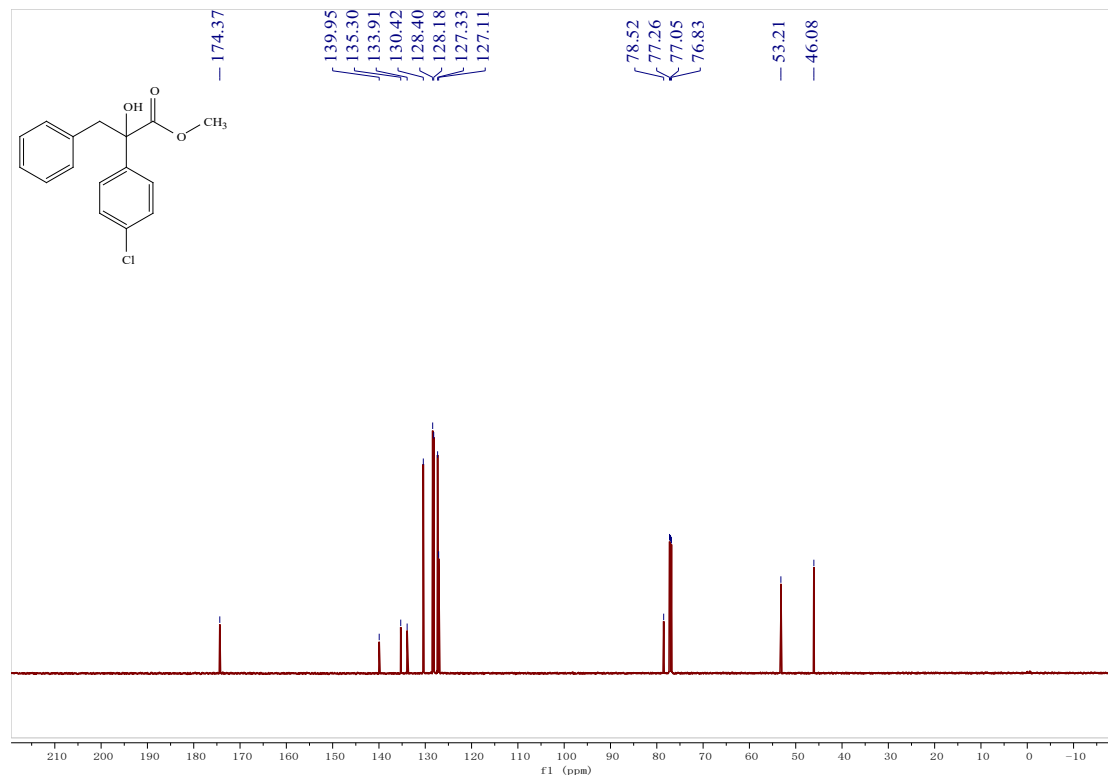
^{19}F NMR (376 MHz, Chloroform-*d*) of **3f**



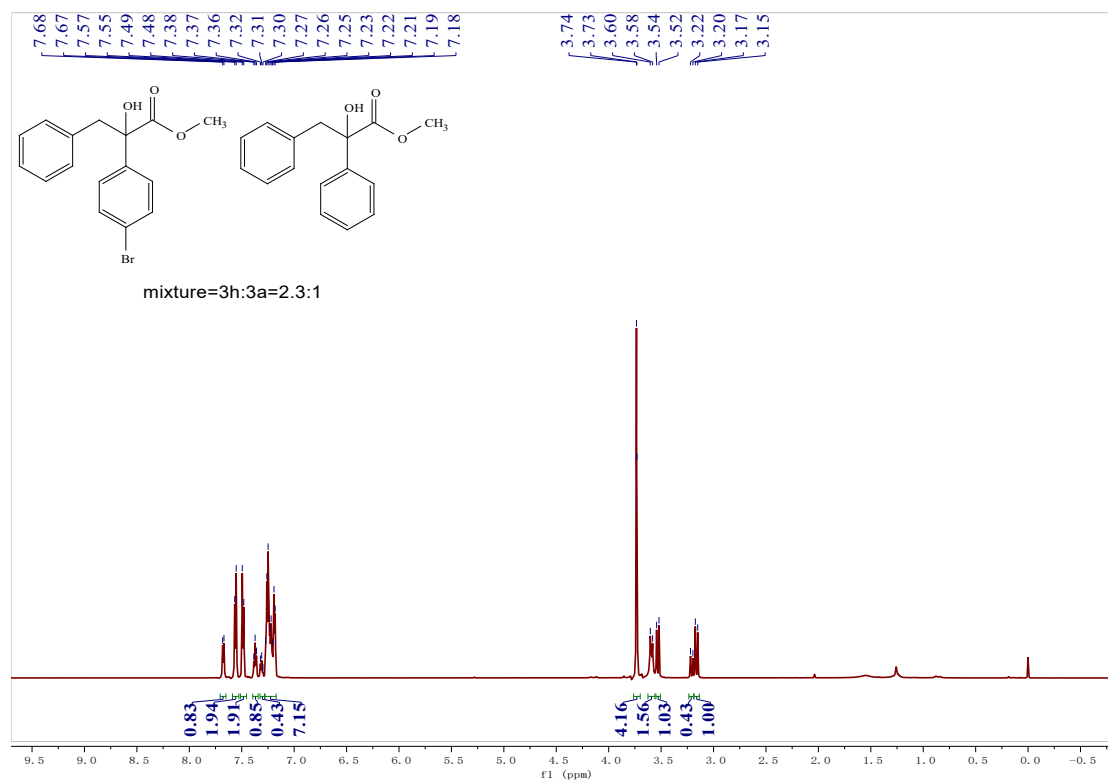
^1H NMR (600 MHz, Chloroform-*d*) of **3g**



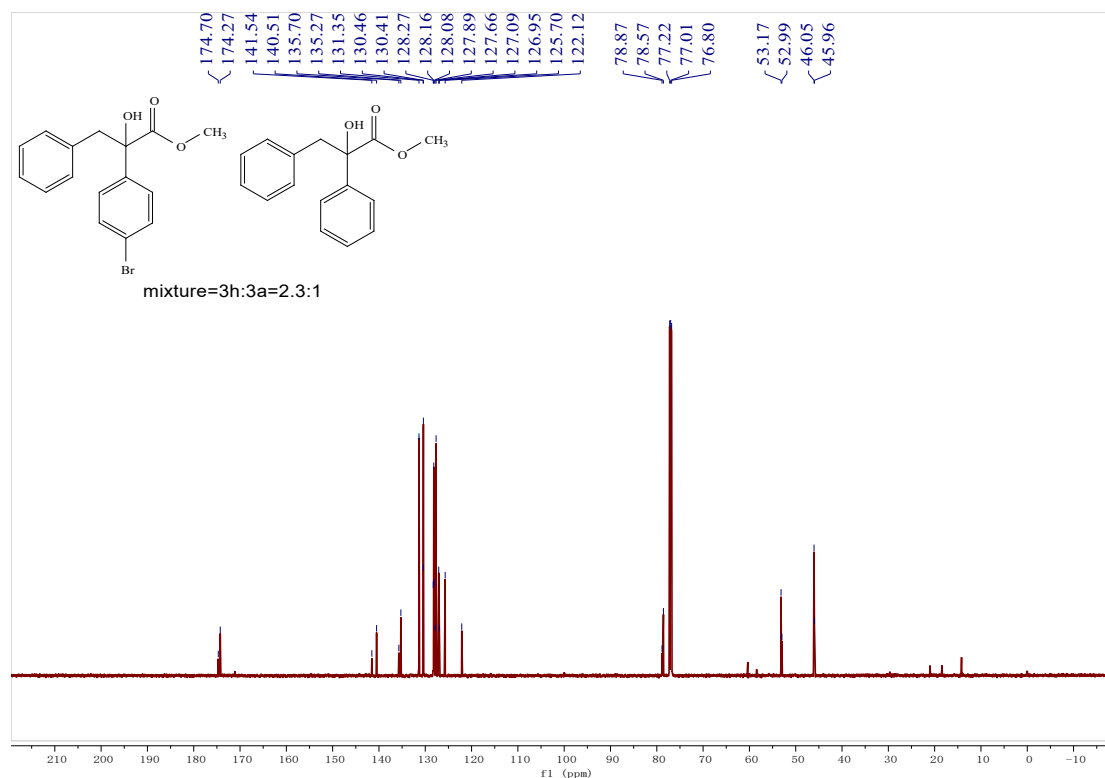
^{13}C NMR (151 MHz, Chloroform-*d*) of **3g**



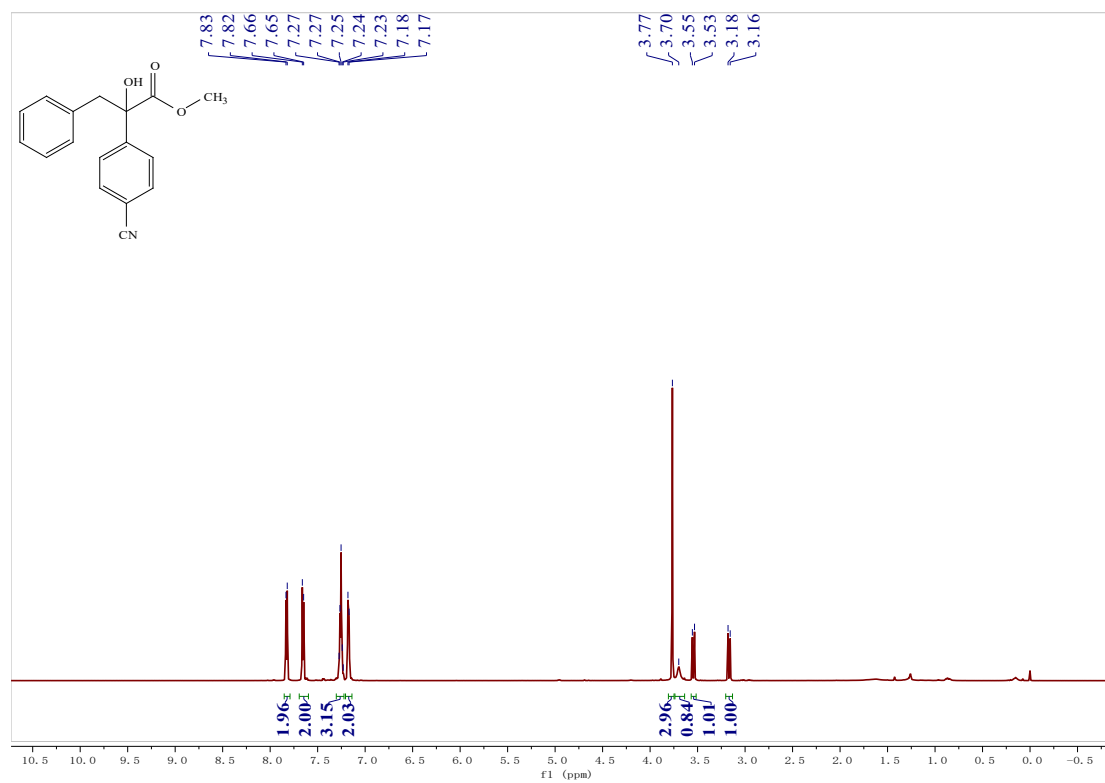
^1H NMR (600 MHz, Chloroform-*d*) of the mixture of **3h** and **3a**



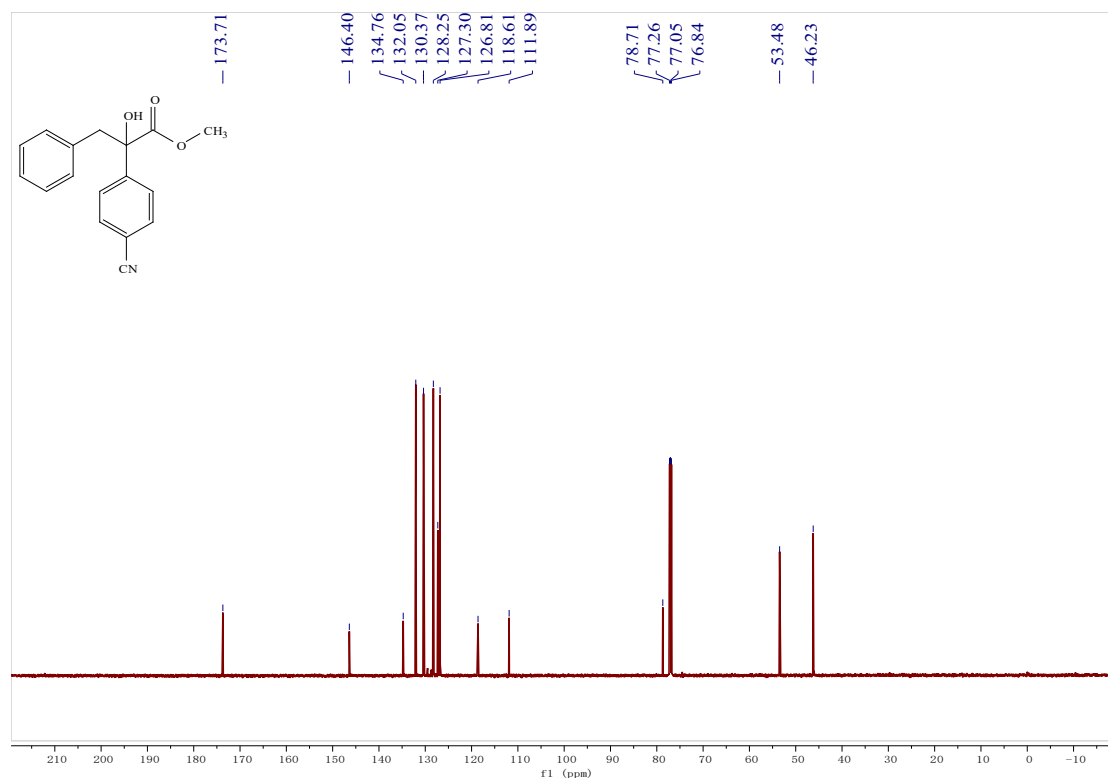
¹³C NMR (151 MHz, Chloroform-*d*) of the mixture of **3h** and **3a**



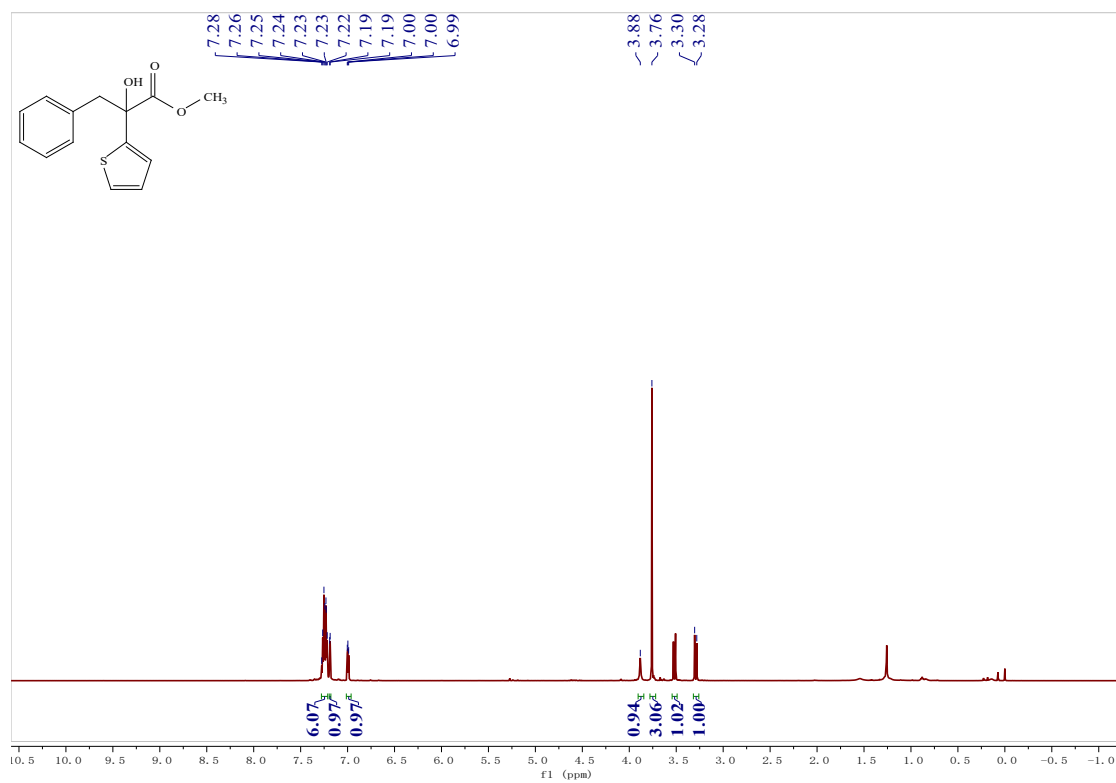
¹H NMR (600 MHz, Chloroform-*d*) of **3i**



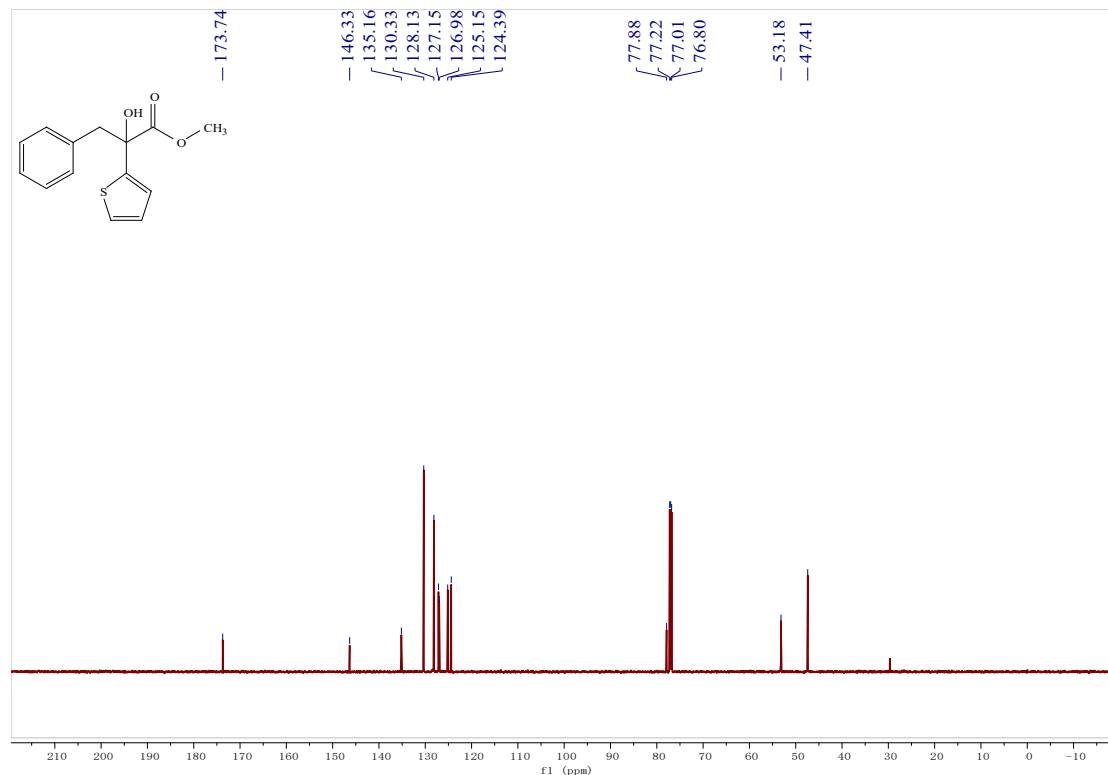
^{13}C NMR (151 MHz, Chloroform-*d*) of **3i**



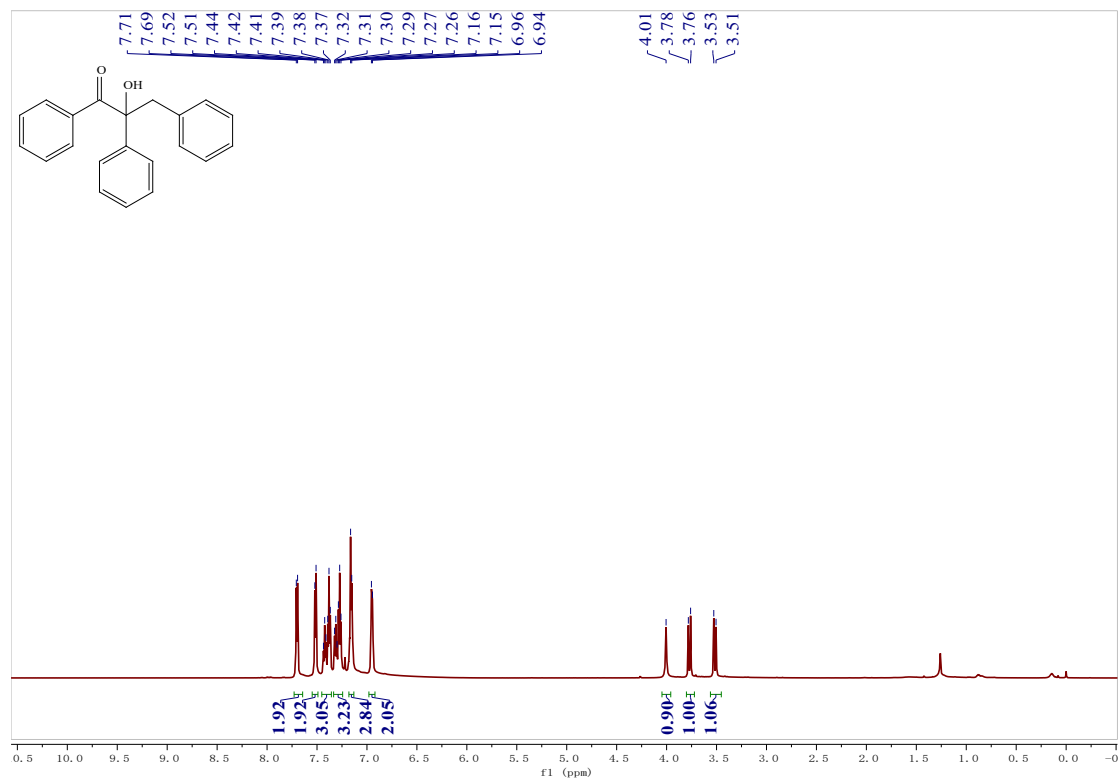
^1H NMR (600 MHz, Chloroform-*d*) of **3j**



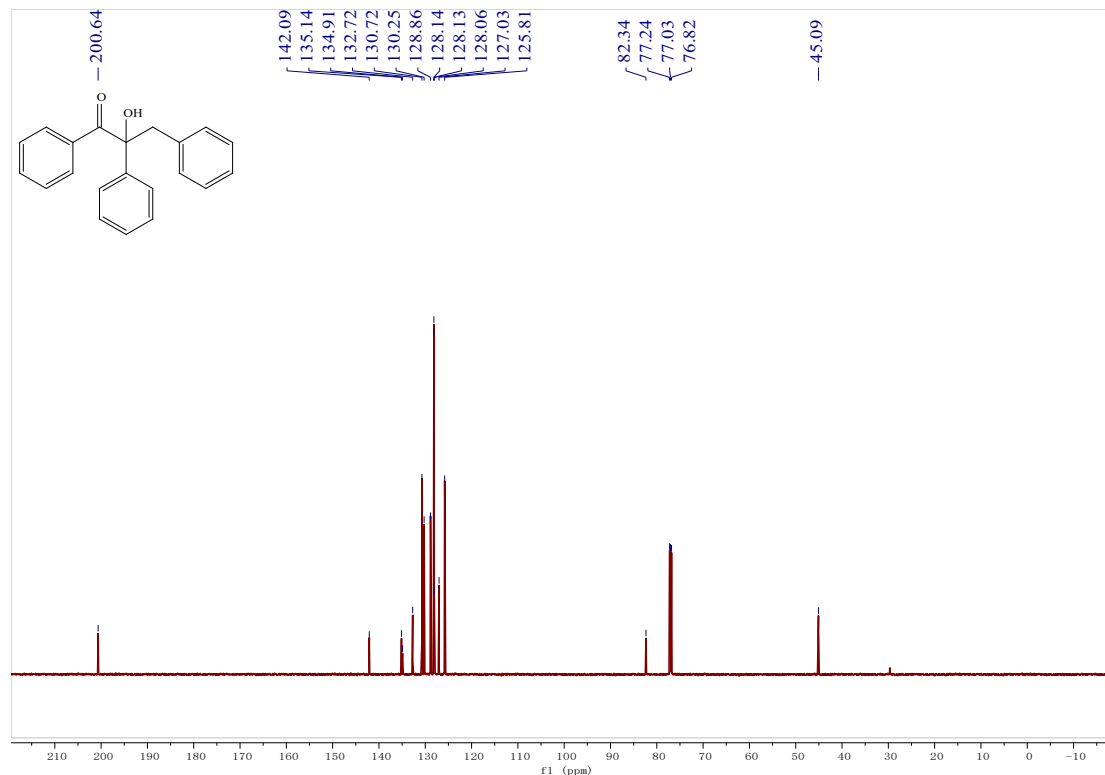
^{13}C NMR (151 MHz, Chloroform-*d*) of **3j**



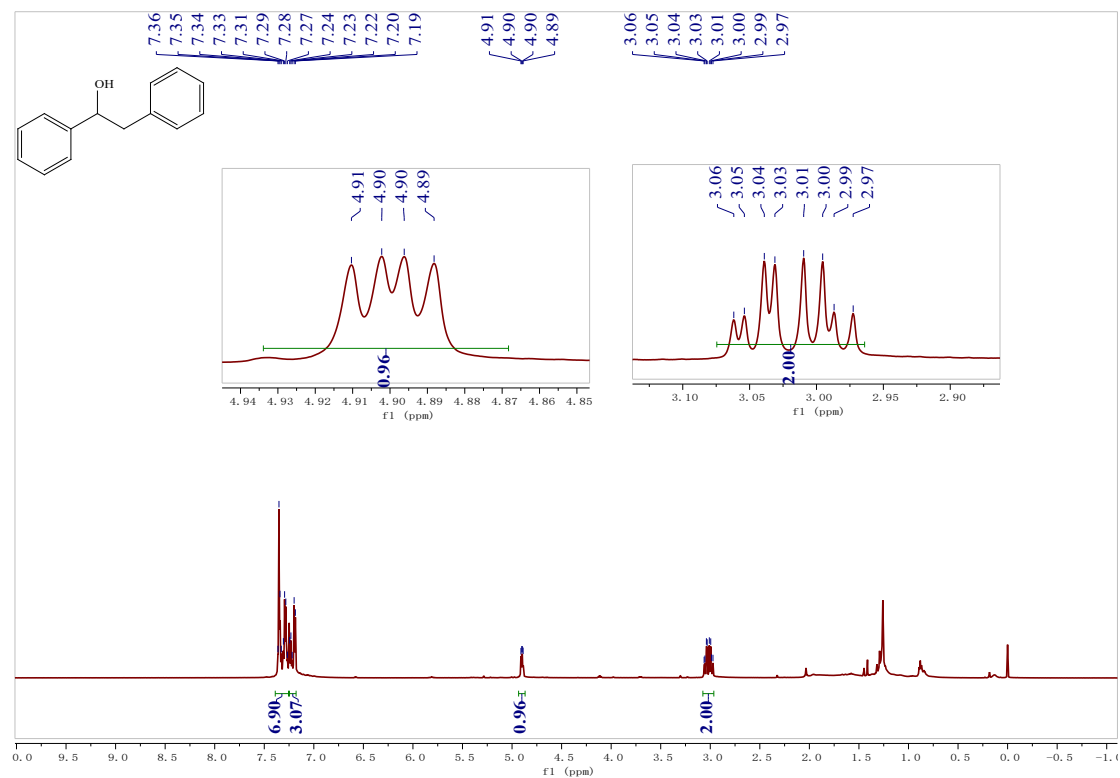
^1H NMR (600 MHz, Chloroform-*d*) of **3k**



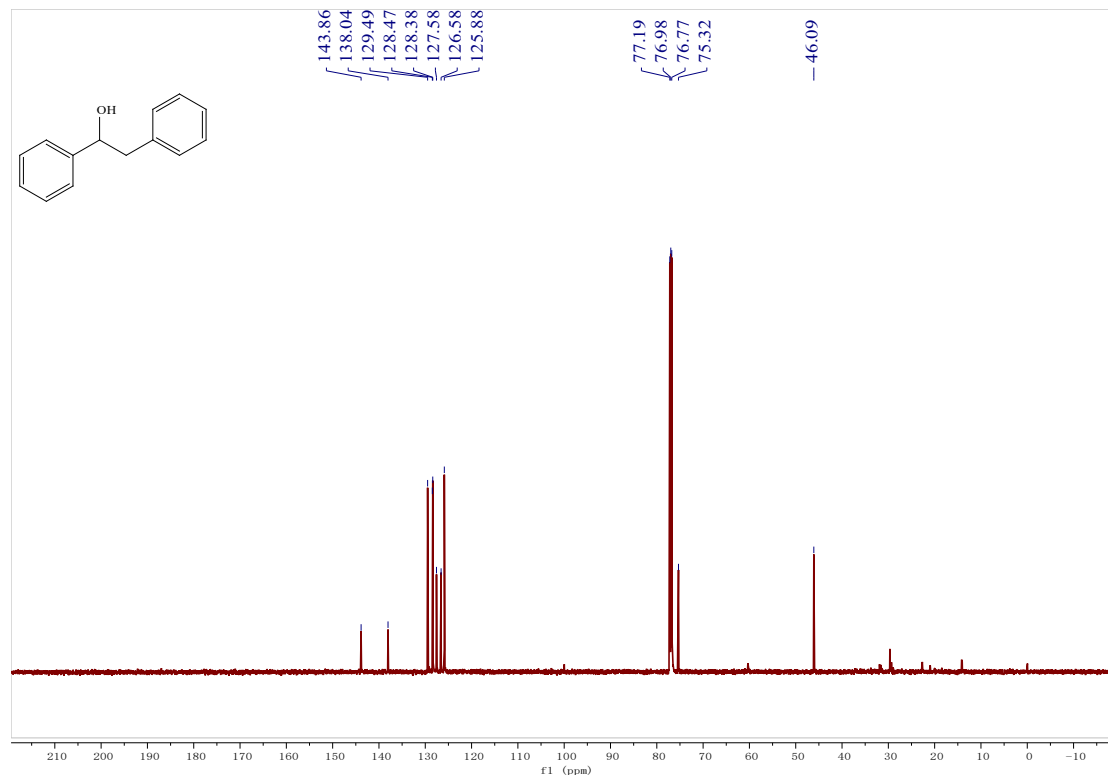
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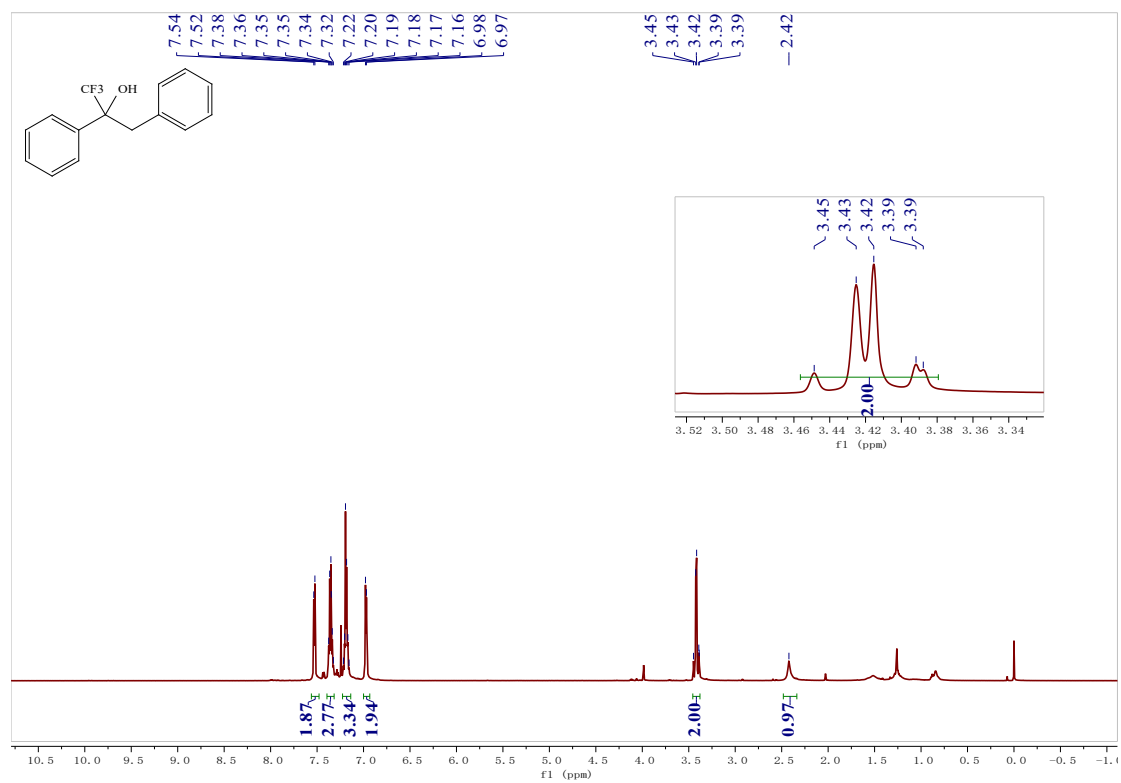
¹H NMR (600 MHz, Chloroform-*d*) of **3l**



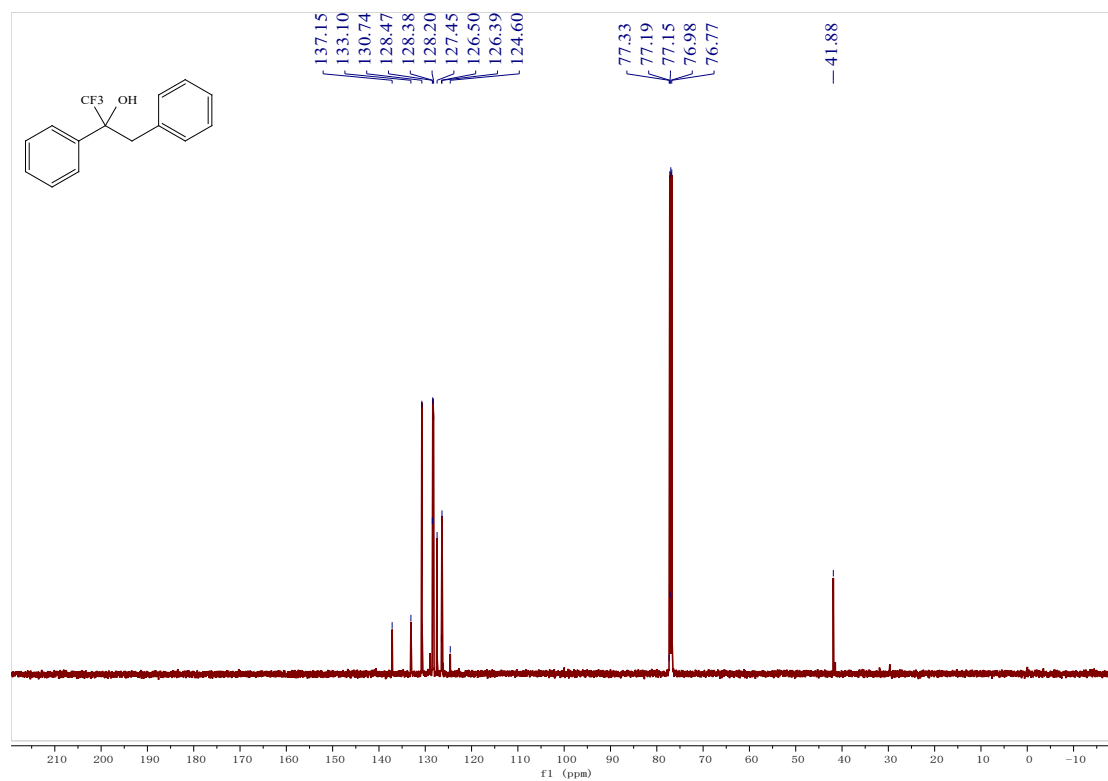
^{13}C NMR (151 MHz, Chloroform-*d*) of **3l**



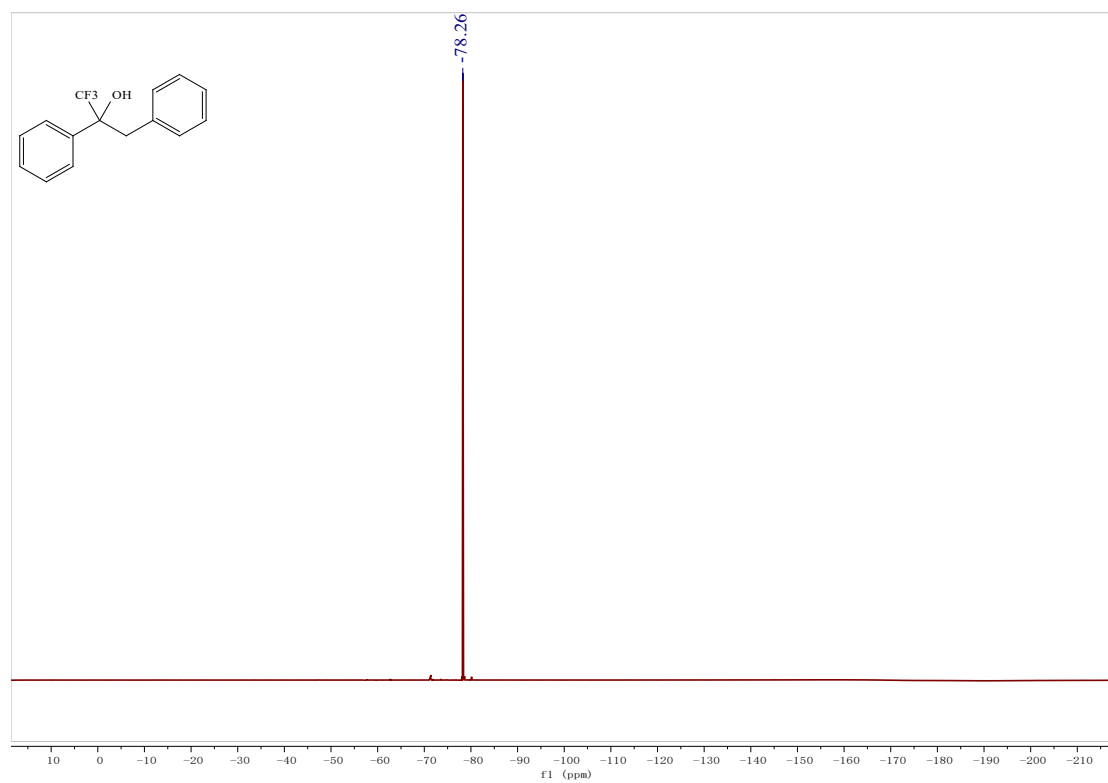
^1H NMR (600 MHz, Chloroform-*d*) of **3m**



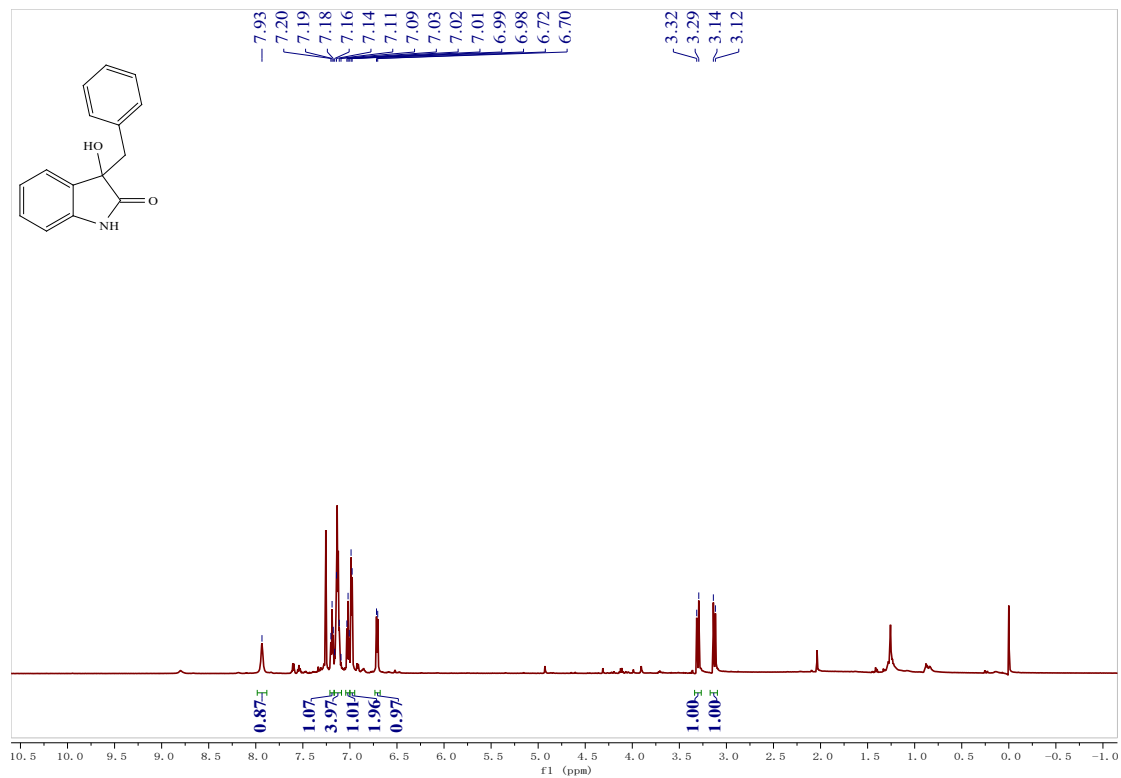
¹³C NMR (151 MHz, Chloroform-*d*) of **3m**



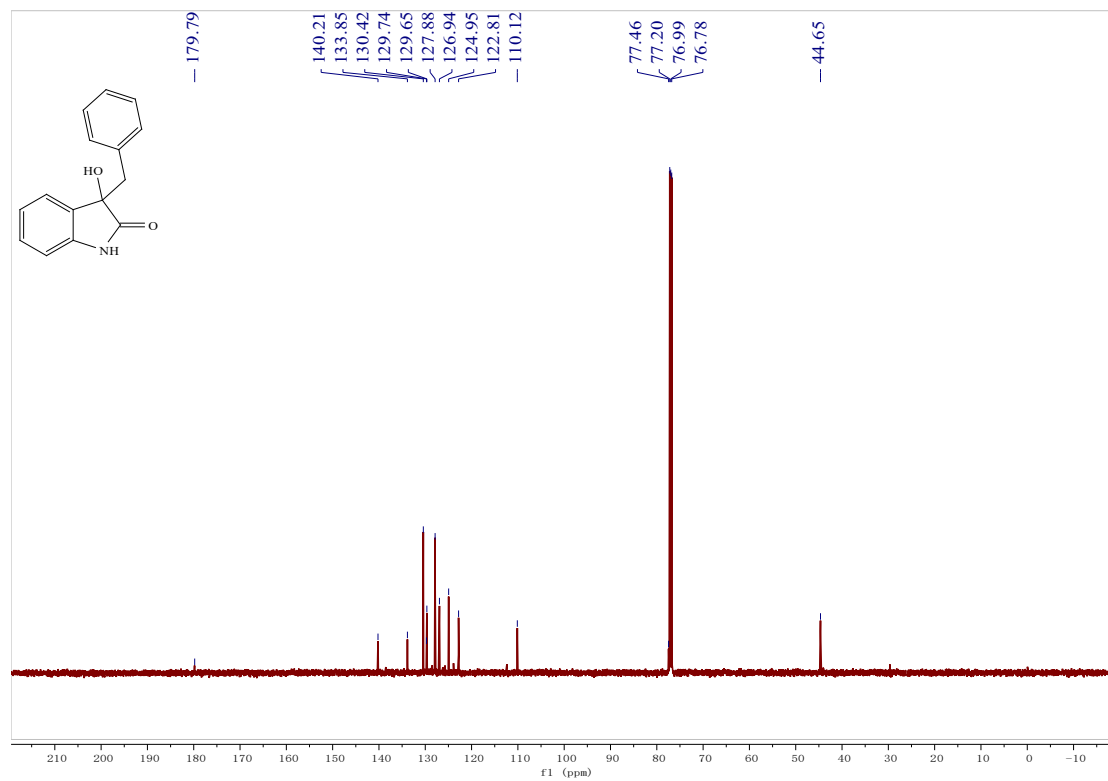
¹⁹F NMR (565 MHz, Chloroform-*d*) of **3m**



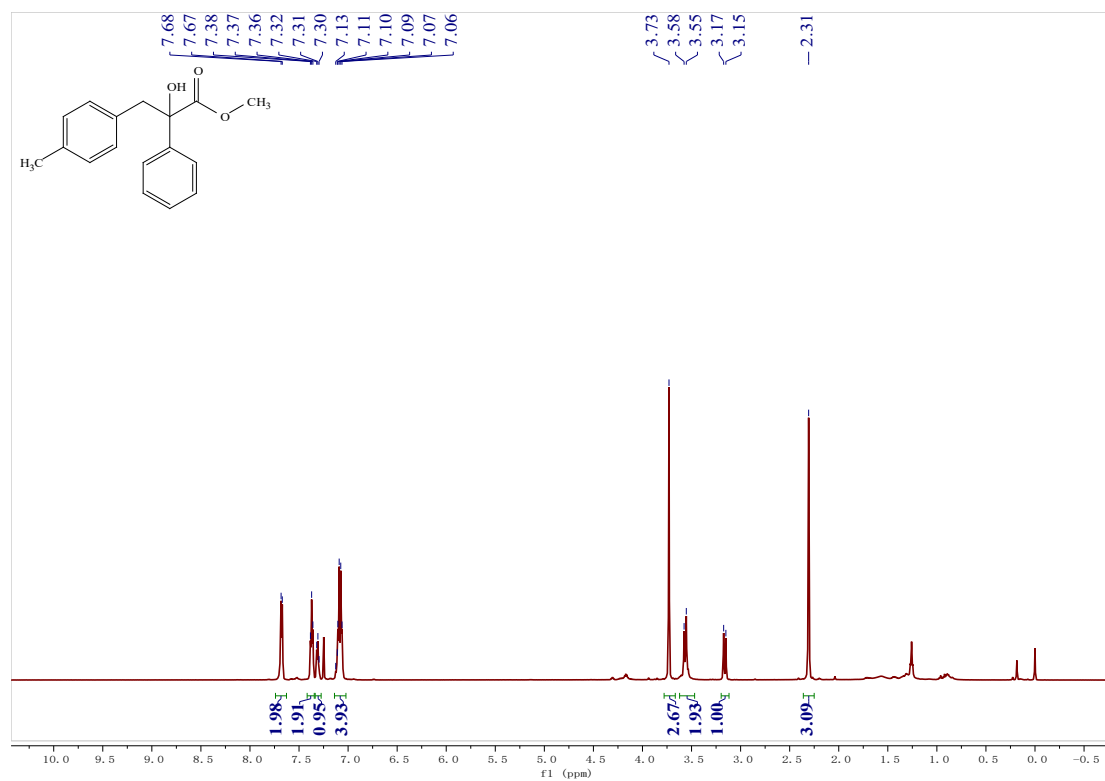
¹H NMR (600 MHz, Chloroform-*d*) of **3n**



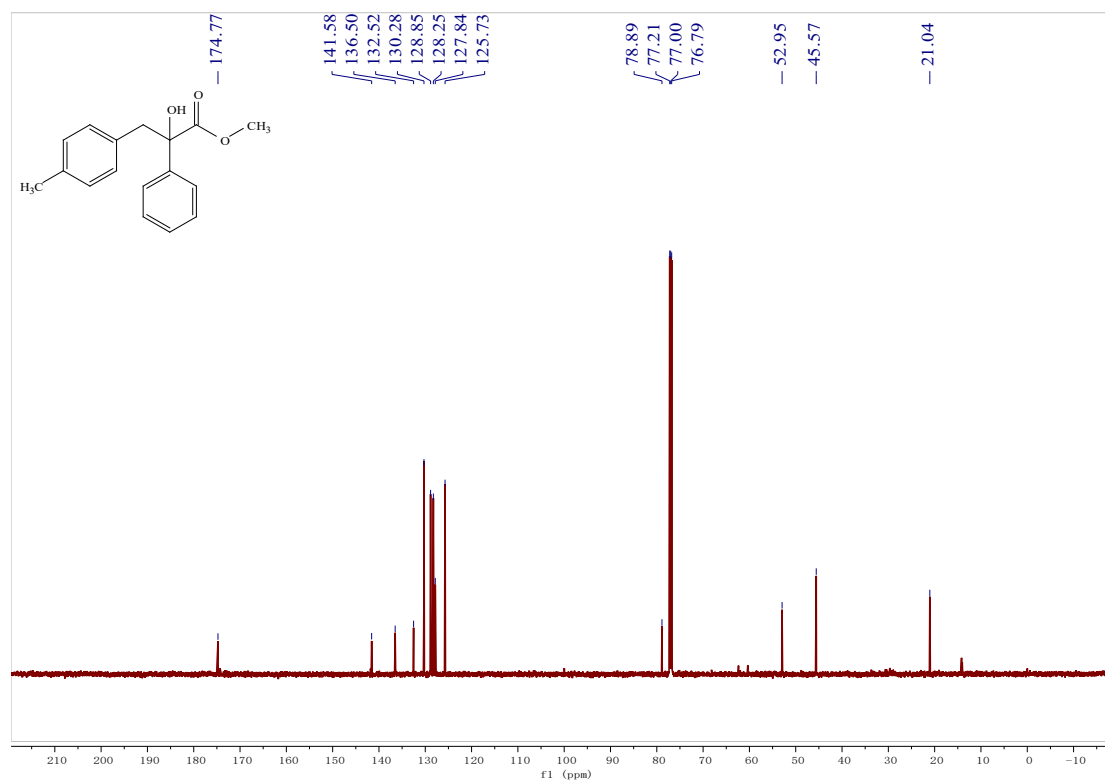
¹³C NMR (151 MHz, Chloroform-*d*) of **3n**



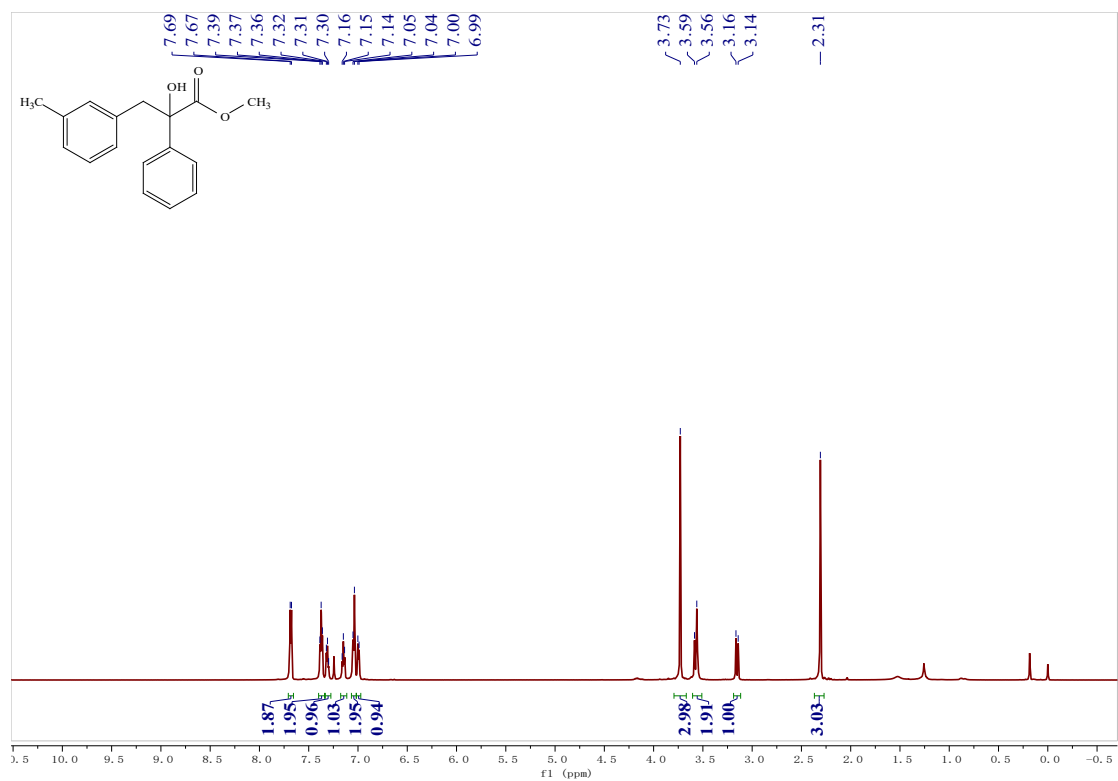
¹H NMR (600 MHz, Chloroform-*d*) of **3o**



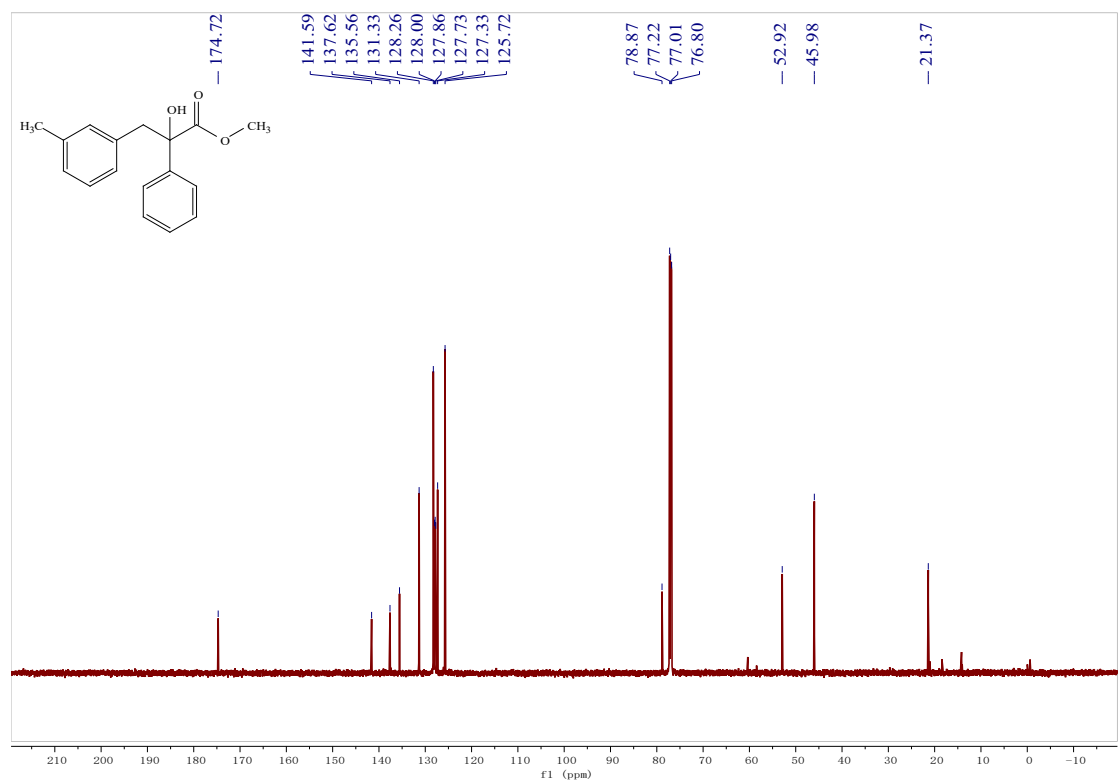
¹³C NMR (151 MHz, Chloroform-*d*) of **3o**



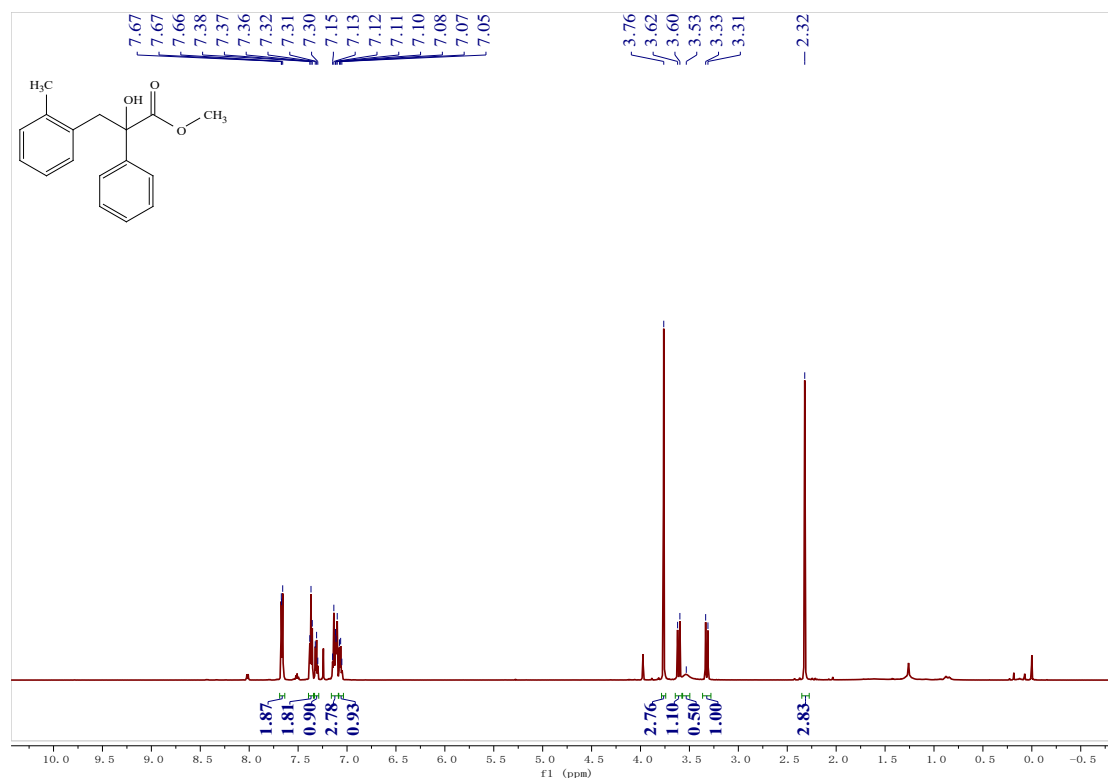
¹H NMR (600 MHz, Chloroform-*d*) of **3p**



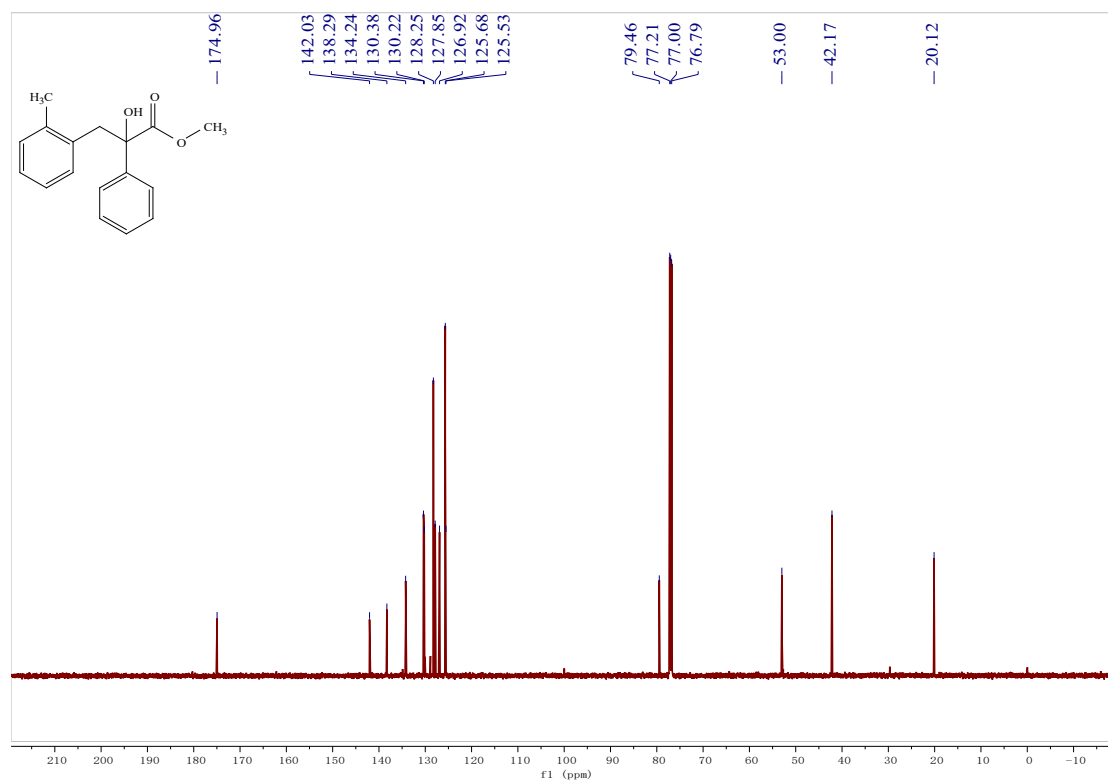
¹³C NMR (151 MHz, Chloroform-*d*) of **3p**



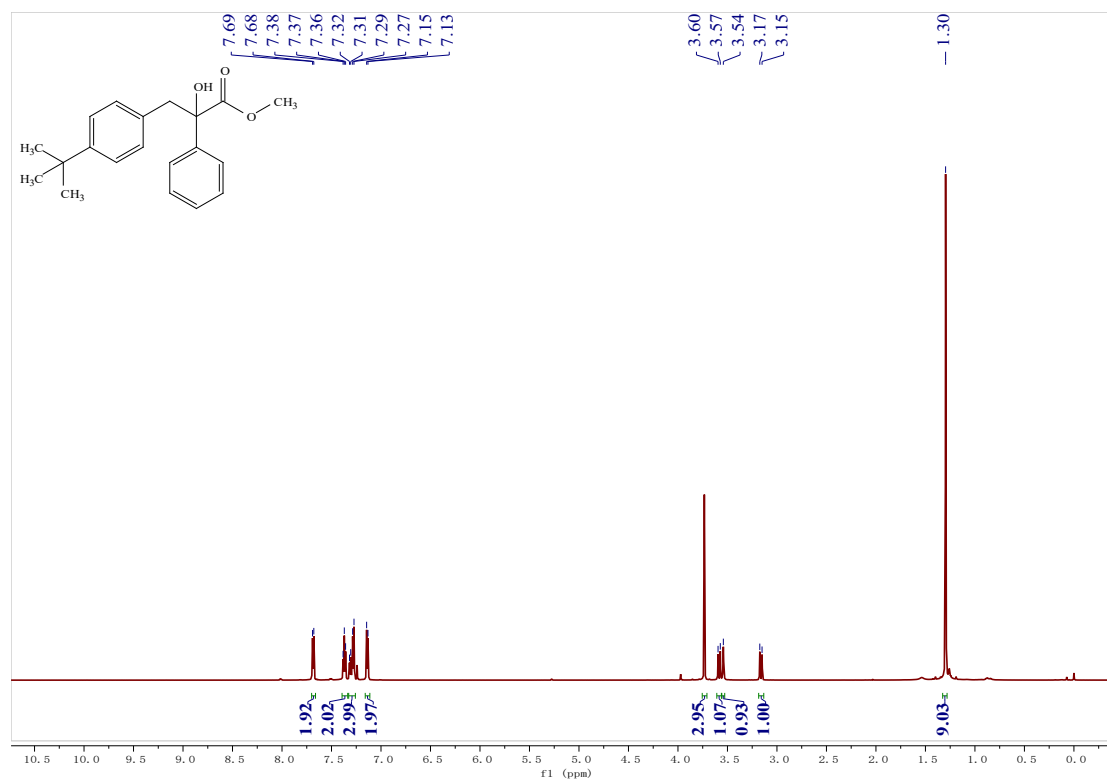
¹H NMR (600 MHz, Chloroform-*d*) of **3q**



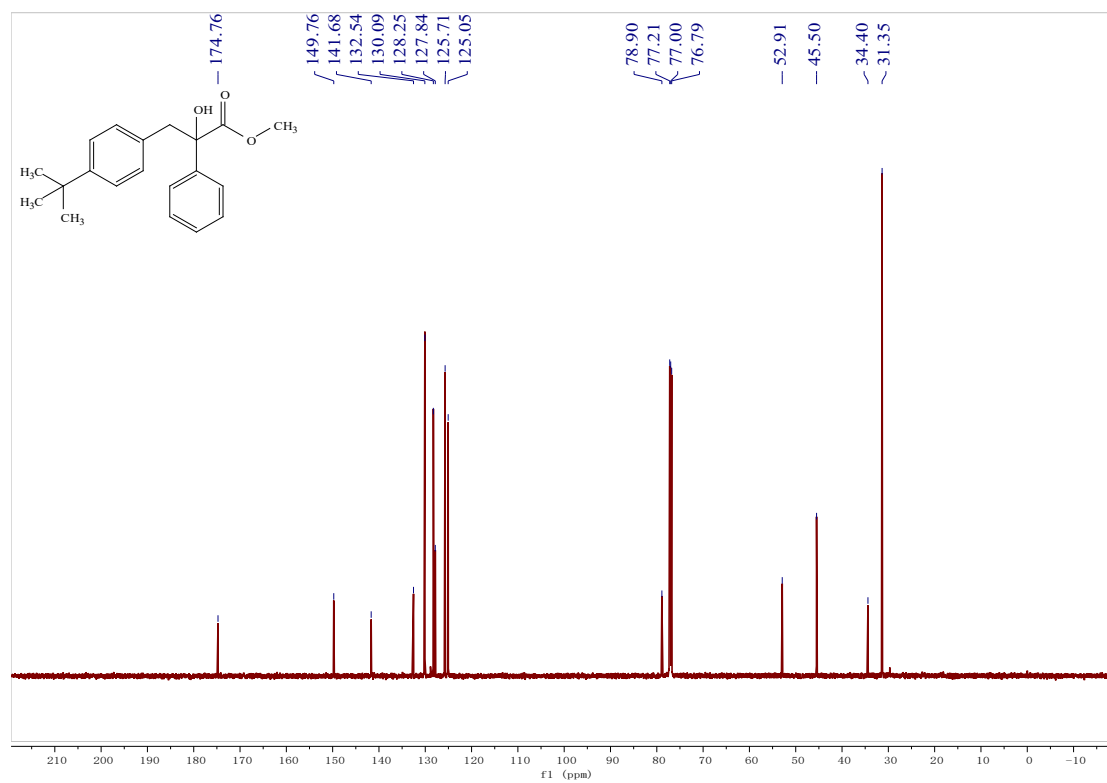
¹³C NMR (151 MHz, Chloroform-*d*) of **3q**



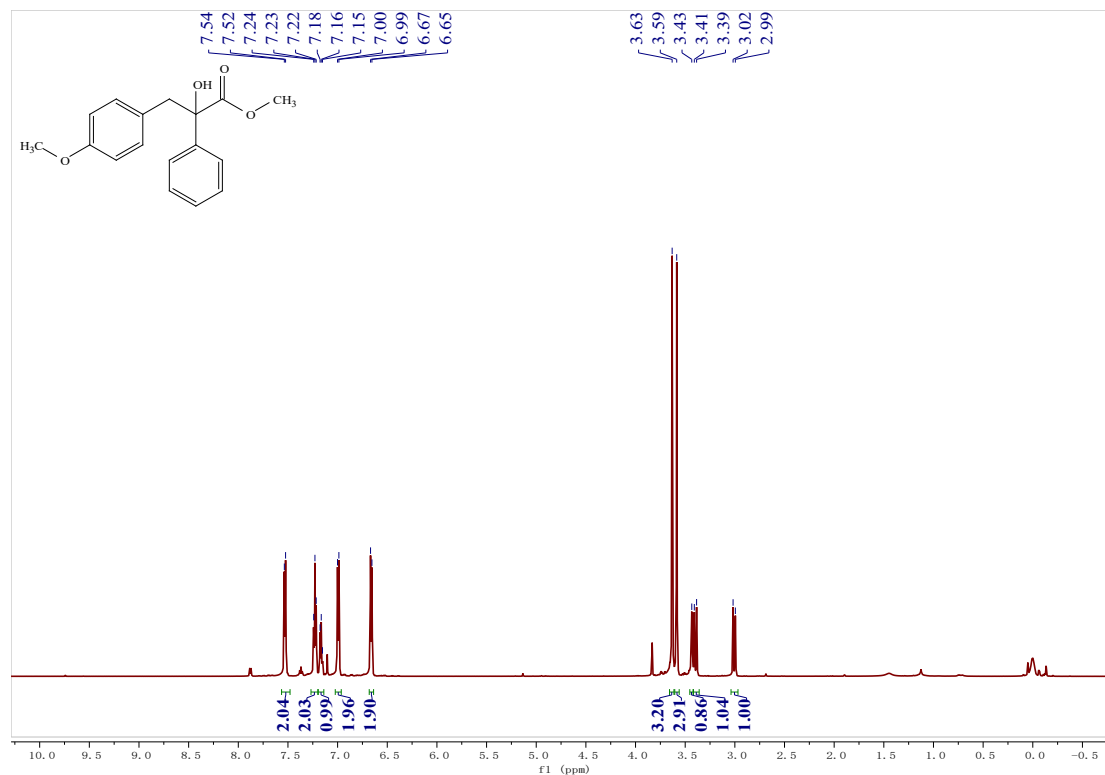
¹H NMR (600 MHz, Chloroform-*d*) of **3r**



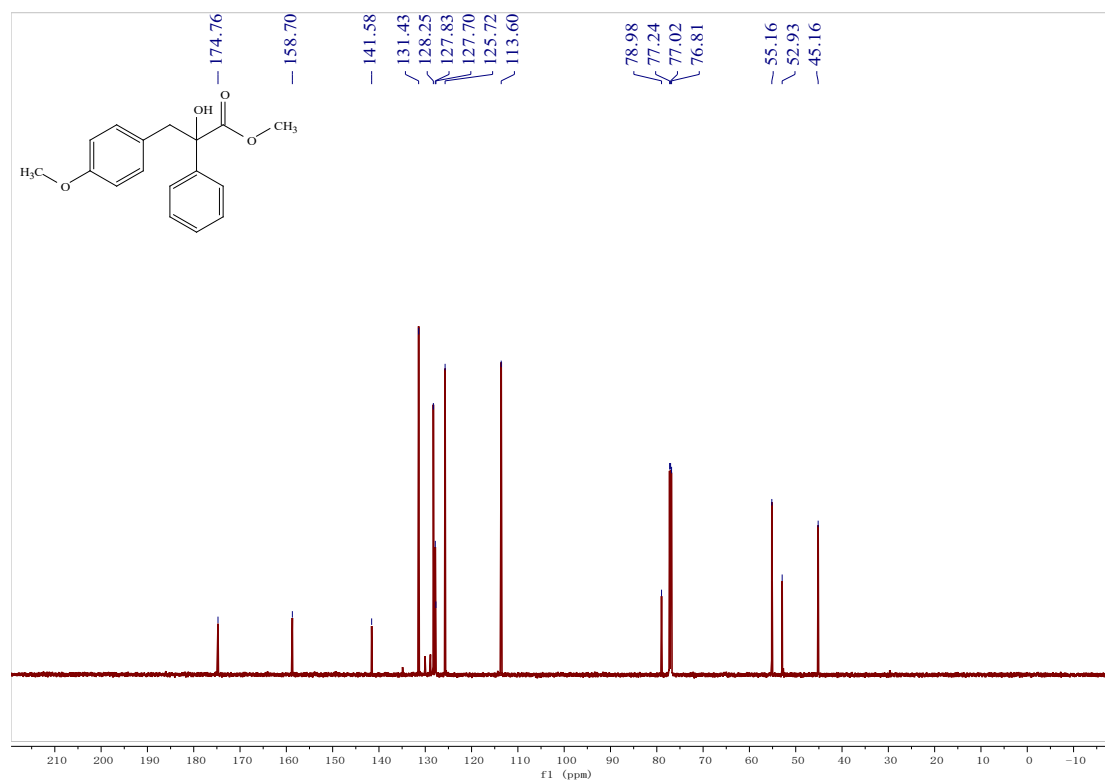
¹³C NMR (151 MHz, Chloroform-*d*) of **3r**



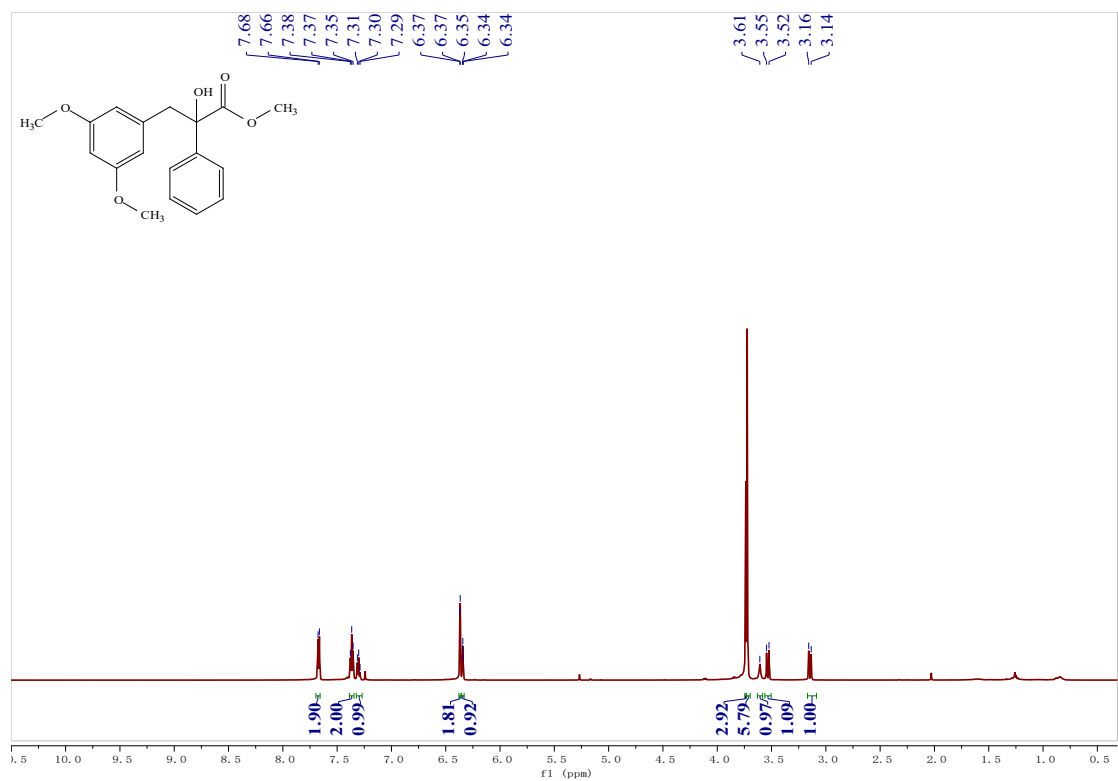
¹H NMR (600 MHz, Chloroform-*d*) of **3s**



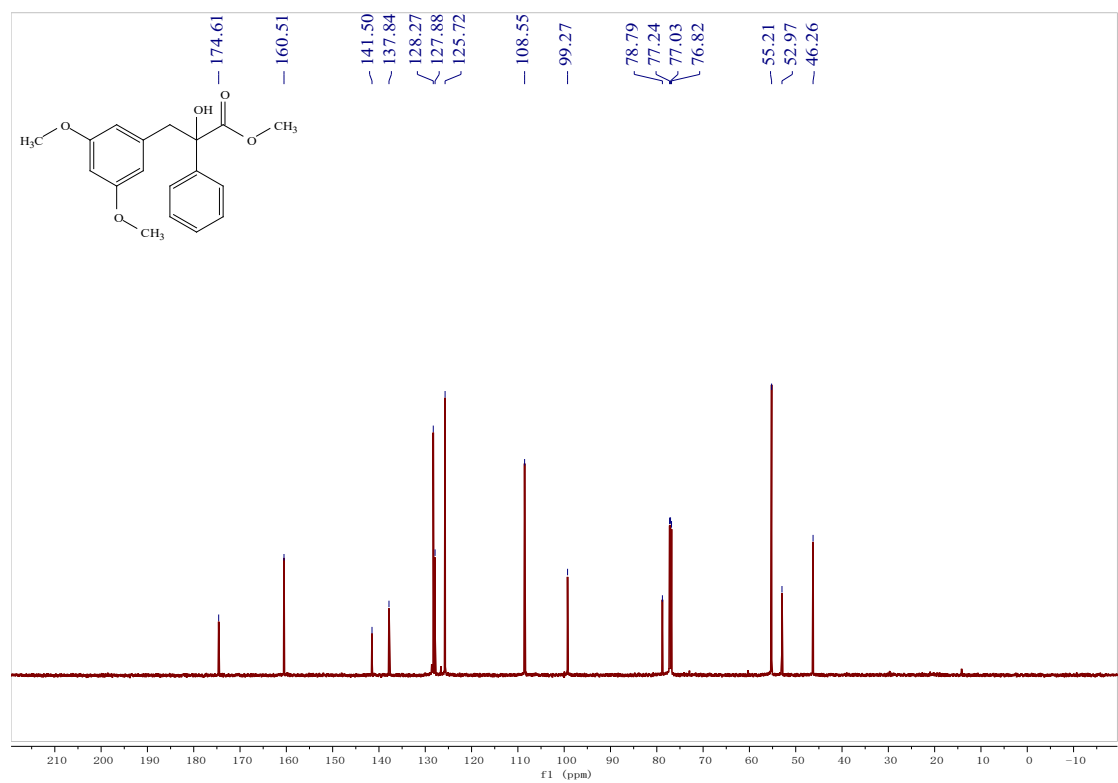
¹³C NMR (151 MHz, Chloroform-*d*) of **3s**



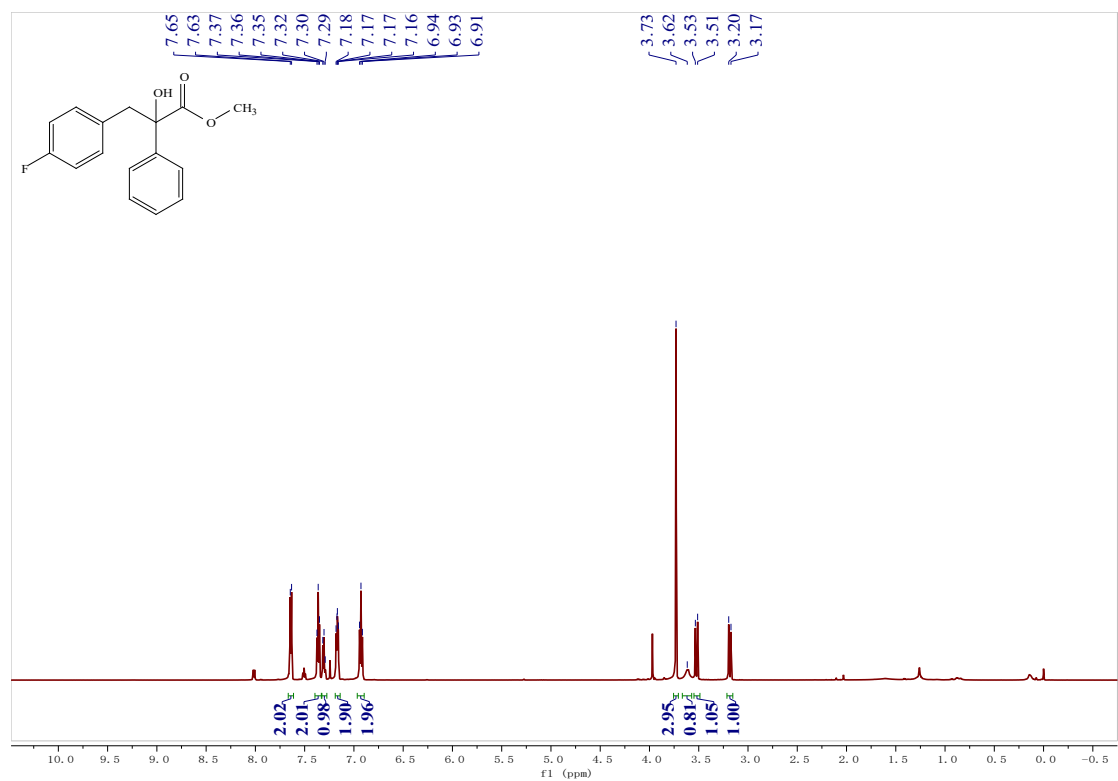
¹H NMR (600 MHz, Chloroform-*d*) of **3t**



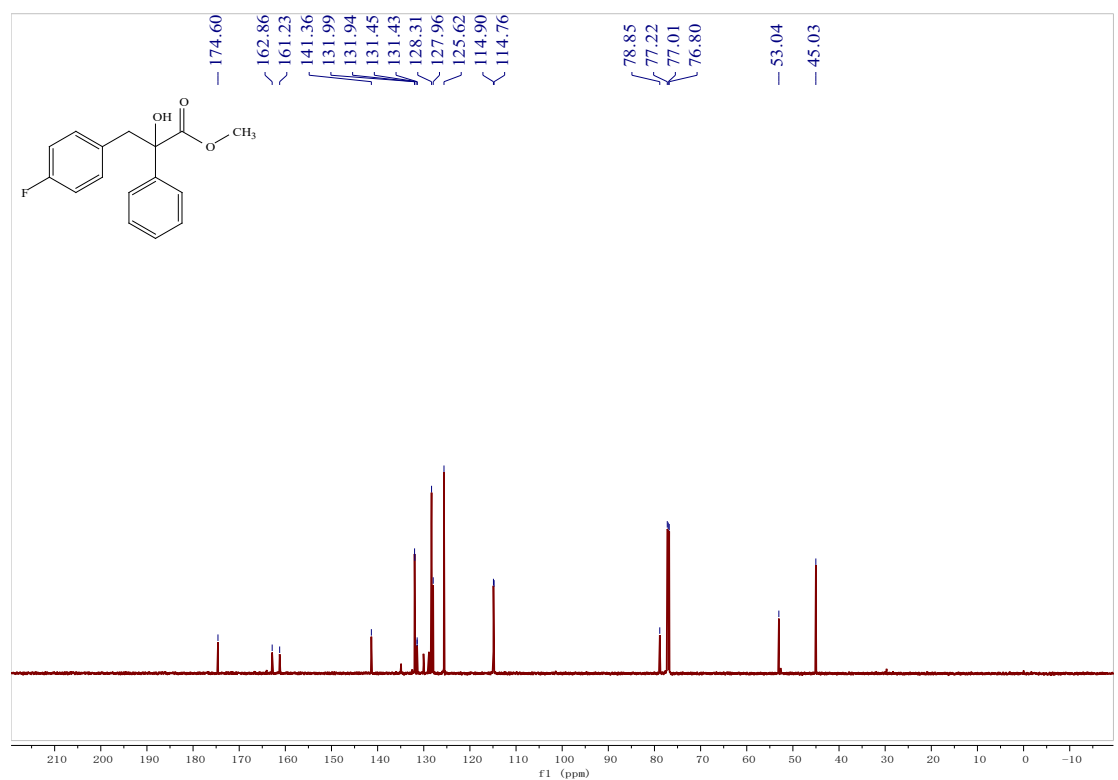
¹³C NMR (151 MHz, Chloroform-*d*) of **3t**



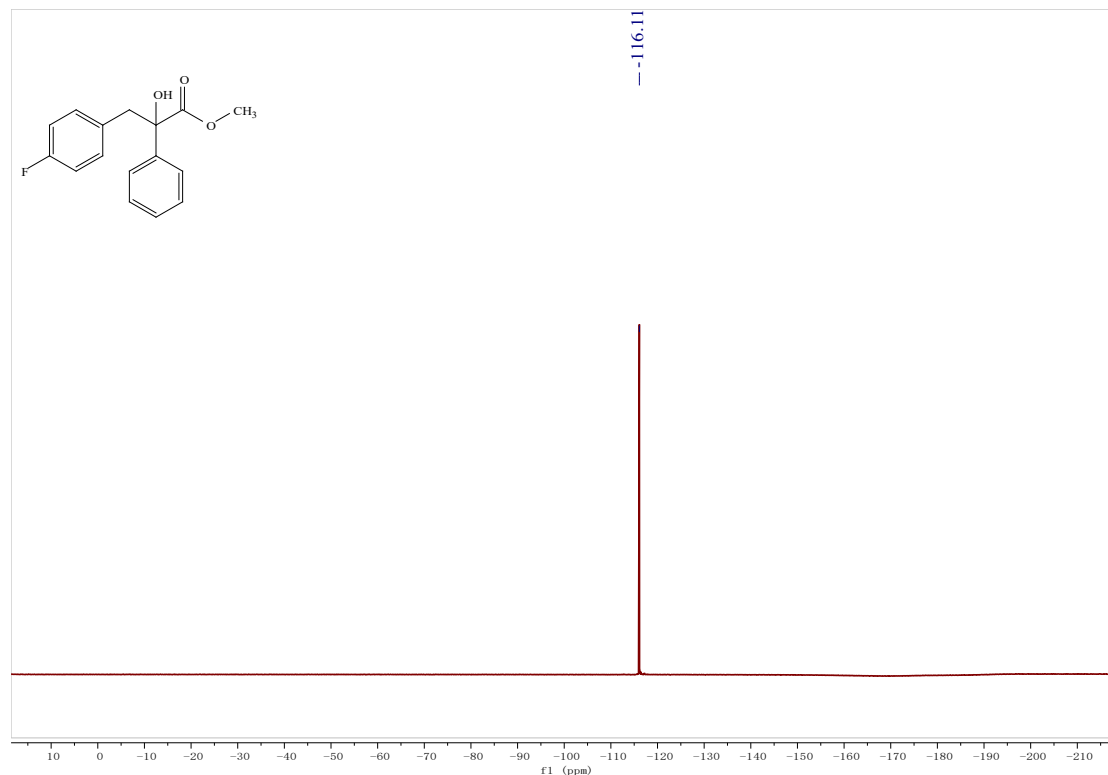
¹H NMR (600 MHz, Chloroform-*d*) of **3u**



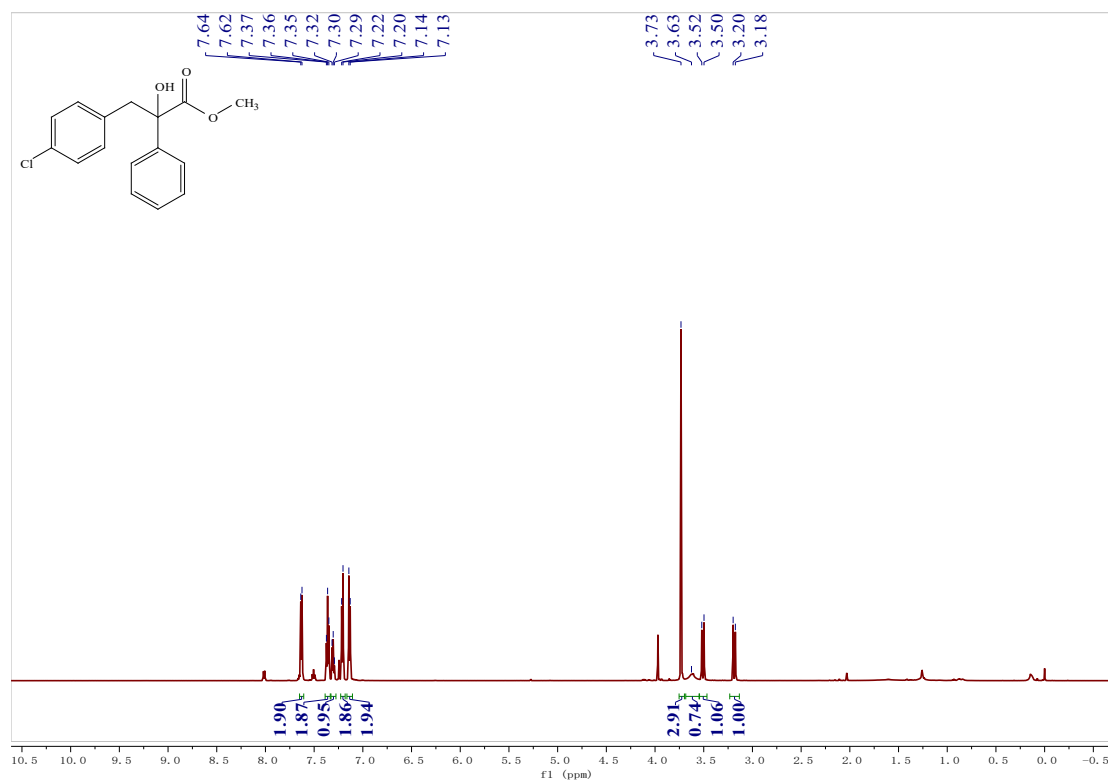
¹³C NMR (151 MHz, Chloroform-*d*) of **3u**



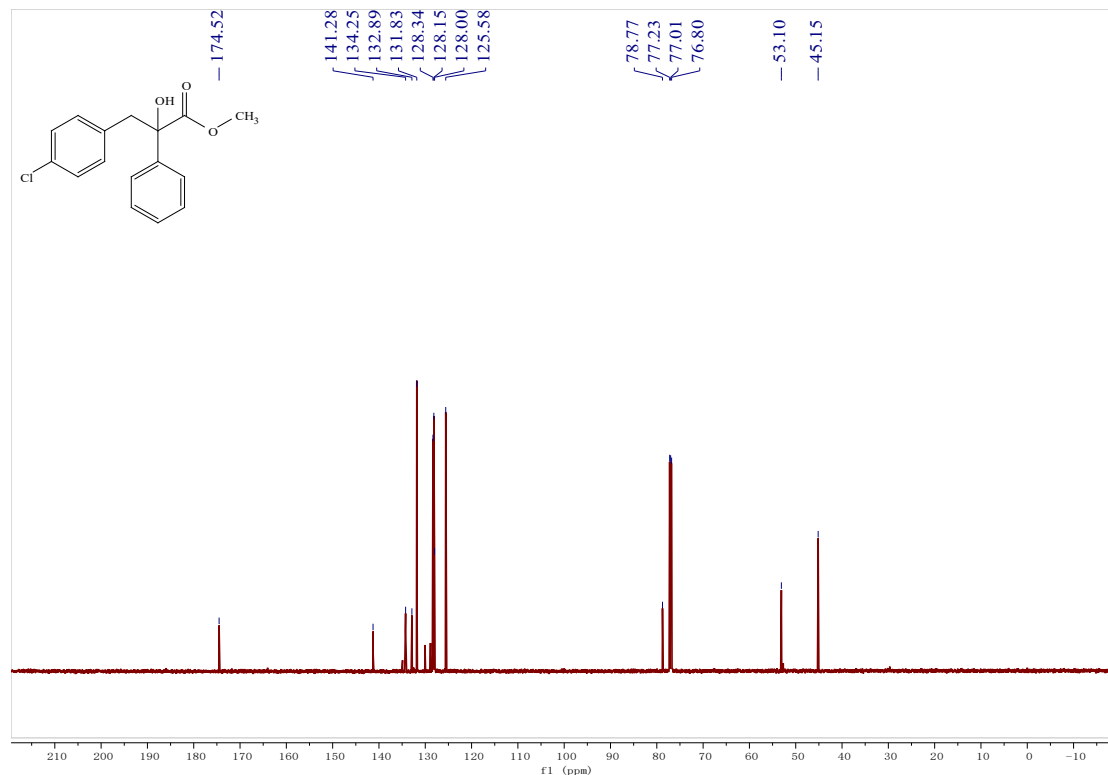
^{19}F NMR (565 MHz, Chloroform-*d*) of **3u**



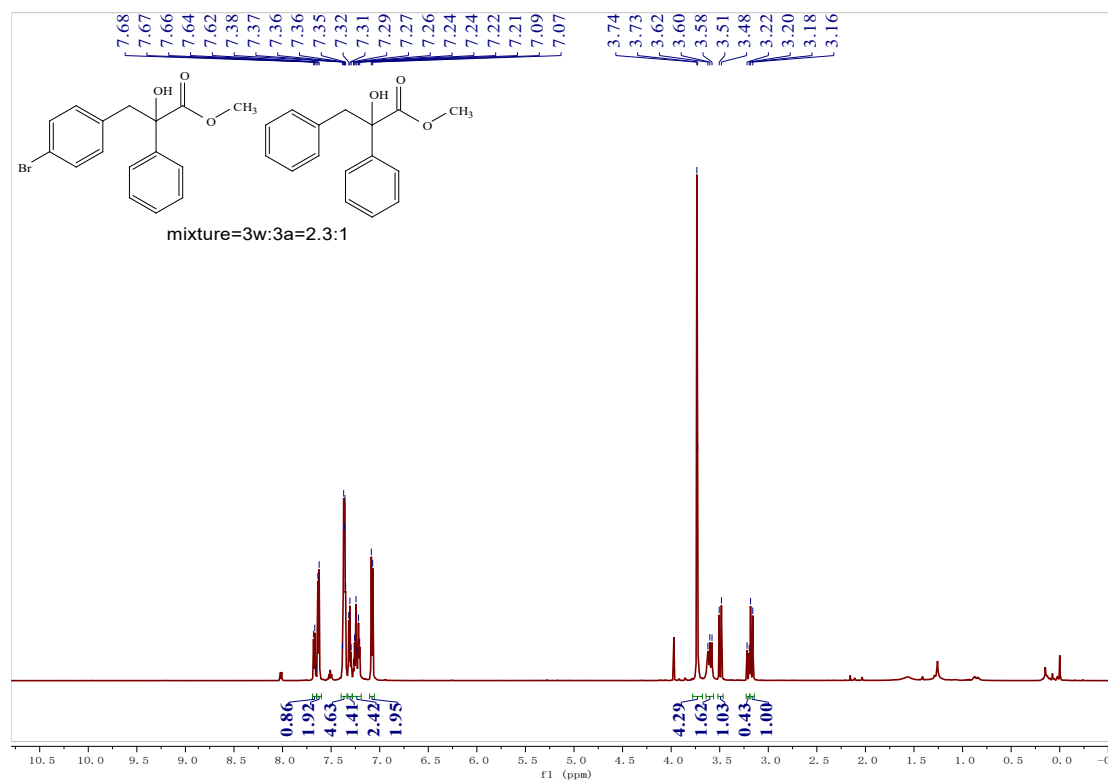
^1H NMR (600 MHz, Chloroform-*d*) of **3v**



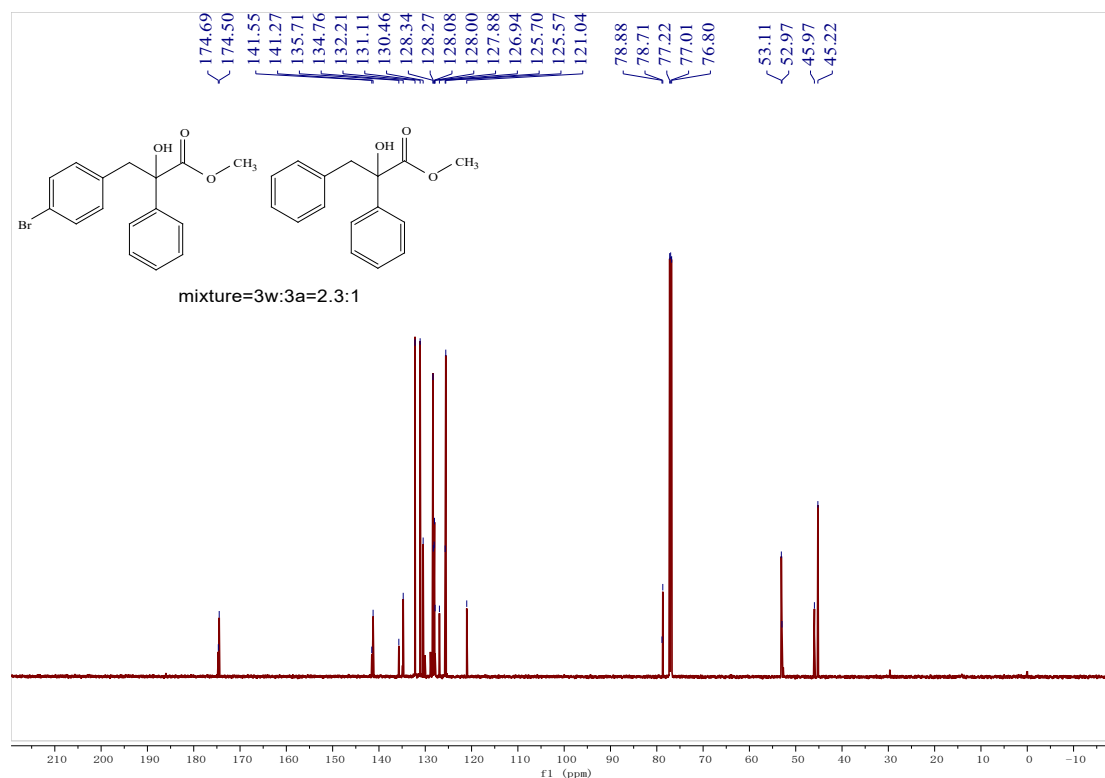
^{13}C NMR (151 MHz, Chloroform-*d*) of **3v**



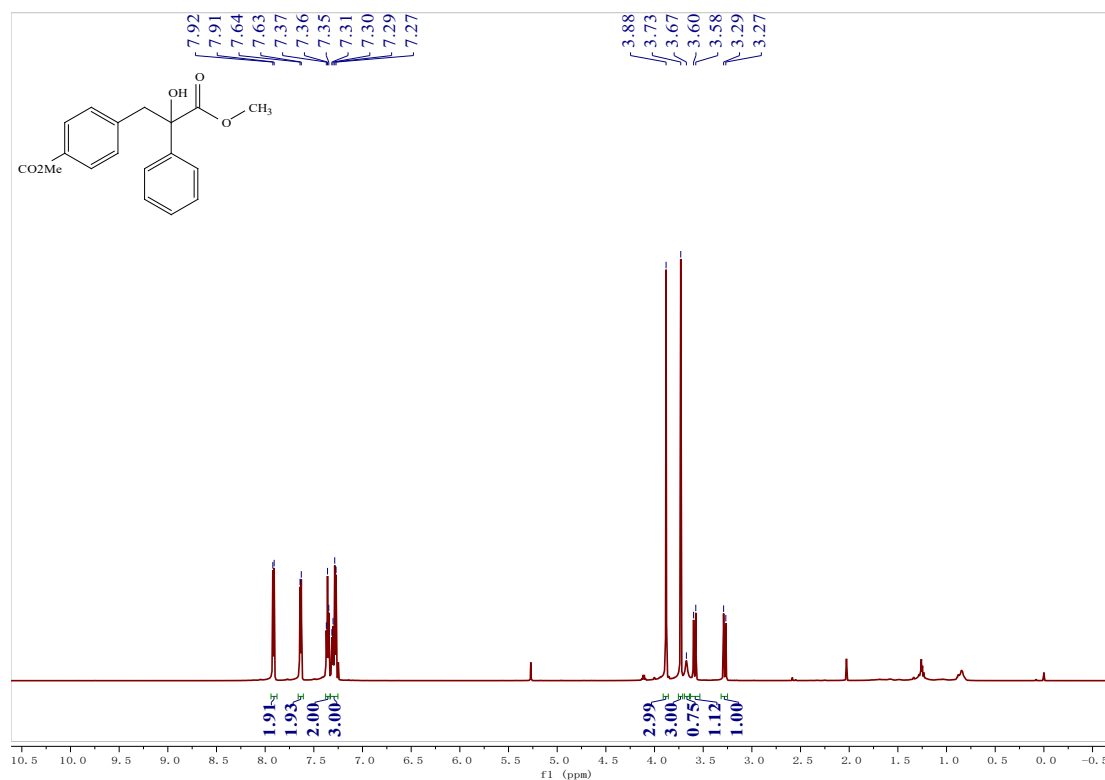
^1H NMR (600 MHz, Chloroform-*d*) of the mixture of **3w** and **3a**



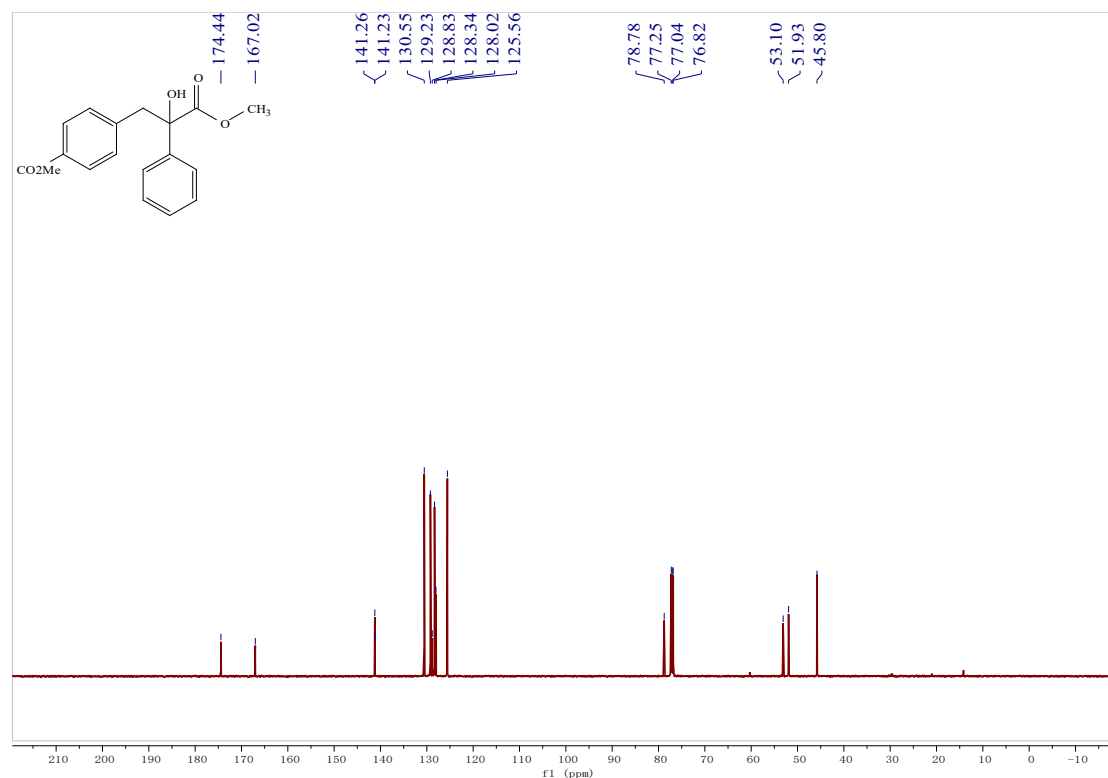
^{13}C NMR (151 MHz, Chloroform-*d*) of the mixture of **3w** and **3a**



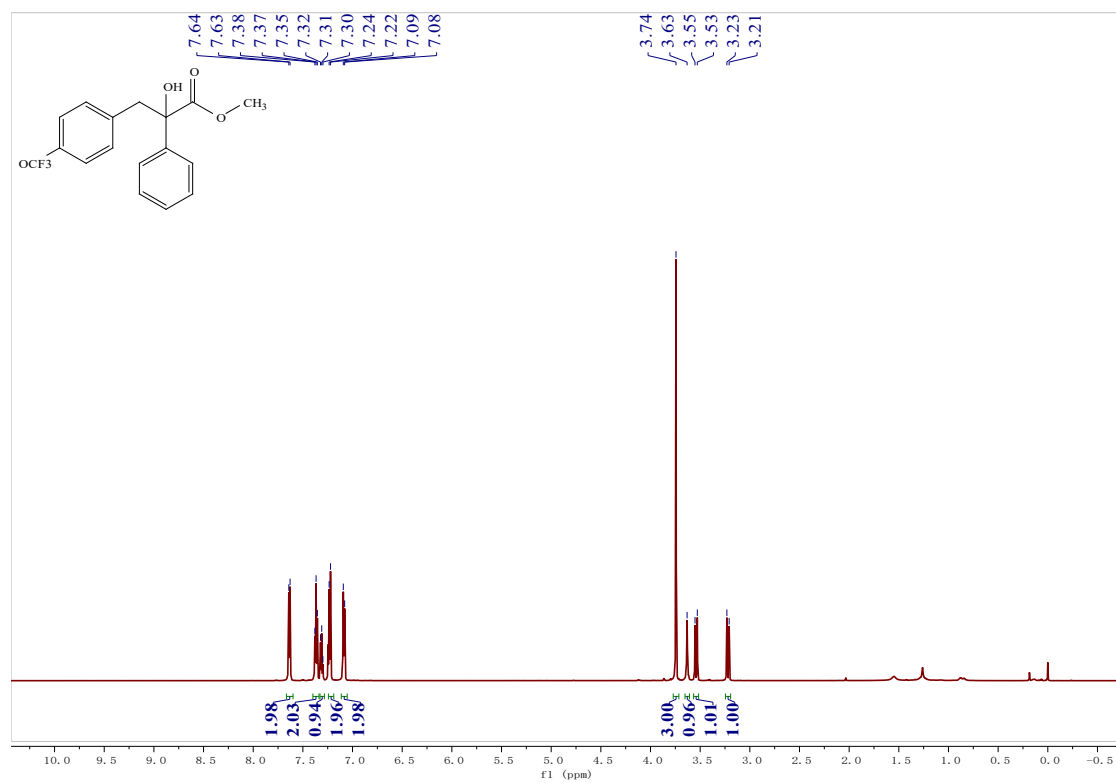
^1H NMR (600 MHz, Chloroform-*d*) of **3x**



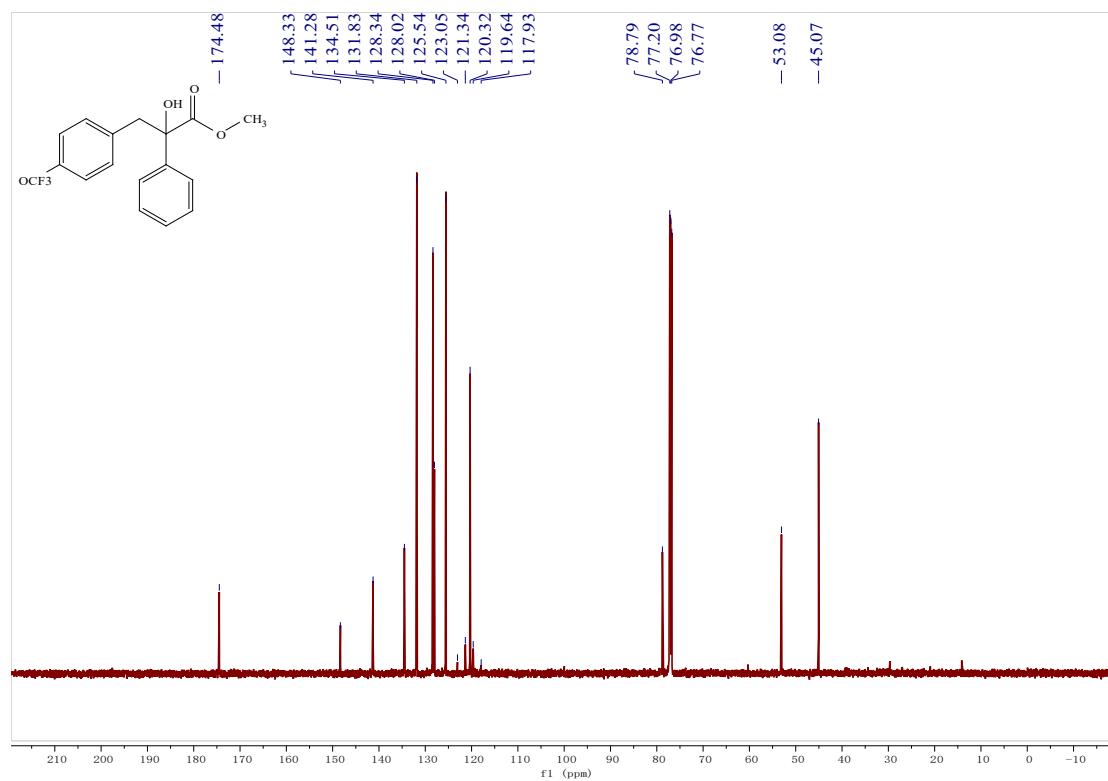
^{13}C NMR (151 MHz, Chloroform-*d*) of **3x**



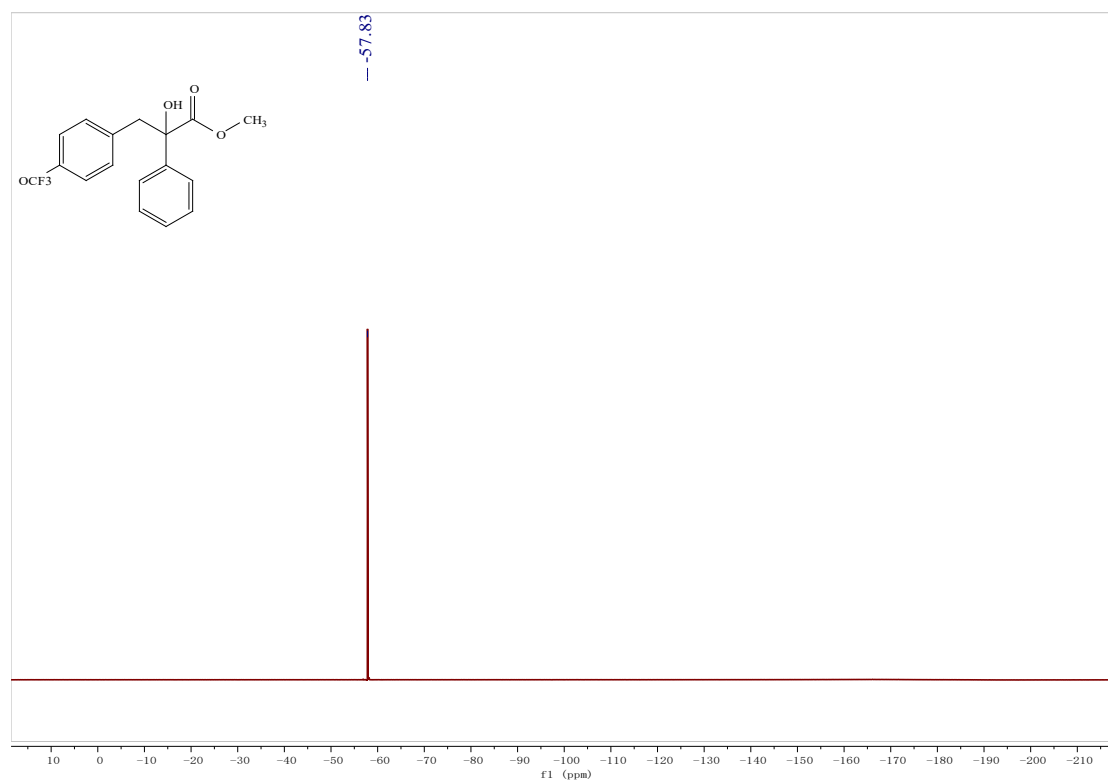
^1H NMR (600 MHz, Chloroform-*d*) of **3y**



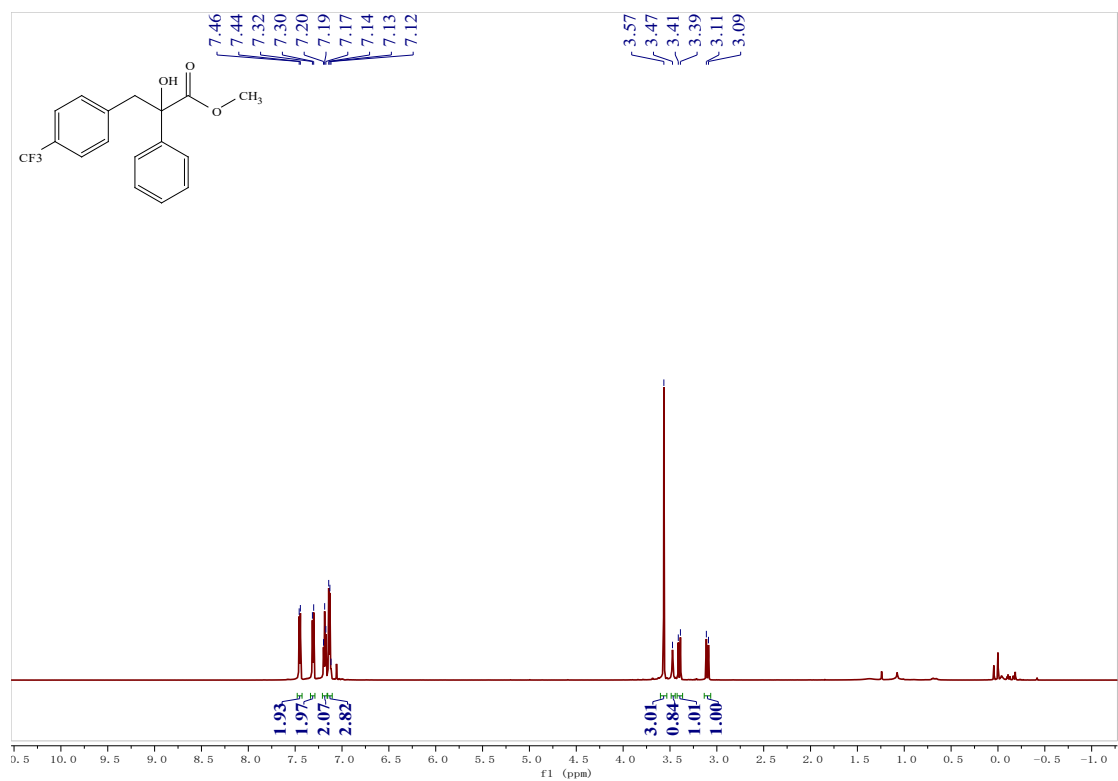
¹³C NMR (151 MHz, Chloroform-*d*) of **3y**



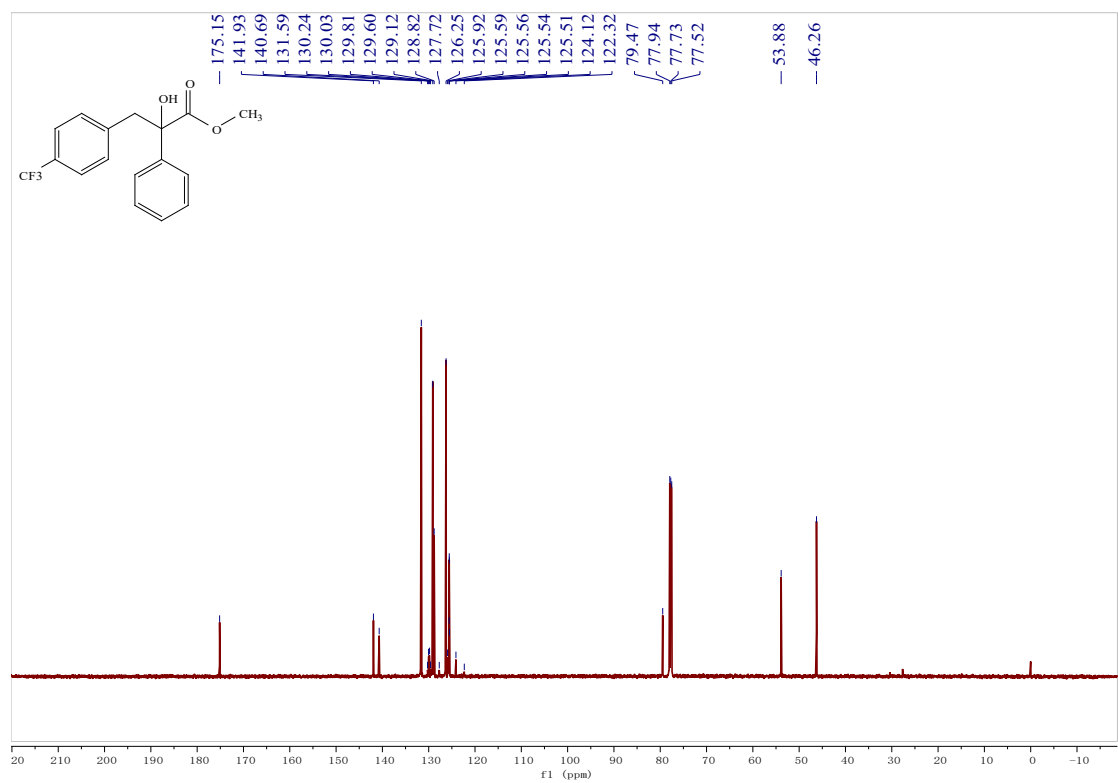
¹⁹F NMR (565 MHz, Chloroform-*d*) of **3y**



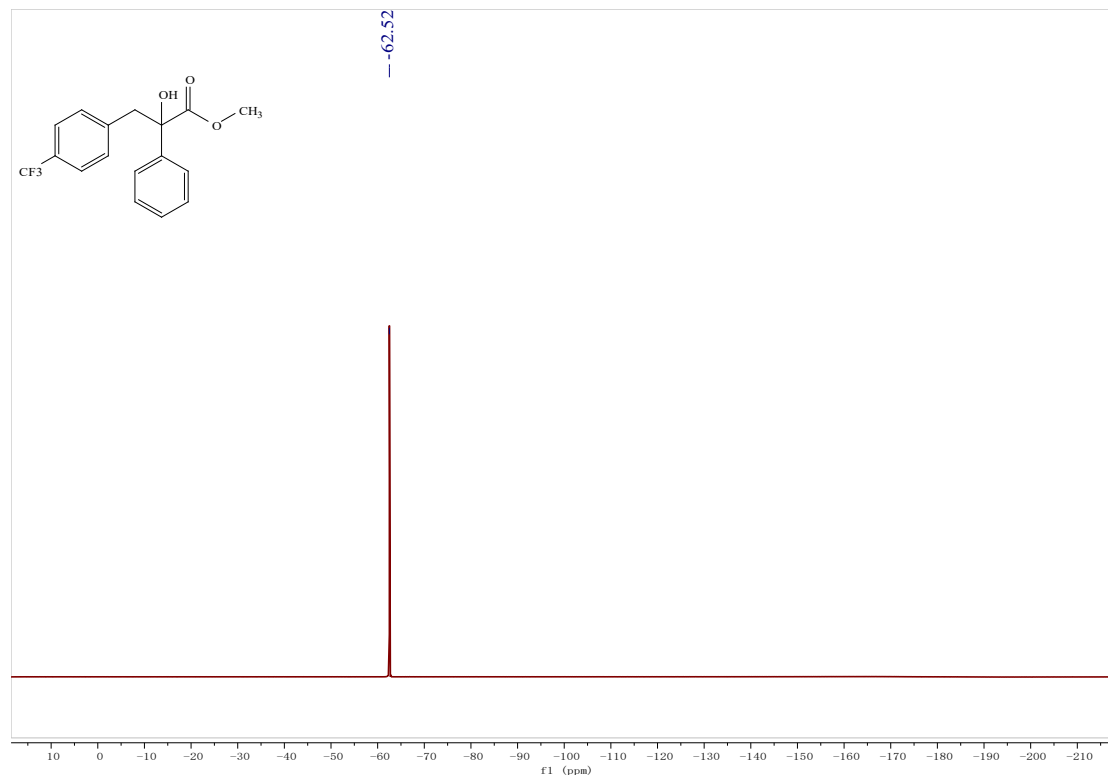
¹H NMR (600 MHz, Chloroform-*d*) of **3z**



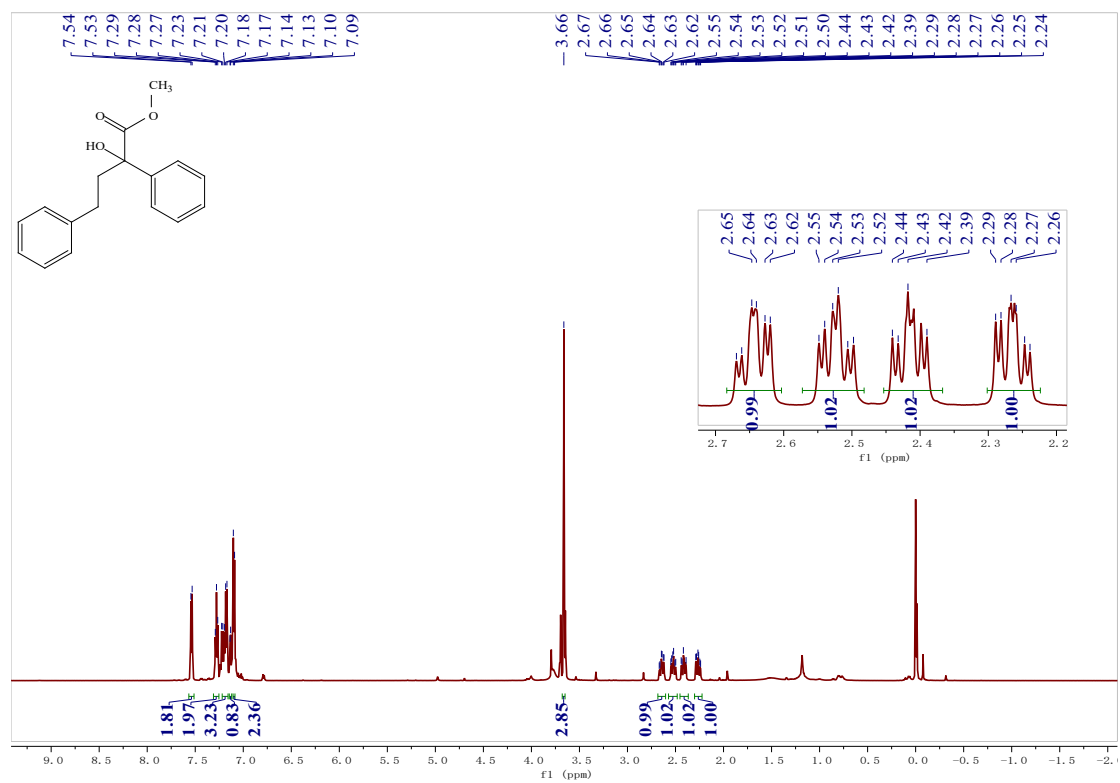
¹³C NMR (151 MHz, Chloroform-*d*) of **3z**



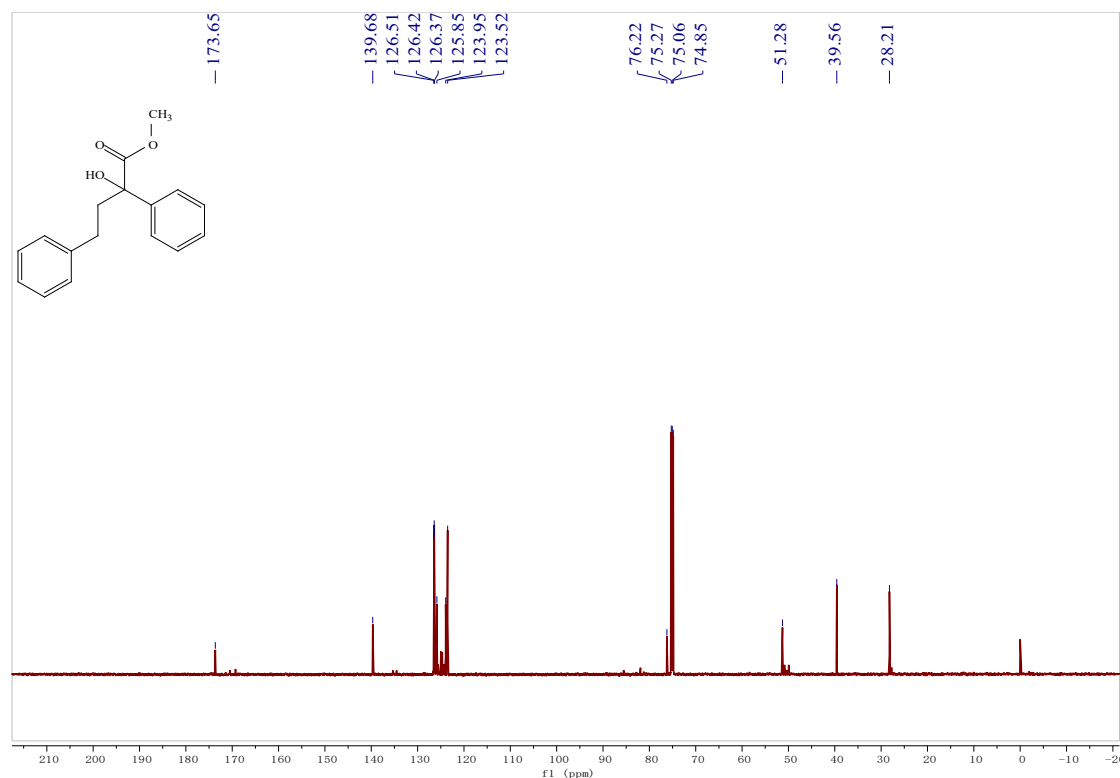
^{19}F NMR (565 MHz, Chloroform-*d*) of **3z**



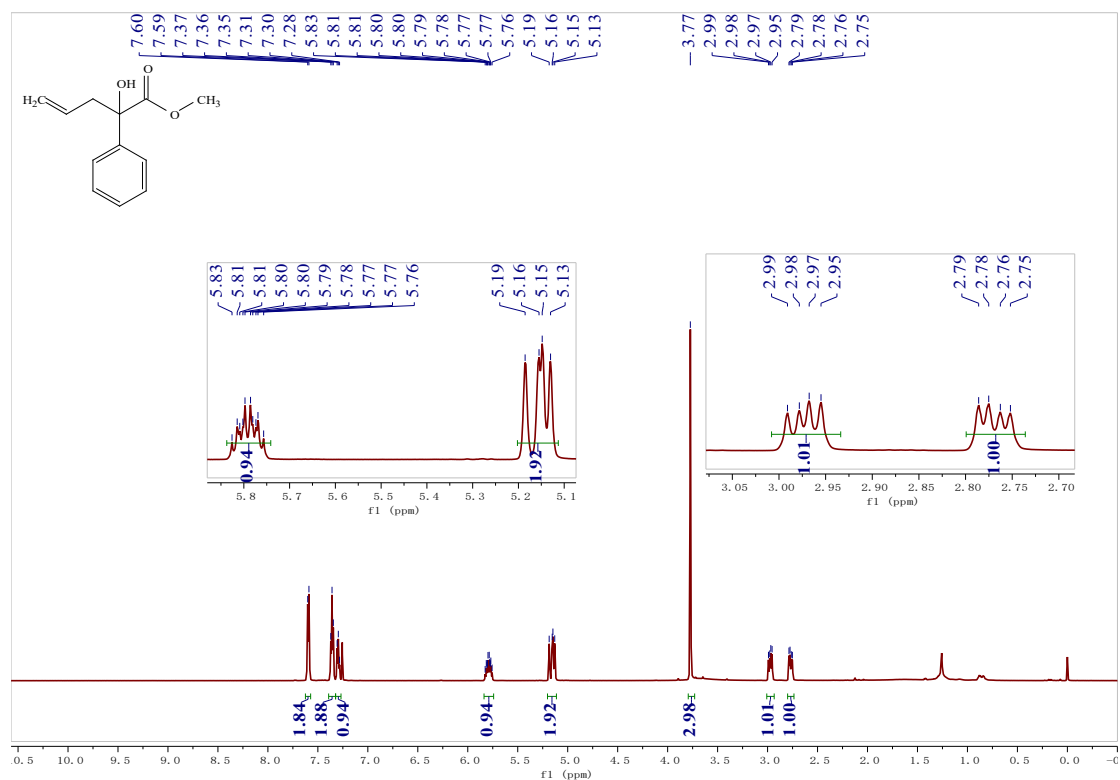
^1H NMR (600 MHz, Chloroform-*d*) of **3aa**



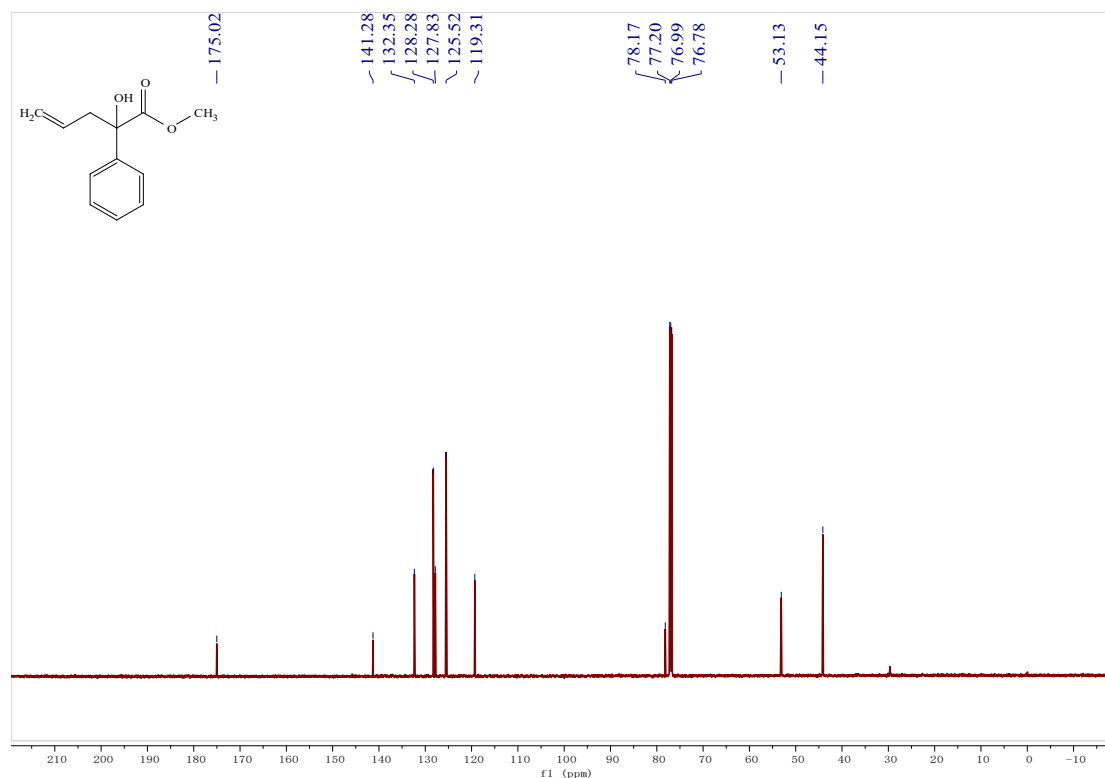
¹³C NMR (151 MHz, Chloroform-*d*) of **3aa**



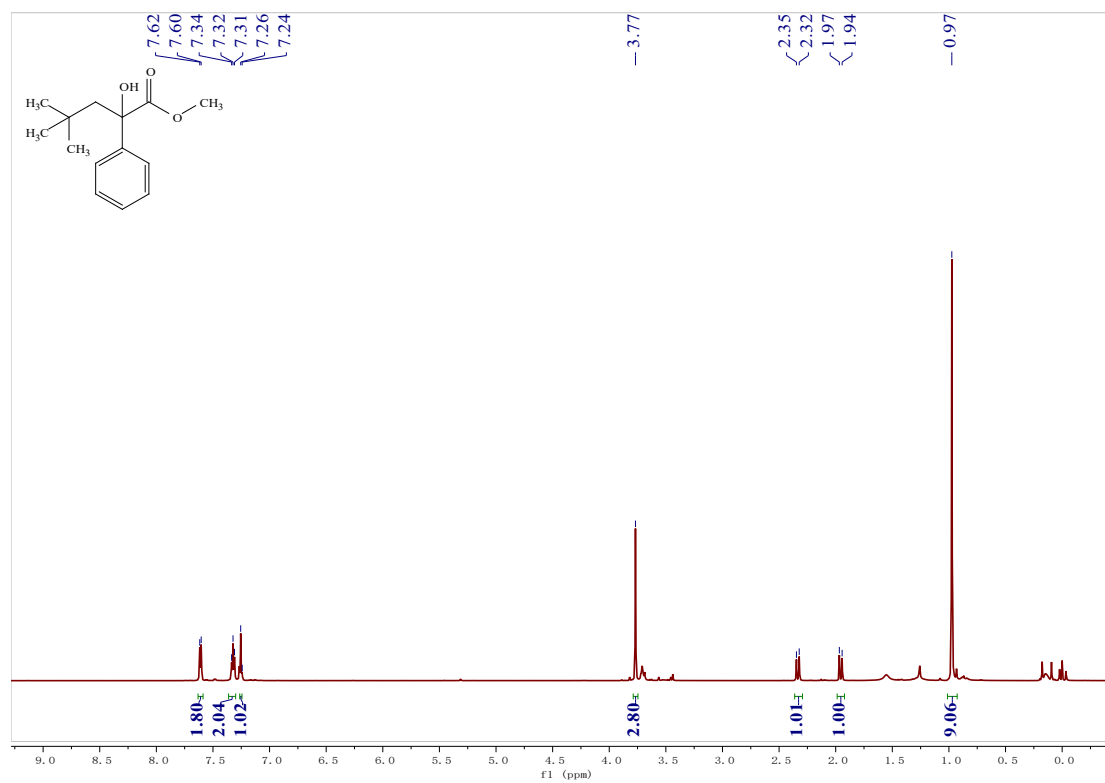
¹H NMR (600 MHz, Chloroform-*d*) of **3ab**



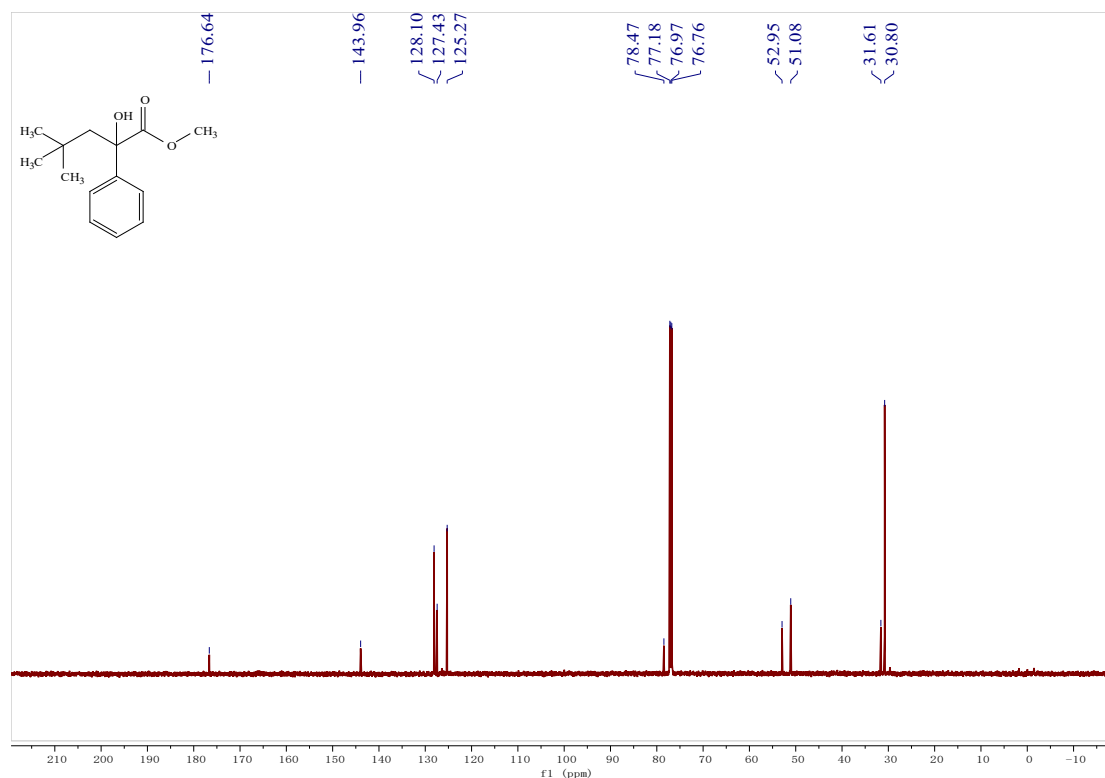
^{13}C NMR (151 MHz, Chloroform-*d*) of **3ab**



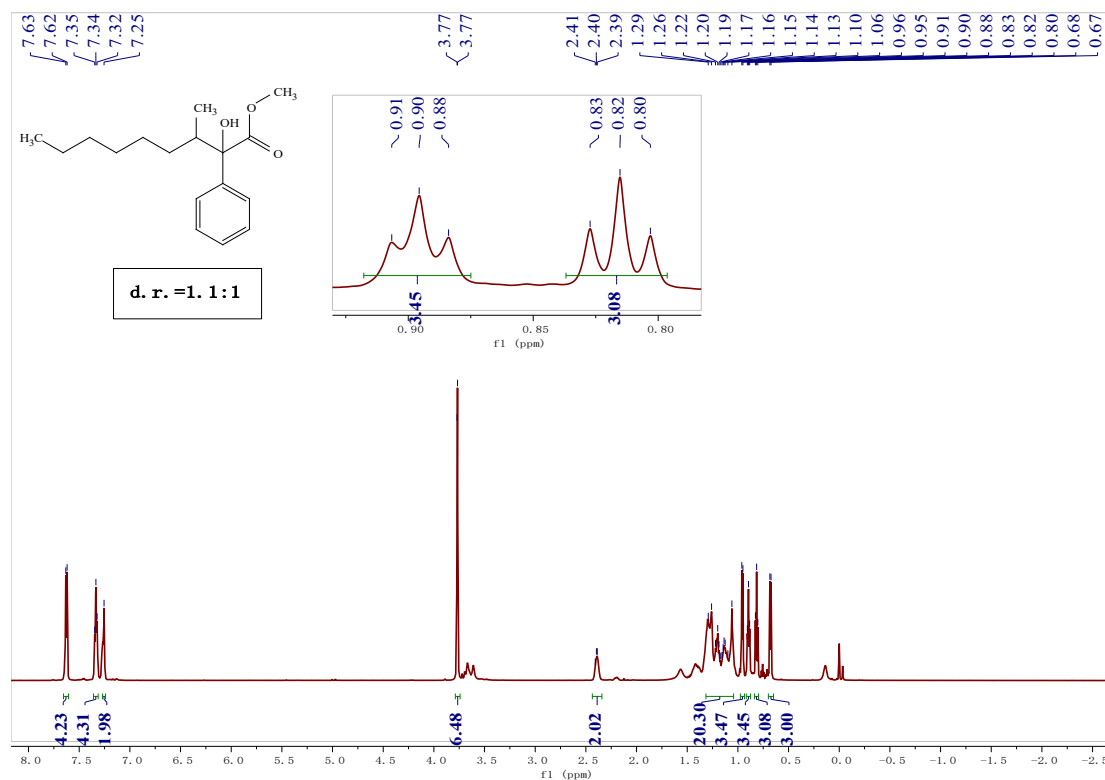
^1H NMR (600 MHz, Chloroform-*d*) of **3ac**



¹³C NMR (151 MHz, Chloroform-*d*) of **3ac**



¹H NMR (600 MHz, Chloroform-*d*) of **3ad**



¹³C NMR (151 MHz, Chloroform-*d*) of **3ad**

