Supporting Information

A general photocatalytic strategy for the synthesis of *β*-hydroxy acid derivatives from alkenes

Meiling Chen, Jingjing Yang, Wei Xiao*, Jian-Qiang Chen* and Jie Wu*

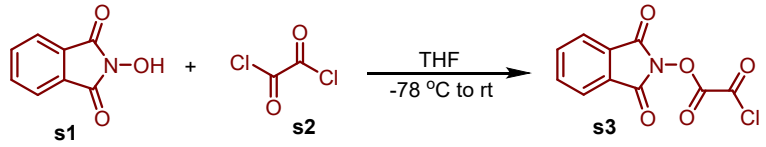
Correspondence and requests for materials should be addressed to W. X. (email: xiaowei1992@tzc.edu.cn), J.-Q. Chen (email: chenjq@tzc.edu.cn) or to J.W. (email: jie_wu@fudan.edu.cn).

Supplementary Methods

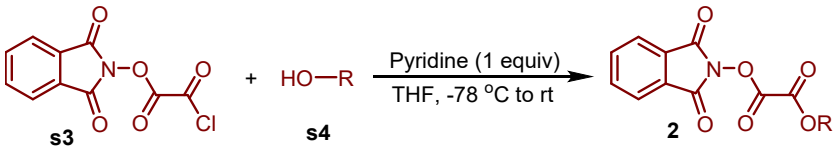
1. General information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200−300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in deuterochloroform ($CDCl_3$) as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. Electrospray–ionisation HRMS data were acquired on a Q–TOF mass spectrometer (Waters SYNAPT G2-Si) LC-MS TOF. All luminescence spectra were surveyed on a Cary Eclipse fluorescence spectrophotometer and equipped with a 1 cm quartz cell. Cyclic voltammetry (CV) studies were carried out on a CHI760E instrument.

2. General experimental procedure for the preparation of substrates

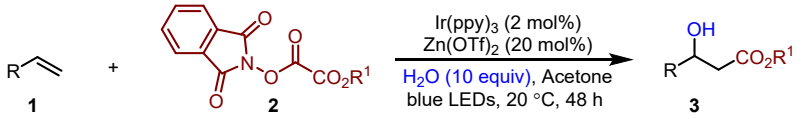


A round-bottom flask was charged with *N*-hydroxyphthalimide (20 mmol, 3.26 g), followed by the addition of THF (300 ml). The resulting solution was then cooled to –78 °C and oxalyl chloride (100 mmol, 8.7 ml) was added dropwise. The solution was then allowed to warm to room temperature and stirred for 12 h. The volatiles were removed under reduced pressure to yield as a white solid **s3**.[1]



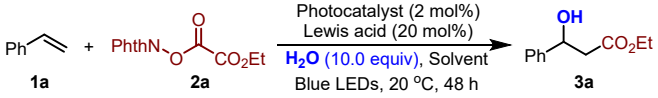
A round-bottom flask was charged with **s3** (5.0 g, 20.0 mmol, 1.0 equiv) followed by the addition of THF (660 mL, 0.03 M). The mixture was cooled to −78 ºC and a solution of **s4** (20 mmol, 1.0 equiv), pyridine (1.6 mL, 20 mmol, 1.0 equiv) in THF (2 mL) was added dropwise. The resulting heterogeneous mixture was warmed to 0 ºC and allowed to stir for 1 h. The reaction was then allowed to warm to room temperature and stirred for another 30 min. The reaction mixture was concentrated under reduced pressure, and the resulting crude residue was dissolved in DCM (45 mL) and washed with sat. aq. $CuSO_4$ (3 x 45 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude residue was dissolved in DCM (55 mL) then poured into pentanes (110 mL). The resulting heterogeneous mixture was filtered through a cotton plug that was then washed with pentanes (2 x 30 mL). The filtrate was concentrated under reduced pressure to yield alkyl *N*-phthalimidoyl oxalate **2** as a colorless solid.[2]

3. General procedure for the synthesis of *β*-substituted *β*-hydroxy acids



All optimization reactions were set up in a glove box under N_2 atmosphere. Substrate **1** (0.2 mmol), **2** (0.4 mmol), H_2O (36 μL, 2.0 mmol) and $Zn(OTf)_2$ (14.5 mg, 0.04 mmol) were added to a solution of $Ir(ppy)_3$ (2.6 mg, 2 mol %) in dry Acetone (4.0 mL) at 20 ℃. The heterogenous mixture was placed in the irradiation apparatus equipped with blue LEDs. The resulting mixture was stirred at 20 ℃ for 48 h. Upon completion of the reaction, the resulting crude residue was concentrated in vacuum and purified by column chromatography to afford the desired product **4**.

4. Optimization of the hydroxyalkoxycarbonylation of 1a



Entry	Photocatalyst	Lewis acid	Solvent	Yield (%)[b]
1	$Ir(ppy)_3$	$Zn(OTf)_2$	Acetone	84
2	$Ir(ppy)_2(dtbbpy)PF_6$	$Zn(OTf)_2$	Acetone	35
3	$Ru(bpy)_3(PF_6)_2$	$Zn(OTf)_2$	Acetone	NR
4	3DPA2FBN	$Zn(OTf)_2$	Acetone	56
5	$Ir(ppy)_3$	$Zn(OTf)_2$	MeCN	19
6	$Ir(ppy)_3$	$Zn(OTf)_2$	THF	31
7	$Ir(ppy)_3$	$Zn(OTf)_2$	DCM	5
8[c]	$Ir(ppy)_3$	$Zn(OTf)_2$	Acetone	53
9	$Ir(ppy)_3$	LiOTf	Acetone	60
10	$Ir(ppy)_3$	$Mg(OTf)_2$	Acetone	71
11	$Ir(ppy)_3$	$Sc(OTf)_3$	Acetone	33
12[d]	$Ir(ppy)_3$	$Zn(OTf)_2$	Acetone	30
13	-	$Zn(OTf)_2$	Acetone	NR
14[e]	$Ir(ppy)_3$	$Zn(OTf)_2$	Acetone	NR

[a] Reaction conditions: styrene **1a** (0.2 mmol), **2a** (0.4 mmol), H_2O (2.0 mmol), photocatalyst (0.004 mmol), Lewis acid (0.04 mmol), solvent (4 mL), 36 W blue LEDs, under a N_2 atmosphere, 20 °C. [b] Determined by ^1H NMR analysis using dibromomethane as an internal standard. [c] H_2O (1.0 mmol). [d] In the absence of $Zn(OTf)_2$. [e] In the dark.

5. Devices for the photocatalytic reactions

Irradiation of visible light was performed with a 36 W Blue LED strip. All photocatalyzed alkoxycarbonylation reactions were carried out at 20 °C. The distance

between tube and lamp was approximately 3 cm.

Manufacture of the light source: LED strip

Manufacturer: Greethink

Model: GT-5050-Blue

Wavelength of peak intensity: 460-470 nm

Material of the irradiation vessel: borosilicate glass

Distance of the irradiation vessel from the light source: approximately 3 cm.

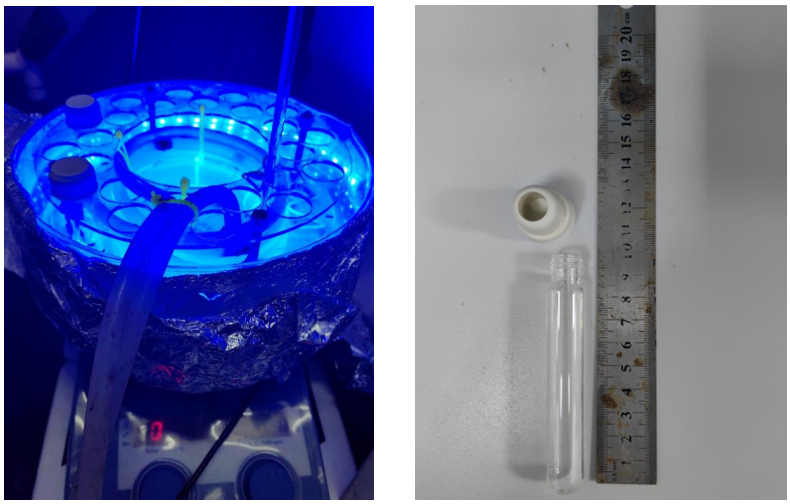


Figure S1. Devices for the photocatalytic reactions

5. Mechanistic studies

(a) Cyclic Voltammetry Studies

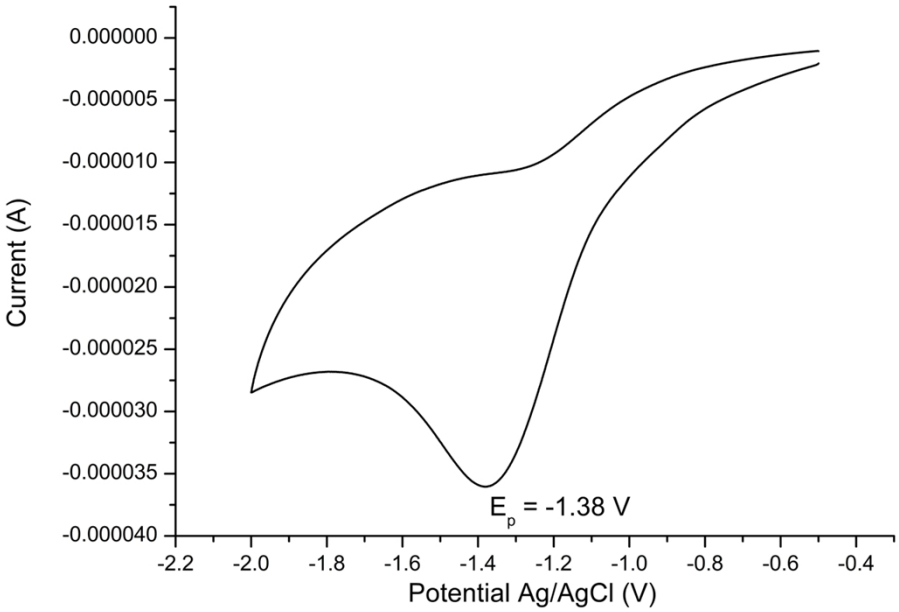


Figure S2. Cyclic voltammogram of **2a** [0.02 M] in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep

rate: 50 mV/s. Glassy carbon working electrode, Ag/AgCl (satd. KCl) reference electrode, Pt wire auxiliary electrode. Irreversible reduction. E_p = -1.38 V.

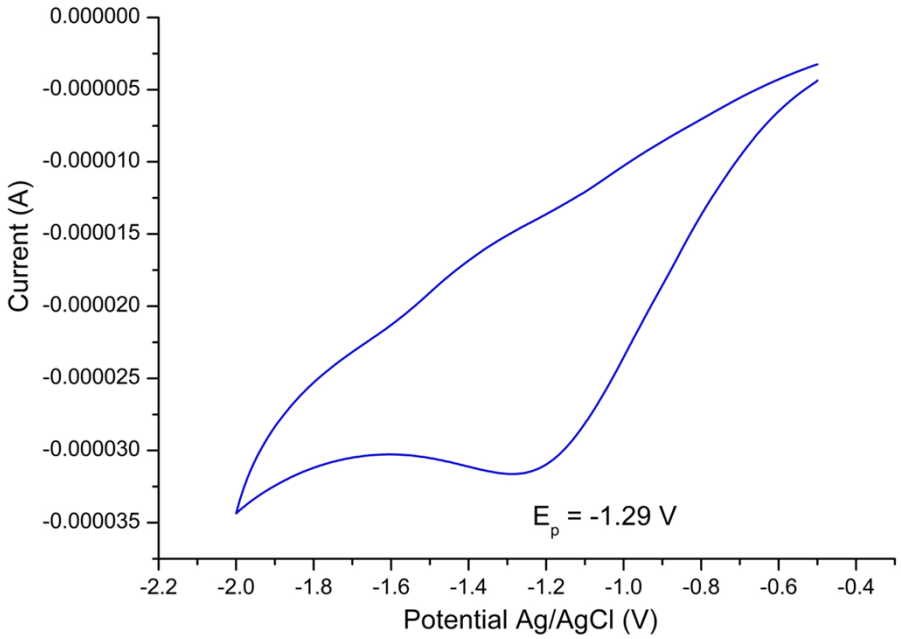


Figure S3. Cyclic voltammogram of **2a** [0.02 M] + $Zn(OTf)_2$ (0.004 M) in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 50 mV/s. Glassy carbon working electrode, Ag/AgCl (satd. KCl) reference electrode, Pt wire auxiliary electrode. Irreversible reduction. E_p = -1.29 V.

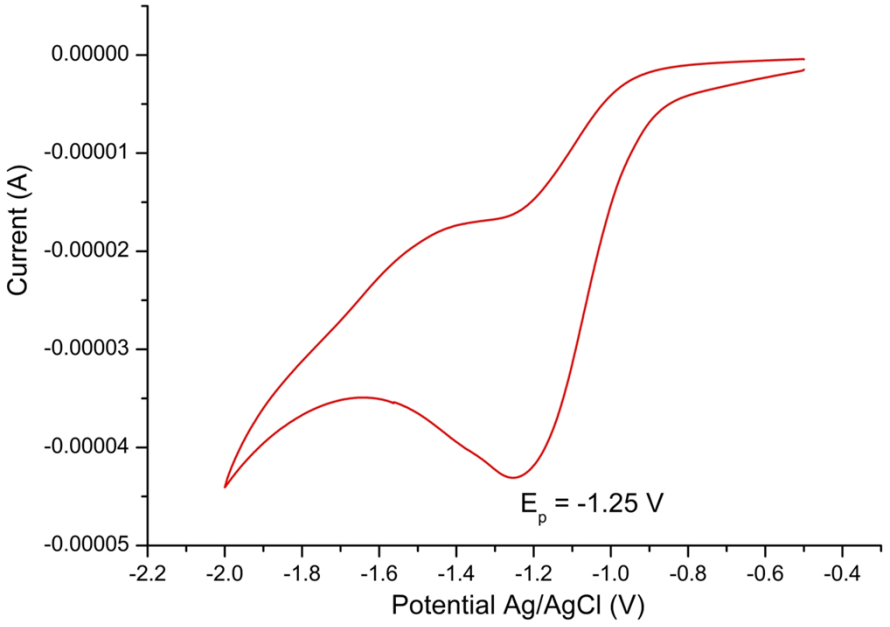


Figure S4. Cyclic voltammogram of **2a** [0.02 M] +H_2O (0.02 M) in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 50 mV/s. Glassy carbon working electrode, Ag/AgCl (satd.

KCl) reference electrode, Pt wire auxiliary electrode. Irreversible reduction. E_p = -1.25 V.

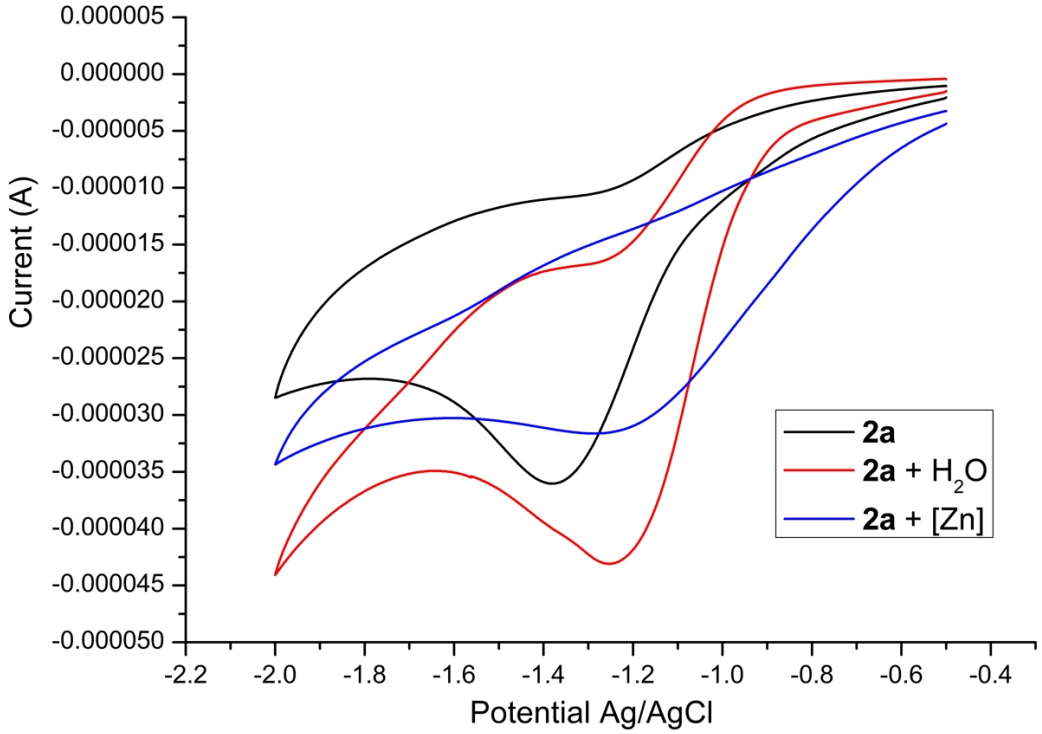


Figure S5. Cyclic voltammetry studies

(b) Stern-Volmer fluorescence quenching experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 0.1 mM $Ir(ppy)_3$ in degassed dry CH_3CN added with the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 395 nm and fluorescence was measured from 450 nm to 650 nm.

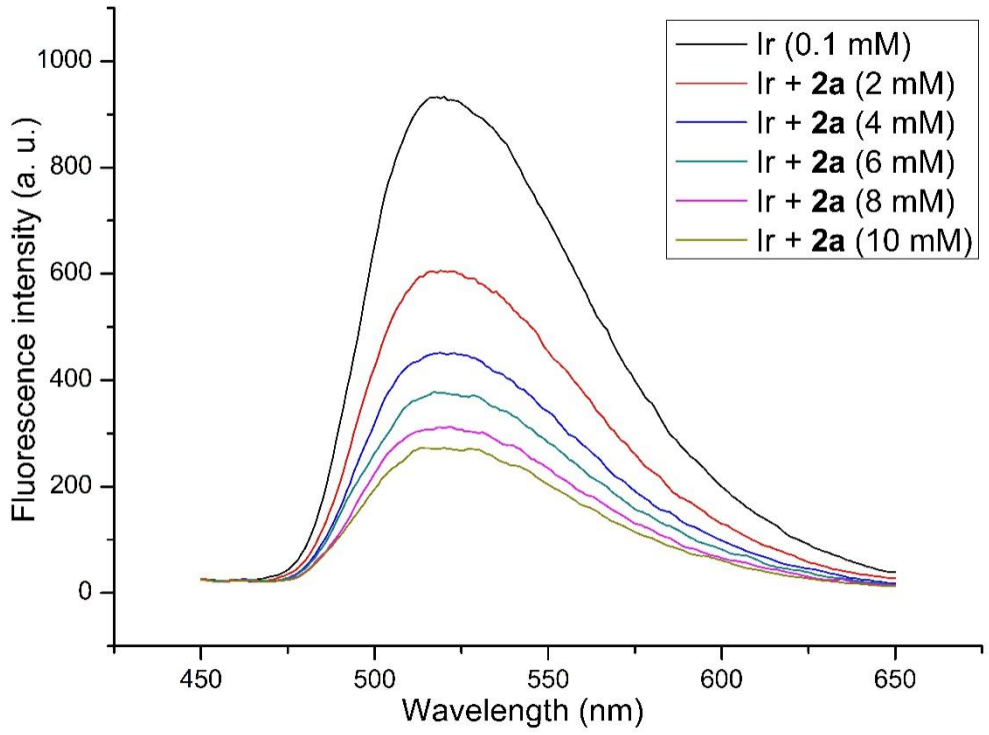


Figure S6. Fluorescence quenching experiments of $Ir(ppy)_3$ and **2a**.

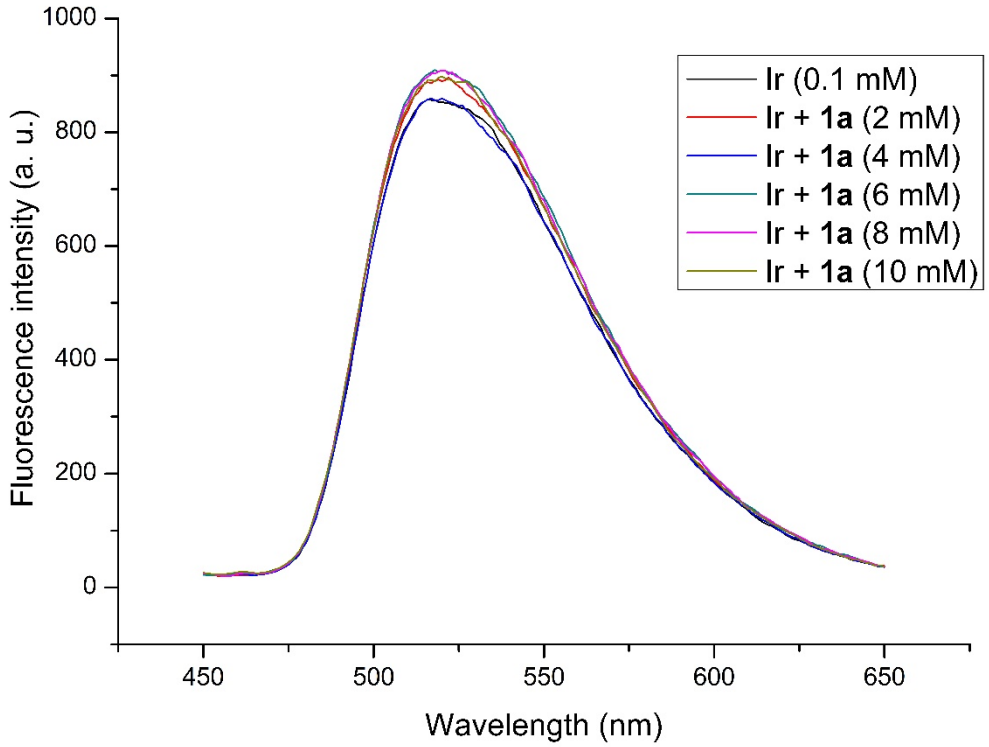


Figure S7. Fluorescence quenching experiments of $Ir(ppy)_3$ and **1a**.

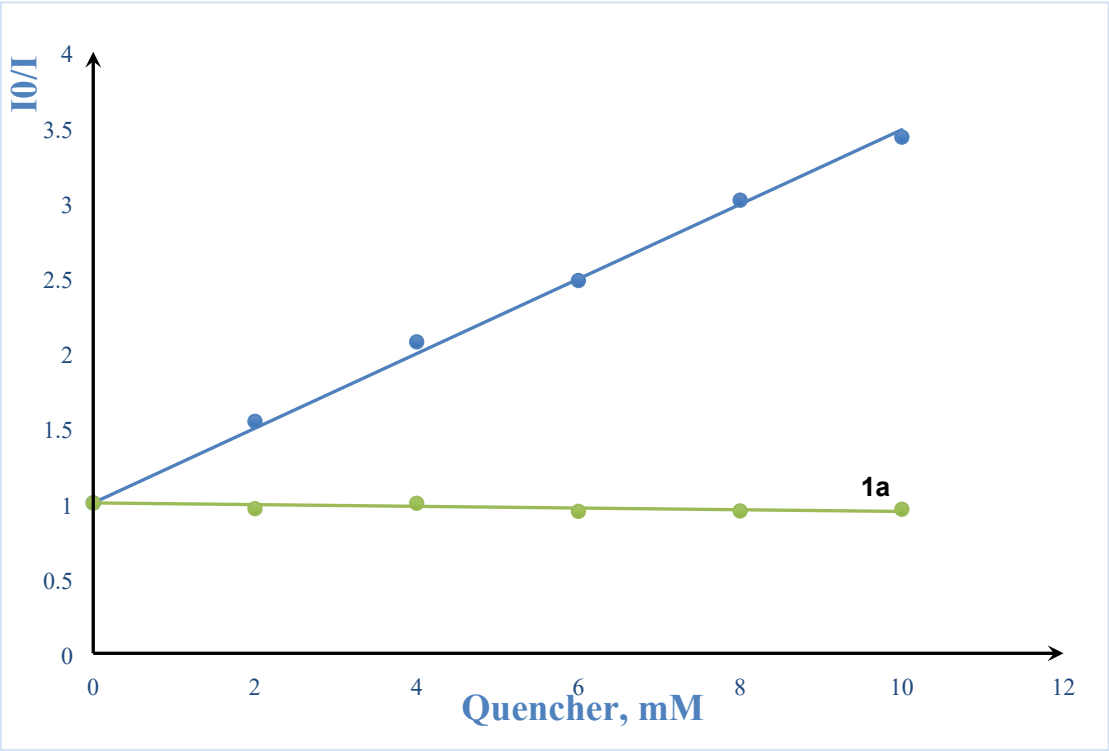
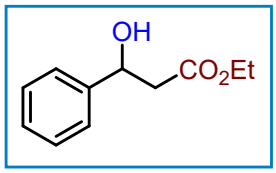


Figure S8. Stern-Volmer plots of $Ir(ppy)_3$ with different quenchers.

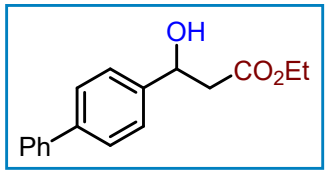
6. Characterization of products

Ethyl 3-hydroxy-3-phenylpropanoate (3a)



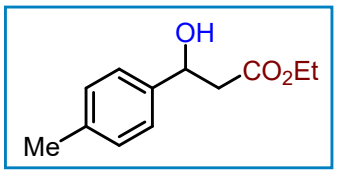
Purification by flash chromatography (PE/EA = 6/1) afforded **3a.** Colorless oil; 80% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.42−7.24 (m, 5H), 5.12 (dd, *J* = 8.7, 3.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.46 (br, 1H), 2.80−2.63 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.3, 142.5, 128.4, 127.7, 125.6, 70.2, 60.8, 43.3, 14.0; HRMS (ESI) for $C_{11}H_{14}NO_3Na$ $[M+Na]^+$ calcd. 217.0841, found 217.0842.

Ethyl 3-([1,1'-biphenyl]-4-yl)-3-hydroxypropanoate (3b)



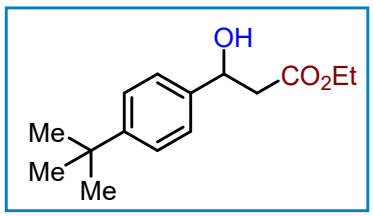
Purification by flash chromatography (PE/EA = 6/1) afforded **3b.** White solid; m.p. = 79−81 °C; 81% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.62−7.55 (m, 4H), 7.48−7.40 (m, 4H), 7.34 (d, *J* = 7.2 Hz, 1H), 5.23−5.13 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.38 (br, 1H), 2.84−2.71 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.4, 141.4, 140.7, 128.7, 127.3, 127.3, 127.0, 126.1, 70.0, 60.9, 43.2, 14.1; HRMS (ESI) for $C_{17}H_{18}NO_3Na$ $[M+Na]^+$ calcd. 293.1148, found 293.1161.

Ethyl 3-hydroxy-3-(p-tolyl)propanoate (3c)



Purification by flash chromatography (PE/EA = 6/1) afforded **3c.** Colorless oil; 81% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.26 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.10 (dd, *J* = 9.1, 3.8 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.27 (br, 1H), 2.80−2.63 (m, 2H), 2.34 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.4, 139.5, 137.4, 129.2, 125.6, 70.1, 60.8, 43.3, 21.1, 14.1; HRMS (ESI) for $C_{12}H_{16}NO_3Na$ $[M+Na]^+$ calcd. 231.0997, found 231.1005.

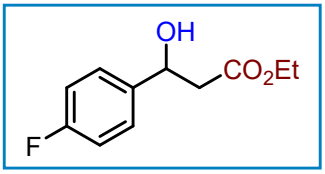
Ethyl 3-(4-(tert-butyl)phenyl)-3-hydroxypropanoate (3d)



Purification by flash chromatography (PE/EA = 6/1) afforded **3d.** Colorless oil; 77% yield; **^{1}H NMR (400**

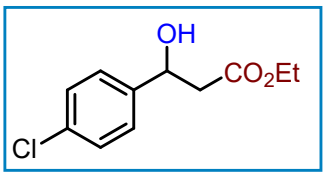
MHz, $CDCl_3$) δ (ppm) 7.38 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.11 (dd, *J* = 9.2, 3.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.24 (br, 1H), 2.82−2.65 (m, 2H), 1.31 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.4, 150.7, 139.5, 125.4, 70.1, 60.8, 43.2, 34.5, 31.3, 14.1; HRMS (ESI) for $C_{15}H_{22}NO_3Na$ $[M+Na]^+$ calcd. 273.1467, found 273.1476.

Ethyl 3-(4-fluorophenyl)-3-hydroxypropanoate (3e)



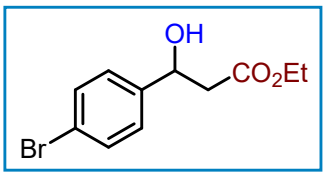
Purification by flash chromatography (PE/EA = 6/1) afforded **3e.** Colorless oil; 78% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.40−7.31 (m, 2H), 7.08−6.99 (m, 2H), 5.11 (dd, *J* = 8.7, 4.1 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.45 (br, 1H), 2.79−2.63 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.3, 162.2 (d, *J* = 244.3 Hz), 138.2 (d, *J* = 3.2 Hz), 127.3 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 21.2 Hz), 69.6, 60.9, 43.3, 14.1; HRMS (ESI) for $C_{11}H_{13}FNO_3Na$ $[M+Na]^+$ calcd. 235.0746, found 235.0749.

Ethyl 3-(4-chlorophenyl)-3-hydroxypropanoate (3f)



Purification by flash chromatography (PE/EA = 6/1) afforded **3f.** Colorless oil; 75% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.38−7.27 (m, 4H), 5.10 (dd, *J* = 8.1, 4.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.52 (br, 1H), 2.77−2.62 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 141.0, 133.4, 128.6, 127.0, 69.6, 61.0, 43.2, 14.1; HRMS (ESI) for $C_{11}H_{13}ClNO_3Na$ $[M+Na]^+$ calcd. 251.0451, found 251.0453.

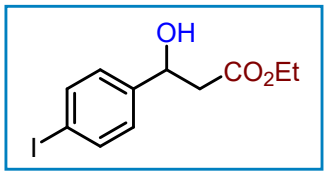
Ethyl 3-(4-bromophenyl)-3-hydroxypropanoate (3g)



Purification by flash chromatography (PE/EA = 6/1) afforded **3g.** Colorless oil; 74% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.51−7.44 (m, 2H), 7.29−7.22 (m, 2H), 5.08 (dd, *J* = 7.8, 4.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.50 (br, 1H), 2.76−2.63 (m,

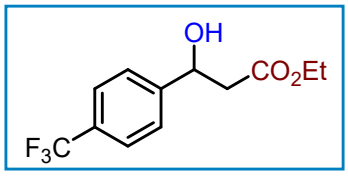
2H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 141.5, 131.6, 127.4, 121.5, 69.6, 61.0, 43.1, 14.1; HRMS (ESI) for $C_{11}H_{13}BrNO_3Na$ $[M+Na]^+$ calcd. 294.9946, found 294.9952.

Ethyl 3-hydroxy-3-(4-iodophenyl)propanoate (3h)



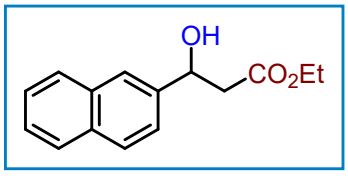
Purification by flash chromatography (PE/EA = 6/1) afforded **3h.** Colorless oil; 75% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.68 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 5.07 (t, J = 6.2 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.47 (br, 1H), 2.74–2.63 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 142.1, 137.5, 127.6, 93.2, 69.6, 61.0, 43.0, 14.1; HRMS (ESI) for $C_{11}H_{13}INO_3Na$ $[M+Na]^+$ calcd. 342.9802, found 342.9802.

Ethyl 3-hydroxy-3-(4-(trifluoromethyl)phenyl)propanoate (3i)



Purification by flash chromatography (PE/EA = 6/1) afforded **3i.** Colorless oil; 32% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.62 (d, J = 8.9 Hz, 2H), 7.50 (d, J = 8.9 Hz, 2H), 5.19 (t, J = 6.2 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.51 (br, 1H), 2.72 (d, J = 6.2 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 146.4, 129.9 (q, J = 32.2 Hz), 126.0, 125.5 (q, J = 3.7 Hz), 124.0 (q, J = 270.3 Hz), 69.6, 61.1, 43.0, 14.1; HRMS (ESI) for $C_{12}H_{13}F_3NO_3Na$ $[M+Na]^+$ calcd. 285.0714, found 285.0723.

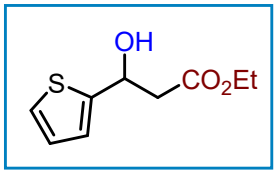
Ethyl 3-hydroxy-3-(naphthalen-2-yl)propanoate (3j)



Purification by flash chromatography (PE/EA = 6/1) afforded **3j.** Colorless oil; 65% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.87–7.77 (m, 4H), 7.51–7.43 (m, 3H), 5.29 (dd, J = 8.5, 4.1 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.52 (br, 1H), 2.88–2.74 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.4, 139.8, 133.2, 132.9, 128.3, 128.0, 127.6, 126.2, 125.9, 124.4, 123.7, 70.4, 60.9, 43.2, 14.1;

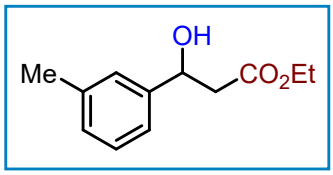
HRMS (ESI) for $C_{15}H_{16}NO_3Na$ $[M+Na]^+$ calcd. 267.0997, found 267.1005.

Ethyl 3-hydroxy-3-(thiophen-2-yl)propanoate (3k)



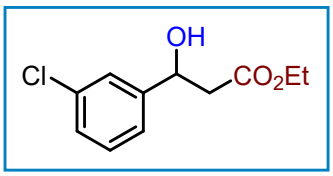
Purification by flash chromatography (PE/EA = 6/1) afforded **3k.** Colorless oil; 45% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.32−7.24 (m, 1H), 7.03−6.94 (m, 2H), 5.38 (dd, *J* = 7.3, 4.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.52 (br, 1H), 2.94−2.80 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.0, 146.2, 126.7, 124.9, 123.6, 66.5, 61.0, 43.1, 14.1; HRMS (ESI) for $C_9H_{12}NO_3SNa$ $[M+Na]^+$ calcd. 223.0405, found 223.0408.

Ethyl 3-hydroxy-3-(m-tolyl)propanoate (3l)



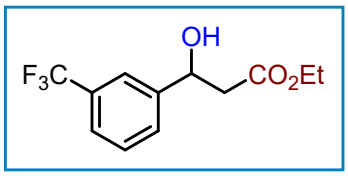
Purification by flash chromatography (PE/EA = 6/1) afforded **3l.** Colorless oil; 78% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.28−7.18 (m, 3H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 5.10 (dd, *J* = 8.9, 3.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.30 (br, 1H), 2.81−2.64 (m, 2H), 2.35 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.5, 142.4, 138.2, 128.5, 128.4, 126.3, 122.7, 70.3, 60.8, 43.3, 21.4, 14.1; HRMS (ESI) for $C_{12}H_{16}NO_3Na$ [M+Na]+ calcd. 231.0992, found 231.1003.

Ethyl 3-(3-chlorophenyl)-3-hydroxypropanoate (3m)



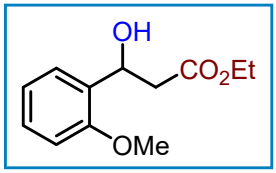
Purification by flash chromatography (PE/EA = 6/1) afforded **3m.** Colorless oil; 58% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.40 (s, 1H), 7.33−7.21 (m, 3H), 5.11 (t, *J* = 6.1 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.43 (br, 1H), 2.71 (d, *J* = 6.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 144.5, 134.4, 129.8, 127.8, 125.9, 123.8, 69.6, 61.0, 43.1, 14.1; HRMS (ESI) for $C_{11}H_{13}ClNO_3Na$ $[M+Na]^+$ calcd. 251.0451, found 251.0455.

Ethyl 3-hydroxy-3-(3-(trifluoromethyl)phenyl)propanoate (3n)



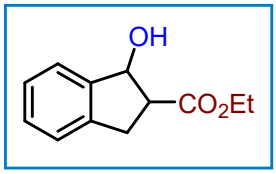
Purification by flash chromatography (PE/EA = 6/1) afforded **3n.** Colorless oil; 50% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.66 (s, 1H), 7.56 (t, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 5.19 (t, *J* = 6.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.59 (br, 1H), 2.74 (d, *J* = 6.3 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 143.4, 130.8 (q, *J* = 32.0 Hz), 129.0, 129.0, 124.6 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 270.7 Hz), 122.5 (q, *J* = 3.8 Hz), 69.6, 61.1, 43.1, 14.1; HRMS (ESI) for $C_{12}H_{23}F_3NO_3Na$ $[M+Na]^+$ calcd. 285.0714, found 285.0720.

Ethyl 3-hydroxy-3-(2-methoxyphenyl)propanoate (3o)



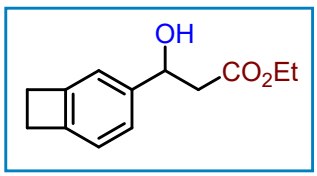
Purification by flash chromatography (PE/EA = 6/1) afforded **3o.** Colorless oil; 77% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.43 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.26 (td, *J* = 7.8, 1.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.41−5.27 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.51 (d, *J* = 4.0 Hz, 1H), 2.81 (dd, *J* = 16.1, 3.5 Hz, 1H), 2.70 (dd, *J* = 16.1, 9.2 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.6, 155.9, 130.5, 128.5, 126.5, 120.7, 110.2, 66.5, 60.6, 55.2, 41.6, 14.1; HRMS (ESI) for $C_{12}H_{16}NO_4Na$ $[M+Na]^+$ calcd. 247.0946, found 247.0951.

Ethyl 1-hydroxy-2,3-dihydro-1H-indene-2-carboxylate (3p)



Purification by flash chromatography (PE/EA = 6/1) afforded **3p.** Colorless oil; 24% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.44 (d, *J* = 6.8 Hz, 1H), 7.33−7.23 (m, 3H), 5.35 (d, *J* = 4.7 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.50−2.34 (m, 2H), 3.11 (dd, *J* = 14.8, 7.1 Hz, 1H), 2.92 (br, 1H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 173.1, 142.6, 141.8, 129.1, 127.2, 125.0, 124.9, 75.8, 60.9, 49.4, 32.8, 14.2; HRMS (ESI) for $C_{12}H_{14}NO_3Na$ $[M+Na]^+$ calcd. 229.0841, found 229.0843.

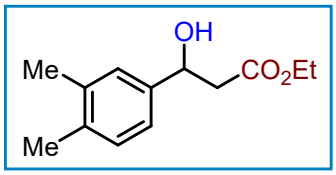
Ethyl 3-(bicyclo[4.2.0]octa-1(6),2,4-trien-3-yl)-3-hydroxypropanoate (3q)



Purification by flash chromatography (PE/EA = 6/1)

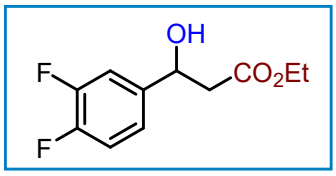
afforded **3q.** Colorless oil; 90% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.18 (d, *J* = 7.5 Hz, 1H), 7.09 (s, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 5.08 (dd, *J* = 9.2, 3.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.37−3.00 (m, 5H), 2.81−2.60 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.4, 146.0, 145.4, 141.3, 124.4, 122.5, 120.0, 71.0, 60.8, 43.6, 29.3, 14.1; HRMS (ESI) for $C_{13}H_{16}O_3Na$ $[M+Na]^+$ calcd. 243.0992, found 243.1000.

Ethyl 3-(3,4-dimethylphenyl)-3-hydroxypropanoate (3r)



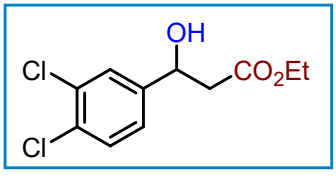
Purification by flash chromatography (PE/EA = 6/1) afforded **3r.** Colorless oil; 77% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.15 (s, 1H), 7.13−7.06 (m, 2H), 5.07 (dd, *J* = 9.2, 3.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.23 (br, 1H), 2.80−2.64 (m, 2H), 2.26 (s, 3H), 2.25 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.5, 139.9, 136.7, 136.1, 129.7, 126.9, 123.0, 70.1, 60.8, 43.3, 19.8, 19.4, 14.1; HRMS (ESI) for $C_{13}H_{18}NO_3Na$ $[M+Na]^+$ calcd. 245.1154, found 245.1163.

Ethyl 3-(3,4-difluorophenyl)-3-hydroxypropanoate (3s)



Purification by flash chromatography (PE/EA = 6/1) afforded **3s.** Colorless oil; 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.27−7.19 (m, 1H), 7.18−7.05 (m, 2H), 5.09 (t, *J* = 6.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.51 (br, 1H), 2.69 (d, *J* = 6.3 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 151.2 (dd, *J* = 62.6, 12.5 Hz), 148.8 (dd, *J* = 62.3, 12.9 Hz), 139.5 (dd, *J* = 5.0, 3.8 Hz), 121.6 (dd, *J* = 6.4, 3.7 Hz), 117.2 (d, *J* = 17.2 Hz), 114.8 (d, *J* = 17.9 Hz), 69.1 (d, *J* = 1.0 Hz), 61.1, 43.1, 14.1; HRMS (ESI) for $C_{11}H_{12}F_2NO_3Na$ [M+Na]+ calcd. 253.0652, found 253.0651.

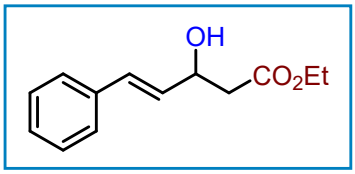
Ethyl 3-(3,4-dichlorophenyl)-3-hydroxypropanoate (3t)



Purification by flash chromatography (PE/EA = 6/1) afforded **3t.** Colorless oil; 57% yield; **^{1}H NMR (400 MHz,**

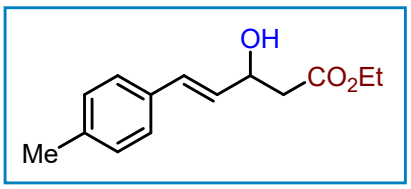
$CDCl_3$) δ (ppm) 7.50 (d, *J* = 1.9 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.21 (dd, *J* = 8.3, 1.9 Hz, 1H), 5.08 (t, *J* = 6.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.54 (br, 1H), 2.69 (d, *J* = 6.3 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.1, 142.7, 132.6, 131.6, 130.5, 127.8, 125.0, 69.1, 61.1, 43.0, 14.1; HRMS (ESI) for $C_{11}H_{12}Cl_2NO_3Na$ $[M+Na]^+$ calcd. 285.0061, found 285.0064.

Ethyl (E)-3-hydroxy-5-phenylpent-4-enoate (3u)



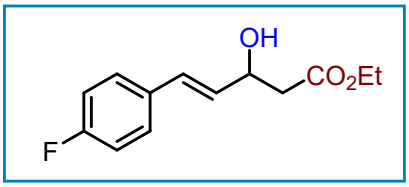
Purification by flash chromatography (PE/EA = 6/1) afforded **3u.** Colorless oil; 61% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.38 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.27−7.21 (m, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.22 (dd, *J* = 15.9, 6.1 Hz, 1H), 4.78−4.65 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.08 (br, 1H), 2.72−2.56 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.3, 136.4, 130.7, 129.9, 128.6, 127.8, 126.5, 68.8, 60.9, 41.4, 14.2; HRMS (ESI) for $C_{13}H_{16}O_3Na$ $[M+Na]^+$ calcd. 243.0992, found 243.1003.

Ethyl (E)-3-hydroxy-5-(p-tolyl)pent-4-enoate (3v)



Purification by flash chromatography (PE/EA = 6/1) afforded **3v.** Colorless oil; 25% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.27 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 6.2 Hz, 1H), 4.77−4.67 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.04 (d, *J* = 4.2 Hz, 1H), 2.72−2.56 (m, 2H), 2.34 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.3, 137.7, 133.6, 130.7, 129.3, 128.8, 126.4, 69.0, 60.8, 41.5, 21.2, 14.2; HRMS (ESI) for $C_{14}H_{18}O_3Na$ $[M+Na]^+$ calcd. 257.1148, found 257.1158.

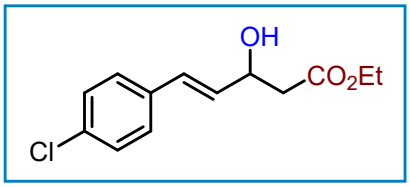
Ethyl (E)-5-(4-fluorophenyl)-3-hydroxypent-4-enoate (3w)



Purification by flash chromatography (PE/EA = 6/1) afforded **3w.** Colorless oil; 36% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.40−7.30 (m, 2H), 7.00 (t, *J*

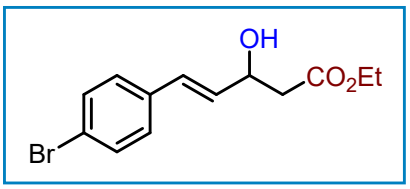
= 8.6 Hz, 2H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 15.9, 6.1 Hz, 1H), 4.80−4.66 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.13 (d, *J* = 4.1 Hz, 1H), 2.73−2.56 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.3, 162.4 (d, *J* = 245.5 Hz), 132.6 (d, *J* = 3.1 Hz), 129.6, 128.0 (d, *J* = 7.9 Hz), 115.6, 115.4, 68.7, 60.9, 41.4, 14.2; HRMS (ESI) for $C_{13}H_{15}FO_3Na$ $[M+Na]^+$ calcd. 261.0897, found 261.0908.

Ethyl (E)-5-(4-chlorophenyl)-3-hydroxypent-4-enoate (3x)



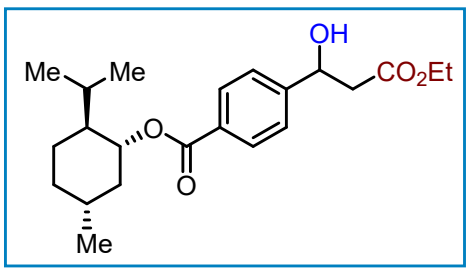
Purification by flash chromatography (PE/EA = 6/1) afforded **3x.** Colorless oil; 51% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.35−7.23 (m, 4H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 15.9, 5.9 Hz, 1H), 4.78−4.67 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.17 (br, 1H), 2.72−2.56 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 134.9, 133.4, 130.5, 129.5, 128.7, 127.7, 68.6, 60.9, 41.3, 14.2; HRMS (ESI) for $C_{13}H_{15}ClO_3Na$ $[M+Na]^+$ calcd. 277.0602, found 277.0616.

Ethyl (E)-5-(4-bromophenyl)-3-hydroxypent-4-enoate (3y)



Purification by flash chromatography (PE/EA = 6/1) afforded **3y.** Colorless oil; 47% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.43 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 5.9 Hz, 1H), 4.76−4.66 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.19 (d, *J* = 4.1 Hz, 1H), 2.71−2.55 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 135.3, 131.6, 130.7, 129.5, 128.0, 121.5, 68.6, 60.9, 41.3, 14.1; HRMS (ESI) for $C_{13}H_{15}BrO_3Na$ $[M+Na]^+$ calcd. 321.0097, found 321.0108.

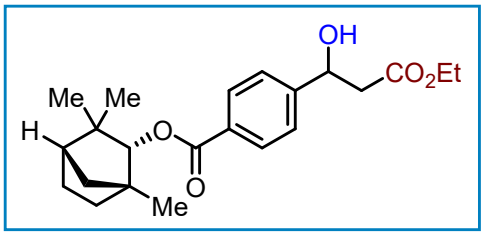
(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-(3-ethoxy-1-hydroxy-3-oxopropyl)benzoate (3z)



Purification by flash chromatography (PE/EA = 6/1) afforded **3z.** Colorless oil; 51% yield; **^{1}H**

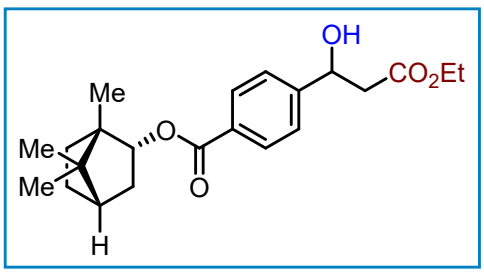
NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 5.19 (t, *J* = 5.7 Hz, 1H), 4.97−4.87 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.60 (br, 1H), 2.77−2.68 (m, 2H), 2.15−2.07 (m, 1H), 2.00−1.90 (m, 1H), 1.77−1.70 (m, 2H), 1.60−1.51 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.17−1.05 (m, 2H), 0.96−0.89 (m, 7H), 0.78 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 165.8, 147.3, 130.1, 129.8, 125.5, 74.8, 69.8, 61.0, 47.2, 43.1, 40.9, 34.2, 31.4, 26.4, 26.4, 23.5, 23.5, 22.0, 20.7, 16.4, 16.4, 14.1; HRMS (ESI) for $C_{22}H_{32}NO_5Na$ $[M+Na]^+$ calcd. 399.2142, found 399.2149.

(1R,2R,4S)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl 4-(3-ethoxy-1-hydroxy-3-oxopropyl)benzoate (3aa)



Purification by flash chromatography (PE/EA = 1/1) afforded **3aa.** Colorless oil; 52% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.05 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 5.19 (t, *J* = 6.1 Hz, 1H), 4.61 (d, *J* = 1.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.59 (br, 1H), 2.73 (d, *J* = 6.1 Hz, 2H), 1.97−1.89 (m, 1H), 1.82−1.75 (m, 2H), 1.69−1.64 (m, 1H), 1.57−1.47 (m, 1H), 1.29−1.24 (m, 4H), 1.21−1.15 (m, 4H), 1.10 (s, 3H), 0.83 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 166.6, 147.4, 130.0, 129.8, 125.6, 86.6, 69.8, 61.0, 48.5, 48.3, 43.1, 41.4, 39.8, 29.7, 26.8, 25.9, 20.2, 19.4, 14.1; HRMS (ESI) for $C_{22}H_{30}NO_5Na$ $[M+Na]^+$ calcd. 397.1985, found 397.1992.

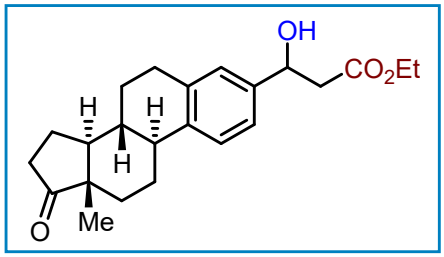
(1S,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-(3-ethoxy-1-hydroxy-3-oxopropyl)benzoate (3ab)



Purification by flash chromatography (PE/EA = 1/1) afforded **3ab.** Colorless oil; 51% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.04 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 5.20 (t, *J* = 6.2 Hz, 1H), 5.13−5.06 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.59 (br, 1H), 2.73 (d, *J* = 6.2 Hz, 2H), 2.52−2.42 (m, 1H), 2.17−2.08

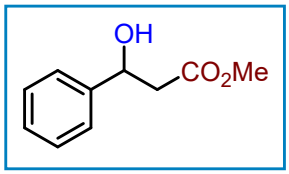
(m, 1H), 1.84−1.77 (m, 1H), 1.74 (t, J = 4.4 Hz, 1H), 1.46−1.37 (m, 1H), 1.34−1.29 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H), 1.11 (dd, J = 13.8, 3.4 Hz, 1H), 0.97 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.2, 166.5, 147.4, 130.2, 129.7, 125.5, 80.5, 69.8, 61.0, 49.0, 47.8, 44.9, 43.1, 36.8, 28.0, 27.3, 19.7, 18.9, 14.1, 13.6; HRMS (ESI) for $C_{22}H_{39}NO_5Na$ $[M+Na]^+$ calcd. 397.1985, found 397.1999.

Ethyl 3-hydroxy-3-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)propanoate (3ac)



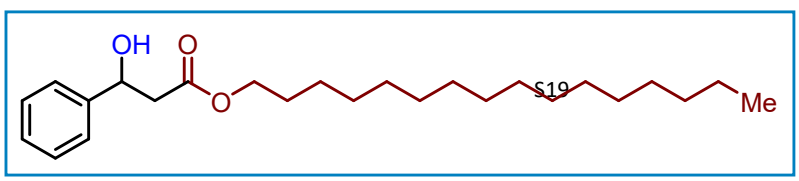
Purification by flash chromatography (PE/EA = 1/1) afforded **3ac.** Colorless oil; 53% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.32−7.25(m, 1H), 7.19−7.10 (m, 2H), 5.09 (dd, J = 9.0, 3.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.27 (br, 1H), 2.96−2.86 (m, 2H), 2.81−2.65 (m, 2H), 2.58−2.36 (m, 2H), 2.33−2.24 (m, 1H), 2.22−1.94 (m, 4H), 1.69−1.42 (m, 5H), 1.33−1.23 (m, 4H), 0.91 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 221.0, 172.5, 139.9, 139.3, 136.7, 126.2, 125.5, 123.1, 123.1, 70.0, 70.0, 60.8, 50.4, 47.9, 44.3, 43.2, 43.1, 38.0, 35.8, 31.5, 29.4, 29.4, 26.4, 25.6, 21.5, 14.1, 13.8; HRMS (ESI) for $C_{23}H_{30}NO_4Na$ $[M+Na]^+$ calcd. 393.2036, found 393.2042.

Methyl 3-hydroxy-3-phenylpropanoate (3aj)



Purification by flash chromatography (PE/EA = 6/1) afforded **3aj.** Colorless oil; 78% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.43−7.23 (m, 5H), 5.14 (dd, J = 8.8, 3.9 Hz, 1H), 3.72 (s, 3H), 3.23 (br, 1H), 2.84−2.66 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.8, 142.4, 128.5, 127.8, 125.6, 70.3, 51.9, 43.1; HRMS (ESI) for $C_{10}H_{12}O_3Na$ $[M+Na]^+$ calcd. 203.0679, found 203.0685.

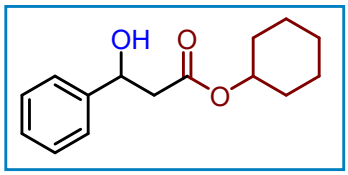
Hexadecyl 3-hydroxy-3-phenylpropanoate (3ak)



Purification by flash

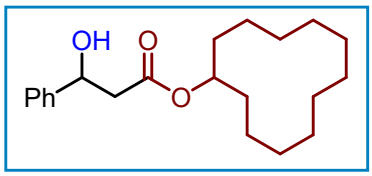
chromatography (PE/EA = 6/1) afforded **3ak.** Colorless oil; 48% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.40−7.26 (m, 5H), 5.17−5.09 (m, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 3.30 (d, *J* = 3.4 Hz, 1H), 2.81−2.66 (m, 2H), 1.64−1.58 (m, 2H), 1.34−1.24 (m, 26H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.5, 142.5, 128.5, 127.8, 125.6, 70.3, 65.1, 43.3, 31.9, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 28.5, 25.8, 22.7, 14.1; HRMS (ESI) for $C_{25}H_{42}O_3Na$ $[M+Na]^+$ calcd. 413.3026, found 413.3026.

Cyclohexyl 3-hydroxy-3-phenylpropanoate (3al)



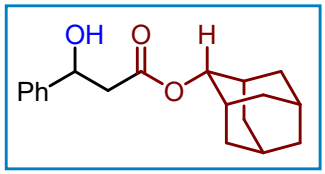
Purification by flash chromatography (PE/EA = 6/1) afforded **3al.** Colorless oil; 41% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.41−7.25 (m, 5H), 5.12 (t, *J* = 3.6 Hz, 1H), 4.87−4.76 (m, 1H), 3.34 (d, *J* = 2.2 Hz, 1H), 2.80−2.66 (m, 2H), 1.89−1.78 (m, 2H), 1.75−1.66 (m, 2H), 1.57−1.50 (m, 1H), 1.45−1.23 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 171.9, 142.5, 128.5, 127.7, 125.7, 73.3, 70.3, 43.6, 31.5, 25.3, 23.7; HRMS (ESI) for $C_{15}H_{20}O_3Na$ $[M+Na]^+$ calcd. 271.1305, found 271.1313.

Cyclohexyl 3-hydroxy-3-phenylpropanoate (3am)



Purification by flash chromatography (PE/EA = 6/1) afforded **3am.** Colorless oil; 39% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.41−7.25 (m, 5H), 5.16−5.02 (m, 2H), 3.37 (d, *J* = 3.6 Hz, 1H), 2.79−2.65 (m, 2H), 1.75−1.64 (m, 2H), 1.53−1.29 (m, 20H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.1, 142.5, 128.5, 127.7, 125.7, 73.0, 70.4, 43.5, 29.1, 29.0, 24.0, 24.0, 23.8, 23.3, 23.3, 23.2, 23.2, 20.8, 20.8; HRMS (ESI) for $C_{21}H_{32}O_3Na$ $[M+Na]^+$ calcd. 355.2244, found 355.2252.

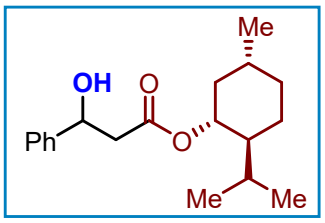
(1R,3S,5r,7r)-Adamantan-2-yl 3-hydroxy-3-phenylpropanoate (3an)



Purification by flash chromatography (PE/EA = 6/1) afforded **3an.** Colorless oil; 60% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.42−7.32 (m, 4H), 7.31−7.25 (m, 1H), 5.18−5.11 (m, 1H), 4.98 (s, 1H), 3.38 (d, *J* = 2.9 Hz, 1H), 2.86−2.72 (m, 2H),

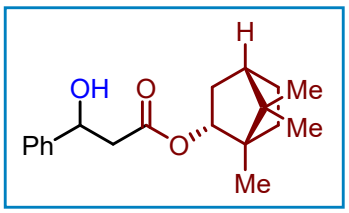
2.00−1.90 (m, 4H), 1.97−1.71 (m, 8H), 1.56 (s, 1H), 1.53 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 171.8, 142.5, 128.5, 127.7, 125.7, 77.8, 70.4, 43.6, 37.3, 36.3, 31.8, 31.8, 31.7, 31.7, 27.1, 26.9; HRMS (ESI) for $C_{19}H_{24}O_3Na$ $[M+Na]^+$ calcd. 323.1618, found 323.1628.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 3-hydroxy-3-phenylpropanoate (3ao)



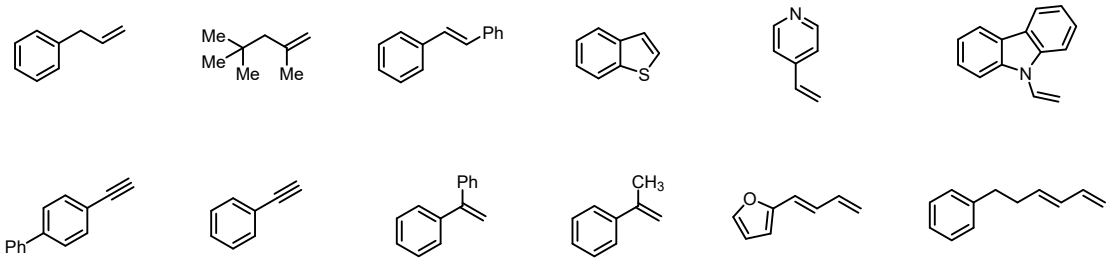
Purification by flash chromatography (PE/EA = 6/1) afforded **3ao.** Colorless oil; 73% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.43−7.24 (m, 5H), 5.17−5.07 (m, 1H), 4.78−4.67 (m, 1H), 3.49−3.25 (m, 1H), 2.81−2.65 (m, 2H), 1.99−1.93 (m, 1H), 1.80−1.71 (m, 1H), 1.70−1.63 (m, 2H), 1.53−1.41 (m, 1H), 1.39−1.30 (m, 1H), 1.06−0.94 (m, 2H), 0.92−0.83 (m, 7H), 0.72 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.1, 171.9, 142.5, 142.5, 128.5, 128.5, 127.7, 127.7, 125.7, 125.6, 74.8, 70.4, 70.2, 46.9, 46.9, 43.5, 43.3, 40.8, 40.8, 34.1, 31.4, 26.2, 26.2, 23.4, 21.9, 20.7, 20.7, 16.3, 16.3; HRMS (ESI) for $C_{19}H_{28}O_3Na$ $[M+Na]^+$ calcd. 327.1931, found 327.1944.

(1S,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 3-hydroxy-3-phenylpropanoate (3ap)



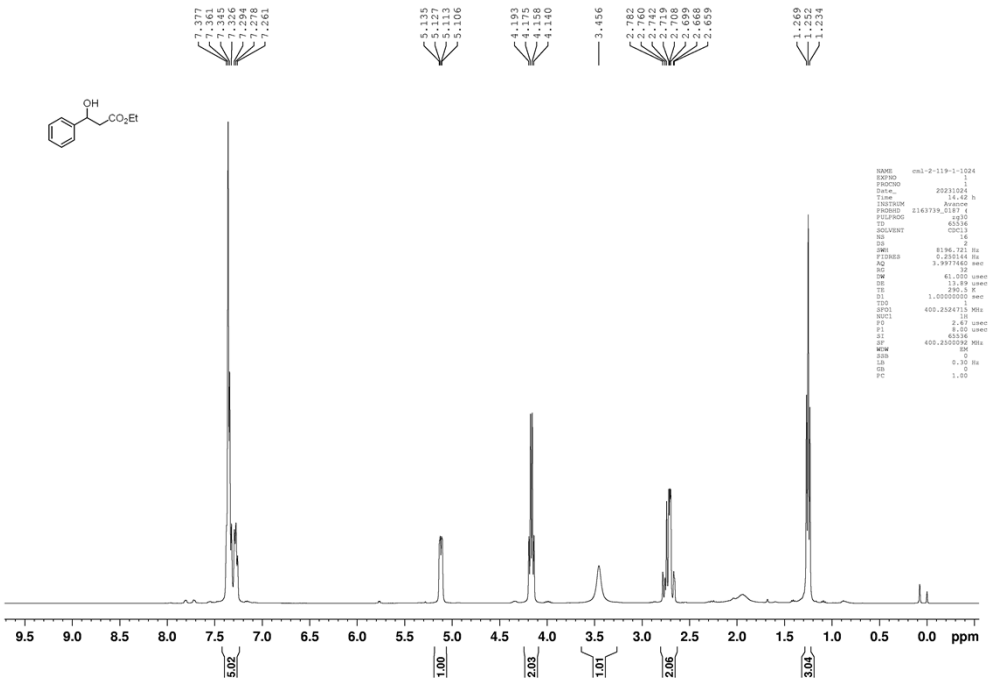
Purification by flash chromatography (PE/EA = 6/1) afforded **3ap.** Colorless oil; 76% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.42−7.24 (m, 5H), 5.18−5.07 (m, 1H), 4.97−4.87 (m, 1H), 3.44−3.28 (m, 1H), 2.85−2.70 (m, 2H), 2.40−2.30 (m, 1H), 1.89−1.81 (m, 1H), 1.77−1.70 (m, 1H), 1.68−1.64 (m, 1H), 1.28−1.23 (m, 1H), 1.22−1.14 (m, 1H), 0.96−0.90 (m, 1H), 0.90 (s, 3H) 0.86 (s, 3H), 0.81−0.78 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.7, 172.6, 142.5, 128.5, 127.7, 125.7, 80.6, 70.4, 70.3, 48.7, 48.7, 47.8, 47.8, 44.8, 43.5, 43.4, 36.6, 36.6, 27.9, 27.9, 27.1, 19.6, 18.8, 13.4, 13.4; HRMS (ESI) for $C_{19}H_{26}O_3Na$ $[M+Na]^+$ calcd. 325.1774, found 325.1787.

7. Unproductive substrates

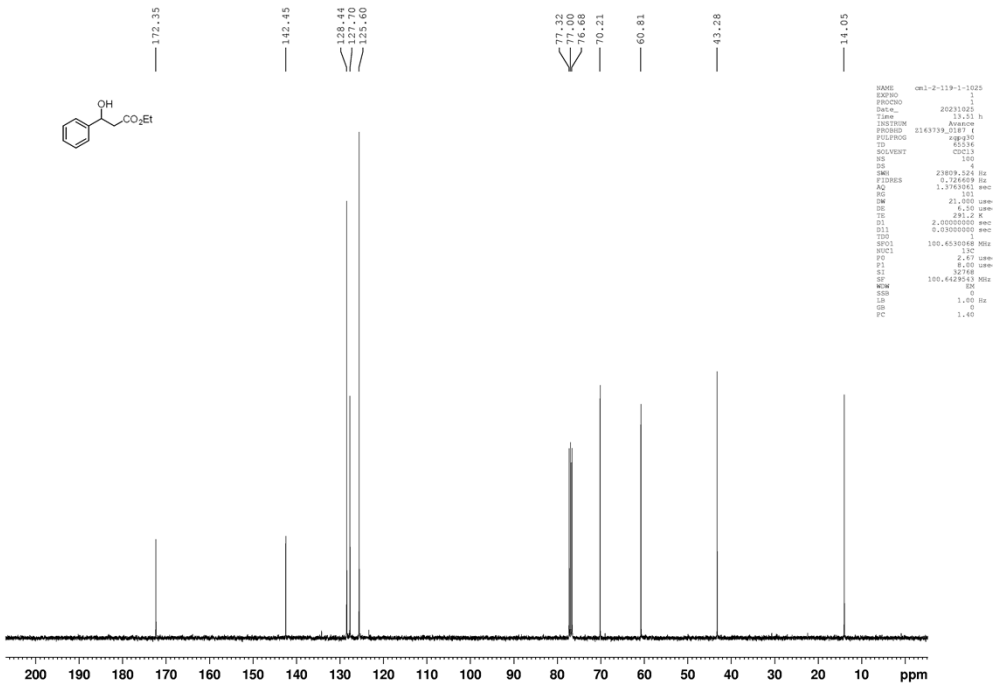


The alkylsubtituted alkenes, 1,2-disubstituted alkenes, vinyl pyridines, teriminal alkynes, (*E*)-2-(buta-1,3-dien-1-yl)furan and (*E*)-hexa-3,5-dien-1-ylbenzene couldn't afford the desired products.

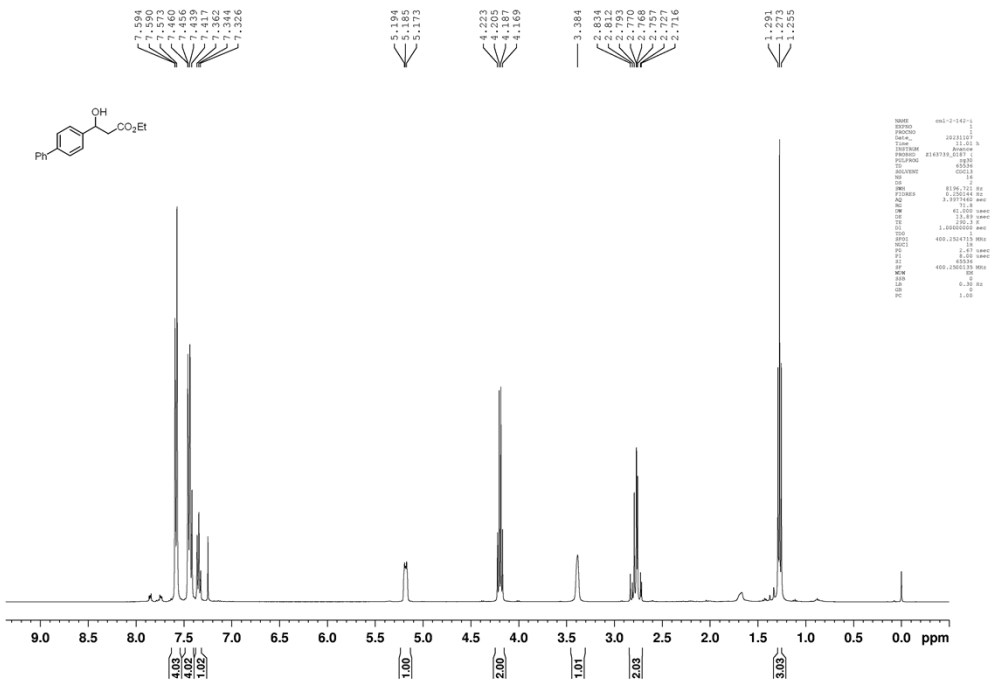
8. NMR spectra of compounds



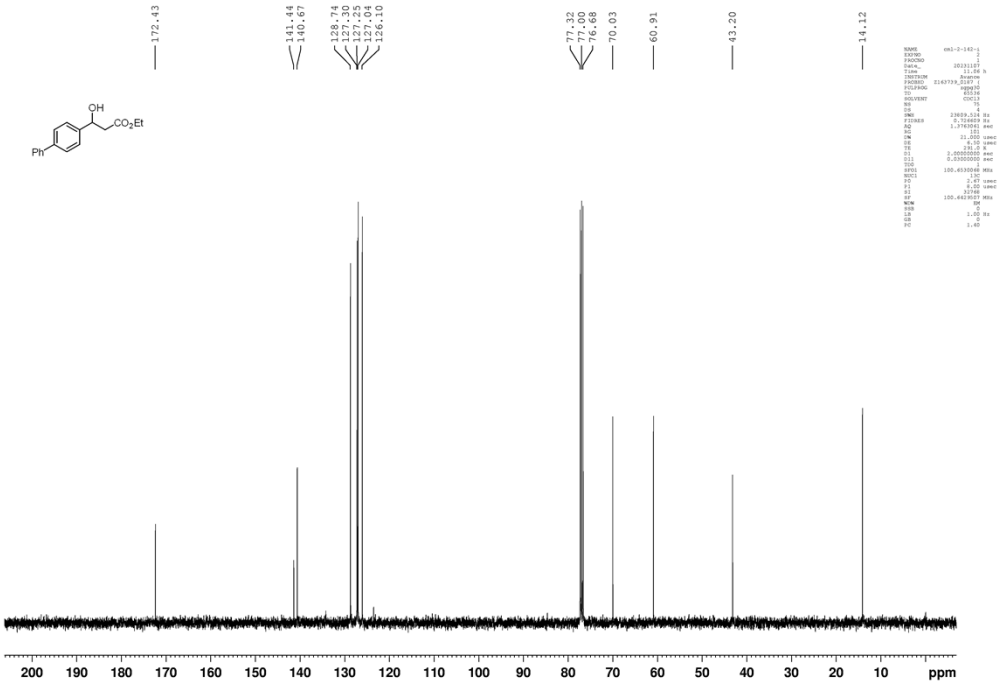
^{1}H NMR spectrum for compound **3a**



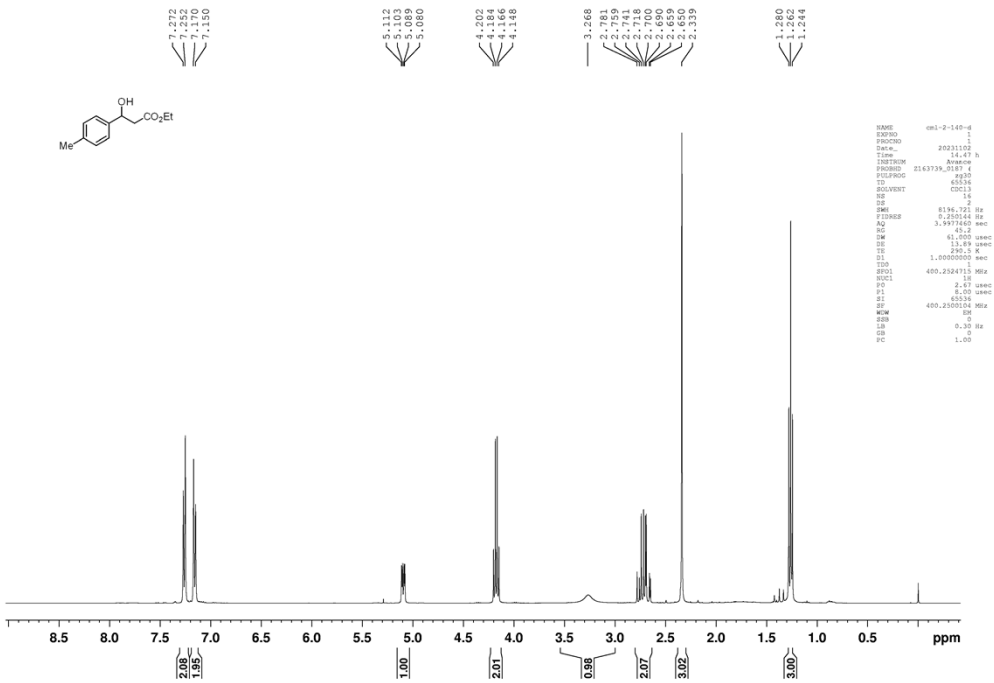
^{13}C NMR spectrum for compound **3a**



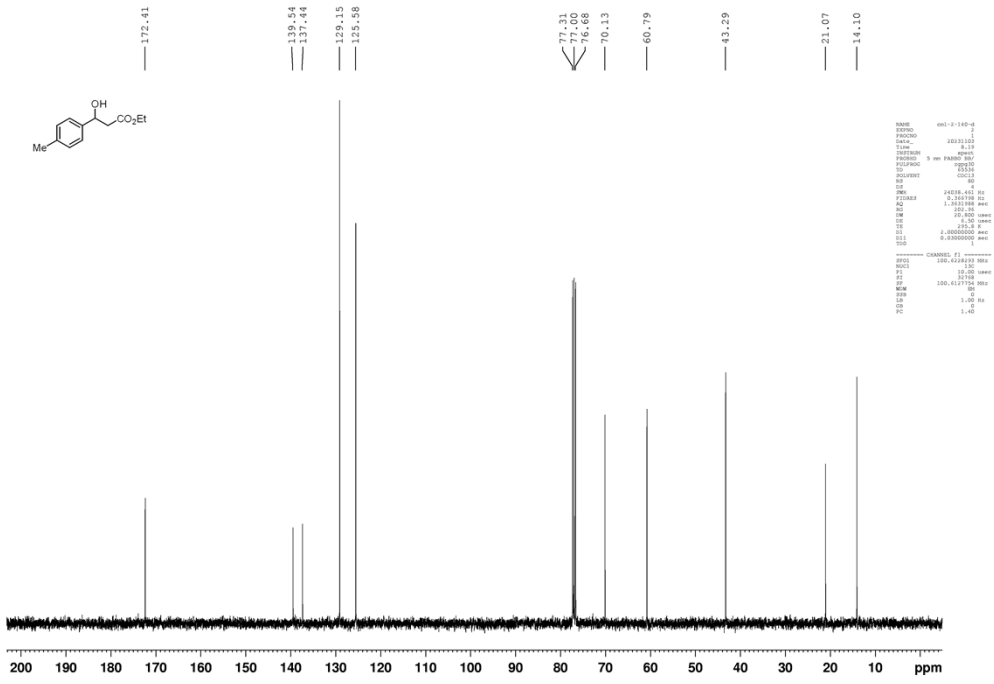
^{1}H NMR spectrum for compound **3b**



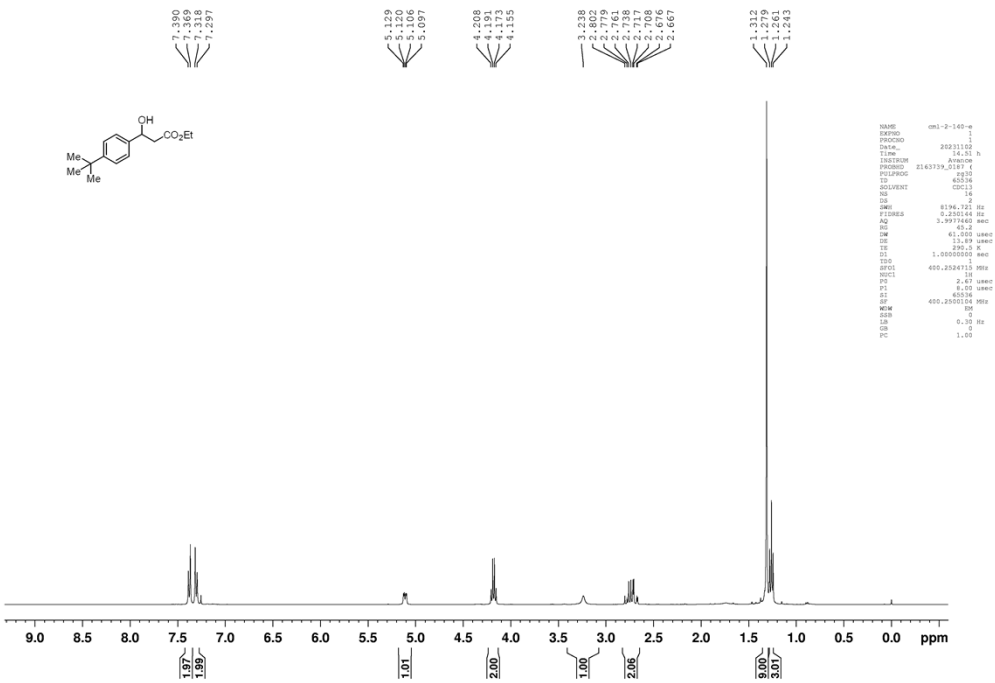
^{13}C NMR spectrum for compound **3b**



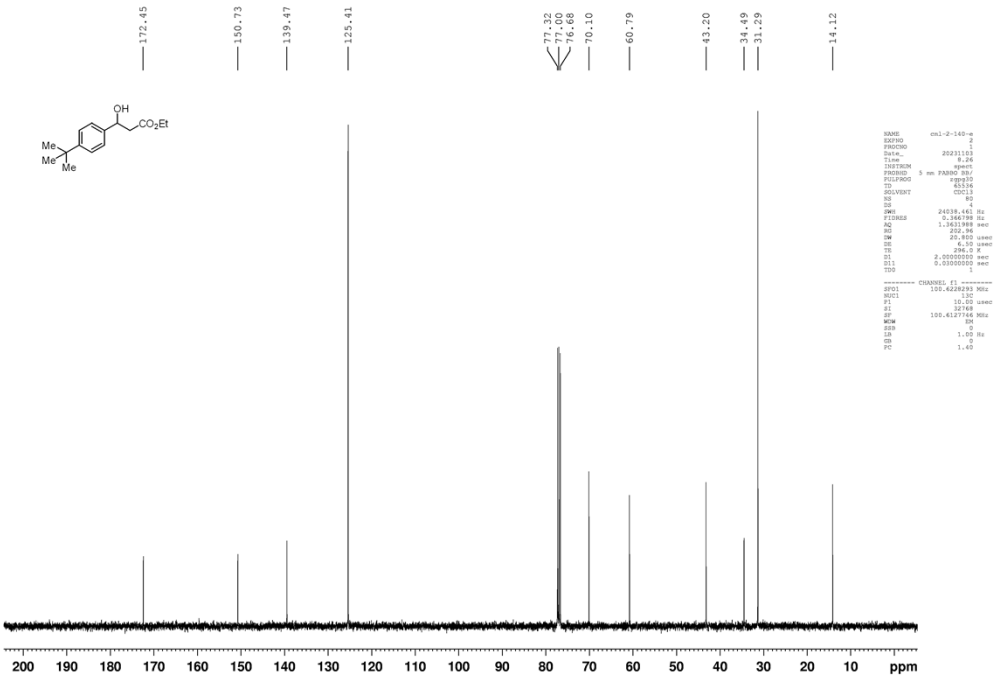
^{1}H NMR spectrum for compound **3c**



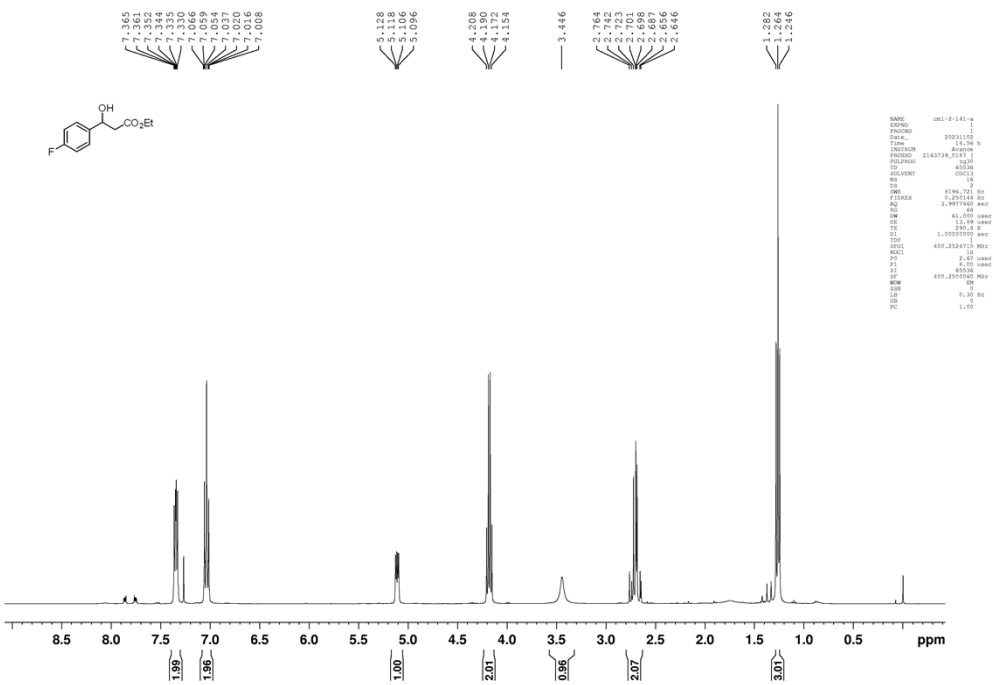
^{13}C NMR spectrum for compound **3c**



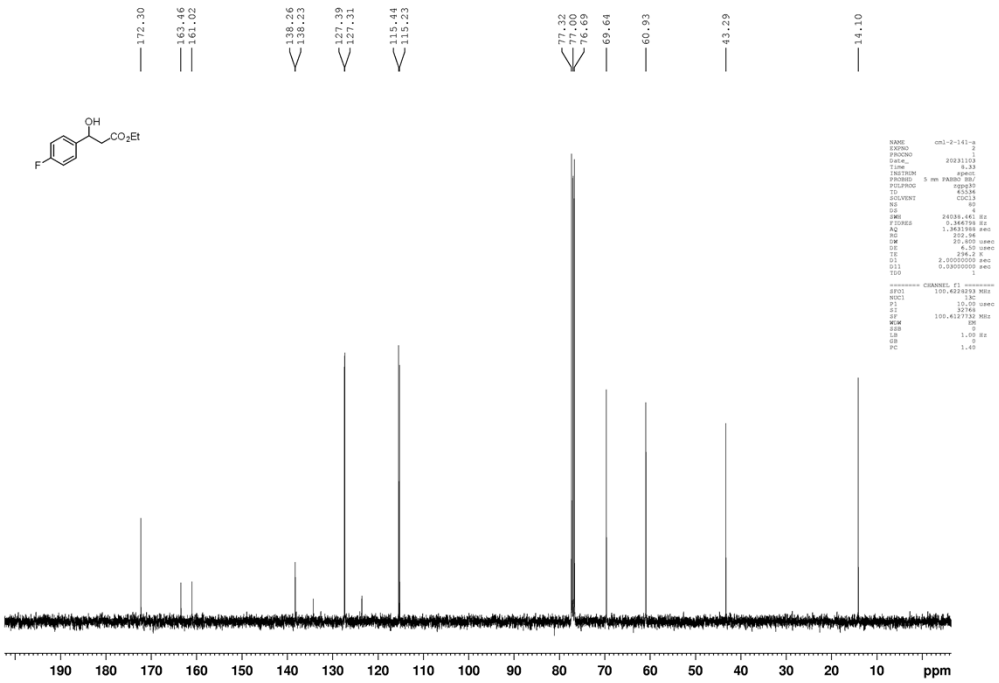
^{1}H NMR spectrum for compound **3d**



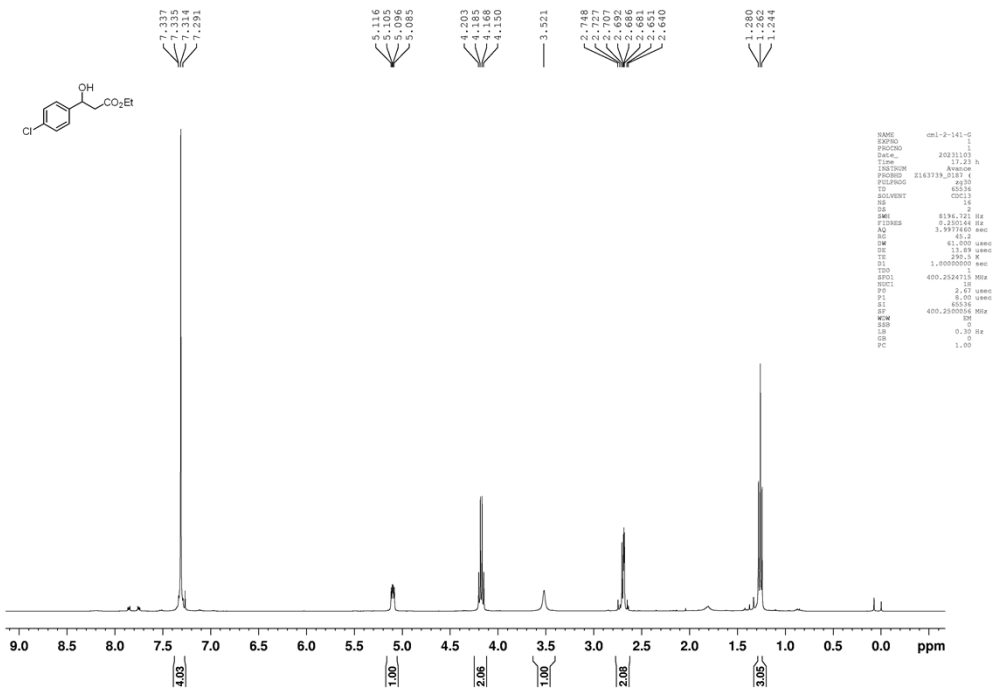
^{13}C NMR spectrum for compound **3d**



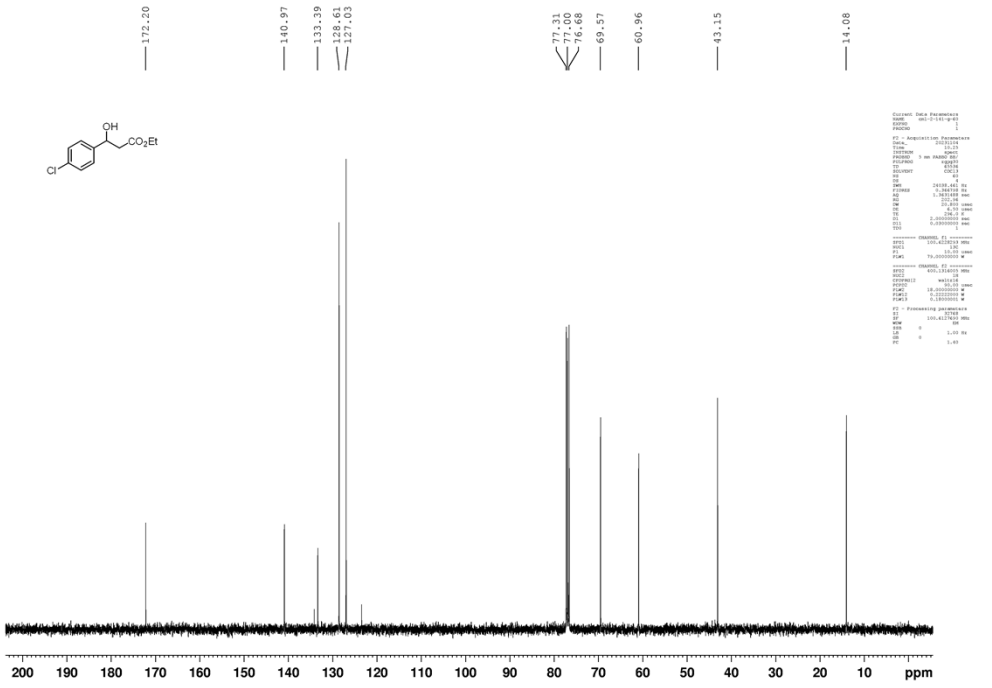
^{1}H NMR spectrum for compound **3e**



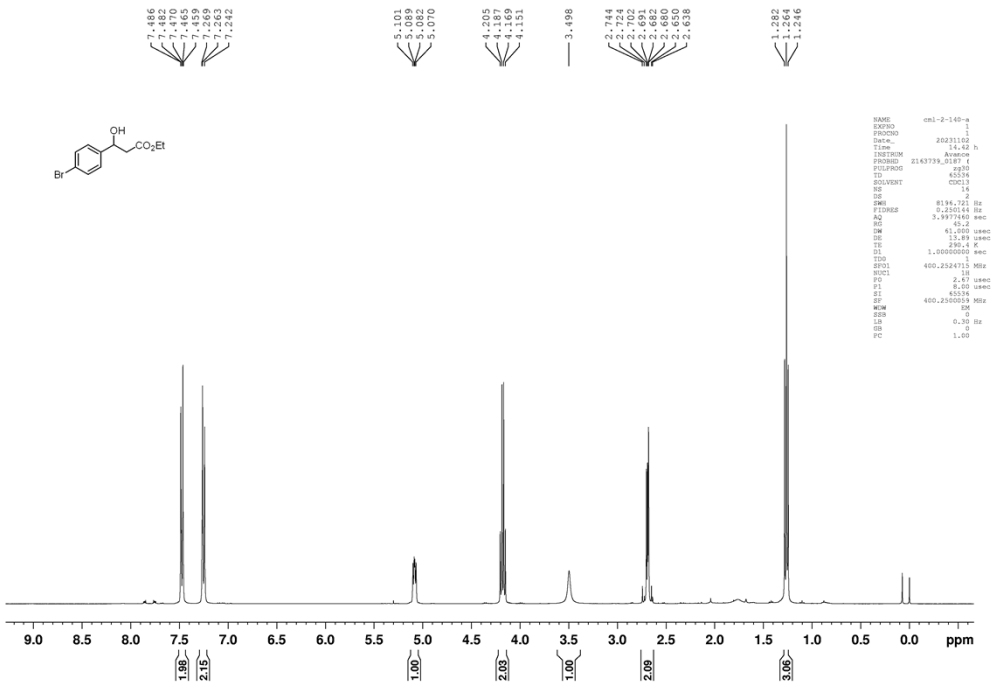
^{13}C NMR spectrum for compound **3e**



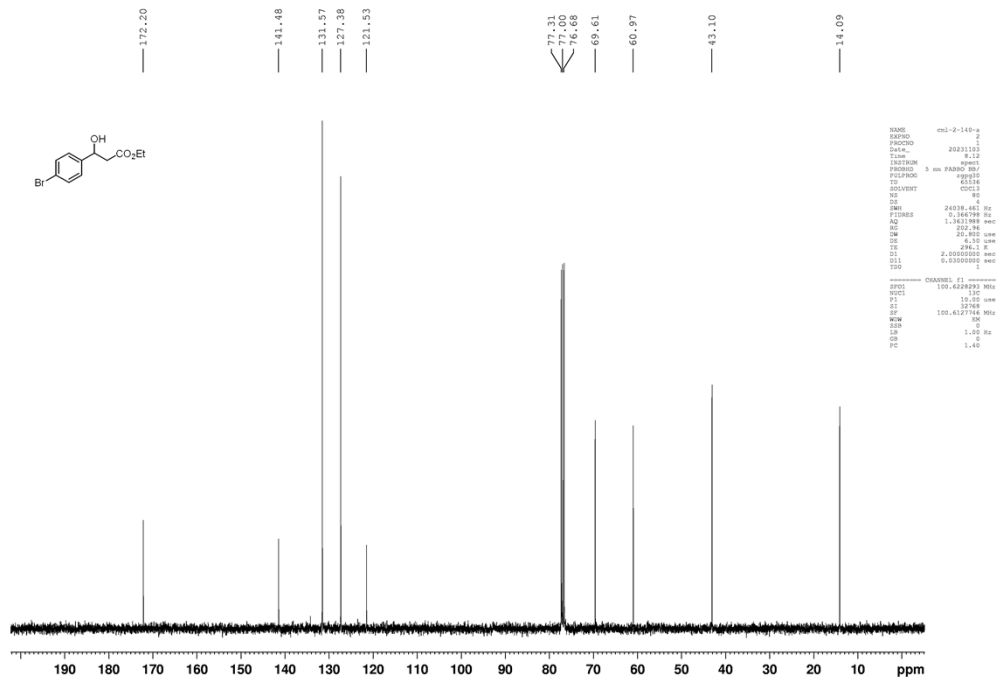
^{1}H NMR spectrum for compound **3f**



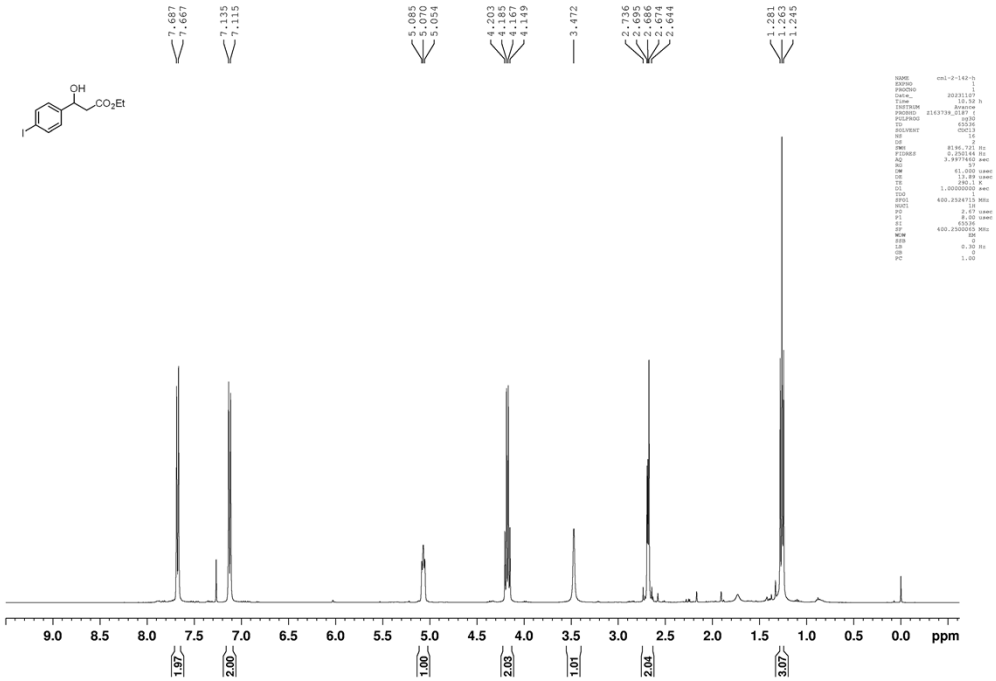
^{13}C NMR spectrum for compound **3f**



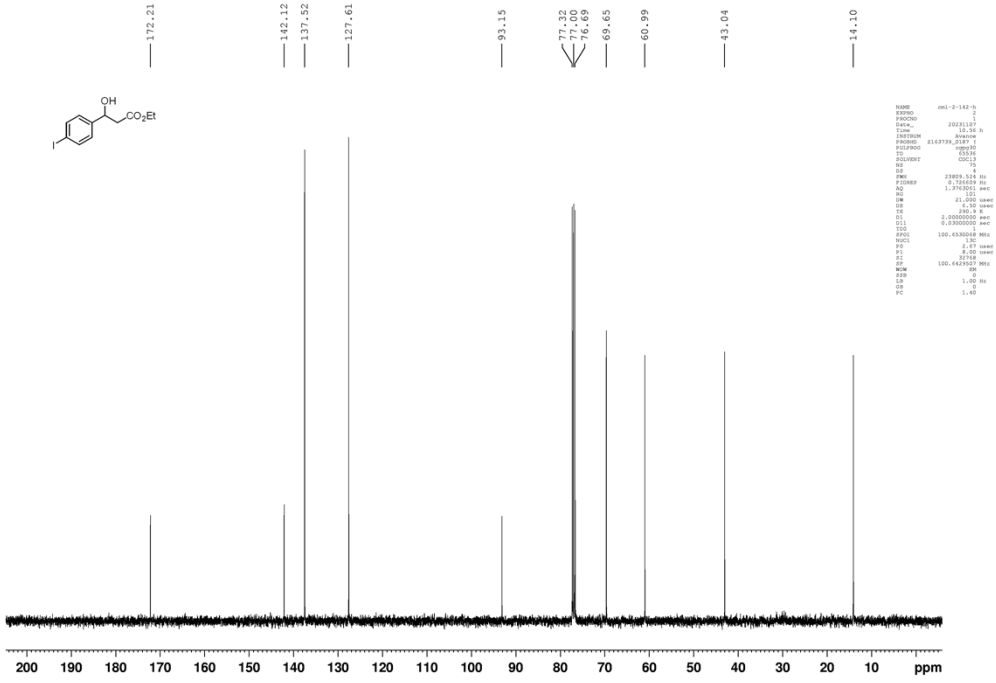
^{1}H NMR spectrum for compound **3g**



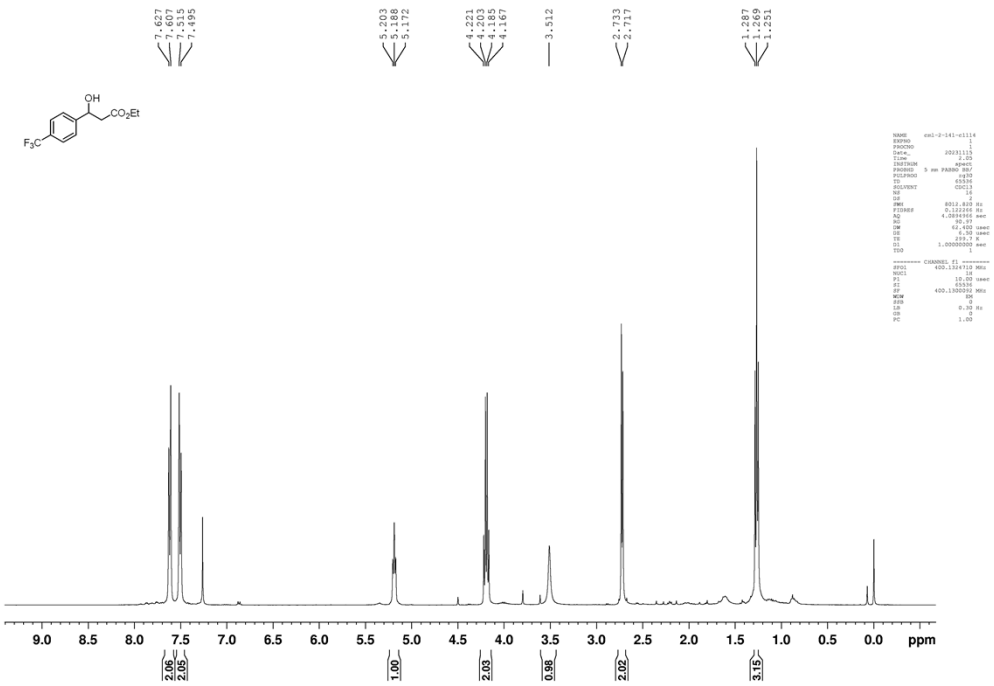
^{13}C NMR spectrum for compound **3g**



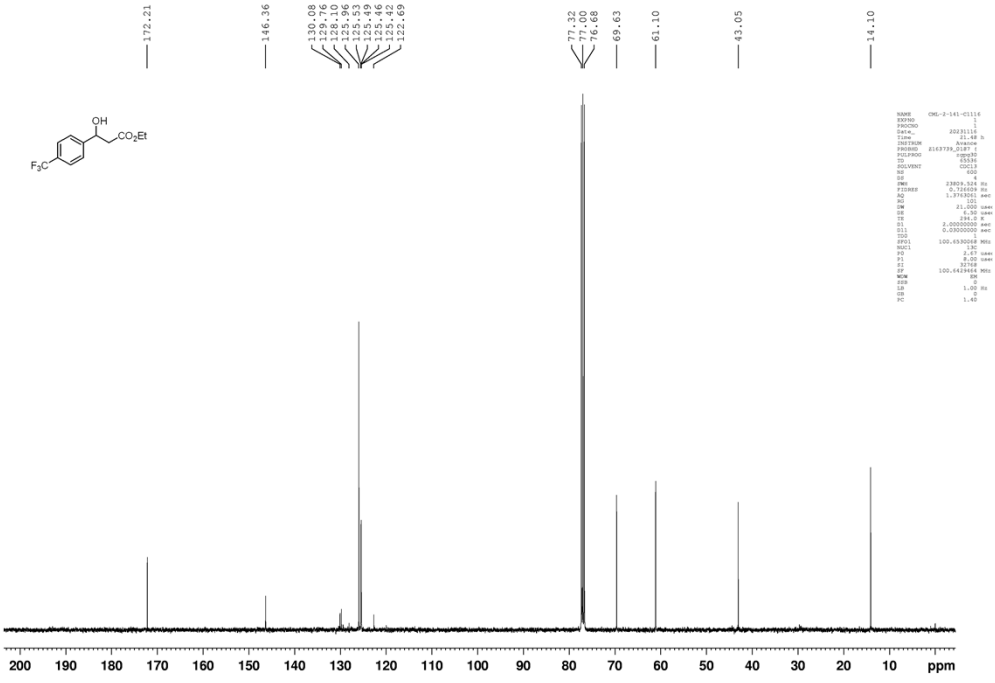
^{1}H NMR spectrum for compound **3h**



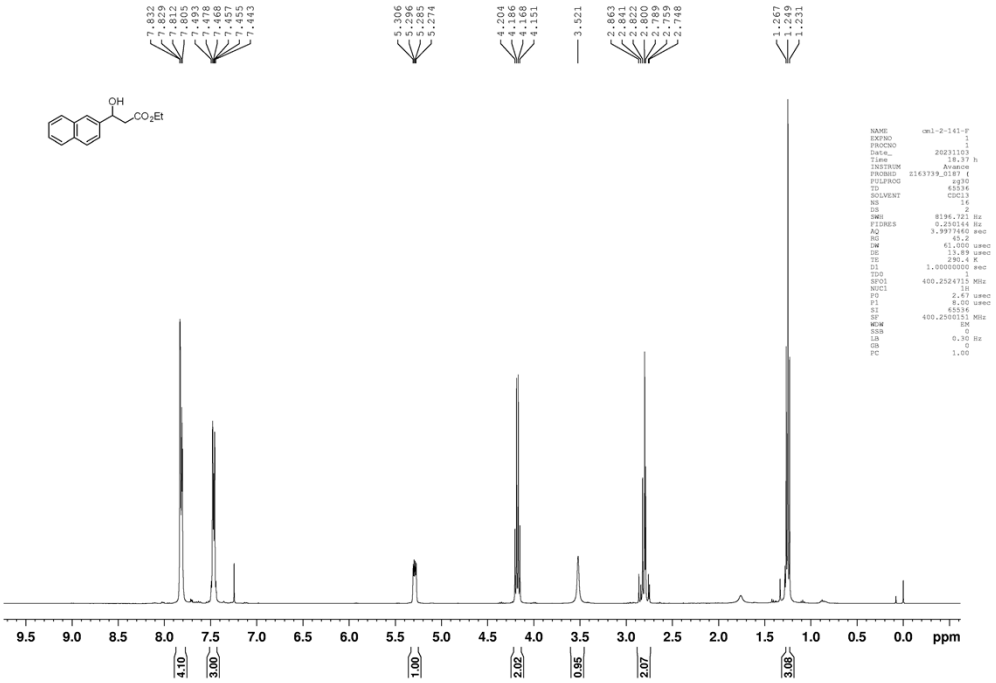
^{13}C NMR spectrum for compound **3h**



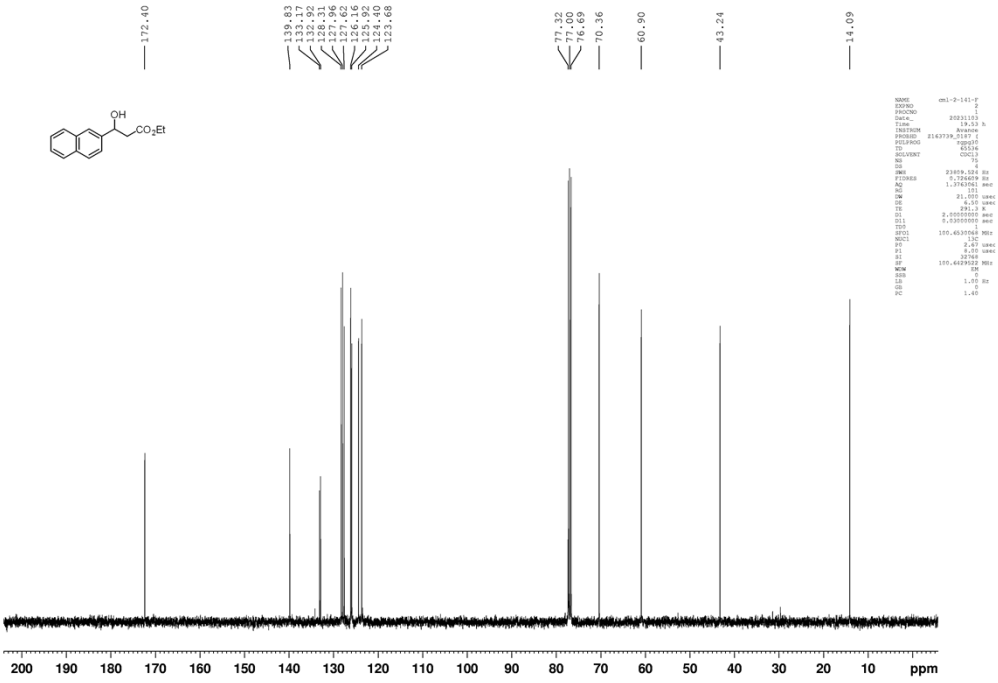
^{1}H NMR spectrum for compound **3i**



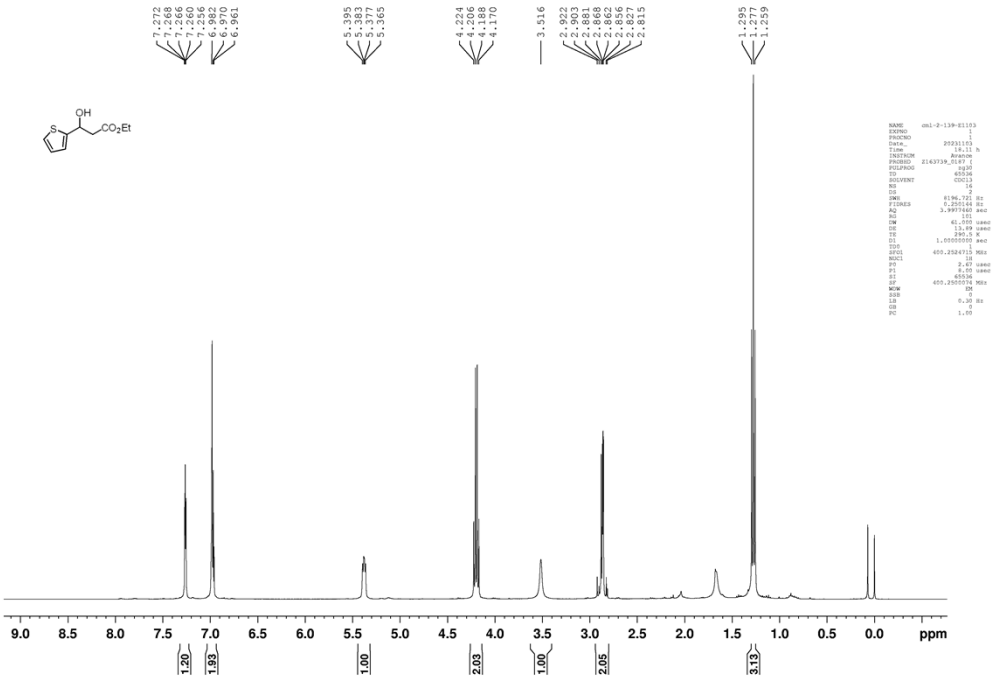
^{13}C NMR spectrum for compound **3i**



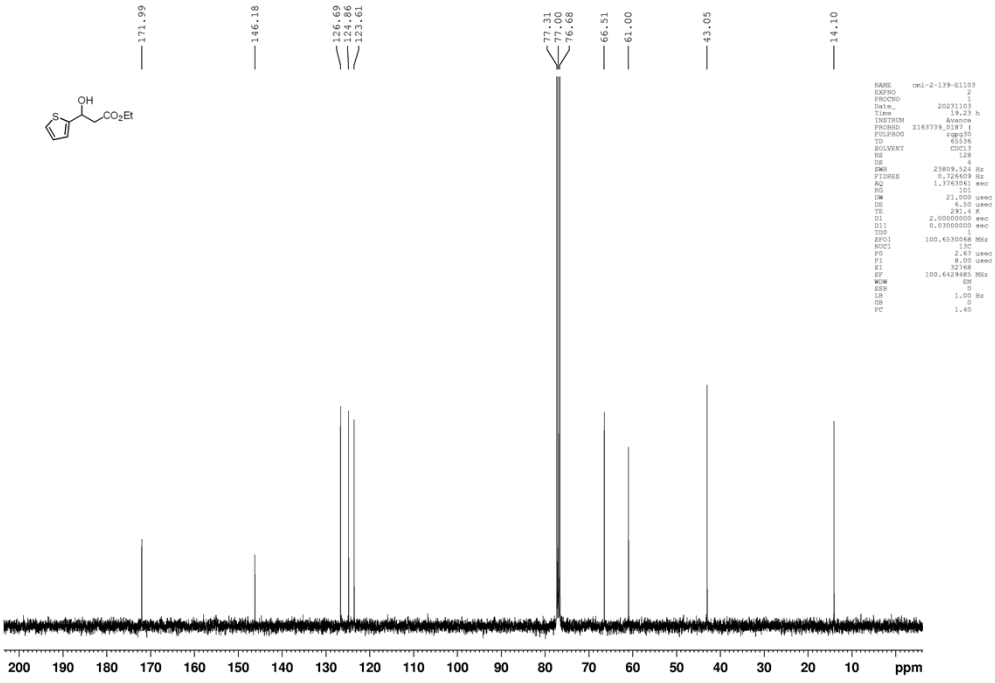
^{1}H NMR spectrum for compound **3j**



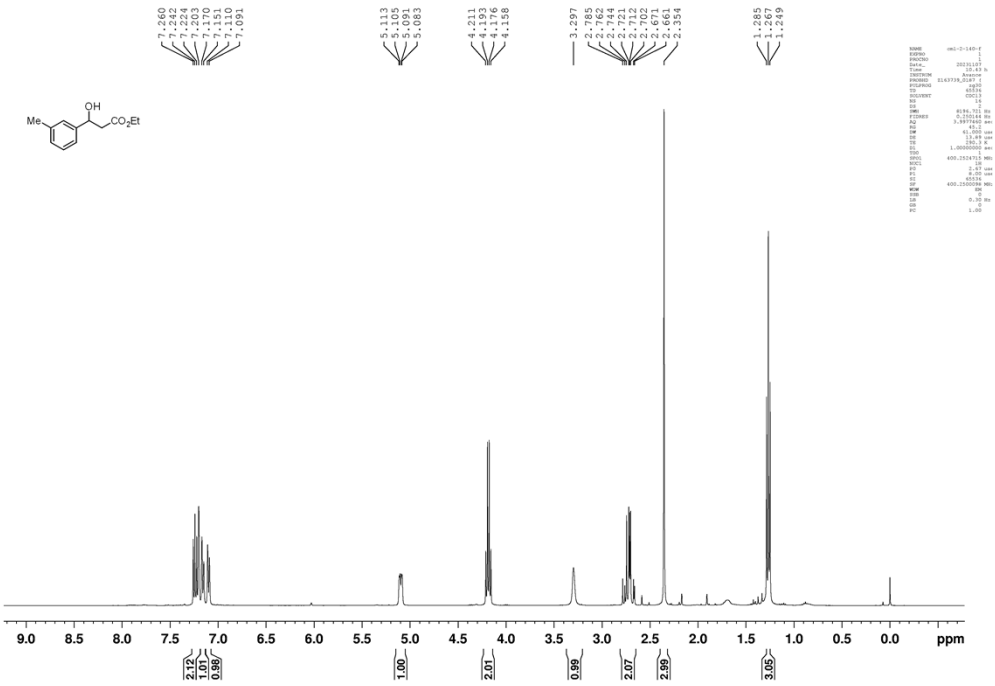
^{13}C NMR spectrum for compound **3j**



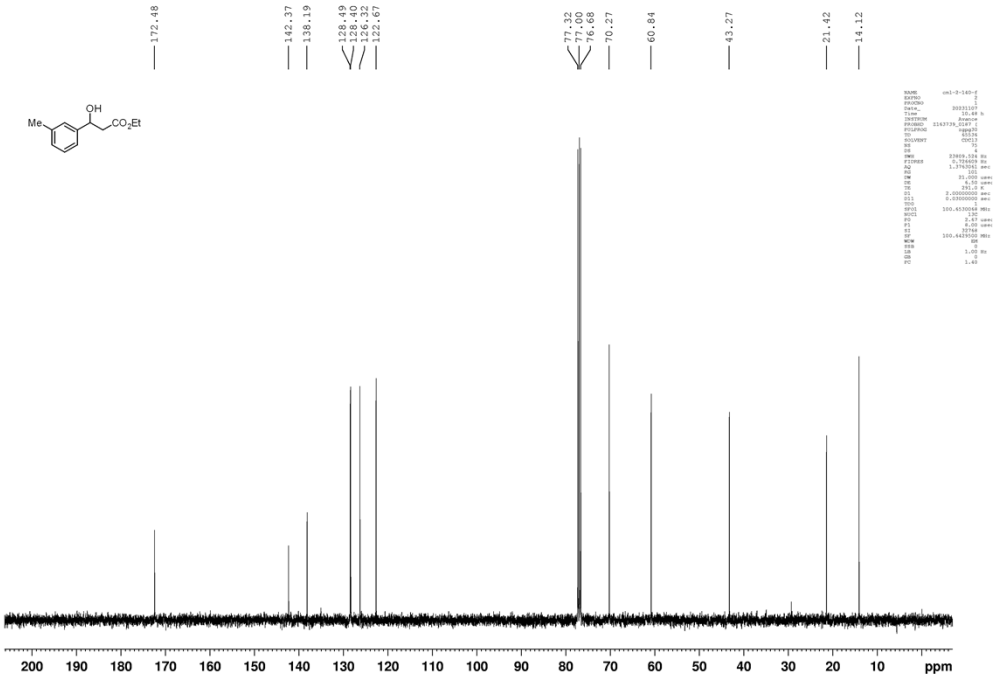
^{1}H NMR spectrum for compound **3k**



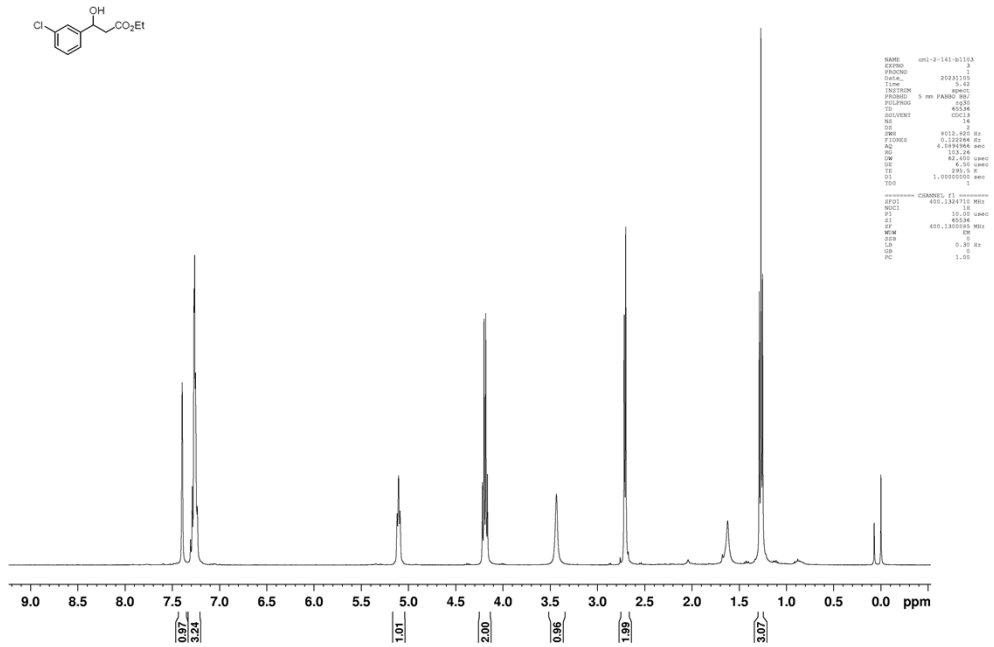
^{13}C NMR spectrum for compound **3k**



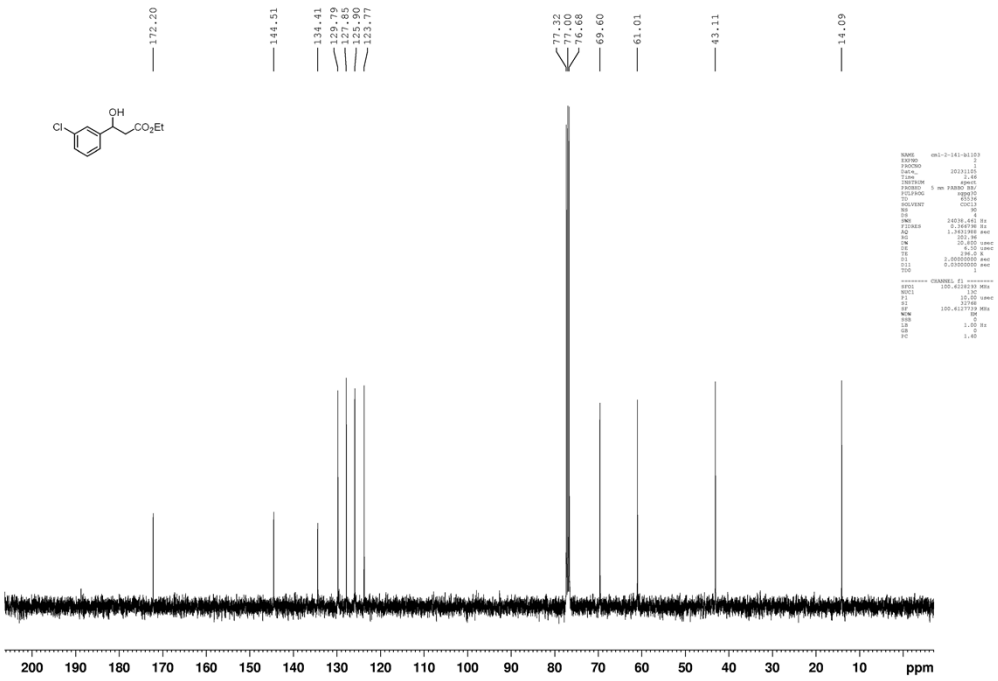
^{1}H NMR spectrum for compound **3l**



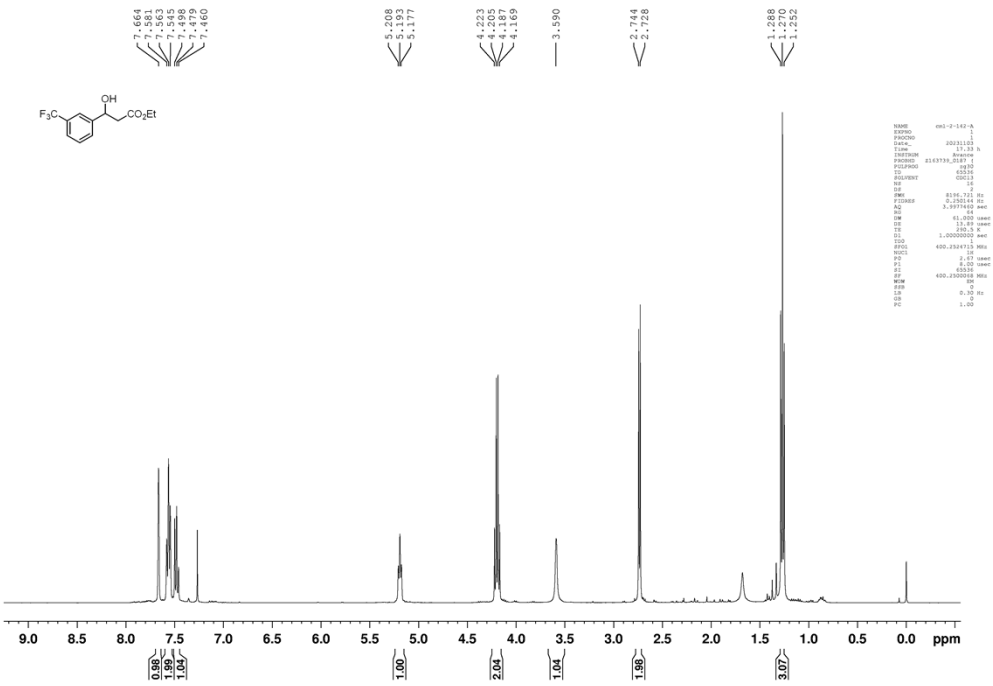
^{13}C NMR spectrum for compound **3l**



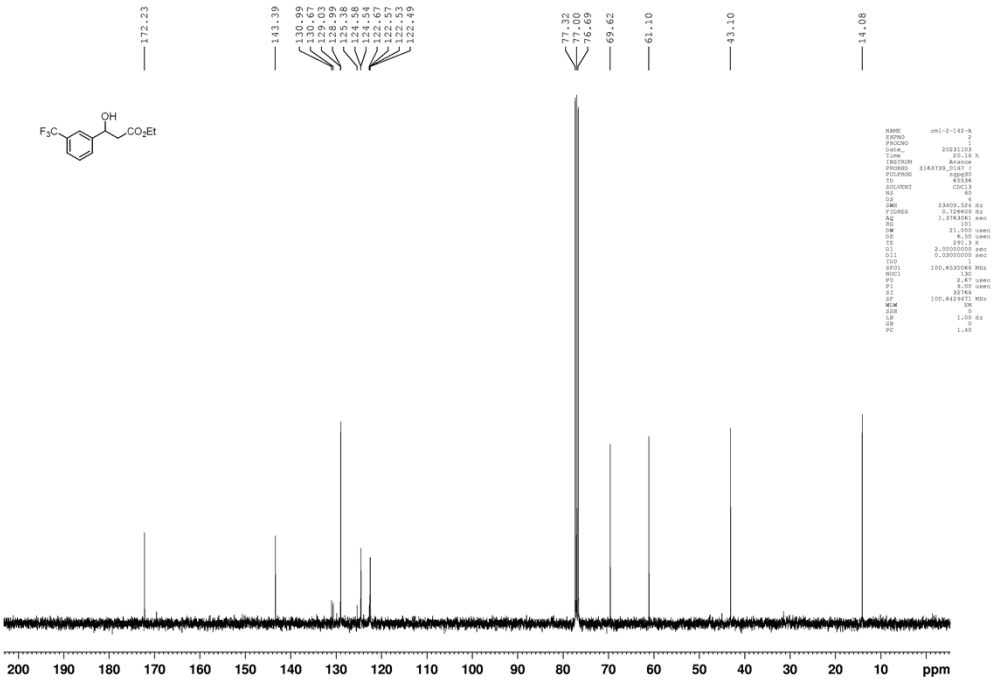
^{1}H NMR spectrum for compound **3m**



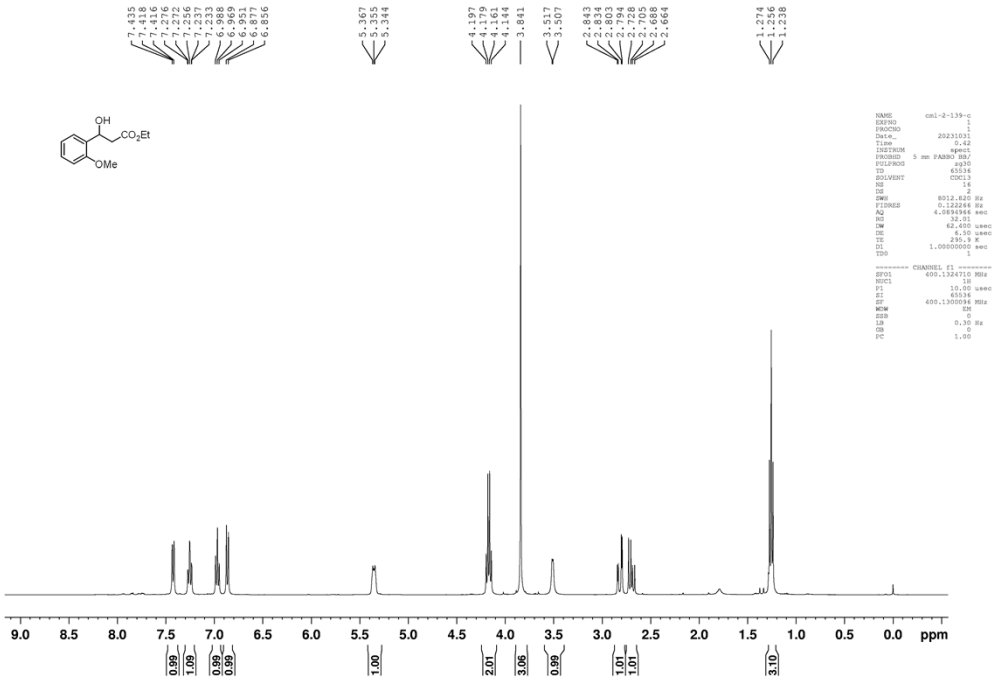
^{13}C NMR spectrum for compound **3m**



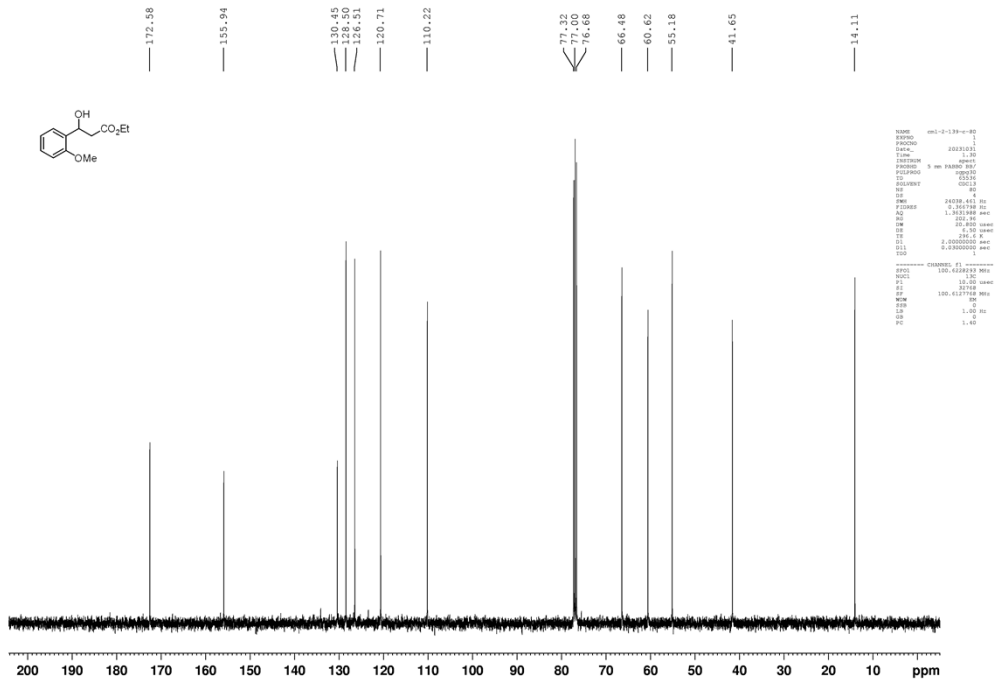
^{1}H NMR spectrum for compound **3n**



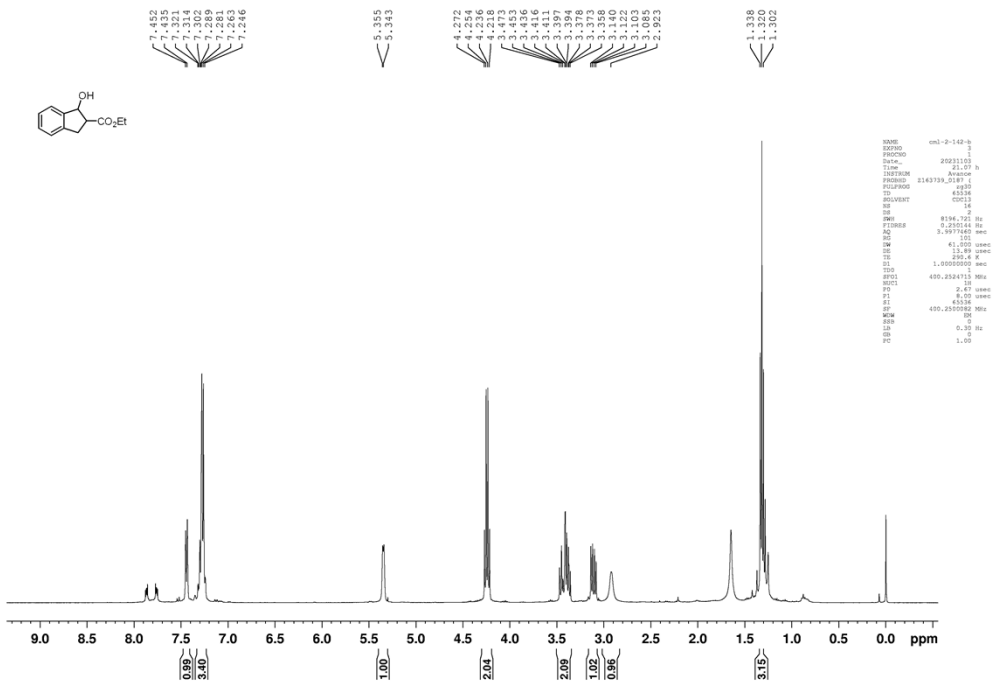
^{13}C NMR spectrum for compound **3n**



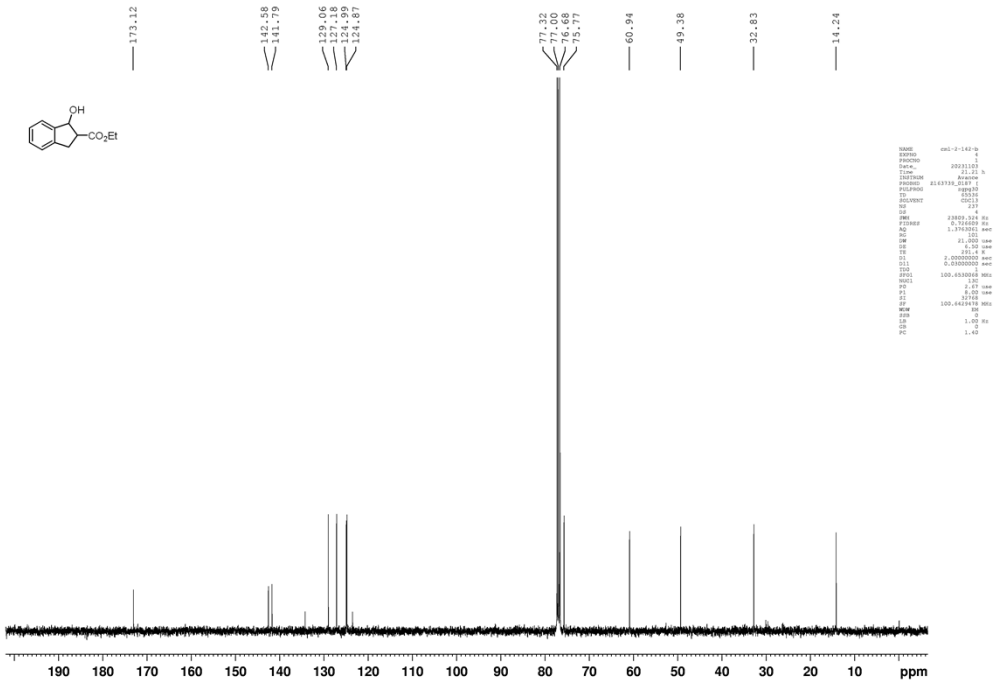
^{1}H NMR spectrum for compound **3o**



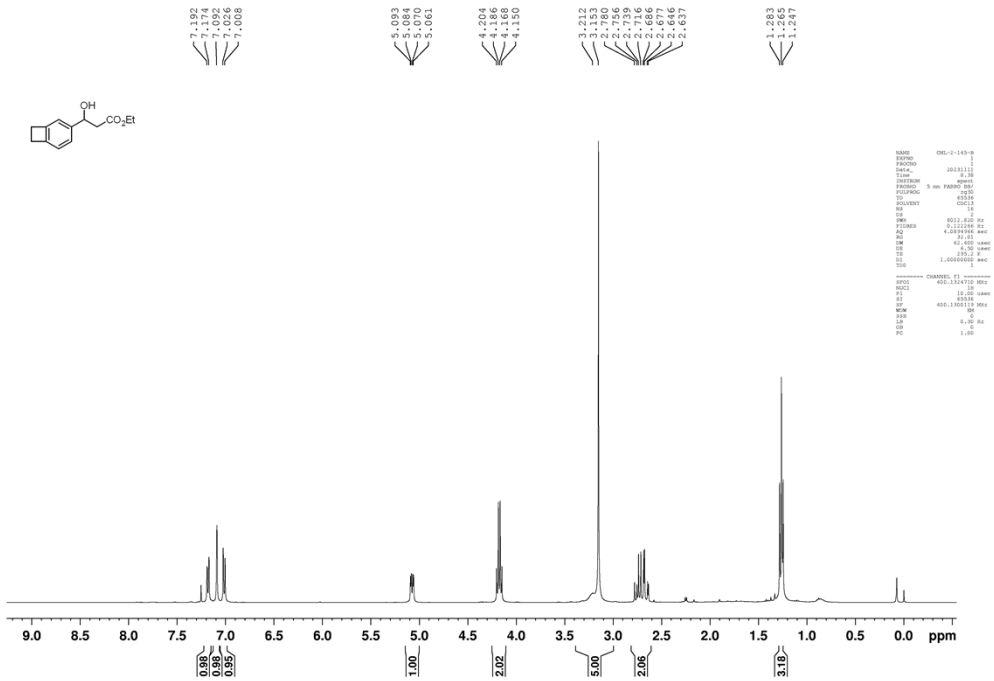
^{13}C NMR spectrum for compound **3o**



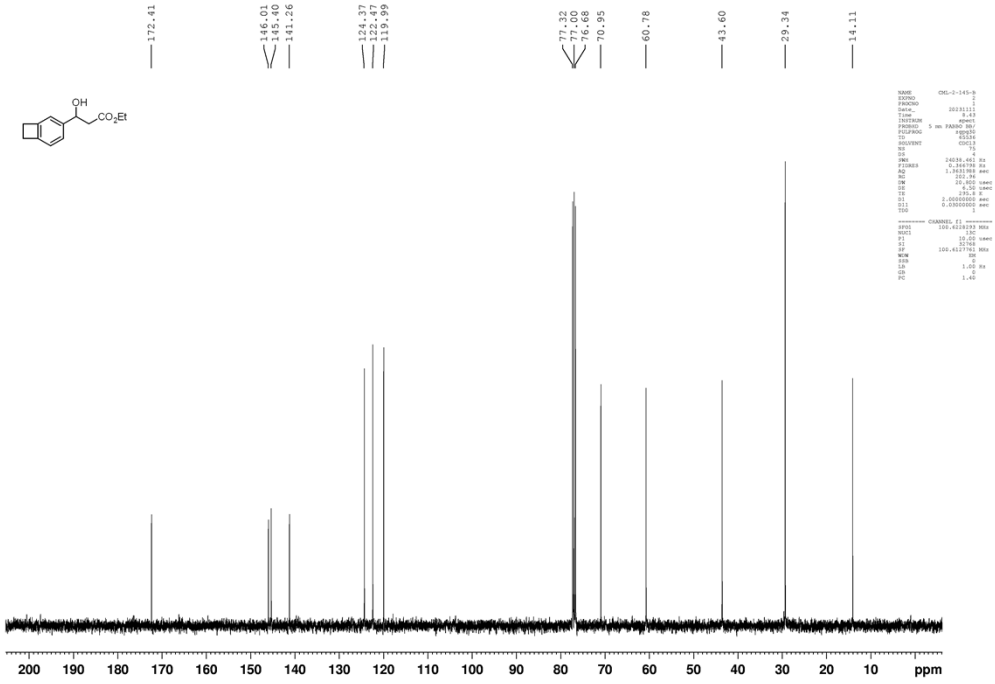
^{1}H NMR spectrum for compound **3p**



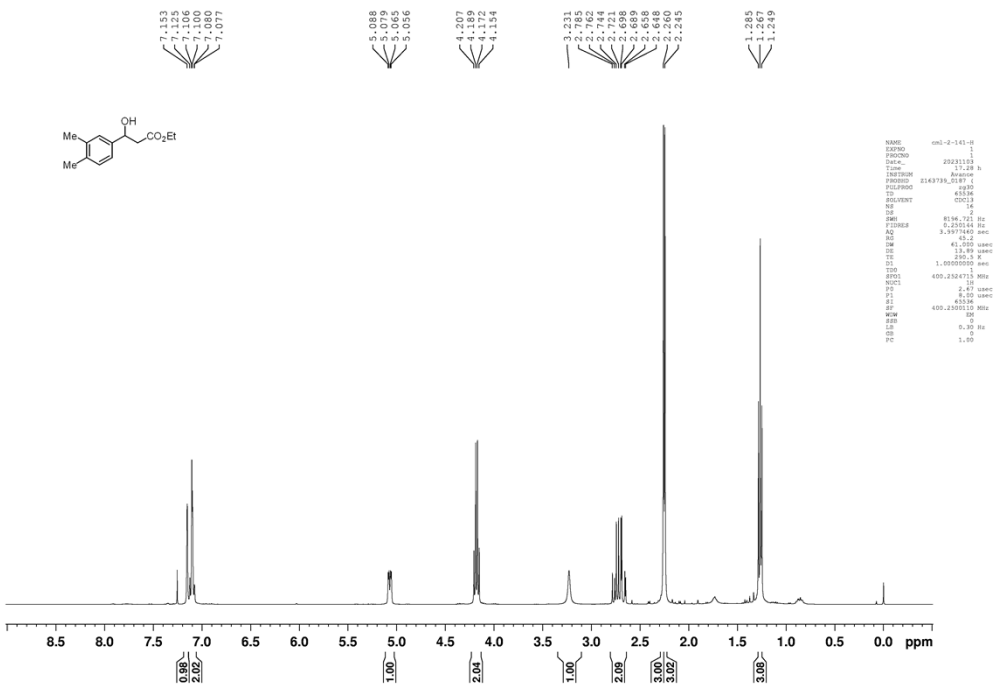
^{13}C NMR spectrum for compound **3p**



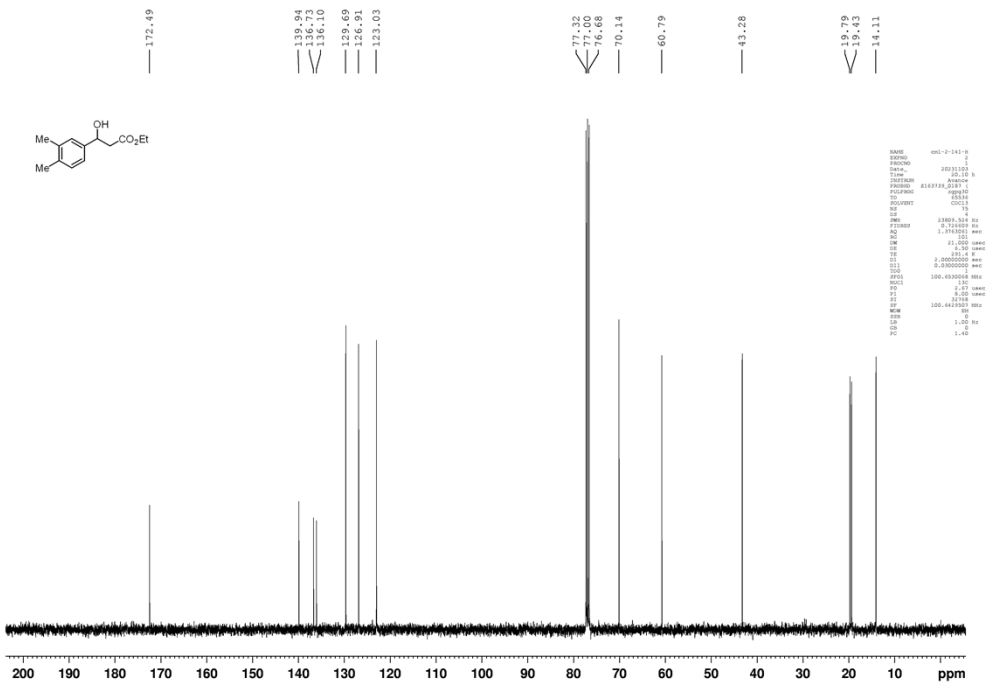
^{1}H NMR spectrum for compound **3q**



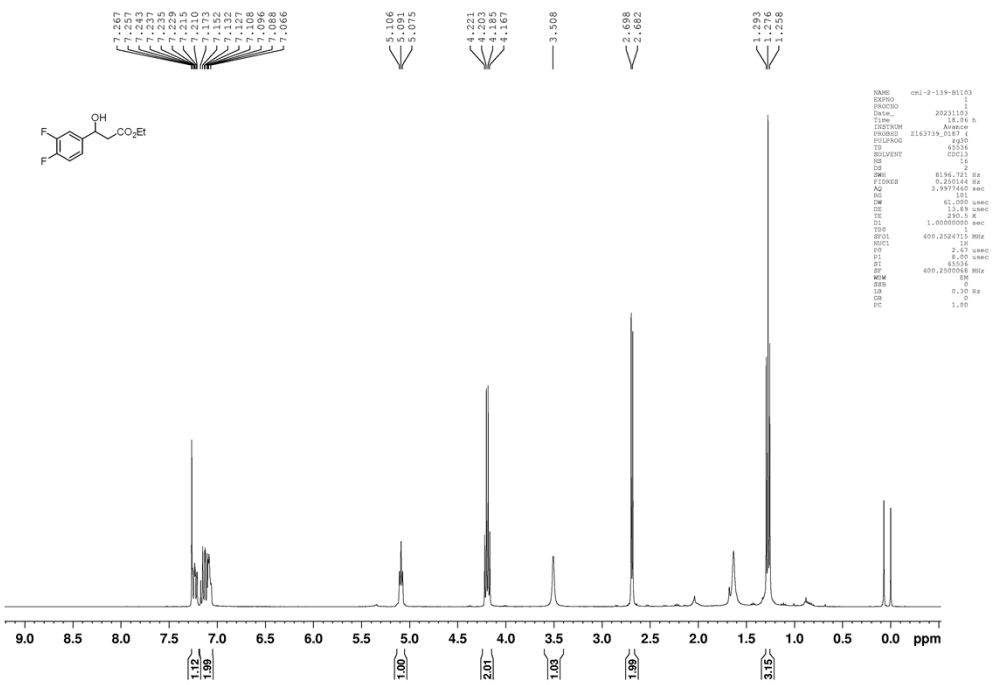
^{13}C NMR spectrum for compound **3q**



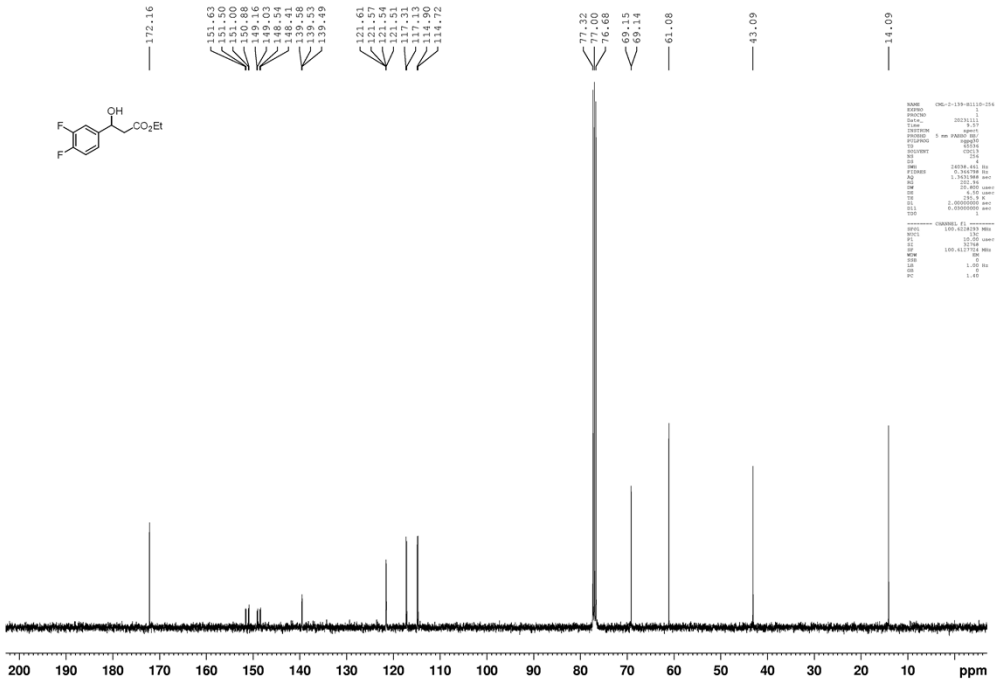
^{1}H NMR spectrum for compound **3r**



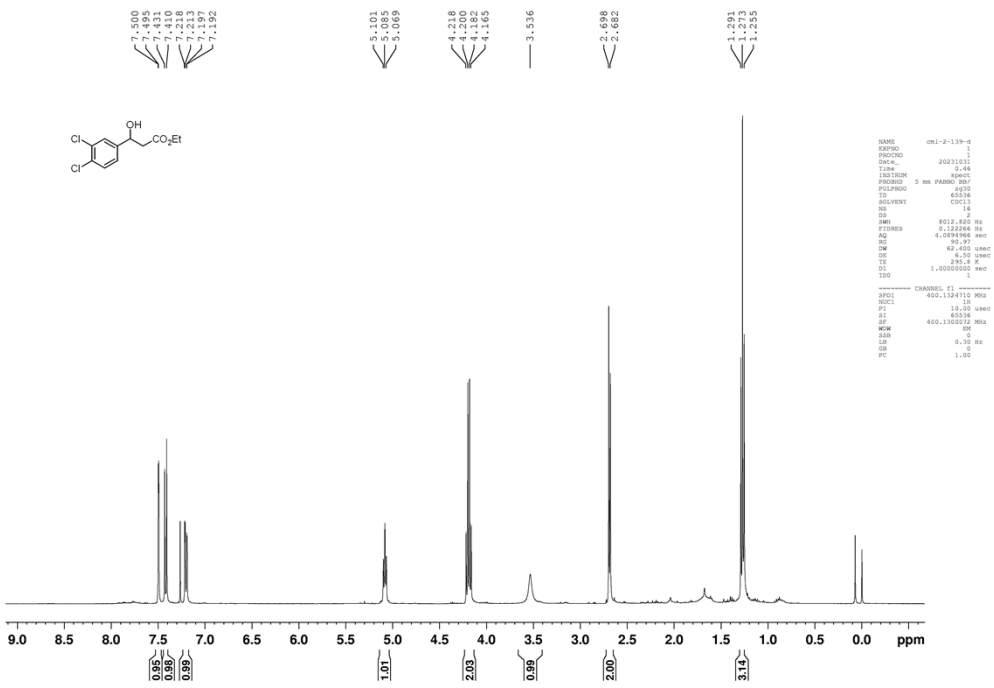
^{13}C NMR spectrum for compound **3r**



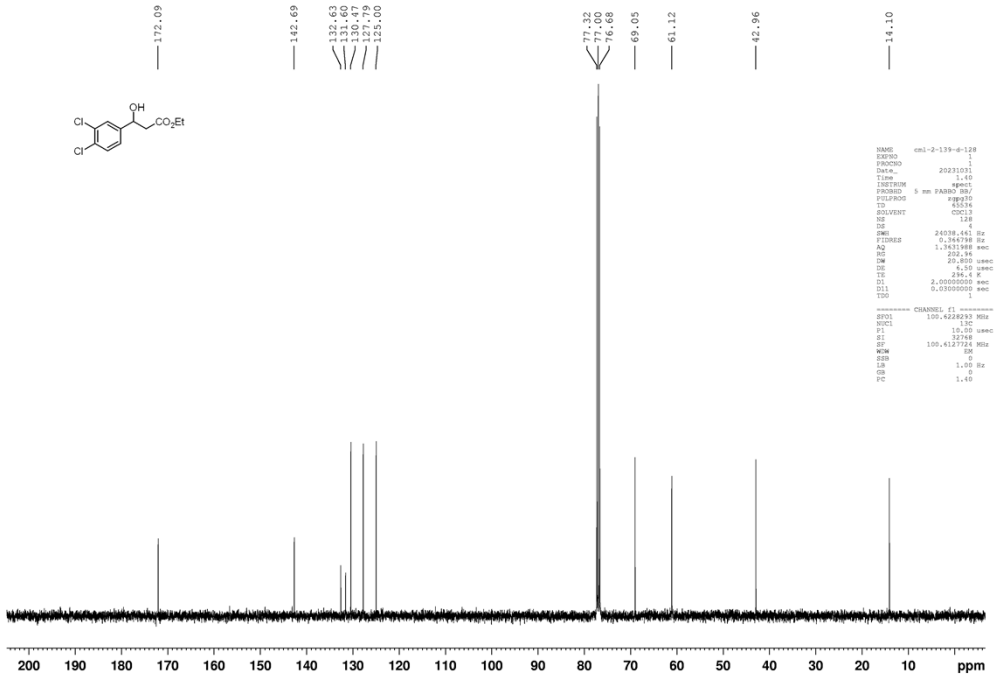
^{1}H NMR spectrum for compound **3s**



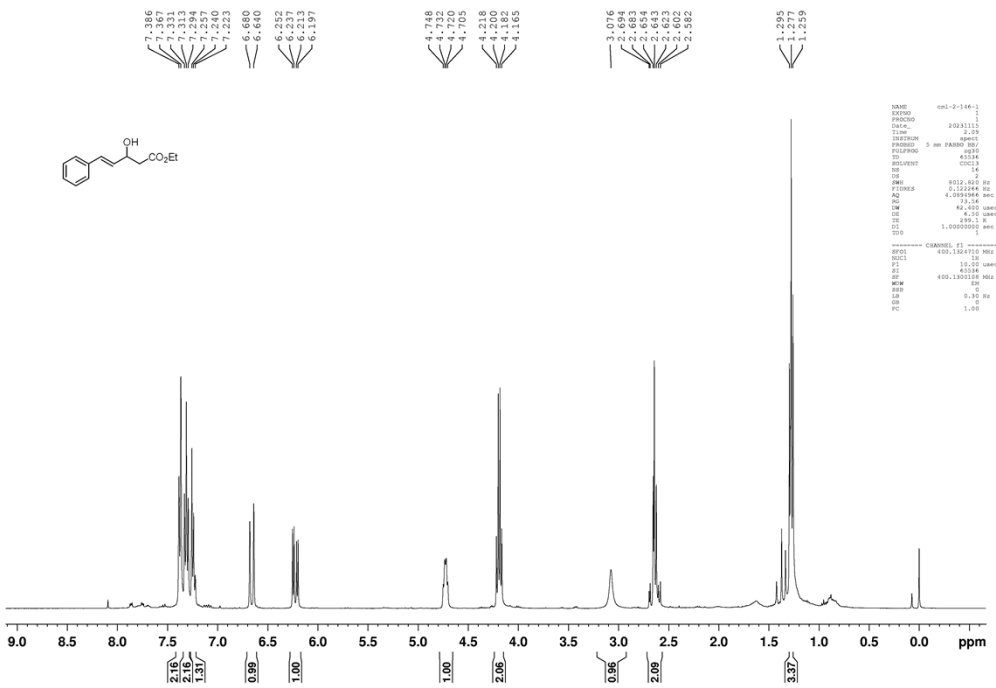
^{13}C NMR spectrum for compound **3s**



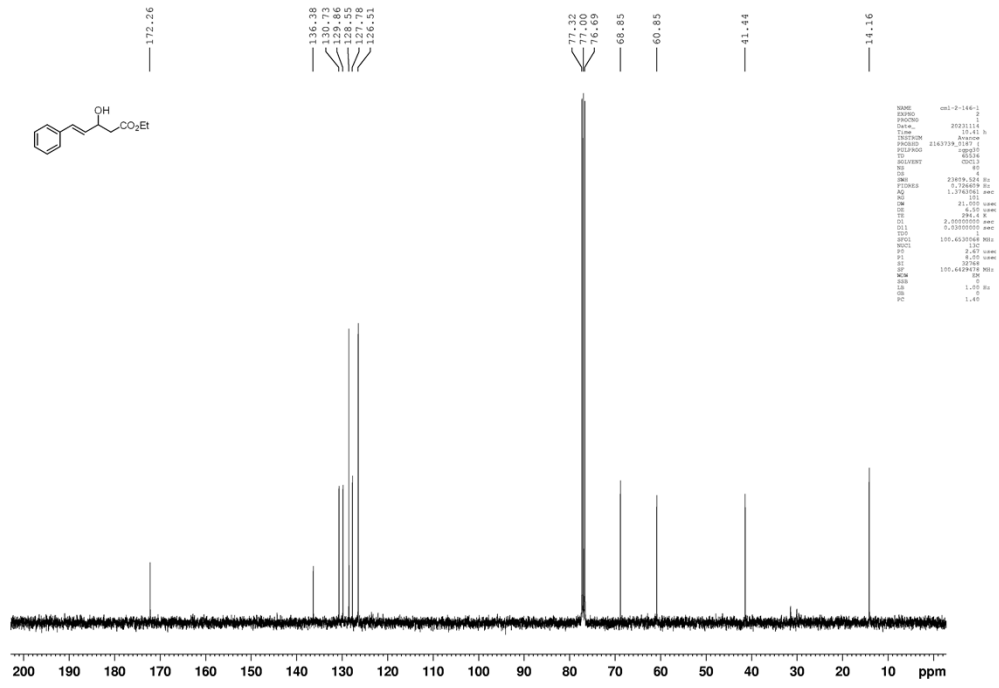
^{1}H NMR spectrum for compound **3t**



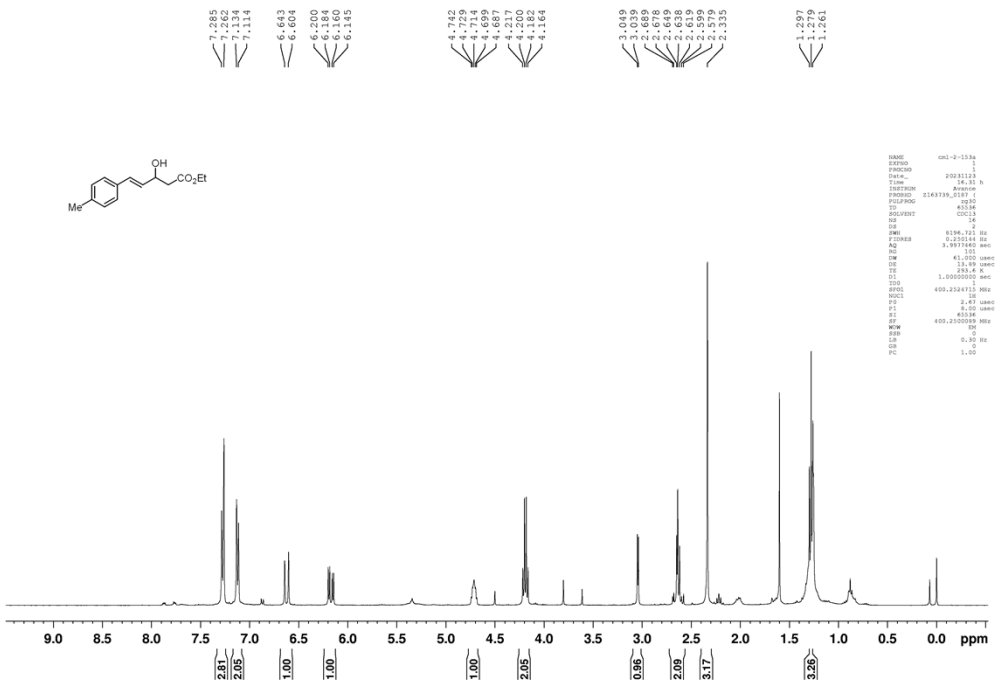
^{13}C NMR spectrum for compound **3t**



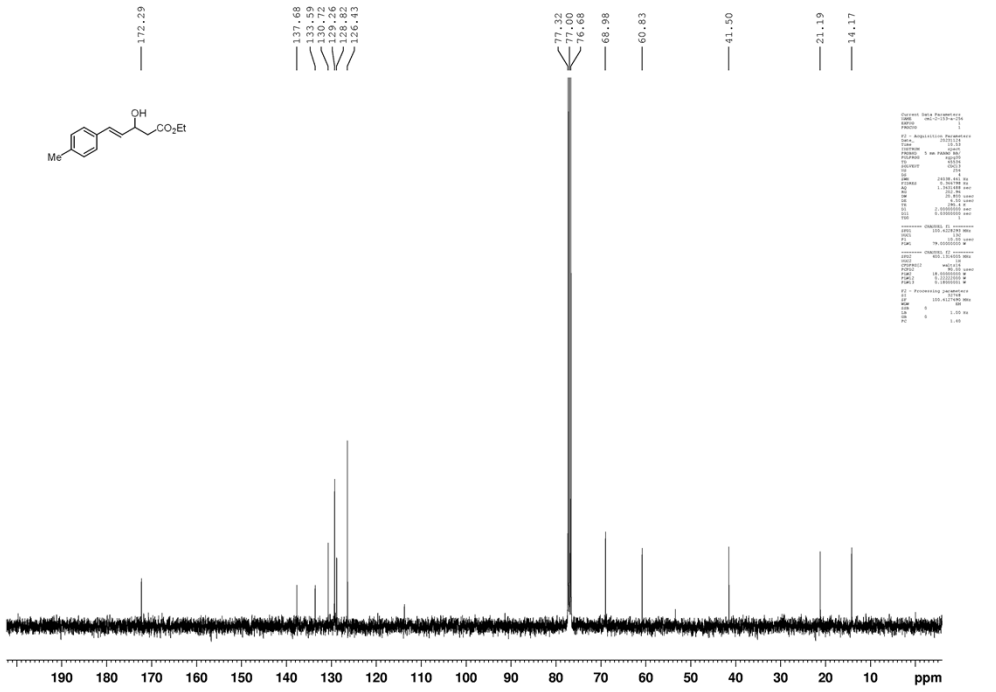
^{1}H NMR spectrum for compound **3u**



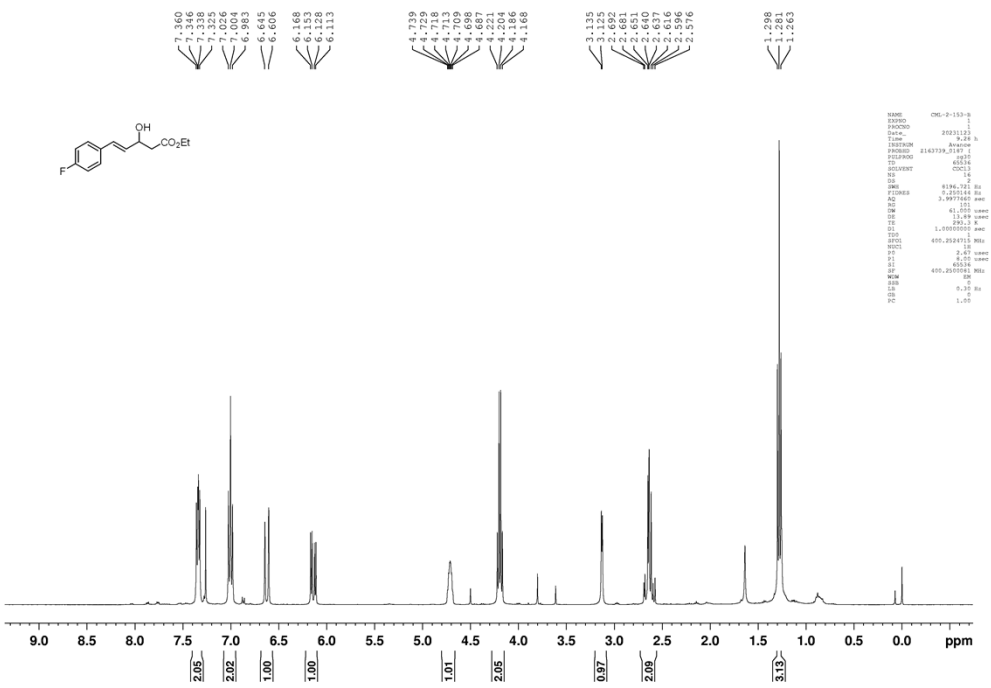
^{13}C NMR spectrum for compound **3u**



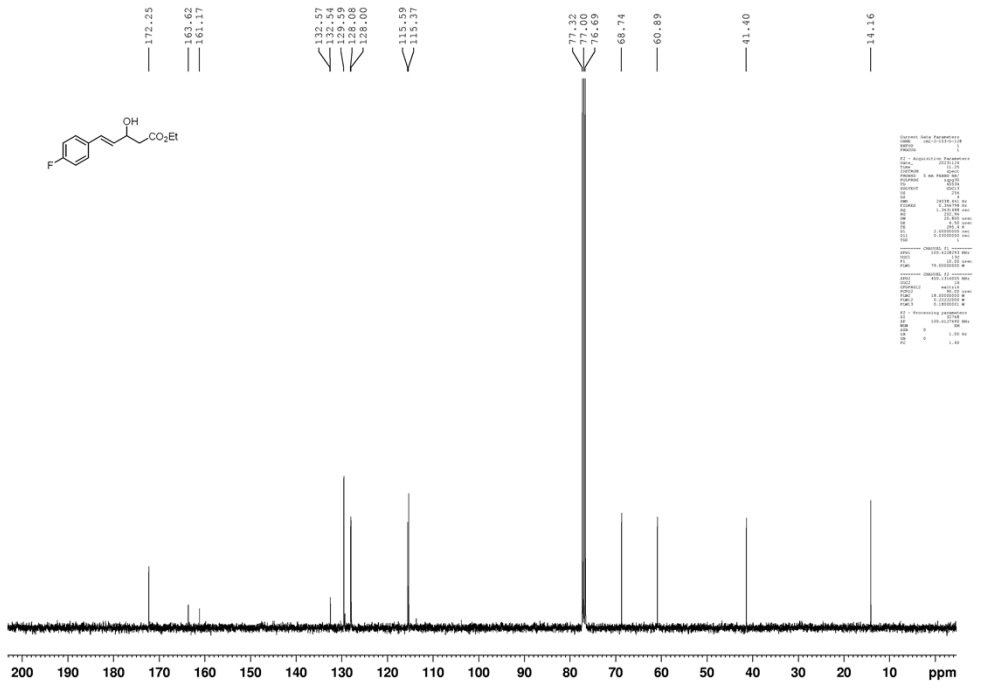
^{1}H NMR spectrum for compound **3v**



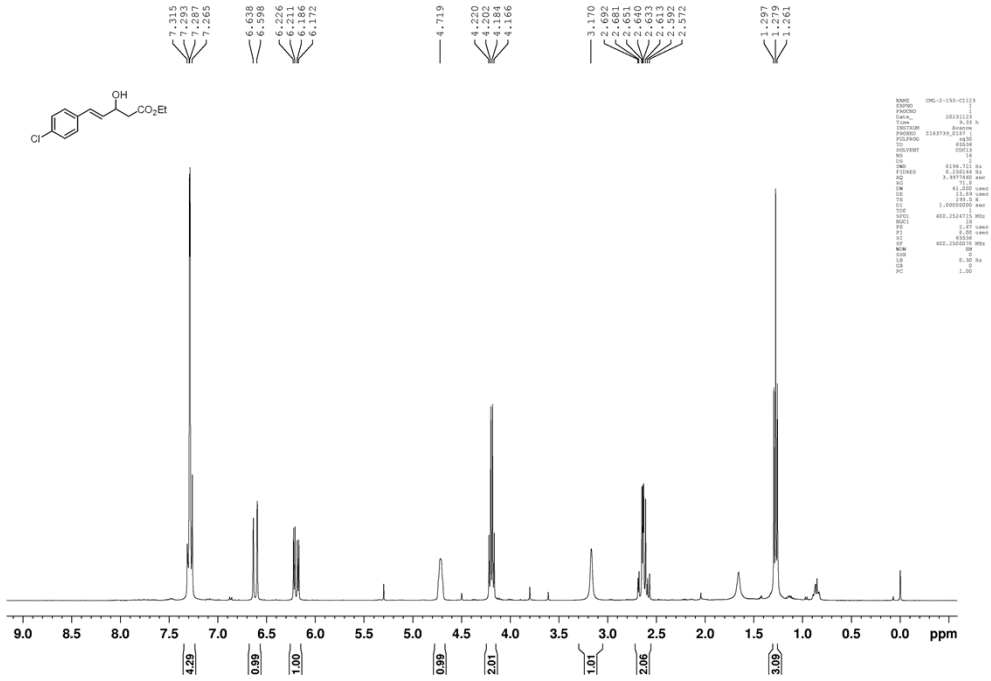
^{13}C NMR spectrum for compound **3v**



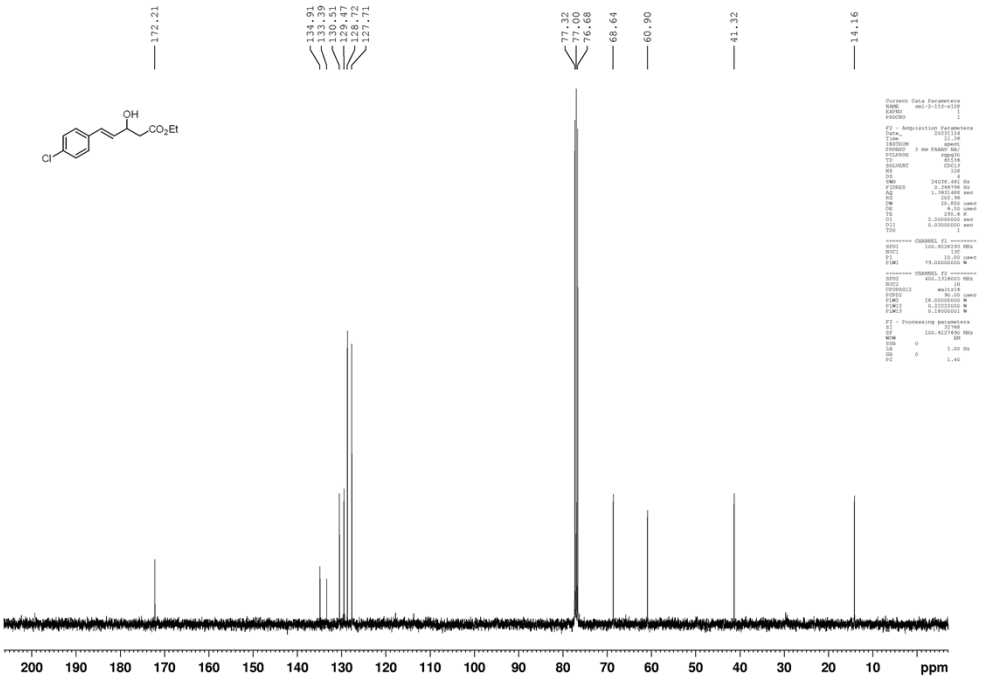
^{1}H NMR spectrum for compound **3w**



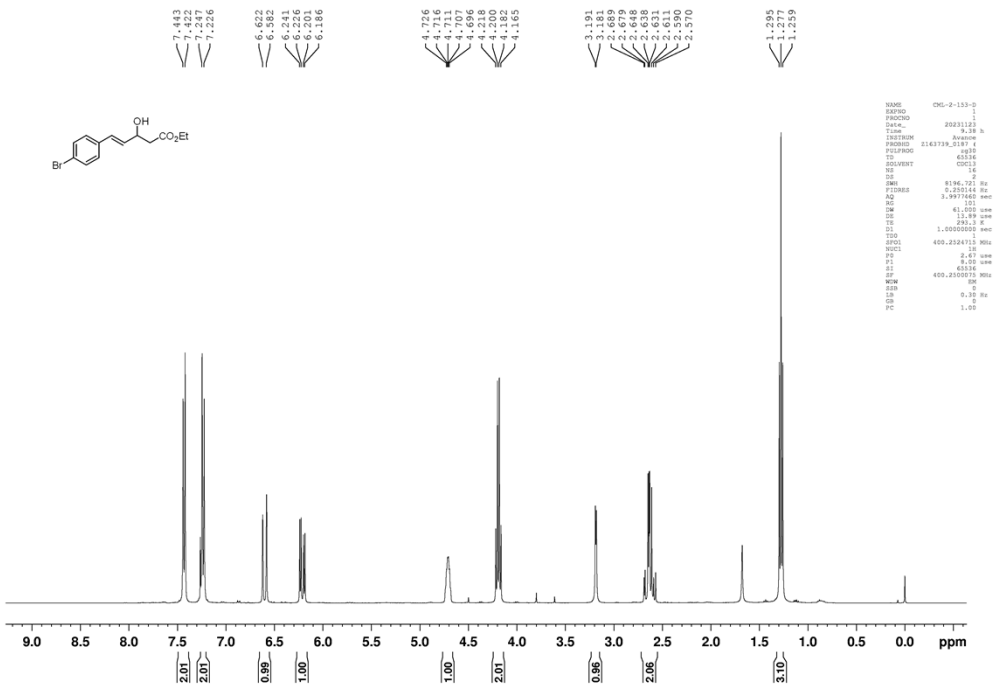
^{13}C NMR spectrum for compound **3w**



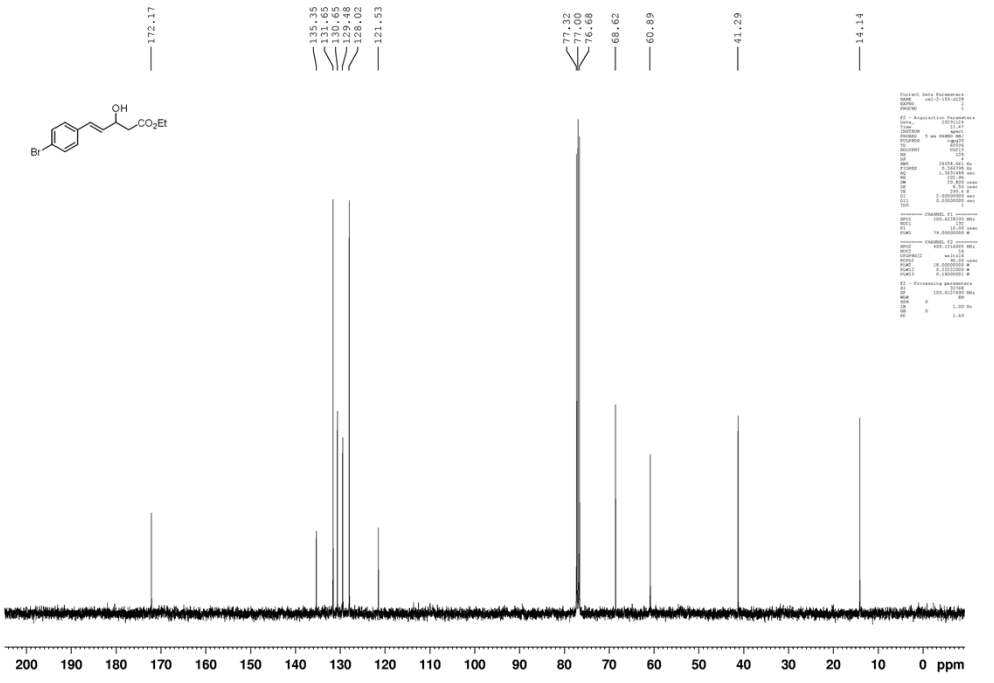
^{1}H NMR spectrum for compound **3x**



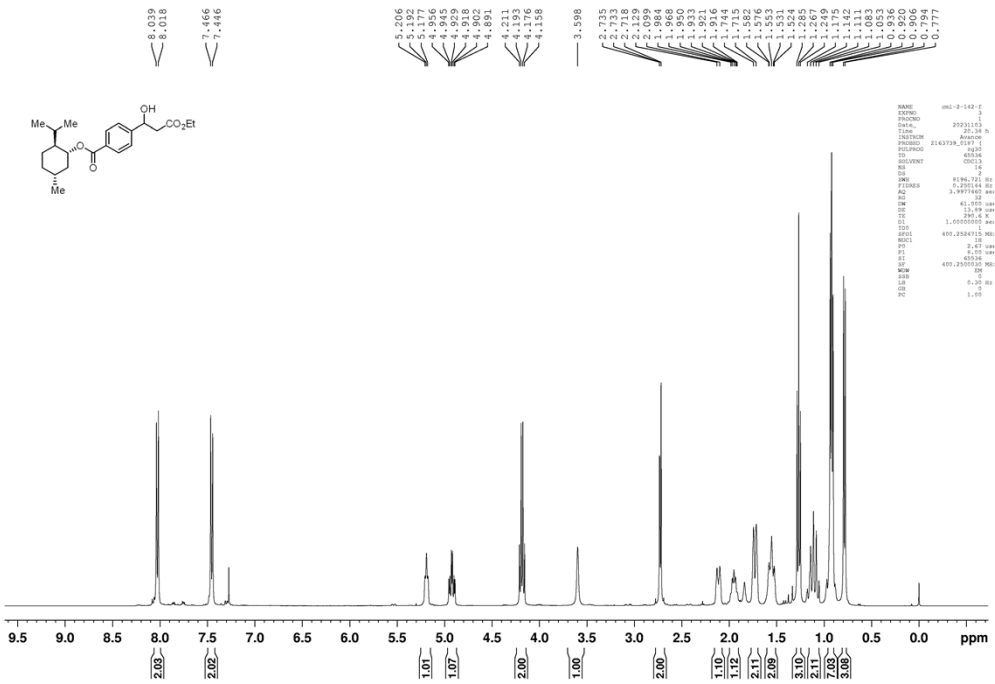
^{13}C NMR spectrum for compound **3x**



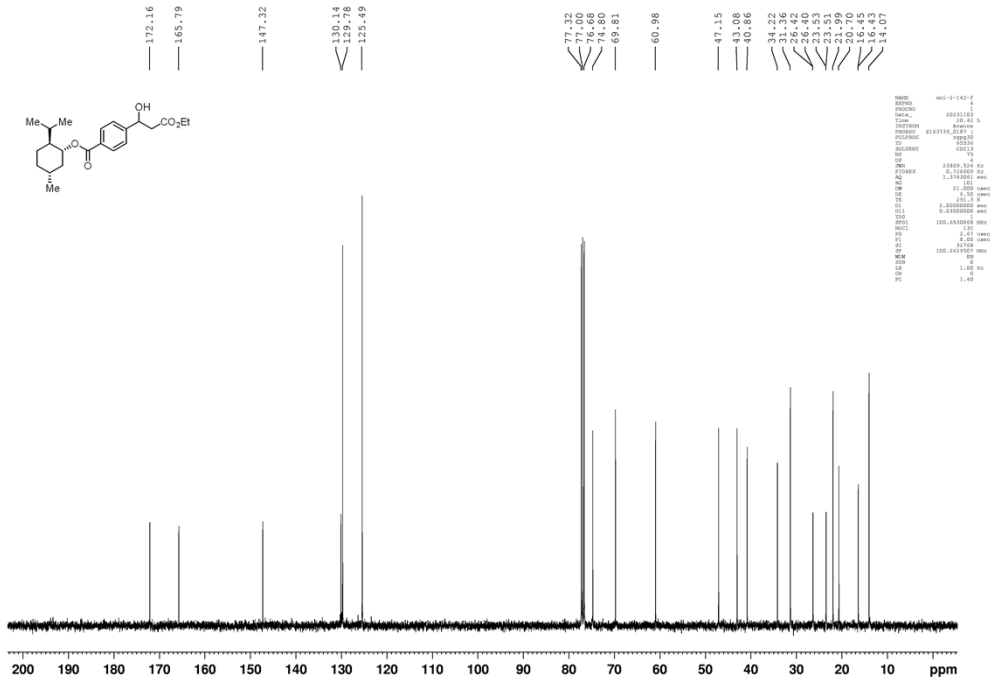
^{1}H NMR spectrum for compound **3y**



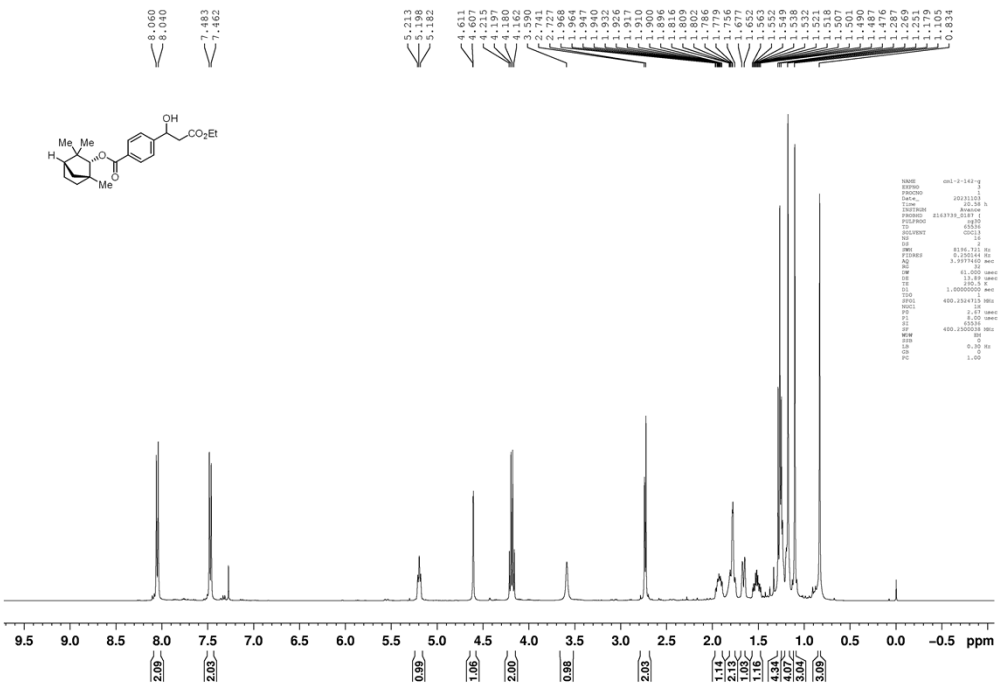
^{13}C NMR spectrum for compound **3y**



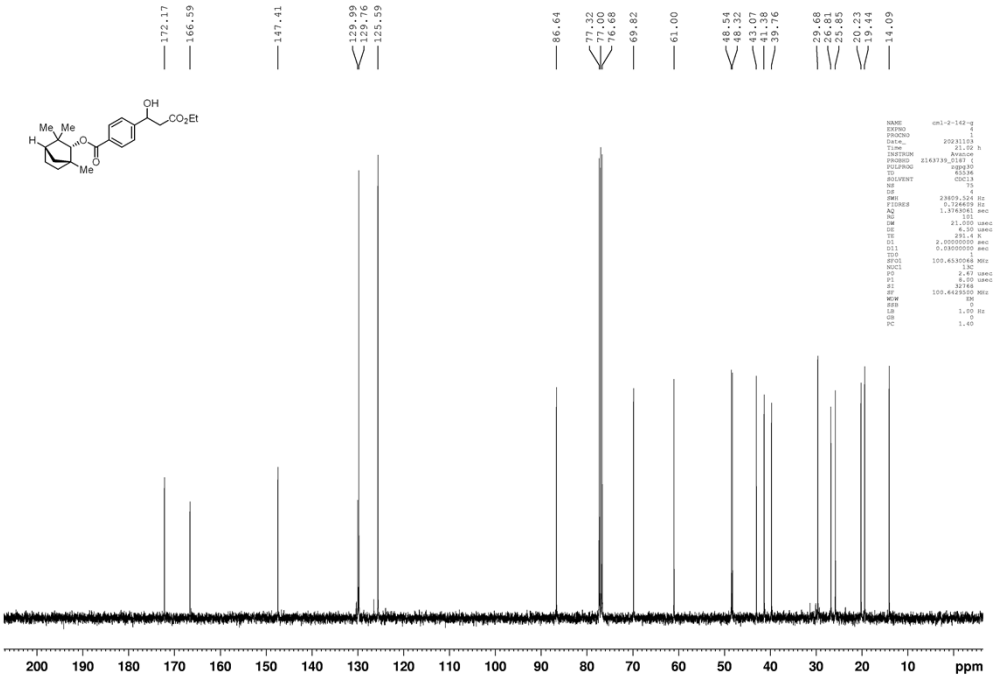
^{1}H NMR spectrum for compound **3z**



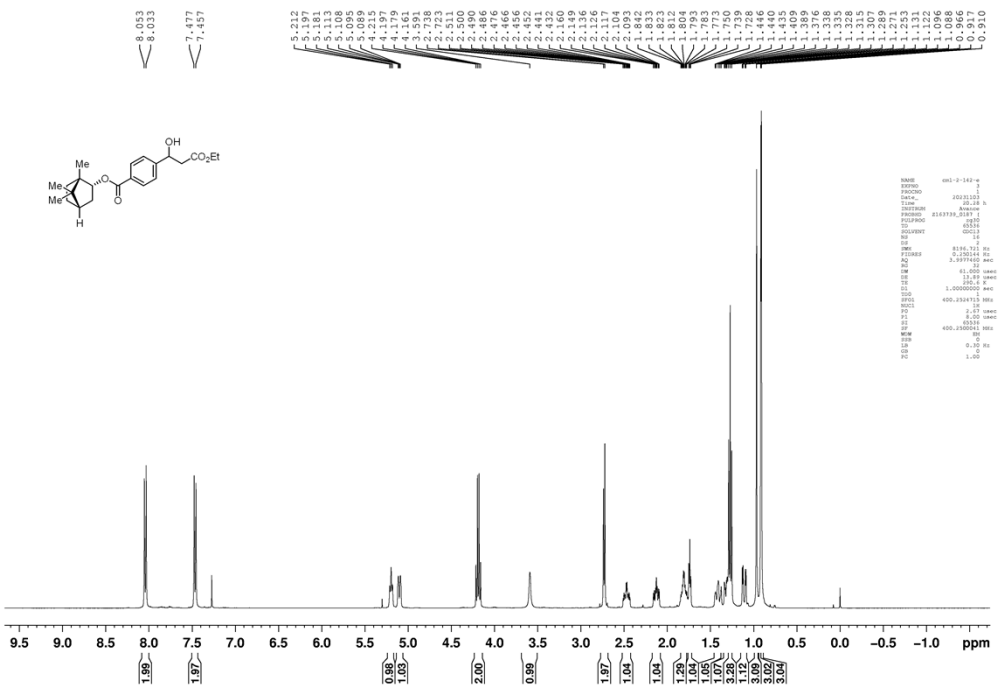
^{13}C NMR spectrum for compound **3z**



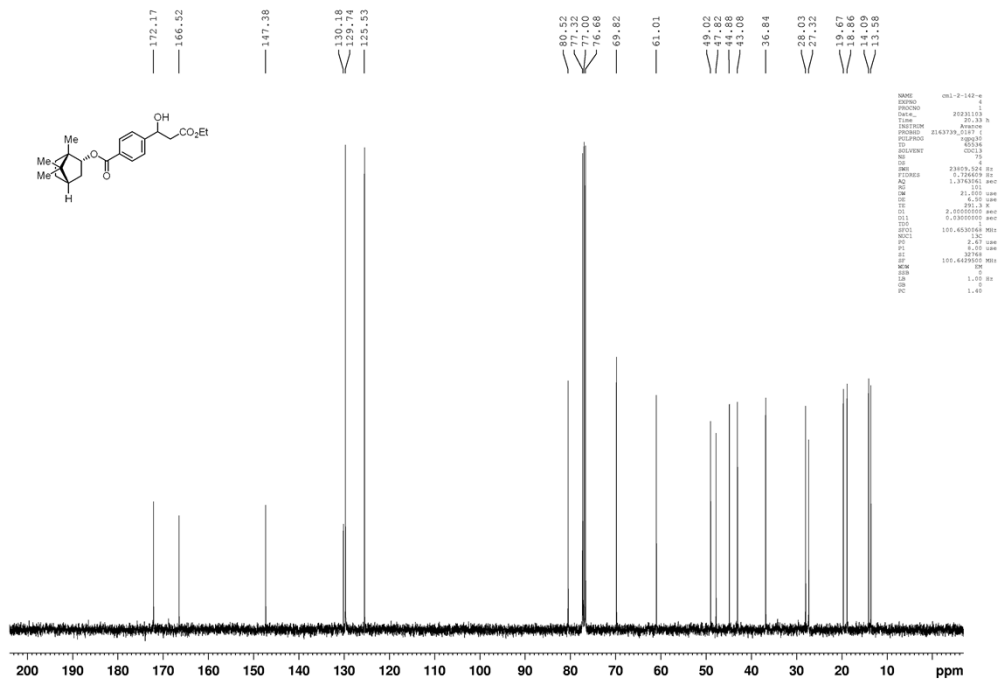
^{1}H NMR spectrum for compound **3aa**



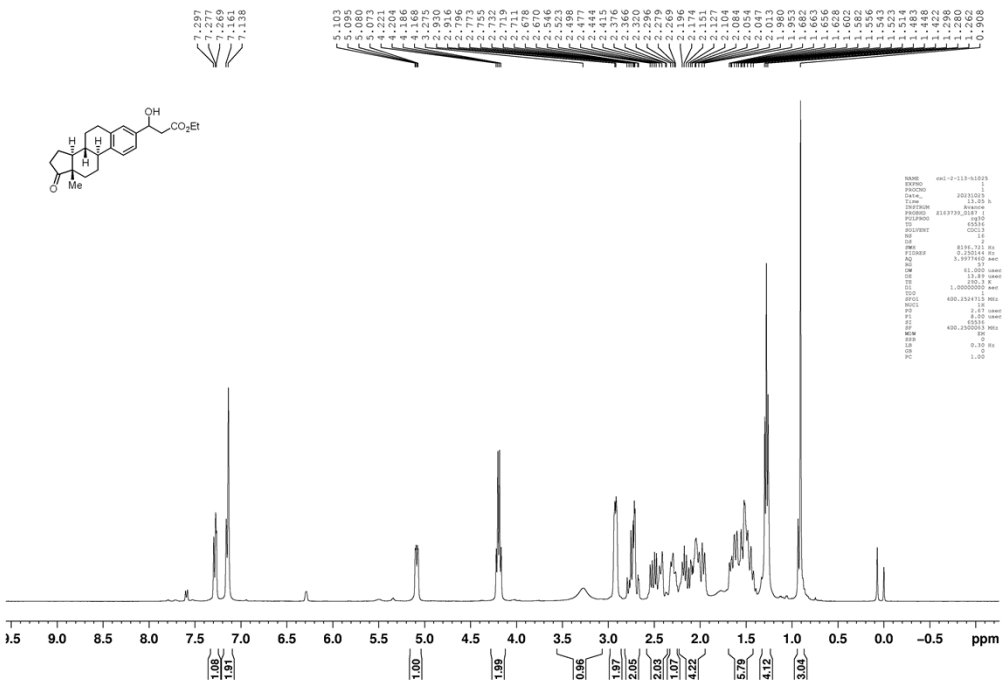
^{13}C NMR spectrum for compound **3aa**



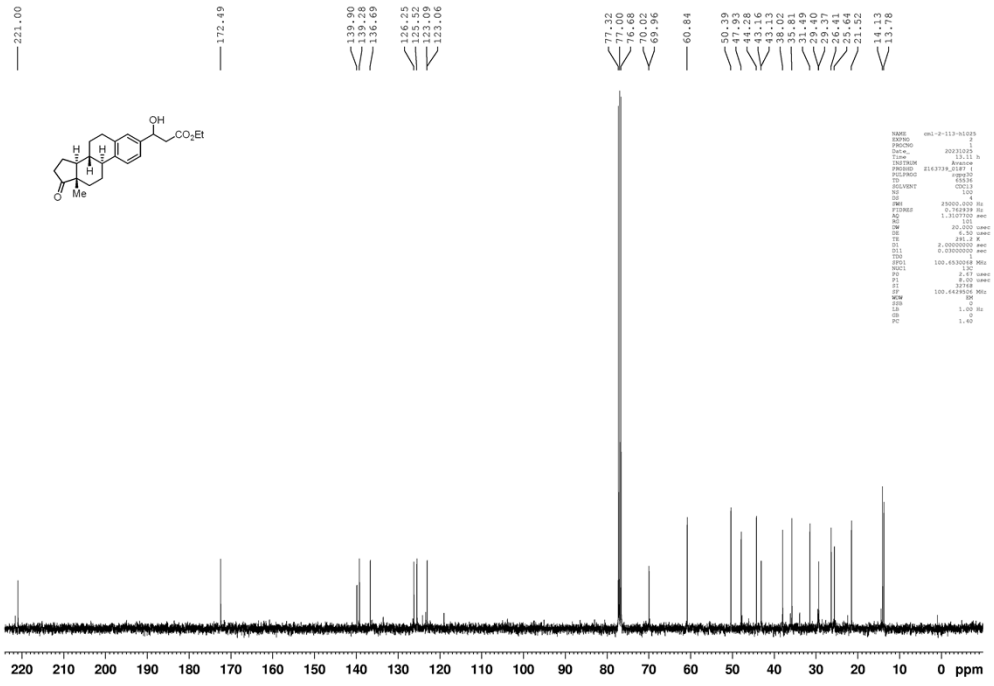
^{1}H NMR spectrum for compound **3ab**



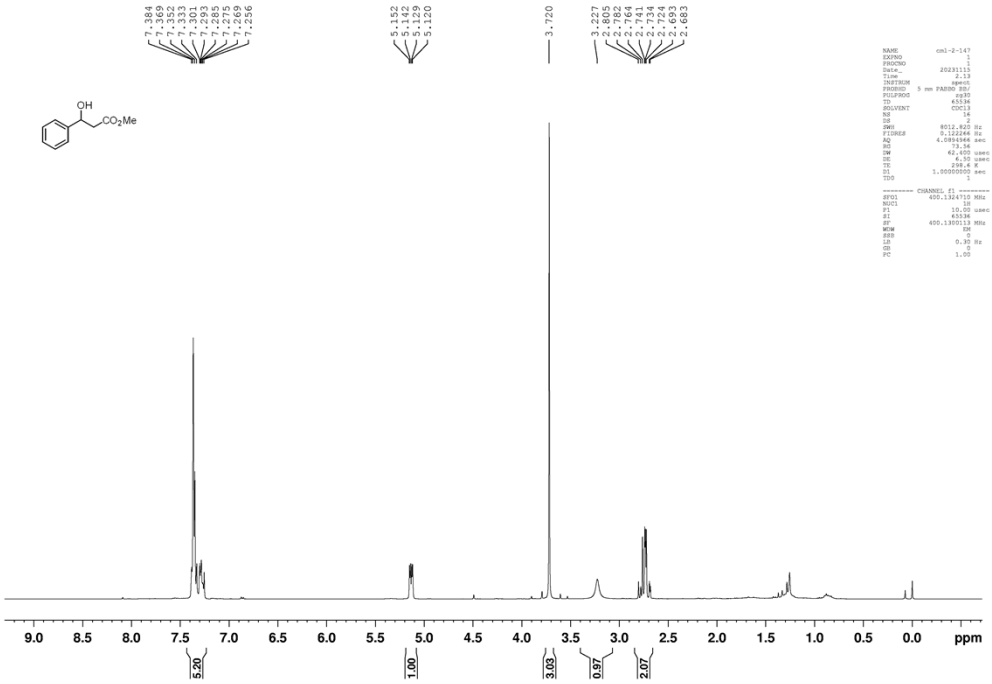
^{13}C NMR spectrum for compound **3ab**



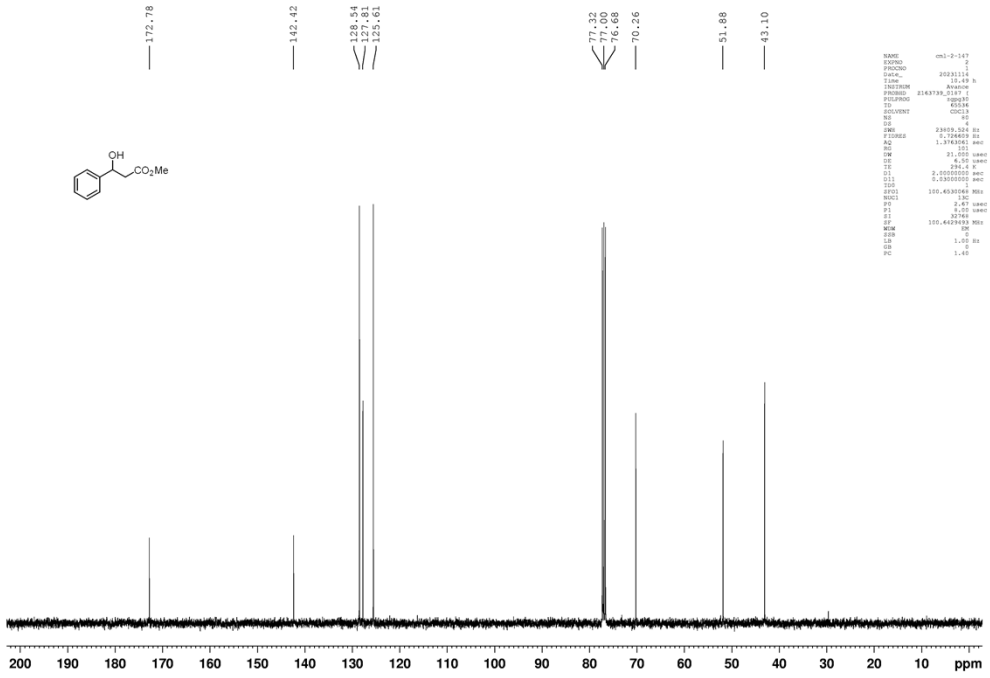
^{1}H NMR spectrum for compound **3ac**



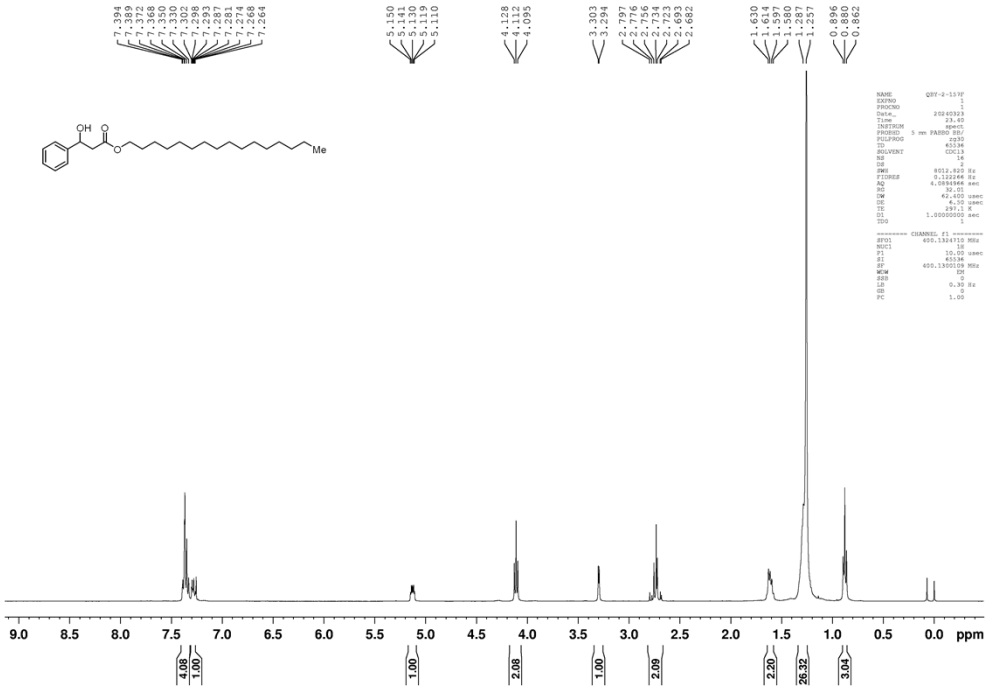
^{13}C NMR spectrum for compound **3ac**



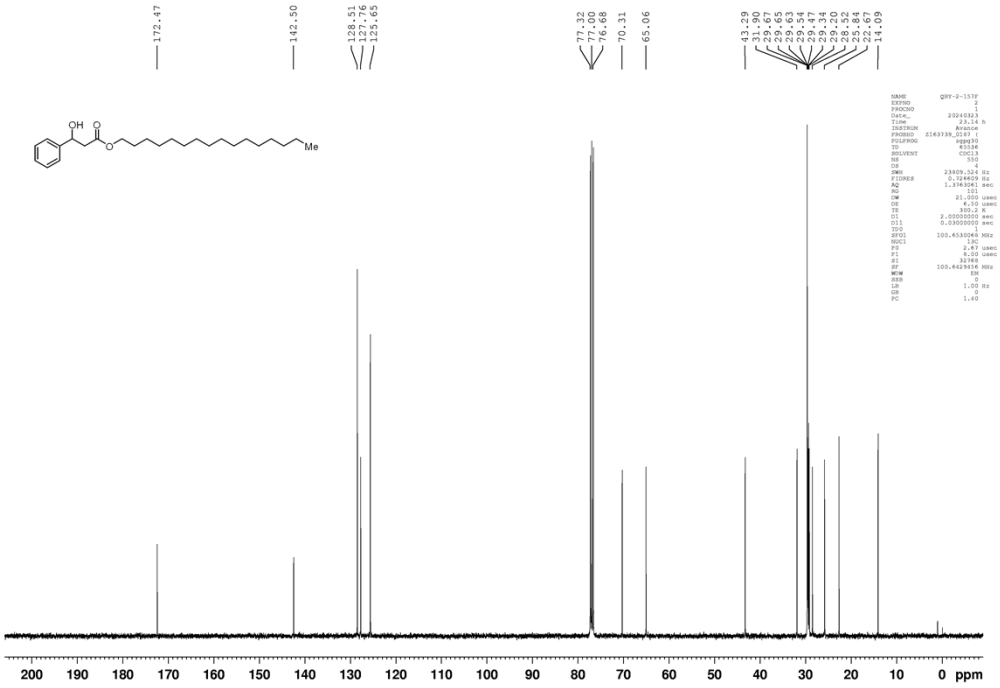
^{1}H NMR spectrum for compound **3aj**



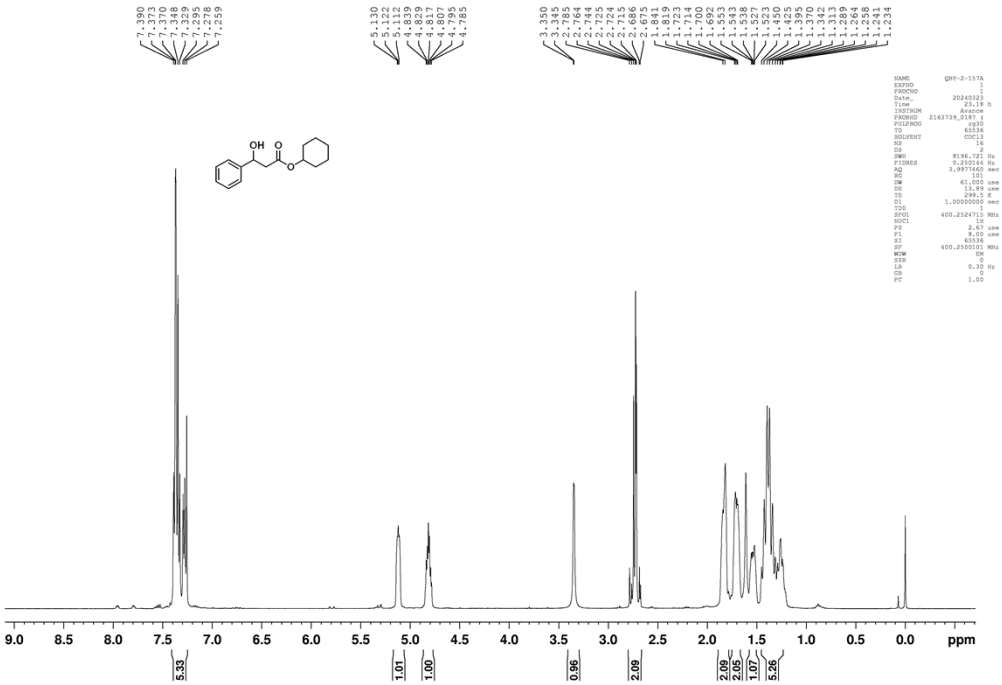
^{13}C NMR spectrum for compound **3aj**



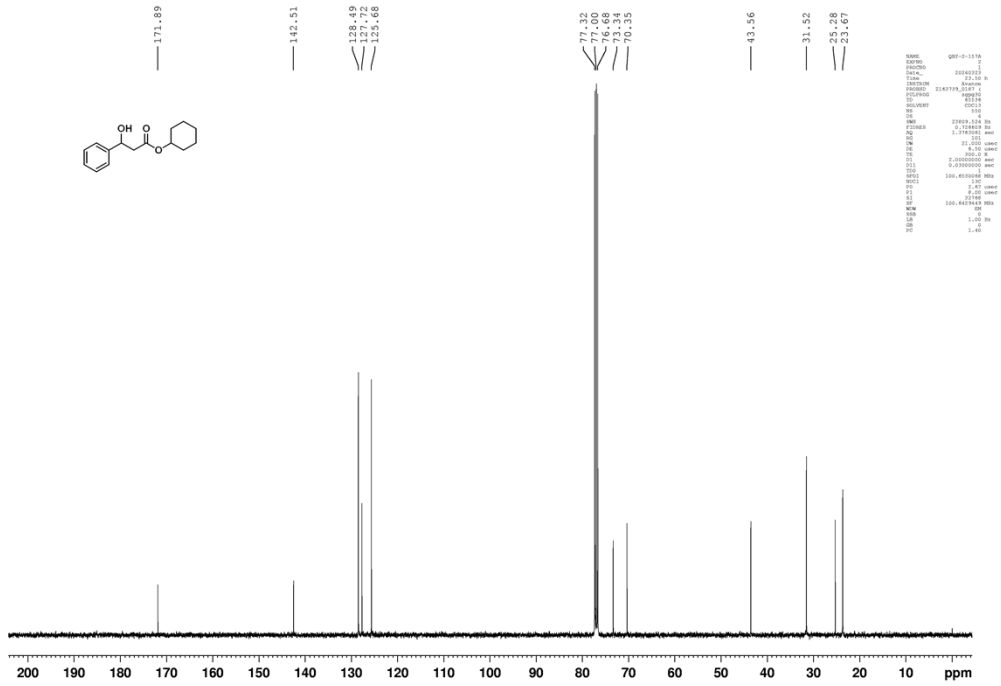
^{1}H NMR spectrum for compound **3ak**



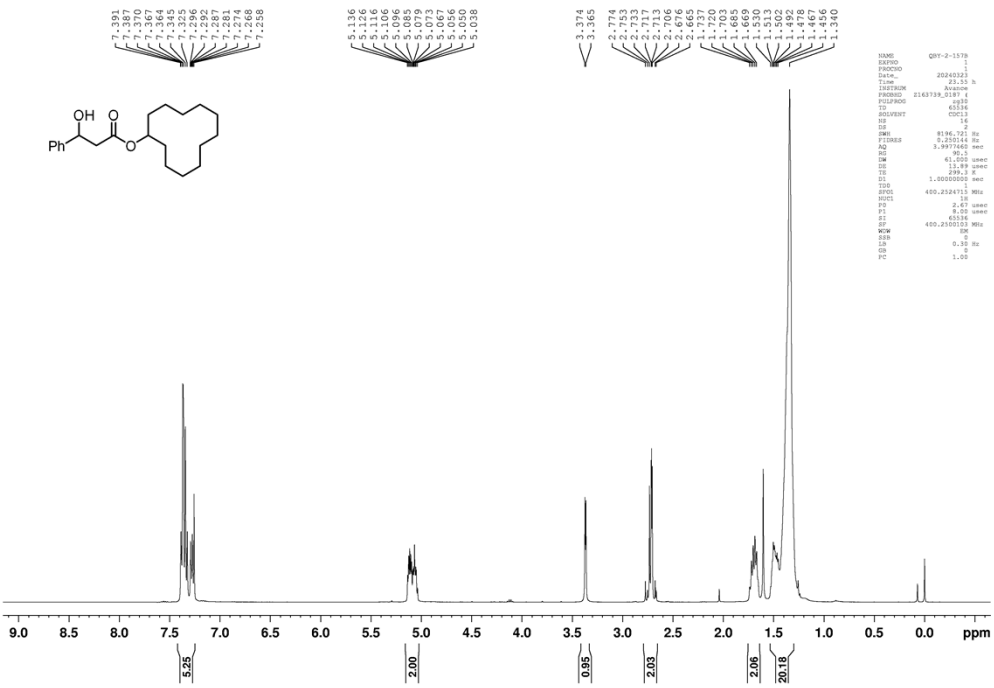
^{13}C NMR spectrum for compound **3ak**



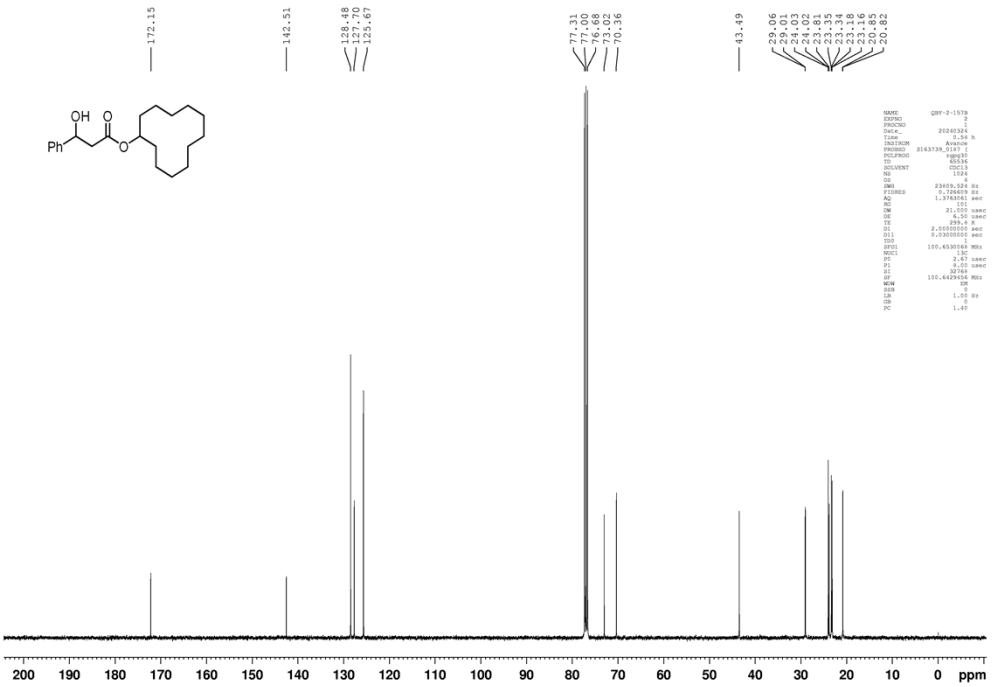
^{1}H NMR spectrum for compound **3al**



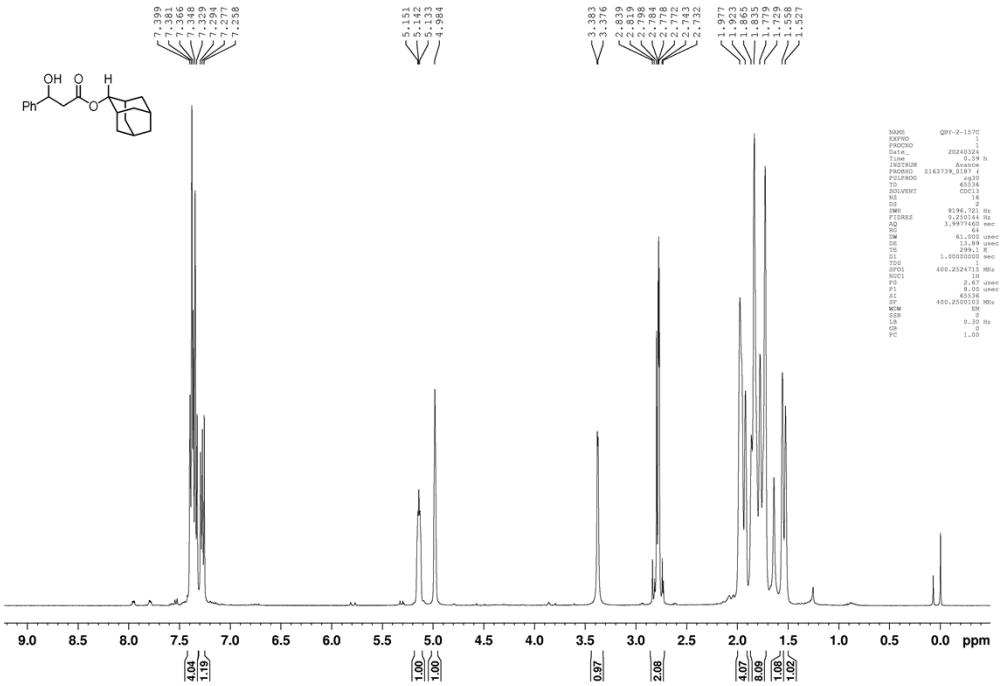
^{13}C NMR spectrum for compound **3al**



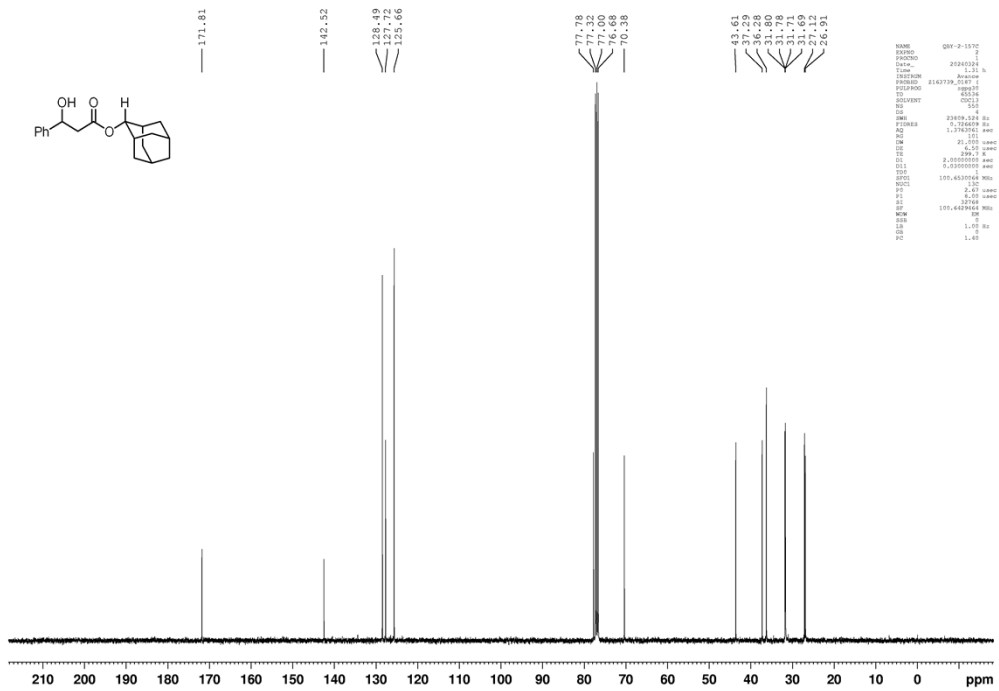
^{1}H NMR spectrum for compound **3am**



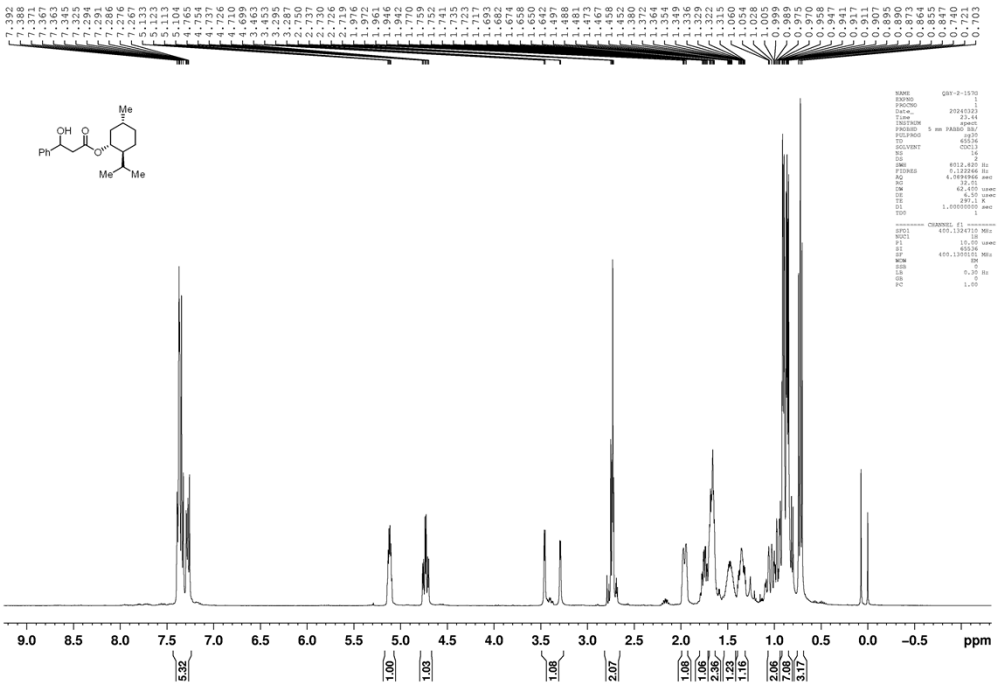
^{13}C NMR spectrum for compound **3am**



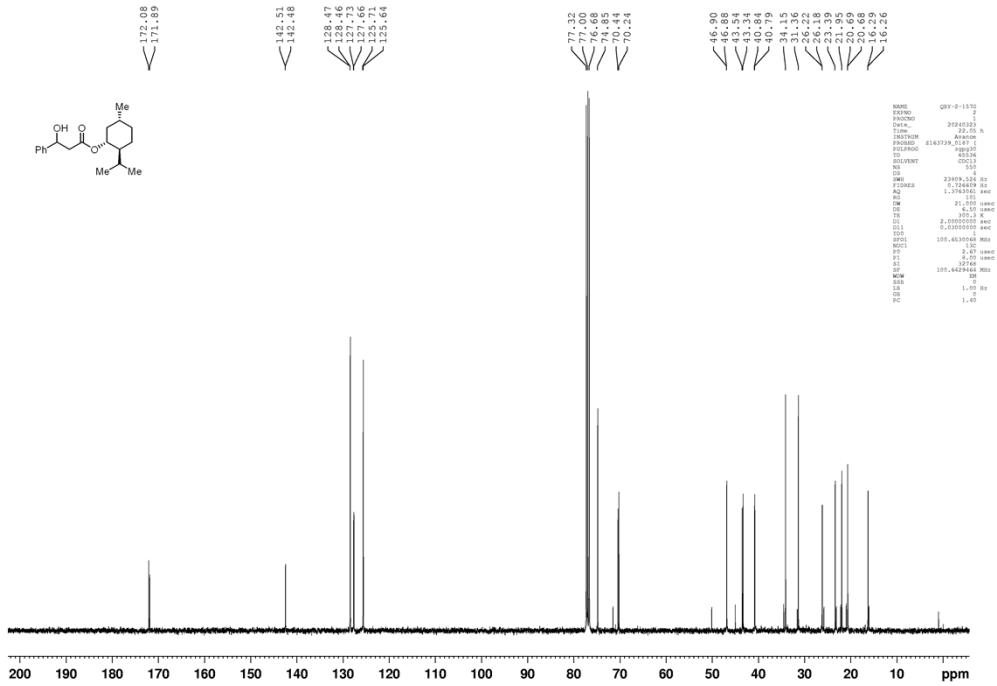
^{1}H NMR spectrum for compound **3an**



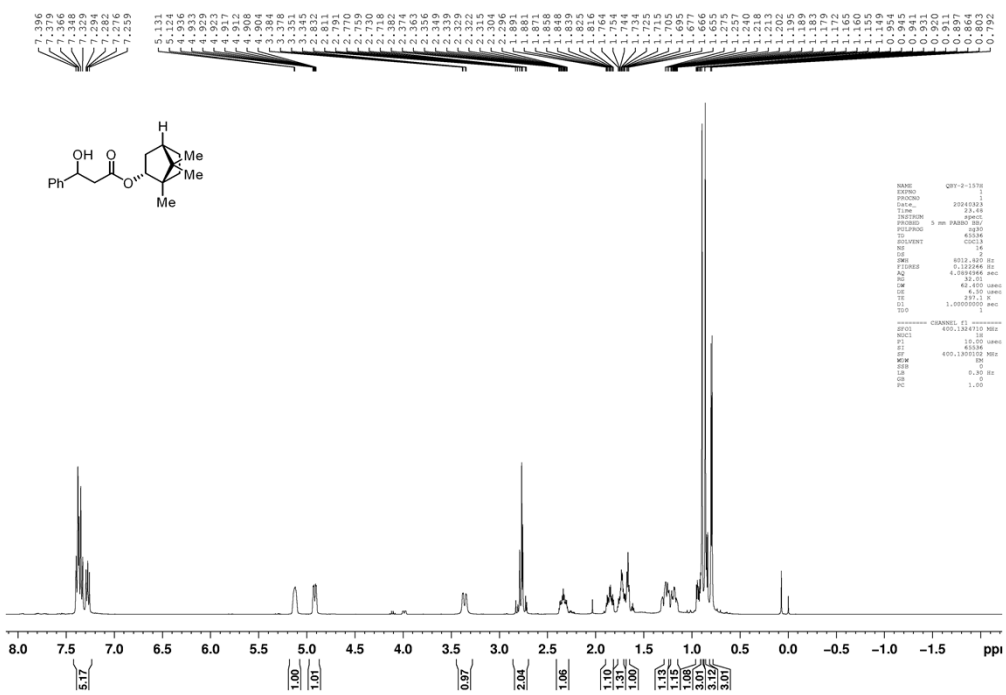
^{13}C NMR spectrum for compound **3an**



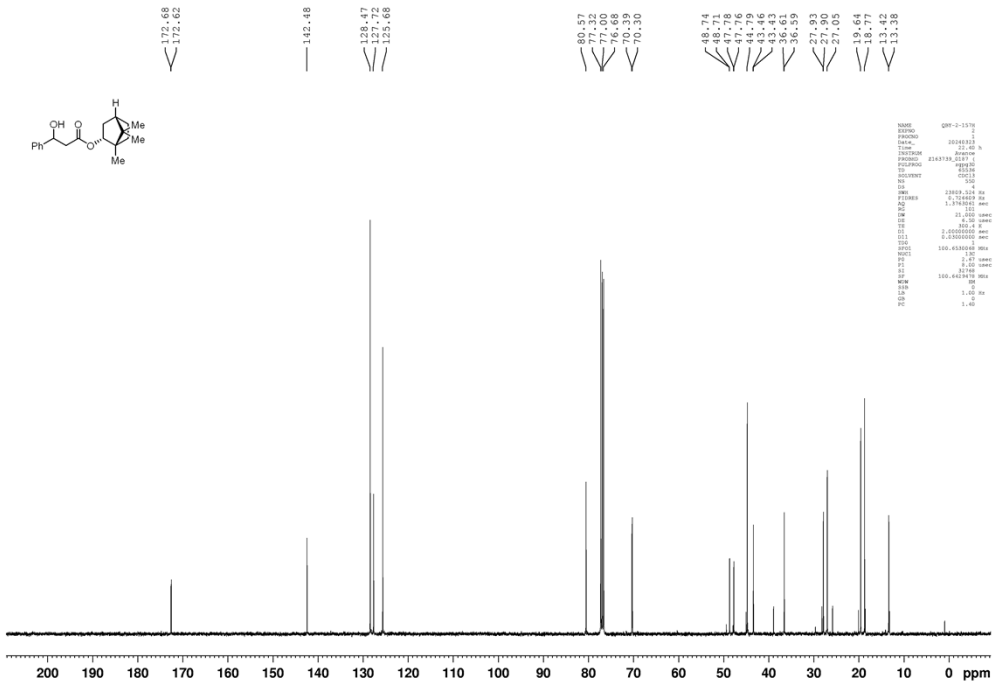
^{1}H NMR spectrum for compound **3ao**



^{1}H NMR spectrum for compound **3ao**



^{1}H NMR spectrum for compound **3ap**



^{1}H NMR spectrum for compound **3ap**

References

1. Gao, C., Li, J., Yu, J., Yang, H. & Fu, H. Visible-light photoredox synthesis of internal alkynes containing quaternary carbons. *Chem. Commun.* 2016, **52**, 7292–7294.
2. Slutskyy, Y. & Overman, L. E. Generation of the methoxycarbonyl radical by visible-light photoredox catalysis and its conjugate addition with electron-deficient olefins. *Org. Lett.* 2016, **18**, 2564–2567.