*Electronic Supplementary Information*

# Permanganate oxidation of α,β-unsaturated carbonyls to vicinal tricarbonyls

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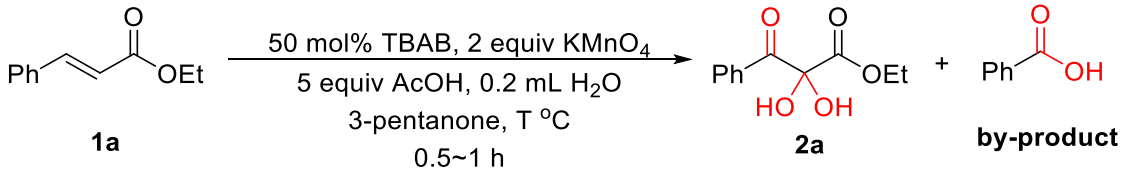
# 1. General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Potassium permanganate was ground into fine powder before use. The reactions were monitored by TLC with Haiyang GF-254 silica gel plates (Qingdao Haiyang chemical industry Co. Ltd, Qingdao, China) using UV light or $KMnO_4$ or Phosphomolybdic acid hydrate as visualizing agents as needed. Flash column chromatography was performed using 300-400 mesh silica gel at increased pressure.

$^1H$ and $^{13}C$ NMR spectra were collected on 400 MHz NMR spectrometers (JNM-ECZ400S). Chemical shifts for protons are reported in parts per million (ppm) downfield and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield and are referenced to the carbon resonances of solvent ($CDCl_3$ = δ 77.00). Data is represented as follows: chemical shift, multiplicity (brs = broad single, s = singlet, d = double, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. High resolution mass spectra (HRMS) were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) and reported in units of mass of charge ratio (m/z). IR spectra were obtained with KBr plates by using an IS10 FT-IR Spectrometer (ThermoFisher Corporation) and reported in wave numbers ($cm^{-1}$). X-ray crystallography analysis was performed on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer.

## 2. Optimization of Reaction Conditions

**Table S1: Optimization of The Reaction Conditions** [a]

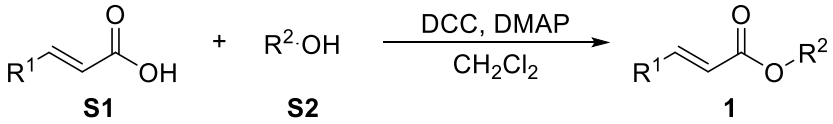



| Entry | Variation from the Standard Condition | Yield of **2a** (%)[b] |
|---|---|---|
| 1 | None | 90 |
| 2 | TBME as solvent | 41 |
| 3 | $CH_2Cl_2$ as solvent | 39 |
| 4 | $PhCH_3$ as solvent | 80 |
| 5 | acetone as solvent | 75 |
| 6 | 2-pentanone as solvent | 60 |
| 7 | THF as solvent | 81 |
| 8 | 2-Methyl-2-butanol as solvent | N.D. |
| 9 | TsOH instead of AcOH | 43 |
| 10 | TFA instead of AcOH | 49 |
| 11 | IBA instead of AcOH | 82 |
| 12 | TFE instead of AcOH | N.D. |
| 13 | HFIP instead of AcOH | N.D. |
| 14 | −10 ℃ instead of 0 ℃ | 45 |
| 15 | 25 ℃ instead of 0 ℃ | 56 |
| 16 | 0.2 equiv TBAB instead of 0.5 equiv | 78 |
| 17 | 10 equiv AcOH instead of 5 equiv | 84 |
| 18 | no water added | N.D. |
| 19 | no AcOH added | N.D. |

[a] Reactions conditions: **1a** (0.2 mmol, 1.0 equiv), $KMnO_4$ (0.4 mmol), AcOH (1.0 mmol), $H_2O$ (0.2 mL), TBAB (0.1 mmol), solvent (2 mL), 0 °C, 1h. [b] Isolated yield. TBAB: tetrabutylammonium bromide; N.D. not detected; TFA: Trifluoroacetic acid; IBA: Isobutyric acid; TFE: 2,2,2-Trifluoroethanol; HFIP: 1,1,1,3,3,3-Hexafluoro-2-propanol.

## 3. Preparation and Characterization of Substrates

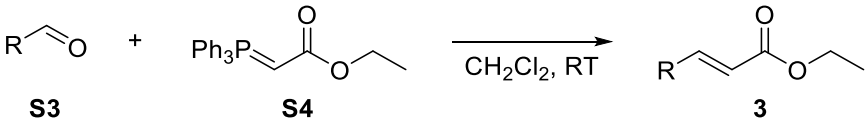
**Method A:**




**S1** **S2** **1**

Acid **S1** (4 mmol) and alcohol **S2** (4 mmol) was mixed in $CH_2Cl_2$ (40 mL) in a 100 mL round bottomed flask equipped with a magnetic stirring bar. After addition of DMAP (2 mmol, 0.5 equiv.) and cooling to 0 ℃, followed by addition of DCC (4 mmol) in $CH_2Cl_2$ dropwise, the reaction was allowed to react at room temperature overnight. After completion, solvent was removed under reduced pressure and the reaction was purified by silica gel column chromatography to afford **1**.

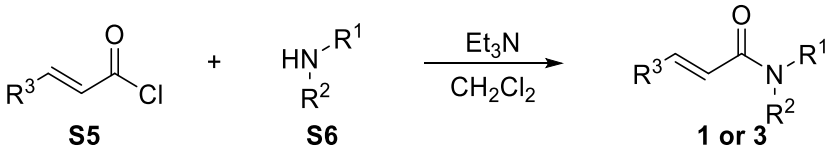
**Method B:**




**S3** **S4** **3**

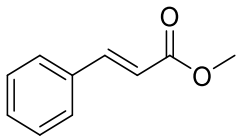
In a 100 mL of round bottomed flask, ethyl (triphenylphosphoranylidene) acetate **S4** (4.4 mmol, 1.1 equiv.) and an aldehyde **S3** (4.0 mmol) were dissolved in $CH_2Cl_2$ (40 mL). The mixture was stirred at room temperature for about 6 h. After completion, solvent was removed under reduced pressure and the reaction was purified by silica gel column chromatography to afford **3**.

**Method C:**

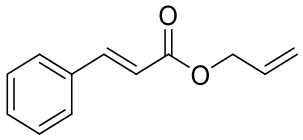



**S5** **S6** **1 or 3**

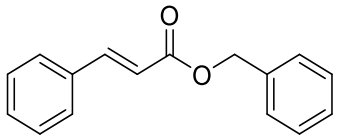
At 0℃, $Et_3N$ (4.8 mmol, 1.2 equiv.) and amine **S6** (4.8 mmol, 1.2 equiv.) were added to a stirred solution of acyl chloride **S5** (4 mmol) in $CH_2Cl_2$. The reaction was allowed to warm to room temperature and stirred overnight. After completion of the reaction, solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography.



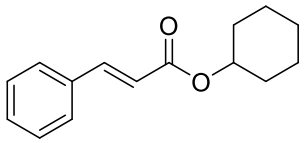
**Methyl cinnamate (1b)[1]:** 93% yield; white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.50–7.45 (m, 2H), 7.36–7.32 (m, 3H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.77 (s, 3H). The data is consistent with previously reported literature.



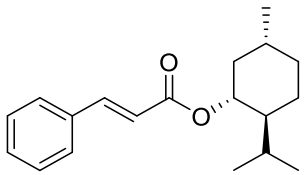
**Allyl cinnamate (1c)[2]:** 99% yield; colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.51–7.46 (m, 2H), 7.38–7.32 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.03–5.93 (m, 1H), 5.38 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.25 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.70 (d, *J* = 6 Hz, 2H). The data is consistent with previously reported literature.



**Benzyl cinnamate (1d)[3]:** 80% yield; colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 16.0 Hz, 1H), 7.56–7.51 (m, 2H), 7.49–7.35 (m, 8H), 6.53 (d, *J* = 16.0 Hz, 1H), 5.32 (s, 2H). The data is consistent with previously reported literature.

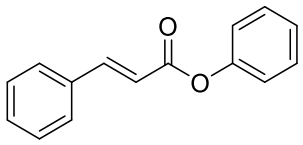


**Cyclohexyl cinnamate(1e)[4]:** 64% yield; white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.52–7.46 (m, 2H), 7.38–7.31 (m, 3H), 6.42 (d, *J* = 16.0Hz, 1H), 4.93–4.84 (m, 1H), 1.96–1.87 (m, 2H), 1.81–1.70 (m, 2H), 1.59–1.31 (m, 6H). The data is consistent with previously reported literature.

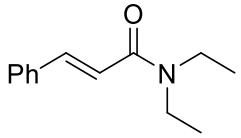


**(-)-Menthyl (*E*)-phenylacrylate (1f)[5]:** 94% yield; colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.52–7.49 (m, 2H), 7.37–7.34 (m, 3H), 6.43 (d, *J*

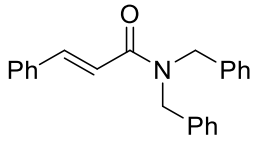
= 16.0 Hz, 1H), 4.83 (td, *J* = 10.4 Hz, 8 Hz, 1H), 2.07 (m, 1H), 1.96–1.89 (m, 1H), 1.73–1.65 (m, 2H), 1.57–1.41 (m, 2H), 1.15–0.99 (m, 2H), 0.94–0.86 (m, 7H), 0.79 (d, *J* = 8 Hz, 3H). The data is consistent with previously reported literature.



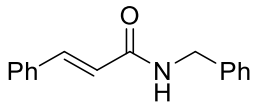

**Phenyl cinnamate(1g)[6]:** 98% yield; white solid; $^1$H NMR(400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 16.0 Hz, 1H), 7.62–7.56 (m, 2H), 7.45–7.38 (m, 5H), 7.28–7.22 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.64 (d, *J* = 16.0 Hz, 1H). The data is consistent with previously reported literature.



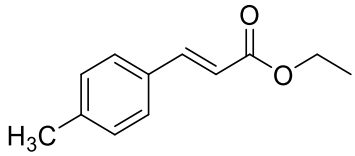

***N*,*N*-diethylcinnamamide (1h)[7]:** 90% yield; white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16 Hz, 1H), 7.48−7.43 (m, 2H), 7.33−7.23 (m, 3H), 6.77 (d, *J* = 15.2 Hz, 1H), 3.47–3.32 (m, 4H), 1.18 (t, *J* = 6.9 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 1H). The data is consistent with previously reported literature.



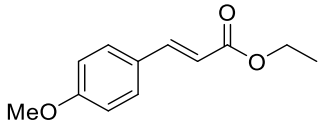

***N*,*N*-dibenzylcinnamamide (1i)[8]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 16 Hz, 1 H), 7.48–7.43 (m, 2H), 7.41–7.26 (m, 11H), 7.24–7.19 (m, 2H), 6.89 (d, *J* = 16 Hz, 1H), 4.71 (s, 2H), 4.60 (s, 2H). The data is consistent with previously reported literature.



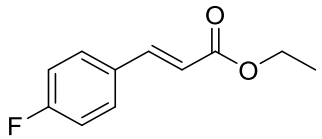

***N*-benzylcinnamamide (1j)[9]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 15.6 Hz, 1 H), 7.54–7.46 (m, 2H), 7.38–7.26 (m, 8H), 6.41 (d, *J* = 15.6 Hz, 1H), 5.96 (s, 1H), 4.57 (d, *J* = 5.76 Hz, 2H). The data is consistent with previously reported literature.



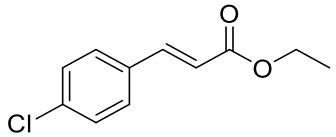
**Ethyl 4-methylcinnamate (3a)[10]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.44–7.40 (m, 2H), 7.21–7.17 (m, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



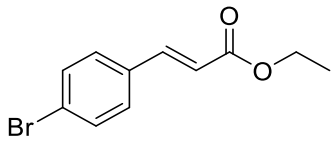
**Ethyl 4-methoxycinnamate (3b)[10]:** *Z:E*=1:25; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.48–7.45 (m, 2H), 6.92–6.87 (m, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



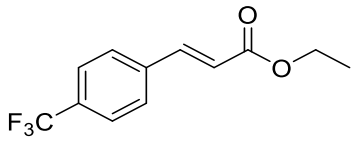
**Ethyl 4-fluorocinnamate (3c)[10]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.53–7.47 (m, 2H), 7.10–7.02 (m, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



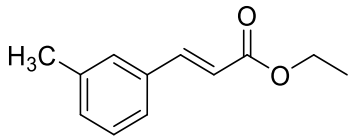
**Ethyl (*E*)-3-(4-chlorophenyl)acrylate (3d)[10]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.0 Hz, 1H), 7.46–7.41 (m, 2H), 7.37–7.33 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



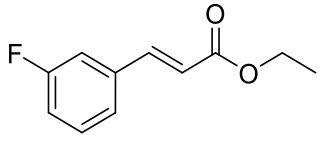

**Ethyl (*E*)-3-(4-bromophenyl)acrylate (3e)[10]:** *Z:E*=3:100; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 16.0 Hz, 1H), 7.58–7.47 (m, 2H), 7.39–7.34 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



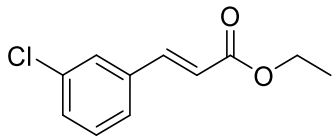

**Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (3f)[10]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.65–7.59 (m, 4H), 6.50 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



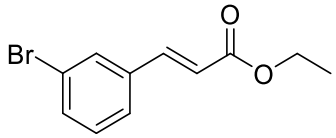

**Ethyl 3-methylcinnamate (3g)[10]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.33–7.29 (m, 2H), 7.28–7.23 (m, 1H), 7.20–7.15 (m, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



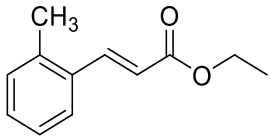

**Ethyl 3- fluorocinnamate (3h)[10]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.38–7.31 (m, 1H), 7.30–7.27 (m, 1H), 7.23–7.18 (m, 1H), 7.10–7.03 (m, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



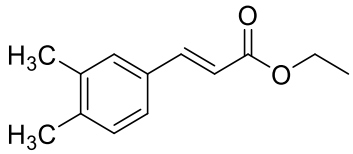

**(*E*)-Ethyl 3-(3-Chlorophenyl)acrylate (3i)[10]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 16.0 Hz, 1H), 7.51 (s, 1H), 7.41–7.29 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



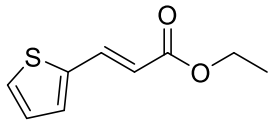

**Ethyl (*E*)-3-(3-chlorophenyl)acrylate (3j)[10]:** *Z:E*=3:100; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67–7.64 (m, 1H), 7.59 (d, *J* = 16.0 Hz, 1H), 7.51–7.41 (m, 2H), 7.27–7.21 (m, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



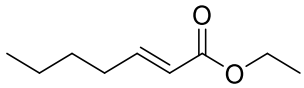

**Ethyl 2-methylcinnamate (3k)[11]:** *Z:E*=3:25; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 16.0 Hz, 1H), 7.56–7.52 (m, 1H), 7.29–7.24 (m, 1H), 7.22–7.16 (m, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H),1.33 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



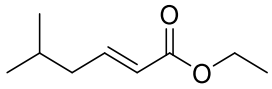

**Ethyl (*E*)-3-(3,4-dimethylphenyl)acrylate (3l)[10]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.30–7.24 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.39 (d, *J* = 16.0Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.28 (s, 6H), 1.33 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



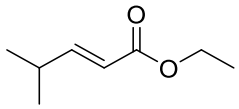
**Ethyl (*E*)-3-(thiophen-2-yl)acrylate (3m)[12]:** *Z:E*=13:100; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.37 (d, *J* = 5.1 Hz, 1H), 7.25 (d, *J* = 3.6 Hz, 1H), 7.05 (dd, *J* = 5.0 Hz, 3.6 Hz ,1H), 6.24 (d, *J* = 15.7 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



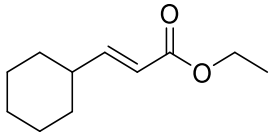
**Ethyl (*E*)-2-heptenoate (3n)[13]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 6.95 (dt, *J* = 14.0 Hz, 7Hz, 1H), 5.80 (d, *J* = 16.0 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.22–2.15 (m, 2H), 1.47–1.38 (m, 2H), 1.37–1.29 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). The data is consistent with previously reported literature.



**Ethyl-(*E*)-5-methyl-2-hexenoate (3o)[14]:** *Z:E*=7:100; $^1$H NMR (400 MHz, $CDCl_3$) δ 6.93 (dt, *J* = 15.5 Hz, 7.5 Hz, 1H), 5.80 (d, *J* = 16.0 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.08 (t, *J* = 7.0Hz, 3H), 1.81–1.68 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 6H). The data is consistent with previously reported literature.

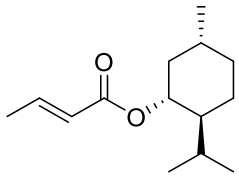


**Ethyl (*E*)-4-methylpent-2-enoate (3p)[15]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 16.0 Hz, 6.7 Hz, 1H), 5.76 (d, *J* = 16.0 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.51–2.41 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 6H). The data is consistent with previously reported literature.

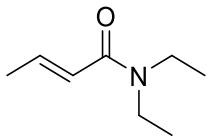


**Ethyl (*E*)-3-cyclohexyl-2-propenoate (3q)[13]:** $^1$H NMR (400 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 16.0 Hz, 7Hz, 1H), 5.74 (d, *J* = 16.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.16–2.06

(m, 1H), 1.78–1.65 (m, 5H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.26–1.06 (m, 5H). The data is consistent with previously reported literature.

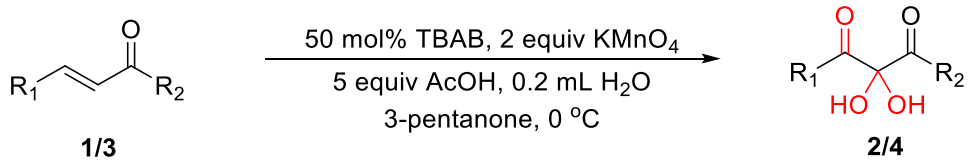


**(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*E*)-but-2-enoate (3r)[16]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.95–6.85 (m,1H), 5.79 (dq, *J* = 16.0 Hz, 4.0 Hz, 1H), 4.69 (td, *J* = 11.2 Hz, 4 Hz, 1H), 1.99–1.92 (m, 1H), 1.86–1.79 (m, 4H), 1.69–1.59 (m, 2H), 1.52–1.41 (m, 1H), 1.40–1.31 (m, 1H), 1.08–0.91 (m, 2H), 0.87–0.81 (m, 7H), 0.72 (d, *J* = 8 Hz, 3H). The data is consistent with previously reported literature.



***N*,*N*-diethylbut-2-enamide (3s):** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.88 (dq, *J* = 14.9 Hz, 6.9Hz, 1H), 6.19 (dq, *J* = 14.9 Hz, 1.68 Hz, 1H), 3.43–3.29 (m, 4H), 1.84 (d, *J* = 6.8 Hz, 1.68 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.77, 141.12, 121.75, 41.97, 40.62, 18.05, 14.68, 13.01.

## 4. General Methods for Permanganate Oxidation




**1/3** **2/4**

(a) 0.2 mmol scale for the optimization of reaction conditions.

At 0 ℃, to a solution of ester **1a** (0.2 mmol), phase transfer catalyst TBAB (0.1 mmol) and acetic acid (57 μL, 1.0 mmol) in 2.0 mL solvent was added dropwise distilled water (0.2 mL), followed by addition of potassium permanganate (0.4 mmol). The reaction was kept to react at 0 ℃ for 1 h. After the reactants were consumed, the reaction mixture was passed through a plug of silica gel (eluent: ethyl acetate). The filtrate was concentrated in vacuo and the residue was purified by flash chromatography affording pure compound **2a**.

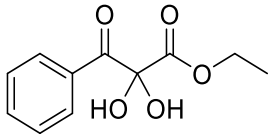
(b) 0.2 mmol scale for substrate scope investigation.

At 0 ℃, to a solution of ester **1/3** (0.2 mmol), phase transfer catalyst TBAB (0.1 mmol) and acetic acid (57 μL, 1.0 mmol) in 2.0 mL 3-pentanone was added dropwise distilled water (0.2 mL), followed by addition of potassium permanganate (0.4 mmol). The reaction was kept to react at 0 ℃ for 1 h. After the reactants were consumed, the reaction mixture was passed through a plug of silica gel (eluent: ethyl acetate). The filtrate was concentrated in vacuo and the residue was purified by flash chromatography affording pure compound **2/4**.

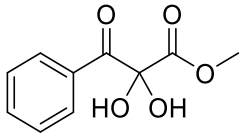
(c) The procedure for scaled-up preparation of **2a**.

At 0 ℃, to a solution of ester **1a** (4 mmol), phase transfer catalyst TBAB (2 mmol) and acetic acid (1.2 mL, 20 mmol) in 40 mL 3-pentanone was added dropwise distilled water (4 mL), followed by addition of potassium permanganate (8 mmol). The reaction was kept to react at 0 ℃ for 1h. After the reactants were consumed, the reaction mixture was passed through a plug of silica gel (eluent: ethyl acetate). The filtrate was concentrated in vacuo and the residue was purified by flash chromatography affording pure compound **2a** (722.7 mg, 81% yield).

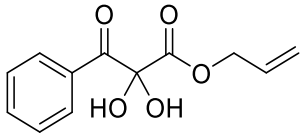
## 5. Characterization of VTCs



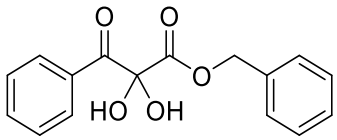
**Ethyl 2,2-dihydroxy-3-oxo-3-phenylpropanoate (2a):** 40.3 mg, 90% yield; yellowish oil; keto form: hydrate form = 3:25; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.10–8.04 (m, 2H), 7.61 (tt, *J* = 7.5 Hz, 1.2 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 5.50 (brs, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.06 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.56, 169.82, 134.60, 131.26, 130.12, 128.71, 91.64, 63.10, 13.59; IR: 1747, 1695, 1600, 1455, 1369, 1240, 1129, 1099, 1009 $cm^{-1}$; HRMS (ESI) calcd for $C_{11}H_{13}O_5$ *m/z* $[M+H]^+$: 225.0763; found: 225.0760.



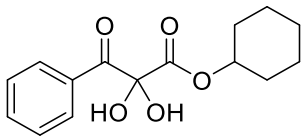
**Methyl 2,2-dihydroxy-3-oxo-3-phenylpropanoate (2b):** 35.2 mg, 84% yield; yellowish oil; keto form: hydrate form = 3:25; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.10–8.04 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 5.34 (brs, 2H), 3.71 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.30, 170.37, 134.73, 131.12, 130.20, 128.81, 91.68, 53.71; IR: 3510, 2986, 1751, 1691, 1600, 1266, 1124, 751, 708 $cm^{-1}$; HRMS (ESI) calcd for $C_{10}H_{11}O_5$ *m/z* $[M+H]^+$: 211.0606; found: 211.0602.



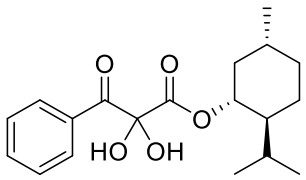
**Allyl 2,2-dihydroxy-3-oxo-3-phenylpropanoate (2c):** 30.6 mg, 65% yield; yellowish oil; keto form: hydrate form = 1:4; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.09–8.04 (m, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 5.71–5.59 (m, 1H), 5.38 (brs, 2H), 5.15–5.07 (m, 2H), 4.62 (dt, *J* = 1.2 Hz, 5.7 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.30, 169.57, 134.71, 131.20, 130.21, 130.12, 128.78, 119.49, 91.62, 67.23; IR: 1747, 1695, 1650, 1597, 1581, 1446, 1236, 1124, 1011 $cm^{-1}$; HRMS (ESI) calcd for $C_{12}H_{13}O_5$ *m/z* $[M+H]^+$: 237.0763; found: 237.0771.



**Benzyl 2,2-dihydroxy-3-oxo-3-phenylpropanoate (2d):** 40.0 mg, 70% yield; yellowish solid; keto form: hydrate form = 7:50; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.26–7.14 (m, 3H), 7.00 (d, *J* = 7.4Hz, 2H), 5.37 (brs, 2H), 5.15 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.22, 169.58, 134.57, 133.95, 131.19, 130.10, 128.72, 128.48, 128.42, 128.02, 91.61, 68.43; IR: 2986, 1747, 1695, 1420, 1266, 1116, 751, 704 $cm^{-1}$; HRMS (ESI) calcd for $C_{16}H_{15}O_5$ *m/z* $[M+H]^+$: 287.0919; found: 287.0911.

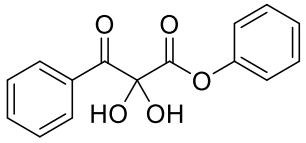


**Cyclohexyl 2,2-dihydroxy-3-oxo-3-phenylpropanoate (2e):** 39.8 mg, 72% yield; yellowish oil; keto form: hydrate form = 1:5; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.10–8.05 (m, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 5.39 (brs, 2H), 4.88–4.81 (m, 1H), 1.65–1.50 (m, 3H), 1.48–1.34 (m, 3H), 1.27–1.19 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.76, 169.26, 134.49, 131.47, 130.03, 128.65, 91.61, 75.79, 30.59, 24.88, 22.91; IR: 2940, 1738, 1691, 1450, 1265, 1117, 1005, 737, 706 $cm^{-1}$; HRMS (ESI) calcd. for $C_{15}H_{18}O_5Na$ *m/z* $[M+Na]^+$: 301.1052; found: 301.1057.

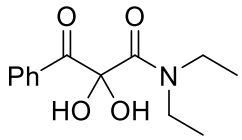


**(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2,2-dihydroxy-3-oxo-3-phenylpropanoate (2f):** 53.5 mg, 80% yield; white solid; keto form: hydrate form =1:50; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.11−8.06 (m, 2H), 7.65−7.59 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 5.43 (brs, 1H), 5.21 (brs, 1H), 4.67 (td, *J* = 11.2 Hz, 4 Hz, 1H), 1.85–1.78 (m, 1H), 1.63–1.55 (m, 3H), 1.44–1.34 (m, 1H), 1.25–1.15 (m, 1H), 1.14–1.05 (m, 1H), 0.93–0.84 (m, 1H), 0.82 (d, *J* = 6.4 Hz, 3H), 0.80–0.72 (m, 1H), 0.59 (d, *J* = 6.4 Hz, 3H), 0.42 (d, *J* = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.55, 169.55,

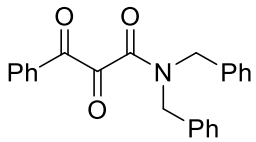
134.52, 131.54, 130.13, 128.69, 91.55, 77.78, 46.37, 39.70, 33.78, 31.21, 25.39, 22.75, 21.77, 20.45, 15.54; IR: 2961, 1742, 1695, 1450, 1262, 1124, 1004, 734, 704 $cm^{-1}$; HRMS (ESI) calcd. for $C_{19}H_{27}O_5$ *m/z* $[M+H]^+$: 335.1858; found: 335.1867.



**Phenyl 2,2-dihydroxy-3-oxo-3-phenylpropanoate (2g):** 40.5 mg, 74% yield; white solid; keto form: hydrate form = 7:100; Hydrate: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 2H), 5.52 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.93, 168.56, 149.76, 134.93, 131.30, 130.22, 129.55, 128.97, 126.67, 120.61, 91.75; IR: 1768, 1695, 1600, 1420, 1266, 1116, 704 $cm^{-1}$; HRMS (ESI) calcd. for $C_{15}H_{12}O_5Na$ *m/z* $[M+Na]^+$: 273.0763; found: 273.0757.

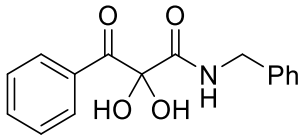


***N*,*N*-diethyl-2,2-dihydroxy-3-oxo-3-phenylpropanamide (2h):** 39.9 mg, 80% yield; yellowish solid; keto form: hydrate form = 9:100; Hydrate: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.40 (s, 1H), 4.91 (brs, 1H), 3.55–3.25 (m, 4H), 1.16–1.10 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 195.23, 167.87, 134.25, 133.85, 129.12, 128.66, 73.65, 41.41, 40.74, 13.73, 12.47; IR: 2982, 1721, 1639, 1579, 1450, 1377, 1219, 708 $cm^{-1}$; HRMS (ESI) calcd. for $C_{13}H_{18}NO_4$ *m/z* $[M+H]^+$: 252.1236; found: 252.1227.

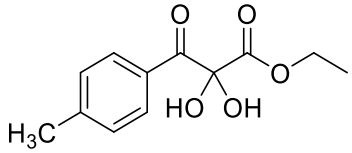


***N*,*N*-dibenzyl-2,2-dihydroxy-3-oxo-3-phenylpropanamide (2i):** 39.7 mg, 60% yield; yellowish solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.2 Hz, 1.1 Hz, 2H), 7.71 (t, *J* = 7.1 Hz, 1H), 7.56 (t, *J* = 7.1 Hz, 2H), 7.43–7.30 (m, 8H), 7.29–7.25 (m, 2H), 4.56 (s, 2H), 4.49 (s, 2H); $^{13}$C NMR(100 MHz, $CDCl_3$) δ 191.60, 184.95, 166.37, 135.32, 135.07, 134.57, 131.87, 130.46, 128.98, 128.92, 128.87, 128.38, 128.34, 128.27,

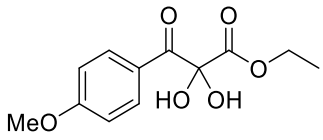
127.90, 50.00, 46.34; IR: 2986, 1691, 1647, 1449, 1266, 1077, 749, 703 $cm^{-1}$; HRMS (ESI) calcd. for $C_{23}H_{19}NO_3Na$ *m/z* $[M+Na]^+$: 380.1263; found: 380.1254.




***N*-benzyl-2,2-dihydroxy-3-oxo-3-phenylpropanamide (2j):** 33.2 mg, 58% yield; yellowish oil; keto form: hydrate form = 7:20; Hydrate: $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.36 Hz, 2H), 7.68 (t, *J* = 7.56 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.41–7.31 (m, 5H), 4.55 (d, *J* = 5.96 Hz, 2H); $^{13}C$ NMR (400 MHz, $CDCl_3$) δ 195.82, 166.83, 137.30, 134.76, 130.86, 129.55, 128.70, 128.38, 127.69,127.62, 75.40, 43.33; IR: 3690, 3055, 1695, 1600, 1446, 1262, 1124, 892 $cm^{-1}$; HRMS (ESI) calcd. for $C_{16}H_{16}NO_4$ *m/z* $[M+H]^+$: 286.1079; found: 286.1075.

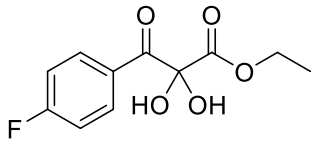



**Ethyl 2,2-dihydroxy-3-oxo-3-(4-tolyl)propanoate (4a):** 39.2 mg, 83% yield; yellowish oil; keto form: hydrate form = 3:20; Hydrate: $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 5.48 (brs, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (400 MHz, $CDCl_3$) δ 191.00, 169.98, 145.90, 130.28, 129.43, 128.63, 91.52, 63.08, 21.80, 13.61; IR: 2982, 1742, 1687, 1605, 1264, 1121, 734, 703 $cm^{-1}$; HRMS (ESI) calcd. for $C_{12}H_{15}O_5$ *m/z* $[M+H]^+$: 239.0919; found: 239.0911.

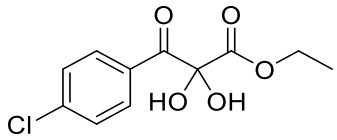



**Ethyl 2,2-dihydroxy-3-(4-methoxyphenyl)-3-oxopropanoate (4b):** 20.5 mg, 40% yield; yellowish oil; keto form: hydrate form: acid = 25:57:17; Hydrate: $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 9 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.46 (brs, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 189.77, 170.20, 164.67, 132.77, 124.02, 114.02, 91.50, 63.06, 55.54, 13.68; IR: 2984, 1743, 1601, 1243, 1174, 1121, 1018 $cm^{-1}$; HRMS (ESI) calcd. for $C_{12}H_{15}O_6$ *m/z*

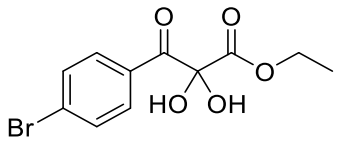
$[M+H]^+$: 255.0869; found: 255.0872.



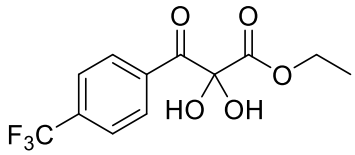
**Ethyl 3-(4-fluorophenyl)-2,2-dihydroxy-3-oxopropanoate (4c):** 32.7mg, 68% yield; yellow solid; keto form: hydrate form = 3:20; Hydrate: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.18–8.09 (m, 2H), 7.18–7.11 (m, 2H), 5.39 (brs, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.10 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.06, 169.74, 166.53 (d, *J* = 258.2 Hz), 133.10 (d, *J* = 9.7 Hz), 127.75 (d, *J* = 3.3 Hz), 116.10 (d, *J* = 22.0 Hz), 91.64, 63.27, 13.67; IR: 3690, 2982, 1747, 1691, 1597, 1420, 1262, 704 $cm^{-1}$; HRMS (ESI) calcd. for $C_{11}H_{12}FO_5$ *m/z* $[M+H]^+$ : 243.0669; found: 243.0675.



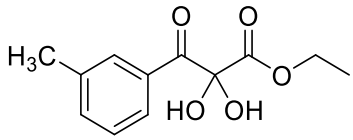
**Ethyl 3-(4-chlorophenyl)-2,2-dihydroxy-3-oxopropanoate (4d):** 20.3 mg, 39% yield; white solid; keto form: hydrate form = 21:100; Hydrate: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.04–7.90 (m, 2H), 7.53–7.40 (m, 2H), 5.30 (brs, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.49, 169.62, 141.37, 132.18, 131.52, 129.18, 91.58, 63.36, 13.69; IR: 2986, 1751, 1691, 1592, 1425, 1270, 742, 704 $cm^{-1}$; HRMS (ESI) calcd. for $C_{11}H_{12}ClO_5$ *m/z* $[M+H]^+$: 259.0373; found: 259.0372.



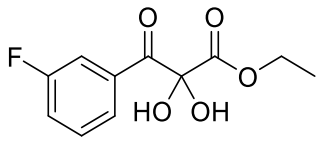
**Ethyl 3-(4-bromophenyl)-2,2-dihydroxy-3-oxopropanoate (4e):** 26.1 mg, 43% yield; white solid; keto form: hydrate form = 1:5; Hydrate: $^1$H NMR (400 MHz, $CDCl_3$) δ7.95–7.92 (m, 2H), 7.64–7.58 (m, 2H), 5.31 (brs, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR(100 MHz, $CDCl_3$) δ 190.73, 169.58, 141.34, 132.16, 131.53, 129.16, 91.61, 63.35, 13.68; IR: 2986, 1747, 1695, 1584, 1425, 1266, 742, 704 $cm^{-1}$; HRMS (ESI) calcd. for $C_{11}H_{12}BrO_5$ *m/z* $[M+H]^+$: 302.9868; found: 302.9862.



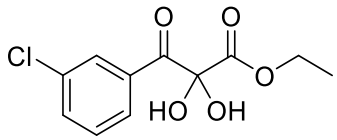
**Ethyl 2,2-dihydroxy-3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate (4f):** 30.3 mg, 52% yield; yellow oil; keto form: hydrate form = 1:4; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.3Hz, 2H), 5.34 (brs, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.95, 169.37, 135.62(d, *J* = 33.1 Hz), 134.17, 130.58, 130.45, 130.36, 125.77 (d, *J* = 4.0 Hz), 91.80, 63.47, 13.65 $cm^{-1}$; IR: 3686, 2986, 1751, 1708, 1425, 1266, 1137, 1009, 897, 738 $cm^{-1}$; HRMS (ESI) calcd. for $C_{12}H_{11}F_3O_5Na$ *m/z* $[M+Na]^+$: 315.0456; found: 315.0446.



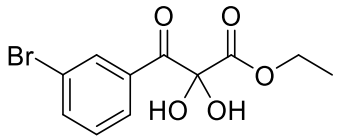
**Ethyl 2,2-dihydroxy-3-oxo-3-(m-tolyl)propanoate (4g):** 33.4 mg, 70% yield; yellowish oil; keto form: hydrate form = 4:25; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.91–7.83 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 5.32 (brs, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (400 MHz, $CDCl_3$) δ 191.63, 169.92, 138.64, 135.47, 131.26, 130.47, 128.58, 127.31, 91.58, 63.12, 21.29, 13.60; IR: 2978, 1747, 1691, 1600, 1257, 1124, 1039, 738, 682 $cm^{-1}$; HRMS (ESI) calcd. for $C_{12}H_{15}O_5$ *m/z* $[M+H]^+$: 239.0919; found: 239.0911.



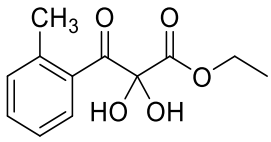
**Ethyl 3-(3-fluorophenyl)-2,2-dihydroxy-3-oxopropanoate (4h):** 26.6 mg, 55% yield; yellowish oil; keto form: hydrate form = 3:50; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.91–7.83 (m, 1H), 7.81–7.74 (m, 1H), 7.49–7.38 (m, 1H), 7.32 (td, *J* = 8.2, 2.4 Hz, 1H), 5.44 (brs, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.68, 169.46, 162.49 (d, *J* = 248.5 Hz), 133.26 (d, *J* = 7.2 Hz), 130.48 (d, *J* = 7.3 Hz), 125.95 (d, *J* = 2.4 Hz), 121.73 (d, *J* = 21.5 Hz), 116.73 (d, *J* = 23.2 Hz), 91.78, 63.30, 13.61; IR: 2986, 1747, 1699, 1494, 1442, 1253, 1189, 1124, 738 $cm^{-1}$; HRMS (ESI) calcd. for $C_{11}H_{11}FO_5Na$ *m/z* $[M+Na]^+$: 265.0488; found: 265.0486.



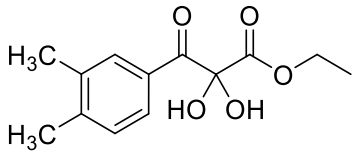
**Ethyl 3-(3-chlorophenyl)-2,2-dihydroxy-3-oxopropanoate (4i):** 25.8 mg, 50% yield; white solid; keto form: hydrate form = 39:100; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.06 (t, *J* = 1.8 Hz, 1H), 7.95 (td, *J* = 7.9 Hz, 1.2 Hz, 1H), 7.60–7.57 (m, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 5.39 (brs, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR(100 MHz, $CDCl_3$) δ 190.60, 169.38, 135.40, 134.52, 132.83, 130.05, 129.90, 128.20, 91.70, 63.34, 13.62; IR: 2986, 1742, 1695, 1570, 1232, 1129, 1021, 740 $cm^{-1}$; HRMS (ESI) calcd. for $C_{11}H_{12}ClO_5$ *m/z* $[M+H]^+$: 259.0373; found: 259.0370.



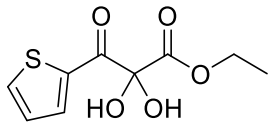
**Ethyl 3-(3-bromophenyl)-2,2-dihydroxy-3-oxopropanoate (4j):** 33.8 mg, 56% yield; white solid; keto form: hydrate form = 1:8; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.23–8.19 (m, 1H), 8.04–7.96 (m, 1H), 7.75 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.37–7.31 (m, 1H), 5.39 (brs, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.52, 169.41, 137.44, 133.03, 132.84, 130.28, 128.65, 122.96, 91.68, 63.38, 13.65; IR: 2982, 1742, 1699, 1562, 1232, 1129, 747, 717 $cm^{-1}$; HRMS (ESI) calcd. for $C_{11}H_{12}BrO_5$ *m/z* $[M+H]^+$: 302.9868; found: 302.9864.



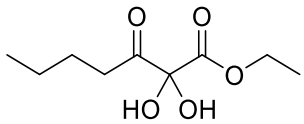
**Ethyl 2,2-dihydroxy-3-oxo-3-(o-tolyl)propanoate (4k):** 35.7 mg, 75% yield; yellowish oil; keto form: hydrate form = 2:5; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.3 Hz, 1.2 Hz, 1H), 7.43 (td, *J* = 7.6 Hz, 1.3 Hz, 1H), 7.34–7.21 (m, 2H), 5.45 (brs, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR(400 MHz, $CDCl_3$) δ 193.43, 169.79, 141.30, 134.36, 133.08, 132.16, 130.40, 125.72, 91.97, 63.00, 21.91, 13.50; IR: 2978, 1747, 1695, 1605, 1455, 1232, 1129, 1017 $cm^{-1}$; HRMS (ESI) calcd. for $C_{12}H_{15}O_5$ *m/z* $[M+H]^+$: 239.0919; found: 239.0912.



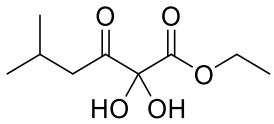
**Ethyl 3-(3,4-dimethylphenyl)-2,2-dihydroxy-3-oxopropanoate (4l):** 35.7 mg, 70% yield; white solid; keto form: hydrate form = 11:50; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.81–7.55 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 5.38 (brs, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.14, 170.12, 144.80, 137.29, 131.07, 129.96, 128.99, 128.01, 91.43, 63.13, 20.24, 19.76, 13.67; IR: 2974, 1756, 1695, 1566, 1450, 1249, 1085 $cm^{-1}$; HRMS (ESI) calcd. for $C_{13}H_{11}O_5$ *m/z* $[M+H]^+$: 253.1076; found: 253.1068.



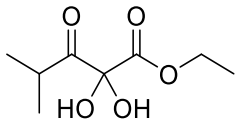
**Ethyl 2,2-dihydroxy-3-oxo-3-(thiophen-2-yl)propanoate (4m):** 18.3 mg, 40% yield; yellowish oil; keto form: hydrate form = 3:20; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 4.0 Hz, 1.1 Hz, 1H), 7.78 (dd, *J* = 4.9 Hz, 1.1 Hz, 1H), 7.16 (dd, *J* = 4.0 Hz, 4.9 Hz, 1H), 5.33 (brs, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 184.84, 169.68, 138.35, 136.60, 136.27, 128.68, 92.00, 63.41, 13.69; IR: 2978, 1751, 1665, 1407, 1240, 1103, 1052, 734 $cm^{-1}$; HRMS (ESI) calcd. for $C_9H_{11}O_5S$ *m/z* $[M+H]^+$: 231.0327; found: 231.0322.



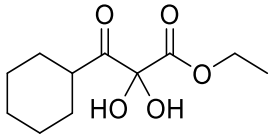
**Ethyl 2,2-dihydroxy-3-oxoheptanoate (4n):** 26.1 mg, 64% yield; yellowish oil; keto form: hydrate form = 3:100; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 5.24 (brs, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.57 (t, *J* = 7.3 Hz, 2H), 1.64–1.55 (m, 2H), 1.29–1.24 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 203.32, 169.18, 92.31, 63.39, 35.36, 25.29, 22.03, 13.89, 13.69; IR: 2961, 1738, 1464, 1369, 1257, 1124, 859 $cm^{-1}$; HRMS (ESI) calcd. for $C_9H_{16}O_5Na$ *m/z* $[M+Na]^+$: 227.0895; found: 227.0902.



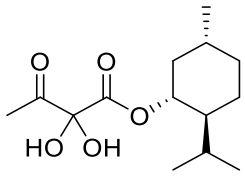
**Ethyl 2,2-dihydroxy-5-methyl-3-oxohexanoate (4o):** 28.1 mg, 69% yield; yellowish oil; keto form: hydrate form = 4:25; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.81 (brs, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.47 (d, *J* = 6.8 Hz, 2H), 2.30–2.17 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.69, 169.16, 92.36, 63.39, 44.47, 23.94, 22.28, 13.86; IR: 2956, 1733, 1469, 1367, 1258, 1135, 1091, 858 $cm^{-1}$; HRMS (ESI) calcd. for $C_9H_{16}O_5Na$ *m/z* $[M+Na]^+$: 227.0895; found: 227.0888.



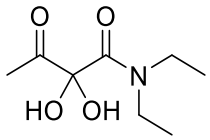
**Ethyl 2,2-dihydroxy-4-methyl-3-oxopentanoate (4p):** 24.3 mg, 64% yield; yellowish oil; keto form: hydrate form = 9:40; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 5.08 (brs, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.00–2.88 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 207.50, 169.26, 92.55, 63.34, 35.29, 19.14, 13.90; IR: 2982, 1725, 1472, 1360, 1257, 1103,1034, 862 $cm^{-1}$; HRMS (ESI) calcd. for $C_8H_{15}O_5$ *m/z* $[M+H]^+$: 191.0919; found: 191.0926.



**Ethyl 3-cyclohexyl-2,2-dihydroxy-3-oxopropanoate (4q):** 35.8 mg, 78% yield; yellowish oil; keto form: hydrate form = 1:5; Hydrate: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 5.09 (brs, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.68 (tt, *J* = 11.6 Hz, 3.3 Hz, 1H), 1.84–1.56 (m, 6H), 1.45–1.33 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 206.24, 169.28, 92.53, 63.26, 45.10, 29.07, 25.45, 25.30, 13.90; IR: 2926, 1751, 1729, 1446, 1262, 1137, 1103, 730 $cm^{-1}$; HRMS (ESI) calcd. for $C_{11}H_{18}O_5Na$ *m/z* $[M+Na]^+$: 253.1052; found: 253.1061.

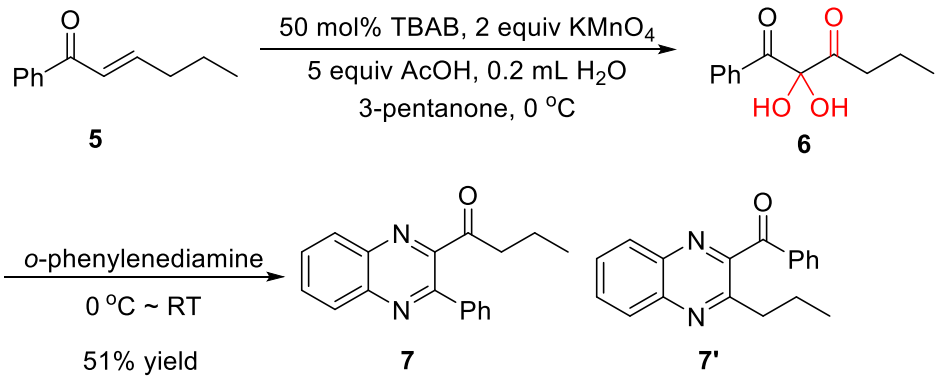


**(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2,2-dihydroxy-3-oxobutanoate (4r):** 42.5 mg, 78% yield; white solid; keto form: hydrate form = 1:25; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 5.01 (s, 1H), 4.95 (s, 1H), 4.80 (td, *J* = 4.4 Hz, 11 Hz, 1H), 2.27 (s, 1H), 2.04–1.95 (m, 1H), 1.82–1.63 (m, 4H), 1.55–1.36 (m, 2H), 1.10–0.96 (m, 2H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.74 (d, *J* = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 200.88, 168.68, 92.43, 78.10, 46.61, 40.07, 33.87, 31.33, 25.99, 23.08, 23.02, 21.85, 20.57, 15.92; IR: 2990, 1727, 1458, 1421, 1276, 1126, 746, 705 cm$^{-1}$; HRMS (ESI) calcd. for $C_{11}H_{18}O_5Na$ *m/z* $[M+Na]^+$: 273.1702; found: 273.1701.



***N*,*N*-diethyl-2,2-dihydroxy-3-oxobutanamide (4s):** 26.9 mg, 71% yield; yellowish solid; keto form: hydrate form = 21:100; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.71 (brs, 2H), 3.65–3.42 (m, 2H), 3.38–3.25 (m, 2H), 2.20 (s, 3H), 1.18–1.10 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 206.63, 167.04, 76.22, 41.47, 41.00, 25.08, 13.61, 12.56; IR: 2982, 1729, 1635, 1385, 1364, 1211, 1135, 789 cm$^{-1}$; HRMS (ESI) calcd. for $C_8H_{16}NO_4$ *m/z* $[M+H]^+$: 190.1079; found: 190.1072.

## 6. Derivatization of VTCs




**1-(3-Phenylquinoxalin-2-yl)butan-1-one (7) and phenyl(3-propylquinoxalin-2-yl)methanone (7′)[17]:**

*Step 1:*α,β-Unsaturated ketone **5** (0.2 mmol × 2) was subjected to permanganate oxidation under standard condition and monitored by TLC. After consumption of the starting material, saturated $Na_2S_2O_3$ aqueous solution was added and the reaction mixture was extracted with dichloromethane. The combined organic layer is dried with anhydrous $Na_2SO_4$, filtered and concentrated to remove dichloromethane.

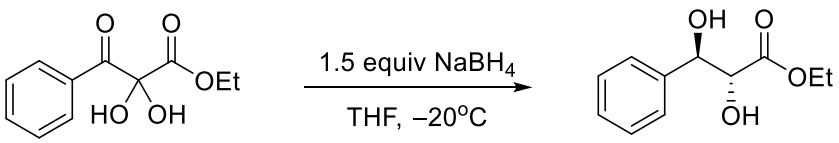
*Step 2:* At 0 °C, *o*-phenylenediamine (64.88 mg, 0.6 mmol, 1.5 equiv.) was added to a solution of the previously obtained crude VTC **6** in 3-pentanone, and then the reaction was allowed to stir at room temperature for about 2 h. The products were purified by column chromatography to obtain the target products **7** + **7'**;

$R_f$ = 0.30 (1:20 EtOAc/hexane); 56.5 mg, 51% yield, yellowish oil; mixture = 4:1;

$^1$H NMR for **7** (400 MHz, $CDCl_3$) δ 8.20–8.13 (m, 2H), 7.87–7.79 (m, 2H), 7.67–7.59 (m, 2H), 7.49–7.45 (m, 3H), 3.10 (t, *J* = 7.3Hz, 2H), 1.77–1.67 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR for **7** (100 MHz, $CDCl_3$) δ 203.69, 152.37, 150.64, 142.19, 139.76, 137.92, 134.13, 131.60, 130.34, 129.50, 129.38, 128.89, 128.60, 42.57, 17.01, 13.67.

$^1$H NMR for **7′** (400 MHz, $CDCl_3$) δ 8.12–8.05 (m, 2H), 7.96–7.91 (m, 2H), 7.79–7.72 (m, 2H), 7.52–7.49 (m, 3H), 3.03 (t, *J* = 7.3Hz, 2H), 1.86–1.77 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR for **7′** (100 MHz, $CDCl_3$) δ194.13, 155.85, 151.03, 139.28, 135.61, 131.04, 130.60, 129.68, 128.75, 128.64, 37.39, 22.63, 14.06; IR: 2871, 2253, 1708, 1455, 1382, 910, 730, 652 $cm^{-1}$; HRMS (ESI) calcd. for $C_{18}H_{16}N_2ONa$ *m/z* $[M+Na]^+$:

299.1160; found: 299.1163.




**2a** **8**

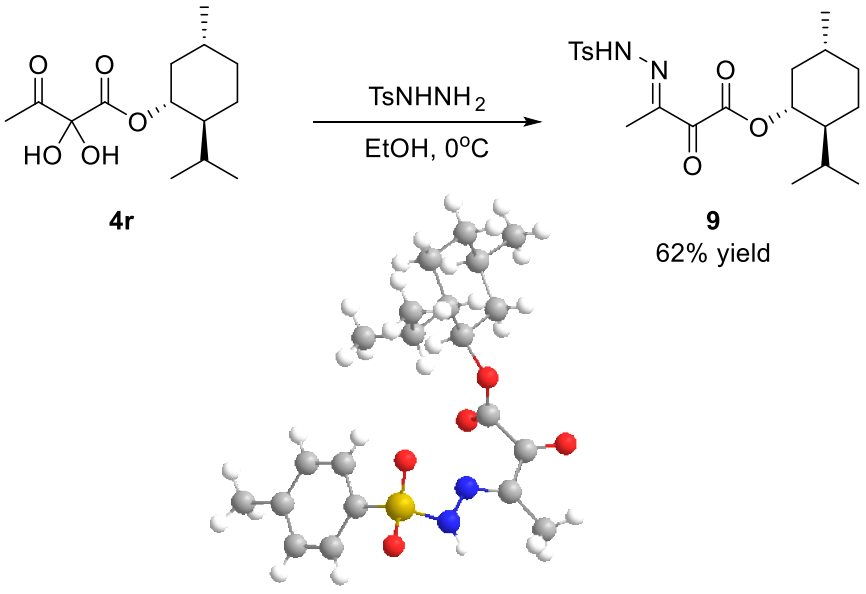
56% yield (25:3 dr)

**Ethyl (2*R*,3*R*)-2,3-dihydroxy-3-phenylpropanoate (8)[18]:**

At –20 ℃, to a solution of **2a** (46.02 mg, 0.2 mmol) in methanol (2.0 mL) was added sodium borohydride (0.2 mmol, 1.5 equiv) and the reaction was stirred for 20 min. Saturated aqueous $NH_4Cl$ was then added and the mixture was allowed to warm to room temperature, followed by addition of saturated aqueous Rochelle's salt. The resultant solution was stirred at room temperature for 12 h. The solution was extracted with EtOAc (×4), and the combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel, providing desired diol **8**.

$R_f$ = 0.20 (1:2 EtOAc/hexane); 23.5 mg, 56% yield, colorless oil;

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.37–7.28 (m, 5H), 5.05–4.99 (m, 1H), 4.51–4.46 (m, 2H), 4.28 (q, *J* = 7.2Hz, 2H), 2.95 (d, *J* = 6.6 Hz, 1H), 2.88 (d, *J* = 6.1 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 3H). The data is consistent with previously reported literature.[19]




**4r** **9**

62% yield

**(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*E*)-3-oxo-2-(2-**

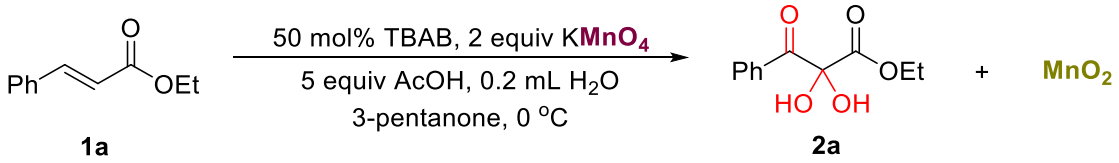
**tosylhydrazono)butanoate (9)[20]:**

At 0 ℃， to a suspension of $TsNHNH_2$ (40.9 mg, 1.1 equiv, 0.22 mmol) in EtOH (1 mL) was added **4r** (51.3mg, 1.0 equiv, 0.2 mmol). The resulted mixture was then stirred for 2.5 h before water (5 mL) was added. The resulting mixture was extracted with ethyl acetate three times, then the combined organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the desired product **9**;

$R_f$ = 0.30 (1:2 EtOAc/hexane); 52.3 mg, 62% yield, white solid;

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 4.94 (td, *J* = 4.5 Hz, 10.6 Hz, 1H), 2.42 (s, 3H), 2.25–2.15 (m, 1H), 2.07–1.95 (m, 1H), 1.89 (s, 3H), 1.78–1.66 (m, 2H), 1.50–1.40 (m, 1H), 1.31–1.09 (s, 4H), 1.00–0.84 (m, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.64, 145.62, 140.66, 135.08, 133.16, 129.89, 128.57, 75.33, 46.79, 40.84, 34.04, 31.37, 26.10, 23.19, 21.95, 21.67, 20.73, 16.13, 9.26; IR: 2982, 1738, 1699, 1425, 1262, 892, 738, 704 $cm^{-1}$; HRMS (ESI) calcd. for $C_{21}H_{30}N_2O_5SNa$ *m/z* $[M+Na]^+$: 445.1773; found: 445.1780.

## 7. Recovery of Manganese Dioxide




At 0 ℃, to a solution of ester **1a** (0.4 mmol), phase transfer catalyst TBAB (0.2 mmol) and acetic acid (114 μL, 2.0 mmol) in 4.0 mL 3-pentanone was added dropwise distilled water (0.4 mL), followed by addition of potassium permanganate (0.8 mmol, 126.4 mg). The reaction was kept to react at 0 ℃ for 1 h. After the reactants were consumed, the reaction mixture was passed through a filtrate. The filter cake was then washed with water (10 mL×3) and ethanol (10 mL×3) to remove water soluble manganese species and $Mn(OAc)_2$. After drying at 60 ℃ for 6 h, brown solid of $MnO_2$ was obtained (two separate experiments performed, 54.5 mg, 78% yield; 60.8 mg, 87% yield).

The obtained sample was characterized by PXRD analysis and the spectrum is as follows. Compared with the spectrum reported in the literature (Fig 1),[21] the structure of obtained $MnO_2$ was determined to be turbostratic structure corresponding to the structure of α-$MnO_2$.

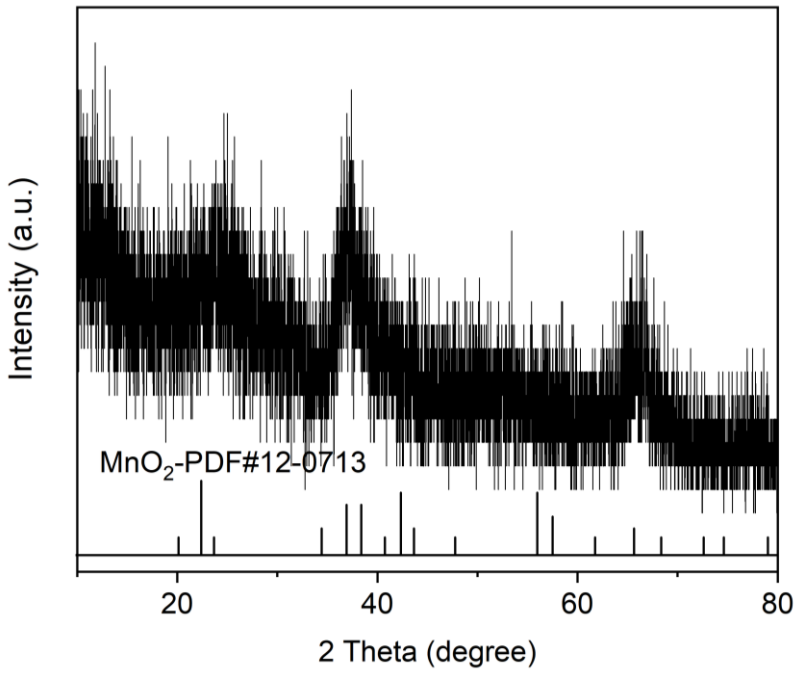



**Figure S1.** PXRD spectrum of $MnO_2$ generated after permanganate oxidation.

## 8. References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## 9. X-ray Crystal Data

**Table S2. Sample And Crystal Data for 2351 (9, CCDC 2181644)**

| | | |
|---|---|---|
| Identification code | 2351 | |
| Chemical formula | $C_{21}H_{30}N_2O_5S$ | |
| Formula weight | 422.53 g/mol | |
| Temperature | 149.99(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal size | 0.14 × 0.13 × 0.12 $mm^3$ | |
| Crystal habit | colorless block | |
| Crystal system | monoclinic | |
| Space group | P 1 21 1 | |
| Unit cell dimensions | a = 11.8685(5) Å | α = 90° |
| | b = 11.8685(5) Å | β = 102.954(4)° |
| | c = 13.3562(4) Å | γ = 90° |
| Volume | 1109.19(8) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.265 $g/cm^3$ | |
| Absorption coefficient | 1.577 $mm^{-1}$ | |
| F(000) | 452.0 | |

# 10. NMR Spectra

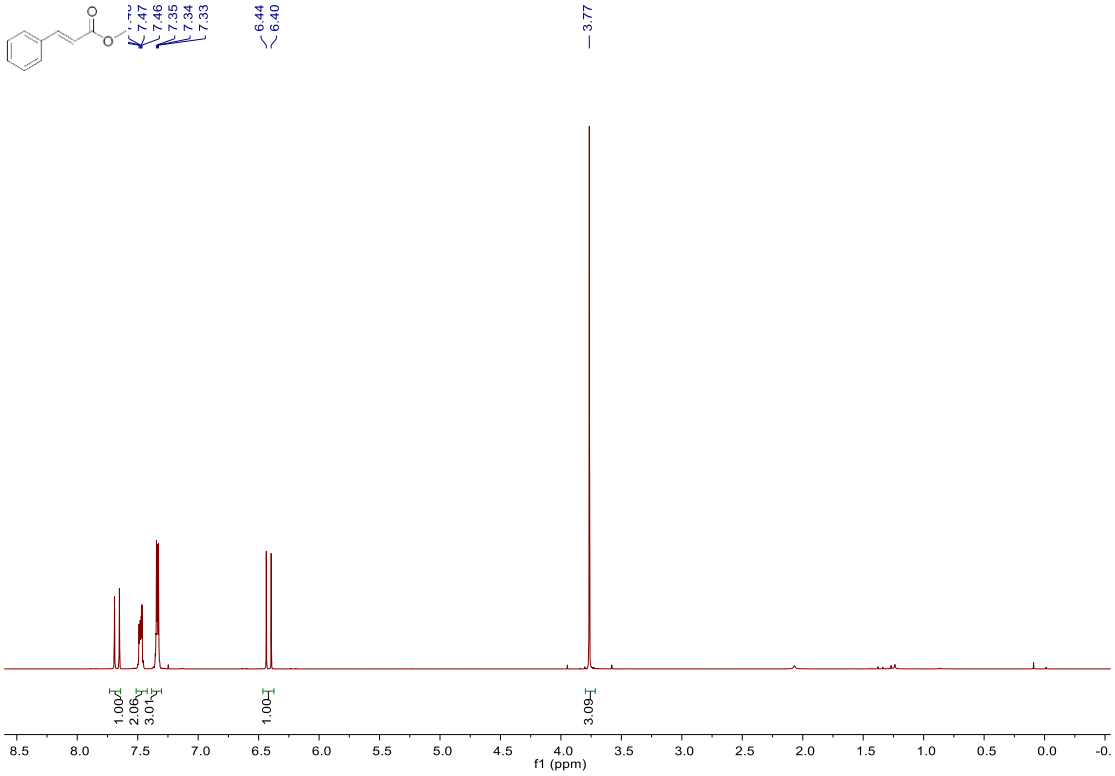


**Figure S2.** $^{1}$H NMR spectra of **1b** in $CDCl_3$.

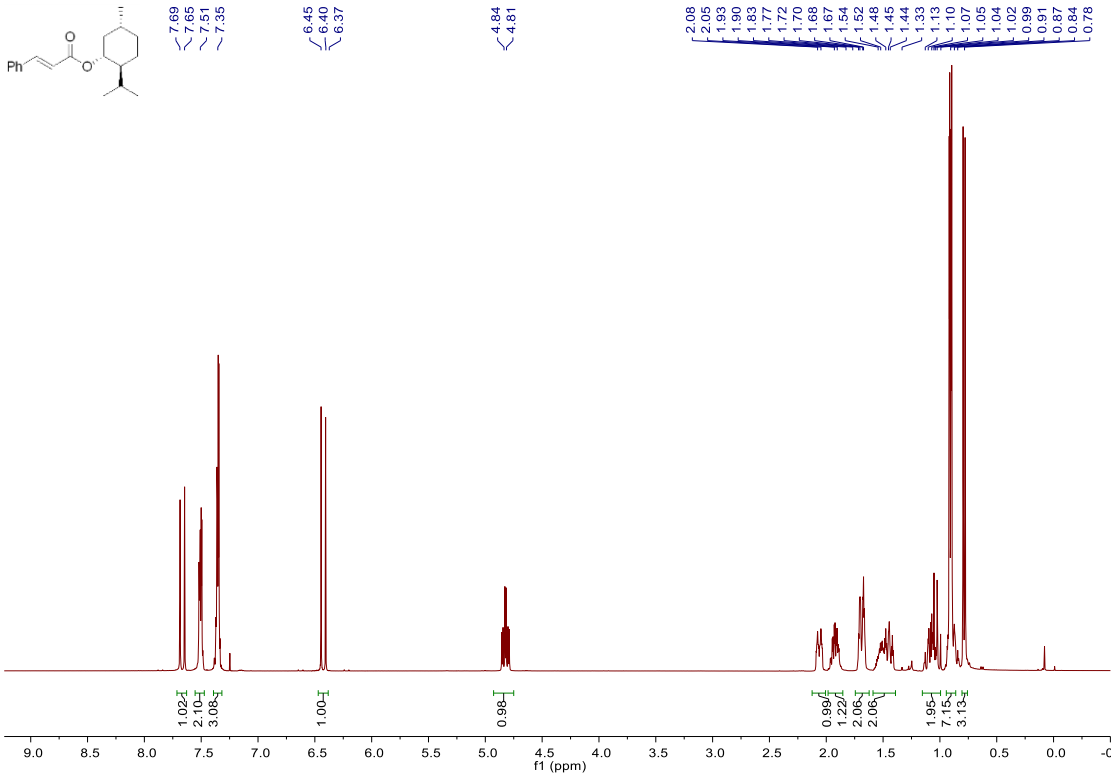


**Figure S3.** $^{1}$H NMR spectra of **1f** in $CDCl_3$.

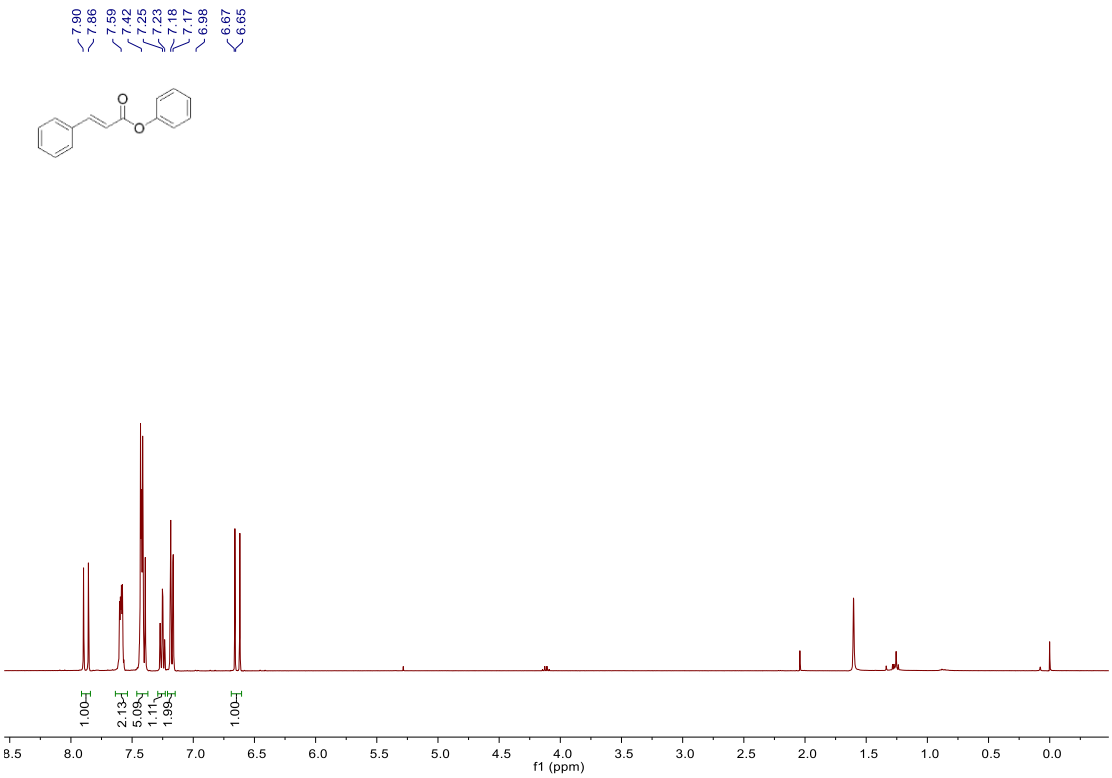


**Figure S4.** $^{1}$H NMR spectra of **1g** in $CDCl_3$.

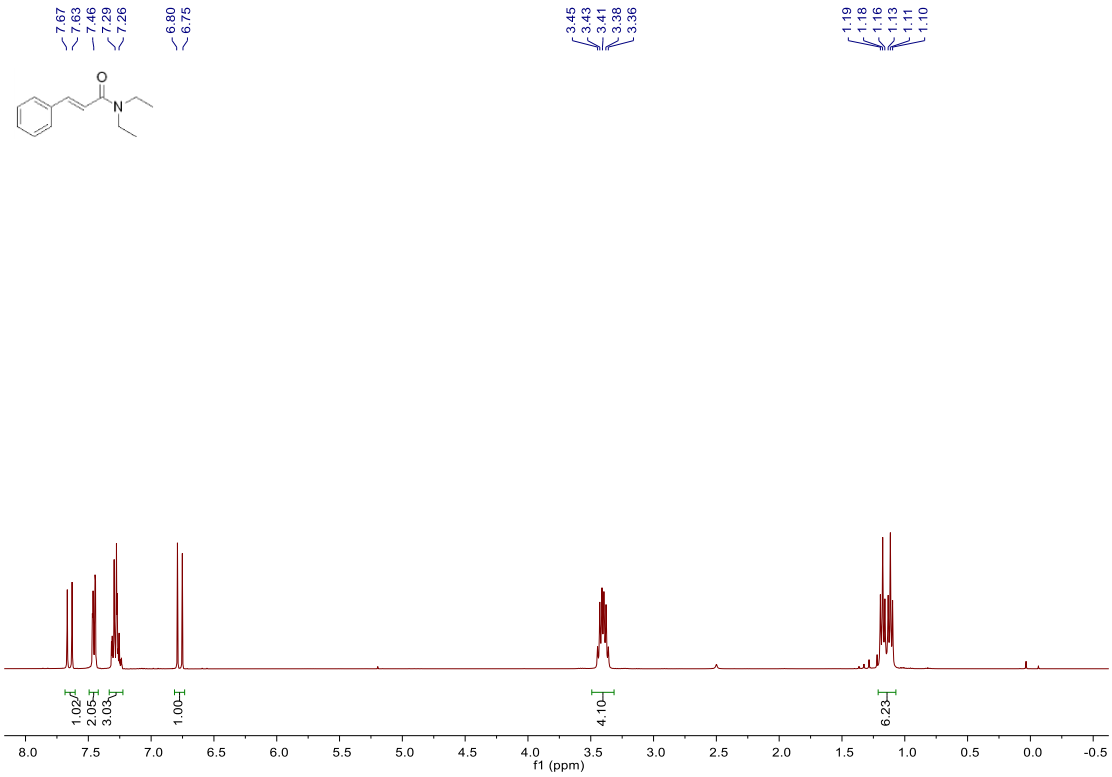


**Figure S5** $^{1}$H NMR spectra of **1h** in $CDCl_3$.

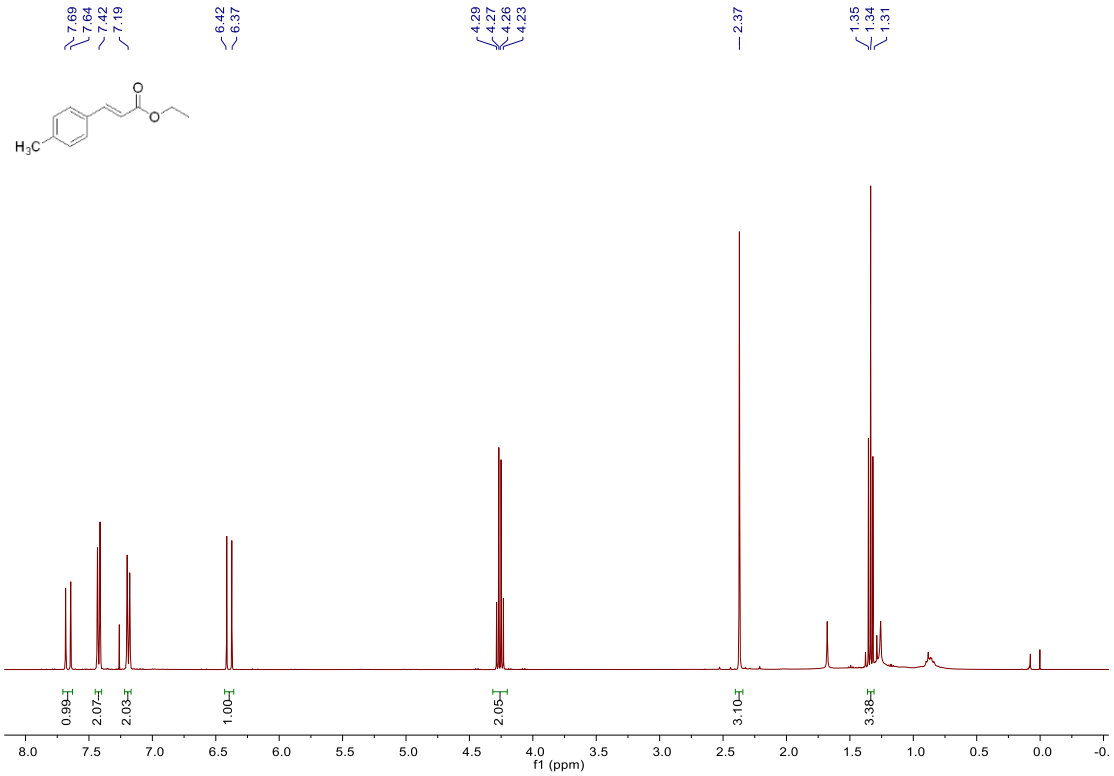


**Figure S6.** $^{1}$H NMR spectra of **3a** in $CDCl_3$.

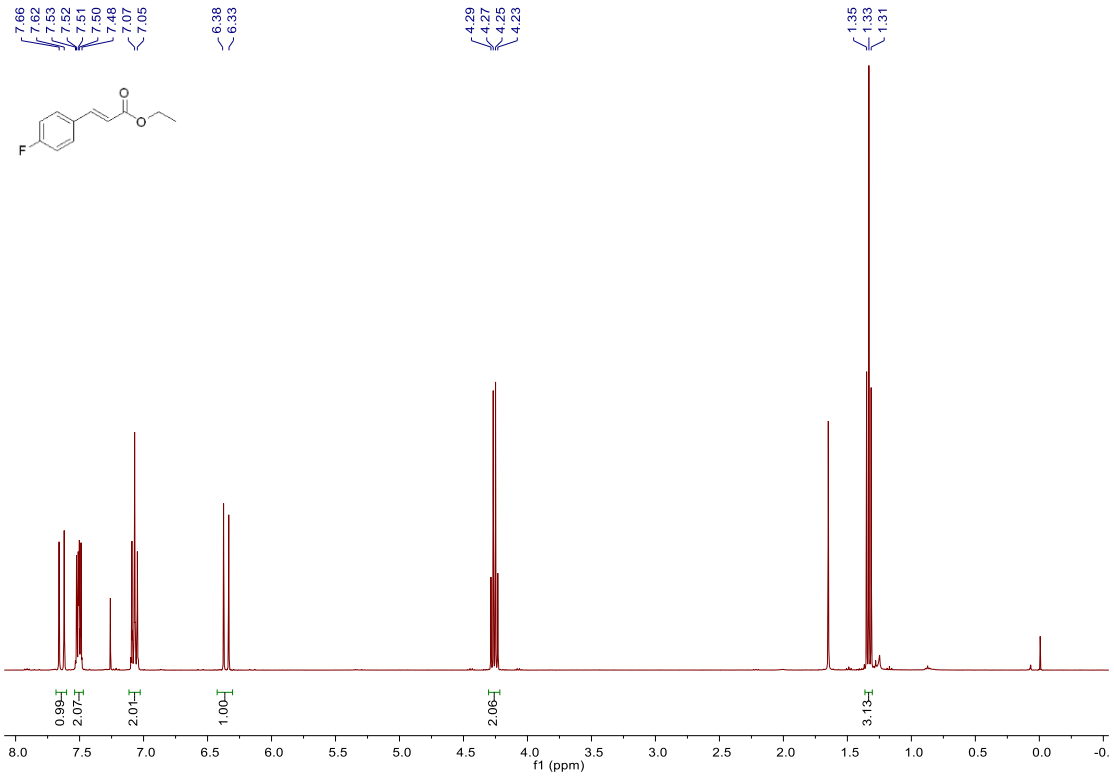


**Figure S7.** $^{1}$H NMR spectra of **3c** in $CDCl_3$.

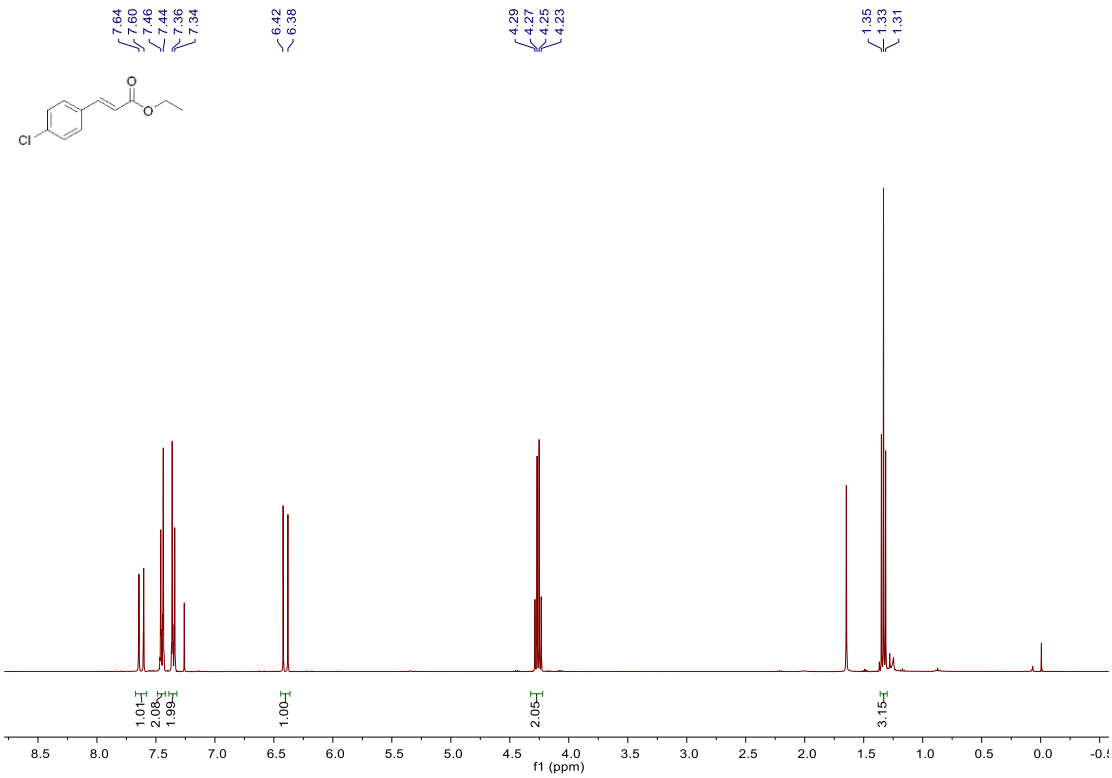


**Figure S8.** $^{1}$H NMR spectra of **3d** in $CDCl_3$.

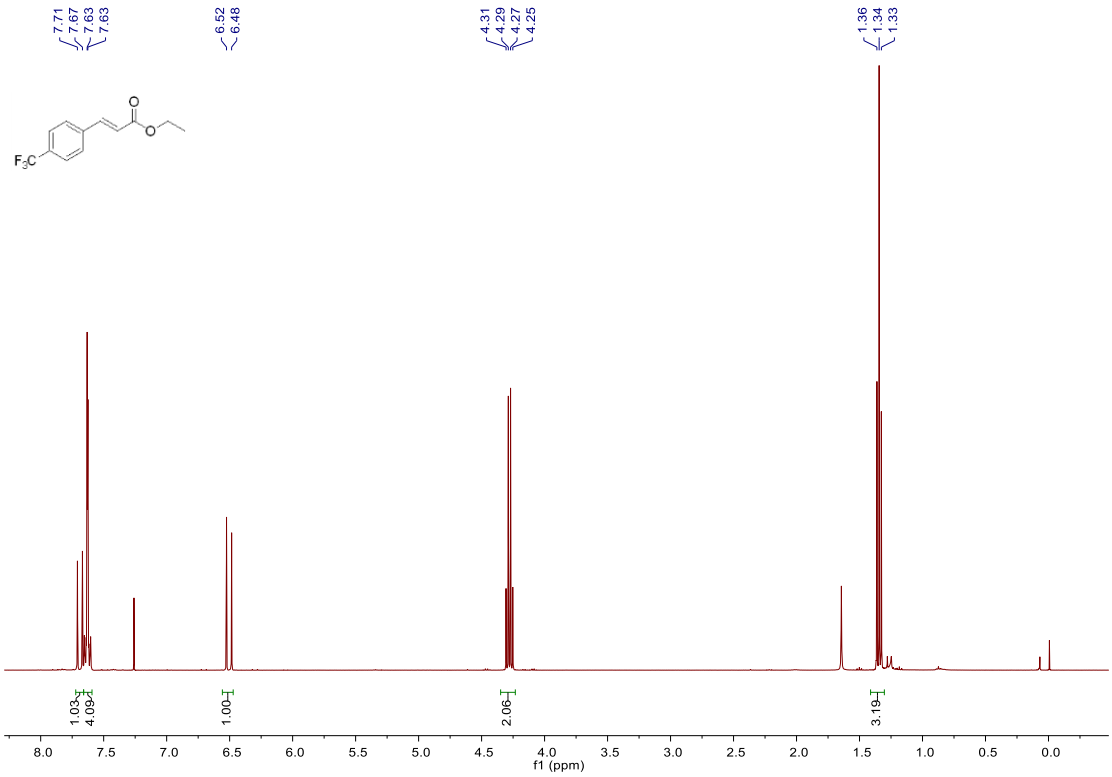


**Figure S9.** $^{1}$H NMR spectra of **3f** in $CDCl_3$.

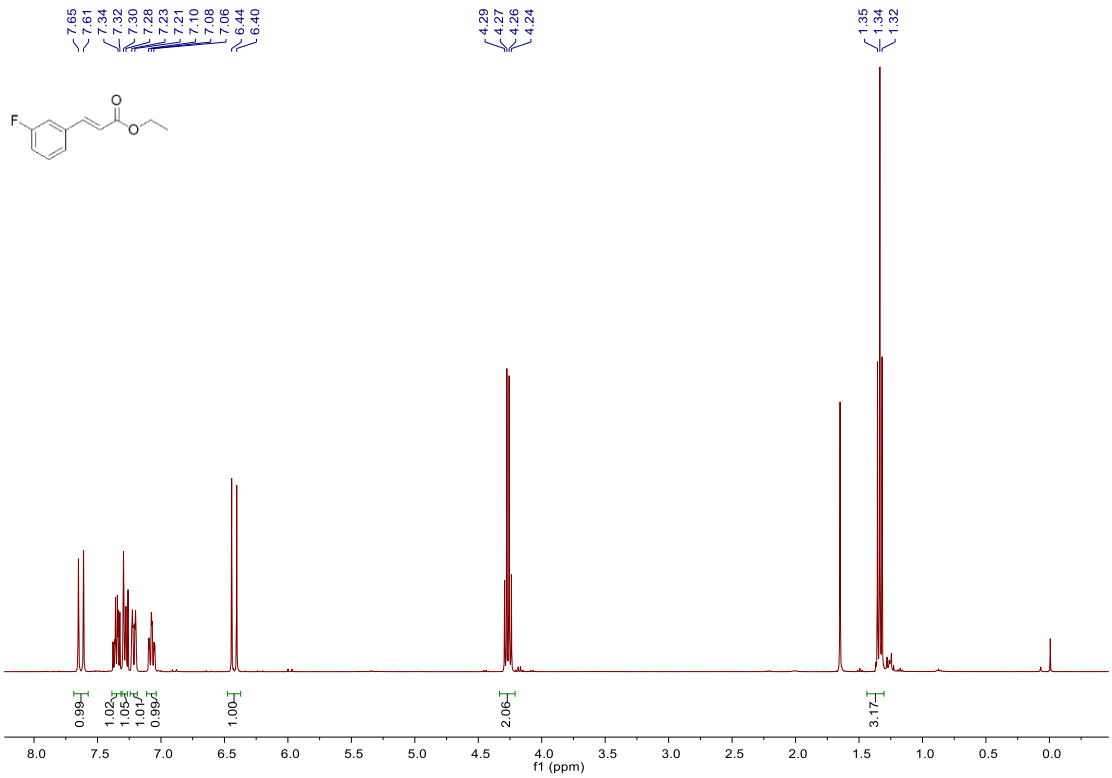


**Figure S10.** $^{1}$H NMR spectra of **3h** in $CDCl_3$.

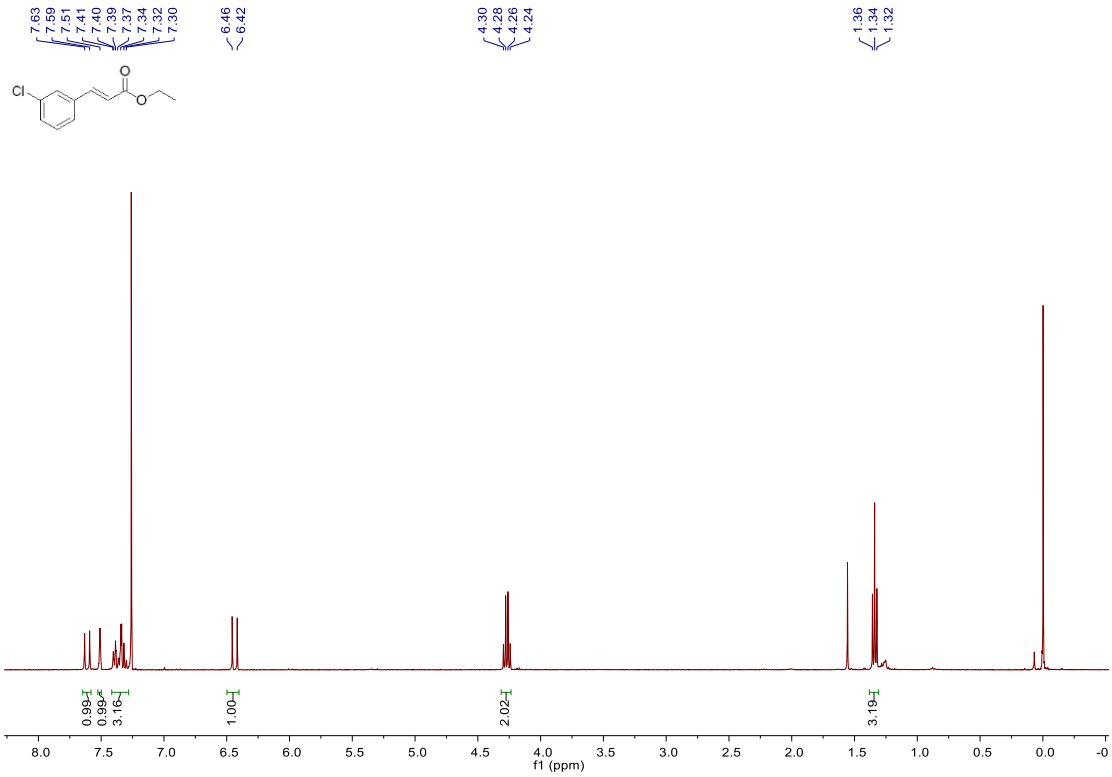


**Figure S11.** $^{1}$H NMR spectra of **3i** in $CDCl_3$.

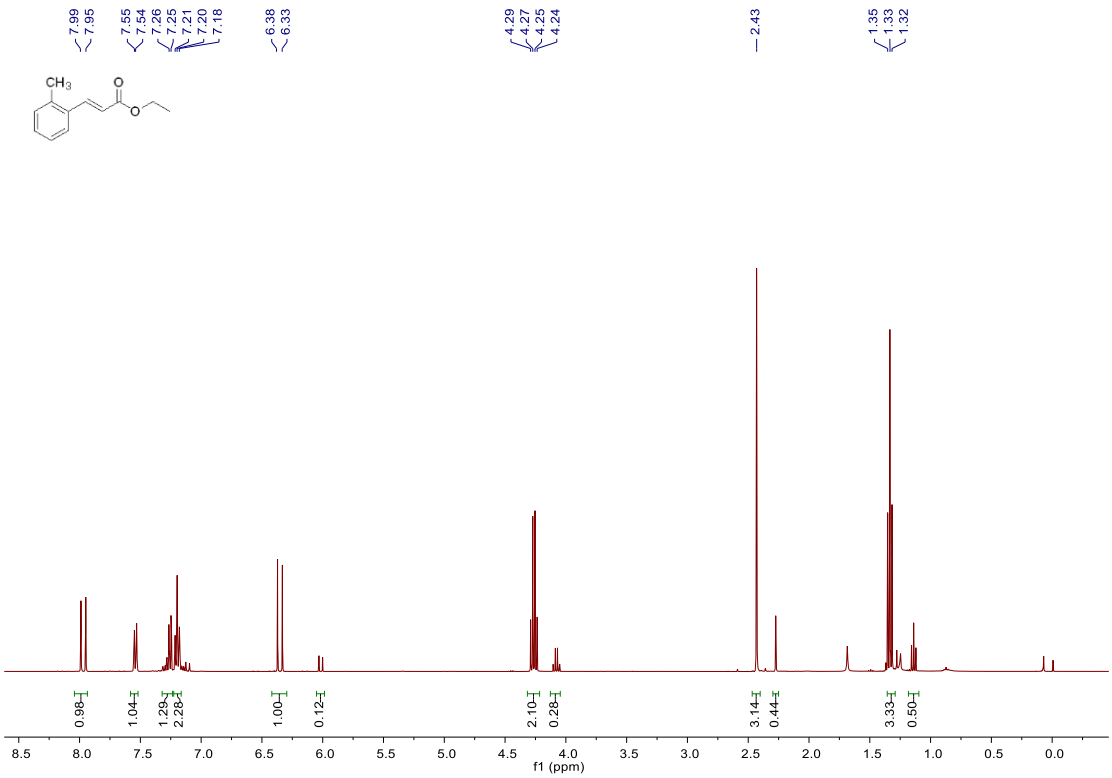


**Figure S12.** $^{1}$H NMR spectra of **3k** in $CDCl_3$.

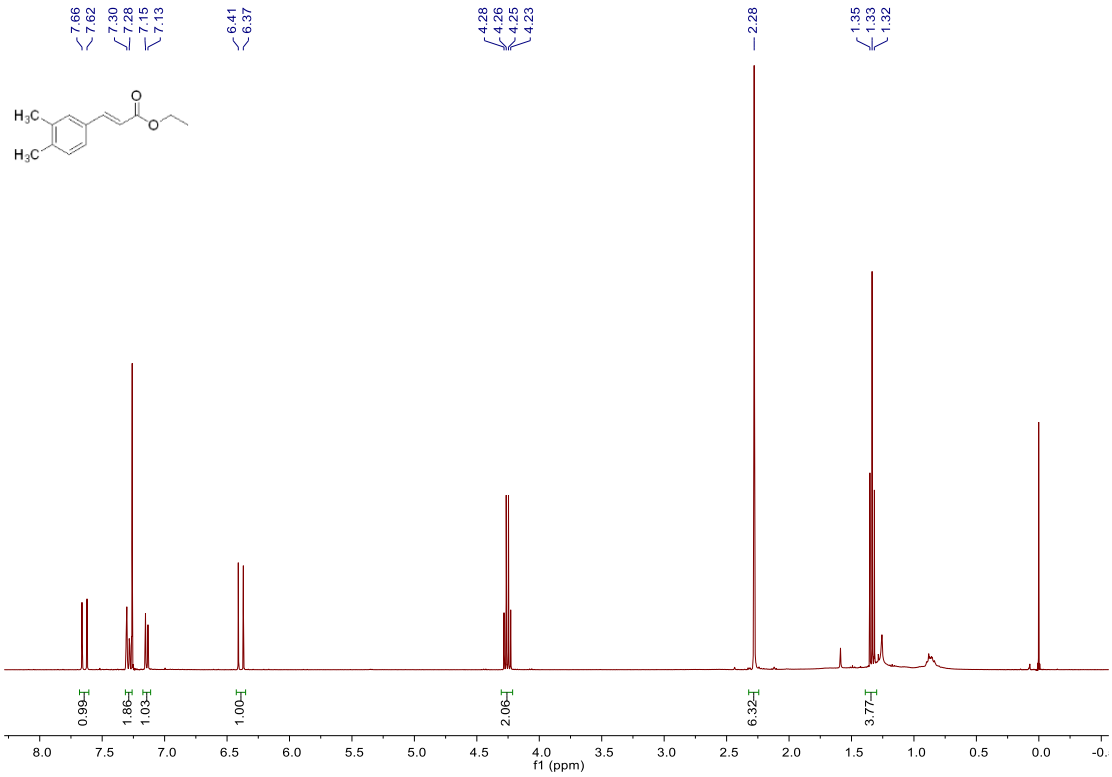


**Figure S13.** $^{1}$H NMR spectra of **3l** in $CDCl_3$.

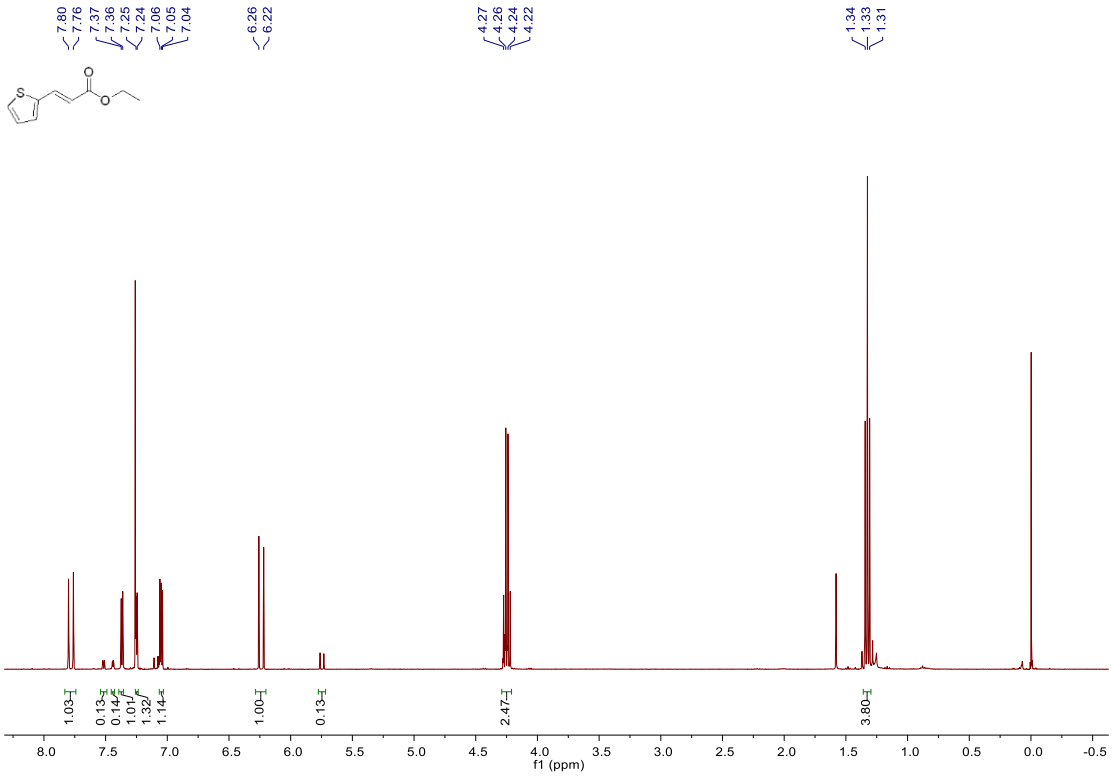


**Figure S14.** $^{1}$H NMR spectra of **3m** in $CDCl_3$.

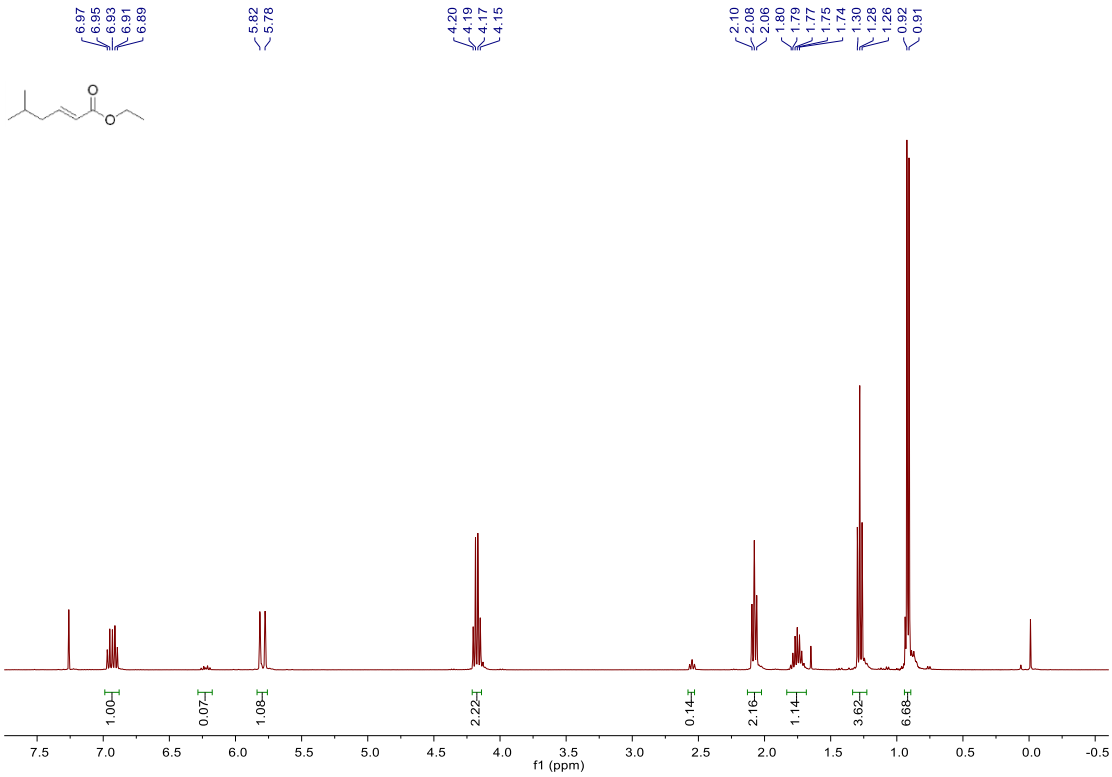


**Figure S15.** $^{1}$H NMR spectra of **3o** in $CDCl_3$.

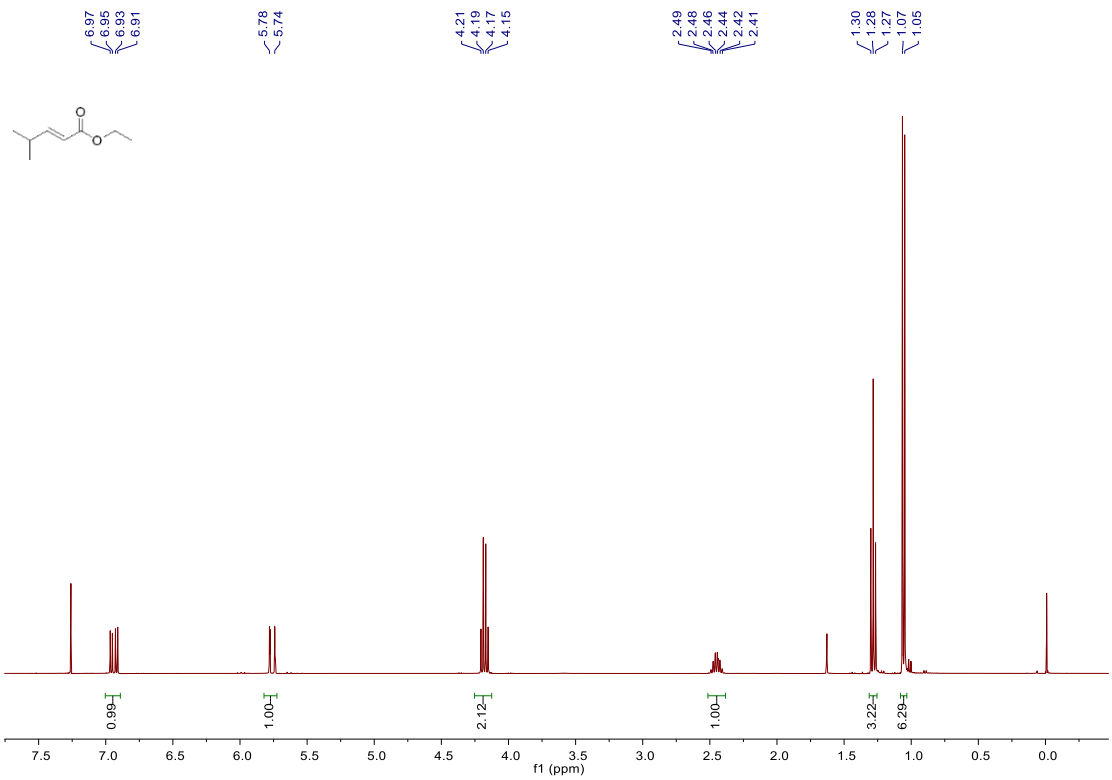


**Figure S16.** $^{1}$H NMR spectra of **3p** in $CDCl_3$.

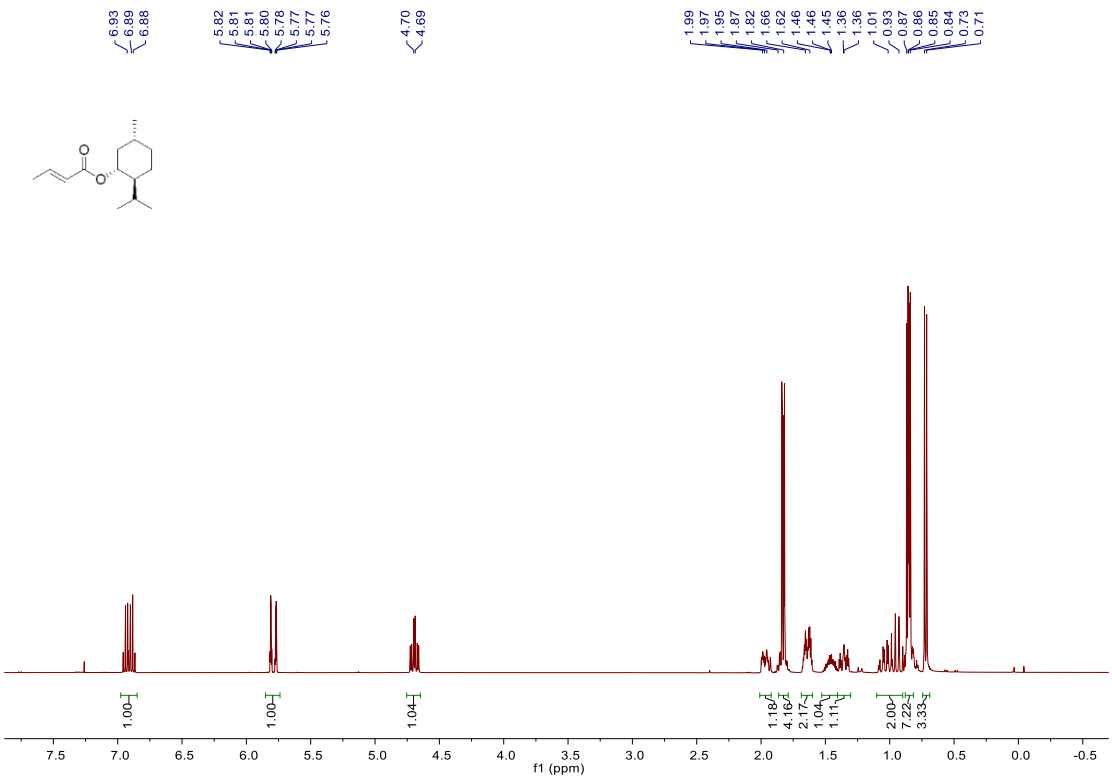


**Figure S17.** $^{1}$H NMR spectra of **3r** in $CDCl_3$.

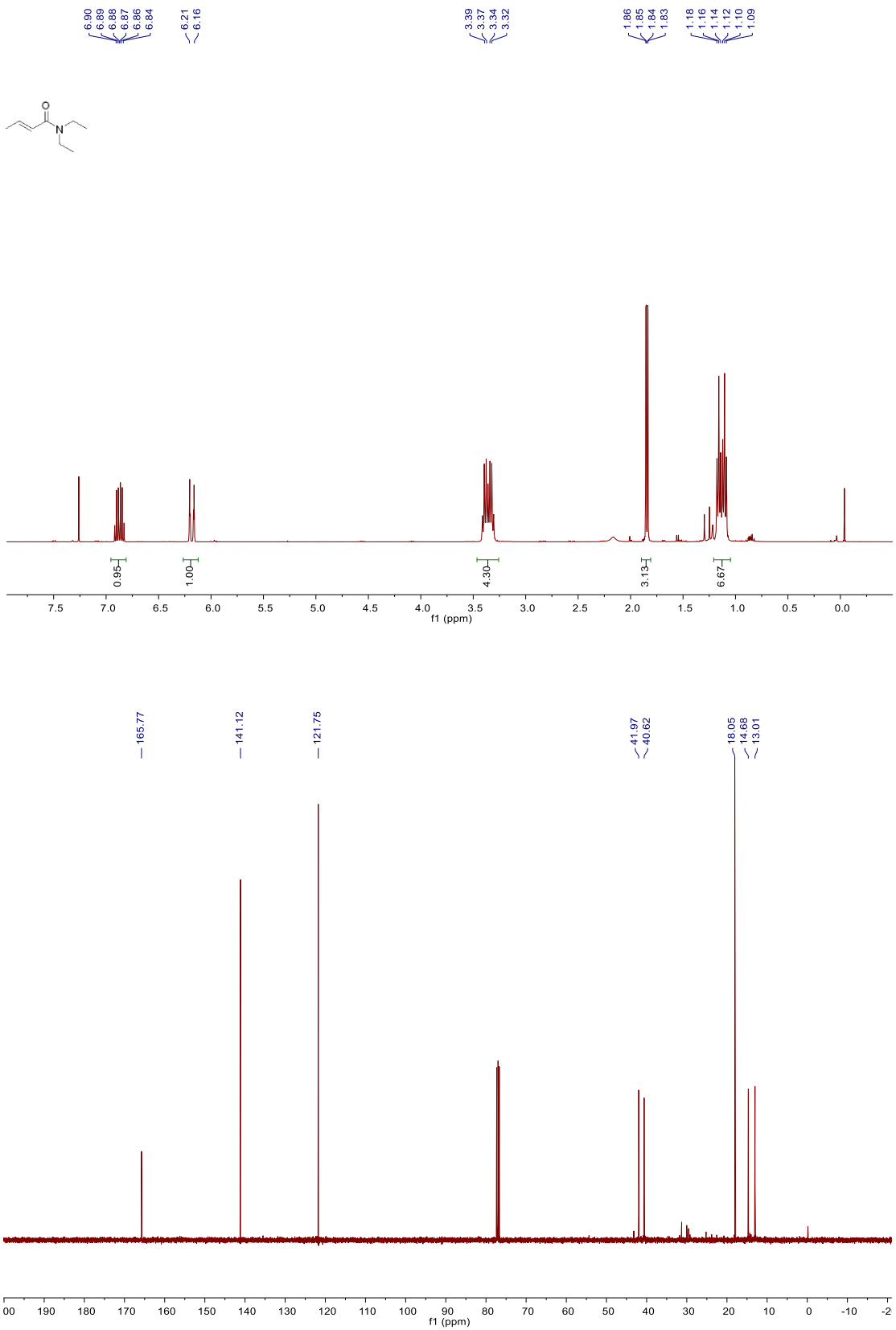


**Figure S18.** $^{1}H$ NMR and $^{13}C$ NMR spectra of **3s** in $CDCl_3$.

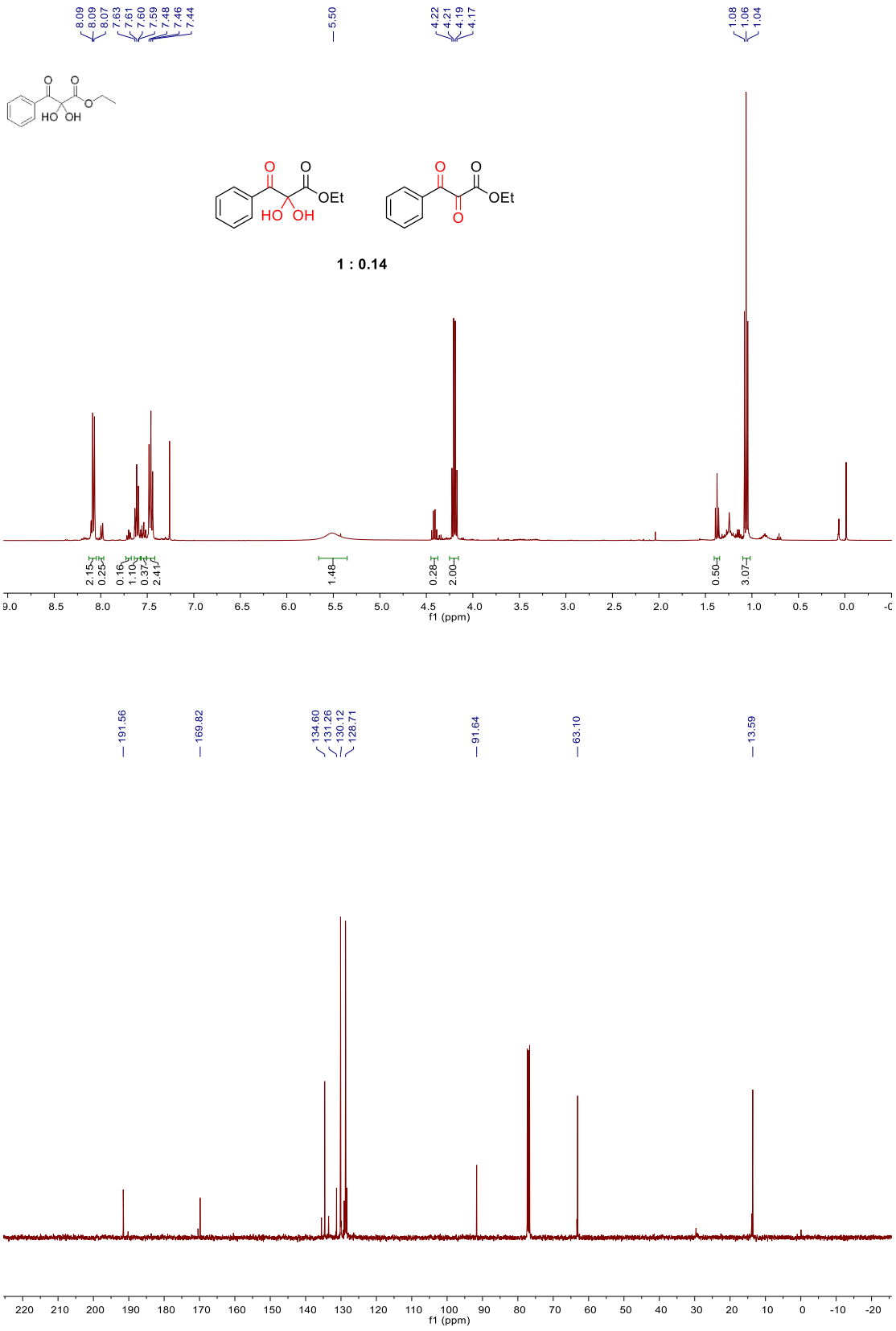


**Figure S19.** $^{1}$H NMR and $^{13}$C NMR spectra of **2a** in $CDCl_3$.

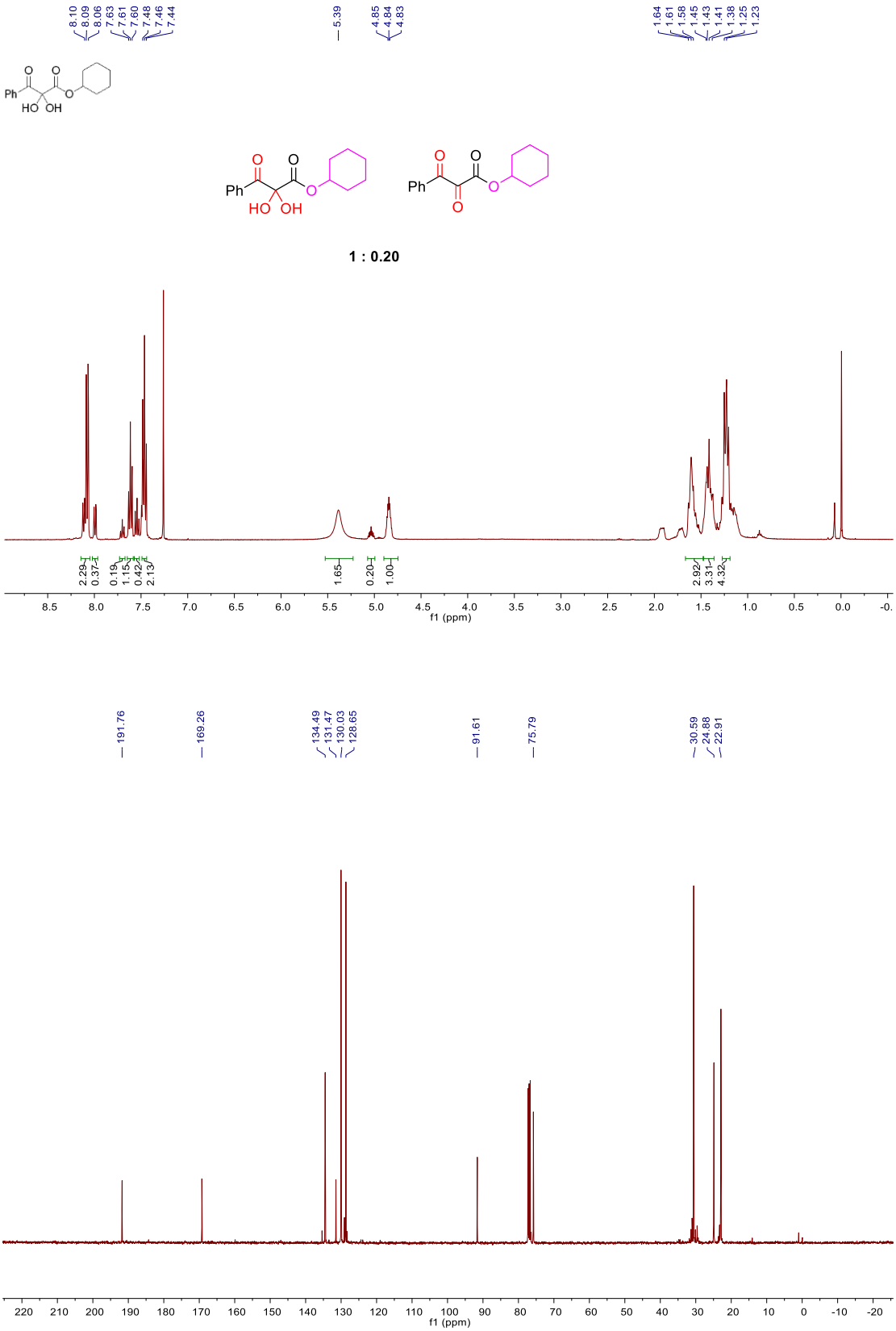


**Figure S20.** $^{1}$H NMR and $^{13}$C NMR spectra of **2e** in $CDCl_3$.

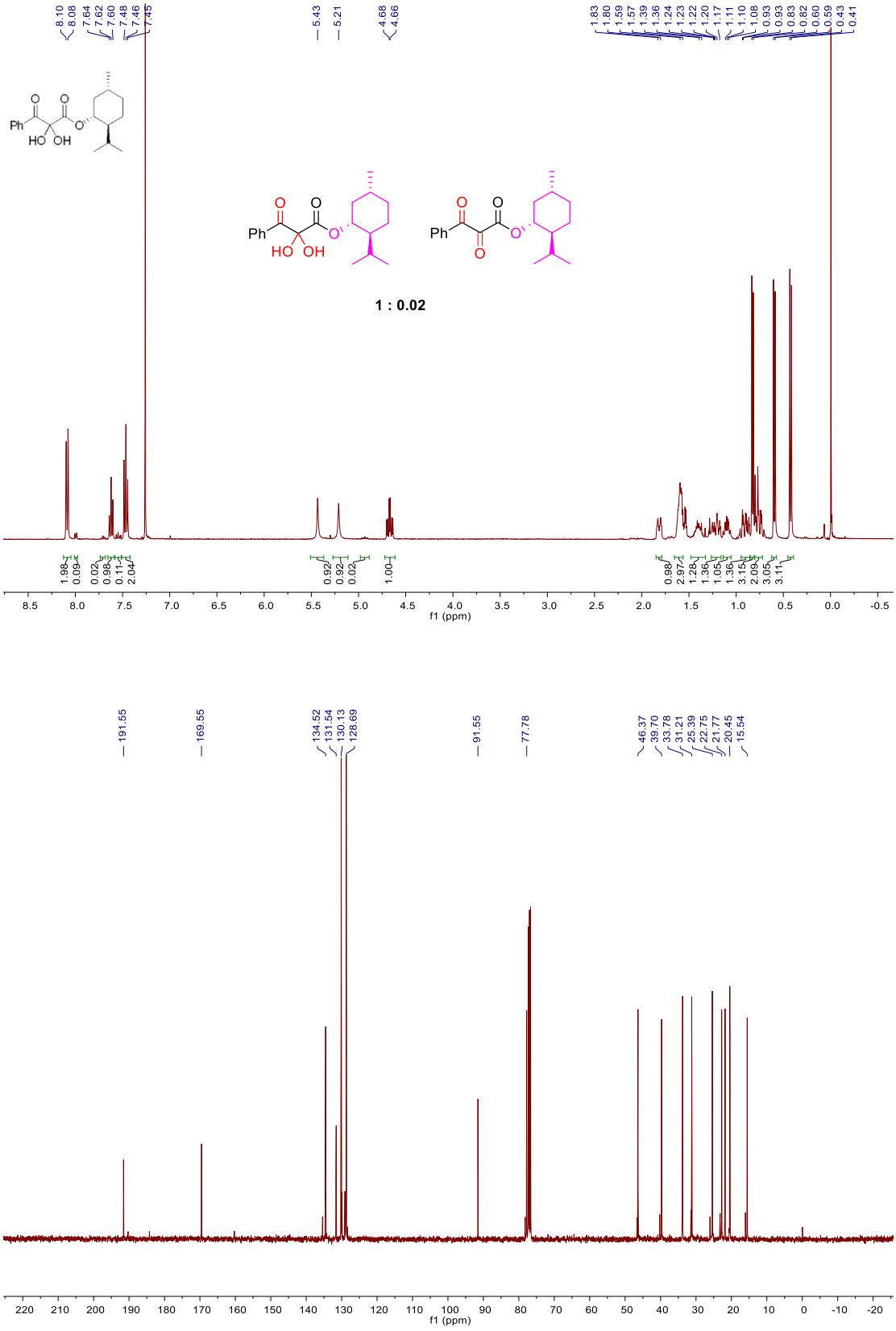


**Figure S21.** $^{1}$H NMR and $^{13}$C NMR spectra of **2f** in $CDCl_3$.

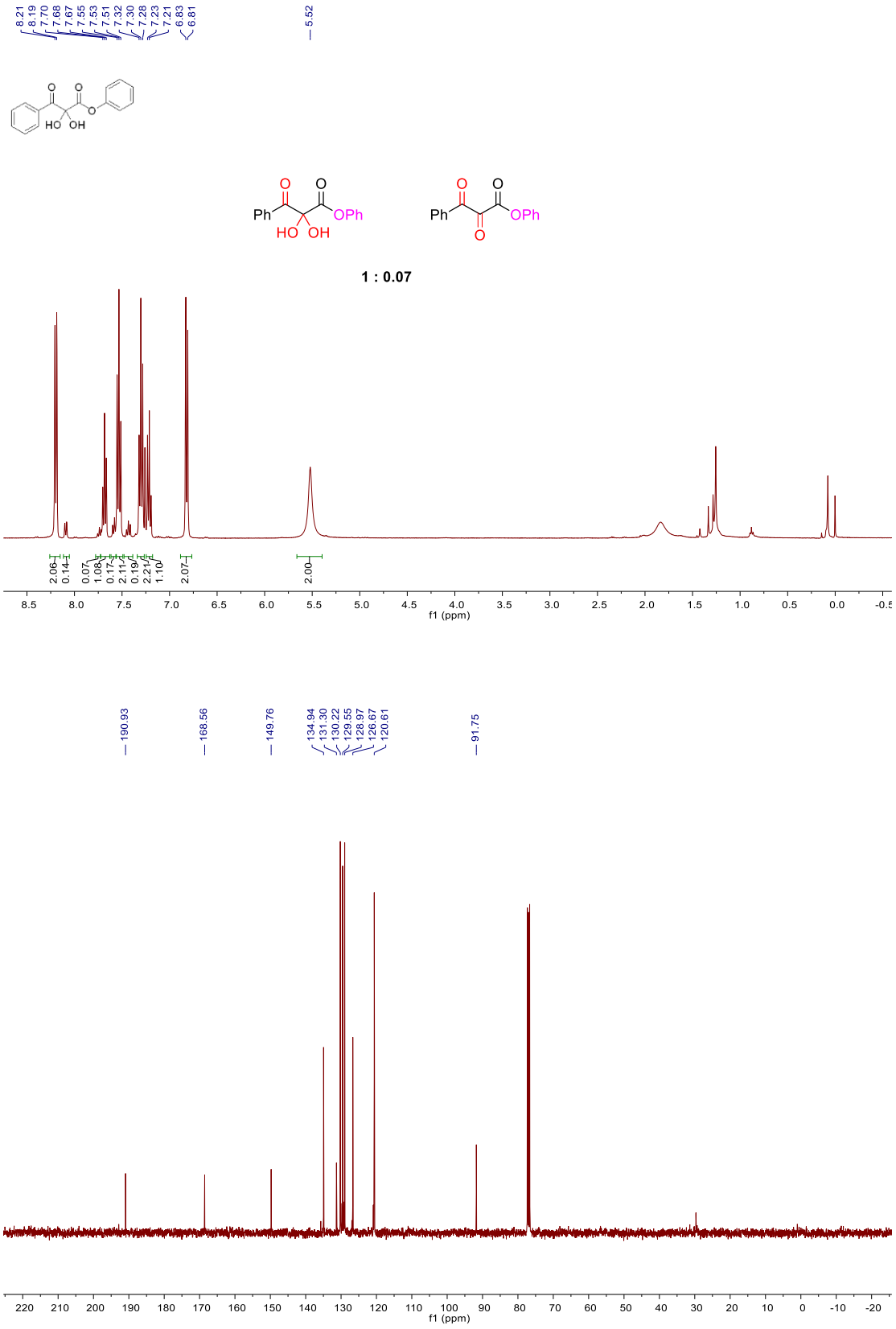


**Figure S22.** $^{1}$H NMR and $^{13}$C NMR spectra of **2g** in $CDCl_3$.

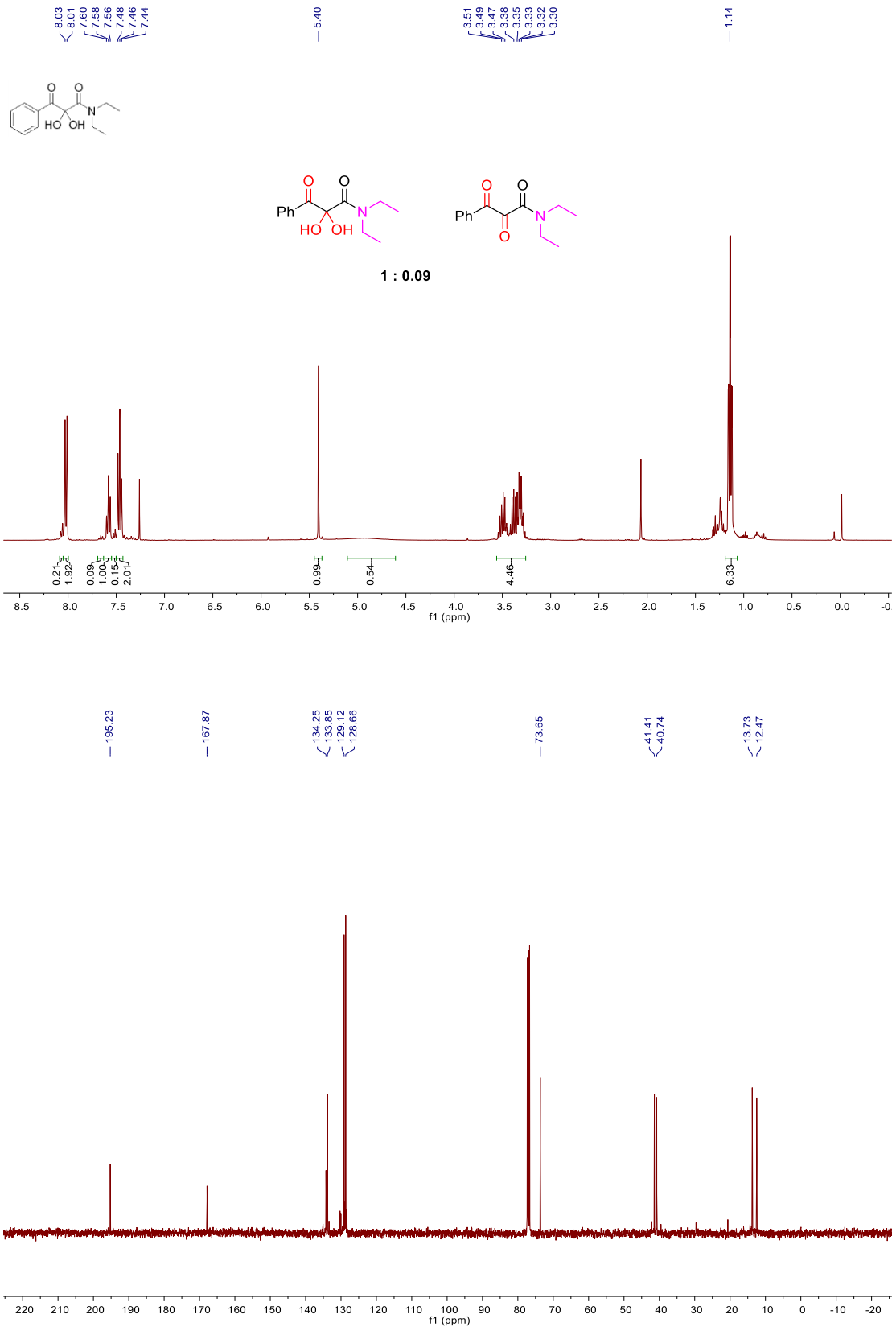


**Figure S23.** $^{1}$H NMR and $^{13}$C NMR spectra of **2h** in $CDCl_3$.

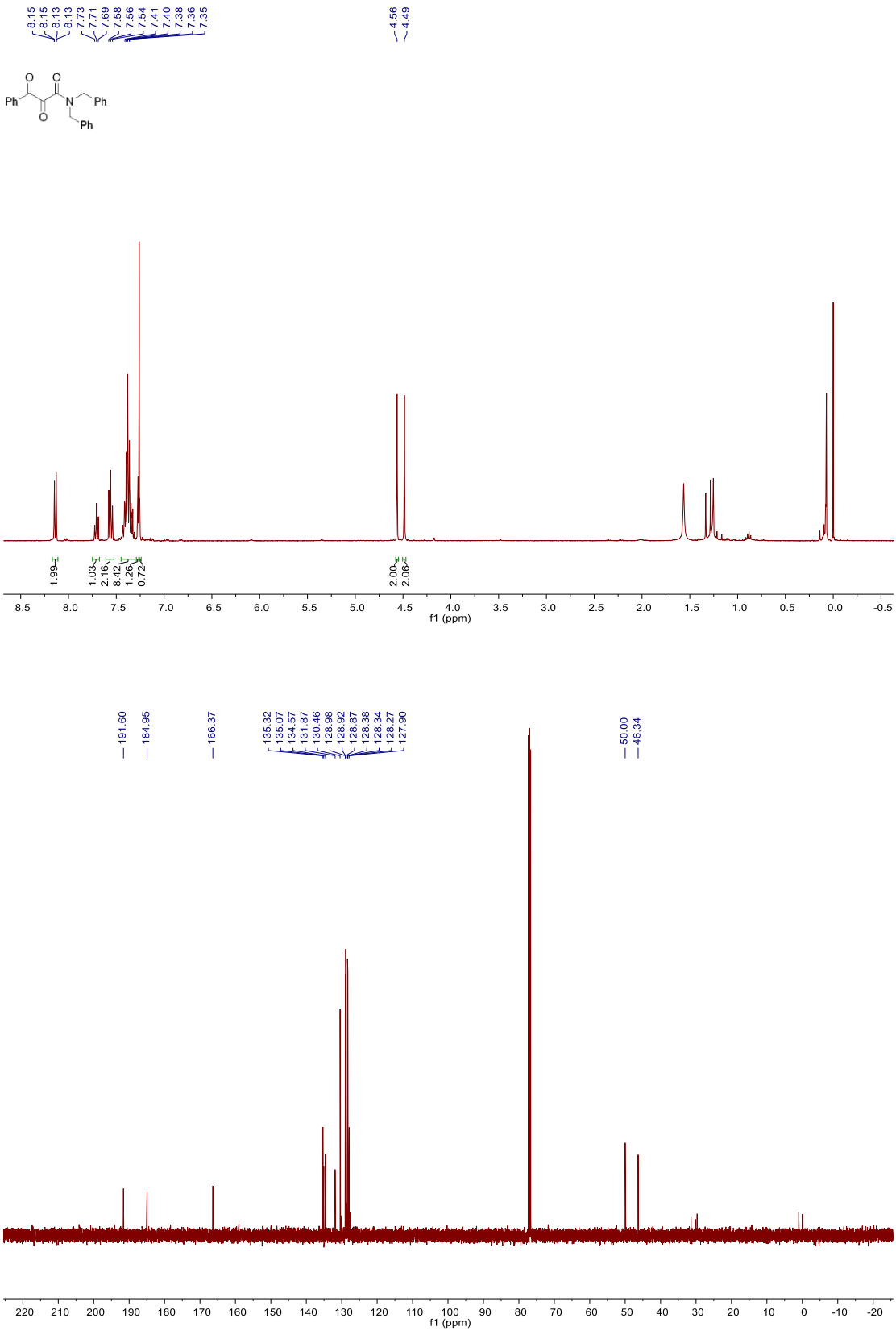


**Figure S24.** $^{1}$H NMR and $^{13}$C NMR spectra of **2i** in $CDCl_3$.

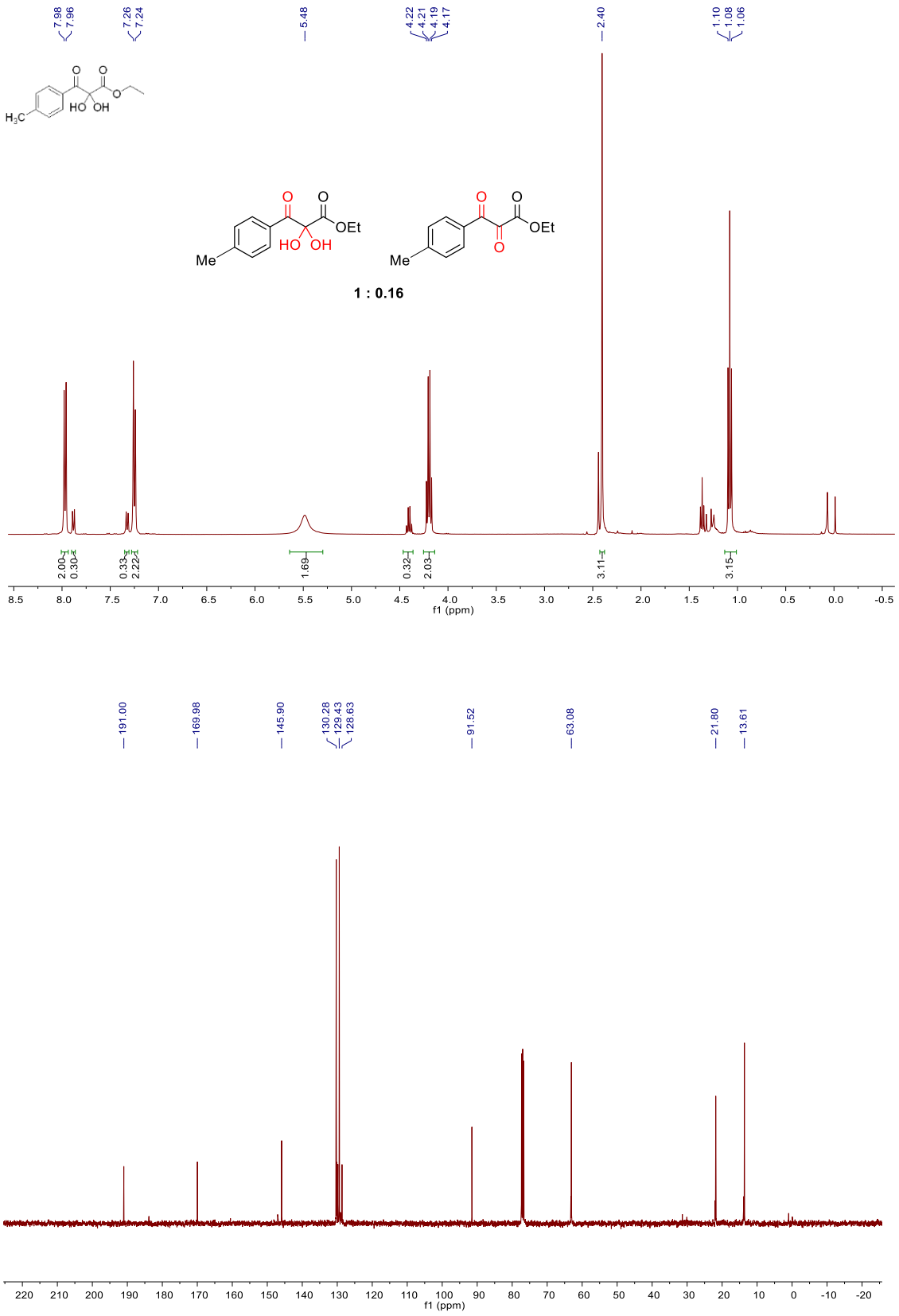


**Figure S25.** $^{1}$H NMR and $^{13}$C NMR spectra of **4a** in $CDCl_3$.

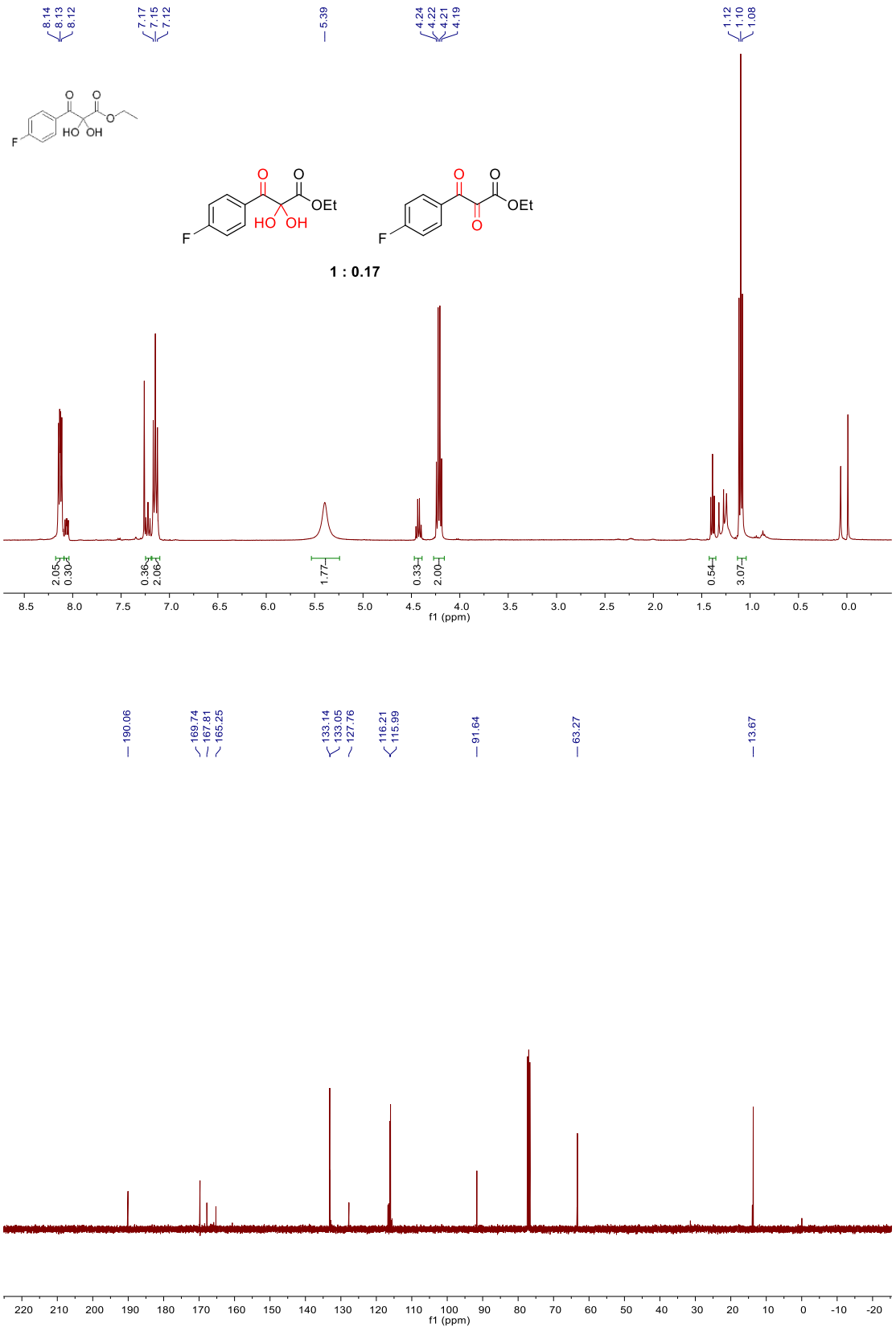


**Figure S26.** $^{1}H$ NMR and $^{13}C$ NMR spectra of **4c** in $CDCl_3$.

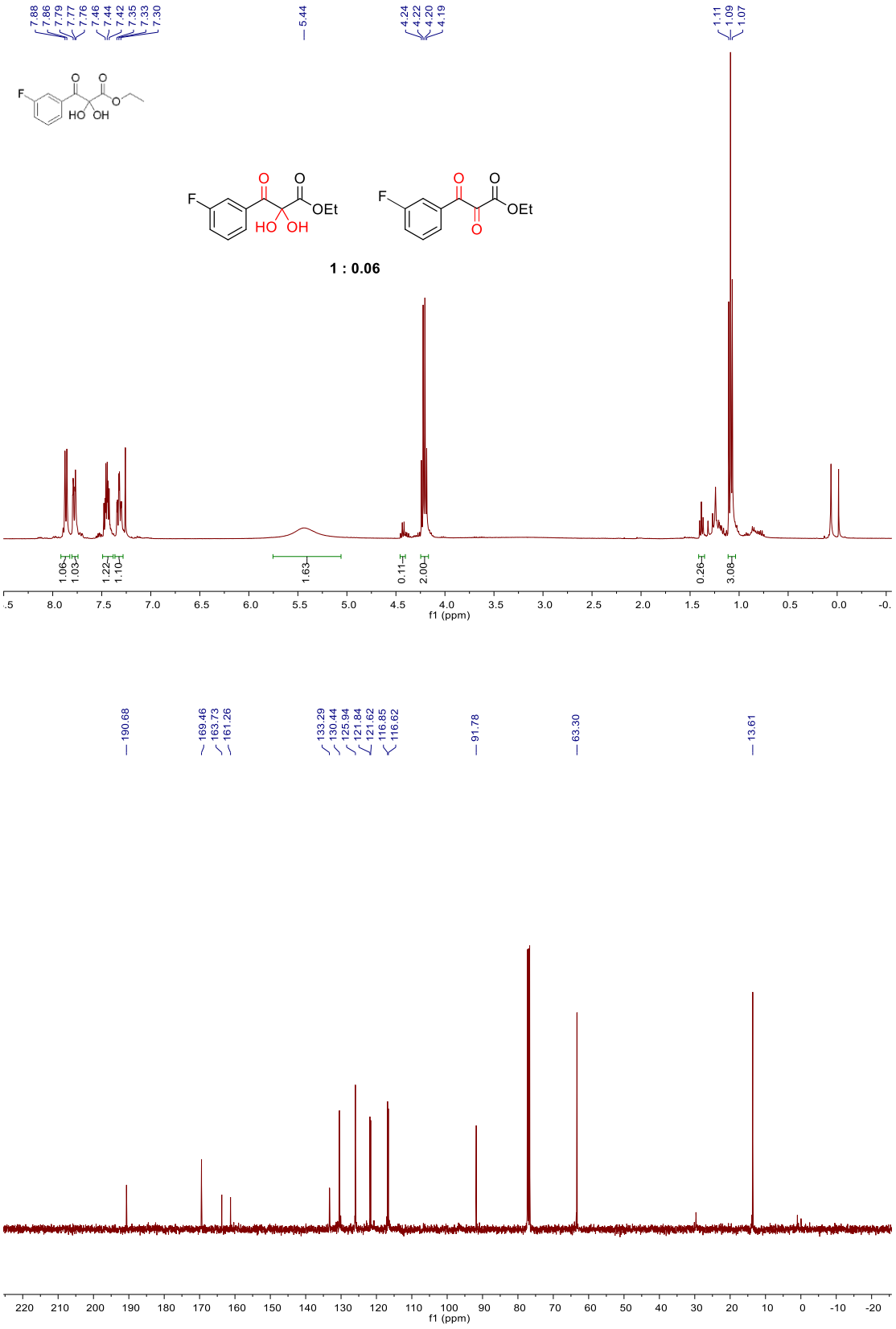


**Figure S27.** $^{1}$H NMR and $^{13}$C NMR spectra of **4h** in $CDCl_3$.

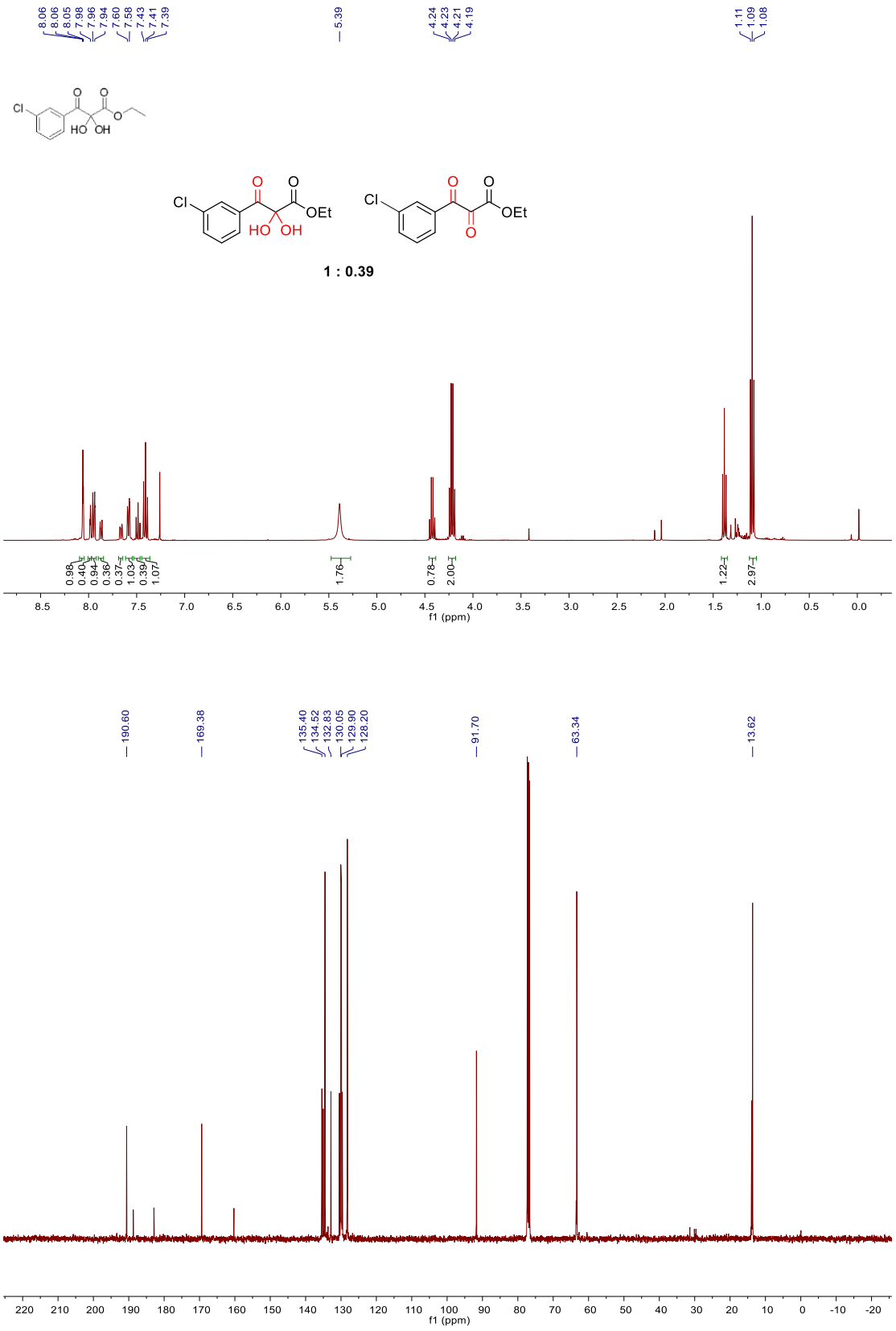


**Figure S28.** $^{1}$H NMR and $^{13}$C NMR spectra of **4i** in $CDCl_3$.

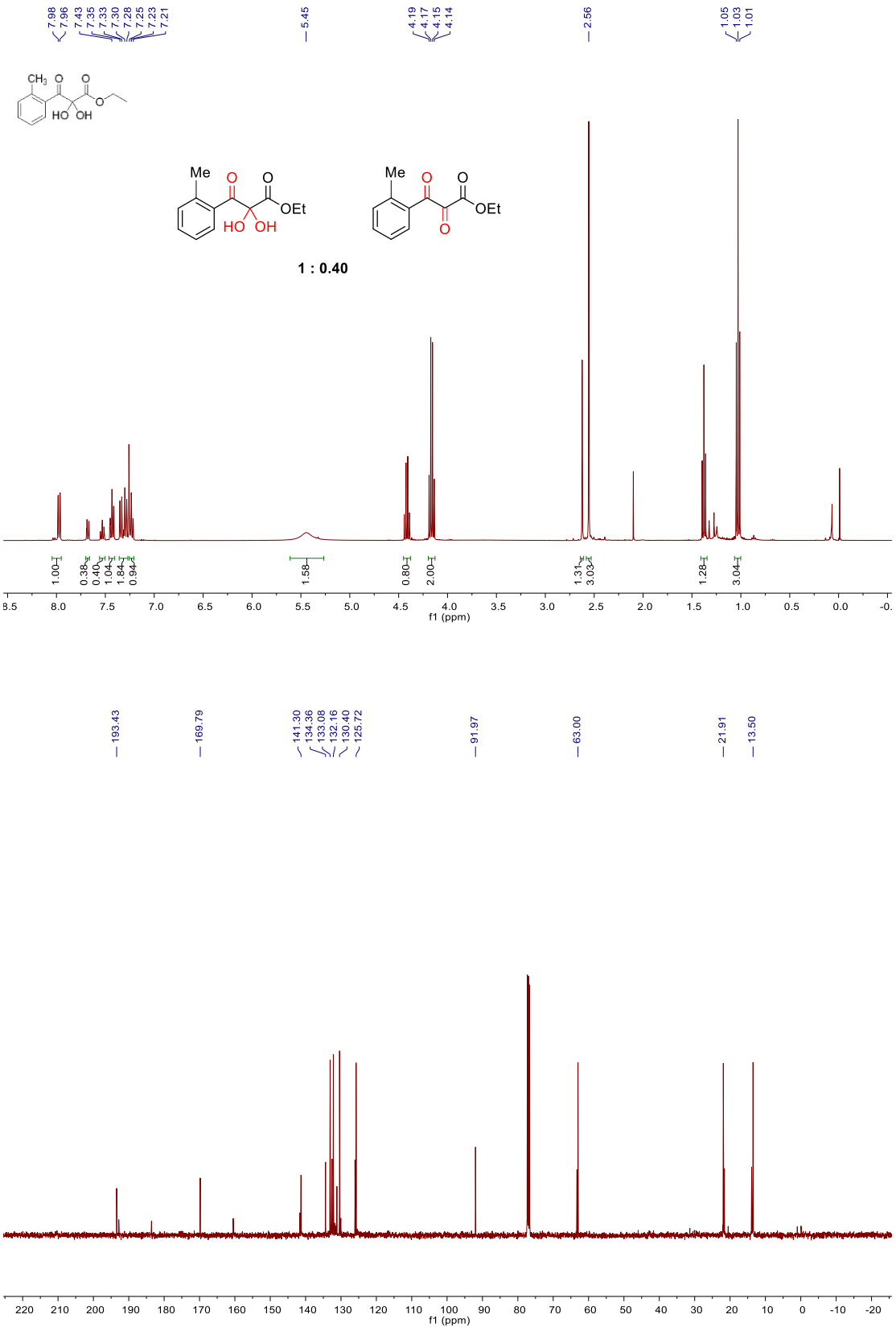


**Figure S29.** $^{1}$H NMR and $^{13}$C NMR spectra of **4k** in $CDCl_3$.

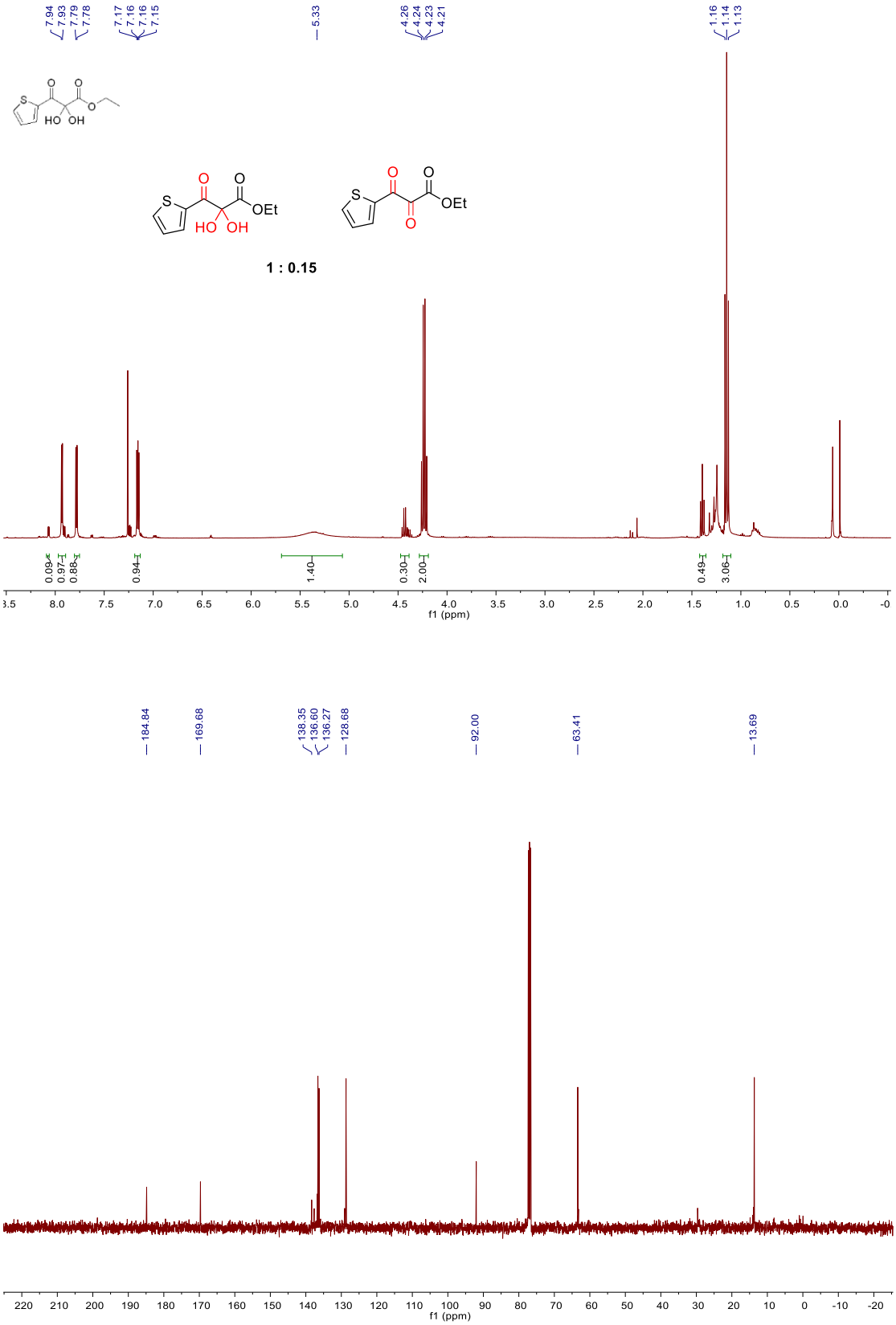


**Figure S30.** $^{1}$H NMR and $^{13}$C NMR spectra of **4m** in $CDCl_3$.

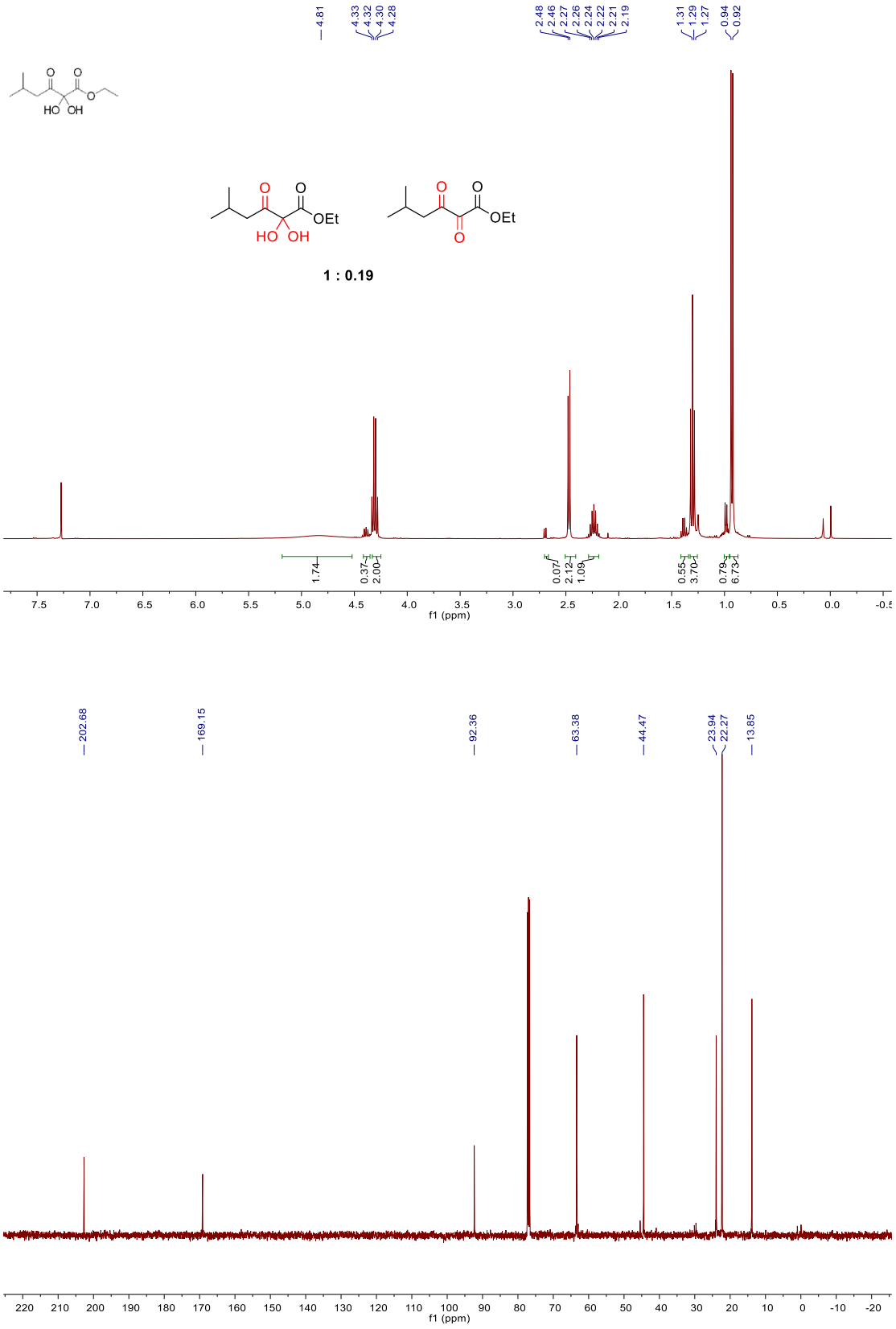


**Figure S31.** $^{1}H$ NMR and $^{13}C$ NMR spectra of **4o** in $CDCl_3$.

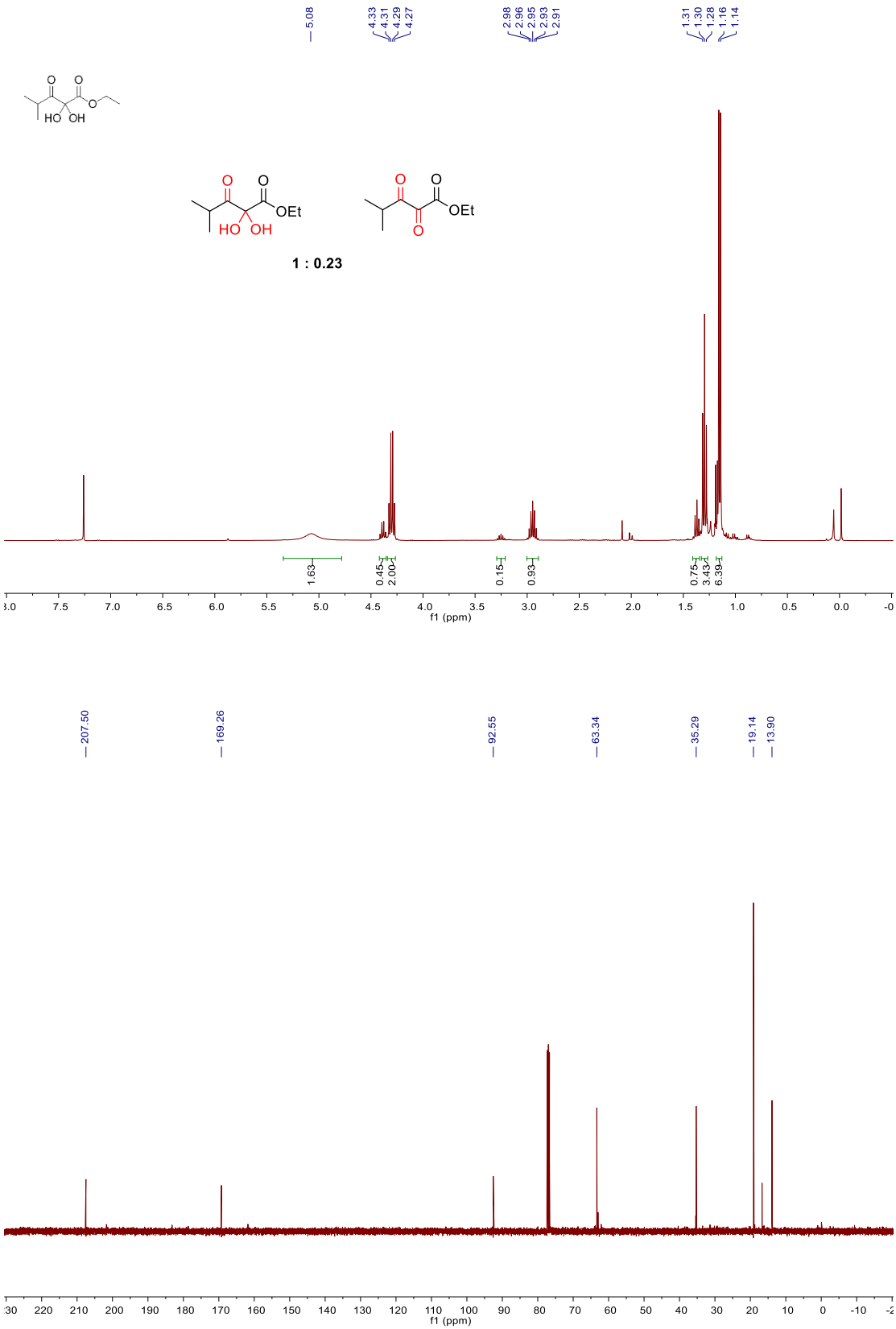


**Figure S32.** $^{1}H$ NMR and $^{13}C$ NMR spectra of **4p** in $CDCl_3$.

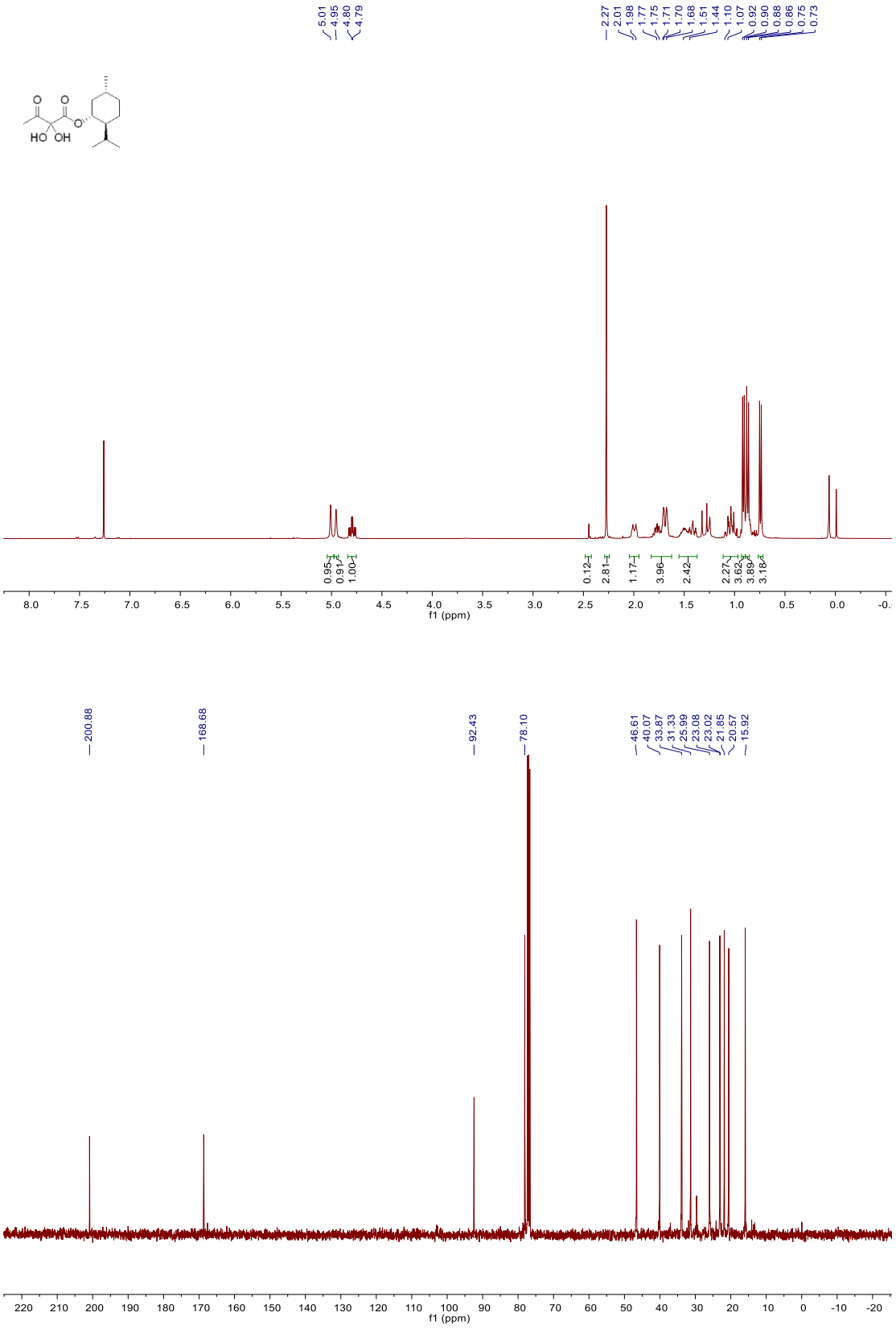


**Figure S33.** $^{1}H$ NMR and $^{13}C$ NMR spectra of **4r** in $CDCl_3$.

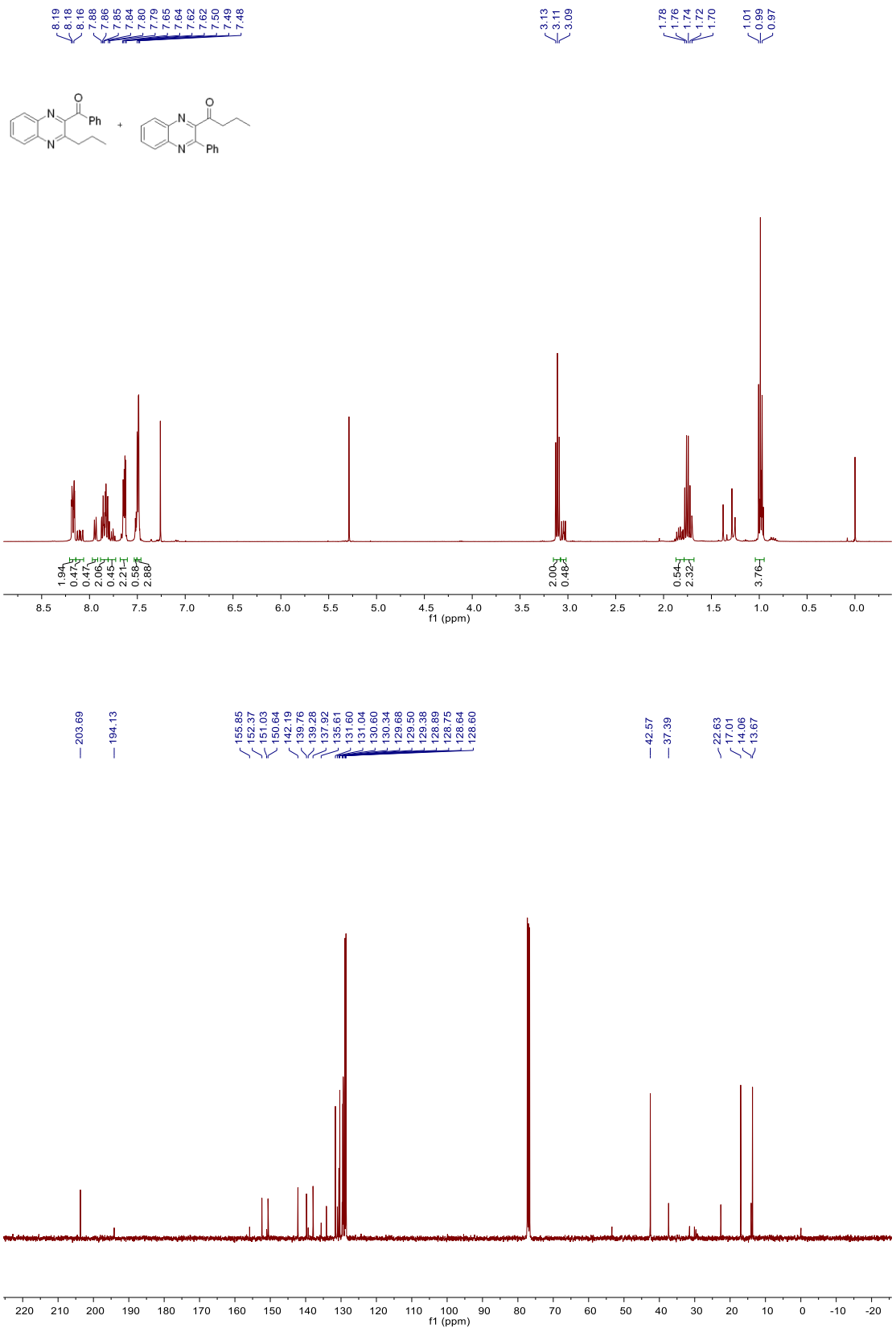


**Figure S34.** $^{1}H$ NMR and $^{13}C$ NMR spectra of **7 + 7'** in $CDCl_3$.

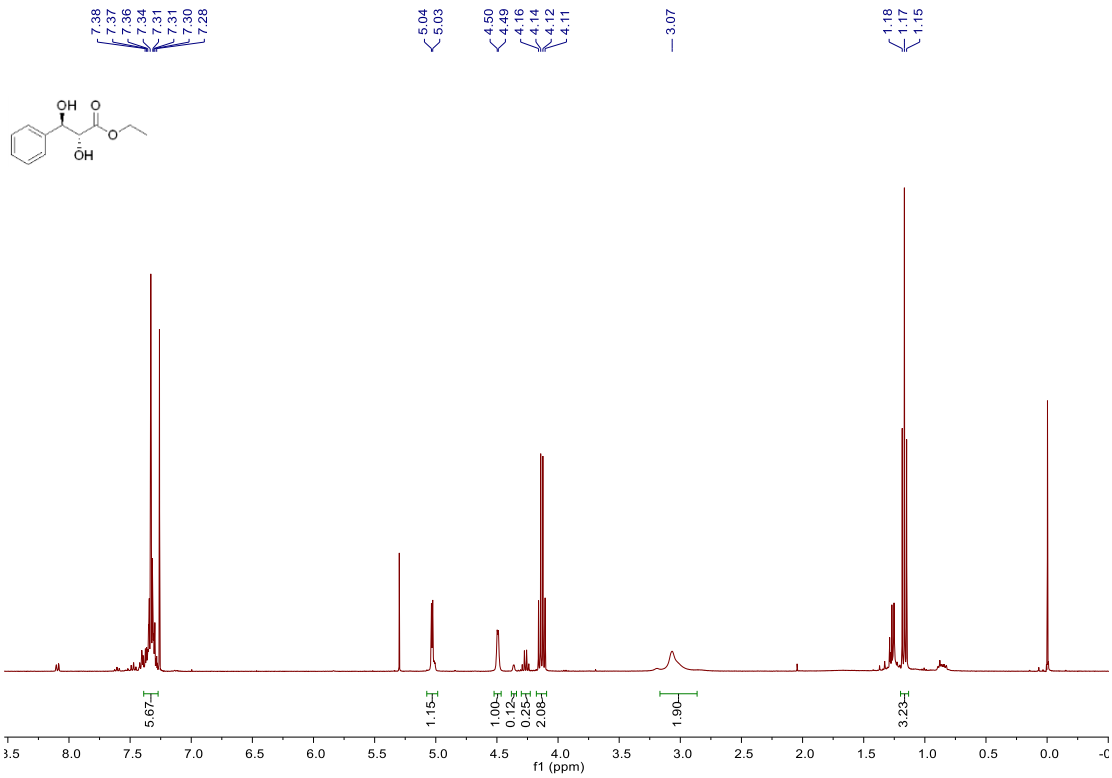


**Figure S35.** $^{1}$H NMR spectra of mixture of *trans*- and *cis*-**8** in $CDCl_3$.

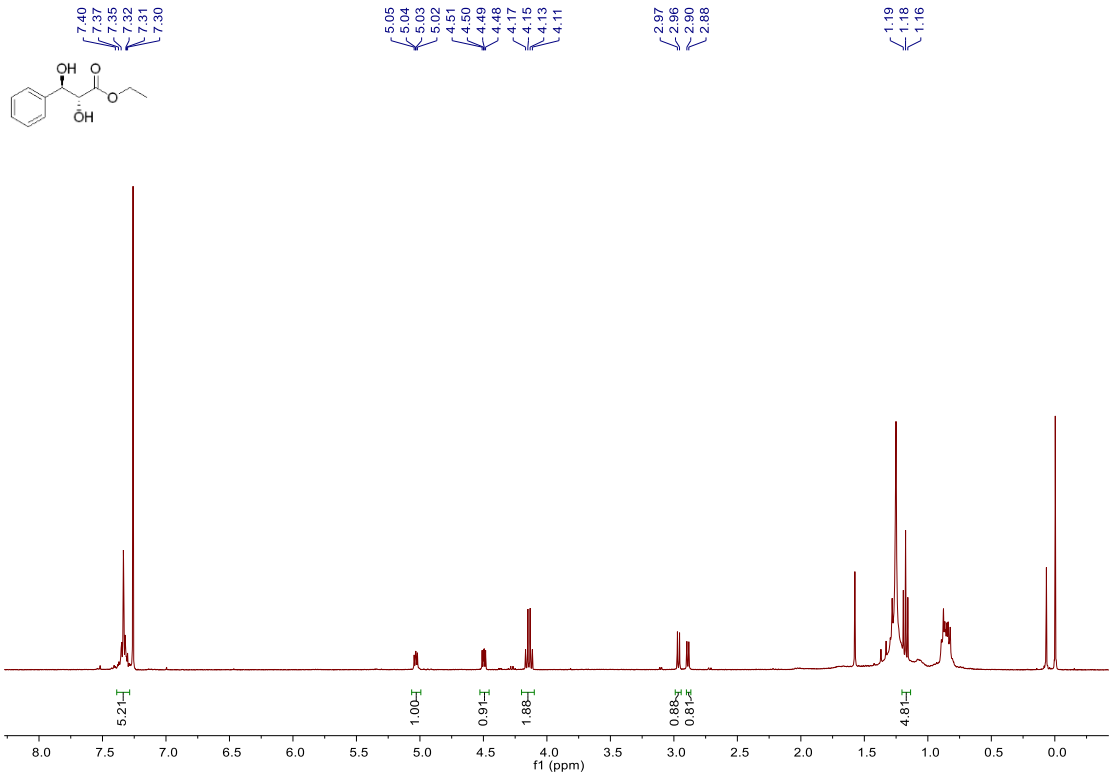


**Figure S36.** $^{1}$H NMR spectra of *trans*-**8** in $CDCl_3$.

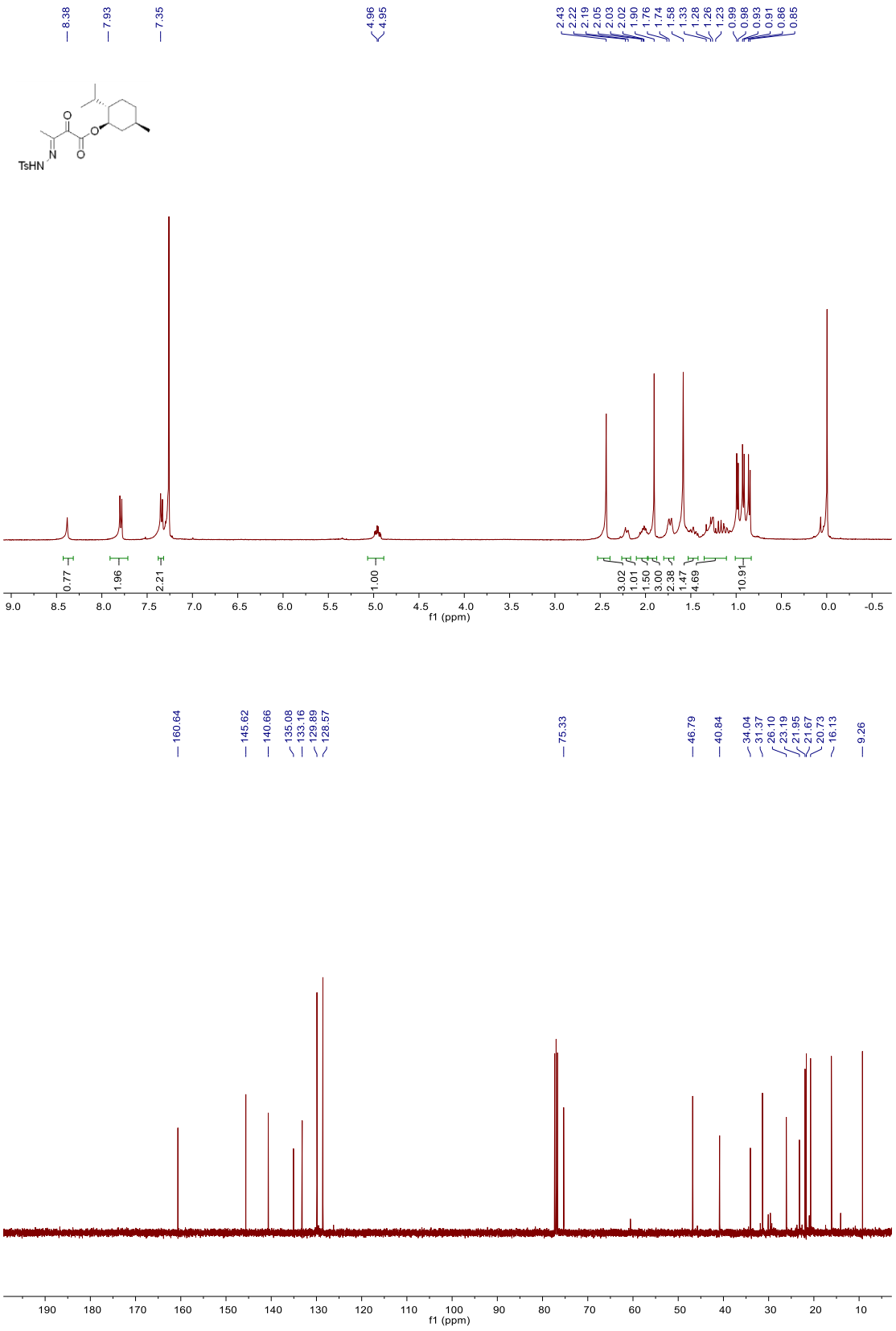


**Figure S37.** $^{1}$H NMR and $^{13}$C NMR spectra of **9** in $CDCl_3$.