Electronic Supplementary Information

Asymmetric Permanganate Dihydroxylation of Enoates: Substrate Scope, Mechanistic Insights and Application in Bicalutamide Synthesis

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1. Materials and Methods

General

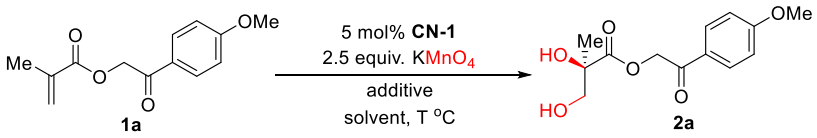
^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance III 400 (400MHz) (100 MHz) or Jeol (400 MHz) (100 MHz) spectrometer. Chemical shifts are recorded as δ in units of parts per million (ppm). The residual solvent peak was used as an internal reference. High resolution mass spectra (HRMS) 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). Enantiomeric excess values were determined by chiral HPLC analysis on Thermo Fischer U3000 HPLC workstations. Optical rotations were measured with a Rudolph-Autopol III Polarimeter at the indicated temperature (20 °C) with a sodium lamp (D line, 589 nm) and reported as follows: $[\alpha]_D^{25}$ (c = g/100 mL, solvent). IR spectra were obtained with KBr plates by using an IS10 FT-IR Spectrometer (ThermoFisher Corporation) and reported in wave numbers (cm^{-1}). Flash chromatography was performed with Qingdao Haiyang flash silica gel (200–300 mesh). Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Visualization was performed using a UV lamp, potassium permanganate stain or phosphomolybdic acid stain.

Materials

THF were distilled over sodium/benzophenone under N_2 atmosphere. Toluene, acetonitrile and dichloromethane were distilled over CaH_2 under N_2 atmosphere. Cinchonine and benzyl bromides were purchased from commercial suppliers. Wittig reagents were purchased from commercial suppliers or prepared from commercially available α-bromoesters. Triethyl phosphonoacetate, triethyl 2-phosphonopropionate and ketones were purchased from commercial suppliers. Potassium permanganate was ground into fine powder before use. All racemates were prepared with stoichiometric amount of tetrabutylammonium bromide. Solvents for asymmetric permanganate dihydroxylation reaction were commercial grade and used as supplied without further purification.

2. Investigation of Asymmetric Dihydroxylation Conditions

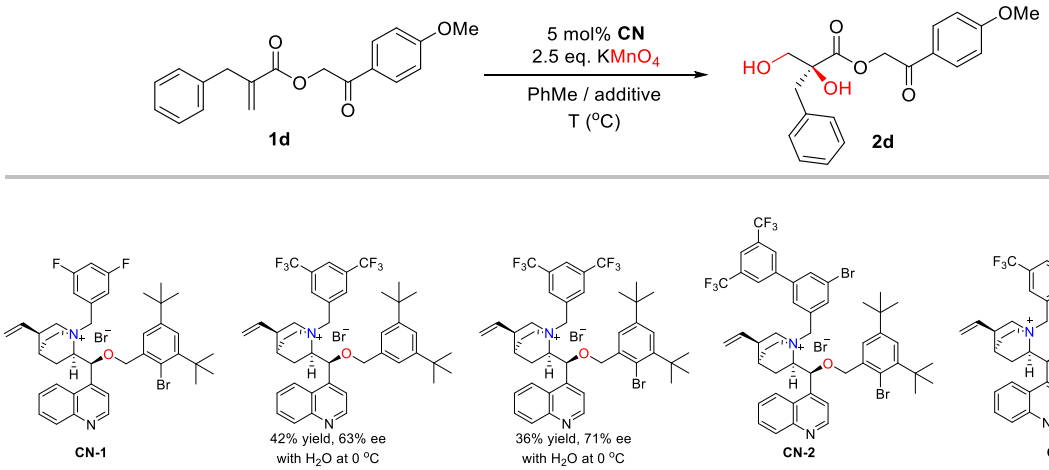
Table S1. Optimization of Conditions for Asymmetric Dihydroxylation of **1a**[a]



entry	T (°C)	solvent	additive	yield of **2a** (*ee*) (%)
1	0	PhMe	H_2O	33 (74)
2[b]	0	PhMe	AcOH / H_2O	22
3[b]	0	PhMe	TFE / H_2O	30
4[b]	0	PhMe	HFIP / H_2O	25
5	−20	PhMe	H_2O	58 (86)
6	−40	PhMe	H_2O	N.D.
7	−20	2-Pentanone	H_2O	35
8	−20	3-Pentanone	H_2O	40
9	−20	2-Methyl-2-butanol	H_2O	N.D.
10	−20	PhMe	1 M aq. $NaHCO_3$	45
11	−20	PhMe	1 M aq. Na_2CO_3	45
12	−20	PhMe	1 M aq. K_2CO_3	N.D.
13	−20	PhMe	1 M aq. Cs_2CO_3	N.D.
14	−20	PhMe	40 wt % aq. KF	43
15[c]	−20	PhMe	DIPEA / H_2O	46
16[c]	−20	PhMe	Et_3N / H_2O	50
17[d]	−20	PhMe	Et_3N / H_2O	42
18[e]	−20	PhMe	Et_3N / H_2O	38

[a]The reaction was conducted on a 0.05 mmol scale in 0.5 mL solvent with 0.05 mL aqueous additive, with isolated yield reported and *ee* determined by chiral HPLC analysis. [b]1 equiv. was used. [c]5 equiv. was used. [d]2.5 equiv. was used. [e]1.25 equiv. was used. N.D. Not detected.

Table S2. Screening of Conditions for Asymmetric Dihydroxylation of **1d**[a]



entry	catalyst	T (°C)	additive	yield (%)	*ee* (%)
1	**CN-1**	0	H_2O	45	72
2	**CN-2**	0	H_2O	38	77
3	**CN-3**	0	H_2O	45	42
4	**CN-1**	0	sat. aq. KNO_3	38	76
5	**CN-1**	0	sat. aq. NaCl	36	75
6	**CN-1**	0	sat. aq. KF	36	78
7	**CN-1**	0	sat. aq. KBr	35	75
8	**CN-1**	0	sat. aq. KPF_6	35	76
9	**CN-1**	0	sat. aq. $NaHSO_3$	33	75
10	**CN-1**	0	sat. aq. $KHSO_4$	40	64
11	**CN-1**	0	40 wt % aq. KF	41	74
12	**CN-2**	−20	H_2O	46	81
13	**CN-2**	−20	sat. aq. KNO_3	48	77
14	**CN-2**	−20	40 wt % aq. KF	45	76
15	**CN-1**	−20	H_2O	48	83
16	**CN-1**	−20	sat. aq. KNO_3	45	81
17	**CN-1**	−20	sat. aq. KPF_6	46	81

[a]The reaction was conducted on a 0.05 mmol scale in 0.5 mL solvent with 0.05 mL aqueous additive, with isolated yield reported and *ee* determined by chiral HPLC analysis.

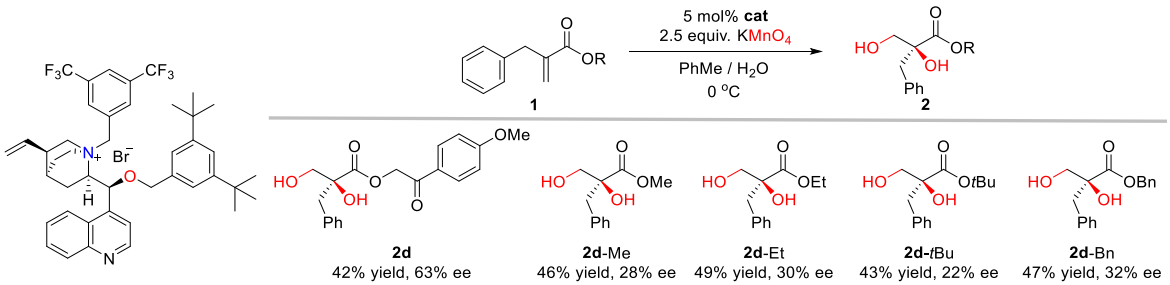


Figure S1. Evaluation of different esters of α-benzyl acrylic acid.

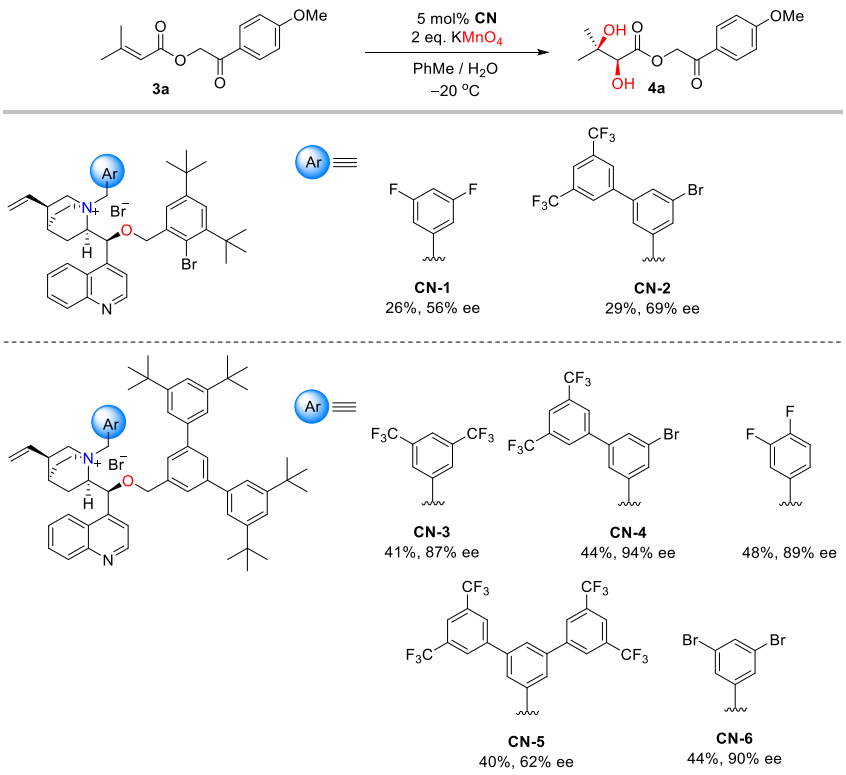
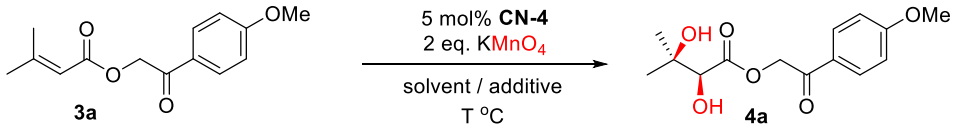


Figure S2. Evaluation of Chiral Cinchoninium Catalysts with **3a**.

Table S3. Screening of Conditions for Asymmetric Dihydroxylation of **3a** with **CN-4**[a]



entry	solvent	T (°C)	additive	yield (%)	*ee* (%)
1	$PhCH_3$	−20	H_2O	44	94
2	$PhCH_3$	−20	1 M aq. Na_2CO_3	20	N.D.
3	$PhCH_3$	−20	1 M aq. $NaHCO_3$	27	N.D.
4	$PhCH_3$	−20	AcOH (1 equiv.) / H_2O	26	N.D.
5	$PhCH_3$	−10	H_2O	33	N.D.
6	$PhCH_3$	−30	H_2O	27	N.D.
7	TBME	−20	H_2O	46	93
8	CH_2Cl_2	−20	H_2O	15	79

[a]The reaction was conducted on 0.10 mmol scale in 1.0 mL solvent with 0.10 mL aqueous additive, with isolated yield reported and *ee* determined by chiral HPLC analysis.

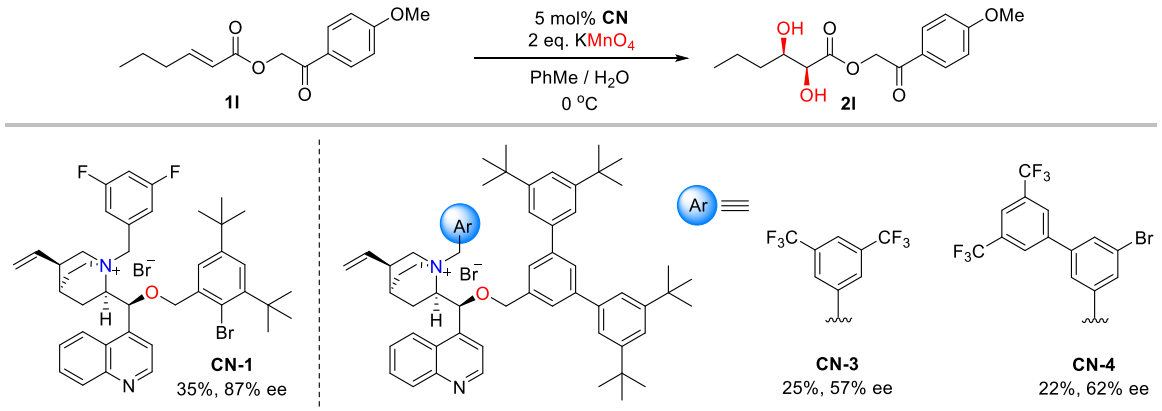
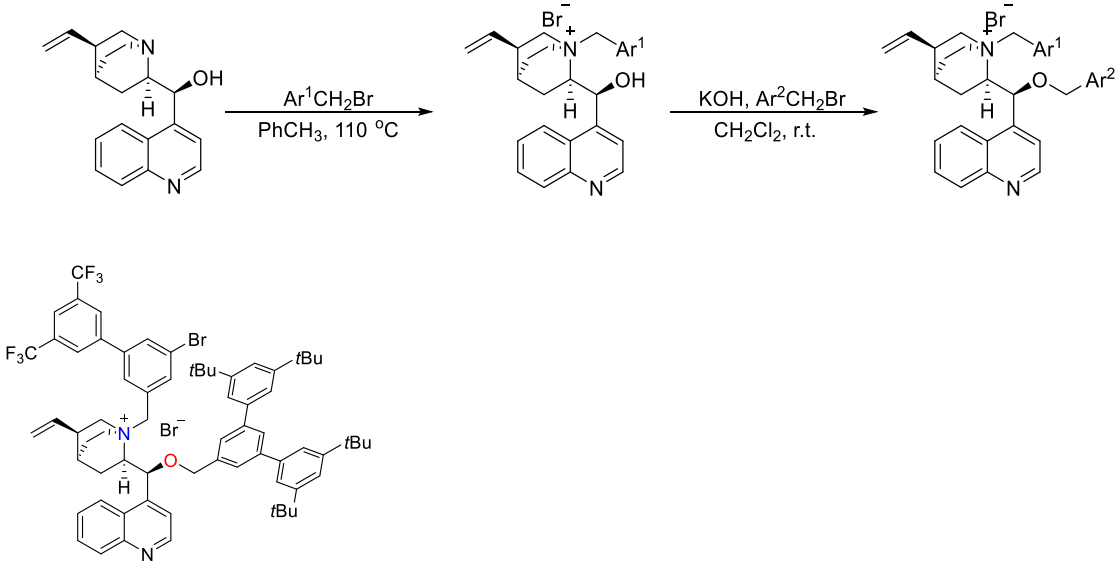


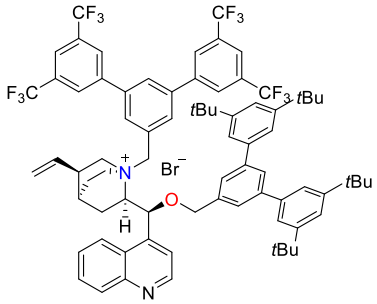
Figure S3. Evaluation of Chiral Cinchoninium Catalysts with **1l**.

3. Preparation and Characterization of Cinchoninium Catalysts

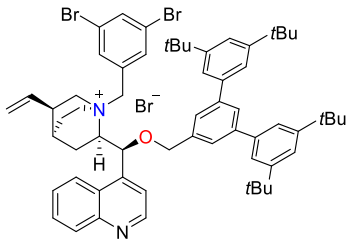
Chiral cinchonidinium catalysts **CN** were prepared from corresponding aryl bromide and commercially available cinchonine with the following procedure according to literature.[1]



CN-4: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 4.4 Hz, 1H), 8.95 – 8.80 (m, 2H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.08 (s, 2H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 9.3 Hz, 2H), 7.83 – 7.71 (m, 3H), 7.62 – 7.55 (m, 2H), 7.48 (s, 2H), 7.40 – 7.29 (m, 5H), 6.92 (s, 1H), 6.44 – 6.17 (m, 2H), 6.06 – 5.88 (m, 1H), 5.56 (s, 1H), 5.37 – 5.20 (m, 1H), 5.11 (d, *J* = 12.3 Hz, 1H), 4.70 (s, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.41 – 4.24 (m, 1H), 4.16 – 3.96 (m, 1H), 3.36 (t, *J* = 11.4 Hz, 1H), 2.81 – 2.60 (m, 1H), 2.60 – 2.35 (m, 2H), 2.06 – 1.60 (m, 4H), 1.33 (s, 36H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.36, 151.31, 149.22, 148.24, 144.48, 141.09, 140.06, 139.73, 139.57, 139.44, 136.63, 135.43, 135.00, 132.78, 132.44, 132.12, 131.96, 131.77, 130.50, 129.94, 129.66, 129.47, 128.11, 127.39, 126.07, 125.73, 124.97, 124.70, 124.29, 122.91, 122.08, 121.93, 121.57, 121.50, 118.90, 118.50, 74.09, 72.24, 66.18, 59.96, 55.67, 54.39, 53.32, 37.71, 34.80, 31.33, 26.99, 24.21, 23.19, 21.62; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.52; **HRMS** (ESI) calcd for $C_{69}H_{76}Br_2F_6N_2O$ m/z $[M–Br]^+$: 1141.5045; found: 1141.5049.



CN-5： **^{1}H NMR** (400 MHz, $CDCl_3$ δ 9.08 (d, *J* = 8.5 Hz, 1H), 9.01 (d, *J* = 4.4 Hz, 1H), 8.41 (br, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.09 (s, 5H), 7.89 (s, 2H), 7.86 – 7.77 (m, 4H), 7.73 (s, 1H), 7.56 (s, 2H), 7.46 (t, *J* = 1.8 Hz, 2H), 7.36 (d, *J* = 1.8 Hz, 4H), 6.75 (d, *J* = 11.3 Hz, 1H), 6.48 (s, 1H), 5.98 – 5.79 (m, 1H), 5.71 (br, 1H), 5.11 (d, *J* = 17.1 Hz, 1H), 5.02 – 4.78 (m, 3H), 4.72 (d, *J* = 11.8 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.39 (t, *J* = 10.3 Hz, 1H), 3.55 (t, *J* = 10.7 Hz, 1H), 2.82 – 2.62 (m, 1H), 2.59 – 2.40 (m, 2H), 2.07 – 1.60 (m, 4H), 1.31 (s, 36H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.31, 149.19, 148.42, 144.23, 141.17, 140.56, 139.76, 136.74, 134.82, 132.87, 132.58, 132.24, 131.91, 130.62, 129.75, 129.49, 128.56, 127.57, 127.10, 125.24, 125.03, 124.33, 122.01, 121.61, 121.51, 118.89, 118.47, 75.04, 72.03, 66.47, 60.75, 55.96, 55.03, 37.72, 34.80, 31.28, 27.10, 23.36, 22.04; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.46; **HRMS** (ESI) calcd for $C_{77}H_{79}BrF_{12}N_2O$ m/z $[M–Br]^+$: 1275.5995; found: 1275.5972.

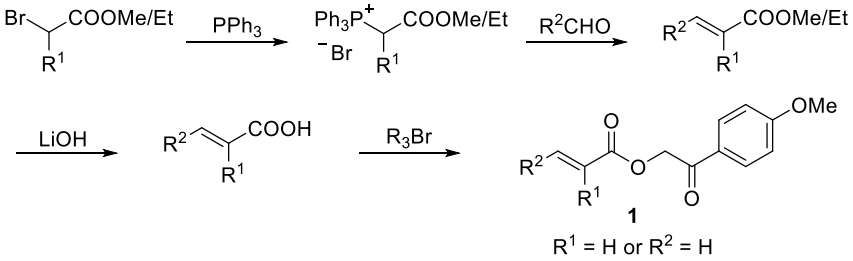


CN-6： **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 4.4 Hz, 1H), 8.84 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.94 (s, 1H), 7.83 (s, 1H), 7.79 – 7.70 (m, 2H), 7.63 (s, 1H), 7.58 – 7.49 (m, 4H), 7.46 (s, 2H), 7.40 – 7.28 (m, 4H), 6.28 (s, 1H), 6.15 (d, *J* = 11.6 Hz, 1H), 6.04 – 5.85 (m, 1H), 5.46 (s, 1H), 5.29 – 5.17 (m, 2H), 5.08 (d, *J* = 12.0 Hz, 1H), 4.69 (s, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.25 (t, *J* = 10.2 Hz, 1H), 4.00 (d, *J* = 11.8 Hz, 1H), 3.21 (t, *J* = 11.5 Hz, 1H), 2.82 – 2.63 (m, 1H), 2.60 – 2.48 (m, 1H), 2.42 (t, *J* = 12.3 Hz, 1H), 2.03 – 1.50 (m, 4H), 1.32 (s, 36H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.19, 151.14, 149.12, 148.06, 144.30, 139.66, 139.43, 139.31, 136.46, 136.02, 134.93, 134.82, 130.37, 130.27, 129.43, 129.15, 128.03, 125.97, 125.72, 124.80, 123.15, 121.91, 121.38, 118.93, 118.26, 74.01, 72.18, 65.76, 59.44, 55.43, 54.12, 37.39, 34.69, 31.24, 26.79, 24.06, 23.02; **HRMS** (ESI) calcd for $C_{61}H_{73}Br_3N_2O$ m/z $[M–Br]^+$: 1007.4090; found: 1007.4094.

4. Preparation and Characterization of Substrates

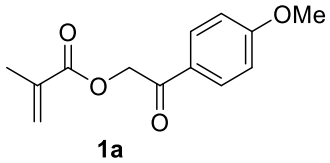
Preparation of disubstituted enoates 1.

2-(4-Methoxyphenyl)-2-oxoethyl (*E*)-enoate substrates were prepared from corresponding methyl/ethyl enoate ester or commercially available enoic acids (**1a**, **1d**, **1i**, **1j**). Methyl/ethyl enoate esters were prepared using Wittig reaction. Wittig reagents are prepared from commercially available α-bromoesters or prepared according to literature. Hydrolysis of methyl/ethyl enoate ester to corresponding enoic acid was performed according to previously reported procedure. Esterification of (*E*)-enoic acids with 2-bromo-1-(4-methoxyphenyl)ethan-1-one provided the enoate substrates.[2]



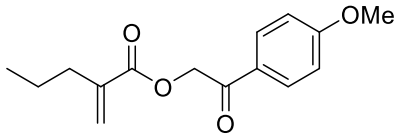
Preparation of methacrylate 1a from methacrylic acid:[3]

To a stirred solution of methacrylic acid (2.2 mmol) in 10 mL DMF was added triethylamine (2.4 mmol) and 2-bromo-1-(4-methoxyphenyl)ethan-1-one (2.0 mmol) at room temperature. The reaction mixture was stirred at 20 °C overnight, and then water and ethyl acetate were added. The aqueous phase was extracted three times with ethyl acetate, and the organic phases were collected and washed ten times with water. The organic phases were combined and washed with brine, dried over anhydrous Na_2SO_4. After removing solvent, the residue was purified by column chromatography on silica gel affording **1a** as a white solid.



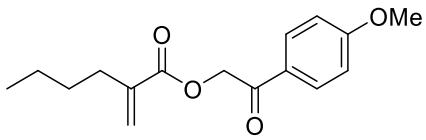
1a

2-(4-methoxyphenyl)-2-oxoethyl methacrylate (1a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.27 (s, 1H), 5.67 (s, 1H), 5.37 (s, 2H), 3.88 (s, 3H), 2.02 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.51, 166.66, 163.85, 135.43, 129.93, 127.04, 126.55, 113.88, 65.83, 55.38, 18.21; **HRMS** (ESI) calcd for $C_{13}H_{15}O_4$ *m/z* $[M+H]^+$: 235.0970; found: 235.0962.

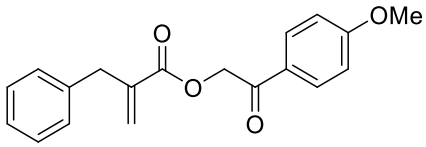


2-(4-methoxyphenyl)-2-oxoethyl 2-methylenepentanoate (1b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.30 (s, 1H), 5.63 (s, 1H), 5.37 (s, 2H), 3.87 (s, 3H), 2.40 – 2.30 (m, 2H), 1.61 – 1.49 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.58, 166.63, 163.88, 139.85, 129.96, 127.16, 125.63, 113.91,

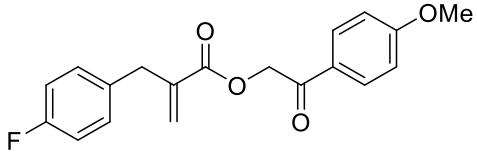
65.78, 55.39, 33.81, 21.35, 13.57; **HRMS** (ESI) calcd for $C_{15}H_{19}O_4$ *m/z* $[M+H]^+$: 263.1283; found: 263.1274.



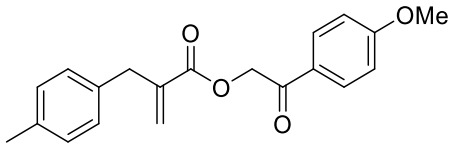
2-(4-methoxyphenyl)-2-oxoethyl 2-methylenehexanoate (1c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.30 (s, 1H), 5.63 (s, 1H), 5.37 (s, 2H), 3.87 (s, 3H), 2.41 – 2.33 (m, 2H), 1.56 – 1.45 (m, 2H), 1.42 – 1.30 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.56, 166.62, 163.83, 140.03, 129.93, 127.09, 125.45, 113.87, 65.78, 55.37, 31.43, 30.28, 22.17, 13.79; **HRMS** (ESI) calcd for $C_{16}H_{21}O_4$ *m/z* $[M+H]^+$: 277.1440; found: 277.1436.



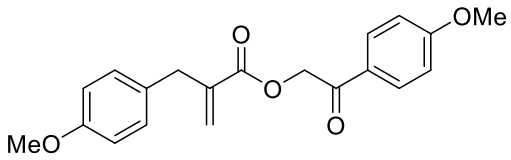
2-(4-methoxyphenyl)-2-oxoethyl 2-benzylacrylate (1d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.34–7.27 (m, 2H), 7.23 (d, *J* = 7.2 Hz, 3H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.42 (s, 1H), 5.56 (s, 1H), 5.35 (s, 2H), 3.88 (s, 3H), 3.71 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.52, 166.27, 163.93, 139.36, 138.45, 130.01, 129.05, 128.38, 127.44, 127.13, 126.30, 113.96, 65.98, 55.43, 37.85; **HRMS** (ESI) calcd for $C_{19}H_{19}O_4$ *m/z* $[M+H]^+$: 311.1283; found: 311.1279.



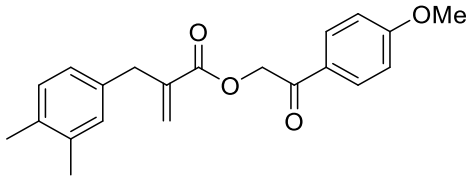
2-(4-methoxyphenyl)-2-oxoethyl 2-(4-fluorobenzyl)acrylate (1e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.19 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.02 – 6.91 (m, 4H), 6.41 (s, 1H), 5.56 (s, 1H), 5.35 (s, 2H), 3.88 (s, 3H), 3.67 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.42, 166.10, 163.94, 161.46 (d, *J* = 244.1 Hz), 139.24, 134.10 (d, *J* = 3.1 Hz), 130.44 (d, *J* = 8.0 Hz), 129.98, 127.45, 127.03, 115.13 (d, *J* = 21.2 Hz) 113.94, 65.98, 55.41, 37.10; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –116.80; **HRMS** (ESI) calcd for $C_{19}H_{18}O_4F$ *m/z* $[M+H]^+$: 329.1189; found: 329.1190.



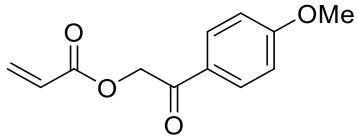
2-(4-methoxyphenyl)-2-oxoethyl 2-(4-methylbenzyl)acrylate (1f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.12 (s, 4H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.40 (s, 1H), 5.55 (s, 1H), 5.35 (s, 2H), 3.88 (s, 3H), 3.66 (s, 2H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.53, 166.31, 163.91, 139.54, 135.77, 135.34, 130.00, 129.07, 128.93, 127.27, 127.12, 113.94, 65.95, 55.43, 37.43, 20.98; **HRMS** (ESI) calcd for $C_{20}H_{21}O_4$ *m/z* $[M+H]^+$: 325.1440; found: 325.1431.



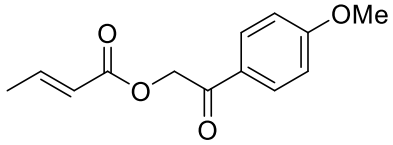
2-(4-methoxyphenyl)-2-oxoethyl 2-(4-methoxybenzyl)acrylate (1g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.39 (s, 1H), 5.54 (s, 1H), 5.35 (s, 2H), 3.88 (s, 3H), 3.79 (s, 3H), 3.64 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.57, 166.35, 163.94, 158.06, 139.74, 130.44, 130.06, 130.03, 127.14, 113.96, 113.77, 65.97, 55.46, 55.15, 37.02; **HRMS** (ESI) calcd for $C_{20}H_{21}O_5$ *m/z* $[M+H]^+$: 341.1389; found: 341.1392.



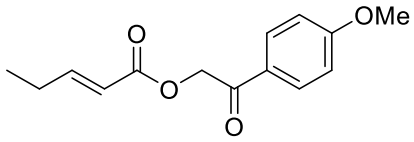
2-(4-methoxyphenyl)-2-oxoethyl 2-(3,4-dimethylbenzyl)acrylate (1h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 6.98 – 6.92 (m, 3H), 6.41 (s, 1H), 5.57 (s, 1H), 5.35 (s, 2H), 3.88 (s, 3H), 3.64 (s, 2H), 2.24 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.47, 166.26, 163.83, 139.51, 136.38, 135.73, 134.33, 130.25, 129.92, 129.54, 127.16, 127.04, 126.32, 113.86, 65.88, 55.33, 37.31, 19.61, 19.21; **HRMS** (ESI) calcd for $C_{21}H_{23}O_4$ *m/z* $[M+H]^+$: 339.1596; found: 339.1603.



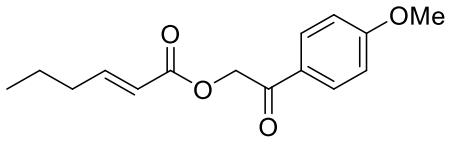
2-(4-methoxyphenyl)-2-oxoethyl acrylate (1i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 17.4 Hz, 1H), 6.28 (dd, *J* = 17.4, 10.4 Hz, 1H), 5.94 (dd, *J* = 10.4, 1.4 Hz, 1H), 5.38 (s, 2H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.39, 165.55, 164.01, 132.03, 130.06, 127.54, 127.13, 114.01, 65.78, 55.50; **HRMS** (ESI) calcd for $C_{12}H_{13}O_4$ *m/z* $[M+H]^+$: 221.0814; found: 221.0816.



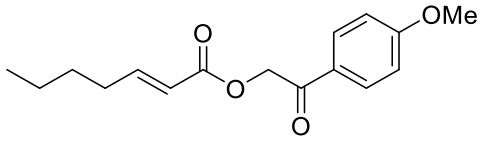
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-but-2-enoate (1j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.17–7.05 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.01 (d, *J* = 17.2 Hz, 1H), 5.35 (s, 2H), 3.87 (s, 3H), 1.92 (dd, *J* = 6.9, 1.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.75, 165.77, 163.92, 146.26, 130.03, 127.19, 121.70, 113.94, 65.52, 55.45, 18.10; **HRMS** (ESI) calcd for $C_{13}H_{15}O_4$ *m/z* $[M+H]^+$: 235.0970; found: 235.0962.



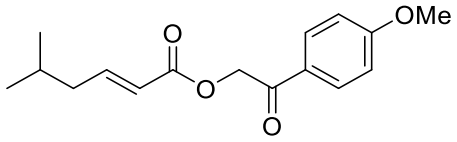
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-pent-2-enoate (1k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.0 Hz, 2H), 7.16 (dt, *J* = 15.7, 6.3 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 2H), 5.98 (dt, *J* = 15.7, 1.8 Hz, 1H), 5.36 (s, 2H), 3.88 (s, 3H), 2.35 – 2.19 (m, 2H), 1.10 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.54, 165.75, 163.69, 152.02, 129.77, 126.91, 119.07, 113.71, 65.33, 55.20, 25.12, 11.71; **HRMS** (ESI) calcd for $C_{14}H_{17}O_4$ *m/z* $[M+H]^+$: 249.1127; found: 249.1121.



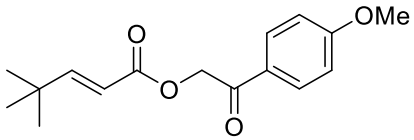
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-hex-2-enoate (1l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.16 – 7.04 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.98 (d, *J* = 15.7 Hz, 1H), 5.35 (s, 2H), 3.87 (s, 3H), 2.22 (q, *J* = 7.1 Hz, 2H), 1.51 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.42, 165.51, 163.60, 150.40, 129.66, 126.82, 120.02, 113.61, 65.24, 55.07, 33.91, 20.77, 13.30; **HRMS** (ESI) calcd for $C_{15}H_{19}O_4$ *m/z* $[M+H]^+$: 263.1283; found: 263.1277.



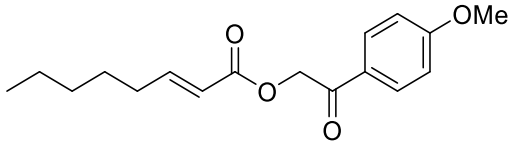
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-hept-2-enoate (1m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.16 – 7.04 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.98 (d, *J* = 15.7 Hz, 1H), 5.35 (s, 2H), 3.87 (s, 3H), 2.30 – 2.19 (m, 2H), 1.54 – 1.30 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.62, 165.79, 163.79, 150.95, 129.88, 127.06, 120.02, 113.81, 65.40, 55.30, 31.82, 29.78, 22.03, 13.64; **HRMS** (ESI) calcd for $C_{16}H_{21}O_4$ *m/z* $[M+H]^+$: 277.1440; found: 277.1431.



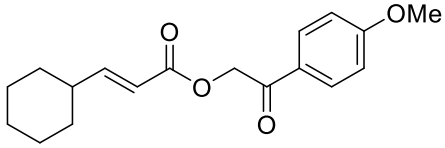
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-5-methylhex-2-enoate (1n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 7.04 (dt, *J* = 15.2, 7.5 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 5.94 (d, *J* = 15.6 Hz, 1H), 5.32 (s, 2H), 3.82 (s, 3H), 2.25 – 1.96 (m, 2H), 1.75 (dt, *J* = 13.3, 6.7 Hz, 1H), 0.91 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.66, 165.73, 163.84, 149.84, 129.93, 127.11, 121.11, 113.85, 65.45, 55.34, 41.42, 27.58, 22.23; **HRMS** (ESI) calcd for $C_{16}H_{21}O_4$ *m/z* $[M+H]^+$: 277.1440; found: 277.1431.



2-(4-methoxyphenyl)-2-oxoethyl (*E*)-4,4-dimethylpent-2-enoate (1o): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.0 Hz, 2H), 7.09 (d, *J* = 15.9 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 5.90 (d, *J* = 15.9 Hz, 1H), 5.35 (s, 2H), 3.86 (s, 3H), 1.09 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.75, 166.55, 163.92, 160.62, 130.02, 127.17, 115.66, 113.94, 65.55, 55.45, 33.92, 28.49; **HRMS** (ESI) calcd for $C_{16}H_{21}O_4$ *m/z* $[M+H]^+$: 277.1440; found: 277.1436.



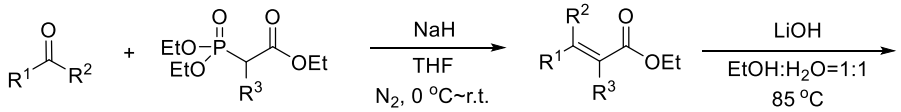
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-oct-2-enoate (1p): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.16–7.05 (m, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.97 (d, *J* = 15.7 Hz, 1H), 5.35 (s, 2H), 3.86 (s, 3H), 2.23 (q, *J* = 8.2 Hz, 2H), 1.53 – 1.43 (m, 2H), 1.33 – 1.28 (m, 4H), 0.91 – 0.86 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.77, 165.97, 163.91, 151.22, 130.02, 127.20, 120.08, 113.93, 65.51, 55.42, 32.22, 31.23, 27.47, 22.34, 13.87; **HRMS** (ESI) calcd for $C_{17}H_{23}O_4$ *m/z* $[M+H]^+$: 291.1596; found: 291.1589.

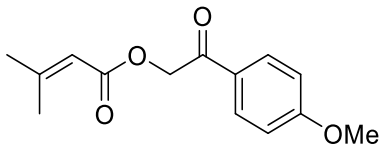


2-(4-methoxyphenyl)-2-oxoethyl (*E*)-3-cyclohexylacrylate (1q): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.05 (dd, *J* = 15.8, 6.7 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.93 (d, *J* = 15.8 Hz, 1H), 5.35 (s, 2H), 3.87 (s, 3H), 2.27 – 2.07 (m, 1H), 1.87 – 1.59 (m, 6H), 1.39 – 1.08 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.70, 166.26, 163.83, 155.84, 129.94, 127.08, 117.69, 113.85, 65.47, 55.38, 40.38, 31.39, 25.76, 25.56; **HRMS** (ESI) calcd for $C_{18}H_{23}O_4$ *m/z* $[M+H]^+$: 303.1596; found: 303.1591.

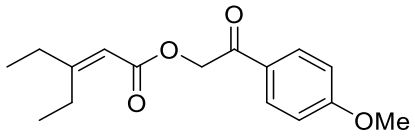
Preparation of β,β-disubstituted enoates 3.

Generally, β,β-disubstituted enoate substrates **3** were prepared from corresponding ethyl enoate esters. Ethyl enoate esters were prepared using Horner-Wadsworth-Emmons reaction from ketones and triethyl phosphonoacetate, or triethyl 2-phosphonopropionate.[4]

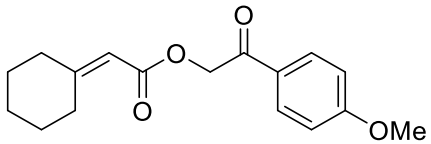




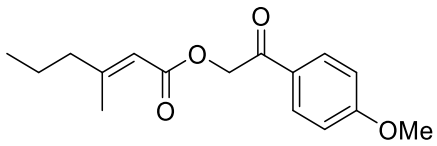
2-(4-methoxyphenyl)-2-oxoethyl 3-methylbut-2-enoate (3a): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.87 (s, 1H), 5.31 (s, 2H), 3.87 (s, 3H), 2.19 (s, 3H), 1.94 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.09, 165.69, 163.83, 158.68, 130.00, 127.23, 115.01, 113.87, 65.00, 55.41, 27.44, 20.30; **HRMS** (ESI) calcd for $C_{14}H_{17}O_4$ *m/z* $[M+H]^+$: 249.1127; found: 249.1120.



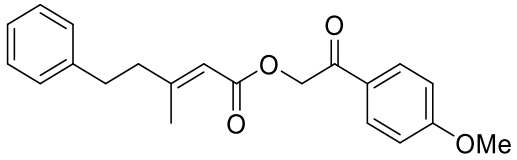
2-(4-methoxyphenyl)-2-oxoethyl 3-ethylpent-2-enoate (3b): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.81 (s, 1H), 5.32 (s, 2H), 3.87 (s, 3H), 2.64 (q, *J* = 7.5 Hz, 2H), 2.24 (q, *J* = 7.4 Hz, 2H), 1.19 – 0.96 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.88, 169.11, 165.31, 163.62, 129.75, 126.99, 113.65, 112.33, 64.80, 55.15, 30.59, 25.36, 12.70, 11.57; **HRMS** (ESI) calcd for $C_{16}H_{21}O_4$ *m/z* $[M+H]^+$: 277.1440; found: 277.1430.



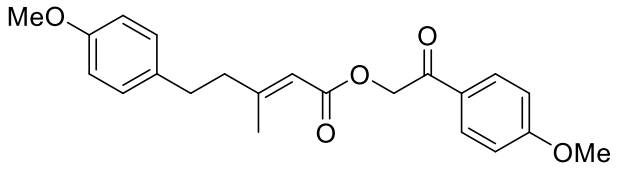
2-(4-methoxyphenyl)-2-oxoethyl 2-cyclohexylideneacetate (3c): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.80 (s, 1H), 5.31 (s, 2H), 3.87 (s, 3H), 2.88 – 2.81 (m, 2H), 2.27 – 2.21 (m, 2H), 1.70 – 1.56 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.12, 165.80, 165.60, 163.85, 130.01, 127.33, 113.89, 111.96, 65.00, 55.41, 37.98, 29.90, 28.47, 27.69, 26.11; **HRMS** (ESI) calcd for $C_{17}H_{21}O_4$ *m/z* $[M+H]^+$: 289.1440; found: 289.1431.



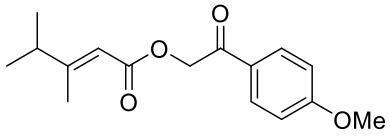
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-3-methylhex-2-enoate (3d)：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.1 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 5.86 (s, 1H), 5.32 (s, 2H), 3.88 (s, 3H), 2.21 – 2.11 (m, 5H), 1.58 – 1.46 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.07, 165.77, 163.78, 162.15, 129.93, 127.20, 114.38, 113.82, 64.94, 55.33, 42.89, 20.34, 18.74, 13.53; **HRMS** (ESI) calcd for $C_{16}H_{21}O_4$ *m/z* $[M+H]^+$: 277.1440; found: 277.1434.



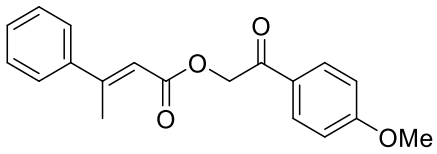
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-3-methyl-5-phenylpent-2-enoate (3e)：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.21 (t, *J* = 8.7 Hz, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.91 (s, 1H), 5.33 (s, 2H), 3.88 (s, 3H), 2.89 – 2.75 (m, 2H), 2.56 – 2.43 (m, 2H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.05, 165.76, 163.88, 161.08, 140.95, 130.02, 128.41, 128.20, 127.29, 126.06, 114.87, 113.91, 65.08, 55.41, 42.72, 33.77, 19.12; **HRMS** (ESI) calcd for $C_{21}H_{23}O_4$ *m/z* $[M+H]^+$: 339.1596; found: 339.1594.



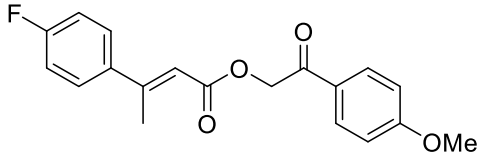
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-5-(4-methoxyphenyl)-3-methylpent-2-enoate (3f)：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.89 (s, 1H), 5.32 (s, 2H), 3.88 (s, 3H), 3.79 (s, 3H), 2.83 – 2.69 (m, 2H), 2.52 – 2.40 (m, 2H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.05, 165.77, 163.86, 161.24, 157.86, 132.98, 130.01, 129.10, 127.26, 114.82, 113.90, 113.78, 65.06, 55.41, 55.14, 43.02, 32.87, 19.12; **HRMS** (ESI) calcd for $C_{16}H_{23}O_6$ *m/z* $[M+H]^+$: 369.1702; found: 369.1696.



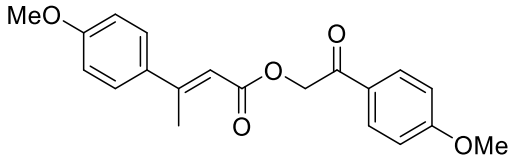
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-3,4-dimethylpent-2-enoate (3g)：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.87 (s, 1H), 5.31 (s, 2H), 3.86 (s, 3H), 2.39 (p, *J* = 6.8 Hz, 1H), 2.15 (s, 3H), 1.09 (s, 3H), 1.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.15, 167.62, 166.16, 163.83, 129.98, 127.24, 113.87, 112.50, 64.98, 55.38, 38.13, 20.70, 16.57; **HRMS** (ESI) calcd for $C_{16}H_{21}O_4$ *m/z* $[M+H]^+$: 277.1440; found: 277.1434.



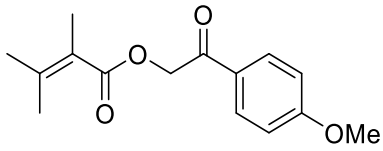
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-3-phenylbut-2-enoate (3h)：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.39 (dd, *J* = 5.1, 2.1 Hz, 3H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.34 (s, 1H), 5.39 (s, 2H), 3.88 (s, 3H), 2.61 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.96, 165.90, 163.90, 157.28, 141.86, 130.03, 129.12, 128.44, 127.24, 126.28, 115.89, 113.93, 65.31, 55.40, 18.05; **HRMS** (ESI) calcd for $C_{19}H_{19}O_4$ *m/z* $[M+H]^+$: 311.1283; found: 311.1281.



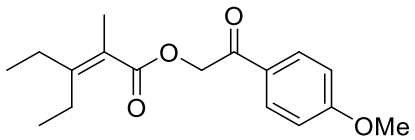
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-3-(4-fluorophenyl)but-2-enoate (3i)：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.50 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.29 (s, 1H), 5.39 (s, 2H), 3.88 (s, 3H), 2.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.86, 165.74, 164.44, 163.88, 161.96, 155.94, 137.81, 137.78, 129.99, 128.15, 128.07, 127.12, 115.74, 115.47, 115.25, 113.90, 65.30, 55.38, 17.99; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –111.92; **HRMS** (ESI) calcd for $C_{19}H_{18}O_4F$ *m/z* $[M+H]^+$: 329.1189; found: 329.1183.



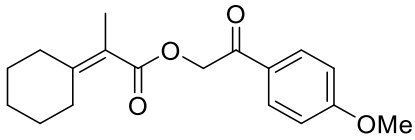
2-(4-methoxyphenyl)-2-oxoethyl (*E*)-3-(4-methoxyphenyl)but-2-enoate (3j)：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.31 (s, 1H), 5.38 (s, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 2.59 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.04, 166.02, 163.80, 160.44, 156.56, 133.76, 129.95, 127.63, 127.15, 113.84, 113.68, 65.17, 55.33, 55.15, 17.62; **HRMS** (ESI) calcd for $C_{20}H_{21}O_5$ *m/z* $[M+H]^+$: 341.1389; found: 341.1382.



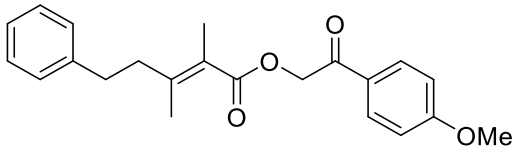
2-(4-methoxyphenyl)-2-oxoethyl 2,3-dimethylbut-2-enoate (3k)：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.36 (s, 2H), 3.87 (s, 3H), 2.09 (s, 3H), 1.96 (s, 3H), 1.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.83, 168.46, 163.69, 145.31, 129.81, 127.08, 121.44, 113.74, 65.34, 55.24, 22.82, 22.50, 15.45; **HRMS** (ESI) calcd for $C_{15}H_{19}O_4$ *m/z* $[M+H]^+$: 263.1283; found: 263.1279.



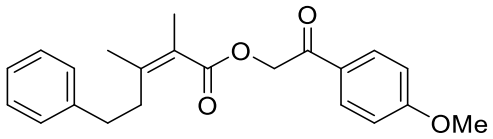
2-(4-methoxyphenyl)-2-oxoethyl 3-ethyl-2-methylpent-2-enoate (3l)：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.1 Hz, 2H), 6.95 (d, *J* = 9.1 Hz, 2H), 5.35 (s, 2H), 3.87 (s, 3H), 2.42 (q, *J* = 7.5 Hz, 2H), 2.18 (q, *J* = 7.6 Hz, 2H), 1.96 (s, 3H), 1.06 (t, *J* = 7.5 Hz, 3H), 1.04 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.95, 168.74, 163.82, 155.52, 129.94, 127.28, 121.00, 113.86, 65.43, 55.36, 26.99, 26.33, 15.05, 13.13, 11.90; **HRMS** (ESI) calcd for $C_{17}H_{23}O_4$ *m/z* $[M+H]^+$: 291.1596; found: 291.1603.



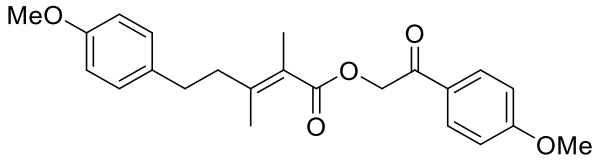
2-(4-methoxyphenyl)-2-oxoethyl 2-cyclohexylidenepropanoate (3m)：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.35 (s, 2H), 3.88 (s, 3H), 2.55 (t, *J* = 5.4 Hz, 2H), 2.26 (t, *J* = 5.6 Hz, 2H), 1.97 (s, 3H), 1.68 – 1.57 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.88, 169.55, 163.80, 149.82, 129.94, 127.21, 118.74, 113.85, 65.50, 55.37, 32.25, 31.28, 28.11, 27.61, 26.34, 15.07; **HRMS** (ESI) calcd for $C_{18}H_{23}O_4$ *m/z* $[M+H]^+$: 303.1596; found: 303.1589.



2-(4-methoxyphenyl)-2-oxoethyl (*E*)-2,3-dimethyl-5-phenylpent-2-enoate (3n):[5,6] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.18 (m, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.37 (s, 2H), 3.88 (s, 3H), 2.78 – 2.70 (m, 2H), 2.51 – 2.43 (m, 2H), 2.12 (s, 3H), 1.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.87, 168.70, 163.79, 147.55, 141.34, 129.93, 128.30, 128.18, 127.17, 125.92, 122.41, 113.85, 65.47, 55.34, 38.34, 33.39, 21.12, 15.11; **HRMS** (ESI) calcd for $C_{22}H_{25}O_4$ *m/z* $[M+H]^+$: 353.1753; found: 353.1761.



2-(4-methoxyphenyl)-2-oxoethyl (*Z*)-2,3-dimethyl-5-phenylpent-2-enoate (3o):[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.31 – 7.23 (m, 4H), 7.17 (t, *J* = 6.7 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.35 (s, 2H), 3.87 (s, 3H), 2.84 – 2.71 (m, 4H), 1.99 (s, 3H), 1.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.87, 168.26, 163.86, 148.36, 142.14, 130.02, 128.40, 128.19, 127.30, 125.67, 122.42, 113.92, 65.52, 55.44, 38.68, 34.80, 20.96, 15.83; **HRMS** (ESI) calcd for $C_{22}H_{25}O_4$ *m/z* $[M+H]^+$: 353.1753; found: 353.1749.



2-(4-methoxyphenyl)-2-oxoethyl (*E*)-5-(4-methoxyphenyl)-2,3-dimethylpent-2-enoate (3p)： **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.35 (s, 2H), 3.85 (s, 3H), 3.77 (s, 3H), 2.75 – 2.63 (m, 2H), 2.48 – 2.39 (m, 2H), 2.12 (s, 3H), 1.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.88, 168.69, 163.78, 157.76, 147.67, 133.38, 129.90, 129.08, 127.16, 122.30, 113.83, 113.65, 65.44, 55.32, 55.04, 38.56, 32.47, 21.11, 15.09; **HRMS** (ESI) calcd for $C_{23}H_{27}O_5$ *m/z* $[M+H]^+$: 383.1858; found: 383.1856.

Determination of *E*/*Z*-geometry of tetrasubstituted enoates

The corresponding ethyl ester **3n**-Et, **3o**-Et were reported in the literature.[5,6] The data is in good agreement with that we obtained which confirmed **3n**-Et to be *E*, **3o**-Et to be *Z*. The geometry of **3p** was assigned by analogy.

^{1}H NMR (400 MHz, $CDCl_3$) for *E*-isomer: δ 7.26–7.31(m, 2H), 7.18–7.22 (m, 3H), 4.18 (q, *J* = 7.3 Hz, 2H), 2.69–2.78 (m, 2H), 2.40–2.44 (m, 2H), 2.02–2.03 (m, 3H), 1.81 (m, 3H), 1.30 (t, *J* = 7.3 Hz, 3H); *Z*-isomer: δ 7.26–7.31 (m, 2H), 7.18–7.22 (m, 3H), 4.18 (q, *J* = 7.3 Hz, 2H), 2.69–2.78 (m, 2H), 2.62–2.66 (m, 2H), 1.86 (m, 3H), 1.82 (m, 3H), 1.29 (t, *J* = 7.3 Hz, 3H).[5]

^{1}H NMR (300 MHz, $CDCl_3$) for *E*-isomer: δ 1.30 (t, *J* = 7.1 Hz, 3H), 1.81 (s, 3H), 2.02 (s, 3H), 2.39−2.45 (m, 2H), 2.69−2.74 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 7.18−7.24 (m, 3H), 7.26−7.31 (m, 2H).[6]

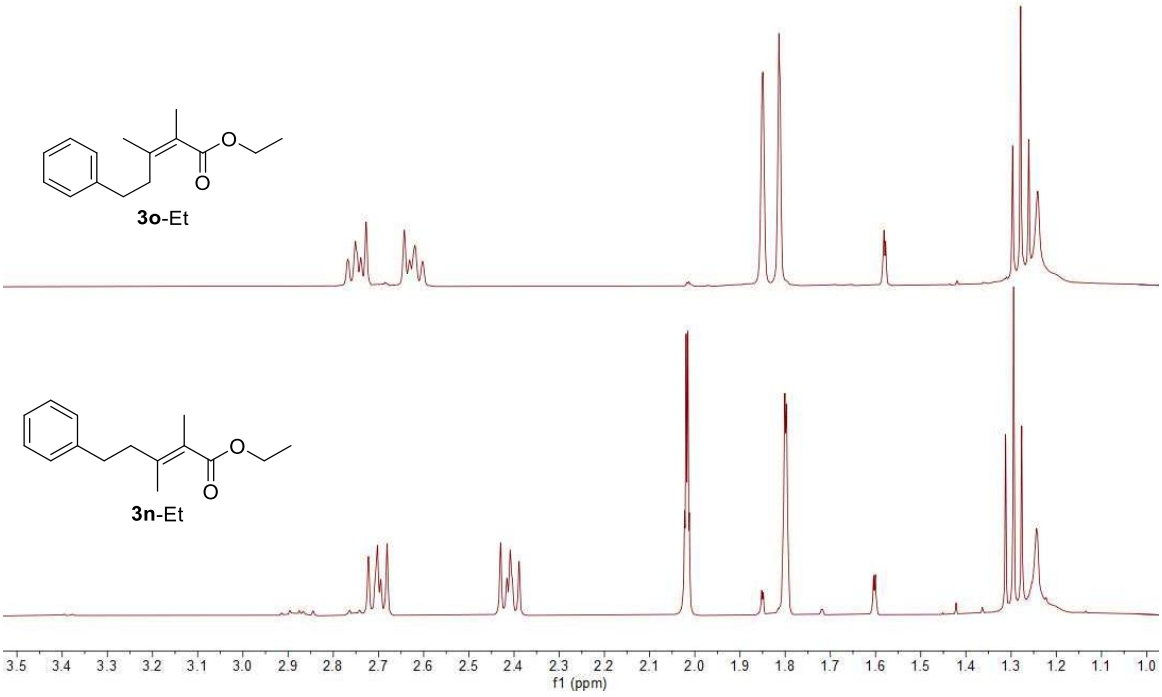


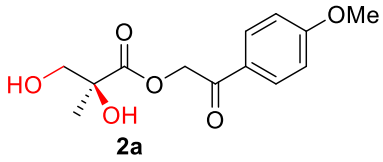
Figure S4. Comparation of partial ^{1}H NMR spectra of **3n**-Et, **3o**-Et with the data reported in the literature.

5. General Methods for Asymmetric Permanganate Oxidation.

Method A: 0.05 mmol scale for optimization of dihydroxylation conditions. At 0 ℃, to a solution of enoate **1a/1d** (0.05 mmol) and the chiral catalyst **CN** (5 mol%) in solvent (0.5 mL), and then 0.05 mL aqueous additive was added. Potassium permanganate was added and the reaction was kept at 0 ℃ for 2h. After the reactants were consumed, the reaction mixture was then passed through a plug of silica gel for the removal of the catalyst (eluent: ethyl acetate). The filtrate was concentrated in vacuo and the residue was purified by flash chromatography on silica gel (1:2 EtOAc/Petroleum ether) affording pure dihydroxylated product **2a/2d** for HPLC analysis.

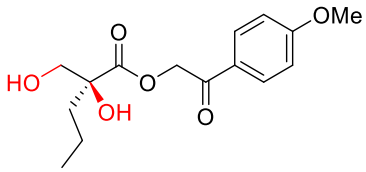
Method B: 0.2 mmol scale for substrate scope investigation. At −20 ℃, to a solution of enoate **1**/**3** (0.2 mmol) and the chiral catalyst **CN** (5 mol%) in toluene (2.0 mL), and then 0.20 mL aqueous additive was added. Potassium permanganate was added and the reaction was kept at −20 ℃ for 10 h. After the reactants were consumed, the reaction mixture was then passed through a plug of silica gel for the removal of the catalyst (eluent: ethyl acetate). The filtrate was concentrated in vacuo and the residue was purified by flash chromatography on silica gel (1:2 EtOAc/Petroleum ether for compound **2**; 1:5 EtOAc/Petroleum ether for compound **4**) affording pure dihydroxylated product **2**/**4** for HPLC analysis. Asymmetric dihydroxylation of enoate **1** performed at 0 ℃ was carried out for 2 h.

6. Characterization of Chiral Dihydroxylation Products.

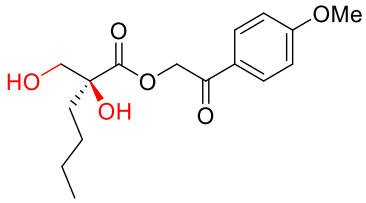


2a

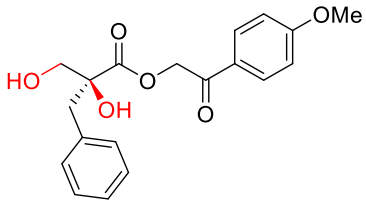
2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2,3-dihydroxy-2-methylpropanoate (2a): 58% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 5.59 (d, *J* = 16.2 Hz, 1H), 5.37 (d, *J* = 16.2 Hz, 1H), 4.03 (d, *J* = 11.6 Hz, 1H), 3.89 (s, 3H), 3.58 (d, *J* = 11.6 Hz, 1H), 1.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.05, 174.93, 164.59, 130.31, 126.29, 114.23, 76.23, 69.68, 66.42, 55.58, 20.79; **IR**: 3449, 2933, 1745, 1685, 1601, 1247, 1172, 967, 837 cm^{-1}; **HRMS** (ESI) calcd for $C_{13}H_{17}O_6$ *m/z* $[M+H]^+$: 269.1025; found: 269.1023; $[\alpha]_D^{25}$ = –0.28 (*c* 0.36, ethyl acetate); **HPLC** analysis: Chiralcel OD-H (Hex/IPA = 90/10, 1.0 mL/min, 254 nm, 25°C), 51.6 (major), 58.7 min, 86% *ee*.



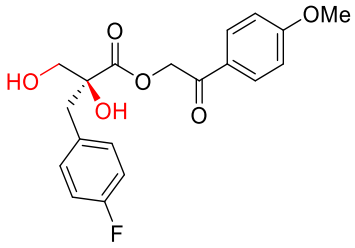
2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2-hydroxy-2-(hydroxymethyl)pentanoate (2b): 42% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 5.63 (d, *J* = 16.2 Hz, 1H), 5.33 (d, *J* = 16.2 Hz, 1H), 4.02 (d, *J* = 11.3 Hz, 1H), 3.89 (s, 3H), 3.60 (d, *J* = 11.5 Hz, 1H), 3.50 (br, 1H), 1.87 – 1.76 (m, 1H), 1.72 – 1.48 (m, 3H), 0.95 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.03, 174.74, 164.58, 130.31, 126.34, 114.23, 79.44, 69.20, 66.39, 55.58, 36.31, 16.58, 14.65; **IR**: 3454, 2962, 1743, 1602, 1514, 1246, 1174, 966, 838 cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{21}O_6$ *m/z* $[M+H]^+$: 297.1338; found: 297.1333; $[\alpha]_D^{25}$= –5.8 (*c* 0.49, ethyl acetate); **HPLC** analysis: Chiralcel OJ-H (Hex/IPA = 60/40, 0.8 mL/min, 210 nm, 25°C), 10.9, 13.4 (major) min, 76% *ee*.



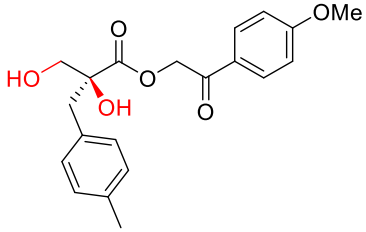
2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2-hydroxy-2-(hydroxymethyl)hexanoate (2c): 47% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.64 (d, *J* = 18.8 Hz, 1H), 5.32 (d, *J* = 16.0 Hz, 1H), 4.02 (d, *J* = 11.5 Hz, 1H), 3.88 (s, 3H), 3.60 (d, *J* = 11.6 Hz, 1H), 1.88–1.79 (m, 1H), 1.68–1.59 (m, 1H), 1.40 – 1. 30 (m, 2H), 1.29 – 1.23 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.05, 174.74, 164.56, 130.30, 126.33, 114.22, 79.44, 69.21, 66.39, 55.57, 33.91, 25.30, 22.83, 13.89; **IR**: 2957, 2933, 1744, 1692, 1602, 1245, 1172, 965, 837 cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{21}O_6$ *m/z* $[M+H]^+$: 311.1495; found: 311.1491; $[\alpha]_D^{25}$= –2.4 (*c* 0.49, ethyl acetate); **HPLC** analysis: Chiralcel AD-H (Hex/IPA = 60/40, 0.9 mL/min, 254 nm, 25°C), 10.8 (major), 13.3 min, 58% *ee*.



2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2-benzyl-2,3-dihydroxypropanoate (2d): 65% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 7.32 – 7.20 (m, 5H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.60 (d, *J* = 16.2 Hz, 1H), 5.31 (d, *J* = 16.2 Hz, 1H), 4.12 (d, *J* = 11.6 Hz, 1H), 3.89 (s, 3H), 3.68 (d, *J* = 11.6 Hz, 1H), 3.18 (d, *J* = 13.8 Hz, 1H), 2.99 (d, *J* = 13.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.98, 173.87, 164.57, 135.18, 130.30, 130.21, 128.17, 126.88, 126.26, 114.20, 79.58, 68.78, 66.37, 55.55, 40.21; **IR**: 3441, 2940, 1743, 1641, 1602, 1426, 1175, 967 cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{21}O_6$ *m/z* $[M+H]^+$: 345.1338; found: 345.1328; $[\alpha]_D^{25}$= +37.2 (*c* 0.72, ethyl acetate); **HPLC** analysis: Chiralcel AZ-H (Hex/IPA = 60/40, 1 mL/min, 254 nm, 25℃), 27.6 (major), 46.1min, 83% *ee*.

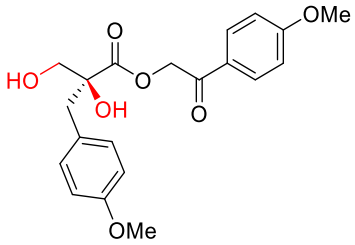


2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2-(4-fluorobenzyl)-2,3-dihydroxypropanoate (2e): 56% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.03 – 6.89 (m, 4H), 5.58 (d, *J* = 16.2 Hz, 1H), 5.33 (d, *J* = 16.2 Hz, 1H), 4.09 (d, *J* = 11.6 Hz, 1H), 3.89 (s, 3H), 3.65 (d, *J* = 11.6 Hz, 1H), 3.15 (d, *J* = 14.0 Hz, 1H), 2.97 (d, *J* = 14.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.00, 173.83, 164.67, 163.19, 160.76, 131.81, 131.73, 130.95, 130.37, 126.22, 115.12, 114.91, 114.27, 79.56, 68.81, 66.48, 55.62, 39.25; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –116.01; **IR**: 3444, 2936, 1753, 1602, 1509, 1173, 1023, 967, 836 cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{20}O_6F$ *m/z* $[M+H]^+$: 363.1244; found: 363.1239; $[\alpha]_D^{25}$= +34.5 (*c* 0.79, ethyl acetate); **HPLC** analysis: Chiralcel AD-H (Hex/IPA = 65/35, 1.0 mL/min, 254 nm, 25℃), 15.9 (major), 19.7 min, 80% *ee*.

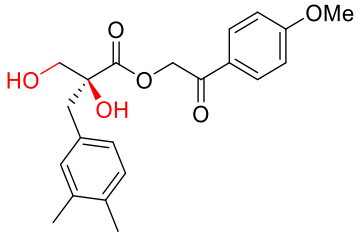


2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2,3-dihydroxy-2-(4-methylbenzyl)propanoate (2f): 48% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.61 (d, *J* = 16.2 Hz, 1H), 5.31 (d, *J* = 16.2 Hz, 1H), 4.12 (d, *J* = 11.5 Hz, 1H), 3.89 (s, 3H), 3.67 (d, *J* = 11.6 Hz, 1H), 3.39 (br, 1H), 3.15 (d, *J* = 13.8 Hz, 1H), 2.95 (d, *J* = 13.8 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.00, 173.93, 164.57, 136.44, 131.98, 130.32, 130.04, 128.92, 126.27, 114.20, 80.13, 68.79, 66.35, 55.57, 39.79, 21.04; **IR**: 3452, 2930, 1745, 1601, 1514,

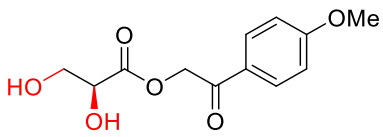
1172,1025, 966, 837 cm^{-1}; **HRMS** (ESI) calcd for $C_{20}H_{23}O_6$ *m/z* $[M+H]^+$: 359.1495; found: 359.1486; $[\alpha]_D^{25}$= +39.0 (*c* 0.62, ethyl acetate); **HPLC** analysis: Chiralcel AD-H (Hex/IPA = 65/35, 1 mL/min, 254 nm, 25℃), 15.3 (major), 18.6 min, 80% *ee*.



2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2,3-dihydroxy-2-(4-methoxybenzyl)propanoate (2g): 56% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.0 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.60 (d, *J* = 16.2 Hz, 1H), 5.32 (d, *J* = 16.2 Hz, 1H), 4.11 (d, *J* = 13.0 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.66 (d, *J* = 11.5 Hz, 1H), 3.38 (br, 1H), 3.13 (d, *J* = 14.0 Hz, 1H), 2.93 (d, *J* = 14.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.00, 173.93, 164.56, 158.49, 131.18, 130.31, 127.11, 126.25, 114.20, 113.59, 79.73, 68.72, 66.35, 55.57, 55.13, 39.33; **IR**: 3461, 2935, 1747, 1601, 1513, 1248, 1030, 966, 836 cm^{-1}; **HRMS** (ESI) calcd for $C_{20}H_{21}O_7$ *m/z* $[M+H]^+$: 373.1287; found: 373.1297; $[\alpha]_D^{25}$ = +33.9 (*c* 0.98, ethyl acetate); **HPLC** analysis: Chiralcel AD-H (Hex/IPA = 65/35, 1 mL/min, 254 nm, 25℃), 21.0 (major), 25.3 min, 85% *ee*.

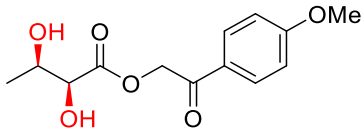


2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2-(3,4-dimethylbenzyl)-2,3-dihydroxypropanoate (2h): 55% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 7.10 – 6.92 (m, 5H), 5.61 (d, *J* = 16.2 Hz, 1H), 5.32 (d, *J* = 16.3 Hz, 1H), 4.12 (d, *J* = 9.9 Hz, 1H), 3.89 (s, 3H), 3.81 (br, 1H), 3.67 (dd, *J* = 11.1, 6.1 Hz, 1H), 3.39 (s, 1H), 3.13 (d, *J* = 13.8 Hz, 1H), 2.92 (d, *J* = 13.8 Hz, 1H), 2.23 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.99, 173.98, 164.56, 136.30, 135.11, 132.39, 131.56, 130.31, 129.47, 127.42, 126.33, 114.20, 79.63, 68.78, 66.32, 55.56, 39.82, 19.76, 19.34; **IR**: 3460, 2936, 1746, 1682, 1602, 1173, 1025, 967, 834 cm^{-1}; **HRMS** (ESI) calcd for $C_{21}H_{25}O_6$ *m/z* $[M+H]^+$: 373.1651; found: 373.1647; $[\alpha]_D^{25}$= +39.1 (*c* 0.77, ethyl acetate); **HPLC** analysis: Chiralcel OD-H (Hex/IPA = 80/20, 1 mL/min, 254 nm, 25℃), 19.5, 28.1 (major) min, 81% *ee*.

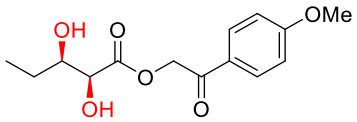


2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2,3-dihydroxypropanoate (2i): 40% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.65 (d, *J* = 16.4 Hz, 1H), 5.31 (d, *J* = 16.3 Hz, 1H), 4.44 (s, 1H), 4.14 (d, *J* = 12.1 Hz, 1H),

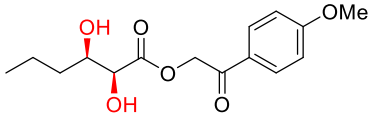
3.96 – 3.82 (m, 1H), 3.87 (s, 3H), 3.56 (s, 1H), 3.41 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.83, 172.78, 164.58, 130.31, 126.26, 114.23, 72.16, 66.44, 64.98, 55.59; **IR**: 3394, 2934, 2360, 1751, 1602 1246, 1174, 969, 835 cm^{-1}; **HRMS** (ESI) calcd for $C_{12}H_{15}O_6$ *m/z* $[M+H]^+$: 255.0869; found: 255.0859; $[\alpha]_D^{25}$= +4.9 (*c* 0.39, ethyl acetate); **HPLC** analysis: Chiralcel OJ-H (Hex/IPA = 60/40, 0.8 mL/min, 254 nm, 25°C), 20.2, 25.7 (major) min, 77% *ee*.



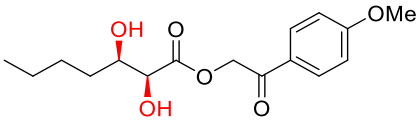
2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxybutanoate (2j): 34% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.62 (d, *J* = 16.2 Hz, 1H), 5.36 (d, *J* = 16.2 Hz, 1H), 4.37 (d, *J* = 5.9 Hz, 1H), 4.23 (d, *J* = 6 Hz, 1H), 3.88 (s, 3H), 3.71 (br, 1H), 3.15 (d, *J* = 9.0 Hz, 1H), 1.37 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.92, 173.01, 164.58, 130.31, 126.26, 114.21, 74.98, 68.96, 66.32, 55.58, 18.40; **IR**: 3437, 2935, 1750, 1687, 1602, 1245, 1175, 973, 836 cm^{-1}; **HRMS** (ESI) calcd for $C_{13}H_{17}O_6$ *m/z* $[M+H]^+$: 269.1025; found: 269.1016; $[\alpha]_D^{25}$= +4.8 (*c* 0.31, ethyl acetate); **HPLC** analysis: Chiralcel OJ-H (Hex/IPA = 60/40, 0.8 mL/min, 254 nm, 25°C), 21.2, 34.4 (major) min, 90% *ee*.



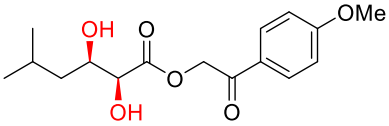
2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxypentanoate (2k): 32% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.61 (d, *J* = 16.3 Hz, 1H), 5.36 (d, *J* = 16.3 Hz, 1H), 4.32 (d, *J* = 5.8 Hz, 1H), 4.07 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 3.72 (br, 1H), 3.23 (d, *J* = 9.0 Hz, 1H), 1.84 – 1.62 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.04, 173.33, 164.56, 130.31, 126.25, 114.20, 74.38, 73.51, 66.29, 55.58, 25.45, 10.37; **IR**: 3431, 2937, 1750, 1689, 1601 1244, 1174, 975, 836 cm^{-1}; **HRMS** (ESI) calcd for $C_{14}H_{19}O_6$ *m/z* $[M+H]^+$: 283.1182; found: 283.1172; $[\alpha]_D^{25}$= +12.4 (*c* 0.42, ethyl acetate); **HPLC** analysis: Chiralcel OJ-H (Hex/IPA = 60/40, 0.8 mL/min, 210 nm, 25°C), 14.9, 17.8 (major) min, 86% *ee*.



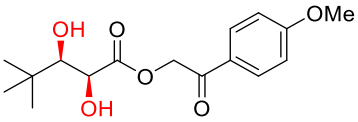
2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxyhexanoate (2l): 35% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.60 (d, *J* = 16.2 Hz, 1H), 5.36 (d, *J* = 16.2 Hz, 1H), 4.28 (d, *J* = 10.6 Hz, 1H), 4.16 (br, 1H), 3.88 (s, 3H), 3.71 (br, 1H), 3.27 (d, *J* = 7.9 Hz, 1H), 1.80 – 1.35 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.05, 173.27, 164.55, 130.30, 126.25, 114.19, 73.93, 72.60, 66.28, 55.57, 34.46, 19.03, 13.97; **IR**: 3445, 2959, 1747 1679, 1602 1244, 1173, 970, 835 cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{21}O_6$ *m/z* $[M+H]^+$: 297.1338; found: 297.1330; $[\alpha]_D^{25}$= +19.5 (*c* 0.43, ethyl acetate); **HPLC** analysis: Chiralcel OJ-H (Hex/IPA = 60/40, 0.8 mL/min, 210 nm, 25°C), 12.4, 13.1 (major) min, 87% *ee*.



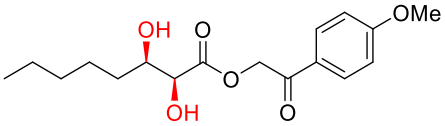
2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxyheptanoate (2m): 45% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.61 (d, *J* = 16.3 Hz, 1H), 5.36 (d, *J* = 16.3 Hz, 1H), 4.30 (d, *J* = 7.2 Hz,, 1H), 4.15 (br, 1H), 3.89 (s, 3H), 3.66 (br, 1H), 3.11 (d, *J* = 9.1 Hz, 1H), 1.80 – 1.33 (m, 6H), 0.93 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.99, 173.30, 164.58, 130.32, 126.29, 114.22, 73.89, 72.89, 66.31, 55.58, 32.11, 28.03, 22.60, 14.03; **IR**: 3453, 2934, 1753, 1681 1602, 1244, 1174, 970, 836 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{23}O_6$ *m/z* $[M+H]^+$: 311.1495; found: 311.1501; $[\alpha]_D^{25}$= +21.8 (*c* 0.28, ethyl acetate); **HPLC** analysis: Chiralcel OD-H (Hex/IPA = 70/30, 1 mL/min, 254 nm, 25°C), 9.9, 11.2 (major) min, 91% *ee*.



2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-5-methylhexanoate (2n): 60% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.62 (d, *J* = 16.2 Hz, 1H), 5.37 (d, *J* = 16.2 Hz, 1H), 4.33 – 4.19 (m, 2H), 3.89 (s, 3H), 3.58 (br, 1H), 3.06 (br, 1H), 1.95 – 1.80 (m, 1H), 1.77 – 1.67 (m, 1H), 1.48 – 1.36 (m, 1H), 1.02 – 0.94 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.03, 173.26, 164.57, 130.32, 126.26, 114.21, 74.29, 71.01, 66.31, 55.58, 41.24, 24.50, 23.20, 22.19; **IR**: 3451, 2955, 1752, 1687, 1602, 1244, 1173, 972, 836 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{23}O_6$ *m/z* $[M+H]^+$: 311.1495; found: 311.1486; $[\alpha]_D^{25}$ = +23.7 (*c* 0.30, ethyl acetate); **HPLC** analysis: Chiralcel OD-H (Hex/IPA = 80/20, 1.0 mL/min, 230 nm, 25°C), 14.8, 15.9 (major) min, 89% *ee*.

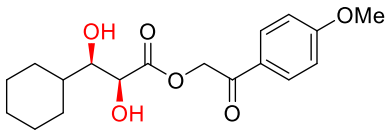


2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-4,4-dimethylpentanoate (2o): 58% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.57 – 5.33 (m, 2H), 4.57 (d, *J* = 6.5 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 1H), 3.45 (br, 1H), 3.12 (br, 1H), 1.08 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.92, 174.19, 164.48, 130.25, 126.41, 114.18, 78.84, 71.65, 66.37, 55.56, 35.10, 26.64; **IR**: 3504, 2957, 1750,1685, 1601, 1243, 1173, 964, 836 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{23}O_6$ *m/z* $[M+H]^+$: 311.1495; found: 311.1487; $[\alpha]_D^{25}$= +9.1 (*c* 0.41, ethyl acetate); **HPLC** analysis: Chiralcel OJ-H (Hex/IPA = 60/40, 1 mL/min, 254 nm, 25°C), 13.3, 14.8 (major) min, 93% *ee*.

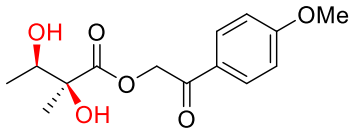


2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxyoctanoate (2p): 65% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.61 (d, *J* = 16.3 Hz, 1H), 5.36 (d, *J* = 16.3 Hz, 1H), 4.30 (s, 1H), 4.15 (t, *J* = 6.1 Hz,

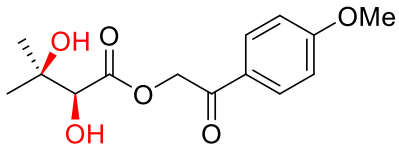
1H), 3.88 (s, 3H), 3.67 (br, 1H), 3.15 (br, 1H), 1.80 – 1.60 (m, 2H), 1.58 – 1.29 (m, 6H), 0.95 – 0.86 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.01, 173.30, 164.57, 130.31, 126.28, 114.21, 73.90, 72.92, 66.30, 55.58, 32.36, 31.71, 25.56, 22.59, 14.02; **IR**: 3453, 2933, 1751, 1687, 1601, 1245, 1173, 972,836 cm^{-1}; **HRMS** (ESI) calcd for $C_{17}H_{25}O_6$ *m/z* $[M+H]^+$: 325.1651; found: 325.1647; $[\alpha]_D^{25}$= +20.4 (*c* 0.36, ethyl acetate); **HPLC** analysis: Chiralcel OD-H (Hex/IPA = 60/40, 1.0 mL/min, 254 nm, 25℃), 7.3, 8.0 (major) min, 86% *ee*.



2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-3-cyclohexyl-2,3-dihydroxypropanoate (2q): 70% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.59 (d, *J* = 16.3 Hz, 1H), 5.35 (d, *J* = 16.3 Hz, 1H), 4.48 (s, 1H), 3.88 (s, 3H), 3.79 (d, *J* = 9.2 Hz, 1H), 3.66 (br, 1H), 3.19 (br, 1H), 2.18 (d, *J* = 13.4 Hz, 1H), 1.85 – 1.63 (m, 5H), 1.35 – 0.96 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.10, 173.86, 164.54, 130.30, 126.28, 114.19, 71.80, 66.26, 55.57, 38.98, 29.83, 28.90, 26.33, 25.88; **IR**: 3455, 2926, 1750, 1681, 1602, 1244, 1173, 968, 836 cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{25}O_6$ *m/z* $[M+H]^+$: 337.1651; found: 337.1643; $[\alpha]_D^{25}$= +25.9 (*c* 0.48, ethyl acetate); **HPLC** analysis: Chiralcel OJ-H (Hex/IPA = 60/40, 0.8 mL/min, 230 nm, 25℃), 11.6 (major), 13.3 min, 91% *ee*.

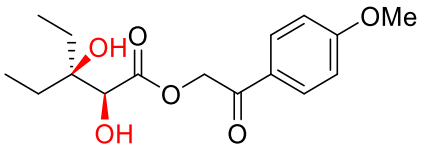


2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-2-methylbutanoate (2r): 35% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.60 (d, *J* = 16.2 Hz, 1H), 5.32 (d, *J* = 16.2 Hz, 1H), 4.23 – 4.12 (m, 1H), 4.10 – 3.98 (m, 1H), 3.88 (s, 3H), 3.40 (s, 1H), 1.42 (s, 3H), 1.27 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.26, 175.61, 164.58, 130.31, 126.28, 114.21, 78.02, 72.03, 66.29, 55.57, 20.95, 15.19; **IR**: 3454, 2360, 1753, 1686, 1632, 1241, 1174, 969, 834 cm^{-1}; **HRMS** (ESI) calcd for $C_{14}H_{19}O_6$ *m/z* $[M+H]^+$: 283.1182; found: 283.1178; $[\alpha]_D^{25}$= +6.3 (*c* 0.30, ethyl acetate); **HPLC** analysis: Chiralcel AZ-H (Hex/IPA = 60/40, 1 mL/min, 254 nm, 25℃), 26.6 (major), 40.2 min, 92% *ee*.

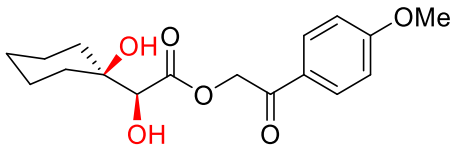


2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2,3-dihydroxy-3-methylbutanoate (4a)： 43% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.58 (d, *J* = 16.2 Hz, 1H), 5.42 (d, *J* = 16.2 Hz, 1H), 4.13 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 3.65 (s, 1H), 3.31 (s, 1H), 1.38 (s, 3H), 1.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.80, 172.83, 164.53, 130.26, 126.24, 114.20, 77.85, 72.25, 66.26, 55.57, 25.82, 24.73; **IR**: 3453, 2937, 1747, 1601, 1245, 1173, 1097, 970, 835 cm^{-1}; **HRMS** (ESI) calcd

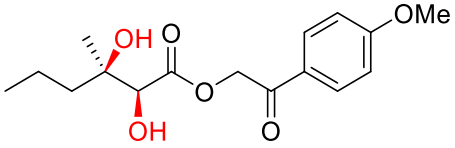
for $C_{14}H_{19}O_6$ *m/z* $[M+H]^+$: 283.1182; found: 283.1180; $[\alpha]_D^{25}$= +15.8 (*c* 0.46, ethyl acetate); **HPLC** analysis: Chiralcel OD-H (Hex/IPA = 80/20, 1.0 mL/min, 254 nm, 25℃), 15.3, 17.1 (major) min, 94% *ee*.



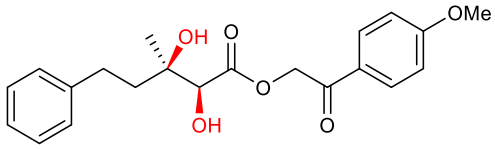
2-(4-methoxyphenyl)-2-oxoethyl (*S*)-3-ethyl-2,3-dihydroxypentanoate (4b): 41% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.65 – 5.39 (m, 2H), 4.28 (s, 1H), 3.88 (s, 3H), 3.38 (s, 1H), 3.33 (br, 1H), 1.77 – 1.56 (m, 4H), 1.04 – 0.90 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.91, 172.49, 164.49, 130.26, 126.30, 114.17, 76.34, 75.16, 66.08, 55.56, 26.85, 26.15, 7.61, 7.55; **IR**: 3460, 2936, 1744, 1601, 1242, 1173, 1097, 974, 833 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{23}O_6$ *m/z* $[M+H]^+$: 311.1495; found: 311.1488; $[\alpha]_D^{25}$= +16.9 (*c* 0.37, ethyl acetate); **HPLC** analysis: Chiralcel AD-H (Hex/IPA = 80/20, 1.0 mL/min, 254 nm, 25℃), 20.5 (major), 28.4 min, 93% *ee*.



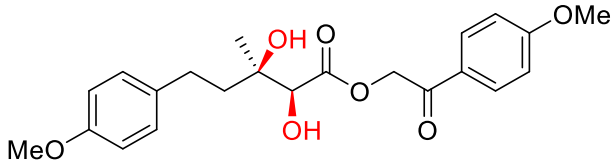
2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2-hydroxy-2-(1-hydroxycyclohexyl)acetate (4c): 45% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.52 (d, *J* = 16.2 Hz, 1H), 5.46 (d, *J* = 16.3 Hz, 1H), 4.14 (d, *J* = 7.3 Hz, 1H), 3.88 (s, 3H), 3.44 (s, 1H), 3.34 (d, *J* = 9.4 Hz, 1H), 1.82 – 1.49 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.04, 172.01, 164.47, 130.25, 126.24, 114.14, 73.15, 66.07, 55.55, 33.68, 32.49, 25.60, 21.57; **IR**: 3462, 2931, 1745, 1686, 1601, 1242, 1173, 976, 835 cm^{-1}; **HRMS** (ESI) calcd for $C_{17}H_{23}O_6$ *m/z* $[M+H]^+$: 323.1495; found: 323.1489; $[\alpha]_D^{25}$= +15.6 (*c* 0.44, ethyl acetate); **HPLC** analysis: Chiralcel AD-H (Hex/IPA = 80/20, 1.0 mL/min, 254 nm, 25℃), 24.0 (major), 35.9 min, 93% *ee*.



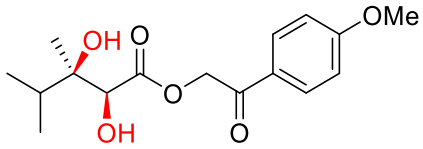
2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-3-methylhexanoate (4d): 41% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.55 – 5.40 (m, 2H), 4.16 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.55 – 3.27 (m, 2H), 1.78 – 1.39 (m, 4H), 1.32 (s, 3H), 0.96 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.78, 172.21, 164.49, 130.23, 126.38, 114.18, 74.09, 66.16, 55.55, 39.72, 22.79, 16.48, 14.60; **IR**: 3463, 2960, 1745, 1602, 1241, 1173, 972, 834, 565 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{23}O_6$ *m/z* $[M+H]^+$: 311.1495; found: 311.1487; $[\alpha]_D^{25}$= +13.7 (*c* 0.49, ethyl acetate); **HPLC** analysis: Chiralcel OD-H (Hex/IPA = 80/20, 1.0 mL/min, 254 nm, 25℃), 12.4, 14.0 (major) min, 94% *ee*.



2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-3-methyl-5-phenylpentanoate (4e)： 52% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.9 Hz, 2H), 7.35 – 7.23 (m, 4H), 7.21 – 7.13 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.65 – 5.39 (m, 2H), 4.25 (d, *J* = 7.6 Hz, 1H), 3.89 (s, 3H), 3.65 (s, 1H), 3.43 (d, *J* = 8.2 Hz, 1H), 2.98 – 2.68 (m, 2H), 2.11 – 1.91 (m, 2H), 1.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.75, 172.15, 164.52, 142.40, 130.24, 128.44, 128.31, 126.32, 125.67, 114.20, 73.95, 66.26, 55.55, 39.21, 29.88, 22.79; **IR**: 3451, 2935, 1745, 1601, 1242, 1172, 969, 833, 700 cm^{-1}; **HRMS** (ESI) calcd for $C_{21}H_{25}O_6$ *m/z* $[M+H]^+$: 373.1651; found: 373.1658; $[\alpha]_D^{25}$= –1.7 (*c* 0.65, ethyl acetate); **HPLC** analysis: Chiralcel OD-H (Hex/IPA = 80/20, 1.0 mL/min, 254 nm, 25℃), 36.9 (major), 42.8 min, 95% *ee*.

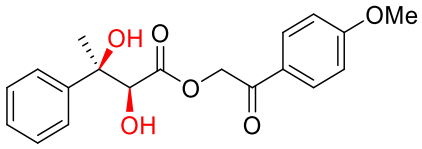


2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-5-(4-methoxyphenyl)-3-methylpentanoate (4f)： 46% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.51 (d, *J* = 16.2 Hz, 1H), 5.46 (d, *J* = 16.2 Hz, 1H), 4.23 (d, *J* = 6.9 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 3.61 (s, 1H), 3.41 (d, *J* = 7.2 Hz, 1H), 2.88 – 2.53 (m, 2H), 2.06 – 1.85 (m, 2H), 1.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.75, 172.16, 164.51, 157.66, 134.44, 130.24, 129.29, 126.33, 114.20, 113.74, 73.95, 66.63, 55.55, 55.21, 39.44, 28.94, 23.17; **IR**: 3451, 2931, 1745, 1512, 1244, 1173, 1031, 970, 931 cm^{-1}; **HRMS** (ESI) calcd for $C_{22}H_{27}O_7$ *m/z* $[M+H]^+$: 403.1757; found: 403.1751; $[\alpha]_D^{25}$= –2.8 (*c* 0.70, ethyl acetate); **HPLC** analysis: Chiralcel AD-H (Hex/IPA = 70/30, 1.0 mL/min, 254 nm, 25℃), 23.6 (major), 26.8 min, 97% *ee*.

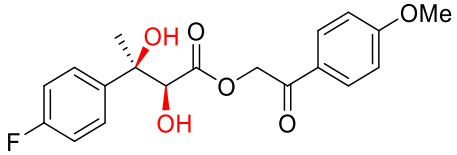


2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-3,4-dimethylpentanoate (4g)： 48% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.66 (d, *J* = 16.4 Hz, 1H), 5.27 (d, *J* = 16.4 Hz, 1H), 4.30 (d, *J* = 6.2 Hz, 1H), 3.87 (s, 3H), 3.67 (d, *J* = 8.4 Hz, 1H), 3.51 (s, 1H), 2.26 (p, *J* = 6.9 Hz, 1H), 1.19 (s, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.16, 172.13, 164.44, 130.22, 126.25, 114.13, 76.30, 75.74, 66.04, 55.53, 32.16, 17.74, 17.36, 16.40; **IR**: 3460, 2962, 1743, 1601, 1240, 1172, 1092, 973, 834 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{23}O_6$ *m/z* $[M+H]^+$: 311.1495; found: 311.1500; $[\alpha]_D^{25}$= –1.1 (*c* 0.46, ethyl acetate); **HPLC** analysis: Chiralcel AZ-H (Hex/IPA = 70/30, 1.0 mL/min, 254 nm, 25℃),

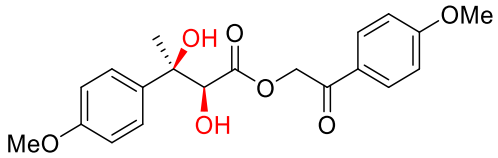
21.1 (major), 30.0 min, 97% *ee*.



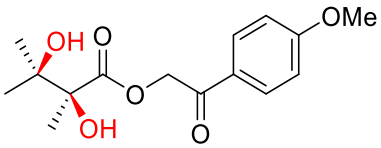
2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-3-phenylbutanoate (4h)： 31% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 7.1 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 5.64 (d, *J* = 16.3 Hz, 1H), 5.34 (d, *J* = 16.3 Hz, 1H), 4.55 (d, *J* = 6.9 Hz, 1H), 4.28 (s, 1H), 3.90 (s, 3H), 3.14 (d, *J* = 9.1 Hz, 1H), 1.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.98, 171.32, 164.61, 143.71, 130.36, 128.19, 127.15, 126.26, 125.17, 114.25, 78.30, 75.64, 66.27, 55.60, 26.82; **IR**: 3456, 2924, 1745, 1686, 1600, 1239, 1172, 972, 701 cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{21}O_6$ *m/z* $[M+H]^+$: 345.1338; found: 345.1330; $[\alpha]_D^{25}$= –24.5 (*c* 0.25, ethyl acetate); **HPLC** analysis: Chiralcel AD-H (Hex/IPA = 80/20, 1.0 mL/min, 254 nm, 25℃), 36.1, 39.0 (major) min, 98% *ee*.



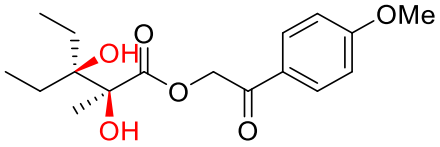
2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-3-(4-fluorophenyl)-2,3-dihydroxybutanoate (4i)： 31% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.52 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 5.59 (d, *J* = 16.3 Hz, 1H), 5.36 (d, *J* = 16.2 Hz, 1H), 4.49 (s, 1H), 3.89 (s, 3H), 1.70 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.93, 171.26, 164.66, 163.12, 160.67, 139.49, 130.35, 127.11, 127.03, 126.20, 115.00, 114.79, 114.26, 78.24, 75.41, 66.30, 55.60, 26.81; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –115.92; **IR**: 3461, 2938, 1744, 1601, 1511, 1236, 1173, 972, 836 cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{20}O_6F$ *m/z* $[M+H]^+$: 363.1244; found: 363.1253; $[\alpha]_D^{25}$= –23.8 (*c* 0.54, ethyl acetate); **HPLC** analysis: Chiralcel AD-H (Hex/IPA = 80/20, 1.0 mL/min, 254 nm, 25℃), 38.3, 42.7 (major) min, 97% *ee*.



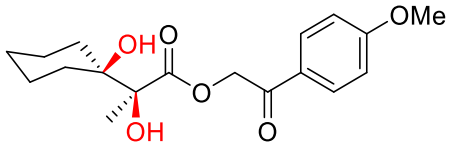
2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-3-(4-methoxyphenyl)butanoate (4j)： 20% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.60 (d, *J* = 16.3 Hz, 1H), 5.34 (d, *J* = 16.3 Hz, 1H), 4.49 (d, *J* = 8.8 Hz, 1H), 4.22 (s, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 3.12 (d, *J* = 9.0 Hz, 1H), 1.70 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.91, 171.42, 164.59, 158.58, 135.72, 130.34, 126.45, 126.30, 114.23, 113.49, 78.33, 75.39, 66.24, 55.59, 55.17, 26.79; **IR**: 3455, 2935, 1744, 1687 1600, 1247, 1174, 972, 833 cm^{-1}; **HRMS** (ESI) calcd for $C_{20}H_{23}O_7$ *m/z* $[M+H]^+$: 323.1444; found: 375.1440; $[\alpha]_D^{25}$= –25.4 (*c* 0.54, ethyl acetate); **HPLC** analysis: Chiralcel AZ-H (Hex/IPA = 60/40, 1.0 mL/min, 254 nm, 25℃), 40.0 (major), 54.0 min, 98% *ee*.



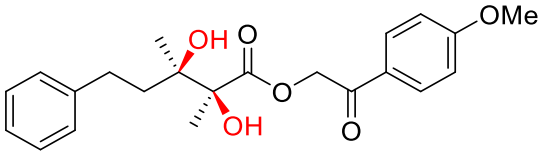
2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2,3-dihydroxy-2,3-dimethylbutanoate (4k)： 62% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.58 (d, *J* = 16.3 Hz, 1H), 5.38 (d, *J* = 16.3 Hz, 1H), 3.94 – 3.72 (m, 5H), 1.49 (s, 3H), 1.34 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.22, 174.59, 164.51, 130.26, 126.25, 114.18, 79.99, 74.35, 66.31, 55.56, 24.48, 23.48, 19.97; **IR**: 3463, 2940, 1740, 1601, 1238, 1174, 1113, 967, 832 cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{21}O_6$ *m/z* $[M+H]^+$: 297.1338; found: 297.1343; $[\alpha]_D^{25}$= +0.14 (*c* 0.72, ethyl acetate); **HPLC** analysis: Chiralcel AZ-H (Hex/IPA = 60/40, 1.0 mL/min, 254 nm, 25°C), 22.0, 31.3 (major) min, 93% *ee*.



2-(4-methoxyphenyl)-2-oxoethyl (*S*)-3-ethyl-2,3-dihydroxy-2-methylpentanoate (4l)： 40% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.60 (d, *J* = 16.3 Hz, 1H), 5.37 (d, *J* = 16.3 Hz, 1H), 3.88 (s, 3H), 3.71 (s, 1H), 3.61 (s, 1H), 1.83 – 1.64 (m, 4H), 1.51 (s, 3H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.15, 174.92, 164.50, 130.27, 126.36, 114.19, 81.01, 66.15, 55.57, 26.81, 25.32, 20.37, 8.92, 8.42; **IR**: 3467, 2940, 1738, 1683, 1601, 1235, 1173, 969, 833 cm^{-1}; **HRMS** (ESI) calcd for $C_{17}H_{25}O_6$ *m/z* $[M+H]^+$: 325.1651; found: 325.1658; $[\alpha]_D^{25}$= +3.5 (*c* 0.63, ethyl acetate); **HPLC** analysis: Chiralcel AZ-H (Hex/IPA = 70/30, 1.0 mL/min, 254 nm, 25°C), 23.2 (major), 26.5 min, 74% *ee*.

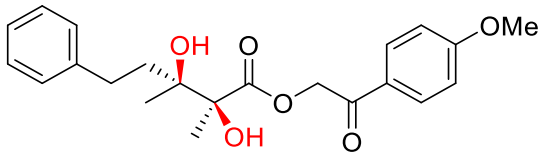


2-(4-methoxyphenyl)-2-oxoethyl (*S*)-2-hydroxy-2-(1-hydroxycyclohexyl)propanoate (4m)： 65% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.54 (d, *J* = 16.3 Hz, 1H), 5.40 (d, *J* = 16.3 Hz, 1H), 3.87 (s, 3H), 3.75 (br, 1H), 3.47 (br, 1H), 1.85 – 1.28 (m, 13H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.12, 174.74, 164.45, 130.24, 126.32, 114.14, 80.40, 74.85, 66.26, 55.54, 30.90, 29.99, 25.72, 21.51, 21.45, 19.42; **IR**: 3465, 2935, 1737, 1601, 1236, 1173, 1139, 970, 828 cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{25}O_6$ *m/z* $[M+H]^+$: 337.1651; found: 337.1660; $[\alpha]_D^{25}$= +7.5 (*c* 0.84, ethyl acetate); **HPLC** analysis: Chiralcel AZ-H (Hex/IPA = 70/30, 1.0 mL/min, 254 nm, 25°C), 22.4 (major), 31.4 min, 80% *ee*.

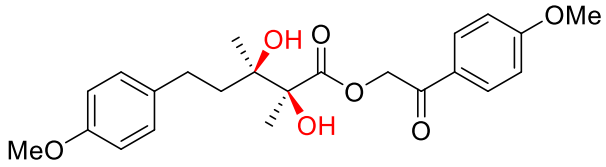


2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-2,3-dimethyl-5-phenylpentanoate (4n)： 57% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d,

J = 8.5 Hz, 2H), 7.39 – 7.09 (m, 5H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.58 (d, *J* = 16.3 Hz, 1H), 5.42 (d, *J* = 16.2 Hz, 1H), 4.07 – 3.66 (m, 5H), 2.96 (t, *J* = 12.4 Hz, 1H), 2.73 (t, *J* = 12.8 Hz, 1H), 2.02 (t, *J* = 11.0 Hz, 1H), 1.93 – 1.75 (m, 1H), 1.50 (s, 3H), 1.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.27, 174.60, 164.53, 142.96, 130.26, 128.52, 128.27, 126.22, 125.57, 114.19, 80.52, 75.60, 66.28, 55.55, 37.15, 29.84, 20.59, 19.73; **IR**: 3450, 2938, 1740, 1601, 1236, 1173, 969, 832, 700 cm^{-1}; **HRMS** (ESI) calcd for $C_{22}H_{27}O_6$ *m/z* $[M+H]^+$: 387.1808; found: 387.1802; $[\alpha]_D^{25}$= –28.1 (*c* 0.70, ethyl acetate); **HPLC** analysis: Chiralcel OD-H (Hex/IPA = 70/30, 1.0 mL/min, 254 nm, 25℃), 16.6 (major), 26.7min, 90% *ee*.

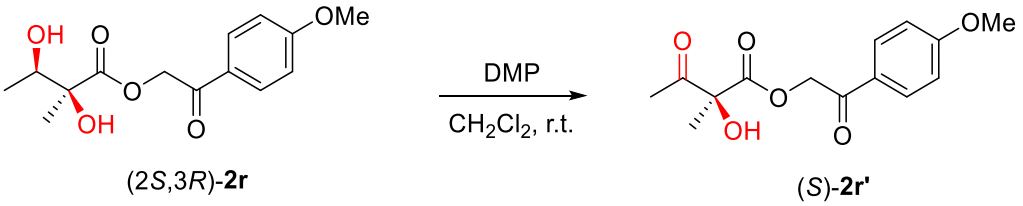


2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*S*)-2,3-dihydroxy-2,3-dimethyl-5-phenylpentanoate (4o): 44% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.20 – 7.12 (m, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.61 (d, *J* = 14.2 Hz, 1H), 5.36 (d, *J* = 16.3 Hz, 1H), 3.97 – 3.74 (m, 5H), 3.06 – 2.89 (m, 1H), 2.82 – 2.67 (m, 1H), 1.94 – 1.78 (m, 2H), 1.50 (s, 3H), 1.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.32, 174.36, 164.55, 142.74, 130.27, 128.52, 128.27, 126.25, 125.59, 114.20, 80.43, 76.06, 66.29, 55.56, 38.07, 29.99, 19.79, 19.56; **IR**: 3454, 2938, 1739, 1601, 1237, 1173, 969, 834, 701 cm^{-1}; **HRMS** (ESI) calcd for $C_{22}H_{27}O_6$ *m/z* $[M+H]^+$: 387.1808; found: 387.1809; $[\alpha]_D^{25}$= +20.2 (*c* 0.62, ethyl acetate); **HPLC** analysis: Chiralcel OD-H (Hex/IPA = 80/20, 1.0 mL/min, 254 nm, 25℃), 15.3 (major), 20.7 min, 62% *ee*.



2-(4-methoxyphenyl)-2-oxoethyl (2*S*,3*R*)-2,3-dihydroxy-5-(4-methoxyphenyl)-2,3-dimethylpentanoate (4p): 62% yield; White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.9 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.57 (d, *J* = 16.3 Hz, 1H), 5.41 (d, *J* = 16.3 Hz, 1H), 3.88 (s, 4H), 3.78 (s, 4H), 2.96 – 2.84 (m, 1H), 2.74 – 2.62 (m, 1H), 2.06 – 1.93 (m, 1H), 1.88 – 1.77 (m, 1H), 1.50 (s, 3H), 1.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.24, 174.64, 164.53, 157.57, 135.00, 130.25, 129.37, 126.27, 114.20, 113.69, 80.52, 75.58, 66.28, 55.55, 55.19, 37.39, 28.88, 20.59, 19.73; **IR**: 3450, 2938, 1677, 1601, 1512, 1239, 1174, 969, 827 cm^{-1}; **HRMS** (ESI) calcd for $C_{23}H_{29}O_7$ *m/z* $[M+H]^+$: 417.1913; found: 417.1906; $[\alpha]_D^{25}$= –28.0 (*c* 0.76, ethyl acetate); **HPLC** analysis: Chiralcel OJ-H (Hex/IPA = 65/35, 1.0 mL/min, 254 nm, 25℃), 46.1 (major), 56.9 min, 80% *ee*.

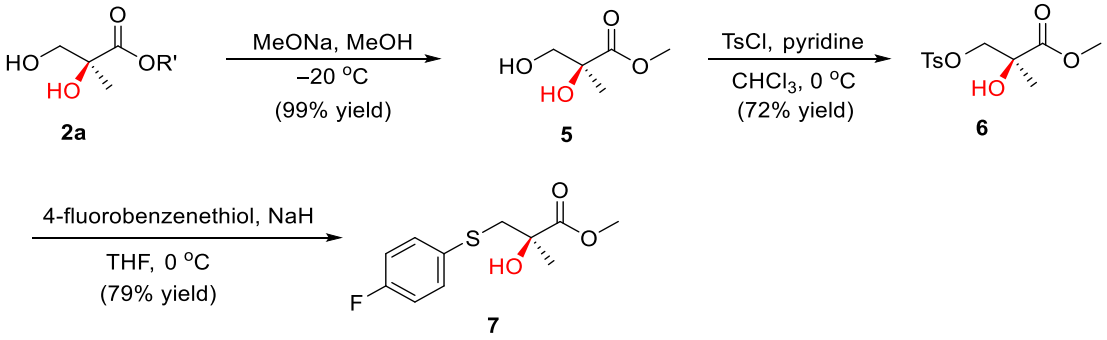
7. Determination of Absolute Configuration of Dihydroxylation Products.



(2*S*,3*R*)-**2r** (*S*)-**2r'**

Figure S5. Determination of Absolute Configuration of Dihydroxylation Products. Absolution of (*S*)-**2r'** was determined by comparison of chiral HPLC traces with previous report.[2] Product **2r** was determined to be (2*S*, 3*R*) based on that permanganate dihydroxylation is *syn*-selective. The absolute configuration of all other dihydroxylation products **2**/**4** was determined by analogy.

8. Application of Dihydroxylation Products in Bicalutamide Synthesis.



Methyl (*R*)-3-((4-fluorophenyl)thio)-2-hydroxy-2-methylpropanoate (7):

Step 1: Sodium methoxide (0.25 mmol) was added to a stirred solution of **2a** (0.25 mmol) in methanol (4 mL) at −20 ℃ and the resulting mixture was stirred for ca. 0.5 hours (t.l.c. control). The reaction was then quenched with water (10 mL), the organic phase was washed with sat. aqueous $NaHCO_3$ solution (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to afford the crude product. Purification by flash column chromatography to afford **5**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.79 (d, *J* = 11.4 Hz, 1H), 3.57 (d, *J* = 11.4 Hz, 1H), 1.35 (s, 3H).

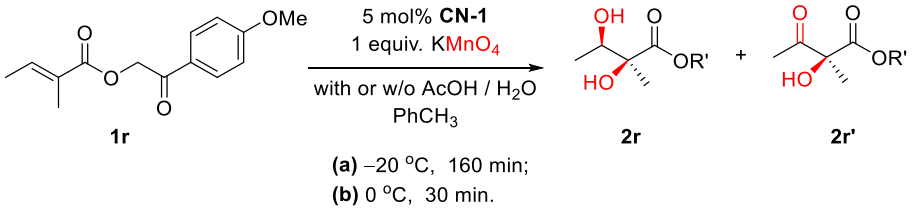
Step 2: **5** (32 mg, 0.24 mmol) was dissolved in chloroform (0.6 mL), pyridine (0.6 mL) was added, the temperature was lowered to 0 ℃, *p*-toluenesulfonyl chloride (68.6 mg, 0.36 mmol) was added, and the reaction solution was stirred at 0 ℃ for 10 minutes. Then warmed to room temperature and stirred for 17 h. 2M HCl (5 mL) was added to the reaction mixture and extracted with dichloromethane (10 mL×3), the organic layer was washed with saturated brine solution (10 mL), then dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. The crude reaction mixture was purified by silica gel column (silica gel, 1:2 EtOAc/Petroleum ether) to give product **6**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 4.22 (d, *J* = 9.8 Hz, 1H), 3.99 (d, *J* = 9.8 Hz, 1H), 3.75 (s, 3H), 3.39 (br, 1H), 2.45 (s, 3H), 1.36 (s, 3H).

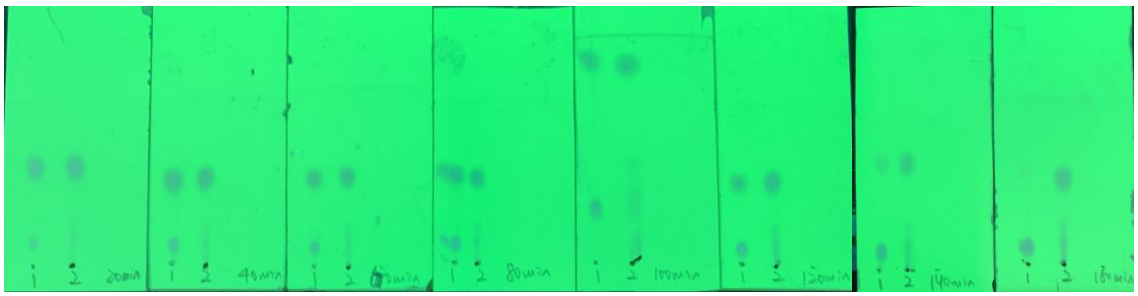
Step 3: Under nitrogen protection, NaH (20.4 mg, 0.51 mmol) was dissolved in THF (2 mL), and *p*-fluorothiophenol (65.4 mg, 0.51 mmol) was added dropwise to the reaction system at 0 ℃, and the reaction was carried out at 0 ℃ for 1 h. Then **6** (49.8 mg, 0.17 mmol) was dissolved in THF (2 mL), added to the reaction solution, and the reaction was carried out at room temperature for 3 h. After the reaction was completed, water (10 mL) was added, and then EtOAc (10 mL×3) was added for extraction. The organic layer was washed with saturated brine (10 mL), then dried, filtered and the solvent was spin-dried. Purification by flash column chromatography (silica gel, 1:10 EtOAc/Petroleum ether) afforded **7** (56% yield for three steps) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.9, 5.2 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 3.53 (s, 3H), 3.34 (d, *J* = 13.9 Hz, 1H), 3.13 (d, *J* = 13.9 Hz, 1H), 1.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.33, 163.25, 160.79, 133.57, 133.49, 130.49, 116.05, 115.83, 74.54, 52.65, 46.03, 25.47; **HRMS** (ESI) calcd for $C_{11}H_{13}O_3SF$ *m/z* $[M+Na]^+$: 267.0467; found: 267.0470; **HPLC** analysis: Chiralcel OJ-H (Hex/IPA = 60/40, 0.8 mL/min, 254 nm, 25℃), 8.2 (major), 8.6 min, 83% *ee*.

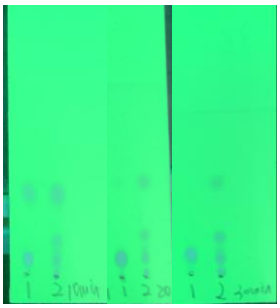
9. Mechanistic Studies.

Reaction kinetics of asymmetric oxohydroxylation and dihydroxylation monitored by thin layer chromatography (TLC) analysis.





(a) Permanganate oxidation reaction at −20 °C for 160 min (Lane 1: oxohydroxylation, with AcOH; Lane 2: dihydroxylation, without AcOH)



(b) Permanganate oxidation reaction at 0 °C for 30 min (Lane 1: oxohydroxylation, with AcOH; Lane 2: dihydroxylation, without AcOH)

Figure S6. Reaction kinetics of permanganate oxidation of **1r** in the presence and absence of AcOH monitored by TLC analysis. The reaction kinetics indicate that permanganate oxidation of **1r** is much faster in the presence of AcOH than in the absence of AcOH.

10. Reference

1. Tozawa, T.; Nagao, H.; Yamane, Y.; Mukaiyama, T., Enantioselective Synthesis of 3,4-Dihydropyran-2-ones by Domino Michael Addition and Lactonization with New Asymmetric Organocatalysts: Cinchona-Alkaloid-Derived Chiral Quaternary Ammonium Phenoxides. *Asian J. Chem.*, **2007**, *2* (1), 123–134.
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3. O. Bertrand, J.-F. Gohy and C.-A. Fustin, Synthesis of diblock copolymers bearing p-methoxyphenacyl side groups. *Polym. Chem.*, **2011**, *2*, 2284−2292.
4. B. B. C. Peters, J. Jongcharoenkamol, S. Krajangsri and P. G. Andersson, Highly Enantioselective Iridium-Catalyzed Hydrogenation of Conjugated Trisubstituted Enones. *Org. Lett.*, **2021**, *23*, 242−246.
5. N. Umemoto, A. Imayoshi and K. Tsubaki, Development of regioselective [2 + 3] cycloaddition reactions of nitrile oxides with alkenes using intramolecular reactions through oxime groups. *Tetrahedron,* **2022**, *120*, 132833.
6. J. H. Kim, Y. S. Chun and S.-g. Lee, Tandem Blaise/retro-Blaise Reaction for the Nitrile-Mediated Regioselective Intermolecular Addition of Unstabilized Zinc Ester Enolates (Reformatsky Reagents) to 1-Alkynes and 1,3-Enynes. *J. Org. Chem.*, **2013**, *78*, 11483−11493.

11. Selected NMR Spectra and HPLC Traces

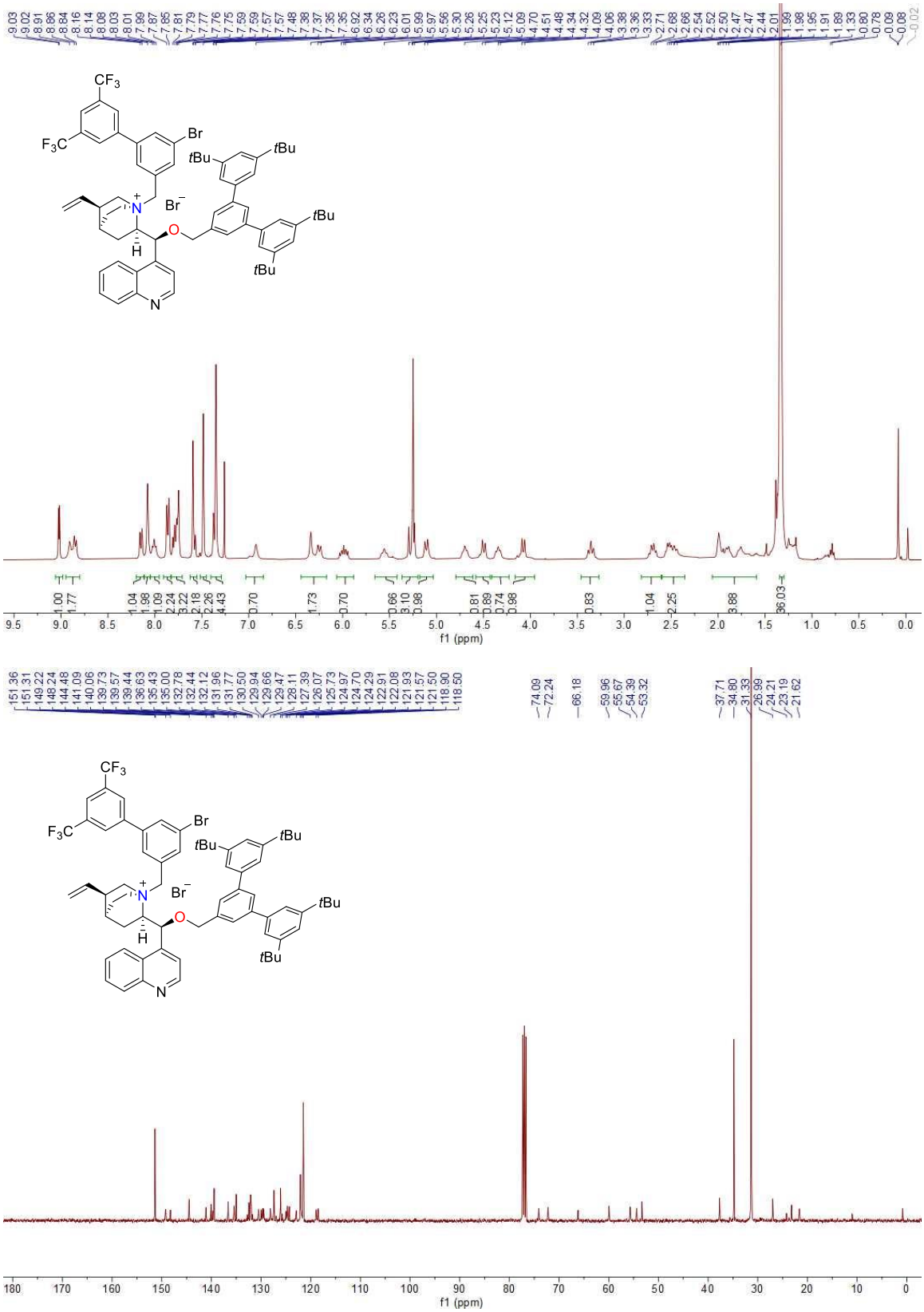


Figure S7. ^{1}H and ^{13}C NMR spectra of **CN-4** in $CDCl_3$.

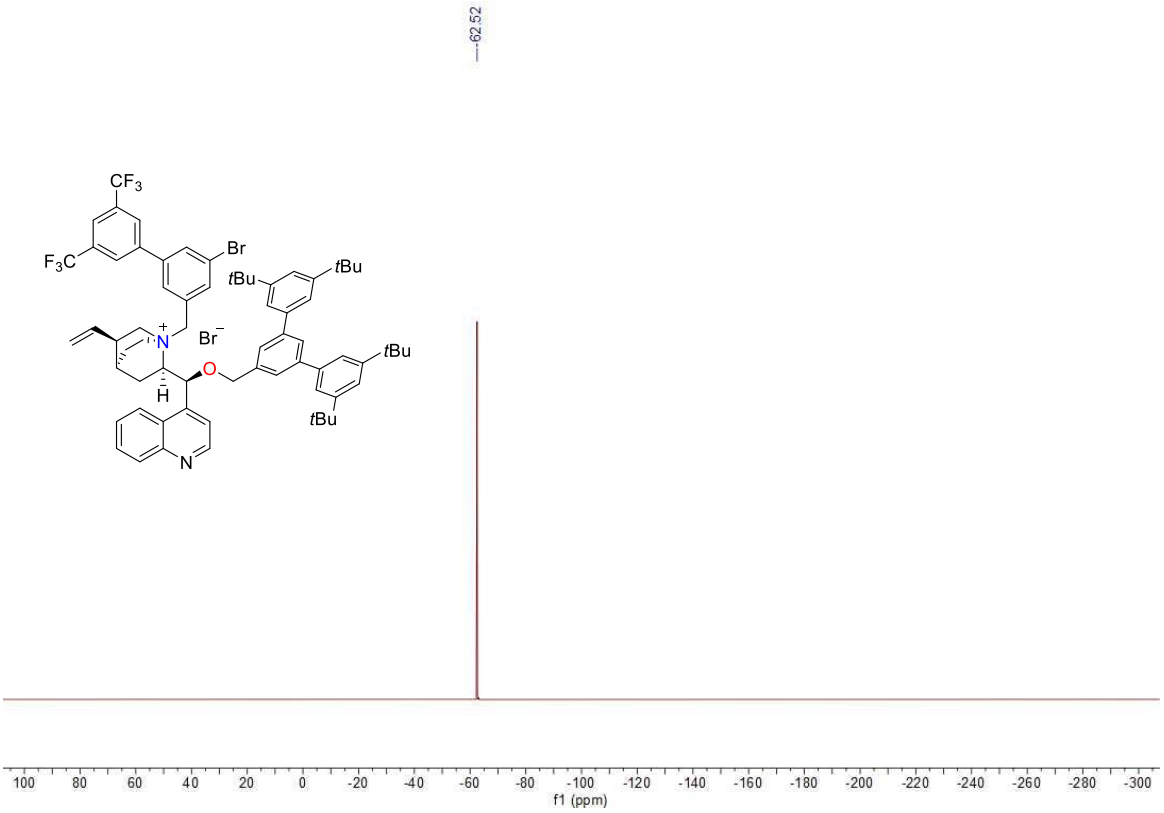


Figure S8. ^{19}F NMR spectra of **CN-4** in $CDCl_3$.

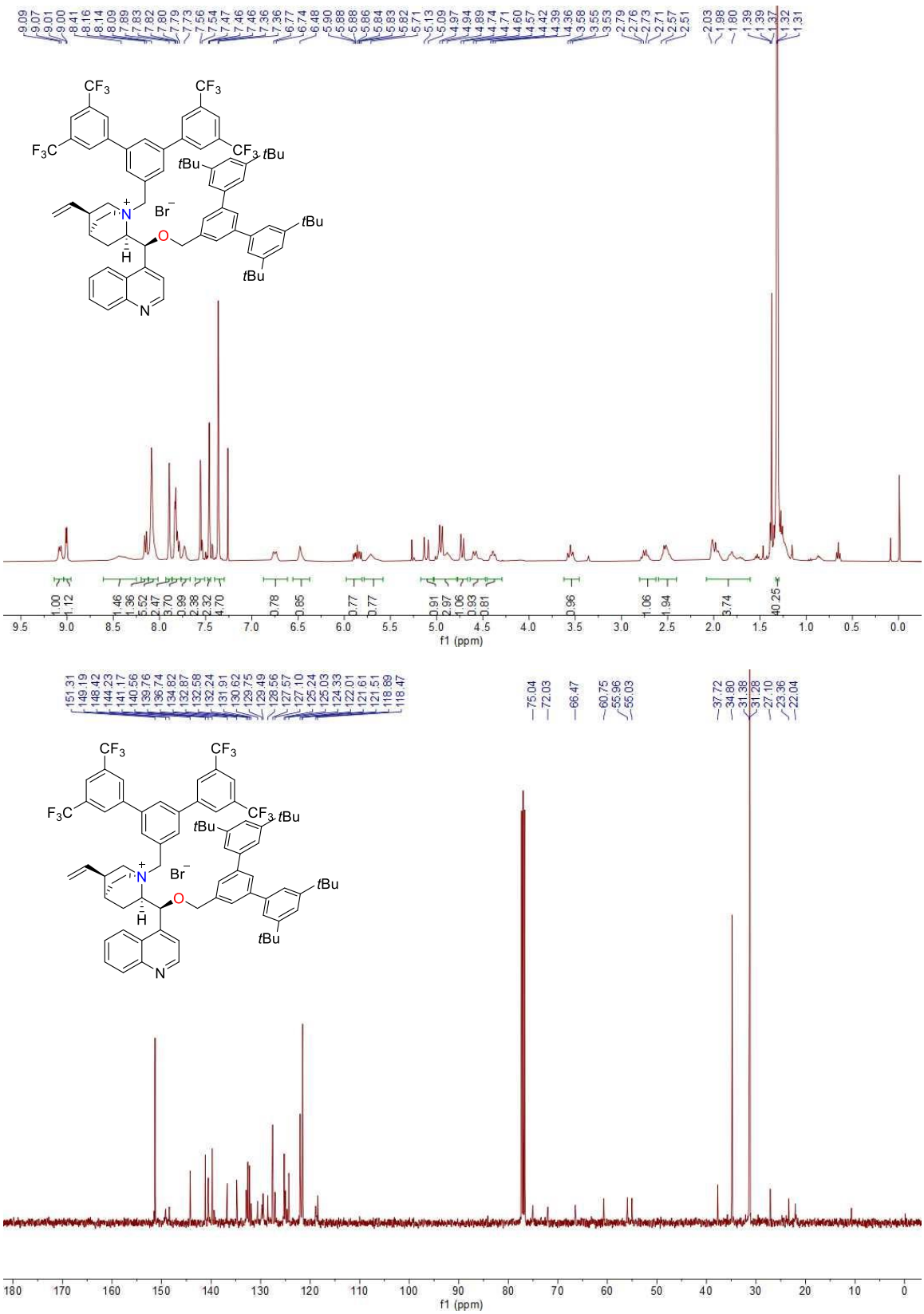


Figure S9. ^{1}H and ^{13}C NMR spectra of **CN-5** in $CDCl_3$.

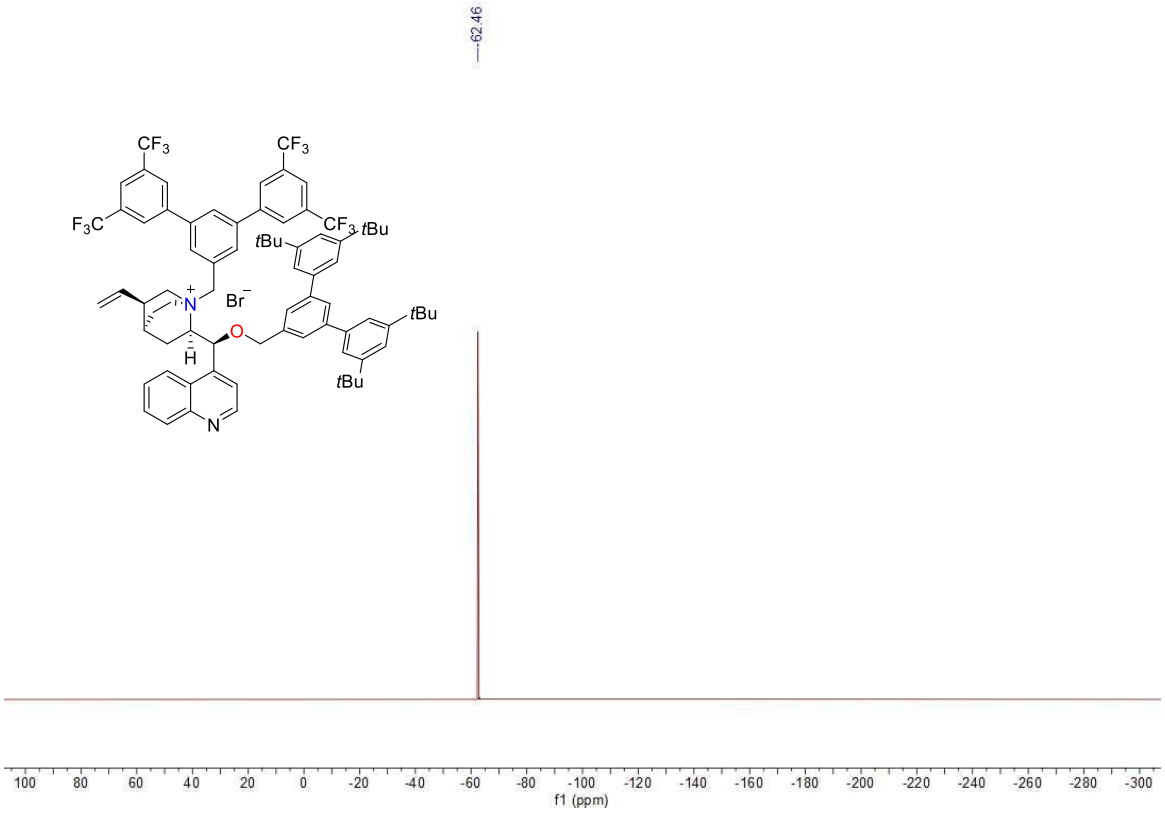


Figure S10. ^{19}F NMR spectra of **CN-5** in $CDCl_3$.

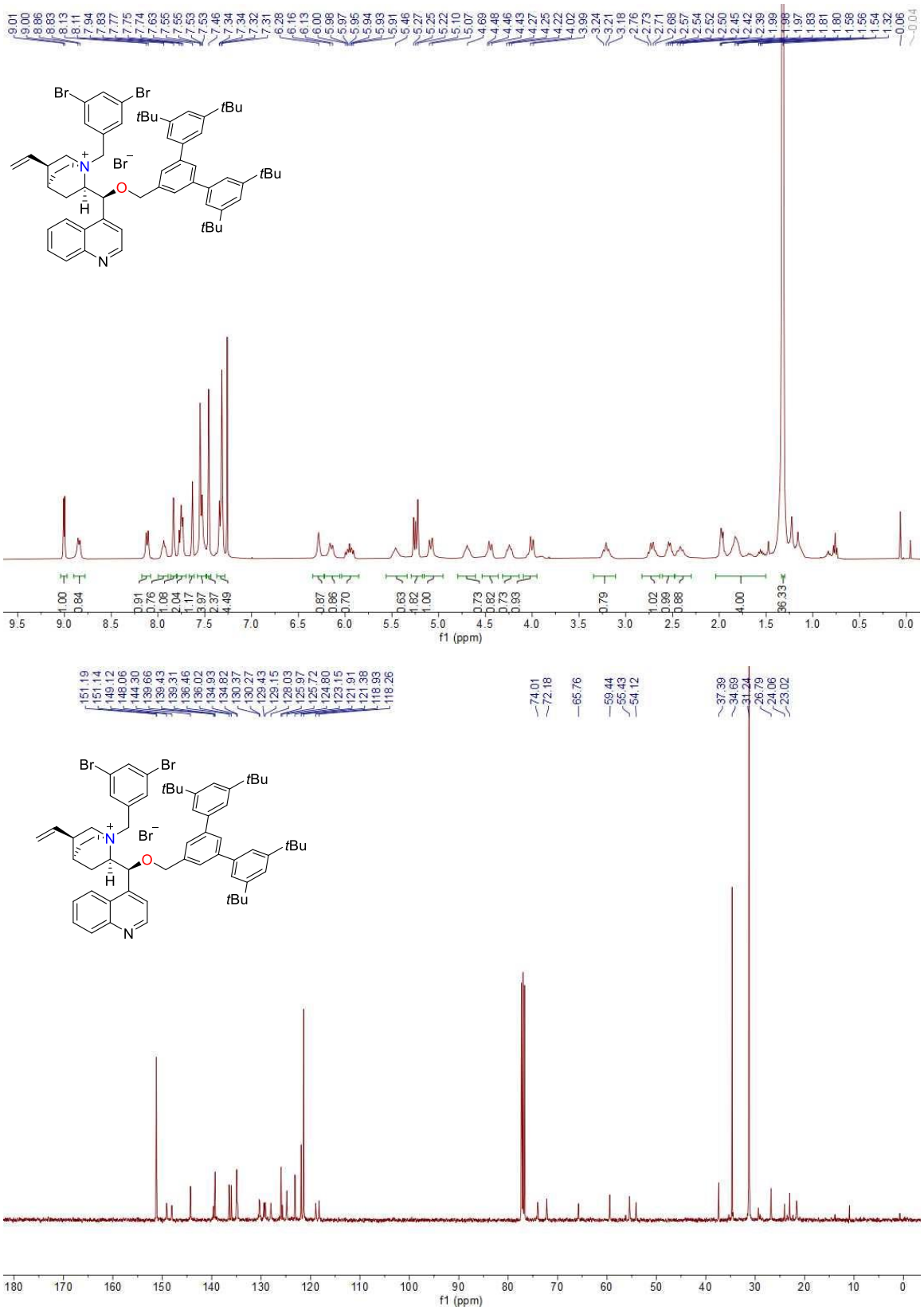


Figure S11. ^{1}H and ^{13}C NMR spectra of **CN-6** in $CDCl_3$.

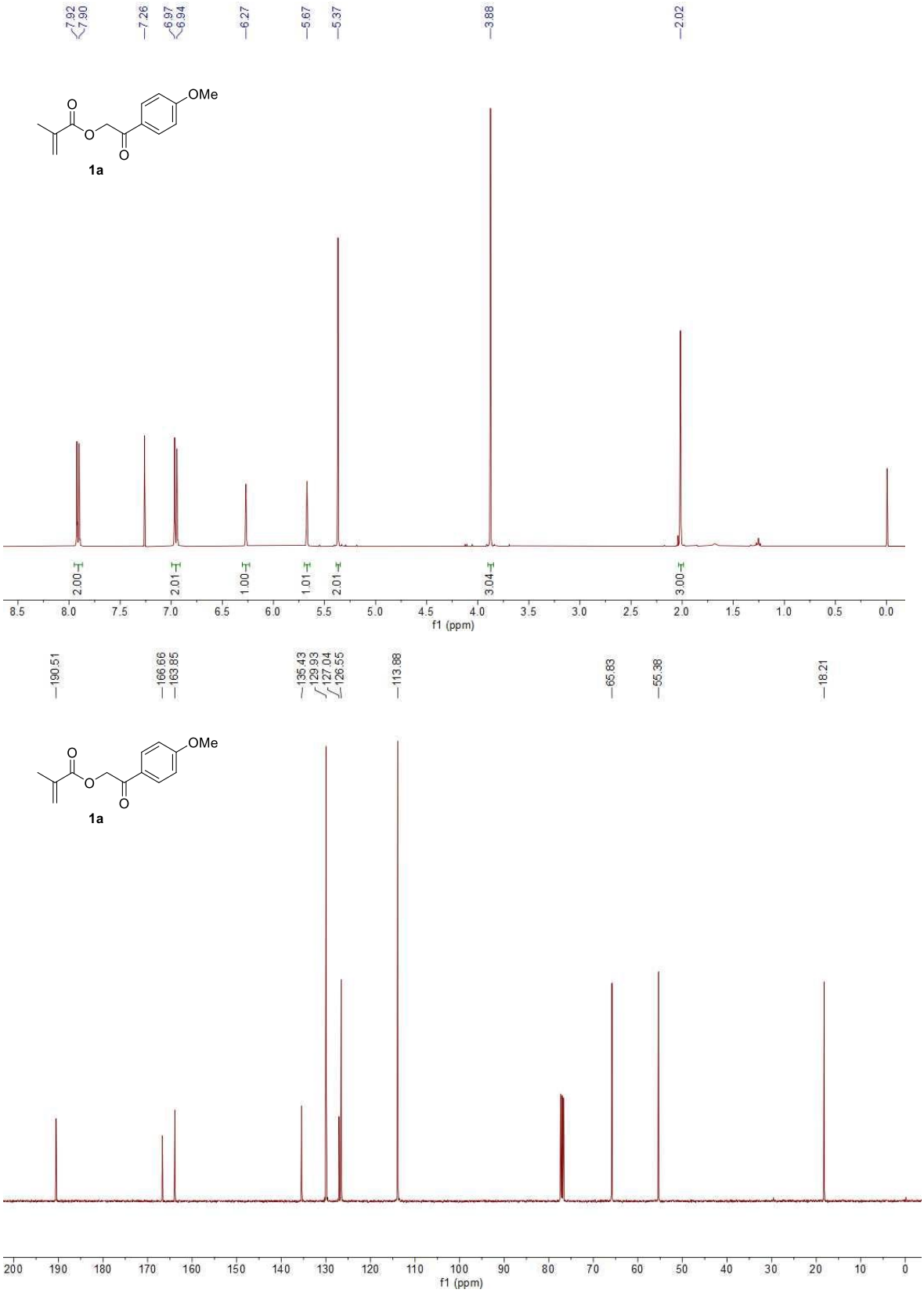


Figure S12. ^{1}H and ^{13}C NMR spectra of **1a** in $CDCl_3$.

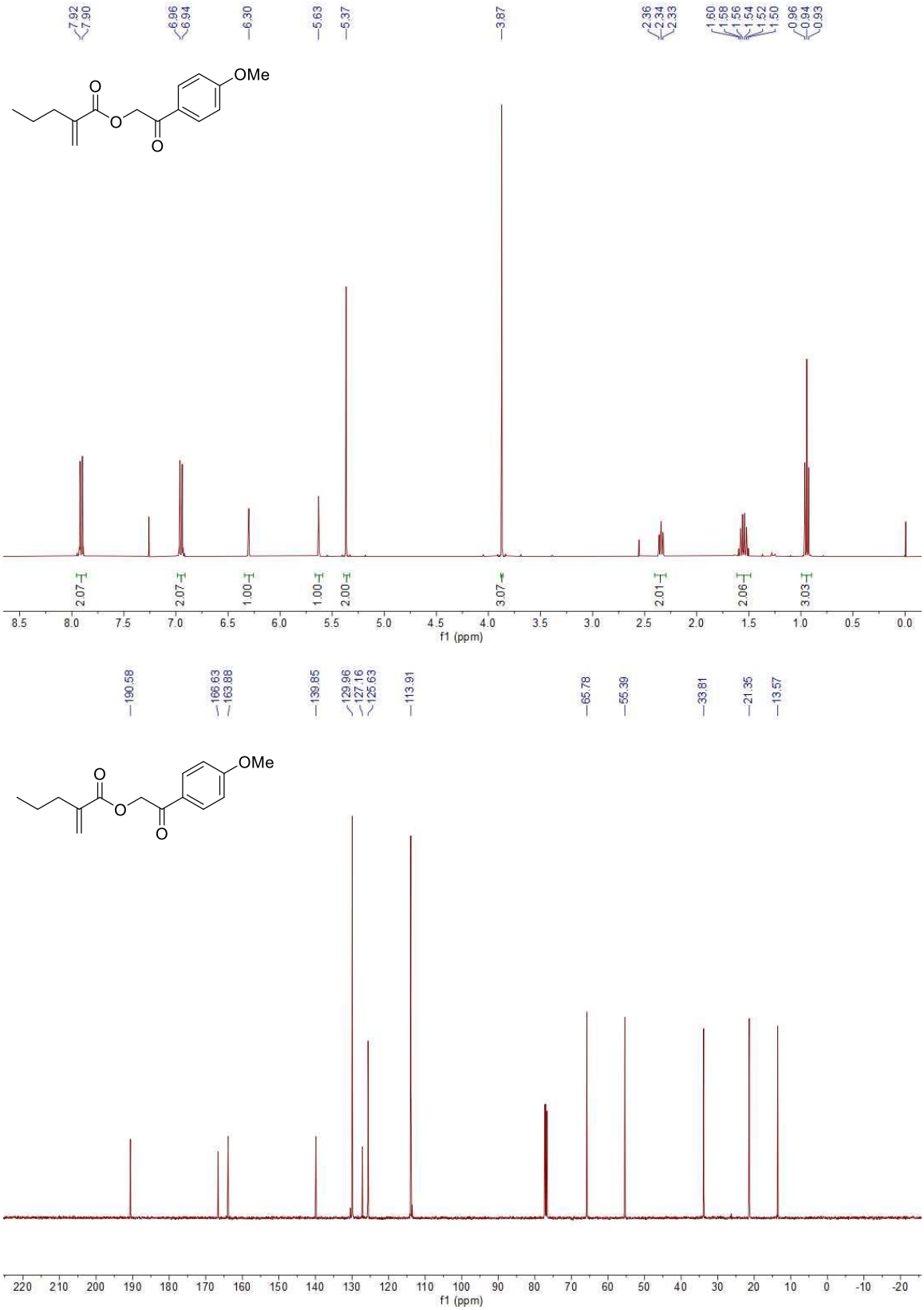


Figure S13. ^{1}H and ^{13}C NMR spectra of **1b** in $CDCl_3$.

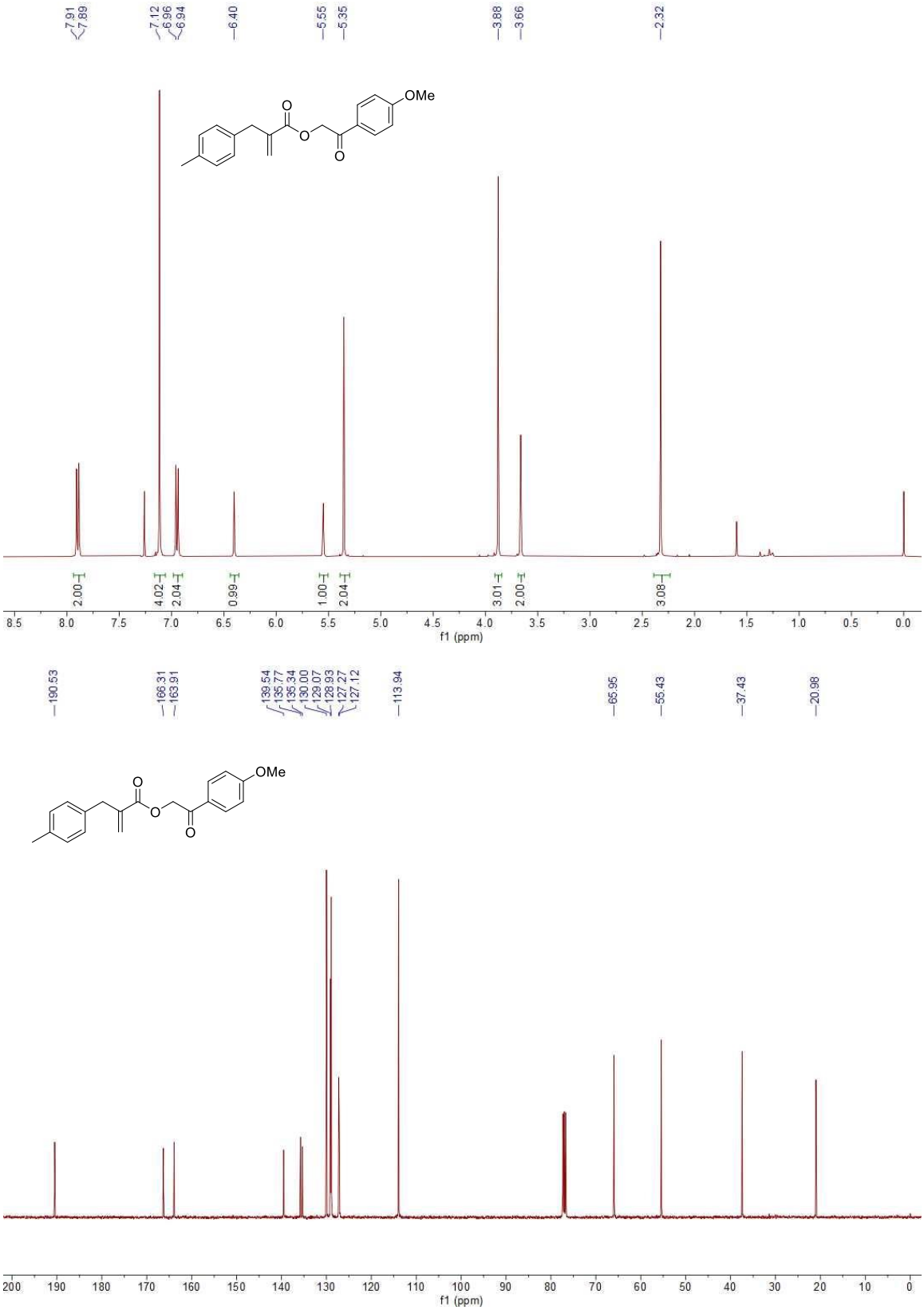


Figure S14. ^{1}H and ^{13}C NMR spectra of **1f** in $CDCl_3$.

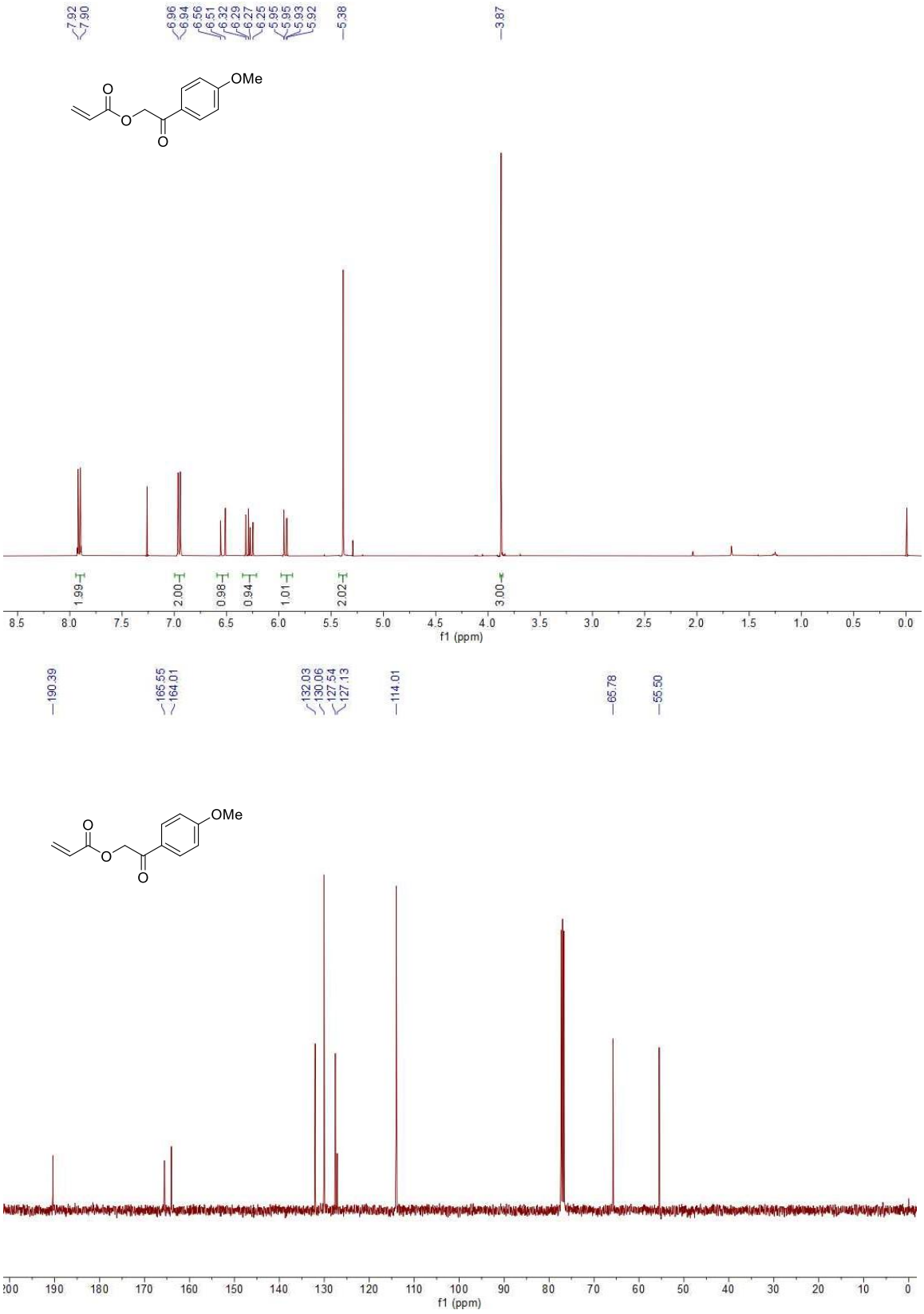


Figure S15. ^{1}H and ^{13}C NMR spectra of **1i** in $CDCl_3$.

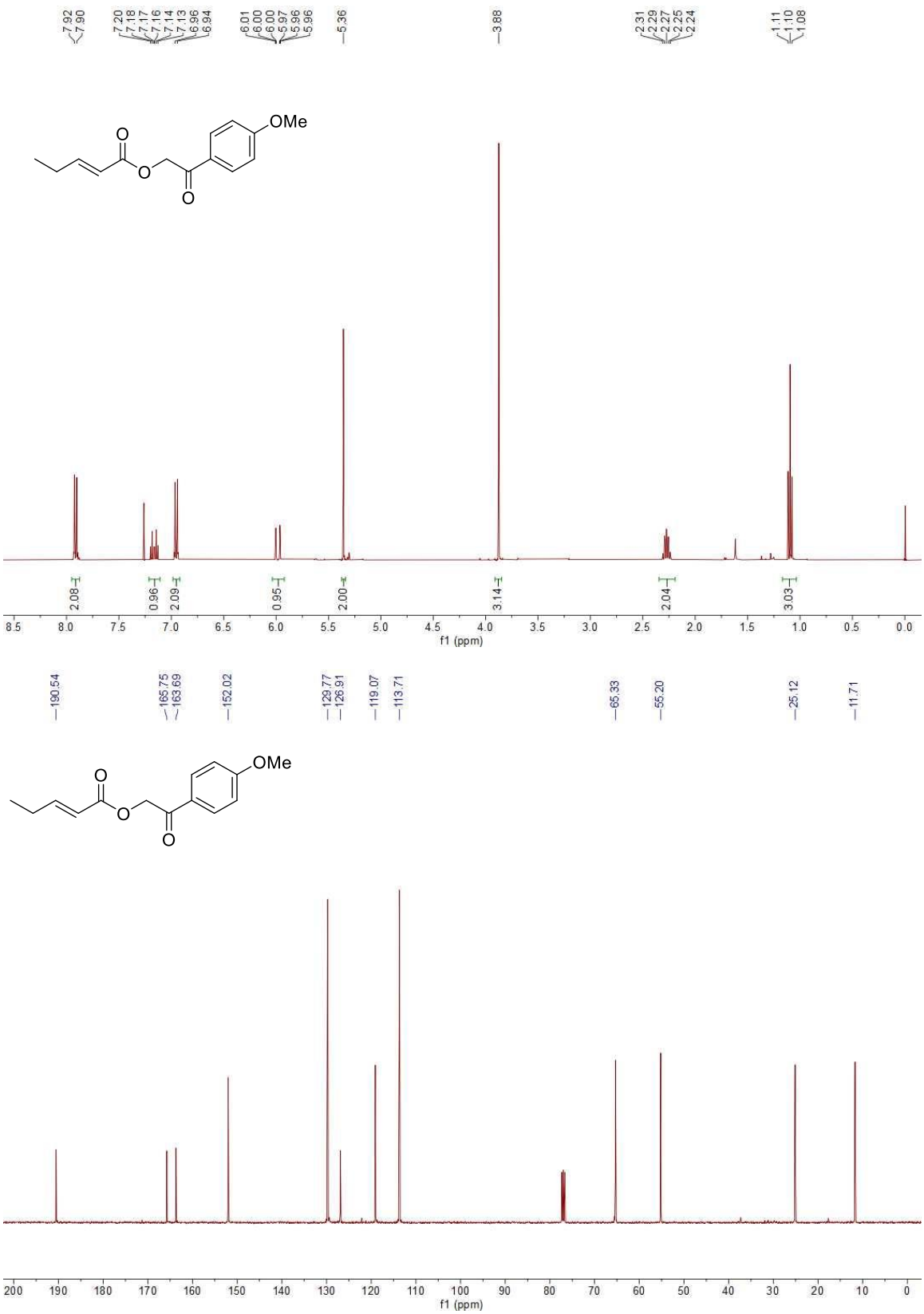


Figure S16. ^{1}H and ^{13}C NMR spectra of **1k** in $CDCl_3$.

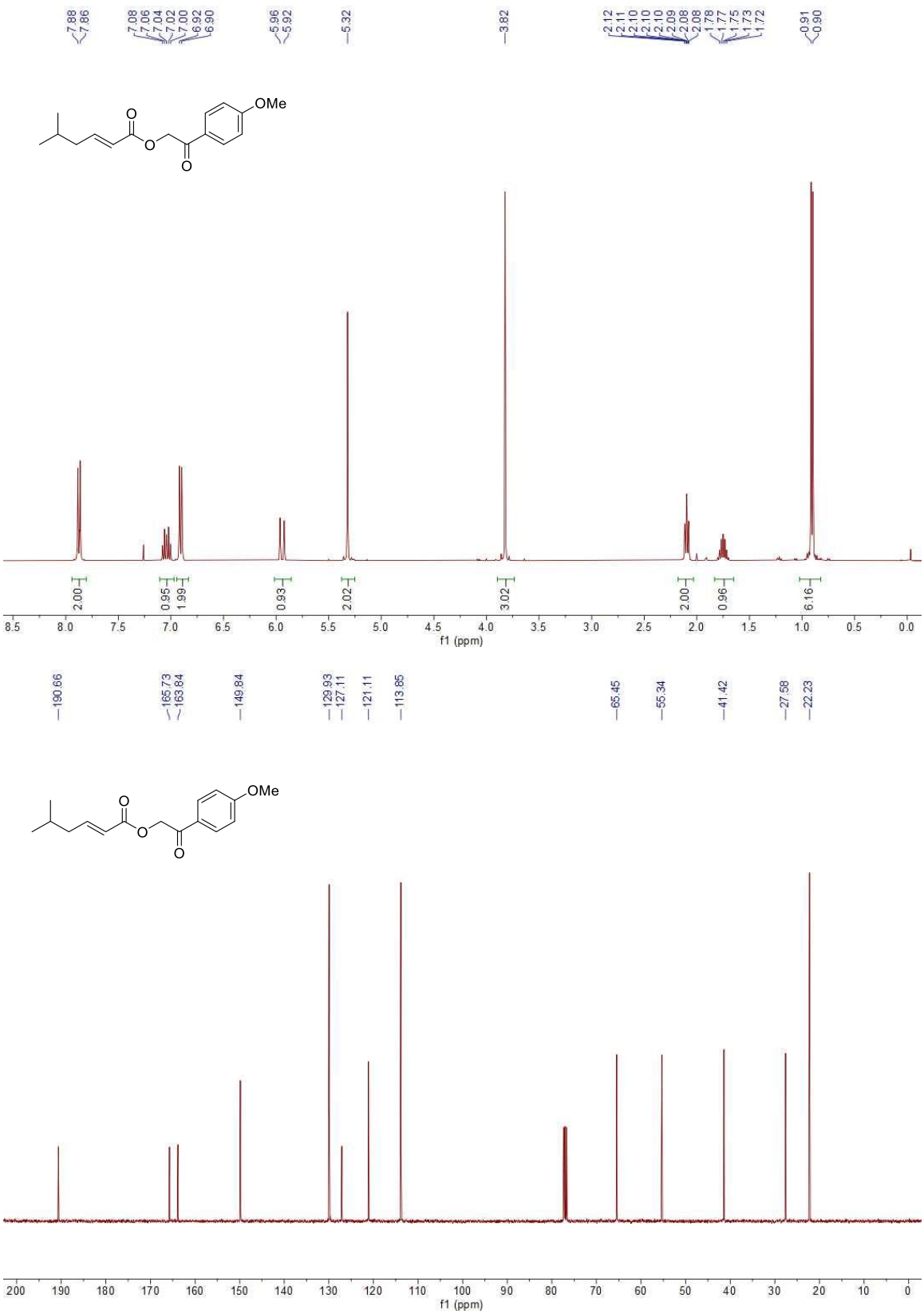


Figure S17. ^{1}H and ^{13}C NMR spectra of **1n** in $CDCl_3$.

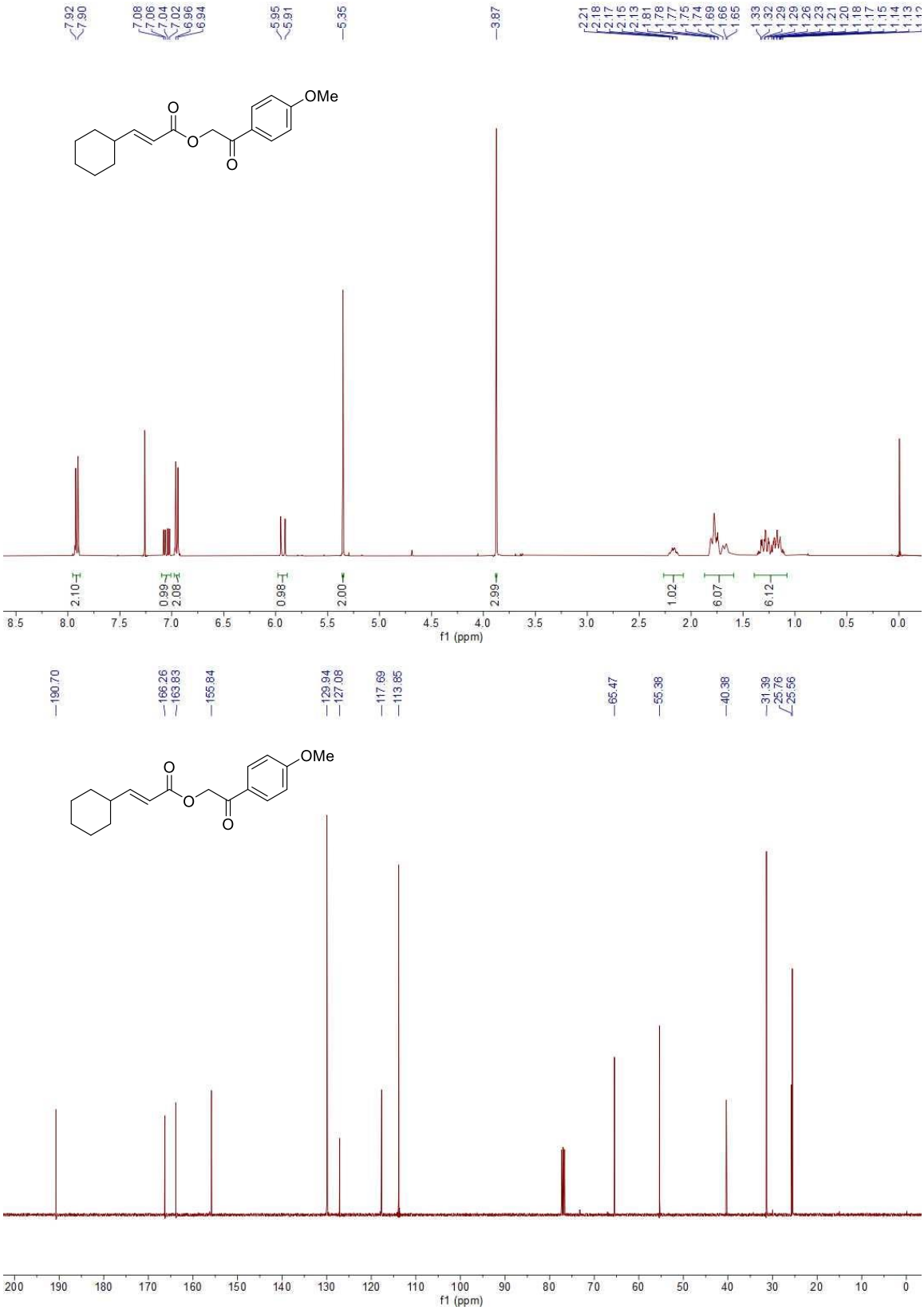


Figure S18. ^{1}H and ^{13}C NMR spectra of **1q** in $CDCl_3$.

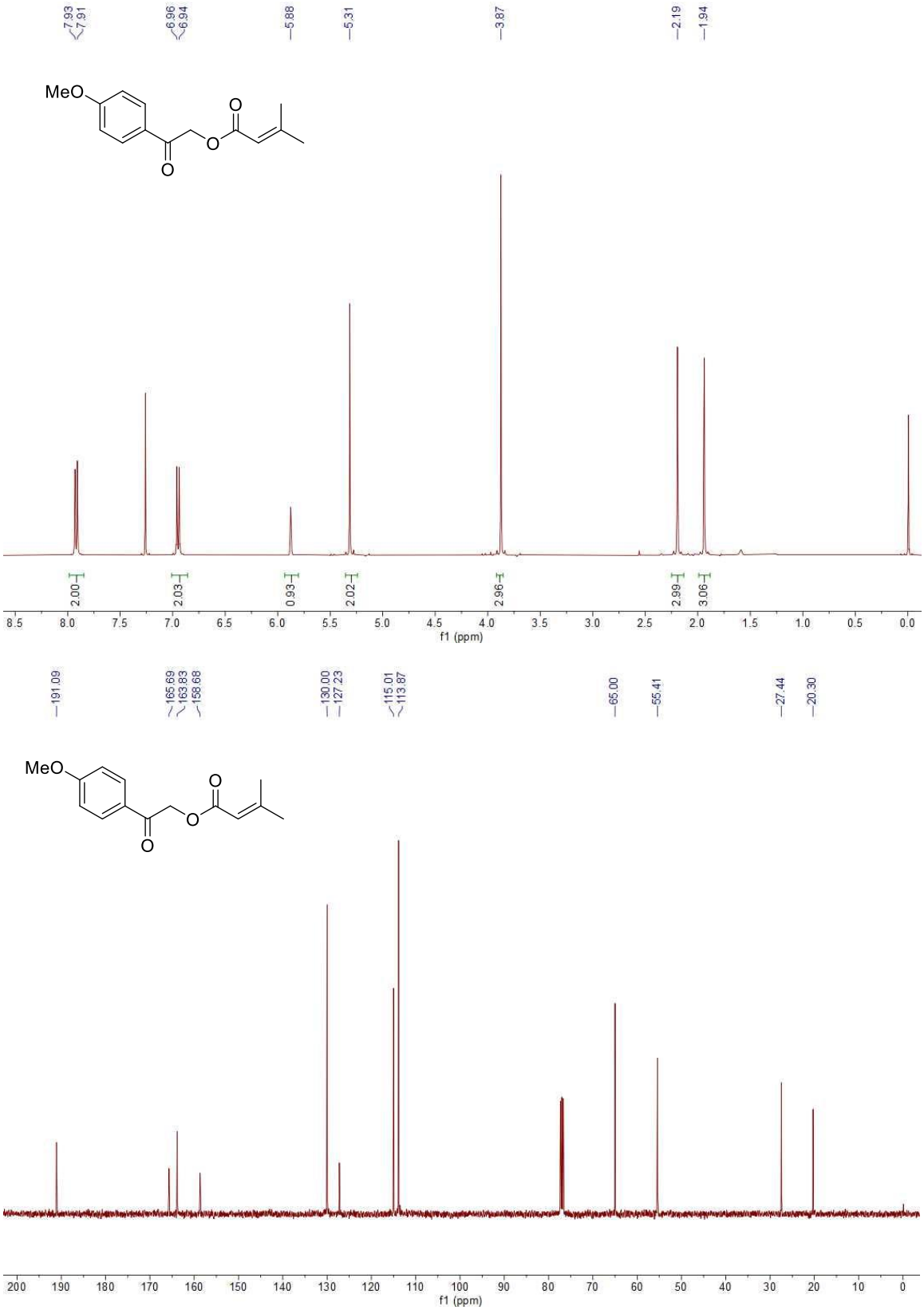


Figure S19. ^{1}H and ^{13}C NMR spectra of **3a** in $CDCl_3$.

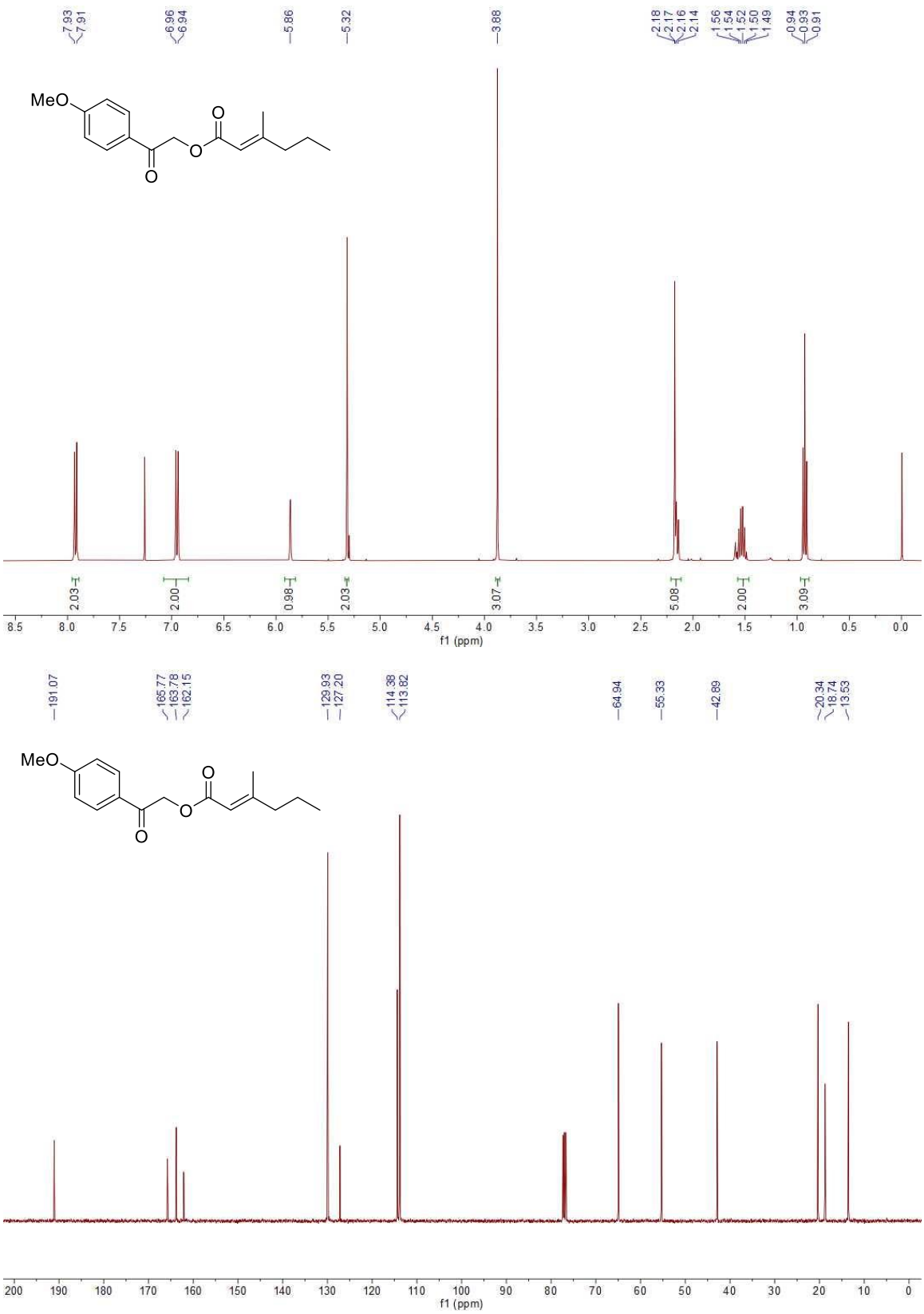


Figure S20. ^{1}H and ^{13}C NMR spectra of **3d** in $CDCl_3$.

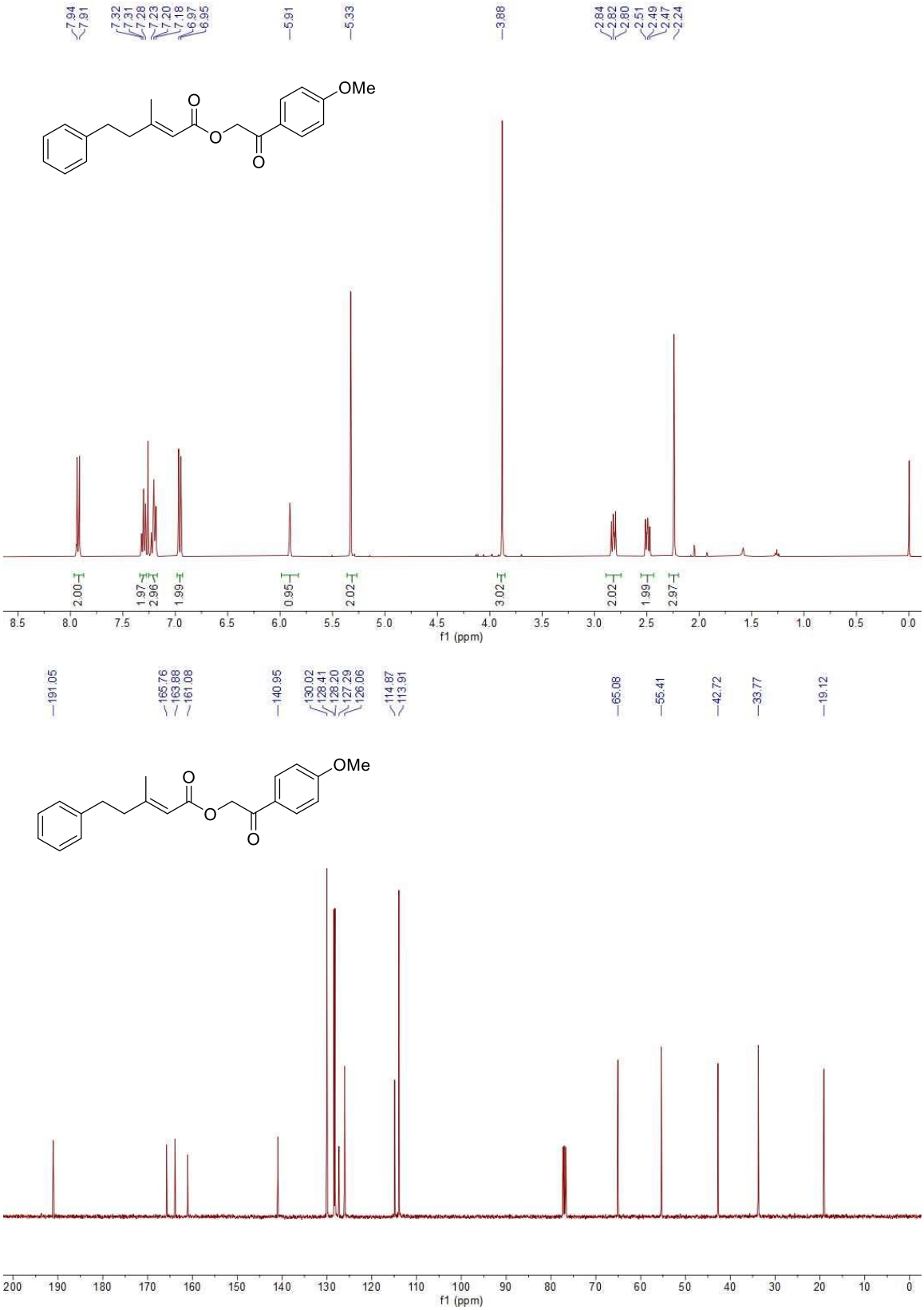


Figure S21. ^{1}H and ^{13}C NMR spectra of **3e** in $CDCl_3$.

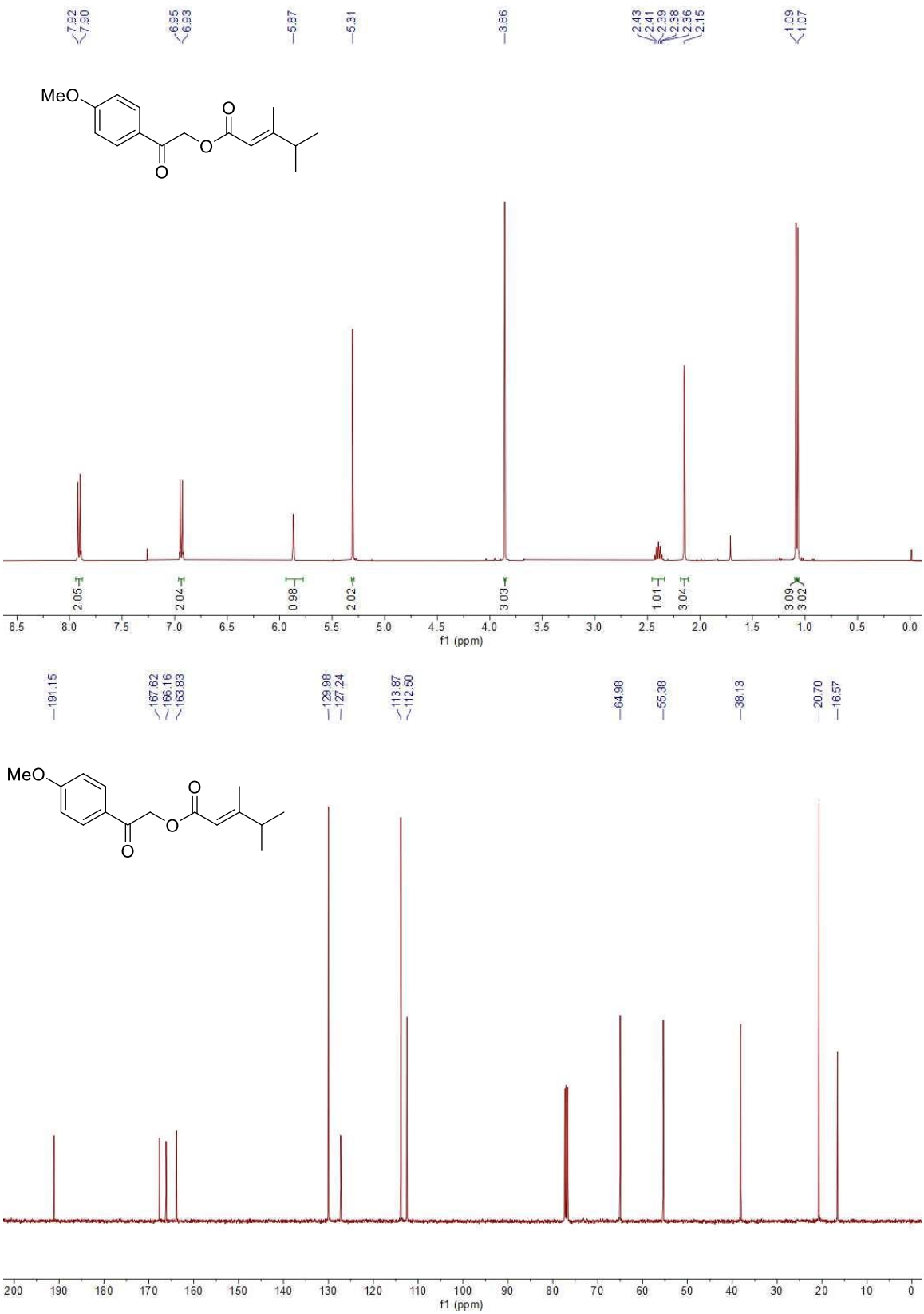


Figure S22. ^{1}H and ^{13}C NMR spectra of **3g** in $CDCl_3$.

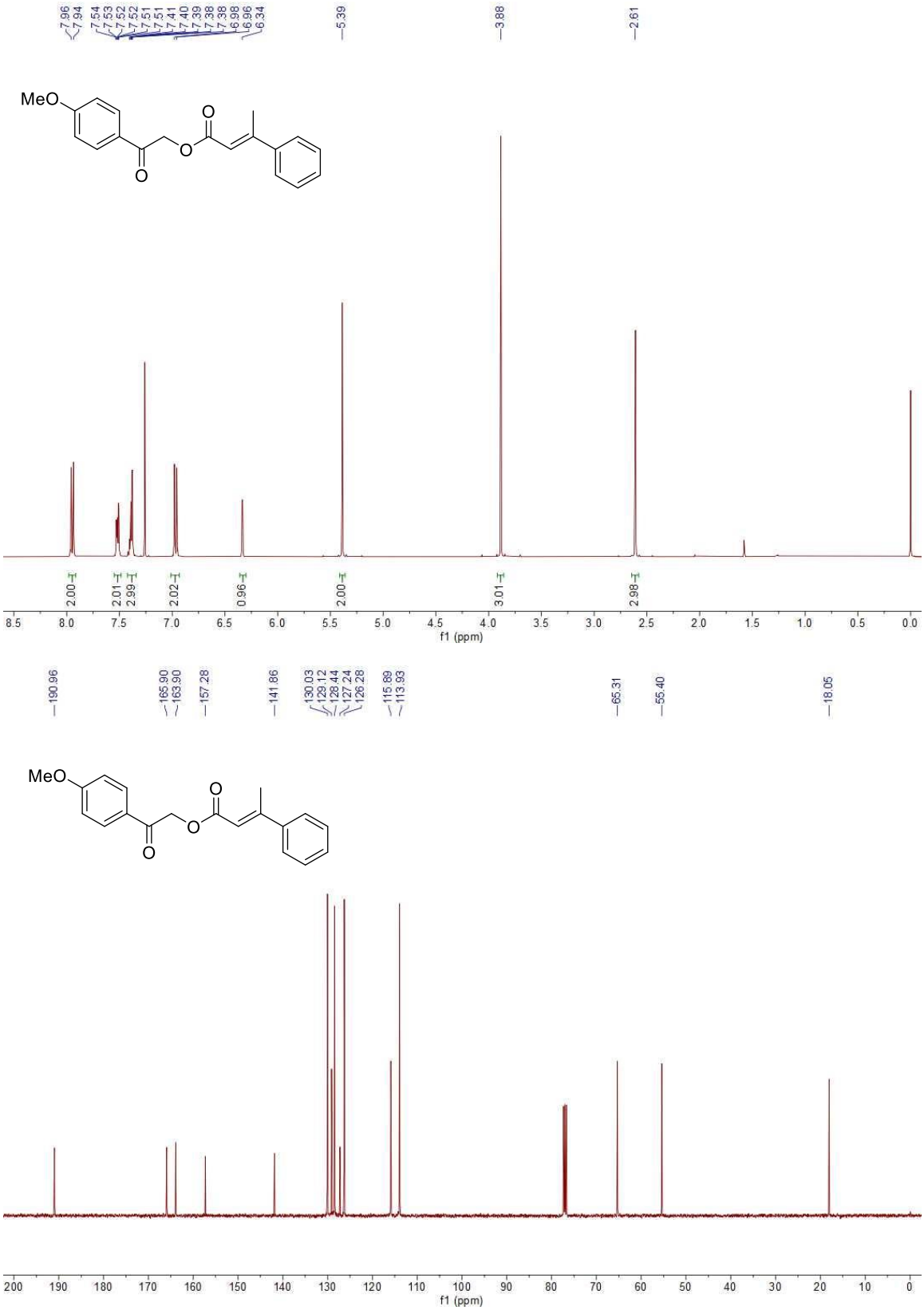


Figure S23. ^{1}H and ^{13}C NMR spectra of **3h** in $CDCl_3$.

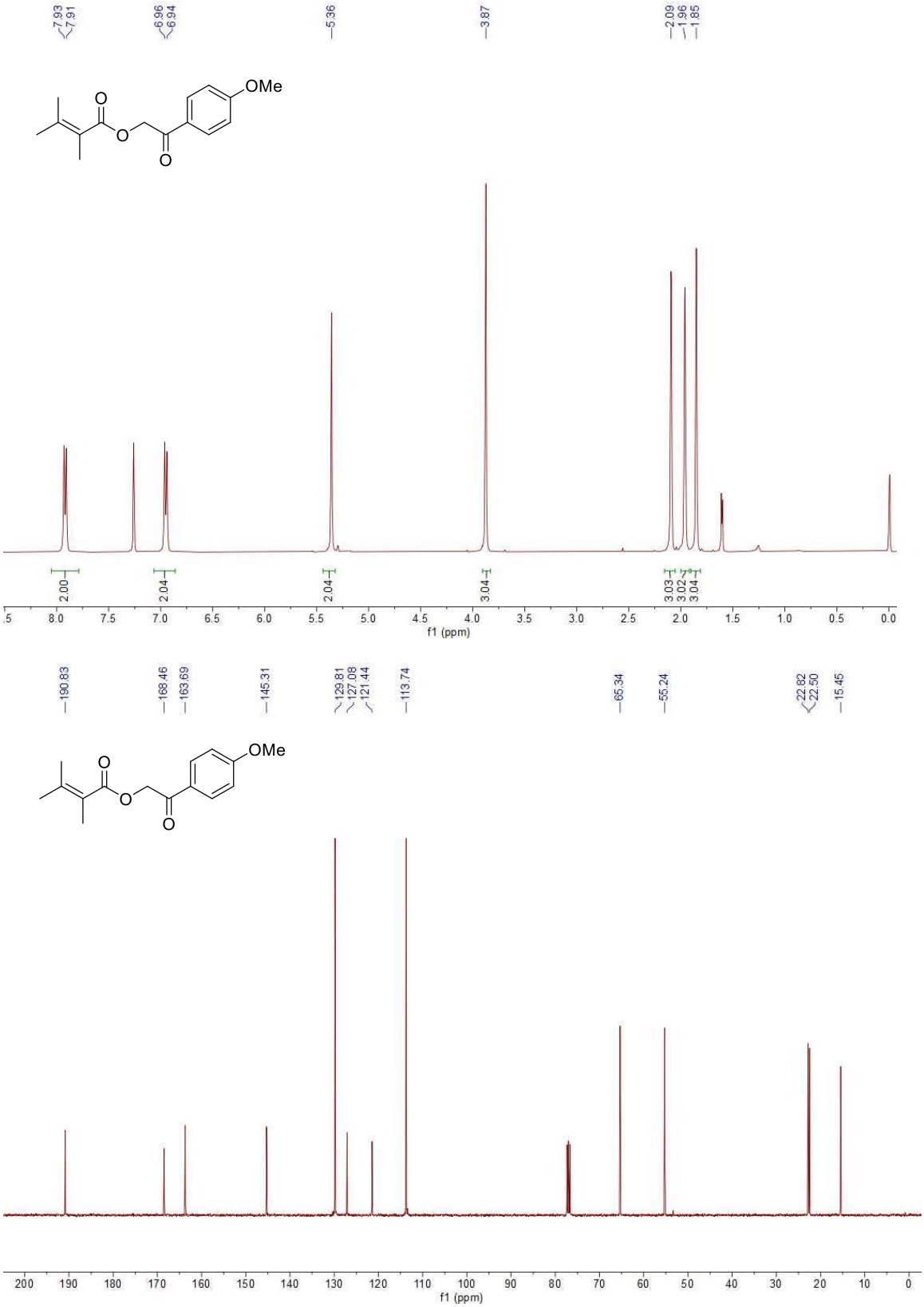


Figure S24. ^{1}H and ^{13}C NMR spectra of **3k** in $CDCl_3$.

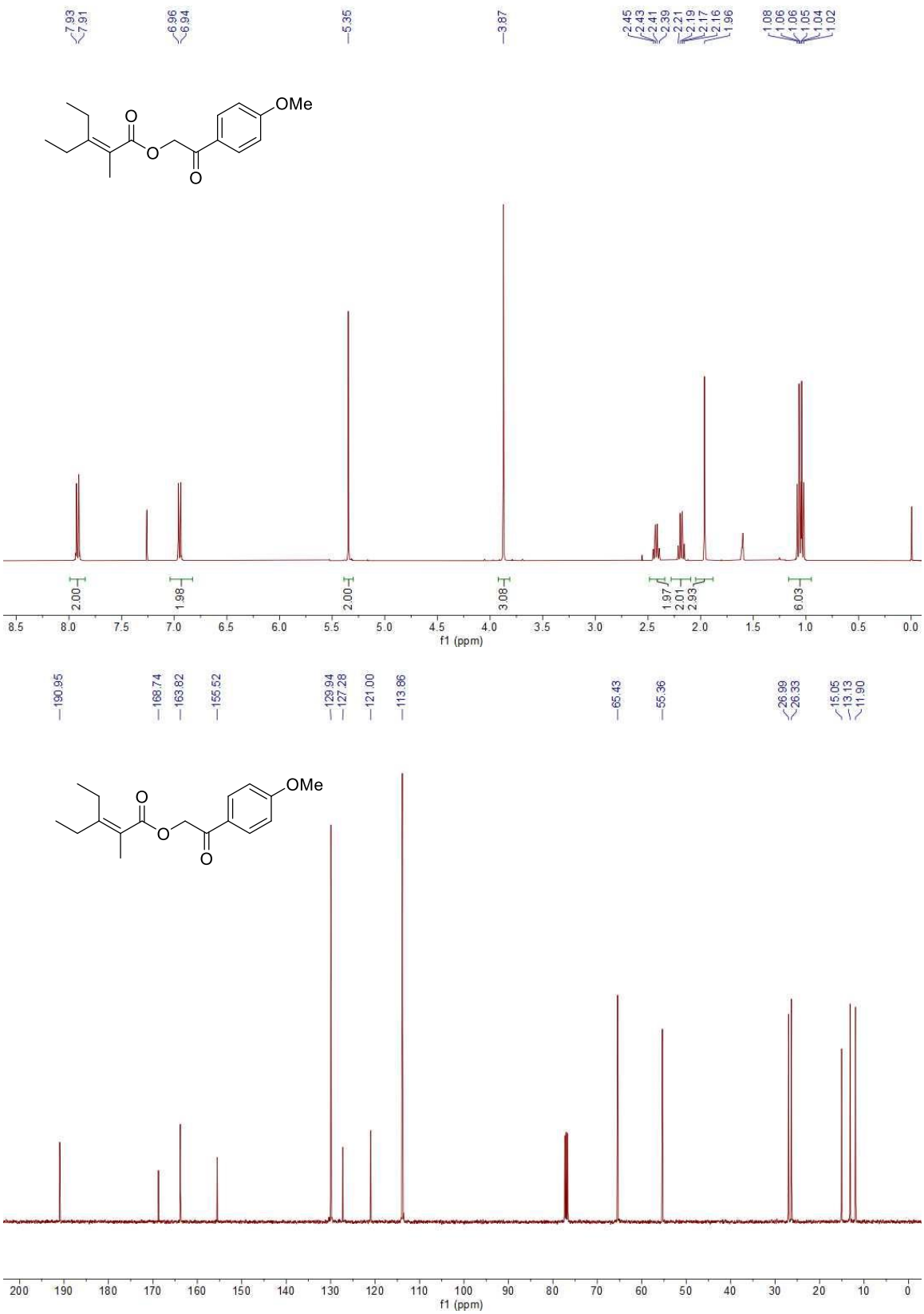


Figure S25. ^{1}H and ^{13}C NMR spectra of **3l** in $CDCl_3$.

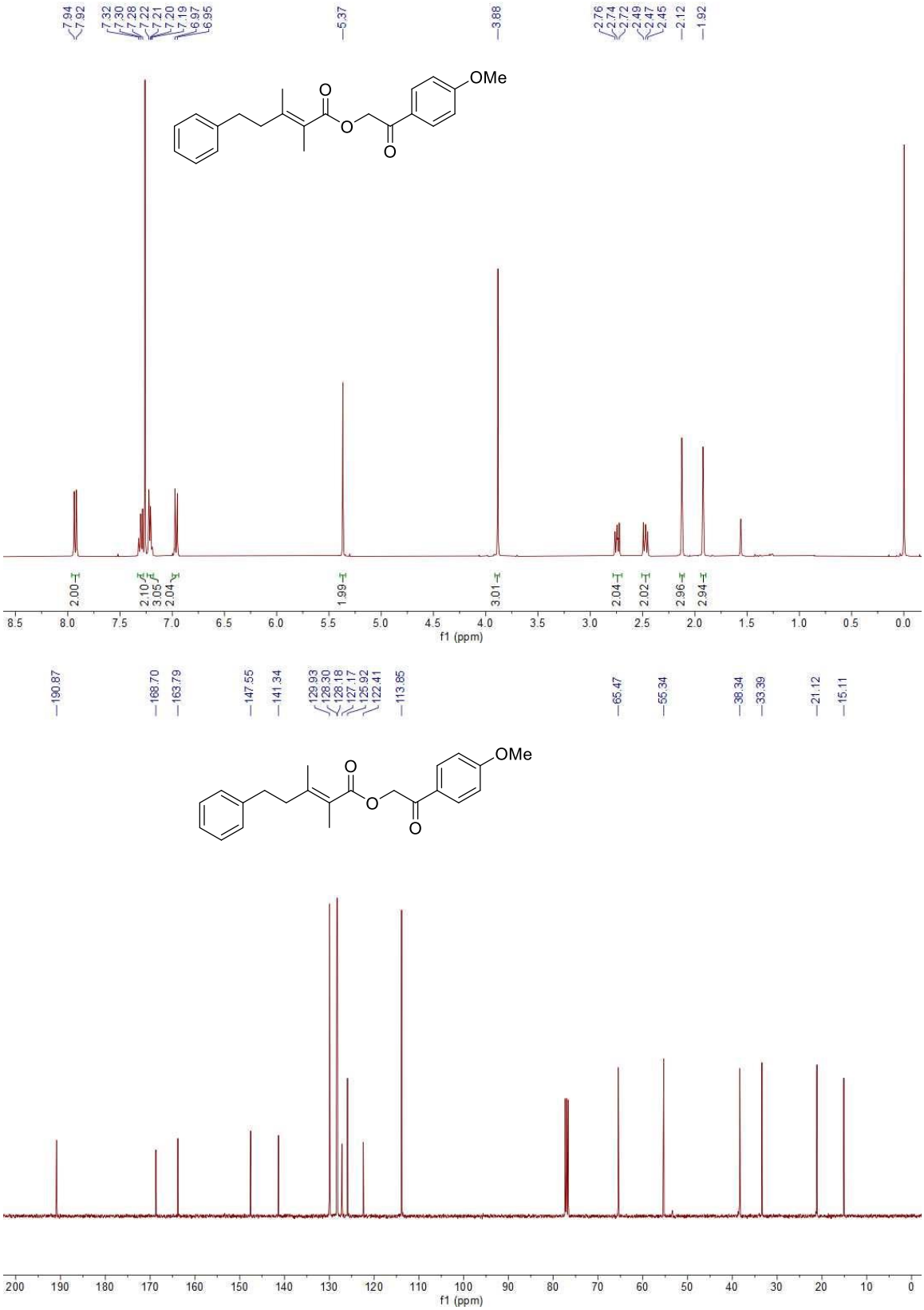


Figure S26. ^{1}H and ^{13}C NMR spectra of **3n** in $CDCl_3$.

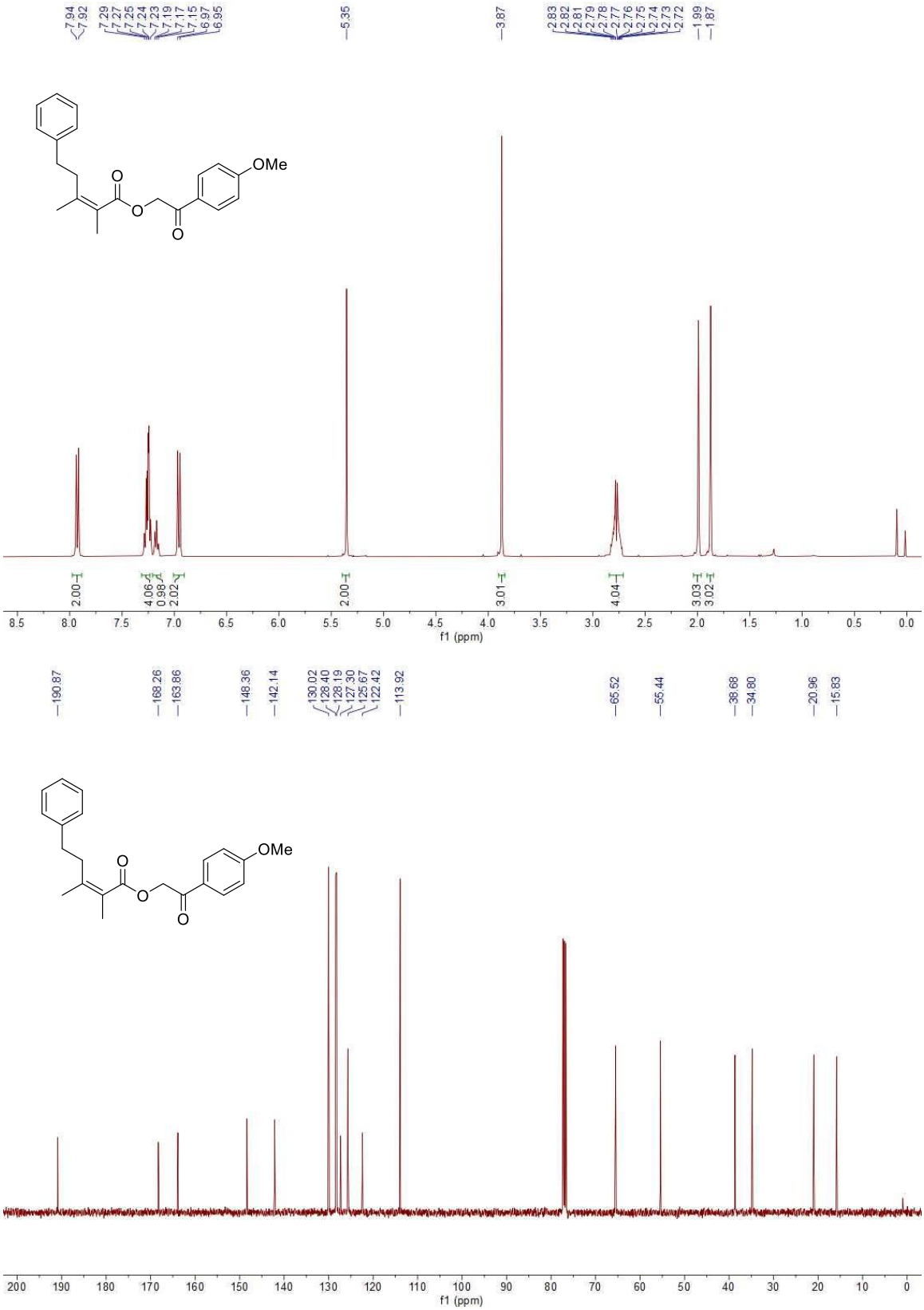


Figure S27. ^{1}H and ^{13}C NMR spectra of **3o** in $CDCl_3$.

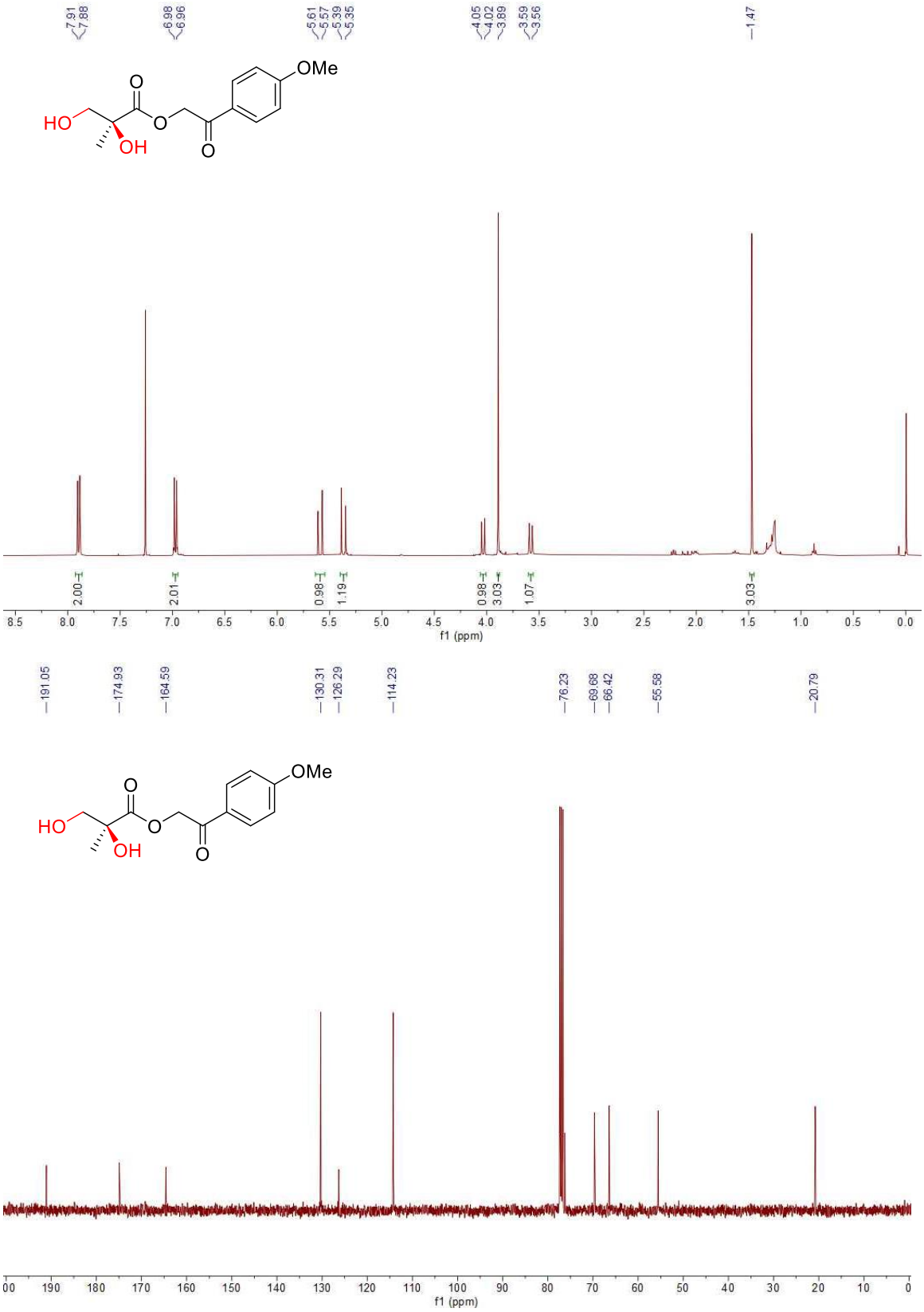


Figure S28. ^{1}H and ^{13}C NMR spectra of **2a** in $CDCl_3$.

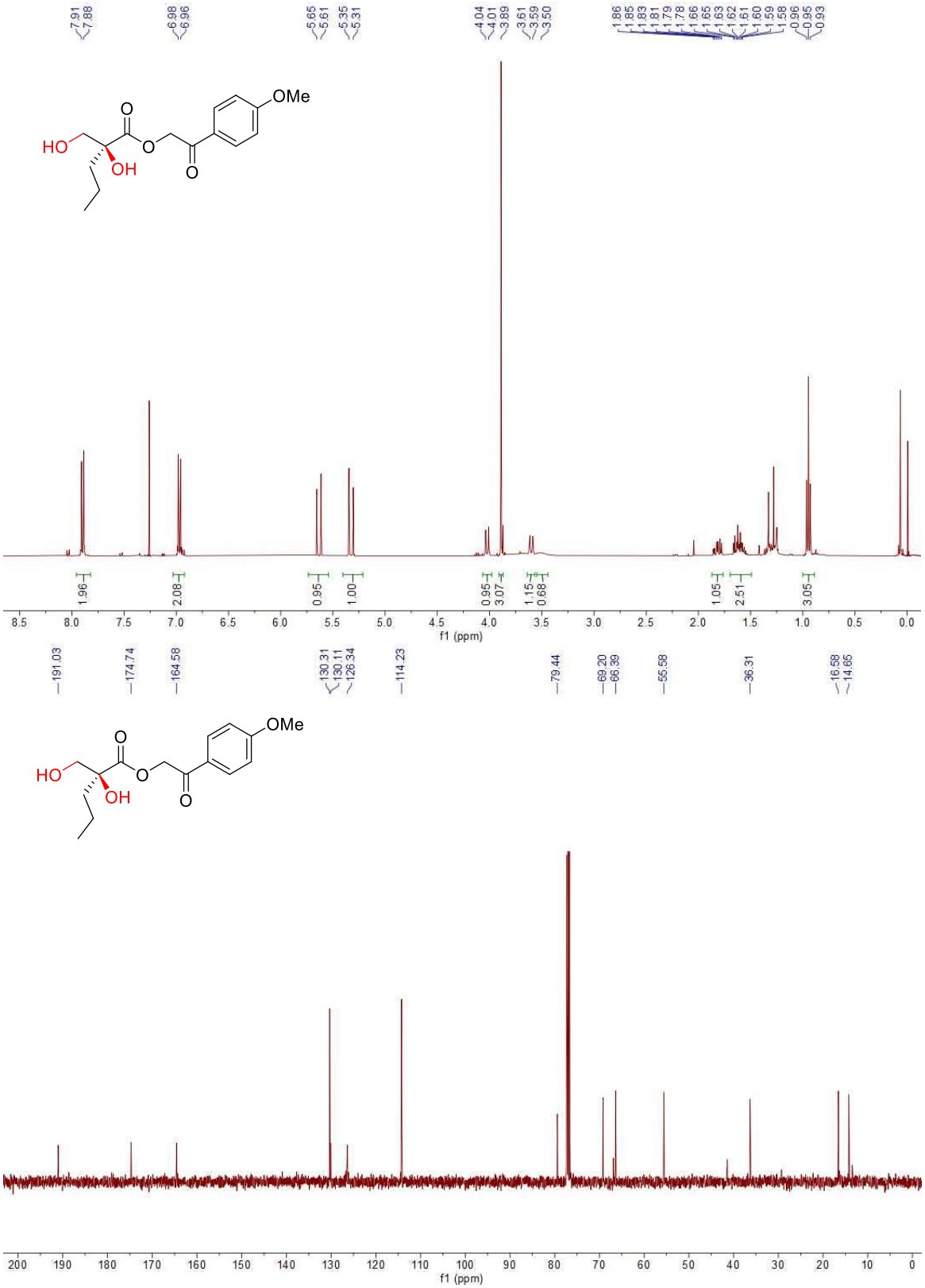


Figure S29. ^{1}H and ^{13}C NMR spectra of **2b** in $CDCl_3$.

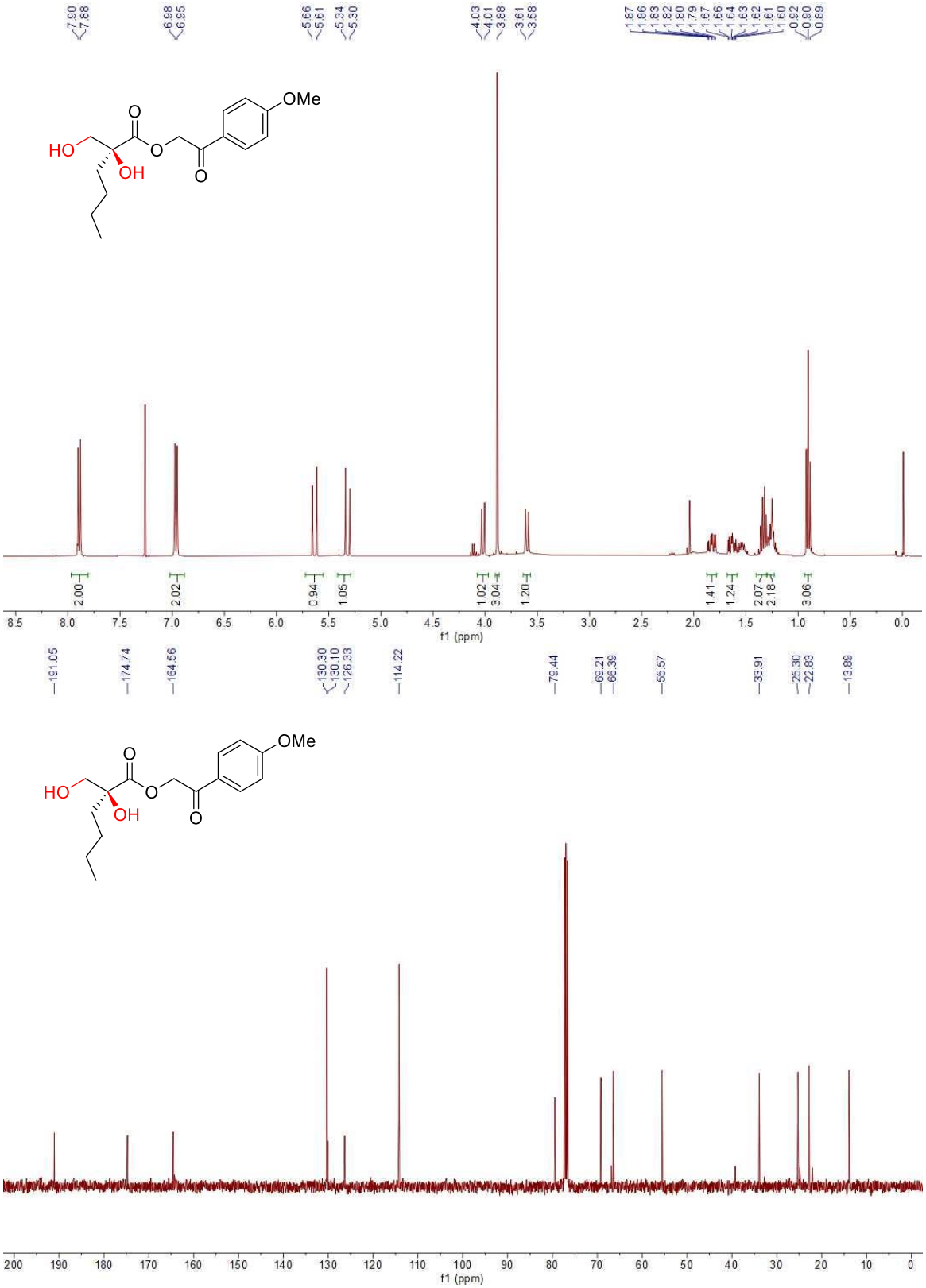


Figure S30. ^{1}H and ^{13}C NMR spectra of **2c** in $CDCl_3$.

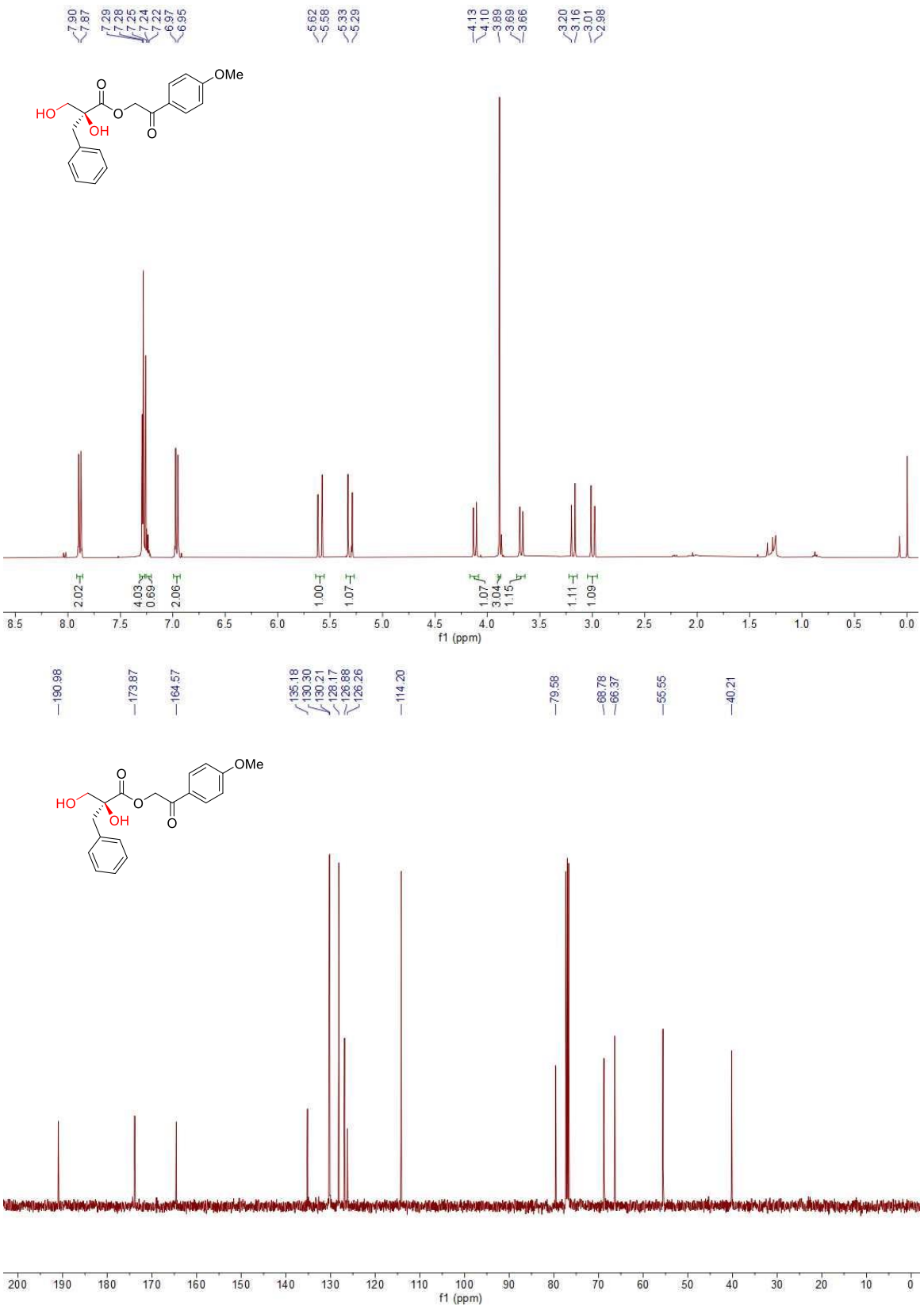


Figure S31. ^{1}H and ^{13}C NMR spectra of **2d** in $CDCl_3$.

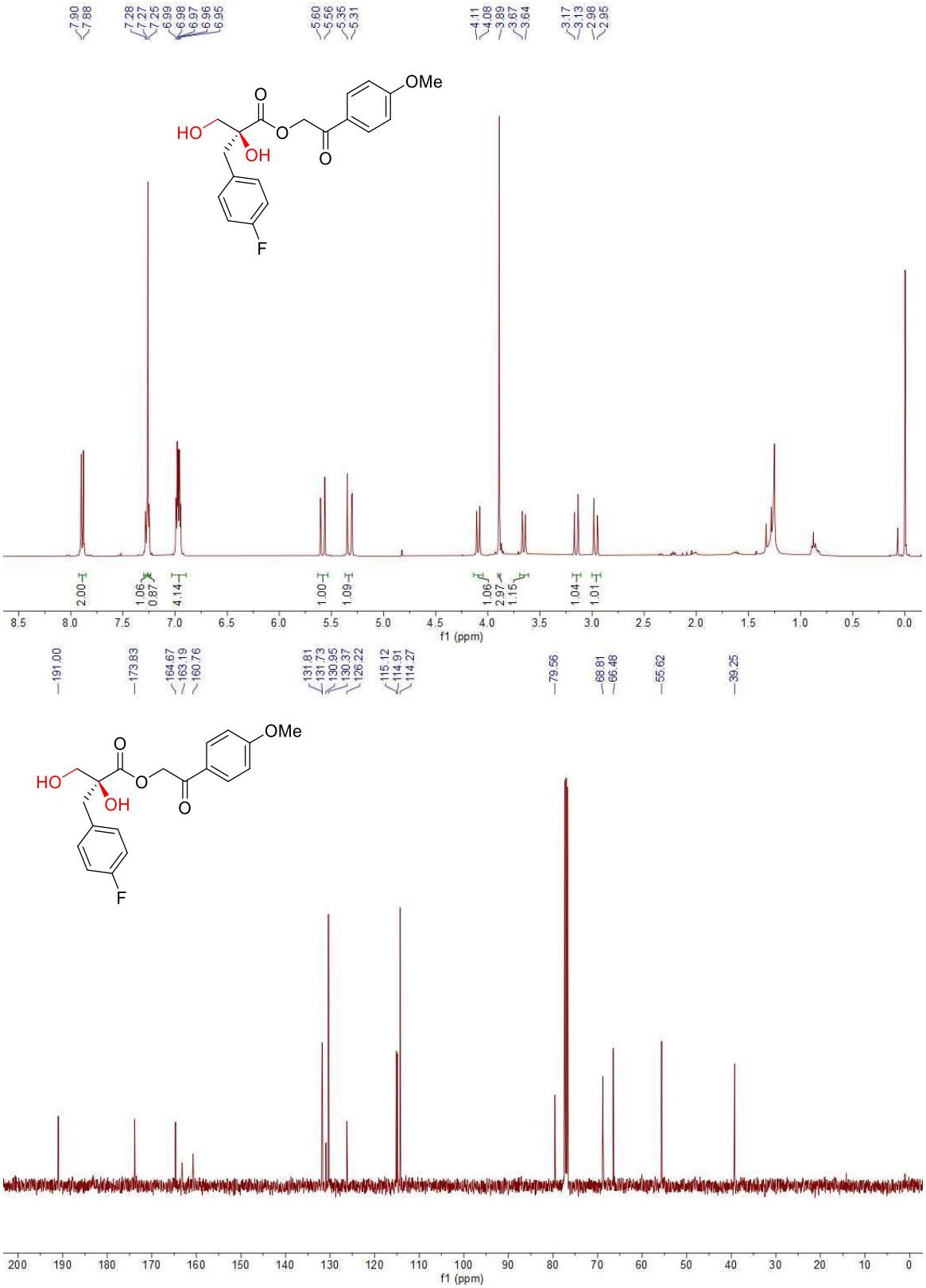


Figure S32. ^{1}H and ^{13}C NMR spectra of **2e** in $CDCl_3$.

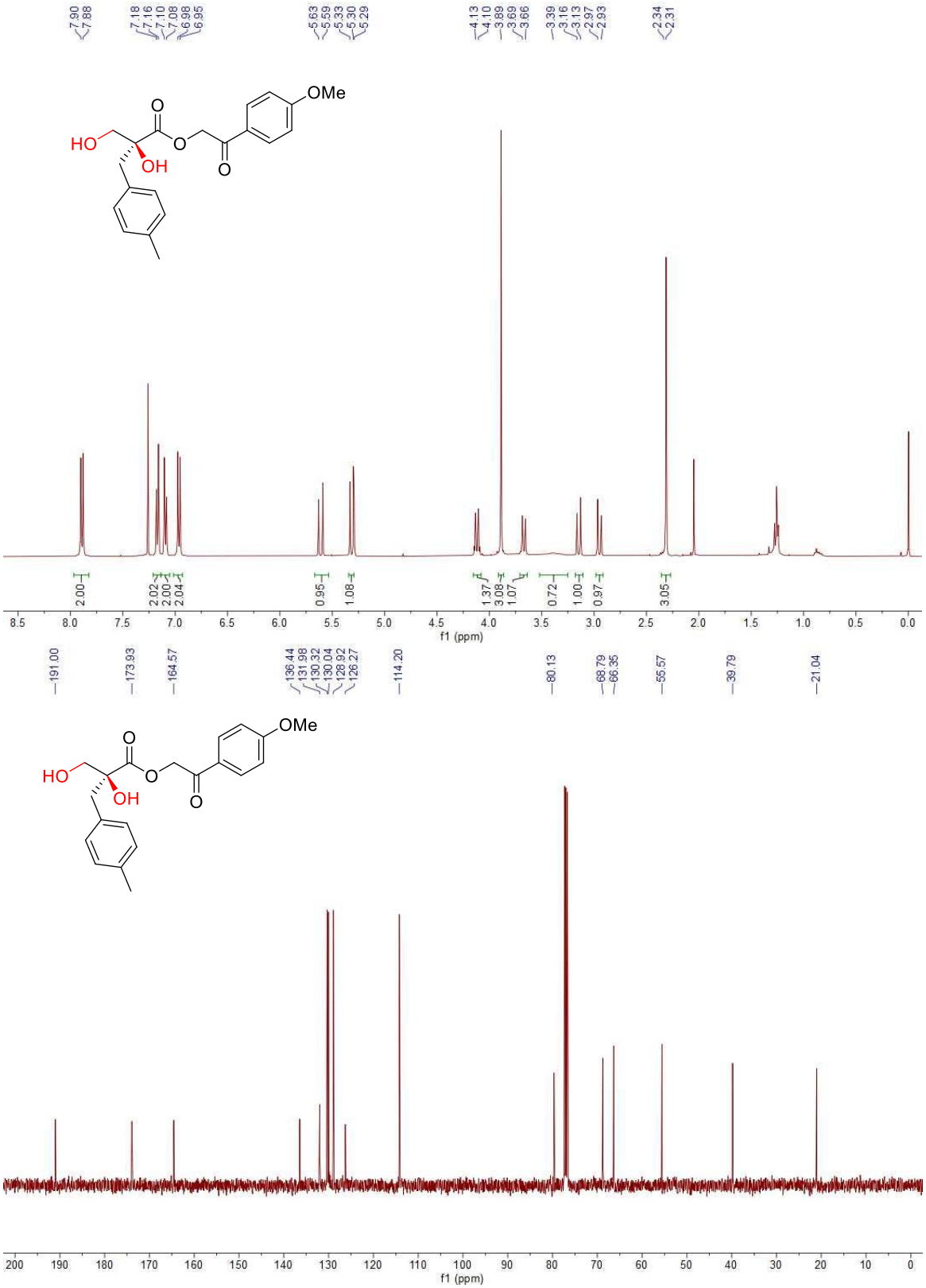


Figure S33. ^{1}H and ^{13}C NMR spectra of **2f** in $CDCl_3$.

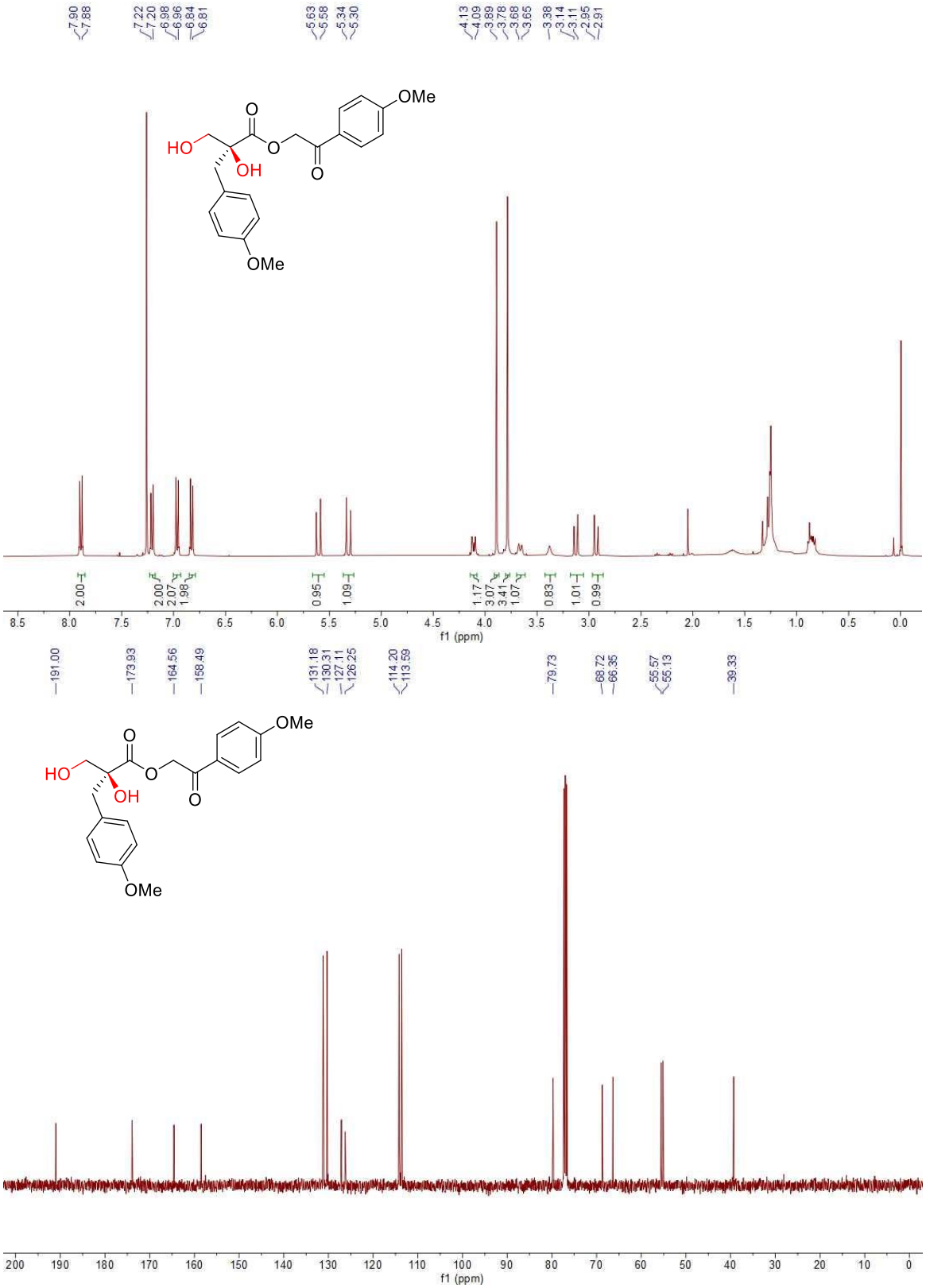


Figure S34. ^{1}H and ^{13}C NMR spectra of **2g** in $CDCl_3$.

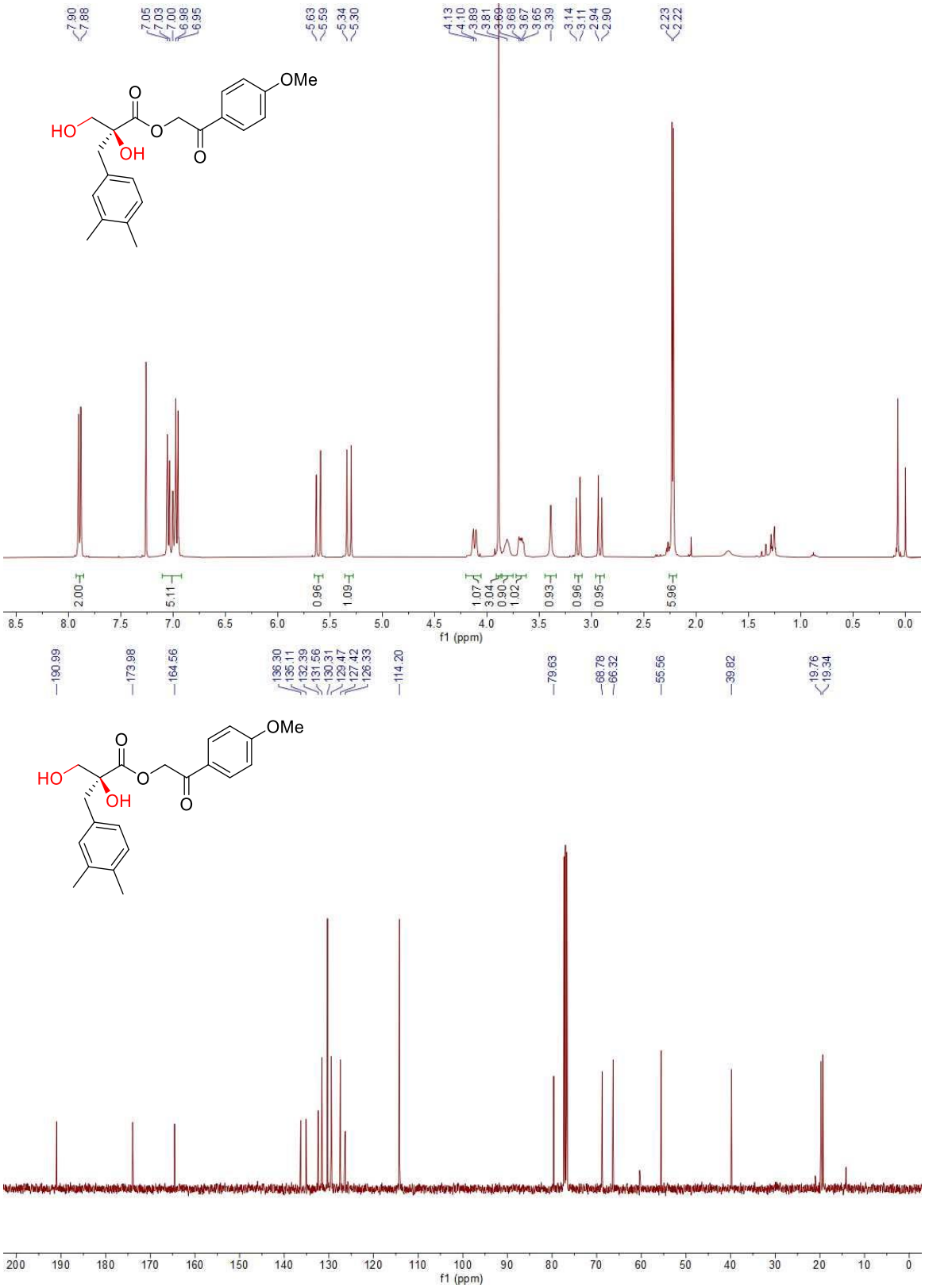


Figure S35. ^{1}H and ^{13}C NMR spectra of **2h** in $CDCl_3$.

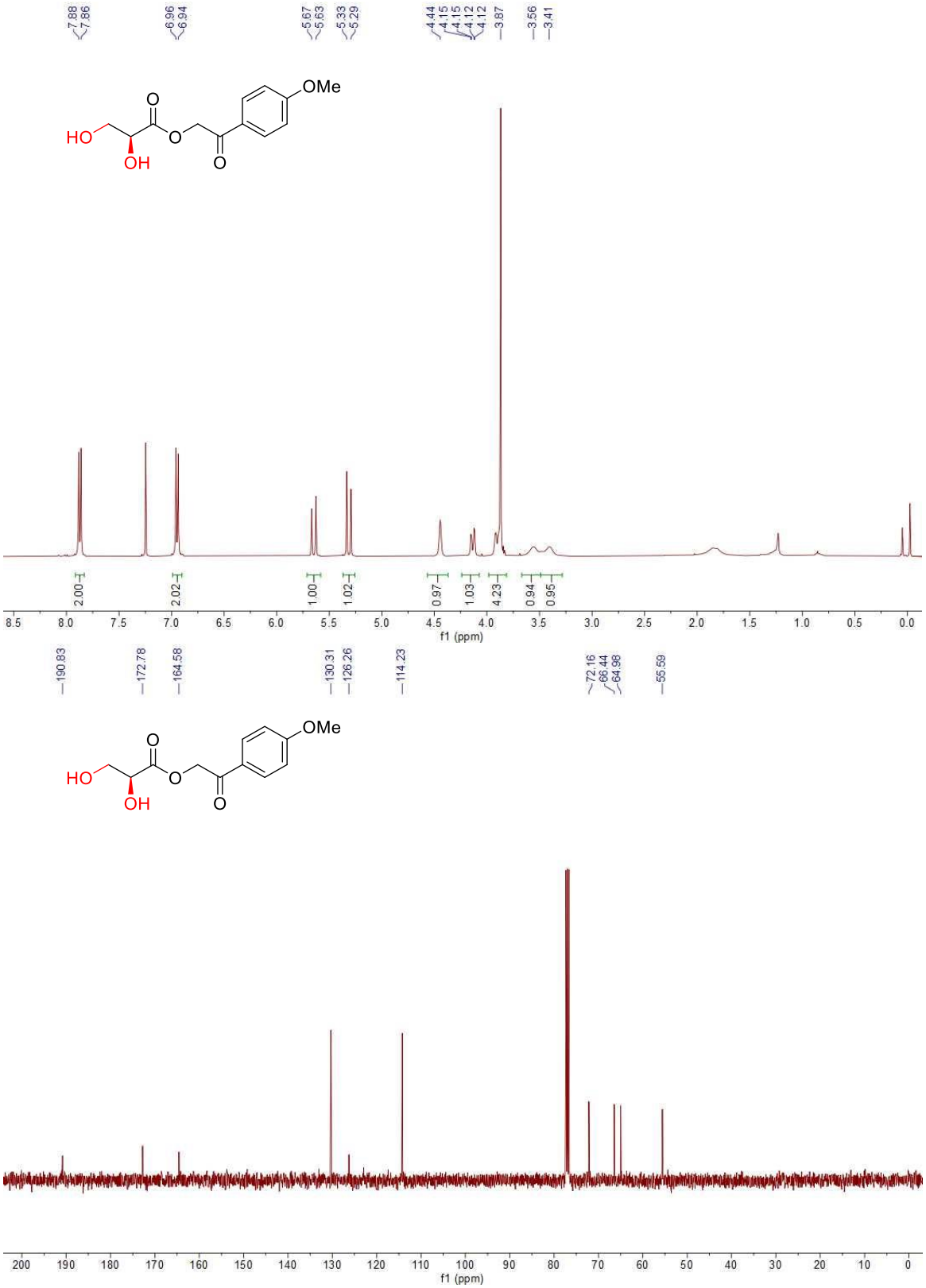


Figure S36. ^{1}H and ^{13}C NMR spectra of **2i** in $CDCl_3$.

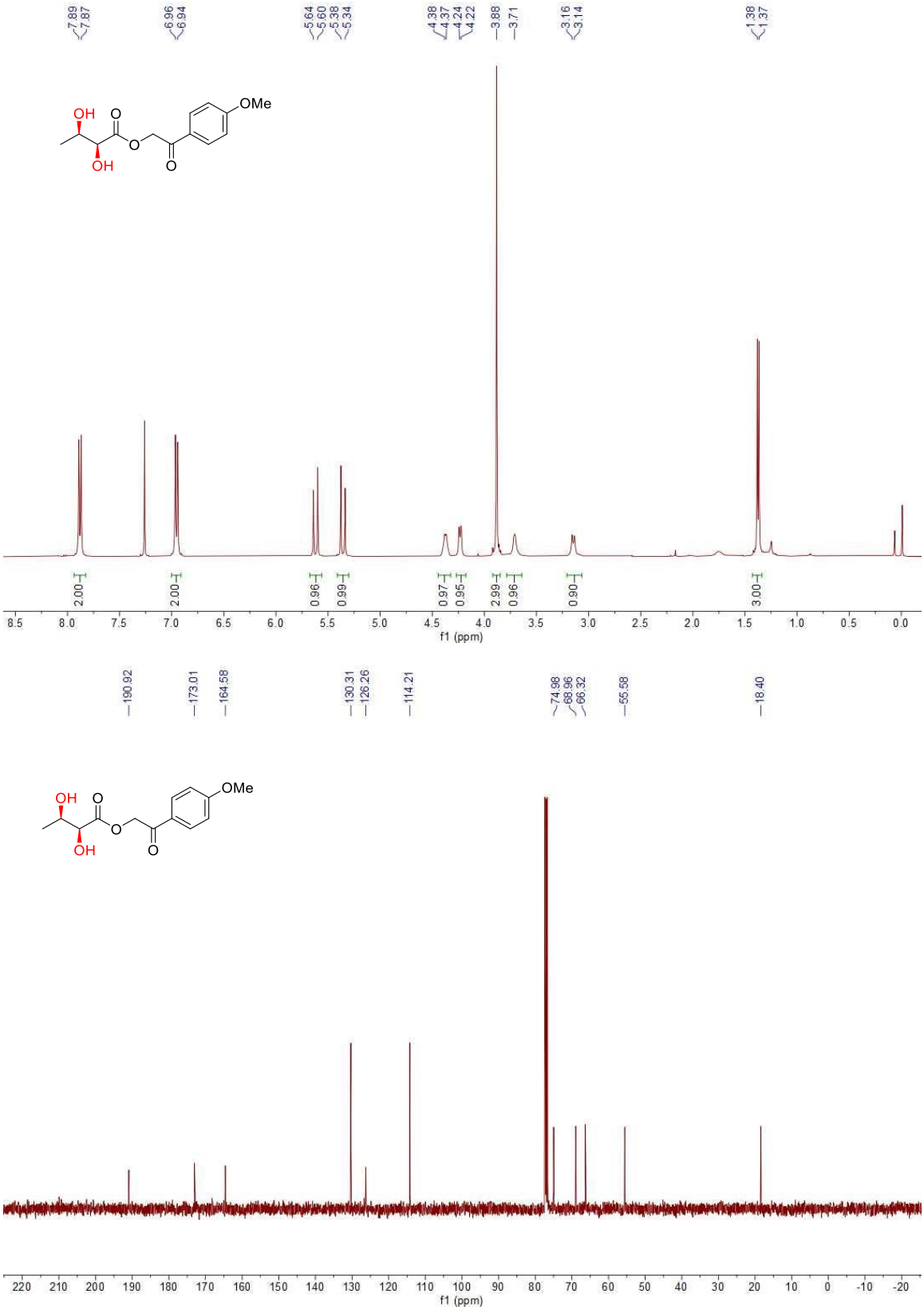


Figure S37. ^{1}H and ^{13}C NMR spectra of **2j** in $CDCl_3$.

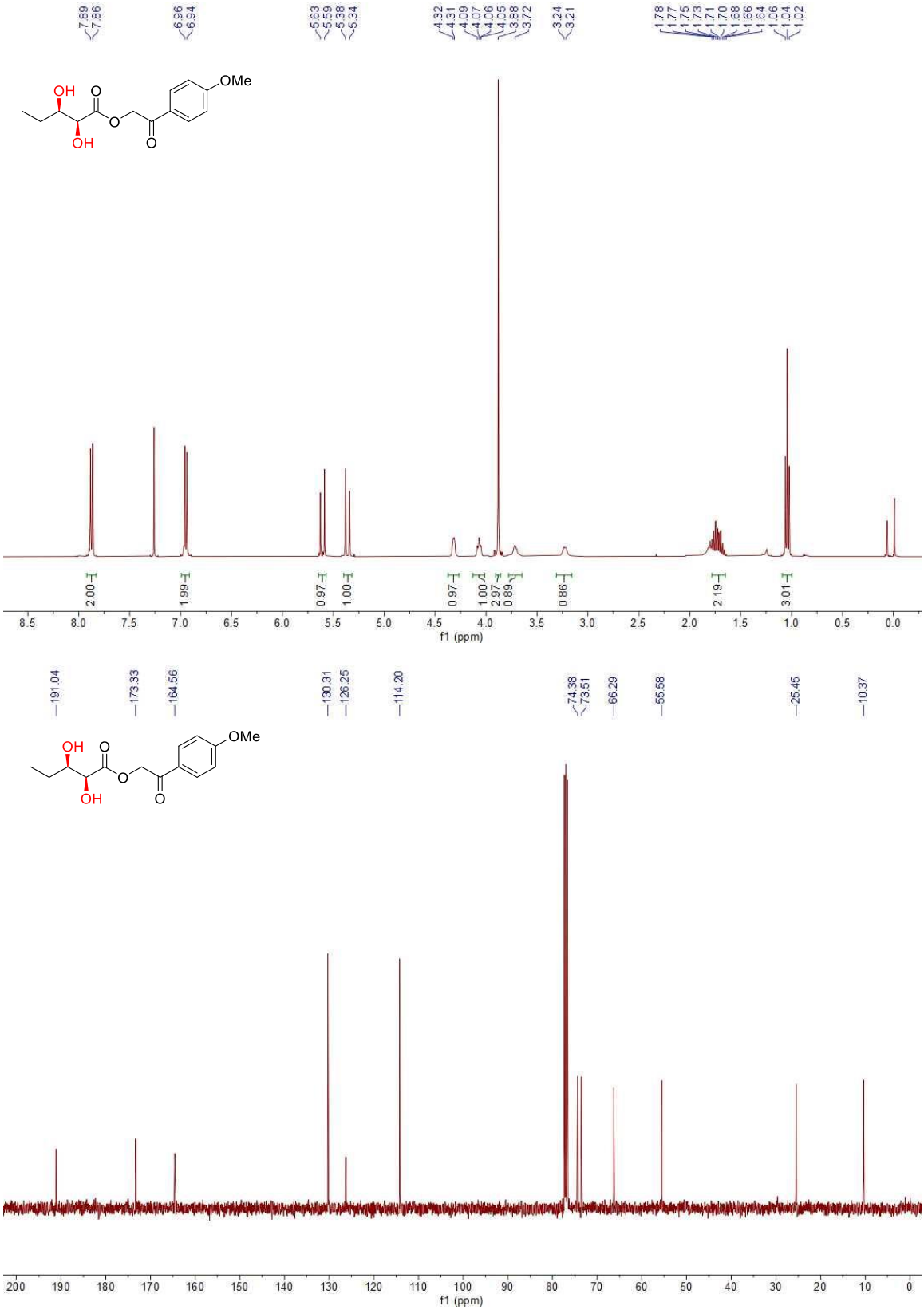


Figure S38. ^{1}H and ^{13}C NMR spectra of **2k** in $CDCl_3$.

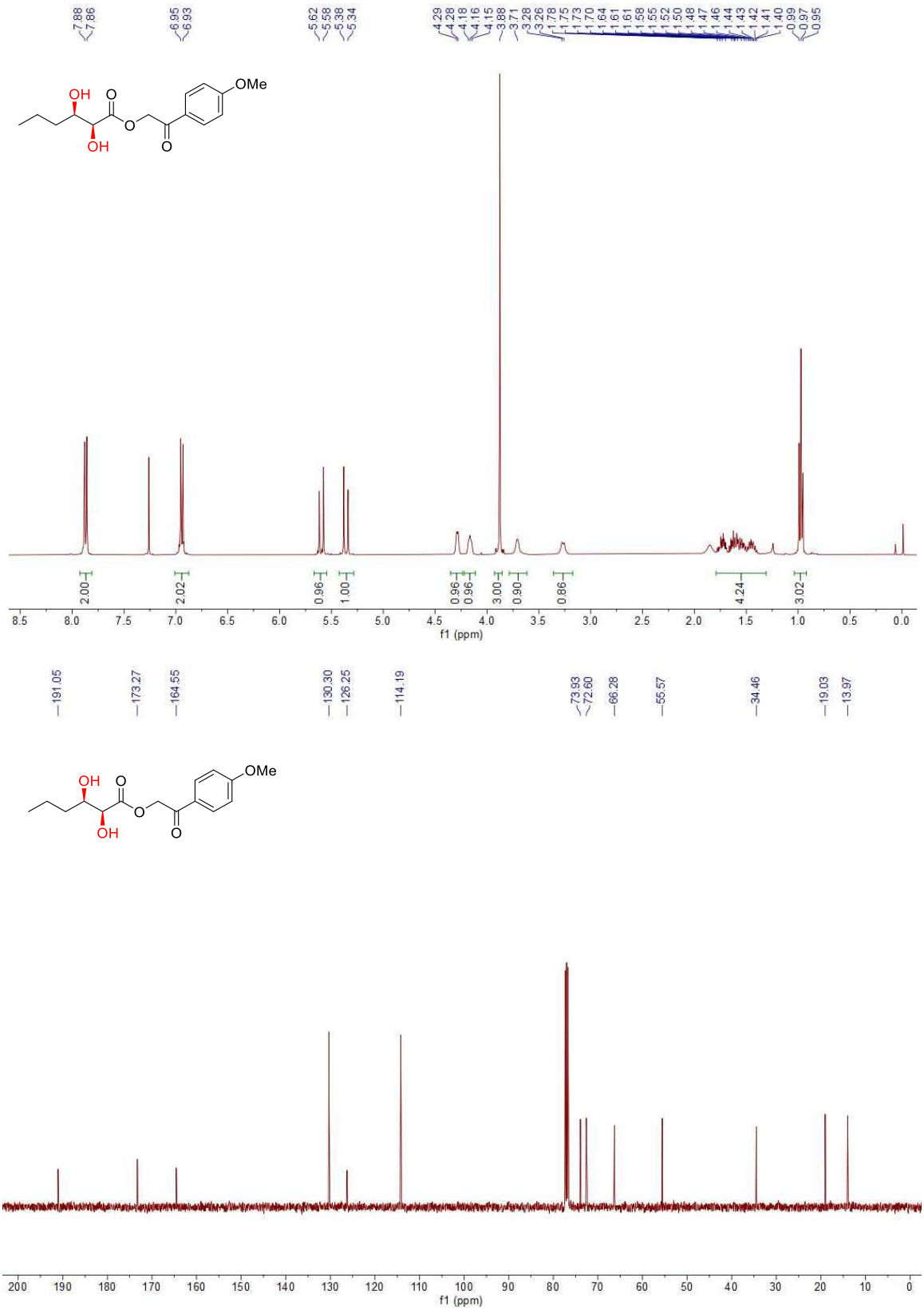


Figure S39. ^{1}H and ^{13}C NMR spectra of **2l** in $CDCl_3$.

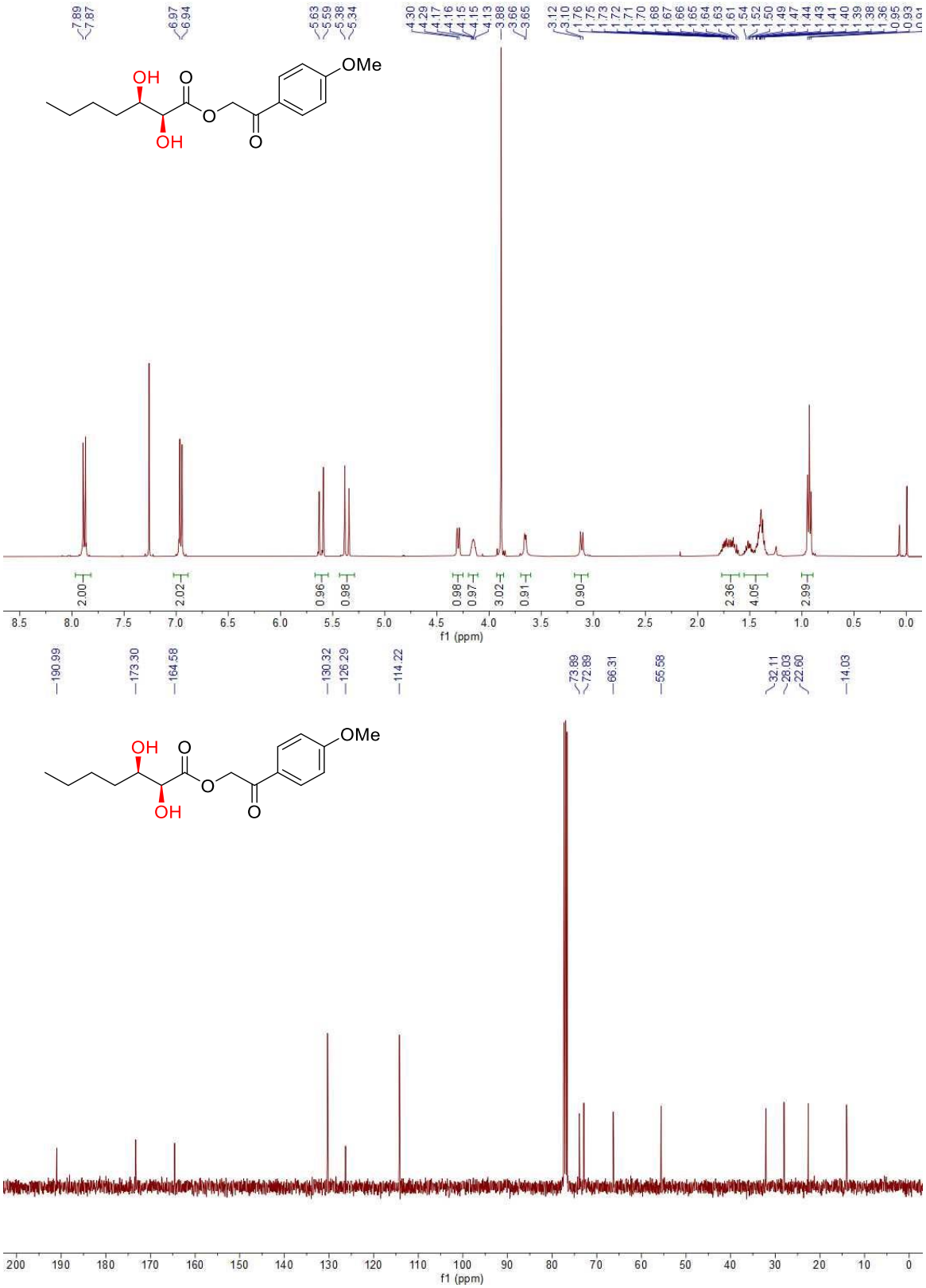


Figure S40. ^{1}H and ^{13}C NMR spectra of **2m** in $CDCl_3$.

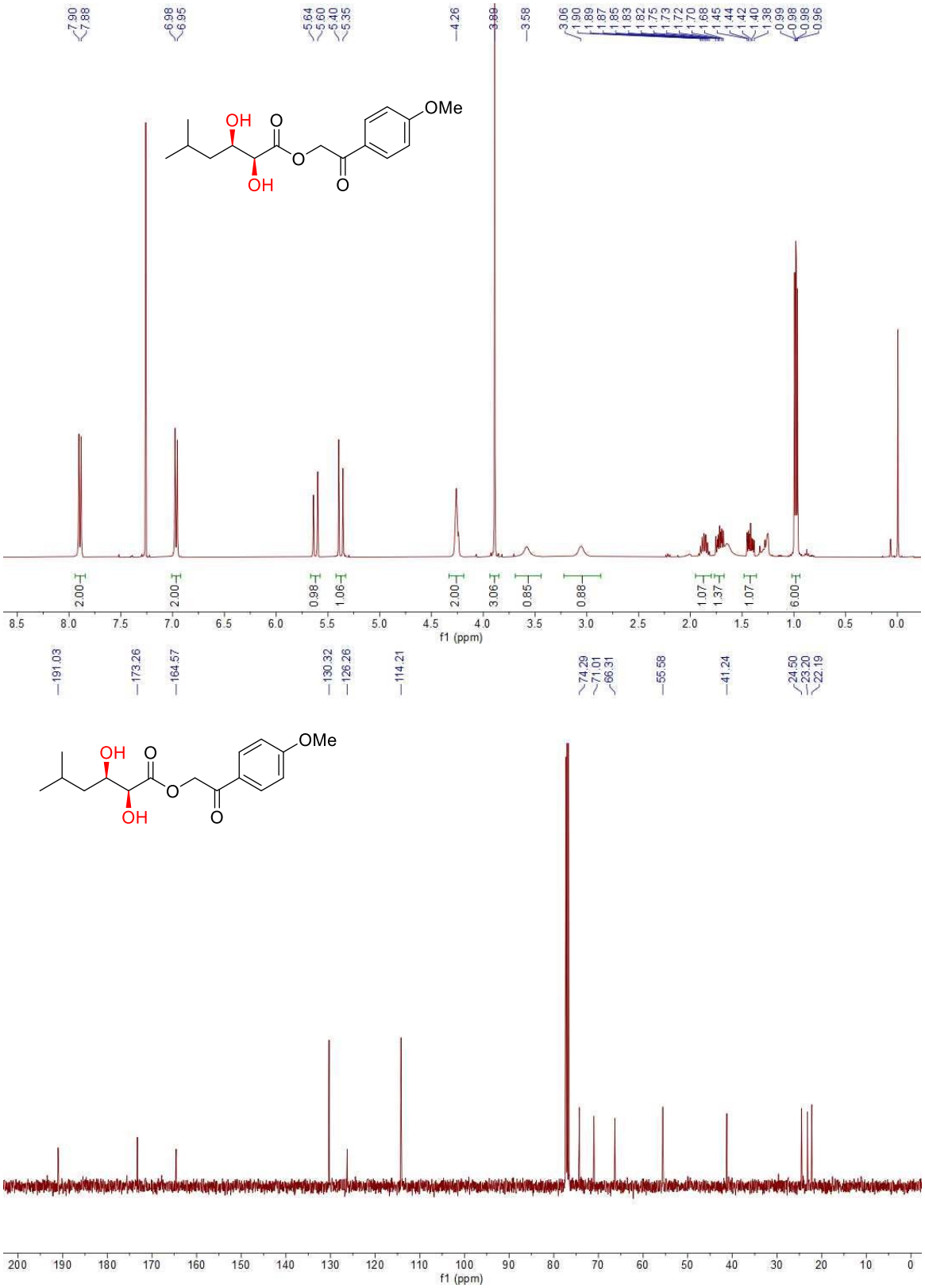


Figure S41. ^{1}H and ^{13}C NMR spectra of **2n** in $CDCl_3$.

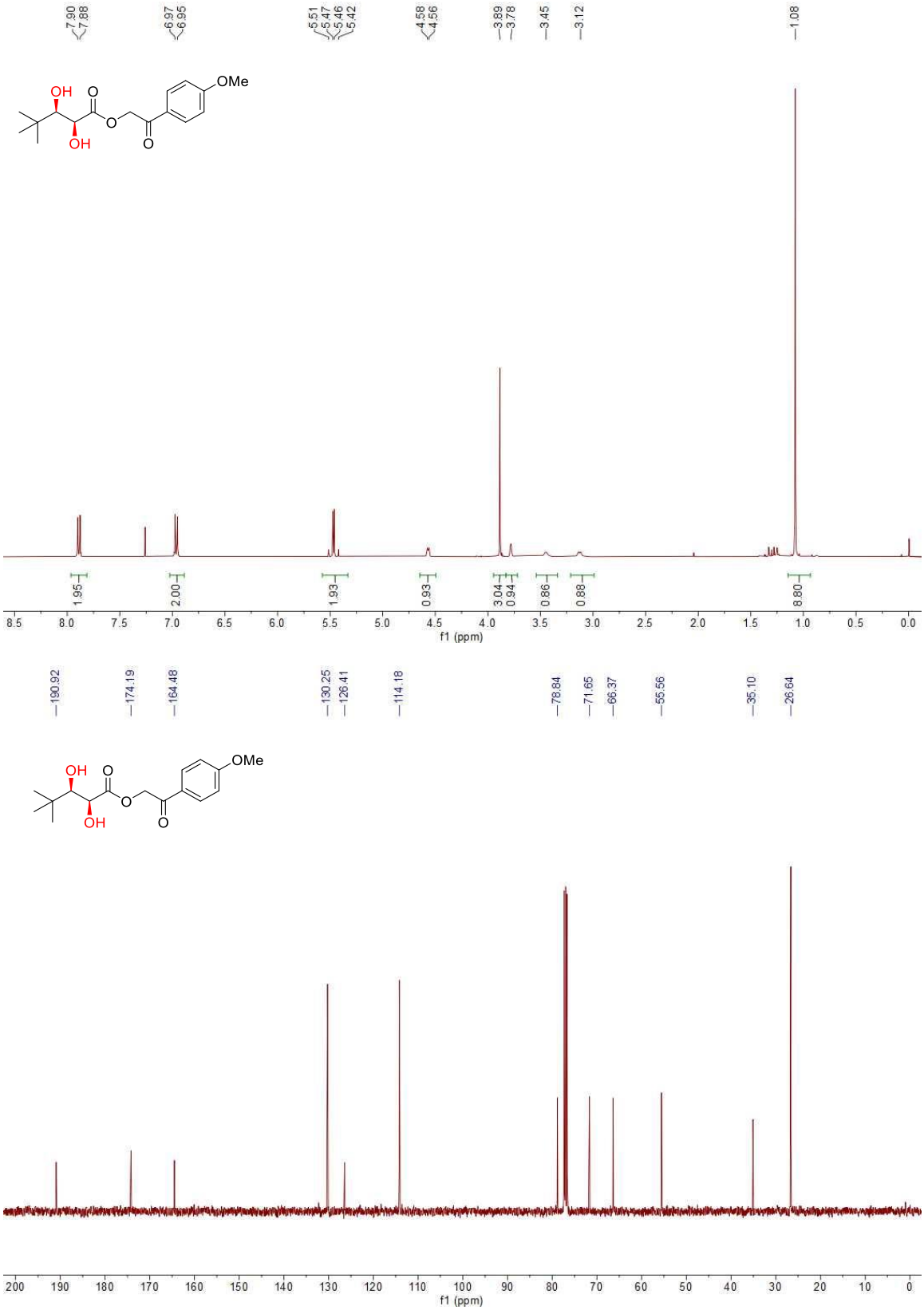


Figure S42. ^{1}H and ^{13}C NMR spectra of **2o** in $CDCl_3$.

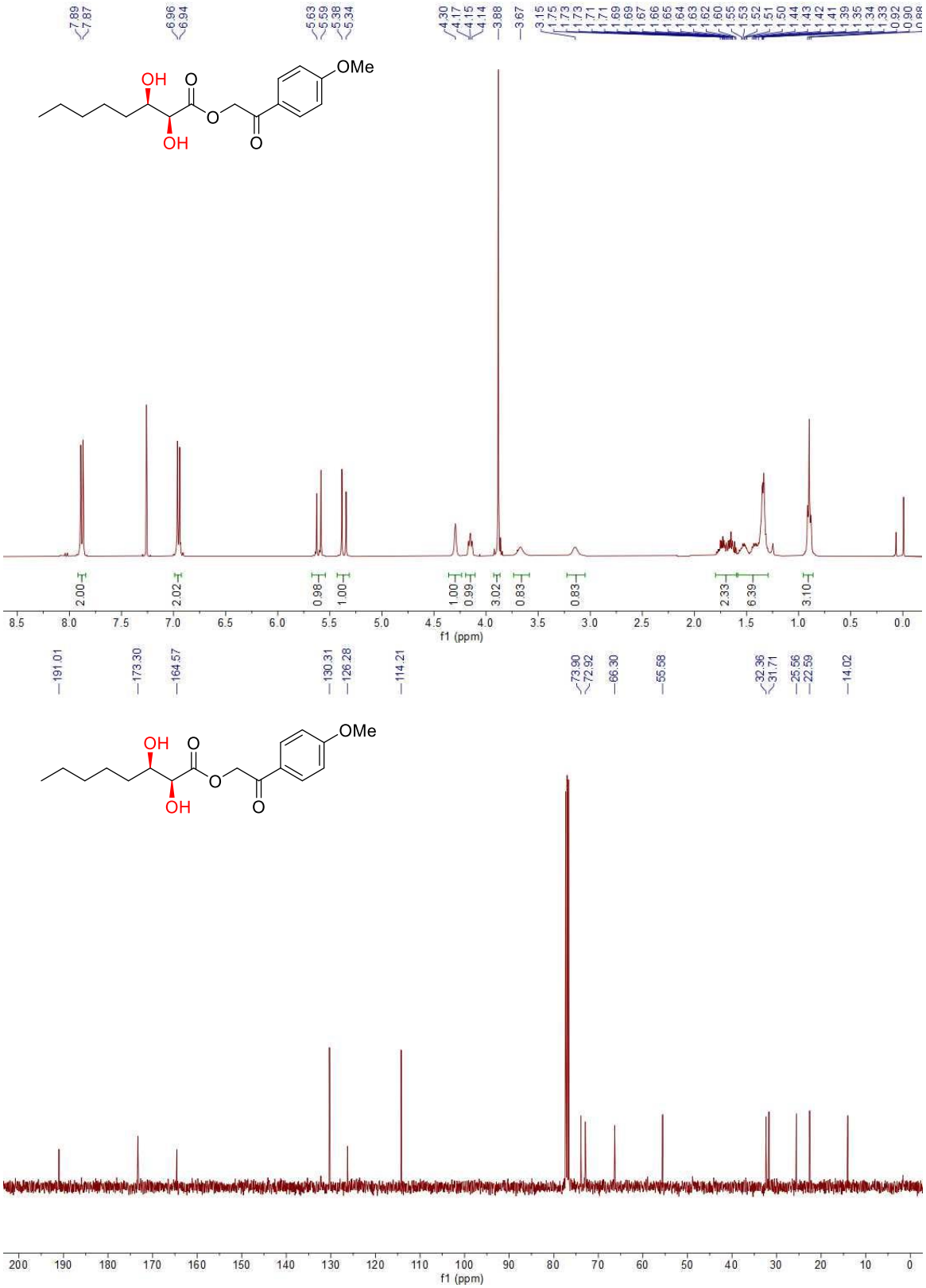


Figure S43. ^{1}H and ^{13}C NMR spectra of **2p** in $CDCl_3$.

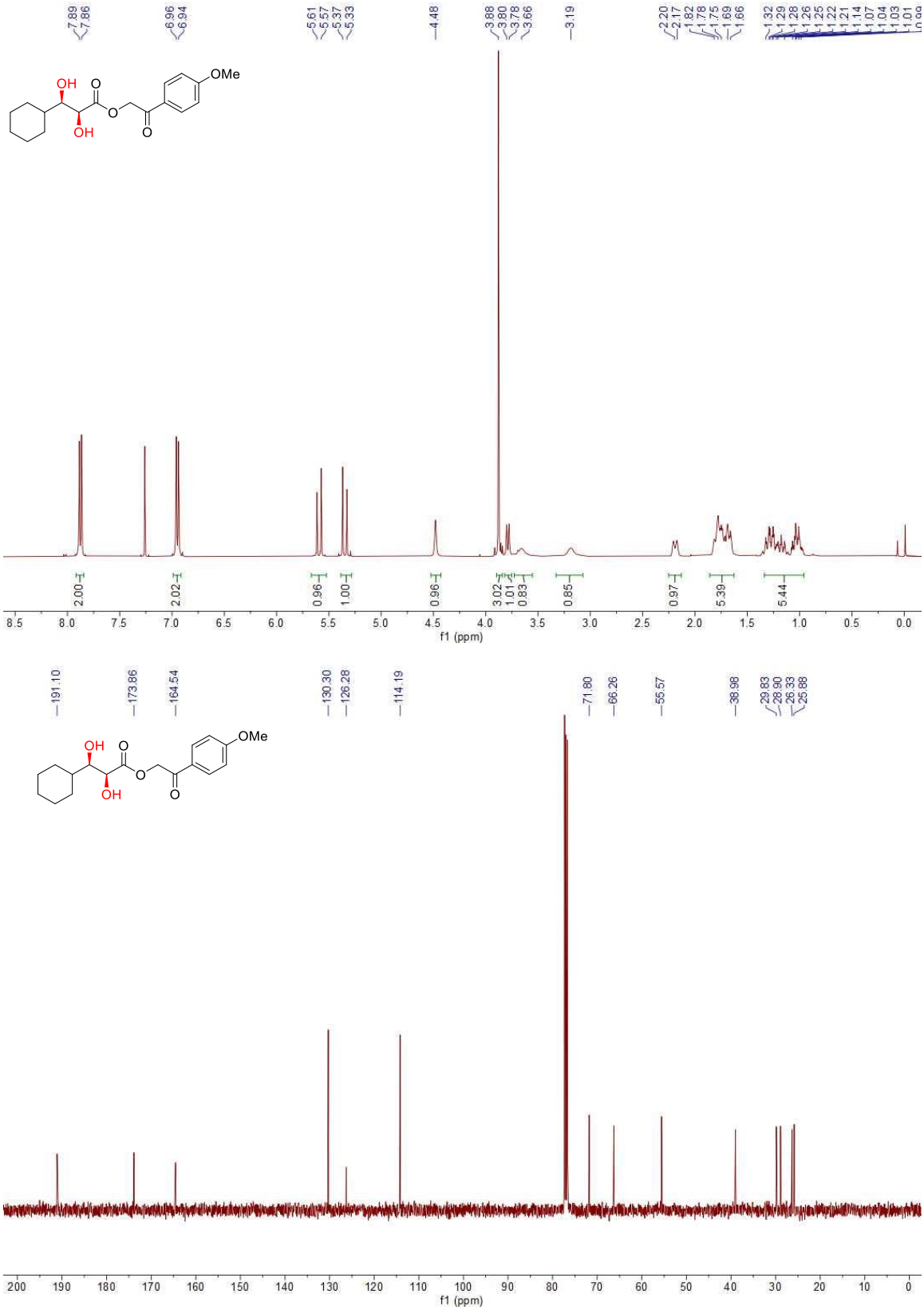


Figure S44. ^{1}H and ^{13}C NMR spectra of **2q** in $CDCl_3$.

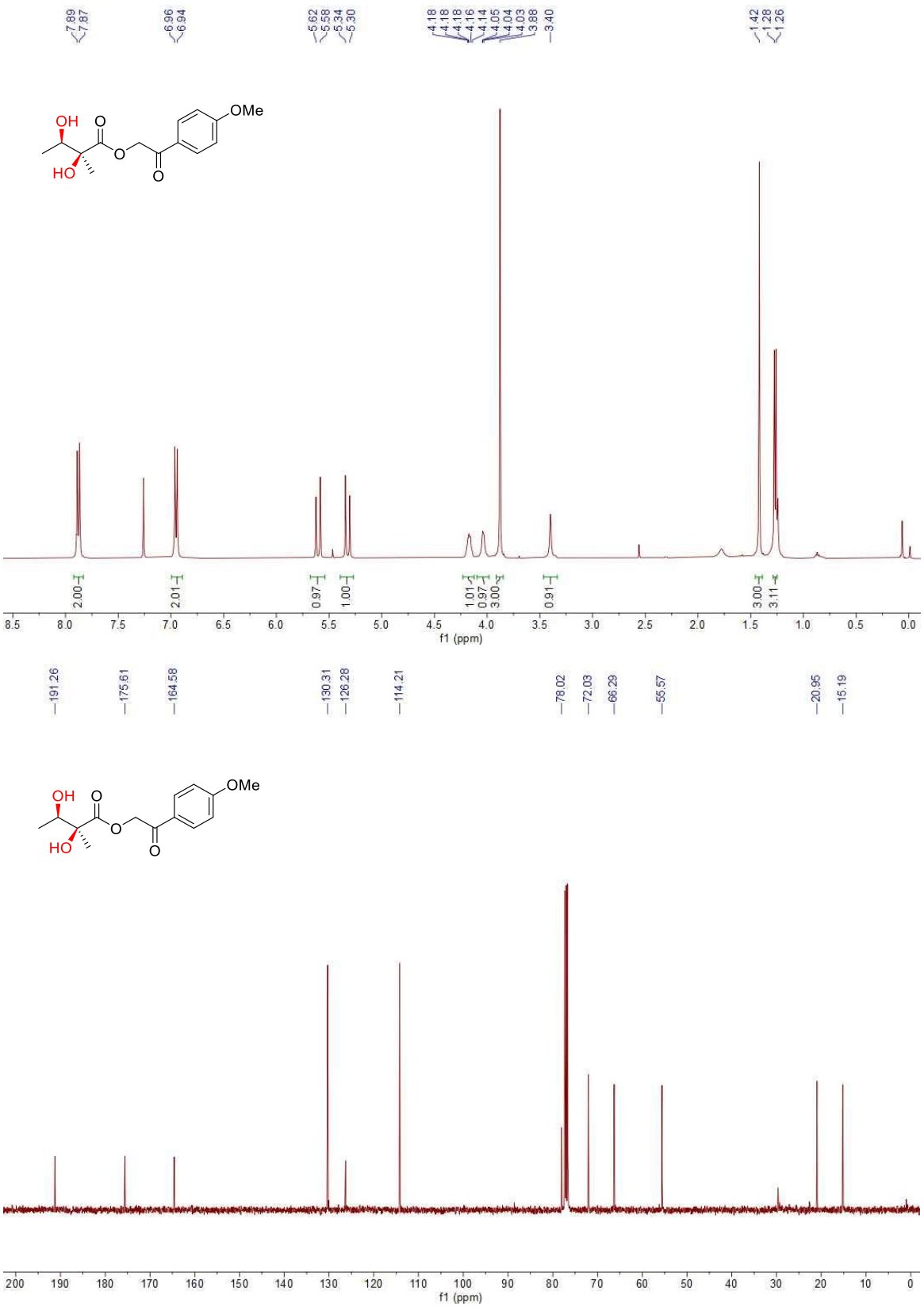


Figure S45. ^{1}H and ^{13}C NMR spectra of **2r** in $CDCl_3$.

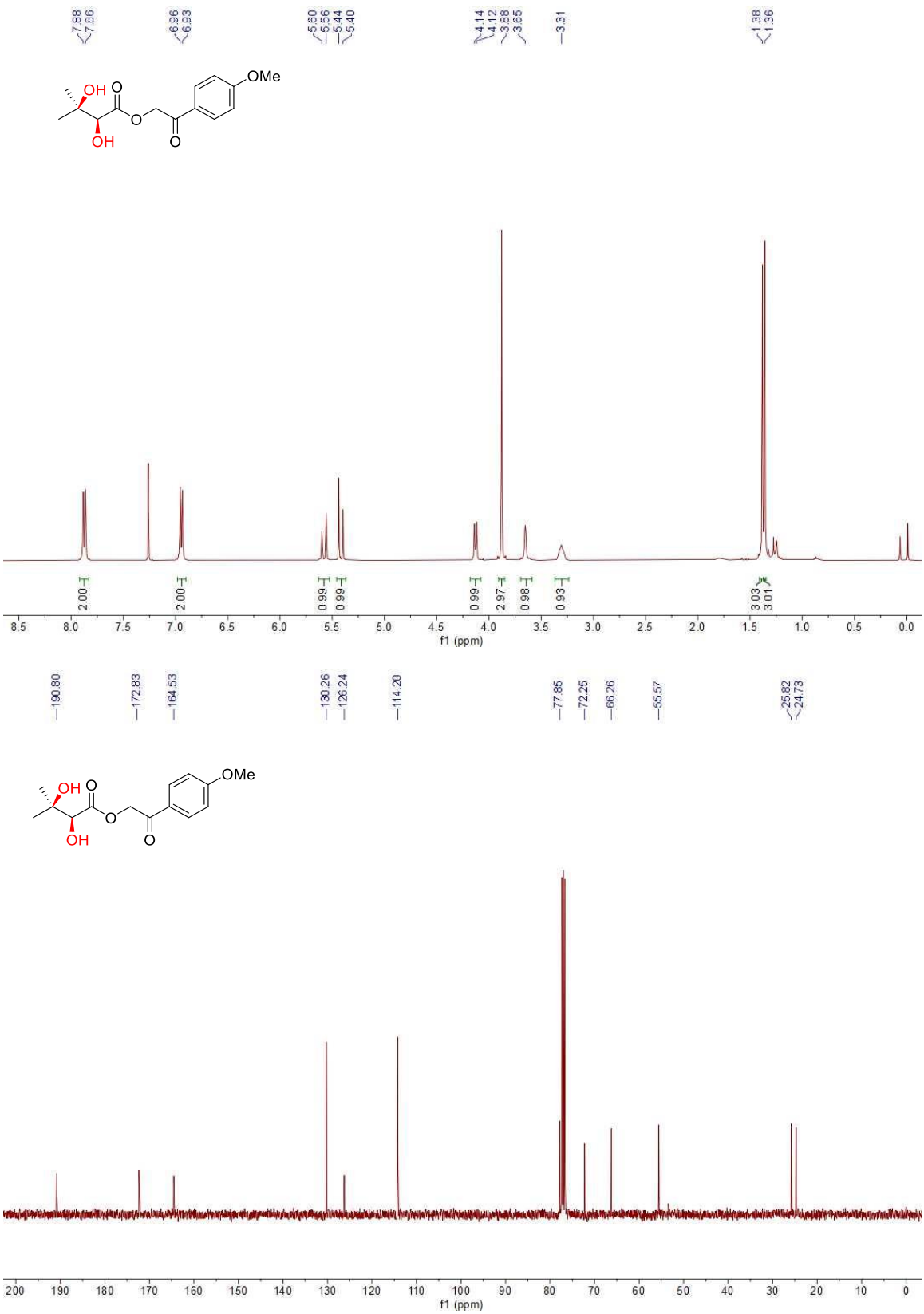


Figure S46. ^{1}H and ^{13}C NMR spectra of **4a** in $CDCl_3$.

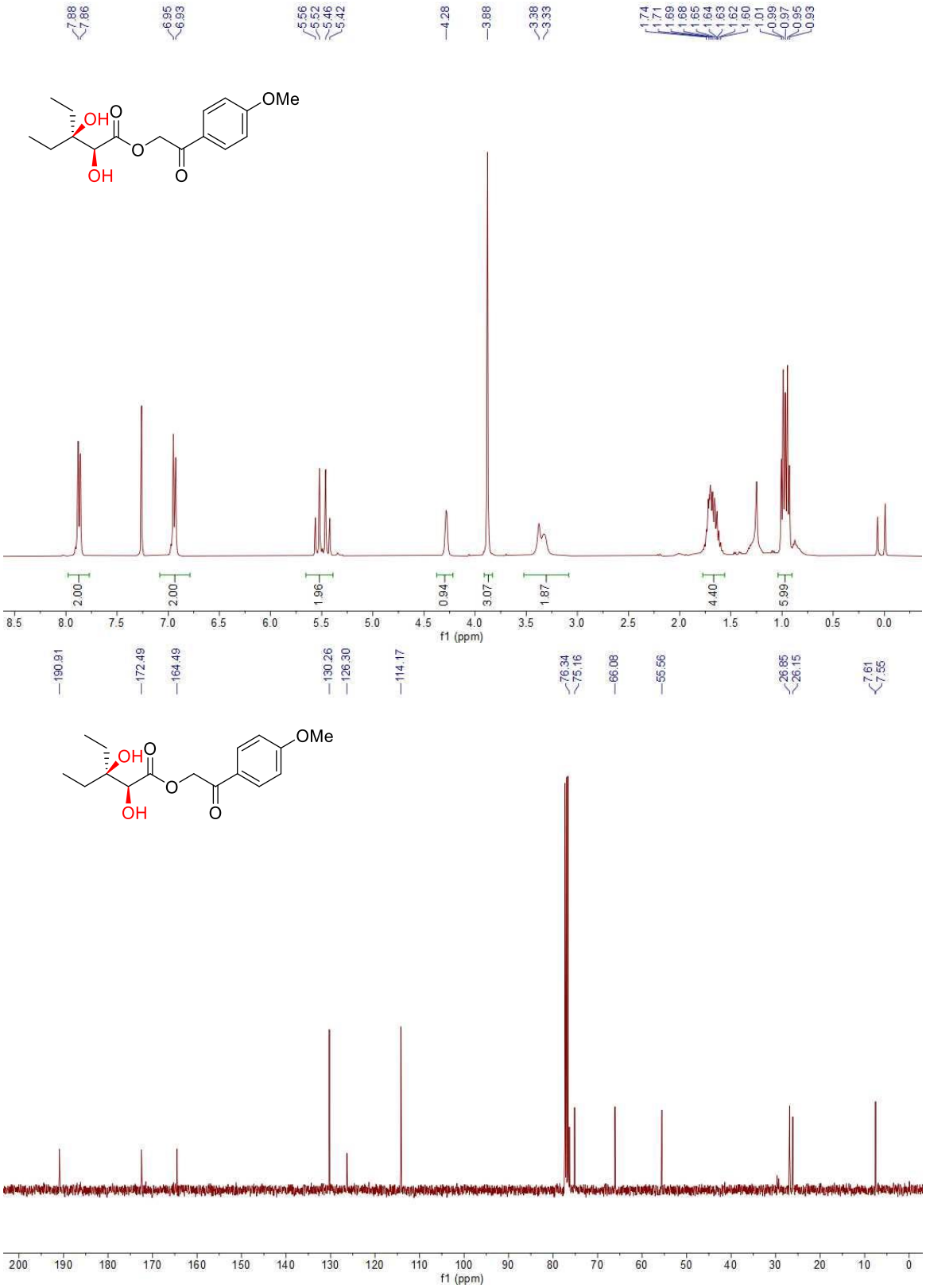


Figure S47. ^{1}H and ^{13}C NMR spectra of **4b** in $CDCl_3$.

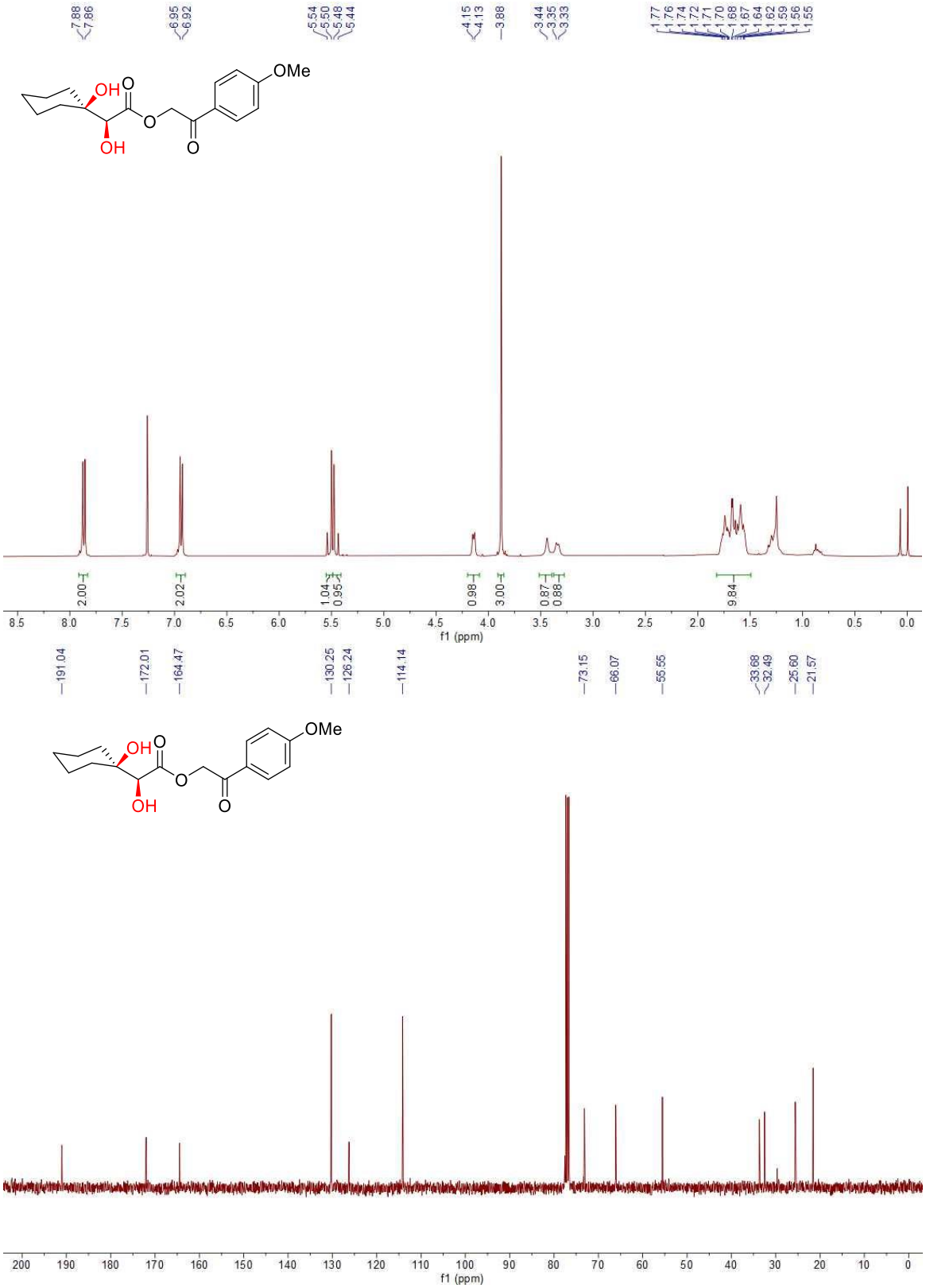


Figure S48. ^{1}H and ^{13}C NMR spectra of **4c** in $CDCl_3$.

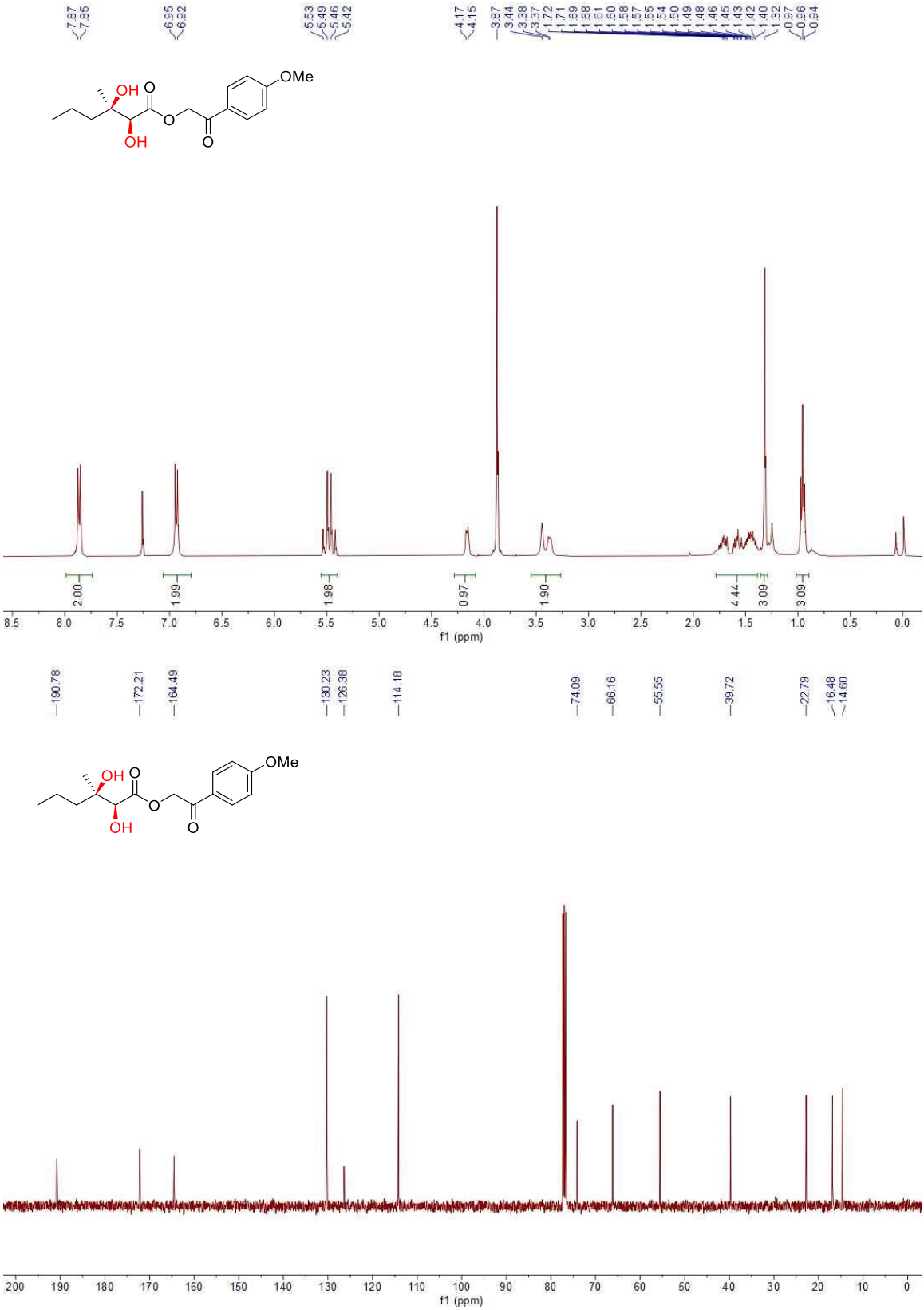


Figure S49. ^{1}H and ^{13}C NMR spectra of **4d** in $CDCl_3$.

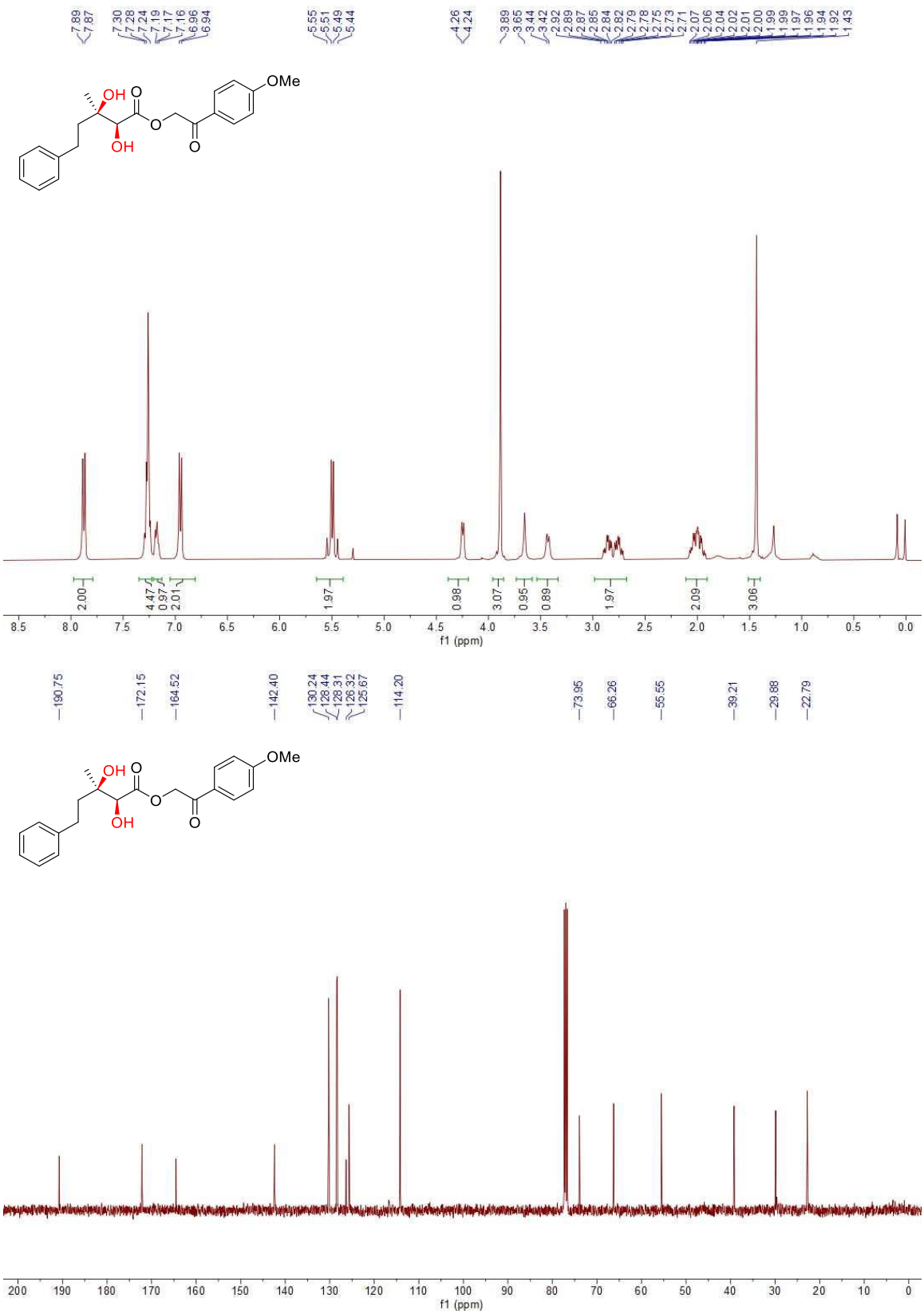


Figure S50. ^{1}H and ^{13}C NMR spectra of **4e** in $CDCl_3$.

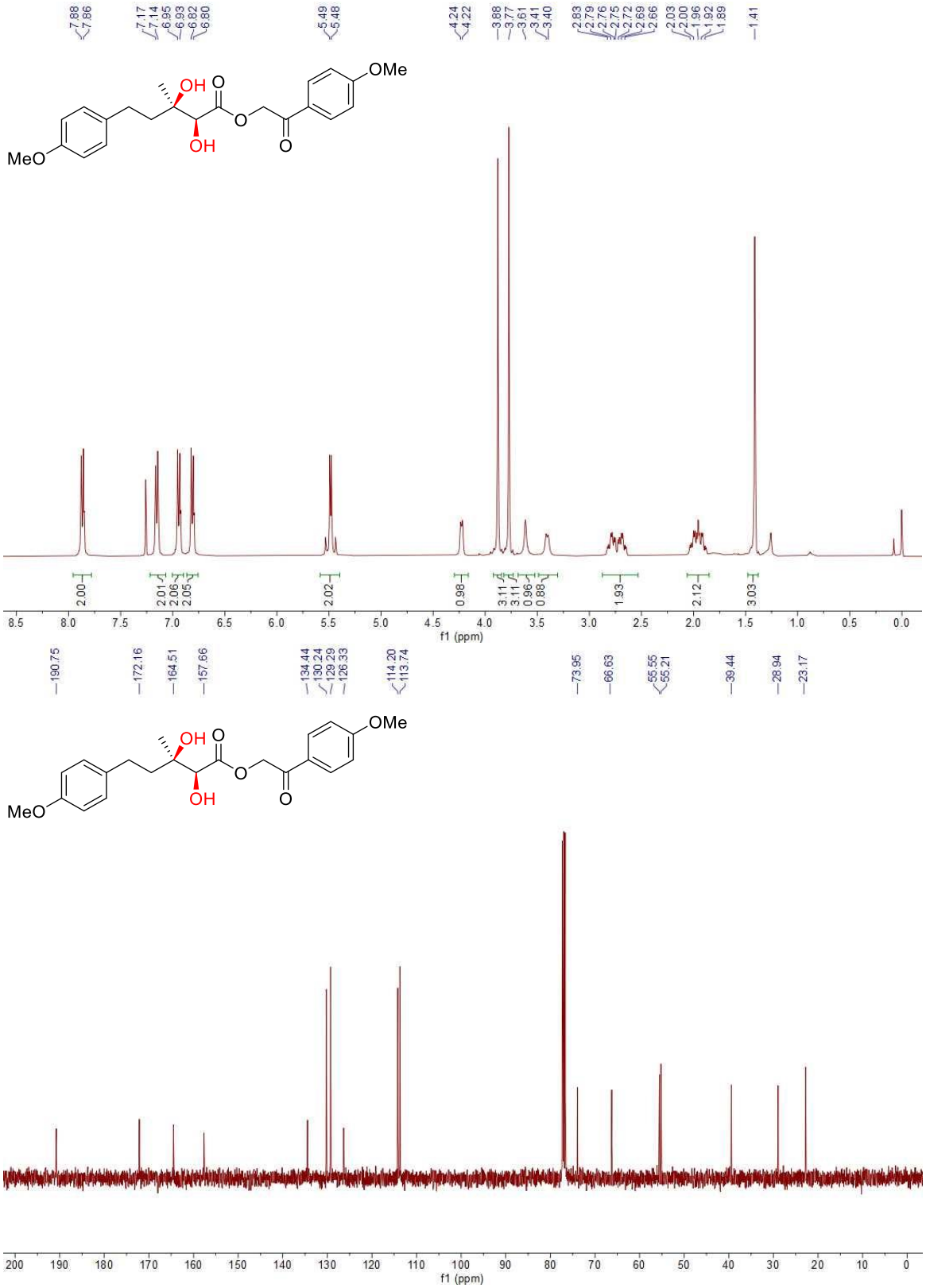


Figure S51. ^{1}H and ^{13}C NMR spectra of **4f** in $CDCl_3$.

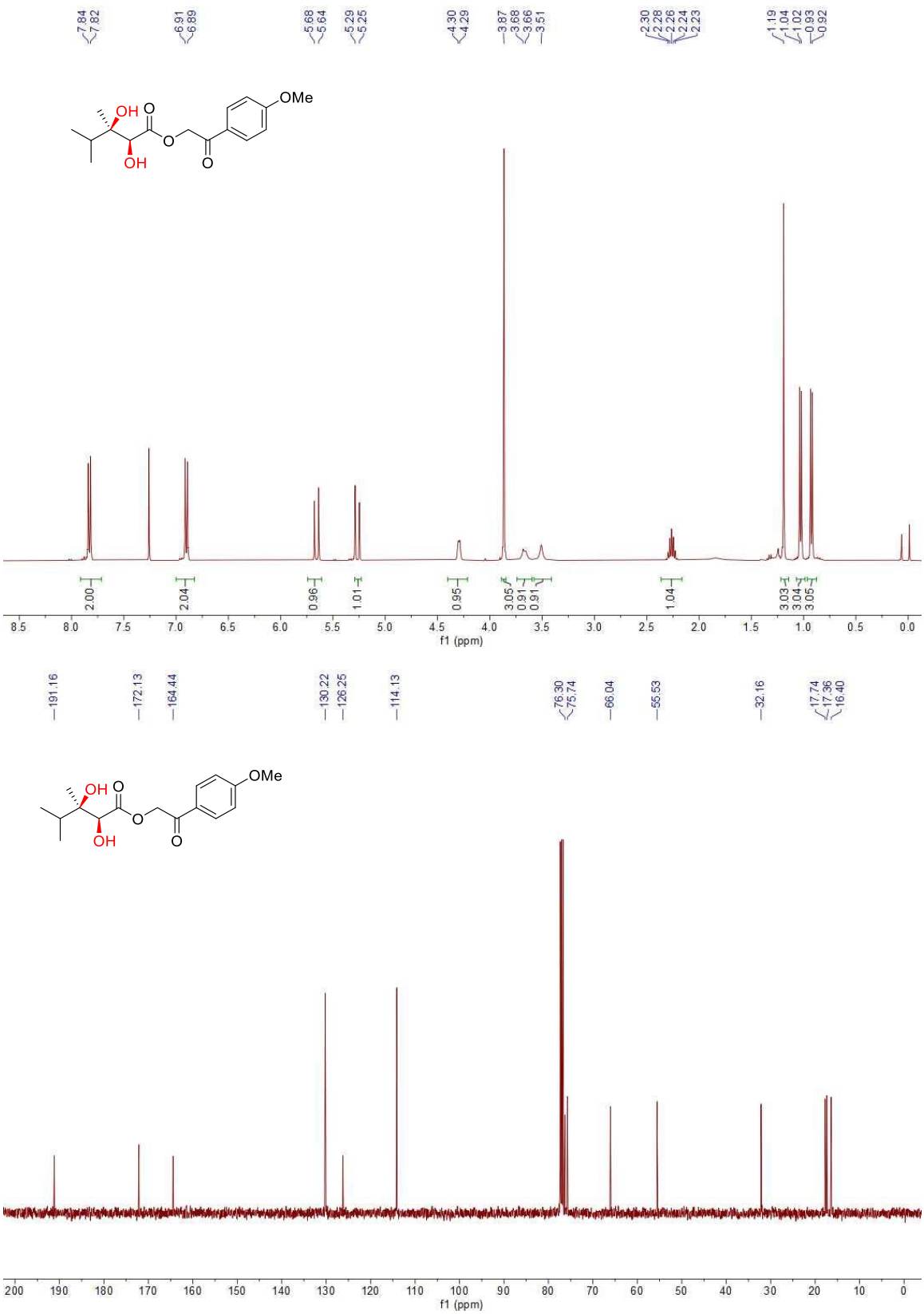


Figure S52. ^{1}H and ^{13}C NMR spectra of **4g** in $CDCl_3$.

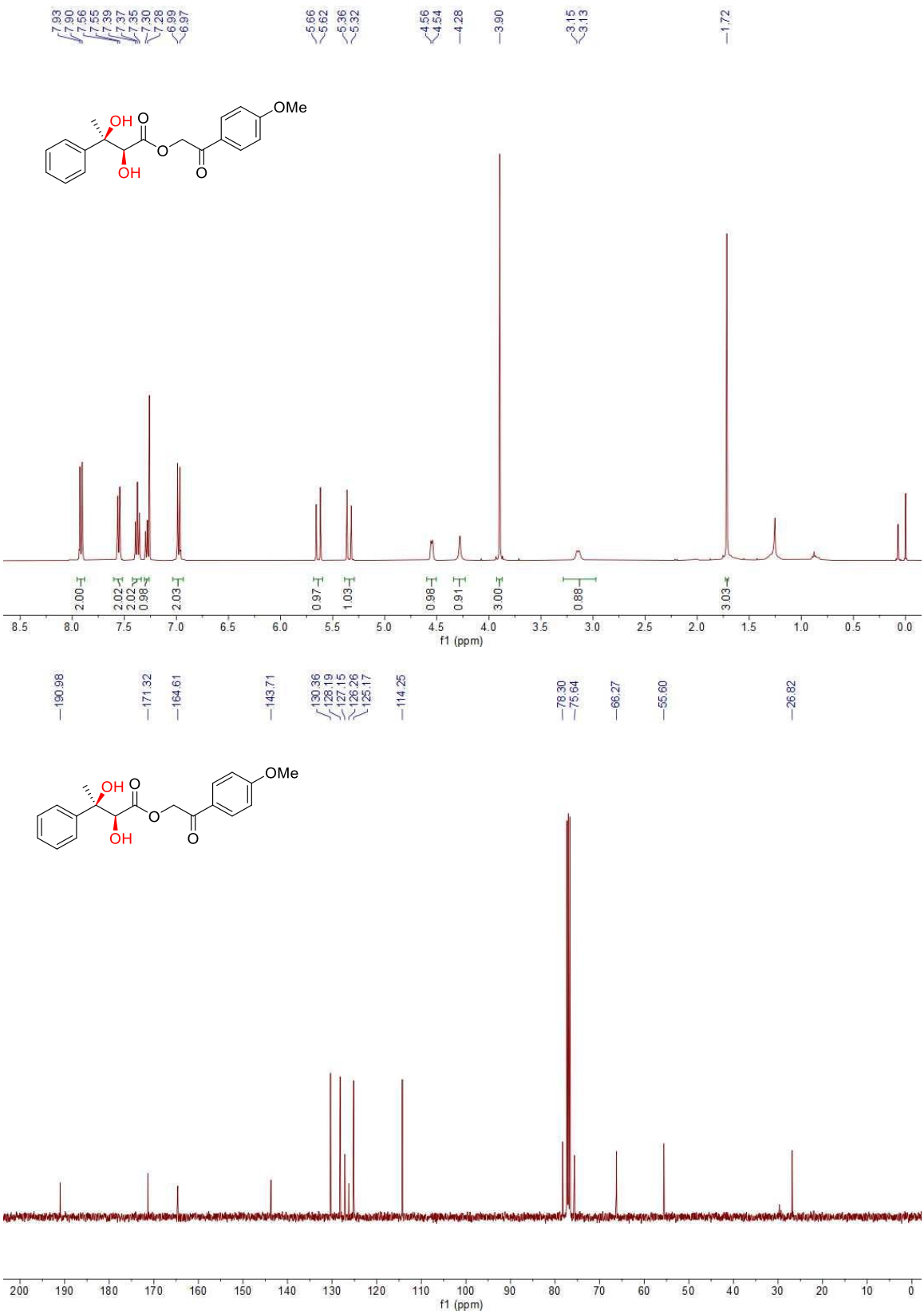


Figure S53. ^{1}H and ^{13}C NMR spectra of **4h** in $CDCl_3$.

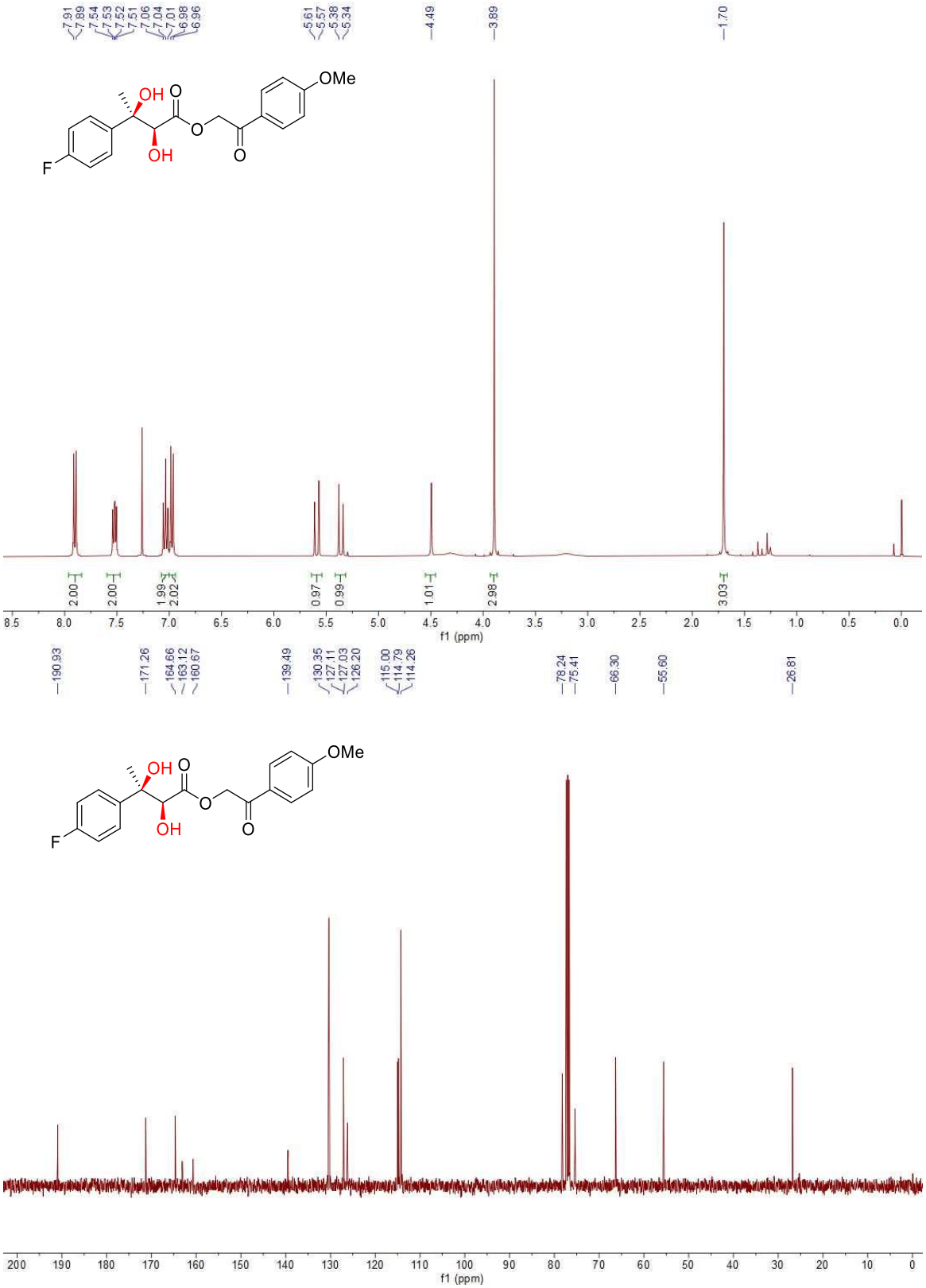


Figure S54. ^{1}H and ^{13}C NMR spectra of **4i** in $CDCl_3$.

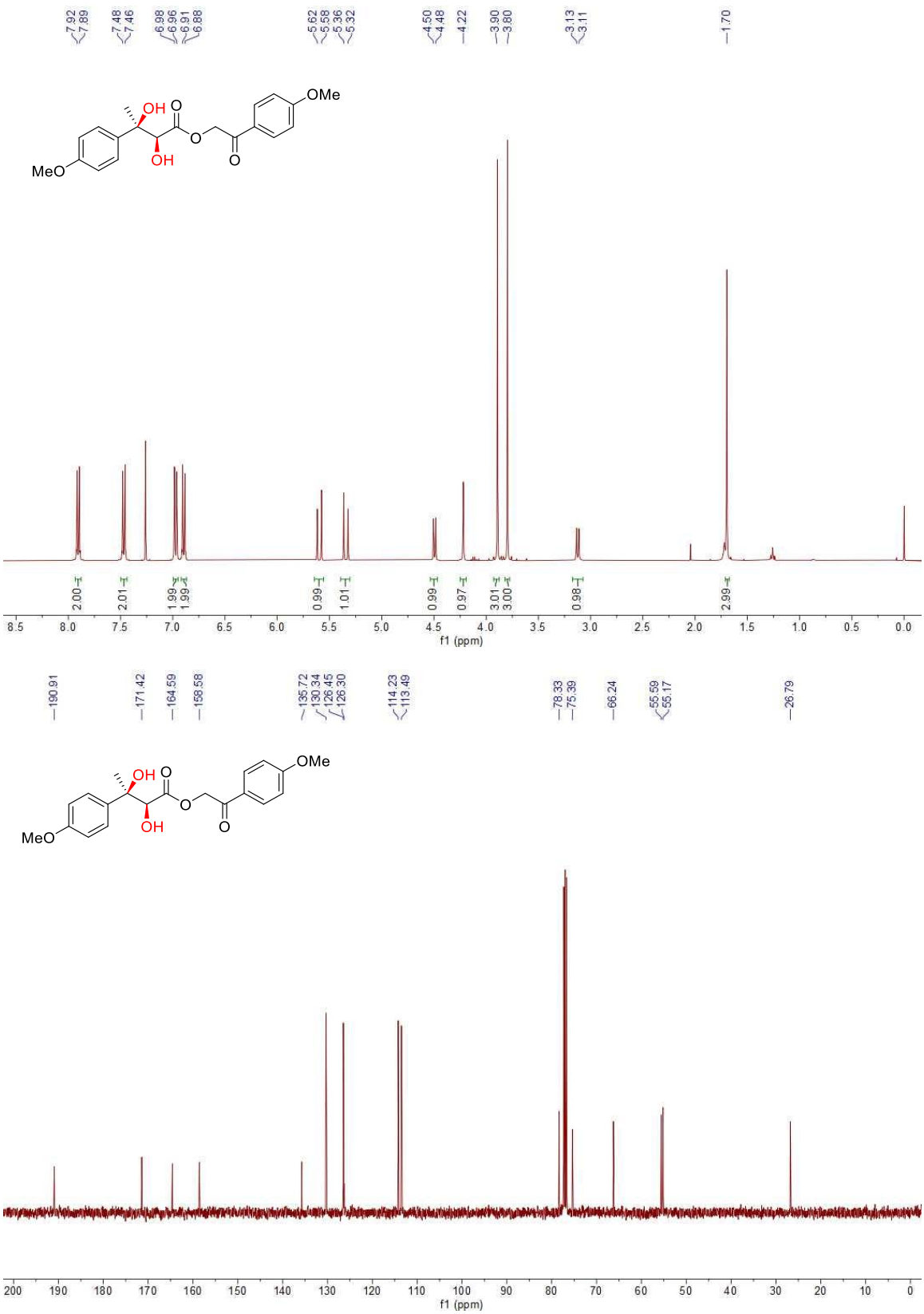


Figure S55. ^{1}H and ^{13}C NMR spectra of **4j** in $CDCl_3$.

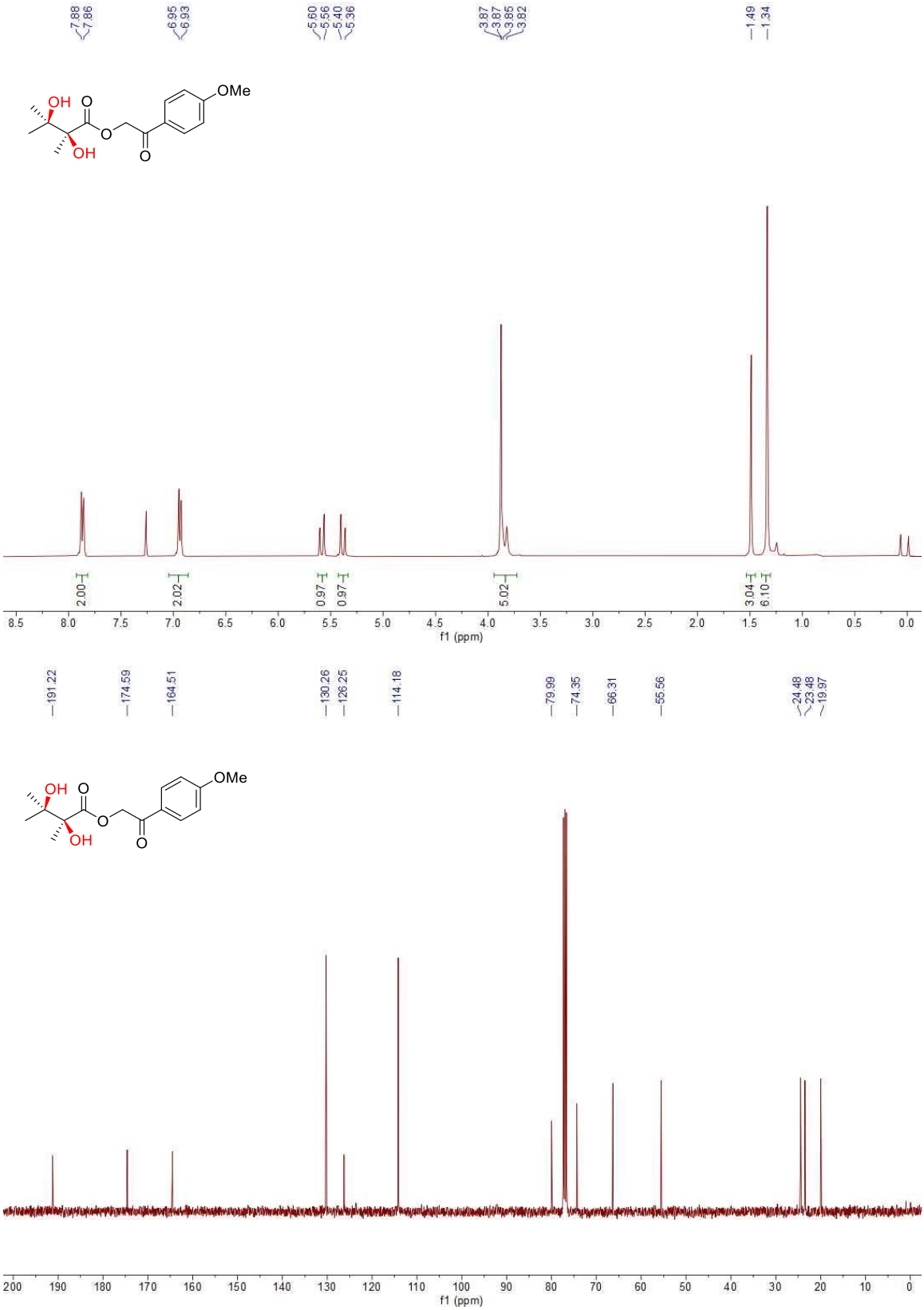


Figure S56. ^{1}H and ^{13}C NMR spectra of **4k** in $CDCl_3$.

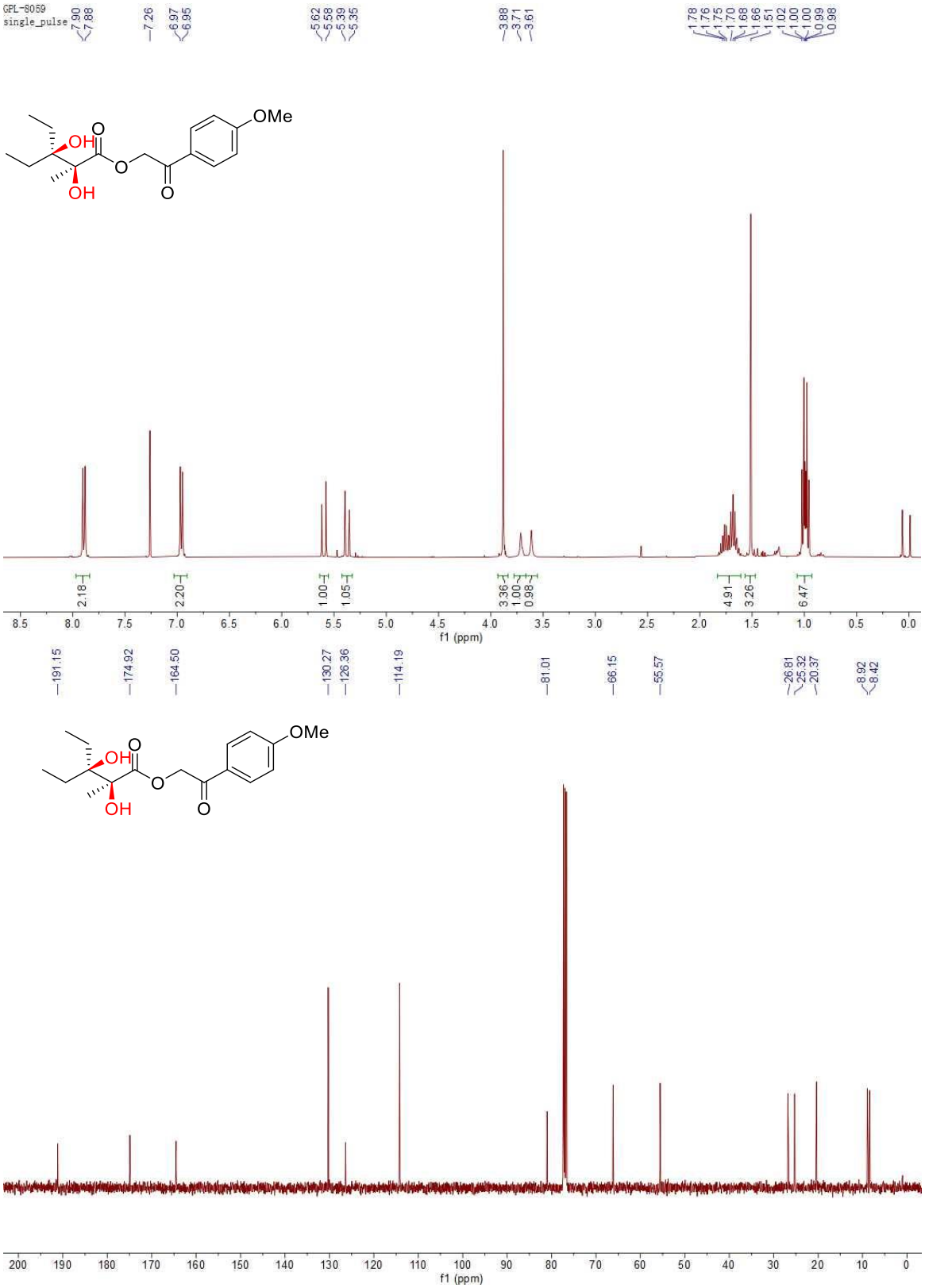


Figure S57. ^{1}H and ^{13}C NMR spectra of **4l** in $CDCl_3$.

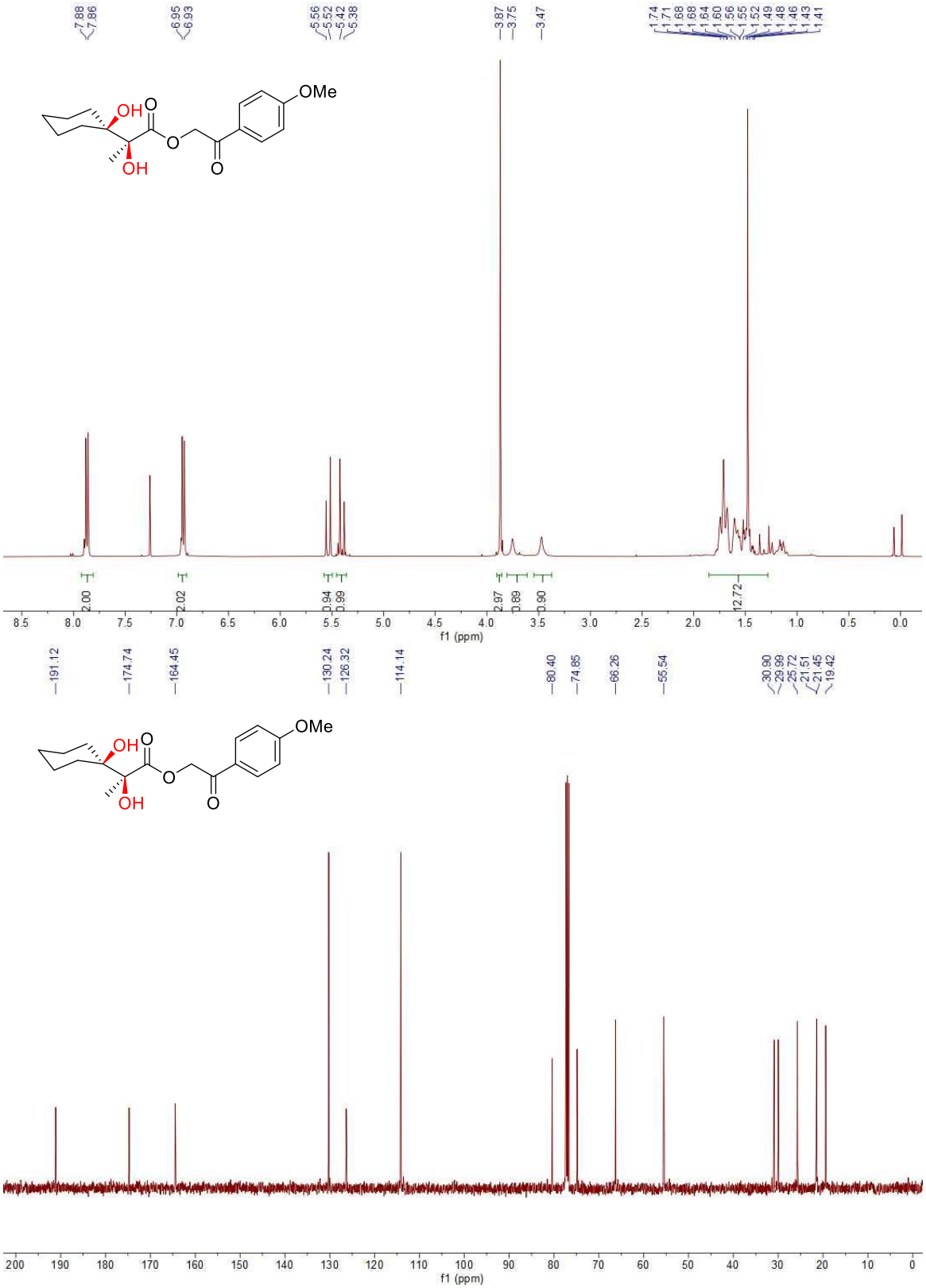


Figure S58. ^{1}H and ^{13}C NMR spectra of **4m** in $CDCl_3$.

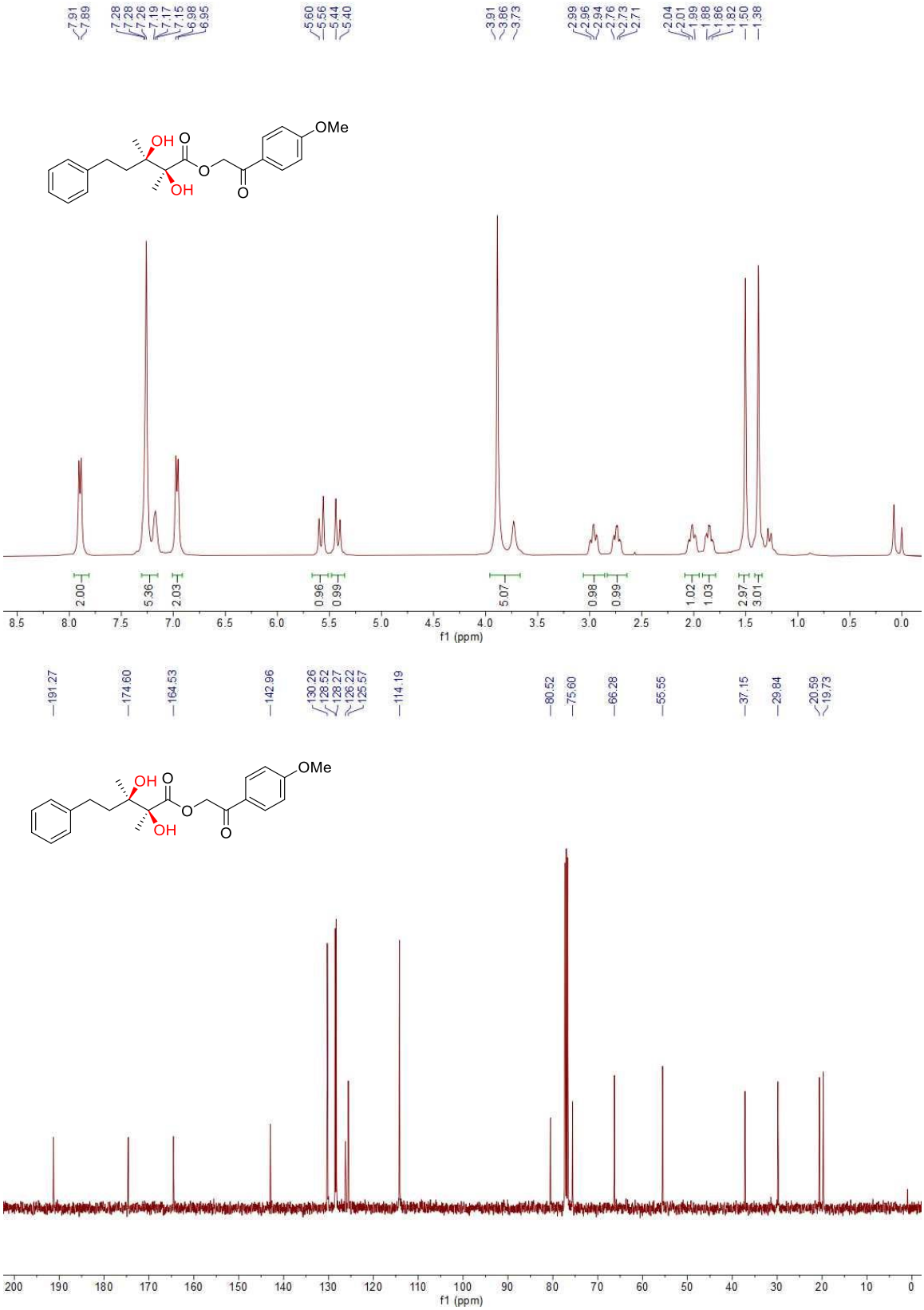


Figure S59. ^{1}H and ^{13}C NMR spectra of **4n** in $CDCl_3$.

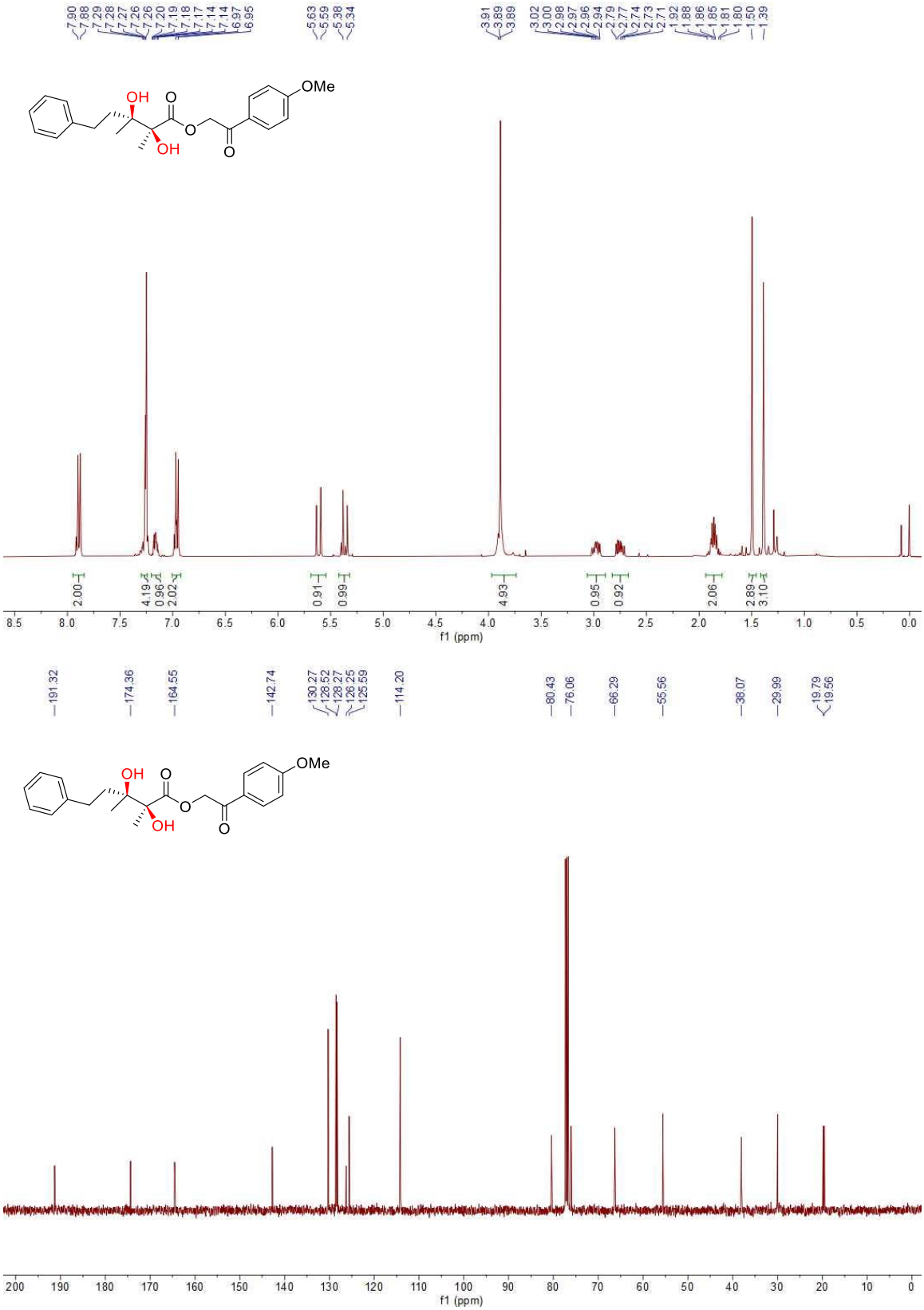


Figure S60. ^{1}H and ^{13}C NMR spectra of **4o** in $CDCl_3$.

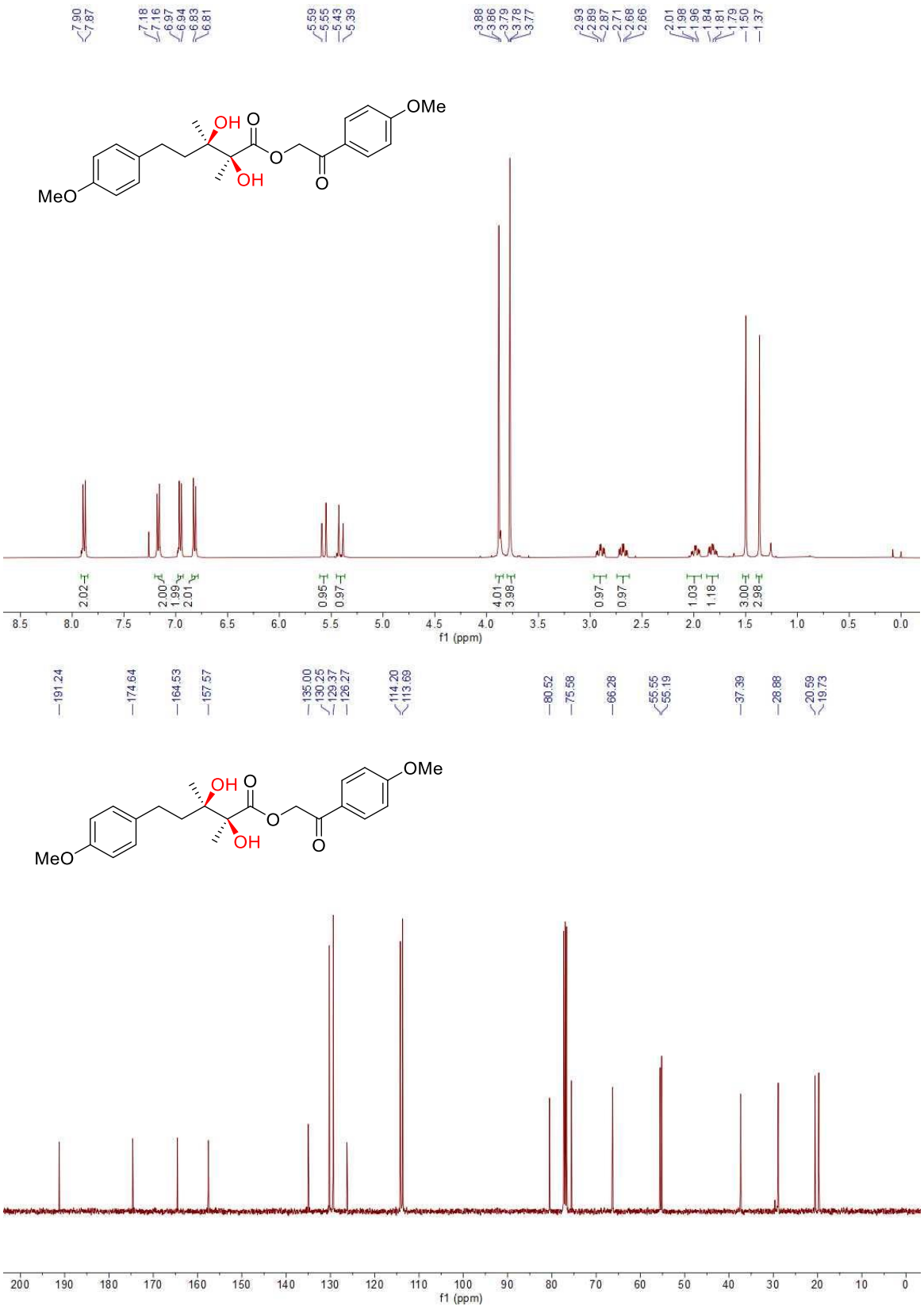


Figure S61. ^{1}H and ^{13}C NMR spectra of **4p** in $CDCl_3$.

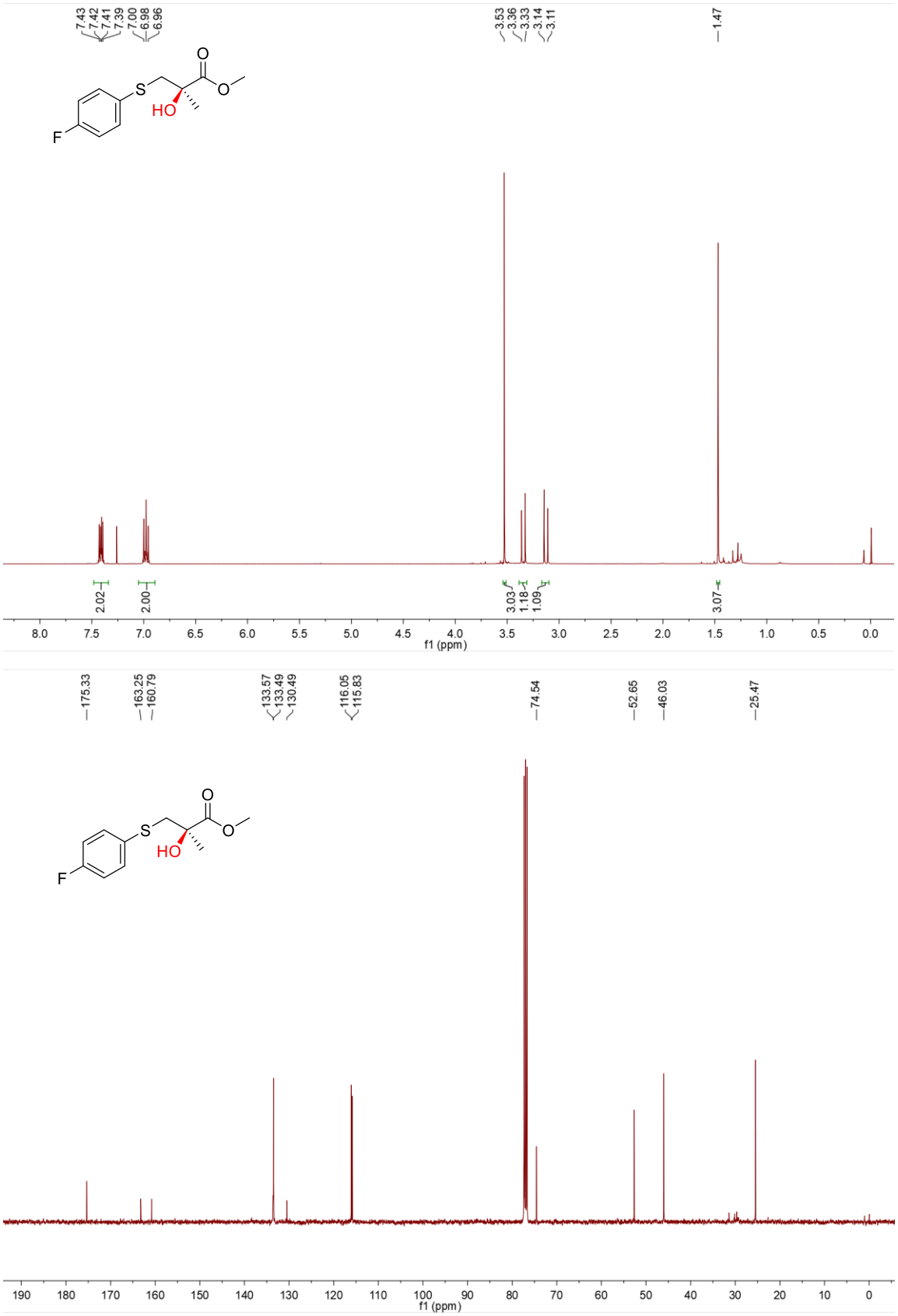
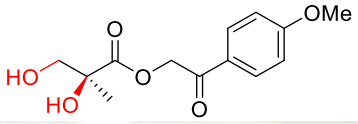
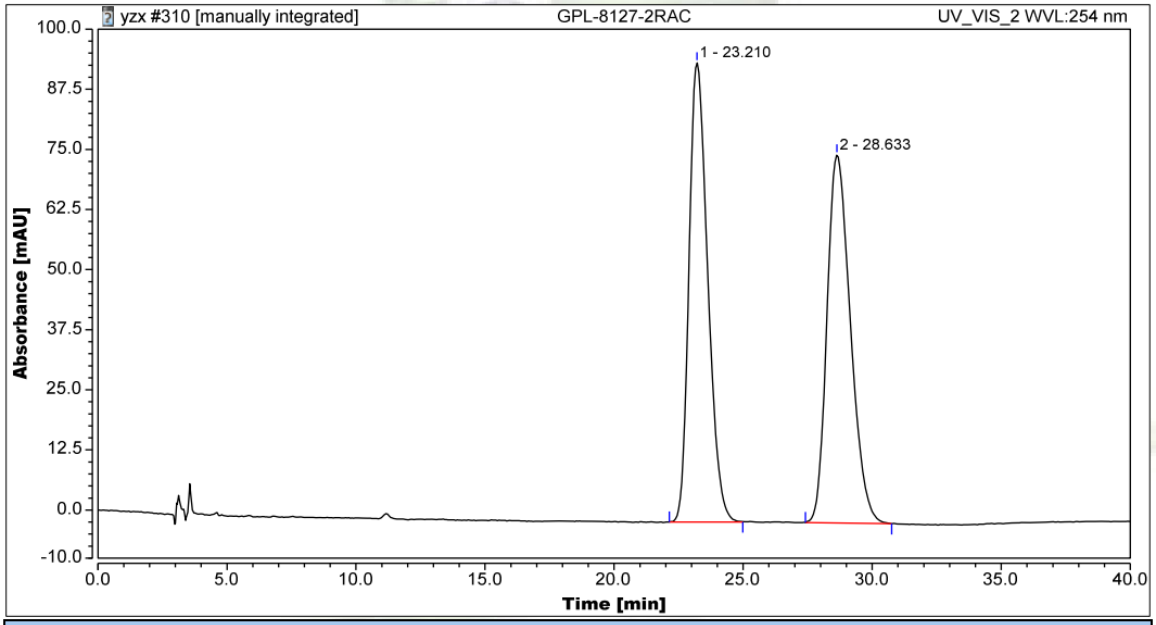


Figure S62. ^{1}H and ^{13}C NMR spectra of **7** in $CDCl_3$.



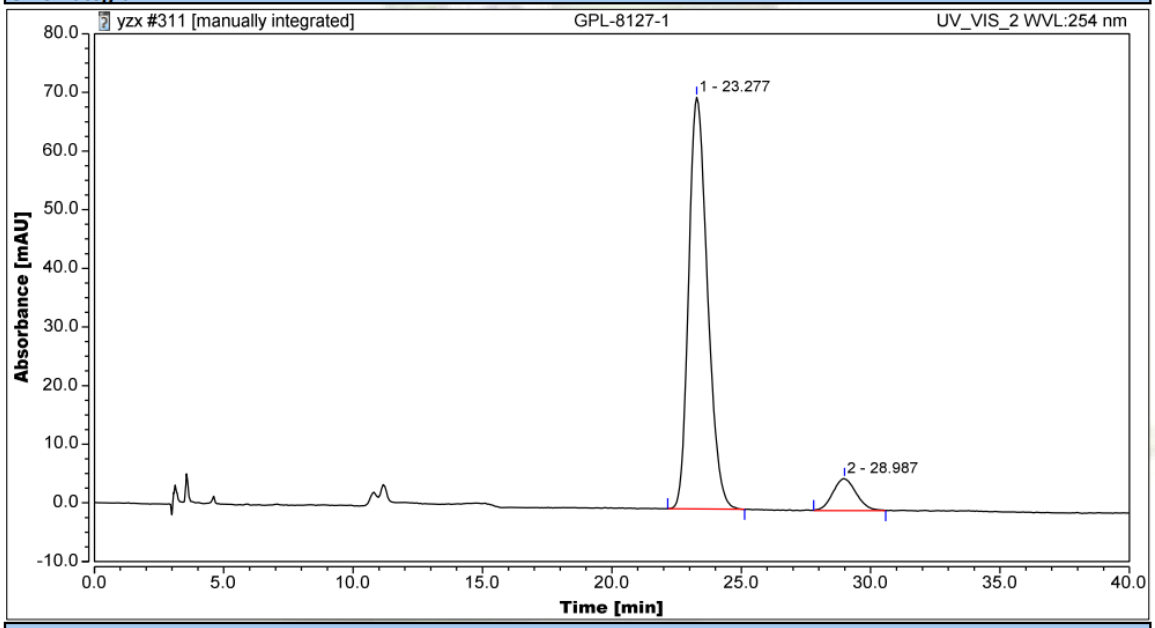
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.210	80.180	95.506	49.92	55.51	n.a.
2		28.633	80.431	76.539	50.08	44.49	n.a.
Total:			**160.611**	**172.045**	**100.00**	**100.00**	

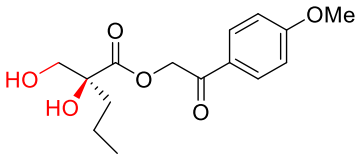
Chromatogram



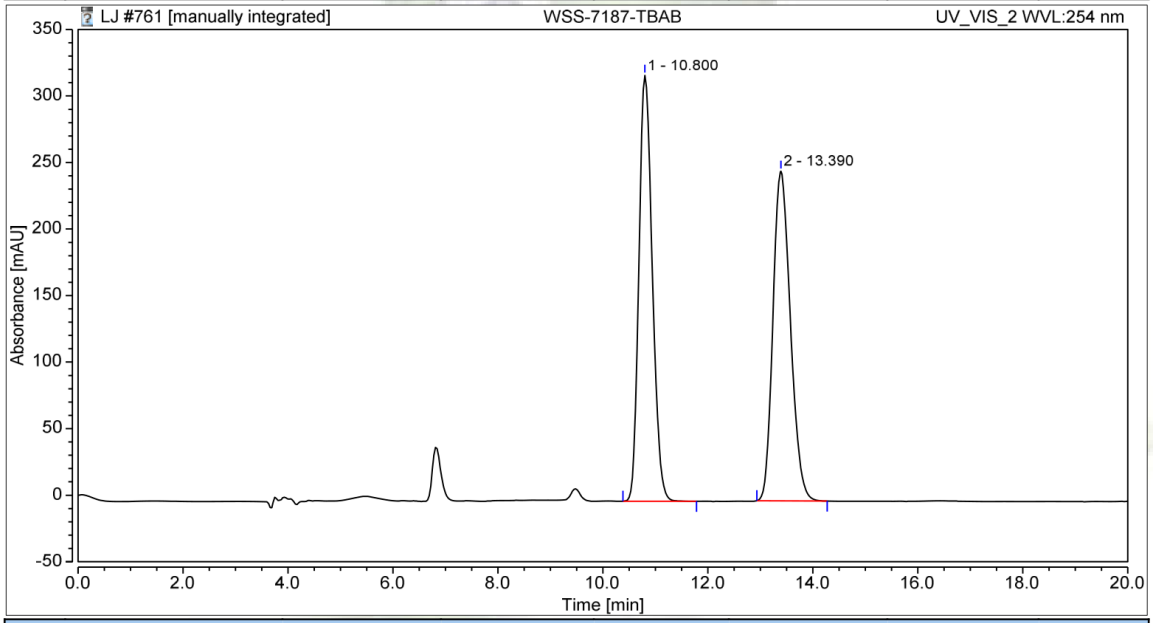
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.277	59.116	70.234	91.20	92.78	n.a.
2		28.987	5.703	5.466	8.80	7.22	n.a.
Total:			**64.818**	**75.699**	**100.00**	**100.00**	

Figure S63. HPLC chromatogram for **2a**.



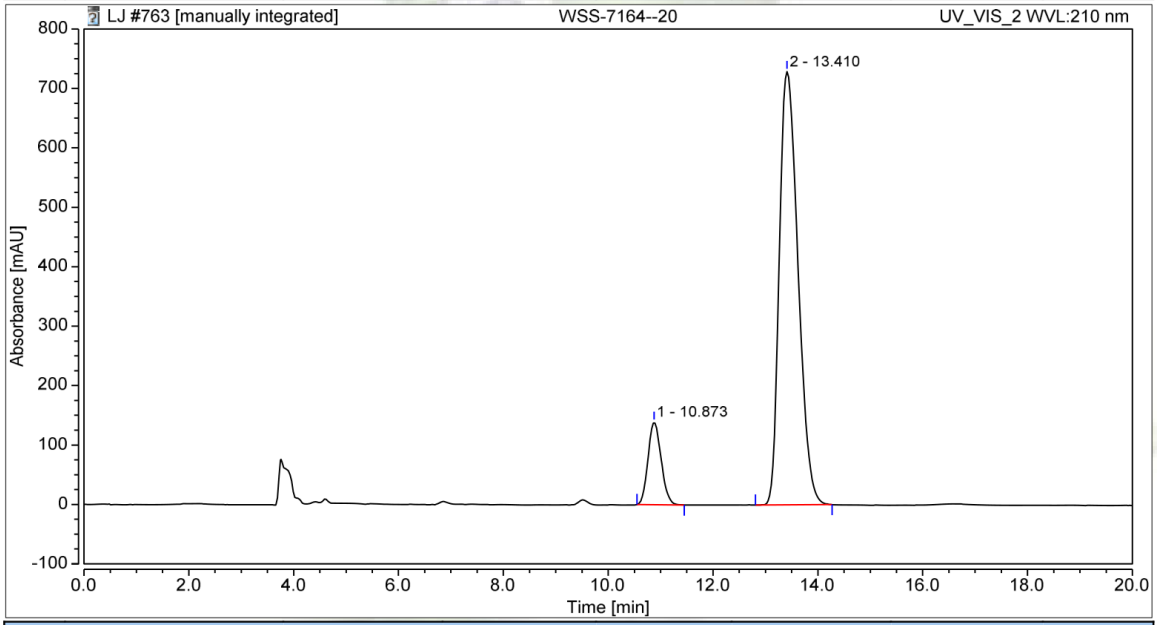
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.800	94.543	320.130	49.79	56.37	n.a.
2		13.390	95.330	247.730	50.21	43.63	n.a.
Total:			**189.873**	**567.859**	**100.00**	**100.00**	

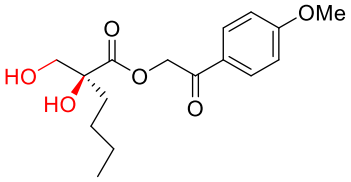
Chromatogram



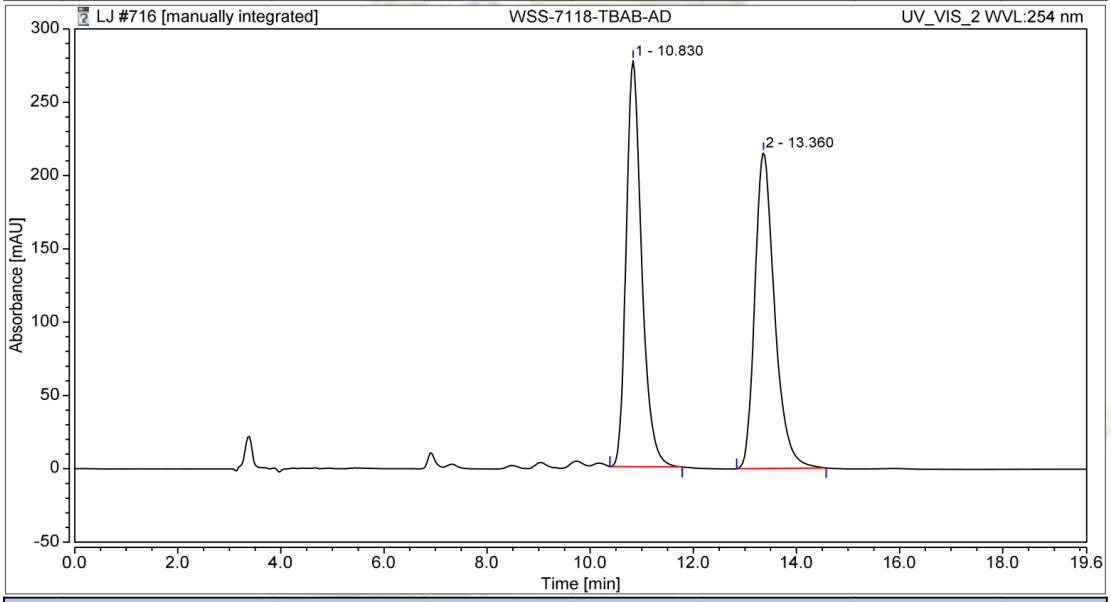
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.873	40.417	138.681	11.84	15.98	n.a.
2		13.410	300.966	729.297	88.16	84.02	n.a.
Total:			**341.383**	**867.978**	**100.00**	**100.00**	

Figure S64. HPLC chromatogram for **2b**.



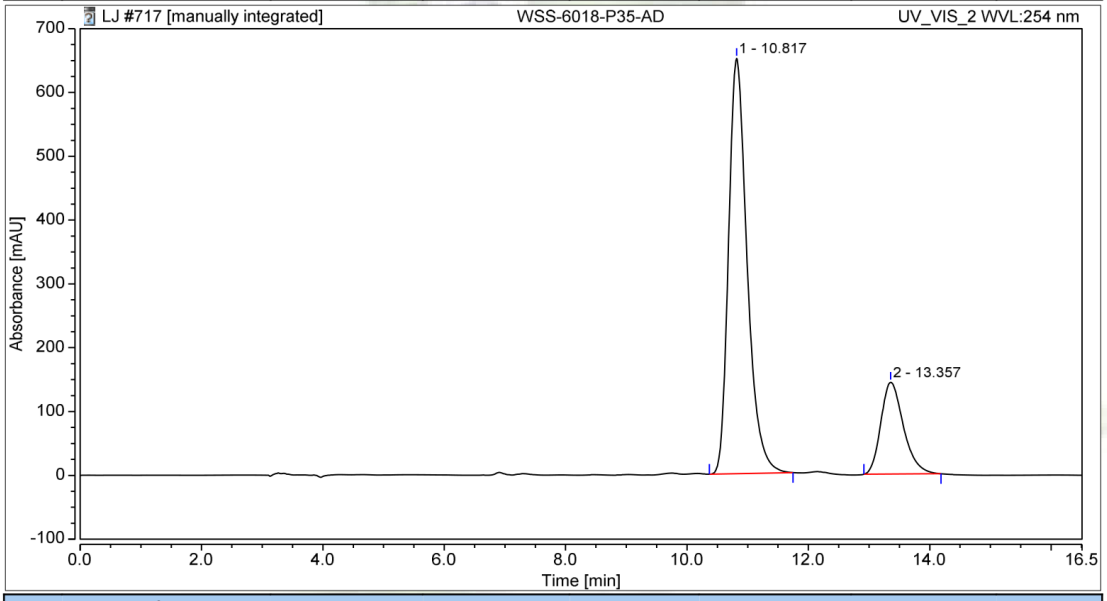
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.830	96.933	277.007	50.32	56.26	n.a.
2		13.360	95.695	215.378	49.68	43.74	n.a.
Total:			**192.628**	**492.385**	**100.00**	**100.00**	

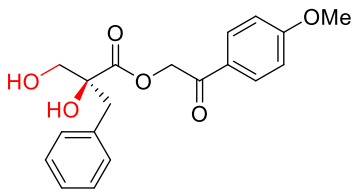
Chromatogram



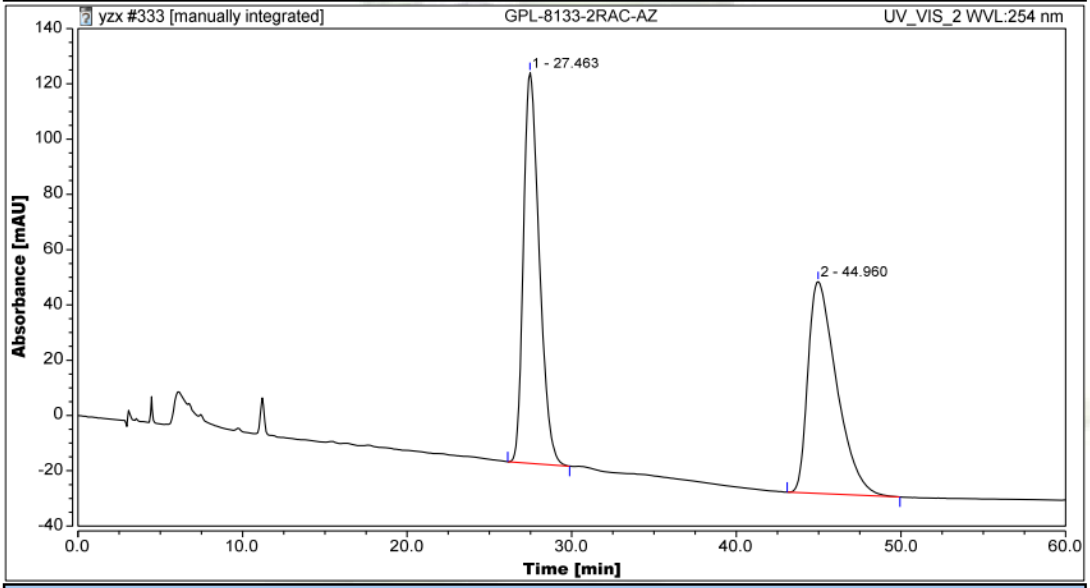
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.817	230.829	650.929	78.80	81.89	n.a.
2		13.357	62.117	143.950	21.20	18.11	n.a.
Total:			**292.945**	**794.878**	**100.00**	**100.00**	

Figure S65. HPLC chromatogram for **2c**.



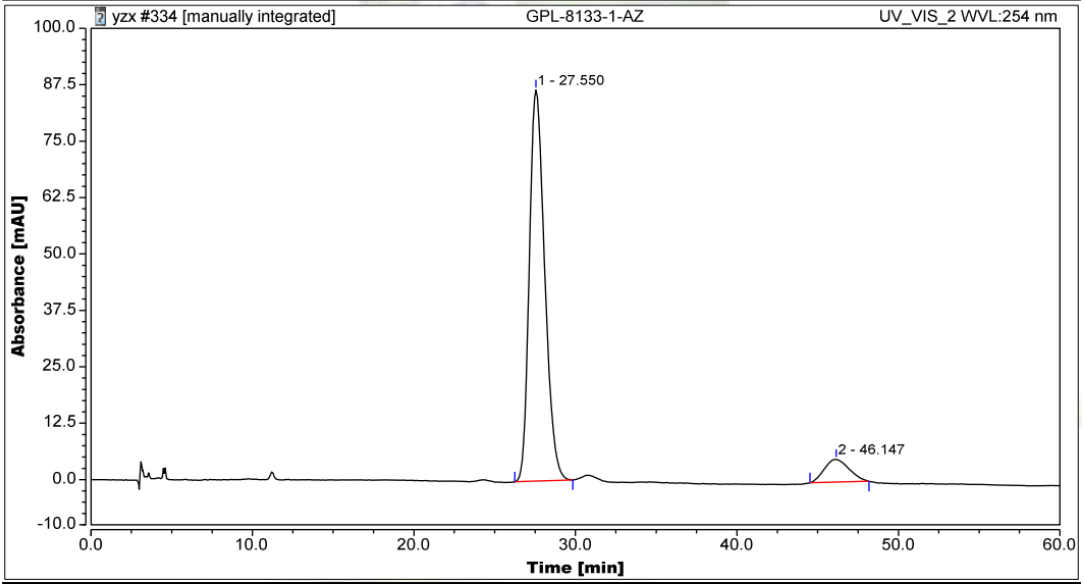
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.463	157.787	141.415	50.51	64.85	n.a.
2		44.960	154.595	76.655	49.49	35.15	n.a.
Total:			**312.382**	**218.070**	**100.00**	**100.00**	

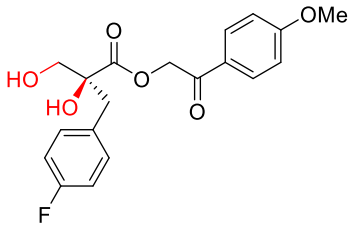
Chromatogram



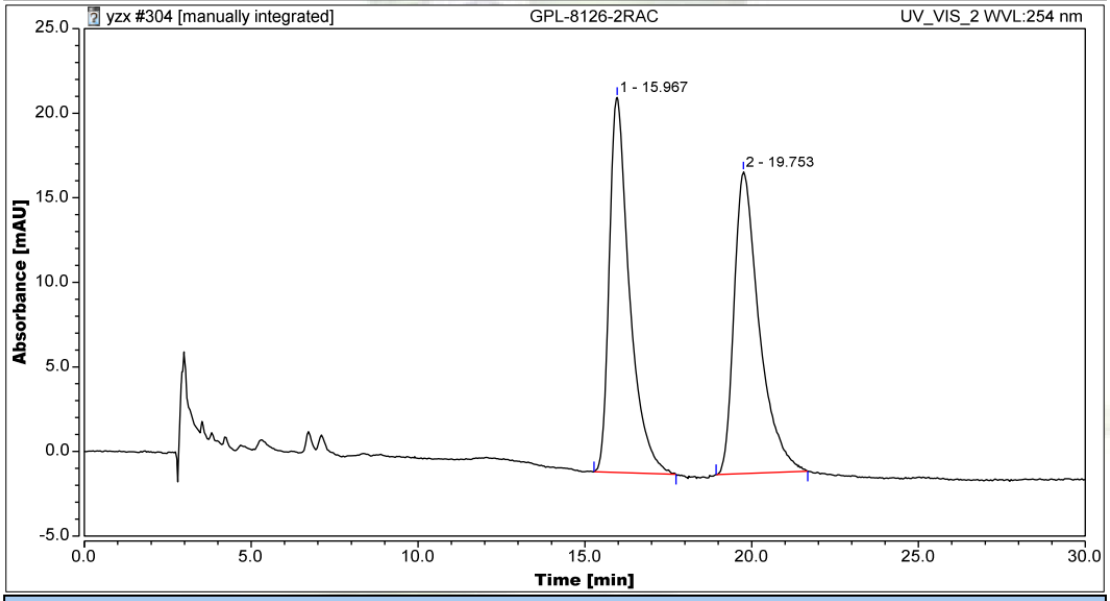
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.550	95.692	86.675	91.46	94.51	n.a.
2		46.147	8.940	5.036	8.54	5.49	n.a.
Total:			**104.632**	**91.711**	**100.00**	**100.00**	

Figure S66. HPLC chromatogram for **2d**.



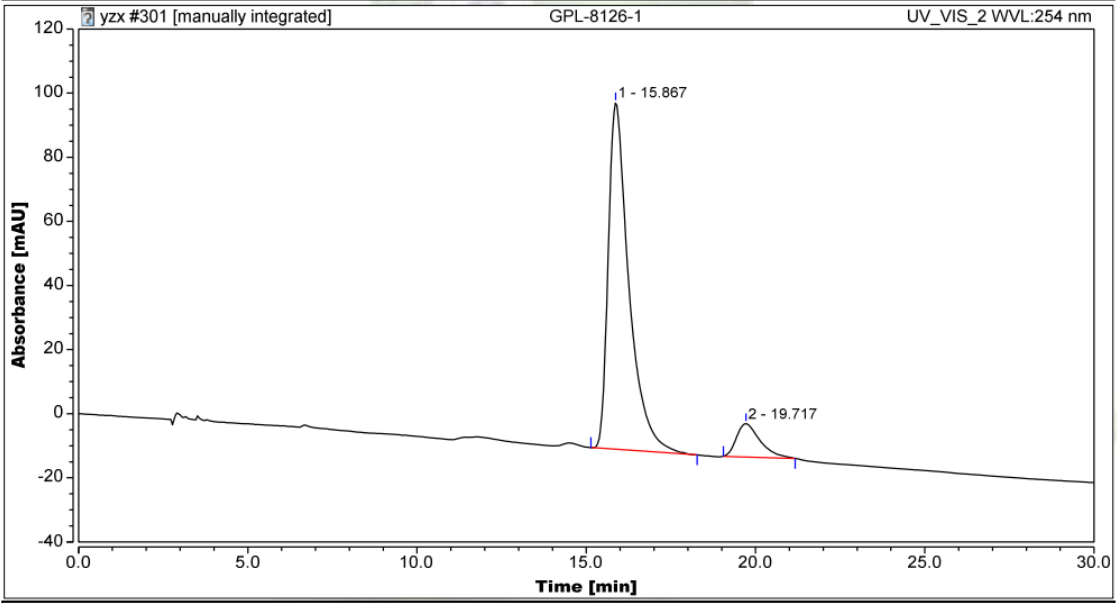
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.967	15.544	22.163	49.90	55.40	n.a.
2		19.753	15.604	17.843	50.10	44.60	n.a.
Total:			**31.147**	**40.006**	**100.00**	**100.00**	

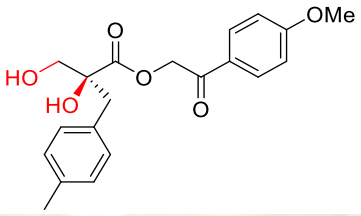
Chromatogram



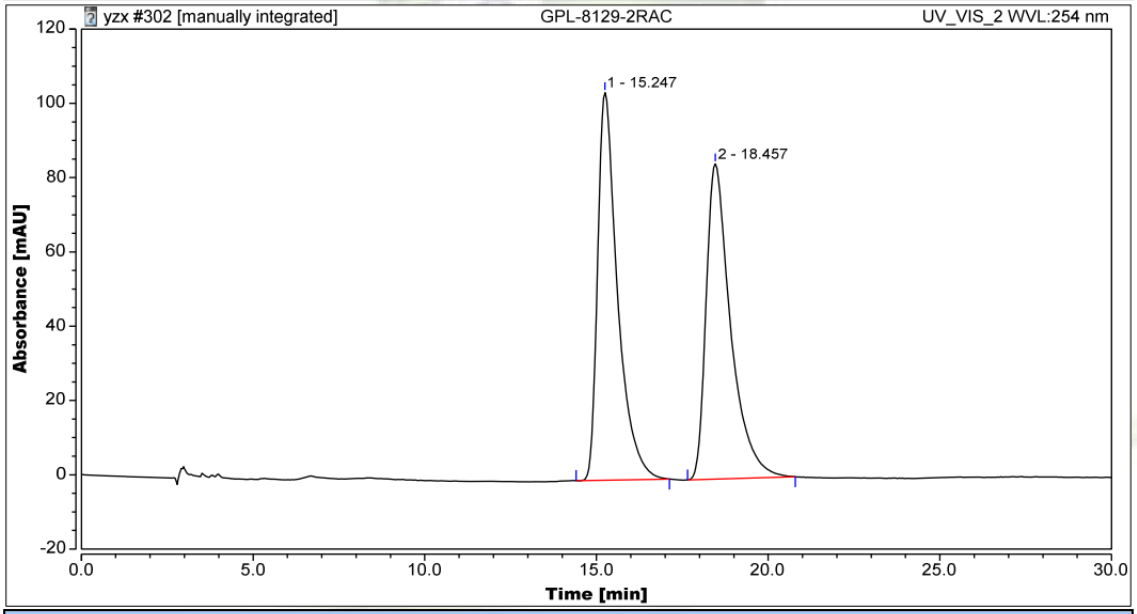
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.867	76.452	108.065	90.10	91.23	n.a.
2		19.717	8.400	10.393	9.90	8.77	n.a.
Total:			**84.851**	**118.458**	**100.00**	**100.00**	

Figure S67. HPLC chromatogram for **2e**.



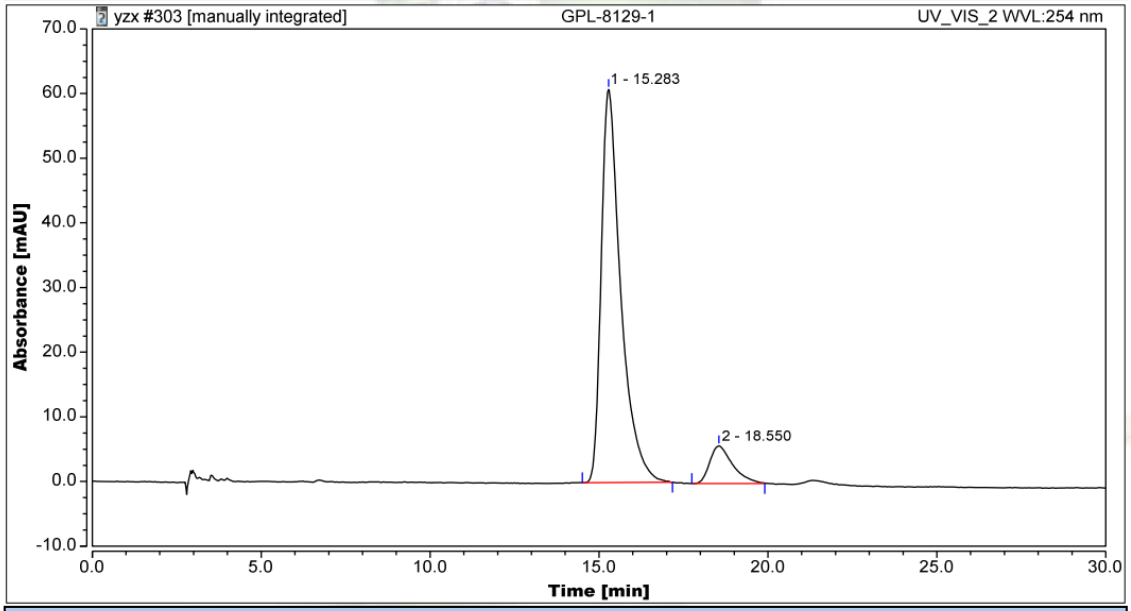
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.247	70.173	104.366	50.02	55.14	n.a.
2		18.457	70.110	84.895	49.98	44.86	n.a.
Total:			**140.283**	**189.260**	**100.00**	**100.00**	

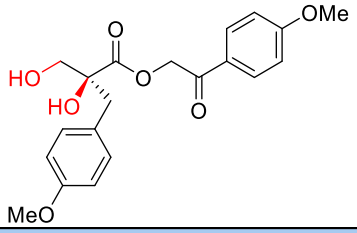
Chromatogram



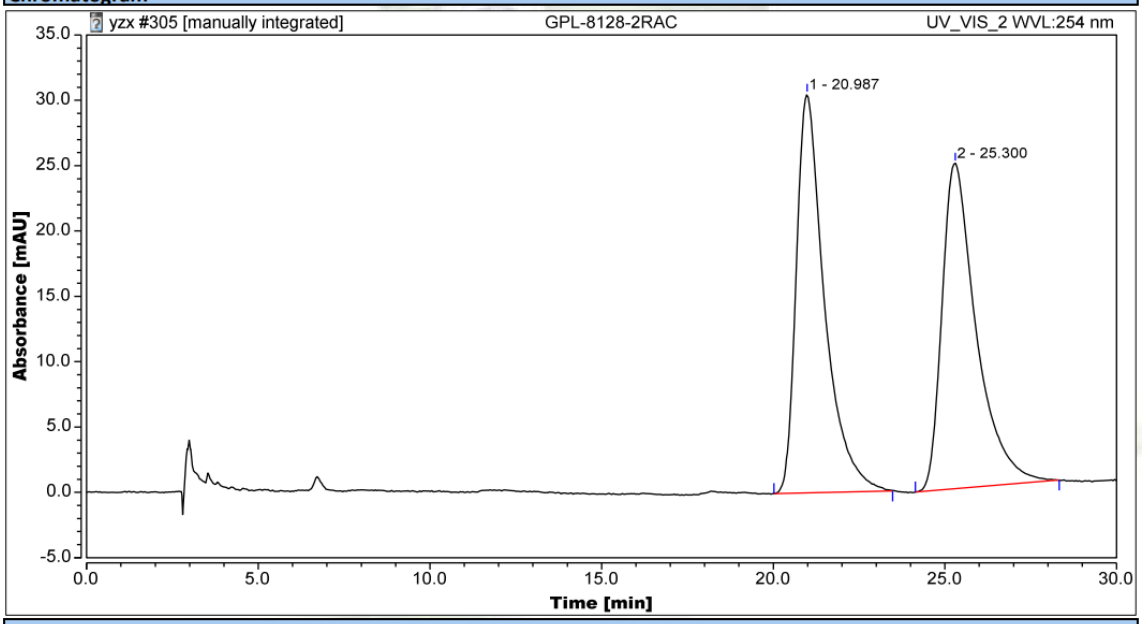
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.283	40.937	60.802	89.93	91.26	n.a.
2		18.550	4.585	5.824	10.07	8.74	n.a.
Total:			**45.523**	**66.626**	**100.00**	**100.00**	

Figure S68. HPLC chromatogram for **2f**.



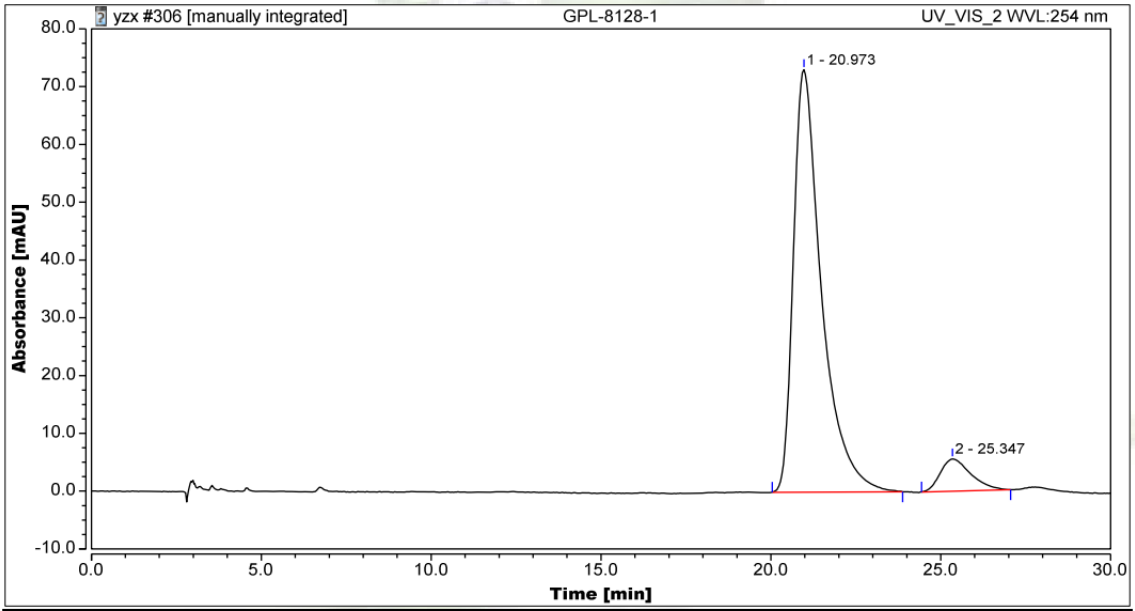
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.987	29.000	30.501	50.24	55.06	n.a.
2		25.300	28.725	24.894	49.76	44.94	n.a.
Total:			**57.725**	**55.395**	**100.00**	**100.00**	

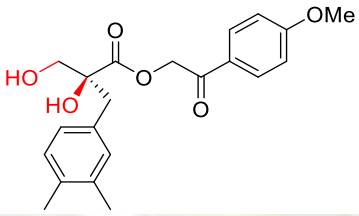
Chromatogram



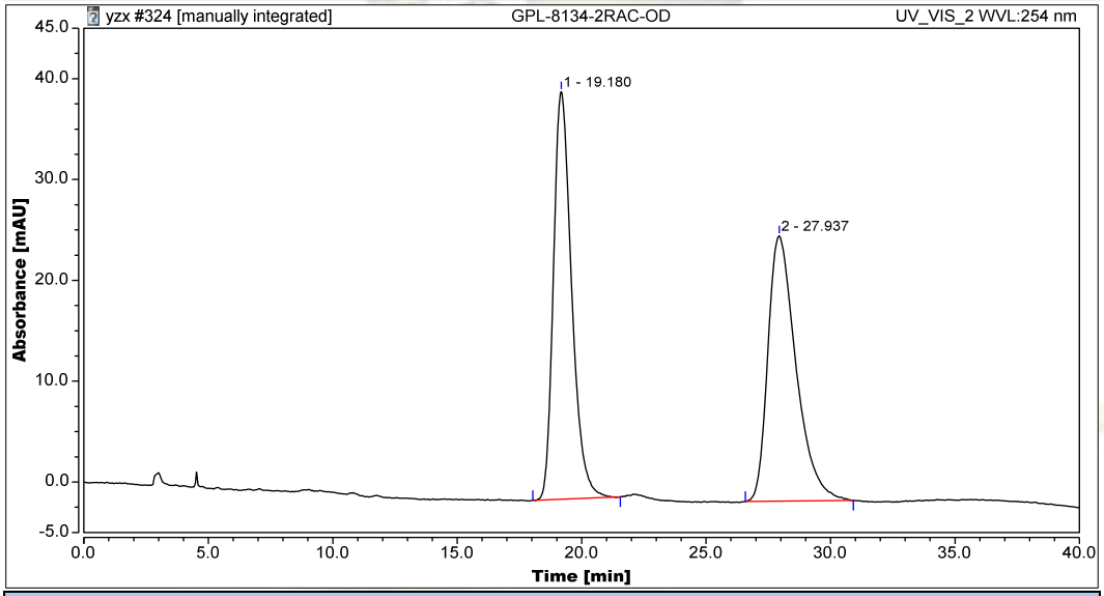
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.973	69.956	73.103	92.36	92.91	n.a.
2		25.347	5.789	5.578	7.64	7.09	n.a.
Total:			**75.744**	**78.681**	**100.00**	**100.00**	

Figure S69. HPLC chromatogram for **2g**.



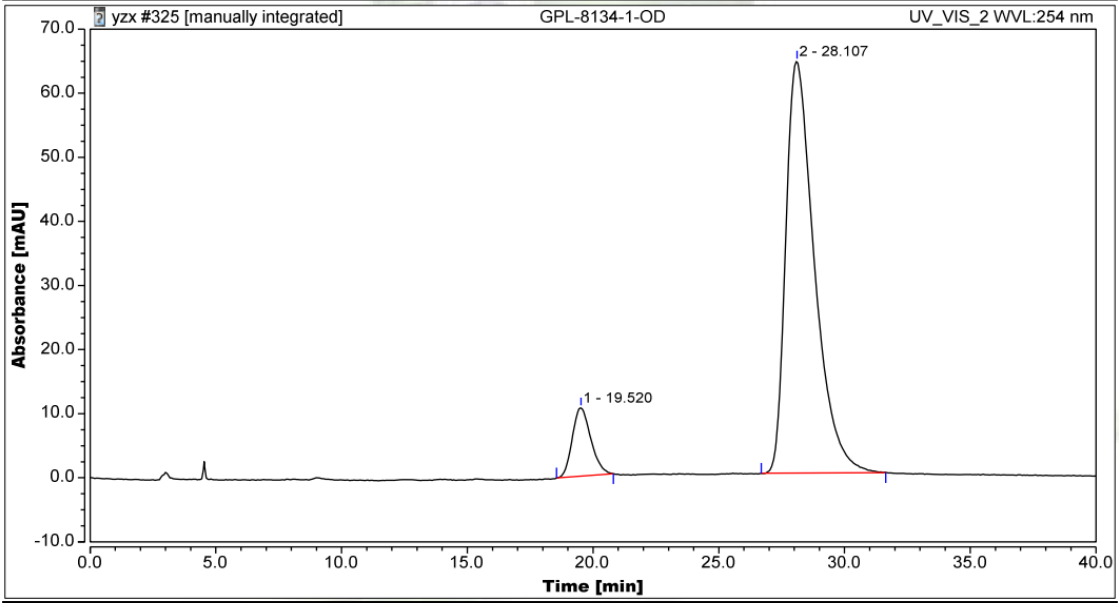
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.180	34.210	40.418	49.87	60.58	n.a.
2		27.937	34.383	26.299	50.13	39.42	n.a.
Total:			**68.593**	**66.717**	**100.00**	**100.00**	

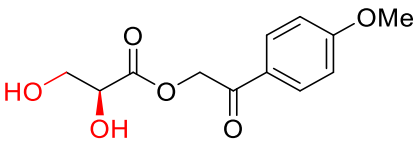
Chromatogram



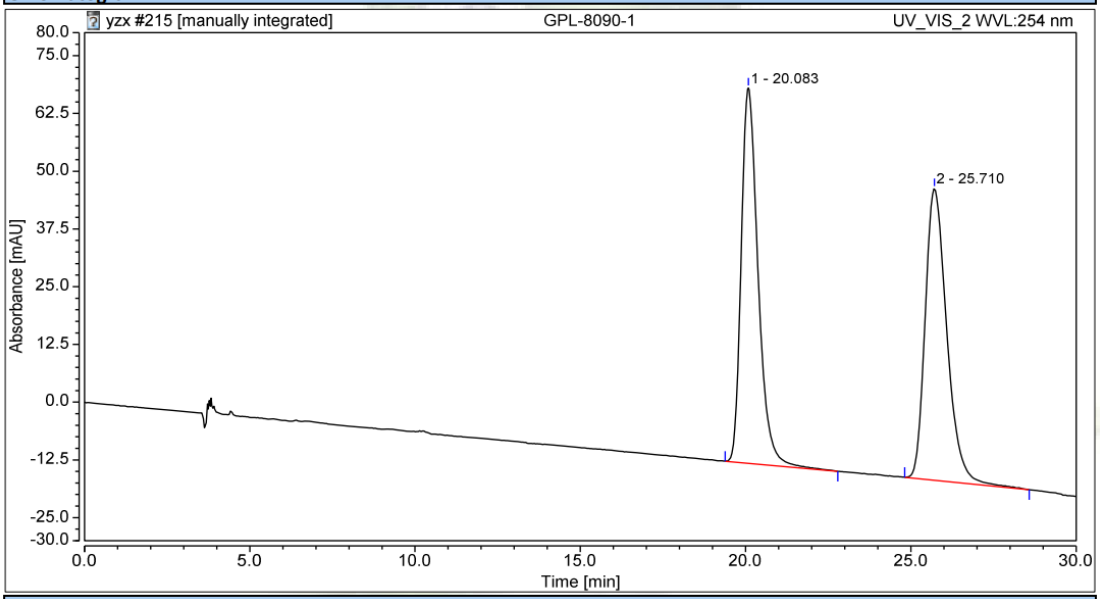
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.520	9.090	10.646	9.68	14.21	n.a.
2		28.107	84.842	64.276	90.32	85.79	n.a.
Total:			**93.932**	**74.922**	**100.00**	**100.00**	

Figure S70. HPLC chromatogram for **2h**.



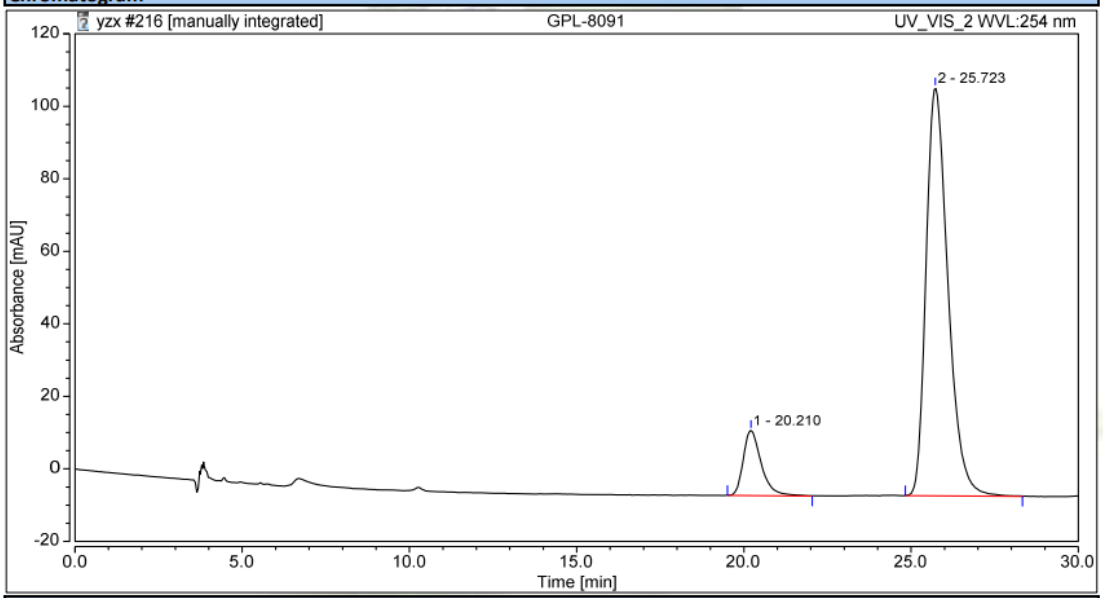
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.083	48.069	81.248	50.04	56.26	n.a.
2		25.710	47.996	63.158	49.96	43.74	n.a.
Total:			**96.065**	**144.405**	**100.00**	**100.00**	

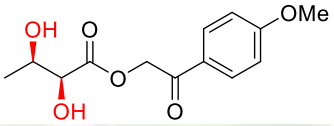
Chromatogram



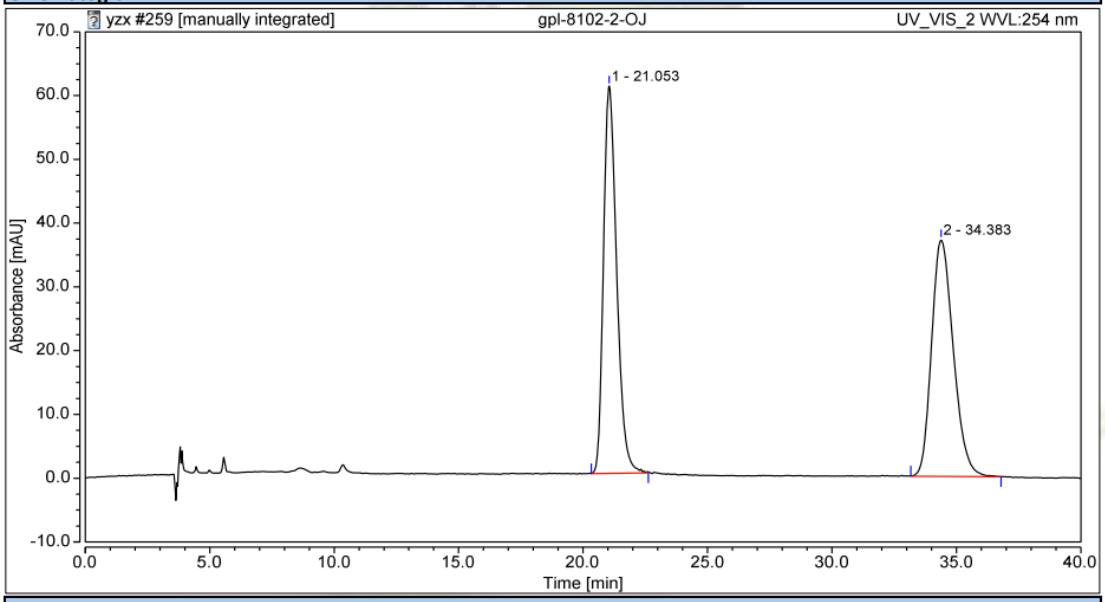
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.210	11.218	17.995	11.63	13.78	n.a.
2		25.723	85.262	112.551	88.37	86.22	n.a.
Total:			**96.480**	**130.546**	**100.00**	**100.00**	

Figure S71. HPLC chromatogram for **2i**.



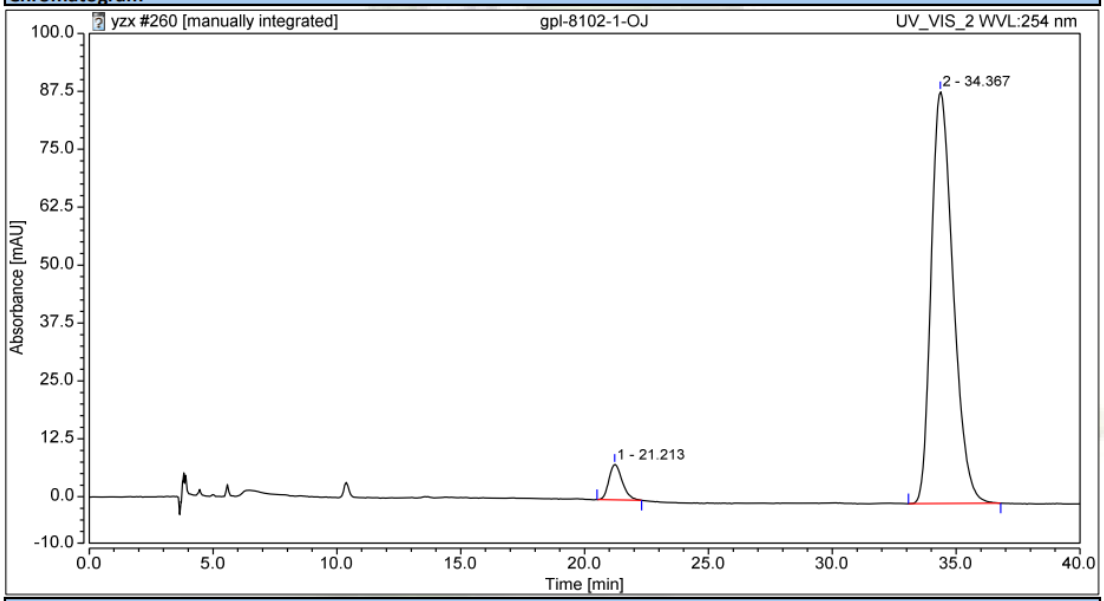
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.053	37.320	60.780	49.86	62.08	n.a.
2		34.383	37.535	37.119	50.14	37.92	n.a.
Total:			**74.855**	**97.899**	**100.00**	**100.00**	

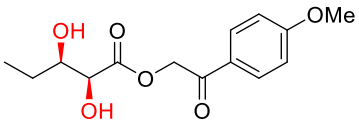
Chromatogram



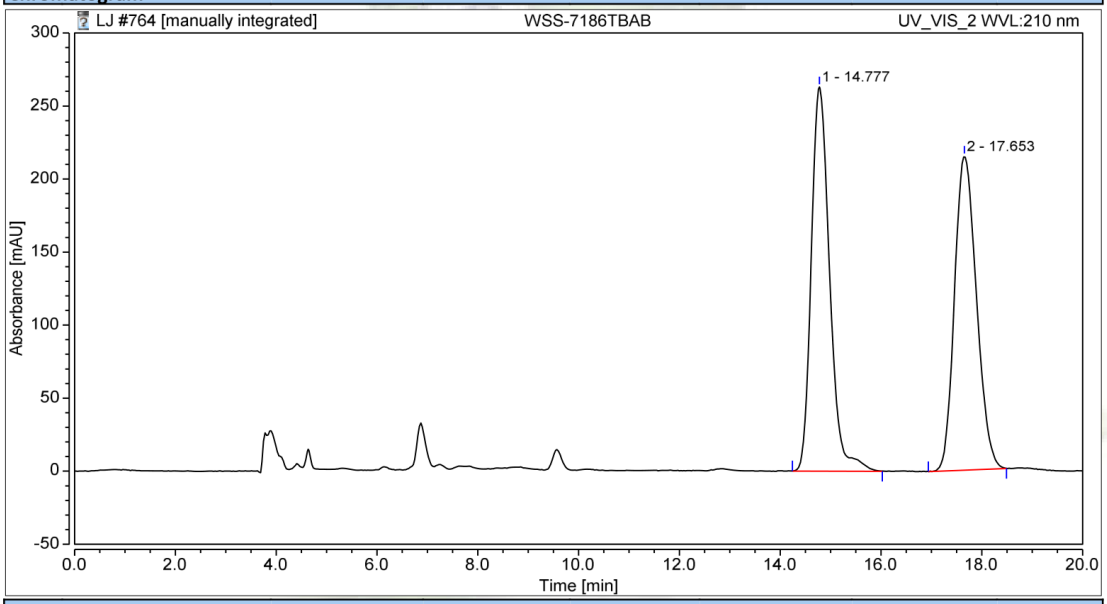
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.213	4.758	7.671	4.96	7.94	n.a.
2		34.367	91.203	88.903	95.04	92.06	n.a.
Total:			**95.962**	**96.574**	**100.00**	**100.00**	

Figure S72. HPLC chromatogram for **2j**.



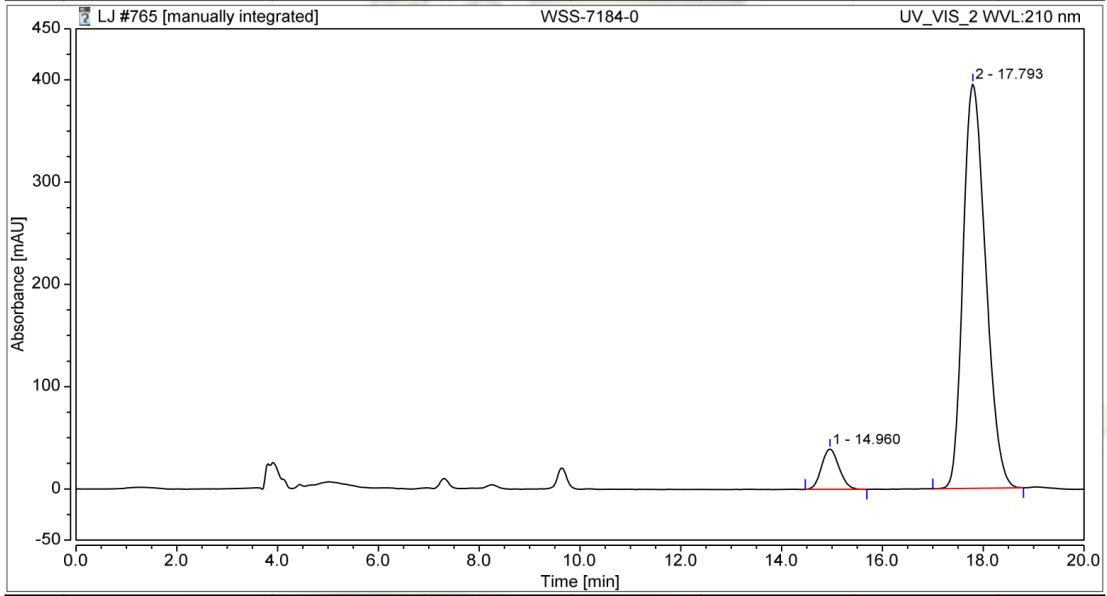
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.777	110.779	263.044	50.58	55.03	n.a.
2		17.653	108.245	214.919	49.42	44.97	n.a.
Total:			**219.024**	**477.963**	**100.00**	**100.00**	

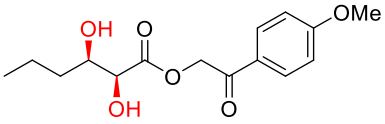
Chromatogram



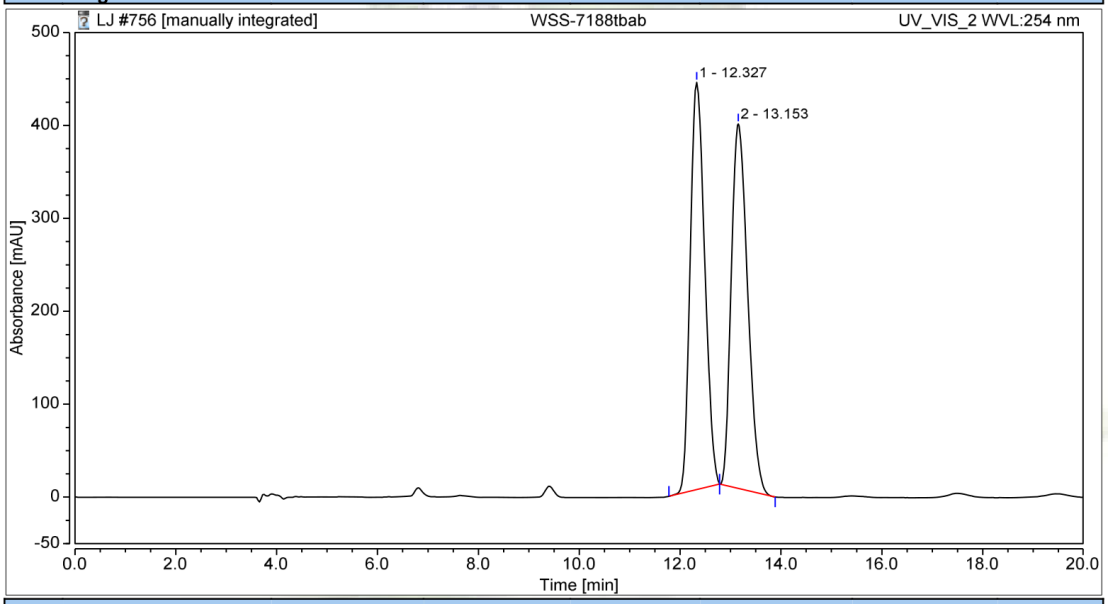
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.960	15.736	39.172	7.12	9.01	n.a.
2		17.793	205.377	395.429	92.88	90.99	n.a.
Total:			**221.113**	**434.601**	**100.00**	**100.00**	

Figure S73. HPLC chromatogram for **2k**.



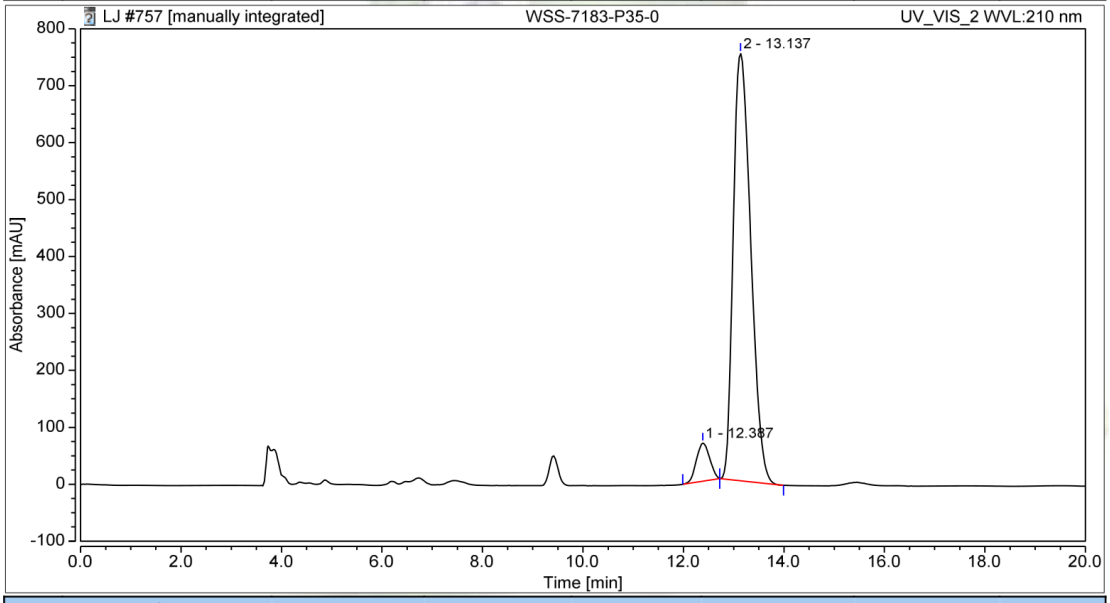
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.327	146.489	438.510	49.83	52.77	n.a.
2		13.153	147.478	392.431	50.17	47.23	n.a.
Total:			**293.967**	**830.941**	**100.00**	**100.00**	

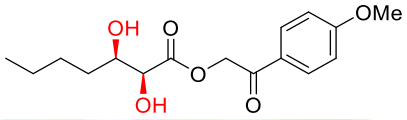
Chromatogram



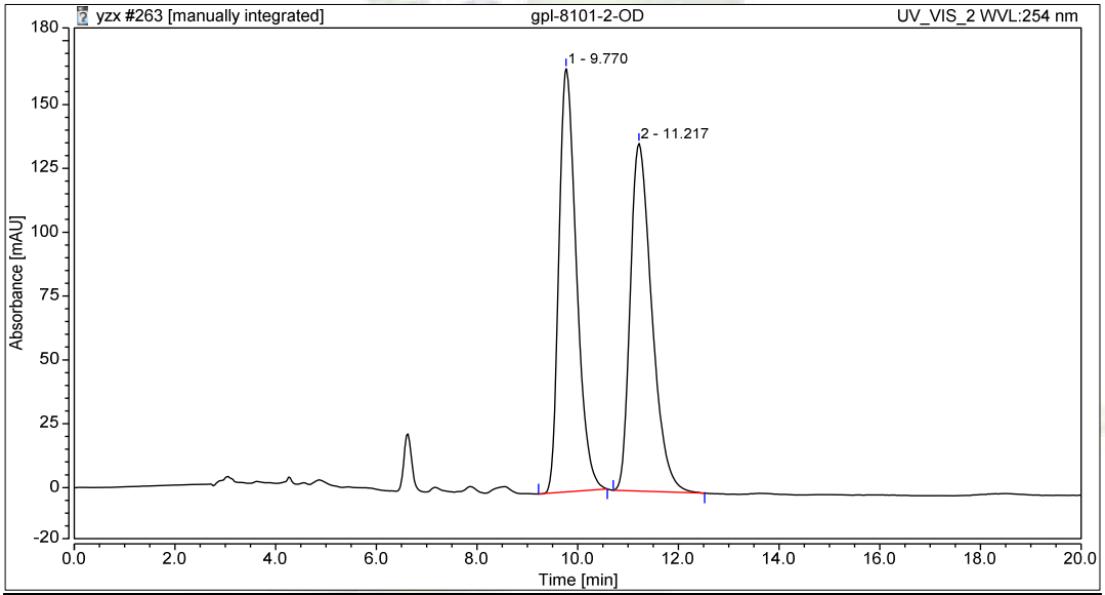
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.387	20.523	66.823	6.34	8.18	n.a.
2		13.137	302.943	750.484	93.66	91.82	n.a.
Total:			**323.466**	**817.307**	**100.00**	**100.00**	

Figure S74. HPLC chromatogram for **2l**.



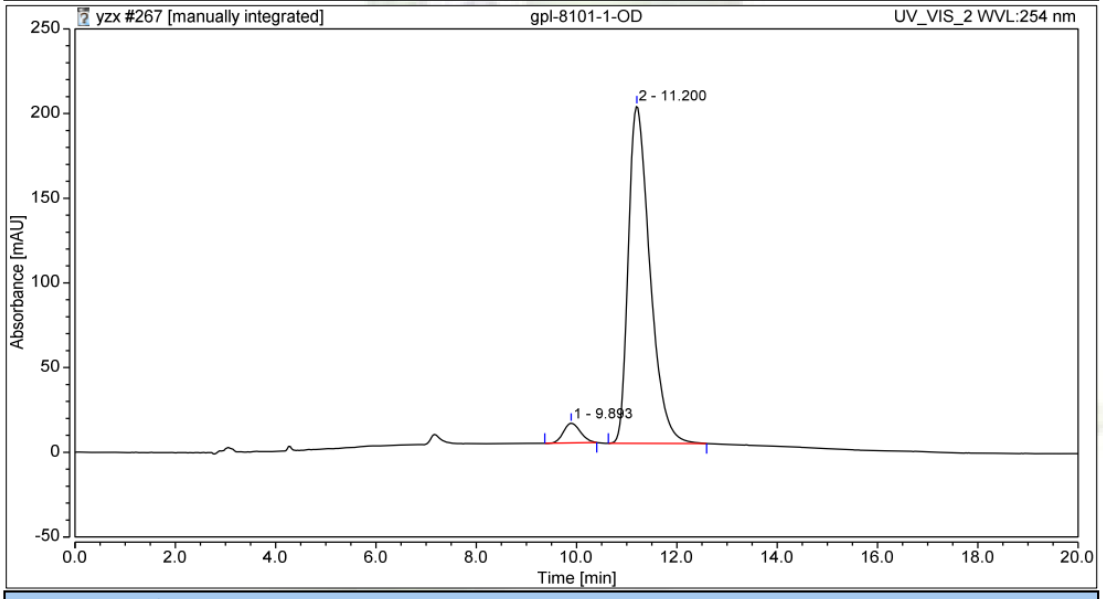
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.770	66.929	165.770	49.78	54.91	n.a.
2		11.217	67.528	136.140	50.22	45.09	n.a.
Total:			**134.457**	**301.910**	**100.00**	**100.00**	

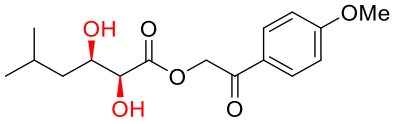
Chromatogram



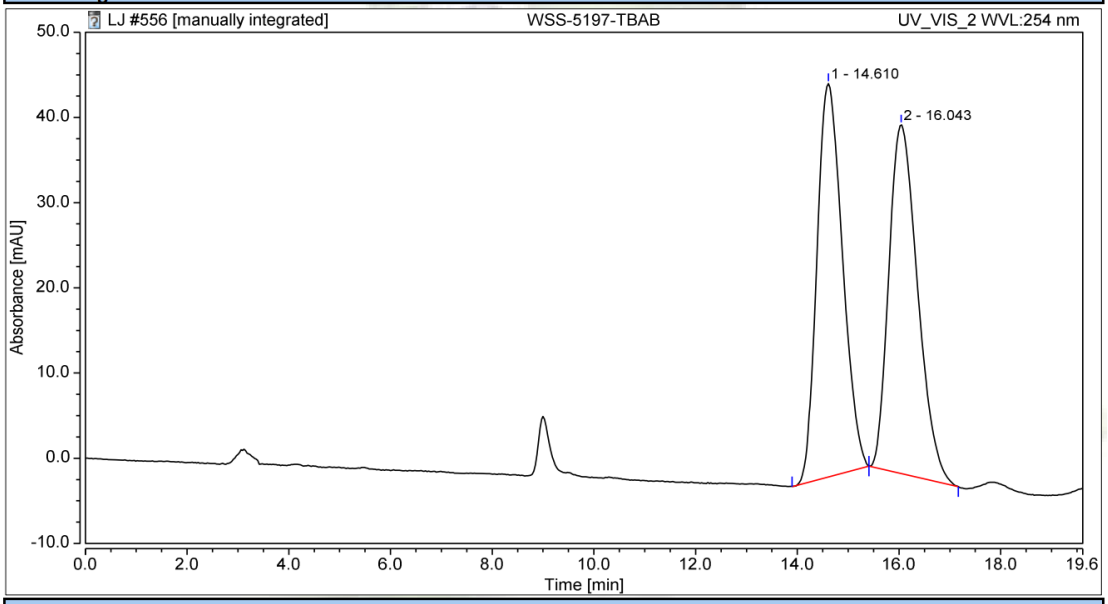
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.893	4.561	11.603	4.38	5.50	n.a.
2		11.200	99.505	199.201	95.62	94.50	n.a.
Total:			**104.067**	**210.804**	**100.00**	**100.00**	

Figure S75. HPLC chromatogram for **2m**.



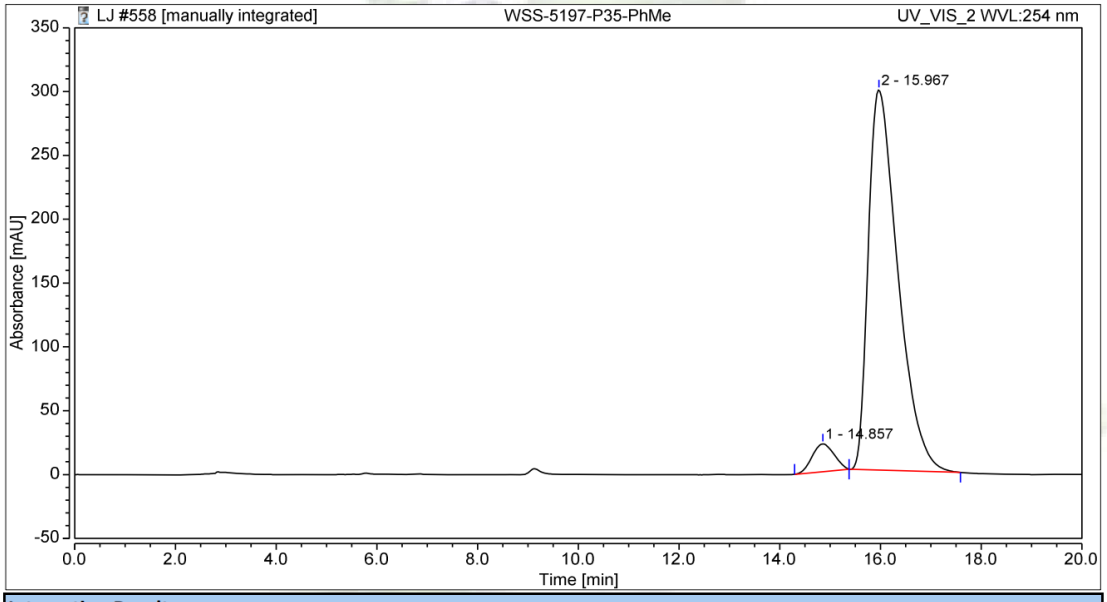
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.610	26.784	46.159	49.98	53.00	n.a.
2		16.043	26.810	40.926	50.02	47.00	n.a.
Total:			**53.594**	**87.085**	**100.00**	**100.00**	

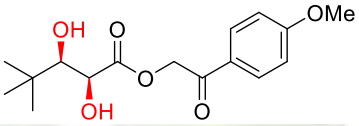
Chromatogram



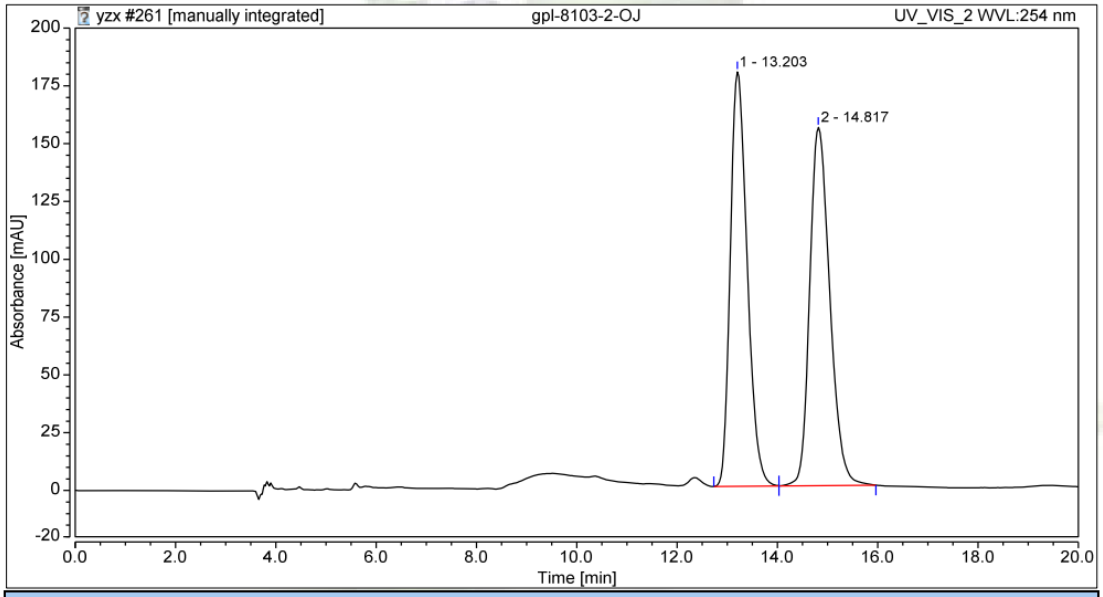
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.857	10.974	21.708	5.14	6.79	n.a.
2		15.967	202.535	297.881	94.86	93.21	n.a.
Total:			**213.509**	**319.588**	**100.00**	**100.00**	

Figure S76. HPLC chromatogram for **2n**.



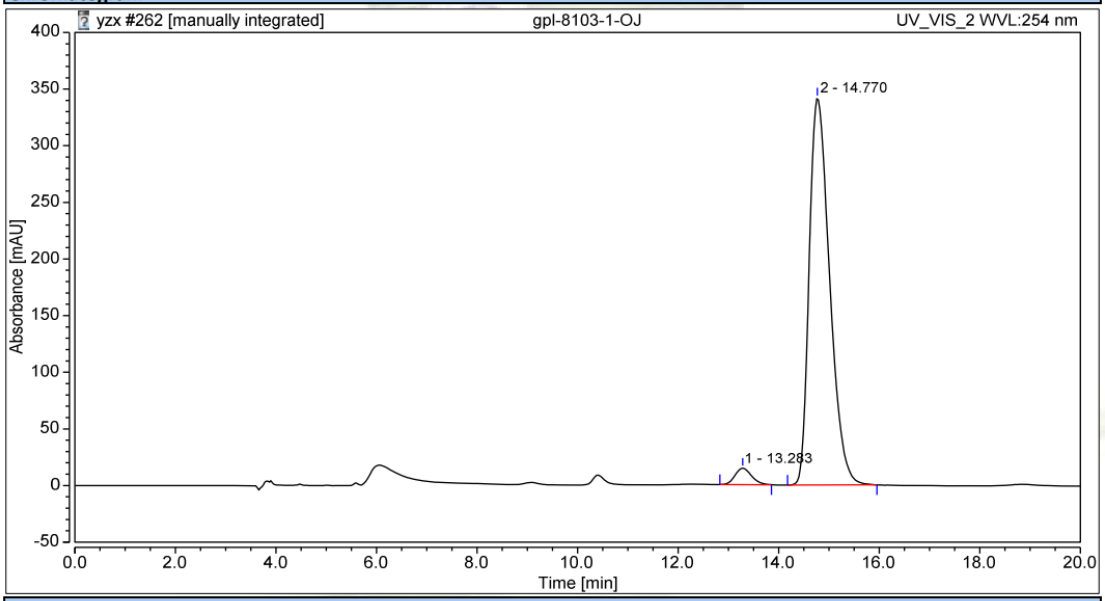
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.203	69.934	179.310	49.34	53.64	n.a.
2		14.817	71.794	154.946	50.66	46.36	n.a.
Total:			**141.728**	**334.256**	**100.00**	**100.00**	

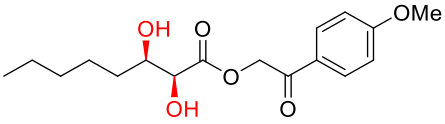
Chromatogram



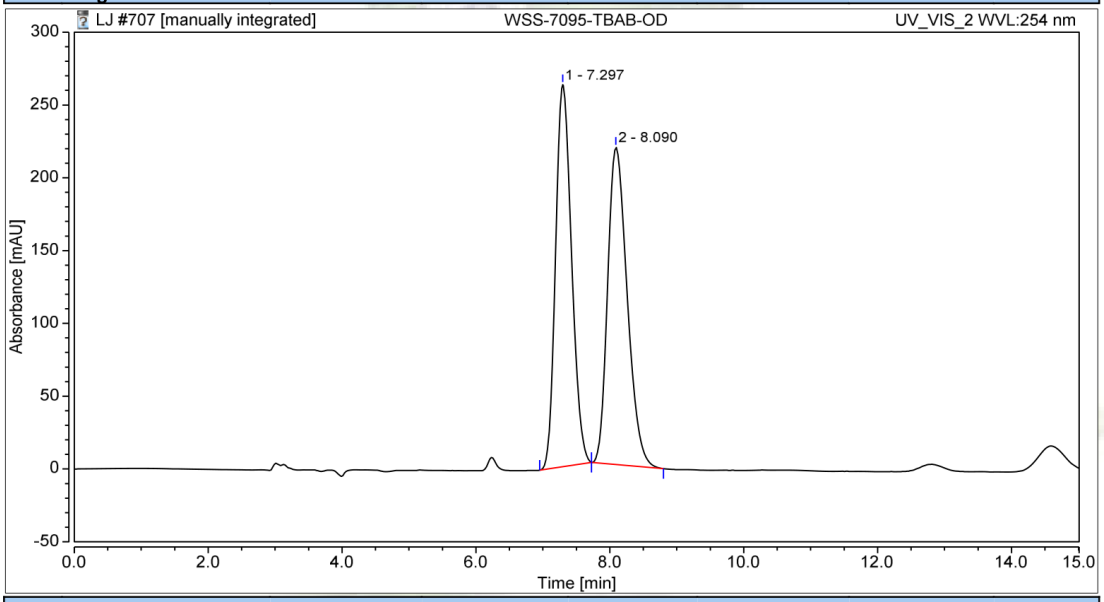
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.283	5.533	14.507	3.34	4.07	n.a.
2		14.770	160.254	341.624	96.66	95.93	n.a.
Total:			**165.787**	**356.131**	**100.00**	**100.00**	

Figure S77. HPLC chromatogram for **2o**.



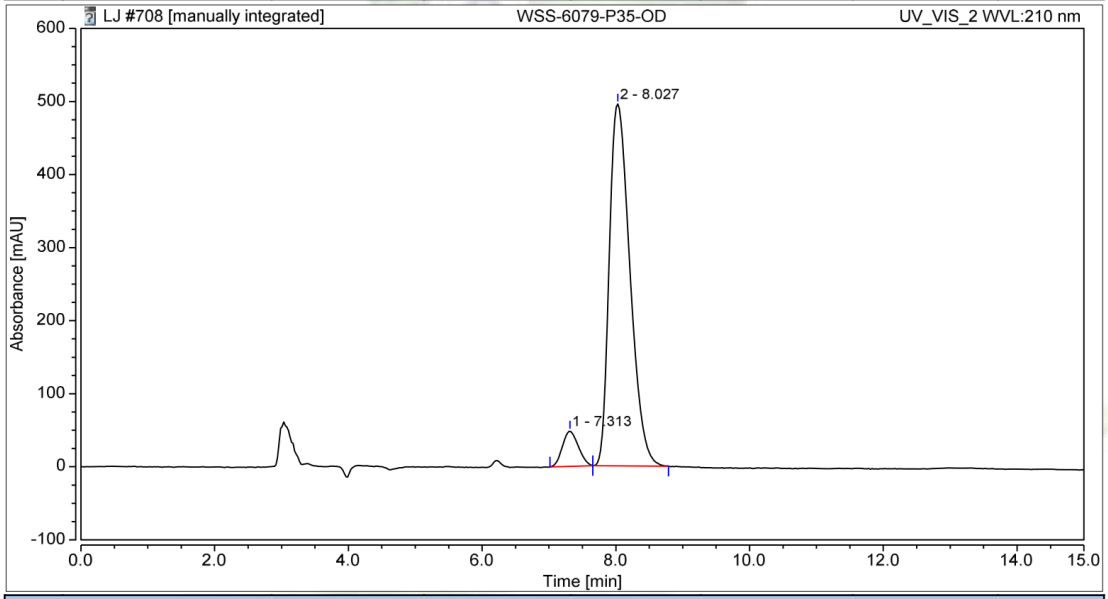
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.297	72.868	262.489	49.63	54.65	n.a.
2		8.090	73.949	217.838	50.37	45.35	n.a.
Total:			**146.817**	**480.328**	**100.00**	**100.00**	

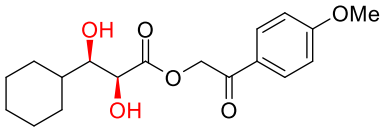
Chromatogram



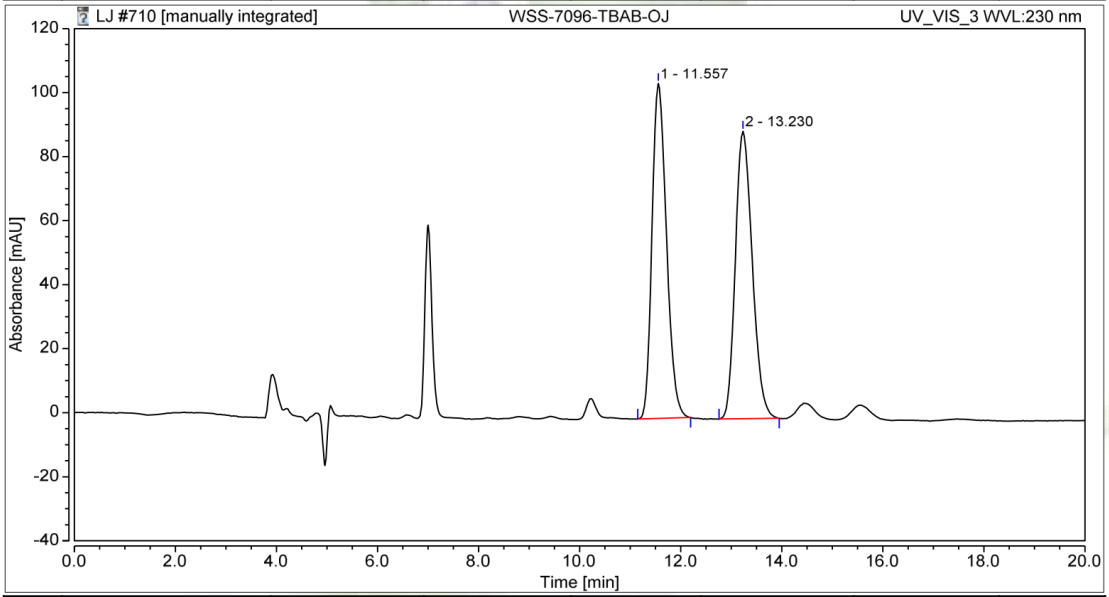
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.313	13.209	48.251	6.93	8.87	n.a.
2		8.027	177.456	495.472	93.07	91.13	n.a.
Total:			**190.665**	**543.723**	**100.00**	**100.00**	

Figure S78. HPLC chromatogram for **2p**.



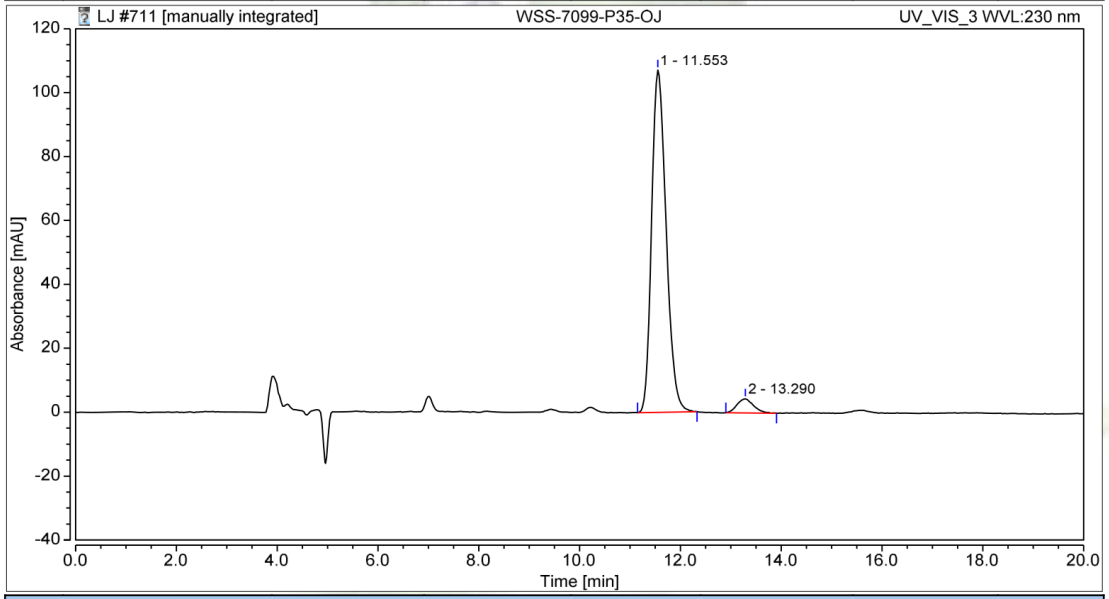
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.557	34.684	104.657	49.87	53.82	n.a.
2		13.230	34.866	89.804	50.13	46.18	n.a.
Total:			**69.550**	**194.461**	**100.00**	**100.00**	

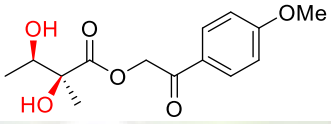
Chromatogram



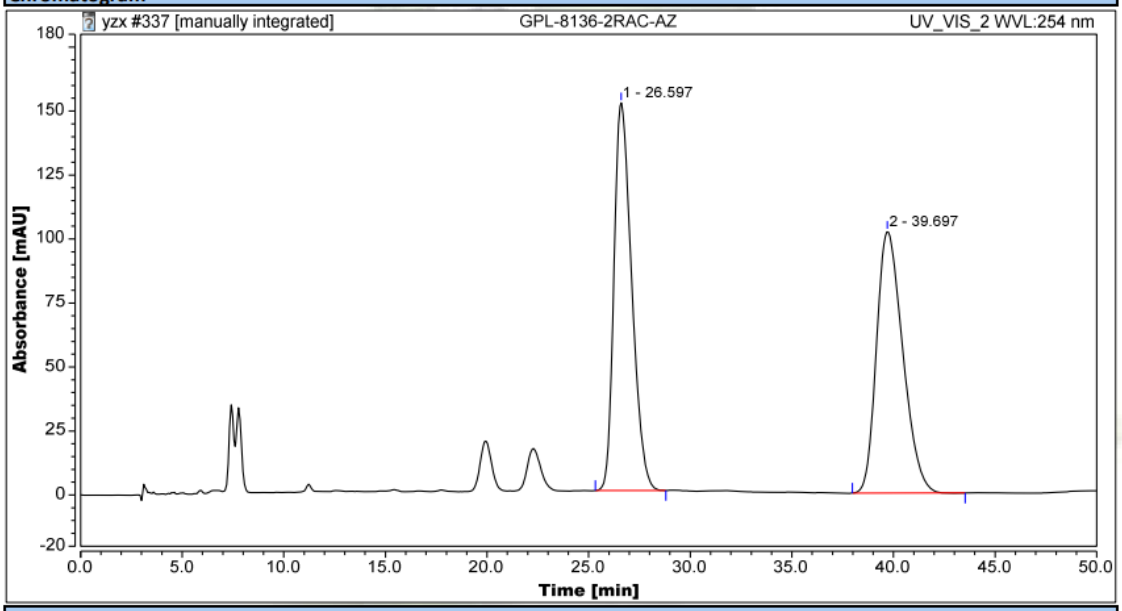
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.553	35.747	107.219	95.53	96.06	n.a.
2		13.290	1.672	4.394	4.47	3.94	n.a.
Total:			**37.419**	**111.613**	**100.00**	**100.00**	

Figure S79. HPLC chromatogram for **2q**.



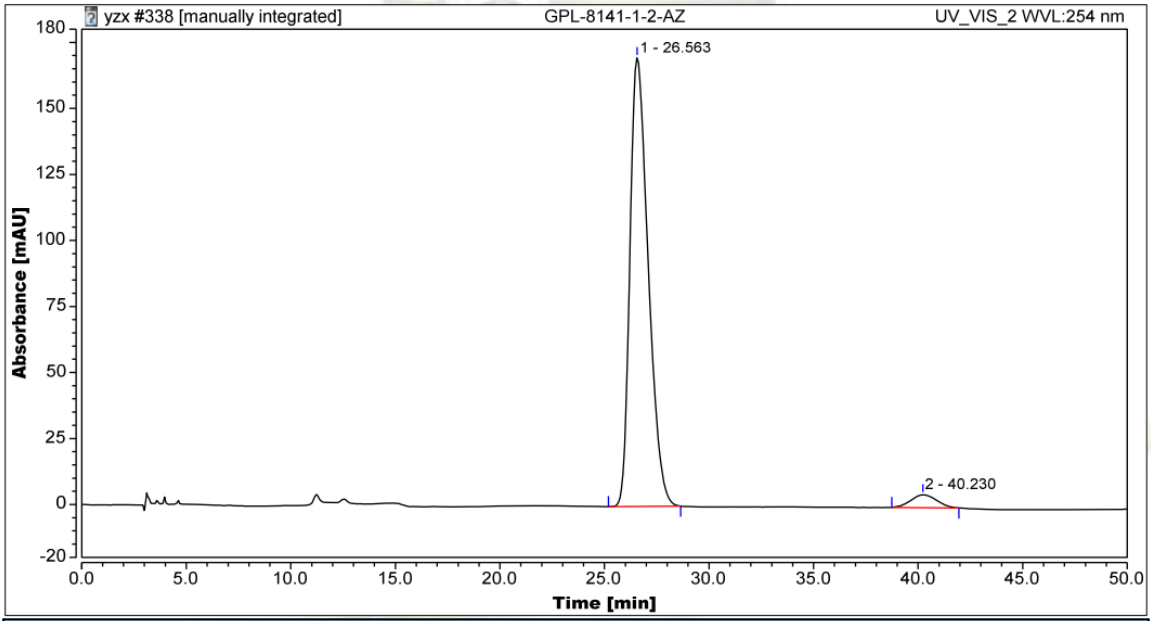
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.597	152.889	151.409	50.01	59.69	n.a.
2		39.697	152.852	102.229	49.99	40.31	n.a.
Total:			**305.740**	**253.638**	**100.00**	**100.00**	

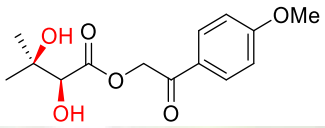
Chromatogram



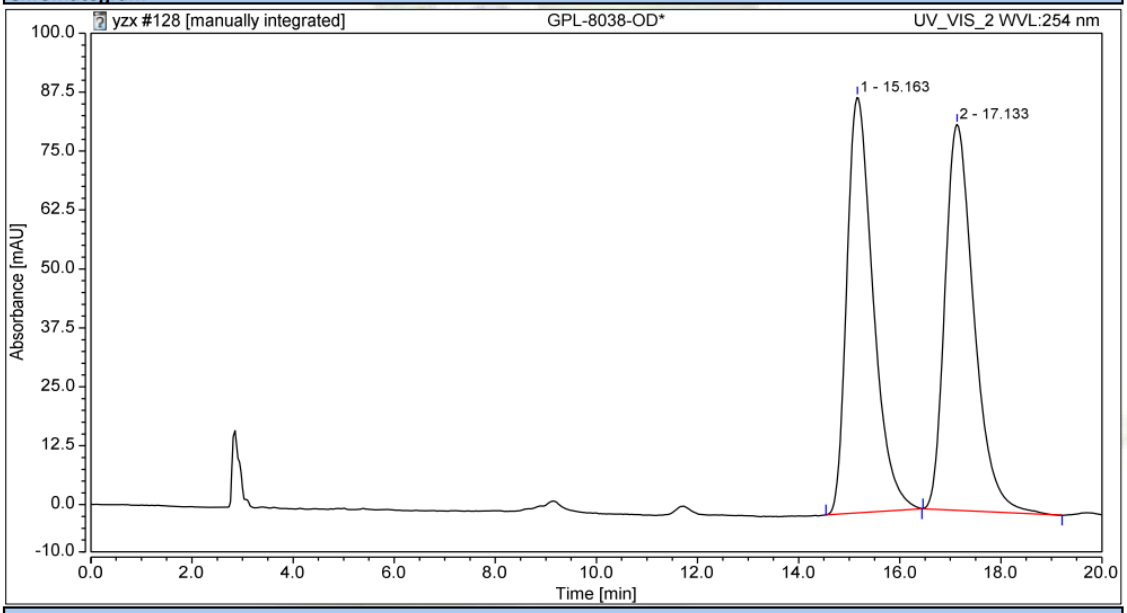
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.563	172.195	169.933	96.11	97.18	n.a.
2		40.230	6.978	4.928	3.89	2.82	n.a.
Total:			**179.173**	**174.861**	**100.00**	**100.00**	

Figure S80. HPLC chromatogram for **2r**.



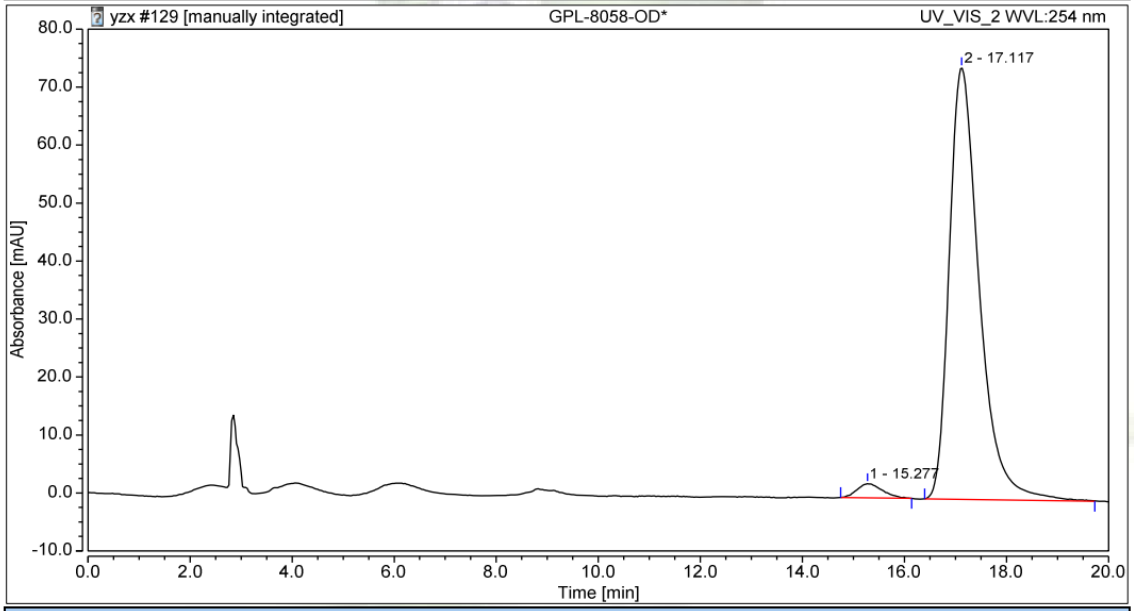
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.163	53.040	88.221	49.38	51.87	n.a.
2		17.133	54.370	81.860	50.62	48.13	n.a.
Total:			**107.410**	**170.081**	**100.00**	**100.00**	

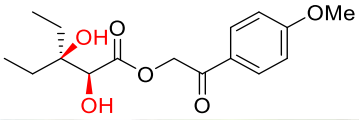
Chromatogram



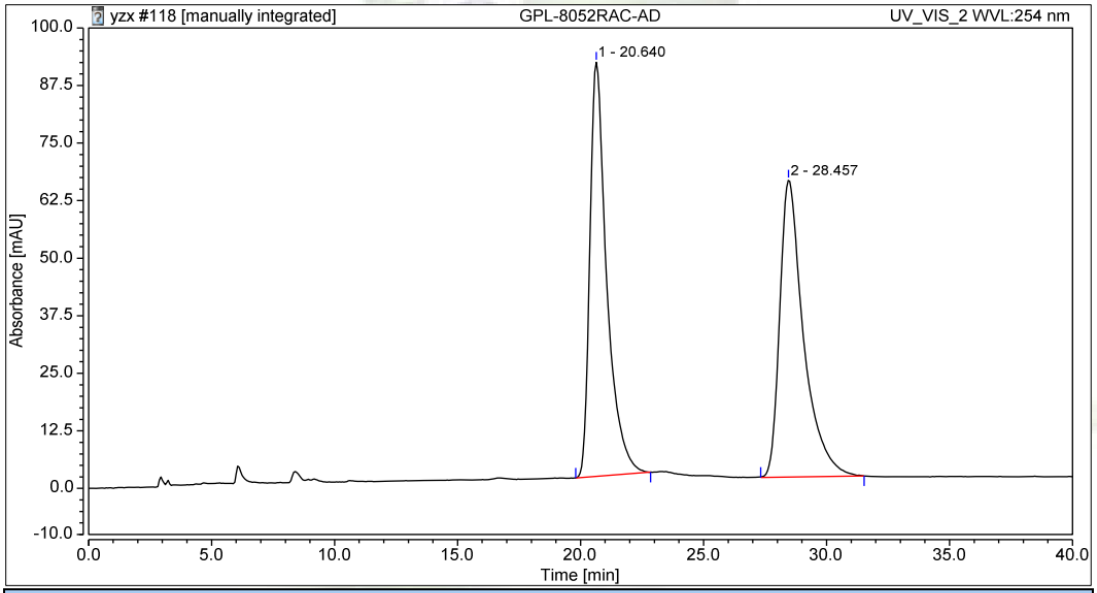
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.277	1.414	2.438	2.71	3.17	n.a.
2		17.117	50.653	74.429	97.29	96.83	n.a.
Total:			**52.066**	**76.867**	**100.00**	**100.00**	

Figure S81. HPLC chromatogram for **4a**.



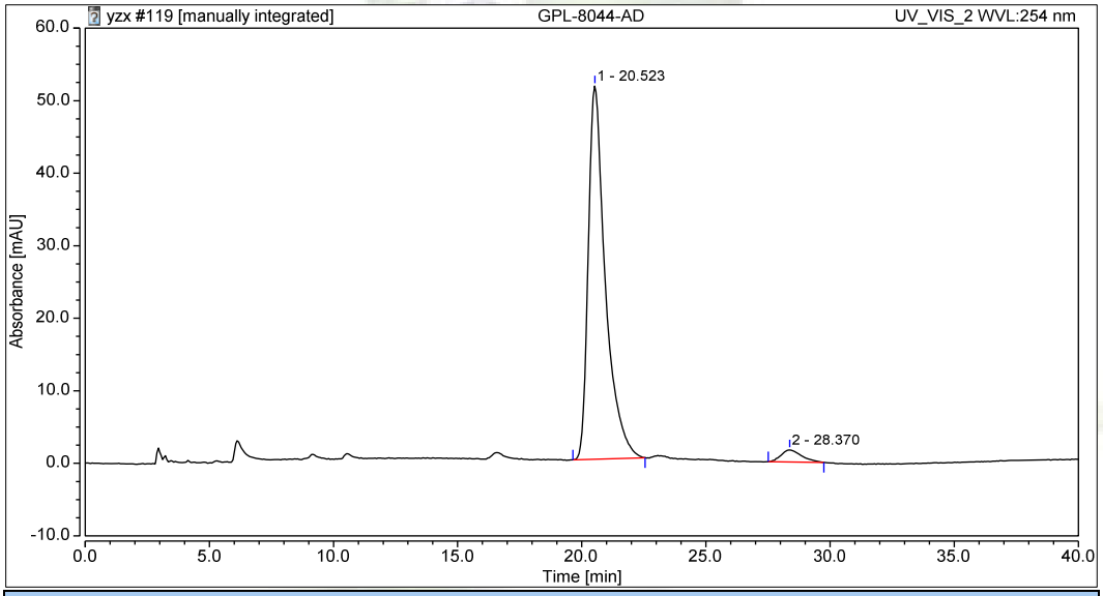
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.640	71.600	89.958	49.83	58.24	n.a.
2		28.457	72.080	64.498	50.17	41.76	n.a.
Total:			**143.679**	**154.456**	**100.00**	**100.00**	

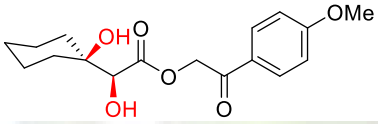
Chromatogram



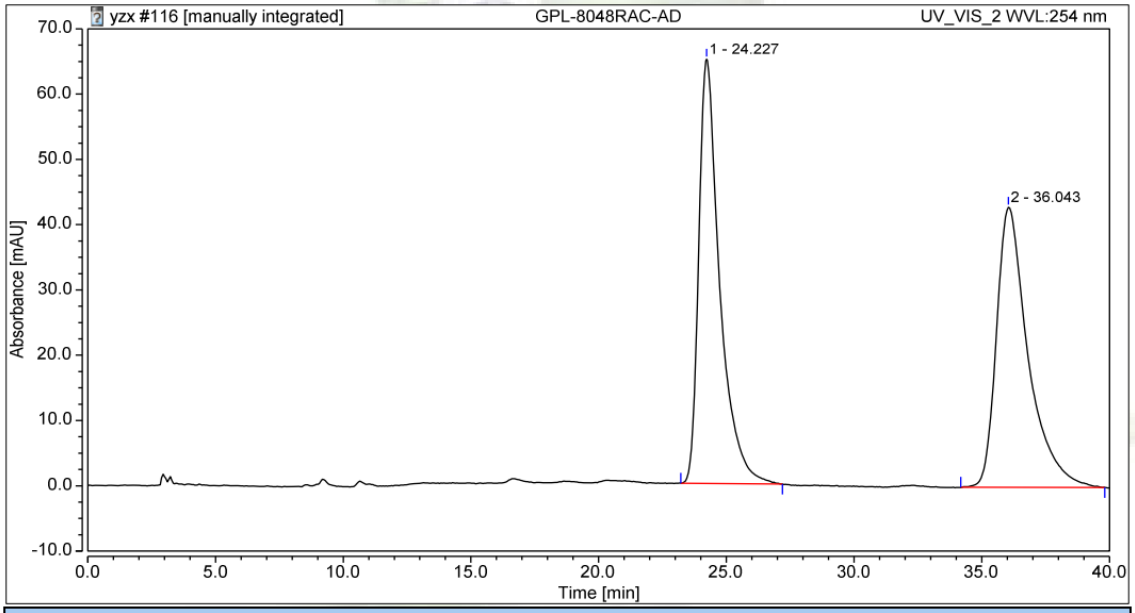
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.523	40.993	51.473	96.33	96.87	n.a.
2		28.370	1.563	1.664	3.67	3.13	n.a.
Total:			**42.556**	**53.136**	**100.00**	**100.00**	

Figure S82. HPLC chromatogram for **4b**.



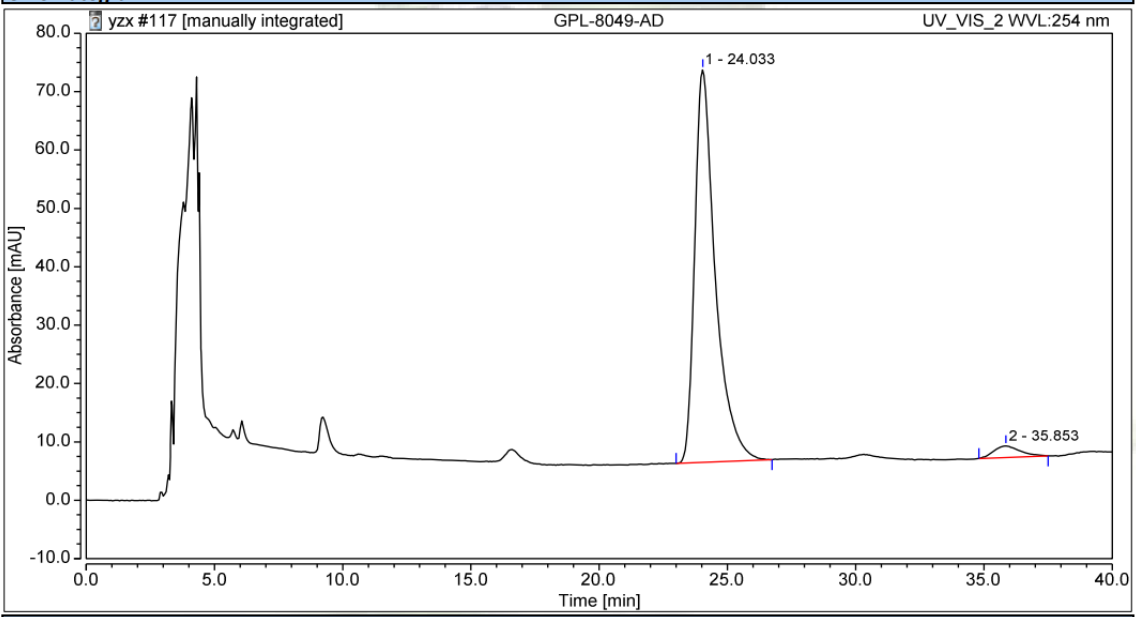
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.227	61.762	64.992	50.16	60.23	n.a.
2		36.043	61.375	42.915	49.84	39.77	n.a.
Total:			**123.137**	**107.907**	**100.00**	**100.00**	

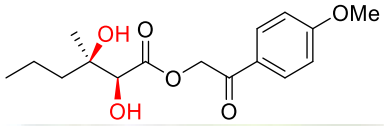
Chromatogram



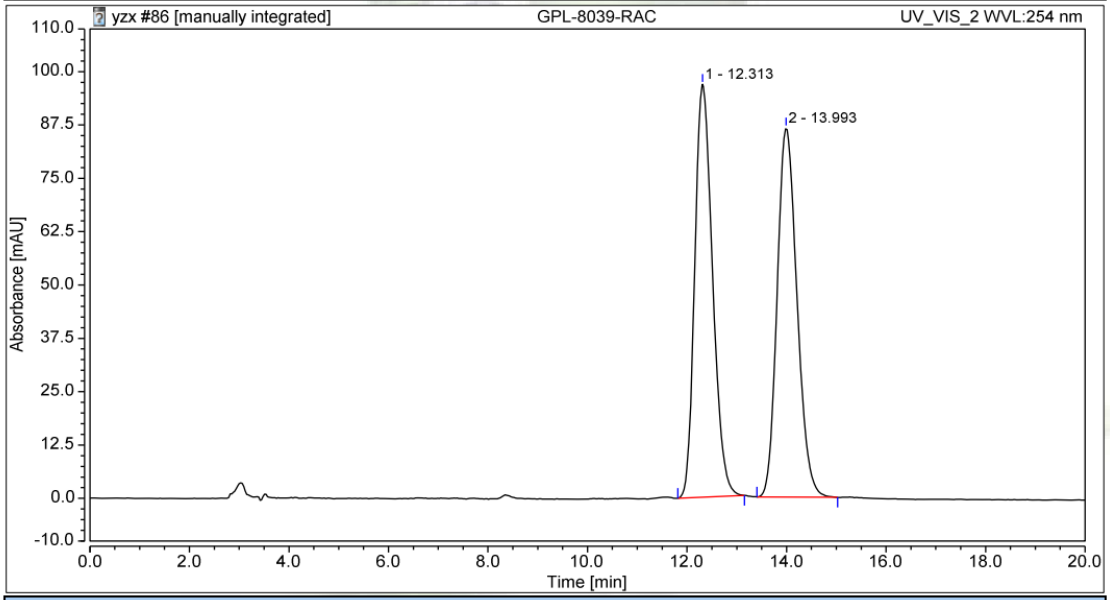
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.033	62.442	67.255	96.31	97.09	n.a.
2		35.853	2.395	2.018	3.69	2.91	n.a.
Total:			**64.838**	**69.273**	**100.00**	**100.00**	

Figure S83. HPLC chromatogram for **4c**.



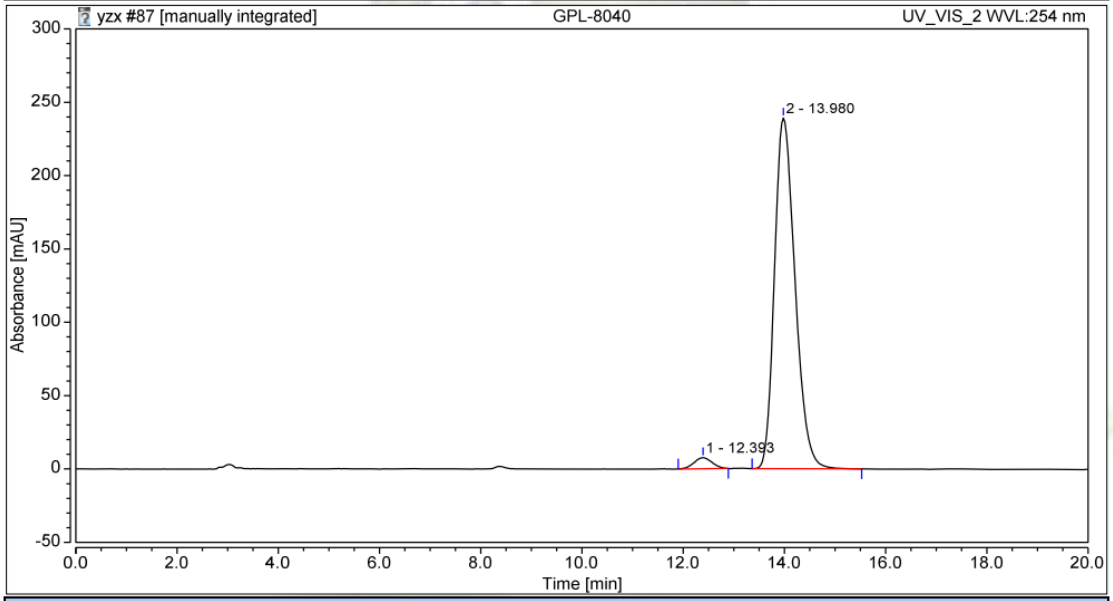
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.313	39.947	96.764	50.05	52.80	n.a.
2		13.993	39.865	86.492	49.95	47.20	n.a.
Total:			**79.812**	**183.257**	**100.00**	**100.00**	

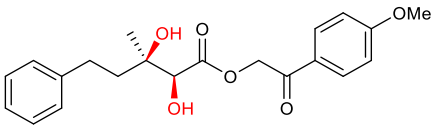
Chromatogram



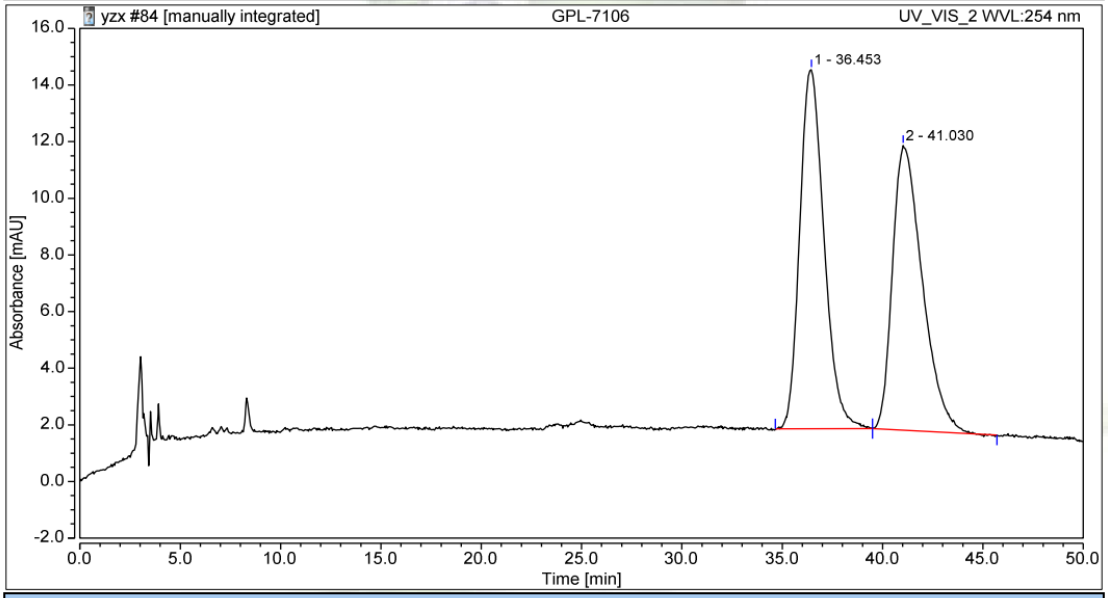
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.393	3.116	7.504	2.70	3.04	n.a.
2		13.980	112.150	238.982	97.30	96.96	n.a.
Total:			**115.265**	**246.487**	**100.00**	**100.00**	

Figure S84. HPLC chromatogram for **4d**.



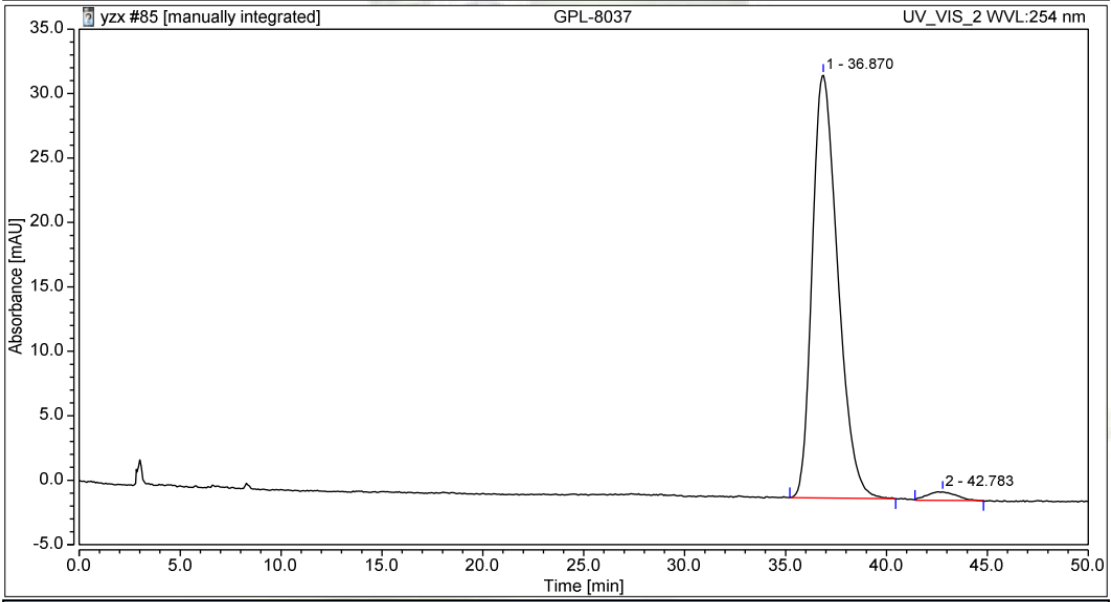
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		36.453	17.767	12.684	50.65	55.78	n.a.
2		41.030	17.310	10.055	49.35	44.22	n.a.
Total:			**35.077**	**22.739**	**100.00**	**100.00**	

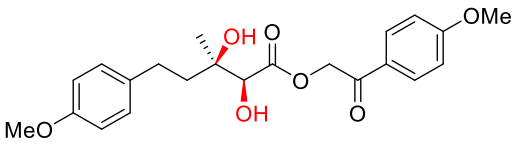
Chromatogram

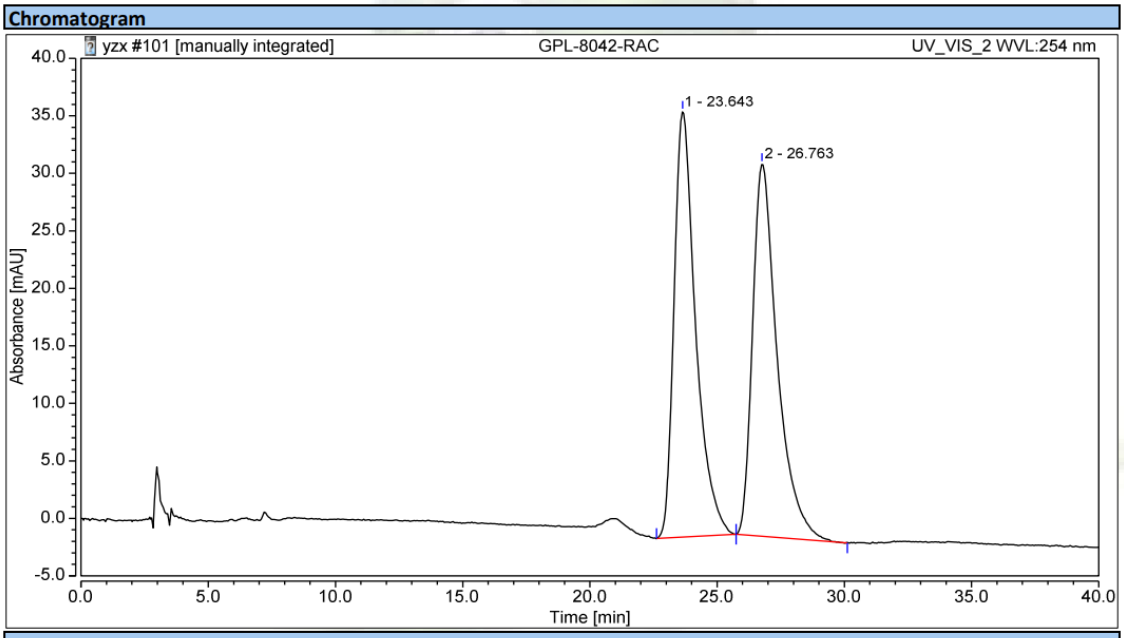


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		36.870	48.186	32.863	97.77	97.91	n.a.
2		42.783	1.097	0.703	2.23	2.09	n.a.
Total:			**49.284**	**33.565**	**100.00**	**100.00**	

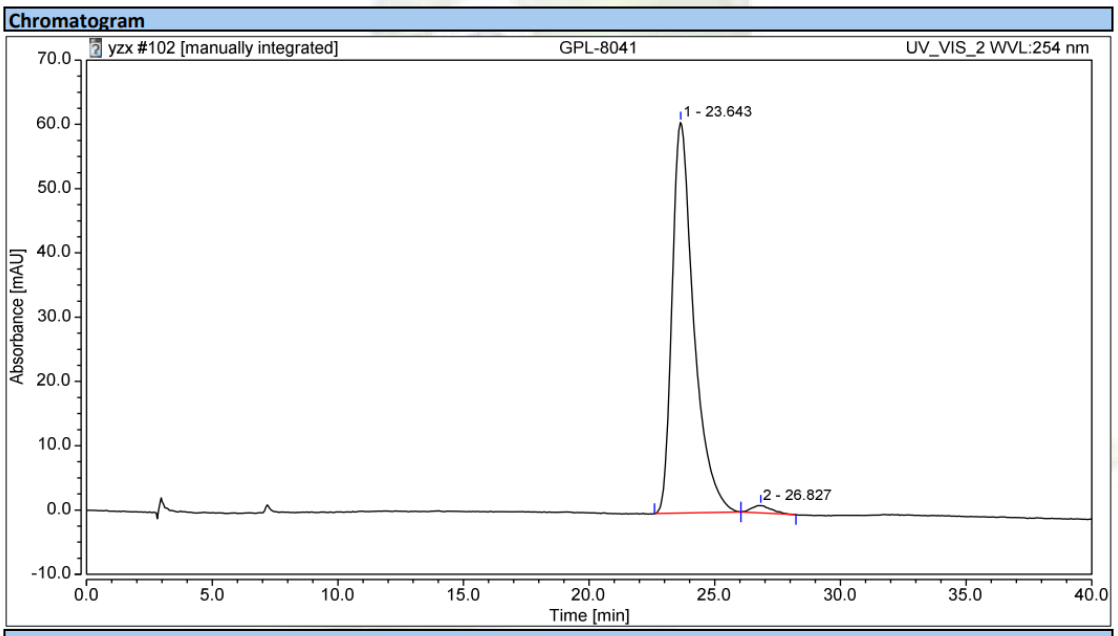
Figure S85. HPLC chromatogram for **4e**.





Integration Results

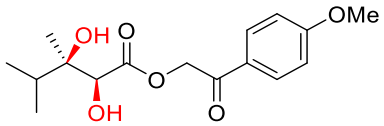
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.643	36.311	37.020	49.99	53.33	n.a.
2		26.763	36.329	32.391	50.01	46.67	n.a.
Total:			**72.640**	**69.411**	**100.00**	**100.00**	



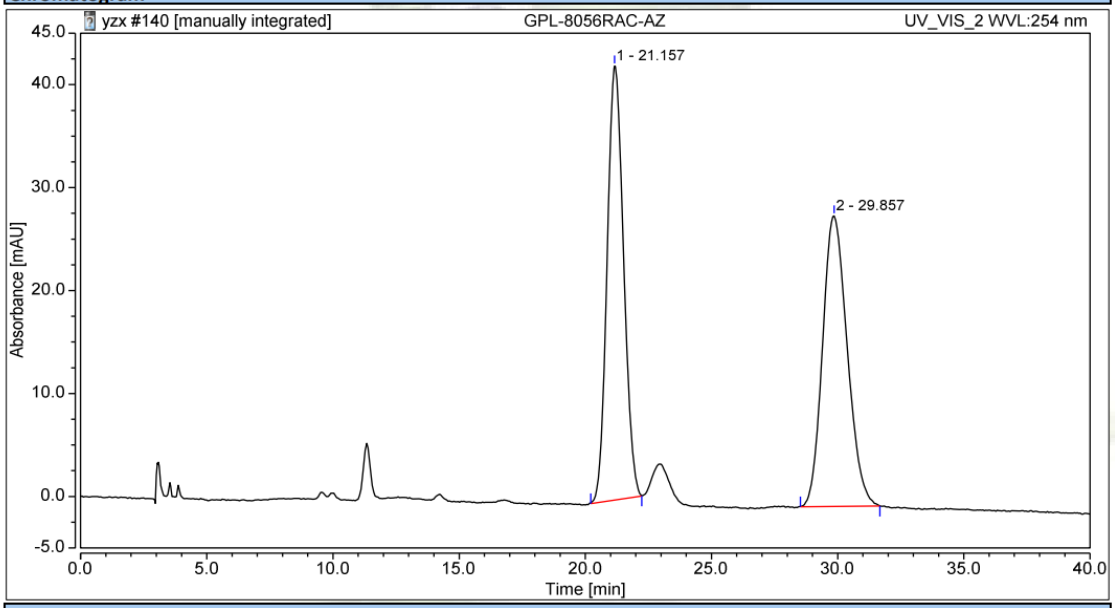
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.643	60.905	60.850	98.33	98.09	n.a.
2		26.827	1.032	1.185	1.67	1.91	n.a.
Total:			**61.937**	**62.034**	**100.00**	**100.00**	

Figure S86. HPLC chromatogram for **4f**.



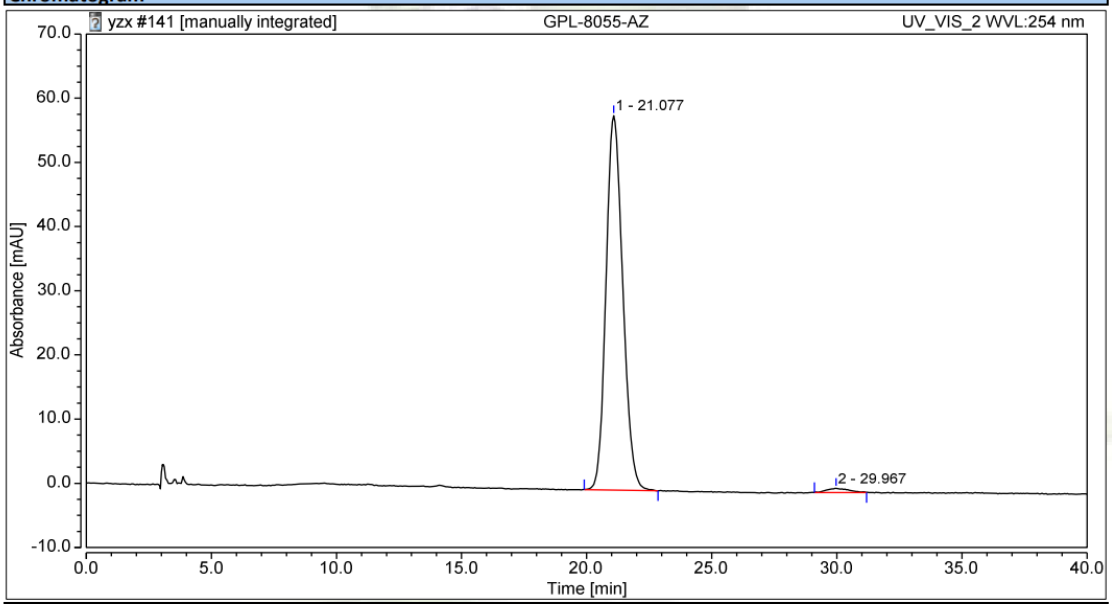
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.157	31.932	42.181	49.96	59.89	n.a.
2		29.857	31.989	28.248	50.04	40.11	n.a.
Total:			**63.921**	**70.429**	**100.00**	**100.00**	

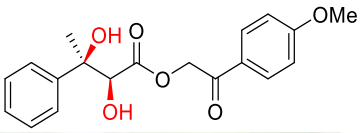
Chromatogram



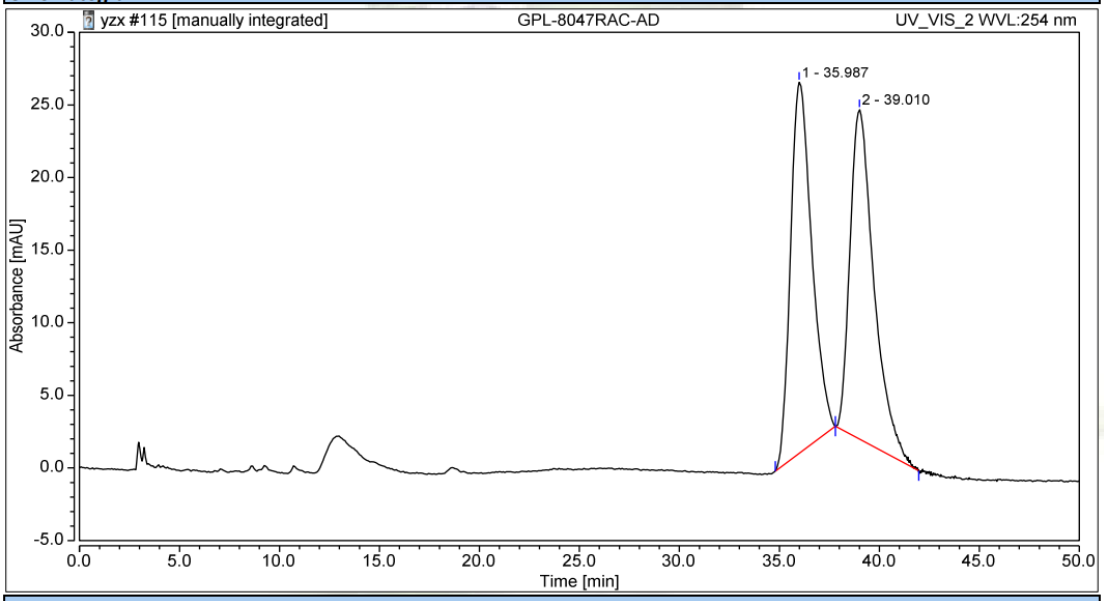
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.077	45.365	58.370	98.53	98.89	n.a.
2		29.967	0.675	0.658	1.47	1.11	n.a.
Total:			**46.040**	**59.028**	**100.00**	**100.00**	

Figure S87. HPLC chromatogram for **4g**.



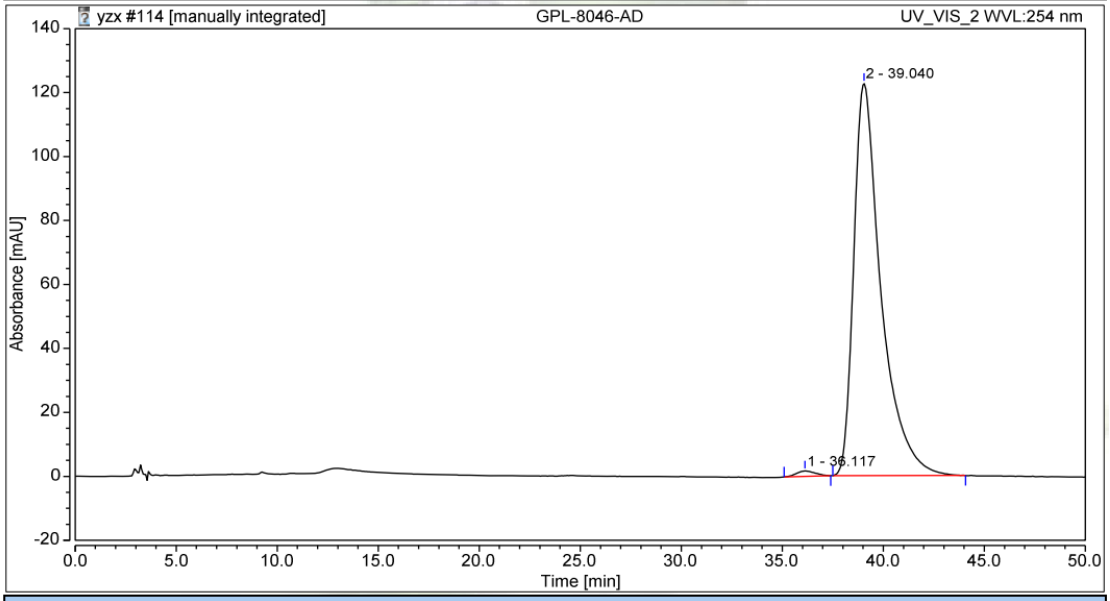
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		35.987	31.349	25.562	49.94	52.97	n.a.
2		39.010	31.429	22.692	50.06	47.03	n.a.
Total:			**62.778**	**48.254**	**100.00**	**100.00**	

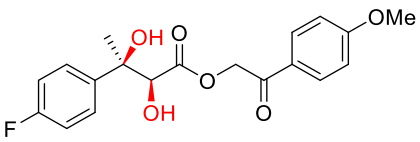
Chromatogram



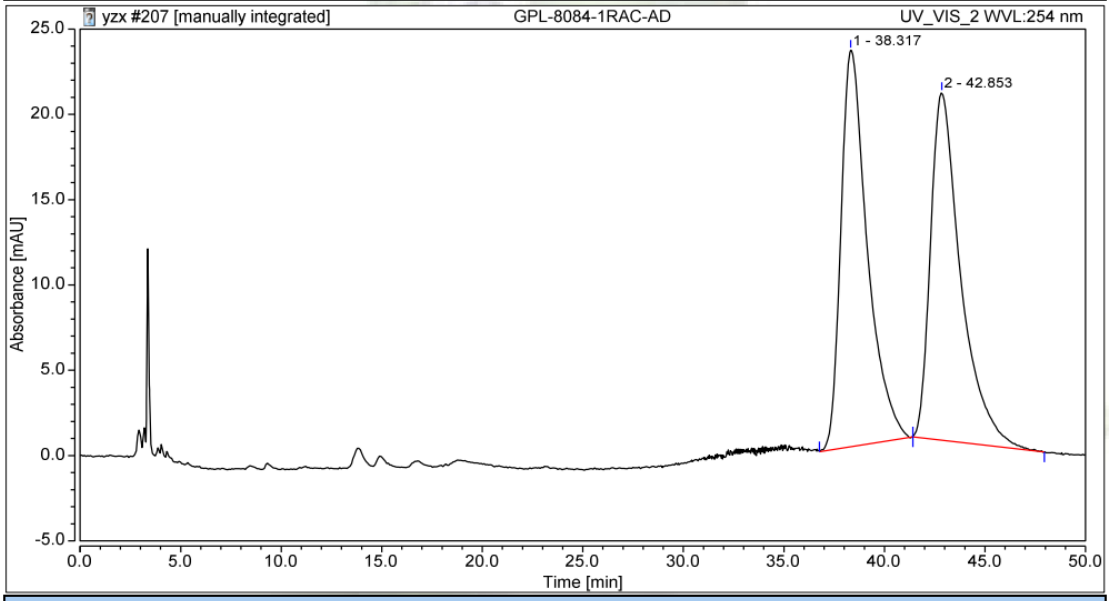
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		36.117	1.835	1.715	0.95	1.38	n.a.
2		39.040	191.627	122.671	99.05	98.62	n.a.
Total:			**193.461**	**124.387**	**100.00**	**100.00**	

Figure S88. HPLC chromatogram for **4h**.



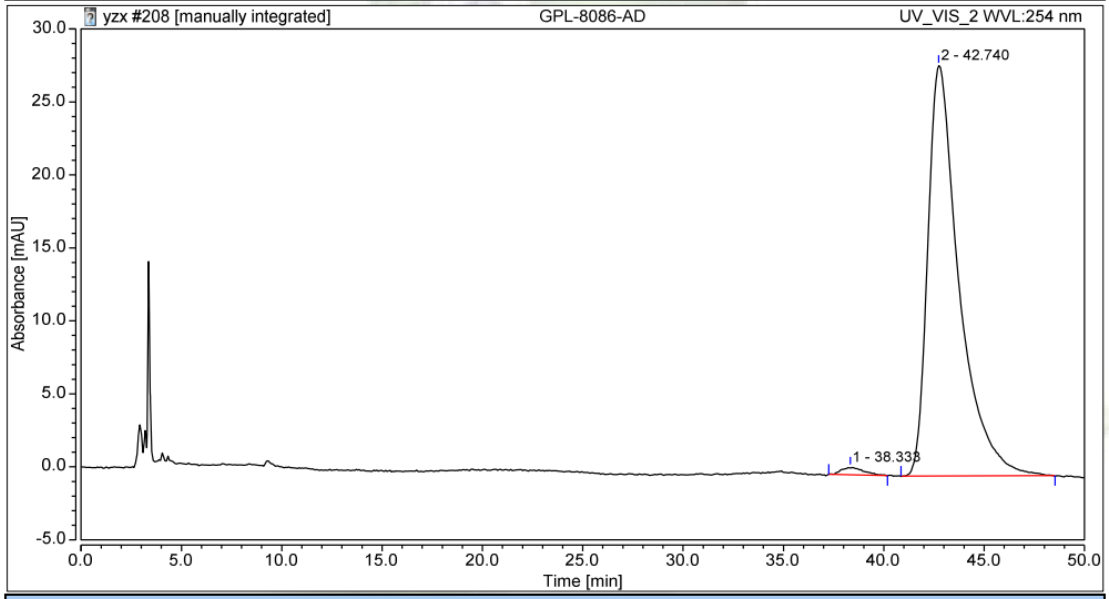
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		38.317	35.477	23.253	49.98	53.29	n.a.
2		42.853	35.498	20.381	50.02	46.71	n.a.
Total:			**70.975**	**43.634**	**100.00**	**100.00**	

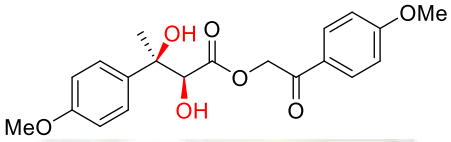
Chromatogram



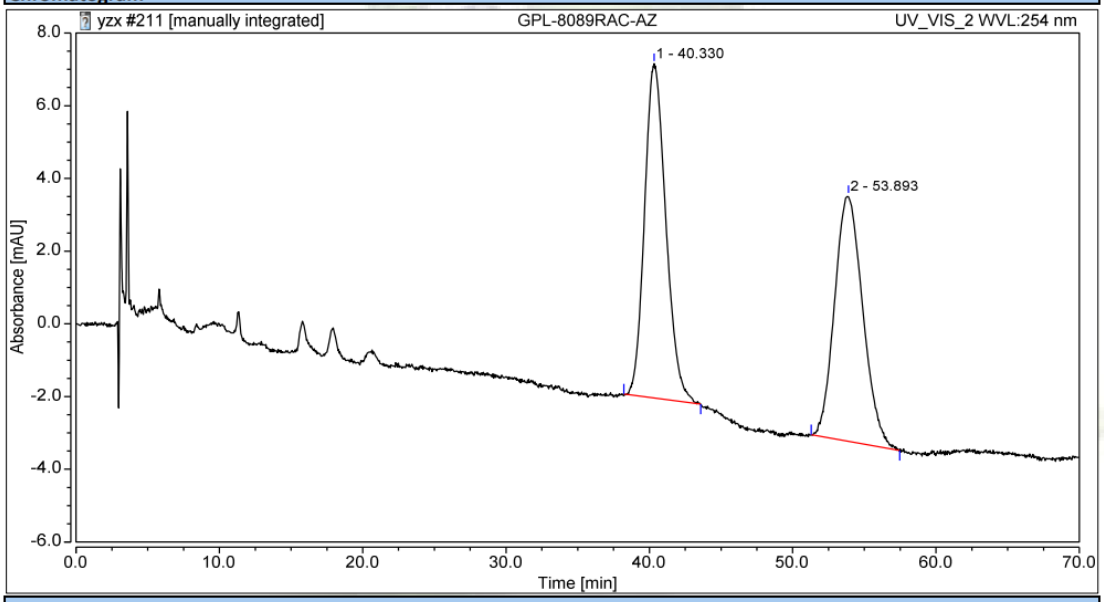
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		38.333	0.660	0.533	1.29	1.86	n.a.
2		42.740	50.696	28.126	98.71	98.14	n.a.
Total:			**51.356**	**28.659**	**100.00**	**100.00**	

Figure S89. HPLC chromatogram for **4i**.



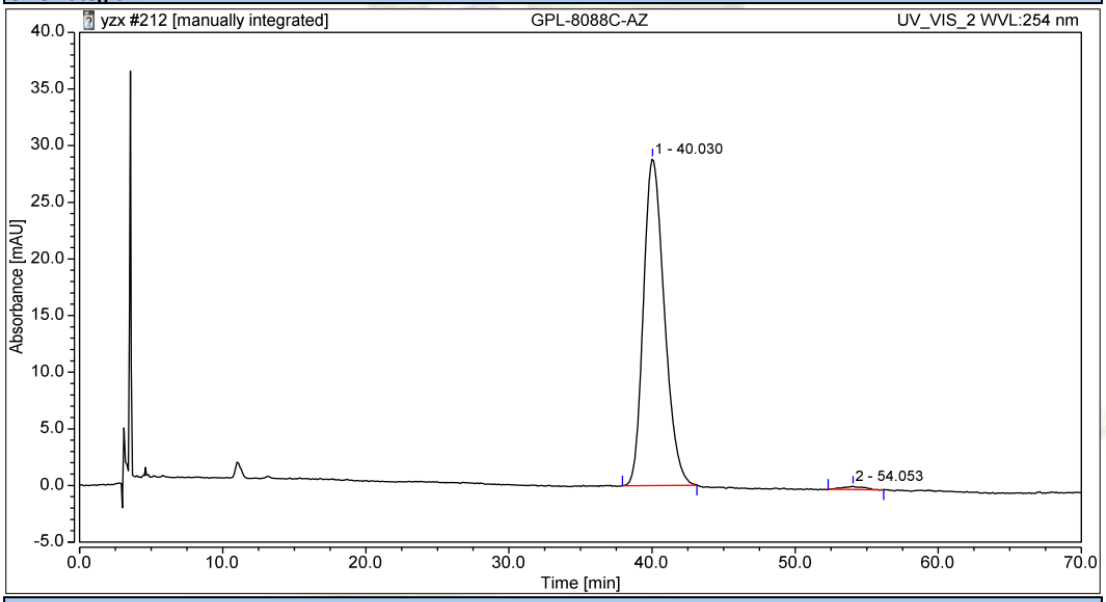
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		40.330	15.794	9.199	50.69	57.62	n.a.
2		53.893	15.365	6.765	49.31	42.38	n.a.
Total:			**31.159**	**15.964**	**100.00**	**100.00**	

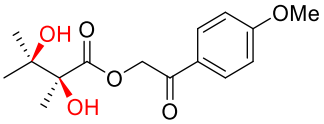
Chromatogram



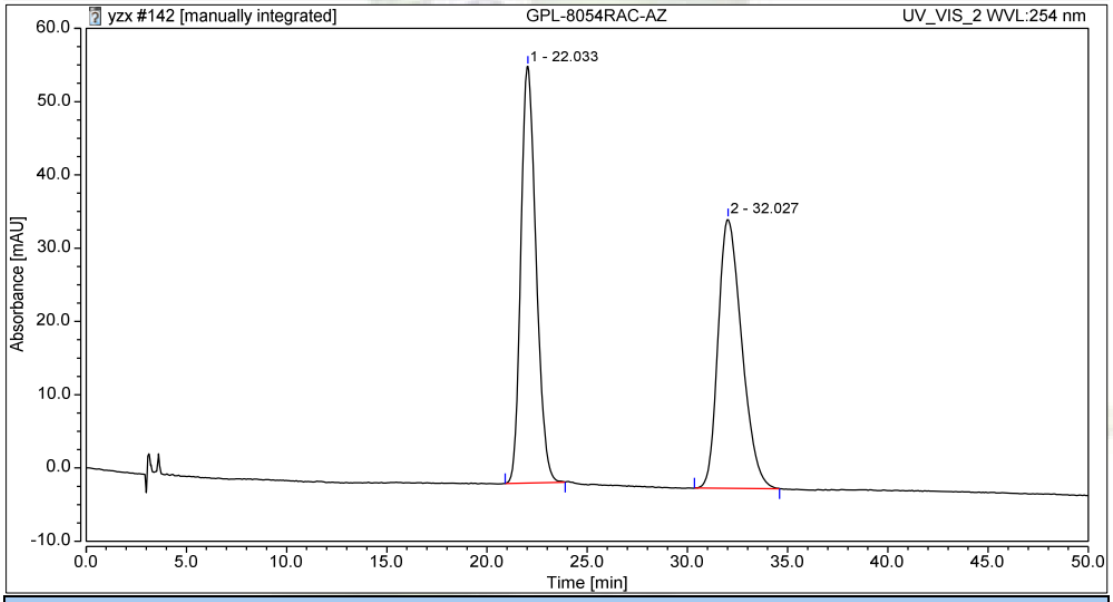
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		40.030	48.811	28.863	99.06	98.96	n.a.
2		54.053	0.462	0.303	0.94	1.04	n.a.
Total:			**49.274**	**29.167**	**100.00**	**100.00**	

Figure S90. HPLC chromatogram for **4j**.



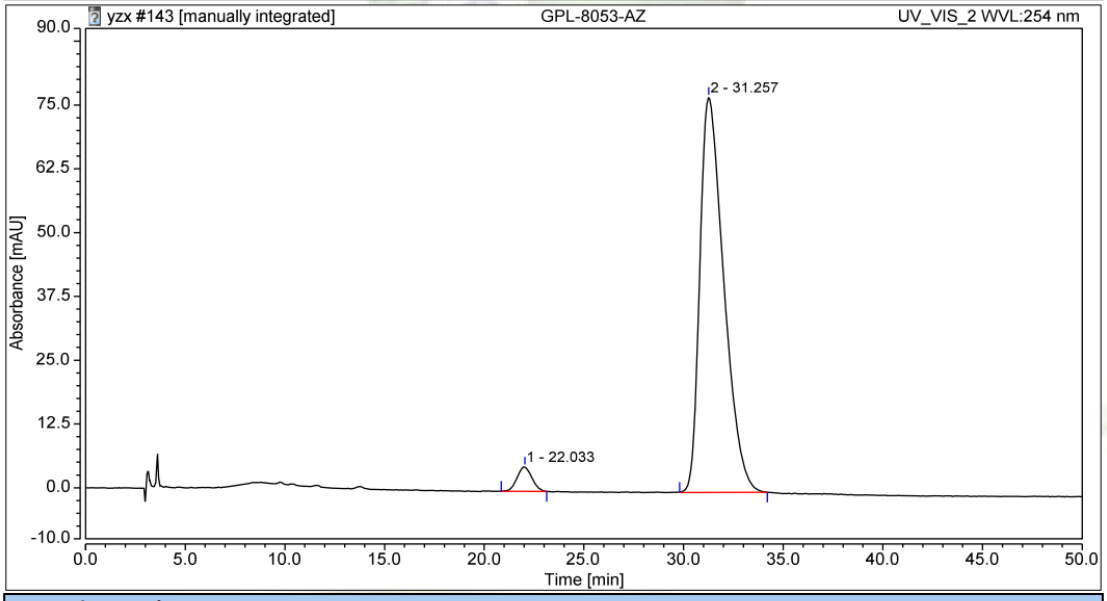
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.033	50.181	56.891	49.95	60.74	n.a.
2		32.027	50.274	36.770	50.05	39.26	n.a.
Total:			**100.455**	**93.661**	**100.00**	**100.00**	

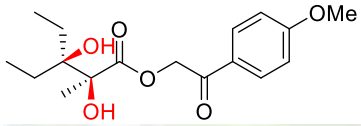
Chromatogram



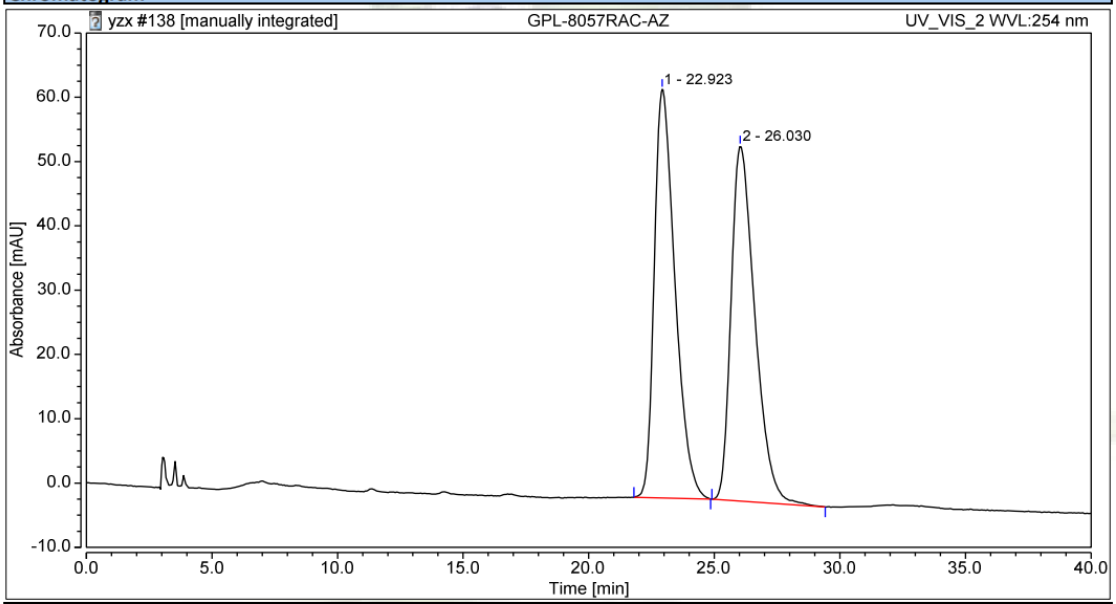
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.033	4.109	4.767	3.67	5.80	n.a.
2		31.257	107.726	77.401	96.33	94.20	n.a.
Total:			**111.835**	**82.168**	**100.00**	**100.00**	

Figure S91. HPLC chromatogram for **4k**.



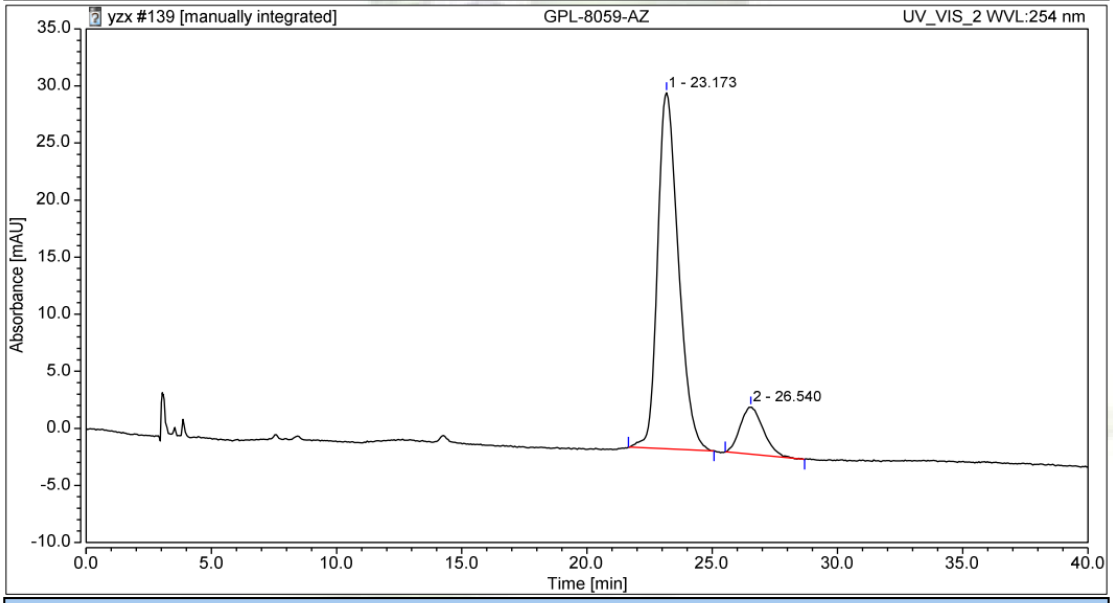
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.923	60.761	63.560	50.05	53.51	n.a.
2		26.030	60.647	55.231	49.95	46.49	n.a.
Total:			**121.408**	**118.791**	**100.00**	**100.00**	

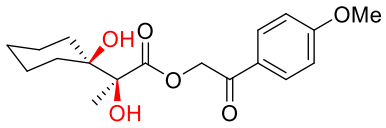
Chromatogram



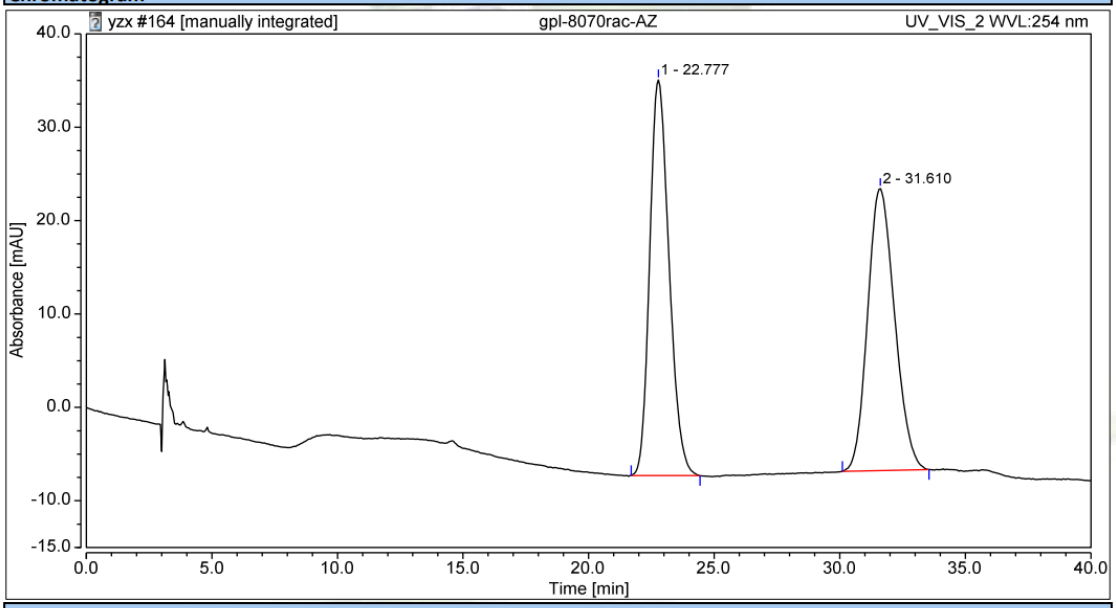
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.173	30.062	31.205	87.20	88.25	n.a.
2		26.540	4.413	4.154	12.80	11.75	n.a.
Total:			**34.476**	**35.359**	**100.00**	**100.00**	

Figure S92. HPLC chromatogram for **4l**.



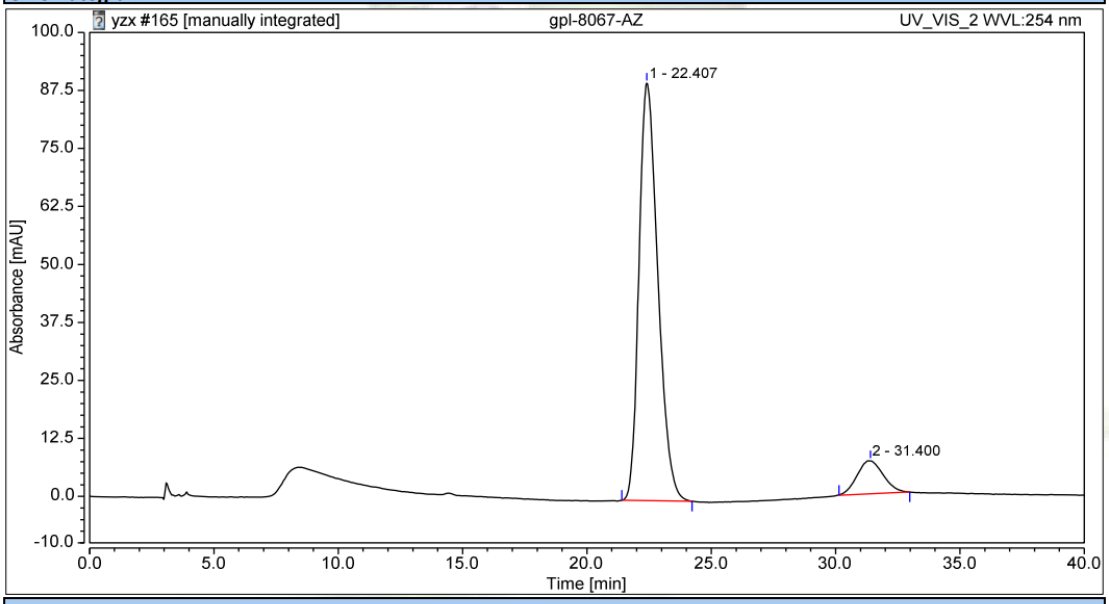
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.777	37.853	42.380	50.15	58.38	n.a.
2		31.610	37.623	30.210	49.85	41.62	n.a.
Total:			**75.476**	**72.589**	**100.00**	**100.00**	

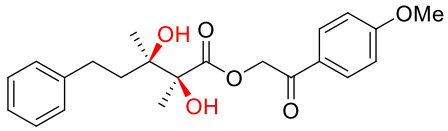
Chromatogram



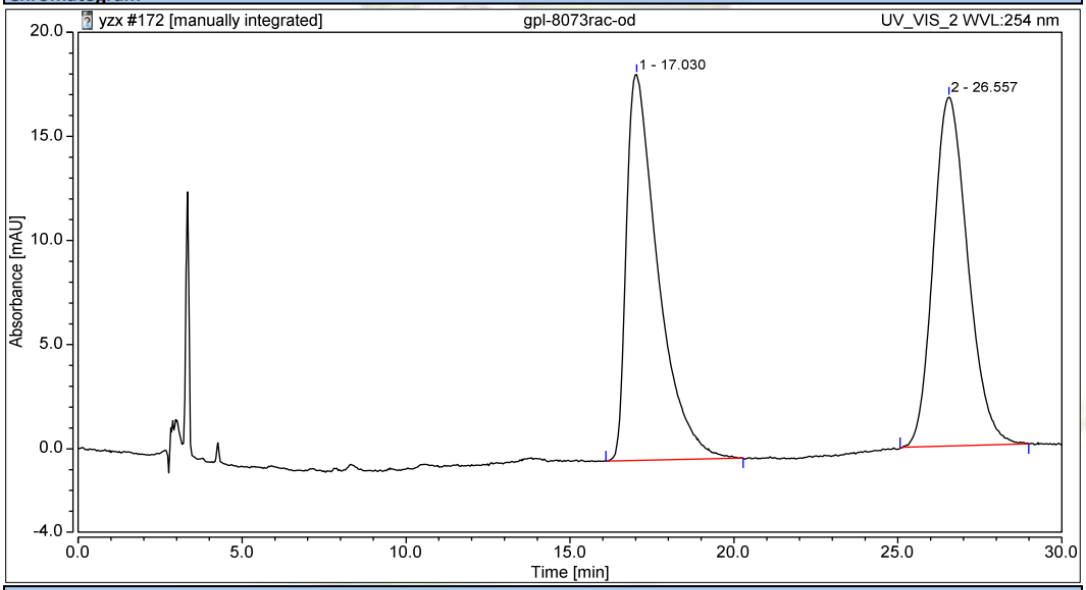
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.407	79.215	89.958	90.13	92.65	n.a.
2		31.400	8.674	7.135	9.87	7.35	n.a.
Total:			**87.889**	**97.092**	**100.00**	**100.00**	

Figure S93. HPLC chromatogram for **4m**.



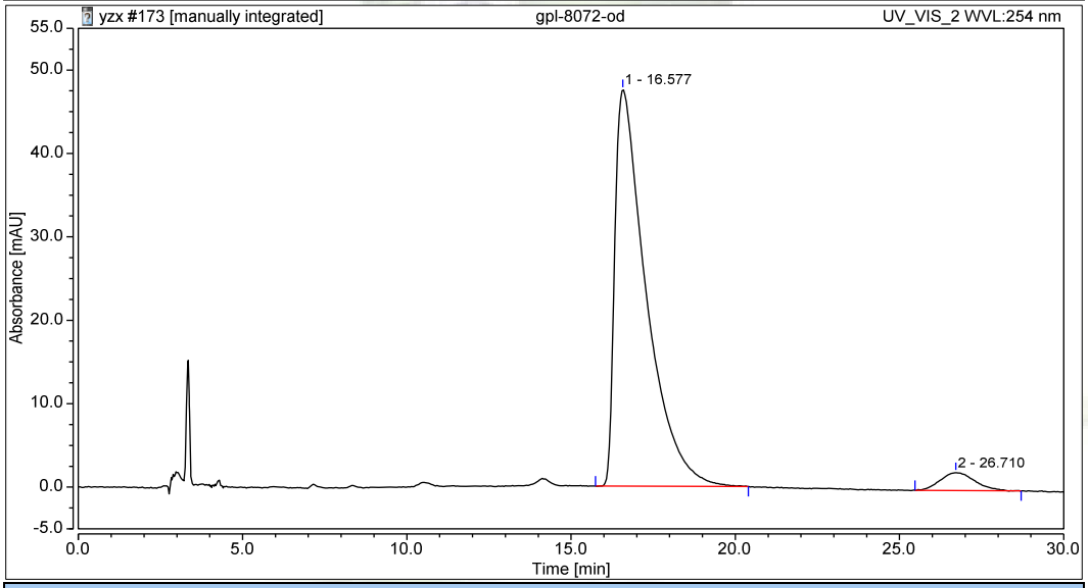
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.030	20.627	18.531	50.29	52.52	n.a.
2		26.557	20.392	16.756	49.71	47.48	n.a.
Total:			**41.019**	**35.287**	**100.00**	**100.00**	

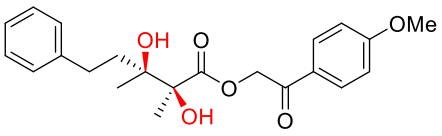
Chromatogram



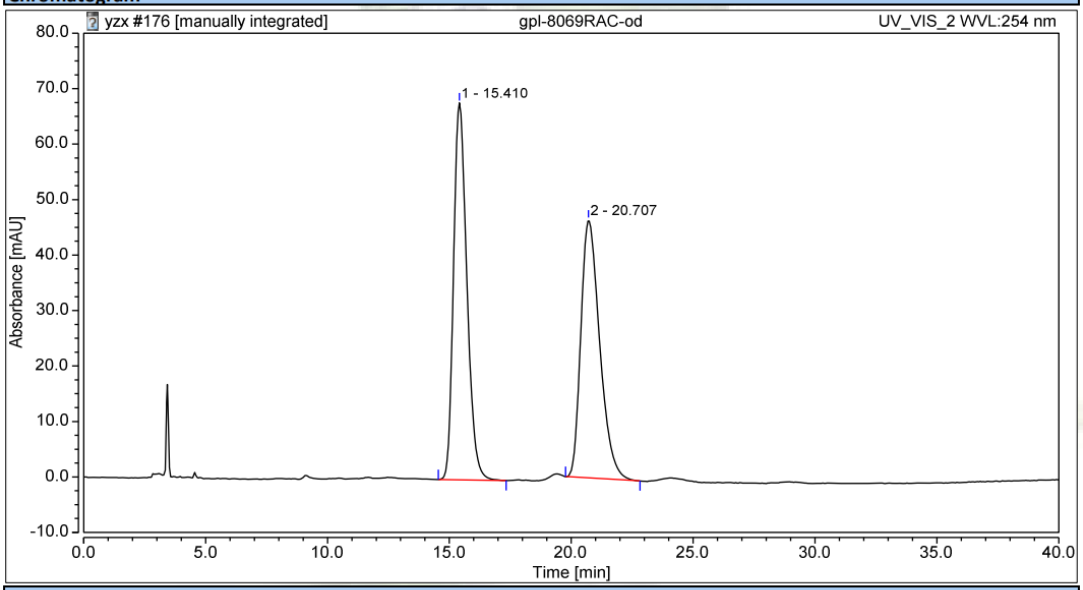
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.577	52.503	47.524	95.26	95.64	n.a.
2		26.710	2.611	2.167	4.74	4.36	n.a.
Total:			**55.114**	**49.691**	**100.00**	**100.00**	

Figure S94. HPLC chromatogram for **4n**.



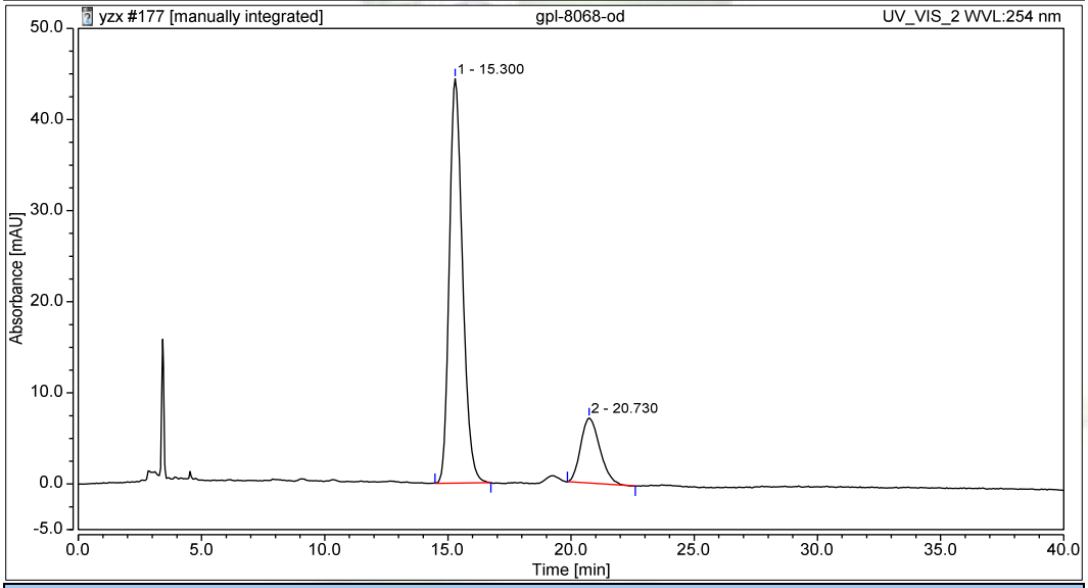
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.410	42.921	67.943	50.82	59.38	n.a.
2		20.707	41.533	46.475	49.18	40.62	n.a.
Total:			**84.454**	**114.418**	**100.00**	**100.00**	

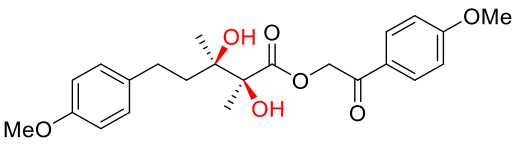
Chromatogram



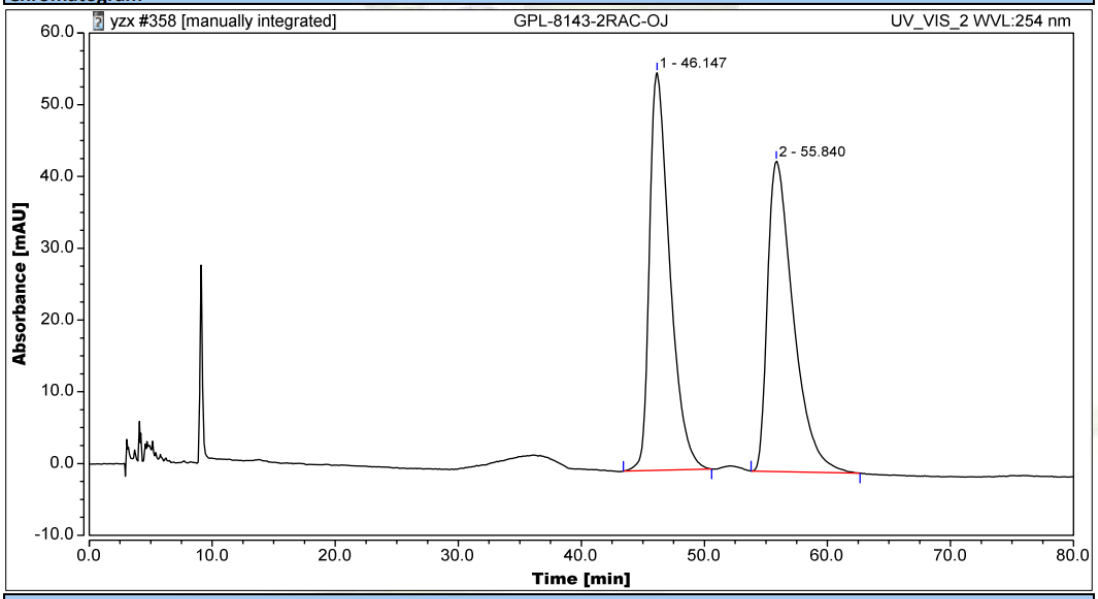
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.300	27.704	44.380	81.25	86.15	n.a.
2		20.730	6.394	7.137	18.75	13.85	n.a.
Total:			**34.098**	**51.517**	**100.00**	**100.00**	

Figure S95. HPLC chromatogram for **4o**.



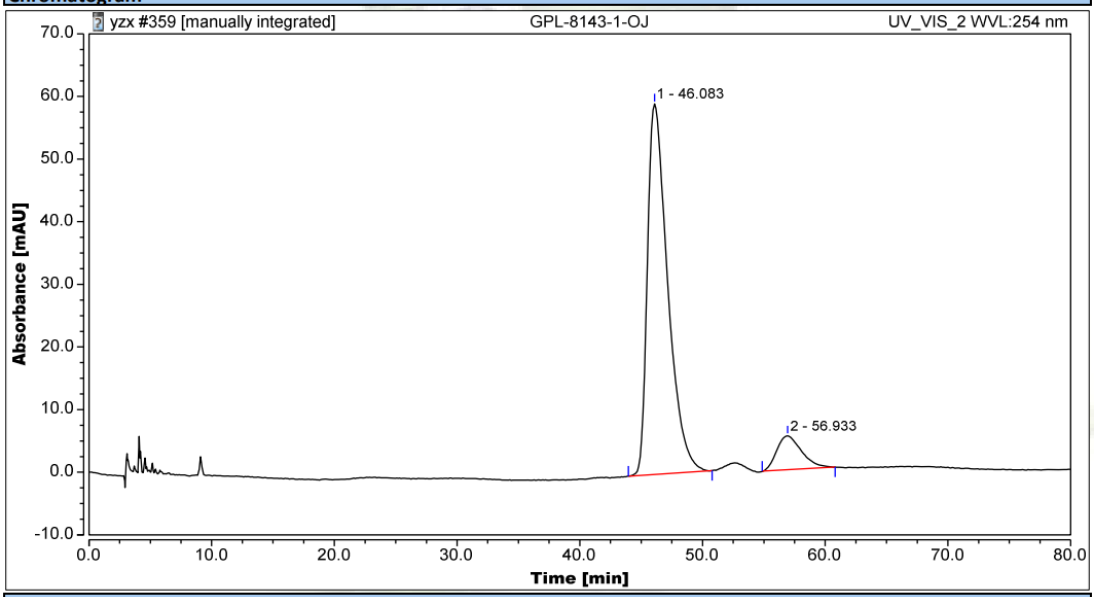
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		46.147	106.355	55.408	50.31	56.16	n.a.
2		55.840	105.030	43.255	49.69	43.84	n.a.
Total:			**211.385**	**98.663**	**100.00**	**100.00**	

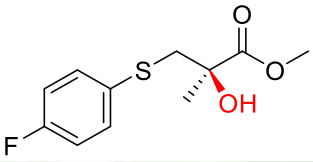
Chromatogram



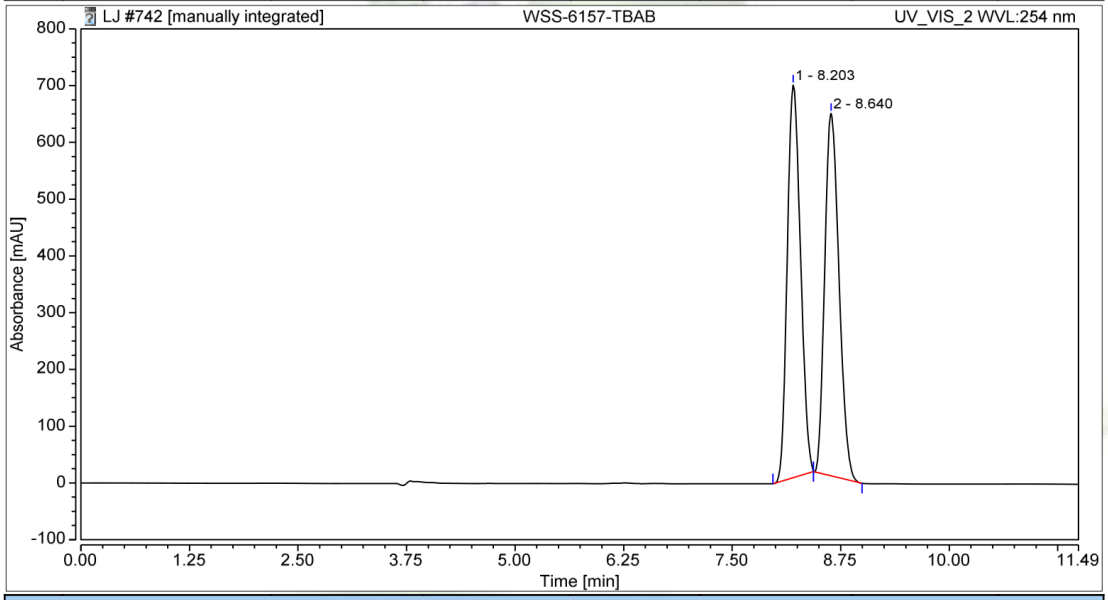
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		46.083	113.285	59.152	89.99	91.63	n.a.
2		56.933	12.596	5.405	10.01	8.37	n.a.
Total:			**125.881**	**64.557**	**100.00**	**100.00**	

Figure S96. HPLC chromatogram for **4p**.



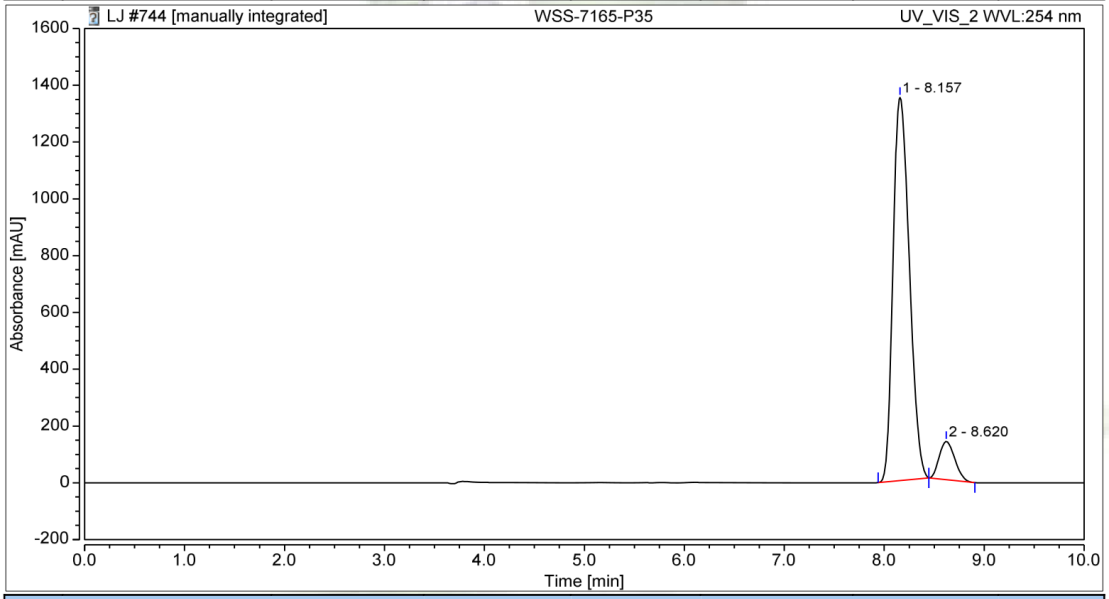
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.203	122.004	691.551	50.04	51.99	n.a.
2		8.640	121.796	638.595	49.96	48.01	n.a.
Total:			**243.799**	**1330.146**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.157	255.640	1349.614	91.30	90.94	n.a.
2		8.620	24.365	134.439	8.70	9.06	n.a.
Total:			**280.004**	**1484.053**	**100.00**	**100.00**	

Figure S97. HPLC chromatogram for **7**.