Supporting Information

Enantioselective Synthesis of Optically Active *cis*-*β*-Thio-*α*-Amino Acid Derivatives Through Organocatalytic Cascade Thio-Michael/Ring Opening Process

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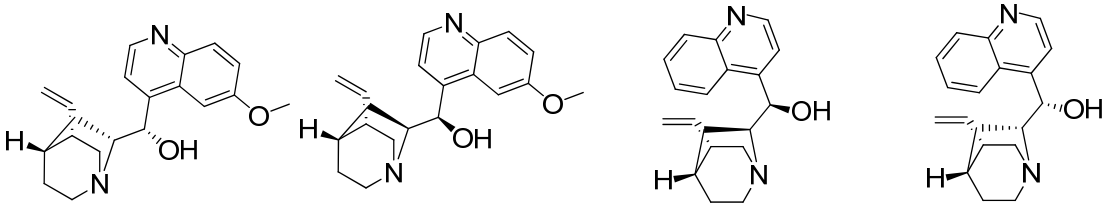
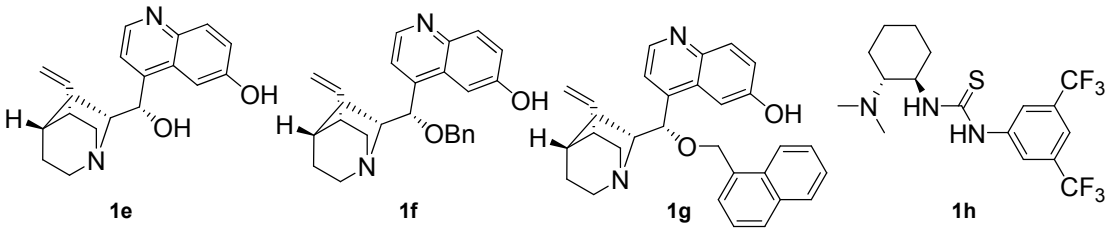
1. General methods

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in air and using undistilled solvent, without any precautions to exclude moisture unless otherwise noted. Organic solutions were concentrated under reduced pressure on an EYELA N-1001 rotary evaporator. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated glass plates (0.2 ± 0.03 mm thickness, GF-254, particle size 0.01–0.04 mm) from Yantai Chemical Industry Research Institute, P. R. China. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using silica gel (particle size 0.04 – 0.05 mm) from Yantai Chemical Industry Research Institute, P. R. China. ^{1}H and ^{13}C NMRspectra were recorded in $CDCl_3$ on Varian Inova (400 MHz or 300 MHz and 100 MHz or 75 MHz, respectively) spectometer. Chemical shifts (δ ppm) are relative to the resonance of the deuterated solvent as the internal standard ($CDCl_3$, δ 7.27 ppm for proton NMR, δ 77.23 ppm for carbon NMR). ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants (*J*) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectra (HRMS) for all the compounds were determined on Micromass GCT-TOF mass spertrometer with ESI resource. Elemental analysis was preformed using a Carlo-Erba EA-1110 instrument. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using a Daicel Chiralpak OD-H, AD-H or AS-H column (0.46cm x 25 cm). X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractomrter. Optical rotations are reported as follows: $[\alpha]_D^{rt}$ (c in g per 100 mL, solvent).

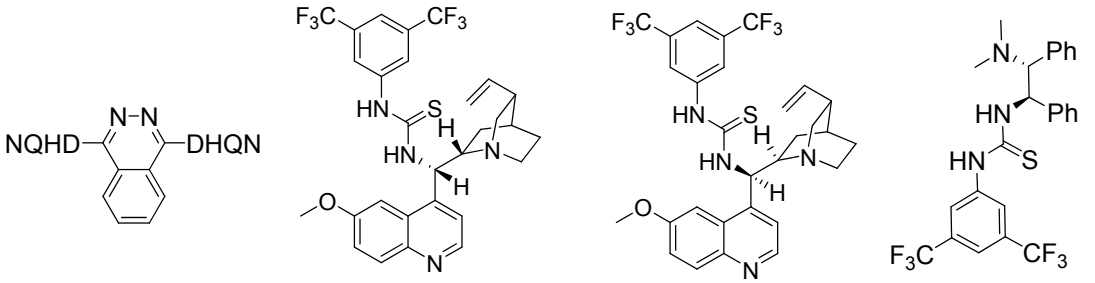
2. Reaction Optimization

Table S2.1. Effects of catalyst

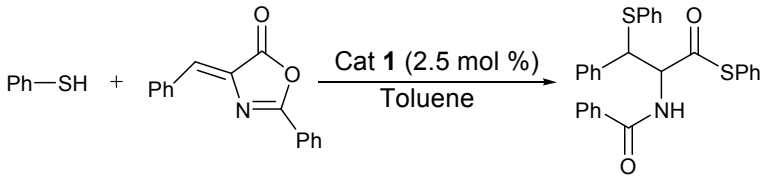




1e **1f** **1g** **1h**



1i **1j** **1k** **1l**

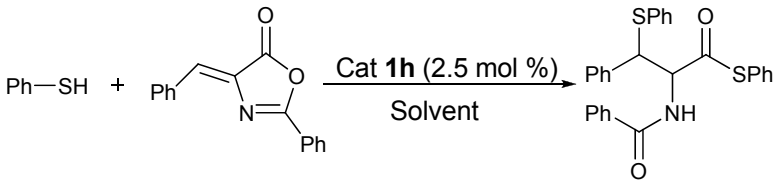


2a **3a** **4a**

Entry[a]	Cat	Temp.	Time (h)	Yield (%)[b]	Dr[c]	Ee (%)[d]
1	**1a**	RT	24	87	53/47	53
2	**1b**	RT	24	87	48/52	47
3	**1c**	RT	24	30	52/48	7
4	**1d**	RT	12	79	81/19	2.5
5	**1e**	RT	12	80	57/43	0.2
6	**1f**	RT	12	90	65/35	28
7	**1g**	RT	12	90	60/40	25
8	**1h**	RT	6	74	85/15	49
9	**1i**	RT	12	85	57/43	18
10	**1j**	RT	6	52	79/21	30
11	**1k**	RT	6	62	74/26	18
12	**1l**	RT	12	65	81/19	12

[a] Unless noted, reactions were carried out with **2a** (1.5 mmol), **3a** (0.3 mmol), **1** (2.5 mol %), and in toluene (2.0mL) at room temperature. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Determined by chiral HPLC analysis.

Table S2.2. Effects of Solvent

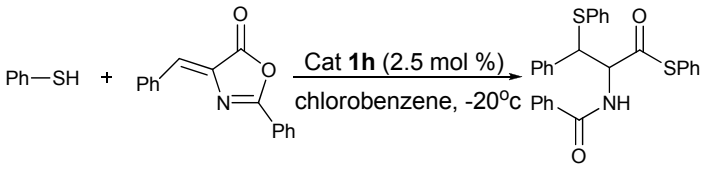


2a **3a** **4a**

Entry [a]	Solvent	Temp.(°C)	Con.	Time (h)	Yield (%) [b]	Dr [c]	Ee (%) [d]
1	THF	RT	0.15 M	24	64	78/22	15
2	$CHCl_3$	RT	0.15 M	24	92	86/14	54
3	PhMe	RT	0.15 M	6	74	85/15	49
4	PhCl	RT	0.15 M	18	94	84/16	50
5	m-Xylene	RT	0.15 M	18	84	85/15	49
6	DCE	RT	0.15 M	24	72	85/15	55

[a] Unless noted, reactions were carried out with **2a** (1.5 mmol), **3a** (0.3 mmol), **1h** (2.5 mol %), and in solvent (2.0 mL). [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Determined by chiral HPLC analysis.

Table S2.3. Effects of substrate concentration and catalyst loading



2a **3a** **4a**

entry[a]	Sol.	Temp.(°C)	Time (h)	Yield (%) [i]	dr[j]	ee[k]
1[b]	PhCl	-20	18	94	93/7	78
2[c]	PhCl	-20	18	94	95/5	86
3[d]	PhCl	-20	18	96	95/5	87
4[e]	PhCl	-20	18	88	95/5	88
5[df]	PhCl	-20	24	75	94/6	84
6[dg]	PhCl	-20	8	96	95/5	86
7[dh]	PhCl	-20	4	97	96/4	85

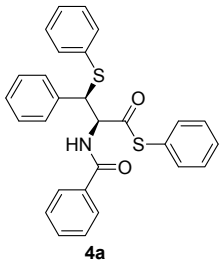
[a] Unless noted, reactions were carried out with **2a** (1.5 mmol), **3a** (0.3 mmol), **1h** (2.5 mol %), and in solvent (2.0 mL). [b] Run in 1.0 ml of chlorobenzene. [c] Run in 3.0 ml of chlorobenzene. [d] Run in 4.0 ml of chlorobenzene. [e] Run in 6.0 ml of chlorobenzene. [f] 2 mol % of **1** was used. [g] 5 mol % of **1h** was used. [h] 10 mol % of **1h** was used. [i] Isolated yield. [j] Determined by chiral HPLC analysis. [k] Determined by chiral HPLC analysis.

3. General Experimental Procedure For Asymmetric Thio-Michael/Ring Opening of Thiols to Olefinic Azlactones

In an ordinary tube equipped with a magnetic stirring bar, the solution of Thiol **2** (0.75 mmol), catalyst **1i** (2.5 mol %) in PhCl (2.0 mL) was stirred at -20 °C for 30 min, and then Olefinic

Azlactone **3** (0.15 mmol) was added. After the reaction mixture was stirred for 16-36 h at -20 ^{o}C. The reaction mixture was directly loaded onto a silica gel and purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 5:1, then dichloromethane) to give desired products **4a**-**4o**.

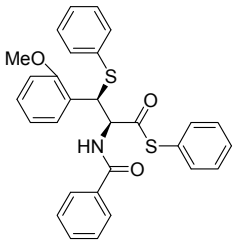
S-phenyl 2-benzamido-3-phenyl-3-(phenylthio)propanethioate 4a



4a

96% yield, 87% ee, dr = 95/5 [Daicel Chiralcel AD-H, hexane/i-PrOH (90:10) , flow rate: 1.0 mL·min^{-1}, λ = 210 nm, t (major) = 31.986, t (minor) = 41.742]; $[\alpha]_D^{26}$ = -38.57 (c 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.39–7.32 (m, 7H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.25–7.23 (m, 4H), 7.16–7.15 (m, 3H), 5.49 (dd, *J* = 8.4 Hz, *J* = 5.2 Hz, 1H), 5.03 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.97, 167.18, 138.05, 134.54, 133.49, 133.20, 132.71, 132.25, 129.64, 129.21, 128.86, 128.78, 128.35, 128.21, 127.98, 127.35, 126.84, 125.65, 63.22, 55.56; IR (KBr) ν_{max}: 3344.9, 1707.4, 1644.0, 1579.6, 1514.0, 1480.9, 747.0, 688.9 cm^{-1}; HRMS (ESI): m/z = 470.1243 (calcd for $C_{28}H_{23}NO_2{}^{32}S_2+H^+$ = 470.1243); Elem. anal. calculated for $C_{28}H_{23}NO_2S_2$: C 71.61, H 4.94, N 2.98; found: C 71.31, H 4.86, N 3.15.

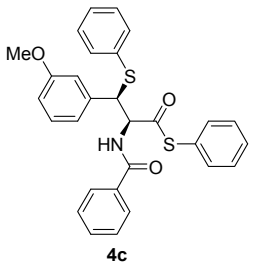
S-phenyl 2-benzamido-3-(2-methoxyphenyl)-3-(phenylthio)propanethioate 4b



4b

92% yield, 85% ee, dr = 97/3 [Daicel Chiralcel AS-H, hexane/i-PrOH (90:10) , flow rate: 1.0 mL·min^{-1}, λ = 210 nm, t (major) = 12.142, t (minor) = 20.575]; $[\alpha]_D^{26}$ = -22.01 (c 1.89, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.45–7.38 (m, 3H), 7.37–7.29 (m, 3H), 7.28–7.17 (m, 5H), 7.13 (d, *J* = 6.0 Hz, 2H), 6.94–6.82 (m, 2H), 5.54 (dd, *J* = 8.4 Hz, *J* = 4.8 Hz, 1H), 5.50 (d, *J* = 4.4 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.93, 167.28, 156.55, 134.65, 134.30, 133.78, 132.15, 132.04, 129.53, 129.45, 129.20, 129.17, 129.04, 128.85, 127.61, 127.31, 127.13, 126.40, 120.81, 110.91, 62.55, 55.82, 50.04; IR (KBr) ν_{max}: 3413.8, 1701.6, 1654.6, 1581.4, 1514.8, 1478.6, 1438.6, 793.7, 746.9, 689.2 cm^{-1}; HRMS (ESI): m/z = 500.1349 (calcd for $C_{29}H_{25}NO_3{}^{32}S_2+H^+$ = 500.1349); Elem. anal. calculated for $C_{29}H_{25}NO_3S_2$: C 69.71, H 5.04, N 2.80; found: C 69.41, H 4.93, N 2.92.

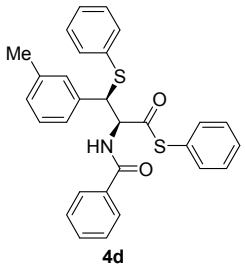
S-phenyl 2-benzamido-3-(3-methoxyphenyl)-3-(phenylthio)propanethioate 4c



4c

96% yield, 89% ee, dr = 97/3 [Daicel Chiralcel AD-H, hexane/i-PrOH (80:20) , flow rate: 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 18.396, t (minor) = 20.888]; $[\alpha]_D^{26}$ = -41.92 (c 0.26, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.43–7.28 (m, 5H), 7.28–7.02 (m, 7H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.48 (dd, *J* = 8.8 Hz, *J* =5.2 Hz, 1H), 5.00 (d, *J* = 5.2 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.06, 167.20, 159.80, 139.55, 134.57, 133.48, 133.21, 132.68, 132.31, 129.82, 129.68, 129.26, 129.24, 128.90, 128.02, 127.35, 126.85, 120.66, 114.07, 113.64, 63.17, 55.50, 55.29; IR (KBr) ν_{max}: 3468.7， 3267.7， 1699.9， 1653.0， 1600.6， 1526.9， 1488.6， 1438.5， 878.2， 743.1， 691.0 cm^{-1}; HRMS (ESI): m/z = 500.1349 (calcd for $C_{29}H_{25}NO_3{}^{32}S_2$+$H^+$ = 500.1349); Elem. anal. calculated for $C_{29}H_{25}NO_3S_2$: C 69.71, H 5.04, N 2.80; found: C 69.23, H 4.96, N 2.87.

S-phenyl 2-benzamido-3-(phenylthio)-3-m-tolylpropanethioate 4d

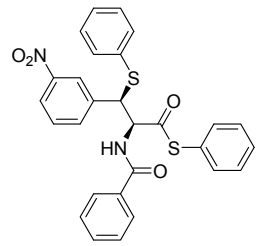


4d

90% yield, 75% ee, dr = 96/4 [Daicel Chiralcel OD-H, hexane/i-PrOH (80:20) , flow rate: 1.0 mL·min^{-1}, λ = 210 nm, t (minor) = 9.718, t (major) = 11.302]; $[\alpha]_D^{26}$ = -17.38 (c 1.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.46–7.37 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 3H), 7.29–7.20 (m, 5H), 7.20–7.12 (m, 2H), 7.09 (d, *J* = 6.8 Hz, 2H), 5.41 (dd, *J* = 8.4 Hz, *J* = 5.2 Hz, 1H), 5.34(d, *J* = 5.2 Hz, 1H), 2.42(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.54, 167.24, 136.55, 135.62, 134.63, 133.64, 133.21, 133.06, 132.34, 130.89, 129.69, 129.36, 129.24, 128.98, 128.24, 128.20, 127.79, 127.41, 126.93, 126.66, 62.73, 51.63, 19.71; IR (KBr) ν_{max}: 3413.4, 1699.6, 1641.3, 1579.8, 1527.3, 1478.2, 1439.1, 888.9, 746.1, 689.4 cm^{-1}; HRMS (ESI): m/z = 484.1398 (calcd for $C_{29}H_{25}NO_2{}^{32}S_2$+$H^+$ = 484.1399); Elem. anal. calculated for $C_{29}H_{25}NO_2S_2$: C 72.02, H 5.21, N 2.90; found: C 71.40, H 4.97, N 2.96.

S-phenyl 2-benzamido-3-(3-nitrophenyl)-3-(phenylthio)propanethioate 4e

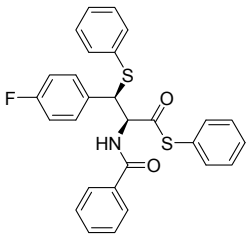
93% yield, 88% ee, dr = 95/5 [Daicel Chiralcel AD-H, hexane/i-PrOH (80:20) , flow rate: 1.0 mL·min^{-1}, λ = 254 nm, t (major) =19.595, t (minor) = 33.325]; $[\alpha]_D^{26}$ = -62.10 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 1H),



4e

7.42–7.32 (m, 5H), 7.30–7.20 (m, 5H), 7.13 (d, J = 8.4 Hz, 1H), 5.53 (dd, J = 8.6 Hz, J =5.0 Hz, 1H), 5.11 (d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.50, 167.48, 148.29, 140.53, 134.61, 134.47, 133.22, 132.61, 131.92, 130.02, 129.79, 129.52, 129.49, 129.07, 128.69, 127.41, 126.37, 123.56, 123.25, 62.86, 55.22; IR (KBr) ν_{max}: 3469.9, 3297.9, 1698.4, 1640.2, 1579.3, 1531.3, 1477.9, 1438.7, 839.3, 748.8, 689.9 cm^{-1}; HRMS (ESI): m/z = 515.1074 (calcd for $C_{28}H_{22}N_2O_4{}^{32}S_2$+H$^+$ = 515.1094); Elem. anal. calculated for $C_{28}H_{22}N_2O_4S_2$: C 65.35, H 4.31, N 5.44; found: C 65.03, H 4.16, N 5.56.

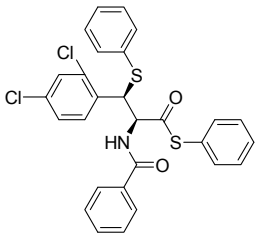
S-phenyl 2-benzamido-3-(4-fluorophenyl)-3-(phenylthio)propanethioate 4f



4f

98% yield, 88% ee, dr = 96/4 [Daicel Chiralcel AD-H, hexane/i-PrOH (80:20) , flow rate: 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 15.299, t (minor) = 23.814]; $[\alpha]_D{}^{26}$ = -42.59 (c 0.27, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.37–7.30 (m, 7H), 7.29–7.20 (m, 3H), 7.18 (d, J = 6.8 Hz, 2H), 7.12 (d, J = 8.8 Hz, 1H), 6.98 (t, J = 8.2 Hz, 2H), 5.47 (dd, J = 8.2 Hz, J = 5.8 Hz, 1H), 5.00 (d, J = 5.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.92, 167.22, 162.45 ($J_{F\text{-}C}$ = 246.0 Hz), 134.59, 133.94, 133.45, 132.94, 132.42, 130.13 ($J_{F\text{-}C}$ = 8.3 Hz), 132.87, 129.82, 129.35, 128.99, 128.24, 127.40, 126.73, 115.77 ($J_{F\text{-}C}$ = 21.8 Hz), 63.20, 54.96; IR (KBr) ν_{max}: 3346.5, 1711.5, 1641.3, 1601.5, 1509.8, 1479.3, 1438.5, 842.4, 743.7, 690.0 cm^{-1}; HRMS (ESI): m/z = 488.1147 (calcd for $C_{28}H_{22}FNO_2{}^{32}S_2$+H$^+$ = 488.1149); Elem. anal. calculated for $C_{28}H_{22}FNO_2S_2$: C 68.97, H 4.55, N 2.87; found: C 68.22, H 4.43, N 2.82.

S-phenyl 2-benzamido-3-(2,4-dichlorophenyl)-3-(phenylthio)propanethioate 4g

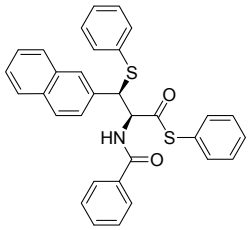


4g

97% yield, 87% ee, dr = 98/2 [Daicel Chiralcel AD-H, hexane/i-PrOH (80:20) , flow rate: 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 10.880, t (minor) = 11.594]; $[\alpha]_D{}^{26}$ = -28.21 (c 0.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 2H), 7.43–7.30 (m, 6H), , 7.30–7.05 (m, 8H), 5.60 (d, J = 4.4 Hz, 1H), 5.53 (dd, J = 9.0 Hz, J = 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.17, 167.23, 134.64, 134.52, 134.48, 134.30, 133.36, 132.47, 132.44, 132.38, 130.63, 129.85, 129.63, 129.41, 129.37, 128.97, 128.27, 127.54, 127.36, 126.51, 61.98, 51.62; IR (KBr) ν_{max}: 3239.7, 1702.8, 1642.6,

1580.9, 1526.2, 1478.0, 1439.0, 790.7, 740.7, 688.9 cm^{-1}; HRMS (ESI): m/z = 538.0464 (calcd for $C_{28}H_{21}{}^{35}Cl_2NO_2{}^{32}S_2+H^+$ = 538.0464); Elem. anal. calculated for $C_{28}H_{21}Cl_2NO_2S_2$: C 62.45, H 3.93, N 2.60; found: C 61.98, H 3.91, N 2.73.

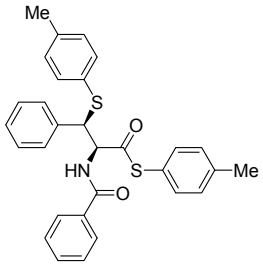
S-phenyl 2-benzamido-3-(naphthalen-2-yl)-3-(phenylthio)propanethioate 4h



4h

98% yield, 85% ee, dr = 96/4 [Daicel Chiralcel AD-H, hexane/i-PrOH (80:20) , flow rate: 1.0 mL·min-1, λ = 254 nm, t (major) = 21.076, t (minor) = 24.000]; $[\alpha]_D{}^{26}$ = -64.00 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.79 (m, 4H), 7.78–7.69 (m, 2H), 7.66–7.54 (m, 2H), 7.53–7.44 (m, 4H), 7.43–7.37 (m, 2H), 7.36–7.29 (m, 3H), 7.24–7.14(m, 4H), 7.14–7.08 (m, 2H), 5.59 (dd, *J* = 8.8 Hz, *J* = 5.6Hz, 1H), 5.16(d, *J* = 5.2Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.08, 167.28, 135.44, 134.58, 133.57, 133.23, 133.07, 132.77, 132.31, 129.70, 129.29, 129.25, 128.92, 128.80, 128.10, 128.08, 127.80, 127.54, 127.39, 126.80, 126.46, 126.06, 63.22, 55.95; IR (KBr) νmax: 3365.8, 1707.1, 1645.4, 1579.2, 1514.0, 1482.8, 762.8, 746.9, 715.6 cm^{-1}; HRMS (ESI): m/z = 520.1399 (calcd for $C_{32}H_{25}NO_2{}^{32}S_2+H^+$ = 520.1399); Elem. anal. calculated for $C_{32}H_{25}NO_2S_2$: C 73.96, H 4.85, N 2.70; found: C 73.47, H 4.77, N 2.79.

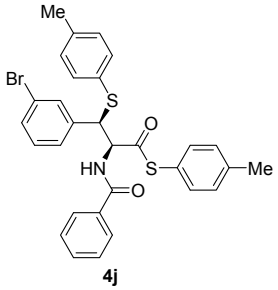
S-p-tolyl 2-benzamido-3-phenyl-3-(p-tolylthio)propanethioate 4i



4i

93% yield, 85% ee, dr = 94/6 [Daicel Chiralcel AD-H, hexane/i-PrOH (90:10) , flow rate: 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 31.500, t (minor) = 54.788]; $[\alpha]_D{}^{26}$ = -24.60 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.23 (m, 5H), 7.23 – 7.18 (m, 1H), 7.17 – 7.12 (m, 2H), 7.11 – 6.95 (m, 4H), 5.45 (dd, *J* = 8.8 Hz, *J* = 4.8 Hz, 1H), 4.99 (d, *J* =4.4 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.42, 167.13, 139.85, 138.31, 138.26, 134.45, 133.56, 133.33, 132.21, 130.00, 129.37, 128.83, 128.73, 128.30, 128.11, 127.34, 123.36, 63.07, 55.85, 21.41, 21.23; IR (KBr) ν_{max}: 3462.7， 3359.1， 3065.9， 1714.1， 1648.6， 1505.3， 1482.8， 809.1， 720.4， 694.2 cm^{-1}; HRMS (ESI): m/z = 498.1557 (calcd for $C_{30}H_{27}NO_2{}^{32}S_2+H^+$ = 498.1558); Elem. anal. calculated for $C_{30}H_{27}NO_2S_2$: C 72.40, H 5.47, N 2.81; found: C 72.05, H 5.29, N 3.04.

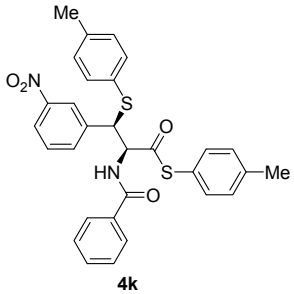
S-p-tolyl 2-benzamido-3-(3-bromophenyl)-3-(p-tolylthio)propanethioate 4j



4j

98% yield, 83% ee, dr = 92/8 [Daicel Chiralcel AD-H, hexane/i-PrOH (80:20) , flow rate: 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 14.704, t (minor) = 18.912]; $[\alpha]_D^{26}$ = -38.71 (c 2.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.6 Hz,, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.54–7.45 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.29–7.26 (m, 3H), 7.18–6.98 (m, 8H), 5.41 (dd, *J* = 9.0 Hz, *J* =5.2 Hz, 1H), 4.88 (d, *J* = 5.2 Hz, 1H), 2.35(s, 3H), 2.31(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.14, 167.25, 140.64, 140.07, 138.68, 134.52, 133.52, 132.32, 131.58, 131.25, 130.29, 130.16, 130.14, 128.92, 128.85, 127.38, 126.92, 123.17, 122.67, 62.90, 55.54, 21.47, 21.29; IR (KBr) ν_{max}: 3468.8, 3290.7, 1698.0, 1643.7, 1596.8, 1530.8, 1489.2, 882.3, 808.8, 691.6 cm^{-1}; HRMS (ESI): m/z = 576.0661 (calcd for $C_{30}H_{26}{}^{80}BrNO_2{}^{32}S_2$+$H^+$ = 576.0661); Elem. anal. calculated for $C_{30}H_{26}BrNO_2S_2$: C 62.49, H 4.55, N 2.43; found: C 61.95, H 4.37, N 2.51.

S-p-tolyl 2-benzamido-3-(3-nitrophenyl)-3-(p-tolylthio)propanethioate 4k

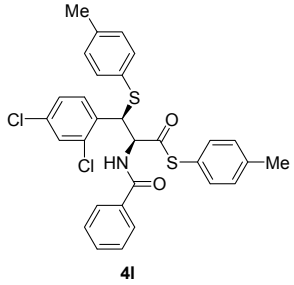


4k

94% yield, 85% ee, dr = 92/8 [Daicel Chiralcel AD-H, hexane/i-PrOH (80:20) , flow rate: 1.0 mL·min^{-1}, λ = 210 nm, t (major) = 17.493, t (minor) = 39.423]; $[\alpha]_D^{26}$ = -48.70 (c 0.54, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.11 (d, *J* = 8.0 Hz,, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.30–7.23 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.16–7.08 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 2H), 5.49 (dd, *J* = 9.0 Hz, *J* = 4.8 Hz, 1H), 5.05(d, *J* = 4.8 Hz, 1H), 2.36(s, 3H), 2.30(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.95, 167.44, 148.24, 140.67, 140.33, 139.11, 134.52, 134.47, 133.76, 133.33, 132.54, 130.29, 129.71, 129.04, 128.11, 127.40, 123.58, 123.15, 122.87, 62.71, 55.50, 21.50, 21.31; IR (KBr) ν_{max}: 3299.5， 1682.9， 1639.4， 1602.2， 1579.5， 1531.2， 1490.1， 1445.4， 835.4， 727.9， 693.1 cm^{-1}; HRMS (ESI): m/z = 543.1375 (calcd for $C_{30}H_{26}N_2O_4{}^{32}S_2$+$H^+$ = 543.1407); Elem. anal. calculated for $C_{30}H_{26}N_2O_4S_2$: C 66.40, H 4.83, N 5.16; found: C 65.94, H 4.69, N 5.00.

S-p-tolyl 2-benzamido-3-(2,4-dichlorophenyl)-3-(p-tolylthio)propanethioate 4l

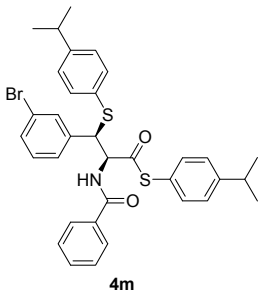
95% yield, 84% ee, dr = 96/4 [Daicel Chiralcel AD-H, hexane/i-PrOH (90:10) , flow rate: 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 14.944, t (minor) = 22.664]; $[\alpha]_D^{26}$ = -17.75 (c 1.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.6 Hz,, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2



4l

Hz, 2H), 7.45 (d, J = 8.4Hz, 1H), 7.39 (s, 1H), 7.32–7.25 (m, 2H), 7.20–7.12 (m, 4H), 7.12–7.02 (m, 4H), 5.54 (d, J = 4.0 Hz, 1H), 5.47 (dd, J = 8.6 Hz, J =4.4 Hz, 1H), 2.35 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.66, 167.19, 140.13, 138.67, 134.66, 134.57, 134.42, 134.31, 133.44, 133.21, 133.14, 132.41, 130.55, 130.19, 129.62, 128.97, 128.56, 127.48, 127.37, 123.03, 61.89, 51.97, 21.50, 21.31; IR (KBr) ν_{max}: 3300.4, 1702.6, 1645.1, 1584.4, 1581.7, 1474.4, 863.1, 808.0, 708.3 cm^{-1}; HRMS (ESI): m/z = 566.0776 (calcd for $C_{30}H_{25}{}^{35}Cl_2NO_2{}^{32}S_2+H^+$ = 566.0777); Elem. anal. calculated for $C_{30}H_{25}Cl_2NO_2S_2$: C 63.60, H 4.45, N 2.47; found: C 63.47, H 4.46, N 2.58.

S-4-isopropylphenyl 2-benzamido-3-(3-bromophenyl)-3-(4-isopropylphenylthio)propane thioate 4m

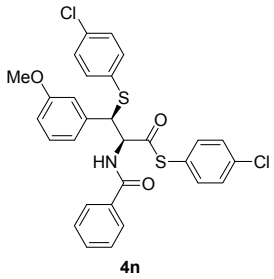


4m

96% yield, 84% ee, dr = 92/8 [Daicel Chiralcel AD-H, hexane/i-PrOH (80:20) , flow rate: 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 7.999, t (minor) = 10.490]; $[\alpha]_D{}^{26}$ = -31.40 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 7.6 Hz,, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.53–7.44 (m, 3H), 7.39 (d, J = 7.6 Hz, 1H), 7.30 (m, 3H), 7.24–7.06 (m, 8H), 5.43 (dd, J = 8.8 Hz, J =5.6 Hz, 1H), 4.88 (d, J = 5.2 Hz, 1H), 3.10–2.70 (m, 2H), 1.25–1.15 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.17, 167.29, 150.76, 149.52, 140.72, 134.53, 133.57, 133.46, 132.35, 131.60, 131.26, 130.33, 129.25, 128.95, 127.59, 127.55, 127.41, 126.92, 123.47, 122.68, 62.95, 55.52, 34.06, 33.90, 23.98, 23.93; IR (KBr) ν_{max}: 3264.4, 2959.3, 1689.2, 1638.9, 1598.6, 1579.7, 1527.4, 1487.6, 889.2, 825.3, 690.1 cm^{-1}; HRMS (ESI): m/z =632.1287 (calcd for $C_{34}H_{34}{}^{80}BrNO_2{}^{32}S_2+H^+$ = 632.1287); Elem. anal. calculated for $C_{34}H_{34}BrNO_2S_2$: C 64.55, H 5.42, N 2.21; found: C 64.31, H 5.30, N 2.30.

S-4-chlorophenyl 2-benzamido-3-(4-chlorophenylthio)-3-(3-methoxyphenyl)propanethioate 4n

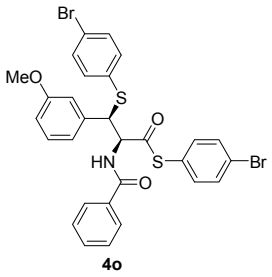
98% yield, 82% ee, dr = 94/6 [Daicel Chiralcel OD-H, hexane/i-PrOH (90:10) , flow rate: 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 14.912, t (major) = 16.990]; $[\alpha]_D{}^{26}$ = -25.60 (c 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 7.6 Hz,, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.2 Hz, 2H), 7.43–7.30 (m, 4H), 7.25–7.18 (m, 3H), 7.14 (d, J = 8.8 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H),



4n

6.99–6.87 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 5.46 (dd, J = 8.8 Hz, J =5.2 Hz, 1H), 4.96 (d, J = 4.8 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.67, 167.22, 159.90, 139.00, 136.20, 135.75, 134.41, 134.21, 133.34, 132.47, 131.46, 129.95, 129.58, 129.41, 128.98, 127.35, 125.26, 120.60, 114.13, 113.80, 63.01, 55.61, 55.33; IR (KBr) ν_{max}: 3286.6, 1702.5, 1643.3, 1598.9, 1524.4, 1474.9, 899.1, 861.3, 747.6, 692.1 cm^{-1}; HRMS (ESI): m/z =568.0569 (calcd for $C_{29}H_{23}{}^{35}Cl_2NO_3{}^{32}S_2+H^+$ = 568.0569); Elem. anal. calculated for $C_{29}H_{23}Cl_2NO_3S_2$: C 61.26, H 4.08, N 2.46; found: C 61.14, H 4.13, N 2.56.

S-4-bromophenyl 2-benzamido-3-(4-bromophenylthio)-3-(3-methoxyphenyl)propanethioate 4o



4o

93% yield, 83% ee, dr = 95/5 [Daicel Chiralcel OD-H, hexane/i-PrOH (90:10) , flow rate: 1.0 mL·min^{-1}, λ = 254 nm, t (minor) = 16.614, t (major) = 19.051]; $[\alpha]_D{}^{26}$ = -21.90 (c 0.79, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.6 Hz,, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.55–7. 43 (m, 4H), 7.36 (d, J = 8.0 Hz, 2H), 7.31–7. 25 (m, 2H), 7.22 (t, J = 8.0 Hz, 1H), 7.14 (d, J = 9.2 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.96–6.88 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 5.45 (dd, J = 8.8 Hz, J =5.2 Hz, 1H), 4.98 (d, J = 4.8 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.57, 167.21, 159.91, 138.96, 135.99, 134.33, 133.32, 132.55, 132.49, 132.36, 132.13, 129.99, 129.00, 127.35, 125.87, 124.52, 122.50, 120.56, 114.14, 113.76, 63.01, 55.41, 55.34; IR (KBr) ν_{max}: 3294.8, 1702.2, 1644.9, 1598.3, 1524.0, 1471.2, 1434.2, 864.2, 815.0, 696.1 cm^{-1}; HRMS (ESI): m/z = 657.9544 (calcd for $C_{29}H_{23}{}^{80}Br_2NO_3{}^{32}S_2+H^+$= 657.9544); Elem. anal. calculated for $C_{29}H_{23}Br_2NO_3S_2$: C 52.98, H 3.53, N 2.13; found: C 52.46, H 3.55, N 2.29.

4. X-ray data of chiral 4f

Identification code	shelxl
Empirical formula	C28 H22 F N O2 S2
Formula weight	487.59
Temperature	293(2) K
Wavelength	0.71070 A
Crystal system, space group	Triclinic, P 1
Unit cell dimensions	a = 5.3494(11) A alpha = 73.698(13) deg.
	b = 10.901(2) A beta = 82.129(15) deg.
	c = 11.123(2) A gamma = 81.024(15) deg.
Volume	611.9(2) A^3
Z, Calculated density	1, 1.323 Mg/m^3
Absorption coefficient	0.251 mm^-1
F(000)	254
Crystal size	0.80 x 0.30 x 0.20 mm
Theta range for data collection	3.09 to 25.35 deg.
Limiting indices	-6<=h<=5, -13<=k<=13, -13<=l<=13
Reflections collected / unique	5973 / 3680 [R(int) = 0.0372]
Completeness to theta = 25.35	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.951 and 0.533
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3680 / 3 / 312
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1300
R indices (all data)	R1 = 0.0666, wR2 = 0.1424
Absolute structure parameter	-0.11(10)
Largest diff. peak and hole	0.259 and -0.463 e.A^-3

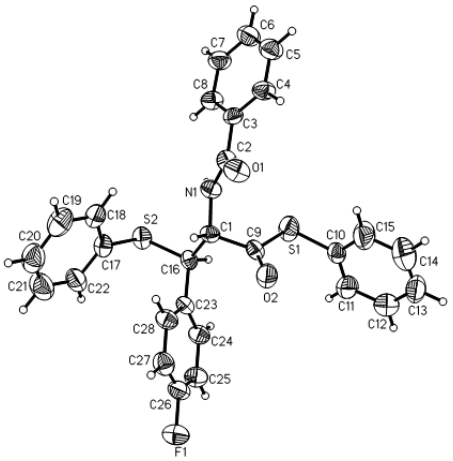


Figure S1. ORTEP drawing of **4f** (40% thermal ellipsoids)

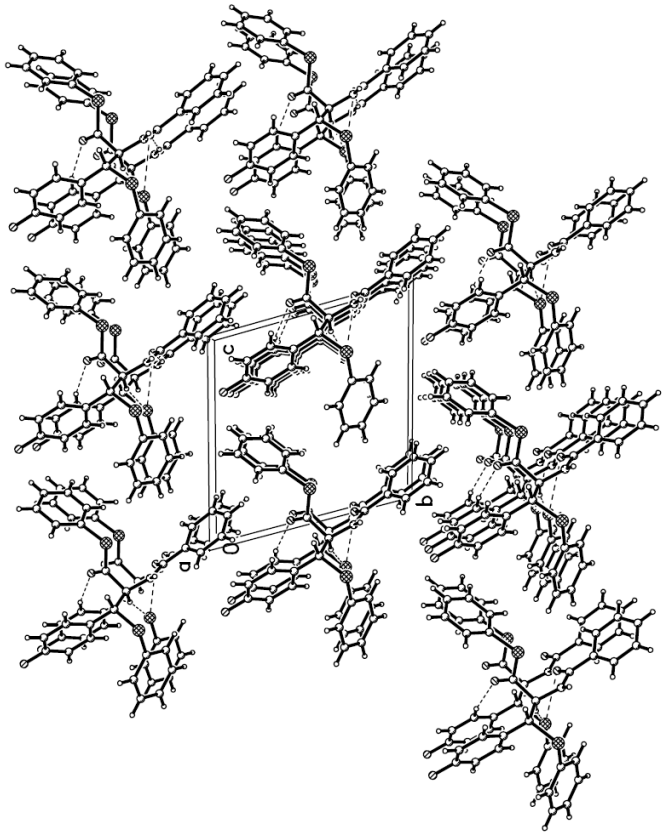
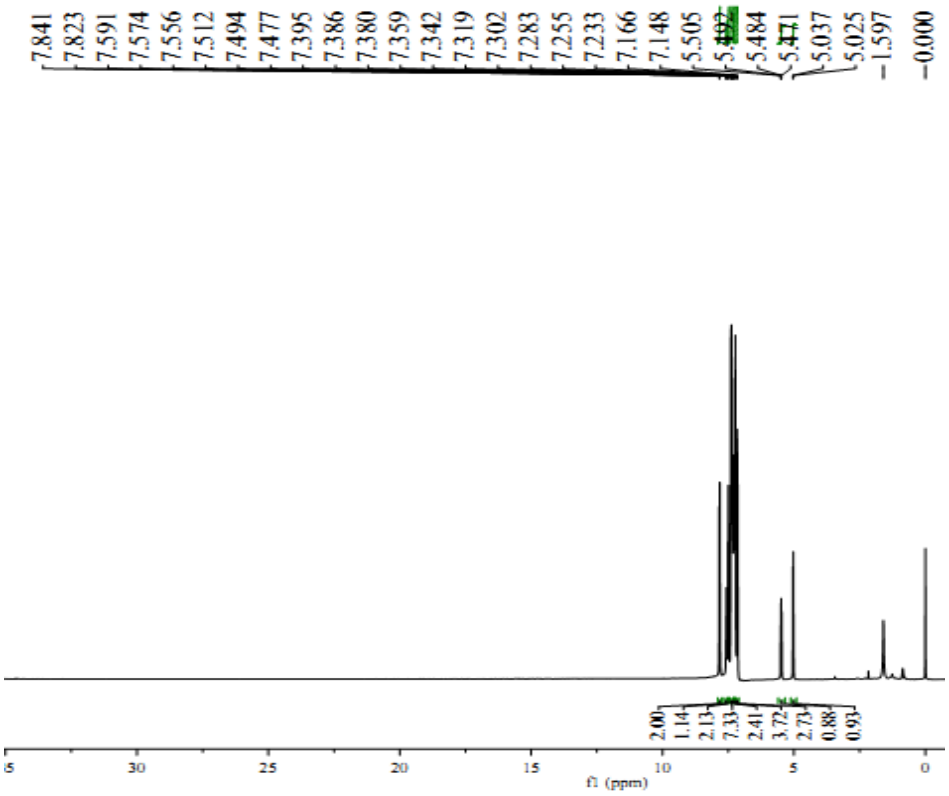


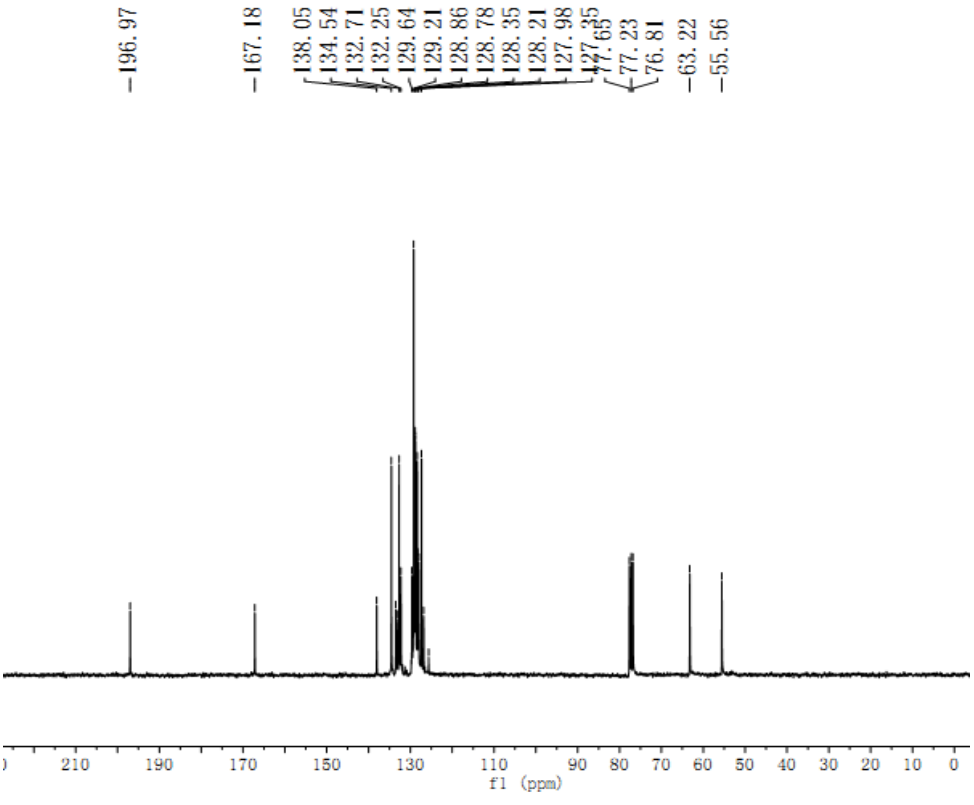
Figure S2. Packing of moleculars in a unit cell for **4f**.

The crystal was prepared from the solution of 4f in petroleum ether/acetyl acetate/$CHCl_3$. CCDC 862831 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

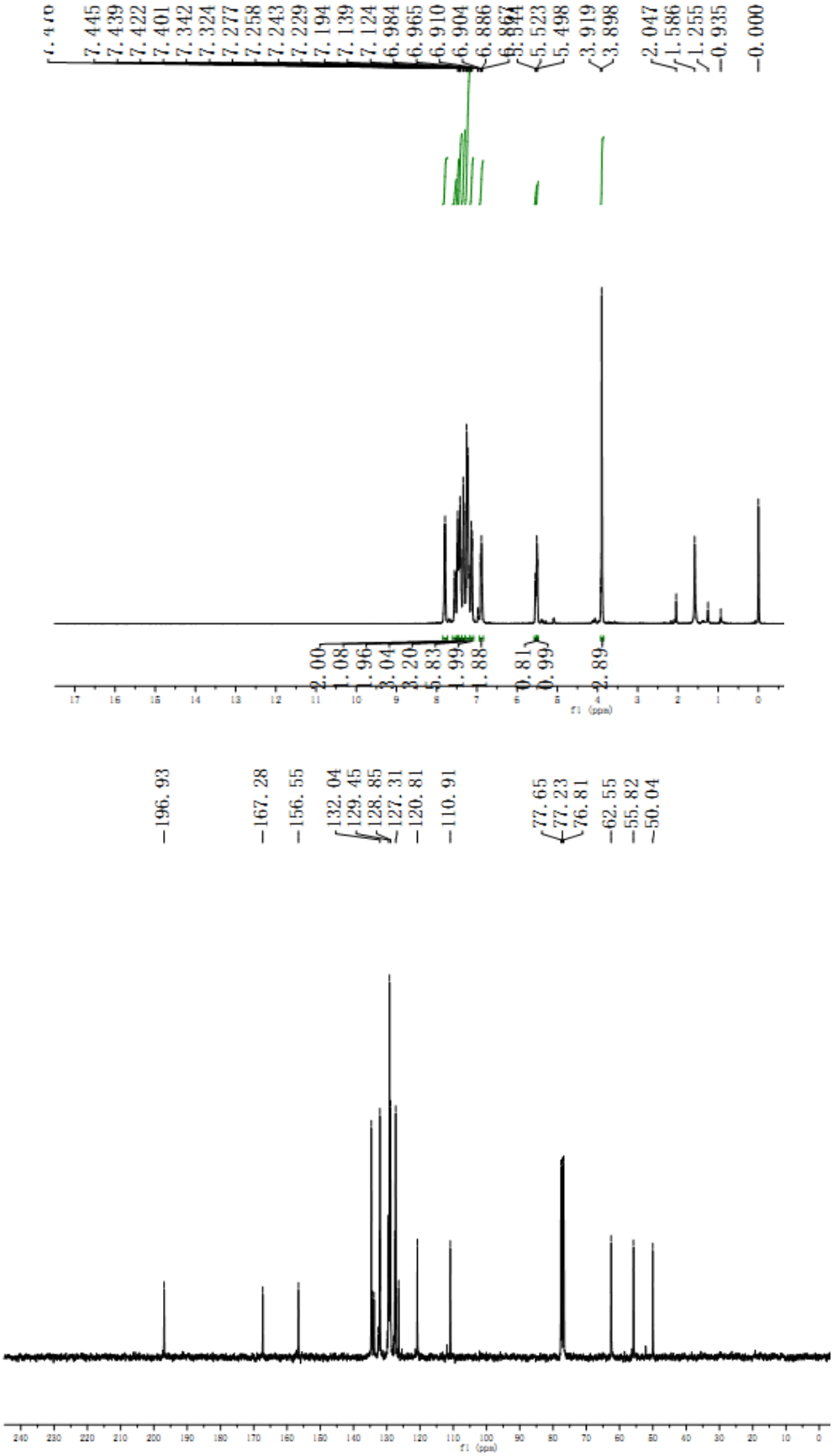
5. ^{1}H NMR and ^{13}C NMR spectra

4a





4b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6.965
6.910
6.904
6.886
5.523
5.498
3.919
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2.047
1.586
1.255
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0.000
2.00
1.08
1.96
3.04
3.20
5.83
1.99
1.88
0.81
0.99
2.89
f1 (ppm)
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132.04
129.45
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127.31
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110.91
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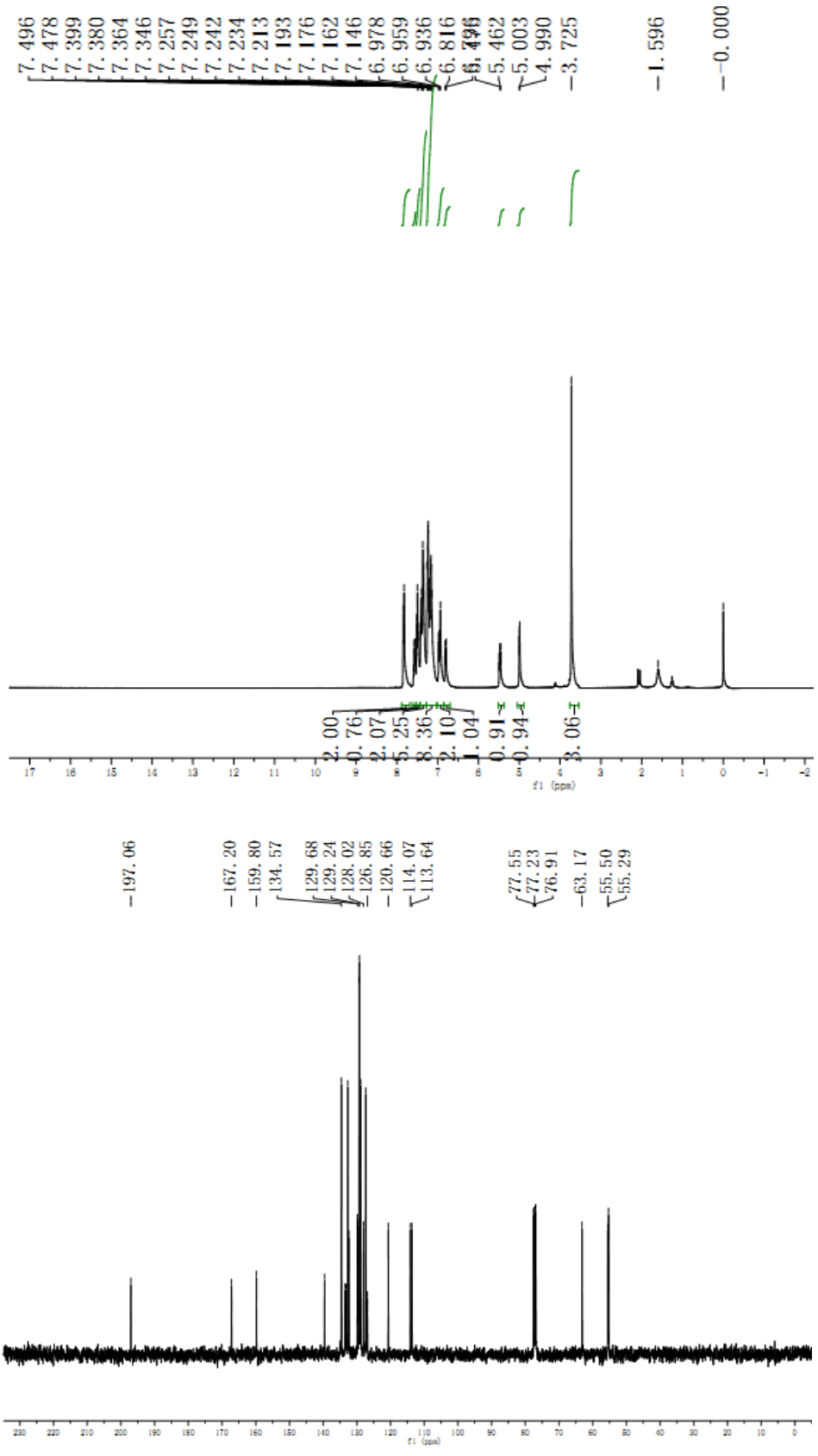
62.55
55.82
50.04
f1 (ppm)

4c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5.003
4.990
3.725
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5.25
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2.10
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0.94
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f1 (ppm)
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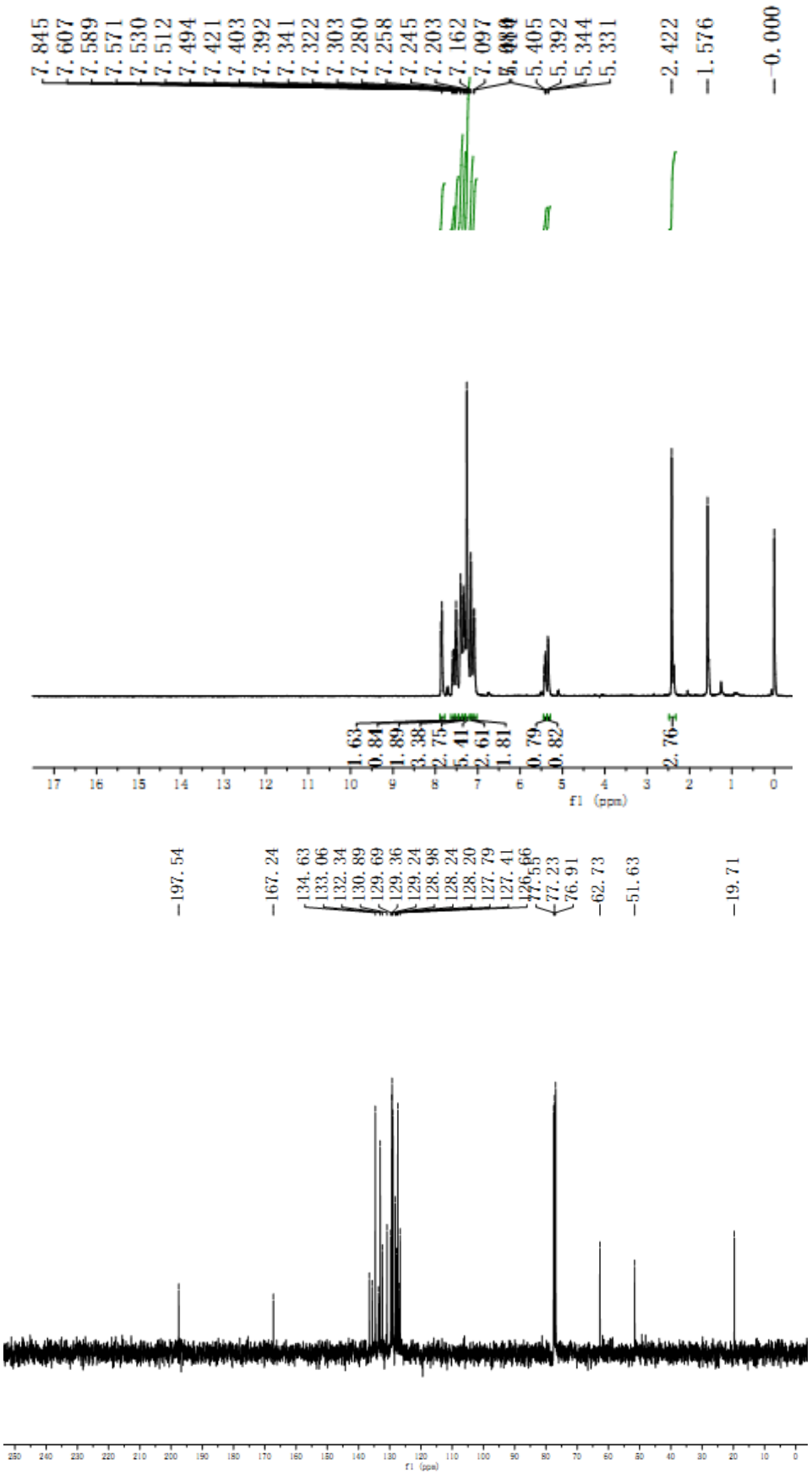
f1 (ppm)

4d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5.392
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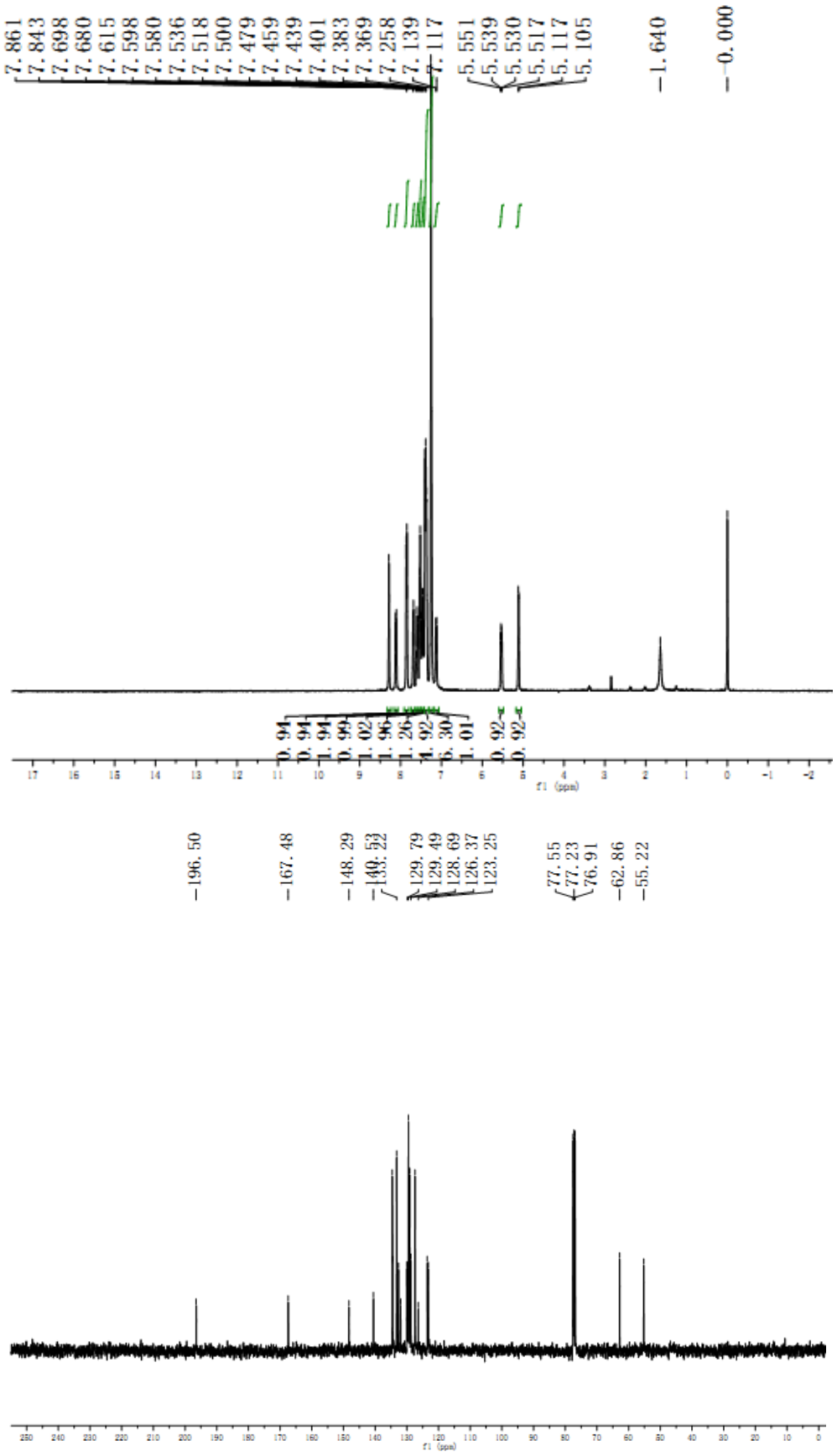
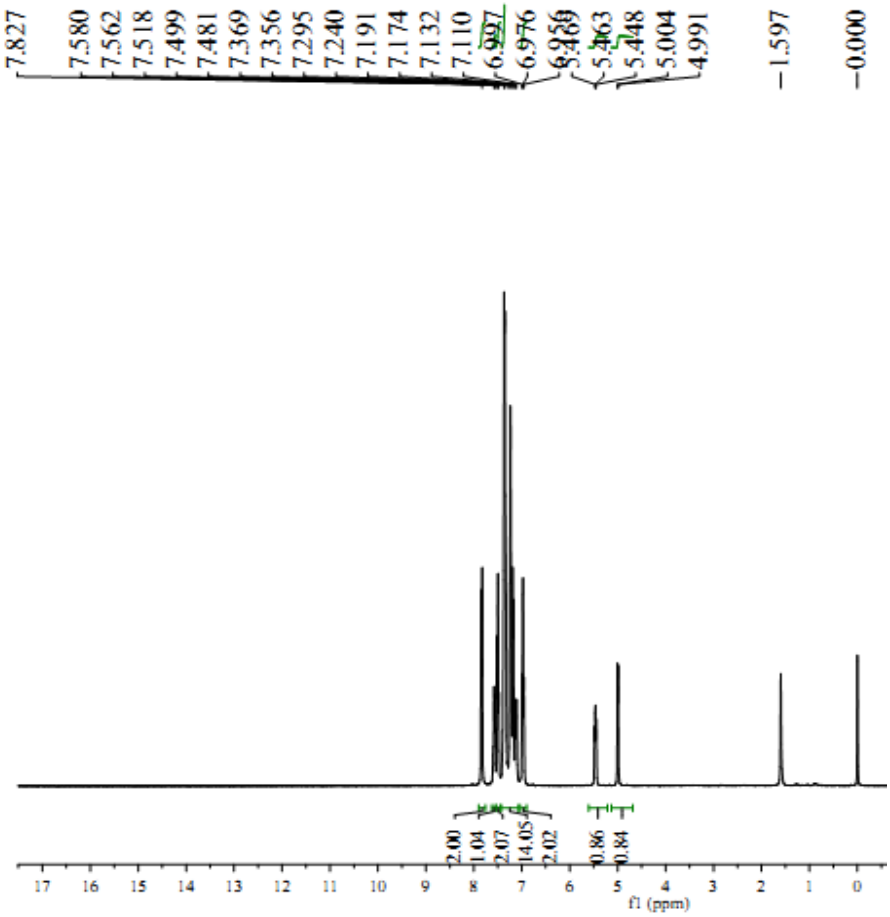
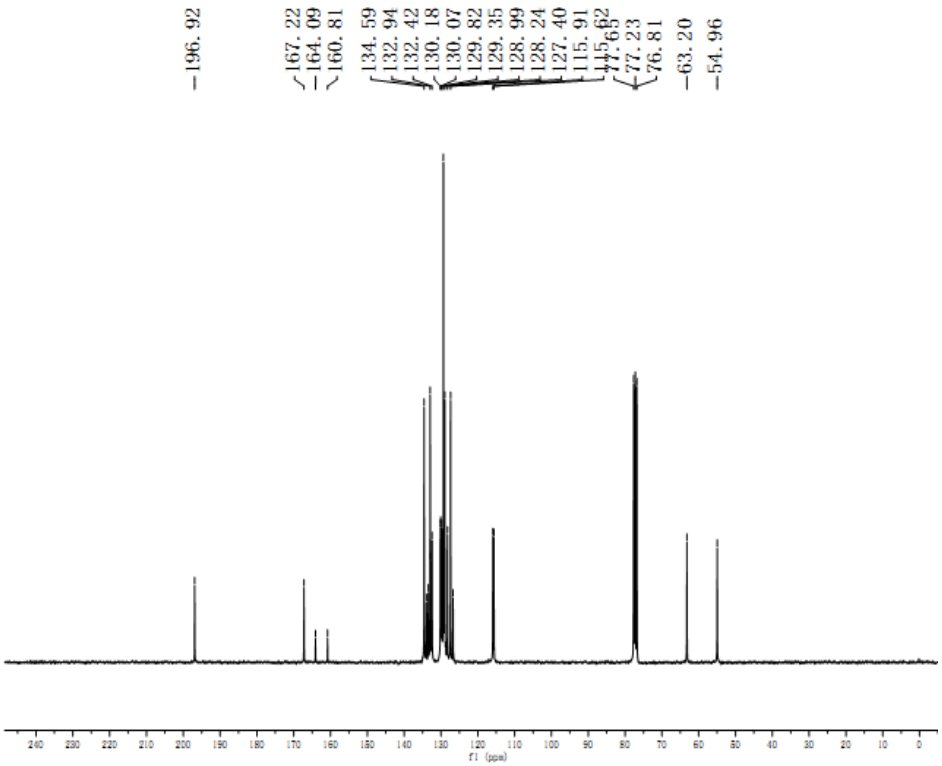
2.75
5.41
2.61
1.81
0.79
0.82
2.76
f1 (ppm)
197.54
167.24
134.63
133.06
132.34
130.89
129.69
129.36
129.24
128.98
128.24
128.20
127.79
127.41
126.66
77.55
77.23
76.91
62.73
51.63
19.71
f1 (ppm)

4e


7.861
7.843
7.698
7.680
7.615
7.598
7.580
7.536
7.518
7.500
7.479
7.459
7.439
7.401
7.383
7.369
7.258
7.139
7.117
5.551
5.539
5.530
5.517
5.117
5.105
1.640
0.000
f1 (ppm)
196.50
167.48
148.29
140.53
133.22
129.79
129.49
128.69
126.37
123.25
77.55
77.23
76.91
62.86
55.22
f1 (ppm)

4f


7.827
7.580
7.562
7.518
7.499
7.481
7.369
7.356
7.295
7.240
7.191
7.174
7.132
7.110
6.997
6.976
5.448
5.004
4.991
1.597
0.000
2.00
1.04
2.07
14.05
2.02
0.86
0.84
f1 (ppm)


196.92
167.22
164.09
160.81
134.59
132.94
132.42
130.18
130.07
129.82
129.35
128.99
128.24
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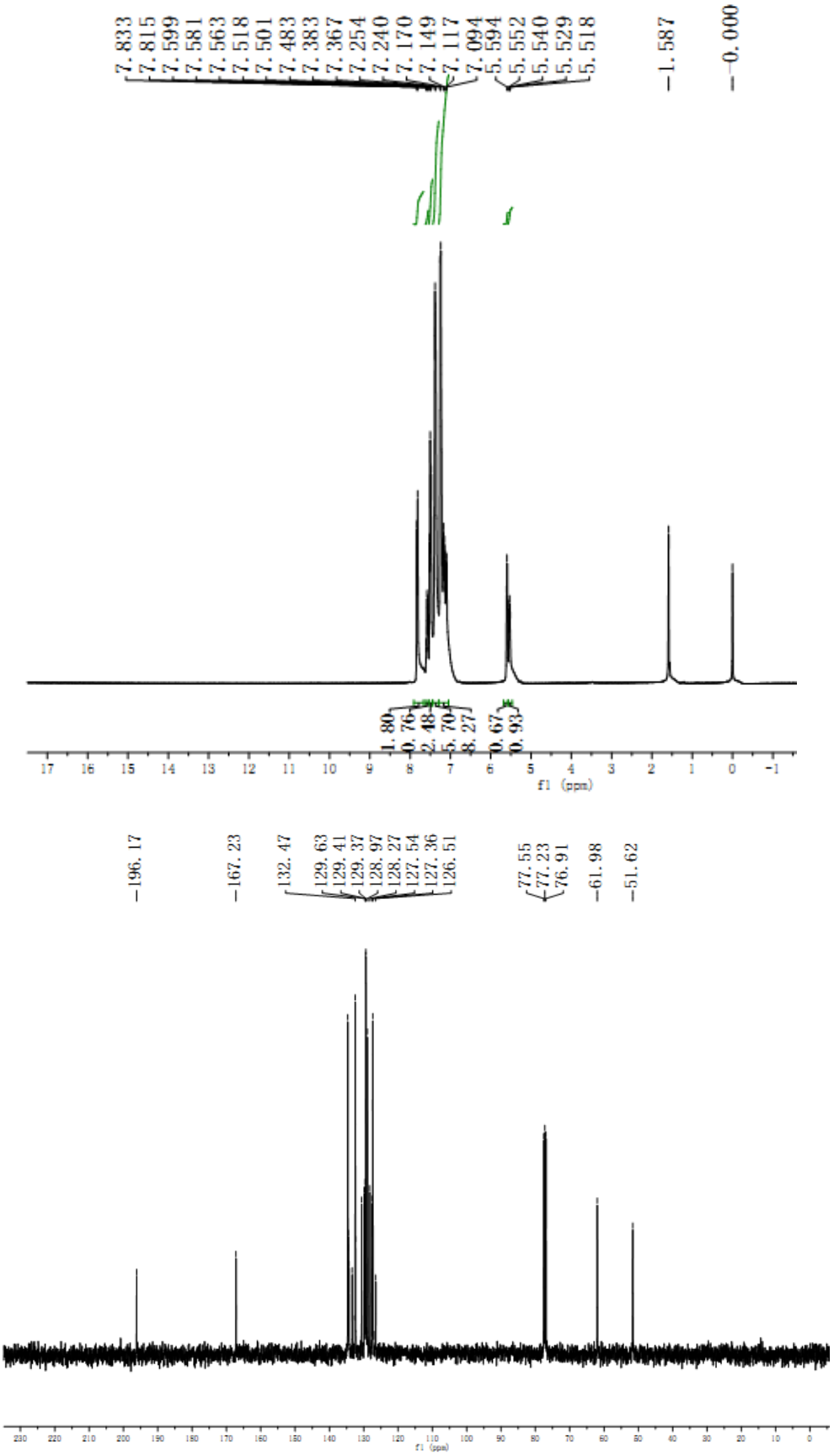
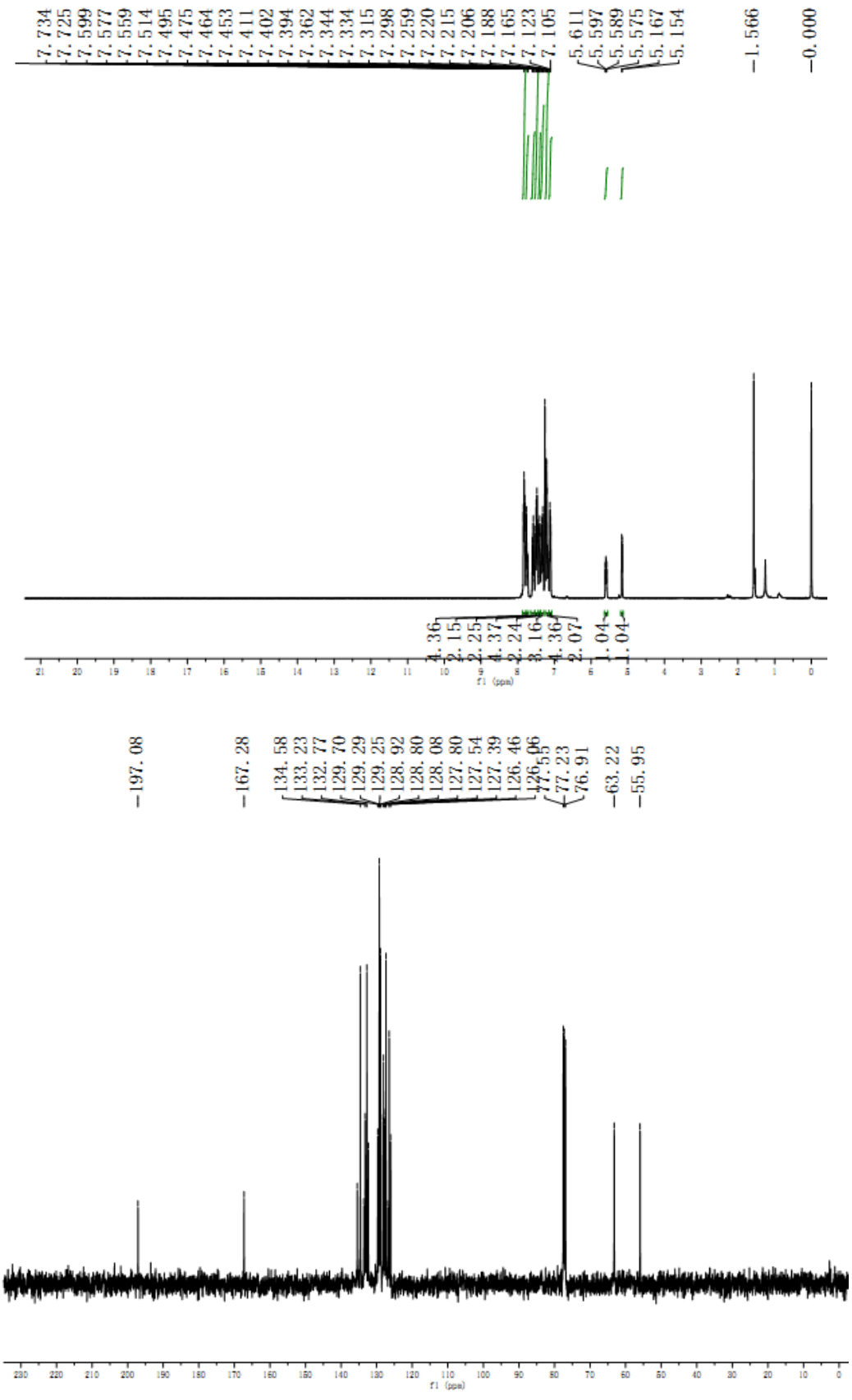
115.91
115.62
77.65
77.23
76.81
63.20
54.96
f1 (ppm)

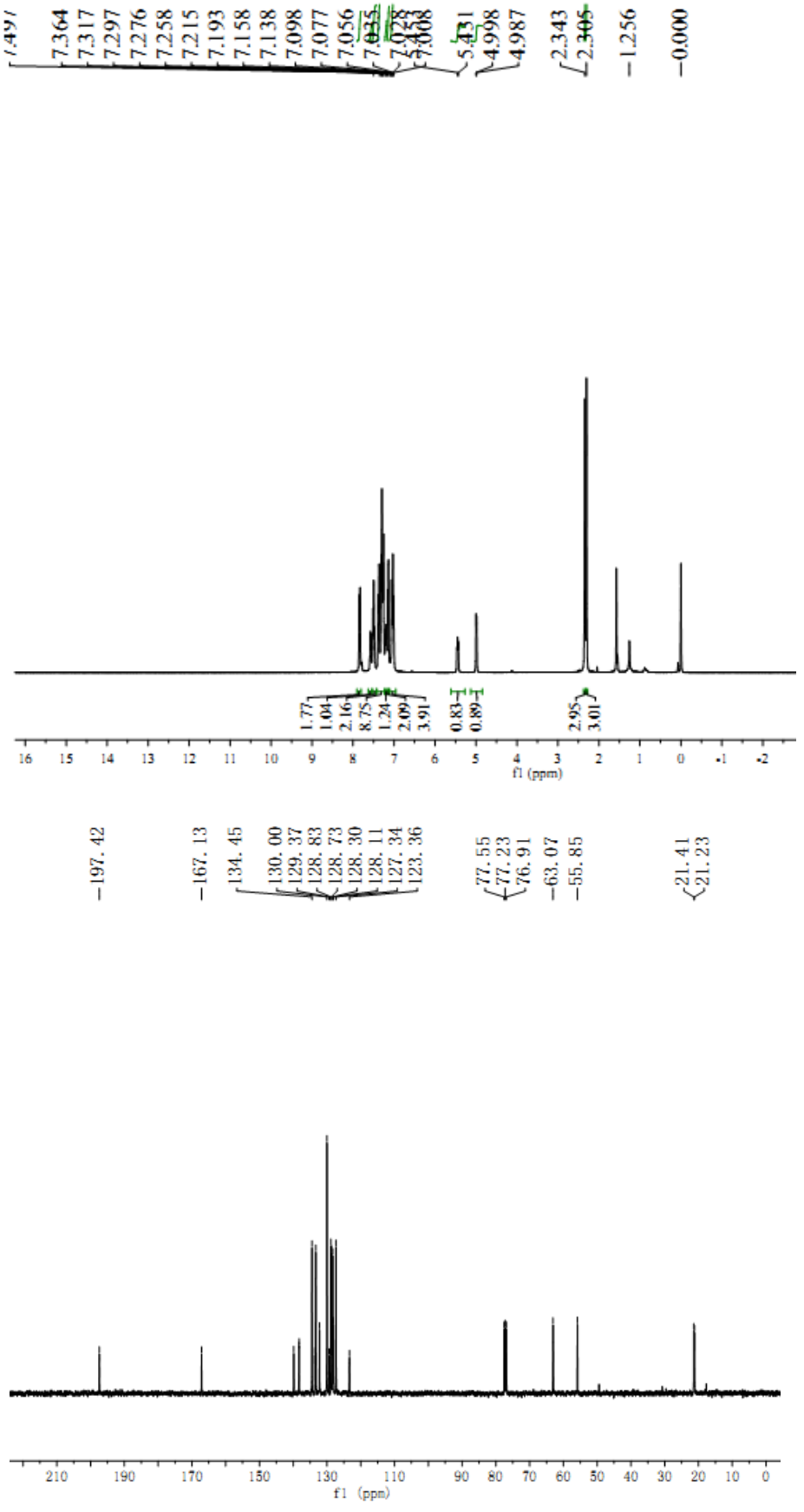
4g


7.833
7.815
7.599
7.581
7.563
7.518
7.501
7.483
7.383
7.367
7.254
7.240
7.170
7.149
7.117
7.094
5.594
5.552
5.540
5.529
5.518
1.587
0.000
1.80
0.76
2.48
5.70
8.27
0.67
0.93
f1 (ppm)
196.17
167.23
132.47
129.63
129.41
129.37
128.97
128.27
127.54
127.36
126.51
77.55
77.23
76.91
61.98
51.62

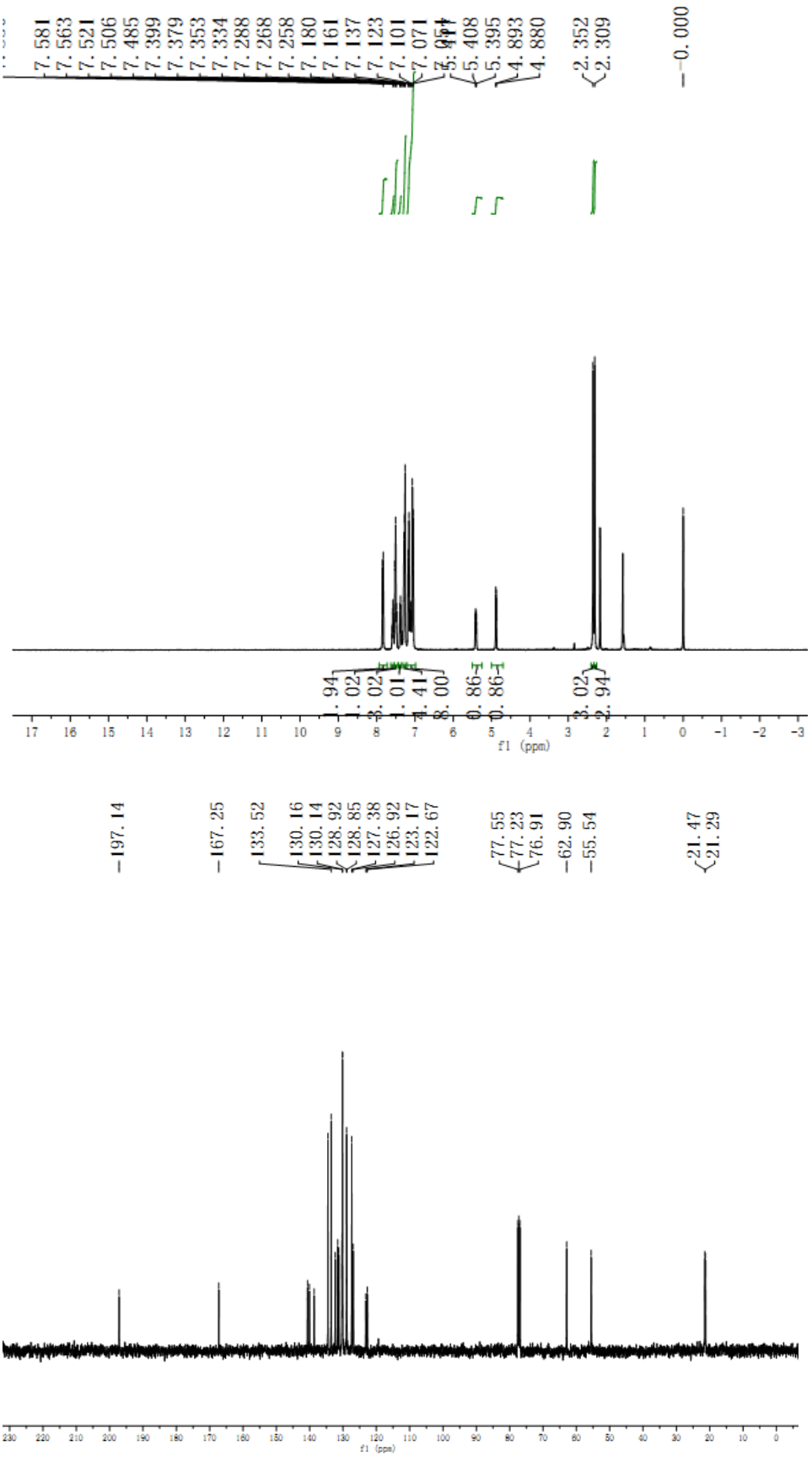
4h


7.734
7.725
7.599
7.577
7.559
7.514
7.495
7.475
7.464
7.453
7.411
7.402
7.394
7.362
7.344
7.334
7.315
7.298
7.259
7.220
7.215
7.206
7.188
7.165
7.123
7.105
5.611
5.597
5.589
5.575
5.167
5.154
1.566
0.000
4.36
2.15
2.25
4.37
2.24
3.16
4.36
2.07
1.04
1.04
f1 (ppm)
197.08
167.28
134.58
133.23
132.77
129.70
129.29
129.25
128.92
128.80
128.08
127.80
127.54
127.39
126.46
126.06
77.55
77.23
76.91
63.22
55.95
f1 (ppm)

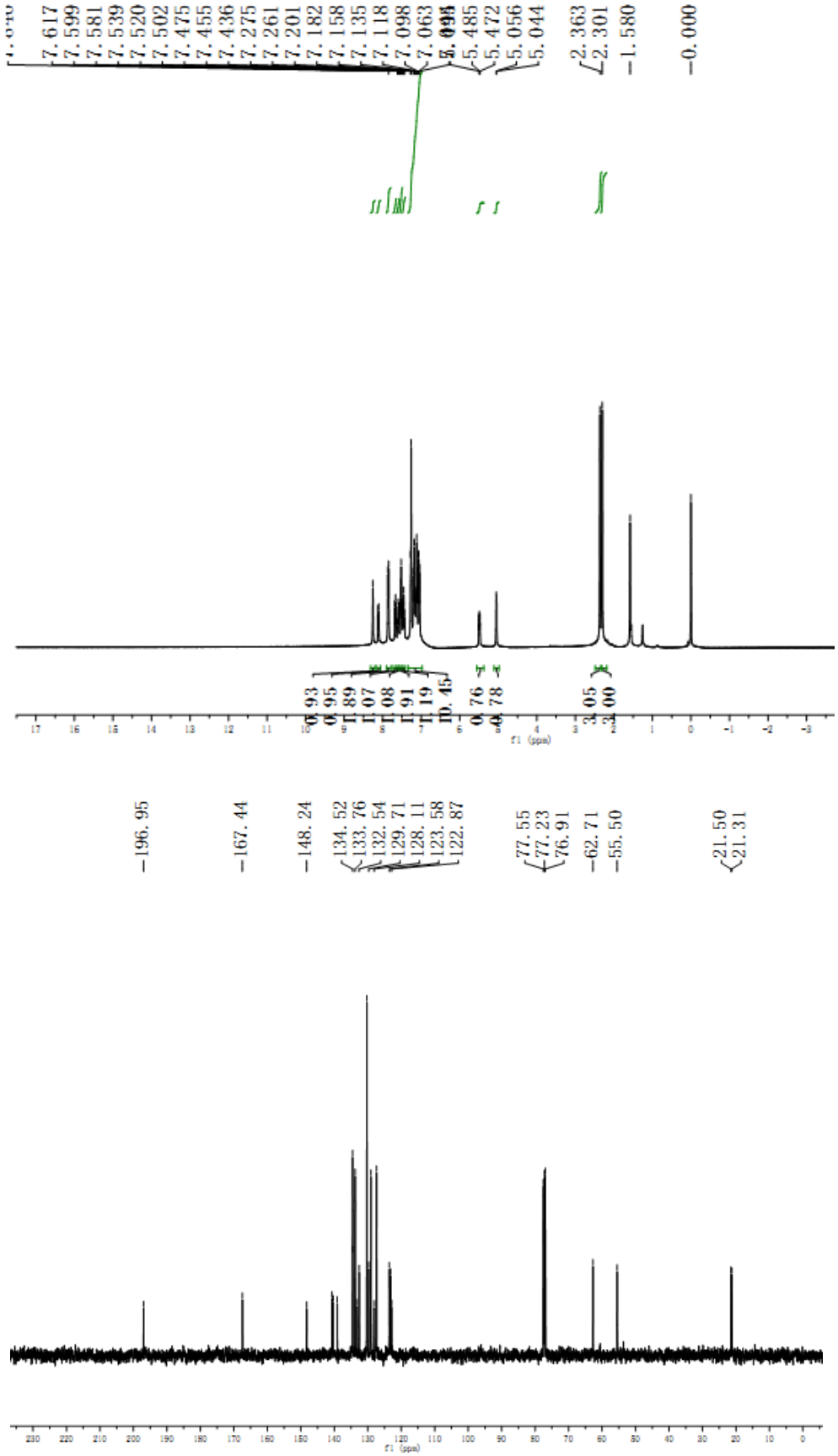
4i


7.364
7.317
7.297
7.276
7.258
7.215
7.193
7.158
7.138
7.098
7.077
7.056
5.431
4.998
4.987
2.343
2.305
1.256
0.000
1.77
1.04
2.16
8.75
1.24
2.09
3.91
0.83
0.89
2.95
3.01
f1 (ppm)
197.42
167.13
134.45
130.00
129.37
128.83
128.73
128.30
128.11
127.34
123.36
77.55
77.23
76.91
63.07
55.85
21.41
21.23
f1 (ppm)

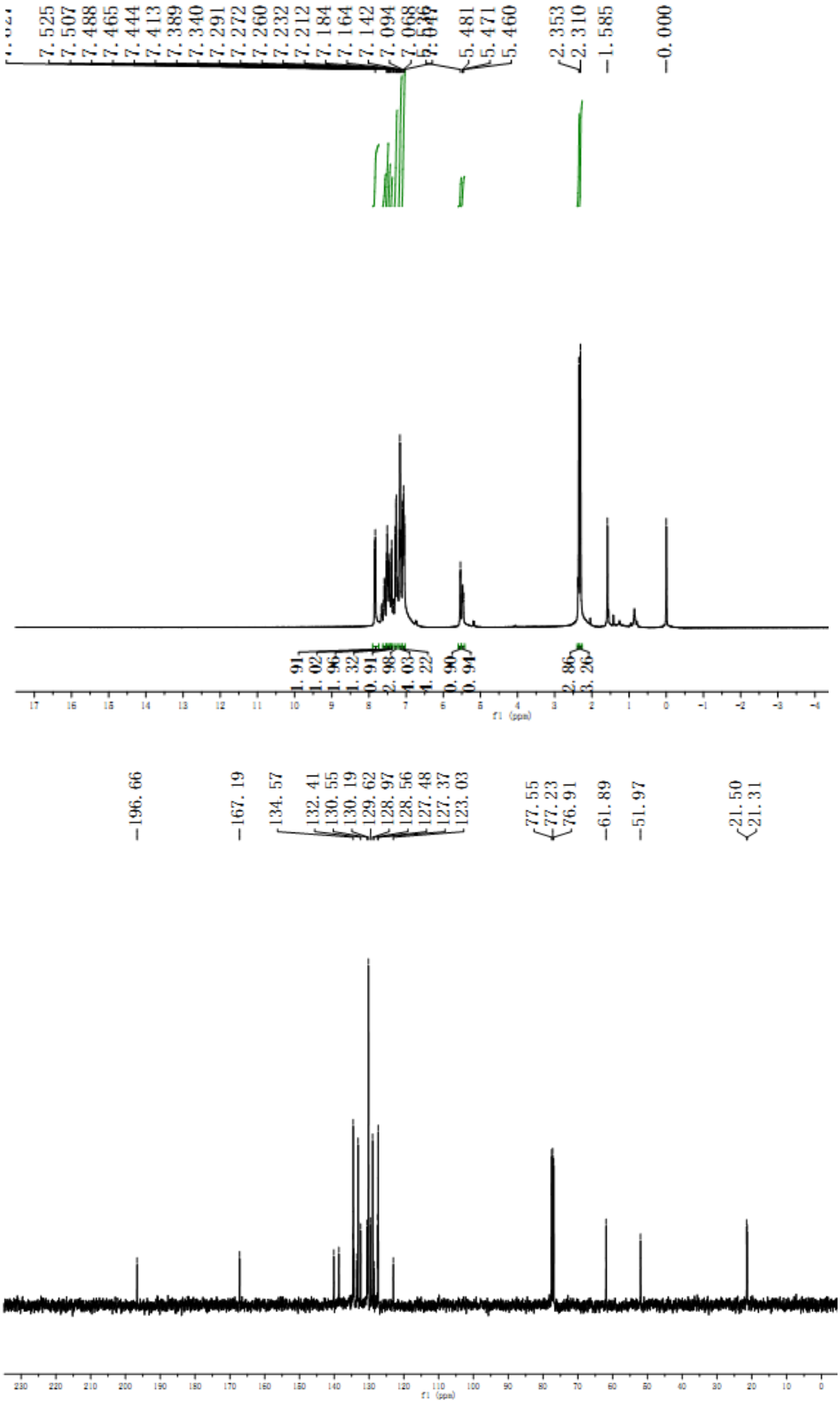
4j


7.581
7.563
7.521
7.506
7.485
7.399
7.379
7.353
7.334
7.288
7.268
7.258
7.180
7.161
7.137
7.123
7.101
7.071
5.408
5.395
4.893
4.880
2.352
2.309
0.000
1.94
1.02
3.02
1.01
4.41
8.00
0.86
0.86
3.02
2.94
f1 (ppm)
197.14
167.25
133.52
130.16
130.14
128.92
128.85
127.38
126.92
123.17
122.67
77.55
77.23
76.91
62.90
55.54
21.47
21.29
f1 (ppm)

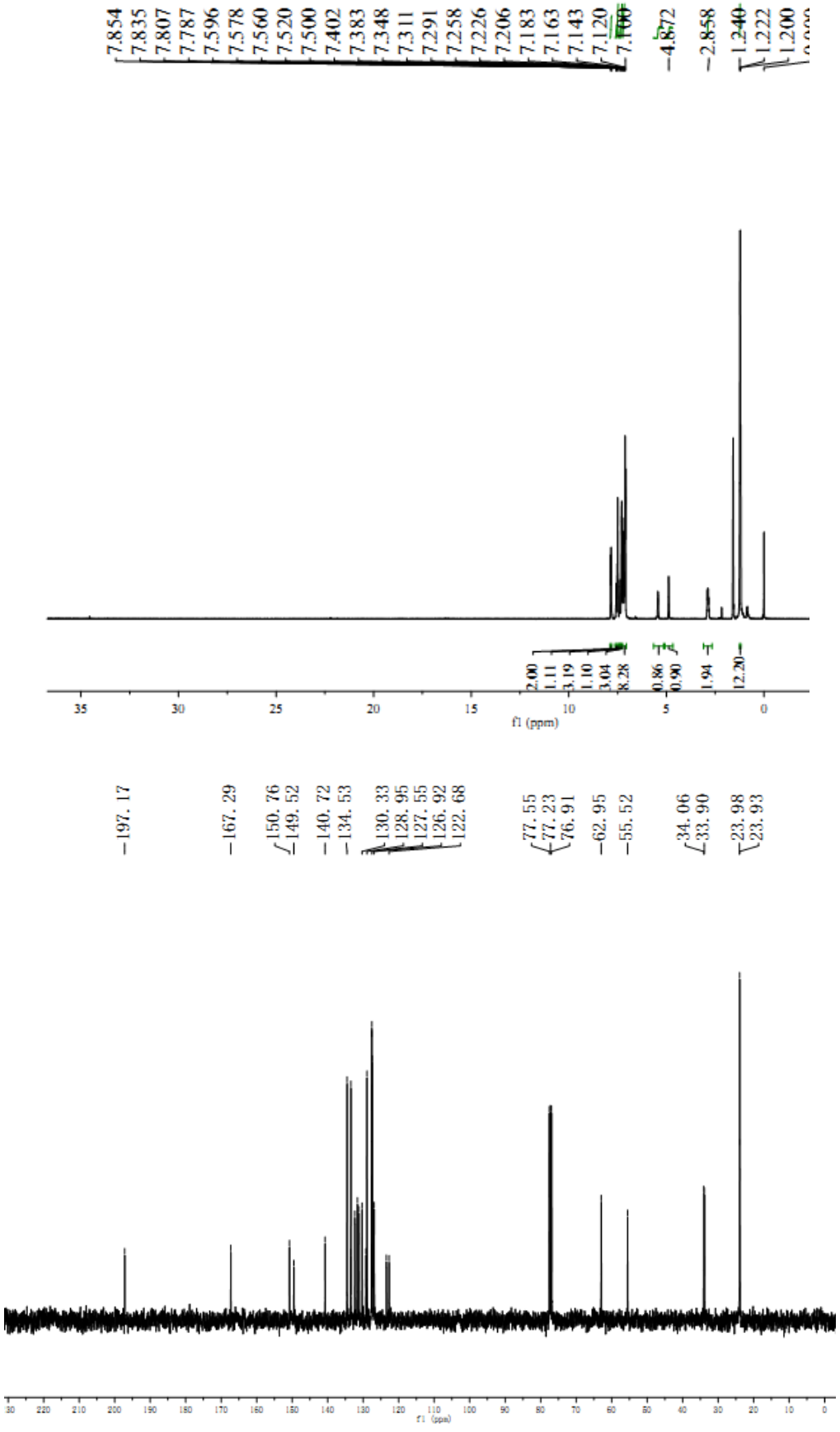
4k


7.617
7.599
7.581
7.539
7.520
7.502
7.475
7.455
7.436
7.275
7.261
7.201
7.182
7.158
7.135
7.118
7.098
7.063
5.485
5.472
5.056
5.044
2.363
2.301
1.580
0.000
0.93
0.95
1.89
1.07
1.08
1.91
1.19
10.45
0.76
0.78
3.05
2.00
f1 (ppm)
196.95
167.44
148.24
134.52
133.76
132.54
129.71
128.11
123.58
122.87
77.55
77.23
76.91
62.71
55.50
21.50
21.31
f1 (ppm)

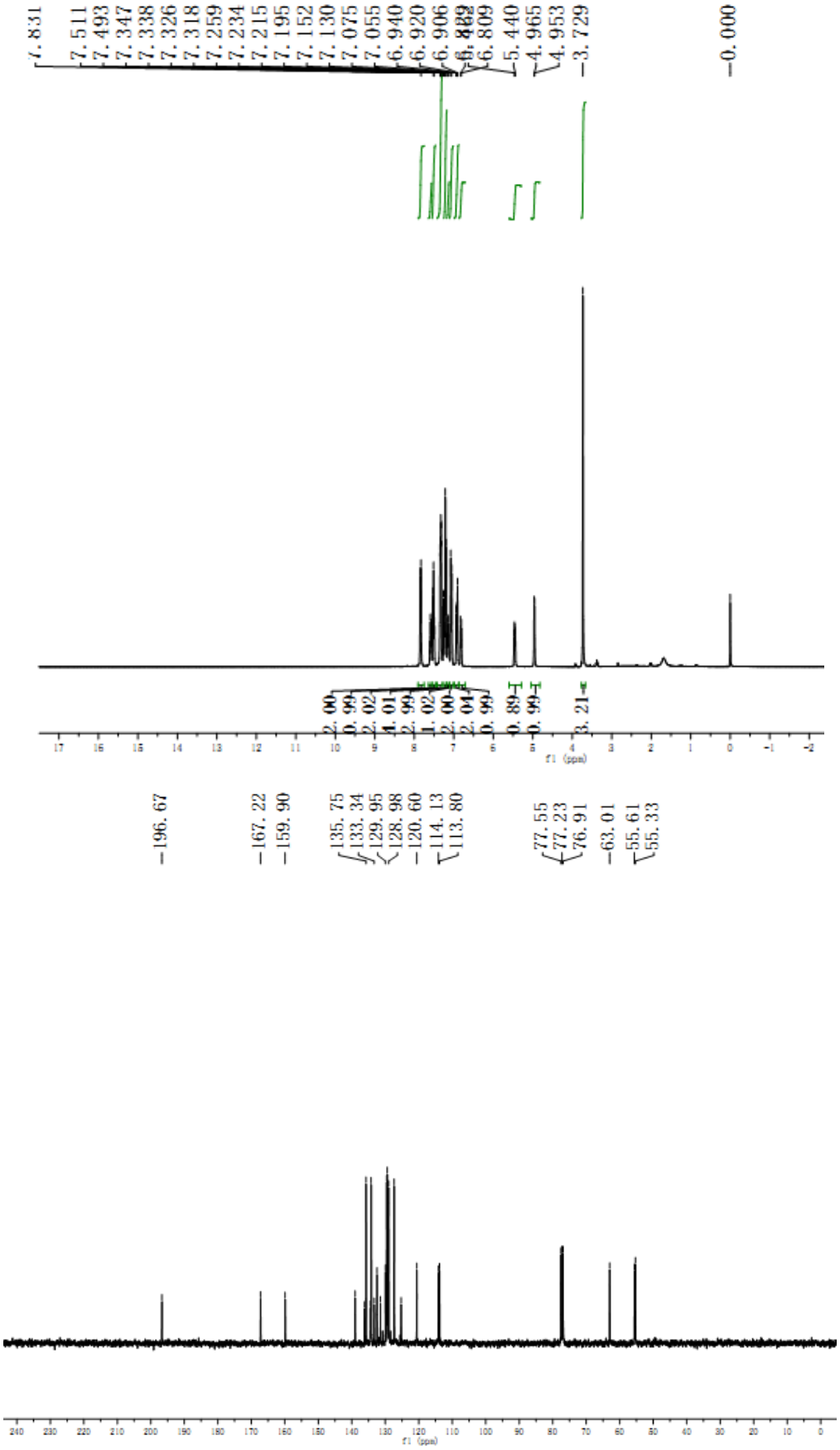
4l


7.525
7.507
7.488
7.465
7.444
7.413
7.389
7.340
7.291
7.272
7.260
7.232
7.212
7.184
7.164
7.142
7.094
7.068
5.481
5.471
5.460
2.353
2.310
1.585
0.000
f1 (ppm)
196.66
167.19
134.57
132.41
130.55
130.19
129.62
128.97
128.56
127.48
127.37
123.03
77.55
77.23
76.91
61.89
51.97
21.50
21.31
f1 (ppm)

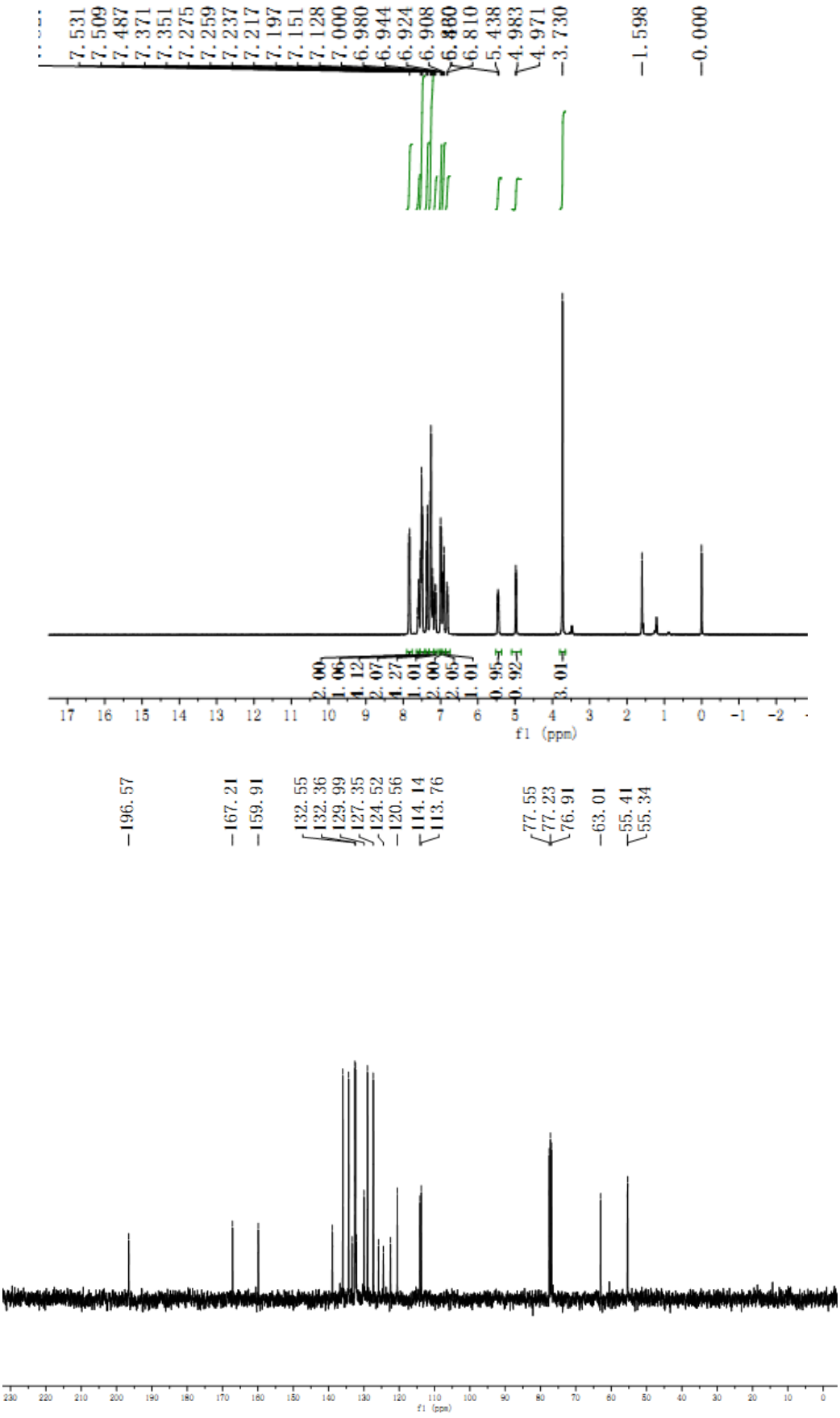
4m


7.854
7.835
7.807
7.787
7.596
7.578
7.560
7.520
7.500
7.402
7.383
7.348
7.311
7.291
7.258
7.226
7.206
7.183
7.163
7.143
7.120
4.872
2.858
1.240
1.222
1.200
2.00
1.11
3.19
1.10
3.04
8.28
0.86
0.90
1.94
12.20
f1 (ppm)
197.17
167.29
150.76
149.52
140.72
134.53
130.33
128.95
127.55
126.92
122.68
77.55
77.23
76.91
62.95
55.52
34.06
33.90
23.98
23.93

4n

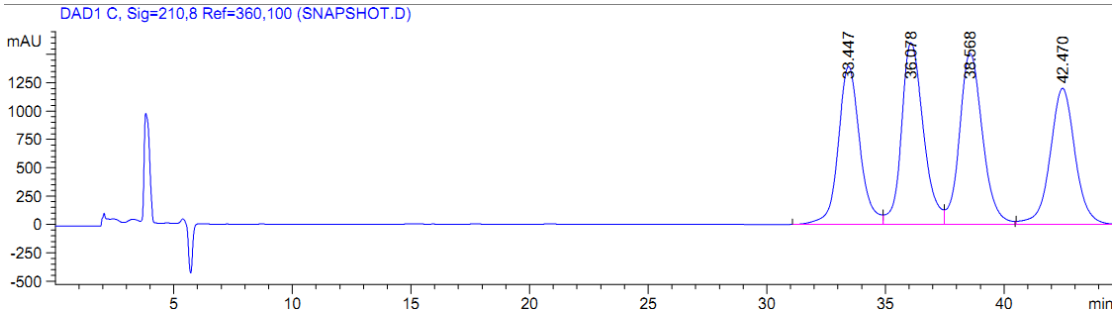

7.831
7.511
7.493
7.347
7.338
7.326
7.318
7.259
7.234
7.215
7.195
7.152
7.130
7.075
7.055
6.940
6.920
6.906
6.809
5.440
4.965
4.953
3.729
0.000
2.00
0.99
0.92
4.01
2.99
1.02
2.00
2.04
0.99
0.89
0.99
3.21
f1 (ppm)
196.67
167.22
159.90
135.75
133.34
129.95
128.98
120.60
114.13
113.80
77.55
77.23
76.91
63.01
55.61
55.33
f1 (ppm)

4o

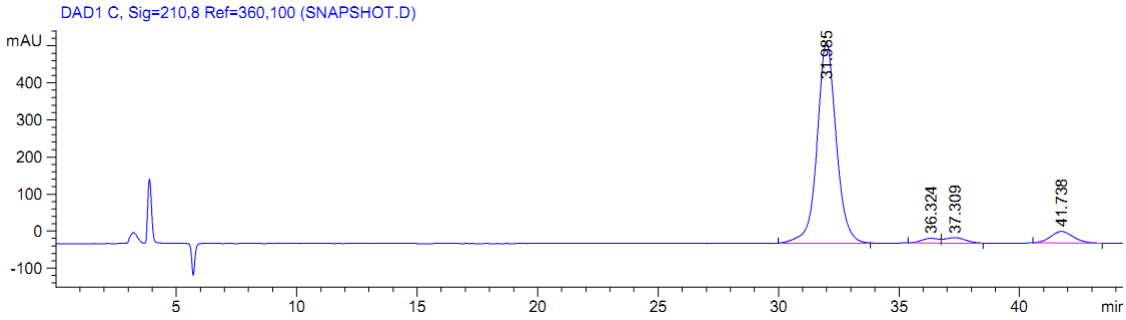

7.531
7.509
7.487
7.371
7.351
7.275
7.259
7.237
7.217
7.197
7.151
7.128
7.000
6.980
6.944
6.924
6.908
6.810
5.438
4.983
4.971
3.730
1.598
0.000
f1 (ppm)
196.57
167.21
159.91
132.55
132.36
129.99
127.35
124.52
120.56
114.14
113.76
77.55
77.23
76.91
63.01
55.41
55.34
f1 (ppm)

6. HPLC spectra

4a

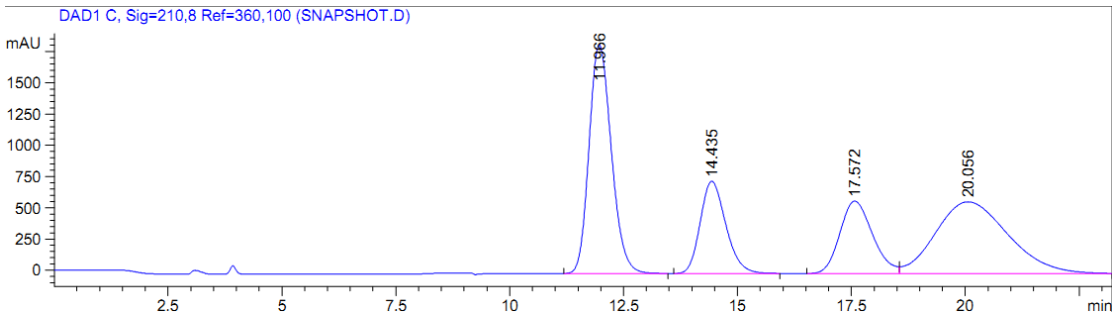


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.447	BV	0.9622	8.82056e4	1393.98547	23.1531
2	36.078	VV	0.9833	1.02905e5	1602.28577	27.0115
3	38.568	VB	1.0385	1.02064e5	1510.12903	26.7909
4	42.470	BBA	1.1144	8.77920e4	1201.54968	23.0445
Totals :				3.80967e5	5707.94995	

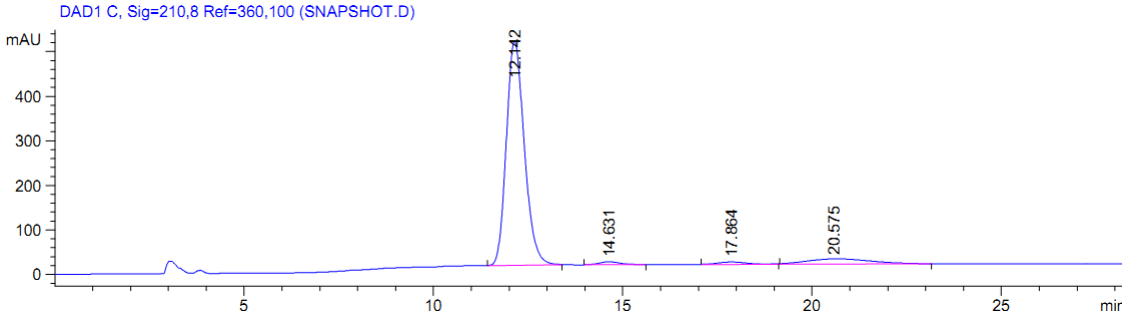


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.985	BB	0.8368	2.98406e4	541.62012	89.3519
2	36.324	BV	0.6992	618.32385	12.36887	1.8514
3	37.309	VB	0.8080	873.66321	14.68619	2.6160
4	41.738	BB	0.9853	2064.12793	31.22101	6.1806
Totals :				3.33967e4	599.89619	

4b

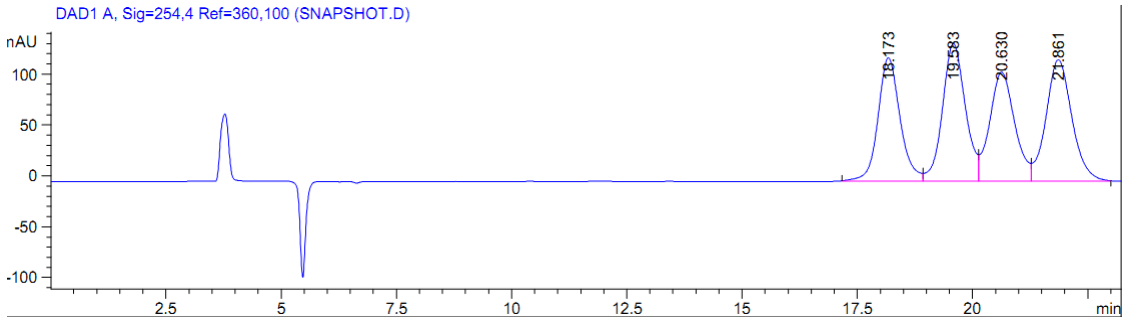


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.966	BB	0.5297	6.23711e4	1829.56226	33.9928
2	14.435	BB	0.6039	2.88324e4	737.86963	15.7139
3	17.572	BV	0.7738	2.89007e4	579.48694	15.7511
4	20.056	VBA	1.7091	6.33791e4	573.60156	34.5422
Totals :				1.83483e5	3720.52039	

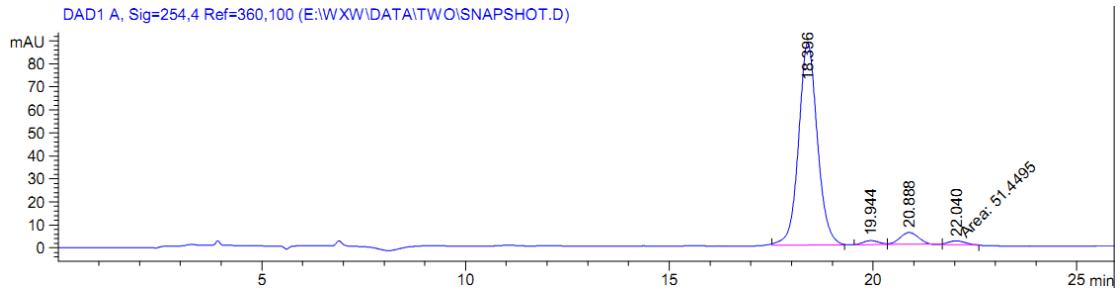


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.142	BB	0.5105	1.66575e4	502.85077	89.4515
2	14.631	BB	0.5991	279.57840	7.01263	1.5014
3	17.864	BB	0.6595	303.88458	5.49267	1.6319
4	20.575	BB	1.4200	1380.84827	11.59001	7.4152
Totals :				1.86218e4	526.94607	

4c

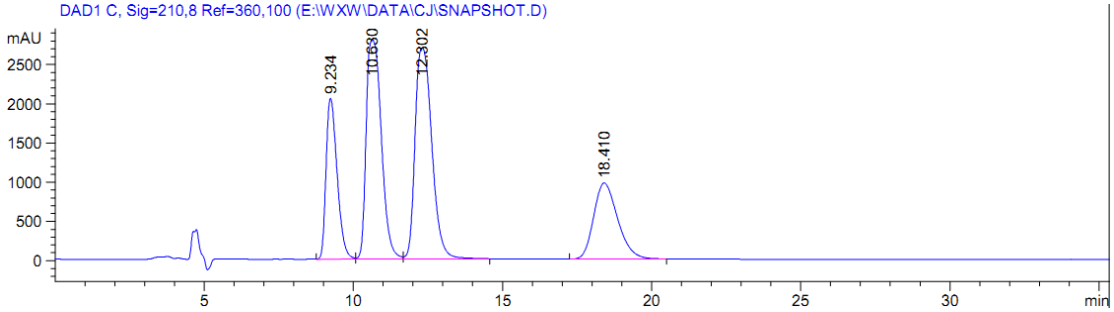


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.173	BV	0.5058	4055.43555	121.36834	23.2053
2	19.583	VV	0.5277	4685.96875	135.40636	26.8133
3	20.630	VV	0.5708	4054.54443	107.30807	23.2002
4	21.861	VB	0.5950	4680.36182	119.47289	26.7812
Totals :				1.74763e4	483.55565	

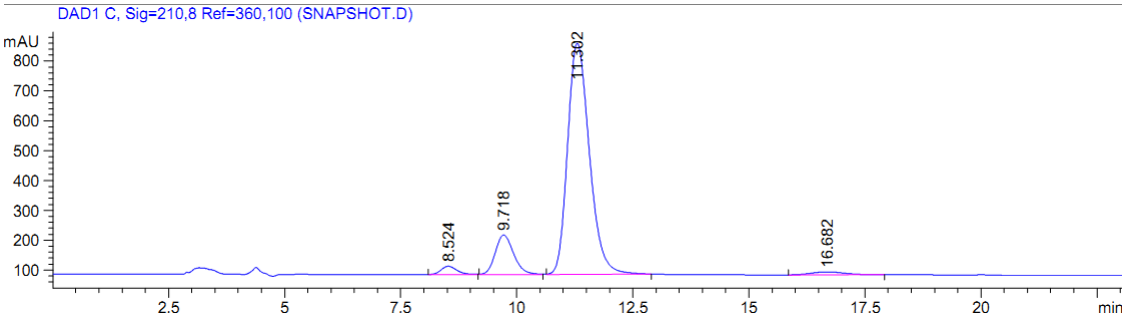


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.396	BB	0.4886	2808.91577	87.94951	91.6590
2	19.944	BV	0.3776	47.59805	1.73760	1.5532
3	20.888	VB	0.4786	156.56615	5.12266	5.1090
4	22.040	MM	0.4886	51.44954	1.75486	1.6789
Totals :				3064.52951	96.56463	

4d

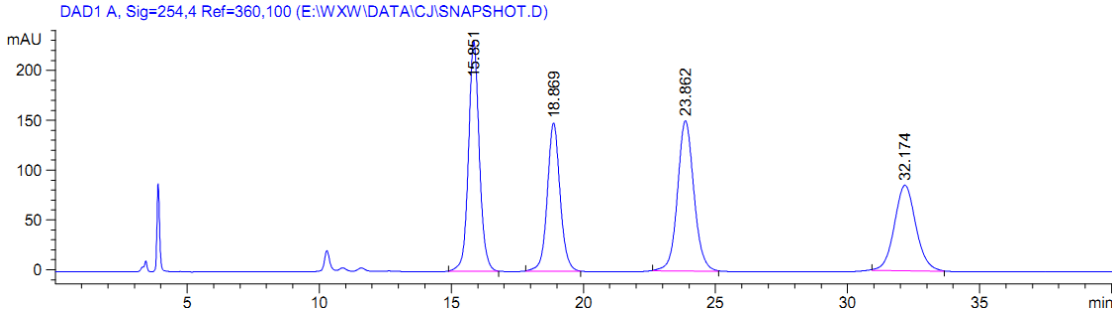


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.234	VV	0.4001	5.27310e4	2049.78149	16.9835
2	10.630	VV	0.5599	9.86250e4	2793.38745	31.7650
3	12.302	VB	0.6152	1.05029e5	2691.76050	33.8277
4	18.410	BB	0.8638	5.40979e4	968.27051	17.4238
Totals :				3.10483e5	8503.19995	

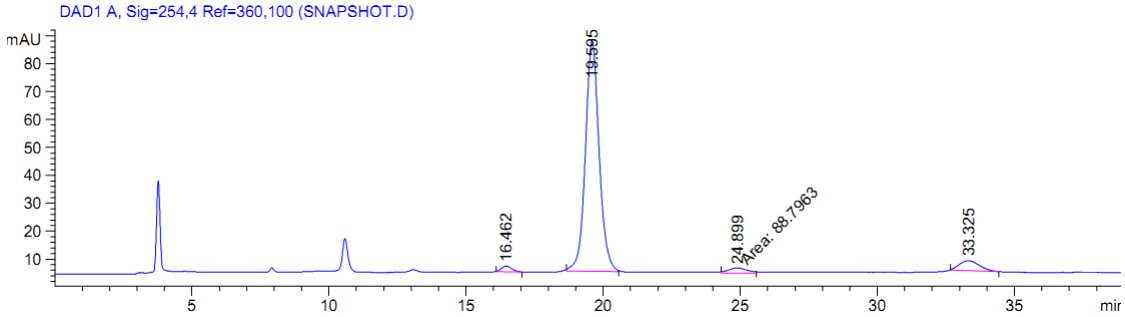


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.524	BB	0.3655	639.80579	27.09198	2.1362
2	9.718	BB	0.4201	3602.73267	132.14867	12.0288
3	11.302	BB	0.5069	2.52401e4	773.01343	84.2716
4	16.682	BB	0.7147	468.27206	9.57327	1.5635
Totals :				2.99509e4	941.82735	

4e

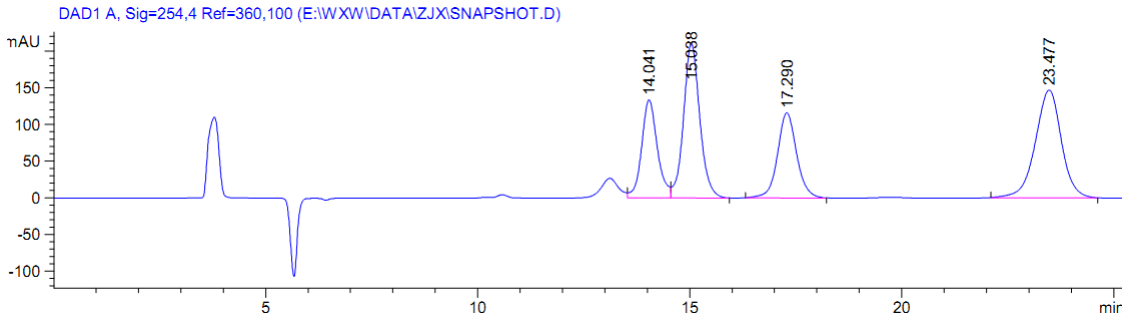


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.851	BB	0.4340	6605.62842	230.72253	28.7299
2	18.869	BB	0.5136	5025.24609	148.93625	21.8564
3	23.862	BB	0.6604	6521.13330	150.84680	28.3624
4	32.174	BB	0.8626	4840.13428	85.73489	21.0513
Totals :				2.29921e4	616.24048	

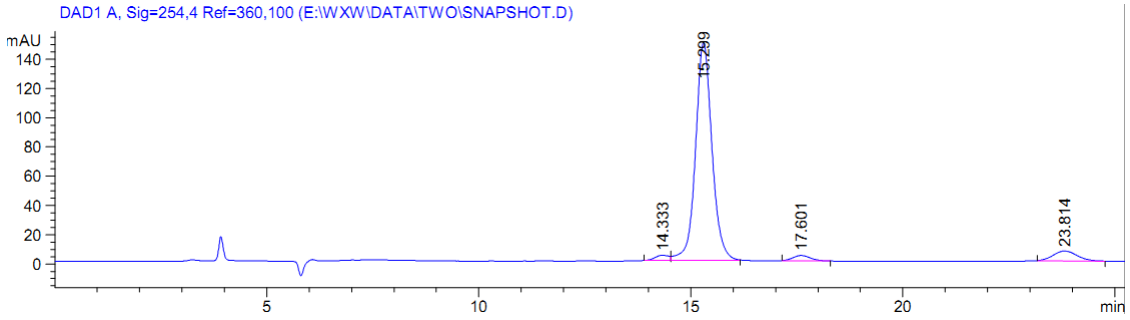


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.462	BB	0.3827	54.50954	2.06005	1.7043
2	19.595	BB	0.5303	2867.02734	82.33336	89.6389
3	24.899	MM	0.8060	88.79632	1.83617	2.7763
4	33.325	BB	0.6546	188.08482	3.62916	5.8806
Totals :				3198.41803	89.85874	

4f

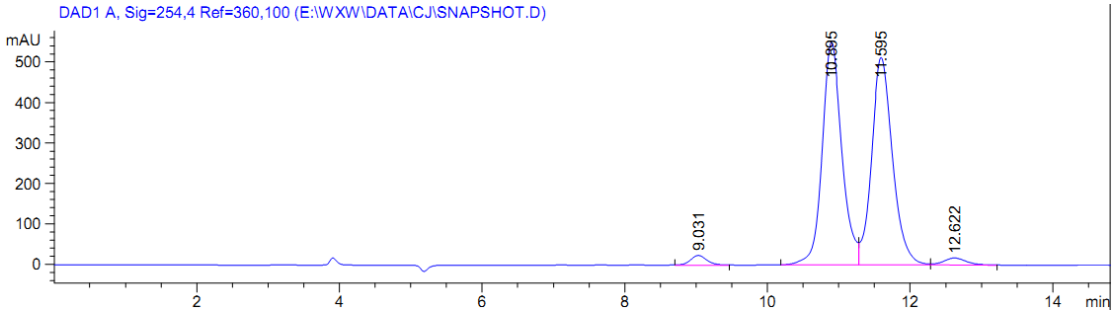


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.041	VV	0.3914	3450.87622	133.56288	18.1330
2	15.038	VB	0.4055	5621.26611	210.55516	29.5376
3	17.290	BB	0.4769	3652.21948	116.13890	19.1910
4	23.477	BB	0.6544	6306.53467	147.04324	33.1384
Totals :				1.90309e4	607.30019	

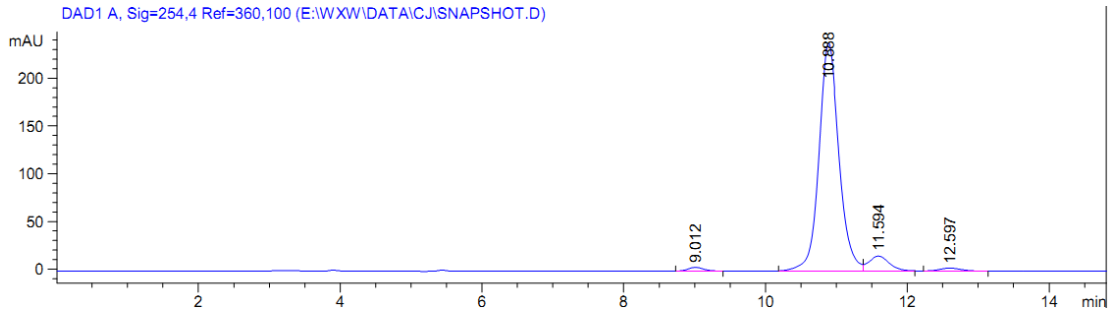


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.333	BV	0.3342	79.58250	3.51446	1.7820
2	15.299	VB	0.4112	4020.37842	148.83188	90.0228
3	17.601	BB	0.4351	102.06685	3.55335	2.2854
4	23.814	BB	0.5845	263.92780	6.77525	5.9098
Totals :				4465.95556	162.67494	

4g

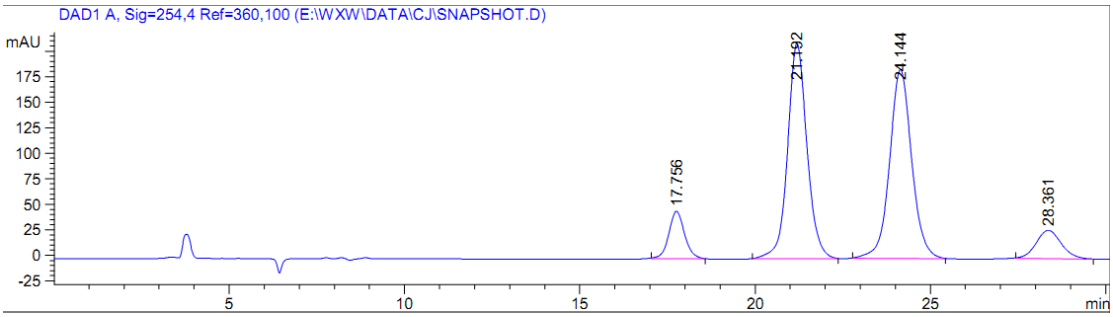


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.031	BB	0.2377	372.86938	23.94442	1.7083
2	10.895	BV	0.2904	1.05876e4	550.39313	48.5084
3	11.595	VV	0.3105	1.04812e4	512.72760	48.0208
4	12.622	VB	0.3392	384.67532	17.17920	1.7624
Totals :				2.18263e4	1104.24435	

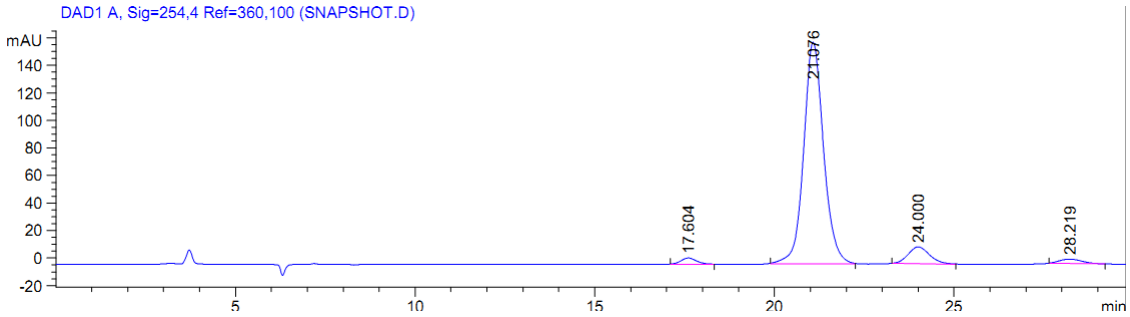


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.012	BB	0.2396	61.31274	3.93839	1.1980
2	10.888	BV	0.2963	4673.00684	238.84068	91.3093
3	11.594	VB	0.3034	317.84186	15.75154	6.2105
4	12.597	BB	0.3277	65.61581	3.09021	1.2821
Totals :				5117.77725	261.62082	

4h

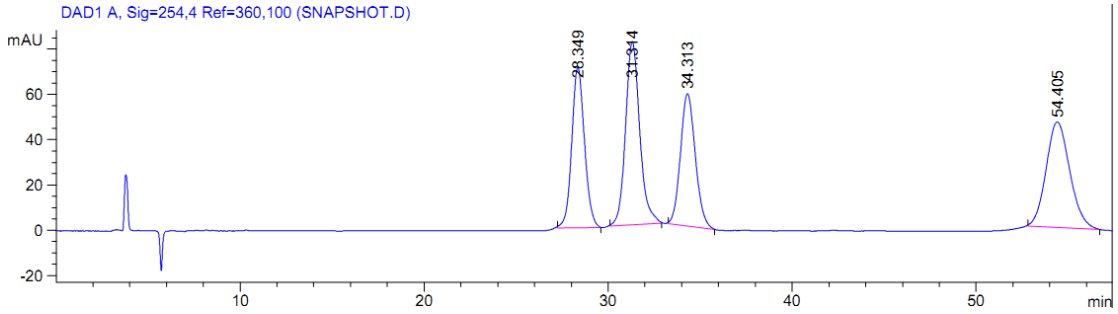


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.756	BB	0.4741	1449.62646	46.45465	7.6118
2	21.192	BB	0.5843	8094.20410	210.65631	42.5018
3	24.144	BB	0.6675	8122.32129	185.26234	42.6495
4	28.361	BB	0.7646	1378.20898	27.69415	7.2368
Totals :				1.90444e4	470.06746	

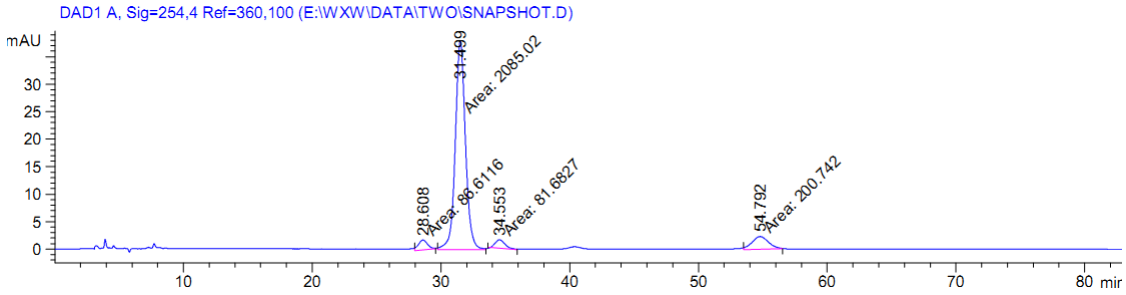


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.604	BB	0.4454	131.37721	4.38654	1.8863
2	21.076	BB	0.5830	6189.06738	160.81990	88.8641
3	24.000	BB	0.6229	502.59644	12.14140	7.2164
4	28.219	BB	0.5908	141.59975	3.18402	2.0331
Totals :				6964.64078	180.53187	

4i

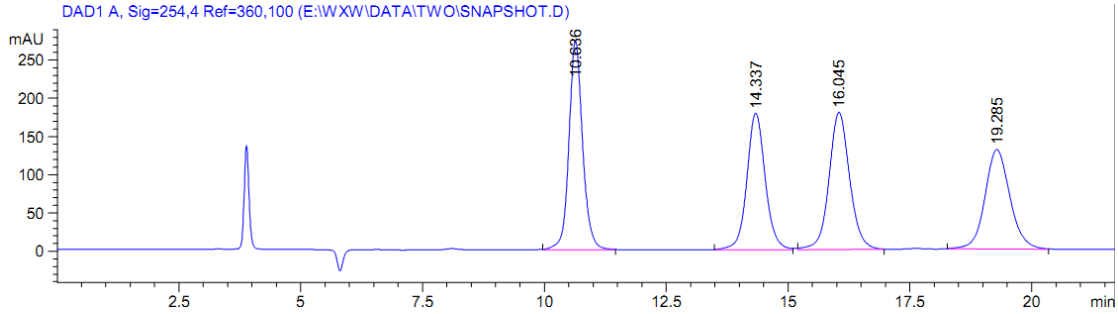


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.349	BB	0.7330	3401.33643	70.73076	22.3369
2	31.314	BB	0.8192	4355.48535	81.01620	28.6028
3	34.313	BB	0.8618	3287.46240	58.48153	21.5890
4	54.405	BB	1.3266	4183.17432	46.62958	27.4713
Totals :				1.52275e4	256.85807	

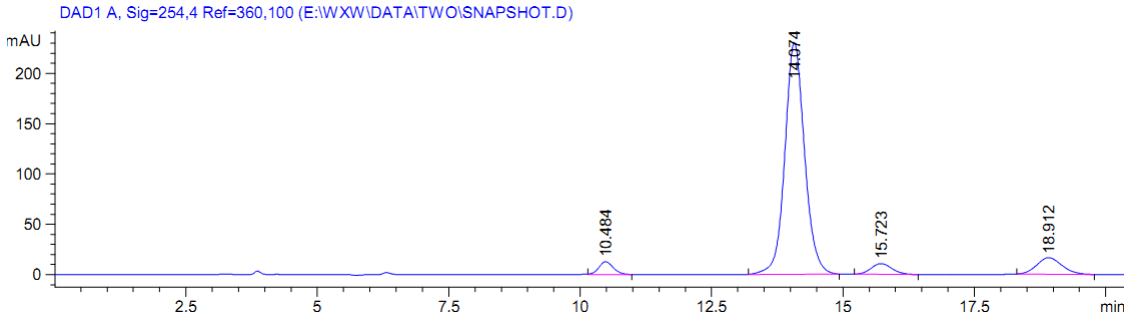


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.608	MM	0.8136	86.61164	1.77421	3.5293
2	31.499	MM	0.9173	2085.01807	37.88144	84.9622
3	34.553	MM	0.8876	81.68272	1.53376	3.3285
4	54.792	MM	1.4739	200.74187	2.26992	8.1800
Totals :				2454.05430	43.45933	

4j

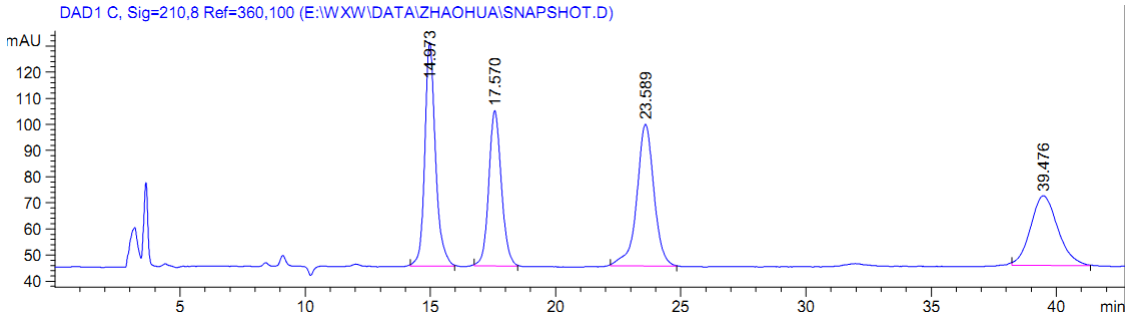


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.636	BB	0.2957	5329.99072	273.09079	26.7589
2	14.337	BB	0.3999	4683.82520	178.60843	23.5149
3	16.045	BB	0.4486	5266.96143	179.36183	26.4425
4	19.285	BB	0.5435	4637.76563	130.21367	23.2837
Totals :				1.99185e4	761.27472	

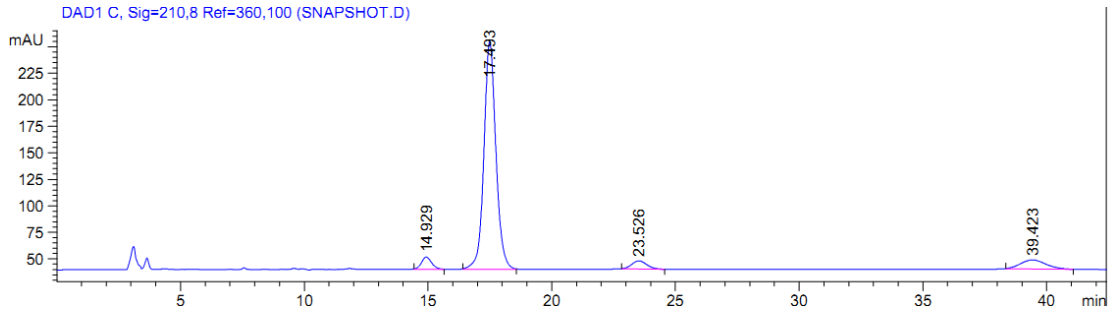


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.484	BB	0.2912	244.71288	12.78953	3.4311
2	14.074	BB	0.3990	6031.04346	230.66344	84.5599
3	15.723	BB	0.4218	298.04117	10.73748	4.1788
4	18.912	BB	0.5144	558.48035	16.51866	7.8303
Totals :				7132.27785	270.70910	

4k

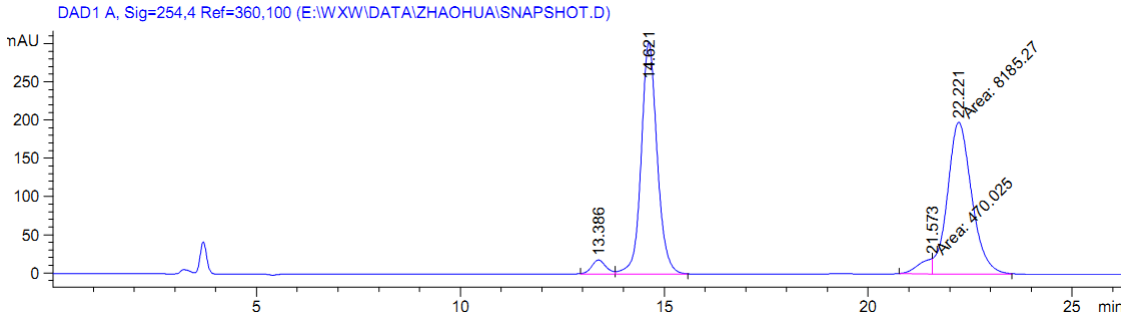


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.973	BB	0.4492	2545.90894	85.55552	27.5980
2	17.570	BB	0.5344	2078.64038	59.38153	22.5328
3	23.589	BB	0.7205	2593.49219	54.17960	28.1138
4	39.476	BB	1.0880	2006.92200	26.60623	21.7553
Totals :				9224.96350	225.72288	

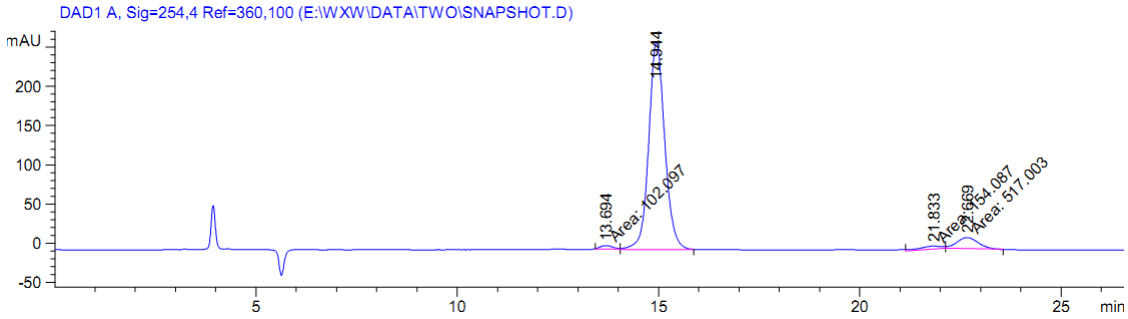


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.929	BB	0.4349	328.91635	11.52714	3.8817
2	17.493	BB	0.5109	7224.87891	214.54095	85.2635
3	23.526	BB	0.6204	320.20148	7.52512	3.7788
4	39.423	BB	0.9115	599.59607	8.37240	7.0761
Totals :				8473.59280	241.96562	

4l

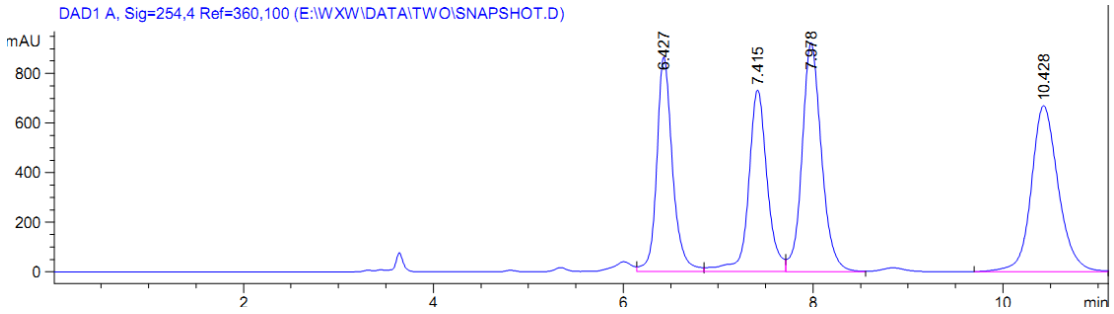


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.386	BV	0.3691	441.32257	18.18883	2.5475
2	14.621	VB	0.4128	8227.46191	303.01169	47.4915
3	21.573	MF	0.3903	470.02521	20.07323	2.7131
4	22.221	FM	0.6876	8185.26611	198.38914	47.2479
Totals :				1.73241e4	539.66290	

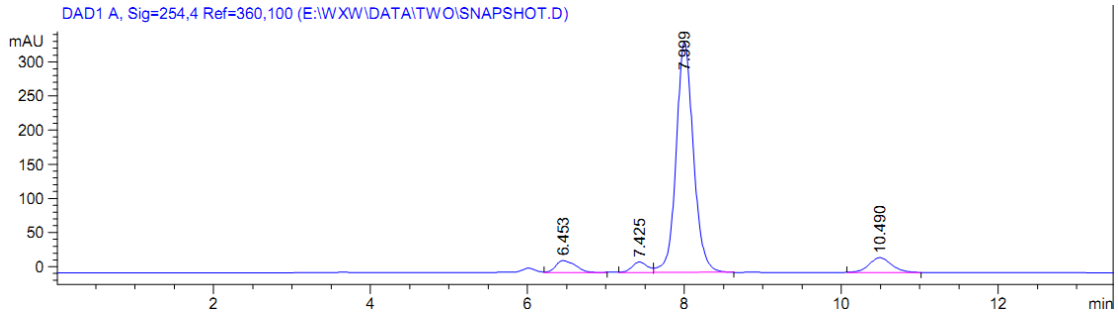


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.694	MM	0.3665	102.09653	4.64303	1.2596
2	14.944	VB	0.4238	7332.04150	264.14264	90.4606
3	21.833	MM	0.7043	154.08650	3.64612	1.9011
4	22.669	MM	0.6154	517.00323	14.00167	6.3786
Totals :				8105.22778	286.43346	

4m

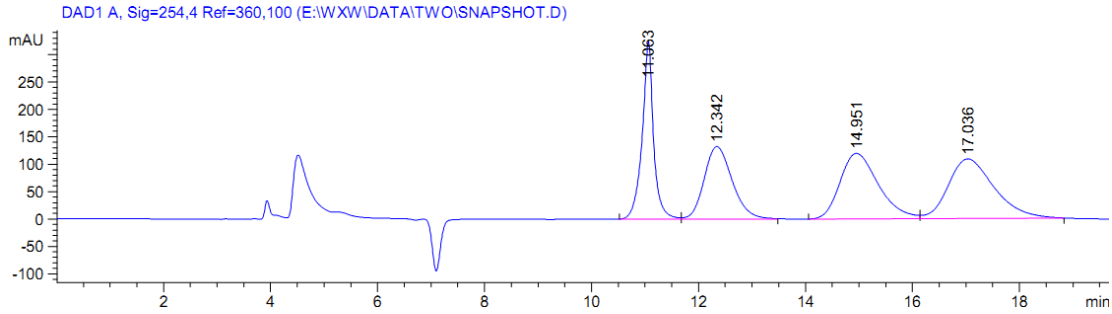


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.427	VV	0.1750	1.00328e4	867.17737	21.5797
2	7.415	VV	0.2055	1.00311e4	733.54822	21.5761
3	7.978	VV	0.2161	1.31529e4	923.80109	28.2908
4	10.428	BBA	0.3011	1.32750e4	670.14386	28.5535
Totals :				4.64918e4	3194.67053	

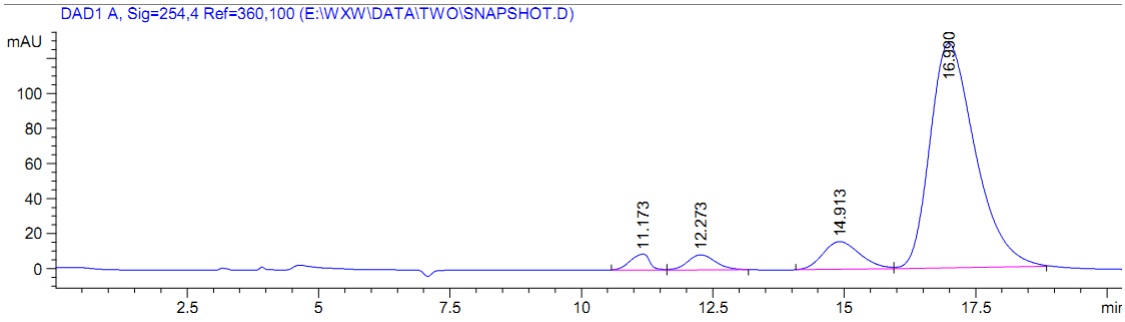


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.453	VB	0.2884	305.49582	17.44050	4.9931
2	7.425	BV	0.2105	211.03787	15.34436	3.4492
3	7.999	VB	0.2333	5164.75342	336.11005	84.4134
4	10.490	BB	0.3070	437.12085	21.70401	7.1444
Totals :				6118.40796	390.59891	

4n

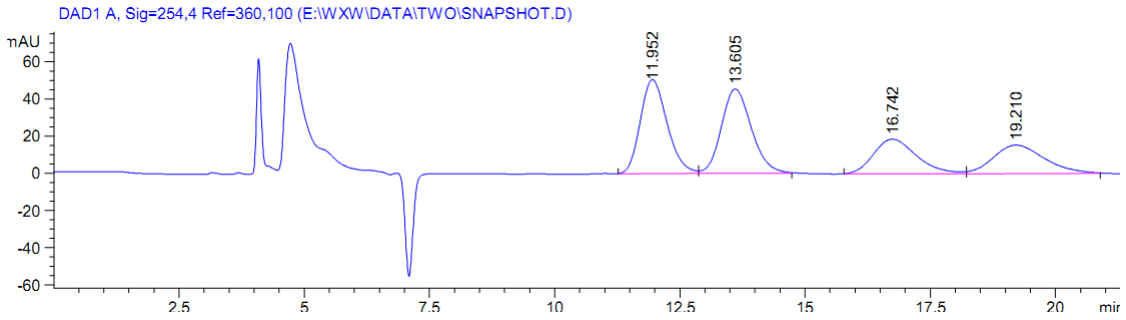


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.063	BV	0.2071	4808.22412	324.07388	21.7325
2	12.342	VB	0.5600	4808.70361	132.30653	21.7347
3	14.951	BV	0.7644	5971.54199	119.62440	26.9906
4	17.036	VB	0.9181	6536.08252	108.91338	29.5422
Totals :				2.21246e4	684.91820	

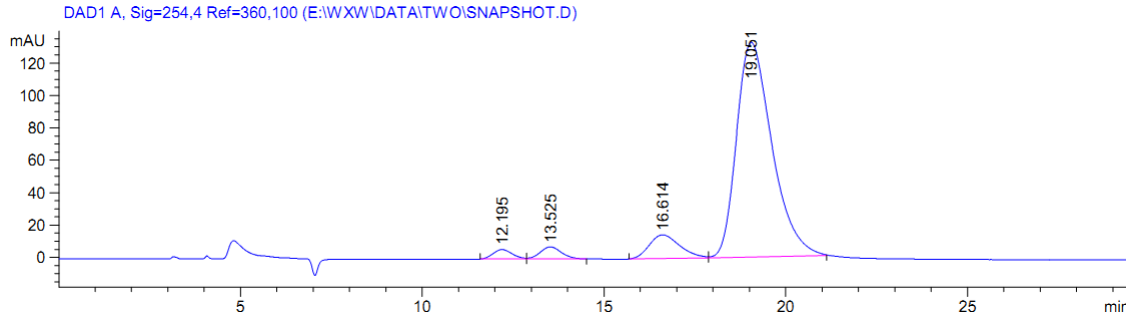


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.173	BV	0.4112	231.74086	9.09739	2.5776
2	12.273	VB	0.5547	318.62402	8.67190	3.5440
3	14.913	BV	0.7468	770.98401	15.75798	8.5756
4	16.990	VB	0.9123	7669.07861	128.13687	85.3027
Totals :				8990.42751	161.66414	

4o



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.952	BV	0.5748	1883.82849	50.54475	31.6182
2	13.605	VB	0.6369	1886.79004	45.40014	31.6679
3	16.742	BB	0.9014	1108.96167	18.60510	18.6128
4	19.210	BB	1.0173	1078.47400	15.28313	18.1011
Totals :				5958.05420	129.83312	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.195	BV	0.5503	216.05608	5.88542	2.0881
2	13.525	VB	0.6166	306.64465	7.47499	2.9635
3	16.614	BV	0.8702	849.69171	14.66058	8.2118
4	19.051	VB	1.0405	8974.82129	132.46201	86.7366
Totals :				1.03472e4	160.48299	