Supporting Information

Rh-Catalyzed One-Pot Sequential Asymmetric Hydrogenation of α-Dehydroamino Ketones for the Synthesis of Chiral Cyclic *trans*-β-Amino Alcohols

Qiupeng Hu,[†] Jianzhong Chen,[‡] Zhenfeng Zhang,*[,†] Yangang Liu[†] and Wanbin Zhang*[,†,‡]

[†]School of Pharmacy and [‡]School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

Tel (Fax): +86 21 54743265

E-mail: wanbin@sjtu.edu.cn; zhenfeng@sjtu.edu.cn

Homepage: http://wanbin.sjtu.edu.cn

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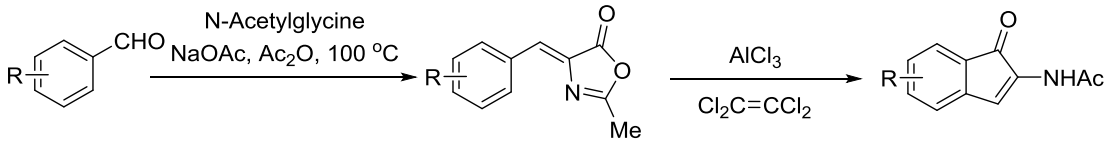
1. General details

All reactions were performed in dried glassware under an atmosphere of dry nitrogen, and the workup was carried out in air, unless otherwise noted. Solvents were dried and distilled by standard procedures. Commercially available reagents were used without further purification. Column chromatography was performed using 100-200 mesh silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer. HRMS was performed on a Waters Micromass Q-TOF Premier Mass Spectrometer at the Instrumental Analysis Center of Shanghai Jiao Tong University. The ee values were determined by HPLC using Daicel Chiralpak columns. Melting points were measured with SGW X-4 micro melting point apparatus. IR was measured with PerkinElmer Spectrum 100 FT-IR Spectrometer. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm. The absolute configuration of **2a** was assigned by H-H Noesy and HPLC spectra according to the literature.[1] The absolute configuration of other products **2b**-**2p** was considered to be the same as **2a**.

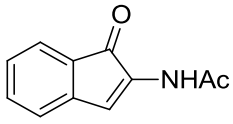
2. Syntheses of α-dehydroamino ketones



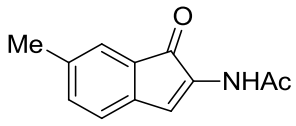
According to a literature procedure.[1]

Benzaldehyde or its derivative (50 mmol), N-acetylglycine (55 mmol), sodium acetate (50 mmol), and acetic anhydride (15 mL) were mixed and heated at 100 ℃ with stirring for 4 h. Then, the mixture was left stirring overnight at 25 ℃. The precipitate was separated by filtration and washed with ice-cold alcohol, then with hot water to obtain the oxazolone (40-77% yields).

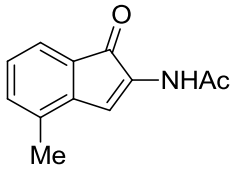
In a 500 mL round-bottom flask, fitted with a dropping funnel and a reflux condenser, was placed 0.036 mol of anhydrous aluminrim chloride and 60 mL of dry acetylene tetrachloride. The mixture was stirred for 1 hour at room temperature. To this was added with stirring a solution containing 0.012 mol of (*Z*)-4-benzylidene-2-methyloxazol-5(4*H*)-one or its derivative in 60 mL of dry acetylene tetrachloride. When all the oxazolone has been added, the reaction mixture was stirred at 60 ℃ or 110 ℃ (by heating on an oil-bath) for 1 hour, then stirring was continued for 2 hours at room temperature. The complex was decomposed with 100 mL of dilute (1/15) hydrochloric acid and two clear layers were obtained. The acetylene tetrachloride layer were separated and the aqueous layer was extracted with dichloromethane. The combined organic phase was dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by silica gel column chromatography to give the pure product (19-58% yields).



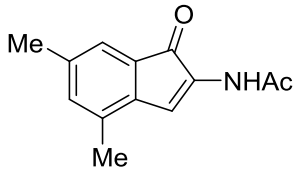
***N*-(1-oxo-1*H*-inden-2-yl)acetamide (1a).**[1] 1.30 g, 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (br s, 1H), 7.46 (s, 1H), 7.35-7.32 (m, 1H), 7.31-7.26 (m, 1H), 7.07-7.02 (m, 1H), 6.95 (d, J = 7.2 Hz, 1H), 2.19 (s, 3H).



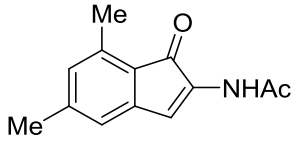
***N*-(6-methyl-1-oxo-1*H*-inden-2-yl)acetamide (1b).**[1] 1.18 g, 49% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (br s, 1H), 7.46 (s, 1H), 7.15 (s, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 2.28 (s, 3H), 2.20 (s, 3H).



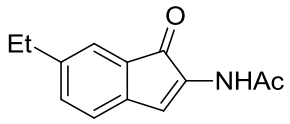
***N*-(4-methyl-1-oxo-1*H*-inden-2-yl)acetamide (1c).**[1] 1.01 g, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.53 (br s, 1H), 7.16 (d, J = 7.2 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 7.2 Hz, 1H), 2.23 (s, 3H), 2.20 (s, 3H).



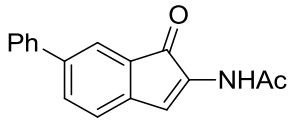
***N*-(4,6dimethyl-1-oxo-1*H*-inden-2-yl)acetamide (1d).** Red solid, 1.03 g, 40% yield; Mp: 206-208 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 8.1 Hz, 1H), 7.44 (s, 1H), 7.13 (d, J = 8.5 Hz, 1H), 7.07 (s, 1H), 2.48 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 165.7, 141.8, 139.8, 131.8, 131.7, 131.5, 129.0, 128.6, 127.4, 21.6, 19.9, 15.7; IR (KBr): ν 3279, 1721, 1669, 1532, 1291, 1244, 846, 784, 720 cm^{-1}; HRMS (ESI): m/z calculated for $C_{13}H_{14}NO_2^+$ $[M+H]^+$ 216.1019, found 216.1019.



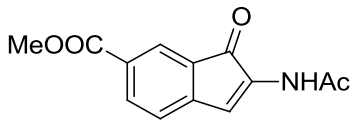
***N*-(5,7-dimethyl-1-oxo-1*H*-inden-2-yl)acetamide (1e).**[1] Red solid, 0.62 g, 25% yield; Mp: 154-156 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (br s, 1H), 7.30 (s, 1H), 6.57 (s, 2H), 2.38 (s, 3H), 2.23 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 168.5, 147.5, 145.7, 138.5, 131.7, 130.1, 122.5, 121.6, 121.5, 24.0, 21.9, 17.3; IR (KBr): ν 3332, 1709, 1683, 1596, 1525, 1381, 1289, 1228, 1131, 1016, 866, 713, 700, 602 cm^{-1}; HRMS (ESI): m/z calculated for $C_{13}H_{14}NO_2^+$ $[M+H]^+$ 216.1019, found 216.1015.



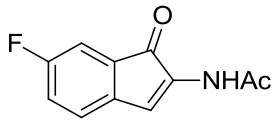
***N*-(6-ethyl-1-oxo-1*H*-inden-2-yl)acetamide (1f).**[1] 0.96 g, 37% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (br s, 1H), 7.44 (s, 1H), 7.17 (s, 1H), 7.08-7.04 (m, 1H), 6.82 (d, J = 7.2 Hz, 1H), 2.54 (q, J = 8.0 Hz, 2H), 2.17 (s, 3H), 1.19 (t, J = 8.0 Hz, 3H).



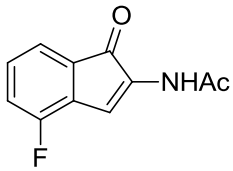
***N*-(1-oxo-6-phenyl-1*H*-inden-2-yl)acetamide (1g).**[1] 0.95 g, 30% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.55 (m, 2H), 7.54-7.50 (m, 3H), 7.50-7.47 (m, 1H), 7.45-7.39 (m, 2H), 7.36-7.32 (m, 1H), 6.99 (d, J = 8.0 Hz, 1H), 2.20 (s, 3H).



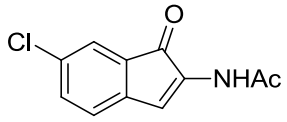
Methyl 2-acetamido-1-oxo-1*H*-indene-6-carboxylate (1h).[1] 0.62 g, 21% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 7.6 Hz, 1H), 7.94 (s, 1H), 7.57 (br s, 1H), 7.51 (s, 1H), 7.01 (d, J = 7.6 Hz, 1H), 3.89 (s, 3H), 2.20 (s, 3H).



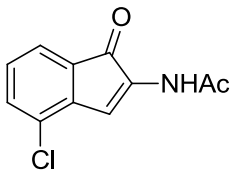
***N*-(6-fluoro-1-oxo-1*H*-inden-2-yl)acetamide (1i).**[1] 1.01 g, 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (br s, 1H), 7.47 (s, 1H), 7.06-7.02 (m, 1H), 6.96-6.90 (m, 1H), 6.89-6.86 (m, 1H), 2.18 (s, 3H).



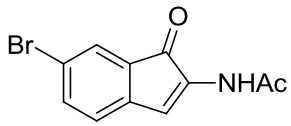
***N*-(4-fluoro-1-oxo-1*H*-inden-2-yl)acetamide (1j).**[1] 1.16 g, 47% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.60 (br s, 1H), 7.15 (s, 1H), 7.06-7.00 (m, 2H), 2.20 (s, 3H).



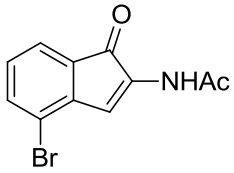
***N*-(6-chloro-1-oxo-1*H*-inden-2-yl)acetamide (1k).**[1] 1.03 g, 39% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (br s, 1H), 7.48 (s, 1H), 7.28-7.26 (m, 1H), 7.24 (dd, J = 2.0 Hz, 7.6 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 2.19 (s, 3H).



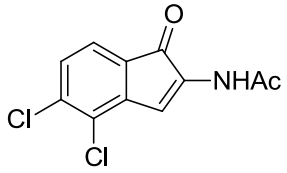
***N*-(4-chloro-1-oxo-1*H*-inden-2-yl)acetamide (1l).**[1] 0.93 g, 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.45 (br s, 1H), 7.25-7.21 (m, 2H), 6.99 (t, J = 7.6 Hz, 1H), 2.20 (s, 3H).



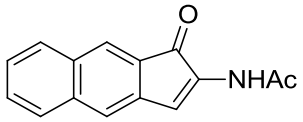
***N*-(6-bromo-1-oxo-1*H*-inden-2-yl)acetamide (1m).**[1] 1.05 g, 33% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.35 (m, 4H), 6.82 (d, J = 8.4 Hz, 1H), 2.19 (s, 3H).



***N*-(4-bromo-1-oxo-1*H*-inden-2-yl)acetamide (1n).**[1] 0.99 g, 31% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.52 (br s, 1H), 7.39 (dd, J = 0.8 Hz, 7.6 Hz, 1H), 7.25 (s, 1H), 6.94-6.90 (m, 1H), 2.21 (s, 3H).

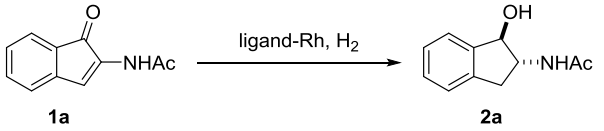


***N*-(4,5-dichloro-1-oxo-1*H*-inden-2-yl)acetamide (1o).**[1] 0.77 g; 25% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.51 (br s, 1H), 7.16 (s, 2H), 2.21 (s, 3H).

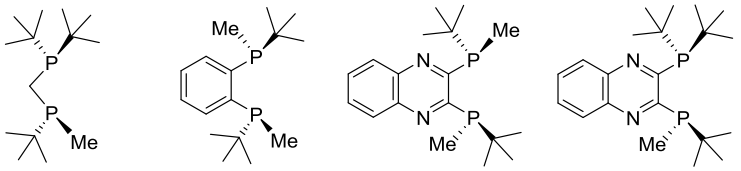


***N*-(1-oxo-1*H*-cyclopenta[*b*]naphthalen-2-yl)acetamide (1p).**[1] 0.54 g, 19% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.74 (s, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.61 (br s, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.21 (s, 1H), 2.21 (s, 3H).

3. The details for solvent screening



1a **2a**

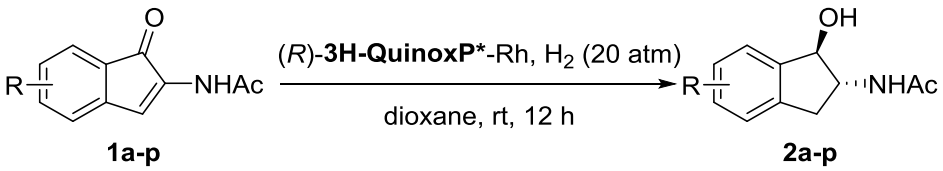


(*S*)-**TCFP** (*S,S*)-**BenzP*** (*R,R*)-**QuinoxP*** (*R*)-**3H-QuinoxP***

entry	ligand	solvent	conv [%] (*trans*/*cis*)[b]	ee [%] (*trans*)[c]
1	**TCFP**	EtOH	34/66	99
2	**TCFP**	EtOAc	33/67	–94
3	**TCFP**	DCM	33/67	–94
4	**BenzP***	EtOH	12/88	–33
5	**BenzP***	EtOAc	8/92	–25
6	**BenzP***	DCM	23/77	39
7	**BenzP***	*i*PrOH	78/22	15
8	**QuinoxP***	EtOH	23/77	39
9	**QuinoxP***	EtOAc	1/99	97
10	**QuinoxP***	DCM	75/25	68
11	**3H-QuinoxP***	EtOH	65/35	97
12	**3H-QuinoxP***	EtOAc	82/18	98
13	**3H-QuinoxP***	DCM	79/21	67
14[d]	**3H-QuinoxP***	MeOH	35/20	93
15	**3H-QuinoxP***	THF	83/17	90
16	**3H-QuinoxP***	toluene	81/19	95
17	**3H-QuinoxP***	dioxane	93/7	93

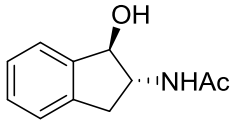
[a] Conditions: **1a** (0.2 mmol), ligand−Rh (1 mol %), H_2 (30 atm), solvent (2 mL), rt, 12 h. [b] Conversions were calculated from ^{1}H NMR spectra. [c] The ee values were determined by HPLC using chiral columns. [d] Product **2a** was obtained in a yield of 55% with α-amino ketone in a yield of 45%.

4. Sequential asymmetric hydrogenation of α-dehydroanimo ketones



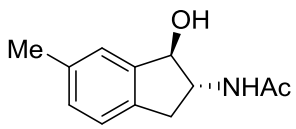
1a-p 2a-p

General procedure: Substrate **1** (0.2 mmol) and [Rh((*R*)-**3H-QuinoxP***)(cod)]SbF_6 (1 mol %) were charged in an autoclave. And the system was evacuated and filled with hydrogen. After repeating this operation 3 times, degassed 1,4-dioxane (2 mL) was added and the hydrogen pressure was adjusted to 20 atm. After vigorous stirring at room temperature for 12 h, the reaction mixture was evaporated under reduced pressure. The conversions were calculated from ^{1}H NMR spectra of crude products, the yields were calculated based on the mixture of *trans*- and *cis*-products isolated by flash chromatography. The ee and dr values were directly determined by HPLC using chiral columns under the following conditions. Then the major *trans*-product **2** was obtained by reslurry (EtOAc/Petroleum ether = 4 mL/12 mL) for additional characterization.

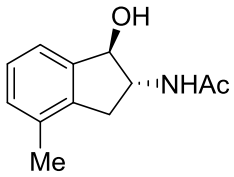


***N*-((1*R*,2*R*)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2a).** White solid, 36.4 mg, 96% yield, 13/1 dr, 94% ee; Mp: 186-188 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 8.44 (br s, 1H), 7.44-7.13 (m, 4H), 4.99 (d, J = 6.4 Hz, 1H), 4.32 (q, J = 6.8 Hz, 1H), 3.31 (dd, J = 15.2, 8.0 Hz, 1H), 2.70 (dd, J = 15.6, 8.0 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 142.6, 139.3, 128.0, 126.7, 124.3, 123.8, 79.4, 59.7, 35.3, 21.2; IR (KBr): ν 3315, 1647, 1544, 1313, 1211, 1065, 741 cm^{-1}; HRMS (ESI): m/z calculated for $C_{11}H_{14}NO_2^+$ $[M+H]^+$ 192.1019, found 190.0874; HPLC conditions: DAICEL Chiralpak OJ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C, t_{major} = 18.4 min, t_{minor} = 44.6 min; $[\alpha]^{20}_D$ = -18 (*c* 0.14, MeOH).

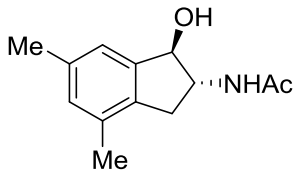
The *trans*-configuration of hydrogenated product **2a** was confirmed by H-H nosey spectra (see Page S40 for the spectra). The hydrogen atoms on the two CH group had an NOE effect with the two hydrogen atoms on CH_2, respectively. The absolute configuration of the *trans*-product was confirmed to be (1*R*, 2*R*) by the known (*R*)-configuration of chiral center connected the nitrogen atom which was reported previously.[1]



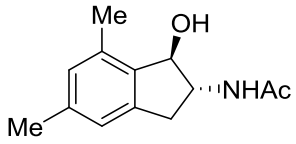
***N*-((1*R*,2*R*)-1-hydroxy-6-methyl-2,3-dihydro-1*H*-inden-2-yl)acetamide (2b).** White solid, 39.0 mg, 95% yield, 10/1 dr, 97% ee; Mp: 193-195 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.17 (s, 1H), 7.07 (s, 2H), 4.94 (d, J = 6.4 Hz, 1H), 4.29 (q, J = 7.8 Hz, 1H), 3.25 (dd, J = 15.5, 7.8 Hz, 1H), 2.63 (dd, J = 15.6, 7.9 Hz, 1H), 2.33 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 142.6, 136.4, 136.2, 128.7, 124.2, 124.1, 79.4, 59.9, 34.9, 21.2, 20.0; IR (KBr): v 3333, 1651, 1542, 1297, 1121, 1063, 1026, 818, 799 cm^{-1}; HRMS (ESI): m/z calculated for $C_{12}H_{16}NO_2^+$ $[M+H]^+$ 206.1176, found 206.1189; HPLC conditions: DAICEL Chiralpak OZ column, Hexene/*i*-PrOH = 95/5, 220 nm, 40 ^{o}C, 1.0 mL/min, t_{major} = 78.8 min, t_{minor} = 66.3 min; $[\alpha]^{20}_D$ = 4 (*c* 0.11, MeOH).



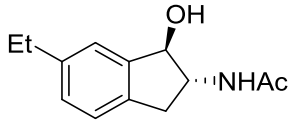
***N*-((1*R*,2*R*)-1-hydroxy-4-methyl-2,3-dihydro-1*H*-inden-2-yl)acetamide (2c).** White solid, 37.9 mg; 93% yield, 13/1 dr, 96% ee; Mp: 182-184 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.24-6.98 (m, 3H), 4.97 (d, J = 6.2 Hz, 1H), 4.29 (q, J = 7.6 Hz, 1H), 3.28 (dd, J = 15.8, 8.0 Hz, 1H), 2.58 (dd, J = 15.8, 7.5 Hz, 1H), 2.25 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 142.2, 138.0, 133.7, 128.7, 126.9, 121.2, 79.7, 59.4, 33.9, 21.2, 17.2; IR (KBr): v 3319, 2939, 1645, 1549, 1383, 1312, 1295, 1105, 790, 748 cm^{-1}; HRMS (ESI): m/z calculated for $C_{12}H_{15}NO_2^+$ $[M+H]^+$ 206.1176, found 206.1190; HPLC conditions: DAICEL Chiralpak AD-H column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C, t_{major} = 10.1 min, t_{minor} = 14.0 min; $[\alpha]^{20}_D$ = -30 (*c* 0.13, MeOH).



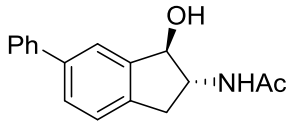
***N*-((1*R*,2*R*)-1-hydroxy-4,6-dimethyl-2,3-dihydro-1*H*-inden-2-yl)acetamide (2d).** White solid, 40.3 mg, 92% yield, 9/1 dr, 99% ee; Mp: 202-204 ℃; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.18 (d, J = 7.1 Hz, 1H), 6.89 (s, 1H), 6.83 (s, 1H), 5.41 (d, J = 6.3 Hz, 1H), 4.79 (t, J = 6.6 Hz, 1H), 4.15-3.98 (m, 1H), 3.05 (dd, J = 15.7, 8.0 Hz, 1H), 2.36 (dd, J = 15.6, 8.0 Hz, 1H), 2.23 (s, 3H), 2.12 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.9, 144.3, 136.1, 135.5, 133.4, 129.5, 122.3, 79.1, 59.6, 34.5, 23.2, 21.4, 18.6; IR (KBr) v: 3270, 1644, 1563, 1440, 1381, 1307, 1102, 861 cm^{-1}; HRMS (ESI): m/z calculated for $C_{13}H_{17}NNaO_2^+$ $[M+Na]^+$ 242.1151, found 242.1156; HPLC conditions: DAICEL Chiralpak AD-H column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C, t_{major} = 22.4 min, t_{minor} = 35.9 min; $[\alpha]^{20}_D$ = 33 (*c* 0.06, CH_2Cl_2).



***N*-((1*R*,2*R*)-1-hydroxy-5,7-dimethyl-2,3-dihydro-1*H*-inden-2-yl)acetamide (2e).** White solid, 41.6 mg; 95% yield, 16/1 dr, 90% ee; Mp: 165-168 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 6.86 (s, 1H), 6.84 (s, 1H), 4.97 (d, J = 2.9 Hz, 1H), 4.29 (q, J = 3.8 Hz, 1H), 3.36 (dd, J = 16.3, 7.3 Hz, 1H), 2.61 (dd, J = 16.2, 4.1 Hz, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.1, 141.2, 138.5, 137.4, 135.3, 128.9, 122.5, 79.3, 59.1, 35.9, 21.1, 20.0, 16.9; IR (KBr) v: 3271, 2945, 1644, 1565, 1439, 1311, 1051, 1033, 850, 711, 611 cm^{-1}; HRMS (ESI): m/z calculated for $C_{13}H_{18}NO_2^+$ $[M+H]^+$ 220.1332, found 220.1342; HPLC conditions: DAICEL Chiralpak OJ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C, t_{major} = 15.0 min, t_{minor} = 23.7 min; $[\alpha]^{20}_D$ = 27 (c 0.17, MeOH).

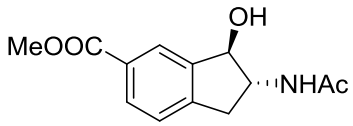


***N*-((1*R*,2*R*)-6-ethyl-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2f).** White solid, 42.1 mg; 96% yield, 12/1 dr, 97% ee; Mp: 179-181 ℃, ^{1}H NMR (400 MHz, CD_3OD): δ 7.19 (s, 1H), 7.09 (s, 2H), 4.94 (d, J = 6.5 Hz, 1H), 4.28 (q, J = 7.7 Hz, 1H), 3.25 (dd, J = 15.5, 7.9 Hz, 1H), 2.67-2.59 (m, 3H), 1.98 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 171.6, 142.3, 141.8, 135.7, 126.9, 123.4, 122.3, 78.7, 59.1, 34.2, 27.6, 20.4, 14.3; IR (KBr): v 3390, 3333, 2960, 1650, 1541, 1492, 1382, 1297, 1120, 1059, 1026, 822 cm^{-1}; HRMS (ESI): m/z calculated for $C_{13}H_{18}NO_2^+$ $[M+H]^+$ 220.1332, found 220.1348; HPLC conditions: DAICEL Chiralpak OJ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C, t_{major} = 20.3 min, t_{minor} = 25.8 min; $[\alpha]^{20}_D$ = 5 (c 0.18, MeOH).

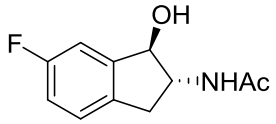


***N*-((1*R*,2*R*)-1-hydroxy-6-phenyl-2,3-dihydro-1*H*-inden-2-yl)acetamide (2g).** White solid, 49.3 mg, 93% yield, 7/1 dr, 95% ee; Mp: 172-173 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.63-7.57 (m, 3H), 7.51 (d, J = 7.8 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.31 (dd, J = 16.2, 7.6 Hz, 2H), 5.04 (d, J = 6.9 Hz, 1H), 4.36 (q, J = 7.7 Hz, 1H), 3.35 (dd, J = 16.0, 7.6 Hz, 1H), 2.73 (dd, J = 15.8, 7.7 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.7, 143.6, 141.4, 140.5, 138.7, 128.7, 127.1, 127.0, 126.8, 125.0, 122.5, 79.6, 60.1, 35.2, 21.4; IR (KBr): v 3277, 1645, 1569, 1481, 1379, 1312, 1172, 1122, 1066, 757, 695, 607 cm^{-1}; HRMS (ESI): m/z calculated for $C_{17}H_{18}NO_2^+$ $[M+H]^+$ 268.1332, found 268.1344; HPLC conditions: DAICEL Chiralpak AD column,

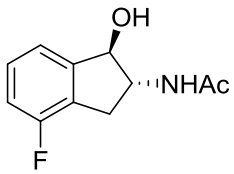
Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 °C, t_{major} = 17.9 min, t_{minor} = 32.1 min; $[\alpha]^{20}_{D}$ = 35 (*c* 0.29, MeOH).



Methyl (2*R*,3*R*)-2-acetamido-3-hydroxy-2,3-dihydro-1*H*-indene-5-carboxylate (2h). White solid, 45.8 mg, 92% yield, 4/1 dr, 89% ee; Mp: 194-196 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.99 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 5.00 (d, *J* = 6.5 Hz, 1H), 4.33 (q, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 3.35 (dd, *J* = 16.4, 9.2 Hz, 1H), 2.74 (dd, *J* = 16.1, 8.0 Hz, 1H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 167.1, 145.2, 143.5, 129.4, 129.0, 125.0, 124.6, 78.7, 59.7, 51.2, 35.4, 21.2; IR (KBr): *v* 3509, 3296, 2956, 1712, 1642, 1560, 1437, 1380, 1308, 1269, 1207, 1129, 1099, 1057, 969, 764 cm^{-1}; HRMS (ESI): m/z calculated for $C_{13}H_{16}NO_4^+$ $[M+H]^+$ 250.1074, found 250.1069; HPLC conditions: DAICEL Chiralpak IE column, Hexene/*i*-PrOH = 90/10, 220 nm, 25 °C, 1.0 mL/min, t_{major} = 71.6 min, t_{minor} = 84.5 min; $[\alpha]^{20}_{D}$ = 8 (*c* 0.10, MeOH).

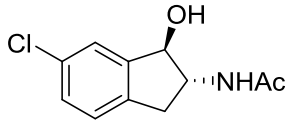


***N*-((1*R*,2*R*)-6-fluoro-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2i).** White solid, 39.7 mg; 95% yield, 6/1 dr, 95% ee; Mp: 177-179 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.19 (dd, *J* = 8.0, 5.3 Hz, 1H), 7.04 (dd, *J* = 8.7, 1.5 Hz, 1H), 6.96 (td, *J* = 9.4, 2.4 Hz, 1H), 4.95 (d, *J* = 6.9 Hz, 1H), 4.31 (q, *J* = 8.0 Hz, 1H), 3.24 (dd, *J* = 15.5, 7.9 Hz, 1H), 2.64 (dd, *J* = 15.4, 8.6 Hz, 1H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 162.4 (d, $J_{C\text{-}F}$ = 242.8 Hz), 145.1 (d, $J_{C\text{-}F}$ = 7.6 Hz), 134.7 (d, $J_{C\text{-}F}$ = 2.6 Hz), 125.8 (d, $J_{C\text{-}F}$ = 8.4 Hz), 114.7 (d, $J_{C\text{-}F}$ = 22.8 Hz), 110.5 (d, $J_{C\text{-}F}$ = 22.6 Hz), 79.0 (d, $J_{C\text{-}F}$ = 1.8 Hz), 60.0, 34.5, 21.2; IR (KBr): *v* 3318, 1651, 1551, 1486, 1445, 1383, 1315, 1301, 1269, 1236, 1156, 1125, 1112, 1058, 1028, 863, 817, 764 cm^{-1}; HRMS (ESI): m/z calculated for $C_{11}H_{13}FNO_2$ $[M+H]^+$ 210.0925, found 210.0937; HPLC conditions: DAICEL Chiralpak AD column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 °C, t_{major} = 10.6 min, t_{minor} = 13.9 min; $[\alpha]^{20}_{D}$ = -33 (*c* 0.10, MeOH).

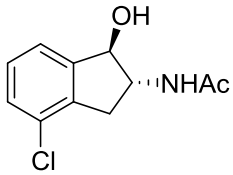


***N*-((1*R*,2*R*)-4-fluoro-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2j).** White solid, 39.3 mg, 94% yield, 6/1 dr, 97% ee; Mp: 194-195 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.33-7.23 (m,

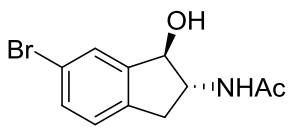
1H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 8.7 Hz, 1H), 4.99 (d, *J* = 6.5 Hz, 1H), 4.33 (q, *J* = 7.6 Hz, 1H), 3.36 (dd, *J* = 16.0, 7.9 Hz, 1H), 2.65 (dd, *J* = 16.0, 7.7 Hz, 1H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 158.9 (d, $J_{C\text{-}F}$ = 246.2 Hz), 146.2 (d, $J_{C\text{-}F}$ = 5.4 Hz), 128.8 (d, $J_{C\text{-}F}$ = 7.0 Hz), 125.4 (d, $J_{C\text{-}F}$ = 18.6 Hz), 119.8 (d, $J_{C\text{-}F}$ = 3.5 Hz), 114.2 (d, $J_{C\text{-}F}$ = 20.6 Hz), 79.1 (d, $J_{C\text{-}F}$ = 2.6 Hz), 59.5, 30.9, 21.2; IR (KBr): *v* 3310, 1647, 1552, 1477, 1271, 1245, 1107, 971, 793, 756 cm^{-1}; HRMS (ESI): m/z calculated for $C_{11}H_{13}FNO_2^+$ $[M+H]^+$ 210.0925, found 210.0931; HPLC conditions: DAICEL Chiralpak OZ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 40 ^{o}C, t_{major} = 41.5 min, t_{minor} = 33.9 min; $[\alpha]^{20}_D$ = -27 (*c* 0.17, MeOH).



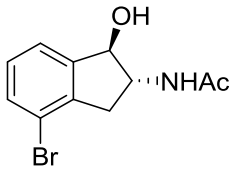
***N*-((1*R*,2*R*)-6-chloro-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2k).** White solid, 42.7 mg, 95% yield, 6/1 dr, 94% ee; Mp: 199-201 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.31 (s, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 4.96 (d, *J* = 6.9 Hz, 1H), 4.30 (q, *J* = 7.3 Hz, 1H), 3.25 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.65 (dd, *J* = 15.6, 8.1 Hz, 1H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 145.0, 137.9, 132.4, 128.0, 125.9, 123.9, 78.9, 59.8, 34.7, 21.2; IR (KBr): *v* 3333, 1652, 1540, 1489, 1073, 889, 817 cm^{-1}; HRMS (ESI): m/z calculated $C_{11}H_{13}ClNO_2^+$ $[M+H]^+$ 226.0629, found 226.0645; HPLC conditions: DAICEL Chiralpak OZ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 40 ^{o}C, t_{major} = 46.0 min, t_{minor} = 32.8 min; $[\alpha]^{20}_D$ = 4 (*c* 0.10, MeOH).



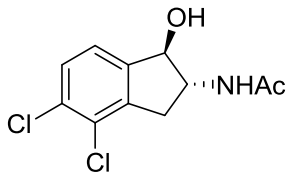
***N*-((1*R*,2*R*)-4-chloro-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2l).** White solid, 42.3 mg, 94% yield, 4/1 dr, 97% ee; Mp: 202-204 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.38-7.11 (m, 3H), 5.01 (d, *J* = 6.4 Hz, 1H), 4.31 (q, *J* = 7.7 Hz, 1H), 3.37 (dd, *J* = 16.3, 8.0 Hz, 1H), 2.67 (dd, *J* = 16.2, 7.7 Hz, 1H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 145.1, 137.5, 130.3, 128.5, 127.8, 122.4, 79.6, 59.0, 34.3, 21.2; IR (KBr): *v* 3274, 1646, 1559, 1450, 1377, 1326, 1307, 1172, 1130, 779 cm^{-1}; HRMS (ESI): m/z calculated for $C_{11}H_{13}ClNO_2^+$ $[M+H]^+$ 226.0629, found 226.0628; HPLC conditions: DAICEL Chiralpak AD column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C, t_{major} = 10.5 min, t_{minor} = 14.1 min; $[\alpha]^{20}_D$ = -51 (*c* 0.11, MeOH).



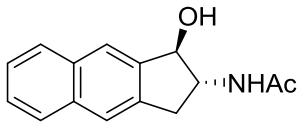
***N*-((1*R*,2*R*)-6-bromo-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2m).** White solid, 50.6 mg, 94% yield, 6/1 dr, 96% ee; Mp: 182-184 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.47 (s, 1H), 7.39 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 4.30 (q, *J* = 7.9 Hz, 1H), 3.25 (dd, *J* = 15.8, 7.8 Hz, 1H), 2.64 (dd, *J* = 15.8, 8.3 Hz, 1H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 145.3, 138.5, 130.9, 127.0, 126.3, 120.2, 78.8, 59.7, 34.8, 21.2; IR (KBr): *v* 3343, 1652, 1540, 1489, 1073, 889, 817 cm^{-1}; HRMS (ESI): m/z calculated for $C_{11}H_{13}BrNO_2^+$ $[M+H]^+$ 270.0124, found 270.1038; HPLC conditions: DAICEL Chiralpak OZ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 40 ^{o}C, t_{major} = 49.1 min, t_{minor} = 34.4 min; $[\alpha]^{20}_D$ = 10 (*c* 0.18, MeOH).



***N*-((1*R*,2*R*)-4-bromo-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2n).** White solid, 49.4 mg, 92% yield, 6/1 dr, 98% ee; Mp 197-199 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.43 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 5.03 (d, *J* = 6.5 Hz, 1H), 4.30 (q, *J* = 7.7 Hz, 1H), 3.33 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.66 (dd, *J* = 16.3, 7.7 Hz, 1H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 145.0, 139.7, 130.9, 128.7, 123.0, 119.4, 79.9, 58.7, 36.4, 21.2; IR (KBr): *v* 3277, 1636, 1559, 1450, 1377, 1326, 1307, 1172, 1130, 779 cm^{-1}; HRMS (ESI): m/z calculated for $C_{11}H_{13}BrNO_2^+$ $[M+H]^+$ 270.0124, found 270.1037; HPLC conditions: DAICEL Chiralpak AD column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C, t_{major} = 11.0 min, t_{minor} = 14.7 min; $[\alpha]^{20}_D$ = -51 (*c* 0.13, MeOH).



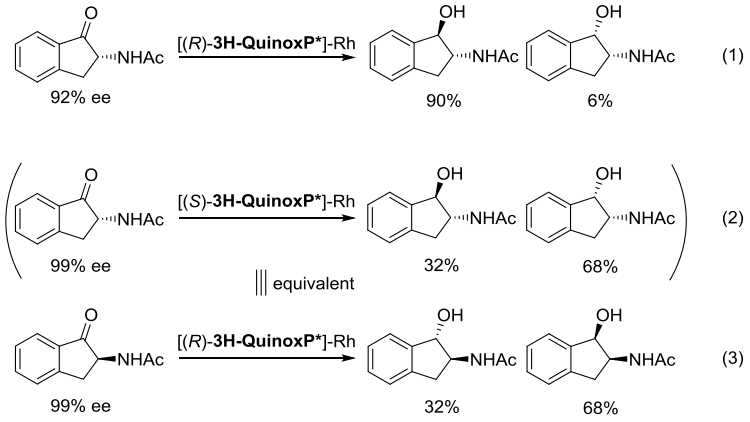
***N*-((1*R*,2*R*)-4,5-dichloro-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2o).** White solid, 47.1 mg, 91% yield, 3/1 dr, 96% ee; Mp: 198-199 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.43 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 5.01 (d, *J* = 6.3 Hz, 1H), 4.34 (q, *J* = 7.6 Hz, 1H), 3.40 (dd, *J* = 16.7, 8.0 Hz, 1H), 2.73 (dd, *J* = 16.4, 7.5 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.4, 143.5, 140.0, 131.5, 129.1, 128.4, 123.4, 79.3, 59.1, 35.0, 21.2; IR (KBr): *v* 3281, 1652, 1562, 1448, 1380, 1320, 1301, 1169, 1082, 1054, 1033, 909, 822, 753, 612 cm^{-1}; HRMS (ESI): m/z calculated for $C_{11}H_{12}Cl_2NO_2^+$ $[M+H]^+$ 260.0240, found 260.0236; HPLC conditions: DAICEL Chiralpak OZ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 40 ^{o}C, t_{major} = 44.9 min, t_{minor} = 35.4 min; $[\alpha]^{20}_D$ = -46 (*c* 0.10, MeOH).



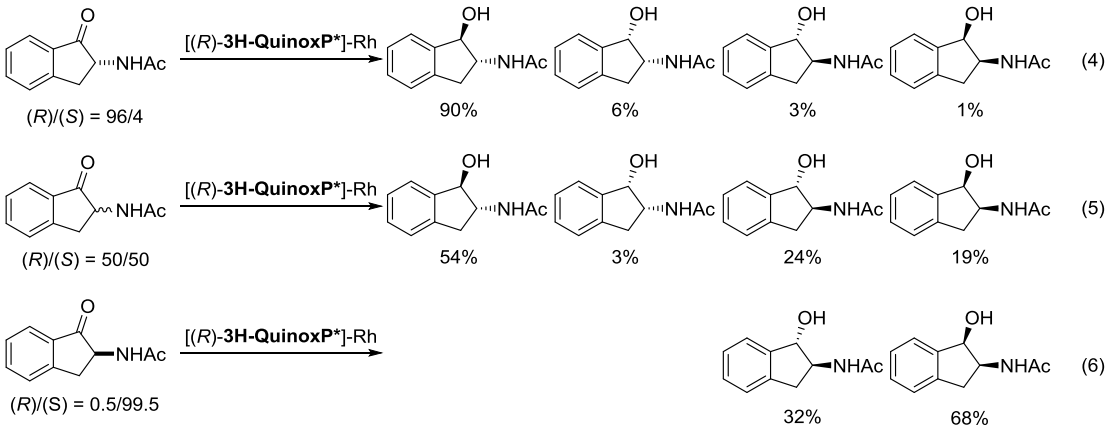
***N*-((1*R*,2*R*)-1-hydroxy-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-2-yl)acetamide (2p).** White solid, 45.3 mg, 94% yield, 5/1 dr, 97% ee; Mp: 242-244 ℃; ^{1}H NMR (400 MHz, CD_3OD): δ 7.85-7.77 (m, 3H), 7.66 (s, 1H), 7.44-7.39 (m, 2H), 5.10 (d, J = 7.0 Hz, 1H), 4.36 (q, J = 7.7 Hz, 1H), 3.43 (dd, J = 15.9, 7.6 Hz, 1H), 2.84 (dd, J = 15.8, 8.6 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ 172.5, 141.6, 137.5, 134.0, 133.2, 127.7, 127.3, 125.4, 125.0, 122.6, 122.4, 78.6, 59.7, 34.8, 21.3; IR (KBr): ν 3310, 1652, 1551, 1477, 1416, 1384, 1270, 1245, 1107, 972, 793, 756 cm^{-1}; HRMS (ESI): m/z calculated for $C_{15}H_{16}NO_2^+$ $[M+H]^+$ 242.1176, found 242.1181; HPLC conditions: DAICEL Chiralpak AD column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C, t_{major} = 18.7 min, t_{minor} = 32.0 min; $[\alpha]^{20}_{D}$ = 31 (*c* 0.11, MeOH).

5. More information about control experiments

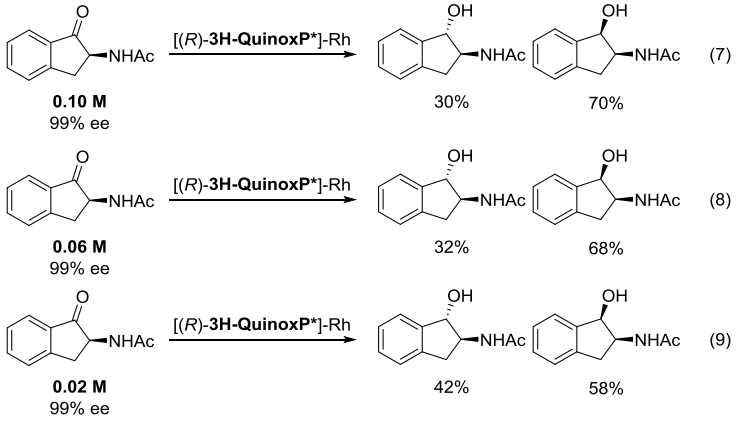
The asymmetric hydrogenation of intermediate (*S*)-alpha-amino ketones using ligand (*R*)-**3H-QuinoxP*** was repeated twice and both gave the desired product with an incomplete conversion (about 90% conv.) and a *trans/cis* ratio of about 32/68 (eq. (3)). Compared with the previous data shown in eq. (1) (hydrogenation of intermediate (*R*)-alpha-amino ketone using the same ligand (*R*)-**3H-QuinoxP***), the configuration of the carbon atom connected to the hydroxyl group in the major product is the same. This result reveals that the reduction of the carbonyl group is predominantly controlled by the catalyst and only partially influenced by the substrate (the intermediate alpha-amino ketone). Additionally there is a "match/mismatch" relationship between the catalyst and intermediate which influences the stereoselectivity and activity of the carbonyl reduction.



Compared to the data shown on the right-hand side of Scheme 4 in the manuscript (hydrogenation of (*S*)-alpha-amino ketone as the minor enantiomer catalyzed by [(*R*)-**3H-QuinoxP***]−Rh, also shown in eq (4)), the above experiment (eq. (3), also shown in eq (6)) in which (*S*)-alpha-amino ketone is the major enantiomer gave an opposite result (the *trans/cis* ratio of products changed from 3%/1% to 32%/68%). Therefore an additional hydrogenation was conducted using the racemic alpha-amino ketone catalyzed by [(*R*)-**3H-QuinoxP***]−Rh. This gave the desired products with a ratio of 54/3/24/19 (shown in eq. (5)). From these data, we can see that: the *trans/cis* ratio of products from (*R*)-alpha-amino ketone in eq. (5) (54/3) is consistent with the data in eq. (4) (90/6); and the *trans/cis* ratio of products from (*S*)-alpha-amino ketone changes under certain conditions.

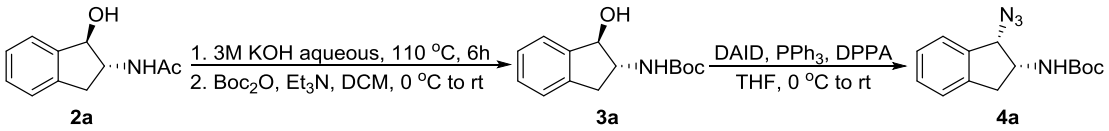


In order to make clear, two more hydrogenation reactions of (*S*)-alpha-amino ketone with different concentrations were set up (eq. (7) and eq. (9)). From the results listed in the following scheme, reducing the concentration of (*S*)-alpha-amino ketone (from 0.10 M to 0.02 M) increased the amount of product with the *trans*-configuration (the *trans/cis* ratio increased from 30/70 to 42/58).



Base on the above results, it's reasonable to assume that there are two different mechanisms (or transition-state intermediates) for the hydrogenation of alpha-amino ketones with opposite configurations catalyzed by [(*R*)-**3H-QuinoxP***]−Rh. Mechanism for the "mismatched" couple ((*S*)-alpha-amino ketone and [(*R*)-**3H-QuinoxP***]−Rh) is more complex because the concentration of the substrate influences the outcome.

6. Application



Gram scale hydrogenation:

Substrate **1a** (6 mmol) and Rh[((*R*)-**3H-QuinoxP***)(cod)]SbF_6 (1 mol %) were charged in an autoclave. The system was evacuated and filled with hydrogen. After repeating this operation 3 times, degassed 1,4-dioxane (30 mL) was added and hydrogen pressure was adjusted to 20 atm. After vigorous stirring at room temperature for 12 h, the reaction mixture was evaporated under reduced pressure. The yield was 94% for the mixture of *trans*- and *cis*-products isolated by flash chromatography (eluent DCM/MeOH = 10/1). The ee value was 91% and the dr value was 9/1 as determined by chiral HPLC.

Further application:

Compound **2a** (96.0 mg, 0.5 mmol) was transferred to a 10 mL round-bottle and dissolved in 3 mL EtOH. 5 mL 3 M KOH aqueous solution was added and the mixture was stirred at 110 ^{o}C for 6 h. After the solution was cooled to room temperature, DCM (20 mL × 3) was added and the mixture was extracted three times. The organic phase was combined, washed by brine and dried over Na_2SO_4. The crude product as a white solid was obtained after evaporating the organic solvent.

The crude amino alcohol was dissolved in 10 mL anhydrous DCM. Then, Et_3N (0.14 mL, 1.0 mmol) and Boc_2O (0.18 mL, 0.8 mmol) were added to the solution under N_2 atmosphere at 0 ^{o}C. The reaction mixture was stirred at room temperature overnight. 10 mL water was added to the solution to quench the reaction. DCM (10 mL × 3) was added to the solution and extracted for three times. The organic phase was combined, washed with brine and dried over Na_2SO_4. White solid **3a** was obtained in 72% yield (for the above two steps) by flash chromatography (eluent PE/EA = 3/1).

***tert*-Butyl ((1*R*,2*R*)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)carbamate (3a).** White solid, 89.6 mg, 72% yield, 90% ee; Mp: 136-137 ^{o}C; ^{1}H NMR (400 MHz, CD_3OD): δ 7.33-7.16 (m, 4H), 4.94 (d, J = 6.7 Hz, 1H), 4.09-3.95 (m, 1H), 3.23 (dd, J = 15.5, 7.8 Hz, 1H), 2.67 (dd, J = 15.5, 8.5 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, CD_3OD): δ 157.2, 142.7, 139.2, 127.8, 126.6, 124.3, 123.6, 79.3, 78.8, 60.9, 35.6, 27.4; IR (KBr): ν 3385, 2976, 2929, 1694, 1668, 1527, 1366, 1173, 1055, 1005, 755 cm^{-1}; HRMS (ESI): m/z calculated for $C_{14}H_{19}NO_3Na^+$ $[M+Na]^+$ 272.1257, found 272.1257.

The product **3a** (89.3 mg, 0.36 mmol) was dissolved in 10 mL anhydrous THF and the solution was cooled in an ice-bath. Triphenylphosphane (188.6 mg, 0.72 mmol), diisopropyl azodicarboxylate (0.14 mL, 0.72 mmol) and diphenylphosphoryl azide (0.16 mL, 0.72 mmol) were added to the solution in sequence. The reaction was stirred at 0 ^{o}C for 2 h and then warmed to room temperature. The solution was extracted by EtOAc and washed with water. The organic

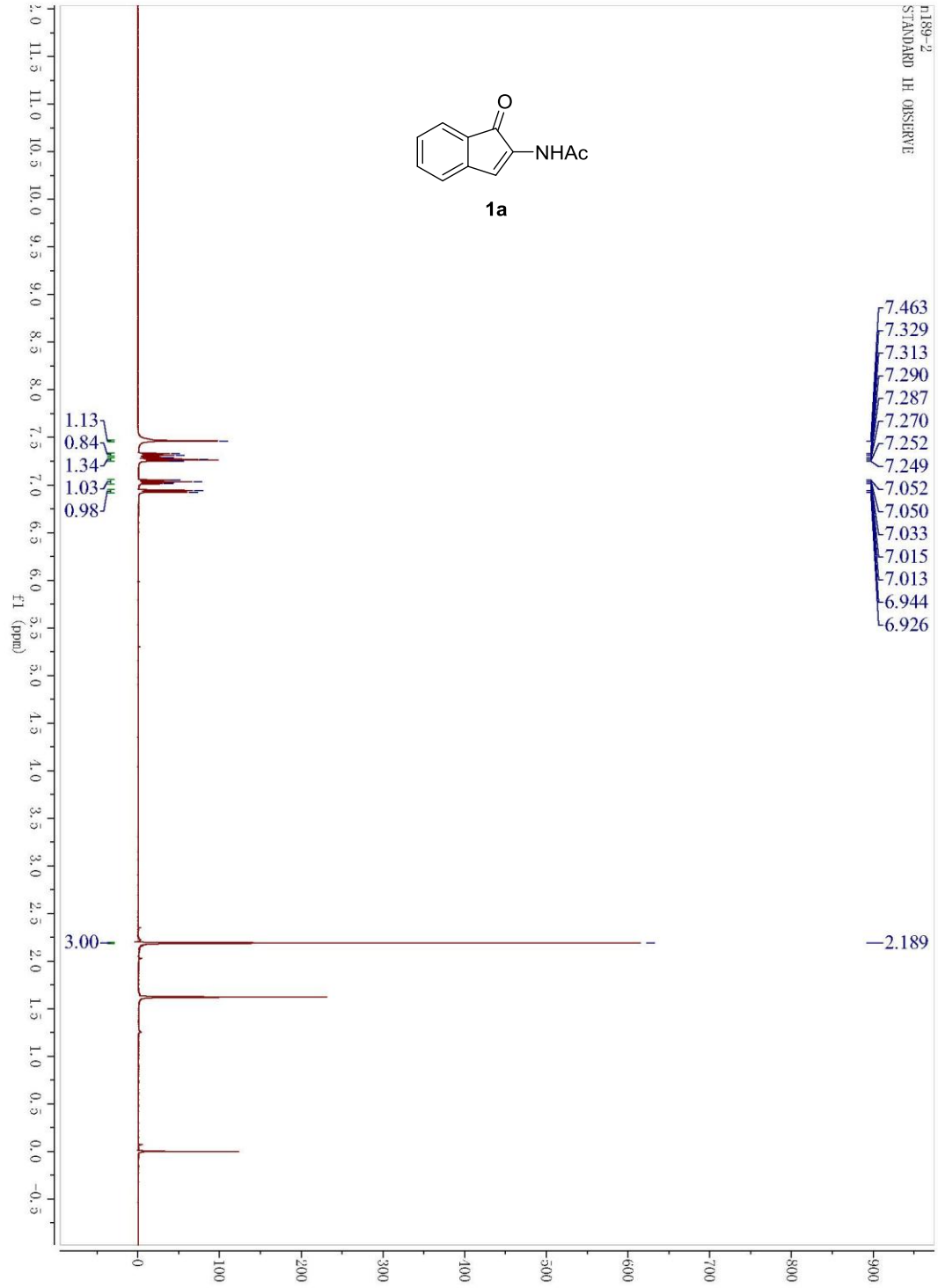
phase was combined, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by flash chromatography (eluent PE/EA = 50/1) to afford **4a** as colorless oil in 67% yield.

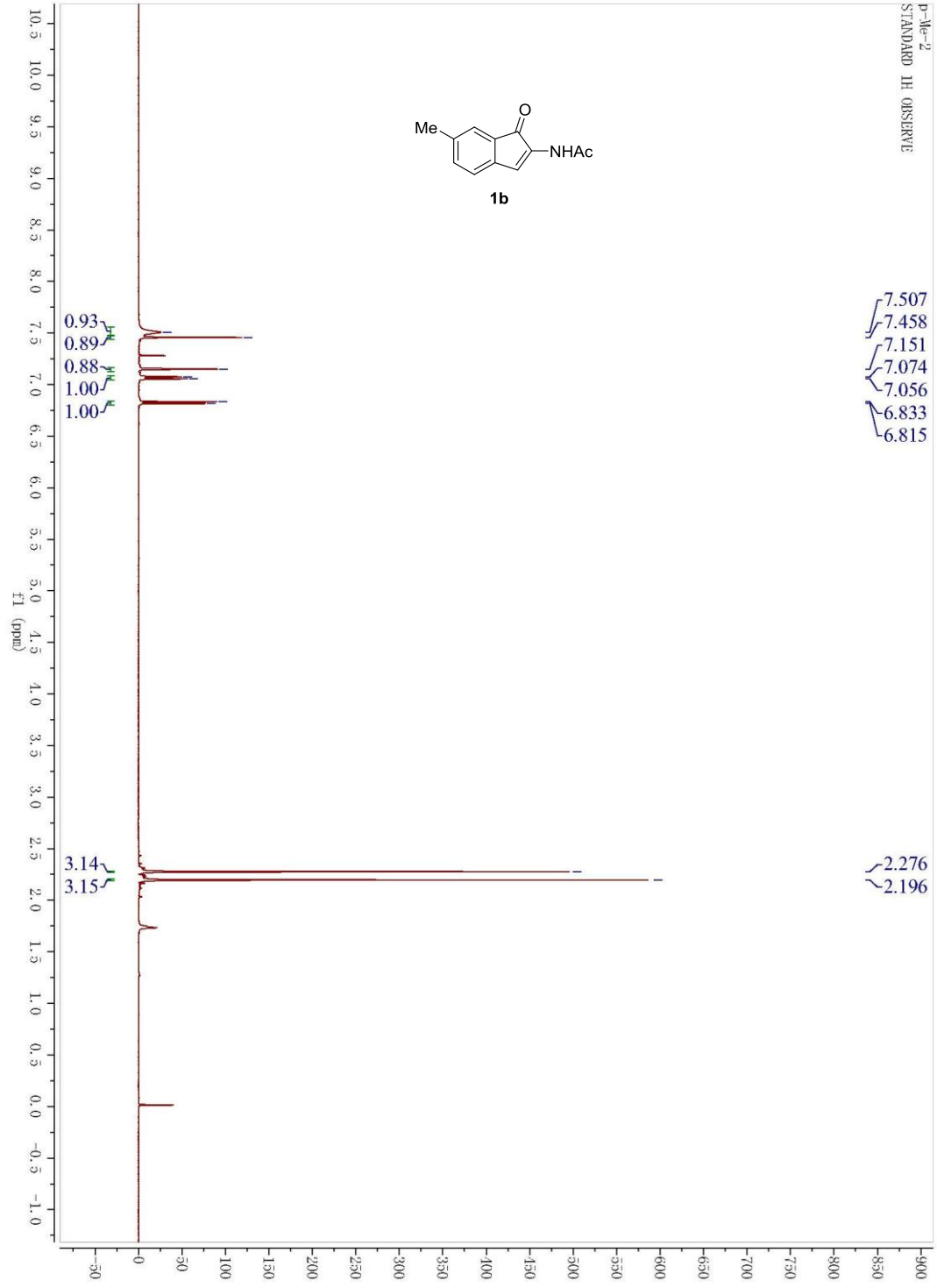
***tert*-Butyl ((1*S*,2*R*)-1-azido-2,3-dihydro-1*H*-inden-2-yl)carbamate (4a).** Colorless oil, 66.2 mg, 67% yield, 88% ee; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.50-7.38 (m, 2H), 7.35-7.19 (m, 3H), 5.00 (d, J = 5.8 Hz, 1H), 4.22 (dt, J = 14.9, 7.5 Hz, 1H), 2.94 (qd, J = 15.8, 8.8 Hz, 2H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.9, 141.8, 139.1, 129.7, 127.4, 126.4, 125.3, 78.5, 66.1, 54.8, 35.0, 28.7; HPLC conditions: DAICEL Chiralpak IC-3 column, Hexene/*i*-PrOH = 98/2, 220 nm, 1.0 mL/min, 25 ^{o}C, t_{major} = 10.5 min, t_{minor} = 12.1 min.

7. Reference

[1] Zhang, Z.; Hu, Q.; Wang, Y.; Chen, J.; Zhang, W. *Org. Lett.* **2015**, *17*, 5380.

8. NMR spectra

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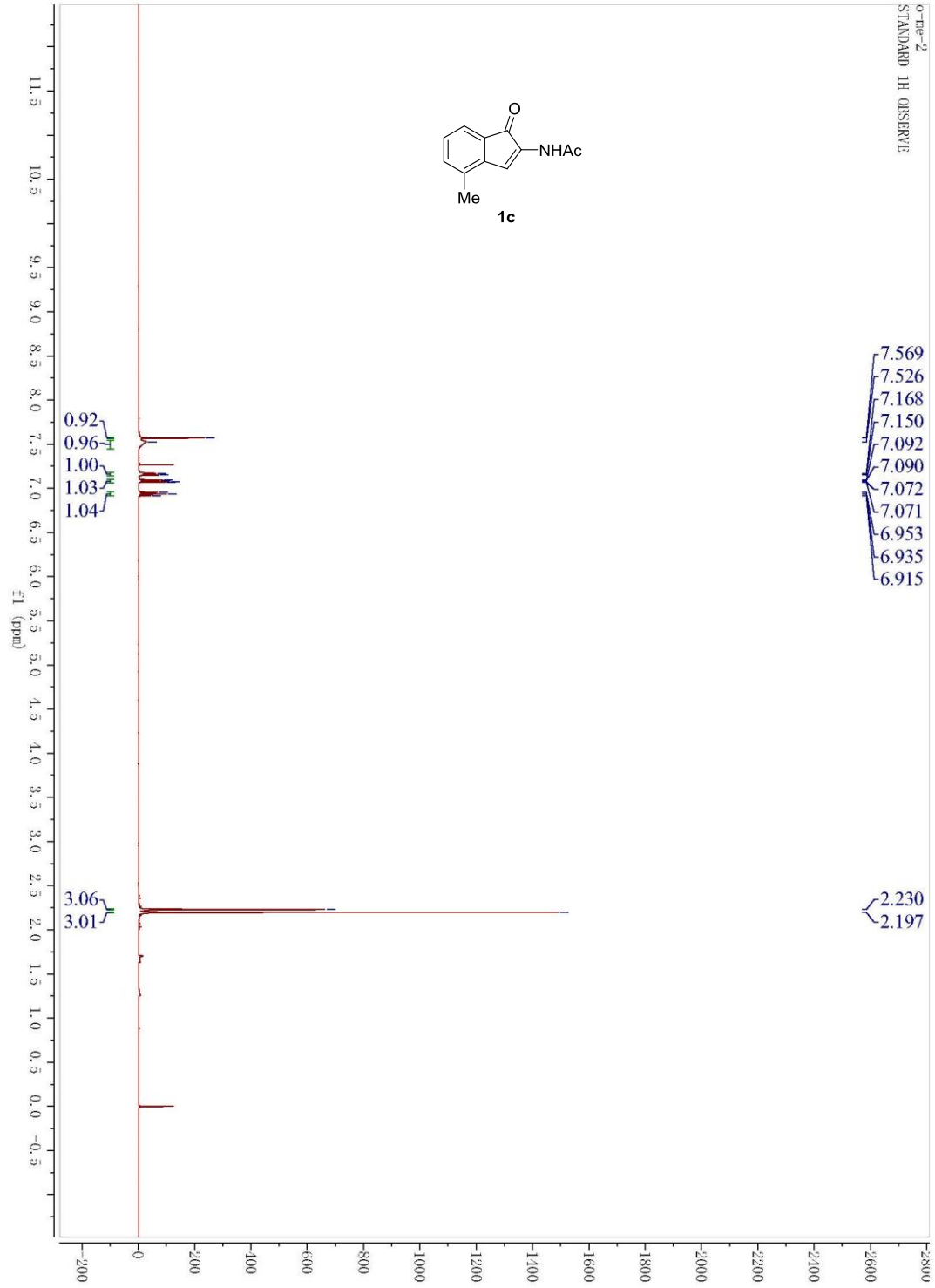
f1 (ppm)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7.071
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0.96
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3.01
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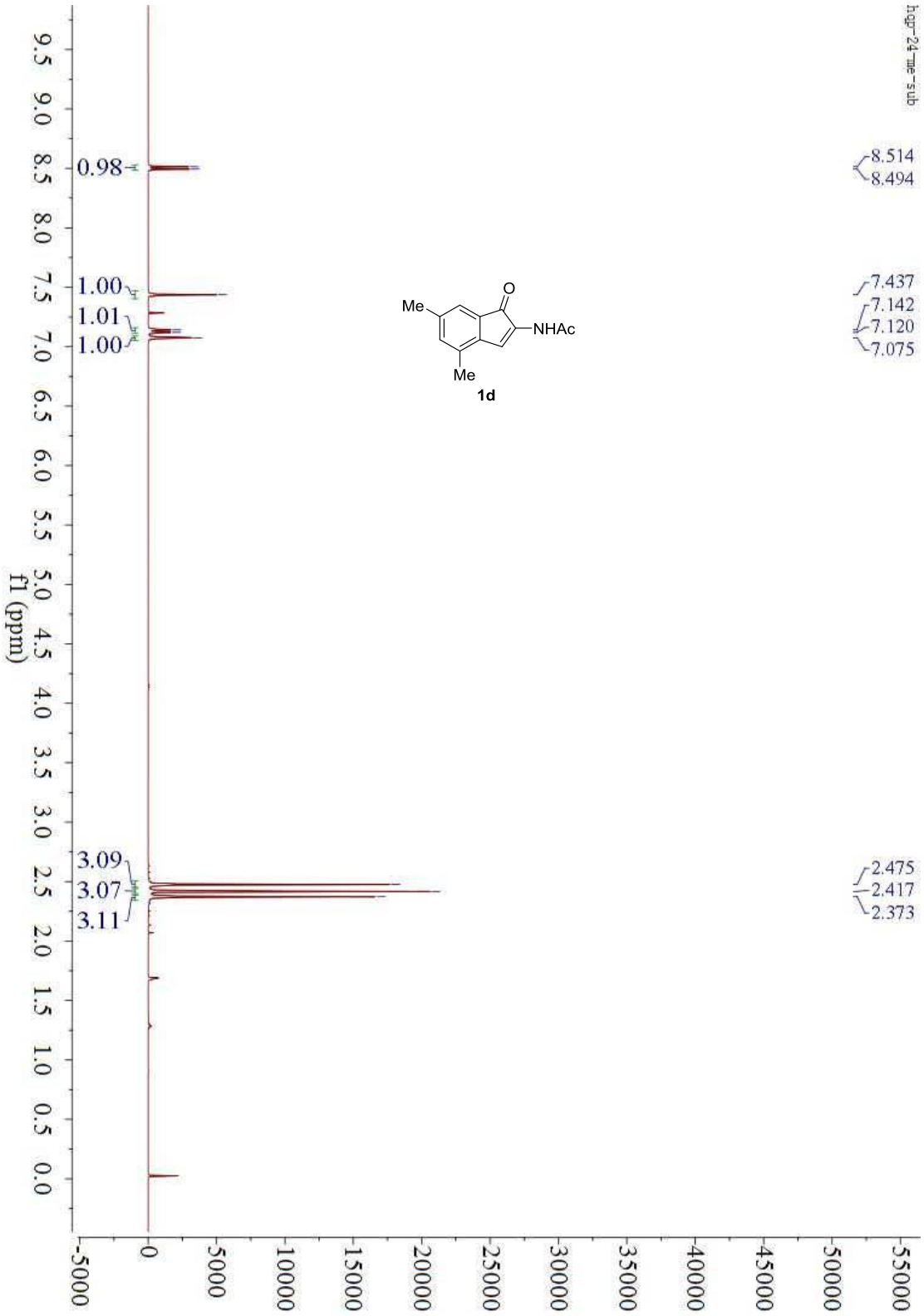
f1 (ppm)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Me
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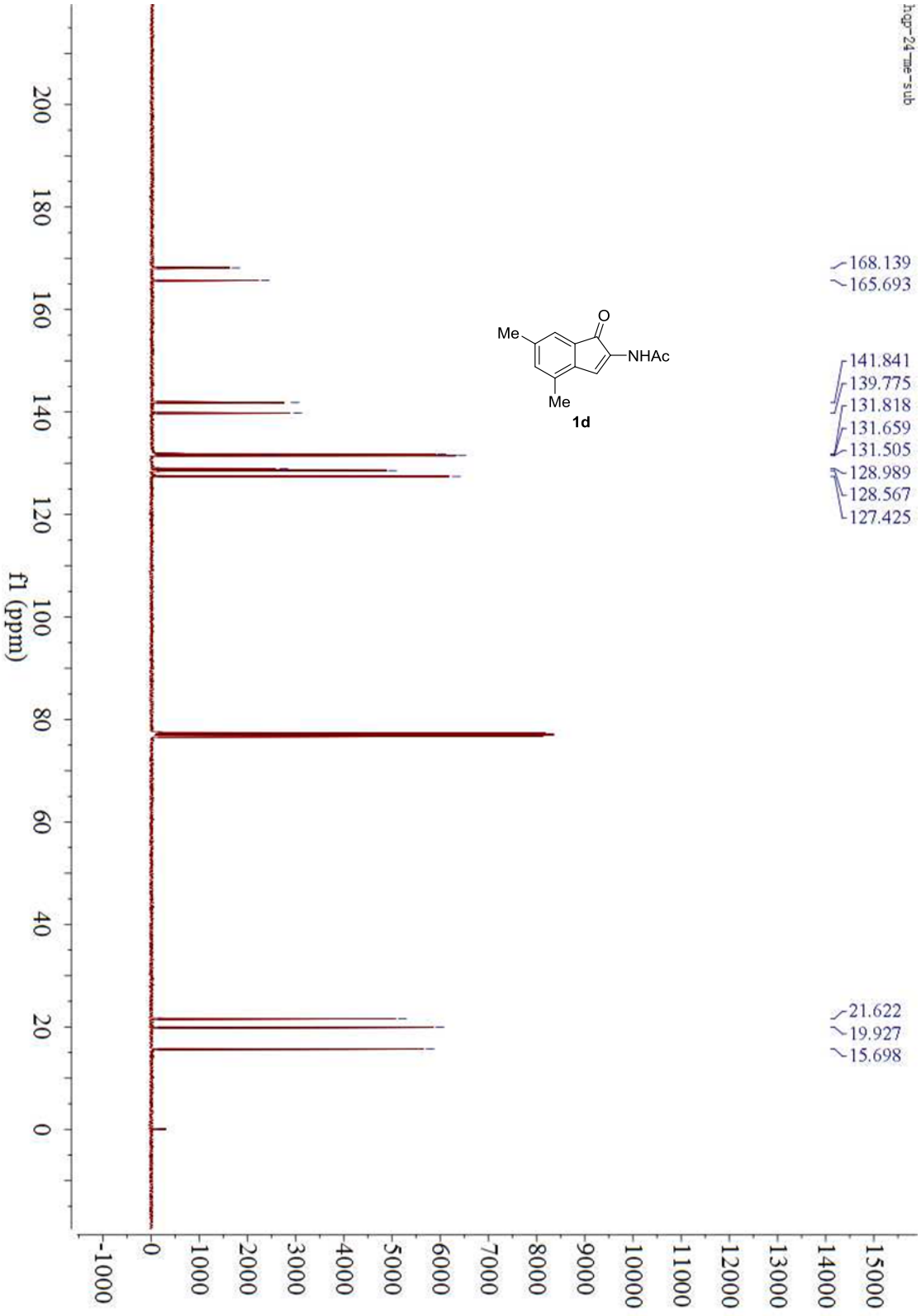
Me
1d
f1 (ppm)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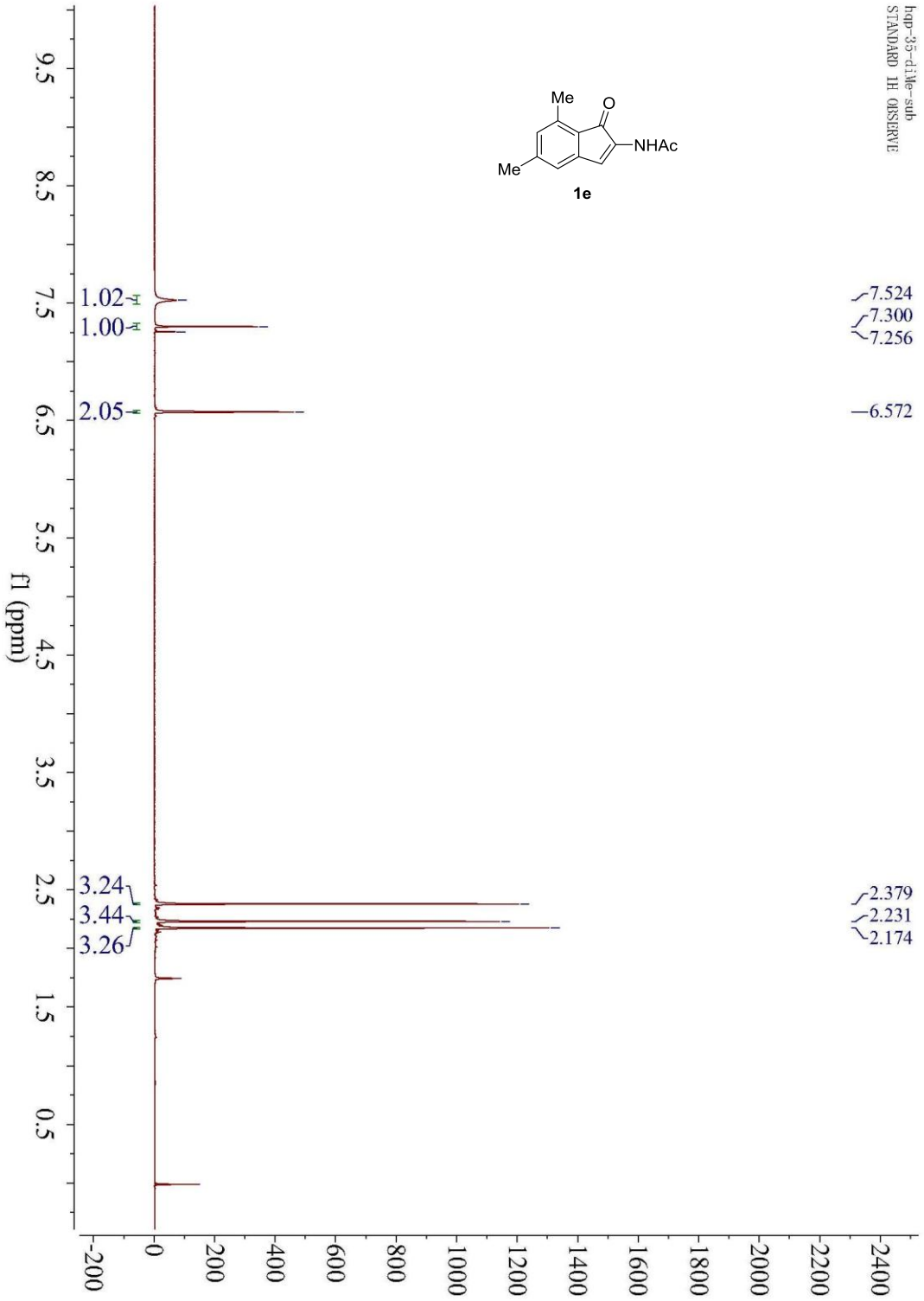
1d
f1 (ppm)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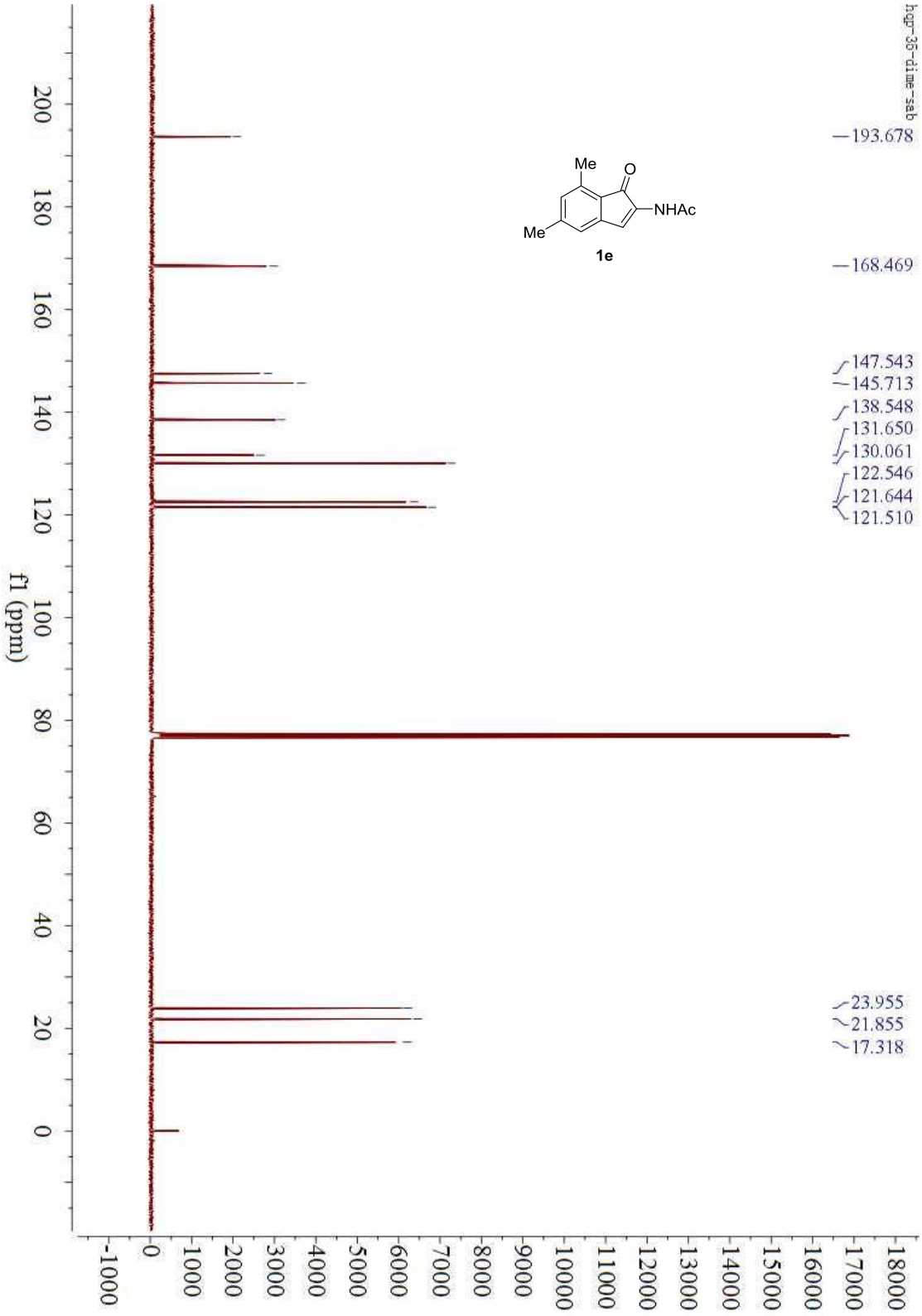
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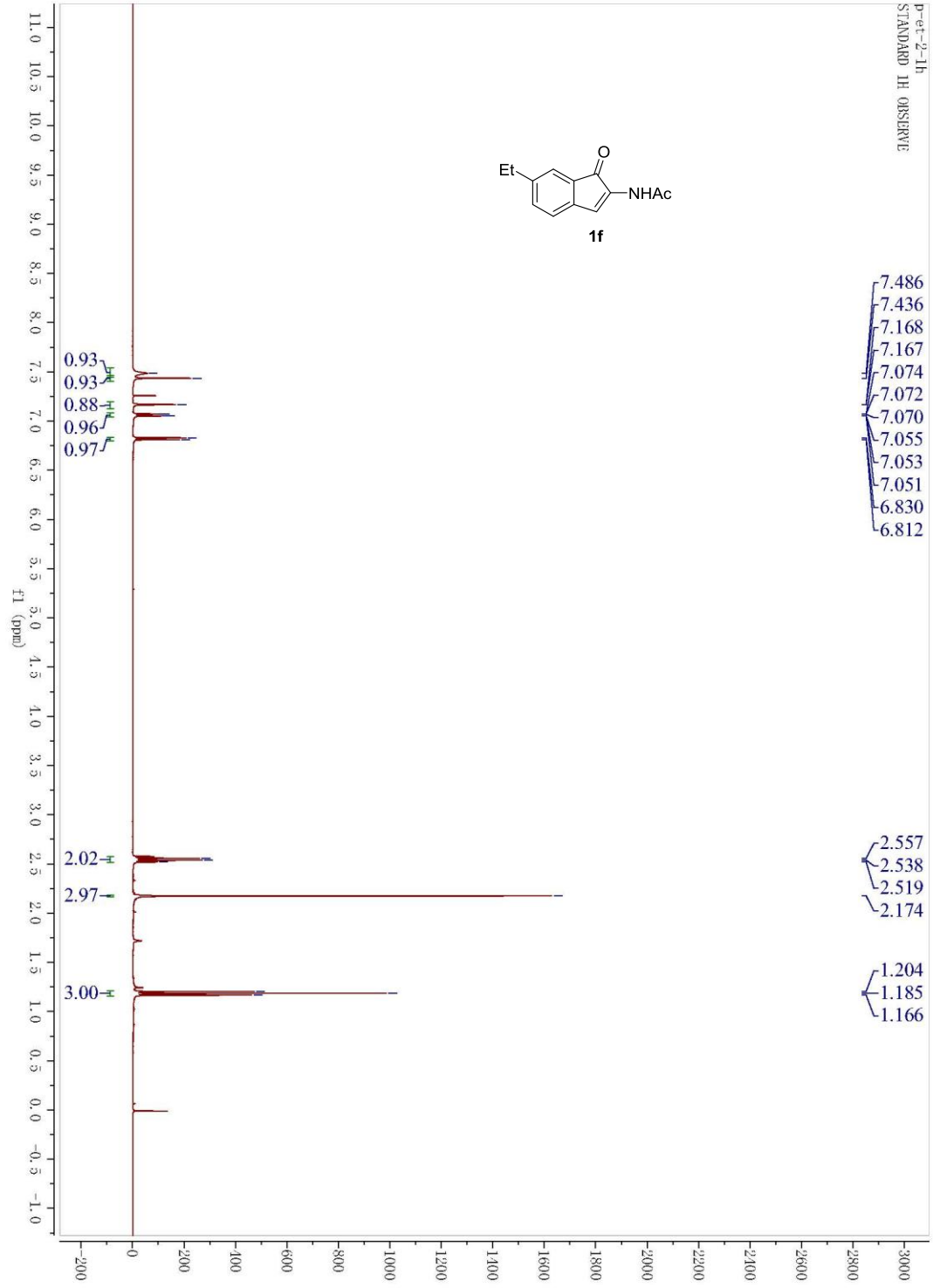
Me
1e
f1 (ppm)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0.88
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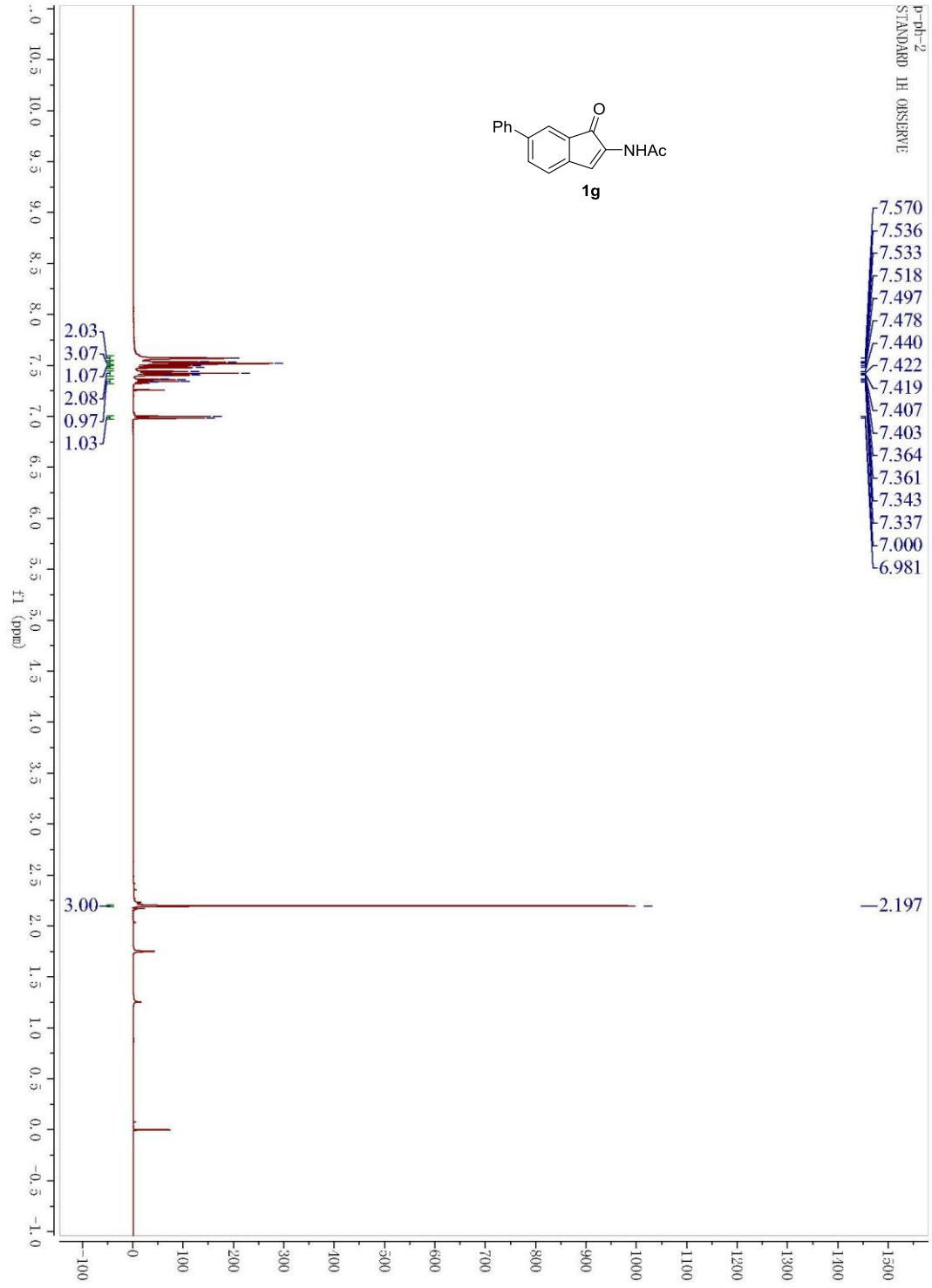
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7.361
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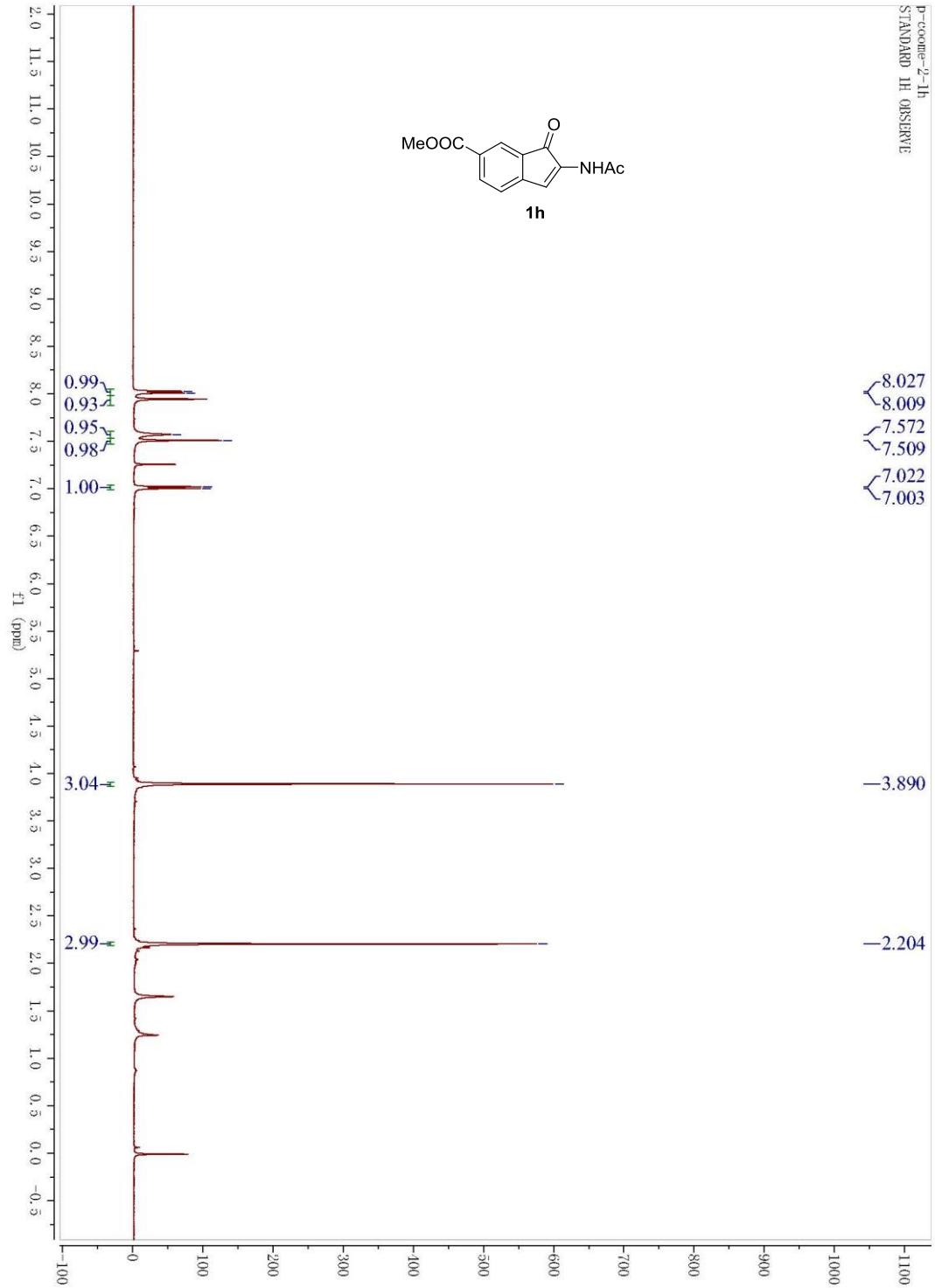
f1 (ppm)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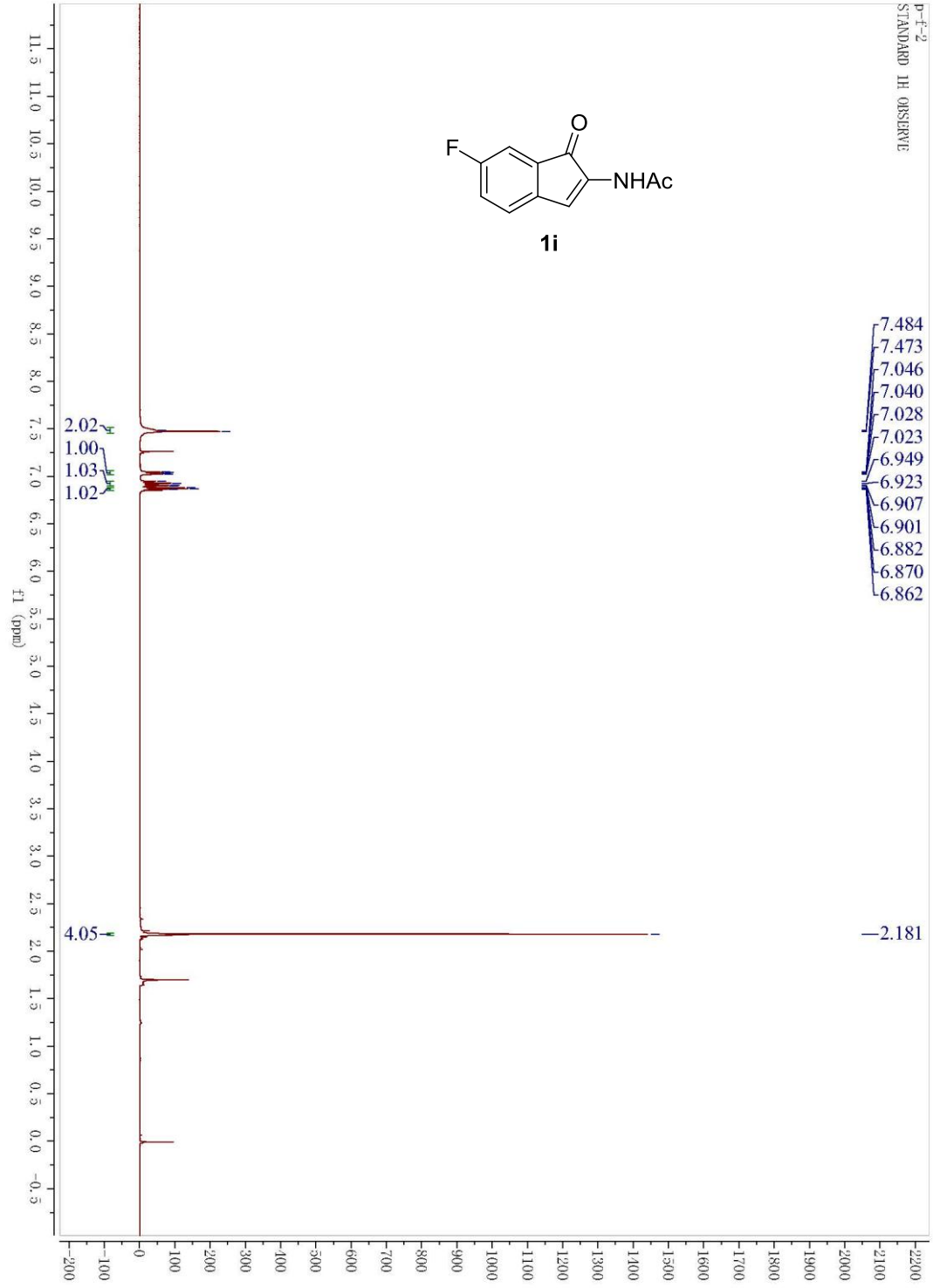
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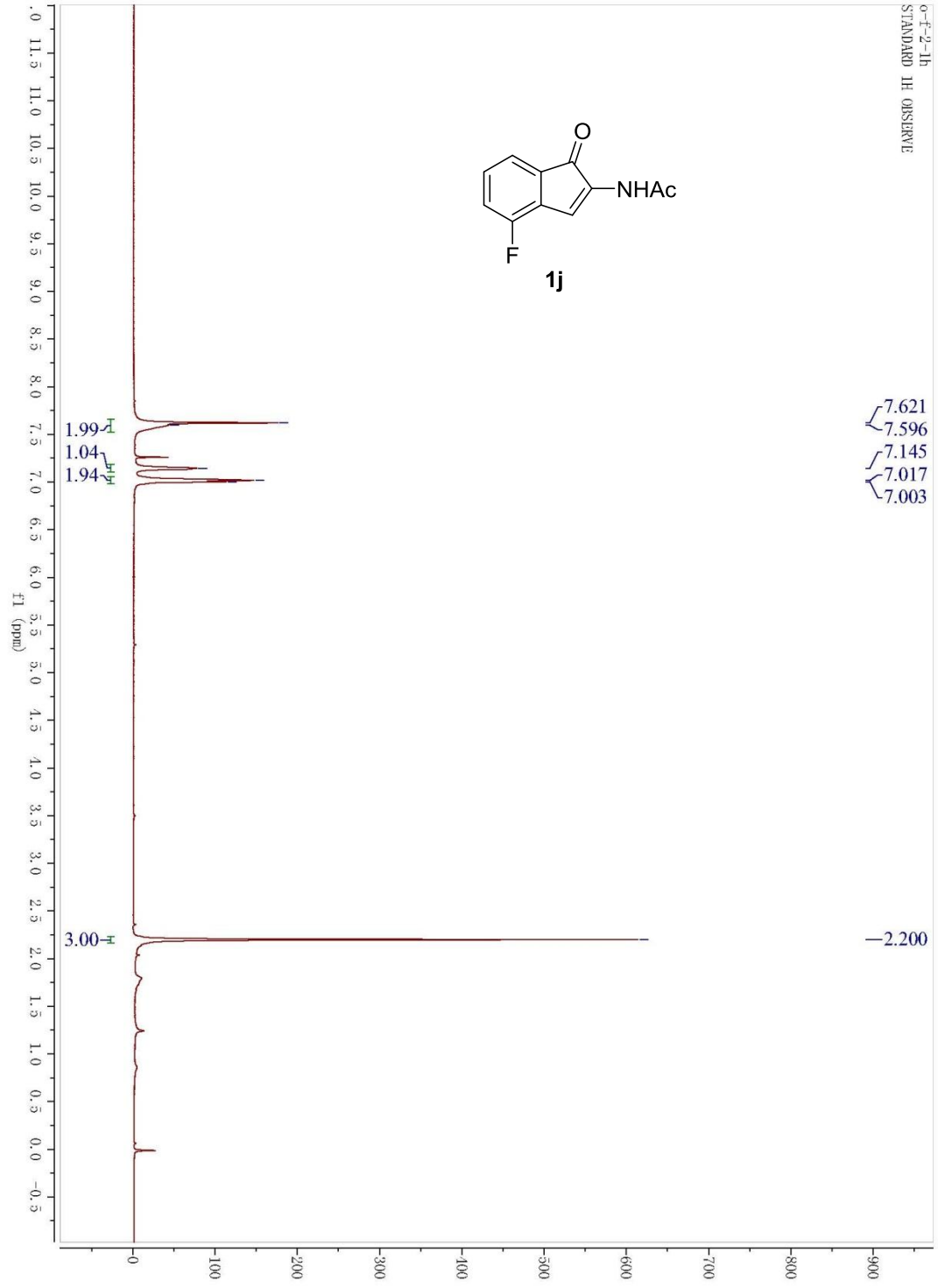
f1 (ppm)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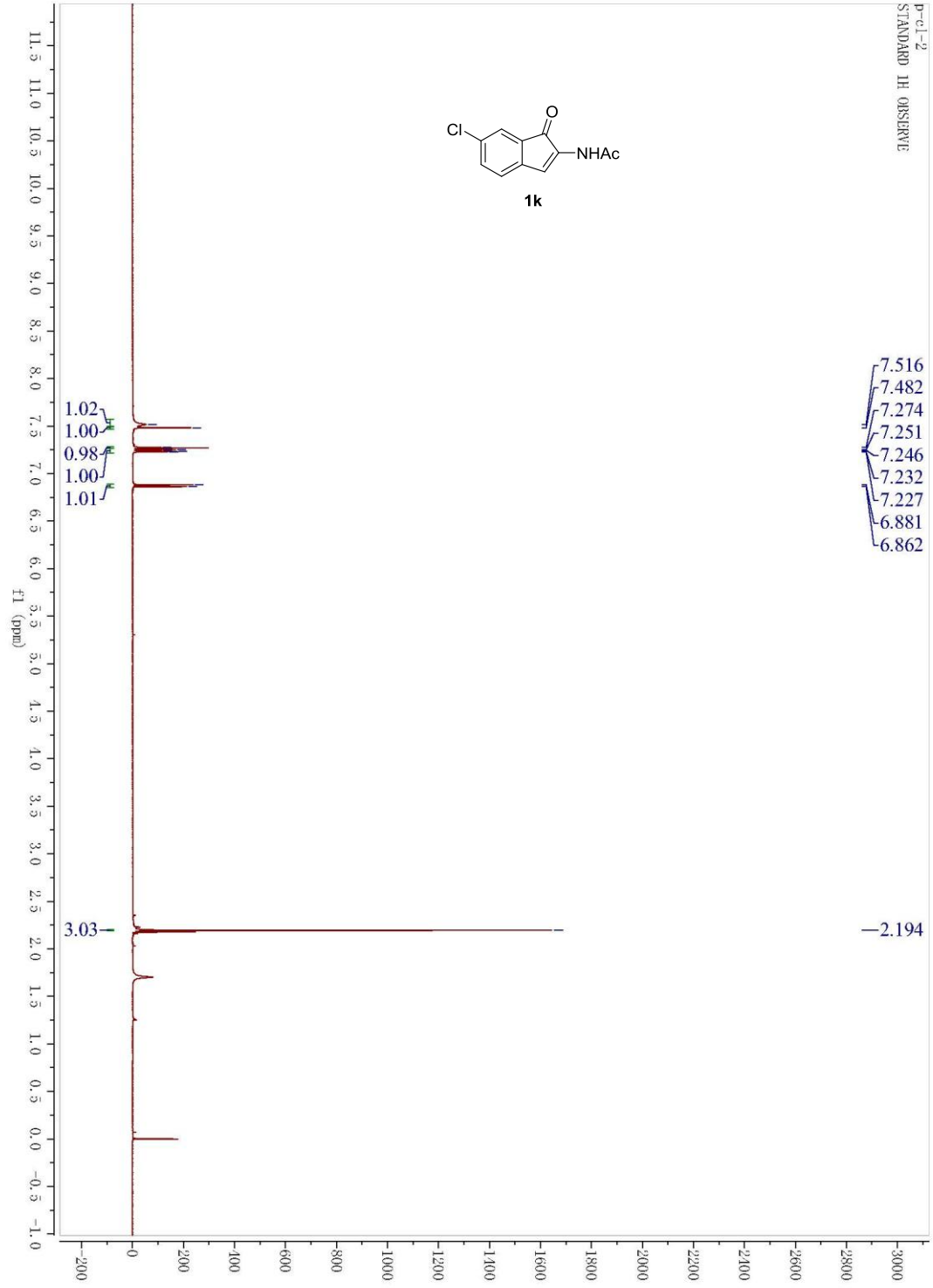
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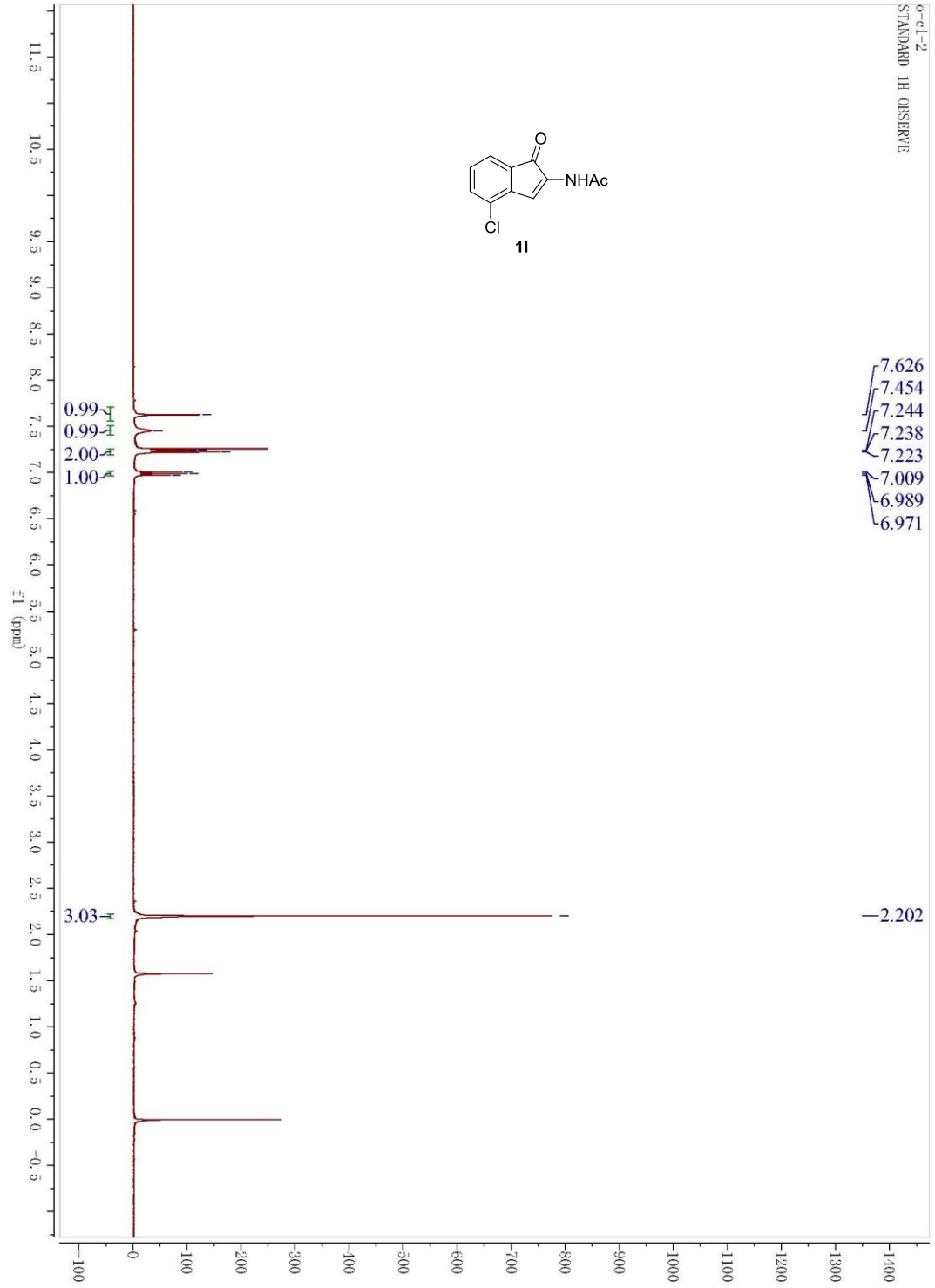
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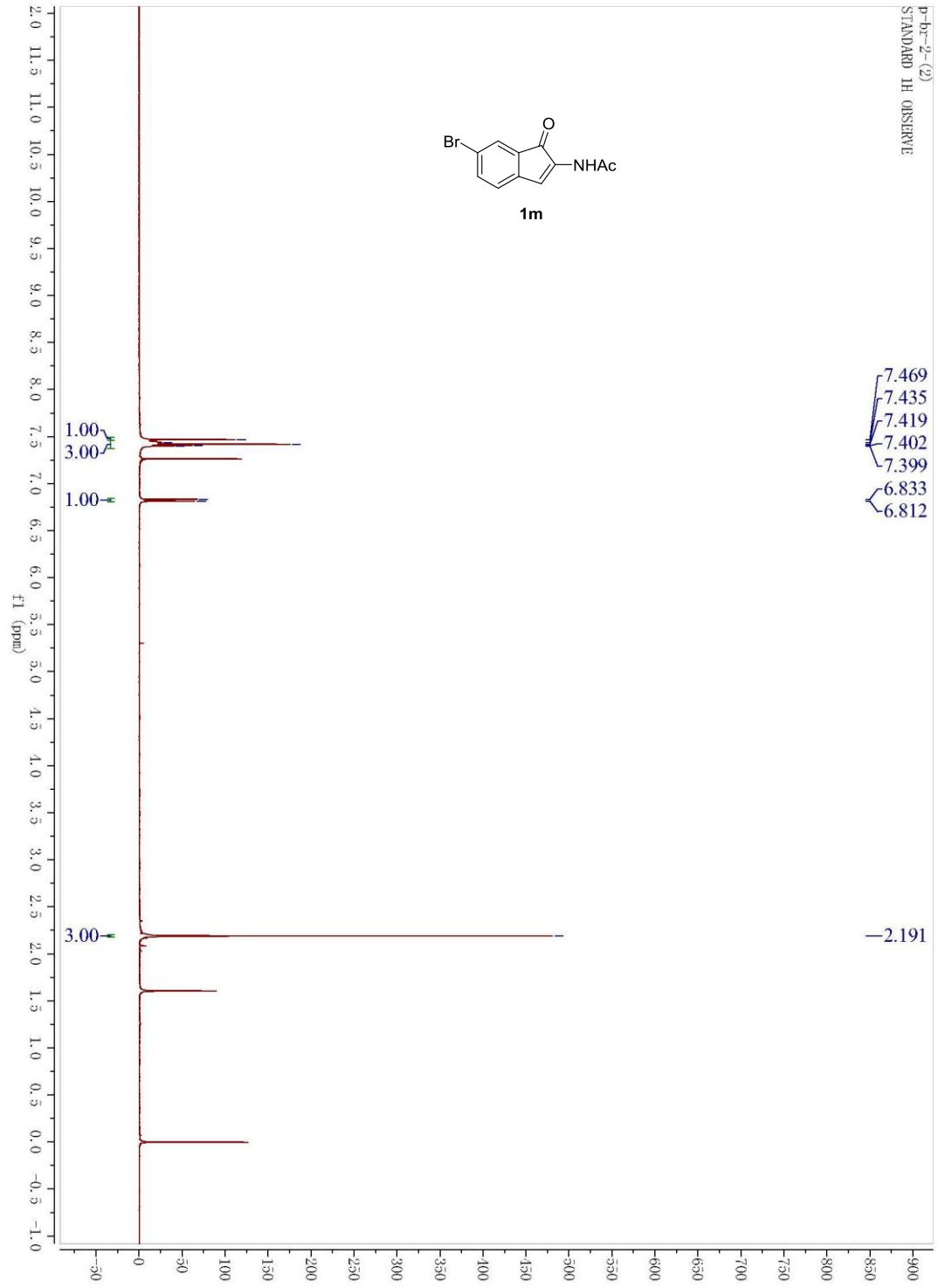
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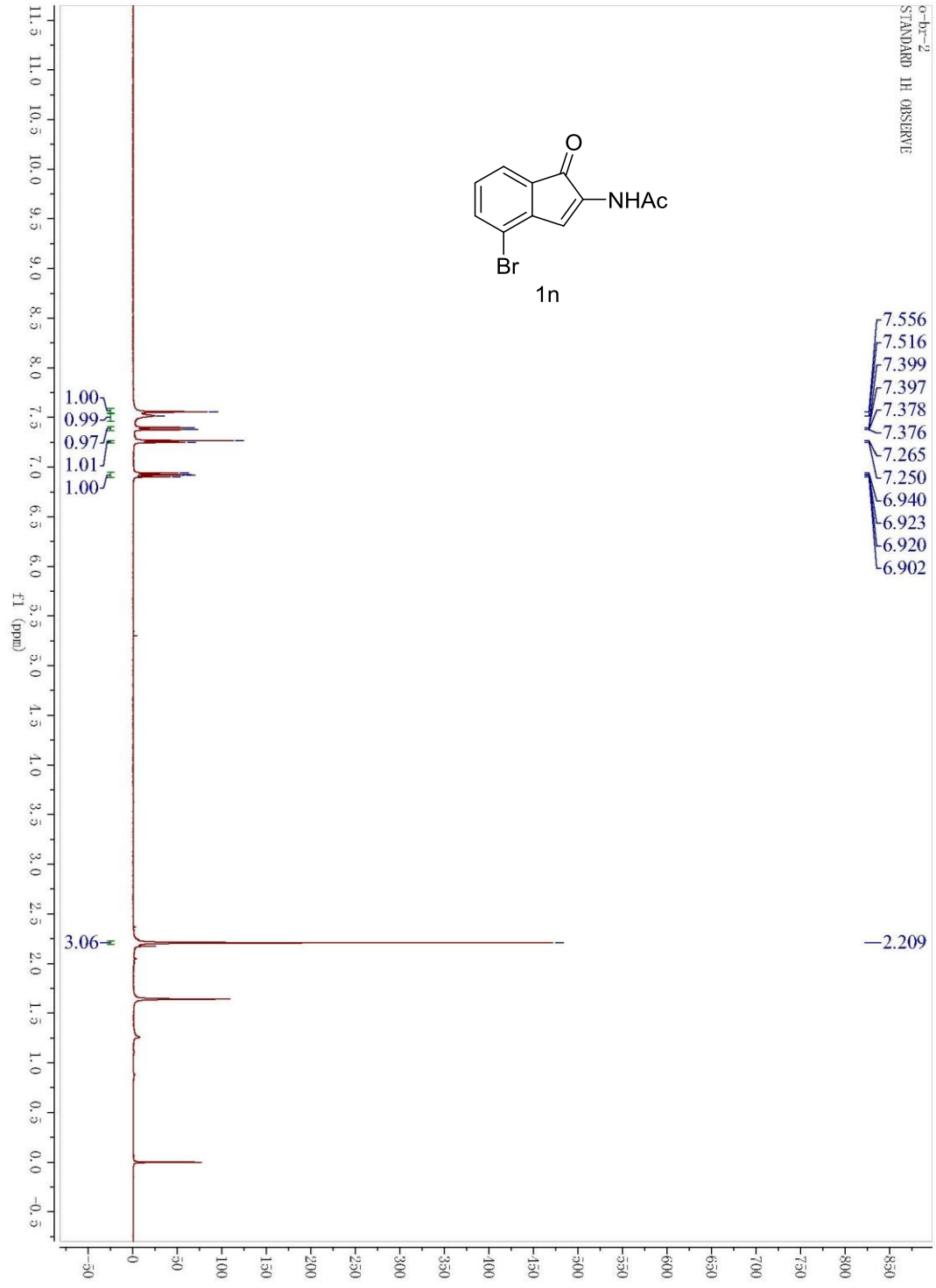
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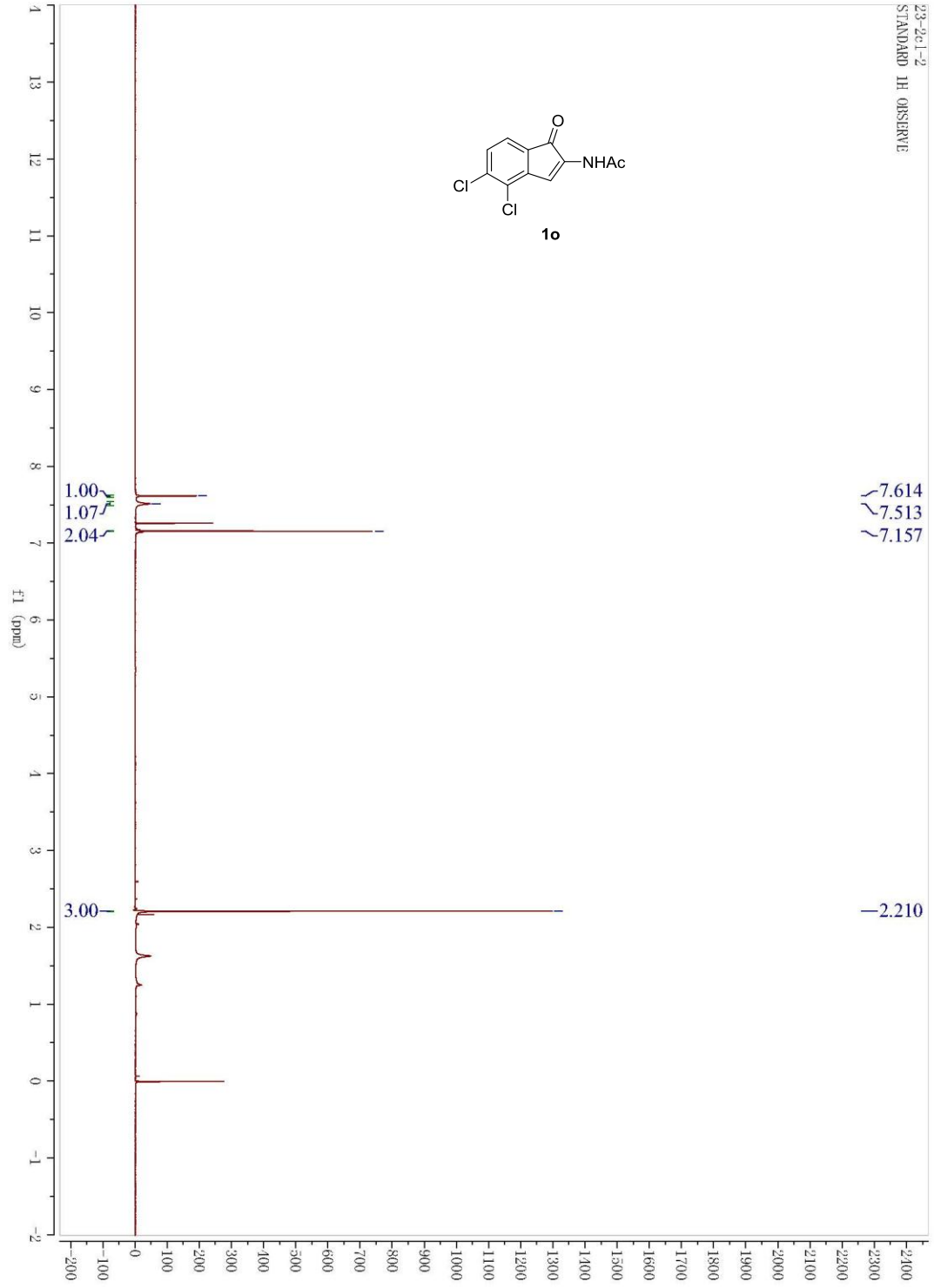
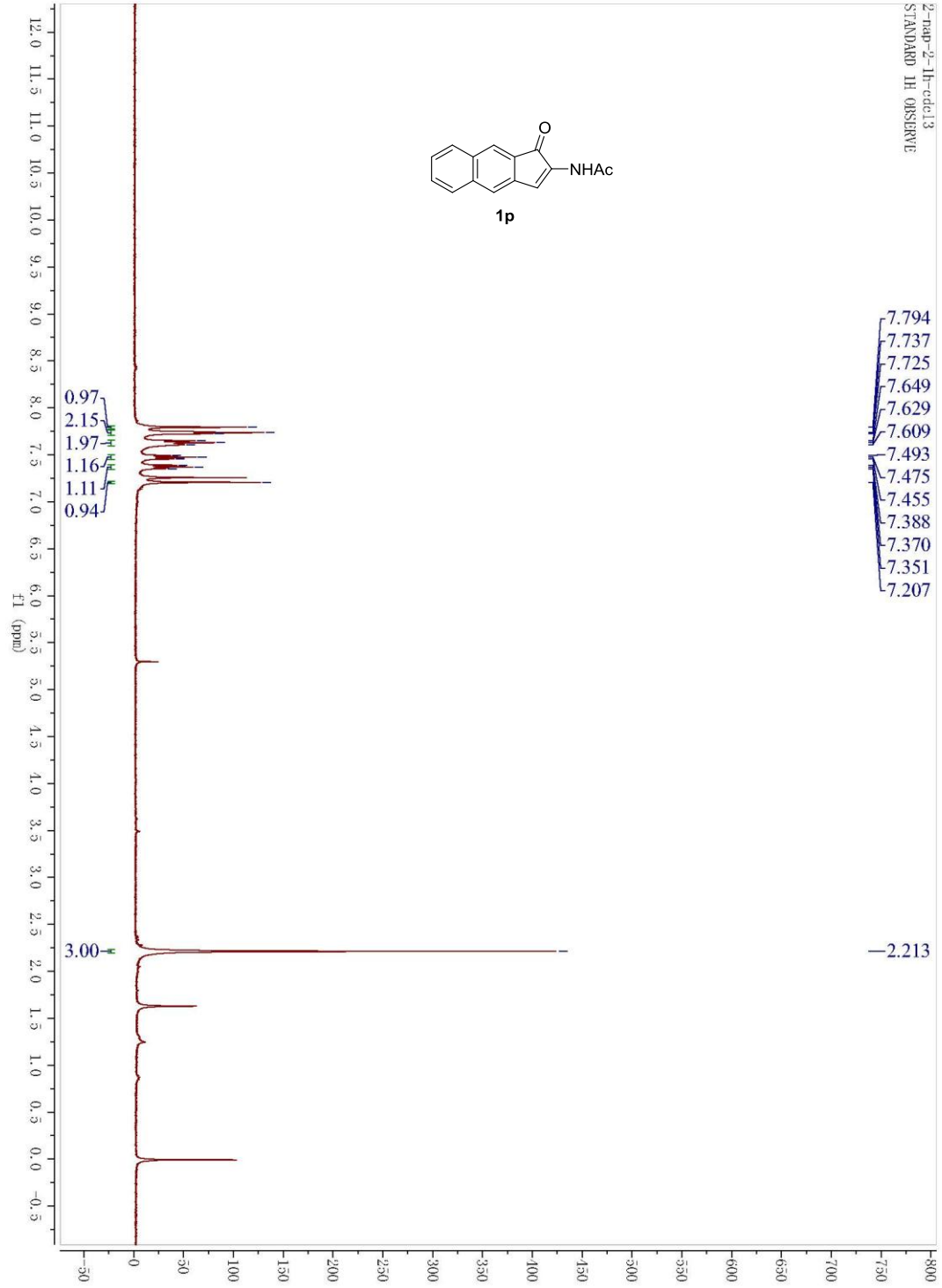
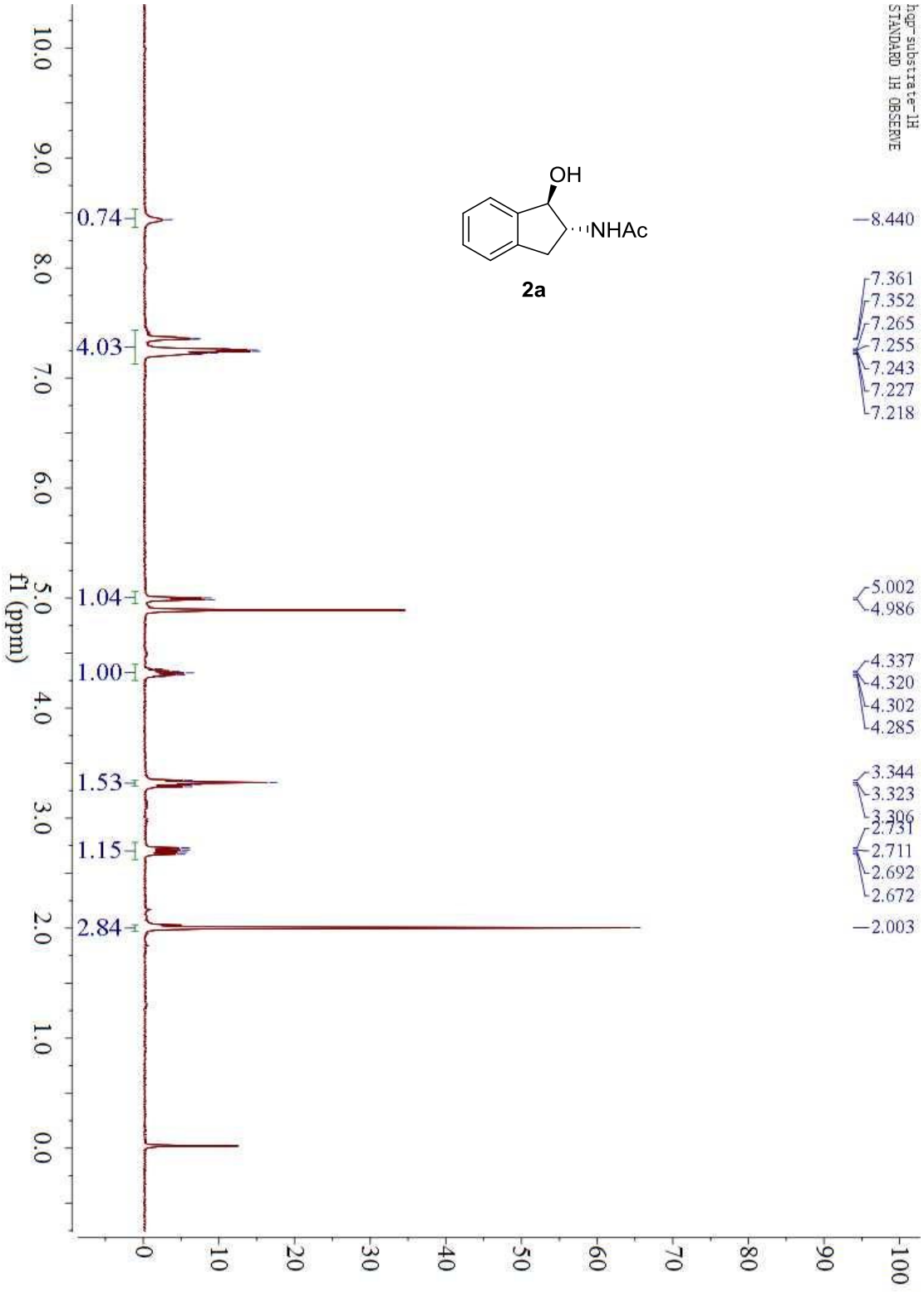
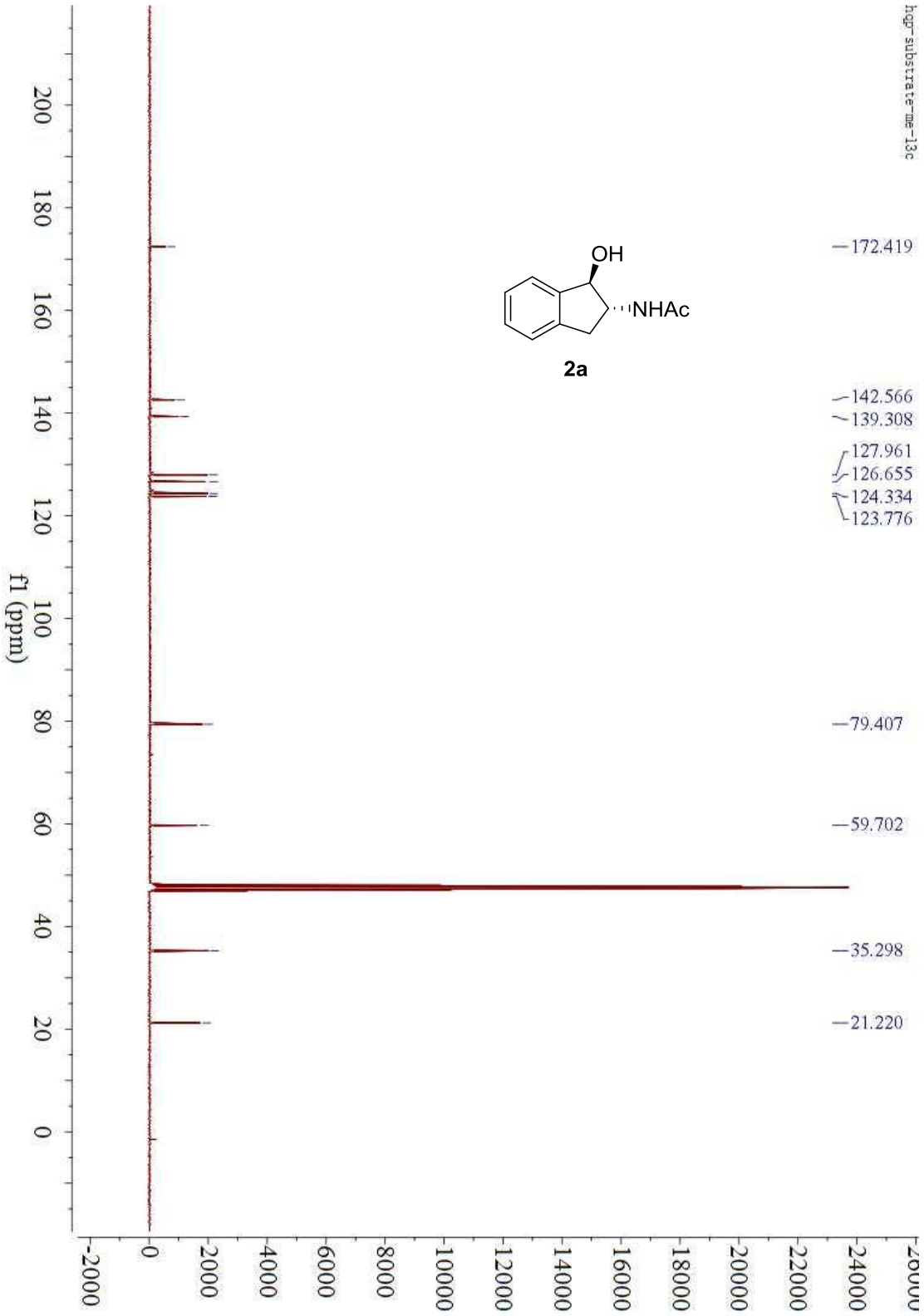
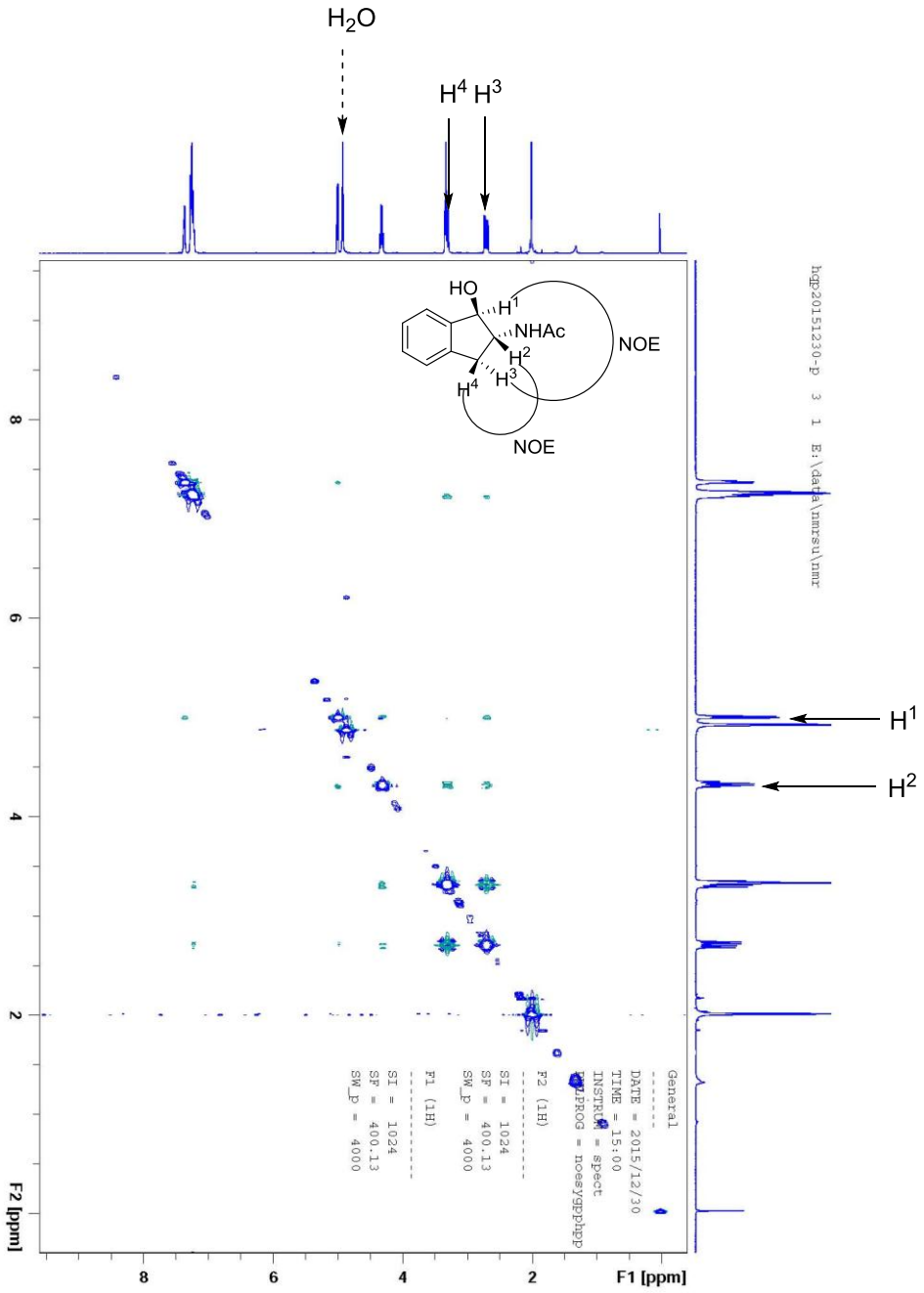
6.923
6.920
6.902
2.209
1.00
0.99
0.97
1.01
1.00
3.06
f1 (ppm)

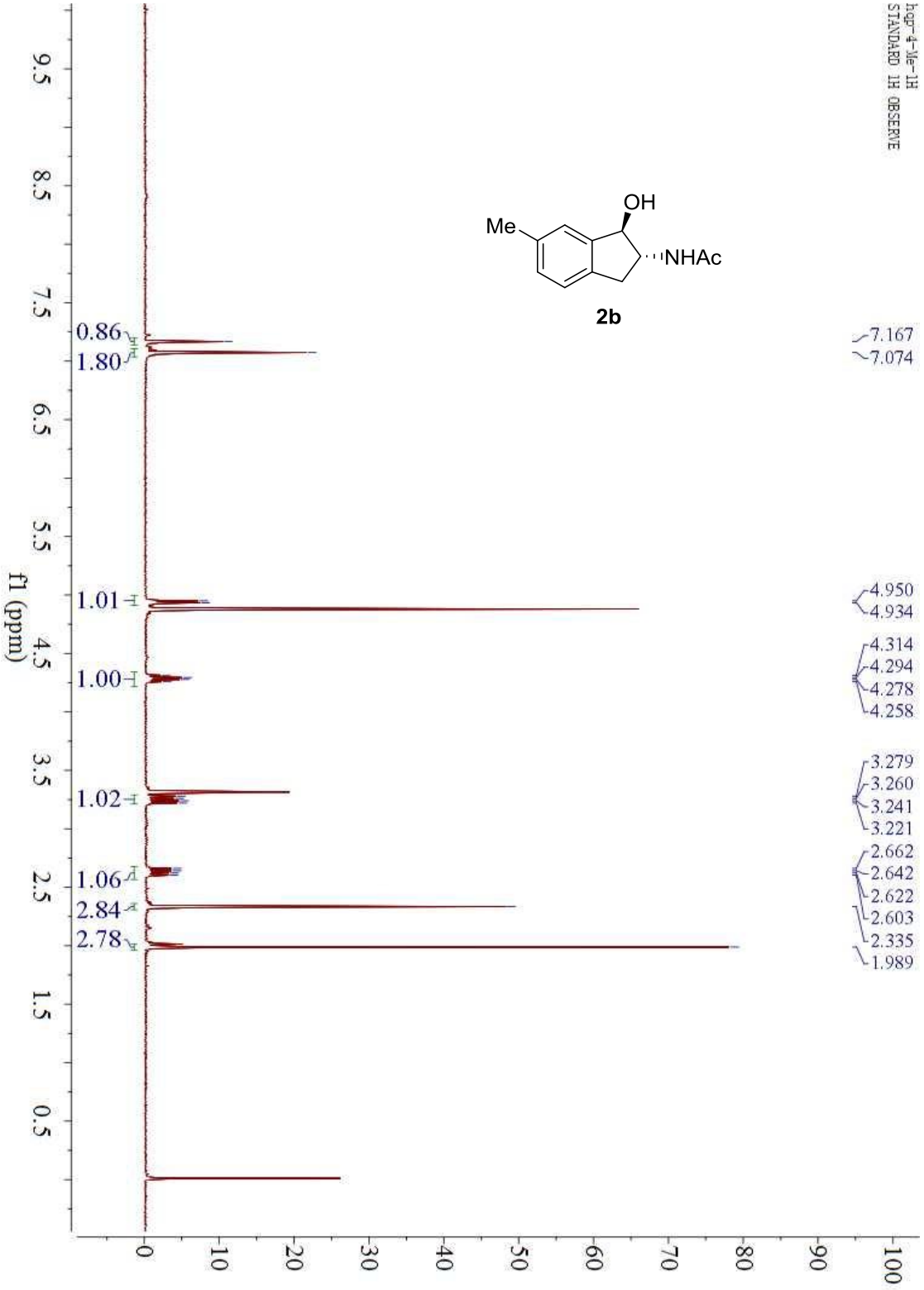

23-2c1-2
STANDARD 1H OBSERVE
O
NHAc
Cl
Cl
1o
1.00
1.07
2.04
3.00
7.614
7.513
7.157
2.210
f1 (ppm)

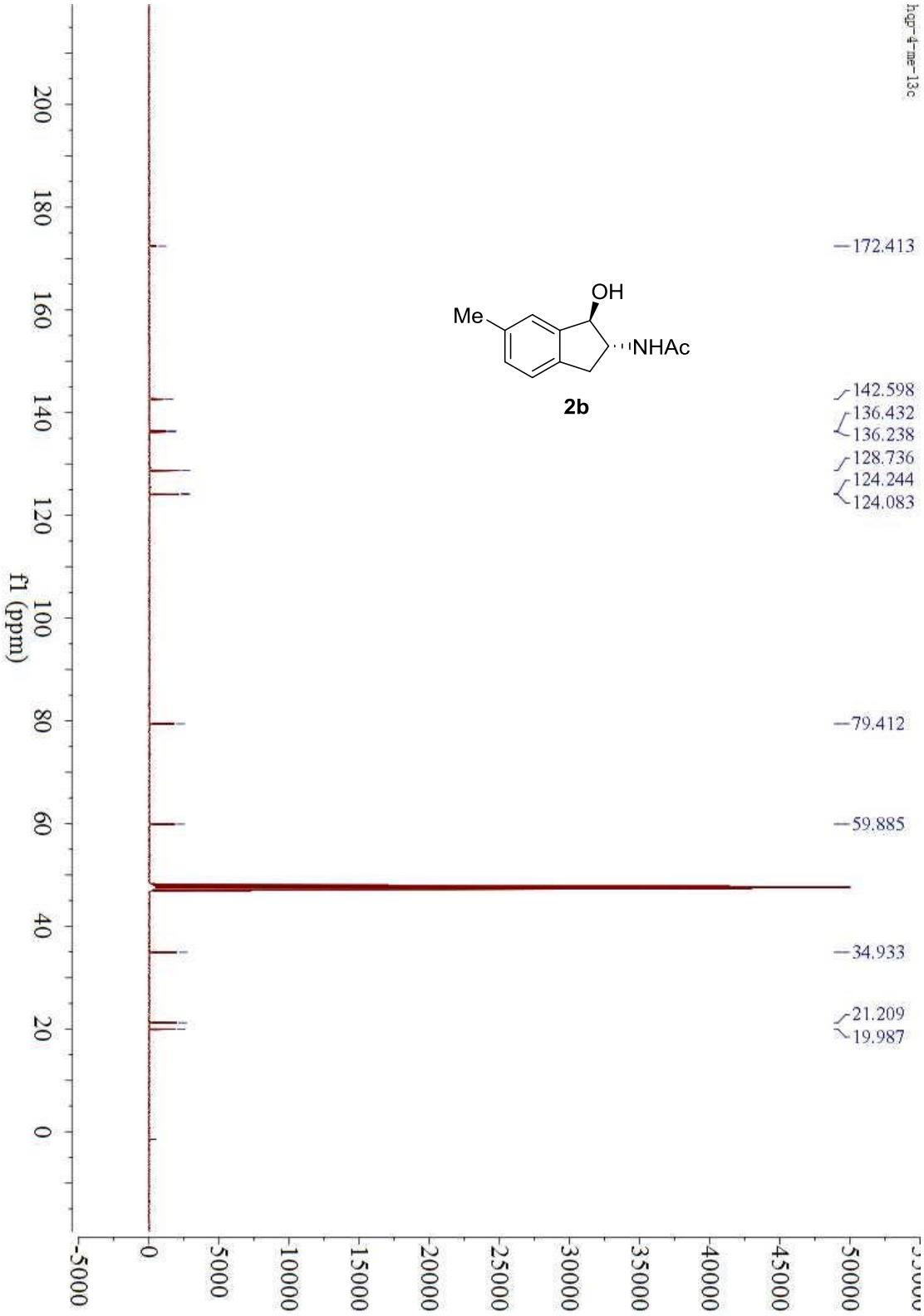

2-nap-2-1h-cdcl3
STANDARD 1H OBSERVE
O
NHAc
1p
7.794
7.737
7.725
7.649
7.629
7.609
7.493
7.475
7.455
7.388
7.370
7.351
7.207
0.97
2.15
1.97
1.16
1.11
0.94
3.00
2.213
f1 (ppm)

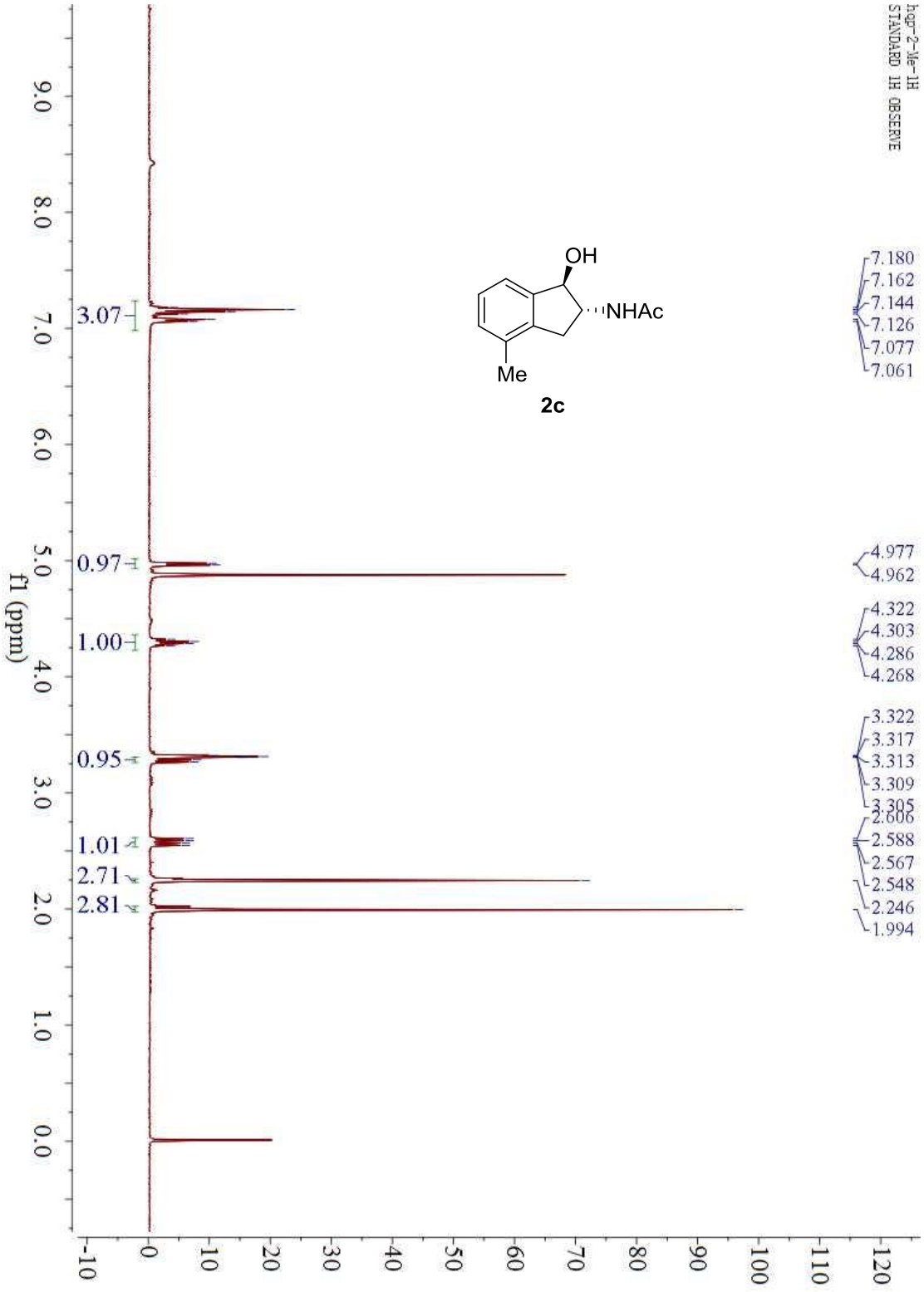

hqp-substrate-1H
STANDARD 1H OBSERVE
OH
NHAc
2a
f1 (ppm)
0.74
4.03
1.04
1.00
1.53
1.15
2.84
8.440
7.361
7.352
7.265
7.255
7.243
7.227
7.218
5.002
4.986
4.337
4.320
4.302
4.285
3.344
3.323
2.731
2.711
2.692
2.672
2.003

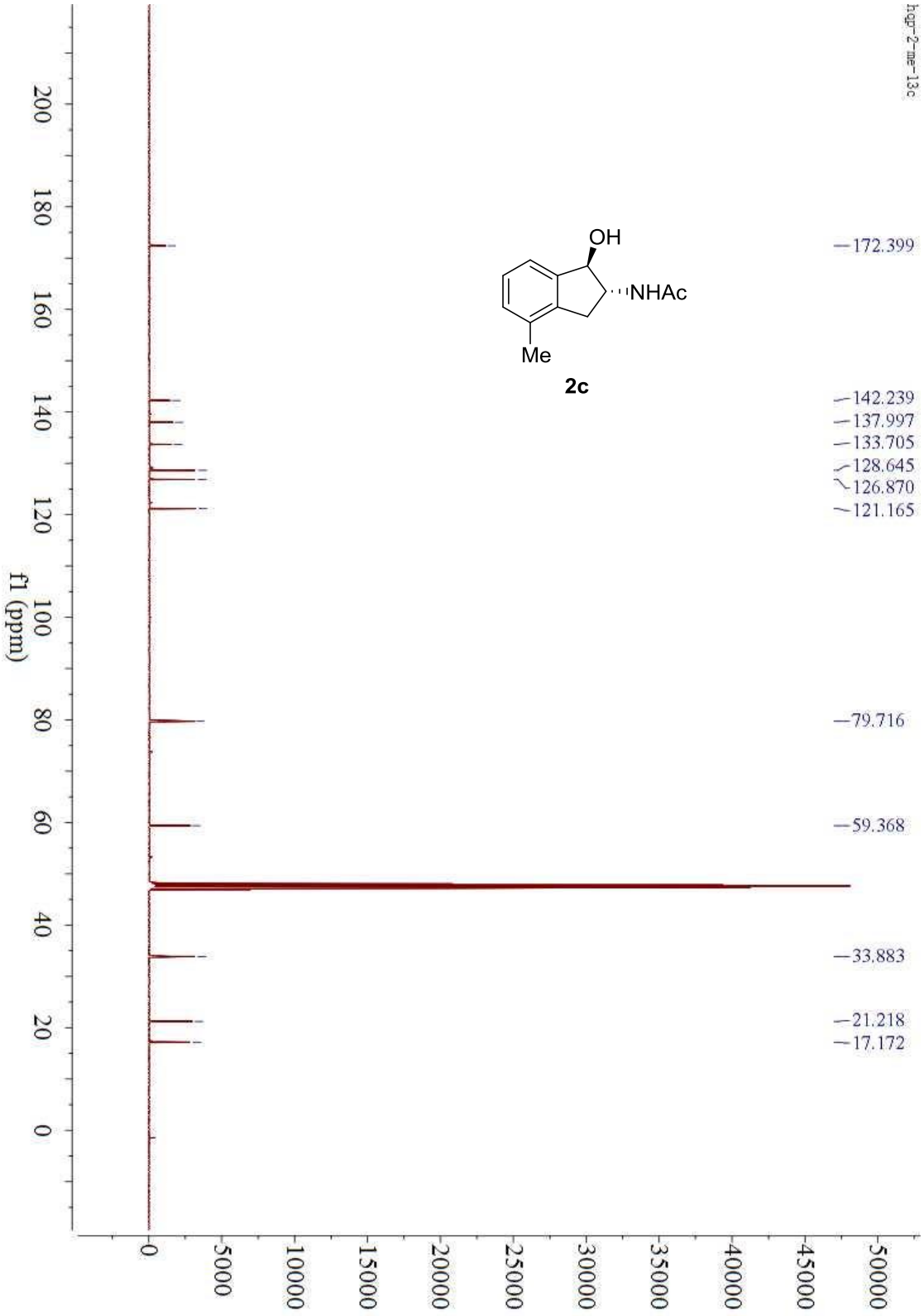

hgp-substrate-me-13c
OH
NHAc
2a
172.419
142.566
139.308
127.961
126.655
124.334
123.776
79.407
59.702
35.298
21.220
f1 (ppm)

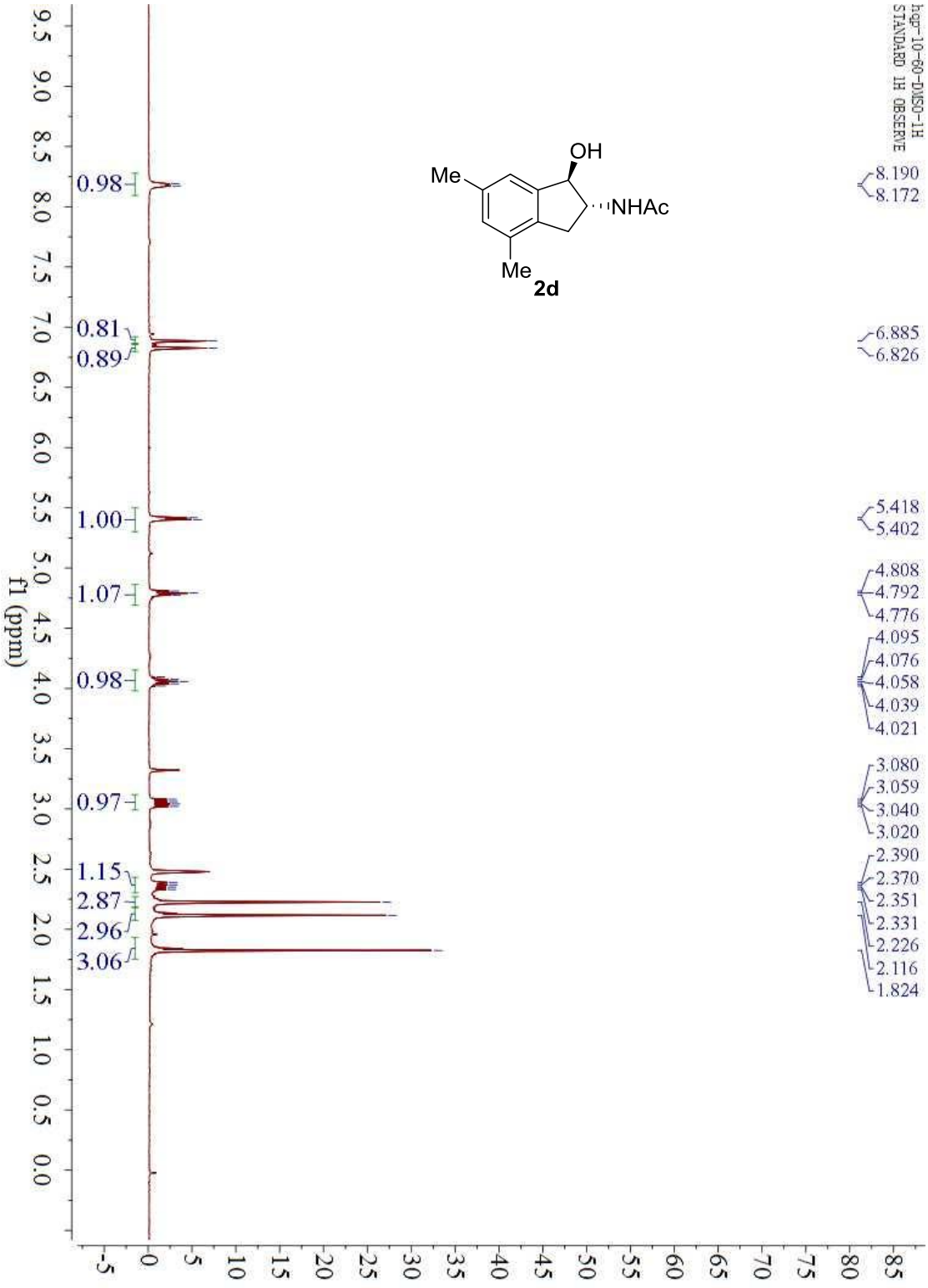

H2O
H4 H3
HO
H1
NHAc
H2
H3
H4
NOE
NOE
H1
H2
F2 [ppm]
F1 [ppm]
8
6
4
2

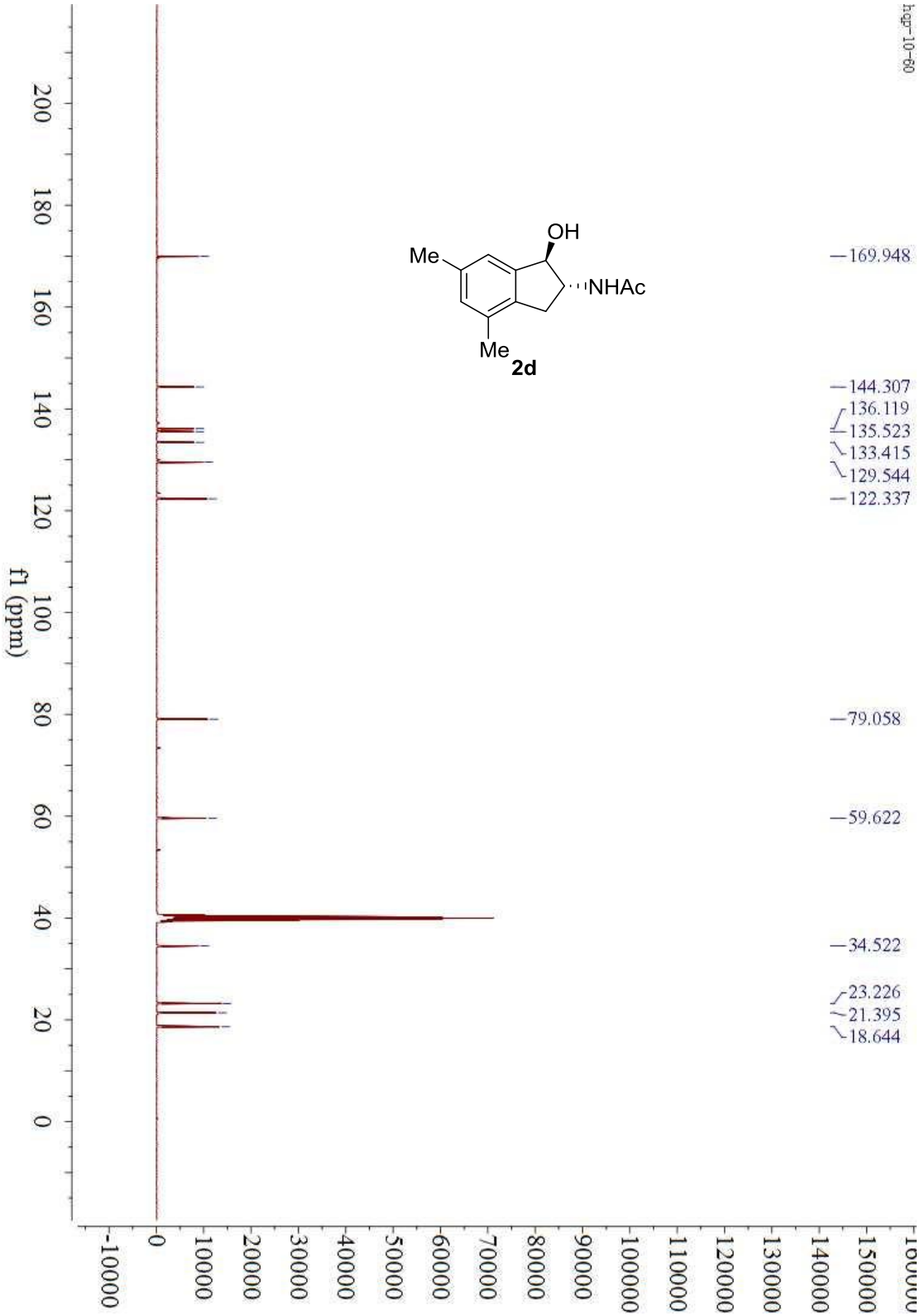

hqp-4-Me-1H
STANDARD 1H OBSERVE
OH
Me
NHAc
2b
f1 (ppm)
0.86
1.80
1.01
1.00
1.02
1.06
2.84
2.78
7.167
7.074
4.950
4.934
4.314
4.294
4.278
4.258
3.279
3.260
3.241
3.221
2.662
2.642
2.622
2.603
2.335
1.989

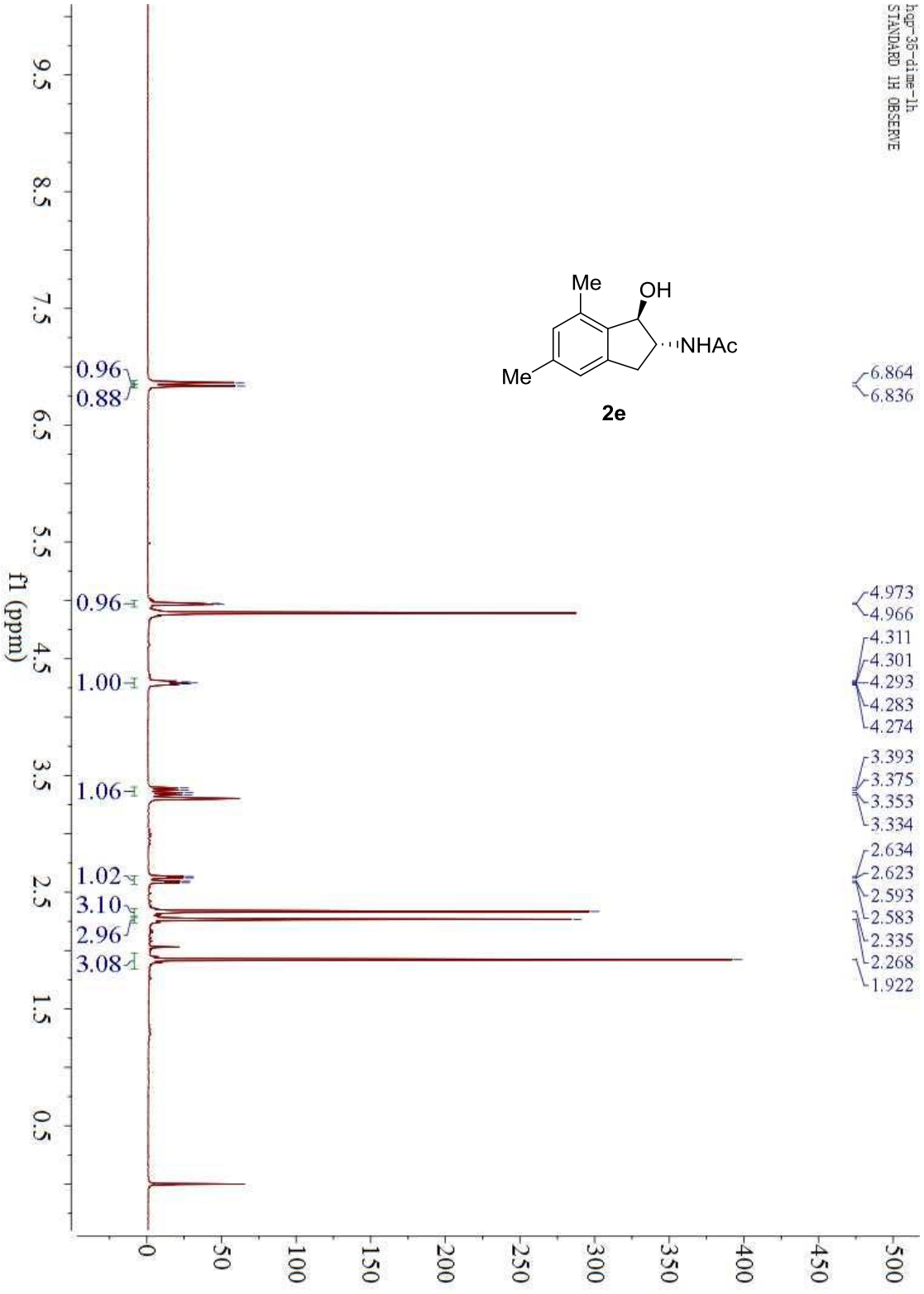

hqp-4-me-13c
OH
Me
NHAc
2b
172.413
142.598
136.432
136.238
128.736
124.244
124.083
79.412
59.885
34.933
21.209
19.987
f1 (ppm)

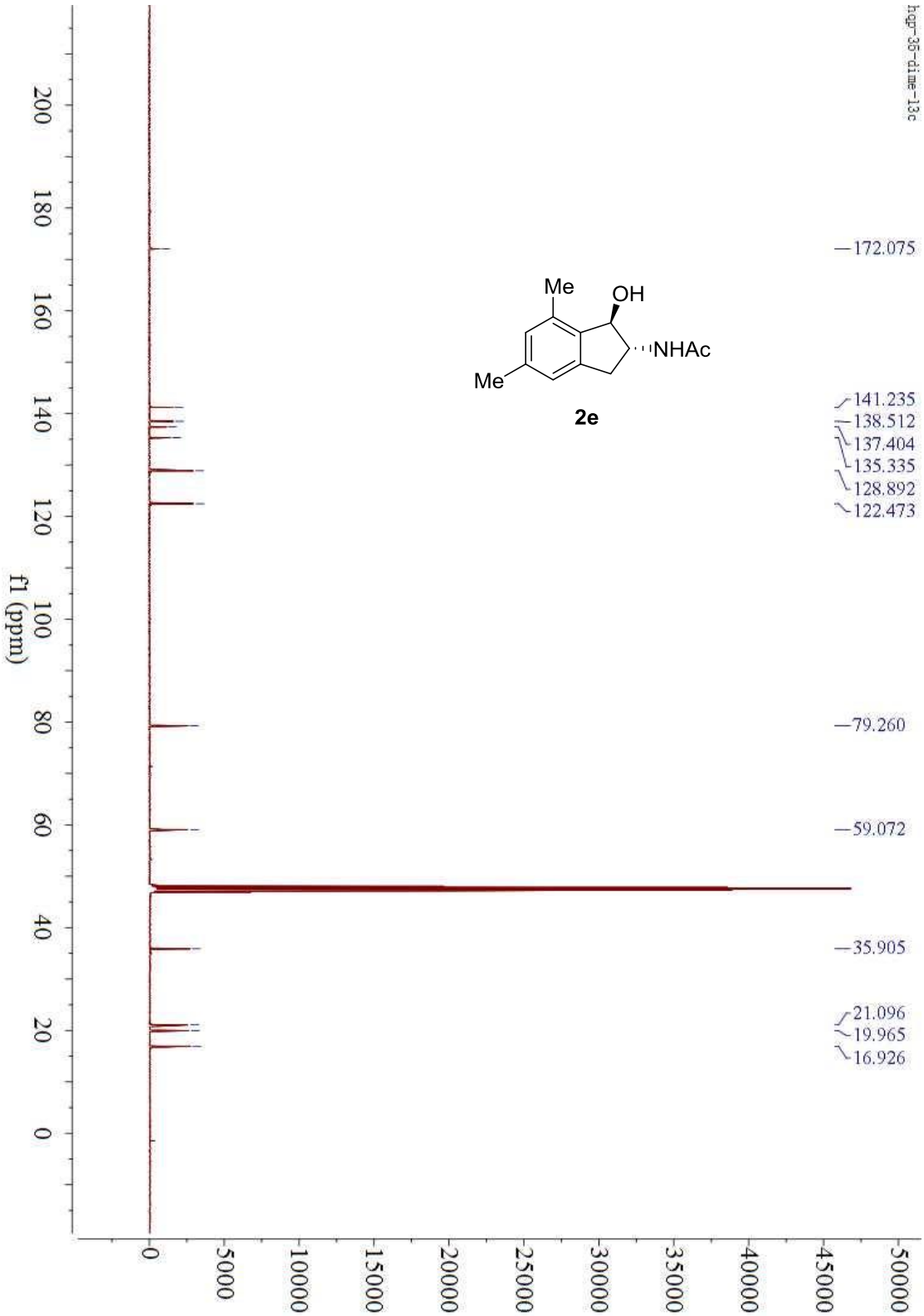

hqp-2-Me-1H
STANDARD 1H OBSERVE
OH
NHAc
Me
2c
7.180
7.162
7.144
7.126
7.077
7.061
4.977
4.962
4.322
4.303
4.286
4.268
3.322
3.317
3.313
3.309
3.305
2.606
2.588
2.567
2.548
2.246
1.994
3.07
0.97
1.00
0.95
1.01
2.71
2.81
f1 (ppm)

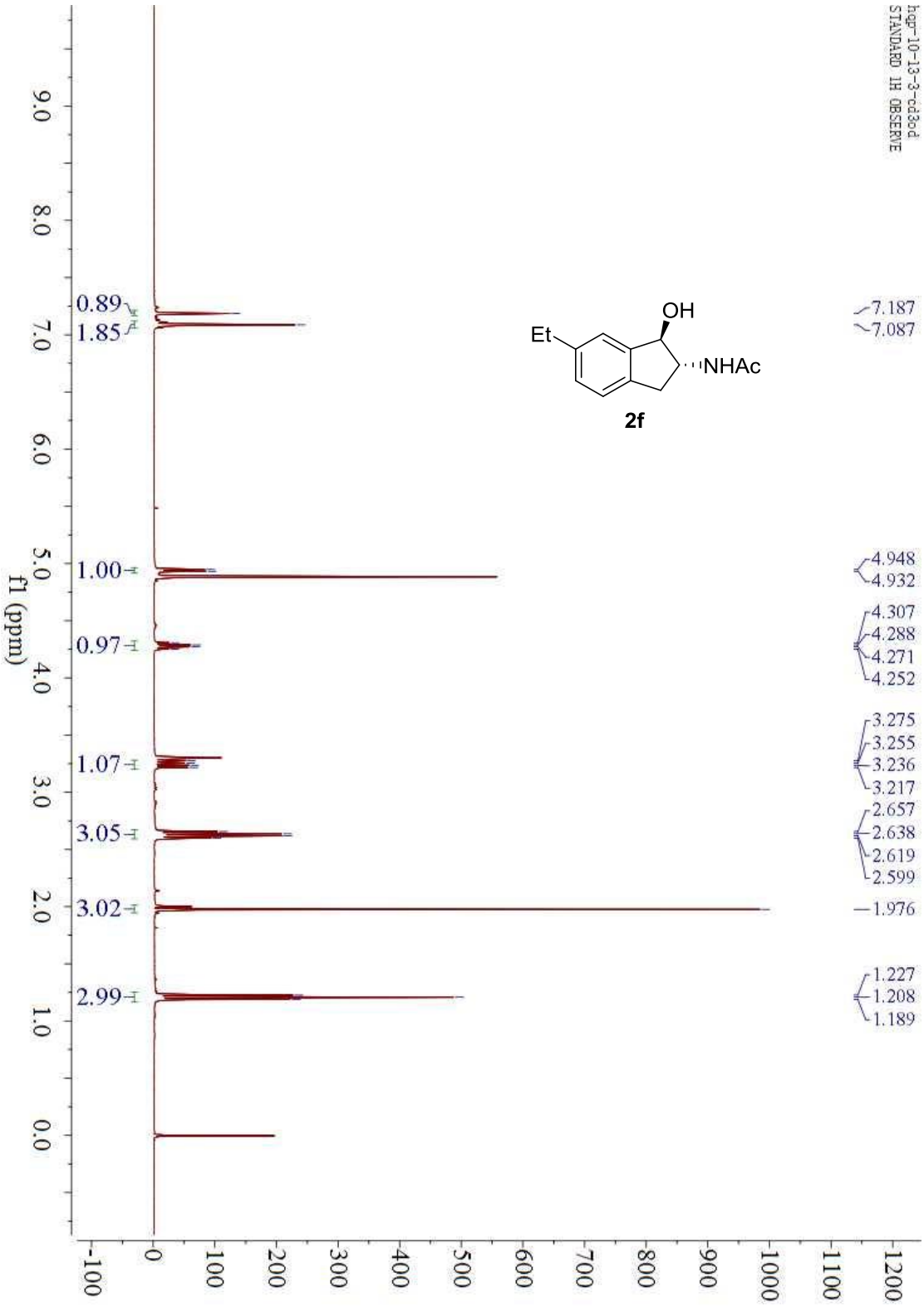

hqp-2-me-13c
OH
NHAc
Me
2c
172.399
142.239
137.997
133.705
128.645
126.870
121.165
79.716
59.368
33.883
21.218
17.172
f1 (ppm)
200
180
160
140
120
100
80
60
40
20
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000

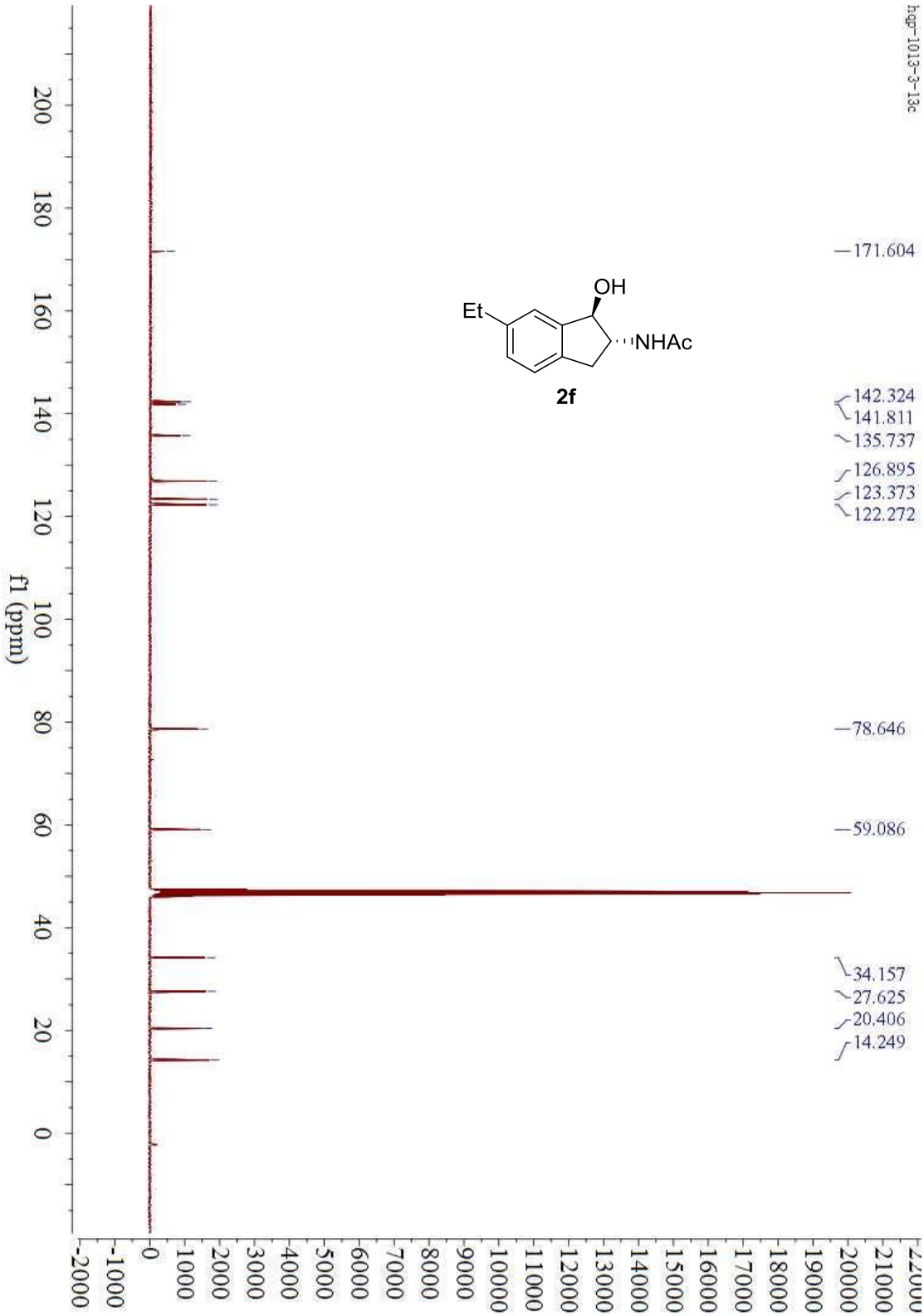

hqp-10-60-DMSO-1H
STANDARD 1H OBSERVE
f1 (ppm)
0.98
0.81
0.89
1.00
1.07
0.98
0.97
1.15
2.87
2.96
3.06
8.190
8.172
6.885
6.826
5.418
5.402
4.808
4.792
4.776
4.095
4.076
4.058
4.039
4.021
3.080
3.059
3.040
3.020
2.390
2.370
2.351
2.331
2.226
2.116
1.824
OH
Me
NHAc
Me
2d

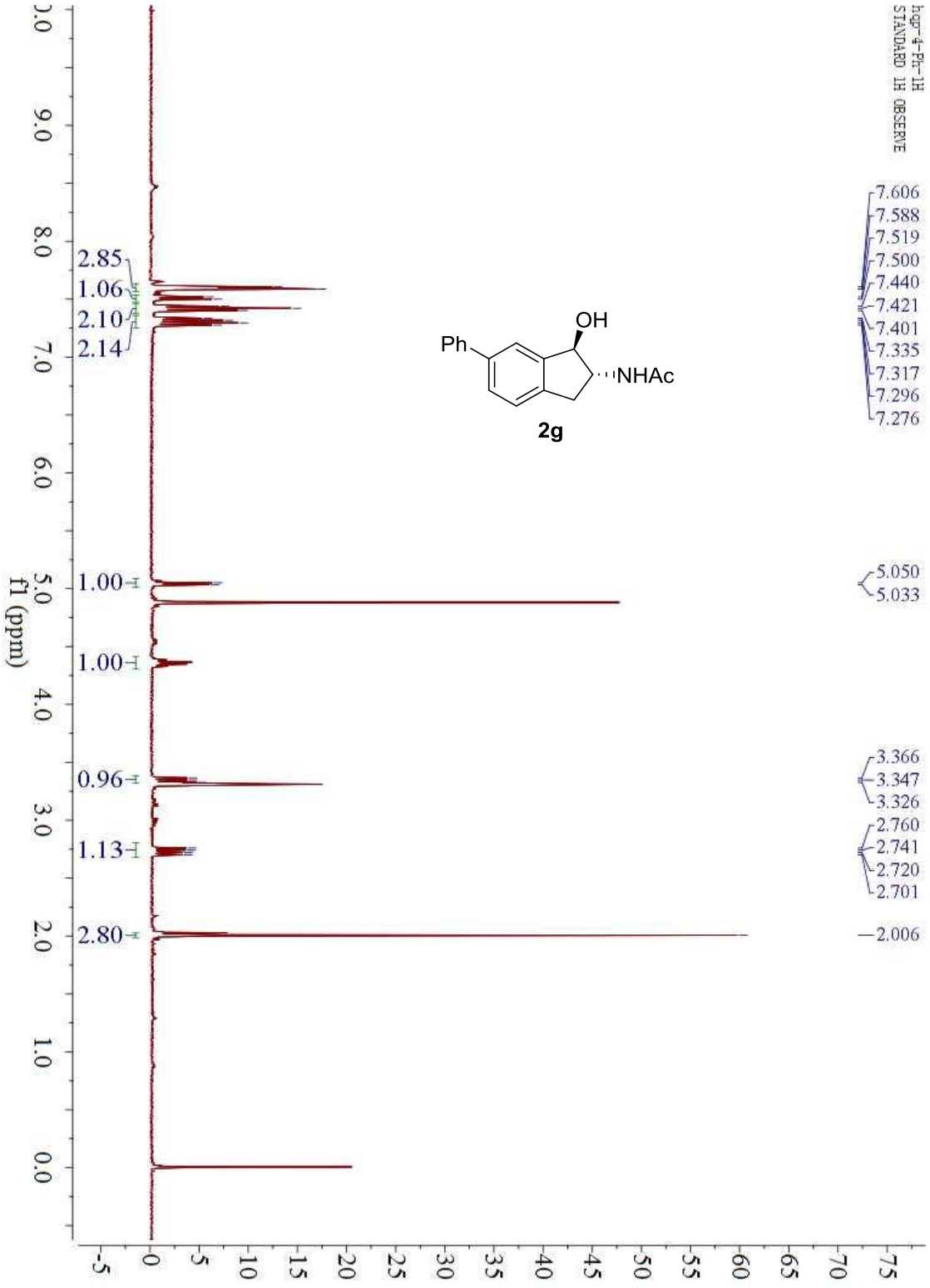

hapr-10-60
OH
Me
NHAc
Me
2d
169.948
144.307
136.119
135.523
133.415
129.544
122.337
79.058
59.622
34.522
23.226
21.395
18.644
f1 (ppm)

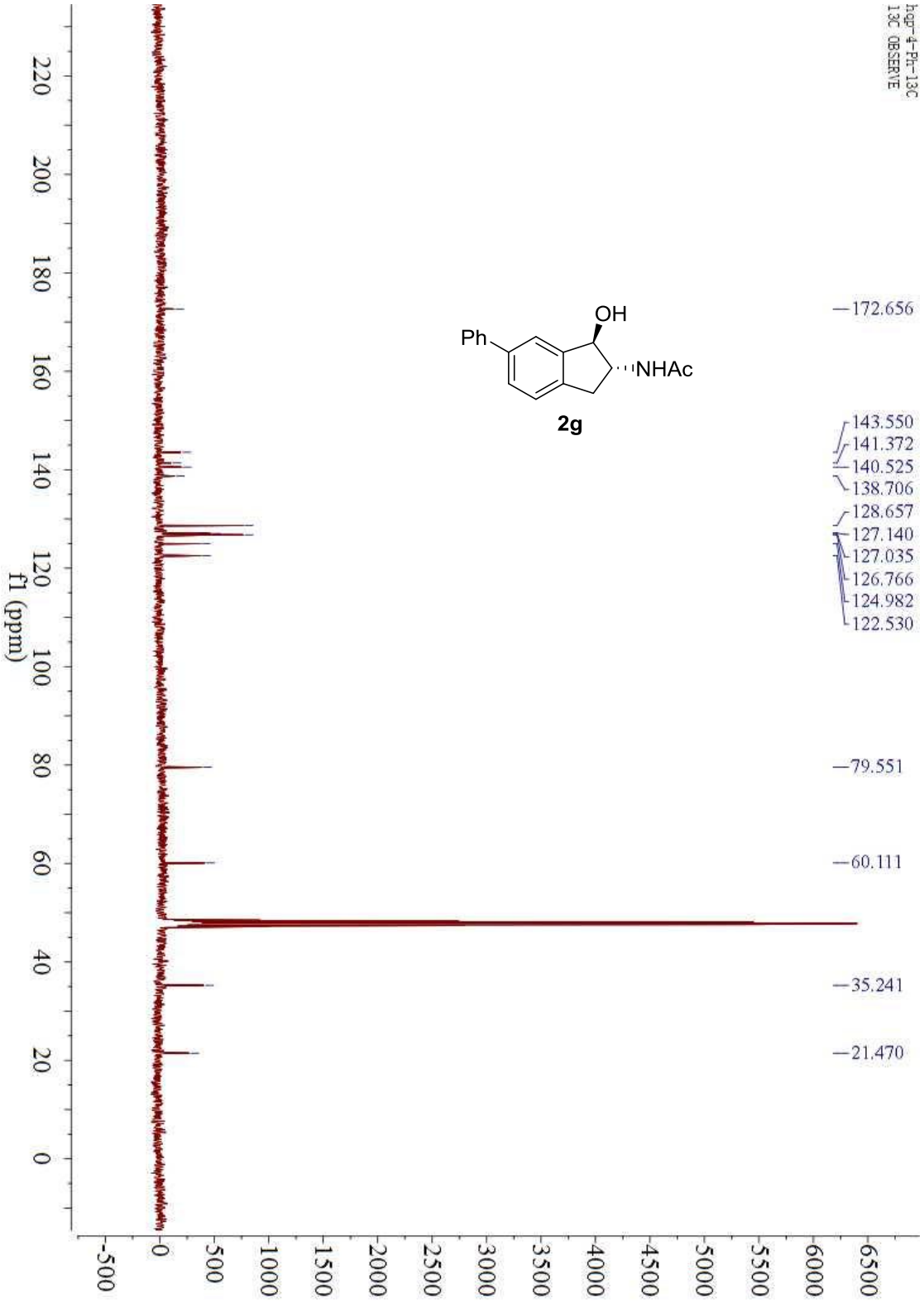

hqp-36-dime-1h
STANDARD 1H OBSERVE
Me
OH
NHAc
Me
2e
f1 (ppm)
0.96
0.88
0.96
1.00
1.06
1.02
3.10
2.96
3.08
6.864
6.836
4.973
4.966
4.311
4.301
4.293
4.283
4.274
3.393
3.375
3.353
3.334
2.634
2.623
2.593
2.583
2.335
2.268
1.922

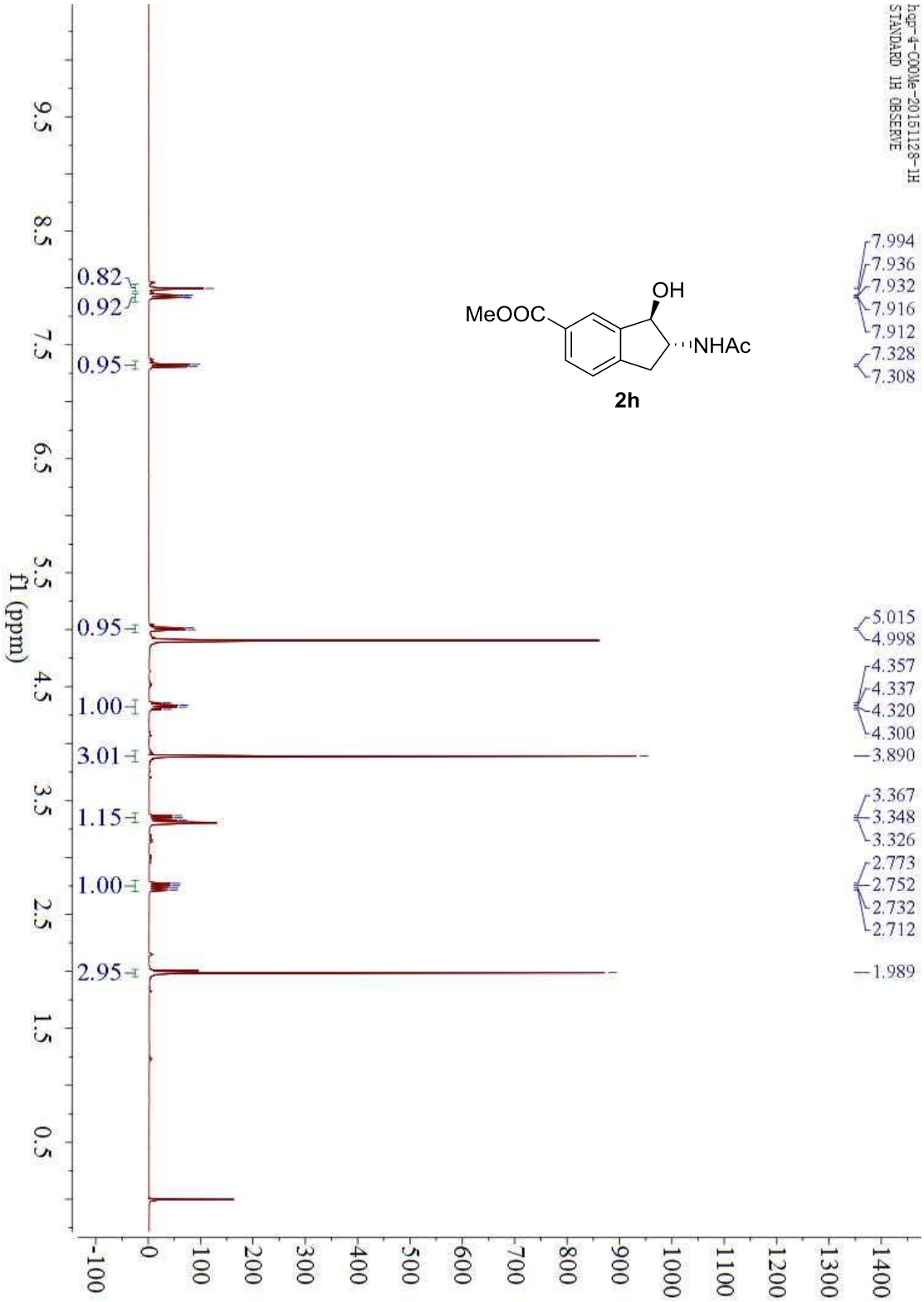

hqpr-36-dime-13c
Me
OH
NHAc
Me
2e
172.075
141.235
138.512
137.404
135.335
128.892
122.473
79.260
59.072
35.905
21.096
19.965
16.926
f1 (ppm)
0
20
40
60
80
100
120
140
160
180
200
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000

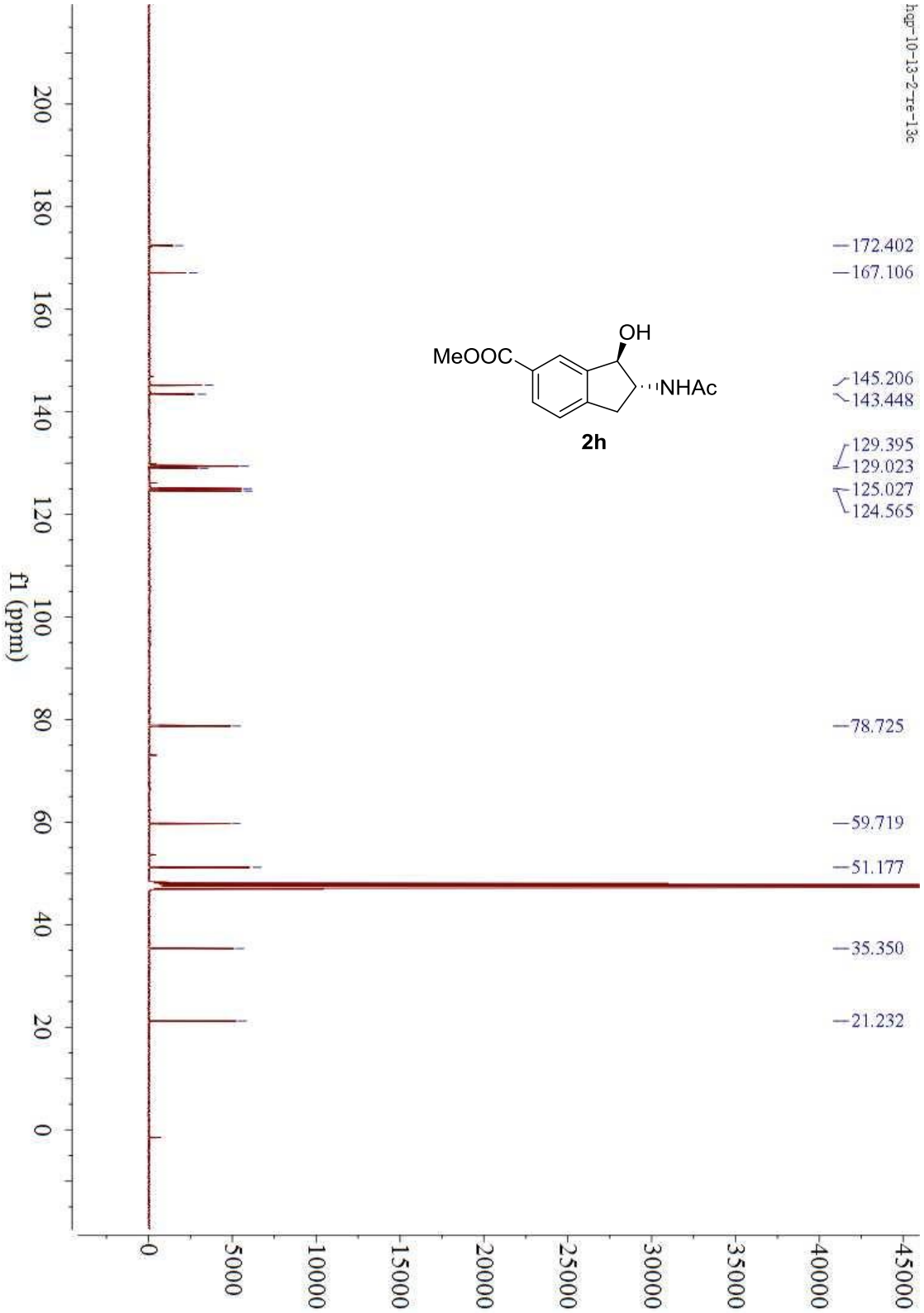

hqp-10-13-3-cd3od
STANDARD 1H OBSERVE
f1 (ppm)
0.89
1.85
1.00
0.97
1.07
3.05
3.02
2.99
OH
Et
NHAc
2f
7.187
7.087
4.948
4.932
4.307
4.288
4.271
4.252
3.275
3.255
3.236
3.217
2.657
2.638
2.619
2.599
1.976
1.227
1.208
1.189

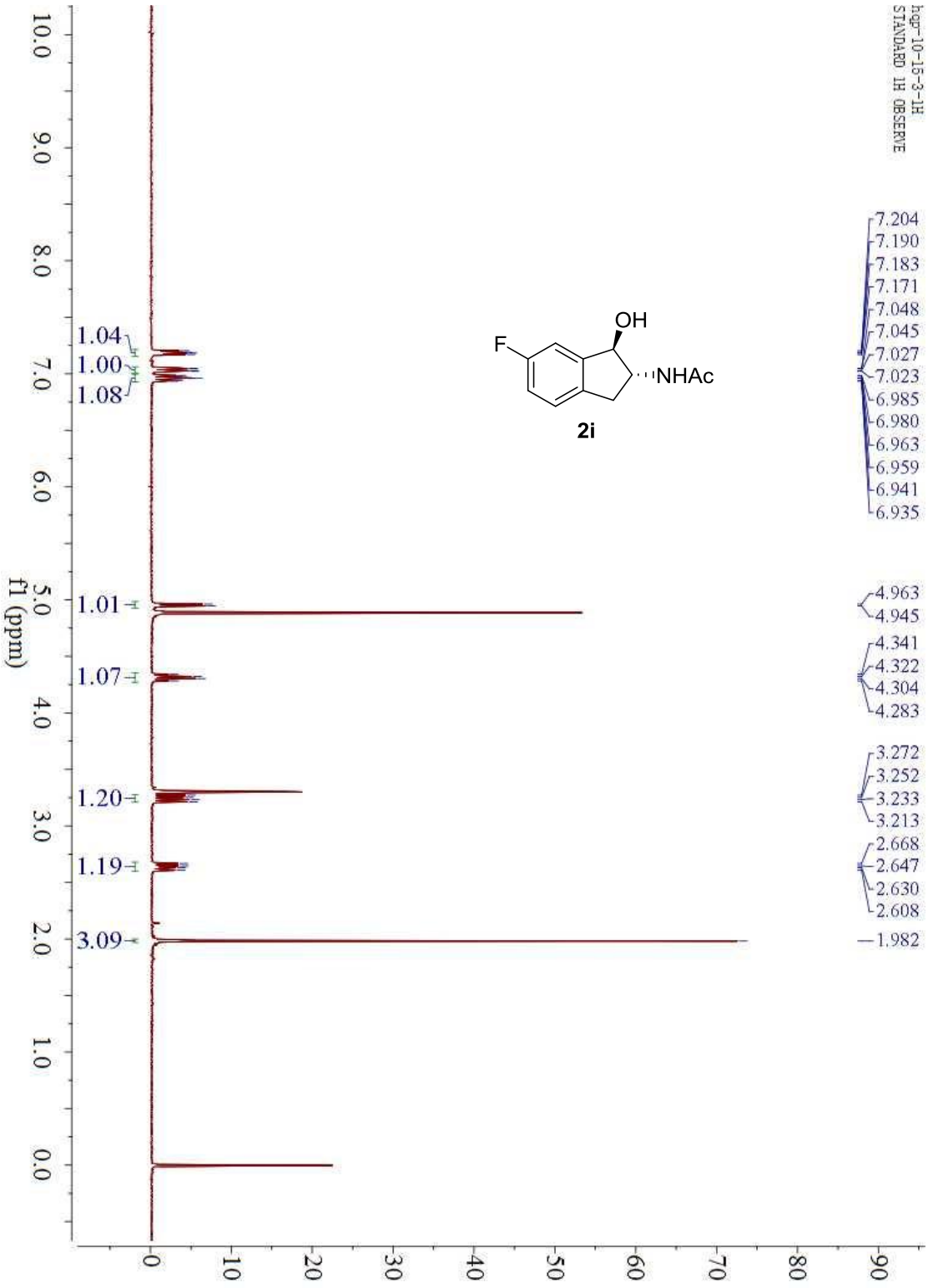

hqp-1013-3-13c
OH
Et
NHAc
2f
171.604
142.324
141.811
135.737
126.895
123.373
122.272
78.646
59.086
34.157
27.625
20.406
14.249
f1 (ppm)

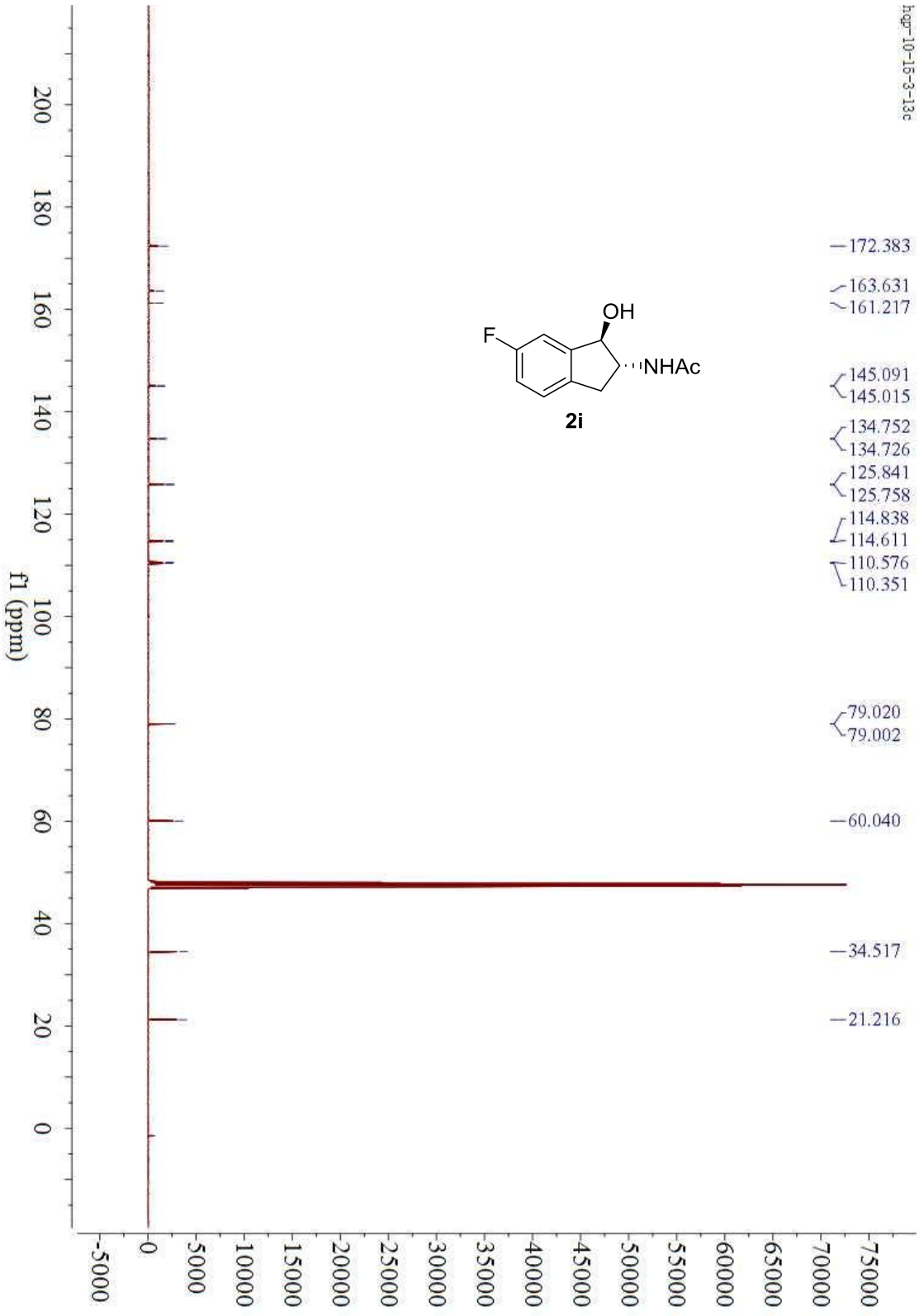

hqp-4-Ph-1H
STANDARD 1H OBSERVE
7.606
7.588
7.519
7.500
7.440
7.421
7.401
7.335
7.317
7.296
7.276
5.050
5.033
3.366
3.347
3.326
2.760
2.741
2.720
2.701
2.006
2.85
1.06
2.10
2.14
1.00
1.00
0.96
1.13
2.80
OH
Ph
NHAc
2g
f1 (ppm)

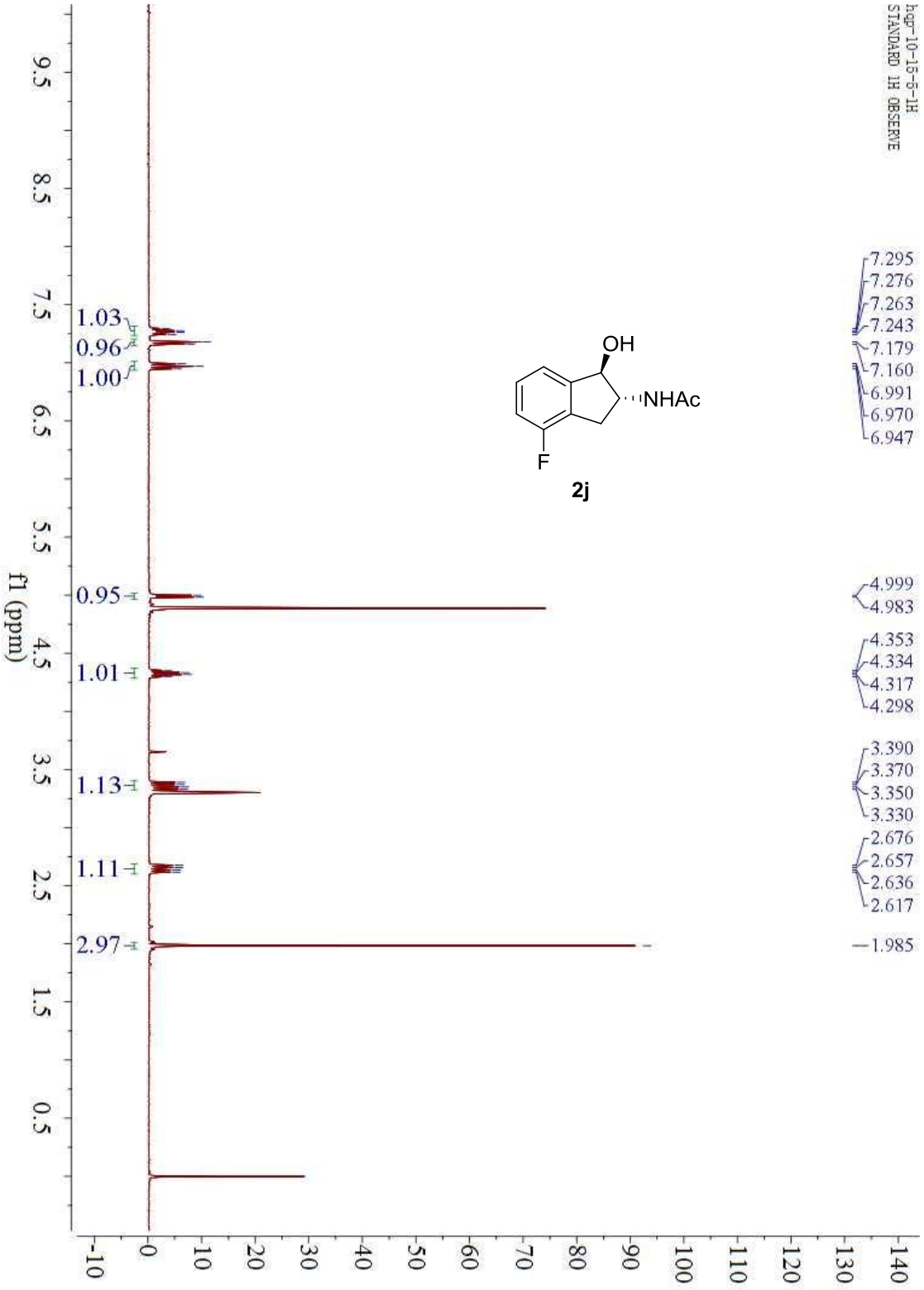

hqp-4-Ph-13C
13C OBSERVE
OH
Ph
NHAc
2g
172.656
143.550
141.372
140.525
138.706
128.657
127.140
127.035
126.766
124.982
122.530
79.551
60.111
35.241
21.470
f1 (ppm)

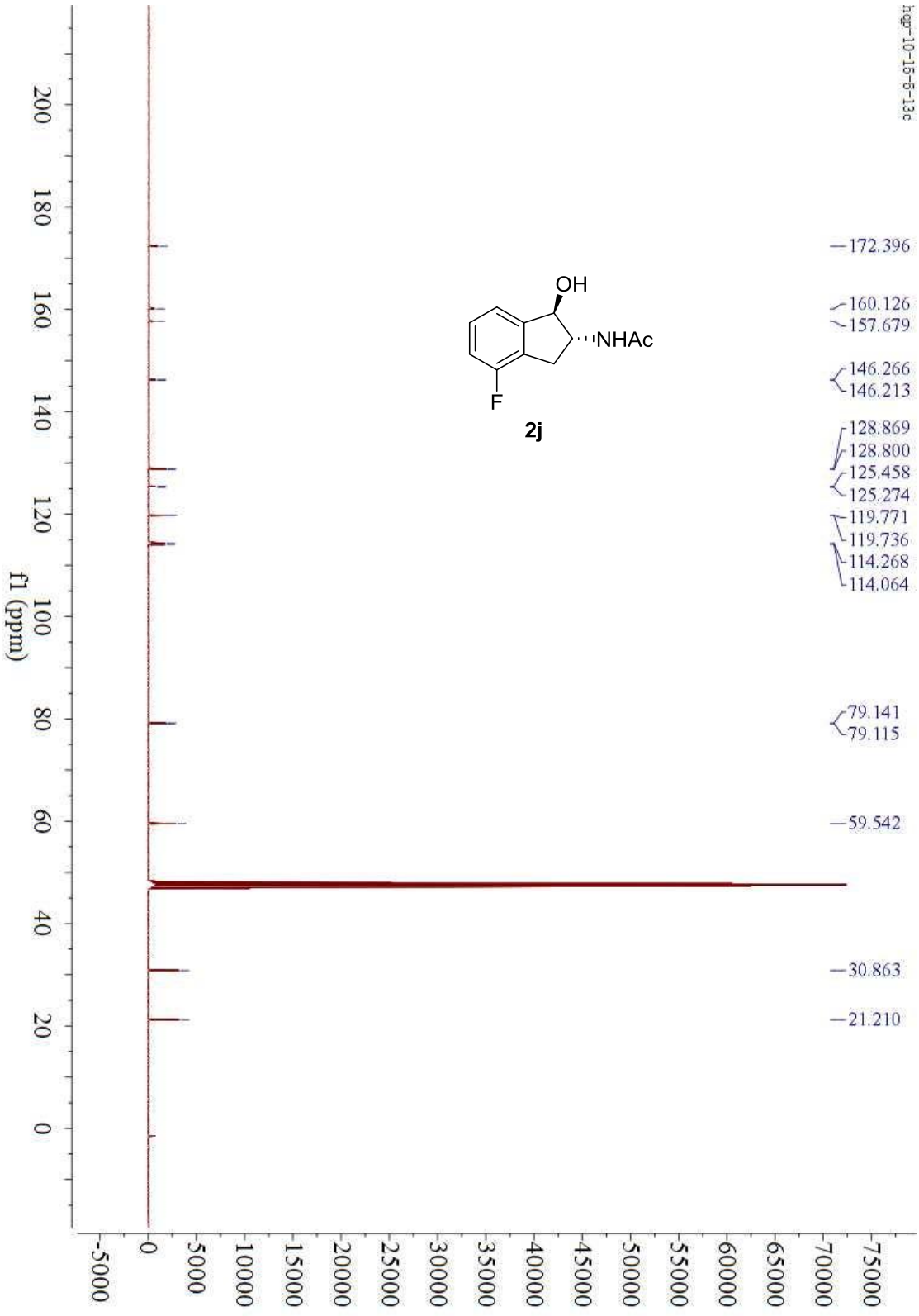

hqp-4-COOMe-20151128-1H
STANDARD 1H OBSERVE
MeOOC
OH
NHAc
2h
f1 (ppm)
0.82
0.92
0.95
0.95
1.00
3.01
1.15
1.00
2.95
7.994
7.936
7.932
7.916
7.912
7.328
7.308
5.015
4.998
4.357
4.337
4.320
4.300
3.890
3.367
3.348
3.326
2.773
2.752
2.732
2.712
1.989

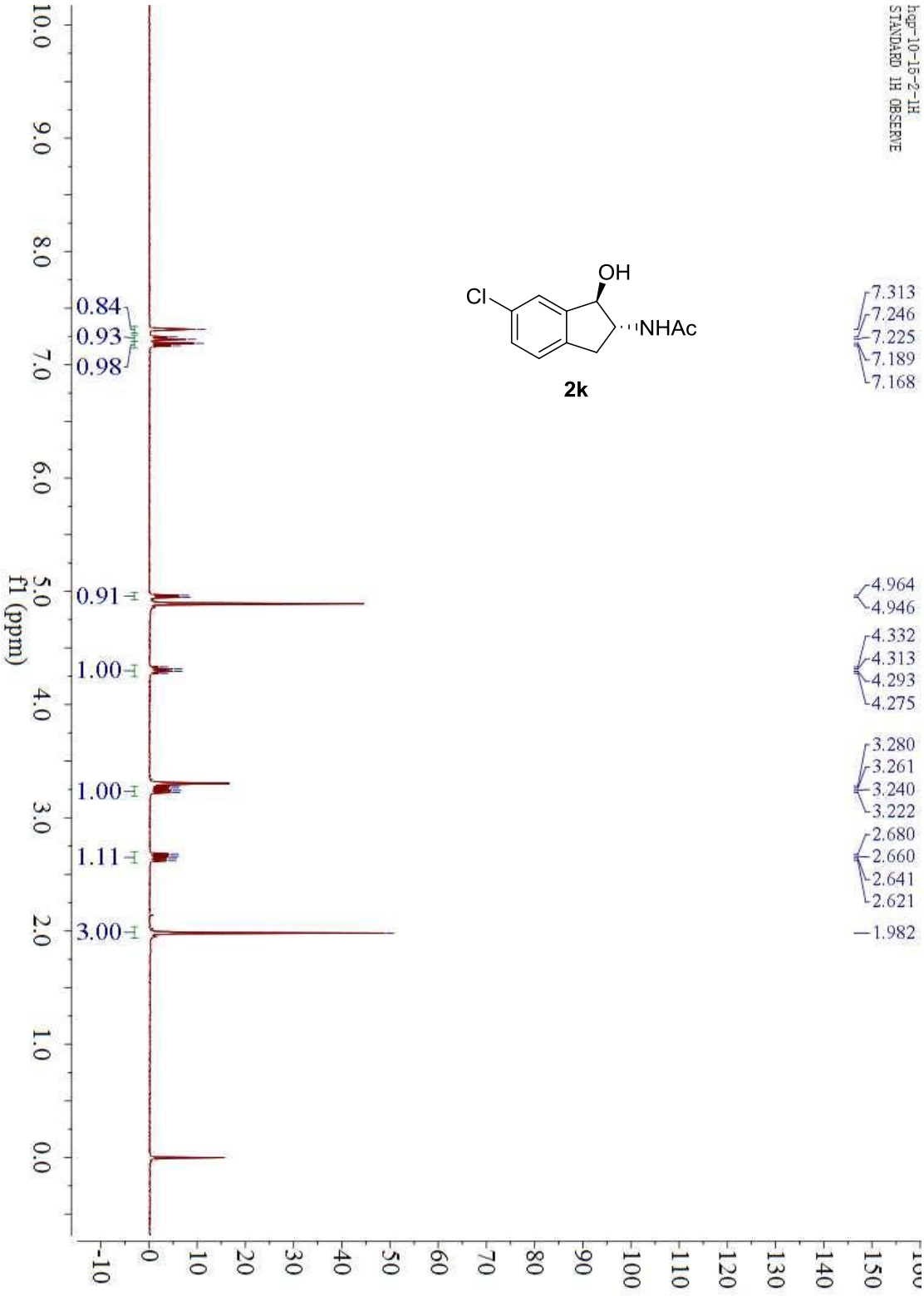

hqp-10-13-2-re-13c
MeOOC
OH
NHAc
2h
172.402
167.106
145.206
143.448
129.395
129.023
125.027
124.565
78.725
59.719
51.177
35.350
21.232
f1 (ppm)
0
20
40
60
80
100
120
140
160
180
200
0
5000
10000
15000
20000
25000
30000
35000
40000
45000

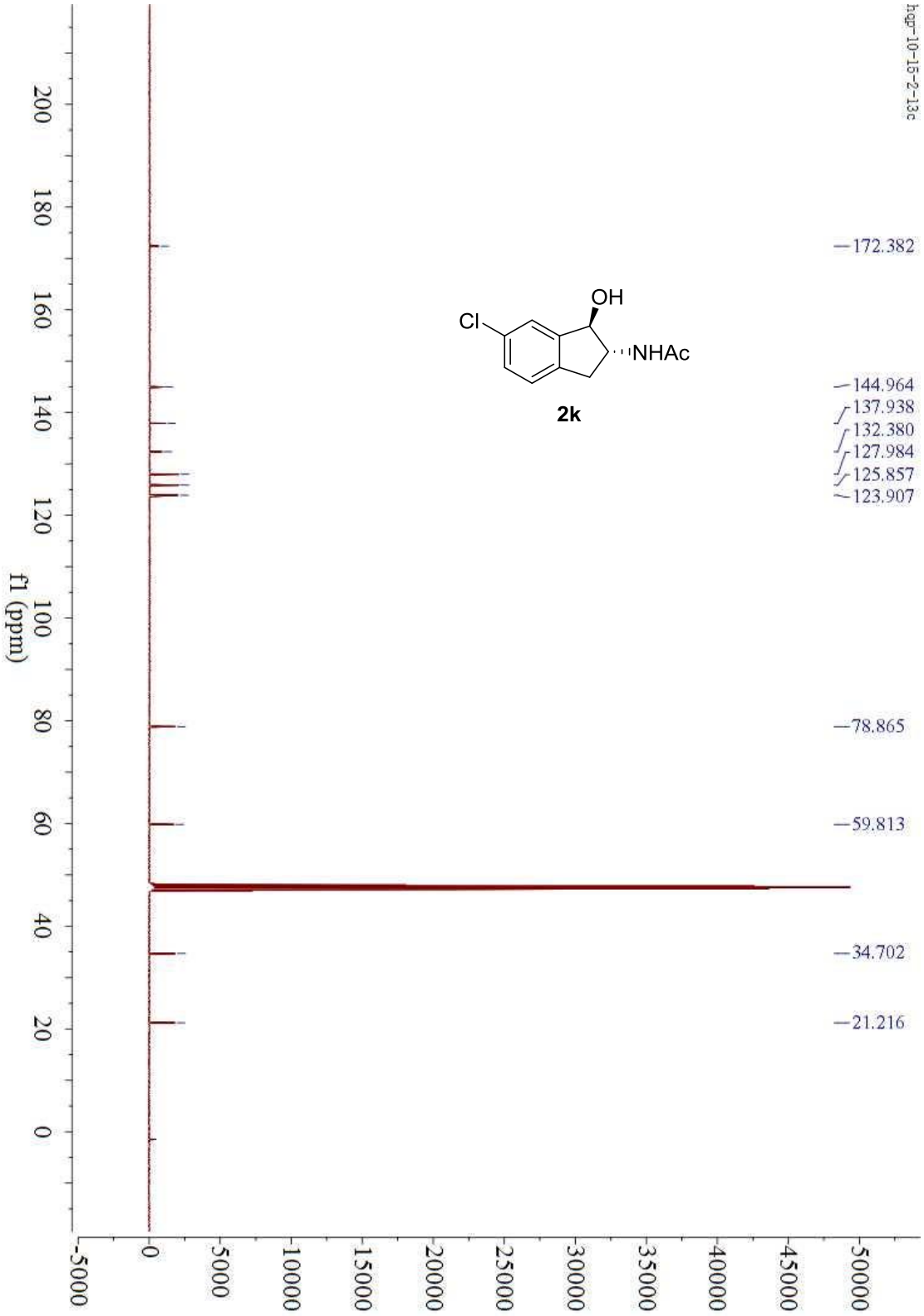

hqp-10-16-3-1H
STANDARD 1H OBSERVE
OH
F
NHAc
2i
7.204
7.190
7.183
7.171
7.048
7.045
7.027
7.023
6.985
6.980
6.963
6.959
6.941
6.935
4.963
4.945
4.341
4.322
4.304
4.283
3.272
3.252
3.233
3.213
2.668
2.647
2.630
2.608
1.982
1.04
1.00
1.08
1.01
1.07
1.20
1.19
3.09
f1 (ppm)

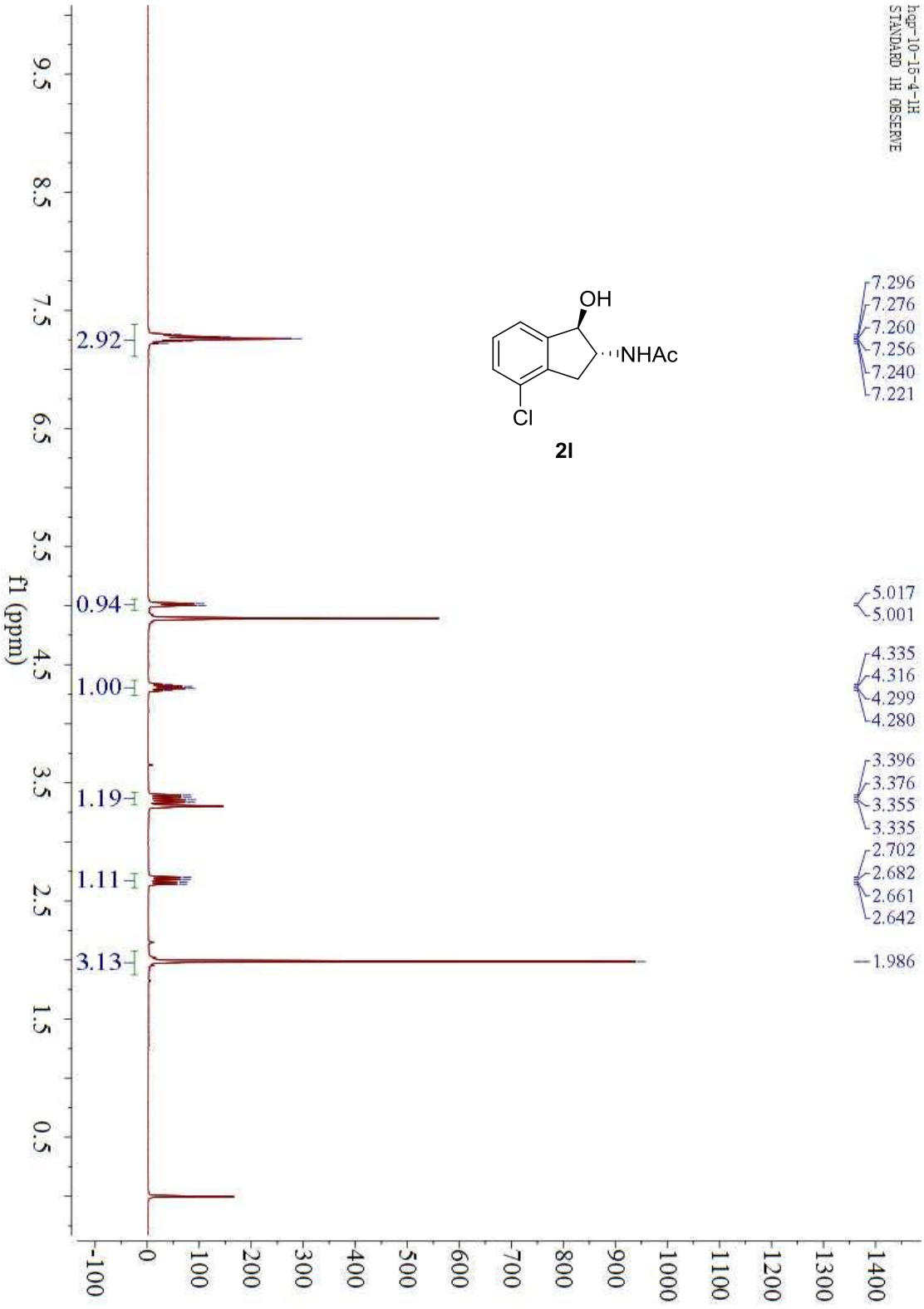

hqp-10-16-3-13c
OH
F
NHAc
2i
172.383
163.631
161.217
145.091
145.015
134.752
134.726
125.841
125.758
114.838
114.611
110.576
110.351
79.020
79.002
60.040
34.517
21.216
f1 (ppm)

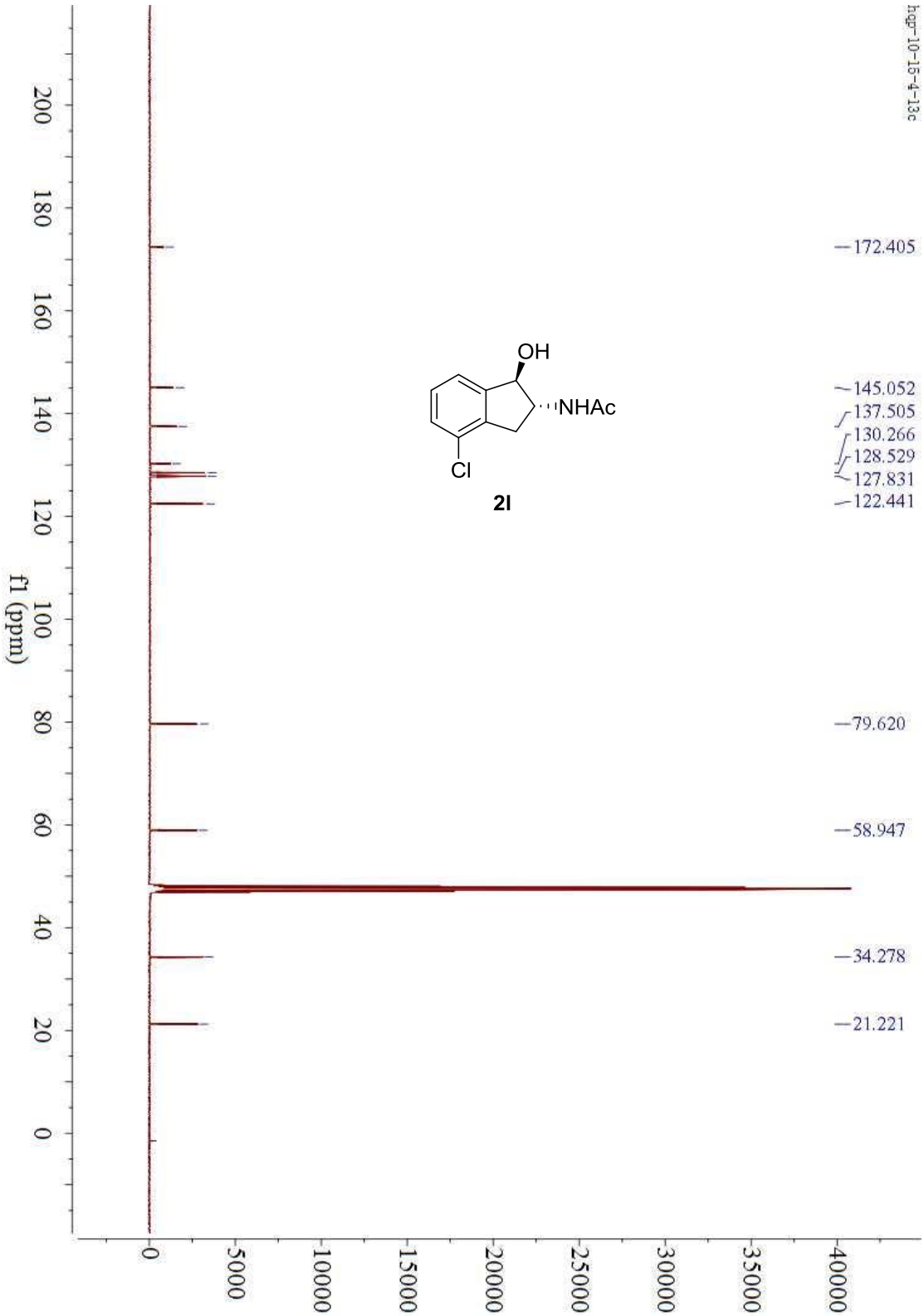

hqp-10-16-6-1H
STANDARD 1H OBSERVE
7.295
7.276
7.263
7.243
7.179
7.160
6.991
6.970
6.947
4.999
4.983
4.353
4.334
4.317
4.298
3.390
3.370
3.350
3.330
2.676
2.657
2.636
2.617
1.985
1.03
0.96
1.00
0.95
1.01
1.13
1.11
2.97
OH
NHAc
F
2j
f1 (ppm)

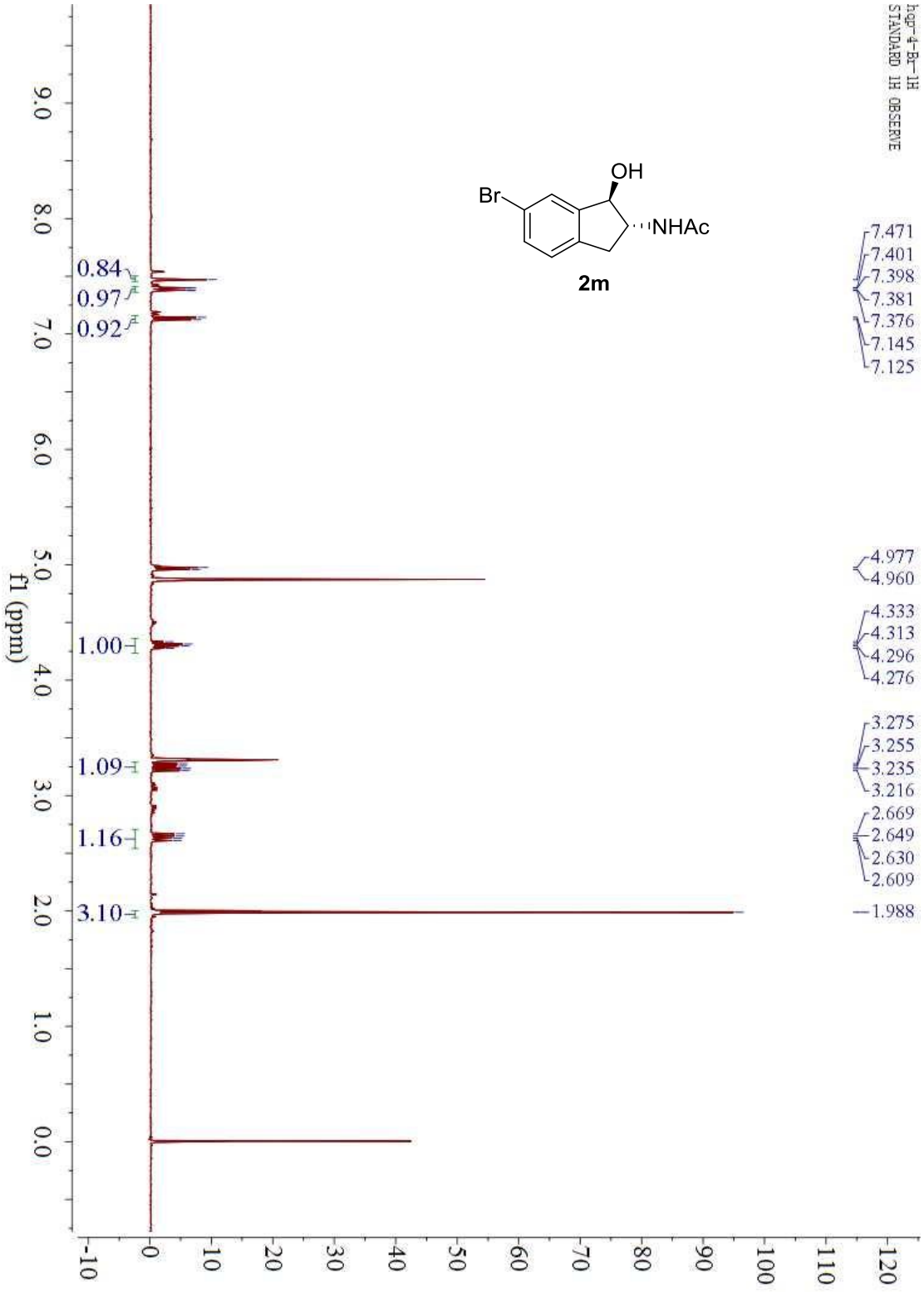

hqp-10-16-6-13c
OH
NHAc
F
2j
172.396
160.126
157.679
146.266
146.213
128.869
128.800
125.458
125.274
119.771
119.736
114.268
114.064
79.141
79.115
59.542
30.863
21.210
f1 (ppm)

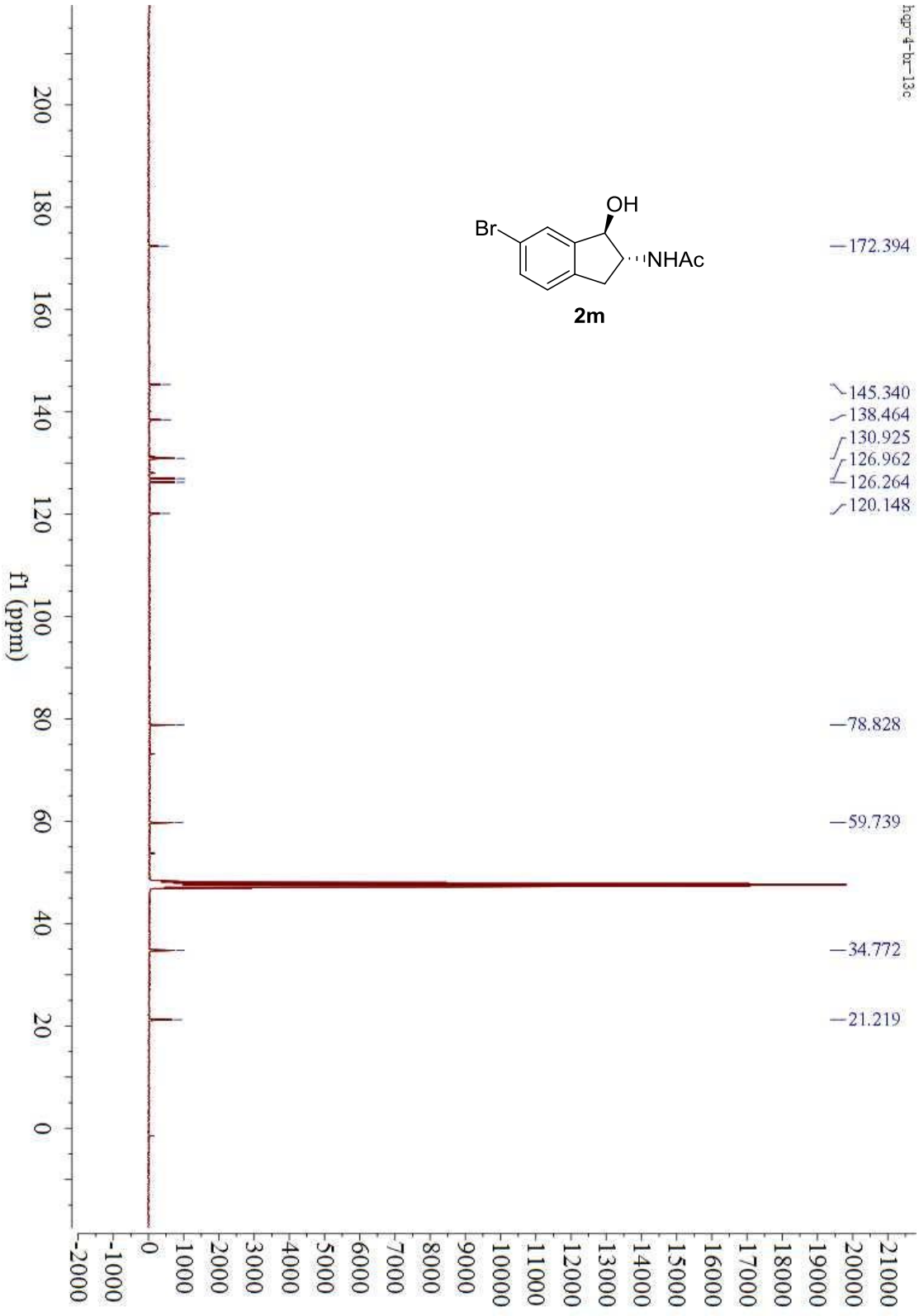

hqp-10-16-2-1H
STANDARD 1H OBSERVE
OH
Cl
NHAc
2k
7.313
7.246
7.225
7.189
7.168
4.964
4.946
4.332
4.313
4.293
4.275
3.280
3.261
3.240
3.222
2.680
2.660
2.641
2.621
1.982
0.84
0.93
0.98
0.91
1.00
1.00
1.11
3.00
f1 (ppm)

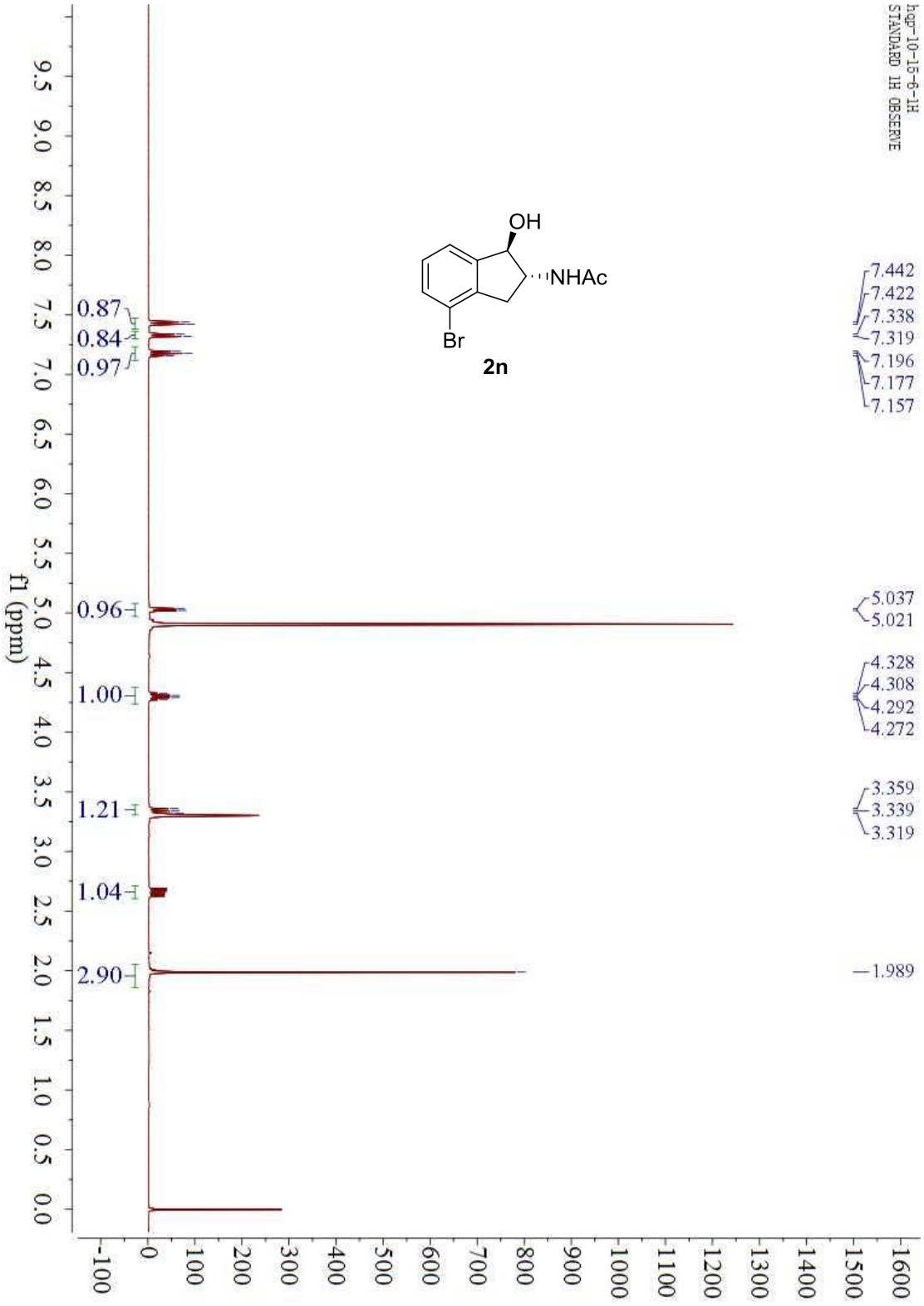

hqp-10-15-2-13c
172.382
144.964
137.938
132.380
127.984
125.857
123.907
78.865
59.813
34.702
21.216
OH
Cl
NHAc
2k
f1 (ppm)

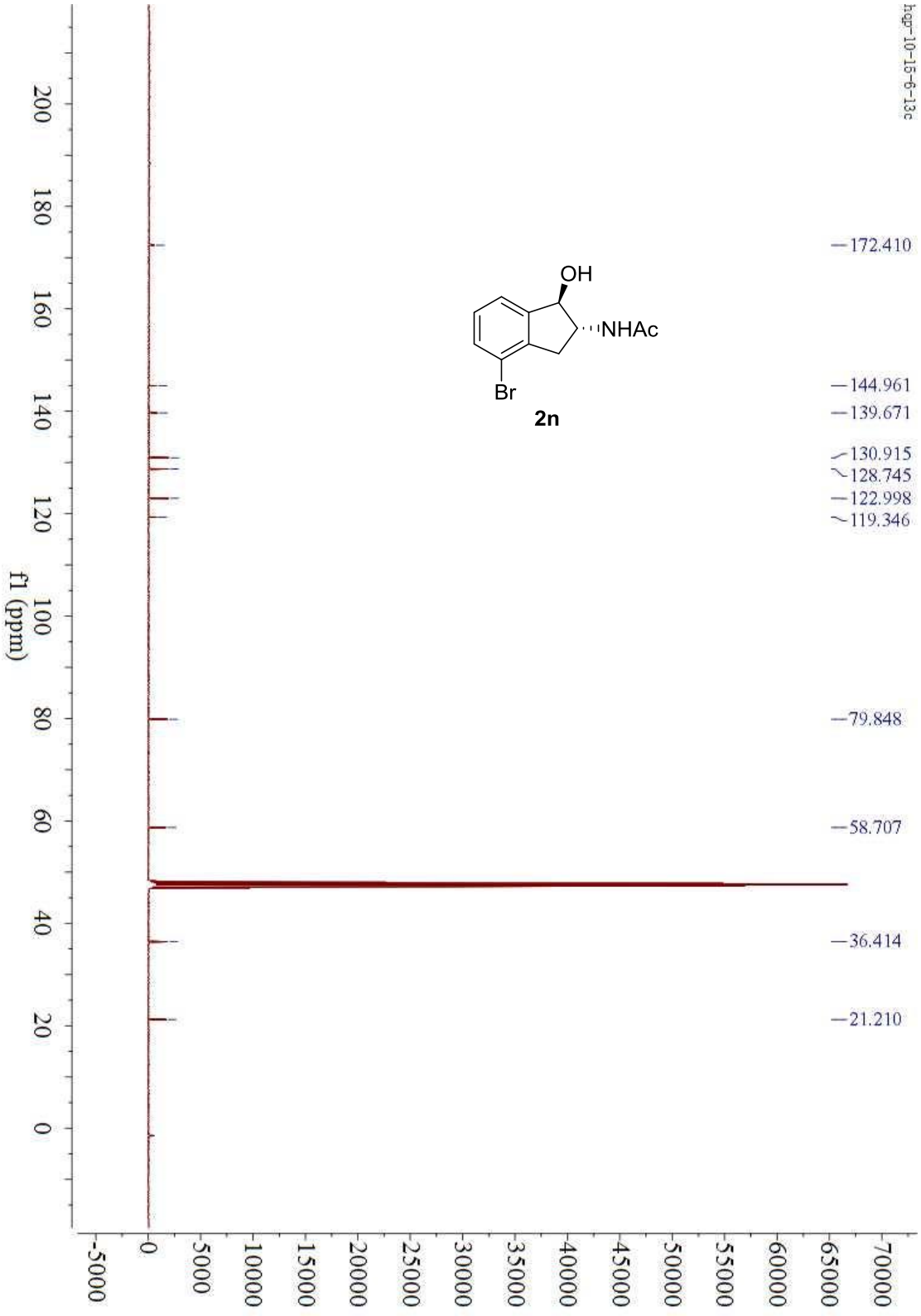

hqp-10-16-4-1H
STANDARD 1H OBSERVE
OH
NHAc
Cl
2l
7.296
7.276
7.260
7.256
7.240
7.221
5.017
5.001
4.335
4.316
4.299
4.280
3.396
3.376
3.355
3.335
2.702
2.682
2.661
2.642
1.986
2.92
0.94
1.00
1.19
1.11
3.13
f1 (ppm)

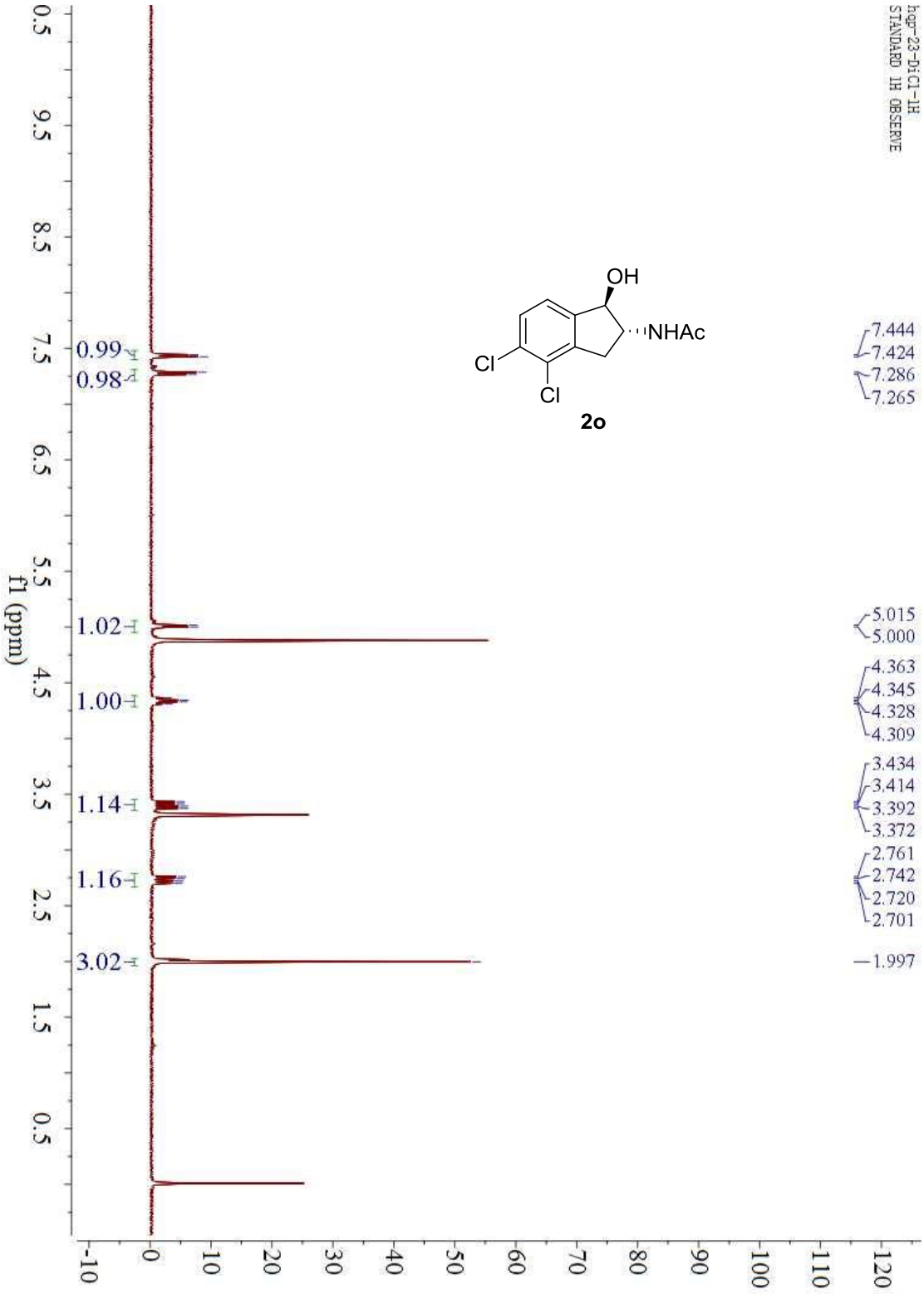

hqp-10-16-4-13c
172.405
145.052
137.505
130.266
128.529
127.831
122.441
79.620
58.947
34.278
21.221
OH
NHAc
Cl
2l
f1 (ppm)
200
180
160
140
120
100
80
60
40
20
0
0
5000
10000
15000
20000
25000
30000
35000
40000

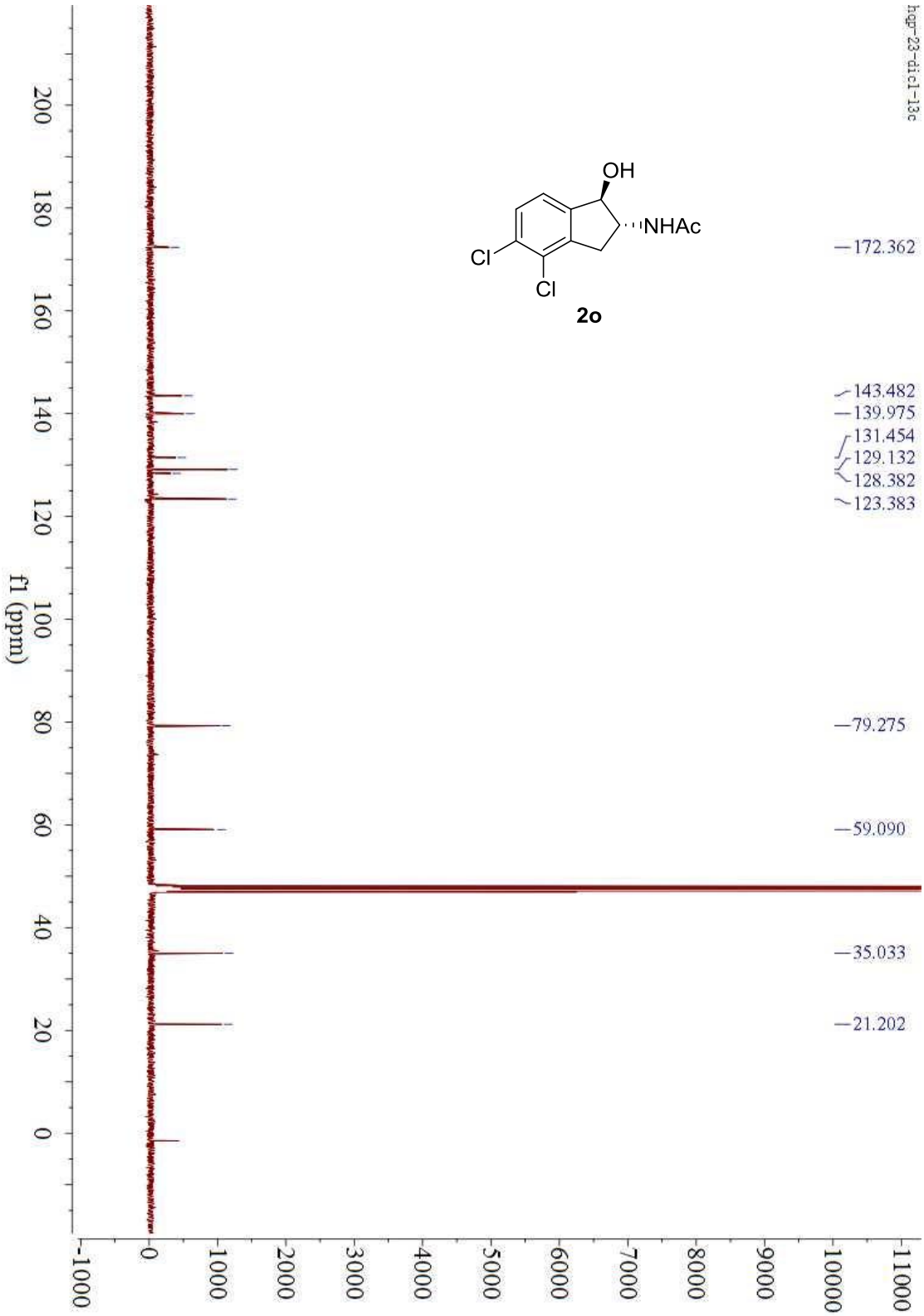

hqp-4-Br-1H
STANDARD 1H OBSERVE
OH
Br
NHAc
2m
7.471
7.401
7.398
7.381
7.376
7.145
7.125
4.977
4.960
4.333
4.313
4.296
4.276
3.275
3.255
3.235
3.216
2.669
2.649
2.630
2.609
1.988
0.84
0.97
0.92
1.00
1.09
1.16
3.10
f1 (ppm)

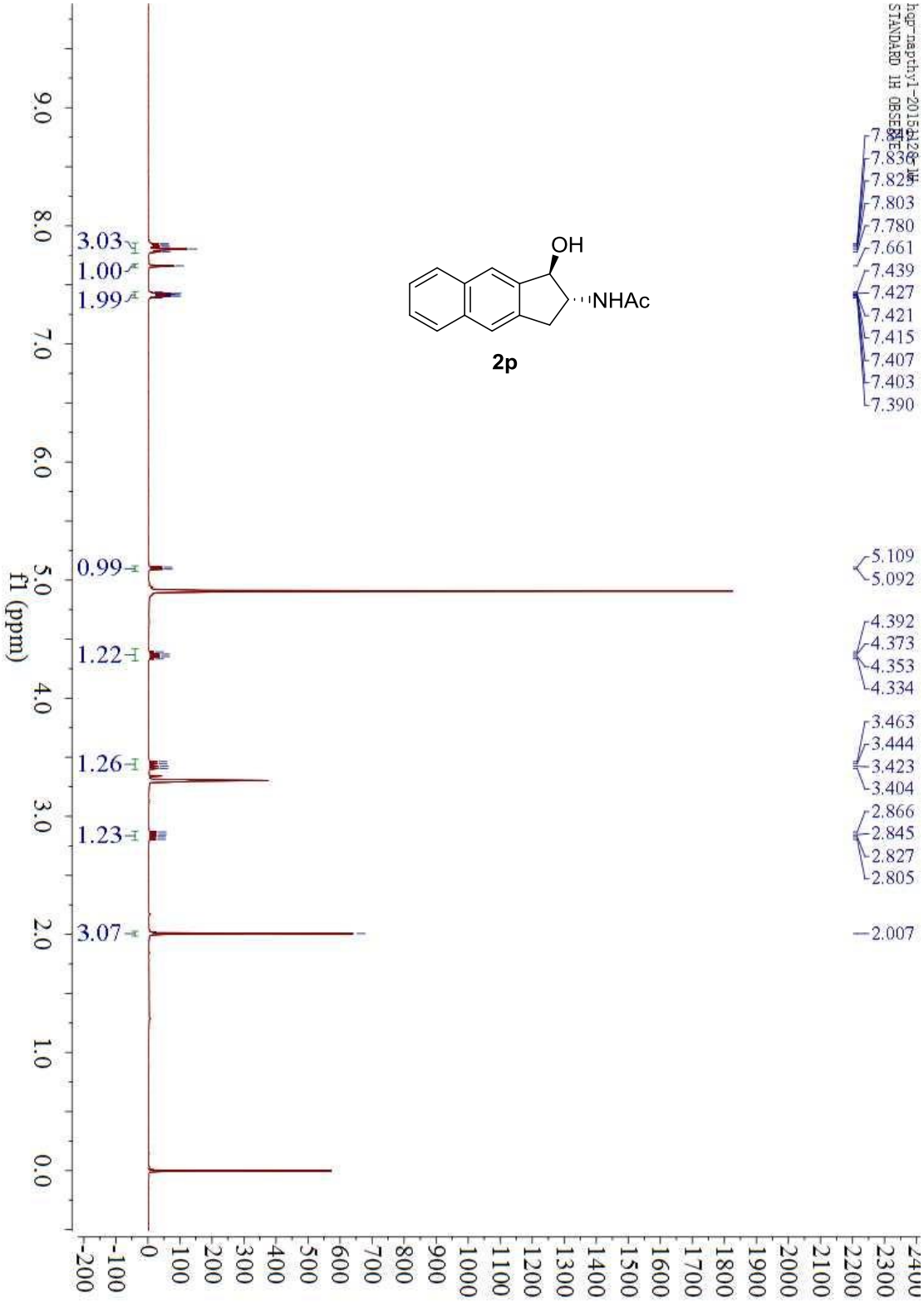

hqpr-4-br-13c
OH
Br
NHAc
2m
172.394
145.340
138.464
130.925
126.962
126.264
120.148
78.828
59.739
34.772
21.219
f1 (ppm)

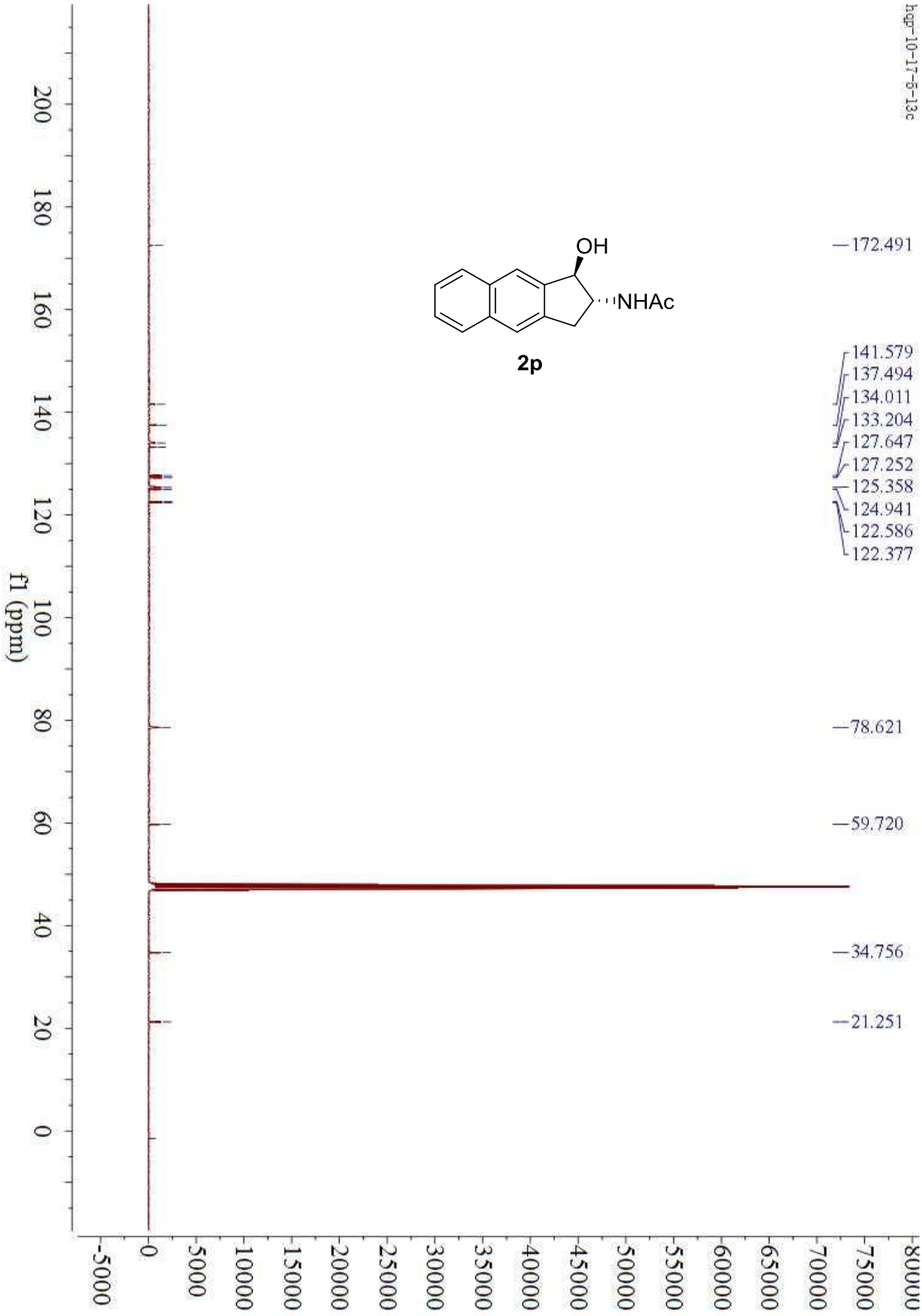

hqp-10-15-6-1H
STANDARD 1H OBSERVE
OH
NHAc
Br
2n
7.442
7.422
7.338
7.319
7.196
7.177
7.157
5.037
5.021
4.328
4.308
4.292
4.272
3.359
3.339
3.319
1.989
0.87
0.84
0.97
0.96
1.00
1.21
1.04
2.90
f1 (ppm)

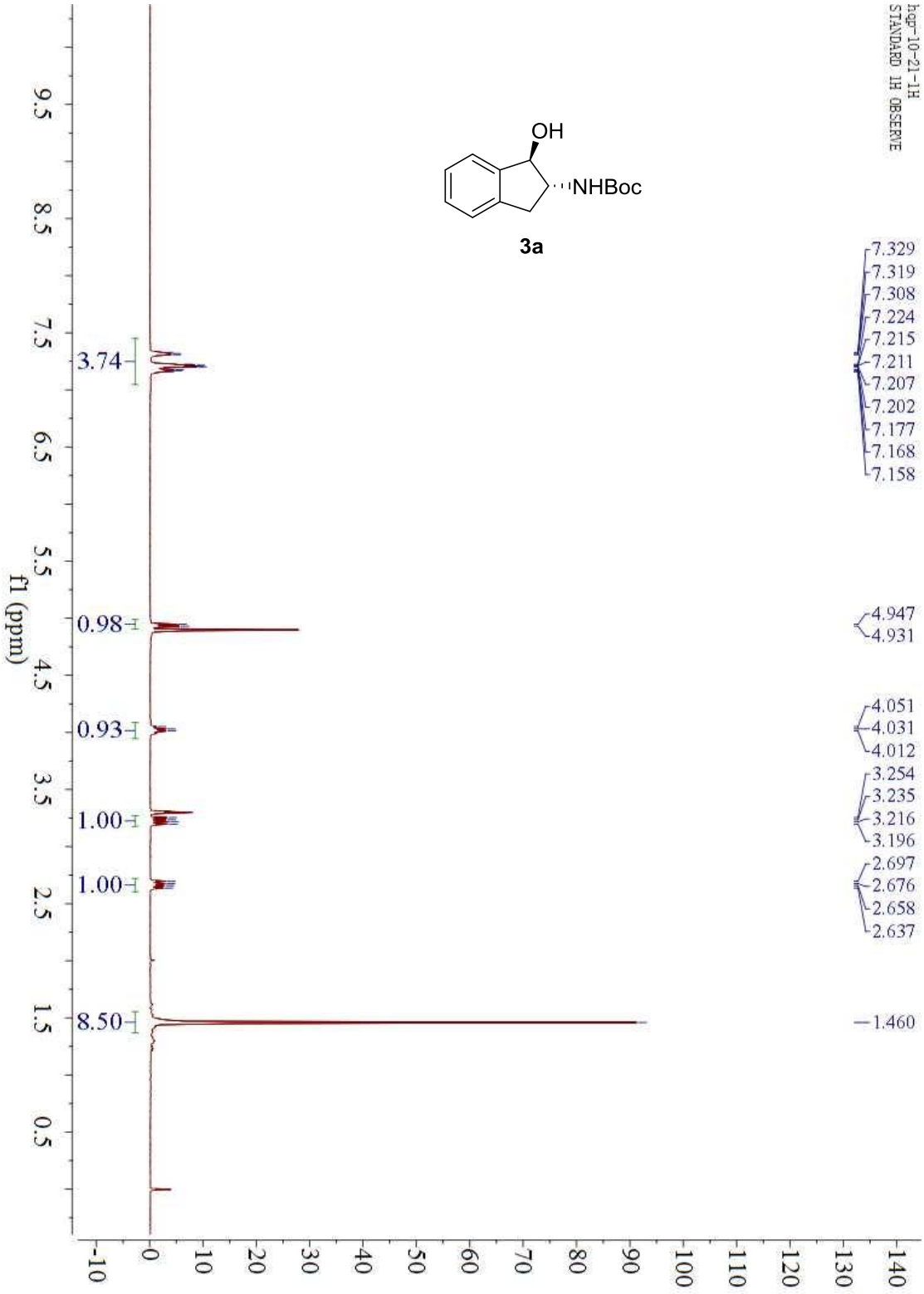

hqp-10-15-6-13c
OH
NHAc
Br
2n
172.410
144.961
139.671
130.915
128.745
122.998
119.346
79.848
58.707
36.414
21.210
f1 (ppm)
200
180
160
140
120
100
80
60
40
20
0
-5000
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
55000
60000
65000
70000

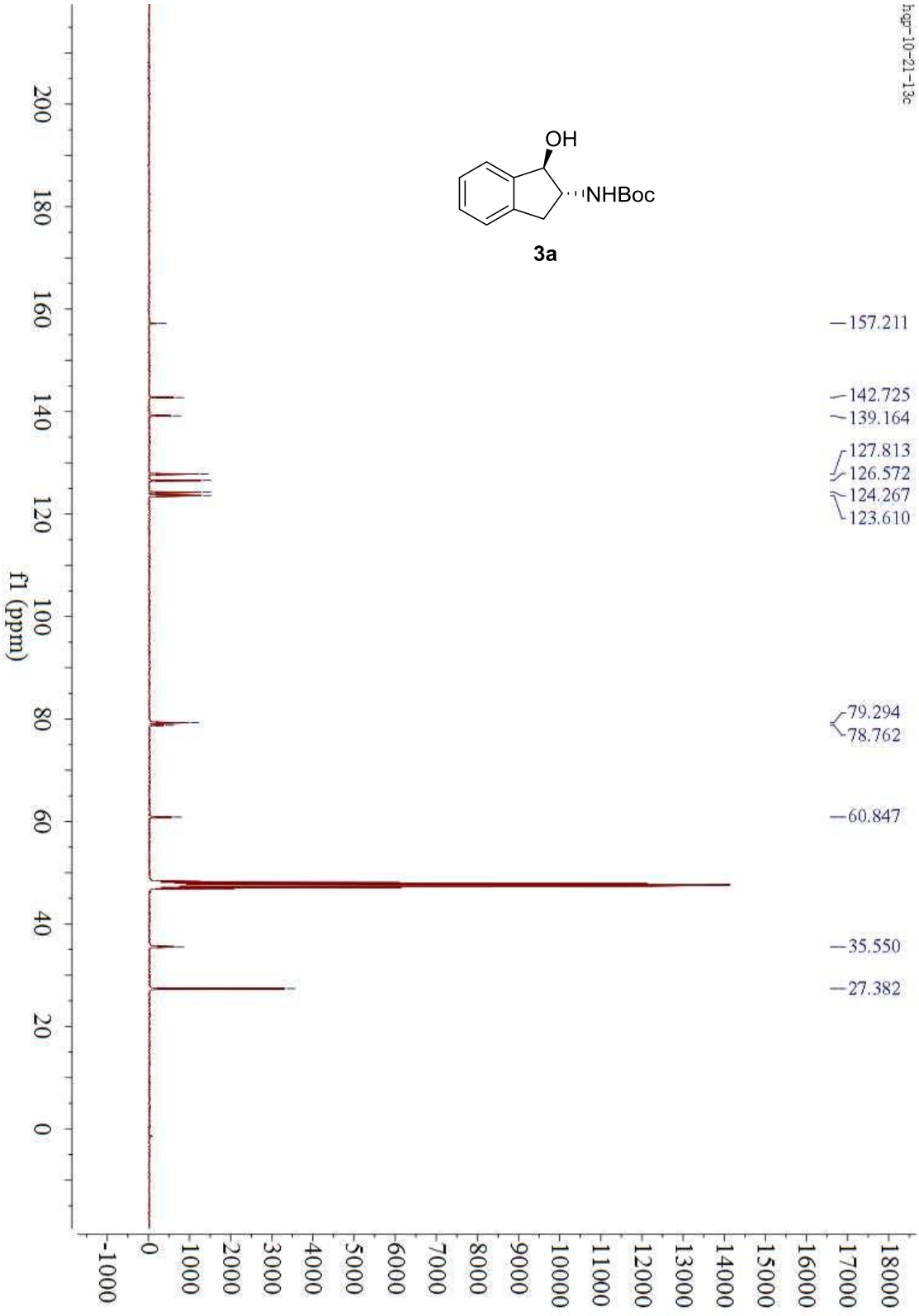

hqp-23-DiCl-1H
STANDARD 1H OBSERVE
OH
NHAc
Cl
Cl
2o
7.444
7.424
7.286
7.265
5.015
5.000
4.363
4.345
4.328
4.309
3.434
3.414
3.392
3.372
2.761
2.742
2.720
2.701
1.997
0.99
0.98
1.02
1.00
1.14
1.16
3.02
f1 (ppm)

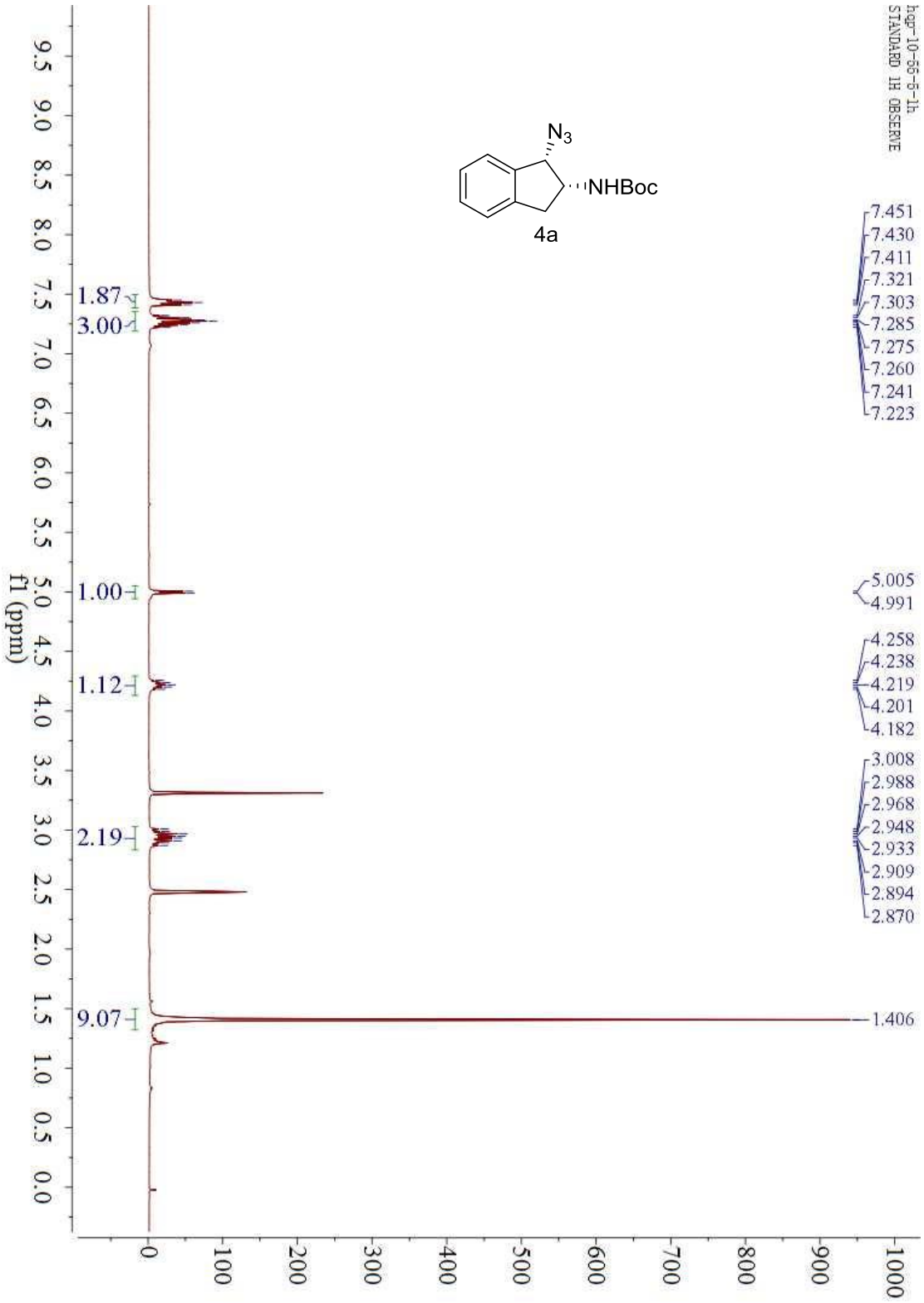

hqp-23-dicl-13c
OH
NHAc
Cl
Cl
2o
172.362
143.482
139.975
131.454
129.132
128.382
123.383
79.275
59.090
35.033
21.202
f1 (ppm)

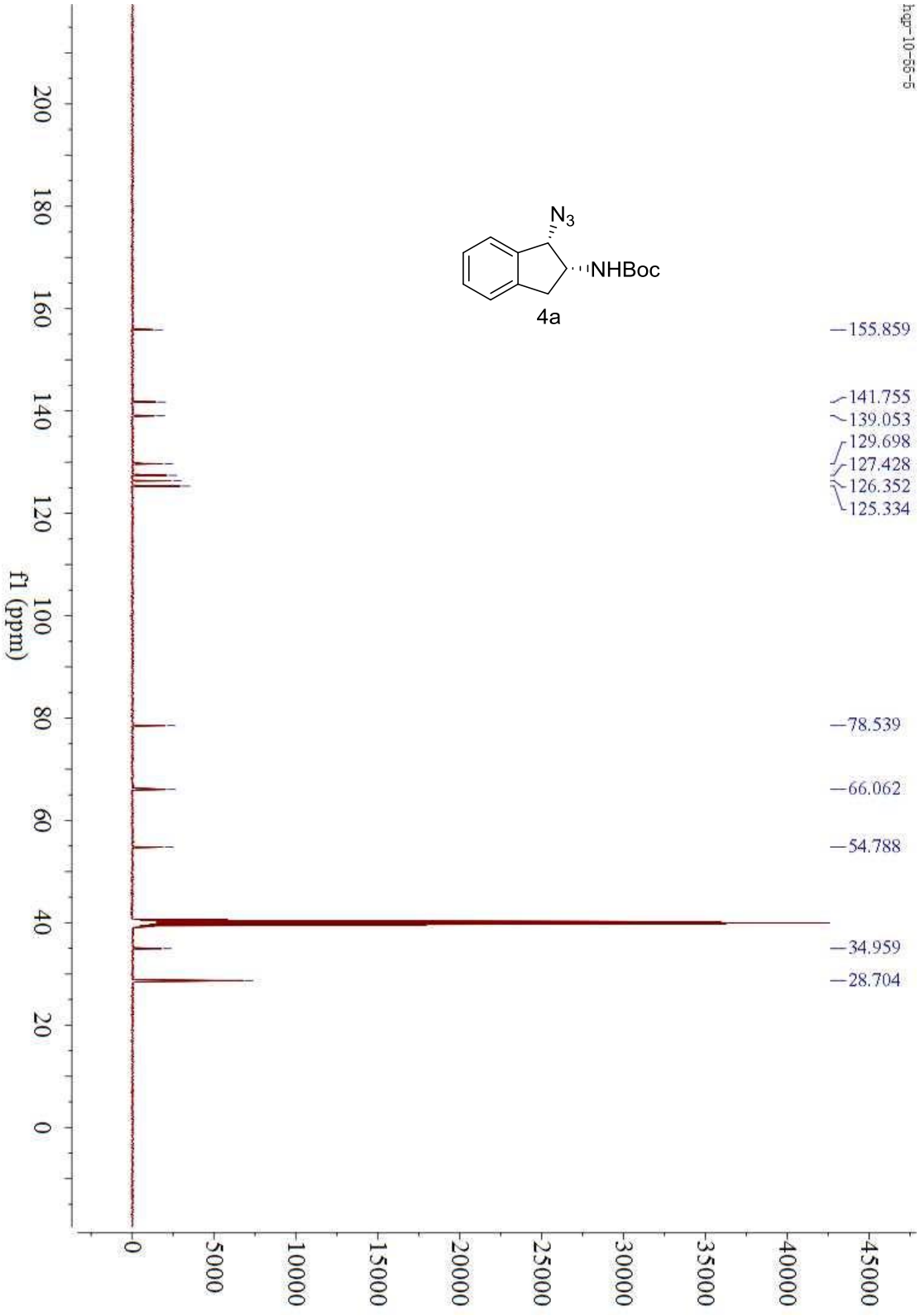

OH
NHAc
2p
3.03
1.00
1.99
0.99
1.22
1.26
1.23
3.07
7.803
7.780
7.661
7.439
7.427
7.421
7.415
7.407
7.403
7.390
5.109
5.092
4.392
4.373
4.353
4.334
3.463
3.444
3.423
3.404
2.866
2.845
2.827
2.805
2.007
f1 (ppm)


hqp-10-17-6-13c
OH
NHAc
2p
172.491
141.579
137.494
134.011
133.204
127.647
127.252
125.358
124.941
122.586
122.377
78.621
59.720
34.756
21.251
f1 (ppm)


hqp-10-21-1H
STANDARD 1H OBSERVE
OH
NHBoc
3a
7.329
7.319
7.308
7.224
7.215
7.211
7.207
7.202
7.177
7.168
7.158
4.947
4.931
4.051
4.031
4.012
3.254
3.235
3.216
3.196
2.697
2.676
2.658
2.637
1.460
3.74
0.98
0.93
1.00
1.00
8.50
f1 (ppm)


hqr-10-21-13c
OH
NHBoc
3a
157.211
142.725
139.164
127.813
126.572
124.267
123.610
79.294
78.762
60.847
35.550
27.382
f1 (ppm)


hqp-10-66-6-1h
STANDARD 1H OBSERVE
N3
NHBoc
4a
7.451
7.430
7.411
7.321
7.303
7.285
7.275
7.260
7.241
7.223
5.005
4.991
4.258
4.238
4.219
4.201
4.182
3.008
2.988
2.968
2.948
2.933
2.909
2.894
2.870
1.406
1.87
3.00
1.00
1.12
2.19
9.07
f1 (ppm)

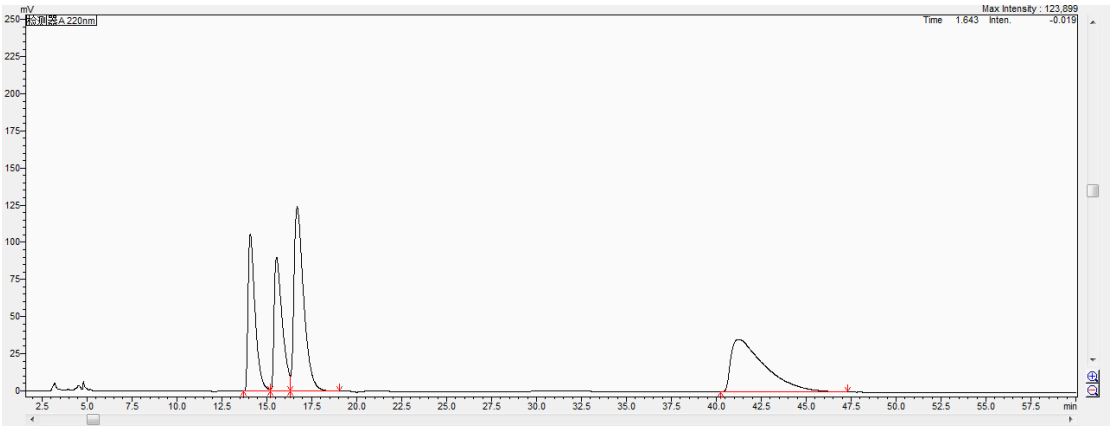

hqp-10-66-5
N3
NHBoc
4a
155.859
141.755
139.053
129.698
127.428
126.352
125.334
78.539
66.062
54.788
34.959
28.704
f1 (ppm)
200
180
160
140
120
100
80
60
40
20
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000

9. HPLC spectra

_N_-((1_R_,2_R_)-1-hydroxy-2,3-dihydro-1_H_-inden-2-yl)acetamide (2a)

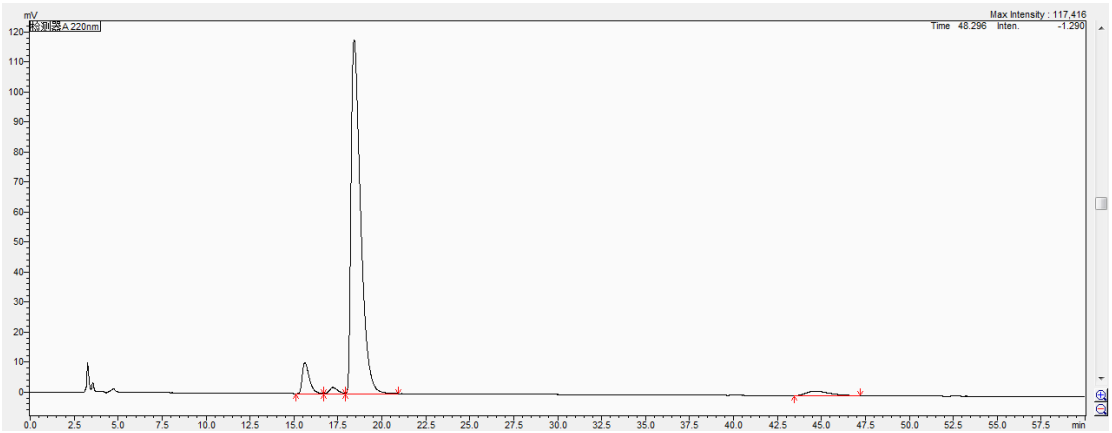
HPLC conditions: DAICEL Chiralpak OJ column, Hexene/_i_-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 °C

Racemic



	Retention Time (min)	Area (%)
Peak 1	14.084	19.350
Peak 2	15.543	18.965
Peak 3	16.690	30.989
Peak 4	41.245	30.697

Chiral

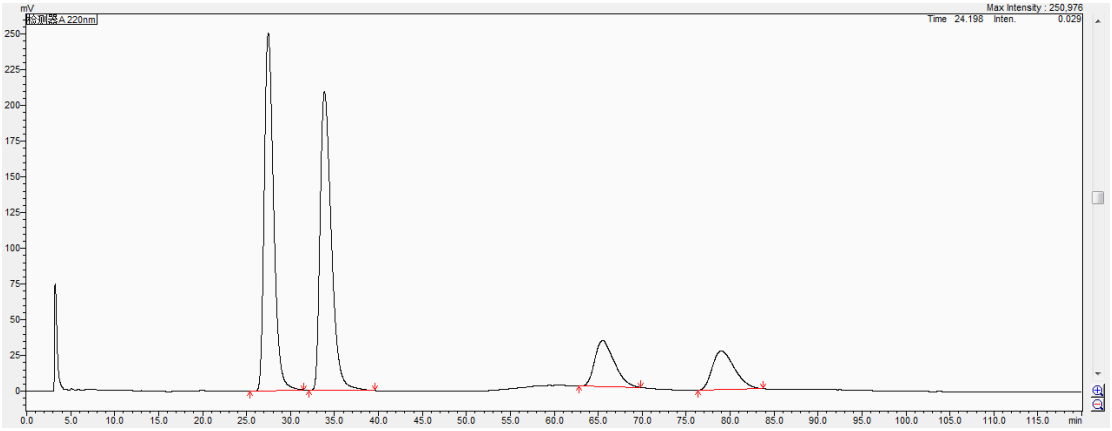


	Retention Time (min)	Area (%)
Peak 1	15.624	5.849
Peak 2	17.218	1.324
Peak 3	18.427	90.071
Peak 4	44.625	2.756

***N*-((1*R*,2*R*)-1-hydroxy-6-methyl-2,3-dihydro-1*H*-inden-2-yl)acetamide (2b).**

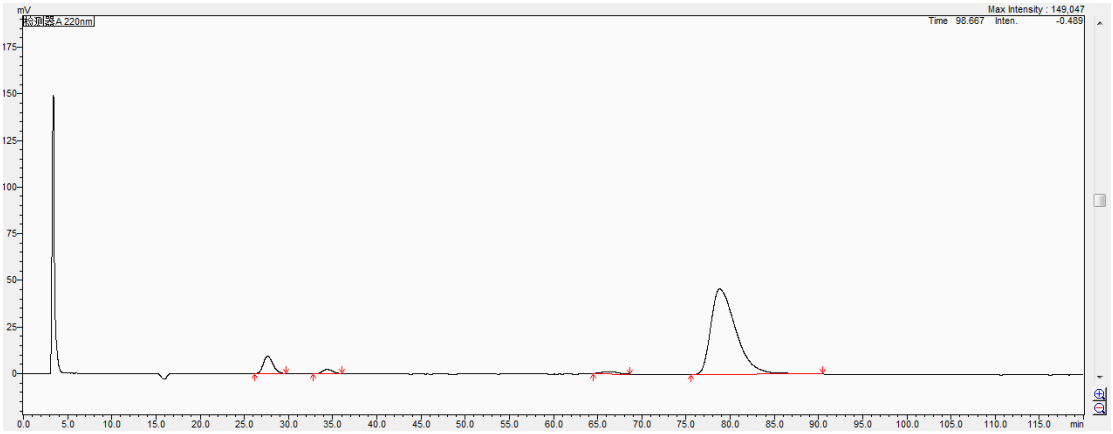
HPLC conditions: DAICEL Chiralpak OZ column, Hexene/*i*-PrOH = 95/5, 220 nm, , 1.0 mL/min, 40 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	27.464	39.485
Peak 2	33.866	39.654
Peak 3	65.506	10.561
Peak 4	78.977	10.300

Chiral

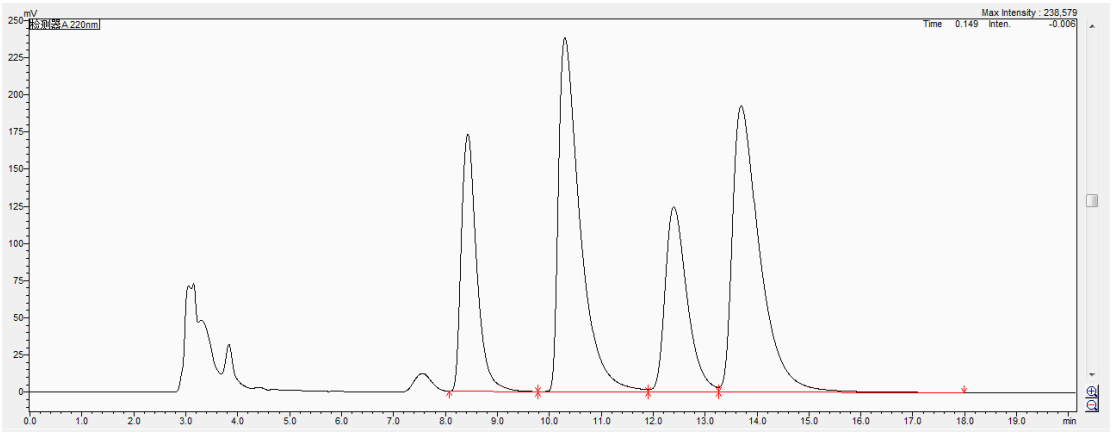


	Retention Time (min)	Area (%)
Peak 1	27.642	7.086
Peak 2	34.387	1.825
Peak 3	66.324	1.545
Peak 4	78.810	89.544

***N*-((1*R*,2*R*)-1-hydroxy-4-methyl-2,3-dihydro-1*H*-inden-2-yl)acetamide (2c).**

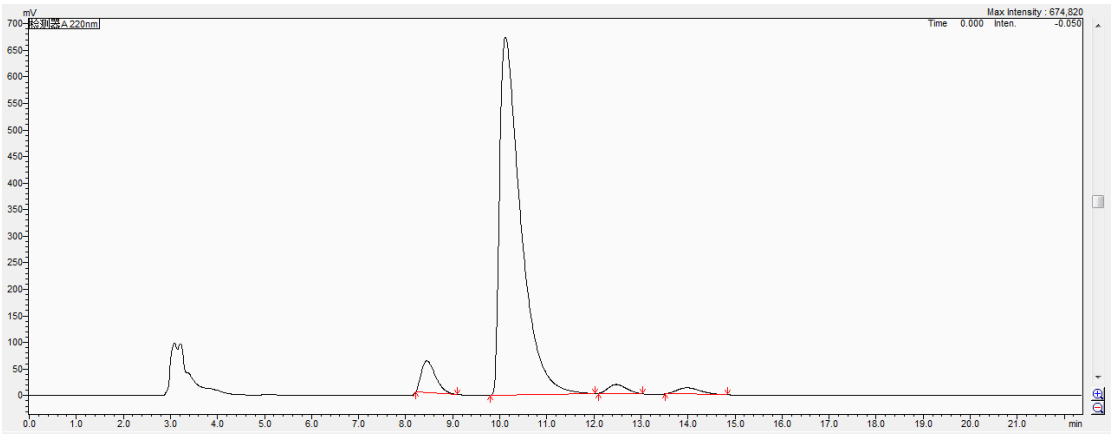
HPLC conditions: DAICEL Chiralpak AD-H column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	8.432	17.034
Peak 2	10.303	32.561
Peak 3	12.399	17.116
Peak 4	13.698	33.289

Chiral

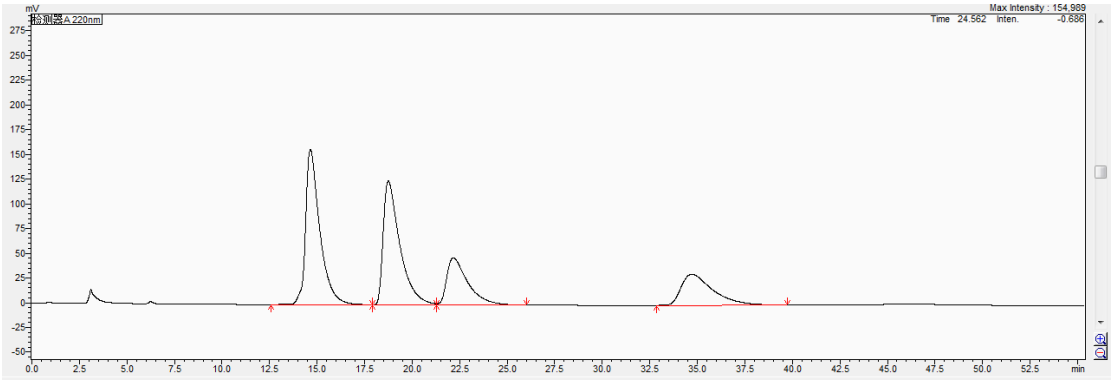


	Retention Time (min)	Area (%)
Peak 1	8.452	5.418
Peak 2	10.121	90.746
Peak 3	12.476	1.995
Peak 4	13.976	1.841

***N*-((1*R*,2*R*)-1-hydroxy-4,6-dimethyl-2,3-dihydro-1*H*-inden-2-yl)acetamide (2d)**

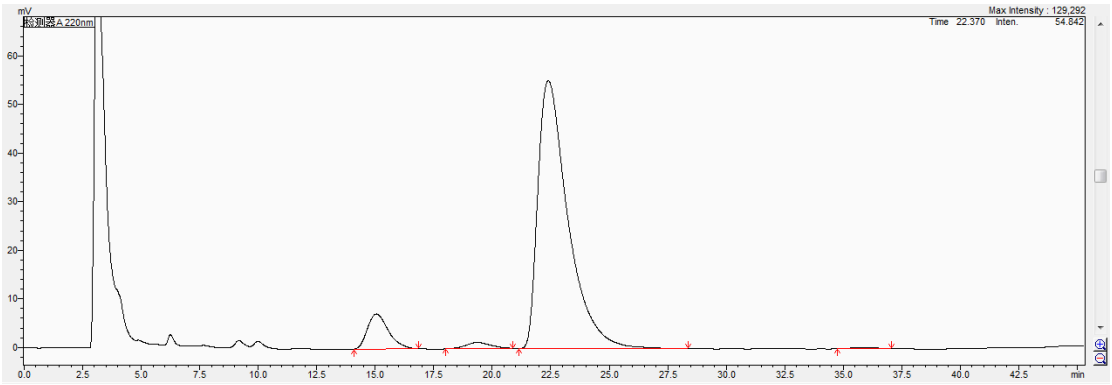
HPLC conditions: DAICEL Chiralpak AD-H column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Rentention Time (min)	Area (%)
Peak 1	14.649	35.372
Peak 2	18.751	32.968
Peak 3	22.164	15.800
Peak 4	34.701	15.861

Chiral

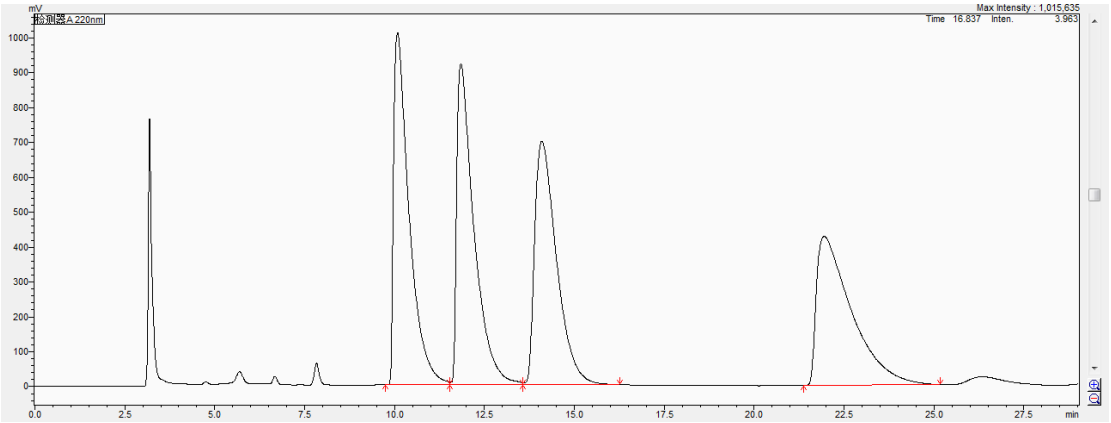


	Rentention Time (min)	Area (%)
Peak 1	15.056	8.083
Peak 2	19.359	1.680
Peak 3	22.398	89.936
Peak 4	35.862	0.301

***N*-((1*R*,2*R*)-1-hydroxy-5,7-dimethyl-2,3-dihydro-1*H*-inden-2-yl)acetamide (2e)**

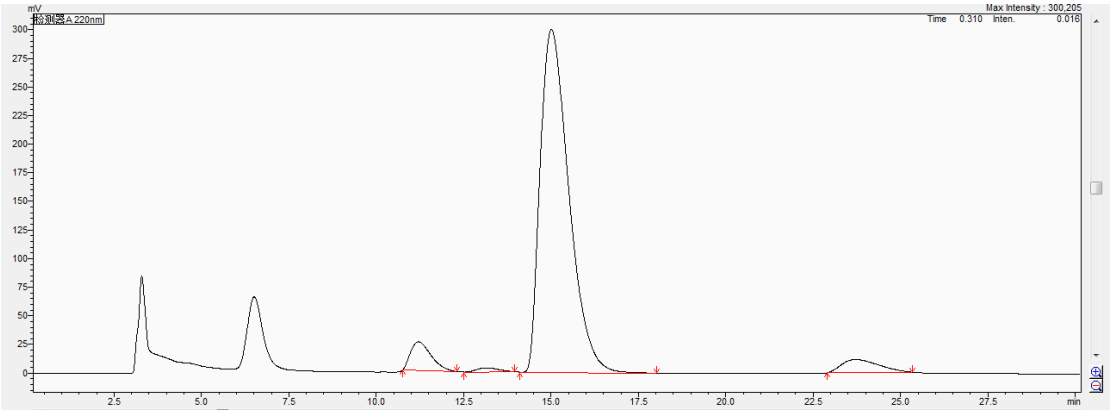
HPLC conditions: DAICEL Chiralpak OJ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	10.082	25.411
Peak 2	11.845	25.725
Peak 3	14.097	24.594
Peak 4	21.945	24.269

Chiral

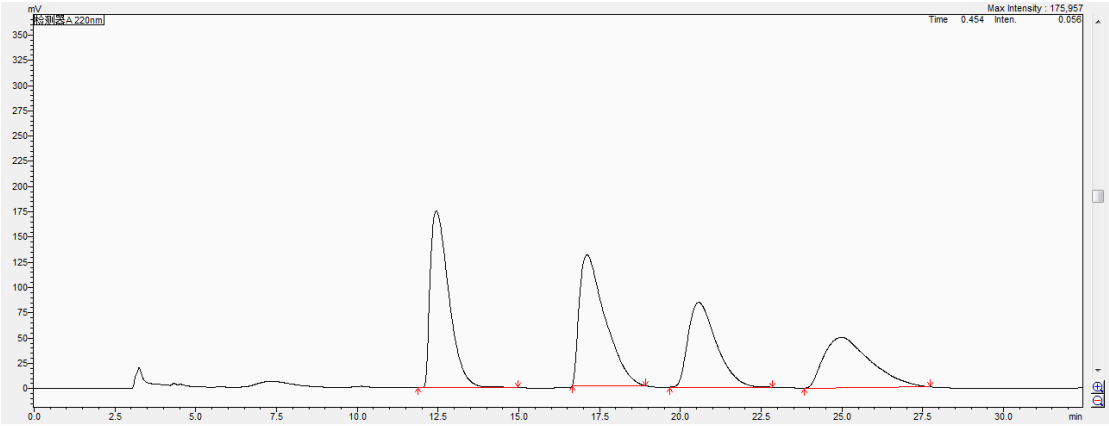


	Retention Time (min)	Area (%)
Peak 1	11.210	5.353
Peak 2	13.170	0.798
Peak 3	15.013	89.398
Peak 4	23.720	4.451

***N*-((1*R*,2*R*)-6-ethyl-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2f)**

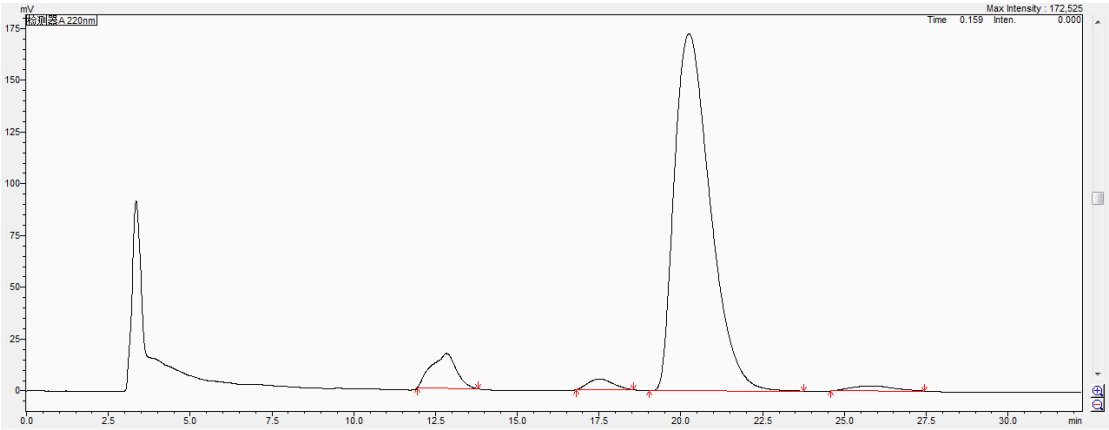
HPLC conditions: DAICEL Chiralpak OJ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	12.443	29.128
Peak 2	17.106	29.561
Peak 3	20.565	20.787
Peak 4	24.983	20.524

Chiral

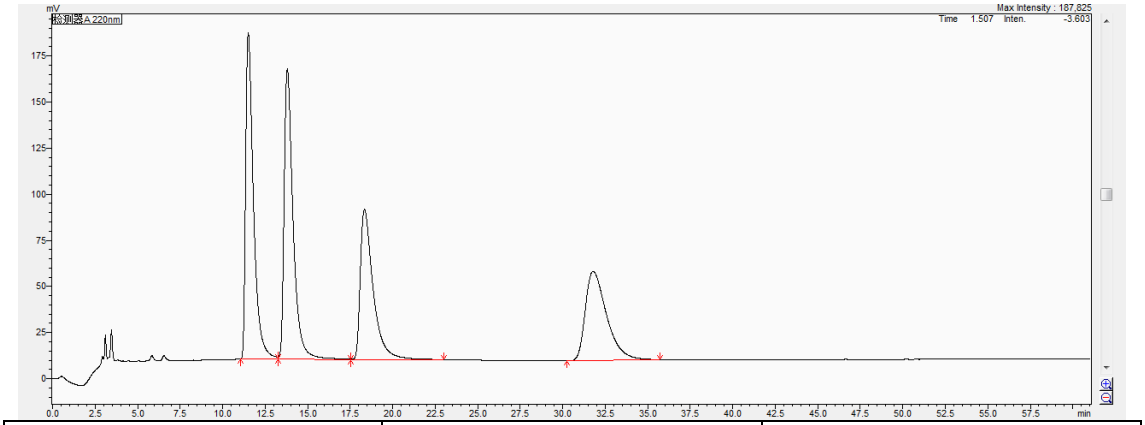


	Retention Time (min)	Area (%)
Peak 1	12.840	6.163
Peak 2	17.515	1.937
Peak 3	20.250	90.374
Peak 4	25.796	1.526

***N*-((1*R*,2*R*)-1-hydroxy-6-phenyl-2,3-dihydro-1*H*-inden-2-yl)acetamide (2g)**

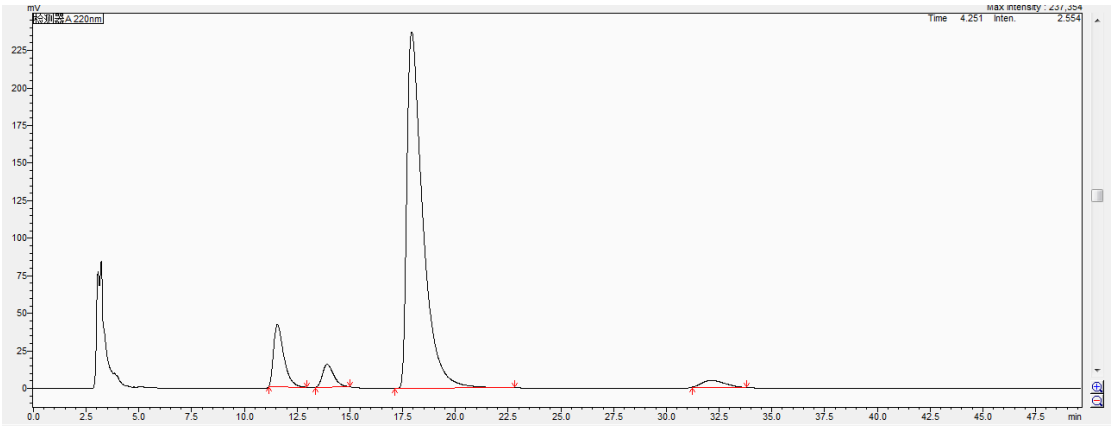
HPLC conditions: DAICEL Chiralpak AD column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	11.508	28.377
Peak 2	13.803	29.166
Peak 3	18.344	21.350
Peak 4	31.797	21.108

Chiral

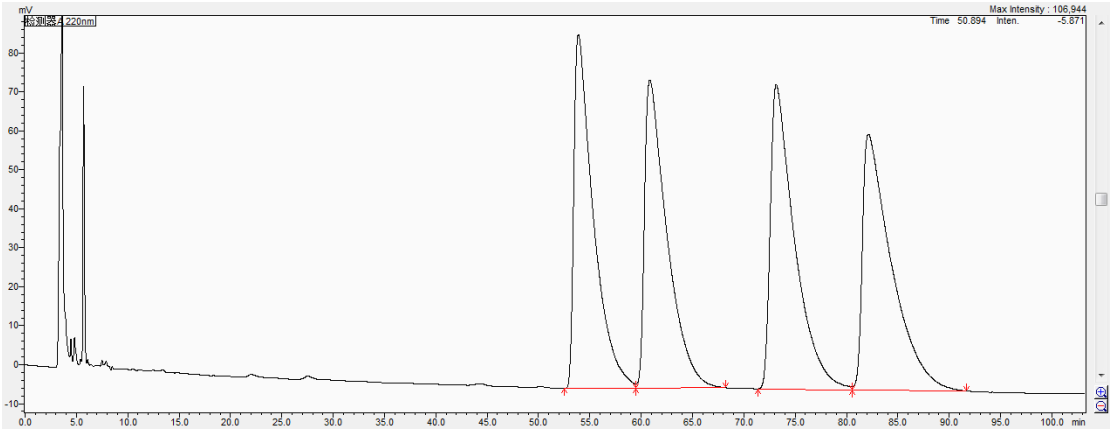


	Retention Time (min)	Area (%)
Peak 1	11.563	9.398
Peak 2	13.920	3.869
Peak 3	17.933	84.393
Peak 4	32.141	2.339

Methyl (2*R*,3*R*)-2-acetamido-3-hydroxy-2,3-dihydro-1*H*-indene-5-carboxylate (2h)

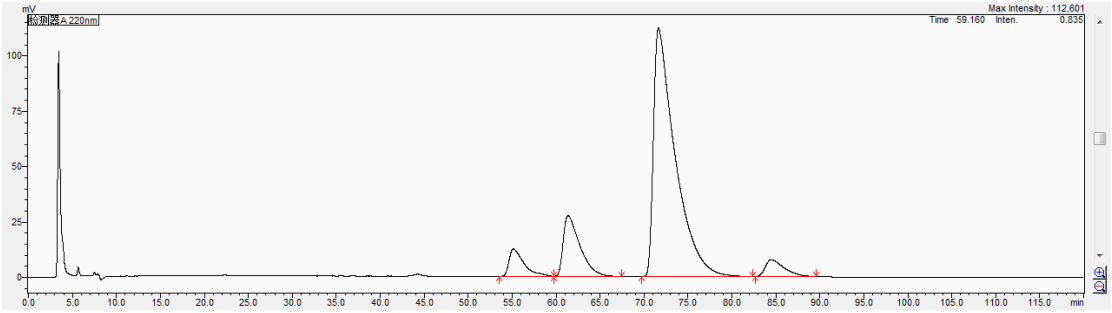
HPLC conditions: DAICEL Chiralpak IE column, Hexene/*i*-PrOH = 90/10, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	53.877	24.164
Peak 2	60.834	24.172
Peak 3	73.149	25.817
Peak 4	82.128	25.847

Chiral

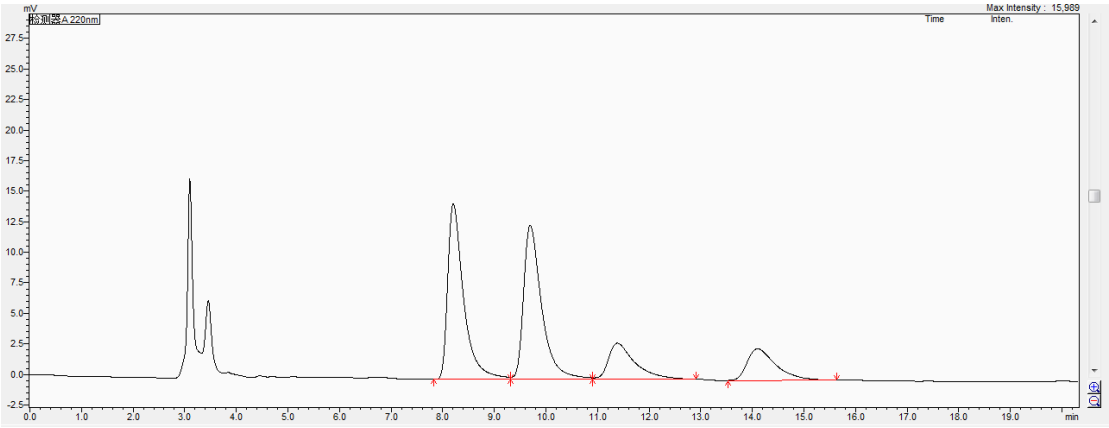


	Retention Time (min)	Area (%)
Peak 1	55.167	5.863
Peak 2	61.365	14.340
Peak 3	71.648	75.329
Peak 4	84.502	4.468

***N*-((1*R*,2*R*)-6-fluoro-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2i)**

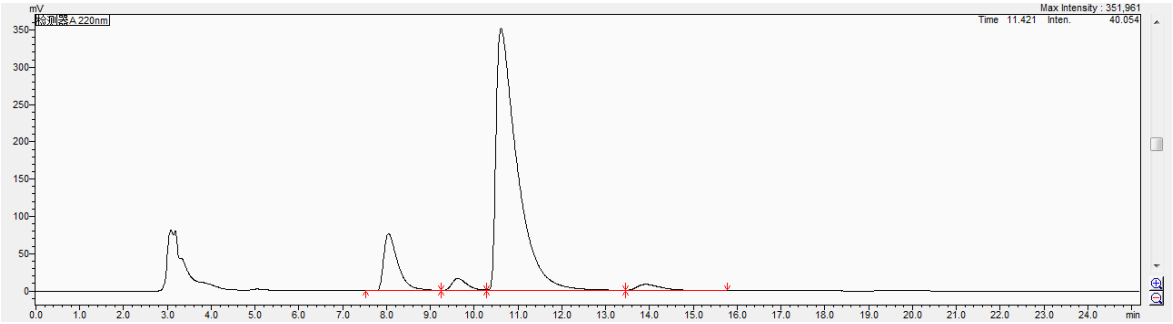
HPLC conditions: DAICEL Chiralpak AD column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	8.208	37.418
Peak 2	9.694	37.509
Peak 3	11.384	12.866
Peak 4	14.100	12.207

Chiral

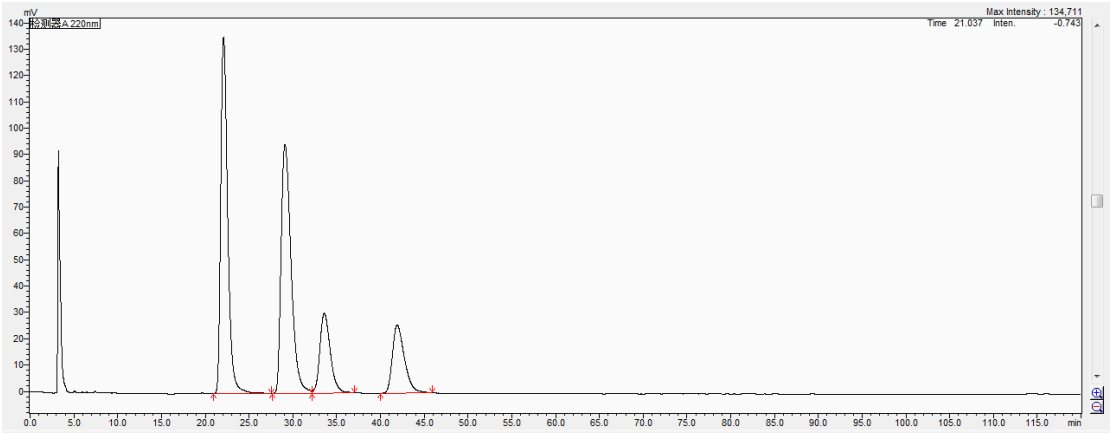


	Retention Time (min)	Area (%)
Peak 1	8.044	12.177
Peak 2	9.626	2.891
Peak 3	10.613	82.607
Peak 4	13.918	2.325

***N*-((1*R*,2*R*)-4-fluoro-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2j)**

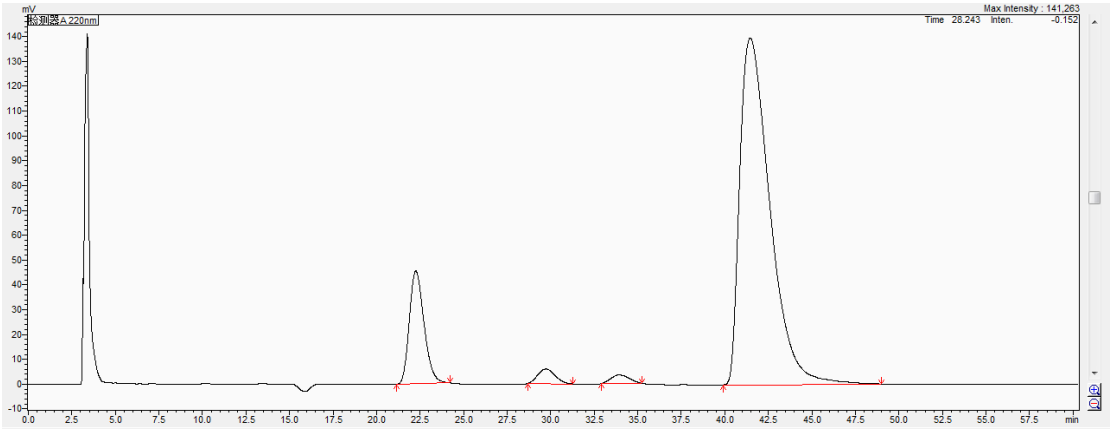
HPLC conditions: DAICEL Chiralpak OZ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 40 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	22.095	37.514
Peak 2	29.108	37.531
Peak 3	33.602	12.588
Peak 4	41.915	12.367

Chiral

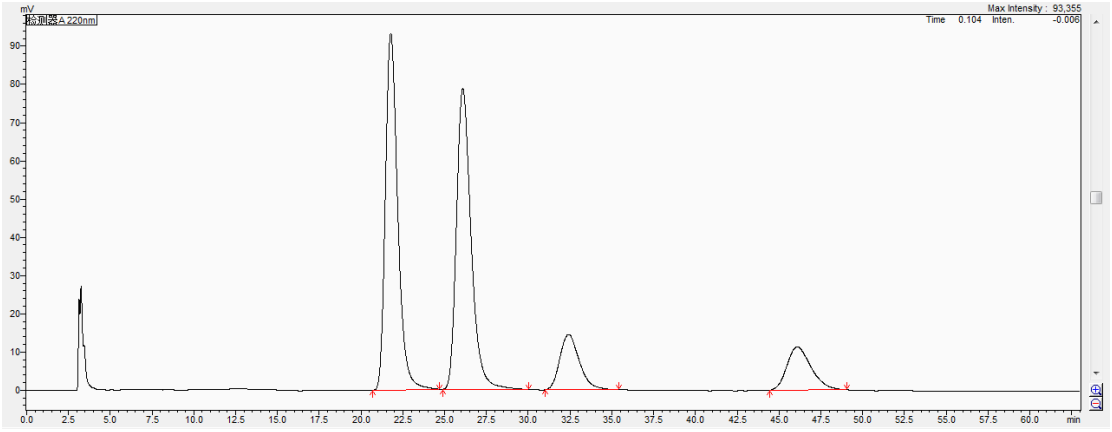


	Retention Time (min)	Area (%)
Peak 1	22.253	13.279
Peak 2	29.732	2.021
Peak 3	33.919	1.241
Peak 4	41.464	83.459

***N*-((1*R*,2*R*)-6-chloro-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2k)**

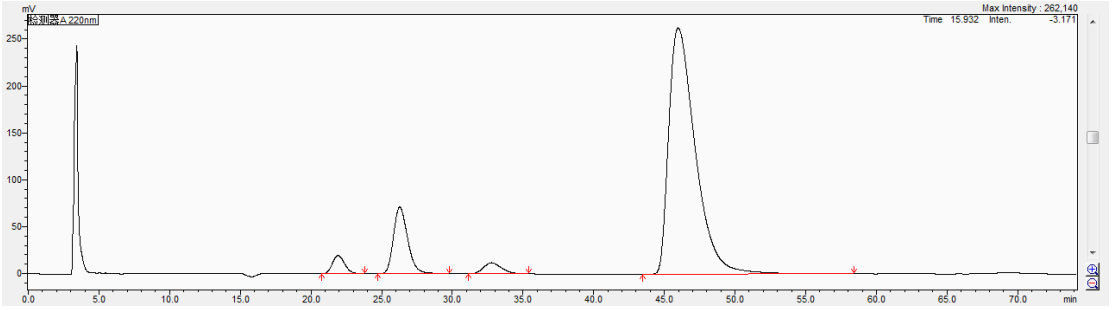
HPLC conditions: DAICEL Chiralpak OZ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 40 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	21.779	40.306
Peak 2	26.086	40.272
Peak 3	32.422	9.829
Peak 4	46.090	9.592

Chiral

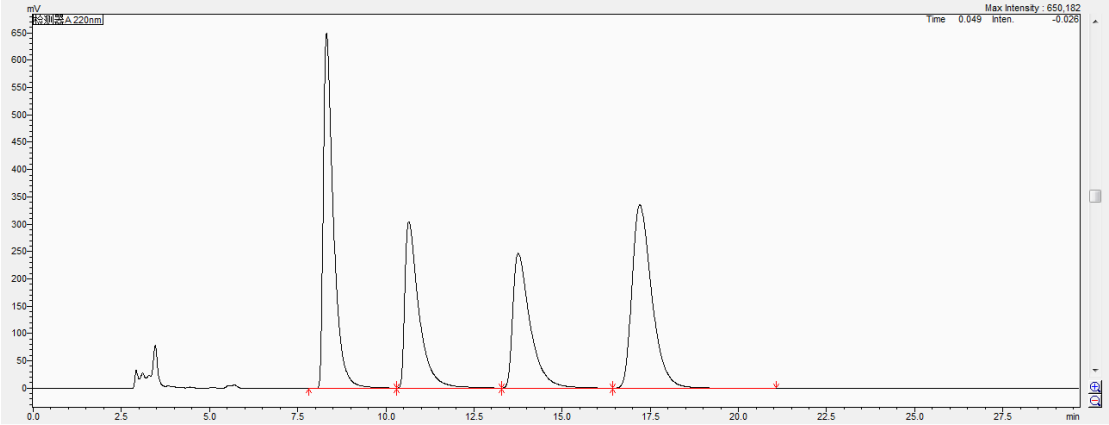


	Retention Time (min)	Area (%)
Peak 1	21.916	2.818
Peak 2	26.276	12.020
Peak 3	32.773	2.532
Peak 4	45.974	82.630

***N*-((1*R*,2*R*)-4-chloro-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2l)**

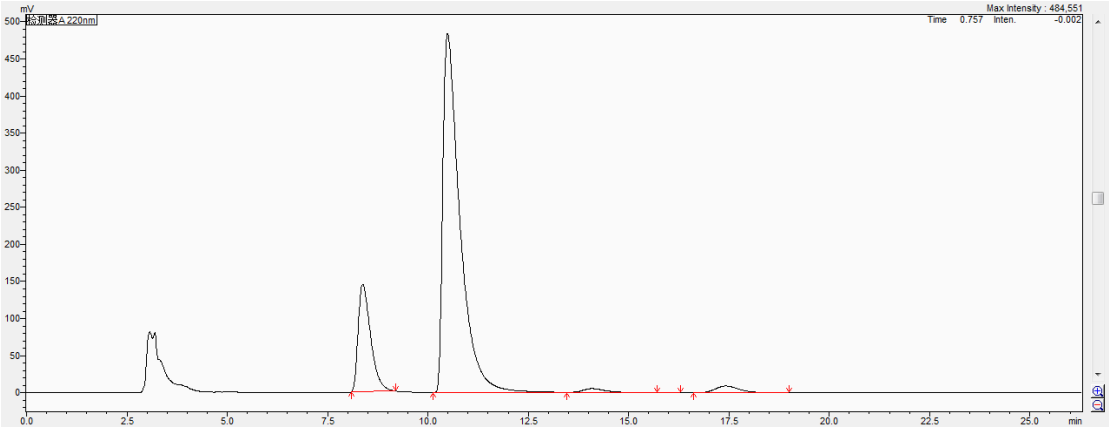
HPLC conditions: DAICEL Chiralpak AD column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	8.317	30.102
Peak 2	10.655	19.799
Peak 3	13.758	19.701
Peak 4	17.205	30.398

Chiral

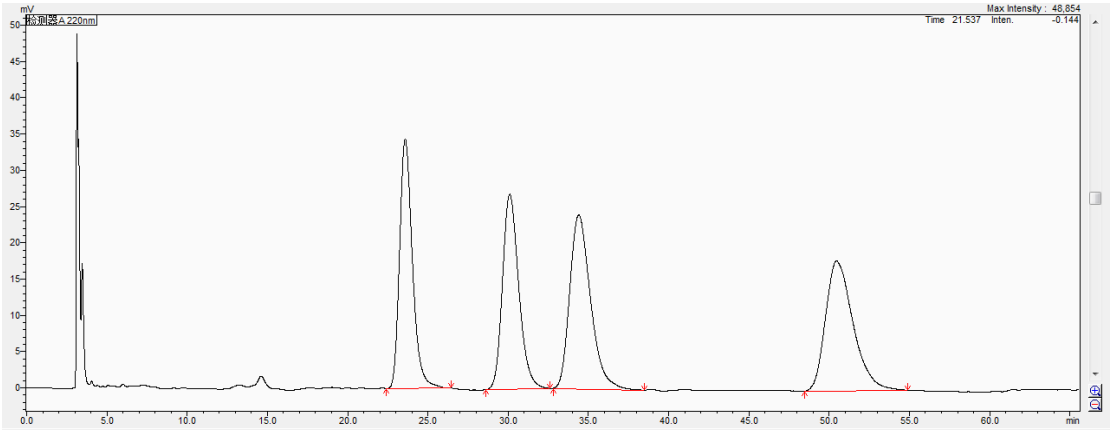


	Retention Time (min)	Area (%)
Peak 1	8.377	17.227
Peak 2	10.491	79.619
Peak 3	14.088	1.073
Peak 4	17.420	2.081

***N*-((1*R*,2*R*)-6-bromo-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2m)**

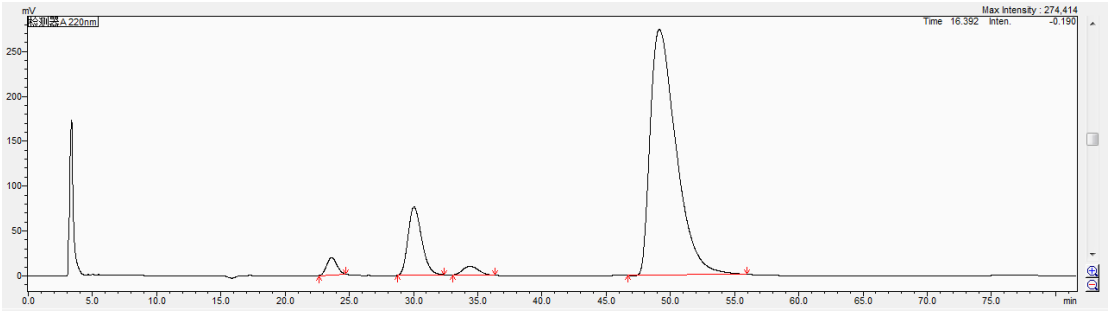
HPLC conditions: DAICEL Chiralpak OZ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 40 °C

Racemic



	Retention Time (min)	Area (%)
Peak 1	23.585	23.534
Peak 2	30.101	23.362
Peak 3	34.398	26.619
Peak 4	50.458	26.486

Chiral

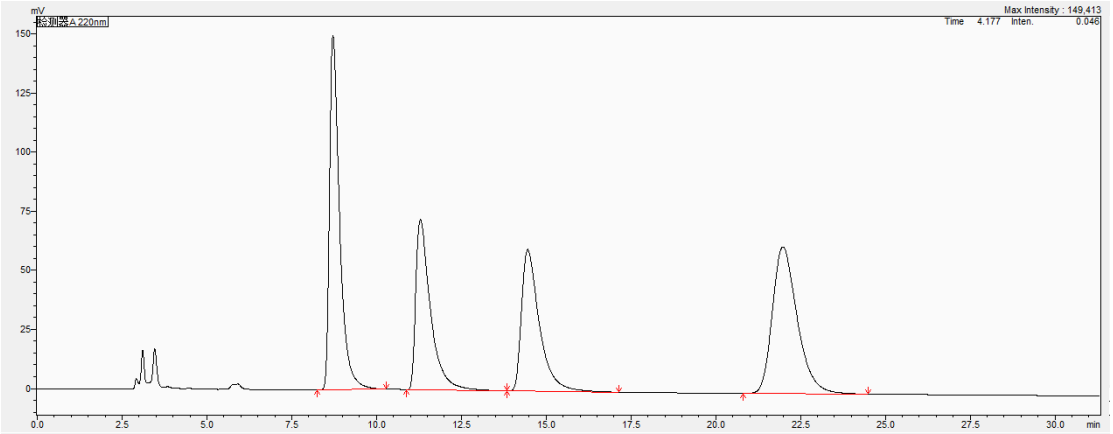


	Retention Time (min)	Area (%)
Peak 1	23.614	2.326
Peak 2	30.030	12.211
Peak 3	34.385	1.857
Peak 4	49.141	83.606

***N*-((1*R*,2*R*)-4-bromo-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2n)**

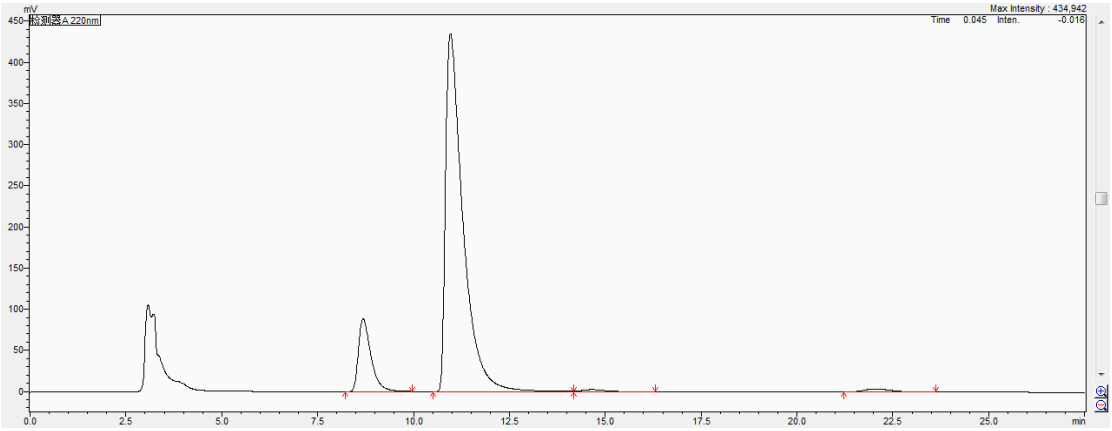
HPLC conditions: DAICEL Chiralpak AD column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	8.719	29.324
Peak 2	11.294	20.504
Peak 3	14.458	20.552
Peak 4	21.981	29.621

Chiral

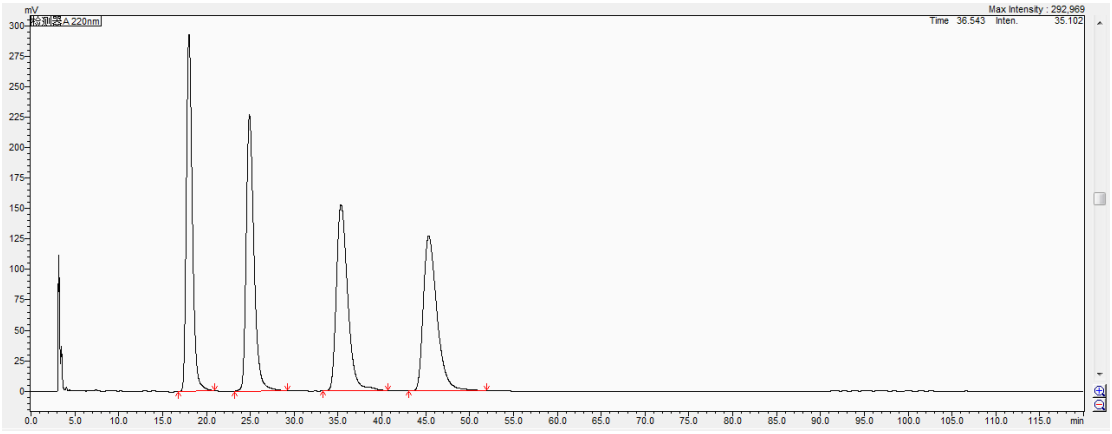


	Retention Time (min)	Area (%)
Peak 1	8.687	12.468
Peak 2	10.964	85.519
Peak 3	14.653	0.742
Peak 4	22.056	1.271

***N*-((1*R*,2*R*)-4,5-dichloro-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)acetamide (2o)**

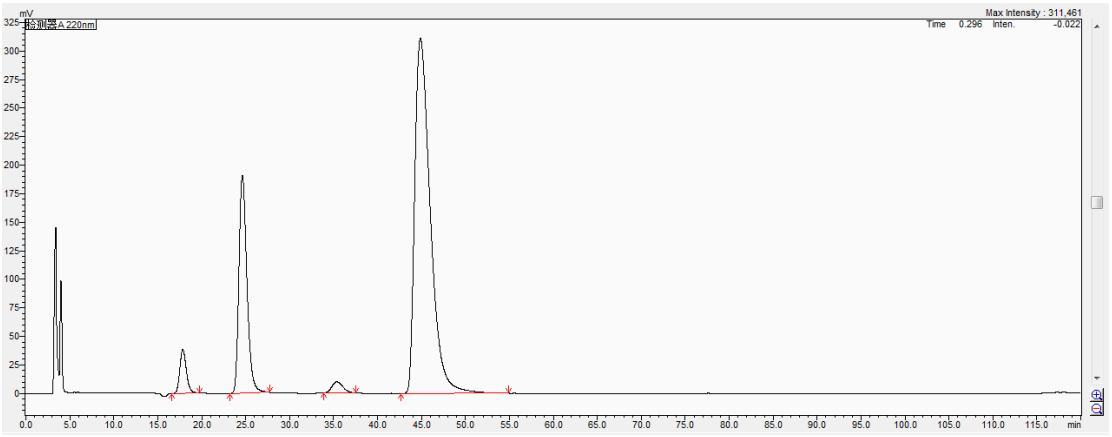
HPLC conditions: DAICEL Chiralpak OZ column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 40 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	18.009	25.016
Peak 2	24.905	25.229
Peak 3	35.345	24.890
Peak 4	45.341	24.866

Chiral

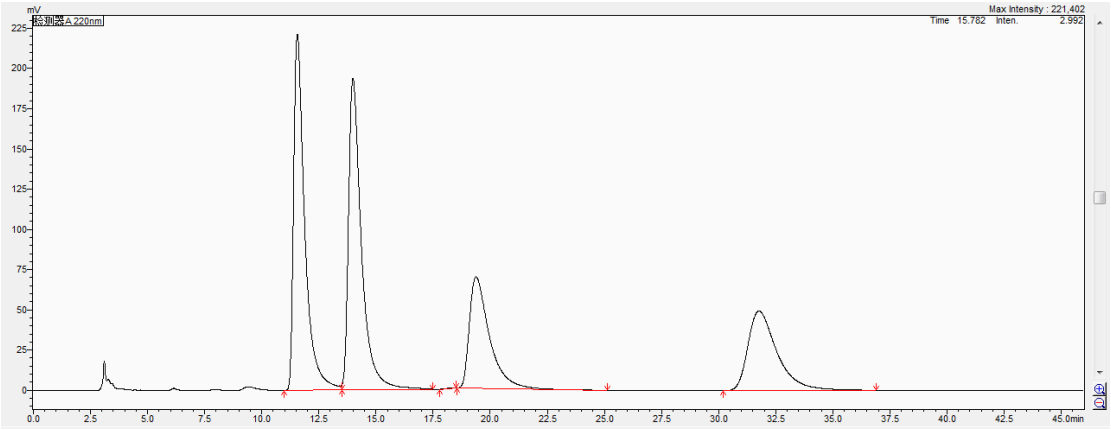


	Retention Time (min)	Area (%)
Peak 1	17.852	3.722
Peak 2	24.630	22.701
Peak 3	35.391	1.627
Peak 4	44.873	71.951

***N*-((1*R*,2*R*)-1-hydroxy-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-2-yl)acetamide (2p)**

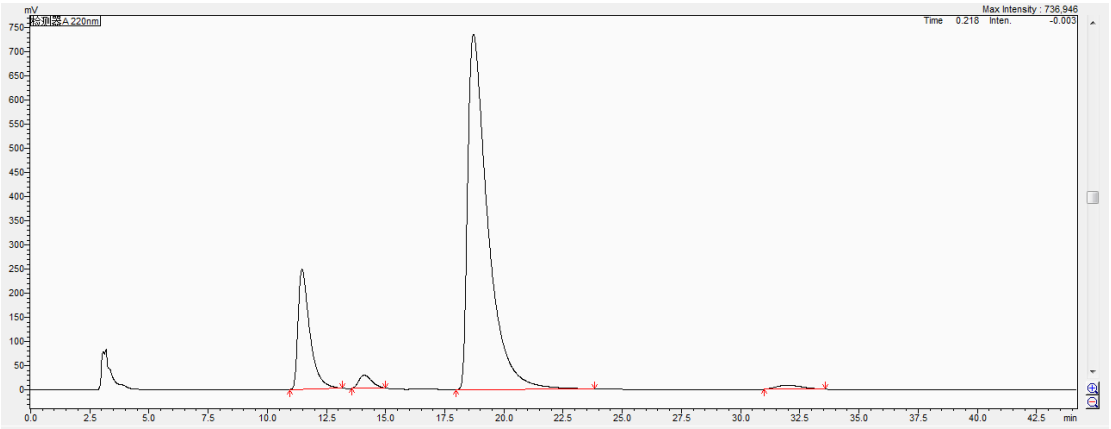
HPLC conditions: DAICEL Chiralpak AD column, Hexene/*i*-PrOH = 95/5, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Retention Time (min)	Area (%)
Peak 1	11.555	31.571
Peak 2	13.993	32.066
Peak 3	19.382	17.846
Peak 4	31.767	18.517

Chiral

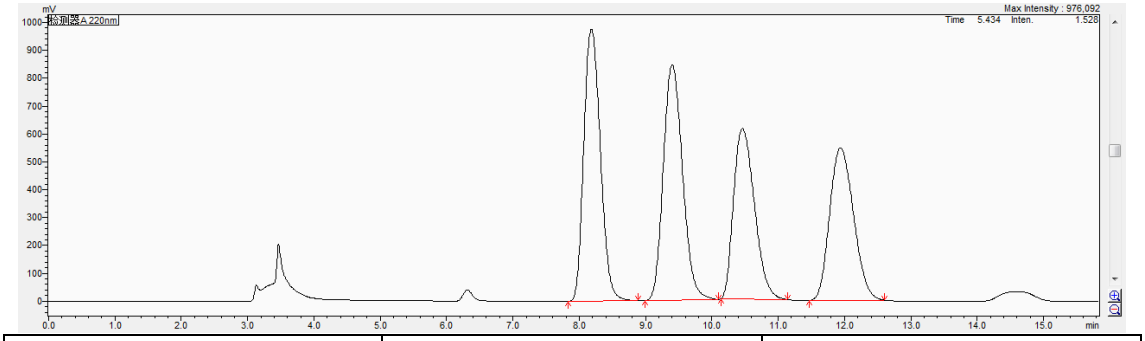


	Retention Time (min)	Area (%)
Peak 1	11.468	16.006
Peak 2	14.091	1.919
Peak 3	18.713	80.870
Peak 4	31.978	1.204

***tert*-Butyl ((1*S*,2*R*)-1-azido-2,3-dihydro-1*H*-inden-2-yl)carbamate (4a)**

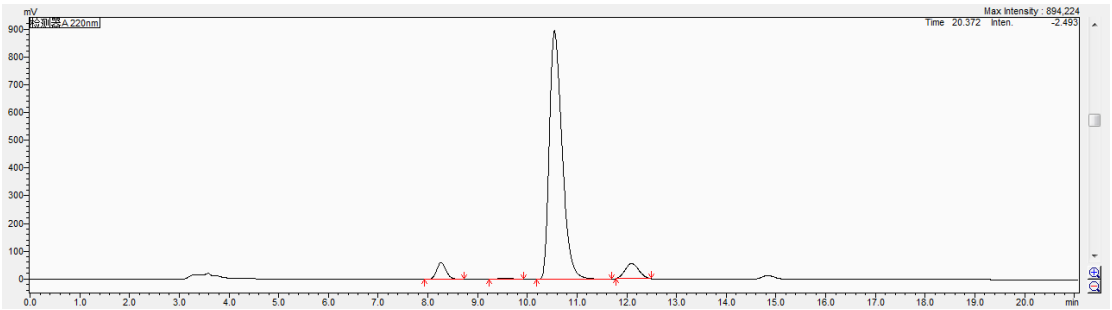
HPLC conditions: DAICEL Chiralpak IC-3 column, Hexene/*i*-PrOH = 98/2, 220 nm, 1.0 mL/min, 25 ^{o}C

Racemic



	Rentention Time (min)	Area (%)
Peak 1	8.183	27.733
Peak 2	9.402	27.890
Peak 3	10.461	21.940
Peak 4	11.940	22.437

Chiral



	Rentention Time (min)	Area (%)
Peak 1	8.264	4.391
Peak 2	9.554	0.458
Peak 3	10.547	89.277
Peak 4	12.097	5.874