

Supporting Information for

Asymmetric Synthesis of Chiral

Pyrazolo[3,4-b]pyridin-6-ones under Carbene Catalysis

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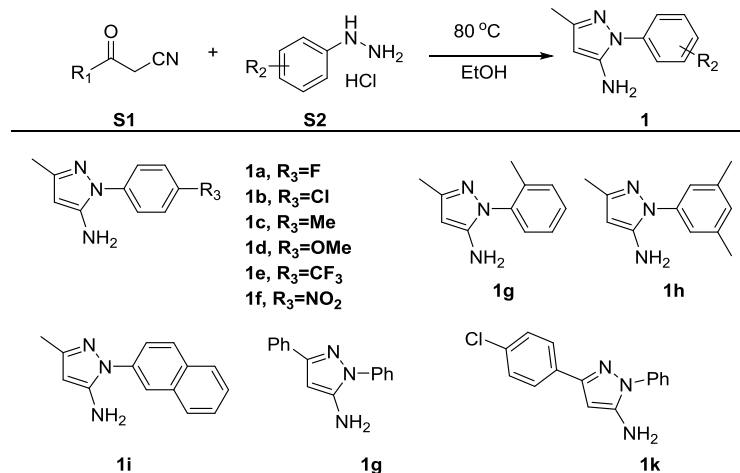
I. General Information

Commercially available materials were purchased from Alfa Aesar and Sigma-Aldrich. THF was distilled over sodium. Other solvents were dried over 4Å molecular sieve prior use. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), triplet of doublets (dt), triplet of triplets (tt), multiplets (m), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on a Waters Q–TOF Premier Spectrometer. The determination of enantiomeric excess was performed *via* chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Jasco P-1030 polarimeter and are reported as follows: $[\alpha]_{\text{D}}^{\text{rt}}$ (c is in gm per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness).

II. General procedure

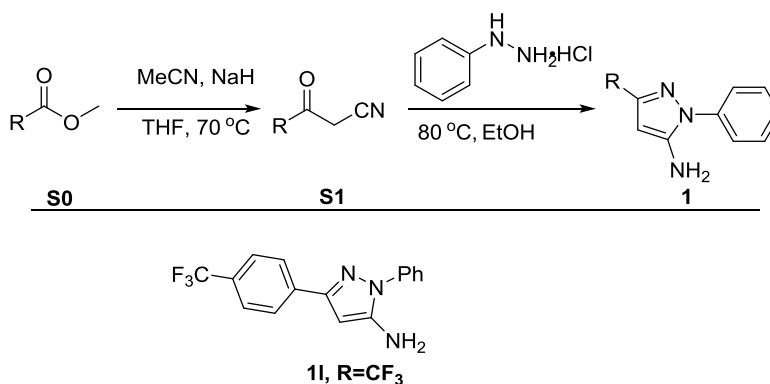
a) General experimental procedure for the synthesis of 5-aminopyrazoles 1

Method 1



S1 (4.5 mmol, 0.9 equiv) was added to the suspension of **S2** (5 mmol, 1.0 equiv.) in EtOH (15 ml), the reaction mixture then was stirred at 80 °C for 18 h. After completion of the reaction (monitored by TLC), EtOH was concentrated in vacuo and then was diluted with EtOAc (30.0 mL) and 15% NaOH (30.0 mL). Then the mixture was extracted with EtOAc (3 × 20.0 mL), and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude residue was purified via column chromatography on silica gel (PE/Ea = 5 /1) to afford compounds **S3**.

Method 2.



To a suspension of NaH (10 mmol, 2.0 equiv.) in anhydrous THF (20 mL) at 0 °C was added acetonitrile (15 mmol, 3.0 equiv.) and ester **S0** (5 mmol, 1.0 equiv.) under

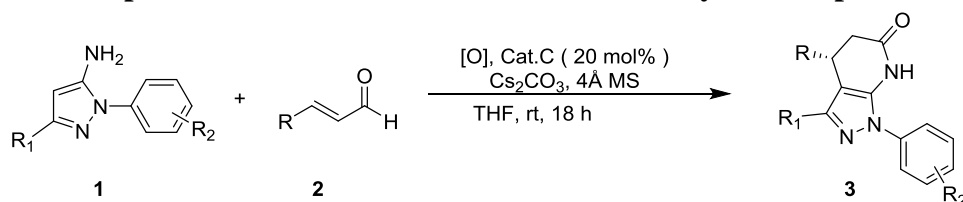
N₂ atmosphere, the reaction mixture was stirred at 70 °C for 5 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to 0 °C, pH of the solution was adjusted to neutral by 1M HCl (aq.) and extracted with ethyl acetate. The organic layer was dried with anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford compound **S1** as a white solid.

According to **Method 1**, the reactions of **S1** with phenylhydrazine hydrochloride to synthesize of **11**.

b) General experimental procedure for the synthesis of enals **2**

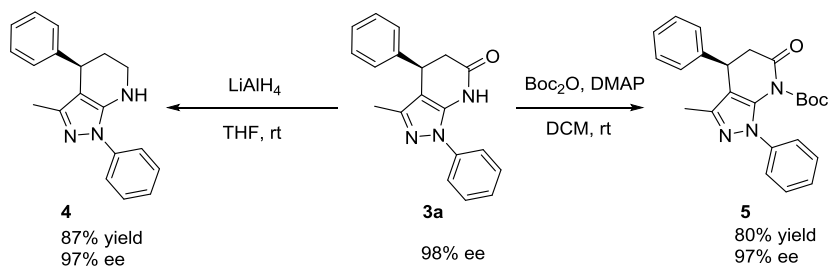
Enals were synthesized according to the literature [1-5]. To a dried 50 mL flask was added formylmethylene triphenylphosphorane (1.521 g, 5 mmol), aldehydes (7 mmol) and 25 mL toluene. The mixture was refluxed overnight (detected by TLC), and then the solvent was removed under reduced pressure. The residue was purified by silicacolumn chromatography to afford the product enals.

c) General procedure for the reactions of **1** with **2** to synthesize products **3**



To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar was added **1** (0.1 mmol, 1.0 equiv.), **2** (0.2 mmol, 2.0 equiv.), Cat.C (0.02 mmol, 0.2 equiv.), 4Å MS (50 mg), DQ (0.2 mmol, 2.0 equiv) and Cs₂CO₃ (0.2 mmol, 2.0 equiv.). To this mixture was added dry THF (1.0 mL), and then the reaction mixture was stirred at 30 °C for 18 hours. The reaction mixture was purified by flash column chromatography on silica gel to afford product **3**.

d) General experimental procedure for the synthesis of **4** or **5**



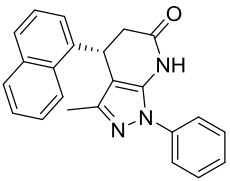
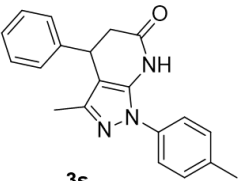
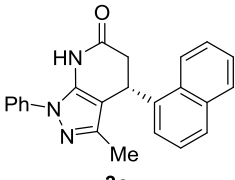
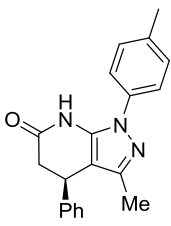
Procedure for the synthesis of compound 4:

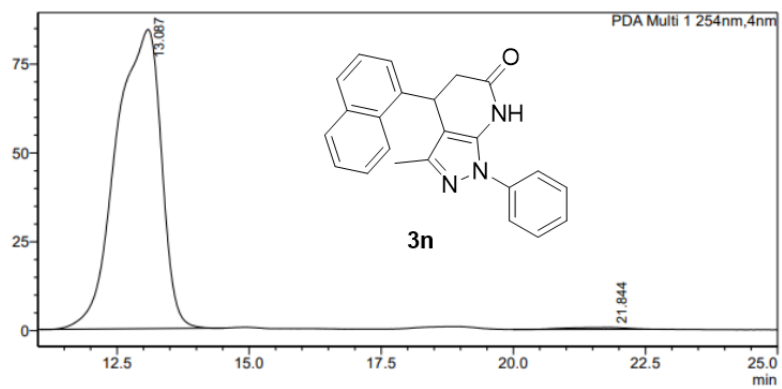
To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar was added **3a** (0.1 mmol) and anhydrous THF (1 mL). The reaction mixture was cooled to 0 °C and added LiAlH₄ (0.4 mmol, 4.0 equiv) in portions, then the reaction mixture was stirred at 30 °C for 5 h. After completion of the reaction (monitored by TLC), the reaction mixture was quenched by water (3.0 mL) and extracted with ethyl acetate (5.0 mL × 3), the combined organic phase washed with brine, dried over Na₂SO₄, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel to afford to give **4** as white solid (87% yield, 97% ee).

Procedure for the synthesis of compound 5:

To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar was added **3a** (0.10 mmol), DMAP (0.01 mmol, 0.1 equiv) and anhydrous THF (1.0 mL). To the reaction mixture was added Di-tert-butyl (0.15 mmol, 1.5 equiv), then the reaction mixture was stirred at 30 °C for overnight. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with saturated salt water (5.0 mL) and extracted with ethyl acetate (5.0 mL × 3), the combined organic phase washed with brine, dried over Na₂SO₄, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel to afford to give **5** as white solid (80% yield, 97% ee).

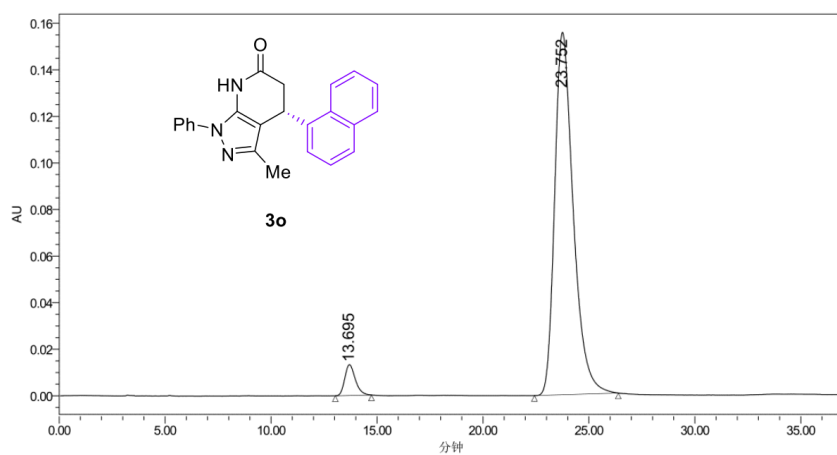
e) Determination of absolute configuration for the product 3.

		Chromatographic column	ee(%)	Ret. Time	Molecular configuration
This work	3n	Chiralpak IC	98	t_R (major) = 13.1 min, t_R (minor) = 21.8 min)	 <p>3n</p>
	3s	Chiralpak IC	99	t_R (major) = 13.4 min, t_R (minor) = 17.4 min)	 <p>3s</p>
Wang group	3o	Chiralpak IC	91	tR(major) = 23.752 min, tR(minor) = 13.695 min.)	 <p>3o</p>
	4a	Chiralpak IC	95	tR(major) = 18.836 min, tR(minor) = 14.342 min.)	 <p>4a</p>



<Peak Table>

Peak#	Ret. Time	Area	Area%	Height
1	13.087	4992892	99.117	84204
2	21.844	44481	0.883	539
Total		5037373	100.000	84743

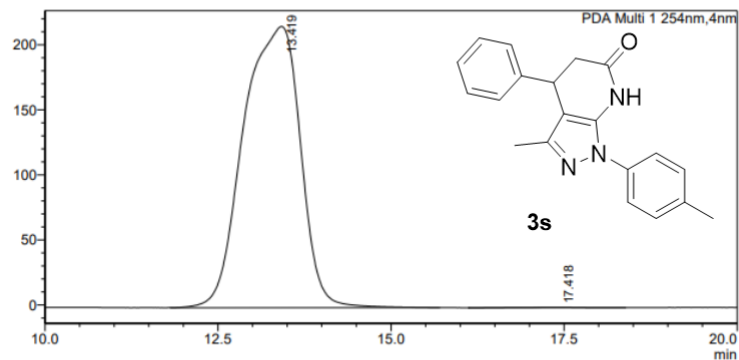


Peak	Ret. Time	Area	Height	Area%	Height%
1	13.695	459395	13267	4.63	7.85
2	23.752	9463916	155655	95.37	92.15
Total		9923311	168922	100.00	100.00

S128

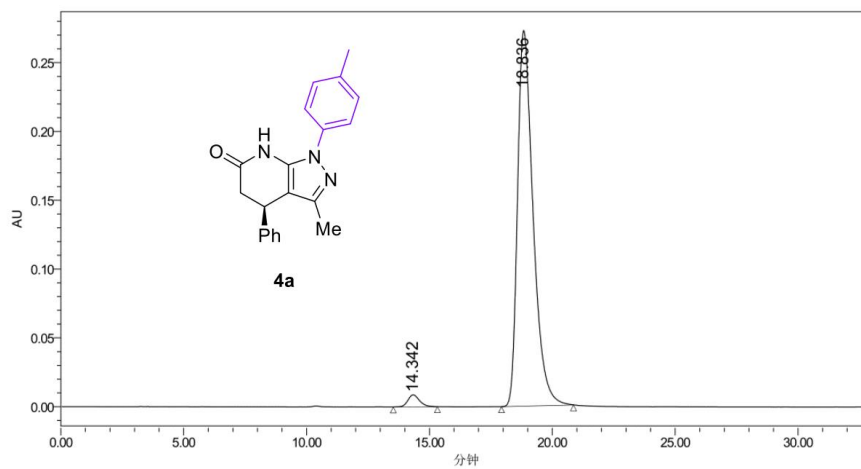
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mAU



<Peak Table>

Peak#	Ret. Time	Area	Area%	Height
1	13.419	12367851	99.817	216289
2	17.418	22701	0.183	376
Total		12390552	100.000	216665



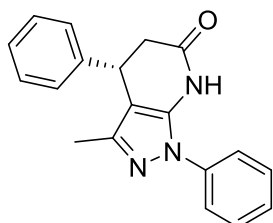
Peak	Ret. Time	Area	Height	Area%	Height%
1	14.342	288443	8755	2.35	3.11
2	18.836	12010864	272974	97.65	96.89
Total		12299307	281729	100.00	100.00

S134

III. Characterizations of products, reference

Structures of known compounds were confirmed by NMR spectral comparison with literature data. The compound not reported before, ^1H NMR and ^{13}C NMR characterization and the corresponding spectra are provided.

a) Characterizations of Products



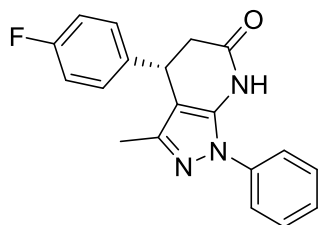
3a

(S)-3-methyl-1,4-diphenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one :

96% yield, 99% ee; $[\alpha]_{\text{D}}^{25} = -76.4$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 90/10, 1.0 mL/min, t_{R} (major) = 16.0 min, t_{R} (minor) = 22.9 min).

^1H NMR (400 MHz, CDCl_3) δ 8.21 (s, 1H), 7.46(d, $J = 4.0$ Hz, 4H), 7.35-7.31 (m, 3H), 7.28-7.21 (m, 3H), 4.21 (t, $J = 6.8$ Hz 1H), 3.04 (dd, $J = 8.8$ Hz, $J = 16.0$ Hz, 1H), 3.04 (dd, $J = 6.8$ Hz, $J = 16.4$ Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 147.0, 142.4, 137.5, 137.5, 129.9, 129.1, 127.8, 127.4, 127.3, 123.1, 102.8, 40.7, 35.5, 12.6.; **HRMS** (ESI) Calcd for $\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 304.1444, found: 304.1448.



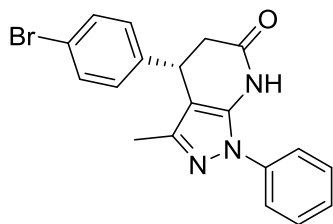
3b

(S)-4-(4-fluorophenyl)-3-methyl-1-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-on

e: 85% yield, 98% ee; $[\alpha]_{\text{D}}^{25} = -24.0$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 90/10, 1.0 mL/min, t_{R} (major) = 14.7 min, t_{R} (minor) = 22.3 min).

^1H NMR (400 MHz, CDCl_3) δ 7.93 (s, 1H), 7.51-7.45 (m, 4H), 7.39-7.35 (m, 1H), 7.20-7.15 (m, 2H), 7.02 (t, $J = 8.8$ Hz 2H), 4.22 (t, $J = 6.8$ Hz, 1H), 3.04 (dd, $J = 7.2$ Hz, $J = 16.4$ Hz, 1H), 2.80 (dd, $J = 6.4$ Hz, $J = 16.4$ Hz, 1H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 163.3, 160.8, 146.9, 138.0, 137.4(d, $J = 17.2$ Hz), 137.4, 130.0, 128.8 (d, $J = 8.0$ Hz), 128.0, 123.0, 115.9 (d, $J = 21.2$ Hz), 102.7, 40.9, 34.8, 12.6.; ^{19}F NMR (376 MHz, CDCl_3) δ -125.2.; **HRMS** (ESI) Calcd for $\text{C}_{19}\text{H}_{17}\text{FN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 322.1350, found: 322.1352.;

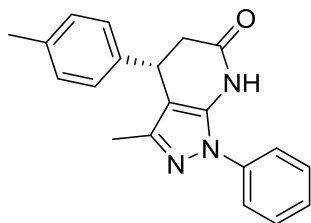


3c

(S)-4-(4-bromophenyl)-3-methyl-1-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 98% yield, 99% ee; $[\alpha]_D^{25} = -56.8$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 90/10, 1.0 mL/min, t_R (major) = 17.1 min, t_R (minor) = 21.3 min).

^1H NMR (400 MHz, CDCl_3) δ 8.23 (s, 1H), 7.49-7.44 (m, 6H), 7.38-7.33 (m, 1H), 7.09 (d, $J = 8.4$ Hz, 2H), 4.18 (t, $J = 6.8$ Hz, 1H), 3.03 (dd, $J = 7.2$ Hz, $J = 16.0$ Hz, 1H), 2.76 (dd, $J = 6.4$ Hz, $J = 16.4$ Hz, 1H), 1.95 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 169.8, 146.8, 141.4, 137.6, 137.4, 132.2, 129.9, 129.0, 127.9, 123.1, 121.2, 102.2, 40.6, 35.0, 12.6.; **HRMS** (ESI) Calcd for $\text{C}_{19}\text{H}_{17}\text{BrN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 382.0550, found: 382.0546.;

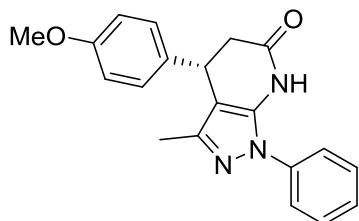


3d

(S)-3-methyl-1-phenyl-4-(p-tolyl)-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 97% yield, 99% ee; $[\alpha]_D^{25} = -110.8$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 90/10, 1.0 mL/min, t_R (major) = 13.0 min, t_R (minor) = 19.6 min).

^1H NMR (400 MHz, CDCl_3) δ 8.25 (s, 1H), 7.47-7.43 (m, 4H), 7.36-7.32 (m, 1H), 7.12 (dd, $J = 8.4$ Hz, $J = 13.2$ Hz, 4H), 4.17 (t, $J = 7.2$ Hz, 1H), 3.01 (dd, $J = 7.2$ Hz, $J = 16.0$ Hz, 1H), 2.81 (dd, $J = 6.4$ Hz, $J = 16.4$ Hz, 1H), 2.33 (s, 3H), 1.95 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.2, 147.0, 139.3, 137.5, 137.4, 137.0, 129.9, 129.7, 127.8, 127.1, 123.0, 103.1, 40.8, 35.1, 21.2, 12.6.; **HRMS** (ESI) Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 318.1601, found: 318.1602.;

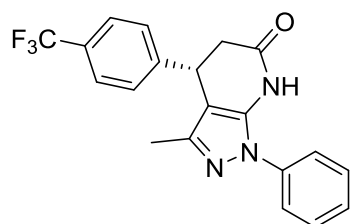


3e

(S)-4-(4-methoxyphenyl)-3-methyl-1-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 93% yield, 99% ee; $[\alpha]_D^{25} = -63.8$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 95/5, 1.0 mL/min, t_R (major) = 44.6 min, t_R (minor) = 52.3 min).

^1H NMR (400 MHz, CDCl_3) δ 8.09 (s, 1H), 7.49-7.44 (m, 4H), 7.37-7.32 (m, 1H), 7.13 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 4.18 (t, $J = 6.8$ Hz, 1H), 3.79 (s, 3H), 3.00 (dd, $J = 7.2$ Hz, $J = 16.4$ Hz, 1H), 2.80 (dd, $J = 6.8$ Hz, $J = 16.4$ Hz, 1H), 1.95 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.2, 158.8, 147.0, 137.5, 137.4, 134.3, 129.9, 128.3, 127.8, 123.0, 114.4, 103.2, 55.4, 40.9, 34.7, 12.6.; **HRMS** (ESI) Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 334.1550, found: 334.1555.;

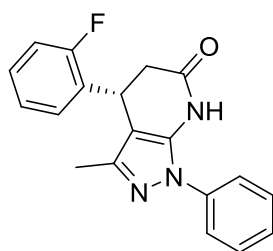


3f

(S)-3-methyl-1-phenyl-4-(4-(trifluoromethyl)phenyl)-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 95% yield, 99% ee; $[\alpha]_D^{25} = -83.8$ ($c=1.0$ in CHCl_3).

HPLC condition: Chiralpak IC (Hex/iPrOH = 95/5, 1.0 mL/min, t_R (major) = 26.8 min, t_R (minor) = 36.7 min).

^1H NMR (400 MHz, CDCl_3) δ 8.21 (s, 1H), 7.59 (d, $J = 8.8$ Hz, 2H), 7.48-7.45 (m, 4H), 7.39-7.32 (m, 3H), 4.29 (t, $J = 6.0$ Hz, 1H), 3.07 (dd, $J = 7.2$ Hz, $J = 16.0$ Hz, 1H), 2.80 (dd, $J = 6.0$ Hz, $J = 16.4$ Hz, 1H), 1.96 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 169.5, 146.8, 146.5, 137.5 (d, $J = 30.0$ Hz), 123.0, 128.0, 127.6, 126.1 (q, $J = 3.8$ Hz), 125.5, 123.1, 122.8, 101.9, 40.4, 35.3, 12.6. **^{19}F NMR** (376 MHz, CDCl_3) δ -62.31.; **HRMS** (ESI) Calcd for $\text{C}_{20}\text{H}_{17}\text{F}_3\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 372.1318, found: 372.1320.;



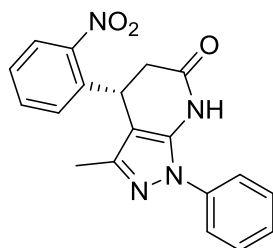
3g

(R)-4-(2-fluorophenyl)-3-methyl-1-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 96% yield, 97% ee; $[\alpha]_D^{25} = -112.4$ ($c=1.0$ in CHCl_3).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 90/10, 1.0 mL/min, t_R (major) = 15.3 min, t_R (minor) = 40.0 min).

^1H NMR (400 MHz, CDCl_3) δ 8.29 (s, 1H), 7.46 (d, $J = 4.4$ Hz, 4H), 7.38-7.33 (m, 1H), 7.26-7.21 (m, 1H), 7.10-7.02 (m, 3H), 4.60-4.52 (m, 1H), 3.06 (dd, $J = 8.0$ Hz, $J = 16.4$ Hz, 1H), 2.83 (dd, $J = 4.8$ Hz, $J = 16.4$ Hz, 1H), 2.00 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 169.9, 161.8, 159.3, 146.9, 137.9, 137.4, 129.9, 129.1 (d, $J = 8.7$ Hz), 128.6 (d, $J = 4.2$ Hz), 128.0, 124.6 (d, $J = 3.6$ Hz), 123.1, 115.9 (d, $J = 21.9$ Hz),

101.2, 38.9, 28.6, 12.3. ^{19}F NMR (376 MHz, CDCl_3) δ -118.08.; HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{17}\text{FN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 322.1350, found: 322.1355.;

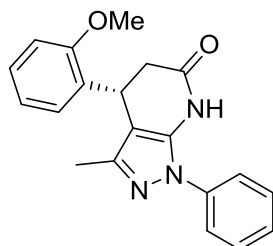


3h

(S)-3-methyl-4-(2-nitrophenyl)-1-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 95% yield, 98% ee; $[\alpha]_{\text{D}}^{25} = -117.8$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IA (Hex/iPrOH = 90/10, 1.0 mL/min, t_{R} (major) = 17.4 min, t_{R} (minor) = 27.3 min).

^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.49-7.46 (m, 4H), 7.45-7.42 (m, 1H), 7.41-7.35 (m, 1H), 7.28-7.27 (m, 1H), 4.88-4.84 (m, 1H), 3.23 (dd, $J = 8.0$ Hz, $J = 16.8$ Hz, 1H), 2.83 (dd, $J = 5.6$ Hz, $J = 16.8$ Hz, 1H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.3, 149.0, 146.8, 138.4, 137.3, 137.0, 133.7, 123.0, 129.6, 128.4, 128.1, 125.1, 123.1, 101.2, 39.8, 30.4, 12.4.; HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_4\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$: 371.1115, found: 371.1112.;

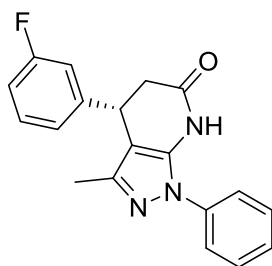


3i

(R)-4-(2-methoxyphenyl)-3-methyl-1-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 70% yield, 98% ee; $[\alpha]_{\text{D}}^{25} = -39.0$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IA (Hex/iPrOH = 95/5, 1.0 mL/min, t_{R} (major) = 19.6 min, t_{R} (minor) = 24.4 min).

^1H NMR (400 MHz, CDCl_3) δ 7.81 (s, 1H), 7.49-7.46 (m, 4H), 7.39-7.34 (m, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 7.6$ Hz, 1H), 7.90-7.84 (m, 2H), 4.53 (q, $J = 4.4$ Hz, 1H), 3.83 (s, 3H), 3.04 (dd, $J = 8.0$ Hz, $J = 16.4$ Hz, 1H), 2.85 (dd, $J = 3.6$ Hz, $J = 16.4$ Hz, 1H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 156.9, 147.1, 137.9, 137.6, 130.1, 123.0, 128.4, 128.1, 127.7, 122.9, 120.7, 110.8, 101.9, 55.1, 38.5, 29.8, 12.4.; HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 334.1550, found: 334.1555.;

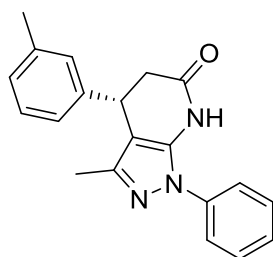


3j

(S)-4-(3-fluorophenyl)-3-methyl-1-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 89% yield, 98% ee; $[\alpha]_D^{25} = -48.0$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IB (Hex/iPrOH = 95/5, 1.0 mL/min, t_R (major) = 24.5 min, t_R (minor) = 31.5 min).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.09 (s, 1H), 7.50-7.45 (m, 4H), 7.39-7.34 (m, 1H), 7.33-7.27 (m, 1H), 7.02-6.88 (m, 3H), 4.22 (t, $J = 7.2$ Hz, 1H), 3.06 (dd, $J = 7.6$ Hz, $J = 16.0$ Hz, 1H), 2.81 (dd, $J = 6.0$ Hz, $J = 16.4$ Hz, 1H), 1.98 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 169.6, 164.5, 162.1, 146.9, 145.0 (d, $J = 6.5$ Hz), 137.6, 137.4, 130.7 (d, $J = 8.2$ Hz), 123.0, 128.0, 123.1, 122.9 (d, $J = 2.8$ Hz), 114.5, 114.3 (d, $J = 6.6$ Hz), 114.1, 102.2, 40.5, 35.2, 12.6. **$^{19}\text{F NMR}$** (376 MHz, CDCl_3) δ -112.09.; **HRMS** (ESI) Calcd for $\text{C}_{19}\text{H}_{17}\text{FN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 322.1350, found: 322.1353.;

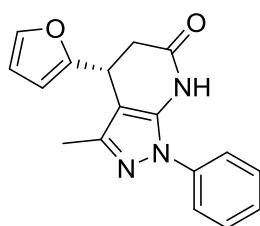


3k

(S)-3-methyl-1-phenyl-4-(m-tolyl)-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 83% yield, 98% ee; $[\alpha]_D^{25} = -50.4$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IC (Hex/iPrOH = 90/10, 1.0 mL/min, t_R (major) = 19.2 min, t_R (minor) = 27.0 min).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 (s, 1H), 7.48-7.47 (m, 4H), 7.38-7.34 (m, 1H), 7.21 (t, $J = 3.2$ Hz, 1H), 7.08-7.00 (m, 3H), 4.18 (t, $J = 6.8$ Hz, 1H), 3.04 (dd, $J = 7.2$ Hz, $J = 16.0$ Hz, 1H), 2.84 (dd, $J = 6.4$ Hz, $J = 16.4$ Hz, 1H), 2.34 (s, 3H), 1.95 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 170.1, 147.0, 142.3, 138.7, 137.5, 137.4, 123.0, 128.9, 128.1, 127.9, 127.9, 124.3, 123.0, 102.9, 40.7, 35.5, 21.6, 12.6. **HRMS** (ESI) Calcd for $\text{C}_{20}\text{H}_{19}\text{N}_3\text{NaO}^+$ $[\text{M}+\text{Na}]^+$: 340.1420, found: 340.1424.;

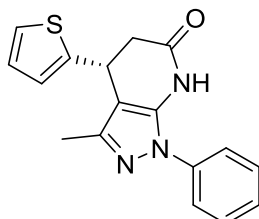


3l

(R)-4-(furan-2-yl)-3-methyl-1-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 93% yield, 98% ee; $[\alpha]_D^{25} = -46.6$ (c=1.0 in CHCl₃).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 95/5, 1.0 mL/min, t_R (major) = 45.0 min, t_R (minor) = 56.8 min).

¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.49-7.42 (m, 4H), 7.38-7.33 (m, 2H), 6.28-6.26 (m, 1H), 6.03 (d, *J* = 3.2 Hz, 1H), 4.29-4.26 (m, 1H), 3.05-2.94 (m, 2H), 2.17 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 169.6, 154.6, 146.8, 142.3, 137.4, 137.4, 129.9, 127.9, 123.0, 110.3, 105.8, 100.9, 37.0, 28.9, 12.1. **HRMS** (ESI) Calcd for C₁₇H₁₆N₃O₂⁺ [M+H]⁺: 294.1237, found: 294.1240.;

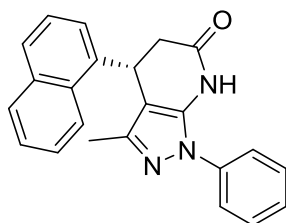


3m

(R)-3-methyl-1-phenyl-4-(thiophen-2-yl)-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 91% yield, 99% ee; $[\alpha]_D^{25} = -42.8$ (c=1.0 in CHCl₃).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 90/10, 1.0 mL/min, t_R (major) = 19.3 min, t_R (minor) = 33.8 min).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (s, 1H), 7.49-7.42 (m, 4H), 7.38-7.33 (m, 1H), 7.19-7.17 (m, 1H), 6.94-6.91 (m, 1H), 6.85-6.83 (m, 1H), 4.51-4.47 (m, 1H), 3.09 (dd, *J* = 7.2 Hz, *J* = 16.4 Hz, 1H), 2.95 (dd, *J* = 4.8 Hz, *J* = 16.4 Hz, 1H), 2.14 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 169.5, 146.6, 146.4, 137.4, 137.2, 123.0, 128.0, 127.1, 124.5, 124.3, 123.1, 103.3, 41.0, 30.5, 12.4. **HRMS** (ESI) Calcd for C₁₇H₁₆N₃OS⁺ [M+H]⁺: 310.1009, found: 310.1010.;



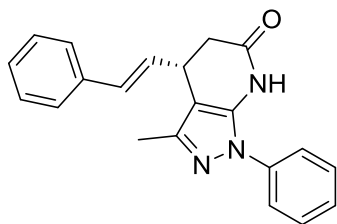
3n

(S)-3-methyl-4-(naphthalen-1-yl)-1-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 89% yield, 98% ee; $[\alpha]_D^{25} = -69.2$ (c=1.0 in CHCl₃).

HPLC condition: Chiralpak IC (Hex/iPrOH = 80/20, 1.0 mL/min, t_R (major) = 13.1 min, t_R (minor) = 21.8 min).

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.4 Hz, 1H), 8.02 (s, 1H), 7.93 (d, *J* = 9.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.62-7.58 (m, 1H), 7.57-7.50 (m, 3H), 7.50-7.45 (m, 2H), 7.40-7.34 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 5.08-7.05 (m, 1H), 3.23 (dd, *J* = 7.6 Hz, *J* = 16.0 Hz, 1H), 3.00 (dd, *J* = 5.2 Hz, *J* = 16.4 Hz, 1H), 1.92 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 169.8, 147.2, 138.3, 137.5, 137.2, 134.4, 130.9, 123.0, 129.5, 128.2, 127.9, 126.6, 125.9, 125.7, 124.7, 123.0, 122.7, 102.2, 39.8, 31.0, 12.5.;

HRMS (ESI) Calcd for C₂₃H₁₉N₃NaO⁺ [M+Na]⁺: 376.1420, found: 376.1417.;

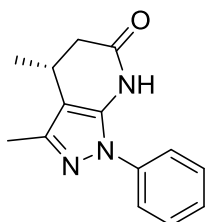


3o

(S,E)-3-methyl-1-phenyl-4-styryl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 90% yield, 98% ee; $[\alpha]_D^{25} = -45.8$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 95/5, 1.0 mL/min, t_R (major) = 27.9 min, t_R (minor) = 36.1 min).

^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.51-7.45 (m, 4H), 7.39-7.34 (m, 3H), 7.33-7.28 (m, 2H), 7.25-7.21 (m, 1H), 6.43 (d, $J = 14.4$ Hz, 1H), 6.2 (dd, $J = 6.4$ Hz, $J = 16.0$ Hz, 1H), 3.82 (q, $J = 7.2$ Hz, 1H), 2.93 (dd, $J = 7.2$ Hz, $J = 16.0$ Hz, 1H), 2.75 (dd, $J = 5.2$ Hz, $J = 16.4$ Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 167.0, 147.0, 137.5, 137.1, 136.6, 130.6, 123.0, 129.8, 128.7, 127.9, 127.8, 126.5, 123.0, 101.8, 38.3, 33.0, 12.6.; **HRMS** (ESI) Calcd for $\text{C}_{21}\text{H}_{20}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 330.1601, found: 330.1600.;

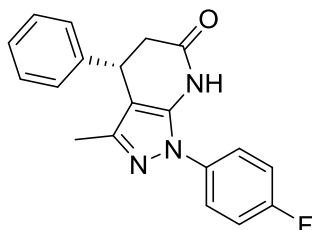


3p

(R)-3,4-dimethyl-1-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one : 65% yield, 98% ee; $[\alpha]_D^{25} = -11.6$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IC (Hex/iPrOH = 90/10, 1.0 mL/min, t_R (major) = 17.4 min, t_R (minor) = 20.1 min).

^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 1H), 7.47 (t, $J = 8.4$ Hz, 2H), 7.44-7.41 (m, 2H), 7.37-7.33 (m, 1H), 3.11 (t, $J = 6.8$ Hz, 1H), 2.81 (dd, $J = 6.8$ Hz, $J = 16.0$ Hz, 1H), 2.48 (dd, $J = 5.2$ Hz, $J = 16.0$ Hz, 1H), 2.28 (s, 3H), 1.25 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.6, 146.2, 137.5, 136.6, 129.9, 127.8, 122.9, 105.1, 40.0, 24.4, 20.8, 12.7. **HRMS** (ESI) Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 242.1288, found: 242.1295.;

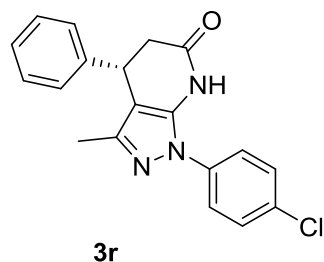


3q

(S)-1-(4-fluorophenyl)-3-methyl-4-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 95% yield, 99% ee; $[\alpha]_D^{25} = -100.8$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 95/5, 1.0 mL/min, t_R (major) = 23.9 min, t_R (minor) = 33.1 min).

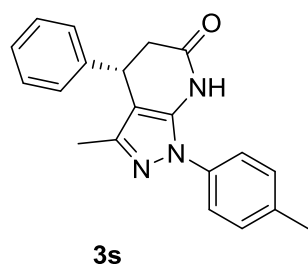
^1H NMR (400 MHz, CDCl_3) δ 7.8 (s, 1H), 7.47-7.43 (m, 2H), 7.34 (t, $J = 6.8$ Hz, 2H), 7.29-7.25 (m, 1H), 7.29-7.25 (m, 4H), 4.23 (t, $J = 7.2$ Hz, 1H), 3.06 (dd, $J = 7.2$ Hz, $J = 16.0$ Hz, 1H), 2.86 (dd, $J = 6.4$ Hz, $J = 16.0$ Hz, 1H), 1.94 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.0, 147.1, 142.2, 137.6, 133.5, 129.1, 127.4, 127.2, 125.2 (d, $J = 23.0$ Hz), 116.9 (d, $J = 8.6$ Hz), 102.8, 40.7, 35.5, 12.6. **^{19}F NMR** (376 MHz, CDCl_3) δ -112.8.; **HRMS** (ESI) Calcd for $\text{C}_{19}\text{H}_{17}\text{FN}_3\text{O}^+ [\text{M}+\text{H}]^+$: 322.1350, found: 322.1353.;



(S)-1-(4-chlorophenyl)-3-methyl-4-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 94% yield, 99% ee; $[\alpha]_D^{25} = -65.6$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IA (Hex/iPrOH = 98/2, 0.8 mL/min, t_R (major) = 72.4 min, t_R (minor) = 80.1 min).

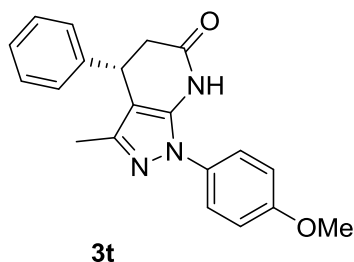
^1H NMR (400 MHz, CDCl_3) δ 8.67 (s, 1H), 7.43-7.39 (m, 4H), 7.34 (t, $J = 6.8$ Hz, 2H), 7.29-7.26 (m, 1H), 7.21 (d, $J = 6.8$ Hz, 2H), 4.21 (t, $J = 6.8$ Hz, 1H), 3.02 (dd, $J = 8.4$ Hz, $J = 17.2$ Hz, 1H), 2.81 (dd, $J = 10.0$ Hz, $J = 16.4$ Hz, 1H), 1.93 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.5, 147.3, 142.1, 137.7, 136.1, 133.3, 129.9, 129.1, 127.4, 127.2, 124.2, 103.2, 40.7, 35.4, 12.6. **HRMS** (ESI) Calcd for $\text{C}_{19}\text{H}_{17}\text{ClN}_3\text{O}^+ [\text{M}+\text{H}]^+$: 338.1055, found: 338.1064.;



(S)-3-methyl-4-phenyl-1-(p-tolyl)-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 96% yield, 99% ee; $[\alpha]_D^{25} = -99.0$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IC (Hex/iPrOH = 80/20, 1.0 mL/min, t_R (major) = 13.4 min, t_R (minor) = 17.4 min).

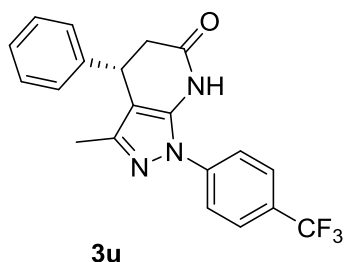
^1H NMR (400 MHz, CDCl_3) δ 8.05 (s, 1H), 7.35-7.31 (m, 4H), 7.28-7.21 (m, 5H), 4.21 (t, $J = 6.8$ Hz, 1H), 3.03 (dd, $J = 7.6$ Hz, $J = 16.4$ Hz, 1H), 2.83 (dd, $J = 6.4$ Hz, $J = 16.0$ Hz, 1H), 2.38 (s, 3H), 1.93 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.0, 146.6, 142.4, 137.9, 137.5, 135.0, 130.4, 129.0, 127.3, 127.3, 123.0, 102.6, 40.7, 35.6, 21.2, 12.6. **HRMS** (ESI) Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}^+ [\text{M}+\text{H}]^+$: 318.1601, found: 318.1606.;



(S)-1-(4-methoxyphenyl)-3-methyl-4-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 97% yield, 99% ee; $[\alpha]_D^{25} = -104.6$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IC (Hex/iPrOH = 80/20, 1.0 mL/min, t_R (major) = 24.4 min, t_R (minor) = 28.8 min).

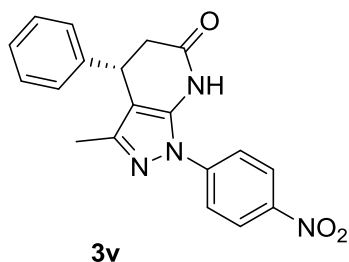
^1H NMR (400 MHz, CDCl_3) δ 8.05 (s, 1H), 7.34 (d, $J = 7.6$ Hz, 4H), 7.27-7.20 (m, 3H), 6.96 (d, $J = 8.8$ Hz, 2H), 4.21 (t, $J = 6.8$ Hz, 1H), 3.83 (s, 3H), 3.02 (dd, $J = 9.2$ Hz, $J = 16.4$ Hz, 1H), 2.82 (dd, $J = 6.4$ Hz, $J = 16.0$ Hz, 1H), 1.93 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.1, 159.3, 146.4, 142.5, 137.6, 130.4, 129.0, 127.3, 127.3, 125.0, 115.0, 102.3, 55.7, 40.8, 35.6, 12.6. **HRMS** (ESI) Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 334.1550, found: 334.1550.;



(S)-3-methyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 92% yield, 99% ee; $[\alpha]_D^{25} = -282.2$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IB (Hex/iPrOH = 95/5, 1.0 mL/min, t_R (major) = 14.4 min, t_R (minor) = 18.7 min).

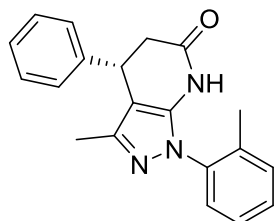
^1H NMR (400 MHz, CDCl_3) δ 9.09 (s, 1H), 7.64 (d, $J = 8.8$ Hz, 2H), 7.34 (t, $J = 7.2$ Hz, 2H), 7.30-7.26 (m, 1H), 7.22-7.20 (m, 2H), 4.21 (t, $J = 6.8$ Hz, 1H), 3.02 (dd, $J = 7.2$ Hz, $J = 16.0$ Hz, 1H), 2.81 (dd, $J = 6.4$ Hz, $J = 16.0$ Hz, 1H), 1.94 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.8, 148.0, 142.0, 140.5, 137.9, 129.1, 127.5, 127.2, 127.0 (q, $J = 3.9$ Hz), 122.6, 103.9, 40.6, 35.3, 12.6. **^{19}F NMR** (376 MHz, CDCl_3) δ -62.23.; **HRMS** (ESI) Calcd for $\text{C}_{20}\text{H}_{17}\text{F}_3\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 372.1318, found: 372.1316.;



(S)-3-methyl-1-(4-nitrophenyl)-4-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 92% yield, 95% ee; $[\alpha]_D^{25} = -68.0$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak AZH (Hex/iPrOH = 90/10, 1.0 mL/min, t_R (major) = 10.0 min, t_R (minor) = 15.3 min).

^1H NMR (400 MHz, CDCl_3) δ 8.54 (s, 1H), 7.45-7.41 (m, 2H), 7.33 (t, $J = 14.4$ Hz, 2H), 7.28-7.24 (m, 1H), 7.22-7.20 (m, 2H), 7.15-7.09 (m, 2H), 4.20 (t, $J = 6.8$ Hz, 1H), 3.01 (dd, $J = 8.8$ Hz, $J = 18.0$ Hz, 1H), 2.81 (dd, $J = 4.4$ Hz, $J = 14.4$ Hz, 1H), 1.93 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.6, 163.1, 160.6, 147.0, 142.3, 137.8, 133.6, 129.1, 127.4, 127.2, 125.3, 125.2, 116.8, 116.6, 102.8, 40.7, 35.5, 12.5.; **HRMS** (ESI) Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_4\text{NaO}_3^+$ [$\text{M}+\text{Na}$] $^+$: 371.1115, found: 371.1112.;

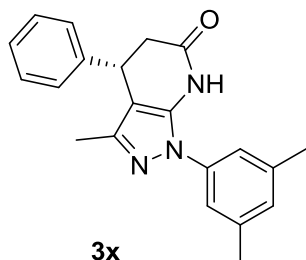


3w

(S)-3-methyl-4-phenyl-1-(o-tolyl)-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 98% yield, 99% ee; $[\alpha]_D^{25} = -64.0$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IA (Hex/iPrOH = 95/5, 1.0 mL/min, t_R (major) = 17.5 min, t_R (minor) = 21.9 min).

^1H NMR (400 MHz, CDCl_3) δ 7.78 (s, 1H), 7.36-7.31 (m, 4H), 7.30-7.25 (m, 3H), 7.23-7.19 (m, 2H), 4.23 (t, $J = 6.4$ Hz, 1H), 3.01 (dd, $J = 7.6$ Hz, $J = 16.4$ Hz, 1H), 2.78 (dd, $J = 6.4$ Hz, $J = 16.4$ Hz, 1H), 2.17 (s, 3H), 1.94 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 169.9, 146.4, 142.7, 138.7, 136.2, 135.6, 131.6, 129.8, 129.0, 127.6, 127.3, 127.2, 127.1, 100.9, 40.9, 35.6, 17.6, 12.6.; **HRMS** (ESI) Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}^+$ [$\text{M}+\text{H}$] $^+$: 318.1601, found: 318.1606.;

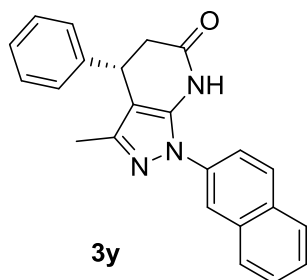


3x

(S)-1-(3,5-dimethylphenyl)-3-methyl-4-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 95% yield, 99% ee; $[\alpha]_D^{25} = -105.0$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak ID (Hex/iPrOH = 96/4, 0.8 mL/min, t_R (major) = 43.2 min, t_R (minor) = 53.8 min).

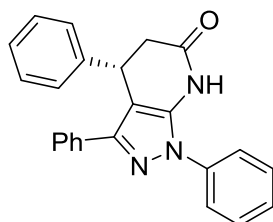
^1H NMR (400 MHz, CDCl_3) δ 8.41 (s, 1H), 7.33 (t, $J = 6.8$ Hz, 2H), 7.27-7.25 (m, 1H), 7.24-7.20 (m, 2H), 7.09 (s, 2H), 6.98 (s, 1H), 4.2 (t, $J = 6.8$ Hz, 1H), 3.03 (dd, $J = 7.2$ Hz, $J = 16.0$ Hz, 1H), 2.83 (dd, $J = 6.4$ Hz, $J = 9.6$ Hz, 1H), 2.34 (s, 6H), 1.94 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 170.2, 146.6, 142.4, 139.8, 137.5, 137.3, 129.5, 129.0, 127.3, 127.3, 120.7, 102.6, 40.8, 35.5, 21.4, 12.6.; **HRMS** (ESI) Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_3\text{O}^+$ [$\text{M}+\text{H}$] $^+$: 332.1757, found: 332.1760.;



(S)-3-methyl-1-(naphthalen-2-yl)-4-phenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 95% yield, 99% ee; $[\alpha]_D^{25} = -128.2$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IB (Hex/iPrOH = 95/5, 1.0 mL/min, t_R (major) = 32.1 min, t_R (minor) = 40.4 min).

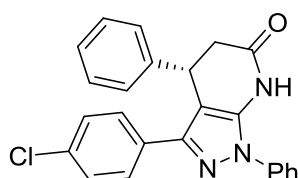
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.57 (s, 1H), 7.93 (d, $J = 8.8$ Hz, 1H), 7.88-7.82 (m, 3H), 7.67-7.64 (m, 1H), 7.55-7.50 (m, 2H), 7.37-7.33 (m, 2H), 7.29-7.27 (m, 1H), 7.24-7.22 (m, 2H), 4.19 (t, $J = 6.8$ Hz, 1H), 3.00 (dd, $J = 7.2$ Hz, $J = 16.4$ Hz, 1H), 2.81 (dd, $J = 6.4$ Hz, $J = 16.0$ Hz, 1H), 1.97 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 170.3, 147.2, 142.3, 137.8, 135.0, 133.4, 132.3, 130.1, 129.1, 128.2, 128.0, 127.4, 127.3, 127.2, 126.7, 121.6, 120.4, 103.0, 40.6, 35.5, 12.6.; **HRMS** (ESI) Calcd for $\text{C}_{23}\text{H}_{20}\text{N}_3\text{O}^+ [\text{M}+\text{H}]^+$: 354.1601, found: 354.1605.;



(S)-1,3,4-triphenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 90% yield, 99% ee; $[\alpha]_D^{25} = -19.8$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IB (Hex/iPrOH = 90/10, 1.0 mL/min, t_R (major) = 13.8 min, t_R (minor) = 21.0 min).

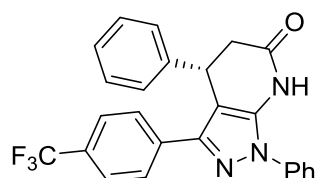
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.18 (s, 1H), 7.60-7.49 (m, 6H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.33-7.28 (m, 5H), 7.26-7.19 (m, 3H), 4.51 (d, $J = 5.6$ Hz, 1H), 3.18 (dd, $J = 8.0$ Hz, $J = 16.0$ Hz, 1H), 2.86 (dd, $J = 2.4$ Hz, $J = 16$ Hz, 1H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 169.7, 148.9, 142.2, 138.7, 137.5, 132.7, 130.0, 129.2, 128.7, 128.3, 128.3, 127.4, 127.1, 127.1, 123.5, 101.9, 41.1, 35.5.; **HRMS** (ESI) Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_3\text{O}^+ [\text{M}+\text{H}]^+$: 366.1601, found: 366.1611.;



(S)-3-(4-chlorophenyl)-1,4-diphenyl-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 98% yield, 99% ee; $[\alpha]_D^{25} = +10.4$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IB (Hex/iPrOH = 95/5, 1.0 mL/min, t_R (major) = 26.2 min, t_R (minor) = 29.2 min).

^1H NMR (400 MHz, CDCl_3) δ 8.57 (s, 1H), 7.58-7.55 (m, 2H), 7.51-7.46 (m, 4H), 7.43-7.38 (m, 1H), 7.22-7.33 (m, 5H), 7.19-7.17 (m, 2H), 4.45 (d, $J = 5.2$ Hz, 1H), 3.16 (dd, $J = 7.6$ Hz, $J = 15.6$ Hz, 1H), 2.83 (d, $J = 13.6$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3) δ 169.8, 147.7, 142.0, 139.0, 137.4, 134.1, 131.2, 123.0, 129.3, 128.8, 128.4, 128.4, 127.6, 127.0, 123.6, 101.9, 41.1, 35.5.; **HRMS** (ESI) Calcd for $\text{C}_{24}\text{H}_{19}\text{ClN}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 400.1211, found: 400.1211.;

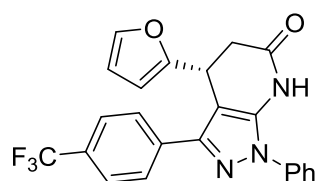


3ab

(S)-1,4-diphenyl-3-(4-(trifluoromethyl)phenyl)-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 97% yield, 99% ee; $[\alpha]_D^{25} = -32.2$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IA (Hex/iPrOH = 90/10, 1.0 mL/min, t_R (major) = 10.9 min, t_R (minor) = 15.8 min).

^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, 1H), 7.67 (d, $J = 8.4$ Hz, 2H), 7.60-7.50 (m, 6H), 7.44 (t, $J = 7.2$ Hz, 1H), 7.33-7.29 (m, 2H), 7.27-7.23 (m, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 4.51-4.48 (m, 1H), 3.18 (dd, $J = 8.0$ Hz, $J = 16.4$ Hz, 1H), 2.88-2.83 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3) δ 169.7, 147.4, 141.9, 139.2, 137.3, 136.2, 130.0, 129.8, 129.4, 128.6, 127.6, 127.2, 127.0, 125.6 (q, $J = 3.7$ Hz), 123.6, 122.9, 102.2, 77.4, 41.1, 35.5. **^{19}F NMR** (376 MHz, CDCl_3) δ -62.47; **HRMS** (ESI) Calcd for $\text{C}_{25}\text{H}_{19}\text{F}_3\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 434.1475, found: 434.1480.;



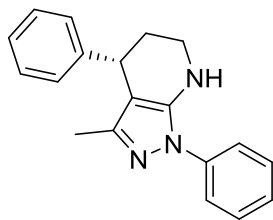
3ac

(R)-4-(furan-2-yl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)-1,4,5,7-tetrahydro-6H-pyrazolo[3,4-b]pyridin-6-one: 67% yield, 96% ee; $[\alpha]_D^{25} = +35.00$ (c=1.0 in CHCl_3).

HPLC condition: Chiralpak IA (Hex/iPrOH = 90/10, 1.0 mL/min, t_R (major) = 10.6 min, t_R (minor) = 15.2 min).

^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1H), 7.87 (d, $J = 4.0$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.57-7.51 (m, 4H), 7.46-7.42 (m, 1H), 7.35 (s, 1H), 6.27-6.25 (m, 1H), 6.04-6.03 (m, 1H), 4.56-4.54 (m, 1H), 3.08-3.06 (m, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 169.3, 154.2, 147.2, 142.7, 138.9, 137.2, 136.2, 130.1, 128.7, 127.2, 125.8 (d, $J = 4.0$ Hz), 123.5, 110.5, 106.7, 100.4, 37.5, 29.7. **^{19}F NMR** (376 MHz, CDCl_3)

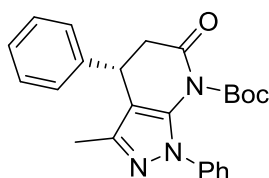
δ -60.77; **HRMS** (ESI) Calcd for $C_{23}H_{17}F_3N_3O_2^+$ $[M+H]^+$: 424.1267, found: 424.1272.;



(S)-3-methyl-1,4-diphenyl-4,5,6,7-tetrahydro-1H-pyrazolo[3,4-b]pyridine: 87% yield, 97% ee; $[\alpha]_D^{25} = -10.4$ ($c=1.0$ in $CHCl_3$).

HPLC condition: Chiralpak ASH (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 13.3 min, t_R (minor) = 25.9 min).

1H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62 (m, 2H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.33-7.19 (m, 6H), 4.04 (t, $J = 5.6$ Hz, 1H), 3.92 (s, 1H), 3.26-3.13 (m, 2H), 2.26-2.18 (m, 1H), 1.97-1.90 (m, 1H), 1.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 145.5, 144.8, 139.3, 129.5, 128.4, 128.1, 126.4, 126.1, 122.0, 101.1, 40.4, 36.6, 33.1, 12.7.; **HRMS** (ESI) Calcd for $C_{19}H_{20}N_3^+$ $[M+H]^+$: 290.1652, found: 290.1655.;



5

tert-butyl(S)-3-methyl-6-oxo-1,4-diphenyl-1,4,5,6-tetrahydro-7H-pyrazolo[3,4-b]pyridine-7-carboxylate: 80% yield, 97% ee; $[\alpha]_D^{25} = -156.4$ ($c=1.0$ in $CHCl_3$).

HPLC condition: Chiralpak IA (Hex/*i*PrOH = 95/5, 1.0 mL/min, t_R (major) = 12.1 min, t_R (minor) = 16.2 min).

1H NMR (400 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.34-7.29 (m, 3H), 7.25-7.19 (m, 3H), 4.21 (t, $J = 5.2$ Hz, 1H), 3.14 (dd, $J = 6.0$ Hz, $J = 15.2$ Hz, 1H), 3.00 (dd, $J = 4.9$ Hz, $J = 14.8$ Hz, 1H), 2.06 (s, 3H), 1.09 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 147.8, 145.8, 140.4, 139.4, 137.0, 129.7, 129.0, 127.5, 127.3, 122.6, 108.9, 85.3, 43.9, 34.8, 27.2, 12.3.; **HRMS** (ESI) Calcd for $C_{24}H_{26}N_3O_3^+$ $[M+H]^+$: 404.1969, found: 404.1972.;

b) References

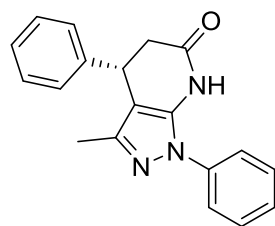
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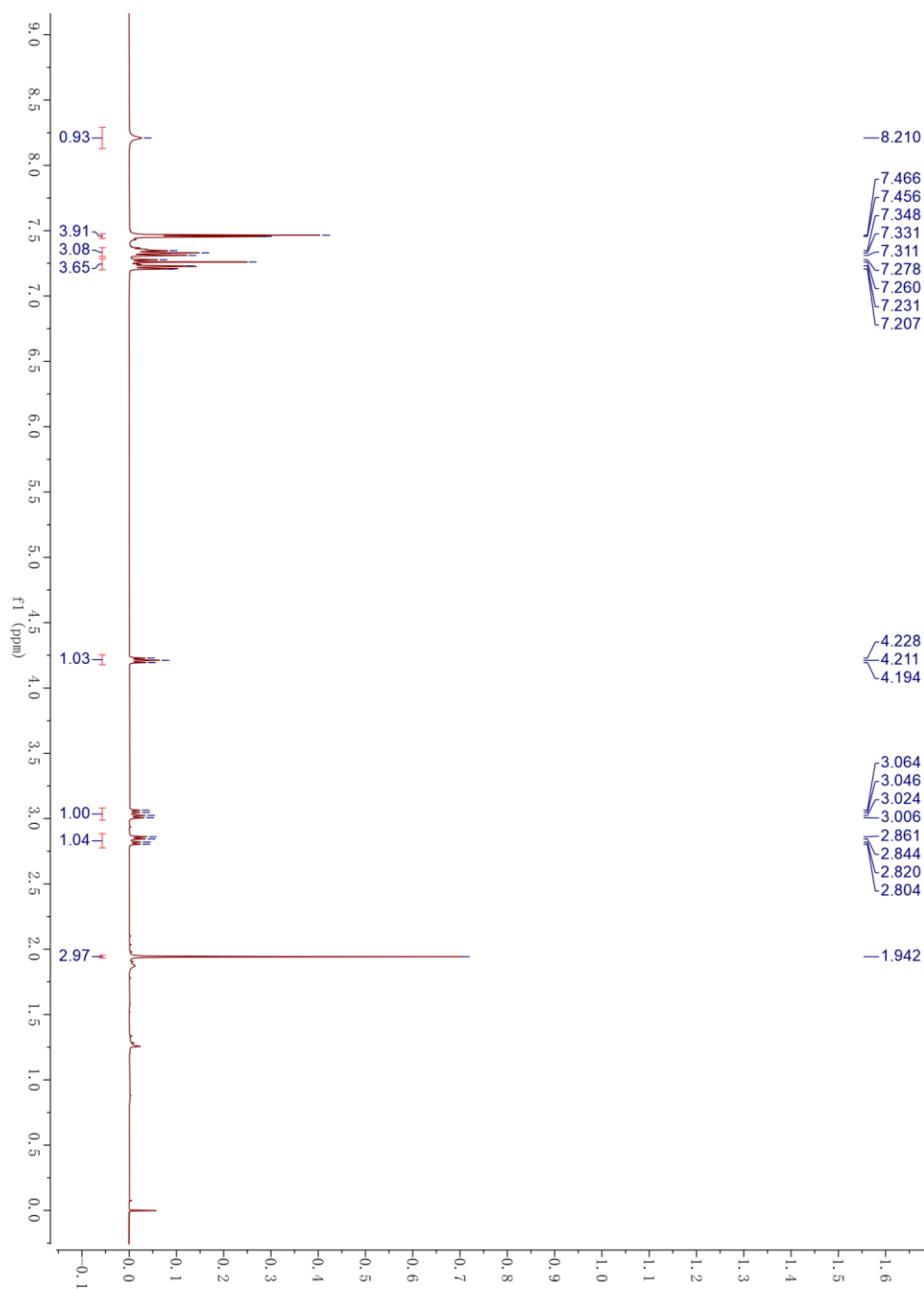
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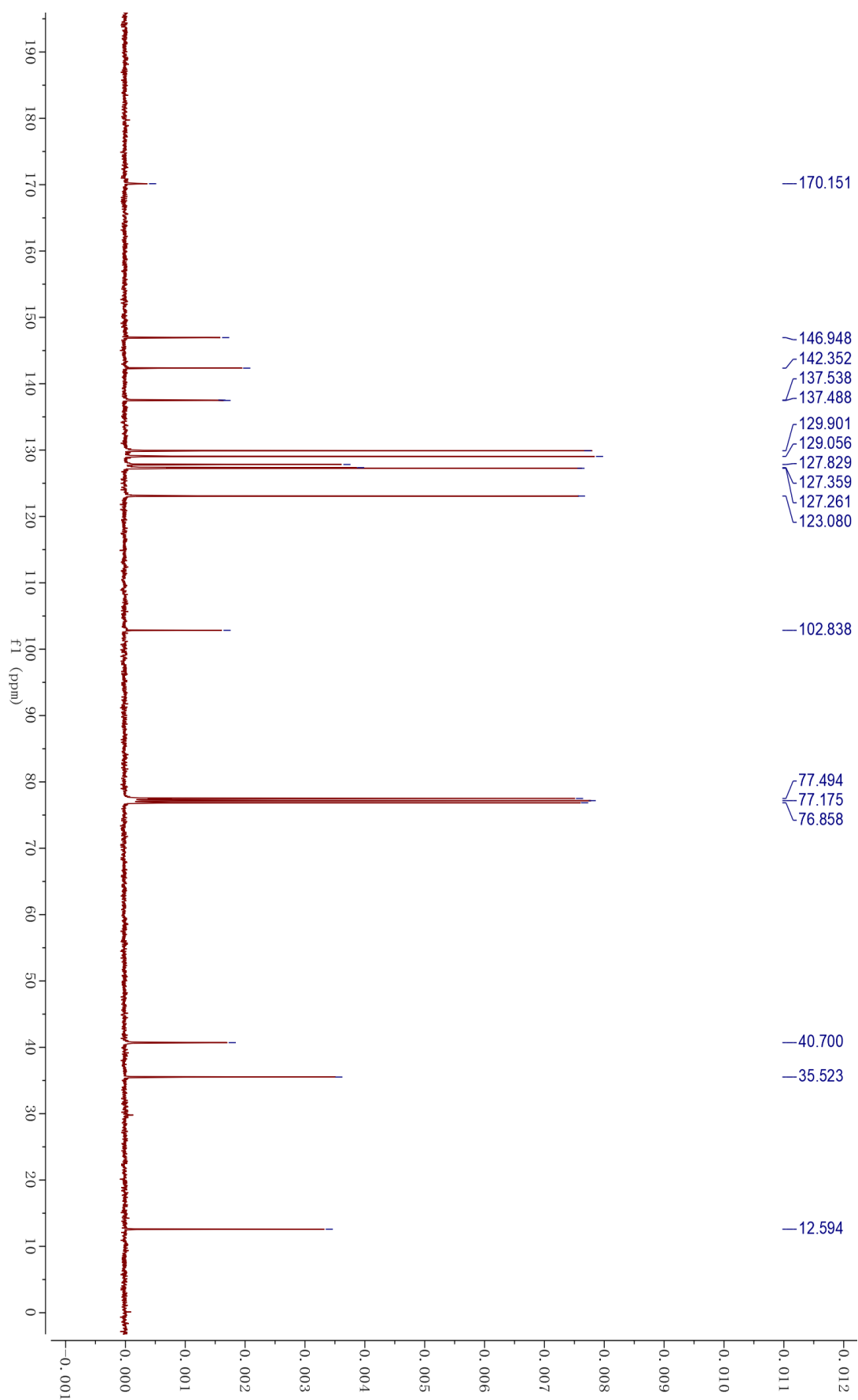
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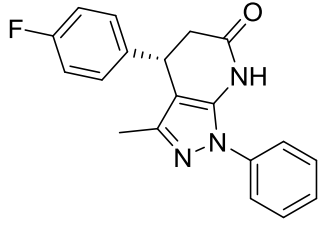
IV: ^1H , ^{13}C , ^{19}F NMR and HPLC data of products



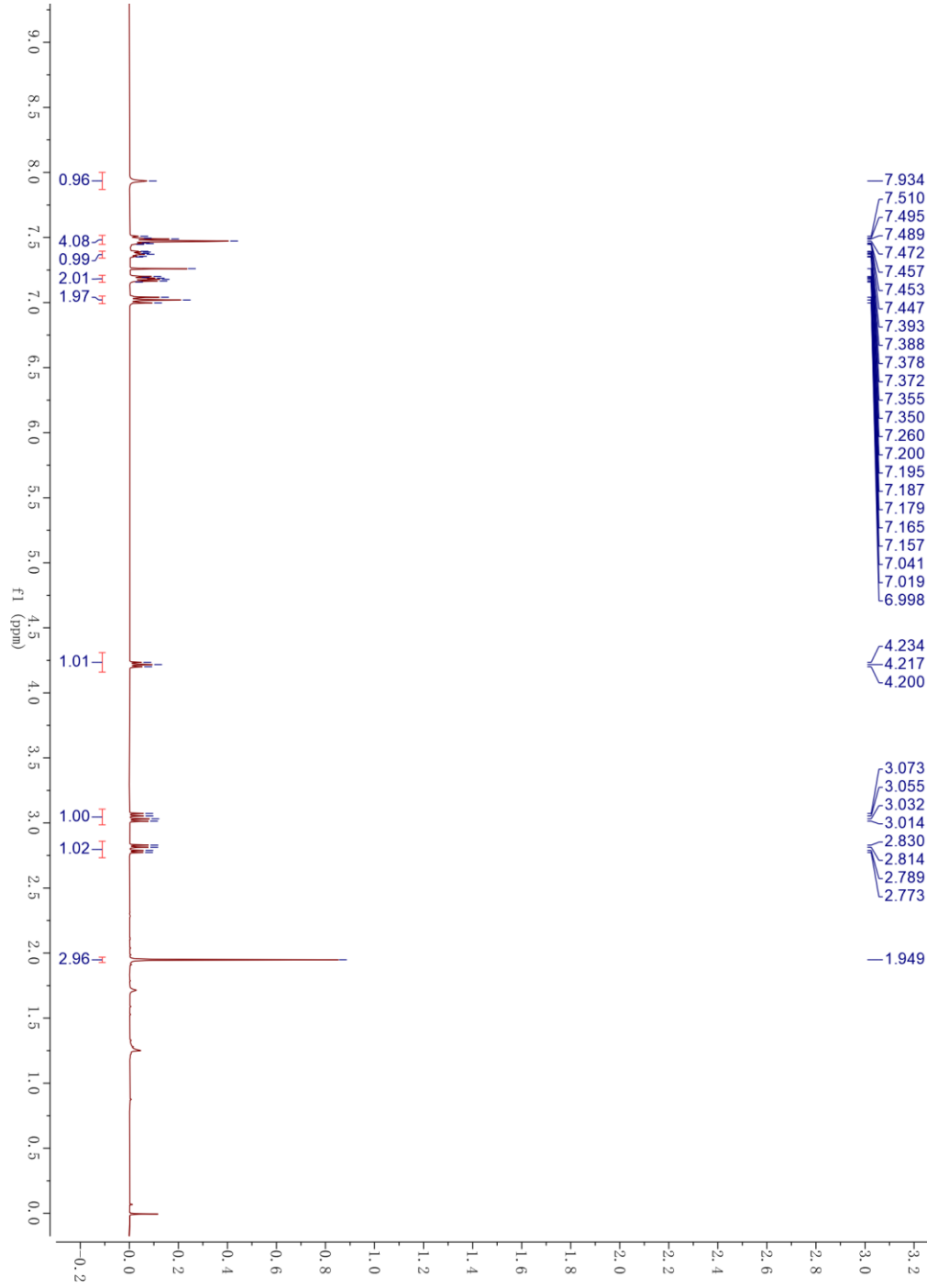
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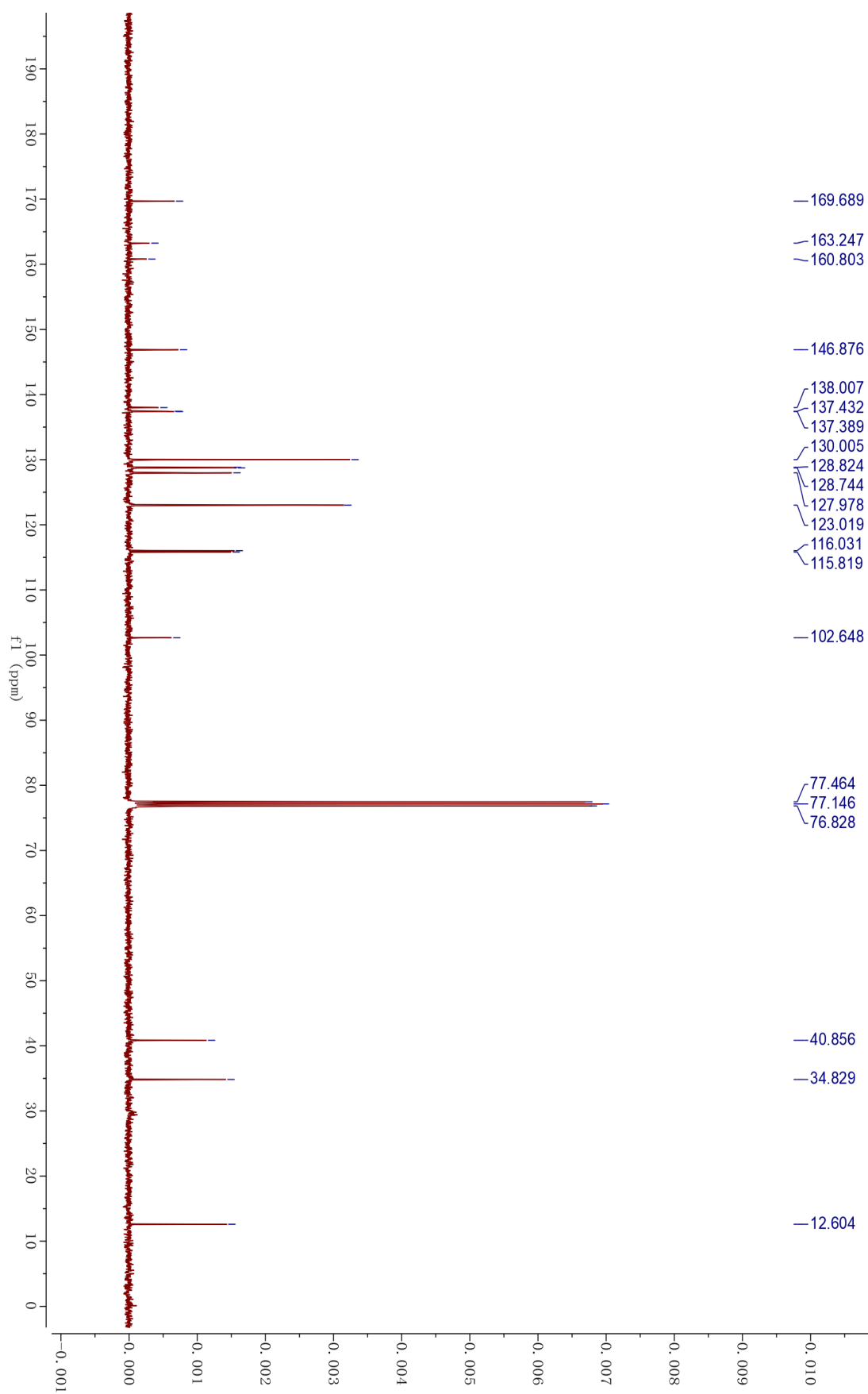


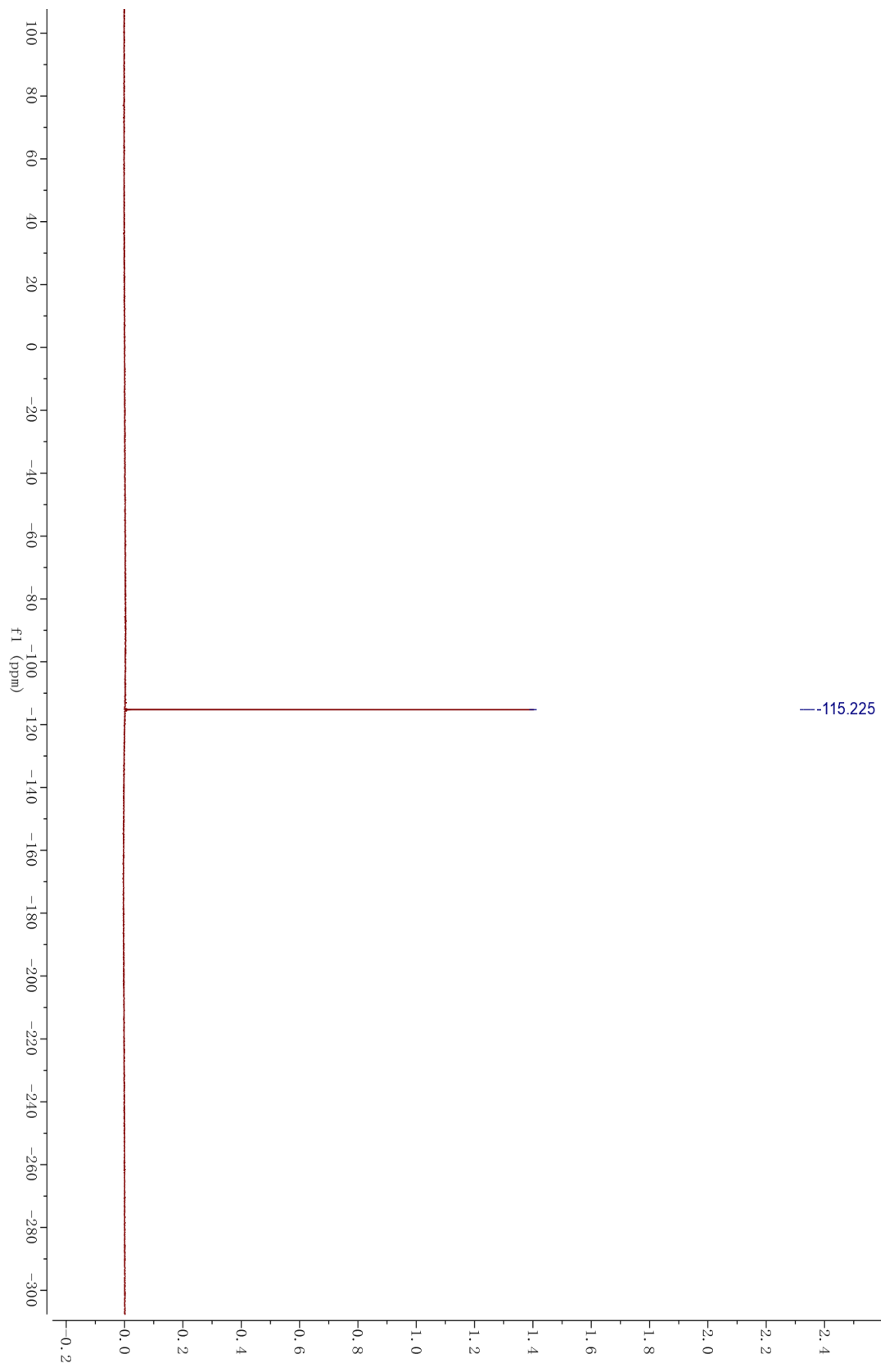


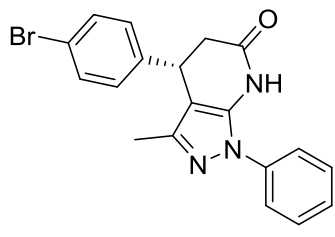


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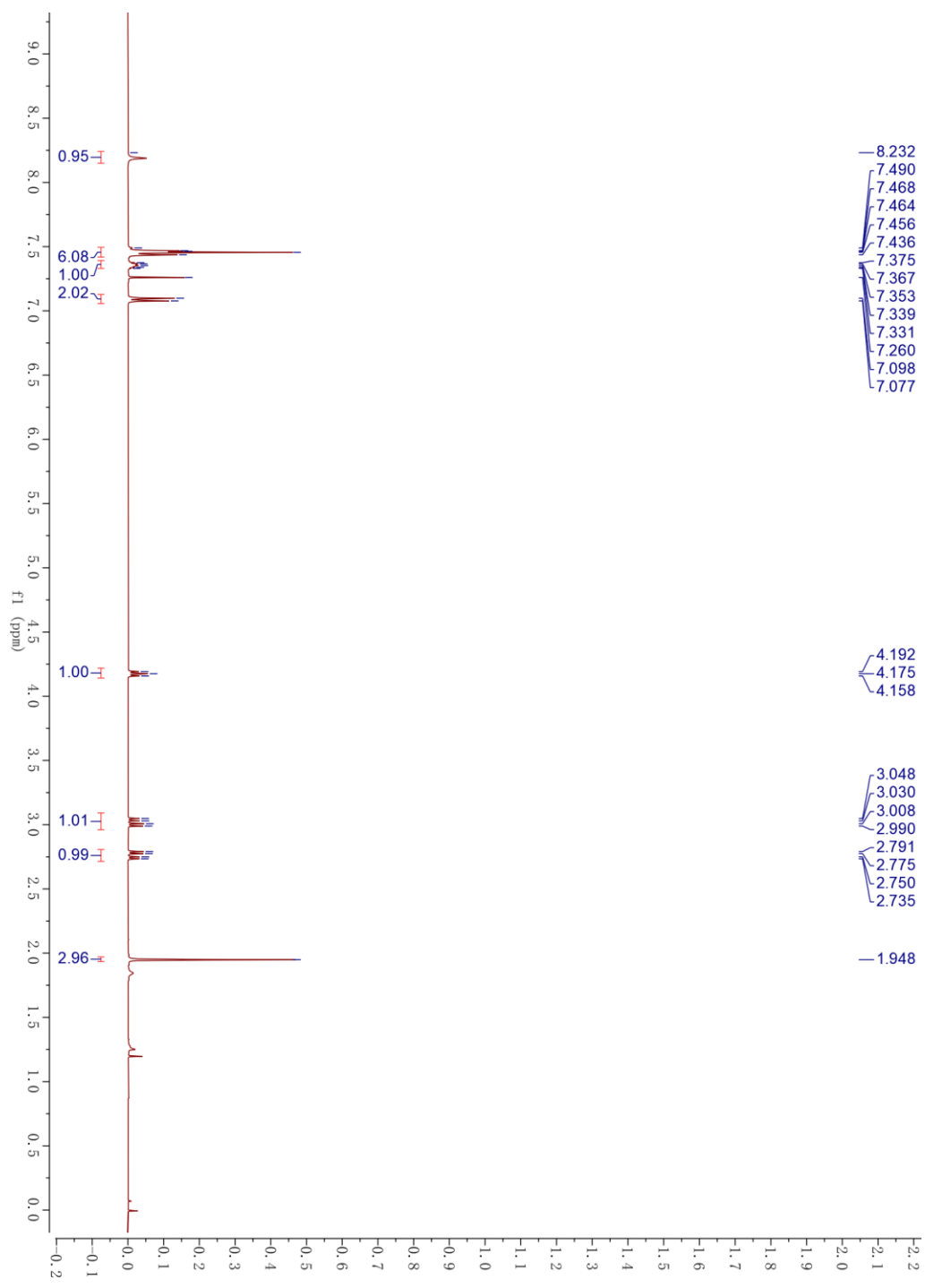


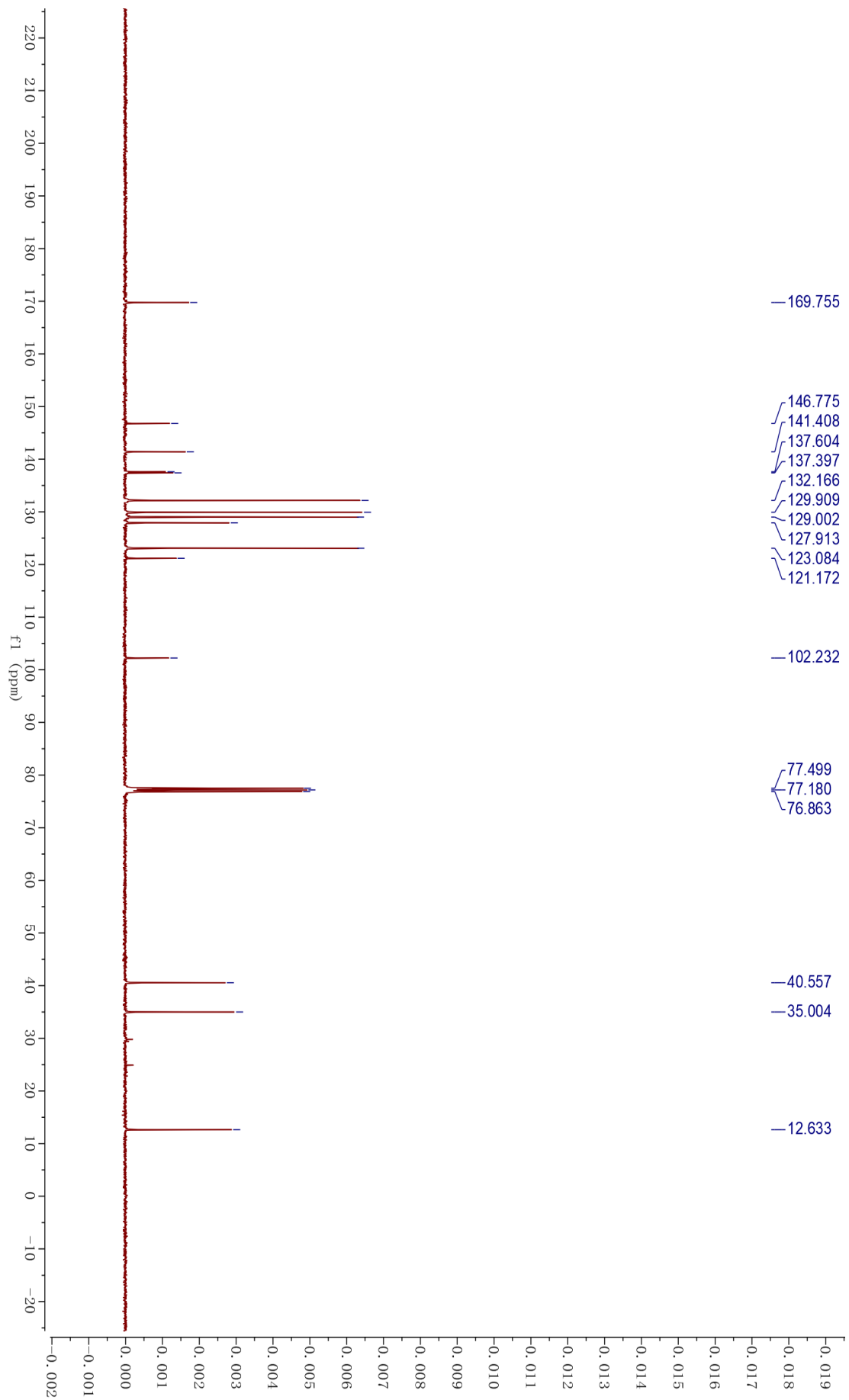


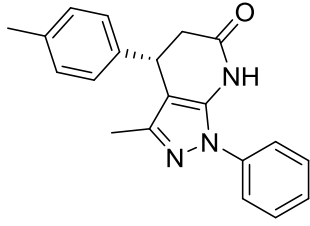




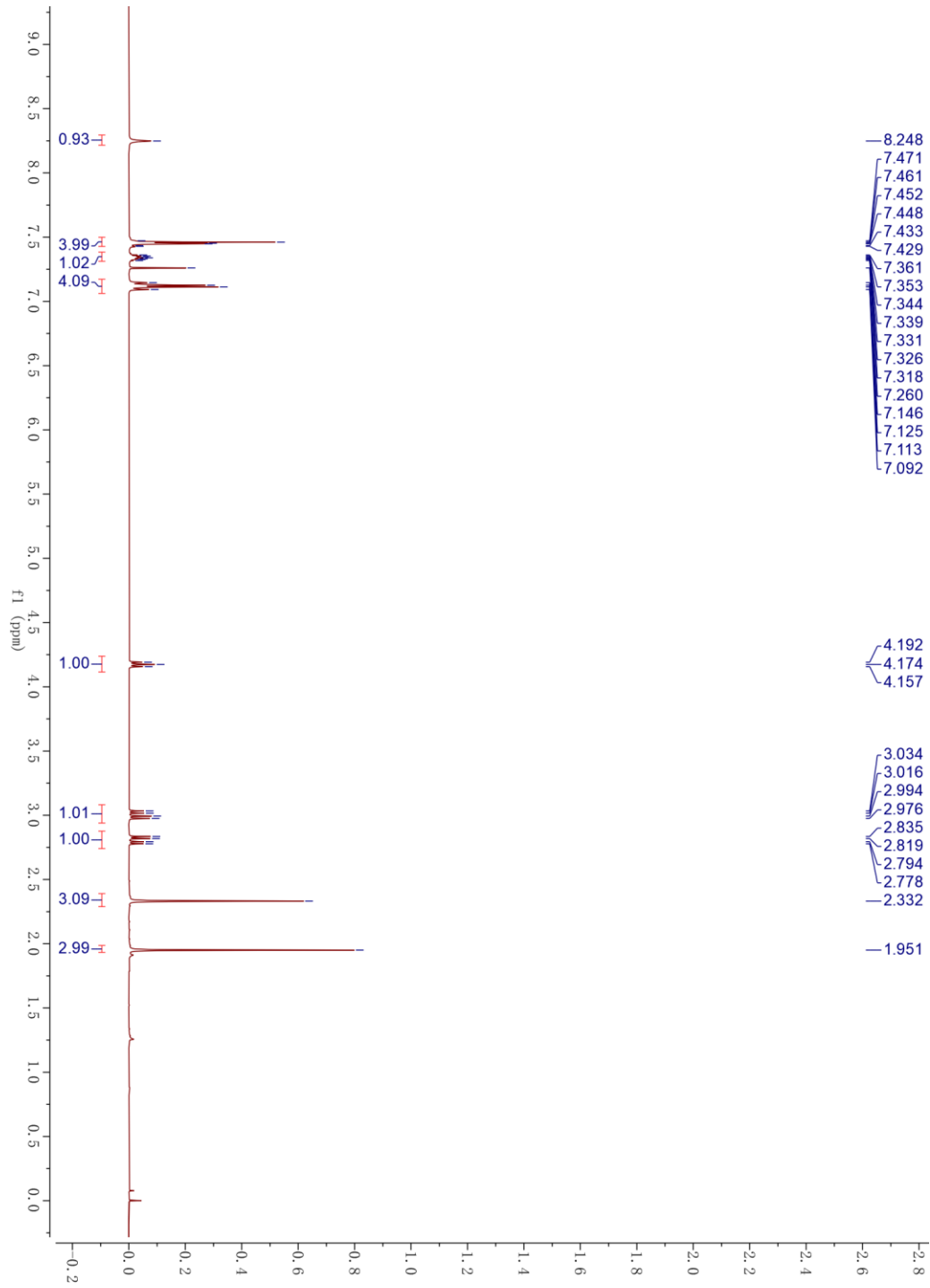
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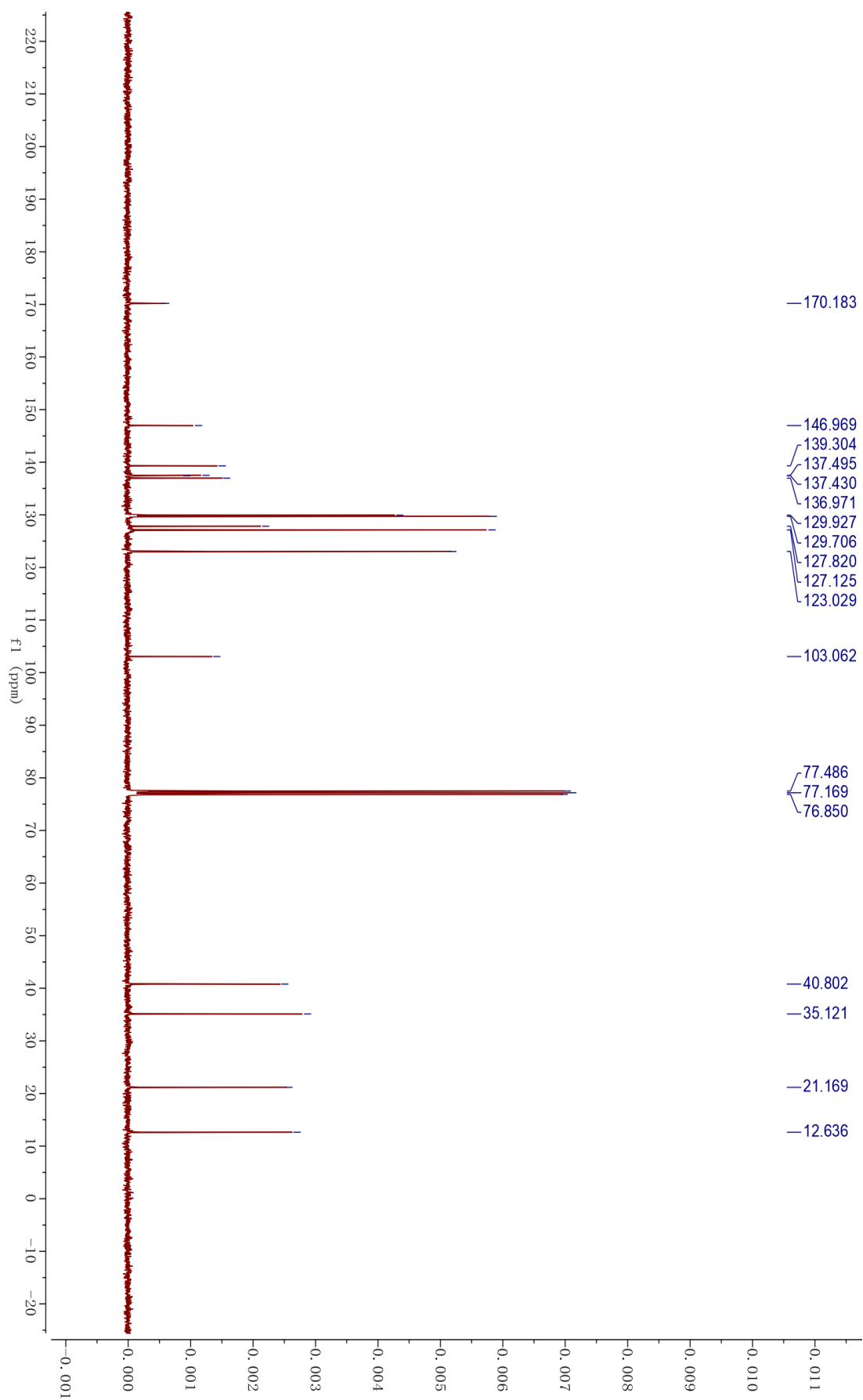


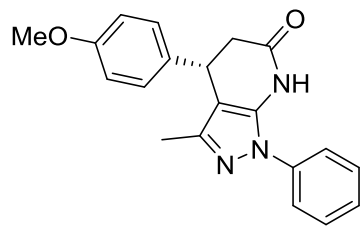




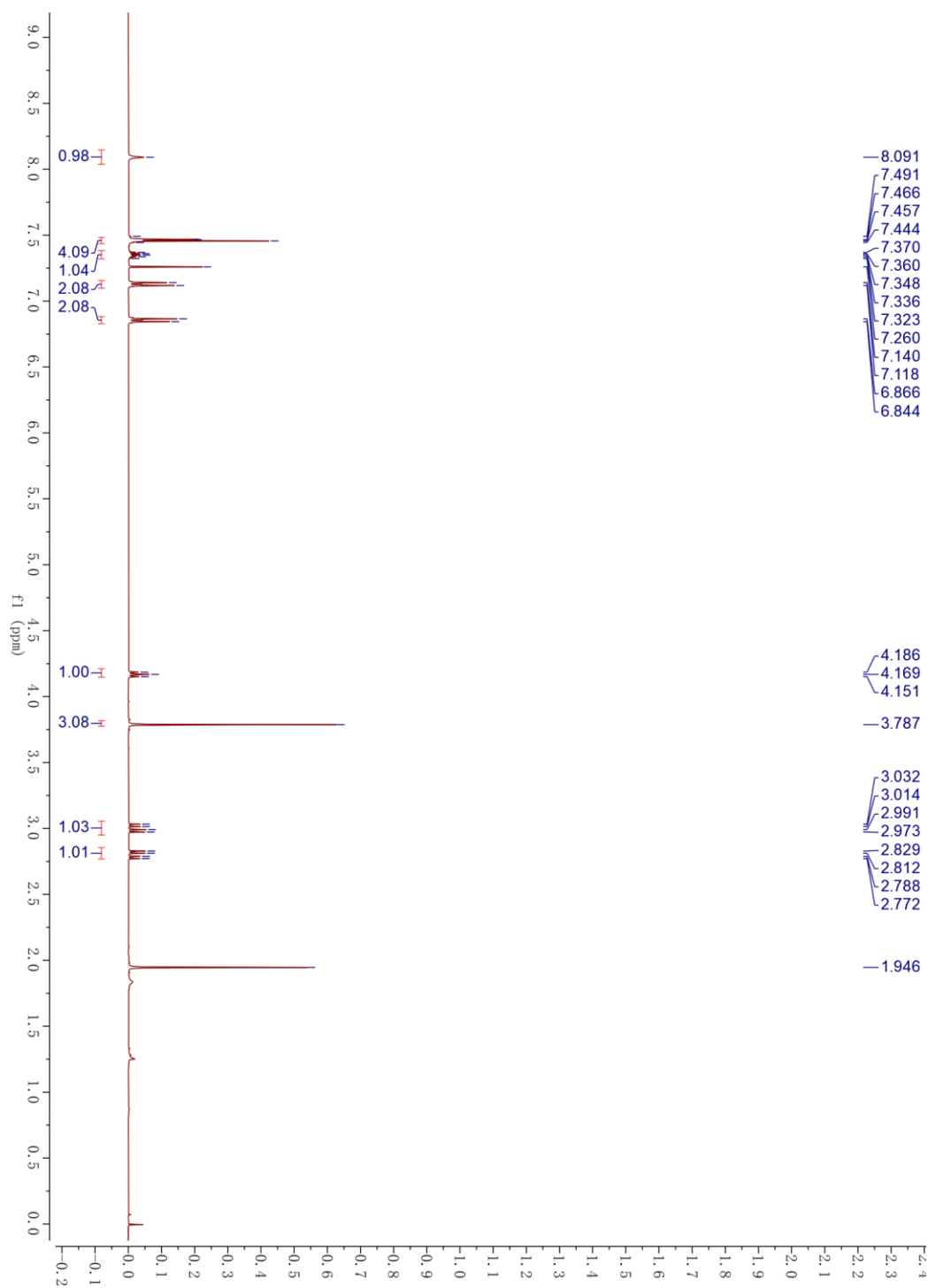
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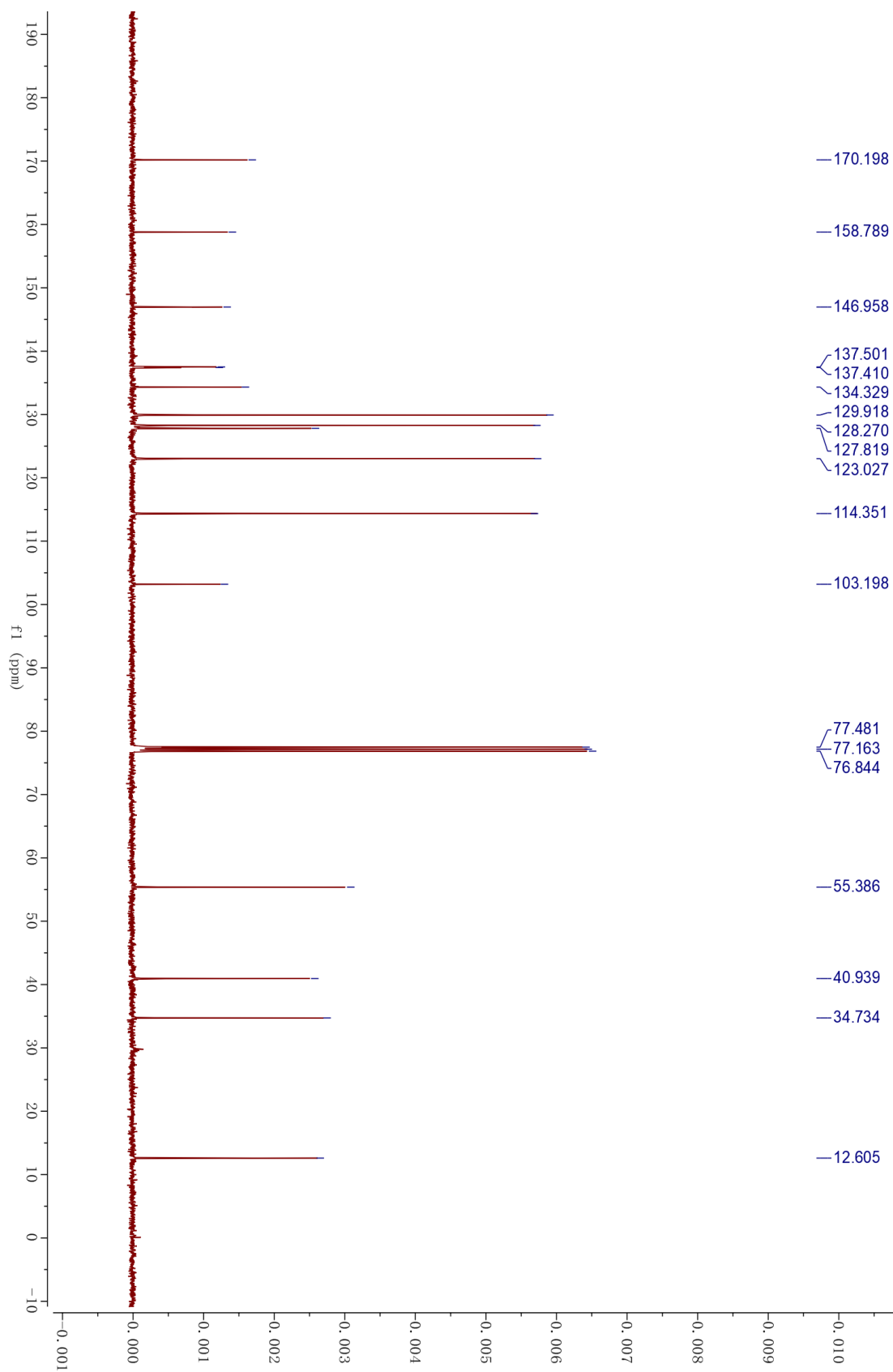


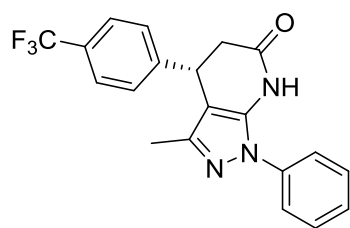




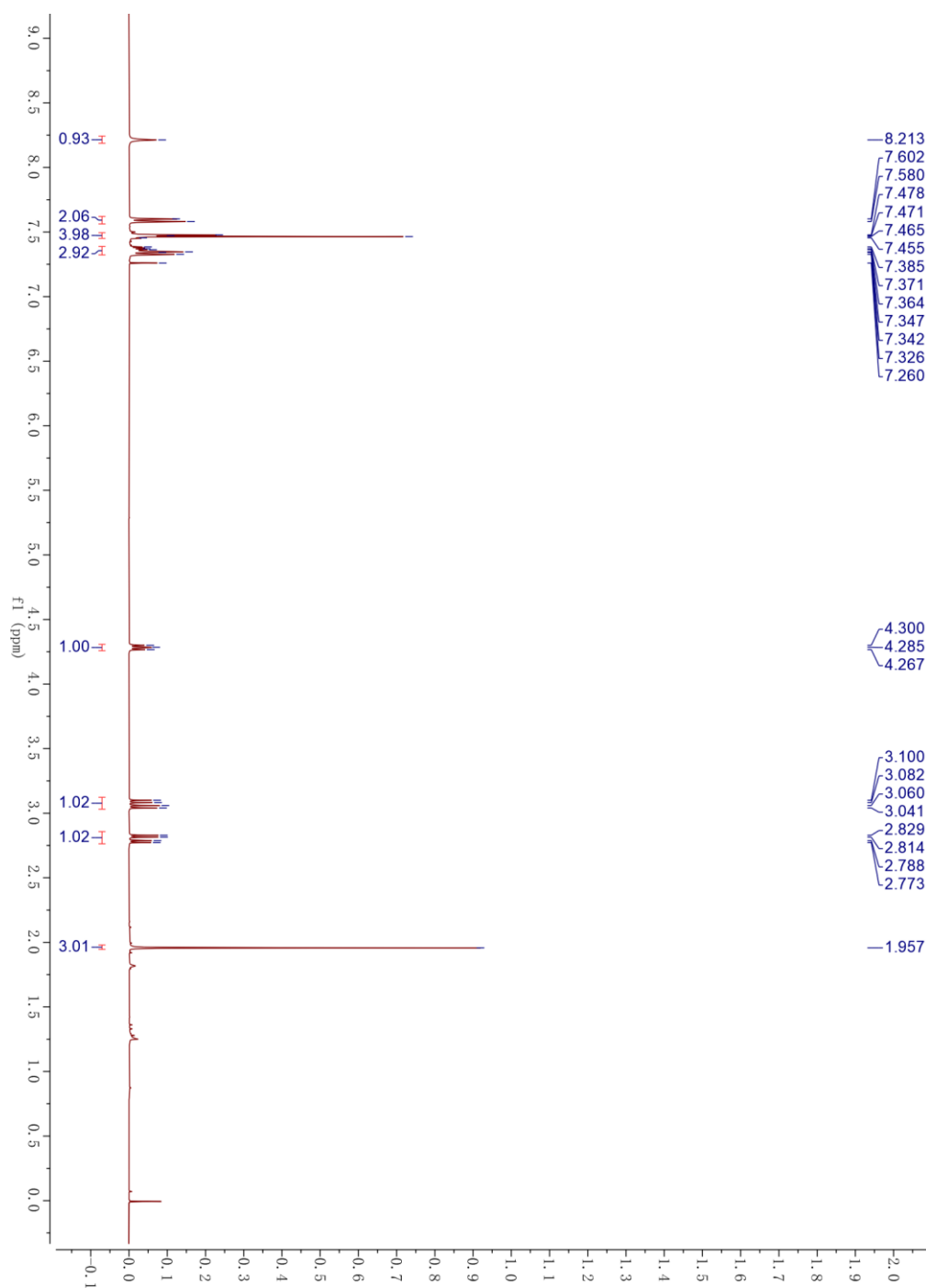
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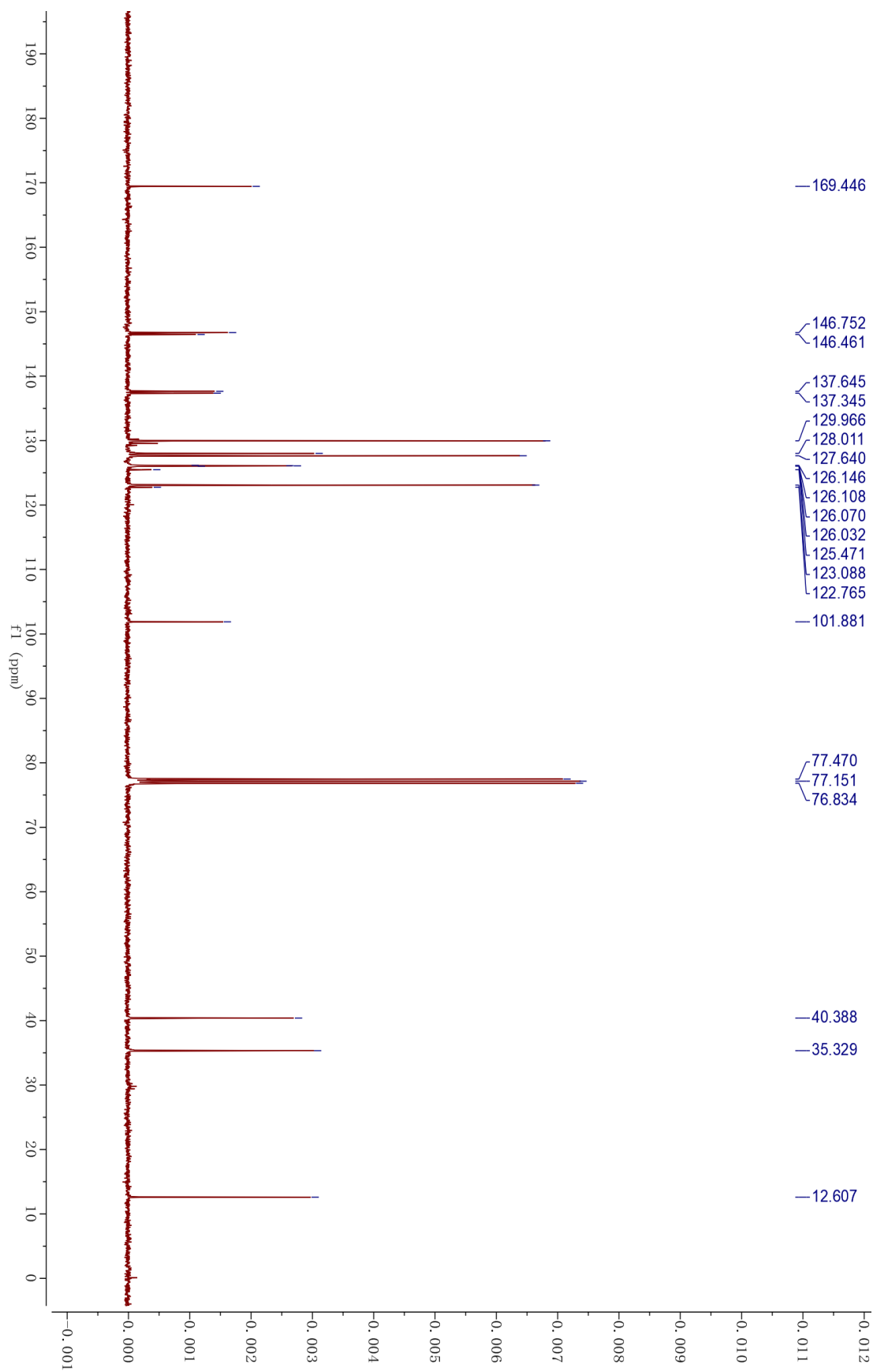


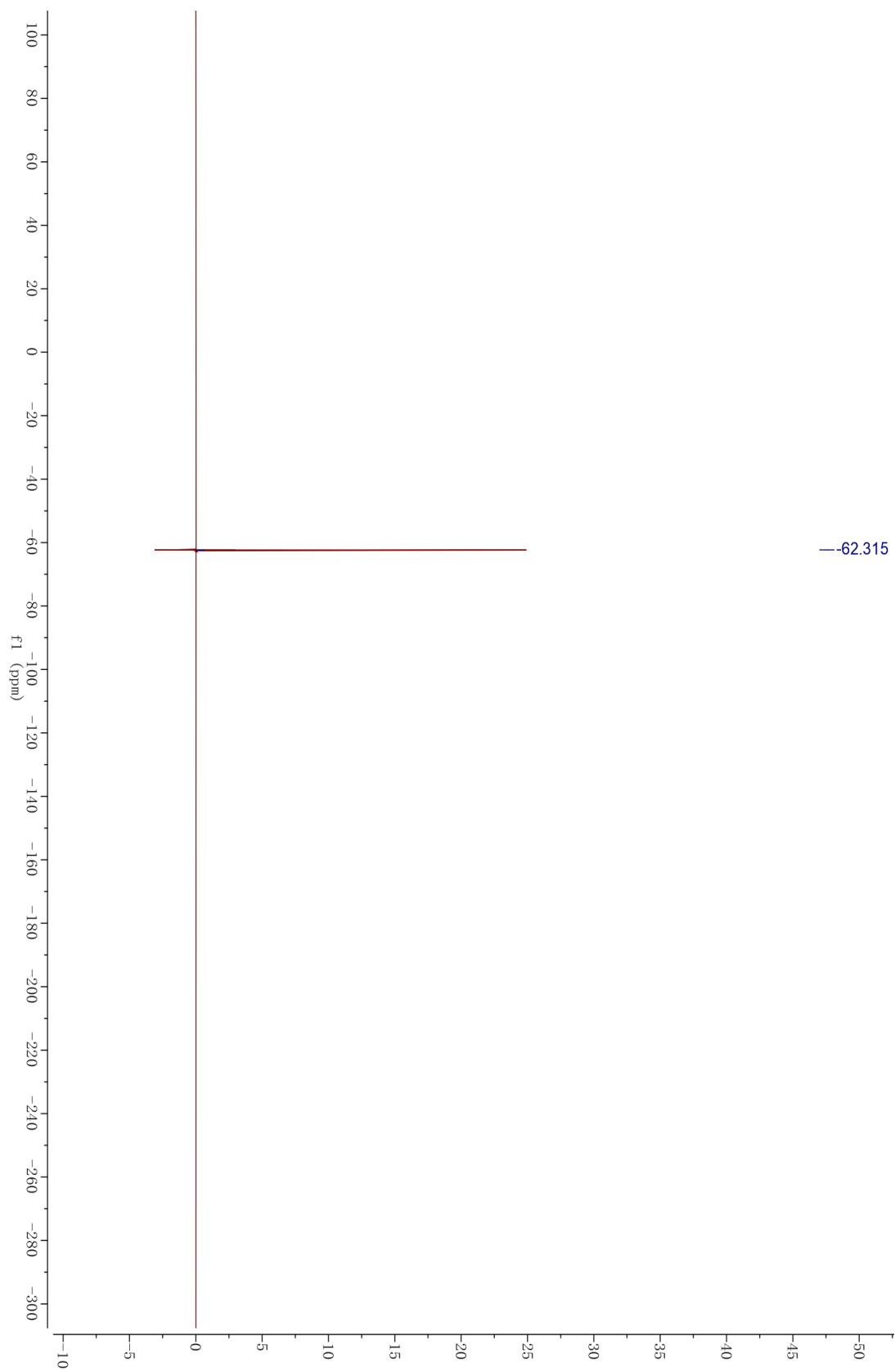


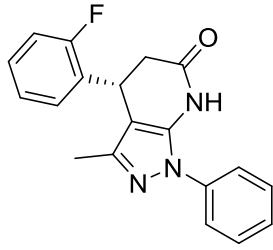


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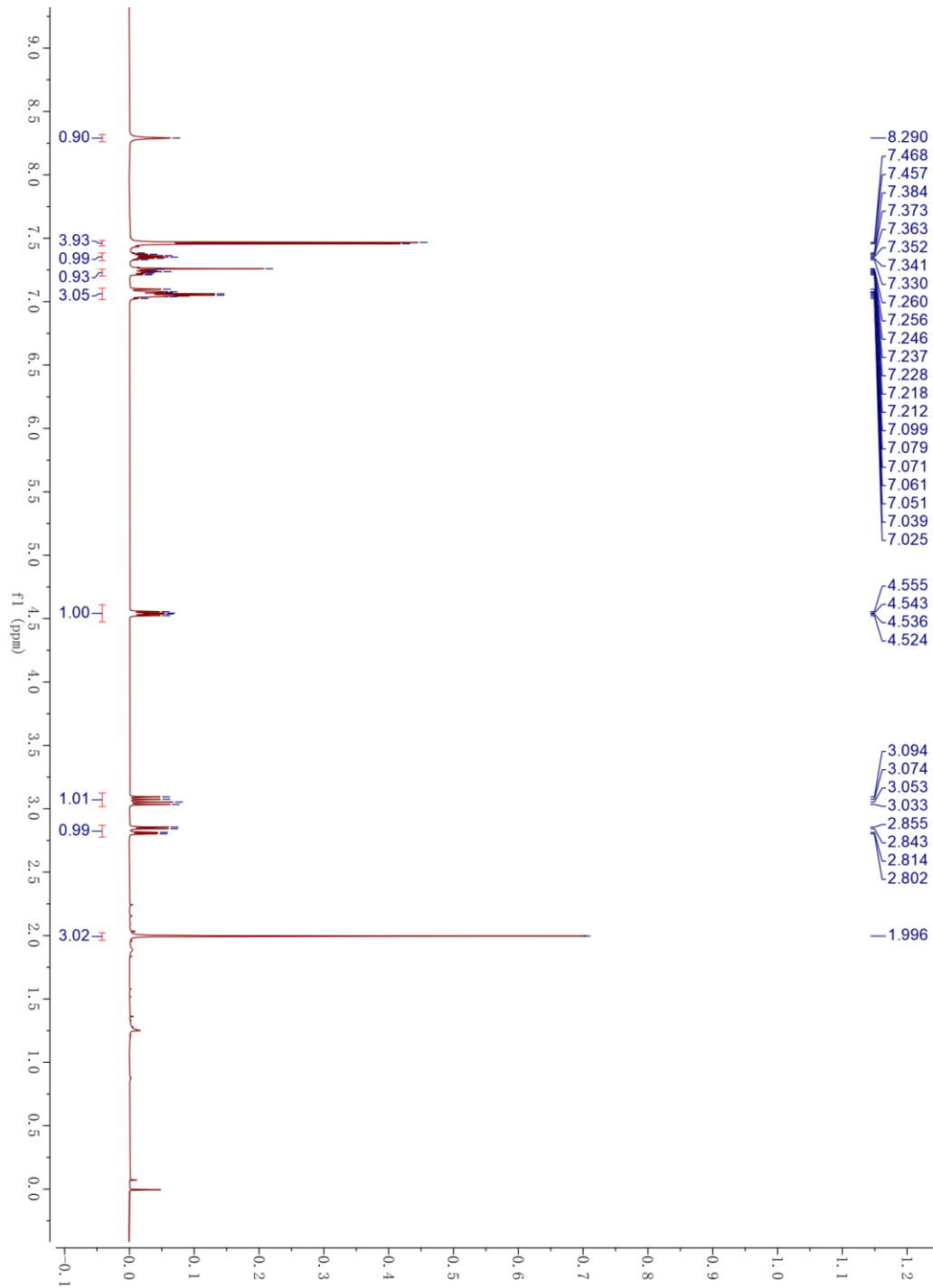


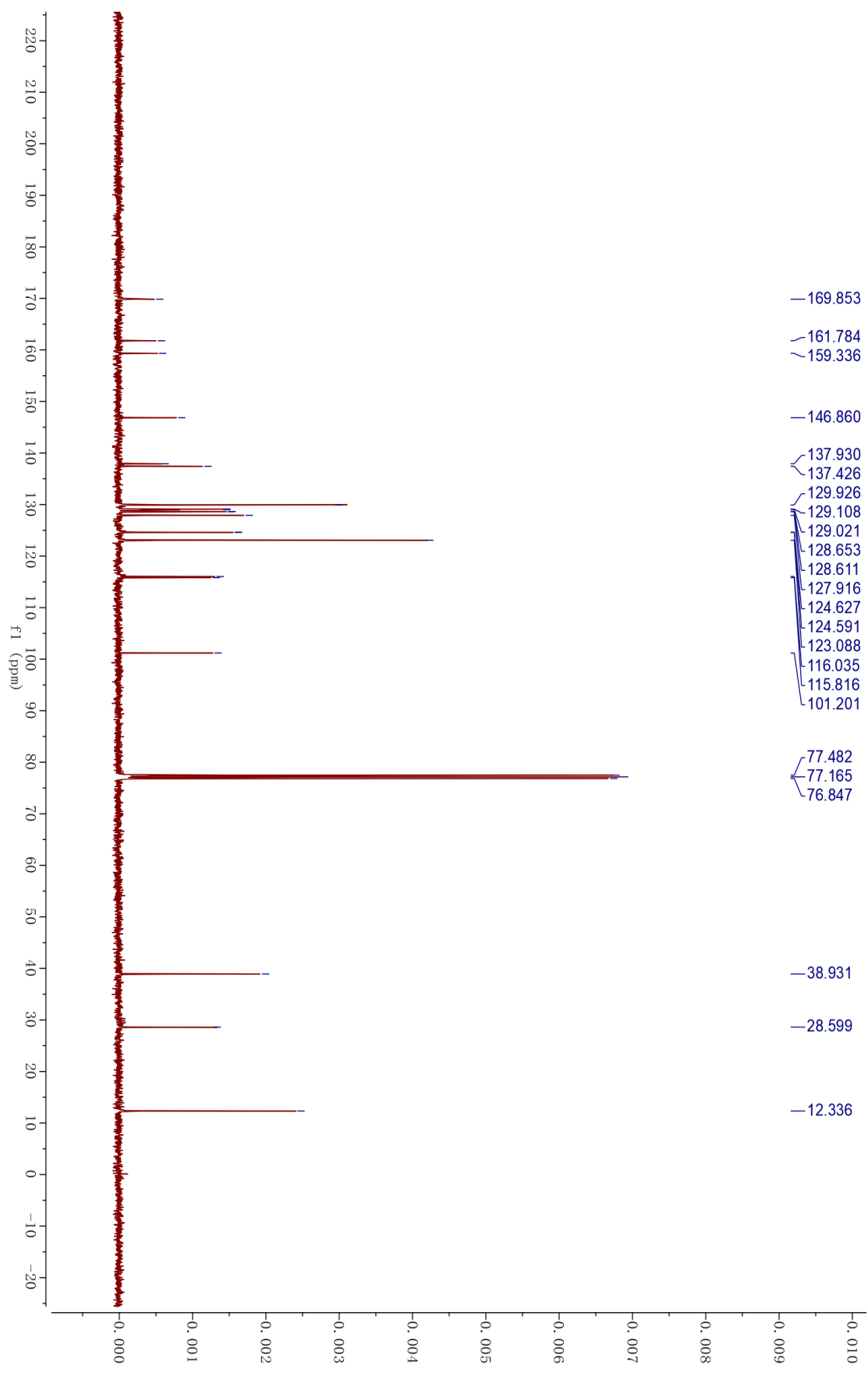


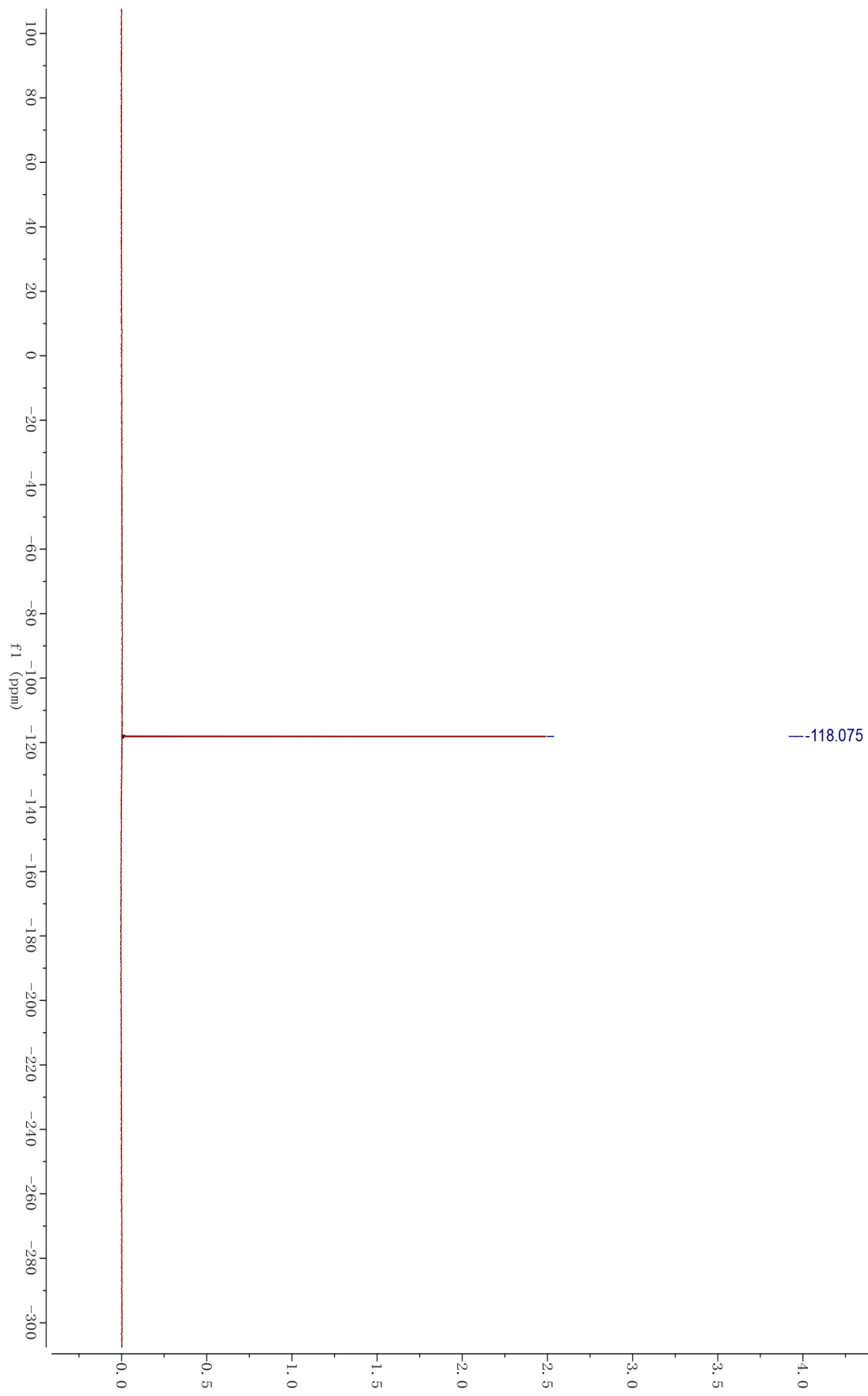


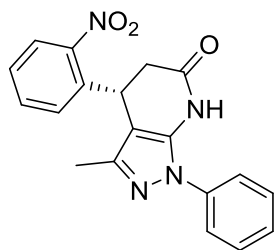


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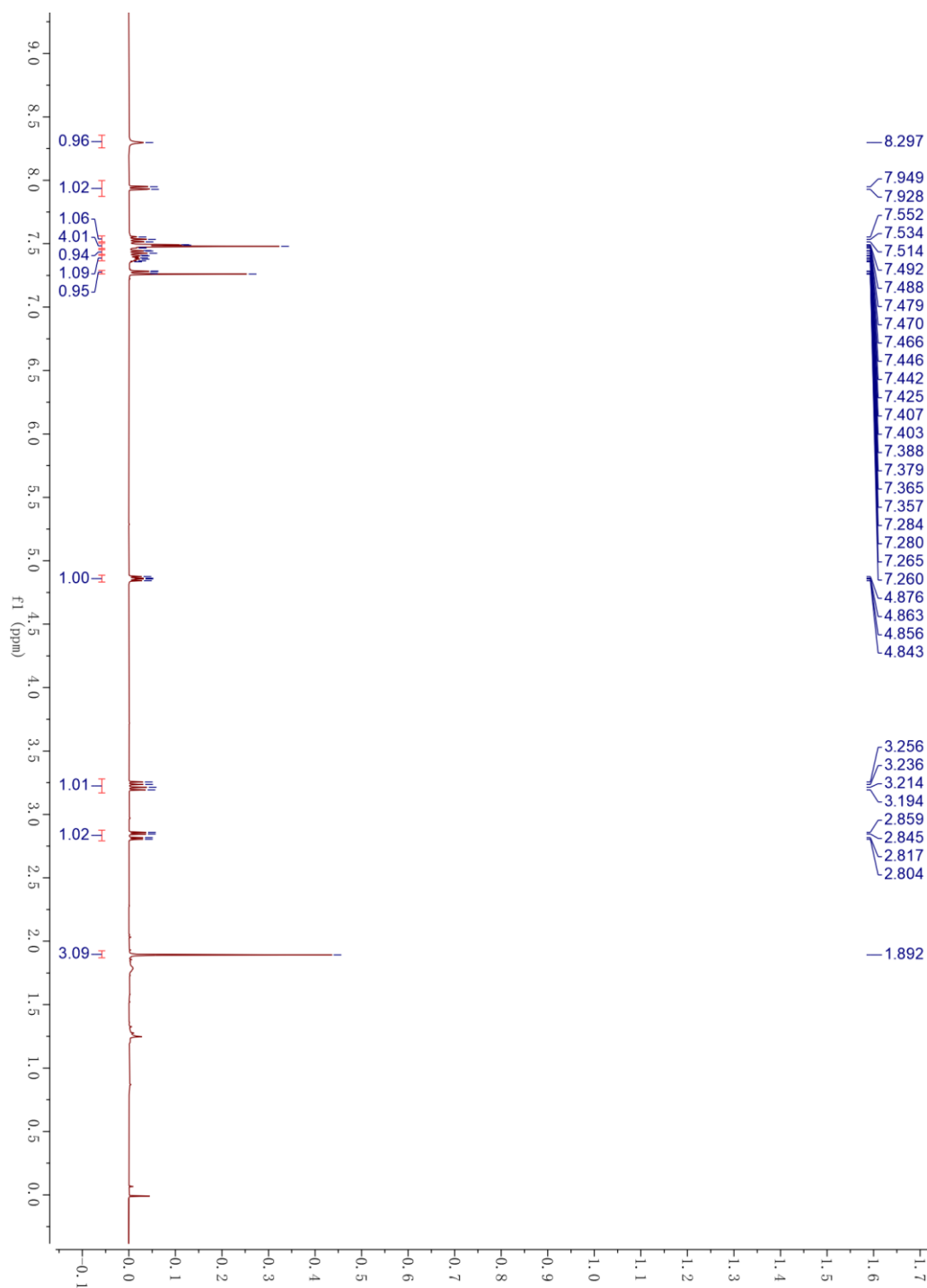


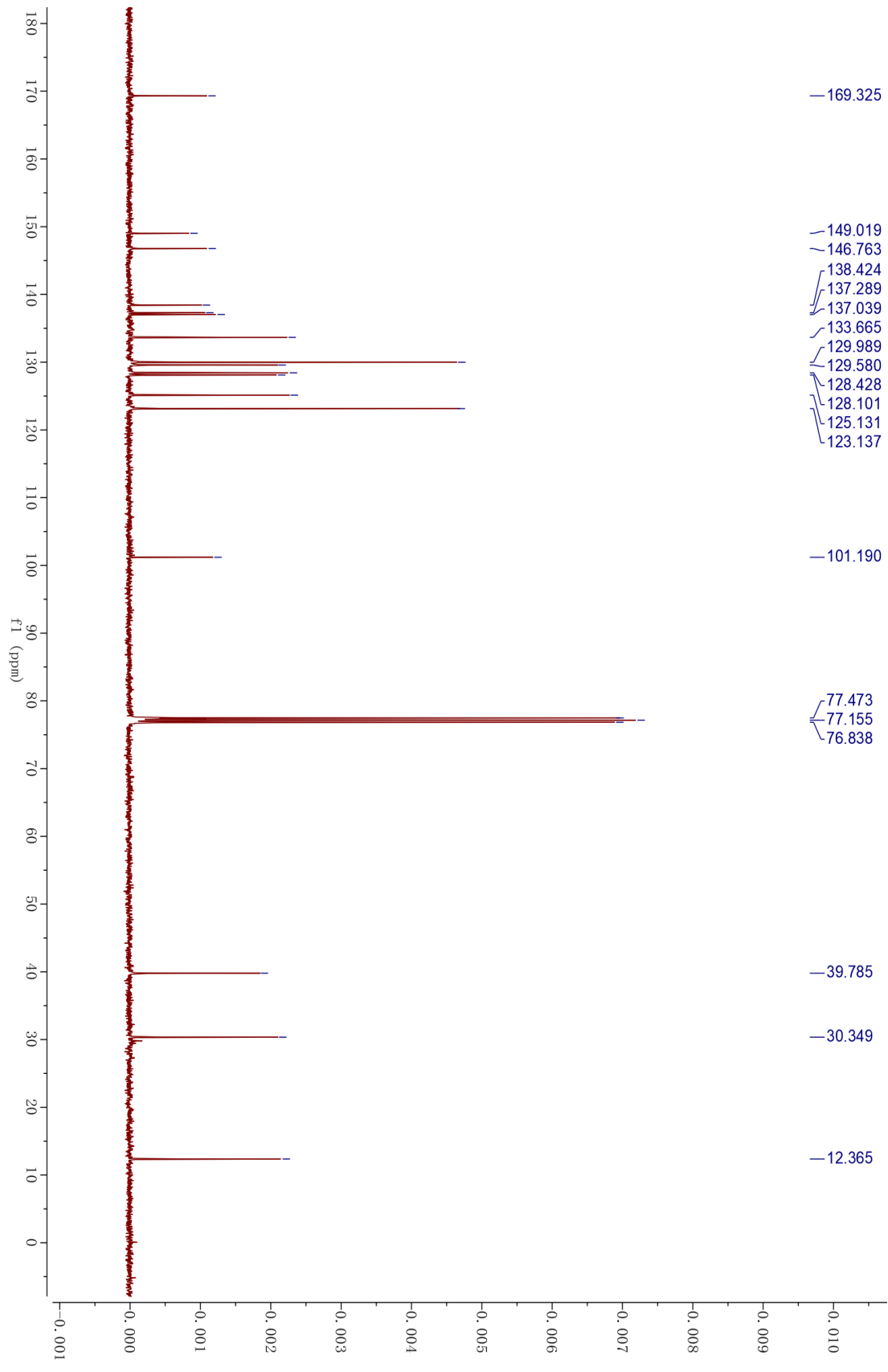


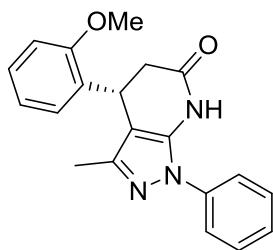




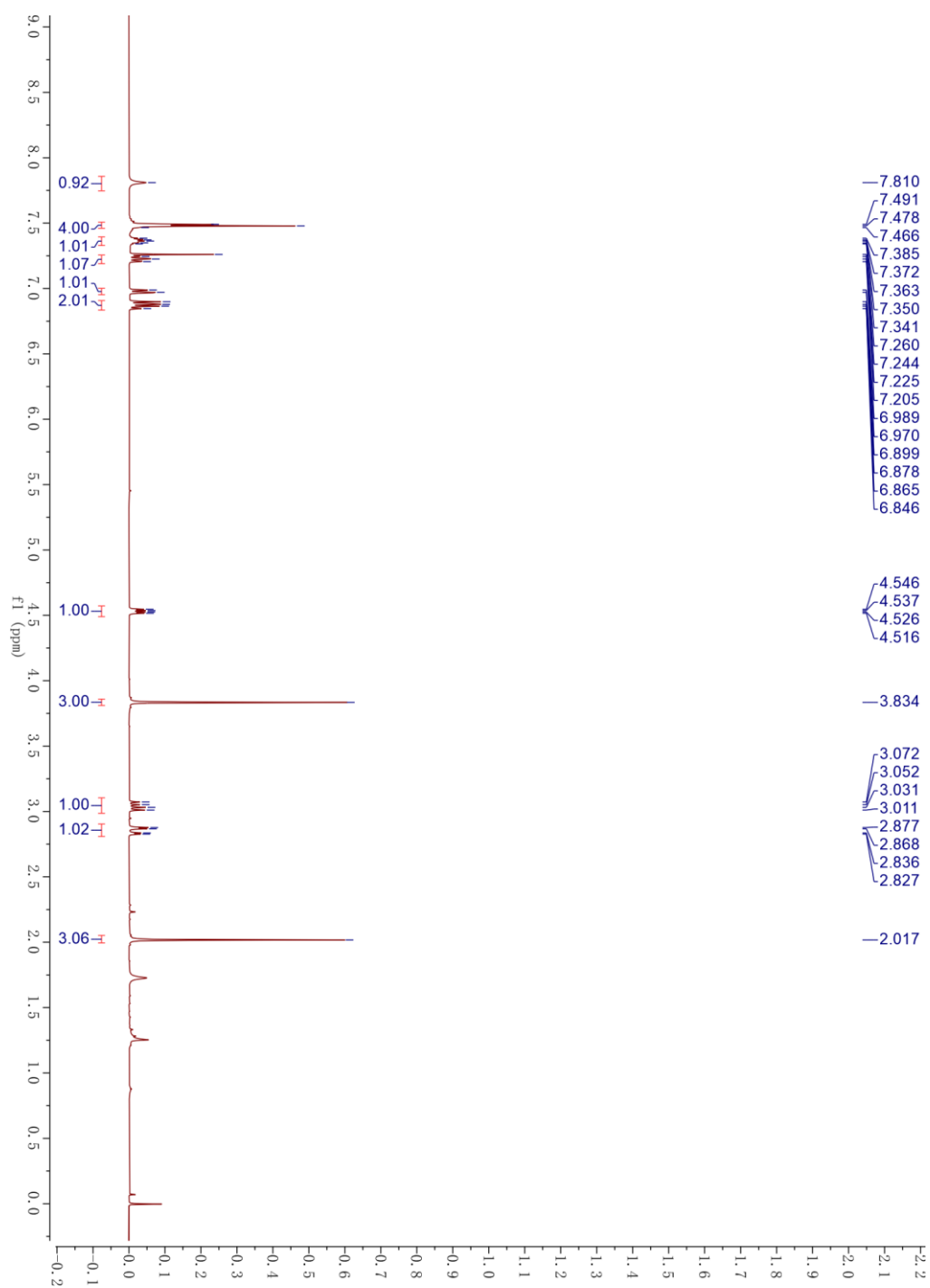
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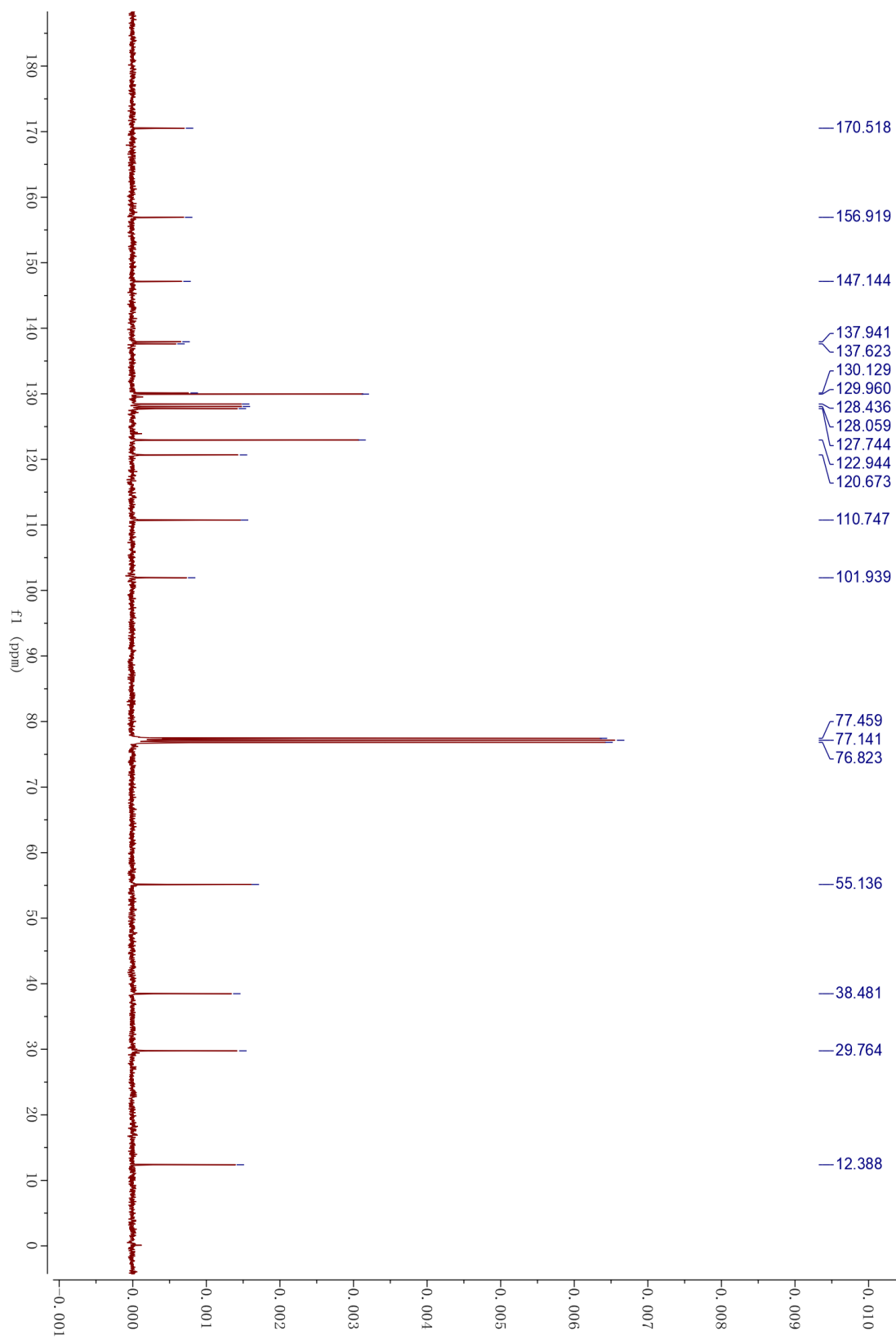


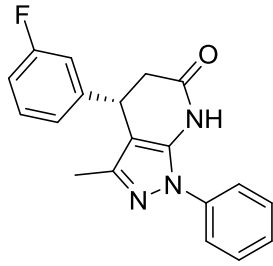




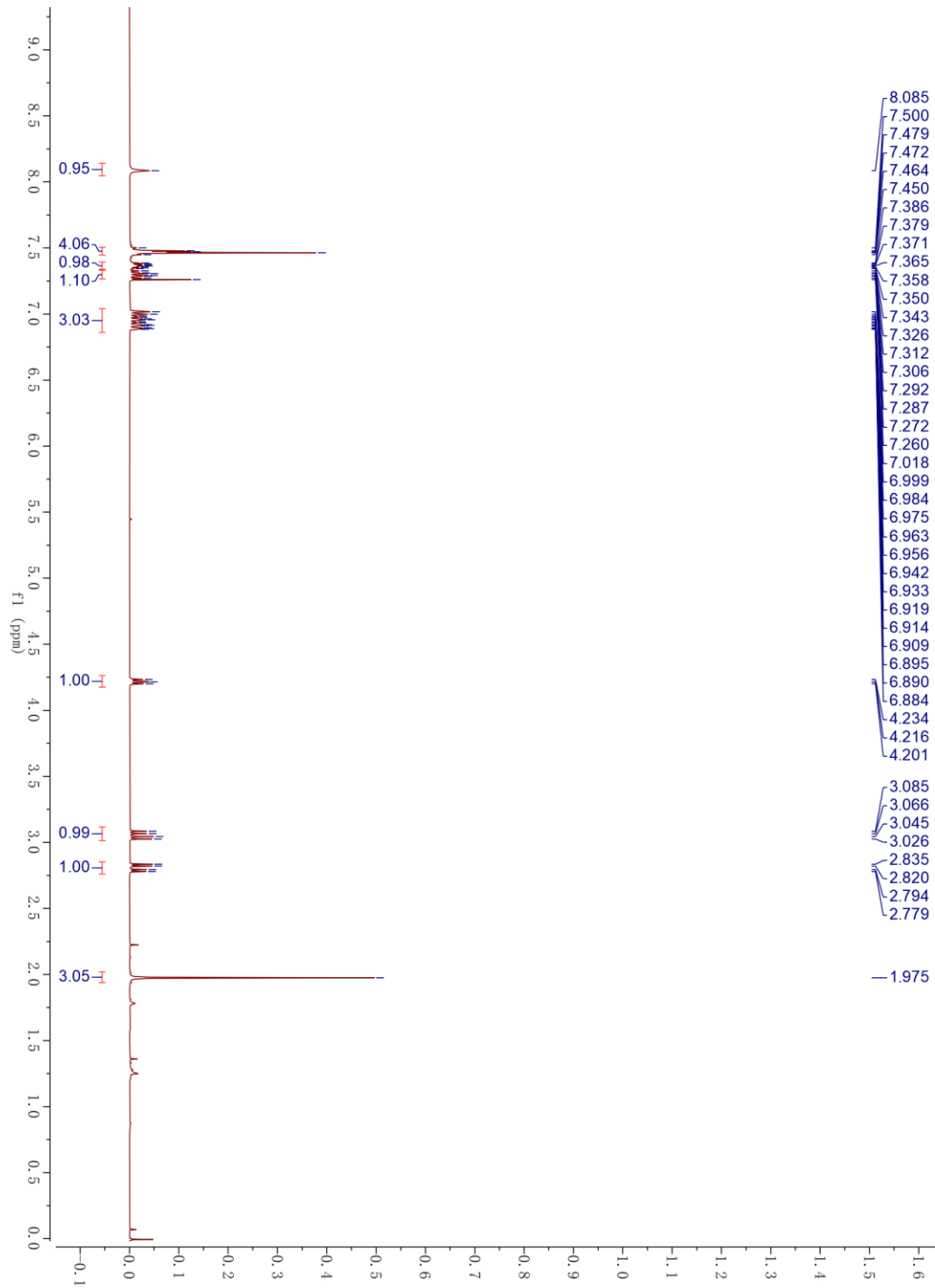
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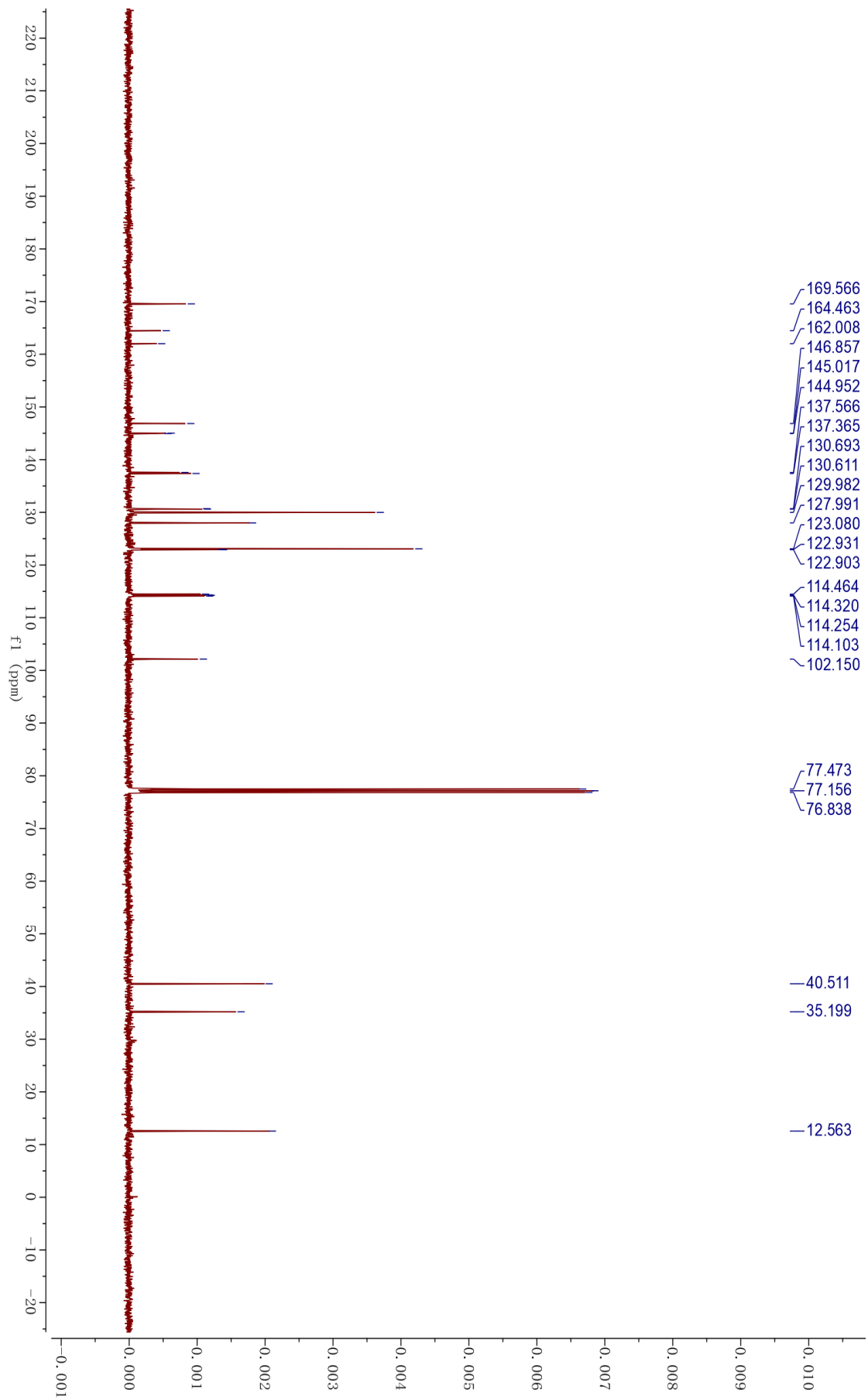


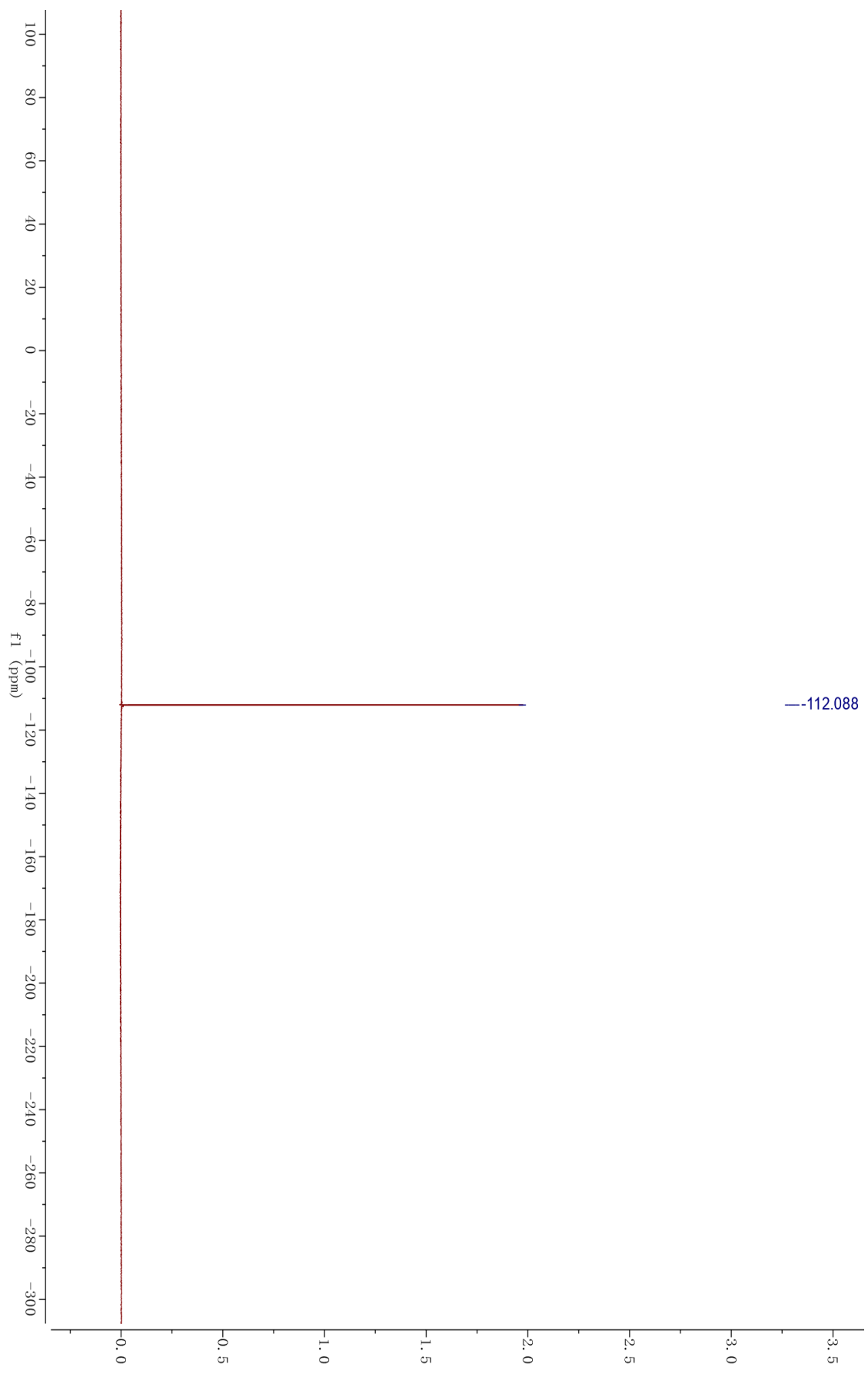


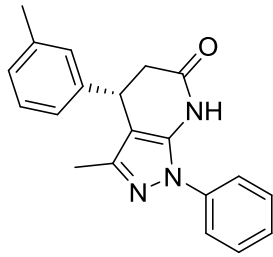


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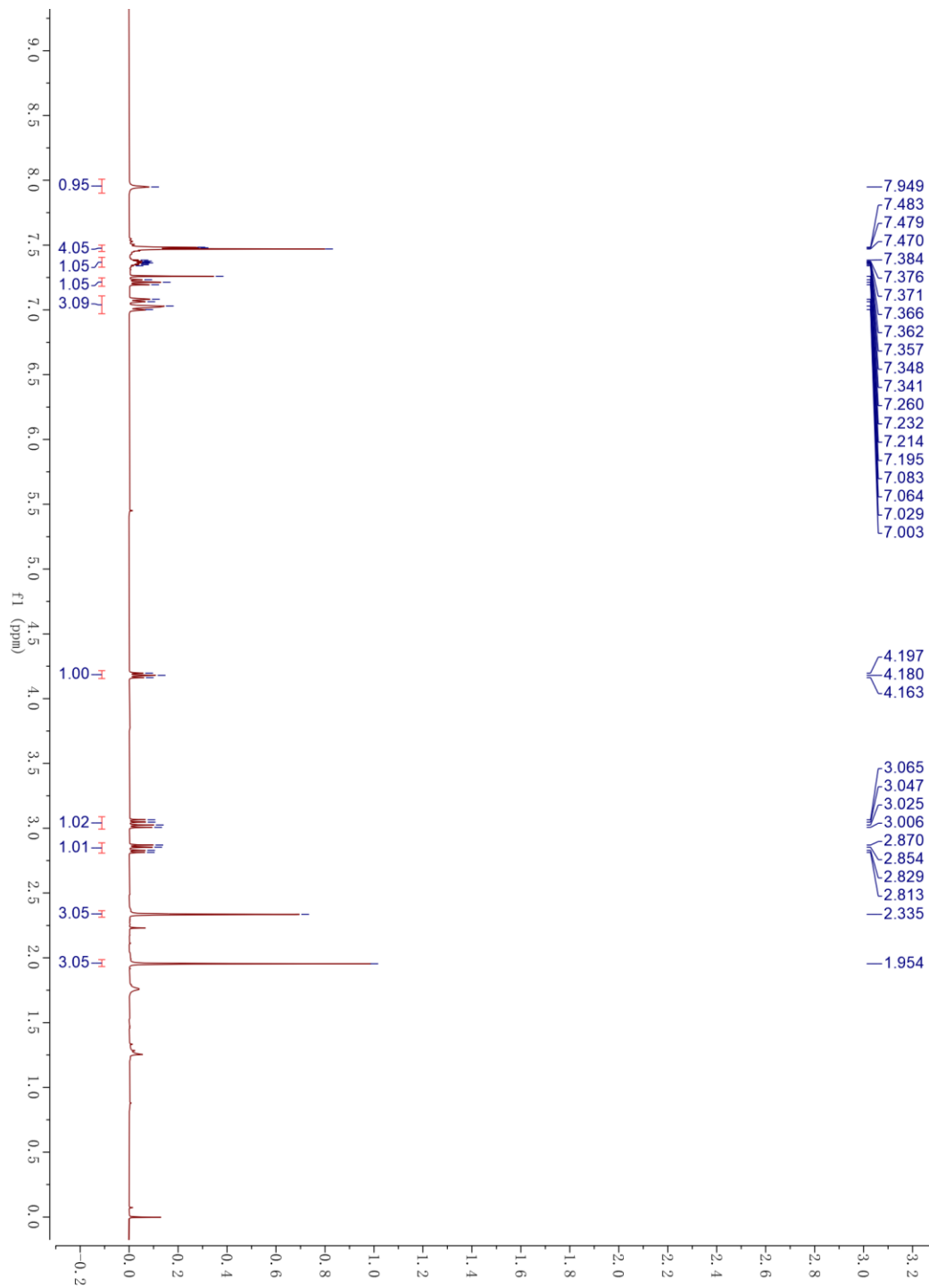


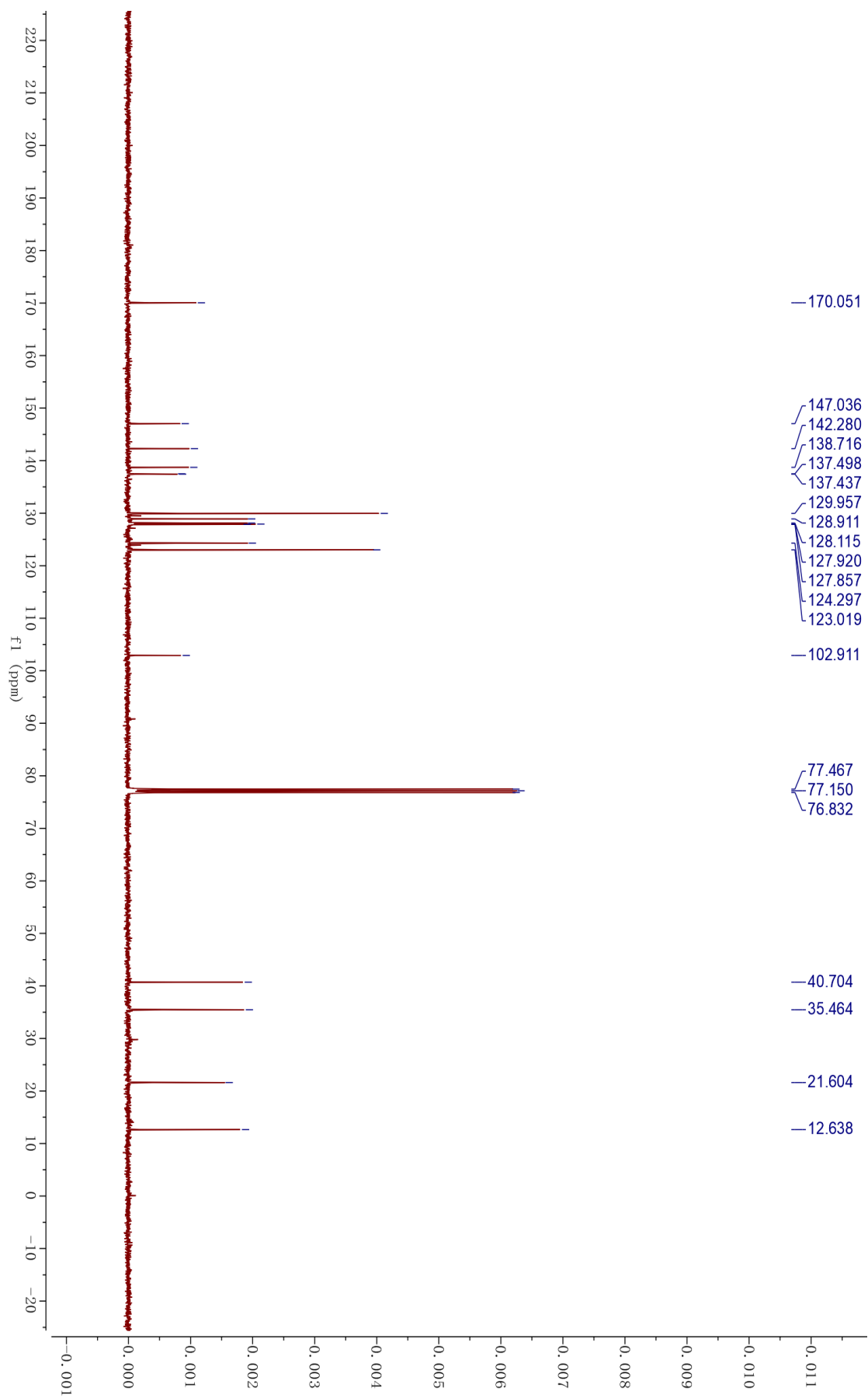


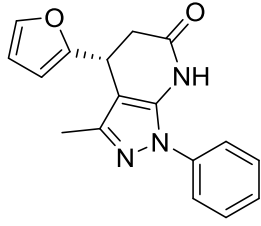




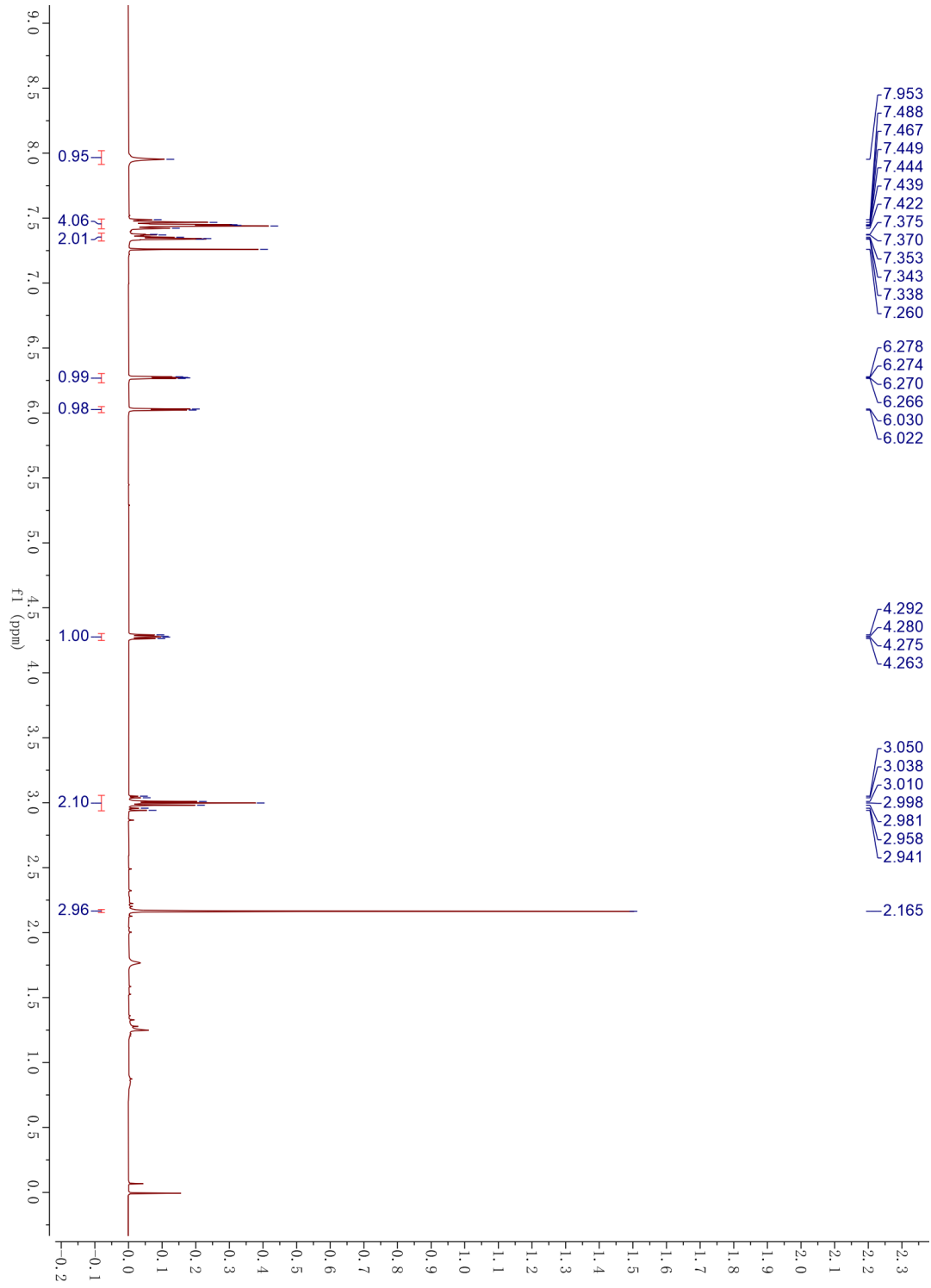
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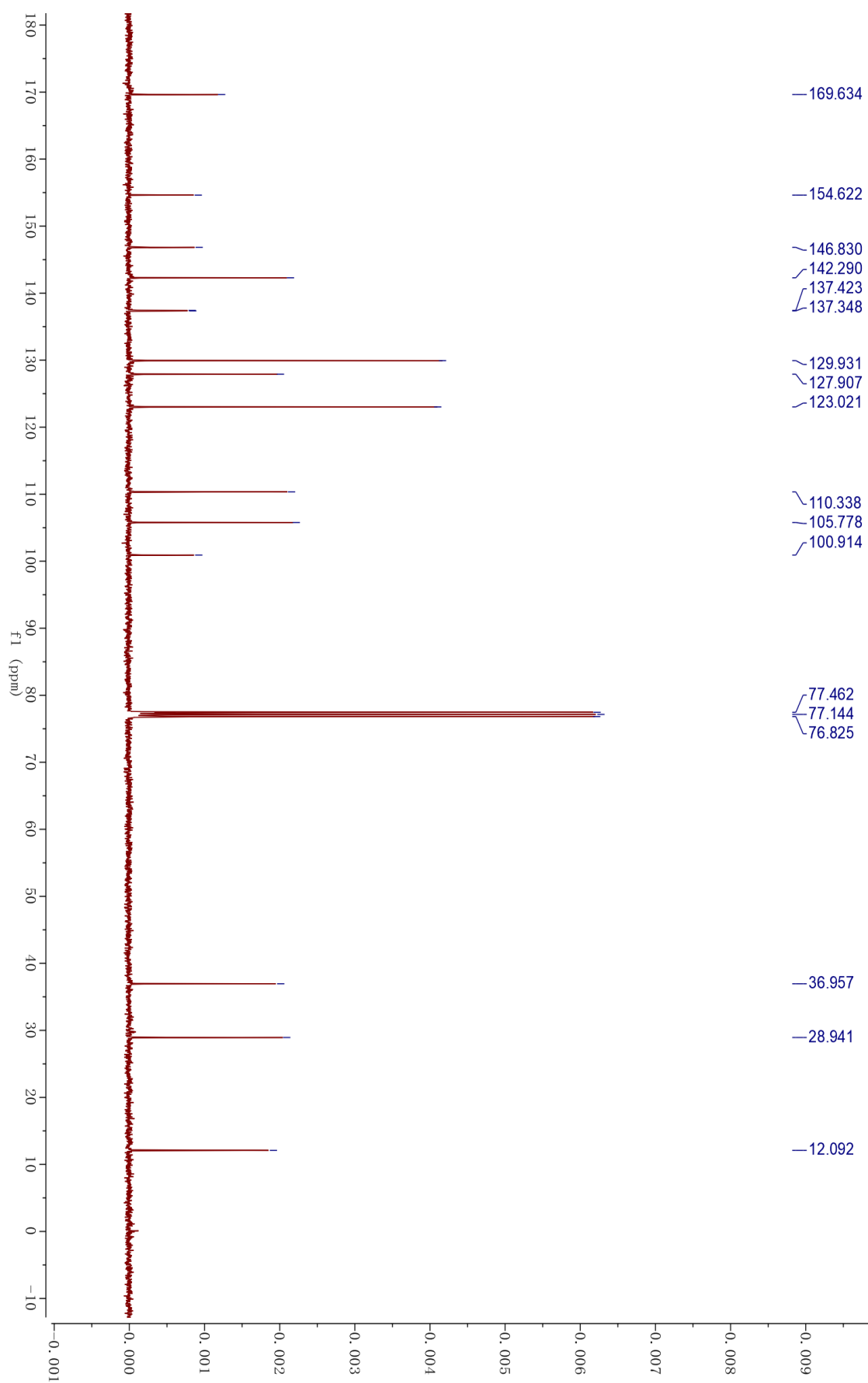


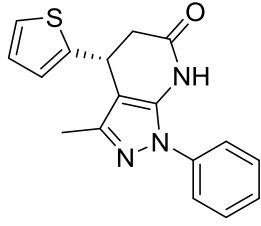




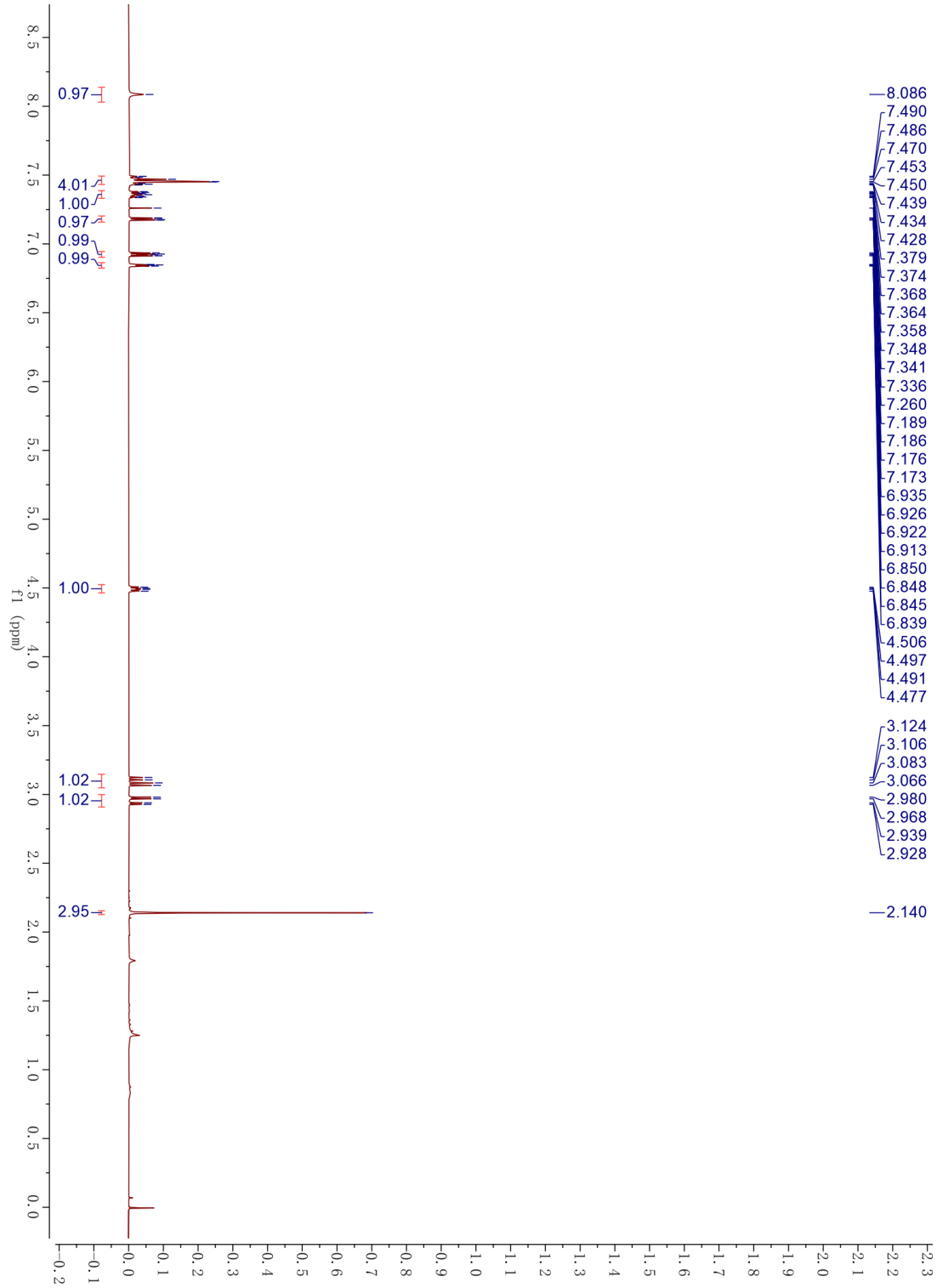
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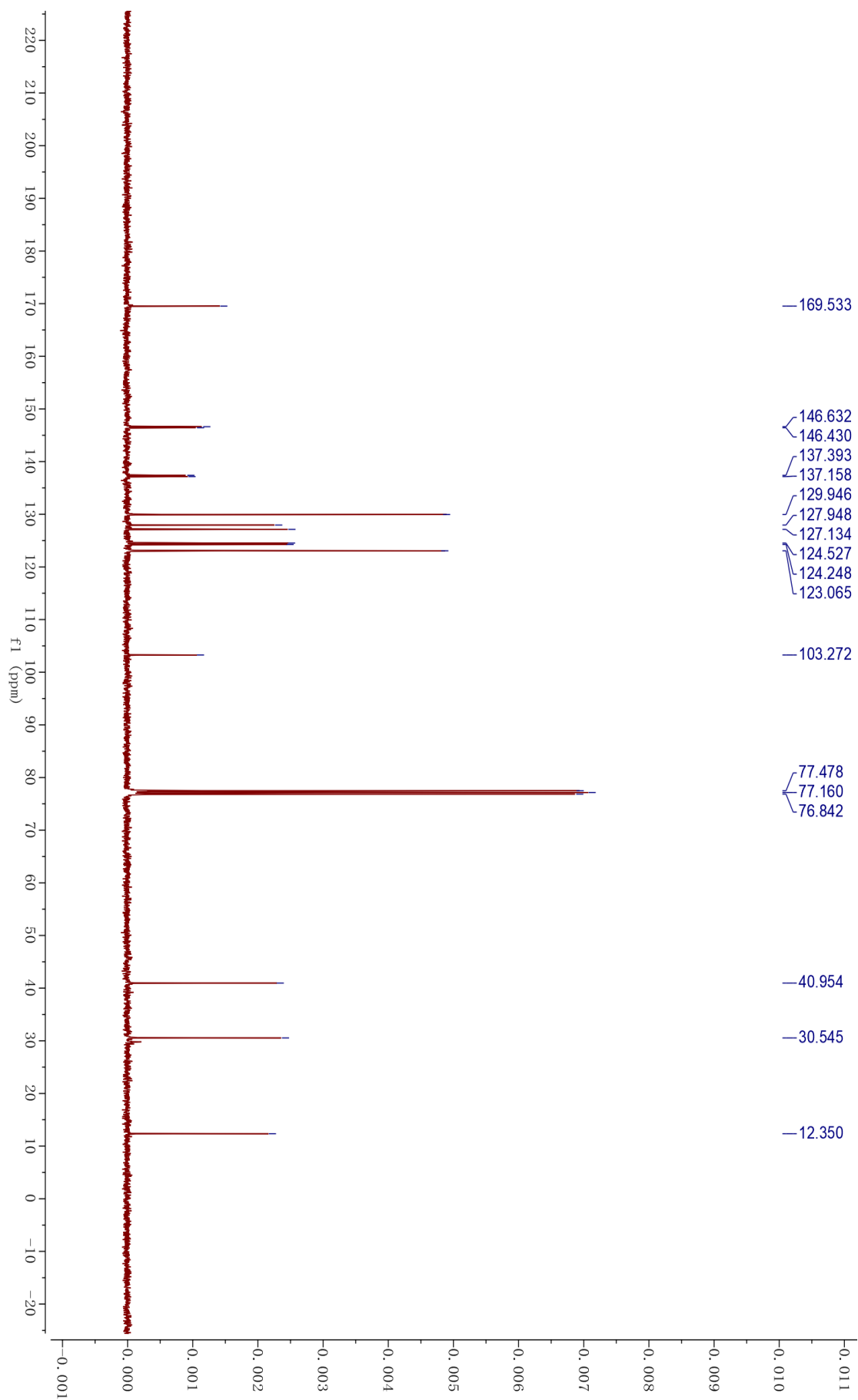


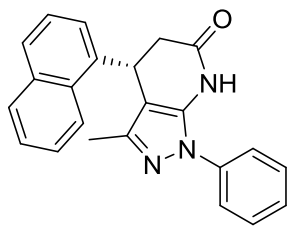




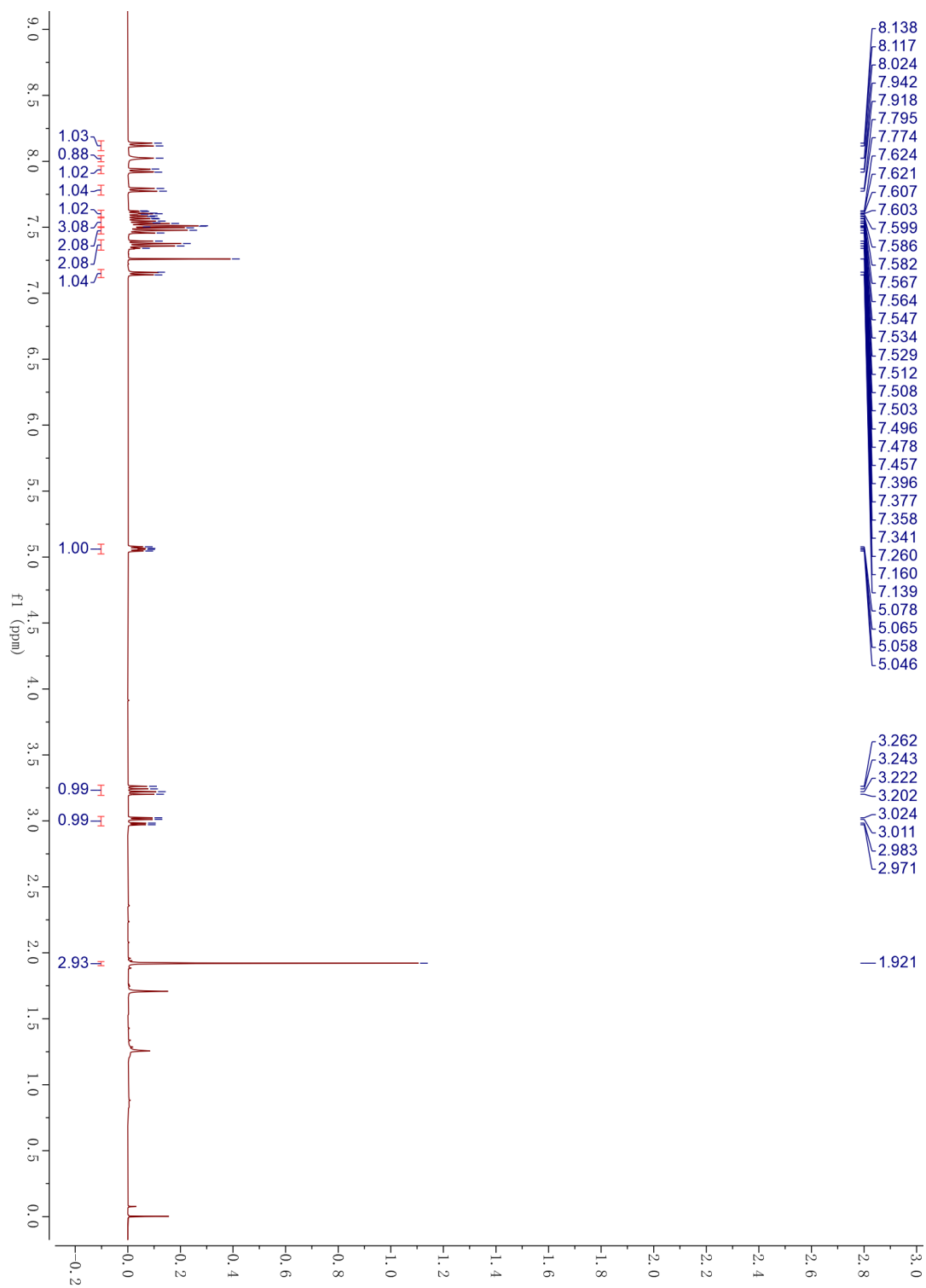
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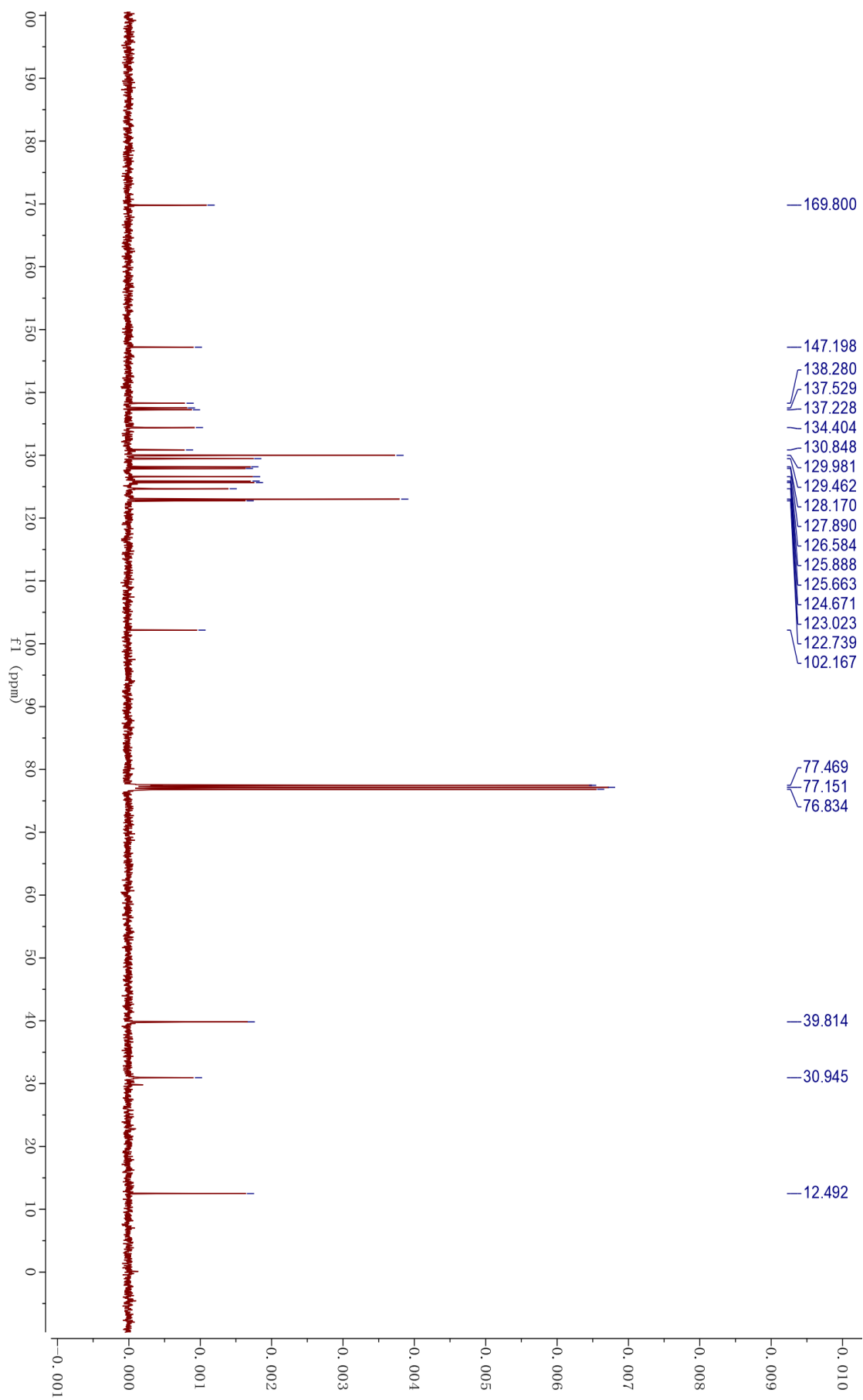


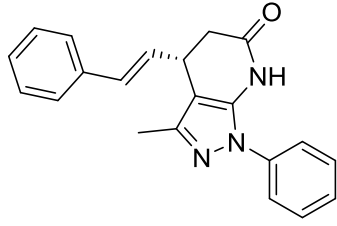




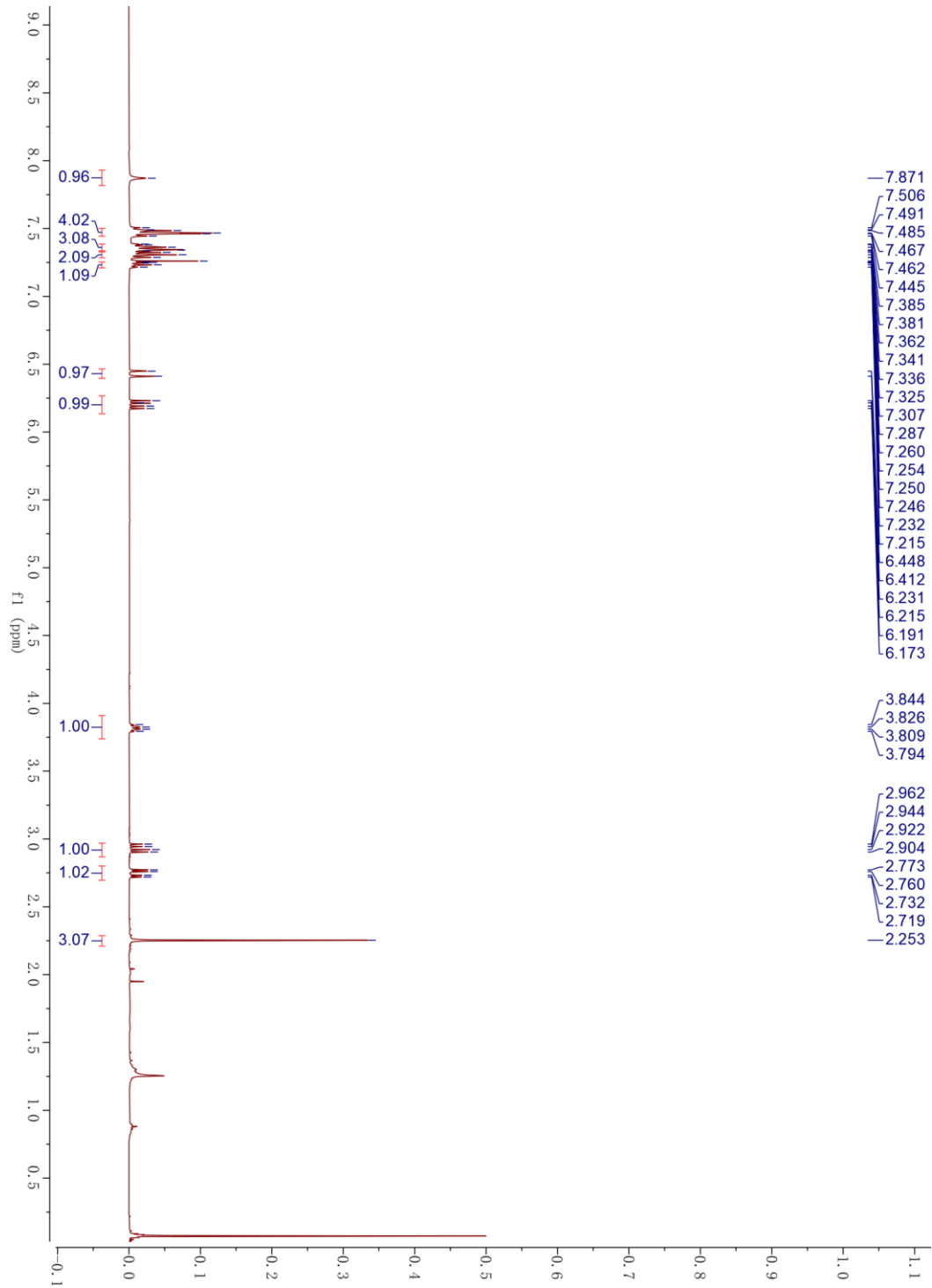
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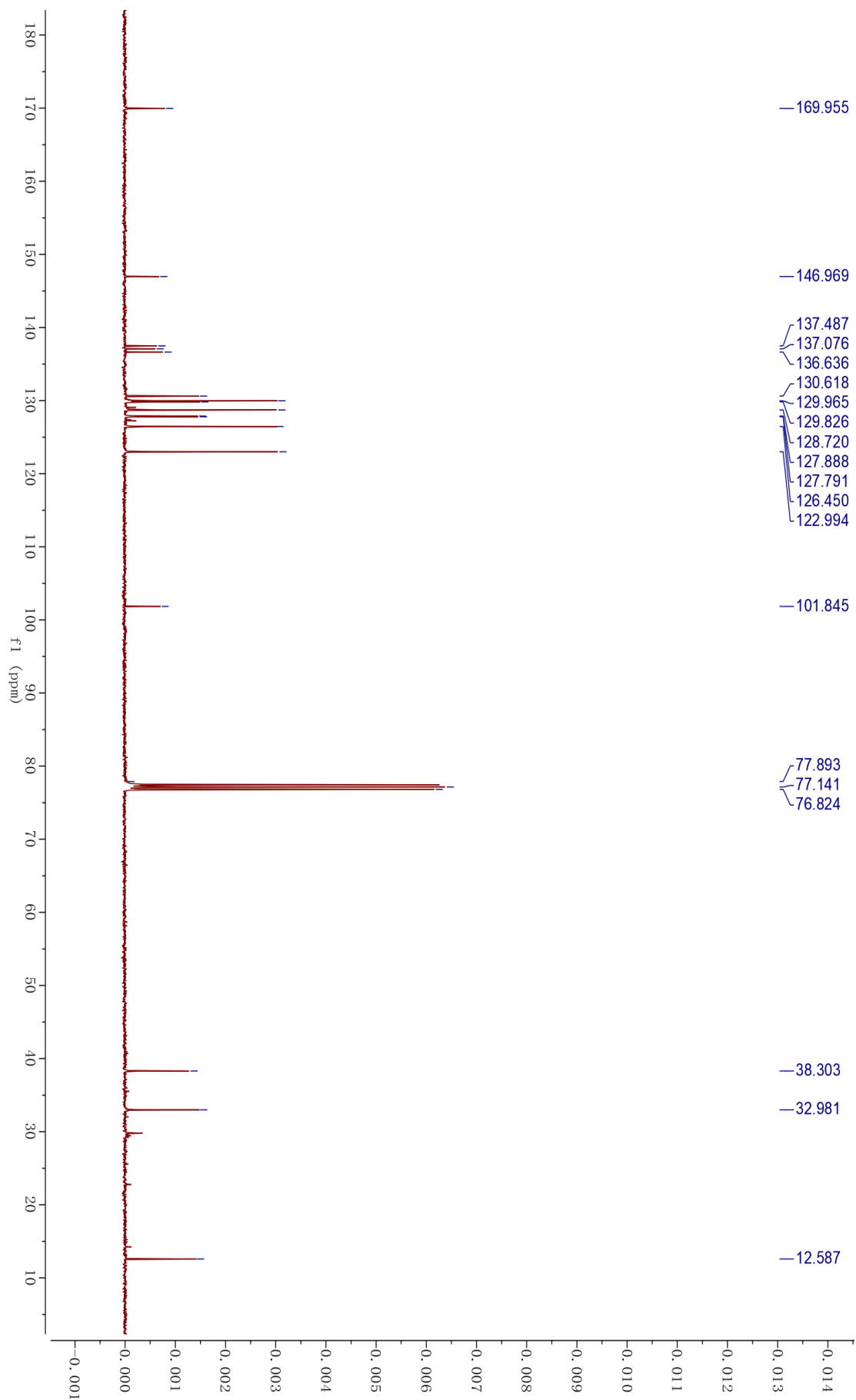


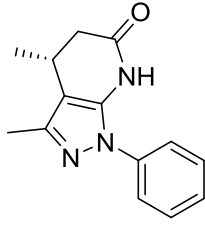




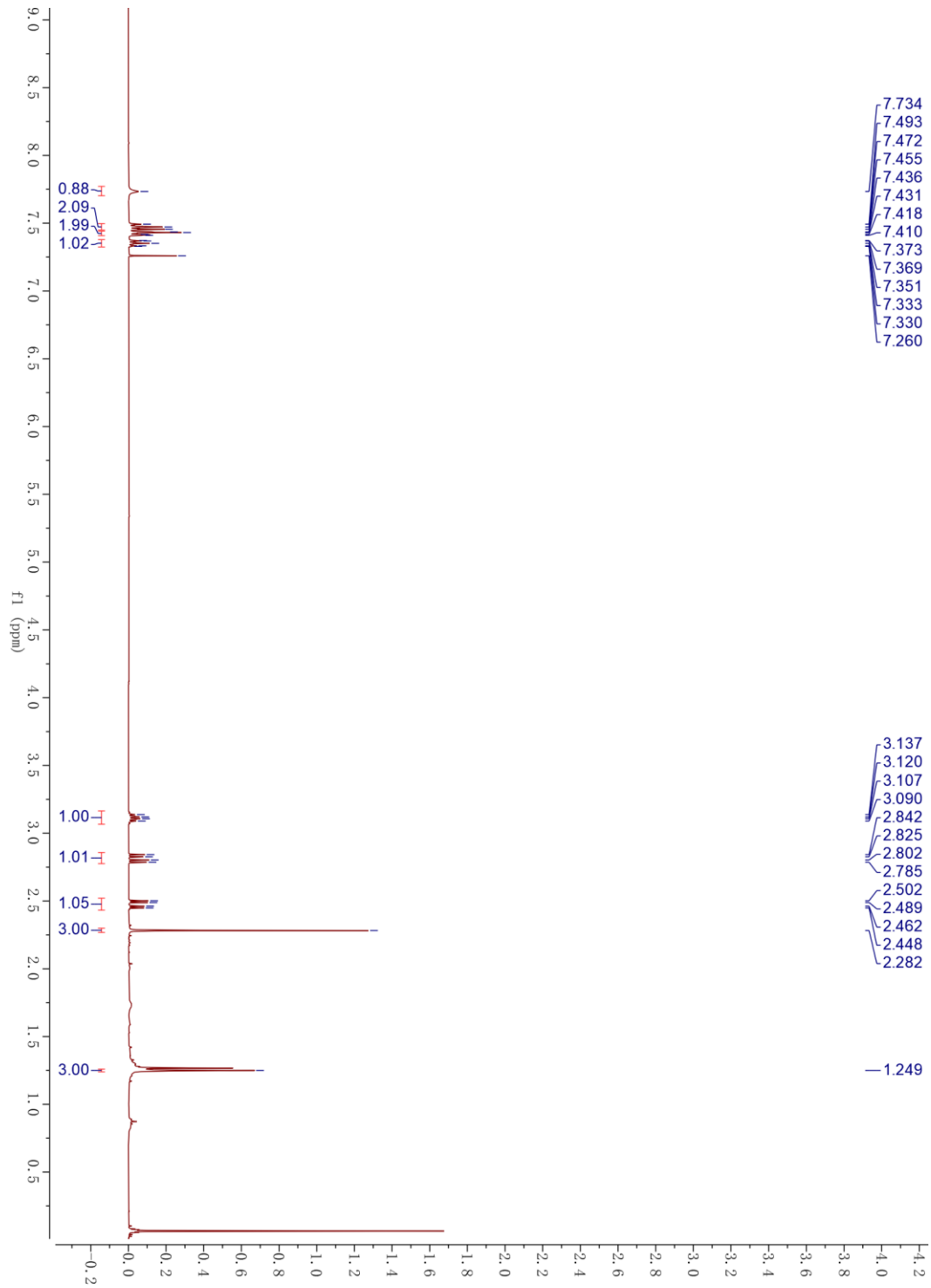
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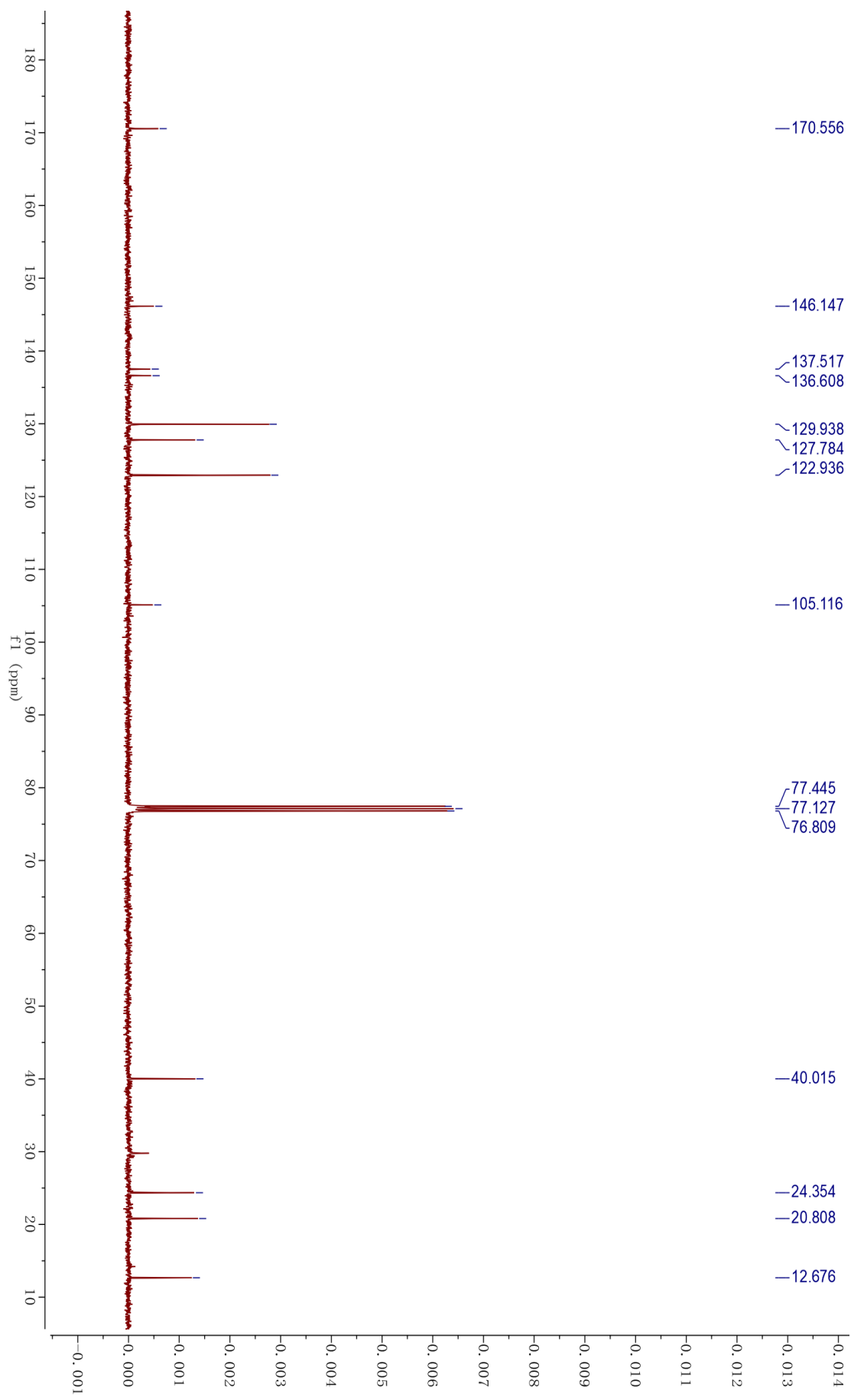


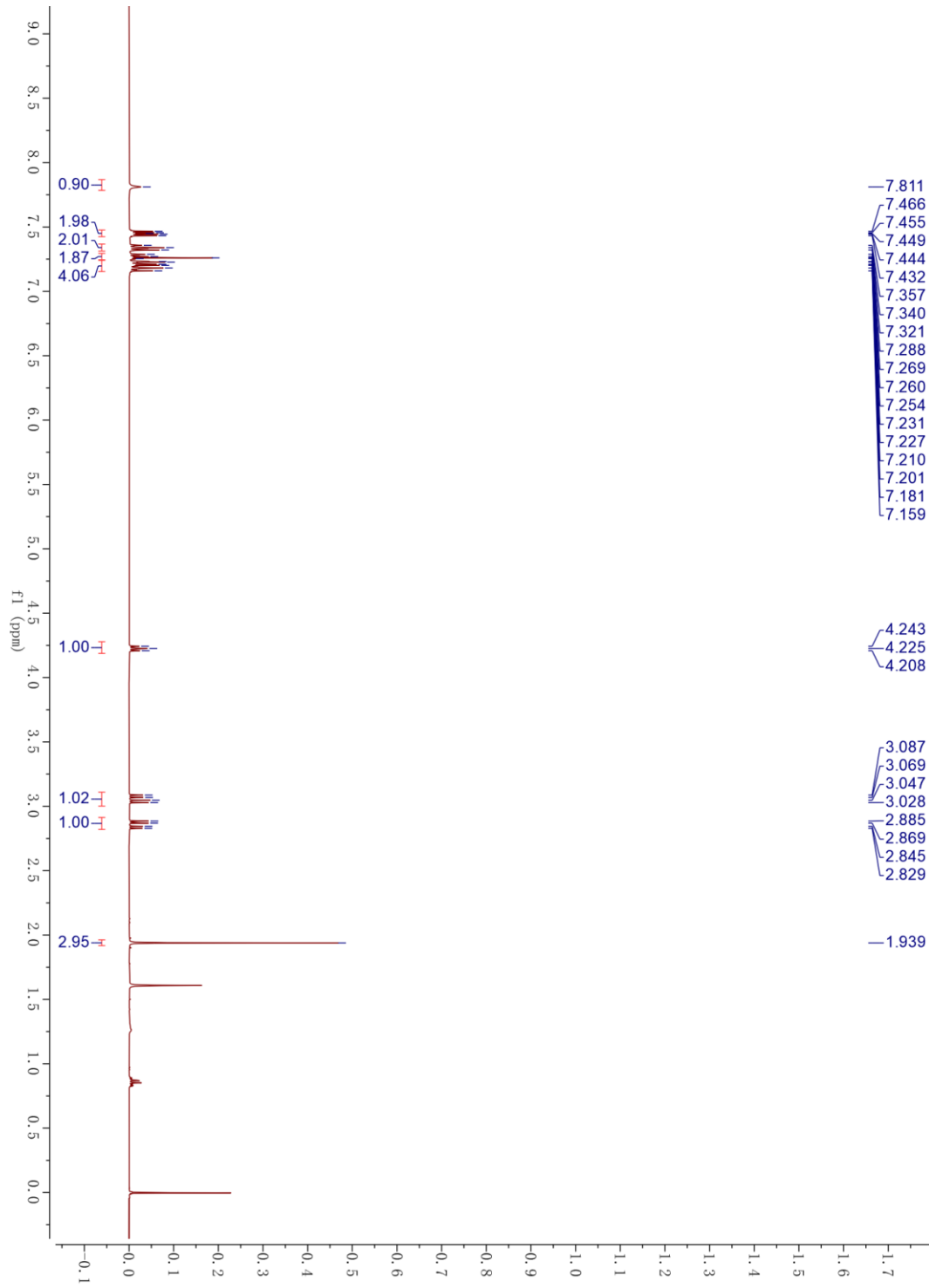
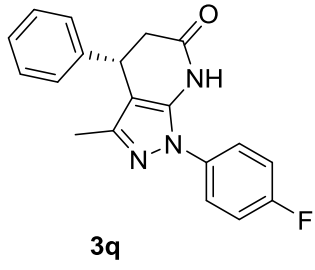


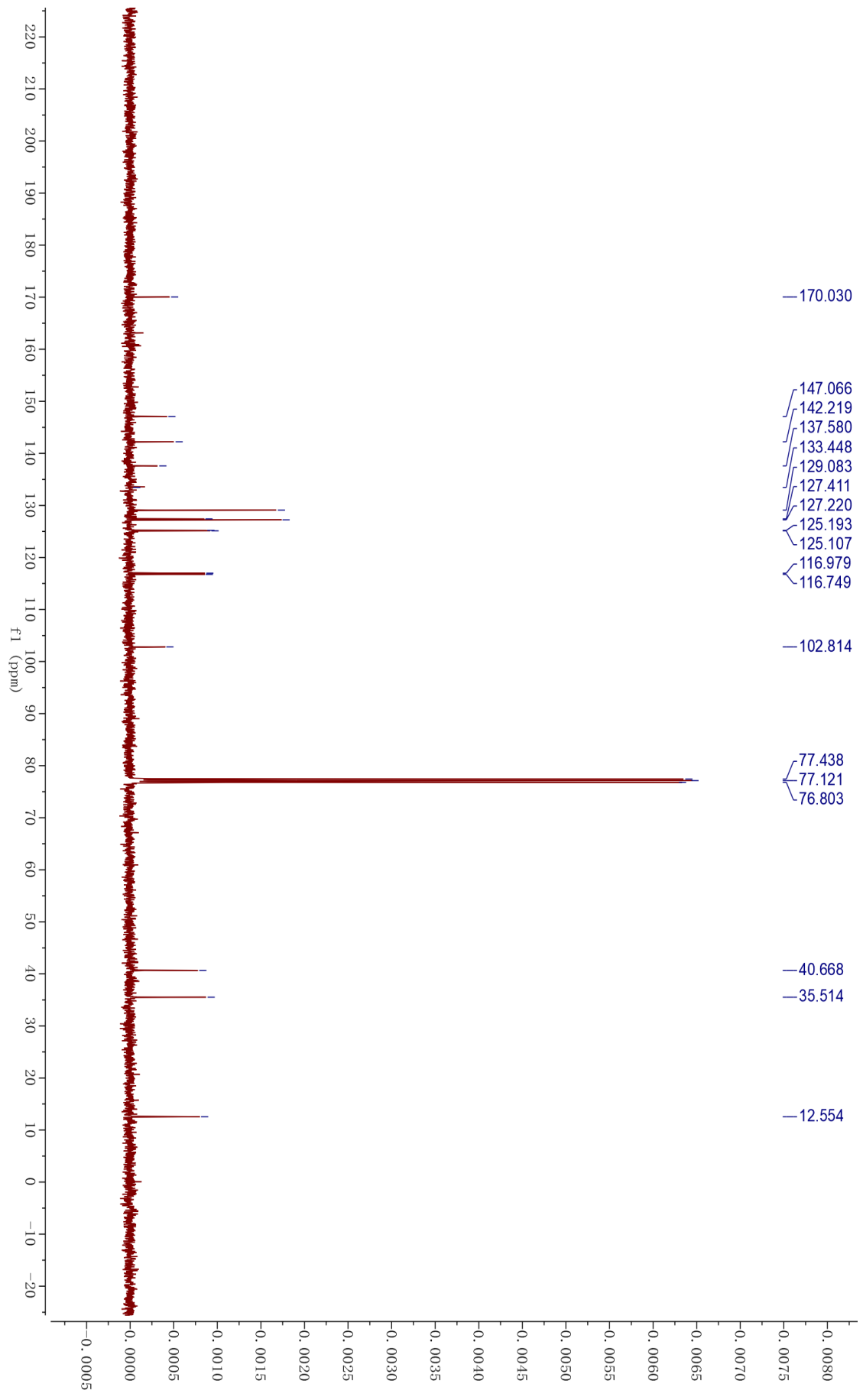


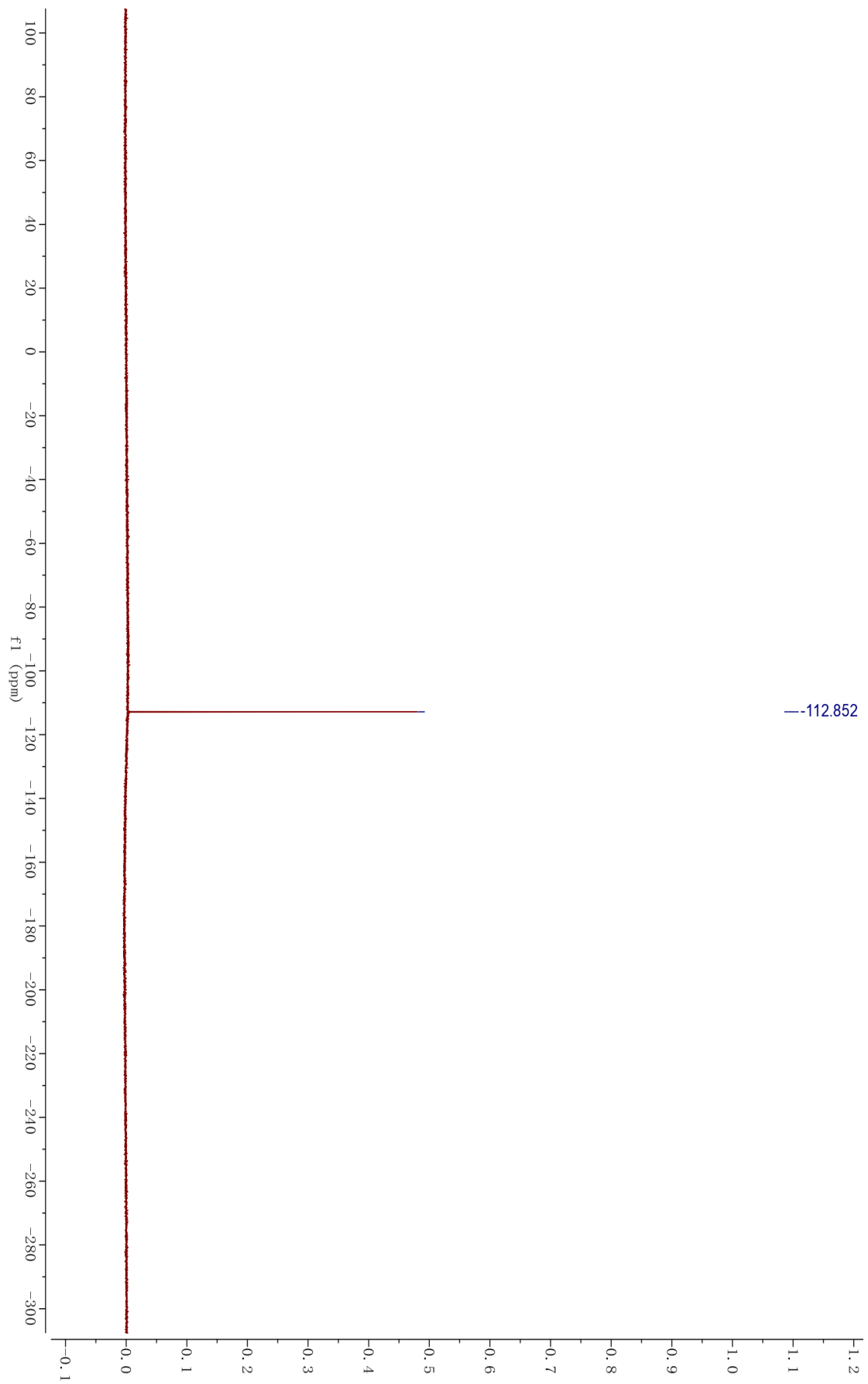
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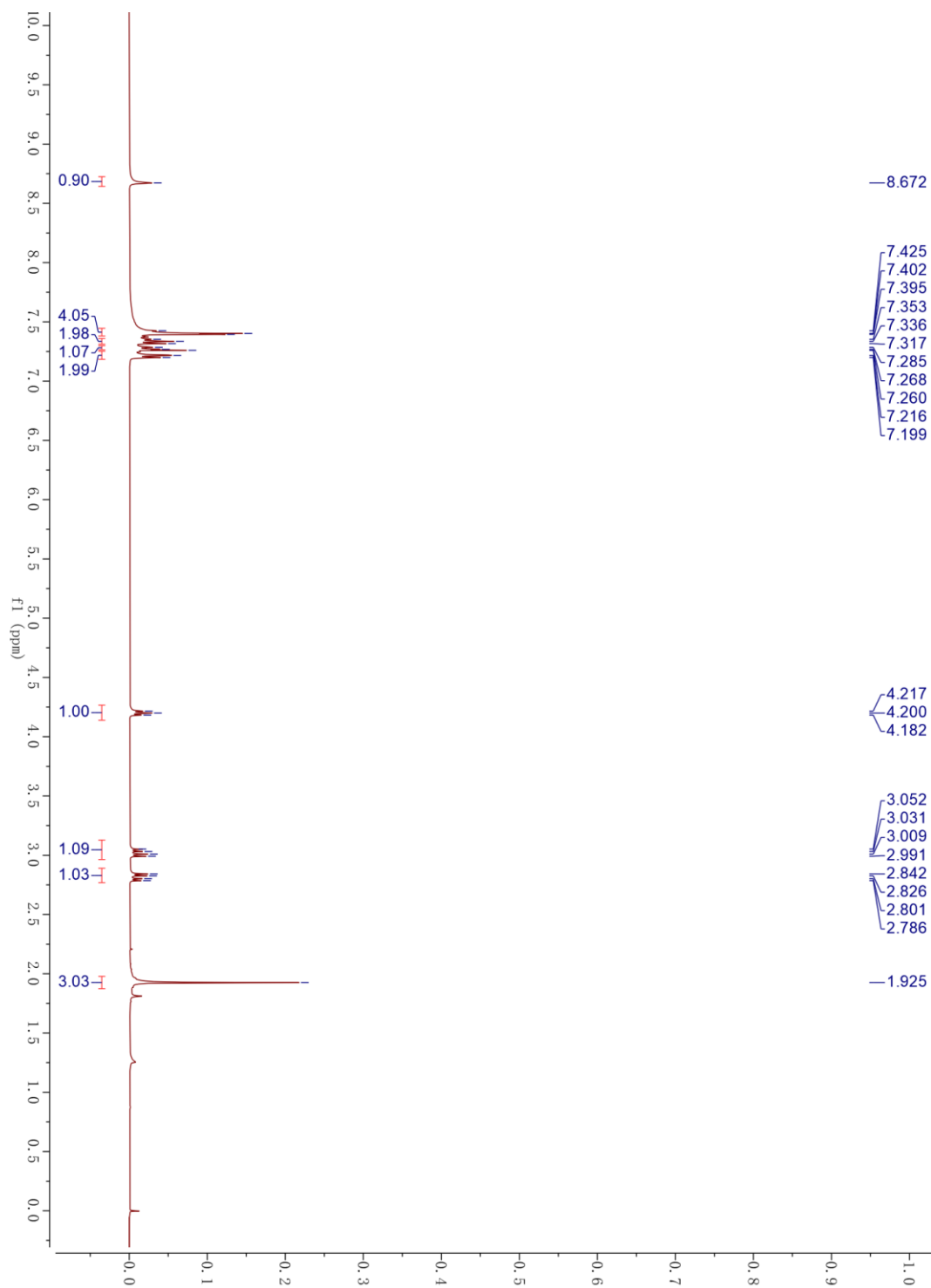
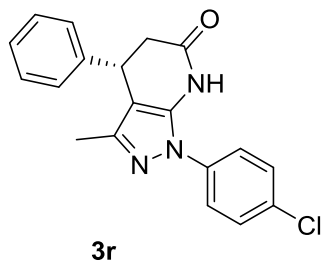


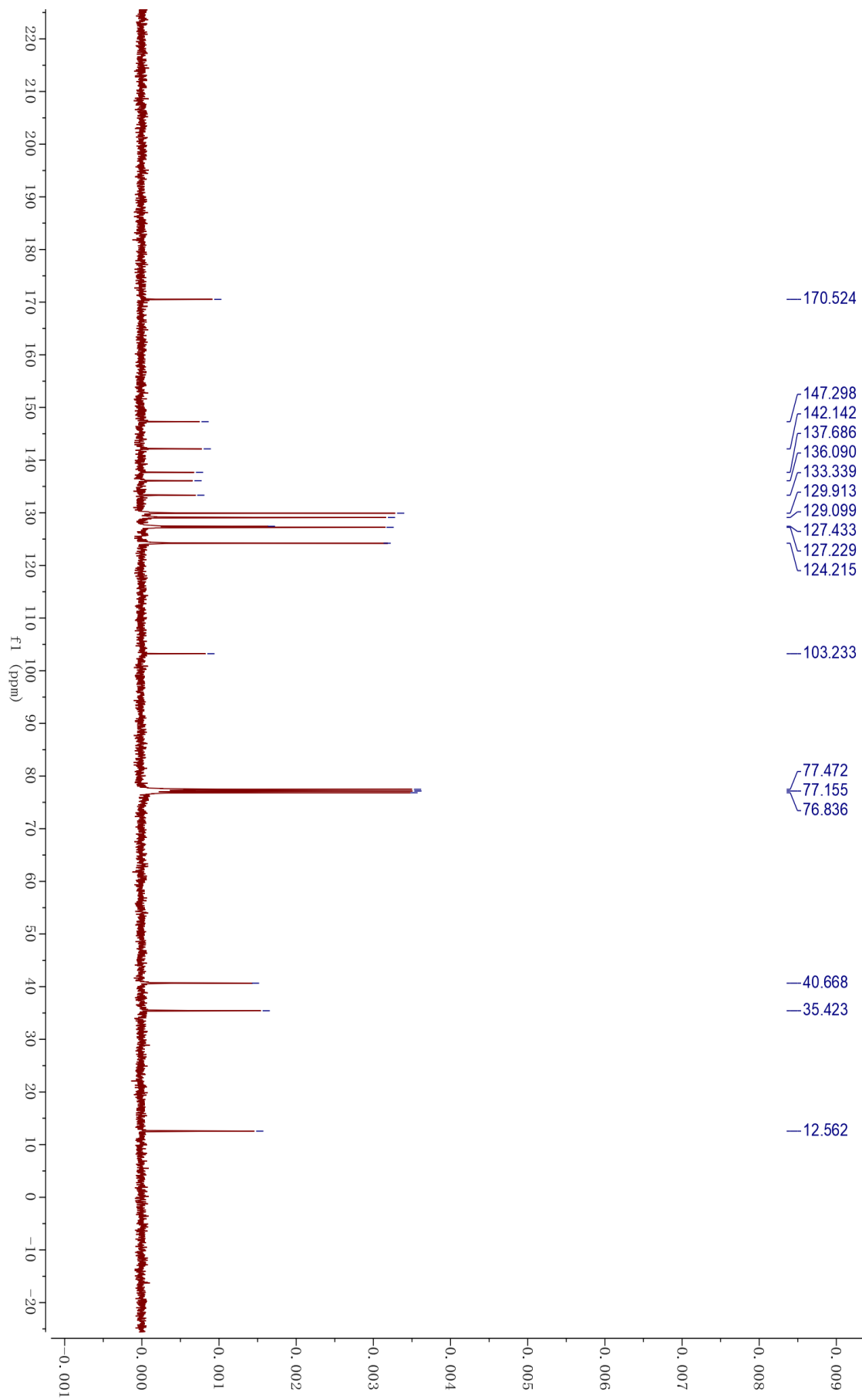


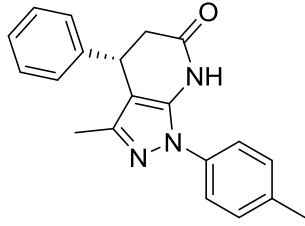




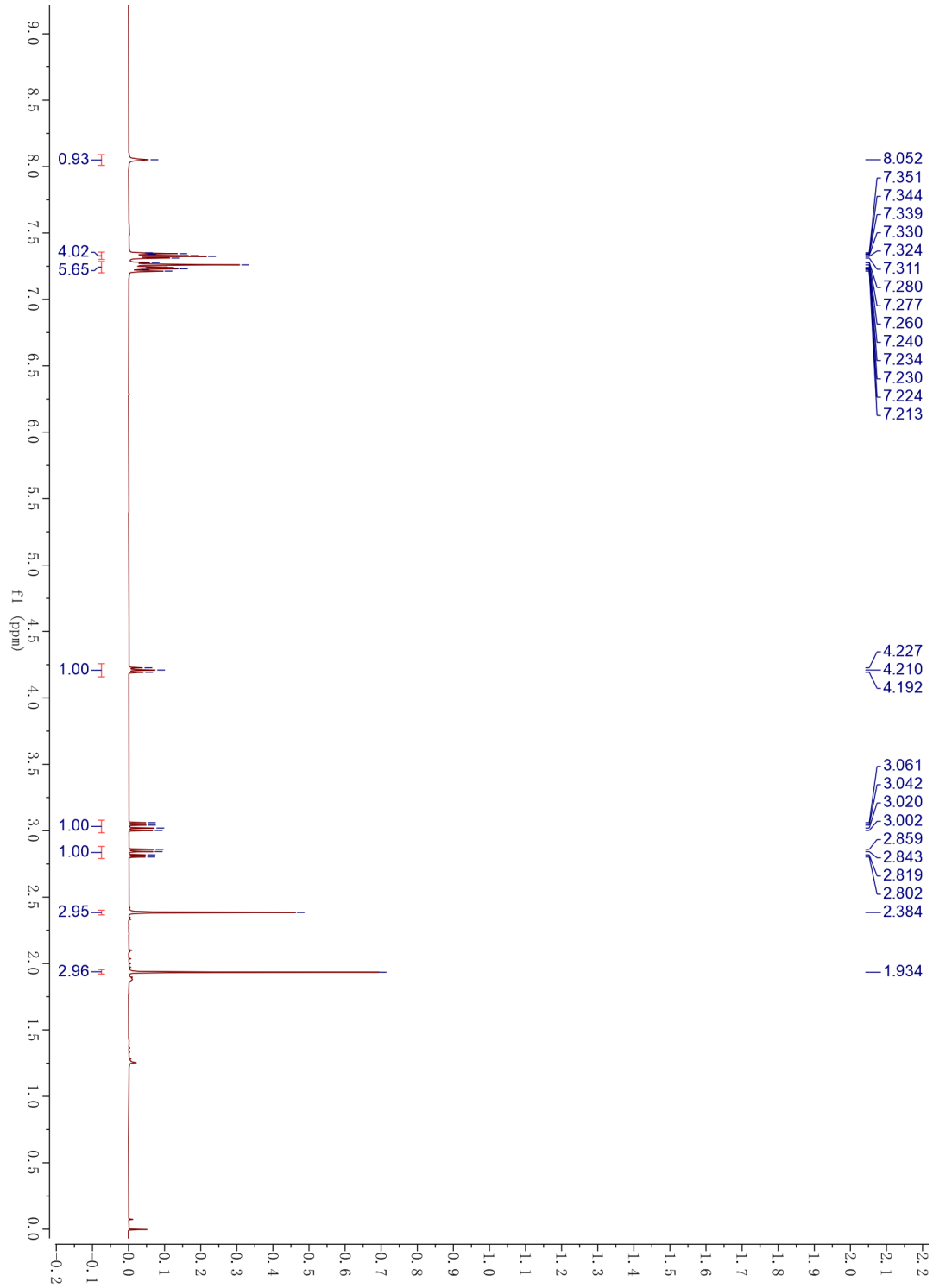


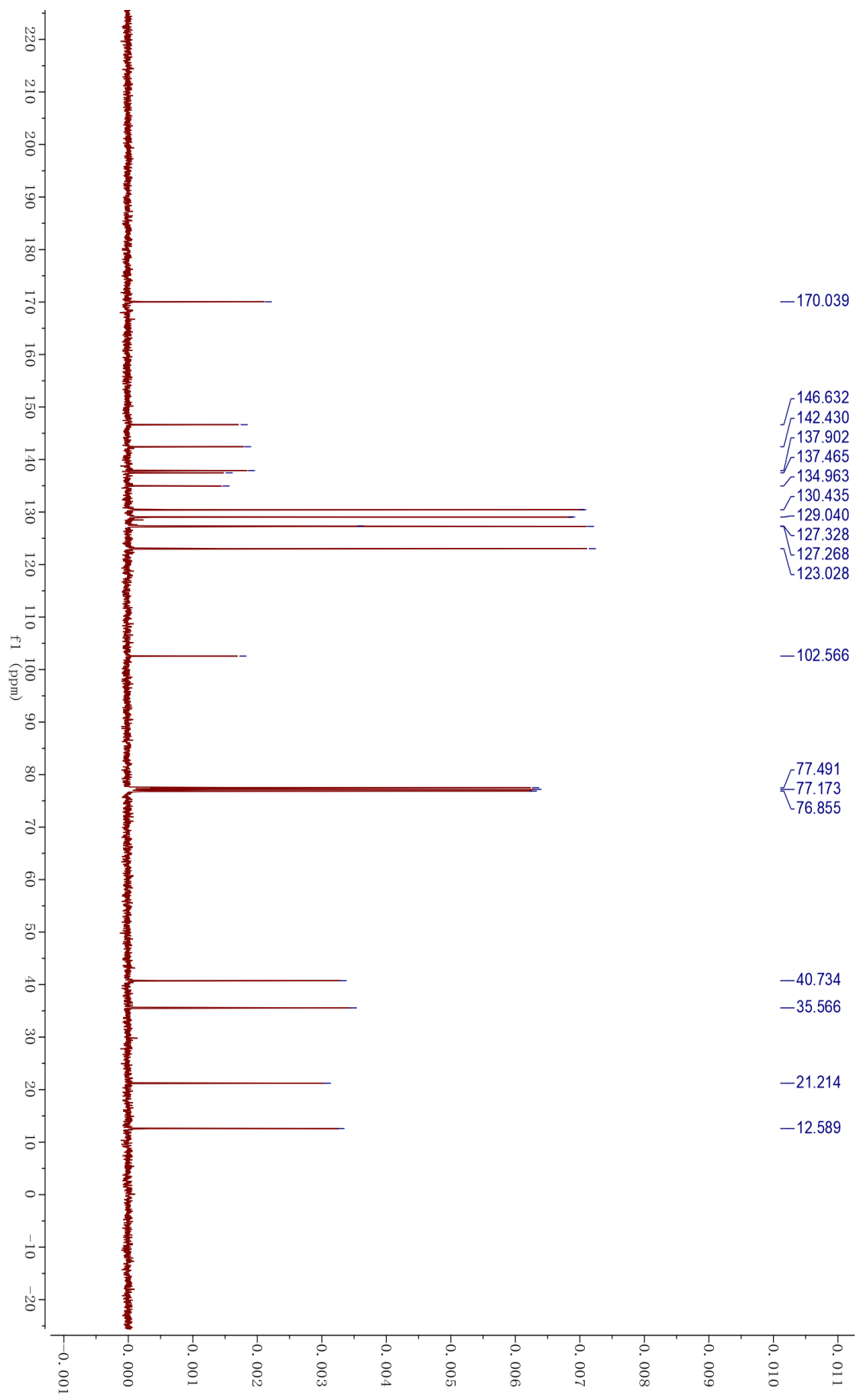


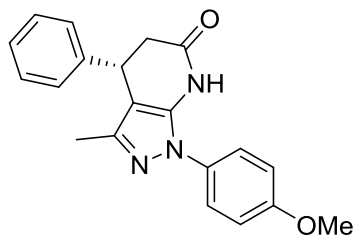




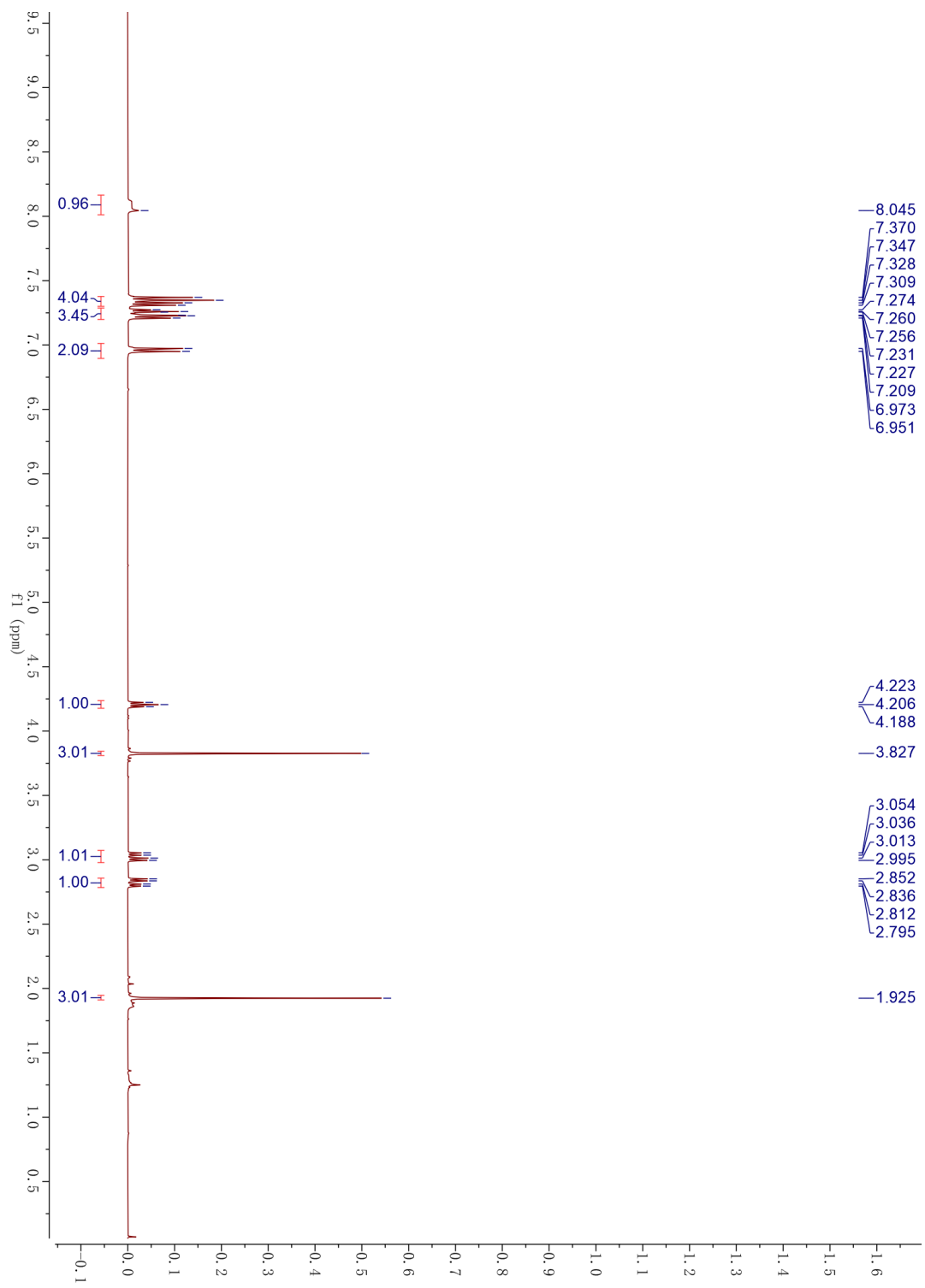
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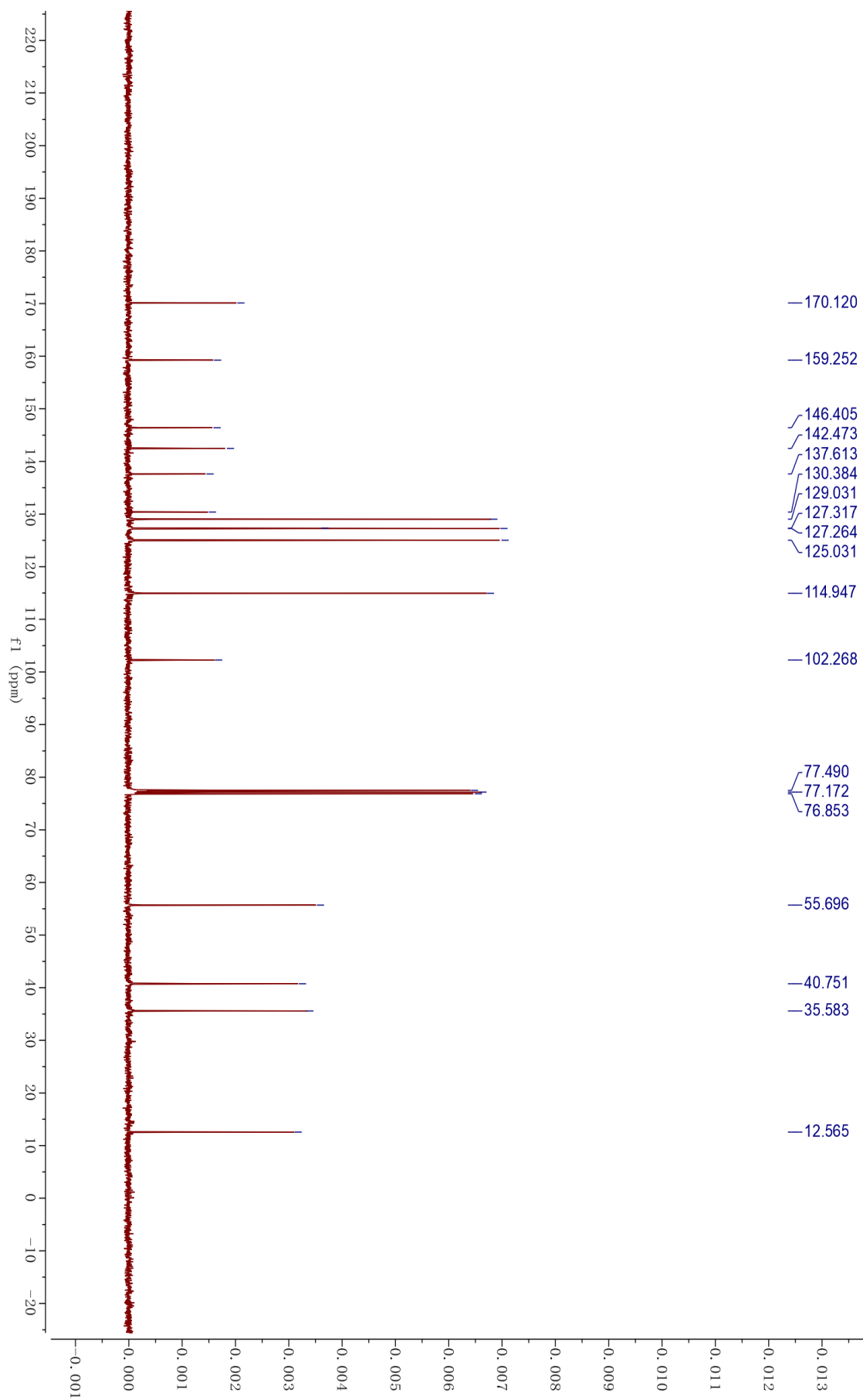


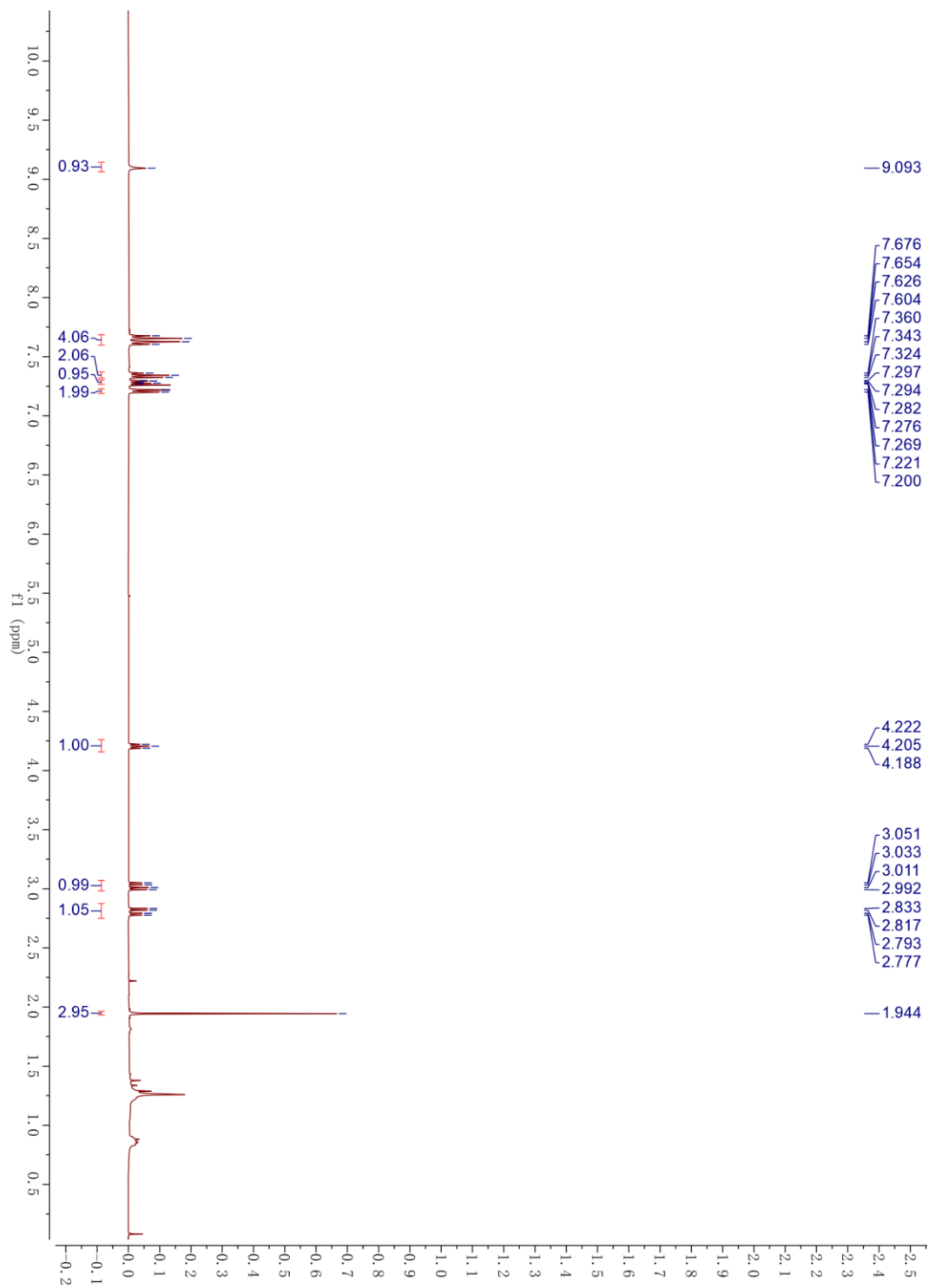
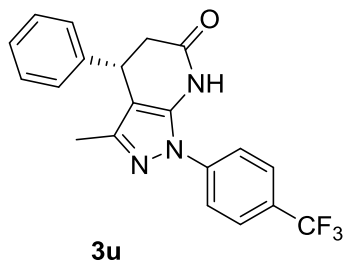


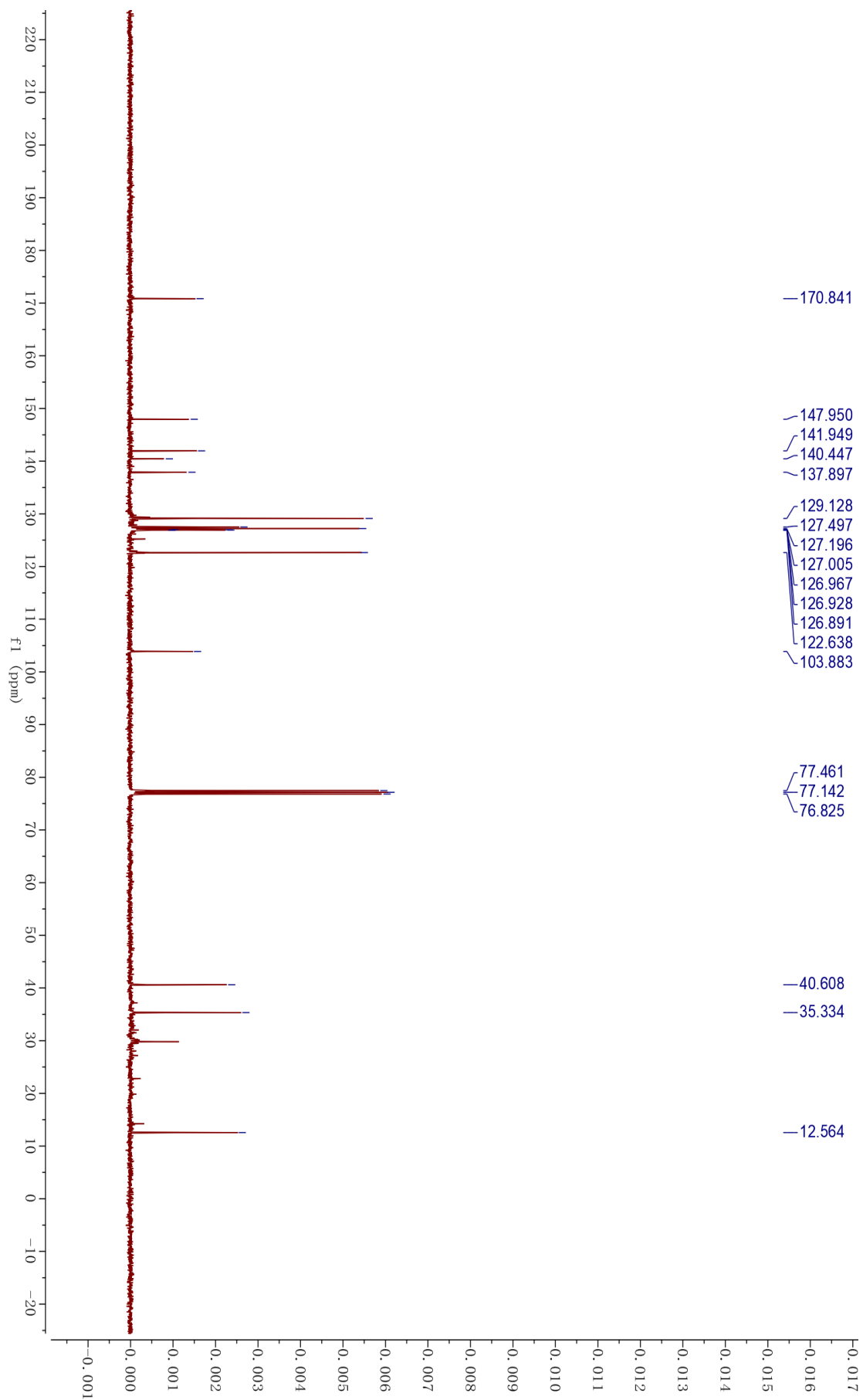


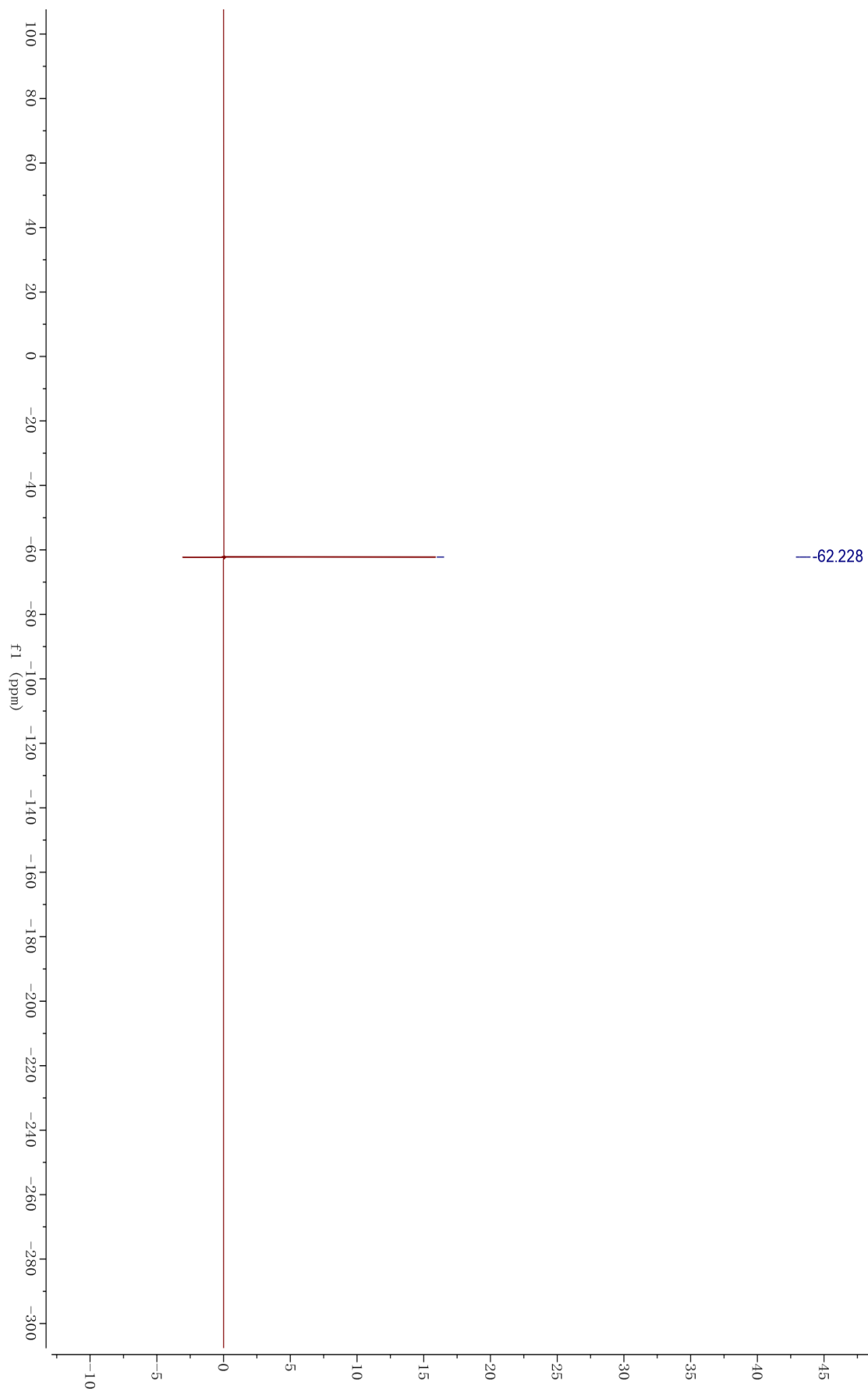
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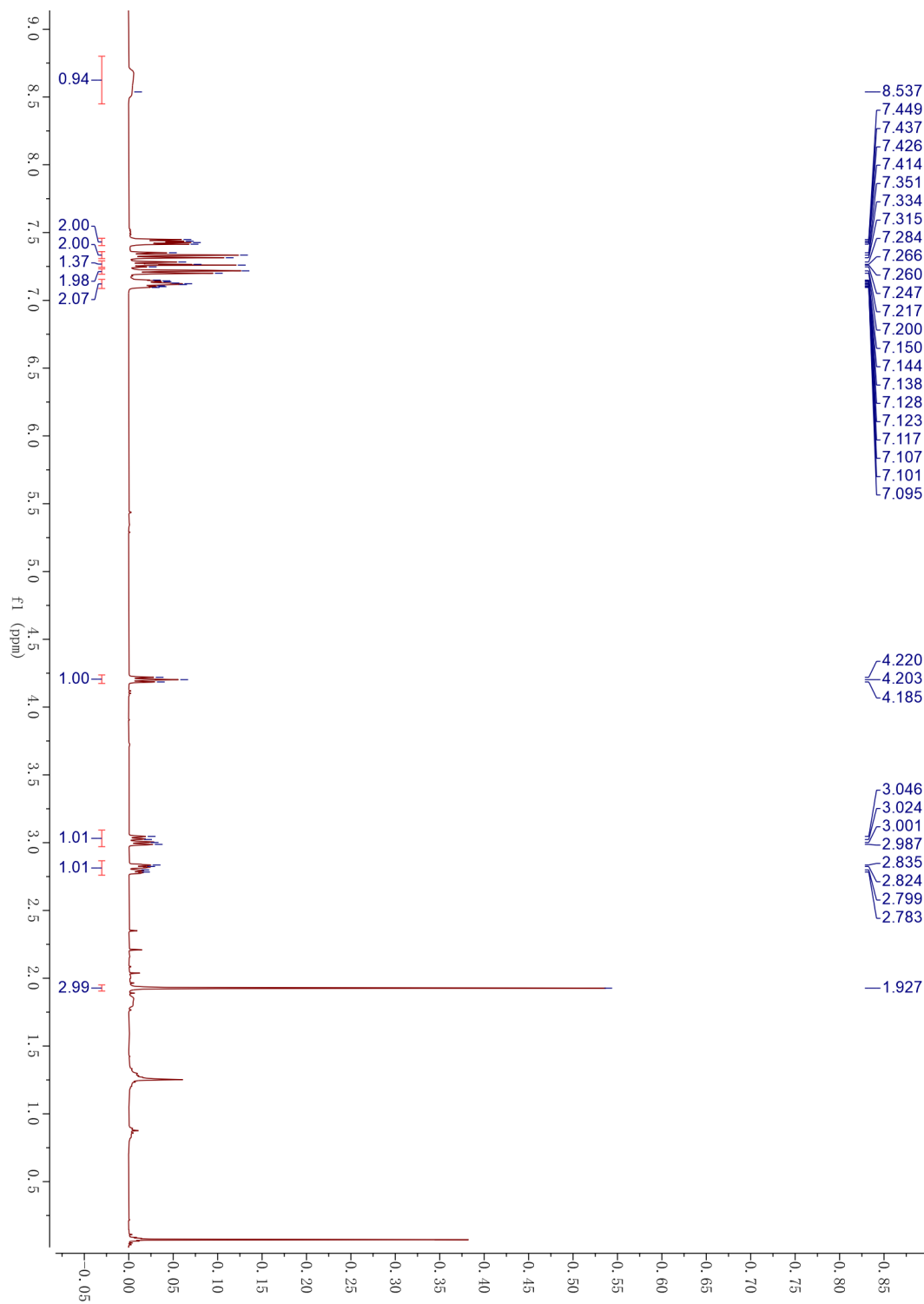
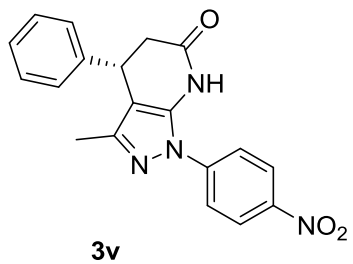


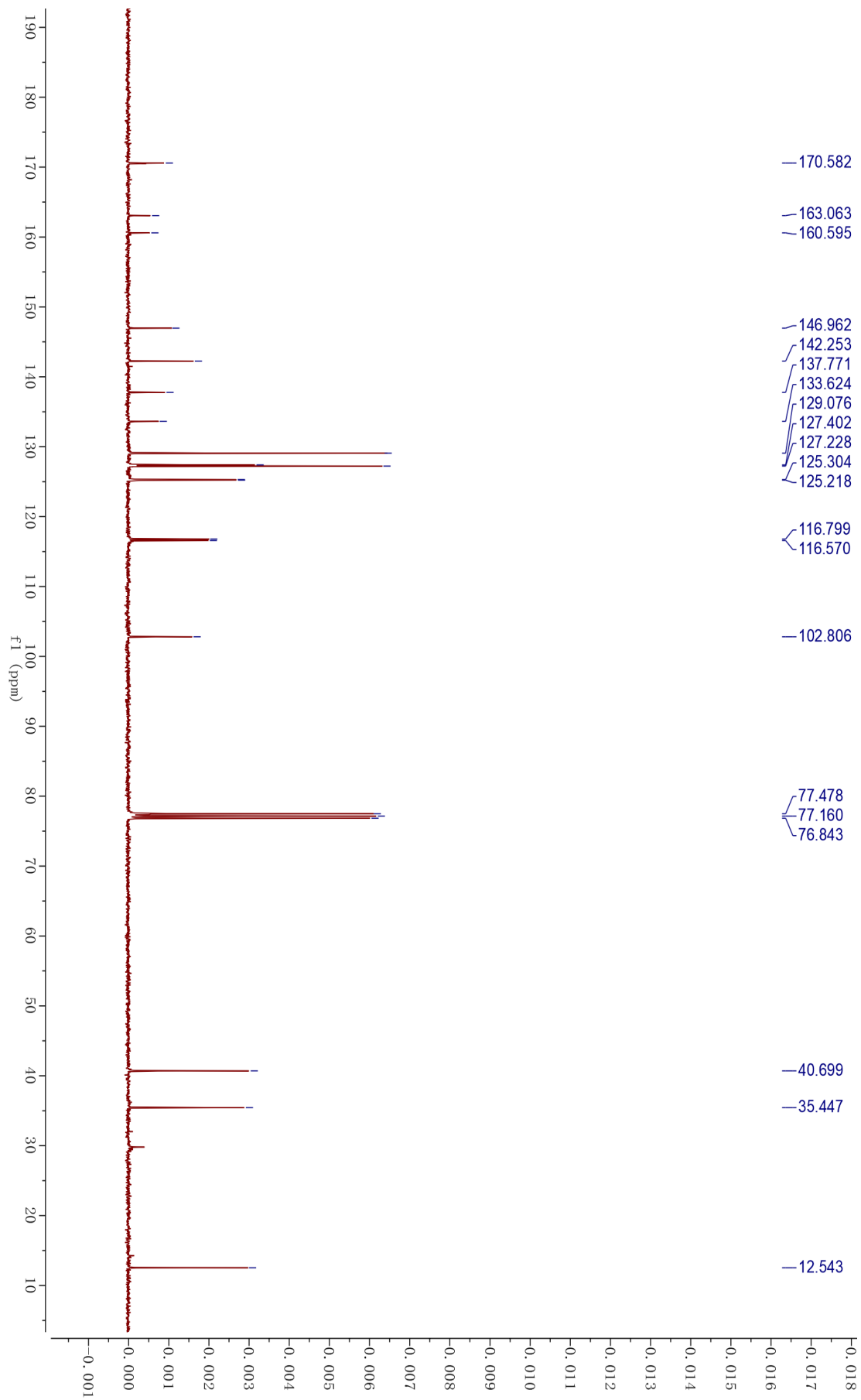


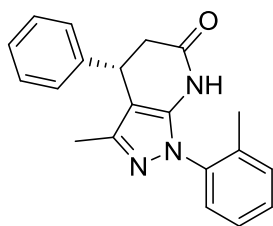




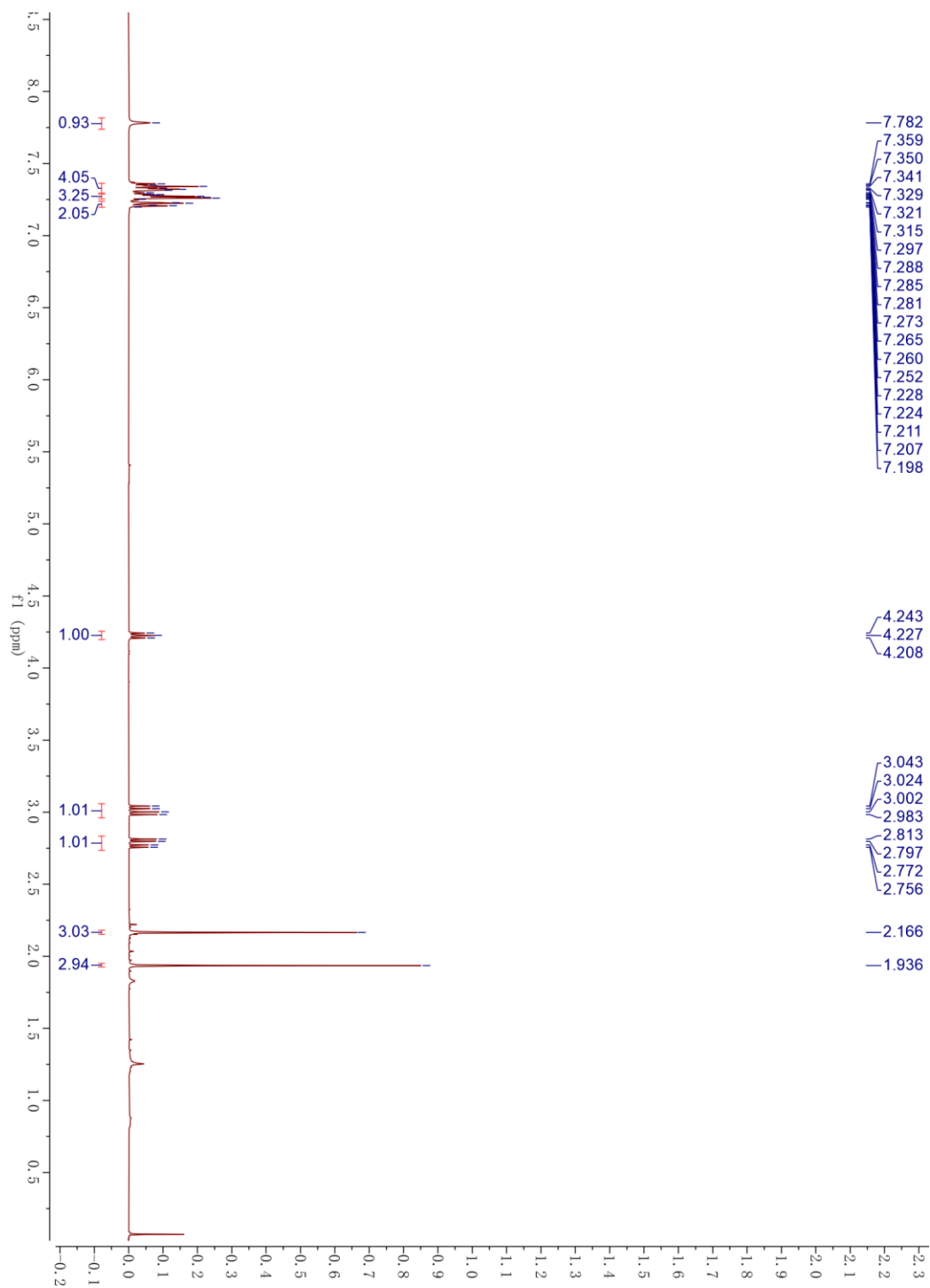


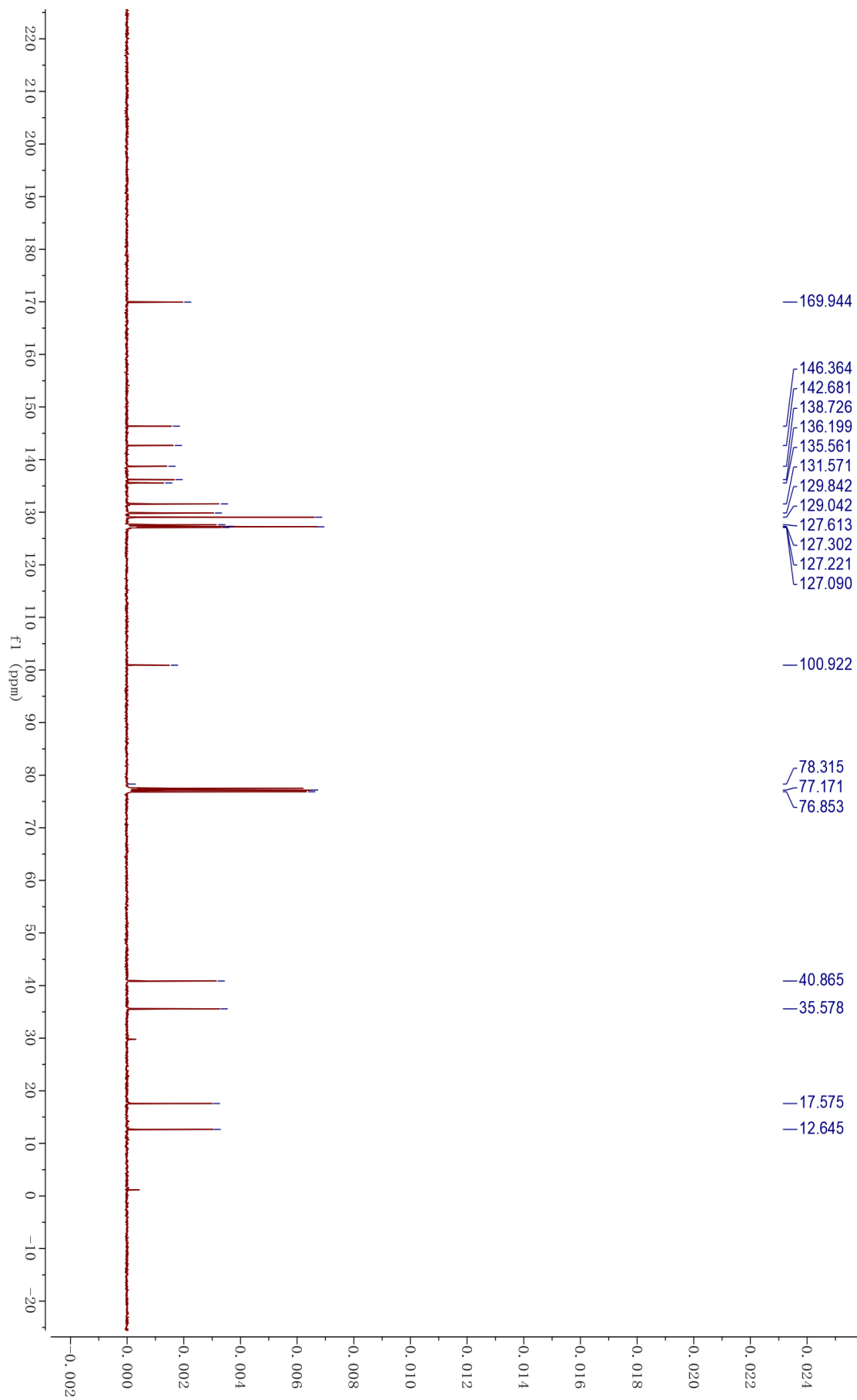


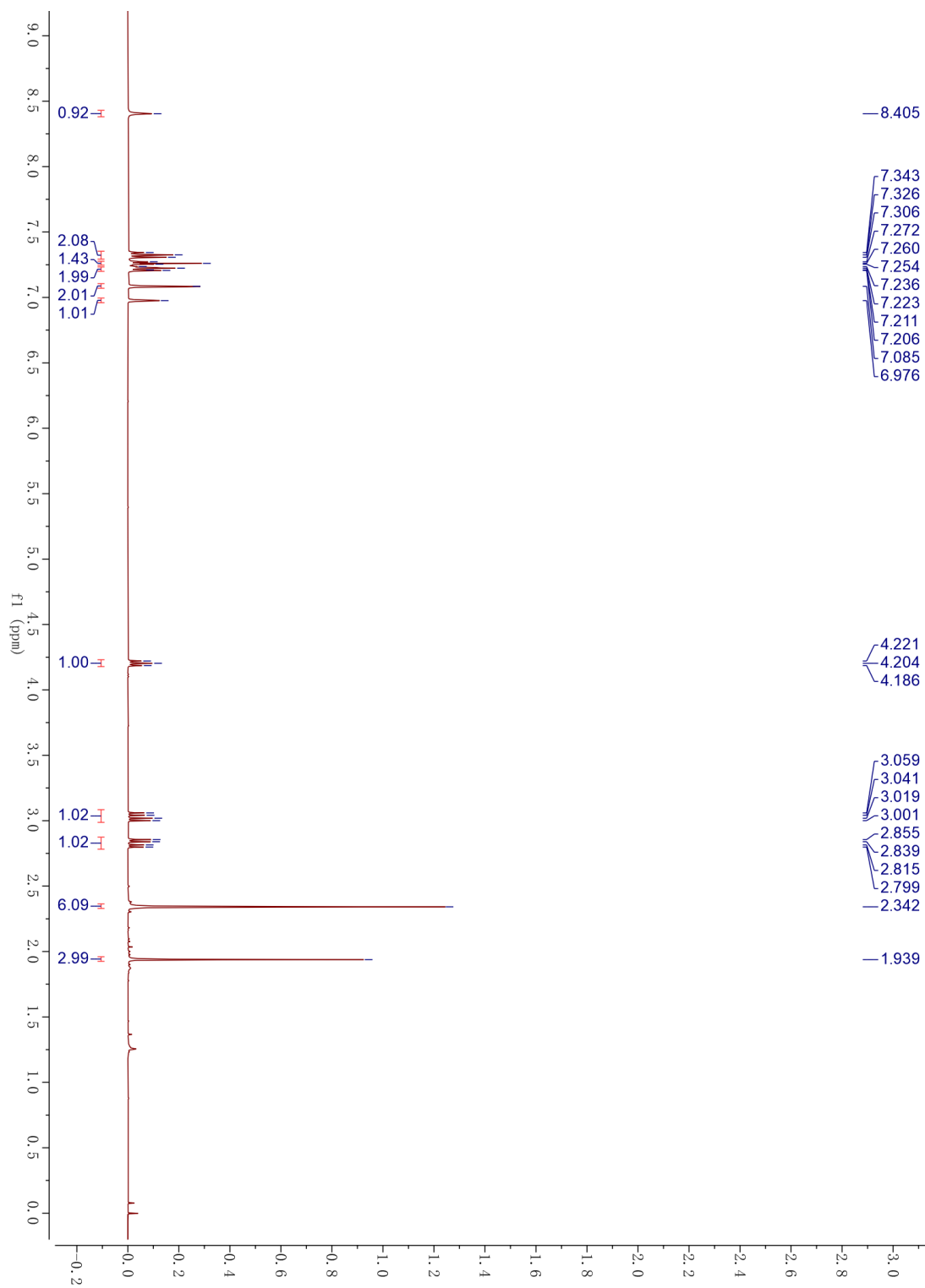
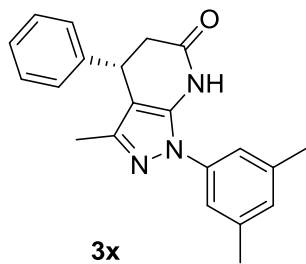


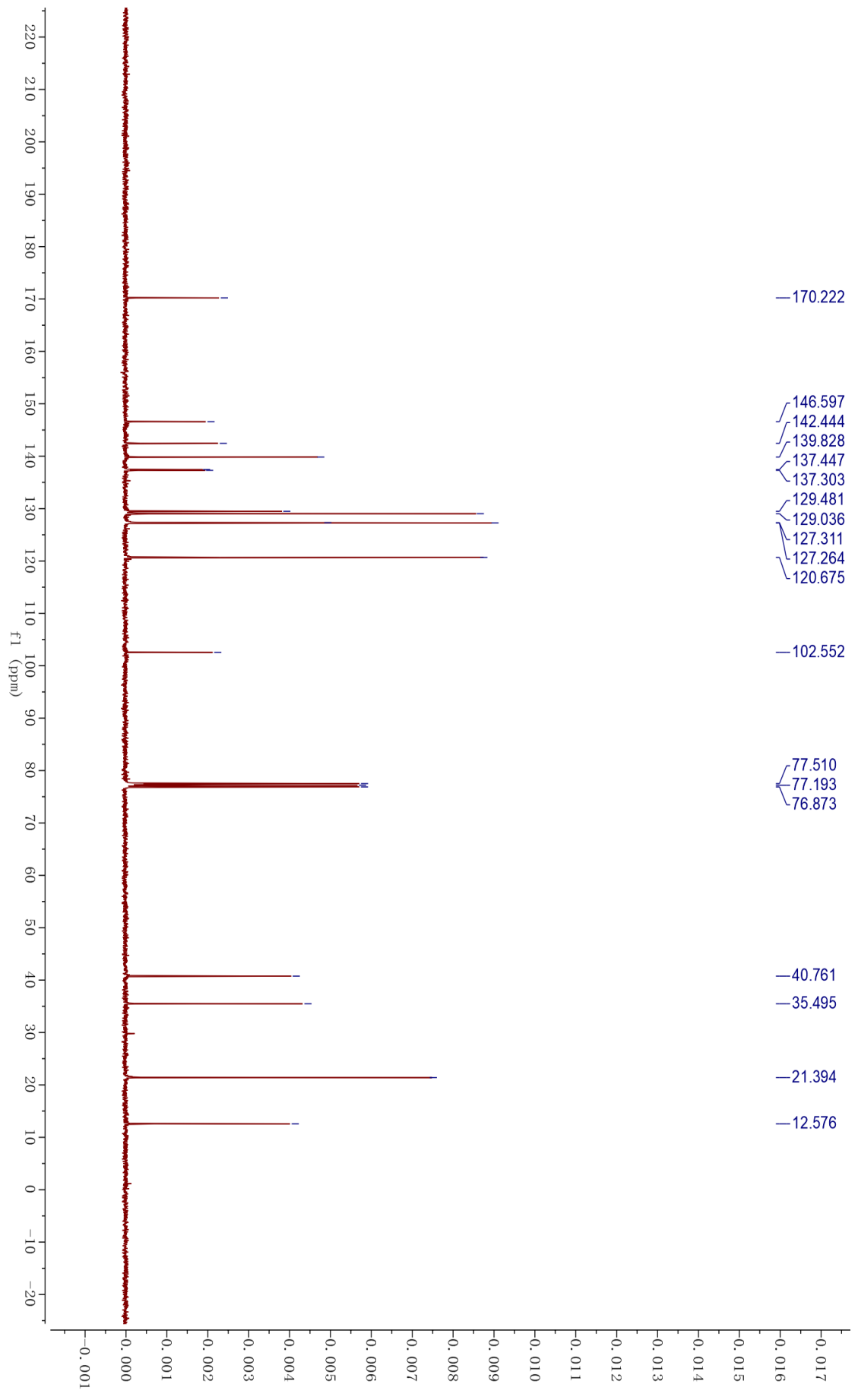


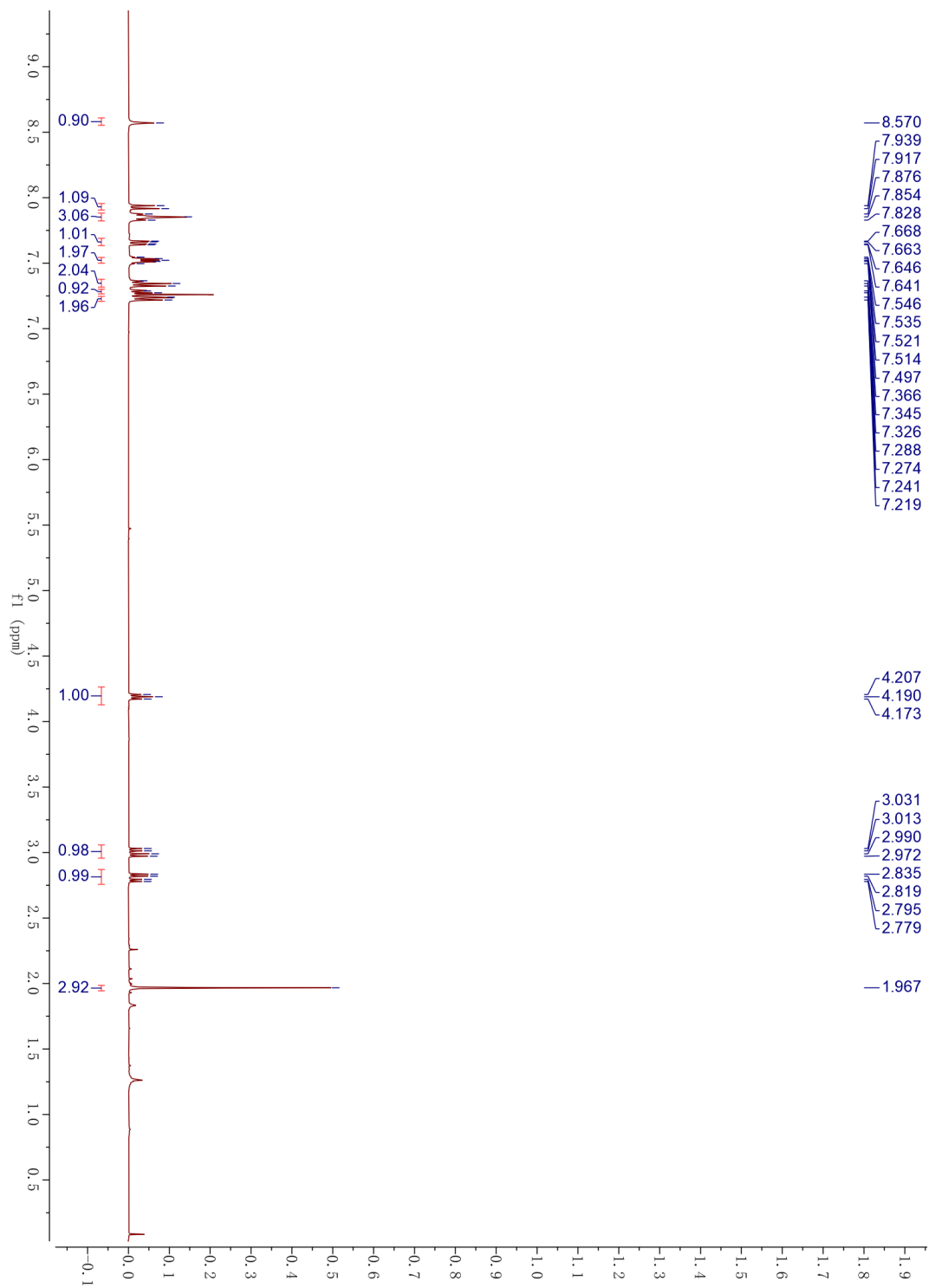
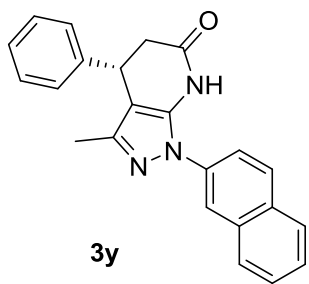
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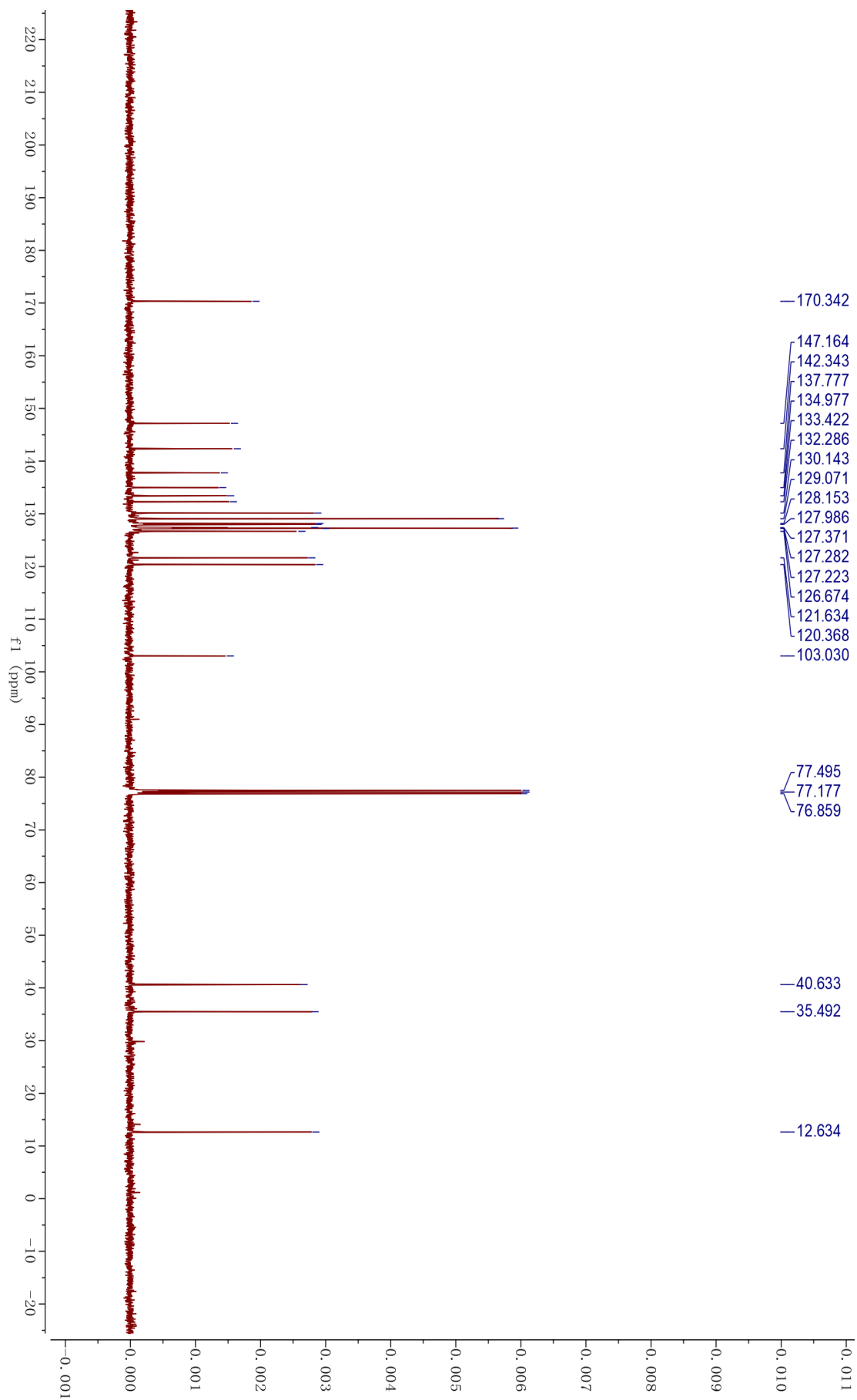


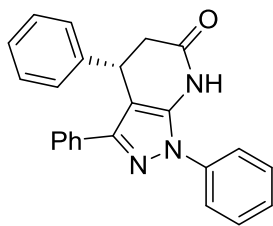




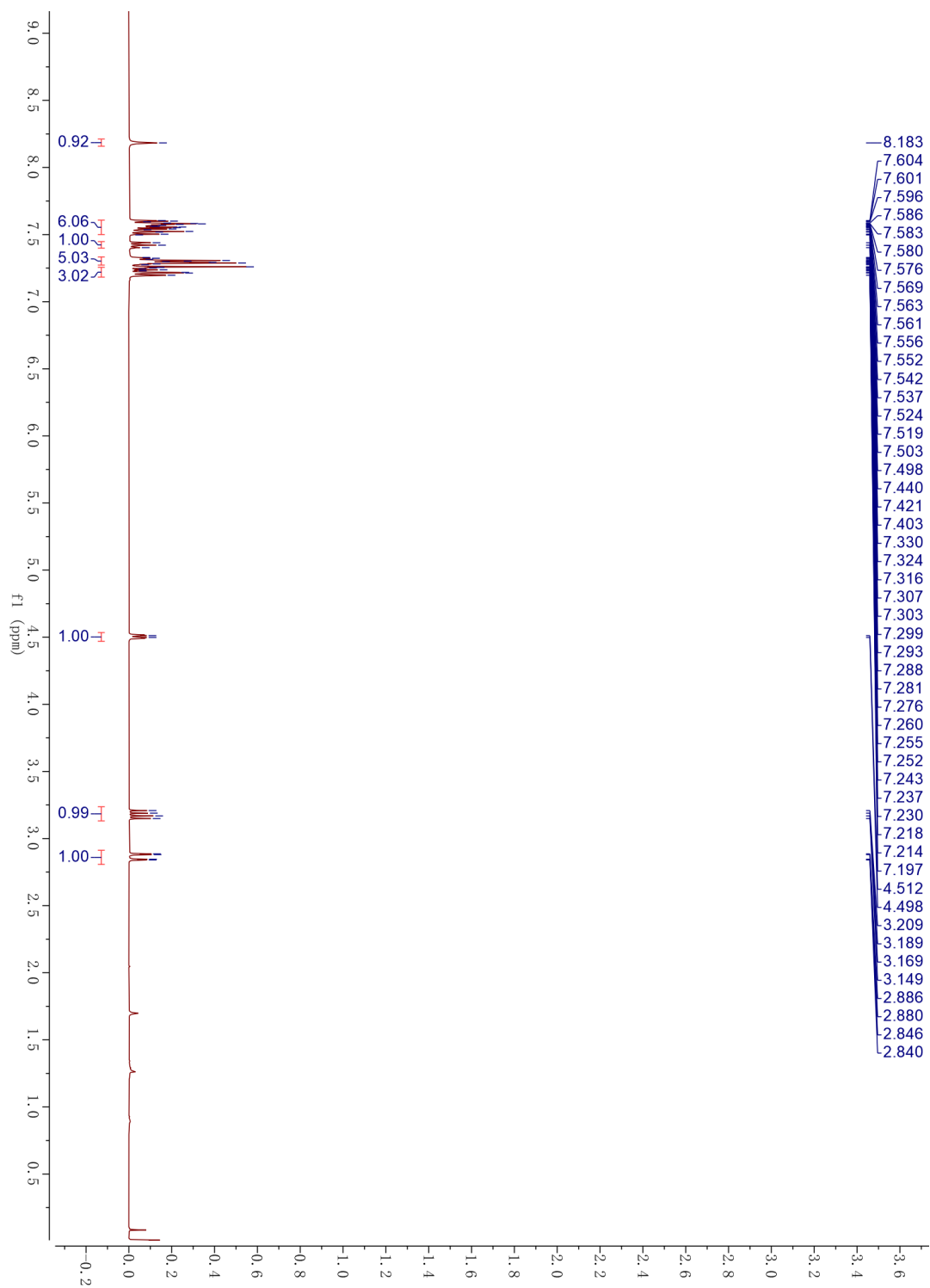


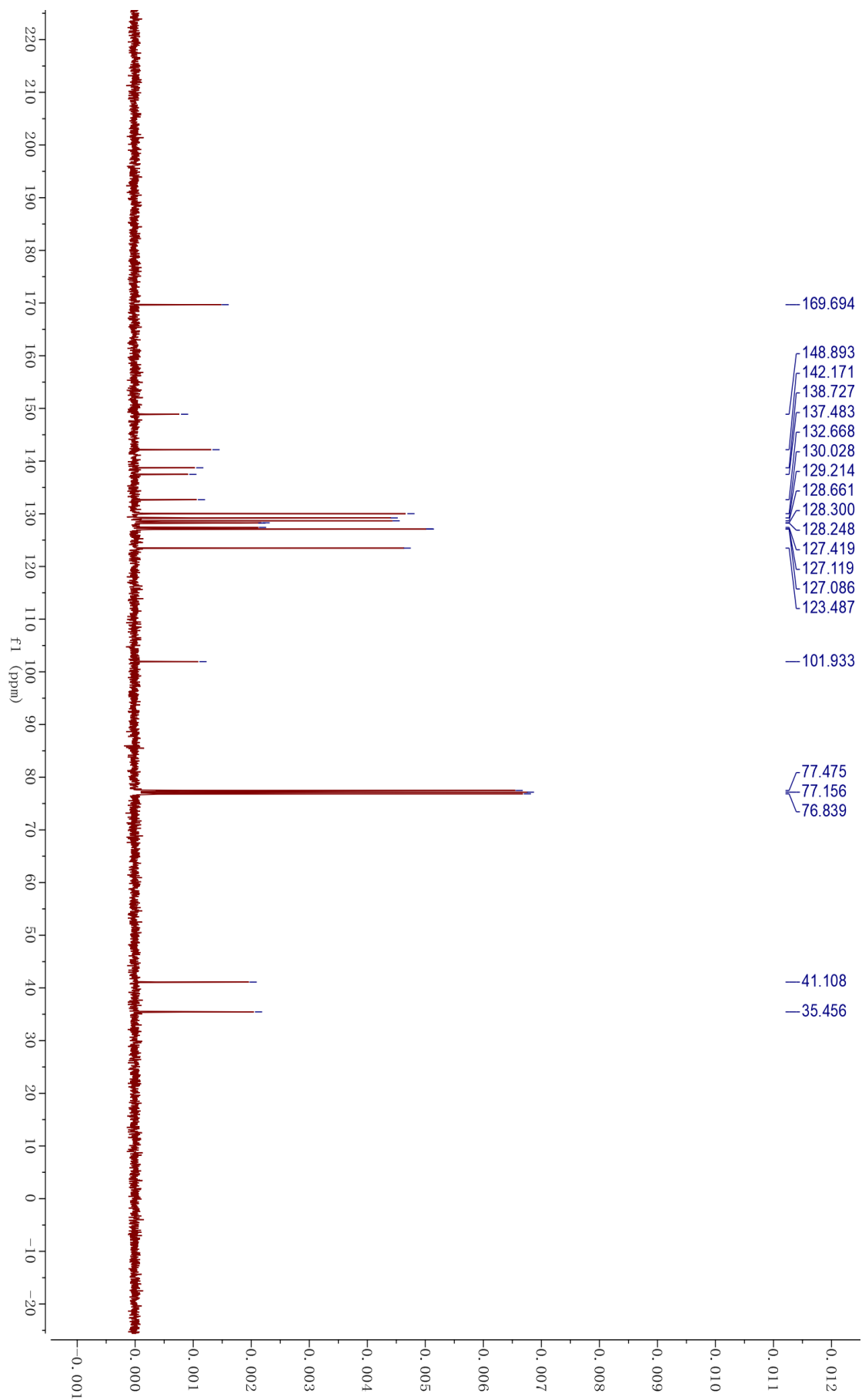


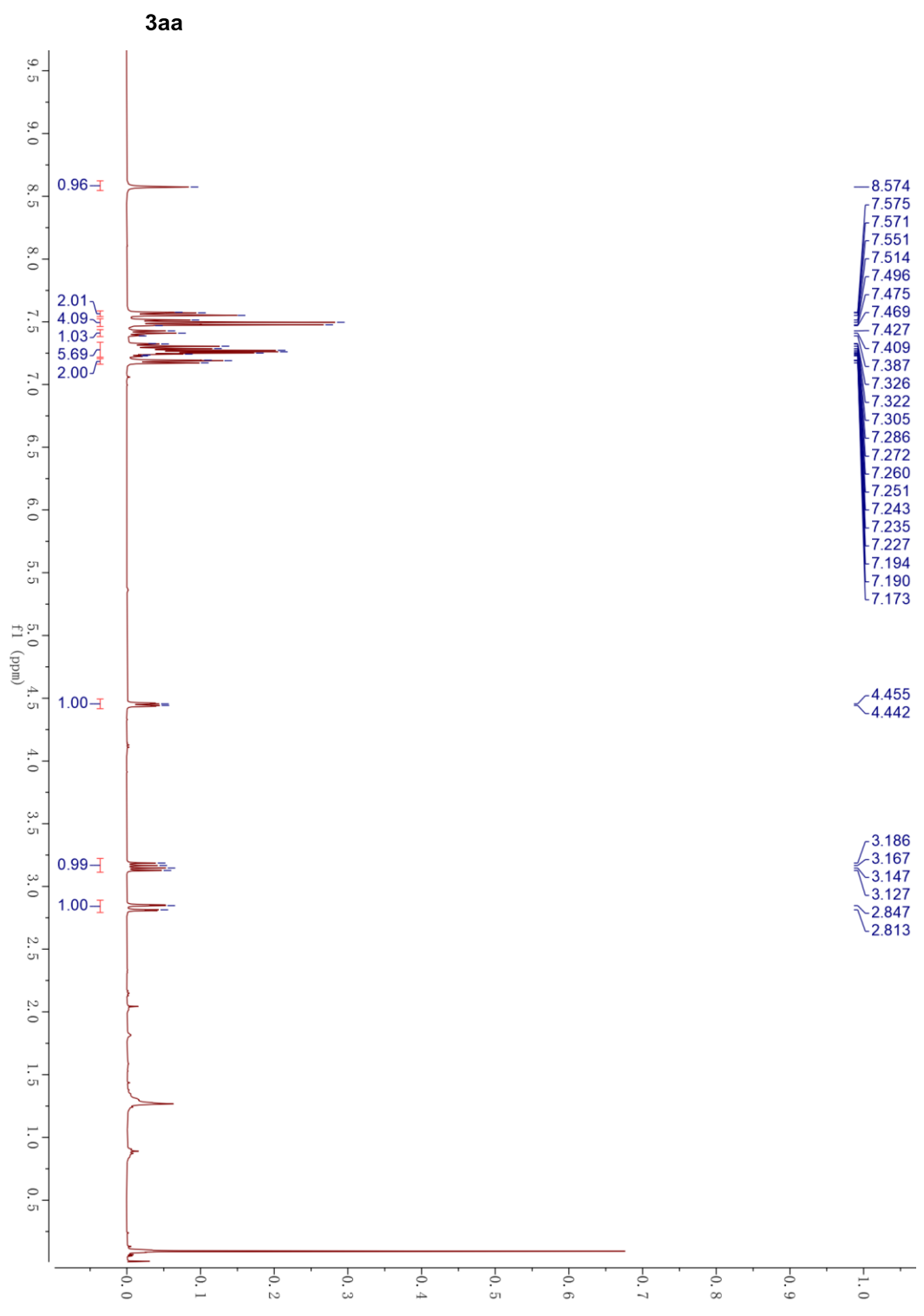
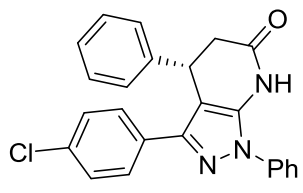


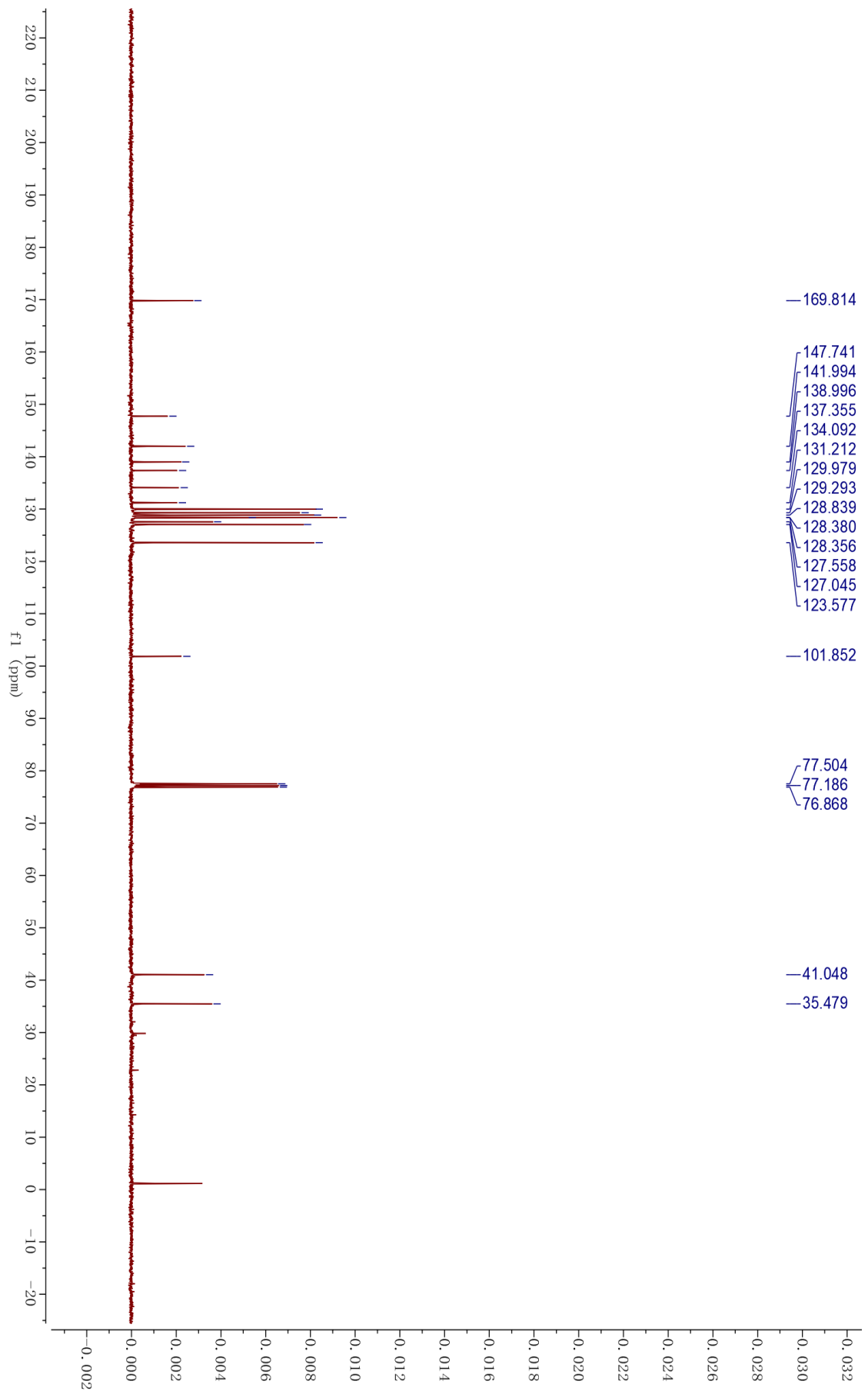


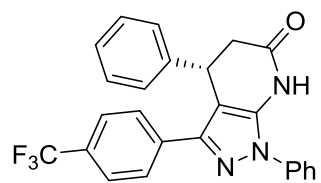
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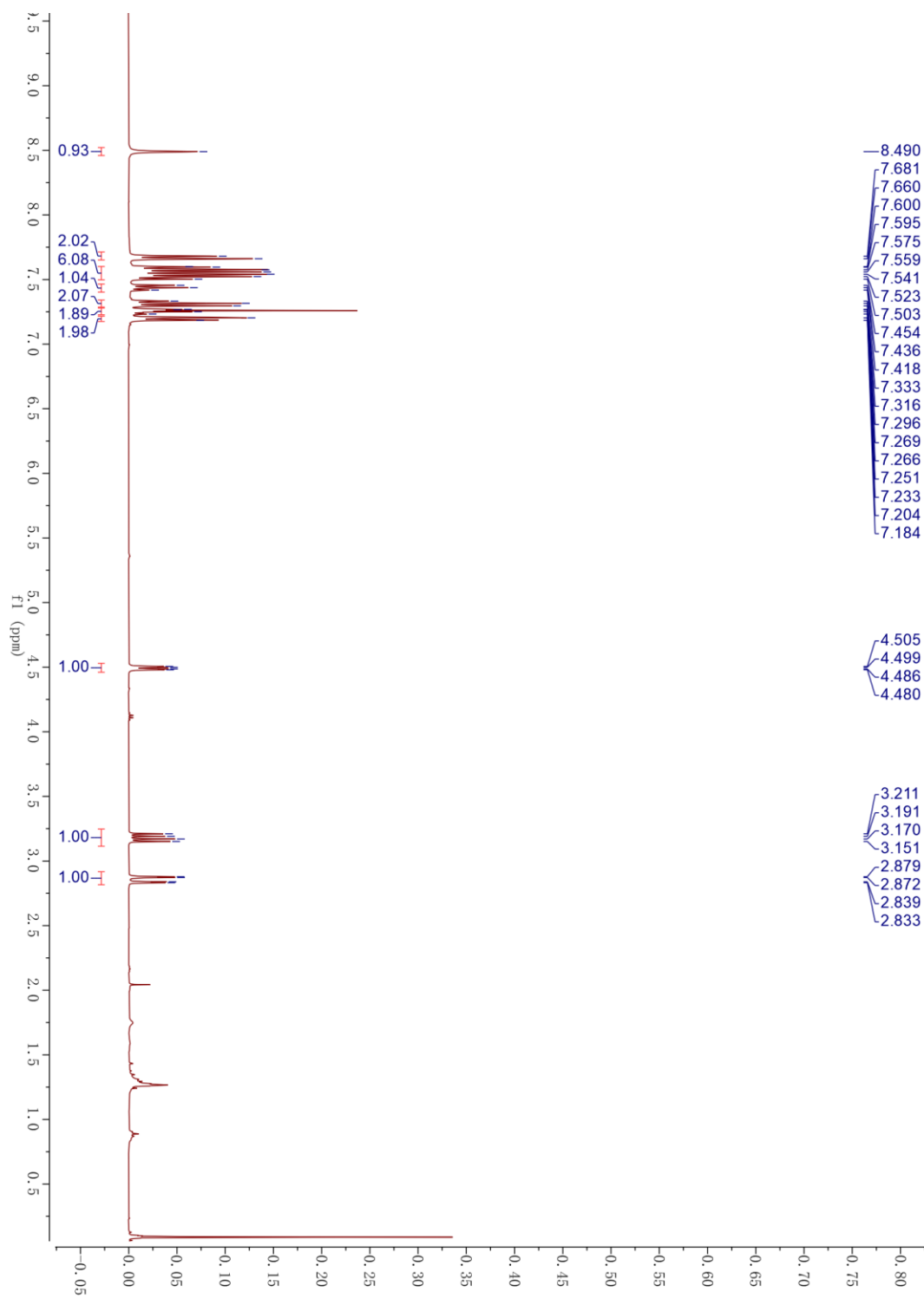


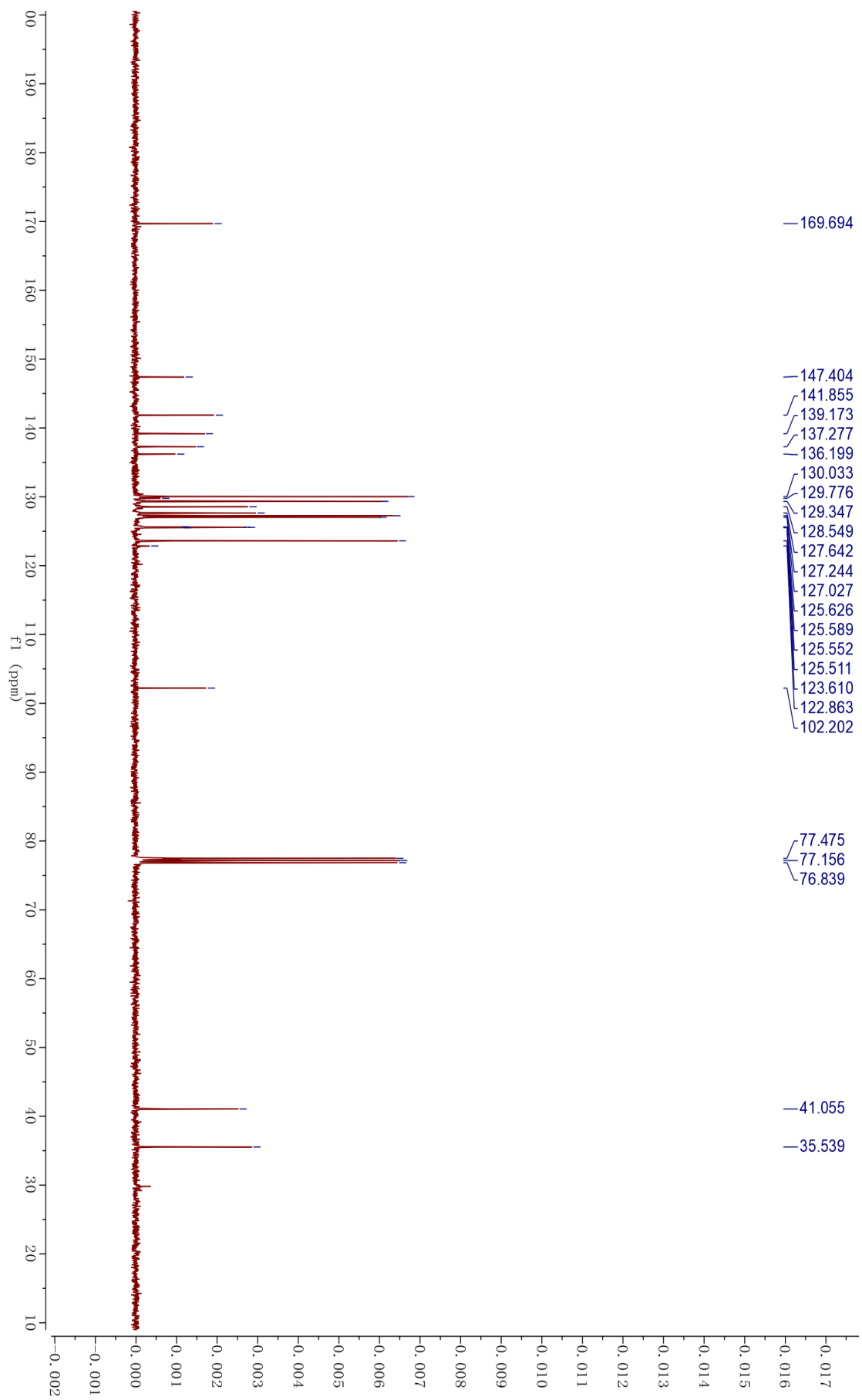


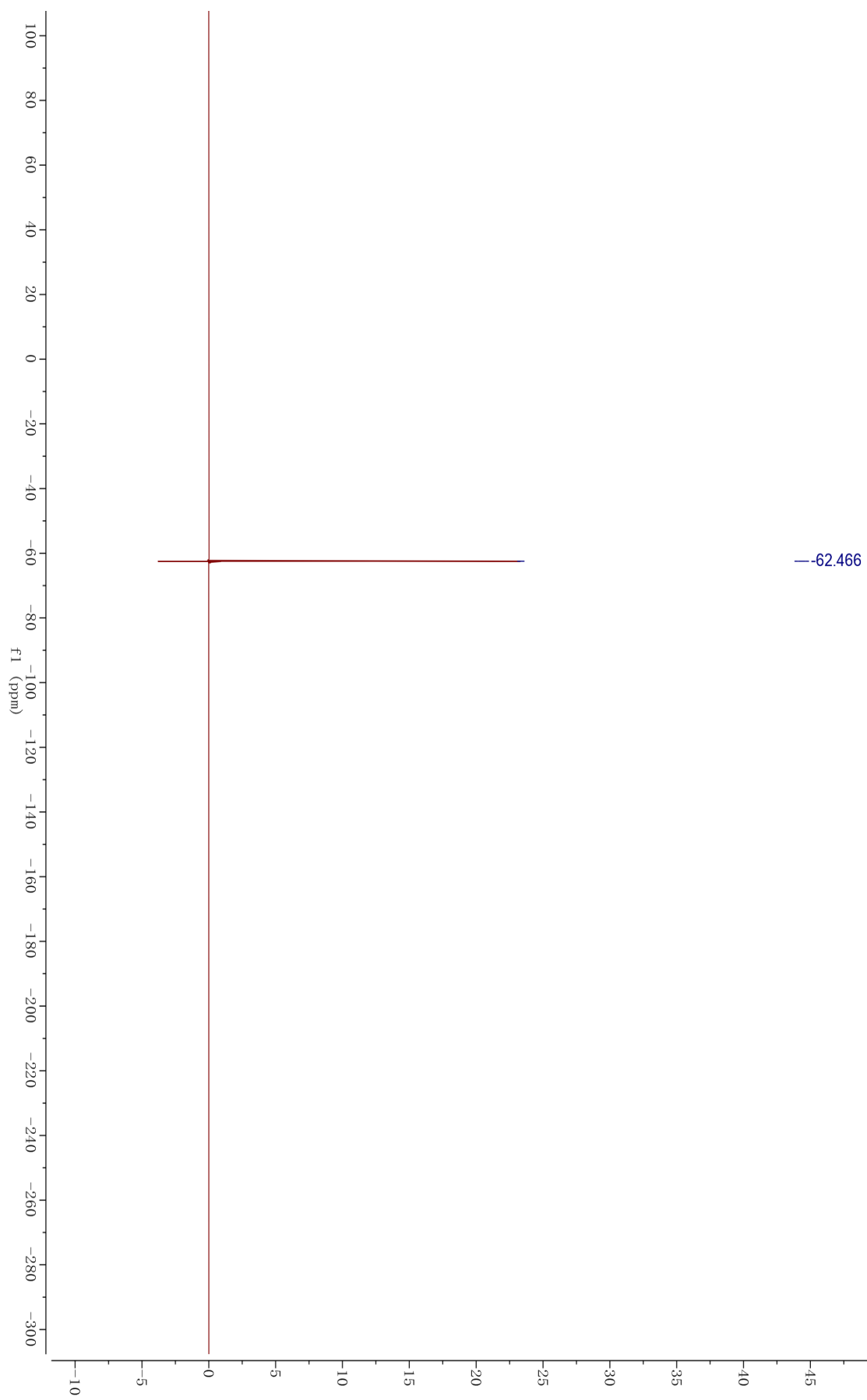


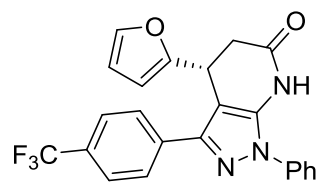


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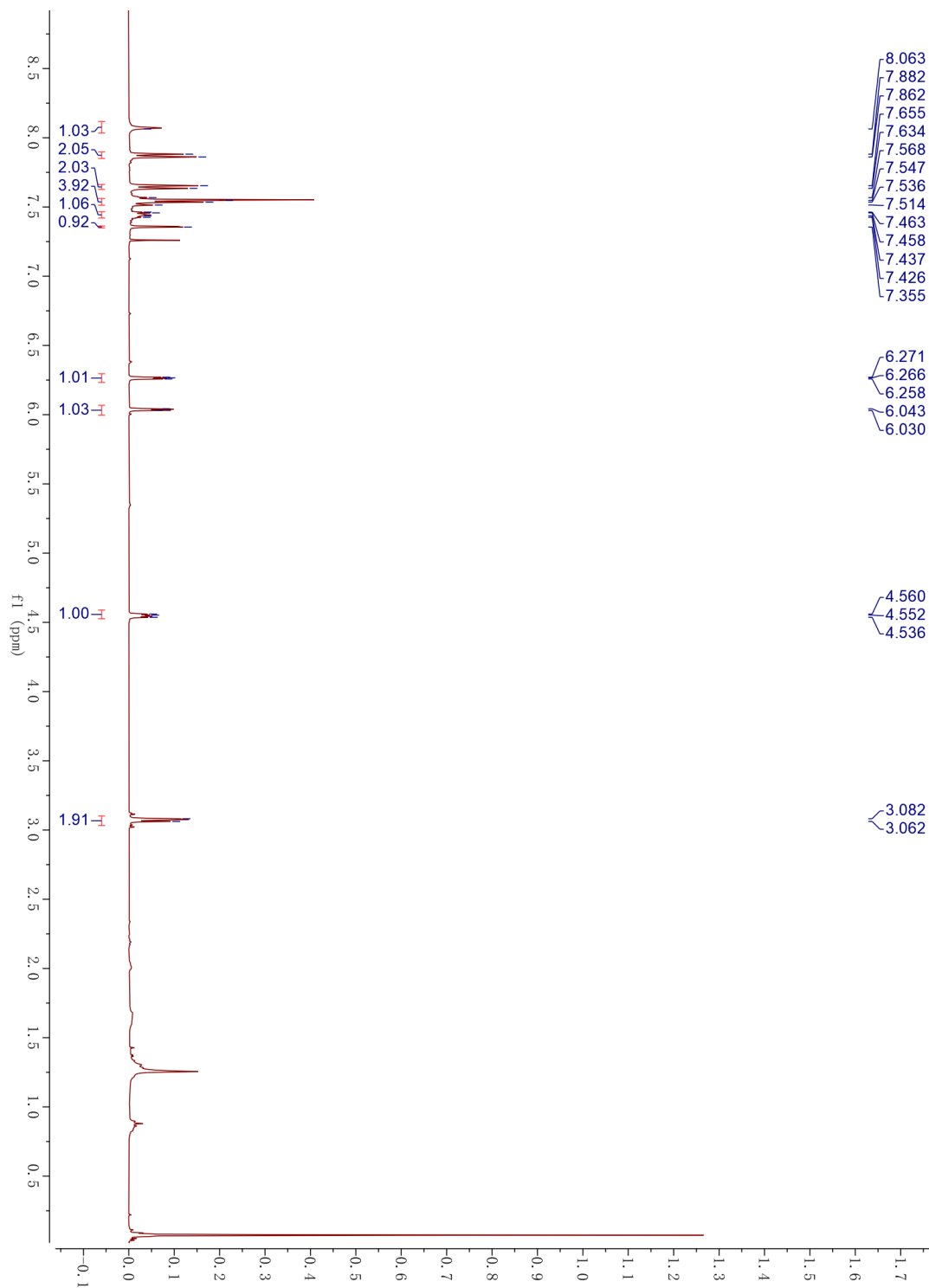


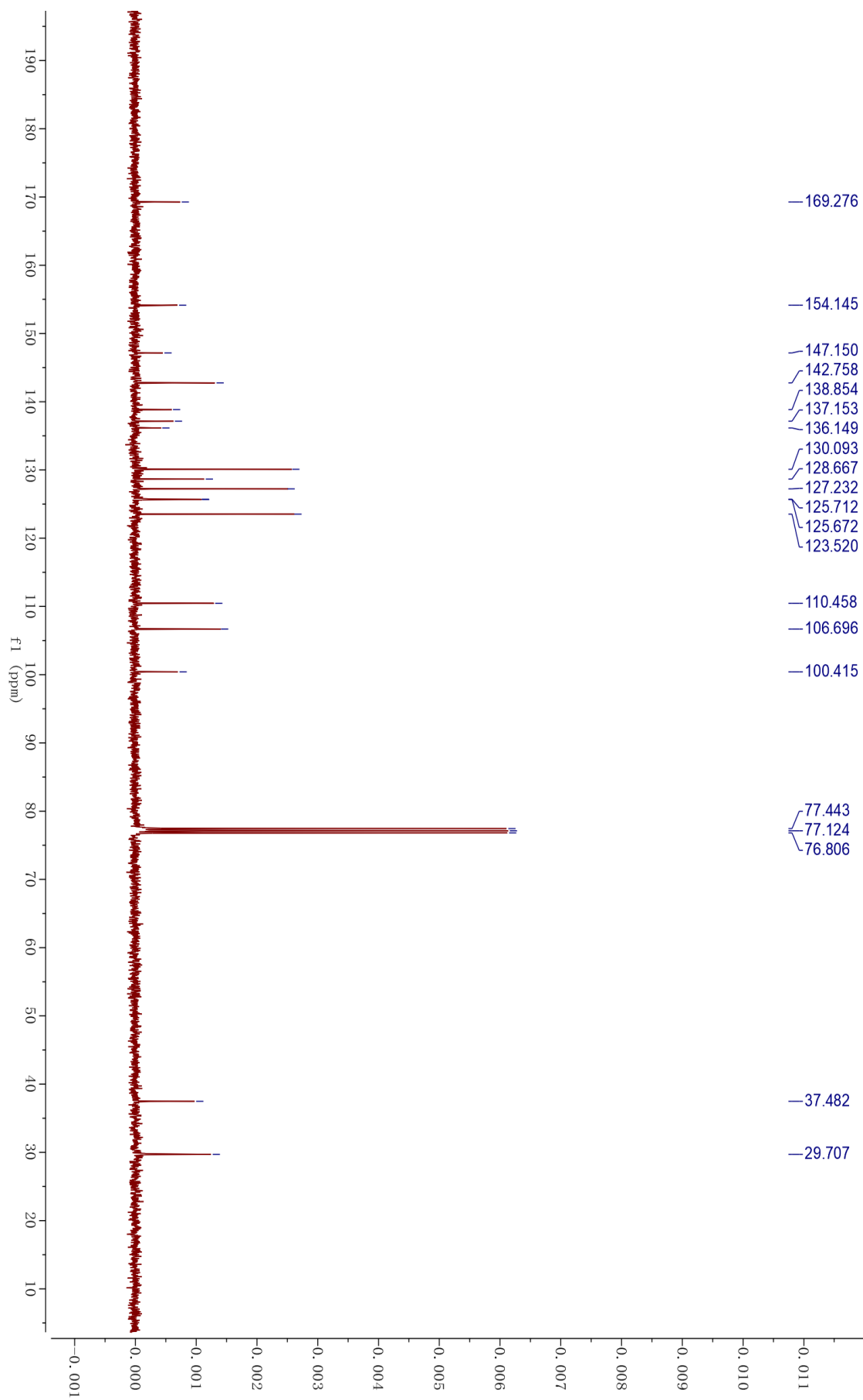


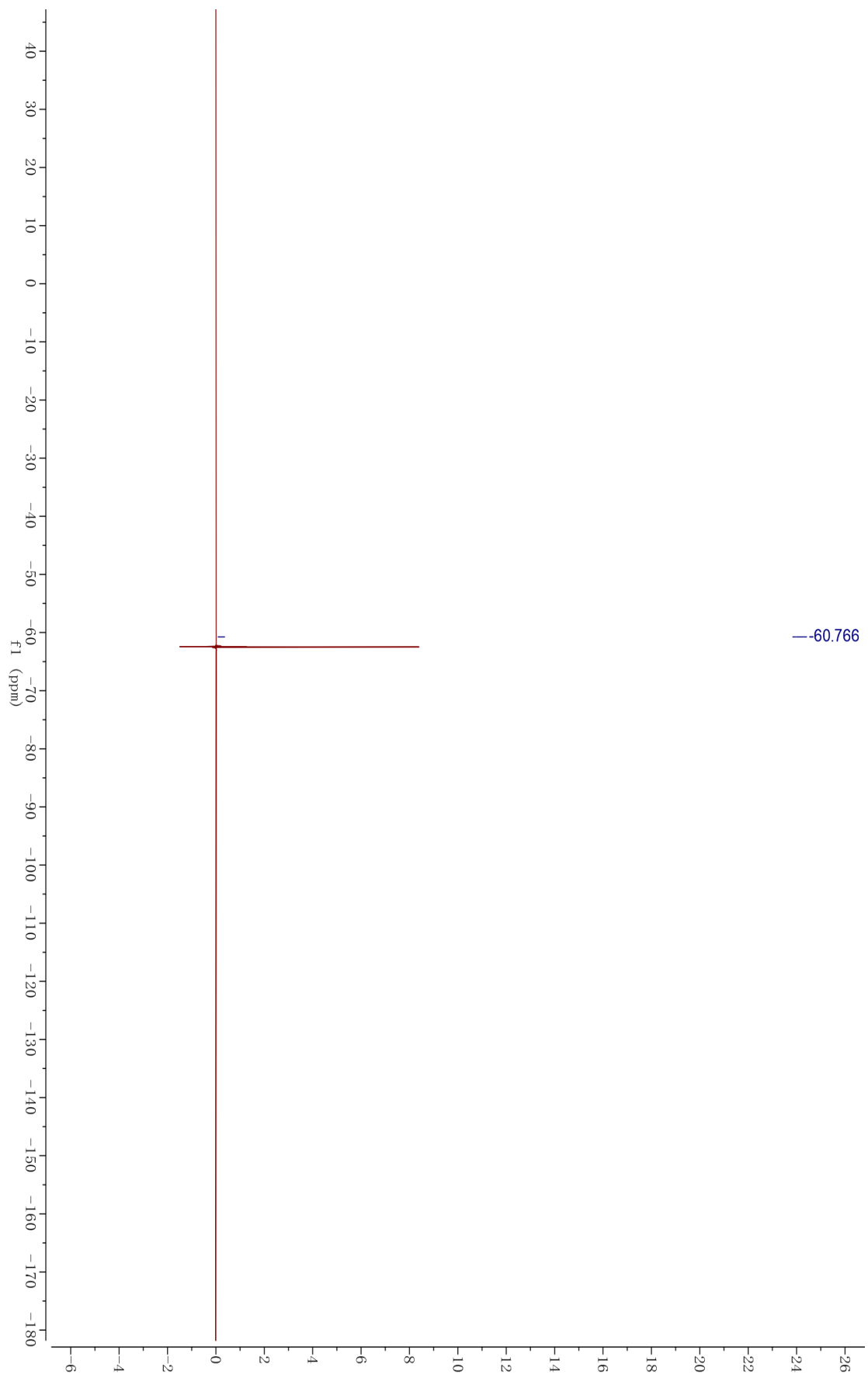


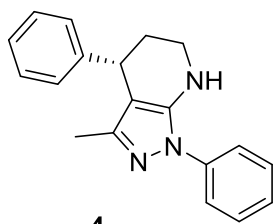


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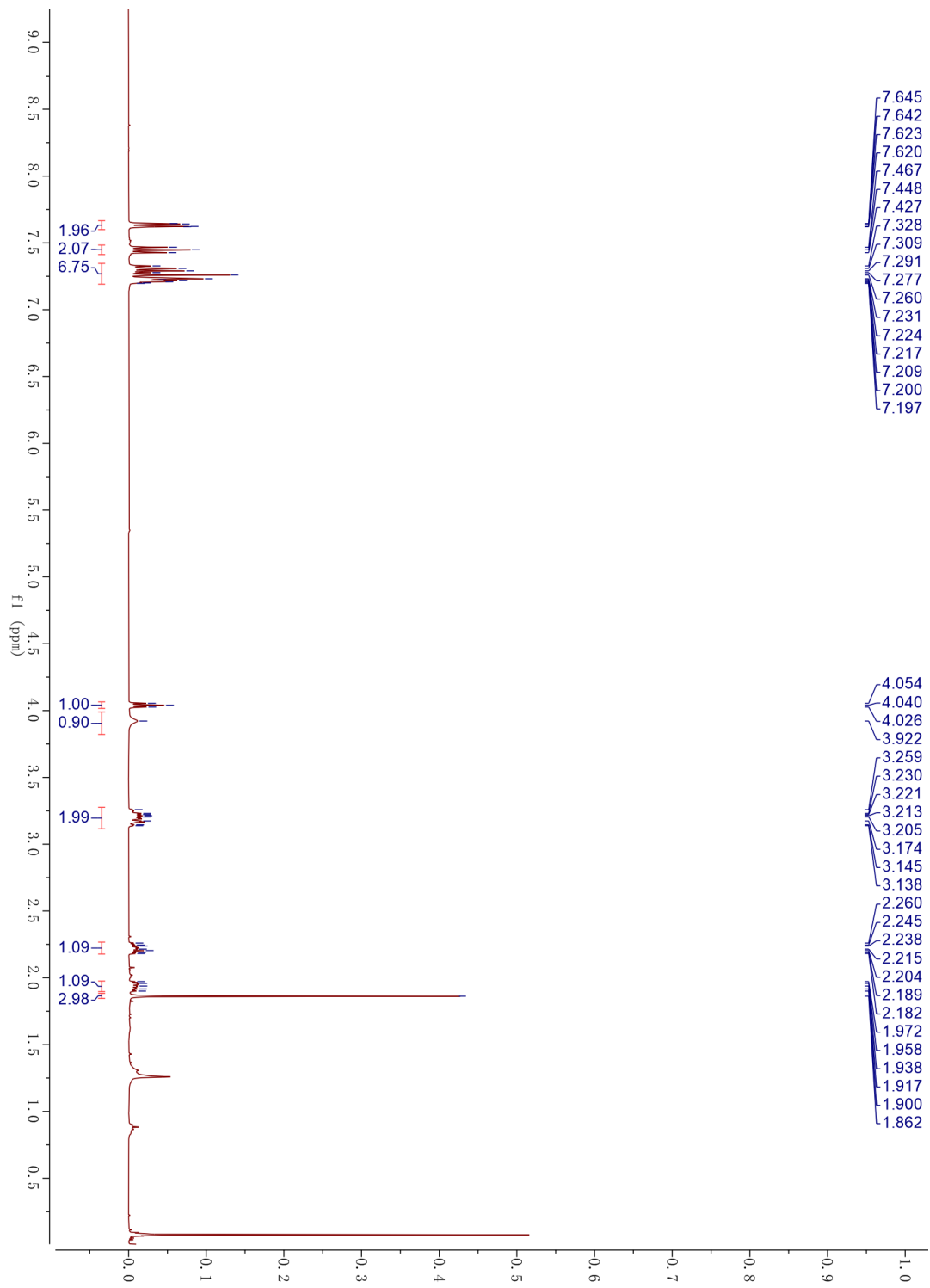


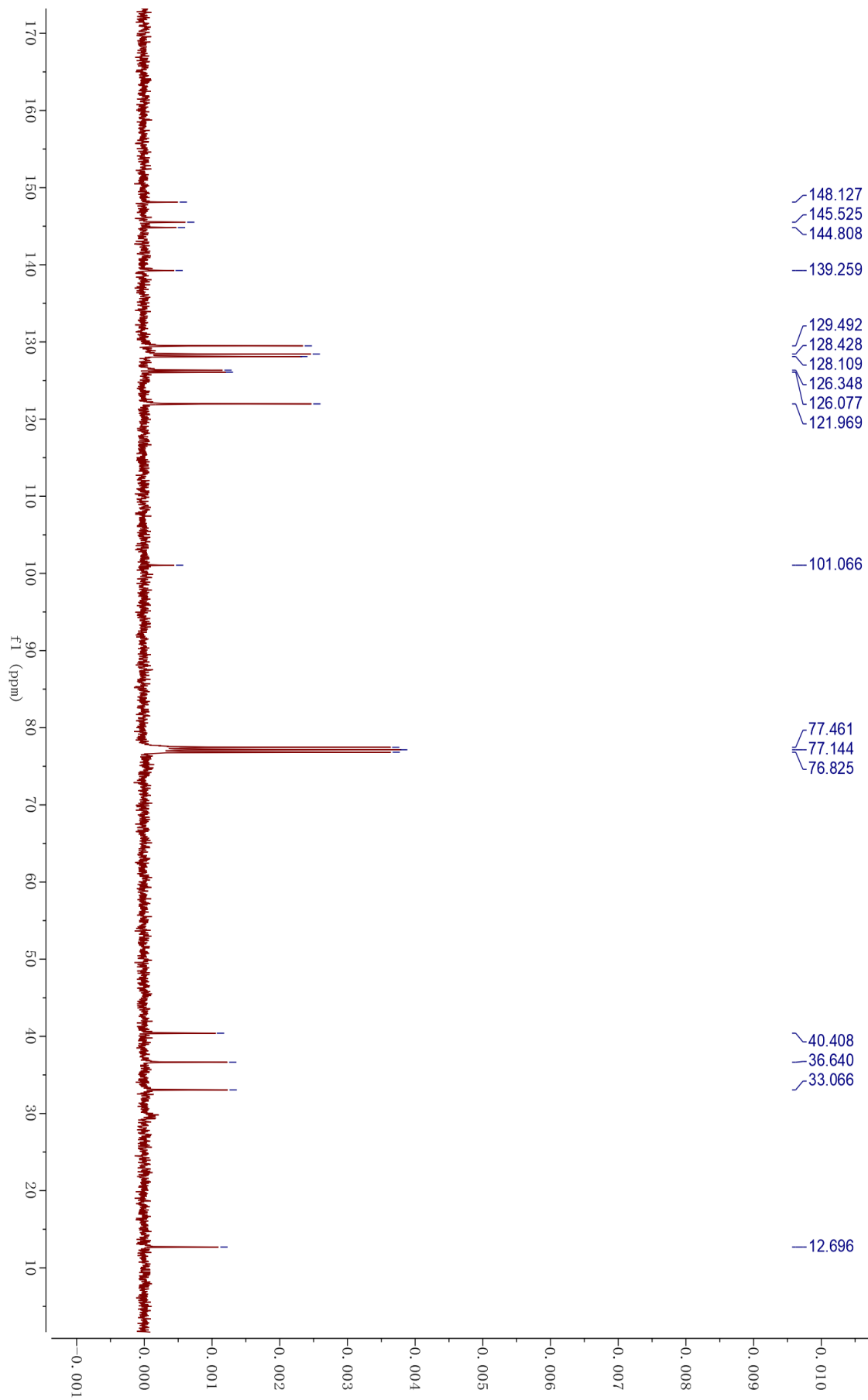


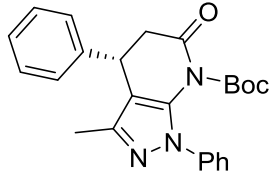




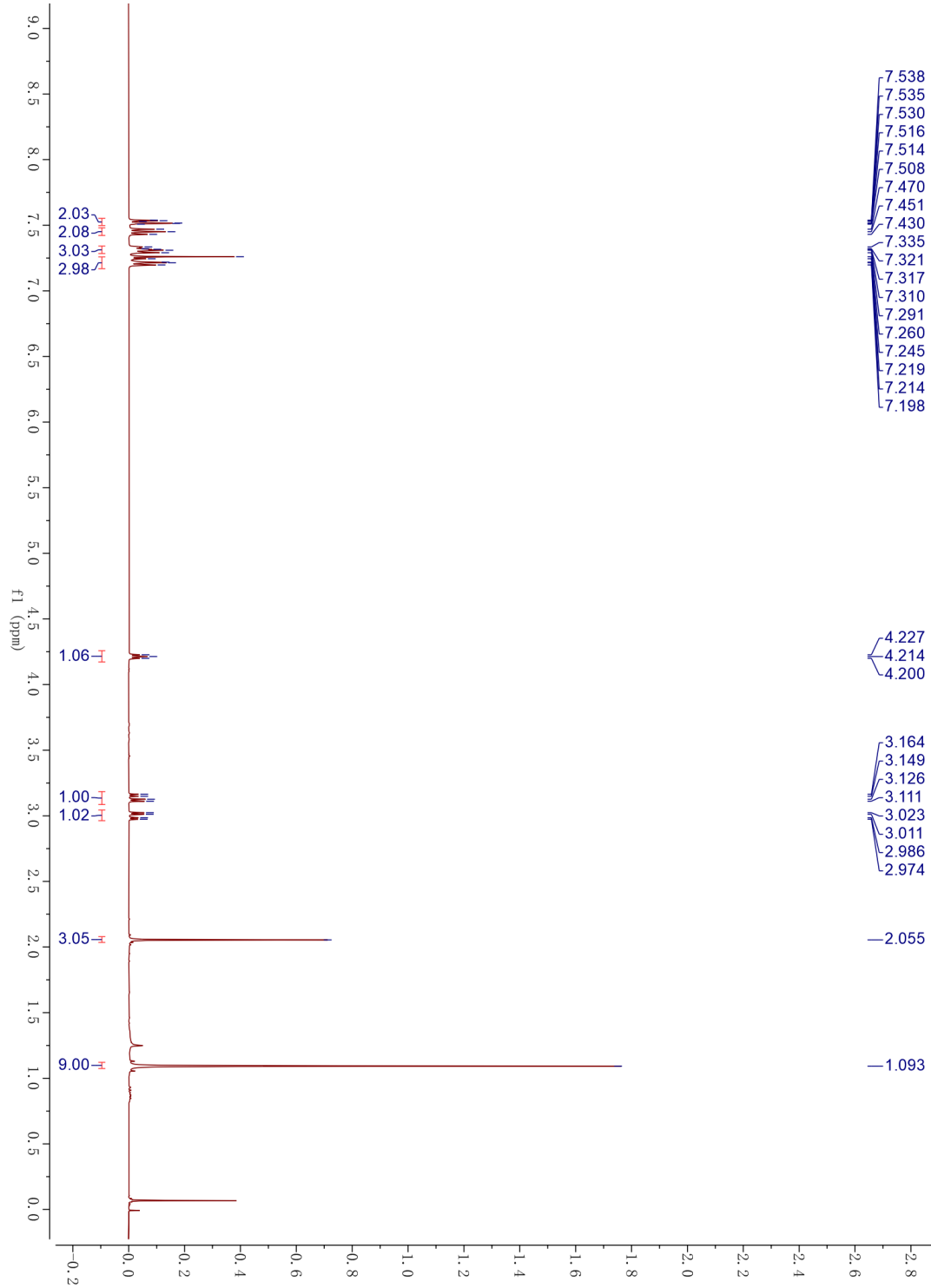
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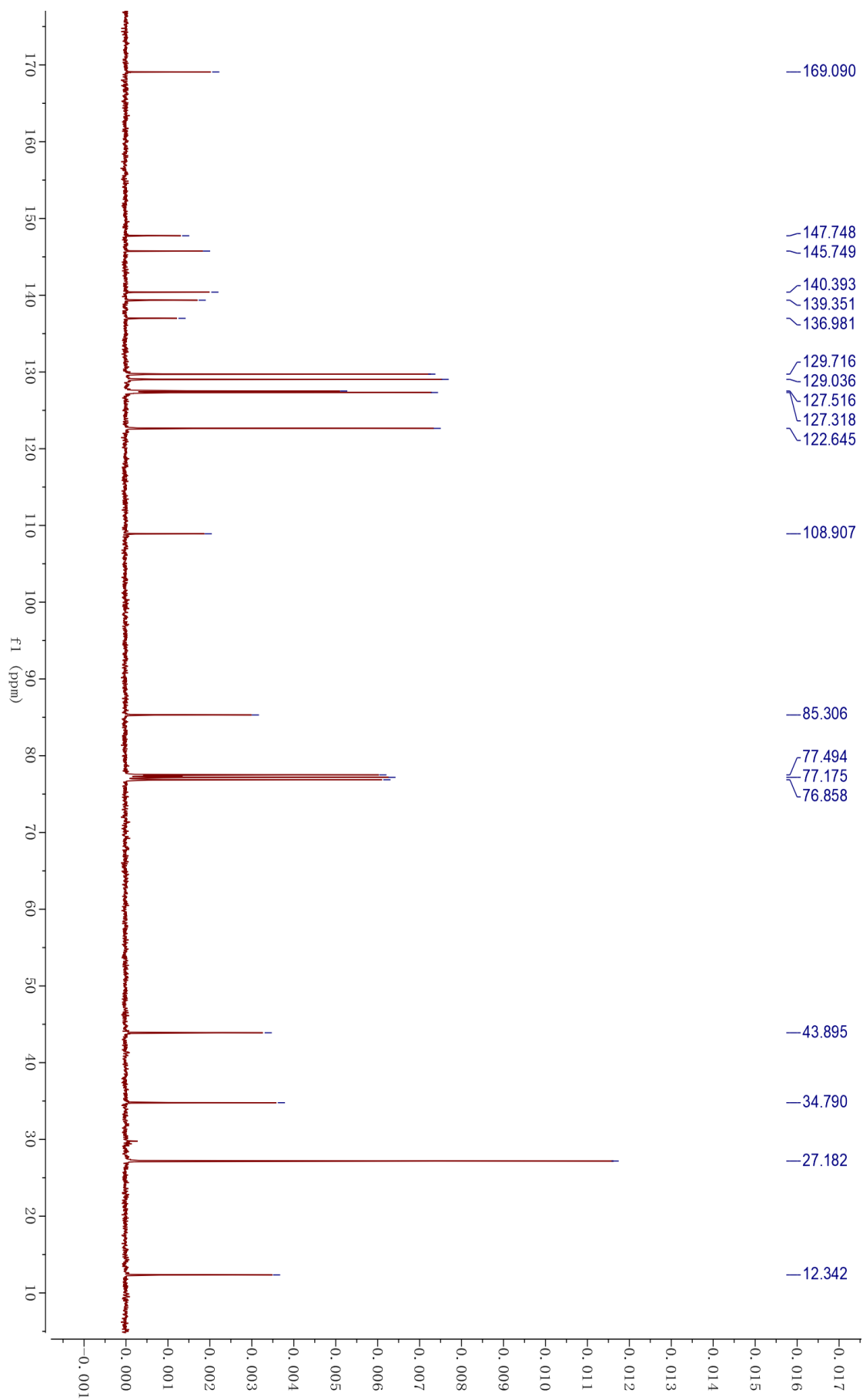


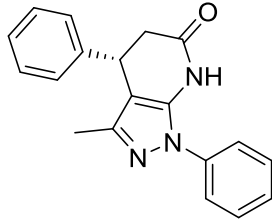




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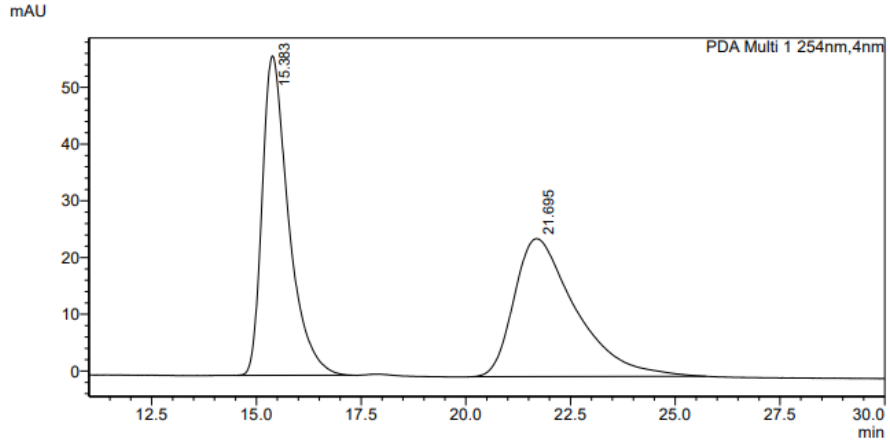






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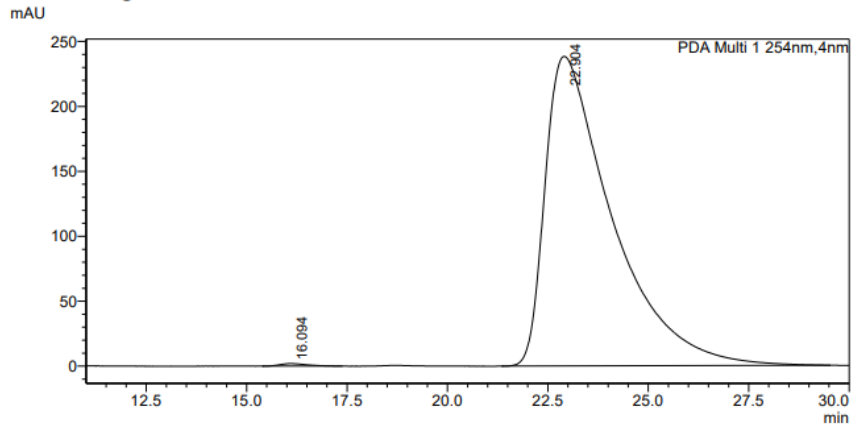
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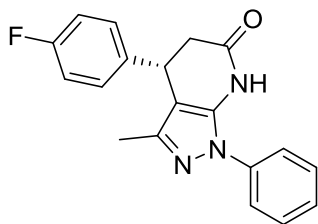
PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	Height
1	15.383	2471915	49.783	56299
2	21.695	2493509	50.217	24324
Total		4965425	100.000	80623

<Chromatogram>



<Peak Table>

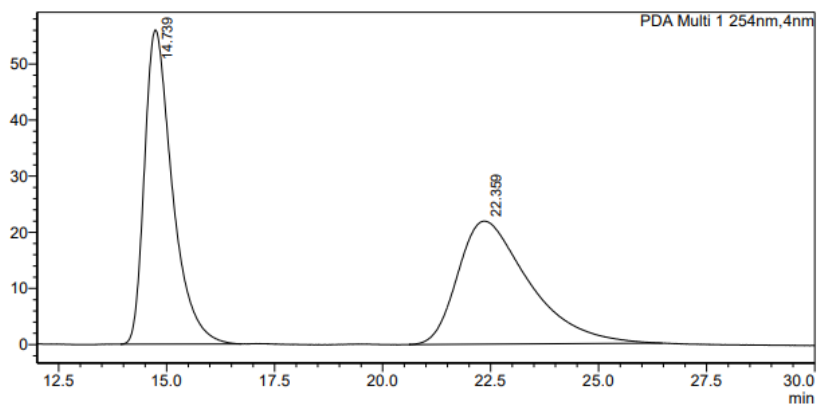
PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	Height
1	16.094	94471	0.340	1981
2	22.904	27688174	99.660	238405
Total		27782645	100.000	240386



3b

<Chromatogram>

mAU



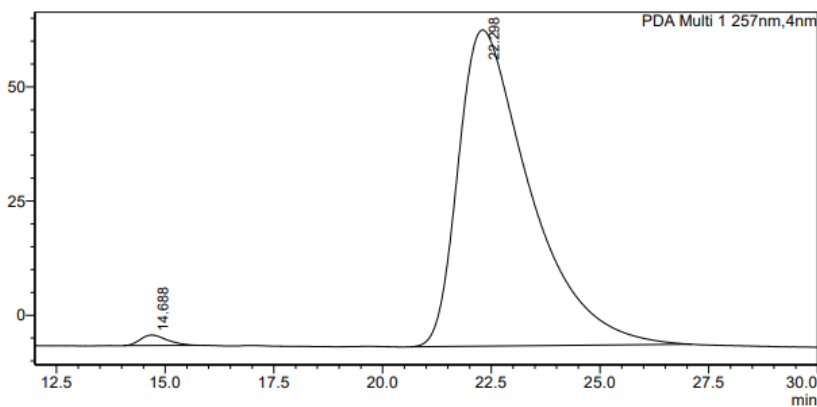
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.739	2514109	49.982	55977
2	22.359	2515952	50.018	21914
Total		5030061	100.000	77891

<Chromatogram>

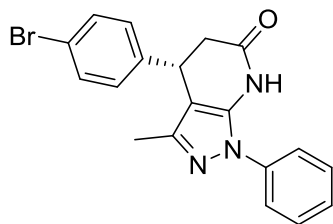
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PDA Ch1 257nm

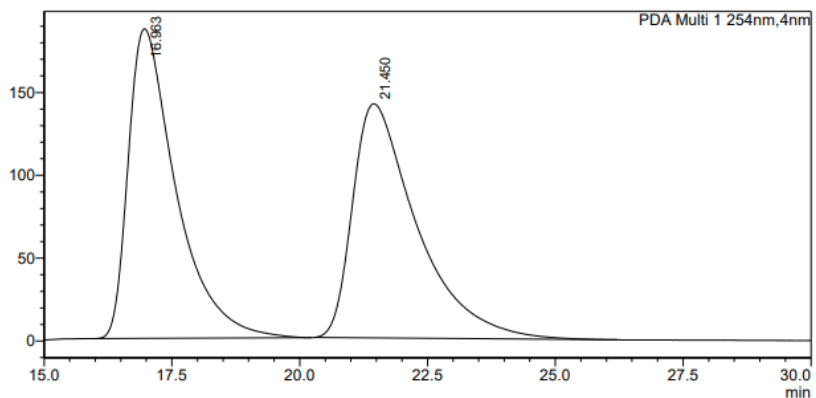
Peak#	Ret. Time	Area	Area%	Height
1	14.688	96848	1.204	2280
2	22.298	7947392	98.796	69199
Total		8044240	100.000	71479



3c

<Chromatogram>

mAU



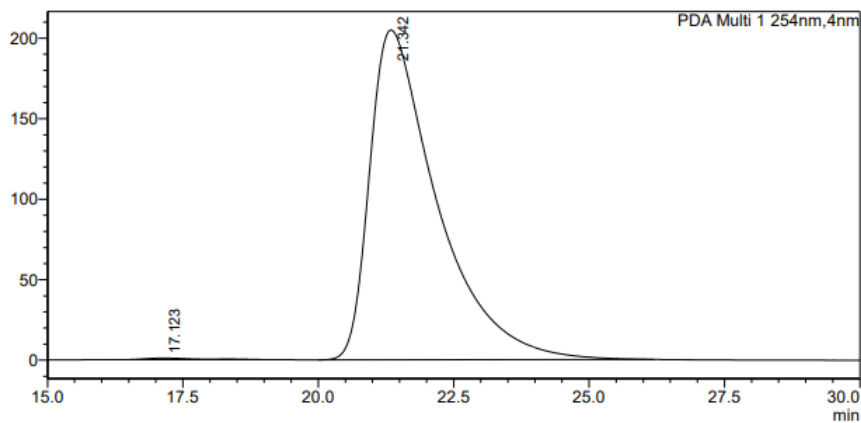
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PDA Ch1 254nm

Peak#	Ret. Time	Area%	Area	Height
1	16.963	49.489	12146340	186873
2	21.450	50.511	12397413	141304
Total		100.000	24543753	328177

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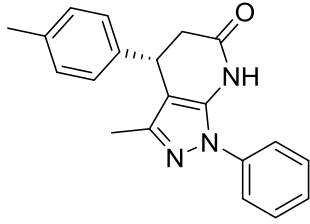
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<Peak Table>

PDA Ch1 254nm

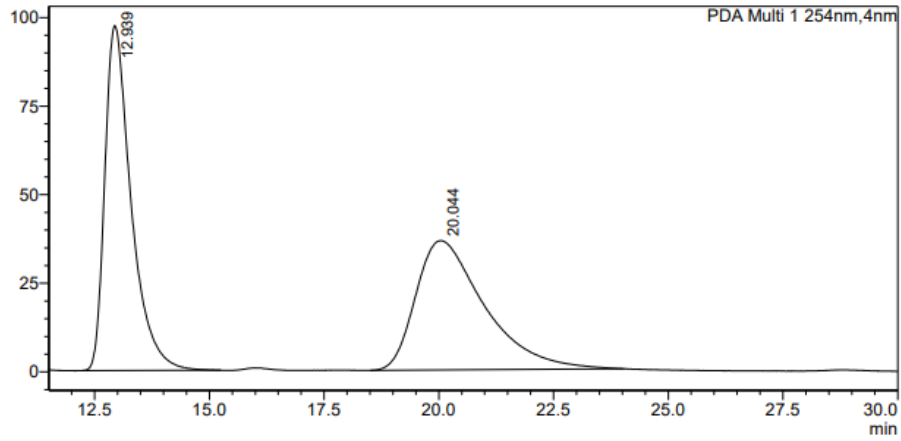
Peak#	Ret. Time	Area	Area%	Height
1	17.123	75932	0.426	1020
2	21.342	17729493	99.574	204849
Total		17805425	100.000	205869



3d

<Chromatogram>

mAU



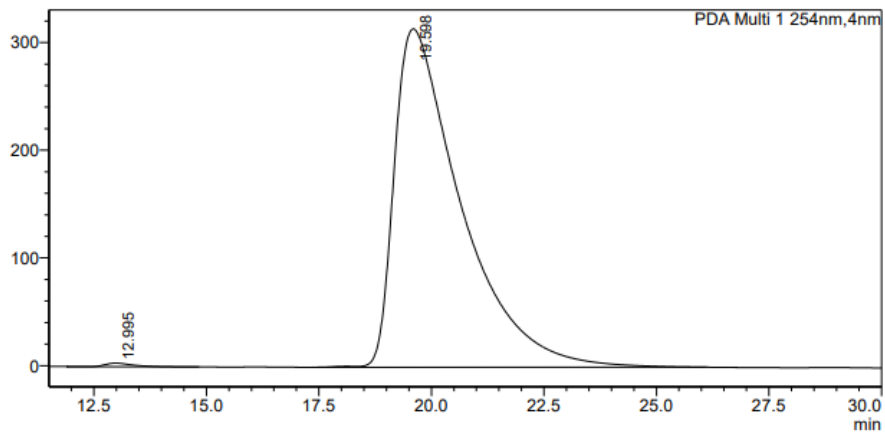
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	12.939	3882343	50.502	97327
2	20.044	3805200	49.498	36528
Total		7687543	100.000	133855

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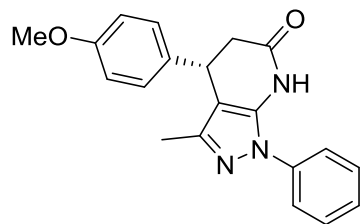
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PDA Ch1 254nm

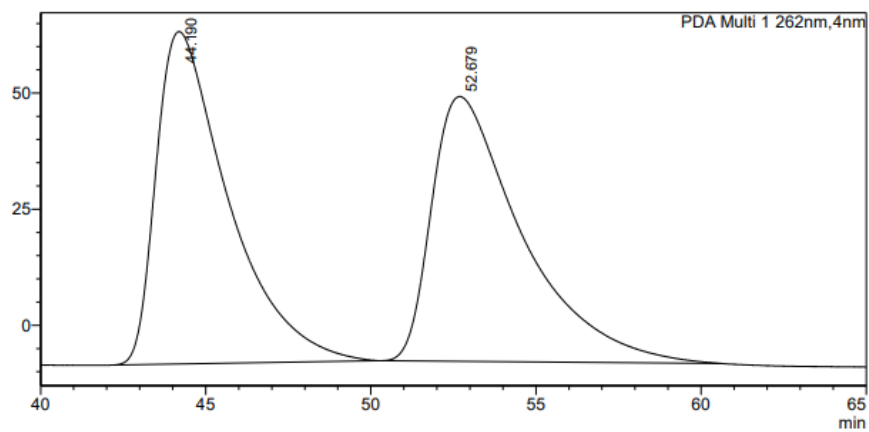
Peak#	Ret. Time	Area	Area%	Height
1	12.995	137234	0.422	3258
2	19.598	32408145	99.578	314129
Total		32545379	100.000	317387



3e

<Chromatogram>

mAU



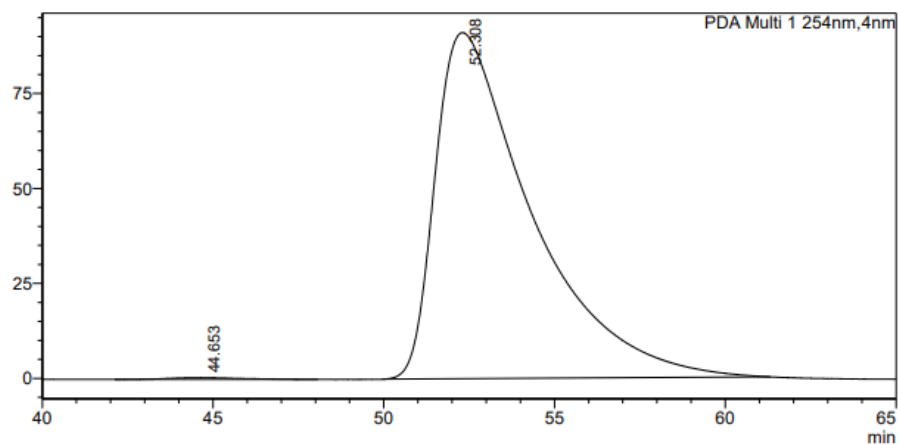
<Peak Table>

PDA Ch1 262nm

Peak#	Ret. Time	Area	Area%	Height
1	44.190	10883016	50.104	71574
2	52.679	10837623	49.896	56997
Total		21720638	100.000	128571

<Chromatogram>

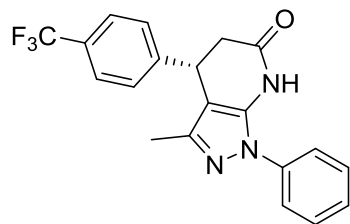
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<Peak Table>

PDA Ch1 254nm

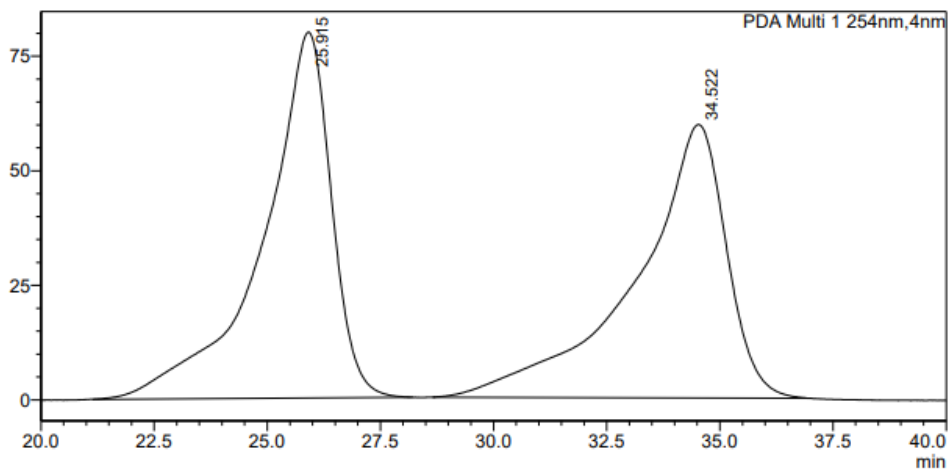
Peak#	Ret. Time	Area	Area%	Height
1	44.653	66577	0.371	476
2	52.308	17885868	99.629	91132
Total		17952445	100.000	91608



3f

<Chromatogram>

mAU



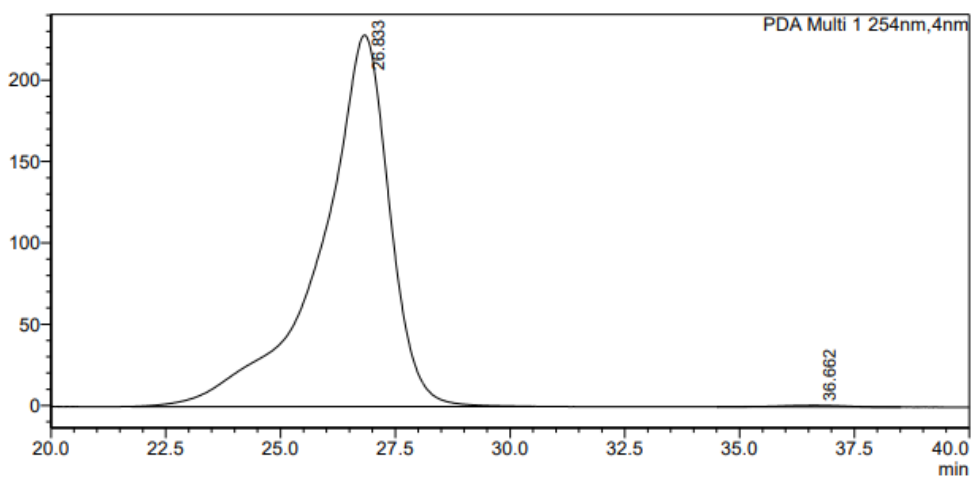
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	25.915	8403156	50.276	79829
2	34.522	8310953	49.724	59661
Total		16714109	100.000	139490

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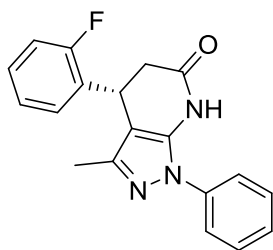
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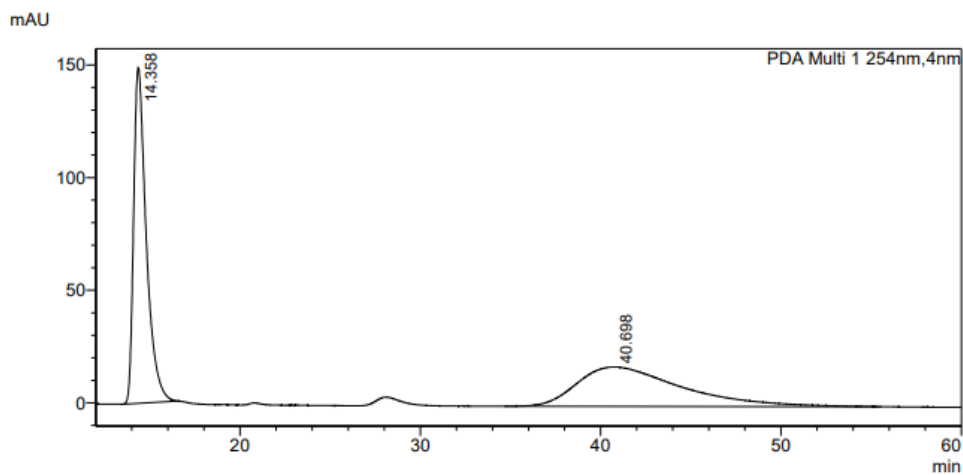
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	26.833	23945406	99.609	228249
2	36.662	94048	0.391	991
Total		24039454	100.000	229240



3g

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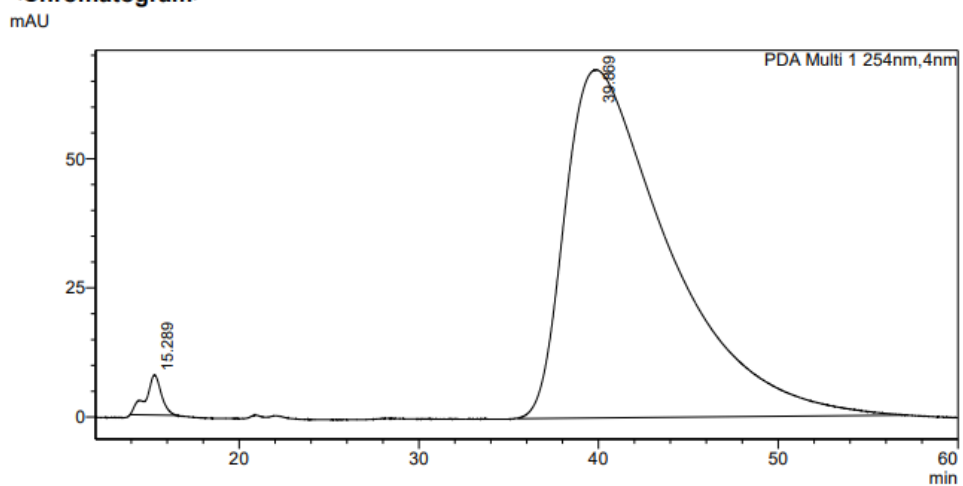


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.358	7248622	50.777	148941
2	40.698	7026713	49.223	17481
Total		14275335	100.000	166422

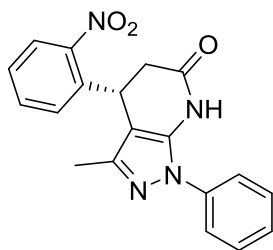
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<Peak Table>

PDA Ch1 254nm

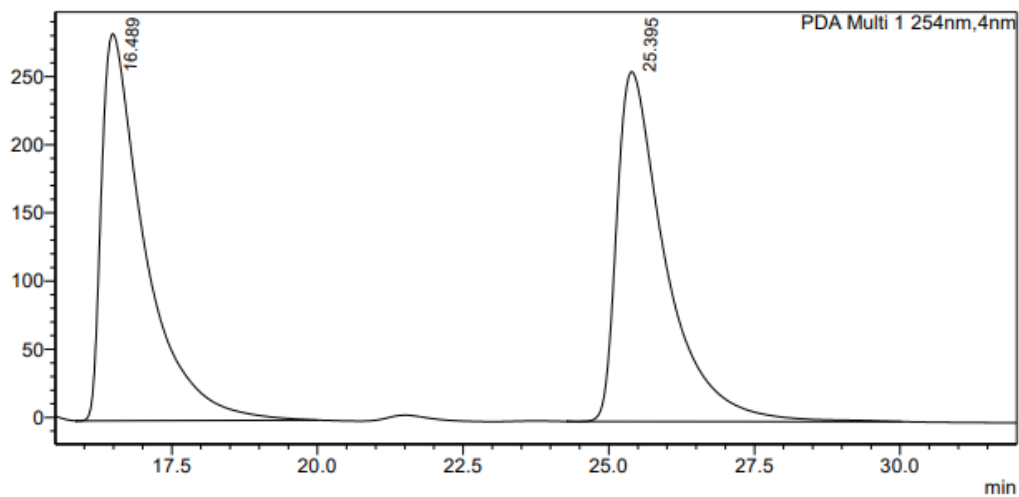
Peak#	Ret. Time	Area	Area%	Height
1	15.289	475230	1.721	7767
2	39.869	27145282	98.279	67381
Total		27620511	100.000	75148



3h

<Chromatogram>

mAU



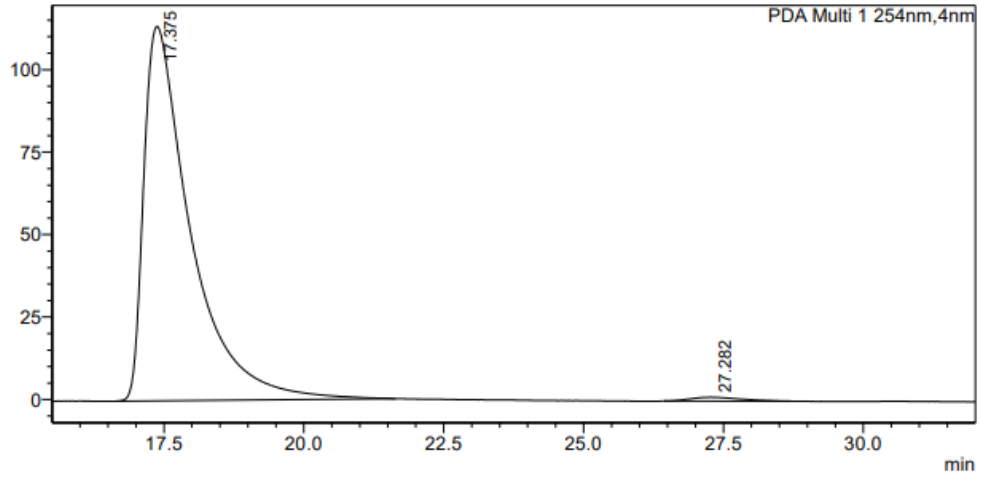
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	16.489	14625466	49.507	283737
2	25.395	14916850	50.493	256435
Total		29542316	100.000	540172

<Chromatogram>

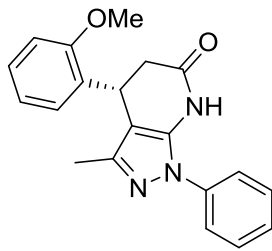
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<Peak Table>

PDA Ch1 254nm

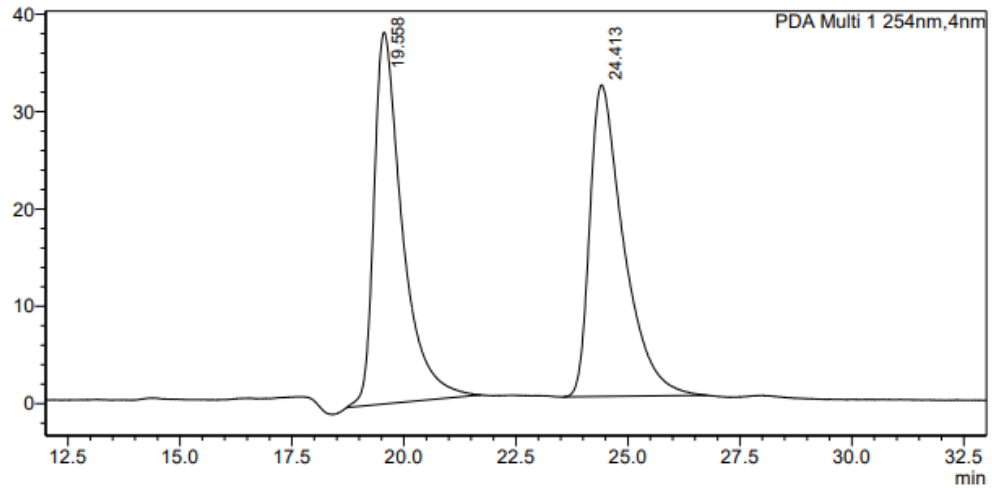
Peak#	Ret. Time	Area	Area%	Height
1	17.375	6589700	98.915	113478
2	27.282	72268	1.085	1165
Total		6661968	100.000	114643



3i

<Chromatogram>

mAU



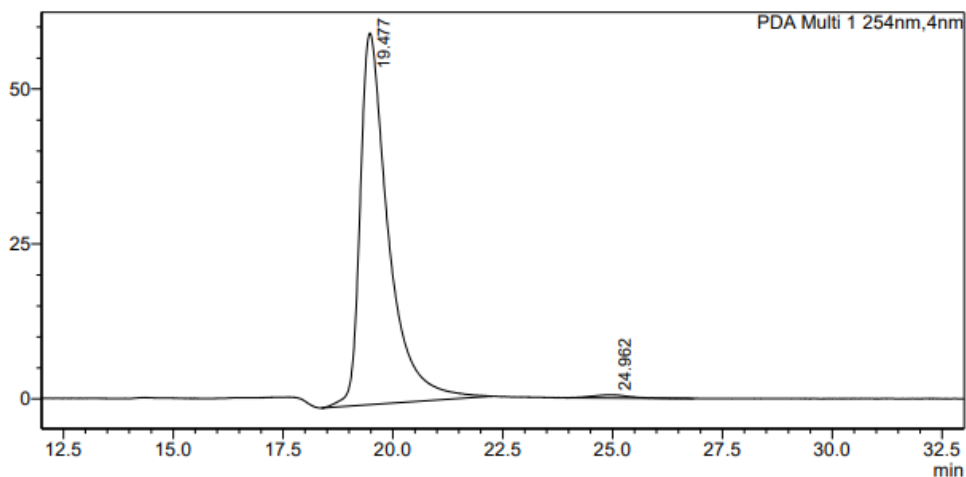
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	19.558	1680318	49.927	38168
2	24.413	1685223	50.073	31994
Total		3365541	100.000	70161

<Chromatogram>

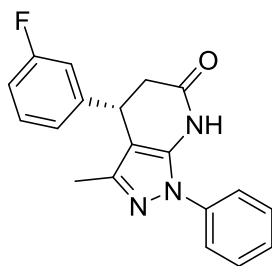
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PDA Ch1 254nm

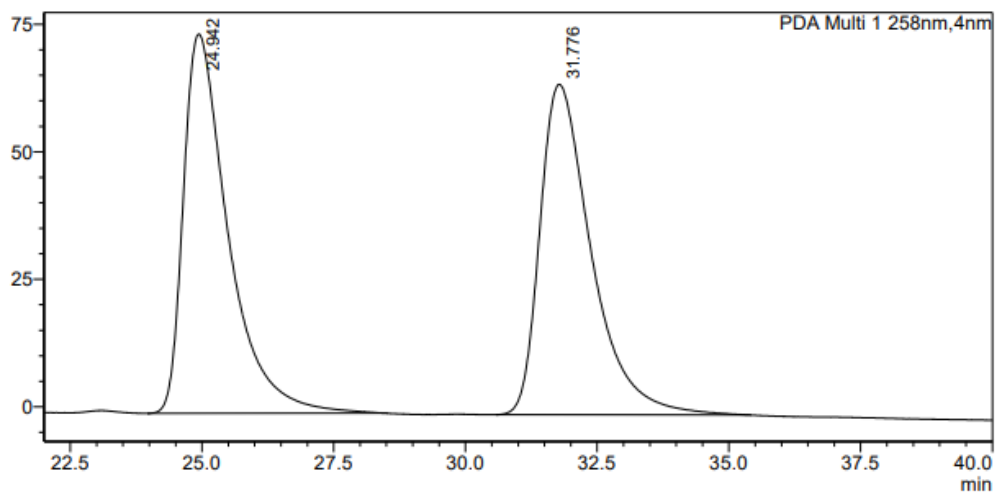
Peak#	Ret. Time	Area	Area%	Height
1	19.477	2691159	98.923	59938
2	24.962	29312	1.077	504
Total		2720470	100.000	60442



3j

<Chromatogram>

mAU

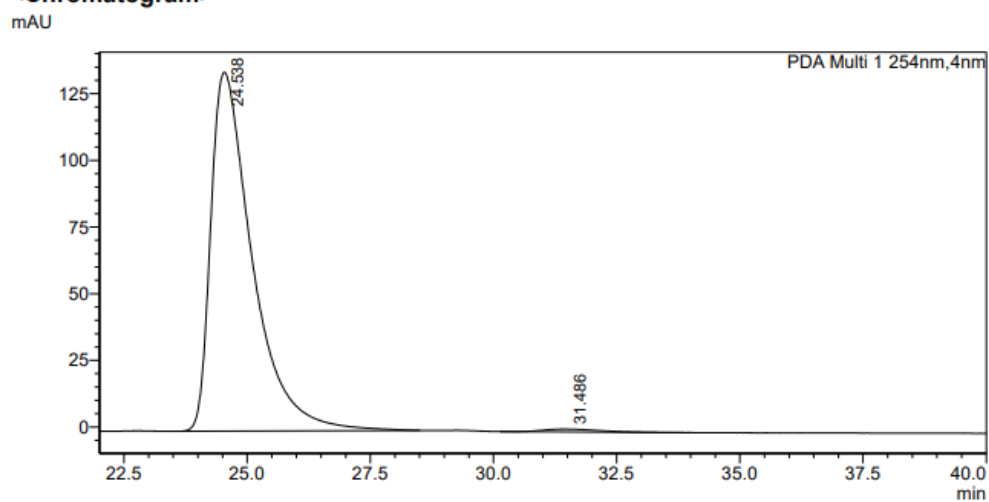


<Peak Table>

PDA Ch1 258nm

Peak#	Ret. Time	Area	Area%	Height
1	24.942	4395929	49.932	74365
2	31.776	4407868	50.068	64790
Total		8803797	100.000	139155

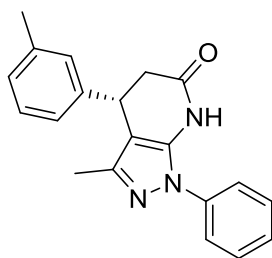
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<Peak Table>

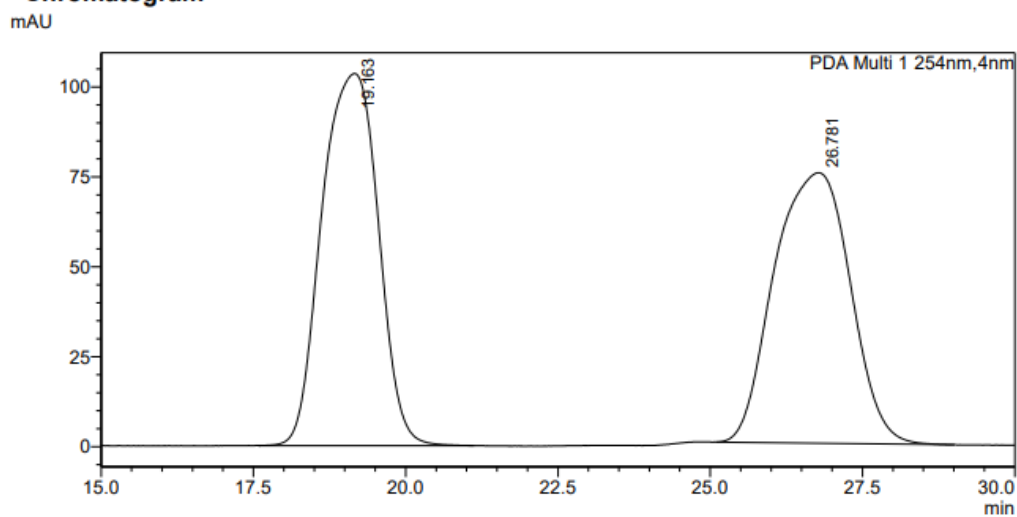
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	24.538	7893799	98.953	134576
2	31.486	83484	1.047	1062
Total		7977283	100.000	135638



3k

<Chromatogram>



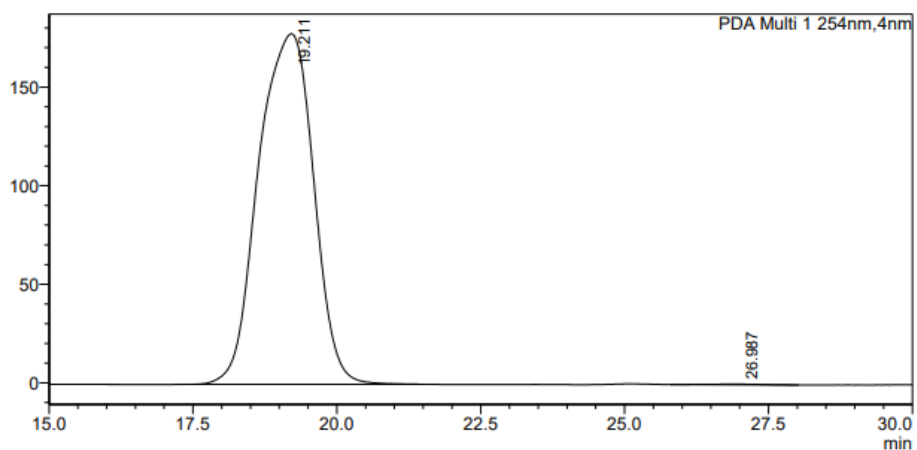
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	19.163	6685476	50.533	103400
2	26.781	6544525	49.467	75170
Total		13230001	100.000	178570

<Chromatogram>

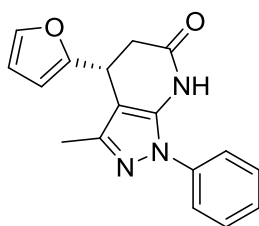
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PDA Ch1 254nm

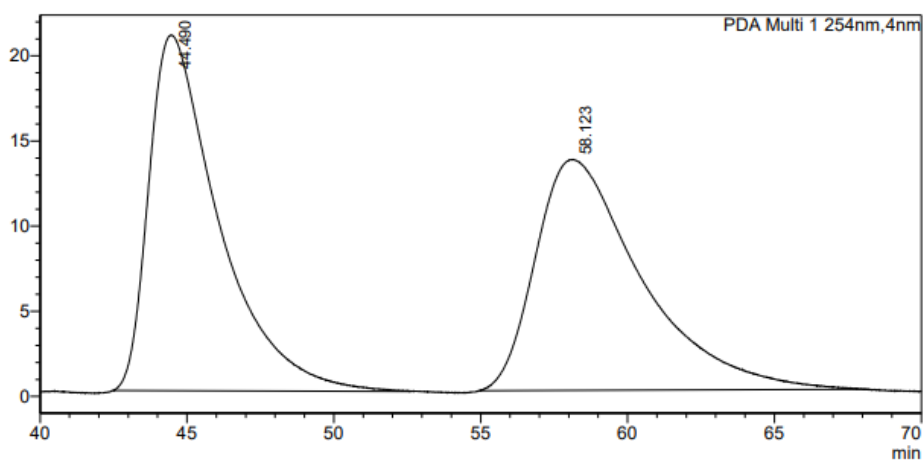
Peak#	Ret. Time	Area	Area%	Height
1	19.211	11848568	99.831	177785
2	26.987	20116	0.169	331
Total		11868684	100.000	178116



31

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mAU



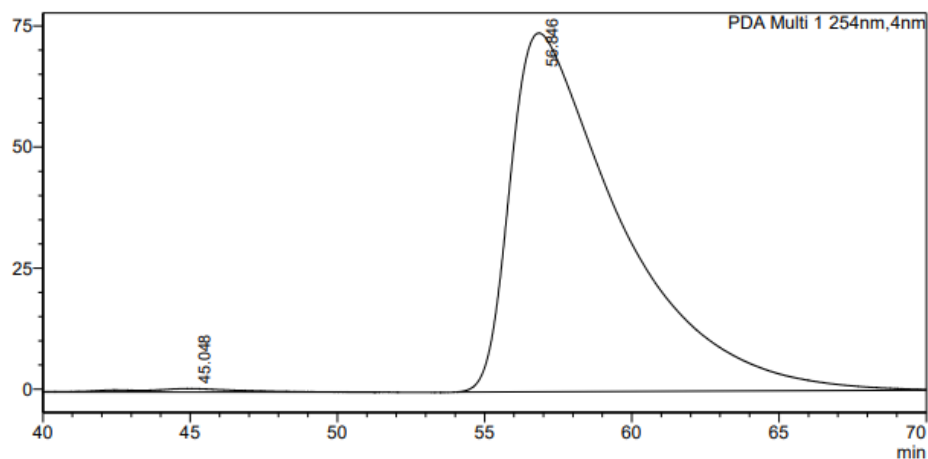
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	44.490	3460612	50.346	20882
2	58.123	3413061	49.654	13567
Total		6873674	100.000	34449

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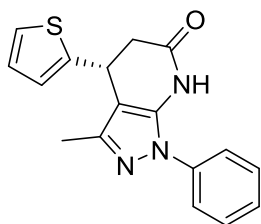
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PDA Ch1 254nm

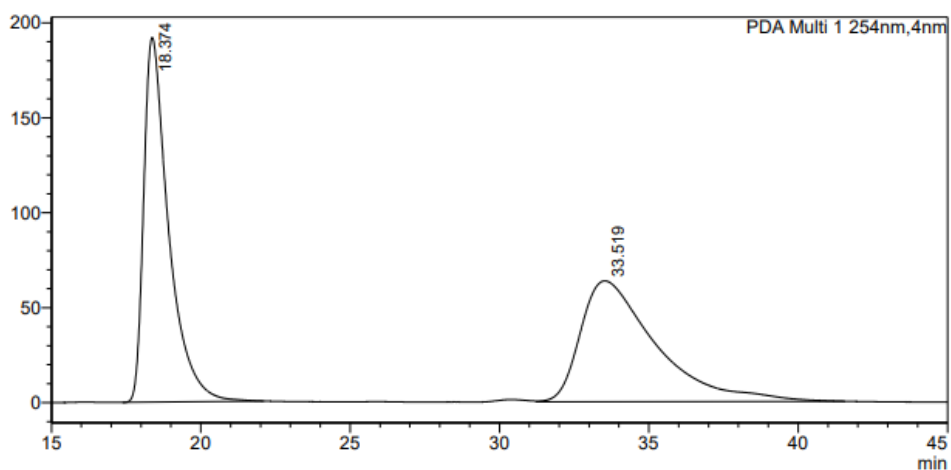
Peak#	Ret. Time	Area	Area%	Height
1	45.048	201696	1.034	750
2	56.846	19304300	98.966	74045
Total		19505996	100.000	74796



3m

<Chromatogram>

mAU



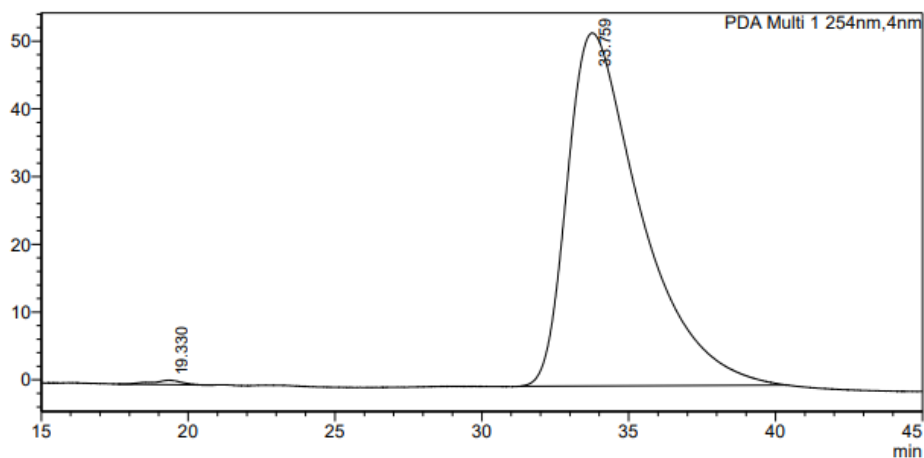
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	18.374	11137937	49.901	191963
2	33.519	11182185	50.099	63653
Total		22320122	100.000	255616

<Chromatogram>

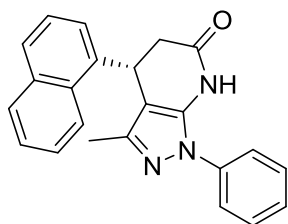
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PDA Ch1 254nm

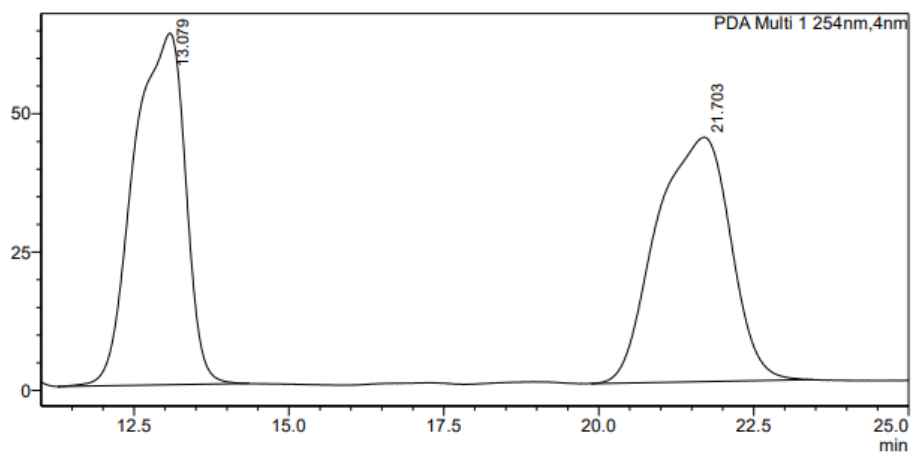
Peak#	Ret. Time	Area	Area%	Height
1	19.330	45994	0.504	666
2	33.759	9077089	99.496	52107
Total		9123083	100.000	52772



3n

<Chromatogram>

mAU



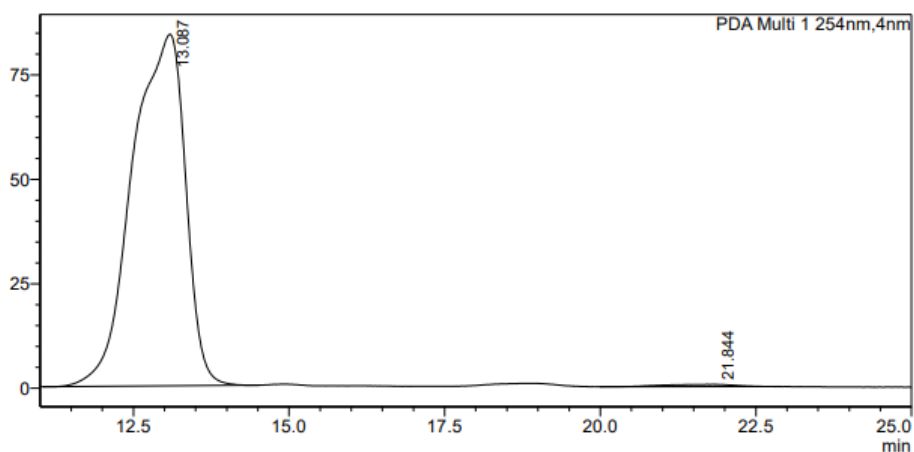
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	13.079	3668116	50.005	63530
2	21.703	3667389	49.995	44155
Total		7335505	100.000	107685

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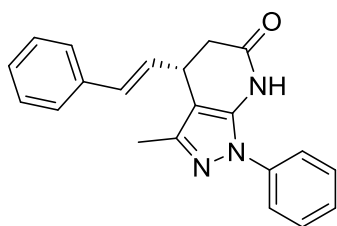
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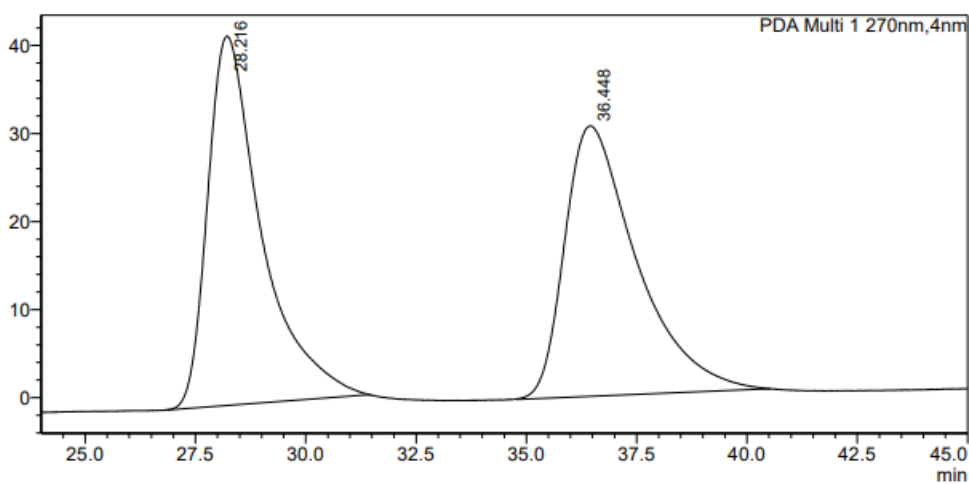
Peak#	Ret. Time	Area	Area%	Height
1	13.087	4992892	99.117	84204
2	21.844	44481	0.883	539
Total		5037373	100.000	84743



3o

<Chromatogram>

mAU



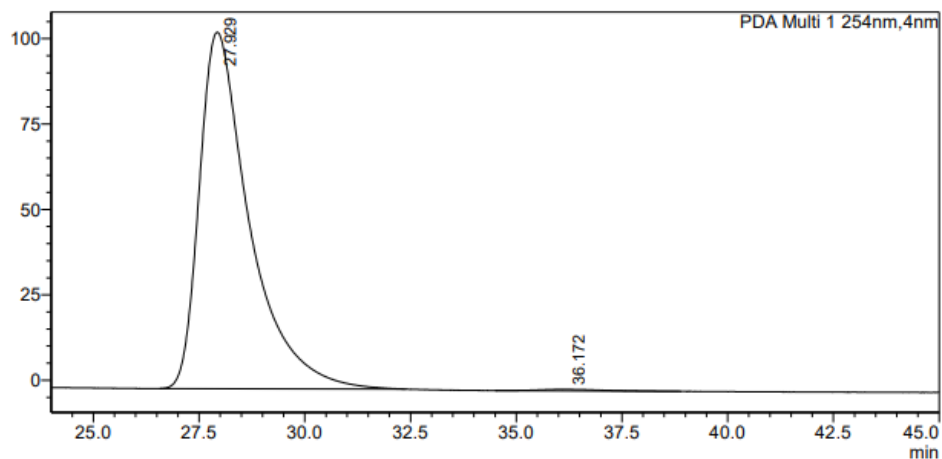
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PDA Ch1 270nm

Peak#	Ret. Time	Area	Area%	Height
1	28.216	3557125	50.490	41927
2	36.448	3488036	49.510	30709
Total		7045161	100.000	72636

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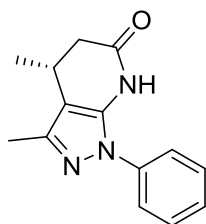
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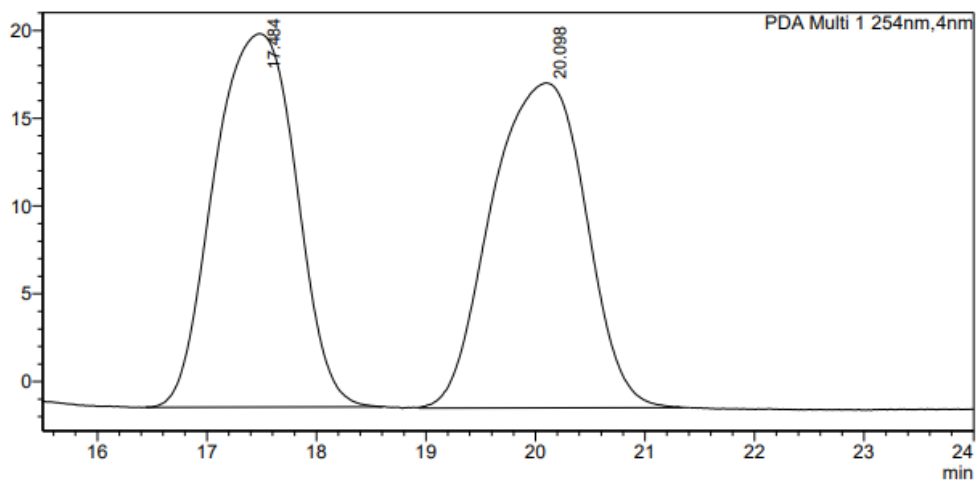
Peak#	Ret. Time	Area	Area%	Height
1	27.929	8611178	99.474	104344
2	36.172	45541	0.526	446
Total		8656719	100.000	104790



3p

<Chromatogram>

mAU



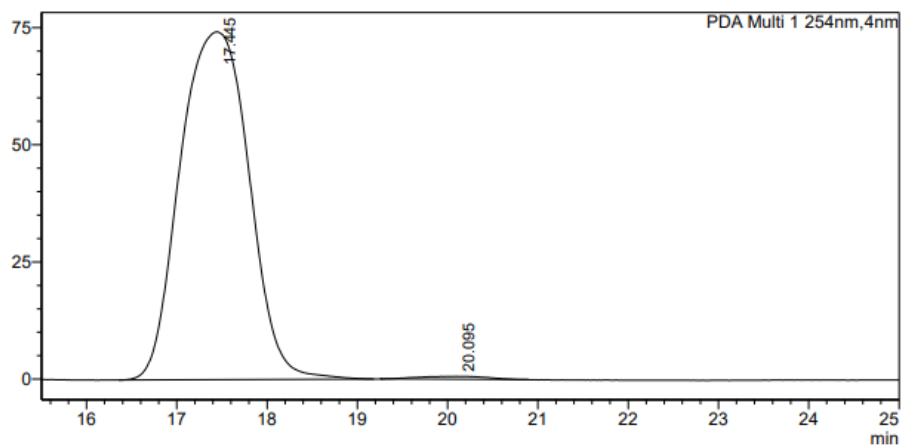
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	17.484	1108603	49.950	21268
2	20.098	1110828	50.050	18512
Total		2219430	100.000	39780

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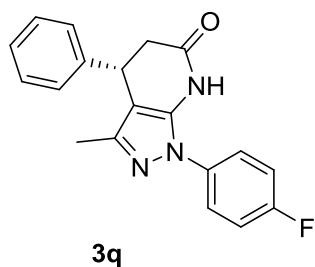
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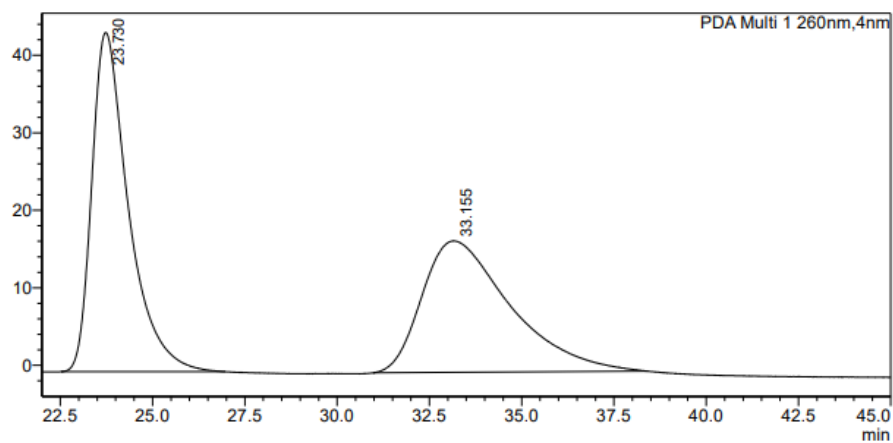
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	17.445	3944562	99.159	74159
2	20.095	33461	0.841	631
Total		3978024	100.000	74790



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mAU



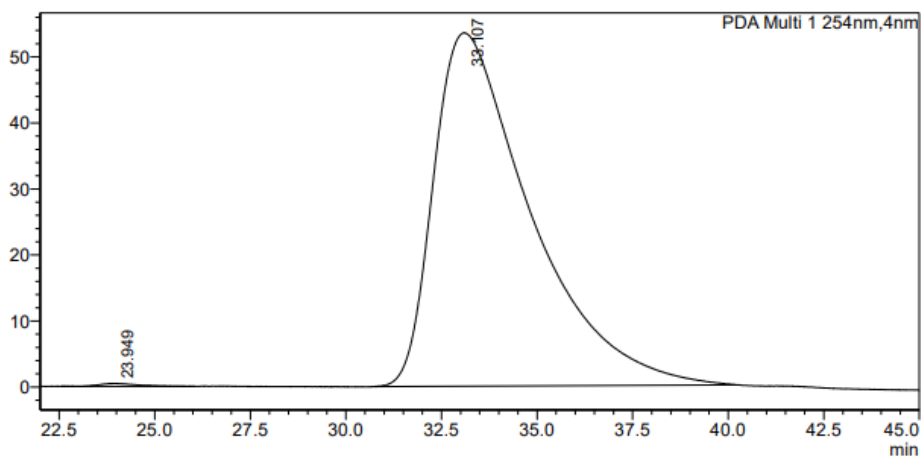
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PDA Ch1 260nm

Peak#	Ret. Time	Area	Area%	Height
1	23.730	3020014	51.718	43749
2	33.155	2819360	48.282	16965
Total		5839375	100.000	60714

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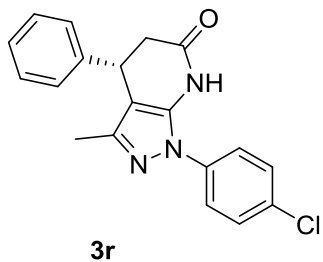
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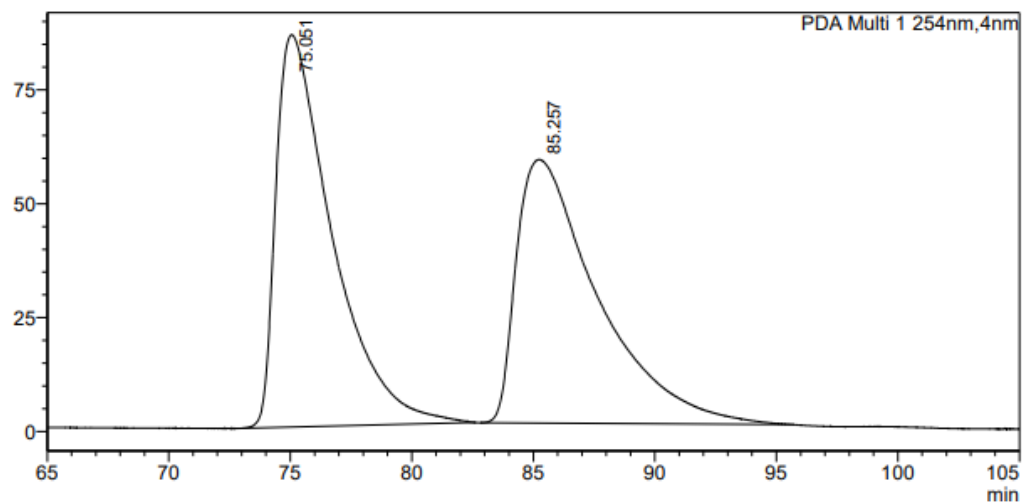
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	23.949	29528	0.311	432
2	33.107	9455836	99.689	53514
Total		9485364	100.000	53946



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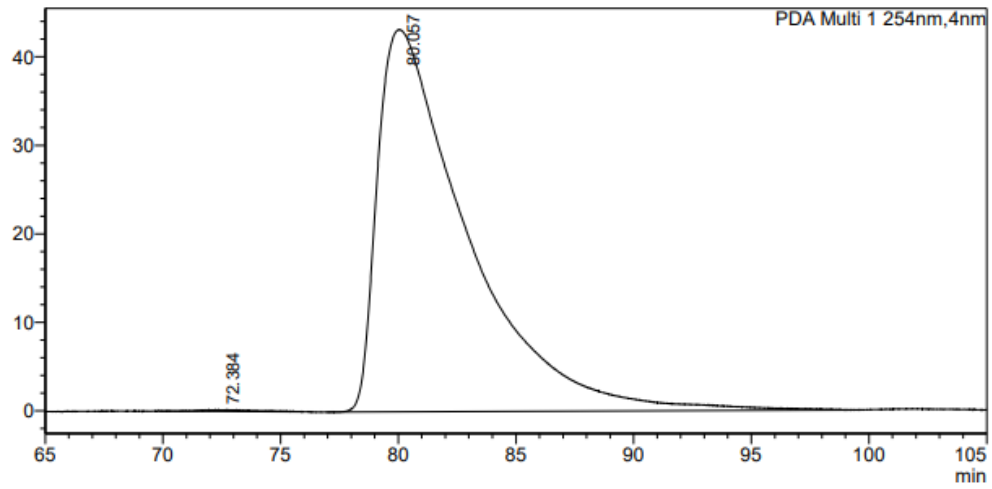
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	75.051	13844279	50.679	86099
2	85.257	13473499	49.321	57850
Total		27317778	100.000	143949

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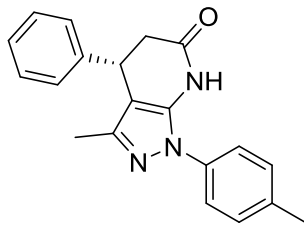
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PDA Ch1 254nm

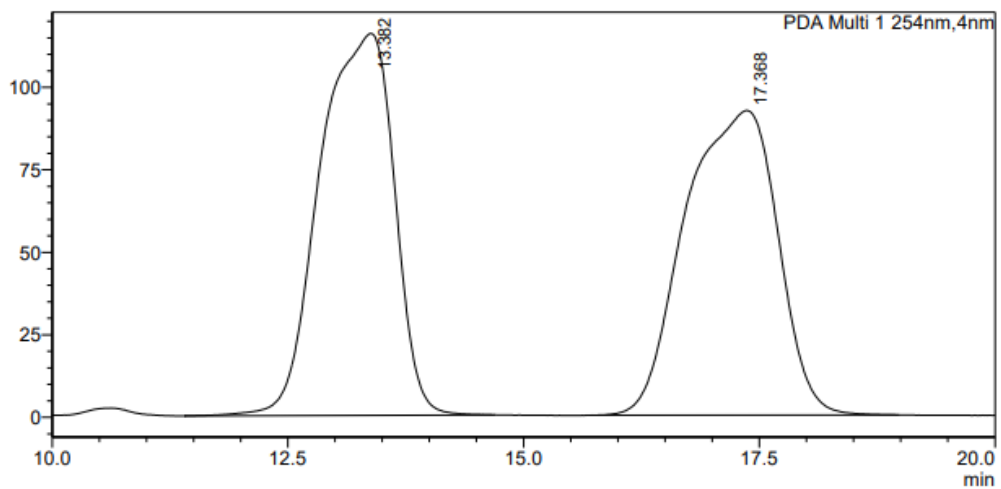
Peak#	Ret. Time	Area	Area%	Height
1	72.384	31333	0.272	180
2	80.057	11496837	99.728	43160
Total		11528170	100.000	43340



3s

<Chromatogram>

mAU



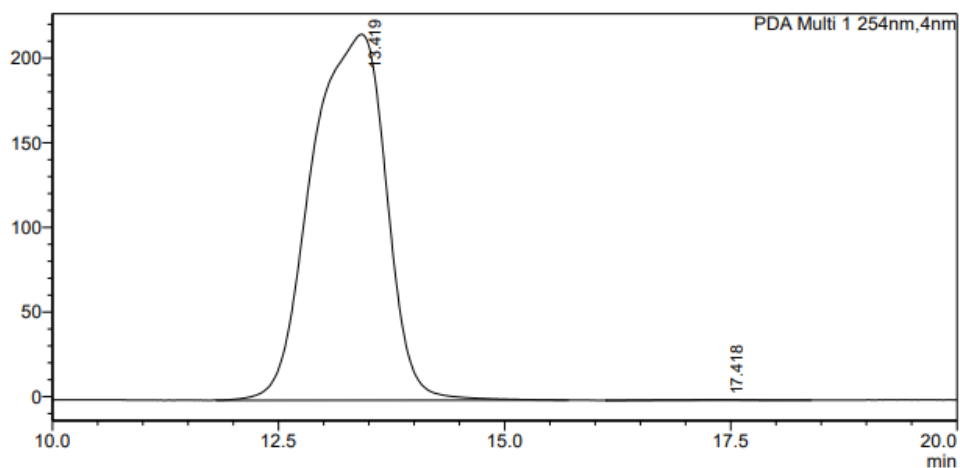
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	13.382	6357659	50.202	115690
2	17.368	6306450	49.798	92309
Total		12664109	100.000	207999

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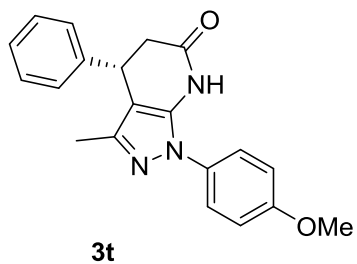
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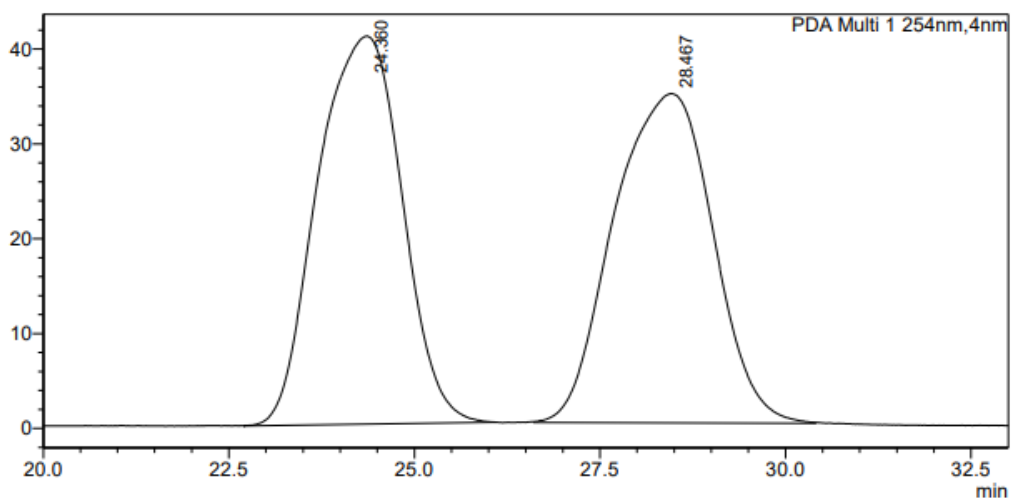
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	13.419	12367851	99.817	216289
2	17.418	22701	0.183	376
Total		12390552	100.000	216665



<Chromatogram>

mAU

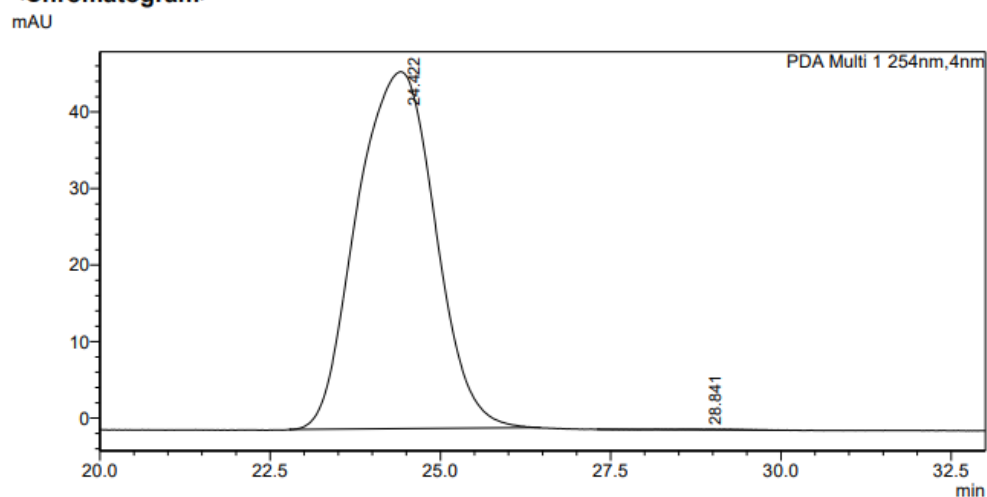


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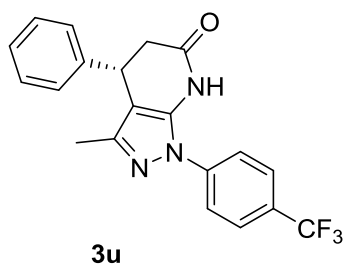
Peak#	Ret. Time	Area	Area%	Height
1	24.360	3242928	50.107	40902
2	28.467	3229109	49.893	34701
Total		6472037	100.000	75603

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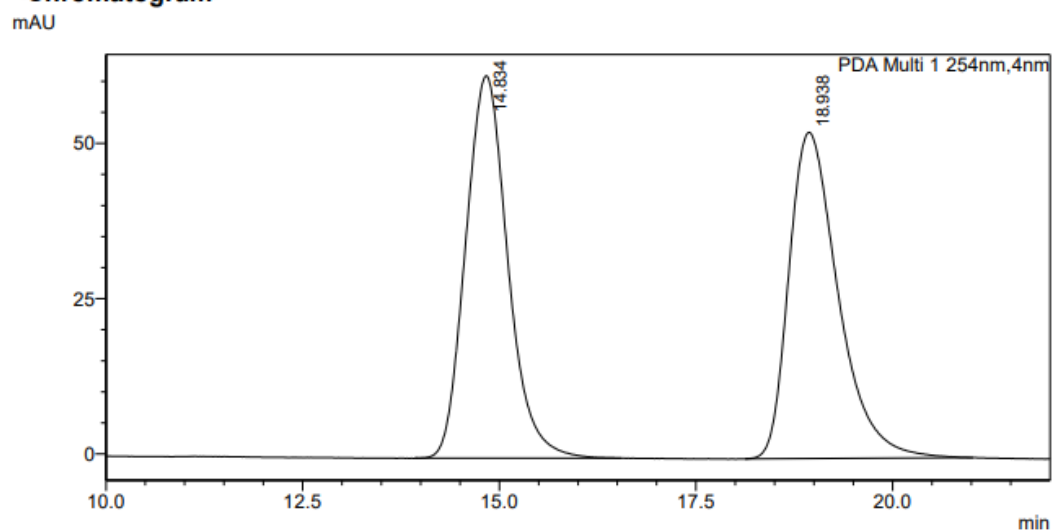


<Peak Table>

PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	Height
1	24.422	3736950	99.853	46633
2	28.841	5484	0.147	92
Total		3742435	100.000	46725



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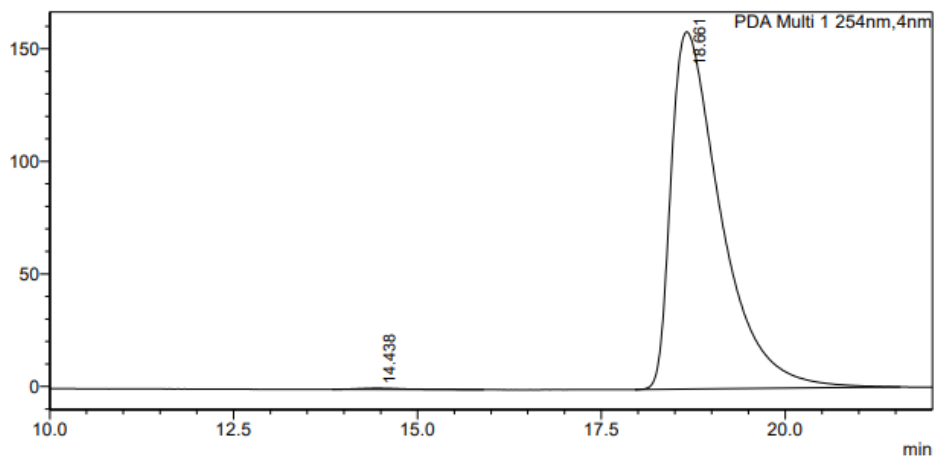


<Peak Table>

PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	Height
1	14.834	2296713	50.134	61524
2	18.938	2284434	49.866	52453
Total		4581147	100.000	113977

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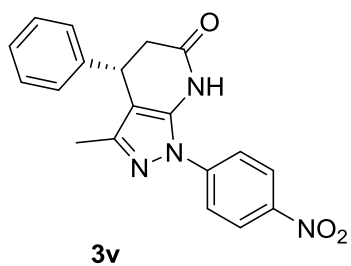
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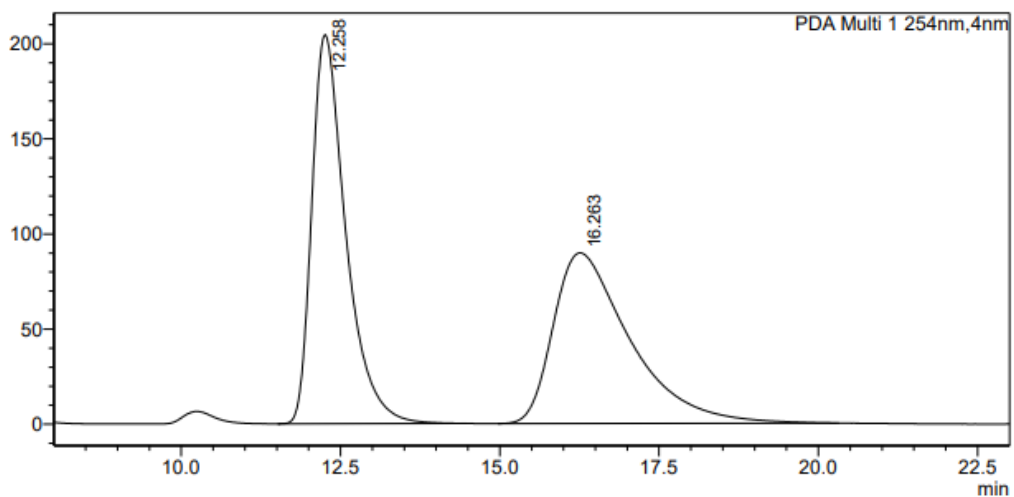
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.438	25589	0.341	574
2	18.661	7486209	99.659	158602
Total		7511798	100.000	159175



<Chromatogram>

mAU



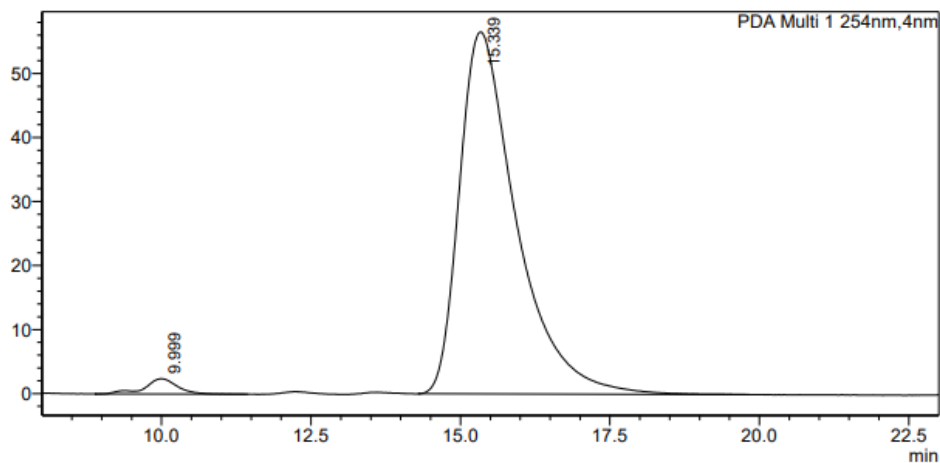
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	12.258	7598966	50.239	204463
2	16.263	7526595	49.761	89669
Total		15125561	100.000	294133

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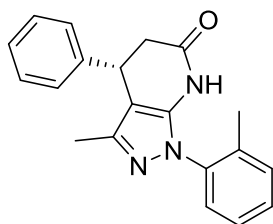
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PDA Ch1 254nm

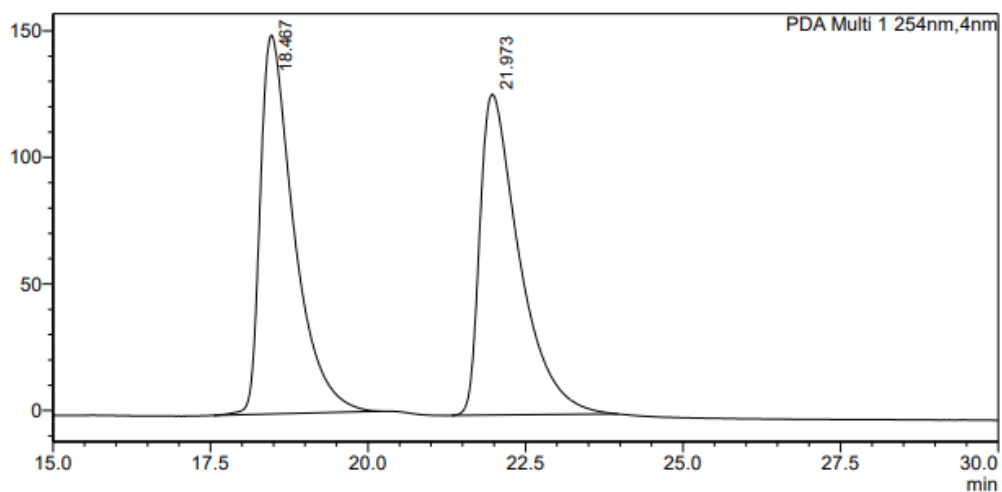
Peak#	Ret. Time	Area	Area%	Height
1	9.999	92720	2.413	2404
2	15.339	3749413	97.587	56530
Total		3842134	100.000	58934



3w

<Chromatogram>

mAU



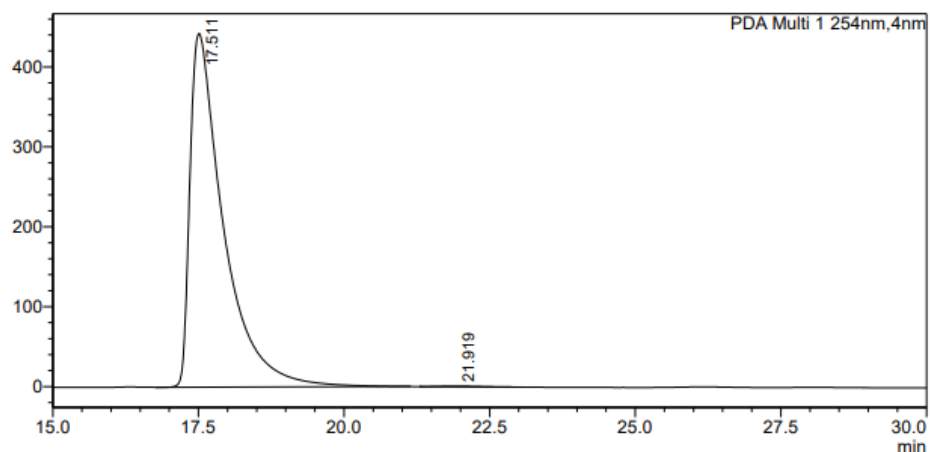
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	18.467	5551204	50.087	149571
2	21.973	5531862	49.913	126732
Total		11083065	100.000	276303

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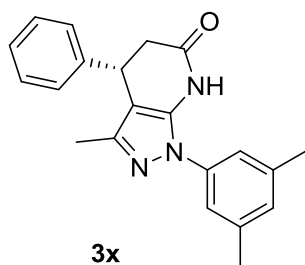
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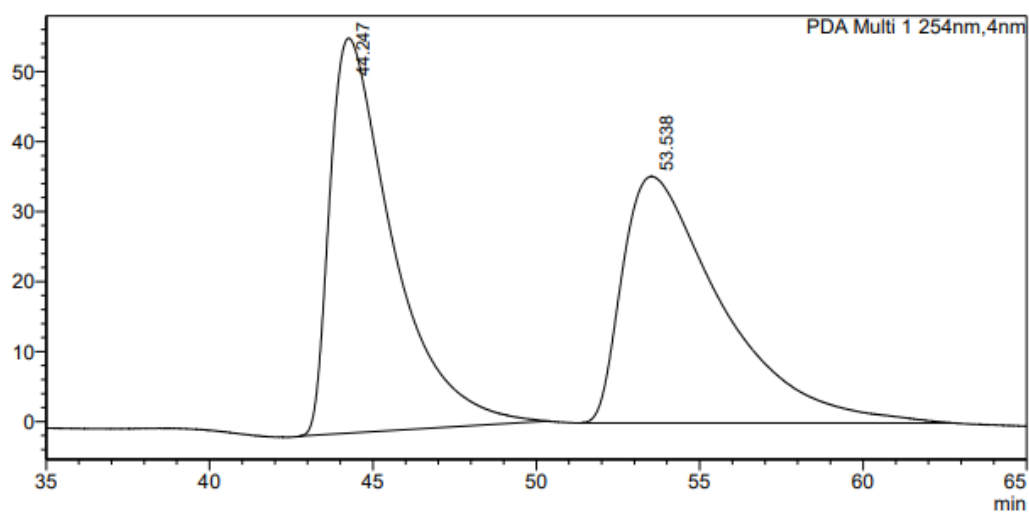
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	17.511	17708337	99.773	442506
2	21.919	40221	0.227	847
Total		17748558	100.000	443354



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mAU



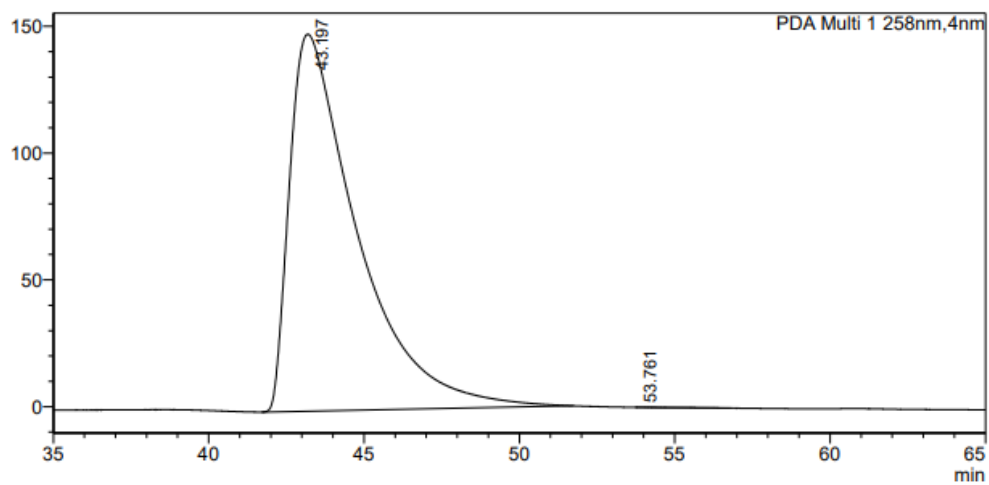
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	44.247	7553116	50.373	56420
2	53.538	7441339	49.627	35224
Total		14994455	100.000	91644

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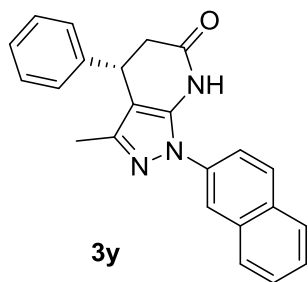
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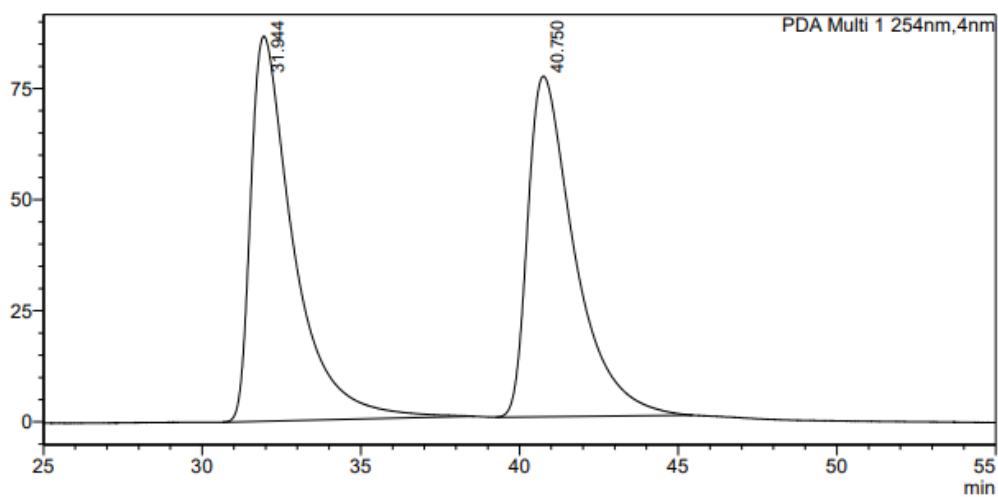
PDA Ch1 258nm

Peak#	Ret. Time	Area	Area%	Height
1	43.197	22560969	99.975	148601
2	53.761	5737	0.025	3
Total		22566705	100.000	148604



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mAU



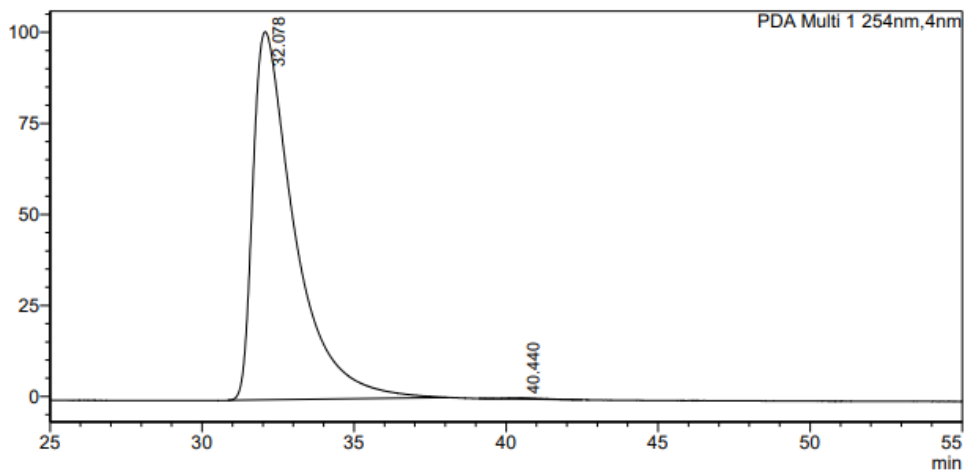
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	31.944	8118664	50.837	86618
2	40.750	7851321	49.163	76621
Total		15969985	100.000	163240

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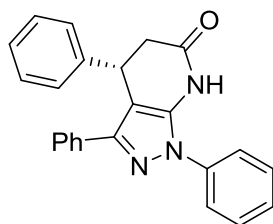
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<Peak Table>

PDA Ch1 254nm

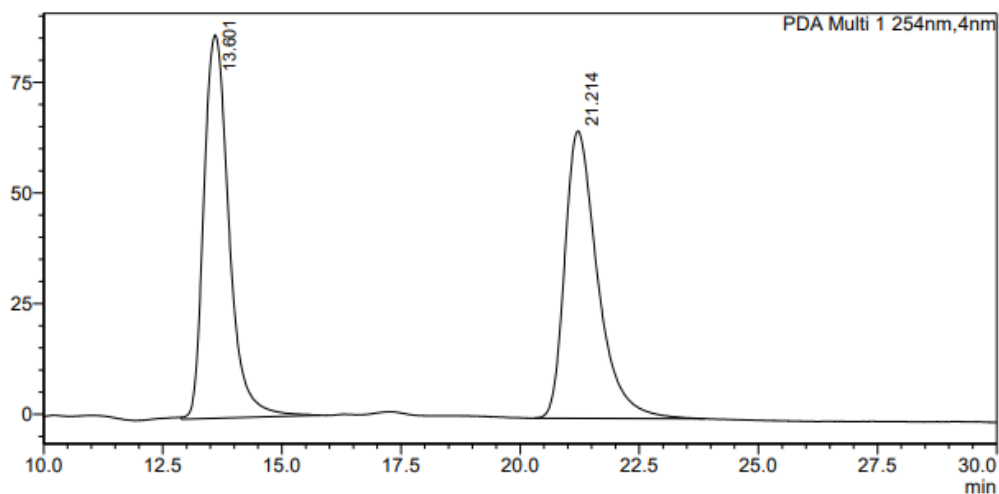
Peak#	Ret. Time	Area	Area%	Height
1	32.078	9648587	99.730	101092
2	40.440	26115	0.270	325
Total		9674703	100.000	101417



3z

<Chromatogram>

mAU

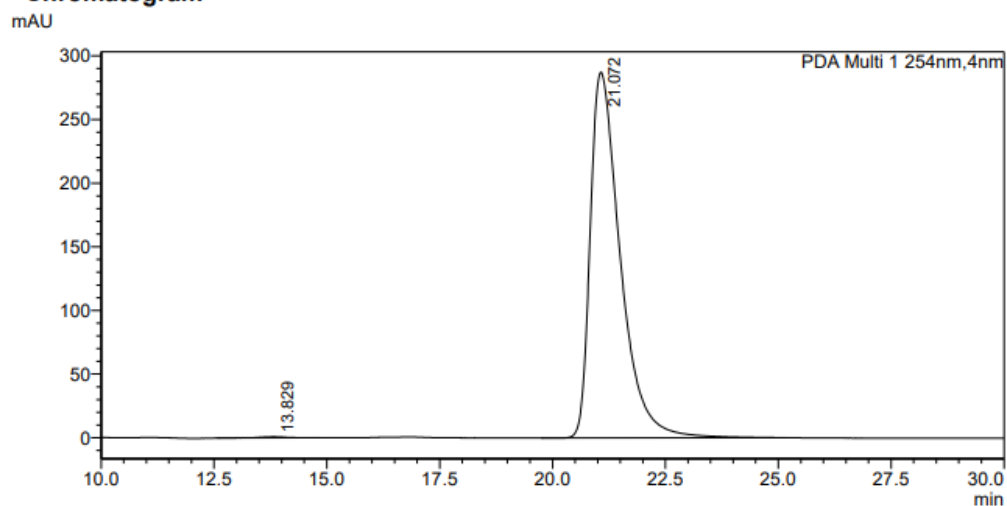


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	13.601	3174362	50.510	86631
2	21.214	3110238	49.490	64921
Total		6284600	100.000	151552

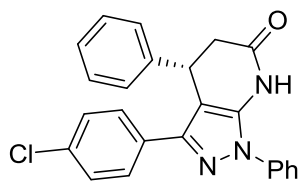
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<Peak Table>

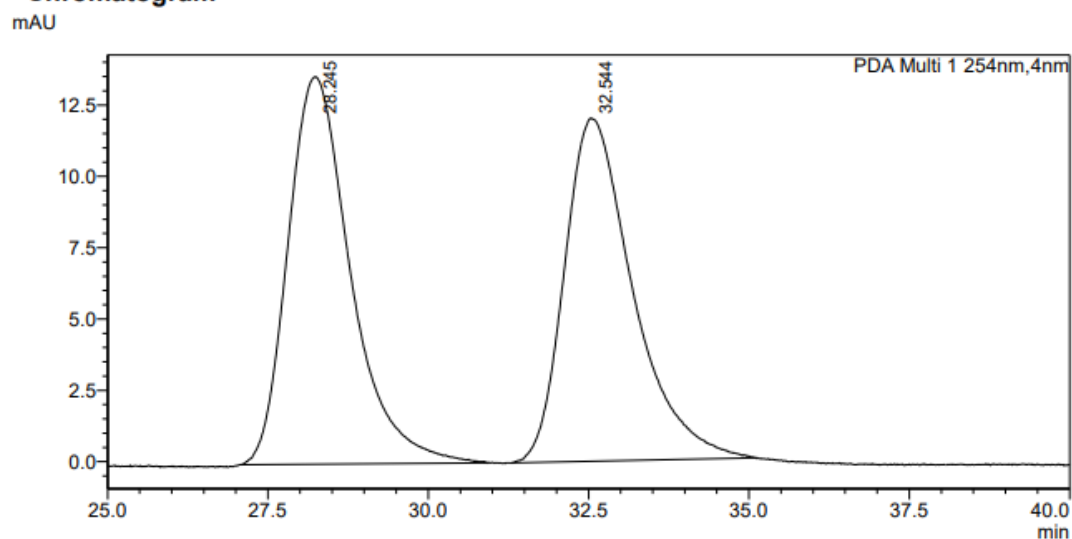
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	13.829	35639	0.268	829
2	21.072	13276800	99.732	287278
Total		13312440	100.000	288107



3aa

<Chromatogram>



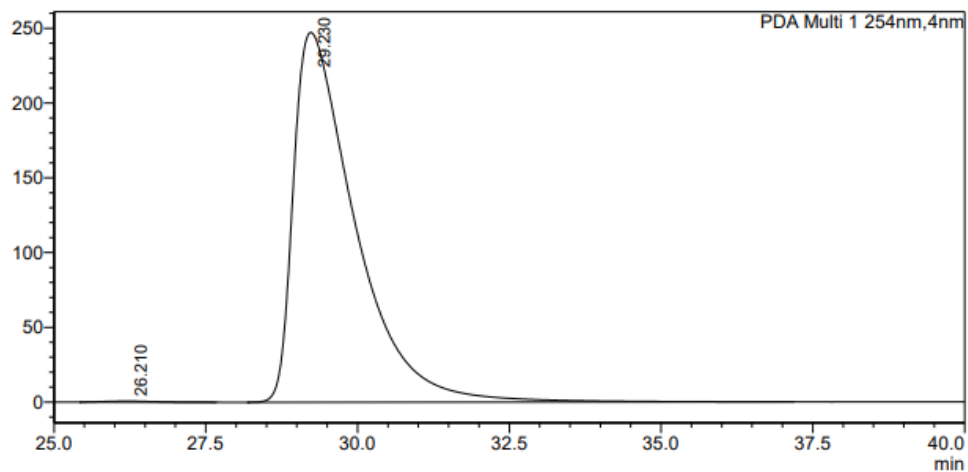
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	28.245	921229	50.857	13579
2	32.544	890190	49.143	12030
Total		1811418	100.000	25609

<Chromatogram>

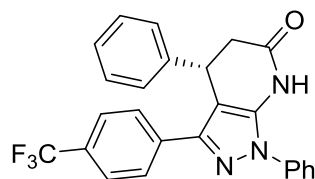
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<Peak Table>

PDA Ch1 254nm

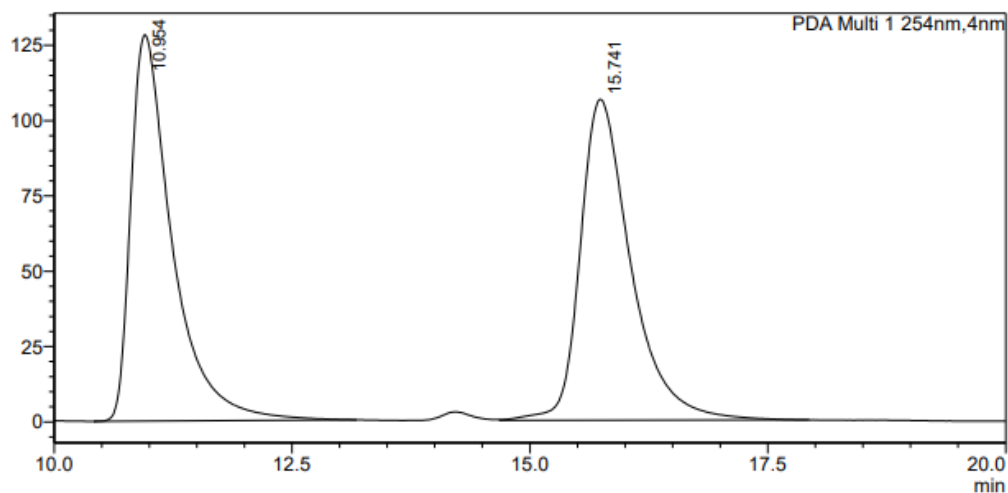
Peak#	Ret. Time	Area	Area%	Height
1	26.210	37497	0.214	660
2	29.230	17524854	99.786	247341
Total		17562351	100.000	248001



3ab

<Chromatogram>

mAU



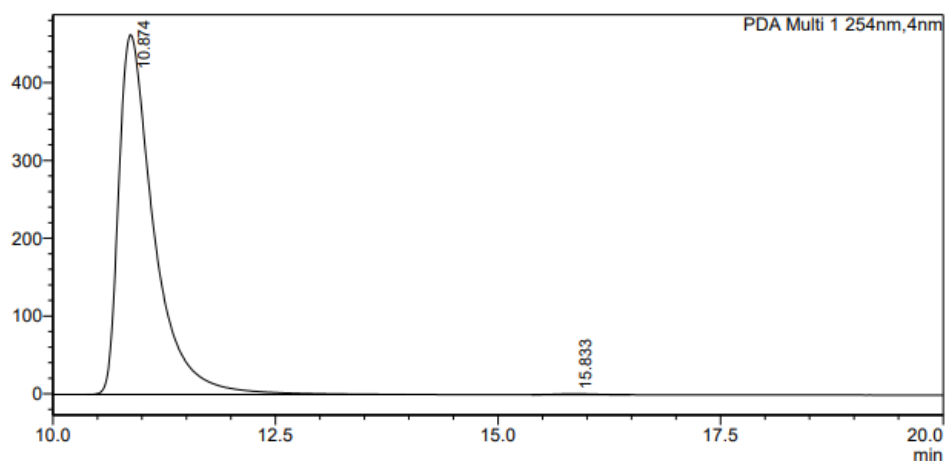
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	10.954	3885168	49.554	128222
2	15.741	3955114	50.446	106498
Total		7840282	100.000	234720

<Chromatogram>

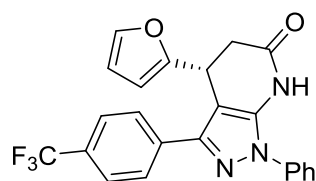
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<Peak Table>

PDA Ch1 254nm

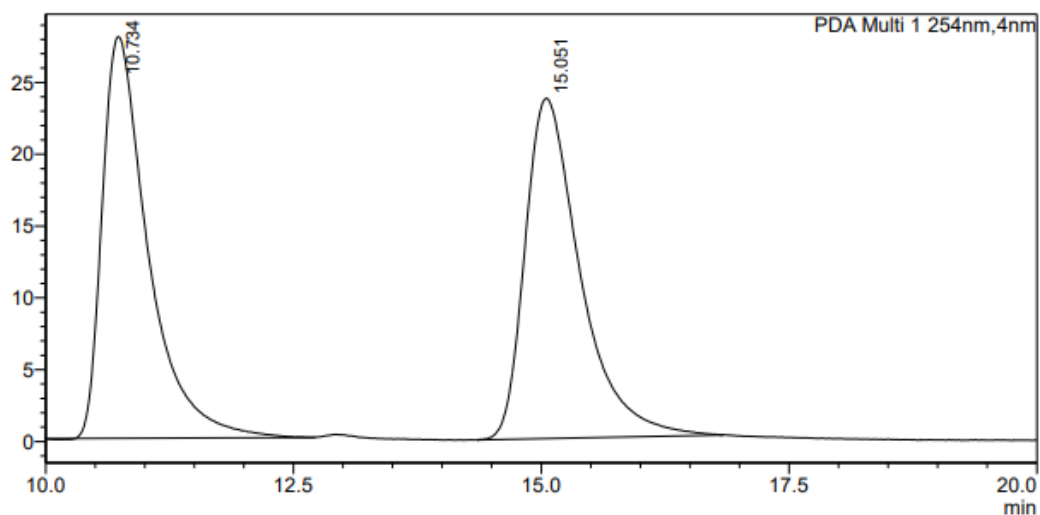
Peak#	Ret. Time	Area	Area%	Height
1	10.874	12704409	99.754	462468
2	15.833	31332	0.246	1002
Total		12735741	100.000	463470



3ac

<Chromatogram>

mAU



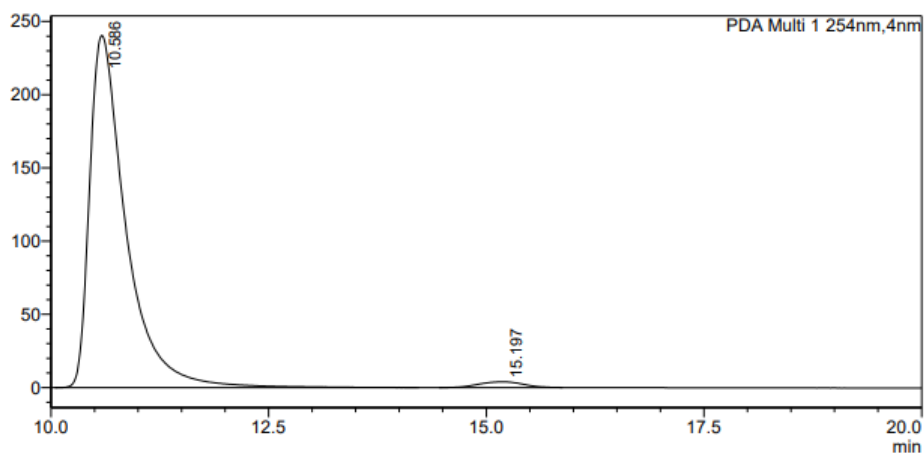
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PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	10.734	900652	49.479	27962
2	15.051	919611	50.521	23692
Total		1820262	100.000	51655

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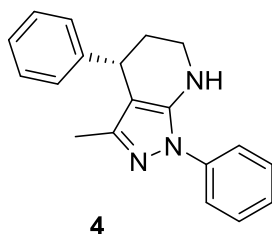
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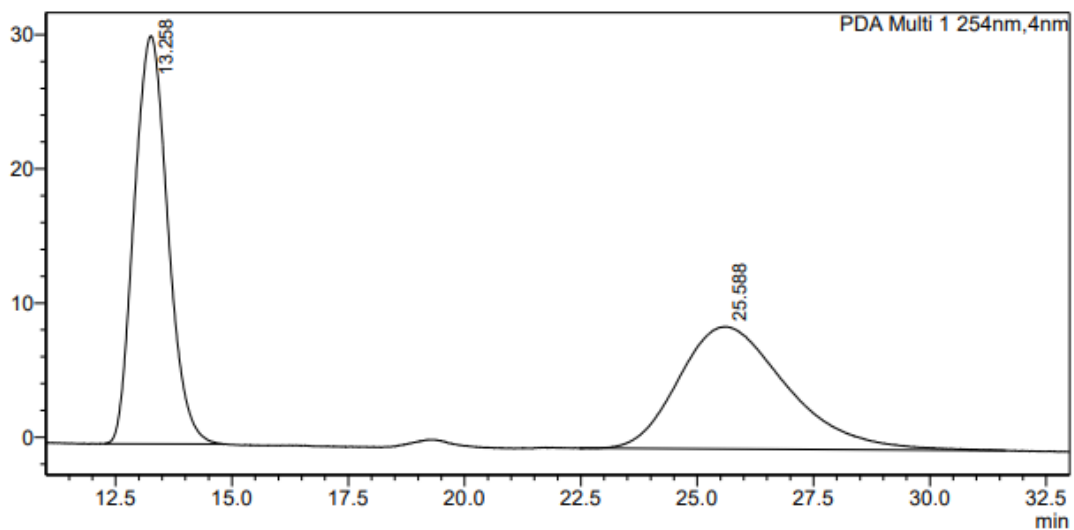
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	10.586	6982109	98.051	240462
2	15.197	138805	1.949	3925
Total		7120914	100.000	244386



<Chromatogram>

mAU



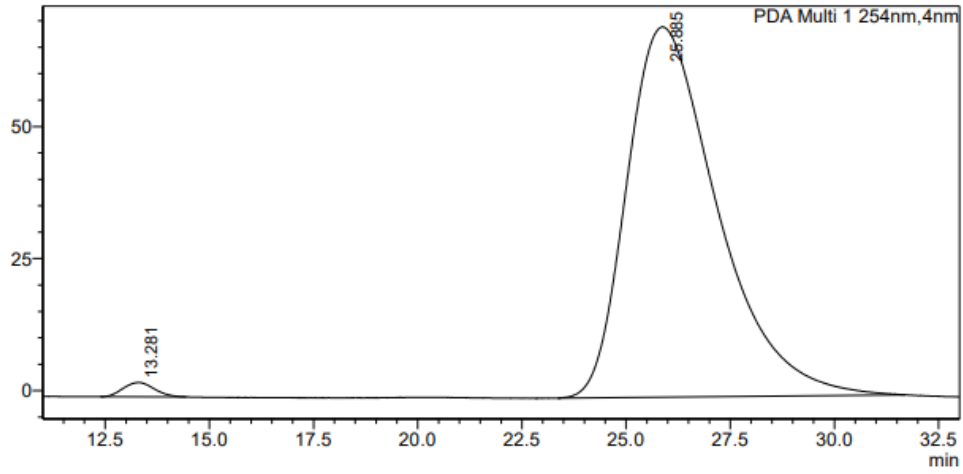
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	13.258	1526313	50.907	30399
2	25.588	1471900	49.093	9108
Total		2998213	100.000	39507

<Chromatogram>

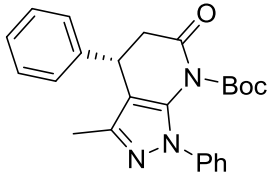
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<Peak Table>

PDA Ch1 254nm

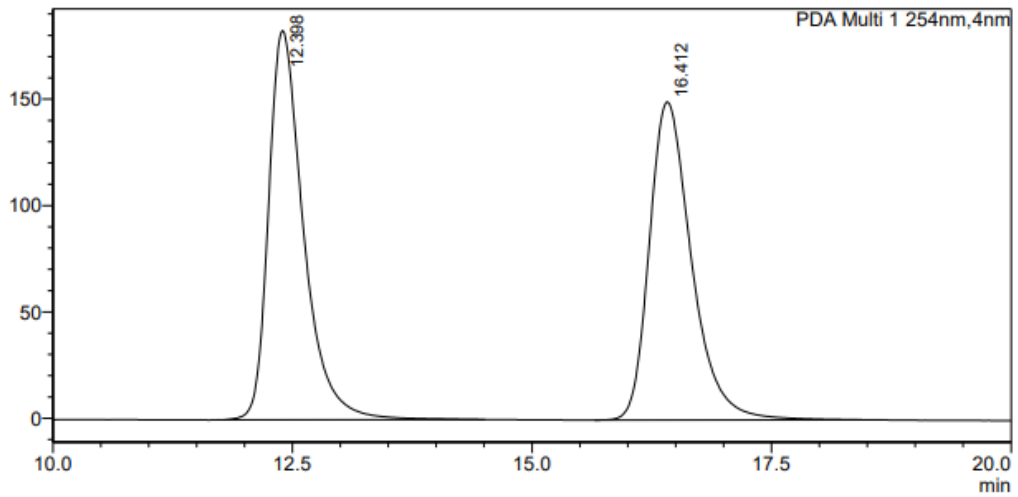
Peak#	Ret. Time	Area	Area%	Height
1	13.281	140287	1.305	2708
2	25.885	10609471	98.695	70079
Total		10749758	100.000	72787



5

<Chromatogram>

mAU



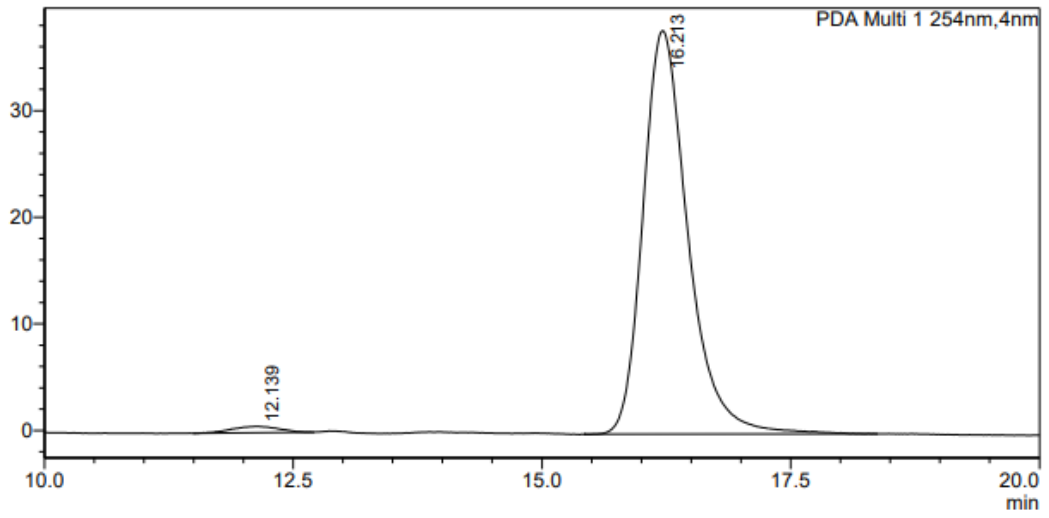
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	12.398	4652174	50.321	182915
2	16.412	4592839	49.679	149562
Total		9245014	100.000	332477

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	12.139	19513	1.611	603
2	16.213	1191912	98.389	37840
Total		1211425	100.000	38443